Supporting Information

Direct Synthesis of Pyrroles via Heterogeneous Catalytic Condensation of Anilines with Bioderived Furans

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1. Materials

1.1 Catalytic materials

H-ZSM-5 (18), H-BEA (12.5), H-MOR (12.5), H-Y (2.6), H-Y (3.2), H-Y (5) were supplied by NanKai University Catalyst Co. Ltd. (Tianjin, China). CeO_2 was supplied by Evonik. MgO was supplied by Alfa Aesar. Commercially available reagents and solvents (Sigma-Aldrich) were used with further purification.

1.2 Catalyst preparation

Preparation of ZrO_2: ZrO_2 powder was prepared by a conventional precipitation method following the reported procedure.[S1] Briefly, 12.9 g $ZrOCl_2 \cdot 8H_2O$ was dissolved in 200 mL deionized water at room temperature, the pH was adjusted to 9.0 by dropwise addition of $NH_3 \cdot H_2O$ (2.5 M). The resultant hydro gel was washed with deionized water until free of chloride ions. The precipitate was then dried at 110 ºC overnight and calcined at 400 ºC for 2 h in air. The BET surface area of the resultant material was 110 $m^2 \cdot g^{-1}$ (Micromeritics TriStar 3000). The crystal phase of ZrO_2 was composed of 56 % monoclinic phase and 44 % tetragonal phase.

Preparation of Nb_2O_5: Nb_2O_5 powder was prepared by calcination of niobium oxalate at 500 ºC for 4 h under air.[S2]

Preparation of SiO_2-Al_2O_3: SiO_2-Al_2O_3 powder was prepared by the addition of TEOS into water containing nitric acid, aluminium nitrate (Si/Al = 1) with vigorous stirring. After the solution became homogeneous it was sealed in a plastic container, and kept at 50 ºC for 20 h for gelation. The obtained gel was dried at 50 ºC for 1 week and then heated at 600 ºC for 2 h.[S3]

2. Supplementary Data

Table S1. The influence of acid strength on the yield of the target pyrrole.

Entry	Catalyst	Si/Al ratio	Desorption temperature of acid site type 1 (°C)	Desorption temperature of acid site type 2 (°C)	Pyrrole yield (%)
1	H-ZSM-5	18	213	412	34
2	H-MOR	12.5	196	419	9
3	H-BEA	12.5	193	314	63
4	H-Y	2.6	203	307	96
5		3.2	211	312	91
6		5	223	320	85

Table S2. The relative ratio of Brønsted acid to Lewis acid.

Entry	Catalyst	Si/Al ratio	B/L ratio	Pyrrole yield (%)
1	H-ZSM-5	18	1:1.04	34
2	H-MOR	12.5	1:0.63	9
3	H-BEA	12.5	1:5.49	63
4	H-Y	2.6	1:0.43	96
5		3.2	1:0.68	91
6		5	1:0.78	85

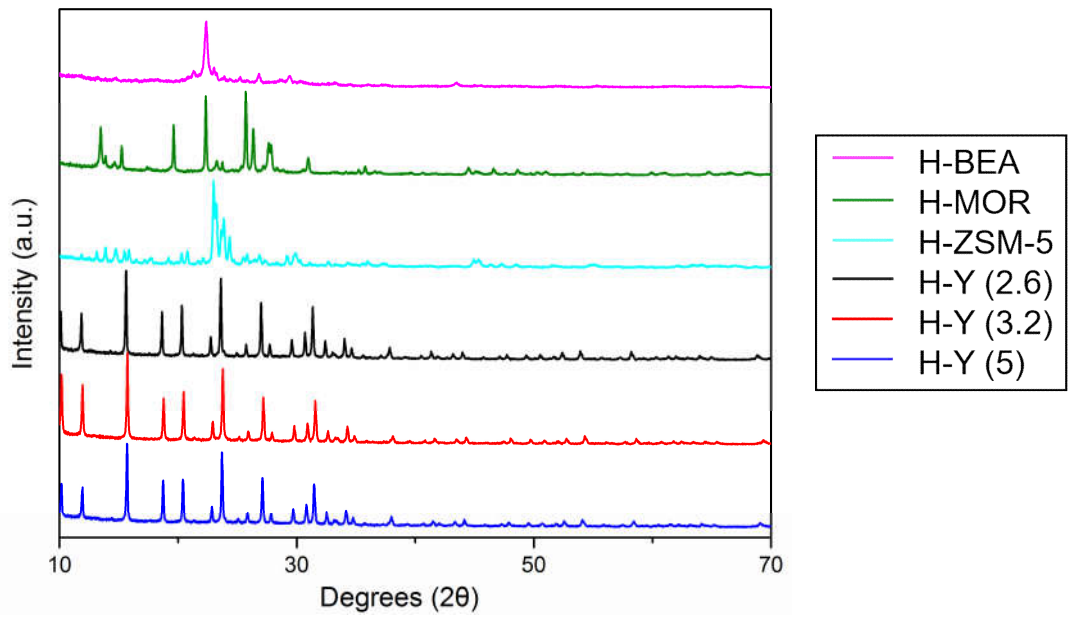


Figure S1. XRD patterns of various zeolite samples.

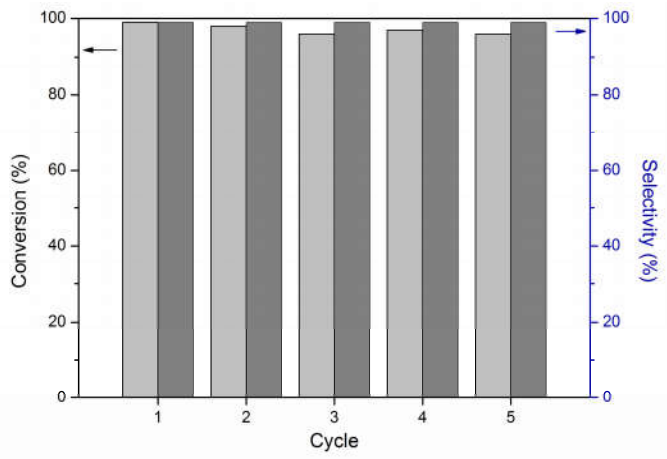


Figure S2. Recycling results of H-Y (2.6) in condensation of 2,5-dimethylfuran with *m*-methylaniline. Reaction conditions: 1 mmol 2,5-dimethylfuran, 1 mmol *m*-methylaniline, 2 mL toluene, 150 mg H-Y (2.6), 150 °C, 5 bar N_2, 0.7 h.

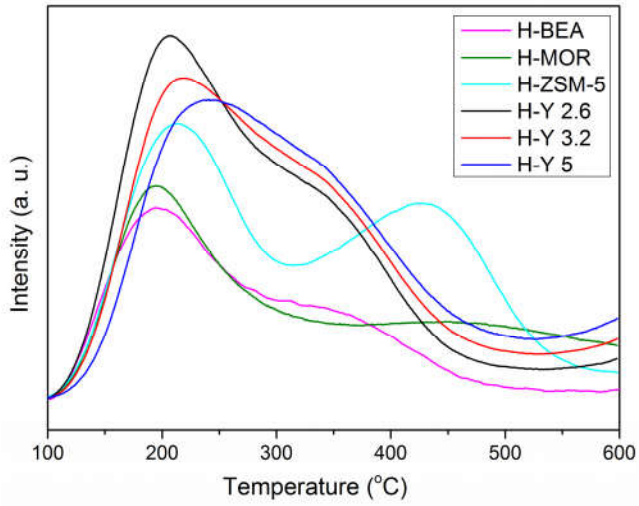


Figure S3. NH_3-TPD profiles of various zeolite samples.

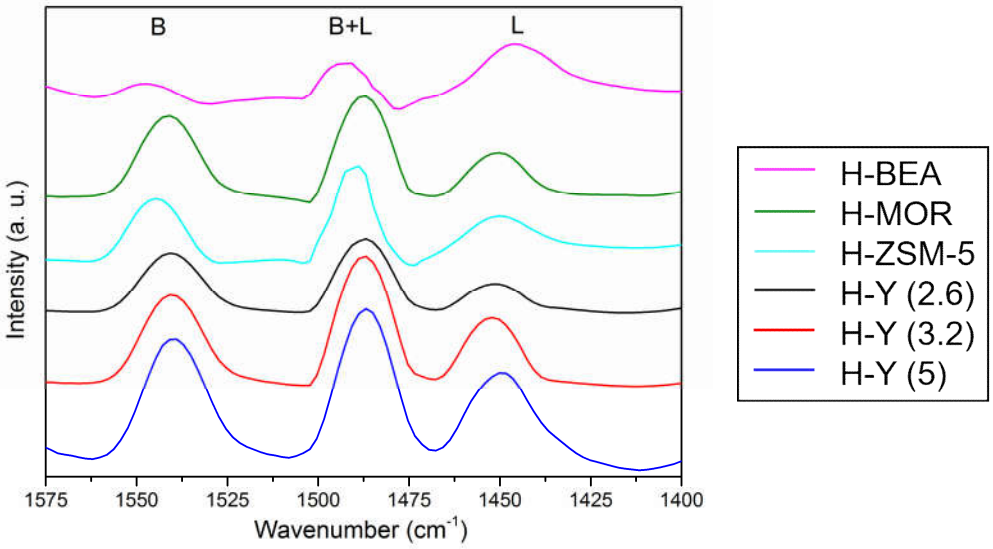


Figure S4. FTIR spectra of pyridine adsorbed onto the various zeolite samples.

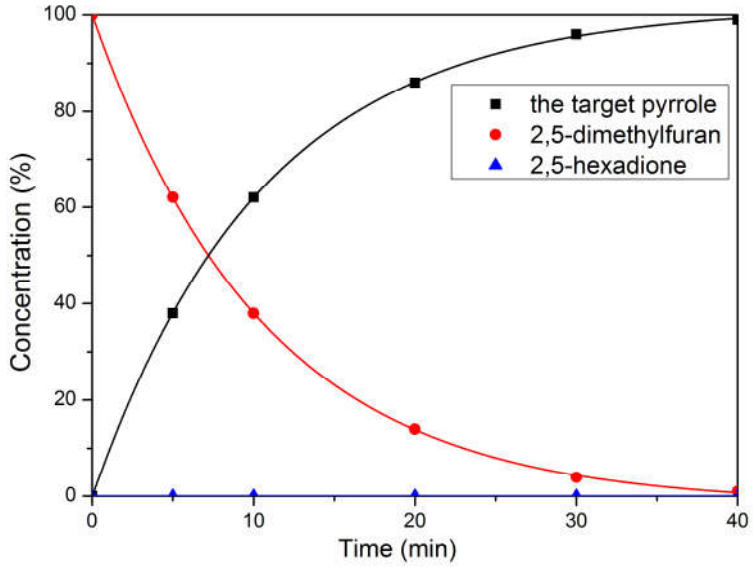


Figure S5. Time-course plot for the direct condensation of 2,5-dimethylfuran with *m*-methylaniline. Reaction conditions: 1 mmol 2,5-dimethylfuran, 1 mmol *m*-methylaniline, 2 mL toluene, 150 mg H-Y (2.6), 150 °C, 5 bar N_2, 0.7 h.

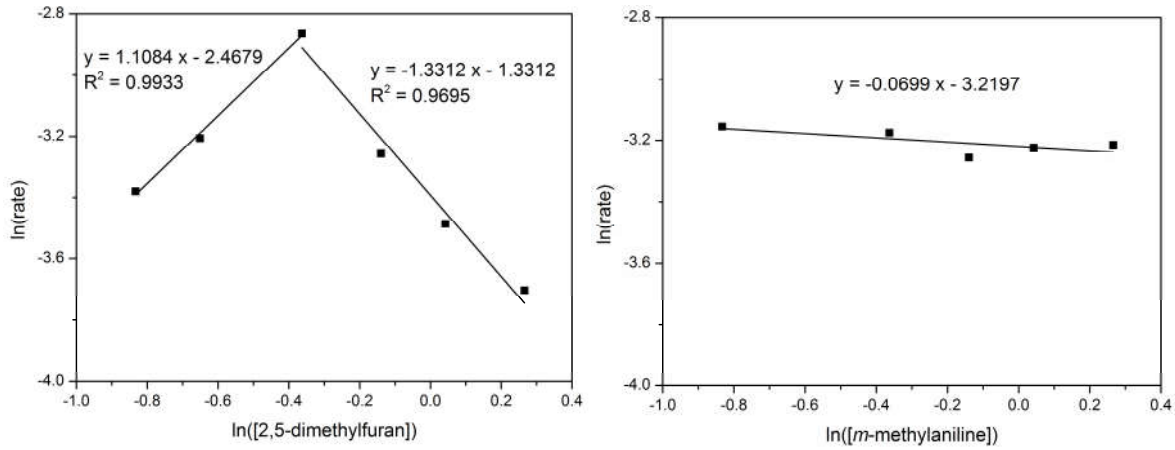


Figure S6. Results of mechanistic studies. Plot of ln(rate) versus ln([2,5-dimethylfuran]) and ln([*m*-methylaniline]).

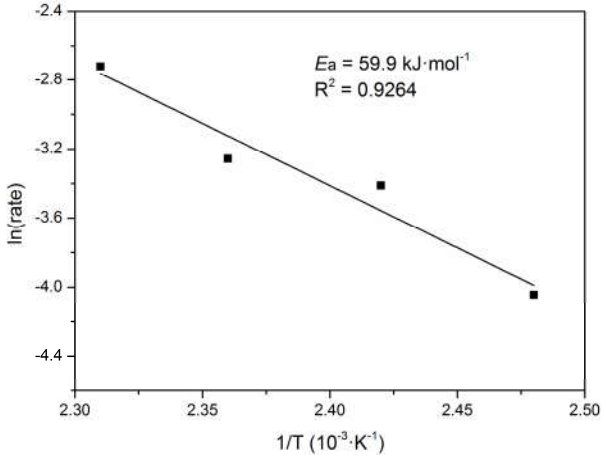
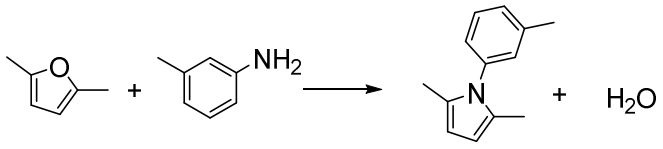
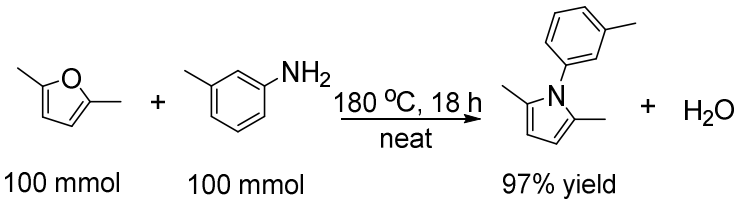


Figure S7. Arrhenius plot for H-Y (2.6) catalyzed direct condensation of 2,5-dimethylfuran with *m*-methylaniline.



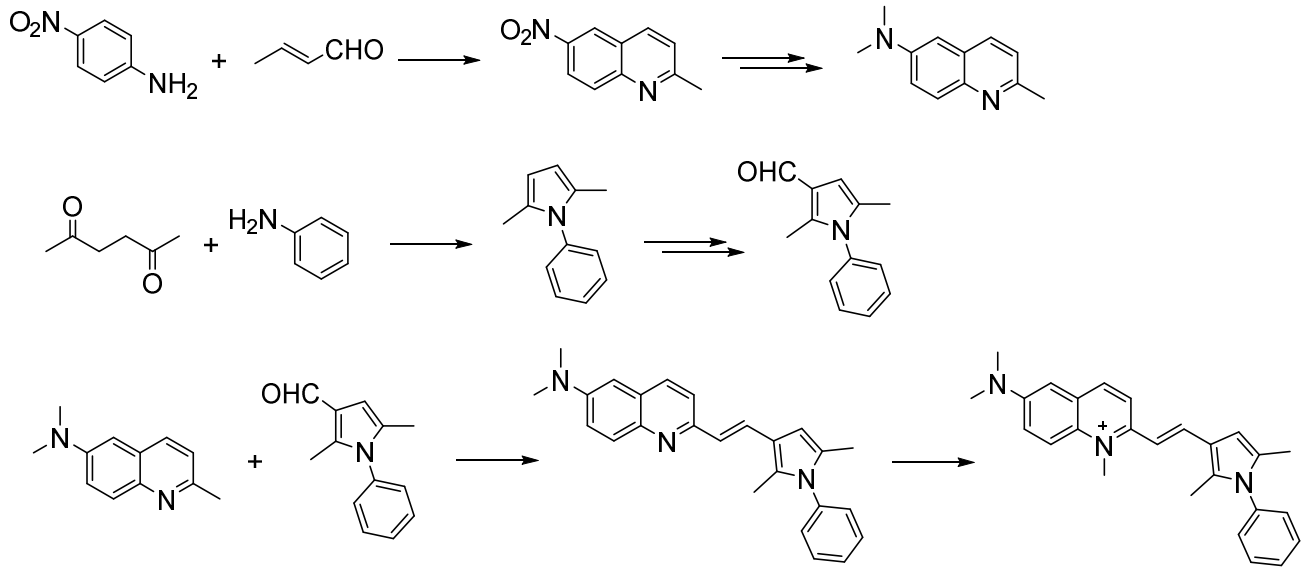
without base: 96% yield
with pyridine: 8% yield
with 2,6-lutidine: 13% yield

Scheme S1. Determination of the role of acid type by selective poisoning experiment. Reaction conditions: 1 mmol 2,5-dimethylfuran, 1 mmol *m*-methylaniline, 2 mL toluene, 150 mg H-Y (2.6), 0.5 mmol additive, 150 °C, 5 bar N_2, 0.5 h



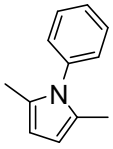
100 mmol 100 mmol 97% yield

Scheme S2. Large-scale condensation of 2,5-dimethylfuran with *m*-methylaniline under neat condition. Reaction conditions: 100 mmol 2,5-dimethylfuran, 100 mmol *m*-methylaniline, 150 mg H-Y (2.6), 180 °C, 5 bar N_2, 18 h

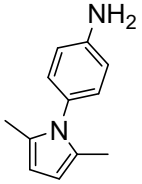


Scheme S3. Traditional synthetic route for Pyrvinium.[S4]

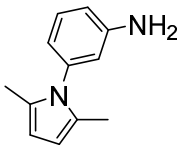
3. ^{1}H-NMR and ^{13}C-NMR spectra of products



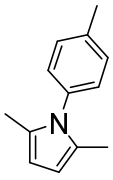
(Scheme 1, entry 1).[S5] ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.45-7.35 (m, 3H), 7.19 (d, J = 7.2 Hz, 2H), 5.90 (s, 2H), 2.02 (s, 6H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 138.9, 128.9, 128.6, 128.1, 127.5 105.6, 12.9.



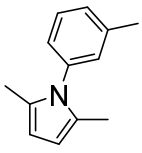
(Scheme 1, entry 2). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 6.96 (d, J = 7.2 Hz, 2H), 6.70 (d, J = 7.2 Hz, 1H), 5.86 (s, 2H), 3.64 (br s, 2H), 2.01 (s, 6H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 145.8, 129.6, 129.0, 115.1, 104.9, 12.9; HRMS (ESI) calculated for $C_{12}H_{14}N_2$ $[M+H]^+$ 187.1230, observed 187.1238.



(Scheme 1, entry 3). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.21 (t, J = 8.0 Hz, 1H), 6.70 (ddd, J = 8.0, 2.4, 0.8 Hz, 1H), 6.59 (ddd, J = 8.0, 2.4, 0.8 Hz, 1H), 6.51 (t, J = 2.0 Hz, 1H), 5.87 (s, 2H), 3.73 (br s, 2H), 2.04 (s, 6H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 147.0, 140.0, 129.7, 128.7, 118.4, 114.8, 114.3, 105.3, 12.9; HRMS (ESI) calculated for $C_{12}H_{14}N_2$ $[M+H]^+$ 187.1230, observed 187.1237.

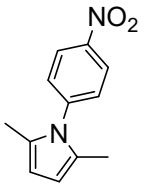


(Scheme 1, entry 4).[S6] ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.24 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 5.89 (s, 2H), 2.41 (s, 3H), 2.02 (s, 6H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 137.4, 136.3, 129.6, 128.8, 127.9, 105.4, 21.1, 12.9.

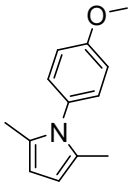


(Scheme 1 entry 5). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.31 (t, J = 7.6 Hz, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.00 (d, J = 8.0 Hz, 2H), 5.88 (s, 2H), 2.39 (s, 3H), 2.02 (s, 6H); ^{13}C-NMR ($CDCl_3$, 100

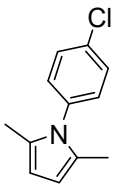
MHz): δ 138.9, 128.8, 128.7, 128.6, 128.3, 125.2, 105.5, 21.2, 12.9; HRMS (ESI) calculated for $C_{13}H_{15}N$ $[M+H]^+$ 186.1277, observed 186.1288.



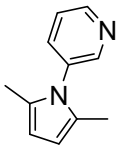
(Scheme 1, entry 6).[S7] ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.35 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 5.96 (s, 2H), 2.08 (s, 6H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 146.7, 144.7, 128.8, 128.5, 124.5, 107.4, 13.1.



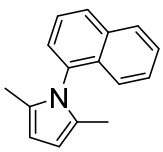
(Scheme 1, entry 7).[S8] ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.12 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 5.88 (s, 2H), 3.85 (s, 3H), 2.01 (s, 6H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 158.8, 131.7, 129.2, 129.0, 114.2, 105.2, 55.4, 12.9.



(Scheme 1, entry 8).[S8] ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.90 (s, 2H), 2.02 (s, 6H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 137.5, 133.5, 129.4, 129.2, 128.6, 106.0, 12.9.

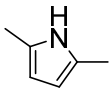


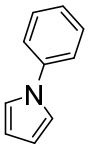
(Scheme 1, entry 9). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 8.66 (d, *J* = 4.0 Hz, 1H), 8.53 (s, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.43 (dd, *J* = 7.2, 4.8 Hz, 1H), 5.94 (s, 2H), 2.04 (s, 6H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ149.3, 148.8, 135.6, 135.5, 128.9, 123.7, 106.6, 13.0; HRMS (ESI) calculated for $C_{11}H_{12}N_2$ $[M+H]^+$ 173.1073, observed 173.1081.

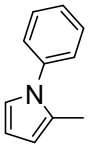


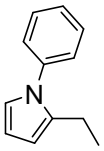
(Scheme 1, entry 10).[S9] ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.52 (quint, *J* = 7.6 Hz, 2H), 7.45 (s, 1H), 7.41 (t, *J* = 6.4 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 6.01 (s, 2H),

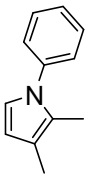
1.89 (s, 6H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 135.8, 134.2, 131.9, 129.8, 128.5, 128.0, 127.2, 126.5, 126.2, 125.3, 123.3, 105.4, 12.5.

 **(Scheme 1, entry 11).**[S10] ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.49 (br s, 1H), 5.73 (d, *J* = 2.8 Hz, 2H), 2.19 (s, 6H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 128.1, 105.7, 12.9.

 **(Scheme 2, entry 1).**[S11] ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.44-7.38 (m, 4H), 7.26-7.22 (m, 1H), 7.09 (t, *J* = 2.0 Hz, 2H), 6.35 (t, *J* = 2.0 Hz, 2H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 140.8, 129.5, 125.6, 120.5, 119.3, 110.4.

 **(Scheme 2, entry 2).** ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.43 (t, *J* = 7.2 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.77 (s, 1H), 6.20 (s, 1H), 6.04 (s, 1H), 2.21 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 140.4, 129.4, 129.0, 126.8, 125.7, 121.3, 108.1, 108.0, 12.9; HRMS (ESI) calculated for $C_{11}H_{11}N$ $[M+H]^+$ 158.0964, observed 158.0955.

 **(Scheme 2, entry 3).** ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.44-7.40 (m, 2H), 7.35-7.29 (m, 3H), 6.74 (t, *J* = 6.4 Hz, 1H), 6.22 (t, *J* = 3.2 Hz, 1H), 6.07 (quint, *J* = 0.8 Hz, 1H), 2.55 (q, *J* = 3.6 Hz, 2H), 1.15 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 140.4, 135.6, 129.0, 127.0, 126.1, 121.5, 107.9, 106.0, 20.1, 13.3; HRMS (ESI) calculated for $C_{12}H_{13}N$ $[M+H]^+$ 172.1121, observed 172.1122.

 **(Scheme 2, entry 4).** ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.42 (t, *J* = 8.0 Hz, 2H), 7.33-7.27 (m, 3H), 6.70 (s, 1H), 6.09 (s, 1H), 2.12 (s, 3H), 2.10 (s, 3H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 140.7, 129.0, 126.5, 125.6, 125.2, 119.9, 116.2, 109.8, 11.5, 10.5; HRMS (ESI) calculated for $C_{12}H_{13}N$ $[M+H]^+$ 172.1121, observed 172.1135.

Reference

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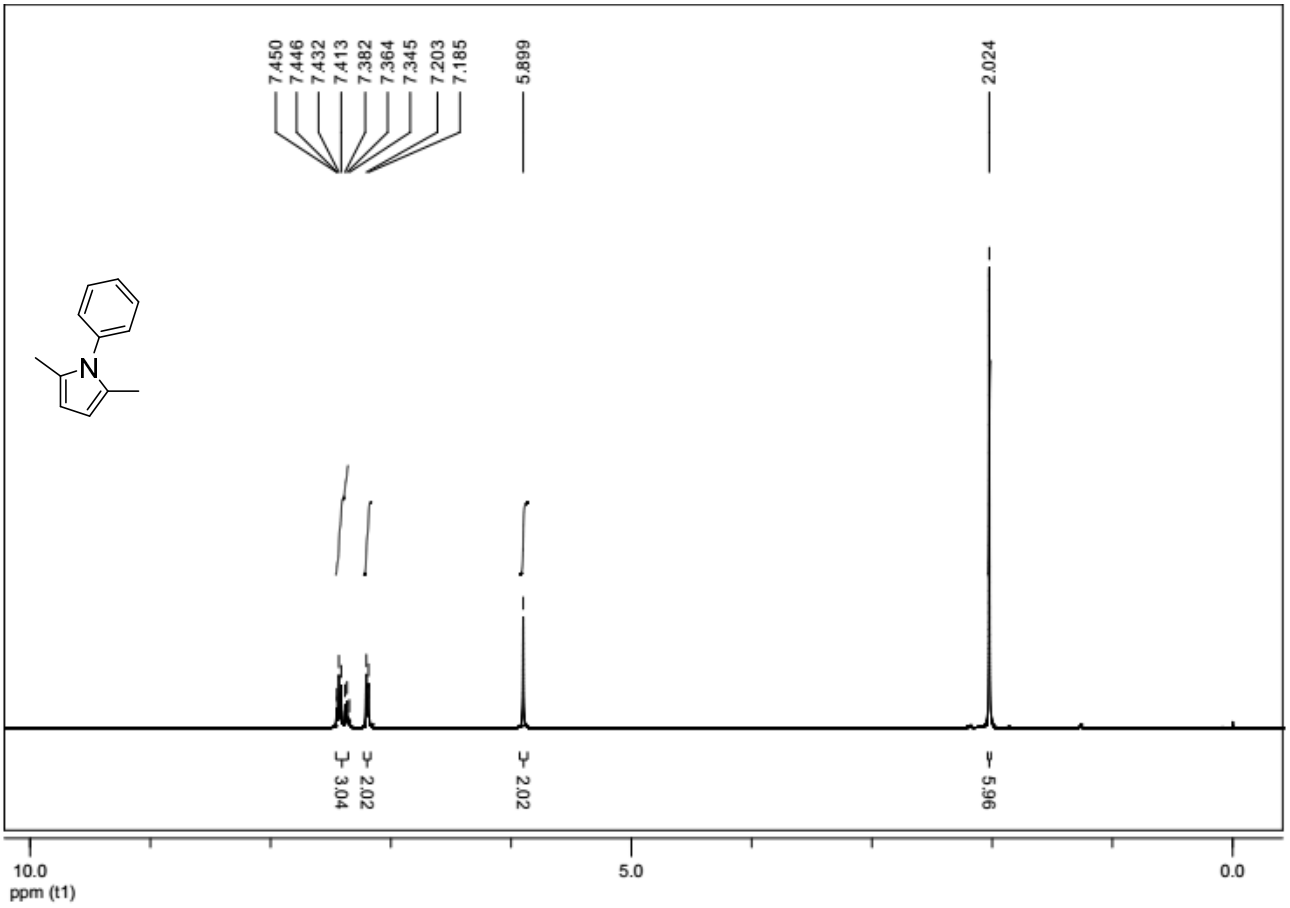
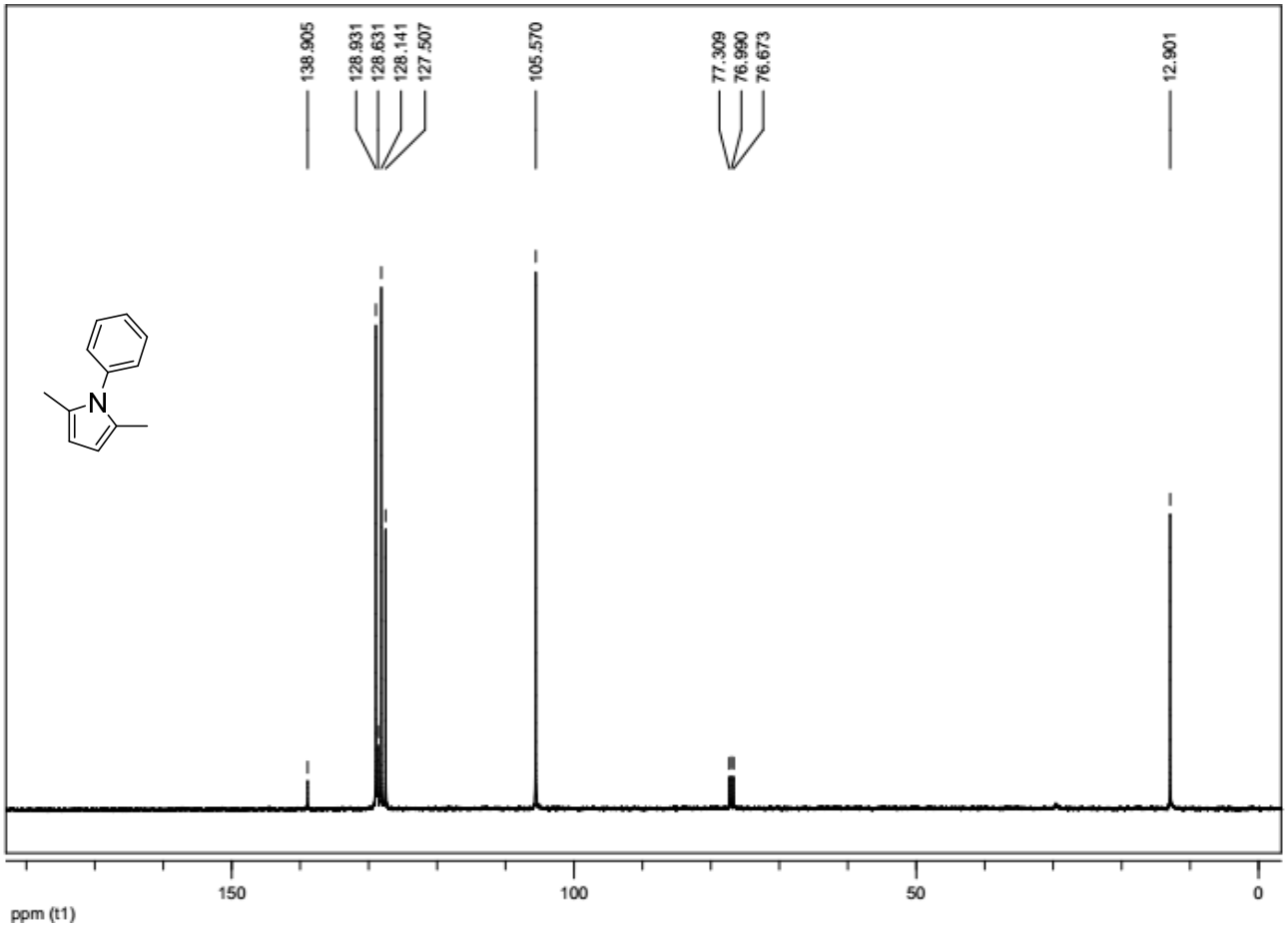
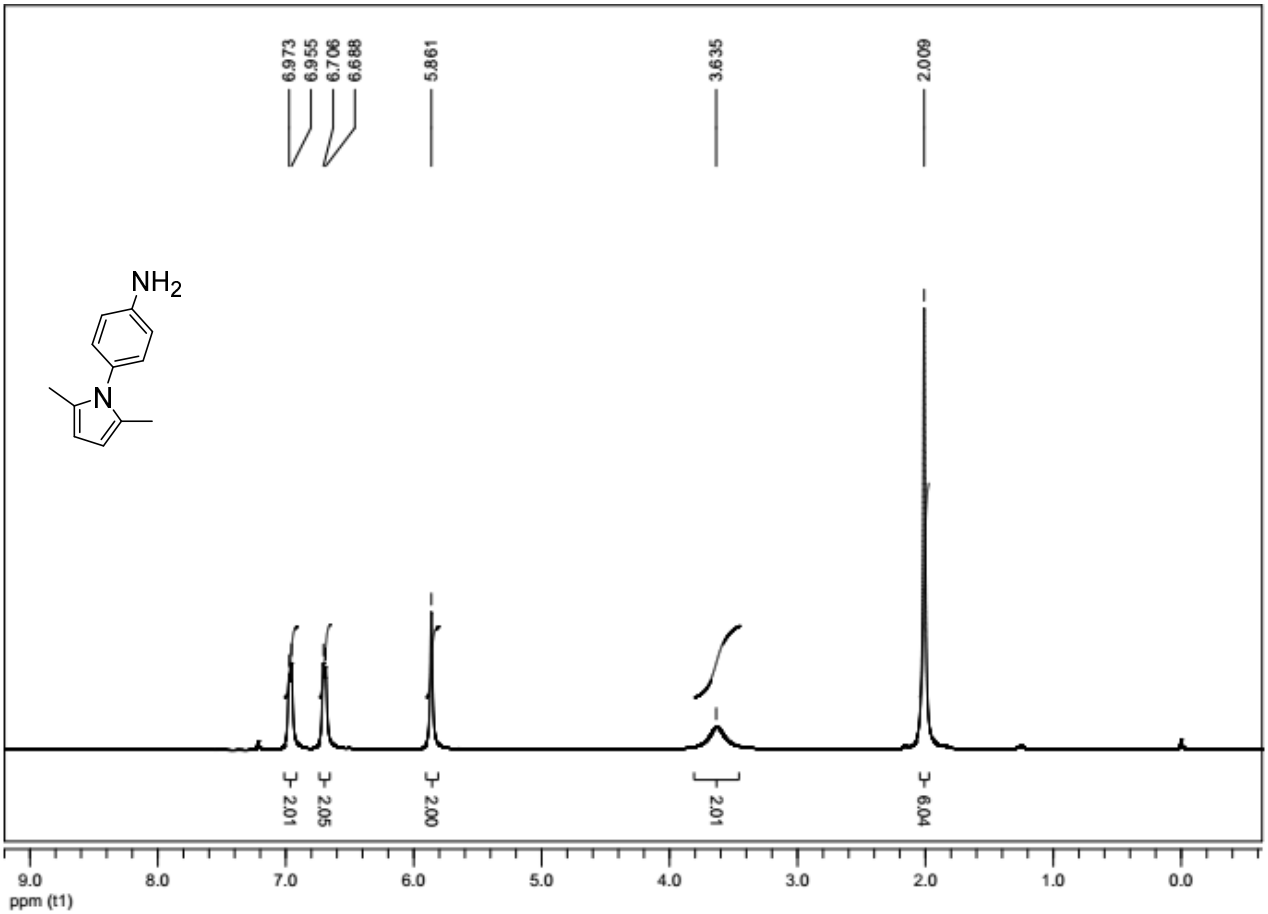
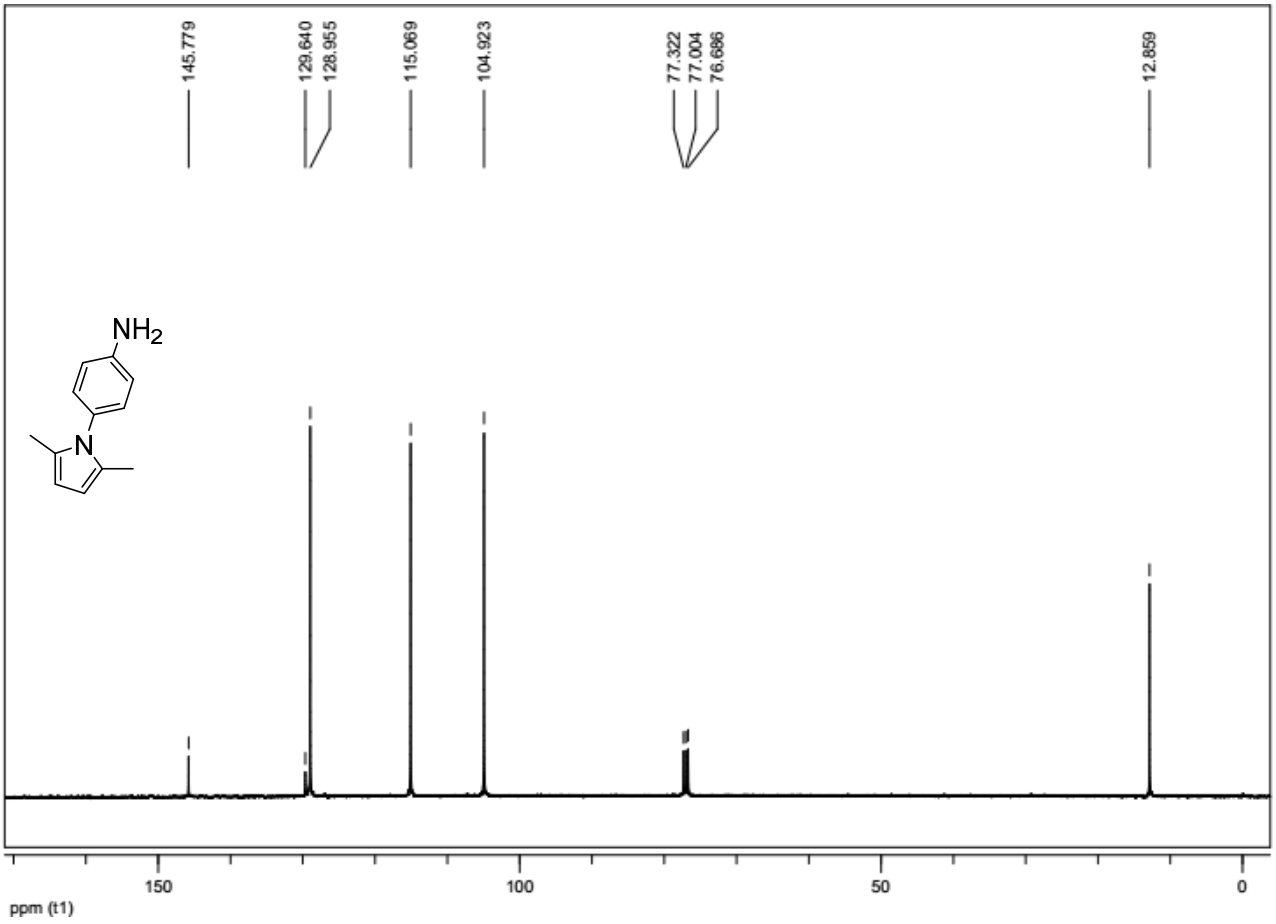
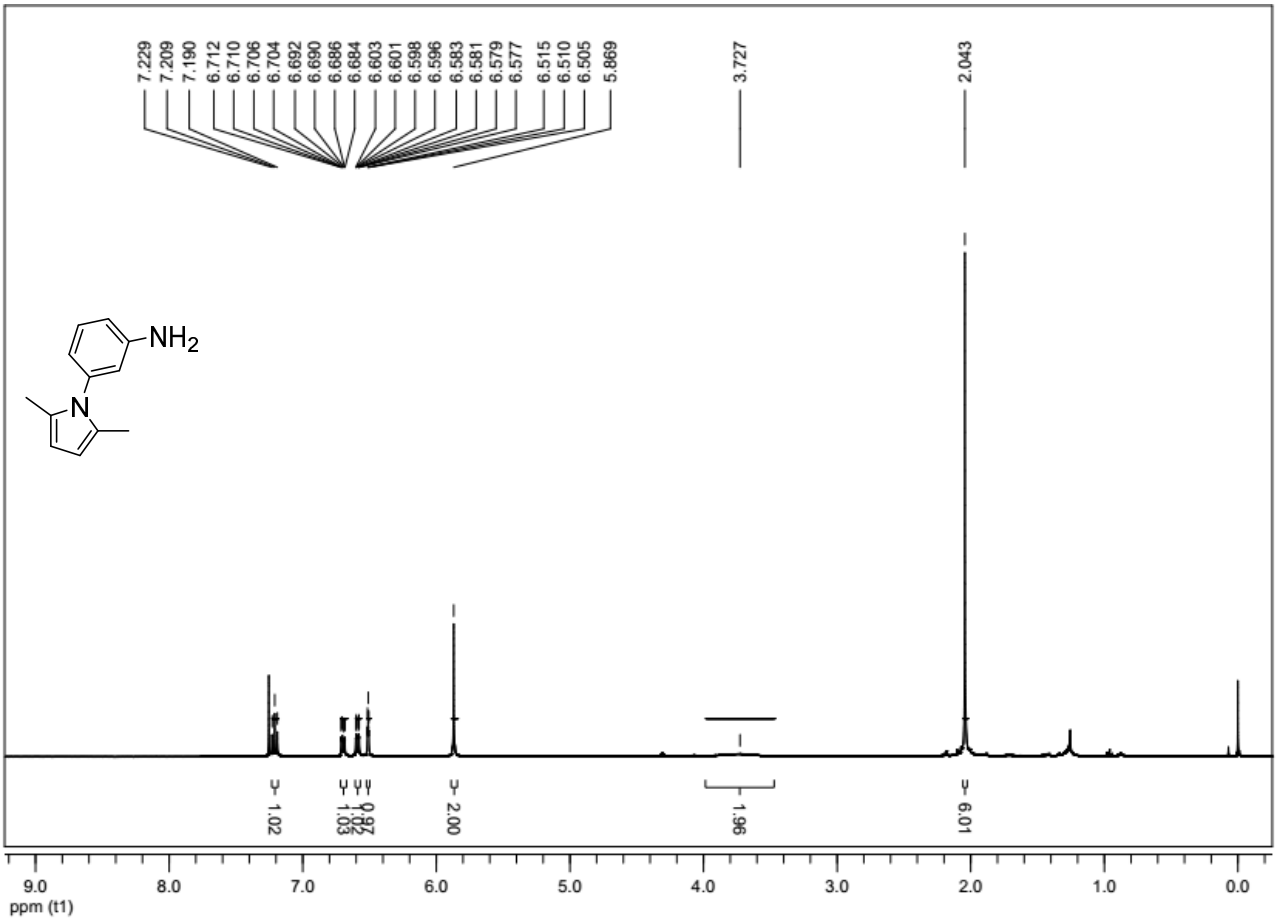
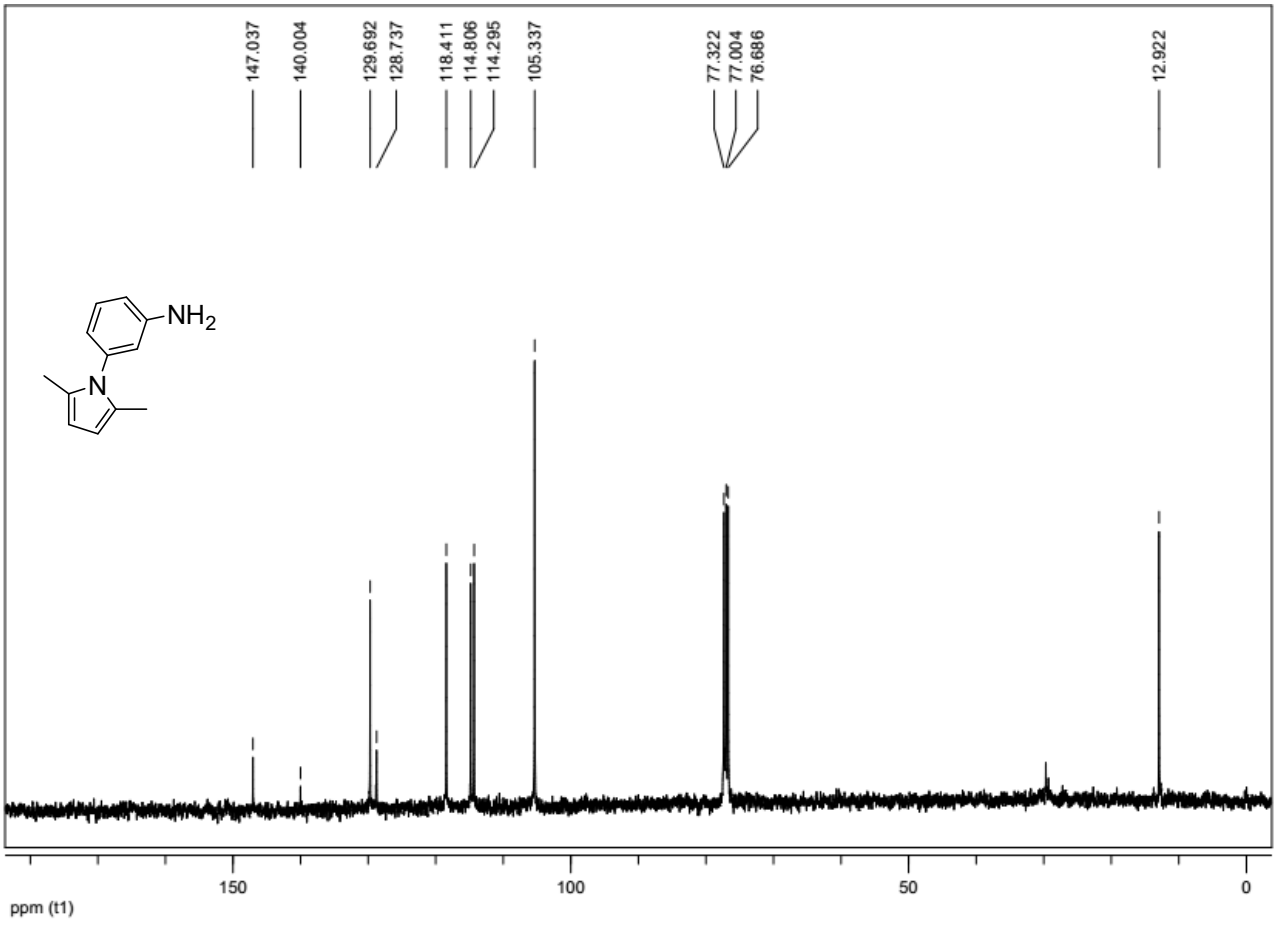

7.450
7.446
7.432
7.413
7.382
7.364
7.345
7.203
7.185
5.899
2.024
3.04
2.02
2.02
5.96
10.0
ppm (t1)
5.0
0.0

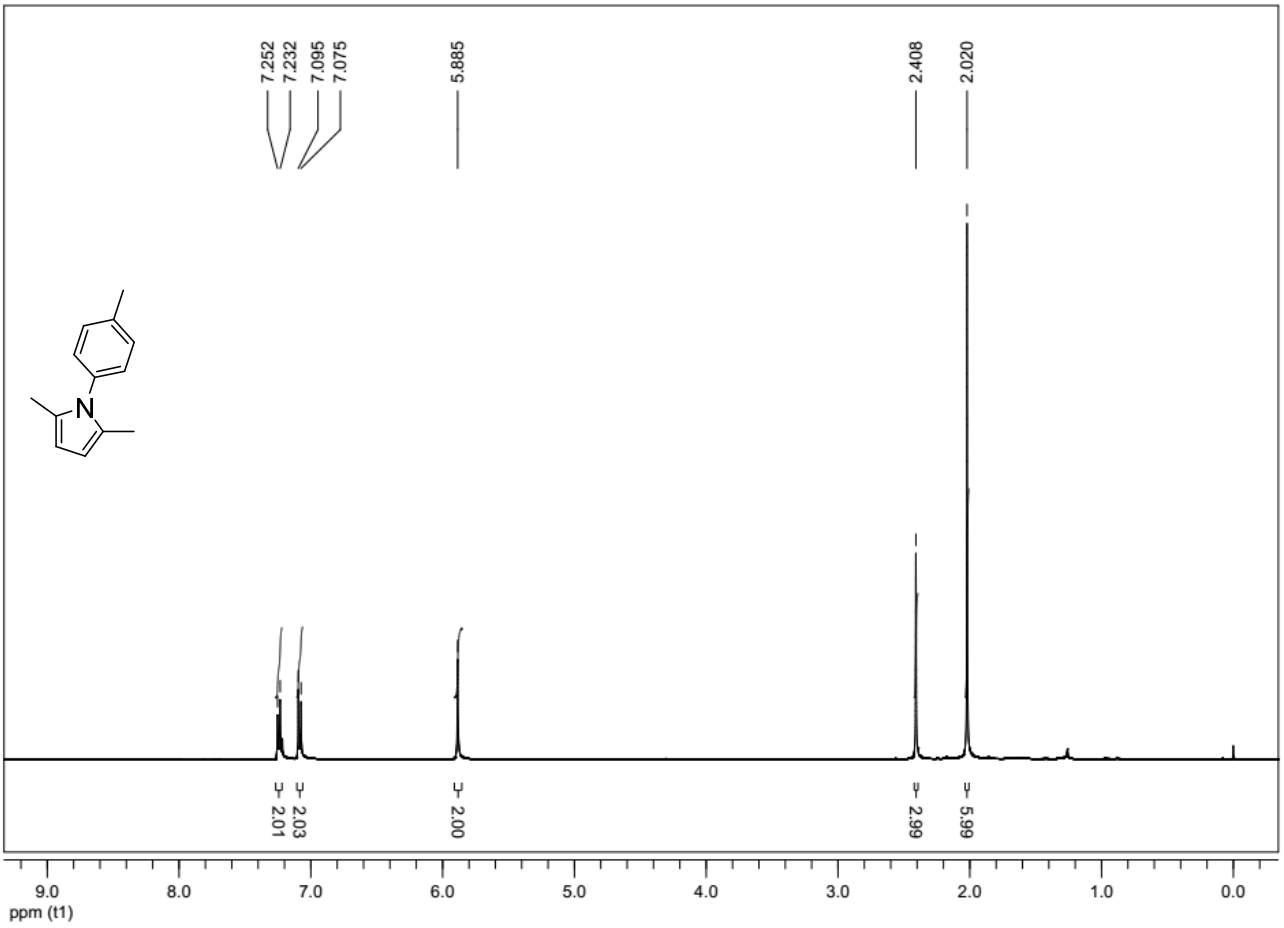

138.905
128.931
128.631
128.141
127.507
105.570
77.309
76.990
76.673
12.901
150
ppm (t1)
100
50
0

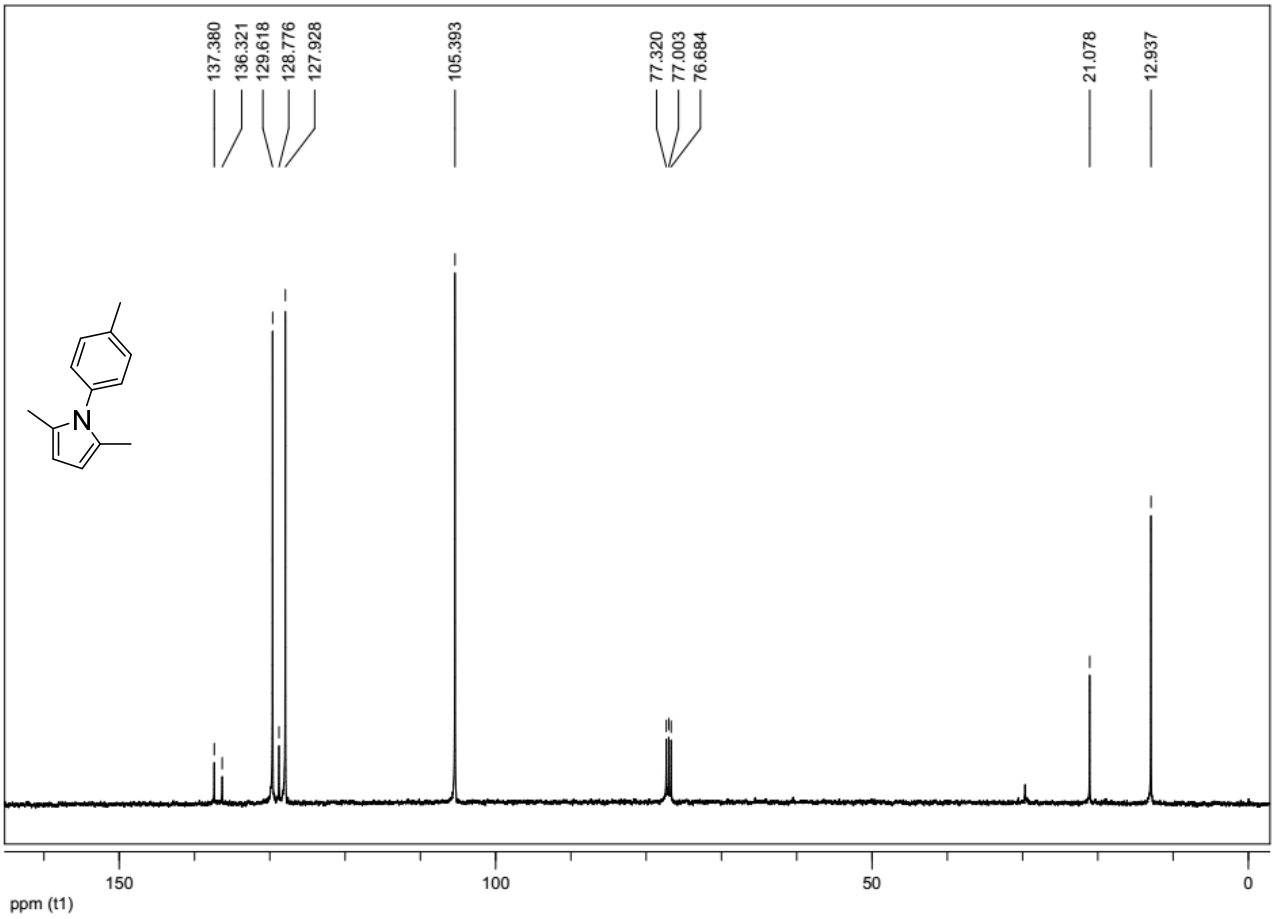

6.973
6.955
6.706
6.688
5.861
3.635
2.009
NH2
N
2.01
2.05
2.00
2.01
6.04
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

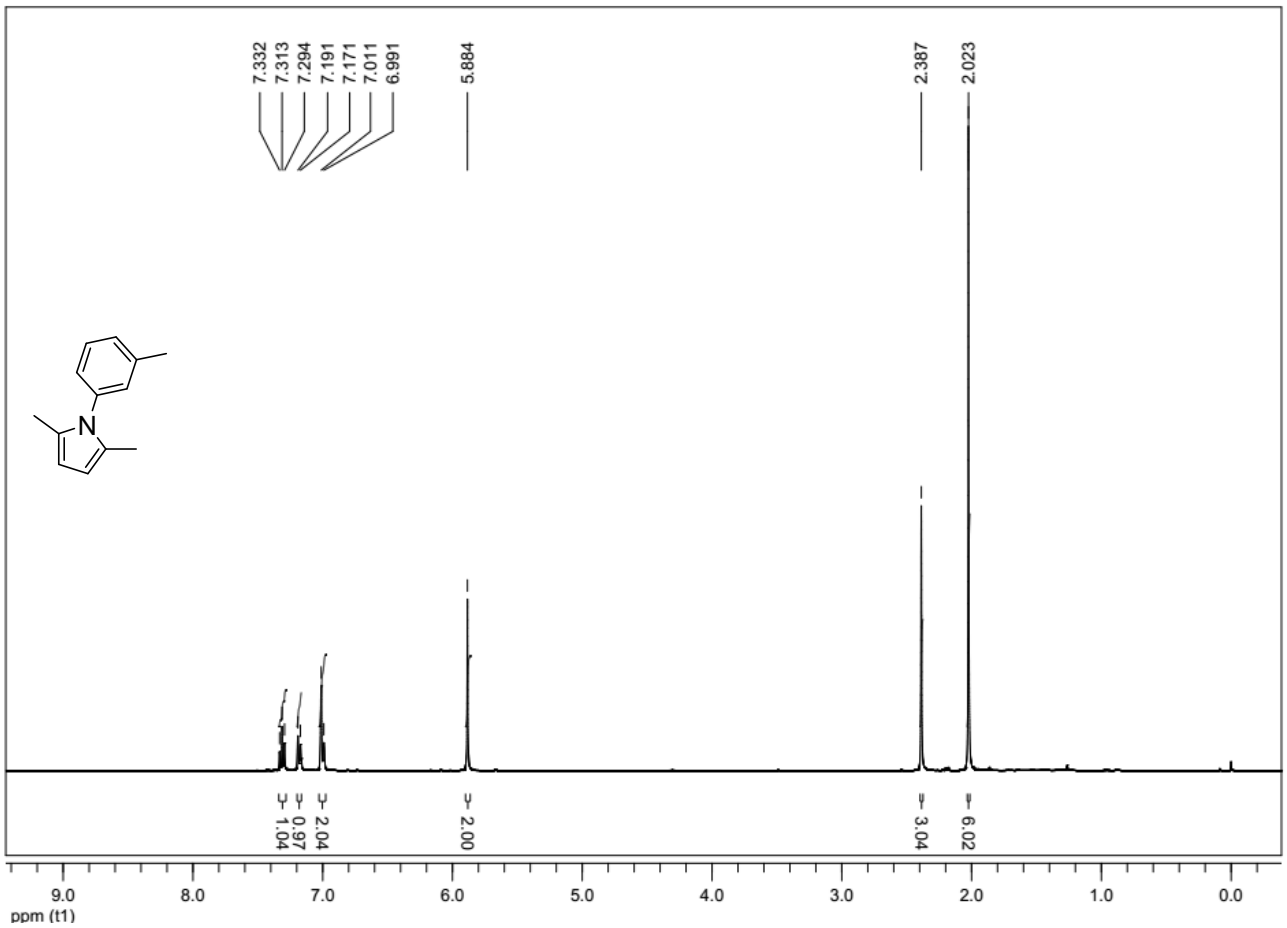

145.779
129.640
128.955
115.069
104.923
77.322
77.004
76.686
12.859
NH2
N
150
100
50
0
ppm (t1)

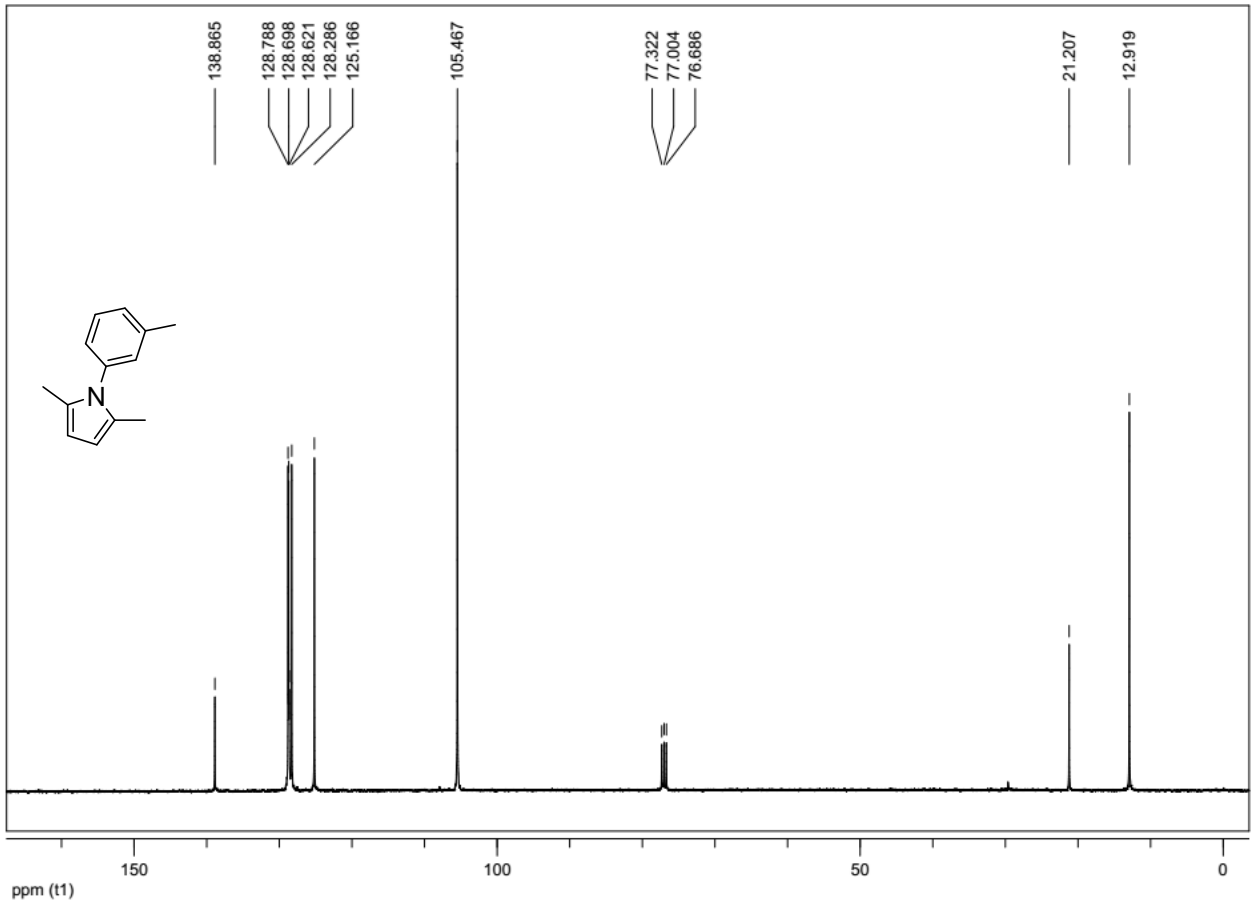

7.229
7.209
7.190
6.712
6.710
6.706
6.704
6.692
6.690
6.686
6.684
6.603
6.601
6.598
6.596
6.583
6.581
6.579
6.577
6.515
6.510
6.505
5.869
3.727
2.043
NH2
N
1.02
2.00
1.96
6.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

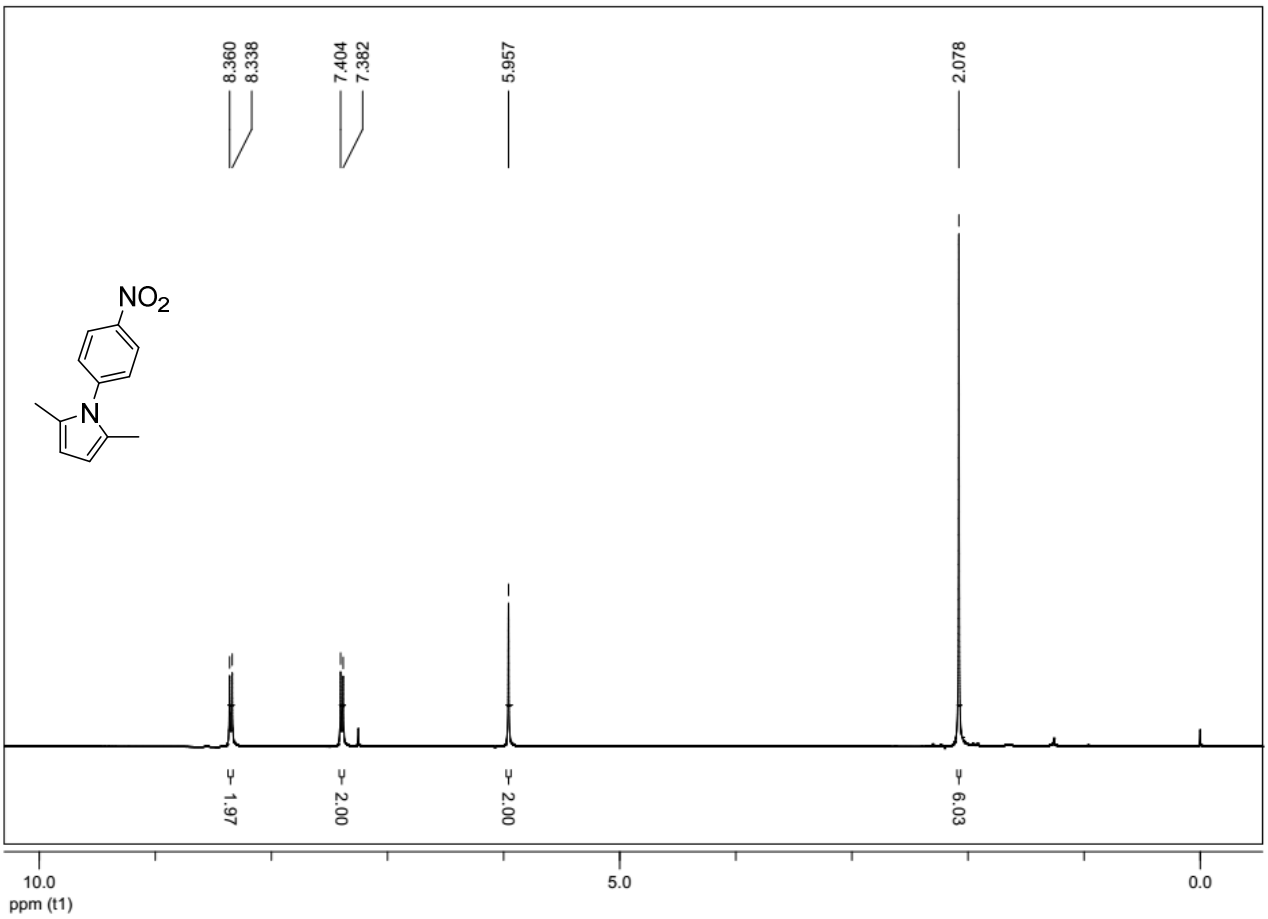

147.037
140.004
129.692
128.737
118.411
114.806
114.295
105.337
77.322
77.004
76.686
12.922
NH2
N
150
100
50
0
ppm (t1)

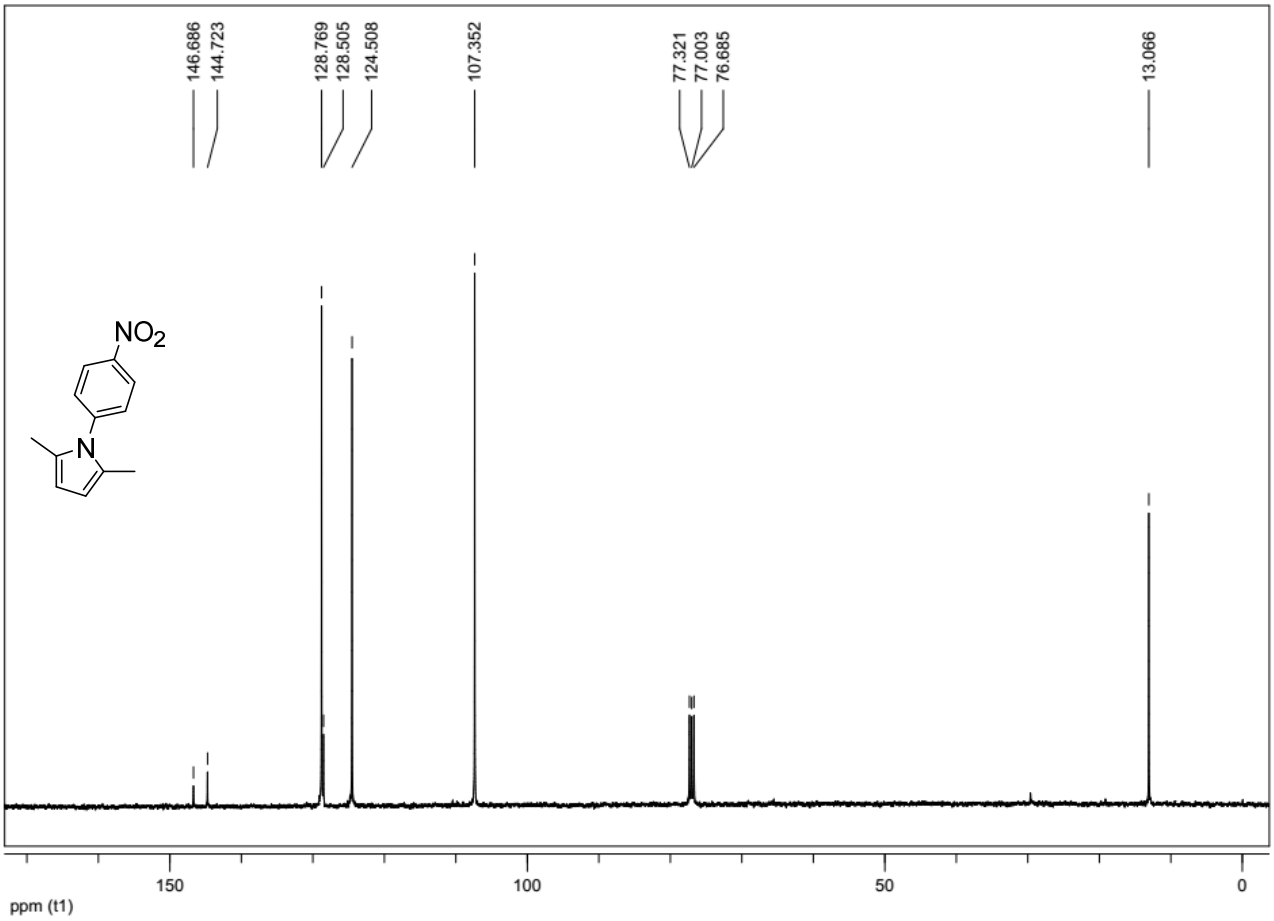

7.252
7.232
7.095
7.075
5.885
2.408
2.020
2.01
2.03
2.00
2.99
5.99
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

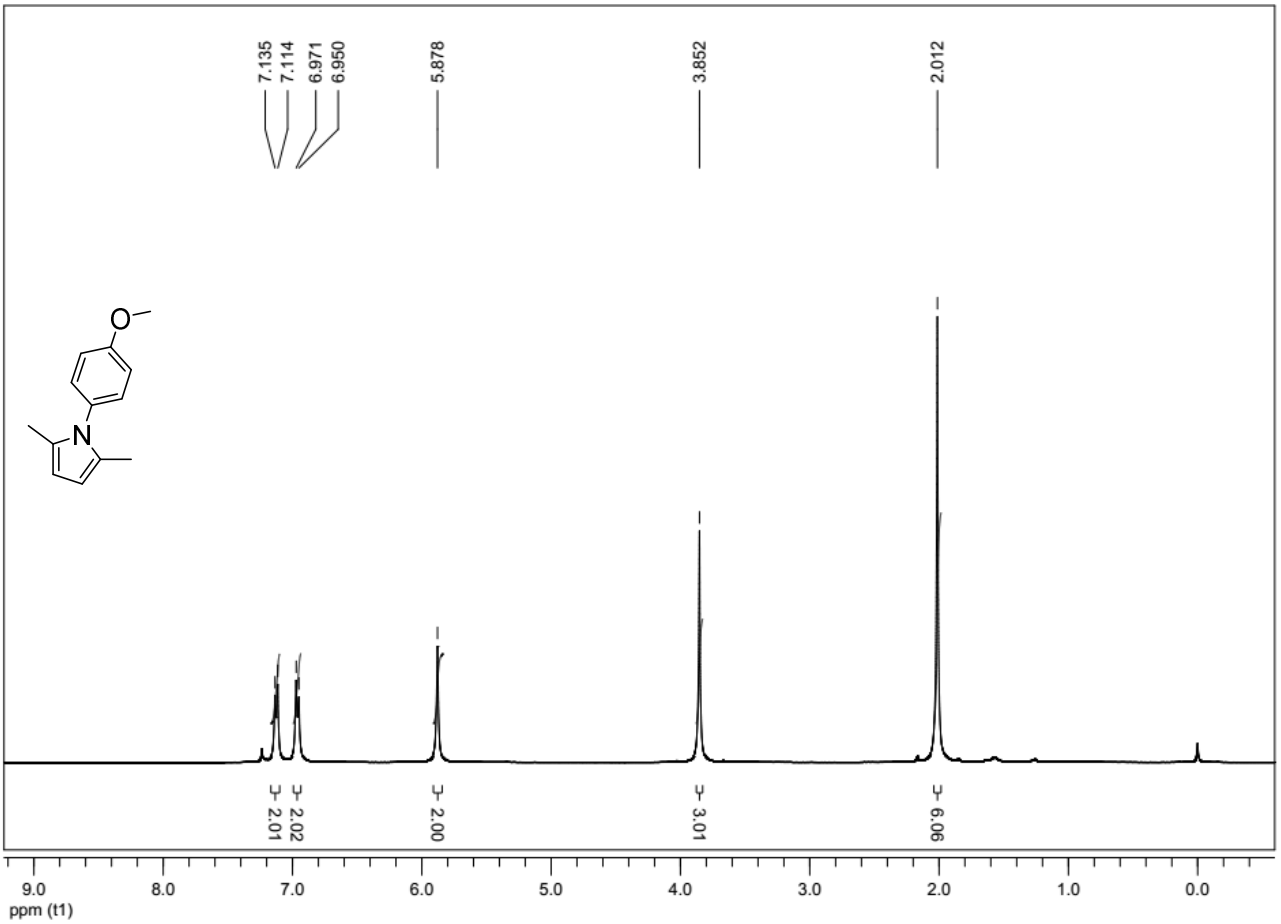

137.380
136.321
129.618
128.776
127.928
105.393
77.320
77.003
76.684
21.078
12.937
150
100
50
0
ppm (t1)

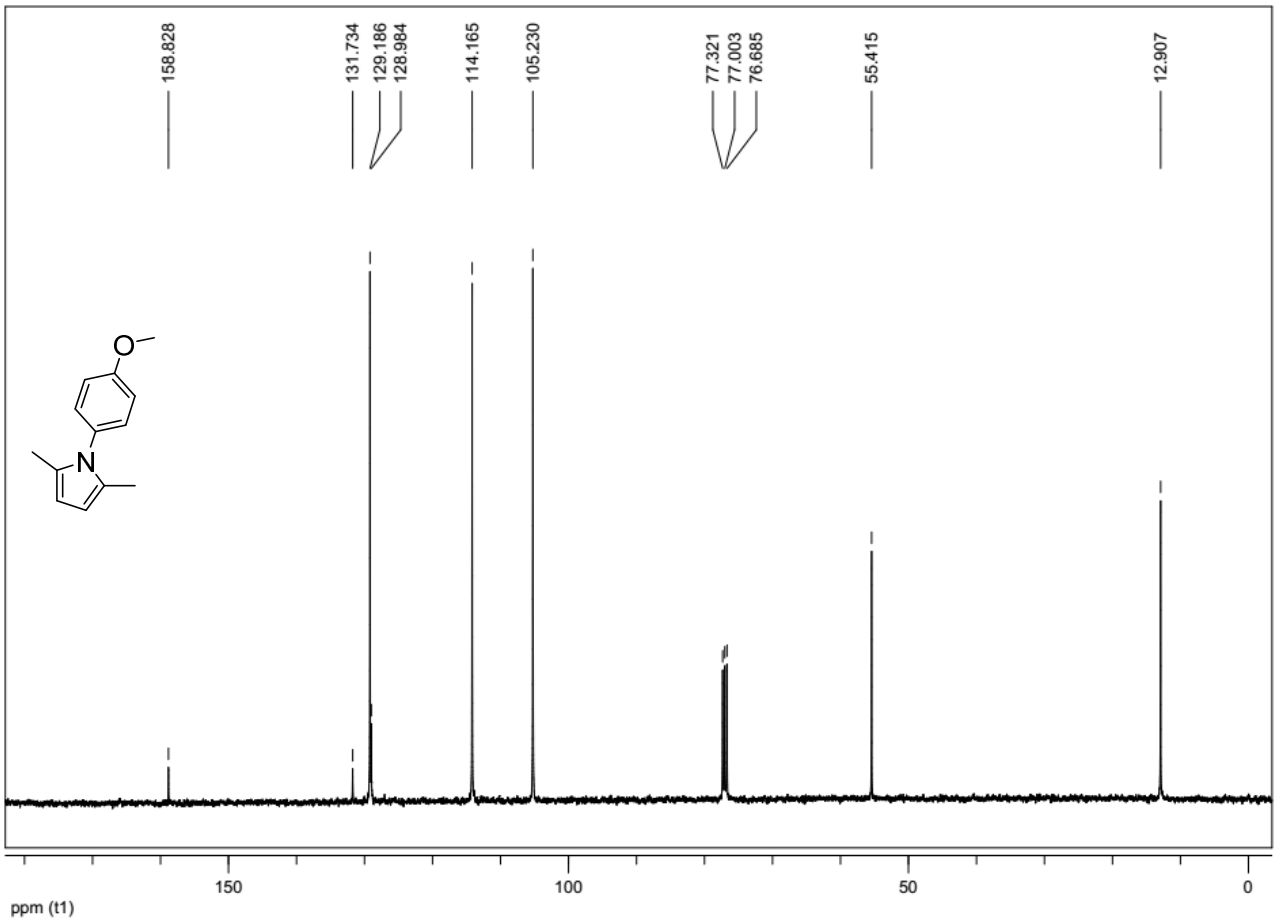

7.332
7.313
7.294
7.191
7.171
7.011
6.991
5.884
2.387
2.023
1.04
0.97
2.04
2.00
3.04
6.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

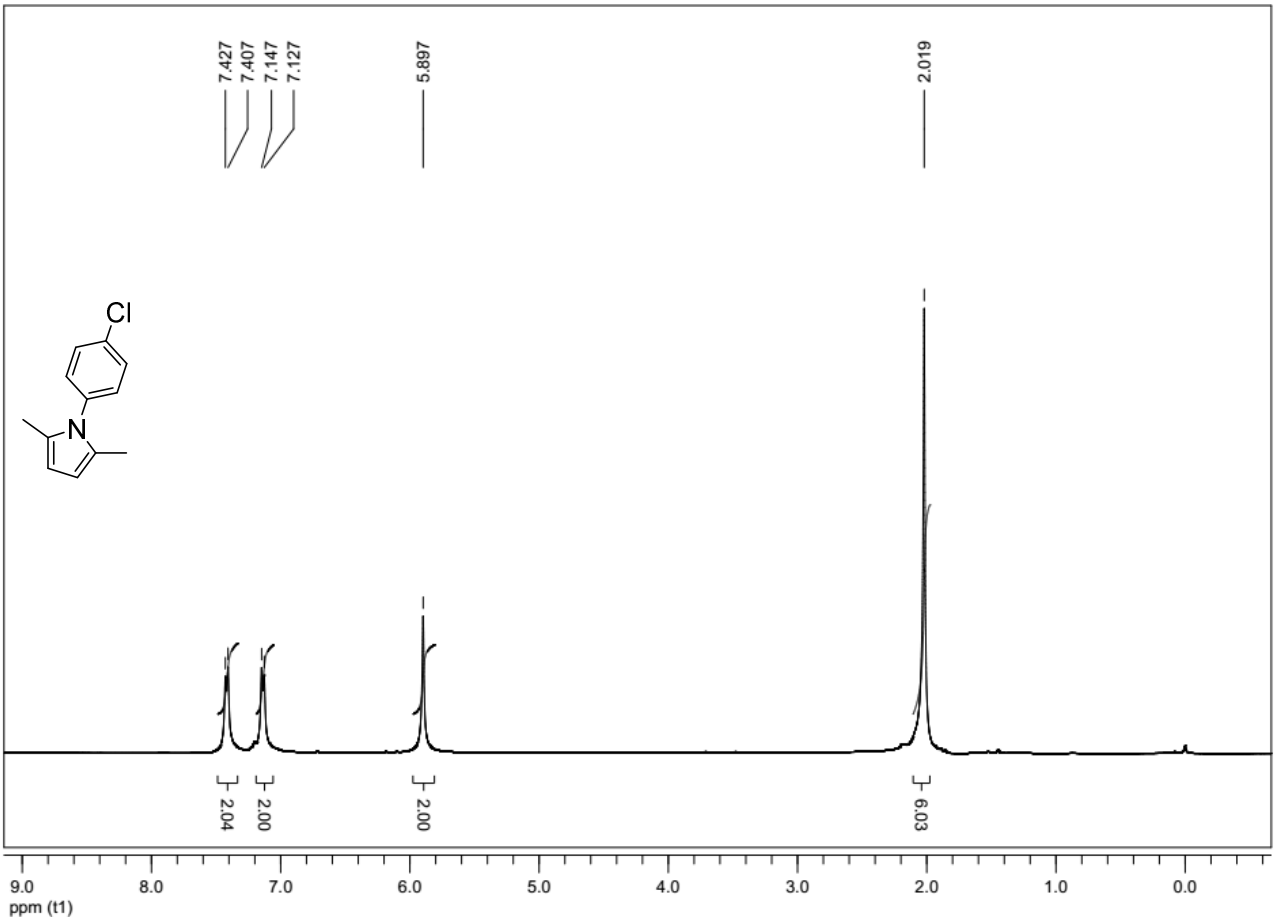

138.865
128.788
128.698
128.621
128.286
125.166
105.467
77.322
77.004
76.686
21.207
12.919
150
100
50
0
ppm (t1)

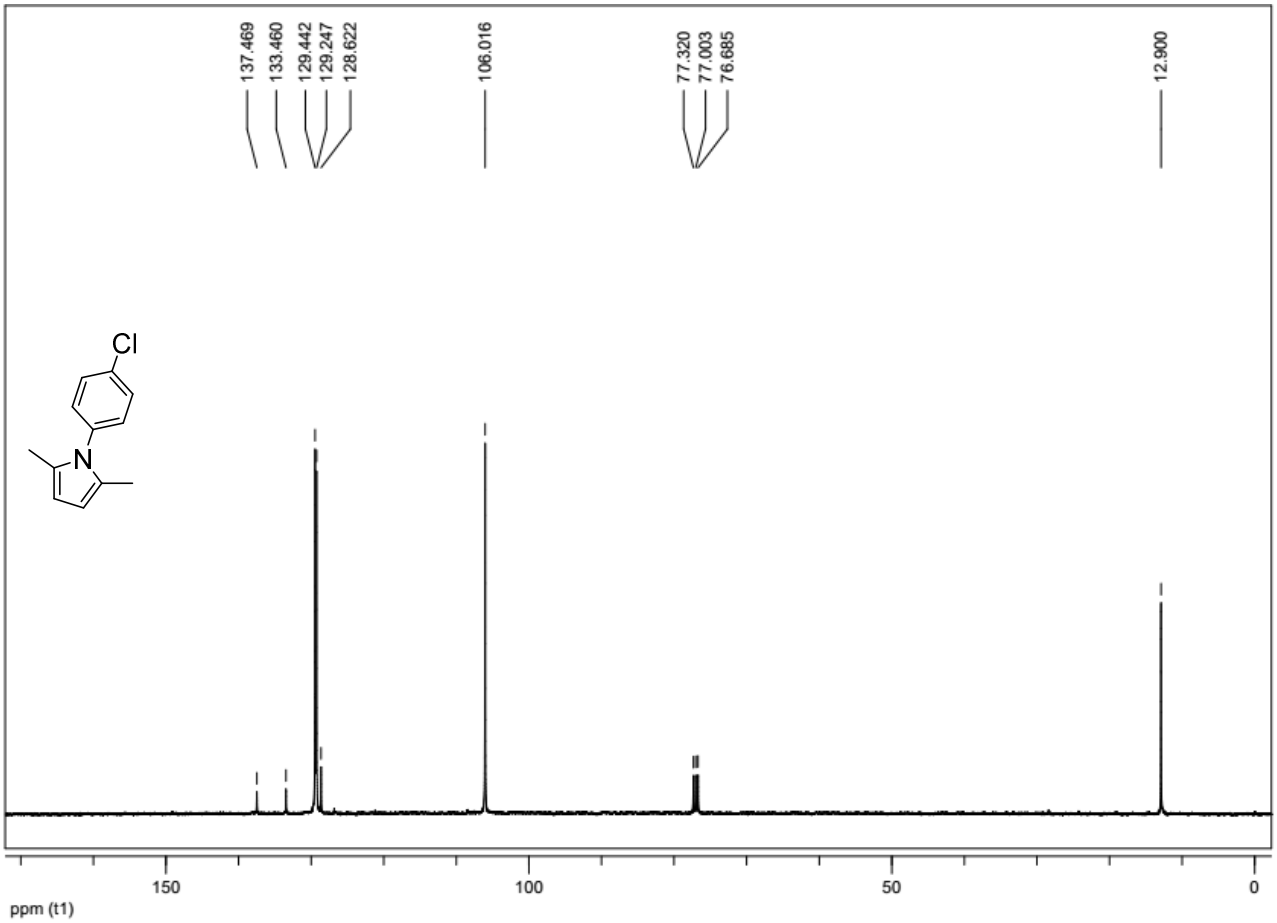

8.360
8.338
7.404
7.382
5.957
2.078
NO2
N
1.97
2.00
2.00
6.03
10.0
5.0
0.0
ppm (t1)

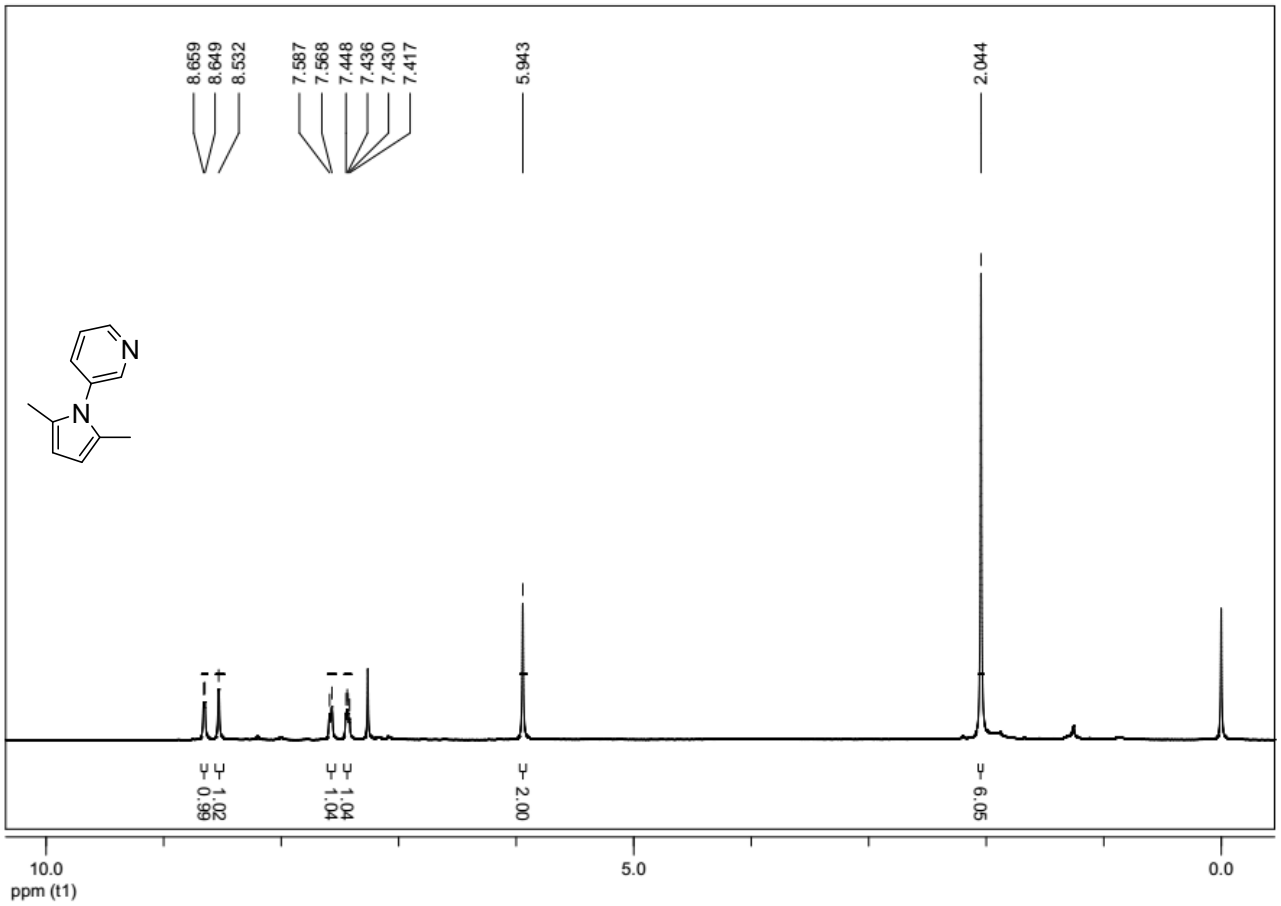

146.686
144.723
128.769
128.505
124.508
107.352
77.321
77.003
76.685
13.066
NO2
N
150
100
50
0
ppm (t1)

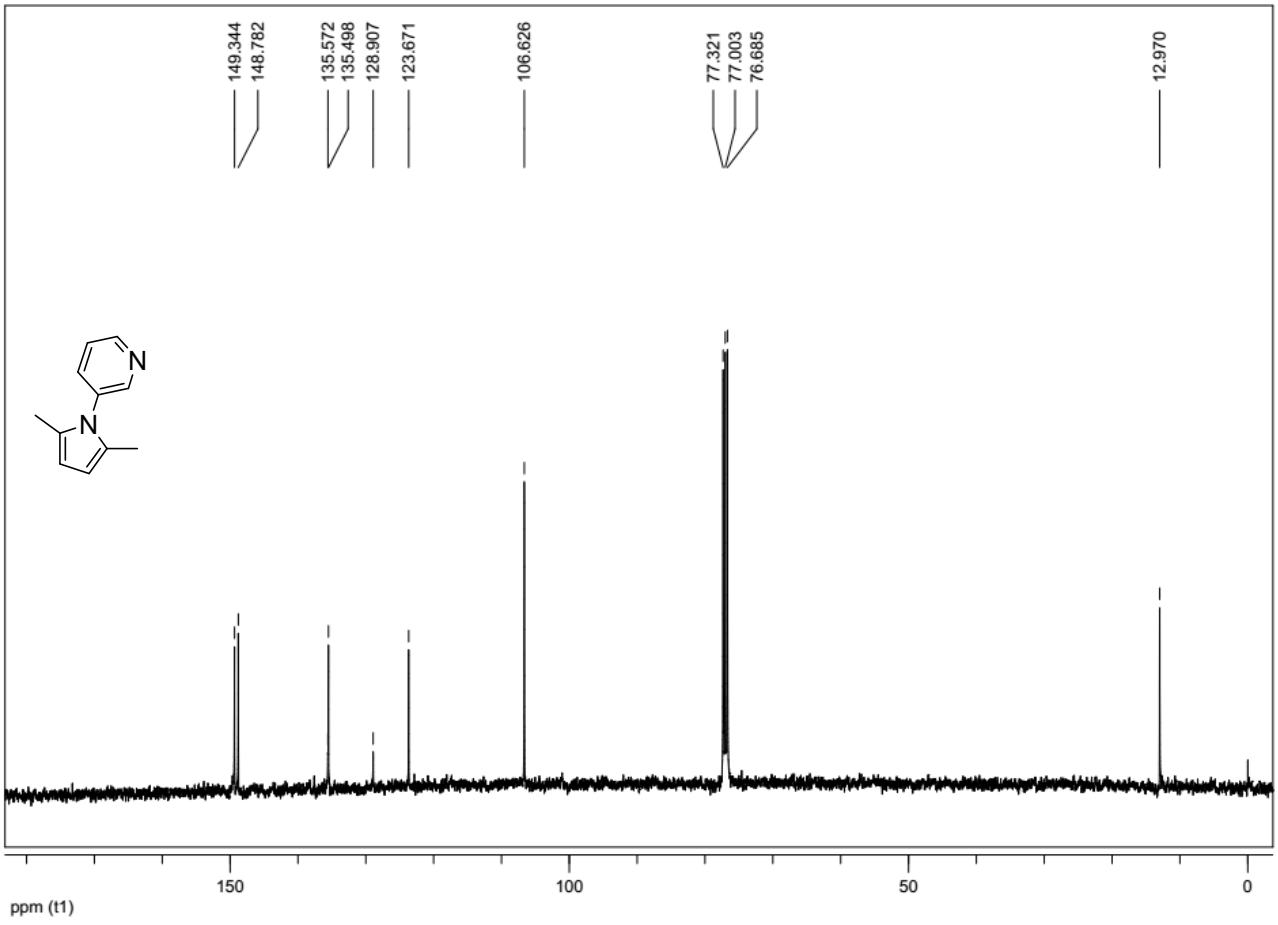

7.135
7.114
6.971
6.950
5.878
3.852
2.012
2.01
2.02
2.00
3.01
6.06
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

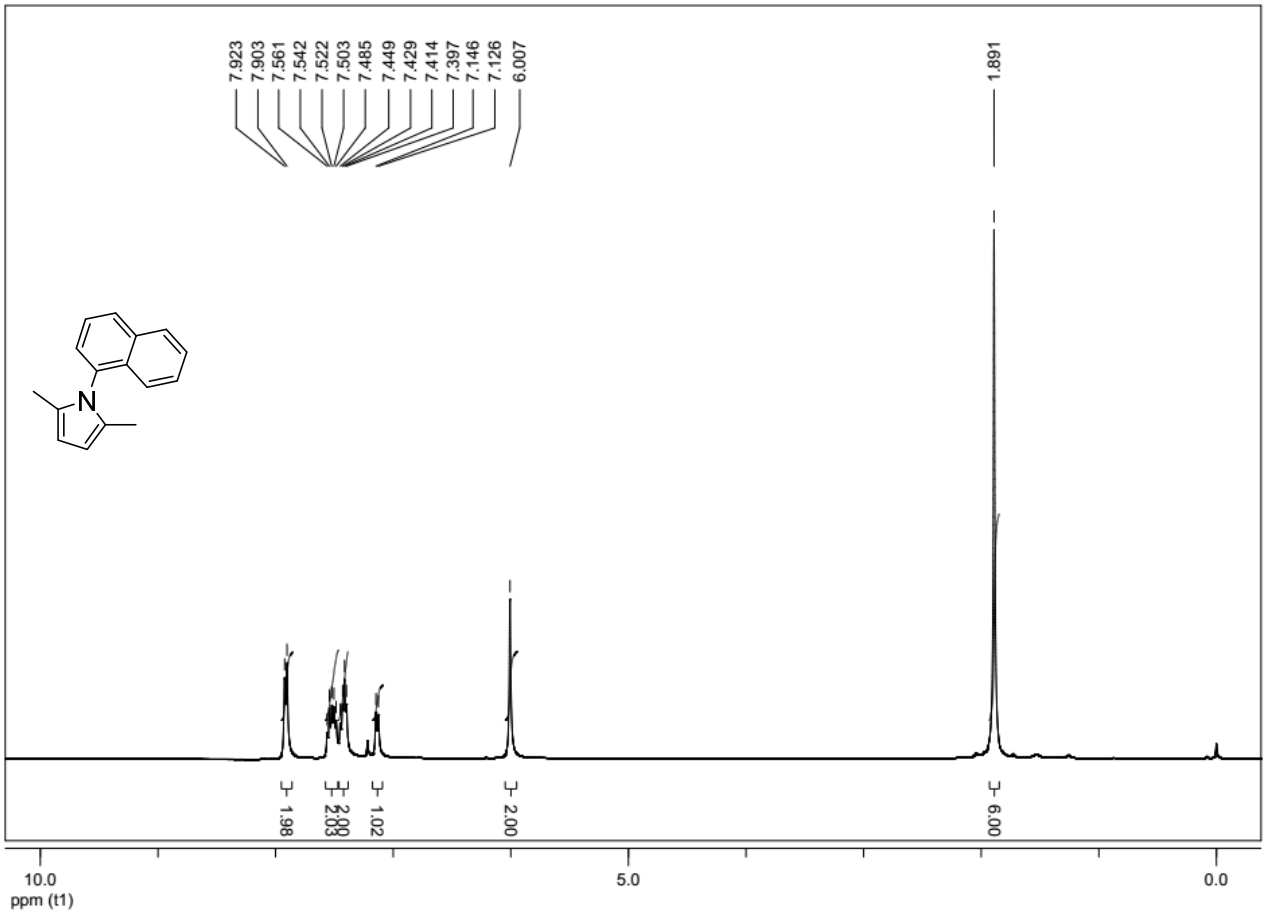

158.828
131.734
129.186
128.984
114.165
105.230
77.321
77.003
76.685
55.415
12.907
150
100
50
0
ppm (t1)

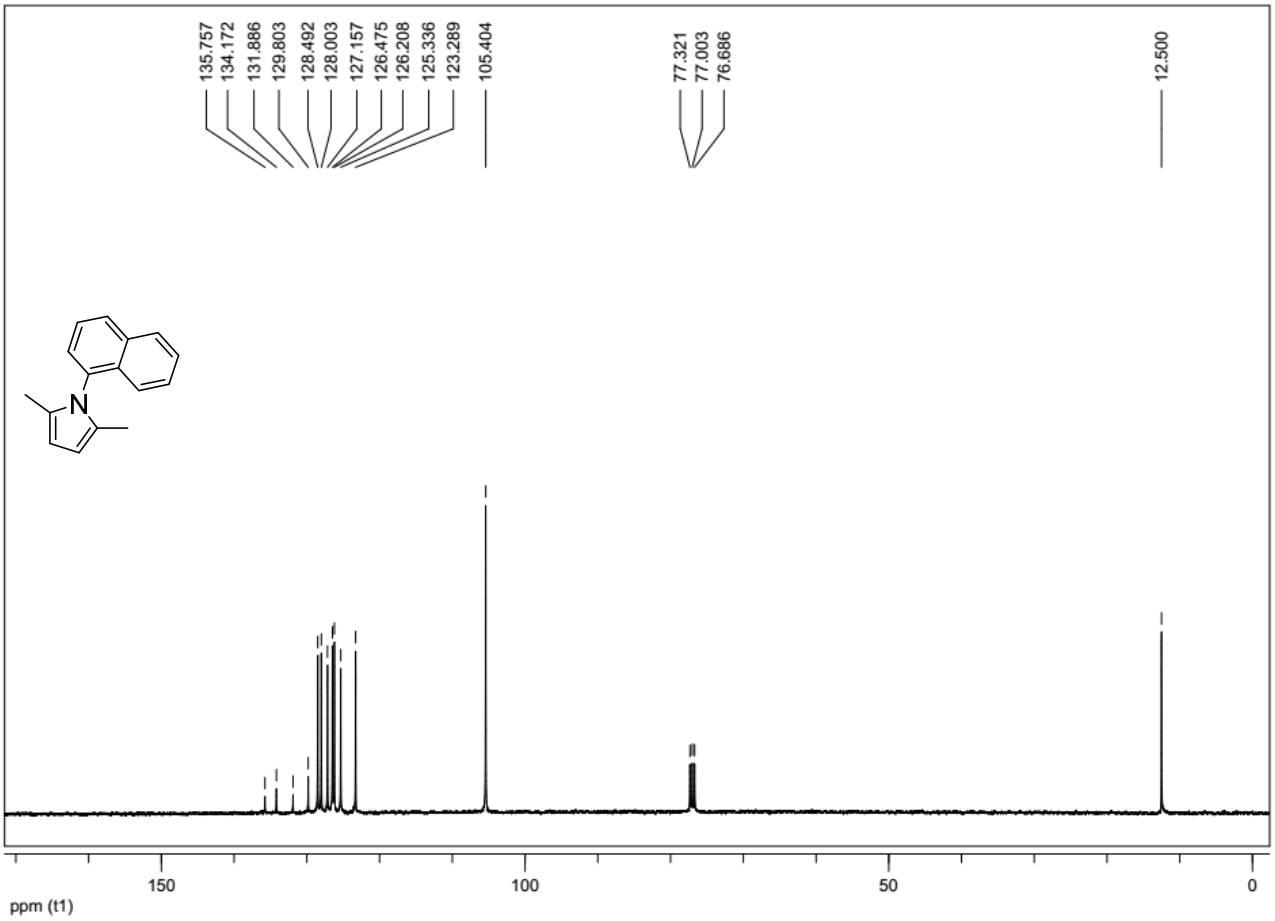

7.427
7.407
7.147
7.127
5.897
2.019
Cl
N
2.04
2.00
2.00
6.03
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

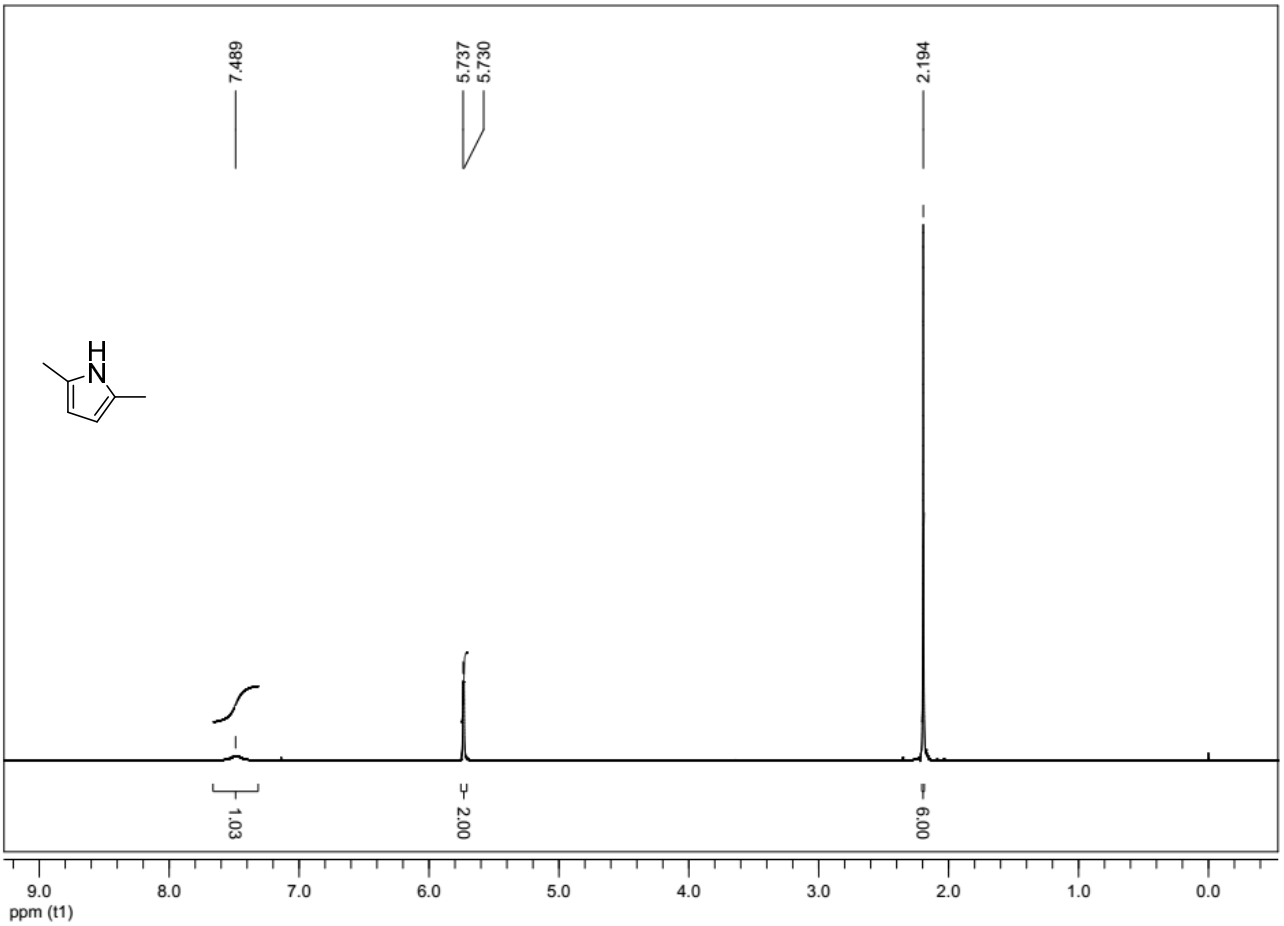

137.469
133.460
129.442
129.247
128.622
106.016
77.320
77.003
76.685
12.900
Cl
N
150
100
50
0
ppm (t1)

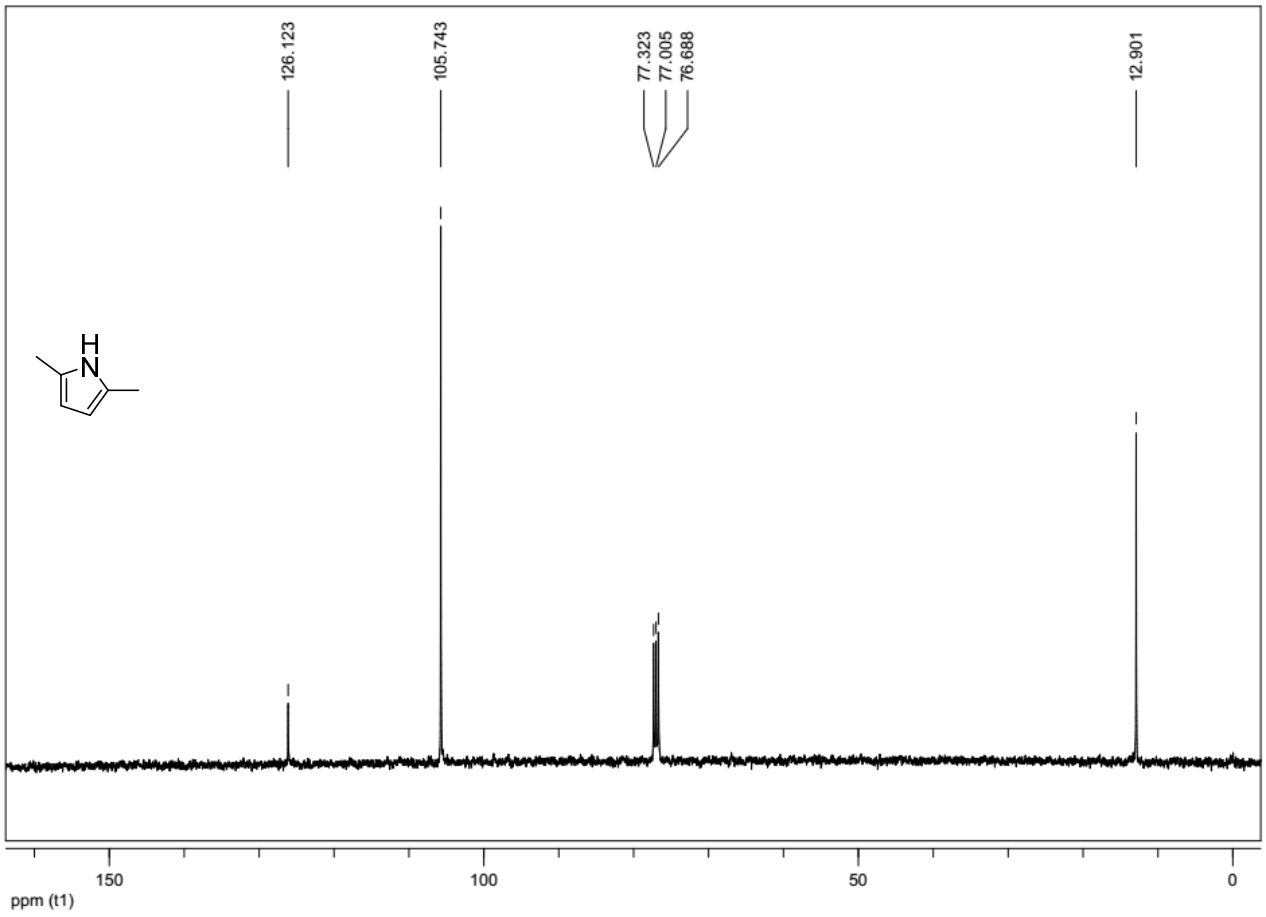

8.659
8.649
8.532
7.587
7.568
7.448
7.436
7.430
7.417
5.943
2.044
0.99
1.02
1.04
1.04
2.00
6.05
10.0
5.0
0.0
ppm (t1)

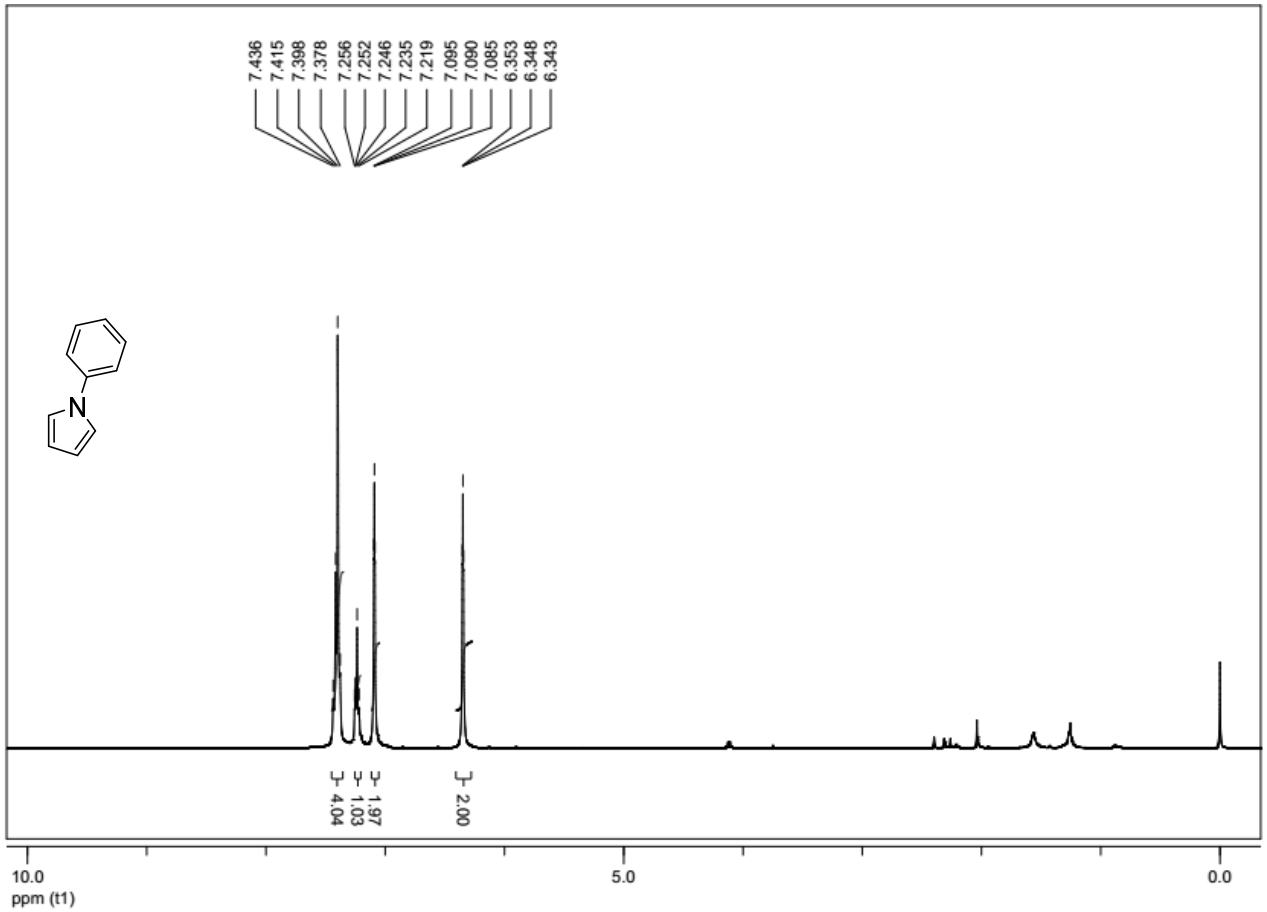

149.344
148.782
135.572
135.498
128.907
123.671
106.626
77.321
77.003
76.685
12.970
150
100
50
0
ppm (t1)

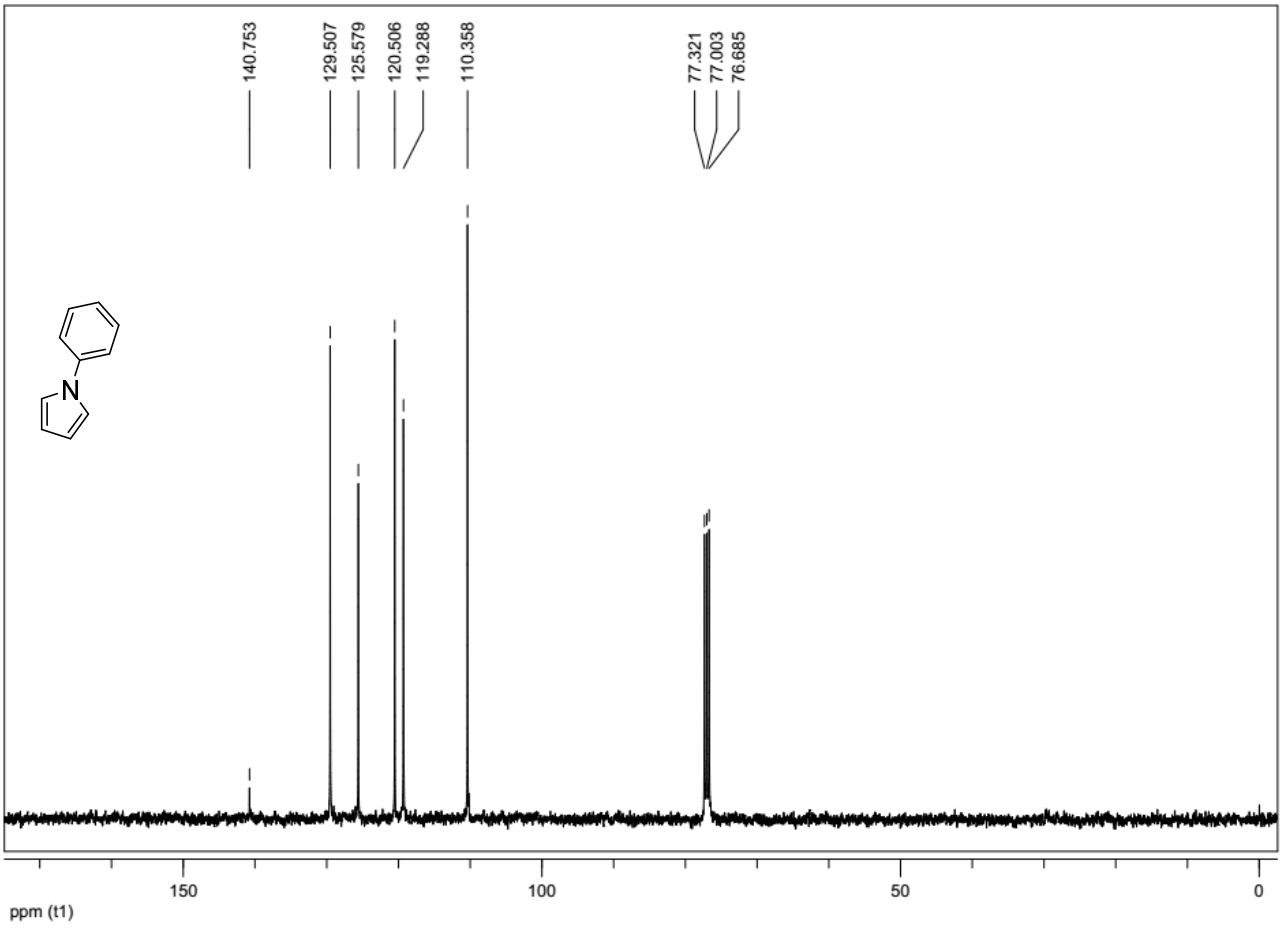

7.923
7.903
7.561
7.542
7.522
7.503
7.485
7.449
7.429
7.414
7.397
7.146
7.126
6.007
1.891
1.98
2.03
1.02
2.00
6.00
10.0
5.0
0.0
ppm (t1)

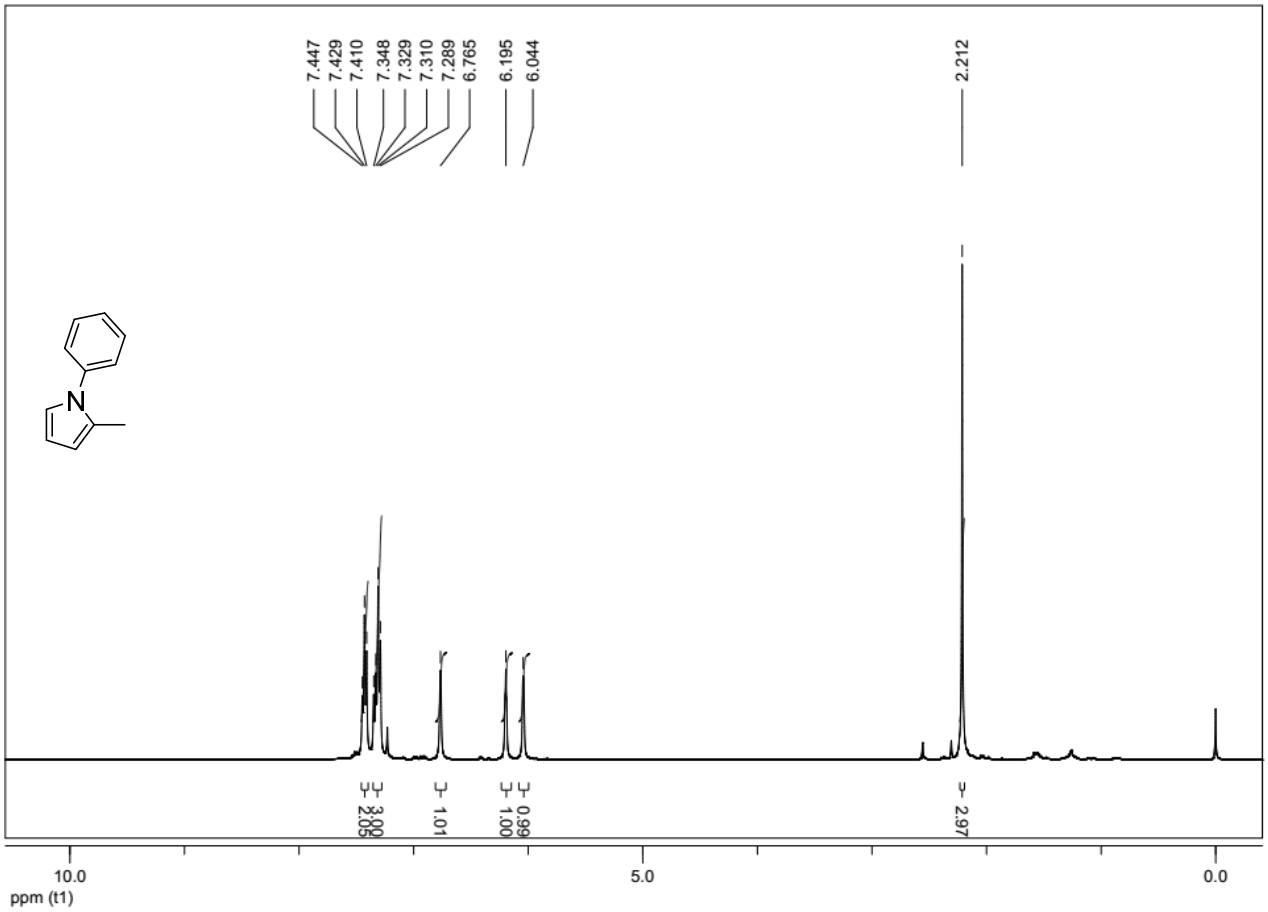

135.757
134.172
131.886
129.803
128.492
128.003
127.157
126.475
126.208
125.336
123.289
105.404
77.321
77.003
76.686
12.500
150
100
50
0
ppm (t1)

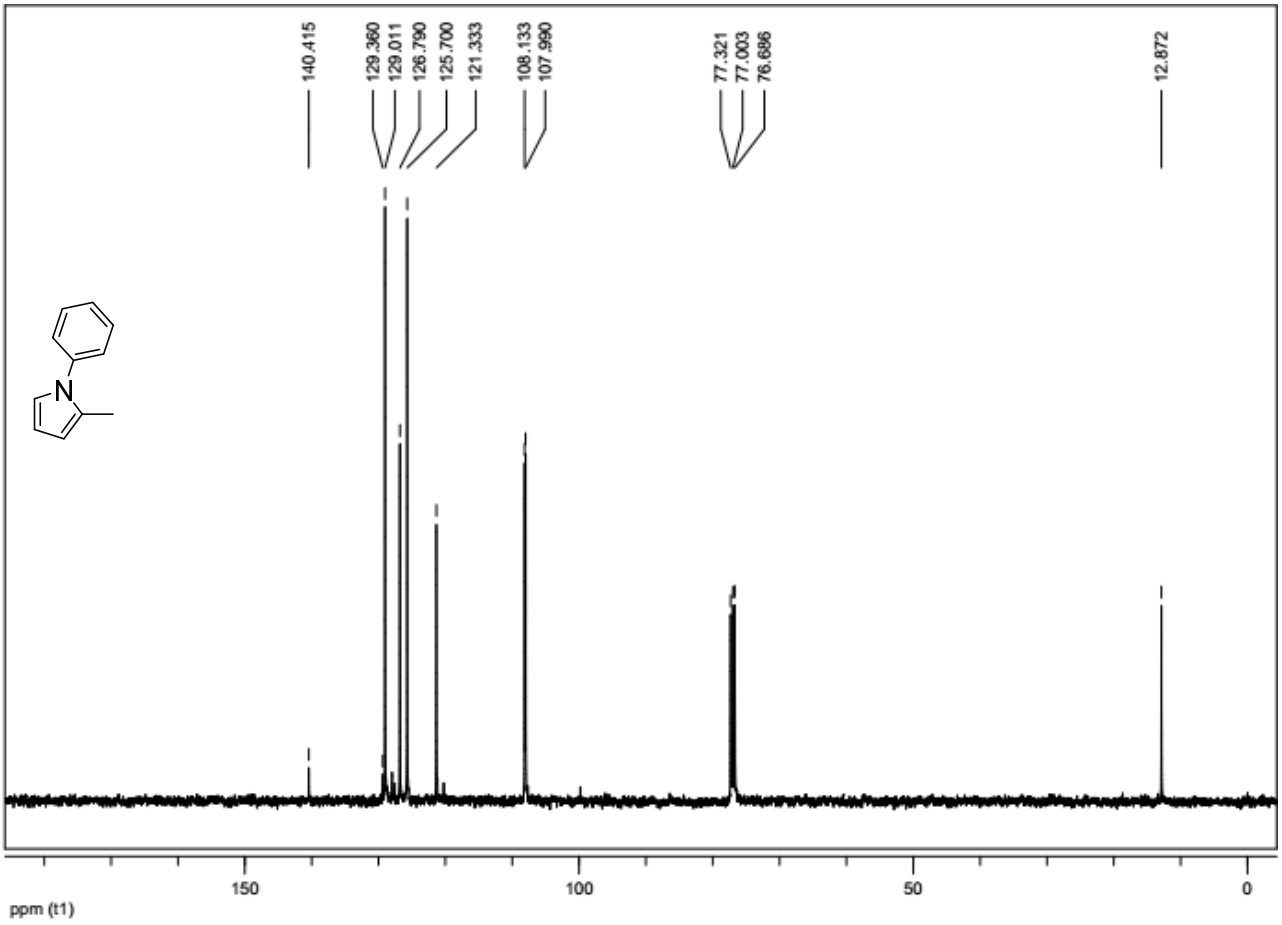

7.489
5.737
5.730
2.194
1.03
2.00
6.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


126.123
105.743
77.323
77.005
76.688
12.901
150
100
50
0
ppm (t1)


7.436
7.415
7.398
7.378
7.256
7.252
7.246
7.235
7.219
7.095
7.090
7.085
6.353
6.348
6.343
4.04
1.03
1.97
2.00
10.0
5.0
0.0
ppm (t1)


140.753
129.507
125.579
120.506
119.288
110.358
77.321
77.003
76.685
150
100
50
0
ppm (t1)


7.447
7.429
7.410
7.348
7.329
7.310
7.289
6.765
6.195
6.044
2.212
2.05
3.00
1.01
1.00
0.99
2.97
10.0
5.0
0.0
ppm (t1)


140.415
129.360
129.011
126.790
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108.133
107.990
77.321
77.003
76.686
12.872
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50
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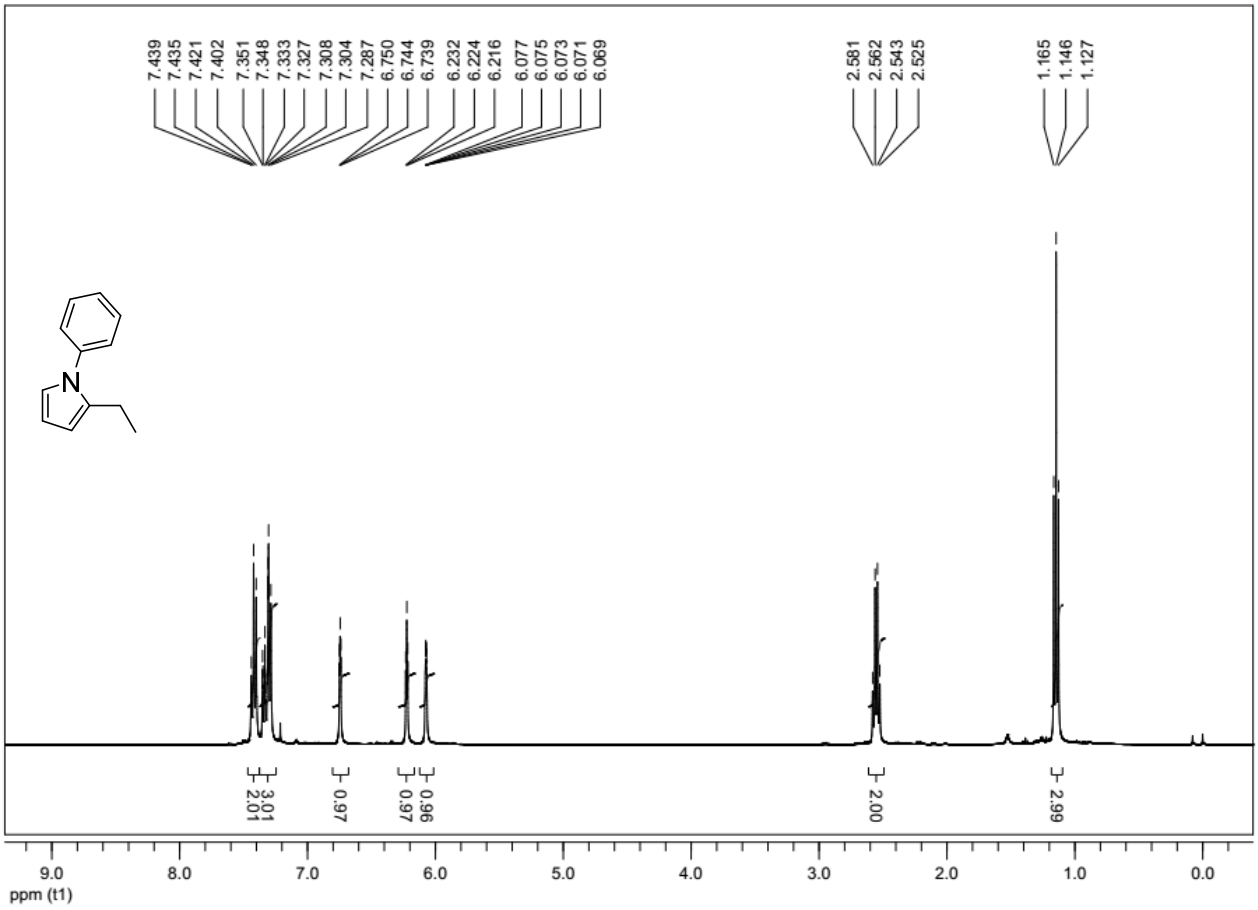
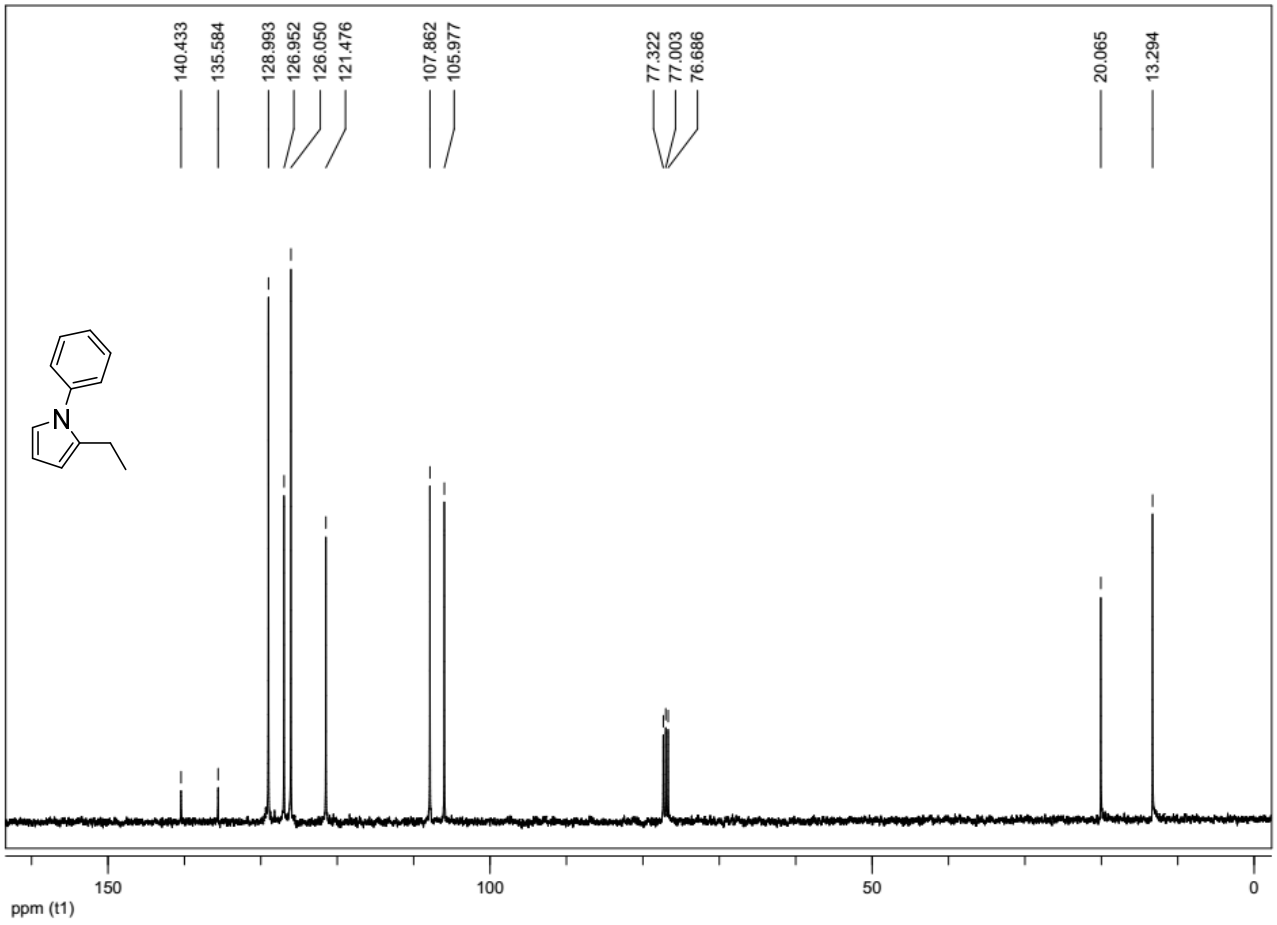
ppm (t1)


7.439
7.435
7.421
7.402
7.351
7.348
7.333
7.327
7.308
7.304
7.287
6.750
6.744
6.739
6.232
6.224
6.216
6.077
6.075
6.073
6.071
6.069
2.581
2.562
2.543
2.525
1.165
1.146
1.127
2.01
3.01
0.97
0.97
0.96
2.00
2.99
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


140.433
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128.993
126.952
126.050
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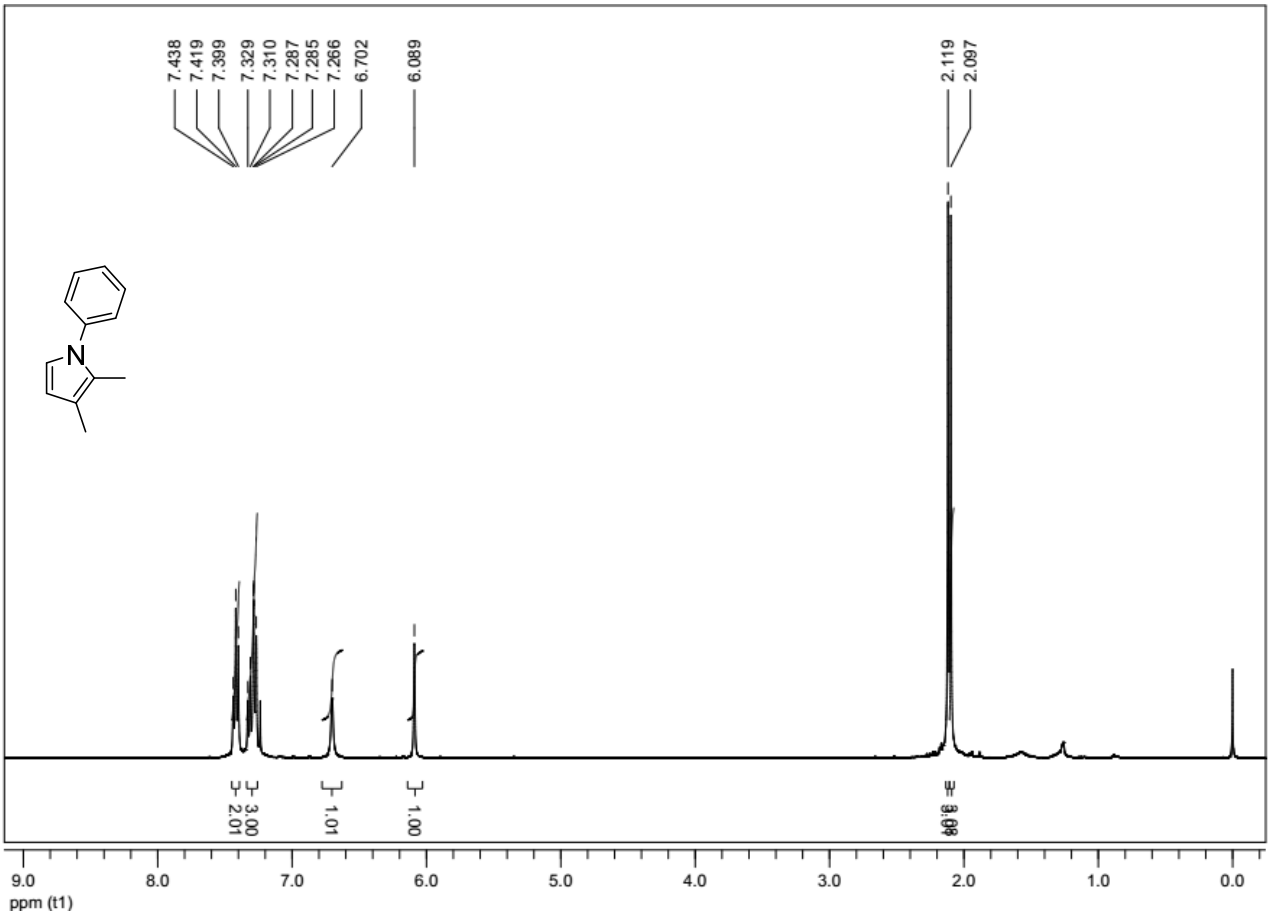
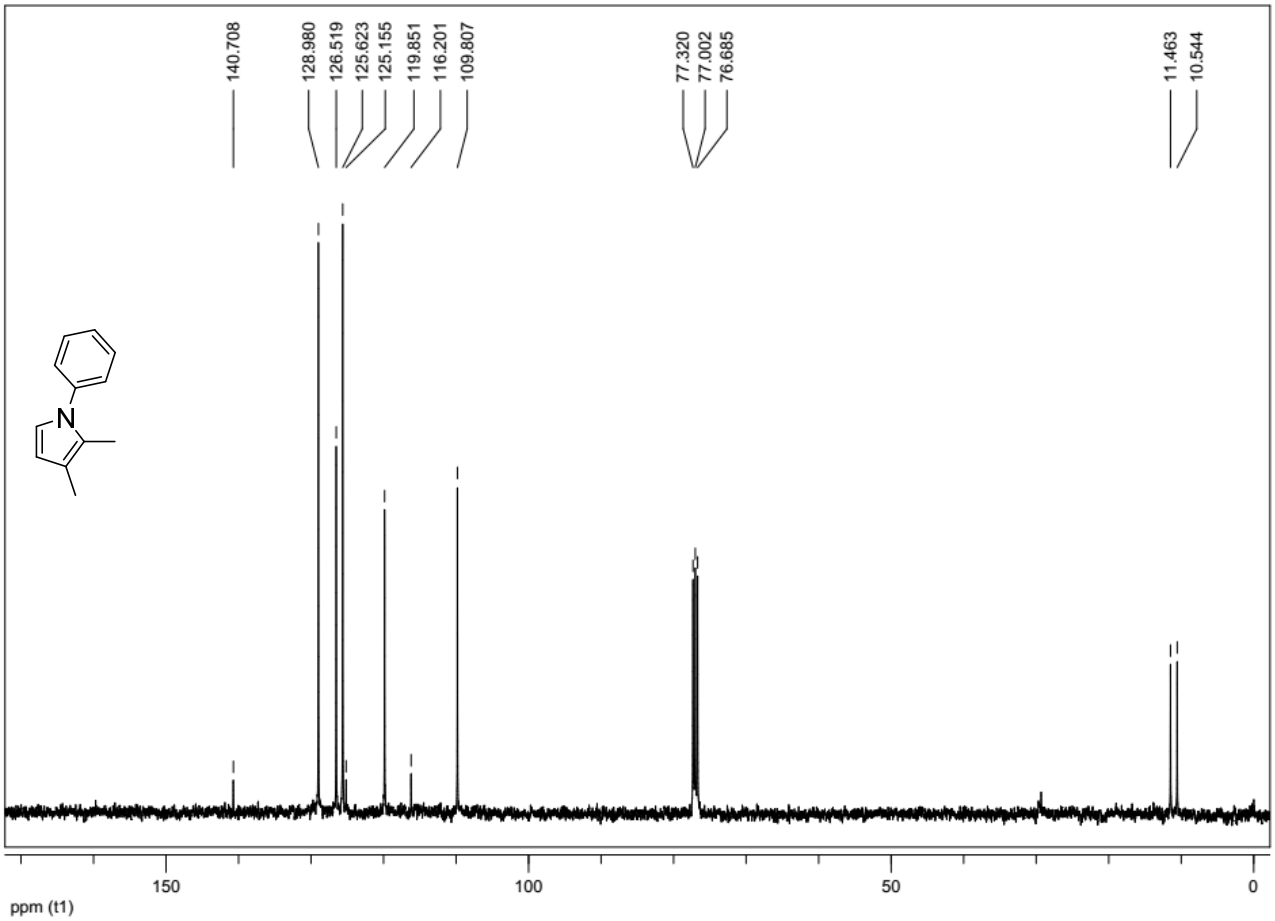
107.862
105.977
77.322
77.003
76.686
20.065
13.294
150
100
50
0
ppm (t1)


7.438
7.419
7.399
7.329
7.310
7.287
7.285
7.266
6.702
6.089
2.119
2.097
3.00
2.01
1.01
1.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


140.708
128.980
126.519
125.623
125.155
119.851
116.201
109.807
77.320
77.002
76.685
11.463
10.544
150
100
50
0
ppm (t1)