Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

SUPPORTING INFORMATION

Preparation of Benzoyl Fluorides and Benzoic Acids from Phenols via Dearomatization−Rearomatization Strategy

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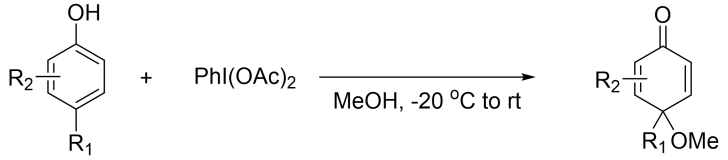
General Information

All reagents were obtained from Adamas, Aladin, Accela, or Acros and used without further purification unless otherwise noted. Solvents were not dried prior to use unless specified as "anhydrous." To prevent moisture, *t*-BuOK was stored and used under inert atmosphere in Glovebox. The products were purified by column chromatography with Huanghai Silica Gel 50-75 um, ultrapure silica gel. ^{1}H and ^{13}C spectra were recorded in $CDCl_3$ (with 0.03% Me_4Si) or DMSO-*d6* using a Bruker 600 or 400 spectrometer. Chemical shifts (δ) are reported in ppm downfield from Me_4Si (δ 0.00 for ^{1}H NMR in $CDCl_3$) or the solvent peak (δ 7.26 for ^{1}H NMR in $CDCl_3$, δ 2.50 for ^{1}H NMR in DMSO-*d6*, δ 77.23 for ^{13}C NMR in $CDCl_3$, and δ 39.52 for ^{13}C NMR in DMSO-*d6*) as an internal reference with coupling constants (*J*) in hertz (Hz). IR spectra were measured on a Shimadzu IRAffinity-1S spectrometer using KBr plates. The high-resolution mass spectra (HRMS) were recorded on Waters SYNAPT G3 spectrometer (ESI).

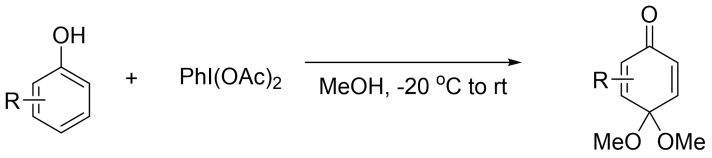
Preparation of compounds 1

General Procedure A for Preparation of Cyclohexadienones:



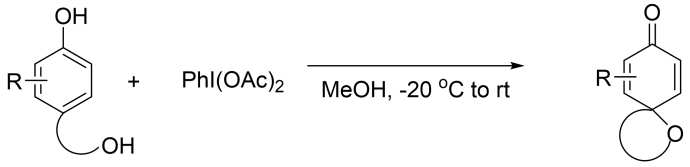
The preparation of cyclohexadienones by phenols dearomatization were accomplished using a known literature procedure.[1] To the solution of phenol (5 mmol) in MeOH (20 mL) was added $PhI(OAc)_2$ (1.2 equiv) in batches at 0 °C, warm to room temperature and stirred until phenol was consumed. The reaction was quenched with sat. $NaHCO_3$ (30 mL), and the resulting mixture was extracted with DCM (15 mL x3). The combined organic layers was washed with brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography to afford the desired cyclohexadienone.

General Procedure B for Preparation of Cyclohexadienones:

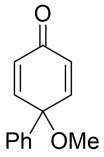


The preparation of cyclohexadienones by phenols dearomatization were accomplished using a known literature procedure.[2] To the solution of phenol (5 mmol) in MeOH (40 mL) was added $PhI(OAc)_2$ (2.2 equiv) in batches at 0 °C, warm to room temperature and stirred until phenol was consumed. The reaction was quenched with sat. $NaHCO_3$ (50 mL), and the resulting mixture was extracted with DCM (15 mL x3). The combined organic layers was washed with brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography to afford the desired cyclohexadienone.

General Procedure C for Preparation of Cyclohexadienones:



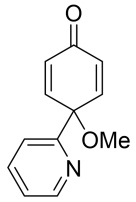
To the solution of phenol (5 mmol) in MeCN (40 mL) was added $PhI(OAc)_2$ (1.2 equiv) in batches at 0 °C, warmed to room temperature and stirred until phenol was consumed. The reaction was quenched with sat. $NaHCO_3$ (50 mL), and the resulting mixture was extracted with DCM (15 mL x3). The combined organic layer was washed with brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography to afford the desired cyclohexadienone.



1a

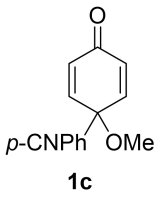
Compound **1a**: Compound **1a** was prepared according to the General Procedure A using commercially available [1,1'-biphenyl]-4-ol (851.1 mg, 5 mmol). The crude product was purified by column chromatography (pet ether: EtOAc = 10:1) to afford 730.8 mg (73%) of compound **1a** as a pale-yellow solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51-7.42 (m, 2H), 7.40-7.26 (m, 3H), 6.80 (d, J = 10.0 Hz, 2H), 6.41 (d, J = 10.0 Hz, 2H), 3.43 (s, 3H). Spectroscopic data was agreement with the literature. (*Org. Lett.* **2022,** *24*, 1812-1816)

Compound **1b**: Compound **1b** was prepared according to the General Procedure A using commercially available 4-(pyridin-2-yl)phenol (856.0 mg, 5 mmol). The crude product was purified by column chromatography (pet ether: EtOAc = 4:1) to afford 492.9 mg (49%) of compound **1b** as a white solid. Mp: 49-51 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 4.8 Hz, 1H), 7.73 (td, J_1 = 7.6, J_2 = 1.2 Hz, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.26-7.19 (m, 1H), 6.86 (d, J = 10.0 Hz, 2H), 6.46 (d, J = 10.0 Hz, 2H), 3.41 (s, 3H). ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.7, 158.8, 149.5, 149.0, 137.5, 131.4, 123.6, 121.3, 77.6, 53.0 ppm; IR (thin film) 1663, 1591, 1460, 1433, 1385, 1350, 1277, 1099, 1075, 857, 716 (cm^{-1}); HRMSMALDI (m/z) calcd for $[C_{12}H_{11}NNaO_2]^+$, 224.0682; found, 224.0692.



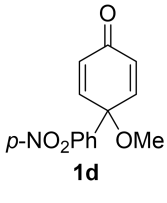
1b

Compound **1c**: Compound **1c** was prepared according to the General Procedure A using 4'-hydroxy-[1,1'-biphenyl]-4-carbonitrile (976.0 mg, 5 mmol). The crude product was purified by column chromatography (pet ether: DCM = 1:2) to afford 843.8 mg (75%) of compound **1c** as a pale-yellow solid. Mp: 84-86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 6.70 (d, J = 10.4 Hz, 2H), 6.43 (d, J = 10.4 Hz, 2H), 3.41 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.0, 149.2, 143.8, 132.7, 131.1, 126.8, 118.5, 112.4, 76.4, 53.1 ppm; IR (thin film) 1660, 1631, 1603, 1388, 1351, 1277, 1166, 1080, 1015, 944, 850, 768 (cm^{-1}); HRMSMALDI (m/z) calcd for $[C_{14}H_{11}NNaO_2]^+$, 248.0682; found, 248.0690.



1c

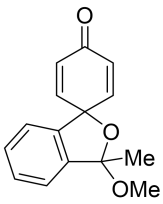
Compound **1d**: Compound **1d** was prepared according to the General Procedure A using 4'-nitro-[1,1'-biphenyl]-4-ol (1.07 g, 5 mmol). The crude product was purified by column chromatography (pet ether: EtOAc = 10:1) to afford 797.0 mg (65%) of compound **1d** as a pale-yellow solid. Mp: 82-84 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8. 8Hz, 2H), 7.64 (d, J = 8.8 Hz, 2H), 6.72 (d, J = 9.6 Hz, 2H), 6.47 (d, J = 9.6 Hz, 2H), 3.44 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.0, 149.1, 147.9, 145.8, 131.2, 127.1, 124.0, 76.5, 53.2 ppm; IR (thin film) 1599, 1519, 1384, 1352, 1276, 1178, 1076, 1013,



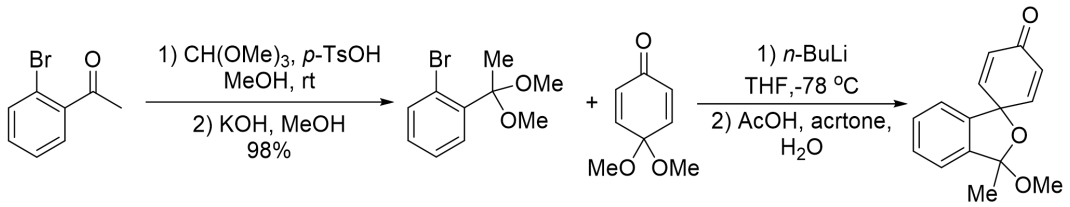
1d

950, 852, 747 (cm^{-1}); HRMSMALDI (m/z) calcd for $[C_{13}H_{11}NNaO_4]^+$, 268.0580; found, 268.0584.

Compound **1e**: Compound **1e** was prepared according to the literature procedure.[4] To a solution of *o*-bromoacetophenone (1.59 g, 8 mmol) in MeOH (20 mL) were added $CH(OMe)_3$ (1.37 mL, 12.0 mmol, 1.5 equiv) and *p*-TsOH (50 mg, 0.29 mmol, 3.6%). Stirred overnight, the reaction mixture was neutralized with 1% KOH solution in MeOH (4 mL), concentrated, and purified by column chromatography (pet ether: EtOAc = 10:1) to afford compound **S1** as colorless oil (1.92 g, 98%).



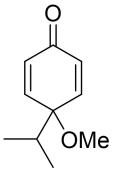
1e



S1 **1e**

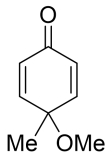
To a solution of **S1** (1.23 g, 5.0 mmol) in THF (20 mL) at -78 °C was added dropwise *n*-BuLi (1.6 M in hexane, 4.1 mL, 6.5 mmol, 1.3 equiv) over 10 min, and the solution was stirred at -78 °C for 2 h. To the mixture was added dropwise 4,4-dimethoxy-2,5-cyclohexadienone (847.9 mg, 5.5 mmol, 1.1 equiv) in THF (5.0 mL) over 10 min, stirred at -78 °C for 1 h and warmed to room temperature. The reaction was quenched with saturated aqueous NH_4Cl (5.0 mL) and extracted with Et_2O (60 mL). The combined organic layer was concentrated in vacuo giving the crude quinol ketal. The crude product was dissolved in acetone (30 mL), 8% aqueous AcOH (6 mL) was added, and the solution was stored at 0 °C for 24 h. After concentration in vacuo, the resulting mixture was extracted with DCM (15 mL x3). The combined organic layer was washed with brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography to afford **1e** (629.9 mg, 52%) as a white solid. ^1H NMR (600 MHz, $CDCl_3$) δ 7.44-7.35 (m, 3H), 7.03 (d, J = 6.6 Hz, 1H), 6.92-6.89 (m, 1H), 6.70-6.66 (m, 1H), 6.25 (d, J = 10.2 Hz, 2H), 3.25 (s, 3H), 1.83 (s, 3H) ppm. Spectroscopic data was agreement with the literature. (*J. Org. Chem.* **1989,** *54* (22), 5364-5371)

Compound **1f**: Compound **1f** was prepared according to the General Procedure A using 4-isopropylphenol (681.0 mg, 5 mmol). The crude product was purified by column chromatography (pet ether: DCM = 1:3) to afford 257.7 mg (31%) of compound **1f** as a pale-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.72 (d, *J* = 10.2 Hz, 2H), 6.41 (d, *J* = 10.2 Hz, 2H), 3.21 (s, 3H), 2.01-1.94 (m, 1H), 0.93 (d, *J* = 7.2 Hz, 6H) ppm.Spectroscopic data was agreement with the literature. (*RSC Adv.* **2015,** *5*, 38499-38502)



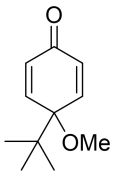
1f

Compound **1g**: Compound **1g** was prepared according to the General Procedure A using *p*-cresol (540.7 mg, 5 mmol). The crude product was purified by column chromatography (pet ether: EtOAc = 10:1) to afford 573.4 mg (83%) of compound **1g** as a pale-yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.77-6.71 (m, 2H), 6.32-6.22 (m, 2H), 3.18 (s, 3H), 1.41 (s, 3H) ppm. Spectroscopic data was agreement with the literature. (*Org. Lett.* **2022,** *24*, 1812-1816)



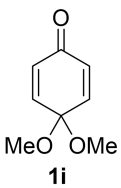
1g

Compound **1h**: Compound **1h** was prepared according to the General Procedure A using 4-(*tert*-butyl)phenol (751.1 mg, 5 mmol). The crude product was purified by column chromatography (pet ether: EtOAc = 10:1) to afford 414.3 mg (46%) of compound **1h** as a pale-yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.87 (d, *J* = 10.2 Hz, 2H), 6.40 (d, *J* = 10.2 Hz, 2H), 3.19 (s, 3H), 1.00 (s, 9H). Spectroscopic data was agreement with the literature. (*RSC Adv.* **2015,** *5*, 38499-38502)



1h

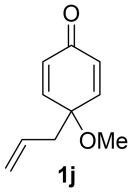
Compound **1i**: Compound **1i** was prepared according to the General Procedure A using 4-methoxyphenol (620.7 g, 5 mmol). The crude product was purified by column chromatography (pet ether: EtOAc = 10:1) to afford 701.5 mg (91%) of compound **1i** as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (d, *J* = 10.4 Hz, 2H), 6.24 (d, *J* = 10.4 Hz, 2H), 3.34 (s,



1i

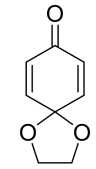
6H). Spectroscopic data was agreement with the literature. (*Org. Lett.* **2018,** *20*, 668-671)

Compound **1j**: Compound **1j** was prepared according to the General Procedure A using 4-allylphenol (670.9 g, 5 mmol). The crude product was purified by column chromatography (pet ether: EtOAc = 10:1) to afford 262.7 mg (32%) of compound **1j** as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.75-6.71 (m, 2H), 6.37-6.32 (m, 2H), 5.73-5.65 (m, 1H), 5.12-5.04 (m, 2H), 3.22 (s, 3H), 2.47 (d, *J* = 7.8 Hz, 2H) ppm. Spectroscopic data was agreement with the literature. (*RSC Adv.* **2015,** *5*, 38499-38502)



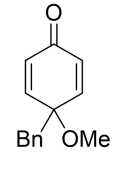
1j

Compound **1k**: Compound **1k** was prepared according to the literature procedure.[3] Added the mixture of 4-methoxyphenol (620.7 mg, 5 mmol, 1.0 equiv) and ethane-1,2-diol (3.1 g, 50 mmol, 10 equiv) in anhydrous DCM (10 mL) to the solution of [Bis(trifluoroacetoxy)iodo]benzene (670.9 g, 5.5 mmol, 1.1 equiv) in anhydrous DCM (10 mL) at 0 °C, then warmed up to room temperature. The reaction was quenched with sat. $NaHCO_3$ (50 mL), and the resulting mixture was extracted with DCM (15 mL x3). The combined organic layer was washed with brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography (pet ether: EtOAc = 10:1) to afford 654.2 mg (86%) of compound **1k** as a pale-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.62 (d, *J* = 10.0 Hz, 2H), 6.16 (d, *J* = 10.0 Hz, 2H), 4.14 (s, 4H). Spectroscopic data was agreement with the literature. (*Org. Lett.* **2012,** *14*, 696-699)



1k

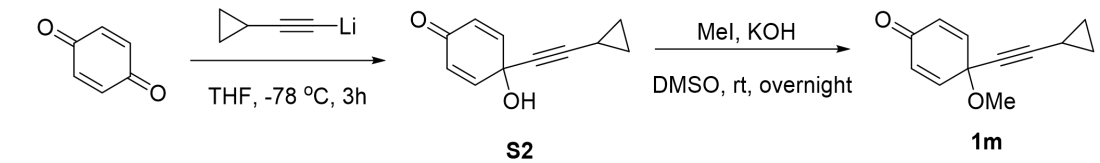
Compound **1l**: Compound **1l** was prepared according to the General Procedure A using 4-benzylphenol (921.0 mg, 5 mmol). The crude product was purified by column chromatography (pet ether: DCM = 2:1) to afford 492.9 mg (46%) of compound **1l** as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.20 (m, 3H), 7.18-7.11 (m, 2H), 6.73 (d, *J* = 10.4 Hz, 2H), 6.29 (d, *J* = 10.4 Hz, 2H), 3.20 (s, 3H), 3.00 (s, 2H) ppm.Spectroscopic data was agreement with



1l

the literature. (*Org. Lett.* **2022**, *24*, 1812-1816)

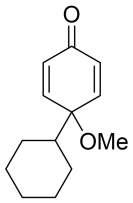
Compound **1m**: To a solution of ethynylbenzene (1.0 mL, 11.7 mmol) in THF (25 mL) was added *n*-BuLi (1.6 M in hexane, 6.8 mL, 10.8 mmol) at -78 °C. After stirring for 1 h at the same temperature, benzoquinone (973 mg, 9.0 mol) was added, the resulting mixture was stirred at -78 °C for 3 h. After the starting material was consumed, the mixture was quenched with saturated NH_4Cl solution, extracted with ethyl acetate, washed with brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under the reduced pressure and the residue was purified by column chromatography on silica gel (pet ether: EtOAc = 6:1) to afford **S2** (1.49 g, 95% yield) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.86 (d, *J* = 9.6 Hz, 2H), 6.13 (d, *J* = 10.2 Hz, 2H), 3.70 (s, 1H), 1.28-1.24 (m, 1H), 0.84-0.79 (m, 2H), 0.73-0.71 (m, 2H) ppm. Spectroscopic data was agreement with the literature. (*Org. Lett*. **2015**, 17, 5926-5929)



To a solution of **S2**(1.49 g, 8.55 mmol) in DMSO (15 mL) was added MeI (1.82g, 12.83 mmol, 1.5 equiv) and KOH (719.8 mg, 12.83 mmol, 1.5 equiv) under room temperature. Stirred overnight, the reaction mixture was neutralized with diluted hydrochloric acid, the organic phase was separated and the aqueous phase was extracted with EtOAc (30 mL x 3). Then the combined organic phases were washed with brine and dried over Na_2SO_4 and concentrated. Flash column chromatography (pet ether: EtOAc = 5: 1) afforded 743 mg (46%) of compound **1m** as white solid. Mp: 39-41 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (d, *J* = 10.0 Hz, 2H), 6.23 (d, *J* = 10.0 Hz, 2H), 3.28 (s, 3H), 1.30 - 1.18 (m, 1H), 0.84 - 0.76 (m, 2H), 0.74 - 0.68 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.9, 145.9, 128.9, 91.7, 69.9, 67.8, 52.2, 8.7, -0.4 ppm; IR (thin film) 1670, 1630, 1605, 1463, 1390, 1351, 1235, 1165, 1091, 1050,

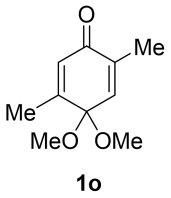
931, 914, 871 (cm^{-1}); HRMSMALDI (m/z) calcd for $[C_{12}H_{12}NaO_2]^+$, 211.0730; found, 211.0740.

Compound **1n**: Compound **1n** was prepared according to the General Procedure A using 4-cyclohexylphenol (881.3 mg, 5 mmol). The crude product was purified by column chromatography (pet ether: EtOAc = 10:1) to afford 546.7 mg (53%) of compound **1n** as a pale-yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.74-6.71 (m, 2H), 6.40-6.36 (m, 2H), 3.20 (s, 3H), 1.89-1.85 (m, 2H), 1.78-1.73 (m, 2H), 1.68-1.62 (m, 2H), 1.23-1.16 (m, 2H), 1.12-1.04 (m, 1H), 0.96-0.89 (m, 2H) ppm. Spectroscopic data was agreement with the literature. (*RSC Adv.* **2015,** *5*, 38499-38502)



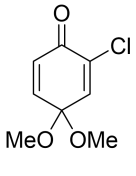
1n

Compound **1o**: Compound **1o** was prepared according to the General Procedure B using 2,5-dimethylphenol (610.9 mg, 5 mmol). The crude product was purified by column chromatography (pet ether: EtOAc = 15:1) to afford 555.8 mg (61%) of compound **1o** as a white solid. Mp: 53-55 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.47 (s, 1H), 6.17 (s, 1H), 3.16 (s, 6H), 1.90 (s, 3H), 1.87 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.8, 155.9, 139.6, 139.2, 123.0, 96.1, 51.0, 16.4, 15.5 ppm; IR (thin film) 1684, 1640, 1454, 1392, 1370, 1271, 1239, 1205, 1160, 1118, 1081, 1054, 959, 742 (cm^{-1}); HRMSMALDI (m/z) calcd for $[C_{10}H_{14}NaO_3]^+$, 205.0835; found, 205.0839.



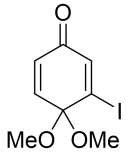
1o

Compound **1p**: Compound **1p** was prepared according to the General Procedure A using 2-chloro-4-methoxyphenol (792.9 mg, 5 mmol). The crude product was purified by column chromatography (pet ether: EtOAc = 15:1) to afford 867.6 mg (92%) of compound **1p** as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (s, 1H), 6.86 (d, J = 10.4 Hz, 1H), 6.36 (d, J = 10.4 Hz, 1H), 3.39 (s, 6H) ppm. Spectroscopic data was agreement with the literature. (*Chem. Sci.*, **2011**,*2*, 1086-1089)



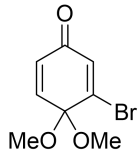
1p

Compound **1q**: Compound **1q** was prepared according to the General Procedure B using 3-iodophenol (1.10 g, 5 mmol). The crude product was purified by column chromatography (pet ether: EtOAc = 10:1) to afford 756.0 mg (54%) of compound **1q** as a pale-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 2.0 Hz, 1H), 6.96 (d, J = 10.0 Hz, 1H), 6.52 (dd, J_1 = 10.0, J_2 = 2.0 Hz, 1H), 3.26 (s, 6H). Spectroscopic data was agreement with the literature. (*Eur. J. Org. Chem.* **2016**, 3809–3816)



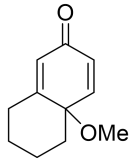
1q

Compound **1r**: Compound **1r** was prepared according to the General Procedure B using 3-bromophenol (865.0 mg, 5 mmol). The crude product was purified by column chromatography (pet ether: EtOAc = 15:1) to afford 862.3 mg (74%) of compound **1r** as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91-6.83 (m, 2H), 6.49 (dd, J_1 = 10.0, J_2 = 2.0 Hz, 1H), 3.30 (s, 6H). Spectroscopic data was agreement with the literature. (*Eur. J. Org. Chem.* **2016**, 3809–3816)



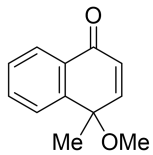
1r

Compound **1s**: Compound **1s** was prepared according to the General Procedure A using 5,6,7,8-tetrahydronaphthalen-2-ol (1.48 g, 5 mmol). The crude product was purified by column chromatography (pet ether: EtOAc = 10:1) to afford 427.8 mg (48%) of compound **1s** as a pale-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.64 (dd, J_1 = 10.0, J_2 = 2.0 Hz, 1H), 6.30 (dt,J_1 = 10.0, J_2 = 2.0 Hz, 1H), 6.18 (d, J = 2.0 Hz, 1H), 3.03 (s, 3H), 2.44-2.27 (m, 2H), 2.14-2.06 (m, 1H), 2.03-1.82 (m, 2H), 1.62-1.54 (m, 1H), 1.42-1.25 (m, 2H). Spectroscopic data was agreement with the literature. (*Org. Lett.* **2018,** *20*, 696-699)



1s

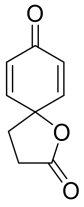
Compound **1t**: Compound **1t** was prepared according to the General Procedure A using 4-methylnaphthalen-1-ol (741.0 mg, 5 mmol). The crude product was purified by column chromatography (pet ether: EtOAc = 10:1) to afford 715.3 mg (76%) of compound **1t** as a pale-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 4.4 Hz, 2H),



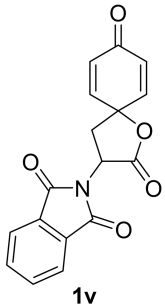
1t

7.50-7.39 (m, 1H), 6.92 (d, J = 10.4 Hz, 1H), 6.49 (d, J = 10.4 Hz, 1H), 3.00 (s, 3H), 1.59 (s, 3H). Spectroscopic data was agreement with the literature. (*Adv. Synth. Catal.* **2016**, *358*, 3683-3687)

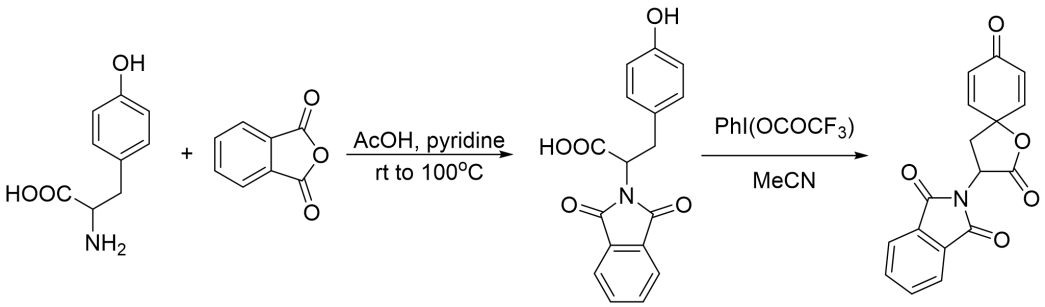
Compound **1u**: Compound **1u** was prepared according to the General Procedure C using 3-(4-hydroxyphenyl)propanoic acid (830.9 mg, 5 mmol). The crude product was purified by column chromatography (pet ether: EtOAc = 10:1) to afford 689.5 mg (84%) of compound **1u** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (d, J = 10.0 Hz, 2H), 6.26 (d, J = 10.0 Hz, 2H), 2.81-2.72 (m, 2H), 2.36 (t, J = 8.4 Hz, 2H). Spectroscopic data was agreement with the literature. (*Angew. Chem., Int. Ed.* **2019**, *58*, 9811-9815)


1u

Compound **1v**: Compound **1v** was prepared according to the literature procedure.[5]


1v

To the mixture of DL-Tyrosine (1.81 g, 10 mmol, 1 equiv), phthalic anhydride (1.48 g, 10 mmol, 1 equiv) in glacial acetic acid (20 mL) was added pyridine until the mixture substances were solved totally. Stirred overnight, warmed up to 100 ℃ and stirred for another 5h. Then removed the solvent under reduced pressure and cooled the mixture, poured the mixture onto crushed ice, collected the precipitate by filtration and recrystallized to afford **S3**.

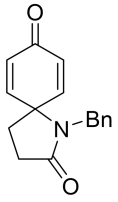


S3 **1v**

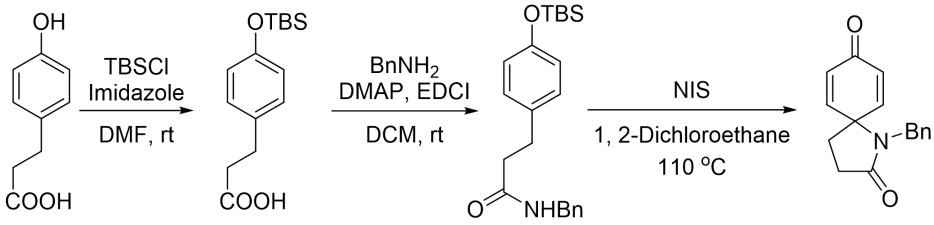
To the solution of **S3** (1.56 g, 5 mmol, 1.o equiv) in MeCN (20 mL) and pyridine (20 mL)was added $PhI(OCOCF_3)_2$ (2.58 g, 6 mmol, 1.2 equiv) in batches at 0 ℃, warm to room temperature and stirred until phenol was consumed. The reaction was

quenched with sat. $NaHCO_3$ (50 mL), and the resulting mixture was extracted with DCM (15 mL x3), and the combined organic layer was washed with brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (pet ether: EtOAc = 3:1) to afford 1.01 g (65%) of compound **1v** as a white solid. Mp: 207-209 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.04-7.74 (m, 4H), 7.54 (dd, J_1 = 10.0, J_2 = 3.2 Hz, 1H), 7.11 (dd, J_1 = 10.0, J_2 = 3.2 Hz, 1H), 6.33 (dd, J_1 = 10.0, J_2 = 2.0 Hz, 1H), 6.29 (dd, J_1 = 10.0, J_2 = 2.0 Hz, 1H), 5.78 (t, J = 10.4 Hz, 1H), 2.83-2.63 (m, 2H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 184.0, 171.9, 166.6, 146.9, 146.6, 135.1, 131.1, 129.0, 127.7, 123.6, 76.4, 47.0, 34.2 ppm; IR (thin film) 1791, 1776, 1710, 1677, 1591, 1402, 1344, 1275, 1253, 1211, 1174, 1125, 1022, 932, 881, 863, 715 (cm^{-1}); HRMSMALDI (m/z) calcd for $[C_{17}H_{11}NNaO_5]^+$, 332.0529; found, 332.0533.

Compound **1w**: Compound **1w** was prepared according to literature procedure.[6] To the mixture of 3-(4-Hydroxyphenyl)propanoic acid (3.32 g, 20 mmol, 1.0 equiv) and *tert*-butyldimethylsilyl chloride (6.64 g, 44 mmol, 2.2 equiv) in DMF (40 mL) was added imidazole (4.08 g, 60 mmol, 3.0 equiv) slowly. The crude product was purified by column chromatography (pet ether: EtOAc = 4:1) to afford 4.21 g (75%) of **S4** as a colorless solid.



1w



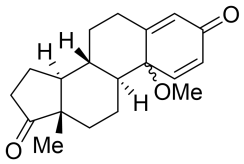
S4 **S5** **1w**

To the mixture of **S4** (2.80 g, 10 mmol, 1.0 equiv), DMAP (1.83 g, 15 mmol, 1.5 equiv) and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride(EDCI) (2.49 g, 13 mmol, 1.3 equiv) in DCM (40 mL) was added benzylamine (1.07 g, 10 mmol, 1.0 equiv), stirred at room temperature for 4 h. The reaction was quenched with H_2O (50 mL), and the resulting mixture was extracted with DCM (20 mL x3), and the combined organic layer was washed with brine (30 mL), dried over Na_2SO_4,

filtered, and concentrated in vacuo. The crude product was purified by column chromatography (pet ether: EtOAc = 4:1) to afford 2.99 g (81%) of compound **S5** as a white solid.

A mixture of **S5** (1.48 g, 4 mmol, 1.0 equiv) and NIS (2.70 g, 12 mmol, 3 equiv.) in 1,2-dichloroethane (20 mL) in pressure tube (purged with Ar) was heated at 110 °C for 10 hours. The reaction mixture was cooled to room temperature, diluted with 50 mL dichloromethane and treated with saturated aqueous $Na_2S_2O_3$ solution. The mixture was extracted with dichloromethane (20 mL x3), and the combined organic layer was washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by column chromatography (pet ether: EtOAc = 1:1) to afford 790.3 mg (78%) of compound **1w** as a pale-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.12 (m, 5H), 6.60-6.48 (m, 2H), 6.20-6.03 (m, 2H), 4.29 (s, 2H), 2.72-2.58 (m, 2H), 2.17-2.07 (m, 2H) ppm. Spectroscopic data was agreement with the literature. (*Org. Biomol. Chem.* **2019**, *17*, 6762-6770)

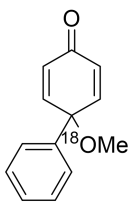
Compound **1x**: Compound **1x** was prepared according to the General Procedure A



1x

using 1,3,5(10)-Estratrien-3-ol-17-one (1.35 g, 5 mmol). The crude product was purified by column chromatography (pet ether: EtOAc = 10:1) to afford 811.1 mg (55%) of compound **1x** as a pale-yellow foam, which is a 6.7:1 mixture of diastereoisomers. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.96 (d, J = 10.4 Hz, 1H), 6.83 (d, J = 10.4 Hz, 0.15H), 6.35 (d, J = 10.4 Hz, 1H), 6.31 (d, J = 10.4 Hz, 0.15H), 6.23 (s, 0.15H), 6.17 (s, 1H), 3.05 (s, 3.45H), 2.52-1.05 (m, 17.25H), 0.94 (s, 3H), 0.77 (s, 0.45H) ppm; HRMSMALDI (m/z) calcd for $[C_{19}H_{25}NO_3]^+$, 301.1798; found, 301.1801.

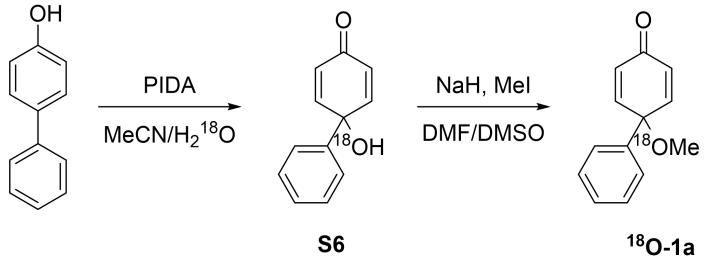
Compound **^{18}O-1a**: To the mixture of [1,1'-biphenyl]-4-ol (255.0 mg, 1.5 mmol),



^{18}O-1a

MeCN (3 mL), and $H_2{}^{18}O$ (1 mL) was added $PhI(OAc)_2$ (1.5 equiv) in batches at 0 °C, warmed to room temperature and stirred until phenol was consumed. The reaction was quenched with sat. $NaHCO_3$ (10 mL), and the resulting mixture was extracted with DCM (10 mL x3). The combined

organic layers was washed with brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography to afford 101.6 mg (36%) of compound **S6**.

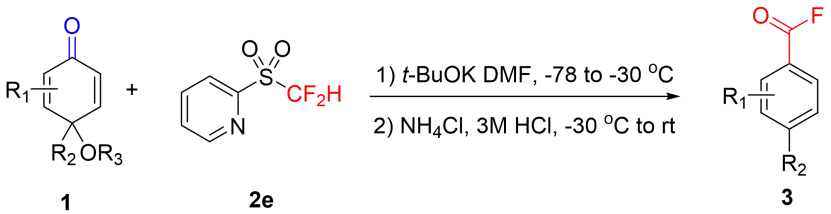


S6 **^{18}O-1a**

The solution of **S6** (101.6 mg, 0.54 mmol) in anhydrous DMF (5.0 mL) was cooled to -78 °C under inert atmosphere, added NaH (60%, 32.4 mg, 0.81 mmol, 1.5 equiv) to the mixture and stirred 20 mins. Then added anhydrous DMSO (0.5 mL) and MeI (0.81 mmol, 1.5 equiv) to the mixture at -78 °C, warmed to room temperature and stirred over night. The reaction was quenched with sat. $NaHCO_3$ (10 mL), and the resulting mixture was extracted with DCM (10 mL x3). The combined organic layers was washed with brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography to afford 86.3 mg (79%) of compound **^{18}O-1a**. Both **S6** and **^{18}O-1a** were confirmed by MS.

Preparation of compounds 3

General Procedure D for Preparation of Benzoyl Fluorides:

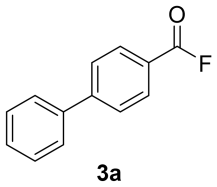


1 **2e** **3**

To the mixture of cyclohexadienones **1** (1.2 mmol, 1.2 equiv) and 2-((difluoromethyl)sulfonyl)pyridine **2e** (1.0 mmol, 1.0 equiv) in anhydrous DMF (5.0 mL) under inert atmosphere was added the solution of *t*-BuOK (1.3 mmol, 1.3 equiv) in anhydrous DMF (2.0 mL) slowly at -78 °C, then warmed up to -30 °C slowly. The reaction was quenched with sat. NH_4Cl (5 mL) and 3M HCl (5 mL) at -30 °C, warmed up to room temperature and extracted with Et_2O (10 x3), the

combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Flash column chromatography afforded product **3**.

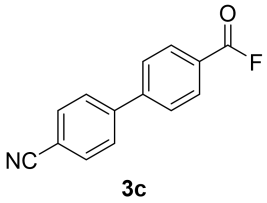
Compound **3a**: Compound **3a** was prepared according to the General Procedure D.



3a

The crude product was purified by column chromatography (pet ether: DCM = 8:1) to afford 162.2 mg (81%) of compound **3a** as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.67-7.63 (m, 2H), 7.51 (t, *J* = 7.2 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.6 (d, *J* = 341.3 Hz), 148.3, 139.4, 132.2 (d, *J* = 3.8 Hz), 129.3, 129.0, 127.8, 127.5, 123.7 (d, *J* = 61.1 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ 18.13 (s, 1F) ppm. Spectroscopic data was agreement with the literature. (*Org. Lett.* **2021,** *23*, 847-852)

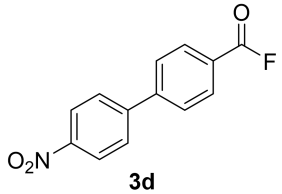
Compound **3c**: Compound **3c** was prepared according to the General Procedure D.



3c

The crude product was purified by column chromatography (pet ether: DCM = 1:1) to afford 168.9 mg (75%) of compound **3c** a white solid. Mp: 153-155 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, *J* =7.8 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.76-7.69 (m, 4H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.1 (d, *J* = 341.9 Hz), 146.1, 143.8, 133.1, 132.4 (d, *J* = 3.8 Hz), 128.3, 128.1, 125.1 (d, *J* = 61.5 Hz), 118.6, 112.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ 18.80 (s, 1F) ppm; IR (thin film) 1803, 1598, 1352, 1257, 1182, 1127, 1040, 995, 865, 827, 765 (cm^{-1}); HRMS-MALDI (m/z) calcd for $[C_{14}H_9FNO]^+$, 226.0663; found, 226.0670.

Compound **3d**: Compound **3d** was prepared according to the General Procedure D.

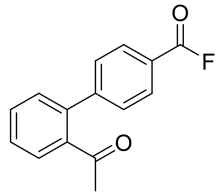


3d

The crude product was purified by column chromatography (pet ether: DCM = 2:1) to afford 181.4 mg (74%) of compound **3d** as a white solid. Mp: 194-196 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (d, *J* = 9.0 Hz, 2H), 8.17 (d, *J* = 8.4 Hz, 2H), 7.81-7.76 (m, 4H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.1 (d, *J* = 342.0 Hz),

148.2, 145.7, 145.6, 132.4 (d, J = 3.6 Hz), 128.5, 128.3, 125.3 (d, J = 61.7 Hz), 124.6 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ 18.90 (s, 1F) ppm; IR (thin film) 1804, 1604, 1517, 1388, 1345, 1259, 1108, 1034, 1001, 855, 840, 741 (cm^{-1}); HRMS-MALDI (m/z) calcd for $[C_{13}H_8FKNO_3]^+$, 284.0120; found, 284.0119.

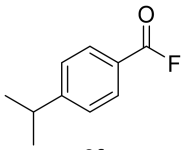
Compound **3e**: Compound **3e** was prepared according to the General Procedure D.



3e

The crude product was purified by column chromatography (pet ether: EtOAc = 10:1) to afford 196.2 mg (81%) of compound **3e** as a white solid. Mp: 79-81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 7.6 Hz, 2H), 7.66 (dd, J_1 = 7.6, J_2 = 1.2 Hz, 1H), 7.57 (td, J_1 = 7.6, J_2 = 1.2 Hz, 1H), 7.54-7.44 (m, 3H), 7.37 (dd, J_1 = 7.6, J_2 = 1.2 Hz, 1H), 2.22 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.9, 157.3 (d, J = 341.6 Hz), 148.6, 140.1, 139.3, 131.8, 131.7, 131.4, 130.6, 129.7, 128.7 (d, J = 5.5 Hz), 124.2 (d, J = 61.3 Hz), 30.4 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ 18.43 (s, 1F) ppm; IR (thin film) 1808, 1681, 1603, 1353, 1246, 1183, 1034, 1006, 956, 762, 696, 597 (cm^{-1}); HRMS-MALDI (m/z) calcd for $[C_{15}H_{11}FNaO_2]^+$, 265.0635; found, 265.0634.

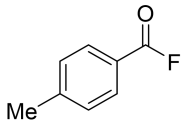
Compound **3f**: Compound **3f** was prepared according to the General Procedure D. The



3f

crude product was purified by column chromatography (pet ether: DCM = 8:1) to afford 121.3 mg (73%) of compound **3f** as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 3.00 (hept, J = 6.8 Hz, 1H), 1.29 (d, J = 6.8 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6 (d, J = 340.7 Hz), 157.4, 131.8 (d, J = 4.0 Hz), 127.4 (d, J = 1.0 Hz), 122.6 (d, J = 60.6 Hz), 34.6, 23.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ 17.50 (s, 1F) ppm. Spectroscopic data was agreement with the literature. (*Organometallics* **2022**, *41*, 883-891)

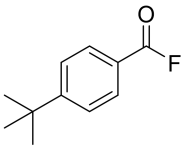
Compound **3g**: Compound **3g** was prepared according to the General Procedure D. The crude product was purified by column chromatography (pet ether: DCM = 8:1) to afford 118.8 mg (86%) of compound **3g** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$)



3g

δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.7 (d, *J* = 340.7 Hz), 146.8, 131.7 (d, *J* = 4.0 Hz), 130.0 (d, *J* = 0.8 Hz), 122.4 (d, *J* = 60.6 Hz), 22.1 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ 17.38 (s, 1F) ppm. Spectroscopic data was agreement with the literature. (*Organometallics* **2022**, *41*, 883-891)

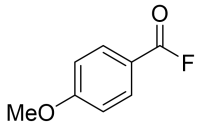
Compound **3h**: Compound **3h** was prepared according to the General Procedure D.



3h

The crude product was purified by column chromatography (pet ether: DCM = 10:1) to afford 135.2 mg (75%) of compound **3h** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 9.0 Hz, 2H), 7.54 (d, *J* = 9.0 Hz, 2H), 1.36 (s, 9H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.7, 157.6 (d, *J* = 340.8 Hz), 131.6 (d, *J* = 3.9 Hz), 126.3, 122.3 (d, *J* = 60.6 Hz), 35.6, 31.1 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ 17.65 (s, 1F) ppm. Spectroscopic data was agreement with the literature. (*Organometallics* **2022**, *41*, 883-891)

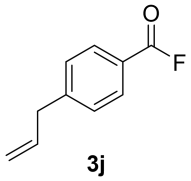
Compound **3i**: Compound **3i** was prepared according to the General Procedure D. The



3i

crude product was purified by column chromatography (pet ether: DCM = 8:1) to afford 140.3 mg (91%) of compound **3i** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.0 Hz, 2H), 6.96 (dd, J_1 = 9.0, J_2 = 1.2 Hz, 2H), 3.87 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.4, 157.4 (d, *J* = 337.8 Hz), 133.8 (d, *J* = 3.9 Hz), 116.9 (d, *J* = 61.5 Hz), 114.6, 55.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ 15.88 (s, 1F) ppm. Spectroscopic data was agreement with the literature. (*J. Am. Chem. Soc.* **2022**, *144*, 9413-9420)

Compound **3j**: Compound **3j** was prepared according to the General Procedure D. The

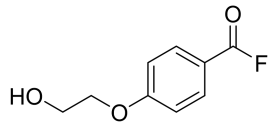


3j

crude product was purified by column chromatography (pet ether: DCM = 8:1) to afford 139.6 mg (85%) of compound **3j** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 6.00-5.91 (m, 1H), 5.22-5.08 (m, 2H), 3.48 (d, *J* = 6.6 Hz, 2H) ppm;

^{13}C NMR (150 MHz, $CDCl_3$) δ 157.6 (d, *J* = 341.1 Hz), 148.7, 135.9, 131.8 (d, *J* = 3.9 Hz), 129.5, 123.1 (d, *J* = 60.6 Hz), 117.4, 40.4 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ 17.72 (s, 1F) ppm; IR (thin film) 2812, 1809, 1712, 1595, 1381, 1351, 1119, 909, 762, 619 (cm^{-1}); HRMS-MALDI (m/z) calcd for $[C_{10}H_{10}FO]^+$, 165.0710; found, 165.0715.

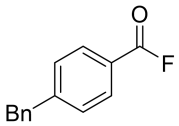
Compound **3k**: Compound **3k** was prepared according to the General Procedure D.



3k

The crude product was purified by column chromatography (pet ether: EtOAc = 2:1) to afford 167.6 mg (91%) of compound **3k** as a white solid. Mp: 62-64 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.0 Hz, 2H), 6.99 (d, *J* = 9.0 Hz, 2H), 4.17 (t, *J* = 4.8 Hz, 2H), 4.01 (t, *J* = 4.8 Hz, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.5, 157.4 (d, *J* = 338.1 Hz), 134.0 (d, *J* = 4.1 Hz), 117.4 (d, *J* = 61.5 Hz), 115.1, 69.9, 61.3 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ 16.20 (s, 1F) ppm; IR (thin film) 1798, 1605, 1381, 1349, 1277, 1255, 1175, 1080, 687, 629 (cm^{-1}); HRMS-MALDI (m/z) calcd for $[C_9H_9FNaO_3]^+$, 207.0428; found, 207.0422.

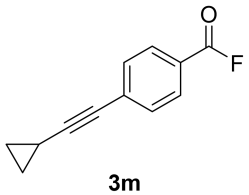
Compound **3l**: Compound **3l** was prepared according to the General Procedure D. The



3l

crude product was purified by column chromatography (pet ether: EtOAc = 6:1) to afford 184.2 mg (86%) of compound **3l** as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.29-7.24 (m, 4H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.16-7.10 (m, 2H), 4.00 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6 (d, *J* = 341.0 Hz), 149.7, 139.6, 131.9 (d, *J* = 4.0 Hz), 129.8, 129.2, 128.9, 126.8, 122.9 (d, *J* = 60.7 Hz), 42.2. ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ 17.86 (s, 1F) ppm; IR (thin film) 1806, 1606, 1353, 1257, 1182, 1118, 1075, 1032, 1011, 908, 740, 726 (cm^{-1}); HRMS-MALDI (m/z) calcd for $[C_{14}H_{12}FO]^+$, 215.0867; found, 215.0860.

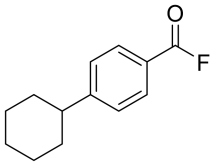
Compound **3m**: Compound **3m** was prepared according to the General Procedure D.



3m

The crude product was purified by column chromatography (pet ether: EtOAc = 2:1) to afford 169.4 mg (90%) of compound **3m** as a white solid. Mp: 45-47 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 1.54-1.42 (m, 1H), 0.97-0.89 (m, 2H), 0.87-0.81 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2 (d, *J* = 341.1 Hz), 132.2, 131.7, 131.4 (d, *J* = 3.9 Hz), 123.4(d, *J* = 61.3 Hz), 99.6, 75.2, 9.2, 0.5 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ 17.96 (s, 1F) ppm; IR (thin film) 1806, 1606, 1353, 1253, 1172, 1027, 1005, 955, 908, 852, 758 (cm^{-1}); HRMS-MALDI (m/z) calcd for $[C_{12}H_{10}FO]^+$, 189.0710; found, 189.0705.

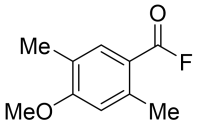
Compound **3n**: Compound **3n** was prepared according to the General Procedure D.



3n

The crude product was purified by column chromatography (pet ether: DCM = 10:1) to afford 169.1 mg (82%) of compound **3n** as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 2.65-2.56 (m, 1H), 1.91-1.84 (m, 4H), 1.81-1.74 (m, 1H), 1.50-1.35 (m, 4H), 1.33-1.22 (m, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.7 (d, *J* = 340.8 Hz), 156.6, 131.8 (d, *J* = 3.9 Hz), 127.8, 122.6 (d, *J* = 60.5 Hz), 45.1, 34.2, 26.8, 26.2 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ 16.47 (s, 1F) ppm. Spectroscopic data was agreement with the literature. (*Org. Lett.* **2021,** *23*, 847-852)

Compound **3o**: Compound **3o** was prepared according to the General Procedure D.

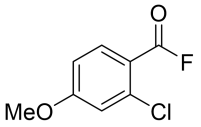


3o

The crude product was purified by column chromatography (pet ether: DCM = 8:1) to afford 83.8 mg (46%) of compound **3o** as a white solid. Mp: 69-71 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (s, 1H), 6.71 (s, 1H), 3.90 (s,3H), 2.62 (s, 3H), 2.19 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.8, 157.0 (d, *J* = 338.4 Hz), 144.7 (d, *J* = 7.2 Hz), 135.0, 125.0, 115.0 (d, *J* = 56.6 Hz), 113.4 (d, *J* = 4.4 Hz), 55.8, 22.4, 15.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$)

δ 26.50 (s, 1F); IR (thin film) 1794, 1611, 1510, 1375, 1340, 1262, 1167, 1116, 1073, 964, 902, 865, 763 (cm^{-1}); HRMS-MALDI (m/z) calcd for $[C_{10}H_{12}FO_2]^+$, 183.0816; found, 183.0808.

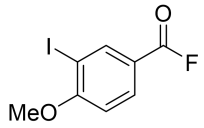
Compound **3p**: Compound **3p** was prepared according to the General Procedure D.



3p

The crude product was purified by column chromatography (pet ether: DCM = 8:1) to afford 86.7 mg (46%) of compound **3p** as a white solid. Mp: 42-44 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, J = 9.0 Hz, 1H), 7.05 (dd, J_1 = 2.4, J_2 = 1.2 Hz, 1H), 6.89 (dd, J_1 = 9.0, J_2 = 2.4 Hz, 1H), 3.89 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 164.9, 154.5 (d, J = 337.5 Hz), 139.3 (d, J = 4.8 Hz), 135.7 (d, J = 2.4 Hz), 117.6 (d, J = 3.8 Hz), 115.4 (d, J = 61.6 Hz), 113.3, 56.2 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ 28.72 (s, 1F); IR (thin film) 1812, 1599, 1496, 1380, 1349, 1245, 1065, 1028, 995, 868, 753, 682, 607 (cm^{-1}); HRMS-MALDI (m/z) calcd for $[C_8H_6ClFO_2]$, 188.0040; found, 188.0049.

Compound **3q**: Compound **3q** was prepared according to the General Procedure D.

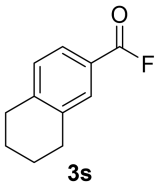


3q

The crude product was purified by column chromatography (pet ether: DCM = 6:1) to afford 168.0 mg (60%) of compound **3q** as a white solid. Mp: 63-65 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.44 (d, J = 2.4 Hz, 1H), 8.05-8.00 (m, 1H), 6.89 (d, J = 9.0 Hz, 1H), 3.99 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.7, 156.1 (d, J = 339.0 Hz), 143.0 (d, J = 3.9 Hz), 134.0 (d, J = 3.8 Hz), 118.9 (d, J = 62.1 Hz), 110.6, 86.2, 57.1 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ 16.67 (s, 1F) ppm; IR (thin film) 1798, 1592, 1491, 1386, 1350, 1315, 1270, 1236, 1014, 825, 750, 660, 613 (cm^{-1}); HRMS-MALDI (m/z) calcd for $[C_8H_6FIO_2]$, 279.9397; found, 279.9396.

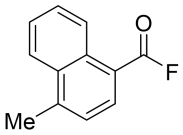
Compound **3s**: Compound **3s** was prepared according to the General Procedure D. The crude product was purified by column chromatography (pet ether: DCM = 10:1) to afford 99.8 mg (56%) of compound **3s** as a colorless oil. ^{1}H NMR (600 MHz,

$CDCl_3$) δ 7.74-7.67 (m, 2H), 7.17 (d, J = 7.8 Hz, 1H), 2.85-2.79 (m, 4H), 1.85-1.80 (m, 4H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.8 (d, J = 340.8 Hz), 146.0, 138.3, 132.4 (d, J = 3.9 Hz), 129.9, 128.3 (d, J = 3.8 Hz), 122.0 (d, J = 60.0 Hz), 29.9, 29.3, 22.8, 22.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ 17.32 (s, 1F) ppm; IR (thin film) 2938, 1806, 1607, 1430, 1350, 1262, 1233, 1165, 1130, 1032, 855, 746, 624 (cm^{-1}); HRMS-MALDI (m/z) calcd for $[C_{11}H_{11}FNaO]^+$, 201.0686; found, 201.0686.



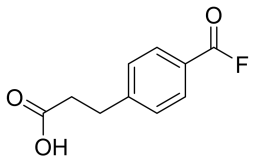
3s

Compound **3t**: Compound **3t** was prepared according to the General Procedure D. The crude product was purified by column chromatography (pet ether: DCM = 6:1) to afford 103.5 mg (55%) of compound **3t** as a white solid. Mp: 64-66 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 9.07 (d, J = 8.4 Hz, 1H), 8.25 (dd, J_1 = 7.2, J_2 = 2.4 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.71 (dd, J_1 = 8.4, J_2 = 7.2 Hz, 1H), 7.64 (dd, J_1 = 8.4, J_2 = 7.2 Hz, 1H), 7.41 (d, J = 7.2 Hz, 1H), 2.80 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.7 (d, J = 340.8 Hz), 144.6, 133.8 (d, J = 2.4 Hz), 133.2 (d, J = 3.9 Hz), 132.4 (d, J = 7.4 Hz), 128.9, 127.0, 125.9, 125.9, 125.0, 118.8 (d, J = 55.8 Hz), 20.6 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ 28.75 (s, 1F) ppm; IR (thin film) 1791, 1514, 1383, 1351, 1244, 1226, 1172, 1087, 984, 907, 763 (cm^{-1}); HRMS-MALDI (m/z) calcd for $[C_{12}H_{10}FO]^+$, 189.0710; found, 189.0716.



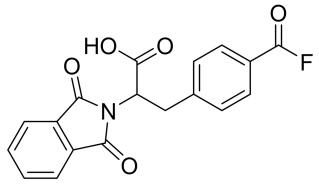
3t

Compound **3u**: Compound **3u** was prepared according to the General Procedure D. The crude product was purified by column chromatography (pet ether: EtOAc = 1:1) to afford 147.1 mg (75%) of compound **3u** as a white solid. Mp: 119-121 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 3.05 (t, J = 7.8 Hz, 2H), 2.73 (t, J = 7.8 Hz, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 178.4, 157.5 (d, J = 341.3 Hz), 148.6, 132.0 (d, J = 3.9 Hz), 129.3, 123.4 (d, J = 60.9 Hz), 34.9, 30.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ 17.93 (s, 1F) ppm; IR (thin film) 1805, 1603, 1381, 1347, 1324, 1288, 1258, 1181, 1002, 730, 681 (cm^{-1}); HRMS-MALDI (m/z) calcd for $[C_{10}H_9FKO_3]^+$, 235.0167; found, 235.0176.



3u

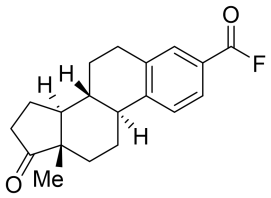
Compound **3v**: Compound **3v** was prepared according to the General Procedure D.



3v

The crude product was purified by column chromatography (EtOAc) to afford 242.3 mg (71%) of compound **3v** as a white solid. Mp: 158-160 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.39 (bs, 1H), 7.88-7.81 (m, 6H), 7.46 (d, J = 8.4 Hz, 2H), 5.31-5.16 (m, 1H), 3.70-3.60 (m, 1H), 3.53-3.40 (m, 1H) ppm; ^{13}C NMR (150 MHz, DMSO-d_6) δ 169.6, 167.0, 156.7 (d, J = 340.7 Hz), 146.3, 134.9, 131.2, 130.6, 129.9, 123.4, 122.3 (d, J = 60.5 Hz), 52.3, 34.2 ppm; ^{19}F NMR (376 MHz, DMSO-d_6) δ 18.58 (s, 1F) ppm; IR (thin film) 1804, 1774, 1708, 1608, 1391, 1349, 1257, 1107, 756, 721, 560, 529 (cm^{-1}); HRMS-MALDI (m/z) calcd for $[C_{18}H_{12}FNNaO_5]^+$, 364.0592; found, 364.0582.

Compound **3x**: To the mixture of **1x** (150.2 mg, 0.5 mmol) and

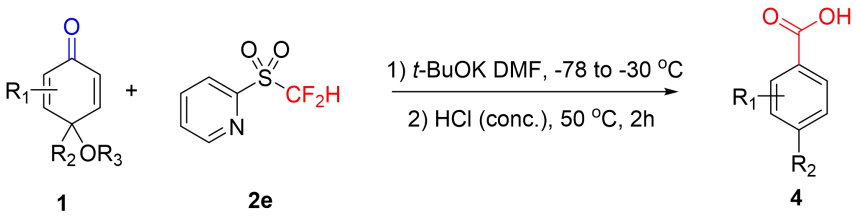


3x

2-((difluoromethyl)sulfonyl)pyridine **2e** (193.2 mg, 1.0 mmol, 2.0 equiv) in anhydrous DMF (5.0 mL) under inert atmosphere was added the solution of *t*-BuOK (145.9 mg, 1.3 mmol, 2.6 equiv) in anhydrous DMF (2.0 mL) slowly at -78 ℃, then warmed up to -30 ℃ slowly. The reaction was quenched with sat. NH_4Cl (5 mL) and 3M HCl (5 mL) at -30 ℃, warmed up to room temperature and extracted with EtOAc (10 x3), the combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Flash column chromatography (pet ether: DCM = 2:1) afforded product **3x** in 34% yield, with 50% **1x** recovery. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.4 Hz, 1H), 7.77 (s, 1H), 7.44 (d, J = 8.4 Hz, 1H), 3.09-2.89 (m, 2H), 2.63-2.32 (m, 3H), 2.23-1.93 (m, 4H), 1.74-1.39 (m, 6H), 0.92 (s, 3H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ 17.79 (s, 1F) ppm. Spectroscopic data was agreement with the literature. (*Org. Lett.* **2021**, *23*, 847-852)

Preparation of compounds 4

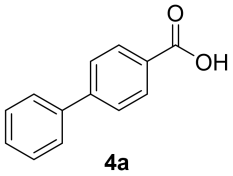
General Procedure E for Preparation of Benzoic Acids:



1 **2e** **4**

To the mixture of cyclohexadienones **1** (1.2 mmol, 1.2 equiv), 2-((difluoromethyl)sulfonyl)pyridine **2e** (1.0 mmol, 1.0 equiv) in anhydrous DMF (5.0 mL) under inert atmosphere was added the solution of *t*-BuOK (1.3 mmol, 1.3 equiv) in DMF (2.0 mL) slowly at -78 ℃, then warmed up to -30 ℃ slowly. The reaction was quenched with concentrated hydrochloric acid (5 mL) at -30 ℃ and stirred at 50 ℃ for 2h. Then the mixture was extracted with EtOAc (10 x3), the combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Flash column chromatography afforded product **4**.

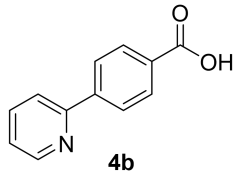
Compound **4a**: Compound **4a** was prepared according to the General Procedure E.



4a

The crude product was purified by column chromatography (pet ether: EtOAc = 4:1) to afford 168.4 mg (85%) of compound **4a** as a white solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.96 (s, 1H), 8.02 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H), 7.73 (d, J =7.8 Hz, 2H), 7.50 (t, J = 7.8 Hz, 2H), 7.42 (t, J = 7.8 Hz, 1H) ppm. Spectroscopic data was agreement with the literature. (*Green Chem.* **2013**,*15*, 635-640)

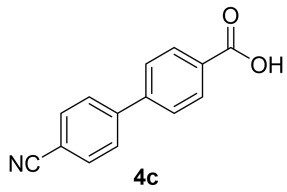
Compound **4b**: Compound **4b** was prepared according to the General Procedure E.



4b

The crude product was purified by column chromatography (pet ether: EtOAc = 4:1) to afford 145.4 mg (73%) of compound **4b** as a white solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.08 (bs, 1H), 8.71 (d, J = 4.8 Hz, 1H), 8.21 (d, J = 8.4 Hz, 2H), 8.08-8.02 (m, 3H), 7.98-7.90 (m, 1H), 7.44-7.39 (m, 1H) ppm. Spectroscopic data was agreement with the literature. (*J. Org. Chem.* **2018**, *83*, 15486-15492)

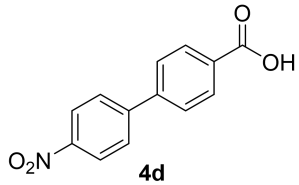
Compound **4c**: Compound **4c** was prepared according to the General Procedure E.



4c

The crude product was purified by column chromatography (pet ether: EtOAc = 2:1) to afford 185.2 mg (83%) of compound **4c** as a white solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.09 (bs, 1H), 8.05 (d, J = 8.4 Hz, 2H), 7.98-7.92 (m, 4H), 7.88 (dd, J_1 = 8.4, J_2 = 1.8 Hz, 2H) ppm. Spectroscopic data was agreement with the literature. (*J. Am. Chem. Soc.* **2019**, *141*, 16003-16013)

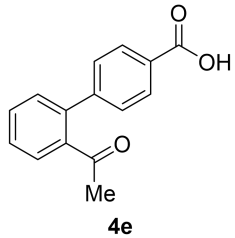
Compound **4d**: Compound **4d** was prepared according to the General Procedure E.



4d

The crude product was purified by column chromatography (pet ether: EtOAc = 2:1) to afford 209.2 mg (86%) of compound **4d** as a white solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 13.12 (bs, 1H), 8.32 (d, J = 8.4 Hz, 2H), 8.07 (d, J = 8.4 Hz, 2H), 8.02 (d, J = 8.4 Hz, 2H), 7.90 (d, J = 8.4 Hz, 2H) ppm. Spectroscopic data was agreement with the literature. (*J. Org. Chem.* **2018**, *83*, 15486-15492)

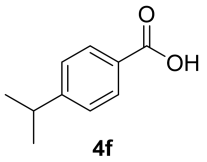
Compound **4e**: Compound **4e** was prepared according to the General Procedure E.



4e

The crude product was purified by column chromatography (pet ether: EtOAc = 8:1) to afford 213.8 mg (89%) of compound **4e** as a white solid. Mp: 93-195 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 7.6 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.51-7.43 (m, 3H), 7.40 (d, J = 7.6 Hz, 1H), 2.13 (s, 3H) ppm; ^{13}C NMR (150 MHz, DMSO-d_6) δ 202.7, 167.1, 145.0, 140.0, 139.1, 131.1, 130.4, 129.8, 129.5, 128.9, 128.1, 128.0, 30.2 ppm; IR (thin film) 1678, 1606, 1353, 1322, 1285, 1250, 1189, 1125, 1001, 961, 908, 864, 758, 710 (cm^{-1}); HRMS-MALDI (m/z) calcd for $[C_{15}H_{12}NaO_3]^+$, 263.0679; found, 263.0682.

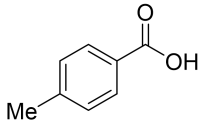
Compound **4f**: Compound **4f** was prepared according to the General Procedure E. The crude product was purified by column chromatography (pet ether: EtOAc = 6:1) to



4f

afford 156.0 mg (95%) of compound **4f** as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 2.99 (hept, J = 6.6 Hz, 1H), 1.29 (d, J = 6.6 Hz, 6H) ppm. Spectroscopic data was agreement with the literature. (*Org. Lett.* **2020**, *22*, 5, 1852-1857)

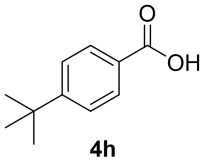
Compound **4g**: Compound **4g** was prepared according to the General Procedure E.



4g

The crude product was purified by column chromatography (pet ether: EtOAc = 6:1) to afford 102.1 mg (75%) of compound **4g** as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, J = 7.8 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 2.43 (s, 3H) ppm. Spectroscopic data was agreement with the literature. (*Org. Biomol. Chem.* **2015**, *13*, 9681-9685)

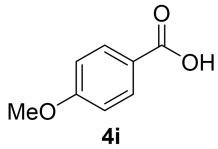
Compound **4h**: Compound **4h** was prepared according to the General Procedure E.



4h

The crude product was purified by column chromatography (pet ether: EtOAc = 6:1) to afford 171.1 mg (96%) of compound **4h** as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.4 Hz, 2H), 1.36 (s, 9H) ppm. Spectroscopic data was agreement with the literature. (*Org. Biomol. Chem.* **2015**, *13*, 9681-9685)

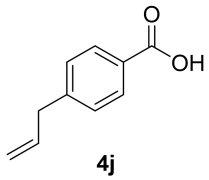
Compound **4i**: Compound **4i** was prepared according to the General Procedure E. The



4i

crude product was purified by column chromatography (pet ether: EtOAc = 6:1) to afford 144.5 mg (95%) of compound **4i** as a white solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.59 (bs, 1H), 7.89 (d, J = 9.0 Hz, 2H), 7.01 (d, J = 9.0 Hz, 2H), 3.82 (s, 3H) ppm. Spectroscopic data was agreement with the literature. (*Org. Biomol. Chem.* **2015**, *13*, 9681-9685)

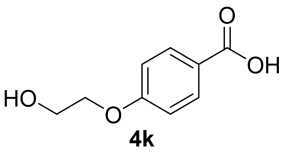
Compound **4j**: Compound **4j** was prepared according to the General Procedure E. The crude product was purified by column chromatography (pet ether: EtOAc = 6:1) to afford 139.5 mg (86%) of compound **4j** as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$)



4j

δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.03-5.93 (m, 1H), 5.16-5.09 (m, 2H), 3.47 (d, *J* = 6.6 Hz, 2H) ppm. Spectroscopic data was agreement with the literature. (*Org. Lett.* **2017**, *19*, 5, 3075-3078)

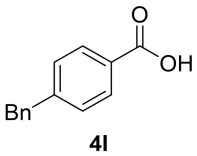
Compound **4k**: Compound **4k** was prepared according to the General Procedure E.



4k

The crude product was purified by column chromatography (EtOAc) to afford 162.1 mg (89%) of compound **4k** as a white solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.56 (s, 1H), 7.88 (d, *J* = 9.0 Hz, 2H), 7.01 (d, *J* =9.0 Hz, 2H), 4.89 (t, *J* = 5.4 Hz, 1H), 4.06 (t, *J* = 5.4 Hz, 2H), 3.73 (q, *J* = 5.4 Hz, 2H) ppm. Spectroscopic data was agreement with the literature. (*Org. Biomol. Chem.* **2014**, *12*, 4747-4753)

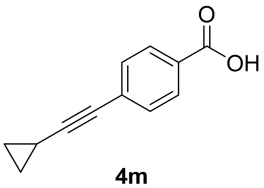
Compound **4l**: Compound **4l** was prepared according to the General Procedure E. The



4l

crude product was purified by column chromatography (pet ether: EtOAc = 6:1) to afford 159.2 mg (75%) of compound **4l** as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.34-7.28 (m, 4H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 2H), 4.04 (s, 2H) ppm. Spectroscopic data was agreement with the literature. (*Green Chem.* **2011**,*13*, 2734-2736)

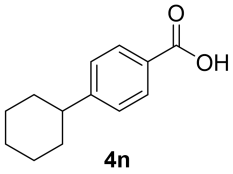
Compound **4m**: Compound **4m** was prepared according to the General Procedure E.



4m

The crude product was purified by column chromatography (pet ether: EtOAc = 6:1) to afford 148.9 mg (80%) of compound **4m** as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 13.02 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 1.82-1.43 (m, 1H), 1.03-0.86 (m, 2H), 0.82-0.48 (m, 2H) ppm. Spectroscopic data was agreement with the literature. (*J. Med. Chem.* **2009**, *52*, 6790-6802)

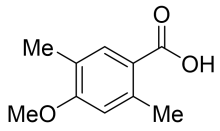
Compound **4n**: Compound **4n** was prepared according to the General Procedure E.



4n

The crude product was purified by column chromatography (pet ether: EtOAc = 8:1) to afford 194.1 mg (95%) of compound **4n** as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 2.65-2.54 (m, 1H), 1.94-1.81 (m, 4H), 1.81-1.74 (m, 1H), 1.51-1.38 (m, 4H), 1.32-1.23 (m, 1H) ppm. Spectroscopic data was agreement with the literature. (*Org. Biomol. Chem.* **2015**, *13*, 9681-9685)

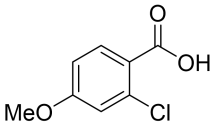
Compound **4o**: Compound **4o** was prepared according to the General Procedure E.



4o

The crude product was purified by column chromatography (pet ether: EtOAc = 6:1) to afford 135.2 mg (75%) of compound **4o** as a white solid. Mp: 149-151 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (s, 1H), 6.67 (s, 1H), 3.88 (s, 3H), 2.66 (s, 3H), 2.21 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.2, 161.5, 142.1, 134.5, 124.2, 120.0, 113.2, 55.6, 22.7, 15.8 ppm; IR (thin film) 1666, 1606, 1468, 1410, 1375, 1284, 1252, 1191, 1166, 1073, 1000, 925, 904, 843, 787, 757, 719 (cm^{-1}); HRMS-MALDI (m/z) calcd for $[C_{10}H_{12}NaO_3]^+$, 203.0679; found, 203.0677.

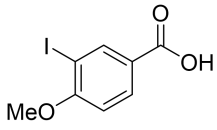
Compound **4p**: Compound **4p** was prepared according to the General Procedure E.



4p

The crude product was purified by column chromatography (pet ether: EtOAc = 2:1) to afford 138.1 mg (74%) of compound **4p** as a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.98 (s, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.10 (d, *J* = 2.8 Hz, 1H), 6.99 (dd, J_1 = 8.8, J_2 = 2.8 Hz, 1H), 3.83 (s, 3H) ppm. Spectroscopic data was agreement with the literature. (*J. Org. Chem.* **2007**, *72*, 3419-3429)

Compound **4q**: Compound **4q** was prepared according to the General Procedure E.

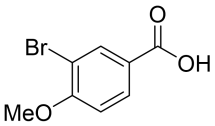


4q

The crude product was purified by column chromatography (pet ether: EtOAc = 4:1) to afford 253.0 mg (91%) of compound **4q** as a white solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.86 (bs, 1H),

8.27 (d, J = 1.8 Hz, 1H), 7.95 (dd, J_1 = 8.4, J_2 = 1.8 Hz, 1H), 7.09 (d, J = 8.4 Hz, 1H), 3.90 (s, 3H) ppm. Spectroscopic data was agreement with the literature. (*J. Org. Chem.* **2008**, *73*, 2130-2137)

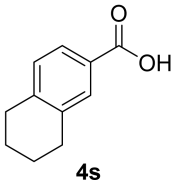
Compound **4r**: Compound **4r** was prepared according to the General Procedure E.



4r

The crude product was purified by column chromatography (pet ether: EtOAc = 6:1) to afford 154.8 mg (67%) of compound **4r** as a white solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.93 (bs, 1H), 8.05 (d, J = 1.8 Hz, 1H), 7.94 (dd, J_1 = 9.0, J_2 = 1.8 Hz, 1H), 7.21 (d, J = 9.0 Hz, 1H), 3.93 (s, 3H) ppm. Spectroscopic data was agreement with the literature. (*J. Org. Chem.* **2019**, *84*, 7405-7410)

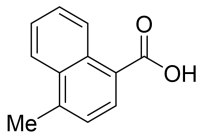
Compound **4s**: Compound **4s** was prepared according to the General Procedure E. The



4s

crude product was purified by column chromatography (pet ether: EtOAc = 4:1) to afford 128.6 mg (73%) of compound **4s** as a white solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84-7.79 (m, 2H), 7.15 (d, J = 7.8 Hz, 1H), 2.83 (s, 4H), 1.86-1.80 (m, 4H) ppm. Spectroscopic data was agreement with the literature. (*Org. Lett.* **2019**, *21*, 4632-4637)

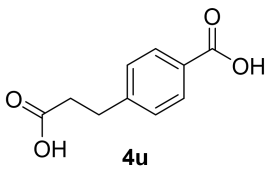
Compound **4t**: Compound **4t** was prepared according to the General Procedure E. The



4t

crude product was purified by column chromatography (pet ether: EtOAc = 1:1) to afford 124.8 mg (67%) of compound **4t** as a white solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.93 (bs, 1H), 8.96-8.91 (m, 1H), 8.13-8.08 (m, 1H), 8.05 (d, J = 7.2 Hz, 1H), 7.67-7.59 (m, 2H), 7.44 (dd, J_1 = 7.2, J_2 = 1.2 Hz, 1H), 2.71 (s, 3H) ppm. Spectroscopic data was agreement with the literature. (*J. Org. Chem.* **2010**, *75*, 7855-7862)

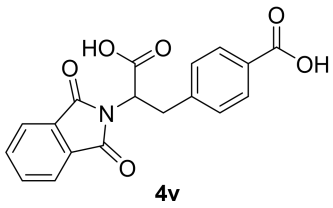
Compound **4u**: Compound **4u** was prepared according to the General Procedure E. The crude product was purified by column chromatography (DCM: MeOH = 10:1) to afford 157.3 mg (81%) of compound **4u** as a white solid. ^{1}H NMR (600 MHz,



4u

DMSO-d_6) δ 12.46 (bs, 2H), 7.85 (d, J = 7.8 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 2.88 (t, J = 7.8 Hz, 2H), 2.57 (t, J = 7.8 Hz, 2H) ppm. Spectroscopic data was agreement with the literature. (*J. Am. Chem. Soc.* **2021**, *143*, 13022-13028)

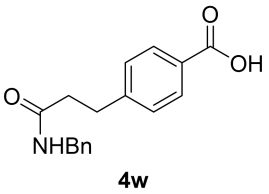
Compound **4v**: Compound **4v** was prepared according to the General Procedure E.



4v

The crude product was purified by column chromatography (DCM: MeOH = 10:1) to afford 278.2 mg (82%) of compound **4v** as a white solid. Mp: 222-224 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.10 (bs, 2H), 7.84 (s, 4H), 7.75 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 5.17 (dd, J_1 = 11.6, J_2 = 4.8 Hz, 1H), 3.55 (dd, J_1 = 14.0, J_2 = 4.8 Hz, 1H), 3.46-3.35 (m, 1H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.9, 167.1, 167.0, 142.7, 135.0, 130.7, 129.4, 129.2, 129.0, 123.5, 52.6, 34.0, 26.3 ppm; IR (thin film) 1712, 1598, 1392, 1353, 1264, 1179, 1114, 1091, 951, 891, 872, 772, 757, 721 (cm^{-1}); HRMS-MALDI (m/z) calcd for $[C_{18}H_{13}NNaO_6]^+$, 362.0635; found, 362.0630.

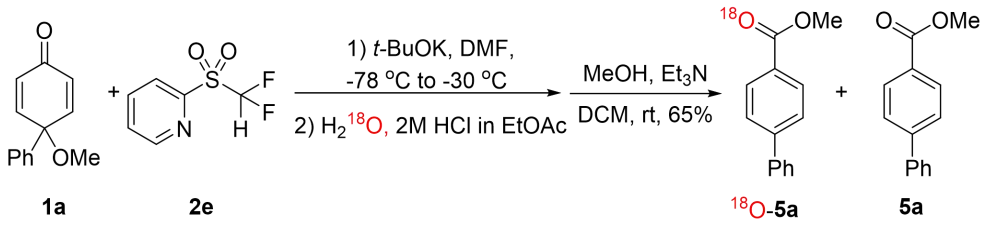
Compound **4w**: Compound **4w** was prepared according to the General Procedure E.

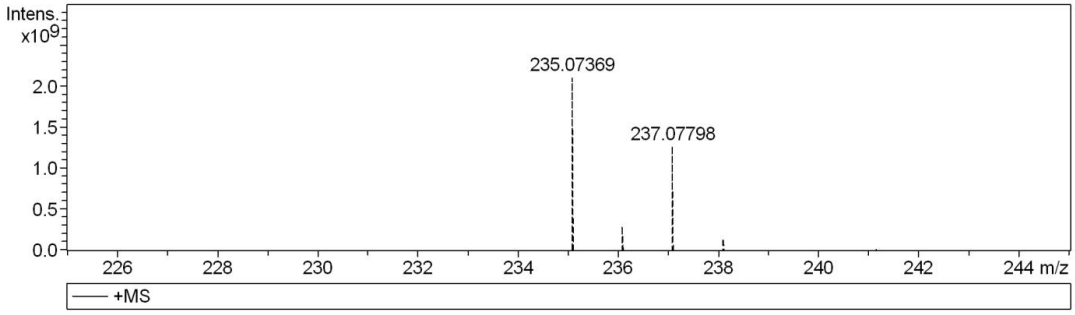


4w

The crude product was purified by column chromatography (pet ether: EtOAc = 1:1) to afford 153.0 mg (54%) of compound **4w** as a white solid. Mp: 171-179 ℃; ^{1}H NMR (600 MHz, DMSO-d_6) δ 12.72 (bs, 1H), 8.26 (s, 1H), 7.92-7.79 (m, 2H), 7.37-7.29 (m, 2H), 7.28-7.16 (m, 3H), 7.10 (t, J = 8.4 Hz, 2H), 4.32-4.16 (m, 2H), 3.06-2.81 (m, 2H), 2.50-2.46 (m, 2H) ppm; ^{13}C NMR (150 MHz, DMSO-d_6) δ 170.9, 167.2, 146.5, 139.4, 129.3, 128.5, 128.4, 128.1, 127.0, 126.6, 41.9, 36.4, 30.9 ppm; IR (thin film) 1693, 1640, 1612, 1453, 1425, 1352, 1315, 1290, 1218, 1178, 1078, 932, 865, 767, 750 (cm^{-1}); HRMS-MALDI (m/z) calcd for $[C_{17}H_{17}NNaO_3]^+$, 306.1101; found, 306.1101.

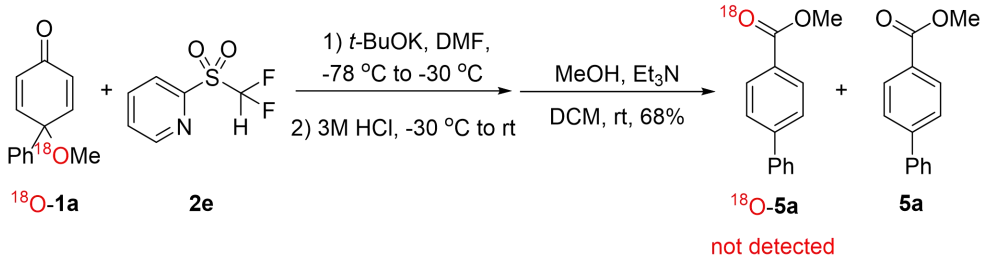
[^{18}O]-Labeling Experiments

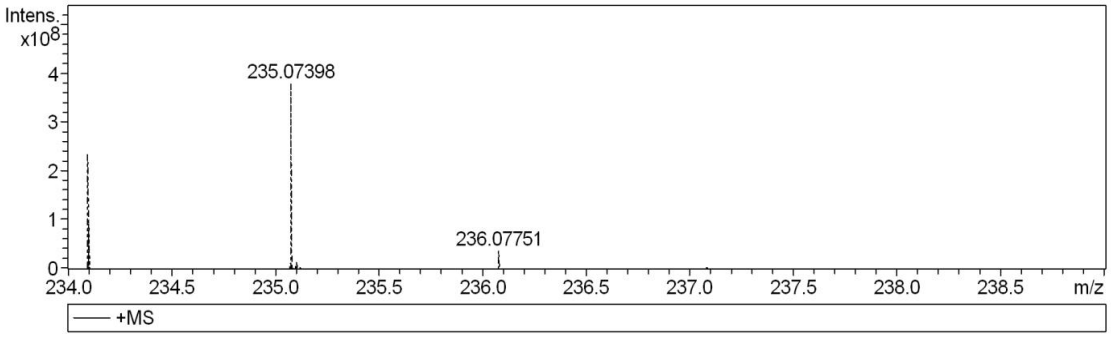




m/z	z	I	Res.
235.07243		190577648	372352
235.07369		2128366592	203367
236.07717		305018528	196540
237.07798		1283649792	200088
301.14250		554189888	158000

Reaction conditions: To the mixture of cyclohexadienone **1a** (0.3 mmol, 1.2 equiv), 2-((difluoromethyl)sulfonyl)pyridine **2e** (0.25 mmol, 1.0 equiv) in anhydrous DMF (2.5 mL) was added the solution of *t*-BuOK (0.33 mmol, 1.3 equiv) in anhydrous DMF (0.5 mL) slowly at -78 °C, then warmed up to -30 °C slowly. The reaction was quenched with [^{18}O]H_2O (0.5 mL) and HCl in EtOAc (2M, 0.6 mL) at -30 °C, the mixture was extracted with Et_2O (5 x3), the combined organic phase was concentrated in vacuo. The crude products ^{18}O-**3a** and **3a** were converted to methyl benzoates ^{18}O-**5a** and **5a** directly. The ^{18}O was determined by HRMS. Two products were detected by HRMS analysis: ^{18}O-**5a** and **5a** with the ratio 1:1.65. **5a**: HRMS-MALDI (m/z) calcd for $[C_{14}H_{12}NaO_2]^+$, 235.0730; found, 235.0737. ^{18}O-**5a**: HRMS-MALDI (m/z) calcd for $[C_{14}H_{12}NaO^{18}O]^+$, 235.0772; found, 237.0780.

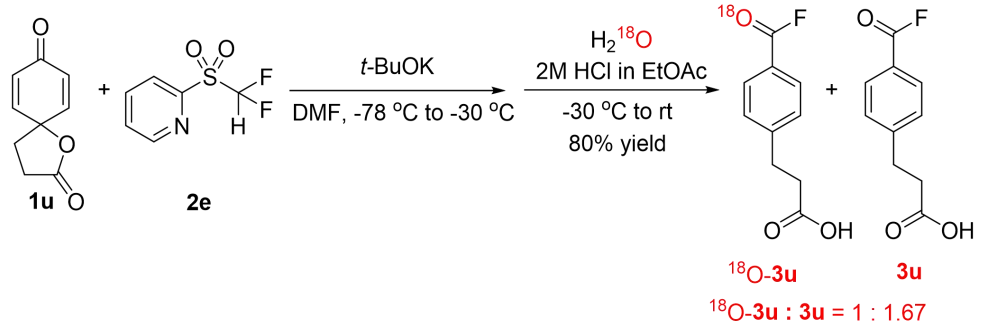


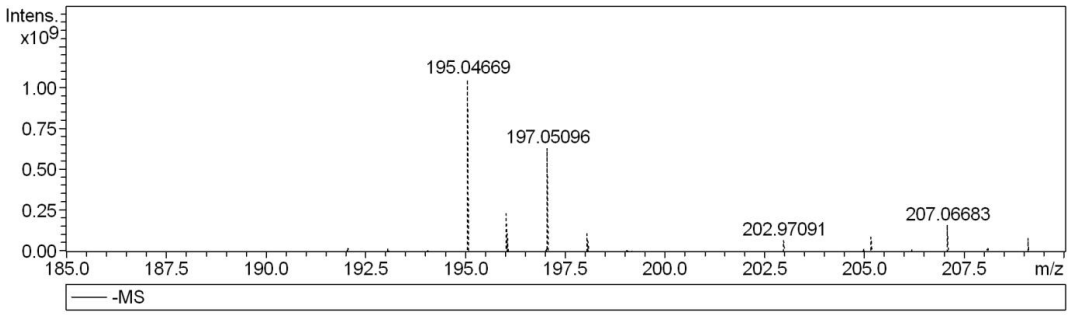


m/z	z	I	Res.
234.09722		237029760	241294
234.09835		95165768	156870
235.07398		380286080	270263
277.10345		319245568	173233

Reaction conditions: To the mixture of cyclohexadienone ^{18}O-**1a** (0.3 mmol, 1.2 equiv), 2-((difluoromethyl)sulfonyl)pyridine **2e** (0.25 mmol, 1.0 equiv) in anhydrous DMF (2.5 mL) was added the solution of *t*-BuOK (0.33 mmol, 1.3 equiv) in anhydrous DMF (0.5 mL) slowly at -78 °C, then warmed up to -30 °C slowly. The reaction was quenched with 3M HCl(1 mL) at -30 °C, warmed up to room temperature and extracted with Et_2O (10 x3), the combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude products ^{18}O-**3a** and **3a** were converted to methyl benzoates ^{18}O-**5a** and **5a** directly. The ^{18}O was determined by HRMS. Only **5a** was detected by HRMS analysis.

5a: HRMS-MALDI (m/z) calcd for $[C_{14}H_{12}NaO_2]^+$, 235.0730; found, 235.0740.





m/z	z	I	Res.
178.03359		186444272	266751
180.04926		129668512	261975
195.04669		1056263936	244177
196.02424		234534752	243821
197.05096		633469888	240982
207.06683		162315264	228383

Reaction conditions: To the mixture of cyclohexadienone **1u** (0.3 mmol, 1.2 equiv), 2-((difluoromethyl)sulfonyl)pyridine **2e** (0.25 mmol, 1.0 equiv) in anhydrous DMF (2.5 mL) was added the solution of *t*-BuOK (0.33 mmol, 1.3 equiv) in anhydrous DMF (0.5 mL) slowly at -78 ℃, then warmed up to -30 ℃ slowly. The reaction was quenched with [^{18}O]H_2O (0.5 mL) and HCl in EtOAc (2M, 0.6 mL) at -30 ℃, the mixture was extracted with EtOAc (5 x3), the combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Flash column chromatography afforded products ^{18}O-**3u** and **3u**. The ^{18}O was determined by HRMS. Two products were detected by HRMS analysis: ^{18}O-**3u** and **3u** with the ratio 1:1.67. **3u**: HRMS-MALDI (m/z) calcd for $[C_{10}H_8FO_3]^-$, 195.0463; found, 195.0467. ^{18}O-**3u**: HRMS-MALDI (m/z) calcd for $[C_{10}H_8FO_2{}^{18}O]^-$, 197.0505; found, 197.0510.

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4. Wang, S.; Morrow, G. W.; Swenton, J. S., Spiro-fused 2,5-cyclohexadienones from the thermal

1,3-alkyl migrations of quinol vinyl ethers. A strategy for conversion of a carbonyl carbon to a quaternary carbon. *J. Org. Chem.* **1989,** *54*, 5364-5371.

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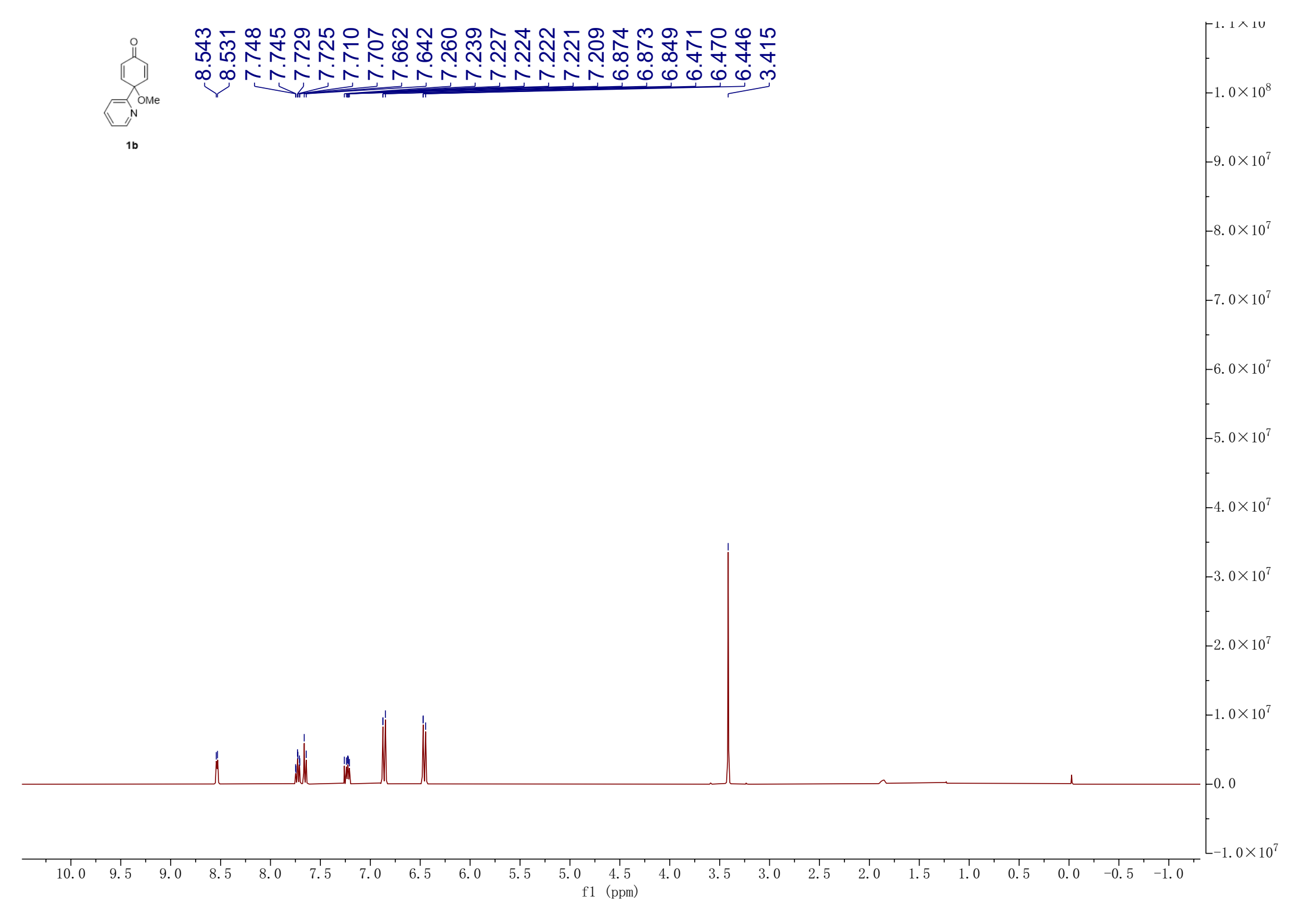
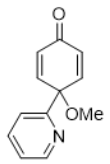
NMR Spectra of Compounds:

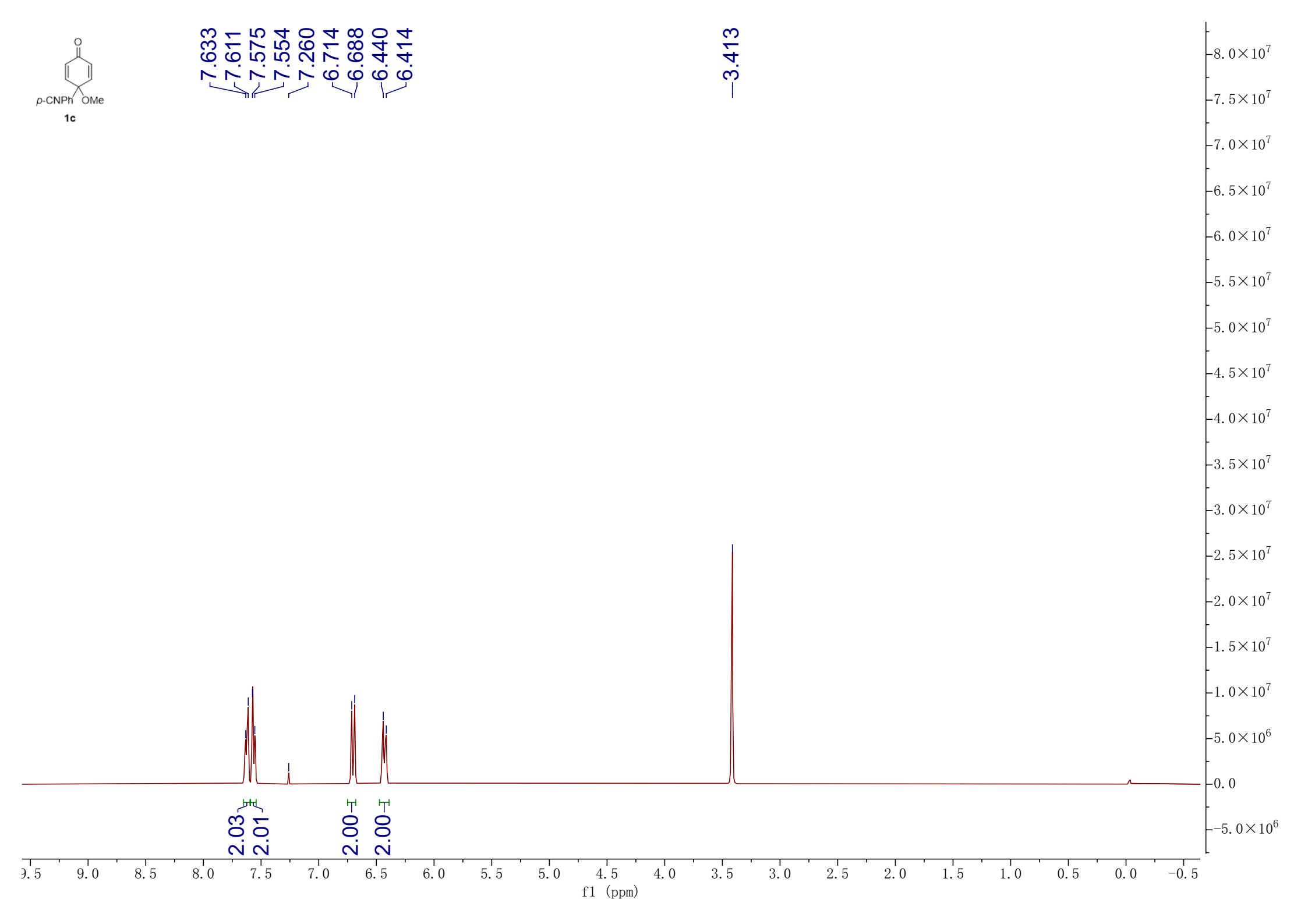

8.543
8.531
7.748
7.745
7.729
7.725
7.710
7.707
7.662
7.642
7.260
7.239
7.227
7.224
7.222
7.221
7.209
6.874
6.873
6.849
6.471
6.470
6.446
3.415
OMe
N
1b
1.1×10
1.0×10^8
9.0×10^7
8.0×10^7
7.0×10^7
6.0×10^7
5.0×10^7
4.0×10^7
3.0×10^7
2.0×10^7
1.0×10^7
0.0
-1.0×10^7
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

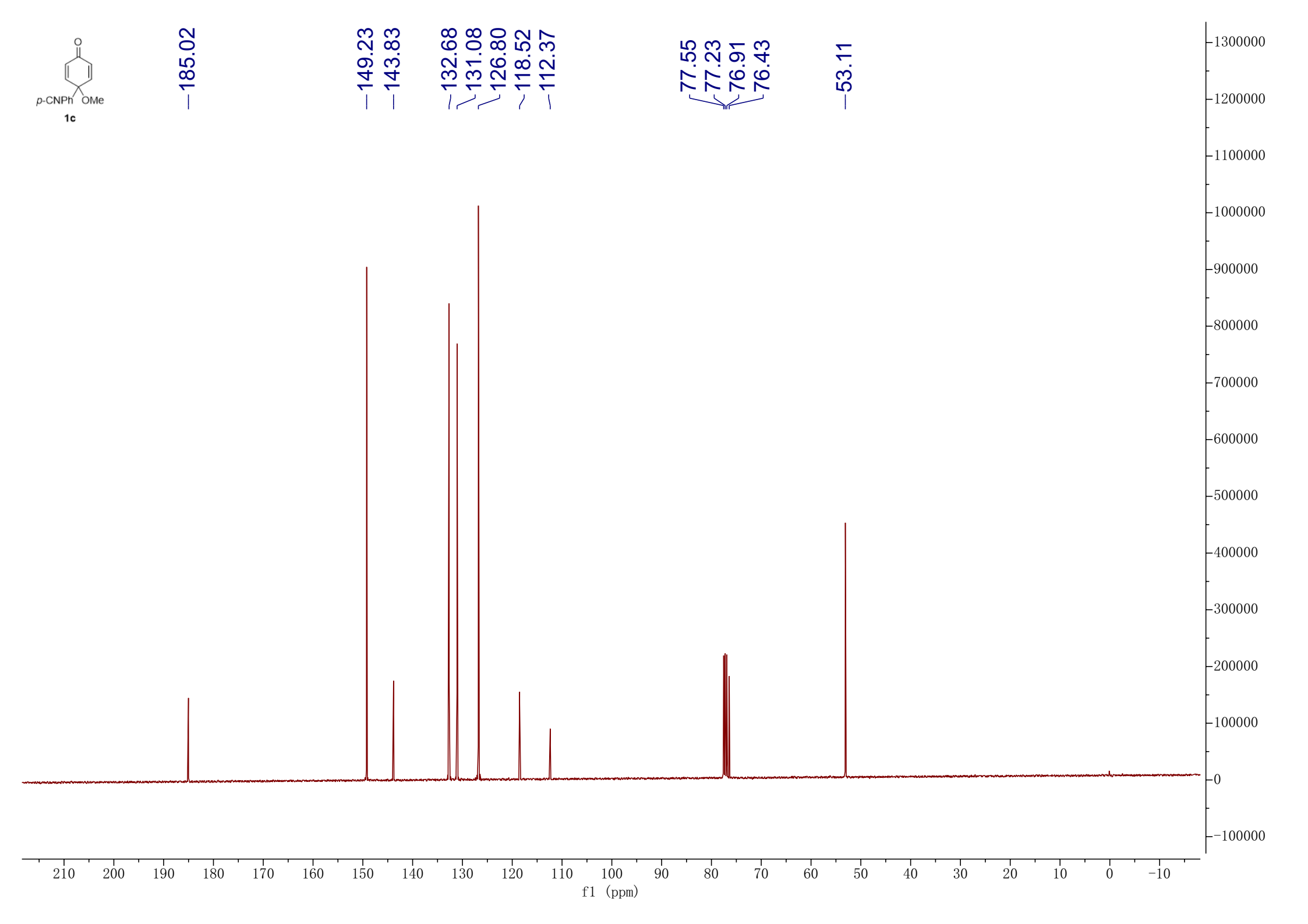


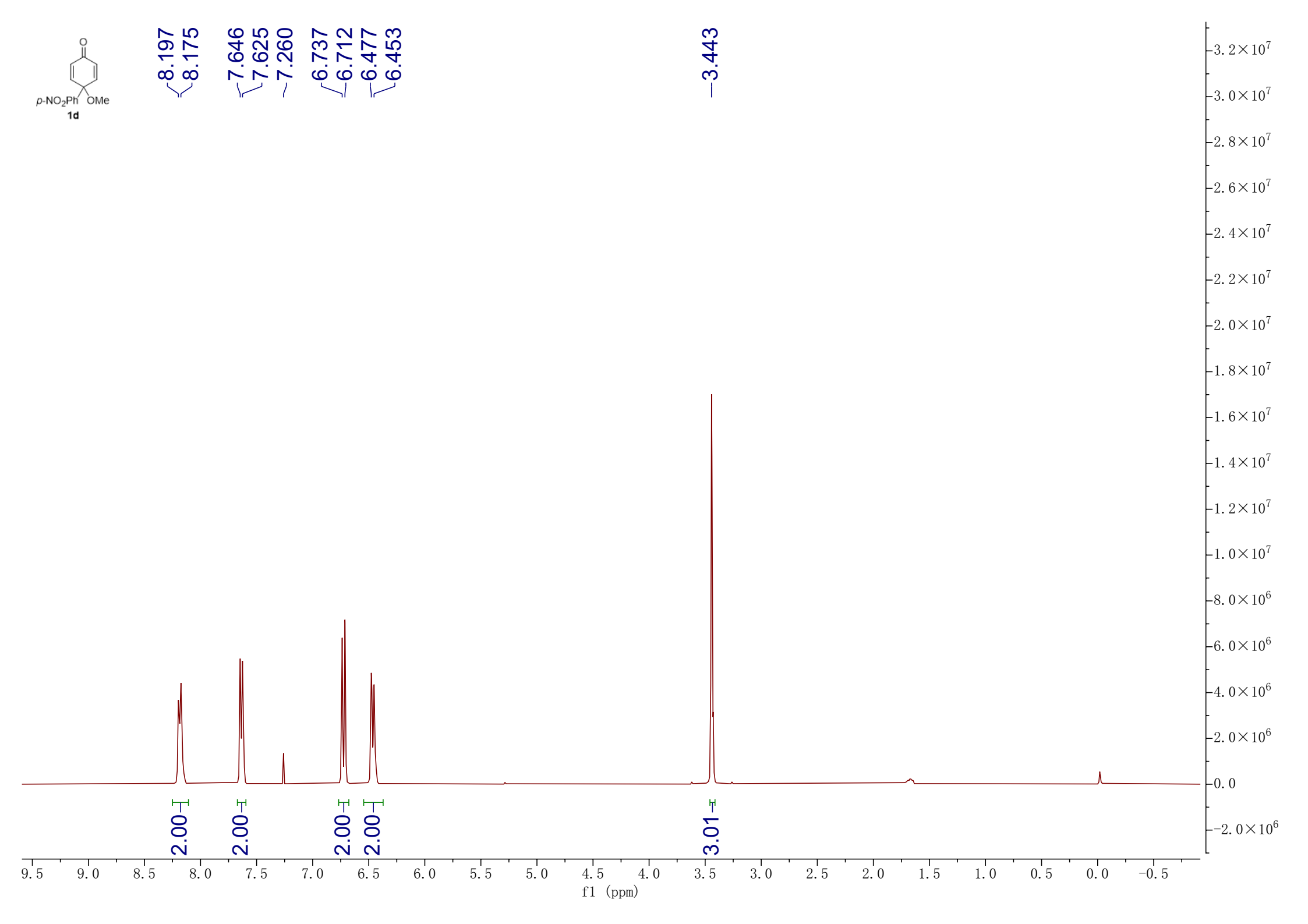
1b

185.74
158.82
149.53
148.99
137.48
131.38
123.56
121.27
77.61
77.55
77.23
76.91
53.00

f1 (ppm)


p-CNPh OMe
1c
7.633
7.611
7.575
7.554
7.260
6.714
6.688
6.440
6.414
3.413
2.03
2.01
2.00
2.00
f1 (ppm)


p-CNPh OMe
1c
185.02
149.23
143.83
132.68
131.08
126.80
118.52
112.37
77.55
77.23
76.91
76.43
53.11
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
−100000
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)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1d
8.197
8.175
7.646
7.625
7.260
6.737
6.712
6.477
6.453
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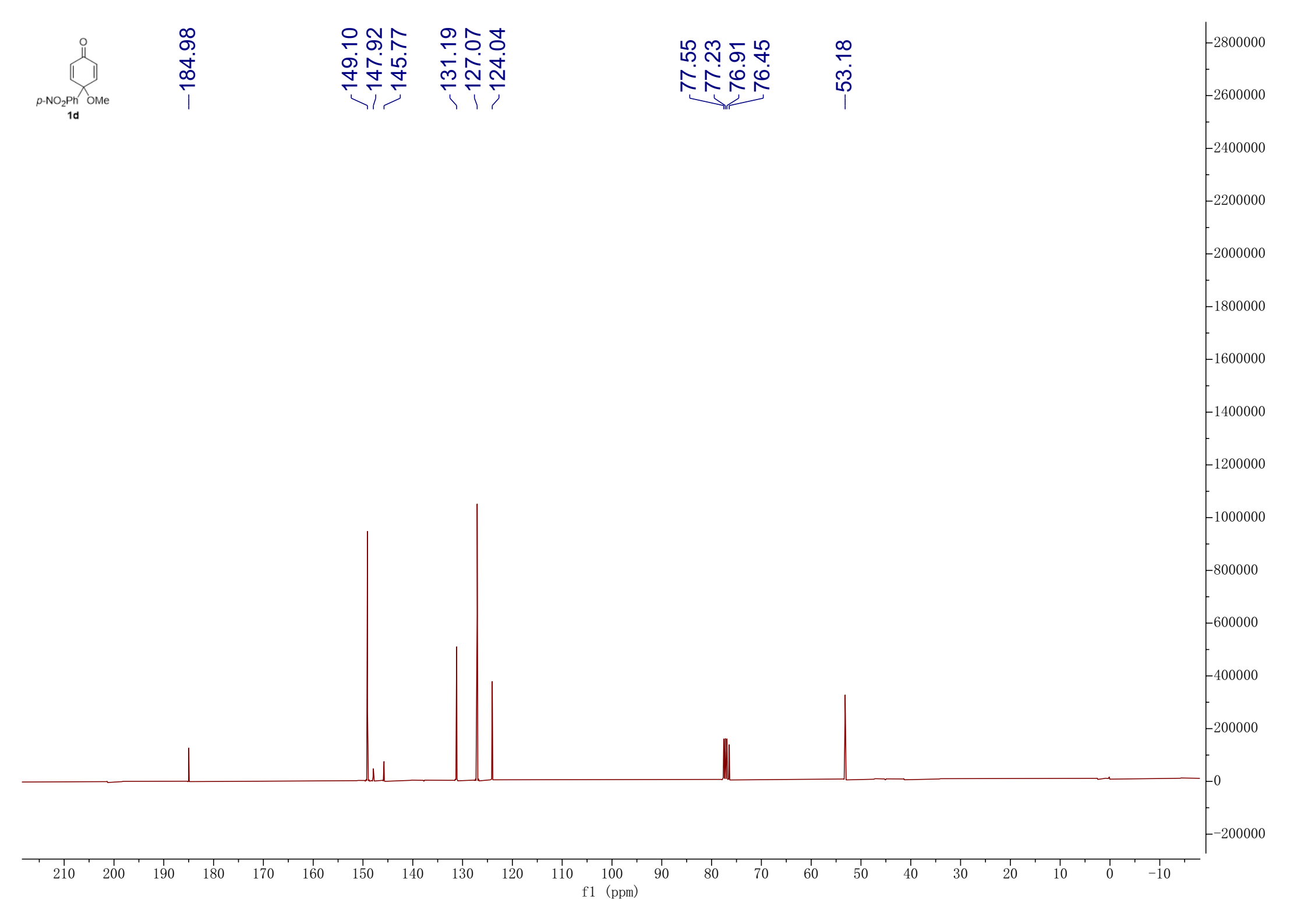
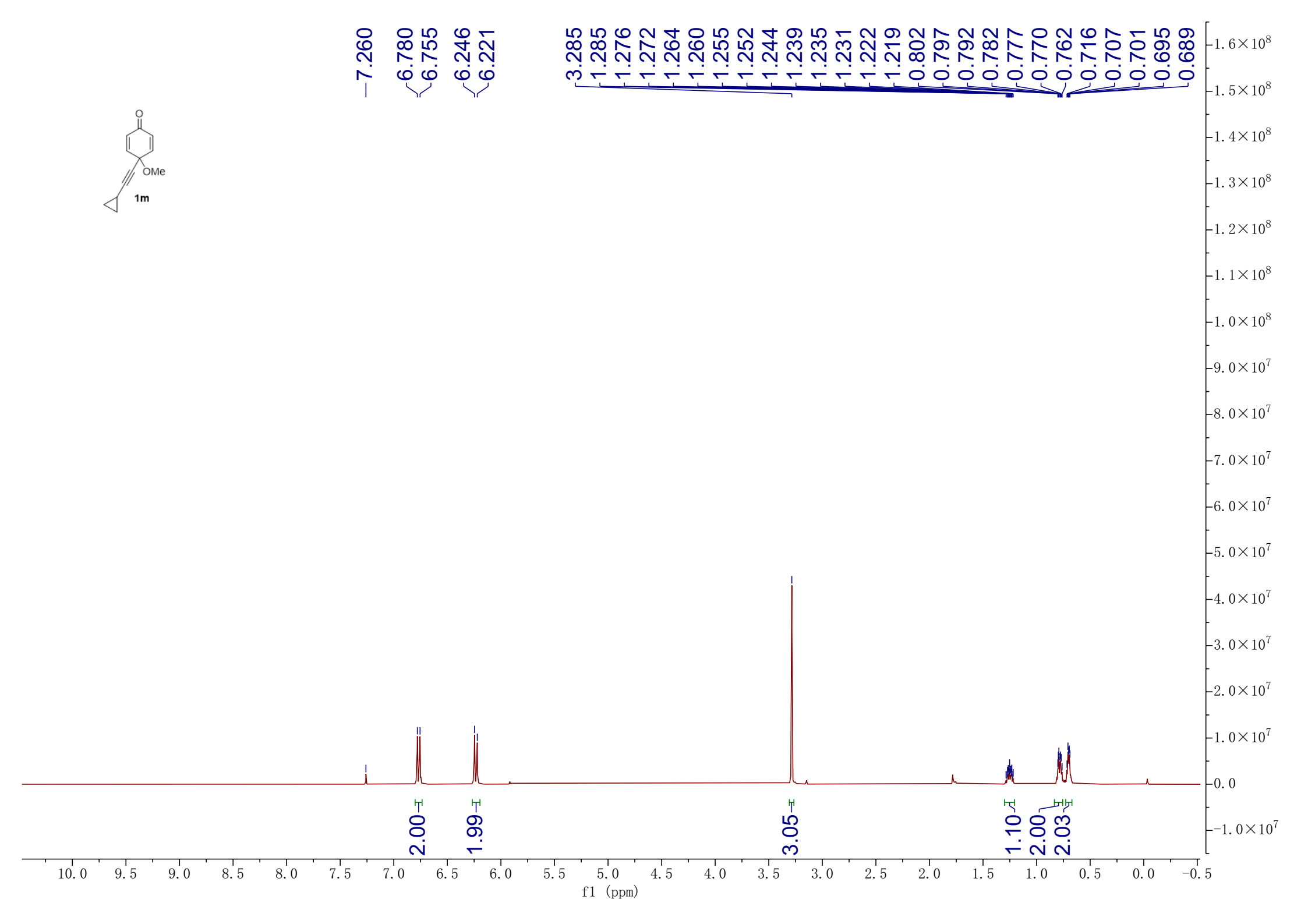
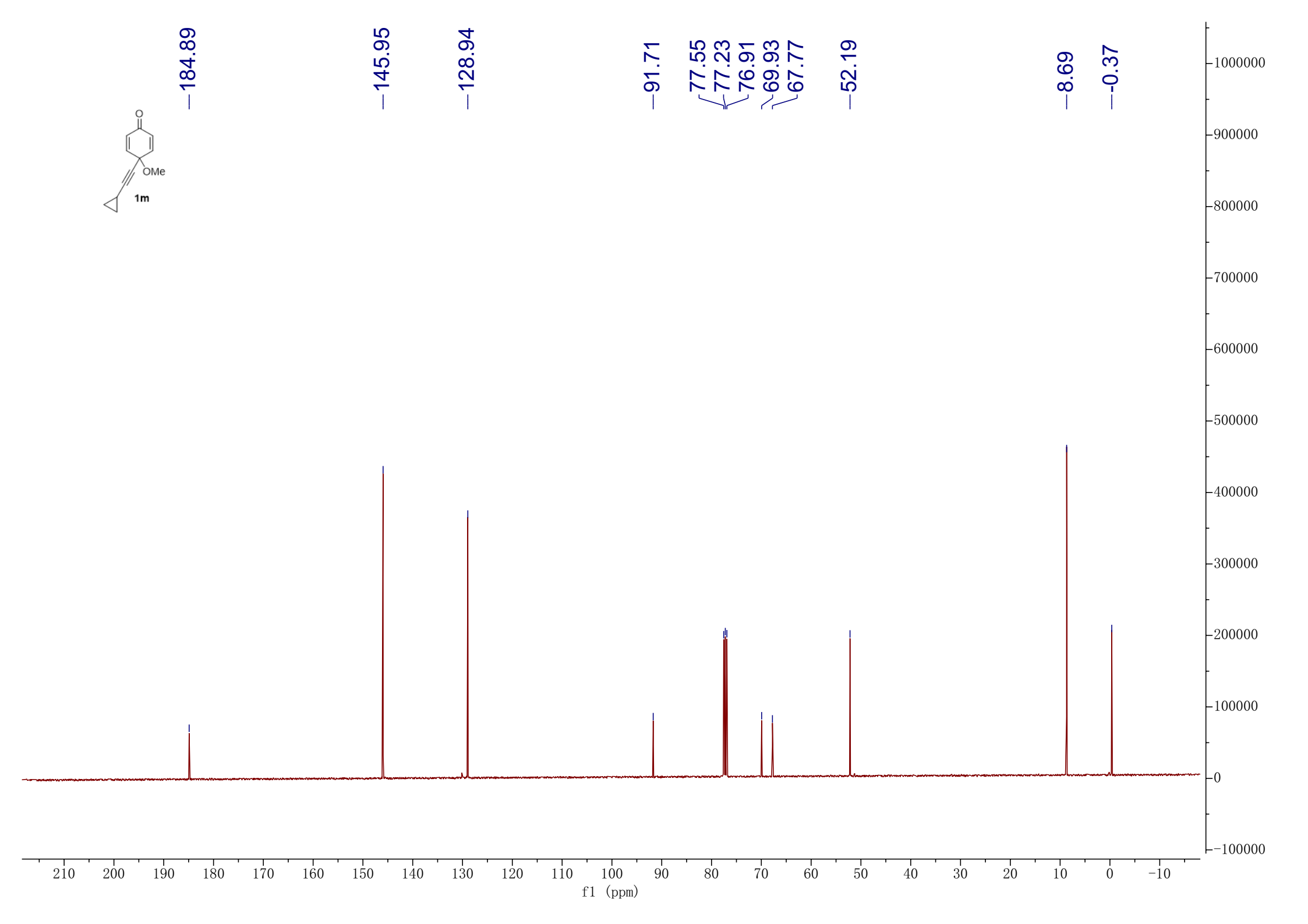
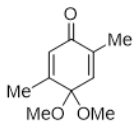
2.00
2.00
2.00
3.01
f1 (ppm)


p-NO2Ph OMe
1d
184.98
149.10
147.92
145.77
131.19
127.07
124.04
77.55
77.23
76.91
76.45
53.18
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
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)

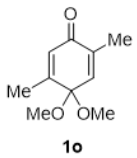

7.260
6.780
6.755
6.246
6.221
3.285
1.285
1.276
1.272
1.264
1.260
1.255
1.252
1.244
1.239
1.235
1.231
1.222
1.219
0.802
0.797
0.792
0.782
0.777
0.770
0.762
0.716
0.707
0.701
0.695
0.689
OMe
1m
2.00
1.99
3.05
1.10
2.00
2.03
f1 (ppm)


184.89
145.95
128.94
91.71
77.55
77.23
76.91
69.93
67.77
52.19
8.69
-0.37
O
OMe
1m
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
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)


O
Me
Me
MeO
OMe

1o

7.260
6.471
6.167
3.159
1.902
1.869
1.00
0.98
6.05
3.10
3.02
9.0×10^7
8.0×10^7
7.0×10^7
6.0×10^7
5.0×10^7
4.0×10^7
3.0×10^7
2.0×10^7
1.0×10^7
0.0
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 -0.5 -1.0 -1.5
f1 (ppm)



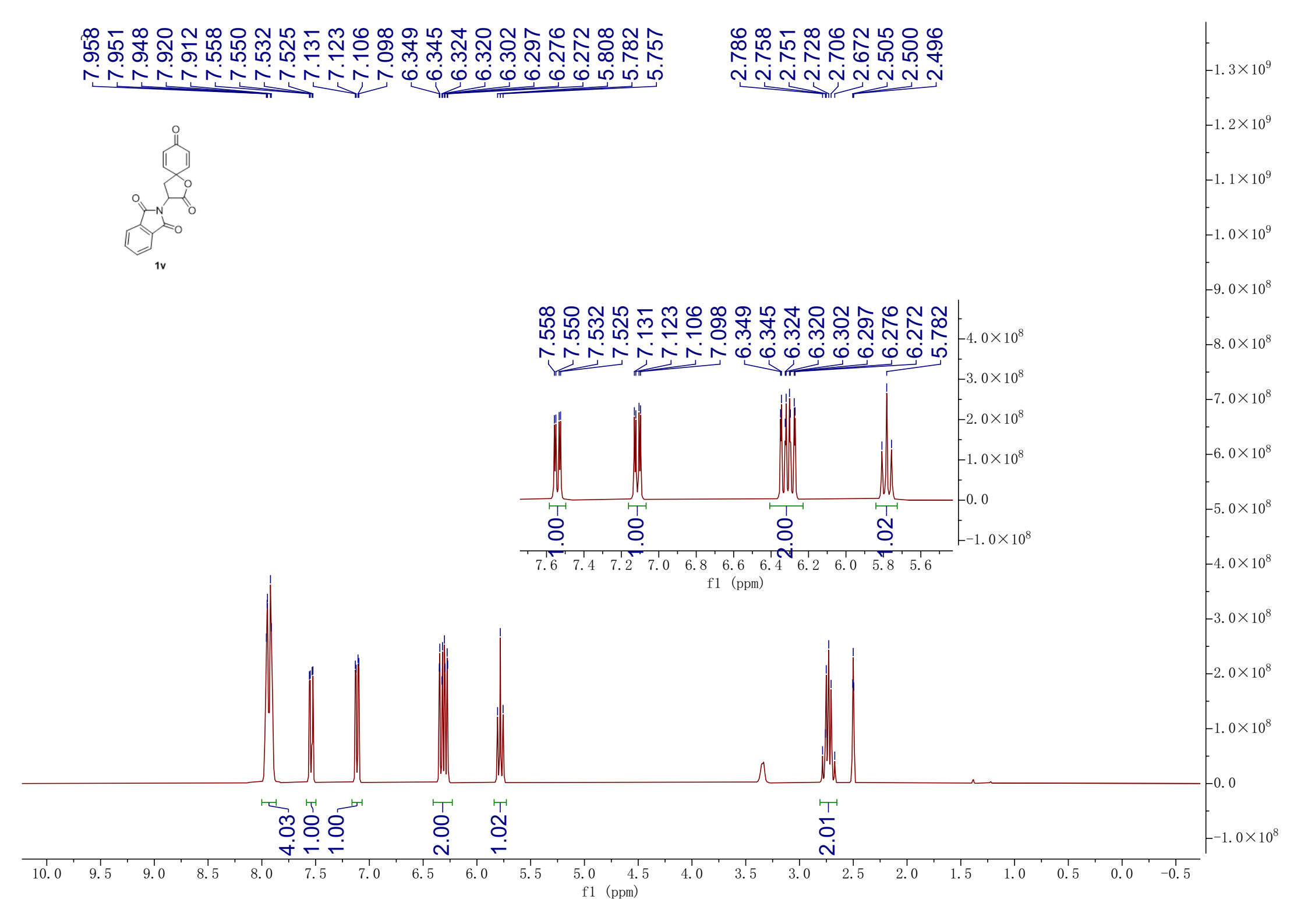
1o

185.81
155.85
139.56
139.22
129.95
96.07
77.55
77.23
76.91
51.00
16.44
15.51

2500000
2000000
1500000
1000000
500000
0

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)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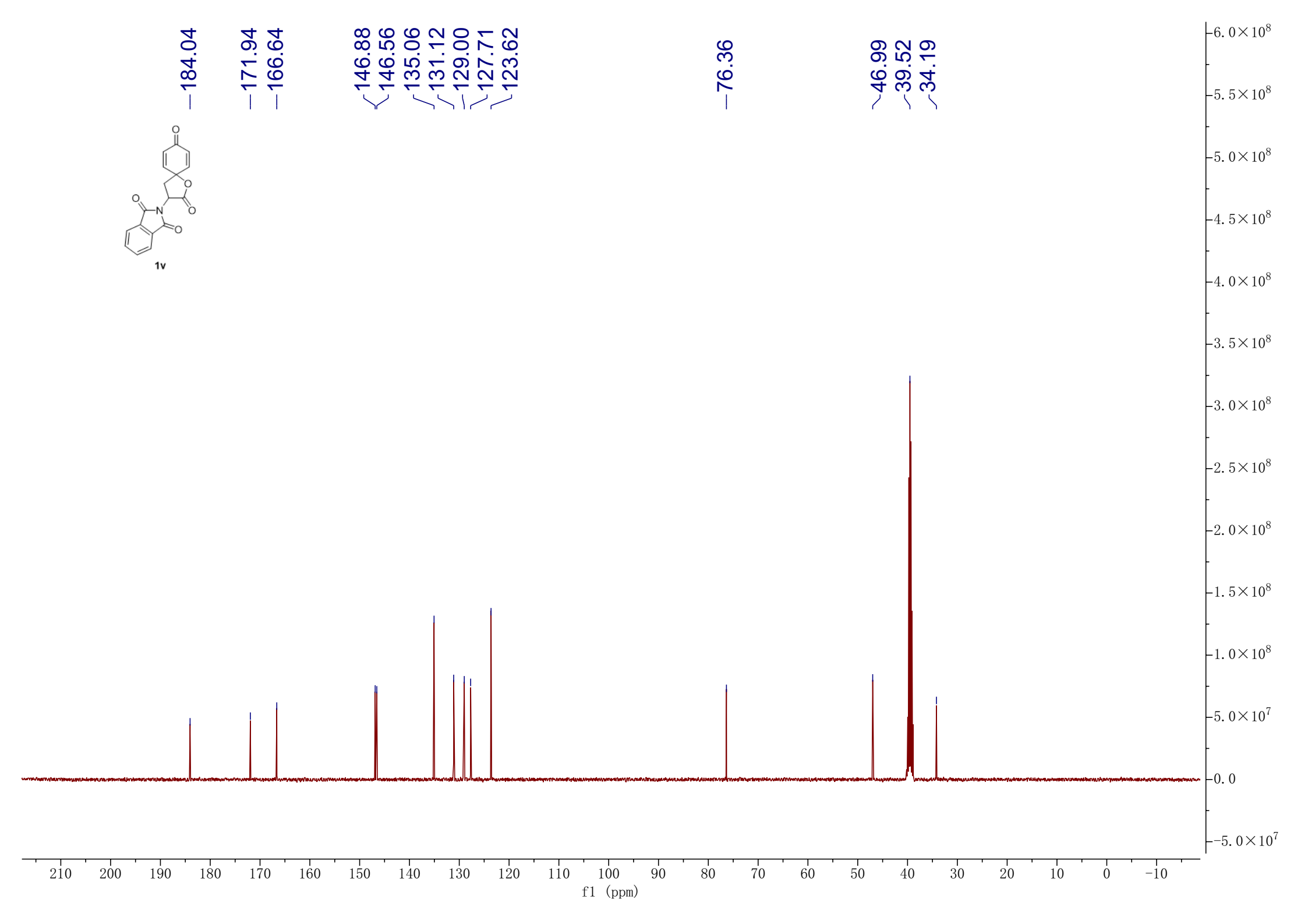
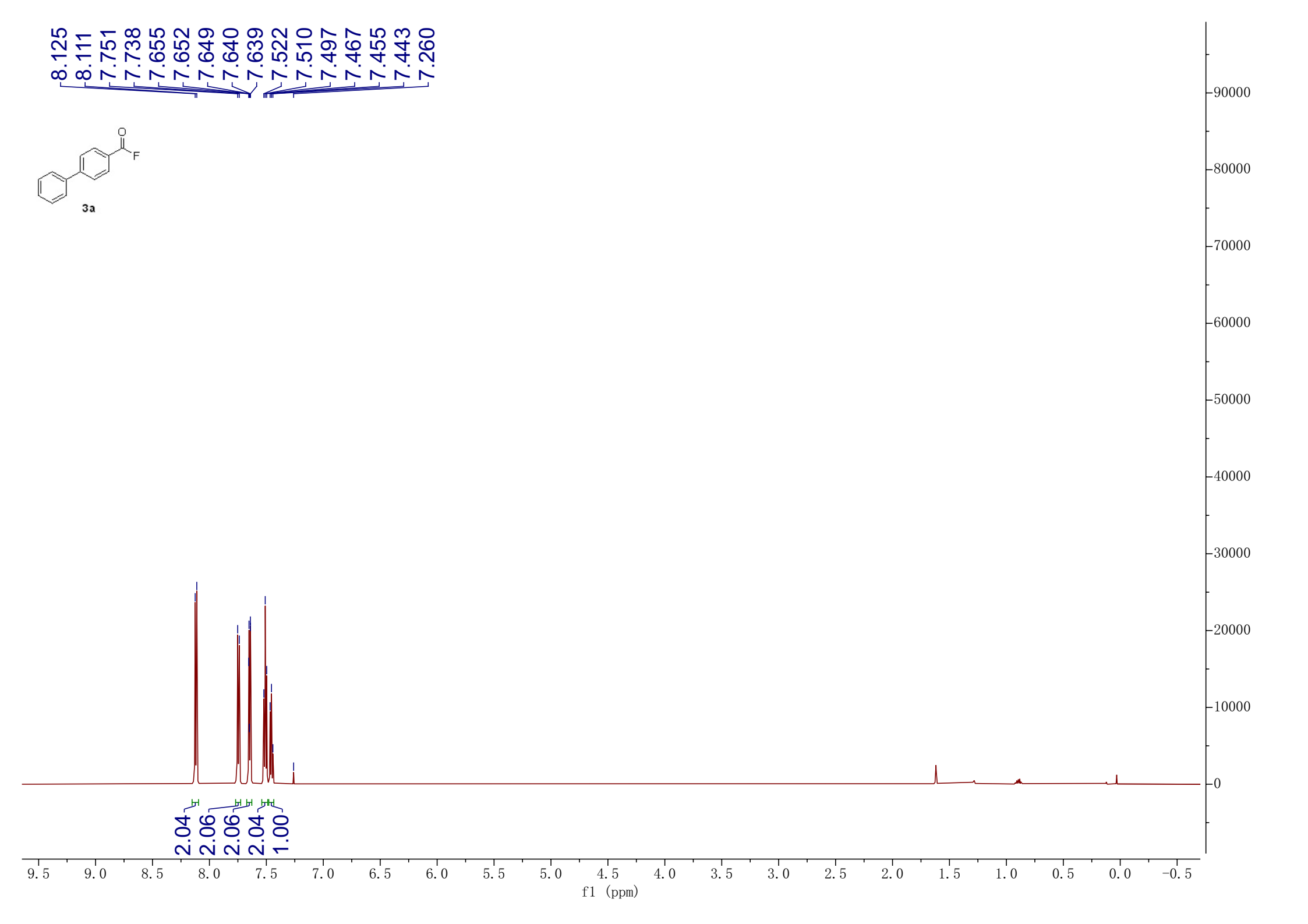
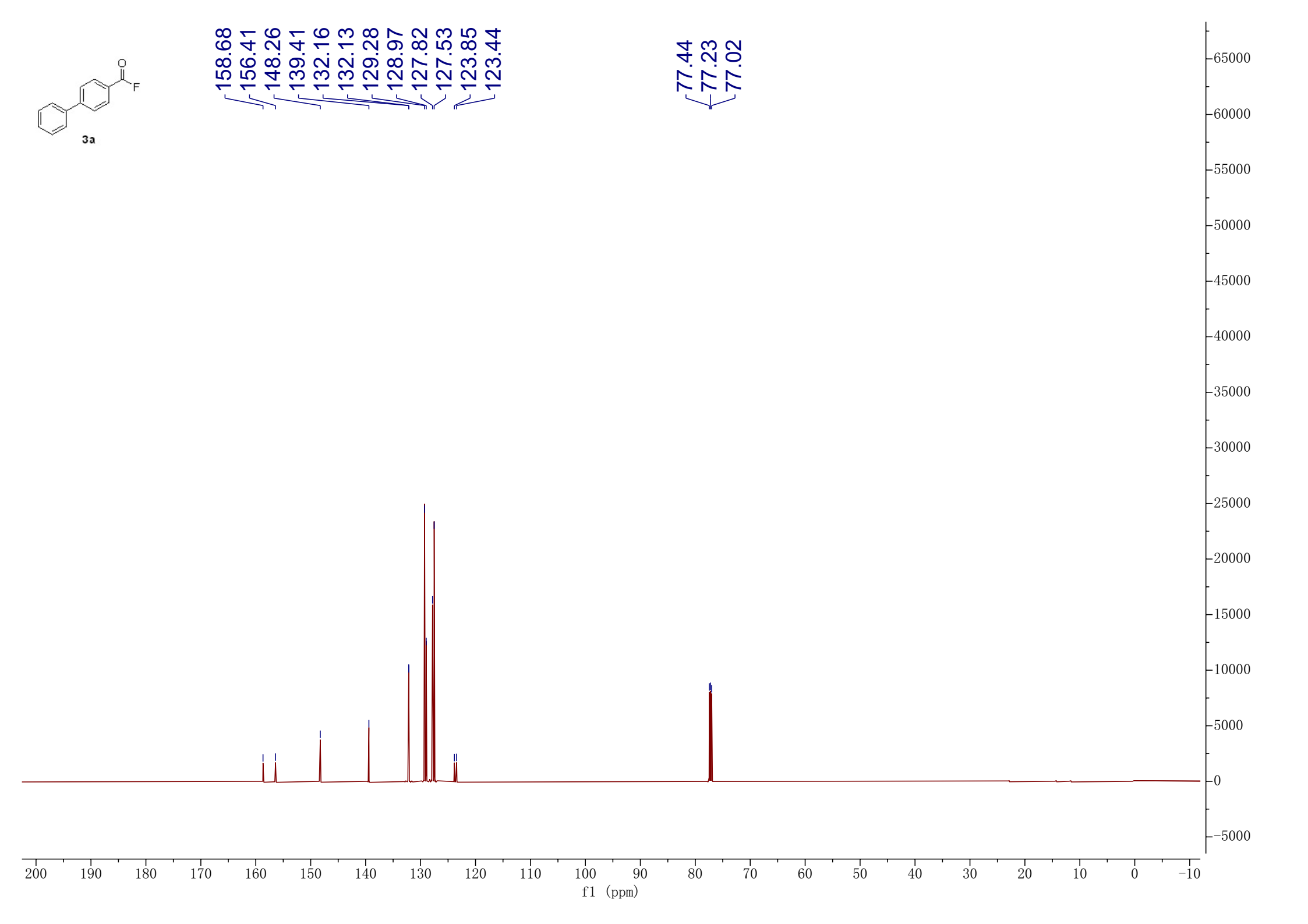
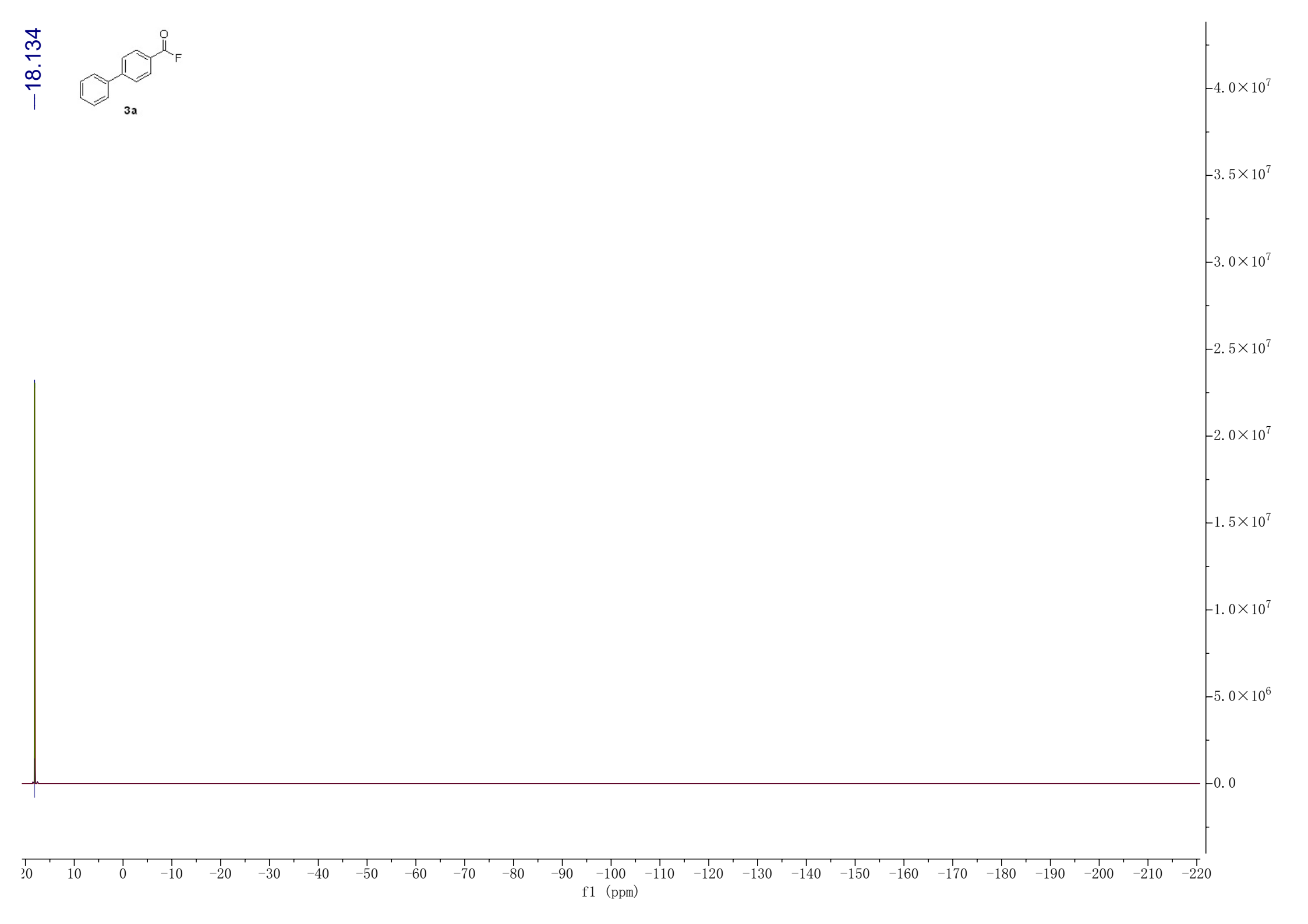
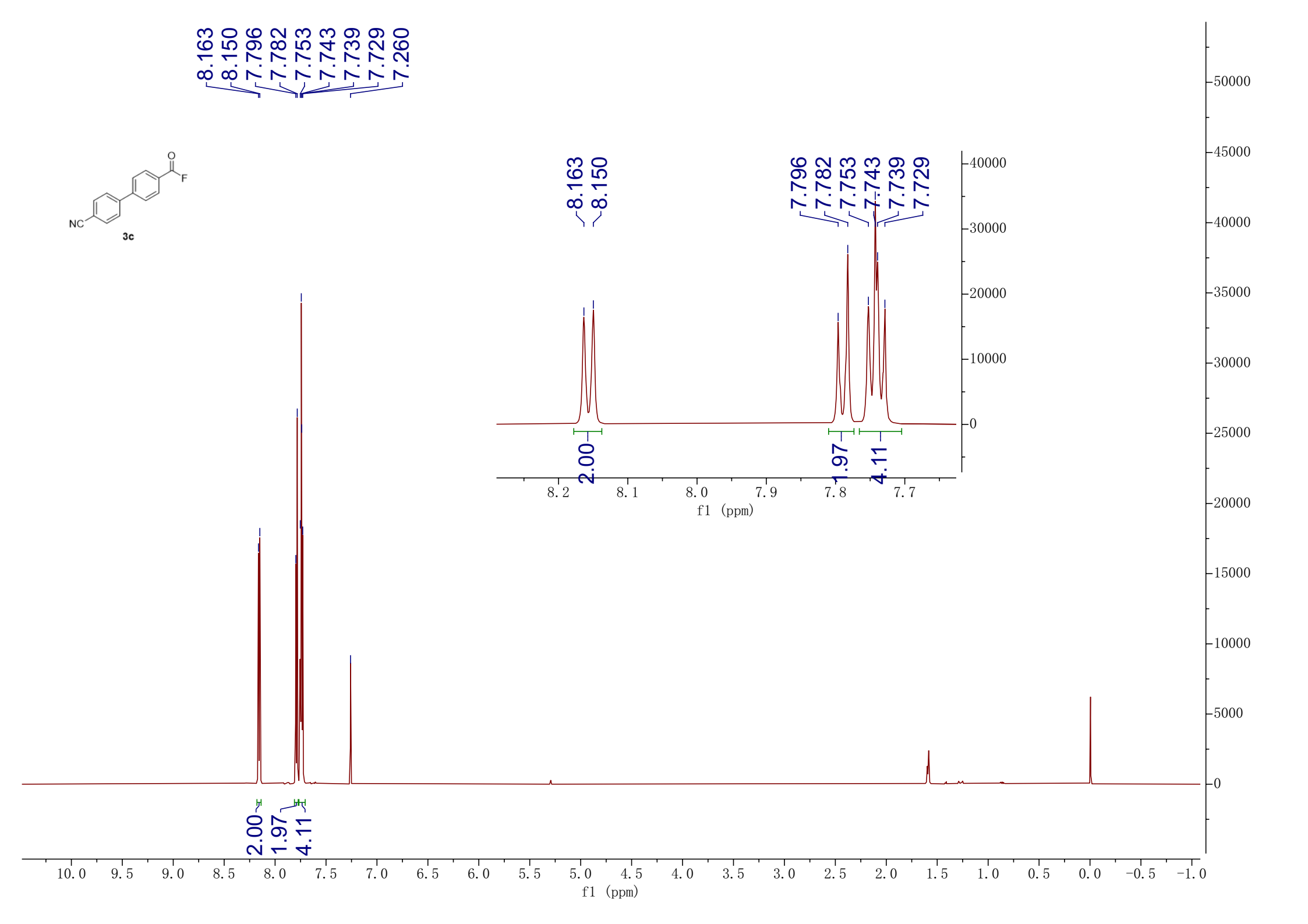
7.948
7.920
7.912
7.558
7.550
7.532
7.525
7.131
7.123
7.106
7.098
6.349
6.345
6.324
6.320
6.302
6.297
6.276
6.272
5.808
5.782
5.757
2.786
2.758
2.751
2.728
2.706
2.672
2.505
2.500
2.496
1v
4.03
1.00
1.00
2.00
1.02
2.01
f1 (ppm)
1.00
1.00
2.00
1.02
f1 (ppm)


184.04
171.94
166.64
146.88
146.56
135.06
131.12
129.00
127.71
123.62
76.36
46.99
39.52
34.19
1v
6.0×10^8
5.5×10^8
5.0×10^8
4.5×10^8
4.0×10^8
3.5×10^8
3.0×10^8
2.5×10^8
2.0×10^8
1.5×10^8
1.0×10^8
5.0×10^7
0.0
-5.0×10^7
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)


8.125
8.111
7.751
7.738
7.655
7.652
7.649
7.640
7.639
7.522
7.510
7.497
7.467
7.455
7.443
7.260
O
F
3a
2.04
2.06
2.06
2.04
1.00
90000
80000
70000
60000
50000
40000
30000
20000
10000
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
-0.5
f1 (ppm)


158.68
156.41
148.26
139.41
132.16
132.13
129.28
128.97
127.82
127.53
123.85
123.44
77.44
77.23
77.02
O
F
3a
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


—18.134
O
F
3a
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)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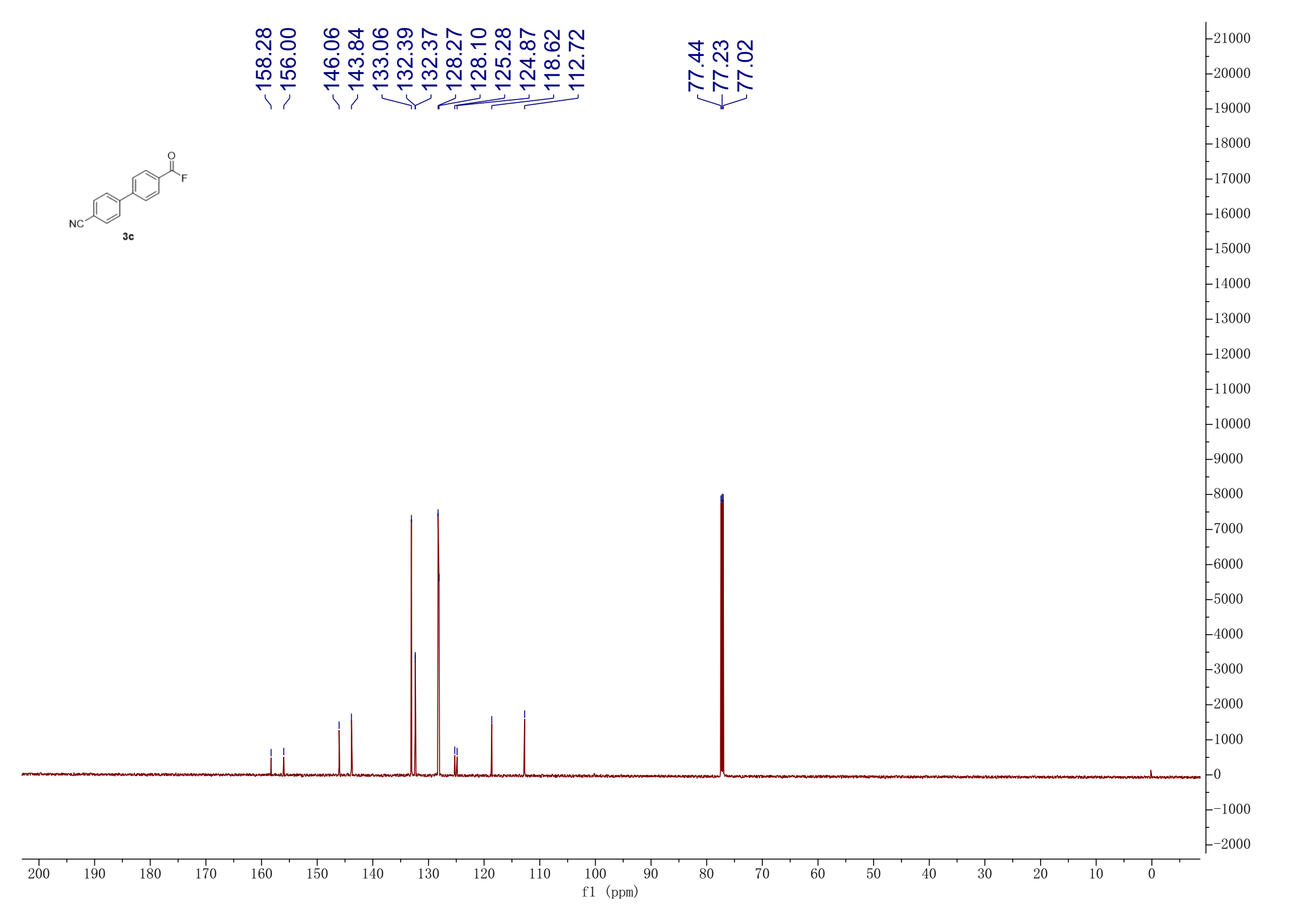
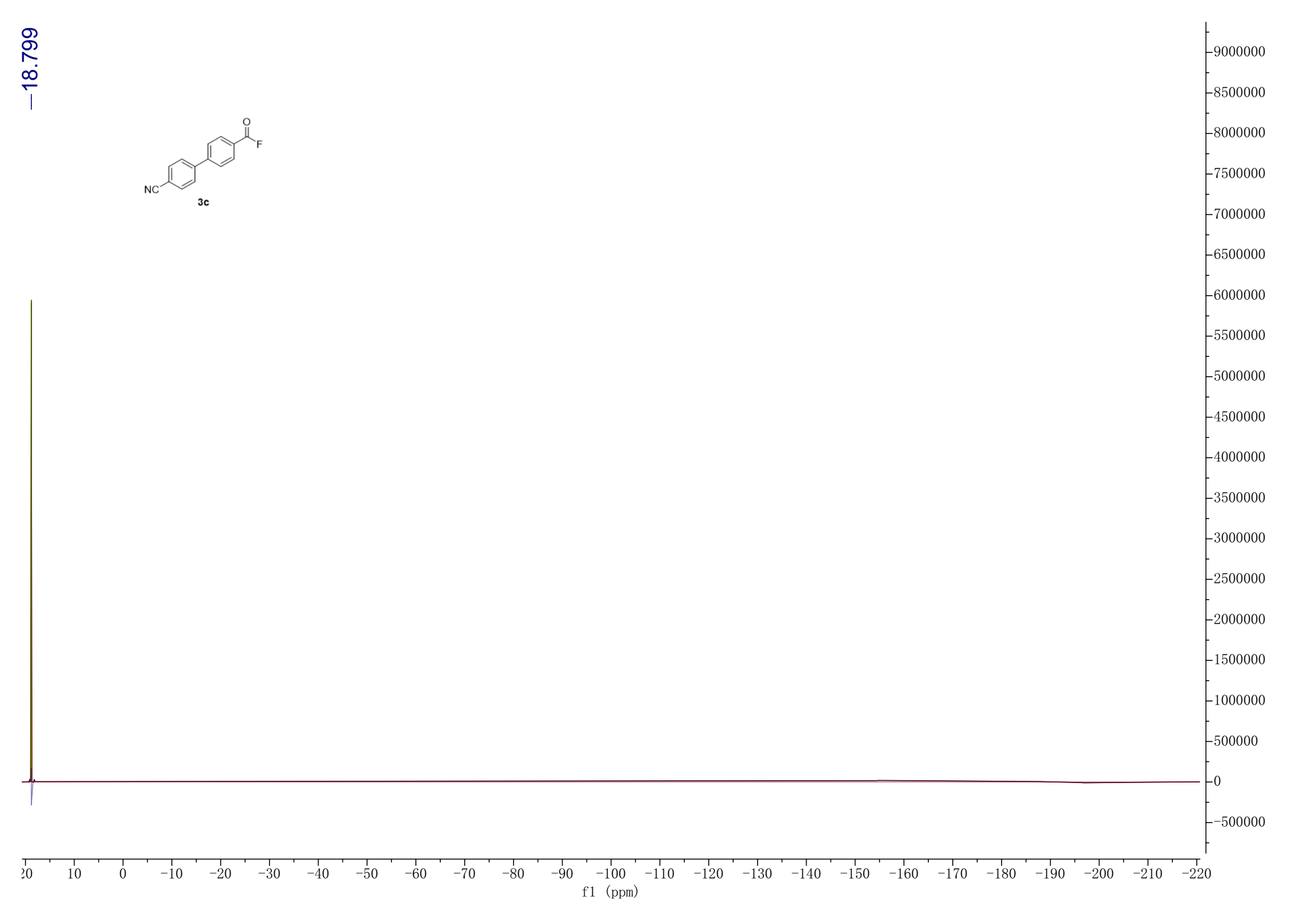
7.796
7.782
7.753
7.743
7.739
7.729
7.260
O
F
NC
3c
2.00
1.97
4.11
f1 (ppm)


158.28
156.00
146.06
143.84
133.06
132.39
132.37
128.27
128.10
125.28
124.87
118.62
112.72
77.44
77.23
77.02
O
F
NC
3c
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000
−2000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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O
F
NC
3c
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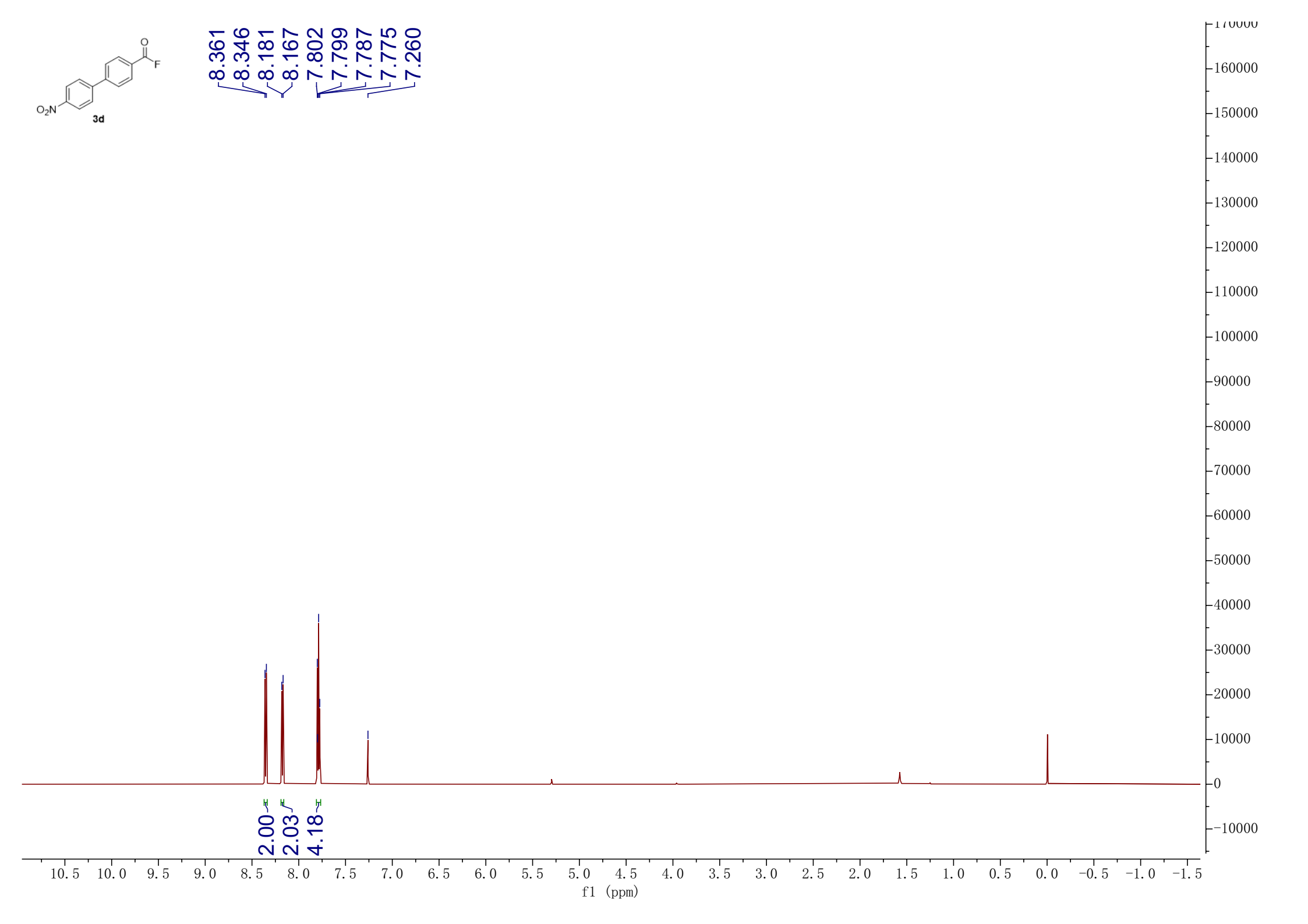
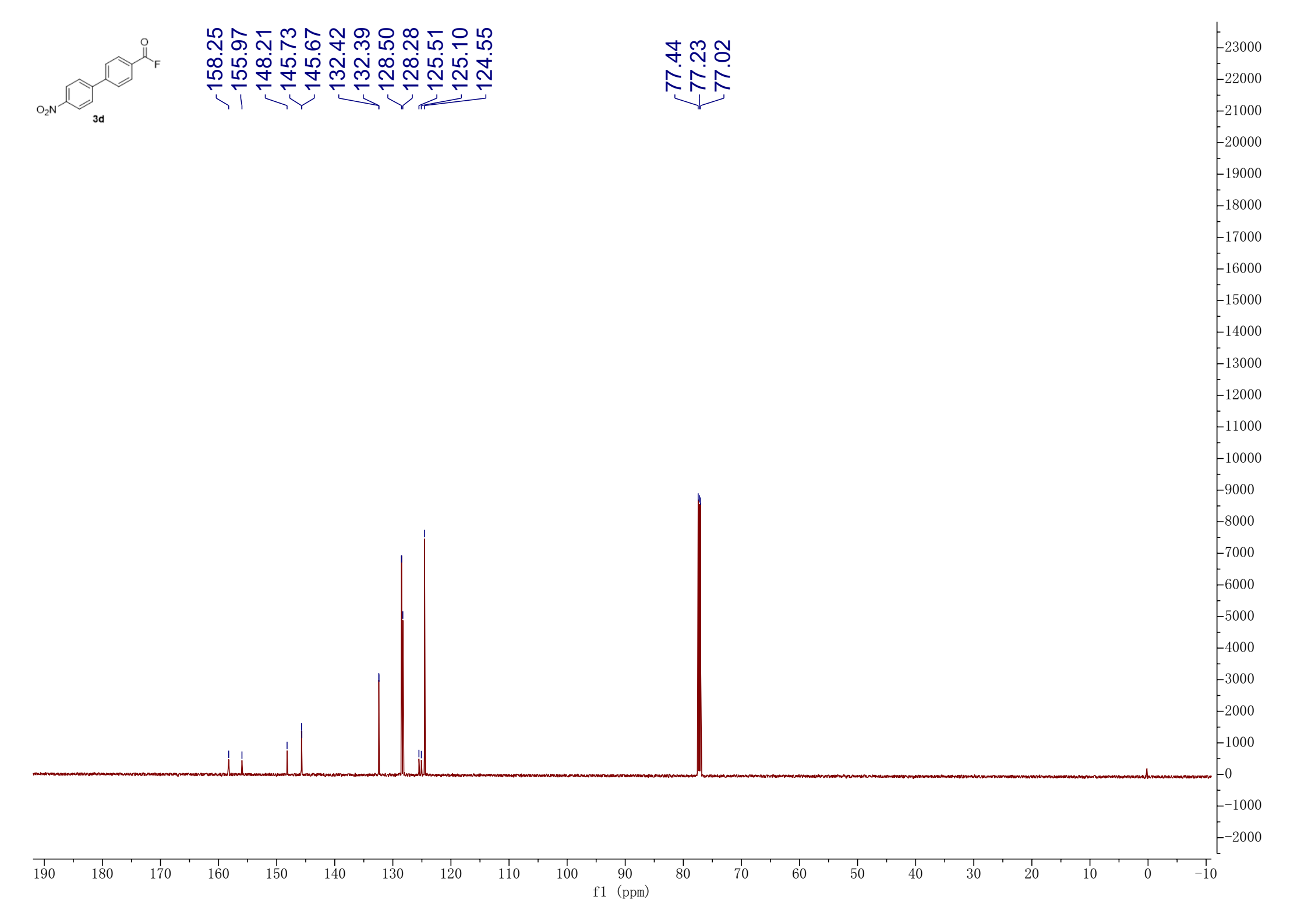
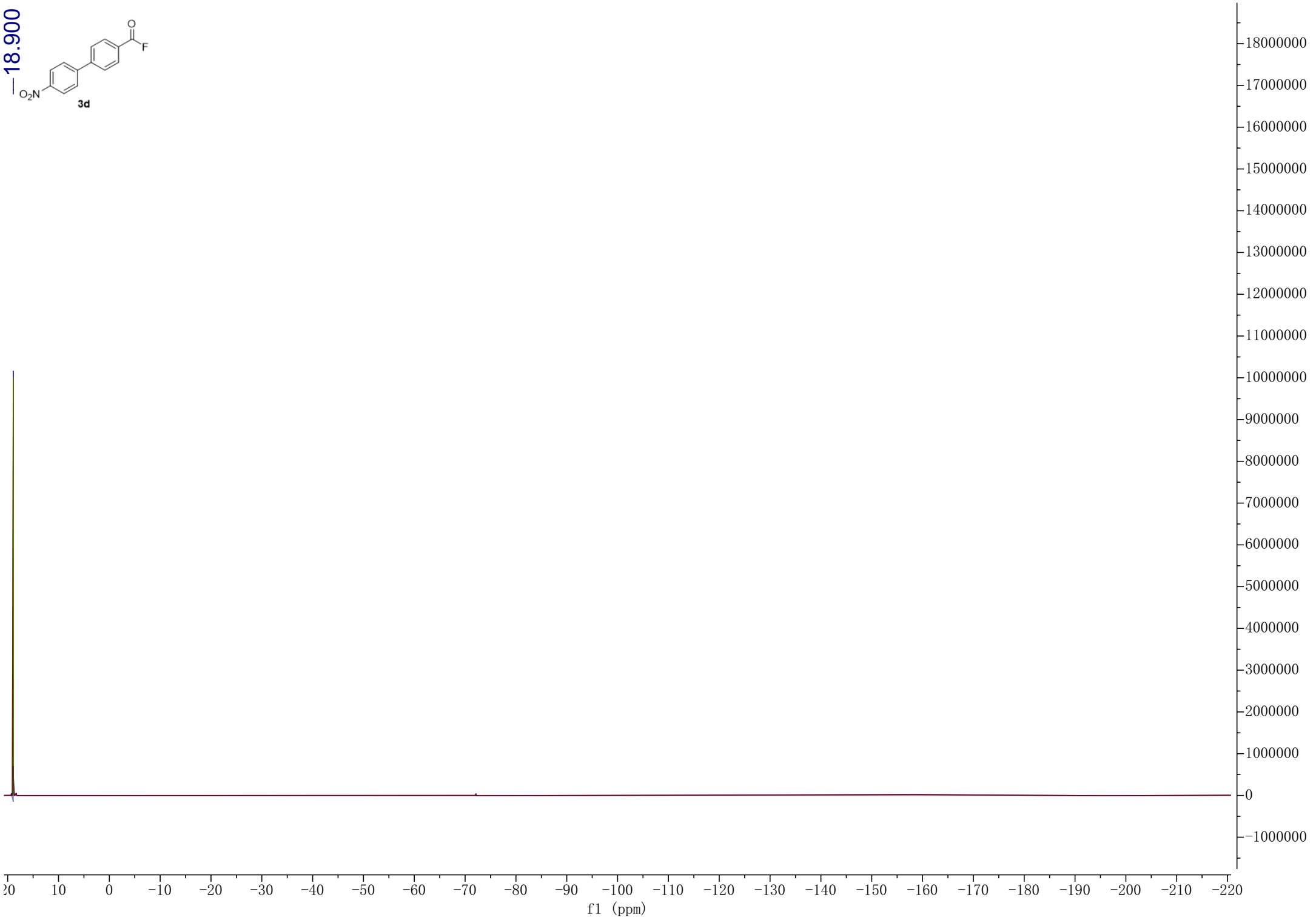
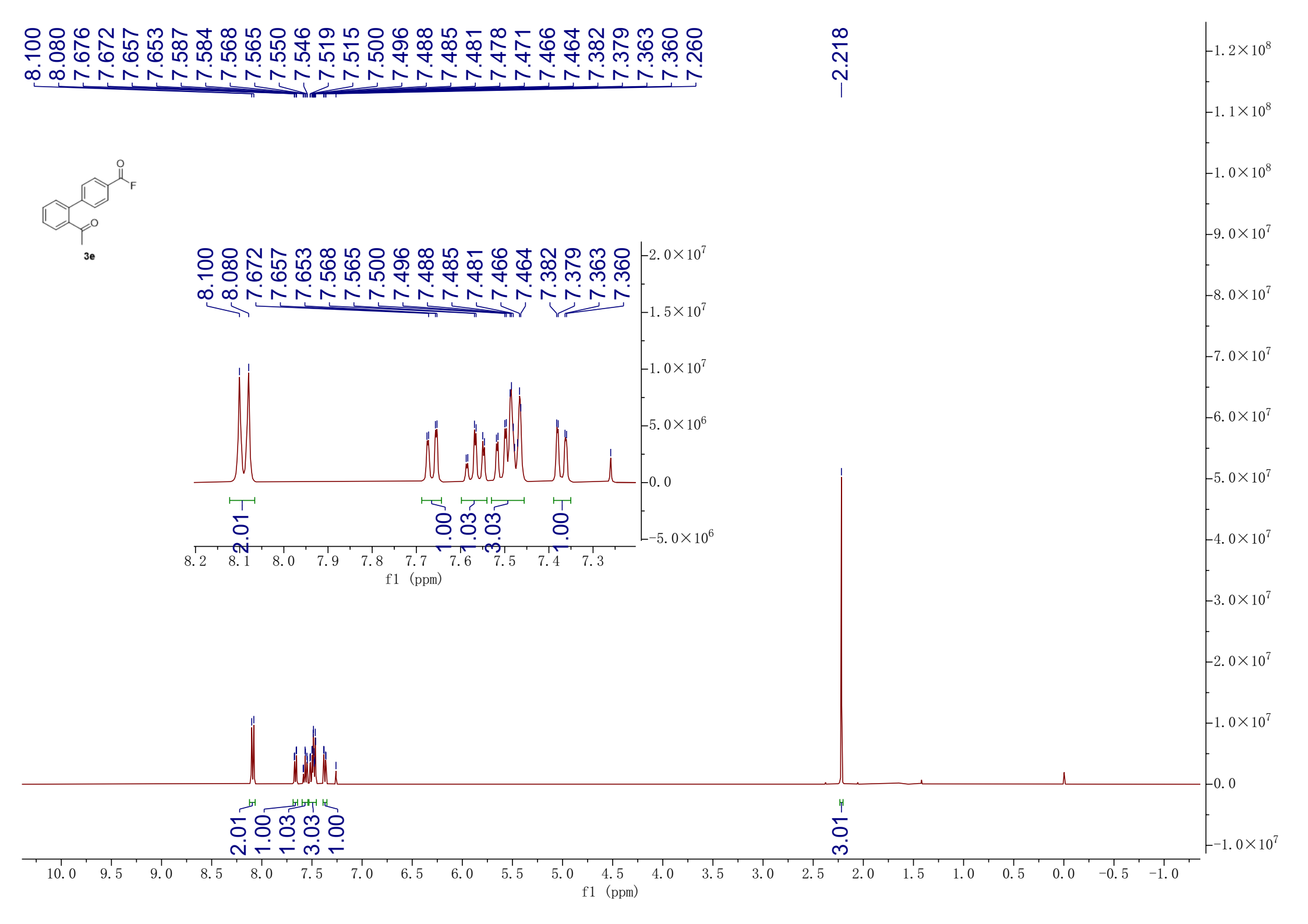
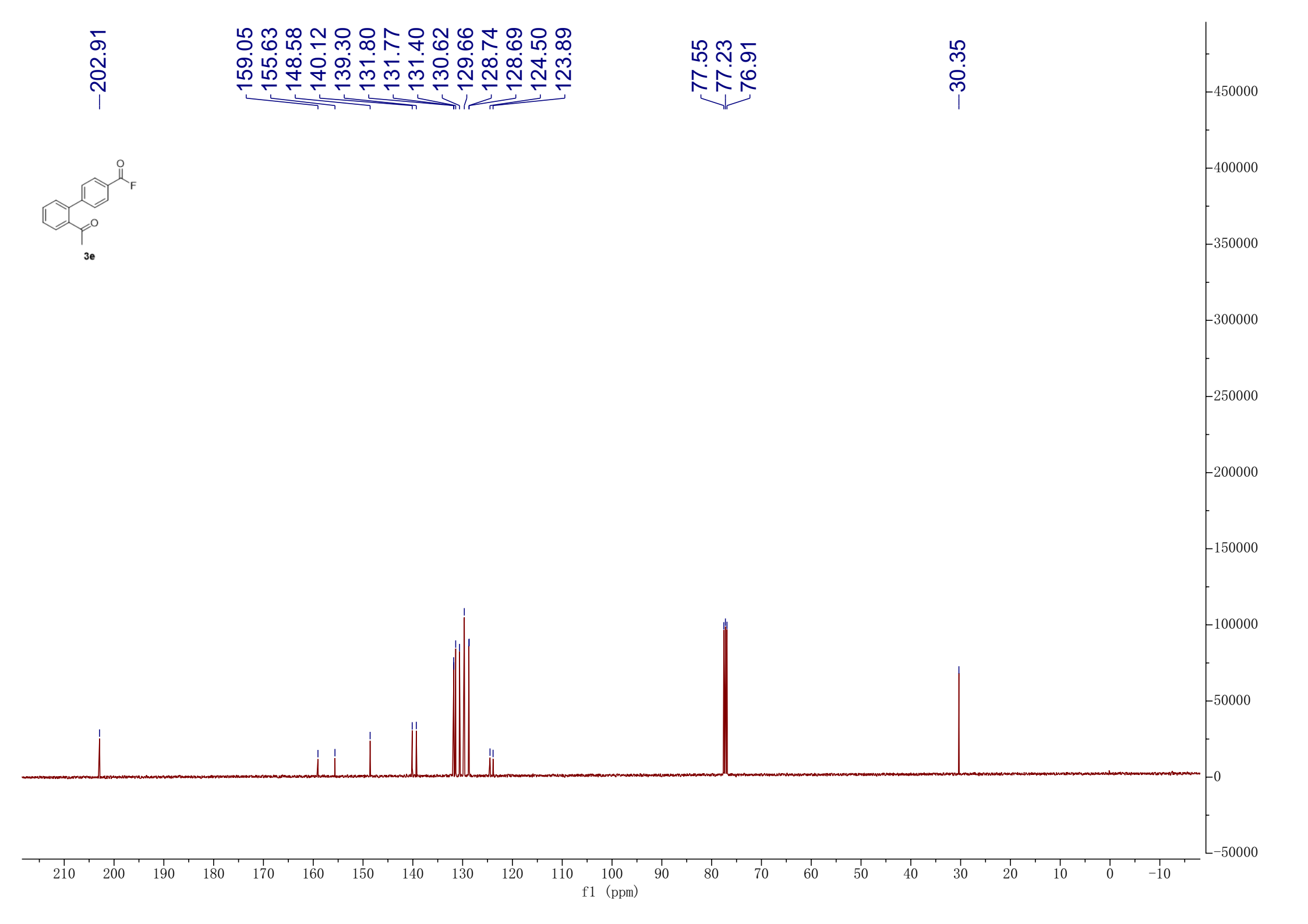
8500000
8000000
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
−500000
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
−220
f1 (ppm)

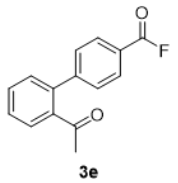

8.361
8.346
8.181
8.167
7.802
7.799
7.787
7.775
7.260
O
F
O2N
3d
2.00
2.03
4.18
f1 (ppm)


O
F
O2N
3d
158.25
155.97
148.21
145.73
145.67
132.42
132.39
128.50
128.28
125.51
125.10
124.55
77.44
77.23
77.02
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


18.900
O
F
O2N
3d
18000000
17000000
16000000
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

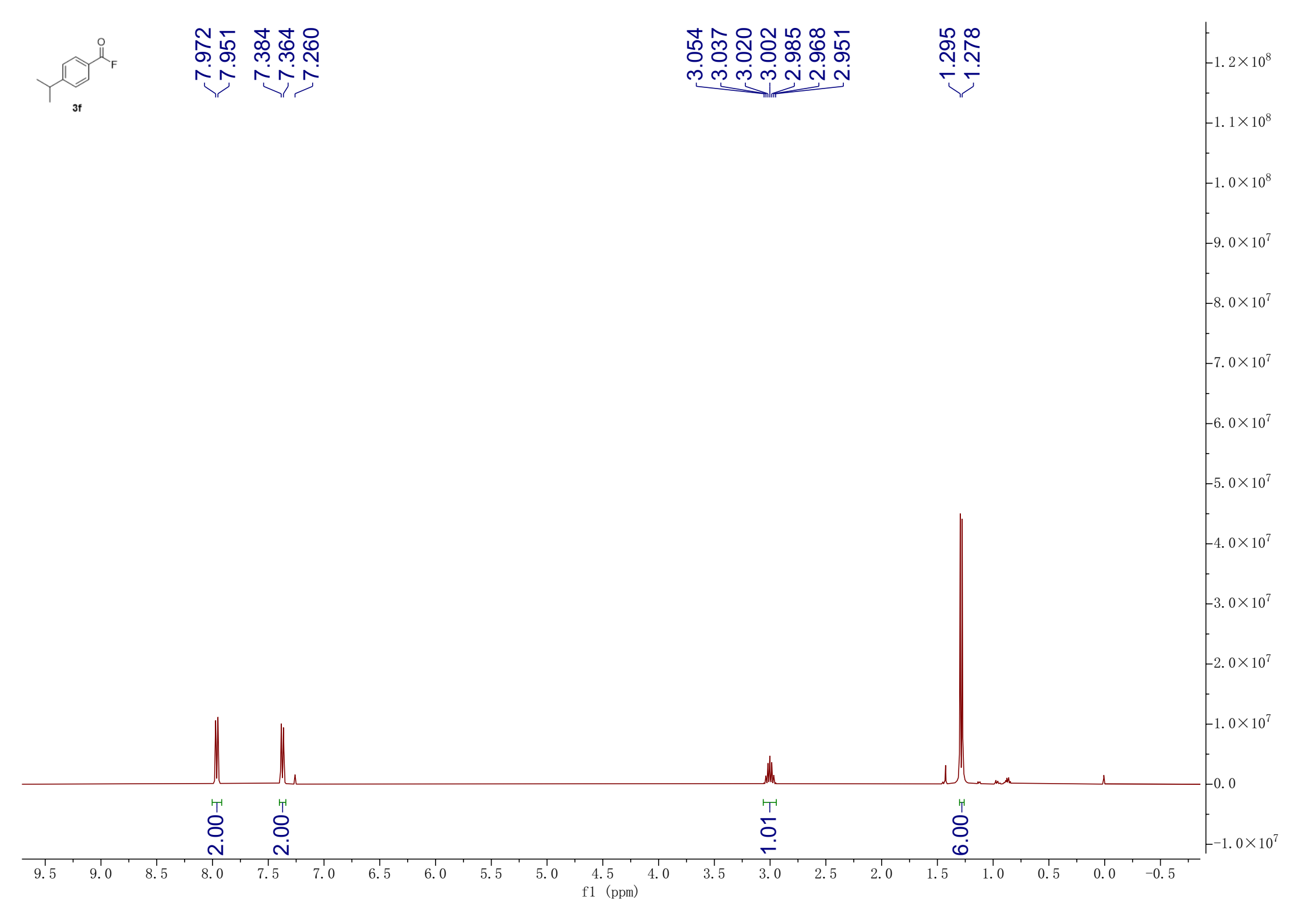

8.100
8.080
7.676
7.672
7.657
7.653
7.587
7.584
7.568
7.565
7.550
7.546
7.519
7.515
7.500
7.496
7.488
7.485
7.481
7.478
7.471
7.466
7.464
7.382
7.379
7.363
7.360
7.260
2.218
3e
f1 (ppm)
2.01
1.00
1.03
3.03
1.00
3.01

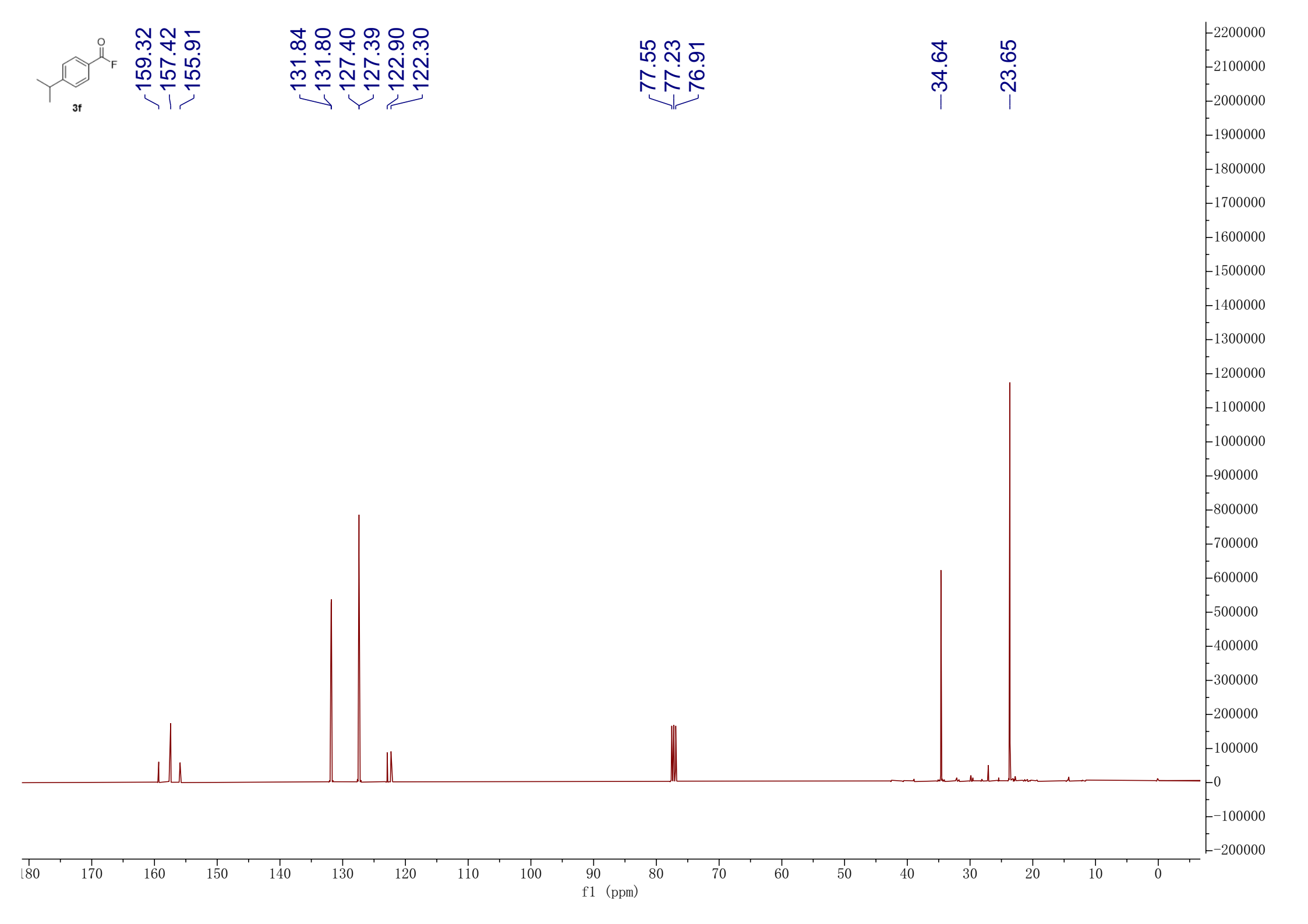

202.91
159.05
155.63
148.58
140.12
139.30
131.80
131.77
131.40
130.62
129.66
128.74
128.69
124.50
123.89
77.55
77.23
76.91
30.35
O
F
O
3e
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

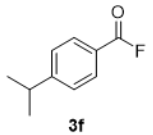

O
F
O

3e

-18.427
7.5×10^7
7.0×10^7
6.5×10^7
6.0×10^7
5.5×10^7
5.0×10^7
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
-5.0×10^6
20 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)


3f
7.972
7.951
7.384
7.364
7.260
3.054
3.037
3.020
3.002
2.985
2.968
2.951
1.295
1.278
2.00
2.00
1.01
6.00
f1 (ppm)


3f
159.32
157.42
155.91
131.84
131.80
127.40
127.39
122.90
122.30
77.55
77.23
76.91
34.64
23.65
f1 (ppm)



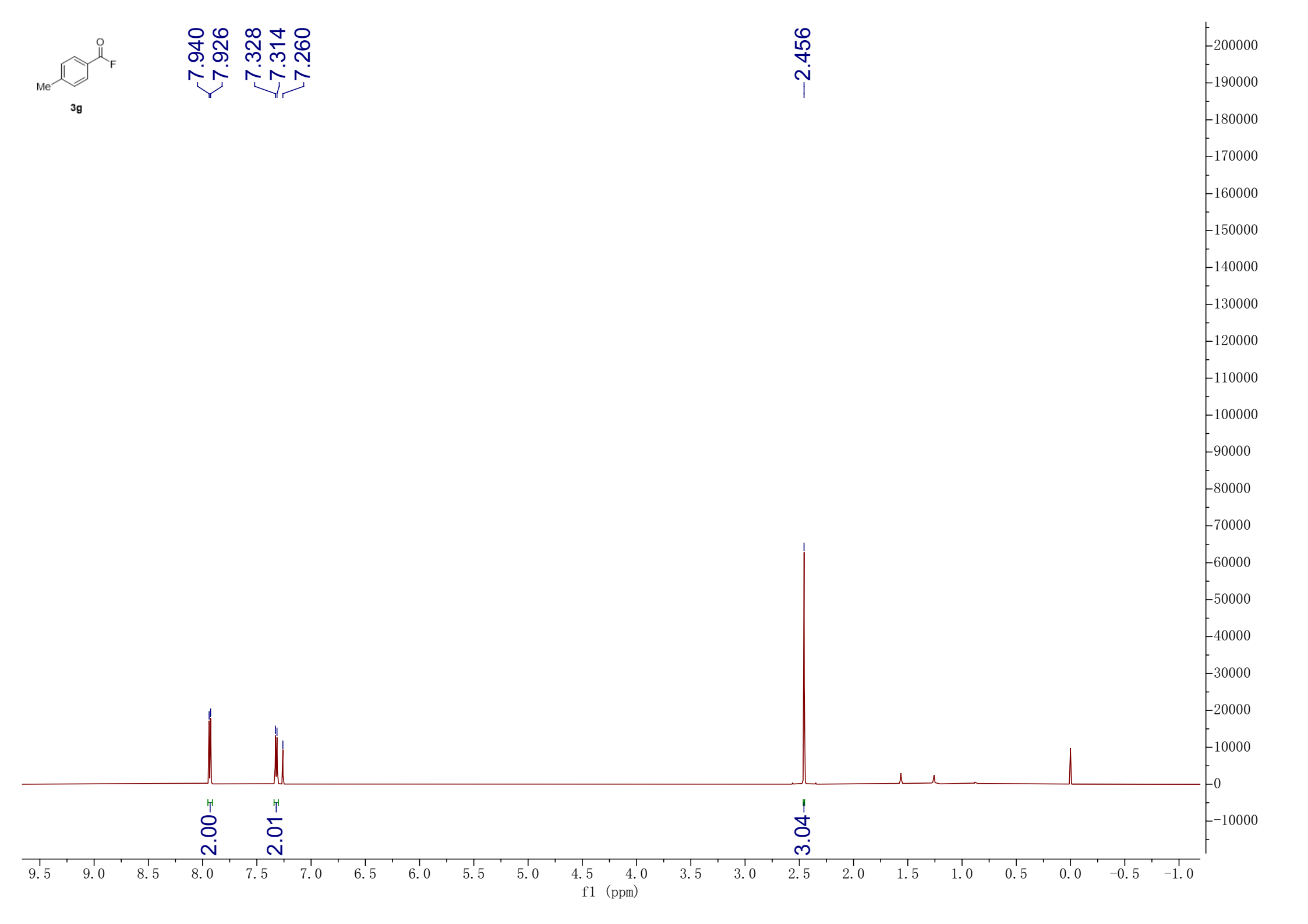
3f

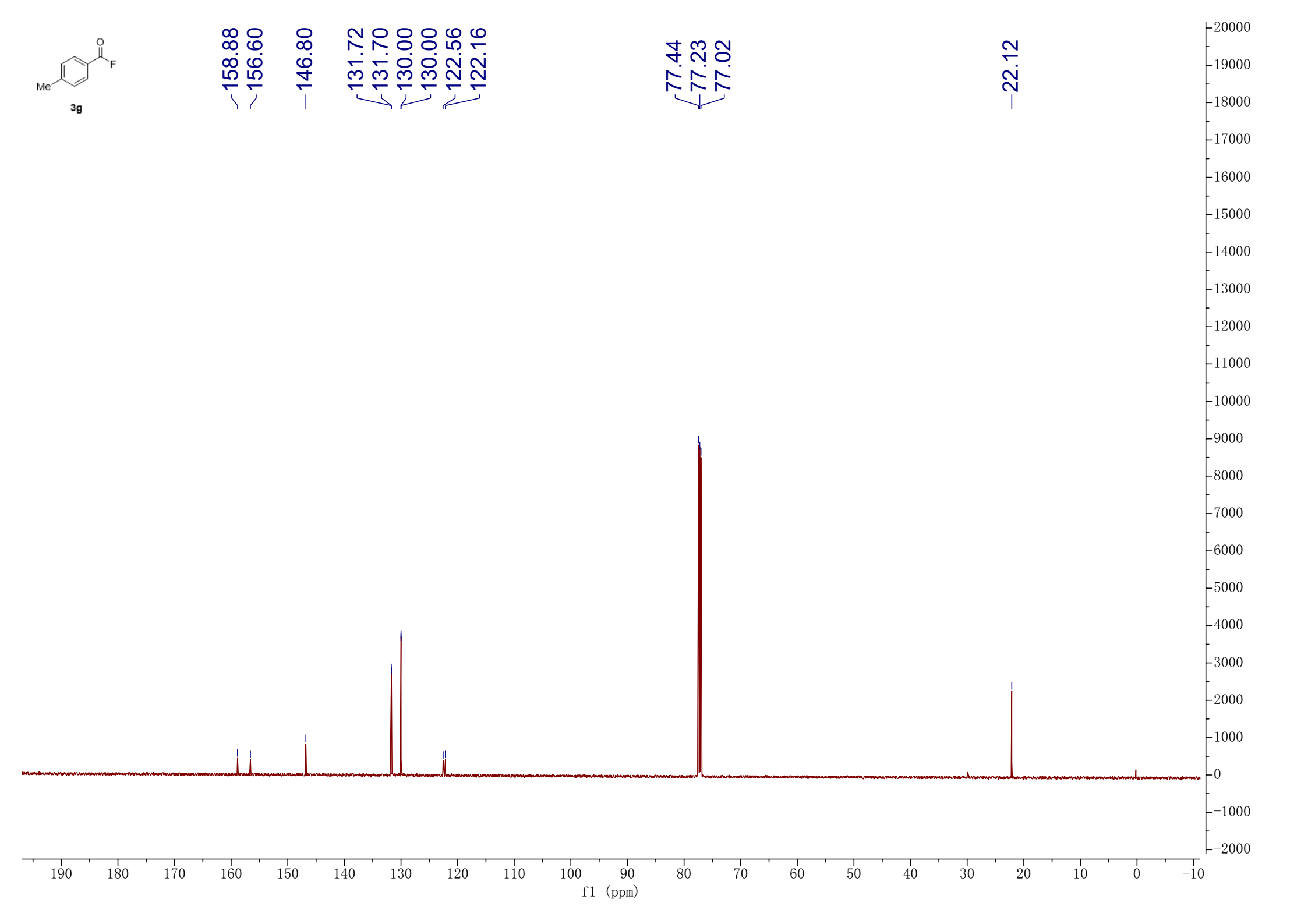
−17.496

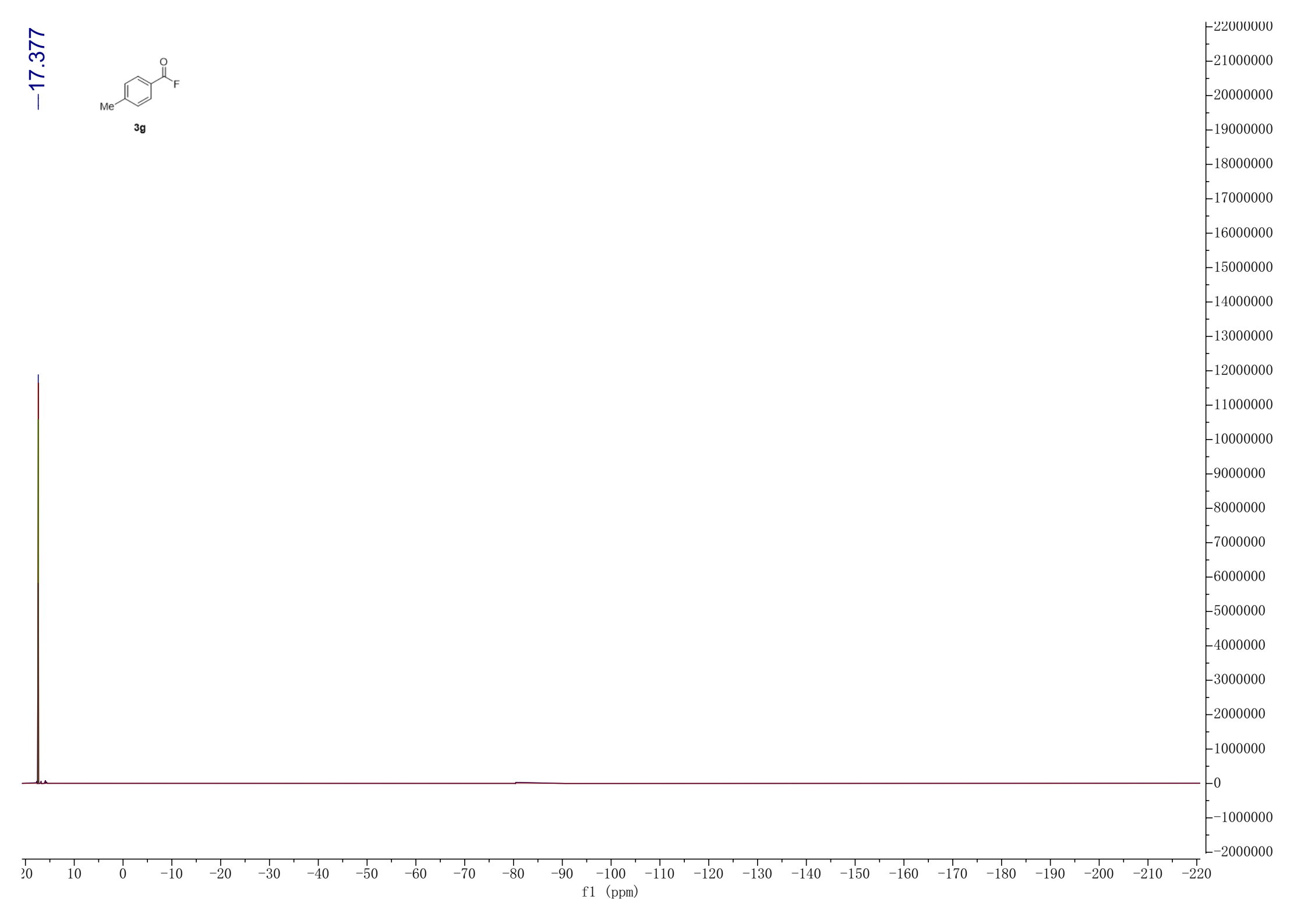
2.00×10^8
1.90×10^8
1.80×10^8
1.70×10^8
1.60×10^8
1.50×10^8
1.40×10^8
1.30×10^8
1.20×10^8
1.10×10^8
1.00×10^8
9.00×10^7
8.00×10^7
7.00×10^7
6.00×10^7
5.00×10^7
4.00×10^7
3.00×10^7
2.00×10^7
1.00×10^7
0.00

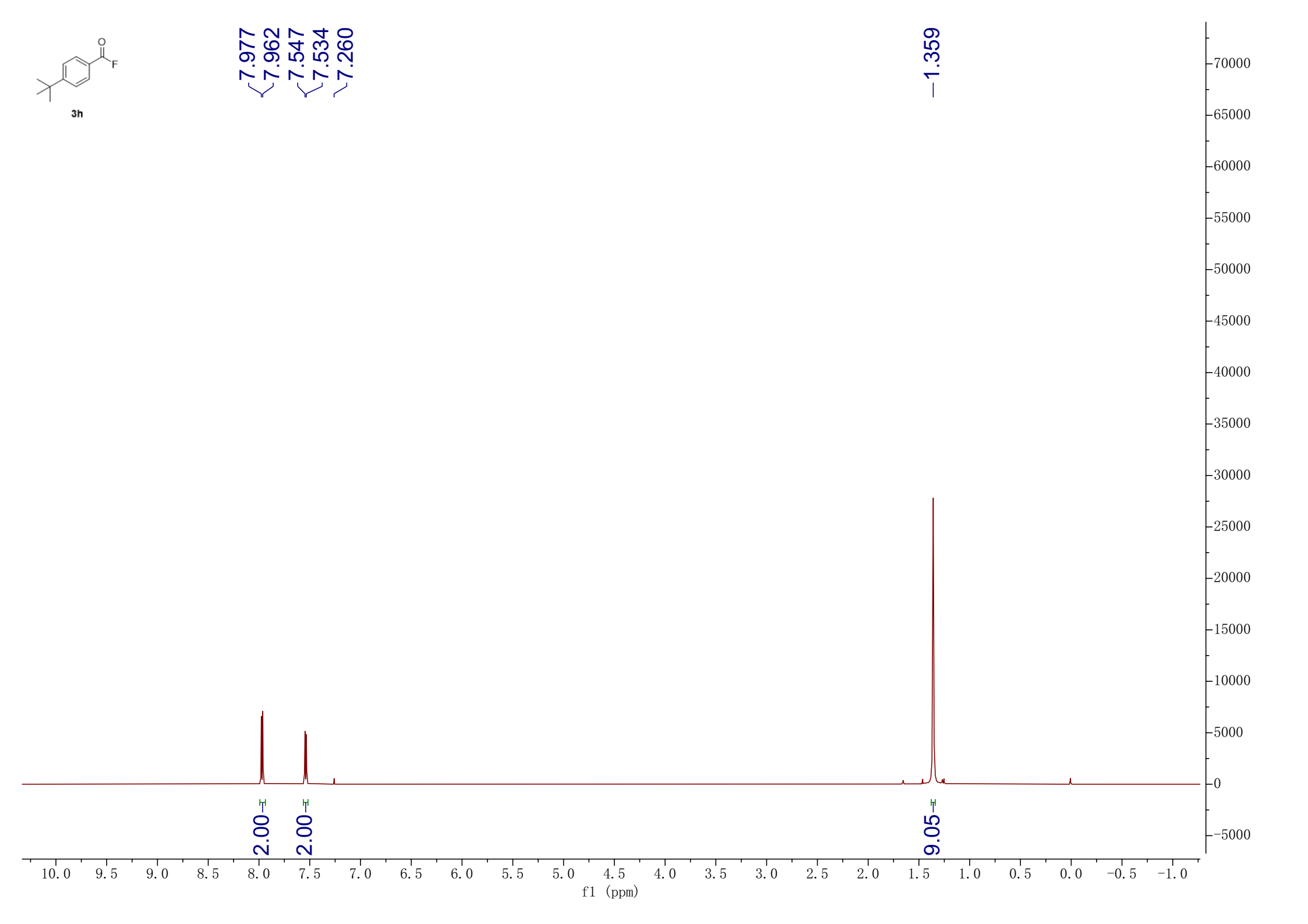
20 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120

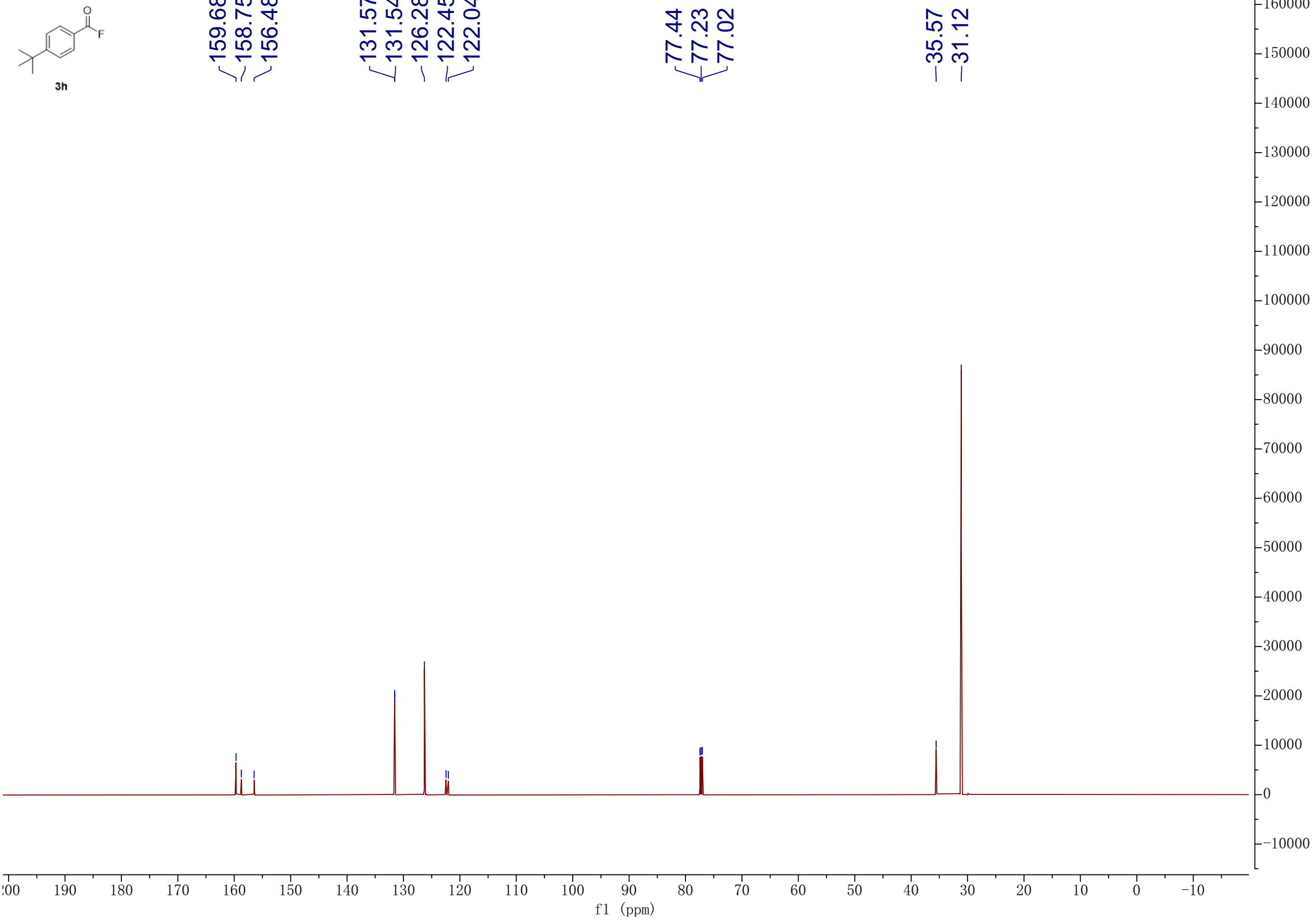
f1 (ppm)

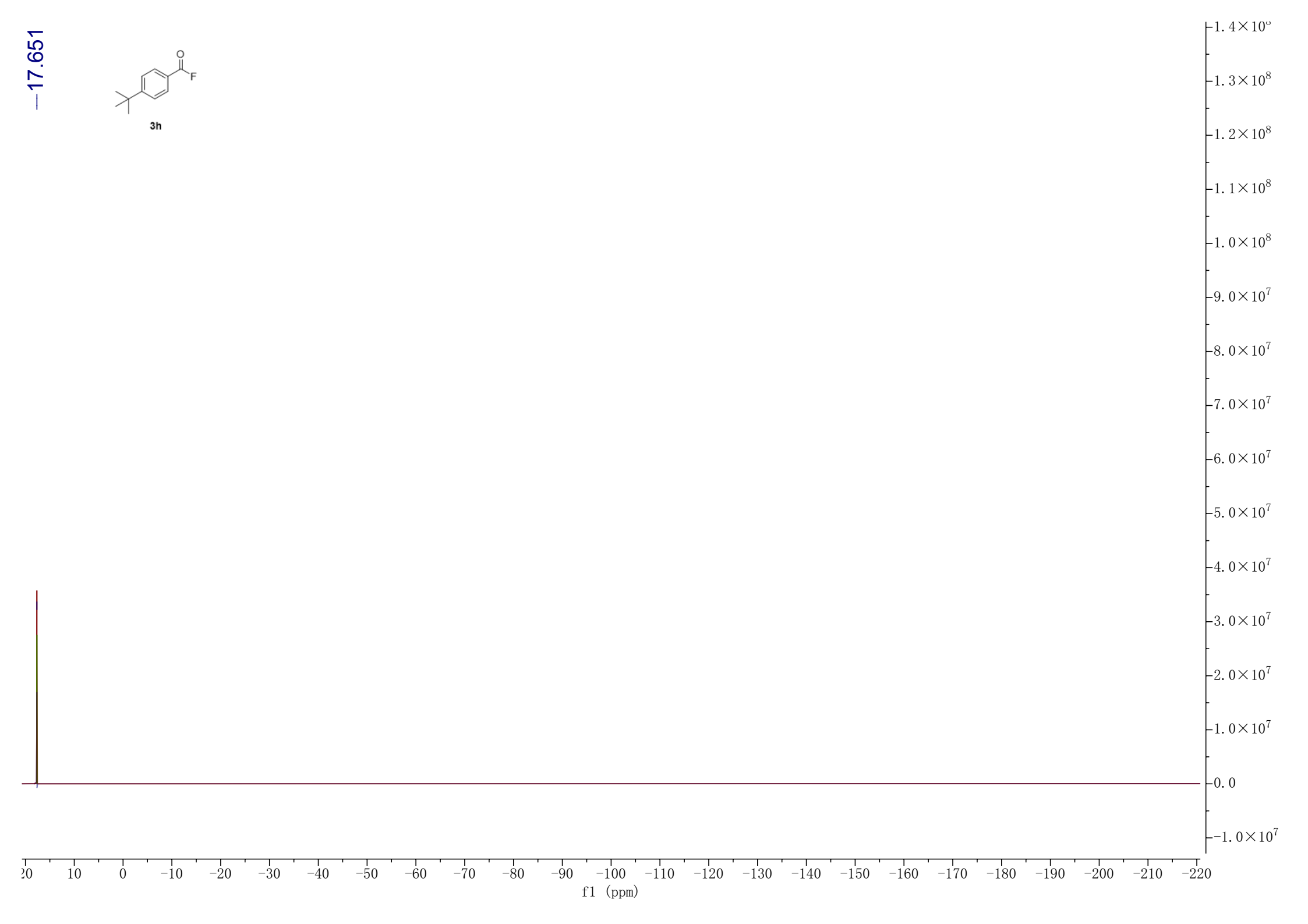

Me
O
F
3g
7.940
7.926
7.328
7.314
7.260
2.456
2.00
2.01
3.04
f1 (ppm)

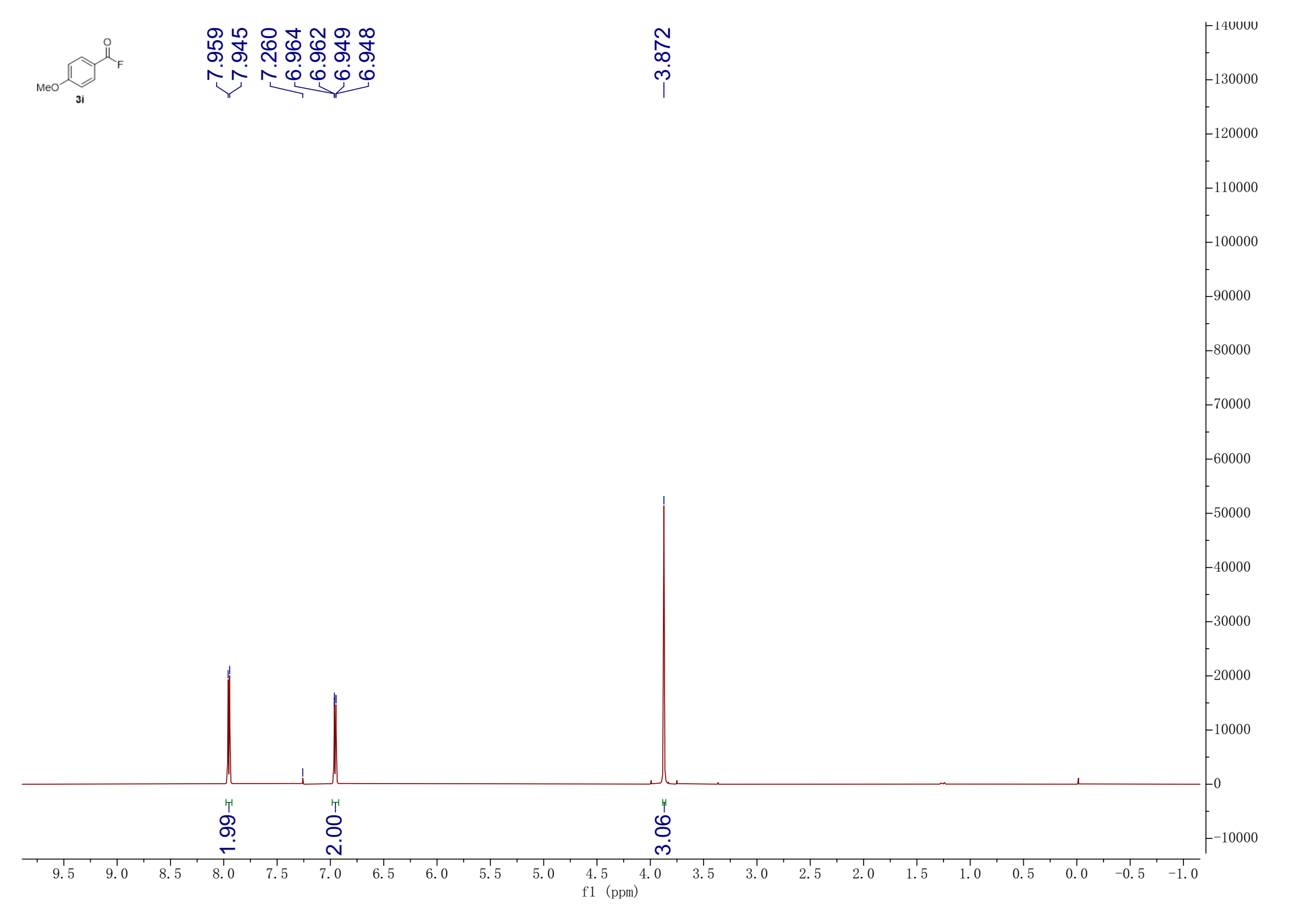

Me
O
F
3g
158.88
156.60
146.80
131.72
131.70
130.00
130.00
122.56
122.16
77.44
77.23
77.02
22.12
f1 (ppm)

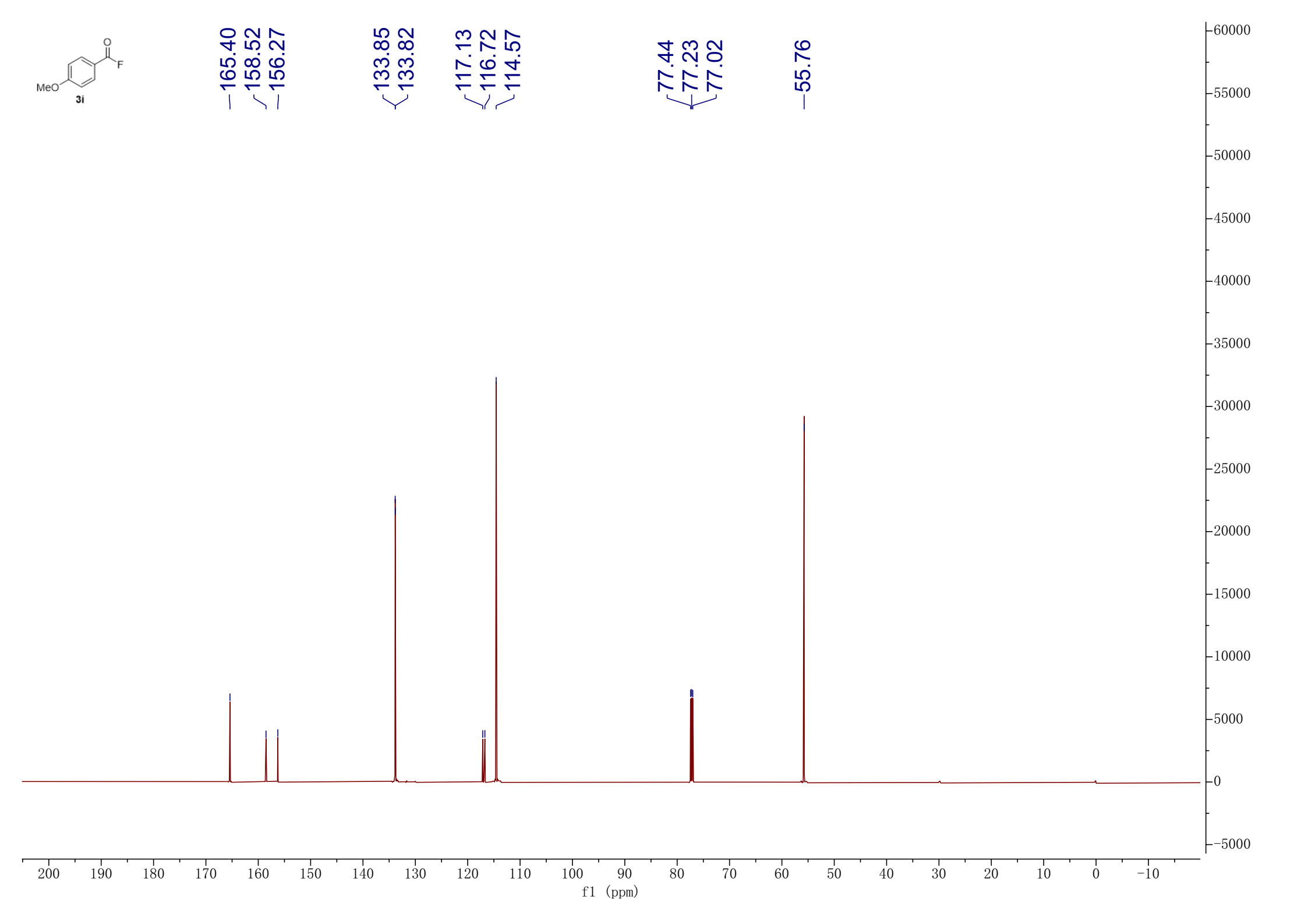

−17.377
O
F
Me
3g
22000000
21000000
20000000
19000000
18000000
17000000
16000000
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
−1000000
−2000000
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)

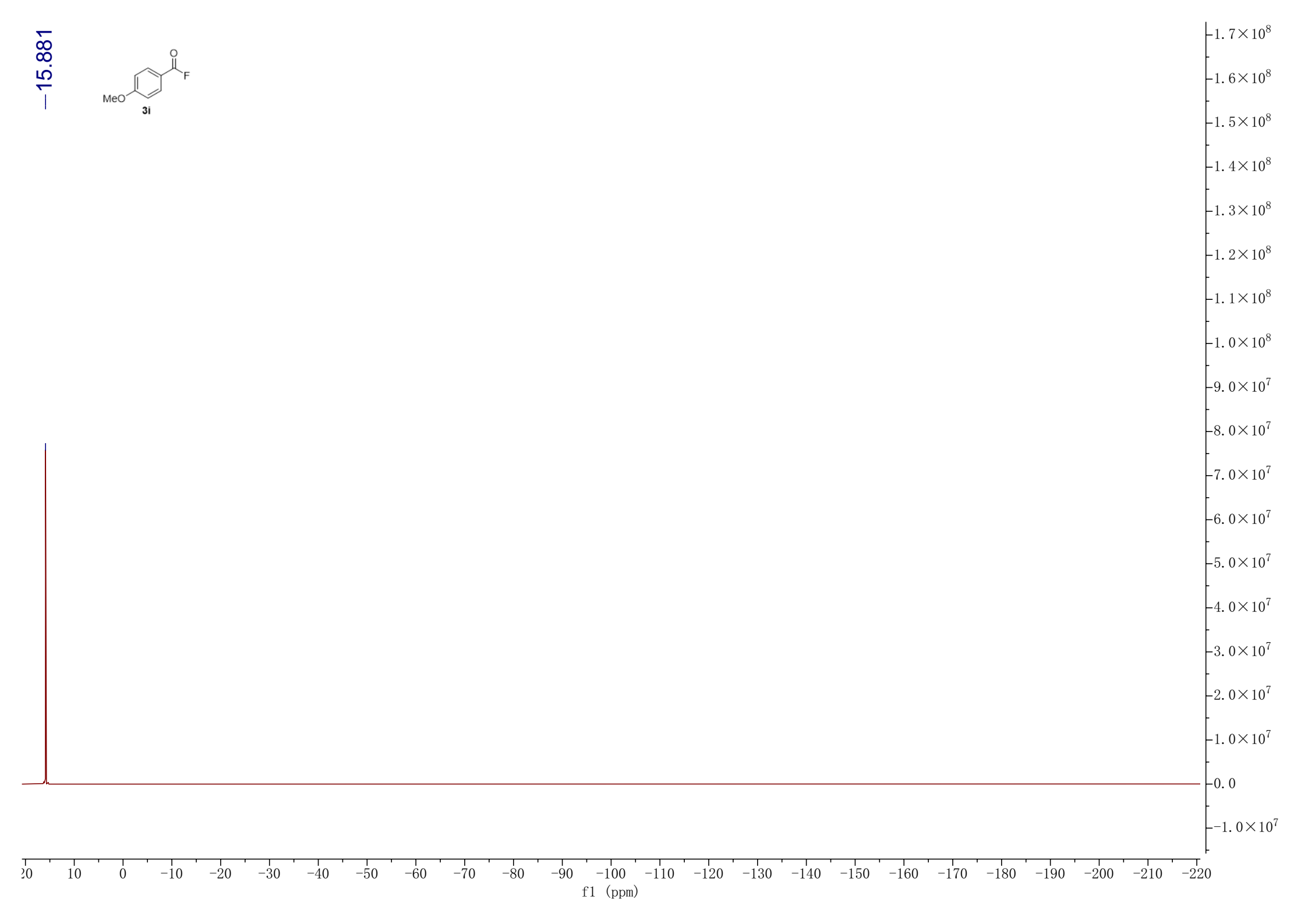

3h
7.977
7.962
7.547
7.534
7.260
1.359
2.00
2.00
9.05
f1 (ppm)

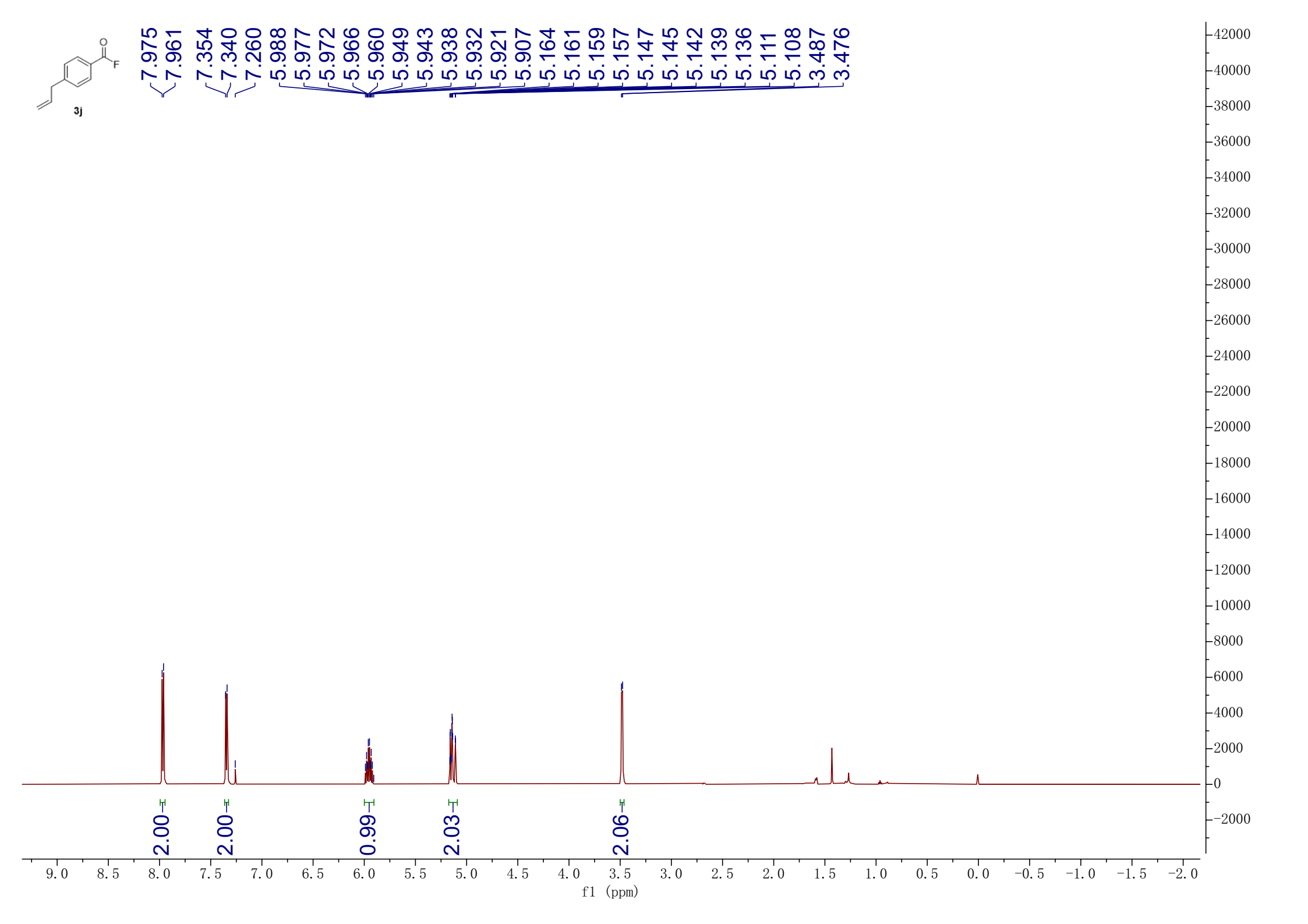

3h
159.68
158.75
156.48
131.57
131.54
126.28
122.45
122.04
77.44
77.23
77.02
35.57
31.12
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
−10000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

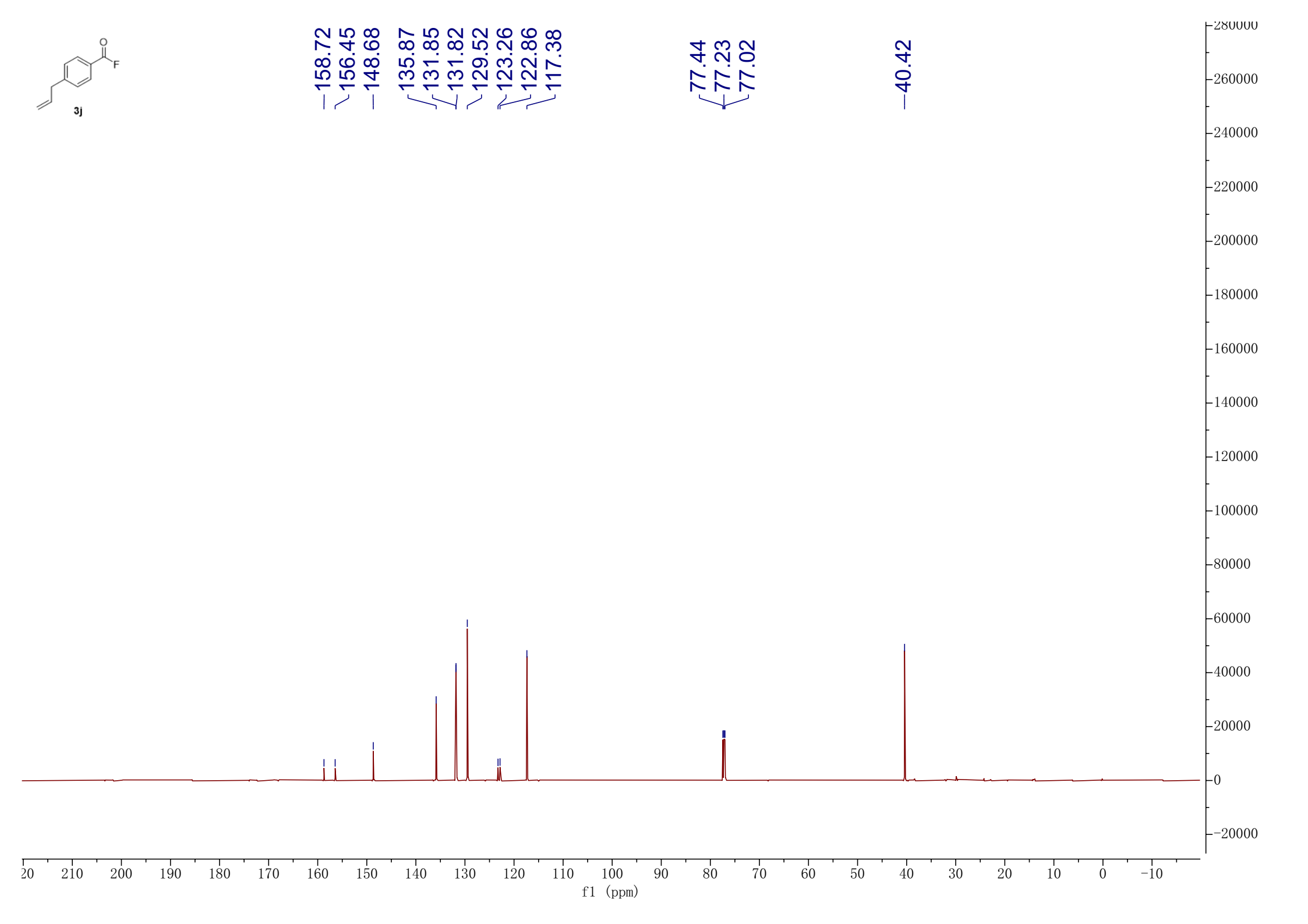

−17.651
O
F
3h
1.4×10⁸
1.3×10⁸
1.2×10⁸
1.1×10⁸
1.0×10⁸
9.0×10⁷
8.0×10⁷
7.0×10⁷
6.0×10⁷
5.0×10⁷
4.0×10⁷
3.0×10⁷
2.0×10⁷
1.0×10⁷
0.0
−1.0×10⁷
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)

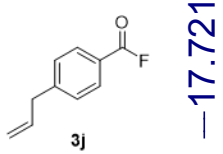

MeO
F
O
3i
7.959
7.945
7.260
6.964
6.962
6.949
6.948
3.872
1.99
2.00
3.06
f1 (ppm)


MeO
O
F
3i
165.40
158.52
156.27
133.85
133.82
117.13
116.72
114.57
77.44
77.23
77.02
55.76
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-15.881
MeO
O
F
3i
1.7×10^8
1.6×10^8
1.5×10^8
1.4×10^8
1.3×10^8
1.2×10^8
1.1×10^8
1.0×10^8
9.0×10^7
8.0×10^7
7.0×10^7
6.0×10^7
5.0×10^7
4.0×10^7
3.0×10^7
2.0×10^7
1.0×10^7
0.0
-1.0×10^7
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)


3j
7.975
7.961
7.354
7.340
7.260
5.988
5.977
5.972
5.966
5.960
5.949
5.943
5.938
5.932
5.921
5.907
5.164
5.161
5.159
5.157
5.147
5.145
5.142
5.139
5.136
5.111
5.108
3.487
3.476
2.00
2.00
0.99
2.03
2.06
f1 (ppm)


3j
158.72
156.45
148.68
135.87
131.85
131.82
129.52
123.26
122.86
117.38
77.44
77.23
77.02
40.42
f1 (ppm)



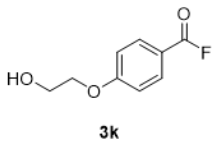
3j

−17.721

4000
3500
3000
2500
2000
1500
1000
500
0
−500

50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220 −230 −240 −250

f1 (ppm)

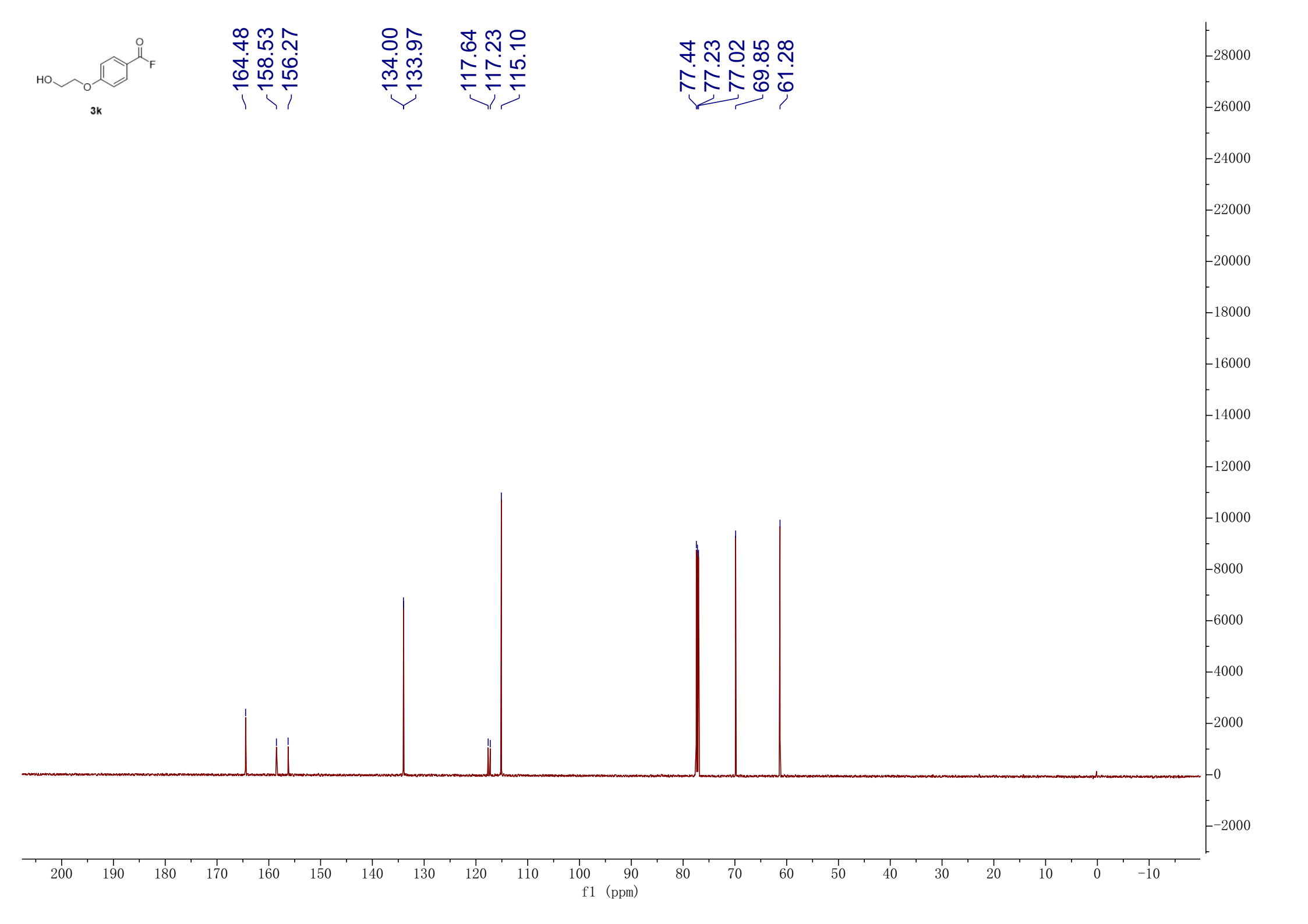


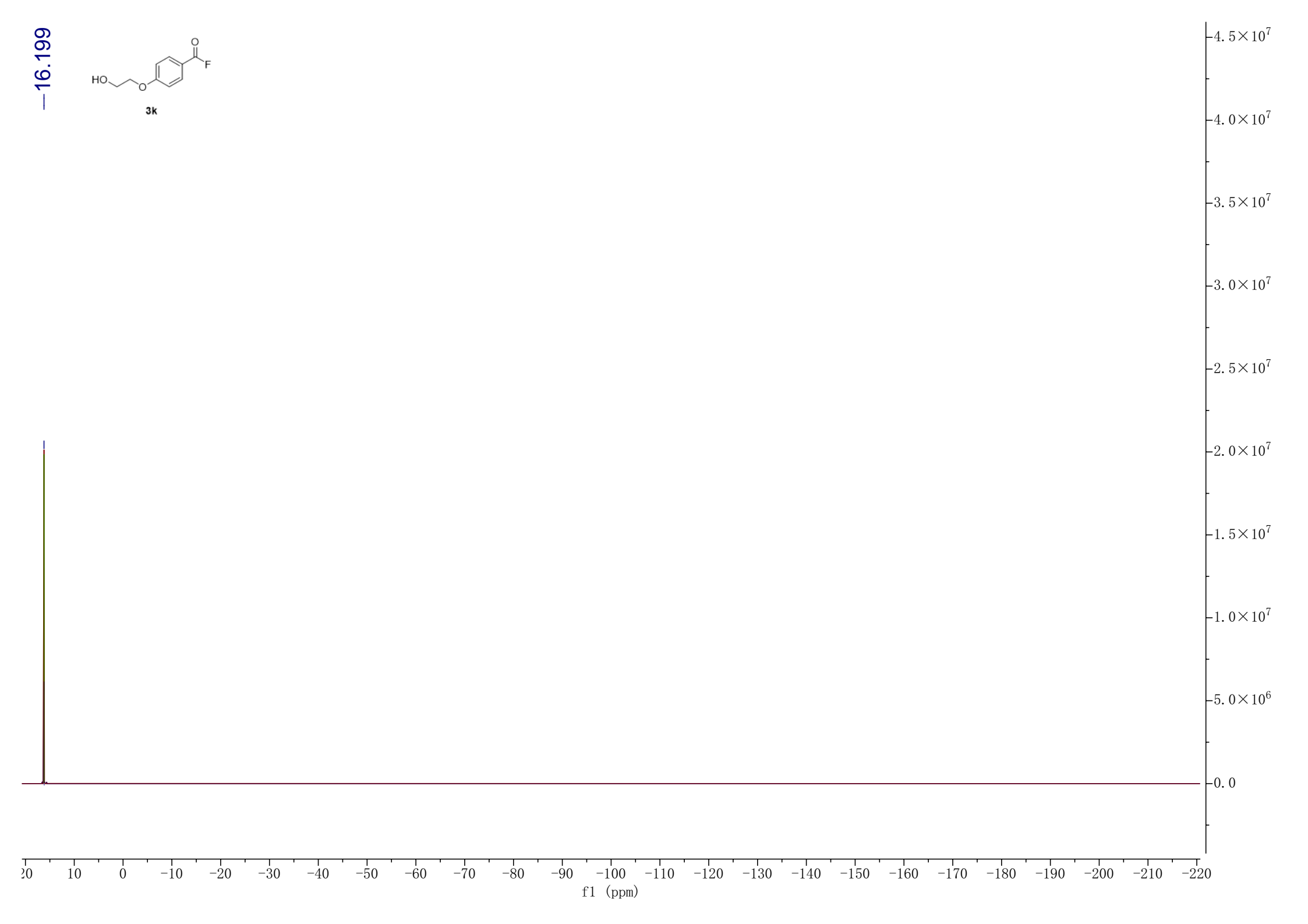
3k

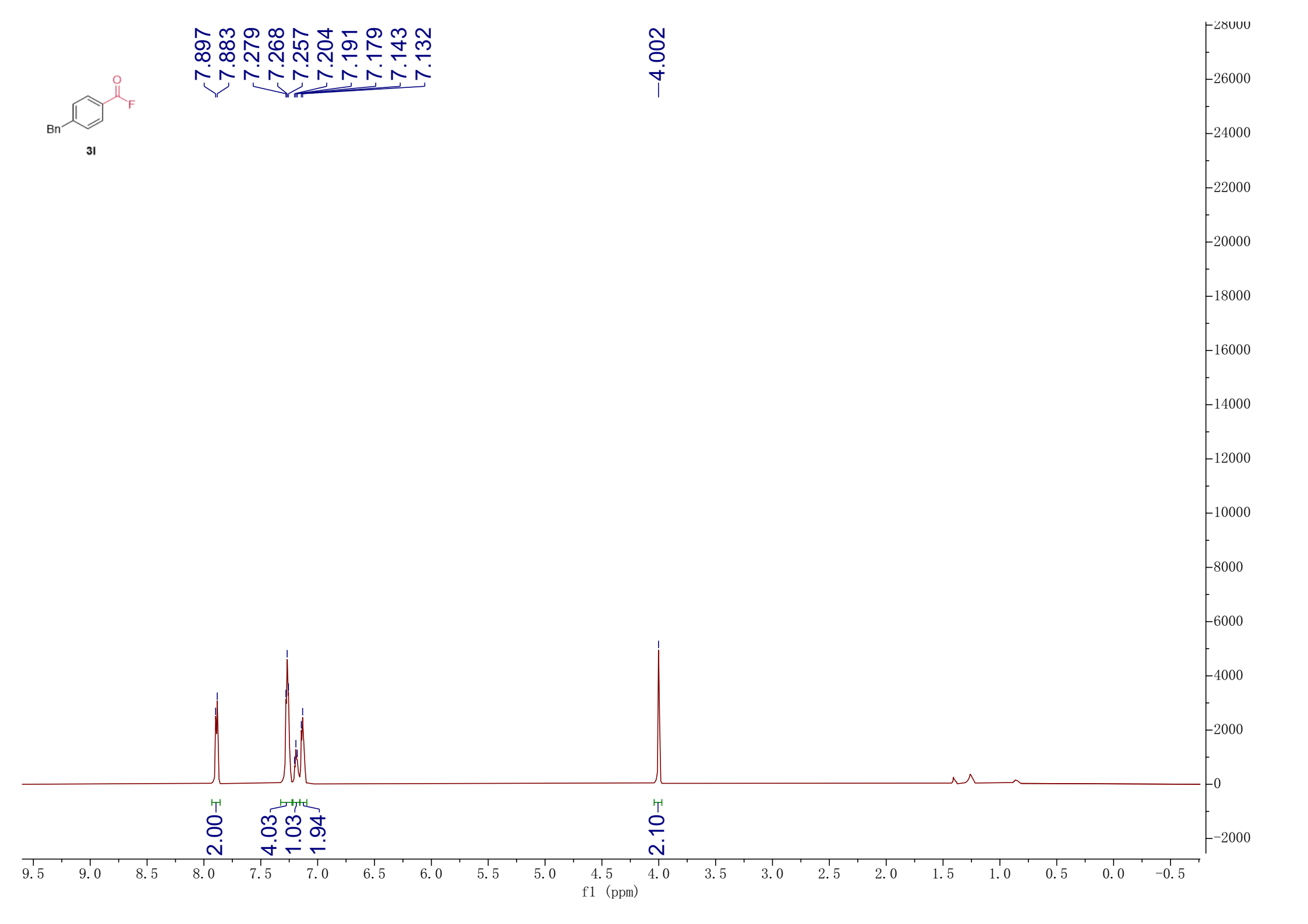
7.986
7.971
7.260
7.002
6.988
4.176
4.169
4.161
4.014
4.006
3.999

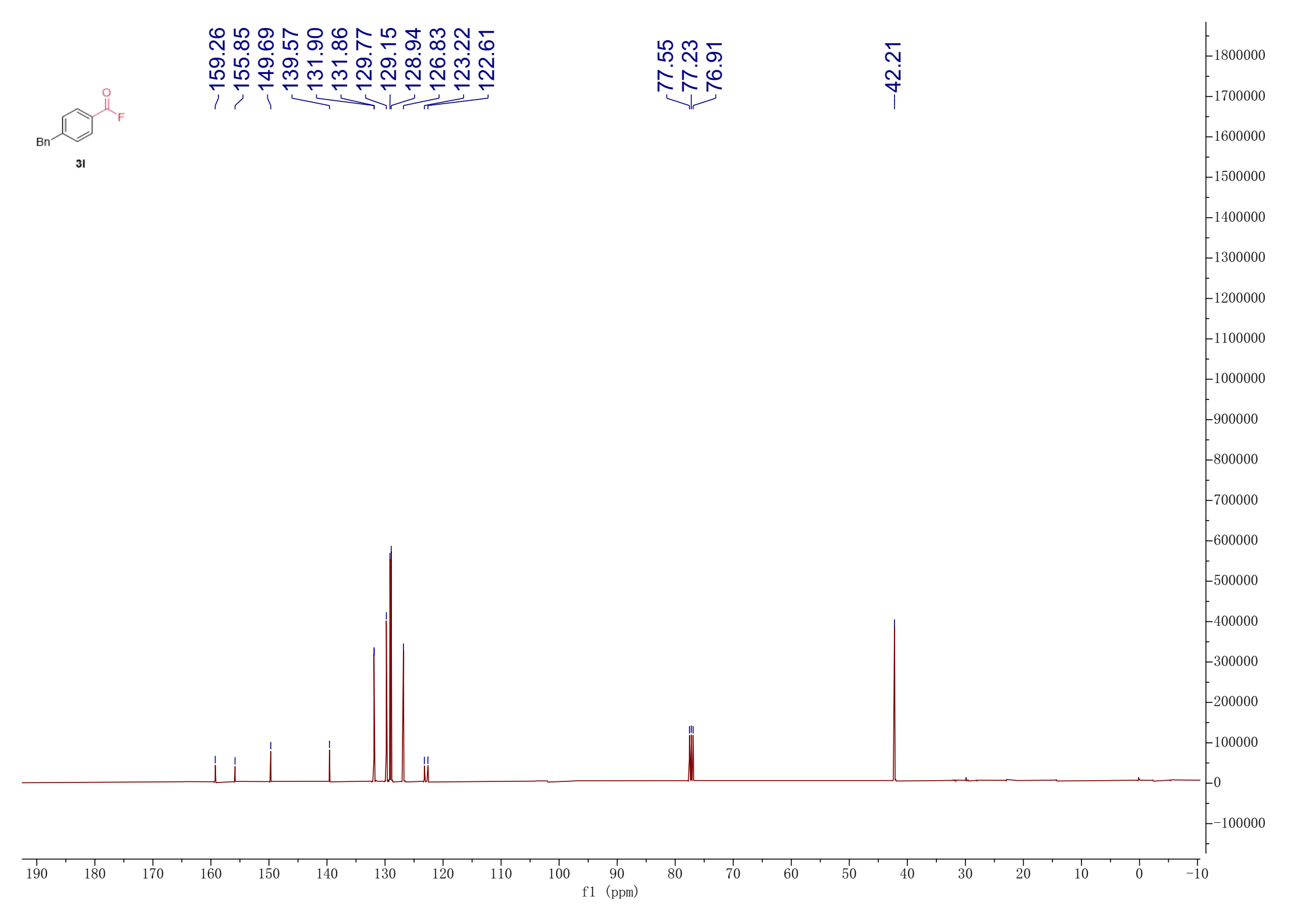
2.00
2.05
2.06
2.01

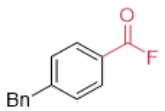
f1 (ppm)


HO
O
O
F
3k
164.48
158.53
156.27
134.00
133.97
117.64
117.23
115.10
77.44
77.23
77.02
69.85
61.28
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
−2000
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


—16.199
HO
O
O
F
3k
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)


7.897
7.883
7.279
7.268
7.257
7.204
7.191
7.179
7.143
7.132
4.002
Bn
O
F
3l
2.00
4.03
1.03
1.94
2.10
f1 (ppm)


159.26
155.85
149.69
139.57
131.90
131.86
129.77
129.15
128.94
126.83
123.22
122.61
77.55
77.23
76.91
42.21
O
F
Bn
3l
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
−100000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)



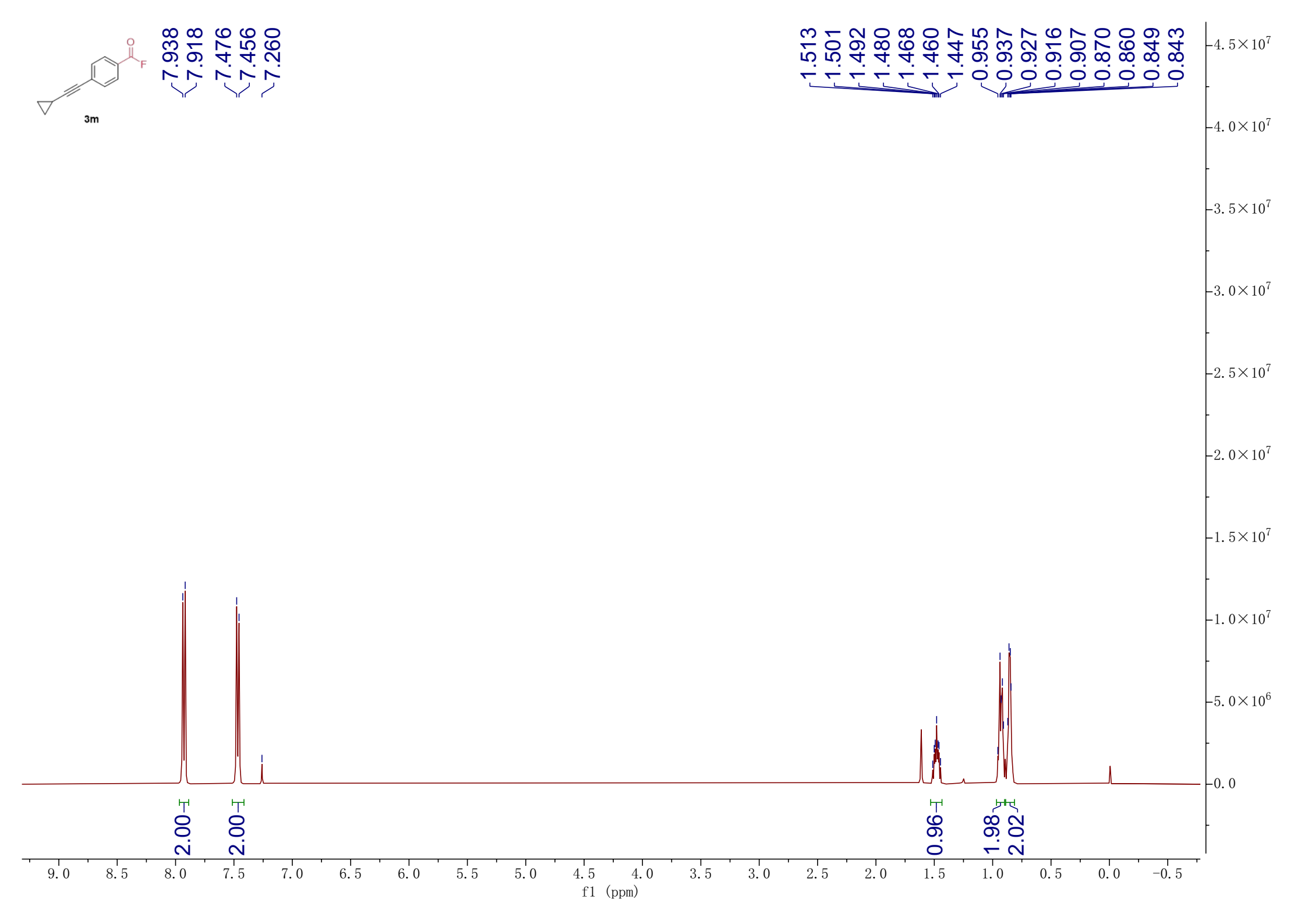
3l

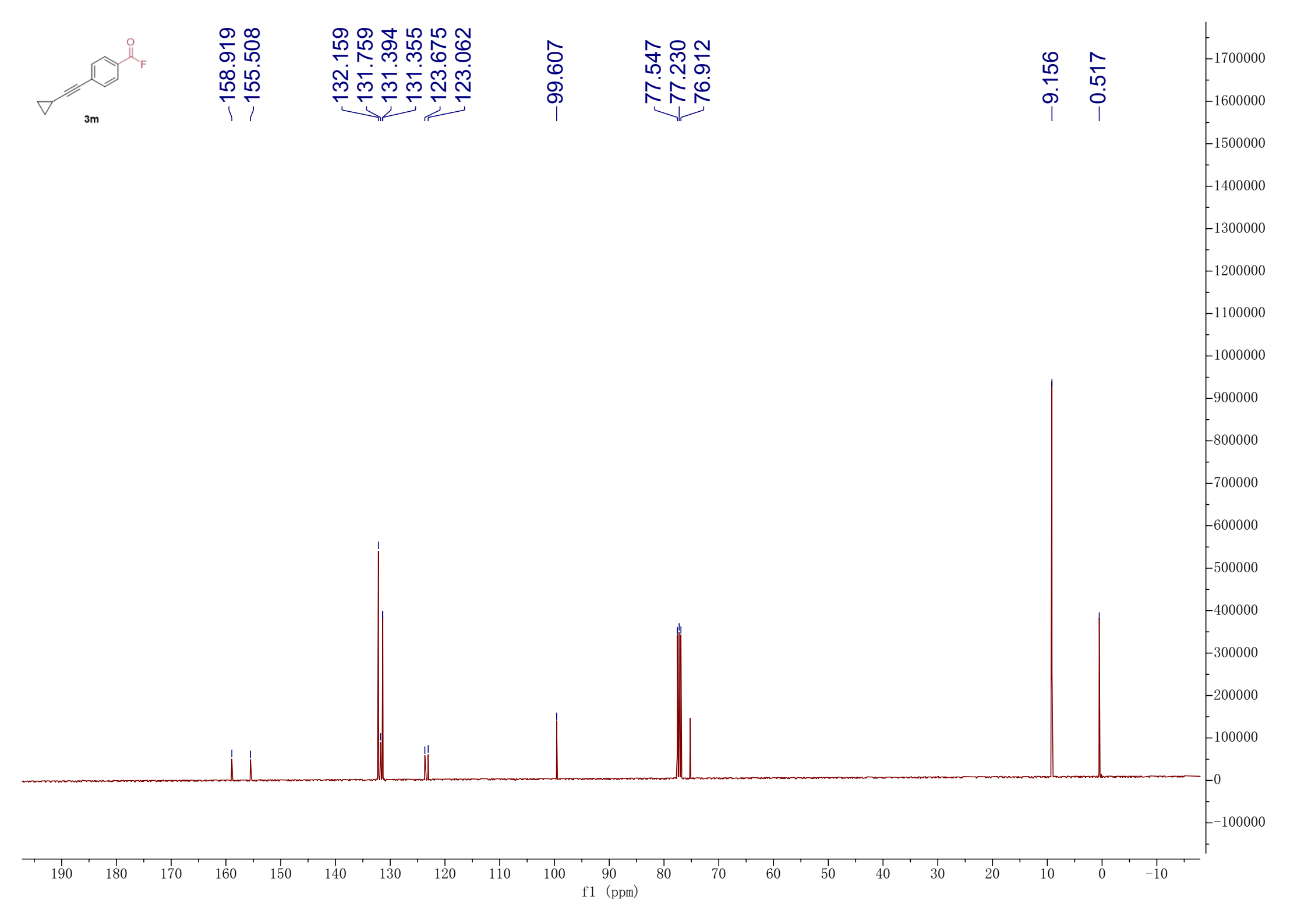
−17.860

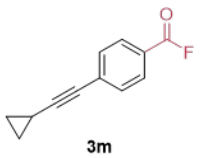
1.3×10^8
1.2×10^8
1.1×10^8
1.0×10^8
9.0×10^7
8.0×10^7
7.0×10^7
6.0×10^7
5.0×10^7
4.0×10^7
3.0×10^7
2.0×10^7
1.0×10^7
0.0
−1.0×10^7

40 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100

f1 (ppm)


3m
7.938
7.918
7.476
7.456
7.260
1.513
1.501
1.492
1.480
1.468
1.460
1.447
0.955
0.937
0.927
0.916
0.907
0.870
0.860
0.849
0.843
2.00
2.00
0.96
1.98
2.02
f1 (ppm)


3m
158.919
155.508
132.159
131.759
131.394
131.355
123.675
123.062
99.607
77.547
77.230
76.912
9.156
0.517
f1 (ppm)



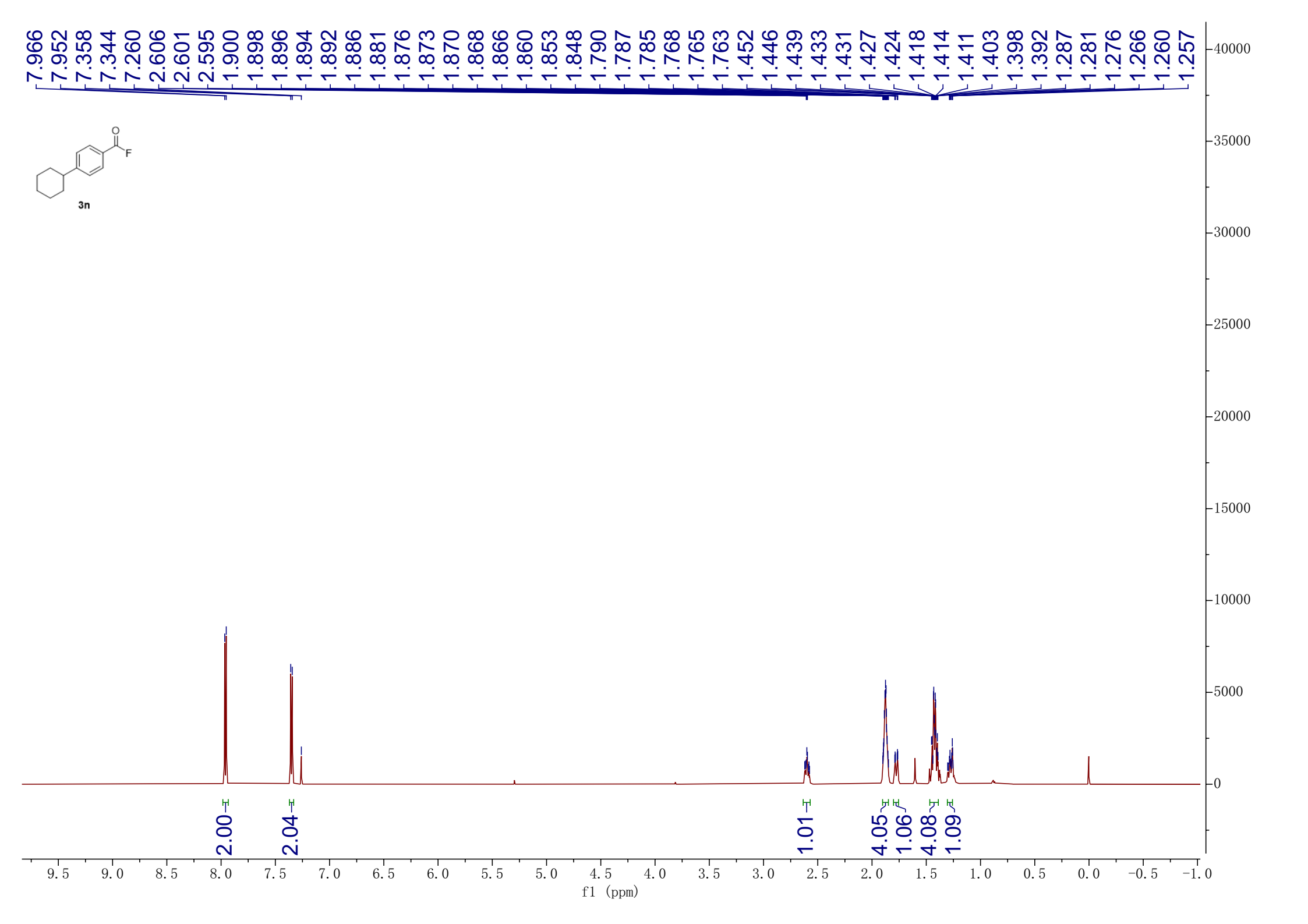
3m

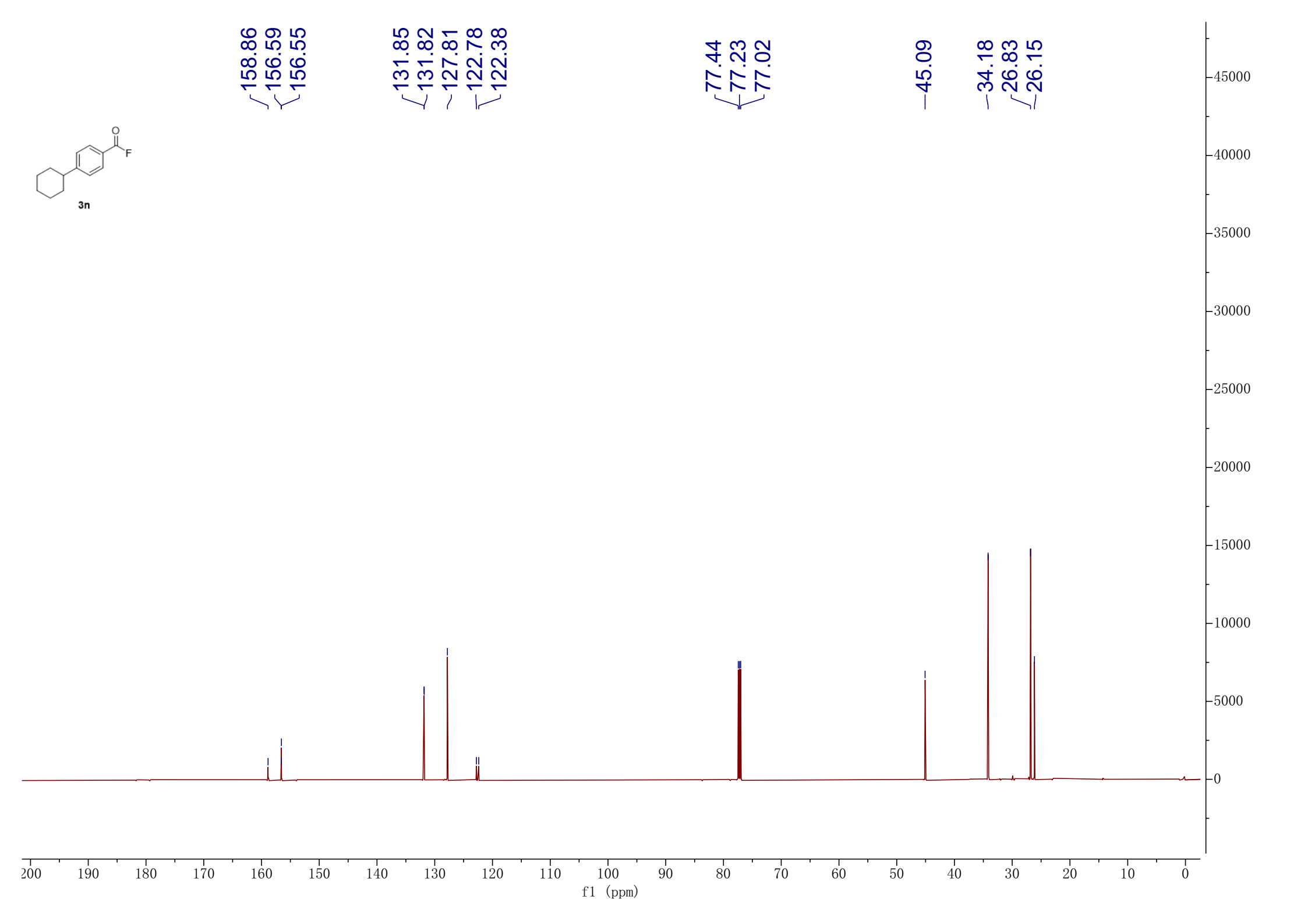
17.96

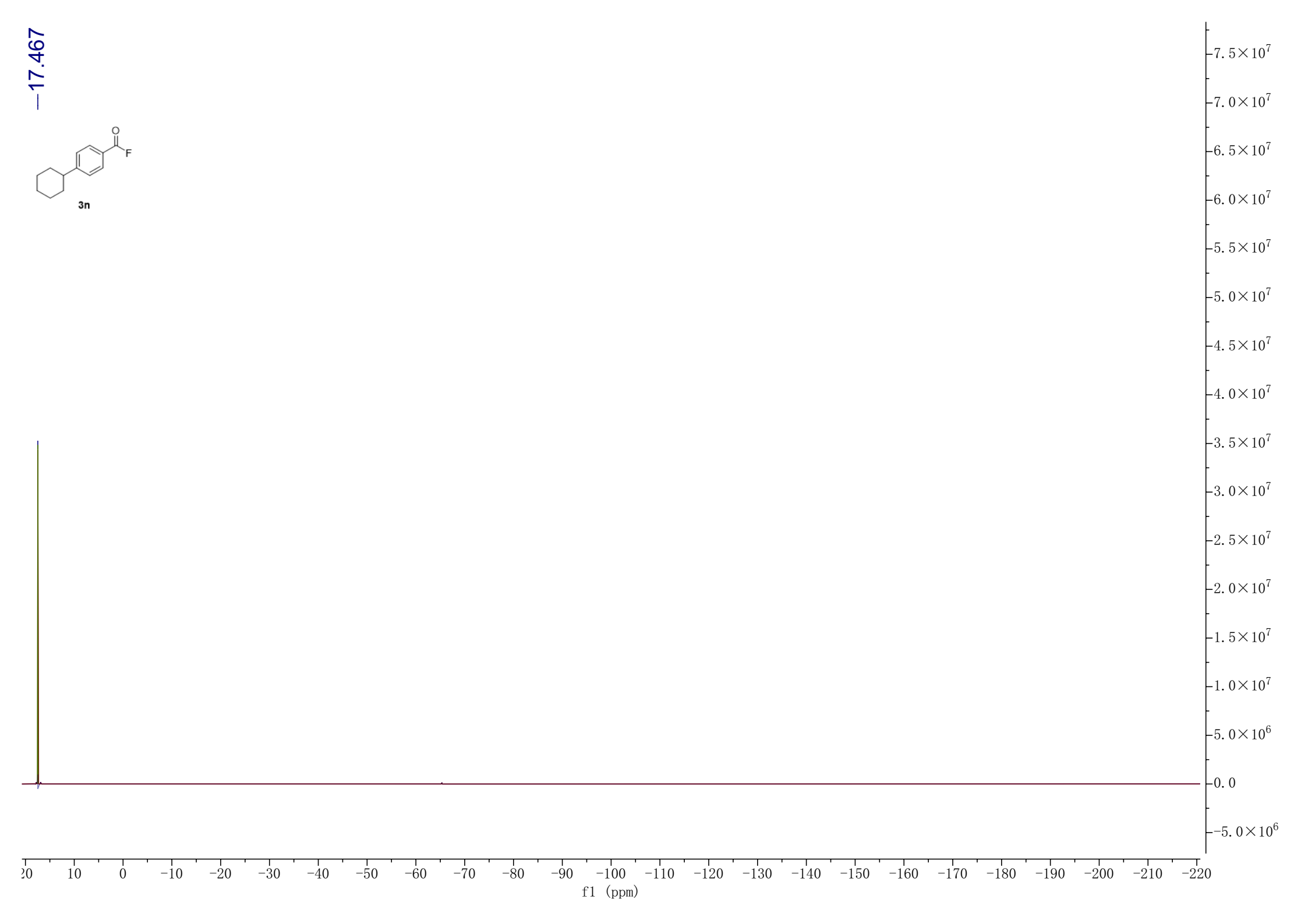
5.5×10^7
5.0×10^7
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
-5.0×10^6

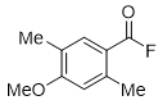
40 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100

f1 (ppm)


7.966
7.952
7.358
7.344
7.260
2.606
2.601
2.595
1.900
1.898
1.896
1.894
1.892
1.886
1.881
1.876
1.873
1.870
1.868
1.866
1.860
1.853
1.848
1.790
1.787
1.785
1.768
1.765
1.763
1.452
1.446
1.439
1.433
1.431
1.427
1.424
1.418
1.414
1.411
1.403
1.398
1.392
1.287
1.281
1.276
1.266
1.260
1.257
O
F
3n
40000
35000
30000
25000
20000
15000
10000
5000
0
2.00
2.04
1.01
4.05
1.06
4.08
1.09
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
-0.5
-1.0
f1 (ppm)


158.86
156.59
156.55
131.85
131.82
127.81
122.78
122.38
77.44
77.23
77.02
45.09
34.18
26.83
26.15
O
F
3n
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


−17.467
O
F
3n
7.5×10^7
7.0×10^7
6.5×10^7
6.0×10^7
5.5×10^7
5.0×10^7
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
−5.0×10^6
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)

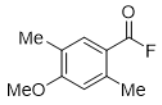


3o

7.755
7.260
6.712
3.900
2.620
2.194

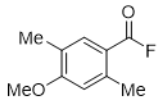
1.01
1.05
3.04
3.07
3.02

f1 (ppm)


Me
O
F
MeO
Me

3o

162.80
158.14
155.88
144.69
144.64
135.00
125.02
115.20
114.82
113.44
113.41
77.44
77.23
77.02
55.77
22.36
15.73
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
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)



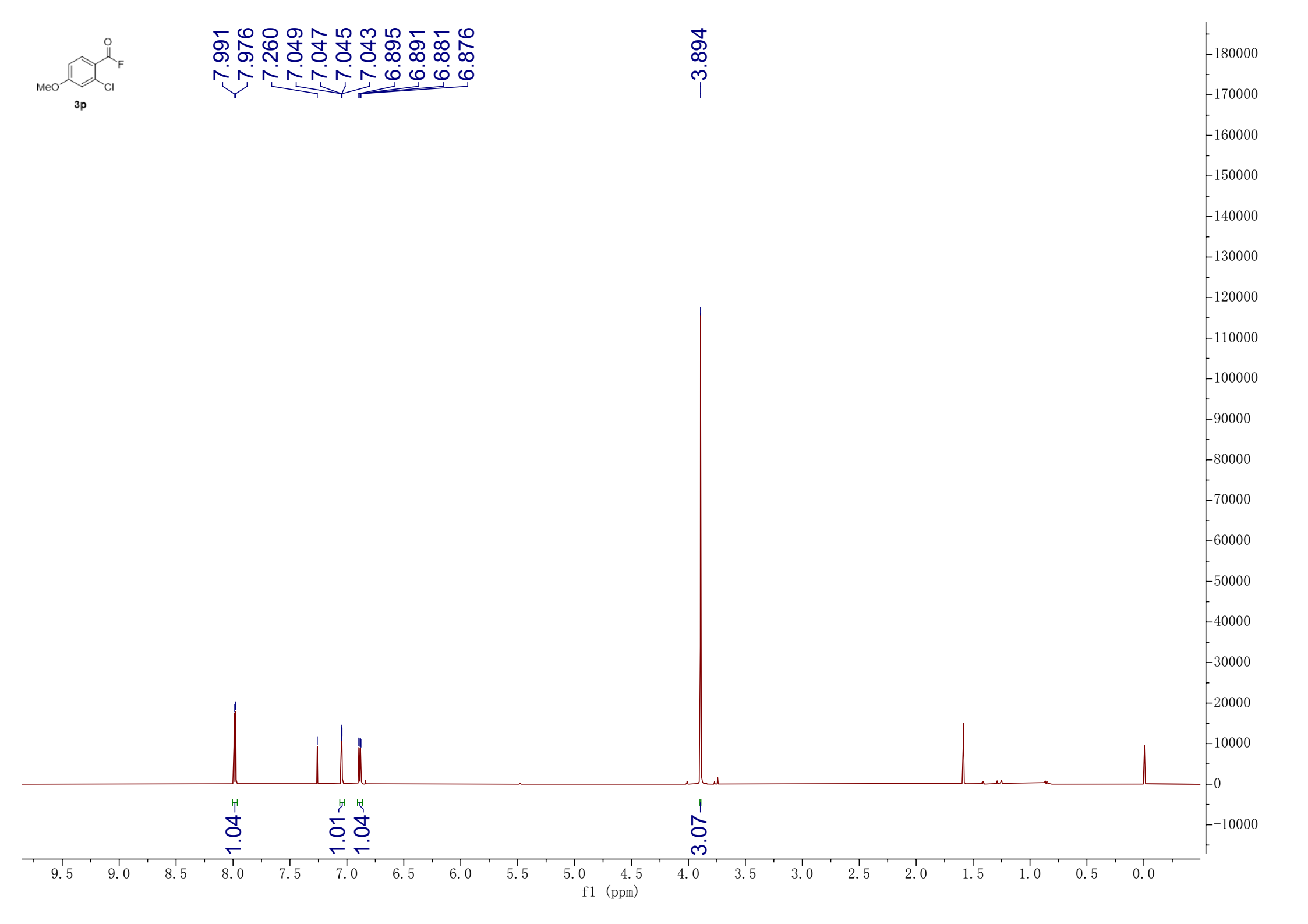
3o

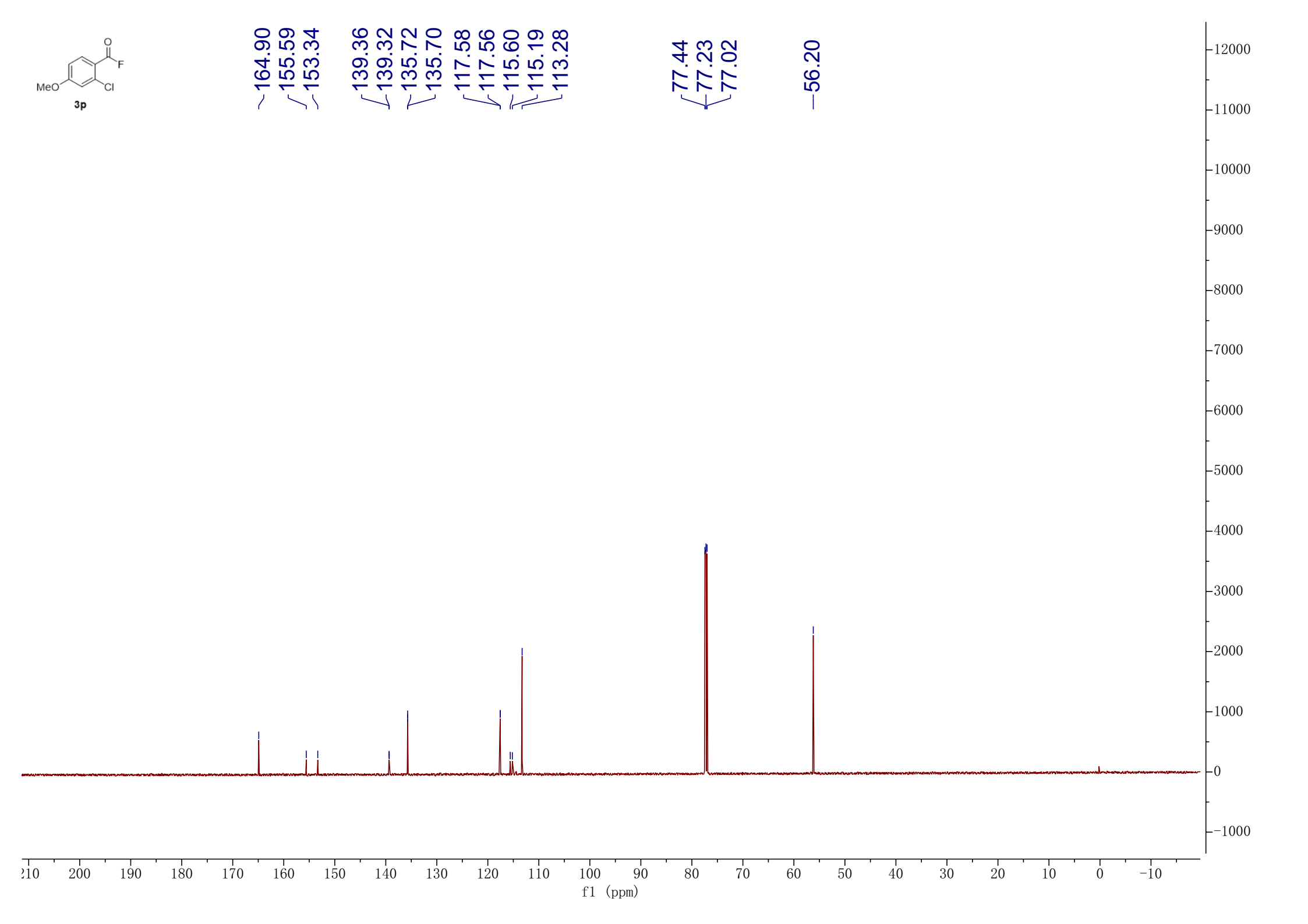
−26.503

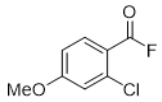
3400000
3200000
3000000
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
−200000

20 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120

f1 (ppm)


3p
7.991
7.976
7.260
7.049
7.047
7.045
7.043
6.895
6.891
6.881
6.876
3.894
1.04
1.01
1.04
3.07
f1 (ppm)


MeO
Cl
F
O
3p
164.90
155.59
153.34
139.36
139.32
135.72
135.70
117.58
117.56
115.60
115.19
113.28
77.44
77.23
77.02
56.20
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
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)



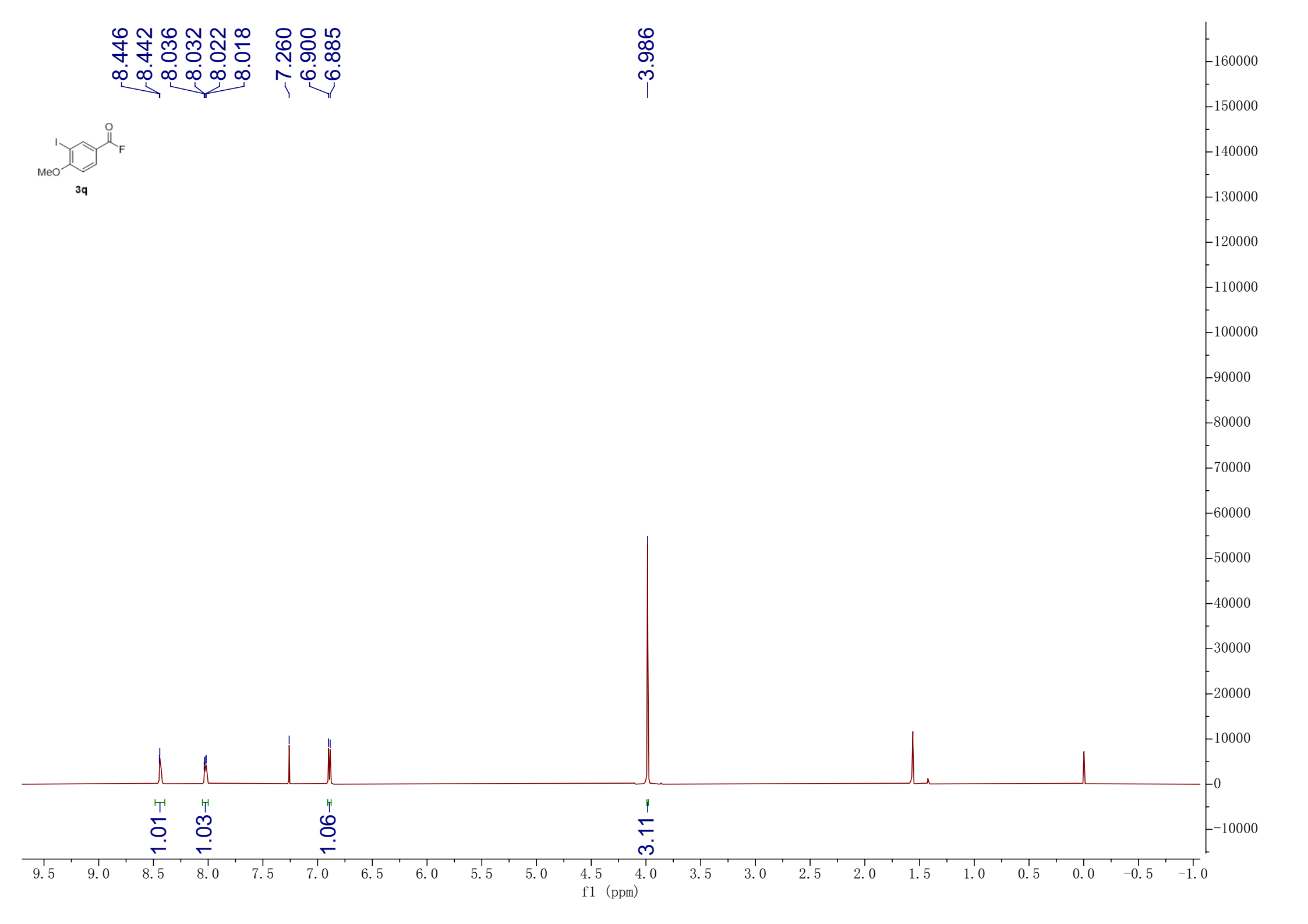
3p

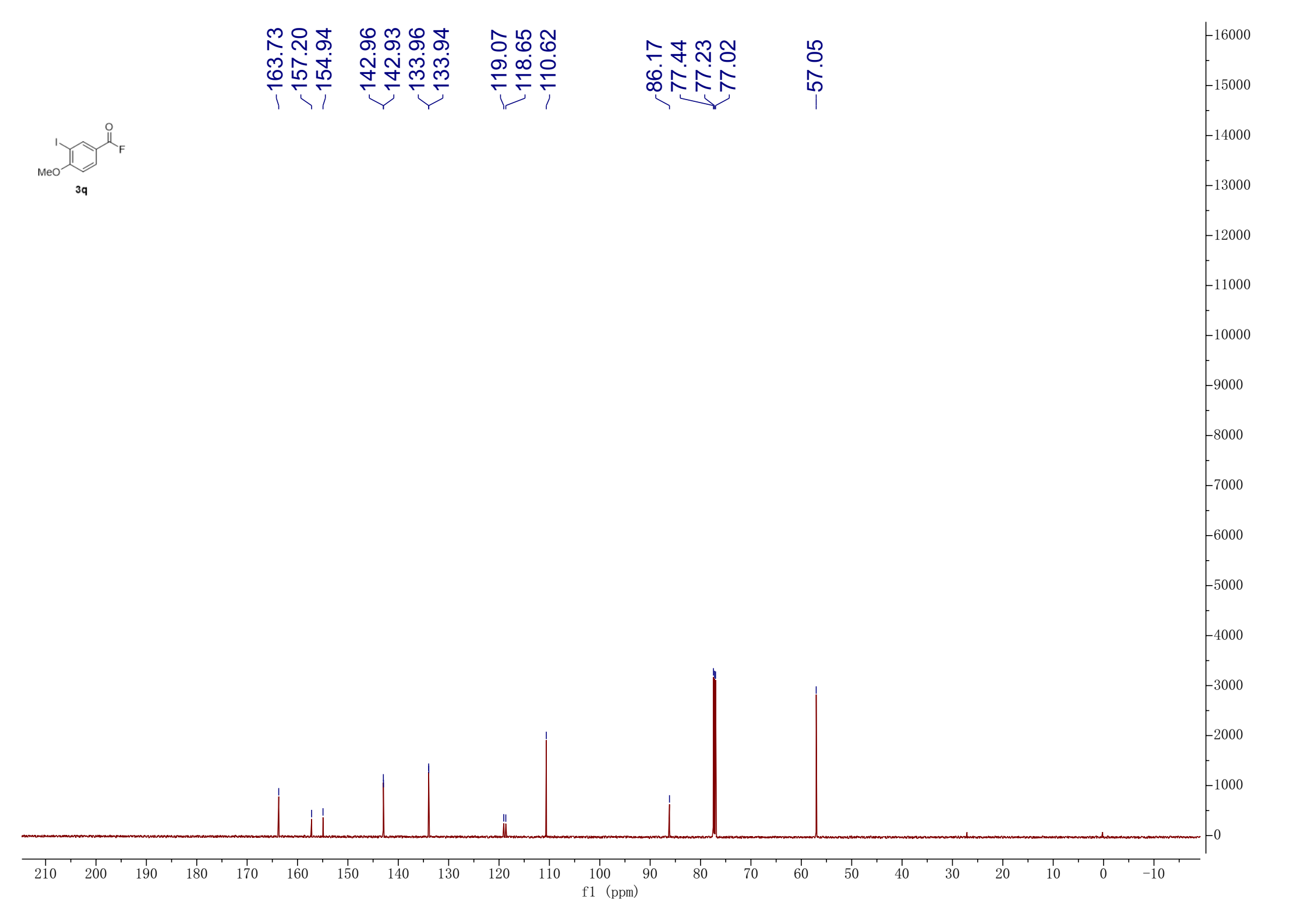
−28.716

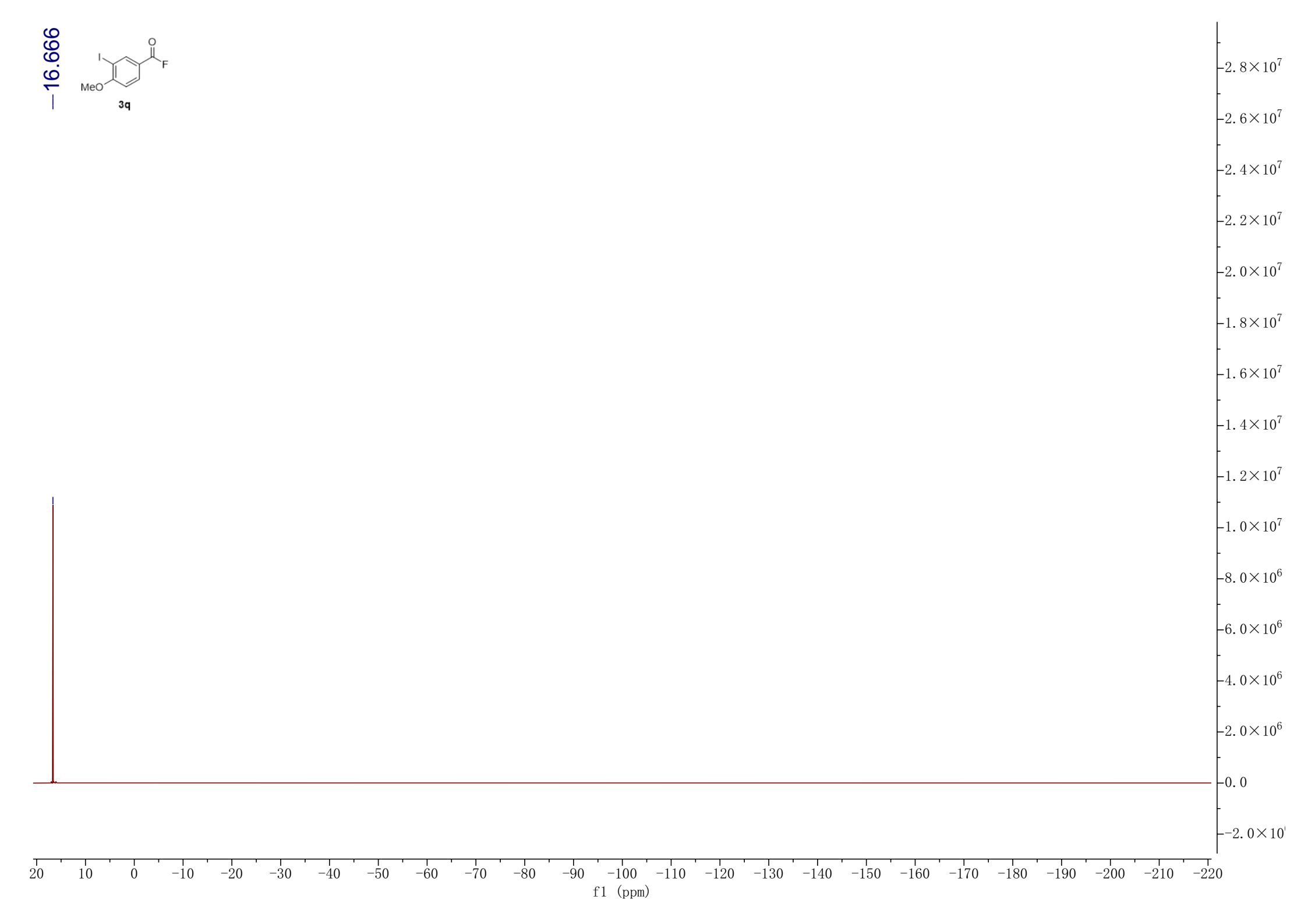
16000000
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
−1000000

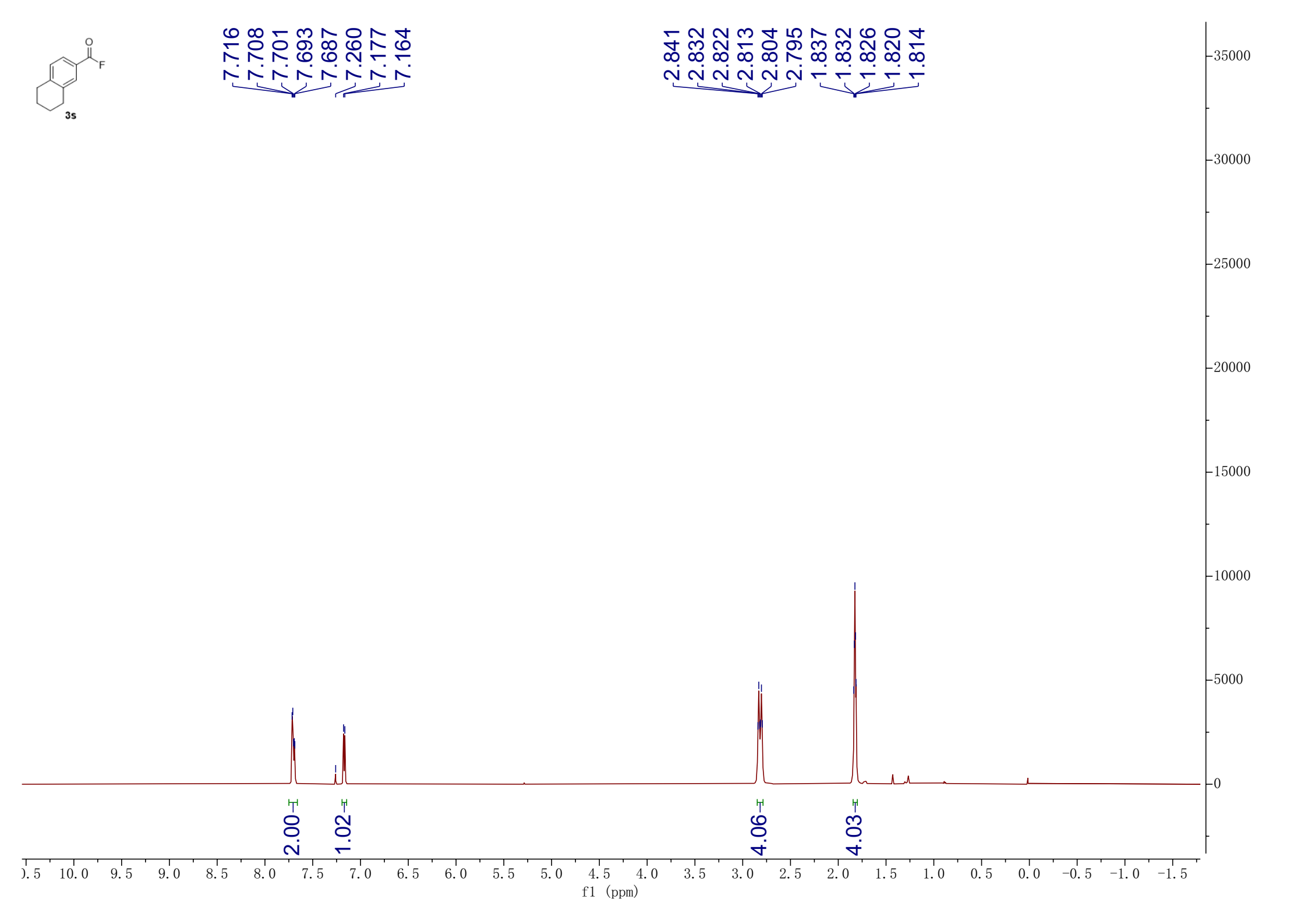
20 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120

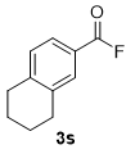
f1 (ppm)


8.446
8.442
8.036
8.032
8.022
8.018
7.260
6.900
6.885
3.986
O
I
F
MeO
3q
1.01
1.03
1.06
3.11
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
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
-0.5
-1.0
f1 (ppm)


163.73
157.20
154.94
142.96
142.93
133.96
133.94
119.07
118.65
110.62
86.17
77.44
77.23
77.02
57.05
I
O
F
MeO
3q
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
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)


16.666
I
O
F
MeO
3q
2.8×10^7
2.6×10^7
2.4×10^7
2.2×10^7
2.0×10^7
1.8×10^7
1.6×10^7
1.4×10^7
1.2×10^7
1.0×10^7
8.0×10^6
6.0×10^6
4.0×10^6
2.0×10^6
0.0
-2.0×10
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)


3s
7.716
7.708
7.701
7.693
7.687
7.260
7.177
7.164
2.841
2.832
2.822
2.813
2.804
2.795
1.837
1.832
1.826
1.820
1.814
2.00
1.02
4.06
4.03
35000
30000
25000
20000
15000
10000
5000
0
f1 (ppm)



158.92
156.65
146.01
138.31
132.36
132.33
129.94
128.32
128.29
122.17
121.77

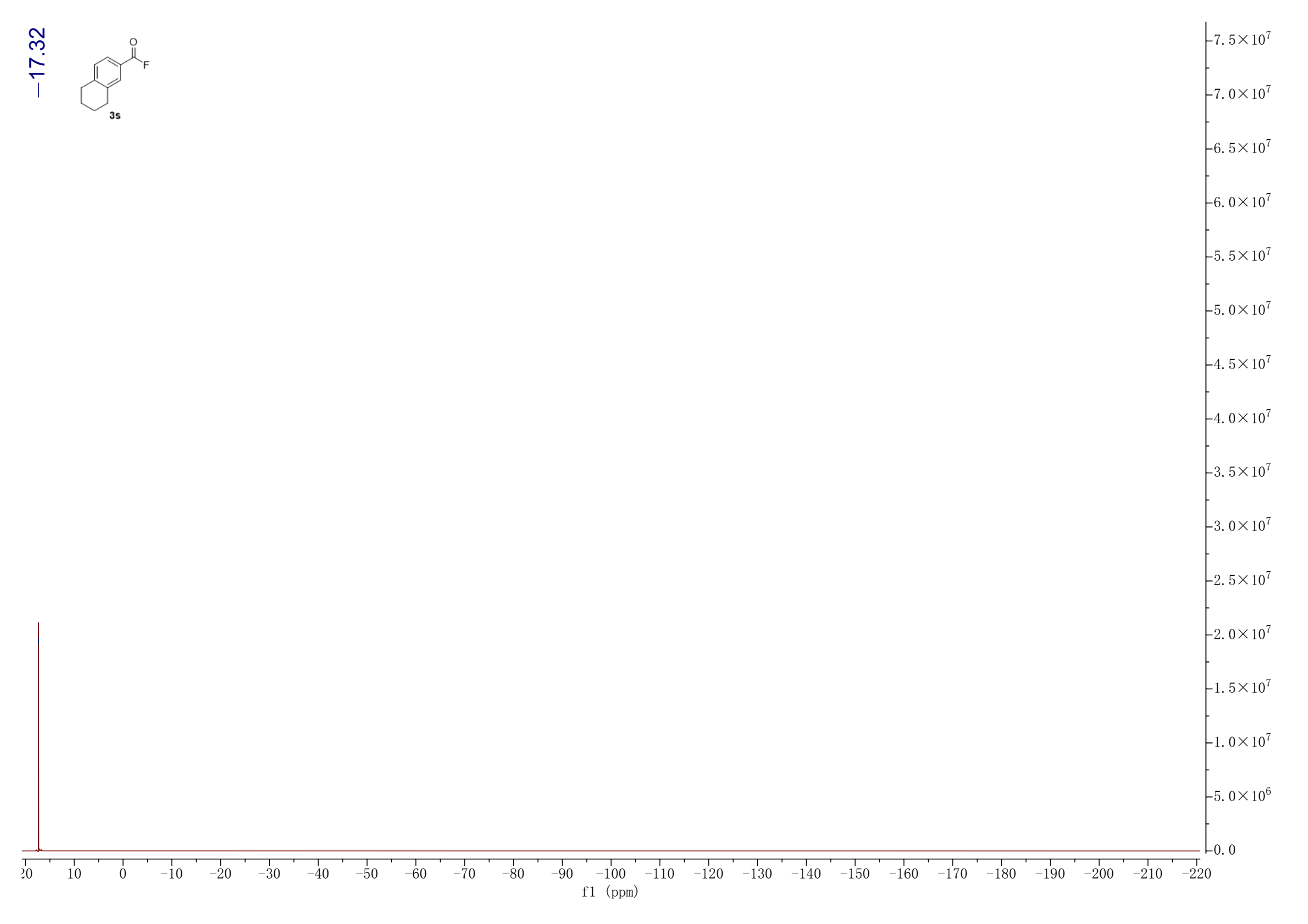
77.44
77.23
77.02

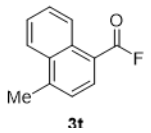
29.91
29.26
22.80
22.68

40000
35000
30000
25000
20000
15000
10000
5000
0

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)


−17.32
O
F
3s
7.5×10^7
7.0×10^7
6.5×10^7
6.0×10^7
5.5×10^7
5.0×10^7
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)

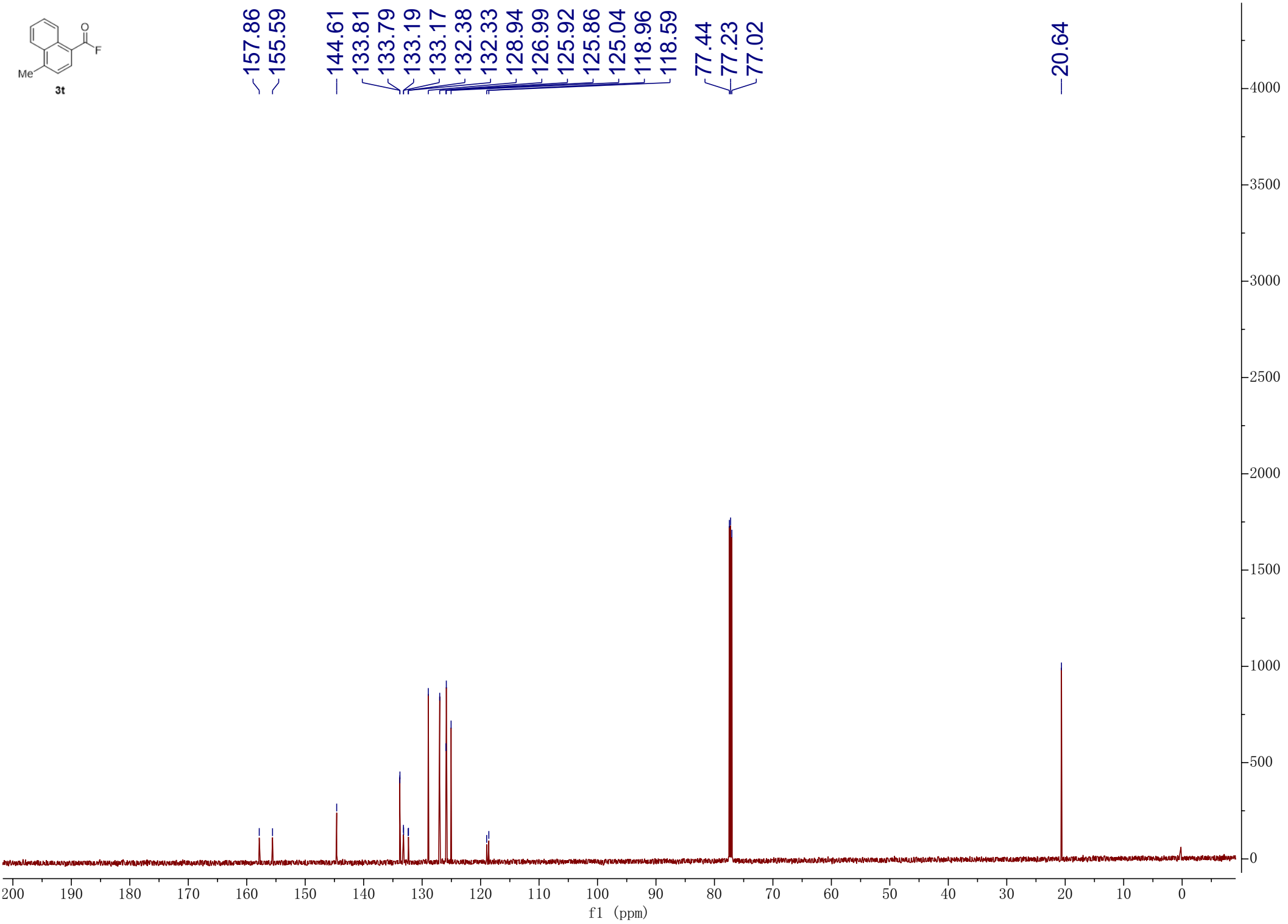


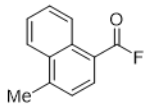
3t

9.078
9.064
8.260
8.256
8.248
8.244
8.231
8.115
8.101
7.727
7.715
7.713
7.701
7.655
7.644
7.641
7.630
7.416
7.404
7.260
2.795

0.96
1.02
1.02
1.01
1.01
1.01
3.33

f1 (ppm)


O
F
Me
3t
157.86
155.59
144.61
133.81
133.79
133.19
133.17
132.38
132.33
128.94
126.99
125.92
125.86
125.04
118.96
118.59
77.44
77.23
77.02
20.64
4000
3500
3000
2500
2000
1500
1000
500
0
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



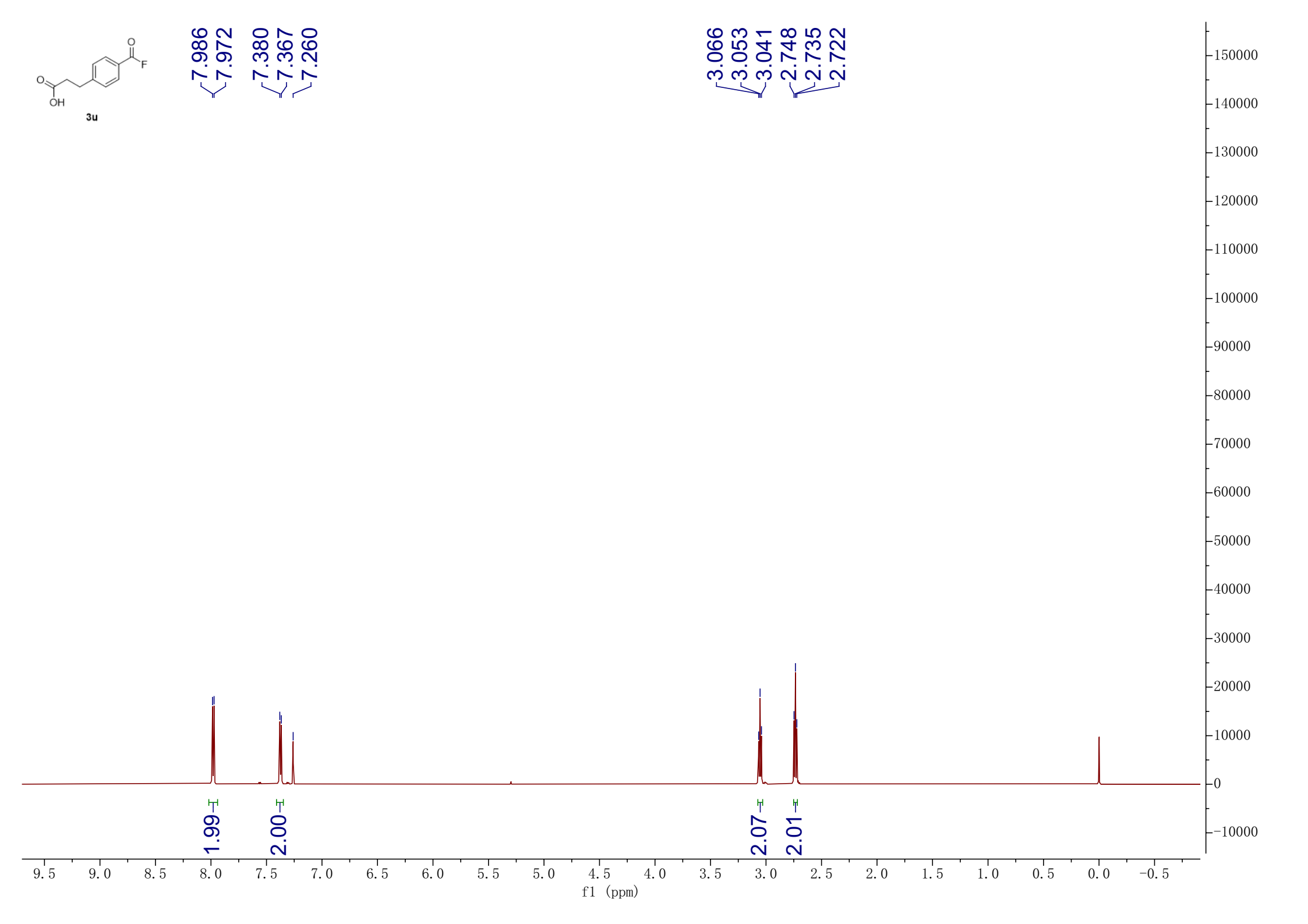
3t

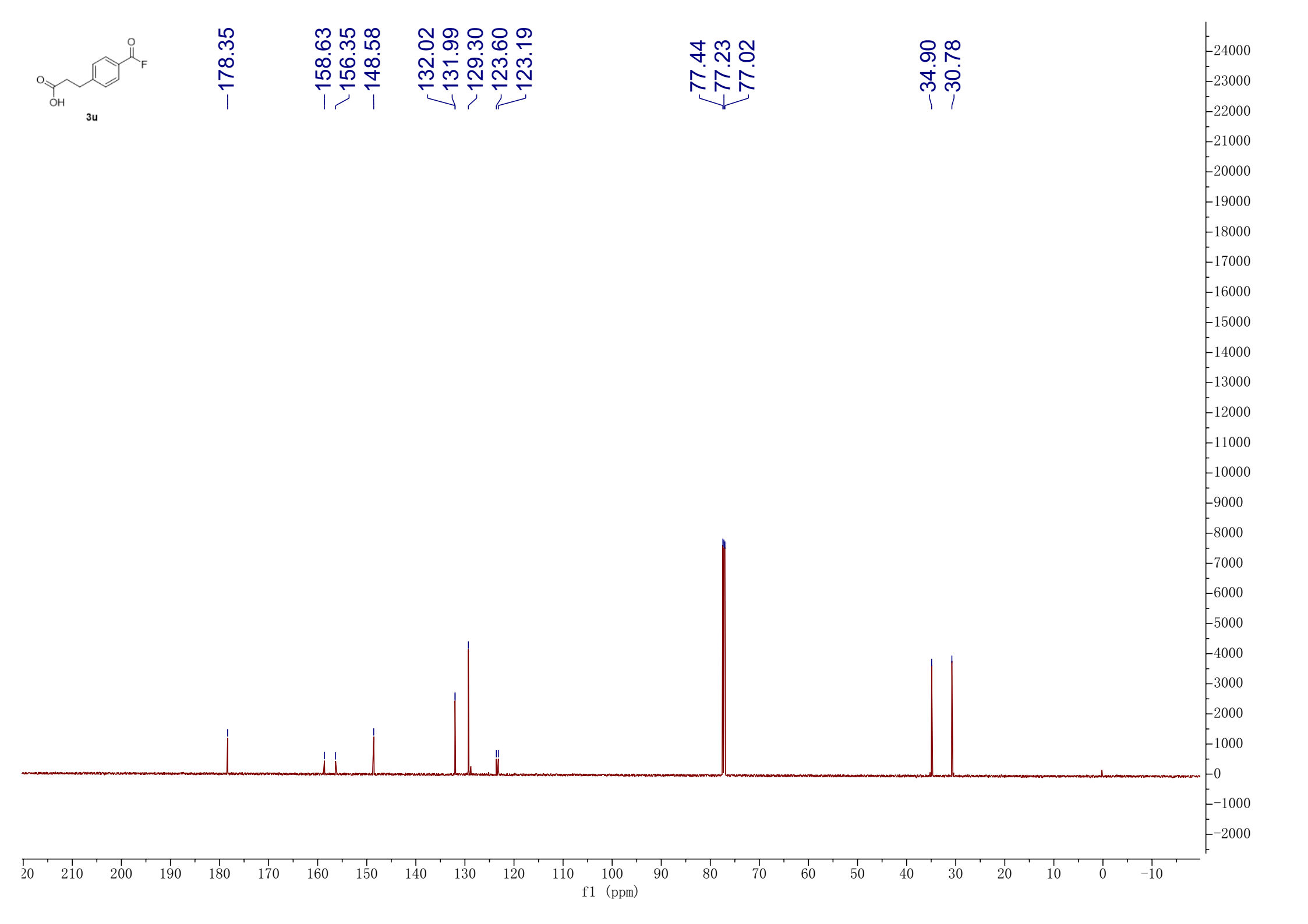
−28.753

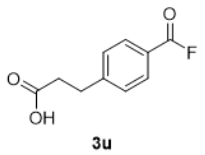
2.8×10^7
2.6×10^7
2.4×10^7
2.2×10^7
2.0×10^7
1.8×10^7
1.6×10^7
1.4×10^7
1.2×10^7
1.0×10^7
8.0×10^6
6.0×10^6
4.0×10^6
2.0×10^6
0.0

20 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120

f1 (ppm)


3u
7.986
7.972
7.380
7.367
7.260
3.066
3.053
3.041
2.748
2.735
2.722
1.99
2.00
2.07
2.01
f1 (ppm)


3u
178.35
158.63
156.35
148.58
132.02
131.99
129.30
123.60
123.19
77.44
77.23
77.02
34.90
30.78
f1 (ppm)



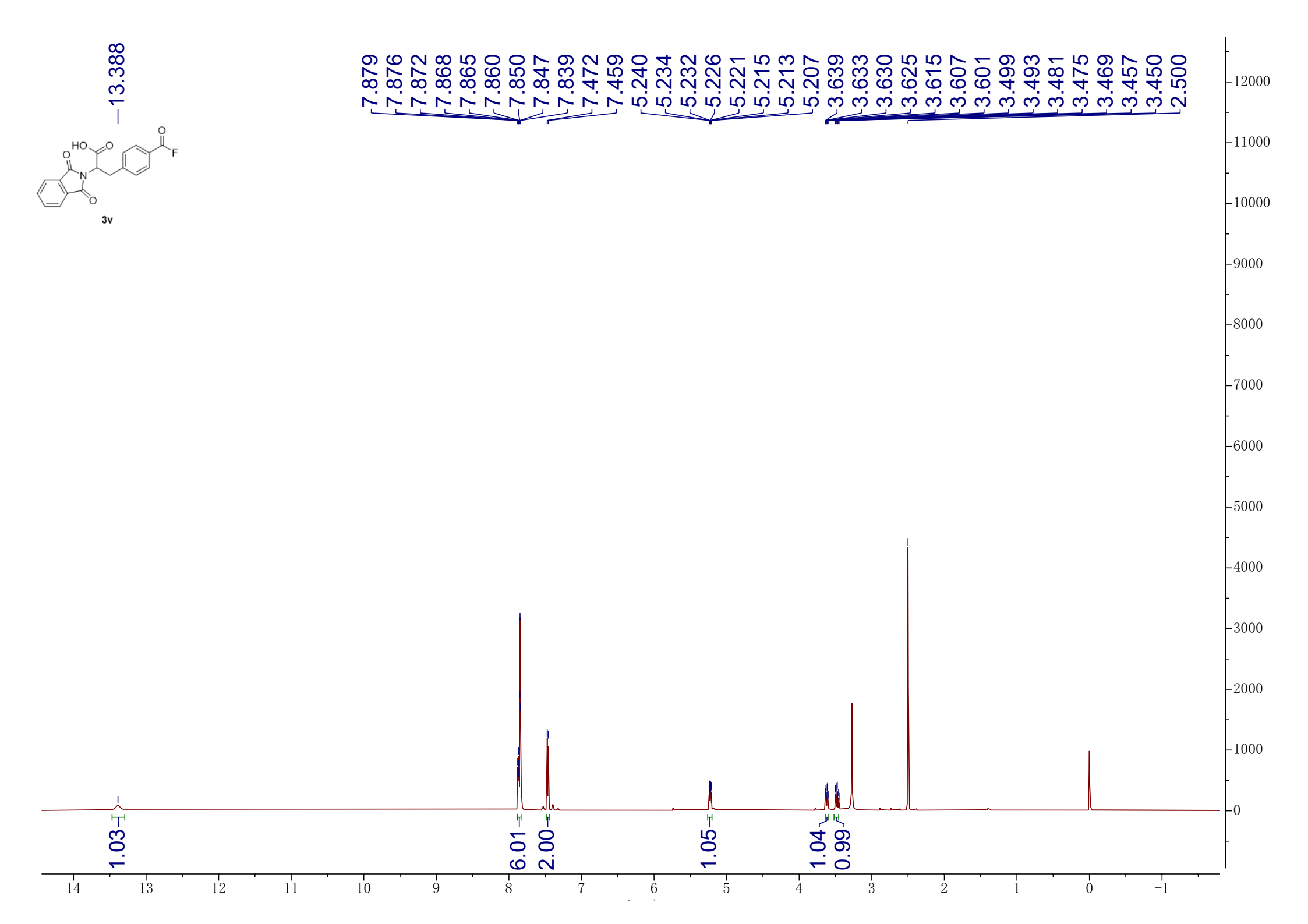
3u

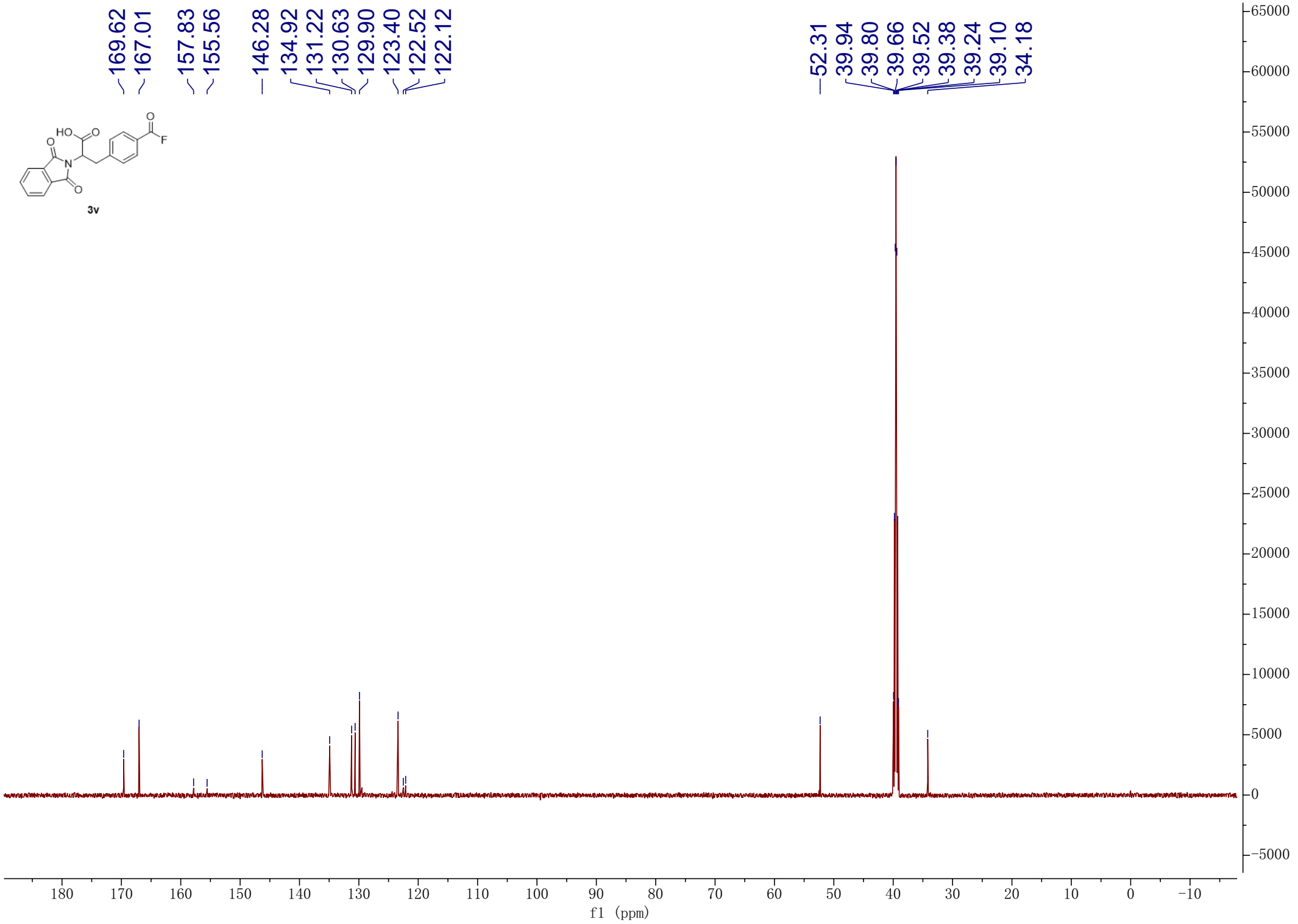
−17.933

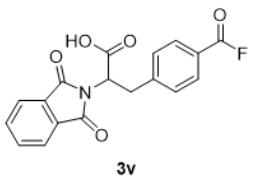
1.3×10^8
1.2×10^8
1.1×10^8
1.0×10^8
9.0×10^7
8.0×10^7
7.0×10^7
6.0×10^7
5.0×10^7
4.0×10^7
3.0×10^7
2.0×10^7
1.0×10^7
0.0
−1.0×10^7

20 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120

f1 (ppm)

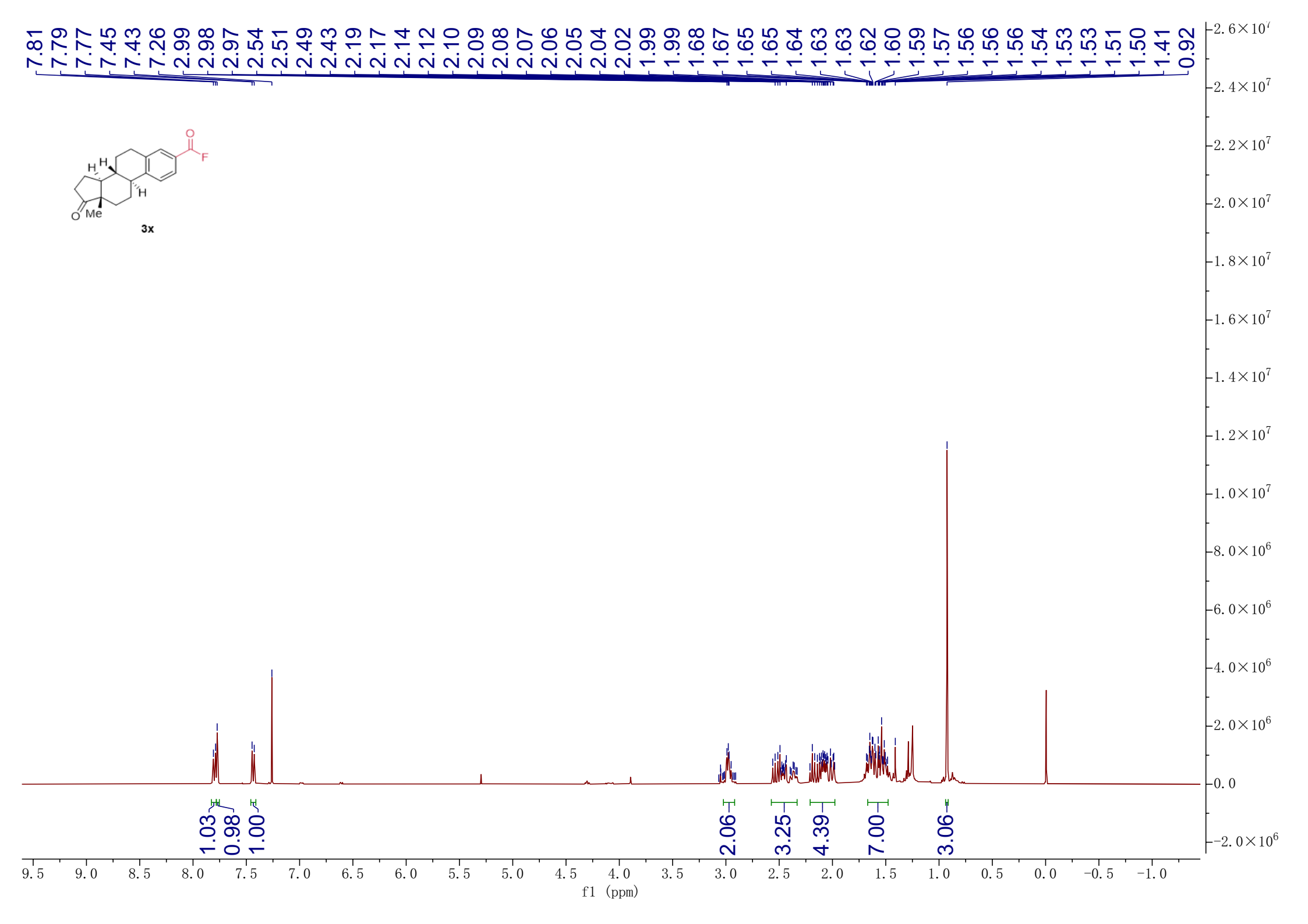

13.388
7.879
7.876
7.872
7.868
7.865
7.860
7.850
7.847
7.839
7.472
7.459
5.240
5.234
5.232
5.226
5.221
5.215
5.213
5.207
3.639
3.633
3.630
3.625
3.615
3.607
3.601
3.499
3.493
3.481
3.475
3.469
3.457
3.450
2.500
HO
O
O
N
O
O
F
3v
1.03
6.01
2.00
1.05
1.04
0.99

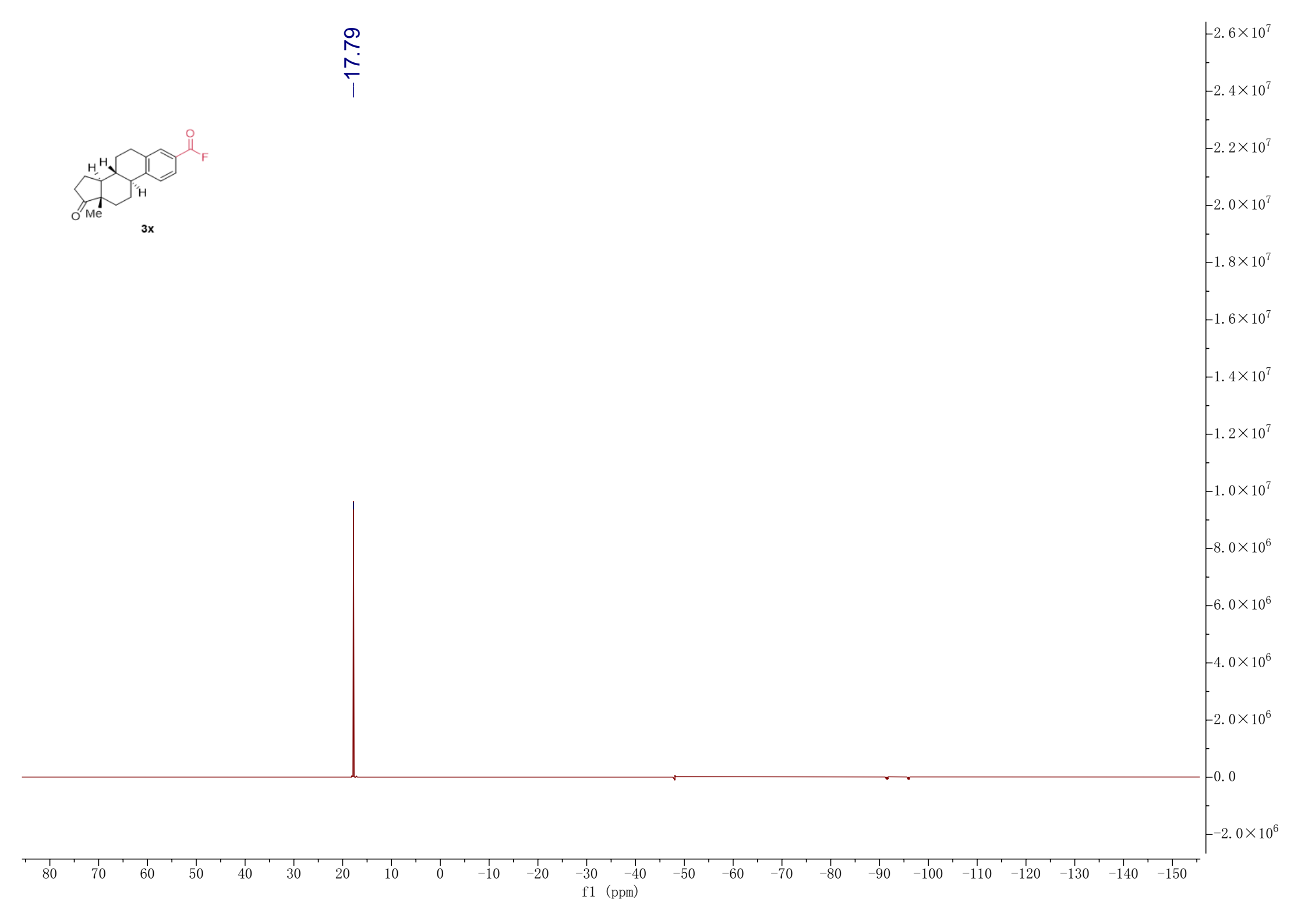

169.62
167.01
157.83
155.56
146.28
134.92
131.22
130.63
129.90
123.40
122.52
122.12
52.31
39.94
39.80
39.66
39.52
39.38
39.24
39.10
34.18
HO
O
O
N
O
O
F
3v
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

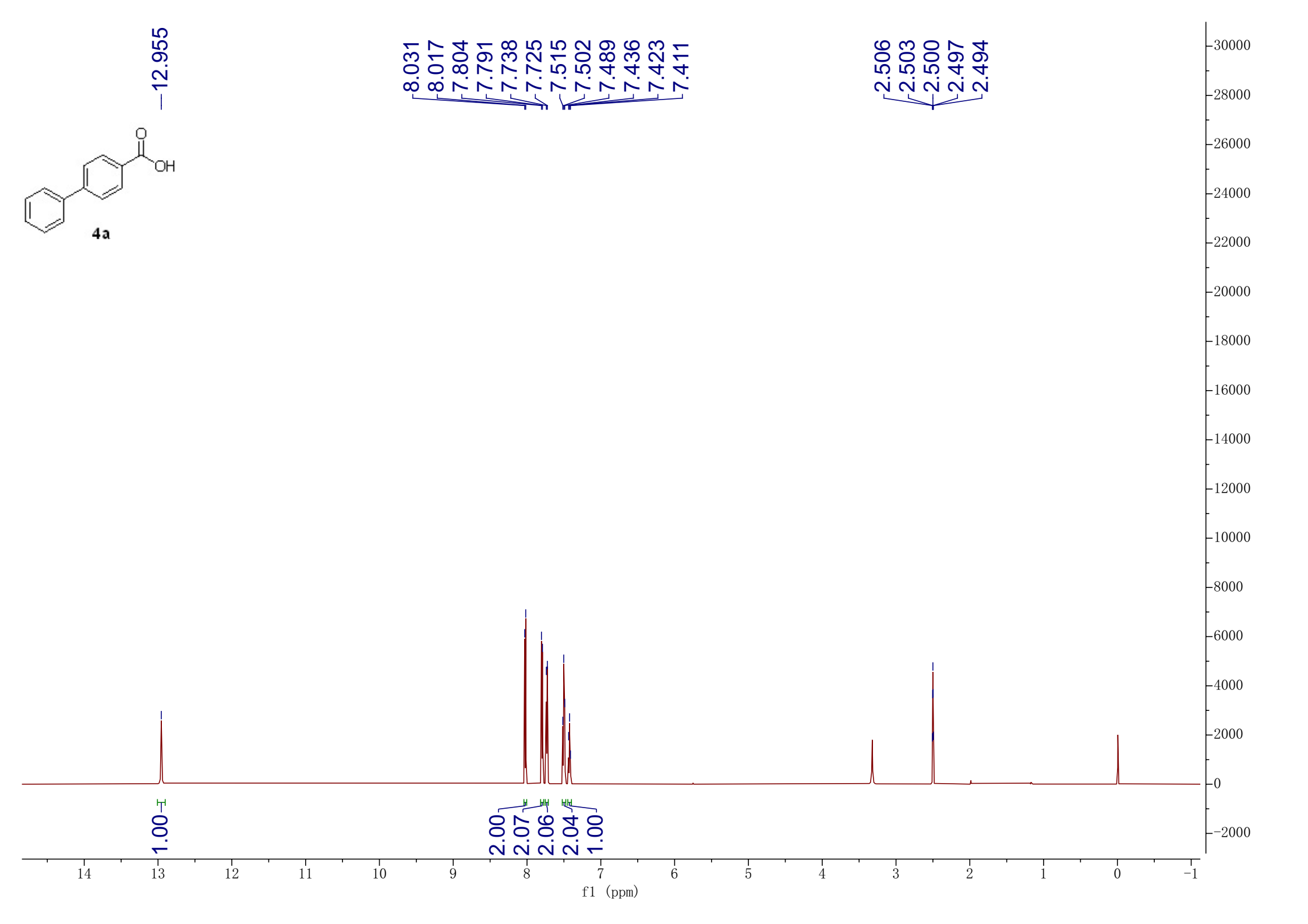

HO
O
O
O
N
O
O
F

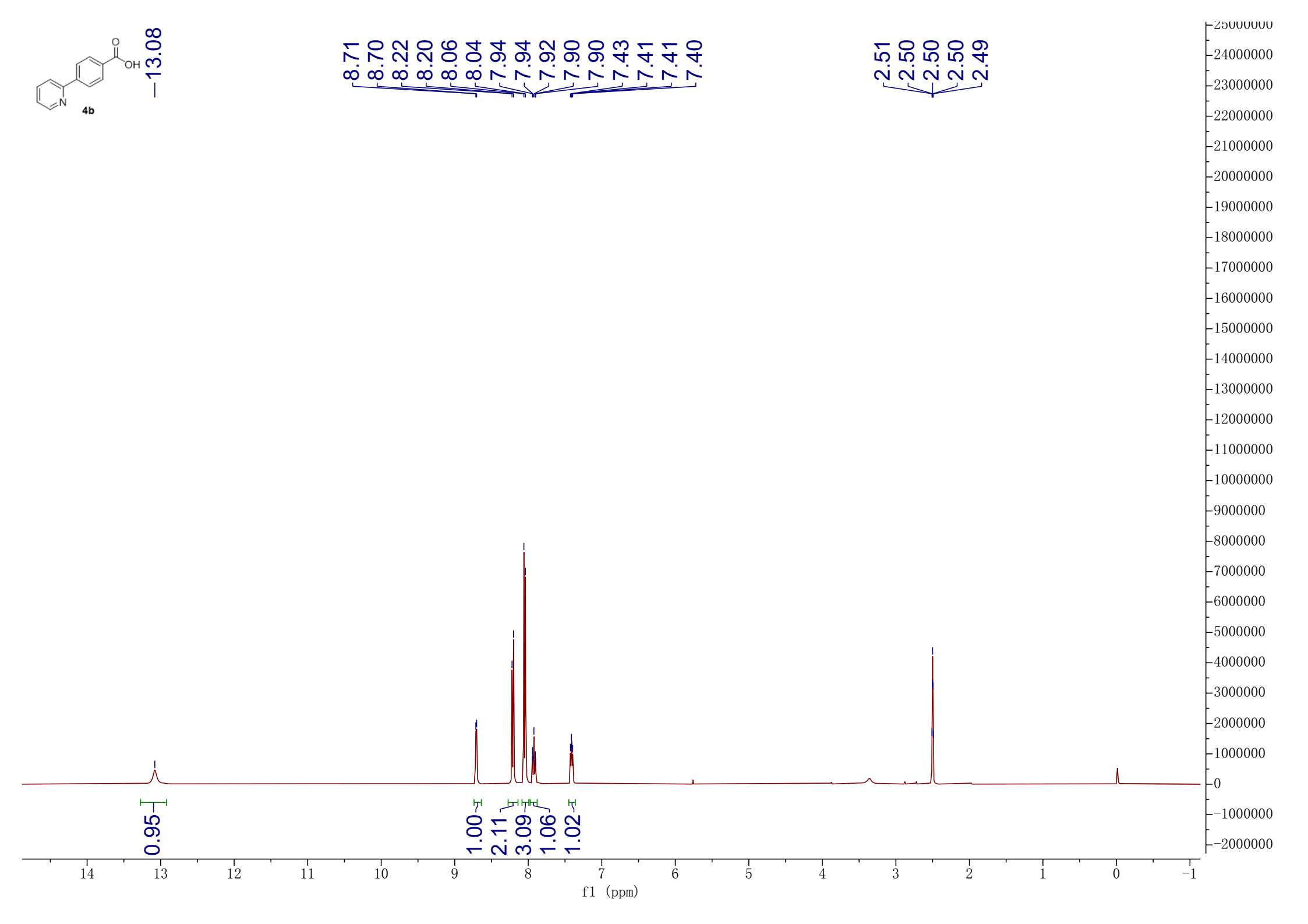
3v

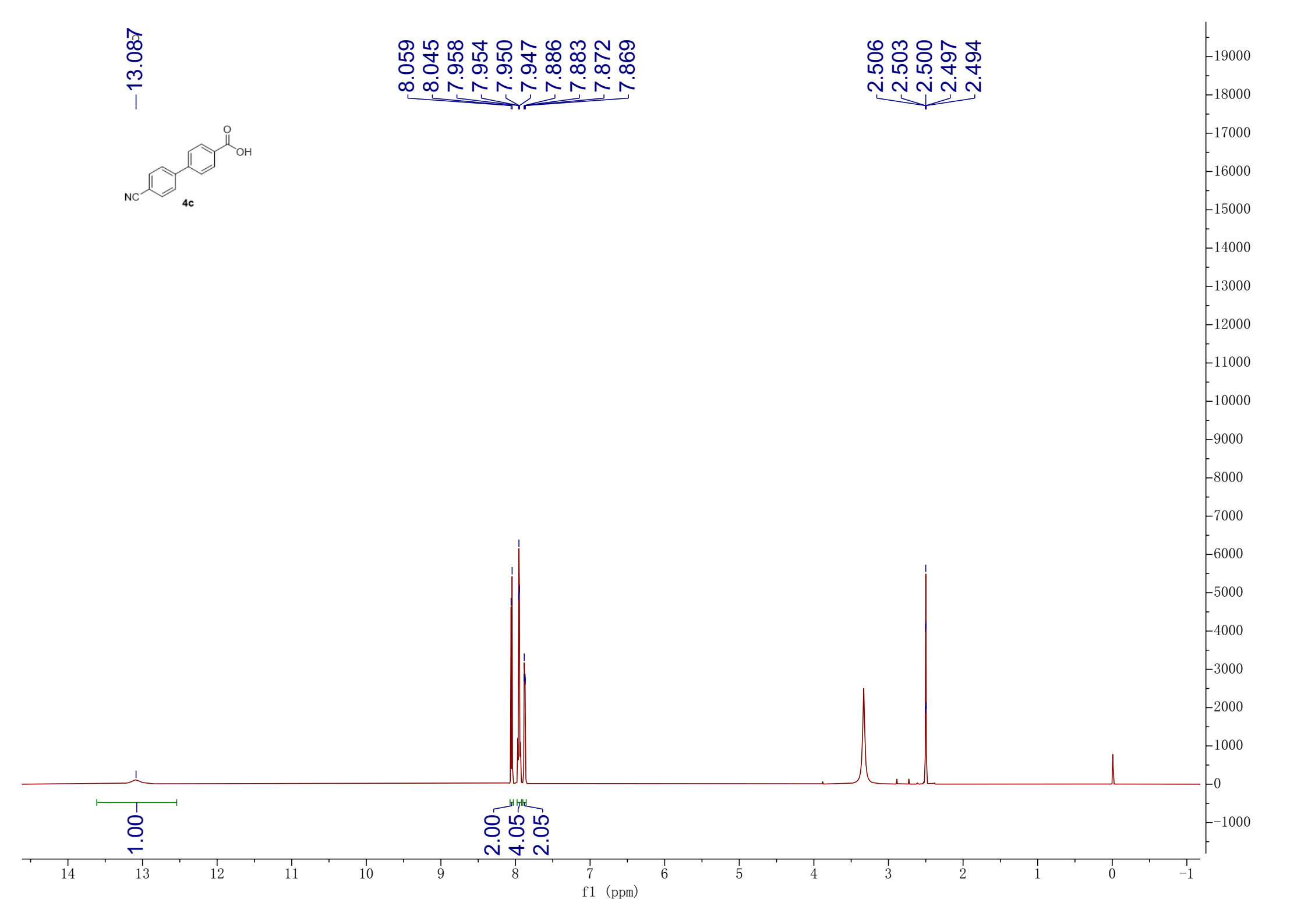
18.572
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
20 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)

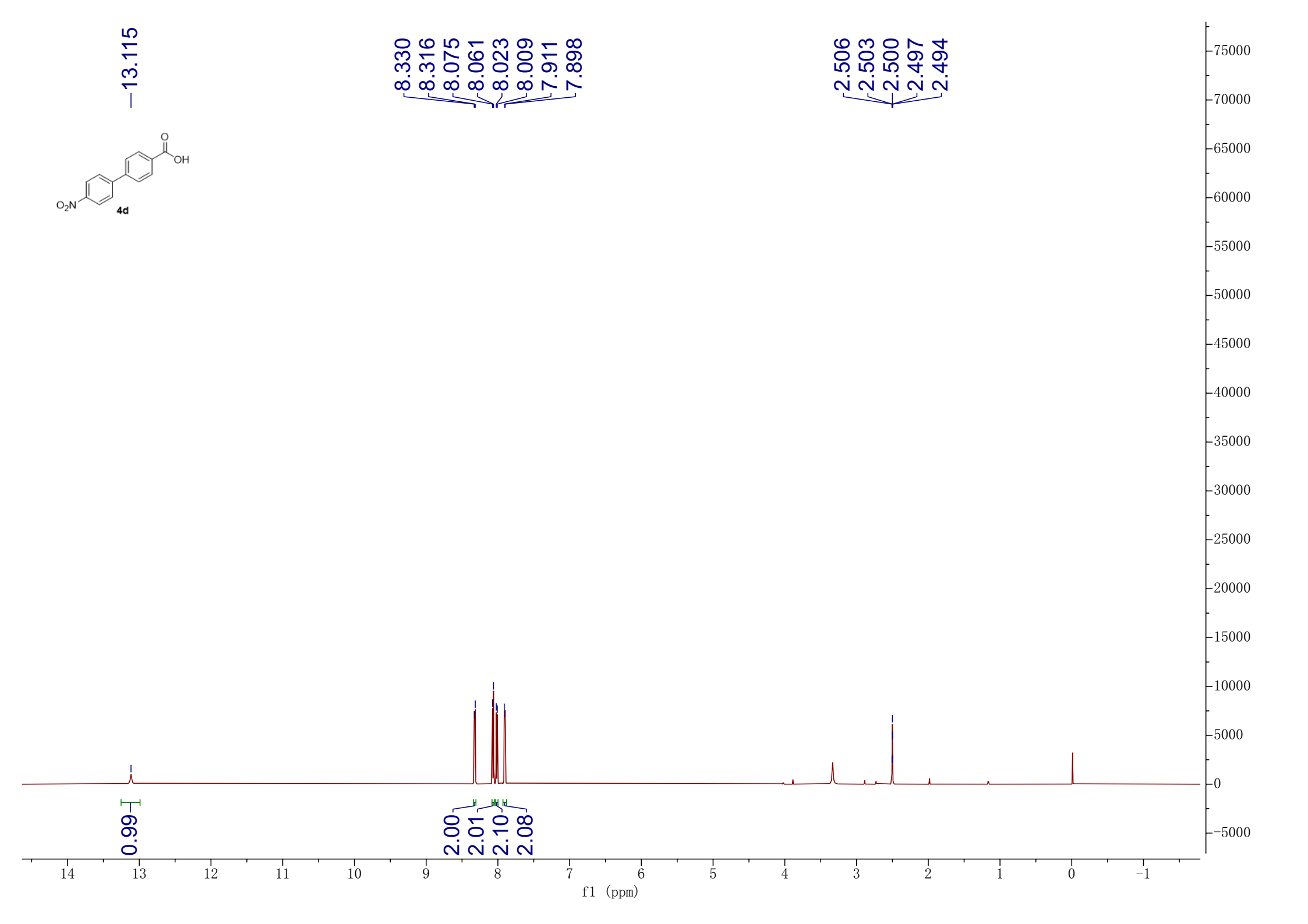

7.81 7.79 7.77 7.45 7.43 7.26 2.99 2.98 2.97 2.54 2.51 2.49 2.43 2.19 2.17 2.14 2.12 2.10 2.09 2.08 2.07 2.06 2.05 2.04 2.02 1.99 1.99 1.68 1.67 1.65 1.65 1.64 1.63 1.63 1.62 1.60 1.59 1.57 1.56 1.56 1.56 1.54 1.53 1.53 1.51 1.50 1.41 0.92
3x
1.03 0.98 1.00 2.06 3.25 4.39 7.00 3.06
f1 (ppm)

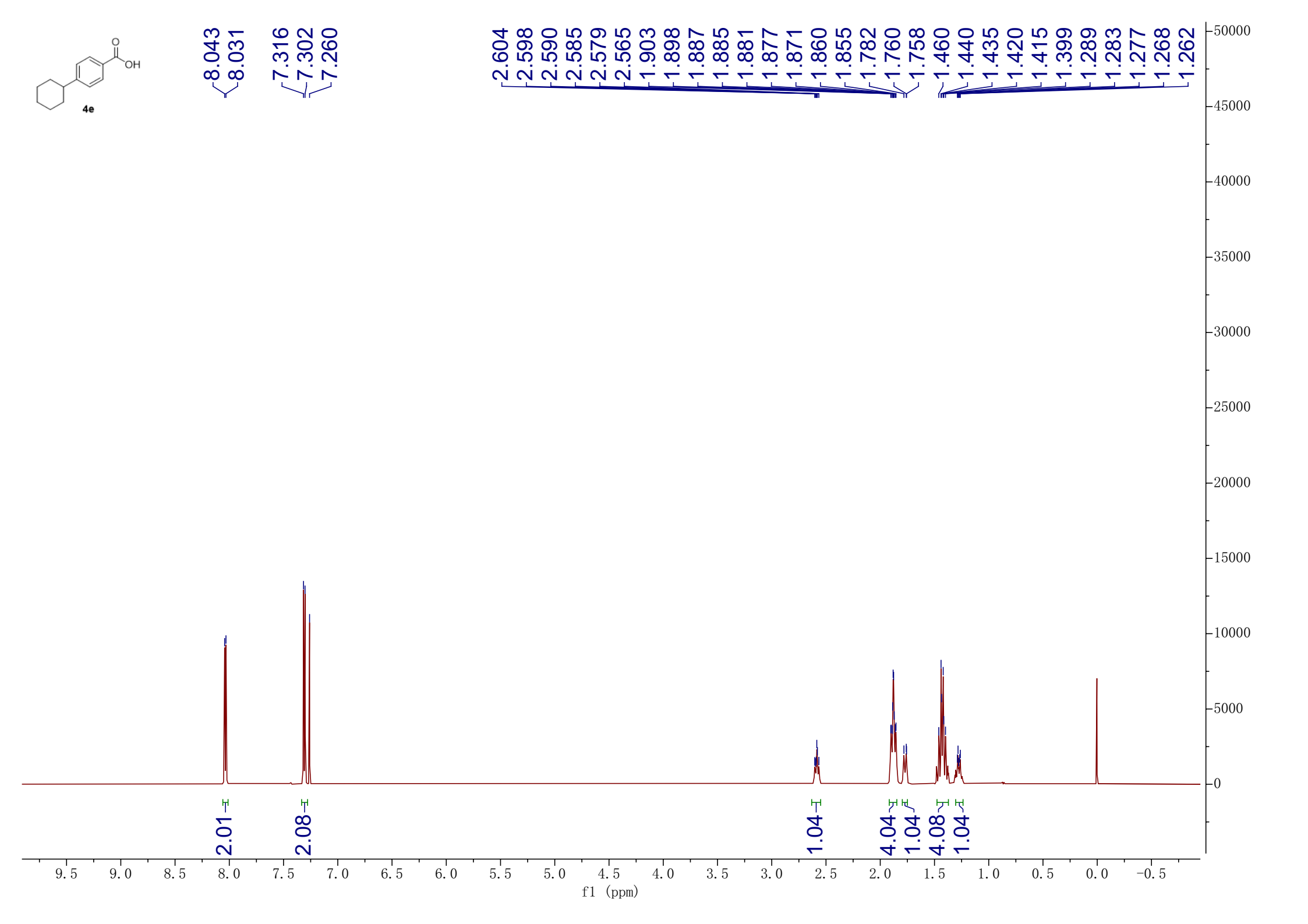

-17.79
O
F
H
H
H
O
Me
3x
2.6×10^7
2.4×10^7
2.2×10^7
2.0×10^7
1.8×10^7
1.6×10^7
1.4×10^7
1.2×10^7
1.0×10^7
8.0×10^6
6.0×10^6
4.0×10^6
2.0×10^6
0.0
-2.0×10^6
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)

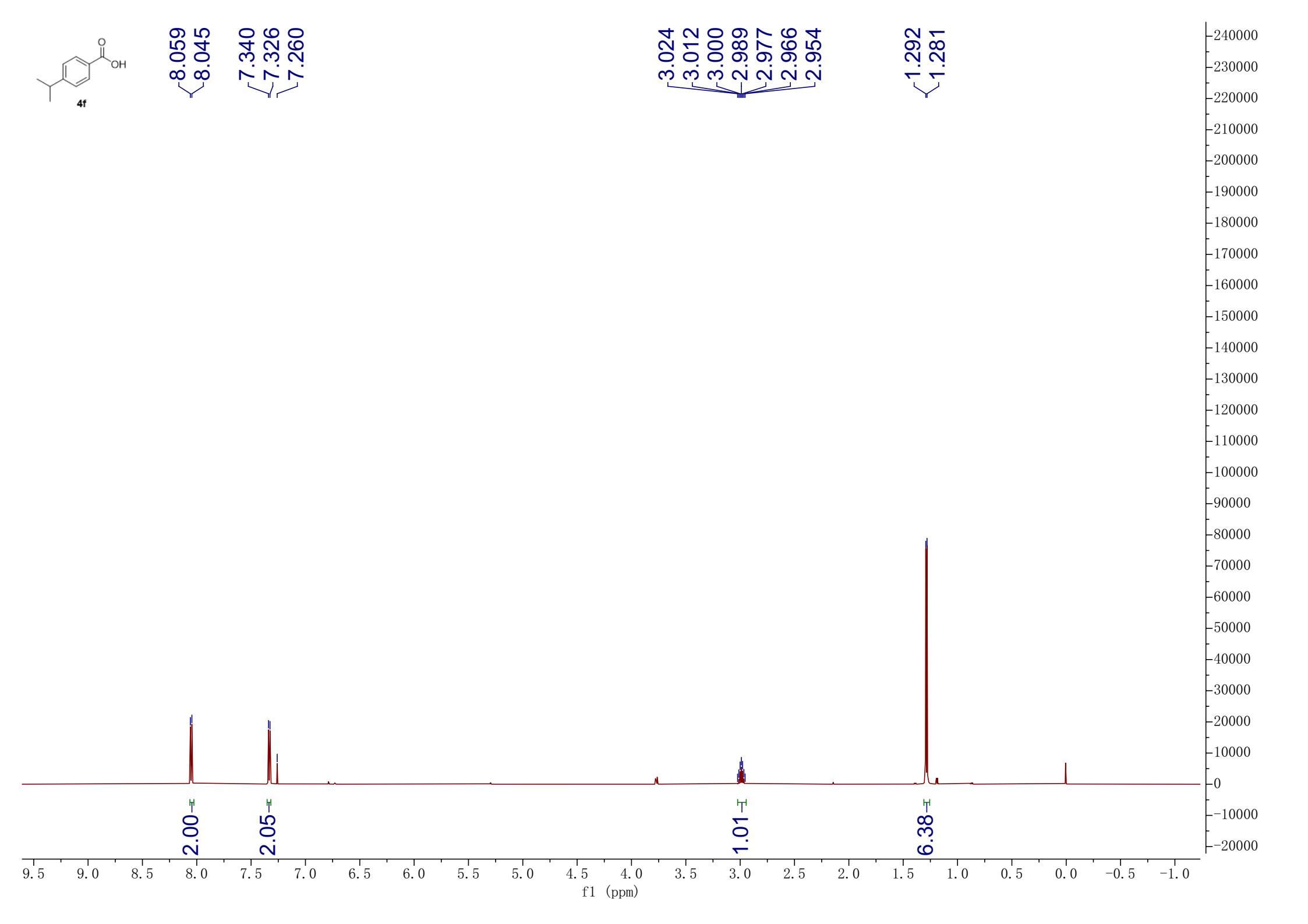

12.955
8.031
8.017
7.804
7.791
7.738
7.725
7.515
7.502
7.489
7.436
7.423
7.411
2.506
2.503
2.500
2.497
2.494
O
OH
4a
1.00
2.00
2.07
2.06
2.04
1.00
f1 (ppm)

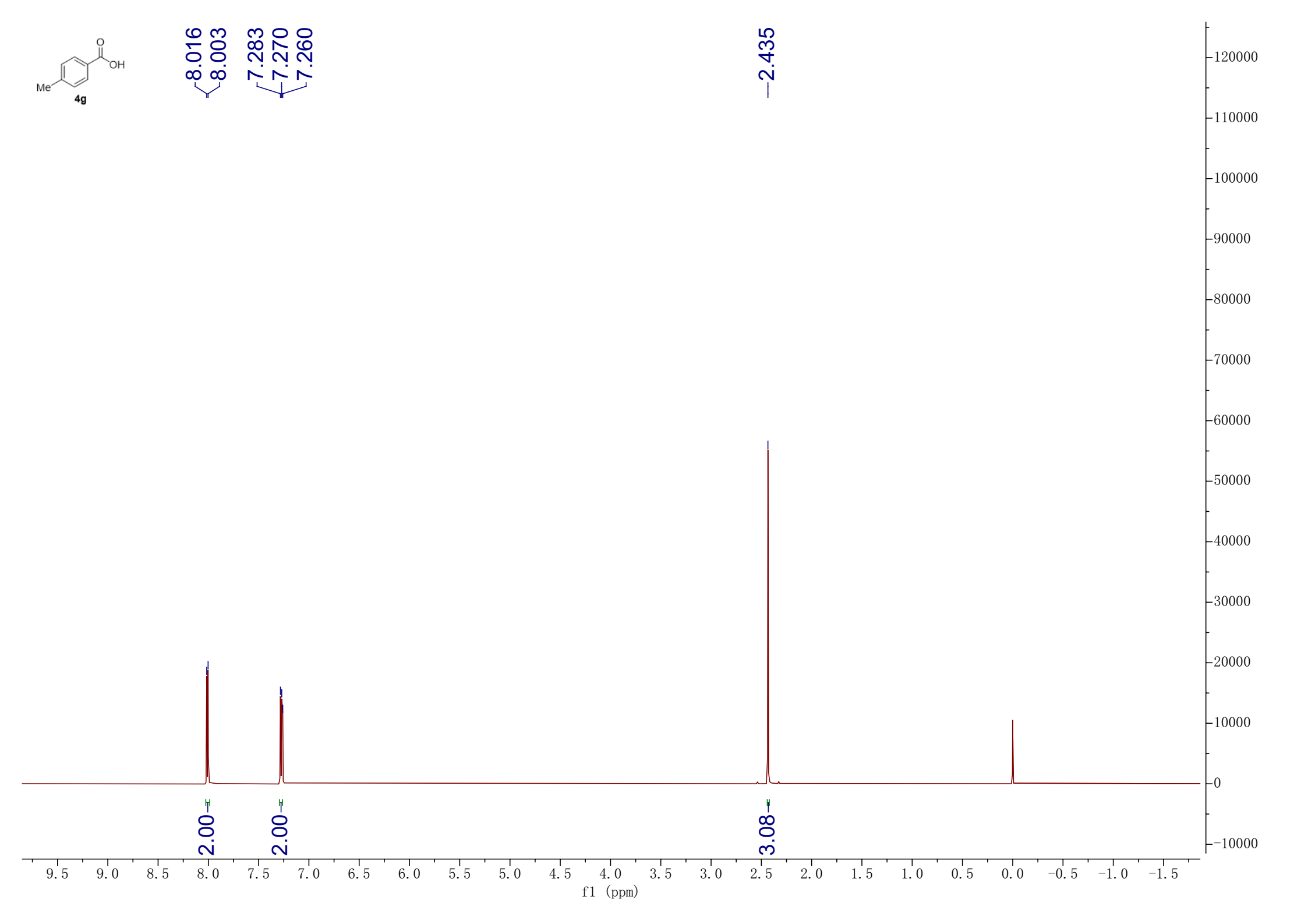

4b
13.08
8.71
8.70
8.22
8.20
8.06
8.04
7.94
7.94
7.92
7.90
7.90
7.43
7.41
7.41
7.40
2.51
2.50
2.50
2.50
2.49
0.95
1.00
2.11
3.09
1.06
1.02
f1 (ppm)

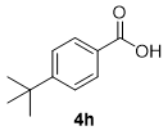

13.087
8.059
8.045
7.958
7.954
7.950
7.947
7.886
7.883
7.872
7.869
2.506
2.503
2.500
2.497
2.494
OH
O
NC
4c
1.00
2.00
4.05
2.05
f1 (ppm)


13.115
8.330
8.316
8.075
8.061
8.023
8.009
7.911
7.898
2.506
2.503
2.500
2.497
2.494
O
OH
O2N
4d
0.99
2.00
2.01
2.10
2.08
f1 (ppm)


4e
8.043
8.031
7.316
7.302
7.260
2.604
2.598
2.590
2.585
2.579
2.565
1.903
1.898
1.887
1.885
1.881
1.877
1.871
1.860
1.855
1.782
1.760
1.758
1.460
1.440
1.435
1.420
1.415
1.399
1.289
1.283
1.277
1.268
1.262
2.01
2.08
1.04
4.04
1.04
4.08
1.04
f1 (ppm)


4f
8.059
8.045
7.340
7.326
7.260
3.024
3.012
3.000
2.989
2.977
2.966
2.954
1.292
1.281
2.00
2.05
1.01
6.38
f1 (ppm)


Me
OH
4g
8.016
8.003
7.283
7.270
7.260
2.435
2.00
2.00
3.08
f1 (ppm)



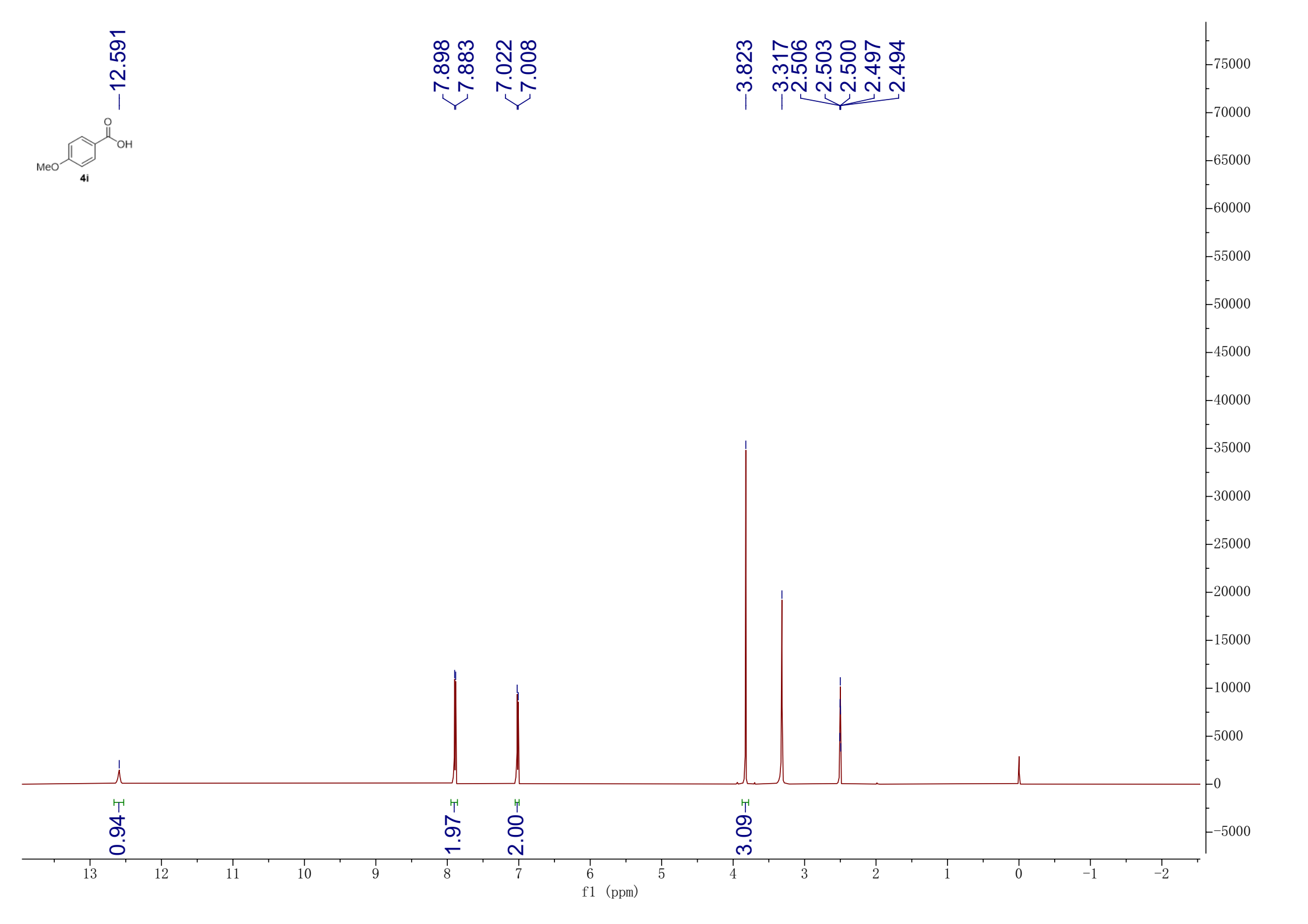
4h

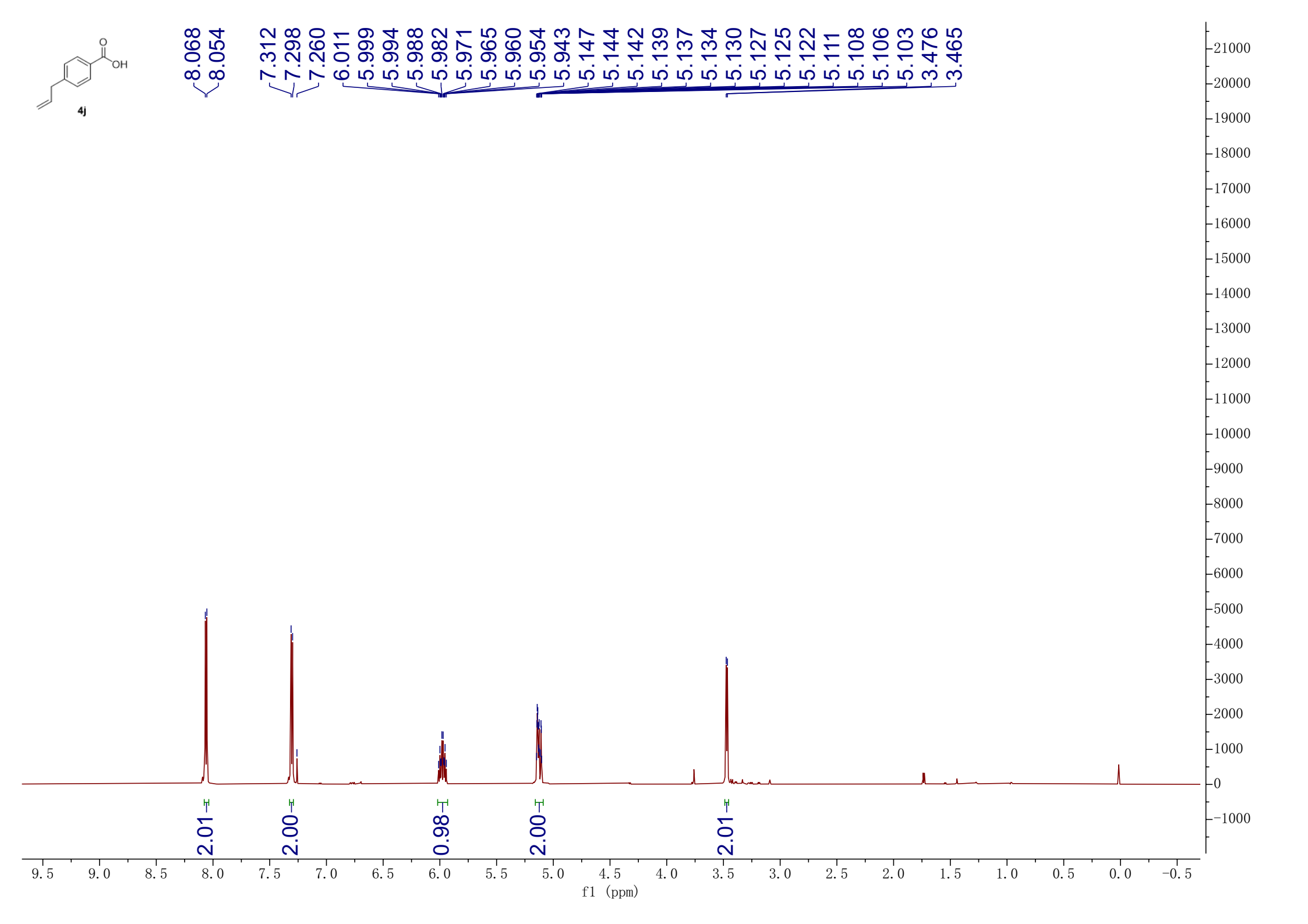
7.978
7.963
7.548
7.534
7.260

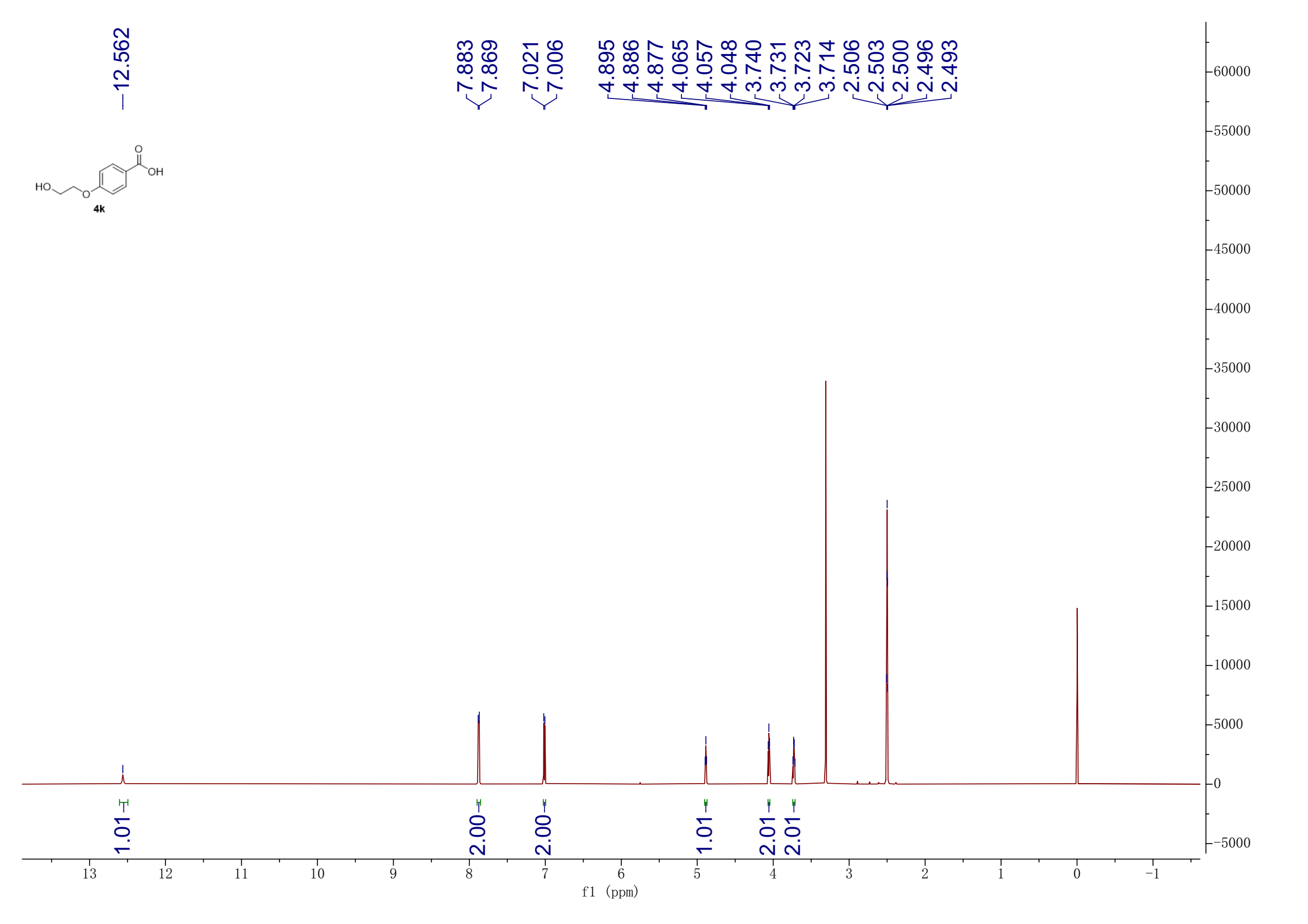
1.359

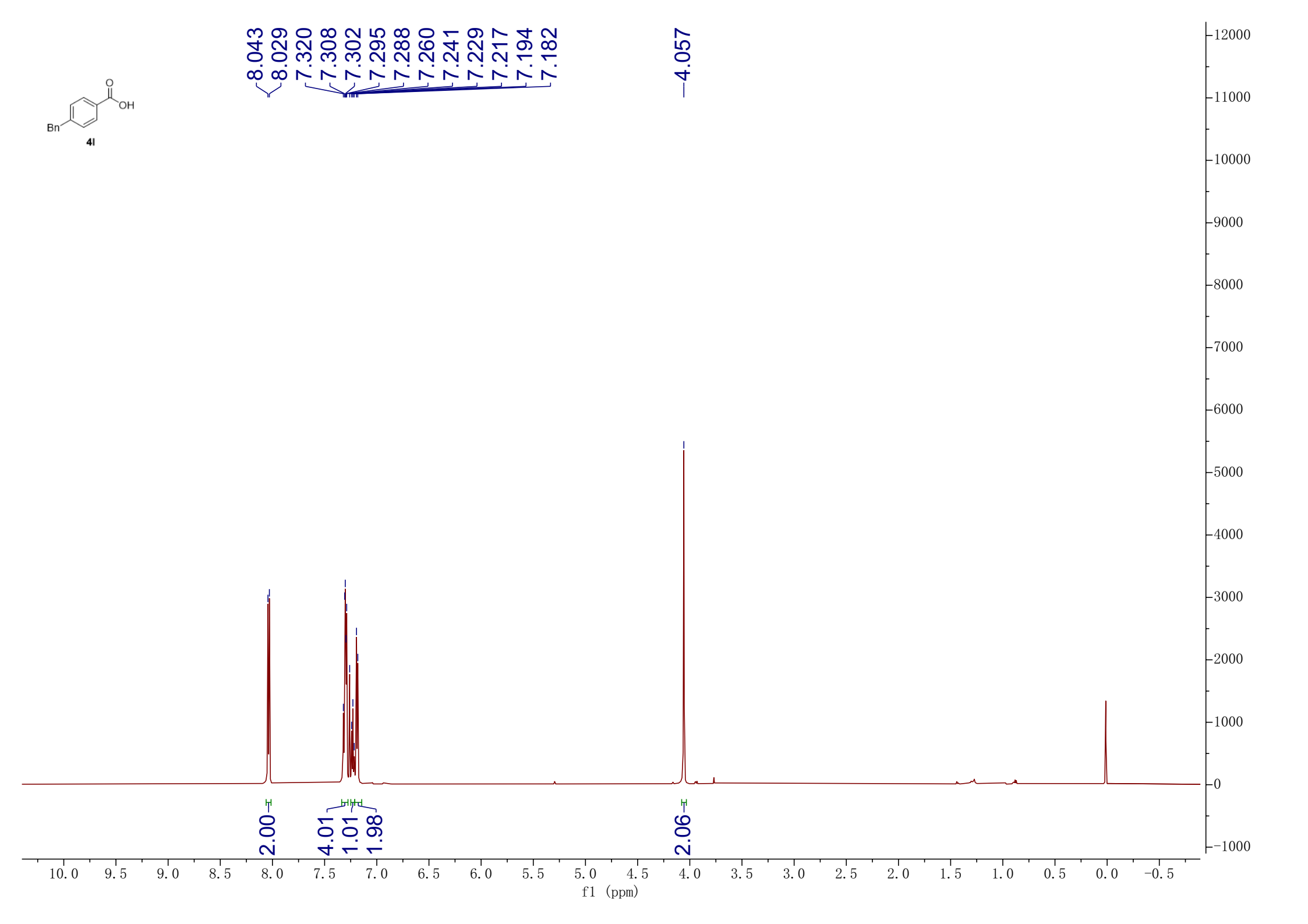
2.00
2.00
9.19

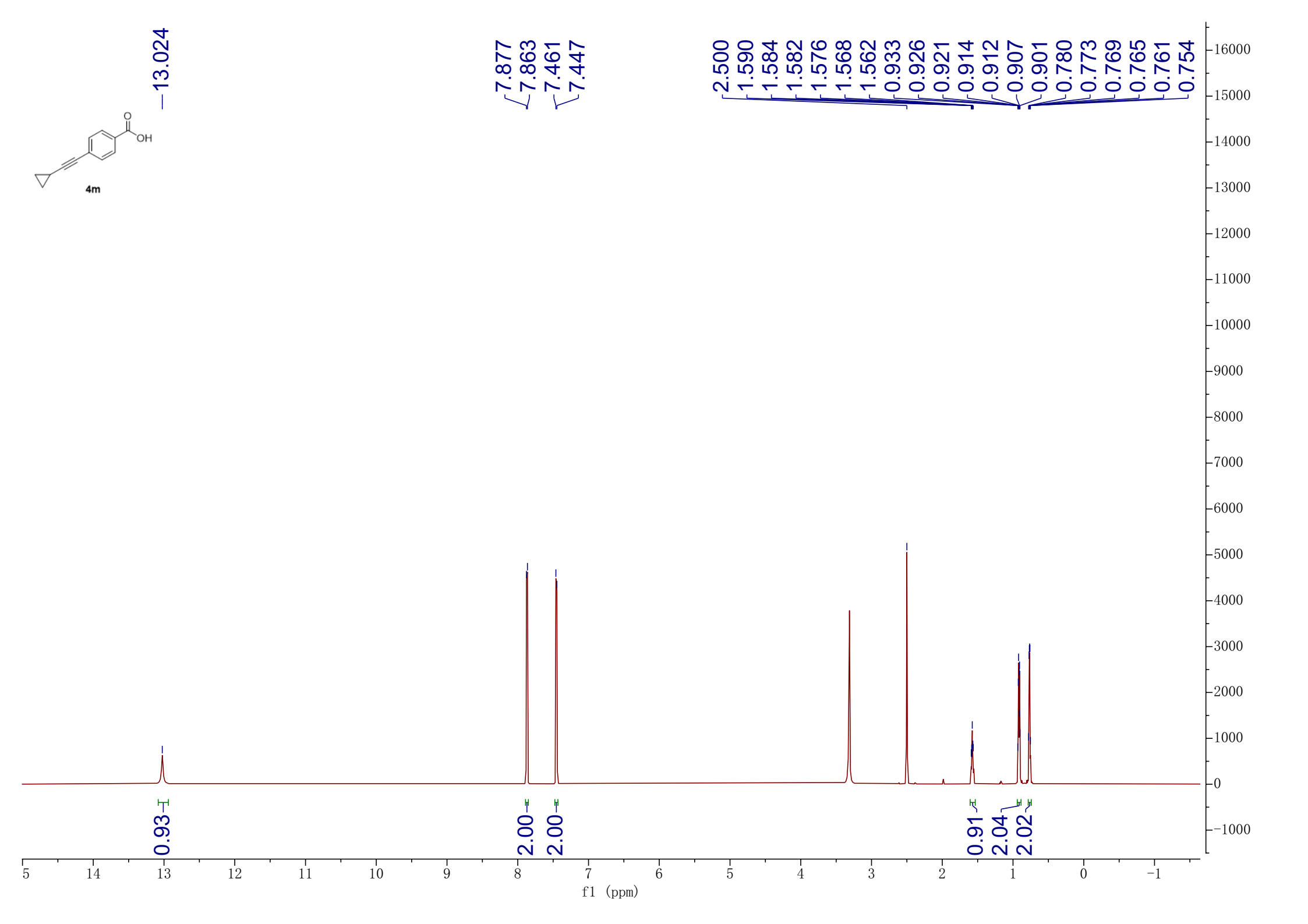
f1 (ppm)

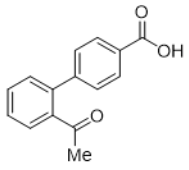

12.591
7.898
7.883
7.022
7.008
3.823
3.317
2.506
2.503
2.500
2.497
2.494
MeO
OH
O
4i
0.94
1.97
2.00
3.09
f1 (ppm)


4j
8.068
8.054
7.312
7.298
7.260
6.011
5.999
5.994
5.988
5.982
5.971
5.965
5.960
5.954
5.943
5.147
5.144
5.142
5.139
5.137
5.134
5.130
5.127
5.125
5.122
5.111
5.108
5.106
5.103
3.476
3.465
2.01
2.00
0.98
2.00
2.01
f1 (ppm)


12.562
7.883
7.869
7.021
7.006
4.895
4.886
4.877
4.065
4.057
4.048
3.740
3.731
3.723
3.714
2.506
2.503
2.500
2.496
2.493
HO
O
OH
4k
1.01
2.00
2.00
1.01
2.01
2.01
f1 (ppm)


8.043
8.029
7.320
7.308
7.302
7.295
7.288
7.260
7.241
7.229
7.217
7.194
7.182
4.057
O
OH
Bn
4l
2.00
4.01
1.01
1.98
2.06
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
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
-0.5
f1 (ppm)


13.024
7.877
7.863
7.461
7.447
2.500
1.590
1.584
1.582
1.576
1.568
1.562
0.933
0.926
0.921
0.914
0.912
0.907
0.901
0.780
0.773
0.769
0.765
0.761
0.754
OH
4m
0.93
2.00
2.00
0.91
2.04
2.02
f1 (ppm)

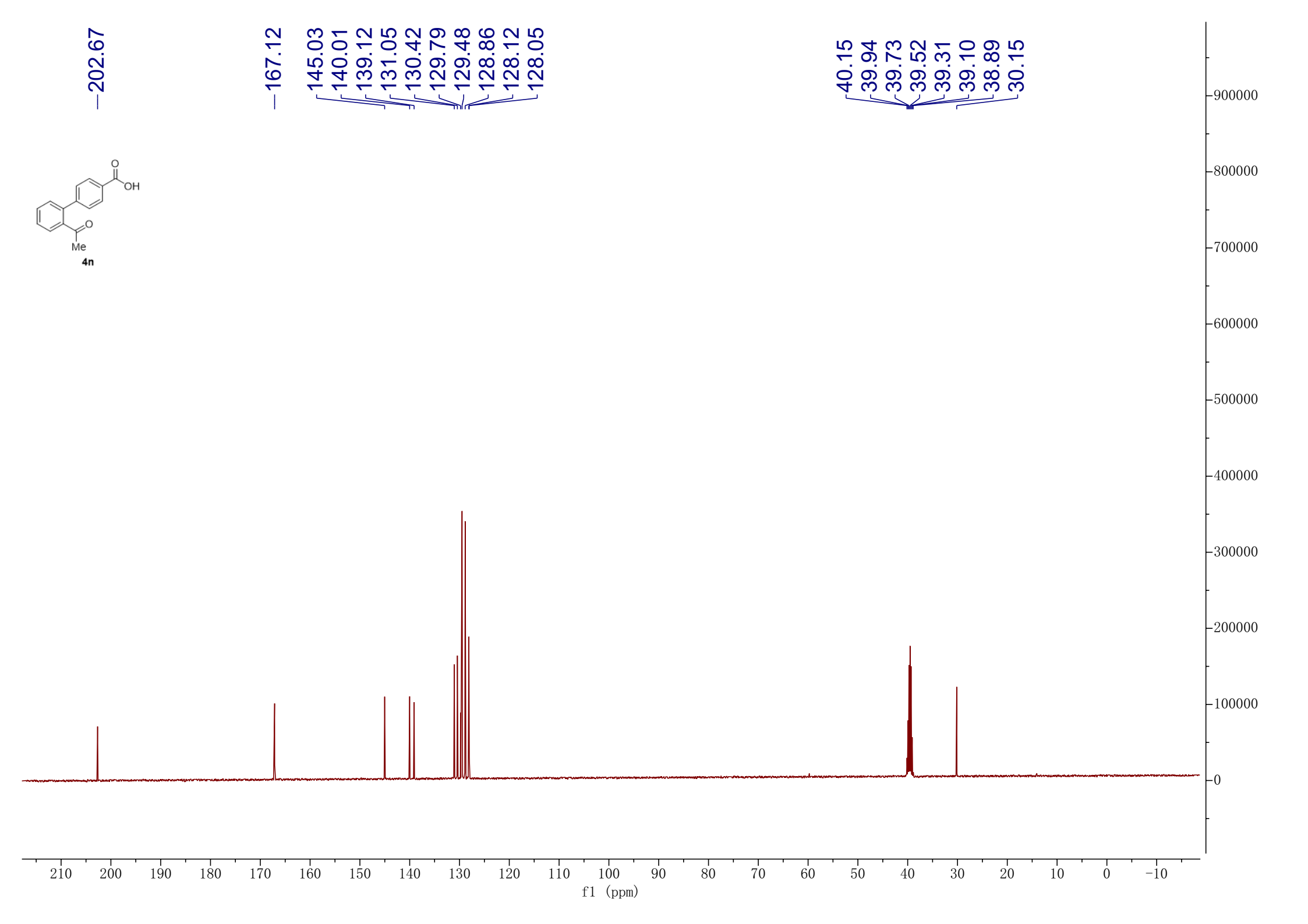


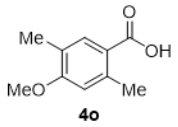
4n

8.189
8.168
7.631
7.612
7.575
7.557
7.538
7.494
7.475
7.467
7.447
7.412
7.260
2.131

2.00
1.01
1.04
3.03
1.03
3.02

f1 (ppm)


202.67
167.12
145.03
140.01
139.12
131.05
130.42
129.79
129.48
128.86
128.12
128.05
40.15
39.94
39.73
39.52
39.31
39.10
38.89
30.15
O
OH
O
Me
4n
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
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)

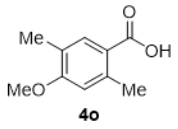


4o

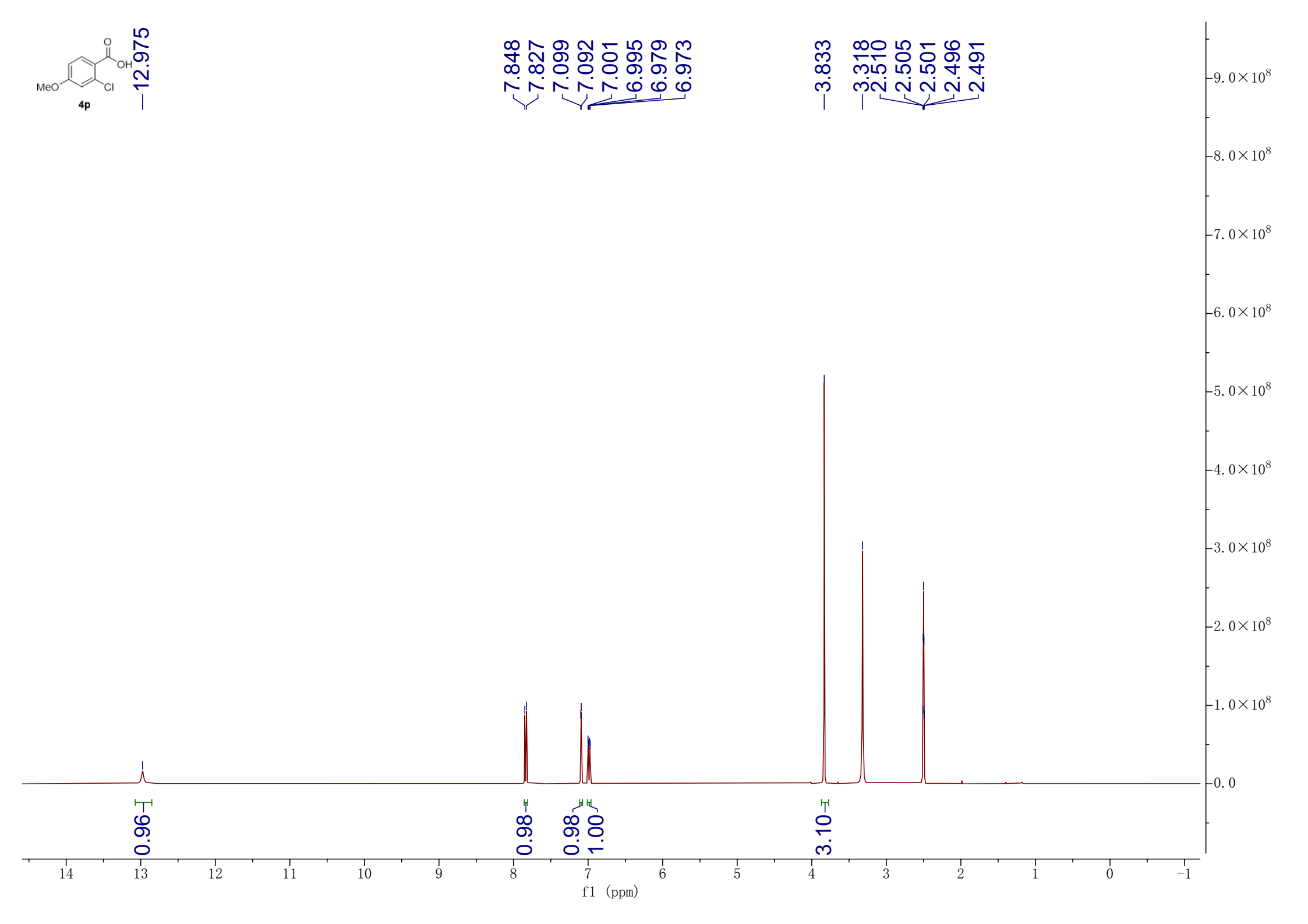
7.898
7.260
6.667
3.882
2.655
2.209

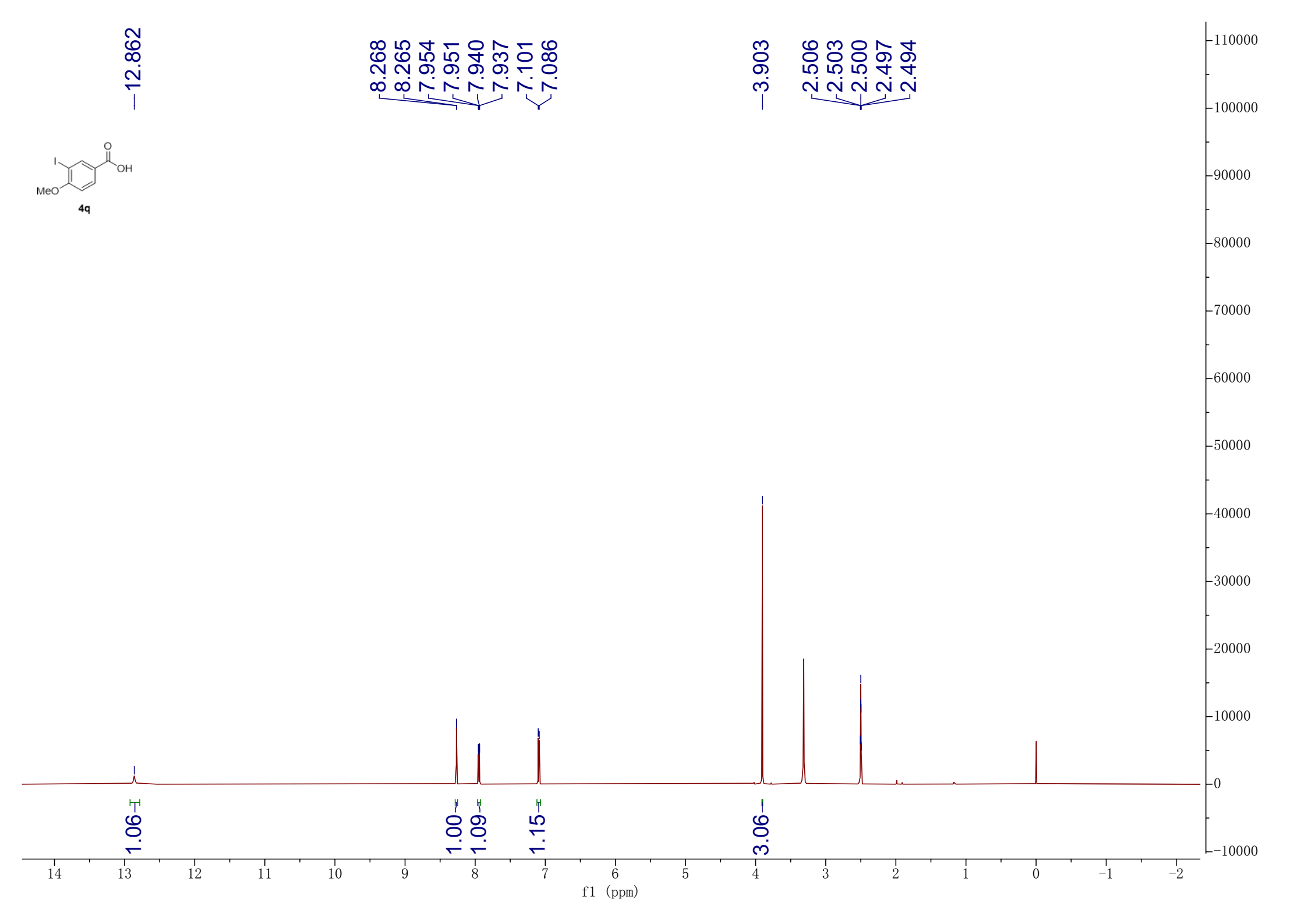
1.00
1.04
3.11
3.00
3.04

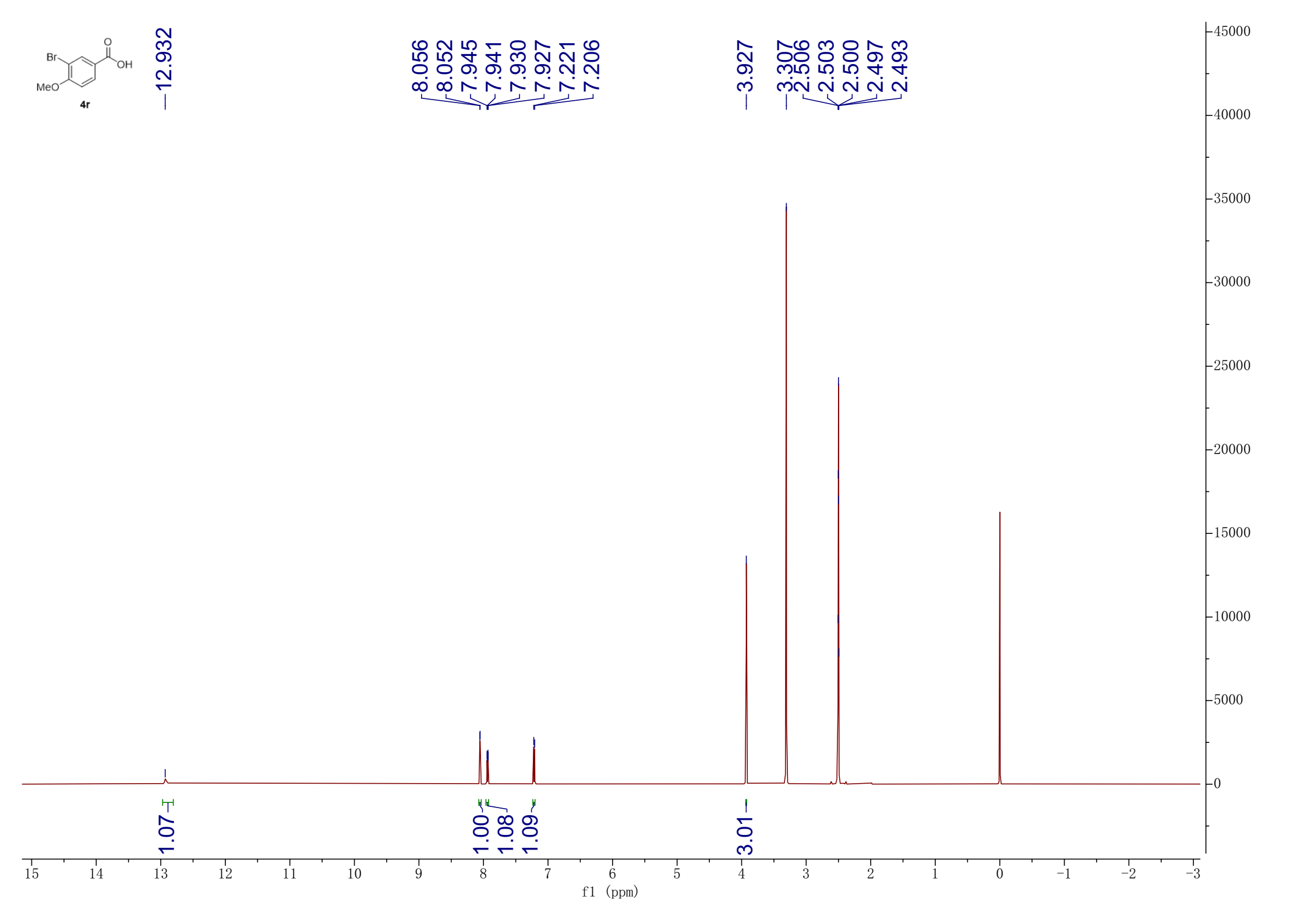
f1 (ppm)

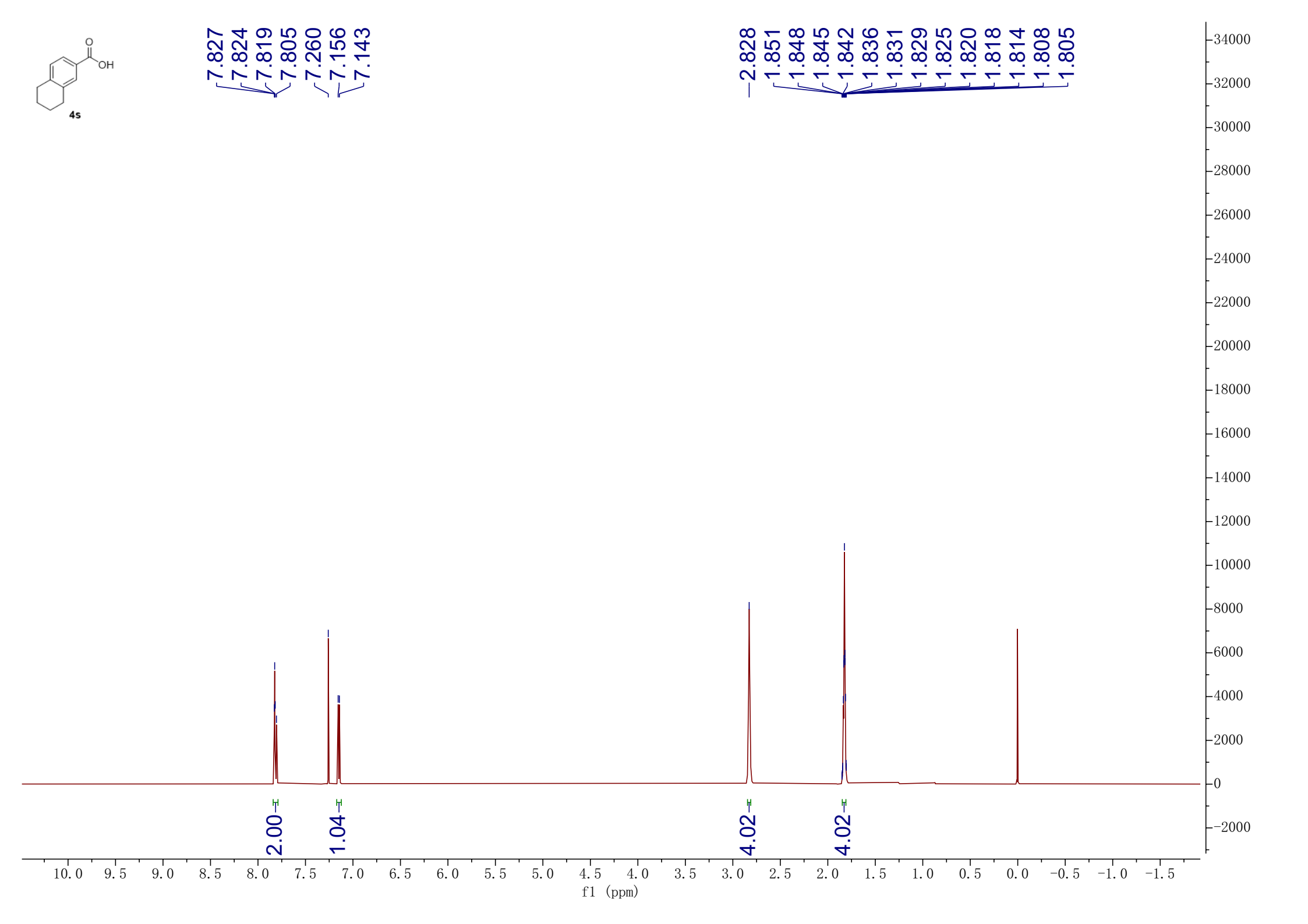

Me
O
OH
MeO
Me
4o

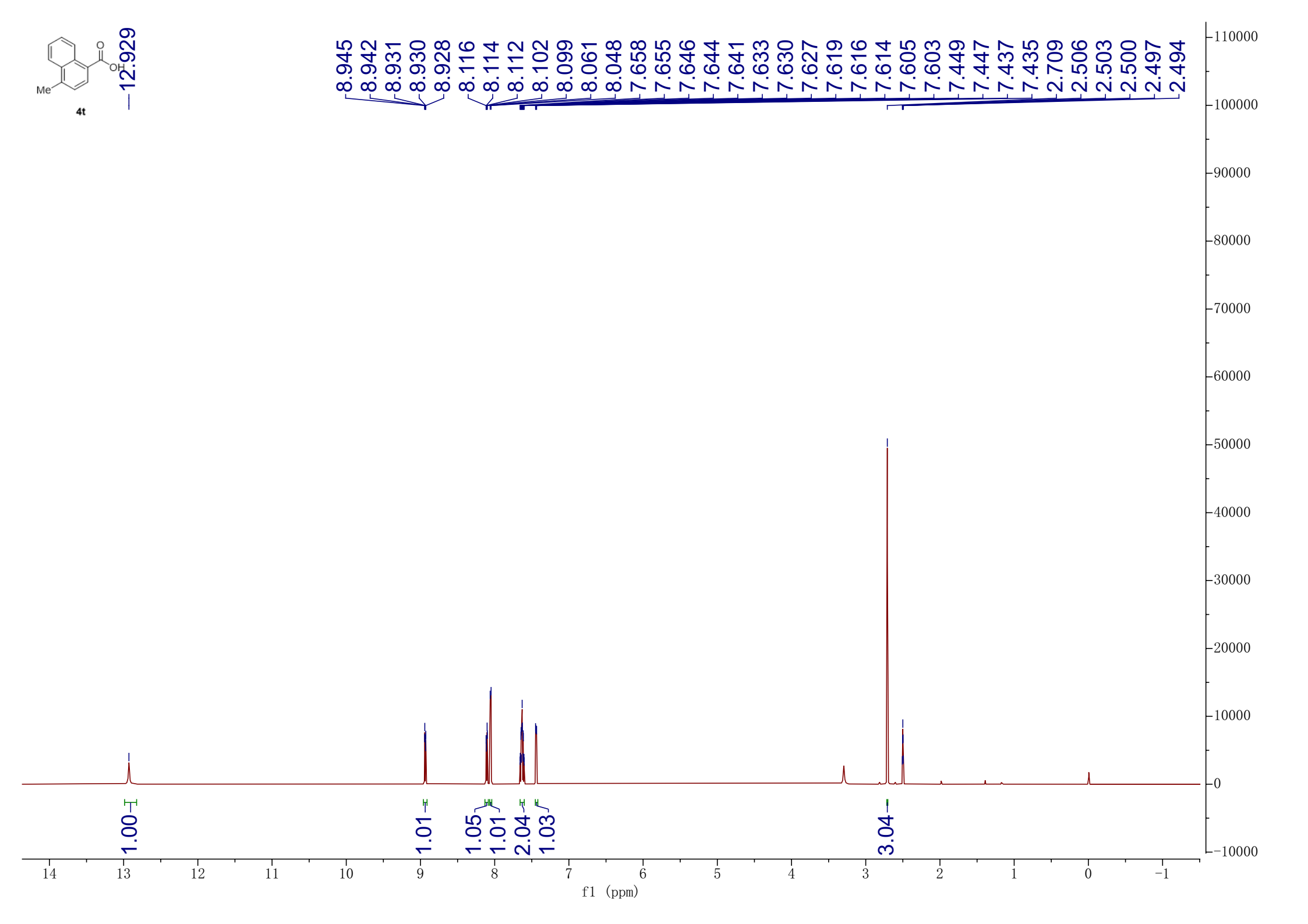
173.21
161.47
142.13
134.46
124.24
120.02
113.21
77.44
77.23
77.02
55.61
22.70
15.75
200000
190000
180000
170000
160000
150000
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

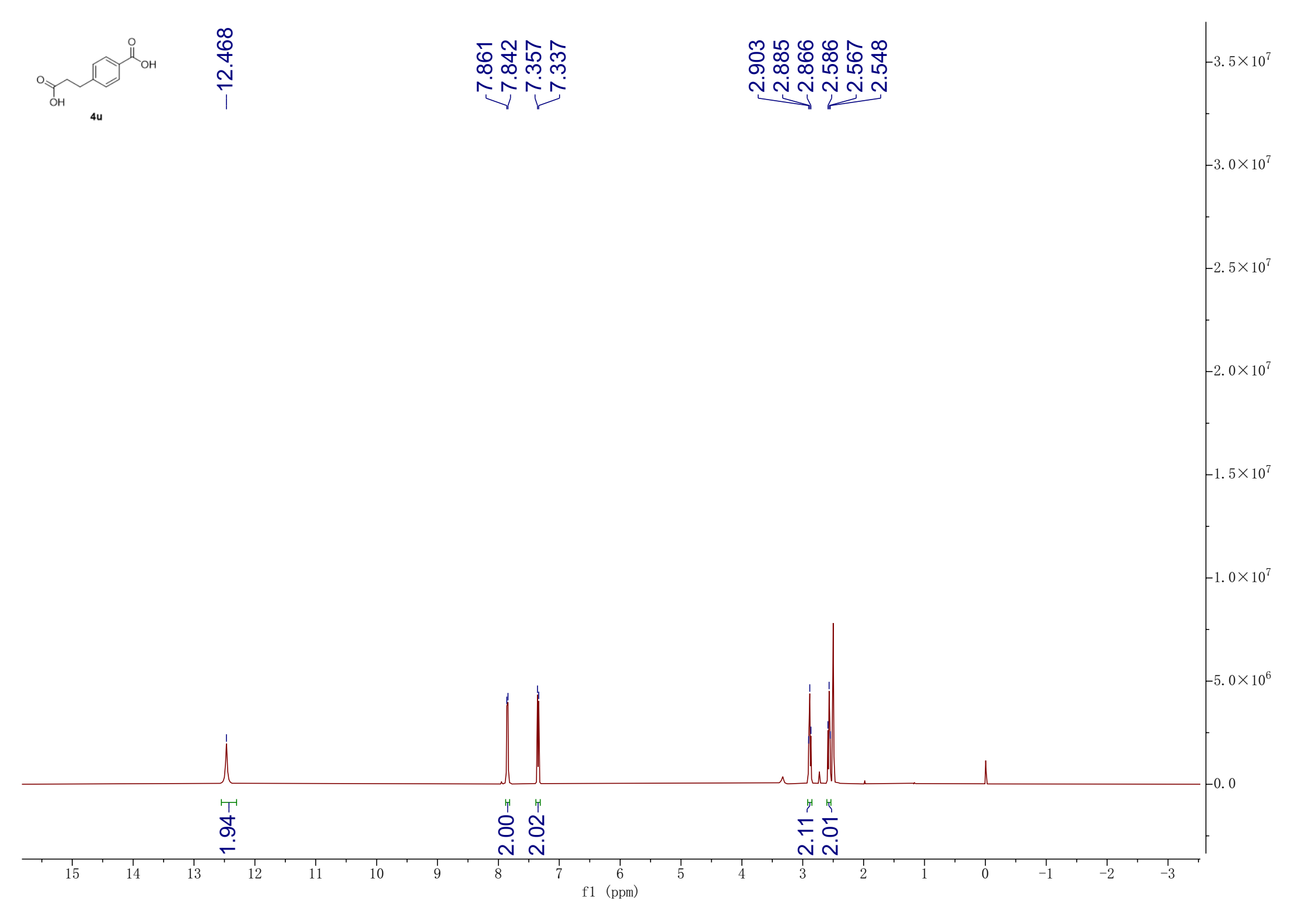

4p
12.975
7.848
7.827
7.099
7.092
7.001
6.995
6.979
6.973
3.833
3.318
2.510
2.505
2.501
2.496
2.491
0.96
0.98
0.98
1.00
3.10
f1 (ppm)

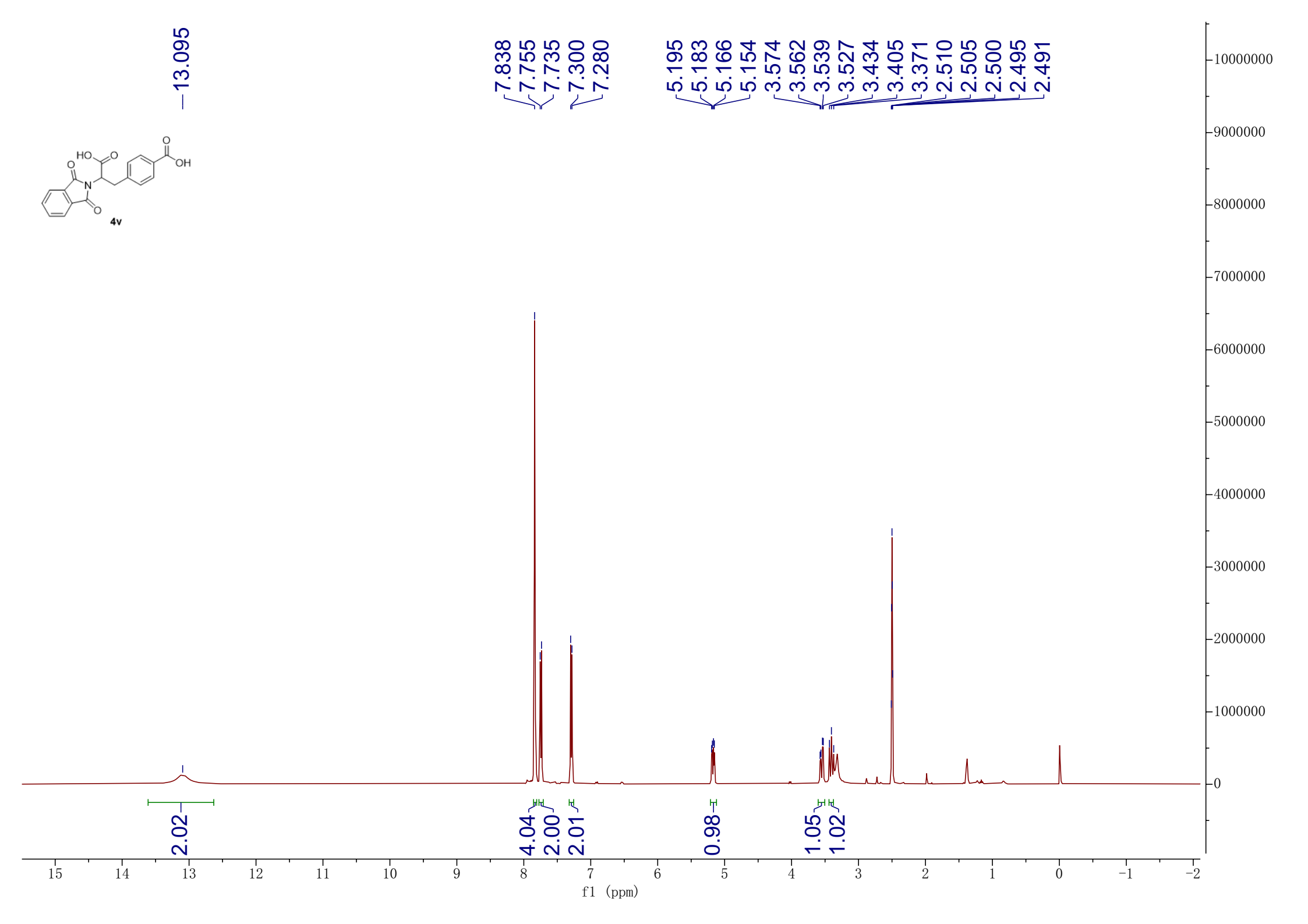

12.862
8.268
8.265
7.954
7.951
7.940
7.937
7.101
7.086
3.903
2.506
2.503
2.500
2.497
2.494
I
O
OH
MeO
4q
1.06
1.00
1.09
1.15
3.06
f1 (ppm)

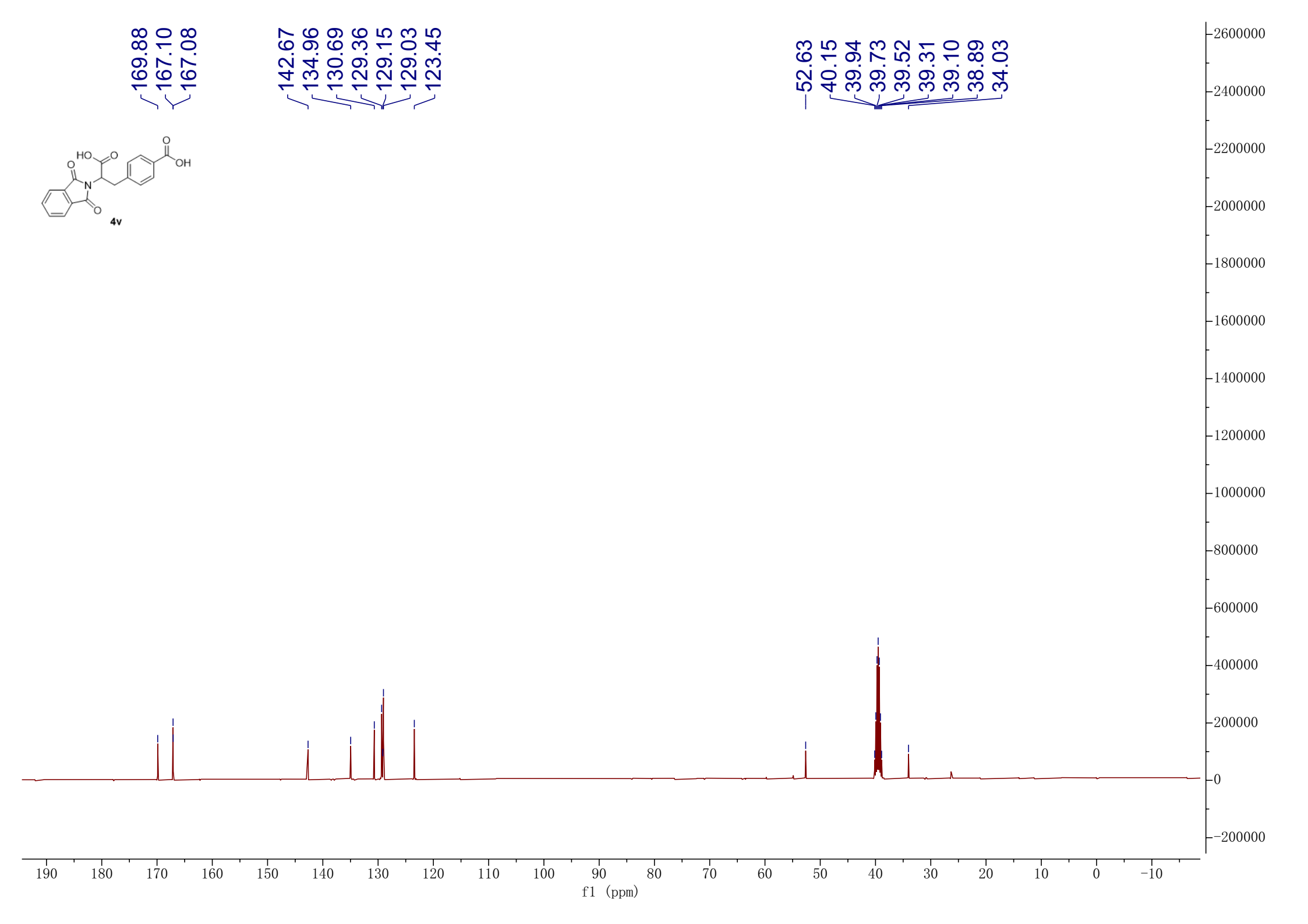

Br
MeO
O
OH
4r
12.932
8.056
8.052
7.945
7.941
7.930
7.927
7.221
7.206
3.927
3.307
2.506
2.503
2.500
2.497
2.493
1.07
1.00
1.08
1.09
3.01
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)

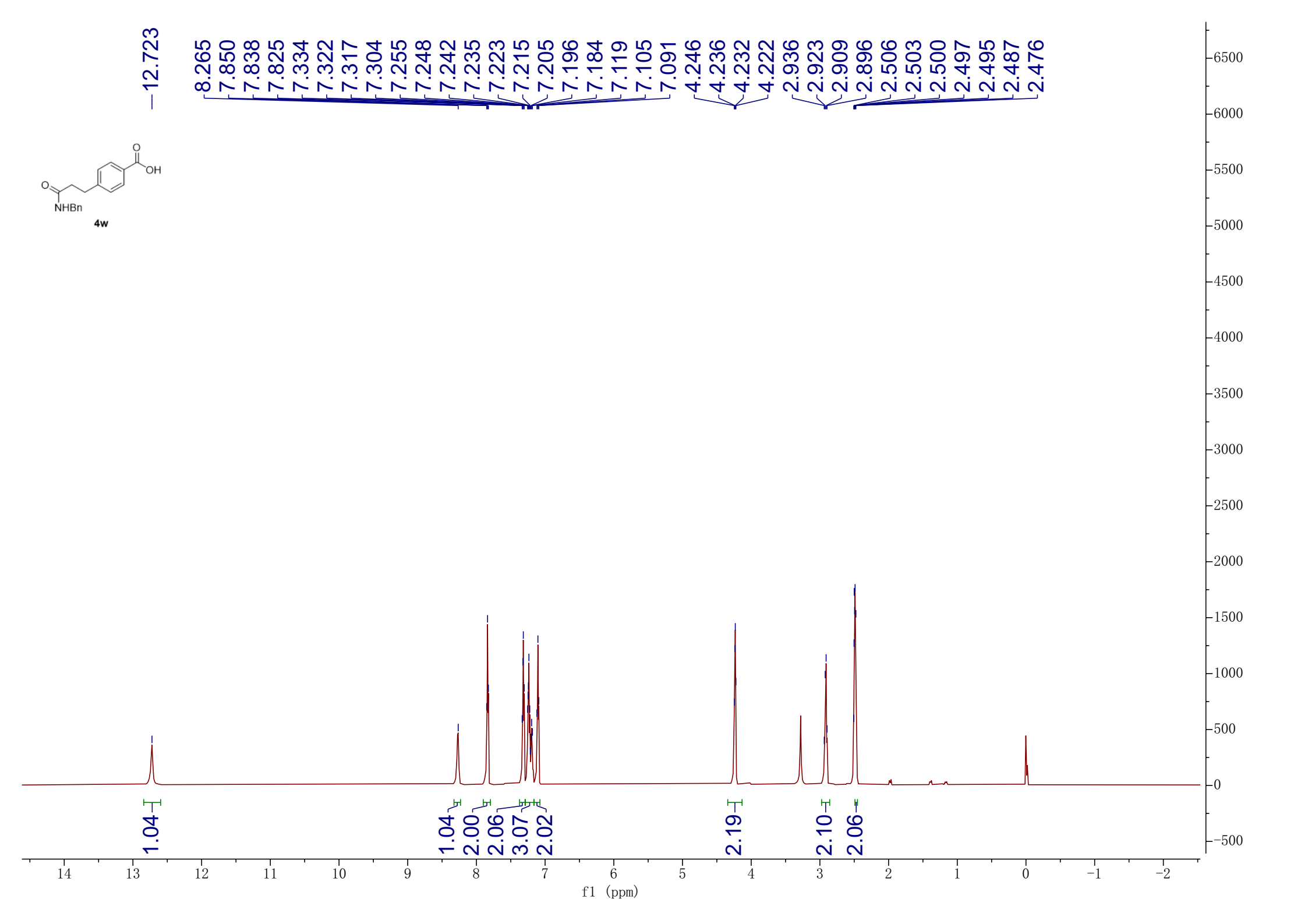

4s
7.827
7.824
7.819
7.805
7.260
7.156
7.143
2.828
1.851
1.848
1.845
1.842
1.836
1.831
1.829
1.825
1.820
1.818
1.814
1.808
1.805
2.00
1.04
4.02
4.02
f1 (ppm)

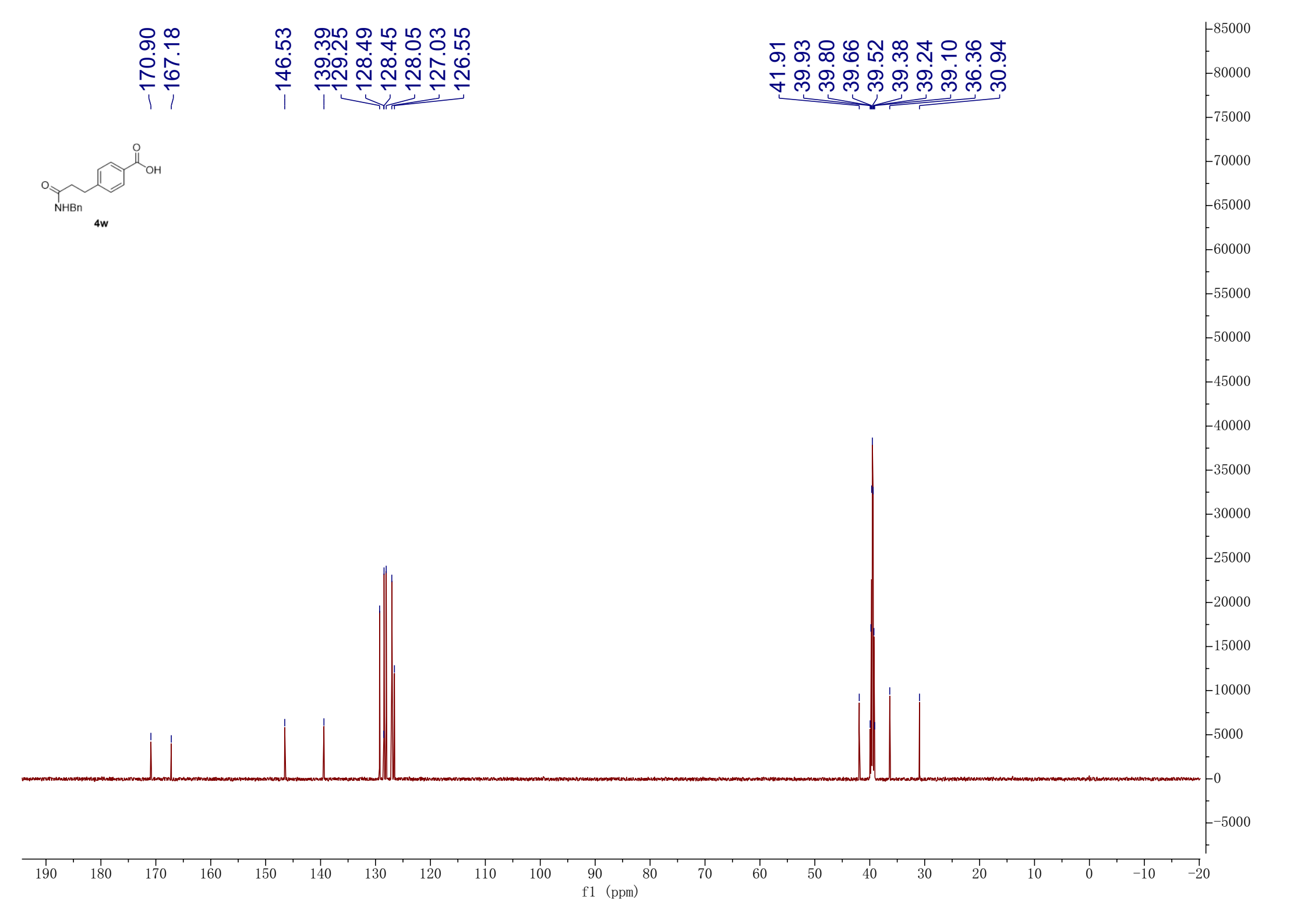

4t
12.929
8.945
8.942
8.931
8.930
8.928
8.116
8.114
8.112
8.102
8.099
8.061
8.048
7.658
7.655
7.646
7.644
7.641
7.633
7.630
7.627
7.619
7.616
7.614
7.605
7.603
7.449
7.447
7.437
7.435
2.709
2.506
2.503
2.500
2.497
2.494
1.00
1.01
1.05
1.01
2.04
1.03
3.04
f1 (ppm)


4u
12.468
7.861
7.842
7.357
7.337
2.903
2.885
2.866
2.586
2.567
2.548
1.94
2.00
2.02
2.11
2.01
f1 (ppm)


13.095
7.838
7.755
7.735
7.300
7.280
5.195
5.183
5.166
5.154
3.574
3.562
3.539
3.527
3.434
3.405
3.371
2.510
2.505
2.500
2.495
2.491
HO
O
O
N
O
O
OH
4v
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
2.02
4.04
2.00
2.01
0.98
1.05
1.02
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
f1 (ppm)


169.88
167.10
167.08
142.67
134.96
130.69
129.36
129.15
129.03
123.45
52.63
40.15
39.94
39.73
39.52
39.31
39.10
38.89
34.03
HO
O
O
OH
N
O
O
4v
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
−200000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


12.723
8.265
7.850
7.838
7.825
7.334
7.322
7.317
7.304
7.255
7.248
7.242
7.235
7.223
7.215
7.205
7.196
7.184
7.119
7.105
7.091
4.246
4.236
4.232
4.222
2.936
2.923
2.909
2.896
2.506
2.503
2.500
2.497
2.495
2.487
2.476
O
OH
O
NHBn
4w
1.04
1.04
2.00
2.06
3.07
2.02
2.19
2.10
2.06
f1 (ppm)


170.90
167.18
146.53
139.39
129.25
128.49
128.45
128.05
127.03
126.55
41.91
39.93
39.80
39.66
39.52
39.38
39.24
39.10
36.36
30.94
O
OH
O
NHBn
4w
f1 (ppm)