Supporting Information For:

Copper-Catalyzed 5-Endo-trig Cyclization of Ketoxime Carboxylates: A Facile Synthesis of 2-Arylpyrroles

Wei Du, Mi-Na Zhao, Zhi-Hui Ren, Yao-Yu Wang and Zheng-Hui Guan*

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, Department of Chemistry & Materials Science, Northwest University, Xi'an 710069, P. R. China

E-mail: guanzhh@nwu.edu.cn

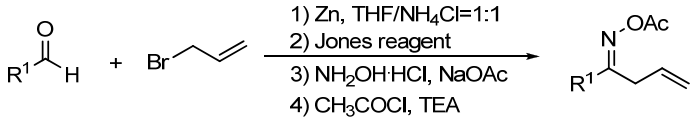
CONTENTS

1. General Information

^{1}H and ^{13}C NMR spectra were recorded on Varian instrument (400 MHz) and (100 MHz), The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants, J were reported in Hertz unit (Hz). Preparative TLC was performed on TLC plate, Analytical thin layer chromatography was performed on 10-25um silica gel GF254, visualization was carried out with UV light. Flash column chromatography was performed with SiO_2 (Silicycle Silica Gel (200-300 mesh)). Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification.

2. General Procedure for Preparation of Ketoxime Acetates

Procedure for Preparation of Ketoxime Acetates 1a-1m:



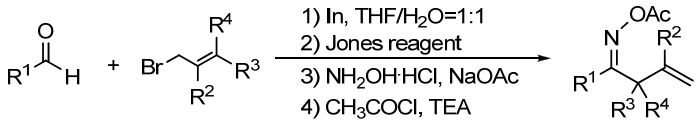
1) To a solution of the aldehyde (1.0 equiv) in anhydrous THF was added the allylbromide (2.0 equiv) and saturated aqueous NH_4Cl. Then, the zinc dust (2.0 equiv) was slowly added to the solution at 0℃ and the resulting suspension was stirred overnight at this temperature. After completion of the reaction, filtered and extracted with ethyl acetate for 3 times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude allylic alcohol product was directly used in the next step without further purification.[1]

2) Allylic alcohol (1.0 equiv) was dissolved in diethyl ether and the solution was kept at 0℃ with stirring. The Jones reagent (2.0-4.0 equiv) was added dropwise at this temperature. Then, the resulting mixture was allowed to warm to room temperature and stirred for 1 h. After completion of the reaction, the diethyl ether layer was separated from the aqueous layer, which was extracted with diethyl ether for 3 times. The combined diethyl ether layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude ketone product was directly used in the next step without further purification.[2]

3) To a solution of hydroxylamine hydrochloride (5.0 equiv) in water was stirred at room temperature. Sodium acetate (7.0 equiv) was dissolved in ethanol and added to the solution. The mixture was stirred at this temperature while the ketone (dissolved in ethanol) was added. The resulting suspension was stirred overnight and concentrated in vacuo. Then, the mixture was extracted with ethyl acetate 3 times and the combined extracts were washed with water and brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude material was purified by flash chromatography on silica gel to afford the corresponding ketoxime.[3]

4) To a solution of the ketoxime (1 equiv) and TEA (Et_3N) (2 equiv) in anhydrous CH_2Cl_2 (20 mL) was stirred at 0℃ while CH_3COCl (1.1 equiv) in CH_2Cl_2 (5 ml) was added dropwise. Then, the resulting mixture was stirred for 2h at the same temperature. After completion of the reaction, water was added and the mixture extracted with CH_2Cl_2 for 3 times. The combined organic extracts were washed with water, brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude material was purified by flash chromatography on silica gel to afford the corresponding ketoxime acetate with hexanes/ethyl acetate as the eluent.[4]

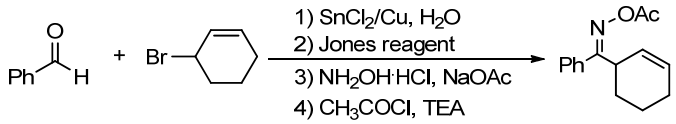
Procedure for Preparation of Ketoxime Acetates 1n and 1p:



1) To a solution of the 3-bromo-2-methylprop-1-ene (1.1 equiv) or its analogue and indium (1.1 equiv) in THF/H_2O (1:1) was stirred at room temperature while the aldehyde (1.0 equiv) was added to the solution. Then, the resulting mixture was stirred for 10-24 h at the same temperature. After completion of the reaction, saturated ammonium chloride was added at 0℃. The THF layer was separated from the aqueous layer, which was extracted with diethyl ether for 3 times. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude allylic alcohol product was directly used in the next step without further purification.[5]

Steps 2), 3), and 4) are same as above-mentioned.

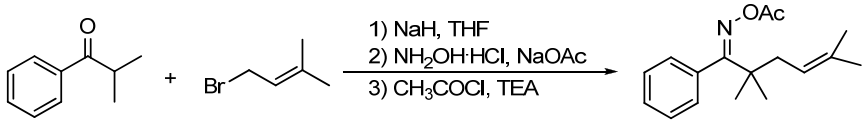
Procedure for Preparation of Ketoxime Acetate 1o:



1) Benzaldehyde (1.0 equiv) and 3-bromo-1-cyclohexene (1.8 equiv) were added in water and the solution was kept at room temperature with stirring while the $SnCl_2 \bullet H_2O$ (2.0 equiv) and copper powder (1.0 equiv) were added. Then, the resulting mixture was vigorously stirred at this temperature for 24 h. After completion of the reaction, the mixture was extracted with ethyl acetate (3×30 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated. The crude material was purified by flash chromatography on silica gel to afford the cyclohex-2-en-1-yl(phenyl)methanol.[6]

Steps 2), 3), and 4) are same as above-mentioned.

Procedure for Preparation of Ketoxime Acetate 1q:



1) To a solution of the isobutyrophenone (0.60 mL, 3.88 mmol) in anhydrous THF (15 mL) was added the NaH (186 mg, 4.65 mmol). The solution was stirred at room temperature for 0.5h. Then, the solution of 1-bromo-3-methylbut-2-ene (0.69 g, 4.66 mmol) in THF (5.0 mL) was slowly added to the solution at this temperature and the resulting suspension was stirred at reflux for 8 h. After completion of the reaction, the reaction mixture was cooled to room temperature. The reaction was quenched by adding saturated aqueous NH_4Cl, and the mixture was extracted with ethyl acetate for 3 times. The combined organic extracts were washed with water, brine, dried over Na_2SO_4, filtered and concentrated in vacuo. The crude material was purified by flash chromatography on silica gel.[7]

Steps 2), and 3) are same as above-mentioned.

Reference:

[1] Dam, J. H.; Fristrup, P.; Madsen, R. *J. Org. Chem.* 2008, **73**, 3228.

[2] Jiang, D.; Peng, J.; Chen, Y. *Org. Lett.* 2008, **10**, 1695.

[3] Garzan, A.; Jaganathan, A.; Marzijarani, N. S.; Yousefi, R.; Whitehead, D. C.; Jackson, J. E.; Borhan, B. *Chem. Eur. J.* 2013, **19**, 9015.

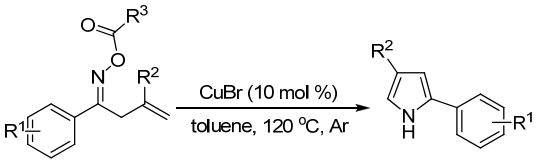
[4] Zaman, S.; Mitsuru, K.; Abell, A. D. *Org. Lett.* 2005, **7**, 609.

[5] Zhu, M.-K.; Zhao, J.-F.; Loh, T.-P. *J. Am. Chem. Soc.* 2010, **132**, 6284.

[6] Tan, X.-H.; Tao, C.-Z.; Hou, Y.-Q.; Luo, L.; Liu, L.; Guo, Q.-X. *Chin. J. Chem.* 2005, **23**, 237.

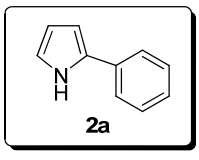
[7] Han, B.; Yang, X.-L.; Fang, R.; Yu, W.; Wang, C.; Duan, X.-Y.; Liu, S. *Angew. Chem., Int. Ed.* 2012, **51**, 8816.

3. General Procedure for Synthesis of 2-Arylpyrroles



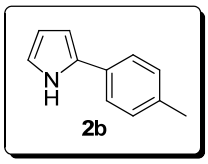
Ketoxime carboxylate (0.3 mmol), CuBr (10 mol%, 4.3 mg), and toluene (3 mL) was charged in a 25 mL round bottom flask. Then, the flask was evacuated and back-filled with Ar (3-times, balloon) and stirred at 120 °C. When the reaction was completed (detected by TLC), the mixture was cooled to room temperature. The reaction was quenched with H_2O (10 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and then evaporated in vacuo. The residue was purified by column chromatography on silica gel to afford the corresponding pyrroles with hexanes/ethyl acetate as the eluent.

4. Spectroscopic Data for Products



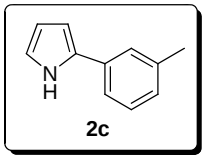
2a

2a: ^{1}H NMR (DMSO-d^6, 400 MHz): δ = 11.28 (s, 1 H), 7.62 (d, J = 7.6 Hz, 2 H), 7.34 (t, J = 7.6 Hz, 2 H), 7.14 (t, J = 7.2 Hz, 1 H), 6.84 (s, 1 H), 6.51 (s, 1 H), 6.11 (s, 1 H); ^{13}C NMR (DMSO-d^6, 100 MHz): δ = 133.0, 131.1, 128.7, 125.4, 123.3, 119.3, 109.1, 105.6. HRMS Calcd (ESI) m/z for $C_{10}H_{10}N$: $[M+H]^+$ 144.0808, found: 144.0814.



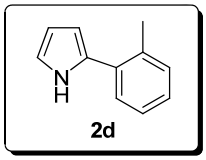
2b

2b: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.38 (s, 1 H), 7.36 (d, *J* = 7.6 Hz, 2 H), 7.17 (d, *J* = 7.2 Hz, 2 H), 6.83 (s, 1 H), 6.48 (s, 1 H), 6.29 (s, 1 H), 2.35 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 135.8, 132.1, 129.9, 129.5, 123.7, 118.4, 109.8, 105.3, 21.1. HRMS Calcd (ESI) m/z for $C_{11}H_{12}N$: $[M+H]^+$ 158.0964, found: 158.0967.



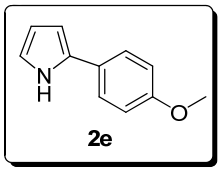
2c

2c: ^{1}H NMR (DMSO-*d*^{6}, 400 MHz): δ = 11.25 (s, 1 H), 7.46-7.41 (m, 2 H), 7.22 (t, *J* = 7.2 Hz, 1 H), 6.96 (d, *J* = 6.8 Hz, 1 H), 6.83 (s, 1 H), 6.49 (s, 1 H), 6.11 (s, 1 H), 2.32 (s, 3 H); ^{13}C NMR (DMSO-*d*^{6}, 100 MHz): δ = 137.7, 133.0, 131.2, 128.6, 126.1, 124.0, 120.6, 119.2, 109.0, 105.5, 21.2. HRMS Calcd (ESI) m/z for $C_{11}H_{10}N$: $[M-H]^+$ 156.0819, found: 156.0823.



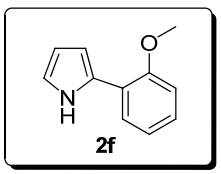
2d

2d: ^{1}H NMR (DMSO-*d*^{6}, 400 MHz): δ = 10.98 (s, 1 H), 7.35 (d, *J* = 7.2 Hz, 1 H), 7.21-7.15 (m, 2 H), 7.11-7.08 (m, 1 H), 6.80 (s, 1 H), 6.19 (s, 1 H), 6.10 (s, 1 H), 2.36 (s, 3 H); ^{13}C NMR (DMSO-*d*^{6}, 100 MHz): δ = 134.1, 133.0, 130.8, 130.3, 127.7, 126.0, 125.8, 118.4, 108.5, 108.4, 21.3. HRMS Calcd (ESI) m/z for $C_{11}H_{12}N$: $[M+H]^+$ 158.0964, found: 158.0960.



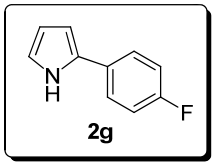
2e

2e: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.33 (s, 1 H), 7.40 (d, *J* = 8.0 Hz, 2 H), 6.91 (d, *J* = 8.4 Hz, 2 H), 6.82 (s, 1 H), 6.41 (s, 1 H), 6.28 (s, 1 H), 3.82 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.1, 132.0, 125.8, 125.2, 118.2, 114.3, 109.8, 104.8, 55.2. HRMS Calcd (ESI) m/z for $C_{11}H_{12}NO$: $[M+H]^+$ 174.0913, found: 174.0920.



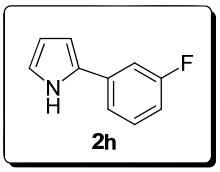
2f

2f: ^{1}H NMR (DMSO-d^6, 400 MHz): δ = 10.94 (s, 1 H), 7.62 (d, J = 7.2 Hz, 1 H), 7.15 (t, J = 7.6 Hz, 1 H), 7.04 (d, J = 8.0 Hz, 1 H), 6.96 (t, J = 7.6 Hz, 1 H), 6.83 (s, 1 H), 6.60 (s, 1 H), 6.12 (s, 1 H), 3.87 (s, 3 H); ^{13}C NMR (DMSO-d^6, 100 MHz): δ = 154.7, 127.9, 126.5, 126.0, 121.4, 120.7, 118.6, 111.8, 108.2, 107.8, 55.3. HRMS Calcd (ESI) m/z for $C_{11}H_{12}NO$: $[M+H]^+$ 174.0913, found: 174.0920.



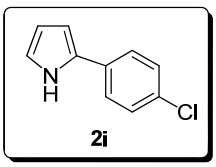
2g

2g: ^{1}H NMR (DMSO-d^6, 400 MHz): δ = 11.28 (s, 1 H), 7.63 (d, J = 5.2 Hz, 2 H), 7.18 (t, J = 7.2 Hz, 2 H), 6.84 (s, 1 H), 6.47 (s, 1 H), 6.11 (s, 1 H); ^{13}C NMR (DMSO-d^6, 100 MHz): δ = 160.4 (d, J_{CF} = 240.6 Hz), 130.2, 129.7, 125.1 (d, J_{CF} = 7.8 Hz), 119.3, 115.5 (d, J_{CF} = 21.3 Hz), 109.1, 105.5. HRMS Calcd (ESI) m/z for $C_{10}H_7FN$: $[M-H]^+$ 160.0568, found: 160.0570.



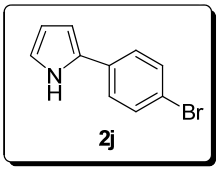
2h

2h: ^{1}H NMR (DMSO-d^6, 400 MHz): δ = 11.37 (s, 1 H), 7.46 (d, J = 8.0 Hz, 2 H), 7.38-7.33 (m, 1 H), 6.94 (t, J = 6.8 Hz, 1 H), 6.88 (s, 1 H), 6.60 (s, 1 H), 6.13 (s, 1 H); ^{13}C NMR (DMSO-d^6, 100 MHz): δ = 162.8 (d, J_{CF} = 240.6 Hz), 135.4 (d, J_{CF} = 8.6 Hz), 130.6 (d, J_{CF} = 8.8 Hz), 129.9, 120.0, 119.3, 111.8 (d, J_{CF} = 21.1 Hz), 109.7 (d, J_{CF} = 22.7 Hz), 109.3, 106.8. HRMS Calcd (ESI) m/z for $C_{20}H_{17}F_2N_2$: $[2M+H]^+$ 323.1354, found: 323.1339.



2i

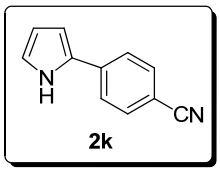
2i: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.41 (s, 1 H), 7.39 (d, J = 8.4 Hz, 2 H), 7.32 (d, J = 8.4 Hz, 2 H), 6.87 (s, 1 H), 6.51 (s, 1 H), 6.30 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 131.6, 131.1, 130.9, 128.9, 124.9, 119.2, 110.2, 106.3. HRMS Calcd (ESI) m/z for $C_{10}H_7ClN$: $[M-H]^+$ 176.0273, found: 176.0275.



2j

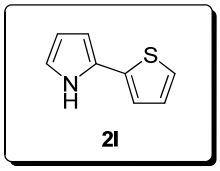
2j: ^{1}H NMR (DMSO-d^6, 400 MHz): δ = 11.37 (s, 1 H), 7.58 (d, J = 8.4 Hz, 2 H), 7.51

(d, J = 8.0 Hz, 2 H), 6.88 (s, 1 H), 6.55 (s, 1 H), 6.13 (s, 1 H); ^{13}C NMR (DMSO-d^6, 100 MHz): δ = 132.2, 131.5, 129.9, 125.2, 119.9, 117.9, 109.3, 106.3. HRMS Calcd (ESI) m/z for $C_{10}H_7BrN$: $[M-H]^+$ 219.9767, found: 219.9778.



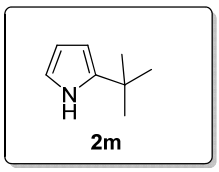
2k

2k: ^{1}H NMR (DMSO-d^6, 400 MHz): δ = 11.55 (s, 1 H), 7.74 (s, 4 H), 6.95 (s, 1 H), 6.71 (s, 1 H), 6.15 (s, 1 H); ^{13}C NMR (DMSO-d^6, 100 MHz): δ = 137.1, 132.7, 129.4, 123.5, 121.7, 119.4, 110.0, 108.7, 106.9. HRMS Calcd (ESI) m/z for $C_{11}H_8N_2Na$: $[M+Na]^+$ 191.0580, found: 191.0579.



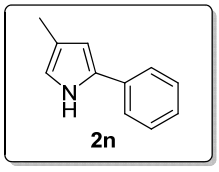
2l

2l: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.29 (s, 1 H), 7.14 (d, J = 4.0 Hz, 1 H), 7.02 (s, 1 H), 7.01 (s, 1 H), 6.80 (s, 1 H), 6.41 (s, 1 H), 6.25 (s, 1 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 136.2, 127.6, 126.6, 122.6, 120.8, 118.5, 109.9, 106.6. HRMS Calcd (ESI) m/z for C_8H_8NS: $[M+H]^+$ 150.0372, found: 150.0374.



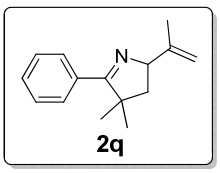
2m

2m: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.92 (s, 1 H), 6.59 (s, 1 H), 6.05 (s, 1 H), 5.87 (s, 1 H), 1.22 (s, 9 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 141.8, 115.9, 107.7, 102.3, 31.3, 30.6.



2n

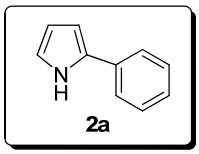
2n: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.08 (s, 1 H), 7.39 (d, J = 7.2 Hz, 2 H), 7.31 (t, J = 7.2 Hz, 2 H), 7.16 (t, J = 7.2 Hz, 1 H), 6.55 (s, 1 H), 6.36 (s, 1 H), 2.14 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 132.8, 131.9, 128.8, 125.9, 123.6, 120.5, 116.8, 107.4, 11.9. HRMS Calcd (ESI) m/z for $C_{11}H_{12}N$: $[M+H]^+$ 158.0964, found: 158.0970.



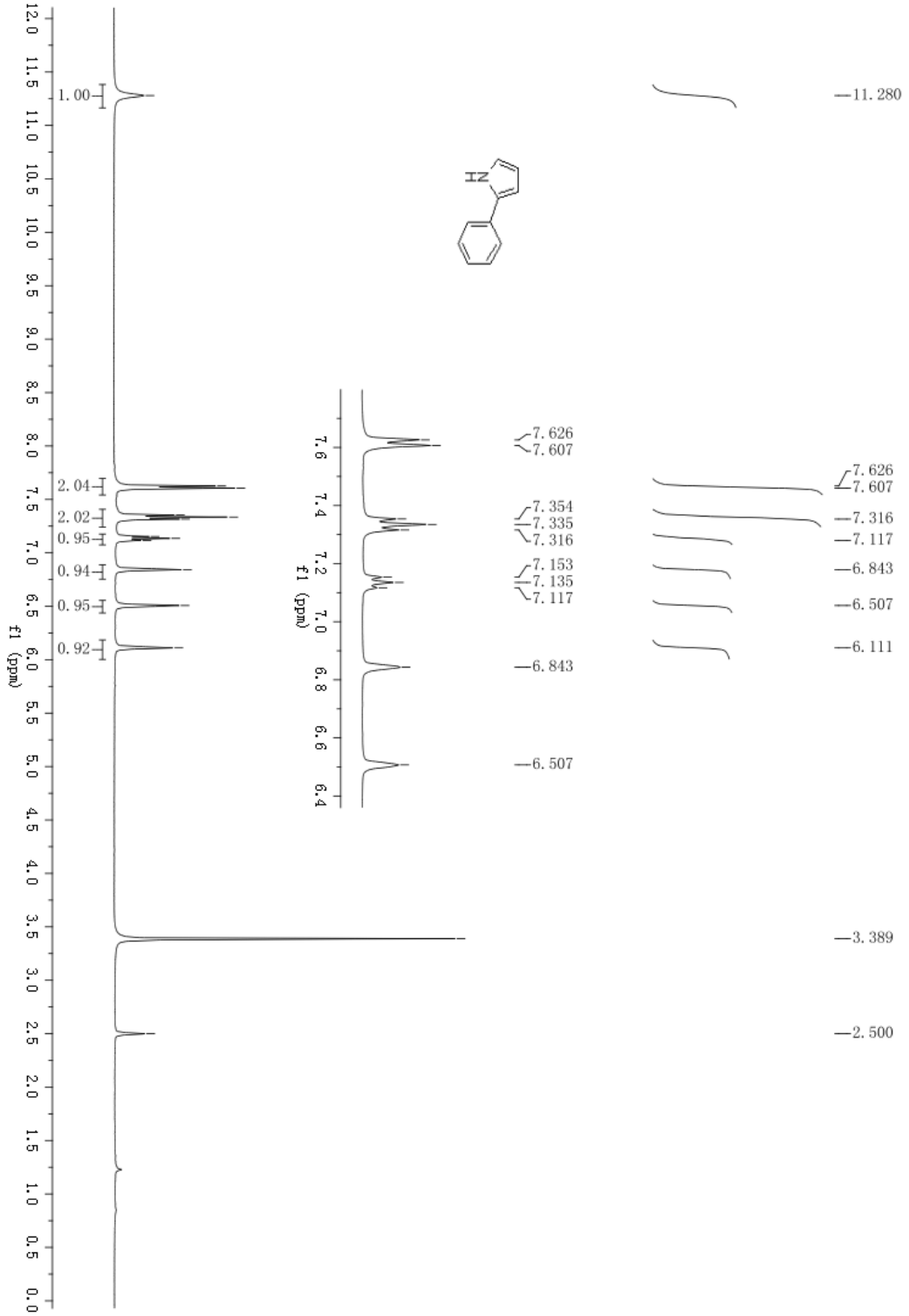
2q

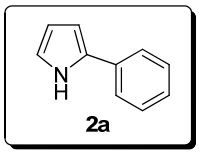
2q: ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.75 (d, *J* = 3.6 Hz, 2 H), 7.38 (s, 3 H), 5.03 (s, 1 H), 4.86 (s, 1 H), 4.51 (t, *J* = 7.6 Hz, 1 H), 2.15-2.10 (m, 1 H), 1.81 (s, 3 H), 1.74 (t, *J* = 9.6 Hz, 1 H), 1.39 (s, 3 H), 1.34 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 179.6, 146.9, 134.6, 129.4, 128.0, 127.8, 110.0, 72.2, 50.3, 47.2, 27.0, 25.8, 19.8. HRMS Calcd (ESI) m/z for $C_{15}H_{20}N$: $[M+H]^+$ 214.1590, found: 214.1597.

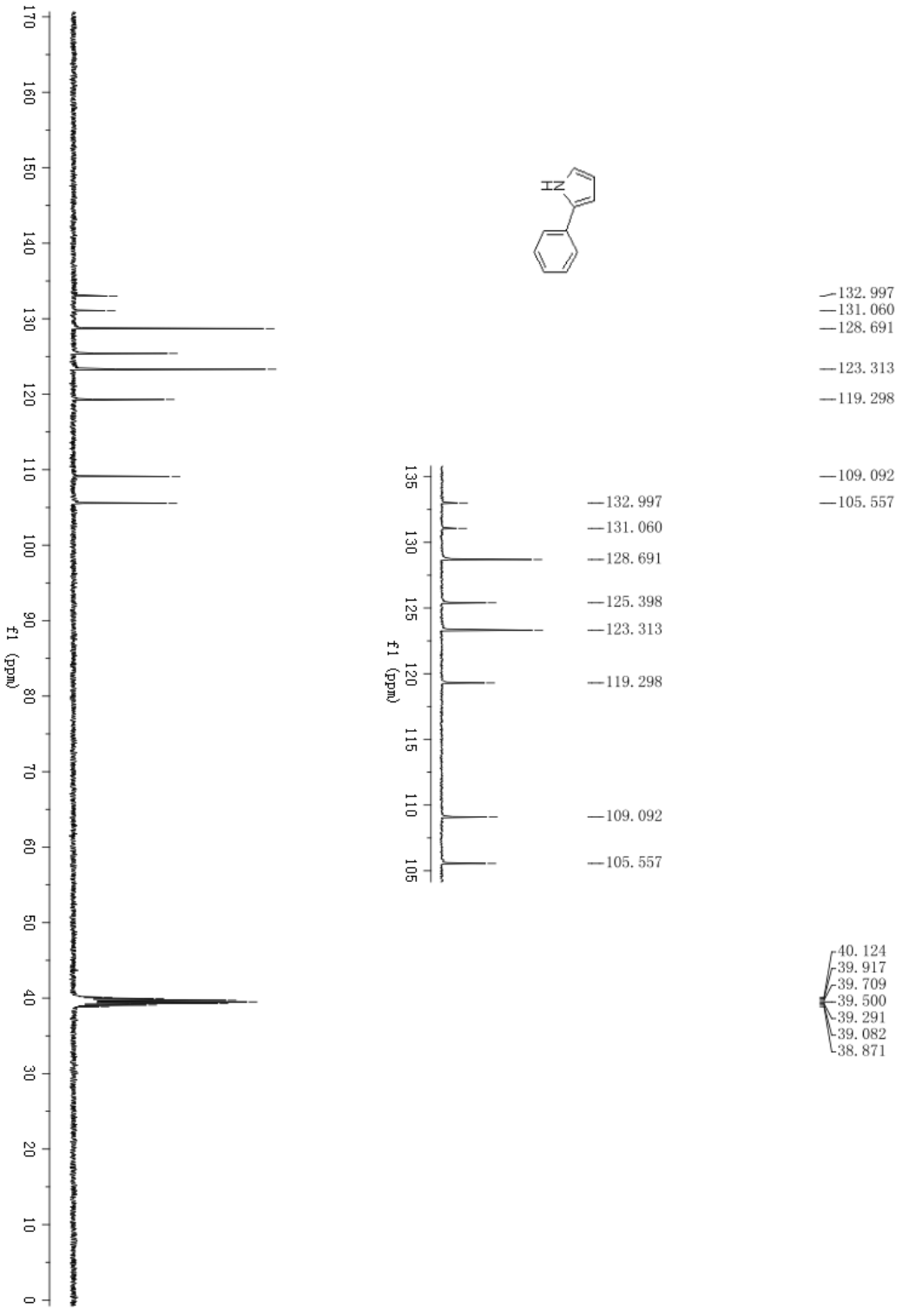
5. Copies of ^{1}H and ^{13}C NMR Spectra

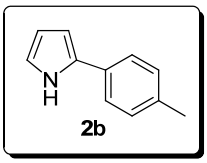


2a

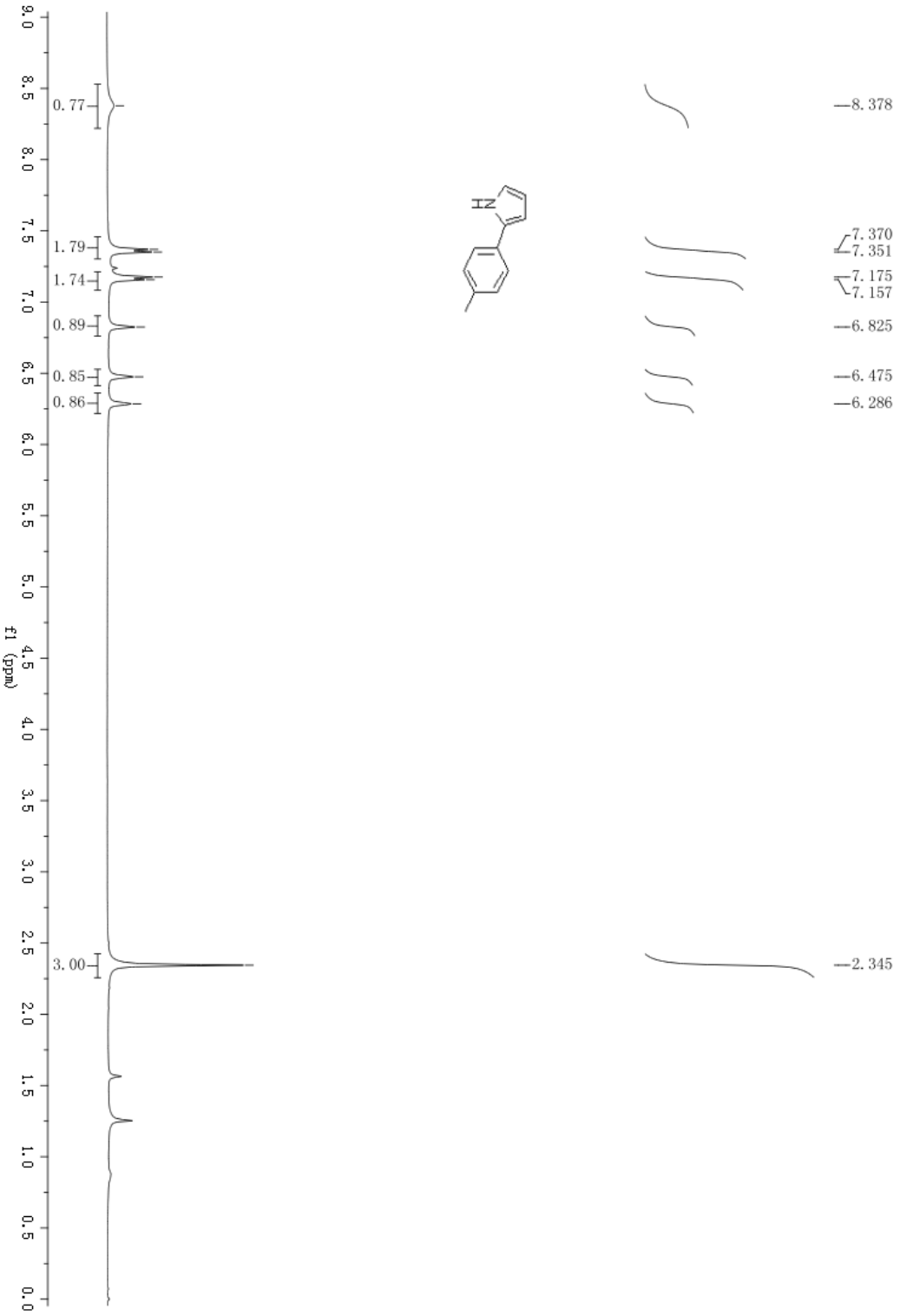


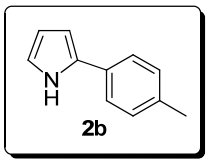

2a

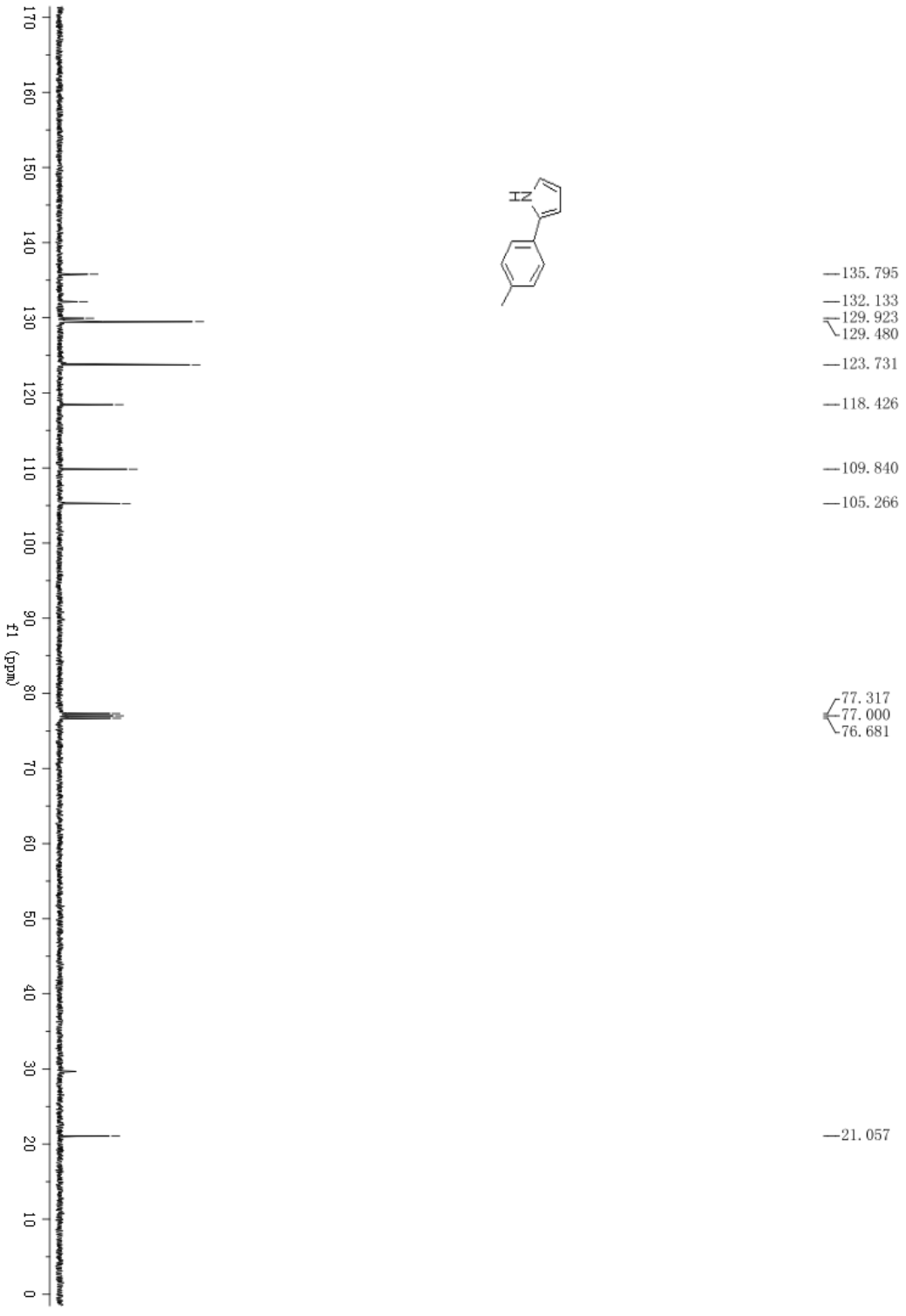

f1 (ppm)
132.997
131.060
128.691
123.313
119.298
109.092
105.557
40.124
39.917
39.709
39.500
39.291
39.082
38.871

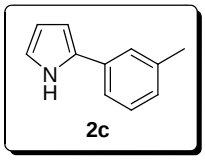

N
H

2b

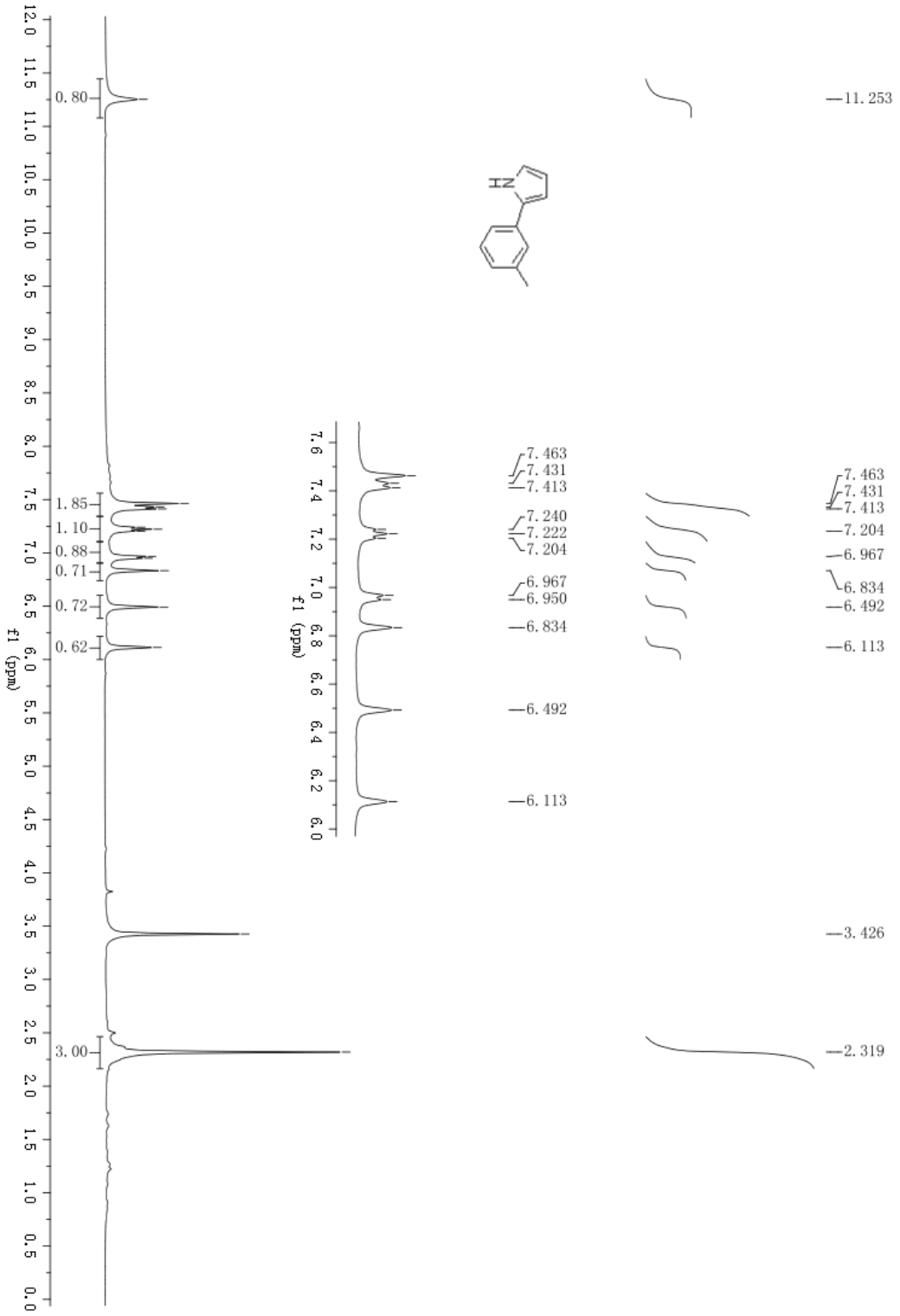

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
0.77
1.79
1.74
0.89
0.85
0.86
3.00
8.378
7.370
7.351
7.175
7.157
6.825
6.475
6.286
2.345

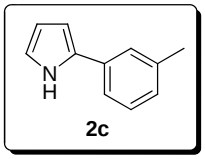

N
H
2b


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
135.795
132.133
129.923
129.480
123.731
118.426
109.840
105.266
77.317
77.000
76.681
21.057

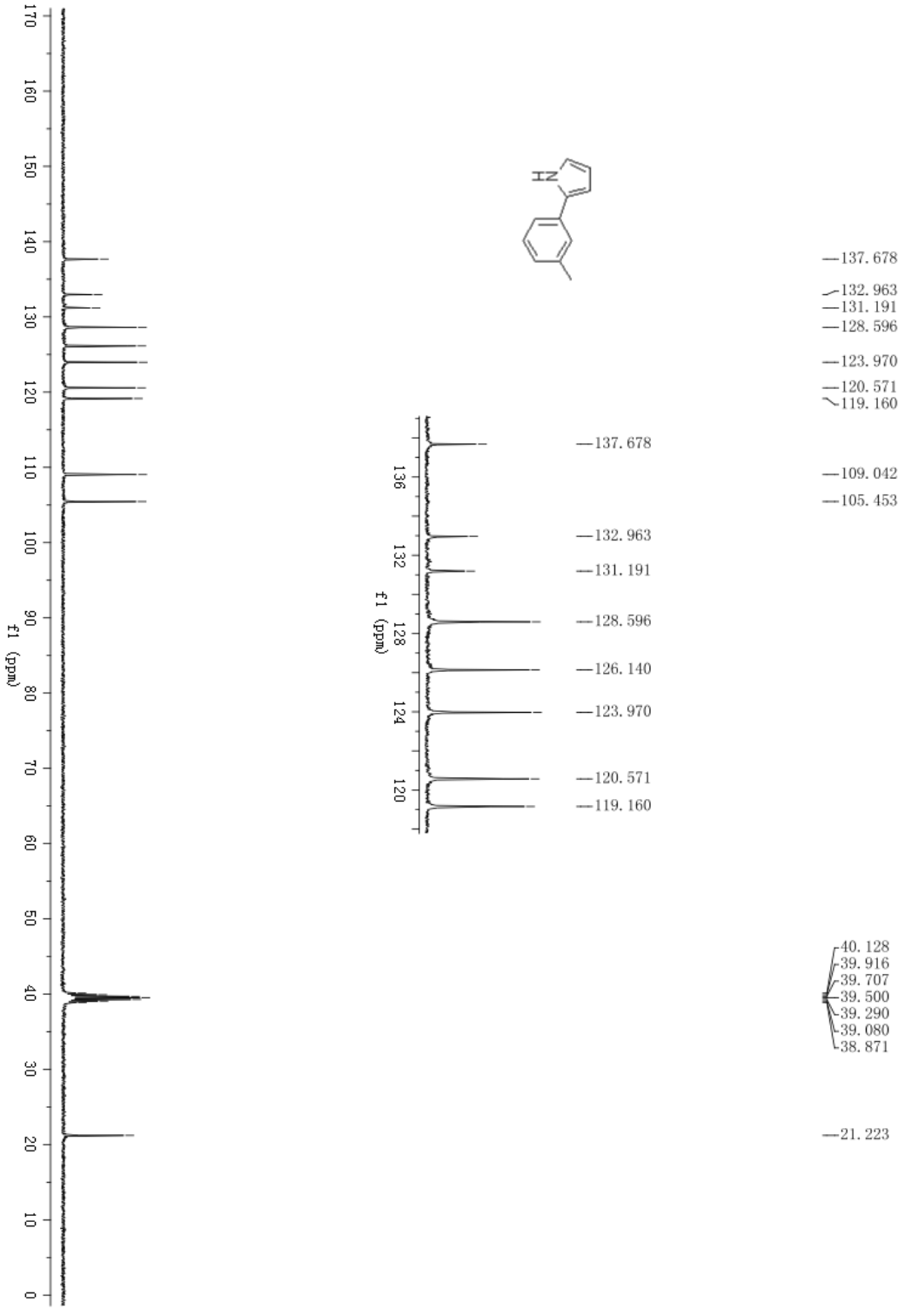

N
H

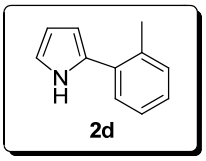
2c


0.80
1.85
1.10
0.88
0.71
0.72
0.62
3.00
f1 (ppm)
7.463
7.431
7.413
7.240
7.222
7.204
6.967
6.950
6.834
6.492
6.113
11.253
3.426
2.319

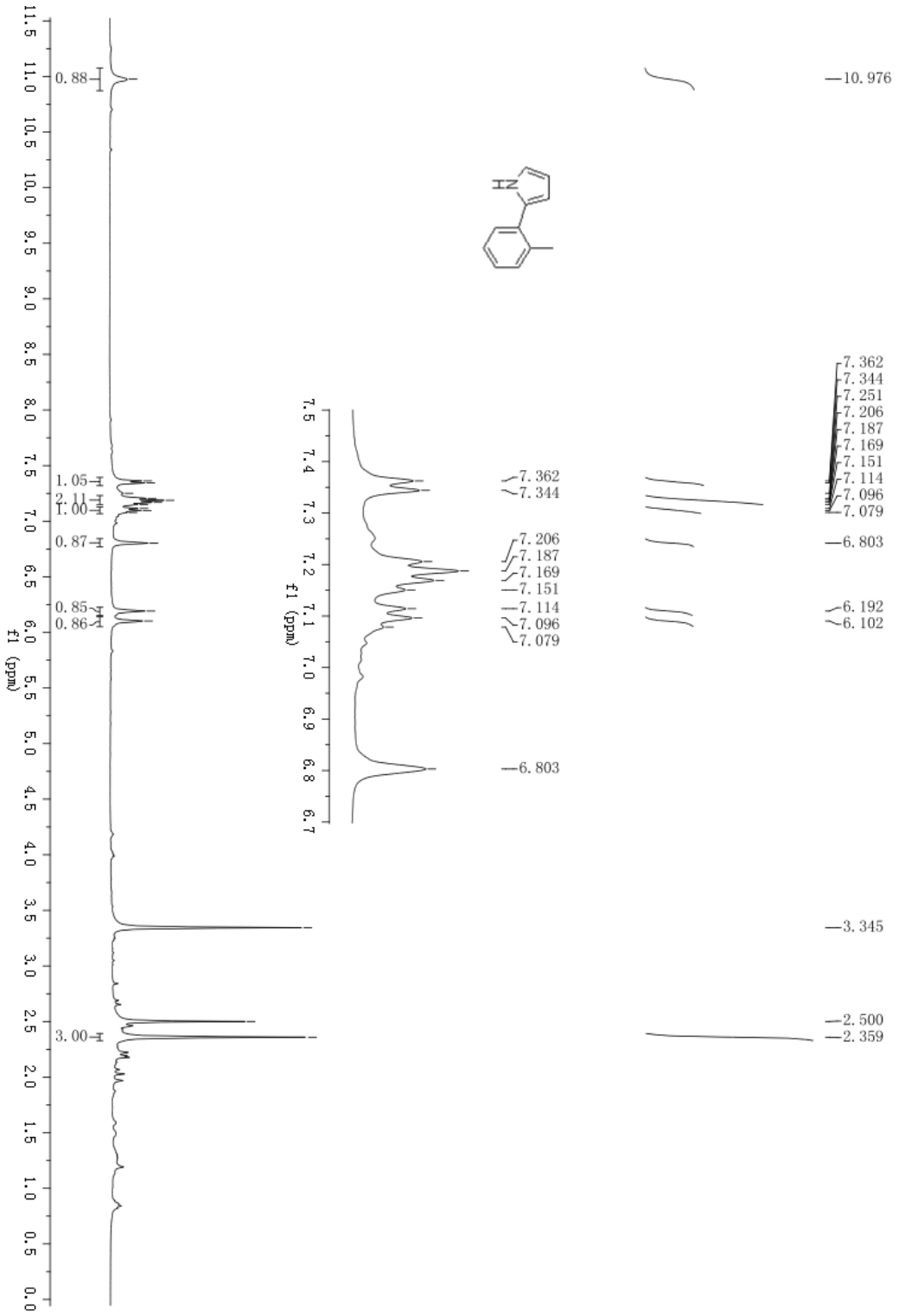

N
H

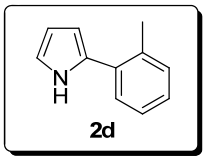
2c

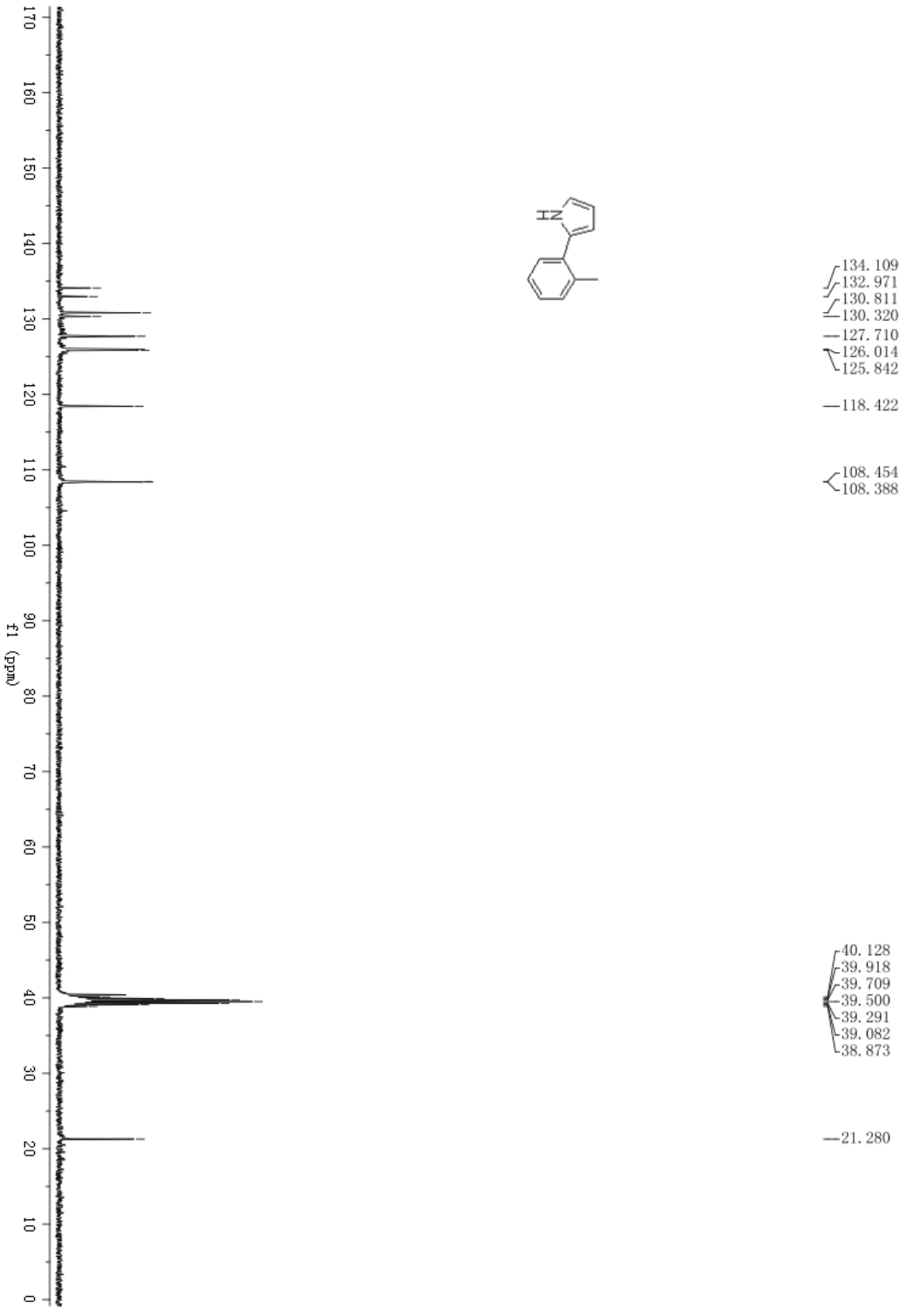

f1 (ppm)
137.678
132.963
131.191
128.596
123.970
120.571
119.160
109.042
105.453
40.128
39.916
39.707
39.500
39.290
39.080
38.871
21.223

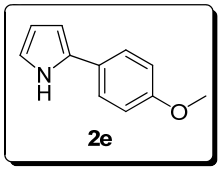

N
H

2d

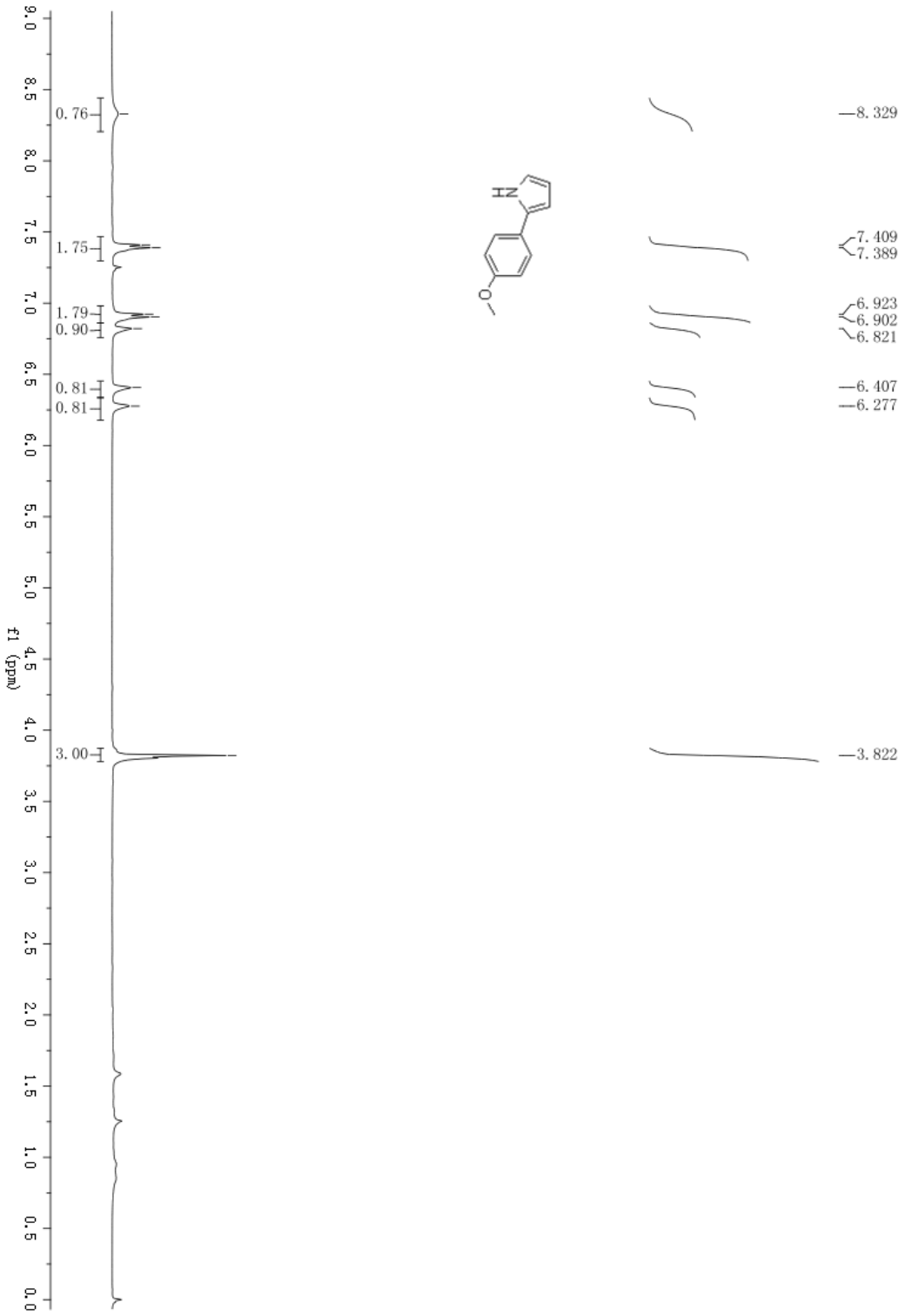

0.88
1.05
2.11
1.00
0.87
0.85
0.86
3.00
f1 (ppm)
7.362
7.344
7.206
7.187
7.169
7.151
7.114
7.096
7.079
6.803
10.976
6.192
6.102
3.345
2.500
2.359

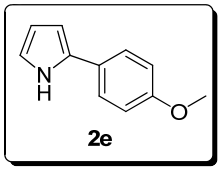

N
H
2d


f1 (ppm)
134.109
132.971
130.811
130.320
127.710
126.014
125.842
118.422
108.454
108.388
40.128
39.918
39.709
39.500
39.291
39.082
38.873
21.280

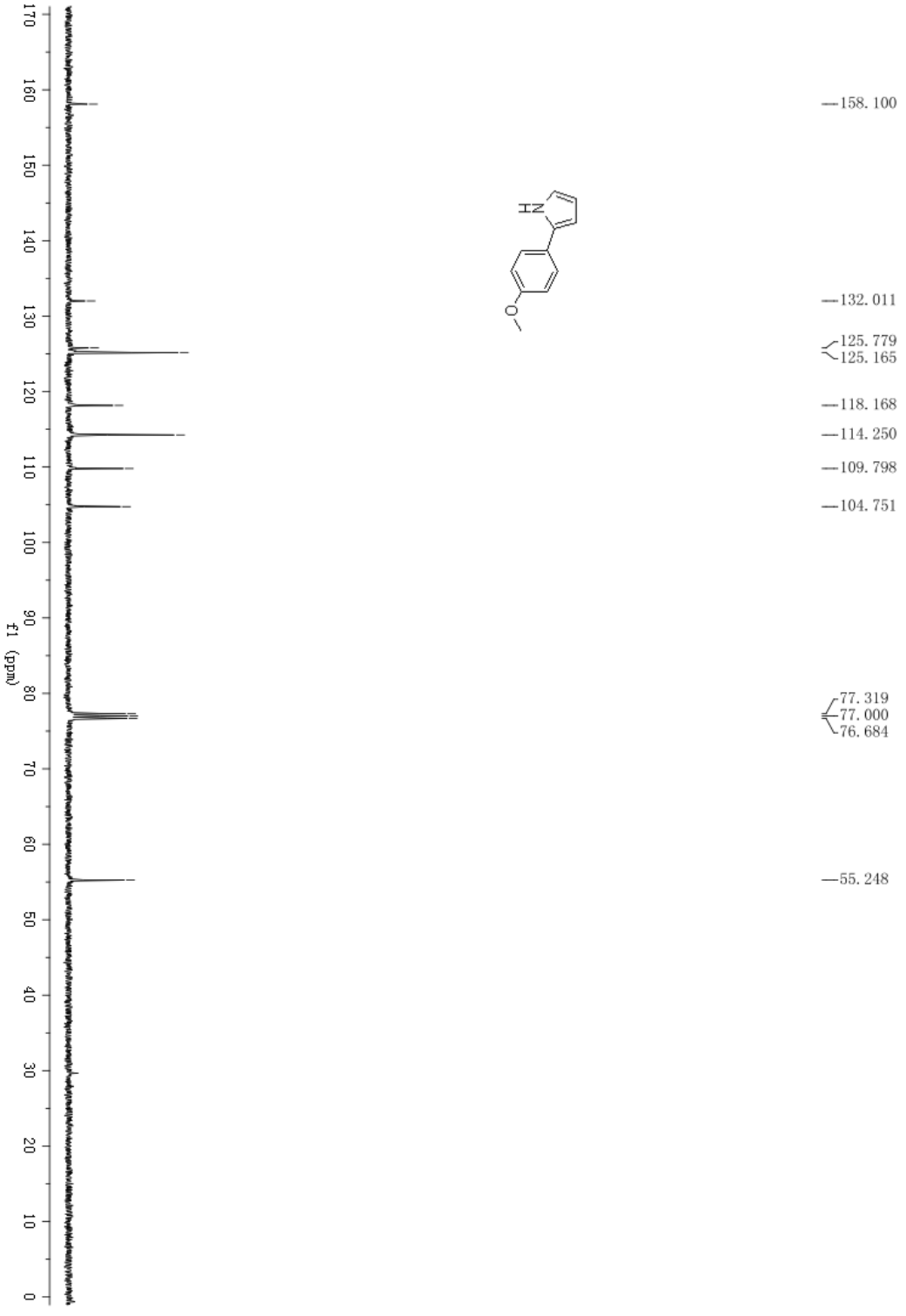

N
H
O

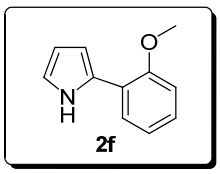
2e


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)
0.76
1.75
1.79
0.90
0.81
0.81
3.00
N
H
O
8.329
7.409
7.389
6.923
6.902
6.821
6.407
6.277
3.822

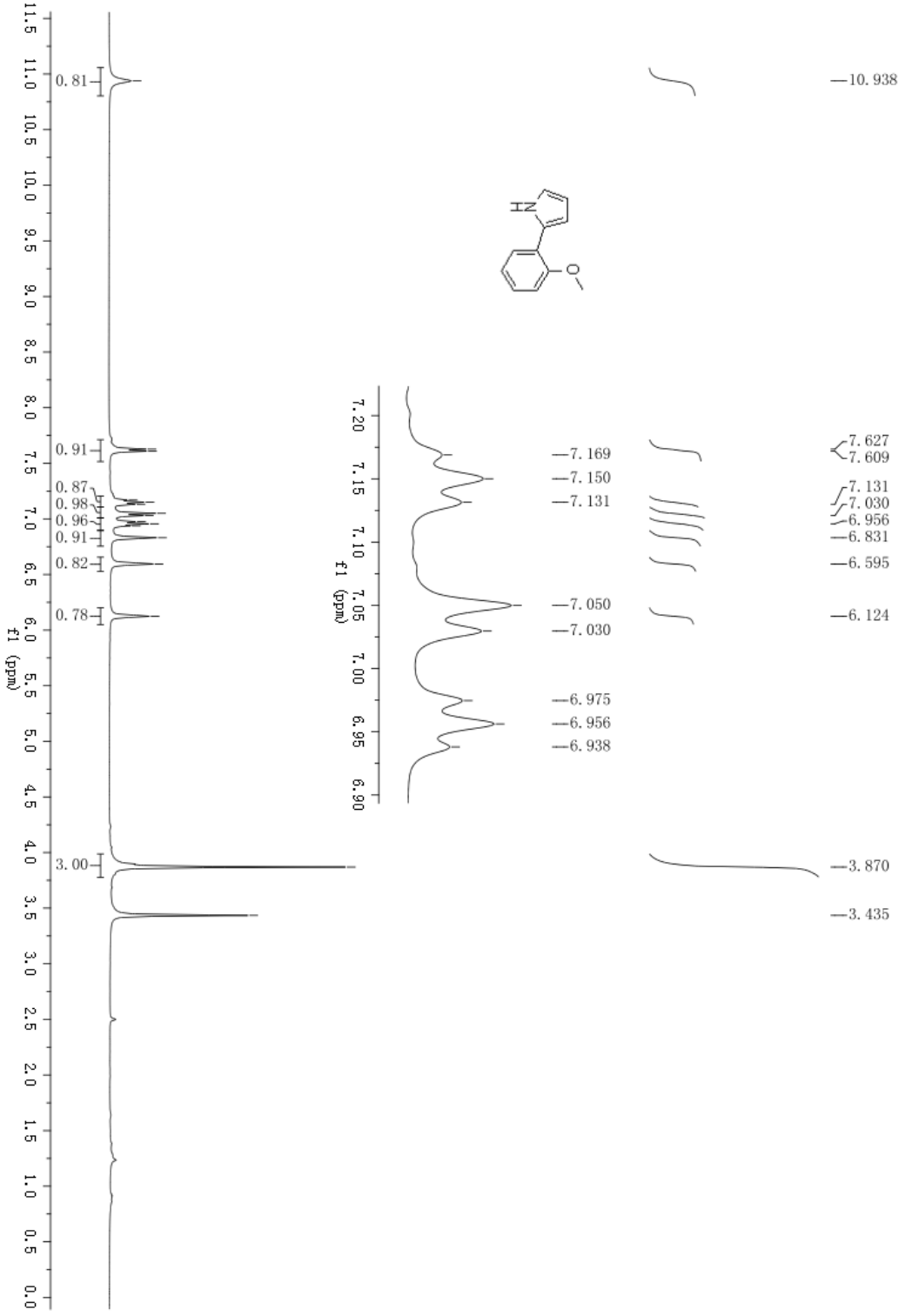

N
H
O

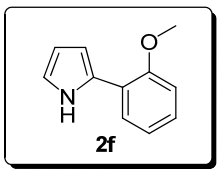
2e


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
158.100
132.011
125.779
125.165
118.168
114.250
109.798
104.751
77.319
77.000
76.684
55.248

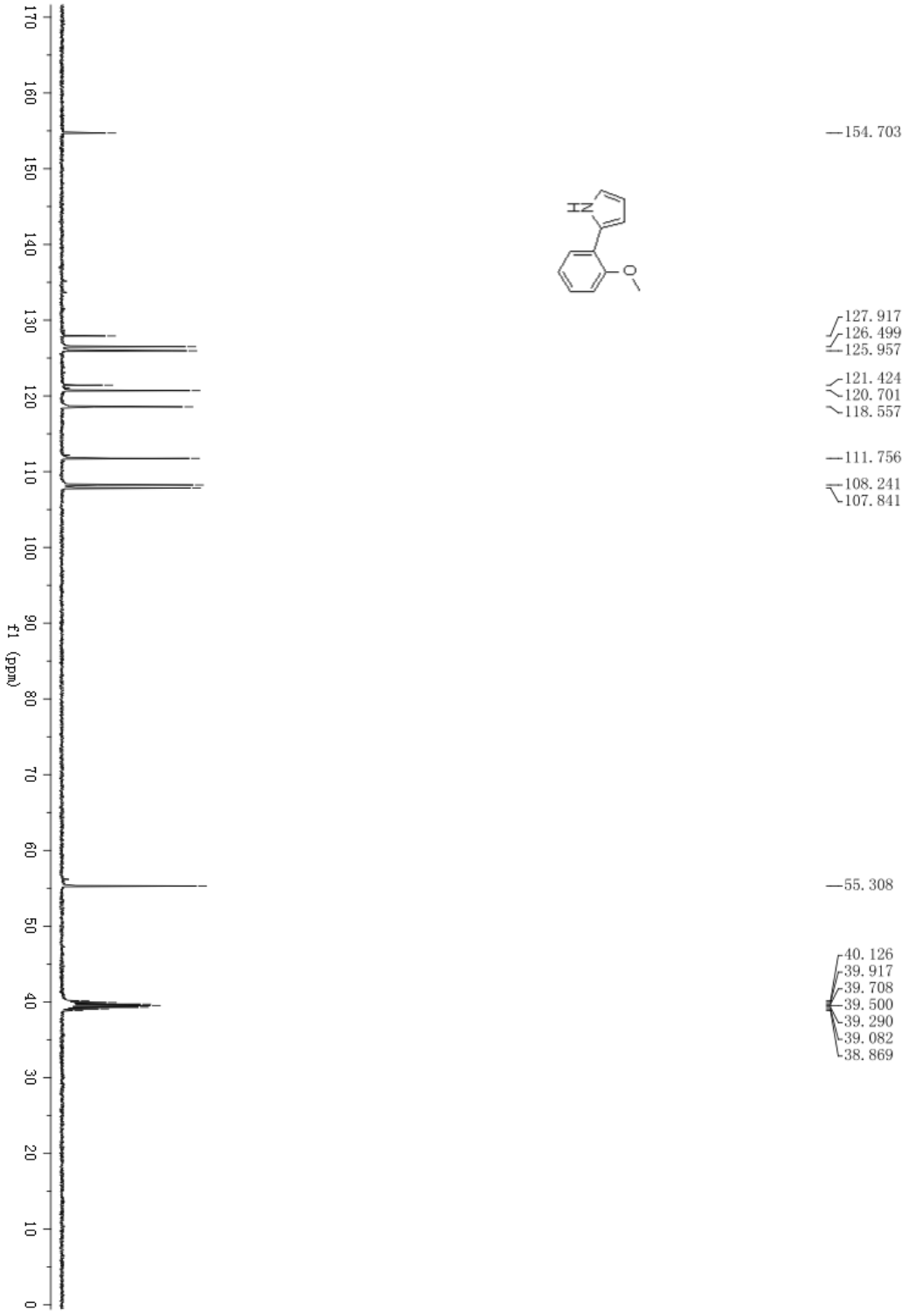

O
N
H

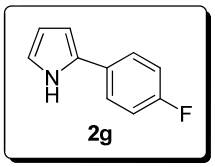
2f

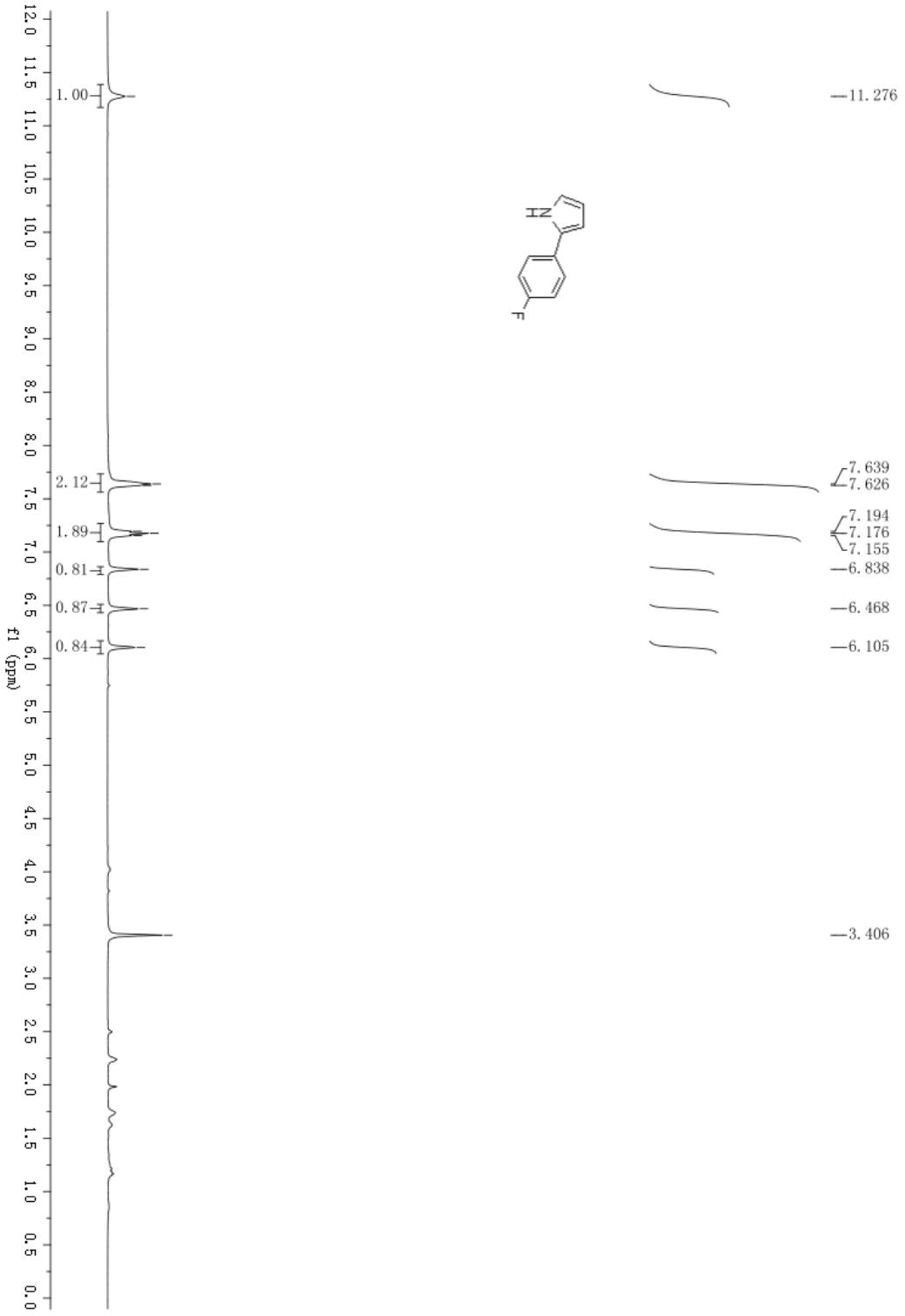

0.81
0.91
0.87
0.98
0.96
0.91
0.82
0.78
3.00
f1 (ppm)
7.169
7.150
7.131
7.050
7.030
6.975
6.956
6.938
10.938
7.627
7.609
7.131
7.030
6.956
6.831
6.595
6.124
3.870
3.435

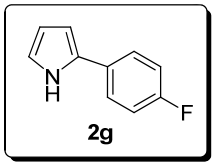

O
N
H

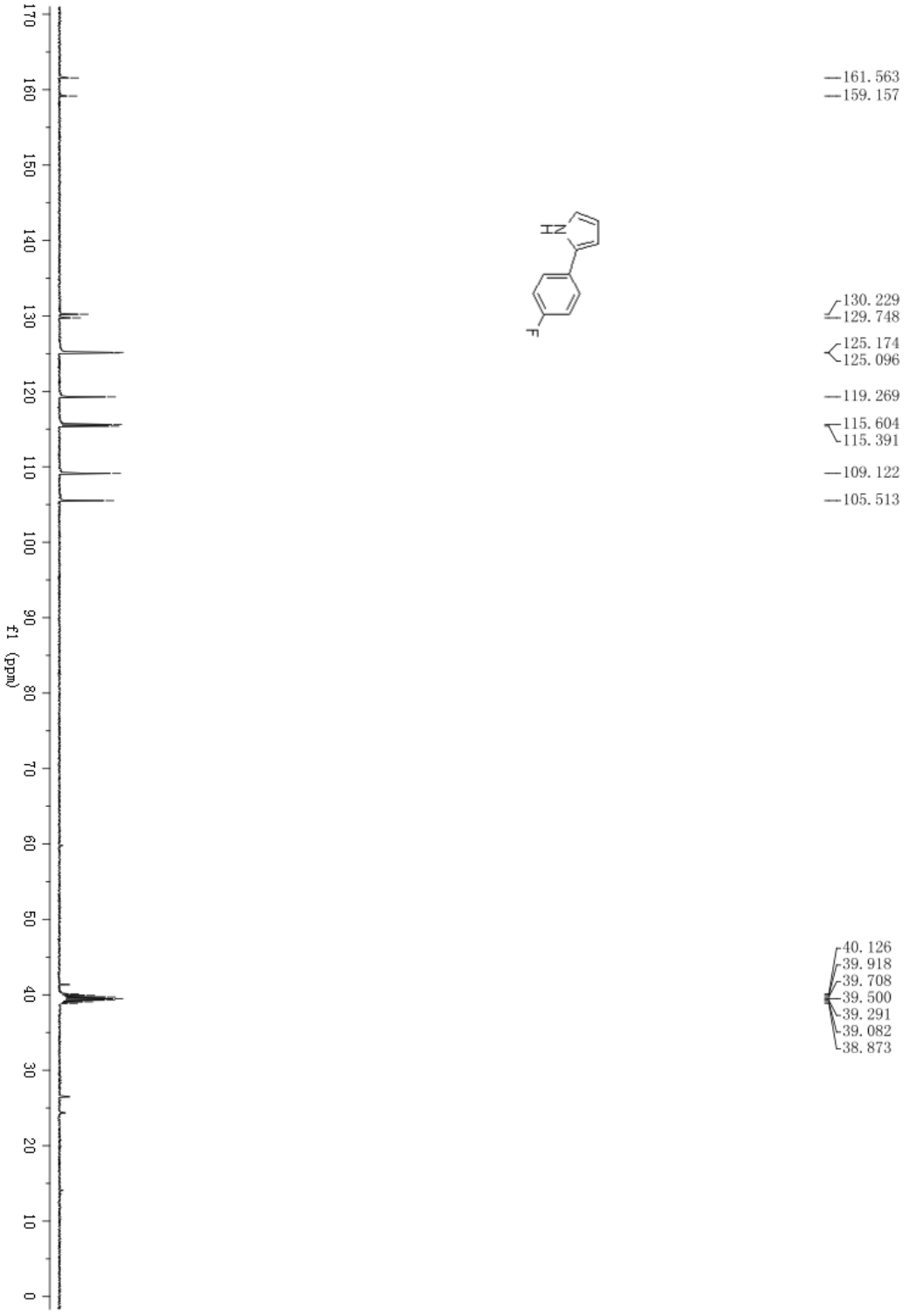
2f

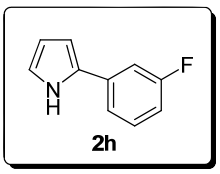

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
154.703
127.917
126.499
125.957
121.424
120.701
118.557
111.756
108.241
107.841
55.308
40.126
39.917
39.708
39.500
39.290
39.082
38.869

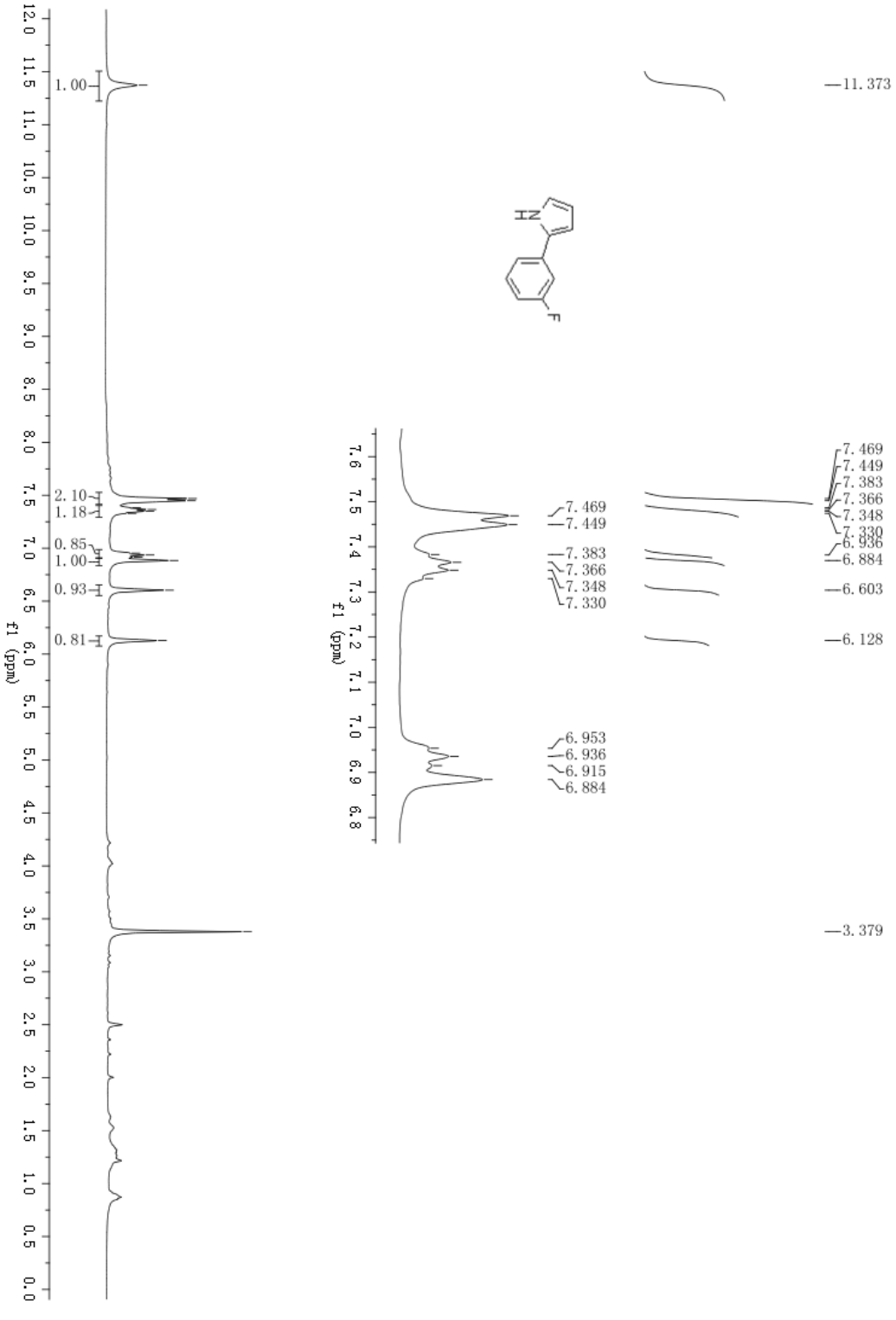

N
H
F
2g

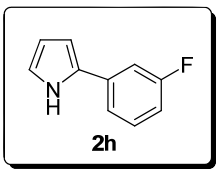

11.276
7.639
7.626
7.194
7.176
7.155
6.838
6.468
6.105
3.406
1.00
2.12
1.89
0.81
0.87
0.84
f1 (ppm)


N
H
F
2g

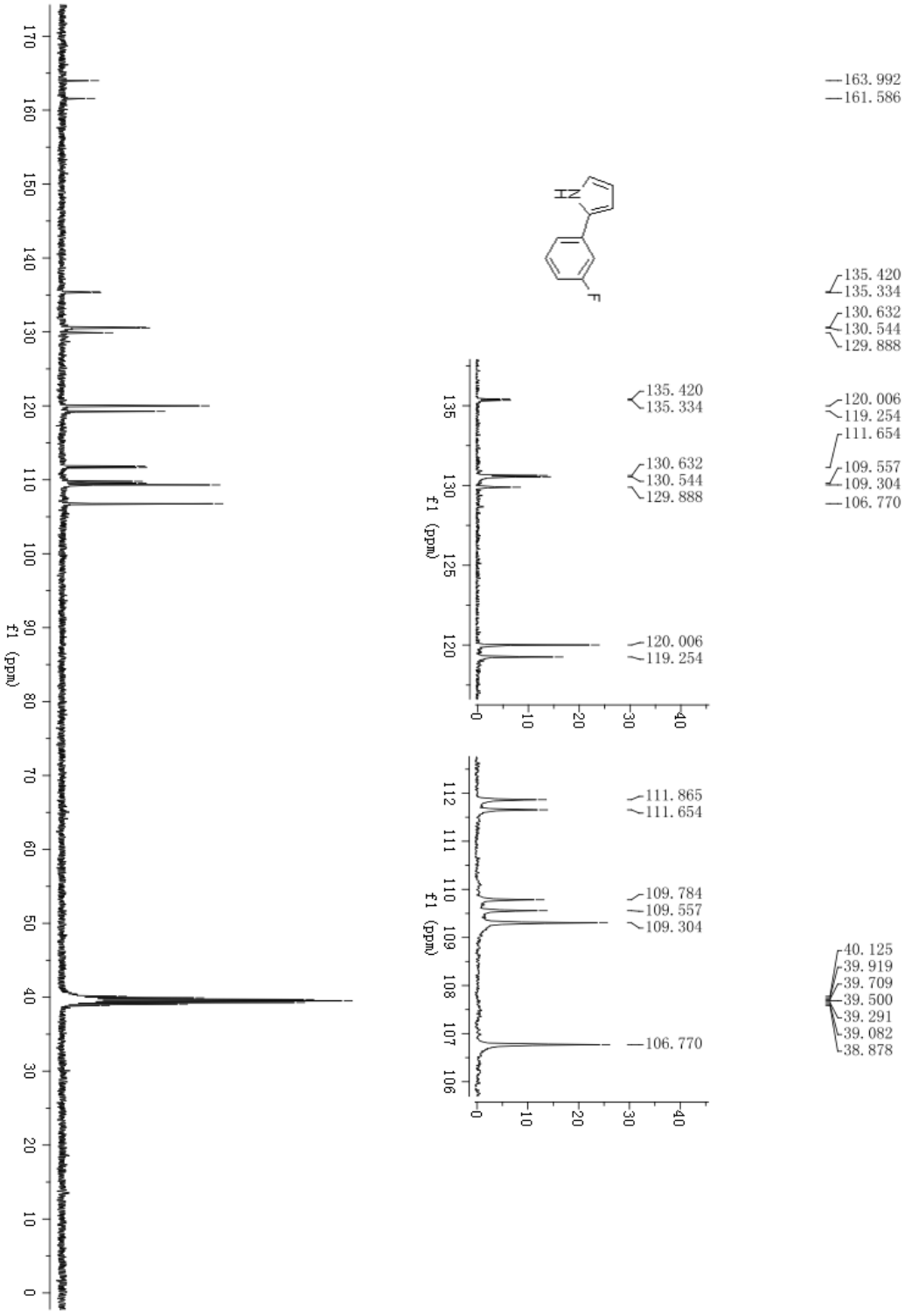

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
161.563
159.157
130.229
129.748
125.174
125.096
119.269
115.604
115.391
109.122
105.513
40.126
39.918
39.708
39.500
39.291
39.082
38.873

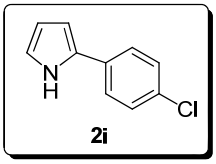

F
N
H
2h


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)
1.00
2.10
1.18
0.85
1.00
0.93
0.81
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
7.469
7.449
7.383
7.366
7.348
7.330
6.953
6.936
6.915
6.884
11.373
7.469
7.449
7.383
7.366
7.348
7.330
6.936
6.884
6.603
6.128
3.379

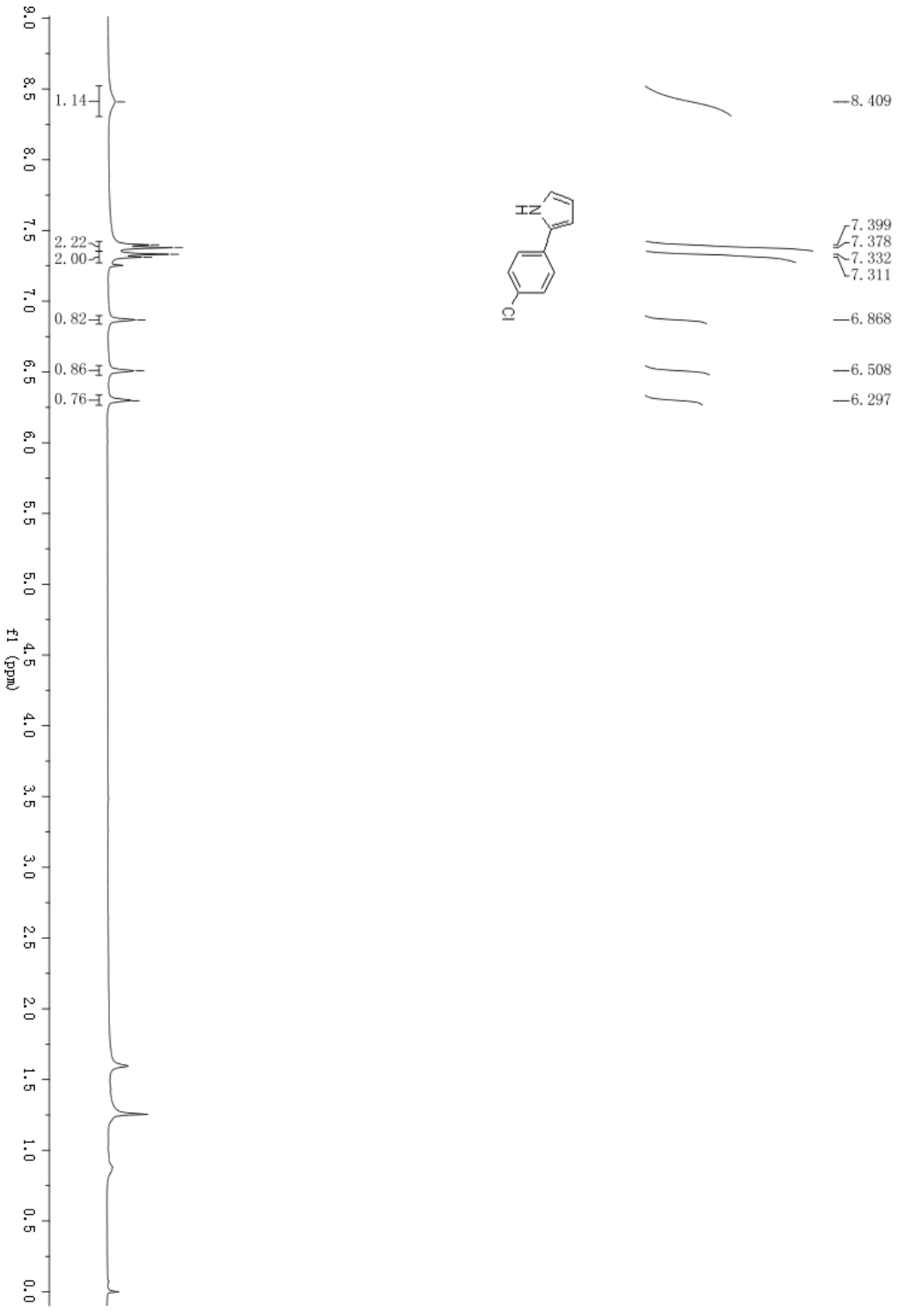

F
N
H

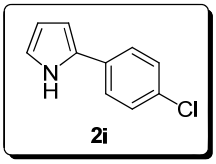
2h


f1 (ppm)
163.992
161.586
135.420
135.334
130.632
130.544
129.888
120.006
119.254
111.654
109.557
109.304
106.770
111.865
109.784
40.125
39.919
39.709
39.500
39.291
39.082
38.878

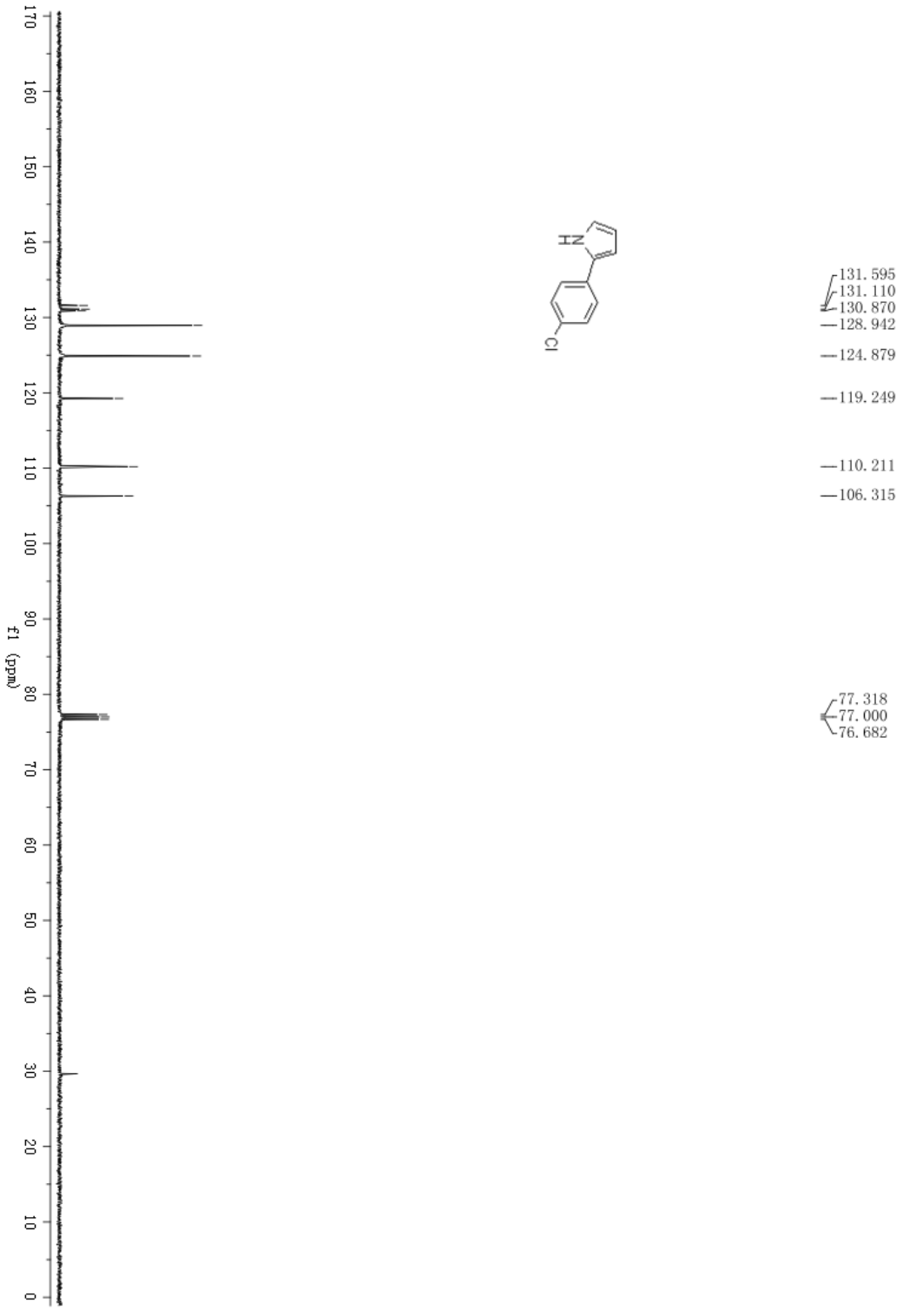

N
H
Cl

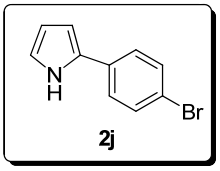
2i


1.14
2.22
2.00
0.82
0.86
0.76
f1 (ppm)
8.409
7.399
7.378
7.332
7.311
6.868
6.508
6.297

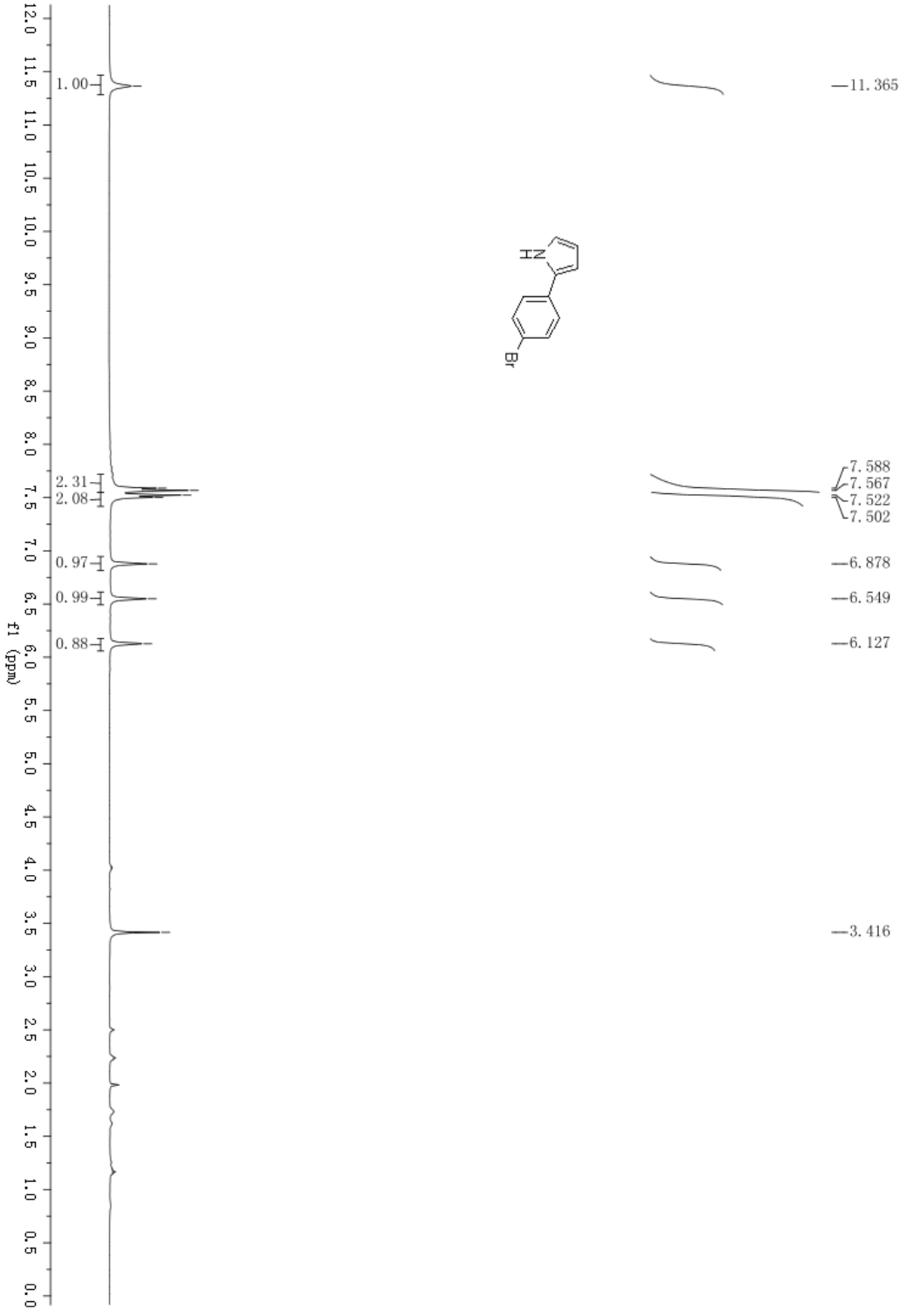

N
H
Cl

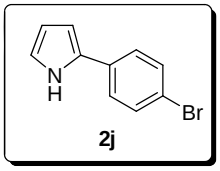
2i


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
131.595
131.110
130.870
128.942
124.879
119.249
110.211
106.315
77.318
77.000
76.682

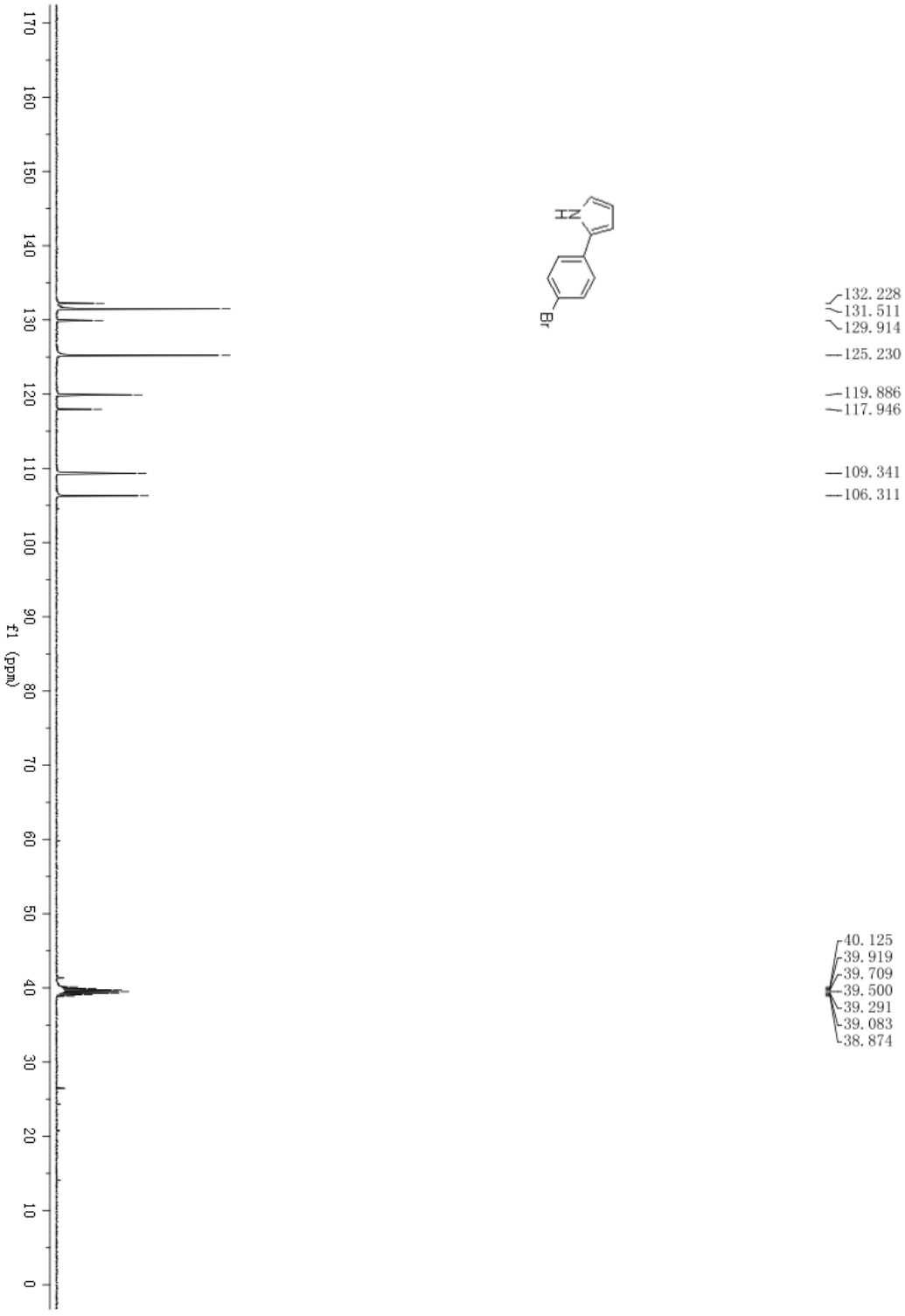

N
H
Br

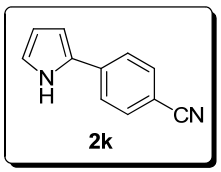
2j


1.00
2.31
2.08
0.97
0.99
0.88
f1 (ppm)
11.365
7.588
7.567
7.522
7.502
6.878
6.549
6.127
3.416

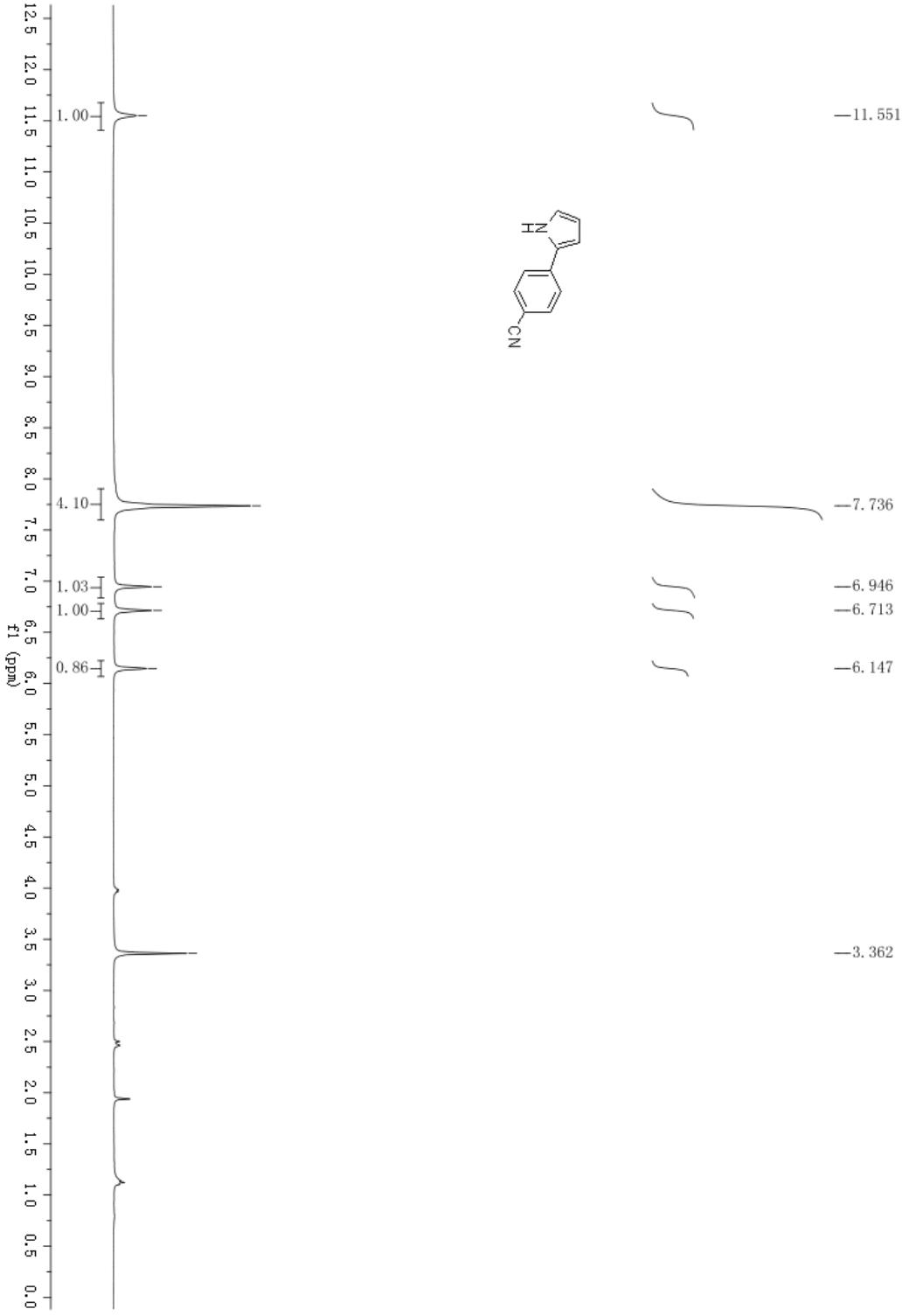

N
H
Br

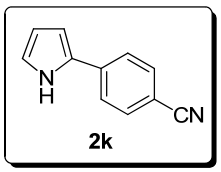
2j


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
N
H
Br
132.228
131.511
129.914
125.230
119.886
117.946
109.341
106.311
40.125
39.919
39.709
39.500
39.291
39.083
38.874

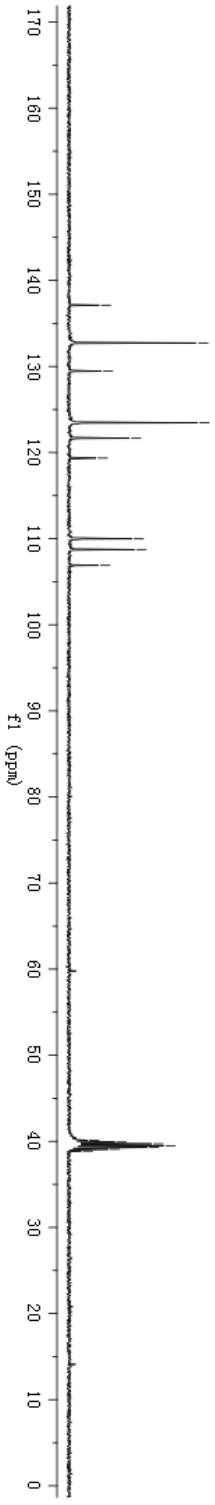


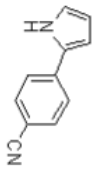
2k



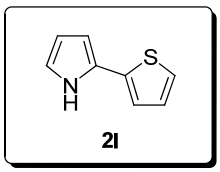


2k

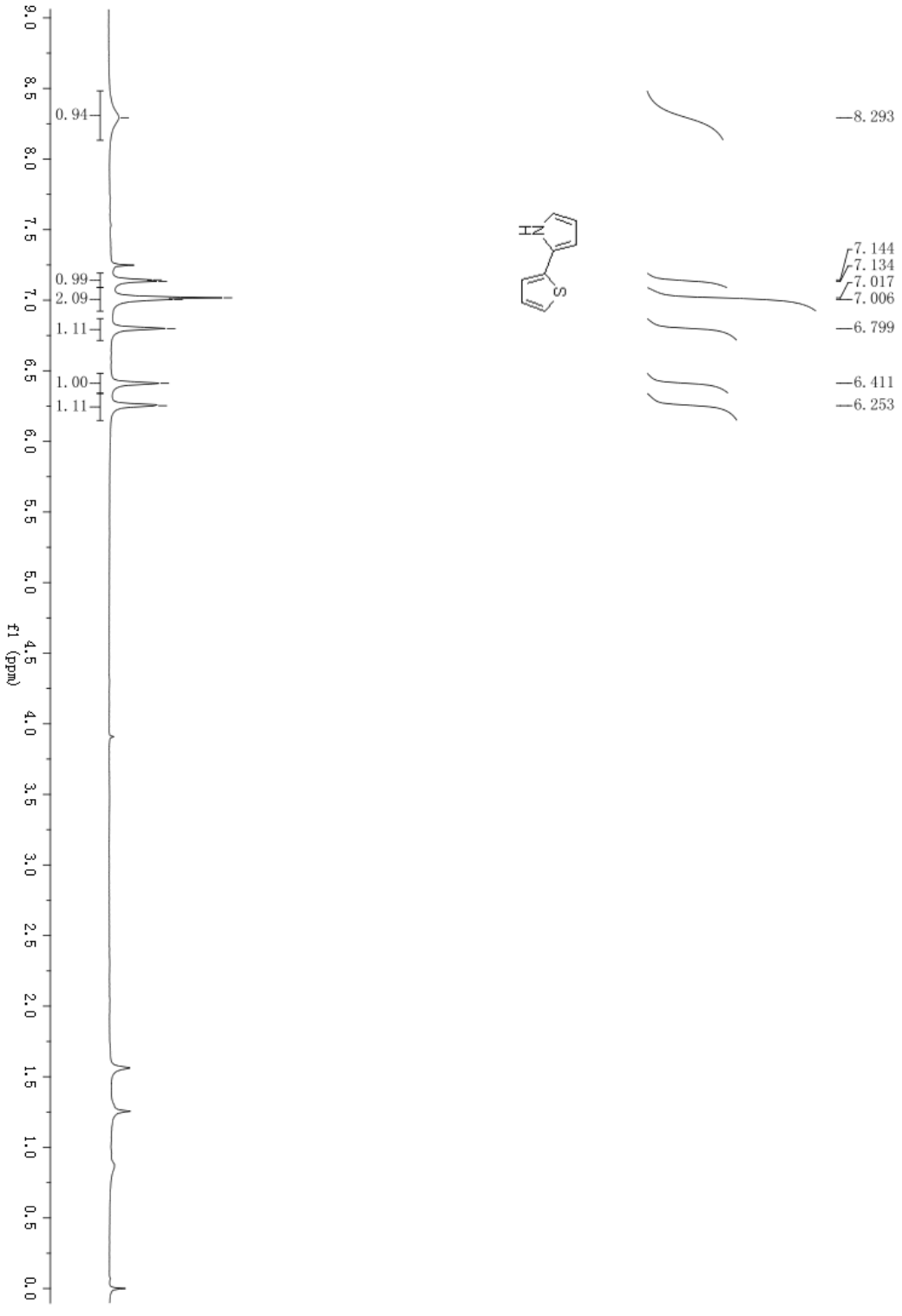


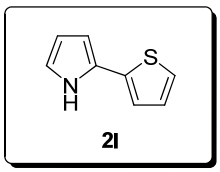


137.119
132.731
129.449
123.451
121.658
119.358
109.979
108.735
106.895
40.123
39.917
39.709
39.500
39.291
39.081
38.874

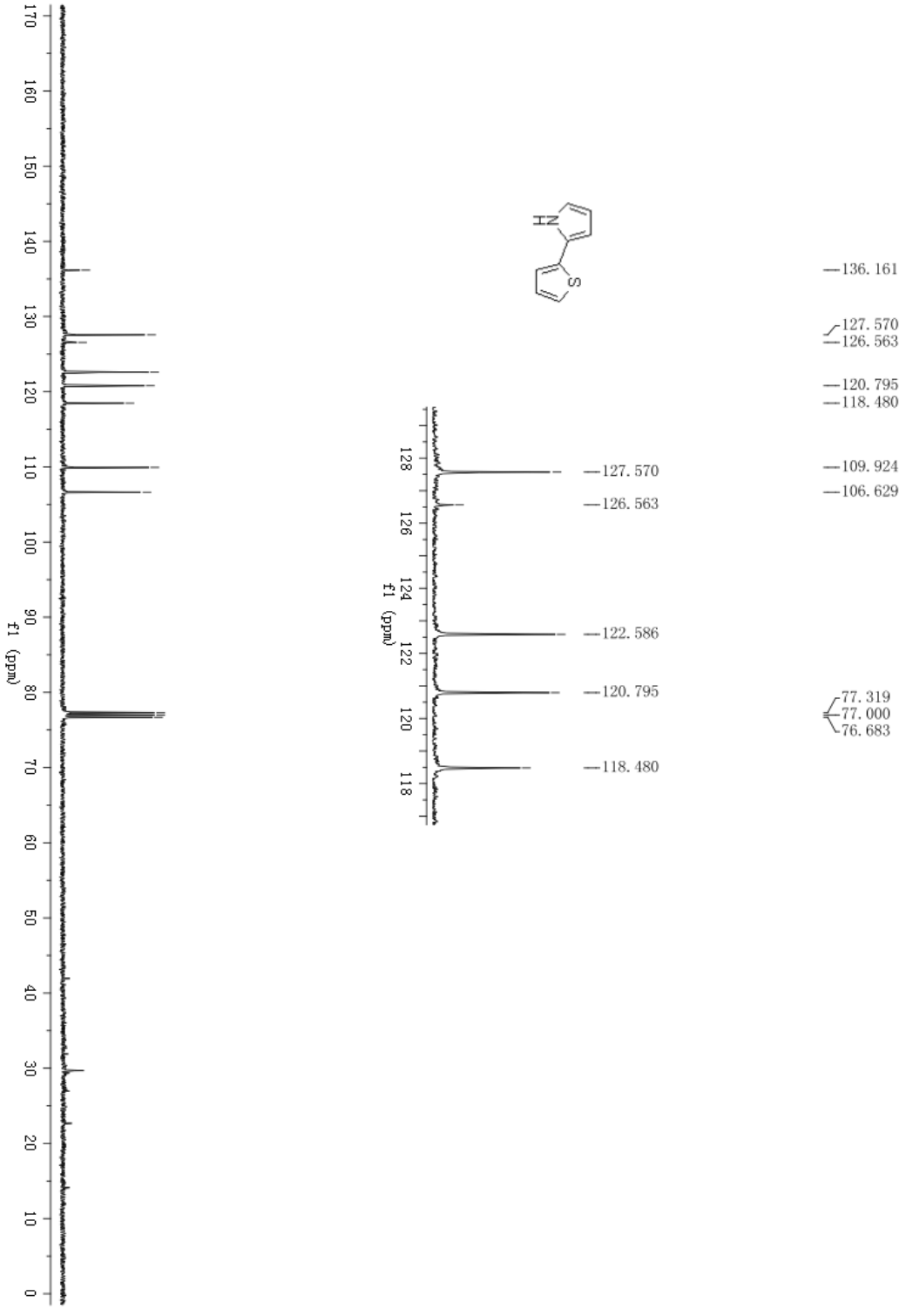

S
N
H

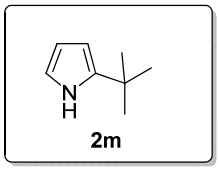
2l

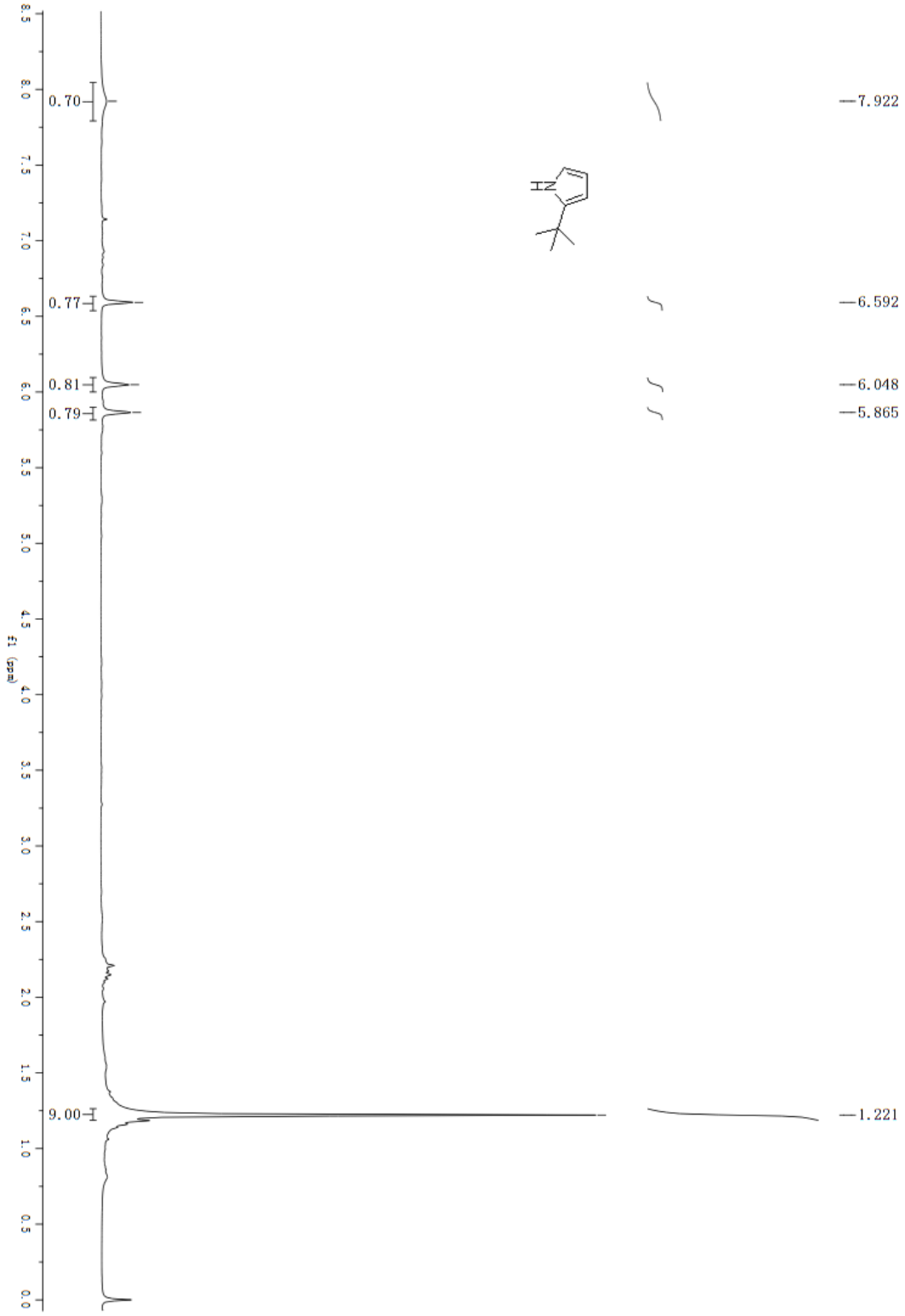

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
0.94
0.99
2.09
1.11
1.00
1.11
N
H
S
8.293
7.144
7.134
7.017
7.006
6.799
6.411
6.253

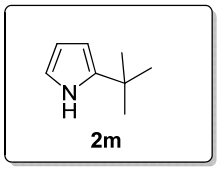

S
N
H

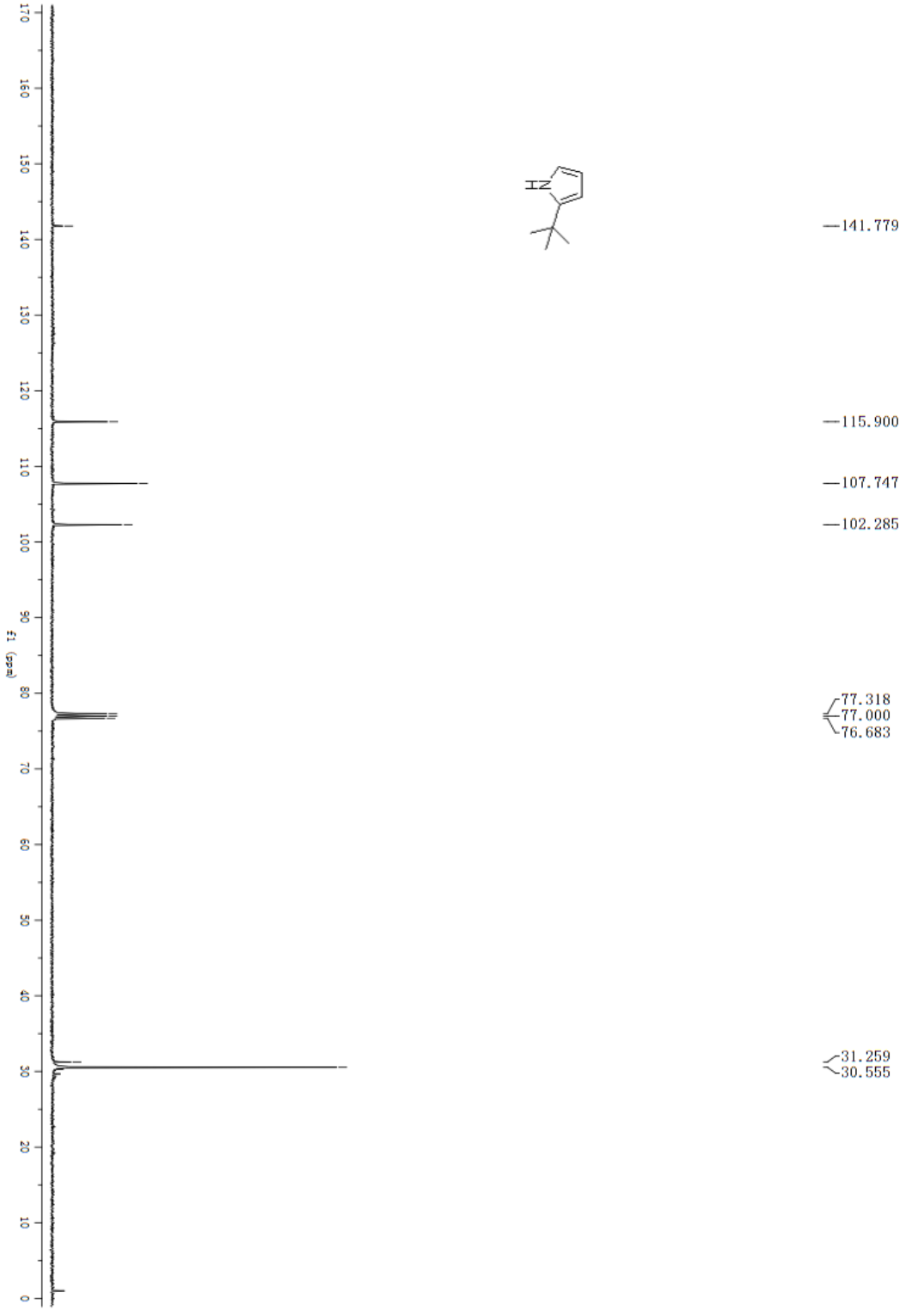
2l

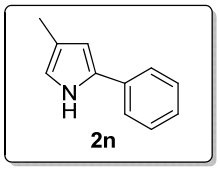

f1 (ppm)
136.161
127.570
126.563
120.795
118.480
109.924
106.629
77.319
77.000
76.683
122.586


2m

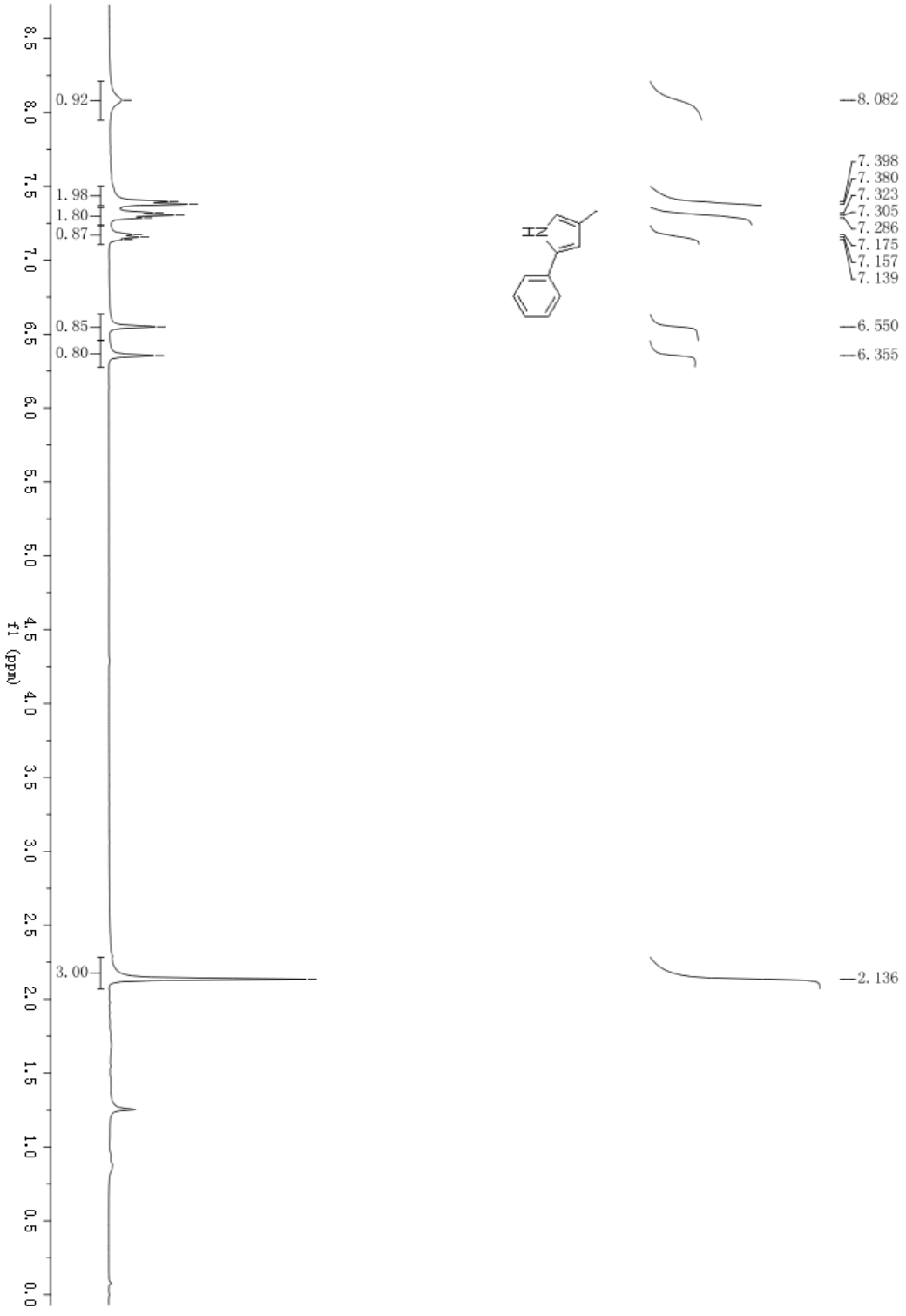

0.70
0.77
0.81
0.79
9.00
7.922
6.592
6.048
5.865
1.221
f1 (ppm)

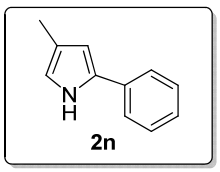

N
H
2m

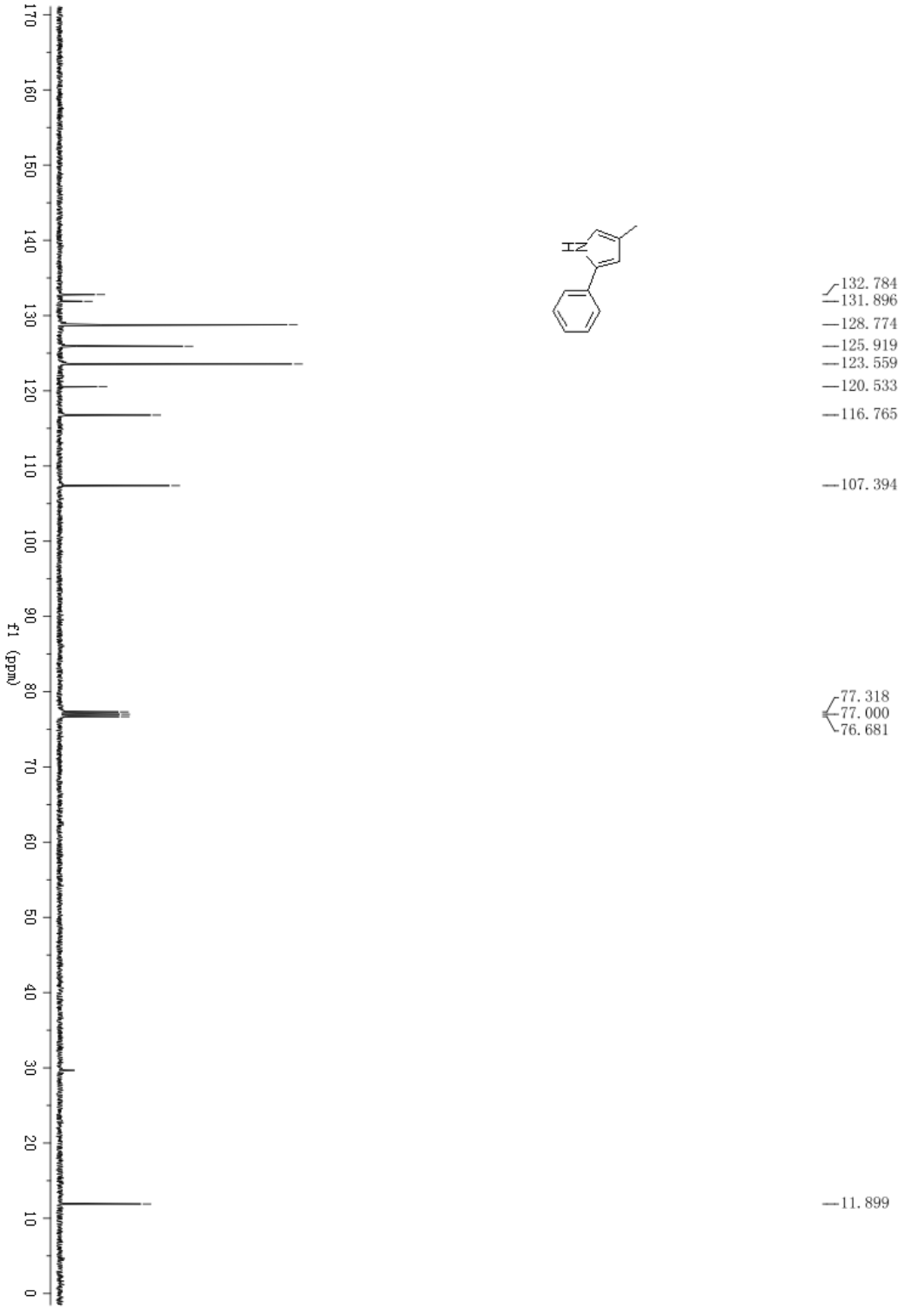

141.779
115.900
107.747
102.285
77.318
77.000
76.683
31.259
30.555
f1 (ppm)

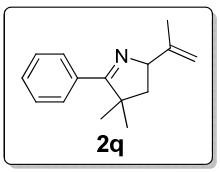

N
H

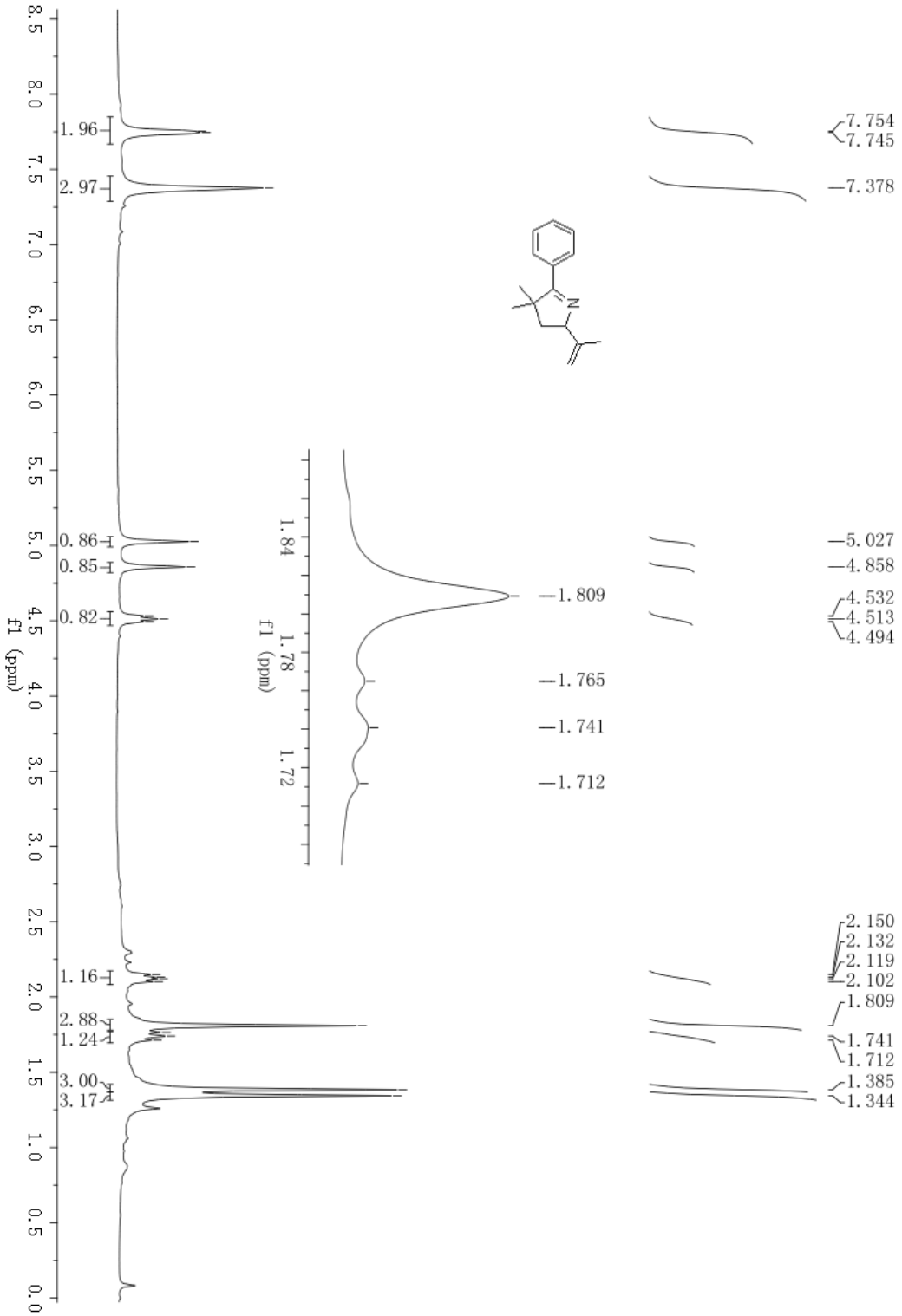
2n

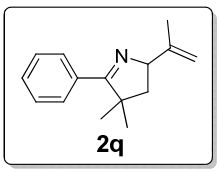

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
0.92
1.98
1.80
0.87
0.85
0.80
3.00
8.082
7.398
7.380
7.323
7.305
7.286
7.175
7.157
7.139
6.550
6.355
2.136

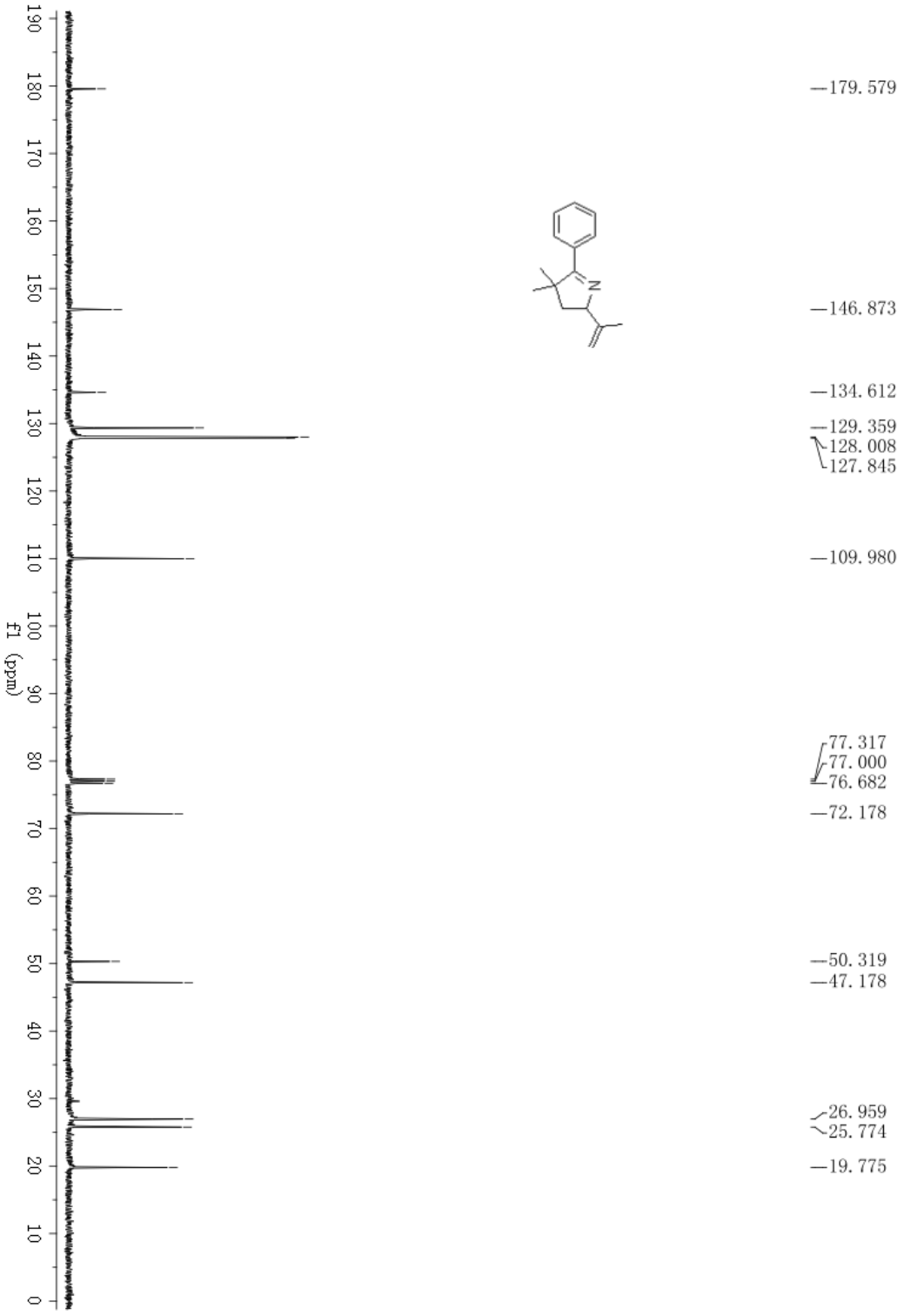

2n


f1 (ppm)
132.784
131.896
128.774
125.919
123.559
120.533
116.765
107.394
77.318
77.000
76.681
11.899


N
2q


f1 (ppm)
1.96
2.97
0.86
0.85
0.82
1.16
2.88
1.24
3.00
3.17
1.84
1.78
1.72
f1 (ppm)
7.754
7.745
7.378
5.027
4.858
4.532
4.513
4.494
1.809
1.765
1.741
1.712
2.150
2.132
2.119
2.102
1.809
1.741
1.712
1.385
1.344


N
2q


f1 (ppm)
179.579
146.873
134.612
129.359
128.008
127.845
109.980
77.317
77.000
76.682
72.178
50.319
47.178
26.959
25.774
19.775