# A silver(I)-catalyzed tandem reaction of 2-alkynylbenzaldoxime with ketene

**Hongliang Liu,[a] Gang Liu,[a] Shouzhi Pu*[a] and Zhiyong Wang*[b]**

[a] *Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science & Technology Normal University, Nanchang 330013, China*

[b] *School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China.*

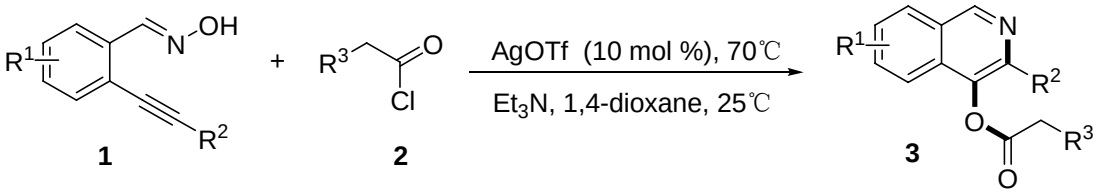
zwang@cqu.edu.cn

## Supporting Information

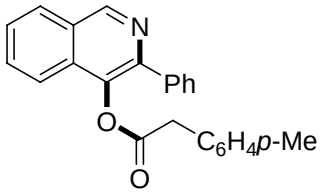
**General experimental methods:**

Unless otherwise stated, all commercial reagents and solvents were used without additional purification. All solvents and $Et_3N$ were dried and distilled according to standard procedures. All reactions were performed in reaction tubes under $N_2$. The Flash column chromatography was performed using silica gel (60-Å pore size, 32–63 μm, standard grade). Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25-35°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane (TMS) on the δ scale.

***General experimental procedure for silver triflate-catalyzed tandem reaction of 2-alkynylbenzaldoxime with ketene.***

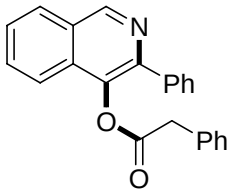



A mixture of Silver triflate (0.03 mmol, 7.7 mg) and 2-alkynylbenzaldoxime **1** (0.3 mmol) in 1,4-dioxane (1.0 mL) was stirred at 70 °C under $N_2$ for 2 hours. Then, $Et_3N$ (0.45 mmol, 46 mg) and ketene precursor **2** (0.45 mmol) in 1,4-dioxane (0.5 mL) were added. The reaction mixture was stirred at room temperature until completion of the reaction. The reaction mixture was diluted with ethyl acetate (5.0 mL), and quenched with water (5.0 mL). The organic layer was washed with brine, dried over $Na_2SO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to provide the desired product **3**.



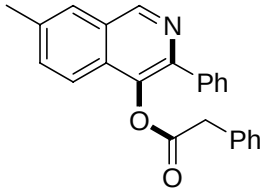

**3-Phenylisoquinolin-4-yl 2-(*p*-tolyl)acetate (3a)**

$^1$H NMR (400 MHz, $CDCl_3$): δ 9.23 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.76-7.73 (m, 2H), 7.67-7.57 (m, 4H), 7.40-7.38 (m, 2H), 7.17-7.16 (m, 4H), 3.82 (s, 2H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 169.5, 150.3, 144.6, 139.6, 137.3, 131.1, 130.9, 129.9, 129.6, 129.5, 129.1, 128.5, 128.4, 127.6, 127.6, 120.8, 41.1, 21.3; HRMS calcd. for $C_{24}H_{20}NO_2^+$ $[M+H]^+$: 354.1489, found 354.1473.



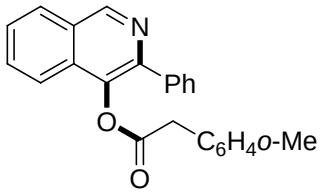

**3-Phenylisoquinolin-4-yl 2-phenylacetate(3b)**

$^1$H NMR (400 MHz, $CDCl_3$): δ 9.23 (s, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.75-7.58 (m, 5H), 7.39-7.28 (m, 8H), 3.85 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 169.1, 150.2, 144.4, 139.4, 137.2, 132.8, 131.0, 130.7, 129.5, 128.9, 128.8, 128.3, 127.5, 120.5; HRMS calcd. for $C_{23}H_{18}NO_2$ $[M+H]^+$: 340.1332, found 340.1315.



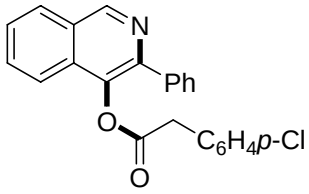

**7-Methyl-3-phenylisoquinolin-4-yl 2-phenylacetate(3c)**

$^1$H NMR (400 MHz, $CDCl_3$): δ 9.14 (s, 1H), 7.76-7.72 (m, 3H), 7.47-7.29 (m, 10H), 3.85 (s, 2H), 2.52 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 169.1, 149.5, 143.6, 137.6, 137.2, 133.3, 132.9, 129.5, 129.3, 129.0, 128.9, 128.8, 128.3, 128.2, 127.5, 126.3, 41.5, 21.6; HRMS calcd. for $C_{24}H_{20}NO_2^+$ $[M+H]^+$: 354.1489, found 354.1454.



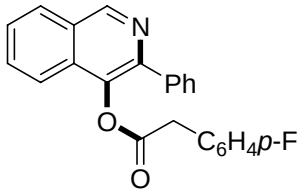
**3-Phenylisoquinolin-4-yl 2-(*o*-tolyl)acetate (3d)**

$^1$H NMR (400 MHz, $CDCl_3$): δ 9.22 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.72-7.57 (m, 5H), 7.43-7.38 (m, 3H), 7.22-7.18 (m, 4H), 3.87 (s, 2H), 2.21 (s, 3H) ; $^{13}$C NMR (100 MHz, $CDCl_3$): δ 169.0, 150.3, 144.7, 139.6, 137.4, 137.2, 131.6, 131.2, 131.0, 130.7, 130.7, 129.1, 128.5, 127.9, 127.7, 127.6, 126.4, 120.6, 39.3, 19.6; HRMS calcd. for $C_{24}H_{20}NO_2^+$ $[M+H]^+$: 354.1489, found 354.1476.



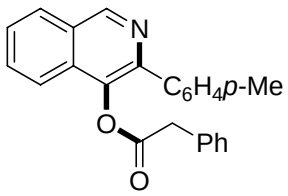

**3-Phenylisoquinolin-4-yl 2-(4-chlorophenyl)acetate (3e)**

$^1$H NMR (400 MHz, $CDCl_3$): δ 9.23 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.71-7.59 (m, 5H), 7.38-7.37 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 3.81 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 168.7, 150.2, 144.5, 139.3, 137.0, 133.5, 131.2, 131.1, 130.7, 130.6, 128.9, 128.3, 127.6, 120.4, 40.6; HRMS calcd. for $C_{23}H_{17}ClNO_2$ $[M+H]^+$: 374.0942, found 374.0946.




**3-Phenylisoquinolin-4-yl 2-(4-fluorophenyl)acetate (3f)**

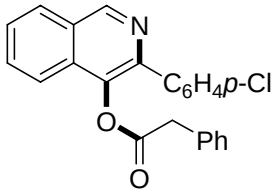
$^1$H NMR (400 MHz, $CDCl_3$): δ 9.24 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.71-7.61 (m, 5H), 7.39-7.38 (m, 3H), 7.25-7.20 (m, 2H), 7.02 (t, *J* = 8.0 Hz, 2H), 3.83 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 169.1, 162.4 (d, $^1J_{CF}$ = 245.8 Hz), 150.4, 144.6, 139.5, 137.2, 131.2, 131.2, 131.1, 130.8, 129.1, 128.4, 127.7, 127.7, 120.6, 115.8 (d, $^2J_{CF}$ = 21.5 Hz), 40.6; HRMS calcd. for $C_{23}H_{17}FNO_2$ $[M+H]^+$: 358.1238, found 358.1221.




**3-(*p*-Tolyl)isoquinolin-4-yl 2-phenylacetate (3g)**

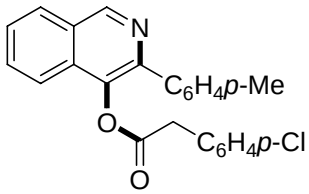
$^1$H NMR (400 MHz, $CDCl_3$): δ 9.21 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.65-7.55 (m,

5H), 7.35-7.29 (m, 5H), 7.19 (d, $J$ = 7.6 Hz, 2H), 3.86 (s, 2H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 169.1, 150.1, 144.5, 139.2, 138.1, 134.3, 132.9, 130.9, 130.8, 129.5, 129.0, 128.8, 128.7, 127.4, 127.3, 120.5, 41.4, 21.3; HRMS calcd. for $C_{24}H_{20}NO_2^+$ $[M+H]^+$ :354.1489, found 354.1488.



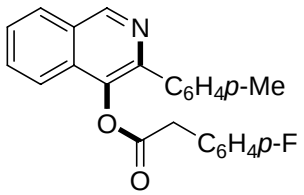

**3-(4-Chlorophenyl)isoquinolin-4-yl 2-phenylacetate (3h)**

$^1$H NMR (400 MHz, $CDCl_3$): δ 9.21 (s, 1H), 8.01 (d, $J$ = 8.0 Hz, 1H), 7.69-7.62 (m, 5H), 7.37-7.28 (m, 7H), 3.87 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 168.9, 150.3, 143.3, 139.5, 135.5, 134.3, 132.5, 131.2, 130.7, 130.2, 129.4, 129.1, 128.8, 128.5, 127.7, 127.64, 127.5, 120.6, 41.5; HRMS calcd. for $C_{23}H_{17}ClNO_2$ $[M+H]^+$: 374.0942, found 374.0953.




**3-(*p*-Tolyl)isoquinolin-4-yl 2-(4-chlorophenyl)acetate (3i)**

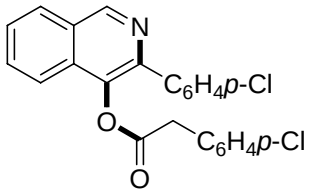
$^1$H NMR (400 MHz, $CDCl_3$): δ 9.21 (s, 1H), 7.99 (d, $J$ = 8.0 Hz, 1H), 7.69-7.57 (m, 5H), 7.30 (d, $J$ = 7.2 Hz, 2H), 7.19-7.15 (m, 4H), 3.82 (s, 2H), 2.40 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 168.8, 150.3, 144.7, 139.3, 138.3, 134.3, 133.6, 131.4, 131.2, 130.9, 130.8, 129.1, 129.0, 128.9, 127.7, 127.5, 120.5, 40.8, 21.4; HRMS calcd. for $C_{24}H_{19}ClNO_2^+$ $[M+H]^+$: 388.1099, found 388.1079.




**3-(*p*-Tolyl)isoquinolin-4-yl 2-(4-fluorophenyl)acetate (3j)**

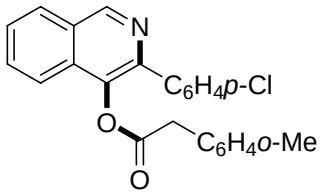
$^1$H NMR (400 MHz, $CDCl_3$): δ 9.22 (s, 1H), 7.99 (d, $J$ = 8.0 Hz, 1H), 7.67-.55 (m, 5H), 7.24-7.17 (m, 4H), 7.02 (t, $J$ = 8.0 Hz, 2H), 3.83 (s, 2H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 168.9, 162.2 (d, $^1J_{CF}$ = 245.8 Hz), 150.1, 144.5, 139.2, 138.2,

134.2, 131.0, 131.0, 130.7, 129.0, 128.8, 128.7, 128.5, 127.5, 127.3, 120.3, 115.6 (d, $^{2}J_{CF}$ = 21.7 Hz), 40.5, 21.3; HRMS calcd. for $C_{24}H_{19}FNO_3^+$ $[M+H]^+$: 372.1394, found 372.1414.



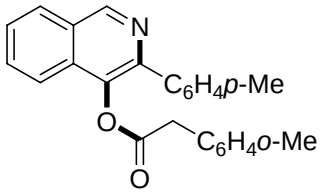

**3-(4-Chlorophenyl)isoquinolin-4-yl 2-(4-chlorophenyl)acetate (3k)**

$^{1}$H NMR (400 MHz, $CDCl_3$): δ 9.21 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.73-7.60 (m, 5H), 7.34-7.30 (m, 4H), 7.20 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 168.5, 150.3, 143.3, 139.4, 135.4, 134.5, 133.7, 131.3, 131.0, 130.7, 130.6, 130.2, 129.1, 129.0, 128.5, 127.8, 127.6, 120.4, 40.7; HRMS calcd. for $C_{23}H_{16}Cl_2NO_2^+$ $[M+H]^+$: 408.0553, found 407.048.




**3-(4-Chlorophenyl)isoquinolin-4-yl 2-(*o*-tolyl)acetate (3l)**

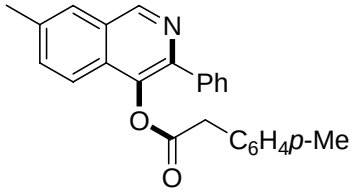
$^{1}$H NMR (400 MHz, $CDCl_3$): δ 9.20 (s, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.70-7.58 (m, 5H), 7.30-7.20 (m, 6H), 3.87 (s, 2H), 2.23 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 168.6, 150.2, 143.3, 139.5, 137.0, 135.5, 134.3, 131.2, 130.7, 130.6, 130.5, 130.2, 129.0, 128.5, 127.9, 127.7, 127.6, 126.3, 120.5, 39.2, 19.4; HRMS calcd. for $C_{24}H_{19}ClNO_2^+$ $[M+H]^+$: 388.1099, found 388.1116.




**3-(*p*-tolyl)isoquinolin-4-yl 2-(*o*-tolyl)acetate (3m)**

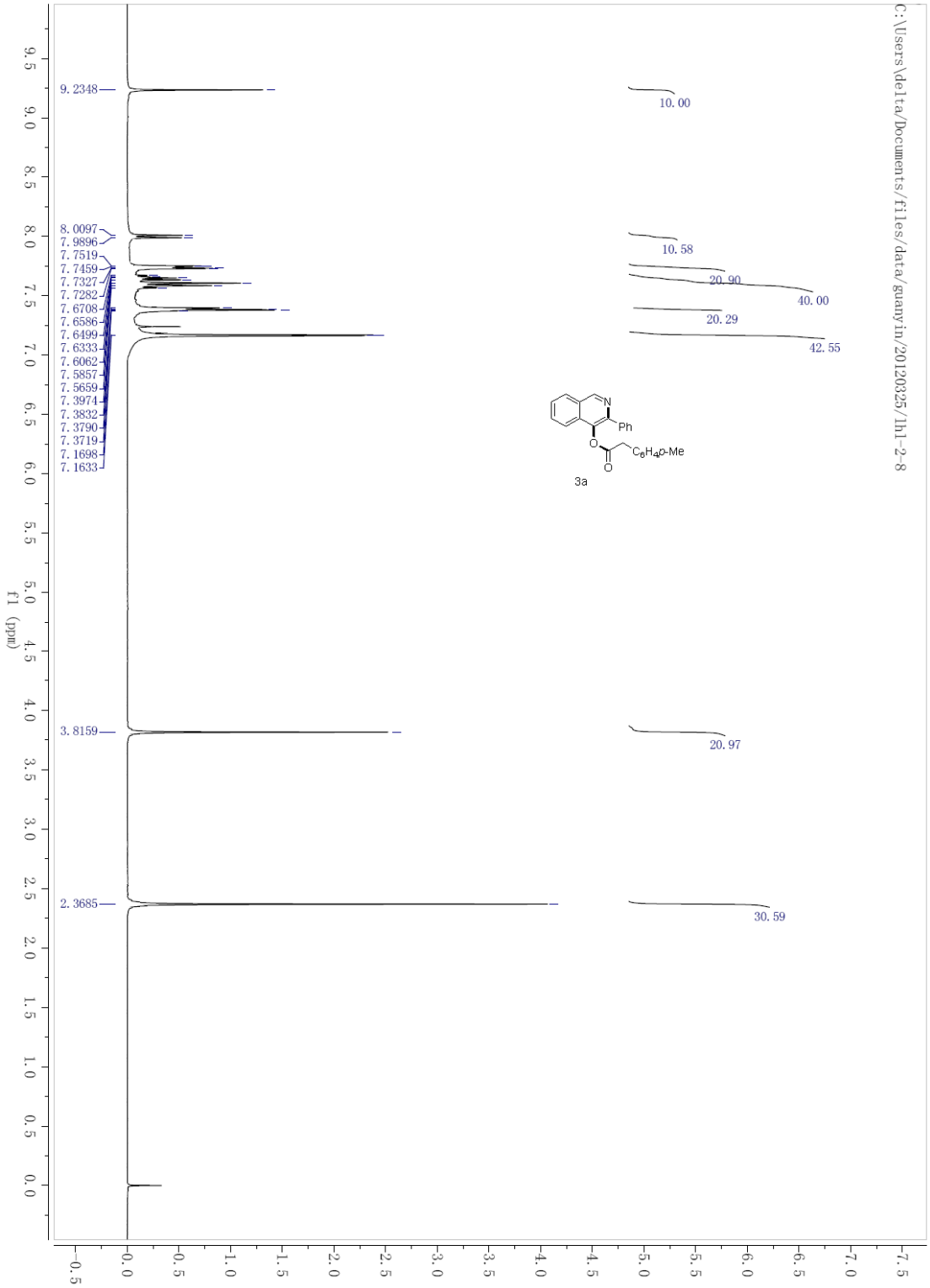
$^{1}$H NMR (400 MHz, $CDCl_3$): δ 9.21 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.66-7.54 (m, 5H), 7.25-7.18 (m, 6H), 3.87 (s, 2H), 2.40 (s, 3H), 2.23 (s, 3H).; $^{13}$C NMR (100 MHz, $CDCl_3$): δ 168.9, 150.0, 144.6, 139.3, 138.1, 137.0, 134.3, 131.5, 130.9, 130.8, 130.5, 129.0, 128.8, 127.7, 127.5, 127.3, 126.2, 120.4, 39.2, 21.3, 19.5; $C_{25}H_{22}NO_2S^+$

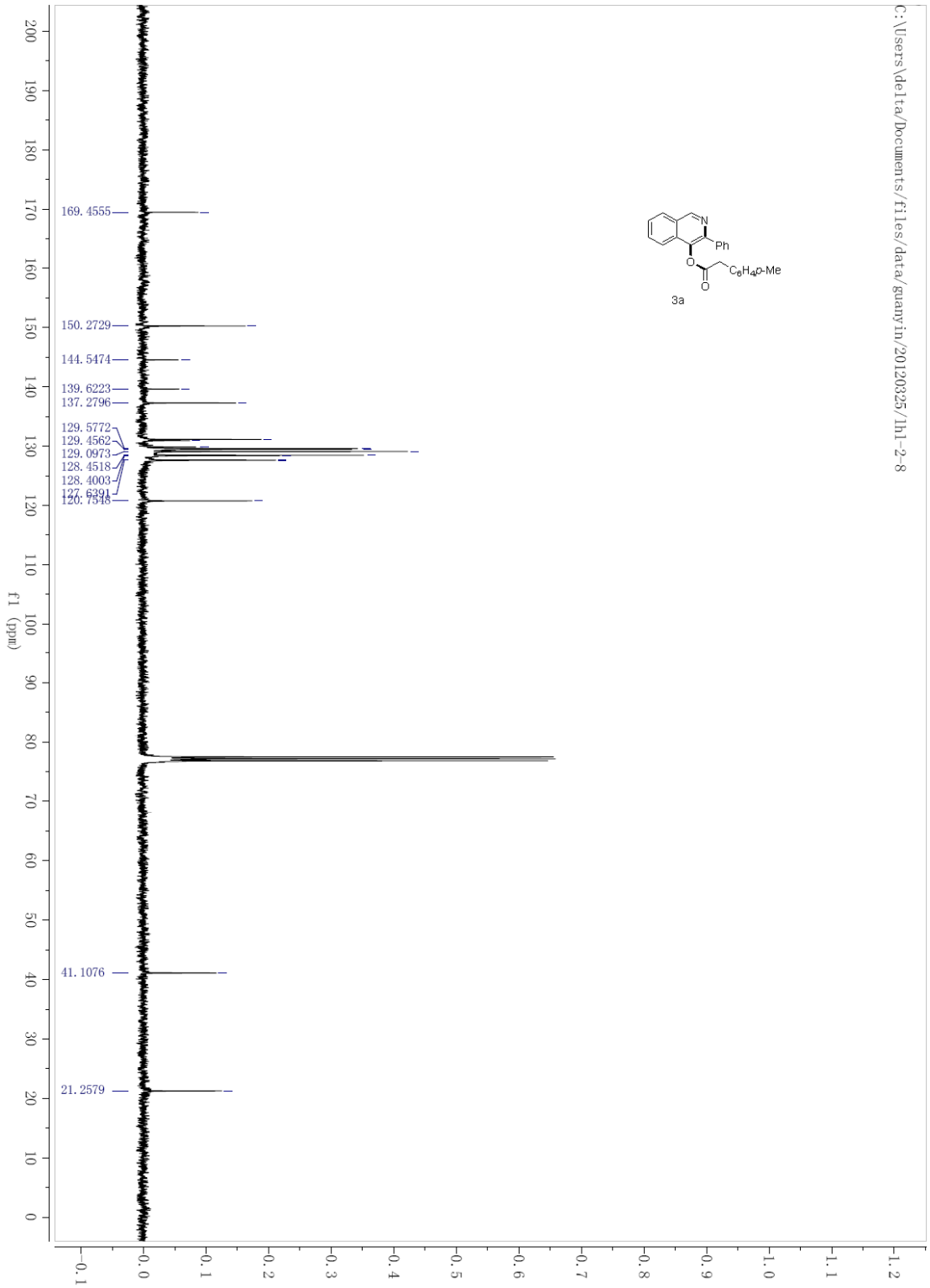
$[M+H]^+$: 368.1645, found 368.1661.




**7-Methyl-3-phenylisoquinolin-4-yl 2-(*p*-tolyl)acetate (3n)**

$^1$H NMR (400 MHz, $CDCl_3$): δ 9.14 (s, 1H), 7.75-7.72 (m, 3H), 7.48-7.37 (m, 5H), 7.18-7.14 (m, 4H), 3.80 (s, 2H), 2.52 (s, 3H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 169.3, 149.5, 143.6, 139.6, 137.6, 137.3, 137.1, 133.3, 129.8, 129.4, 129.3, 129.0, 128.9, 128.3, 128.1, 126.2, 120.5, 41.0, 21.6, 21.1; HRMS calcd. for $C_{25}H_{22}NO_2^+$ $[M+H]^+$: 368.1645, found 368.1665.

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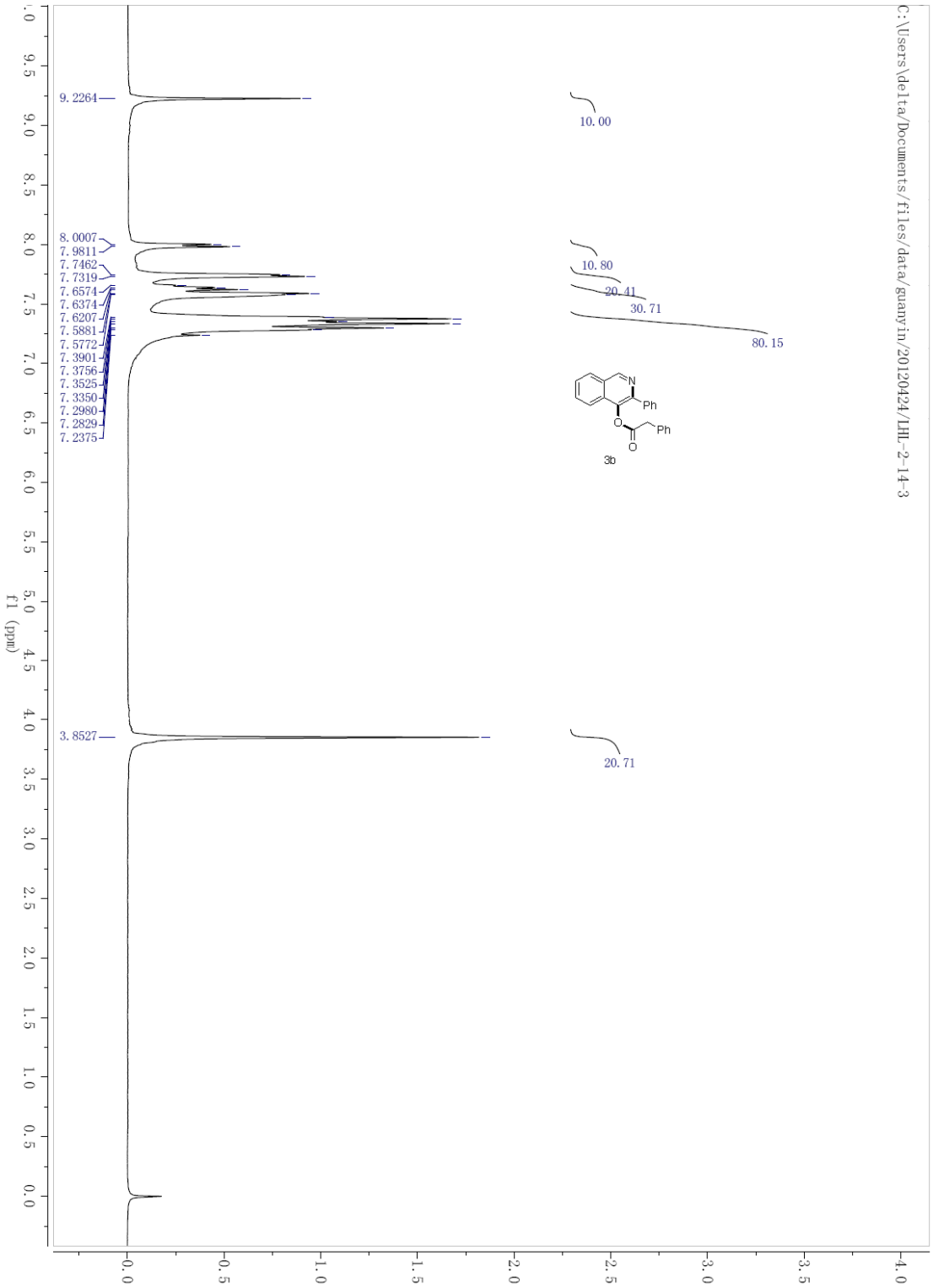

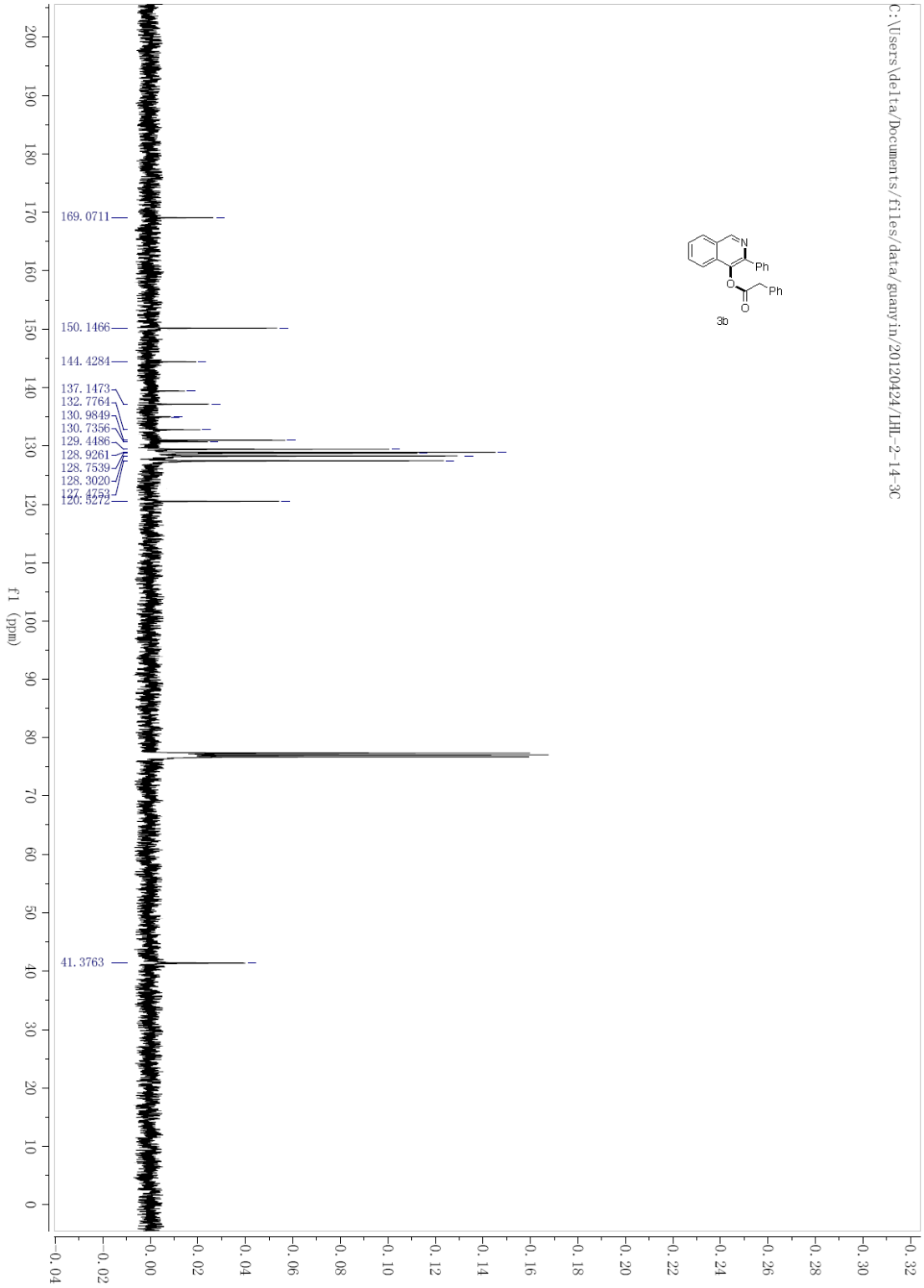

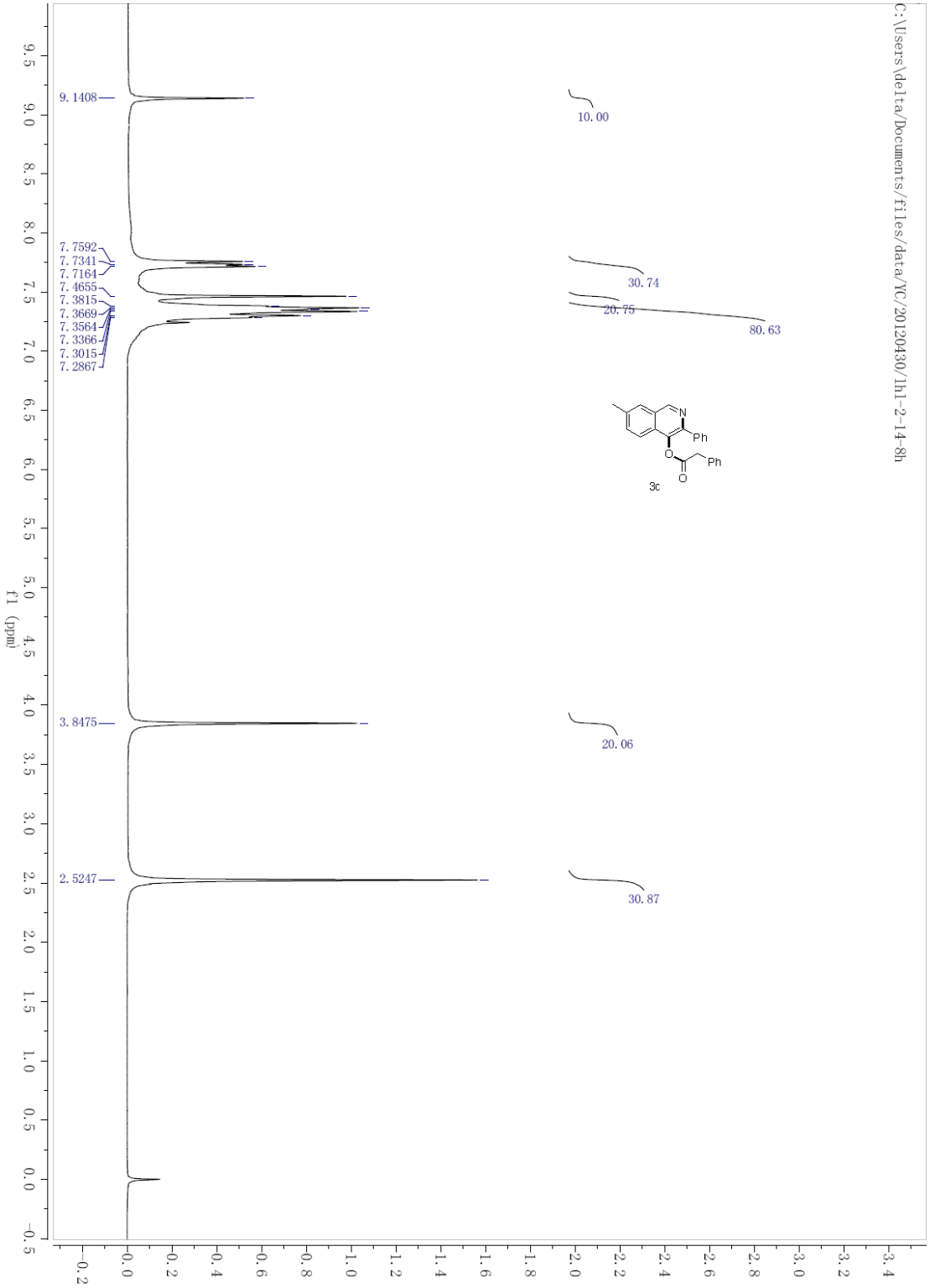

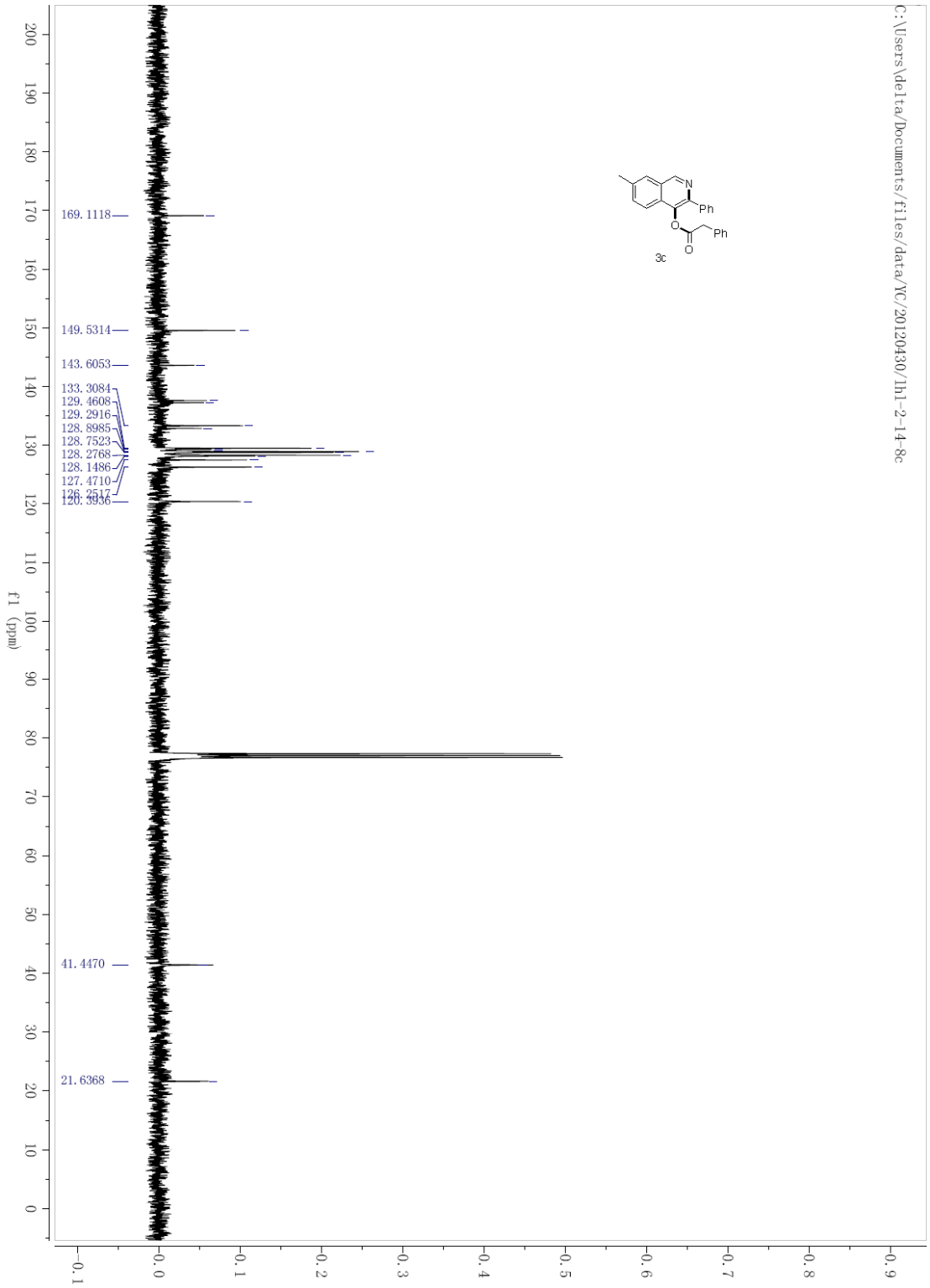

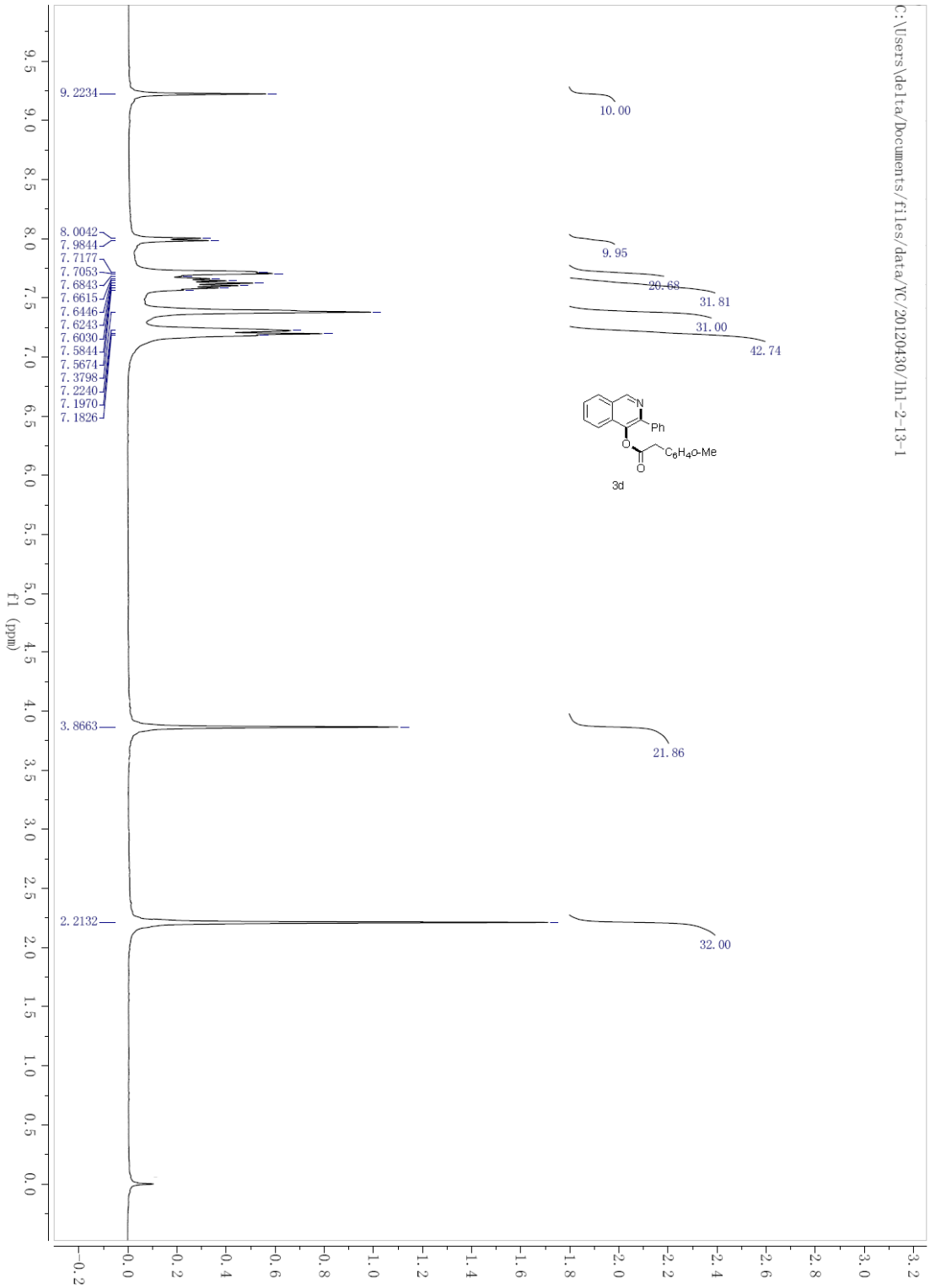

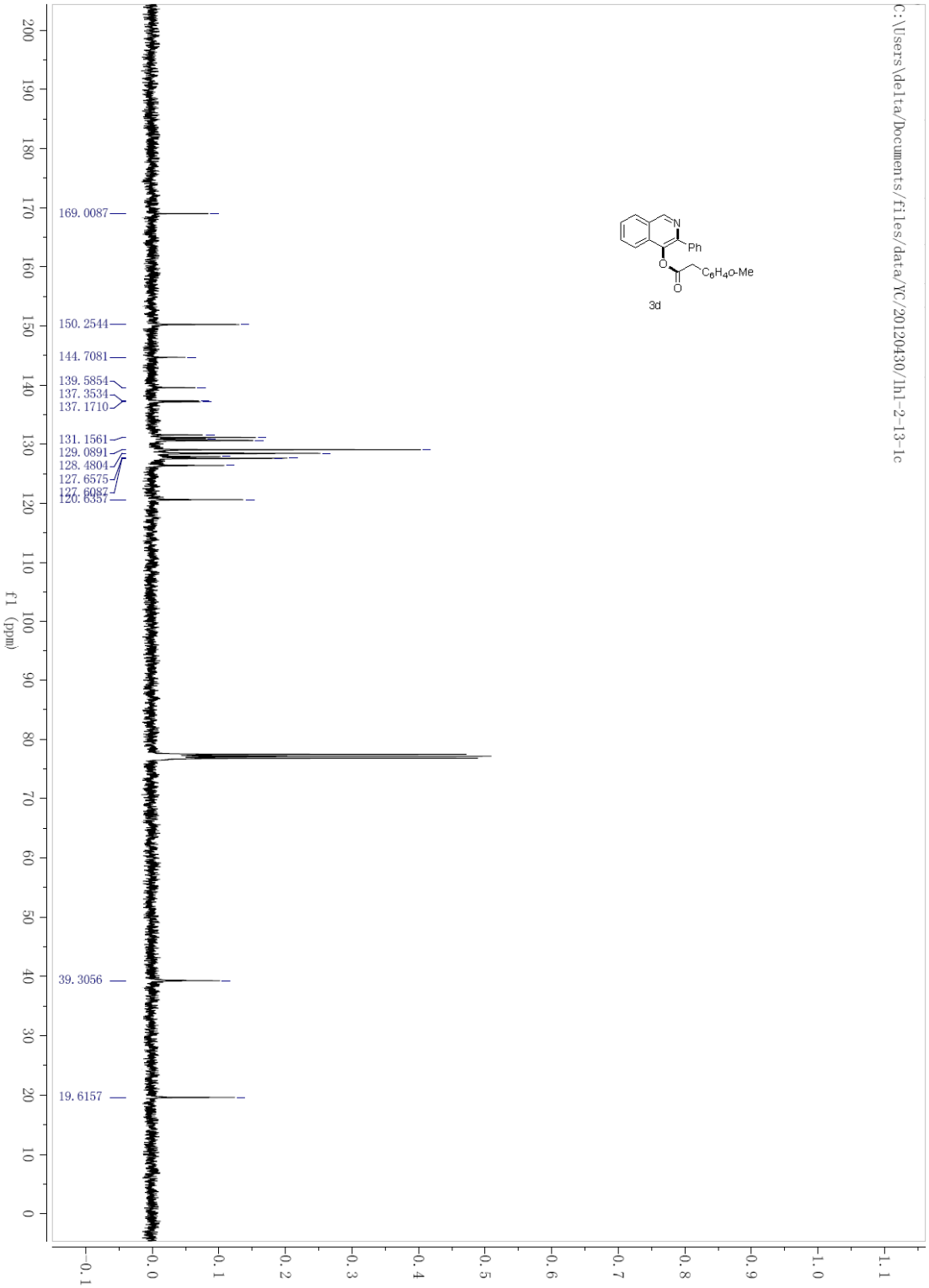
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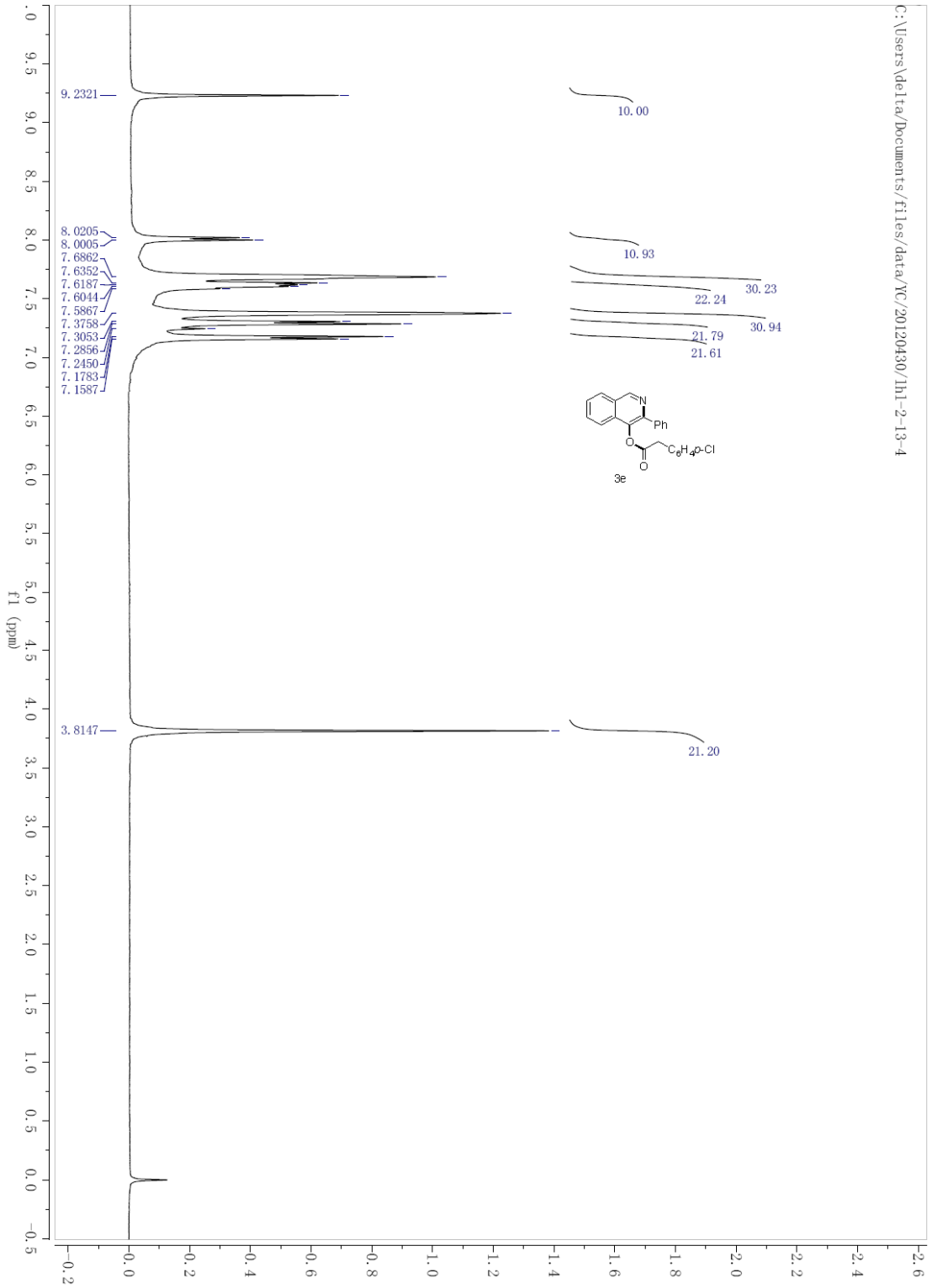
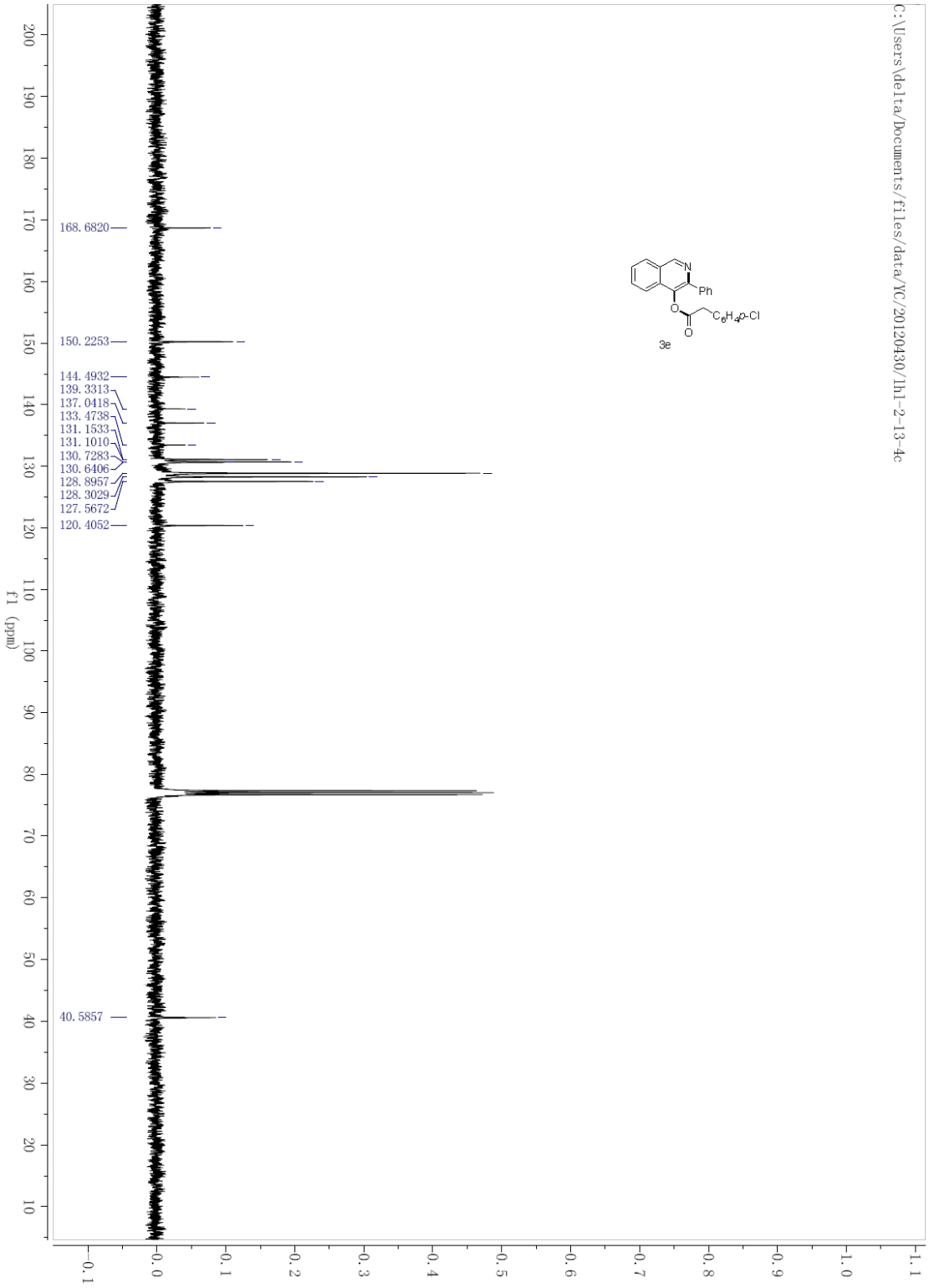
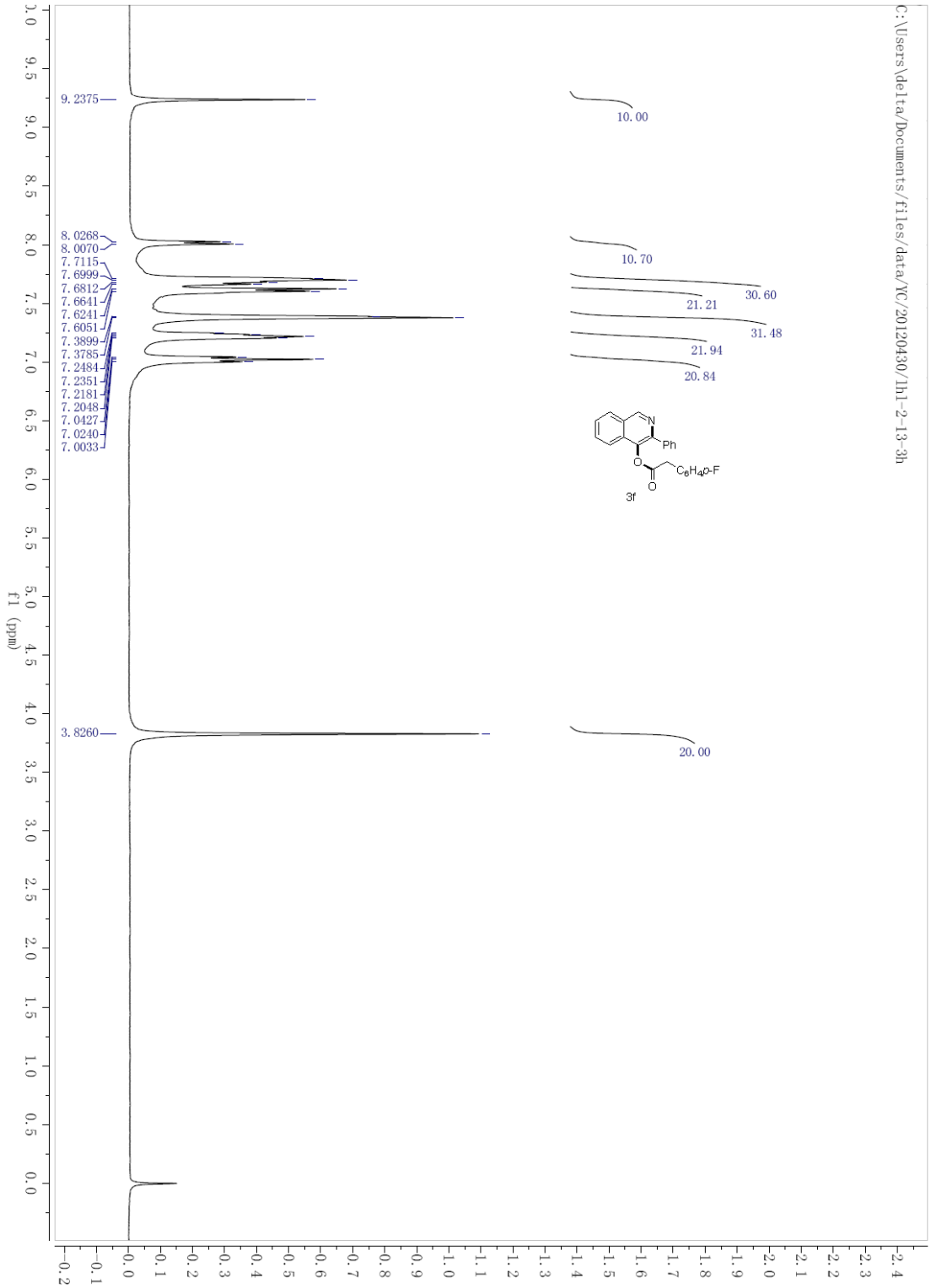
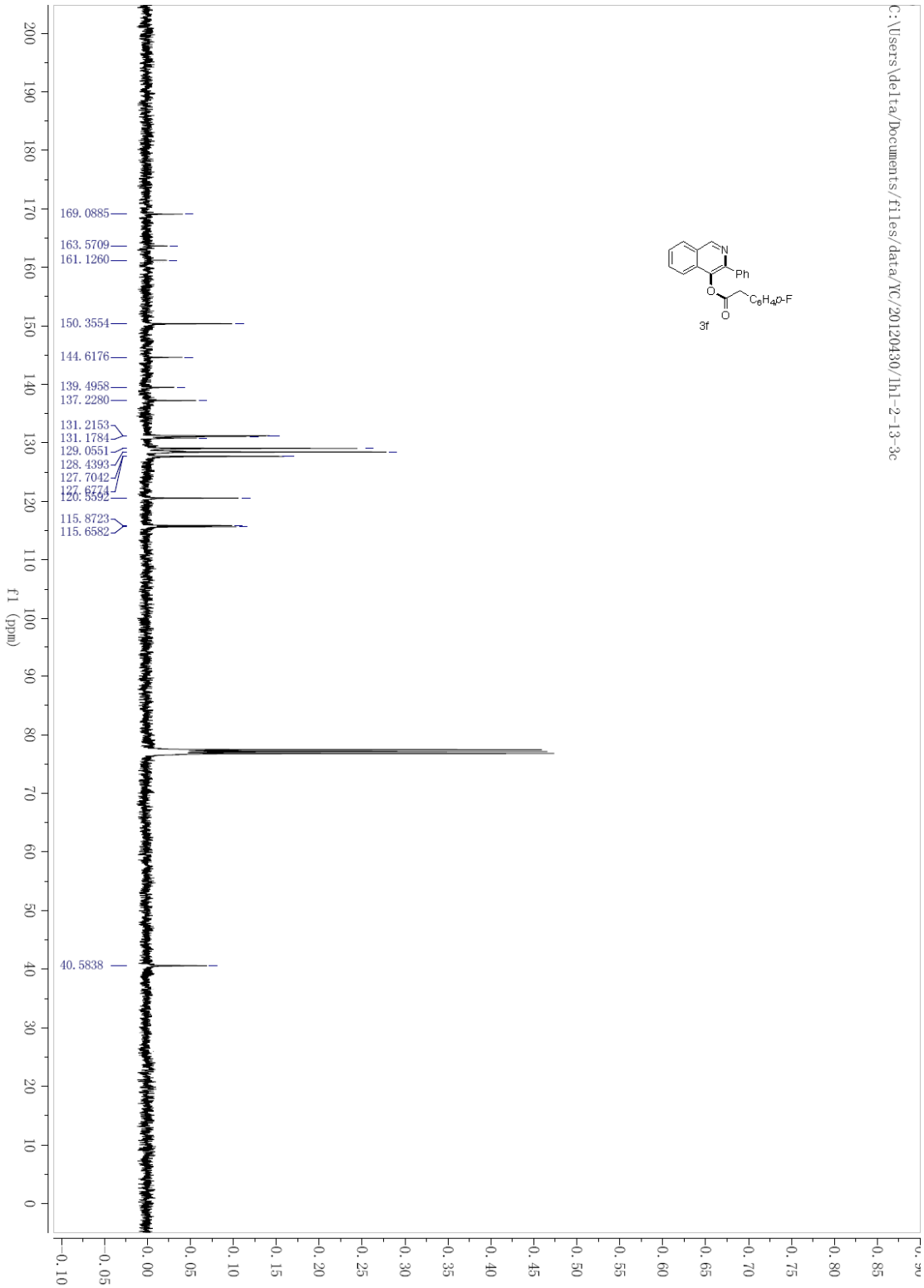
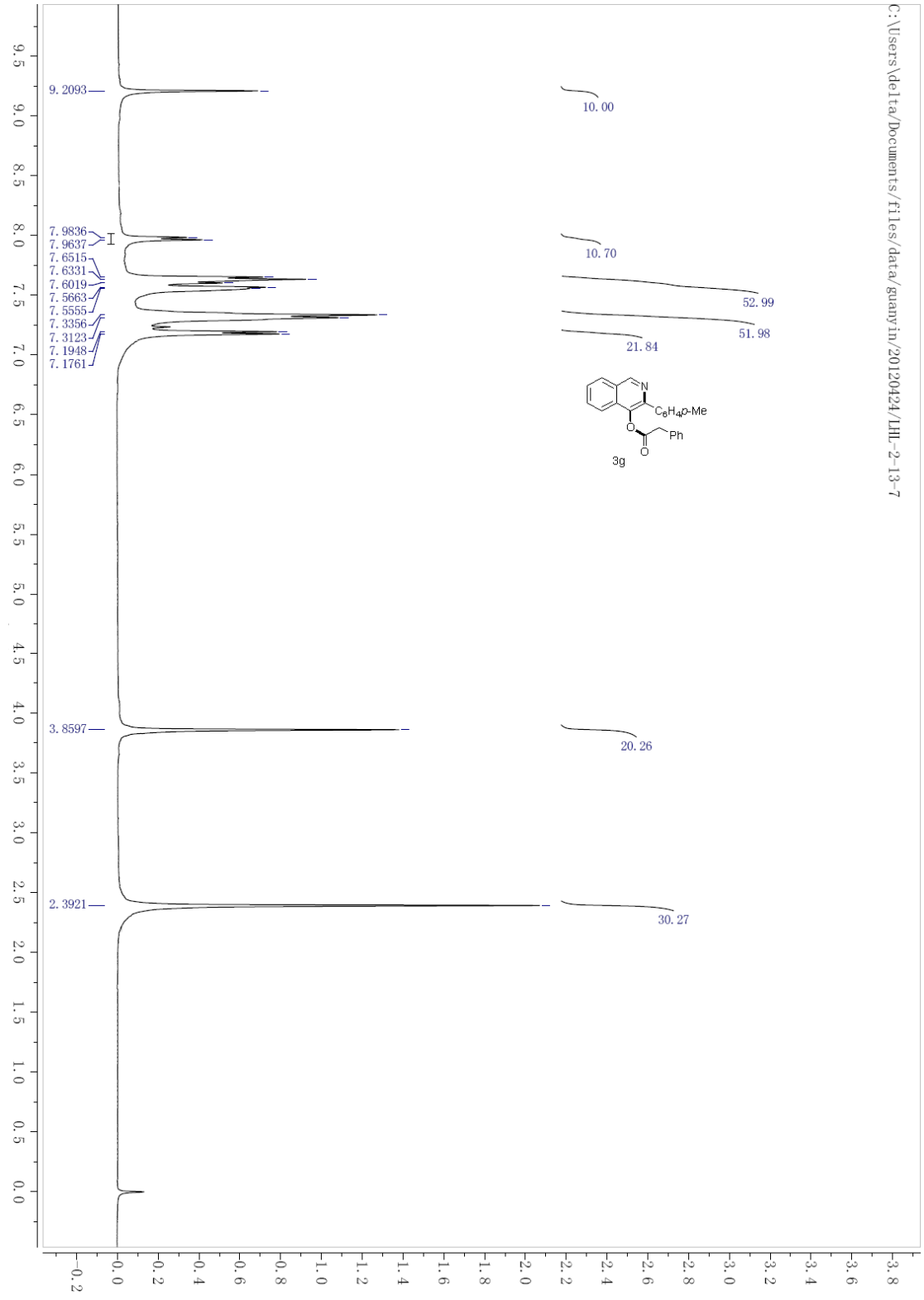
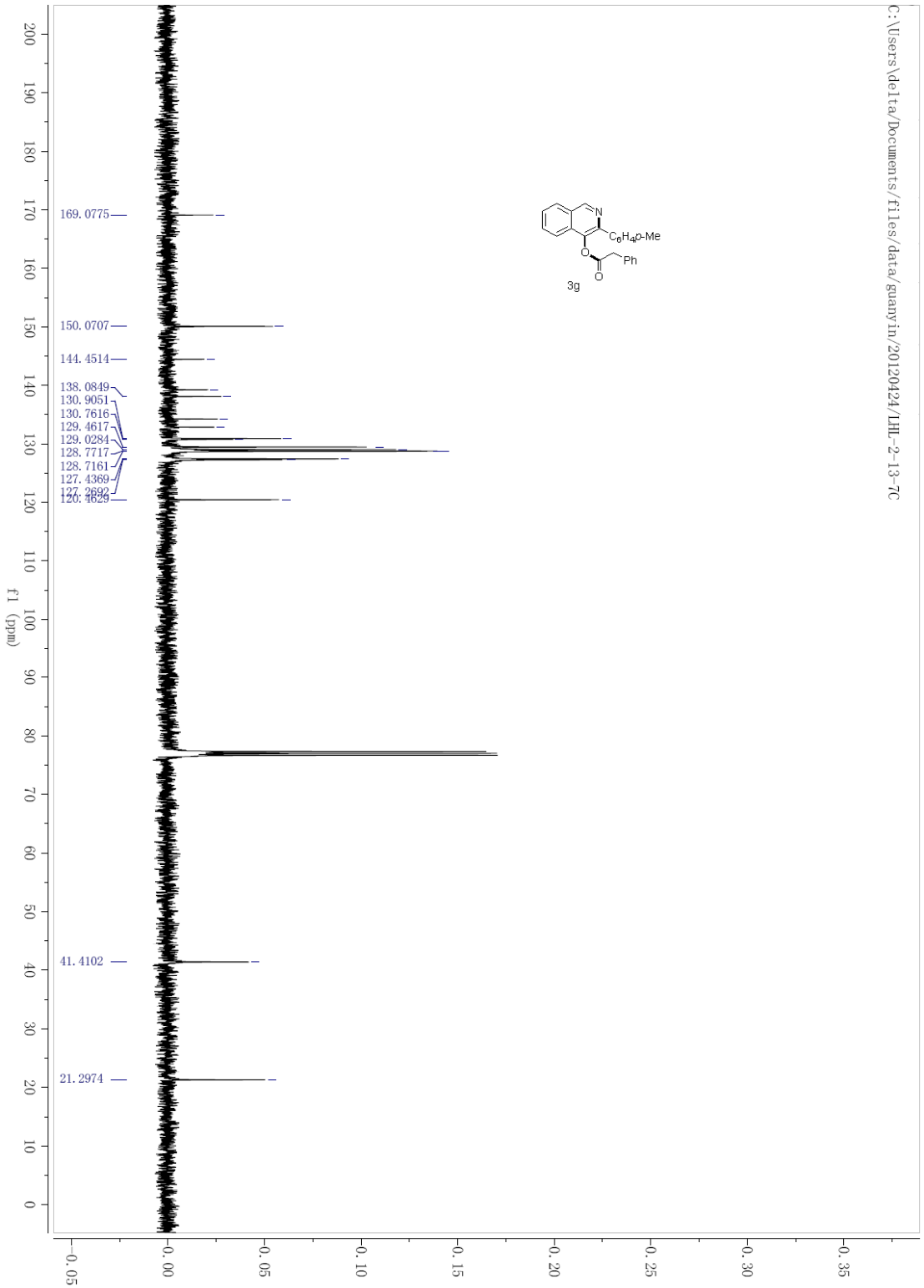


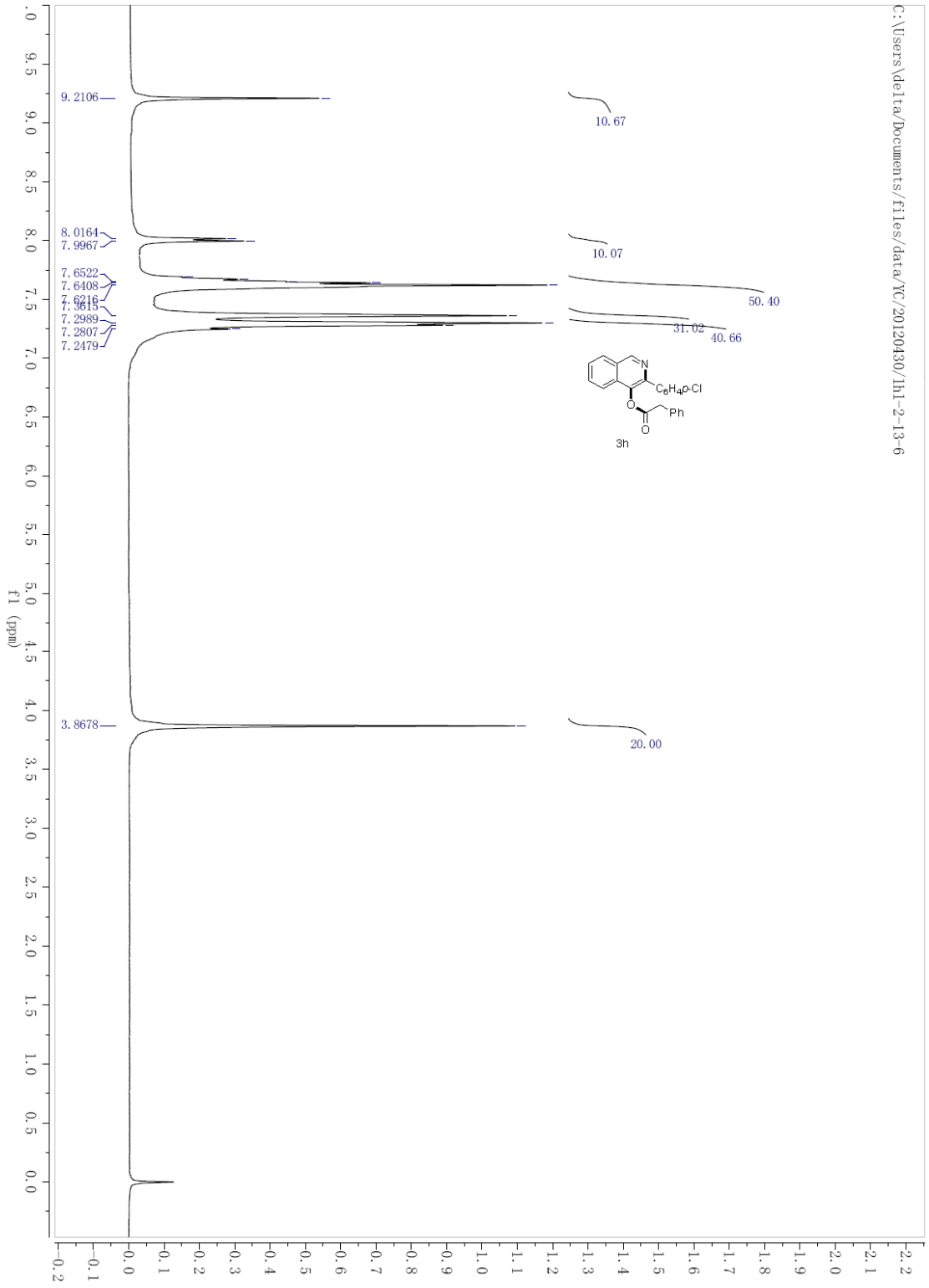


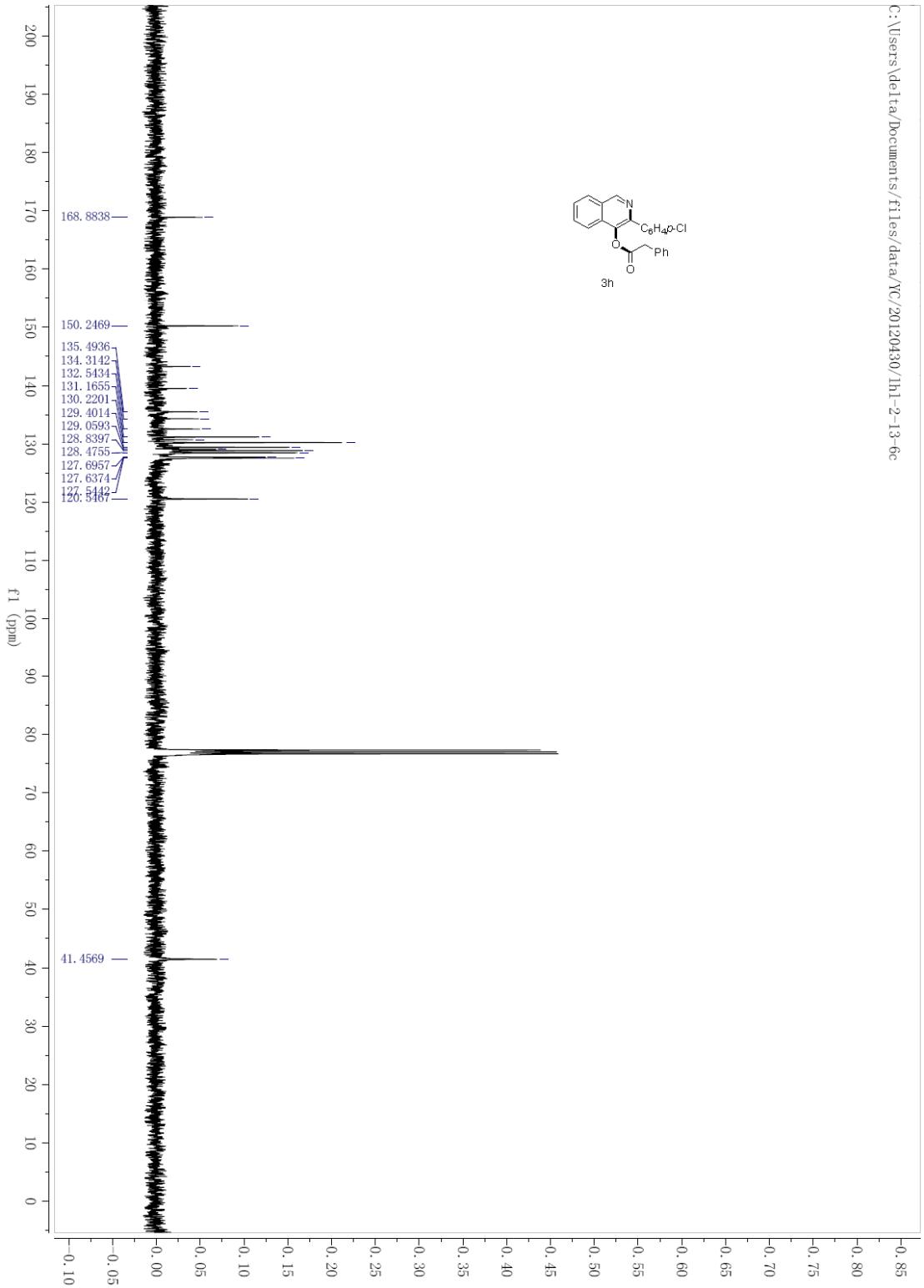


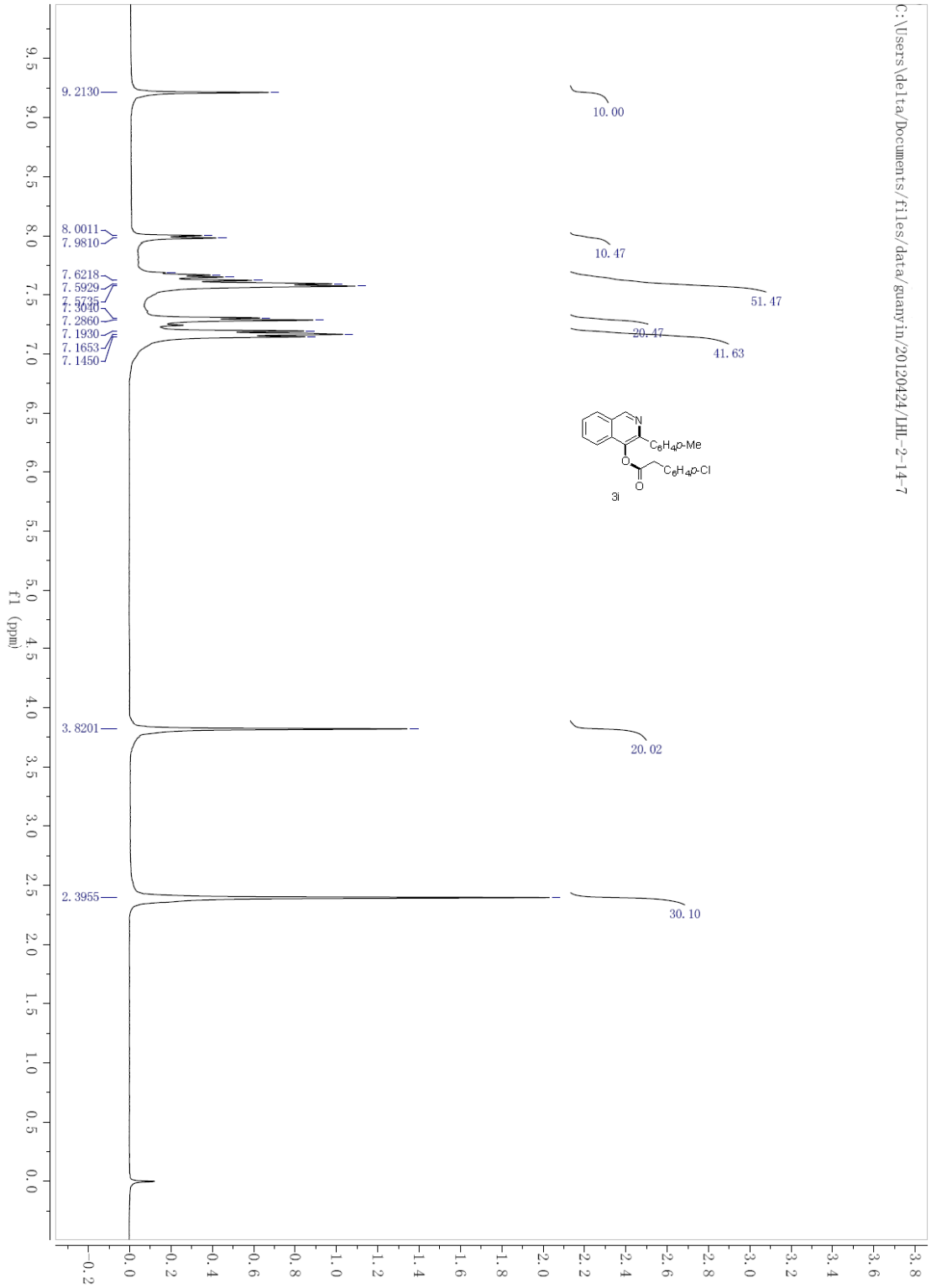


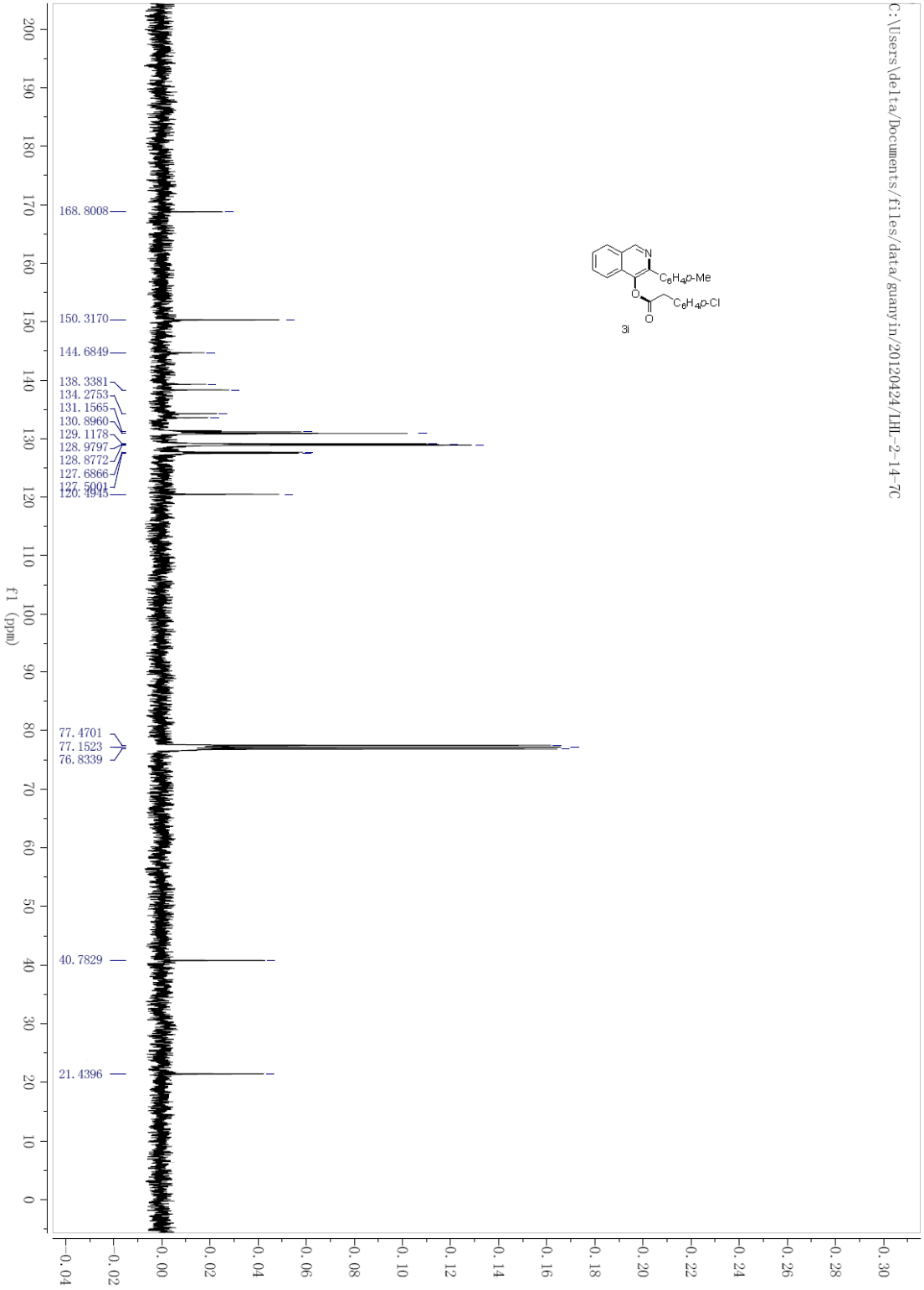


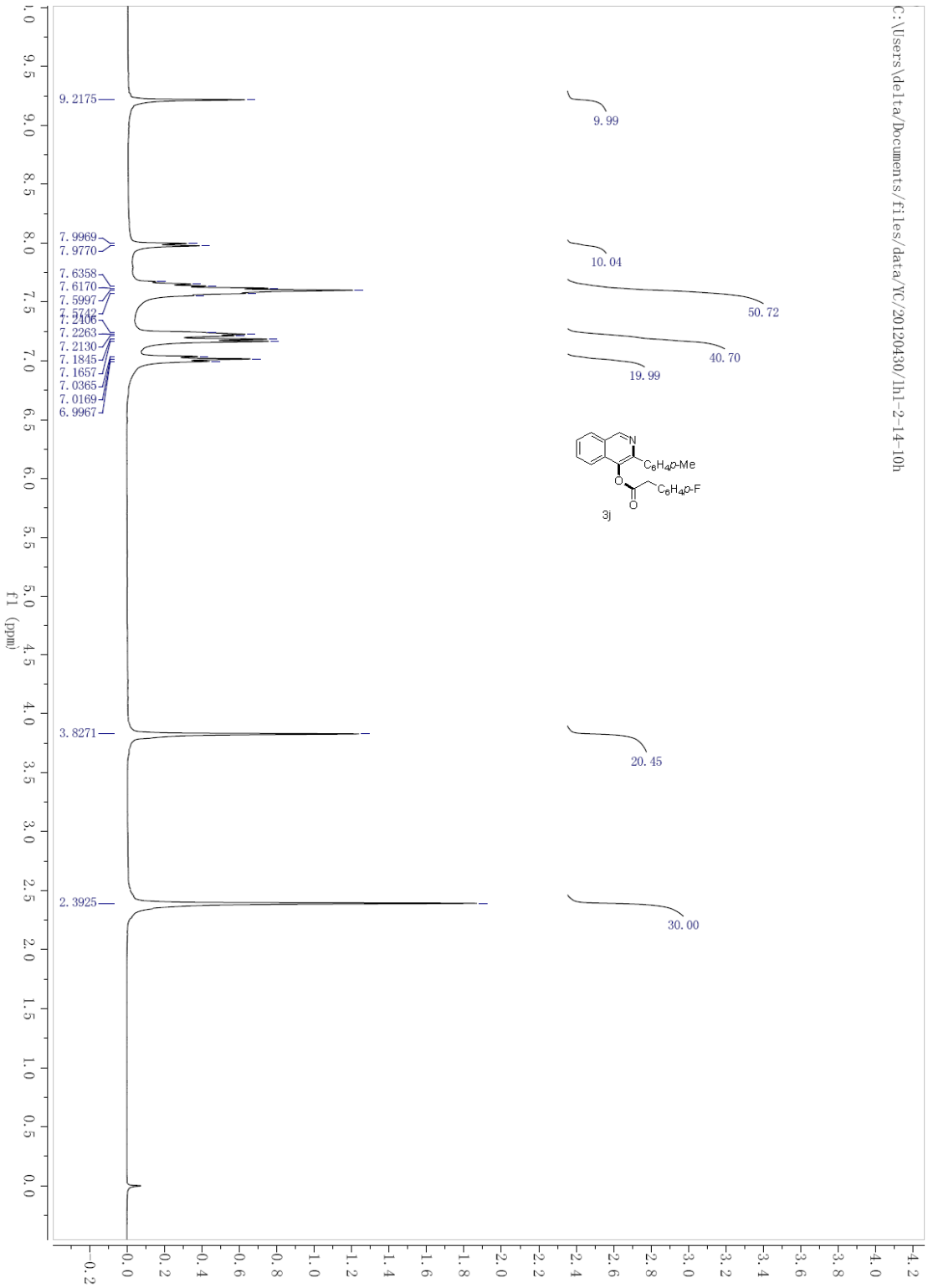

C:\Users\delta\Documents\files\data\guanyin\20120424\1HL-2-13-7C
169.0775
150.0707
144.4514
138.0849
130.9051
130.7616
129.4617
129.0284
128.7717
128.7161
127.4369
127.2692
120.4629
41.4102
21.2974
f1 (ppm)
$C_6H_4$p-Me
Ph
3g

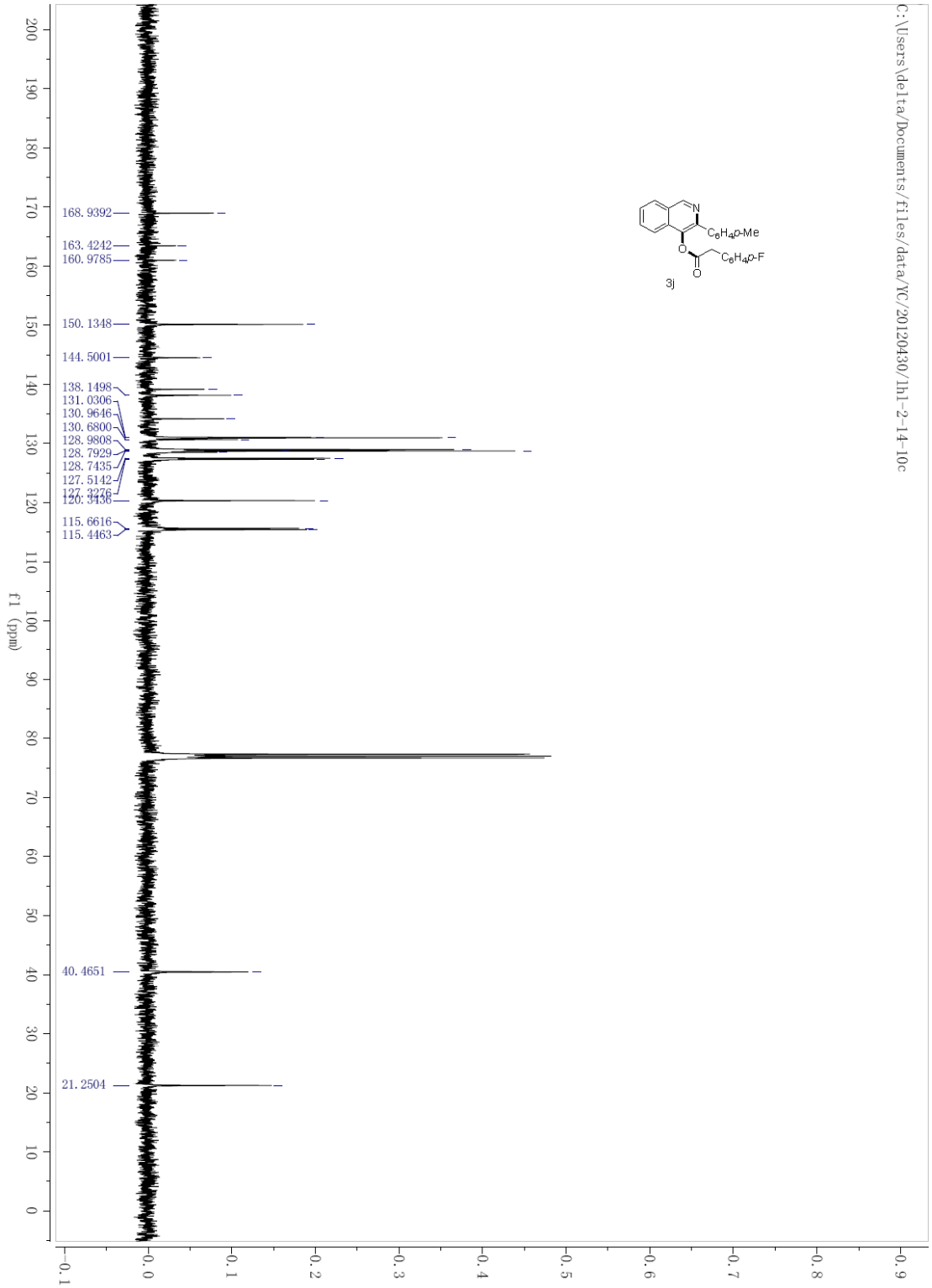


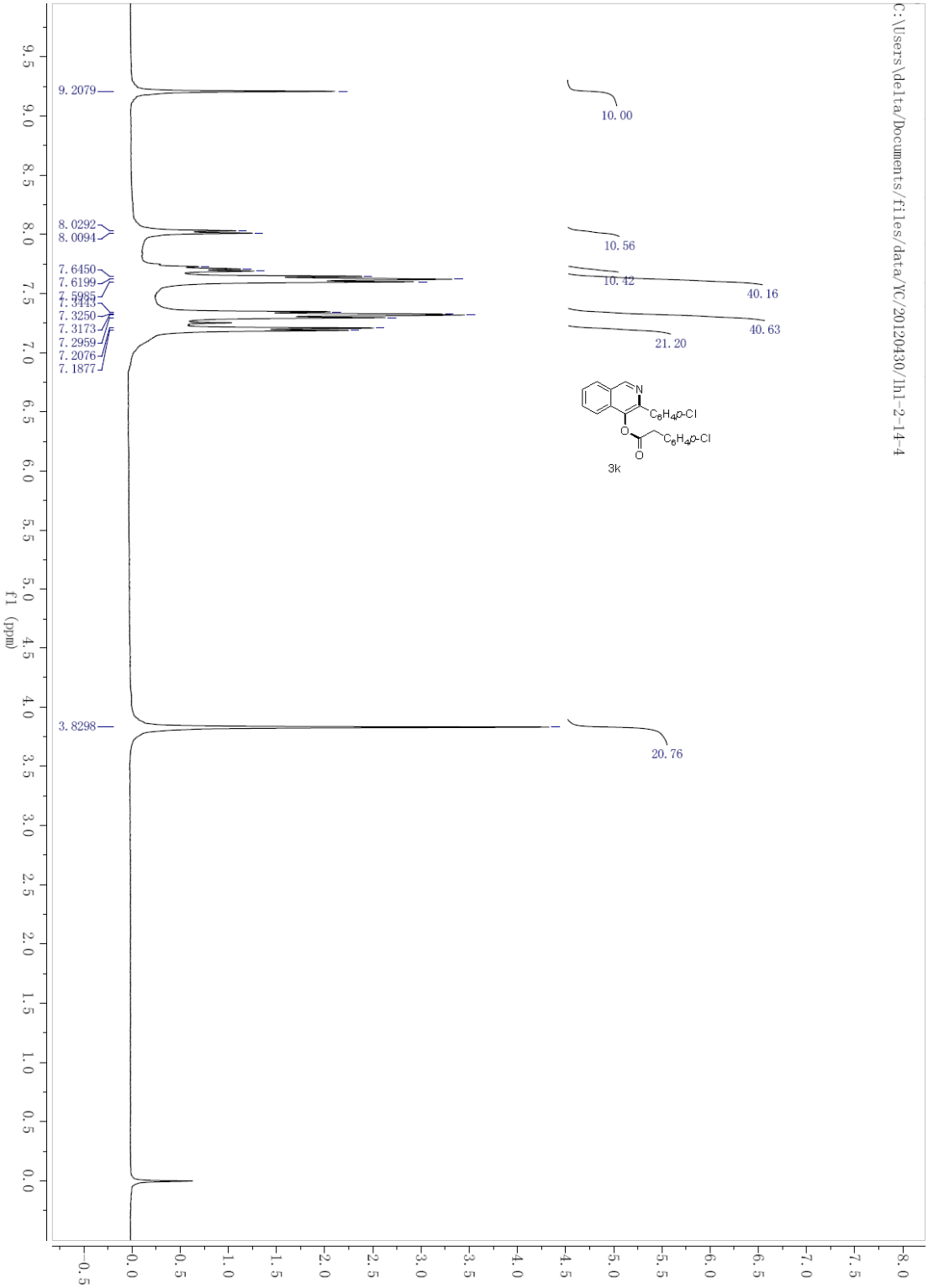

C:\Users\delta\Documents\files\data\YC\20120430\1h1-2-13-6c
168.8838
150.2469
135.4936
134.3142
132.5434
131.1655
130.2201
129.4014
129.0593
128.8397
128.4755
127.6957
127.6374
127.5442
120.5467
41.4569
f1 (ppm)
3h
Ph
O
N

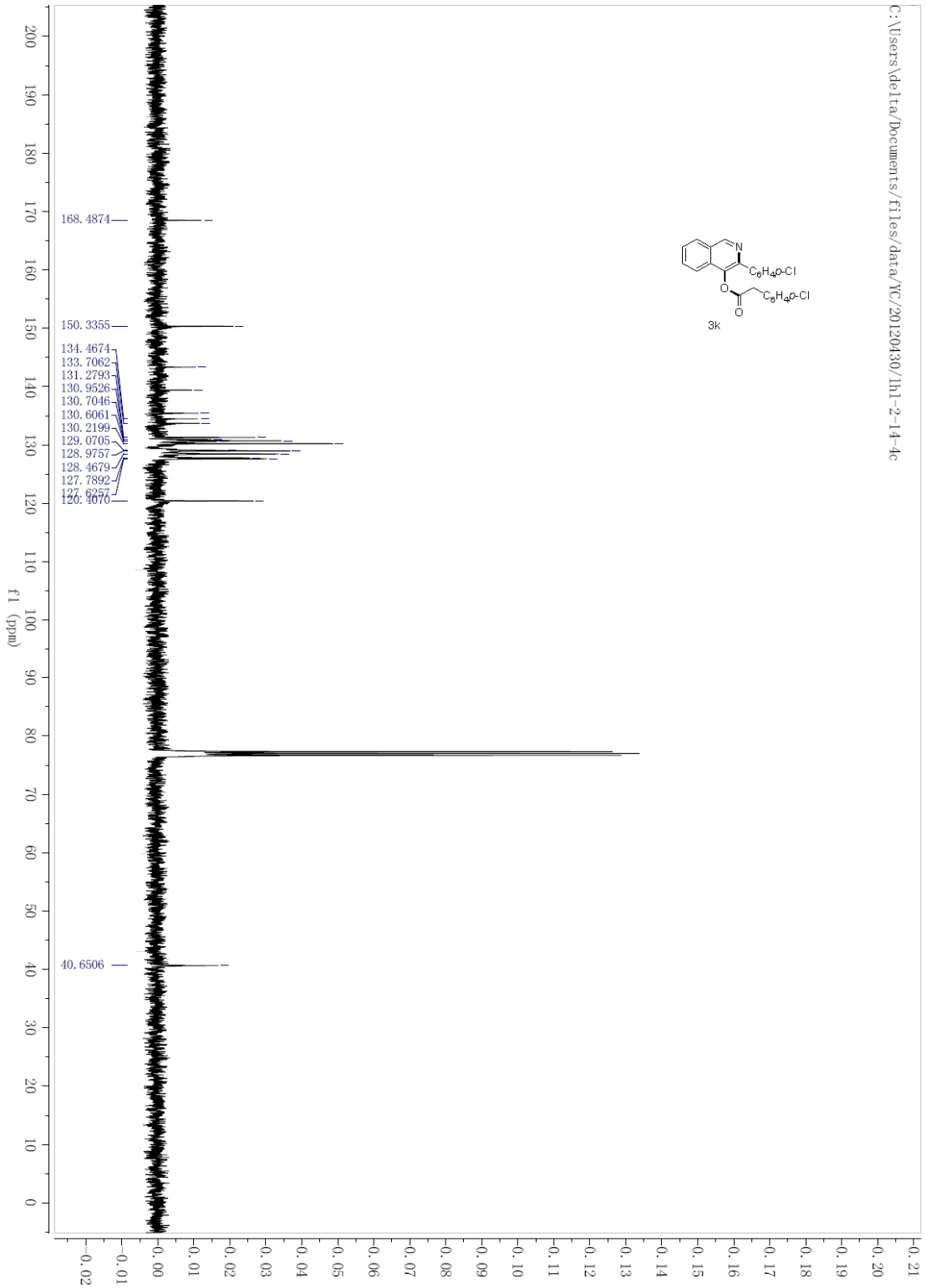


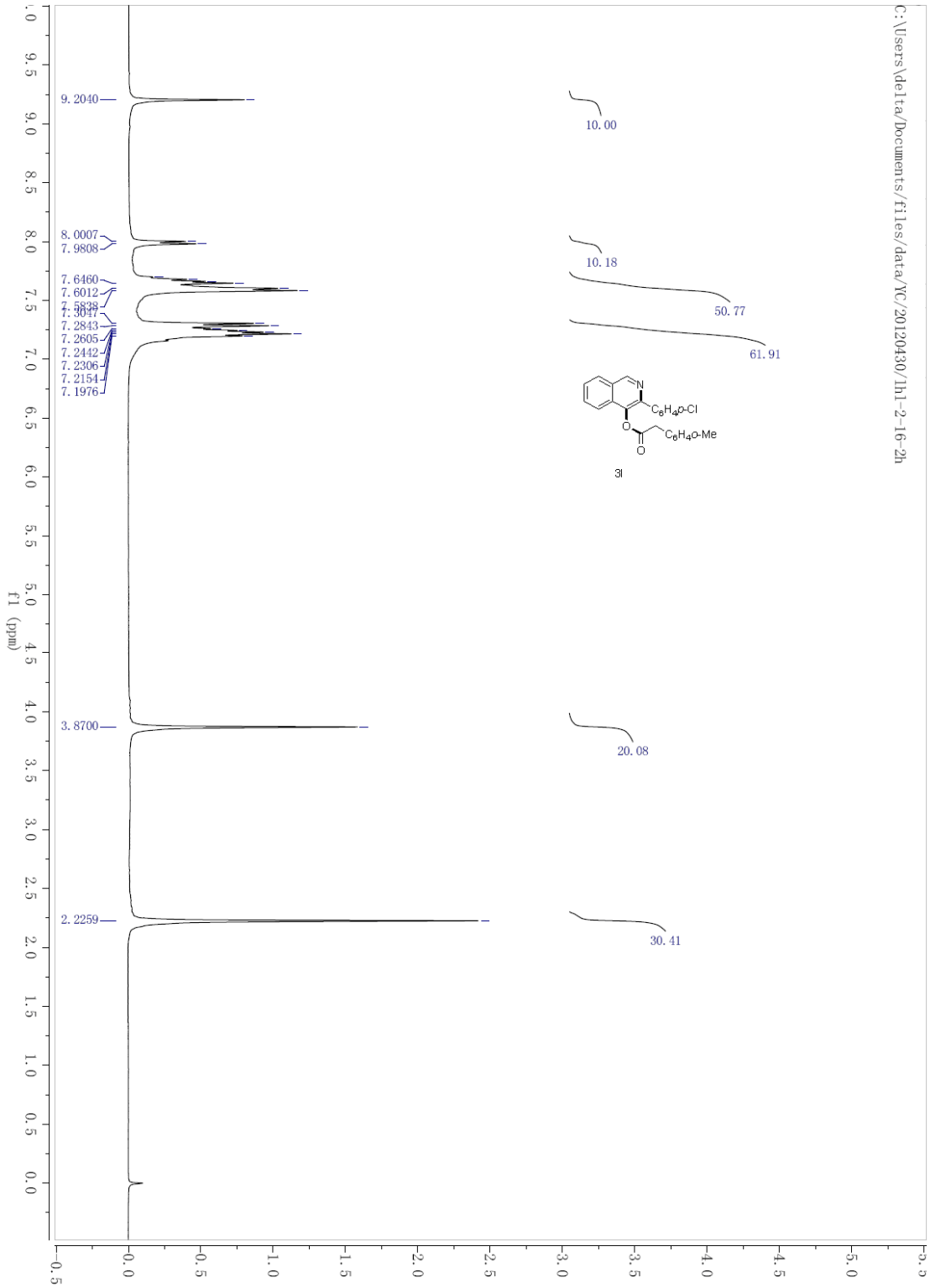


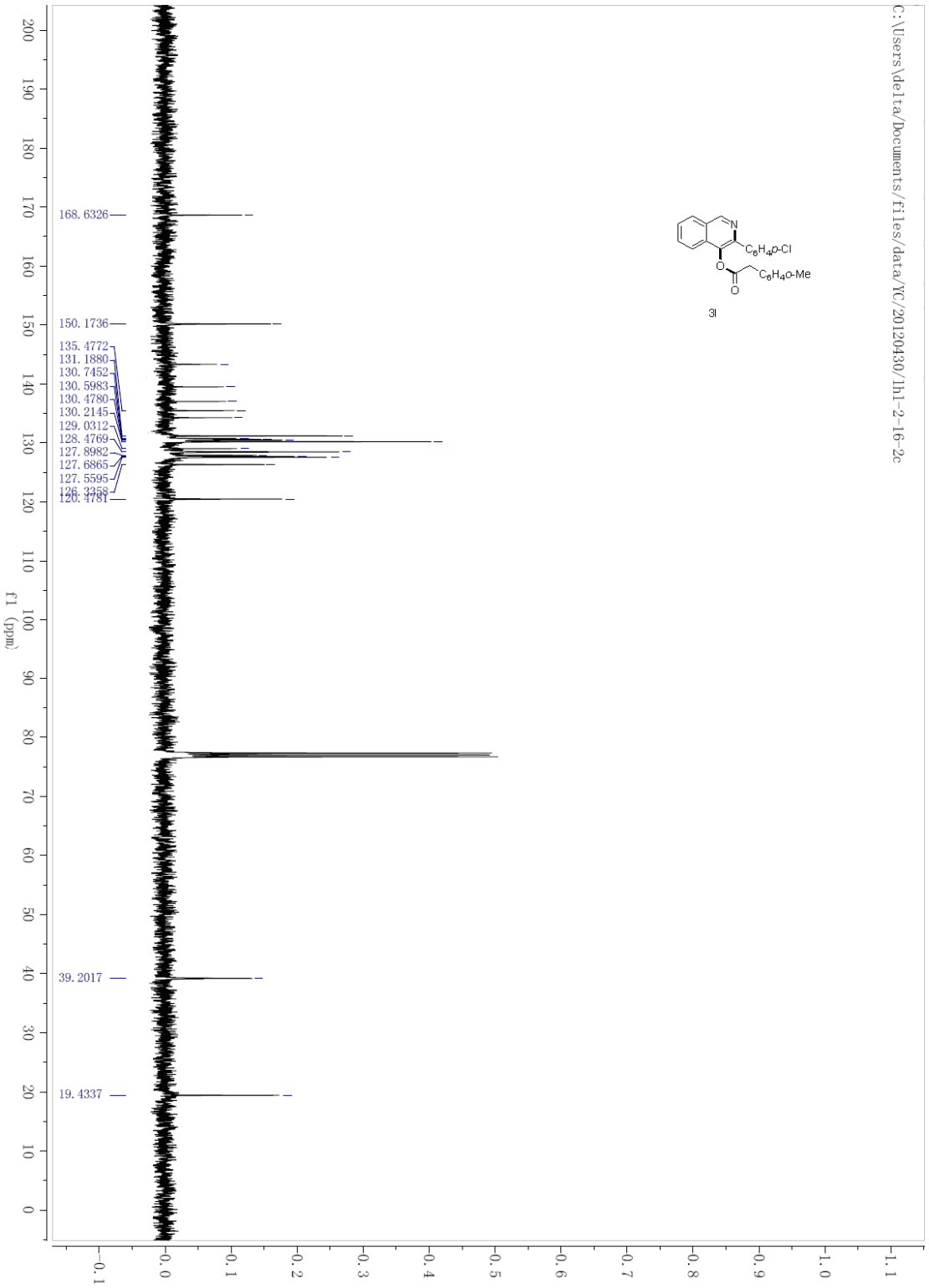


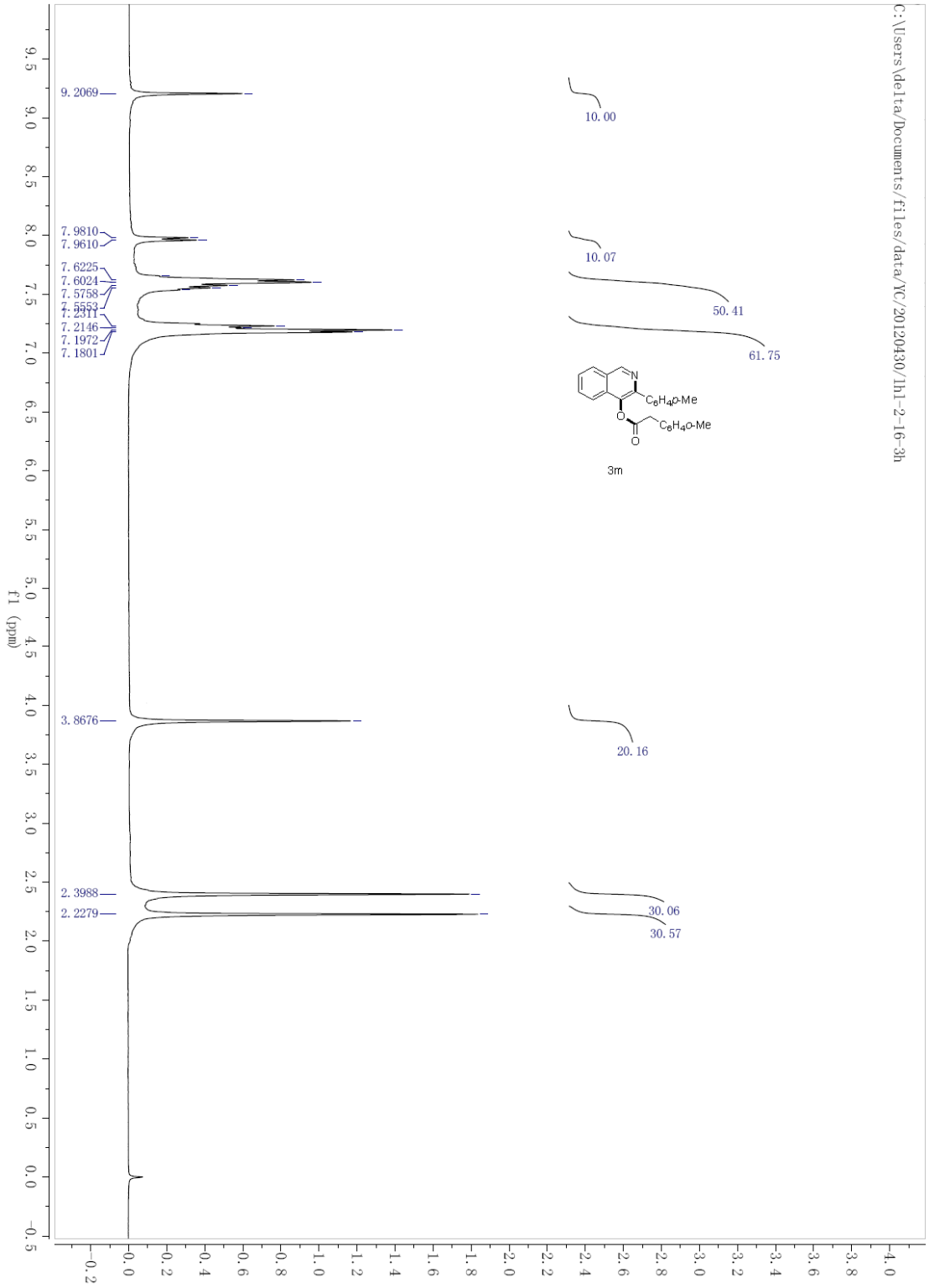


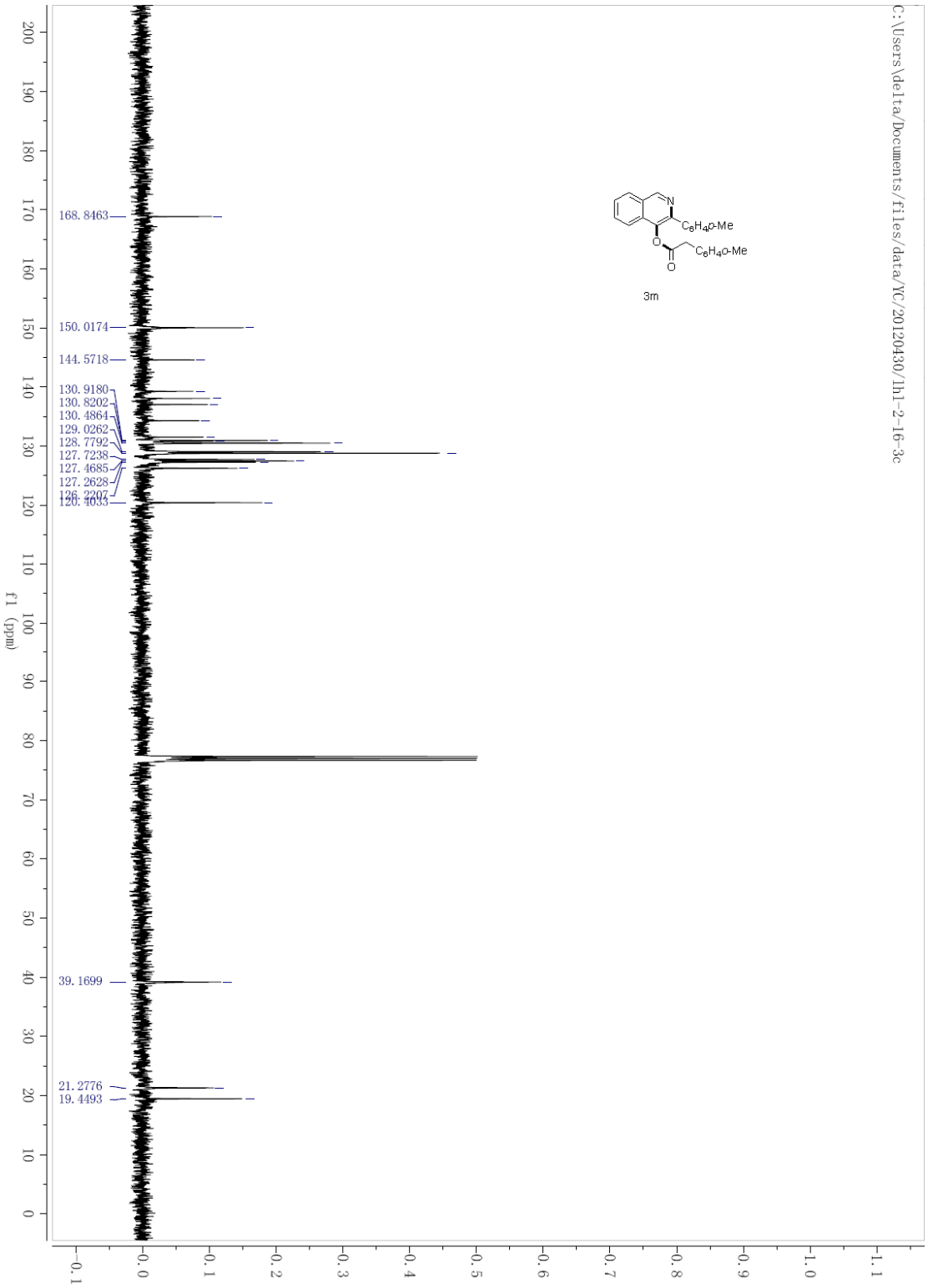

C:\Users\delta\Documents\files\data\YC\20120430\lh1-2-14-4
9.2079
8.0292
8.0094
7.6450
7.6199
7.5985
7.3443
7.3250
7.3173
7.2959
7.2076
7.1877
3.8298
10.00
10.56
10.42
40.16
40.63
21.20
20.76
C6H4p-Cl
C6H4p-Cl
3k
f1 (ppm)

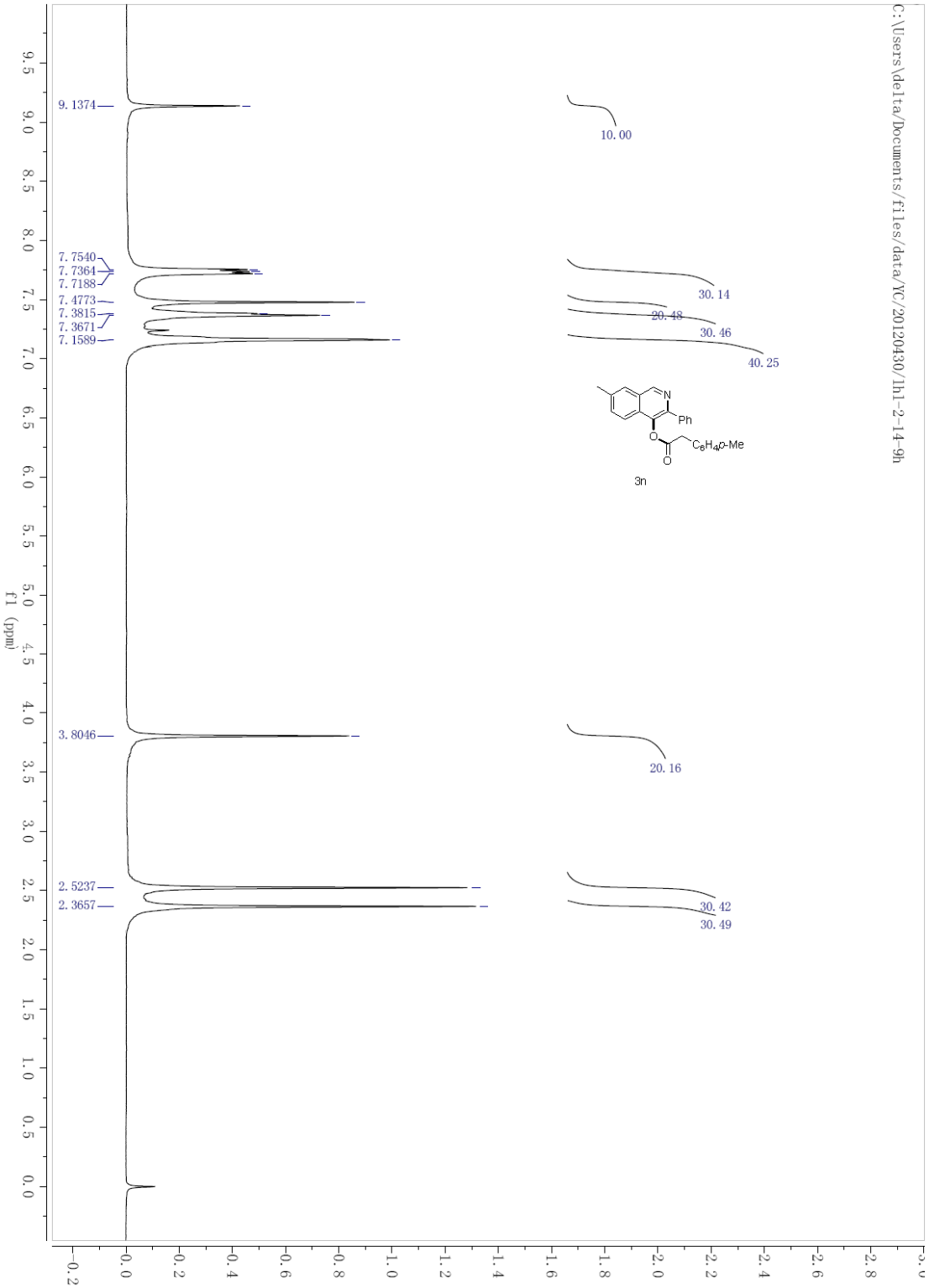


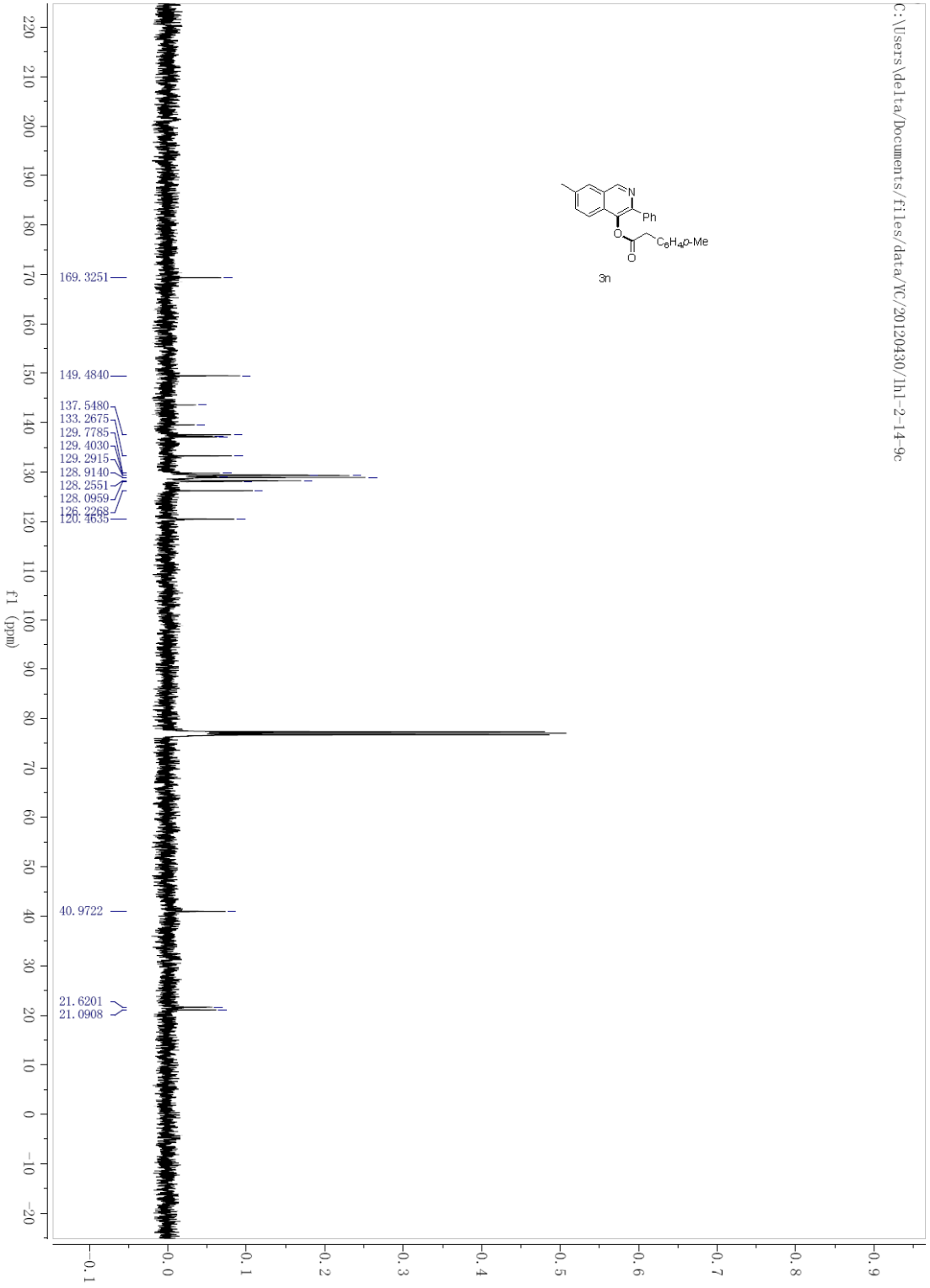







C:\Users\delta\Documents\files\data\YC\20120430\lh1-2-16-3c
168.8463
150.0174
144.5718
130.9180
130.8202
130.4864
129.0262
128.7792
127.7238
127.4685
127.2628
126.2207
120.4033
39.1699
21.2776
19.4493
f1 (ppm)
C6H4p-Me
C6H4o-Me
3m


C:\Users\delta\Documents\files\data\YC\20120430\lhl-2-14-9h
9.1374
7.7540
7.7364
7.7188
7.4773
7.3815
7.3671
7.1589
3.8046
2.5237
2.3657
10.00
30.14
20.48
30.46
40.25
20.16
30.42
30.49
Ph
O
O
C6H4p-Me
3n
f1 (ppm)


C:\Users\delta\Documents\files\data\YC\20120430\lhl-2-14-9c
169.3251
149.4840
137.5480
133.2675
129.7785
129.4030
129.2915
128.9140
128.2551
128.0959
126.2268
120.4635
40.9722
21.6201
21.0908
f1 (ppm)
Ph
C6H4p-Me
3n

# checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

No syntax errors found. CIF dictionary Interpreting this report

## Datablock: a20611b

---

```
Bond precision:  C-C = 0.0071 A          Wavelength=0.71073

Cell:            a=17.532(4)     b=7.5384(19)         c=13.756(3)
                 alpha=90        beta=100.059(4)      gamma=90
Temperature:     293 K
```

| | Calculated | Reported |
|---|---|---|
| Volume | 1790.1(7) | 1790.1(8) |
| Space group | P 21/c | P2(1)/c |
| Hall group | -P 2ybc | ? |
| Moiety formula | C23 H16 F N O2 | ? |
| Sum formula | C23 H16 F N O2 | C23 H16 F N O2 |
| Mr | 357.37 | 357.37 |
| Dx,g cm-3 | 1.326 | 1.326 |
| Z | 4 | 4 |
| Mu (mm-1) | 0.092 | 0.092 |
| F000 | 744.0 | 744.0 |
| F000’ | 744.38 | |
| h,k,lmax | 20,8,16 | 20,8,16 |
| Nref | 3150 | 3148 |
| Tmin,Tmax | 0.989,0.993 | 0.989,0.993 |
| Tmin’ | 0.989 | |

```
Correction method= MULTI-SCAN

Data completeness= 0.999          Theta(max)= 25.010

R(reflections)= 0.0694( 1151)     wR2(reflections)= 0.1420( 3148)

S = 0.922                 Npar= 244
```

---

The following ALERTS were generated. Each ALERT has the format
**test-name_ALERT_alert-type_alert-level**.
Click on the hyperlinks for more details of the test.

---

**Alert level B**

PLAT026_ALERT_3_B Ratio Observed / Unique Reflections too Low .... 37 Perc.

---

**Alert level C**

```
RINTA01_ALERT_3_C  The value of Rint is greater than 0.12
           Rint given   0.136
PLAT241_ALERT_2_C Check High      Ueq as Compared to Neighbors for        C11
PLAT242_ALERT_2_C Check Low       Ueq as Compared to Neighbors for        C12
PLAT242_ALERT_2_C Check Low       Ueq as Compared to Neighbors for        C15
PLAT334_ALERT_2_C Small Average Benzene  C-C Dist. C12    -C17          1.36 Ang.
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ..............    0.0071 Ang
```

---

**Alert level G**

```
PLAT005_ALERT_5_G No _iucr_refine_instructions_details in CIF ....         ?
PLAT199_ALERT_1_G Check the Reported _cell_measurement_temperature       293 K
PLAT200_ALERT_1_G Check the Reported   _diffrn_ambient_temperature       293 K
```

---

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   1 ALERT level B = A potentially serious problem, consider carefully
   6 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   3 ALERT level G = General information/check it is not something unexpected

   2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   4 ALERT type 2 Indicator that the structure model may be wrong or deficient
   3 ALERT type 3 Indicator that the structure quality may be low
   0 ALERT type 4 Improvement, methodology, query or suggestion
   1 ALERT type 5 Informative message, check
```

---

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

**Publication of your CIF in IUCr journals**

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

**Publication of your CIF in other journals**

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

---

**PLATON version of 19/04/2012; check.def file version of 14/04/2012**

**Datablock a20611b** - ellipsoid plot