Supporting Information

Transition-metal-free access to 2-aminopyridine derivatives from 2-fluoropyridine and acetamidine hydrochloride

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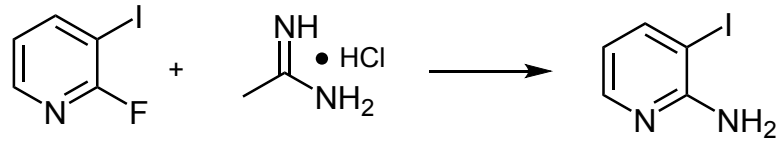
I. General methods and materials

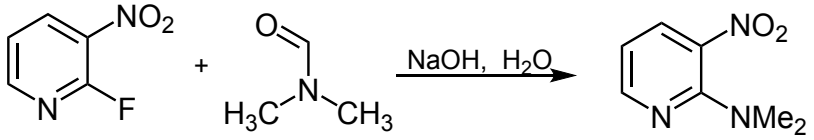
Unless otherwise noted, all commercial materials and solvents were used without further purification and all the reactions were carried out in a Schlenk tube equipped with magnetic stir bar. ^{1}H NMR spectra were recorded in $CDCl_3$ at 400 MHz and ^{13}C NMR spectra were recorded in $CDCl_3$ at 100 MHz respectively, ^{1}H and ^{13}C NMR were referenced to $CDCl_3$ at δ 7.260 and 77.0 respectively. GC–MS was obtained using electron ionization (Agilent Technologies 7890A/5975C). HRESIMS spectra were acquired using an Agilent 6210 ESI/TOF mass spectrometer. IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Brucker Vector 22 spectrometer. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm. All the other chemicals were purchased from Aldrich Chemicals. Commercial reagents were used without further purification.

II. General methods for the synthesis of 2-aminopyridine derivatives



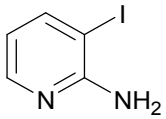
A mixture of 2-fluoro-3-iodopyridine (1 mmol), acetamidine hydrochloride (1.2 mmol), NaOH (2.5 mmol), H_2O (5 equiv.) and DMSO (2.5 mL) was added successively in a 25 mL Schlenk tube. After stirring for 24 h at 130 °C, the solution was filtered though a small amount of silica gel. Then the residue was concentrated in vacuo and the crude was purified by flash chromatography with n-hexane/ethyl acetate (2/1, v/v) to afford the 3-iodopyridin-2-amine as a pale-yellow solid in 95% yield.

III General methods for the Synthesis of *N,N*-dimethylpyridin-2-amines



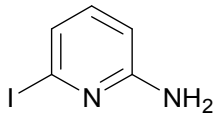
A mixture of 2-fluoro-3-nitropyridine (1 mmol), acetamidine hydrochloride (1.2 mmol), NaOH (2.0 mmol) and DMF (3 mL) was added successively in a 25 mL Schlenk tube. After stirring for 24 h at 130 °C, the solution was filtered though a small amount of silica gel. Then the residue was concentrated in vacuo and the crude was purified by flash chromatography with n-hexane/ethyl acetate (1/1, v/v) to afford the *N,N*-dimethyl-3-nitropyridin-2-amine as a pale-yellow solid in 93% yield.

IV. Characterization data for all prepared compounds



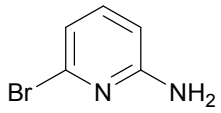
3-iodopyridin-2-amine[1]

GC-MS (EI, 70 Ev) m/z. 220, 127, 93, 66. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.86 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.39 (dd, *J* = 7.7, 4.9 Hz, 1H), 5.00 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.55, 147.80, 147.14, 115.33, 77.65.



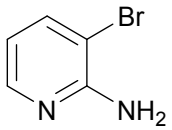
6-iodopyridin-2-amine[2]

GC-MS (EI, 70 Ev) m/z. 220, 127, 93, 66. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10 – 6.92 (m, 2H), 6.41 (d, *J* = 7.6 Hz, 1H), 4.64 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.50, 138.93, 124.30, 115.68, 107.28.



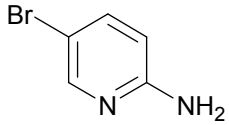
6-bromopyridin-2-amine[3]

GC-MS (EI, 70 Ev) m/z. 174, 172, 93, 63. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.8 Hz, 1H), 6.74 (d, *J* = 7.5 Hz, 1H), 6.37 (d, *J* = 8.1 Hz, 1H), 4.93 (s, 2H) ; ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.73, 139.76, 139.70, 116.57, 106.77.



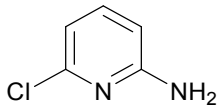
3-bromopyridin-2-amine[4]

GC-MS (EI, 70 Ev) m/z. 174, 172, 145, 93. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 4.8 Hz, 1H), 7.68 – 7.56 (m, 1H), 6.51 (dd, *J* = 7.7, 4.9 Hz, 1H), 5.11 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.60, 146.88, 140.26, 114.82, 104.38.



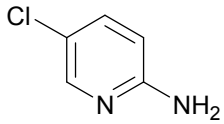
5-bromopyridin-2-amine[5]

GC-MS (EI, 70 Ev) m/z.172, 145, 93, 66. ^{1}H NMR (600 MHz, Acetone) δ 7.85 (d, *J* = 2.4 Hz, 1H), 7.36 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.40 (dd, *J* = 8.8, 0.5 Hz, 1H), 5.52 (s, 2H). ^{13}C NMR (150 MHz, Acetone) δ 158.72, 148.30, 139.33, 109.90, 106.06.



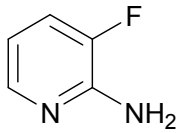
6-chloropyridin-2-amine[6]

GC-MS (EI, 70 Ev) m/z. 128, 101, 93, 66. ^{1}H NMR (600 MHz, Acetone) δ 7.38 (t, *J* = 7.8 Hz, 1H), 6.54 (d, *J* = 7.5 Hz, 1H), 6.48 (d, *J* = 8.1 Hz, 1H), 5.83 (s, 2H). ^{13}C NMR (150 MHz, Acetone) δ 160.95, 149.83, 140.64, 111.92, 107.08.



5-chloropyridin-2-amine[7]

GC-MS (EI, 70 Ev) m/z.128, 101, 93, 66. ^{1}H NMR (600 MHz, Acetone) δ 7.77 (d, *J* = 3 Hz, 1H), 7.25 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.43 (dd, *J* = 8.8, 0.6 Hz, 1H), 5.49 (s, 2H). ^{13}C NMR (150 MHz, Acetone) δ 158.53, 146.00, 136.75, 118.73, 109.20.

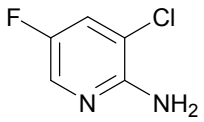


3-fluoropyridin-2-amine[8]

GC-MS (EI, 70 Ev) m/z. 112, 85, 57. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 5.0 Hz, 1H), 7.17 (ddd, *J* = 10.9, 7.9, 1.3 Hz, 1H), 6.59 (ddd, *J* = 8.3, 5.0, 3.5 Hz, 1H), 4.78 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.53 (d, J_{C-F} = 12.52 Hz, 1C), 146.91 (d, J_{C-F} = 252.5 Hz, 1C), 142.84 (d, J_{C-F} = 5.96 Hz, 1C), 121.39 (d, J_{C-F} = 15.35 Hz, 1C), 113.79 (d, J_{C-F} = 1.72 Hz, 1C).

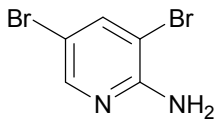
3-fluoro-4-iodopyridin-2-amine[9]

GC-MS (EI, 70 Ev) m/z. 238, 221, 84, 57. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 5.3 Hz, 1H), 6.98 (dd, J = 5.3, 3.9 Hz, 1H), 4.76 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.16 (d, $J_{C\text{-}F}$ = 37.57 Hz, 1C), 146.84 (d, $J_{C\text{-}F}$ = 199.07 Hz, 1C), 143.44 (d, $J_{C\text{-}F}$ = 6.97 Hz,1C), 123.48 (d, $J_{C\text{-}F}$ =2.83 Hz, 1C), 90.49 (d, $J_{C\text{-}F}$ = 20.2 Hz, 1C).



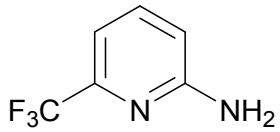
3-chloro-5-fluoropyridin-2-amine

GC-MS(EI, 70 Ev) m/z. 146, 119, 111, 84. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 2.6 Hz, 1H), 7.34 (dd, J = 7.5, 2.6 Hz, 1H), 4.81 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.94 (s, 1C), 151.54 (d, $J_{C\text{-}F}$ = 12.02 Hz, 1C), 133.16 (d, $J_{C\text{-}F}$ = 24.04 Hz, 1C), 124.95 (d, $J_{C\text{-}F}$ = 22.83 Hz, 1C), 144.35 (d, $J_{C\text{-}F}$ = 4.9 Hz, 1C).



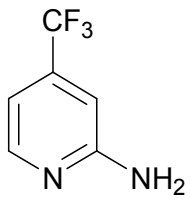
3,5-dibromopyridin-2-amine[10]

GC-MS (EI, 70 Ev) m/z. 254, 252, 249, 170. ^{1}H NMR (600 MHz, Acetone) δ 8.03 (d, J = 2.4 Hz, 1H), 7.88 (d, J = 1.8 Hz, 1H), 5.96 (s, 2H). ^{13}C NMR (150 MHz, Acetone) δ 156.33, 148.40, 142.31, 106.14, 104.48.



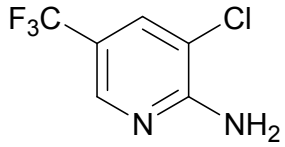
6-(trifluoromethyl)pyridin-2-amine[11]

GC-MS (EI, 70 Ev) m/z.162, 143, 135, 115, 93, 66. ^{1}H NMR (600 MHz, Acetone) δ 7.46 (t, J = 7.8 Hz, 1H), 6.80 (d, J = 7.2 Hz, 1H), 6.65 (d, J = 8.4 Hz, 1H), 5.84 (s, 2H). ^{13}C NMR (150 MHz, Acetone) δ 160.049 (s, 1C), 145.82 (dd, $J_{C\text{-}F}$=66.59, 66.44 Hz, 1C), 138.23 (s, 1C), 122.00 (d, $J_{C\text{-}F}$=273.31 Hz, 1C), 111.756 (s, 1C), 108.38 (dd, $J_{C\text{-}F}$=6.80,6.80Hz, 1C)



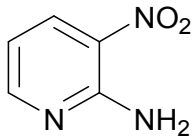
4-(trifluoromethyl)pyridin-2-amine[12]

GC-MS (EI, 70 Ev) m/z.162, 143, 135, 116. ^{1}H NMR (600 MHz, Acetone) δ 8.17 (d, J = 4.8 Hz, 1H), 6.81 (s, 1H), 6.77 (d, J = 4.8 Hz, 1H), 5.94 (s, 2H). ^{13}C NMR (150 MHz, Acetone) δ 161.31 (s, 1C), 150.68 (s, 1C), 139.56 (dd, $J_{C\text{-}F}$ = 65.53, 65.69 Hz, 1C), 124.36 (dd, $J_{C\text{-}F}$ = 544.36, 544.51 Hz, 1C), 108.03 (t, $J_{C\text{-}F}$ = 3.322 Hz, 1C), 104.25 (t, $J_{C\text{-}F}$ = 4.228 Hz, 1C).



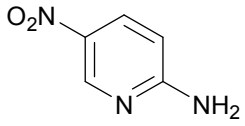
3-chloro-5-(trifluoromethyl)pyridin-2-amine[13]

GC-MS (EI, 70 Ev) m/z.196, 177, 169, 161, 141. ^{1}H NMR (151 MHz, Acetone) δ 16.99 (d, J = 1.8 Hz, 1H), 13.80 (d, J = 3.9 Hz, 1H), 3.66 (s, 2H). ^{13}C NMR (150 MHz, Acetone) δ 158.18 (s, 1C), 144.10 (dd, $J_{C\text{-}F}$ = 8.91, 8.76Hz, 1C), 133.41(dd, $J_{C\text{-}F}$ = .80, 6.80 Hz, 1C), 124.07(dd, $J_{C\text{-}F}$ = 540.28, 540.28 Hz, 1C), 115.59 (dd $J_{C\text{-}F}$ = 66.44, 66.59 Hz, 1C), 113.48 (s, 1C).



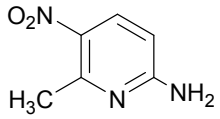
3-nitropyridin-2-amine[14]

GC-MS (EI, 70 Ev) m/z. 139, 122, 93, 66. ^{1}H NMR (600 MHz, Acetone) δ 8.51 – 8.23 (m, 2H), 7.46 (s, 2H), 6.80 (dd, J = 8.3, 4.5 Hz, 1H). ^{13}C NMR (150 MHz, Acetone) δ 156.85, 154.91, 135.60, 128.56, 113.70.



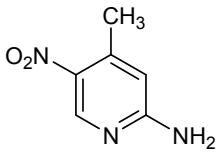
5-nitropyridin-2-amine [15]

GC-MS (EI,70 Ev) m/z.139, 109, 93, 66. ^{1}H NMR (600 MHz, Acetone) δ 8.91 (d, J = 2.8 Hz, 1H), 8.20 (dd, J = 9.2, 2.8 Hz, 1H), 6.89 (s, 2H), 6.73 – 6.63 (m, 1H). ^{13}C NMR (150 MHz, Acetone) δ 163.81, 147.11, 136.11, 133.11, 107.47.



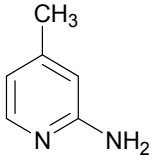
6-methyl-5-nitropyridin-2-amine [16]

GC-MS(EI,70Ev) m/z 153, 136, 80. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 9.1 Hz, 1H), 6.90 (s, 2H), 5.92 (d, *J* = 9.1 Hz, 1H), 2.15 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.71, 146.56, 125.22, 124.74, 96.21, 15.49.



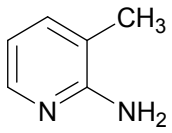
4-methyl-5-nitropyridin-2-amine[16]

GC-MS(EI, 70Ev) m/z.153, 136, 80, 53. ^{1}H NMR (600 MHz, CD_3Cl+DMSO) δ 8.76 (s, 1H), 7.29 (s, 2H), 6.31 (s, 1H), 2.47 (s, 3H). ^{13}C NMR (150 MHz, CD_3Cl+DMSO) δ 160.46, 146.47, 142.22, 133.57, 106.87, 19.15.



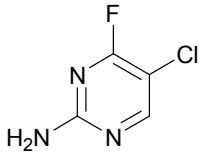
4-methylpyridin-2-amine[17]

GC-MS (EI, 70 Ev) m/z. 108, 93, 51. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 5.4 Hz, 1H), 6.44 (d, *J* = 5.4 Hz, 1H), 6.28 (s, 1H), 4.69 (s, 2H), 2.18 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.61, 148.47, 147.37, 115.08, 108.71, 20.71.



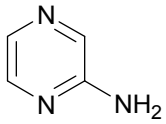
3-methylpyridin-2-amine[18]

GC-MS (EI, 70 Ev) m/z. 108, 93, 51. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.22 (ddd, *J* = 7.2, 1.7, 0.8 Hz, 1H), 6.57 (dd, *J* = 7.2, 5.1 Hz, 1H), 4.47 (s, 2H), 2.08 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.07, 145.44, 137.61, 116.45, 114.23, 17.00.



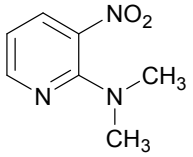
5-chloro-4-fluoropyrimidin-2-amine

GC-MS (EI, 70 Ev) m/z.147, 120, 114, 40; ESI-HRMS (m/z): $[M+H]^+$, caculated for $C_4H_4ClFN_3$, 148.0072, found 148.0074; ^{1}H NMR (600 MHz, Acetone) δ 8.13 (s, 1H), 7.16 (d, J = 180.3 Hz, 2H). ^{13}CNMR (150MHz, Acetone) δ 163.47 (d, $J_{C\text{-}F}$ = 18.57 Hz, 1C), 162.11 (d, $J_{C\text{-}F}$ = 210.65 Hz, 1C), 156.47 (d, $J_{C\text{-}F}$ = 57.08 Hz, 1C) ,111.21 (d, $J_{C\text{-}F}$ = 6.49 Hz, 1C).



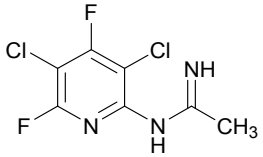
pyrazin-2-amine[19]

GC-MS (EI, 70 Ev) m/z. 95, 68, 41. ^{1}H NMR (600 MHz, Acetone) δ 7.98 (d, J = 1.2 Hz, 1H), 7.89 (dd, J = 2.4, 2.4 Hz, 1H), 7.73 (d, J = 2.7 Hz, 1H), 5.84 (s, 2H). ^{13}C NMR (150 MHz, Acetone) δ 156.97, 142.74, 133.5, 133.4.



N,N-dimethyl-3-nitropyridin-2-amine[20]

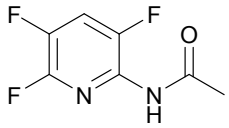
GC-MS (EI, 70 Ev) m/z. 167, 119, 93, 79, 66. ^{1}H NMR (600 MHz, Acetone) δ 8.35 (dd, J = 4.4, 1.6 Hz, 1H), 8.15 (dd, J = 8.0, 1.6 Hz, 1H), 6.78 (dd, J = 8.0, 4.5 Hz, 1H), 3.03 (s, 6H). ^{13}C NMR (150 MHz, Acetone) δ 153.61, 152.31, 136.02, 132.79, 112.72, 40.11 (2C).



N-(3,5-dichloro-4,6-difluoropyridin-2-yl)acetamidine

GC-MS (EI, 70 Ev) m/z. 239, 223, 204, 177. ESI-HRMS (m/z): $[M+H]^+$, caculated for $C_7H_6Cl_2F2N_3$, 239.9901, found 239.9906, ^{1}H NMR (600 MHz, Acetone) δ 6.72 (s, 1H), 6.27 (s, 1H), 2.06 (s, 3H). ^{13}C NMR (150 MHz, Acetone) δ 161.20 (t, $J_{C\text{-}F}$ = 3.93Hz, 1C), 159.01

(s, 1C), 156.66 (d, $J_{C\text{-}F}$ = 18.72 Hz, 1C), 155.08 (d, $J_{C\text{-}F}$ = 18.72 Hz, 1C), 106.83 (dd, $J_{C\text{-}F}$ = 25.07, 25.07 Hz, 2C), 20.78 (s, 1C).



N-(3,5,6-trifluoropyridin-2-yl)acetamide

GC-MS (EI, 70 Ev) m/z. 190, 148, 121. ESI-HRMS (m/z): $[M+H]^+$, caculated for $C_7H_6F_3N_2O$, 191.0413, found 191.0430; ^{1}H NMR (600 MHz, Acetone) δ 9.36 (s, 1H), 7.97 (dd, J = 16.0, 8.4 Hz, 1H), 2.16 (s, 3H). ^{13}C NMR (150 MHz, Acetone) δ 168.8, 149.70 (d, J = 259.2 Hz, 1C), 145.83 (dd, J = 235.3, 16.4 Hz, 1C), 143.94 – 141.54 (m, 1C), 133.20 (t, J = 12.9 Hz, 1C), 121.51 – 117.37 (m, 1C), 23.1.

References:

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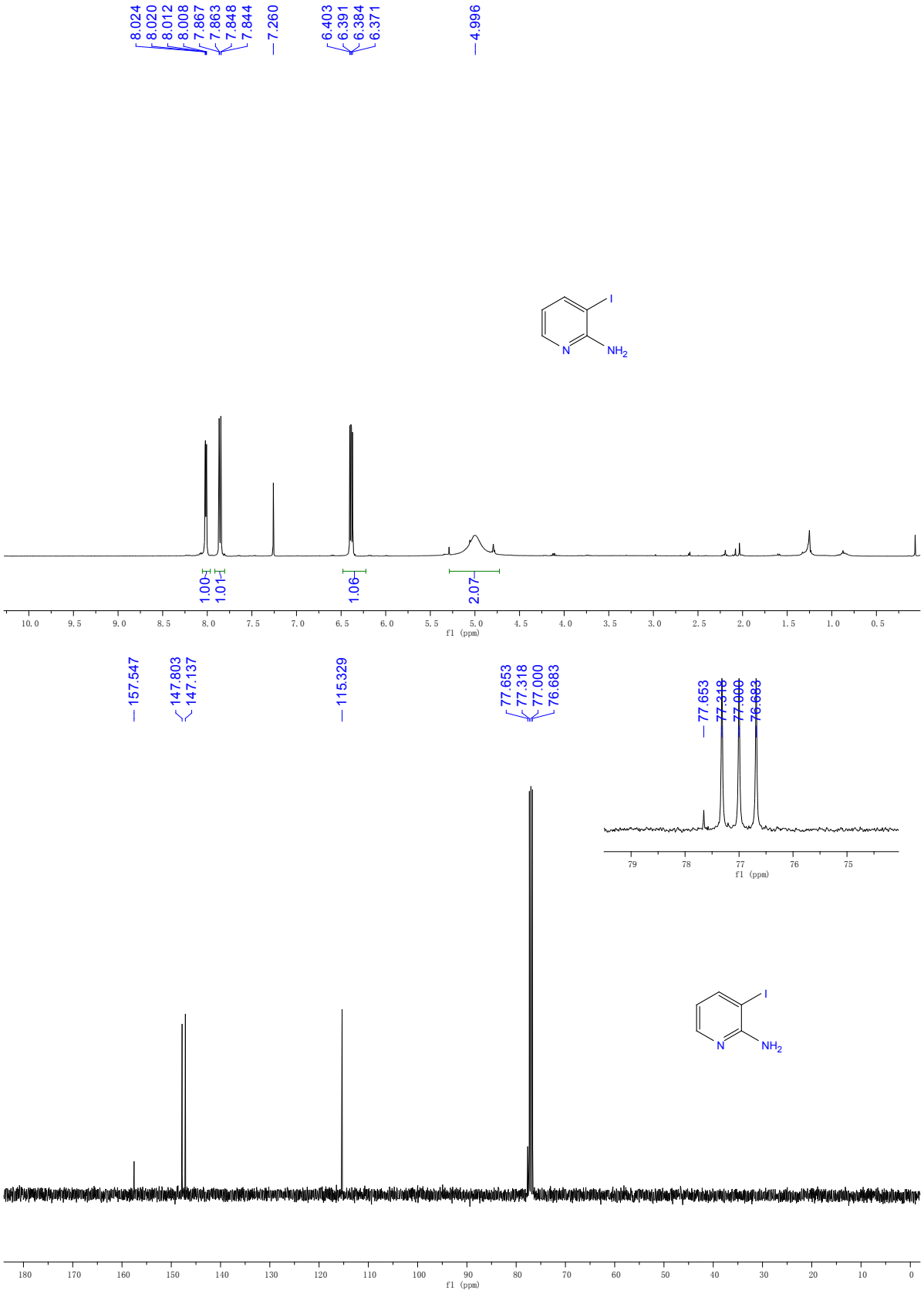
V. NMR Data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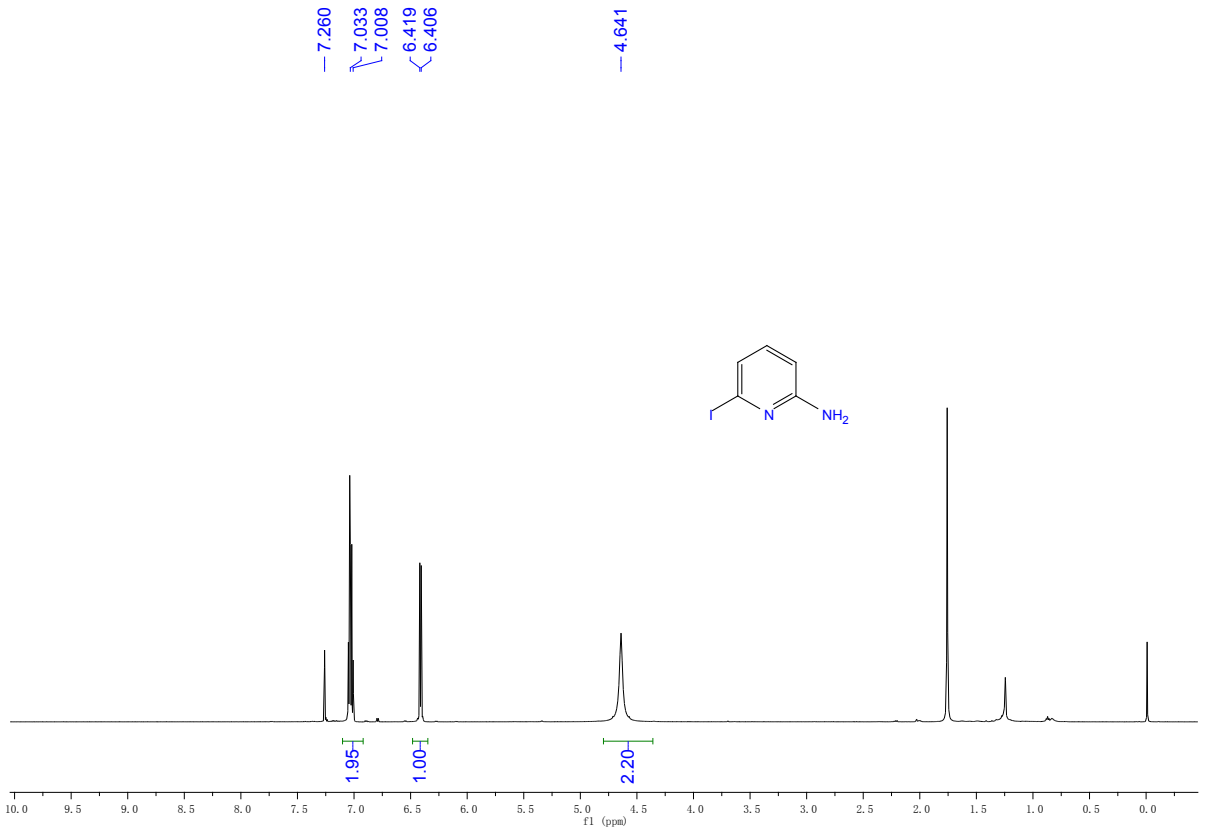
7.260
6.403
6.391
6.384
6.371
4.996
I
N
NH2
1.00
1.01
1.06
2.07
f1 (ppm)
157.547
147.803
147.137
115.329
77.653
77.318
77.000
76.683
f1 (ppm)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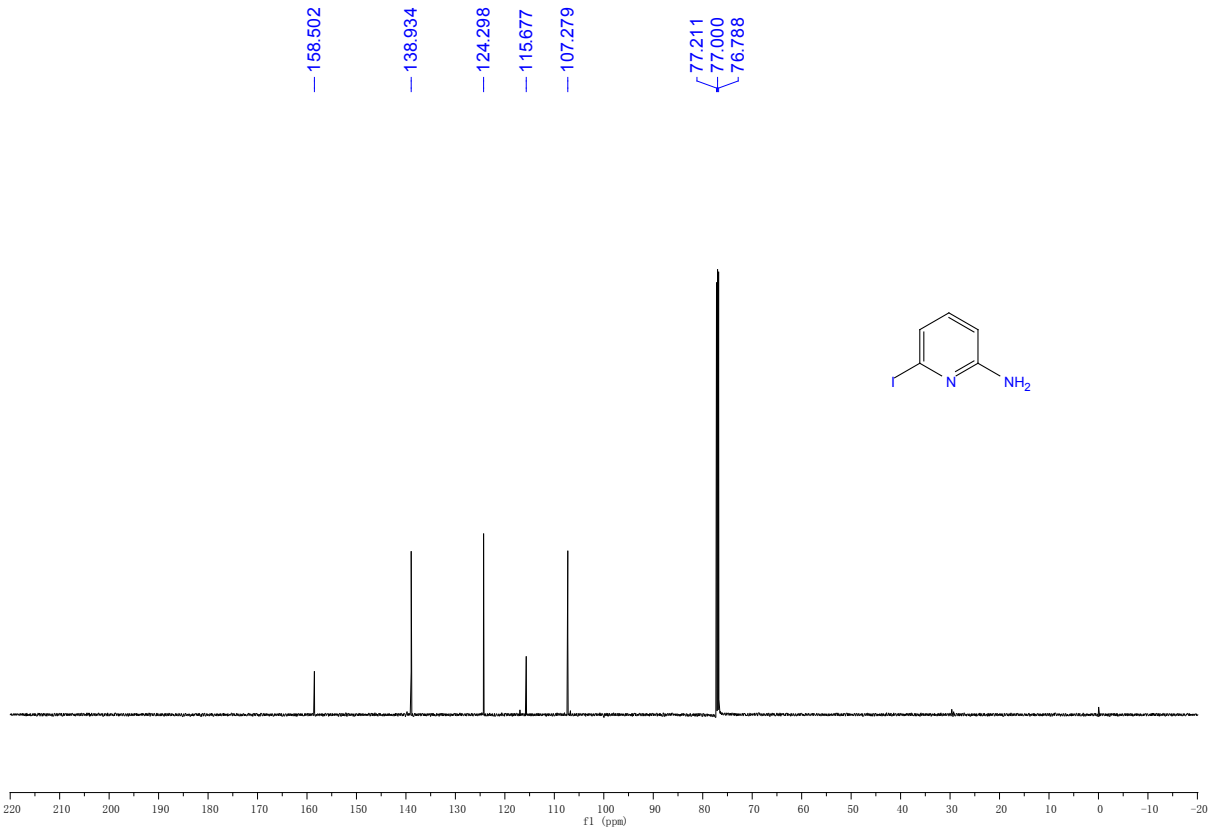
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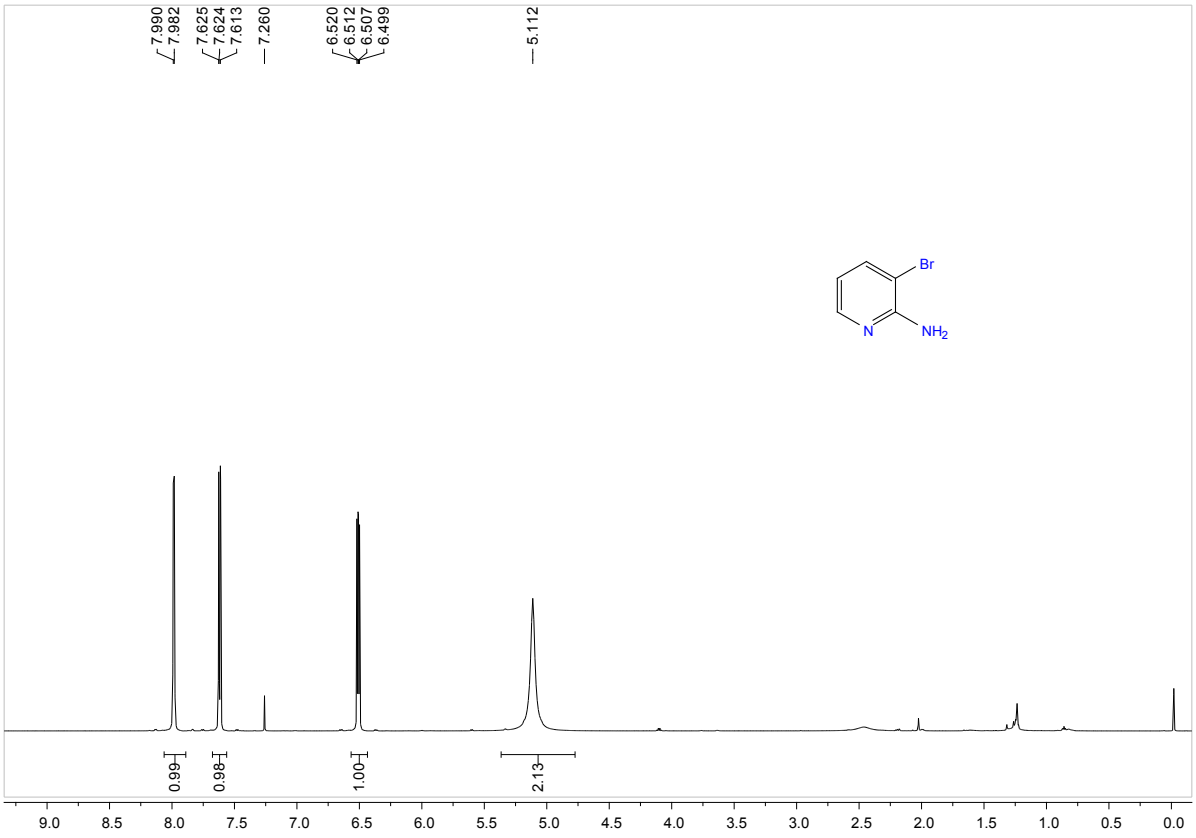
107.279
77.211
77.000
76.788
I
N
NH2
f1 (ppm)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7.613
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6.507
6.499
5.112
Br
N
NH2
0.99
0.98
1.00
2.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.5
4.0
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2.0
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1.0
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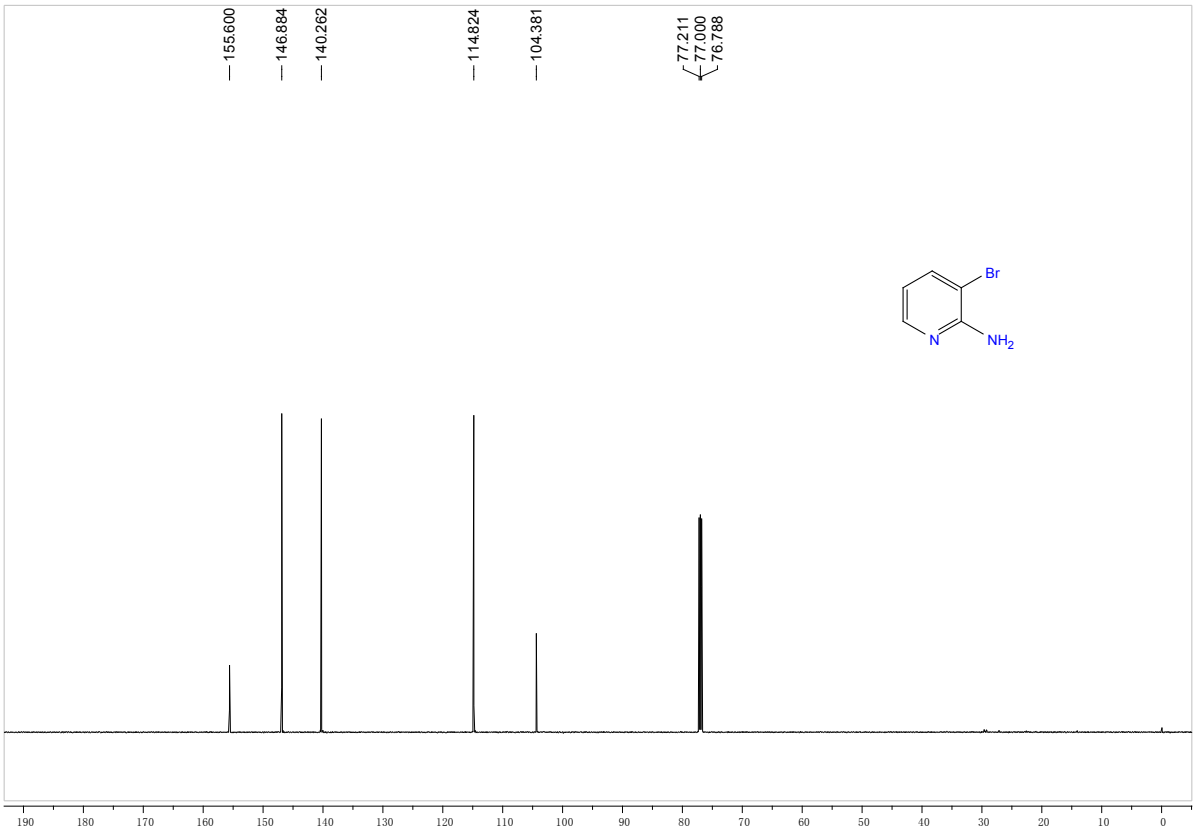
0.0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104.381
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76.788
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NH2
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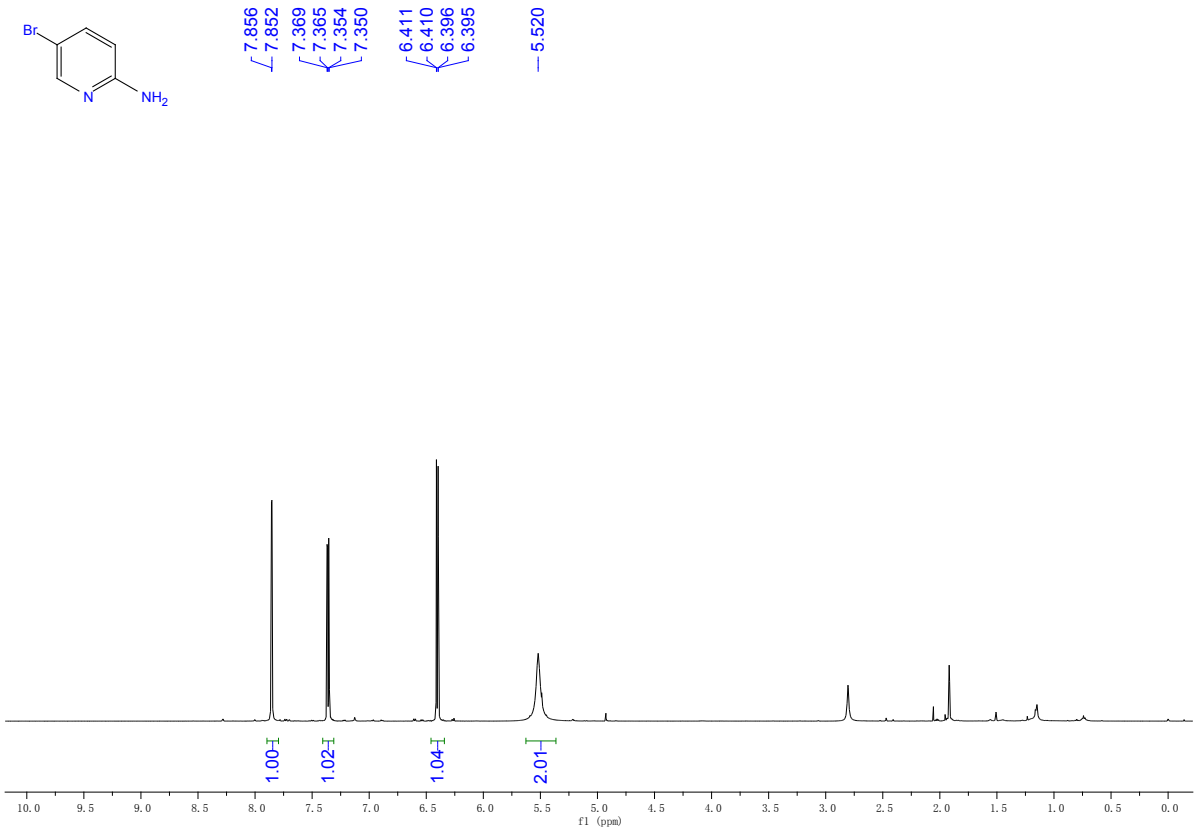
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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1.02
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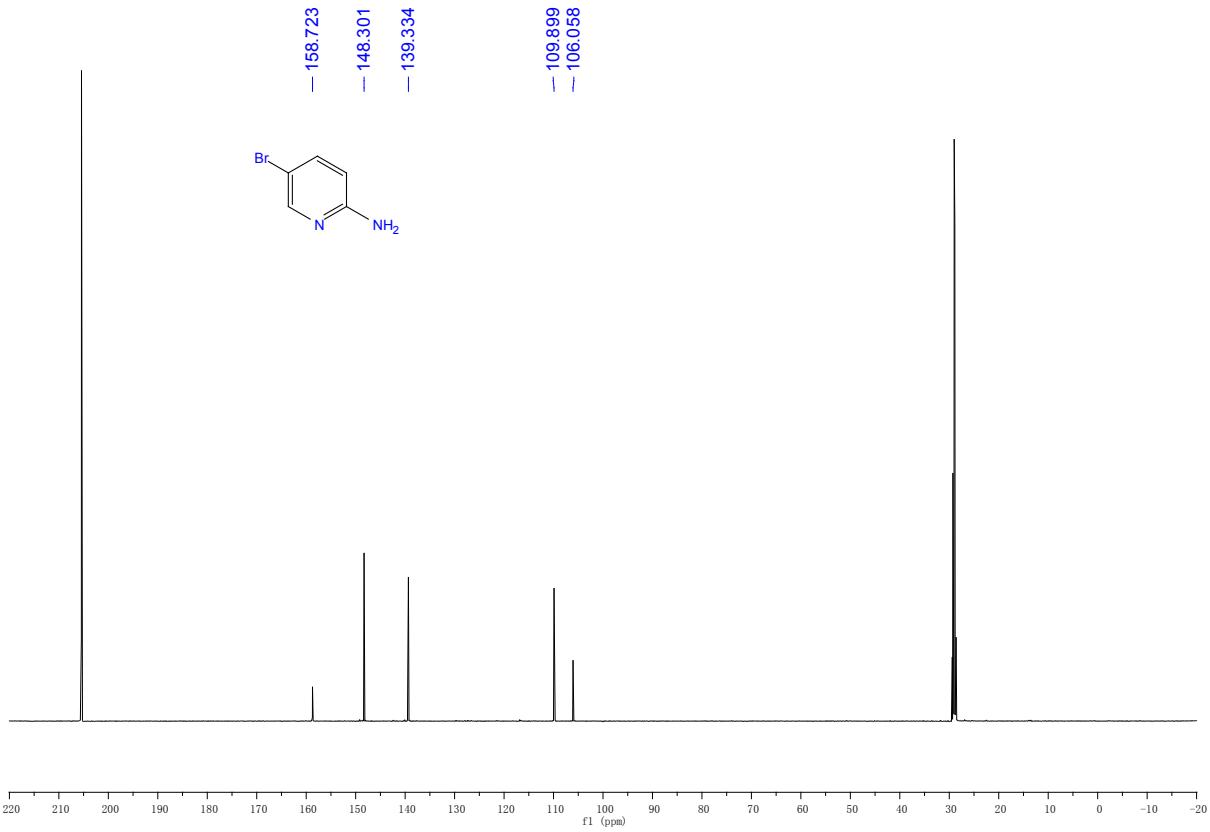
2.01
f1 (ppm)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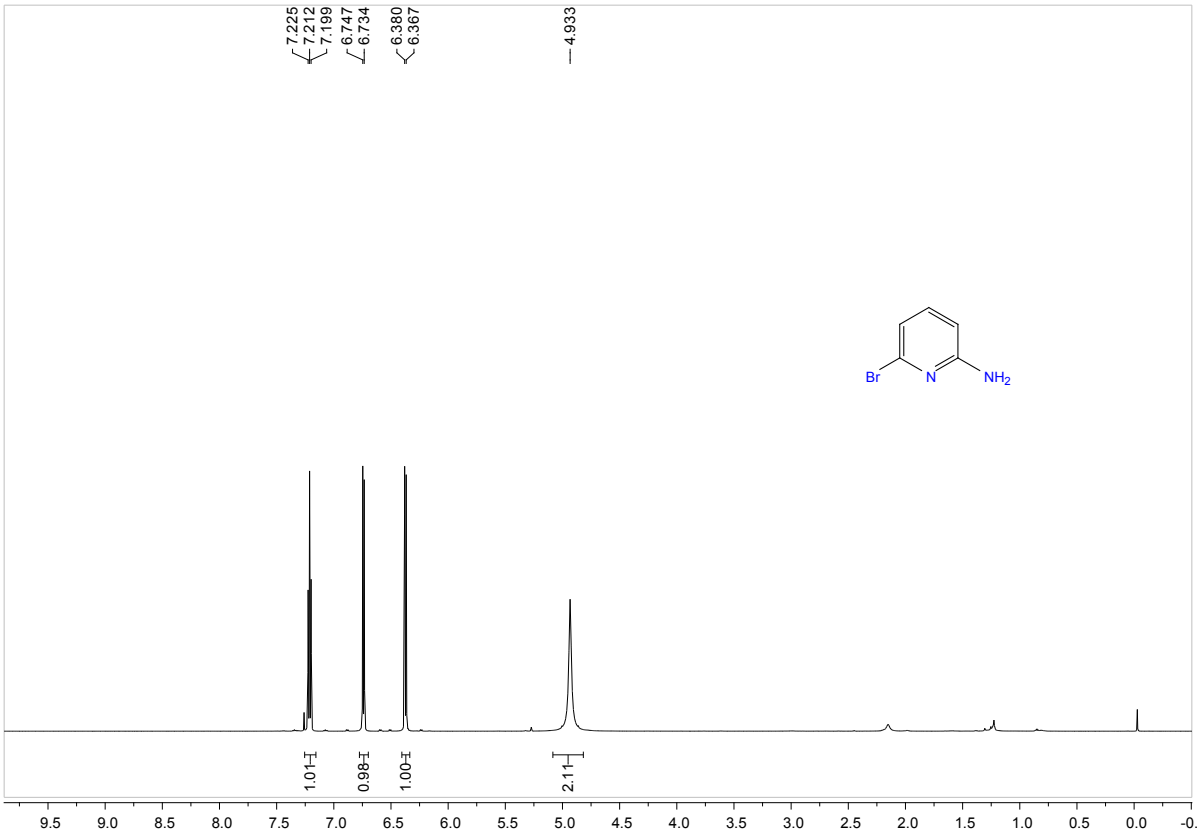
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0.98
1.00
2.11
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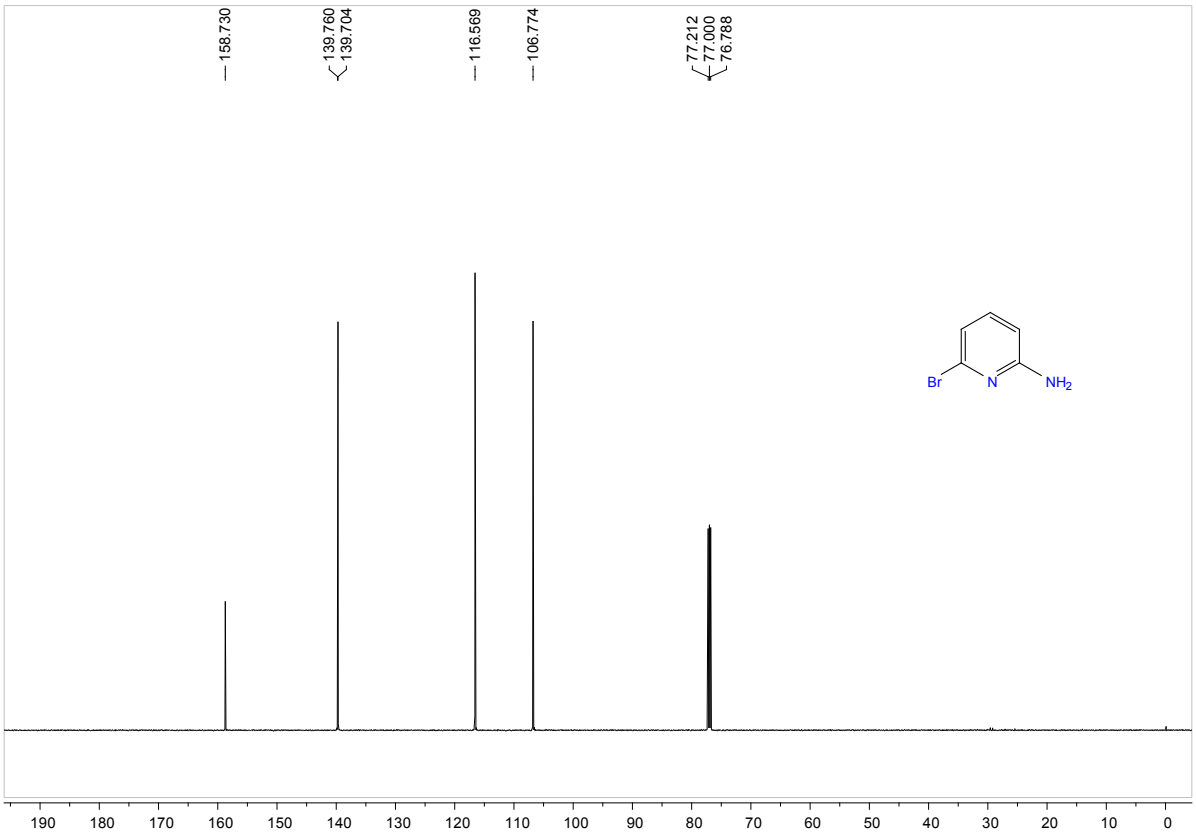
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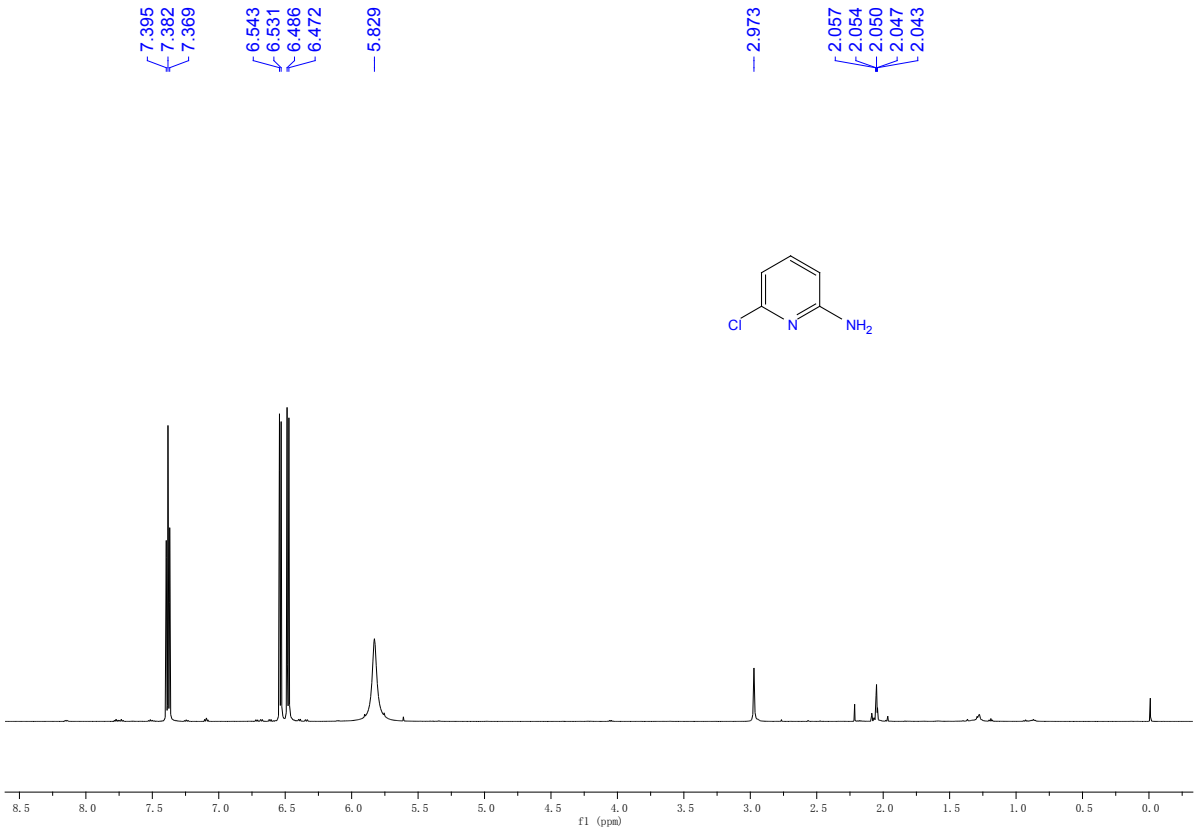
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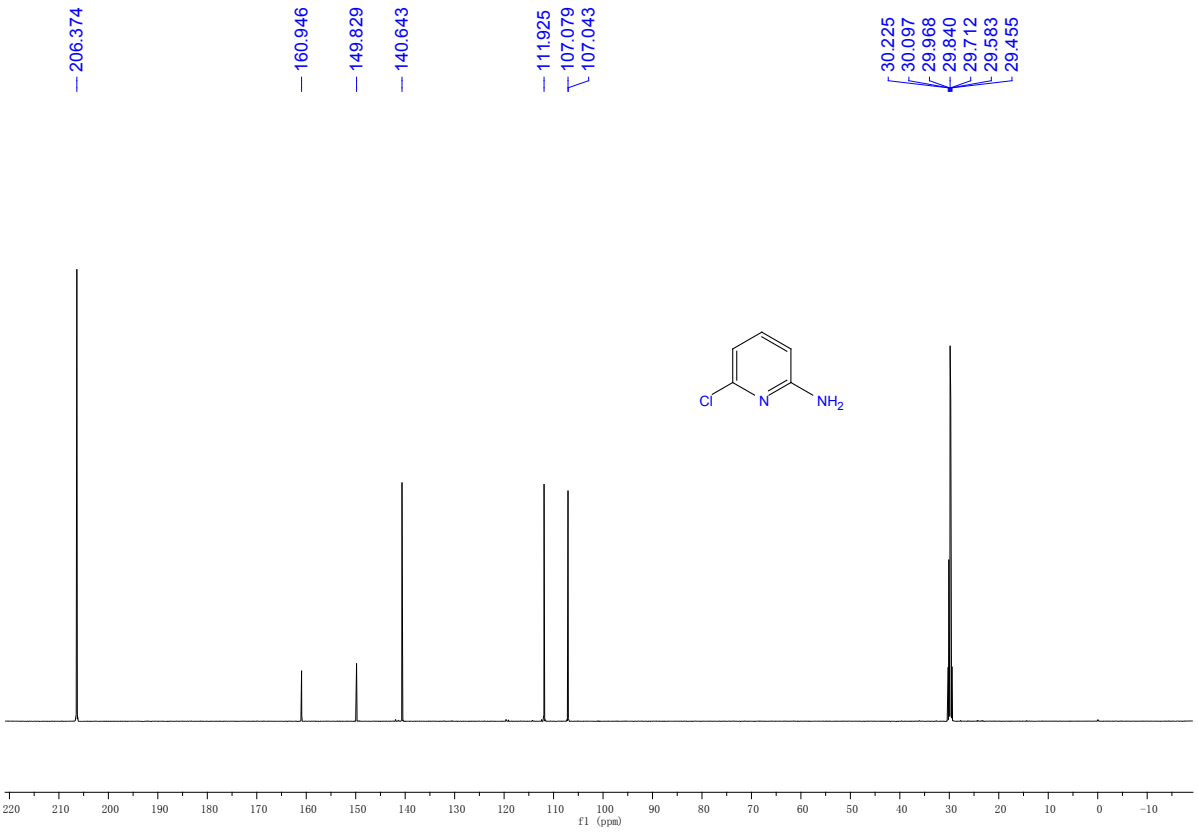
NH2
f1 (ppm)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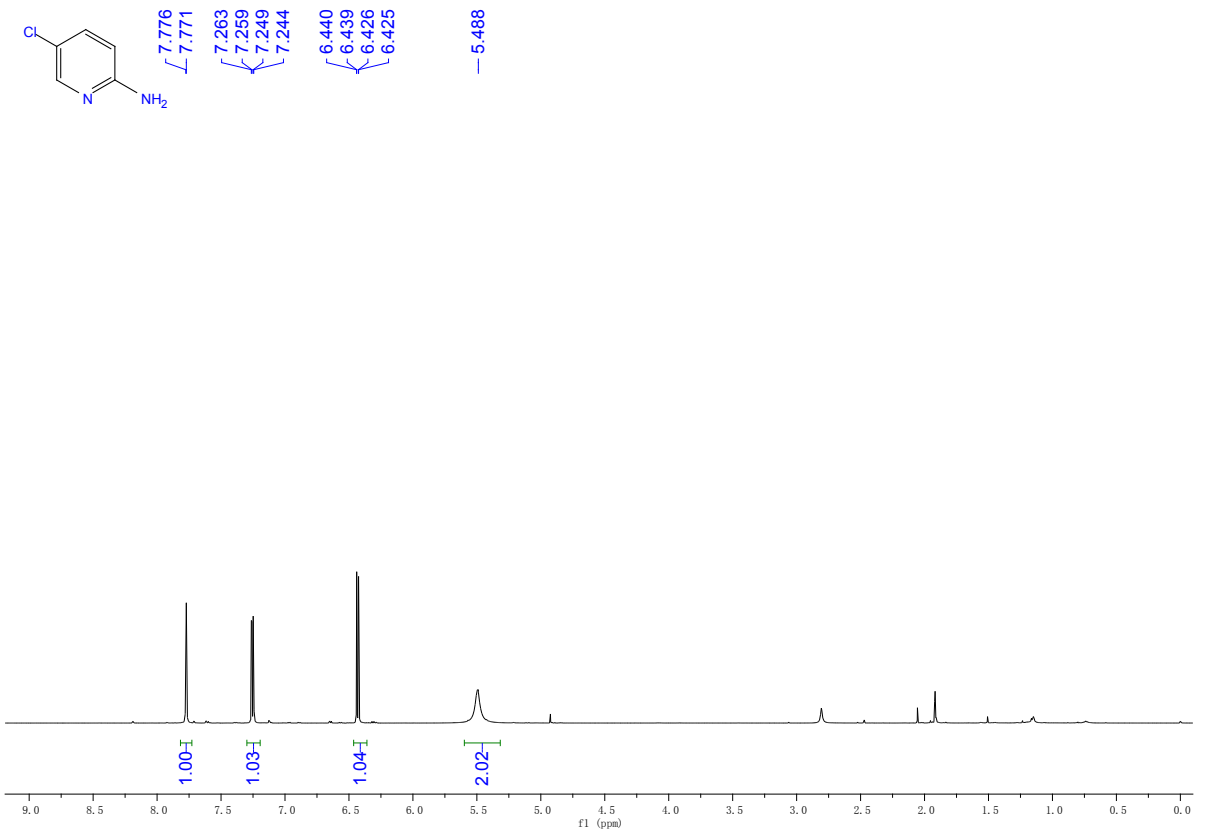
f1 (ppm)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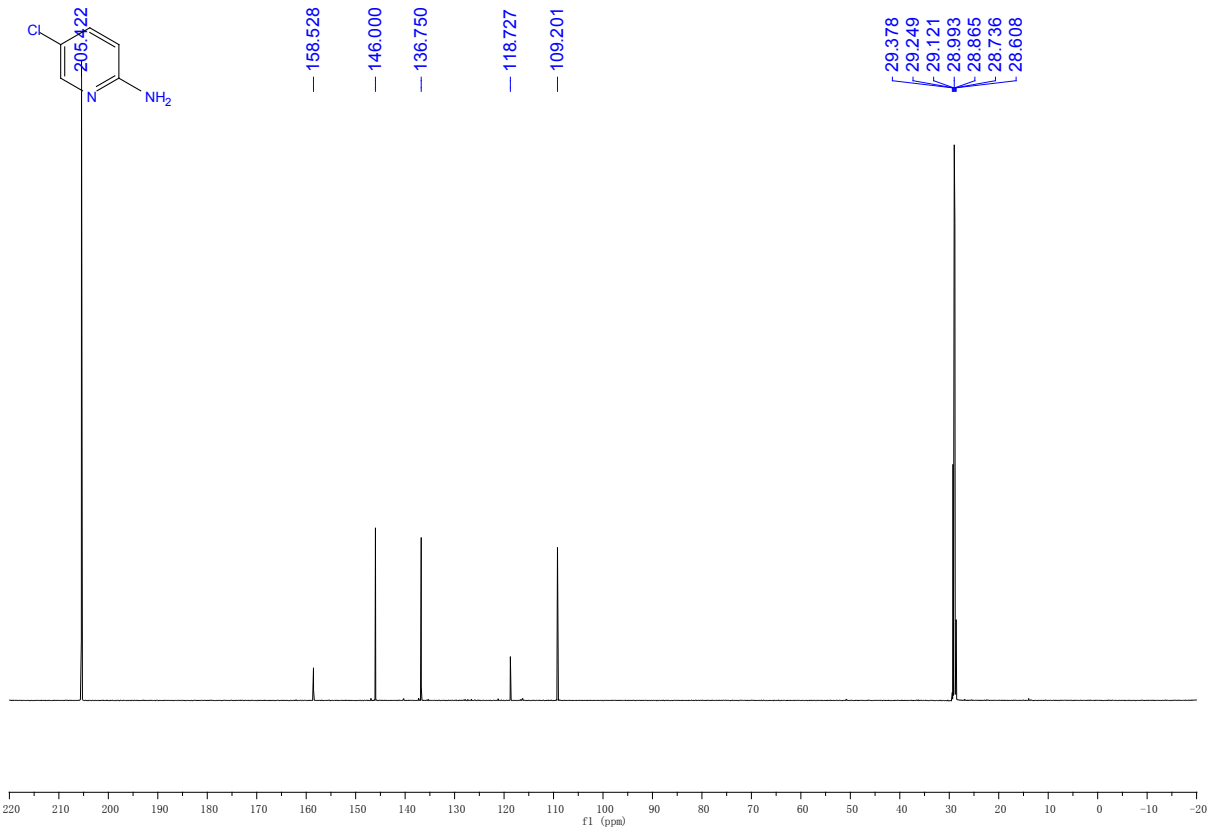
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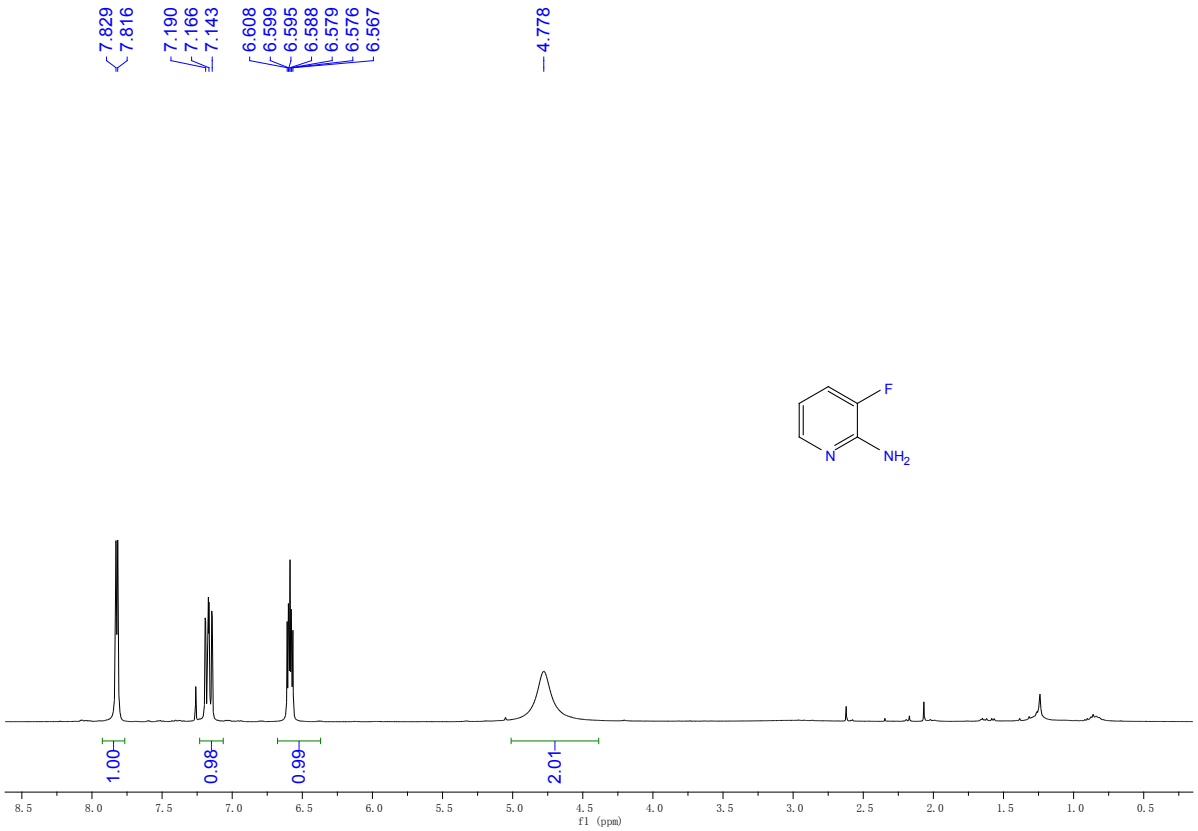
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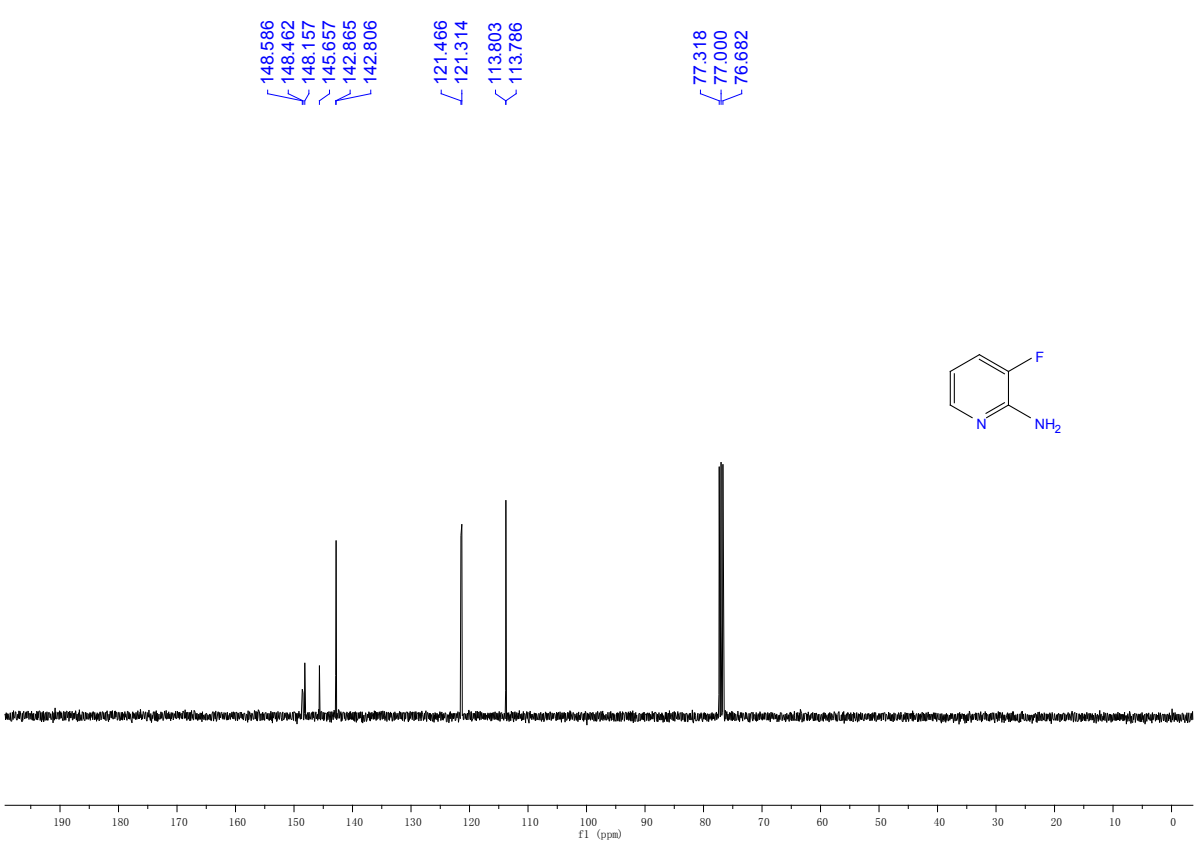
0.99
2.01
f1 (ppm)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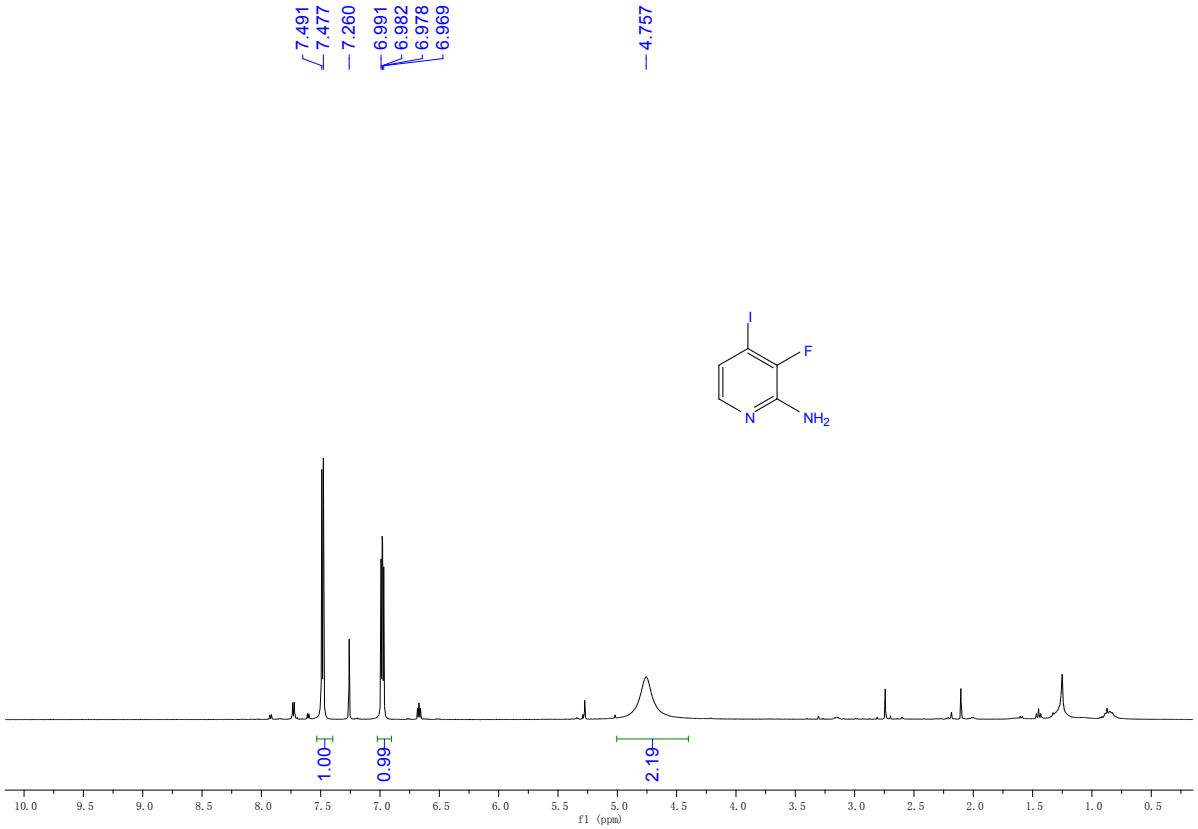
N
NH2
f1 (ppm)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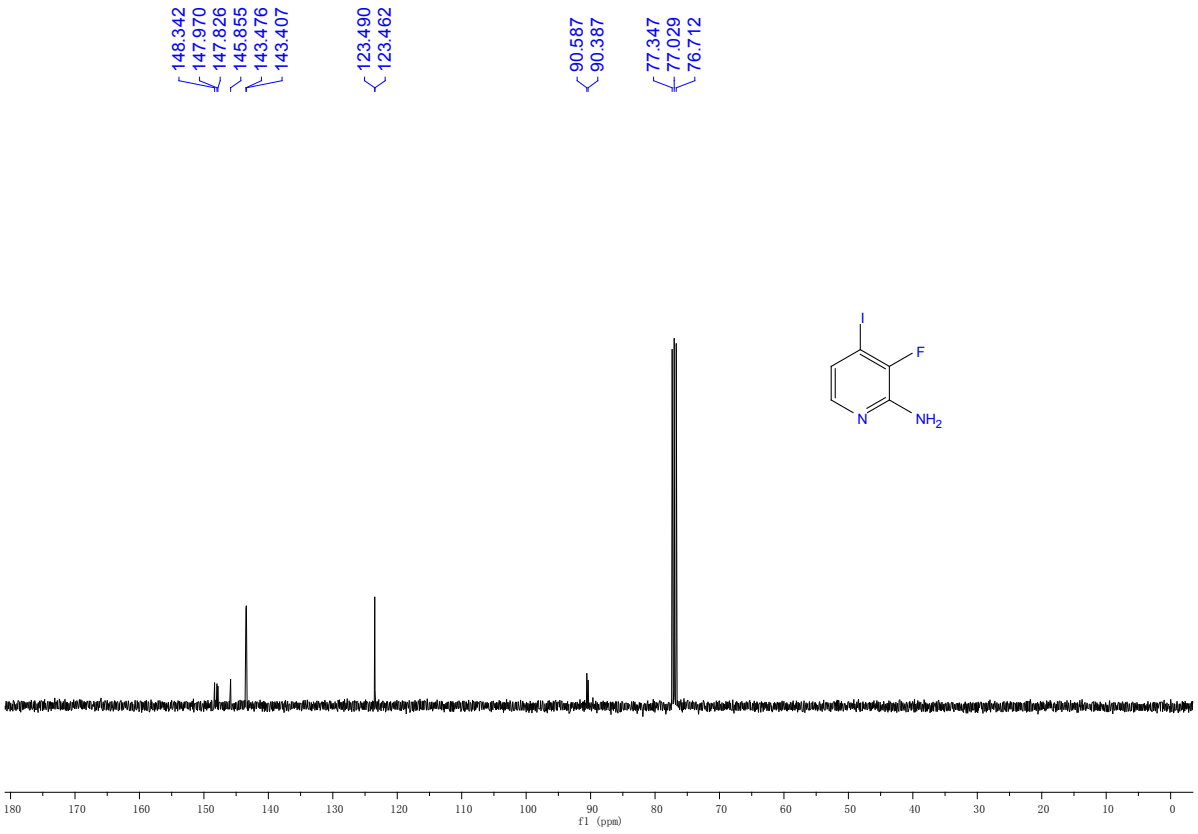
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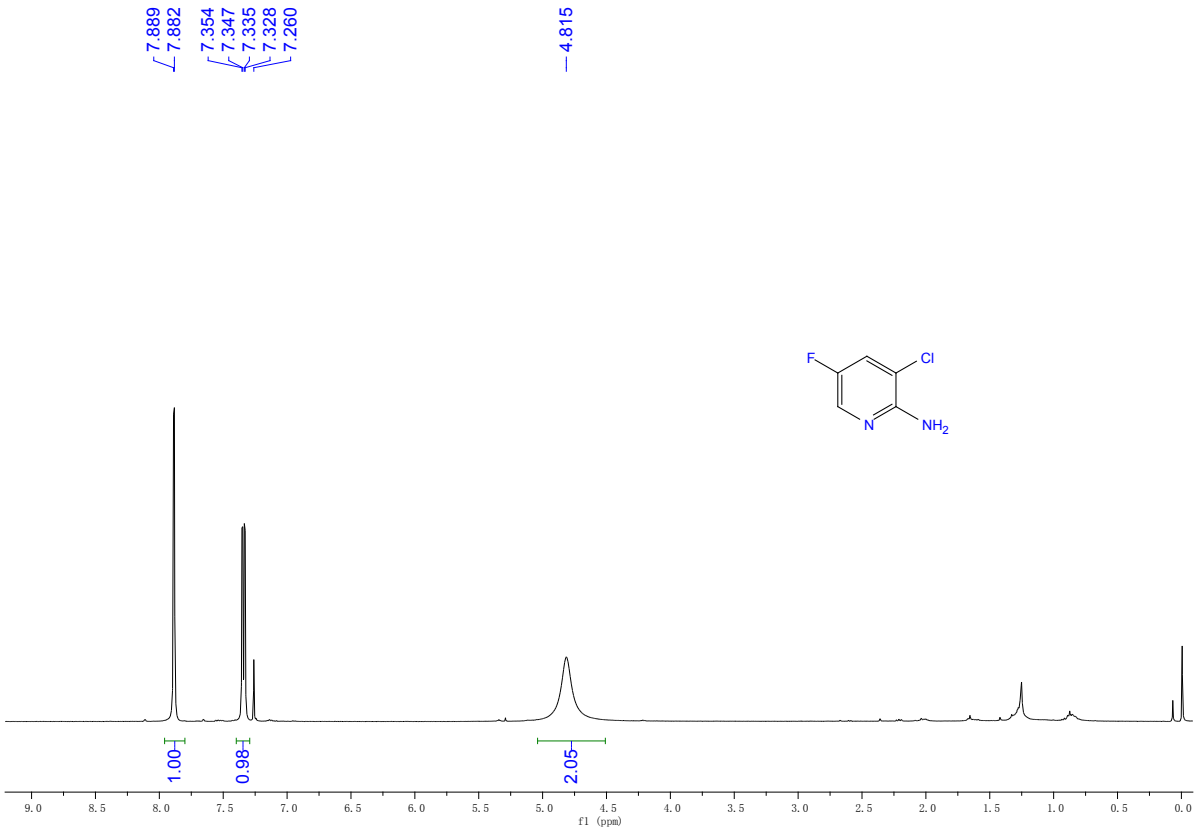
N
NH2
f1 (ppm)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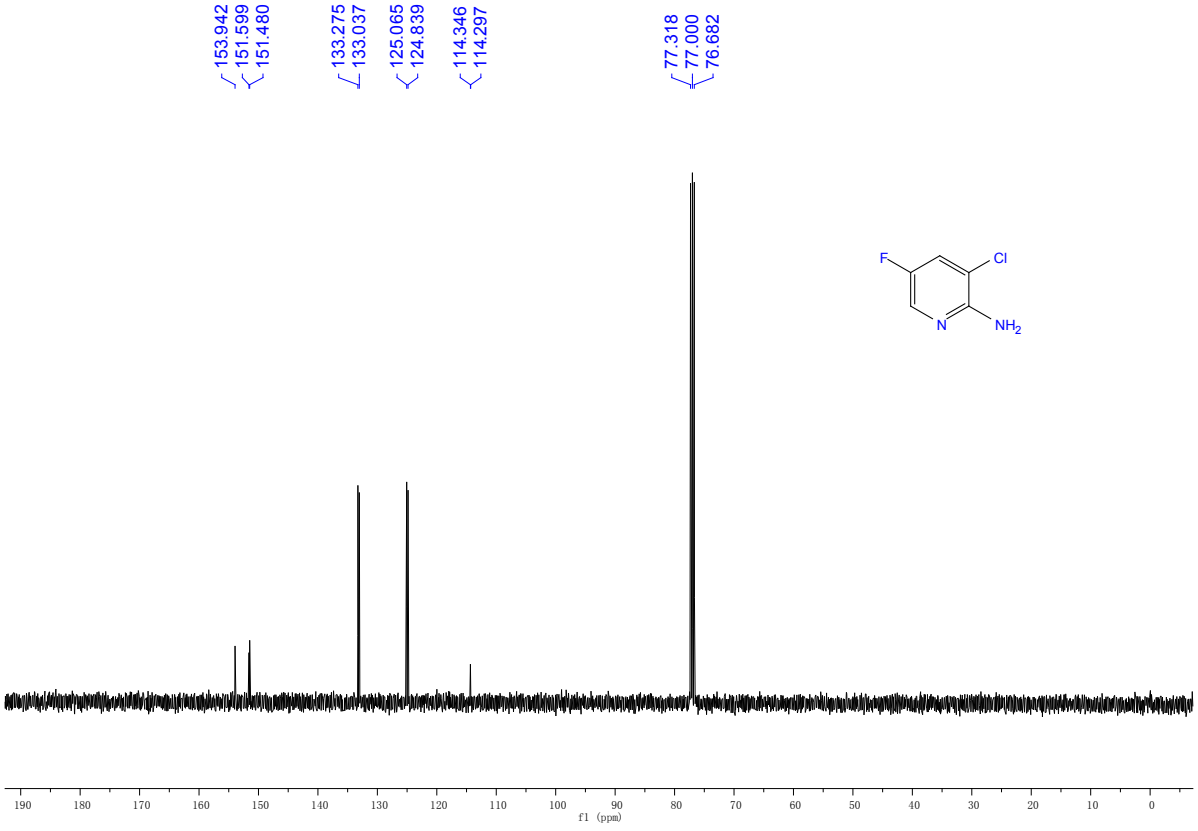
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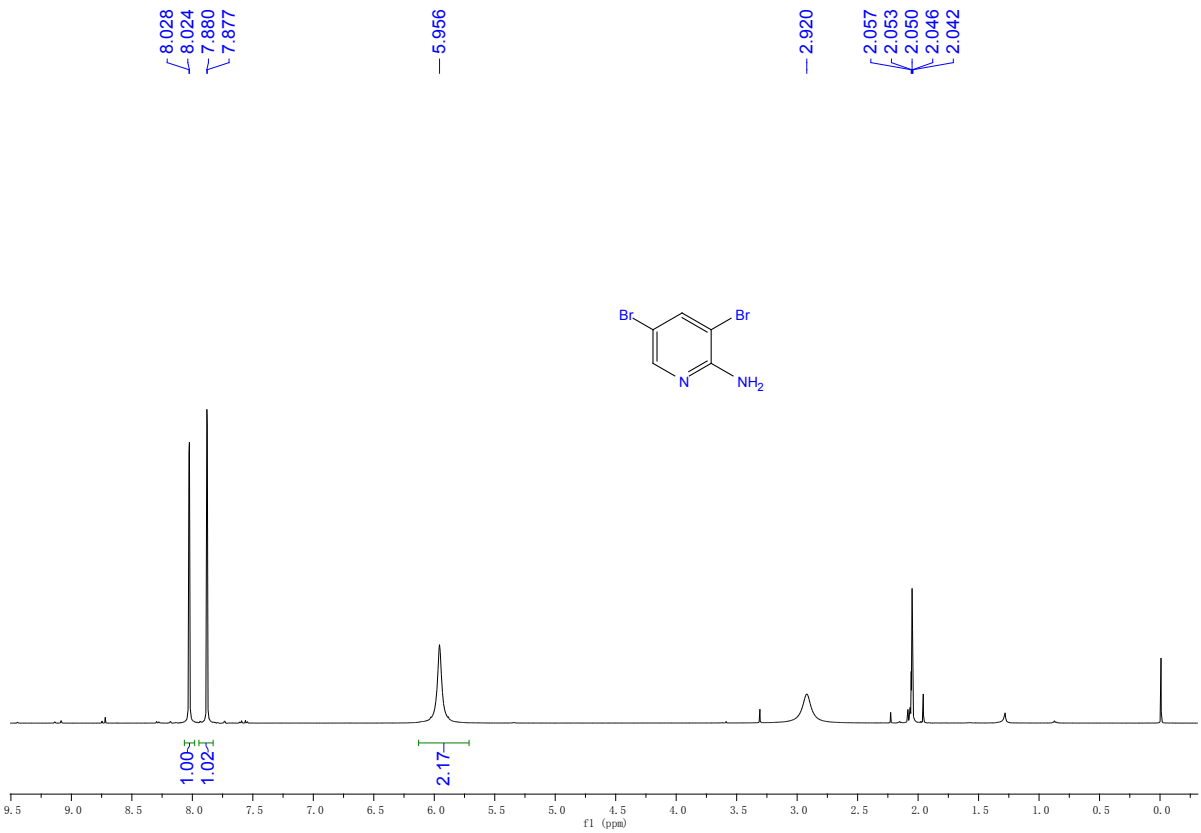
f1 (ppm)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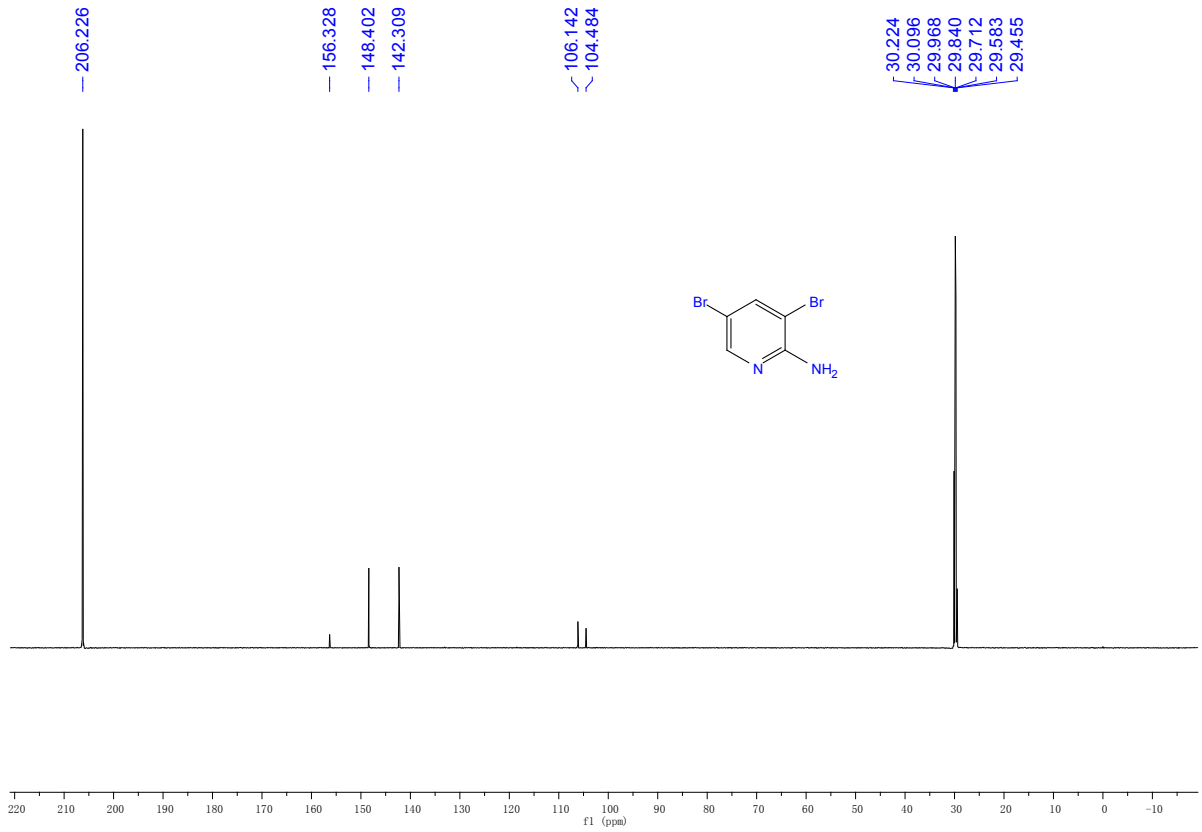
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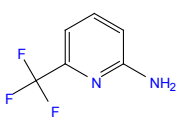
N
NH2
f1 (ppm)



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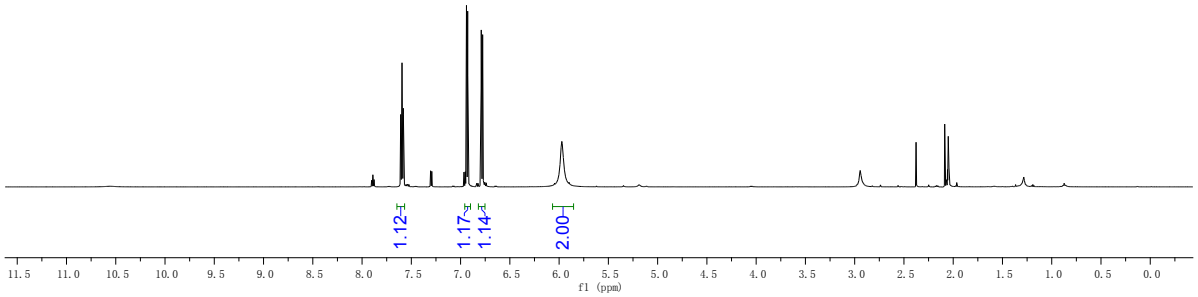

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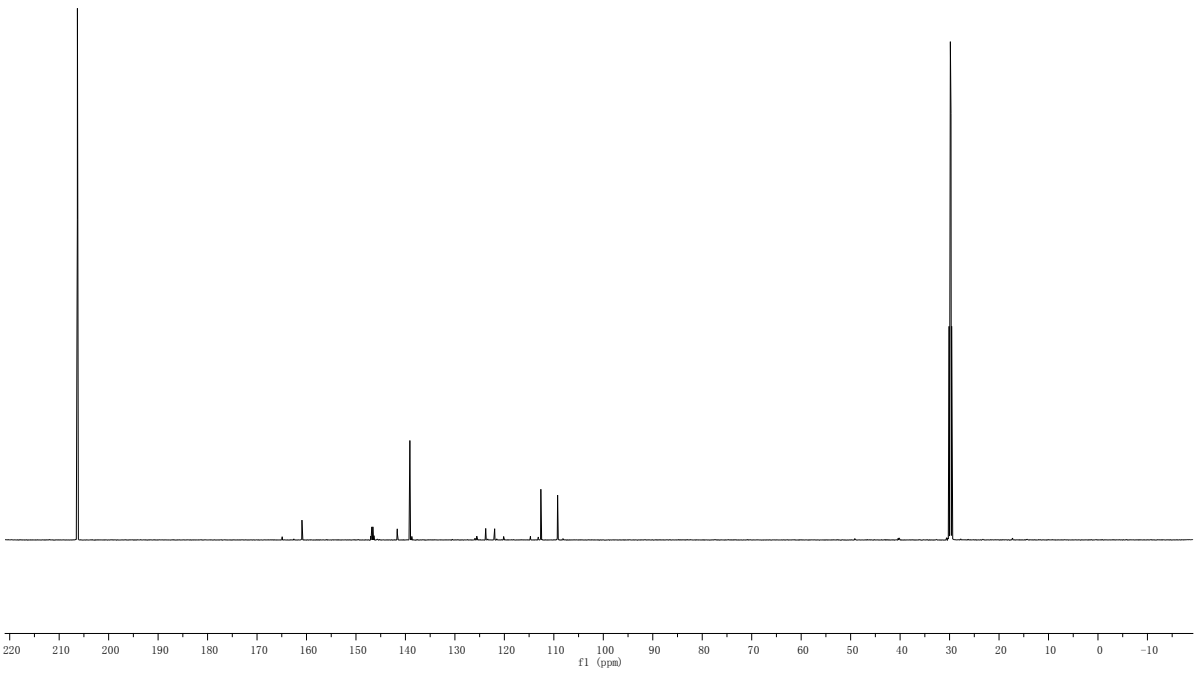

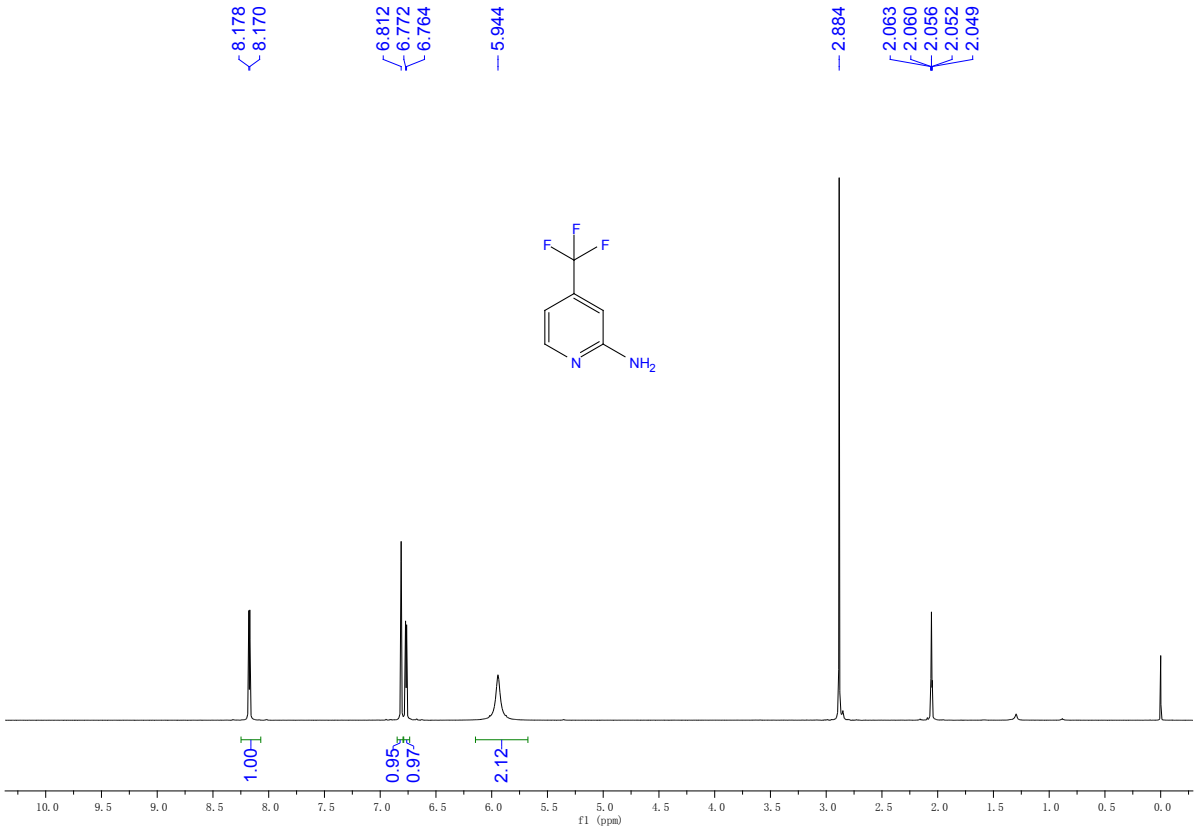
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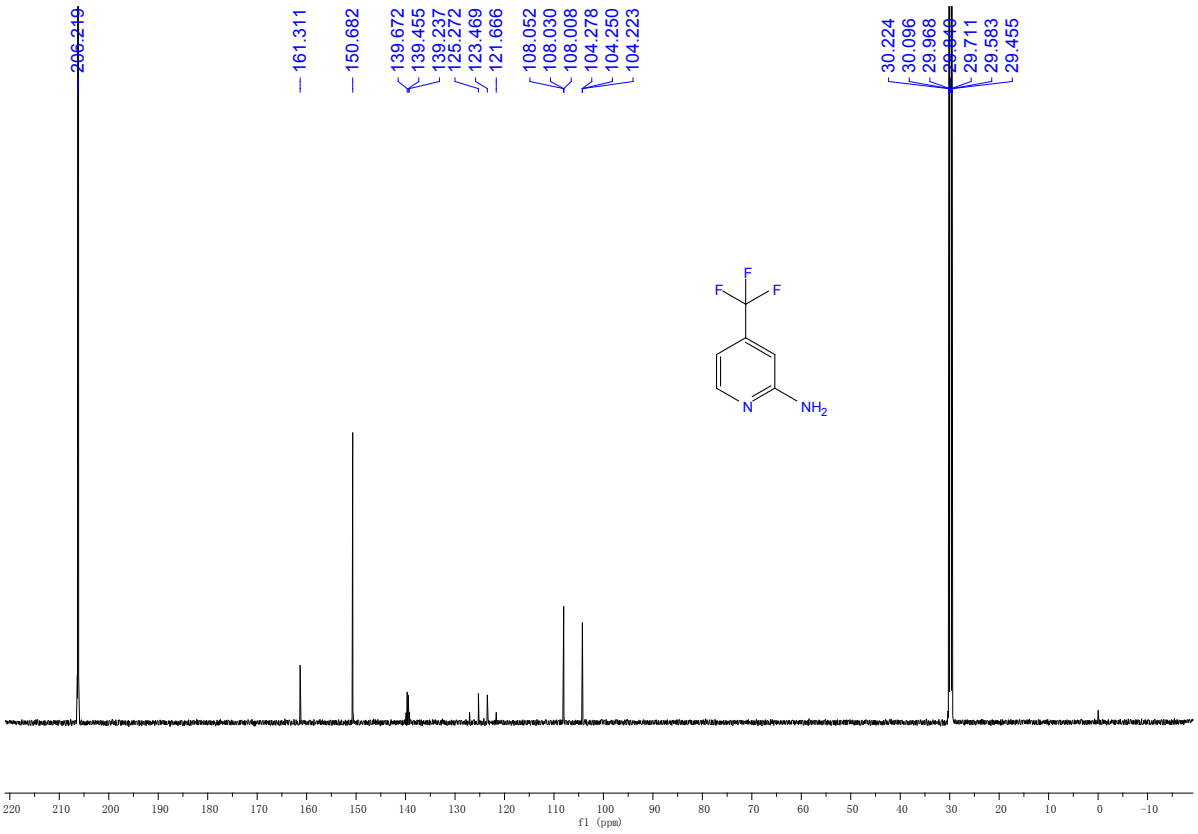
F
F
F
N
NH2
1.00
0.95
0.97
2.12
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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104.250
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30.224
30.096
29.968
29.711
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F
F
F
N
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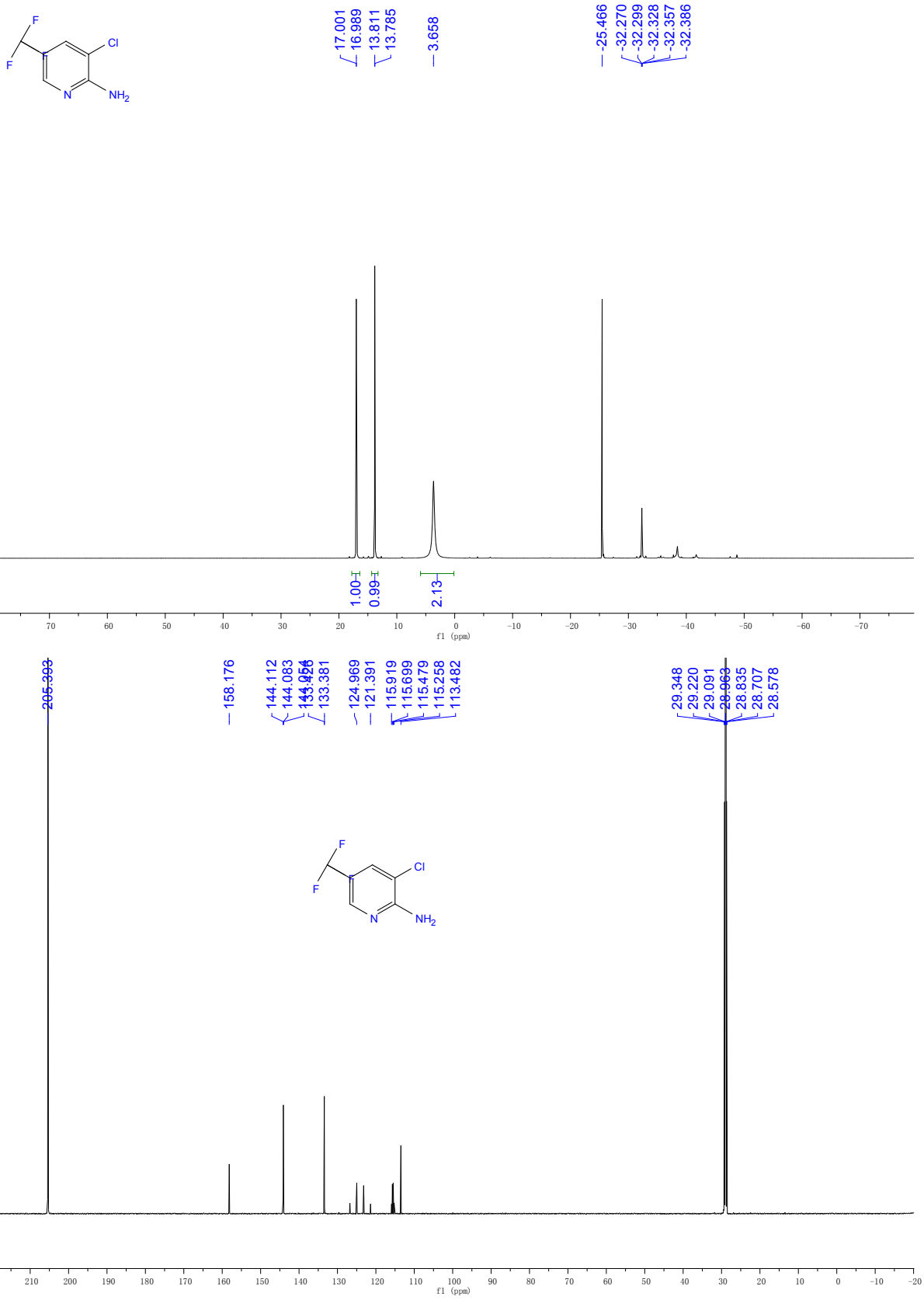
f1 (ppm)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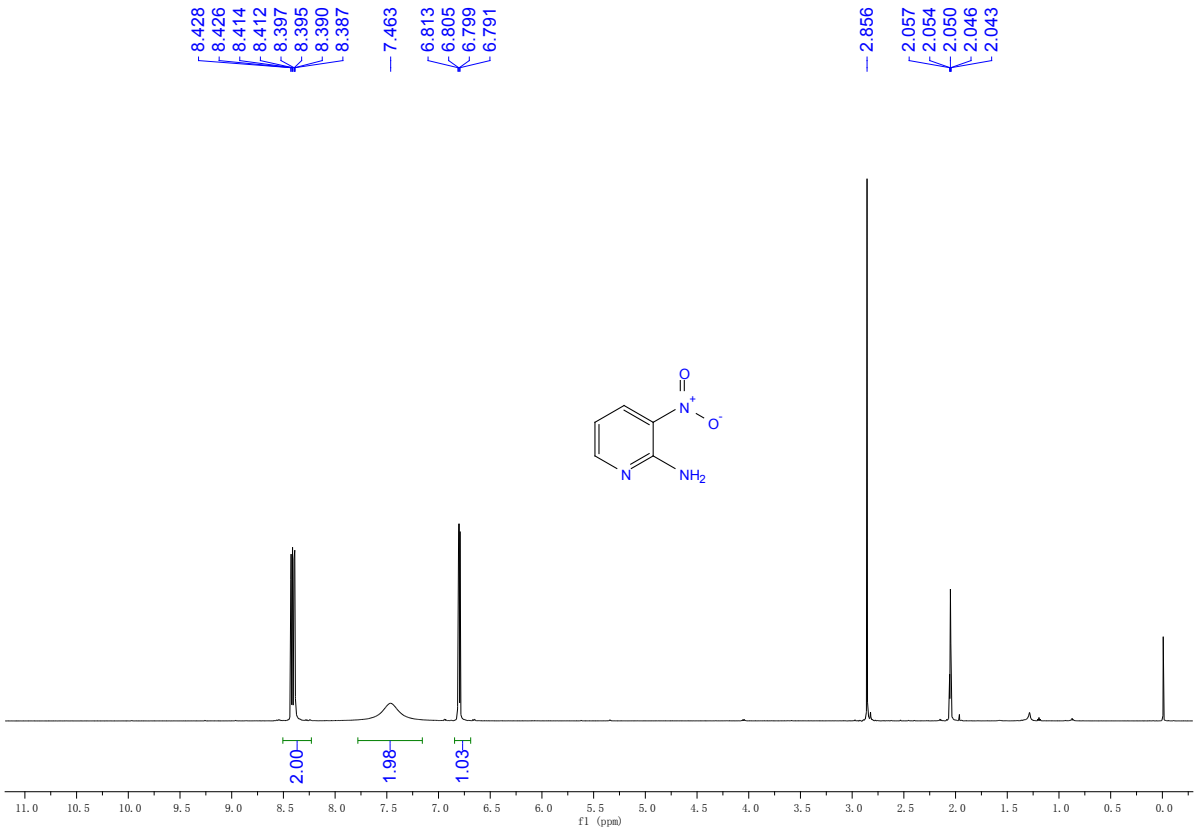
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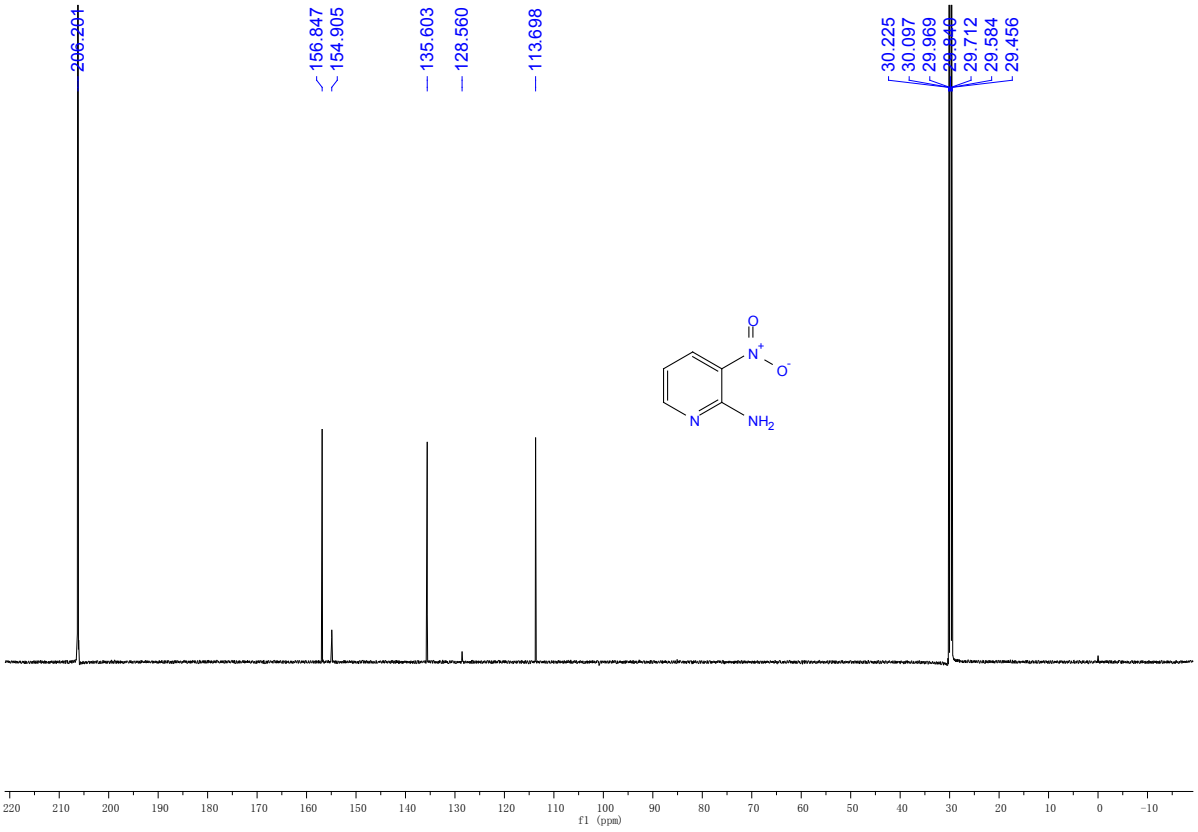
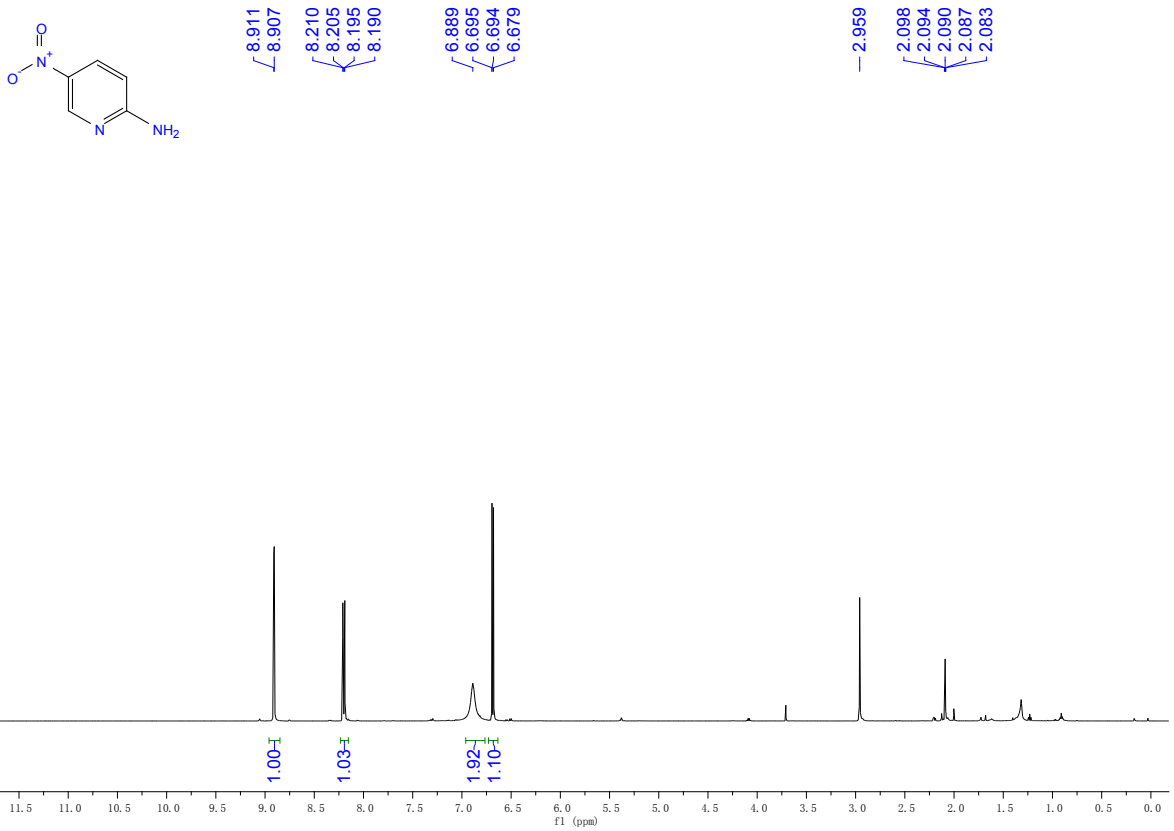
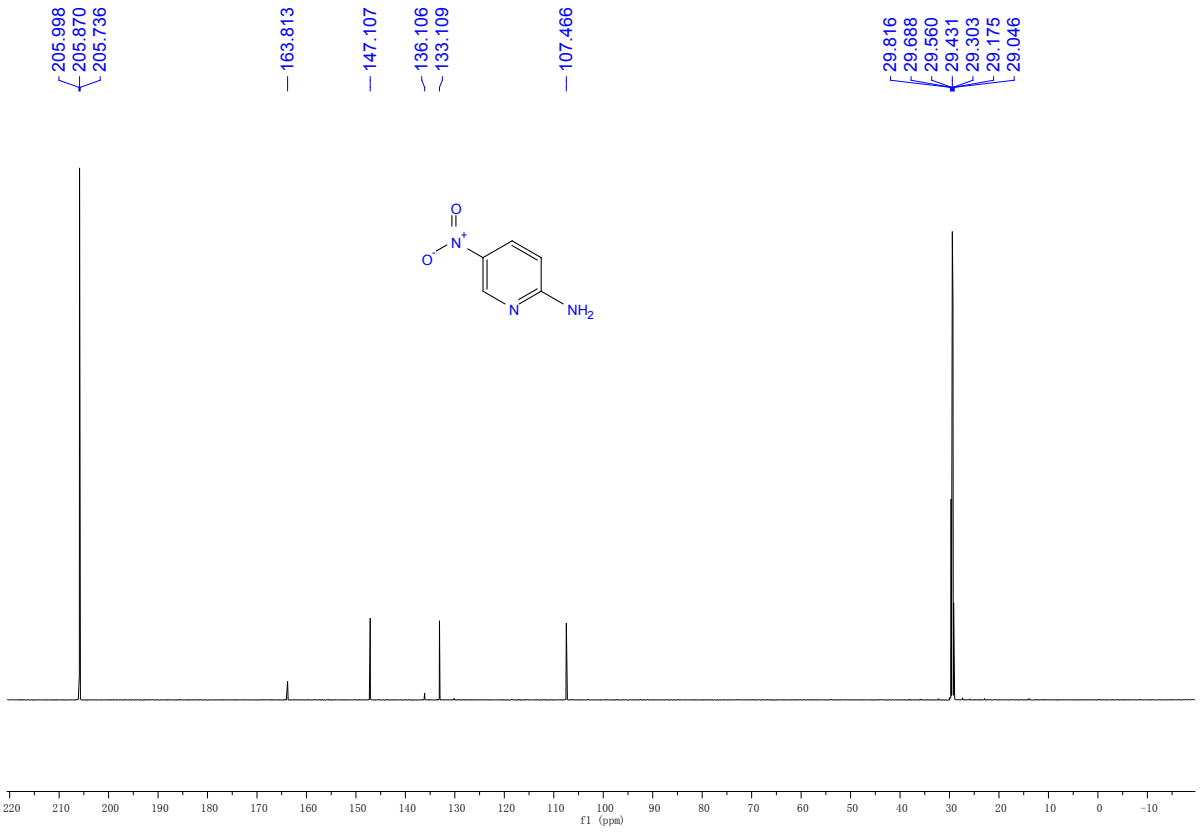
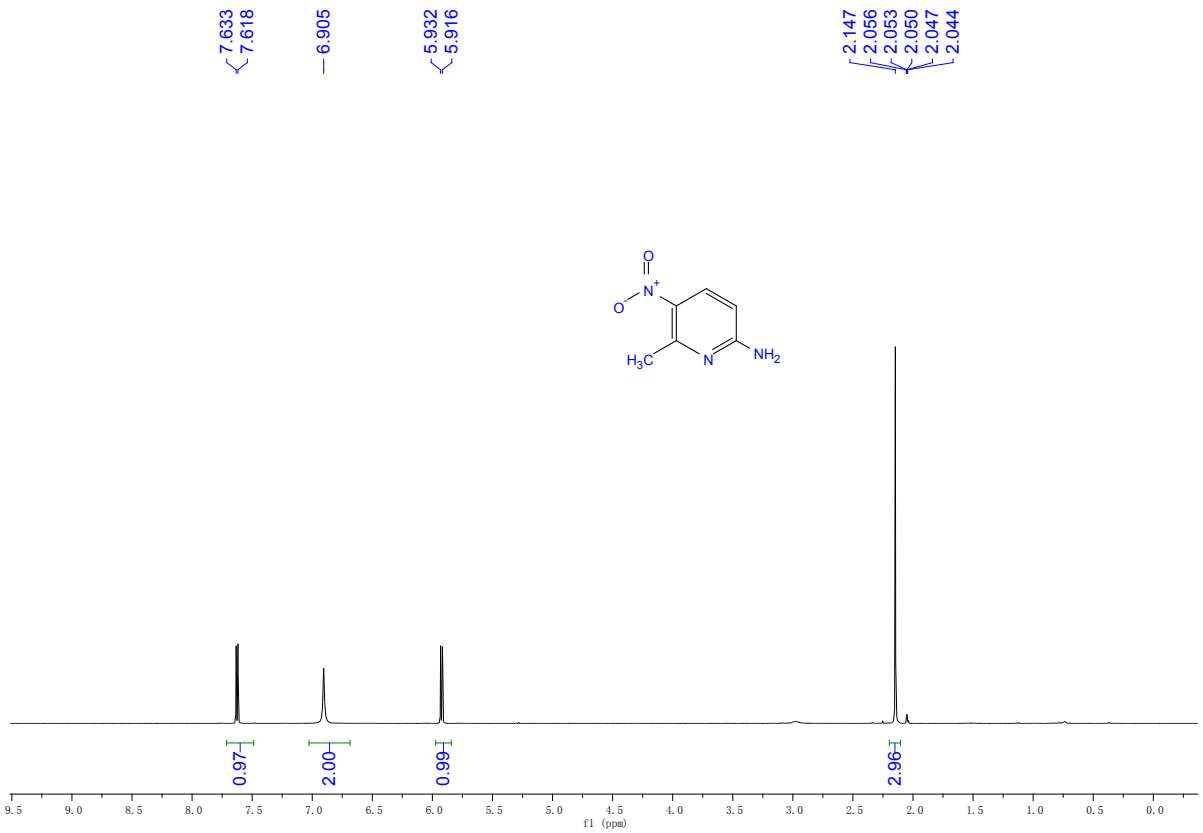
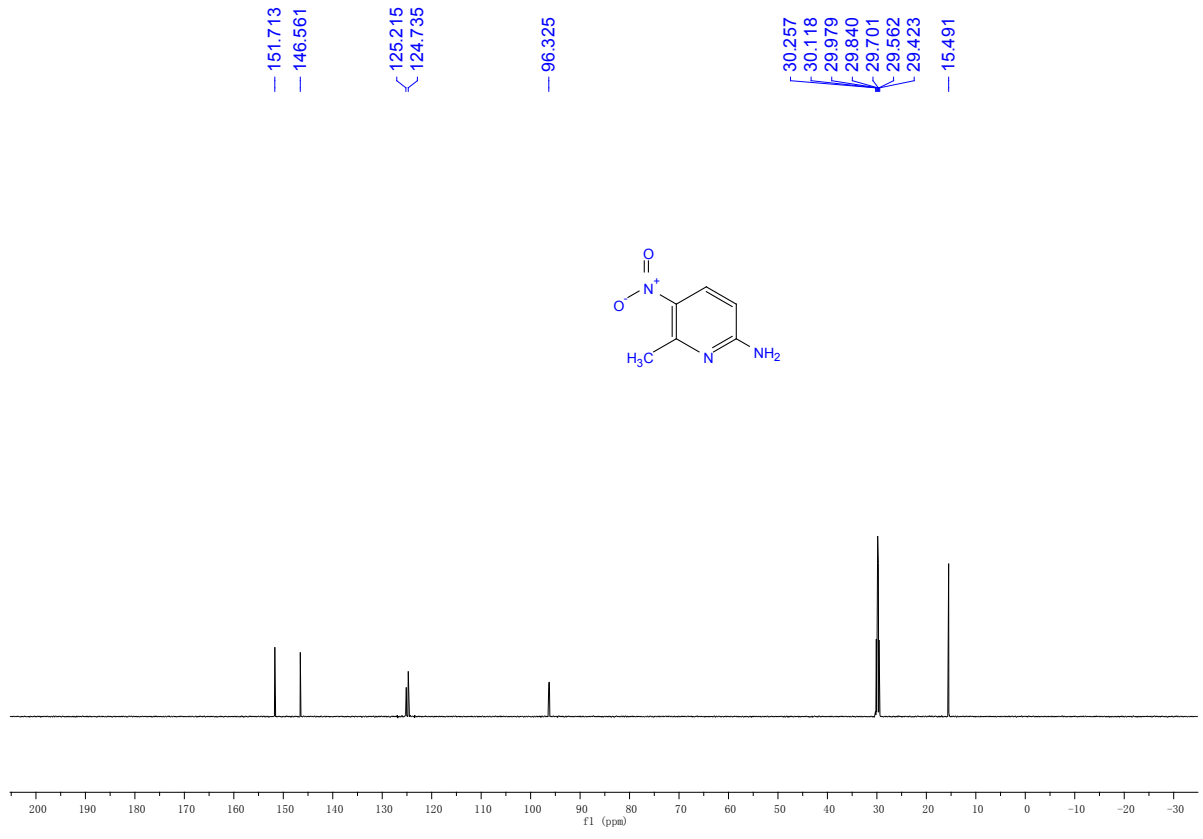
2.856
2.057
2.054
2.050
2.046
2.043
O
N+
O-
N
NH2
2.00
1.98
1.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

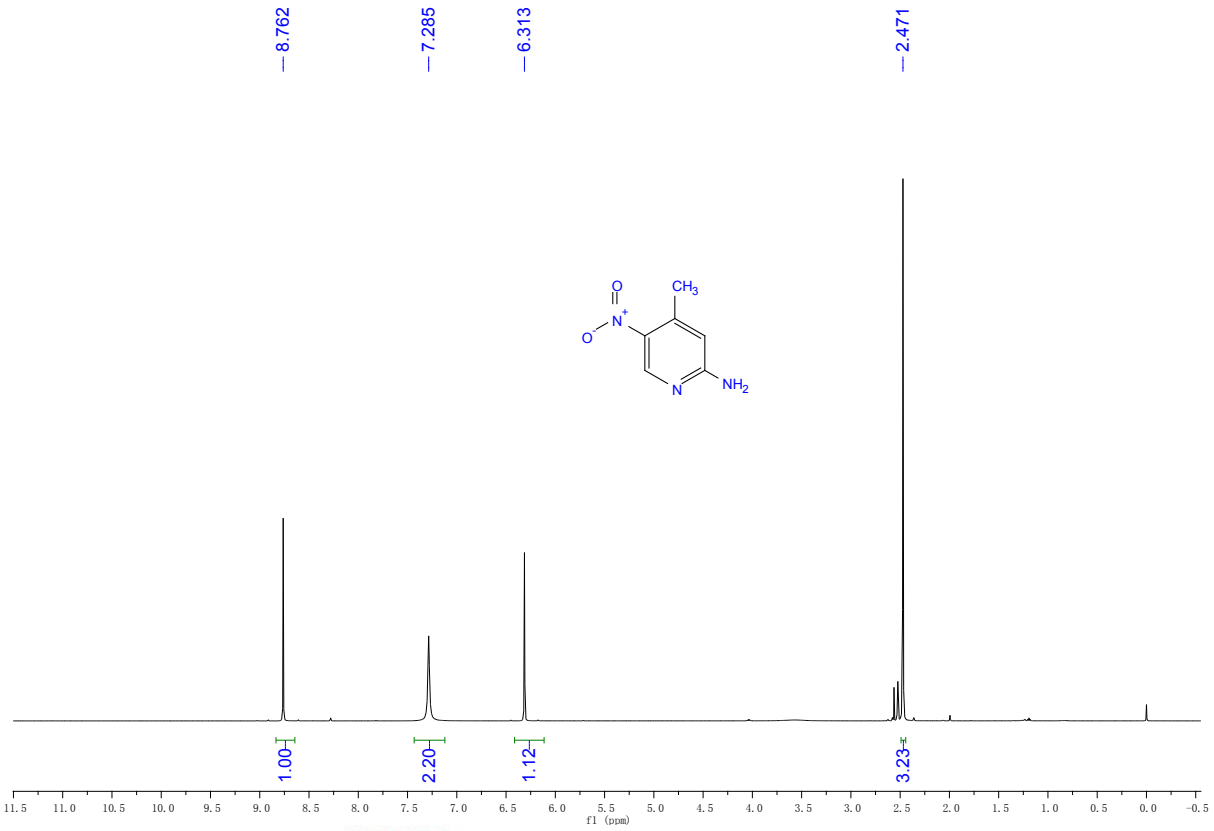

206.201
156.847
154.905
135.603
128.560
113.698
30.225
30.097
29.969
29.840
29.712
29.584
29.456
O
N+
O-
N
NH2
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

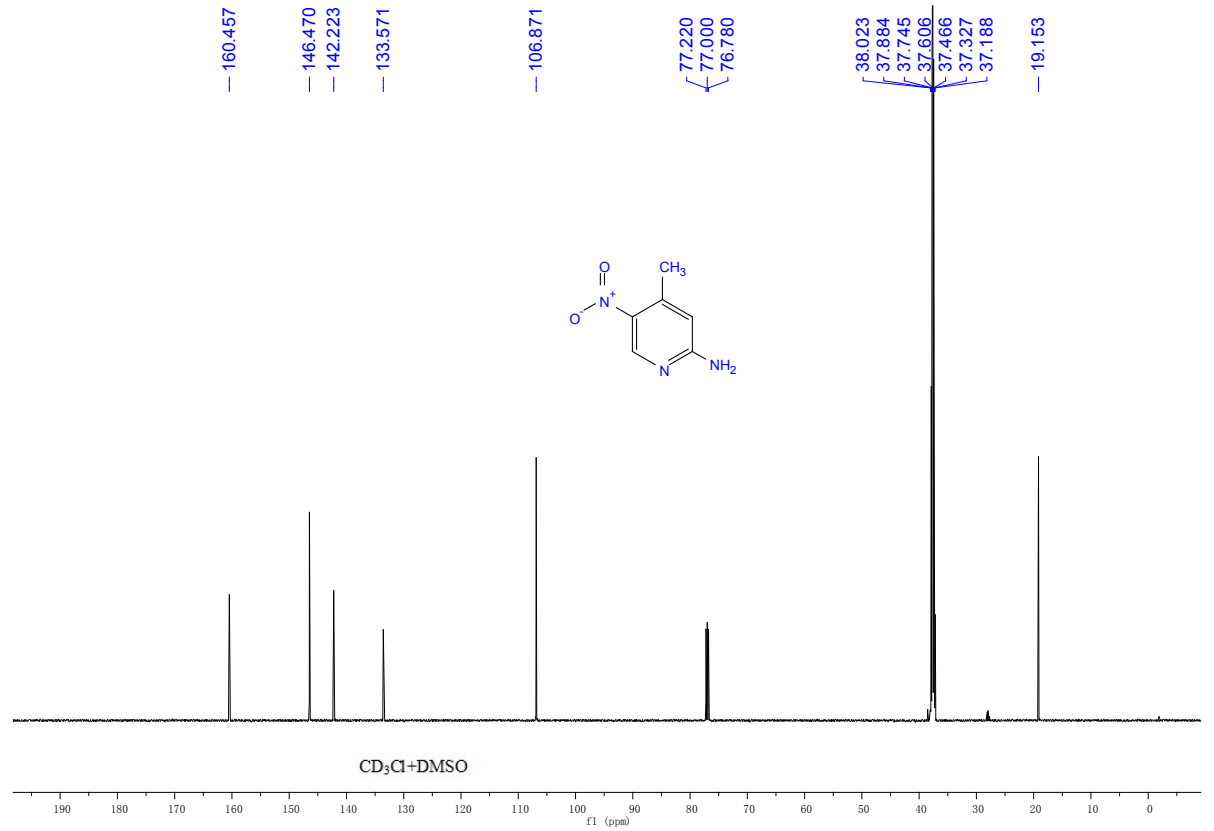

8.911
8.907
8.210
8.205
8.195
8.190
6.889
6.695
6.694
6.679
2.959
2.098
2.094
2.090
2.087
2.083
1.00
1.03
1.92
1.10
f1 (ppm)

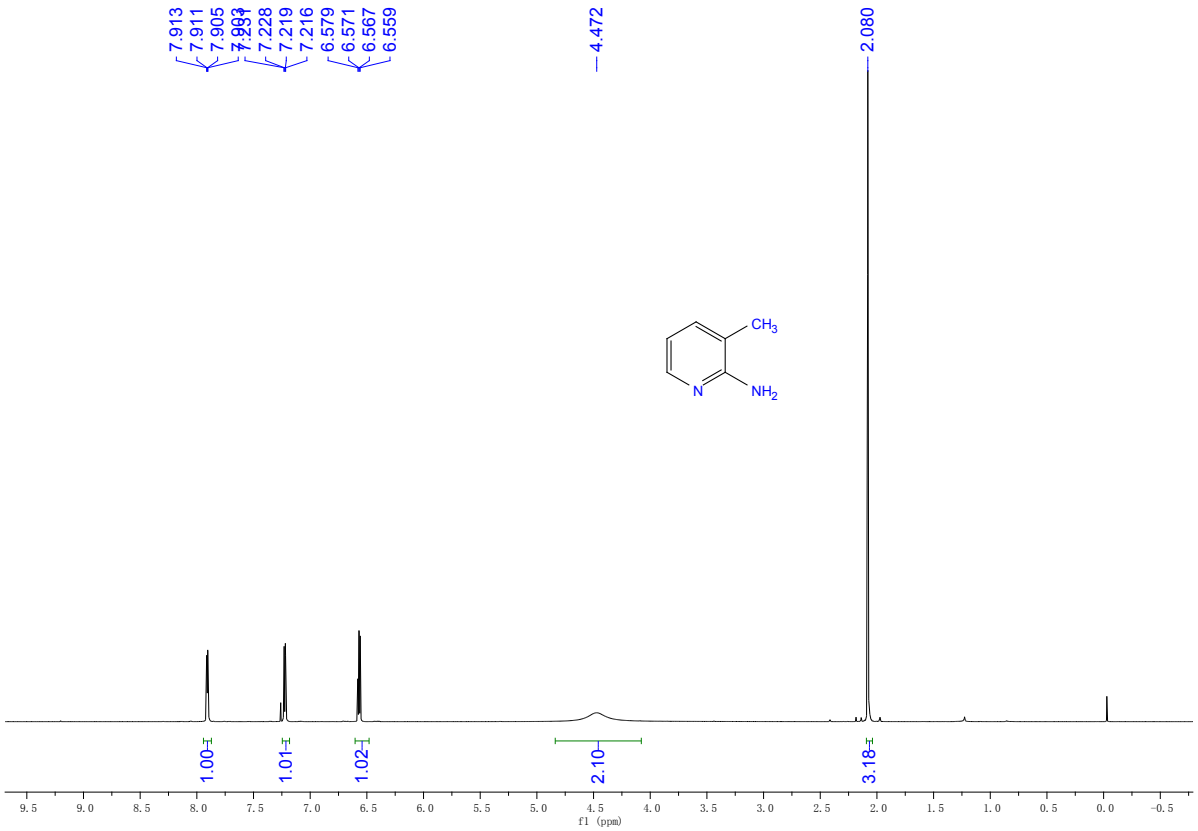

205.998
205.870
205.736
163.813
147.107
136.106
133.109
107.466
29.816
29.688
29.560
29.431
29.303
29.175
29.046
f1 (ppm)

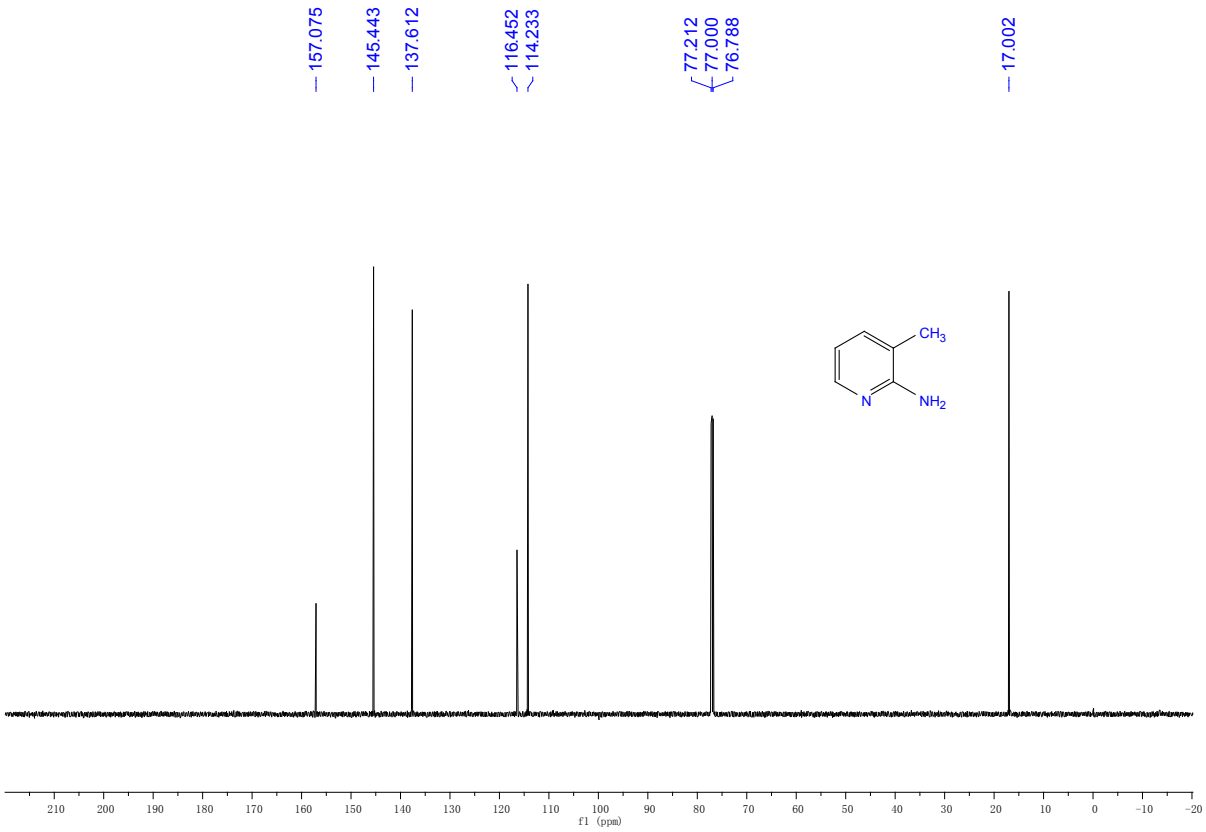

7.633
7.618
6.905
5.932
5.916
2.147
2.056
2.053
2.050
2.047
2.044
O
N+
O
H3C
N
NH2
0.97
2.00
0.99
2.96
f1 (ppm)

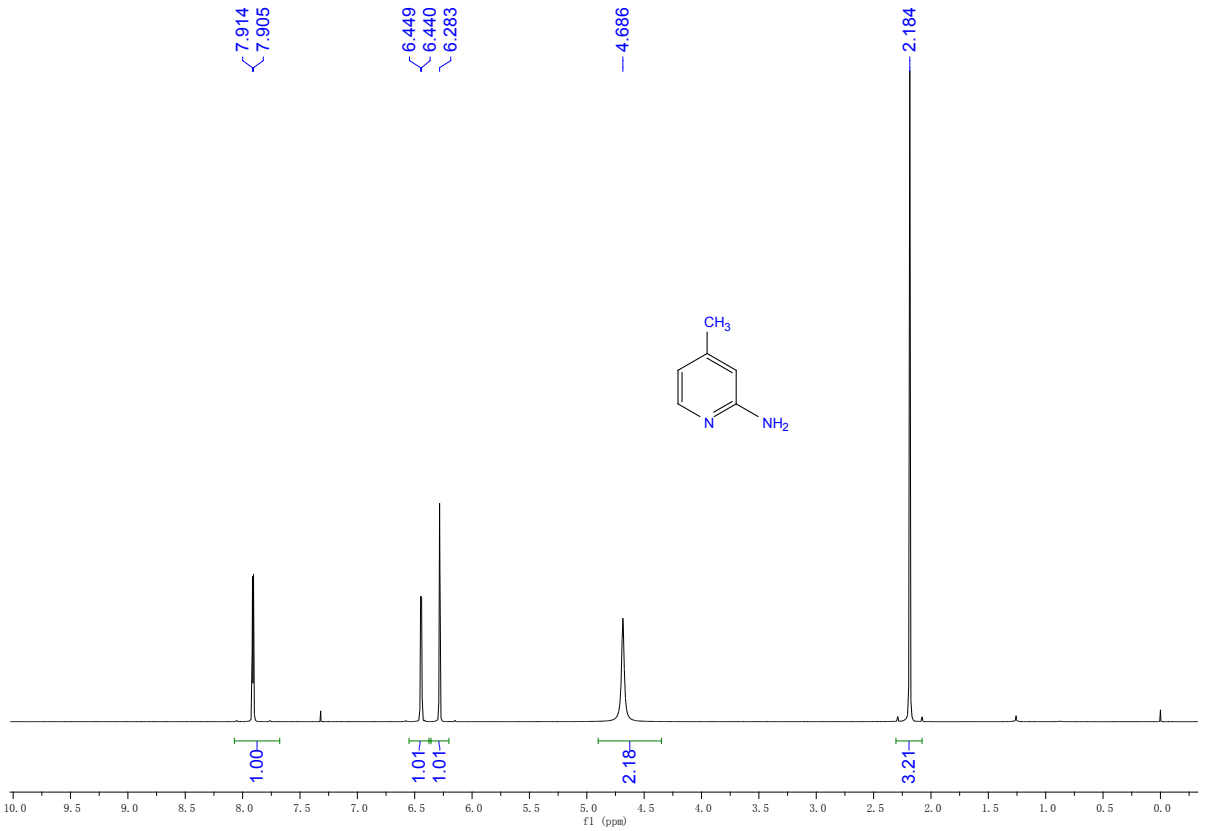

151.713
146.561
125.215
124.735
96.325
30.257
30.118
29.979
29.840
29.701
29.562
29.423
15.491
O
N+
O
H3C
N
NH2
f1 (ppm)

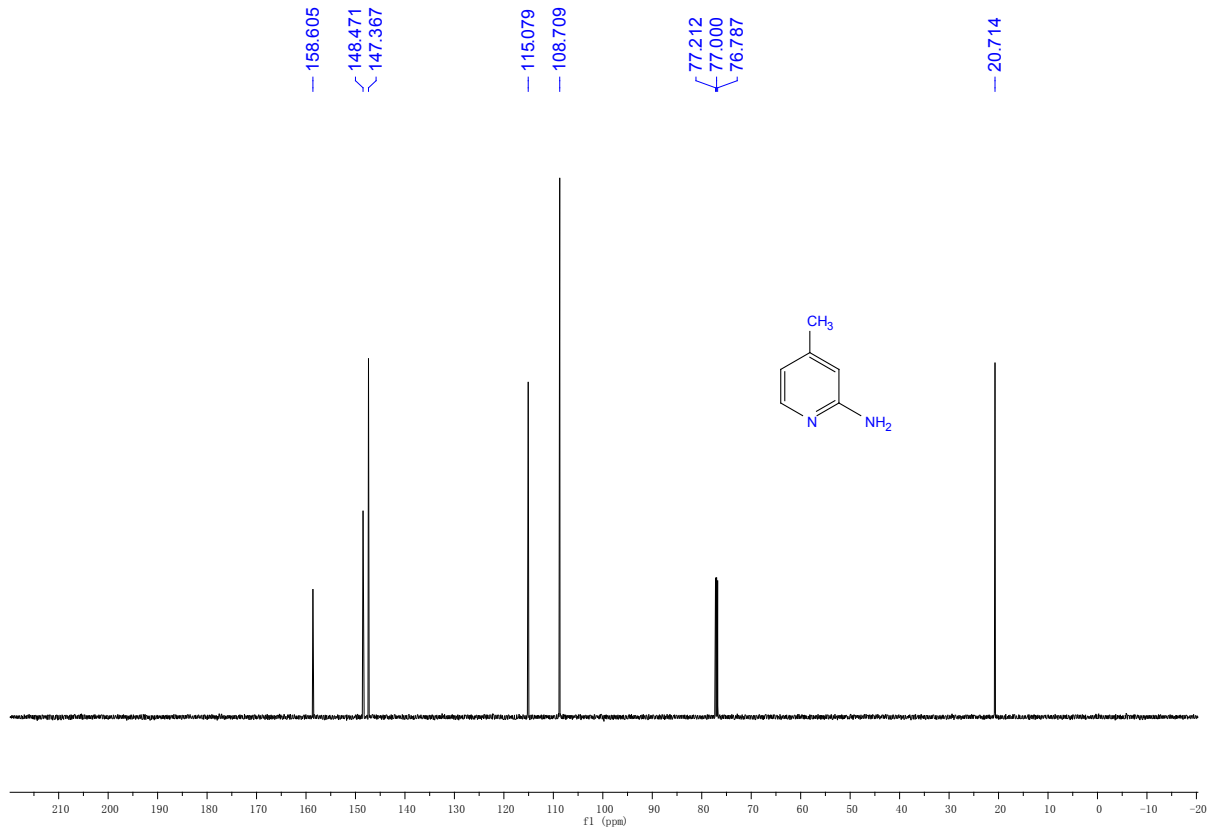

8.762
7.285
6.313
2.471
1.00
2.20
1.12
3.23
f1 (ppm)
CD3Cl+DMSO

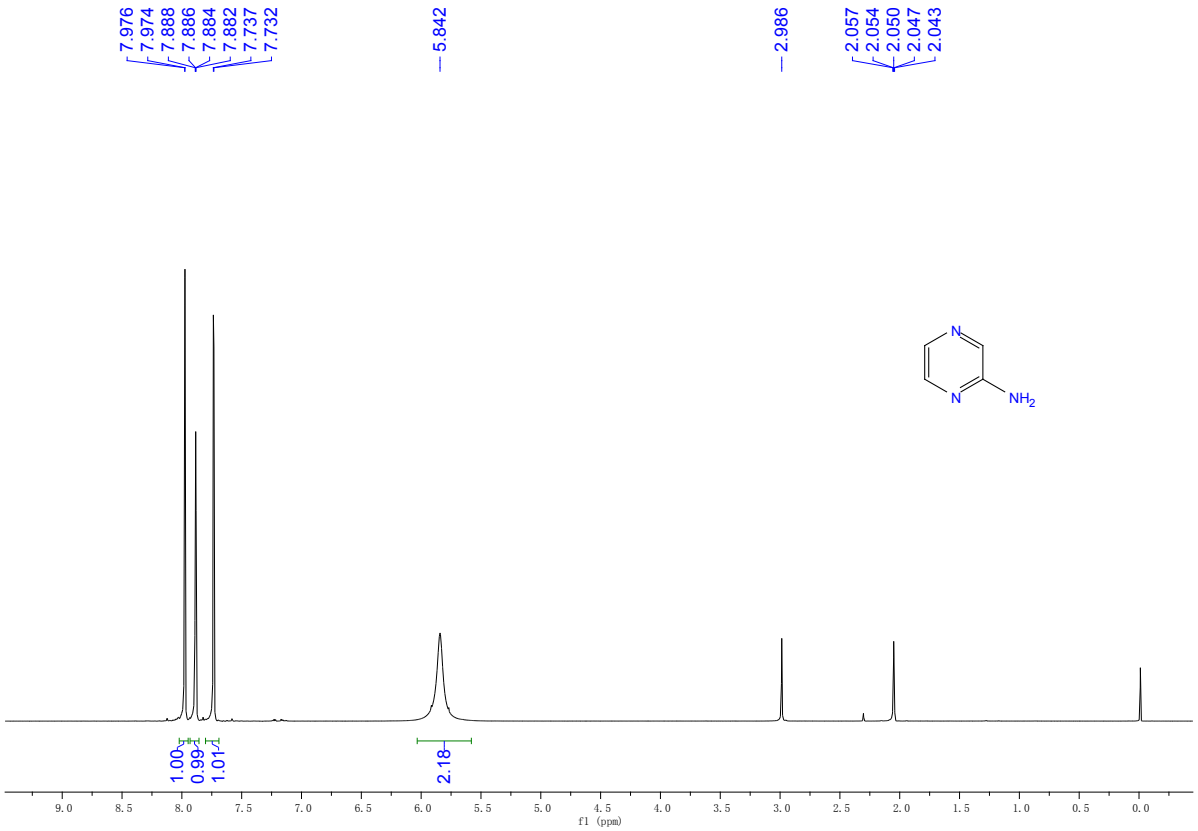

160.457
146.470
142.223
133.571
106.871
77.220
77.000
76.780
38.023
37.884
37.745
37.606
37.466
37.327
37.188
19.153
CD3Cl+DMSO
f1 (ppm)

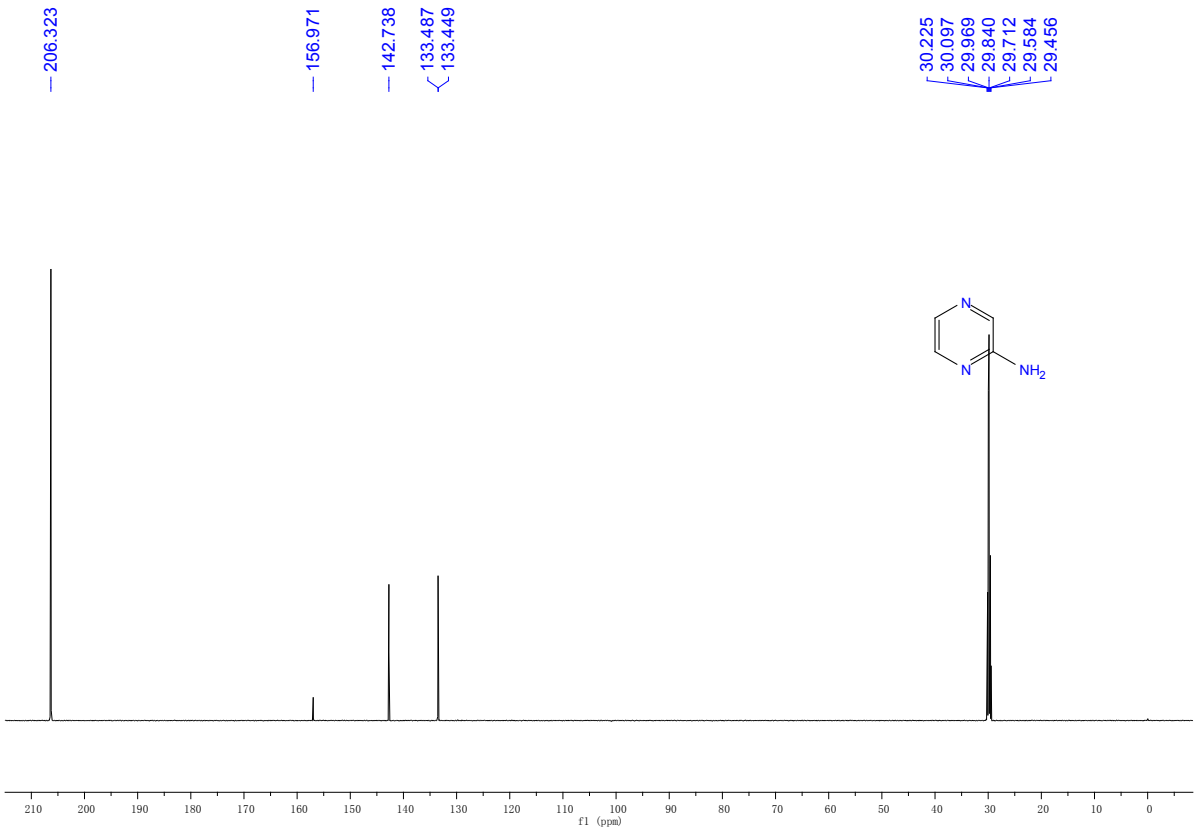

7.913
7.911
7.905
7.228
7.219
7.216
6.579
6.571
6.567
6.559
4.472
2.080
CH3
NH2
N
1.00
1.01
1.02
2.10
3.18
f1 (ppm)

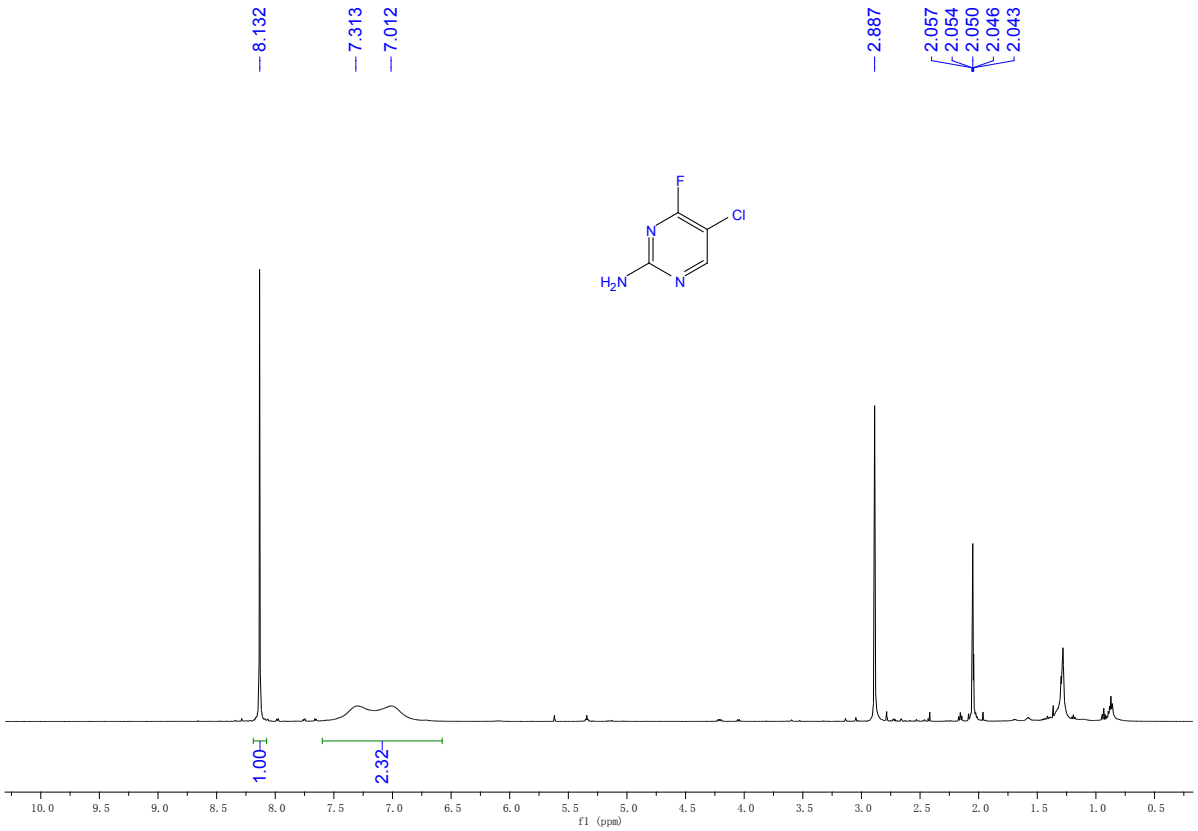

157.075
145.443
137.612
116.452
114.233
77.212
77.000
76.788
17.002
CH3
NH2
N
f1 (ppm)

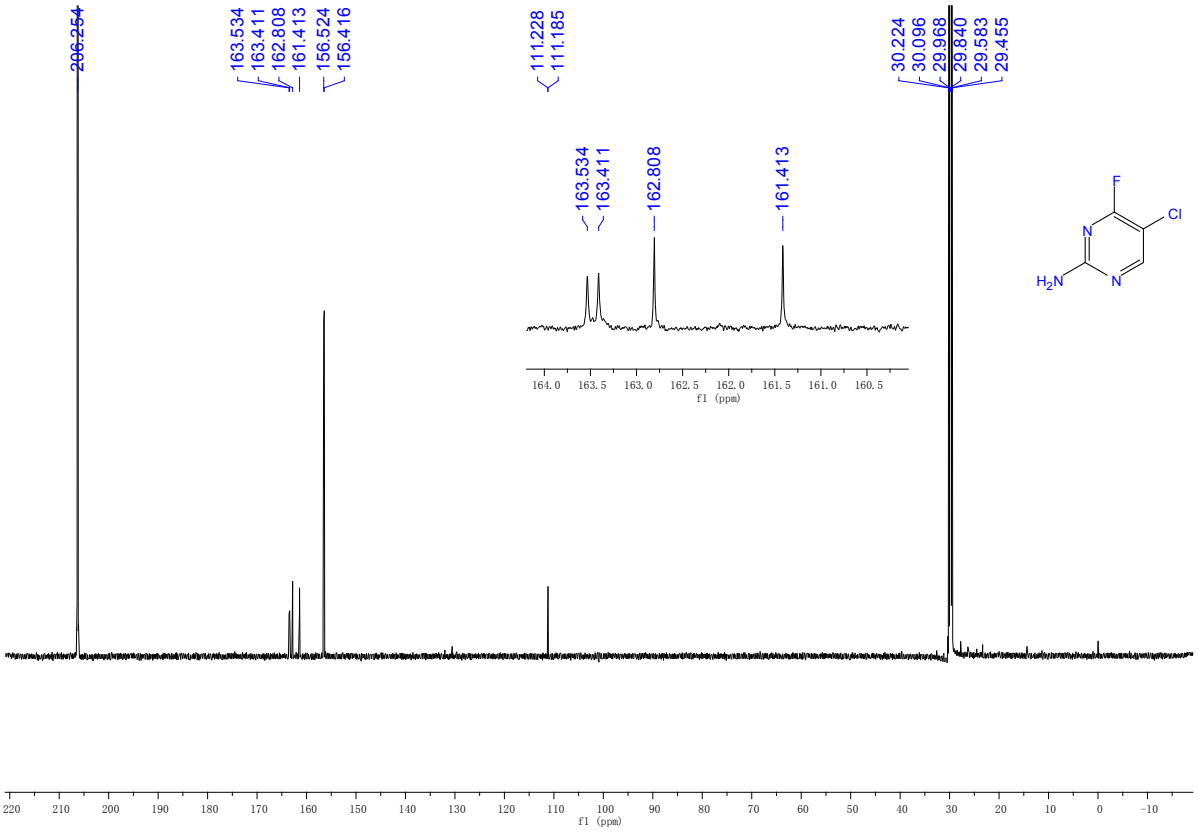

7.914
7.905
6.449
6.440
6.283
4.686
2.184
CH3
NH2
N
1.00
1.01
1.01
2.18
3.21
f1 (ppm)

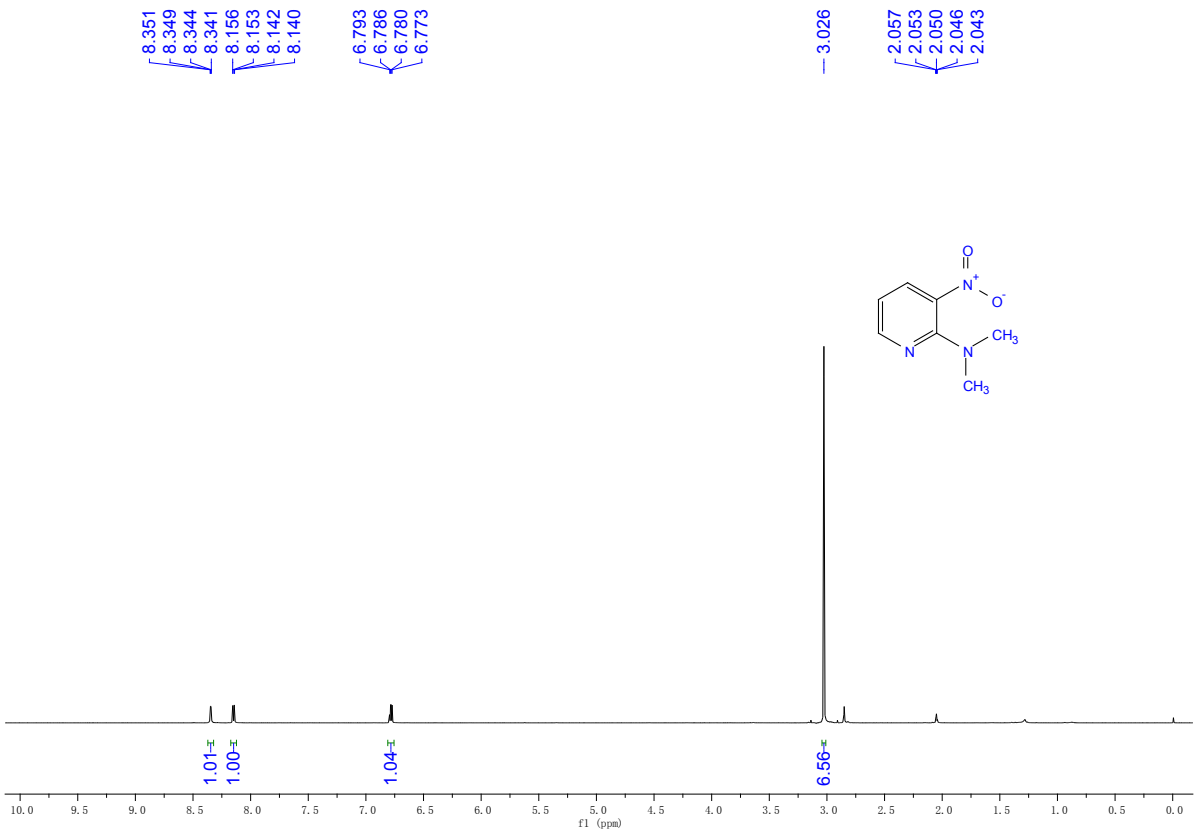

158.605
148.471
147.367
115.079
108.709
77.212
77.000
76.787
20.714
CH3
NH2
N
f1 (ppm)

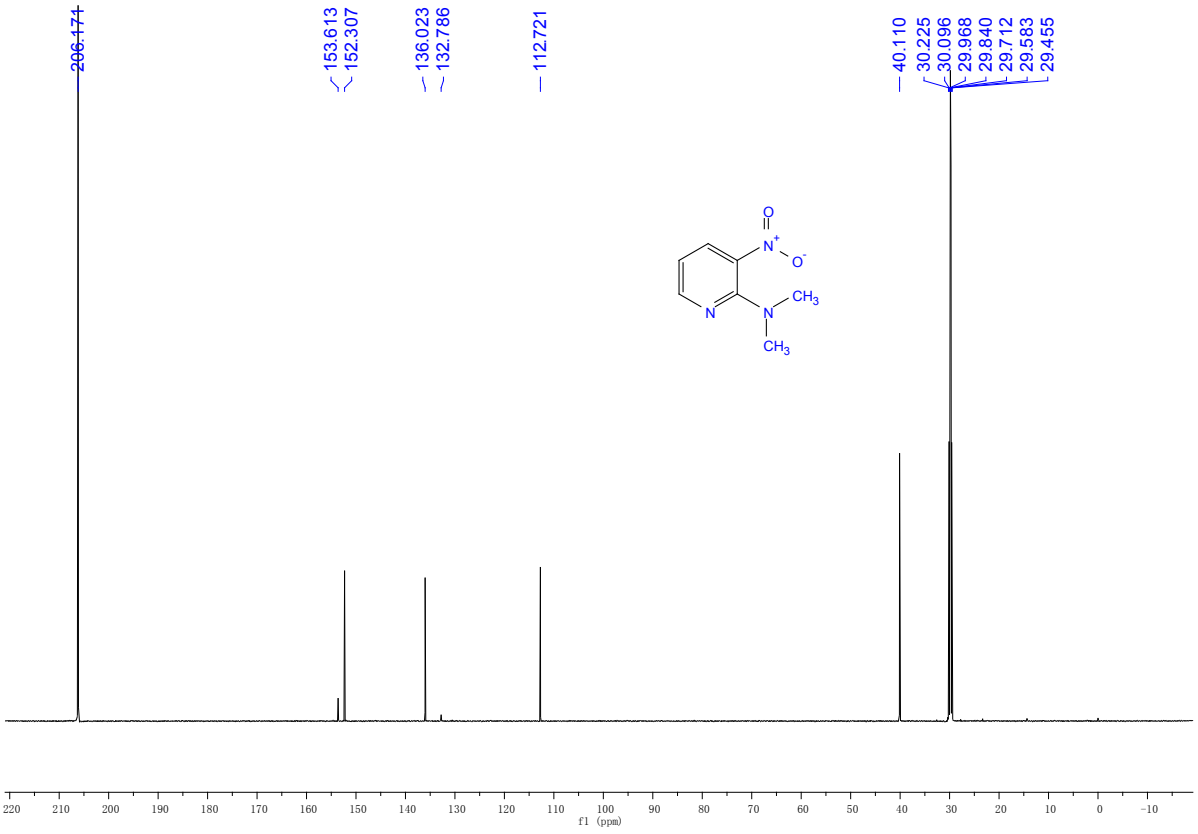

7.976
7.974
7.888
7.886
7.884
7.882
7.737
7.732
5.842
2.986
2.057
2.054
2.050
2.047
2.043
N
N
NH2
1.00
0.99
1.01
2.18
f1 (ppm)

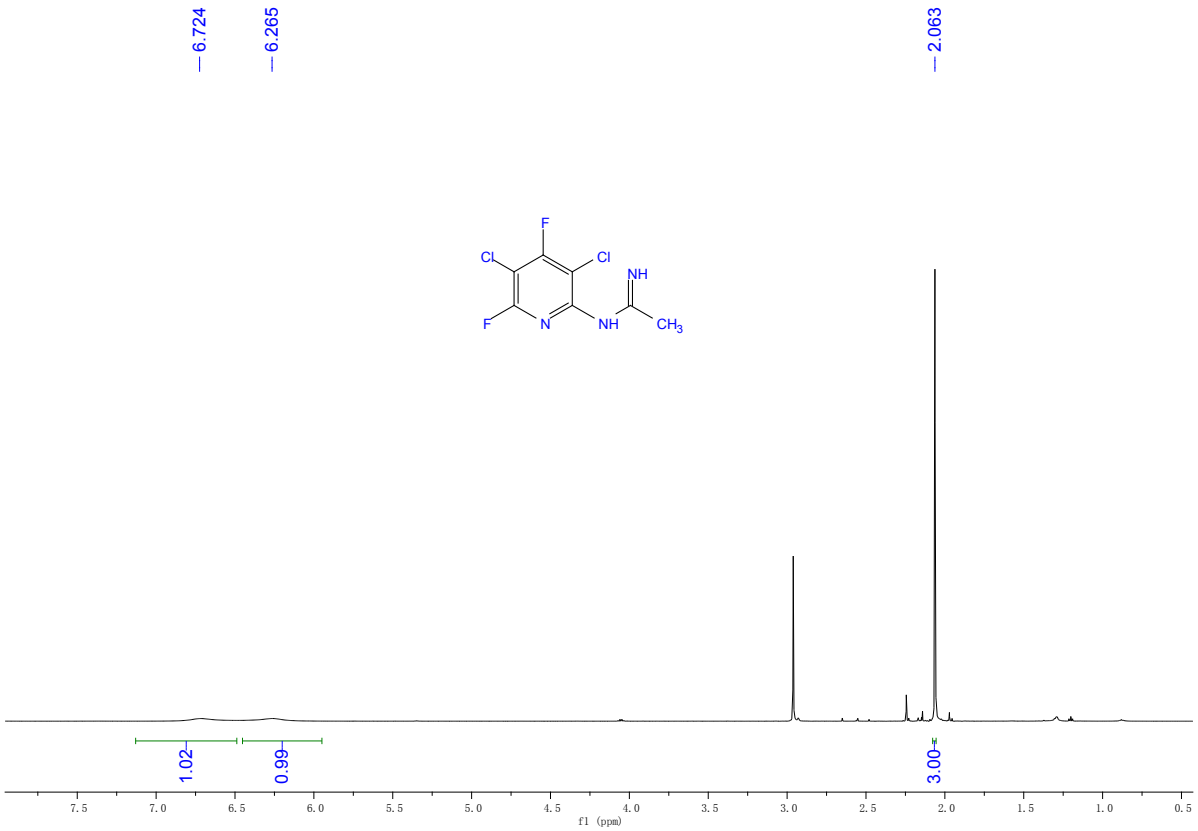

206.323
156.971
142.738
133.487
133.449
30.225
30.097
29.969
29.840
29.712
29.584
29.456
N
N
NH2
f1 (ppm)

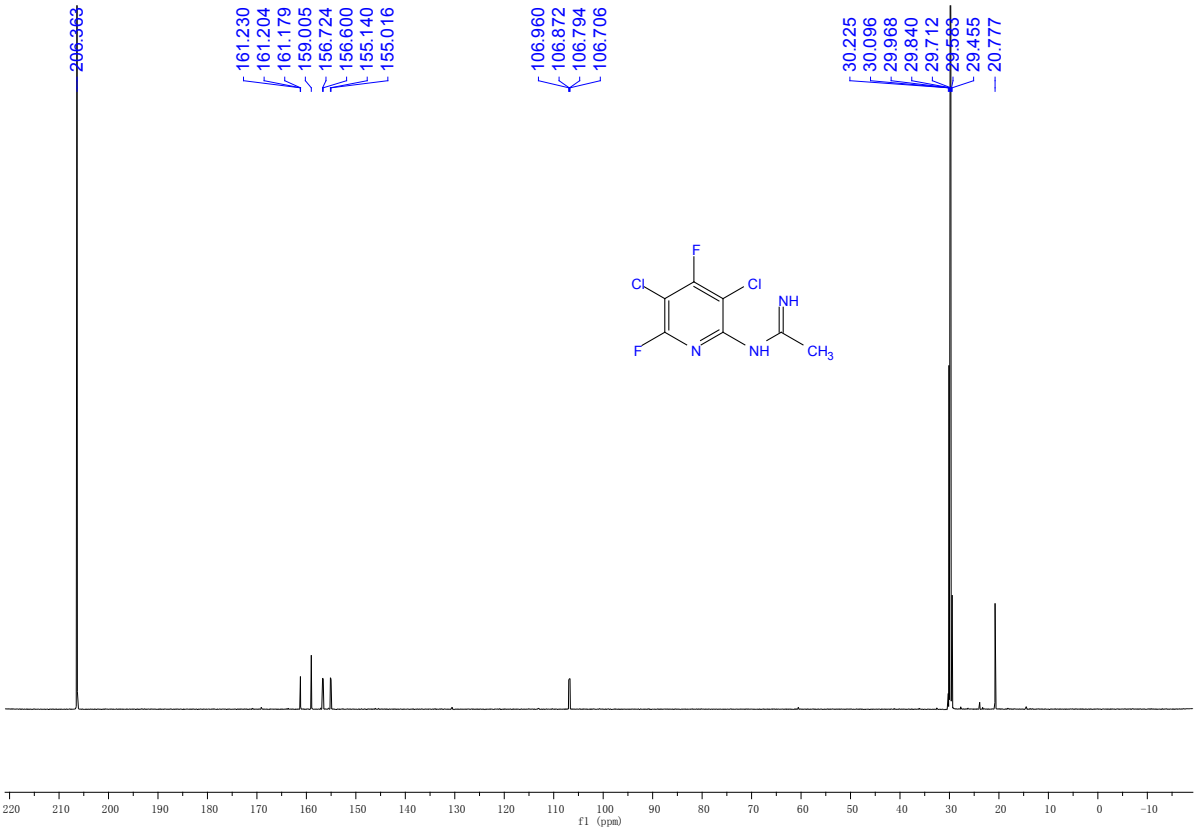

8.132
7.313
7.012
2.887
2.057
2.054
2.050
2.046
2.043
F
Cl
N
H2N
N
1.00
2.32
f1 (ppm)

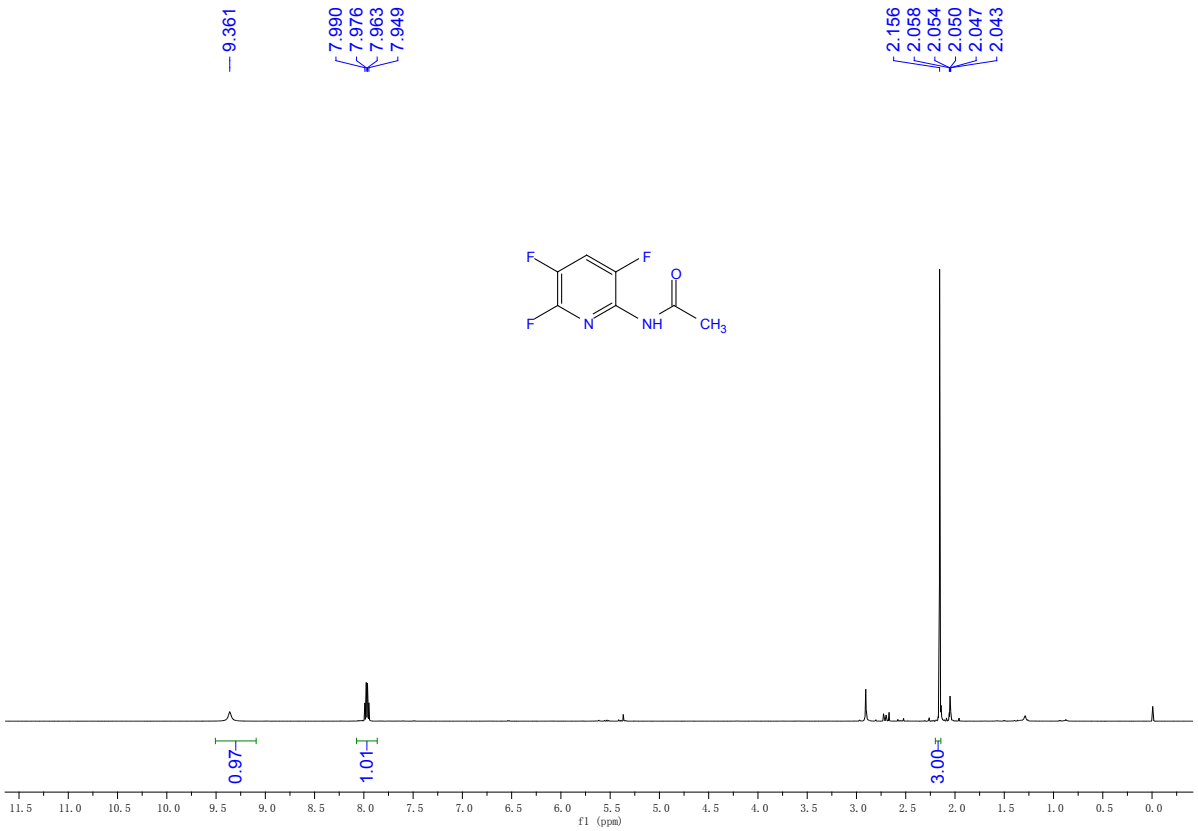

206.254
163.534
163.411
162.808
161.413
156.524
156.416
111.228
111.185
30.224
30.096
29.968
29.840
29.583
29.455
163.534
163.411
162.808
161.413
164.0
163.5
163.0
162.5
162.0
161.5
161.0
160.5
f1 (ppm)
F
Cl
N
H2N
N
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

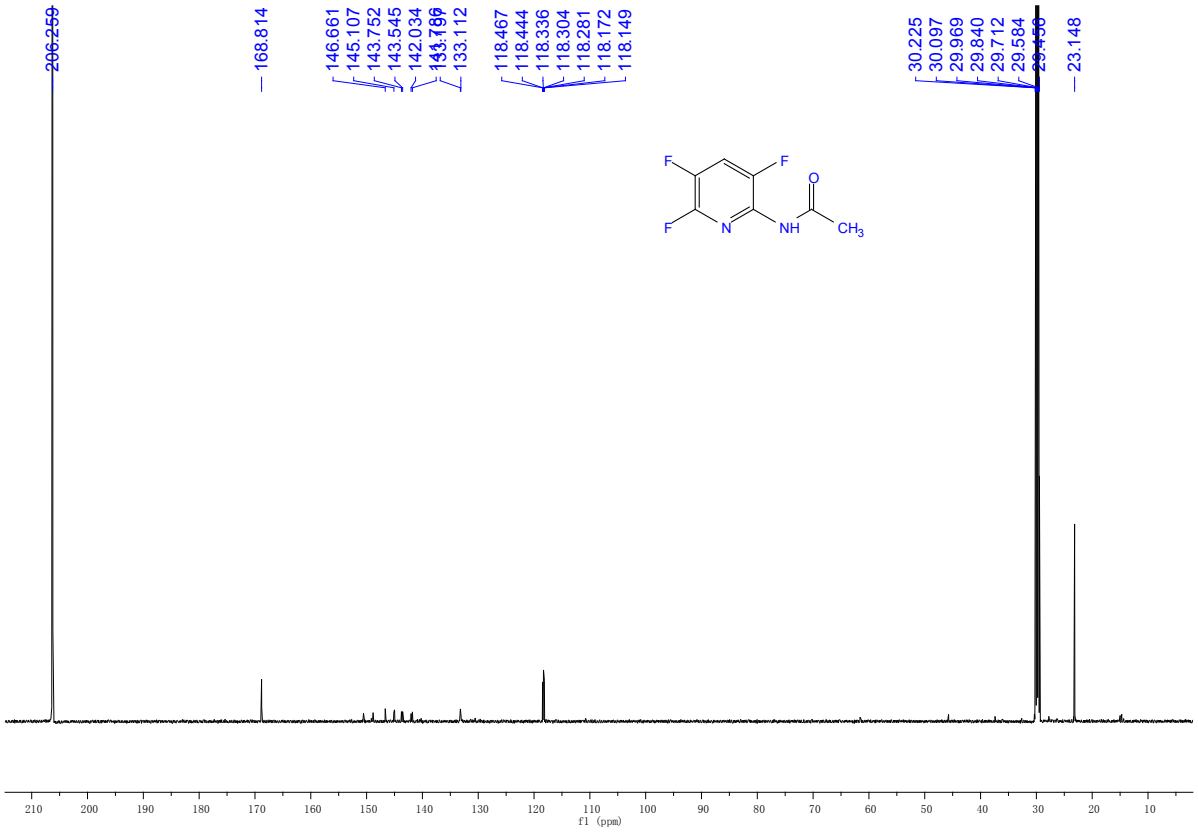

8.351
8.349
8.344
8.341
8.156
8.153
8.142
8.140
6.793
6.786
6.780
6.773
3.026
2.057
2.053
2.050
2.046
2.043
1.01
1.00
1.04
6.56
f1 (ppm)


206.171
153.613
152.307
136.023
132.786
112.721
40.110
30.225
30.096
29.968
29.840
29.712
29.583
29.455
f1 (ppm)


6.724
6.265
2.063
F
Cl
Cl
NH
F
N
NH
CH3
1.02
0.99
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


206.363
161.230
161.204
161.179
159.005
156.724
156.600
155.140
155.016
106.960
106.872
106.794
106.706
30.225
30.096
29.968
29.840
29.712
29.583
29.455
20.777
F
Cl
Cl
NH
F
N
NH
CH3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


9.361
7.990
7.976
7.963
7.949
2.156
2.058
2.054
2.050
2.047
2.043
F
F
O
F
N
NH
CH3
0.97
1.01
3.00
f1 (ppm)


206.259
168.814
146.661
145.107
143.752
143.545
142.034
133.112
118.467
118.444
118.336
118.304
118.281
118.172
118.149
30.225
30.097
29.969
29.840
29.712
29.584
23.148
F
F
O
F
N
NH
CH3
f1 (ppm)