Electronic Supplementary Information (ESI)

The amino side chains do matter: chemoselectivity in the one-pot three-component synthesis of 2-amino-4*H*-chromenes by supramolecular catalysis with amino-appended β-cyclodextrins (ACDs) in water

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Contents

1. Analytical data of ACDs

1.1 mp, ^{1}H NMR and HRMS of ACDs

a0: mp: 234 ℃ (decomp.); ^{1}H NMR (500 MHz, D_2O) δ 4.99 (s, 7 H, H-1 of CD), 3.90-3.76 (m, 28 H, H-3, 5, 6 of CD), 3.58-3.47 (m, 14 H, H-2,4 of CD), 3.09-3.05 (m, 2H); HRMS (ESI) *m*/*z*: calcd for $C_{42}H_{71}NO_{34}$ $[M+H]^+$: 1134.3936, found $[M+H]^+$: 1134.3954.

a1: mp: 257 ℃ (decomp.); ^{1}H NMR (500 MHz, D_2O) δ 4.92 (s, 7 H, H-1 of CD), 3.83-3.69 (m, 28 H, H-3, 5, 6 of CD), 3.51-3.41 (m, 14 H, H-2,4 of CD), 2.93-2.78 (m, 4H, en); HRMS (ESI) *m*/*z*: calcd for $C_{44}H_{76}N_2O_{34}$ $[M+H]^+$: 1177.4358, found $[M+H]^+$: 1177.4370.

a2: mp: 272 ℃ (decomp.); ^{1}H NMR (500 MHz, D_2O) δ 4.98 (s, 7 H, H-1 of CD), 3.89-3.76 (m, 28 H, H-3, 5, 6 of CD), 3.58-3.47 (m, 14 H, H-2,4 of CD), 2.78-2.65 (m, 8H, en); HRMS (ESI) *m*/*z*: calcd for $C_{46}H_{81}N_3O_{34}$ $[M+H]^+$: 1220.4780, found $[M+H]^+$: 1220.4792.

a3: mp: 283 ℃ (decomp.); ^{1}H NMR (500 MHz, D_2O) δ 4.96 (s, 7 H, H-1 of CD), 3.86-3.73 (m, 28 H, H-3, 5, 6 of CD), 3.56-3.46 (m, 14 H, H-2,4 of CD), 2.78-2.59 (m, 12 H, en); HRMS (ESI) *m*/*z*: calcd for $C_{48}H_{86}N_4O_{34}$ $[M+H]^+$: 1263.5202, found $[M+H]^+$: 1263.5194.

a4: mp: 295 ℃ (decomp.); ^{1}H NMR (500 MHz, D_2O) δ 4.96 (s, 7 H, H-1 of CD), 3.84-3.72 (m, 28 H, H-3, 5, 6 of CD), 3.54-3.45 (m, 14 H, H-2,4 of CD), 2.77-2.53 (m, 16 H, en); HRMS (ESI) *m*/*z*: calcd for $C_{50}H_{91}N_5O_{34}$ $[M+H]^+$: 1306.5624, found $[M+H]^+$: 1306.5601.

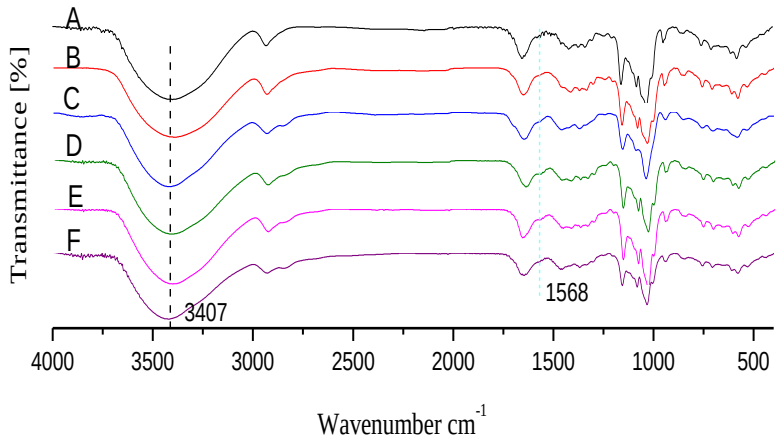
a5: mp: >300 ℃; ^{1}H NMR (500 MHz, D_2O) δ 4.98 (s, 7 H, H-1 of CD), 3.85-3.72 (m, 28 H, H-3, 5, 6 of CD), 3.57-3.48 (m, 14 H, H-2,4 of CD), 2.78-2.56 (m, 20 H, en); HRMS (ESI) *m*/*z*: calcd for $C_{52}H_{96}N_6O_{34}$ $[M+H]^+$: 1349.6046, found $[M+H]^+$: 1349.6069.

1.2 Water solubility test of ACDs

Water solubilities of **a0**-**a5** were determined by the method of preparing the saturated solution. Excess amounts of **a0**-**a5** was placed in 2 mL of water (ca. pH 7.0) respectively, sheltered from light and the mixture was stirred vigorously for 1 h at 25±2 ℃. The solution is then filtered on a 0.45 μm cellulose acetate membrane. The filtrate was evaporated under reduced pressure to dryness and the water solubilities of **a0**-**a5** were calculated.

1.3 Fourier Transform Infrared Spectroscopy (FT-IR)

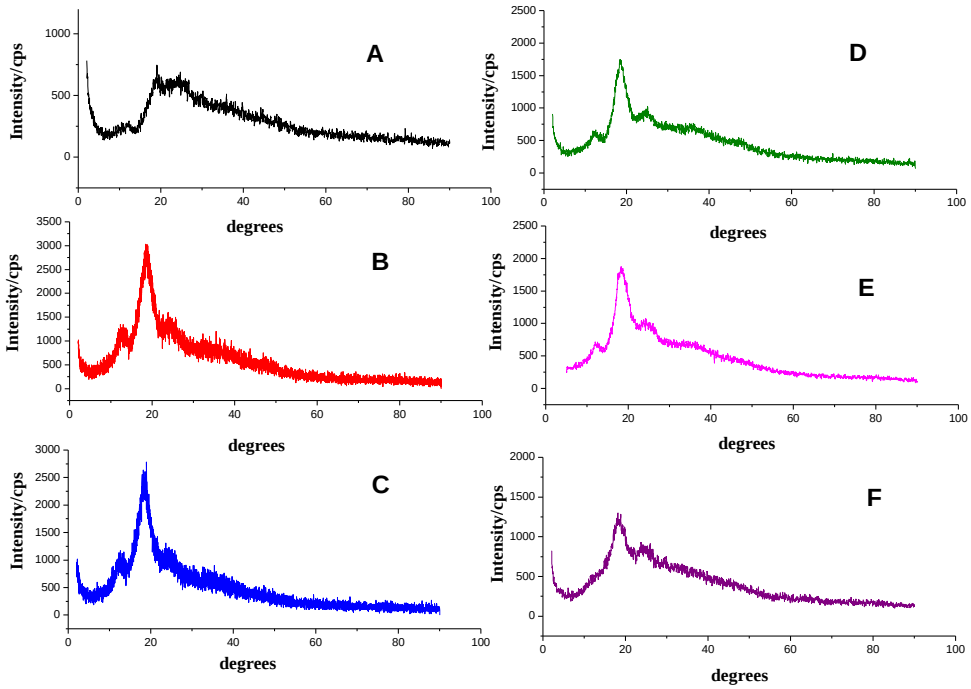
The FT-IR spectra of **a0**-**a5** were collected between 4000 and 400 cm^{-1} by the KBr method.



IR spectra of (A) **a0**; (B) **a1**; (C) **a2**; (D) **a3**; (E) **a4**; (F) **a5**

1.4 X-ray Diffractometry

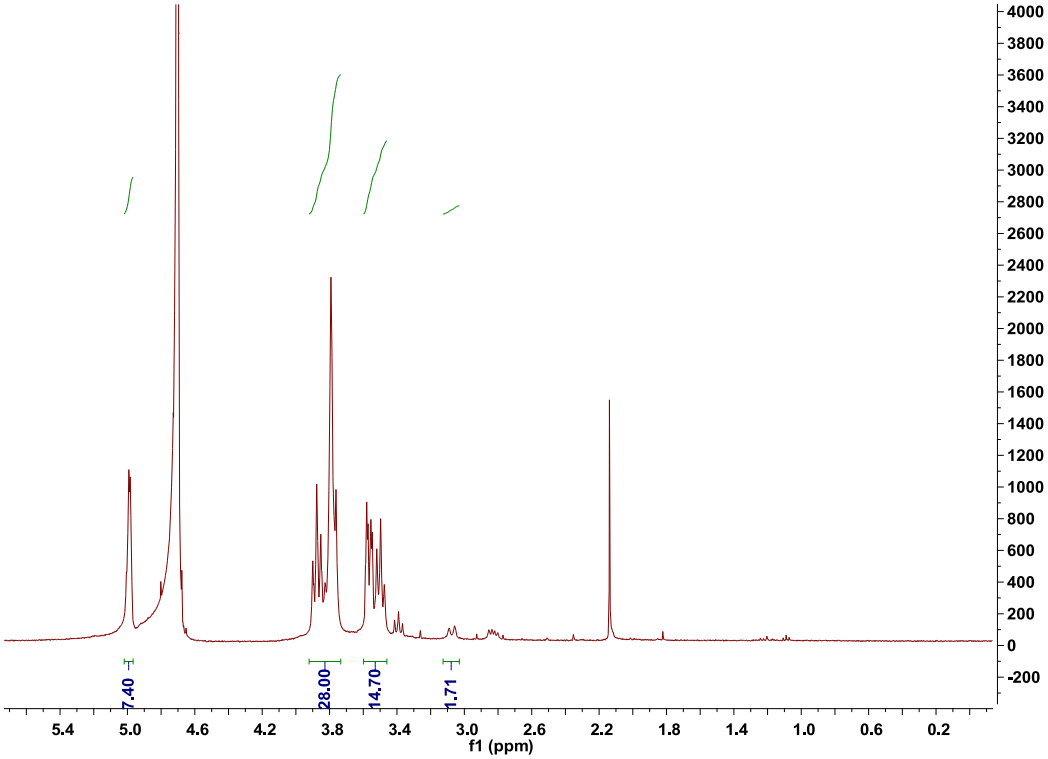
A D/Max-3B diffractometer (Cu-Kα (k=1.5460 Å)) was used for XRD. Experimental conditions: Voltage: 40 kV; scanning rate: 5 °/min; scanning with a step size of 2θ=0.02° between 2θ=5° and 70°.

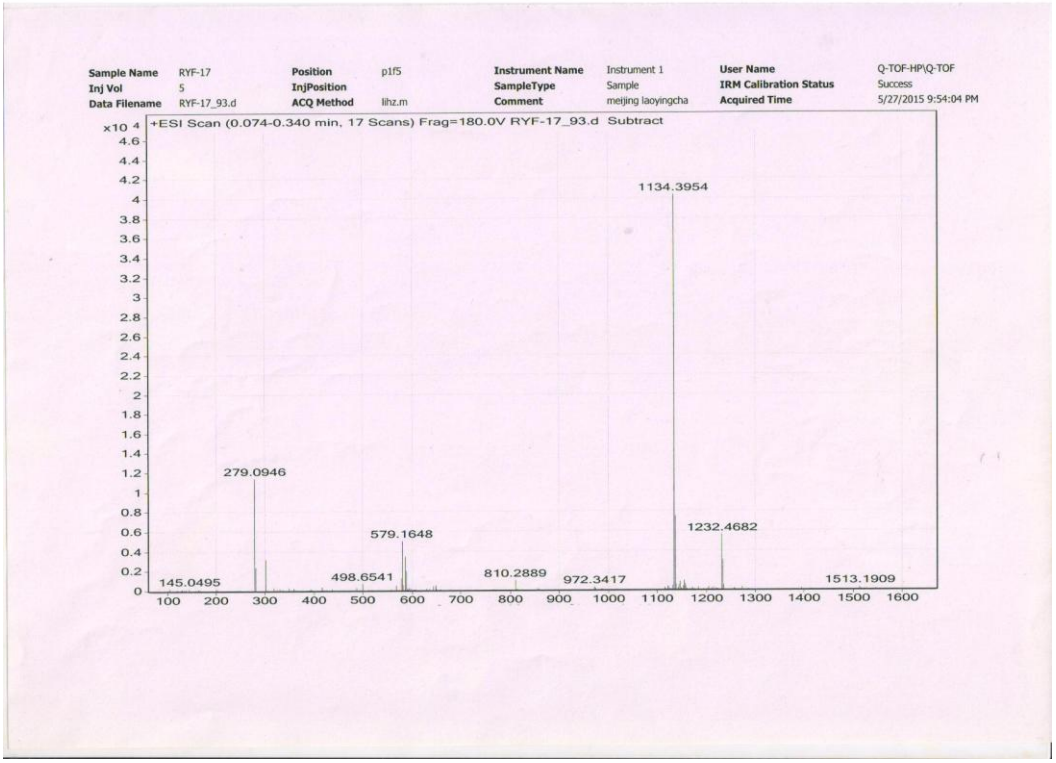


XRD patterns: (A) **a0**; (B) **a1**; (C) **a2**; (D) **a3**, (E) **a4**; (F) **a5**

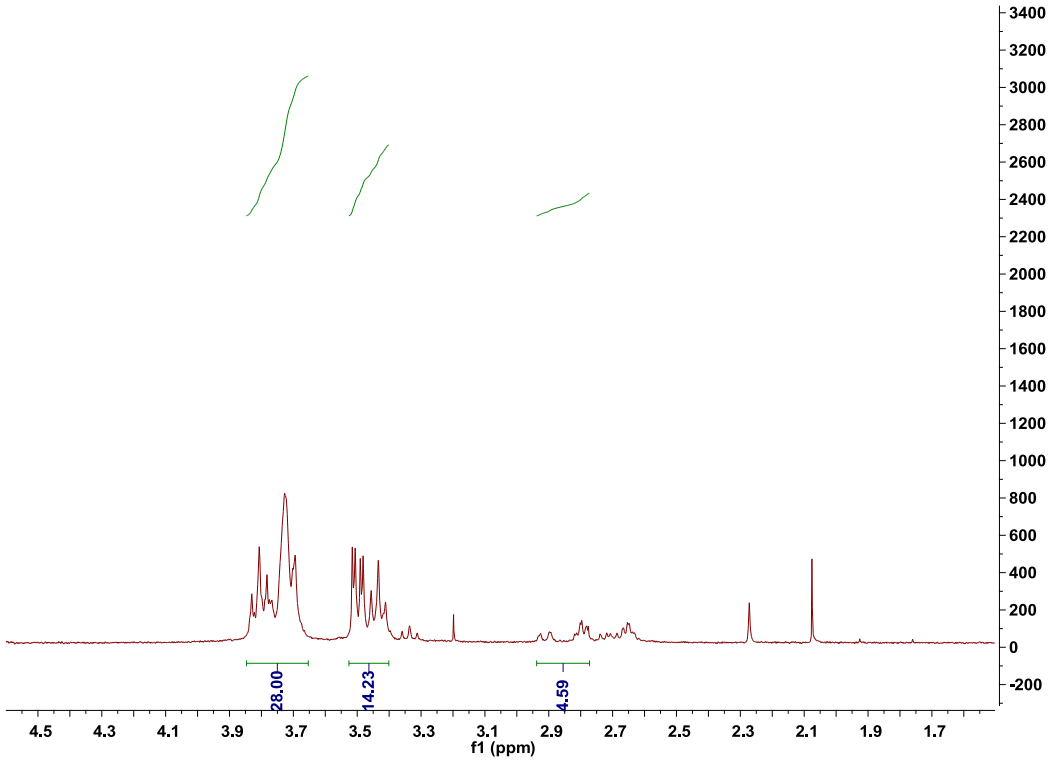
2. Proton NMR and HRMS copies of ACDs

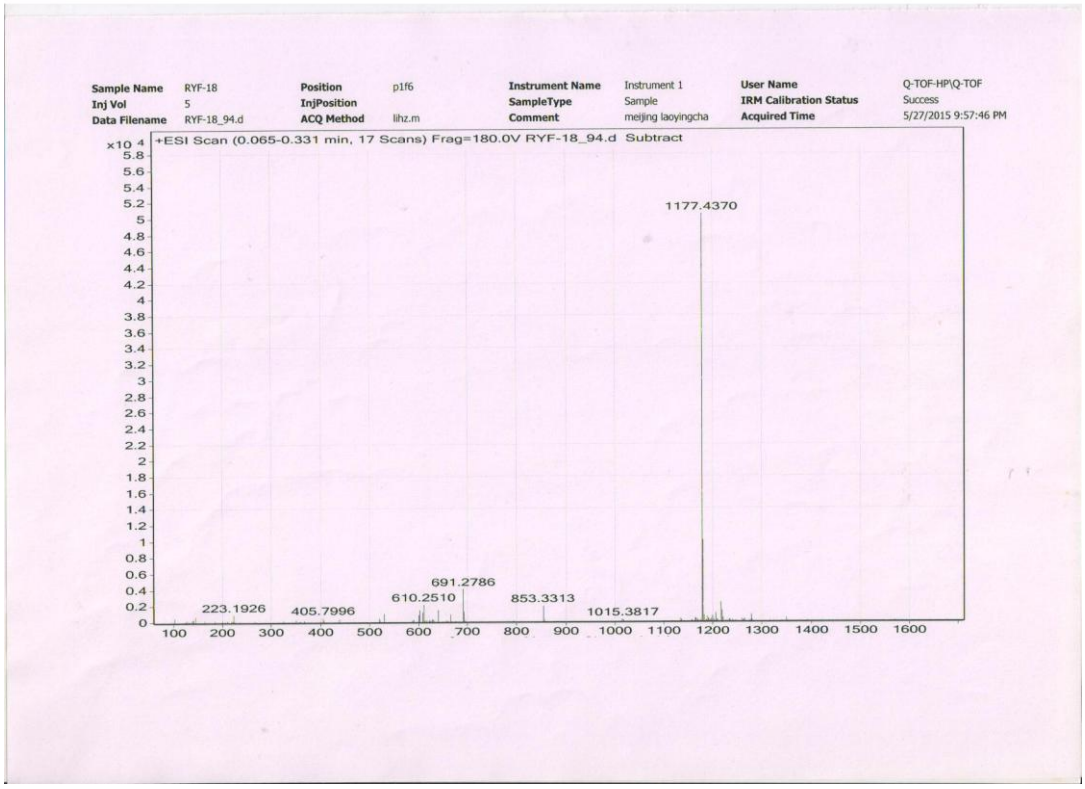
a0：





a1:


28.00
14.23
4.59
f1 (ppm)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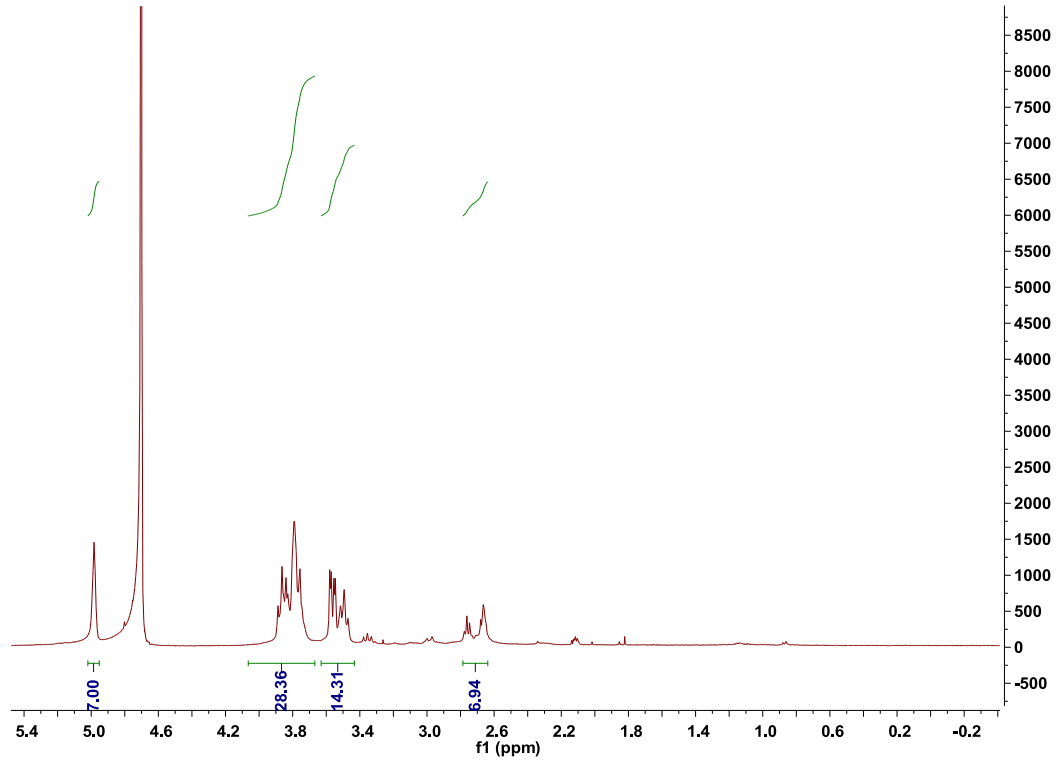
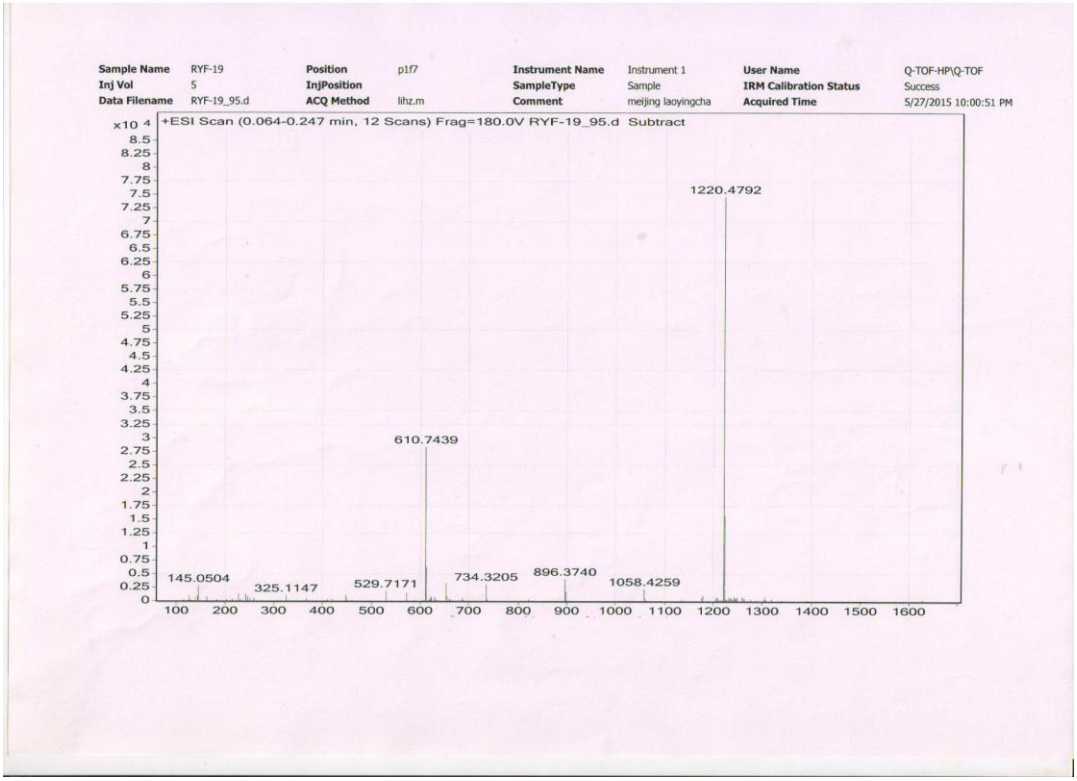
Inj Vol 5
Data Filename RYF-18_94.d
Position p1f6
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment meijing laoyingcha
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 5/27/2015 9:57:46 PM
+ESI Scan (0.065-0.331 min, 17 Scans) Frag=180.0V RYF-18_94.d Subtract
1177.4370
691.2786
610.2510
853.3313
223.1926
405.7996
1015.3817

a2:


7.00
28.36
14.31
6.94
f1 (ppm)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Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 5
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename RYF-19_95.d
ACQ Method lihz.m
Comment meijing laoyingcha
Acquired Time 5/27/2015 10:00:51 PM
+ESI Scan (0.064-0.247 min, 12 Scans) Frag=180.0V RYF-19_95.d Subtract
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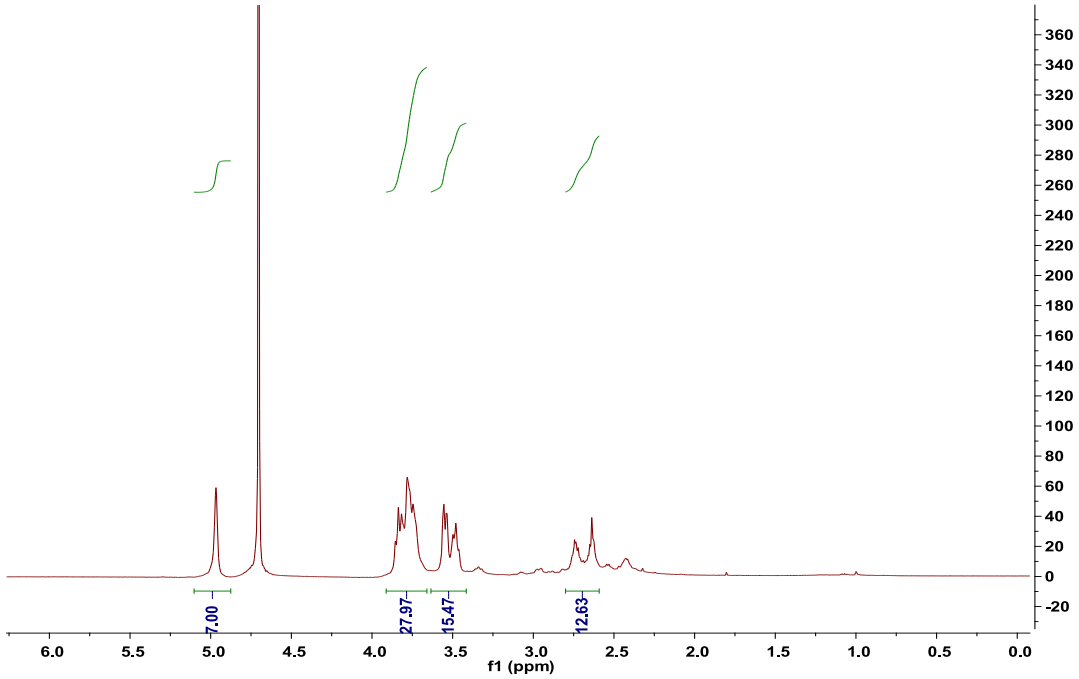
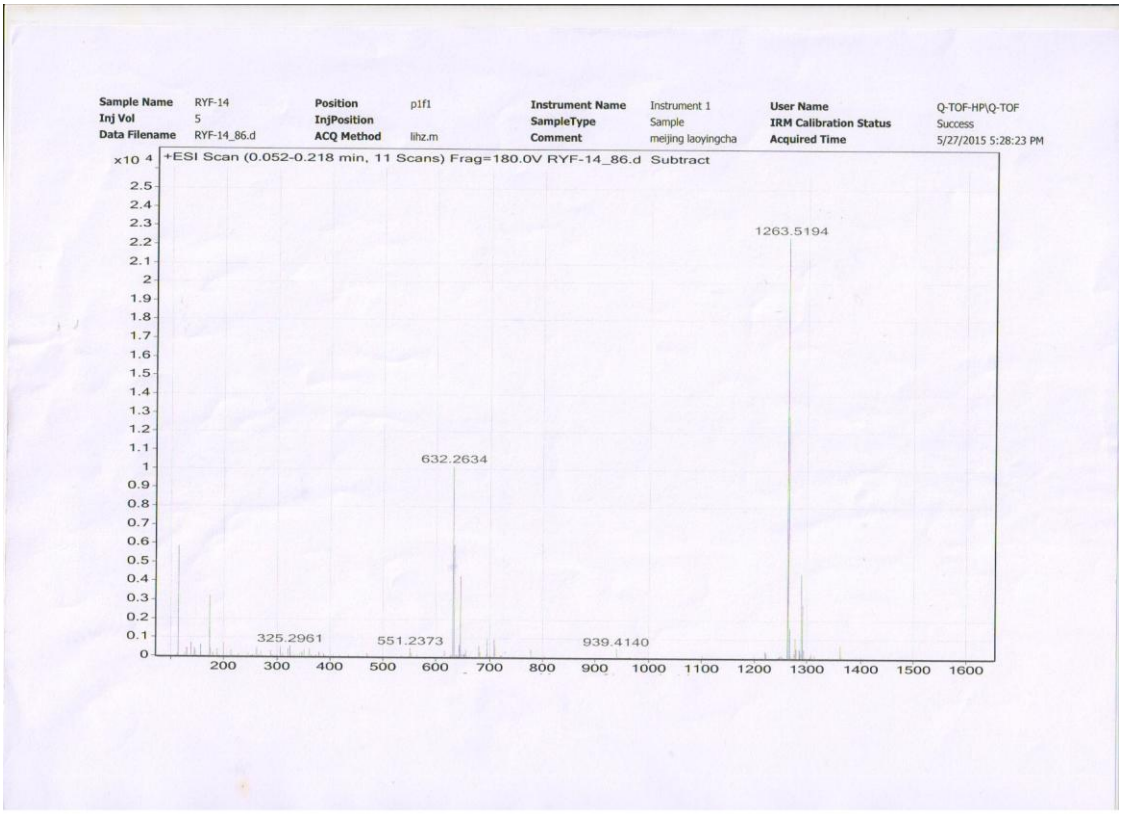
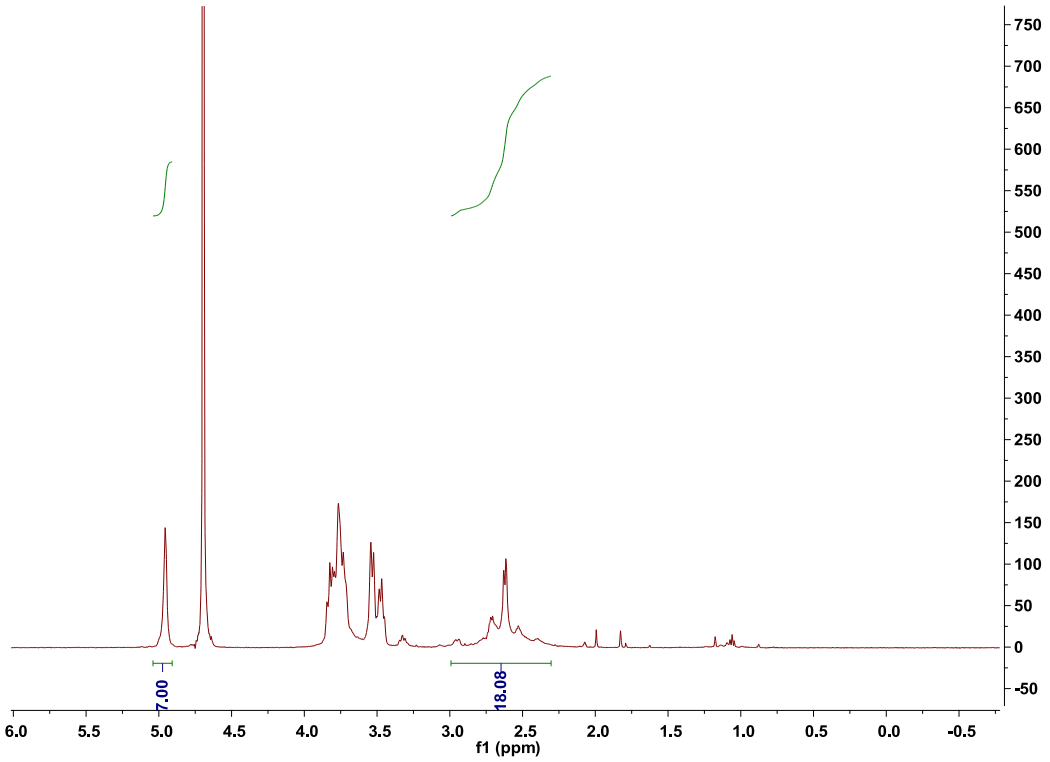
610.7439
145.0504
325.1147
529.7171
734.3205
896.3740
1058.4259

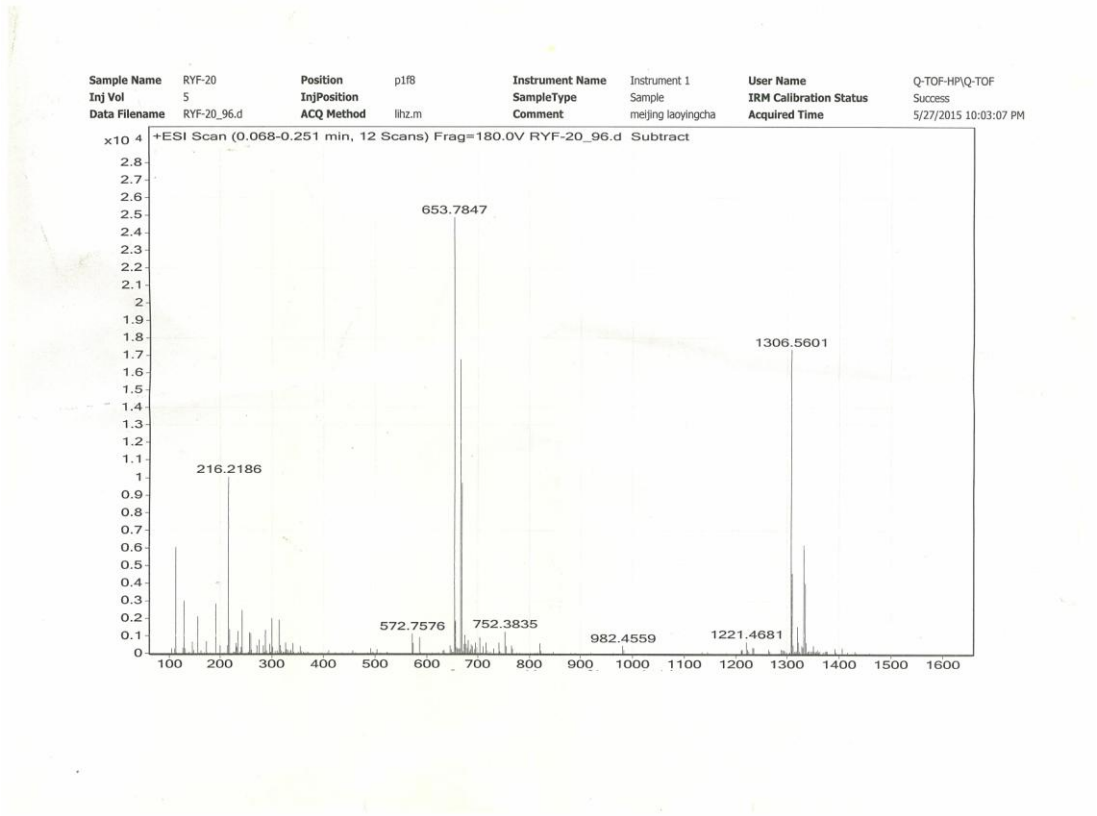
a3:


7.00
27.97
15.47
12.63
f1 (ppm)


Sample Name RYF-14
Inj Vol 5
Data Filename RYF-14_86.d
Position p1f1
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment meijing laoyingcha
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 5/27/2015 5:28:23 PM
+ESI Scan (0.052-0.218 min, 11 Scans) Frag=180.0V RYF-14_86.d Subtract
1263.5194
632.2634
325.2961
551.2373
939.4140

a4:


7.00
18.08
f1 (ppm)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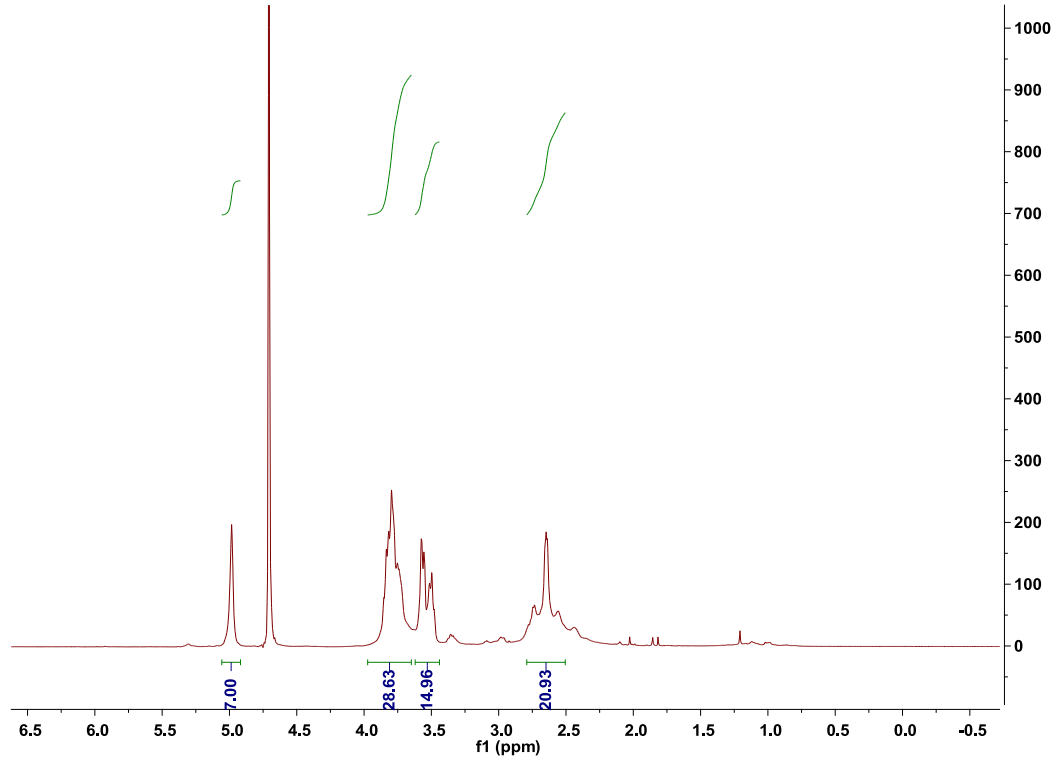
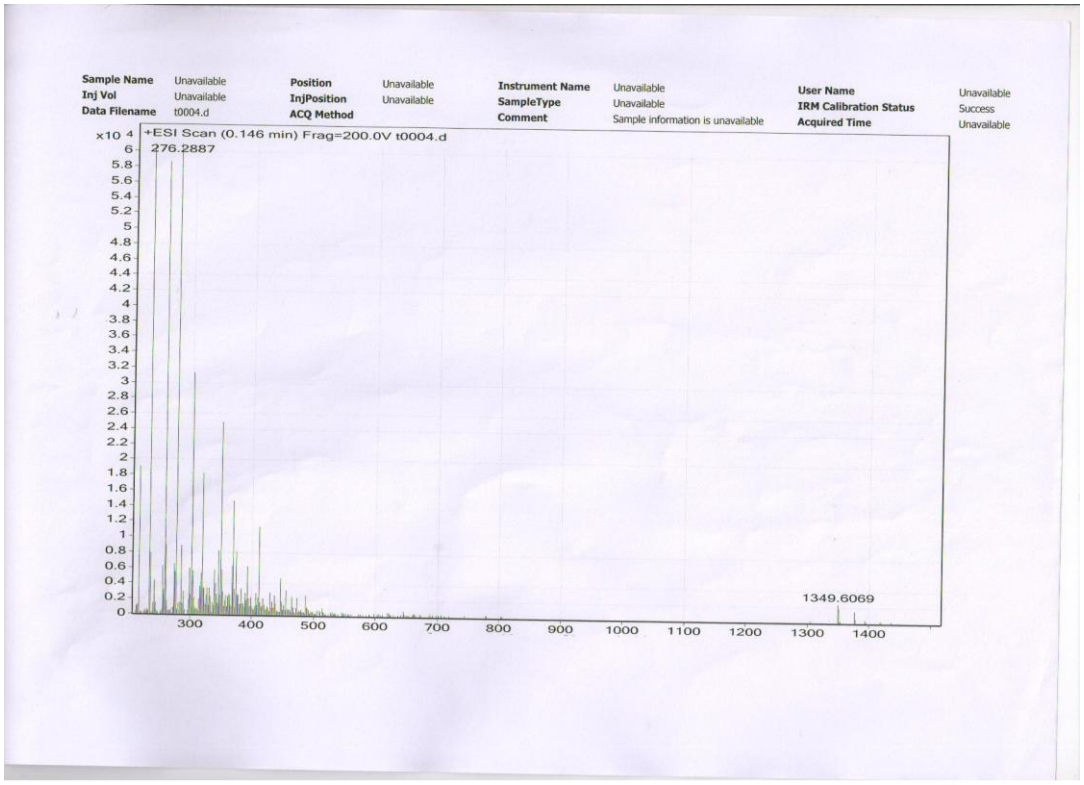
Position p1f8
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 5
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename RYF-20_96.d
ACQ Method lihz.m
Comment meijing laoyingcha
Acquired Time 5/27/2015 10:03:07 PM
+ESI Scan (0.068-0.251 min, 12 Scans) Frag=180.0V RYF-20_96.d Subtract
653.7847
1306.5601
216.2186
572.7576
752.3835
982.4559
1221.4681

a5:


7.00
28.63
14.96
20.93
f1 (ppm)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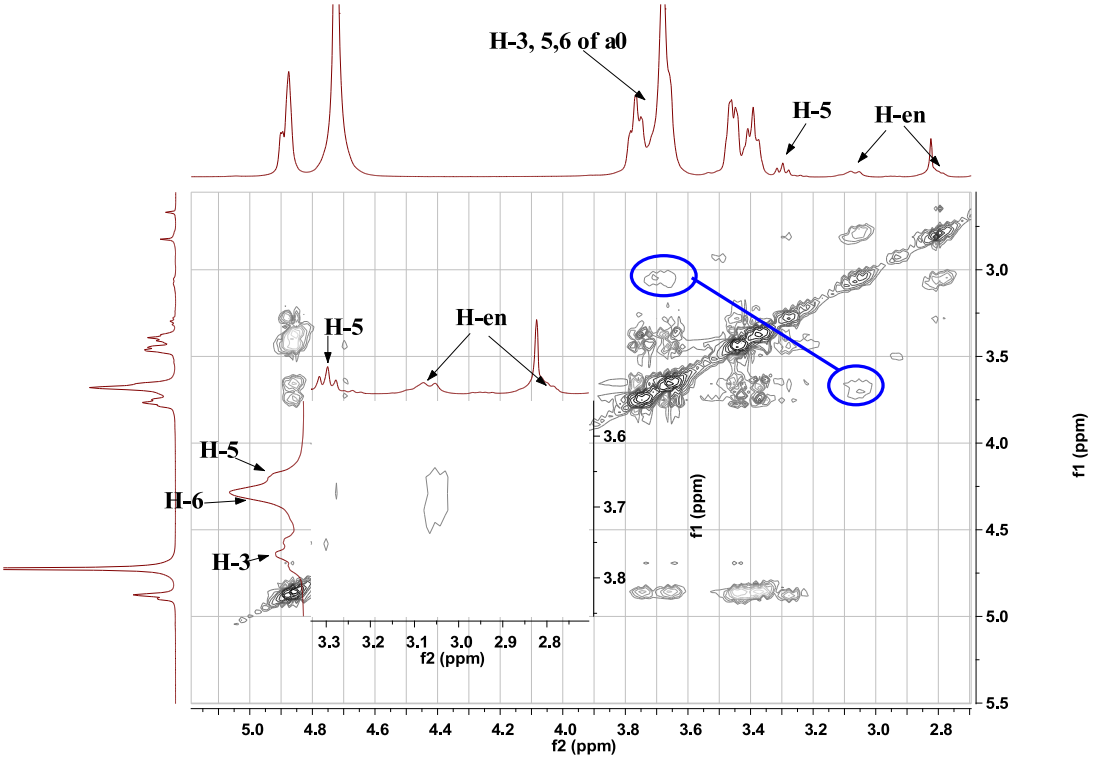
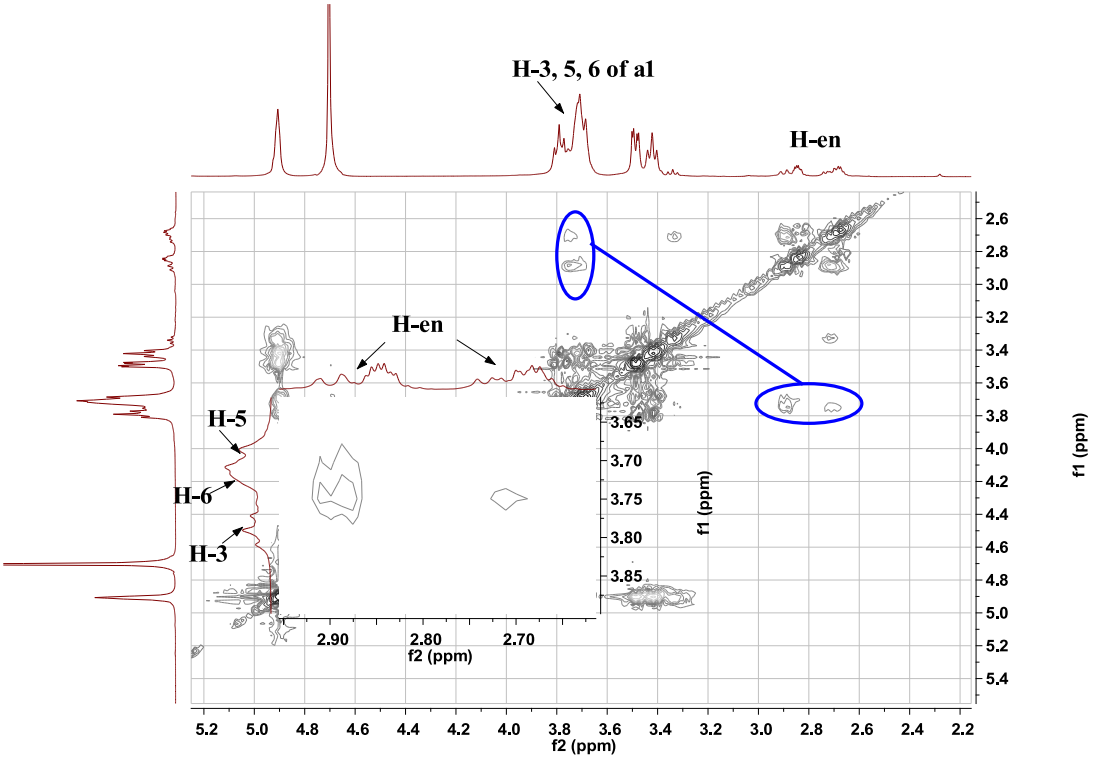
Inj Vol Unavailable
Data Filename t0004.d
Position Unavailable
InjPosition Unavailable
ACQ Method
Instrument Name Unavailable
SampleType Unavailable
Comment Sample information is unavailable
User Name
IRM Calibration Status Success
Acquired Time Unavailable
+ESI Scan (0.146 min) Frag=200.0V t0004.d
276.2887
1349.6069

3. ROESY spectra of ACDs (500 MHz, 298 K in D_2O, 25 mg/mL)

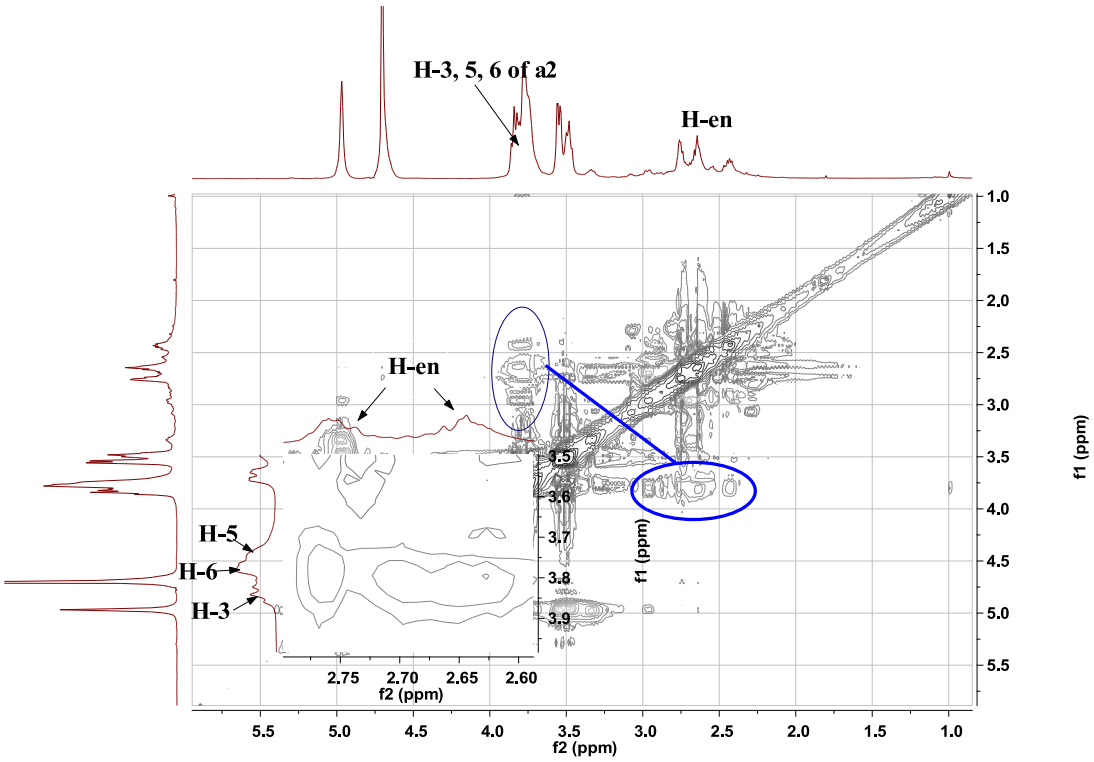
a0:



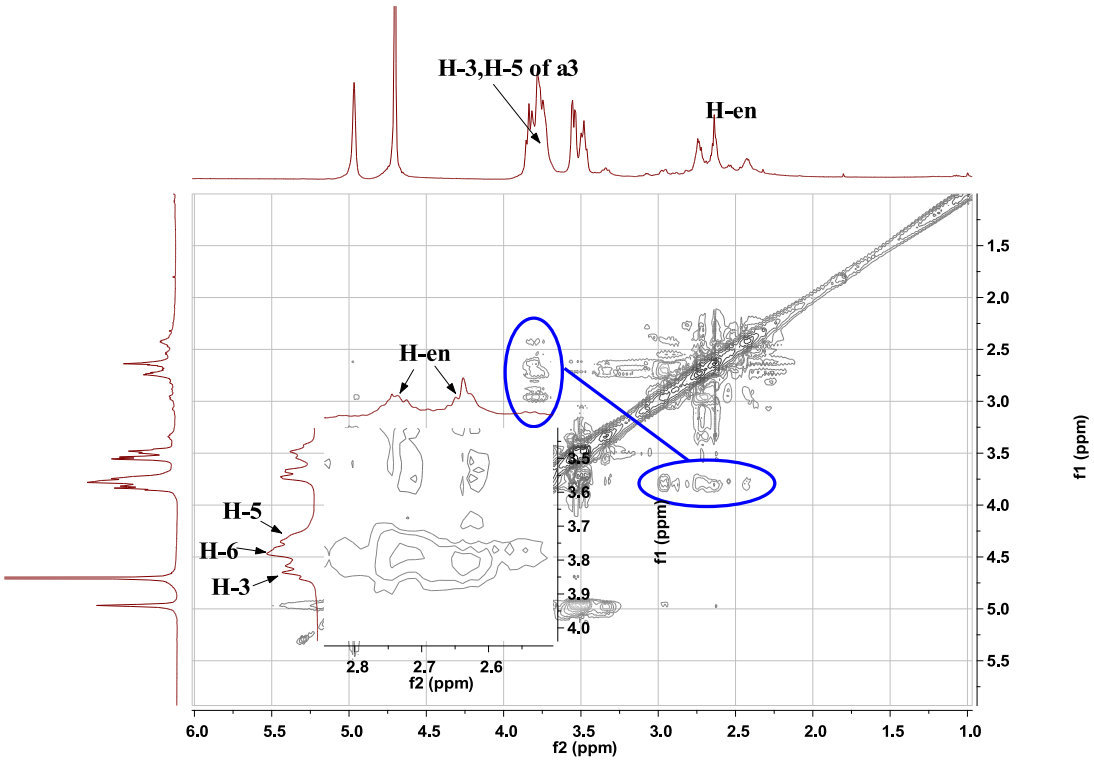
a1:



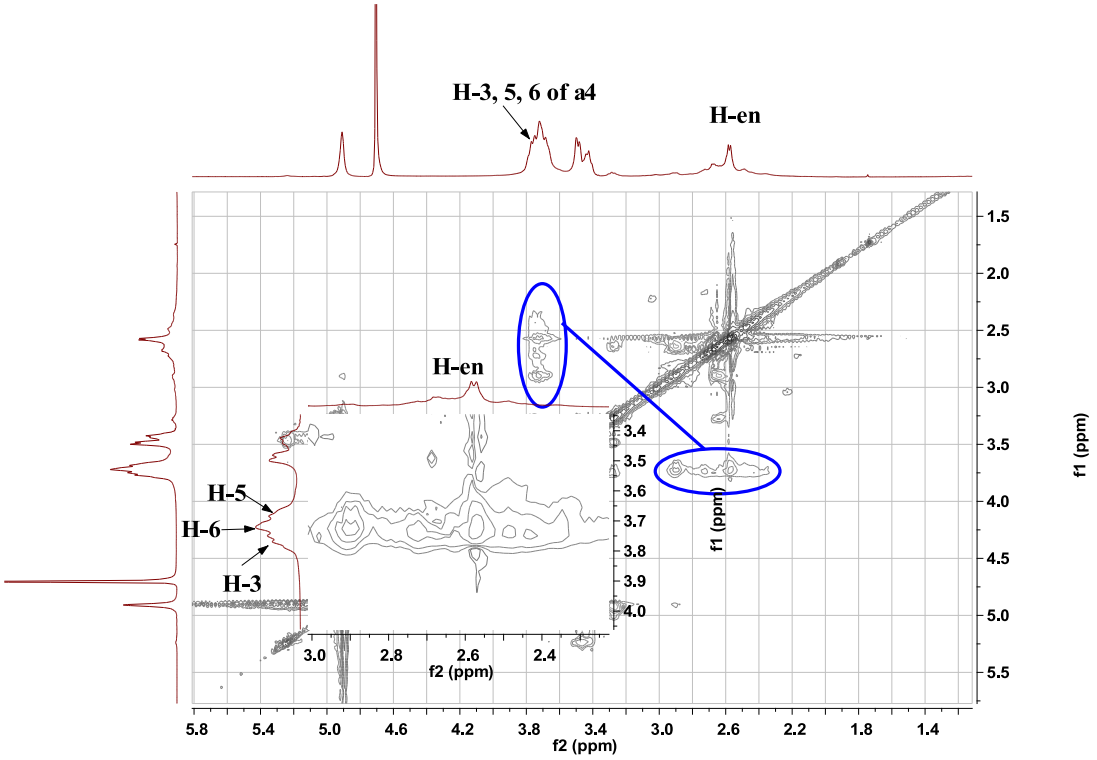
a2:



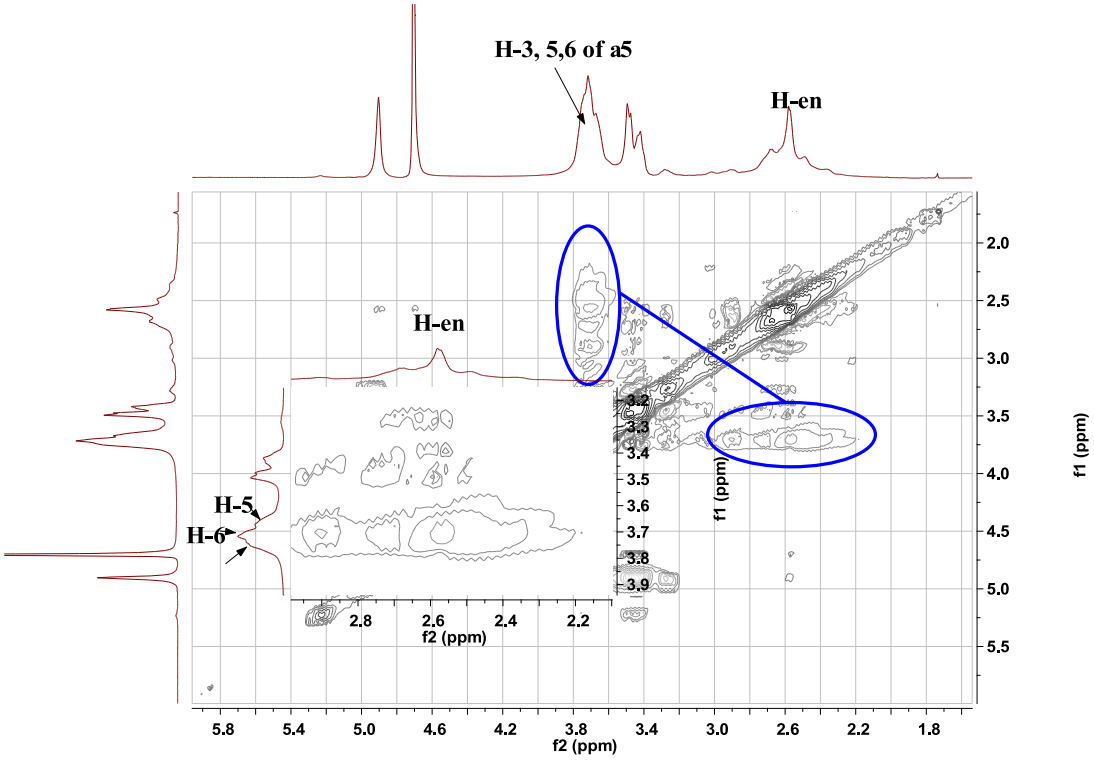
a3:



a4:

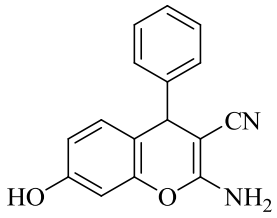


a5:



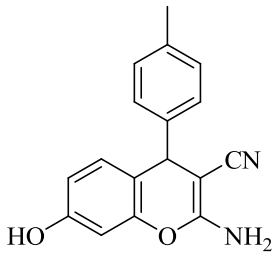
4. Analytical data of 2-amino-4*H*-chromenes (4a-4ff)

4a.



mp：232-233 ℃; IR (KBr) (ν_{max} cm^{-1}): 3495 (OH), 3338 (NH_2), 2183 (CN), 1652 (C=C vinyl nitrile), 1621, 1589, 1505 (C=C, aromatic)；^{1}H NMR (500 MHz, DMSO-d_6) δ 9.71 (s, 1H, OH), 7.29 (d, *J* = 7.5 Hz, 2H, Ar-H), 7.20 (t, *J* = 7.3 Hz, 1H, Ar-H), 7.16 (d, *J* = 7.3 Hz, 2H, Ar-H), 6.87 (s, 2H, NH_2), 6.80 (d, *J* = 8.5 Hz, 1H, Ar-H), 6.48 (dd, *J* = 8.4, 2.3 Hz, 1H, Ar-H), 6.40 (d, *J* = 2.3 Hz, 1H, Ar-H), 4.61 (s, 1H); HRMS (ESI) *m*/*z*：calcd for $C_{16}H_{12}N_2O_2$ $[M+H]^+$: 287.0796, found $[M+H]^+$: 287.0795.

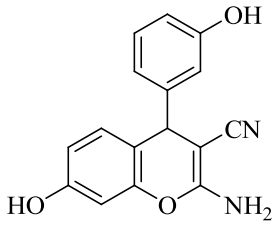
4b.



mp：162-164 ℃; IR (KBr) (ν_{max} cm^{-1}): 3481 (OH), 3333 (NH_2), 2920 (CH_3), 2201 (CN), 1649 (C=C vinyl nitrile), 1589, 1507 (C=C, aromatic), 1400(CH_3); ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.66 (s, 1H, OH), 7.10 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.04 (d, *J* = 7.9 Hz, 2H, Ar-H), 6.81 (s, 2H, NH_2), 6.77 (d, *J* = 8.4 Hz, 1H, Ar-H), 6.46 (dd, *J* = 8.5, 2.2 Hz, 1H, Ar-H), 6.39 (d, *J* = 2.1 Hz, 1H, Ar-H), 4.56 (s, 1H), 2.25 (s, 3H, CH_3); HRMS (ESI)

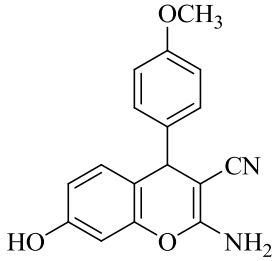
m/*z*：calcd for $C_{17}H_{14}N_2O_2$ $[M+H]^+$: 301.0953, found $[M+H]^+$: 301.0947.

4c.



mp：215-216 ℃；IR (KBr) (ν_{max} cm^{-1}): 3445 (OH), 3343 (NH_2), 2197 (CN), 1650 (C=C vinyl nitrile), 1620, 1585, 1509 (C=C, aromatic)；^1H NMR (500 MHz, DMSO-d_6) δ 9.69 (s, 1H, OH), 9.33 (s, 1H, OH), 7.07 (s, 1H, Ar-H), 6.85 (s, 2H, NH_2), 6.80 (s, 1H, Ar-H), 6.59 (d, *J* = 12.4 Hz, 2H, Ar-H), 6.50 (d, *J* = 15.6 Hz, 2H, Ar-H), 6.39 (s, 1H, Ar-H), 4.49 (s, 1H); HRMS (ESI) *m*/*z*：calcd for $C_{16}H_{12}N_2O_3$ $[M+H]^+$: 303.0746, found $[M+H]^+$: 303.0725.

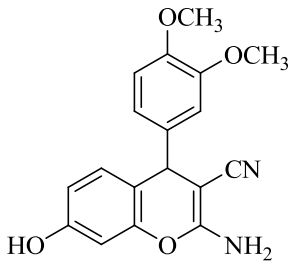
4d.



mp: 111-113 ℃; IR (KBr) (ν_{max} cm^{-1}): 3417 (OH), 3337 (NH_2), 2191 (CN), 1648 (C=C vinyl nitrile), 1507, 1460, 1405 (C=C, aromatic); ^1H NMR (500 MHz, DMSO-d_6) δ 9.66 (s, 1H, OH), 7.05 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.84 (d, *J* = 8.6 Hz, 2H, Ar-H), 6.80 (s, 2H, NH_2), 6.75 (d, *J* = 8.5 Hz, 1H, Ar-H), 6.45 (dd, *J* = 8.4, 2.4 Hz, 1H, Ar-H), 6.37 (d, *J* = 2.3 Hz, 1H, Ar-H), 4.54 (s, 1H), 3.69 (s, 3H, OCH_3); HRMS (ESI) *m*/*z*：calcd for

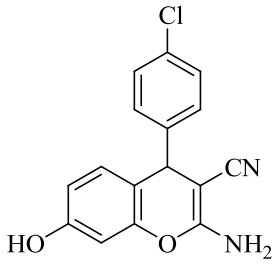
$C_{17}H_{14}N_2O_3$ $[M+H]^+$: 295.1083, found $[M+H]^+$: 295.1076.

4e.



mp: ℃; IR (KBr) (ν_{max} cm^{-1}): 3434 (OH), 3344 (NH_2), 2192 (CN), 1647 (C=C vinyl nitrile), 1590, 1509, 1459 (C=C, aromatic); ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.66 (s, 1H, OH), 6.86 (d, J = 8.3 Hz, 1H, Ar-H), 6.81 (m, 1H, Ar-H, 2H, NH_2), 6.76 (d, J = 1.9 Hz, 1H, Ar-H), 6.64 (dd, J = 8.2, 1.9 Hz, 1H, Ar-H), 6.46 (dd, J = 8.4, 2.4 Hz, 1H, Ar-H), 6.37 (d, J = 2.3 Hz, 1H, Ar-H), 4.54 (s, 1H), 3.69 (d, J = 3.6 Hz, 6H, 2×OCH_3); HRMS (ESI) m/z：calcd for $C_{18}H_{16}N_2O_4$ $[M+H]^+$: 325.1188, found $[M+H]^+$: 325.1180.

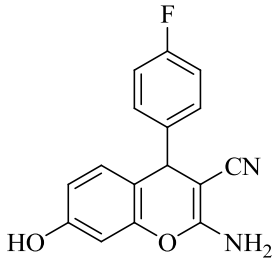
4f.



mp：165-166 ℃; IR (KBr) (ν_{max} cm^{-1}): 3462 (OH), 3341 (NH_2), 2192 (CN), 1641 (C=C vinyl nitrile), 1615, 1589, 1506 (C=C, aromatic)；^{1}H NMR (400 MHz, DMSO-d_6) δ 9.76 (s, 1H, OH), 7.37 (d, J = 8.4 Hz, 2H，Ar-H), 7.19 (d, J = 8.4 Hz, 2H，Ar-H), 6.95 (s, 2H，NH_2), 6.79 (d, J = 8.5

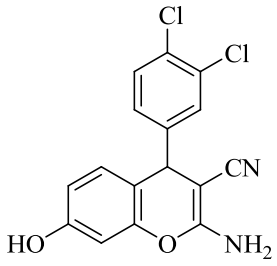
Hz, 1H，Ar-H), 6.49 (dd, *J* = 8.4, 2.4 Hz, 1H，Ar-H), 6.41 (d, *J* = 2.3 Hz, 1H，Ar-H), 4.67 (s, 1H); HRMS (ESI) *m*/*z*：calcd for $C_{16}H_{11}ClN_2O_2$ $[M+H]^+$: 321.0407, found $[M+H]^+$: 321.0400.

4g.



mp：185-187 ℃；IR (KBr) (ν_{max} cm^{-1}): 3430 (OH), 3343 (NH_2), 2187 (CN), 1646 (C=C vinyl nitrile), 1618, 1585, 1505 (C=C, aromatic)；^{1}H NMR (400 MHz, DMSO-d_6) δ 9.75 (s, 1H, OH), 7.20 (dd, *J* = 8.6, 5.7 Hz, 2H, Ar-H), 7.13 (t, *J* = 8.8 Hz, 2H, Ar-H), 6.92 (s, 2H, NH_2), 6.79 (d, *J* = 8.5 Hz, 1H, Ar-H), 6.49 (dd, *J* = 8.4, 2.3 Hz, 1H, Ar-H), 6.40 (d, *J* = 2.3 Hz, 1H, Ar-H), 4.66 (s, 1H); HRMS (ESI) *m*/*z*：calcd for $C_{16}H_{11}FN_2O_2$ $[M+H]^+$: 305.0702, found $[M+H]^+$: 305.0701.

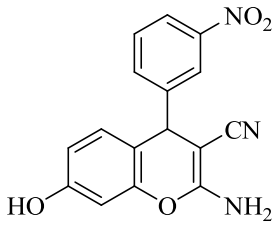
4h.



mp：245 ℃; IR (KBr) (ν_{max} cm^{-1}): 3477 (OH), 3342 (NH_2), 2192 (CN), 1641 (C=C vinyl nitrile), 1617, 1588, 1506 (C=C, aromatic); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.81 (s, 1H, OH), 7.59 (d, *J* = 8.3 Hz, 1H, Ar-H),

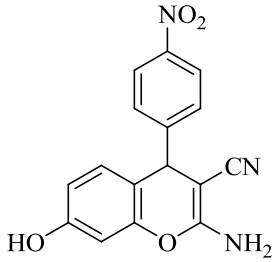
7.45 (d, *J* = 1.9 Hz, 1H, Ar-H), 7.16 (dd, *J* = 8.3, 2.0 Hz, 1H, Ar-H), 7.03 (s, 2H, NH_2), 6.82 (d, *J* = 8.5 Hz, 1H, Ar-H), 6.51 (dd, *J* = 8.4, 2.3 Hz, 1H, Ar-H), 6.42 (d, *J* = 2.3 Hz, 1H, Ar-H), 4.74 (s, 1H); HRMS (ESI) *m*/*z*：calcd for $C_{16}H_{10}Cl_2N_2O_2$ $[M+H]^+$: 321.0407, found $[M+H]^+$: 321.0400.

4i.



mp：190-193 ℃; IR (KBr) (ν_{max} cm^{-1}): 3411 (OH), 3335 (NH_2), 2191 (CN), 1655 (C=C vinyl nitrile), 1623, 1587, 1529 (C=C, aromatic), 1153 (NO_2); ^1H NMR (500 MHz, DMSO-d_6) δ 9.81 (s, 1H, OH), 8.11 (m, 1H, Ar-H), 8.03 (m, 1H, Ar-H), 7.66 (m, 2H, Ar-H), 7.05 (s, 2H, NH_2), 6.85 (d, *J* = 8.5 Hz, 1H, Ar-H), 6.52 (dd, *J* = 8.4, 2.4 Hz, 1H, Ar-H), 6.45 (d, *J* = 2.4 Hz, 1H, Ar-H), 4.92 (s, 1H); HRMS (ESI) *m*/*z*：calcd for $C_{16}H_{11}N_3O_4$ $[M+H]^+$: 310.0828, found $[M+H]^+$: 310.0821.

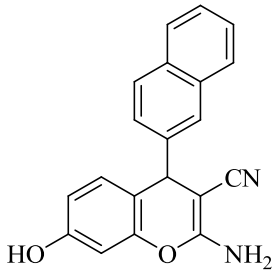
4j.



mp：210-212 ℃; IR (KBr) (ν_{max} cm^{-1}): 3472 (OH), 3341 (NH_2), 2195 (CN), 1643 (C=C vinyl nitrile), 1617, 1587, 1518 (C=C, aromatic), 1156 (NO_2); ^1H NMR (500 MHz, DMSO-d_6) δ 9.80 (s, 1H, OH), 8.20 (m, 2H,

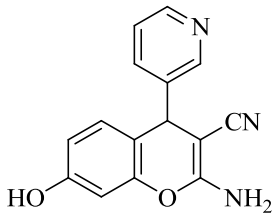
Ar-H), 7.45 (d, *J* = 8.6 Hz, 2H, Ar-H), 7.04 (s, 2H, NH_2), 6.81 (d, *J* = 8.5 Hz, 1H, Ar-H), 6.51 (dd, *J* = 8.4, 2.3 Hz, 1H, Ar-H), 6.44 (d, *J* = 2.3 Hz, 1H, Ar-H), 4.87 (s, 1H); HRMS (ESI) *m*/*z*：calcd for $C_{16}H_{11}N_3O_4$ $[M+H]^+$: 332.0647, found $[M+H]^+$: 332.0647.

4k.



mp：258-261℃; IR (KBr) (ν_{max} cm^{-1}): 3480 (OH), 3343 (NH_2), 2191 (CN), 1642 (C=C vinyl nitrile), 1614, 1586, 1505 (C=C, aromatic); ^1H NMR (500 MHz, DMSO-d_6) δ 9.73 (s, 1H, OH), 7.90 (d, *J* = 7.7 Hz, 1H, Ar-H), 7.86 (m, 2H, Ar-H), 7.76 (s, 1H, Ar-H), 7.50 (m, 2H, Ar-H), 7.25 (d, *J* = 8.5 Hz, 1H, Ar-H), 6.93 (s, 2H, NH_2), 6.82 (d, *J* = 8.4 Hz, 1H, Ar-H), 6.46 (m, 2H, Ar-H), 4.81 (s, 1H); HRMS (ESI) *m*/*z*：calcd for $C_{20}H_{14}N_2O_2$ $[M+H]^+$: 315.1134, found $[M+H]^+$: 315.1121.

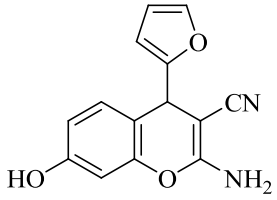
4l.



mp：298 ℃；IR (KBr) (ν_{max} cm^{-1}): 3386 (OH), 3334 (NH_2), 2192 (CN), 1657 (C=C vinyl nitrile), 1623 1598, 1584 (C=C, aromatic)；^1H NMR (400 MHz, DMSO-d_6) δ 9.80 (s, 1H, OH), 8.45 (d, *J* = 2.0 Hz, 2H, Ar-H),

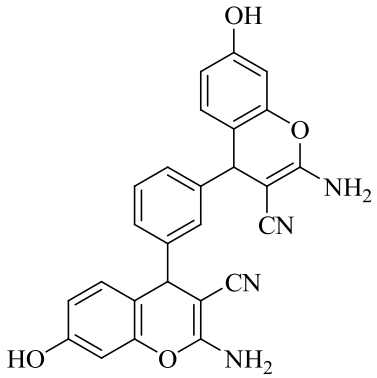
7.51 (dt, *J* = 7.9, 1.9 Hz, 1H, Ar-H), 7.34 (dd, *J* = 7.8, 4.7 Hz, 1H, Ar-H), 7.01 (s, 2H, NH_2), 6.80 (s, 1H, Ar-H), 6.50 (dd, *J* = 8.4, 2.4 Hz, 1H, Ar-H), 6.42 (d, *J* = 2.4 Hz, 1H, Ar-H), 4.73 (s, 1H); HRMS (ESI) *m*/*z*：calcd for $C_{15}H_{11}N_3O_2$ $[M+H]^+$: 288.0749, found $[M+H]^+$: 288.0742.

4m.



mp：208-210 ℃；IR (KBr) (ν_{max} cm^{-1}): 3476 (OH), 3333 (NH_2), 2194 (CN), 1655 (C=C vinyl nitrile), 1623, 1590, 1508(C=C, aromatic)；^1H NMR (500 MHz, DMSO-d_6) δ 9.75 (s, 1H, OH), 7.51 (s, 1H, Ar-H), 6.96 (s, 1H, Ar-H), 6.94(s, 2H, NH_2), 6.53 (d, *J* = 8.5 Hz, 1H, Ar-H), 6.39 (s, 1H, Ar-H), 6.34 (s, 1H, Ar-H), 6.13 (d, *J* = 2.7 Hz, 1H, Ar-H), 4.76 (s, 1H); HRMS (ESI) *m*/*z*：calcd for $C_{14}H_{10}N_2O_3$ $[M+H]^+$: 277.0589, found $[M+H]^+$: 277.0580.

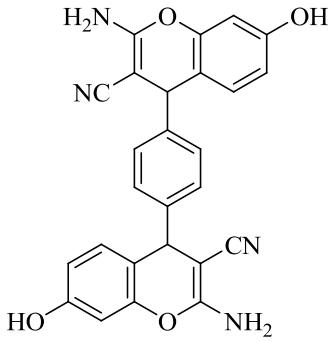
4n.



mp：230-232 ℃; IR (KBr) (ν_{max} cm^{-1}): 3447 (OH), 3338 (NH_2), 2188 (CN), 1648 (C=C vinyl nitrile), 1582, 1507(C=C, aromatic) ; ^1H NMR

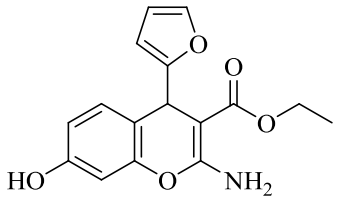
(500 MHz, DMSO-d_6) δ 9.67 (s, 2H, OH), 7.21 (d, *J* = 5.8 Hz, 1H, Ar-H), 7.13 (d, *J* = 15.5 Hz, 1H, Ar-H), 6.95 (d, *J* = 7.7 Hz, 1H, Ar-H), 6.88 (d, *J* = 7.7 Hz, 1H, Ar-H), 6.84 (d, *J* = 9.6 Hz, 4H, NH_2), 6.80 (d, *J* = 8.5 Hz, 1H, Ar-H), 6.74 (d, *J* = 8.5 Hz, 1H, Ar-H), 6.44 (td, *J* = 8.0, 2.2 Hz, 2H, Ar-H), 6.37 (dd, *J* = 4.9, 2.3 Hz, 2H, Ar-H), 4.59 (d, *J* = 4.9 Hz, 2H); HRMS (ESI) *m*/*z*：calcd for $C_{26}H_{18}N_4O_4$ $[M+H]^+$: 451.1406, found $[M+H]^+$: 451.1404.

4o.



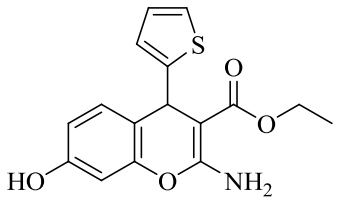
mp：215-217 ℃; IR (KBr) (ν_{max} cm^{-1}): 3442 (OH), 3338 (NH_2), 2190 (CN), 1649 (C=C vinyl nitrile), 1588, 1507(C=C, aromatic); ^1H NMR (500 MHz, DMSO-d_6) δ 9.68 (s, 2H, OH), 7.08 (s, 4H, NH_2), 6.83 (d, *J* = 5.4 Hz, 4H, Ar-H), 6.81 (t, *J* = 4.3 Hz, 2H, Ar-H), 6.48 (d, *J* = 2.2 Hz, 1H, Ar-H), 6.47 (d, *J* = 2.2 Hz, 1H, Ar-H), 6.39 (d, *J* = 2.3 Hz, 2H, Ar-H), 4.57 (s, 2H); HRMS (ESI) *m*/*z*：calcd for $C_{26}H_{18}N_4O_4$ $[M+H]^+$: 451.1406, found $[M+H]^+$: 451.1399.

4p.



mp：214-216 ℃; IR (KBr) (ν_{max} cm^{-1}): 3412 (OH), 3330 (NH_2), 1661 (C=O), 1511, 1458 (C=C, aromatic); ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.66 (s, 1H, OH), 7.63 (s, 2H, NH_2), 7.39 (d, *J* = 0.7 Hz, 1H, Ar-H), 7.11 (d, *J* = 8.4 Hz, 1H, Ar-H), 6.54 (dd, *J* = 8.3, 2.3 Hz, 1H, Ar-H), 6.43 (d, *J* = 2.3 Hz, 1H, Ar-H), 6.26 (dd, *J* = 3.0, 1.9 Hz, 1H, Ar-H), 5.93 (d, *J* = 3.1 Hz, 1H, Ar-H), 4.91 (s, 1H), 4.03 (m, 2H, CH_2), 1.12 (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, DMSO-d_6) δ 168.57, 161.89, 159.29, 157.48, 149.94, 141.60, 130.00, 114.25, 112.30, 110.53, 104.08, 102.53, 73.81, 58.92, 33.06, 14.76; HRMS (ESI) *m*/*z*：calcd for $C_{16}H_{15}NO_5$ $[M+H]^+$: 302.1028, found $[M+H]^+$: 302.1025.

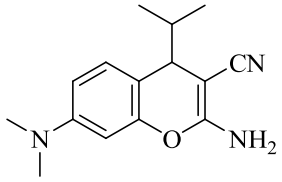
4q.



mp：206-208 ℃; IR (KBr) (ν_{max} cm^{-1}): 3410 (OH), 3299 (NH_2), 2979 (CH_3, CH_2), 1656 (C=O), 1503, 1459 (C=C, aromatic); ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.68 (s, 1H, OH), 7.62 (s, 2H, NH_2), 7.20 (dd, *J* = 5.1, 1.1 Hz, 1H, Ar-H), 7.15 (d, *J* = 8.4 Hz, 1H, Ar-H), 6.84 (dd, *J* = 5.0, 3.6 Hz, 1H, Ar-H), 6.73 (d, *J* = 3.3 Hz, 1H, Ar-H), 6.55 (dd, *J* = 8.4, 2.4 Hz, 1H, Ar-H), 6.44 (d, *J* = 2.2 Hz, 1H, Ar-H), 5.13 (s, 1H), 4.04 (m, 2H,

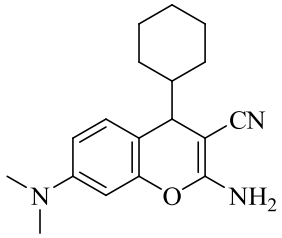
CH_2), 1.14 (t, *J* = 7.1 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, DMSO-d_6) δ 168.48, 161.59, 157.43, 153.85, 149.66, 130.07, 126.93, 123.82, 122.94, 116.67, 112.49, 102.48, 77.34, 59.02, 34.34, 14.75; HRMS (ESI) *m*/*z*：calcd for $C_{16}H_{15}NO_4S$ $[M+H]^+$: 318.0800, found $[M+H]^+$: 318.0797.

4r.



mp：192-194 ℃; IR (KBr) (ν_{max} cm^{-1}): 3440, 3319 (NH_2), 2966, 2868 (CH_3, CH_2), 2172 (CN), 1645 (vinyl nitrile), 1595, 1557, 1522 (C=C, aromatic); ^1H NMR (500 MHz, DMSO-d_6) δ 6.98 (d, *J* = 8.5 Hz, 1H, Ar-H), 6.72 (s, 2H, NH_2), 6.52 (dd, *J* = 8.5, 2.5 Hz, 1H, Ar-H), 6.22 (d, *J* = 2.5 Hz, 1H, Ar-H), 3.24 (d, *J* = 3.4 Hz, 1H), 2.88 (s, 6H, 2×CH_3), 1.79 (m, 1H), 0.82 (d, *J* = 6.8 Hz, 3H, CH_3), 0.72 (d, *J* = 6.8 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.86, 151.10, 150.43, 129.13, 122.26, 110.87, 109.16, 98.96, 52.79, 40.93, 36.86, 19.19, 18.15; HRMS (ESI) *m*/*z*：calcd for $C_{15}H_{20}N_3O$ $[M+H]^+$: 258.1606, found $[M+H]^+$: 258.1603.

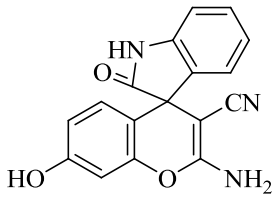
4s.



mp：148-150 ℃; IR (KBr) (ν_{max} cm^{-1}): 3486, 3307, 3175 (NH_2), 2922, 2851 (CH_3, CH_2), 2176 (CN), 1638 (vinyl nitrile), 1595, 1560, 1520

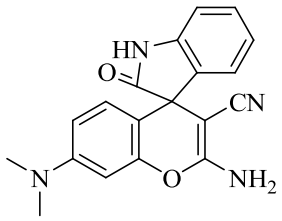
(C=C, aromatic); ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.96 (d, J = 8.5 Hz, 1H, Ar-H), 6.71 (s, 2H, NH2), 6.52 (dd, J = 8.5, 2.4 Hz, 1H, Ar-H), 6.21 (d, J = 2.4 Hz, 1H, Ar-H), 3.20 (d, J = 3.3 Hz, 1H), 2.88 (s, 6H, 2×CH_3), 1.62 (dt, J = 25.2, 13.8 Hz, 4H), 1.39 (m, 2H), 1.11 (dd, J = 25.8, 12.9 Hz, 2H), 0.95 (m, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.84, 151.19, 150.38, 129.13, 122.27, 111.06, 109.11, 98.96, 53.33, 47.26, 29.33, 28.56, 26.41, 26.20, 14.21; HRMS (ESI) m/z：calcd for $C_{18}H_{23}N_3O$ $[M+H]^+$: 298.1919, found $[M+H]^+$: 298.1915.

4t.



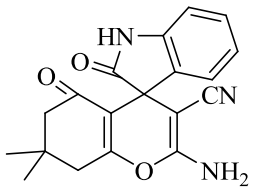
mp：238-240 ℃; IR (KBr) (ν_{max} cm^{-1}): 3428 (OH, NH_2, NH), 2196 (CN), 1715 (C=O), 1620 (C=C, aromatic); ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.49 (s, 1H, NH), 9.87 (s, 1H, OH), 7.26 (td, J = 7.6, 1.3 Hz, 1H, Ar-H), 7.16 (s, 2H, NH_2), 7.02 (m, 2H, Ar-H), 6.93 (d, J = 7.7 Hz, 1H, Ar-H), 6.47 (dd, J = 6.7, 2.2 Hz, 2H, Ar-H), 6.31 (m, 1H, Ar-H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 179.49, 161.76, 158.25, 149.77, 142.30, 135.04, 129.25, 127.86, 125.10, 122.94, 119.02, 113.16, 111.32, 110.17, 102.91, 54.62, 50.31; HRMS (ESI) m/z：calcd for $C_{17}H_{11}N_3O_3$ $[M+H]^+$: 328.0698, found $[M+H]^+$: 328.0701.

4u.



mp：>300 ℃; IR (KBr) (ν_{max} cm^{-1}): 3467, 3319 (NH_2, NH), 2203 (CN), 1716 (C=O), 1655, 1628 (C=C, aromatic); ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.44 (s, 1H, NH), 7.24 (ddd, *J* = 7.8, 6.9, 2.2 Hz, 1H, Ar-H), 7.09 (s, 2H, NH_2), 6.99 (dd, *J* = 9.8, 3.8 Hz, 2H，Ar-H), 6.92 (d, *J* = 7.7 Hz, 1H, Ar-H), 6.41 (dd, *J* = 8.8, 2.5 Hz, 1H, Ar-H), 6.28 (d, *J* = 4.6 Hz, 1H, Ar-H), 6.27 (d, *J* = 1.4 Hz, 1H, Ar-H), 2.86 (s, 6H, 2×CH_3); ^{13}C NMR (126 MHz, DMSO-d_6) *δ* 179.68, 161.95, 151.17, 149.87, 142.32, 135.26, 129.13, 127.25, 125.04, 122.84, 119.19, 110.10, 109.97, 107.86, 99.05, 54.90, 50.23; HRMS (ESI) *m*/*z*：calcd for $C_{19}H_{16}N_4O_2$ $[M+H]^+$: 355.1171, found $[M+H]^+$: 355.1168.

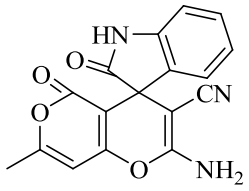
4v.



mp：269-271 ℃; IR (KBr) (ν_{max} cm^{-1}): 3315, 3140 (NH_2, NH), 2959, 2926, 2885 (CH_3, CH_2), 2192 (CN), 1722 (C=O), 1682 (C=C vinyl nitrile), 1655, 1604(C=C, aromatic); ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.37 (s, 1H, NH), 7.20 (s, 2H, NH_2), 7.12 (t, *J* = 7.4 Hz, 1H, Ar-H), 6.96 (d, *J* = 7.2 Hz, 1H, Ar-H), 6.88 (t, *J* = 7.4 Hz, 1H, Ar-H), 6.77 (d, *J* = 7.7 Hz, 1H, Ar-H), 2.54 (dd, *J* = 5.6 Hz, 2H), 2.12 (dd, *J* = 37.8, 16.0 Hz, 2H), 1.02 (s,

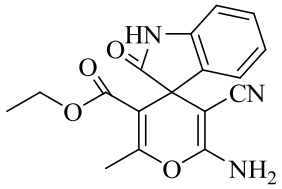
3H, CH_3), 0.99 (s, 3H, CH_3); HRMS (ESI) *m*/*z*： calcd for $C_{19}H_{17}N_3O_3$ $[M+H]^+$: 336.1348, found $[M+H]^+$: 336.1343.

4w.



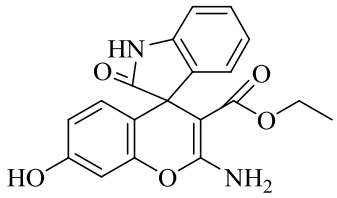
mp：278-279 ℃; IR (KBr) (ν_{max} cm^{-1}): 3455, 3335 (NH_2, NH), 2199 (CN), 1713 (C=O), 1617 (C=C vinyl nitrile); ^1H NMR (500 MHz, DMSO-d_6) δ 10.58 (s, 1H, NH), 7.44 (s, 2H, NH_2), 7.20 (t, *J* = 7.7 Hz, 1H, Ar-H), 7.11 (d, *J* = 7.3 Hz, 1H, Ar-H), 6.94 (t, *J* = 7.5 Hz, 1H, Ar-H), 6.83 (d, *J* = 7.7 Hz, 1H, Ar-H), 6.36 (s, 1H, =CH), 2.25 (s, 3H, CH_3); HRMS (ESI) *m*/*z*： calcd for $C_{17}H_{11}N_3O_4$ $[M+H]^+$: 322.0828, found $[M+H]^+$: 322.0828.

4x.



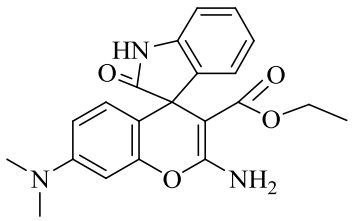
mp：258-260 ℃; IR (KBr) (ν_{max} cm^{-1}): 3373, 3190 (NH_2, NH), 2980 (CH_3, CH_2), 2198 (CN), 1729 (C=O), 1605 (C=C, aromatic); ^1H NMR (500 MHz, DMSO-d_6) δ 10.40 (s, 1H, NH), 7.19 (dd, *J* = 8.1, 7.2 Hz, 1H, Ar-H), 7.14 (s, 2H, NH_2), 7.06 (d, *J* = 7.2 Hz, 1H, Ar-H), 6.94 (t, *J* = 7.5 Hz, 1H, Ar-H), 6.80 (d, *J* = 7.7 Hz, 1H, Ar-H), 3.77 (m, 2H, CH_2), 2.32 (s, 3H, CH_3), 0.79 (t, *J* = 7.1 Hz, 3H, CH_3); HRMS (ESI) *m*/*z*： calcd for $C_{17}H_{15}N_3O_4$ $[M+H]^+$: 348.0960, found $[M+H]^+$: 348.0957.

4y.



mp：290-292 ℃; IR (KBr) (ν_{max} cm^{-1}): 3421 (OH, NH_2, NH), 2959 (CH_3, CH_2), 1699 (C=O), 1621 (C=C, aromatic); ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.31 (s, 1H, NH), 9.78 (s, 1H, OH), 7.85 (s, 2H, NH_2), 7.13 (m, 1H, Ar-H), 6.84 (dd, J = 14.4, 6.8 Hz, 3H, Ar-H), 6.43 (s, 3H, Ar-H), 3.71 (m, 2H, CH_2), 0.73 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, DMSO-d_6) δ 181.46, 168.20, 161.49, 157.81, 148.61, 142.40, 140.01, 127.94, 127.67, 123.09, 122.01, 113.07, 112.75, 109.38, 102.36, 73.84, 58.91, 49.84, 13.54; HRMS (ESI) *m*/*z*：calcd for $C_{19}H_{16}N_2O_5$ $[M+H]^+$: 353.1137, found $[M+H]^+$: 353.1136.

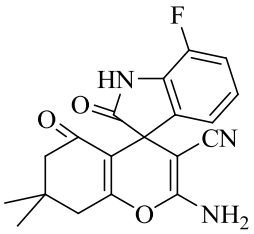
4z.



mp：276-278 ℃; IR (KBr) (ν_{max} cm^{-1}): 3397, 3298, 3082 (NH_2, NH), 1717 (C=O), 1671, 1631, 1612 (C=C, aromatic); ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.29 (s, 1H, NH), 7.82 (s, 2H, NH_2), 7.12 (td, J = 7.5, 1.6 Hz, 1H, Ar-H), 6.82 (m, 3H, Ar-H), 6.41 (t, J = 6.0 Hz, 2H, Ar-H), 6.25 (d, J = 1.8 Hz, 1H, Ar-H), 3.71 (m, 2H, CH_2), 2.86 (s, 6H, 2×CH_3), 0.73 (t, J = 7.1 Hz, 3H, CH_3); ^{13}C NMR (126 MHz, DMSO-d_6) δ 181.61,

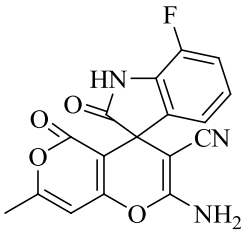
168.28, 161,73, 150.80, 148.69, 142,40, 140.15, 127.54, 127.41, 123.03, 121.94, 110.02, 109.45, 109.29, 98.62, 73.96, 58.87, 49.71, 13.55; HRMS (ESI) *m*/*z*：calcd for $C_{21}H_{21}N_3O_4$ $[M+H]^+$: 380.1610, found $[M+H]^+$: 380.1608.

4aa.



mp：>300 ℃; IR (KBr) (ν_{max} cm^{-1}): 3357, 3276, 3167 (NH_2, NH), 2961, 2927 (CH_3, CH_2), 2197 (CN), 1732 (C=O), 1682 (C=C vinyl nitrile), 1656, 1602(C=C, aromatic); ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.92 (s, 1H, NH), 7.32 (s, 2H, NH_2), 7.08 (m, 1H, Ar-H), 6.93 (td, *J* = 7.9, 4.6 Hz, 1H, Ar-H), 6.87 (d, *J* = 7.2 Hz, 1H, Ar-H), 2.58 (d, *J* = 4.8 Hz, 2H, CH_2), 2.16 (d, *J* = 19.4 Hz, 2H, CH_2), 1.04 (s, 3H, CH_3), 1.01 (s, 3H, CH_3); HRMS (ESI) *m*/*z*：calcd for $C_{19}H_{16}FN_3O_3$ $[M+H]^+$: 376.1073, found [M+H^+: 376.1063.

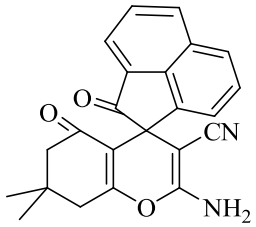
4bb.



mp：>300 ℃; IR (KBr) (ν_{max} cm^{-1}): 3461, 3262 (NH_2, NH), 2199 (CN), 1715 (C=O); ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.12 (s, 1H, NH), 7.53 (s,

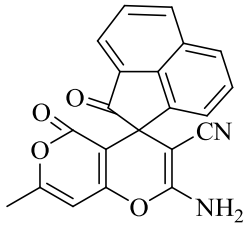
2H, NH_2), 7.14 (m, 1H, Ar-H), 7.01 (d, *J* = 7.0 Hz, 1H, Ar-H), 6.96 (m, 1H, Ar-H), 6.38 (s, 1H, =CH), 2.26 (s, 3H, CH_3); HRMS (ESI) *m*/*z*：calcd for $C_{17}H_{10}FN_3O_4$ $[M+H]^+$: 340.0734, found $[M+H]^+$: 340.0731.

4cc.



mp：260-261 ℃; IR (KBr) (ν_{max} cm^{-1}): 3360, 3170 (NH_2, NH), 2954 (CH_3, CH_2), 2194 (CN), 1665 (C=O), 1610 (C=C, aromatic); ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.26 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.93 (dd, *J* = 7.6, 3.9 Hz, 1H, Ar-H), 7.83 (m, 1H, Ar-H), 7.65 (dd, *J* = 8.1, 7.2 Hz, 1H, Ar-H), 7.39 (d, *J* = 6.9 Hz, 1H, Ar-H), 7.31 (s, 2H, NH_2), 2.63 (dd, 1H), 2.08 (d, *J* = 7.9 Hz, 1H), 1.04 (s, 3H, CH_3), 1.02 (s, 3H, CH_3); HRMS (ESI) *m*/*z*：calcd for $C_{23}H_{18}N_2O_3$ $[M+H]^+$: 371.1396, found $[M+H]^+$: 371.1393.

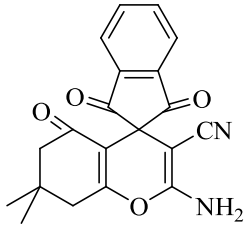
4dd.



mp：>300 ℃; IR (KBr) (ν_{max} cm^{-1}): 3466, 3339 (NH_2, NH), 2183 (CN), 1708 (C=O), 1630 (C=C, aromatic); ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.33 (d, *J* = 8.1 Hz, 1H, Ar-H), 8.00 (dd, *J* = 7.6, 3.5 Hz, 2H, Ar-H), 7.87 (s, 1H, Ar-H), 7.70 (s, 1H, Ar-H), 7.54 (s, 1H, Ar-H), 7.53 (s, 2H, NH_2),

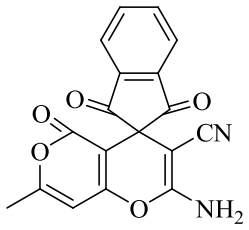
6.43 (s, 1H, =CH), 2.25 (s, 3H, CH_3); HRMS (ESI) *m*/*z*：calcd for $C_{21}H_{12}N_2O_4$ $[M+H]^+$: 357.0875, found $[M+H]^+$: 357.0875.

4ee.



mp：289-291 ℃; IR (KBr) (ν_{max} cm^{-1}): 3375, 3194 (NH_2, NH), 2957 (CH_3, CH_2), 2189 (CN), 1656 (C=O), 1593 (C=C, aromatic); ^1H NMR (500 MHz, DMSO-d_6) δ 8.04 (dd, *J* = 5.8, 3.0 Hz, 2H, Ar-H), 8.00 (dd, *J* = 5.8, 3.0 Hz, 2H, Ar-H), 7.64 (s, 2H, NH_2), 2.62 (s, 1H), 2.20 (s, 1H), 1.04 (s, 3H); HRMS (ESI) *m*/*z*： calcd for $C_{20}H_{16}N_2O_4$ $[M+Na]^+$: 371.1008, found $[M+Na]^+$: 371.0997.

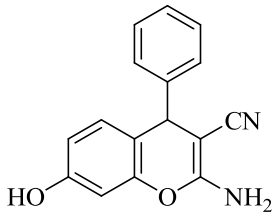
4ff.

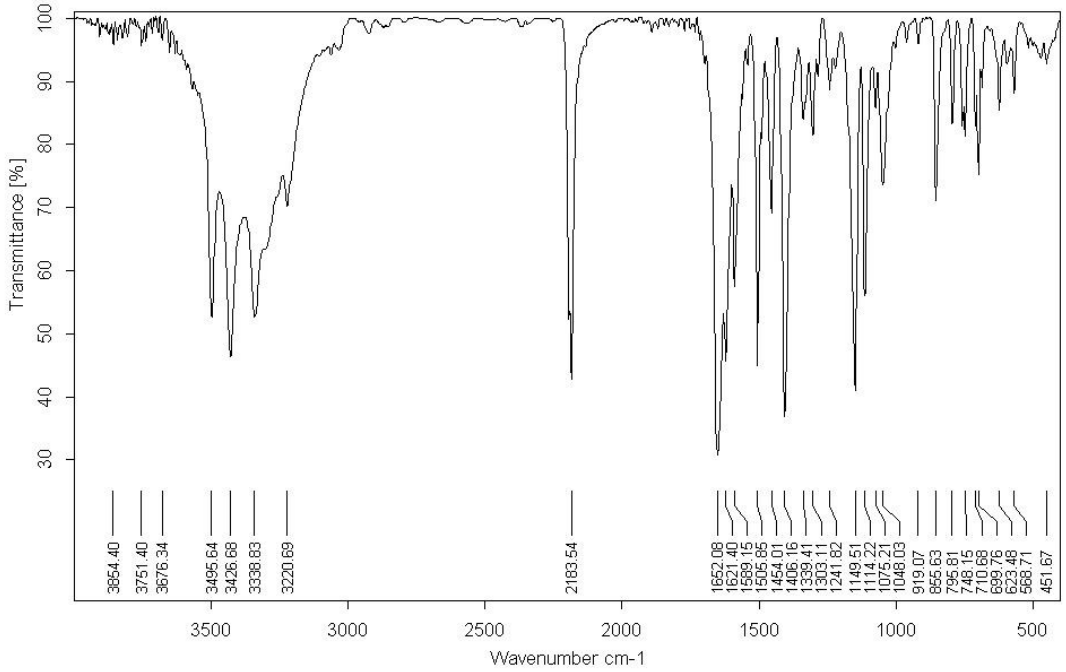


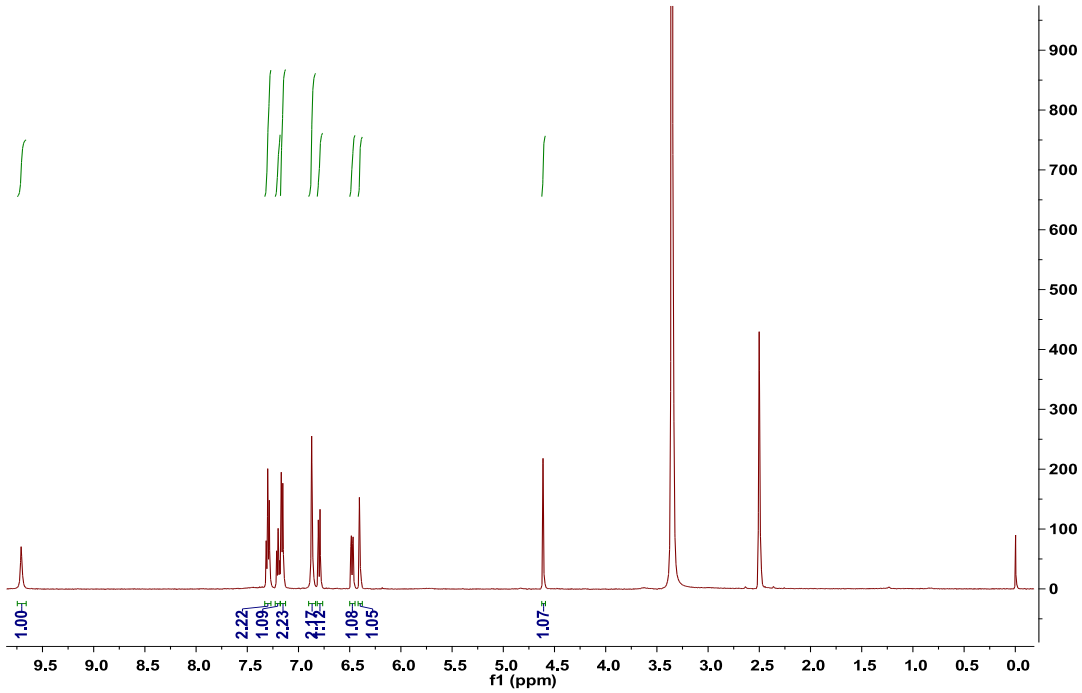
mp：290-292 ℃; IR (KBr) (ν_{max} cm^{-1}): 3351, 3164 (NH_2, NH), 2190 (CN), 1705 (C=O), 1630 (C=C, aromatic); ^1H NMR (500 MHz, DMSO-d_6) δ 8.09 (m, 4H, Ar-H), 7.88 (s, 2H, NH_2), 6.47 (s, 1H, =CH), 2.29 (s, 3H, CH_3); HRMS (ESI) *m*/*z*： calcd for $C_{18}H_{10}N_2O_5$ $[M+H]^+$: 335.0668, found $[M+H]^+$: 335.0668.

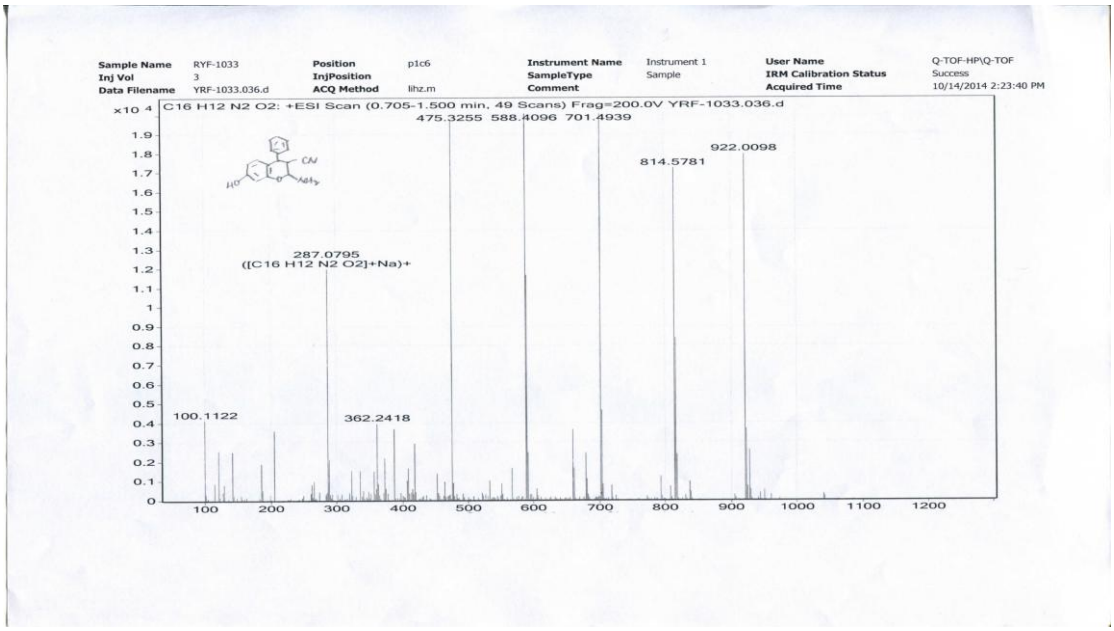
5. IR and NMR copies of 2-amino-4*H*-chromenes (4a-4ff)

4a.





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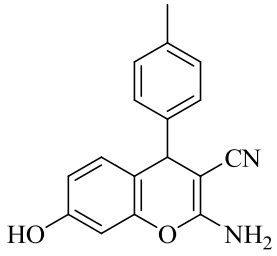
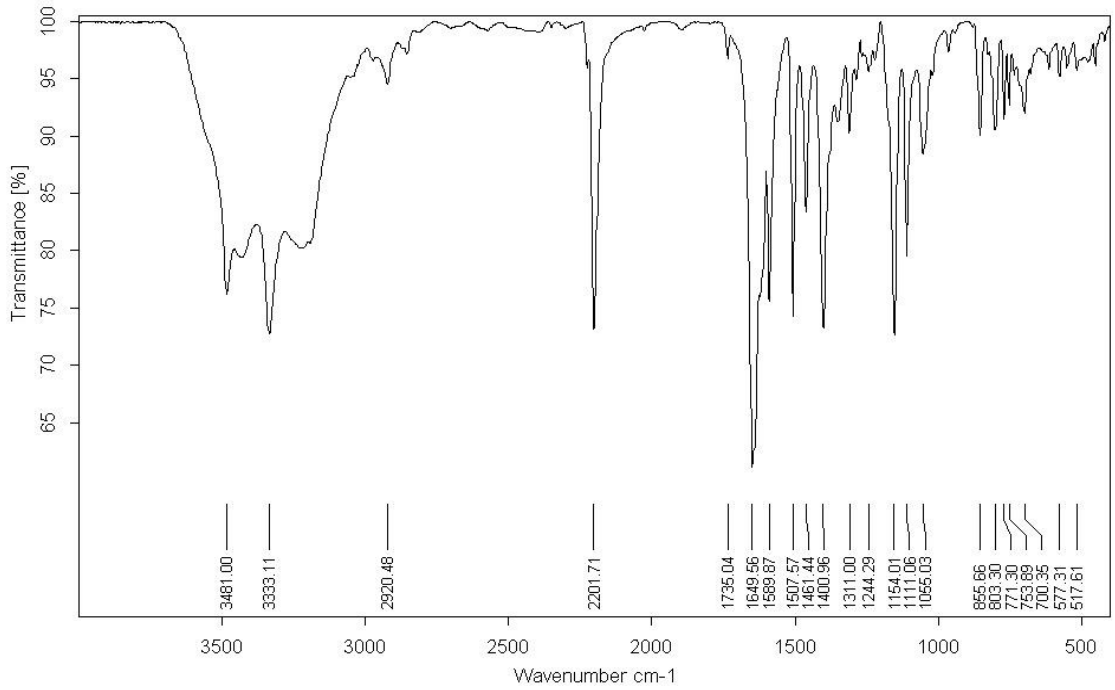
Inj Vol 3
Data Filename YRF-1033.036.d
Position p1c6
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 10/14/2014 2:23:40 PM
C16 H12 N2 O2: +ESI Scan (0.705-1.500 min, 49 Scans) Frag=200.0V YRF-1033.036.d
475.3255 588.4096 701.4939
922.0098
814.5781
287.0795
([C16 H12 N2 O2]+Na)+
100.1122
362.2418
x10 4

4b.


CN
HO
O
NH2


Transmittance [%]
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75
70
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2201.71
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1649.56
1589.87
1507.57
1461.44
1400.96
1311.00
1244.29
1154.01
1111.06
1055.03
855.66
803.30
771.30
753.89
700.35
577.31
517.61
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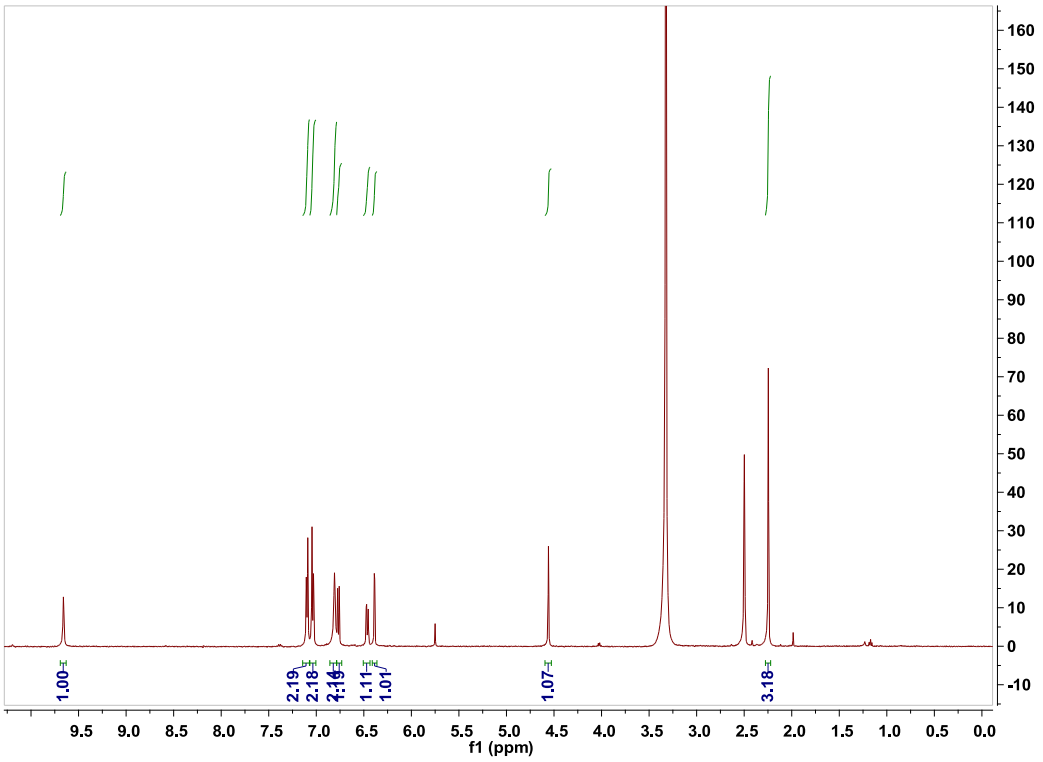
3000
2500
2000
1500
1000
500
Wavenumber cm-1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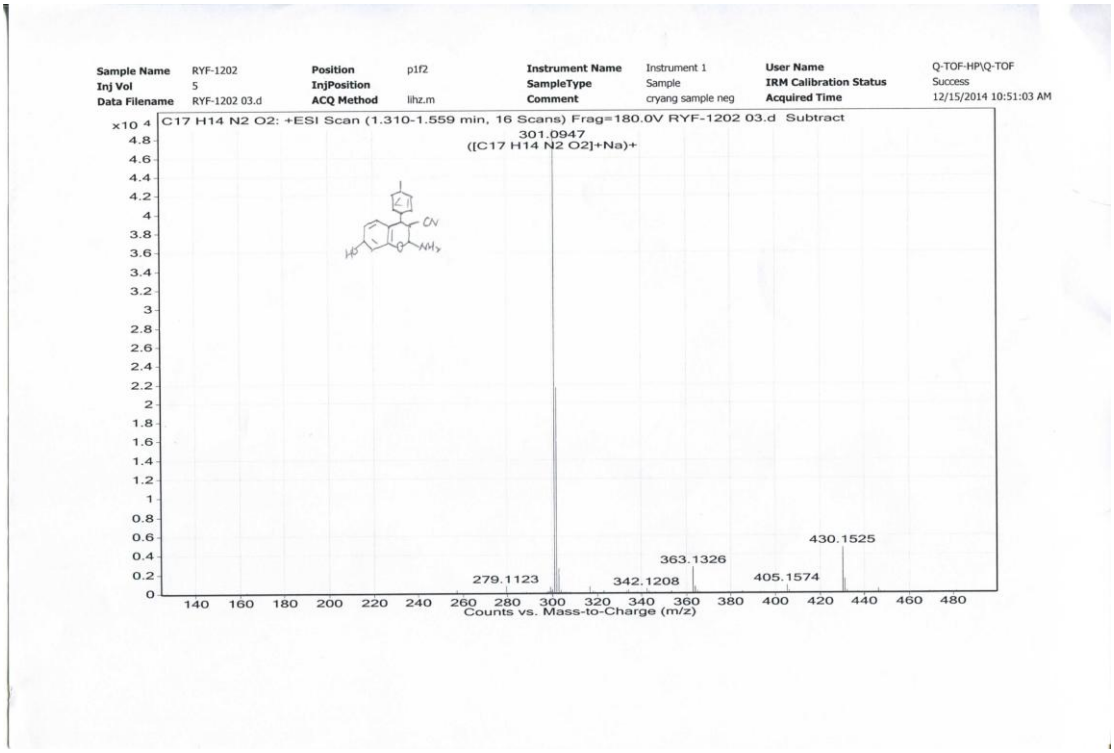
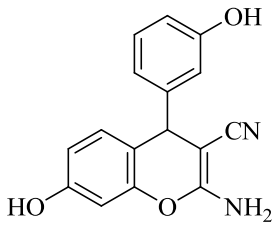
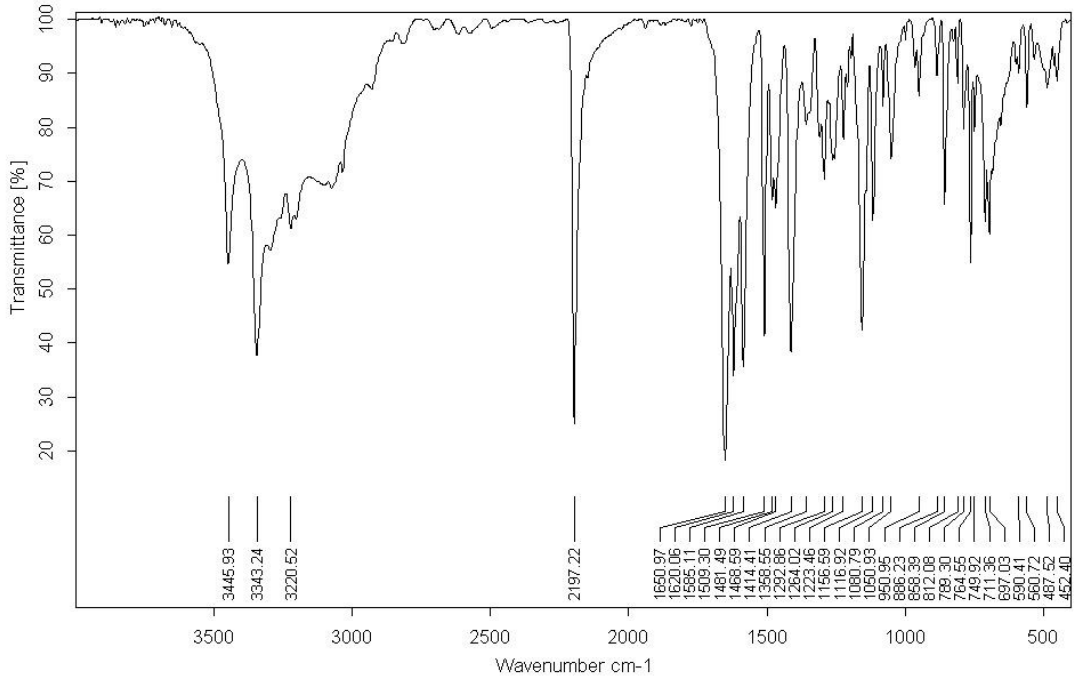
2.19
2.18
1.11
1.01
1.07
3.18
f1 (ppm)


Sample Name RYF-1202
Inj Vol 5
Data Filename RYF-1202 03.d
Position p1f2
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment cryang sample neg
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 12/15/2014 10:51:03 AM
C17 H14 N2 O2: +ESI Scan (1.310-1.559 min, 16 Scans) Frag=180.0V RYF-1202 03.d Subtract
301.0947
([C17 H14 N2 O2]+Na)+
279.1123
342.1208
363.1326
405.1574
430.1525
Counts vs. Mass-to-Charge (m/z)

4c.


OH
CN
HO
O
NH2


Transmittance [%]
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1620.06
1585.11
1509.30
1481.49
1468.59
1414.41
1358.55
1292.88
1264.02
1223.46
1156.59
1116.92
1080.79
1050.93
950.95
886.23
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812.08
789.30
764.55
749.92
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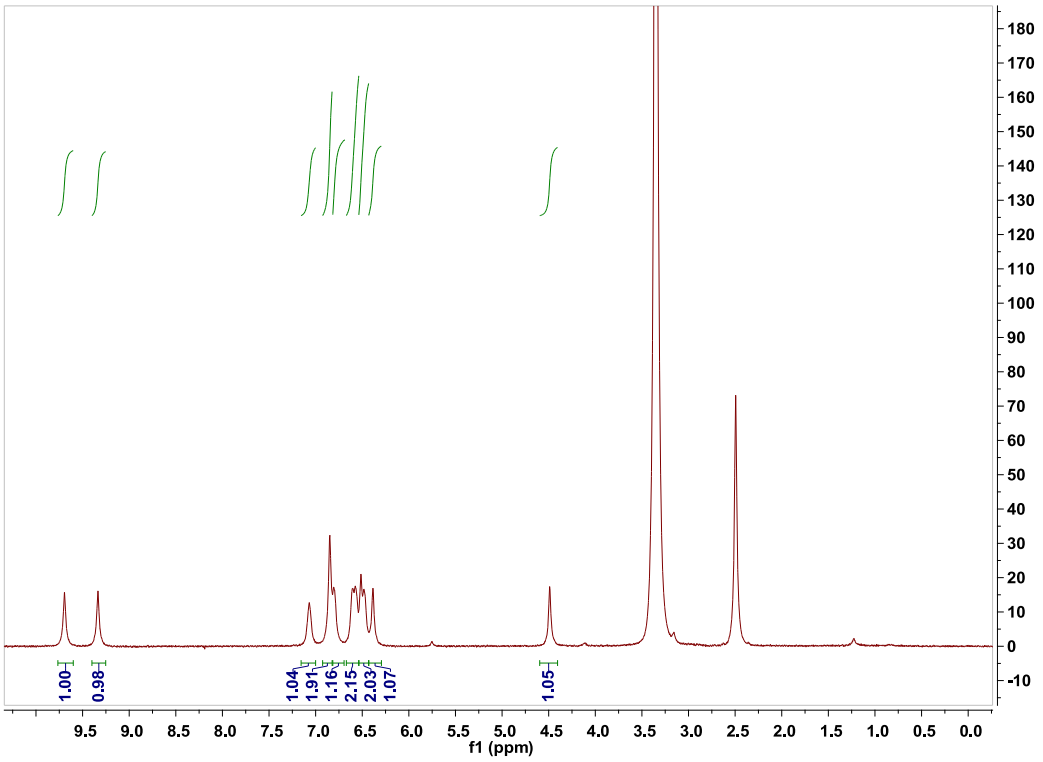
1000
500
Wavenumber cm-1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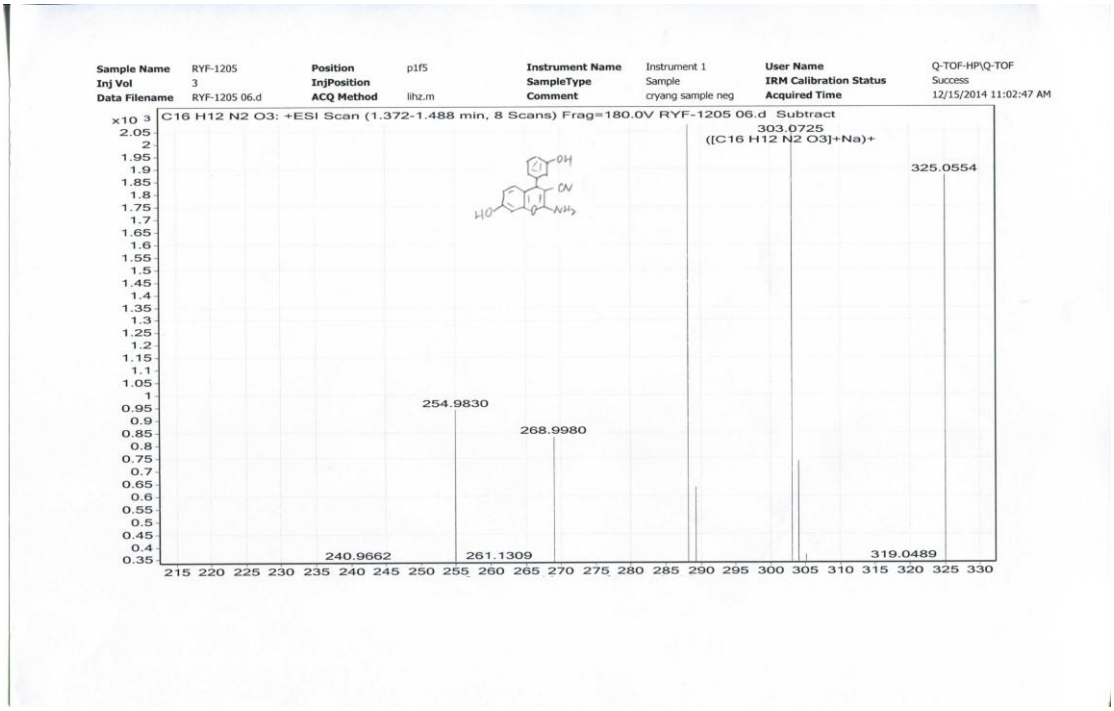
1.91
1.16
2.15
2.03
1.07
1.05
f1 (ppm)


Sample Name RYF-1205
Position p1f5
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 3
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename RYF-1205 06.d
ACQ Method lihz.m
Comment cryang sample neg
Acquired Time 12/15/2014 11:02:47 AM
C16 H12 N2 O3: +ESI Scan (1.372-1.488 min, 8 Scans) Frag=180.0V RYF-1205 06.d Subtract
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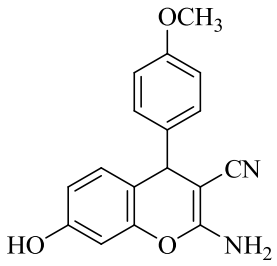
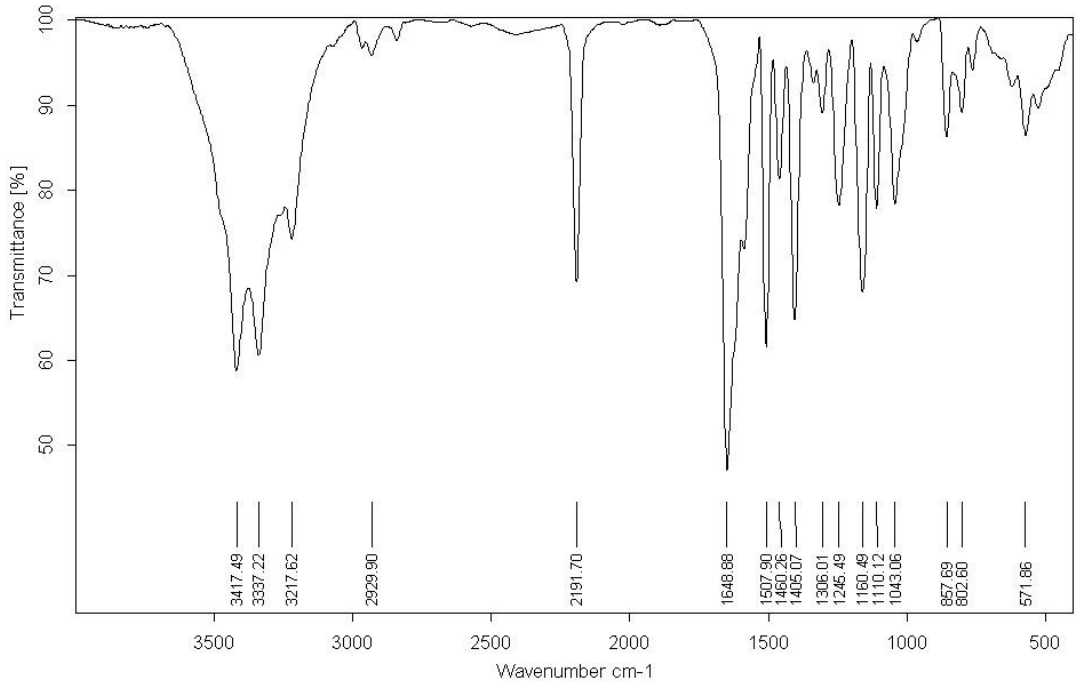
325.0554
254.9830
268.9980
240.9662
261.1309
319.0489

4d.


OCH3
CN
HO
O
NH2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2191.70
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1507.90
1460.26
1405.07
1306.01
1245.49
1160.49
1110.12
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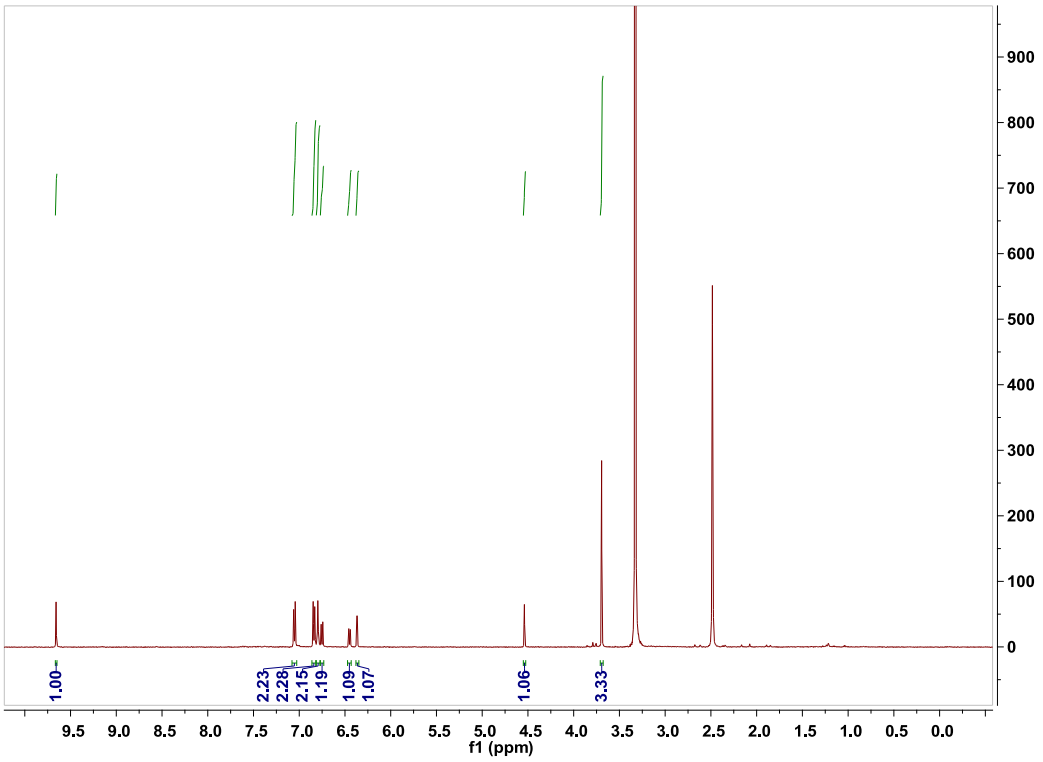
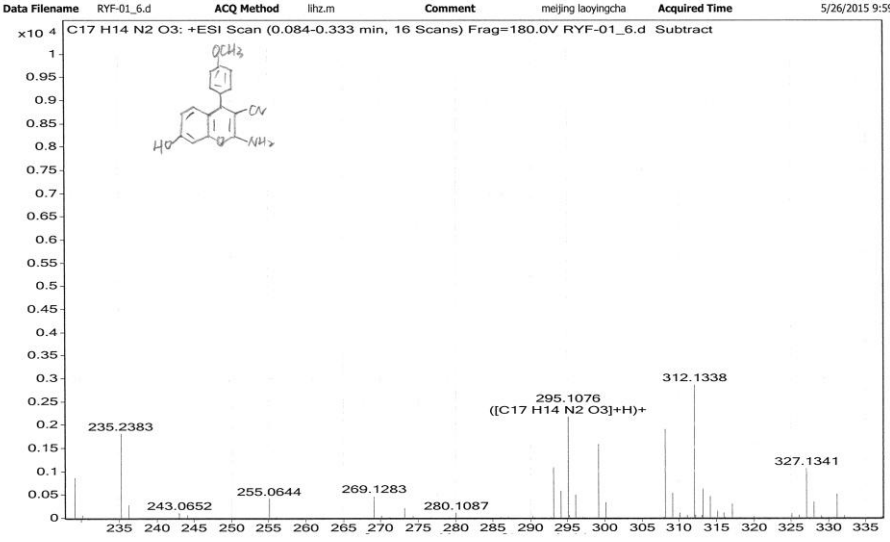
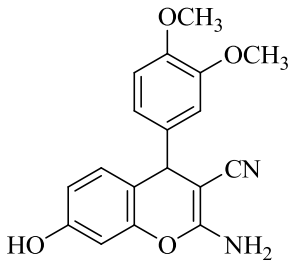
857.69
802.60
571.86
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

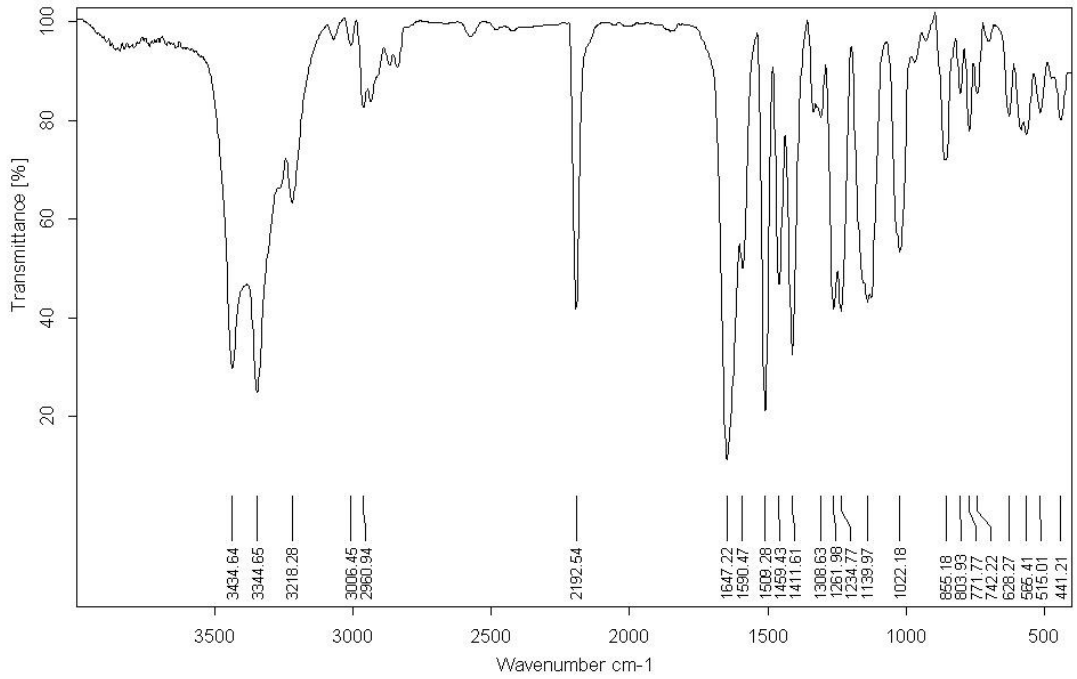


Sample Name	RYF-01	**Position**	p1f1	**Instrument Name**	Instrument 1	**User Name**	Q-TOF-HP\Q-TOF
Inj Vol	3	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	RYF-01_6.d	**ACQ Method**	lihz.m	**Comment**	meijing laoyingcha	**Acquired Time**	5/26/2015 9:59:48 AM



4e.


OCH3
OCH3
CN
HO
O
NH2


Transmittance [%]
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3344.65
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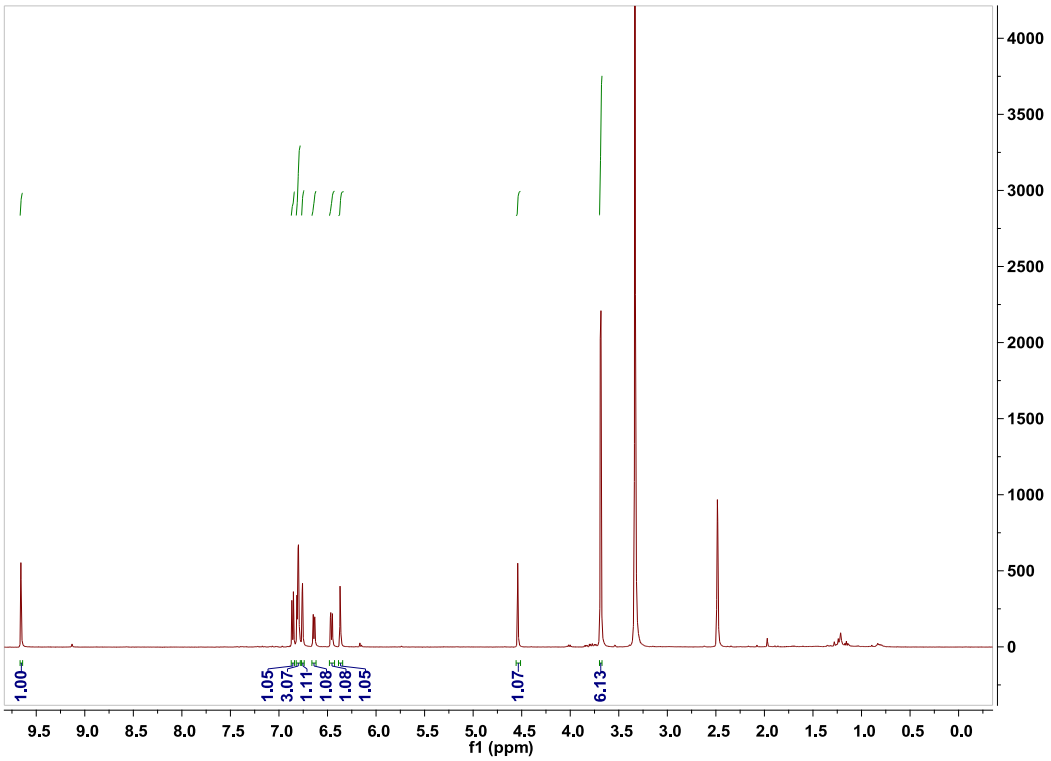
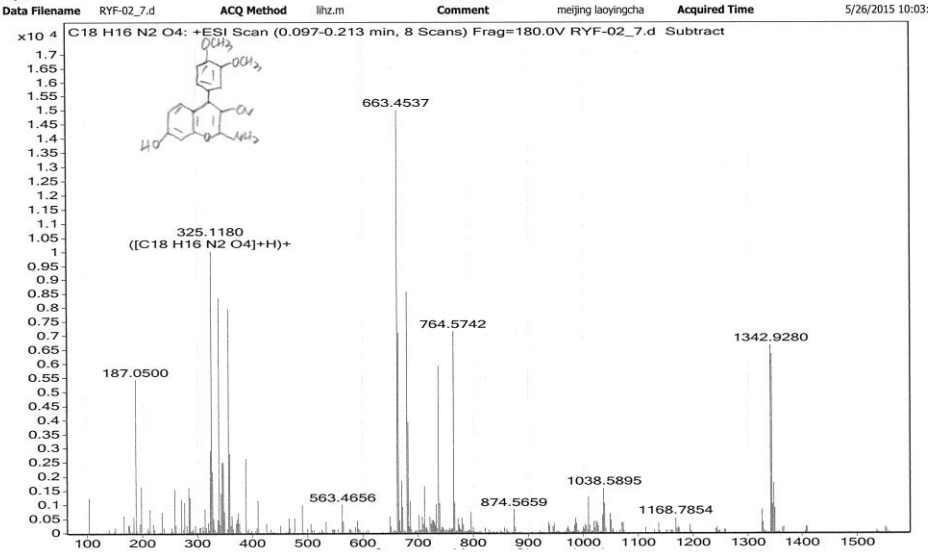
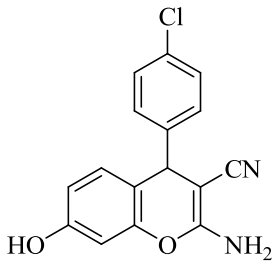
2960.94
2192.54
1647.22
1590.47
1509.28
1459.43
1411.61
1308.63
1261.98
1234.77
1139.97
1022.18
855.18
803.93
771.77
742.22
628.27
566.41
515.01
441.21
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

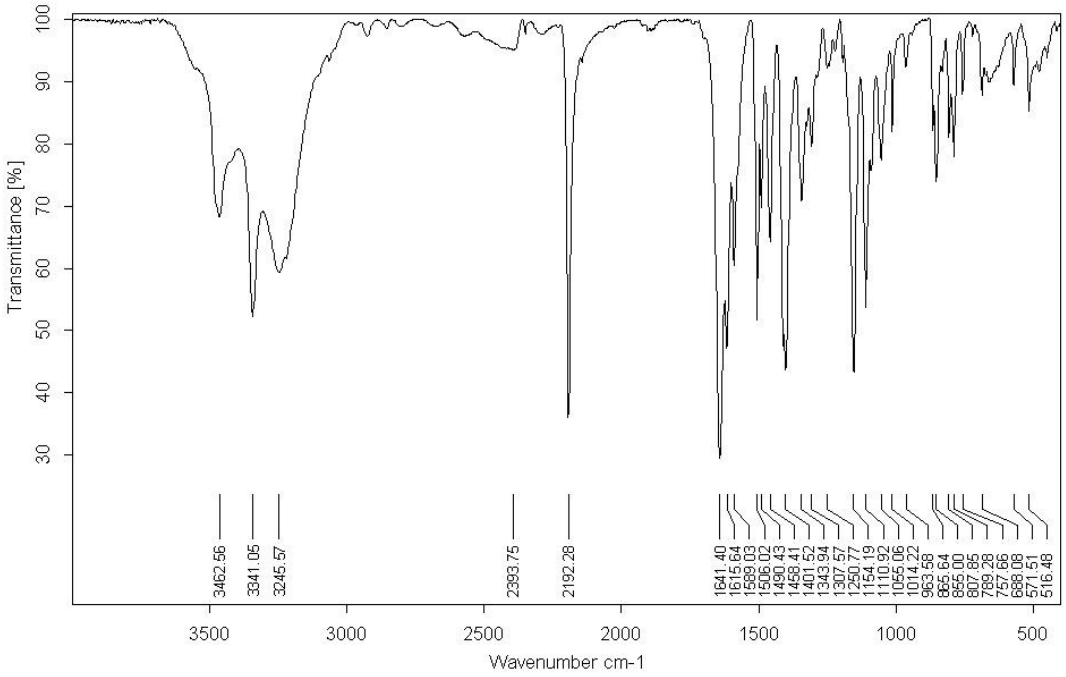


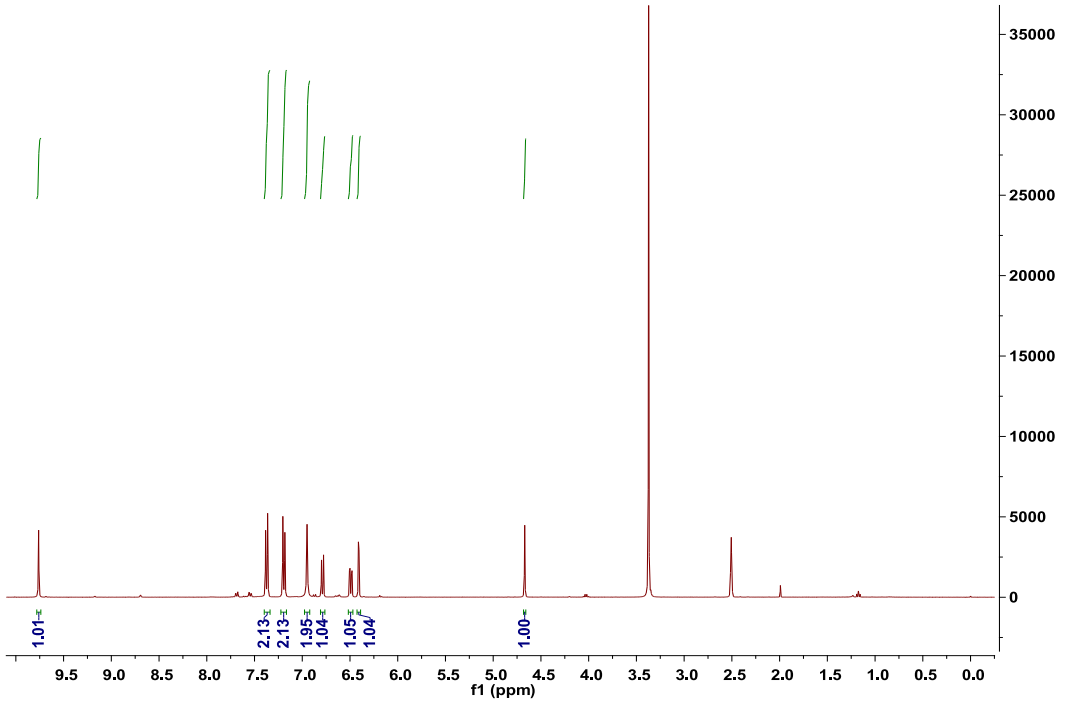
Sample Name	RYF-02	**Position**	p1f2	**Instrument Name**	Instrument 1	**User Name**	Q-TOF-HP\Q-TOF
Inj Vol	3	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	RYF-02_7.d	**ACQ Method**	lihz.m	**Comment**	meijing laoyingcha	**Acquired Time**	5/26/2015 10:03:29 AM

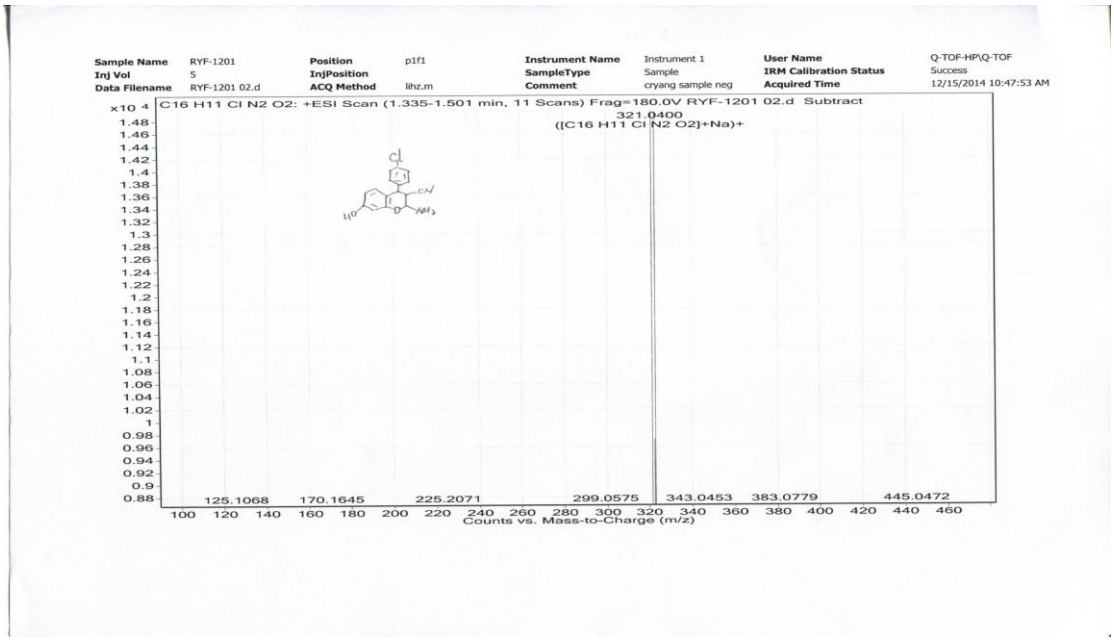


4f.

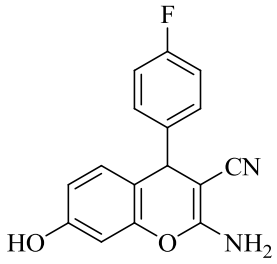

Cl
CN
HO
O
NH2

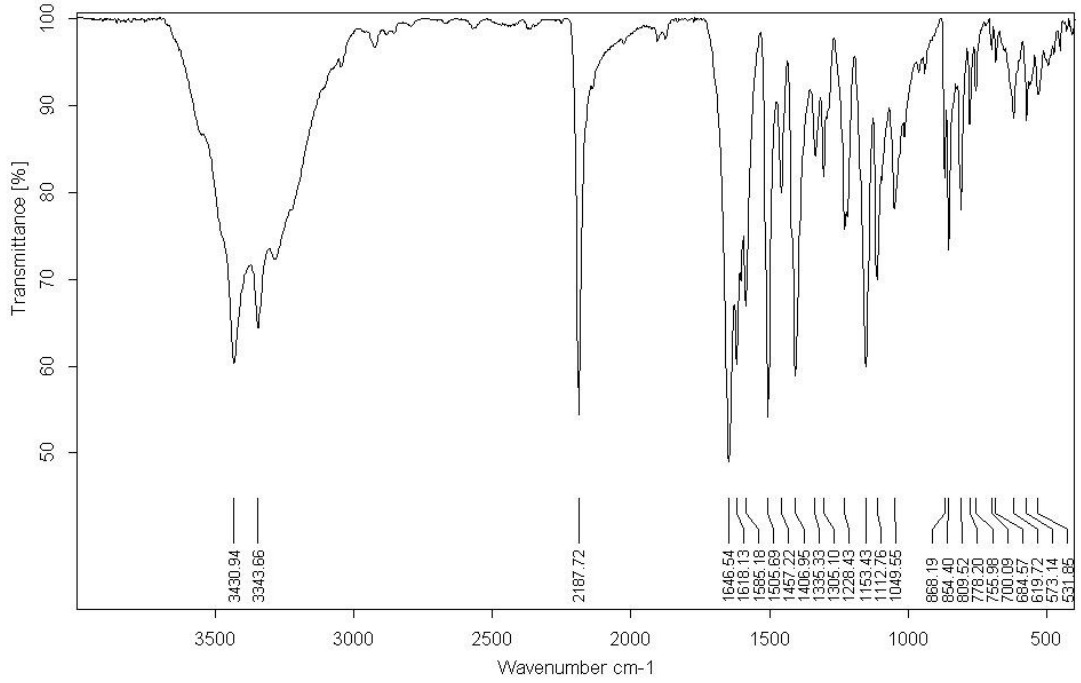

Transmittance [%]
100
90
80
70
60
50
40
30
3462.56
3341.05
3245.57
2393.75
2192.28
1641.40
1615.64
1589.03
1506.02
1490.43
1458.41
1401.52
1343.94
1307.57
1250.77
1154.19
1110.92
1055.06
1014.22
963.58
865.64
855.00
807.85
789.28
757.66
688.08
571.51
516.48
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

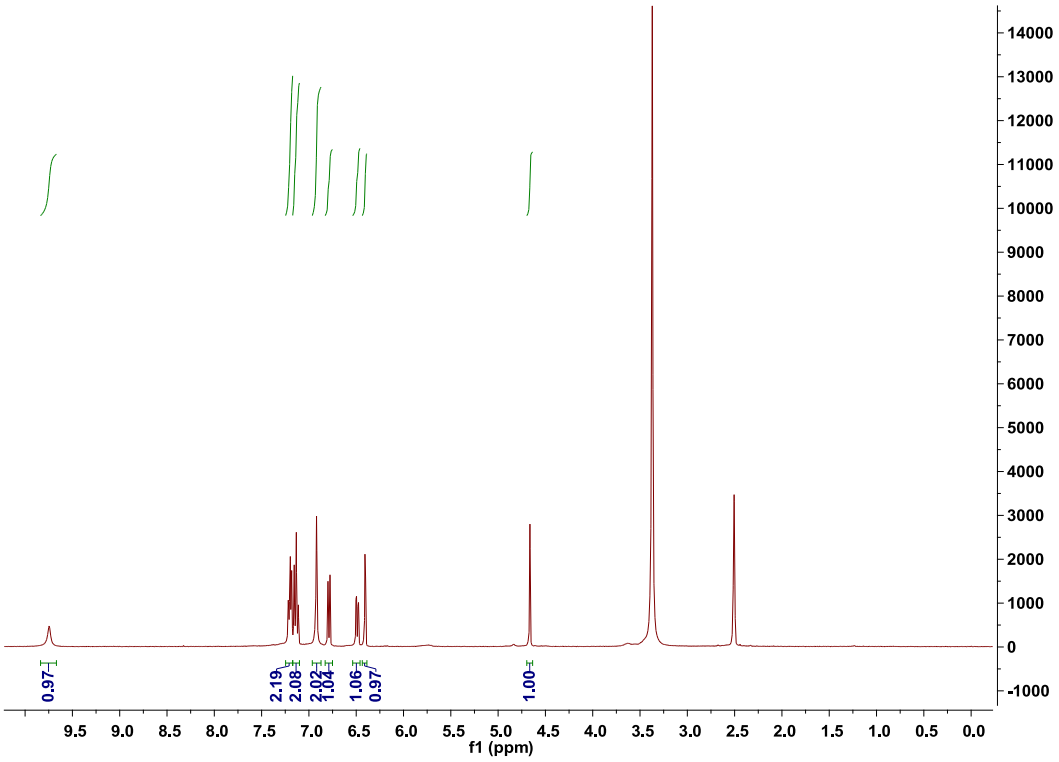

35000
30000
25000
20000
15000
10000
5000
0
1.01
2.13
2.13
1.95
1.04
1.05
1.04
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

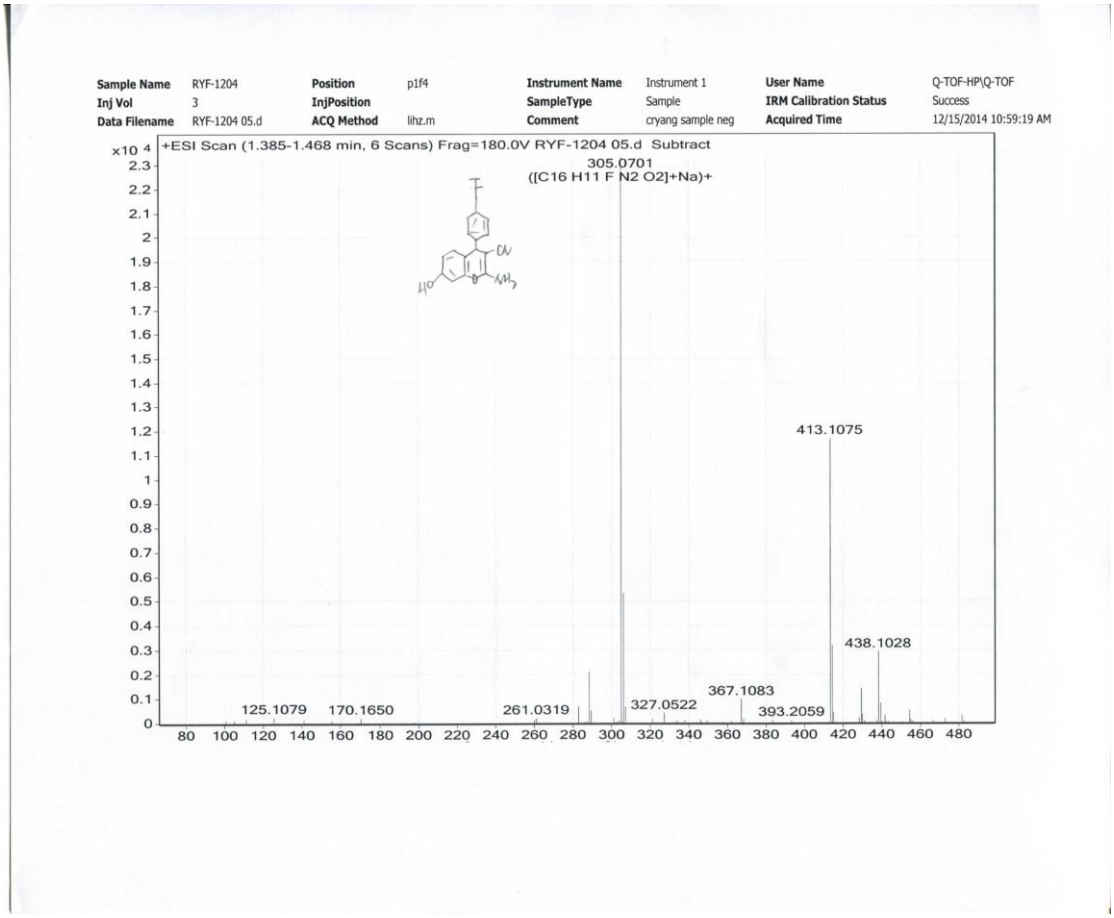

Sample Name RYF-1201
Position p1f1
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 5
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename RYF-1201 02.d
ACQ Method lihz.m
Comment cryang sample neg
Acquired Time 12/15/2014 10:47:53 AM
C16 H11 Cl N2 O2: +ESI Scan (1.335-1.501 min, 11 Scans) Frag=180.0V RYF-1201 02.d Subtract
321.0400
([C16 H11 Cl N2 O2]+Na)+
125.1068
170.1645
225.2071
299.0575
343.0453
383.0779
445.0472
Counts vs. Mass-to-Charge (m/z)

4g.

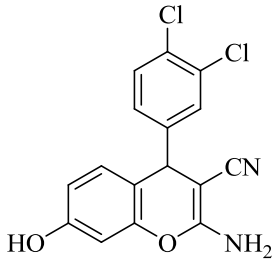

F
CN
HO
O
NH2

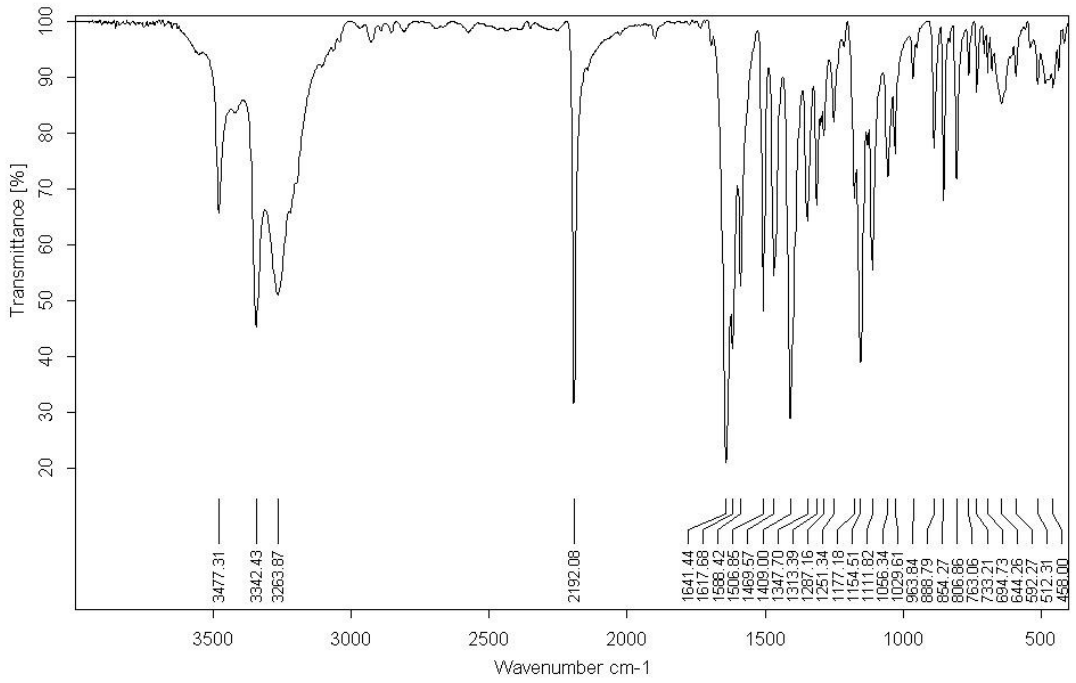

Transmittance [%]
100
90
80
70
60
50
3430.94
3343.66
2187.72
1646.54
1618.13
1585.18
1505.69
1457.22
1406.95
1335.33
1305.10
1228.43
1153.43
1112.76
1049.55
868.19
854.40
809.52
779.20
755.98
700.09
684.57
619.72
573.14
531.86
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

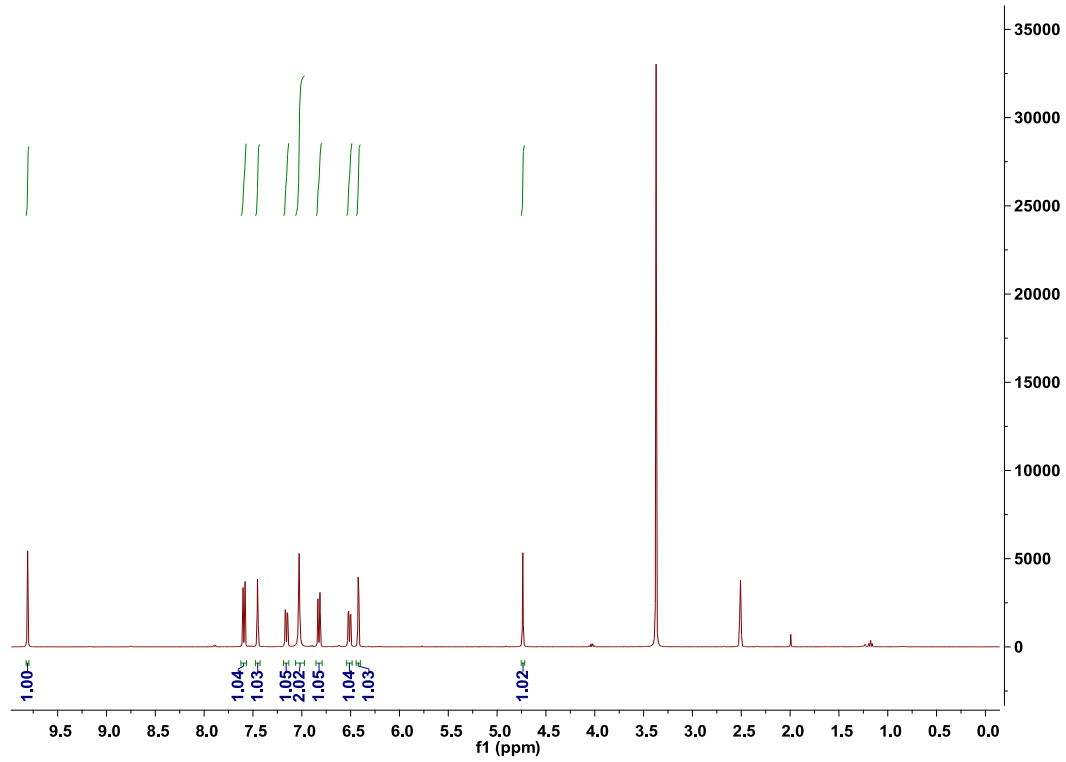

0.97
2.19
2.08
2.02
1.04
1.06
0.97
1.00
f1 (ppm)

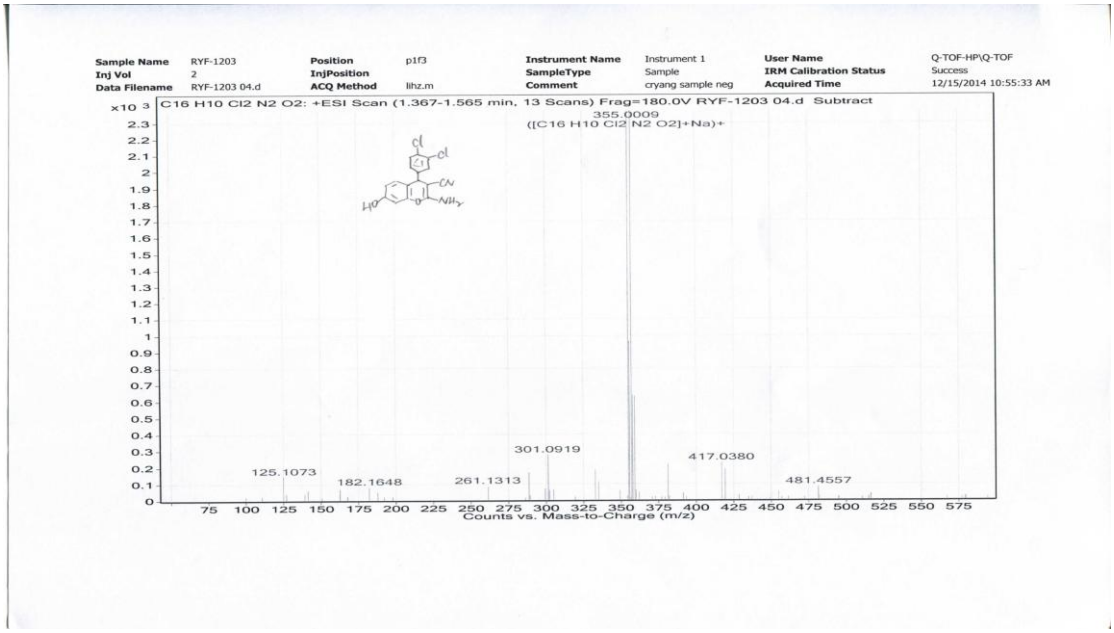

Sample Name RYF-1204
Position p1f4
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 3
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename RYF-1204 05.d
ACQ Method lihz.m
Comment cryang sample neg
Acquired Time 12/15/2014 10:59:19 AM
+ESI Scan (1.385-1.468 min, 6 Scans) Frag=180.0V RYF-1204 05.d Subtract
305.0701
([C16 H11 F N2 O2]+Na)+
413.1075
438.1028
367.1083
125.1079
170.1650
261.0319
327.0522
393.2059

4h.

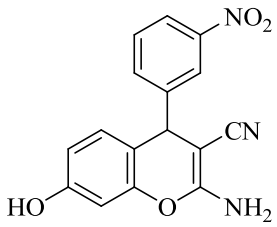

Cl
Cl
CN
HO
O
NH2

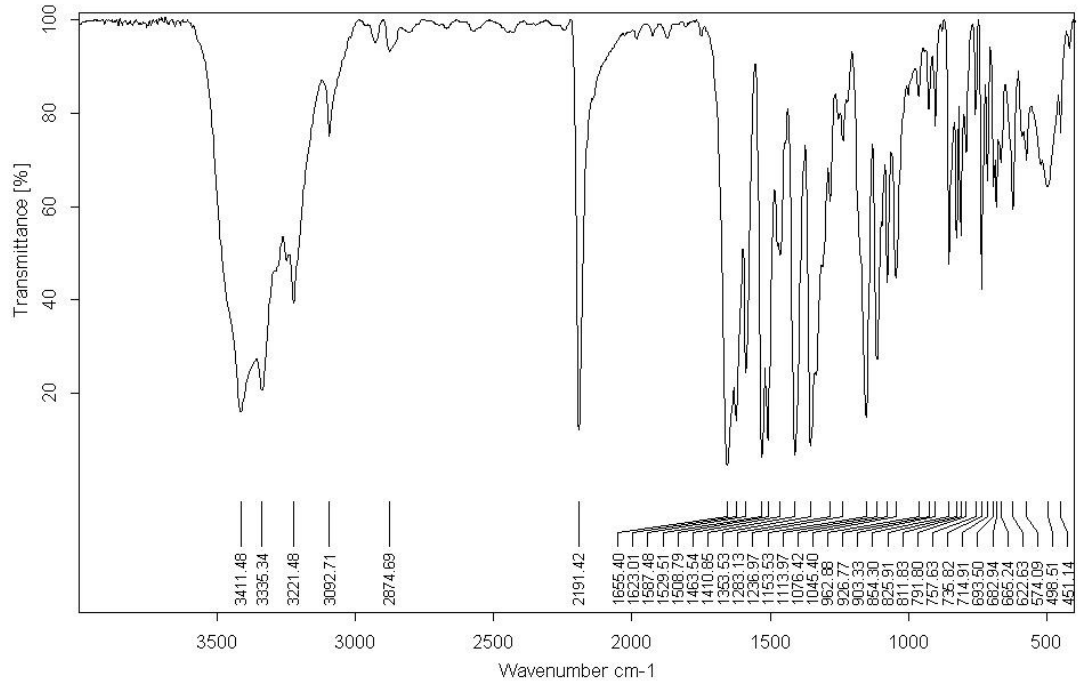

Transmittance [%]
100
90
80
70
60
50
40
30
20
3477.31
3342.43
3263.87
2192.08
1641.44
1617.68
1588.42
1506.85
1469.57
1409.00
1347.70
1313.39
1287.16
1251.34
1177.18
1154.51
1111.82
1056.34
1029.61
963.84
888.79
854.27
806.86
763.06
733.21
694.73
644.26
592.27
512.31
468.00
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

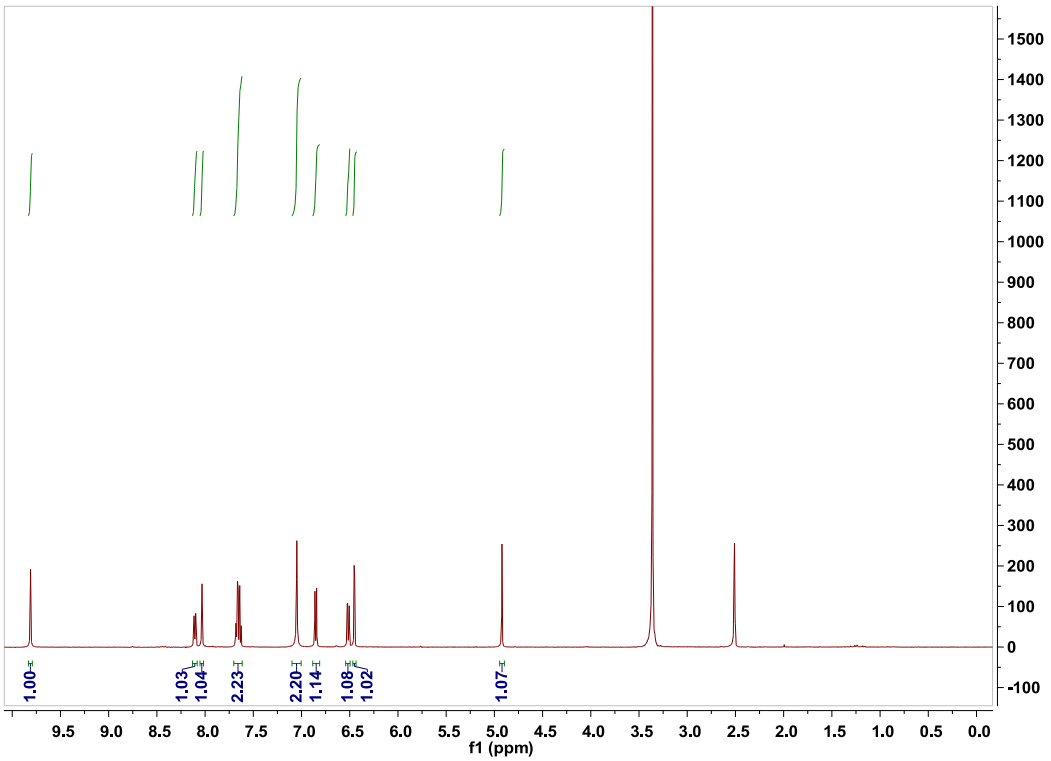

35000
30000
25000
20000
15000
10000
5000
0
1.00
1.04
1.03
1.05
2.02
1.05
1.04
1.03
1.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Sample Name RYF-1203
Inj Vol 2
Data Filename RYF-1203 04.d
Position p1f3
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment cryang sample neg
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 12/15/2014 10:55:33 AM
C16 H10 Cl2 N2 O2: +ESI Scan (1.367-1.565 min, 13 Scans) Frag=180.0V RYF-1203 04.d Subtract
355.0009
([C16 H10 Cl2 N2 O2]+Na)+
301.0919
417.0380
125.1073
182.1648
261.1313
481.4557
Counts vs. Mass-to-Charge (m/z)

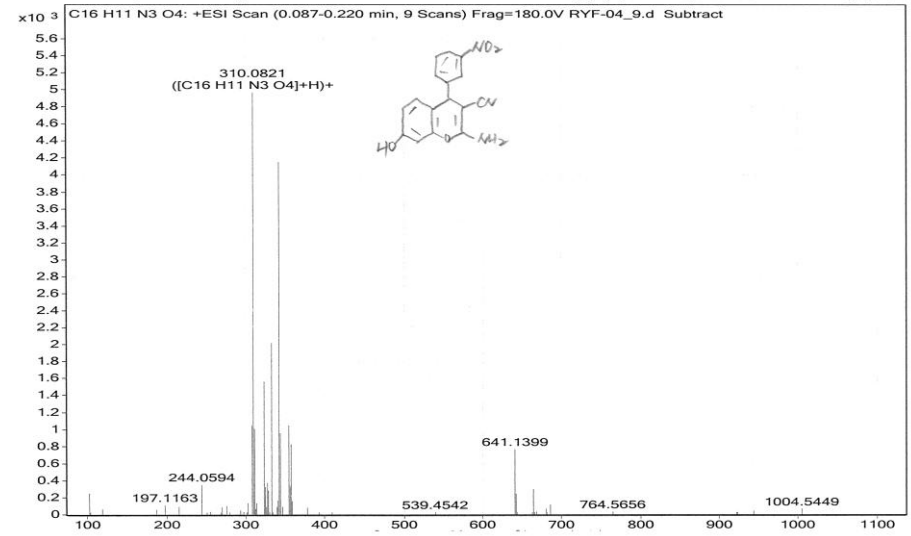
4i.


NO2
CN
HO
O
NH2

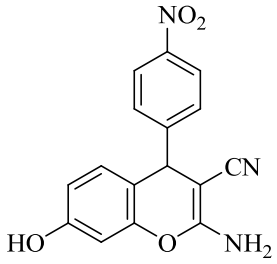

Transmittance [%]
100
80
60
40
20
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
3411.48
3335.34
3221.48
3092.71
2874.69
2191.42
1655.40
1623.01
1587.48
1529.51
1508.79
1463.54
1410.86
1363.53
1283.13
1236.97
1153.53
1113.97
1076.42
1045.40
962.88
926.77
903.33
854.30
825.91
811.83
791.80
757.63
735.82
714.91
693.50
682.94
665.24
622.63
574.09
498.51
451.14

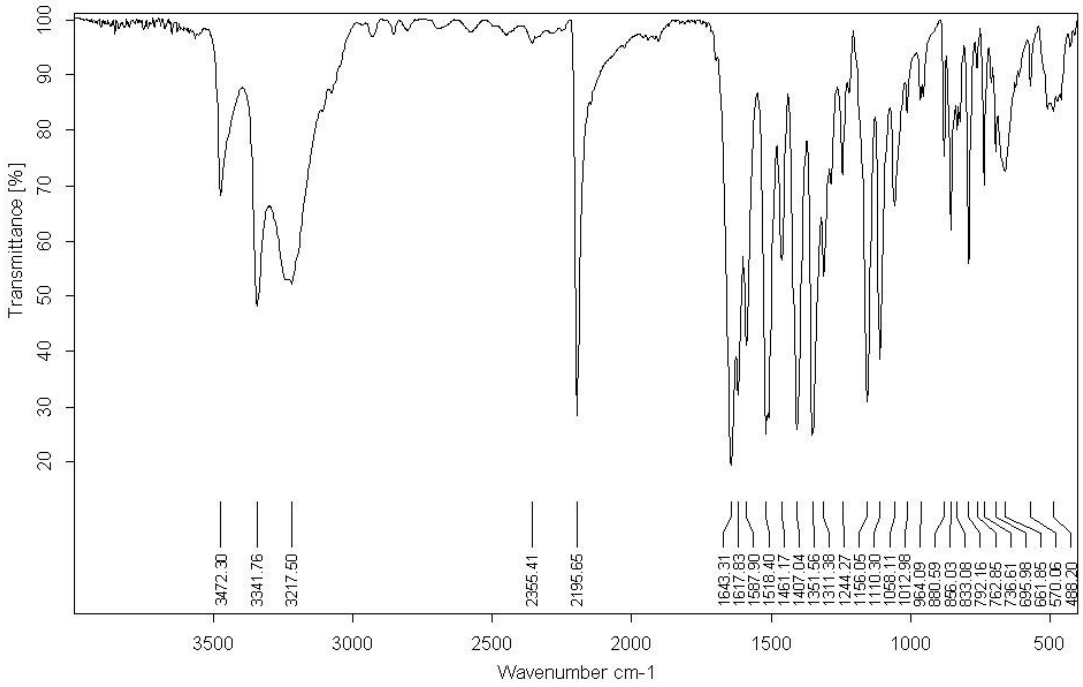

1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
1.00
1.03
1.04
2.23
2.20
1.14
1.08
1.02
1.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

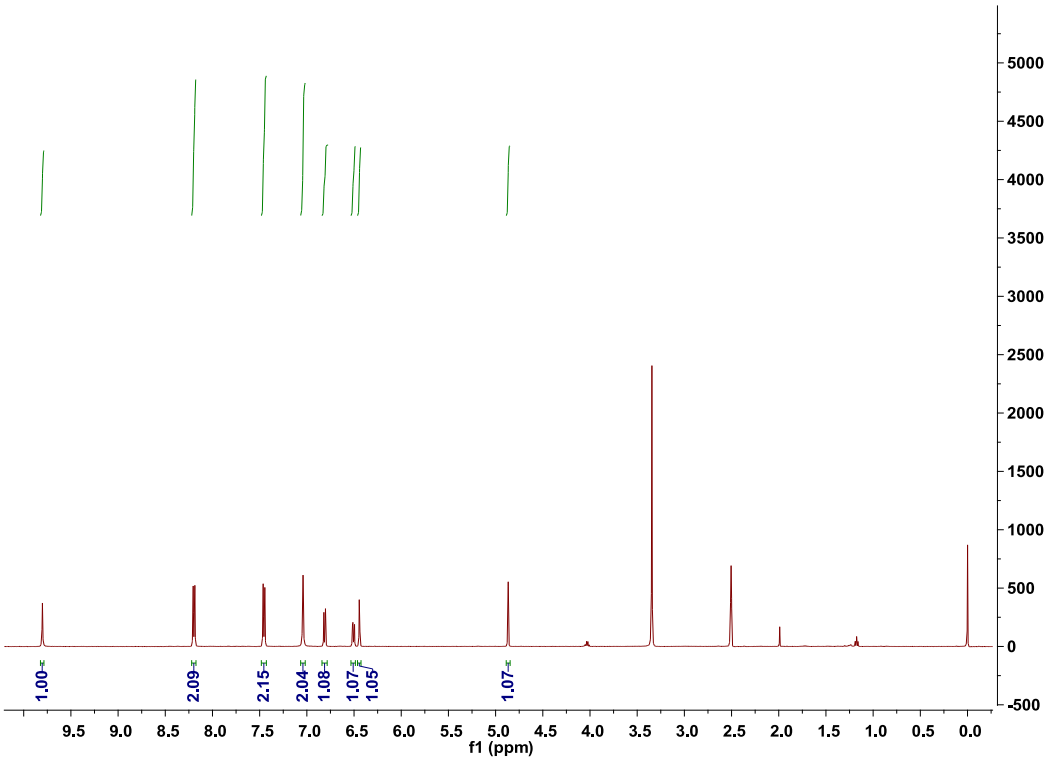
Sample Name	RYF-04	**Position**	p1f4	**Instrument Name**	Instrument 1	**User Name**	Q-TOF-HP\Q-TOF
Inj Vol	3	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	RYF-04_9.d	**ACQ Method**	lihz.m	**Comment**	meijing laoyingcha	**Acquired Time**	5/26/2015 10:09:51 AM



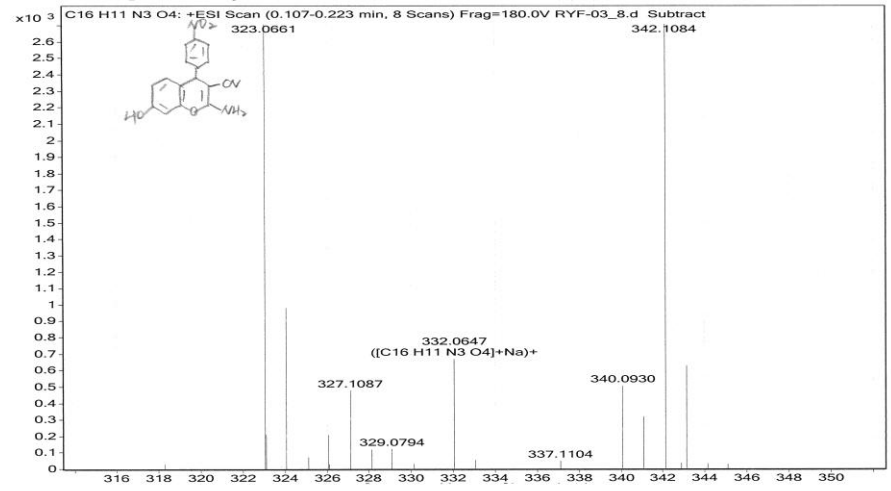
4j.


NO2
CN
HO
O
NH2

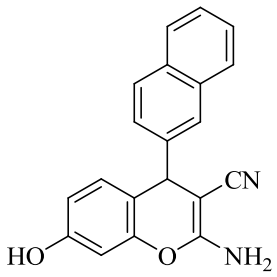

Transmittance [%]
100
90
80
70
60
50
40
30
20
3472.30
3341.76
3217.50
2355.41
2195.65
1643.31
1617.83
1587.90
1518.40
1461.17
1407.04
1351.56
1311.38
1244.27
1156.05
1110.30
1058.11
1012.98
964.09
880.59
856.03
833.08
792.16
762.85
736.61
695.98
661.85
570.06
488.20
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

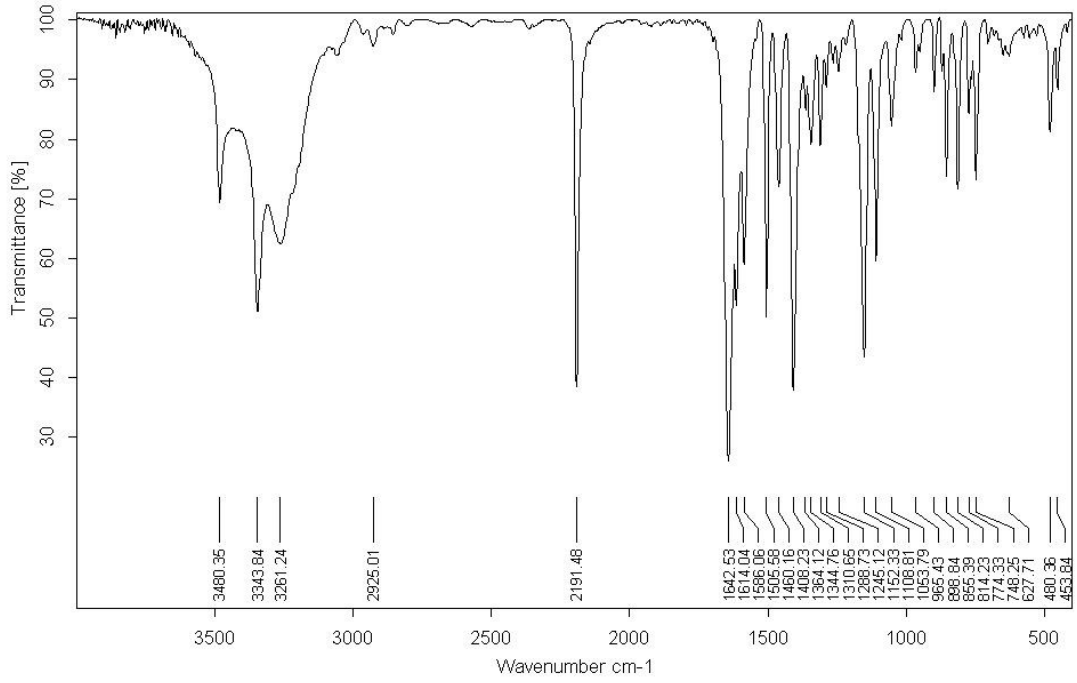


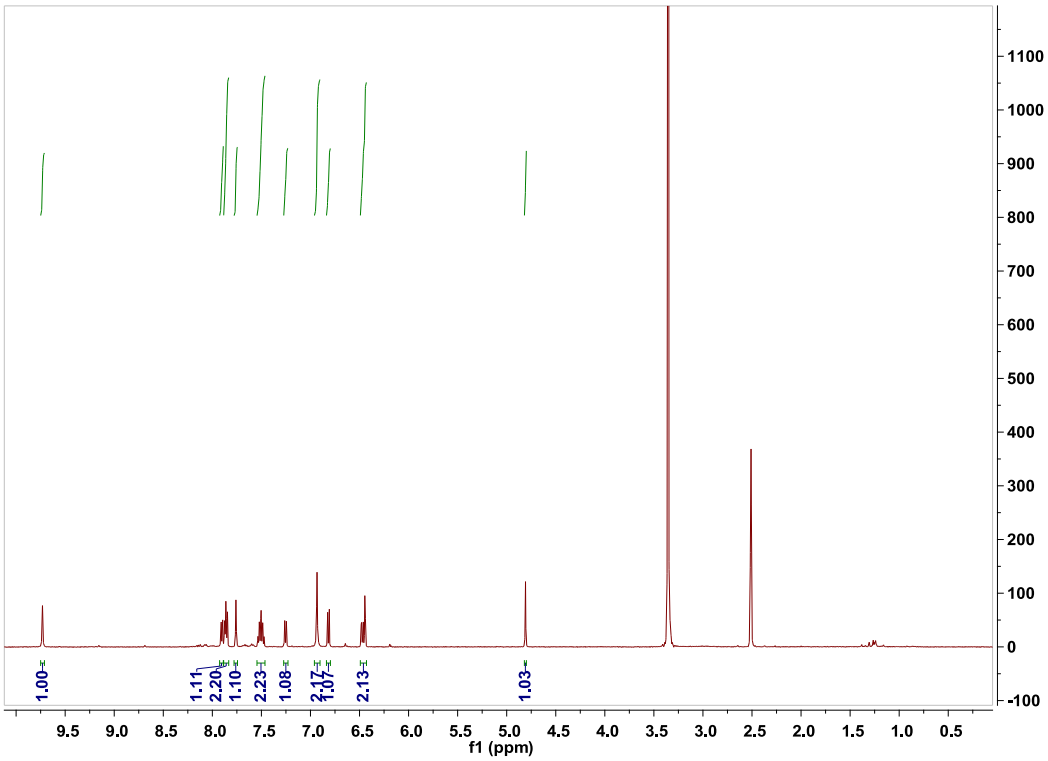
Sample Name	RYF-03	**Position**	p1f3	**Instrument Name**	Instrument 1	**User Name**	Q-TOF-HP\Q-TOF
Inj Vol	3	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	RYF-03_8.d	**ACQ Method**	lihz.m	**Comment**	meijing laoyingcha	**Acquired Time**	5/26/2015 10:05:34 AM



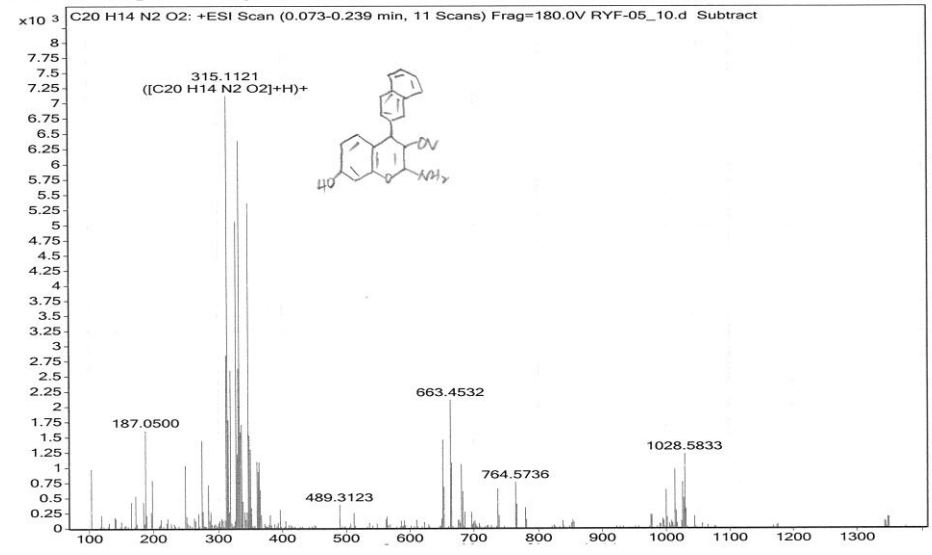
4k.


CN
HO
O
NH2

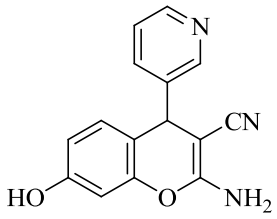

Transmittance [%]
100
90
80
70
60
50
40
30
3480.35
3343.84
3261.24
2925.01
2191.48
1642.53
1614.04
1586.06
1505.58
1460.16
1408.23
1364.12
1344.76
1310.65
1288.73
1245.12
1152.33
1108.81
1053.79
965.43
898.84
855.39
814.23
774.33
748.25
627.71
480.36
453.84
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

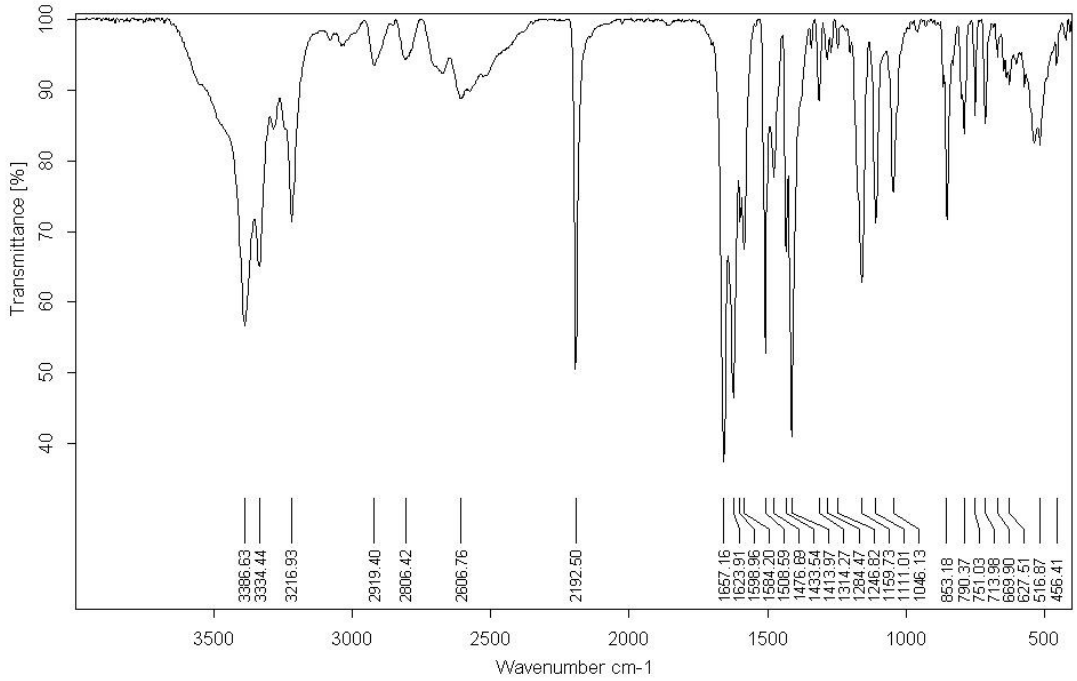


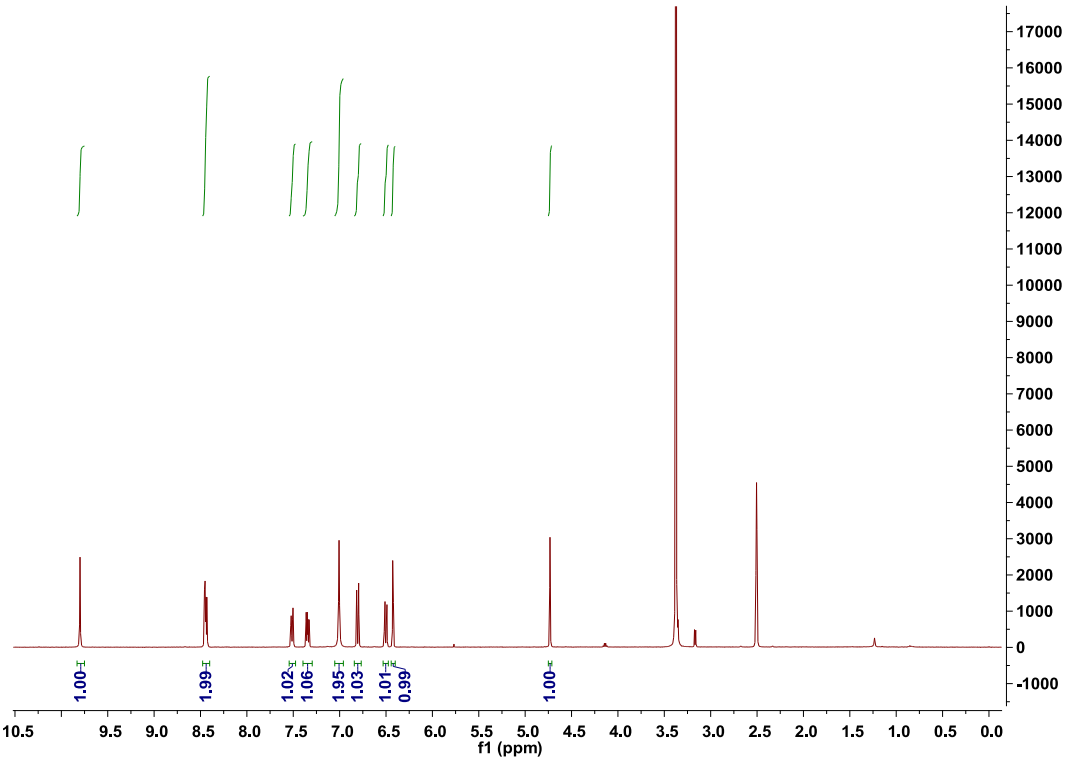
Sample Name	RYF-05	**Position**	p1f5	**Instrument Name**	Instrument 1	**User Name**	Q-TOF-HP\Q-TOF
Inj Vol	4	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	RYF-05_10.d	**ACQ Method**	lihz.m	**Comment**	meijing laoyingcha	**Acquired Time**	5/26/2015 10:13:21 AM



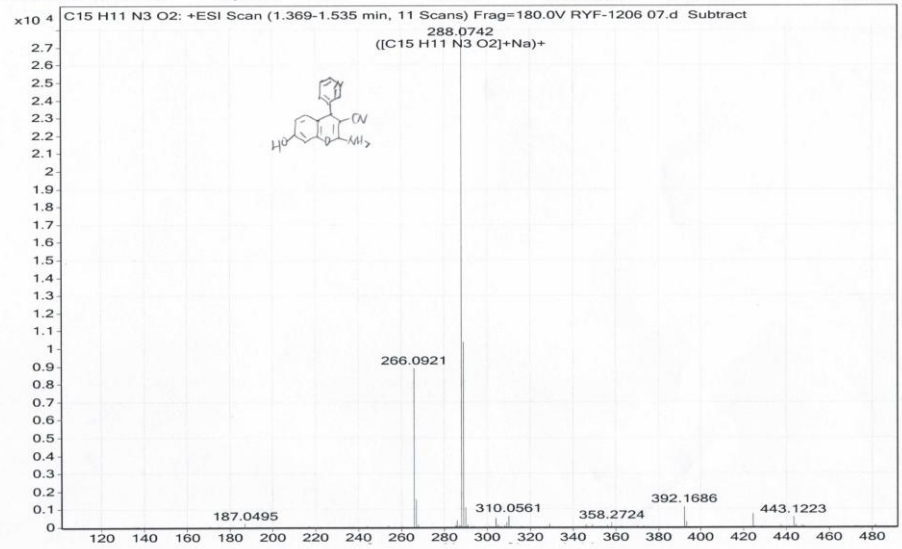
4l.


N
CN
HO
O
NH2

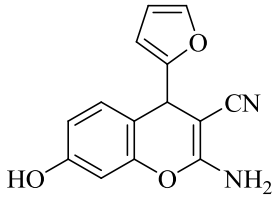

Transmittance [%]
100
90
80
70
60
50
40
3386.63
3334.44
3216.93
2919.40
2806.42
2606.76
2192.50
1657.16
1623.91
1598.96
1584.20
1508.59
1476.89
1433.54
1413.97
1314.27
1284.47
1246.82
1159.73
1111.01
1046.13
853.18
790.37
751.03
713.98
669.90
627.51
516.87
456.41
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

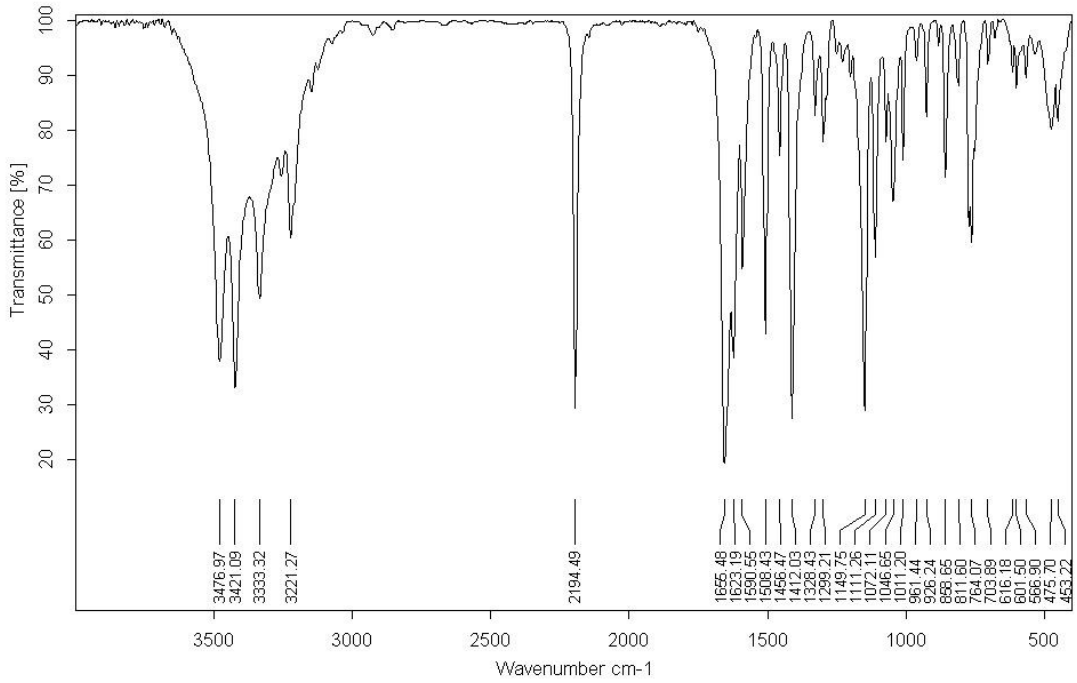

17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
1.00
1.99
1.02
1.06
1.95
1.03
1.01
0.99
1.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

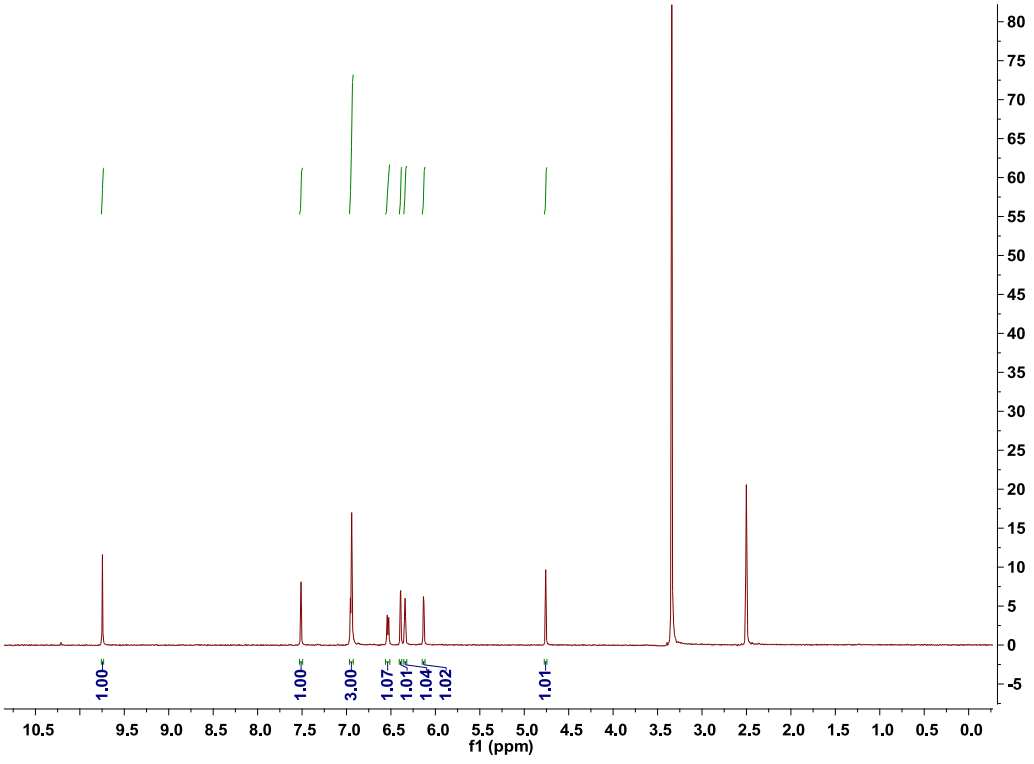
Sample Name	RYF-1206	**Position**	p1f6	**Instrument Name**	Instrument 1	**User Name**	Q-TOF-HP\Q-TOF
Inj Vol	3	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	RYF-1206 07.d	**ACQ Method**	lihz.m	**Comment**	cryang sample neg	**Acquired Time**	12/15/2014 11:06:25 AM

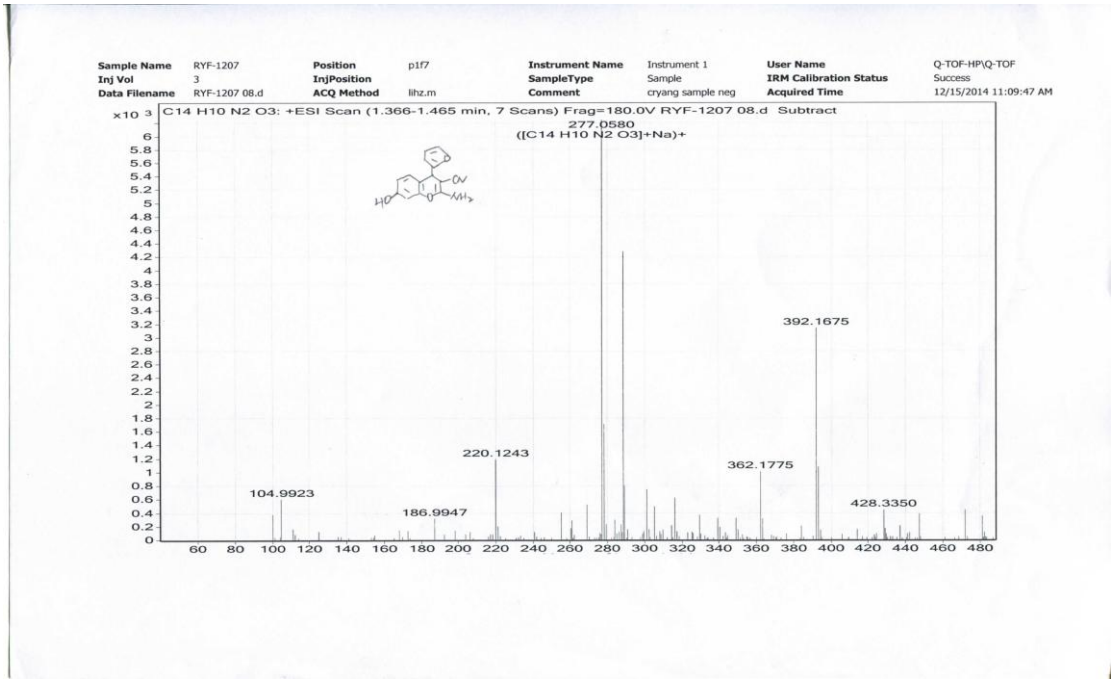


4m.

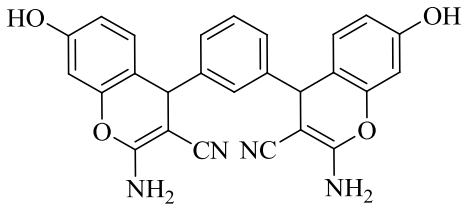

O
CN
HO
O
NH2

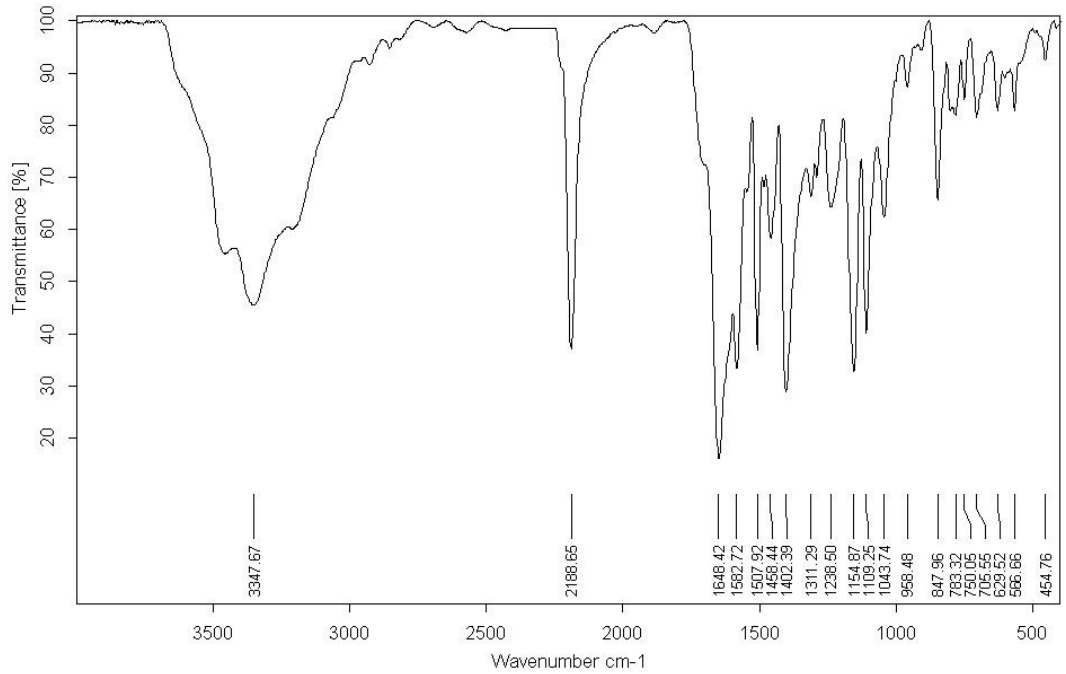

Transmittance [%]
100
90
80
70
60
50
40
30
20
3476.97
3421.09
3333.32
3221.27
2194.49
1655.48
1623.19
1590.55
1508.43
1456.47
1412.03
1328.43
1299.21
1149.75
1111.26
1072.11
1046.65
1011.20
961.44
926.24
858.65
811.60
764.07
703.89
616.18
601.50
566.90
475.70
453.22
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

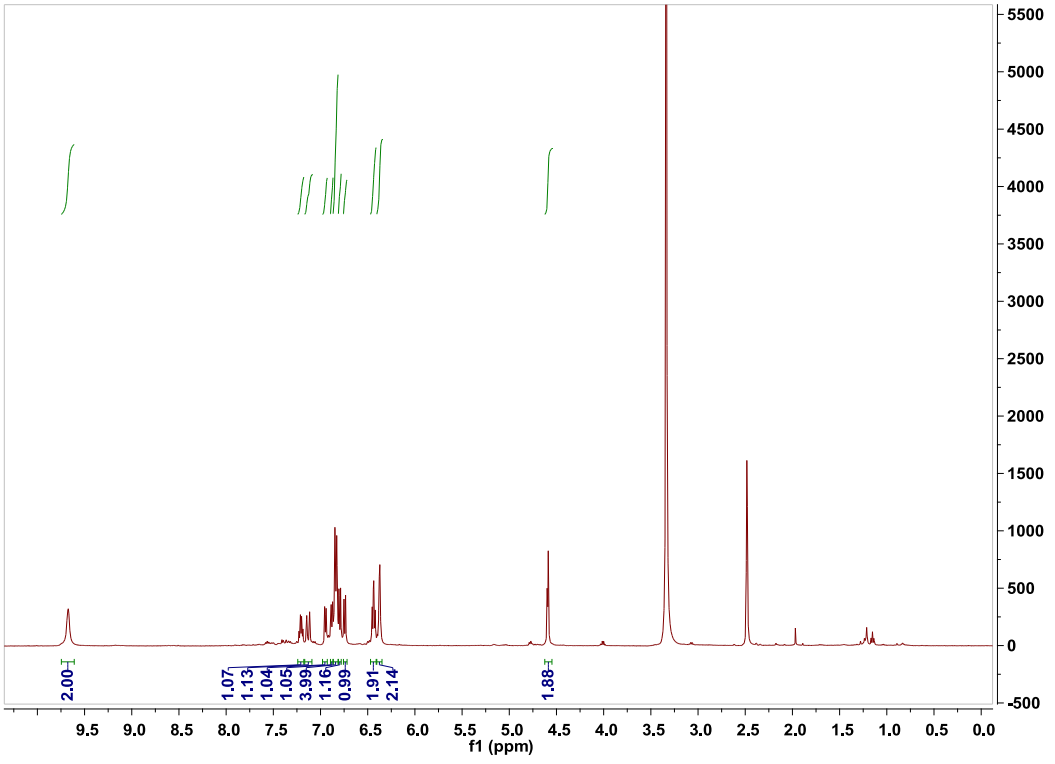

1.00
1.00
3.00
1.07
1.01
1.04
1.02
1.01
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Sample Name RYF-1207
Position p1f7
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 3
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename RYF-1207 08.d
ACQ Method lihz.m
Comment cryang sample neg
Acquired Time 12/15/2014 11:09:47 AM
C14 H10 N2 O3: +ESI Scan (1.366-1.465 min, 7 Scans) Frag=180.0V RYF-1207 08.d Subtract
277.0580
([C14 H10 N2 O3]+Na)+
392.1675
220.1243
362.1775
104.9923
186.9947
428.3350

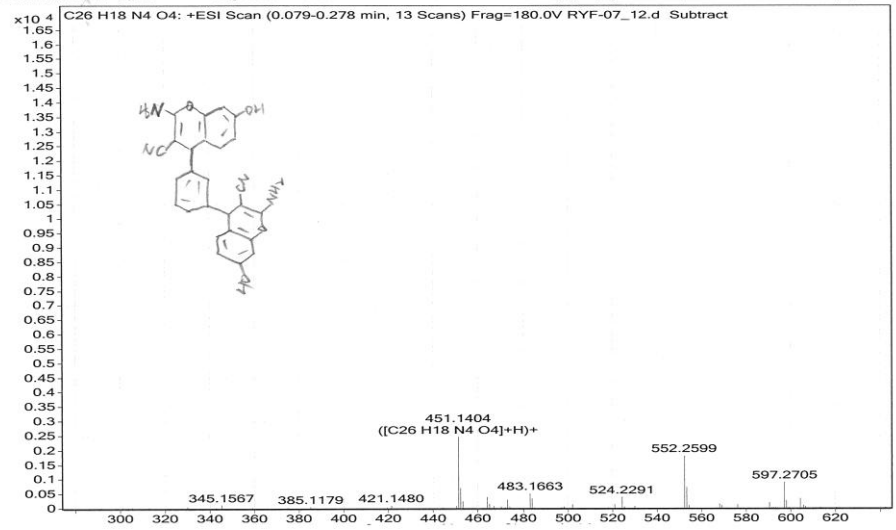
4n.


HO
OH
O
CN NC
O
NH2
NH2

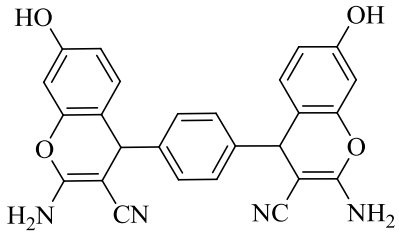

Transmittance [%]
100
90
80
70
60
50
40
30
20
3347.67
2188.65
1648.42
1582.72
1507.92
1458.44
1402.39
1311.29
1238.50
1154.87
1109.25
1043.74
958.48
847.96
783.32
750.05
705.55
629.52
566.66
454.76
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

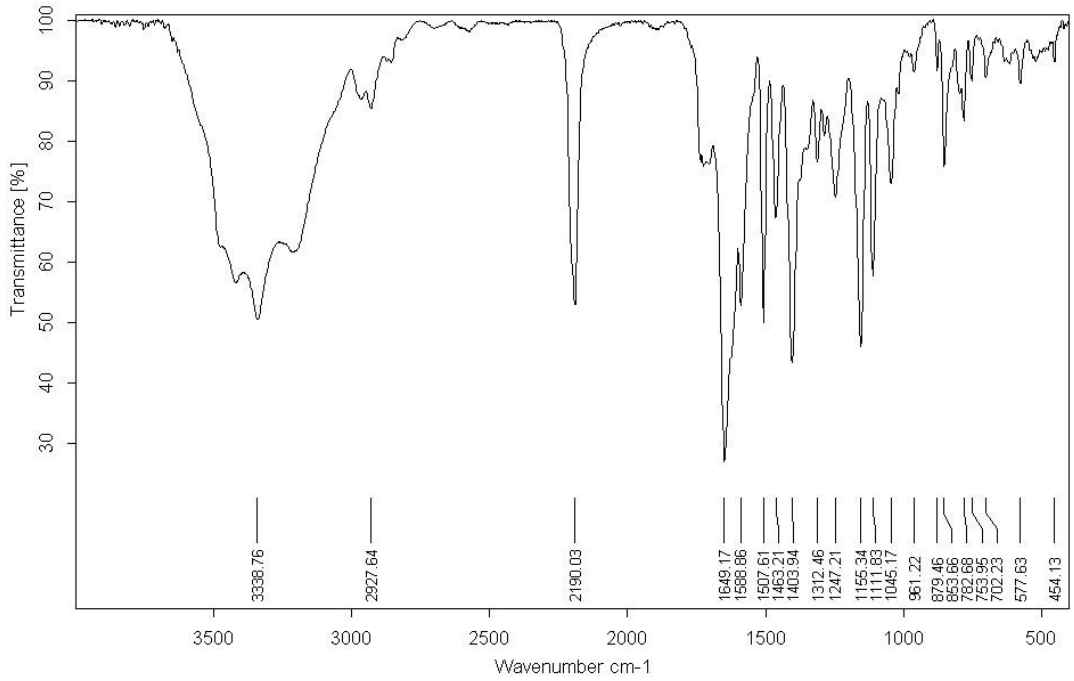

5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
2.00
1.07
1.13
1.04
1.05
3.99
1.16
0.99
1.91
2.14
1.88
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

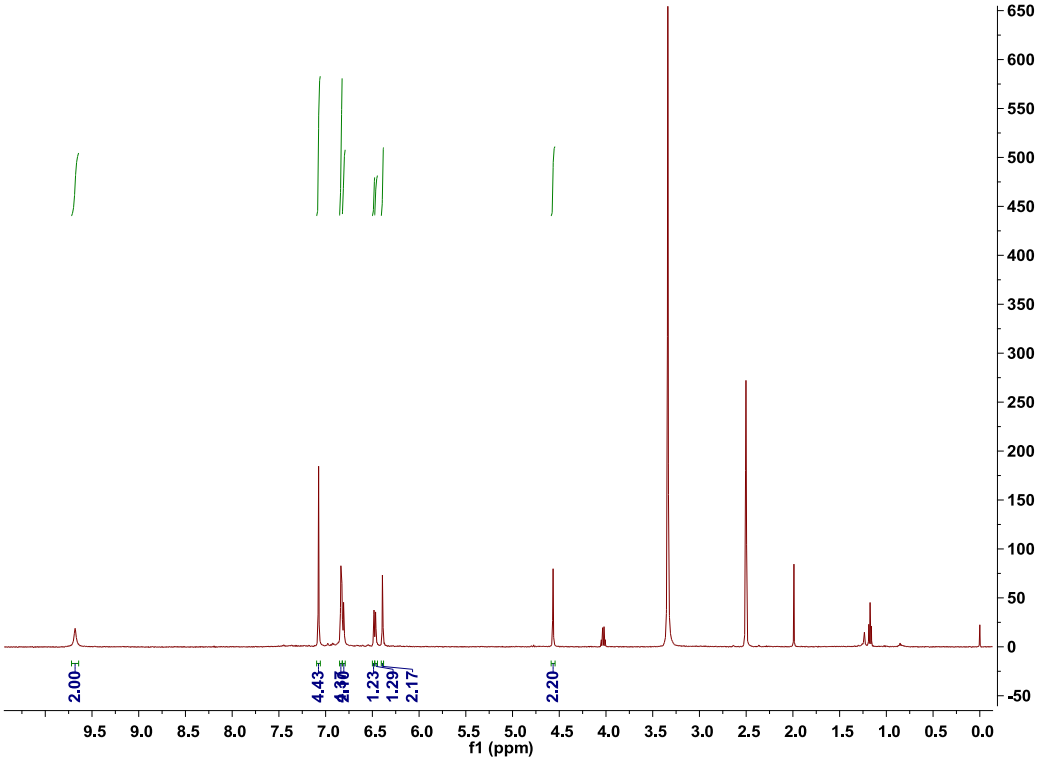
Sample Name	RYF-07	**Position**	p1f7	**Instrument Name**	Instrument 1	**User Name**	Q-TOF-HP\Q-TOF
Inj Vol	4	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	RYF-07_12.d	**ACQ Method**	lihz.m	**Comment**	meijing laoyingcha	**Acquired Time**	5/26/2015 10:18:44 AM



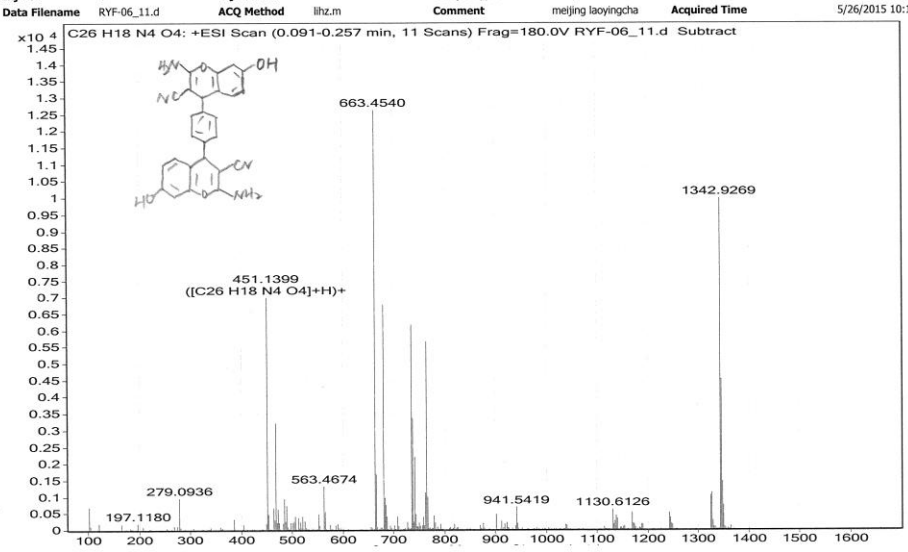
4o.


HO
OH
O
O
H_2N
CN
NC
NH_2

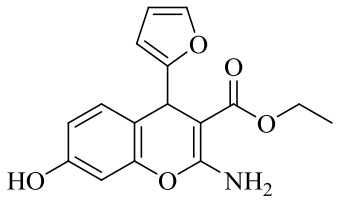

Transmittance [%]
100
90
80
70
60
50
40
30
3338.76
2927.64
2190.03
1649.17
1588.86
1507.61
1463.21
1403.94
1312.46
1247.21
1155.34
1111.83
1045.17
961.22
879.46
853.66
782.68
753.95
702.23
577.63
454.13
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

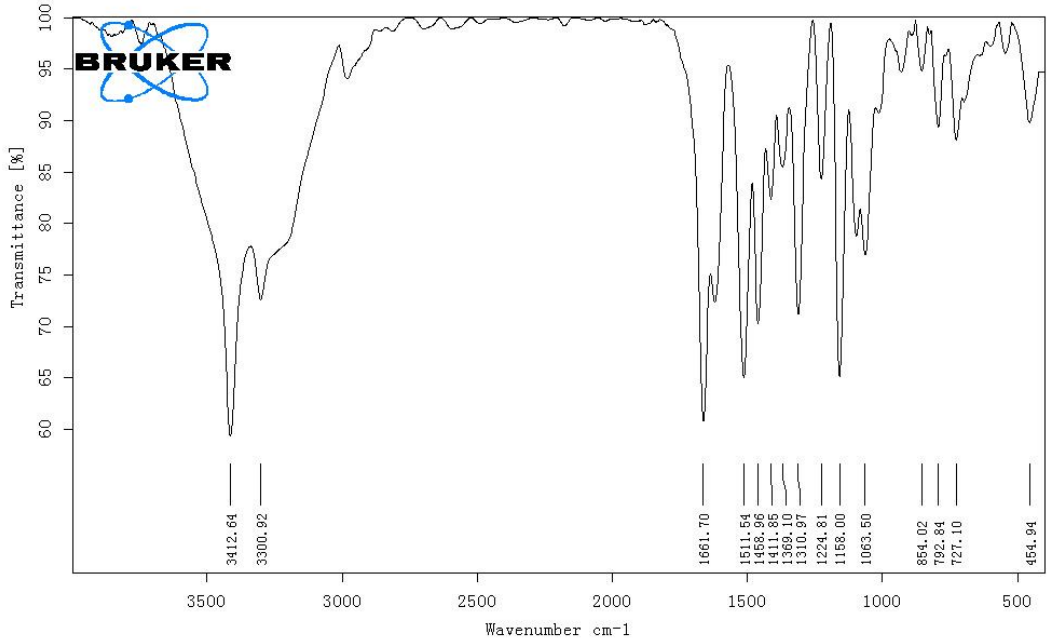

650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
2.00
4.43
1.23
1.29
2.17
2.20
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

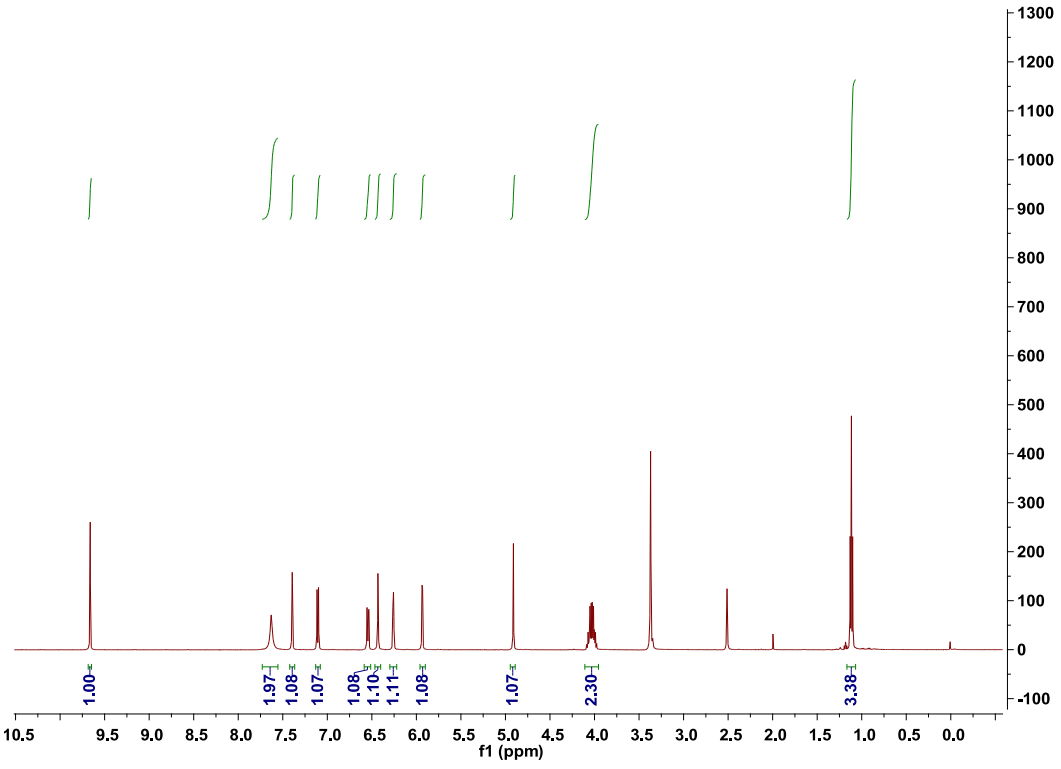
Sample Name	RYF-06	**Position**	p1f6	**Instrument Name**	Instrument 1	**User Name**	Q-TOF-HP\Q-TOF
Inj Vol	4	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	RYF-06_11.d	**ACQ Method**	lihz.m	**Comment**	meijing laoyingcha	**Acquired Time**	5/26/2015 10:16:27 AM

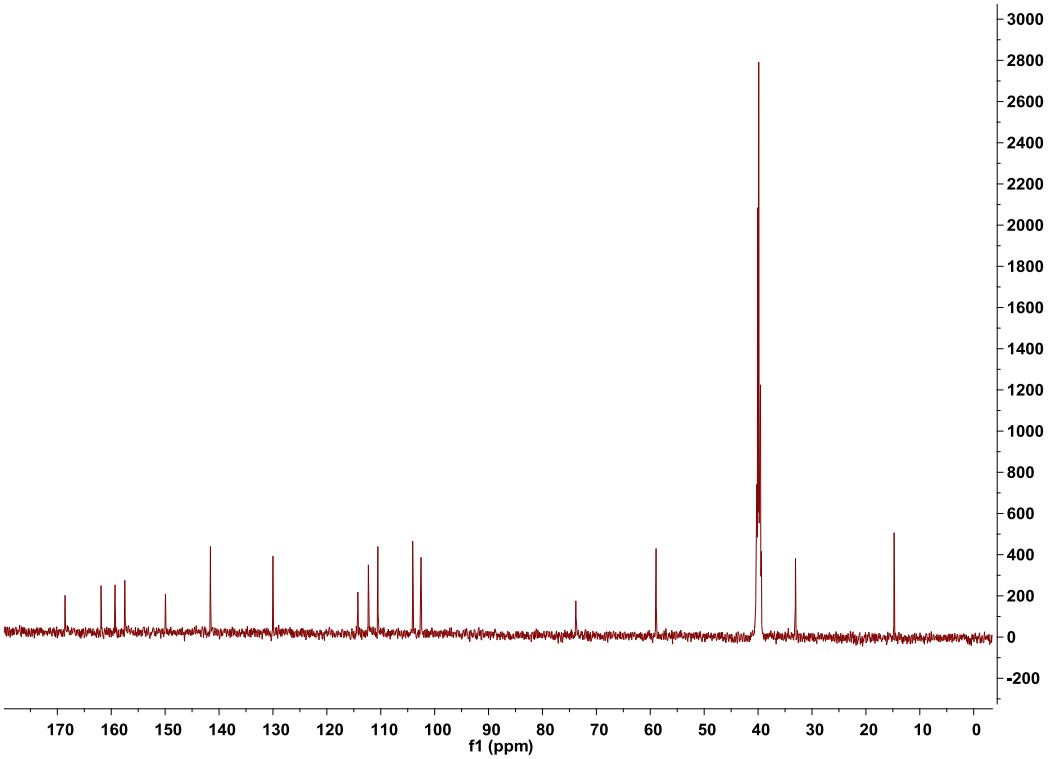


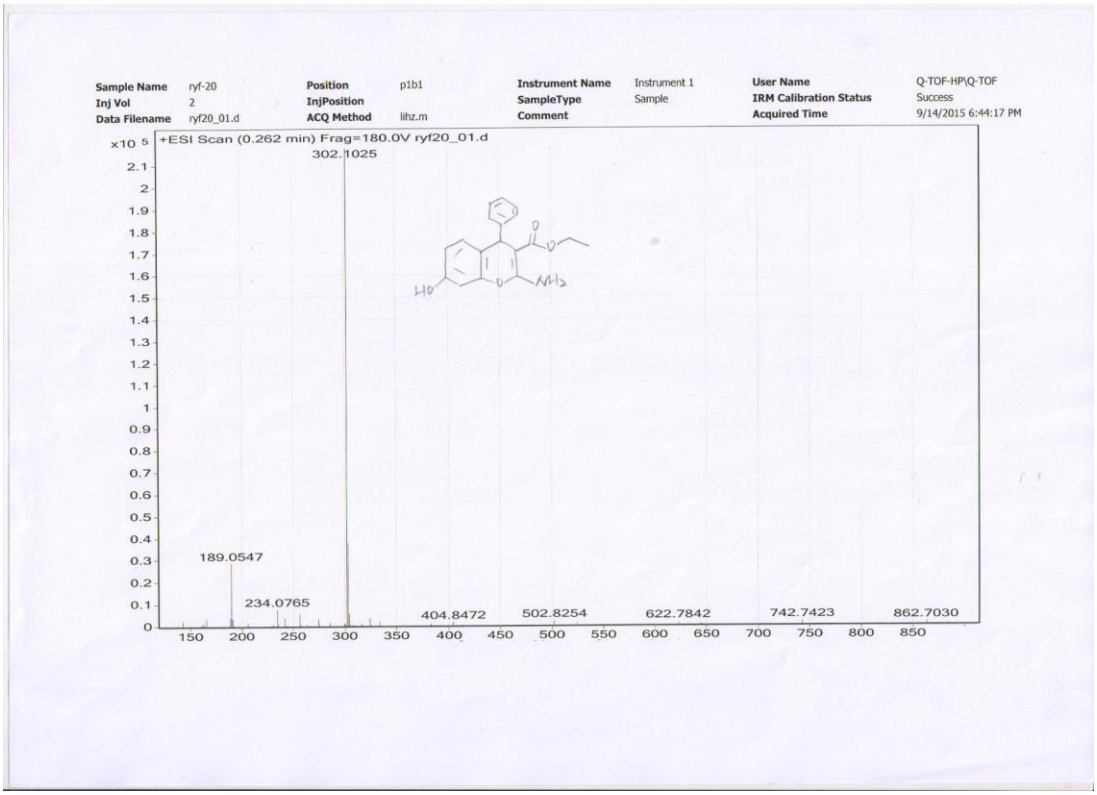
4p.


O
O
O
HO
O
NH2

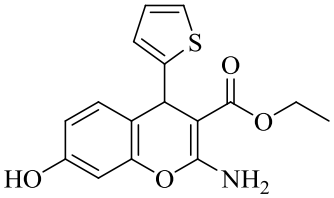

BRUKER
Transmittance [%]
100
95
90
85
80
75
70
65
60
3412.64
3300.92
1661.70
1511.54
1458.96
1411.85
1369.10
1310.97
1224.81
1158.00
1063.50
854.02
792.84
727.10
454.94
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

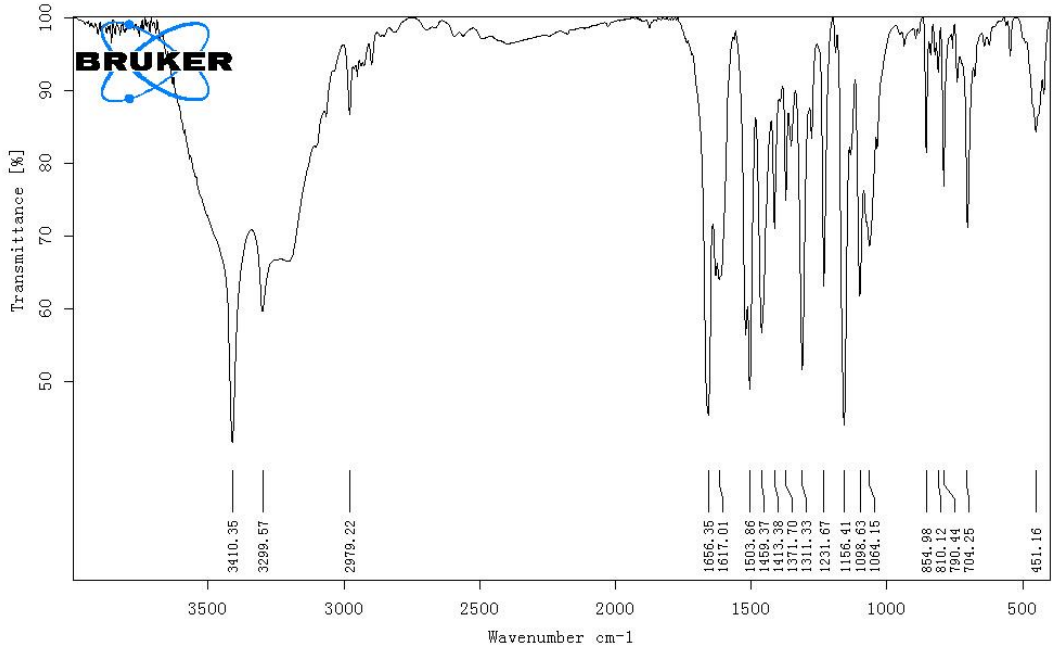

1.00
1.97
1.08
1.07
1.08
1.10
1.11
1.08
1.07
2.30
3.38
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

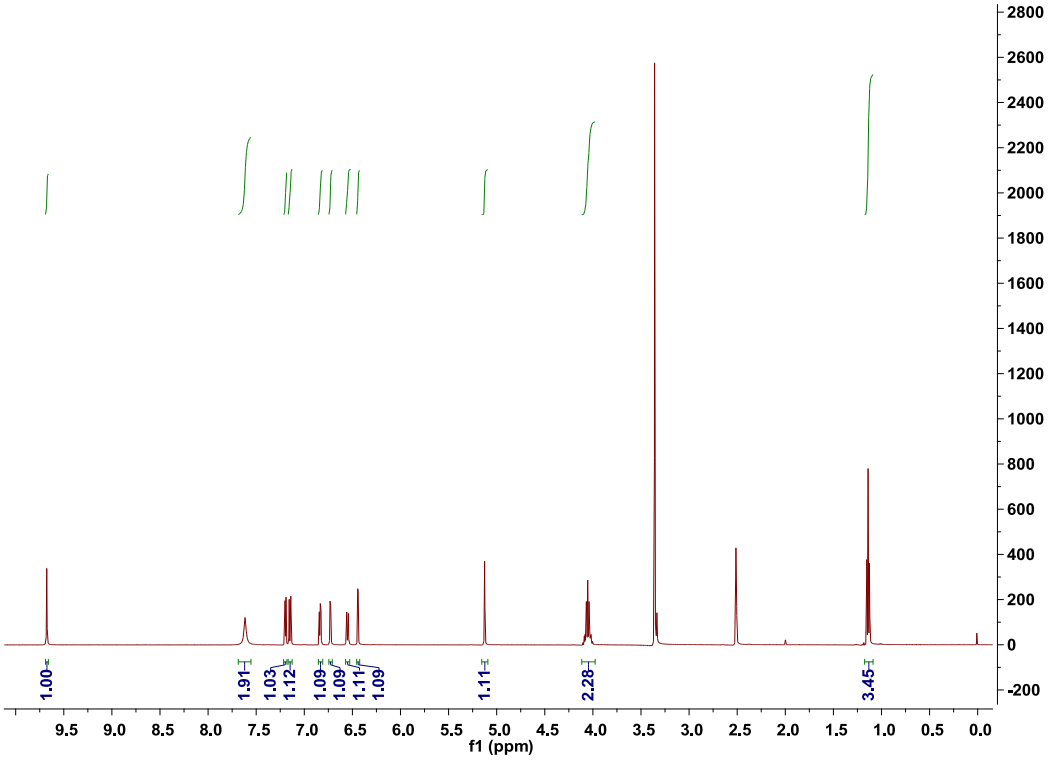

3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

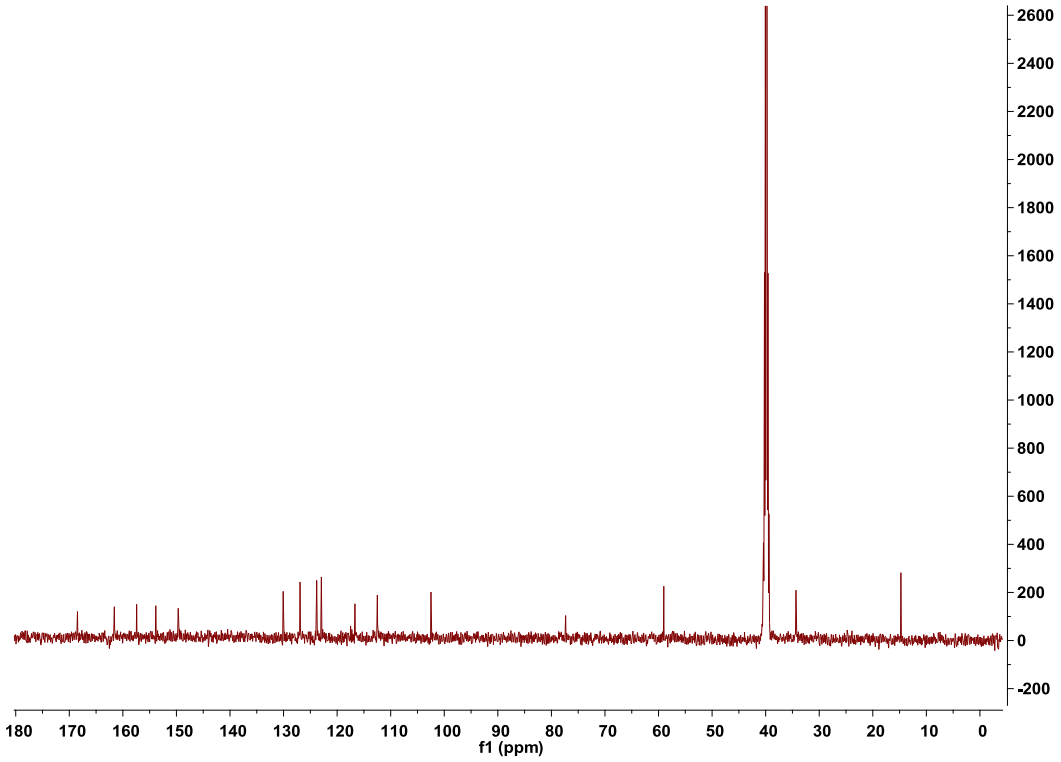

Sample Name ryf-20
Inj Vol 2
Data Filename ryf20_01.d
Position p1b1
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 9/14/2015 6:44:17 PM
+ESI Scan (0.262 min) Frag=180.0V ryf20_01.d
x10 5
302.1025
189.0547
234.0765
404.8472
502.8254
622.7842
742.7423
862.7030
150 200 250 300 350 400 450 500 550 600 650 700 750 800 850

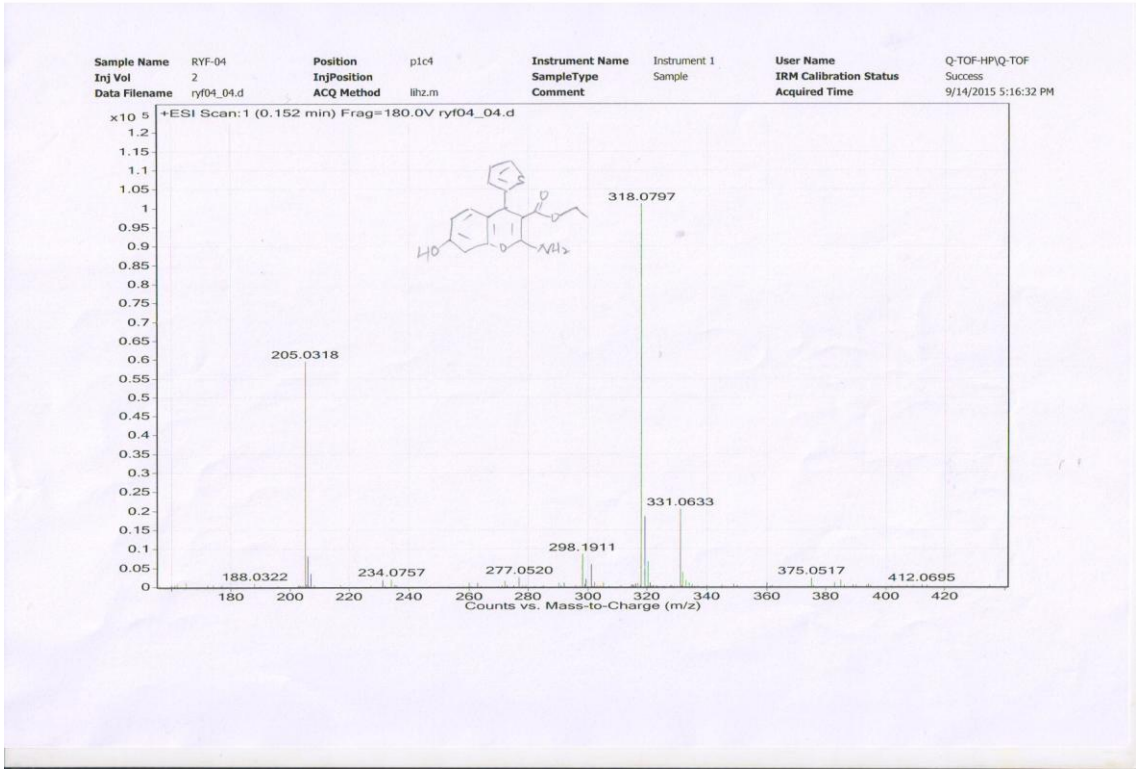
4q.


S
O
O
HO
O
NH2

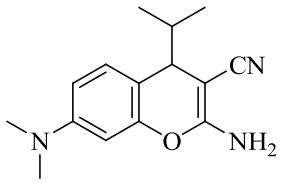

BRUKER
Transmittance [%]
100
90
80
70
60
50
3410.35
3299.57
2979.22
1656.35
1617.01
1503.86
1459.37
1413.38
1371.70
1311.33
1231.67
1156.41
1098.63
1064.15
854.98
810.12
790.44
704.25
451.16
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

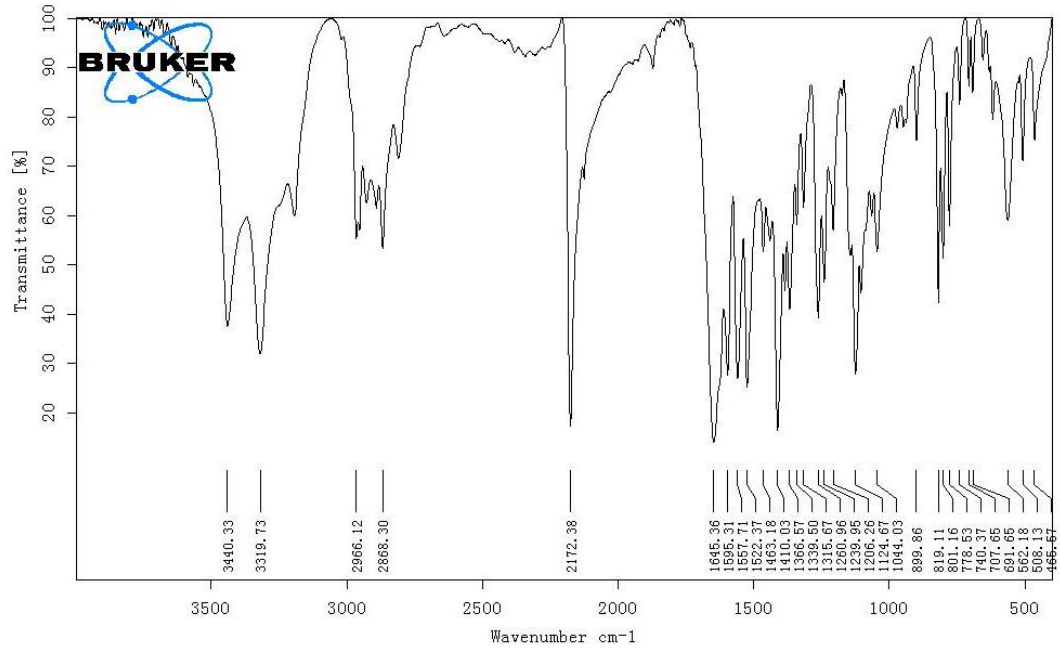

2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
1.00
1.91
1.03
1.12
1.09
1.09
1.11
1.09
1.11
2.28
3.45
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

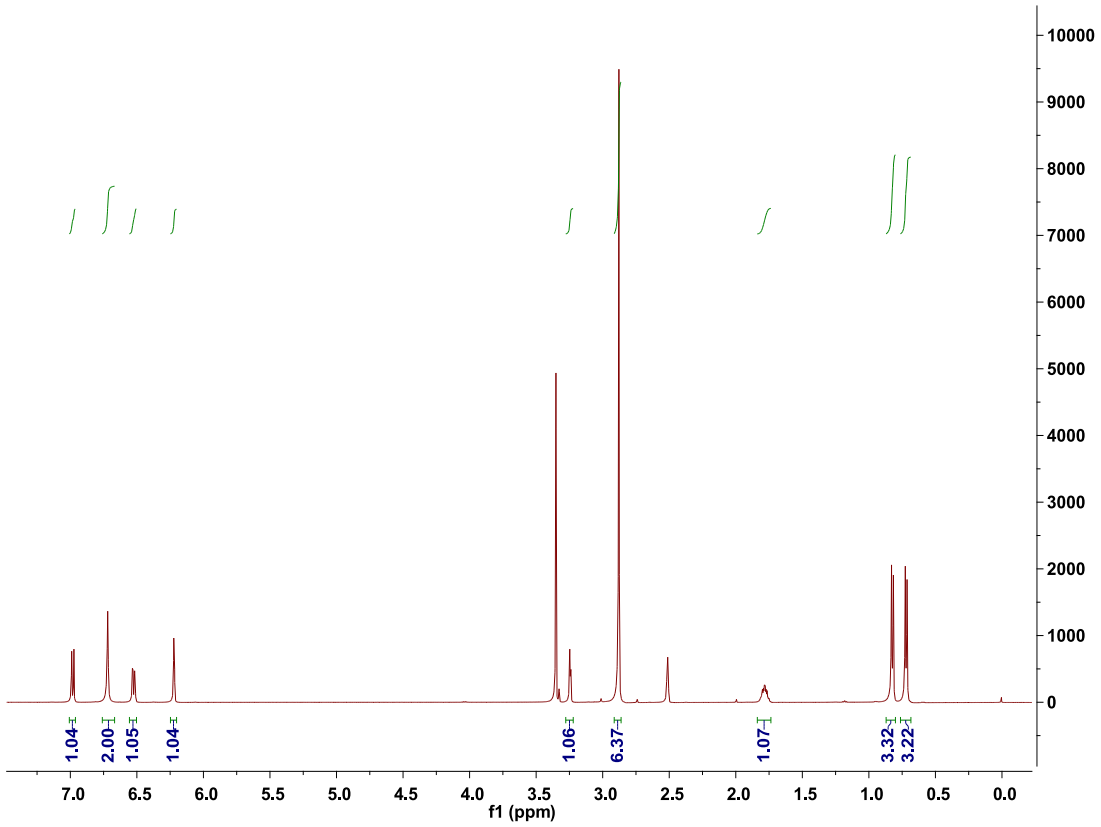

2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

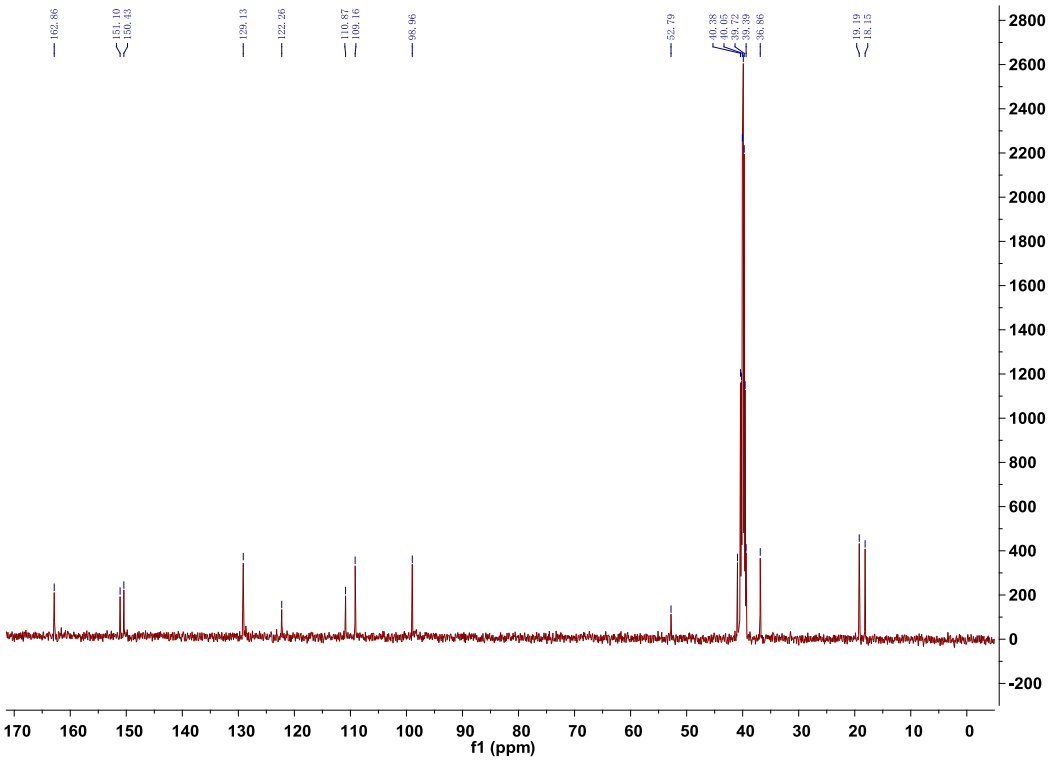

Sample Name RYF-04
Position p1c4
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 2
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename ryf04_04.d
ACQ Method lihz.m
Comment
Acquired Time 9/14/2015 5:16:32 PM
+ESI Scan:1 (0.152 min) Frag=180.0V ryf04_04.d
x10 5
318.0797
205.0318
331.0633
298.1911
188.0322
234.0757
277.0520
375.0517
412.0695
Counts vs. Mass-to-Charge (m/z)

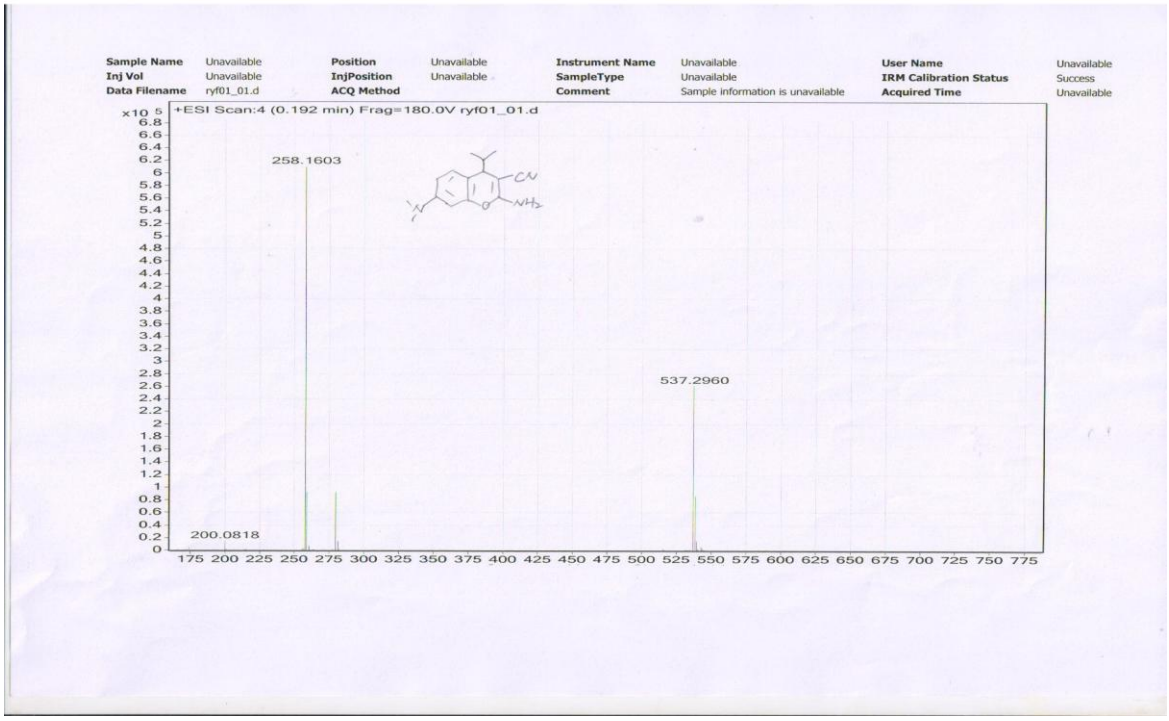
4r.


CN
N
O
NH2

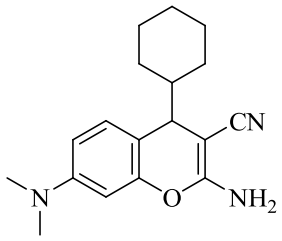

BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
20
3440.33
3319.73
2966.12
2868.30
2172.38
1645.36
1596.31
1557.71
1522.37
1463.18
1410.03
1366.57
1339.50
1315.67
1260.96
1239.95
1206.26
1124.67
1044.03
899.86
819.11
801.16
778.53
740.37
707.65
691.65
562.18
508.13
485.67
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

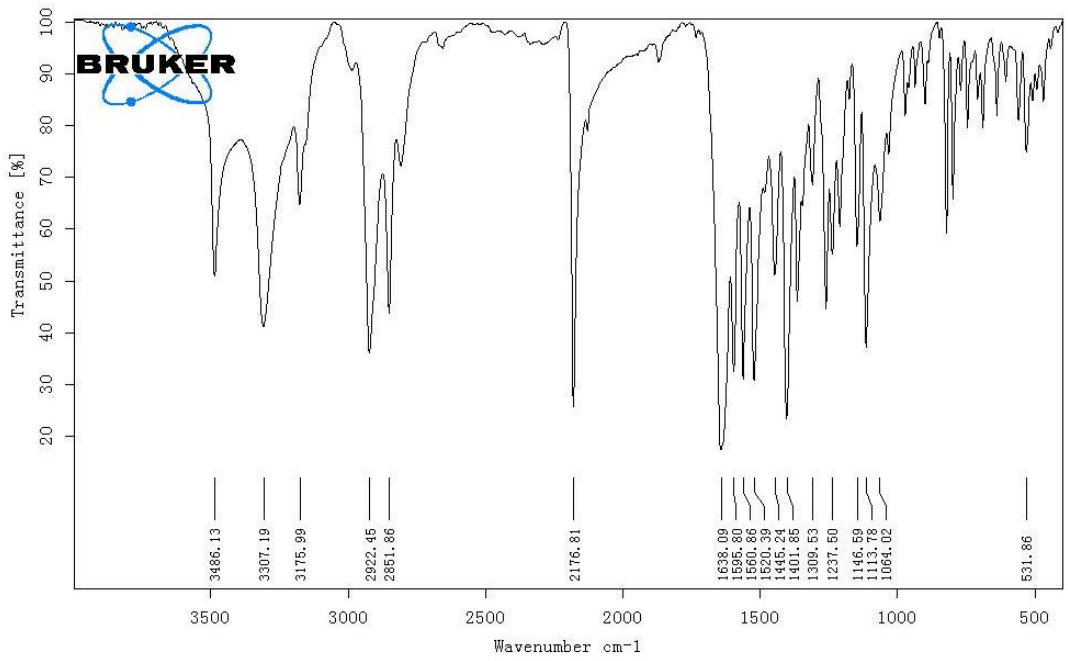

10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
1.04
2.00
1.05
1.04
1.06
6.37
1.07
3.32
3.22
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

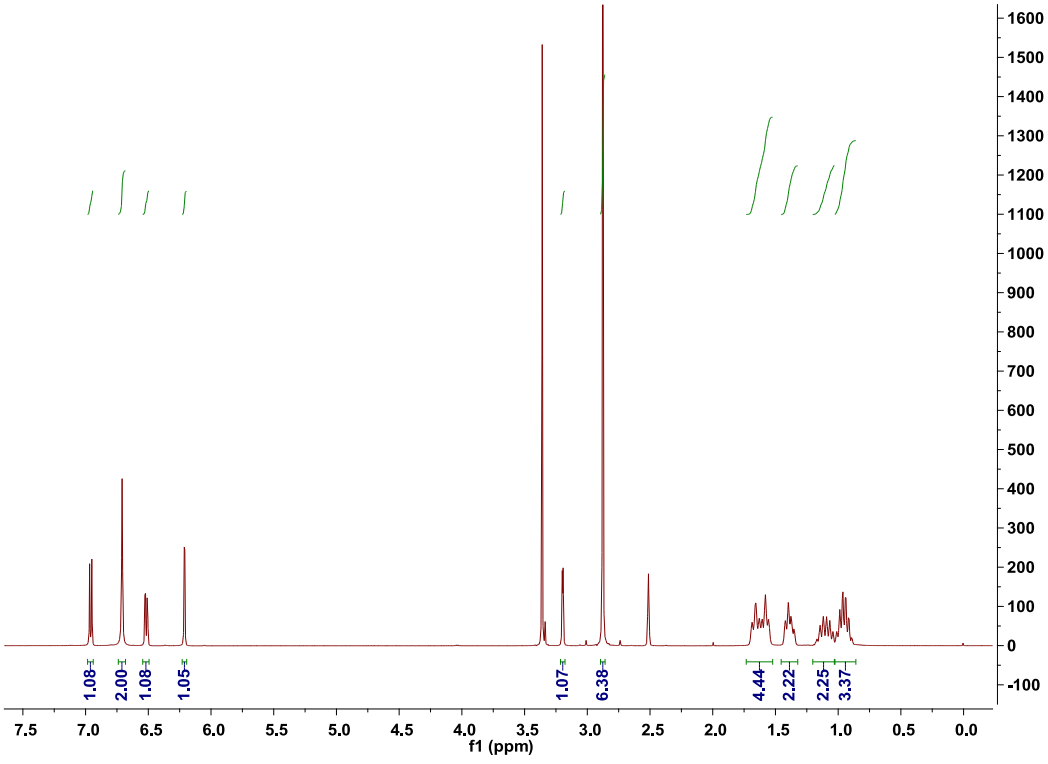

162.86
151.10
150.43
129.13
122.26
110.87
109.16
98.96
52.79
40.38
40.05
39.72
39.39
35.86
19.19
18.15
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

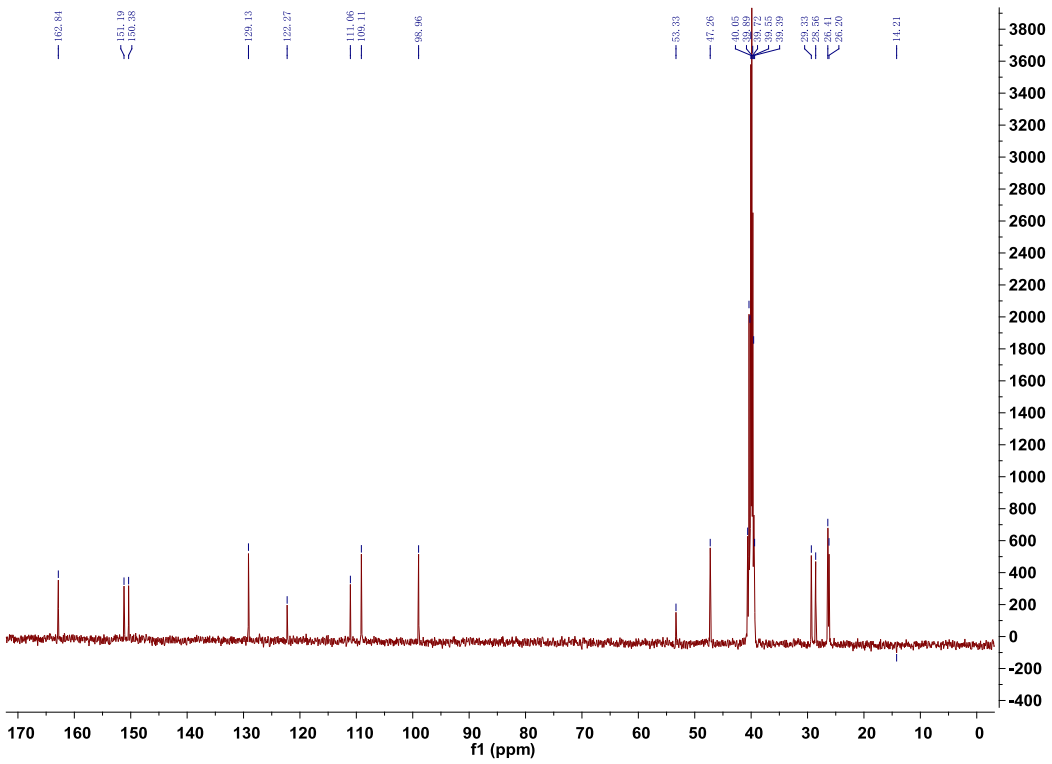

Sample Name Unavailable
Inj Vol Unavailable
Data Filename ryf01_01.d
Position Unavailable
InjPosition Unavailable
ACQ Method
Instrument Name Unavailable
SampleType Unavailable
Comment Sample information is unavailable
User Name Unavailable
IRM Calibration Status Success
Acquired Time Unavailable
+ESI Scan:4 (0.192 min) Frag=180.0V ryf01_01.d
x10 5
258.1603
537.2960
200.0818
CN
NH2
175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 625 650 675 700 725 750 775

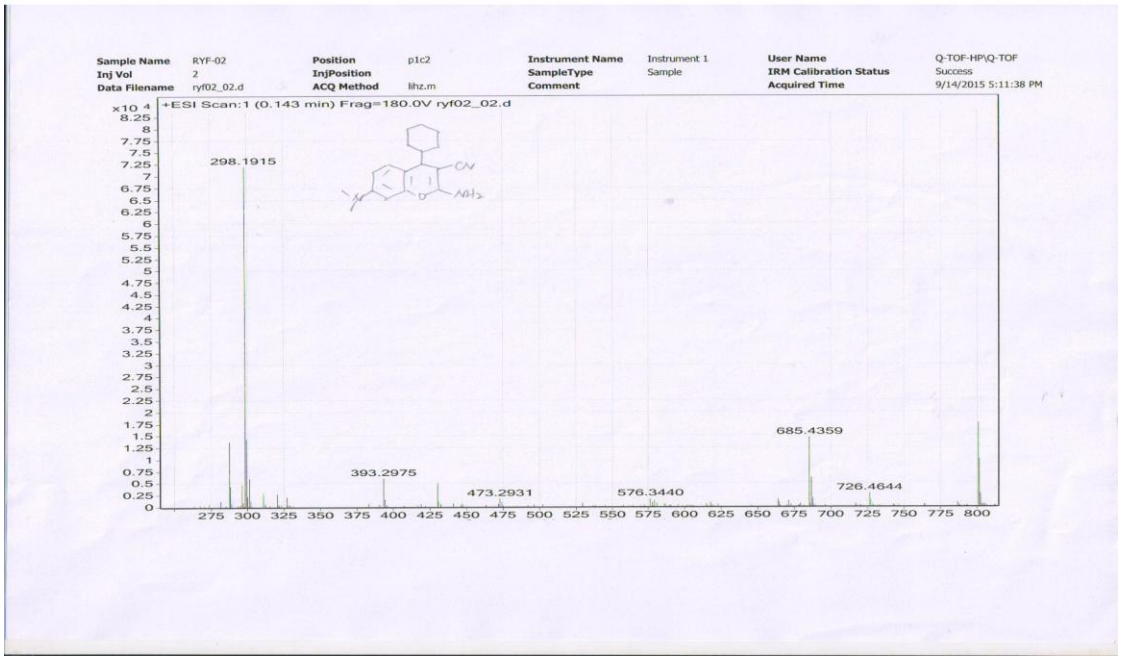
4s.


CN
N
O
NH2

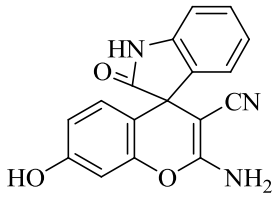

BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
20
3486.13
3307.19
3175.99
2922.45
2851.86
2176.81
1638.09
1595.80
1560.86
1520.39
1445.24
1401.85
1309.53
1237.50
1146.59
1113.78
1064.02
531.86
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

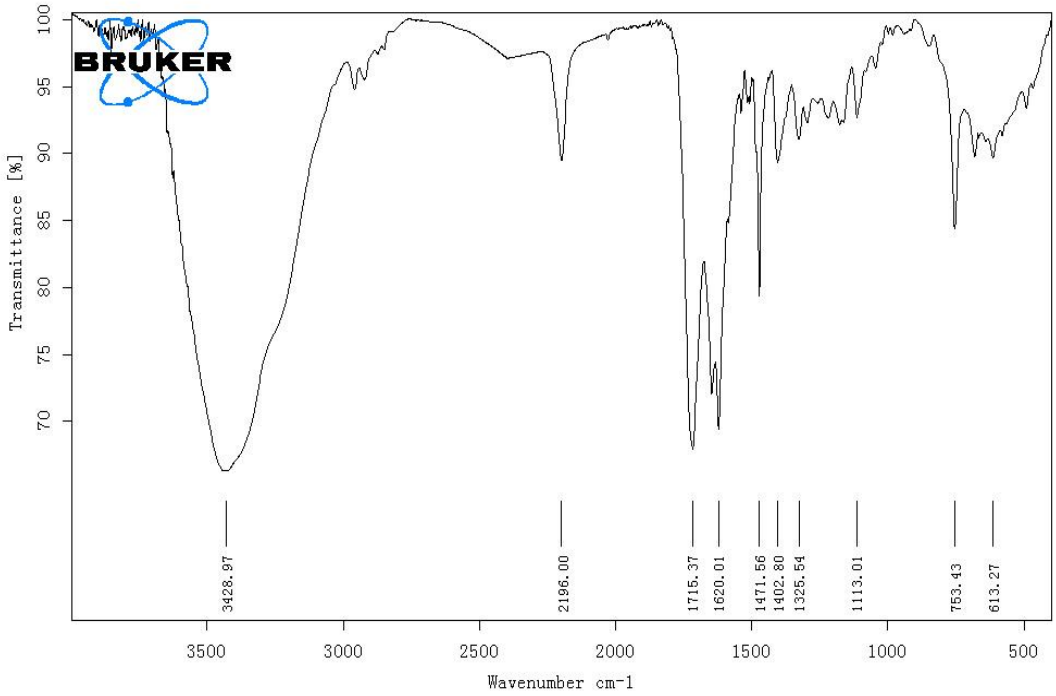

1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
1.08
2.00
1.08
1.05
1.07
6.38
4.44
2.22
2.25
3.37
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

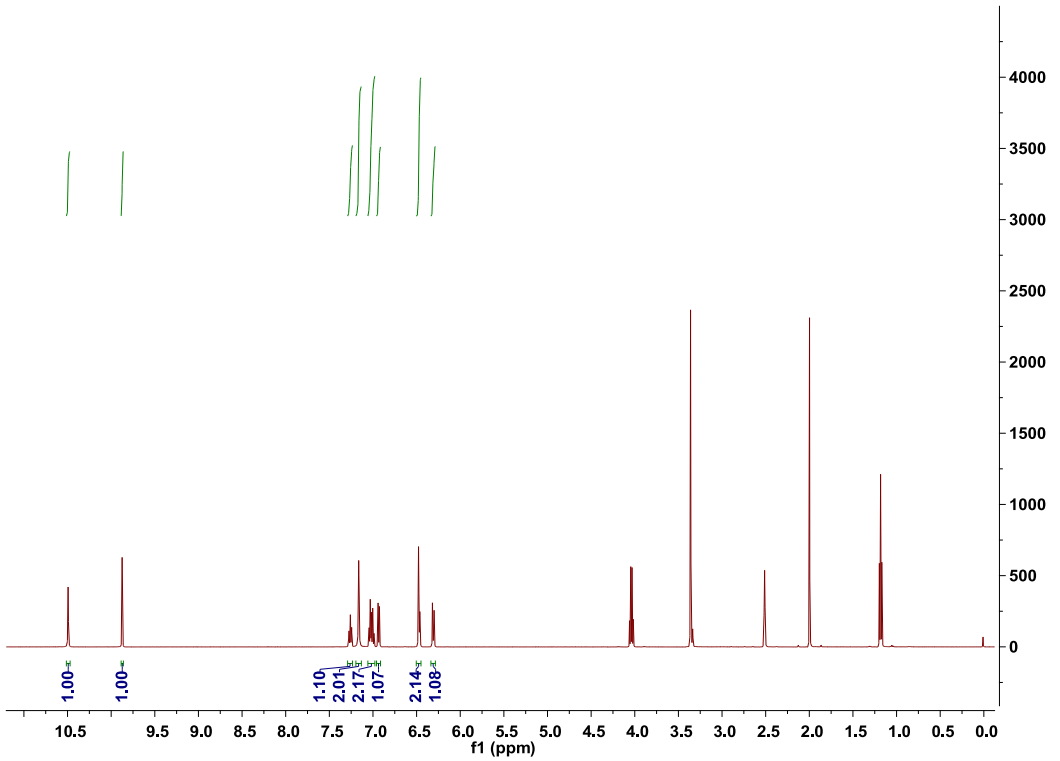

162.84
151.19
150.38
129.13
122.27
111.06
109.11
98.96
53.33
47.26
40.05
39.89
39.72
39.55
39.39
29.33
28.56
26.41
26.20
14.21
f1 (ppm)

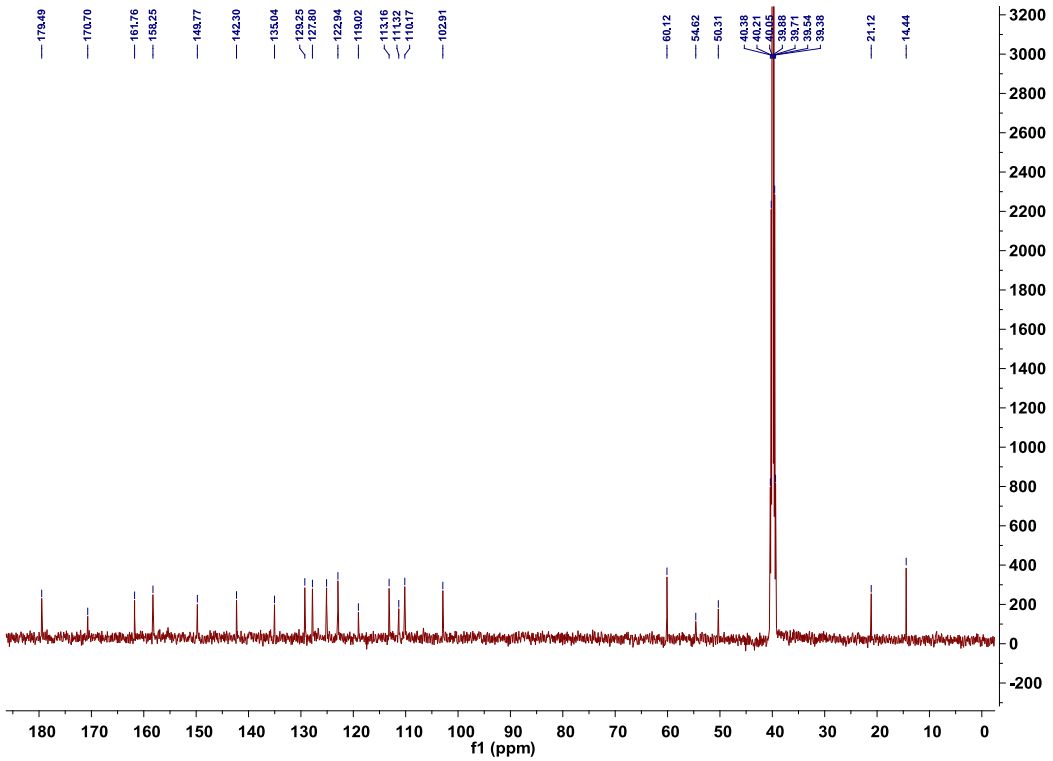

Sample Name RYF-02
Inj Vol 2
Data Filename ryf02_02.d
Position p1c2
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 9/14/2015 5:11:38 PM
+ESI Scan:1 (0.143 min) Frag=180.0V ryf02_02.d
298.1915
393.2975
473.2931
576.3440
685.4359
726.4644

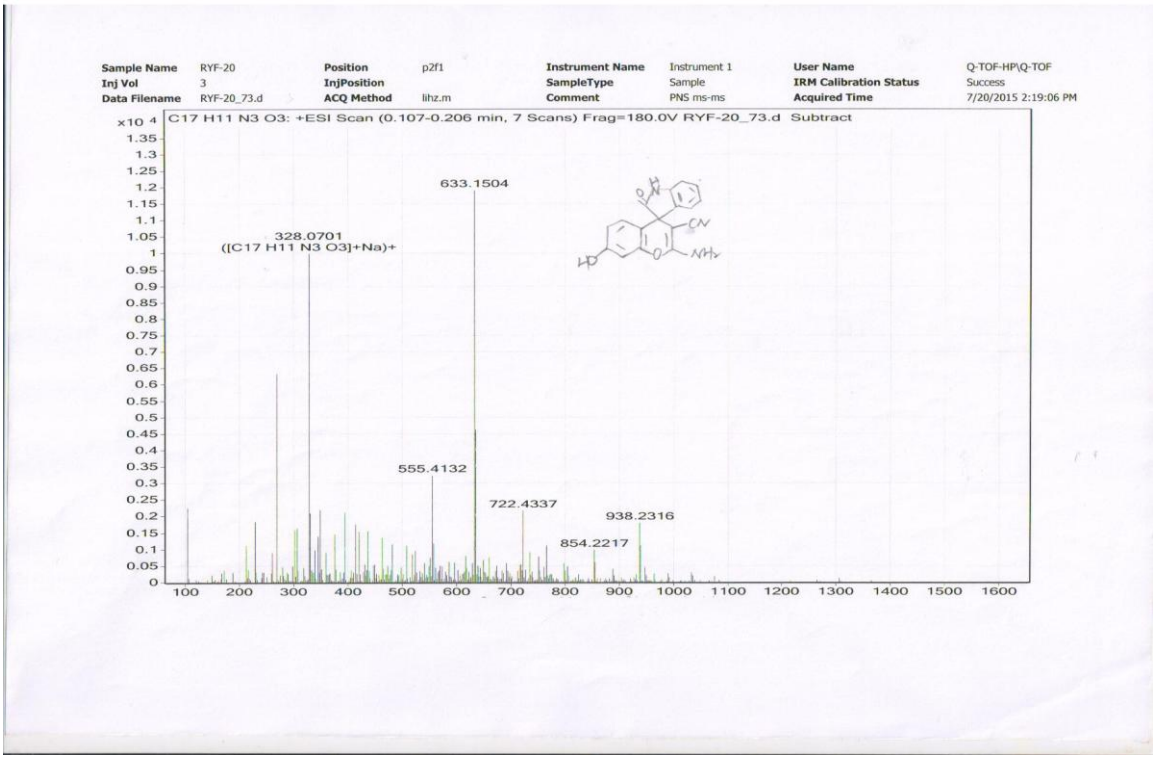
4t.


HN
O
CN
HO
O
NH2

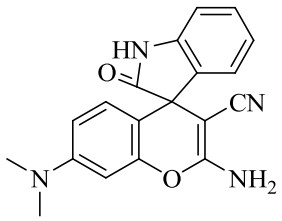

BRUKER
Transmittance [%]
100
95
90
85
80
75
70
3428.97
2196.00
1715.37
1620.01
1471.56
1402.80
1325.54
1113.01
753.43
613.27
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

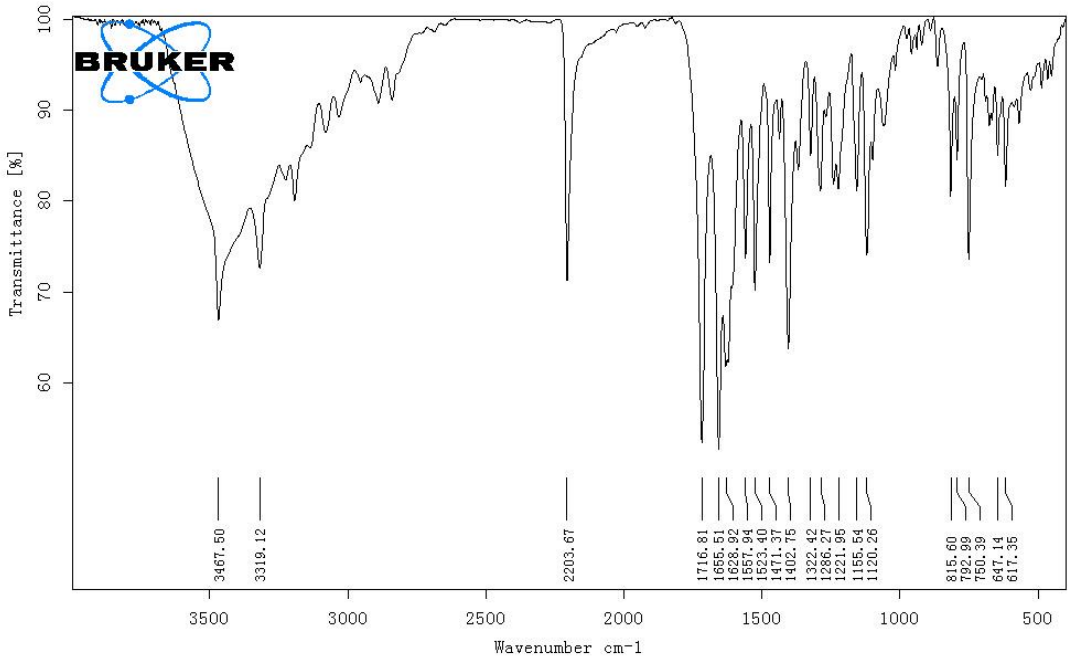

4000
3500
3000
2500
2000
1500
1000
500
0
1.00
1.00
1.10
2.01
2.17
1.07
2.14
1.08
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

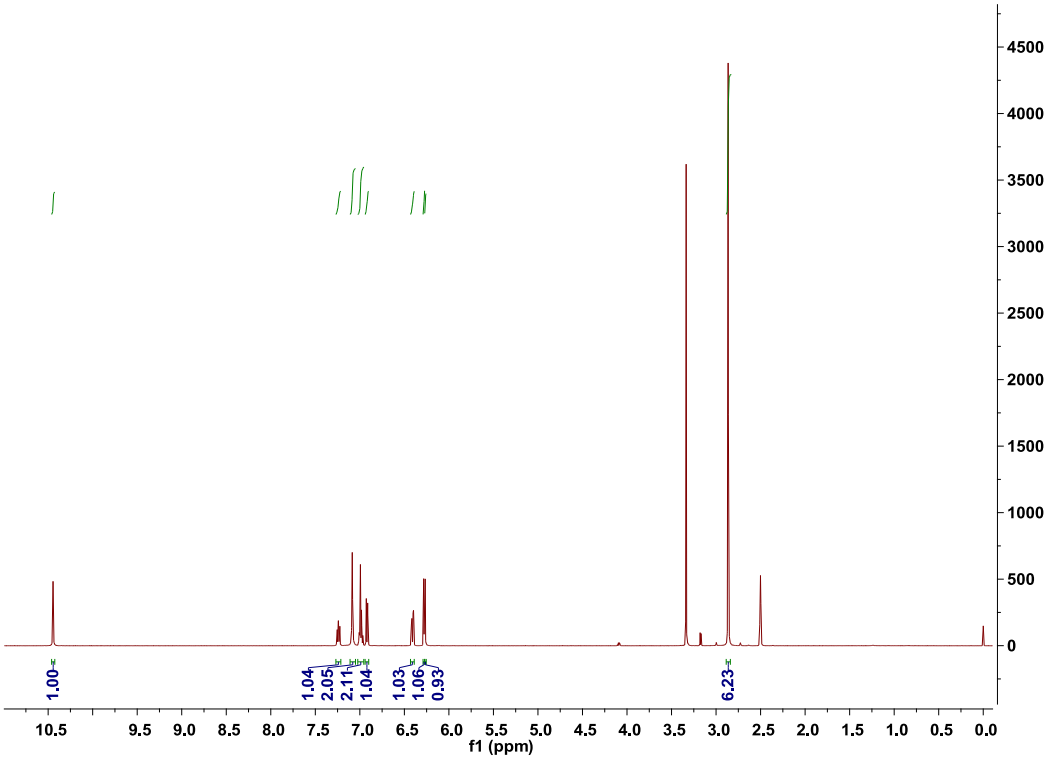

179.49
170.70
161.76
158.25
149.77
142.30
135.04
129.25
127.80
122.94
119.02
113.16
111.32
110.17
102.91
60.12
54.62
50.31
40.38
40.21
40.05
39.88
39.71
39.54
39.38
21.12
14.44
f1 (ppm)

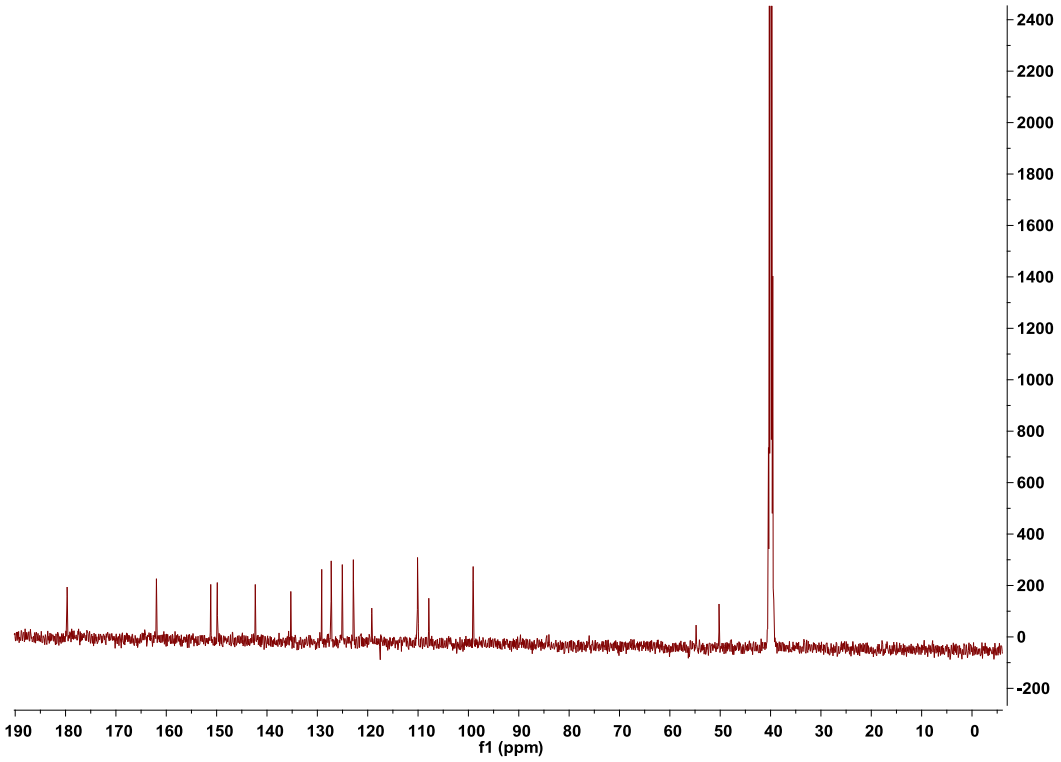

Sample Name RYF-20
Inj Vol 3
Data Filename RYF-20_73.d
Position p2f1
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment PNS ms-ms
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 7/20/2015 2:19:06 PM
C17 H11 N3 O3: +ESI Scan (0.107-0.206 min, 7 Scans) Frag=180.0V RYF-20_73.d Subtract
x10 4
633.1504
328.0701
([C17 H11 N3 O3]+Na)+
555.4132
722.4337
938.2316
854.2217

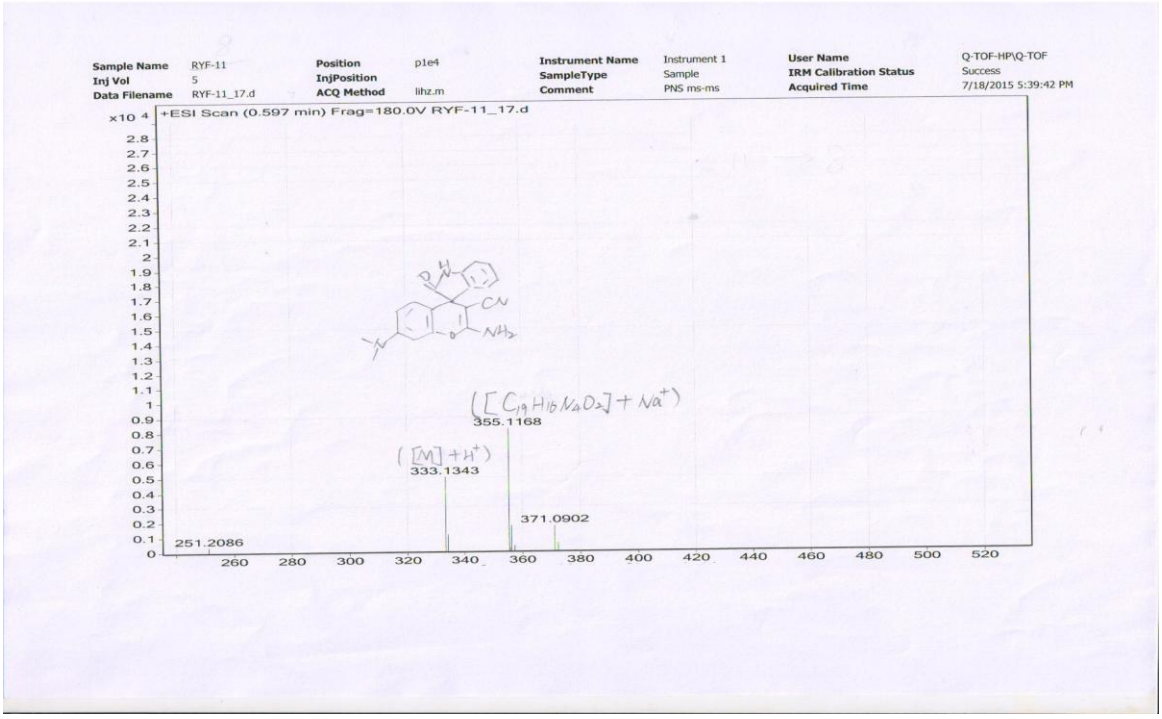
4u.


HN
O
CN
N
O
NH2

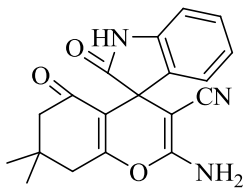

BRUKER
Transmittance [%]
100
90
80
70
60
3467.50
3319.12
2203.67
1716.81
1655.51
1628.92
1557.94
1523.40
1471.37
1402.75
1322.42
1286.27
1221.95
1155.54
1120.26
815.60
792.99
750.39
647.14
617.35
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

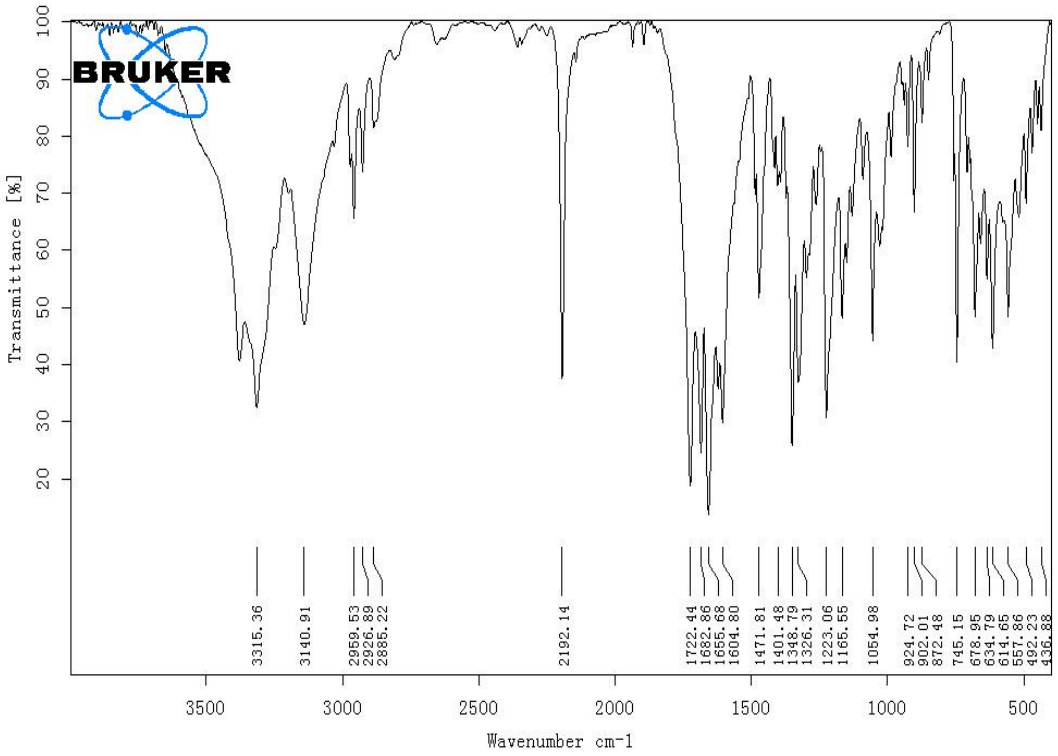

4500
4000
3500
3000
2500
2000
1500
1000
500
0
1.00
1.04
2.05
2.11
1.04
1.03
1.06
0.93
6.23
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

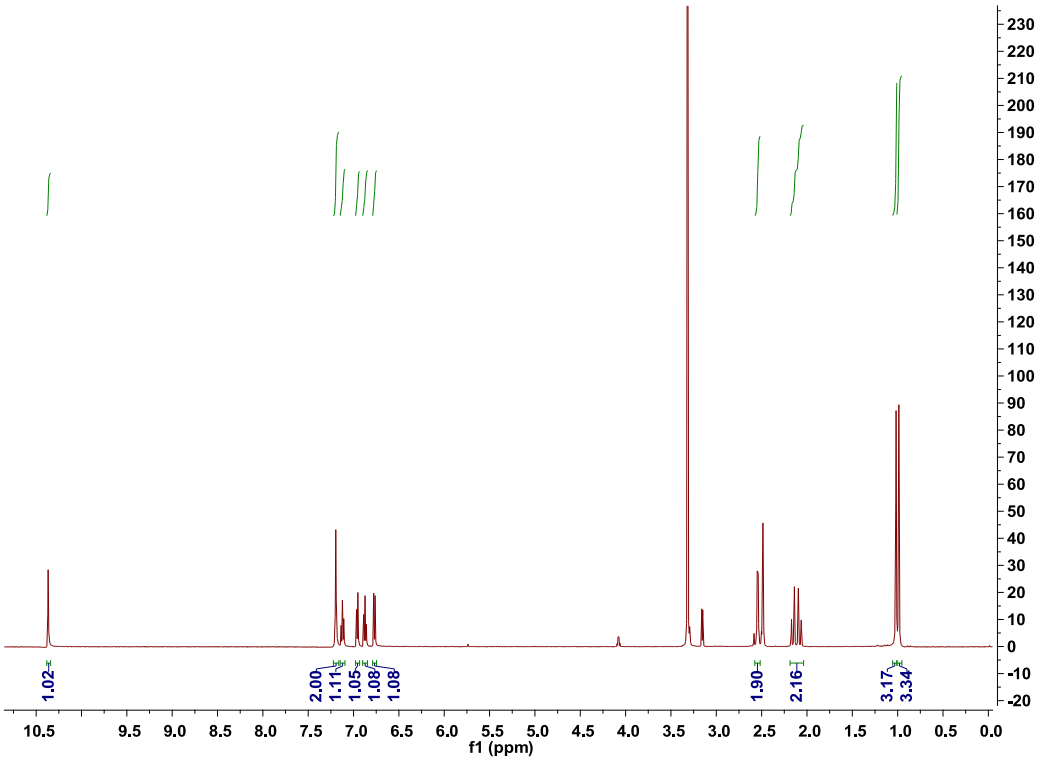

2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

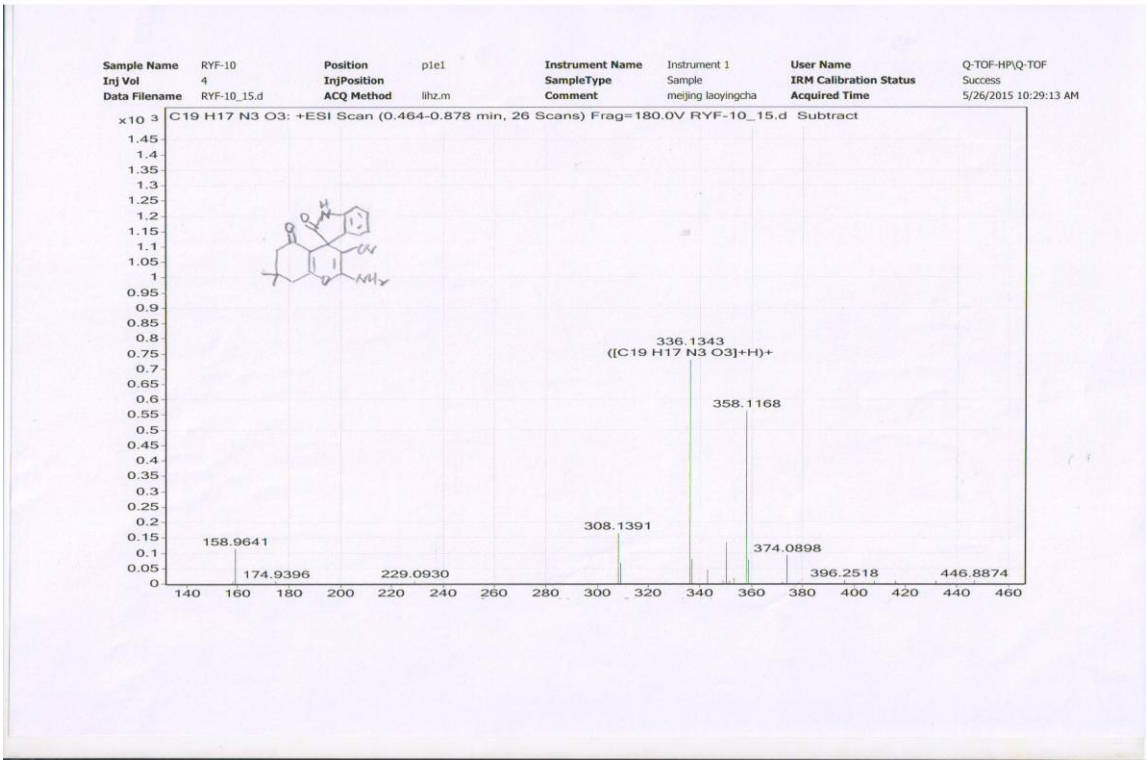

Sample Name RYF-11
Inj Vol 5
Data Filename RYF-11_17.d
Position p1e4
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment PNS ms-ms
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 7/18/2015 5:39:42 PM
+ESI Scan (0.597 min) Frag=180.0V RYF-11_17.d
x10 4
355.1168
333.1343
371.0902
251.2086
260 280 300 320 340 360 380 400 420 440 460 480 500 520

4v.

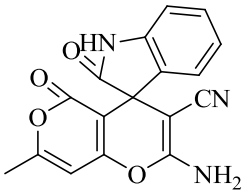

HN
O
O
CN
O
NH2

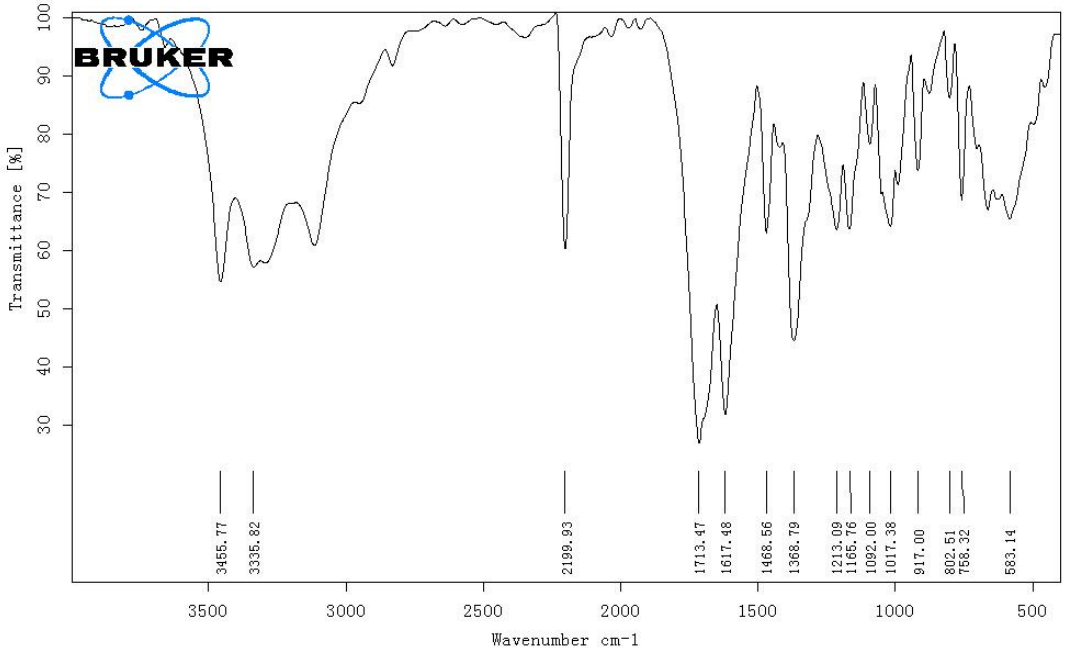

BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
20
3315.36
3140.91
2959.53
2926.89
2885.22
2192.14
1722.44
1682.86
1655.68
1604.80
1471.81
1401.48
1348.79
1326.31
1223.06
1165.55
1054.98
924.72
902.01
872.48
745.15
678.95
634.79
614.65
557.86
492.23
436.88
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

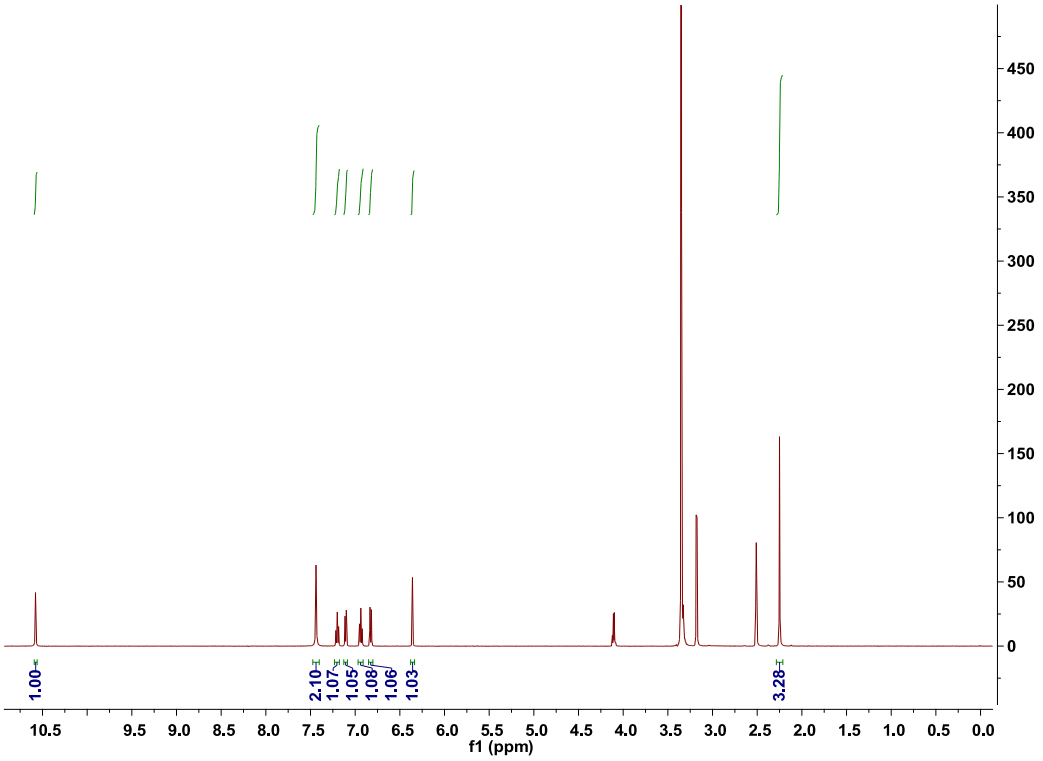

1.02
2.00
1.11
1.05
1.08
1.08
1.90
2.16
3.17
3.34
f1 (ppm)

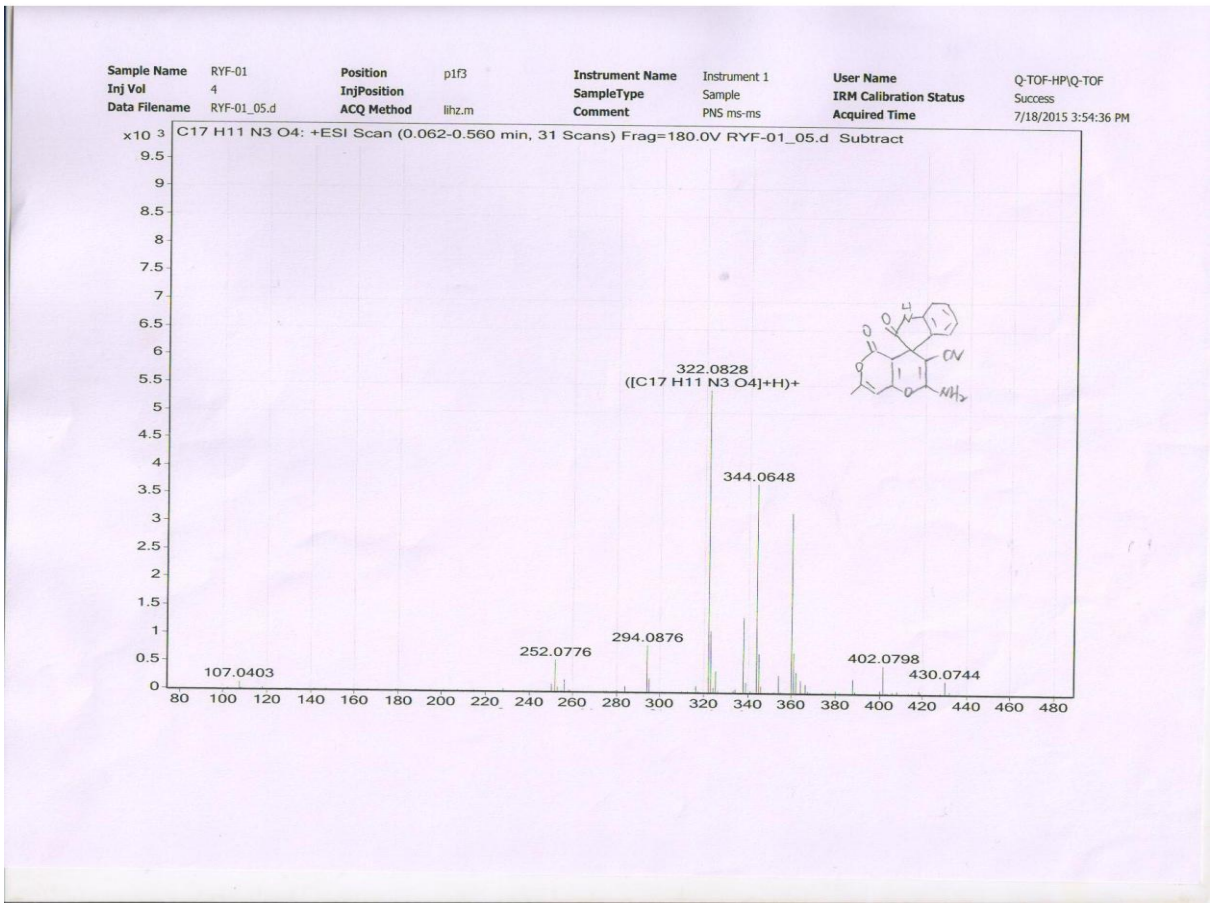

Sample Name RYF-10
Inj Vol 4
Data Filename RYF-10_15.d
Position p1e1
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment meijing laoyingcha
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 5/26/2015 10:29:13 AM
C19 H17 N3 O3: +ESI Scan (0.464-0.878 min, 26 Scans) Frag=180.0V RYF-10_15.d Subtract
336.1343
([C19 H17 N3 O3]+H)+
358.1168
308.1391
374.0898
158.9641
174.9396
229.0930
396.2518
446.8874

4w.

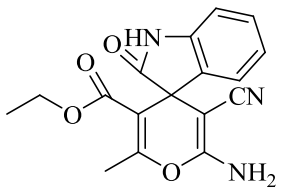

HN
O
O
O
CN
O
NH2

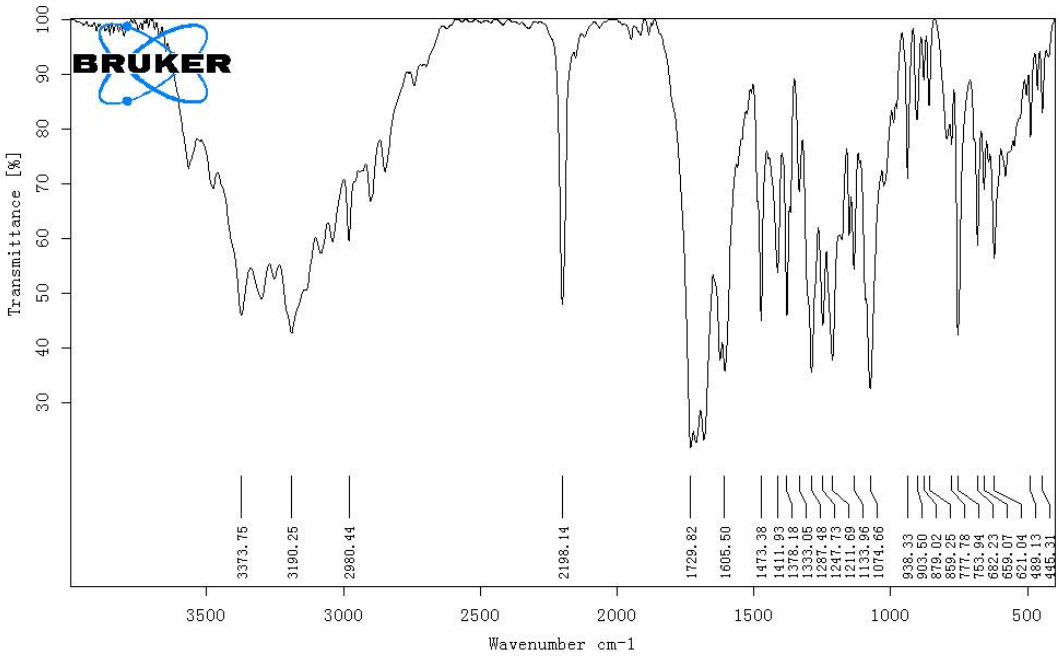

BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
3455.77
3335.82
2199.93
1713.47
1617.48
1468.56
1368.79
1213.09
1165.76
1092.00
1017.38
917.00
802.51
768.32
583.14
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

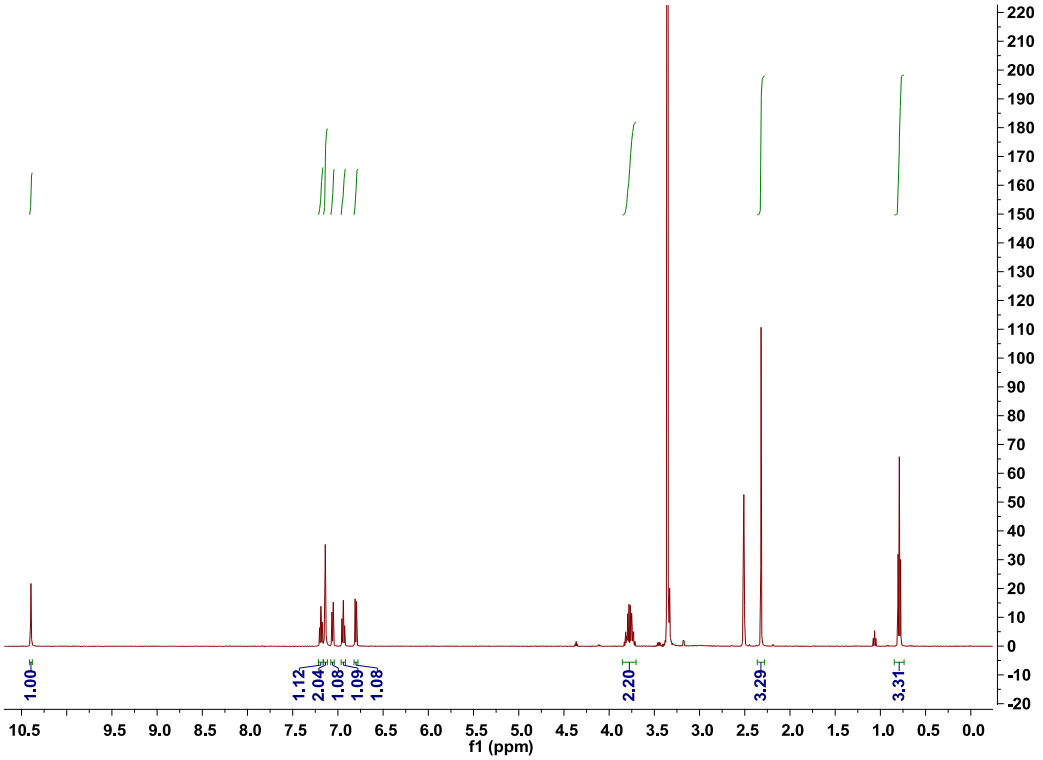

450
400
350
300
250
200
150
100
50
0
1.00
2.10
1.07
1.05
1.08
1.06
1.03
3.28
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

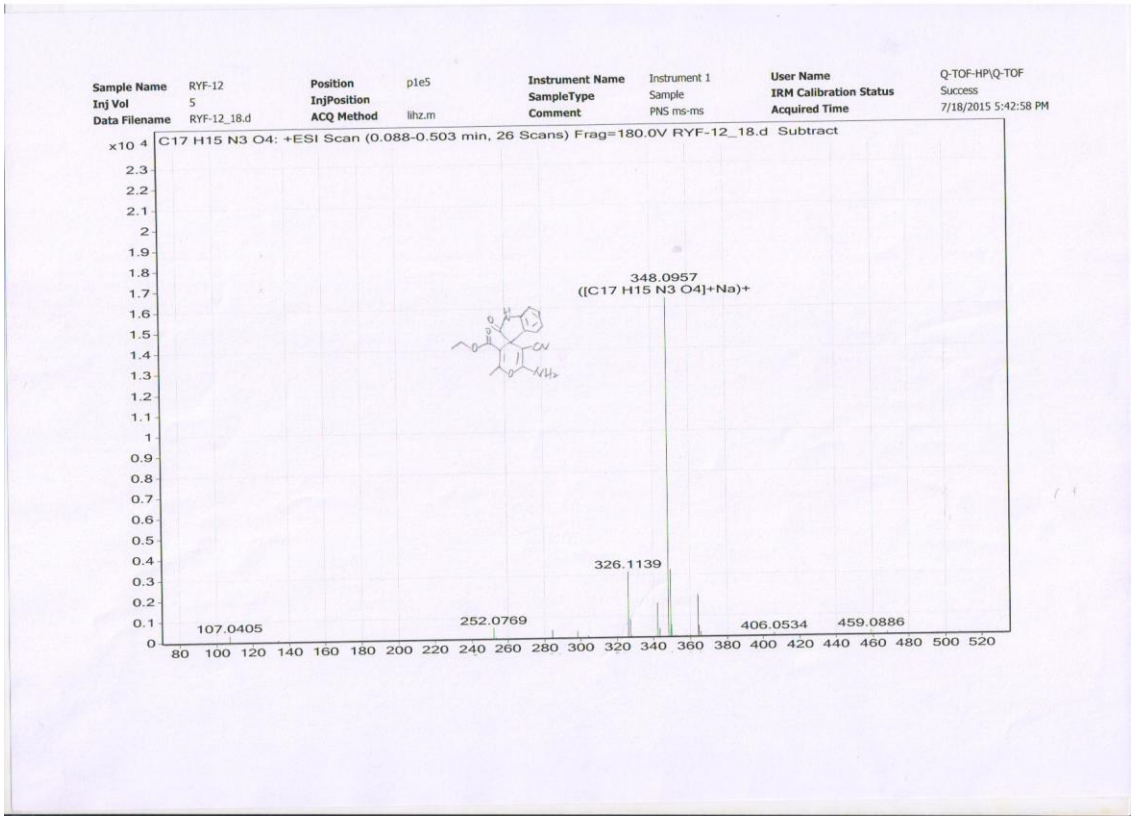

Sample Name RYF-01
Inj Vol 4
Data Filename RYF-01_05.d
Position p1f3
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment PNS ms-ms
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 7/18/2015 3:54:36 PM
x10 3
C17 H11 N3 O4: +ESI Scan (0.062-0.560 min, 31 Scans) Frag=180.0V RYF-01_05.d Subtract
322.0828
([C17 H11 N3 O4]+H)+
344.0648
294.0876
252.0776
107.0403
402.0798
430.0744
CN
NH2

4x.

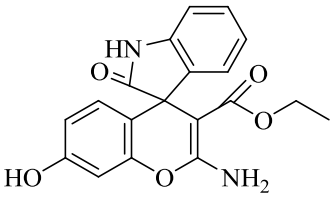

O
HN
O
CN
O
O
NH2

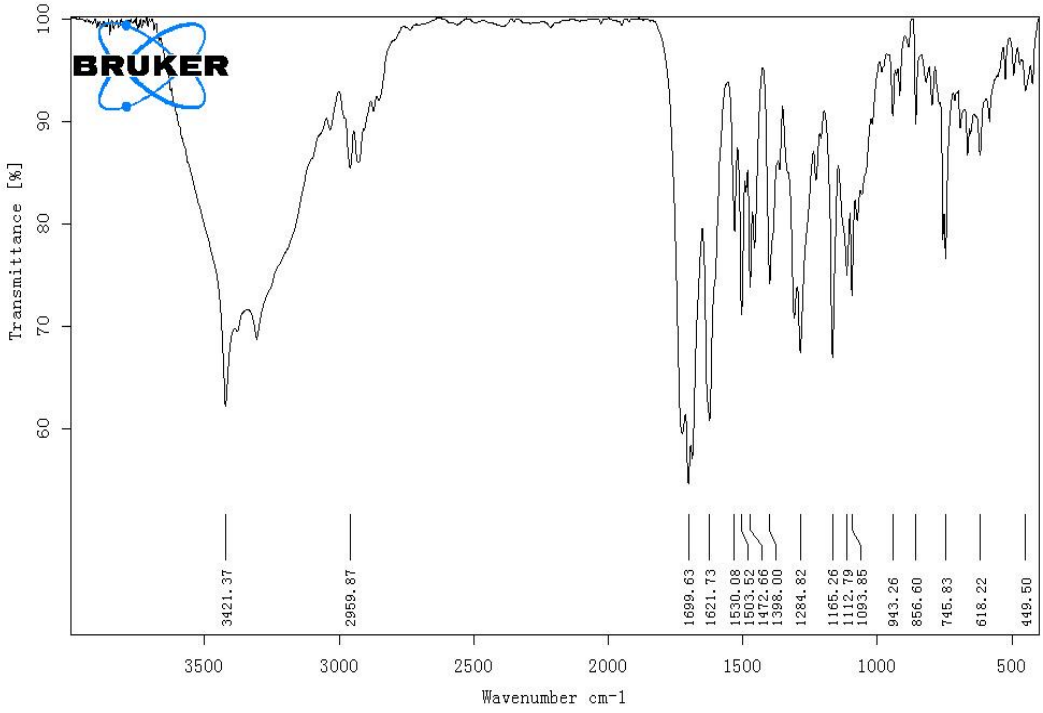

BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
3373.75
3190.25
2980.44
2198.14
1729.82
1605.50
1473.38
1411.93
1378.18
1333.05
1287.48
1247.73
1211.69
1133.96
1074.66
938.33
903.50
879.02
859.25
777.78
753.94
682.23
659.07
621.04
489.13
445.31
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

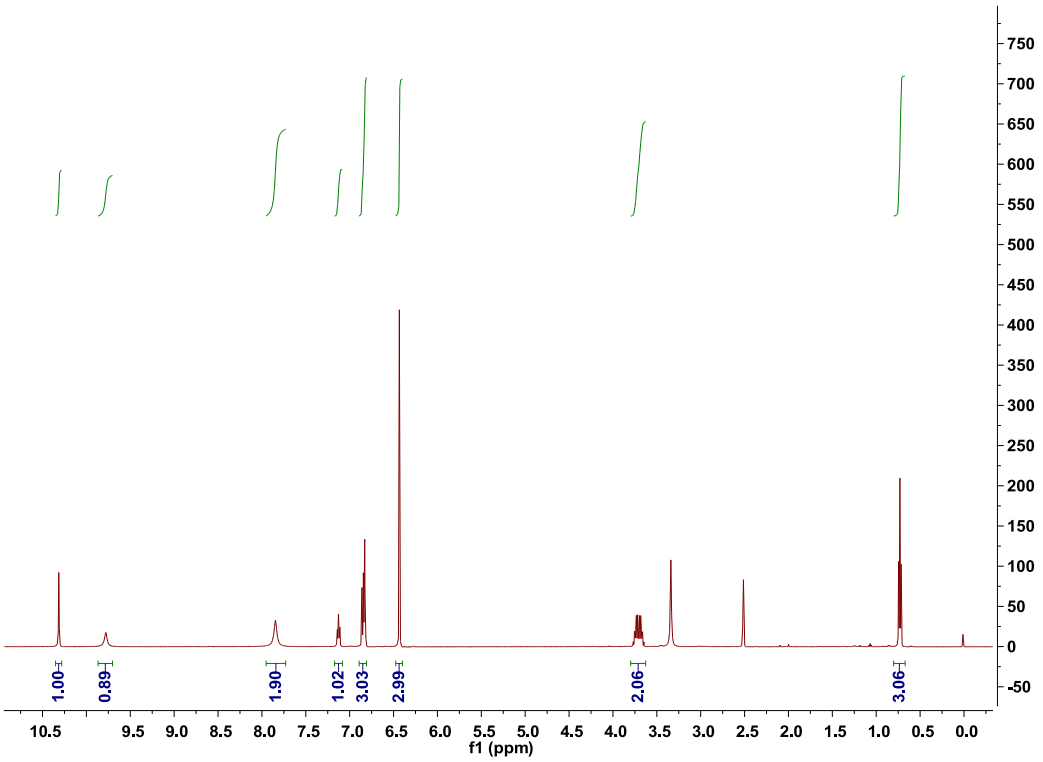

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
1.00
1.12
2.04
1.08
1.09
1.08
2.20
3.29
3.31
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

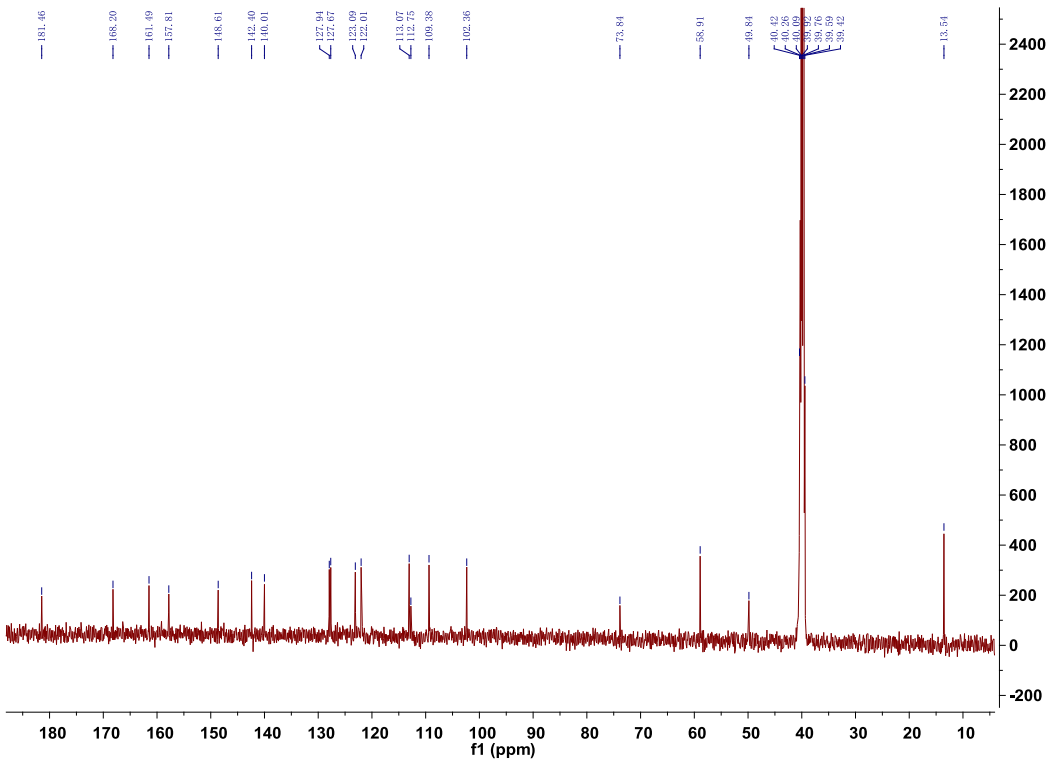

Sample Name RYF-12
Inj Vol 5
Data Filename RYF-12_18.d
Position p1e5
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment PNS ms-ms
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 7/18/2015 5:42:58 PM
C17 H15 N3 O4: +ESI Scan (0.088-0.503 min, 26 Scans) Frag=180.0V RYF-12_18.d Subtract
x10 4
348.0957
([C17 H15 N3 O4]+Na)+
326.1139
107.0405
252.0769
406.0534
459.0886

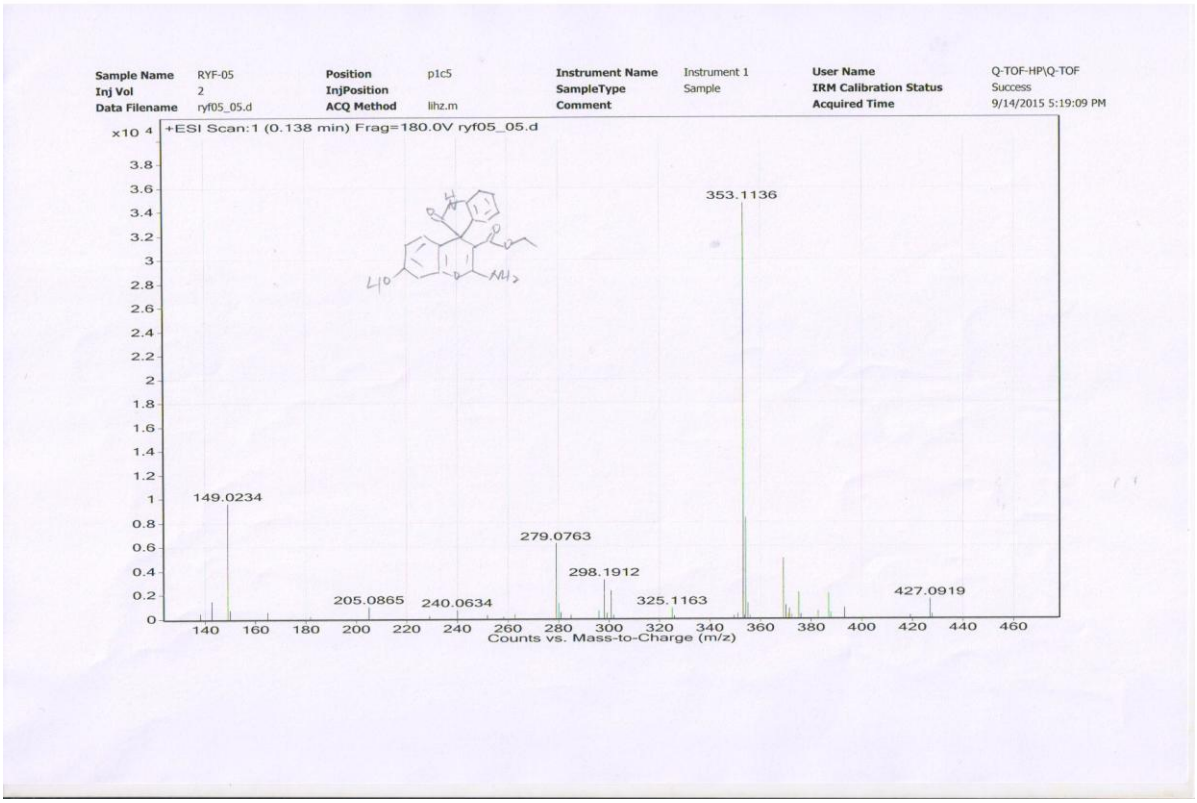
4y.


HN
O
O
O
HO
O
NH2

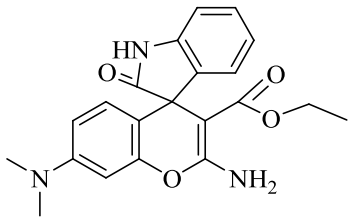

BRUKER
Transmittance [%]
100
90
80
70
60
3421.37
2959.87
1699.63
1621.73
1530.08
1503.52
1472.66
1398.00
1284.82
1165.26
1112.79
1093.85
943.26
856.60
745.83
618.22
449.50
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

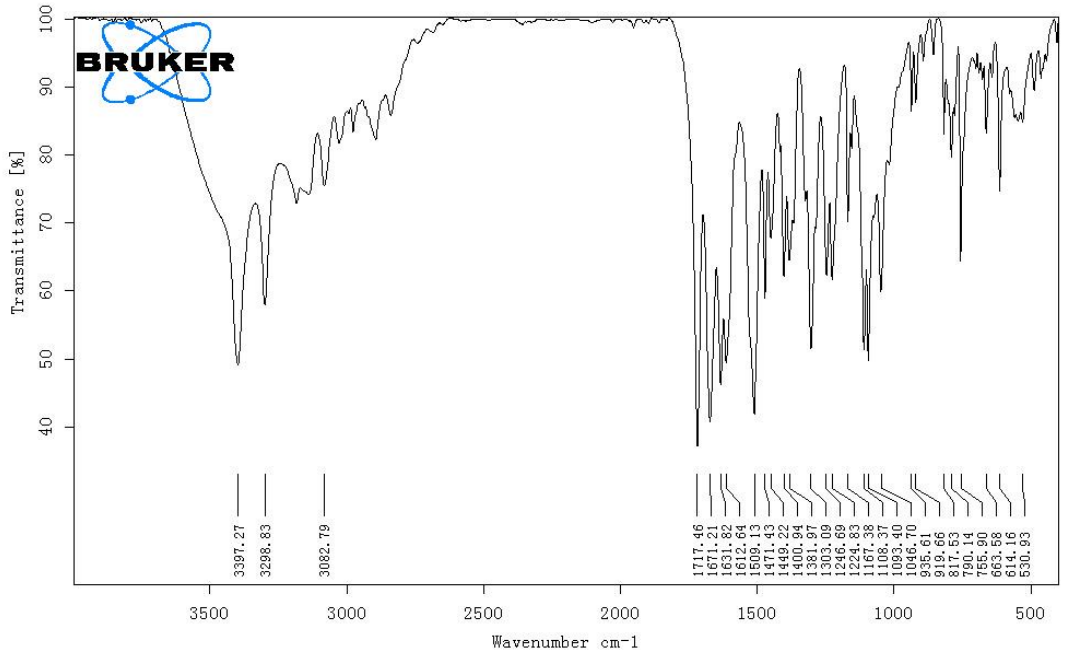

1.00
0.89
1.90
1.02
3.03
2.99
2.06
3.06
f1 (ppm)

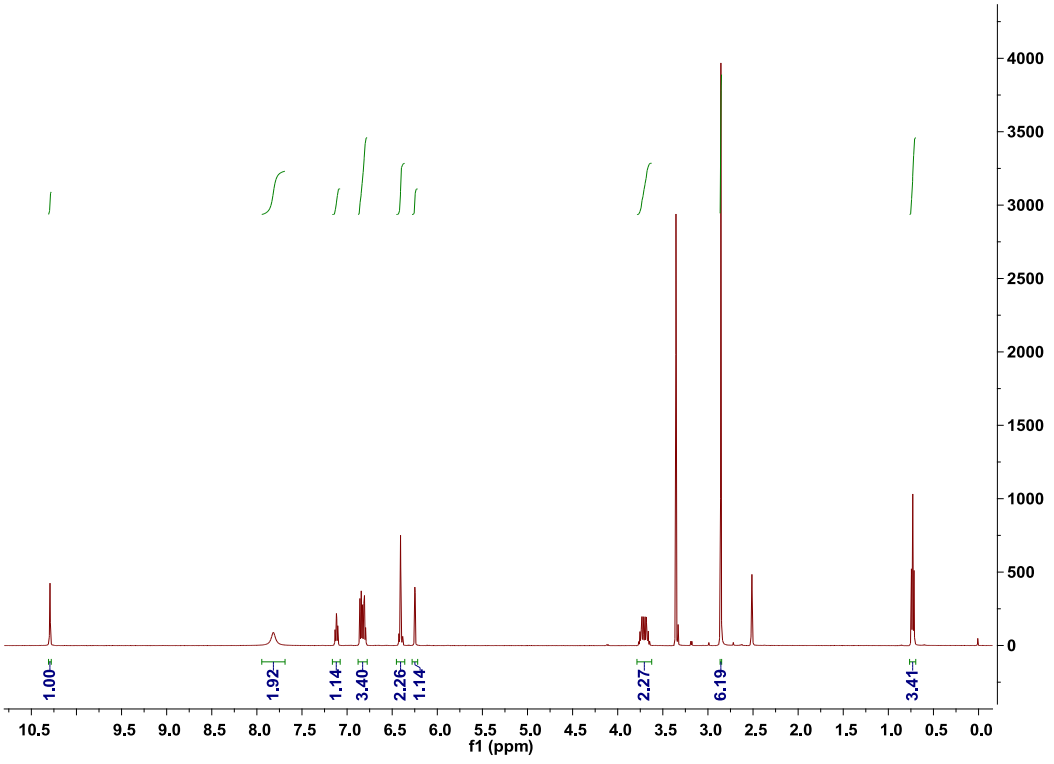

181.46
168.20
161.49
157.81
148.61
142.40
140.01
127.94
127.67
123.09
122.01
113.07
112.75
109.38
102.36
73.84
58.91
49.84
40.42
40.26
40.09
39.92
39.76
39.59
39.42
13.54
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

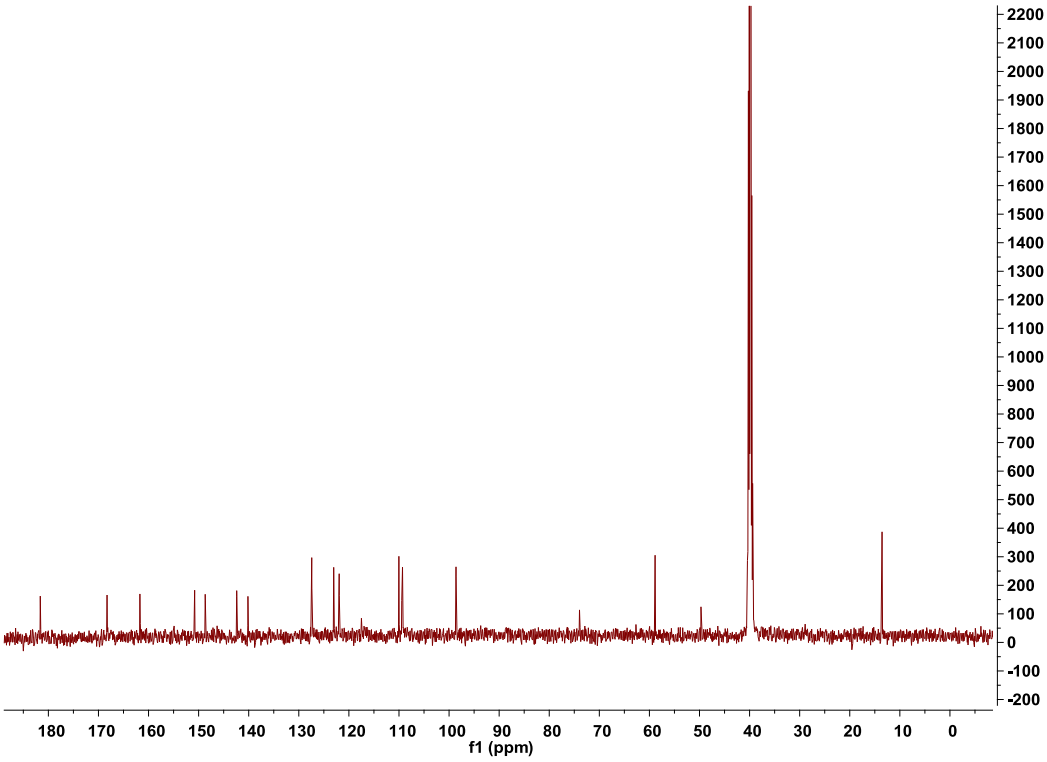

Sample Name RYF-05
Inj Vol 2
Data Filename ryf05_05.d
Position p1c5
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 9/14/2015 5:19:09 PM
+ESI Scan:1 (0.138 min) Frag=180.0V ryf05_05.d
x10 4
353.1136
149.0234
279.0763
298.1912
205.0865
240.0634
325.1163
427.0919
Counts vs. Mass-to-Charge (m/z)

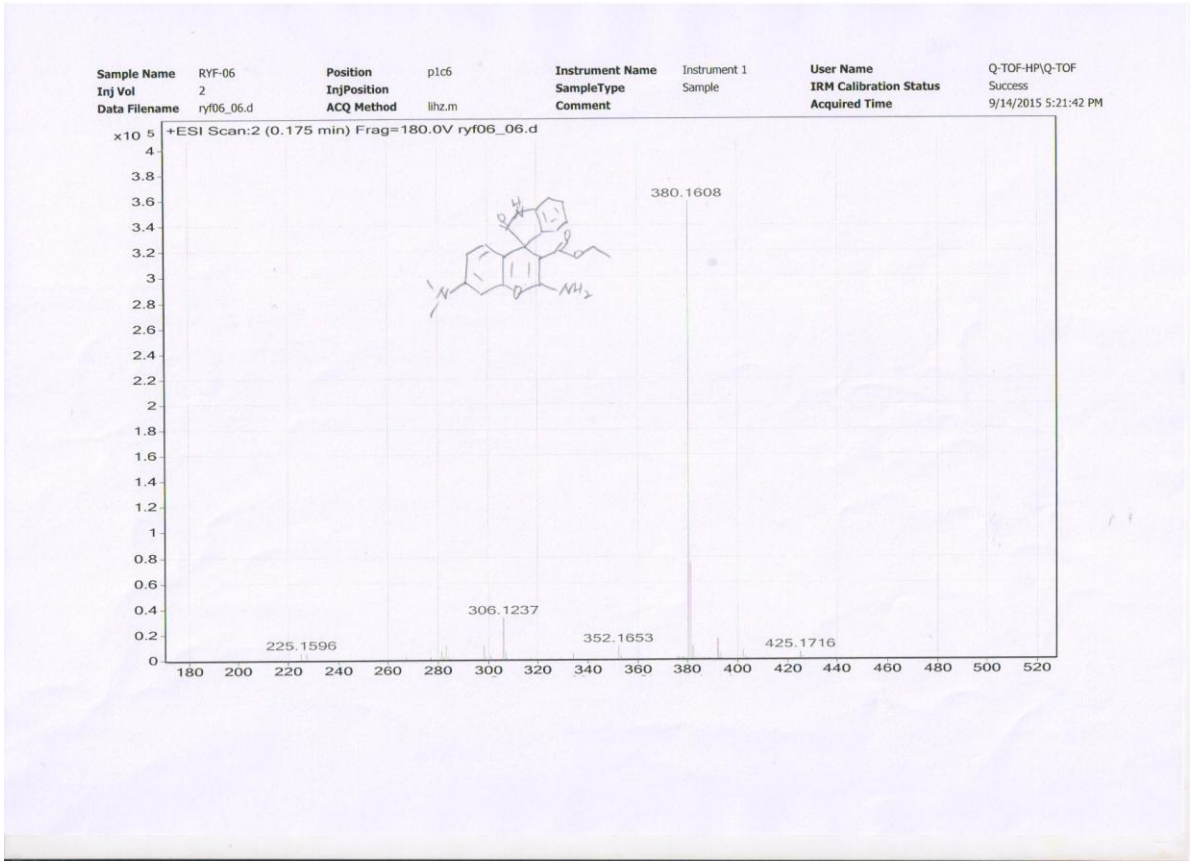
4z.


HN
O
O
O
N
O
NH2

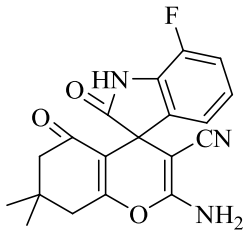

BRUKER
Transmittance [%]
100
90
80
70
60
50
40
3397.27
3298.83
3082.79
1717.46
1671.21
1631.82
1612.64
1509.13
1471.43
1449.22
1400.94
1381.97
1303.09
1246.69
1224.83
1167.38
1108.37
1093.40
1046.70
935.61
919.66
817.53
790.14
755.90
663.58
614.16
530.93
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

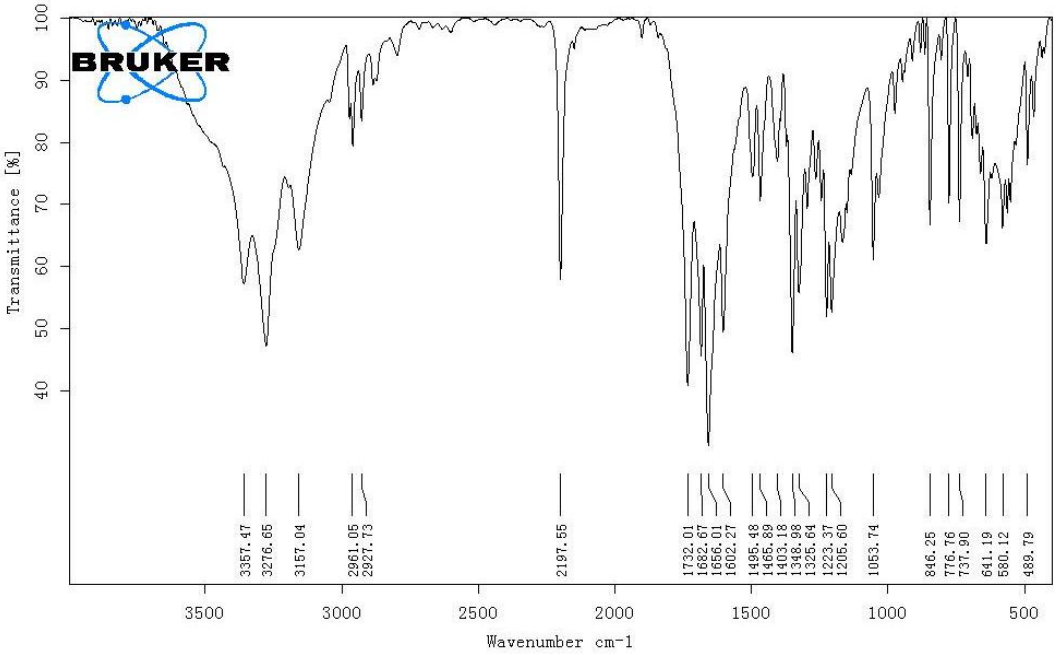

4000
3500
3000
2500
2000
1500
1000
500
0
1.00
1.92
1.14
3.40
2.26
1.14
2.27
6.19
3.41
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

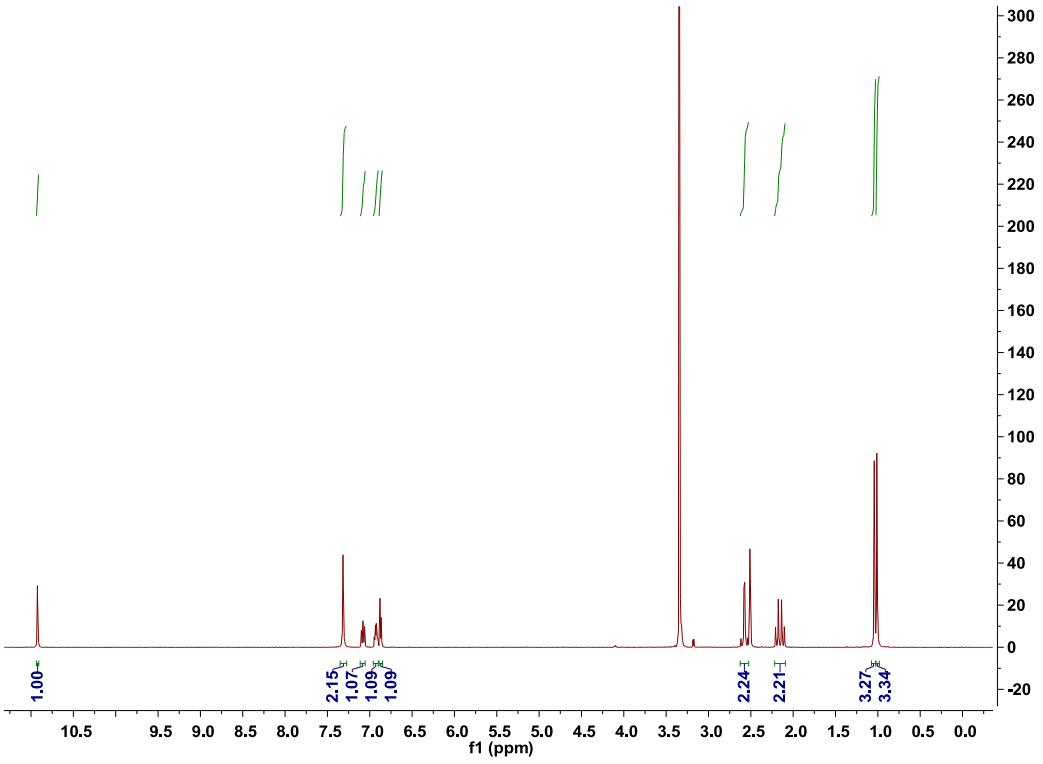

2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Sample Name RYF-06
Inj Vol 2
Data Filename ryf06_06.d
Position p1c6
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 9/14/2015 5:21:42 PM
+ESI Scan:2 (0.175 min) Frag=180.0V ryf06_06.d
x10 5
380.1608
306.1237
225.1596
352.1653
425.1716
180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520

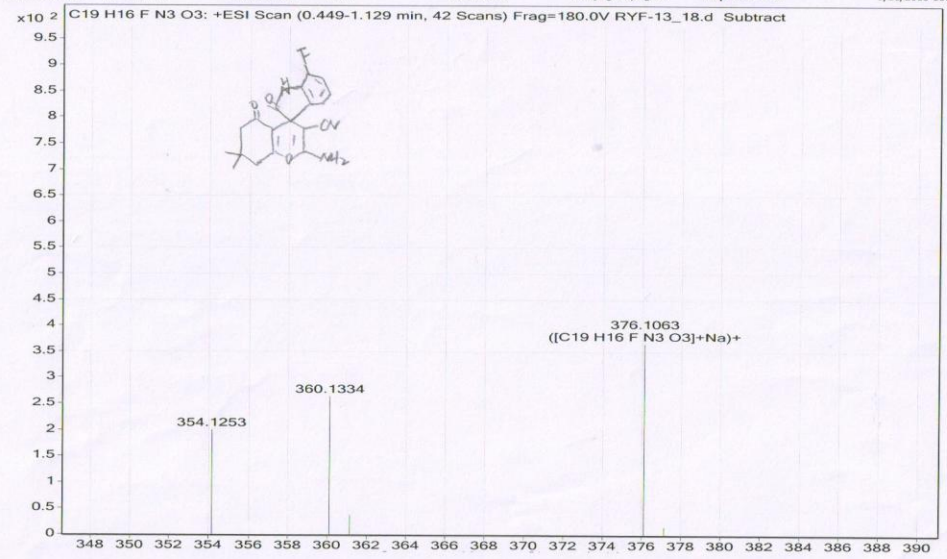
4aa.


F
HN
O
O
CN
O
NH2

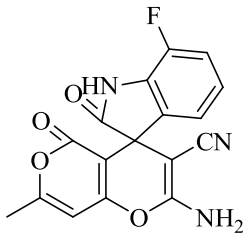

BRUKER
Transmittance [%]
100
90
80
70
60
50
40
3357.47
3276.65
3157.04
2961.05
2927.73
2197.55
1732.01
1682.67
1656.01
1602.27
1495.48
1465.89
1403.18
1348.98
1325.64
1223.37
1205.60
1053.74
846.25
776.76
737.90
641.19
580.12
489.79
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

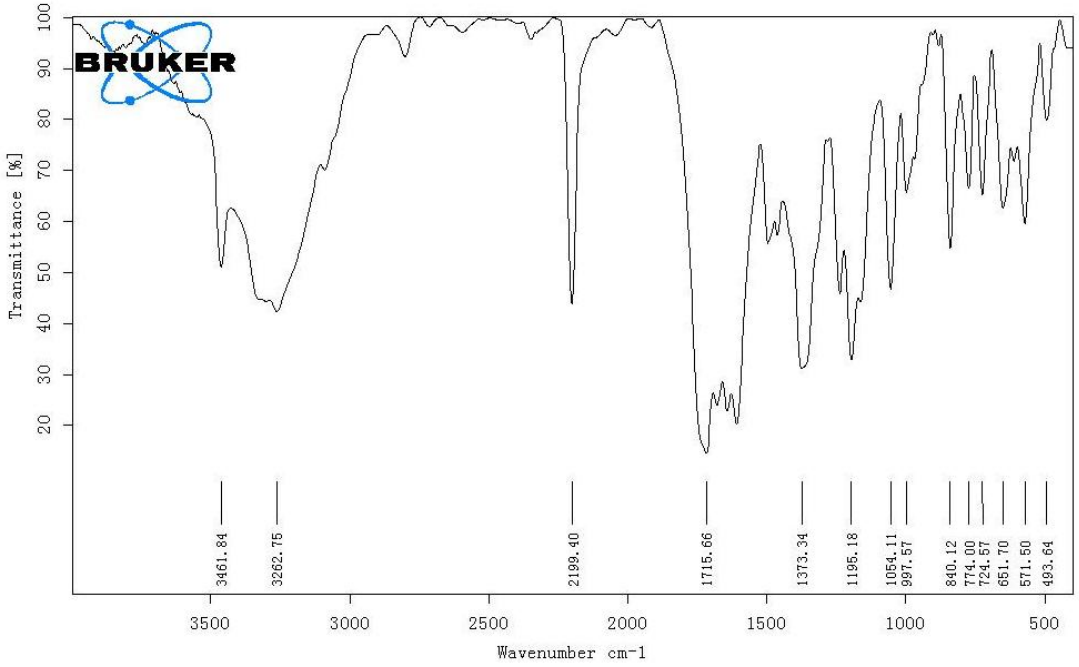

300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
1.00
2.15
1.07
1.09
1.09
2.24
2.21
3.27
3.34
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

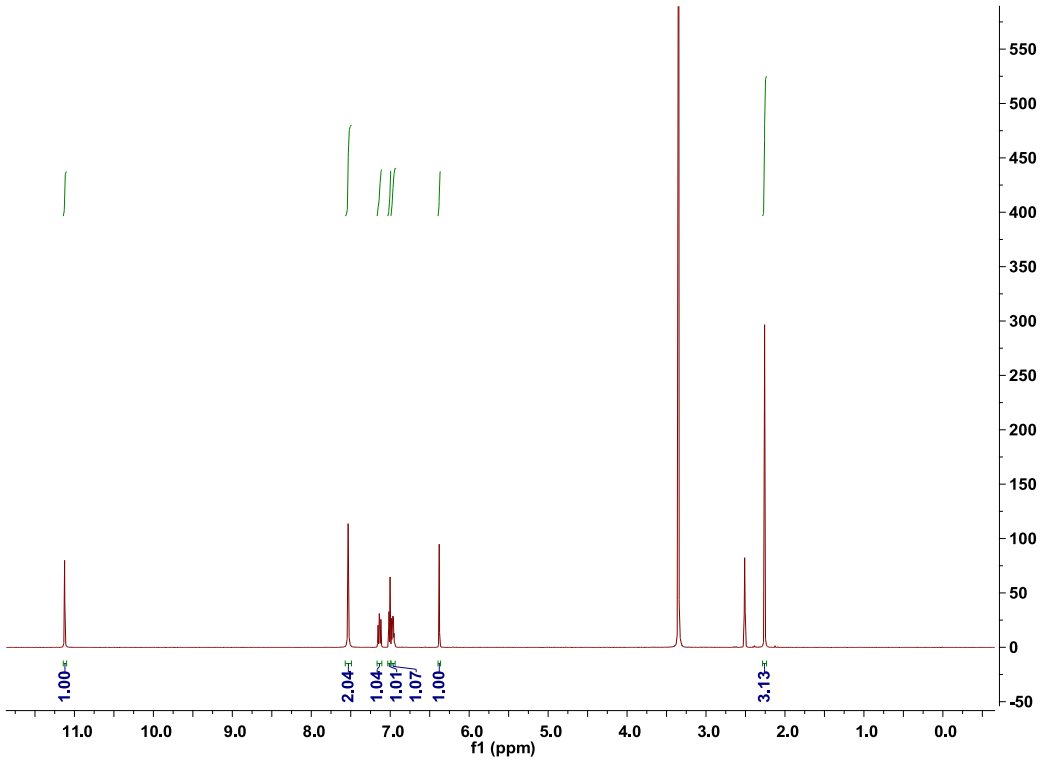
Sample Name	RYF-13	**Position**	p1e4	**Instrument Name**	Instrument 1	**User Name**	Q-TOF-HP\Q-TOF
Inj Vol	4	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	RYF-13_18.d	**ACQ Method**	lihz.m	**Comment**	meijing laoyingcha	**Acquired Time**	5/26/2015 10:41:10 AM



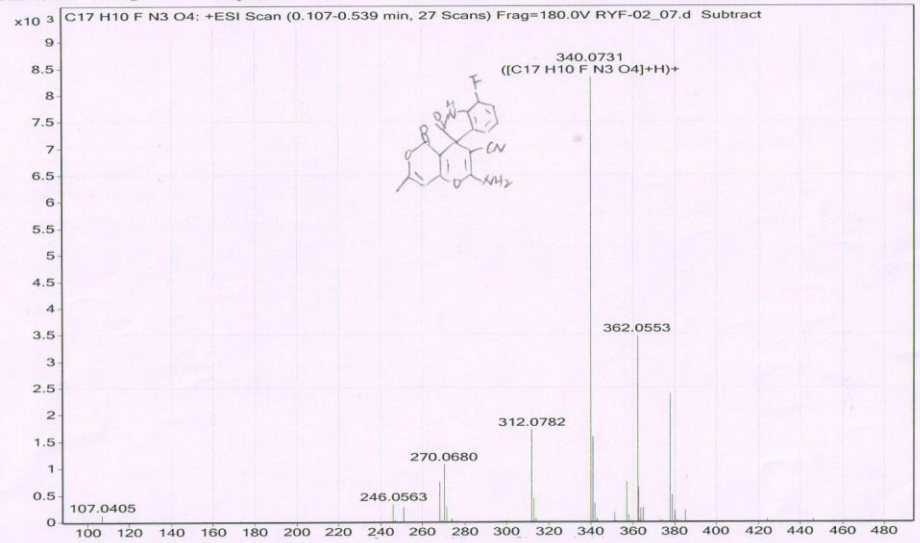
4bb.


F
HN
O
O
O
CN
O
NH2

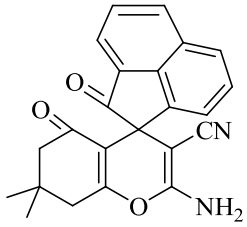

BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
20
3461.84
3262.75
2199.40
1715.66
1373.34
1196.18
1054.11
997.57
840.12
774.00
724.57
651.70
571.50
493.64
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

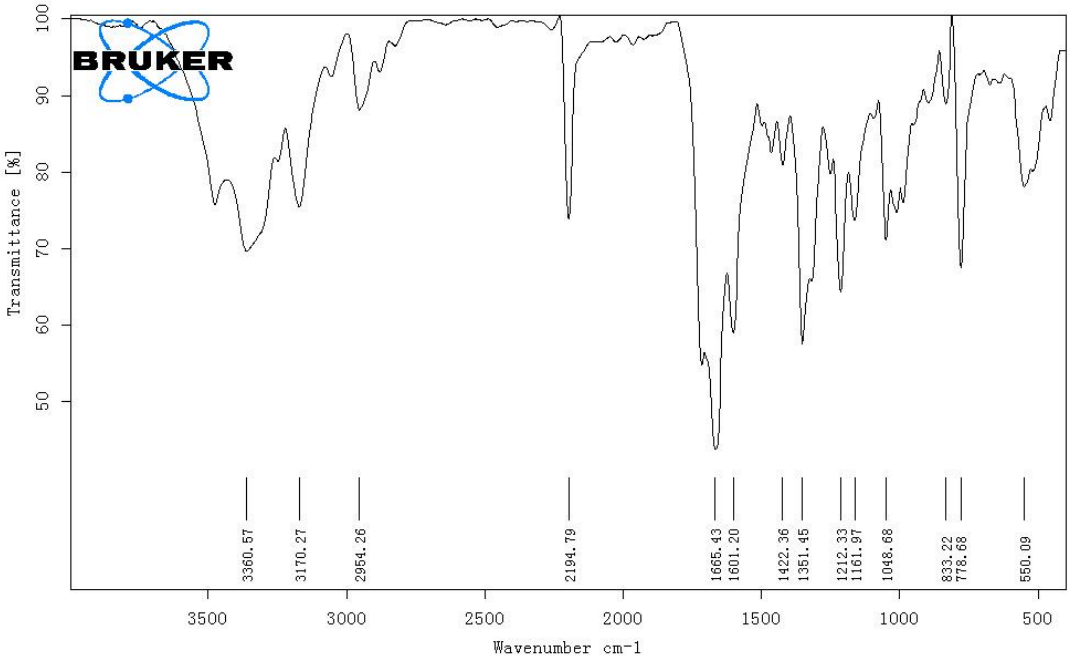

1.00
2.04
1.04
1.01
1.07
1.00
3.13
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
550
500
450
400
350
300
250
200
150
100
50
0
-50

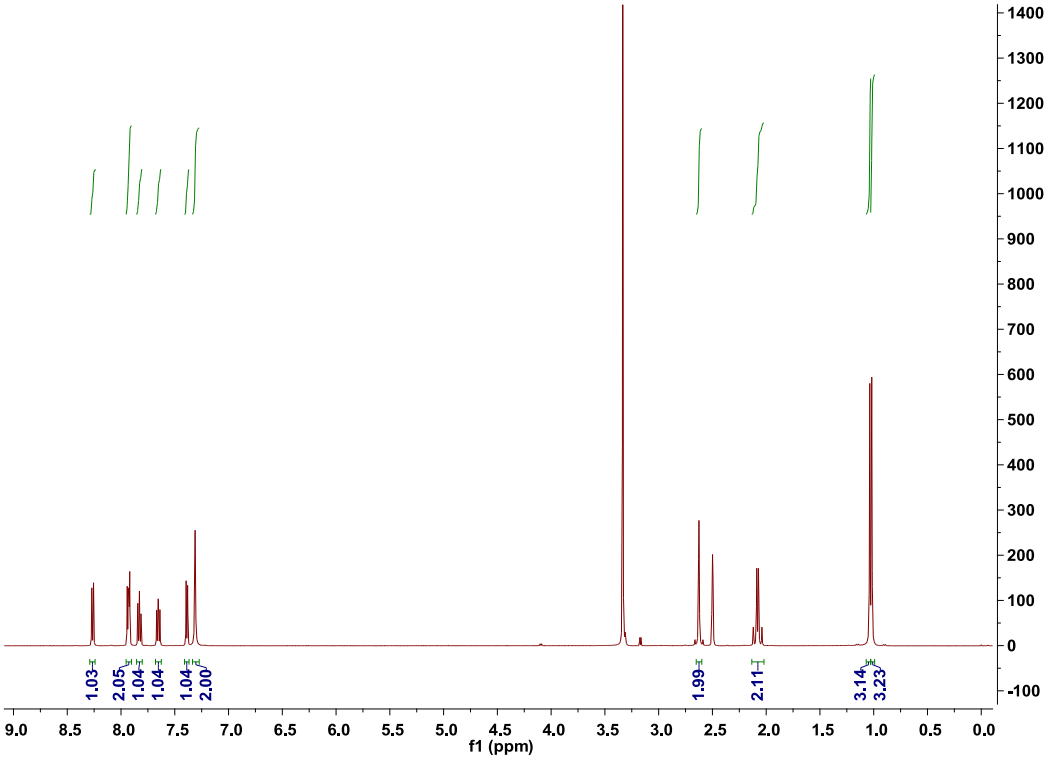
Sample Name	RYF-02	**Position**	p1f4	**Instrument Name**	Instrument 1	**User Name**	Q-TOF-HP\Q-TOF
Inj Vol	5	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	RYF-02_07.d	**ACQ Method**	lihz.m	**Comment**	PNS ms-ms	**Acquired Time**	7/18/2015 4:02:58 PM



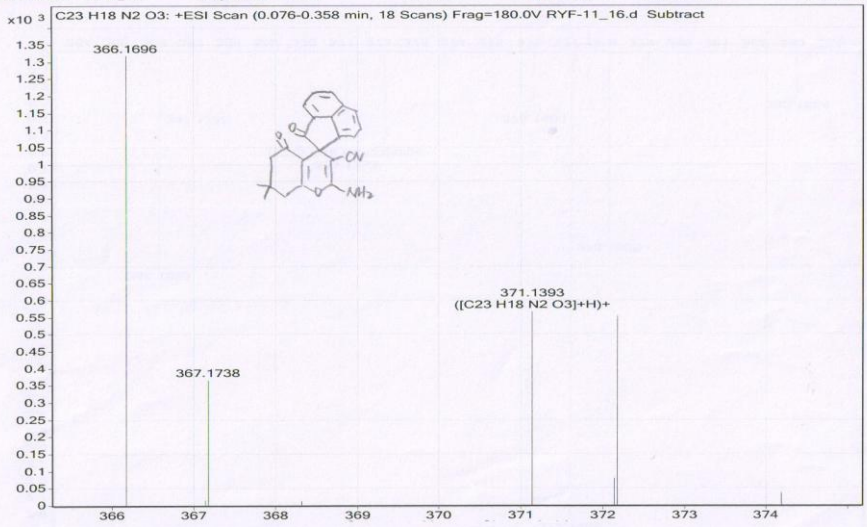
4cc.


O
O
CN
O
NH2

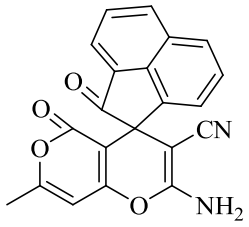

BRUKER
Transmittance [%]
100
90
80
70
60
50
3360.57
3170.27
2954.26
2194.79
1665.43
1601.20
1422.36
1351.45
1212.33
1161.97
1048.68
833.22
778.68
550.09
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

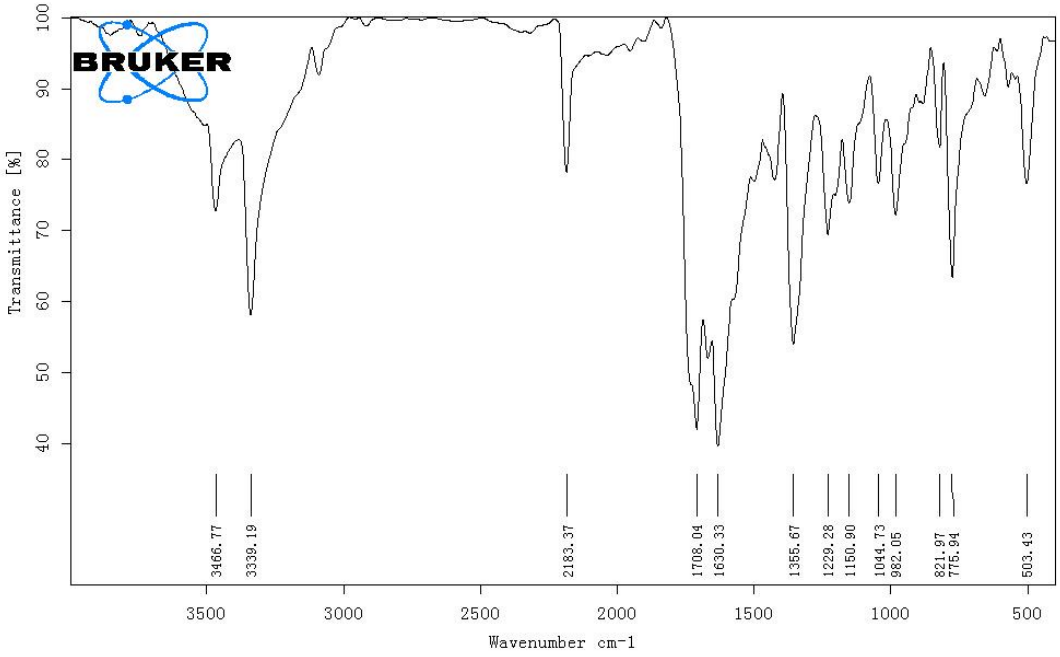

1.03
2.05
1.04
1.04
1.04
2.00
1.99
2.11
3.14
3.23
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

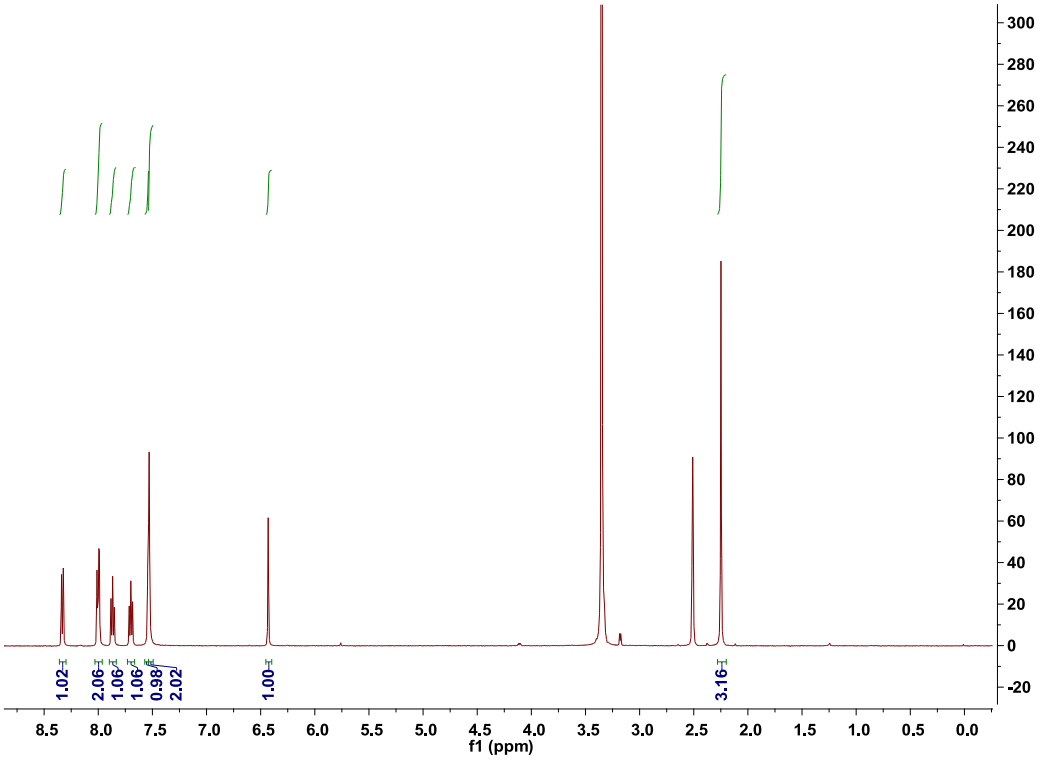
Sample Name	RYF-11	**Position**	p1e2	**Instrument Name**	Instrument 1	**User Name**	Q-TOF-HP\Q-TOF
Inj Vol	4	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	RYF-11_16.d	**ACQ Method**	lihz.m	**Comment**	meijing laoyingcha	**Acquired Time**	5/26/2015 10:33:30 AM

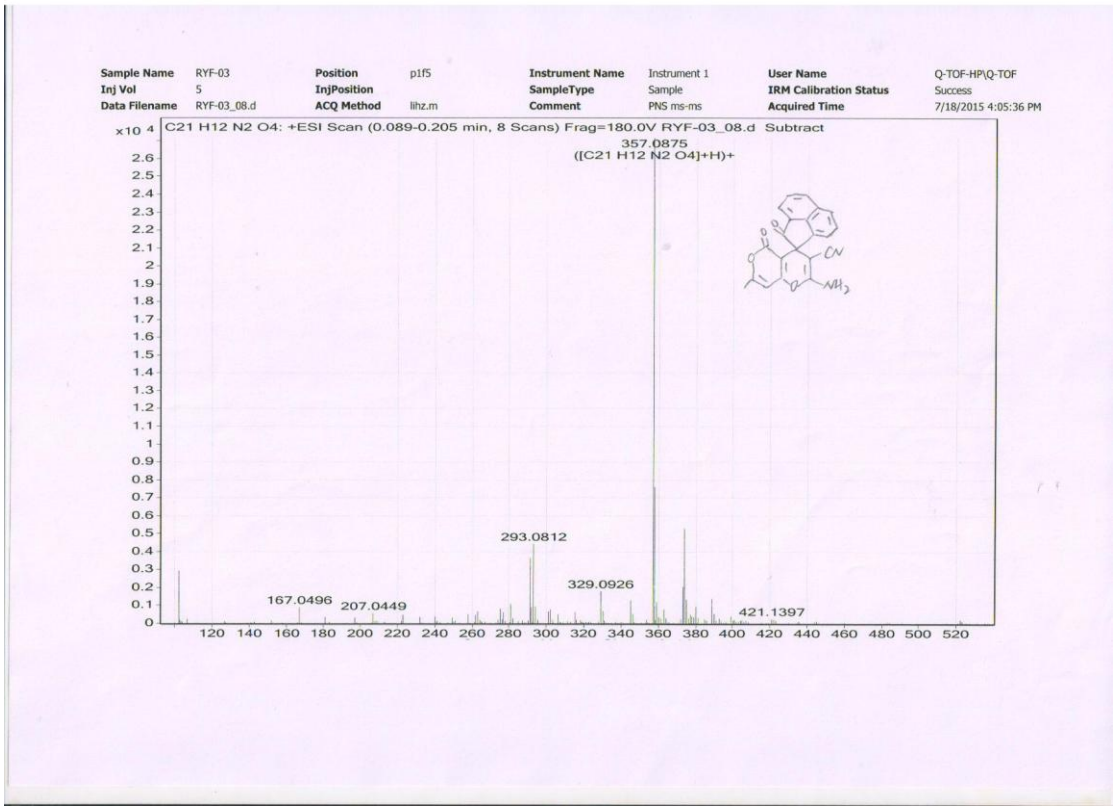


4ee.

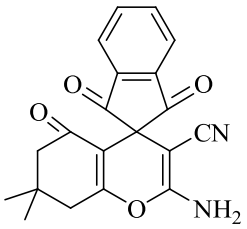

O
O
O
CN
O
NH2

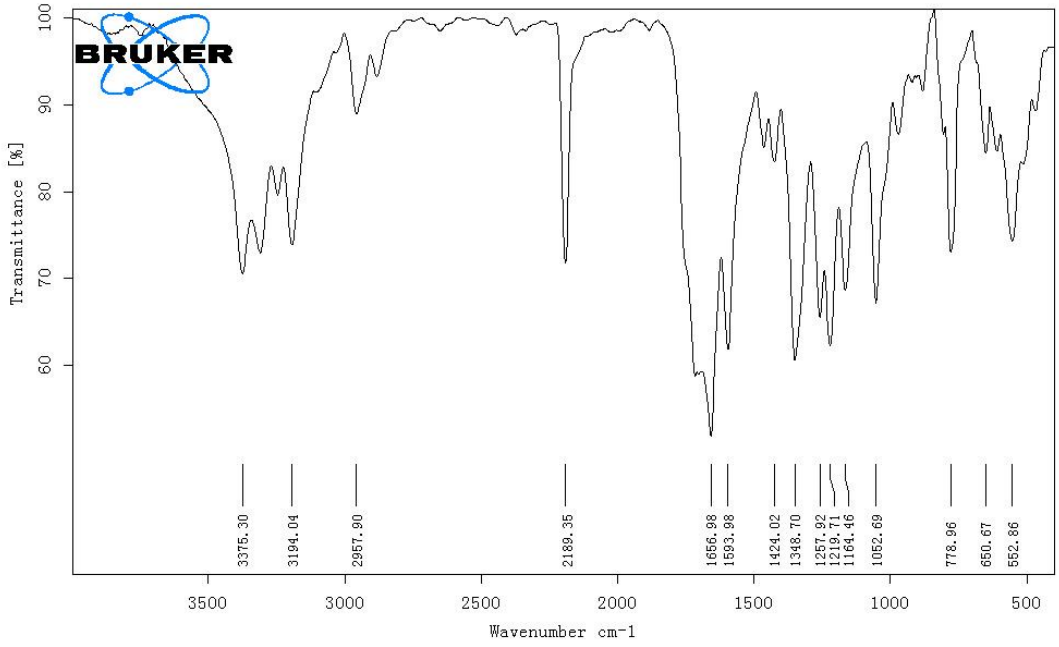

BRUKER
Transmittance [%]
100
90
80
70
60
50
40
3466.77
3339.19
2183.37
1708.04
1630.33
1355.67
1229.28
1150.90
1044.73
982.05
821.97
775.94
503.43
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

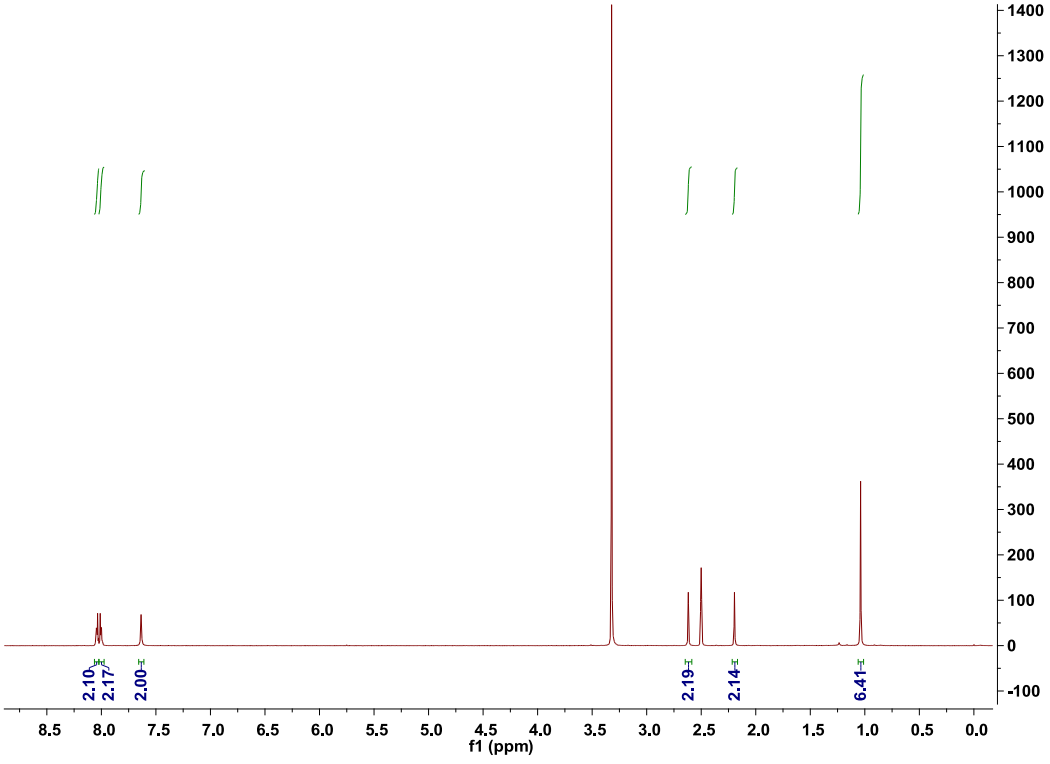

1.02
2.06
1.06
1.06
0.98
2.02
1.00
3.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20


Sample Name RYF-03
Position p1f5
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 5
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename RYF-03_08.d
ACQ Method lihz.m
Comment PNS ms-ms
Acquired Time 7/18/2015 4:05:36 PM
C21 H12 N2 O4: +ESI Scan (0.089-0.205 min, 8 Scans) Frag=180.0V RYF-03_08.d Subtract
x10 4
357.0875
([C21 H12 N2 O4]+H)+
293.0812
329.0926
167.0496
207.0449
421.1397
CN
NH2

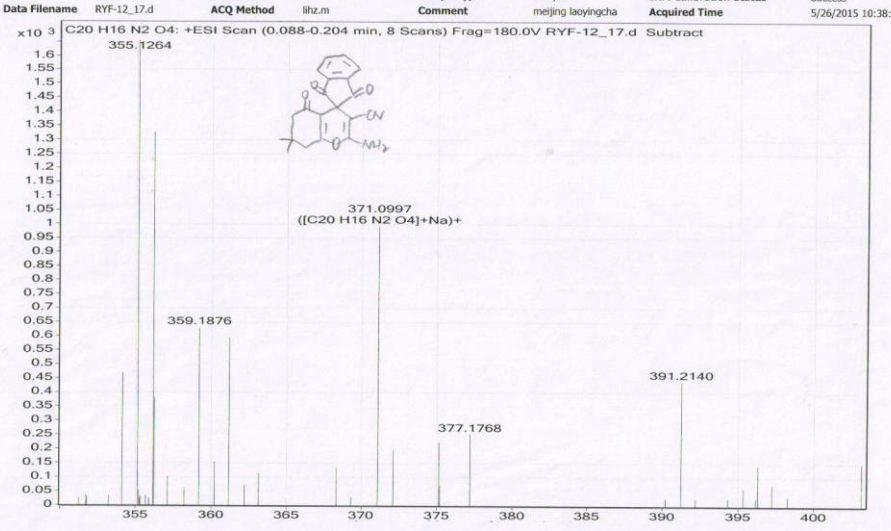
4ff.


O
O
O
CN
O
NH2

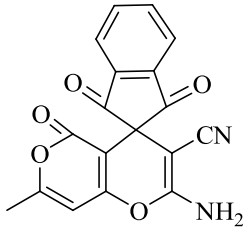

BRUKER
Transmittance [%]
100
90
80
70
60
3375.30
3194.04
2957.90
2189.35
1656.98
1593.98
1424.02
1348.70
1257.92
1219.71
1164.46
1052.69
778.96
650.67
552.86
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

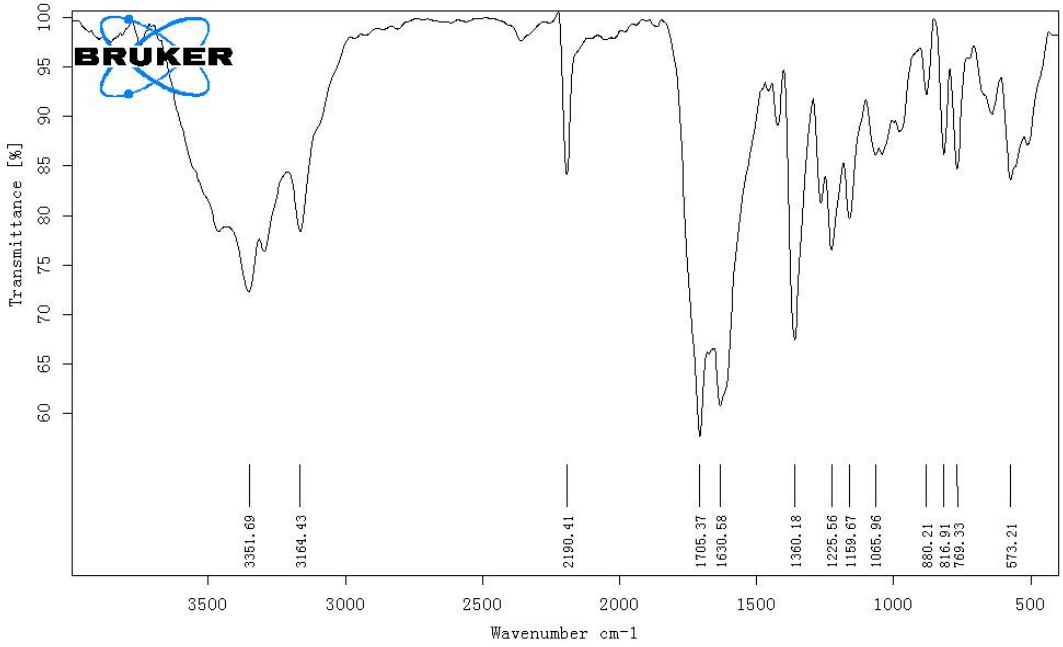

1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
2.10
2.17
2.00
2.19
2.14
6.41
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

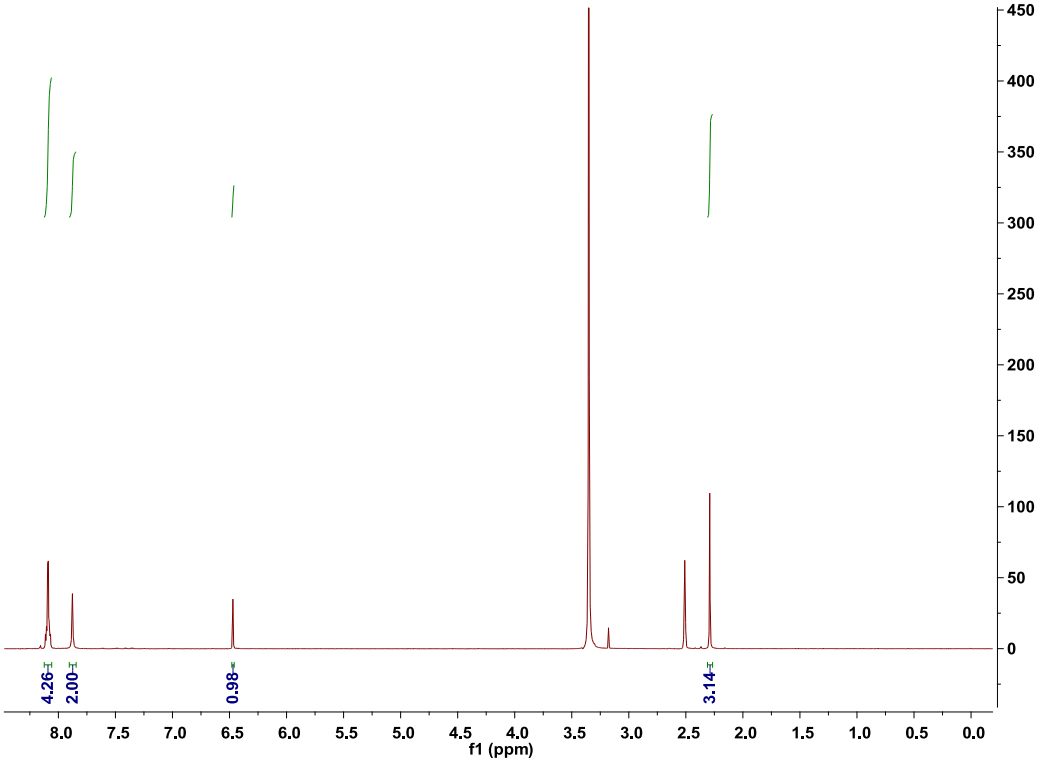
Sample Name	RYF-12	**Position**	p1e3	**Instrument Name**	Instrument 1	**User Name**	Q-TOF-HP\Q-TOF
Inj Vol	4	**InjPosition**		**SampleType**	Sample	**IRM Calibration Status**	Success
Data Filename	RYF-12_17.d	**ACQ Method**	lihz.m	**Comment**	meijing laoyingcha	**Acquired Time**	5/26/2015 10:38:05 AM

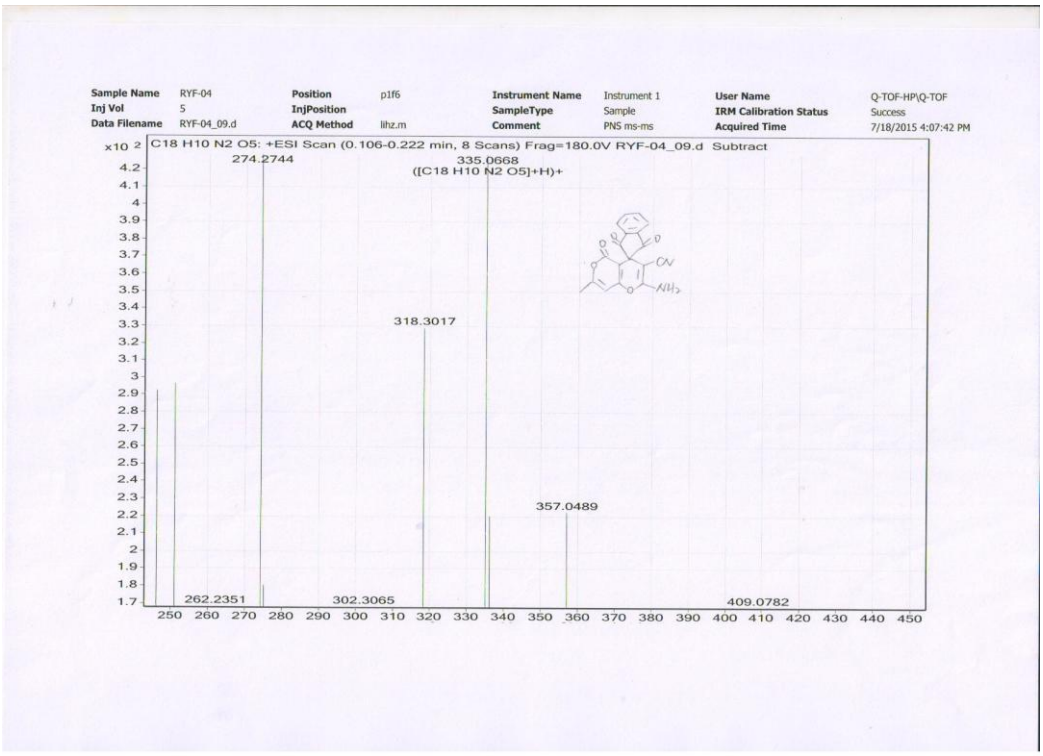


6m、


O
O
O
O
CN
O
NH2


BRUKER
Transmittance [%]
100
95
90
85
80
75
70
65
60
3351.69
3164.43
2190.41
1705.37
1630.58
1360.18
1225.56
1159.67
1065.96
880.21
816.91
769.33
573.21
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1


450
400
350
300
250
200
150
100
50
0
4.26
2.00
0.98
3.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Sample Name RYF-04
Position p1f6
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 5
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename RYF-04_09.d
ACQ Method lihz.m
Comment PNS ms-ms
Acquired Time 7/18/2015 4:07:42 PM
C18 H10 N2 O5: +ESI Scan (0.106-0.222 min, 8 Scans) Frag=180.0V RYF-04_09.d Subtract
x10 2
274.2744
335.0668
([C18 H10 N2 O5]+H)+
318.3017
357.0489
262.2351
302.3065
409.0782