Supporting Information

Silver-catalyzed intermolecular amination of fluoroarenes

Yu Wang,*[a] Chenlong Wei,[a] Ruyun Tang,[a] Haosheng Zhan,[a] Jing Lin,[a] Zhenhua Liu,[b] Weihua Tao[a] and Zhongxue Fang*[a]

[a]School of Chemistry and Environmental Engineering, Yancheng Teachers University, Yancheng City 224007, Jiangsu Province, People's Republic of China.
E-mail: fangzhongxue120@163.com
[b]College of Chemistry, Chemical Engineering and Materials Science, Shandong Normal University, Jinan 250014, People's Republic of China.

Contents

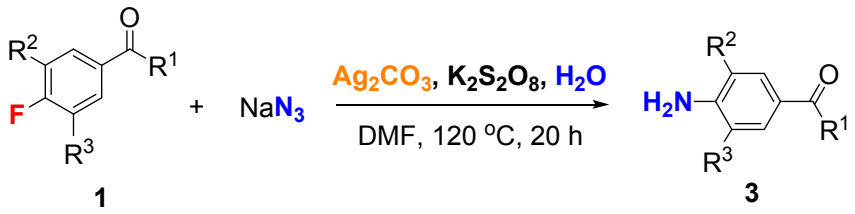
1. General information

Unless otherwise noted, all chemicals were purchased from commercial suppliers (Adamas, Aladdin, J&K etc) and used without further purification. **^{1}H NMR** and **^{13}CNMR** were recorded at ambient temperature on a 400 or 500 MHz spectrometer (100 or 125 MHz for ^{13}C NMR). NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.0 ppm) as the internal standard. The coupling constants J are given in Hertz. Mass spectra were recorded on BRUKER AutoflexIIISmartbeam MS-spectrometer. High resolution mass spectra (HRMS) were recorded on Bruck microTof by using ESI method. Column chromatography was performed using EM silica gel 60 (300−400 mesh).

2. General procedures and characterization data for all reaction products

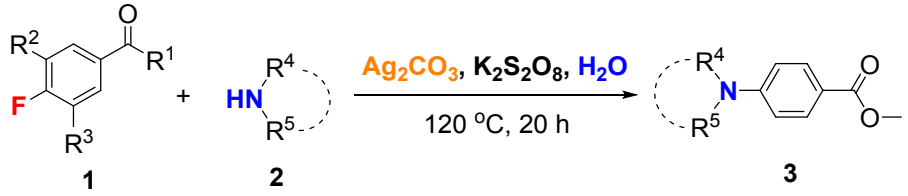
Synthesis of 4-acetylphenylsiluer

All experiments were carried out under dry, purified nitrogen using Schlenk-typeglassware. Liquids were handled by syringe techniques. Solvents were purified,distilled under nitrogen, and stored under nitrogen over molecular sieves.Diphenylzinc was prepared as described by Knochel[1].1.0 g (5.9 mmol) of finely ground $AgNO_3$ was added with stirring to a solutionof 3.33 g (11.0 mmol) of $(4\text{-}CH_3COPh)_2Zn$ in 40ml of diethyl ether at 0°C. A part-orange,part-white precipitate formed immediately. The orange colour disappeared after2 h stirring and the amount of white precipitate correspondingly increased. Afterdecantation of the green supermatant liquid, the solid was washed five times with25 ml of diethyl ether and dried in vacua.[2]



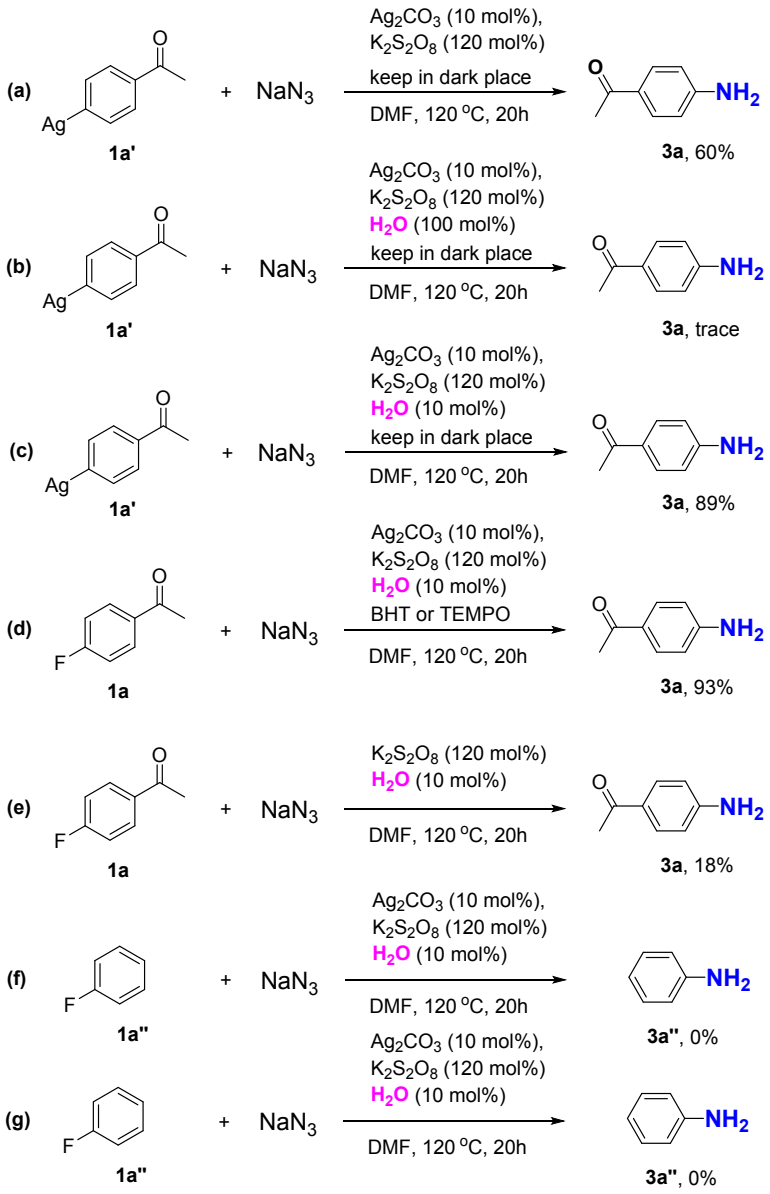
Scheme S1

The typical experimental procedure for synthesis of 4-aminoacetophenone **3a**: 4-fluoroacetophenone **1a** (0.4 mmol, 48.0μL), NaN_3 (1.2 mmol, 78.0 mg), Ag_2CO_3 (0.04 mmol, 11.0 mg), $K_2S_2O_8$ (0.48 mmol, 129.7 mg), H_2O (0.04 mmol, 7.2μL) and DMF (2 mL) were placed into a sealed dry tube (15 mL) with a magnetic stirrer bar. The reaction was heated under anair atmosphere at 120 °C for 20 h. After the reaction finished, the catalyst was separated by centrifugation and filtration to obtain the liquid phase. The pure product **3a** was obtained by flash column chromatography on silica gel by using petroleum ether (30-60 °C) and ethyl acetate as eluents (petroleum ether /ethyl acetate = 4/1).

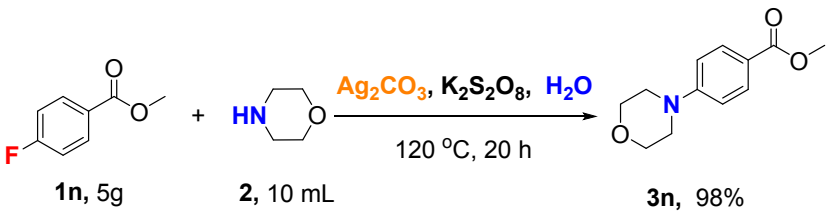


Scheme S2

The typical experimental procedure for synthesis of 4-aminoacetophenone **3m**: 4-fluoroacetophenone **1a** (0.4 mmol, 48.0μL), morpholine (0.5mL), Ag_2CO_3 (0.04 mmol, 11.0 mg), $K_2S_2O_8$ (0.48 mmol, 129.7 mg) and H_2O (0.04 mmol, 7.2 μL) were placed into a sealed dry tube (15 mL) with a magnetic stirrer bar. The reaction was heated under an air atmosphere at 120 °C for 20 h. After the reaction finished, the catalyst was separated by centrifugation and filtration to obtain the liquid phase. The pure product **3m** was obtained by flash column chromatography on silica gel by using petroleum ether (30-60 °C) and ethyl acetate as eluents (petroleum ether /ethyl acetate = 3/1).

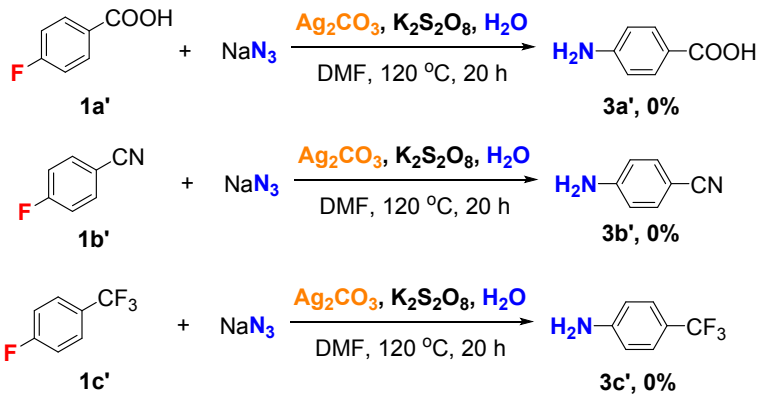


Scheme S3



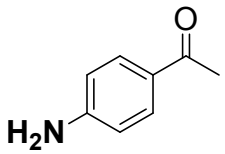
Scheme S4 Scale-up experiment.

Scale-up experiment: we examined the scalability of our catalytic system (Scheme S4). To demonstrate the utility of our environmentally benign, efficient and simple protocol, a gram scale reaction of **1n** with morpholine in the presence of Ag_2CO_3 (10 mol%), H_2O (10 mol%) and $K_2S_2O_8$ (120 mol%) was carried out. The gram-scale synthesis of the desired product **3n** was achieved successfully in 98% isolated yield.



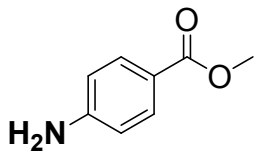
Scheme S5 Fluoroarenes with other electron withdrawing groups.

Analytical data



1-(4-aminophenyl)ethanone (3a)

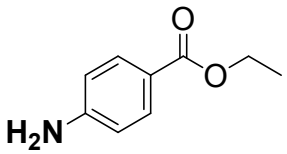
White Solid, m.p. 105-106°C; The pure product was obtained by flash column chromatography on silica gel by using petroleum ether (30-60 °C) and ethyl acetate as eluents (petroleum ether /ethyl acetate = 4/1); **^{1}H NMR** (500 MHz, DMSO) δ 7.67 (d, *J* = 9.0 Hz, 2H), 6.57 (d, *J* = 8.5 Hz, 2H), 6.02 (s, 2H), 2.38 (s, 3H); **^{13}C NMR** (125 MHz, DMSO) δ 194.9, 153.5, 130.5, 124.8, 112.4, 25.8; **HRMS** (ESI) Calcd. for $C_8H_{10}NO$ $[M+H]^+$, 136.0762. Found: m/z 136.0764. The crude product was purified by flash column chromatography to afford **3a** as a white solid in 96% yield (51.9 mg).



Methyl 4-aminobenzoate (3b)

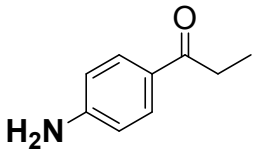
White Solid, m.p. 110-111°C; The pure product was obtained by flash column

chromatography on silica gel by using petroleum ether (30-60 °C) and ethyl acetate as eluents (petroleum ether /ethyl acetate = 4/1); **^{1}H NMR** (400 MHz, DMSO) δ 7.59 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 8.8 Hz, 2H), 5.90 (s, 2H), 3.67 (s, 3H); **^{13}C NMR** (100 MHz, DMSO) δ166.3, 153.4, 131.0, 115.7, 112.6, 51.1; **HRMS** (ESI) Calcd. for $C_8H_{10}NO_2$ $[M+H]^+$, 152.0712. Found: m/z 152.0713.



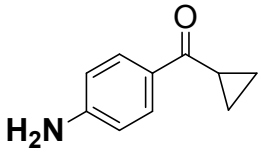
Ethyl 4-aminobenzoate (3c)

White Solid, m.p. 92-93^{o}C; The pure product was obtained by flash column chromatography on silica gel by using petroleum ether (30-60 °C) and ethyl acetate as eluents (petroleum ether /ethyl acetate = 4/1); **^{1}H NMR** (400 MHz, DMSO) δ 7.60 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 8.8 Hz, 2H), 5.89 (s, 2H), 4.17 (q, *J* = 7.2 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, DMSO) δ 166.3, 153.9, 131.4, 116.5, 113.1, 59.9, 14.8; **HRMS** (ESI) Calcd. for $C_9H_{12}NO_2$ $[M+H]^+$, 166.0868. Found: m/z 166.0869.



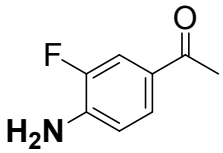
1-(4-aminophenyl)propan-1-one (3d)

White Solid, m.p. 136-137^{o}C; The pure product was obtained by flash column chromatography on silica gel by using petroleum ether (30-60 °C) and ethyl acetate as eluents (petroleum ether /ethyl acetate = 4/1); **^{1}H NMR** (400 MHz, DMSO) δ 7.61 (d, *J* = 8.8 Hz, 2H), 6.49 (d, *J* = 8.8 Hz, 2H), 5.90 (s, 2H), 2.75 (q, *J* = 7.2 Hz, 2H), 0.96 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, DMSO) δ 197.6, 153.4, 130.1, 124.4, 112.5, 30.1, 8.73; **HRMS** (ESI) Calcd. for $C_9H_{12}NO$ $[M+H]^+$, 150.0919. Found: m/z 150.0920.



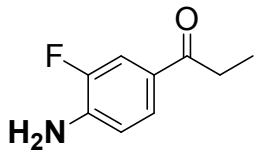
(4-aminophenyl)(cyclopropyl)methanone (3e)

White Solid, m.p. 115-116°C; The pure product was obtained by flash column chromatography on silica gel by using petroleum ether (30-60 °C) and ethyl acetate as eluents (petroleum ether /ethyl acetate = 4/1); **^{1}H NMR** (400 MHz, DMSO) δ 7.72 (d, *J* = 8.4 Hz, 2H), 6.53 (d, *J* = 8.4 Hz, 2H), 5.95 (s, 2H), 2.70-2.55 (m, 1H), 0.87-0.73 (m, 4H); **^{13}C NMR** (100 MHz, DMSO) δ 196.5, 153.5, 130.2, 125.1, 112.5, 15.2, 9.9; **HRMS** (ESI) Calcd. for $C_{10}H_{12}NO$ $[M+H]^+$, 162.0919. Found: m/z 162.0923.



1-(4-amino-3-fluorophenyl)ethanone (3f)

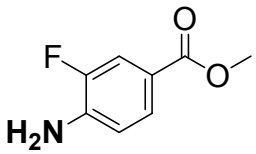
White Solid, m.p. 86-87°C; The pure product was obtained by flash column chromatography on silica gel by using petroleum ether (30-60 °C) and ethyl acetate as eluents (petroleum ether /ethyl acetate = 4/1); **^{1}H NMR** (400 MHz, DMSO) δ 7.52-7.43 (m, 2H), 6.71 (t, *J* = 9.2 Hz, 1H), 6.04 (s, 2H), 2.35 (s, 3H); **^{13}C NMR** (100 MHz, DMSO) δ 194.7, 150.5 (d, *J* = 236.8 Hz), 141.9 (d, *J* = 13.1 Hz), 136.4 (d, *J* = 1.9 Hz), 124.9 (d, *J* = 4.7 Hz), 114.7 (d, *J* = 18.1 Hz), 114.4 (d, *J* = 4.9 Hz), 25.9; **^{19}F NMR**(376.5 MHz, $CDCl_3$) δ 135.88; **HRMS** (ESI) Calcd. for C_8H_9FNO $[M+H]^+$, 154.0668. Found: m/z 154.0669.



1-(4-amino-3-fluorophenyl)propan-1-one (3g)

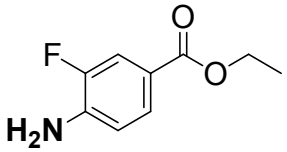
White Solid, m.p. 92-93°C; The pure product was obtained by flash column chromatography on silica gel by using petroleum ether (30-60 °C) and ethyl acetate as

eluents (petroleum ether /ethyl acetate = 4/1); **^{1}H NMR** (400 MHz, DMSO) δ 7.59-7.43 (m, 2H), 6.72 (t, *J* = 9.2 Hz, 1H), 6.00 (s, 2H), 2.81 (q, *J* = 7.2 Hz, 2H), 0.98 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, DMSO) δ 197.8, 151.0 (d, *J* = 236.5 Hz), 142.1 (d, *J* = 13.2 Hz), 126.4 (d, *J* = 2.1 Hz), 125.0 (d, *J* = 4.5 Hz), 114.9, 114.8 (d, *J* = 14.1 Hz), 30.7, 8.98; **^{19}F NMR**(376.5 MHz, $CDCl_3$) δ 135.855; **HRMS** (ESI) Calcd. for $C_9H_{11}FNO$ $[M+H]^+$, 168.0825. Found: m/z 168.0827.



Methyl 4-amino-3-fluorobenzoate (3h)

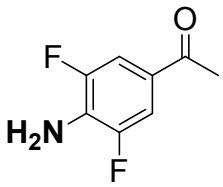
White Solid, m.p. 76-77^{o}C; The pure product was obtained by flash column chromatography on silica gel by using petroleum ether (30-60 °C) and ethyl acetate as eluents (petroleum ether /ethyl acetate = 4/1); **^{1}H NMR** (400 MHz, DMSO) δ 7.53-7.36 (m, 2H), 6.73 (t, *J* = 8.4 Hz, 1H), 6.01 (s, 2H), 3.71 (s, 3H); **^{13}C NMR** (100 MHz, DMSO) δ 165.6 (d, *J* = 2.8 Hz), 150.3 (d, *J* = 236.2 Hz), 141.7 (d, *J* = 12.8 Hz), 126.8 (d, *J* = 2.1 Hz), 116.0 (d, *J* = 6.0 Hz), 115.7 (d, *J* = 19.2 Hz), 114.7 (d, *J* = 4.9 Hz), 51.5; **^{19}F NMR**(376.5 MHz, $CDCl_3$) δ 136.015; **HRMS** (ESI) Calcd. for $C_8H_9FNO_2$ $[M+H]^+$, 170.0617. Found: m/z 170.0620.



Ethyl 4-amino-3-fluorobenzoate (3i)

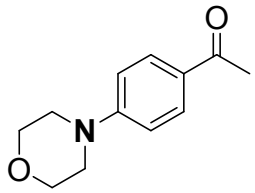
White Solid, m.p. 68-69^{o}C; The pure product was obtained by flash column chromatography on silica gel by using petroleum ether (30-60 °C) and ethyl acetate as eluents (petroleum ether /ethyl acetate = 4/1); **^{1}H NMR** (400 MHz, DMSO) δ 7.55-7.41 (m, 2H), 6.76 (t, *J* = 8.8 Hz, 1H), 6.02 (s, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, DMSO) δ165.1 (d, *J* = 2.7 Hz), 150.3 (d, *J* = 236.1 Hz), 141.7 (d, *J* = 12.8 Hz), 126.7 (d, *J* = 2.2 Hz), 116.3 (d, *J* = 6.0 Hz), 115.6 (d, *J* = 19.2 Hz), 114.7 (d, *J* = 5.0 Hz), 59.9, 14.2; **^{19}F NMR**(376.5 MHz, $CDCl_3$) δ 136.011; **HRMS** (ESI) Calcd. for $C_9H_{11}FNO_2$ $[M+H]^+$,

184.0774. Found: m/z 184.0774.



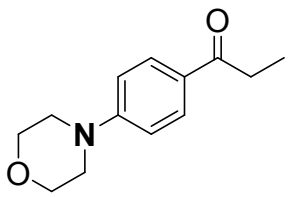
1-(4-amino-3,5-difluorophenyl)ethanone (3j)

White Solid, m.p. 85-86°C; The pure product was obtained by flash column chromatography on silica gel by using petroleum ether (30-60 °C) and ethyl acetate as eluents (petroleum ether /ethyl acetate = 4/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52-7.41 (m, 2H), 4.25 (s, 2H), 2.50 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ194.8, 151.9 (dd, *J* = 7.7, 240.1 Hz), 129.2 (t, *J* = 16.1 Hz), 125.7 (t, *J* = 6.5 Hz), 111.5 (m), 25.9; **^{19}F NMR**(376.5 MHz, $CDCl_3$) δ 136.281; **HRMS** (ESI) Calcd. for $C_8H_8F_2NO$ $[M+H]^+$, 172.0574 . Found: m/z 172.0575.



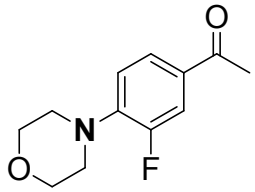
1-(4-morpholinophenyl)ethan-1-one (3k)

White solid, m.p. 65-66 °C; The pure product was obtained by flash column chromatography on silica gel by using petroleum ether (30-60 °C) and ethyl acetate as eluents (petroleum ether /ethyl acetate = 3/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.90 (d, *J* = 9.2 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.86 (t, *J* = 4.8 Hz, 4H), 3.30 (t, *J* = 5.2 Hz, 4H), 2.53 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.5, 154.1, 130.3, 128.1, 113.2, 66.5, 47.4, 26.1; **HRMS** (ESI) Calcd. for $C_{12}H_{16}NO_2$ $[M+H]^+$, 206.1181. Found: m/z 206.1182.



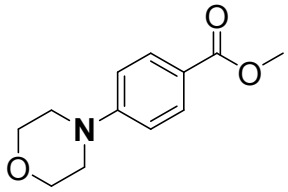
1-(4-morpholinophenyl)propan-1-one (3l)

White Solid, m.p. 83-84 ^{o}C; The pure product was obtained by flash column chromatography on silica gel by using petroleum ether (30-60 °C) and ethyl acetate as eluents (petroleum ether /ethyl acetate = 3/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.91 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 9.2 Hz, 2H), 3.85 (t, *J* = 5.2 Hz, 4H), 3.29 (t, *J* = 5.2 Hz, 4H), 2.93 (q, *J* = 7.2, 14.4 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.2, 154.1, 129.9, 127.8, 113.3, 66.5, 47.5, 31.2, 8.6; **HRMS** (ESI) Calcd. for $C_{13}H_{18}NO_2$ $[M+H]^+$, 220.1338. Found: m/z 220.1339.



1-(3-fluoro-4-morpholinophenyl)ethan-1-one (3m)

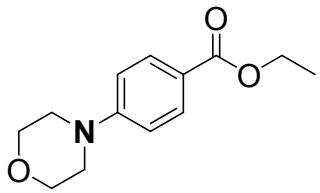
White Solid, m.p. 92-93 ^{o}C; The pure product was obtained by flash column chromatography on silica gel by using petroleum ether (30-60 °C) and ethyl acetate as eluents (petroleum ether /ethyl acetate = 3/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.71-7.60 (m, 2H), 6.92 (t, *J* = 8.4 Hz, 1H), 3.87 (t, *J* = 4.4 Hz, 4H), 3.21 (t, *J* = 4.8 Hz, 4H), 2.54 (s, 3H); **^{13}C NMR** (100 MHz,$CDCl_3$) δ195.8 (d, *J* = 6.8 Hz), 155.6, 153.2, 144.0 (d, *J* = 32.4 Hz), 131.0 (d, *J*= 24.4 Hz), 125.5 (d, *J* = 11.6 Hz), 117.3 (d, *J* = 13.2 Hz), 116.1 (d, *J* = 87.2 Hz), 66.7, 50.0 (d, *J* = 18.0 Hz), 26.2;**^{19}F NMR**(376.5 MHz,$CDCl_3$) δ 131.386; **HRMS** (ESI) Calcd. for $C_{12}H_{15}FNO_2$ $[M+H]^+$, 224.1087. Found: m/z 224.1088.



methyl 4-morpholinobenzoate (3n)

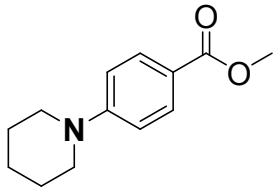
White Solid, m.p. 154-155^{o}C; The pure product was obtained by flash column chromatography on silica gel by using petroleum ether (30-60 °C) and ethyl acetate as

eluents (petroleum ether /ethyl acetate = 3/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.96-7.90 (m, 2H), 6.88-6.84 (m, 2H), 3.89-3.83 (m, 7H), 3.28 (t, *J* = 4.8 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ167.0, 154.1, 131.2, 120.3, 113.4, 66.5, 51.6, 47.7; **HRMS** (ESI) Calcd. for $C_{12}H_{16}NO_3$ $[M+H]^+$, 222.1130. Found: m/z 222.1133.



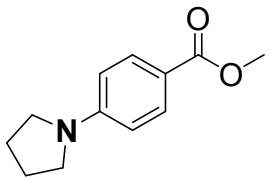
ethyl 4-morpholinobenzoate(3o)

White Solid, m.p. 83-84 °C;The pure product was obtained by flash column chromatography on silica gel by using petroleum ether (30-60 °C) and ethyl acetate as eluents (petroleum ether /ethyl acetate = 3/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.95 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 4.33 (q, *J* = 7.2, 14.4 Hz, 2H), 3.84 (t, *J* = 5.2 Hz, 4H), 3.26 (t, *J* = 4.8 Hz, 4H), 1.38 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.4, 154.0, 131.0, 120.5, 113.3, 66.4, 60.2, 47.5, 14.3; **HRMS** (ESI) Calcd. for $C_{13}H_{18}NO_3$ $[M+H]^+$, 236.1287. Found: m/z 236.1289.



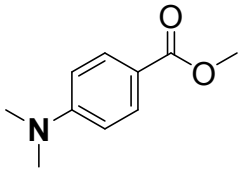
methyl 4-(piperidin-1-yl)benzoate (3p)

White Solid, m.p. 94-95 °C; The pure product was obtained by flash column chromatography on silica gel by using petroleum ether (30-60 °C) and ethyl acetate as eluents (petroleum ether /ethyl acetate = 3/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.89 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 3.34-3.22 (m, 4H), 1.69-1.55 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.9, 154.2, 131.0, 118.3, 113.3, 51.3, 48.5, 25.1, 24.1; **HRMS** (ESI) Calcd. for $C_{13}H_{18}NO_2$ $[M+H]^+$, 220.1338. Found: m/z 220.1339.



methyl 4-(pyrrolidin-1-yl)benzoate (3q)

White Solid, m.p.67-68 ^{o}C; The pure product was obtained by flash column chromatography on silica gel by using petroleum ether (30-60 °C) and ethyl acetate as eluents (petroleum ether /ethyl acetate = 3/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.89 (d, *J* = 8.8 Hz, 2H), 6.49 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 3.32 (t, *J* = 6.8 Hz, 4H), 2.05-1.95 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.5, 150.7, 131.2, 116.0, 110.5, 51.3, 47.3, 25.3; **HRMS** (ESI) Calcd. for $C_{12}H_{16}NO_2$ $[M+H]^+$, 206.1181. Found: m/z 206.1182.



methyl 4-(dimethylamino)benzoate(3r)

White Solid, m.p. 237-238 ^{o}C; The pure product was obtained by flash column chromatography on silica gel by using petroleum ether (30-60 °C) and ethyl acetate as eluents (petroleum ether /ethyl acetate = 4/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.91 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.03 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.4, 153.2, 131.2, 116.8, 110.6, 51.4, 40.0; **HRMS** (ESI) Calcd. for $C_{10}H_{14}NO_2$ $[M+H]^+$, 180.1025. Found: m/z 180.1027.

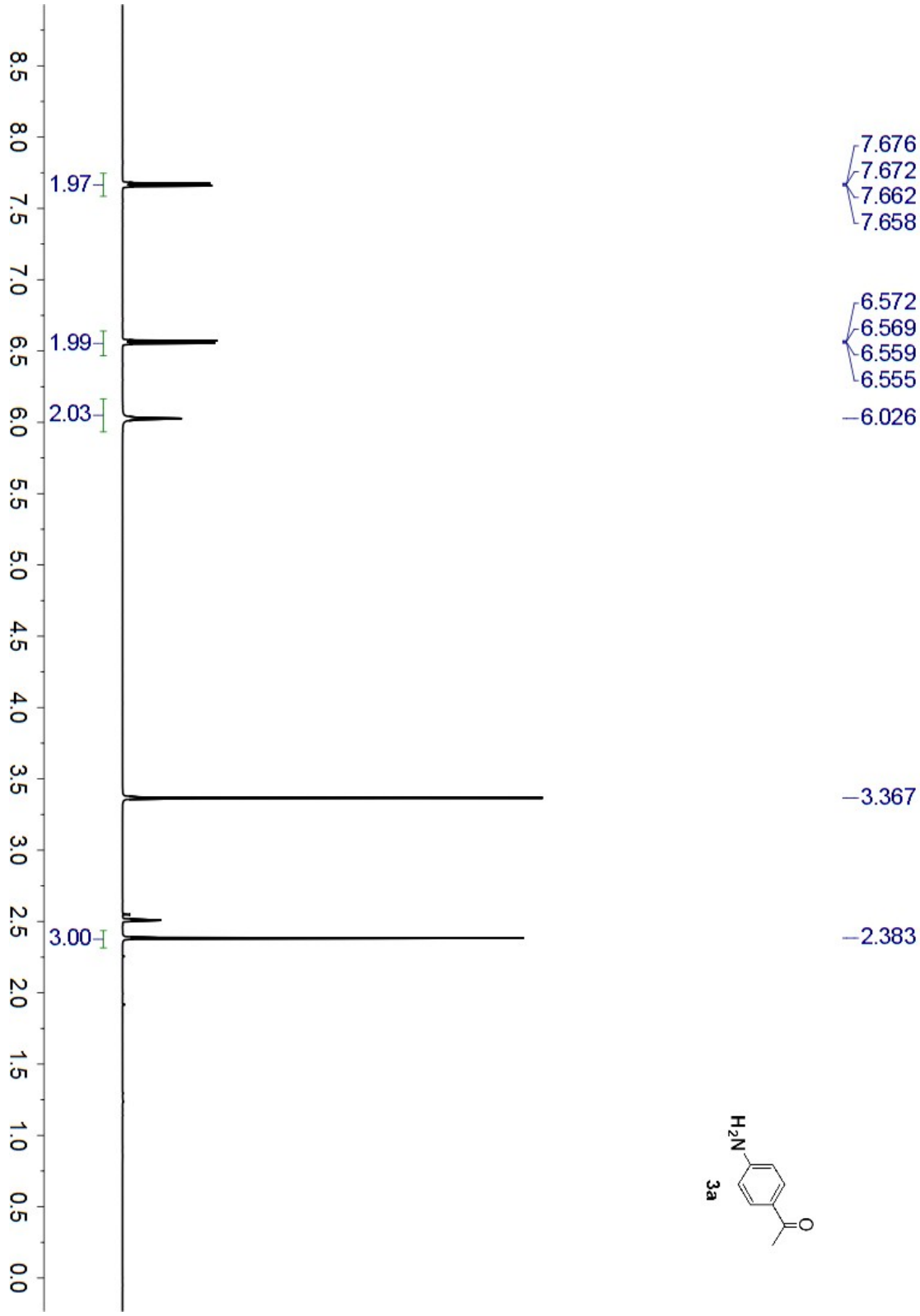
---

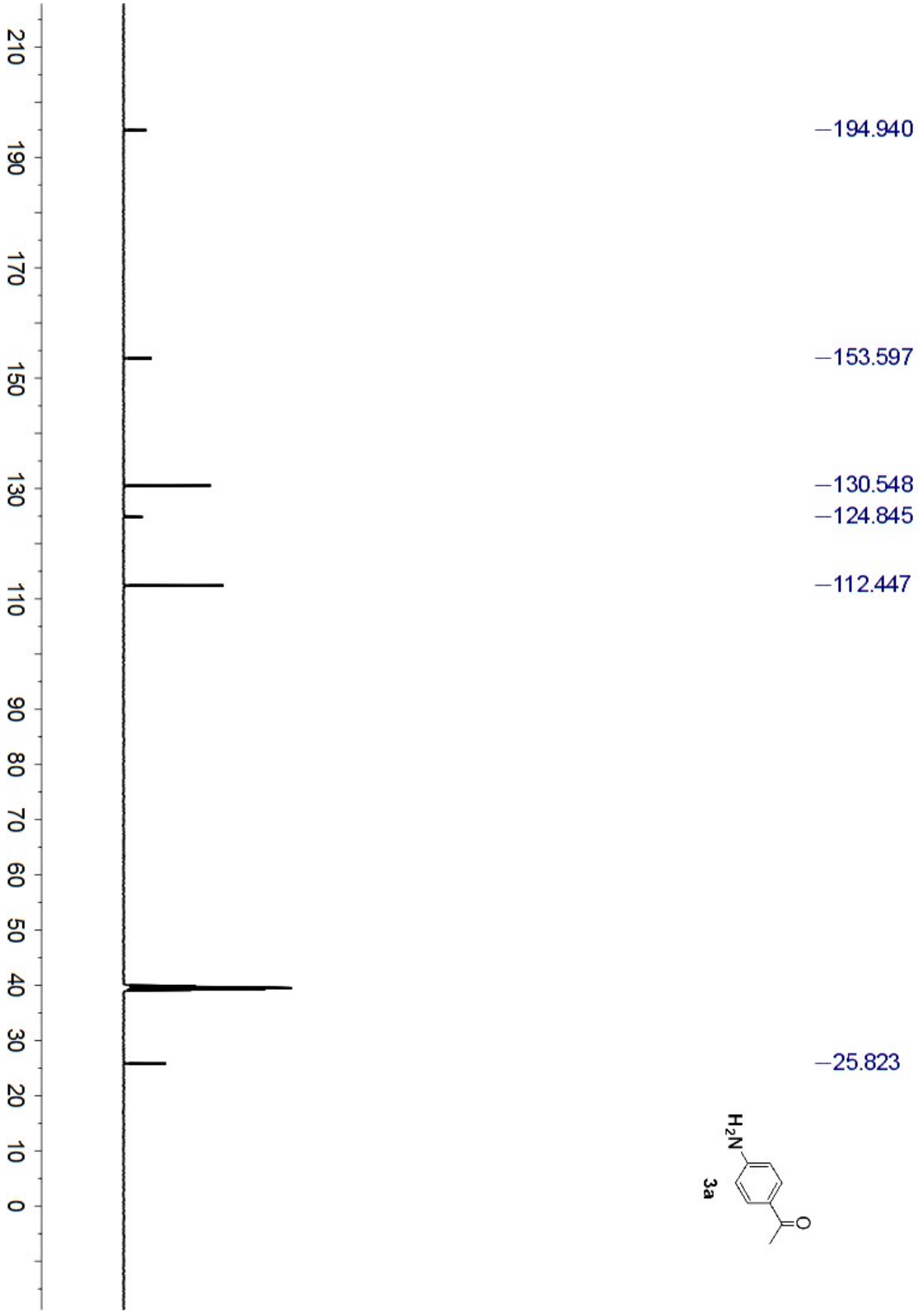
3. References

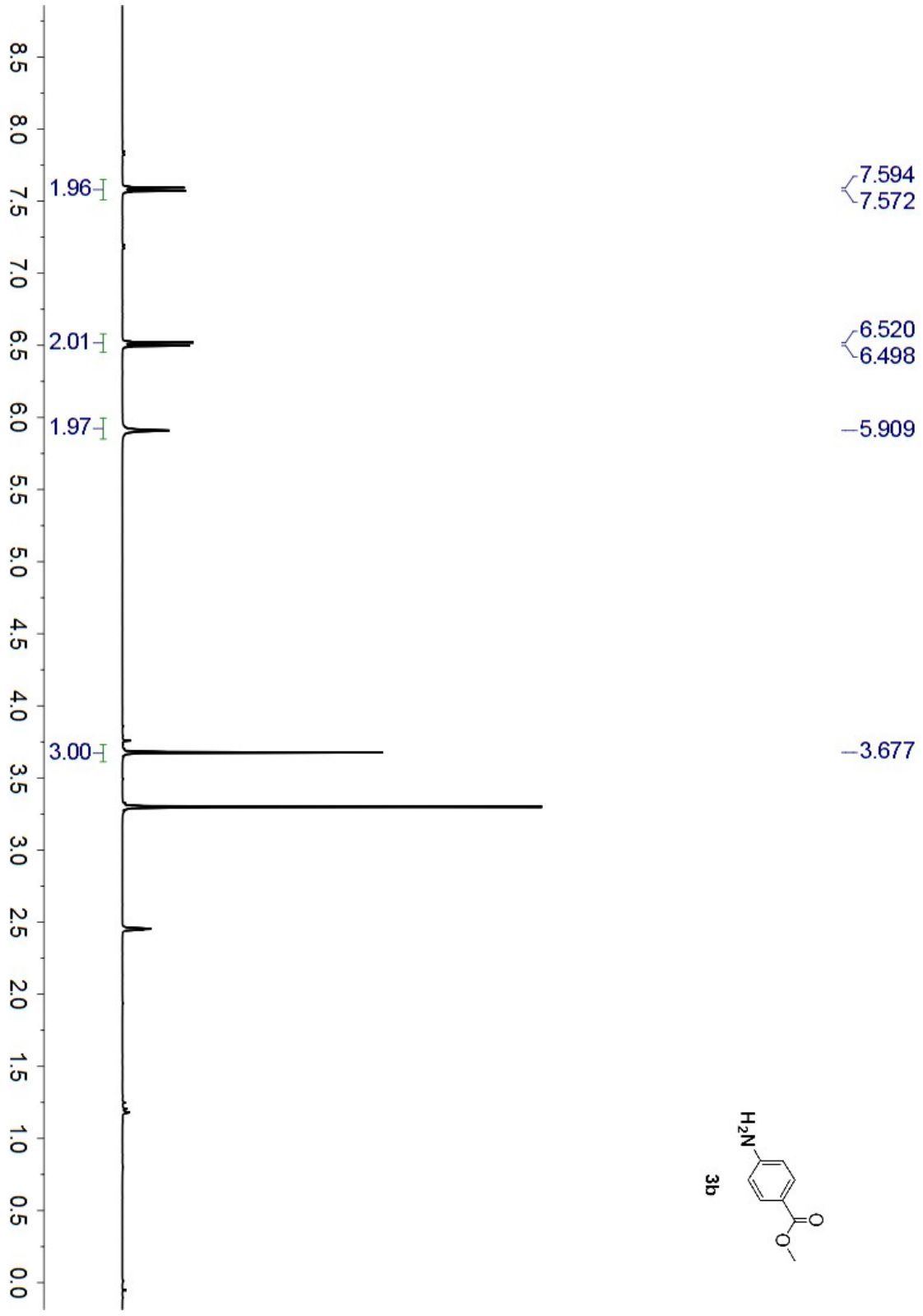
1. M. J. Rozema, A. Sidduri, and P. Knochel, *J. Org. Chem.*, 1992, **57**, 1956-1958.

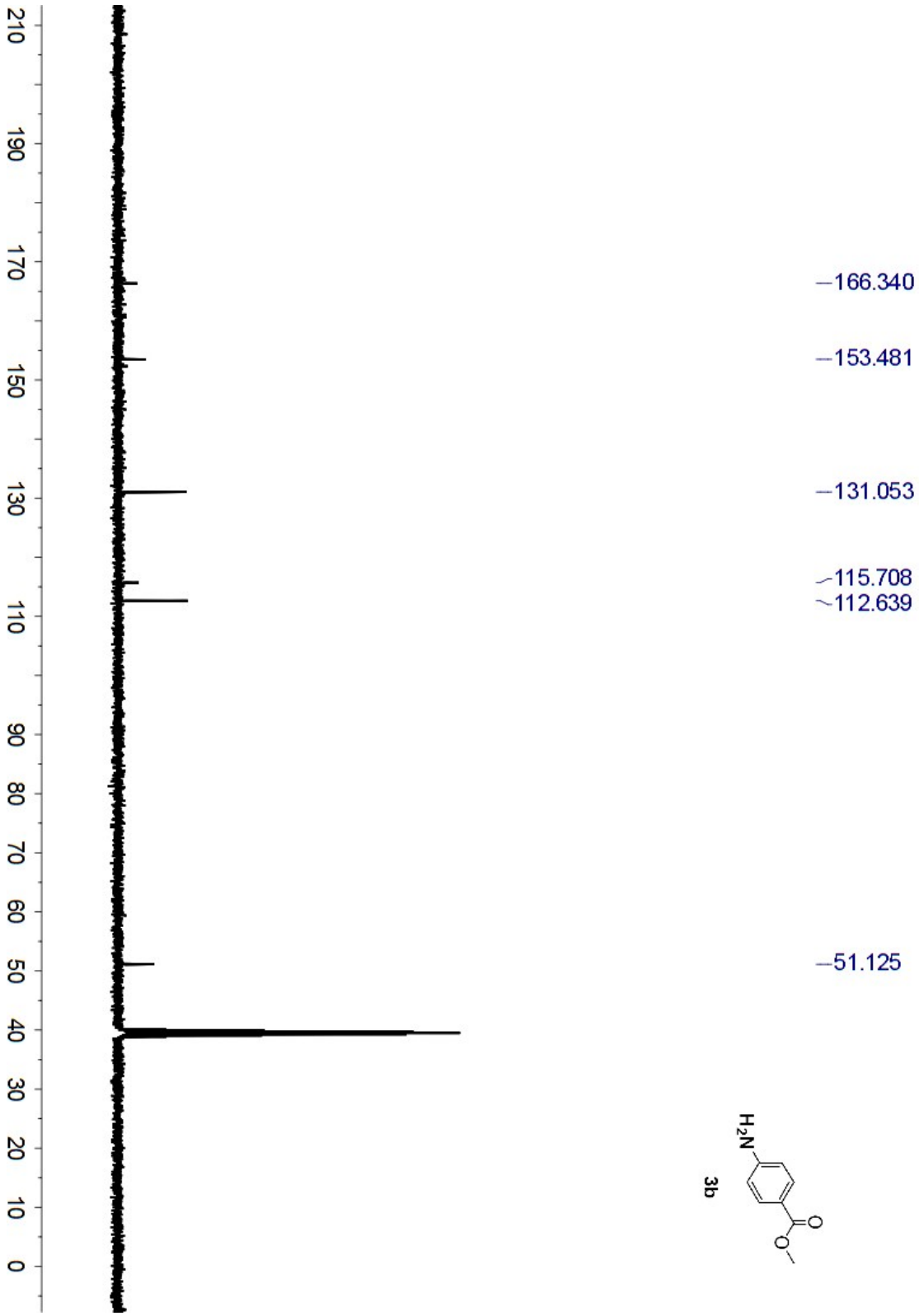
2. J. Boersma, F. J. A. Des Tombe, F. Weijers and G. J. M. V. Der Kerk, *J. Organomet. Chem.*, 1977, **124**, 229-233.

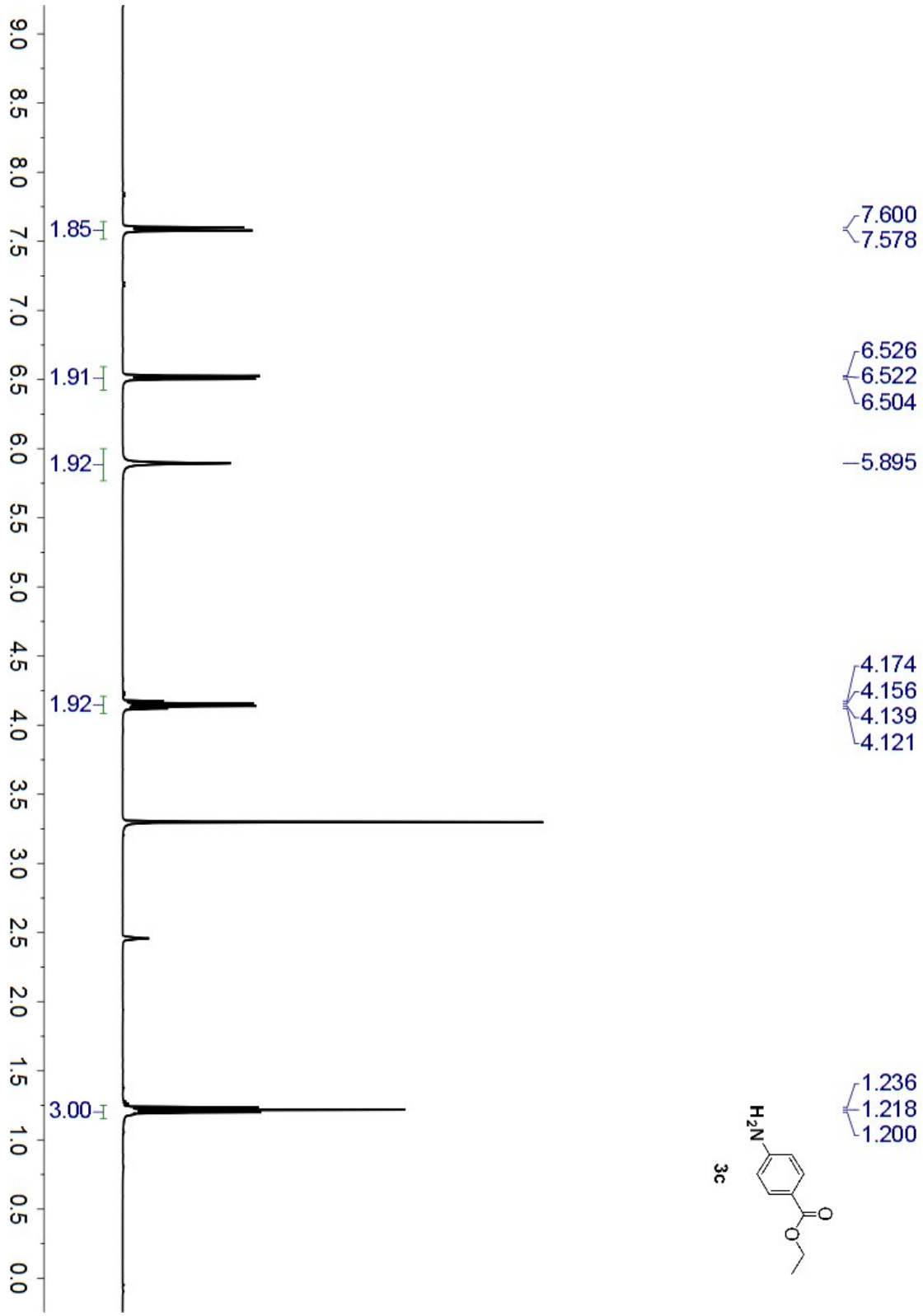
4. NMRspectra copies

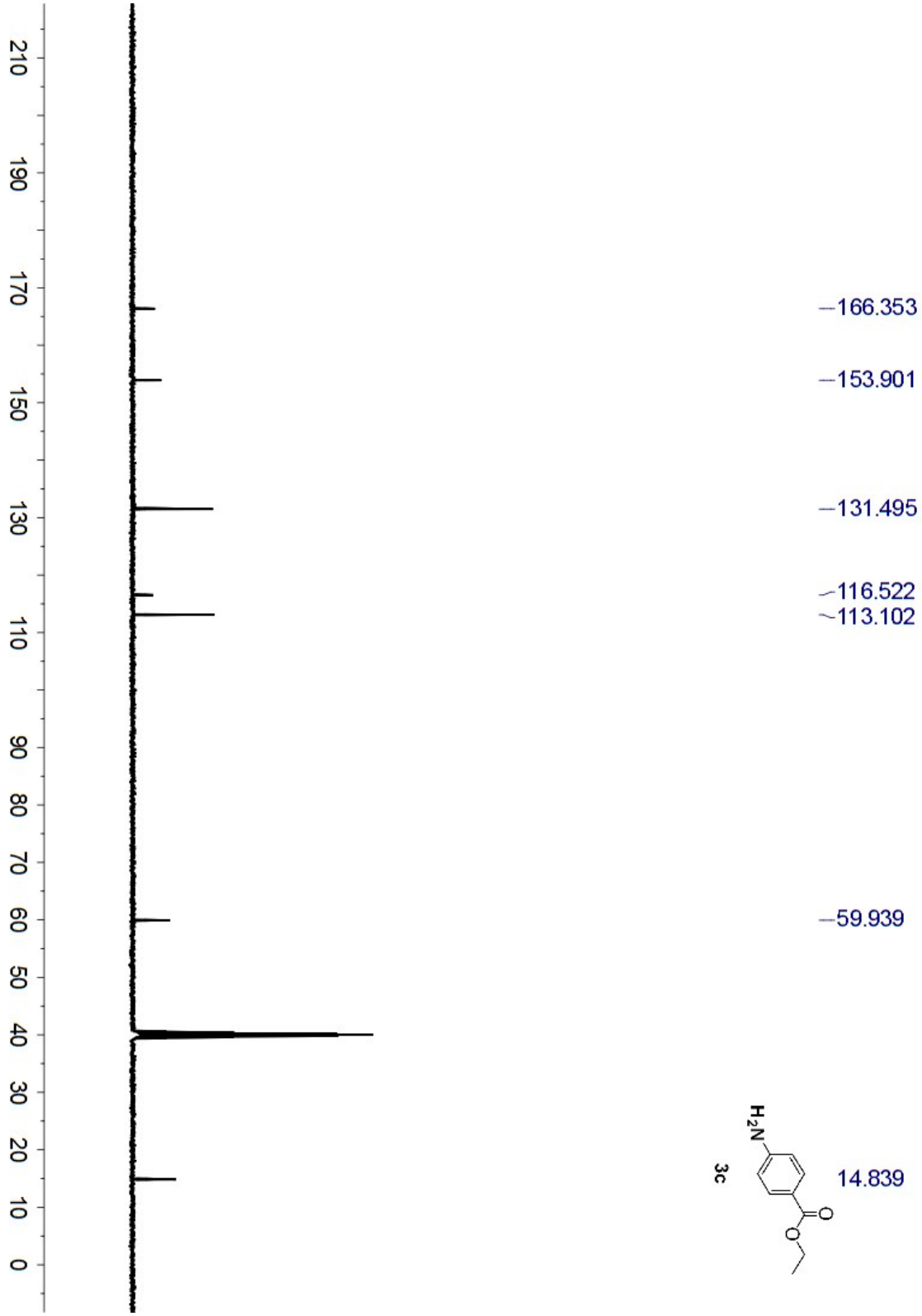


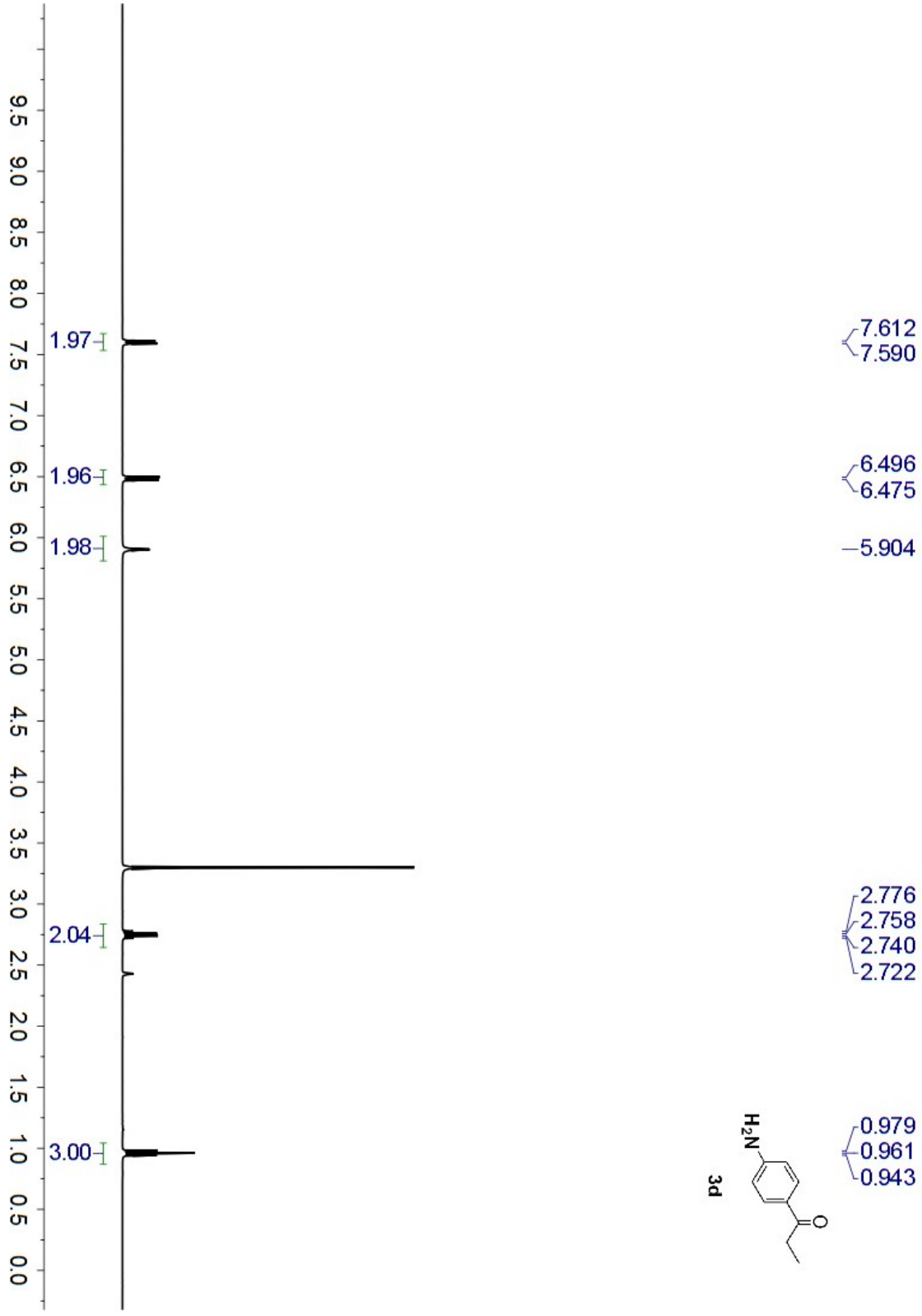

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
194.940
153.597
130.548
124.845
112.447
25.823
H2N
O
3a

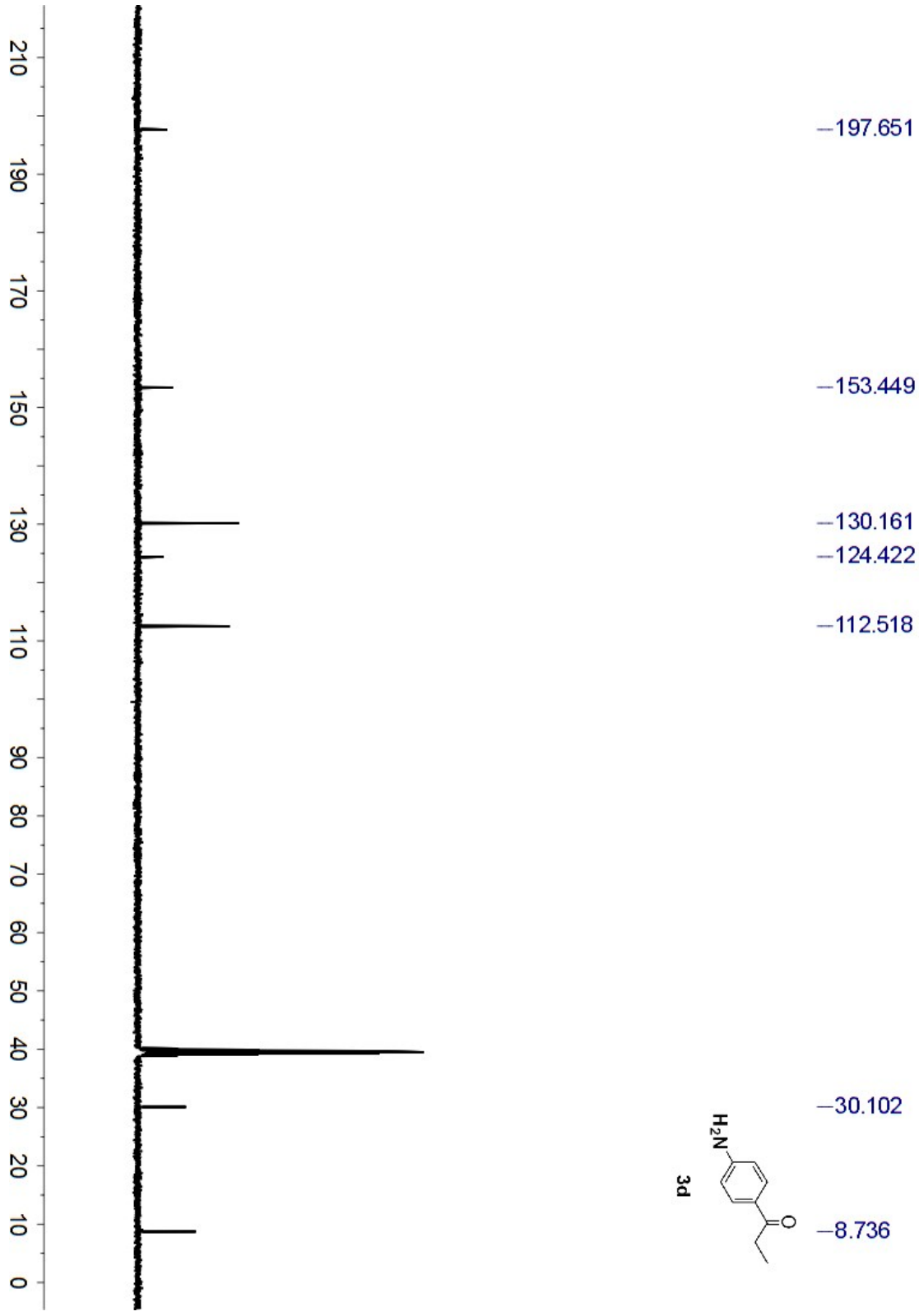

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.96
2.01
1.97
3.00
7.594
7.572
6.520
6.498
5.909
3.677
H2N
O
O
3b

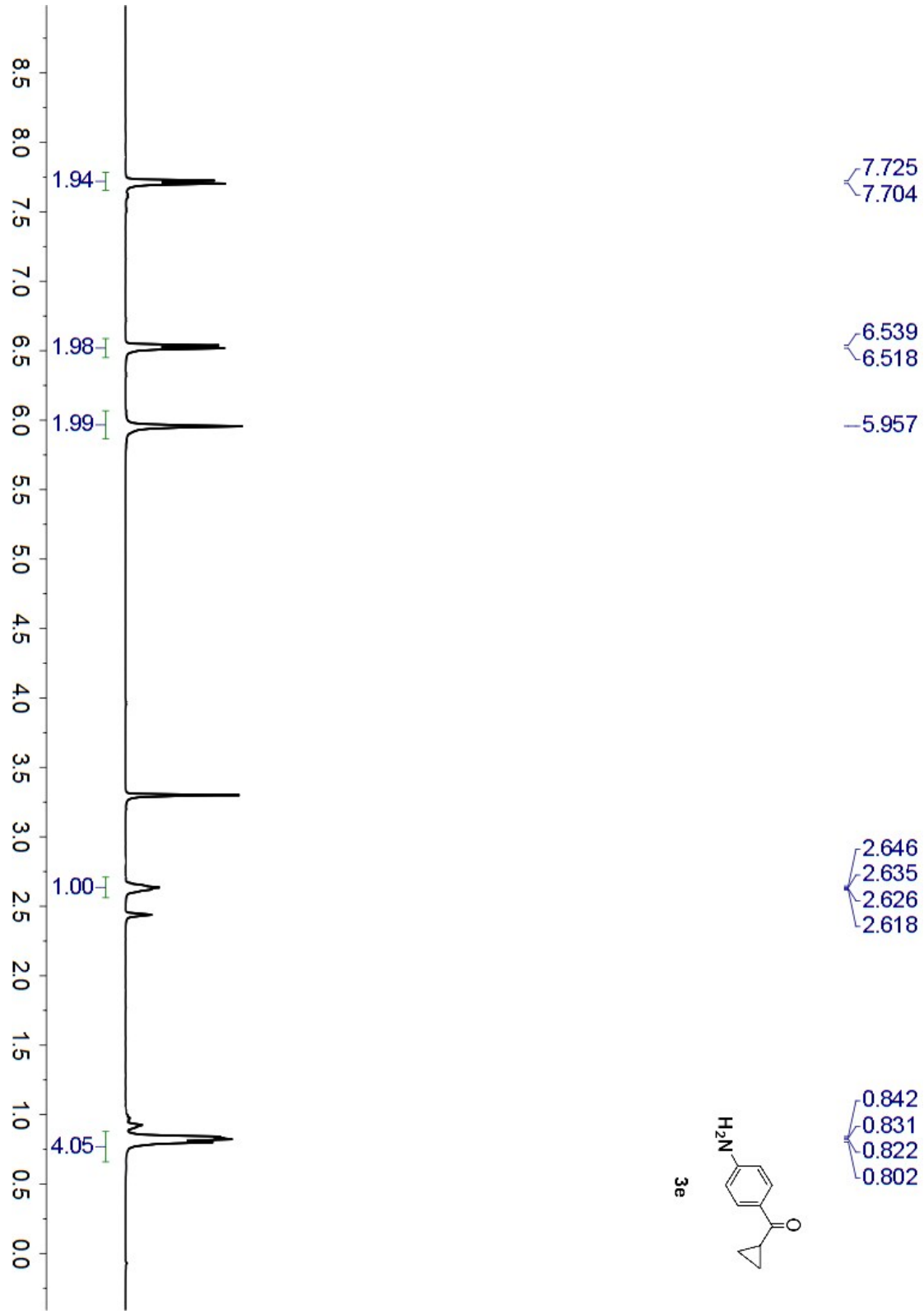

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
166.340
153.481
131.053
115.708
112.639
51.125
H2N
O
O
3b

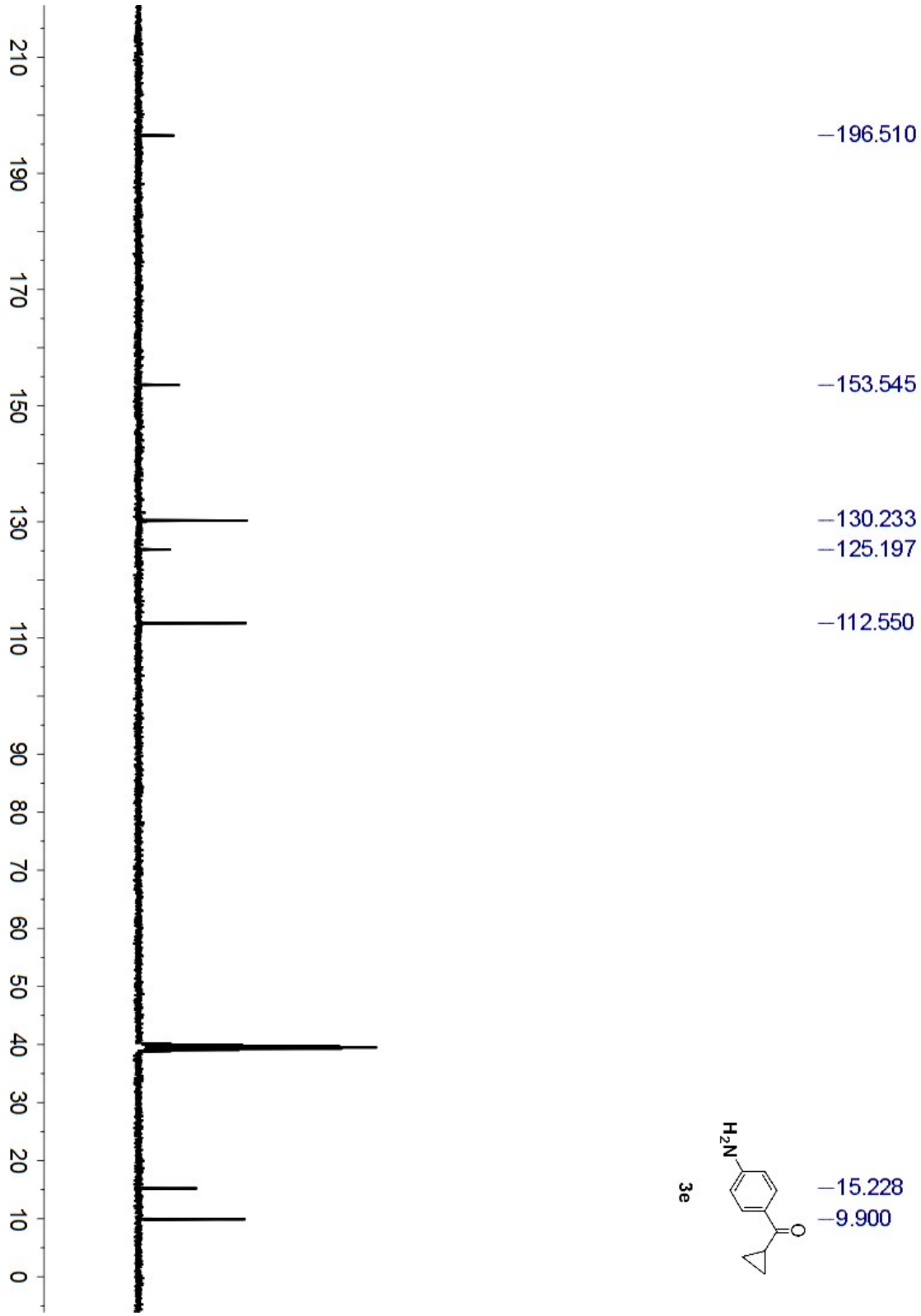

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.85
1.91
1.92
1.92
3.00
7.600
7.578
6.526
6.522
6.504
5.895
4.174
4.156
4.139
4.121
1.236
1.218
1.200
H2N
O
O
3c

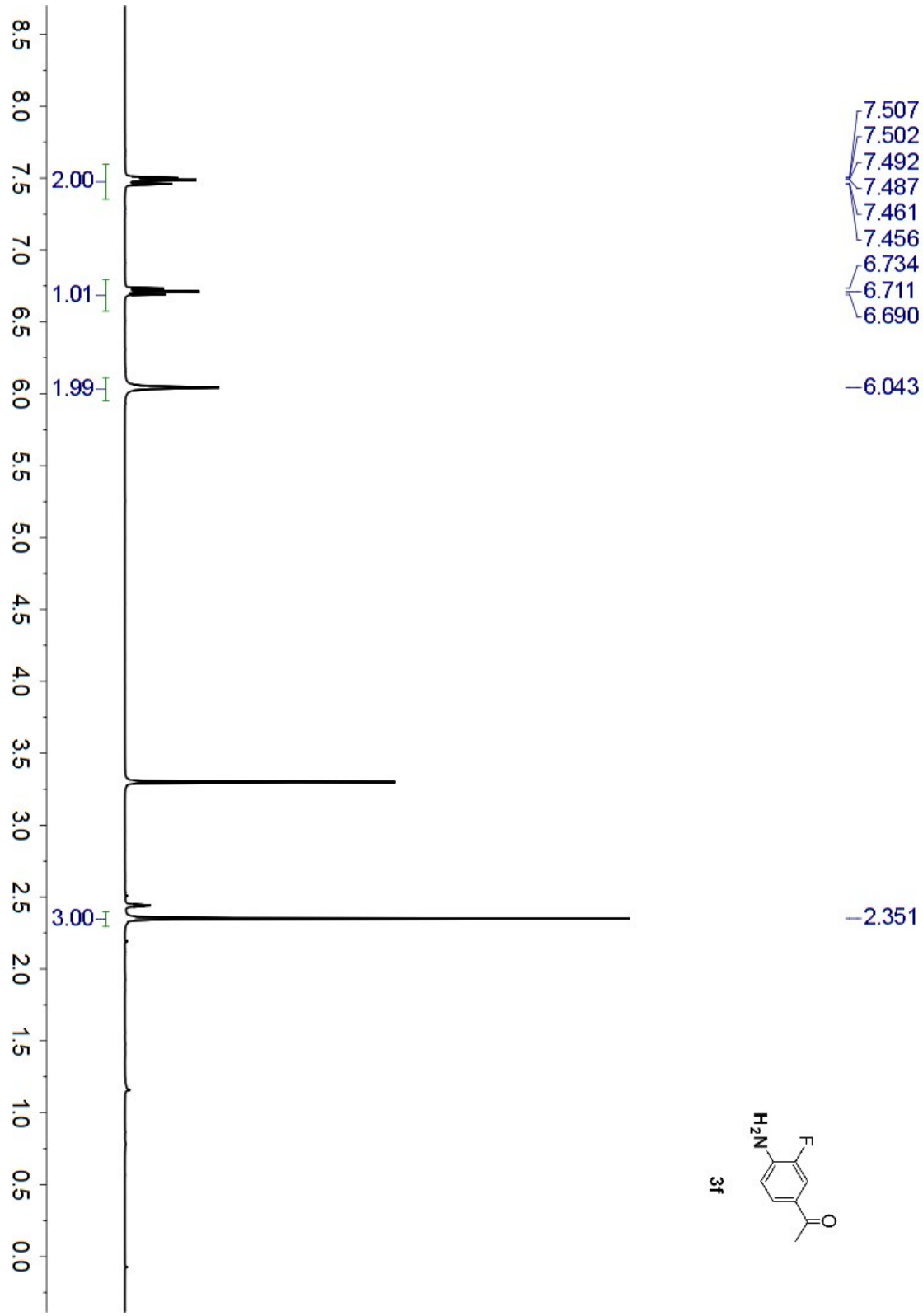

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
166.353
153.901
131.495
116.522
113.102
59.939
14.839
3c
H2N
O
O

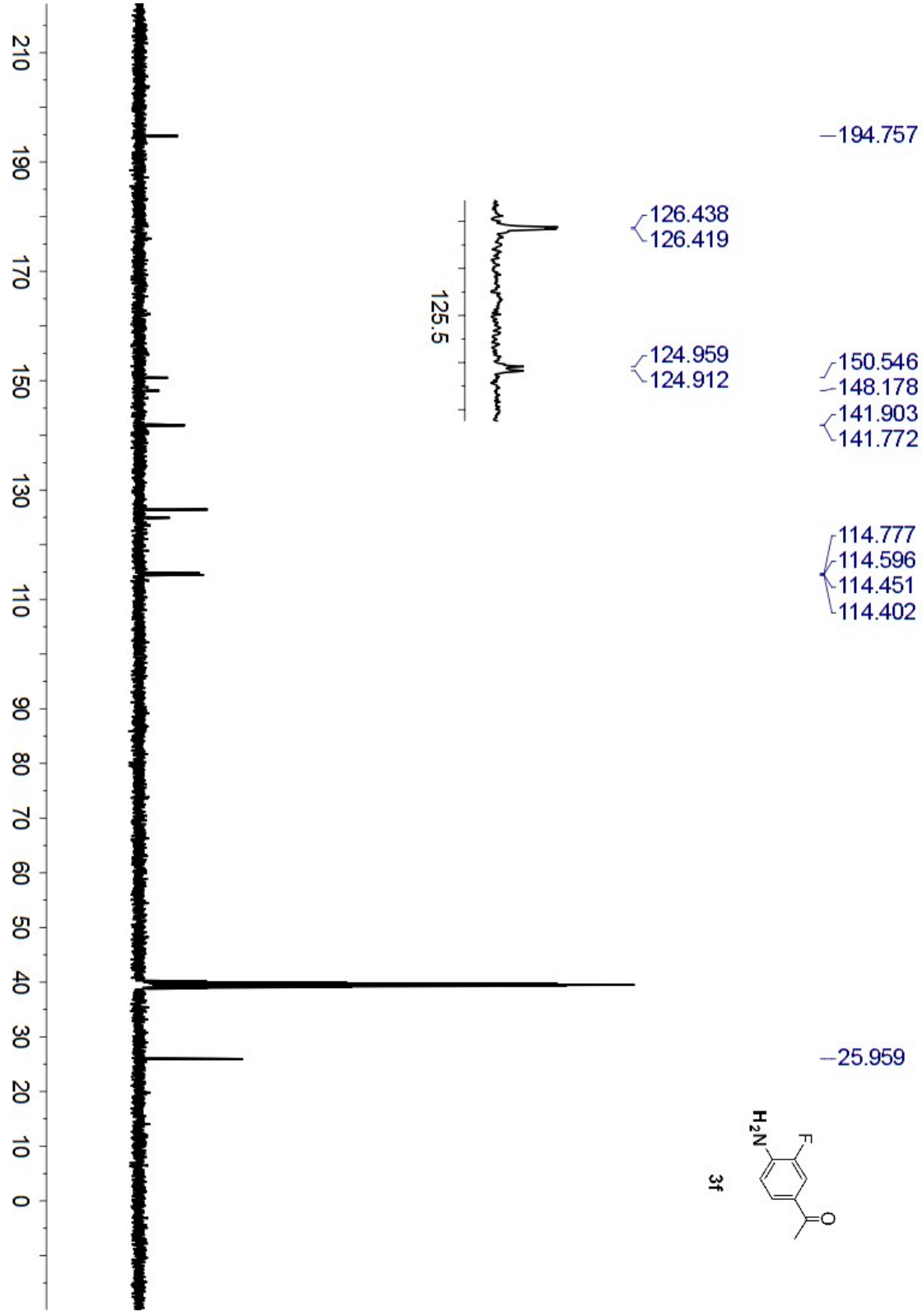

9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
1.97
1.96
1.98
2.04
3.00
7.612
7.590
6.496
6.475
5.904
2.776
2.758
2.740
2.722
0.979
0.961
0.943
H2N
O
3d

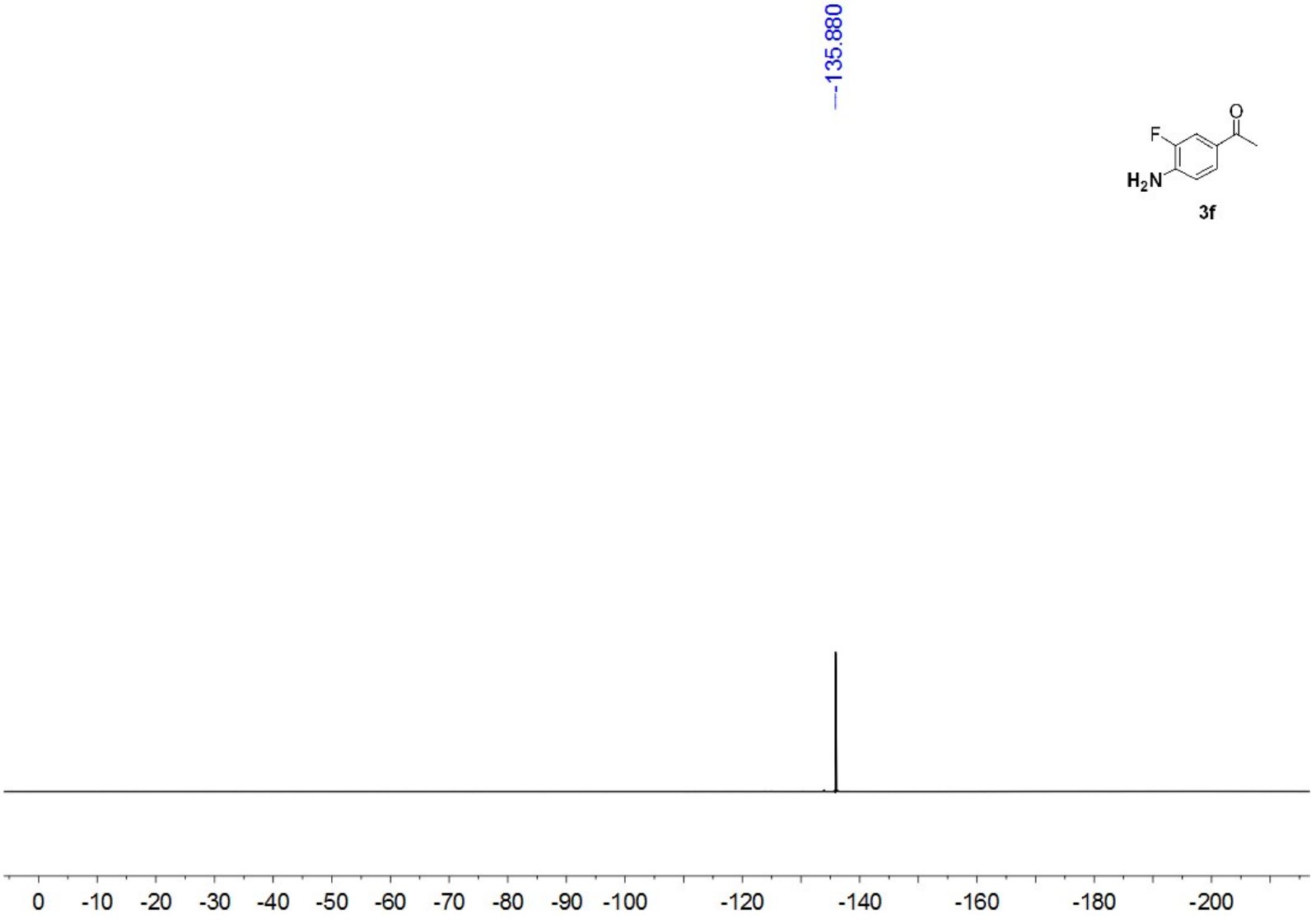

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
197.651
153.449
130.161
124.422
112.518
30.102
8.736
H2N
O
3d

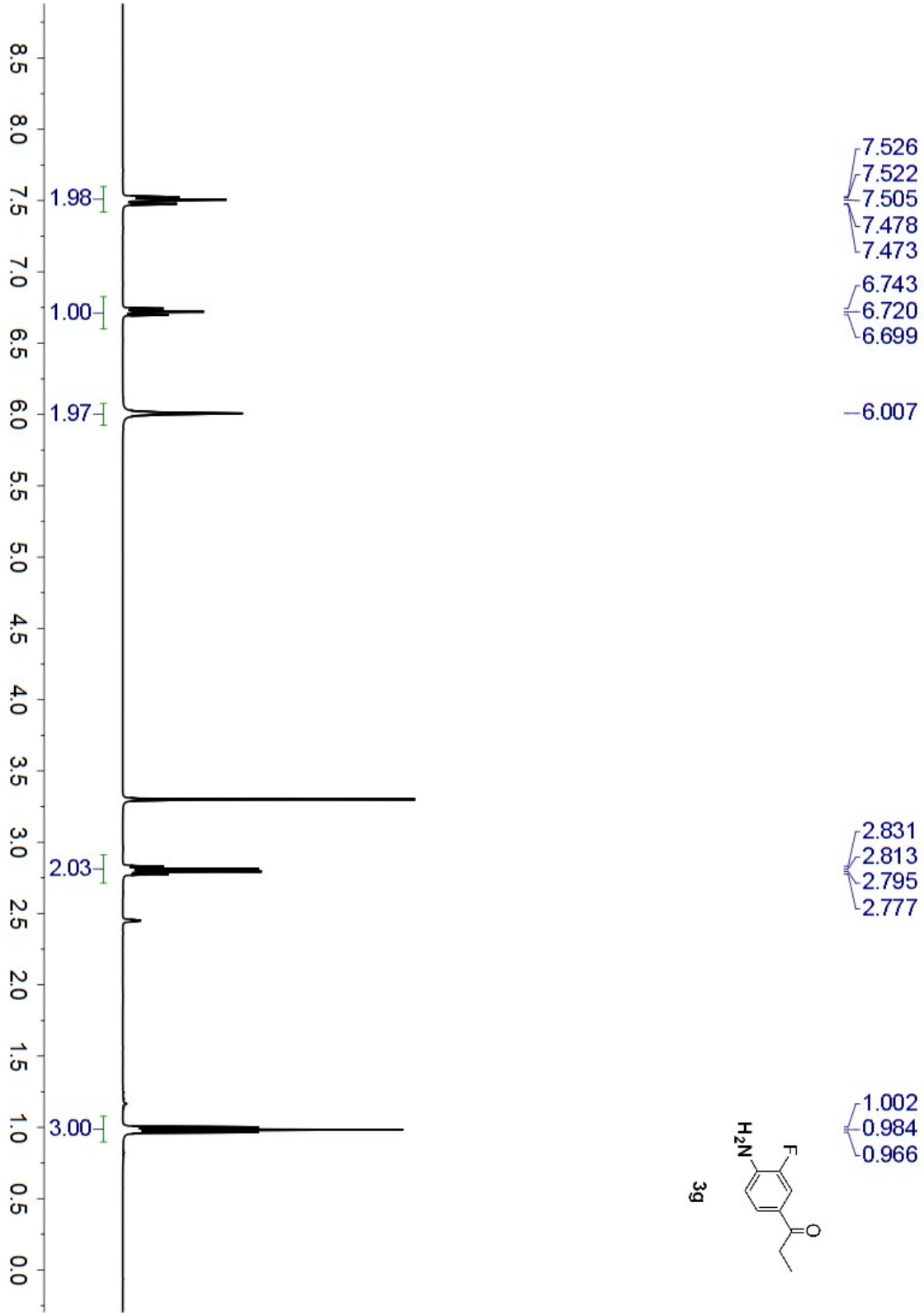

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.94
1.98
1.99
1.00
4.05
7.725
7.704
6.539
6.518
5.957
2.646
2.635
2.626
2.618
0.842
0.831
0.822
0.802
H2N
O
3e

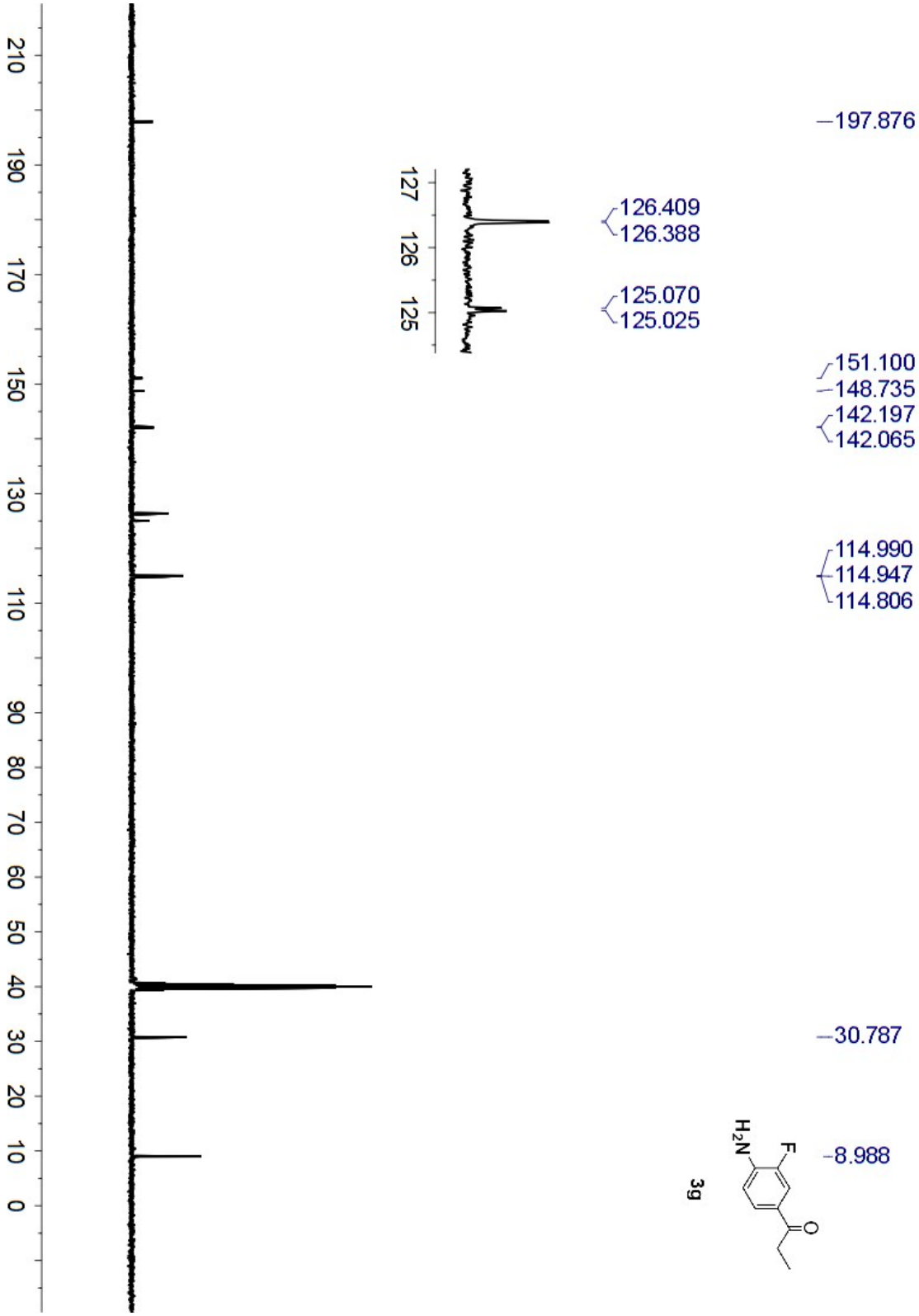

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
196.510
153.545
130.233
125.197
112.550
15.228
9.900
H2N
O
3e

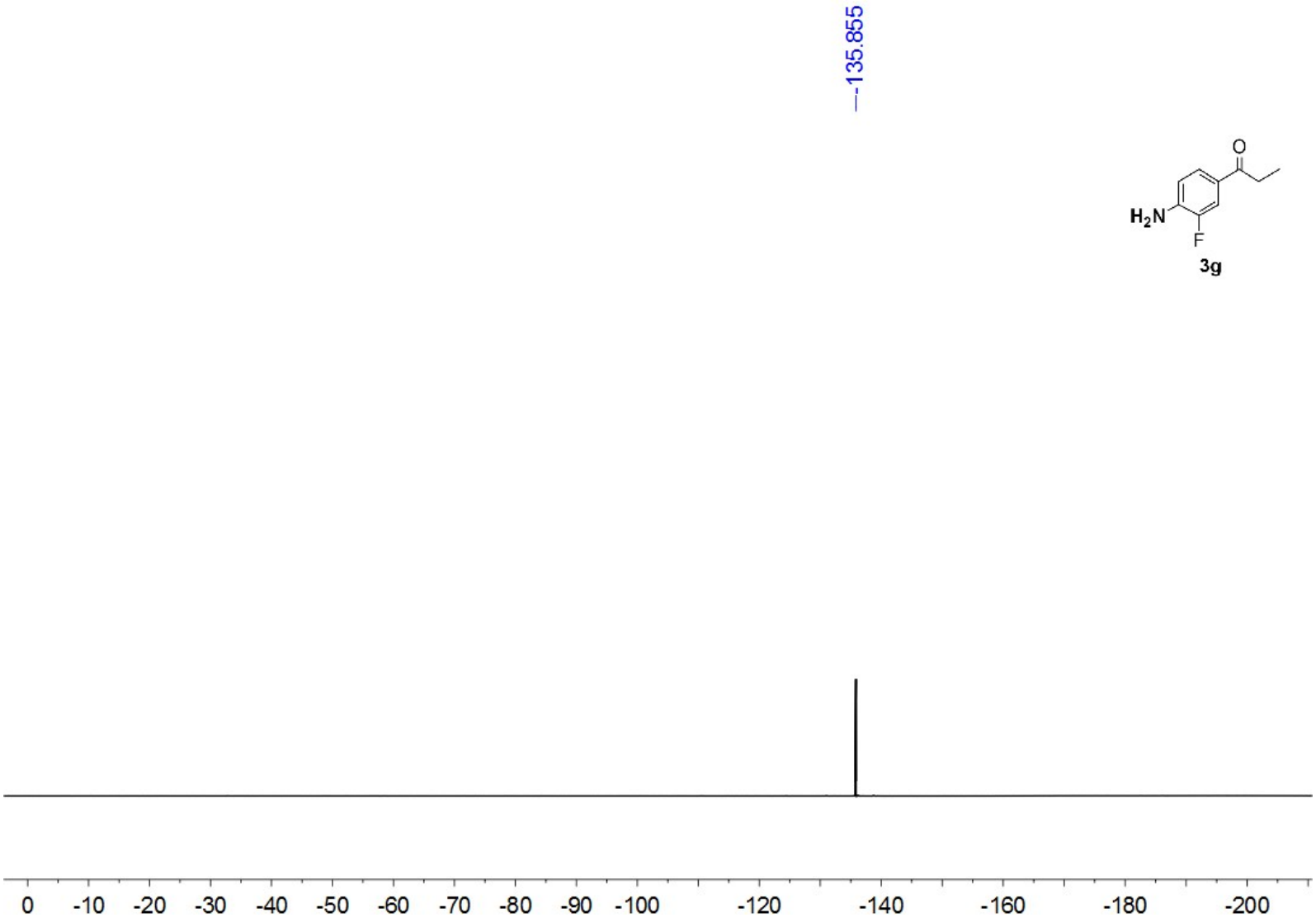

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2.00
1.01
1.99
3.00
7.507
7.502
7.492
7.487
7.461
7.456
6.734
6.711
6.690
6.043
2.351
H2N
F
O
3f

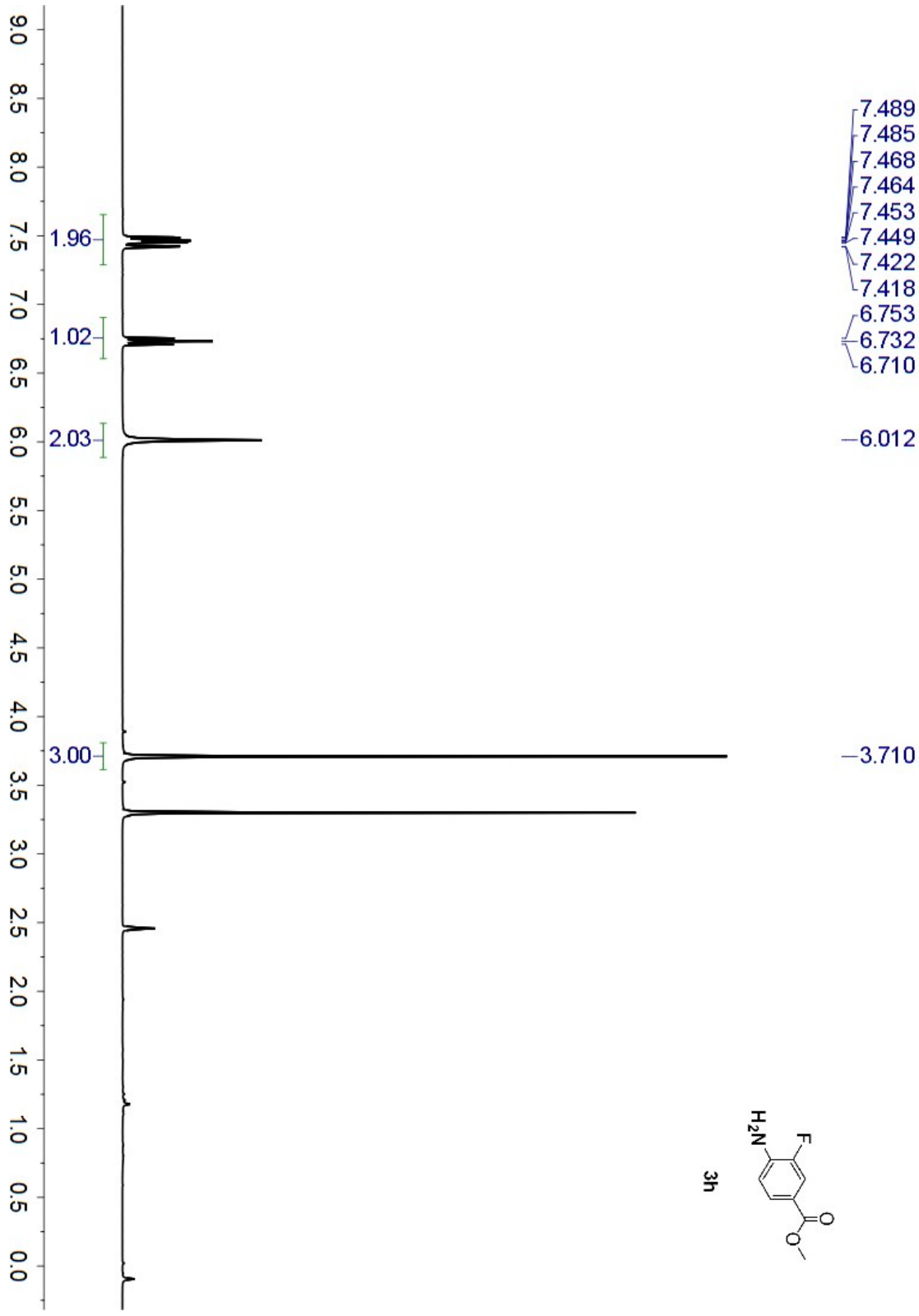

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
125.5
194.757
126.438
126.419
124.959
124.912
150.546
148.178
141.903
141.772
114.777
114.596
114.451
114.402
25.959
H2N
F
O
3f

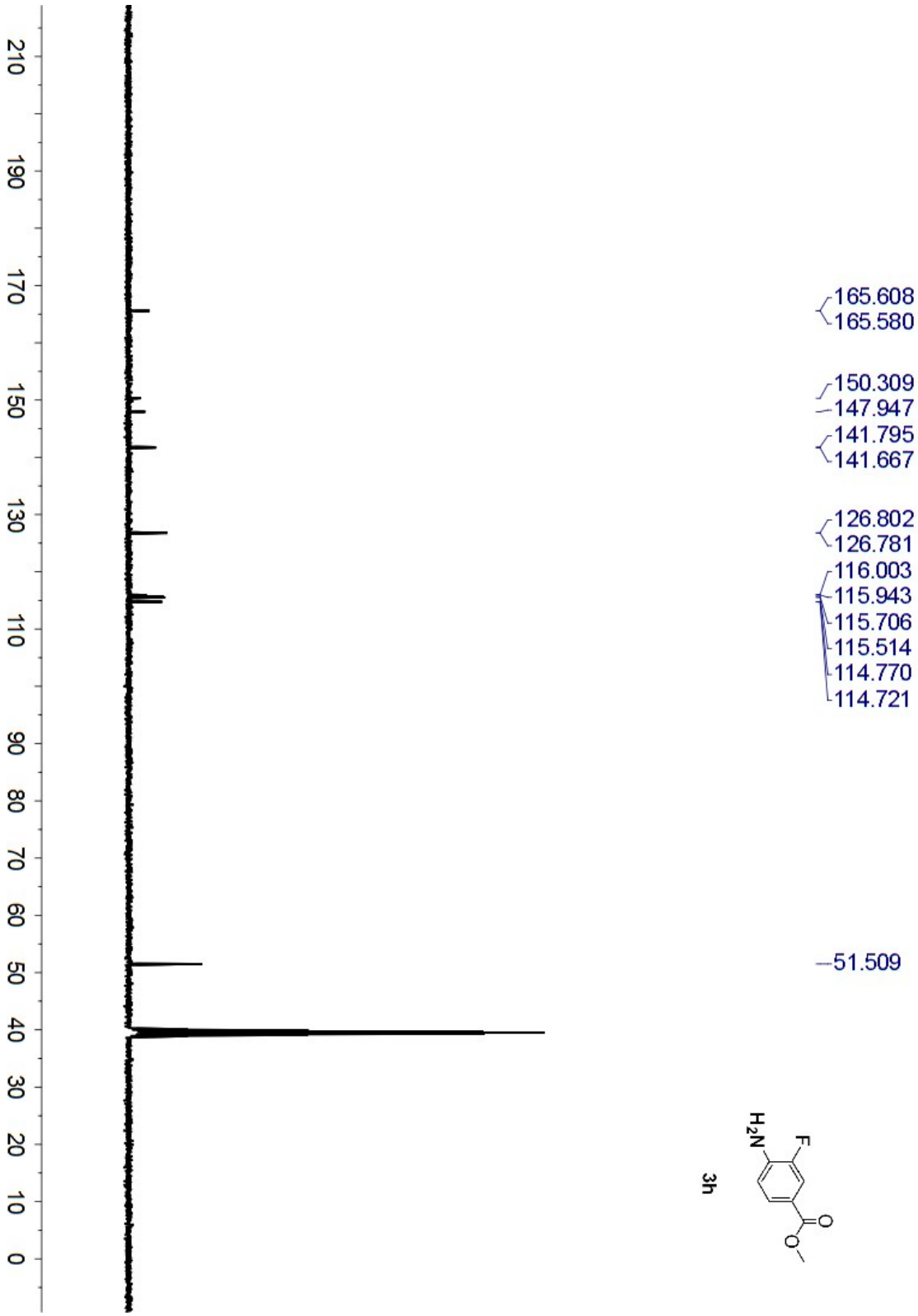

-135.880
F
O
H_2N
3f
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

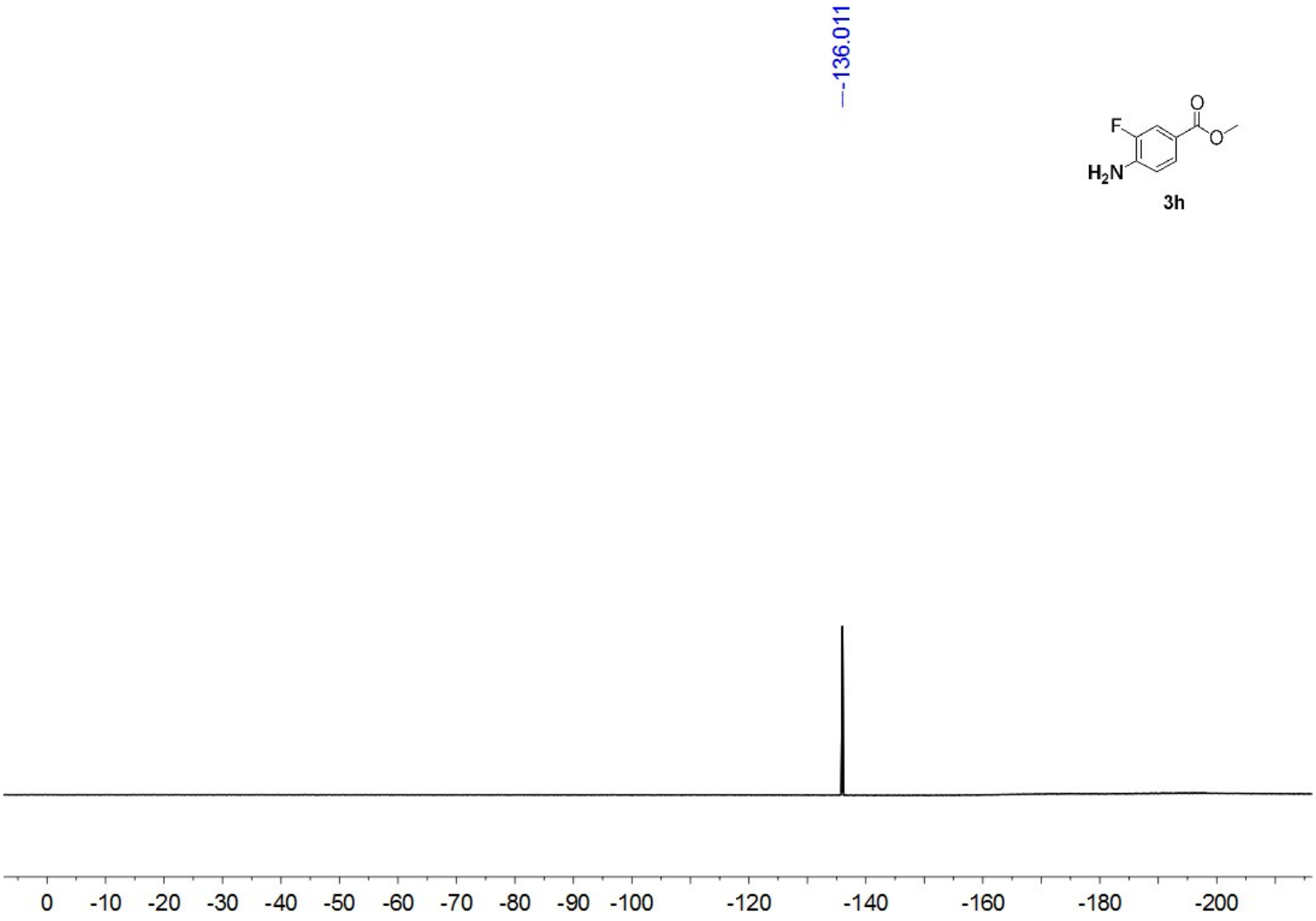

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.98
1.00
1.97
2.03
3.00
7.526
7.522
7.505
7.478
7.473
6.743
6.720
6.699
6.007
2.831
2.813
2.795
2.777
1.002
0.984
0.966
H2N
F
O
3g

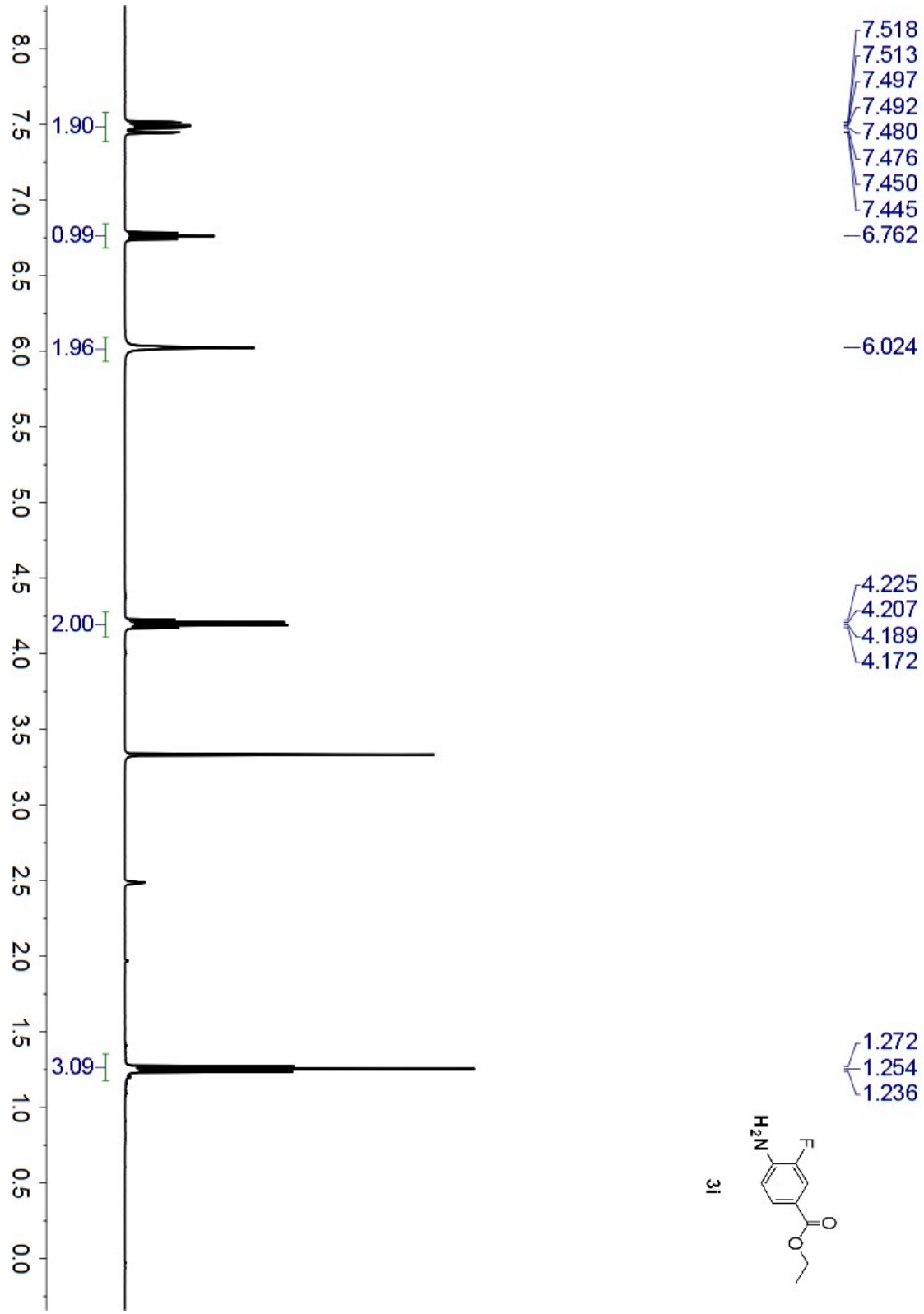

197.876
126.409
126.388
125.070
125.025
151.100
148.735
142.197
142.065
114.990
114.947
114.806
30.787
8.988
3g

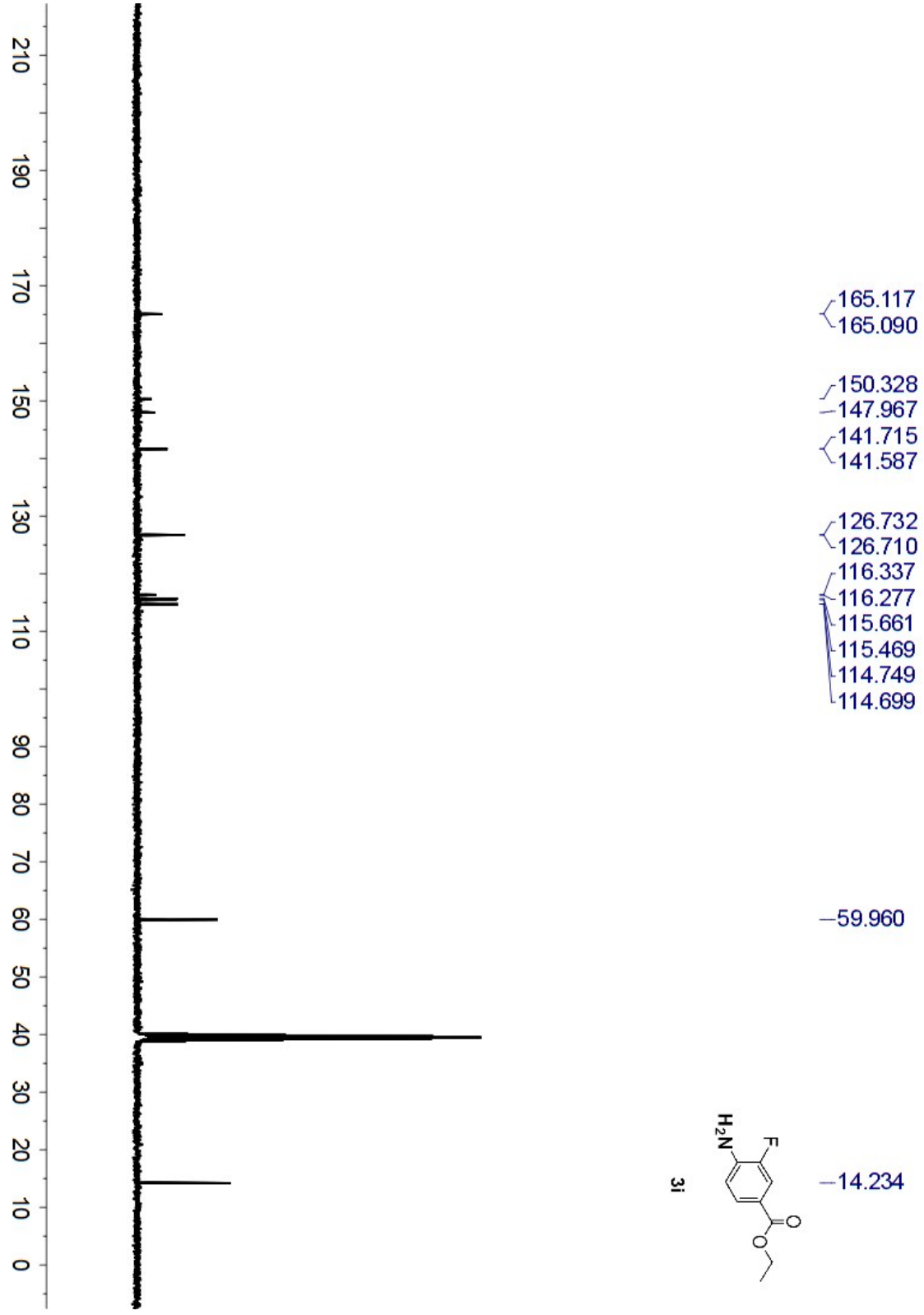

-135.855
O
H2N
F
3g
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

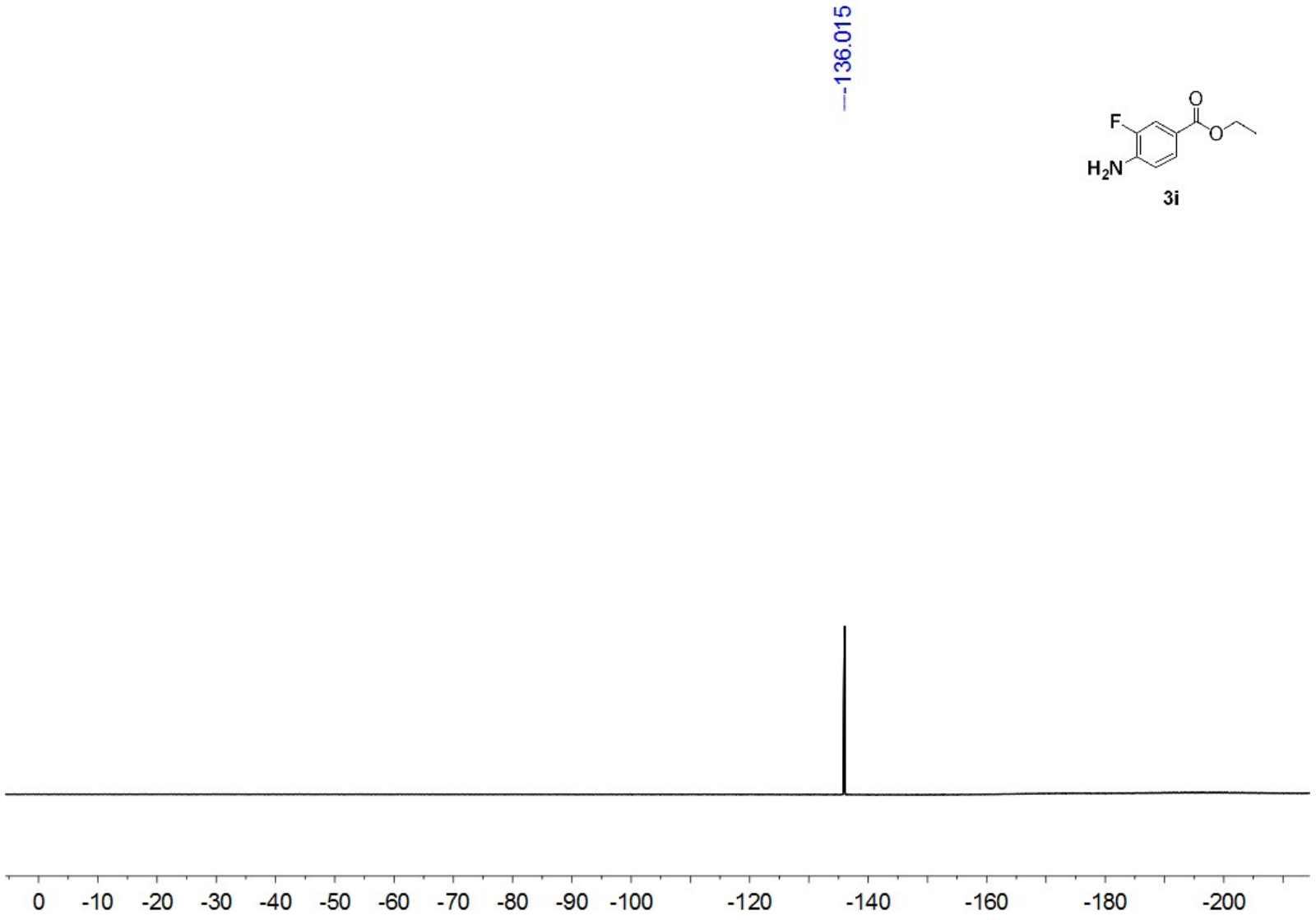

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.96
1.02
2.03
3.00
7.489
7.485
7.468
7.464
7.453
7.449
7.422
7.418
6.753
6.732
6.710
6.012
3.710
3h
H2N
F
O
O

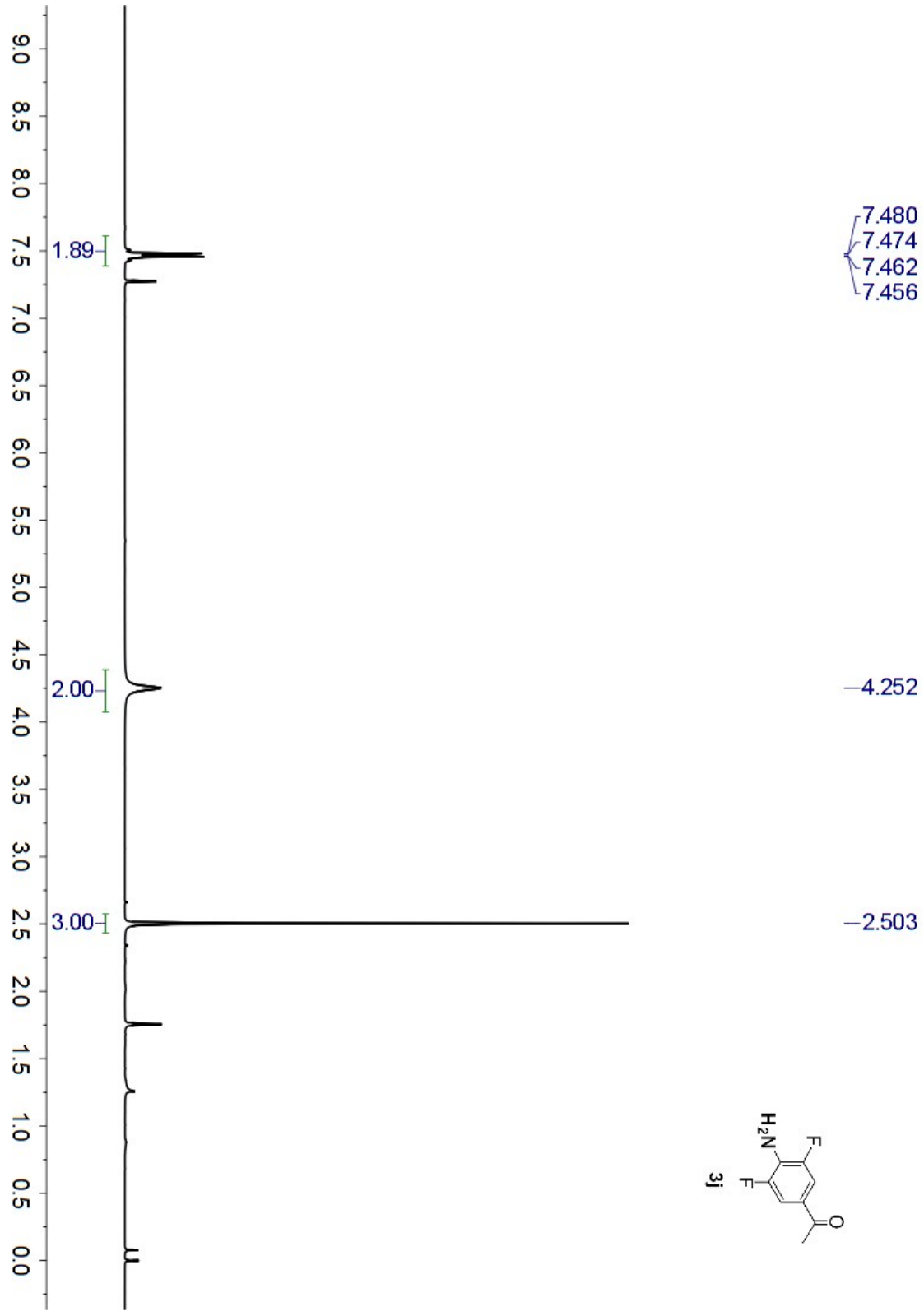

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
165.608
165.580
150.309
147.947
141.795
141.667
126.802
126.781
116.003
115.943
115.706
115.514
114.770
114.721
51.509
3h
H2N
F
O
O

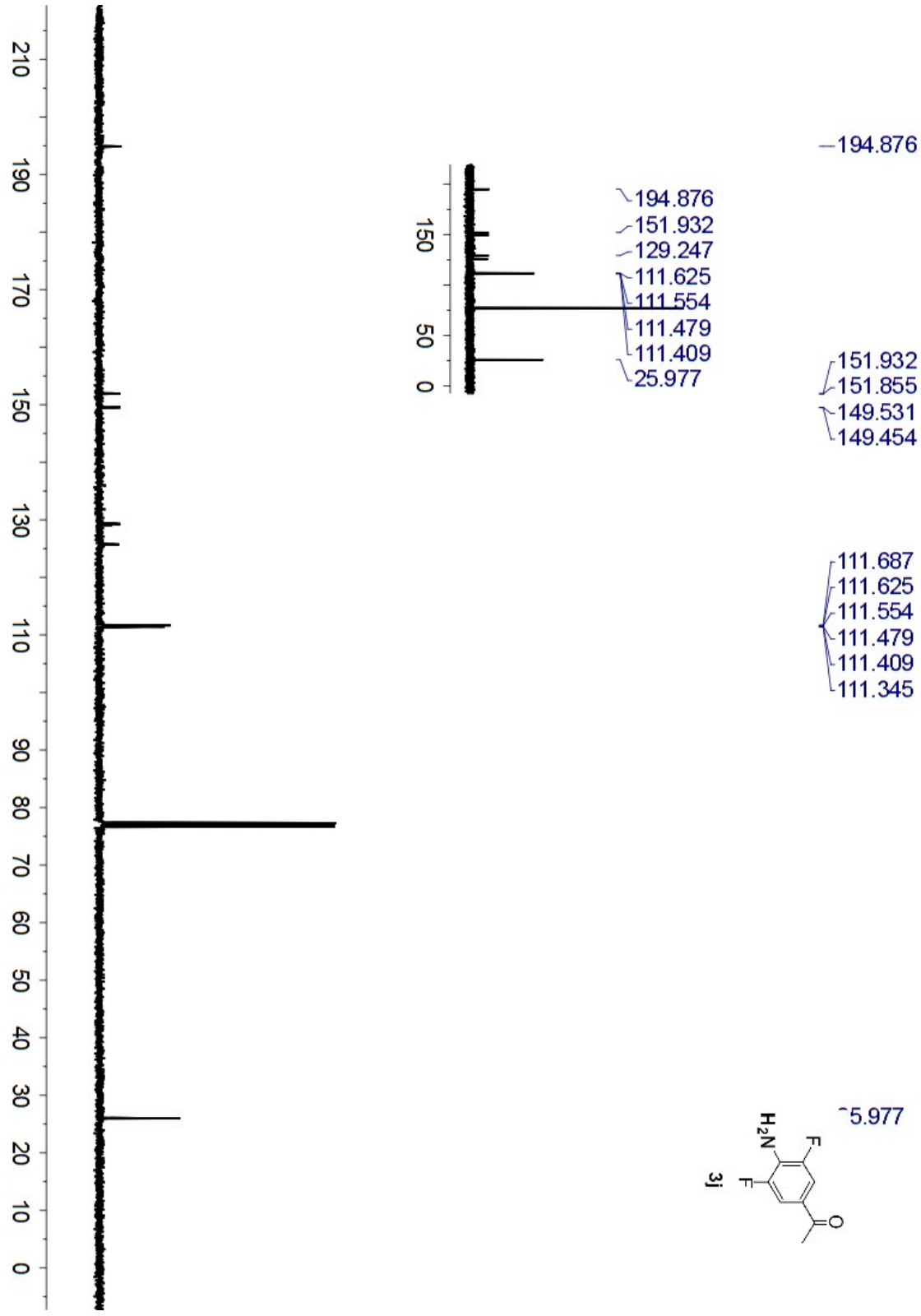

-136.011
F
O
O
H2N
3h
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200


7.518
7.513
7.497
7.492
7.480
7.476
7.450
7.445
6.762
6.024
4.225
4.207
4.189
4.172
1.272
1.254
1.236
1.90
0.99
1.96
2.00
3.09
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
H2N
F
O
O
3i

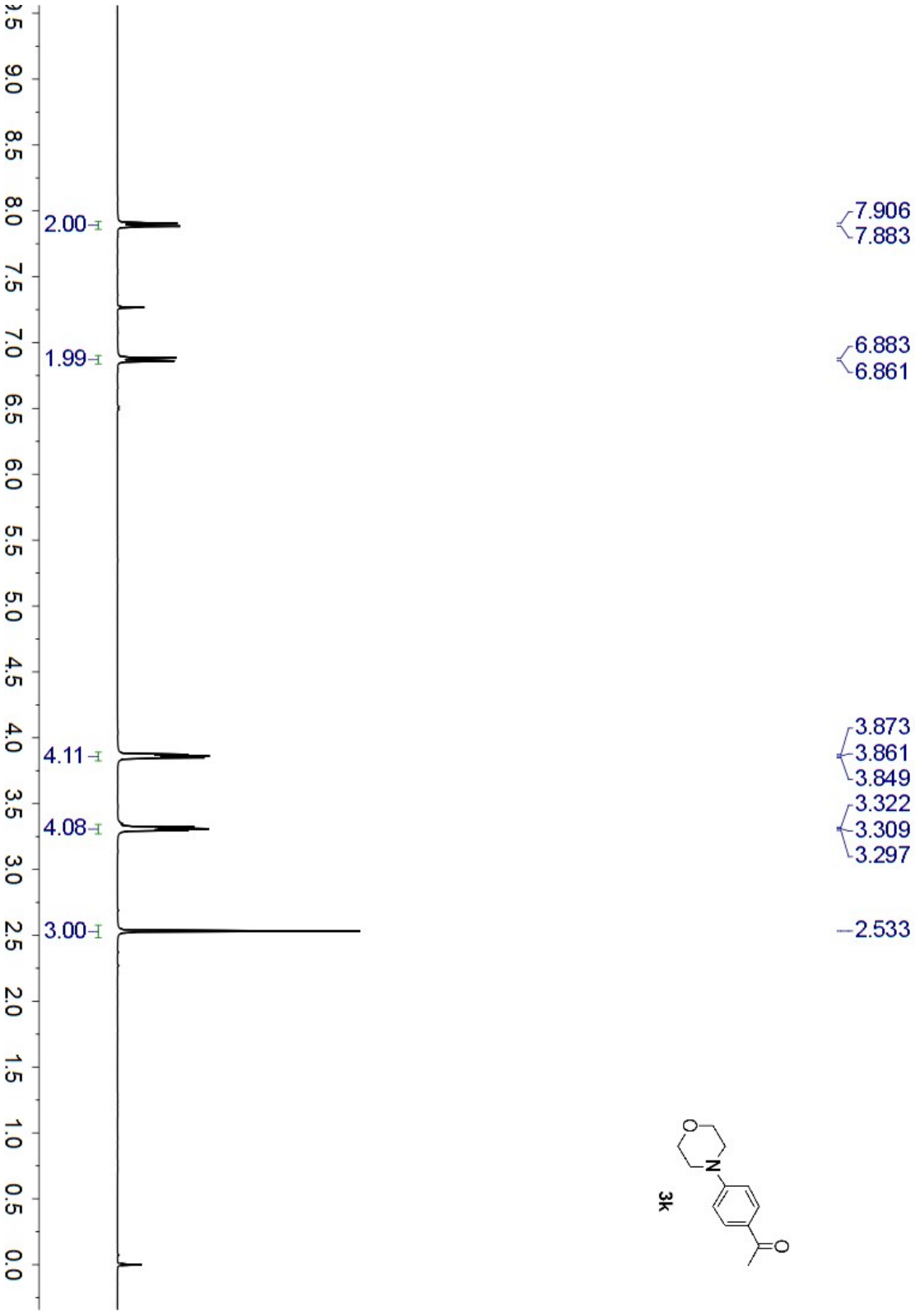

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
165.117
165.090
150.328
147.967
141.715
141.587
126.732
126.710
116.337
116.277
115.661
115.469
114.749
114.699
59.960
14.234
3i
H2N
F
O
O

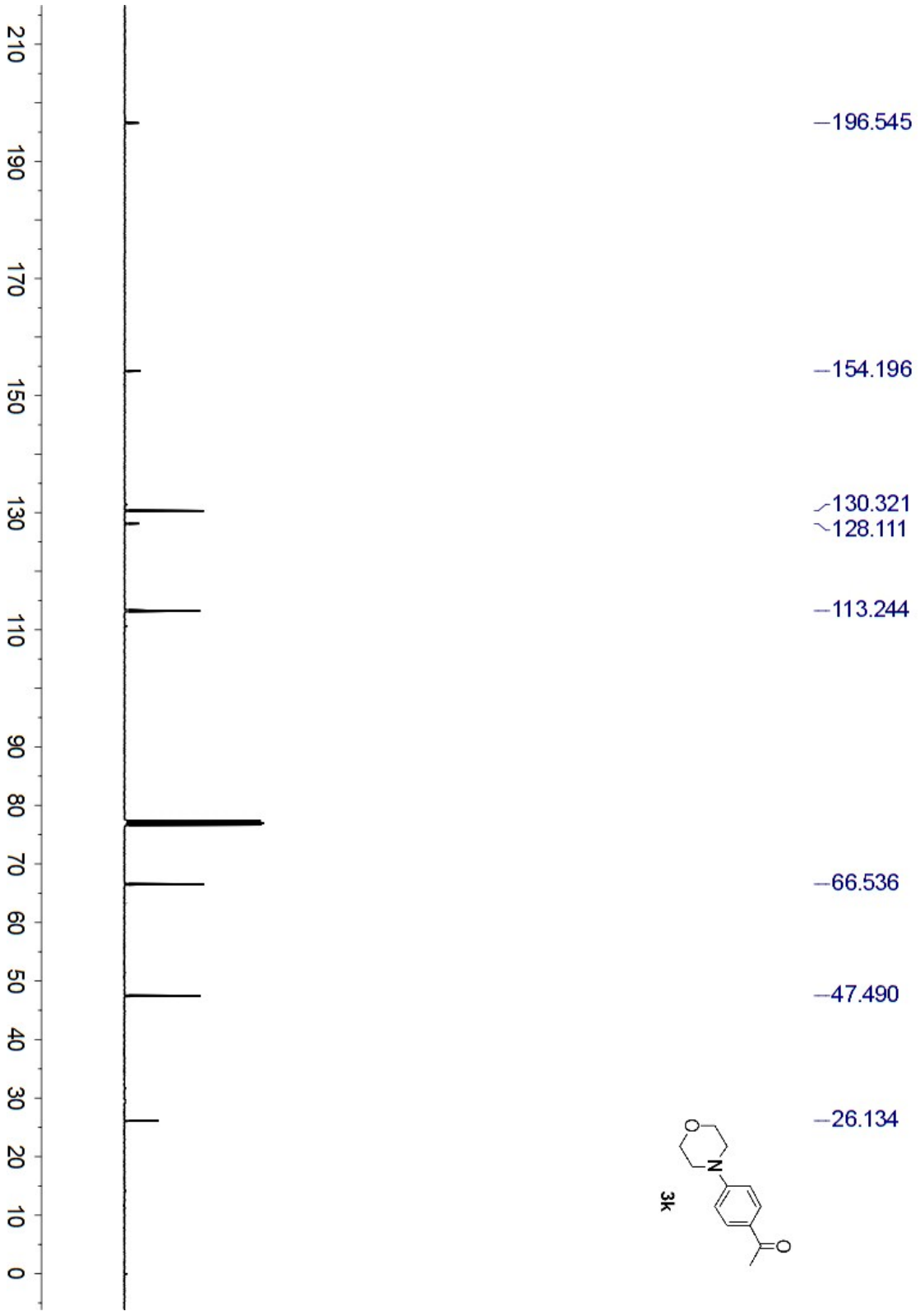

-136.015
F
O
O
H_2N
3i
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200

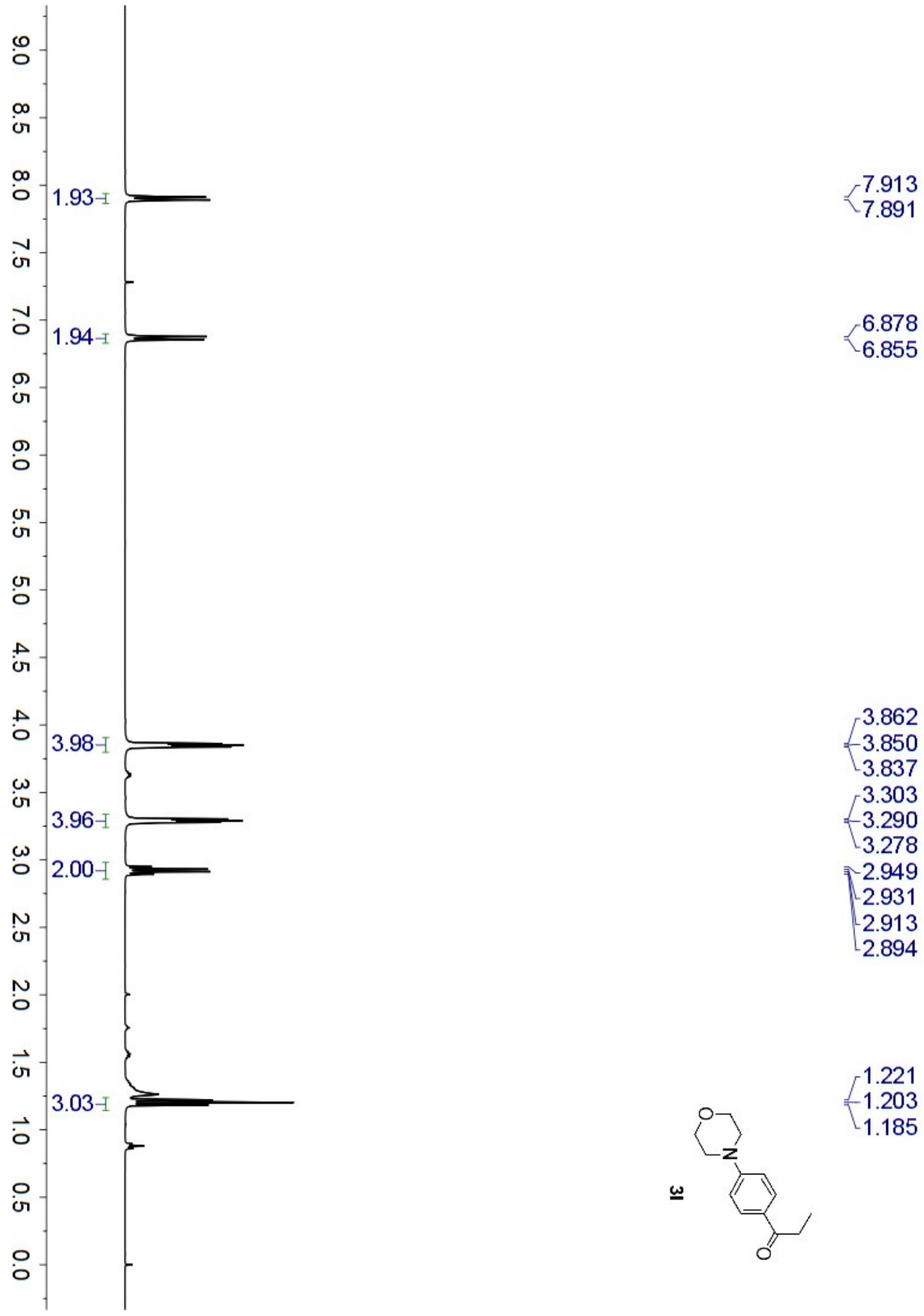

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.89
2.00
3.00
7.480
7.474
7.462
7.456
4.252
2.503
H2N
F
F
O
3j

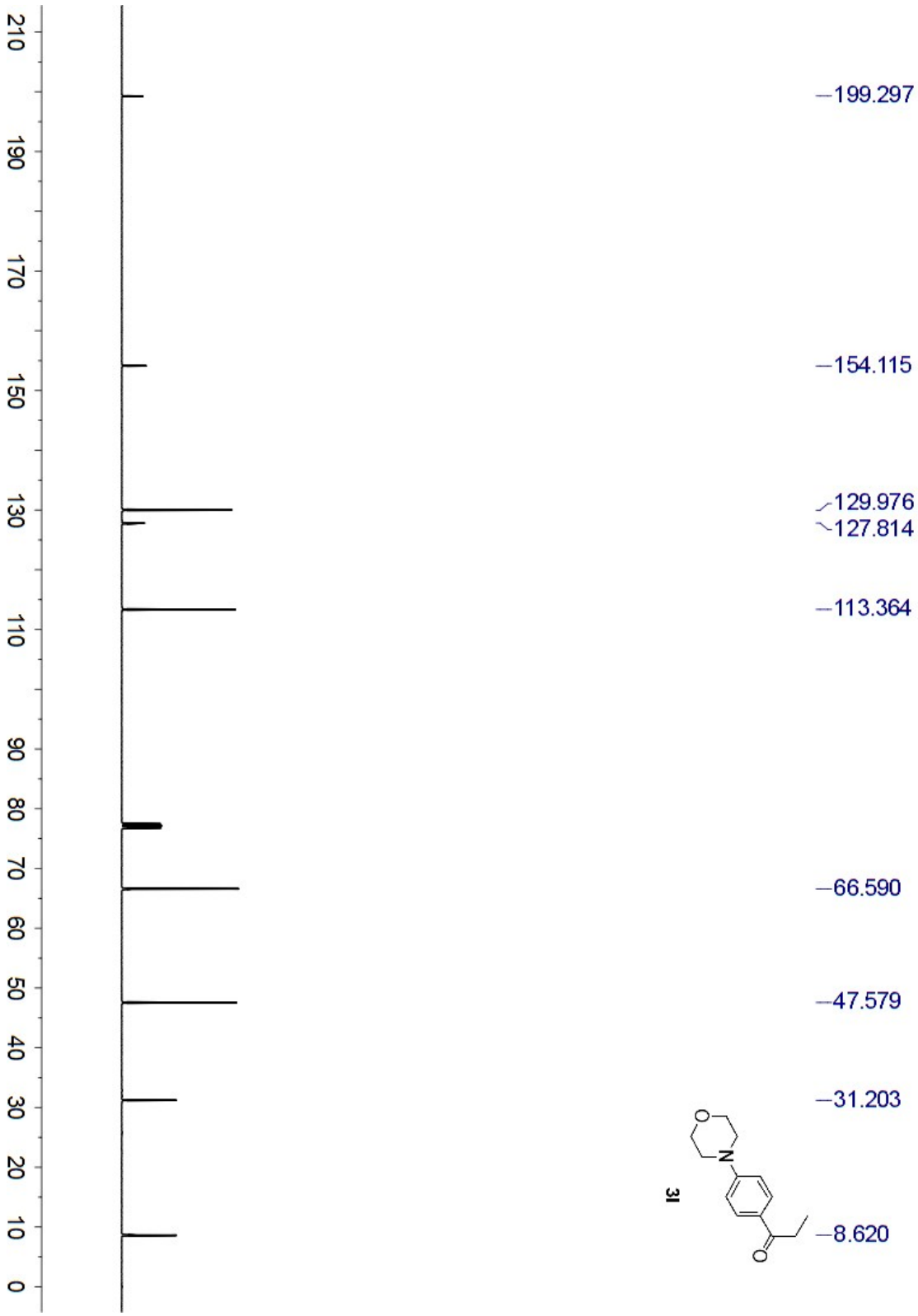

194.876
194.876
151.932
129.247
111.625
111.554
111.479
111.409
25.977
151.932
151.855
149.531
149.454
111.687
111.625
111.554
111.479
111.409
111.345
5.977
3j

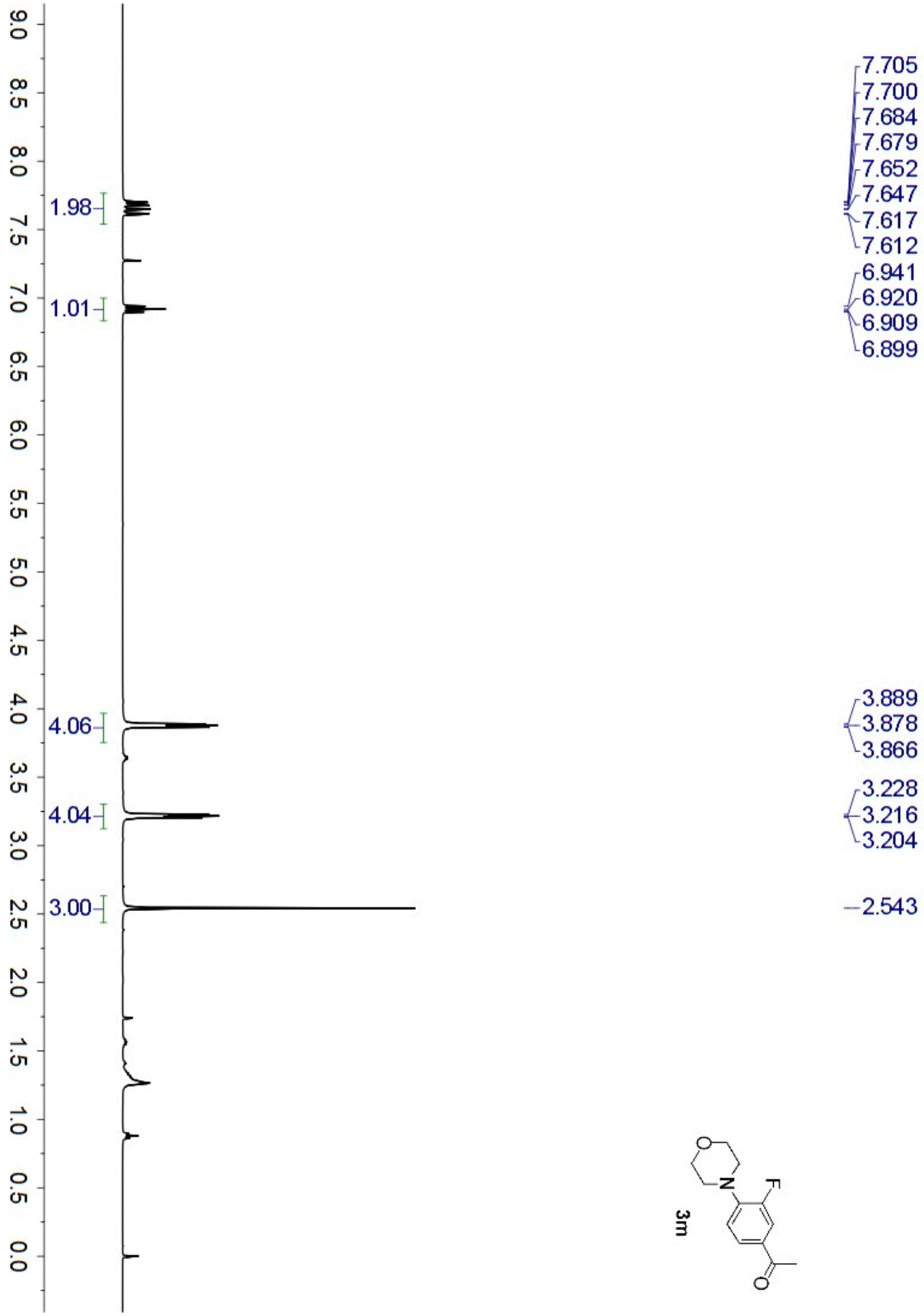
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-132.681
H2N
F
F
O
3j

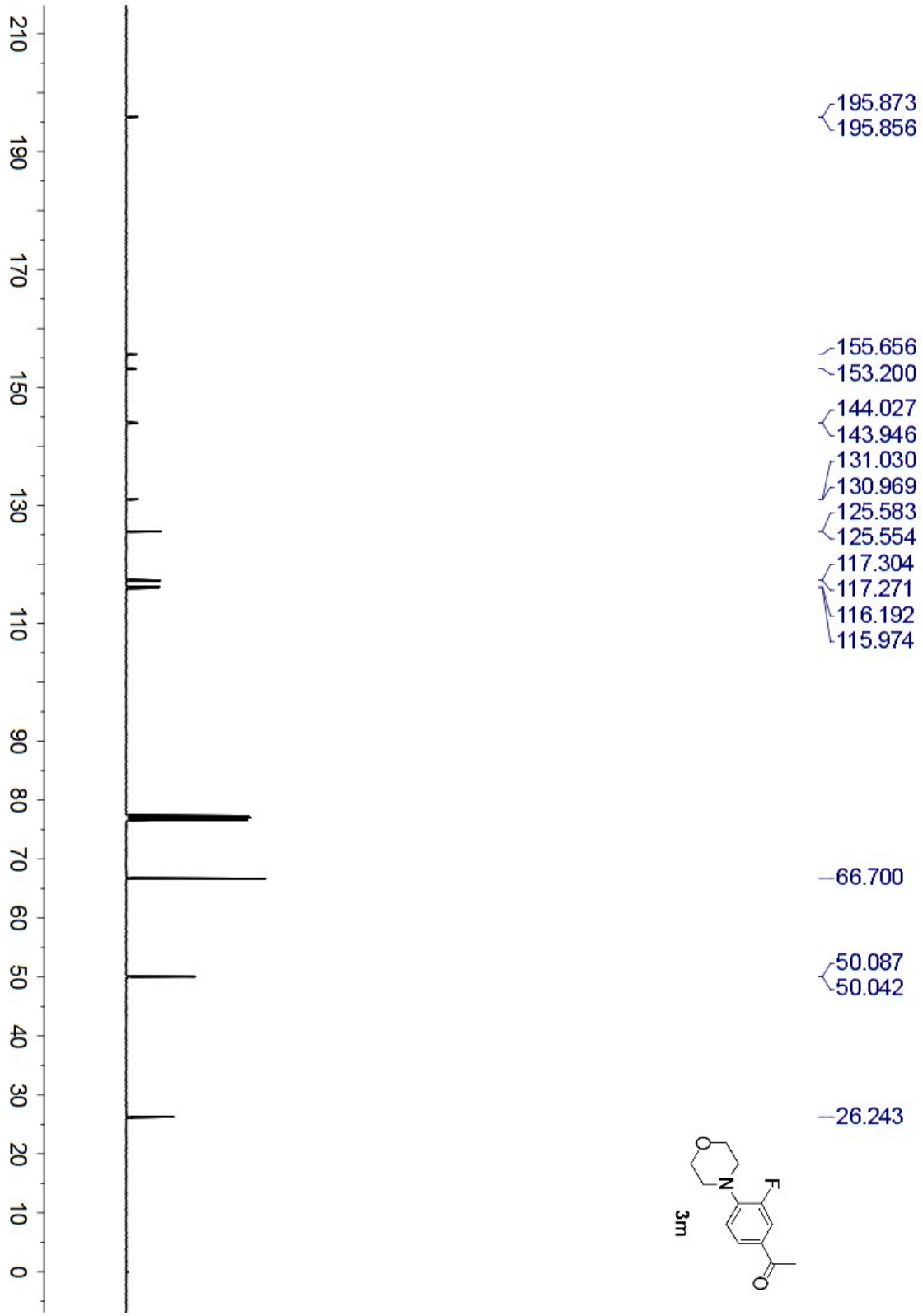

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2.00
1.99
4.11
4.08
3.00
7.906
7.883
6.883
6.861
3.873
3.861
3.849
3.322
3.309
3.297
2.533
O
N
O
3k

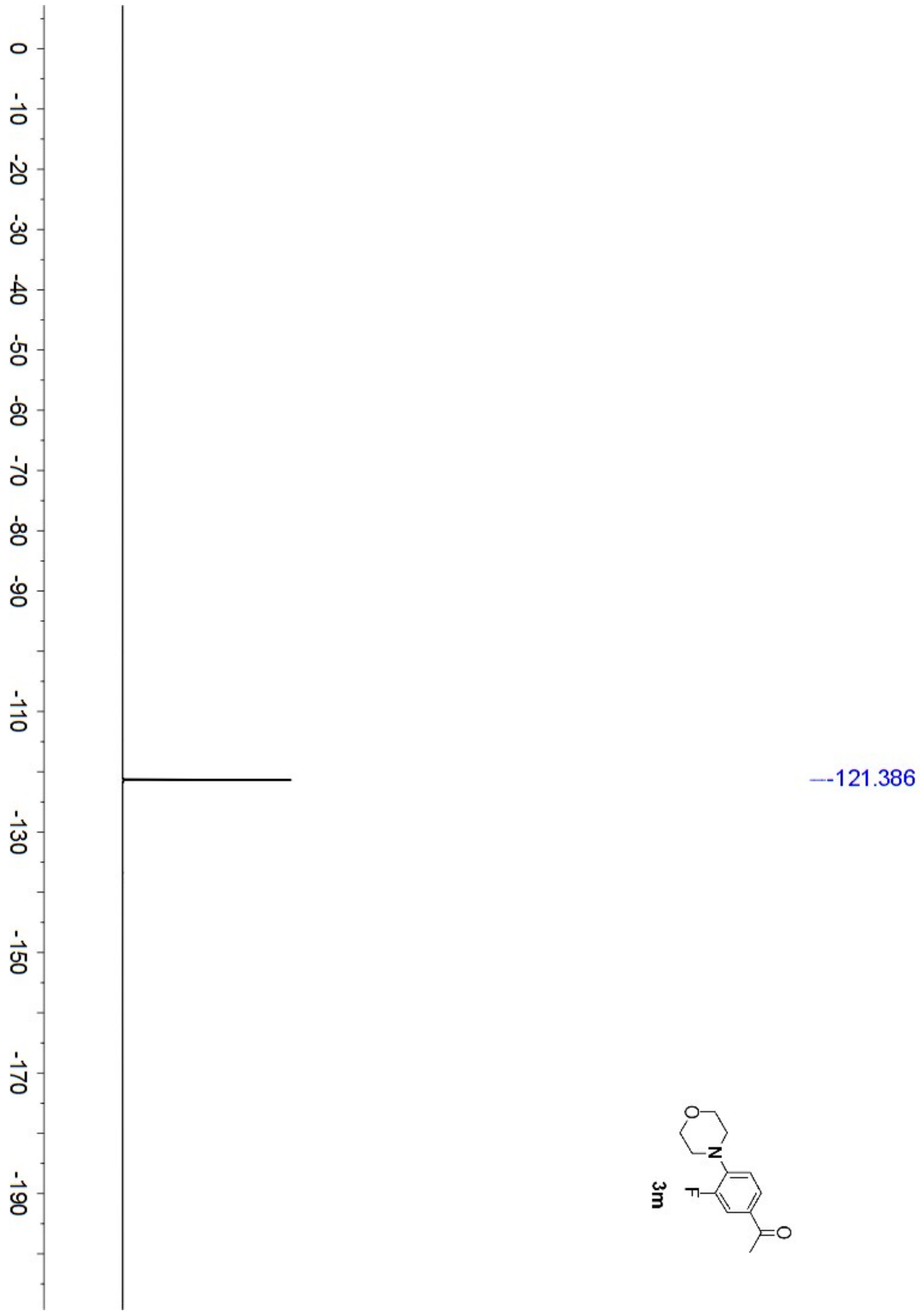

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
196.545
154.196
130.321
128.111
113.244
66.536
47.490
26.134
O
N
O
3k

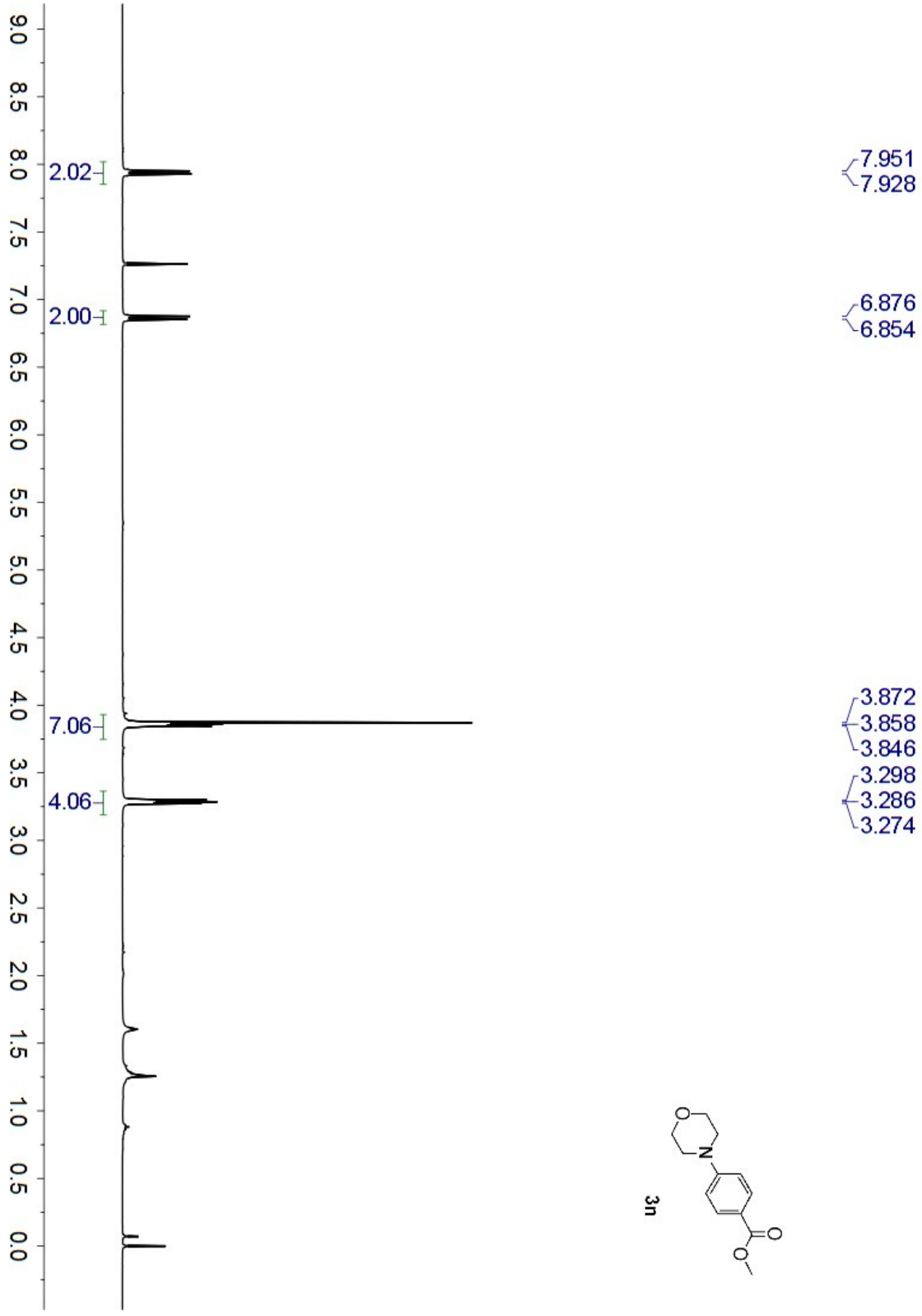

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.93
1.94
3.98
3.96
2.00
3.03
7.913
7.891
6.878
6.855
3.862
3.850
3.837
3.303
3.290
3.278
2.949
2.931
2.913
2.894
1.221
1.203
1.185
3l
N
O
O

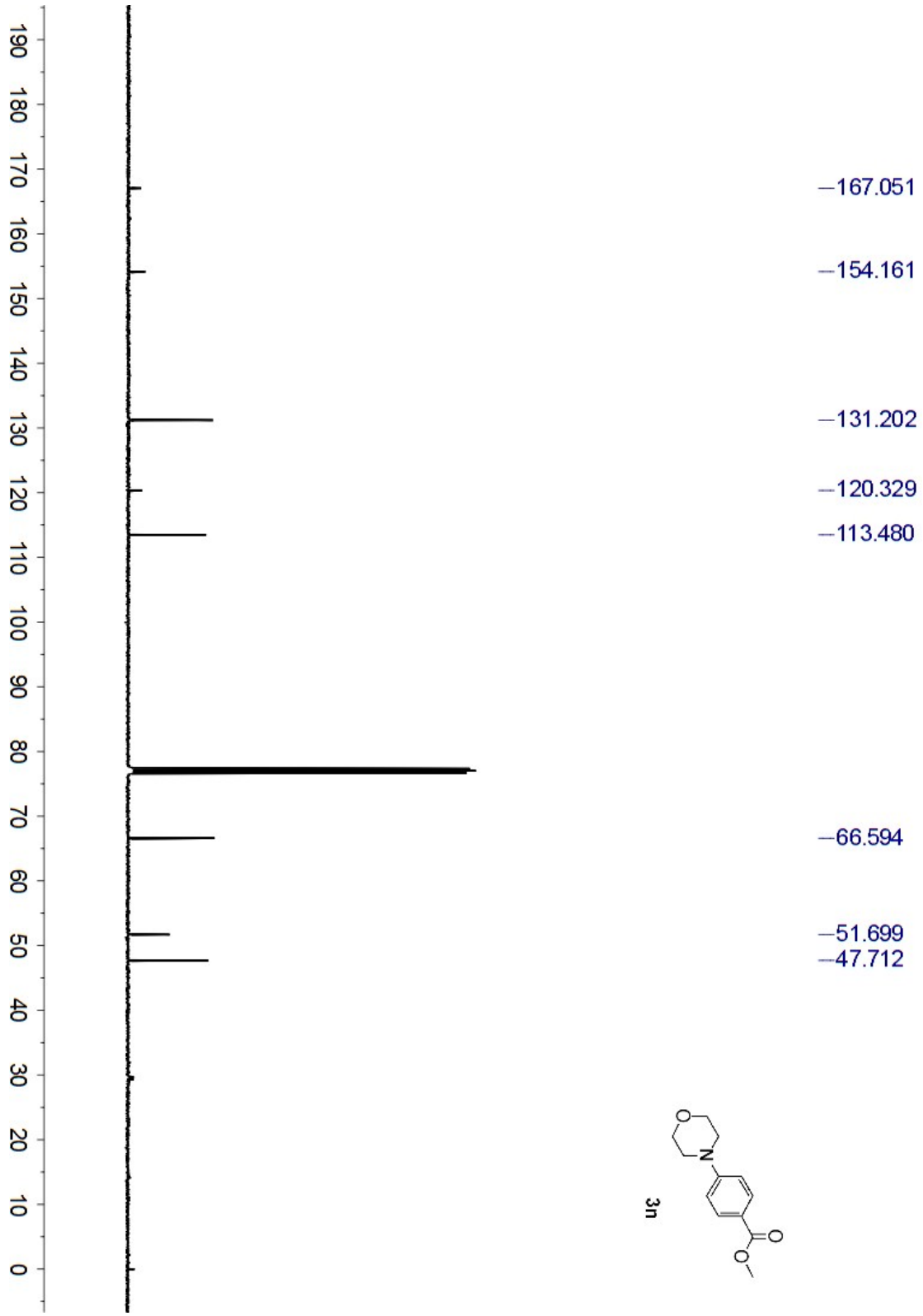

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
199.297
154.115
129.976
127.814
113.364
66.590
47.579
31.203
8.620
N
O
O
3l

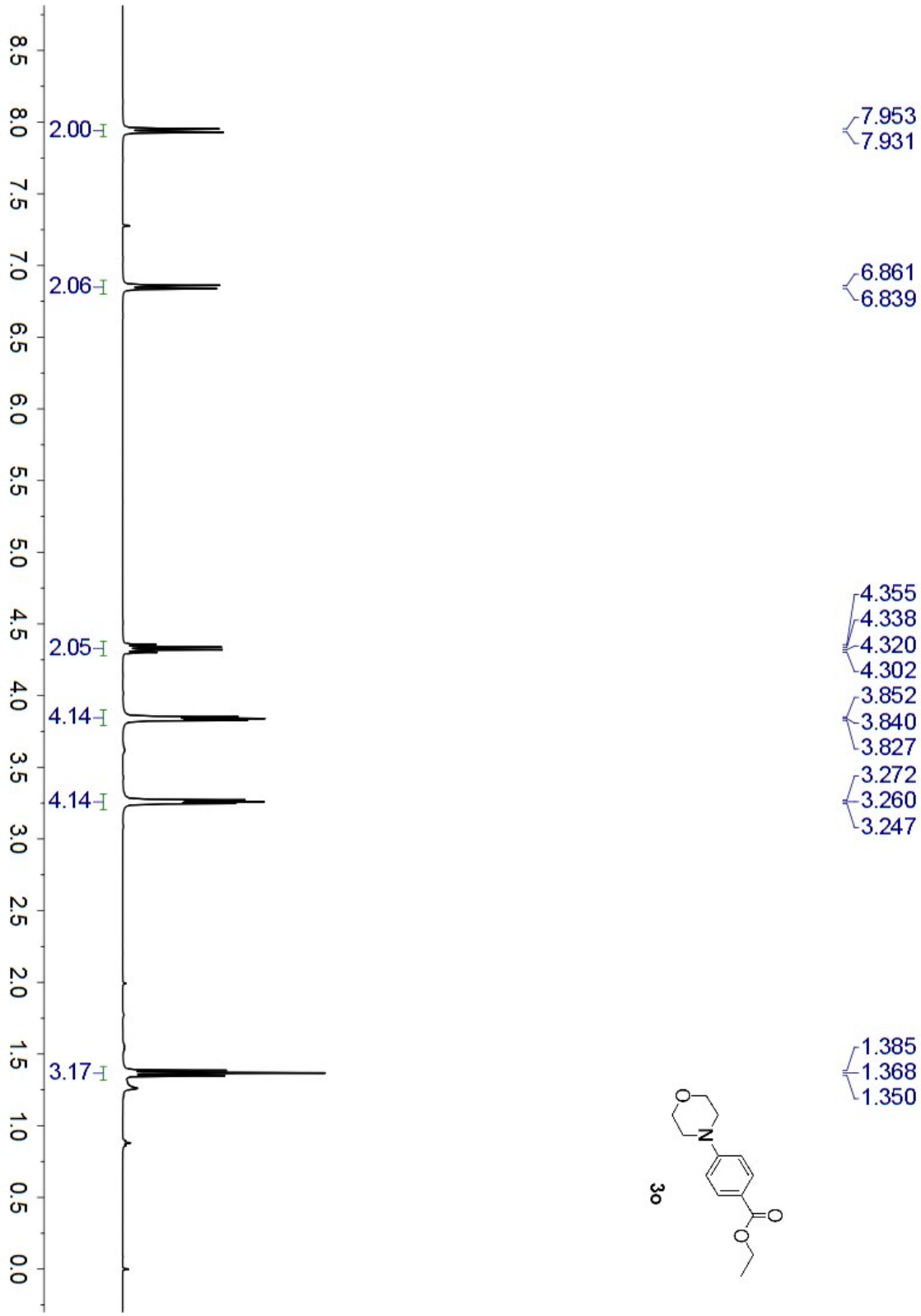

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.98
1.01
4.06
4.04
3.00
7.705
7.700
7.684
7.679
7.652
7.647
7.617
7.612
6.941
6.920
6.909
6.899
3.889
3.878
3.866
3.228
3.216
3.204
2.543
F
N
O
O
3m

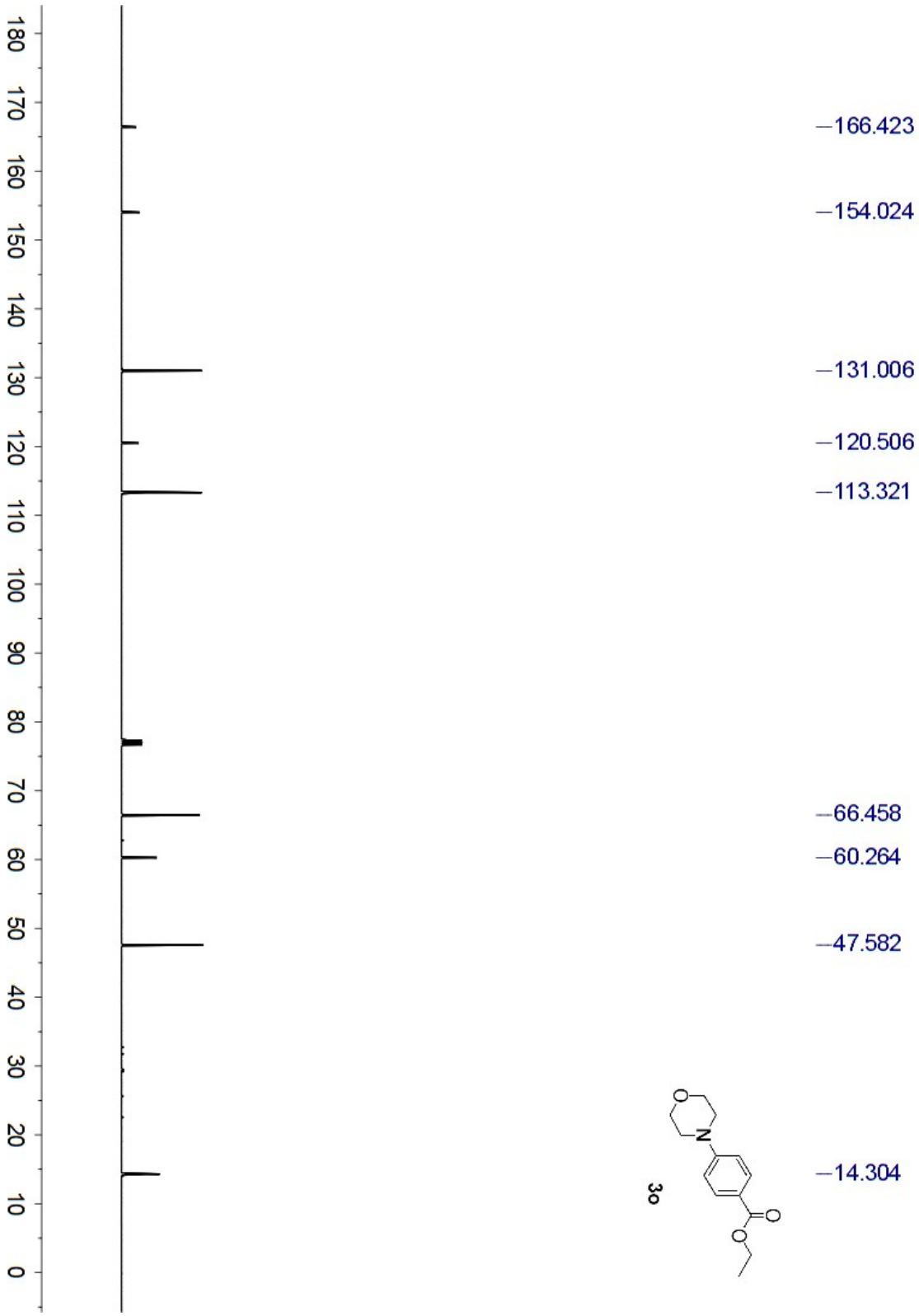

210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
195.873
195.856
155.656
153.200
144.027
143.946
131.030
130.969
125.583
125.554
117.304
117.271
116.192
115.974
66.700
50.087
50.042
26.243
F
N
O
O
3m

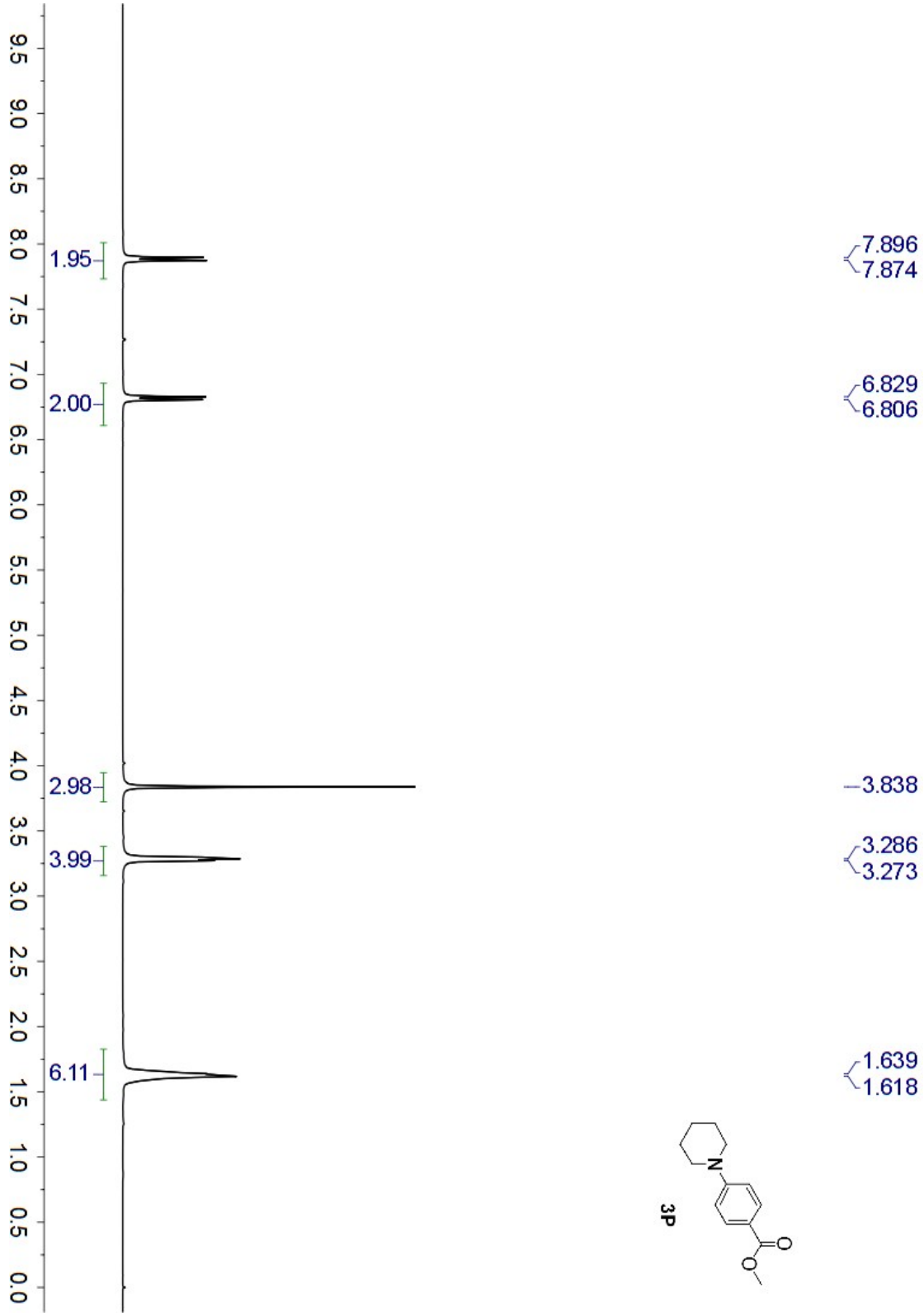

0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-121.386
O
N
F
O
3m

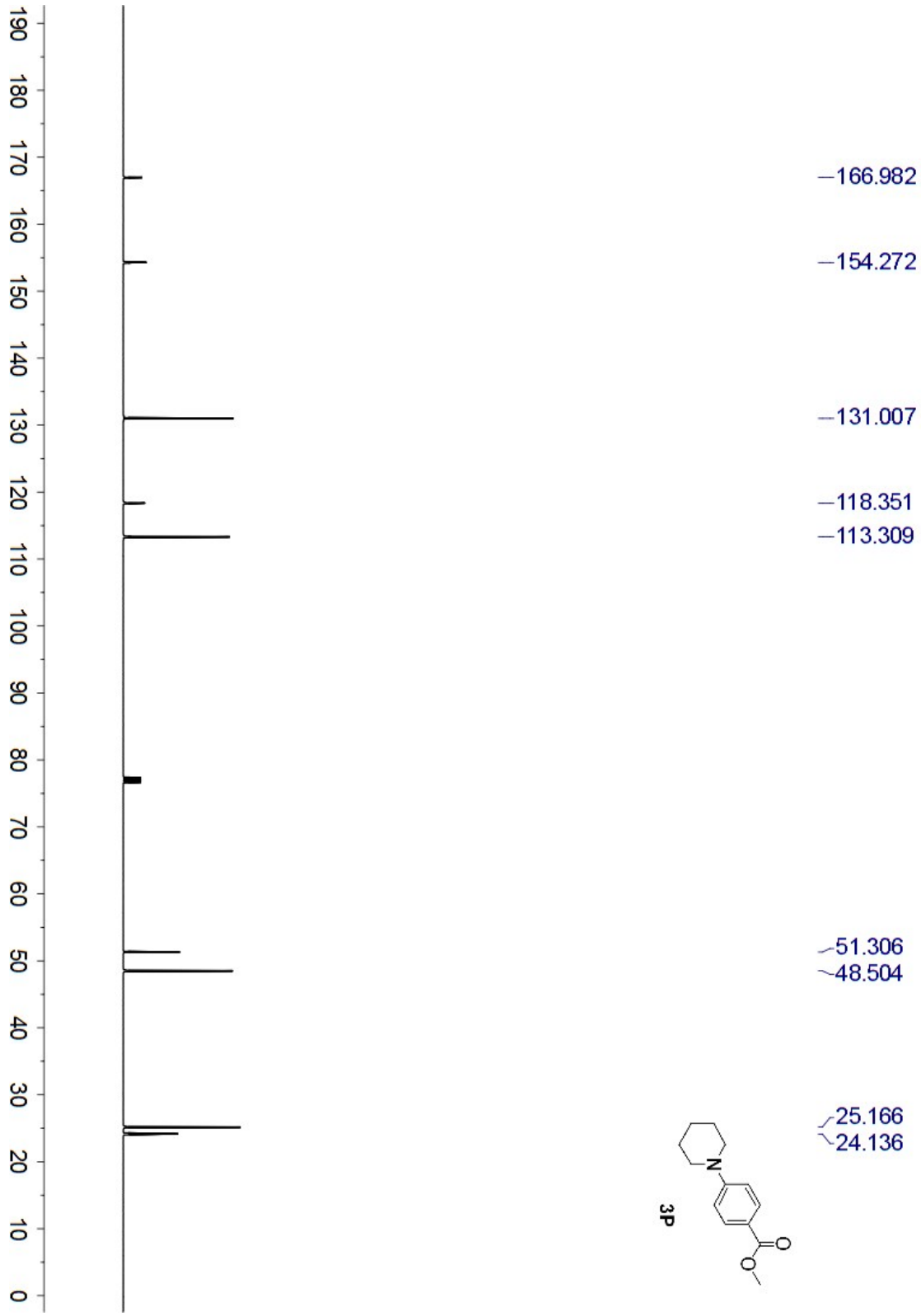

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2.02
2.00
7.06
4.06
7.951
7.928
6.876
6.854
3.872
3.858
3.846
3.298
3.286
3.274
O
N
O
O
O
3n

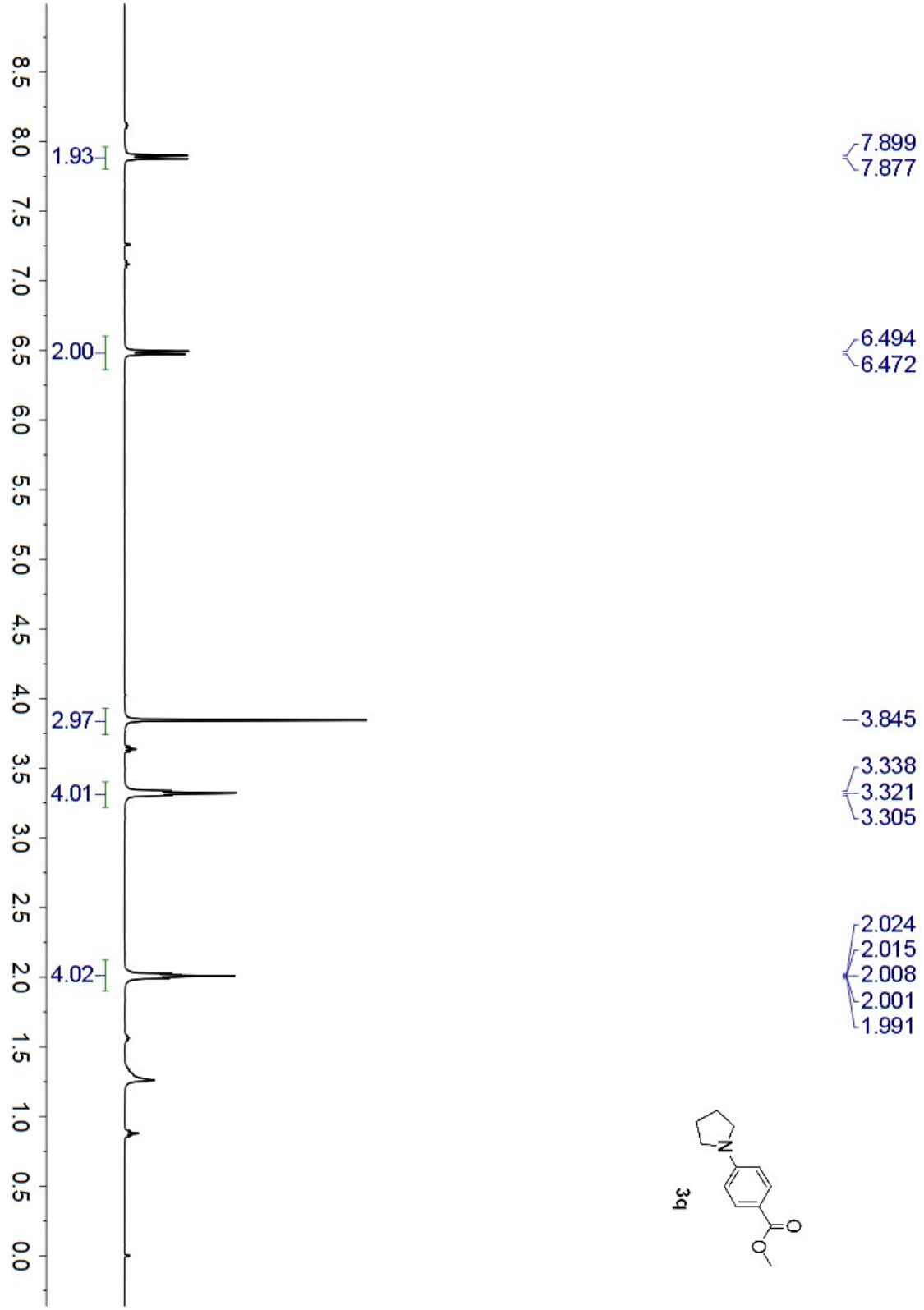

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
167.051
154.161
131.202
120.329
113.480
66.594
51.699
47.712
O
N
O
O
O
3n

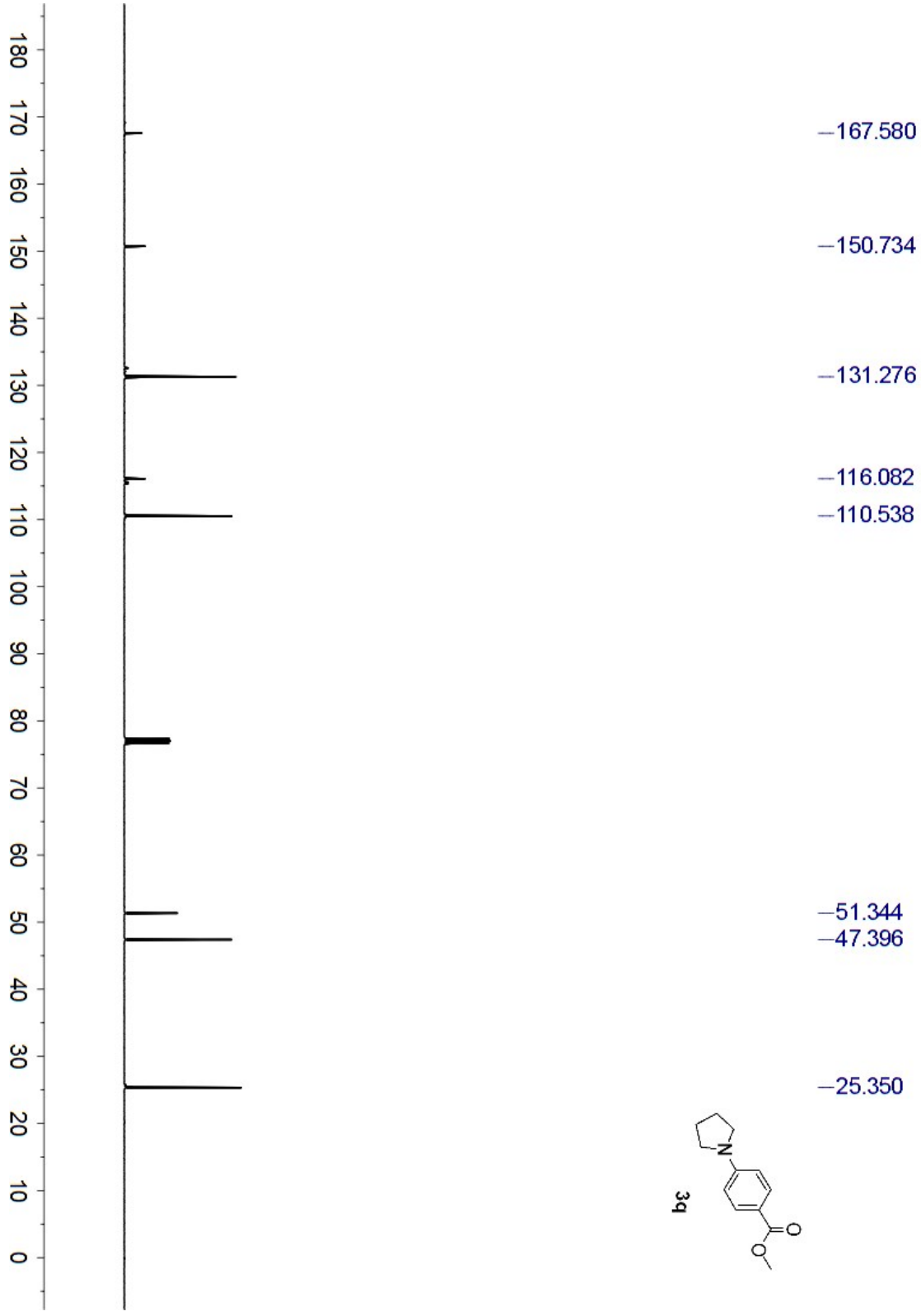

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2.00
2.06
2.05
4.14
4.14
3.17
7.953
7.931
6.861
6.839
4.355
4.338
4.320
4.302
3.852
3.840
3.827
3.272
3.260
3.247
1.385
1.368
1.350
O
N
O
O
3o

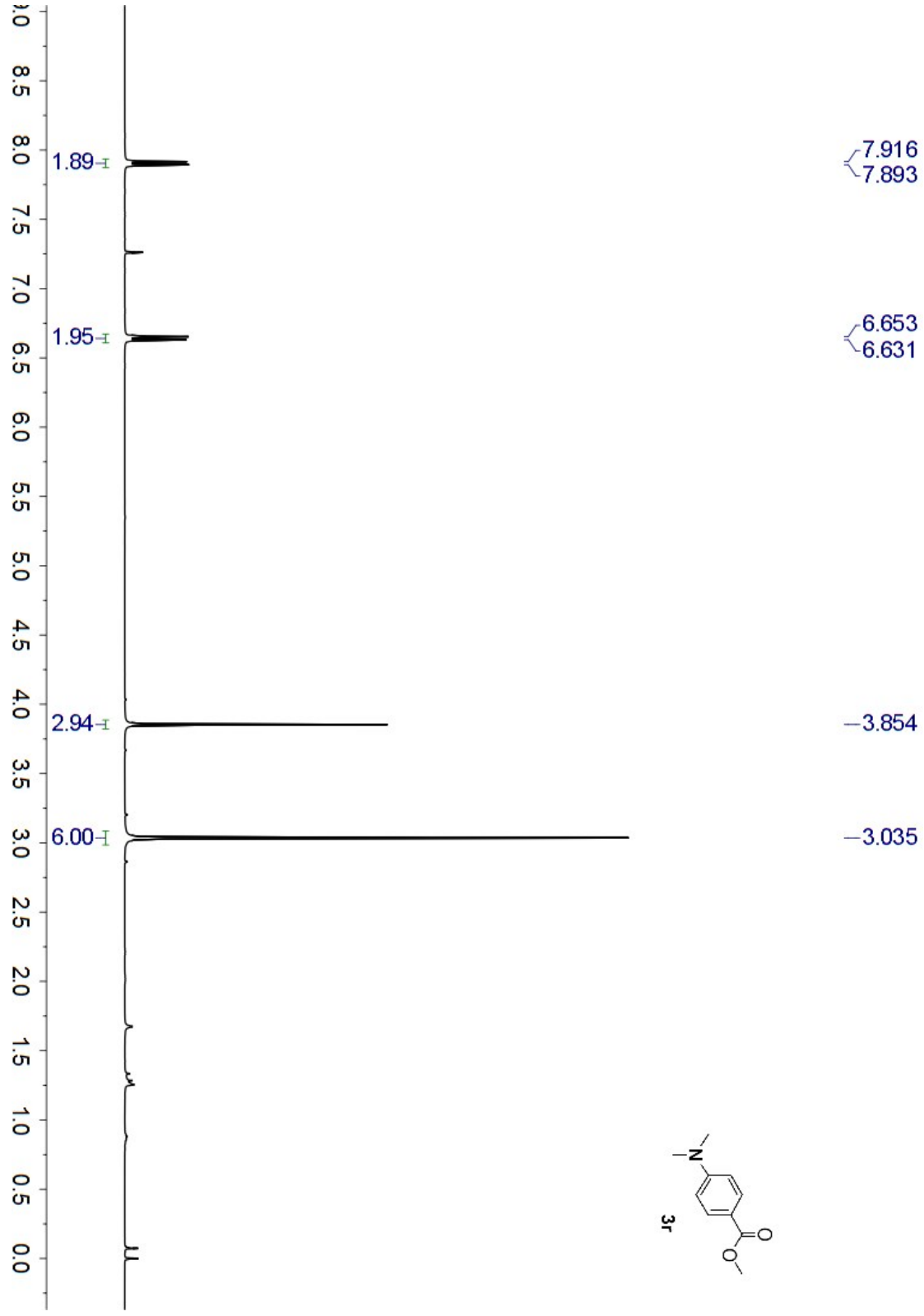

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
166.423
154.024
131.006
120.506
113.321
66.458
60.264
47.582
14.304
O
N
O
O
3o

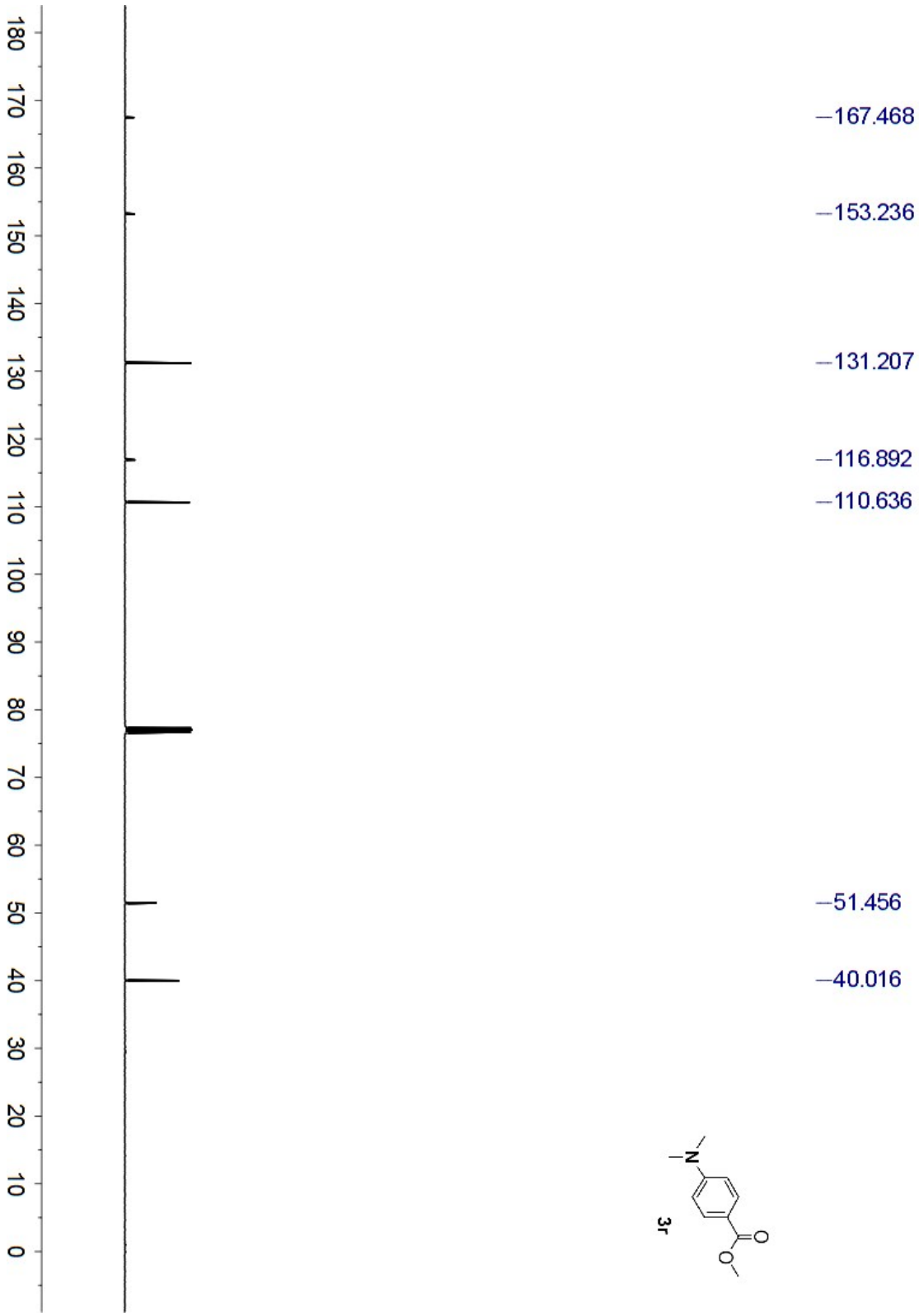

9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.95
2.00
2.98
3.99
6.11
7.896
7.874
6.829
6.806
3.838
3.286
3.273
1.639
1.618
N
O
O
3P


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
166.982
154.272
131.007
118.351
113.309
51.306
48.504
25.166
24.136
N
O
O
3P


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
1.93
2.00
2.97
4.01
4.02
7.899
7.877
6.494
6.472
3.845
3.338
3.321
3.305
2.024
2.015
2.008
2.001
1.991
N
O
O
3q


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
167.580
150.734
131.276
116.082
110.538
51.344
47.396
25.350
N
O
O
3q


1.89
1.95
2.94
6.00
7.916
7.893
6.653
6.631
3.854
3.035
3r


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
167.468
153.236
131.207
116.892
110.636
51.456
40.016
3r