Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Post-Polymerisation Diversification of Conjugated Polymer by Inverse Electron Demand Diels-Alder Reaction

Zhuang Mao Png, Xiang Yun Debbie Soo, Jun Xiang Damian Liew, Ming Hui Chua, Shanxin Xiong, Qiang Zhu, Jianwei Xu*

Materials and Methods

General Experimental Procedure

Commercial reagents were used as supplied from Sigma Aldrich, Alfa Aesar, or Combi blocks without further purification. Tetrazine **1** was prepared by modification of previously reported procedures.[1]

Nuclear magnetic resonance (NMR) spectra were recorded on a Jeol 500 MHz using $CDCl_3$ as the solvent. Data are reported as follows: chemical shift (integration, splitting (s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, sxt = sextet, spt = septet, m = multiplet), coupling constant, assignment).

Infrared spectra (FT-IR) were recorded using a Perkin-Elmer Paragon 1000 Fourier transform Spectrometer and with samples pelletized with KBr, and absorption maxima (λ_{max}) being quoted in wavenumbers (cm^{-1}). UV spectra were recorded on a Shimadzu UV3101PC UV-vis-NIR spectrophotometer with chloroform as the solvent and at a monomer concentration of about 2.5 x 10^{-5} M. High Resolution Mass Spectrometry (HRMS) was carried out by the National University of Singapore Mass Spectrometry Service using a Bruker MicrOTOF-QII positive ion nano-electrospray.

Proportion of protonated polymer was estimated using the following equation:

$$\frac{[HP^+]}{[P]} \approx \frac{\varepsilon_f - \varepsilon_x}{\varepsilon_f}$$

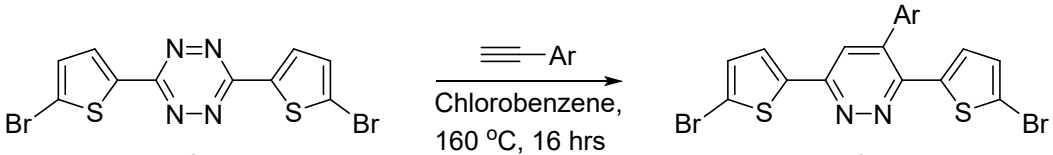
Whereby ε_f = ε of polymer at local maxima between 538 nm to 574 nm when amount of TFA added is 20 μL, and ε_x = ε of polymer at local maxima between 538 to 574 nm when the amount of TFA added is x μL.

Emission ratio was calculated by the following equation:

$$Emission\ ratio = \frac{Emission_x}{Initial\ emission}$$

Whereby "initial emission" refers to the average measured emission (between 460 to 700 nm) of the polymer when no metal ions is added, and $emission_x$ refers to the measured emission of the polymer (between 460 to 700 nm) when x amount of metal ions is added.

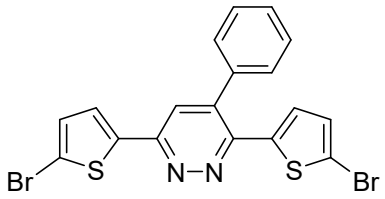
General method A for small molecule iEDDA reaction



1 **3a-e**

To a red solution of tetrazine **1** (404 mg, 1 mmol, 1 eq) in chlorobenzene (5 mL) was added the corresponding aryl alkyne (5 eq). The solution was stirred at 160 °C for 16 hours, with the solution turning from red to yellowish brown, then cooled to RT, and concentrated in *vacuo* to remove excess chlorobenzene. The solid was then re-dissolved in minimum chloroform and reprecipitated in methanol, and filtered to obtain a yellowish-brown powder, which was dried and used without further purification.

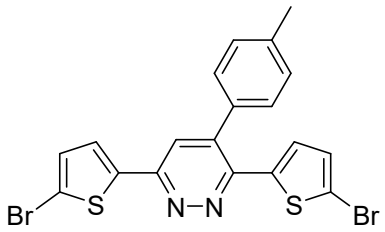
3,6-bis(5-bromothiophen-2-yl)-4-phenylpyridazine (3a)



3a

General procedure A was applied to tetrazine **1** with phenylacetylene (548 µL, 5 mmol). A yellowish-brown powder was obtained (444 mg, 92%). IR (λ_{max}/cm^{-1}) 3058, 1578, 1492, 1484, 1380, 1237,1077. ^{1}H NMR (500.1 MHz, $CDCl_3$) 7.51-7.49 (4H, m), 7.37 – 7.35 (3H, m), 7.10 (1H, d, *J* = 4.2 Hz), 6.78 (1H, d, *J* = 3.8 Hz), 6.35 (1H, d, *J* = 4.2 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) 152.0, 151.6,141.4,141.3,138.4, 136.3, 131.3, 130.6, 130.0, 129.7, 129.4, 128.4, 128.4, 126.8, 123.3, 117.7, 117.6. HRMS (FTMS +p NSI) m/z: $[M + H]^+$ calculated for $C_{18}H_{11}Br_2N_2S_2$ 476.8725, found = 476.8723, Δ = 0.42 ppm.

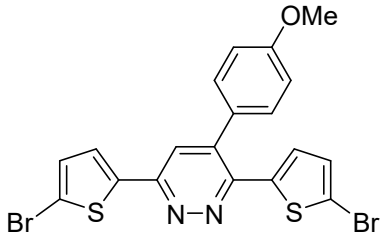
3,6-bis(5-bromothiophen-2-yl)-4-(p-tolyl)pyridazine (3b)



3b

General procedure A was applied to tetrazine **1** with *p*-tolylacetylene (633 µL, 5 mmol). A yellowish-brown powder was obtained (442 mg, 90%). IR (λ_{max}/cm^{-1}). 3031, 2917, 1610, 1578, 1509, 1484, 1374, 1236, 1212, 1178, 1073. ^{1}H NMR (500.1 MHz, $CDCl_3$) 7.61 (1H, d, *J* = 3.6 Hz), 7.54 (1H, s), 7.32 – 7.25 (4H, m), 7.13 (1H, d, *J* = 3.6 Hz), 6.84 (1H, d, *J* = 3.8 Hz), 6.65 (1H, d, *J* = 3.7 Hz), 2.46 (3H, s), ^{13}C NMR (100.6 MHz, $CDCl_3$) 151.7, 151.6, 140.6, 140.3, 140.2, 139.5, 132.9, 131.5, 130.7, 130.5, 130.1, 128.4, 128.3, 127.7, 124.3, 118.2, 118.0, 21.6. HRMS (FTMS +p NSI) m/z: $[M + H]^+$ calculated for $C_{19}H_{13}Br_2N_2S_2$ 490.8880 found = 490.8881, Δ = 0.20 ppm.

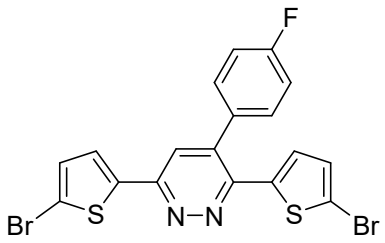
3,6-bis(5-bromothiophen-2-yl)-4-(4-methoxyphenyl)pyridazine (3c)



3c

General procedure A was applied to tetrazine **1** with 4-ethynylanisole (647 µL, 5 mmol). A yellowish-brown powder was obtained (447 mg, 88%). IR (λ_{max}/cm^{-1}) 2963, 1607, 1581, 1537, 1569, 1425, 1385, 1247, 1174, 1020. ^{1}H NMR (500.1 MHz, $CDCl_3$) 7,48 (1H, s), 7.38 (1H, d, *J* = 3.6 Hz), 7.29 (2H, d, *J* = 8.2 Hz), 7.10 (1H, d, *J* = 3.6 Hz), 7.01 (2H, d, *J* = 8.2 Hz), 6.81 (1H, d, *J* = 4.2 Hz), 6.51 (1H, d, *J* = 4.2 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$) 160.8, 152.0, 151.9, 141.3, 141.1, 138.5, 131.3, 130.7, 130.0, 129.9, 128.1, 127.0, 123.6, 117.8, 117.5, 114.8, 55.6. HRMS (FTMS +p NSI) m/z: $[M + H]^+$ calculated for $C_{19}H_{13}Br_2N_2OS_2$ 506.8831 found = 506.8829, Δ = 0.39 ppm.

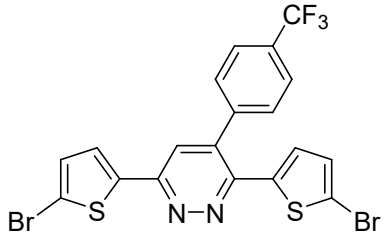
3,6-bis(5-bromothiophen-2-yl)-4-(4-fluorophenyl)pyridazine (3d)



3d

General procedure A was applied to tetrazine **1** with 1-ethynyl-4-fluorobenzene (572 µL, 5 mmol). A brown powder was obtained (430 mg, 87%). IR (λ_{max}/cm^{-1}) 3047, 1606, 1509, 1435, 1380, 1236, 1162, 1078. ^{1}H NMR (500.1 MHz, $CDCl_3$) 7.47 (1H, s), 7.37 – 7.34 (3H, m), 7.20 (2H, t, *J* = 8.3 Hz) 7.10 (1H, d, *J* = 4.7 Hz), 6.82 (1H, d, *J* = 4.1 Hz), 6.41 (1H, d, *J* = 4.1 Hz). ^{19}F NMR (470.6 MHz, $CDCl_3$) -110.6 ^{13}C NMR (100.6 MHz, $CDCl_3$) 163.5 (d, J = 247.9 Hz), 152.1, 151.7, 141.2, 137.3, 132.2, 131.3, 130.7, 130.5, 130.4, 129.9, 126.8, 123.3, 117.7, 116.8, 116.6. HRMS (FTMS +p NSI) m/z: $[M + H]^+$ calculated for $C_{18}H_{10}Br_2FN_2S_2$ 494.8631 found = 494.8637, Δ = 1.21 ppm.

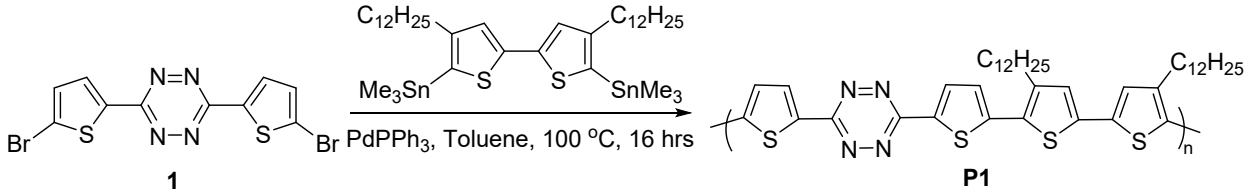
3,6-bis(5-bromothiophen-2-yl)-4-(4-(trifluoromethyl)phenyl)pyridazine (3e)



3e

General procedure A was applied to tetrazine **1** with 4-ethynyl-α,α,α-trifluorotoluene (817 µL, 5 mmol). A brown powder was obtained (435 mg, 80%). IR (λ_{max}/cm^{-1}) 3047, 1617, 1581, 1439, 1386, 1165, 1125, 1068. ^{1}H NMR (500.1 MHz, $CDCl_3$) 7.77 (2H, d, *J* = 7.8 Hz) 7.52 (2H, d, *J* = 7.8 Hz), 7.47 (1H, s), 7.37 (1H, d, *J* = 3.9 Hz), 7.11 (1H, d, *J* = 3.9 Hz), 6.82 (1H, d, *J* = 4.1 Hz), 6.32 (1H, d, *J* = 4.1 Hz). ^{19}F NMR (470.6 MHz, $CDCl_3$) -62.6 ^{13}C NMR (100.6 MHz, $CDCl_3$) 152.1, 151.1, 141.0, 140.9, 140.8, 140.0, 136.8, 132.1, 131.3, 130.8, 129.9, 129.0, 127.0, 126.5, 124.9, 123.1, 118.1, 118.0. HRMS (FTMS +p NSI) m/z: $[M + H]^+$ calculated for $C_{19}H_{10}Br_2F_3N_2S_2$ 544.8599 found = 544.8596, Δ = 0.55 ppm.

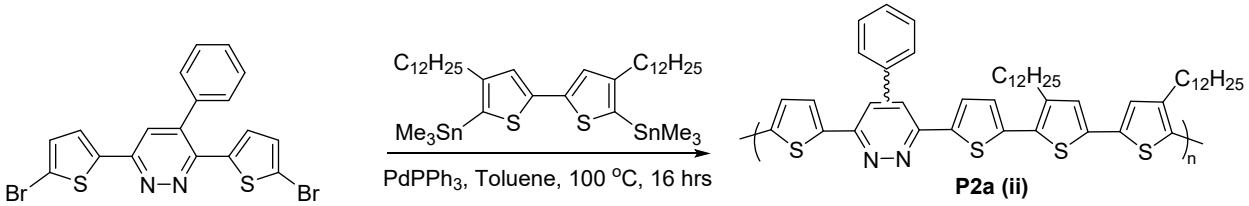
Stille Coupling of P1



1 **P1**

To a 100 mL round-bottomed flask with a large oval stirrer bar was added tetrazine **1** (404 mg, 1 mmol), (4,4'-didodecyl-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane) (828 mg, 1 mmol), and tetrakis(triphenylphosphine)palladium(0) (57.8 mg, 0.05 mmol). The flask was sealed with a septum and evacuated / backfilled with nitrogen three times. Degassed toluene (10 mL) was then added *via* syringe. The mixture was heated at 120 °C for 24 hours. The solution was allowed to cool, then precipitated in methanol (100 mL). Filtration gave the crude polymer as a purple powder. The polymer was purified by Soxhlet extraction by acetone (3 hours), hexane (3 hours), and finally chloroform (3 hours). Chloroform was then removed in *vacuo* and the polymer was re-dissolved in a minimum amount of chloroform. The polymer was then re-precipitated in methanol, filtered, and dried under vacuum to yield a purple solid (475 mg, 63%, M_n = 5.0 kDa, PDI = 1.42). IR (λ_{max}/cm^{-1}) 2922, 2851, 2344, 1444, 1388,1080, 1063, 1001. ^{1}H NMR (500.1 MHz, $CDCl_3$) 8.20 (br), 7.03 (br), 2.82 (br), 2.80 (br), 1.80 – 0.85 (m, alkyl peaks). Note: Increasing the reaction time to 72 hours lead to lower yields (~ 10%) due to greater amount of insoluble residue after Soxhlet extraction with chloroform. M_n of chloroform portion remains similar at about ~ 5 kDa.

Stille Coupling of P2a (ii)

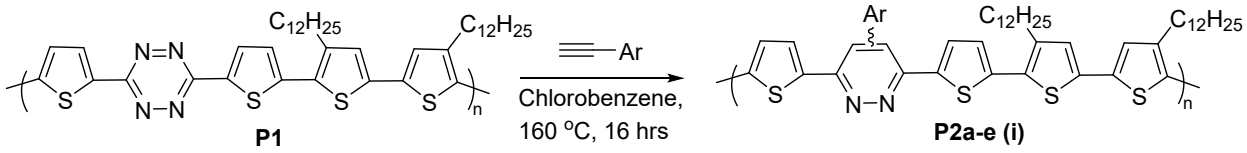


3a **P2a (ii)**

To a 100 mL round-bottomed flask with a large oval stirrer bar was added 3,6-bis(5-bromothiophen-2-yl)-4-phenylpyridazine **3a** (93 mg, 0.2 mmol), (4,4'-didodecyl-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylstannane) (165 mg, 0.2 mmol), and tetrakis(triphenylphosphine)palladium(0) (11.5 mg, 0.01 mmol). The flask was sealed with a septum and evacuated / backfilled with nitrogen three times. Degassed toluene (2 mL) was then added *via* syringe. The mixture was heated at 120 °C for 24 hours. The solution was allowed to cool, then precipitated in methanol (100 mL). Filtration gave the crude polymer as an orange-red powder. The polymer was purified by Soxhlet extraction by acetone (3 hours), hexane (3 hours), and finally chloroform (3 hours). Chloroform was then removed in *vacuo* and the polymer was re-

dissolved in a minimum amount of chloroform. The polymer was then re-precipitated in methanol, filtered, and dried under vacuum to yield a yellow solid (110 mg, 67 %, M_n = 8.9 kDa, PDI = 1.69). IR (λ_{max}/cm^{-1}) 2921, 2850, 1442, 1380, 1078, 792. ^{1}H NMR (500.1 MHz, $CDCl_3$) 7.60 – 7.48 (br), 7.47 – 7.38 (br), 7.20 – 7.14 (br), 7.05 – 6.96 (br), 6.90 – 6.84 (br), 6.60 – 6.58 (br), 2.87 – 2.71 (br), 1.75 – 1.08 (m, alkyl peaks), 0.93 – 0.78 (br).

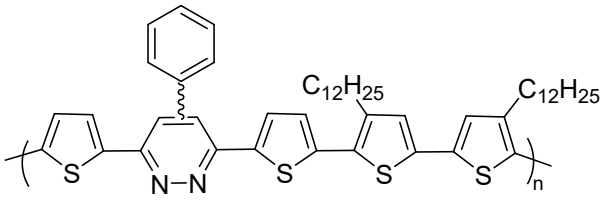
General method B for polymer iEDDA reaction



P1 **P2a-e (i)**

To a dark purple solution of polymer **P1** (37.8 mg, 0.05 mmol) in chlorobenzene (3 mL) was added the corresponding aryl alkyne (2 mmol, 10 eq). The solution was stirred at 160 °C for 16 hours, cooled to RT, then precipitated in methanol and filtered. The filtrate was then re-dissolved in minimum chloroform (~ 1 mL) and re-precipitated in methanol a second time to obtain an orange-red solid, which was dried in *vacuo*.

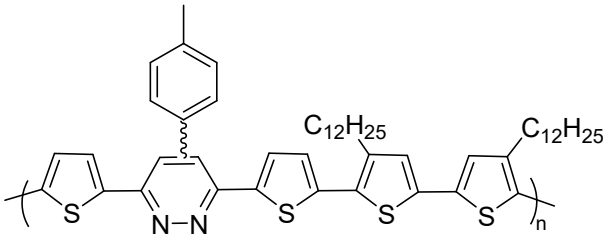
P2a(i)



P2a (i)

General procedure B was applied to polymer **P1** with phenylacetylene (219 µL, 2 mmol). An orange powder was obtained (35.6 mg, 87%, M_n = 5.3 kDa, PDI = 1.47). IR (λ_{max}/cm^{-1}) 2922, 2851, 1446, 1384, 1073, 758. ^{1}H NMR (500.1 MHz, $CDCl_3$) 7.63 – 7.48 (br), 7.47 – 7.38 (br), 7.20 – 7.15 (br), 7.06 – 6.95 (br), 6.90 – 6.84 (br), 6.61 – 6.48 (br), 2.94 – 2.47 (br), 1.75 – 1.08 (m, alkyl peaks), 0.91 – 0.78 (br).

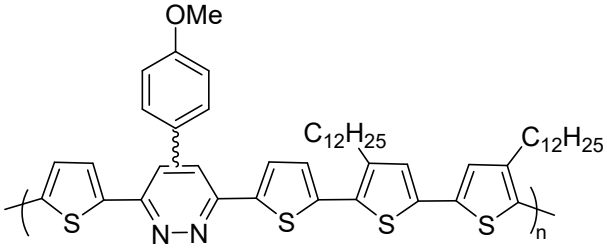
P2b(i)



P2b(i)

General procedure B was applied to polymer **P1** with *p*-tolylacetylene (253 µL, 2 mmol). An orange powder was obtained (32.1 mg, 77%, M_n = 6.0 kDa, PDI = 1.42). IR (λ_{max}/cm^{-1}) 2920, 2849, 1437, 1377, 1076, 794. ^{1}H NMR (500.1 MHz, $CDCl_3$) 7.60 – 7.51 (br), 7.38 – 7.24 (br), 7.20 – 7.15 (br), 7.07 – 6.97 (br), 6.62 – 6.61 (br), 6.55 (br), 2.90 – 2.72 (br), 2.50 – 2.41 (br, phenyl CH_3), 1.75 – 1.03 (m, alkyl peaks), 0.90 – 0.78 (br).

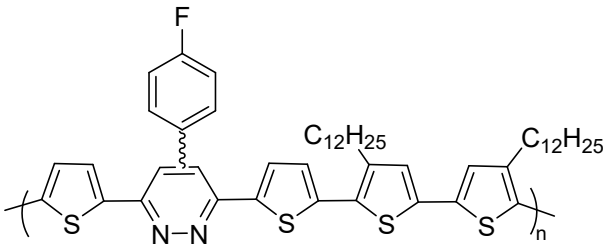
P2c(i)



P2c(i)

General procedure B was applied to polymer **P1** with 4-ethynylanisole (258 µL, 2 mmol). An orange powder was obtained (37.2 mg, 88%, M_n = 5.9 kDa, PDI = 1.43). IR (λ_{max}/cm^{-1}) 2920, 2850, 1607, 1438, 1378, 1290, 1248, 1174, 1030, 830, 793. ^{1}H NMR (500.1 MHz, $CDCl_3$) 7.60 – 7.50 (br), 7.38 – 7.30 (br), 7.20 – 7.15 (br), 7.10 – 6.95 (br), 6.92 – 6.85 (br), 6.70 – 6.65 (br), 3.91 (s, OMe), 2.88 – 2.72 (br), 1.75 – 0.92 (m, alkyl peaks), 0.89 – 0.77 (br).

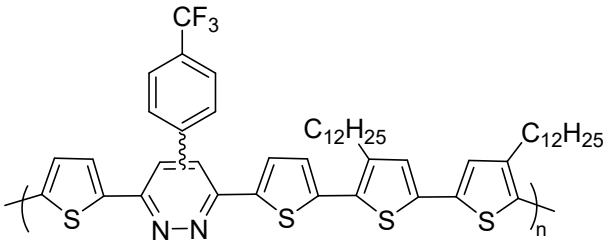
P2d(i)



P2d(i)

General procedure B was applied to polymer **P1** with 1-ethynyl-4-fluorobenzene (228 µL, 2 mmol). An orange powder was obtained (25.9 mg, 62%, M_n = 6.2 kDa, PDI = 1.38). IR (λ_{max}/cm^{-1}) 2921, 2850, 1437, 1379, 1231, 1158, 1077, 835, 790. ^{1}H NMR (500.1 MHz, $CDCl_3$) 7.62 – 7.50 (br), 7.45 – 7.38 (br), 7.30 – 7.20 (br), 7.05 – 6.96 (br), 6.92 – 6.88 (br), 6.62 (s), 6.54 (s), 2.87 – 2.48 (br), 2.26 (s), 1.78 (s), 1.73 – 0.95 (m, alkyl peaks), 0.92 – 0.76 (br). ^{19}F NMR (470.6 MHz, $CDCl_3$) 111.1.

P2e(i)



P2e(i)

General procedure B was applied to polymer **P1** with 4-ethynyl-α,α,α-trifluorotoluene (327 µL, 2 mmol). An orange powder was obtained (28.9 mg, 65%, M_n = 5.4 kDa, PDI = 1.43). IR (λ_{max}/cm^{-1}) 2922, 2851, 1578, 1441, 1380, 1322, 1167, 1129, 1068, 843, 791. ^{1}H NMR (500.1 MHz, $CDCl_3$) 7.82 – 7.79 (br), 7.62 – 7.50 (br), 7.20 – 7.15 (br), 7.06 – 6.95 (br), 6.92 – 6.85 (br), 6.62 (s), 6.54 – 6.50 (br), 2.87 – 2.48 (br), 2.26 (s), 1.77 (s), 1.74 – 1.03 (m, alkyl peaks), 0.91 – 0.77 (br). ^{19}F NMR (470.6 MHz, $CDCl_3$) 62.5.

UV Spectra of partially modified polymer

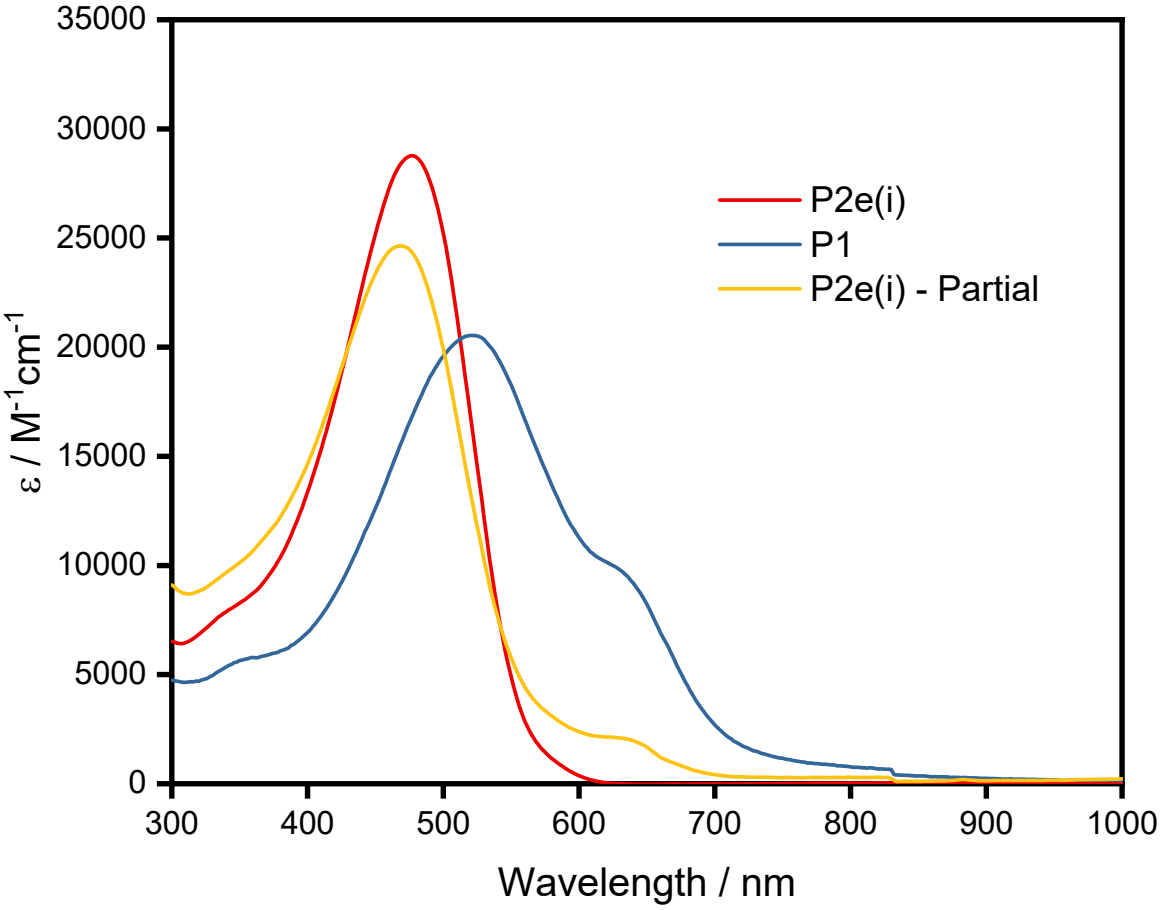


Figure S1: UV Spectra of P1 reacted with 1 eq of arylalkyne (**P2e(i) partial**) and 10 eq of aryl alkyne (**P2e(i)**).

UV spectra of polymers with addition of TFA

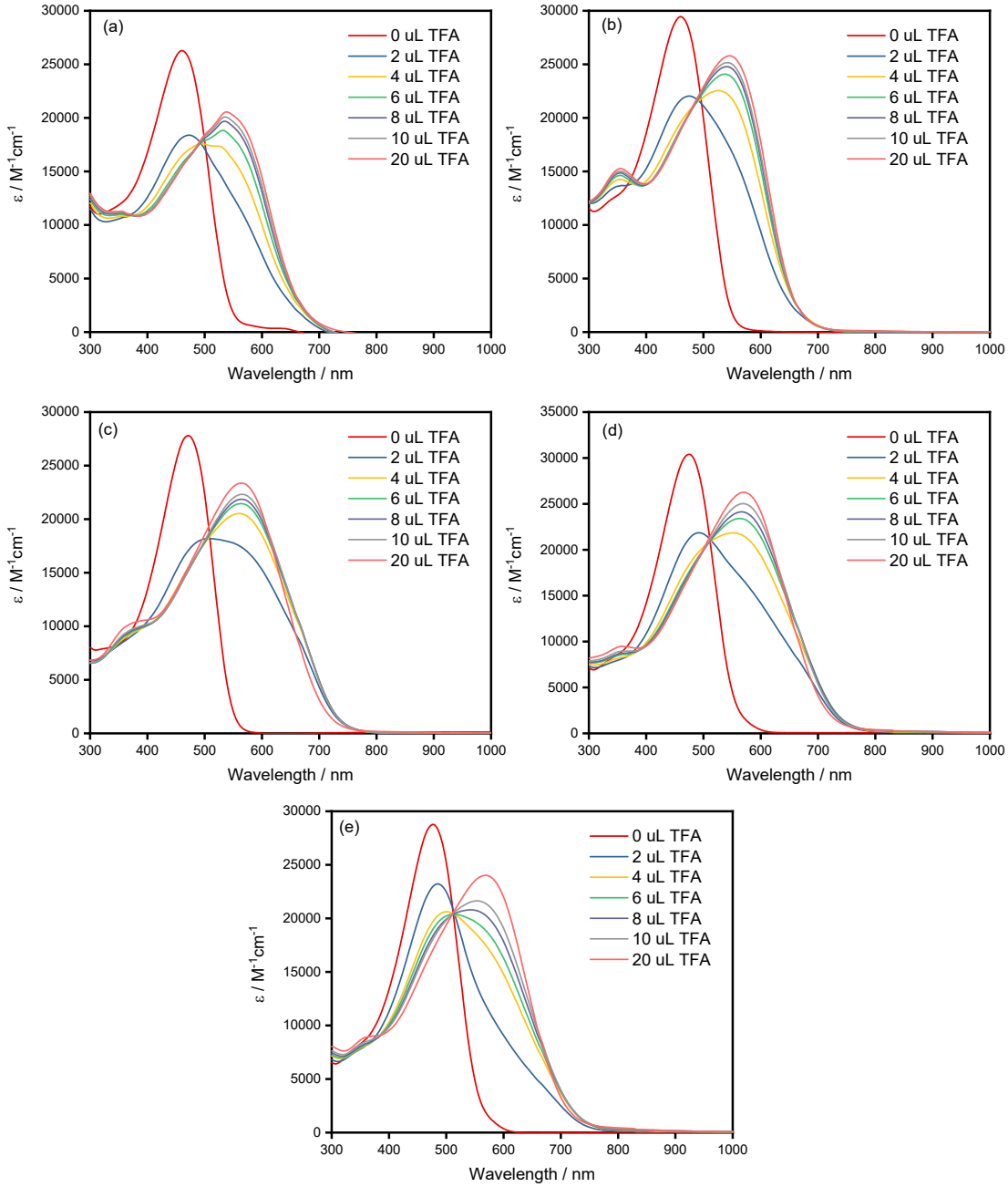


Figure S2: UV Spectra of polymers with iterative addition of TFA. (a) **P2a(i)**. (b) **P2b(i)**. (c) **P2c(i)**. (d) **P2d(i)**. (e) **P2e(i)**.

Fluorescence quenching of polymers with metal ions

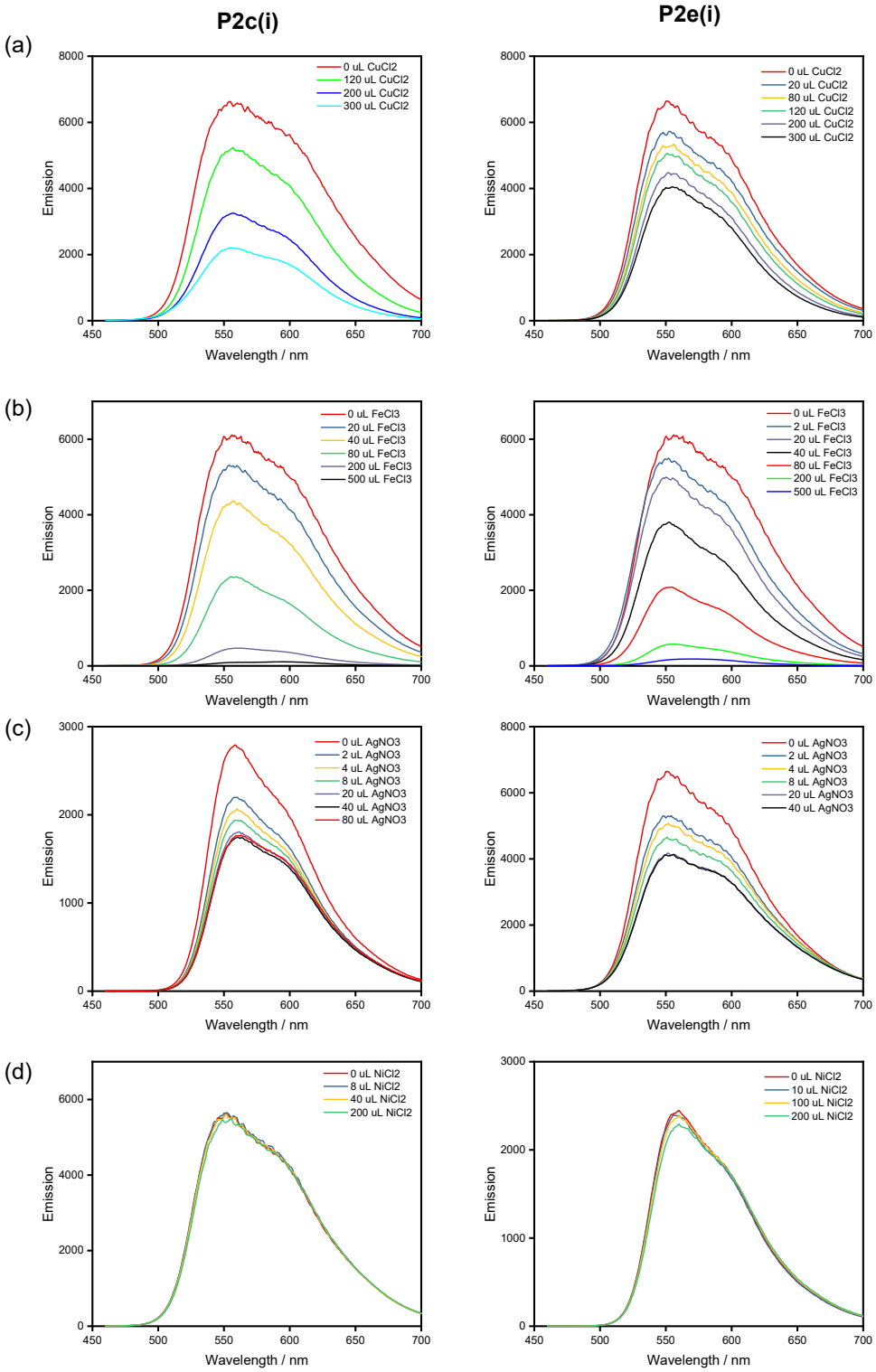
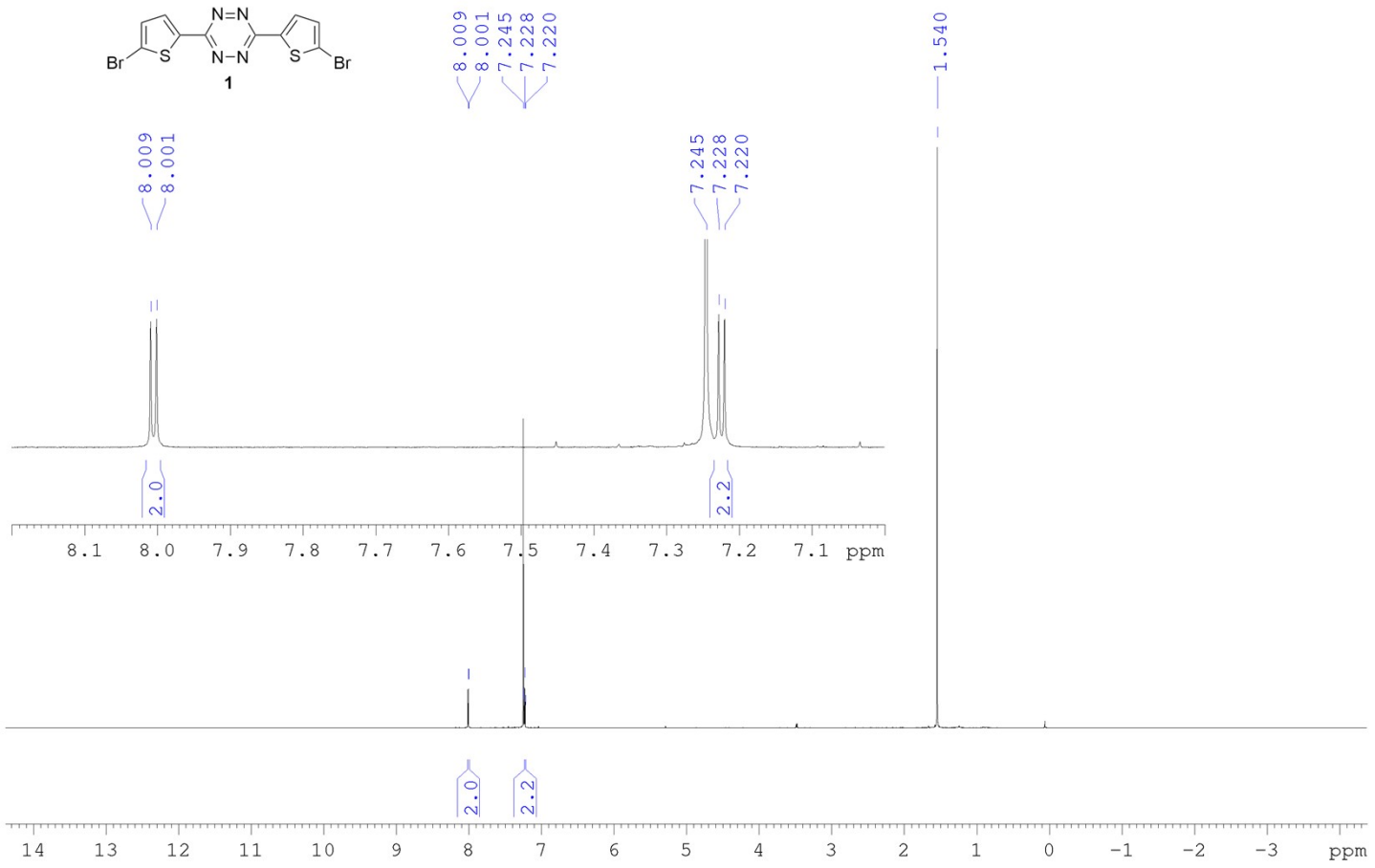


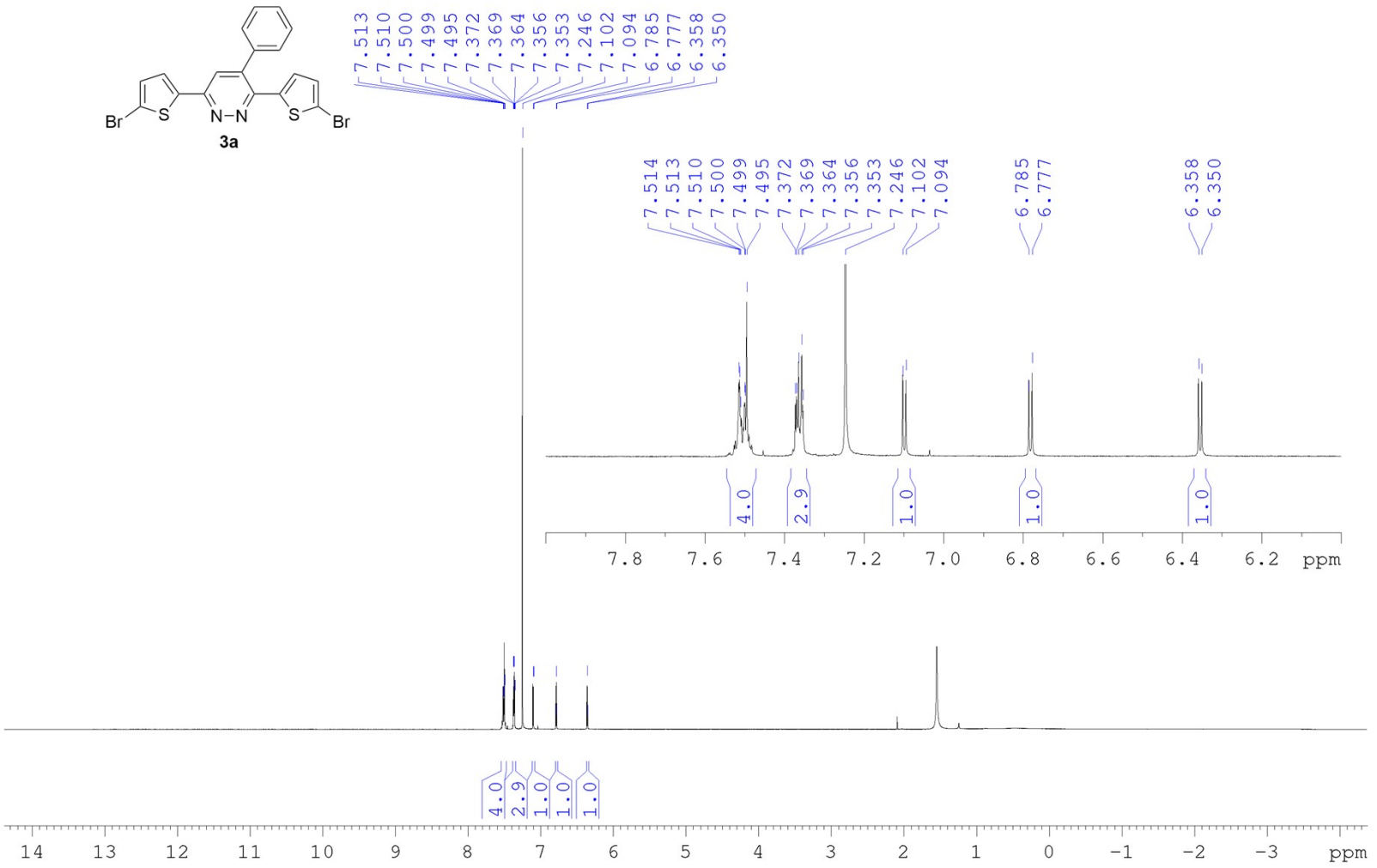
Figure S3: Emission spectra of polymers with iterative addition of metal ions. Left: **P2c(i)**, right: **P2e(i)**. (a) Addition of $CuCl_2$, (b) $FeCl_3$, (c) $AgNO_3$, (d) $NiCl_2$. All metal concentrations were 100 $mgmL^{-1}$ in water. Measurements were conducted in THF with a concentration of ~ 2.5 X 10^{-5} M.

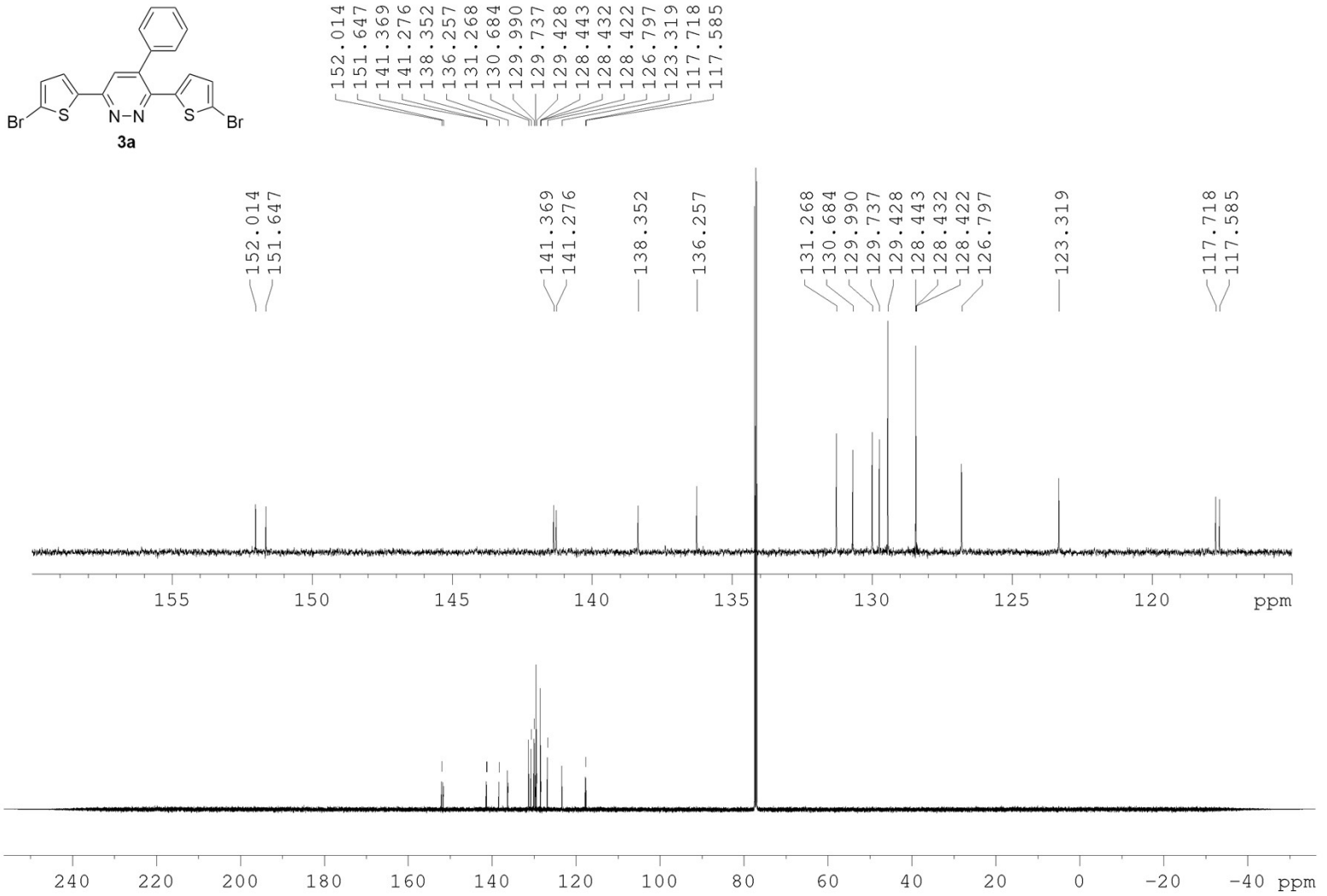
References

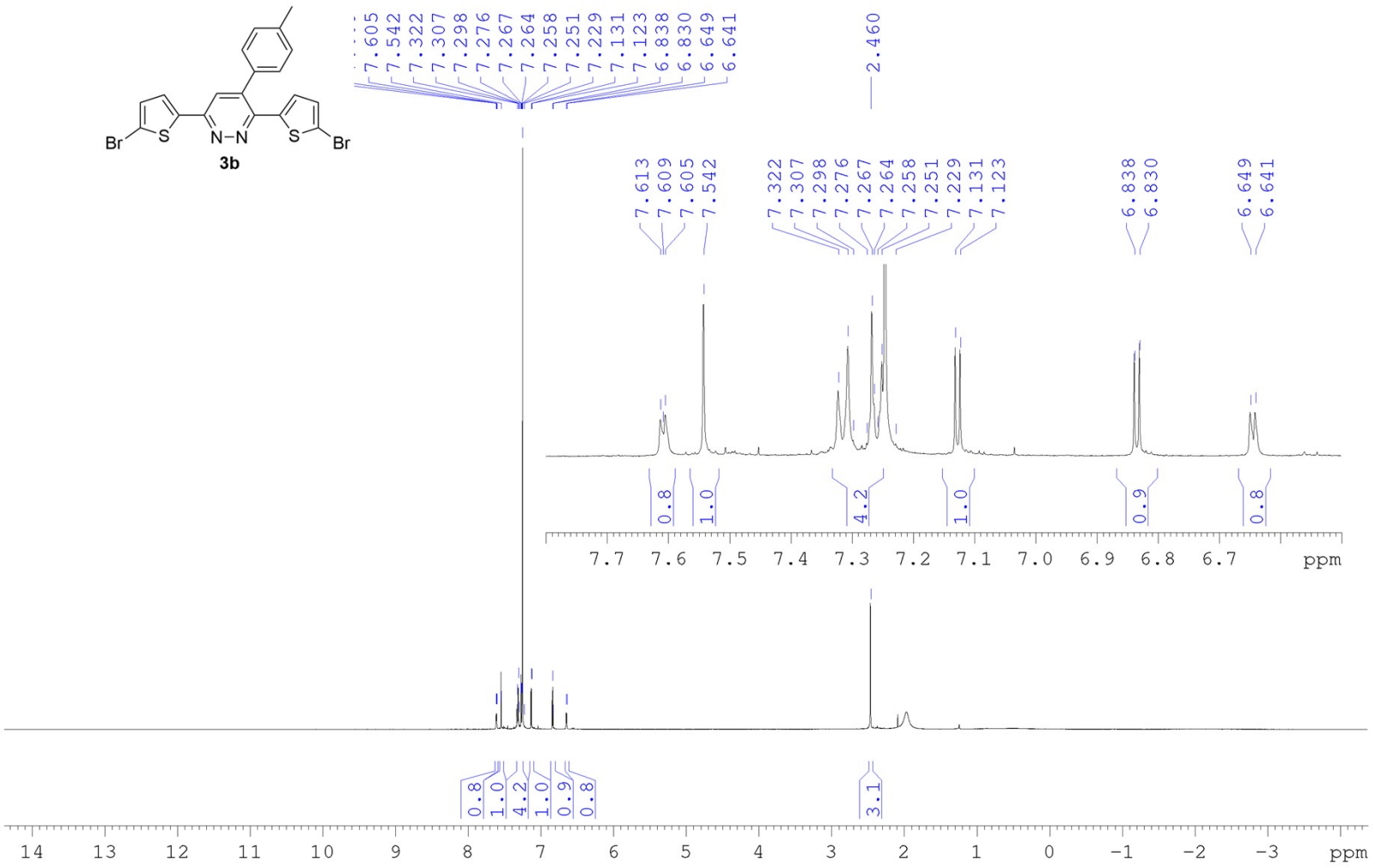
1 Q. Ye, W. T. Neo, C. M. Cho, S. W. Yang, T. Lin, H. Zhou, H. Yan, X. Lu, C. Chi and J. Xu, *Org. Lett.*, 2014, **16**, 6386–6389.

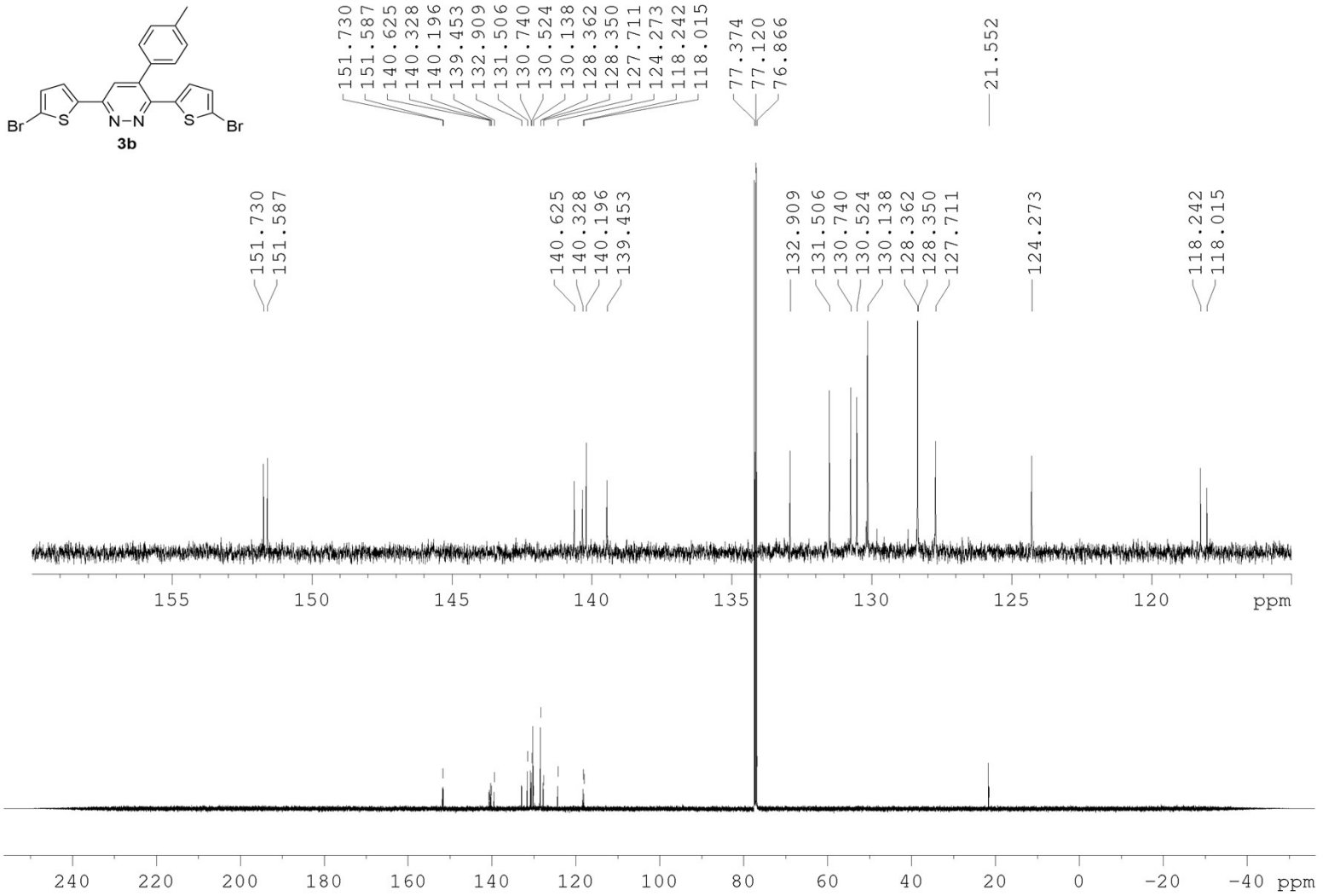
Appendix A: ^{1}H, ^{13}C and ^{19}F NMR spectra

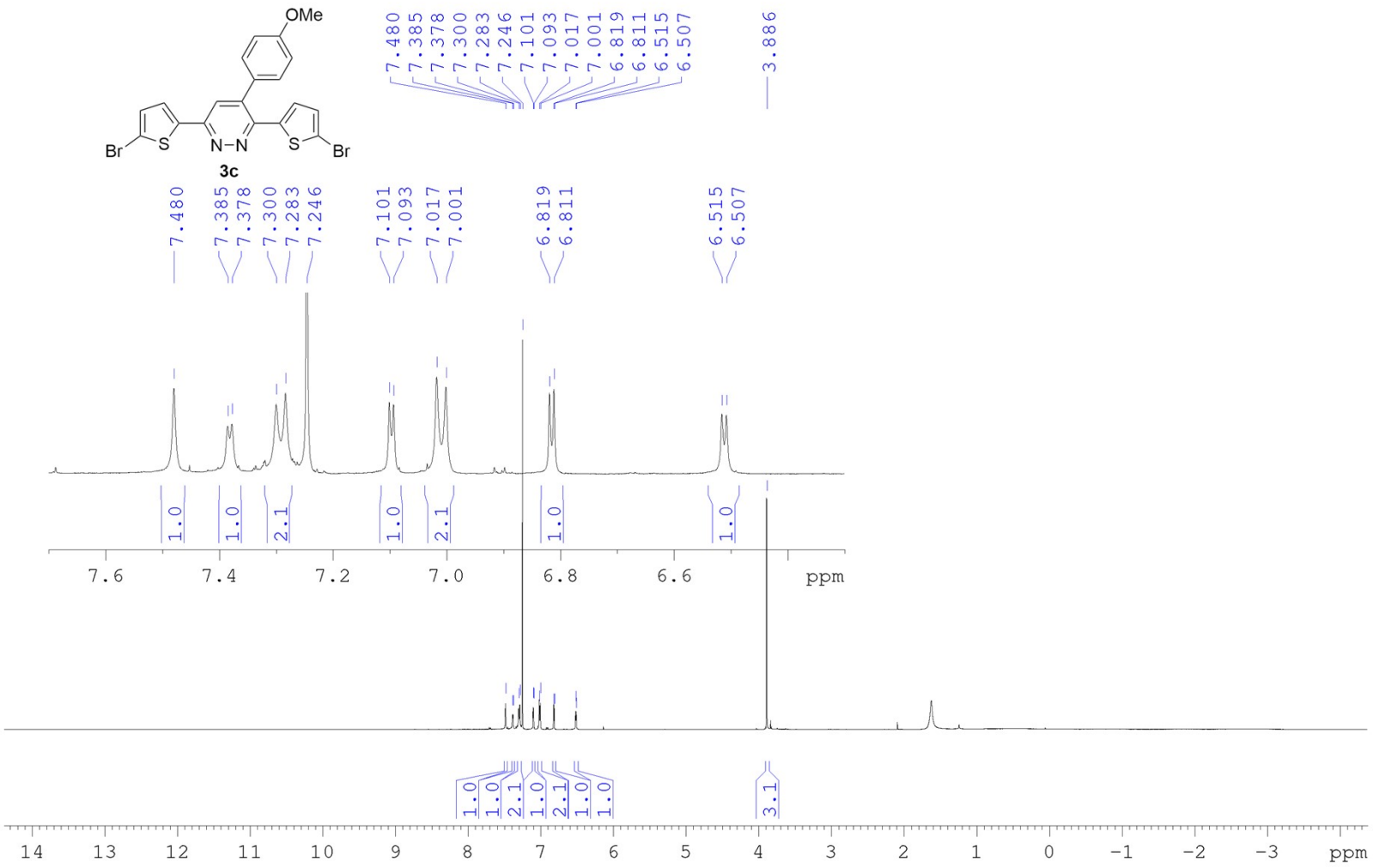


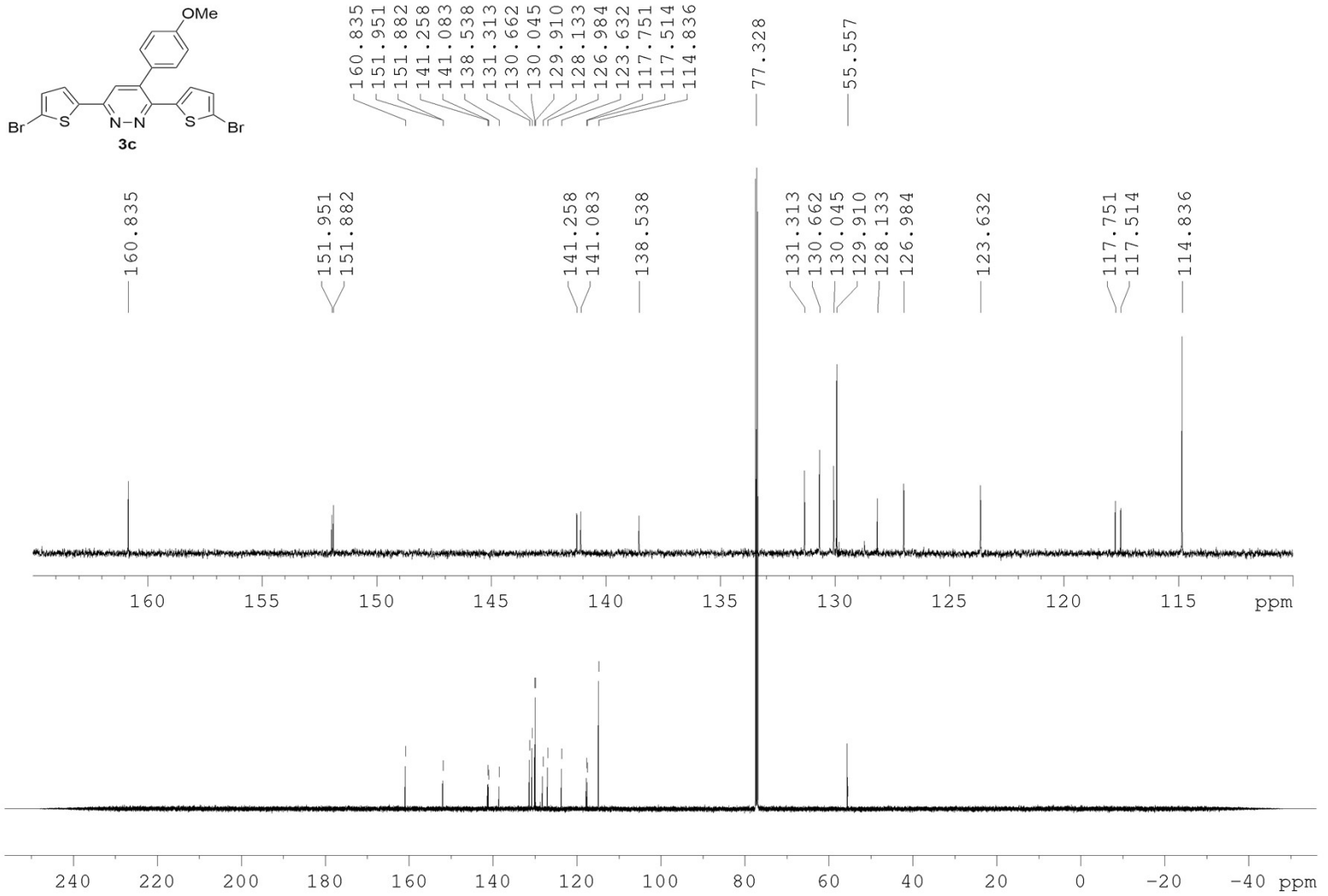

Br
S
N–N
S
Br
3a
7.513
7.510
7.500
7.499
7.495
7.372
7.369
7.364
7.356
7.353
7.246
7.102
7.094
6.785
6.777
6.358
6.350
4.0
2.9
1.0
1.0
1.0
ppm

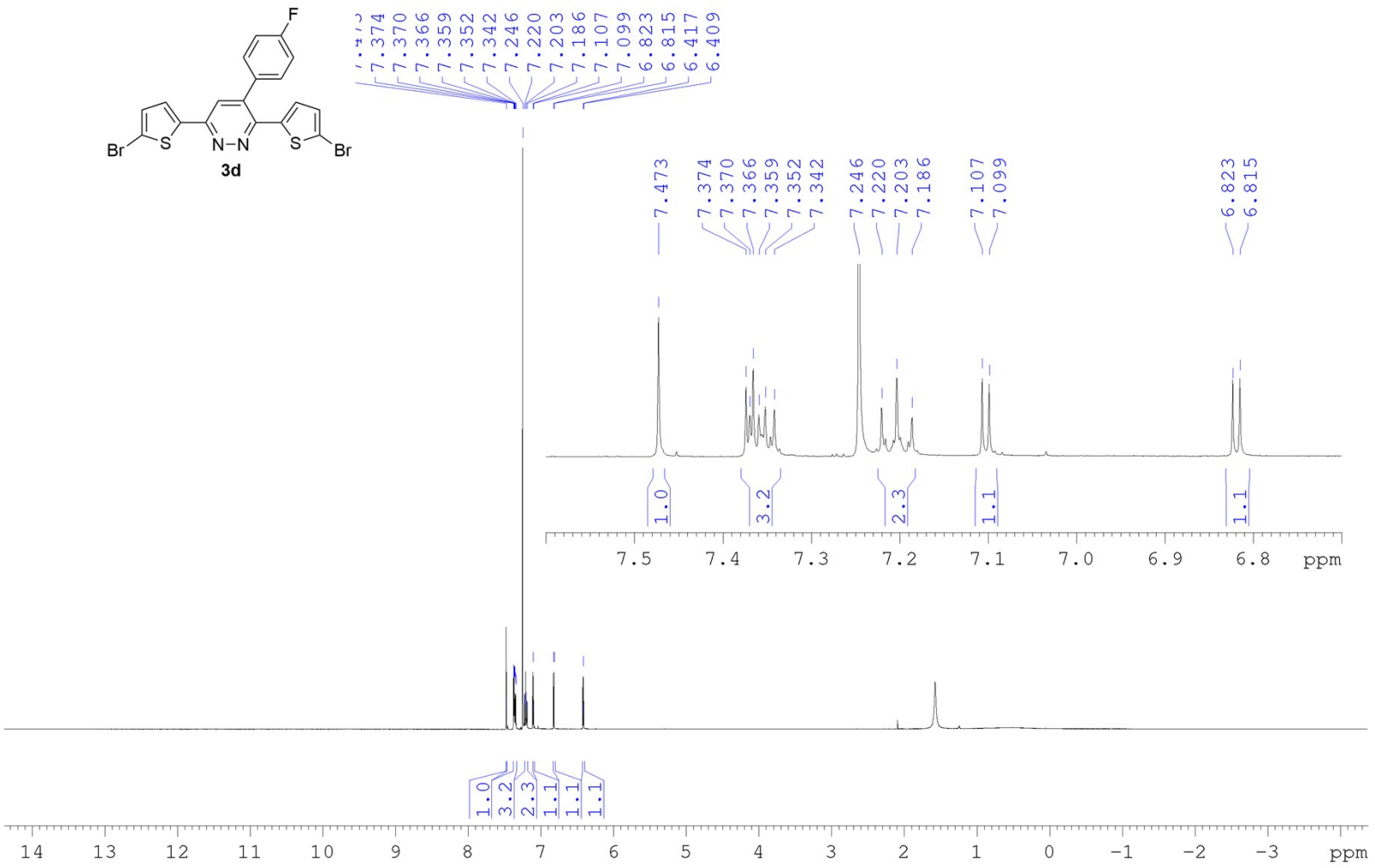

Br
S
N–N
S
Br
3a
152.014
151.647
141.369
141.276
138.352
136.257
131.268
130.684
129.990
129.737
129.428
128.443
128.432
128.422
126.797
123.319
117.718
117.585
155
150
145
140
135
130
125
120
ppm
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
ppm

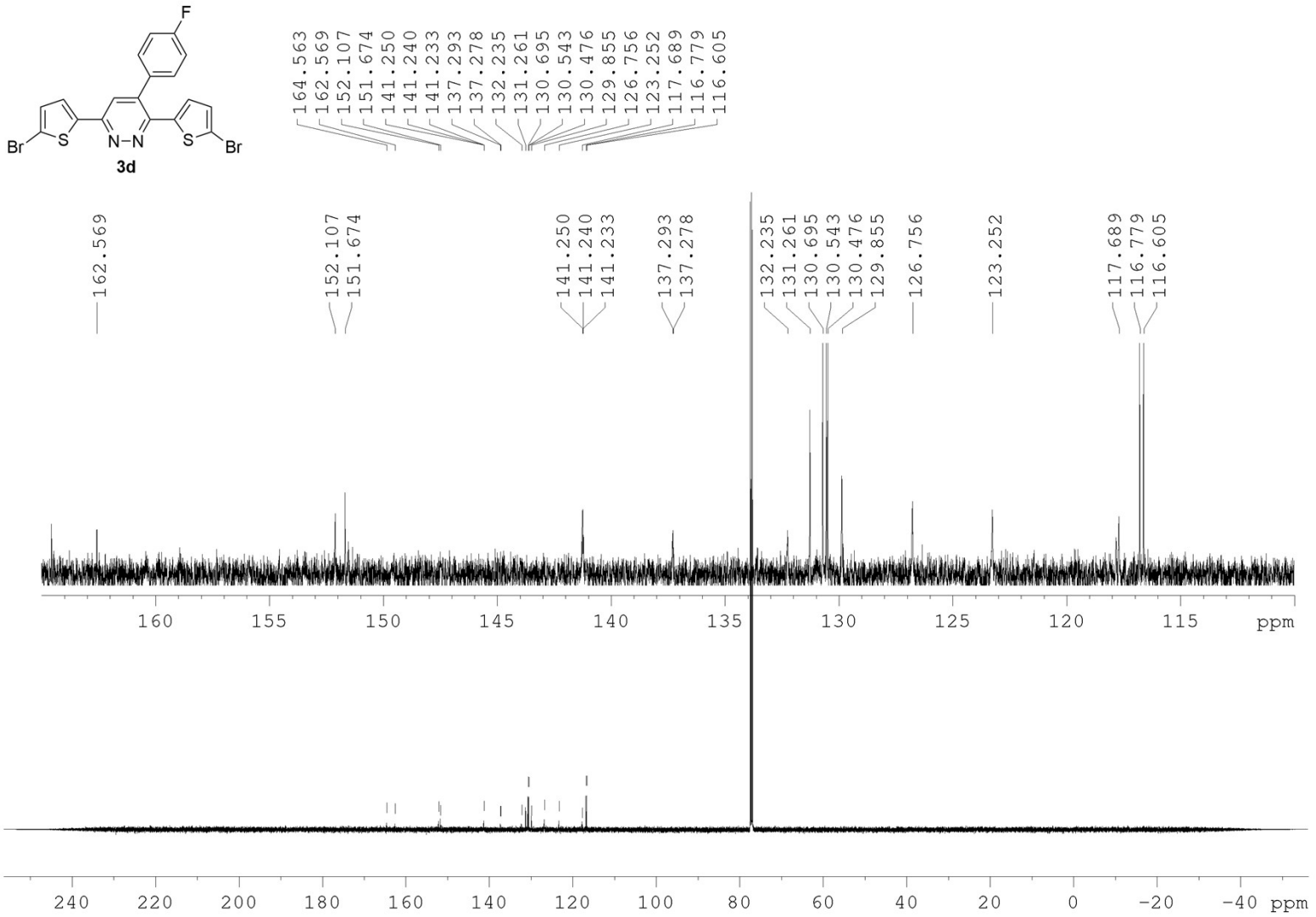

Br
S
N–N
S
Br
3b
7.605
7.542
7.322
7.307
7.298
7.276
7.267
7.264
7.258
7.251
7.229
7.131
7.123
6.838
6.830
6.649
6.641
2.460
7.613
7.609
7.605
7.542
7.322
7.307
7.298
7.276
7.267
7.264
7.258
7.251
7.229
7.131
7.123
6.838
6.830
6.649
6.641
0.8
1.0
4.2
1.0
0.9
0.8
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 ppm
0.8
1.0
4.2
1.0
0.9
0.8
3.1
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 ppm

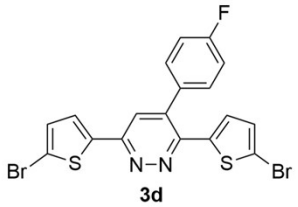

Br
S
N–N
S
Br
3b
151.730
151.587
140.625
140.328
140.196
139.453
132.909
131.506
130.740
130.524
130.138
128.362
128.350
127.711
124.273
118.242
118.015
77.374
77.120
76.866
21.552
155
150
145
140
135
130
125
120
ppm
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
ppm


OMe
Br
S
N–N
S
Br
3c
7.480
7.385
7.378
7.300
7.283
7.246
7.101
7.093
7.017
7.001
6.819
6.811
6.515
6.507
3.886
1.0
1.0
2.1
1.0
2.1
1.0
1.0
7.6
7.4
7.2
7.0
6.8
6.6
ppm
1.0
1.0
2.1
1.0
2.1
1.0
1.0
3.1
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
ppm


OMe
Br
S
N–N
S
Br
3c
160.835
151.951
151.882
141.258
141.083
138.538
131.313
130.662
130.045
129.910
128.133
126.984
123.632
117.751
117.514
114.836
77.328
55.557
ppm
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40

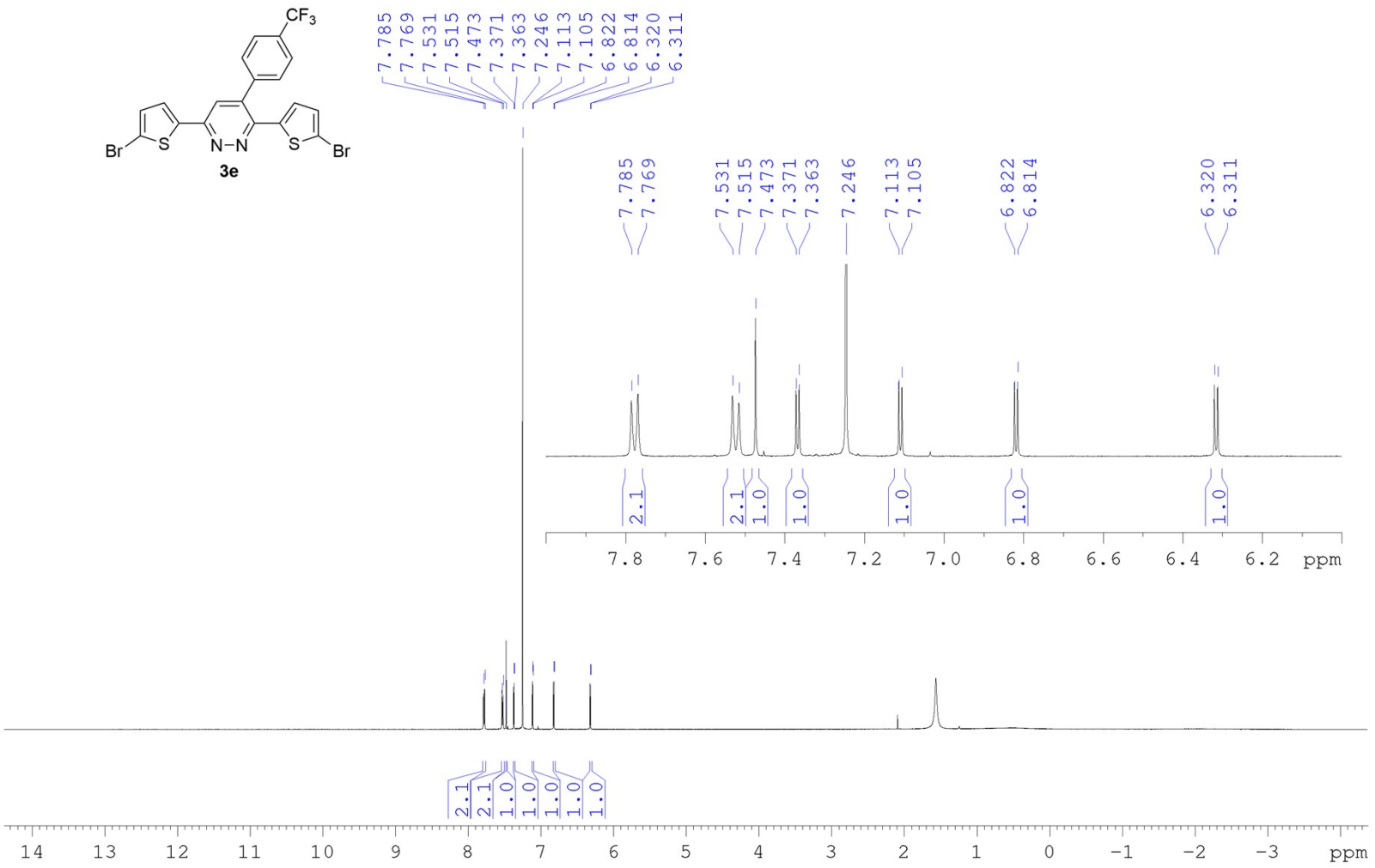

F
Br
S
N–N
S
Br
3d
7.473
7.374
7.370
7.366
7.359
7.352
7.342
7.246
7.220
7.203
7.186
7.107
7.099
6.823
6.815
6.417
6.409
1.0
3.2
2.3
1.1
1.1
1.1
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
ppm
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
ppm

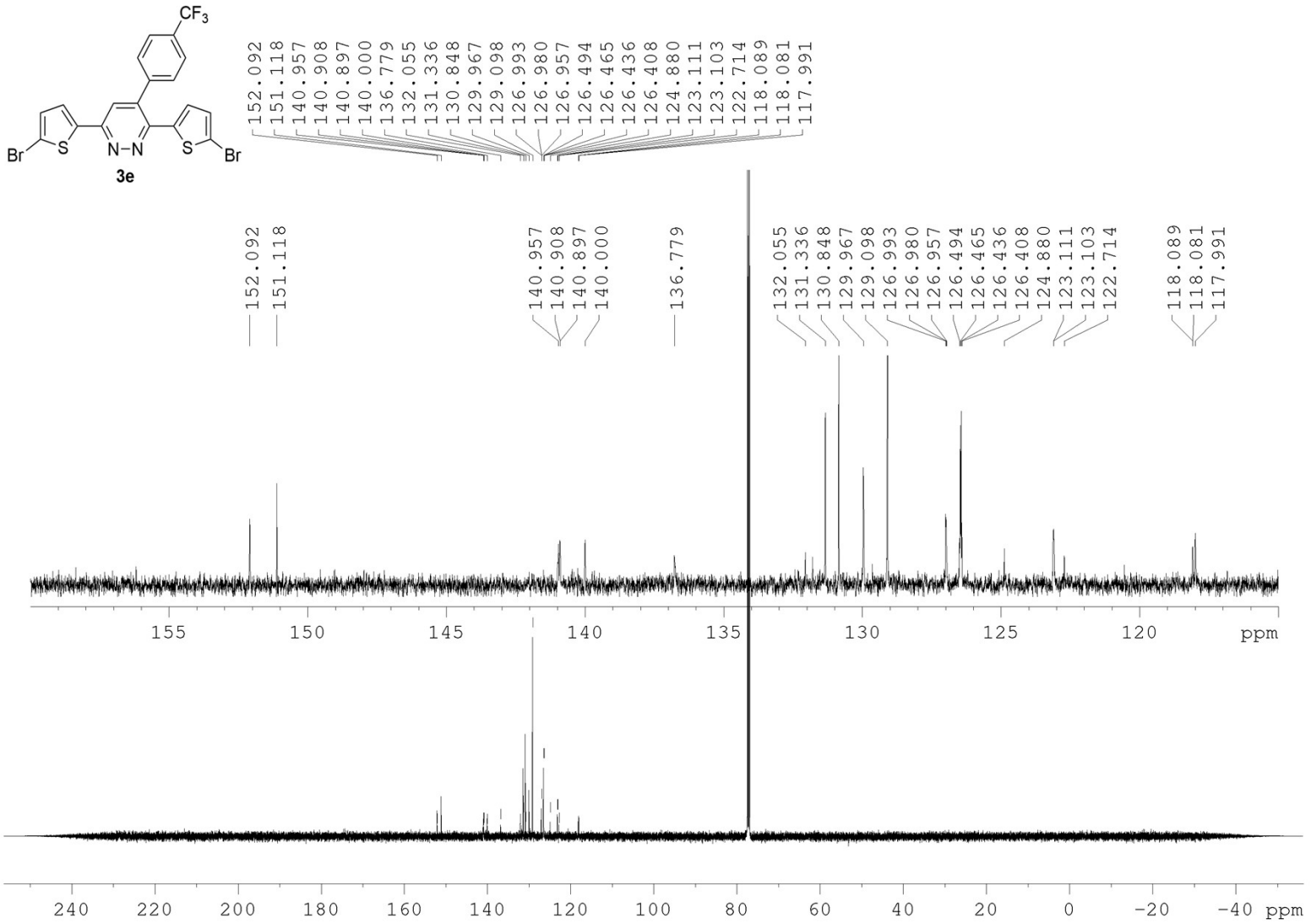

F
Br
S
N–N
S
Br
3d
164.563
162.569
152.107
151.674
141.250
141.240
141.233
137.293
137.278
132.235
131.261
130.695
130.543
130.476
129.855
126.756
123.252
117.689
116.779
116.605
160
155
150
145
140
135
130
125
120
115
ppm
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
ppm

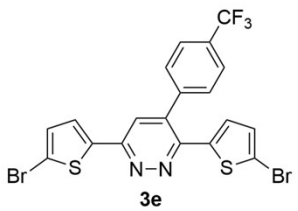

F
Br
S
N–N
S
Br

3d

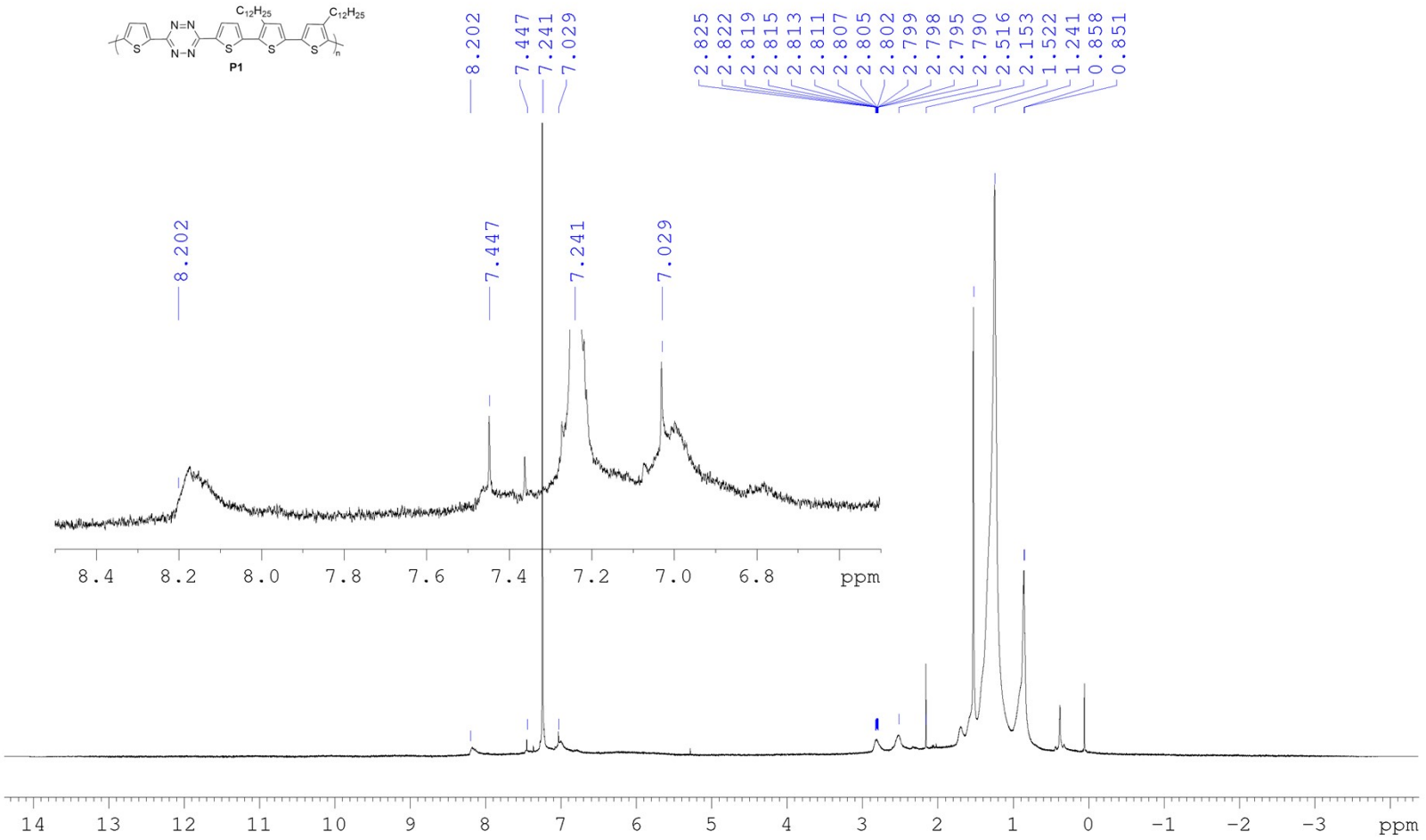
-110.602
-110.609
-110.620
-110.631
-110.638
100
50
0
-50
-100
-150
-200
-250
-300
ppm

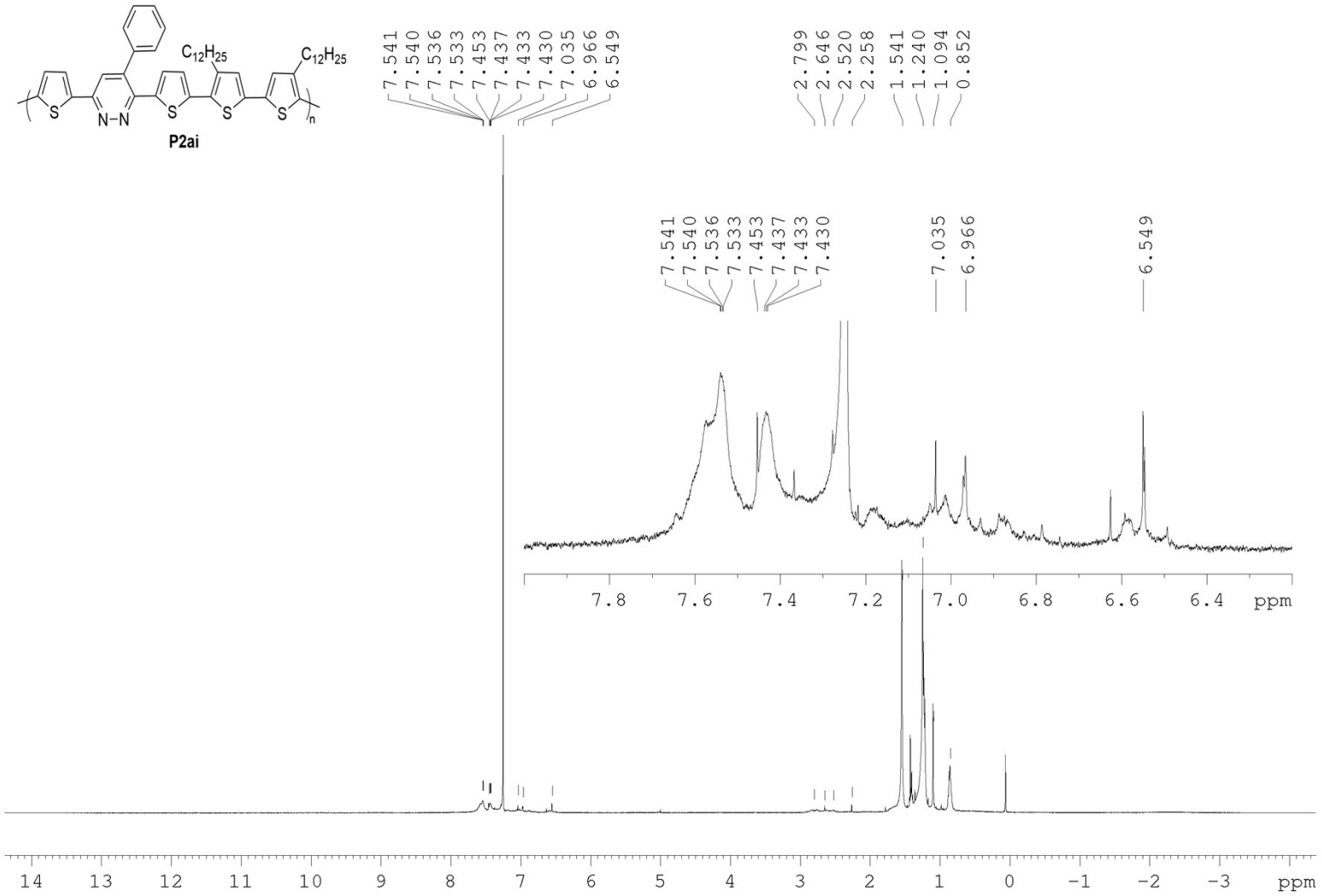

CF3
Br
S
N–N
S
Br
3e
7.785
7.769
7.531
7.515
7.473
7.371
7.363
7.246
7.113
7.105
6.822
6.814
6.320
6.311
2.1
2.1
1.0
1.0
1.0
1.0
1.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
ppm
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
ppm

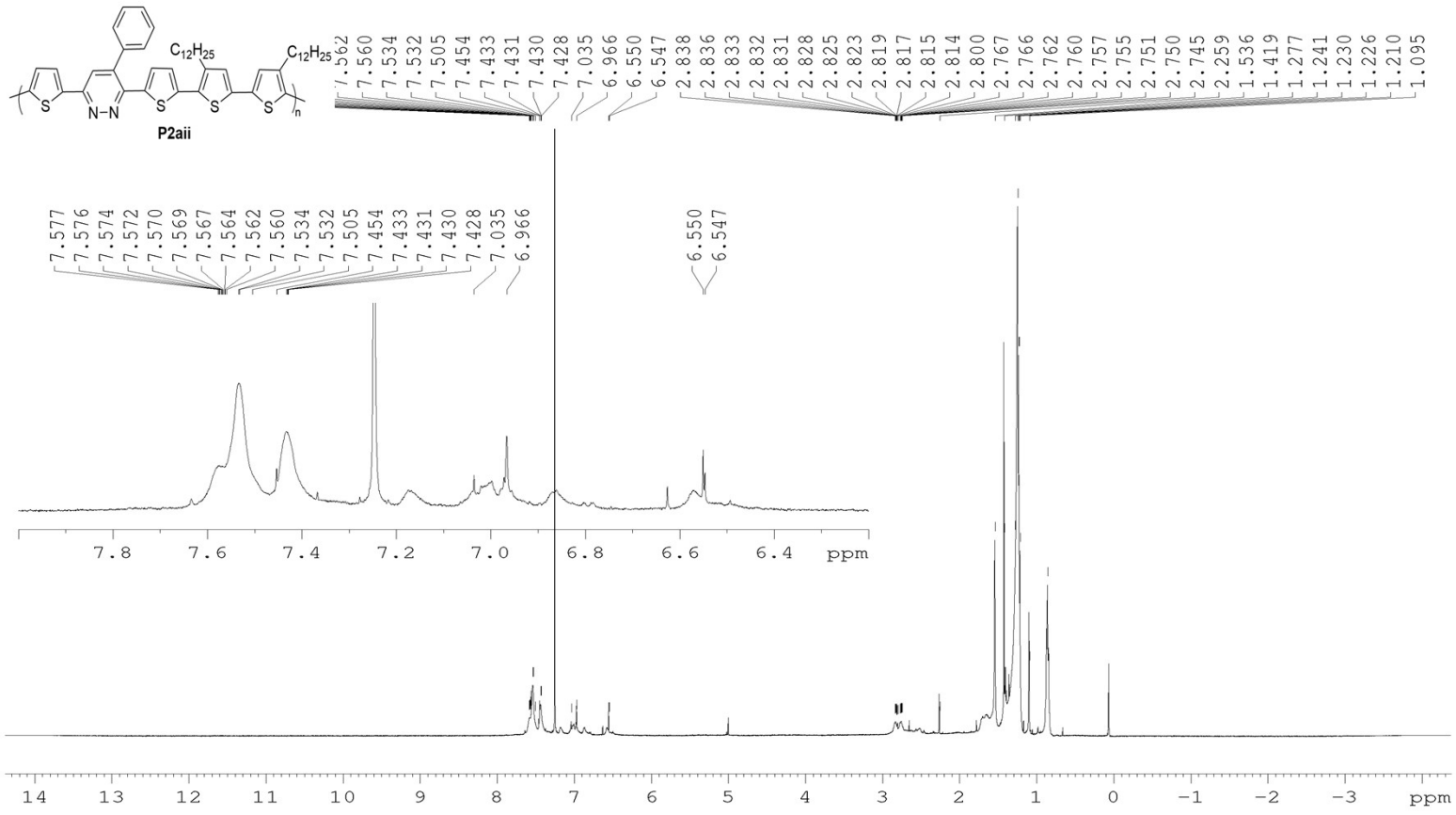

CF3
Br
S
N–N
S
Br
3e
152.092
151.118
140.957
140.908
140.897
140.000
136.779
132.055
131.336
130.848
129.967
129.098
126.993
126.980
126.957
126.494
126.465
126.436
126.408
124.880
123.111
123.103
122.714
118.089
118.081
117.991
155
150
145
140
135
130
125
120
ppm
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
ppm

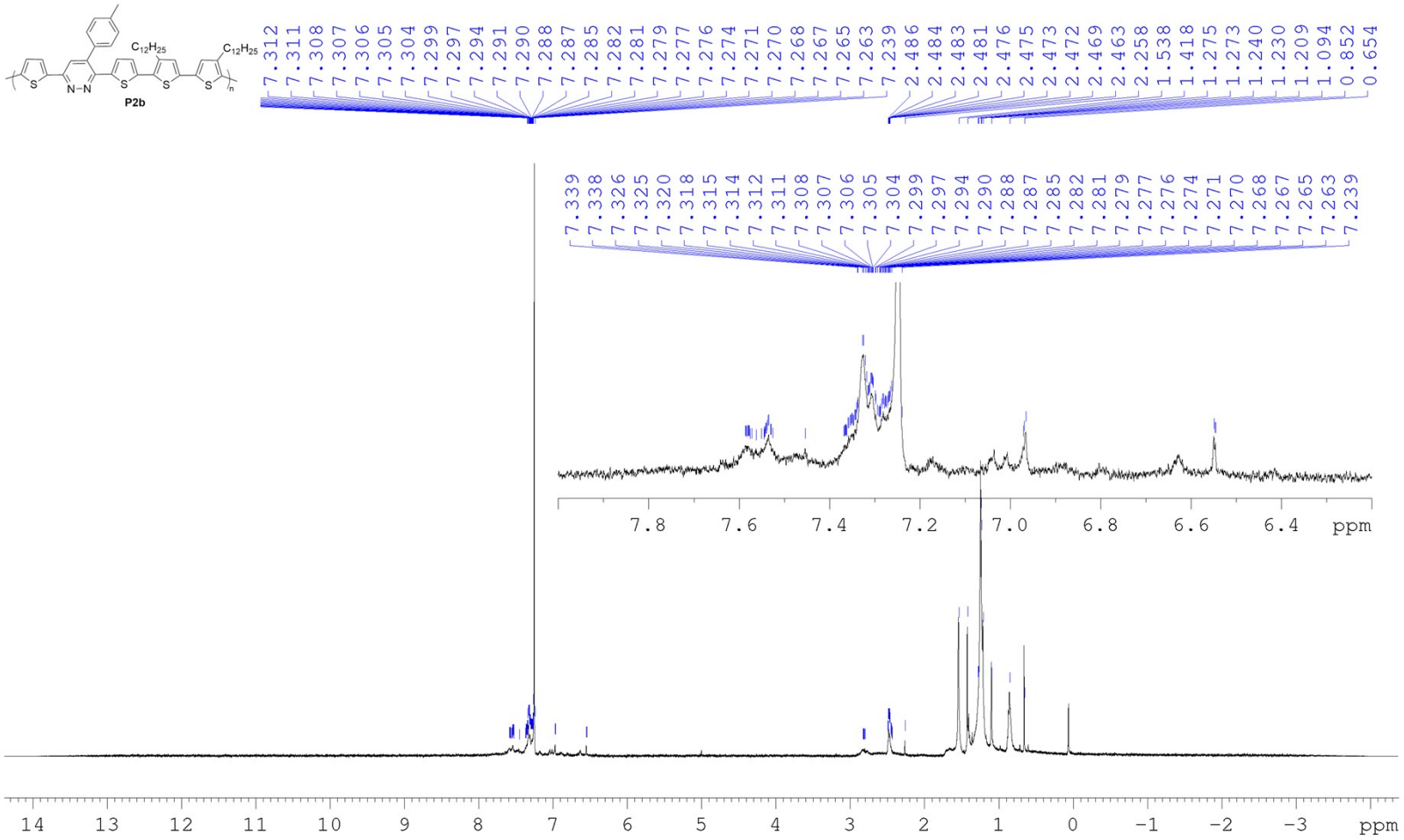


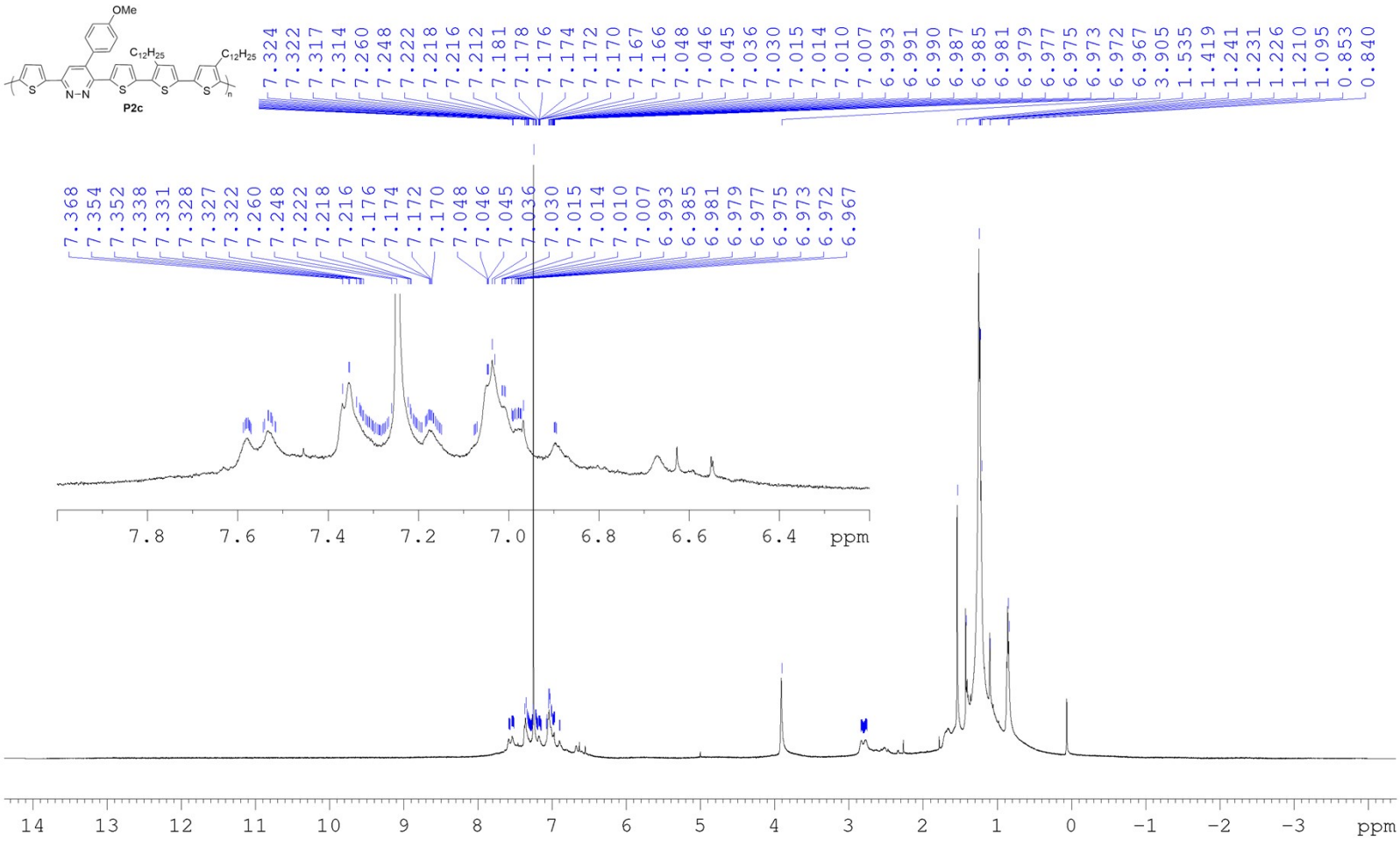
3e

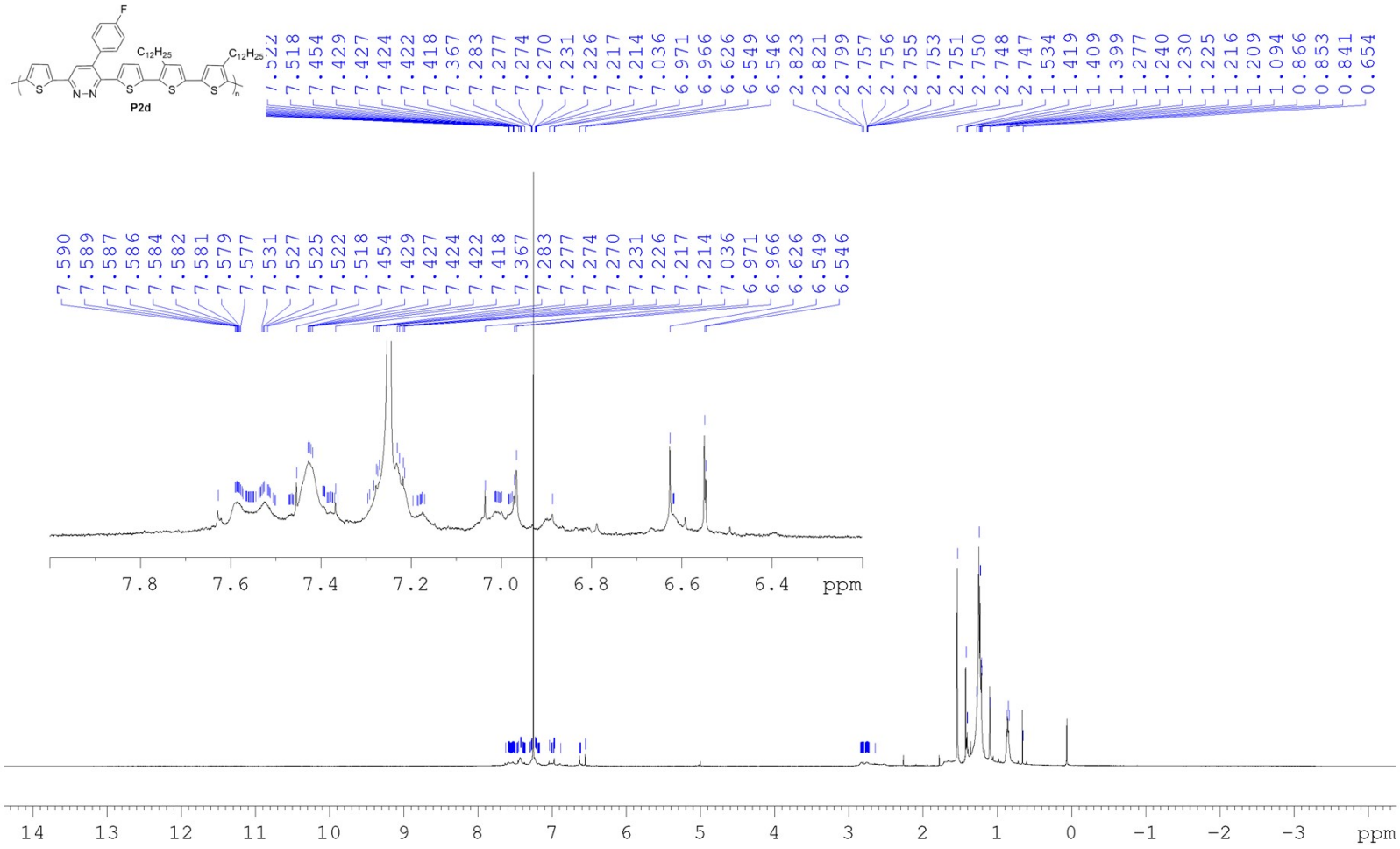

P1
8.202
7.447
7.241
7.029
2.825
2.822
2.819
2.815
2.813
2.811
2.807
2.805
2.802
2.799
2.798
2.795
2.790
2.516
2.153
1.522
1.241
0.858
0.851
ppm
ppm

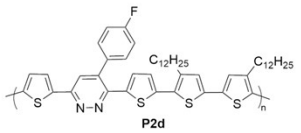

C12H25
C12H25
S
N–N
S
S
S
n
P2ai
7.541
7.540
7.536
7.533
7.453
7.437
7.433
7.430
7.035
6.966
6.549
2.799
2.646
2.520
2.258
1.541
1.240
1.094
0.852
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
ppm
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
ppm


P2aii
7.562
7.560
7.534
7.532
7.505
7.454
7.433
7.431
7.430
7.428
7.035
6.966
6.550
6.547
2.838
2.836
2.833
2.832
2.831
2.828
2.825
2.823
2.819
2.817
2.815
2.814
2.800
2.767
2.766
2.762
2.760
2.757
2.755
2.751
2.750
2.745
2.259
1.536
1.419
1.277
1.241
1.230
1.226
1.210
1.095
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
ppm
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
ppm


P2b
7.312
7.311
7.308
7.307
7.306
7.305
7.304
7.299
7.297
7.294
7.291
7.290
7.288
7.287
7.285
7.282
7.281
7.279
7.277
7.276
7.274
7.271
7.270
7.268
7.267
7.265
7.263
7.239
2.486
2.484
2.483
2.481
2.476
2.475
2.473
2.472
2.469
2.463
2.258
1.538
1.418
1.275
1.273
1.240
1.230
1.209
1.094
0.852
0.654
7.339
7.338
7.326
7.325
7.320
7.318
7.315
7.314
7.312
7.311
7.308
7.307
7.306
7.305
7.304
7.299
7.297
7.294
7.290
7.288
7.287
7.285
7.282
7.281
7.279
7.277
7.276
7.274
7.271
7.270
7.268
7.267
7.265
7.263
7.239
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
ppm
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
ppm

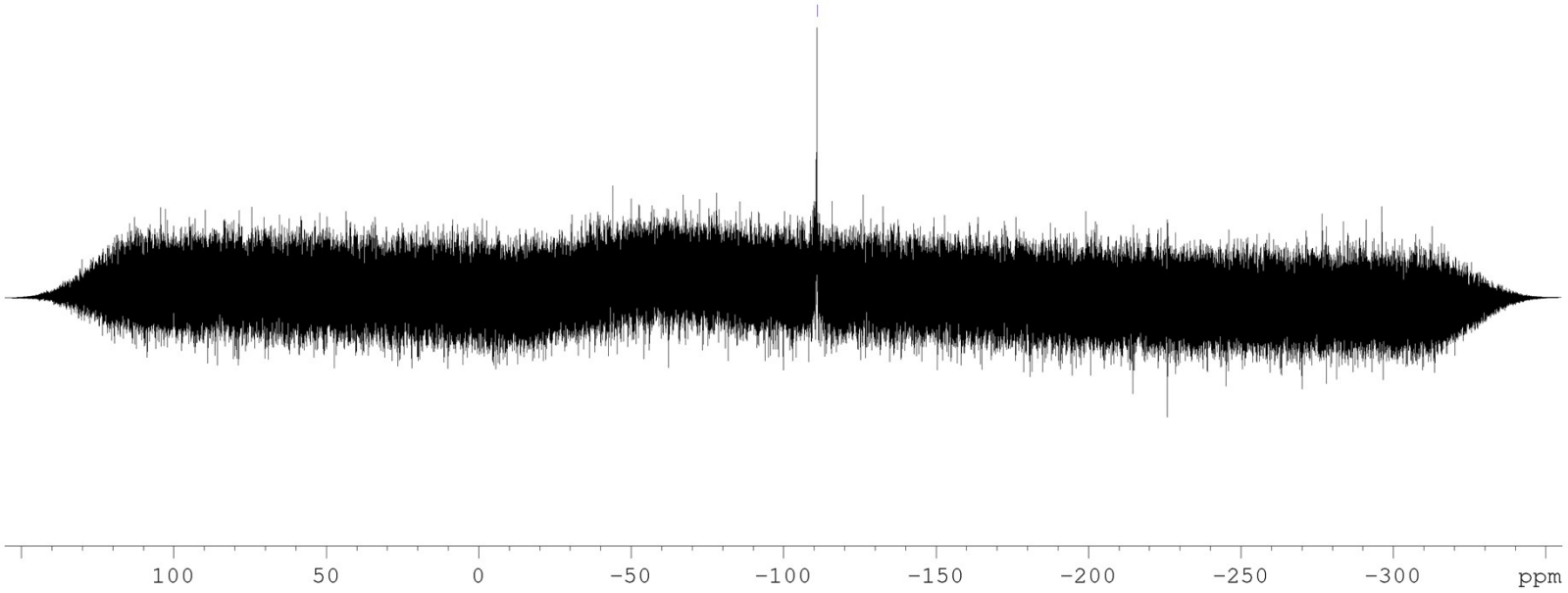

OMe
C12H25
C12H25
N–N
S
n
P2c
7.324
7.322
7.317
7.314
7.260
7.248
7.222
7.218
7.216
7.212
7.181
7.178
7.176
7.174
7.172
7.170
7.167
7.166
7.048
7.046
7.045
7.036
7.030
7.015
7.014
7.010
7.007
6.993
6.991
6.990
6.987
6.985
6.981
6.979
6.977
6.975
6.973
6.972
6.967
3.905
1.535
1.419
1.241
1.231
1.226
1.210
1.095
0.853
0.840
7.368
7.354
7.352
7.338
7.331
7.328
7.327
7.322
7.260
7.248
7.222
7.218
7.216
7.176
7.174
7.172
7.170
7.048
7.046
7.045
7.036
7.030
7.015
7.014
7.010
7.007
6.993
6.985
6.981
6.979
6.977
6.975
6.973
6.972
6.967
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
ppm
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
ppm

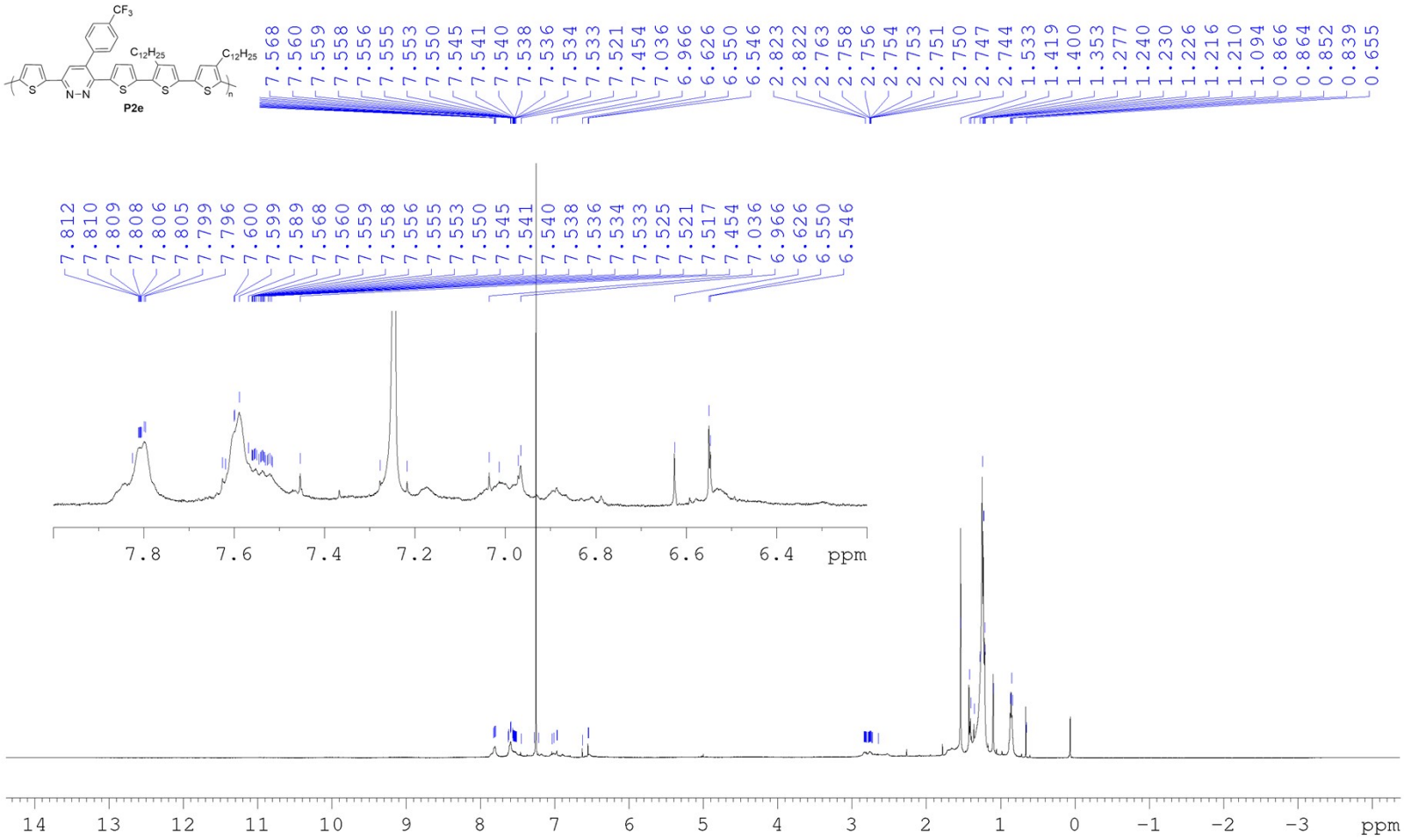

F
C12H25
C12H25
S
N–N
S
S
S
n
P2d
7.590
7.589
7.587
7.586
7.584
7.582
7.581
7.579
7.577
7.531
7.527
7.525
7.522
7.518
7.454
7.429
7.427
7.424
7.422
7.418
7.367
7.283
7.277
7.274
7.270
7.231
7.226
7.217
7.214
7.036
6.971
6.966
6.626
6.549
6.546
2.823
2.821
2.799
2.757
2.756
2.755
2.753
2.751
2.750
2.748
2.747
1.534
1.419
1.409
1.399
1.277
1.240
1.230
1.225
1.216
1.209
1.094
0.866
0.853
0.841
0.654
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
ppm
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
ppm

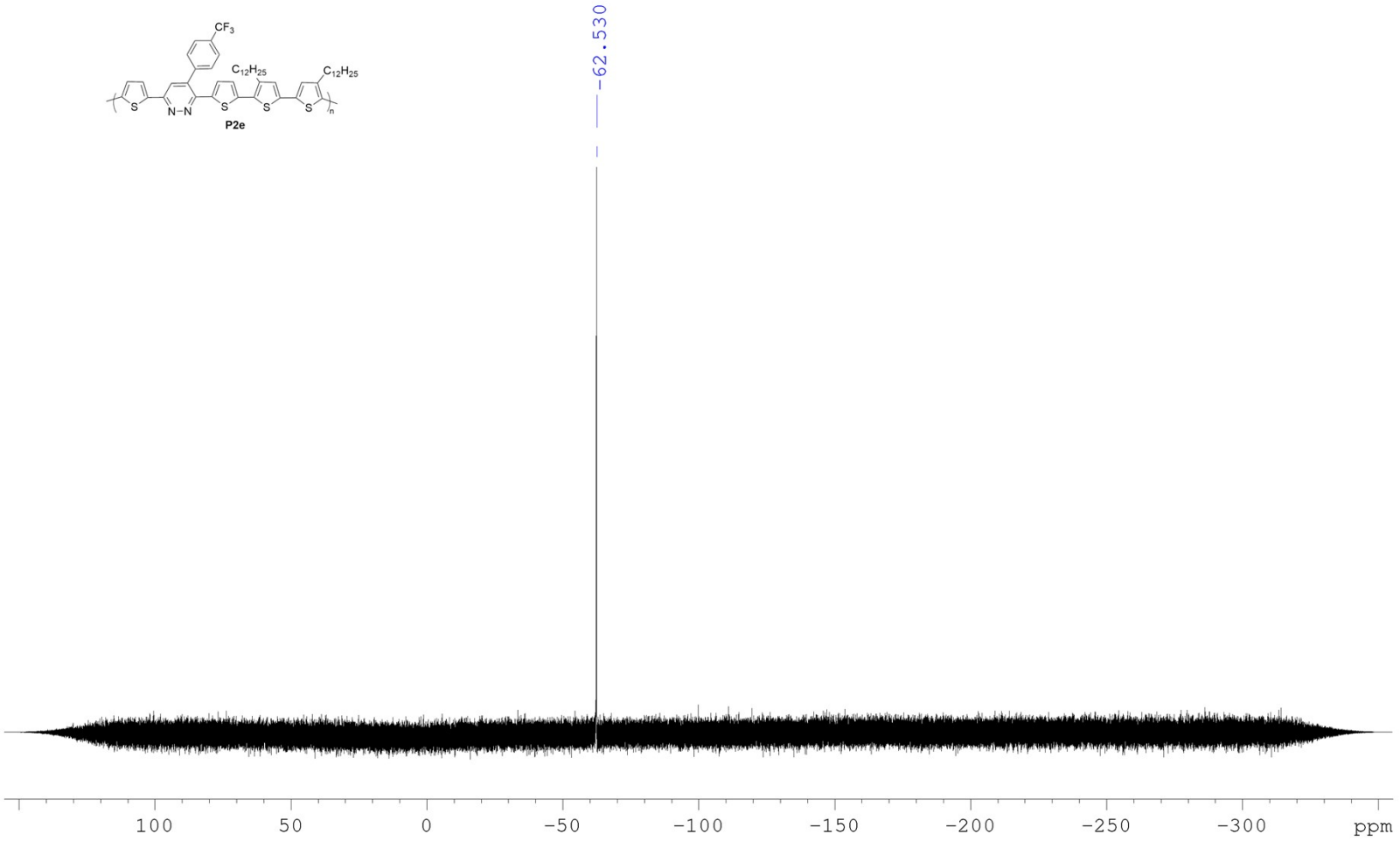


P2d

-111.067
-111.073
-111.079
-111.083
-111.088
-111.094




CF3
C12H25
C12H25
N-N
S
S
S
n
P2e
7.568
7.560
7.559
7.558
7.556
7.555
7.553
7.550
7.545
7.541
7.540
7.538
7.536
7.534
7.533
7.521
7.454
7.036
6.966
6.626
6.550
6.546
2.823
2.822
2.763
2.758
2.756
2.754
2.753
2.751
2.750
2.747
2.744
1.533
1.419
1.400
1.353
1.277
1.240
1.230
1.226
1.216
1.210
1.094
0.866
0.864
0.852
0.839
0.655
7.812
7.810
7.809
7.808
7.806
7.805
7.799
7.796
7.600
7.599
7.589
7.568
7.560
7.559
7.558
7.556
7.555
7.553
7.550
7.545
7.541
7.540
7.538
7.536
7.534
7.533
7.525
7.521
7.517
7.454
7.036
6.966
6.626
6.550
6.546
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
ppm
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
ppm


CF3
C12H25
C12H25
S
N–N
S
S
S
n
P2e
-62.530
100
50
0
-50
-100
-150
-200
-250
-300
ppm