Electronic Supplementary Information (ESI)

Merging supramolecular catalysis and aminocatalysis: amino-appended β-cyclodextrins (ACDs) as efficient and recyclable supramolecular catalysts for the synthesis of tetraketones

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1. Analytical data of ACDs (a0-a3).

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.

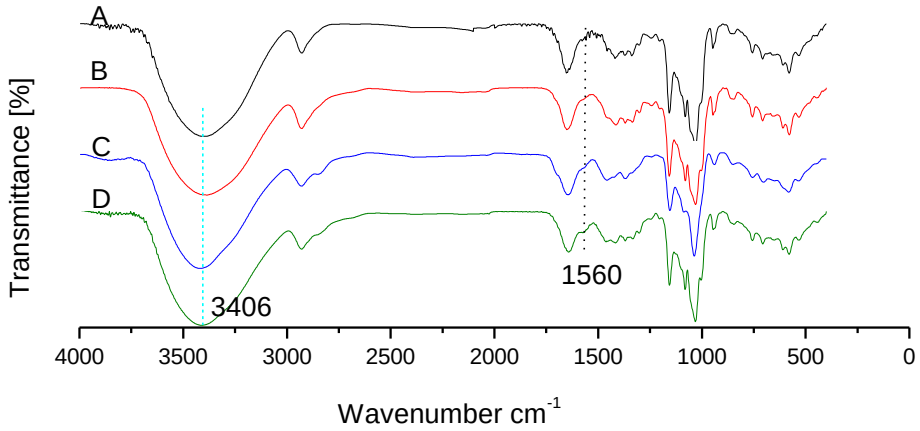
a1: mp: 257 ℃ (decomp.); ^{1}H NMR (500 MHz, D_2O) δ 4.92 (s, 7 H, H-1 of CD), 3.83-3.69 (m, 28 H, H-3, 5, 6 of CD), 3.51-3.41 (m, 14 H, H-2,4 of CD), 2.93-2.78 (m, 4H, en); HRMS (ESI) *m/z*: calcd for $C_{44}H_{76}N_2O_{34}$ $[M+H]^+$: 1177.4358, found $[M+H]^+$: 1177.4370.

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, 6H, 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 (400 MHz, D_2O) δ 5.08 (s, 7 H, H-1 of CD), 3.89-3.38 (m, H-2, 3, 4, 5, 6 of CD), 2.85-2.61 (m, 12 H, en). HRMS (ESI) *m/z*: calcd for $C_{48}H_{87}N_4O_{34}$ $[M+H]^+$: 1263.5196, found $[M+H]^+$: 1263.5194.

1.2 IR of catalyst **a0-a3**.

The FT-IR spectra of **a0-a3** (Figure S1) were collected between 4000 and 400 cm^{-1} by the KBr method.



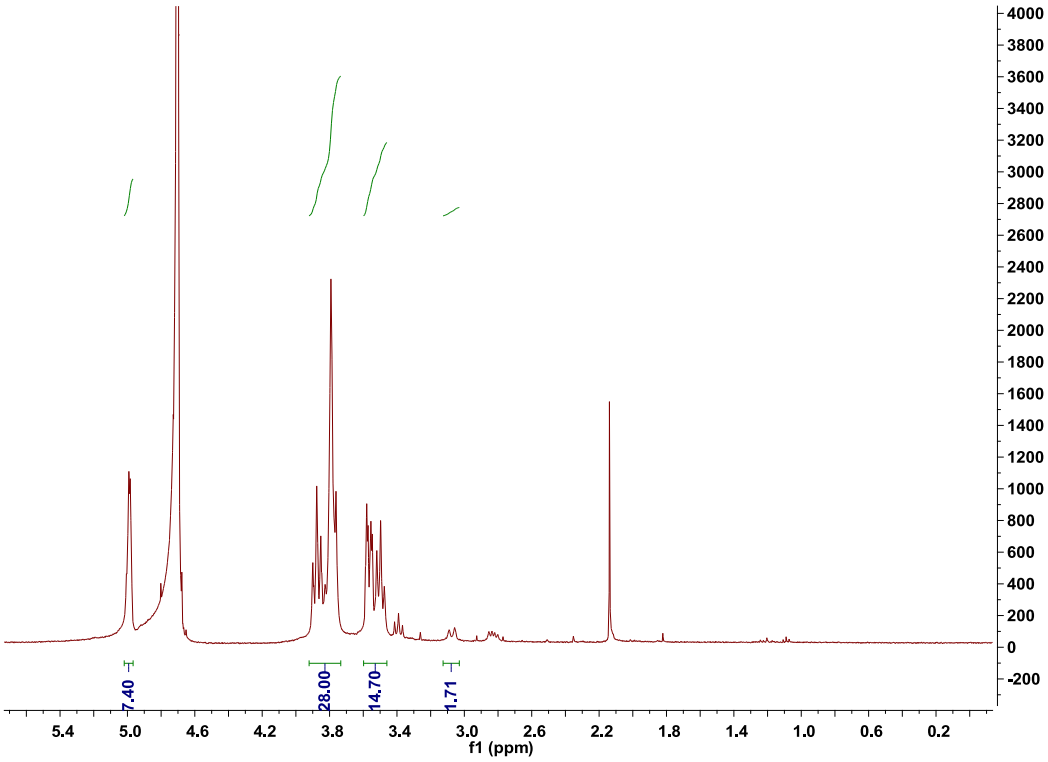
IR spectra of ACDs: (A) **a0**; (B) **a1**; (C) **a2**; (D) **a3**.

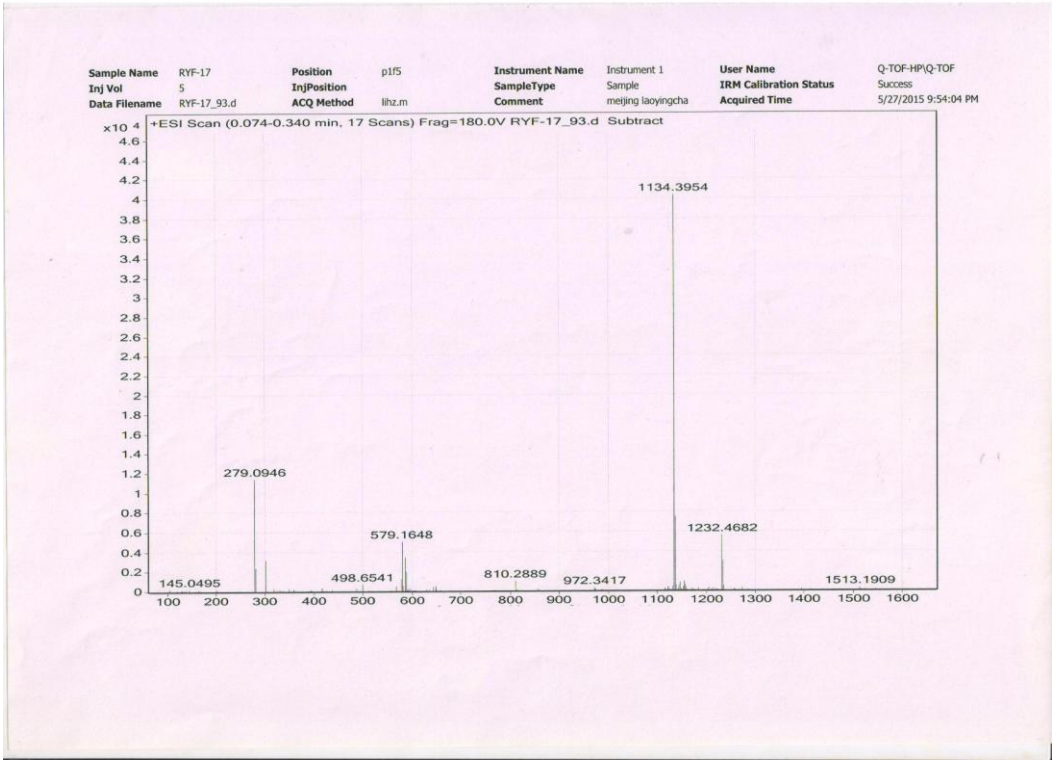
1.3 Water solubilities of ACDs

Water solubilities of **a0-a3** were determined by preparing their saturated aqueous solutions. Excess amounts of **a0-a3** was placed in 2 mL of water (ca. pH 7.0) respectively, and the mixture was stirred vigorously for 1 h in dark 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-a3** were calculated to be 79.6, 208.9, 393.9 and 656.9 mg/mL, respectively.

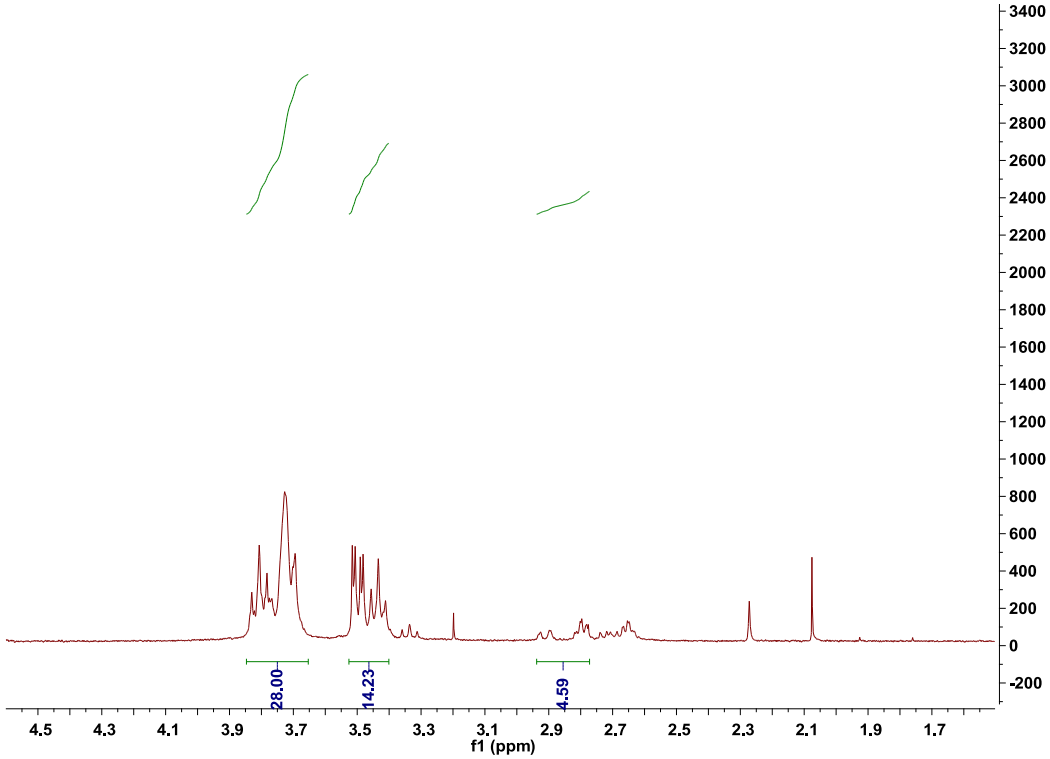
2. NMR and MS spectral copies of ACDs

a0





a1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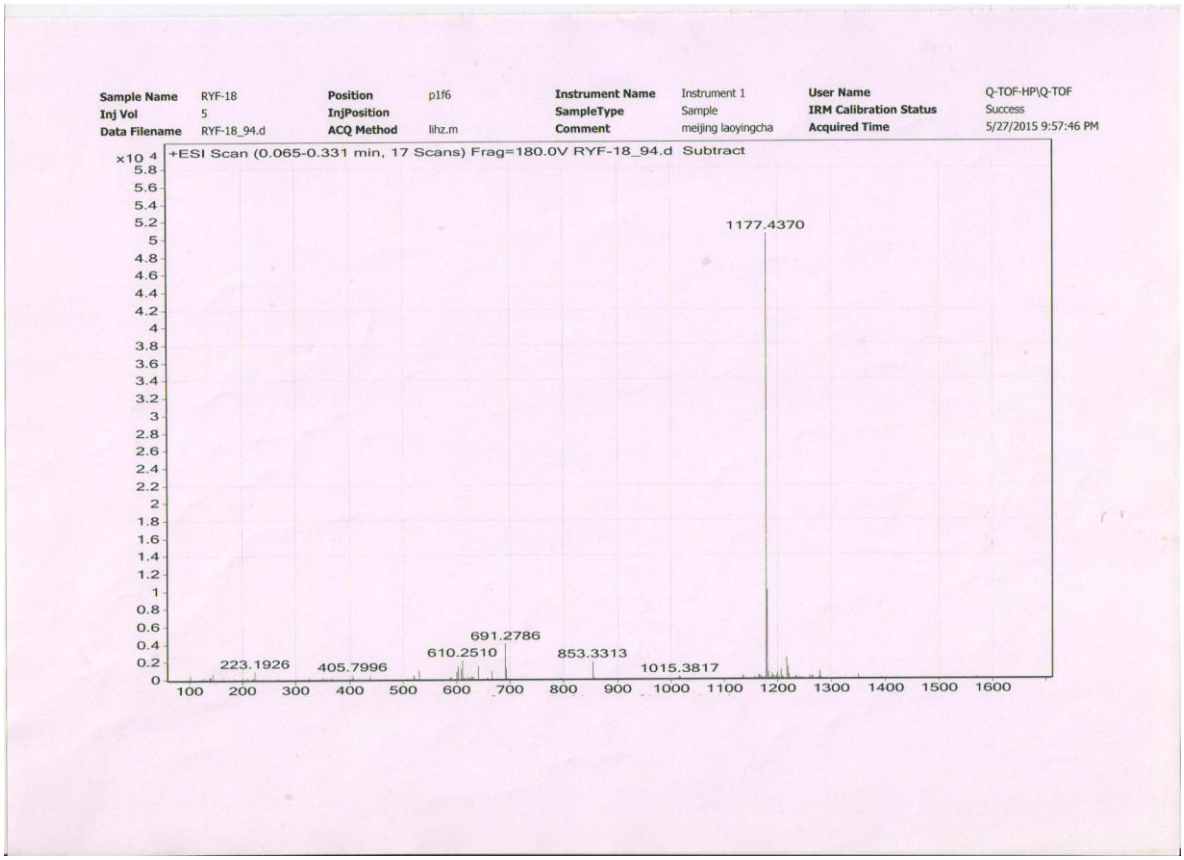
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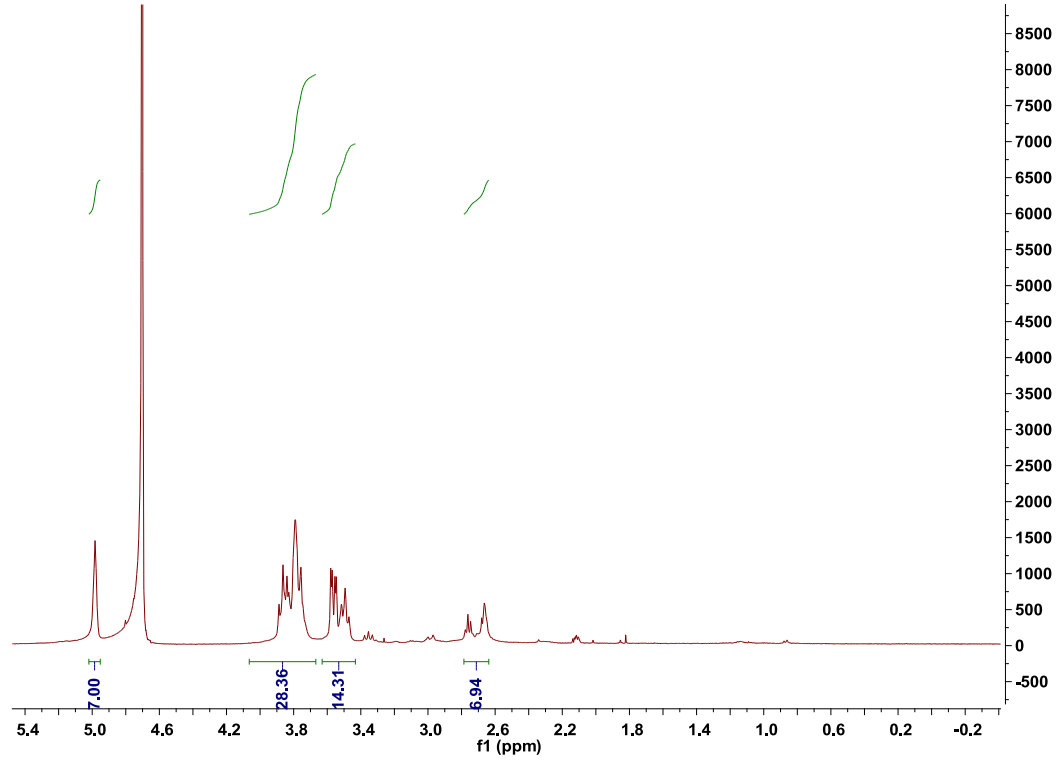
a2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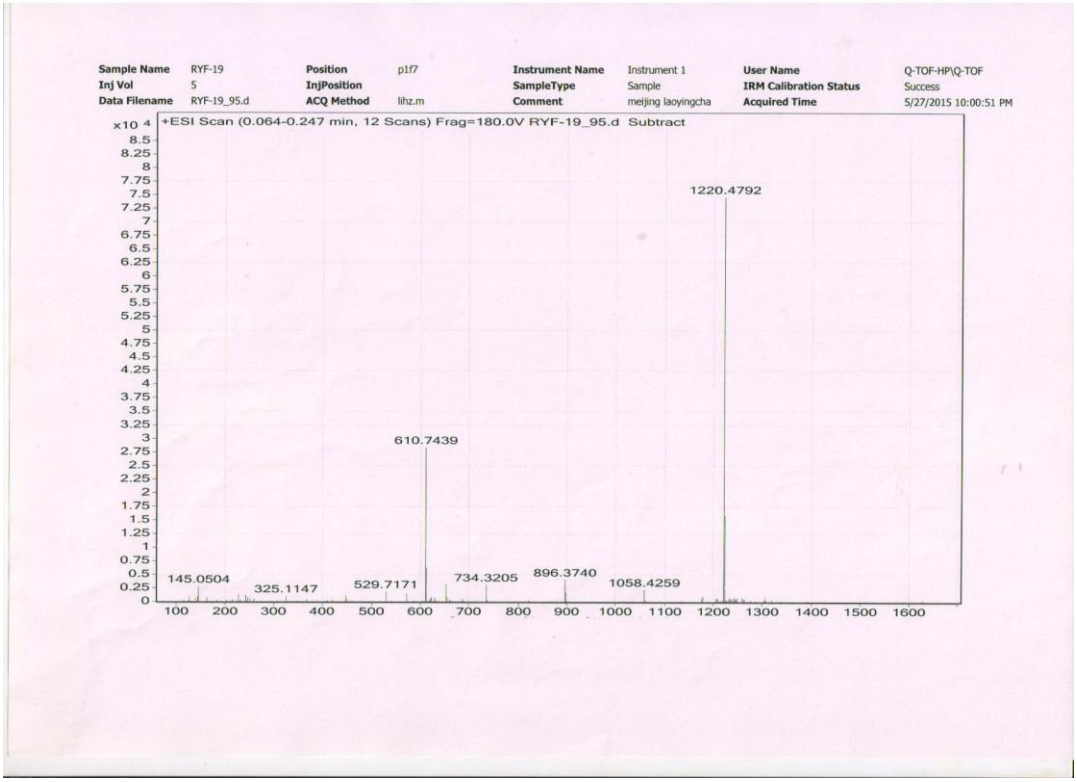
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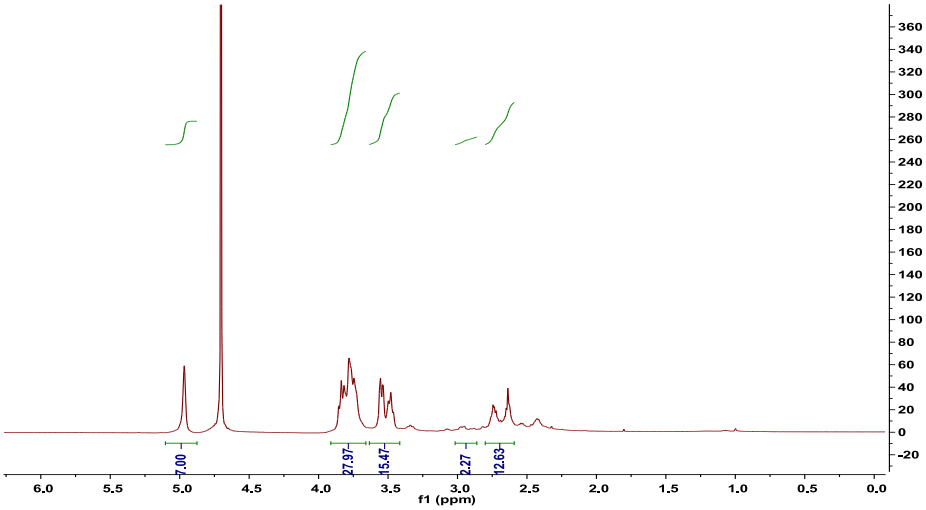
a3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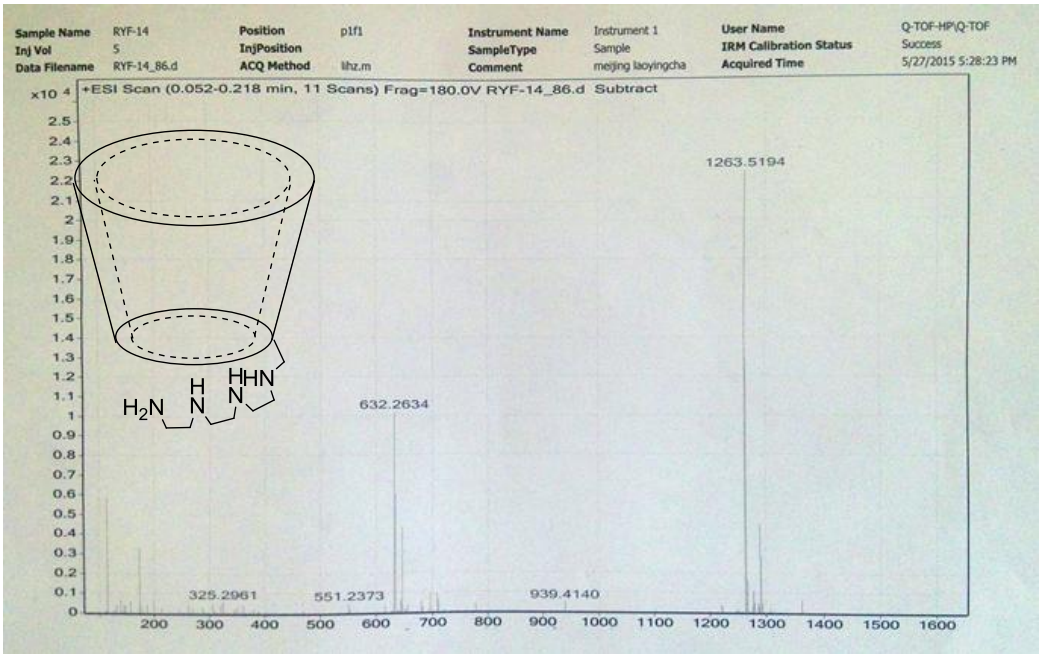
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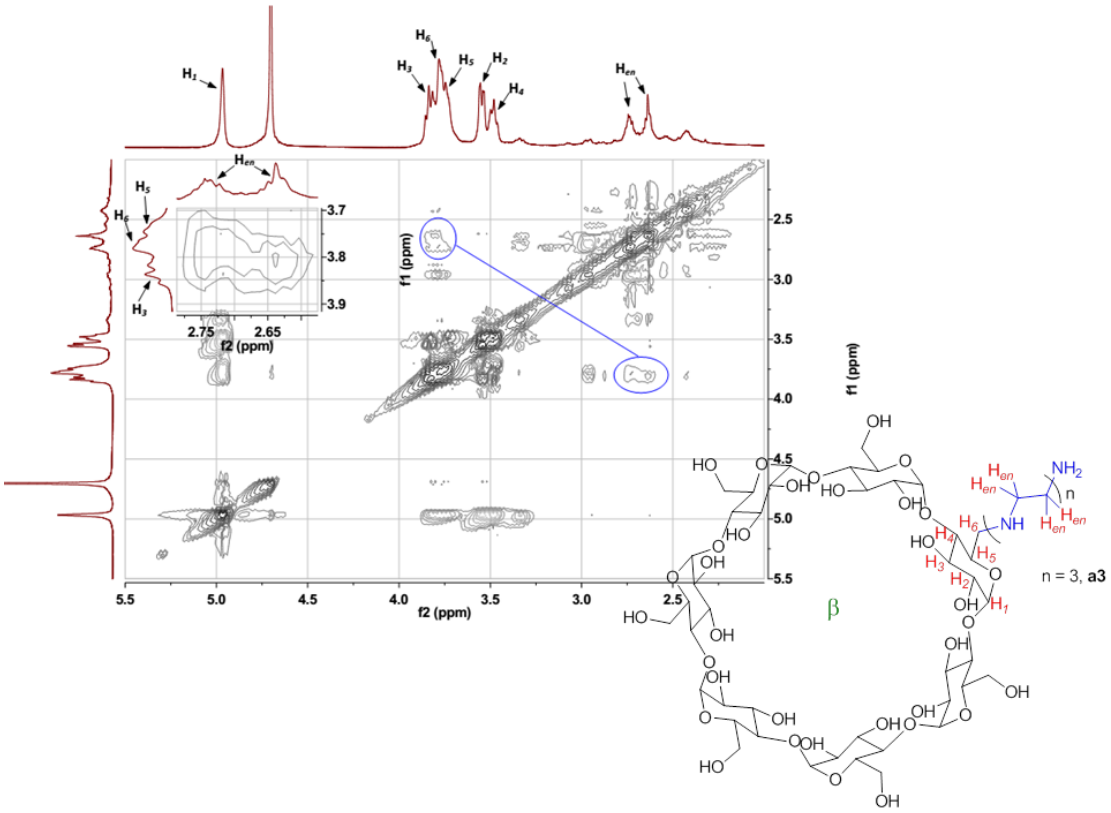

ROESY of **a3** in D_2O at 25 ℃

3. Analytical data of tetraketones 3

3.1 Phenyl-2, 2′-methylenebis-(5, 5-dimethylcyclohexane-1, 3-dione) (**3a**)
Yield: 96%; mp: 205-207 ℃ (Lit.: 204 ℃)[1]; IR (KBr)cm^{-1} 3442(OH), 2968, 2929, 2877(C-H), 1600(C=O), 1503, 1457, 1424(C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.92(s, 1H), 7.28 (d, *J*=7.9 Hz, 1H, Ar-H), 7.25 (s, 1H, Ar-H), 7.17 (t, *J*=7.3 Hz, 1H, Ar-H), 7.10 (d, *J*=7.3 Hz, 2H, Ar-H), 5.54(s, 1H, H-7), 2.51-2.26(m, 8H, H-4/H-6/H-4′/H-6′), 1.24(s, 6H, 2×CH_3), 1.11(s, 6H, 2×CH_3); HRMS (ESI) m/z: calcd for $C_{23}H_{28}O_4$ $[M+H]^+$: 369.2066, found $[M+H]^+$: 369.2063.

3.2 4-Tolyl-2, 2′-methylenebis-(5, 5-dimethylcyclohexane-1, 3-dione) (**3b**)
Yield: 90%; mp: 135-136 ℃ (Lit.: 132-133 ℃)[2]; IR (KBr)cm^{-1} 3429(OH), 2969, 2916, 2871(C-H), 1607(C=O), 1515, 1451, 1386(C=C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.92(s, 1H), 7.09 (d, *J*=8.1 Hz, 2H, Ar-H), 6.99 (d, *J*=7.8 Hz, 2H, Ar-H), 5.52(s, 1H, H-7), 2.49-2.34(m, 8H, H-4/H-6/H-4′/H-6′), 2.31(s, 3H), 1.24(s, 6H, 2×CH_3), 1.11(s, 6H, 2×CH_3); HRMS (ESI) m/z calcd for $C_{24}H_{30}O_4$ $[M+H]^+$: 383.2222, found $[M+H]^+$: 383.2222.

3.3 3-Hydroxyphenyl-2, 2′-methylenebis-(5,5-dimethylcyclohexane-1,3-dione) (**3c**)
Yield: 95%; mp: 243 ℃ (Lit. 248-250 ℃)[3]; IR (KBr)cm^{-1} 3546(Ar-OH), 3384(OH), 2955, 2877, 2825(C-H), 1593(C=O), 1477, 1450, 1386(C=C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.94(s, 1H), 7.12 (t, *J*=7.9 Hz, 1H, Ar-H), 6.67 (d, *J*=7.8 Hz, 1H, Ar-H), 6.65–6.61 (m, 1H, Ar-H), 6.57 (s, 1H, Ar-H), 5.49(s, 1H, H-7), 2.38 (dt, *J*=31.2, 17.6 Hz, 8H, H-4/H-6/H-4′/H-6′), 1.23(s, 6H, 2×CH_3), 1.09(s, 6H, 2×CH_3); HRMS (ESI) m/z calcd for $C_{23}H_{28}O_5$ $[M+H]^+$: 385.20125 found $[M+H]^+$: 385.2013.

3.4 4-Hydroxyphenyl-2, 2′-methylenebis-(5,5-dimethylcyclohexane-1,3-dione) (**3d**)
Yield: 91%; mp: 196-197 ℃ (Lit.: 187-189 ℃)[4]; IR (KBr)cm^{-1} 3773(Ar-OH), 3416(OH), 2949(C-H), 1625(C=O), 1515, 1385(C=C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.89(s, 1H), 6.94 (d, *J*=8.3 Hz, 2H, Ar-H), 6.71 (d, *J*=8.1 Hz, 2H, Ar-H), 5.47(s, 1H, H-7), 2.48-2.27(m, 8H, H-4/H-6/H-4′/H-6′), 1.22(s, 6H, 2×CH_3), 1.10(s, 6H, 2×CH_3); HRMS (ESI) m/z： calcd for $C_{23}H_{28}O_5$ $[M+Na]^+$: 407.1834, found $[M+Na]^+$: 407.1832.

3.5 4-Methoxyphenyl-2, 2′-methylenebis-(5, 5-dimethylcyclohexane-1, 3-dione) (**3e**)
Yield: 93%; mp: 143 ℃ (Lit.: 138 ℃)[2]; IR (KBr)cm^{-1} 3429OH), 2968, 2936, 2903(C-H), 1600(C=O), 1515, 1444, 1392(C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.91(s, 1H), 7.03–6.96 (d, *J*=8.4 Hz, 2H, Ar-H), 6.84–6.77 (d, *J*=8.8 Hz, 2H, Ar-H), 5.48(s, 1H, H-7), 3.77(s, 3H, OCH_3), 2.50-2.25(m, 8H, H-4/H-6/H-4′/H-6′), 1.22(s, 6H, 2×CH_3), 1.10(s, 6H, 2×CH_3); HRMS (ESI) m/z： calcd for $C_{24}H_{30}O_5$ $[M+H]^+$: 399.2171, found $[M+H]^+$: 399.2171.

3.6 3, 4-Dimethoxyphenyl-2, 2′-methylenebis-(5, 5-dimethylcyclohexane-1, 3-dione) (**3f**)

Yield: 91%; mp: 183 ℃ (Lit.: 186-189 ℃)[5]; IR (KBr)cm^{-1} 3448OH), 2968, 2936, 2877, 2832(C-H), 1593(C=O), 1509, 1476, 1444(C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.98(s, 1H), 6.78 (d, *J*=8.0 Hz, 1H, Ar-H), 6.67–6.60 (m, 2H, Ar-H), 5.51(s, 1H, H-7), 3.84(s, 3H, OCH_3), 3.77(s, 3H, OCH_3), 2.50-2.28(m, 8H, H-4/H-6/H-4′/H-6′), 1.24(s, 6H, 2×CH_3), 1.11(s, 6H, 2×CH_3); HRMS (ESI) m/z： calcd for $C_{25}H_{32}O_6$ $[M+H]^+$: 429.2277, found $[M+H]^+$: 429.2274.

3.7 2, 5-Dimethoxyphenyl-2, 2′-methylenebis-(5, 5-dimethylcyclohexane-1, 3-dione) (**3g**)

Yield: 93%; mp: 154-156 ℃ (Lit.: 146-148 ℃)[6]; IR (KBr)cm^{-1} 3390(OH), 2962, 2829(C-H), 1619(C=O), 1496, 1470, 1431(C=C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83(s, 1H, Ar-H), 6.70(s, 2H，Ar-H), 5.55(s, 1H, H-7), 3.73(s, 3H, OCH_3), 3.67(s, 3H, OCH_3), 2.34(s, 10H, H-2/H-4/H-6/H-2′/H-4′/H-6′), 1.11(s, 12H, 4×CH_3); HRMS (ESI) m/z： calcd for $C_{25}H_{32}O_6$ $[M+Na]^+$: 451.2097, found $[M+Na]^+$: 451.2093.

3.8 3, 4, 5-Trimethoxyphenyl-2, 2′-methylenebis-(5, 5-dimethylcyclohexane-1, 3-dione) (**3h**)

Yield: 96%; mp: 195-196 ℃ (Lit.: 189-191 ℃)[7]; IR (KBr)cm^{-1} 3370(OH), 2955, 2825(C-H), 1625(C=O), 1483, 1392(C=C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.03(s, 1H), 6.35(s, 2H, Ar-H), 5.50(s, 1H, H-7), 3.82(s, 3H, OCH_3), 3.75(s, 6H, 2×OCH_3), 2.42 (dd, *J*=32.2, 21.5 Hz, 8H, H-4/H-6/H-4′/H-6′), 1.25(s, 6H, 2×CH_3), 1.13(s, 6H, 2×CH_3); HRMS (ESI) m/z： calcd for $C_{26}H_{34}O_7$ $[M+H]^+$: 459.2383, found $[M+H]^+$: 459.2379.

3.9 3-Methoxy-4-hydroxyphenyl-2, 2′-methylenebis-(5, 5-dimethylcyclohe -xane-1, 3-dione) (**3i**)

Yield: 94%; mp: 206-209 ℃ (Lit.: 196-197 ℃)[8]; IR (KBr)cm^{-1} 3520, 3442(OH), 2968, 2936, 2877(C-H), 1613(C=O), 1522, 1470, 1431(C=C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.97(s, 1H), 6.81 (d, *J*=8.2 Hz, 1H, Ar-H), 6.70–6.49 (m, 2H, Ar-H), 5.49(s, 2H), 3.77(s, 3H, OCH_3), 2.48-2.30(m, 8H, H-4/H-6/H-4′/H-6′), 1.23(s, 6H, 2×CH_3), 1.11(s, 6H, 2×CH_3); HRMS (ESI) m/z： calcd for $C_{24}H_{30}O_6$ $[M+Na]^+$: 4371940, found $[M+Na]^+$: 437.1938.

3.10 4- Chlorophenyl-2, 2′-methylenebis-(5, 5-dimethylcyclohexane-1, 3-dione) (**3j**)

Yield: 87%; mp: 147-148 ℃ (Lit.: 146-148 ℃)[5]; IR (KBr)cm^{-1} 3403(OH), 2942, 2877, 2813(C-H), 1600(C=O), 1496, 1463, 1380(C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.88(s, 1H), 7.26–7.19 (d, *J*=8.4Hz, 2H, Ar-H), 7.07–6.98(d, *J*=8Hz, 2H, Ar-H), 5.47(s, 1H, H-7), 2.39 (dq, *J*=26.2, 17.6 Hz, 8H, H-4/H-6/H-4′/H-6′), 1.22(s, 6H, 2×CH_3), 1.10(s, 6H, 2×CH_3); HRMS (ESI) m/z: calcd for $C_{23}H_{27}ClO_4$ $[M+H]^+$: 403.1676, found $[M+H]^+$: 403.1675.

3.11 4-Fluorophenyl-2, 2′-methylenebis-(5, 5-dimethylcyclohexane-1, 3-dione) (**3k**)

Yield: 94%; mp: 193-195 ℃ (Lit.: 190-192 ℃)[5]; IR (KBr)cm^{-1} 3397(OH), 2949, 2903(C-H), 1600(C=O), 1515, 1457, 1398(C=C); ^{1}H NMR (500 MHz, $CDCl_3$) δ

11.88(s, 1H), 7.04 (dd, *J*=7.9, 5.4 Hz, 2H, Ar-H), 6.95 (t, *J*=8.6 Hz, 2H, Ar-H), 5.48(s, 1H, H-7), 2.39 (dq, *J*=32.6, 17.6 Hz, 8H, H-4/H-6/H-4′/H-6′), 1.22(s, 6H, 2×CH_3), 1.09(s, 6H, 2×CH_3); HRMS (ESI) m/z： calcd for $C_{23}H_{27}FO_4$ $[M+H]^+$: 387.1972, found $[M+H]^+$: 387.1969.

3.12 3, 4-Dichlorophenyl-2, 2′-methylenebis-(5, 5-dimethylcyclohexane-1, 3-dione) (**3l**)

Yield: 85%; mp: 194℃; IR (KBr)cm^{-1} 3448OH), 2968, 2936, 2877, 2832(C-H), 1593(C=O), 1509, 1476, 1444(C=C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.88(s, 1H), 7.32 (d, *J*=8.4 Hz, 1H, Ar-H), 7.15 (s, 1H, Ar-H), 6.91 (d, *J*=8.4 Hz, 1H, Ar-H), 5.44(s, 1H, H-7), 2.54-2.23(m, 8H, H-4/H-6/H-4′/H-6′), 1.24(s, 6H, 2×CH_3), 1.10(s, 6H, 2×CH_3); HRMS (ESI) m/z: calcd for $C_{23}H_{26}Cl_2O_4$ $[M+H]^+$: 437.1286, found $[M+H]^+$: 437.1284.

3.13 2-Nitrophenyl-2, 2′-methylenebis-(5, 5-dimethylcyclohexane-1, 3-dione) (**3m**)

Yield: 96%; mp: 191-193℃ (Lit.: 188-190℃)[3]; IR (KBr)cm^{-1} 3403(OH), 2975, 2923, 2890, 2832(C-H), 1730(C=O), 1625, 1470, 1398(C=C), 1535, 1295(NO_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.60(s, 1H), 7.55 (dd, *J*=7.9, 1.1 Hz, 1H, Ar-H), 7.50–7.44 (m, 1H, Ar-H), 7.32 (t, *J*=7.7 Hz, 1H, Ar-H), 7.25 (d, *J*=8.0 Hz, 1H, Ar-H), 6.04(s, 1H, H-7), 2.51-2.20(m, 8H, H-4/H-6/H-4′/H-6′), 1.15(s, 6H, 2×CH_3), 1.02(s, 6H, 2×CH_3); HRMS (ESI) m/z： calcd for $C_{23}H_{27}NO_6$ $[M+H]^+$: 414.1917, found $[M+H]^+$: 414.1915.

3.14 3-Nitrophenyl-2, 2′-methylenebis-(5, 5-dimethylcyclohexane-1, 3-dione) (**3n**)

Yield: 93%; mp: 202-205℃ (Lit.: 197-198℃)[4]; IR (KBr)cm^{-1} 3442(OH), 2975, 2936, 2887(C-H), 1620(C=O), 1542, 1379(C=C), 1457, 1282(NO_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.86(s, 1H), 8.07–7.99 (m, 2H, Ar-H), 7.47–7.38 (m, 2H, Ar-H), 5.55(s, 1H, H-7), 2.42 (dq, *J*=28.5, 17.7 Hz, 8H, H-4/H-6/H-4′/H-6′), 1.28(s, 6H, 2×CH_3), 1.12(s, 6H, 2×CH_3); HRMS (ESI) m/z： calcd for $C_{23}H_{27}NO_6$ $[M+H]^+$: 414.1917, found $[M+H]^+$: 414.1917.

3.15 4-Nitrophenyl-2, 2′-methylenebis-(5, 5-dimethylcyclohexane-1, 3-dione) (**3o**)

Yield: 95%; mp: 195℃ (Lit.: 190℃)[1]; IR (KBr)cm^{-1} 3461(OH), 2968, 2871(C-H), 1613(C=O), 1522, 1347(C=C), 1522, 1248(NO_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.80(s, 1H), 8.14-8.12(d, *J*=8.8 Hz, 2H, Ar-H), 7.26-7.24(d, *J*=9.2Hz, 2H, Ar-H), 5.55(s, 1H, H-7), 2.54-2.30(m, 8H, H-4/H-6/H-4′/H-6′), 1.24(s, 6H, 2×CH_3), 1.12(s, 6H, 2×CH_3); HRMS (ESI) m/z： calcd for $C_{23}H_{27}NO_6$ $[M+H]^+$: 414.1917, found $[M+H]^+$: 414.1914.

3.16 2-Naphthyl-2, 2′-methylenebis-(5, 5-dimethylcyclohexane-1, 3-dione) (**3p**)

Yield: 96%; mp: 218℃; IR (KBr)cm^{-1} 3435(OH), 2962, 2916, 2871(C-H), 1606(C=O), 1509, 1392(C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.95(s, 1H), 7.74 (ddd, *J*=16.3, 9.1, 6.8 Hz, 3H, Ar-H), 7.51 (s, 1H, Ar-H), 7.47–7.35 (m, 2H, Ar-H), 7.23 (dd, *J* = 8.6, 1.7 Hz, 1H, Ar-H), 5.68(s, 1H, H-7), 2.55-2.30(m, 8H, H-4/H-6/H-4′/H-6′),

1.30(s, 6H, 2×CH_3), 1.10(s, 6H, 2×CH_3); HRMS (ESI) m/z calcd for $C_{27}H_{30}O_4$ $[M+Na]^+$: 441.2042, found $[M+Na]^+$: 441.2040.

3.17 3-Pyridinyl-2, 2′-methylenebis-(5,5-dimethylcyclohexane-1,3-dione) (**3q**)

Yield: 93%; mp: 98 ℃; IR (KBr)cm^{-1} 3481(Ar-OH), 2923, 2877(C-H), 1613(C=O); ^1H NMR (500 MHz, $CDCl_3$) δ 11.88(s, 1H), 8.42 (d, *J*=4.4 Hz, 1H), 8.38 (s, 1H), 7.38 (d, *J*=8.0 Hz, 1H), 7.20 (dd, *J*=8.0, 4.8 Hz, 1H), 5.53(s, 1H, H-7), 2.54-2.25(m, 8H, H-4/H-6/H-4′/H-6′), 1.23(s, 6H, 2×CH_3), 1.11(s, 6H, 2×CH_3); HRMS (ESI) m/z calcd for $C_{22}H_{27}NO_4$ $[M+H]^+$: 370.2018, found $[M+H]^+$: 370.2019.

3.18 2-Thienyl-2, 2′-methylenebis-(5, 5-dimethylcyclohexane-1, 3-dione) (**3r**)

Yield: 92%; mp: 160-162 ℃ (Lit.: 156-157 ℃)[9]; IR (KBr)cm^{-1} 3448(OH), 2968, 2884(C-H), 1606(C=O), 1450, 1392(C=C); ^1H NMR (400 MHz, $CDCl_3$) δ 12.32(s, 1H), 7.11 (dd, *J*=4.2, 1.0 Hz, 1H), 6.87 (dd, *J*=5.1, 3.5 Hz, 1H), 6.66–6.62 (m, 1H), 5.63(s, 1H, H-7), 2.47-2.26(m, 8H, H-4/H-6/H-4′/H-6′), 1.22(s, 6H, 2×CH_3), 1.10(s, 6H, 2×CH_3); HRMS (ESI) m/z calcd for $C_{21}H_{26}O_4S$ $[M+Na]^+$: 397.1449, found $[M+Na]^+$: 397.1448.

3.19 1, 4-Bis(2, 2′-methylenebis-(5, 5-dimethylcyclohexane-1, 3-dione))benzene (**3s**)

Yield: 97%; mp: 322-323 ℃; IR (KBr)cm^{-1} 3429(OH), 2962, 2929, 2871(C-H), 1606(C=O), 1515, 1457, 1424(C=C); ^1H NMR (500 MHz, $CDCl_3$) δ 11.87(s, 2H), 7.04(s, 4H, Ar-H), 5.50(s, 2H, H-7), 2.49-2.27(m, 16H, H-4/H-6/H-4′/H-6′), 1.23(s, 12H, 4×CH_3), 1.10(s, 12H, 4×CH_3); HRMS (ESI) m/z: calcd for $C_{40}H_{50}O_8$ $[M+Na]^+$: 681.3403, found$[M+Na]^+$: 681.3400.

3.20 1, 3-Bis(2,2′-methylenebis-(5, 5-dimethylcyclohexane-1,3-dione))benzene (**3t**)

Yield: 90%; mp: 303-305 ℃; IR(KBr)cm^{-1} 3416(OH), 2929, 2877(C-H), 1600(C=O), 1476, 1457, 1392(C=C); ^1H NMR (400 MHz, $CDCl_3$) δ 11.90(s, 2H), 7.18 (t, *J*=7.8 Hz, 1H, Ar-H), 6.92 (d, *J*=7.9 Hz, 2H, Ar-H), 6.87 (s, 1H, Ar-H), 5.51(s, 2H, H-7), 2.47-2.22(m, 16H,H-4/H-6/H-4′/H-6′), 1.18(s, 12H, 4×CH_3), 1.07(s, 12H, 4×CH_3); HRMS (ESI) m/z: calcd for $C_{40}H_{50}O_8$ $[M+Na]^+$: 681.3403, found $[M+Na]^+$: 681.3402.

3.21 2, 2′-methylenebis-(5, 5-dimethylcyclohexane-1, 3-dione) (**3u**)

Yield: 95%; mp: 188-190 ℃ (Lit.: 192-193 ℃)[8]; IR(KBr)cm^{-1} 3455(OH), 2968, 2936, 2877(C-H), 1619(C=O); ^1H NMR (400 MHz, $CDCl_3$) δ 11.58(s, 1H), 3.16(s, 2H), 2.29(d, *J*=4.4 Hz, 8H, H-4/H-6/H-4′/H-6′), 1.05(s, 12H, 4×CH_3); HRMS (ESI) m/z : calcd for $C_{17}H_{24}O_4$ $[M+Na]^+$: 315.1572, found $[M+Na]^+$: 315.1573.

3.22 Methyl-2, 2′-methylenebis-(5, 5-dimethylcyclohexane-1, 3-dione) (**3v**)

Yield: 92%; mp: 185-186 ℃ (Lit.: 182-184 ℃)[8]; IR(KBr)cm^{-1} 3416(OH), 2968, 2936, 2871(C-H), 1613(C=O); ^1H NMR (400 MHz, $CDCl_3$) δ 12.53(s, 1H), 4.15 (d, *J*=7.4 Hz, 1H, H-7), 2.29(m, 8H, H-4/H-6/H-4′/H-6′), 1.49(d, *J*=7.4 Hz 3H, CH_3), 1.05(s, 12H, 4×CH_3); HRMS (ESI) m/z: calcd for $C_{18}H_{26}O_4$ $[M+Na]^+$: 329.1729, found $[M+Na]^+$: 329.1733.

3.23 Ethyl formate-2, 2′-methylenebis-(5, 5-dimethylcyclohexane-1, 3-dione) (**3w**)
Yield: 94%; mp: 100-101 ℃; IR(KBr)cm^{-1} 3442(OH), 2962, 2877(C-H), 1606C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.72(s, H), 4.84(s, H), 4.15 (q, *J*=7.1 Hz, 2H), 2.34(s, 8H), 1.20 (t, *J*=7.1 Hz, 3H), 1.11 (s, 12H); HRMS (ESI) m/z: calcd for $C_{20}H_{28}O_6$ $[M+Na]^+$: 387.1784, found $[M+Na]^+$: 387.1785.

3.24 Propyl-2, 2′-methylenebis-(5, 5-dimethylcyclohexane-1, 3-dione) (**3x**)
Yield: 97%; mp: 120-122 ℃ (Lit.: 130 ℃)[1]; IR(KBr)cm^{-1} 3429(OH), 2962, 2923, 2871(C-H), 1587(C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.51(s, 1H), 3.95(t, *J*=8.0 Hz, 1H, H-7), 2.30(m, 8H, H-4/H-6/H-4′/H-6′), 2.00(dd, *J*=15.5, 7.9 Hz, 2H, CH_2), 1.23(m, 2H, CH_2), 1.07(d, *J*=3.4 Hz 12H, 4×CH_3), 0.87-0.90(t, *J*=7.3 Hz 3H, CH_3); HRMS (ESI) m/z: calcd for $C_{20}H_{30}O_4$ $[M+Na]^+$: 357.2042, found$[M+Na]^+$: 357.2044.

3.25 Isopropyl-2, 2′-methylenebis-(5, 5-dimethylcyclohexane-1, 3-dione) (**3y**)
Yield: 96%; mp: 153 ℃ (Lit.: 153-154 ℃)[4]; IR(KBr)cm^{-1} 3442(OH), 2968, 2884(C-H), 1580(C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.44(s, 1H), 3.46(d, *J*=11.2 Hz, 1H, H-7), 2.89-2.98(m, 1H, CH), 2.38-2.21(m, 8H, H-4/H-6/H-4′/H-6′), 1.08(s, 6H, 2×CH_3), 1.06(s, 6H, 2×CH_3), 0.85(s, 3H, CH_3), 0.83(s, 3H, CH_3); HRMS (ESI) m/z: calcd for $C_{20}H_{30}O_4$ $[M+Na]^+$: 357.2042, found$[M+Na]^+$: 357.2041.

3.26 Isobutyl-2, 2′-methylenebis-(5, 5-dimethylcyclohexane-1, 3-dione) (**3z**)
Yield: 94%; mp: 170-171 ℃; IR(KBr)cm^{-1} 3461(OH), 2975, 2942, 2884(C-H), 1613(C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.52(s, 1H), 4.3(t, *J*=8.1 Hz, 1H, H-7), 2.27(m, 8H,H-4/H-6/H-4′/H-6′), 1.87(t, *J*=7.7 Hz, 2H, CH_2), 1.34-1.41(m, 1H) 1.05(s, 12H, 4×CH_3), 0.86(s, 3H, CH_3), 0.84(s, 3H, CH_3); HRMS (ESI) m/z: calcd for $C_{21}H_{32}O_4$ $[M+Na]^+$: 371.2198, found$[M+Na]^+$: 371.2198.

3.27 Cyclohexyl-2, 2′-methylenebis-(5, 5-dimethylcyclohexane-1, 3-dione) (**3aa**)
Yield: 95%; mp: 185-186 ℃; IR(KBr)cm^{-1} 3442(OH), 2936, 2851(C-H), 1600(C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.42(s, 1H), 3.72 (dd, *J*=14.0, 7.0 Hz, 2H), 3.58(d, *J*=11.1 Hz, 1H, H-7), 2.57 (d, *J*=10.9 Hz, 1H), , 2.30 (dt, *J*=29.9, 13.1 Hz, 9H), 1.24(t, *J*=7.0 Hz, 6H), 1.07(s, 6H, 2×CH_3), 1.05(s, 6H, 2×CH_3), 0.74 (d, *J*=10.5 Hz, 2H); HRMS (ESI) m/z: calcd for $C_{23}H_{34}O_4$ $[M+Na]^+$: 397.2355, found $[M+Na]^+$: 397.2355.

3.28 7-Fluoro-3, 3-bis-(5,5-dimethylcyclohexane-1, 3-dione)-1, 3-dihydro-indol-2-one (**3bb**)
Yield: 58%; mp: 308 ℃; IR(KBr)cm^{-1} 3442(OH), 3260(NH), 2975, 2910,(C-H), 1729, 1710(C=C), 1606C=O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.94 (s, 1H, NH), 6.99 (t, *J*=9.2 Hz, 1H, Ar-H), 6.91 (m, 1H, Ar-H), 6.63 (d, *J*=7.4 Hz, 1H, Ar-H), 3.51 (s, 1H), 2.26 (m, 8H), 1.14 (d, *J* = 9.2 Hz, 6H), 1.09 (s, 3H), 1.04 (s, 3H); HRMS (ESI) m/z: calcd for $C_{24}H_{26}FNO_5$ $[M+Na]^+$: 450.1693, found$[M+Na]^+$: 450.1688.

3.29 Phenyl-2, 2′-methylenebis-(cyclohexane-1, 3-dione) (**3cc**)

Yield: 96%; mp: 213-215 ℃ (Lit.: 207-208 ℃)[10]; IR(KBr)cm^{-1} 3305(OH), 2968, 2916, 2890, 2825(C-H), 1613(C=O), 1736, 1638 (C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.36(s, H), 7.26 (t, *J*=7.3 Hz, 2H, Ar-H), 7.17 (t, *J*=7.0 Hz, 1H, Ar-H), 7.10 (d, *J*=7.9 Hz, 2H, Ar-H), 5.47(s, H), 2.61 (dd, *J*=21.9, 18.4 Hz, 4H), 2.42 (ddd, *J*=34.6, 17.4, 8.5 Hz, 4H), 2.03 (m, 4H); HRMS (ESI) m/z: calcd for $C_{19}H_{20}O_4$ $[M+Na]^+$: 335.1259, found $[M+Na]^+$: 335.1257.

3.30 Phenyl-3, 3'-methylenebis(4-hydroxy-6-methyl-2H-pyran-2-one) (**3dd**)

Yield: 90%; mp: 174-175 ℃ (Lit.: 167-169 ℃)[10]; IR(KBr)cm^{-1} 3429(OH), 3091, 3020(=C-H), 2936, 2858(C-H), 1684(C=O), 1619, 1574, 1502 (C=C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.93(s, H), 7.20(m, 5H, Ar-H), 6.03(s, 2H), 5.73(d, *J*=21.6 Hz, 1H, H-7), 2.27(d, *J*=21.5 Hz , 6H, 2×CH_3); HRMS (ESI) m/z: calcd for $C_{19}H_{16}O_6$ $[M+Na]^+$: 363.0845, found $[M+Na]^+$: 363.0836.

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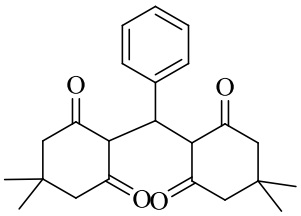

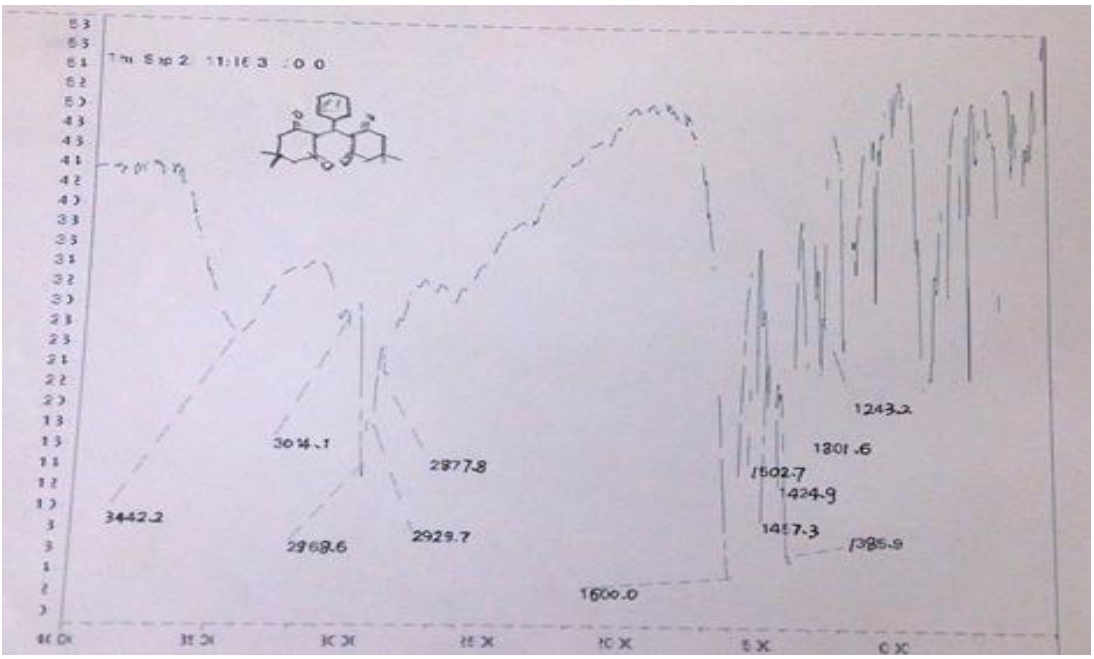

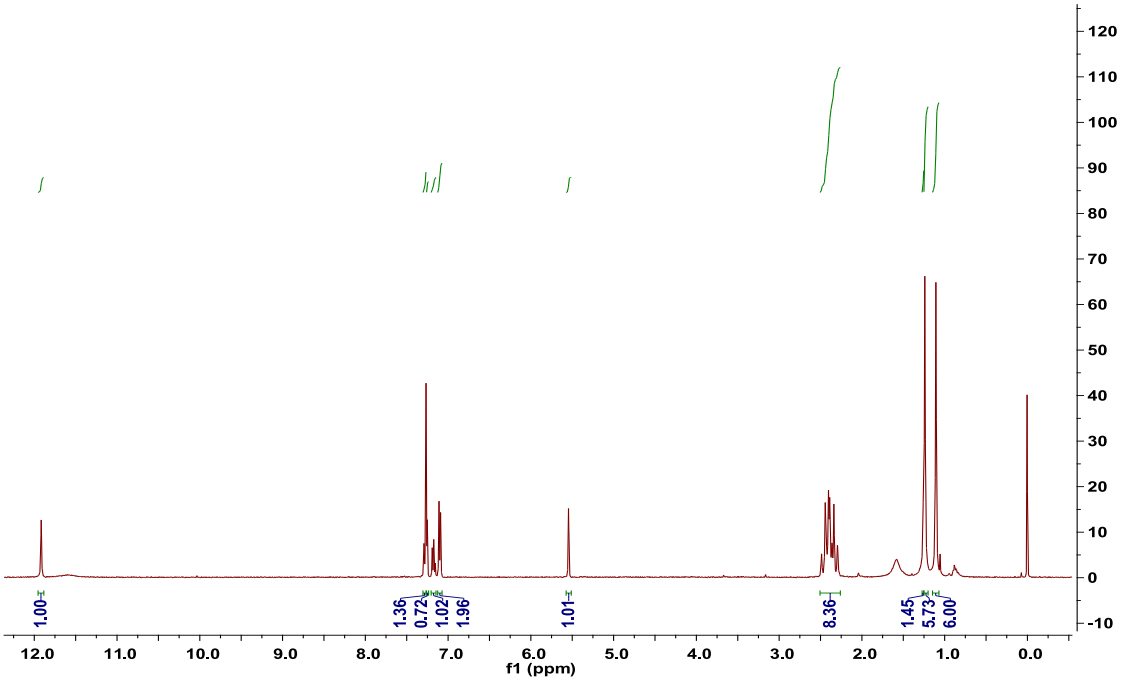

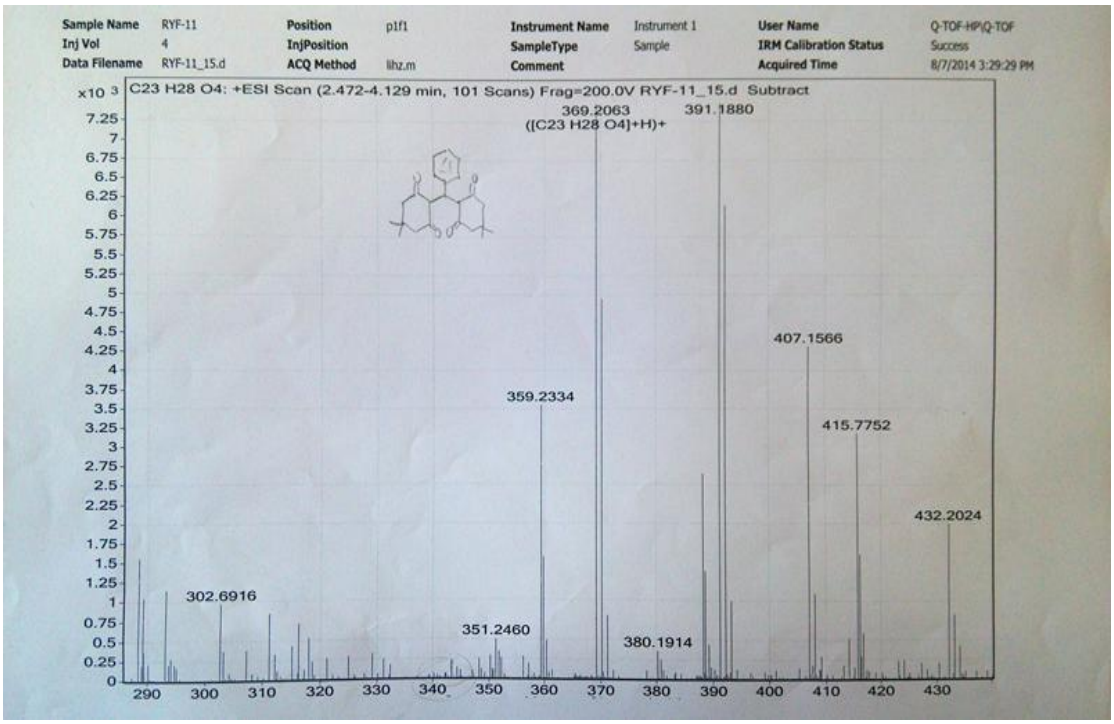
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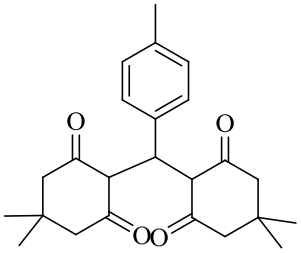
3b.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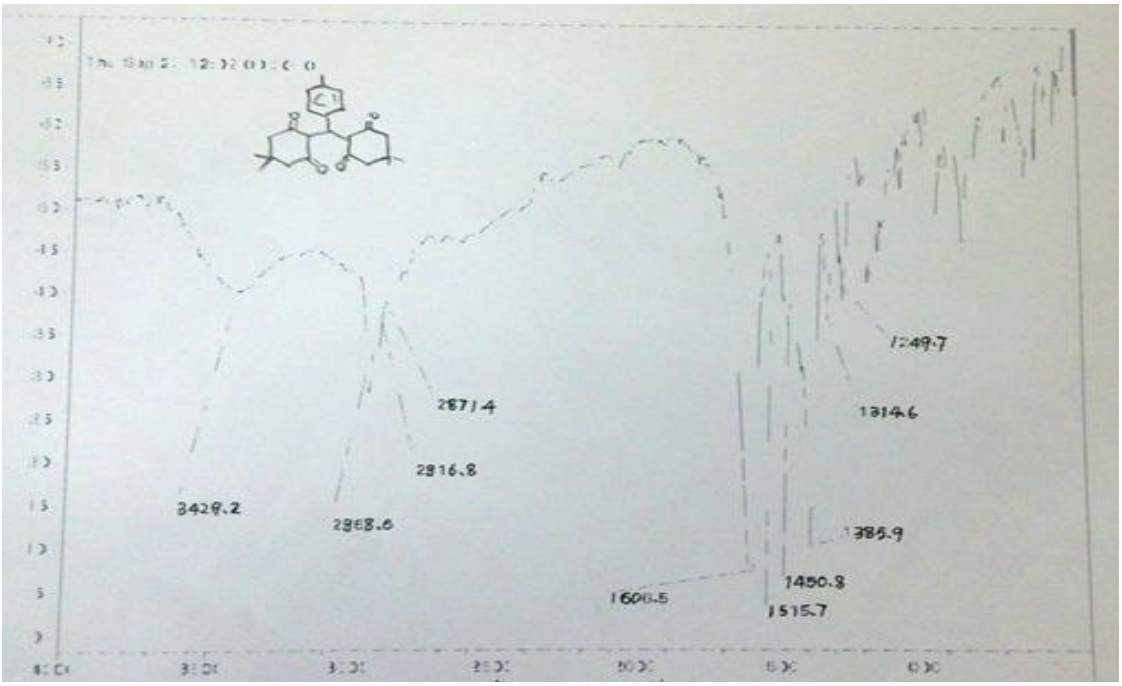
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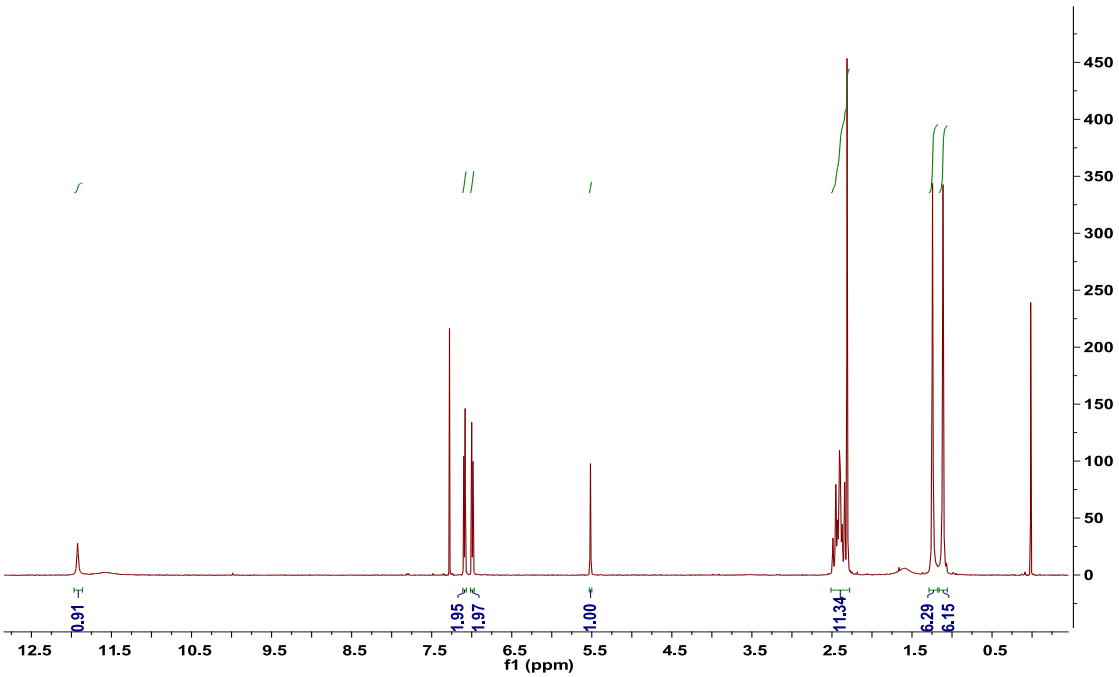
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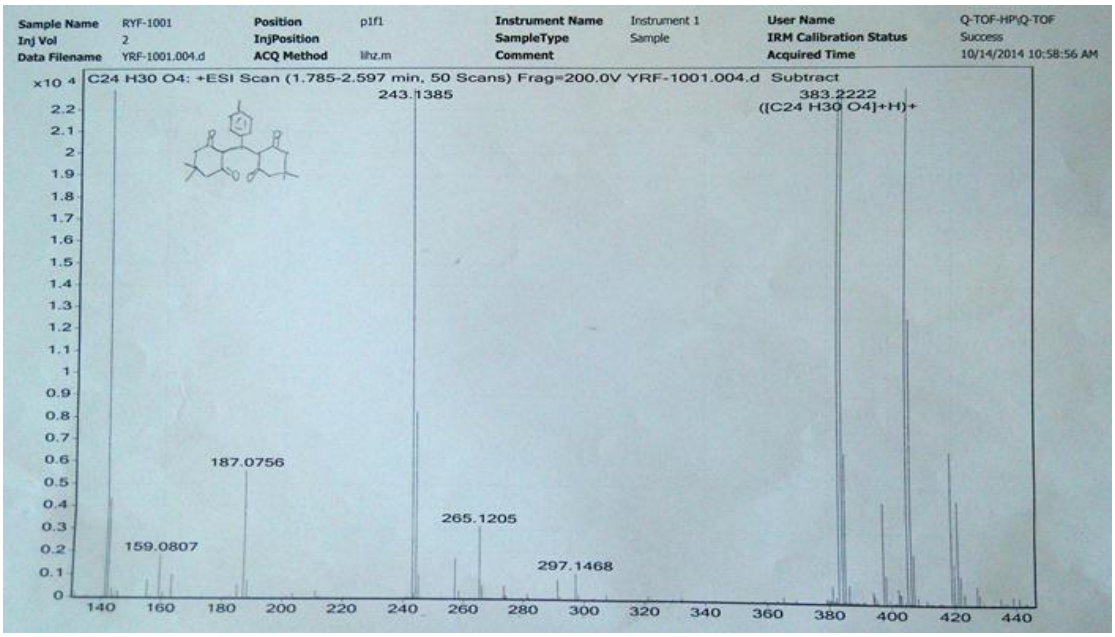
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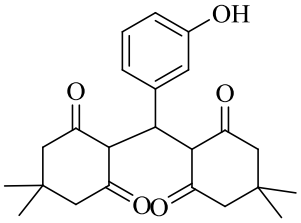
3c.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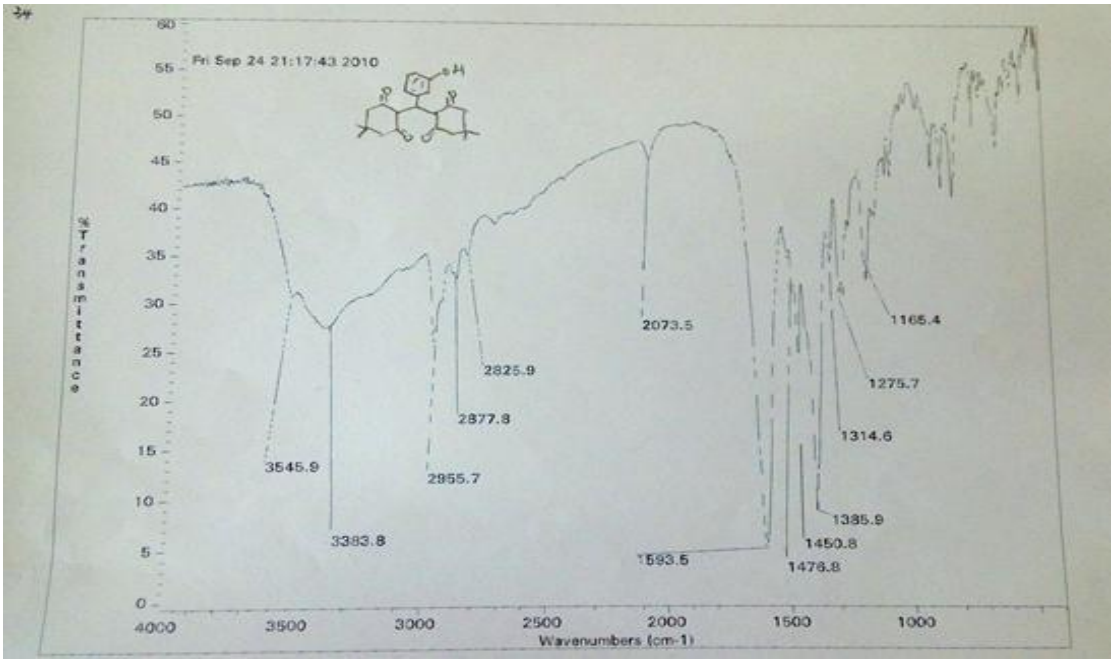
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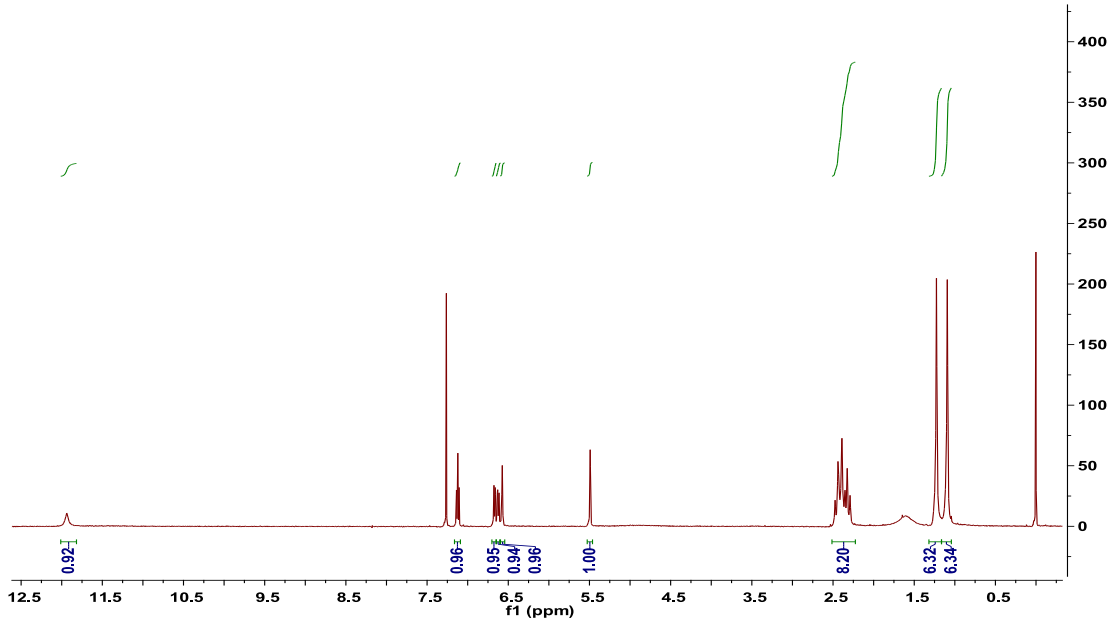
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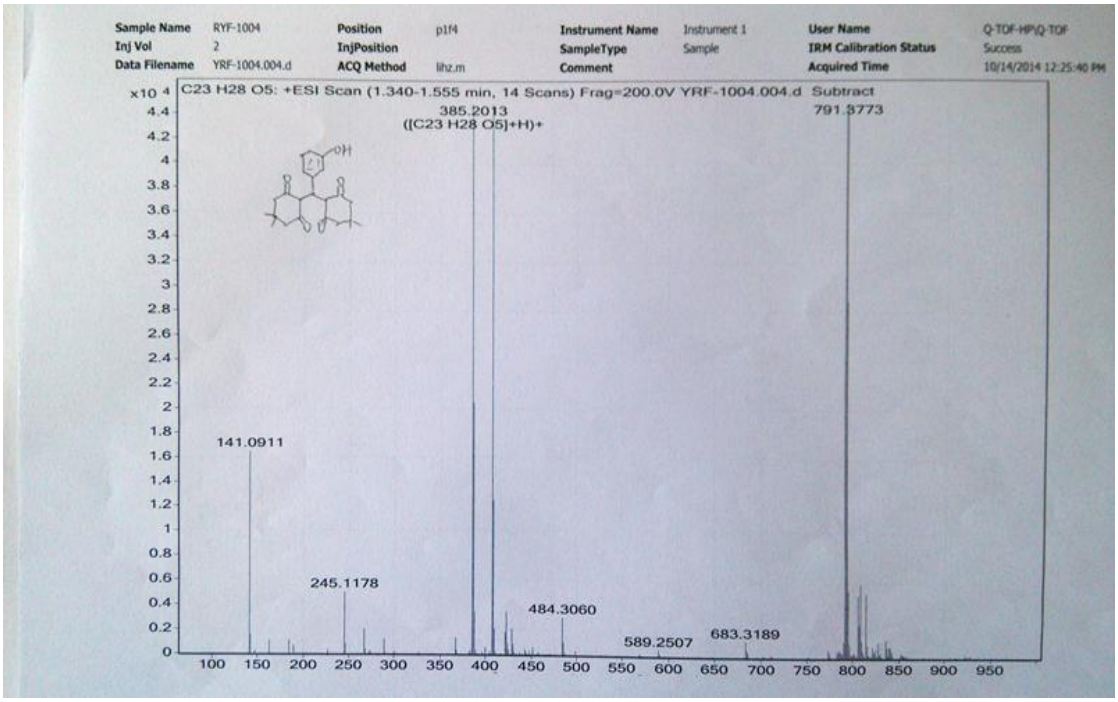
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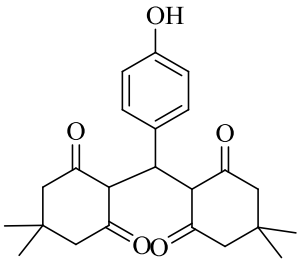
3d.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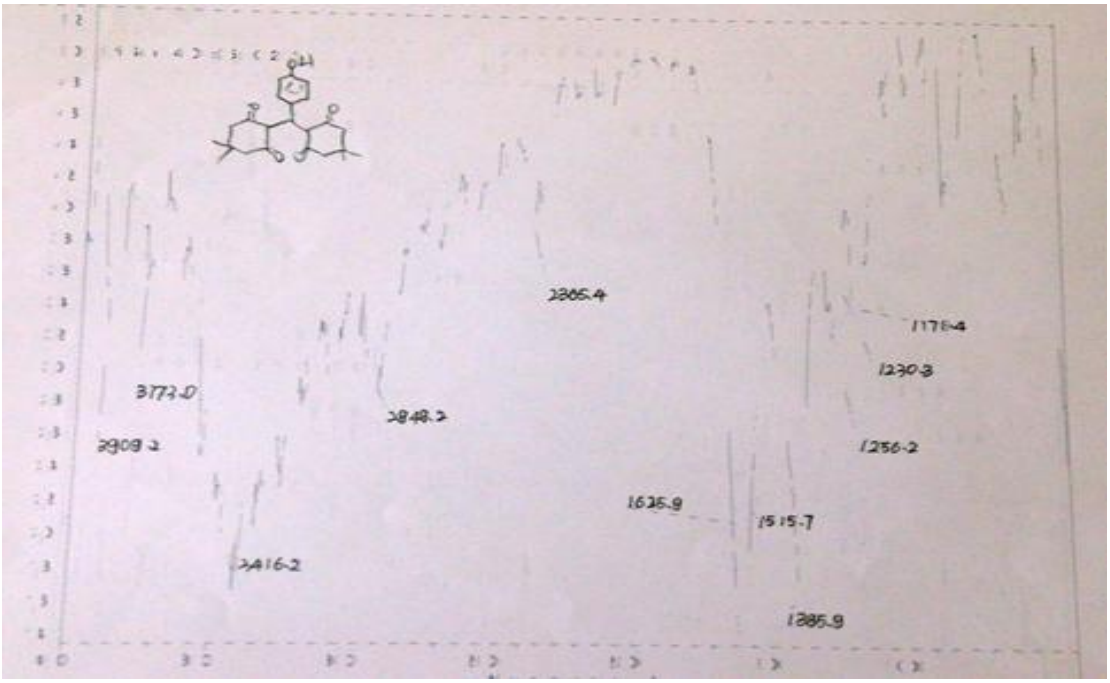
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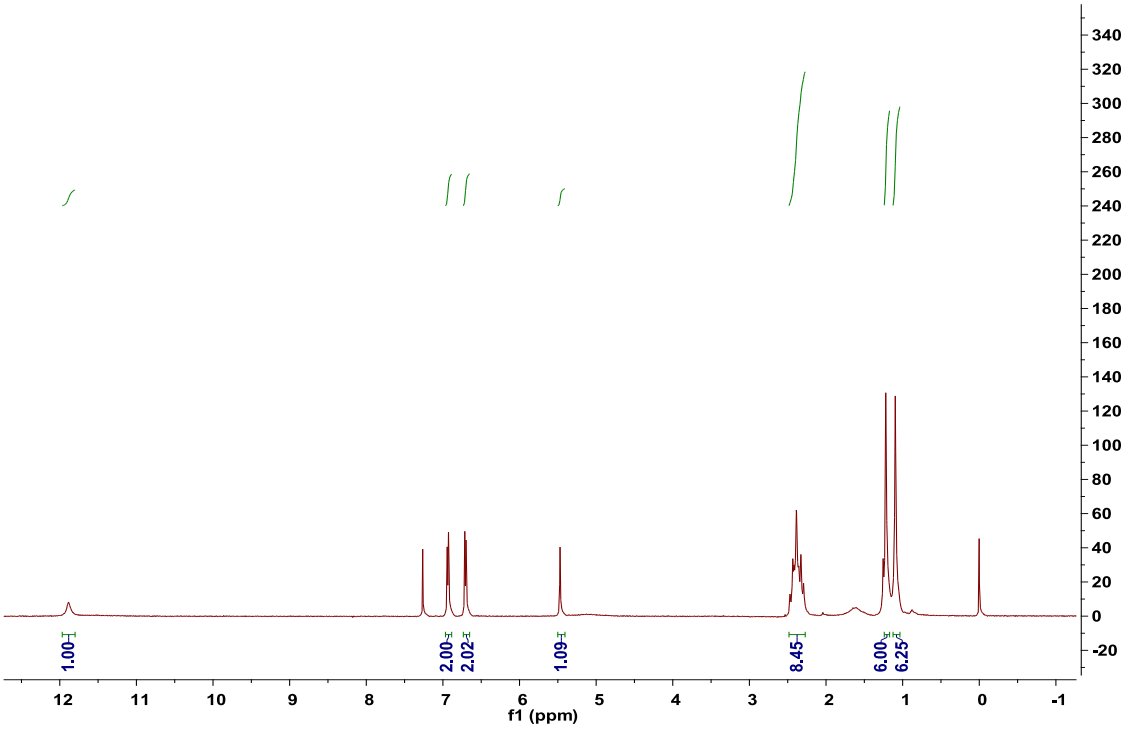
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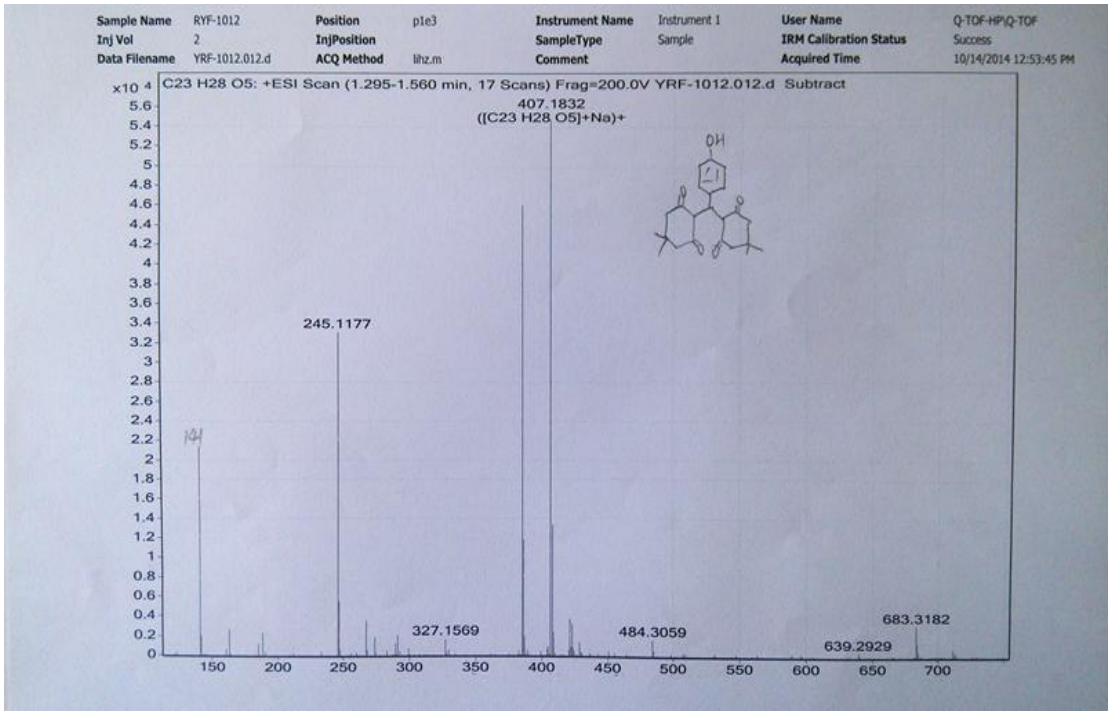
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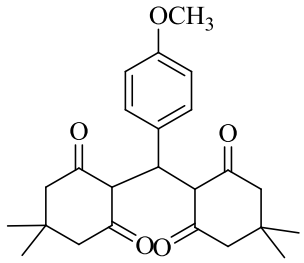
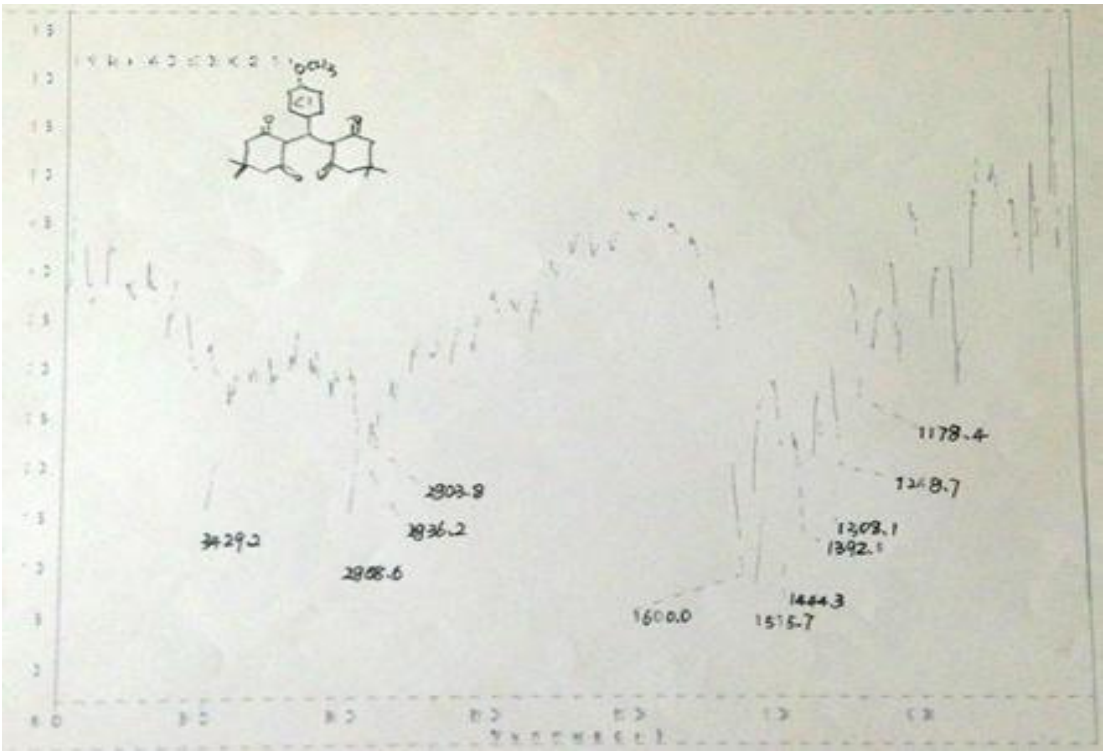
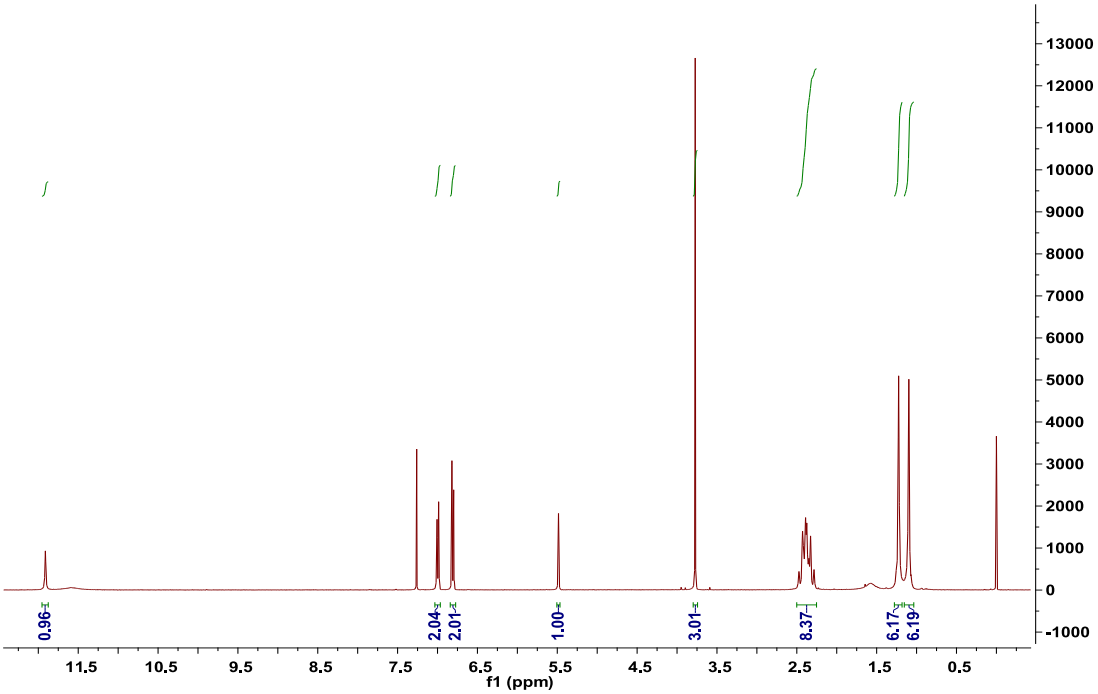
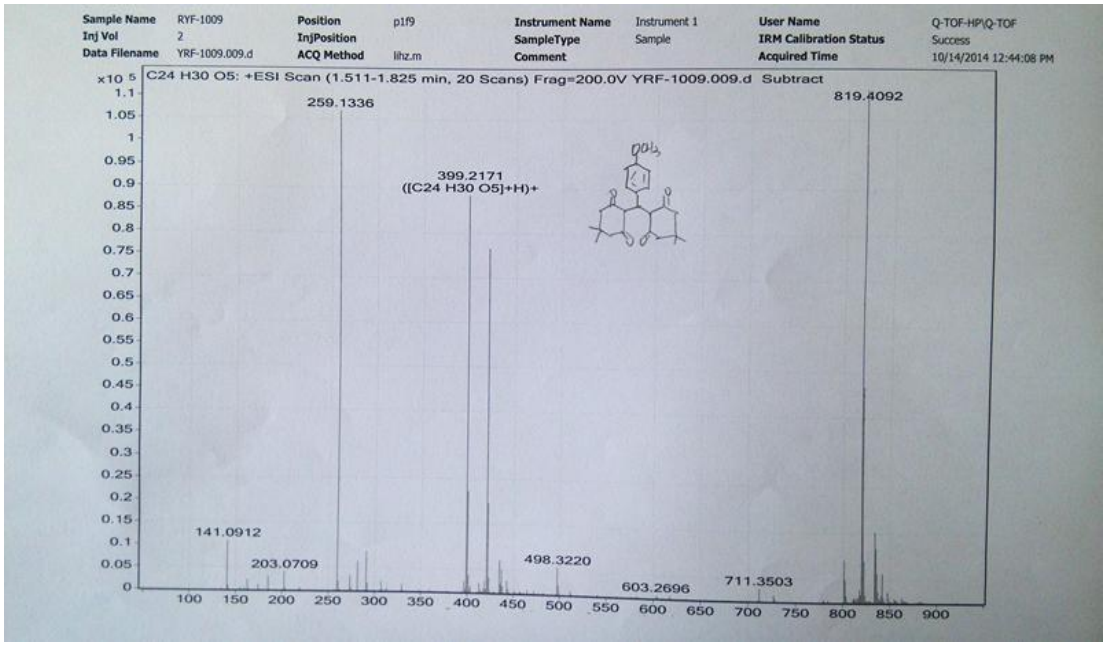
683.3182

3e.

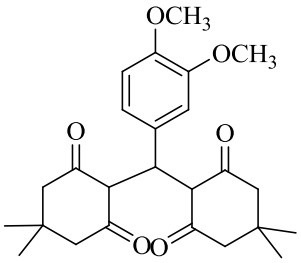

OCH3
O
O
O
O

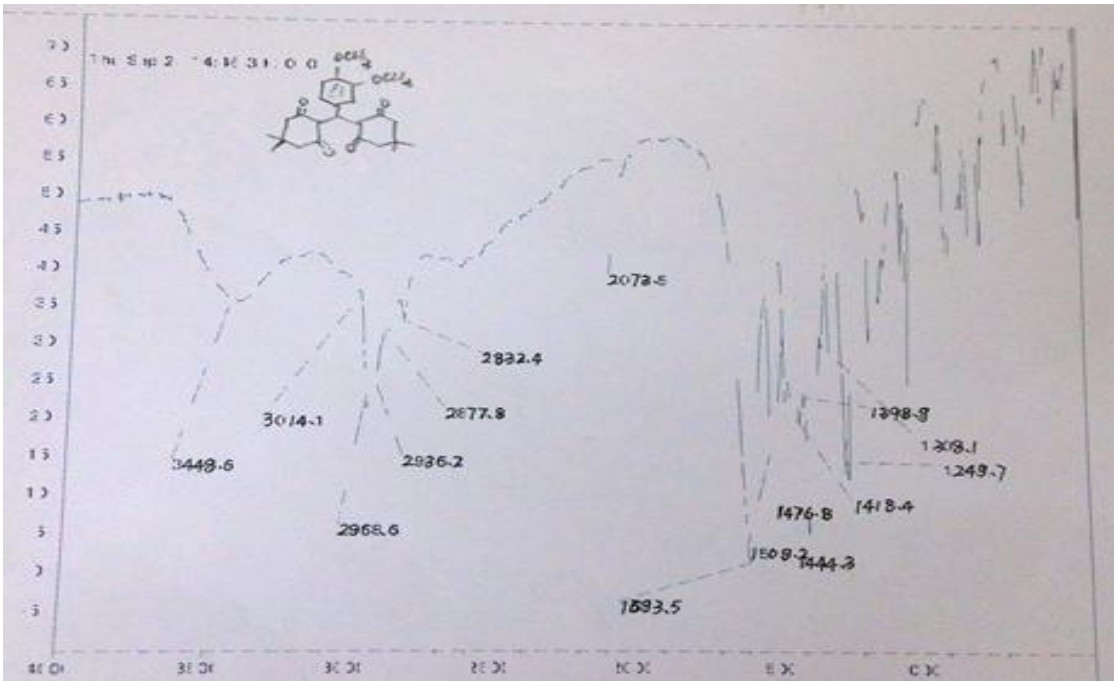

3429.2
2958.6
2903.9
2836.2
1600.0
1515.7
1444.3
1392.1
1308.1
1178.4

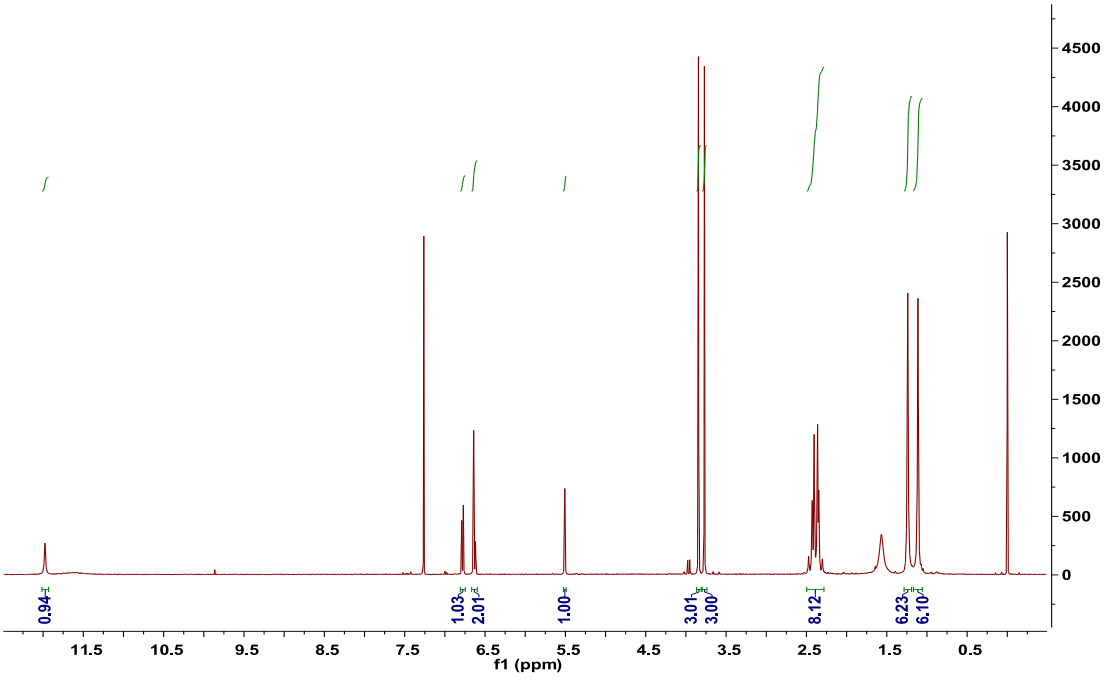

0.96
2.04
2.01
1.00
3.01
8.37
6.17
6.19
f1 (ppm)

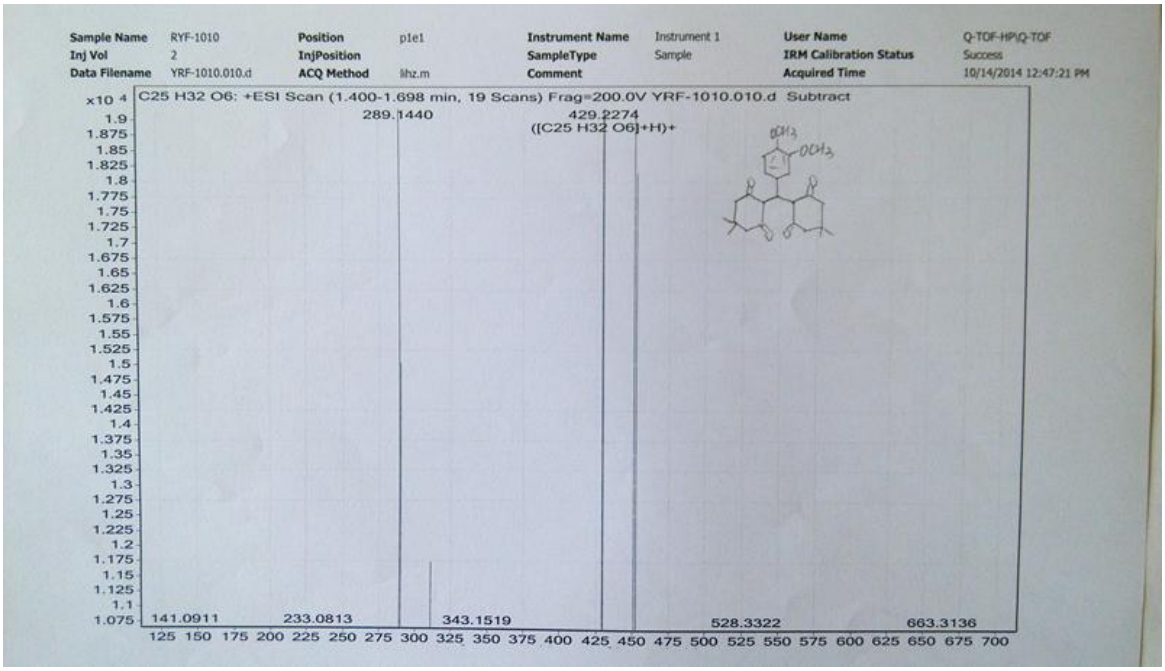

Sample Name RYF-1009
Inj Vol 2
Data Filename YRF-1009.009.d
Position p1f9
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 10/14/2014 12:44:08 PM
C24 H30 O5: +ESI Scan (1.511-1.825 min, 20 Scans) Frag=200.0V YRF-1009.009.d Subtract
x10 5
259.1336
819.4092
399.2171
([C24 H30 O5]+H)+
141.0912
203.0709
498.3220
603.2696
711.3503

3f.

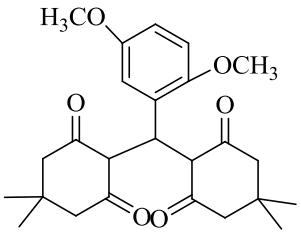

OCH3
OCH3
O
O
O
O

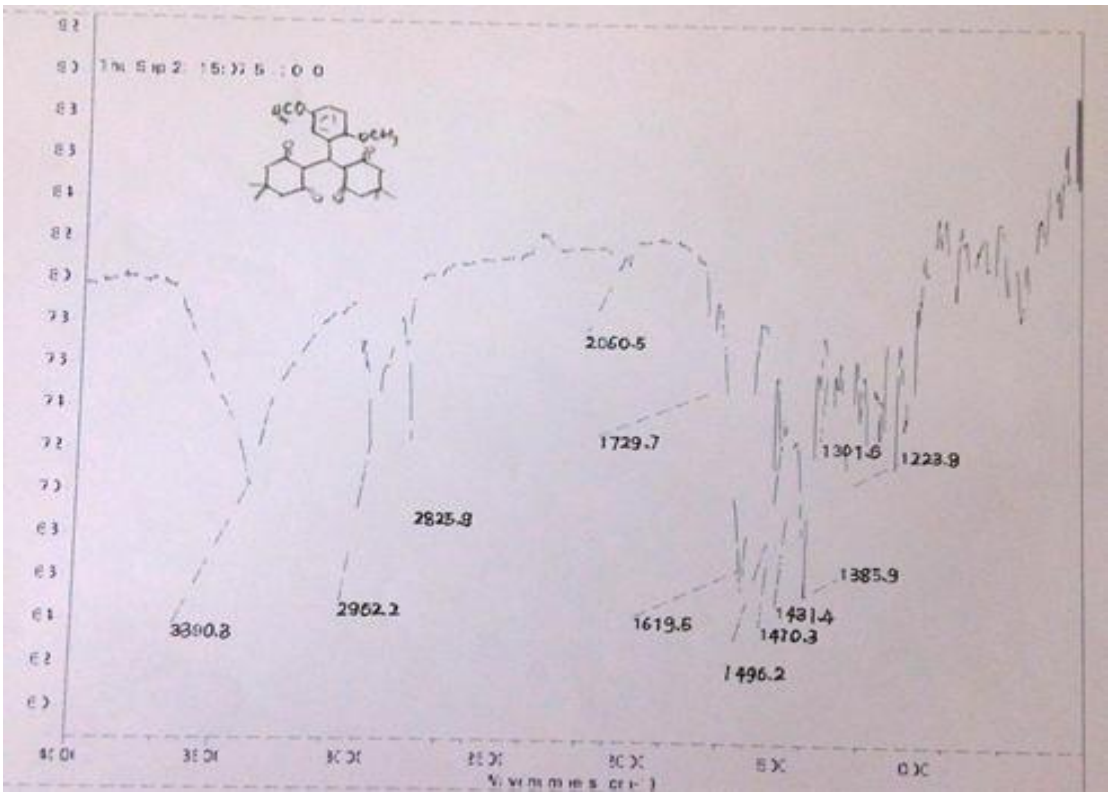

3448.6
3014.1
2968.6
2936.2
2877.8
2832.4
2073.5
1893.5
1509.2
1476.8
1444.3
1418.4
1398.8
1308.1
1249.7

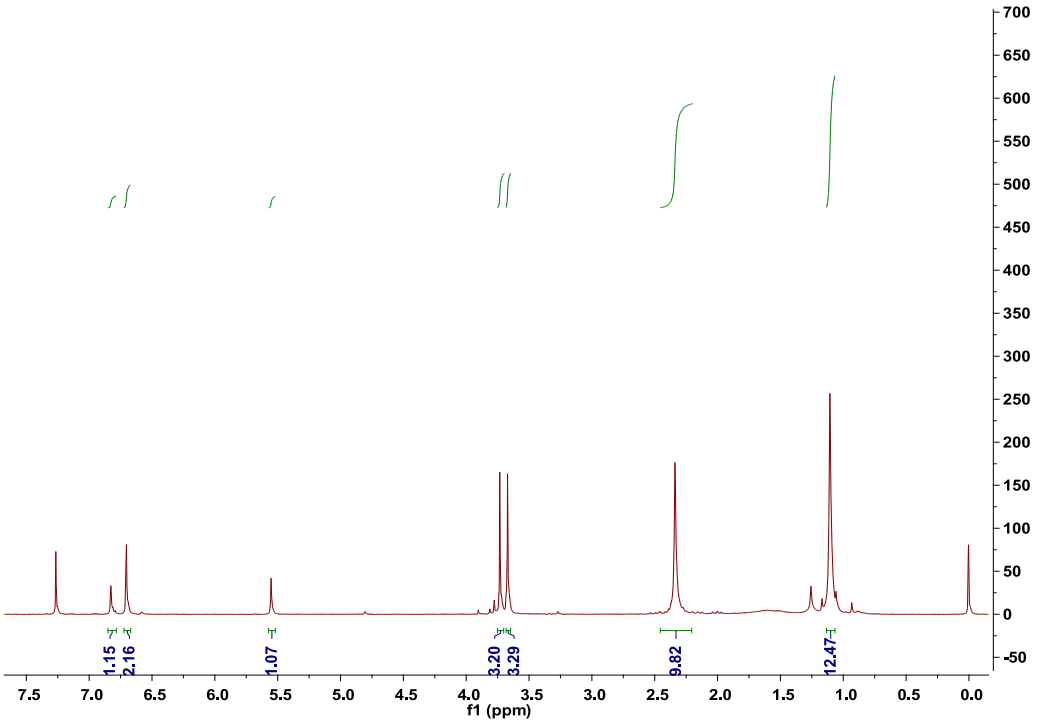

0.94
1.03
2.01
1.00
3.01
3.00
8.12
6.23
6.10
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0

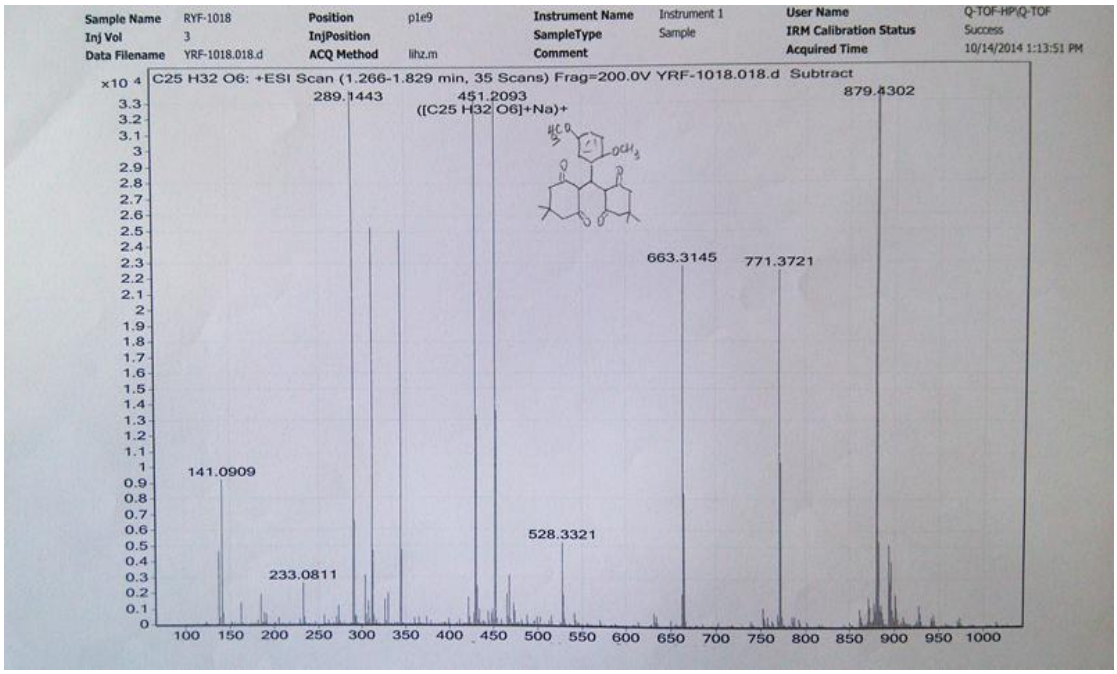

Sample Name RYF-1010
Position p1e1
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 2
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename YRF-1010.010.d
ACQ Method lihz.m
Comment
Acquired Time 10/14/2014 12:47:21 PM
C25 H32 O6: +ESI Scan (1.400-1.698 min, 19 Scans) Frag=200.0V YRF-1010.010.d Subtract
289.1440
429.2274
([C25 H32 O6]+H)+
141.0911
233.0813
343.1519
528.3322
663.3136
x10 4

3g.

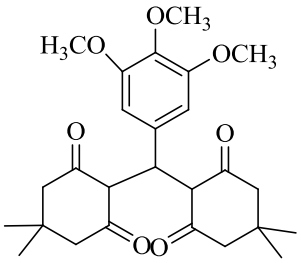

H3CO
OCH3
O
O
O
O

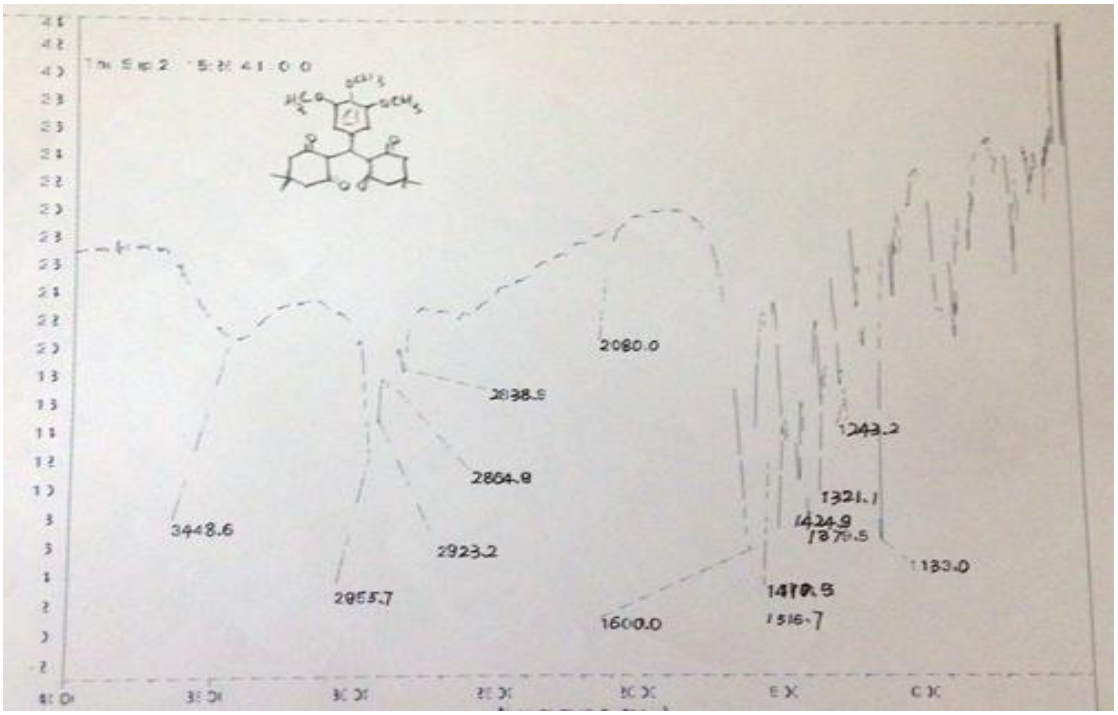

3390.8
2962.2
2825.8
2060.5
1729.7
1619.6
1496.2
1470.3
1431.4
1385.9
1301.6
1223.8

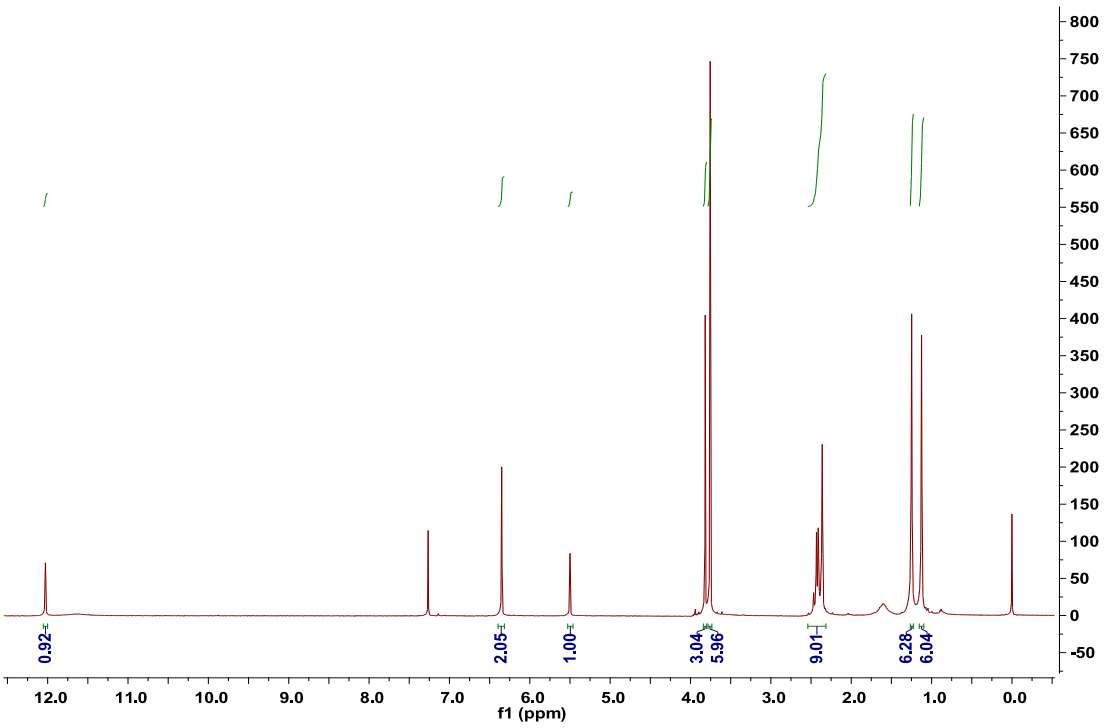

1.15
2.16
1.07
3.20
3.29
9.82
12.47
f1 (ppm)

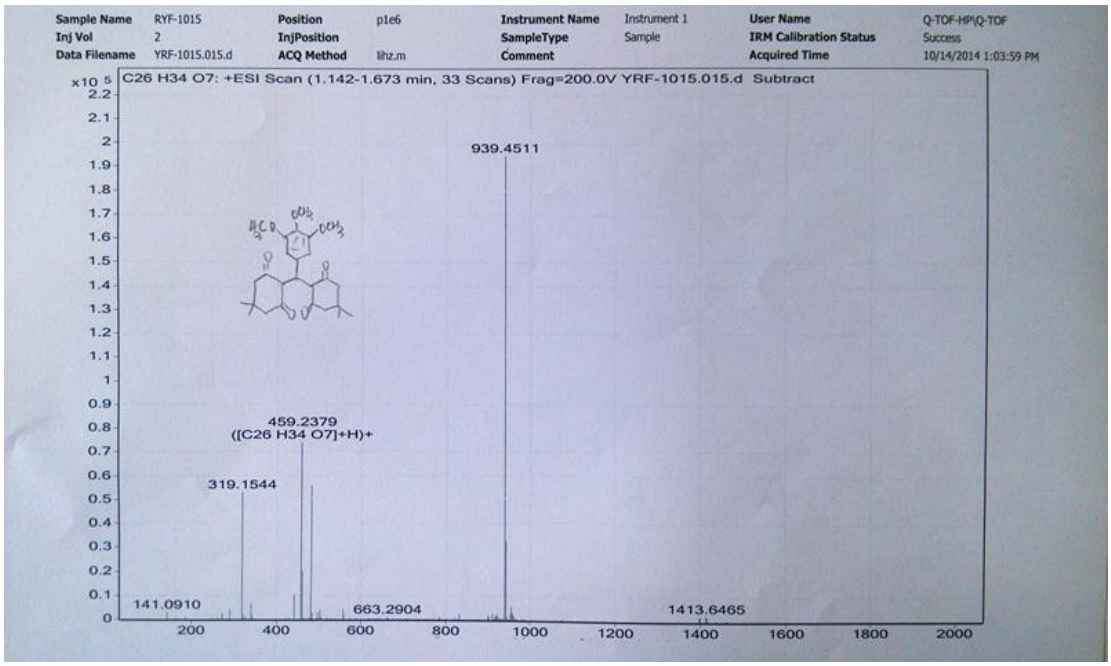

Sample Name RYF-1018
Inj Vol 3
Data Filename YRF-1018.018.d
Position p1e9
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 10/14/2014 1:13:51 PM
C25 H32 O6: +ESI Scan (1.266-1.829 min, 35 Scans) Frag=200.0V YRF-1018.018.d Subtract
x10 4
289.1443
451.2093
([C25 H32 O6]+Na)+
879.4302
663.3145
771.3721
141.0909
528.3321
233.0811

3h.

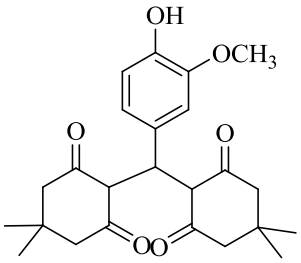

OCH3
H3CO
OCH3
O
O
O
O

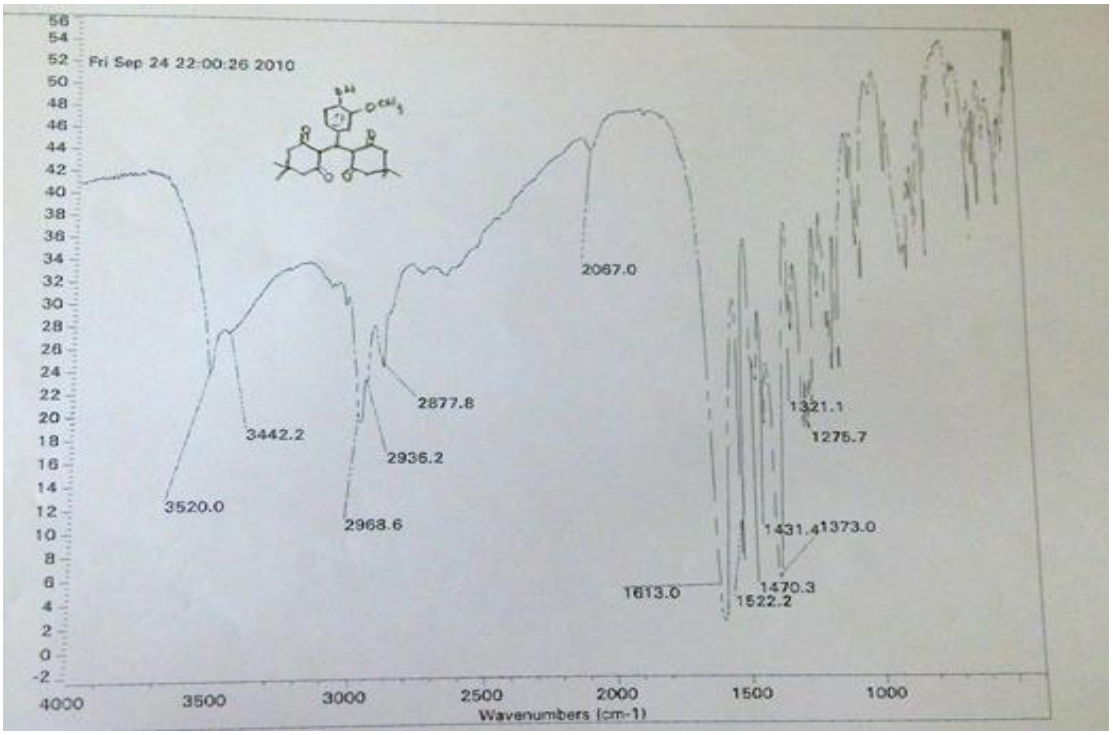

3448.6
2923.2
2855.7
2864.9
2838.9
2080.0
1600.0
1516.7
1321.1
1424.9
1243.2
1183.0

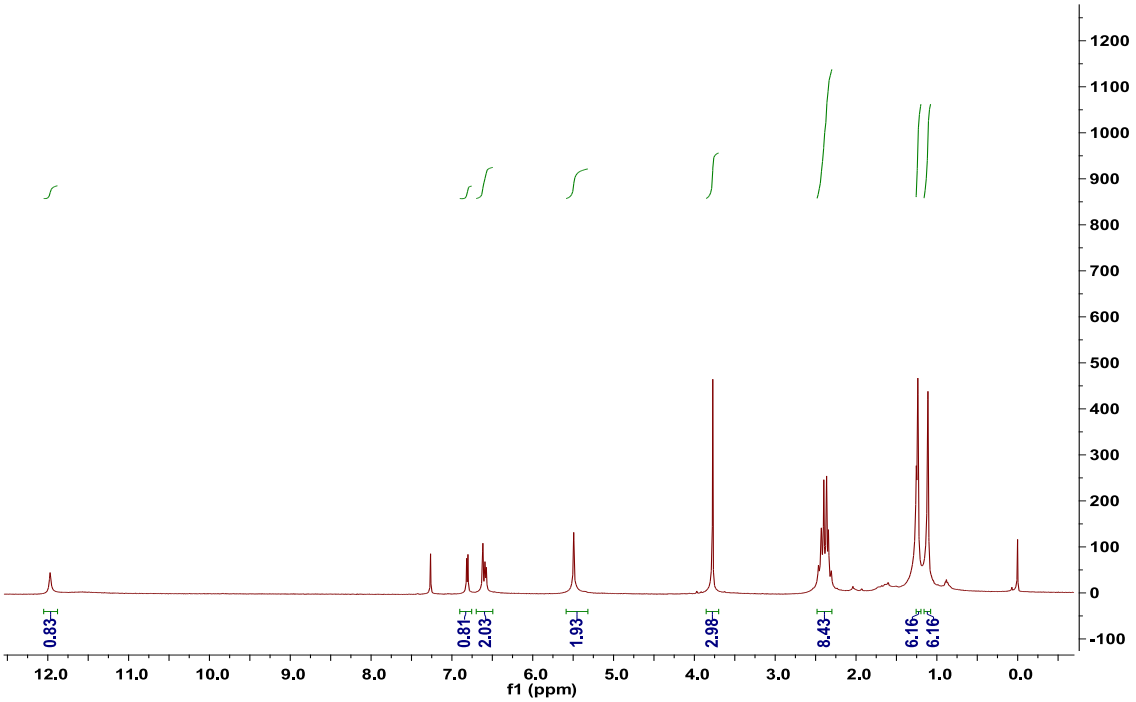

0.92
2.05
1.00
3.04
5.96
9.01
6.28
6.04
f1 (ppm)

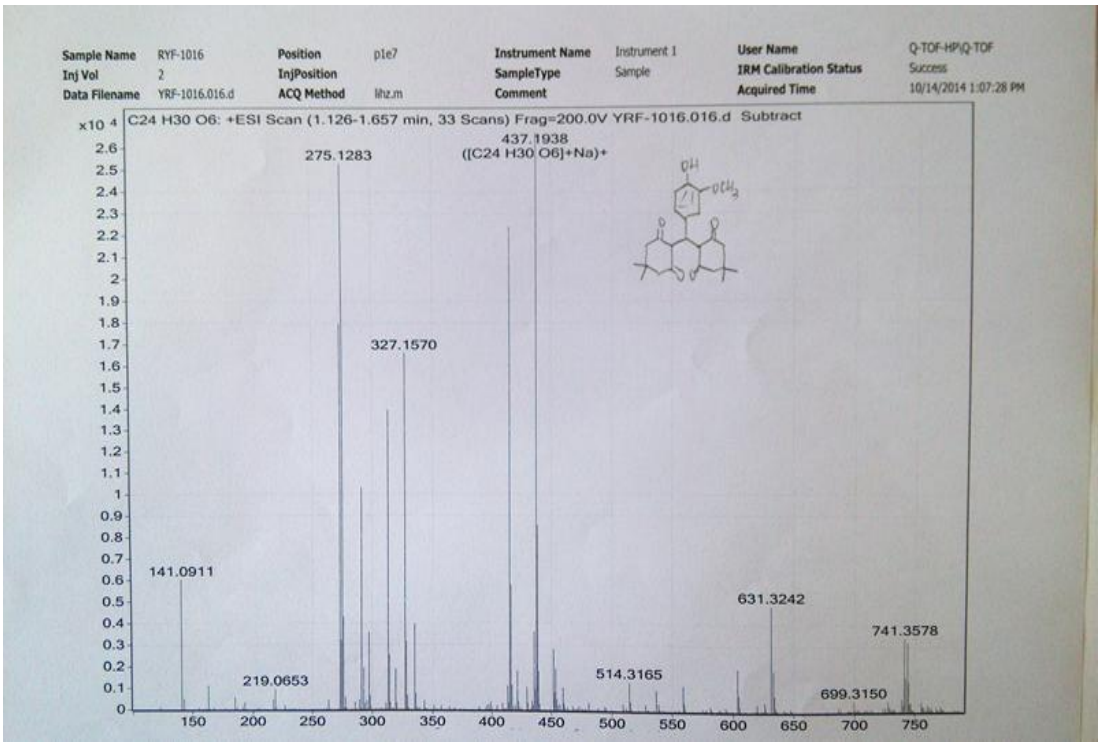

Sample Name RYF-1015
Position p1e6
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 2
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename YRF-1015.015.d
ACQ Method lihz.m
Comment
Acquired Time 10/14/2014 1:03:59 PM
C26 H34 O7: +ESI Scan (1.142-1.673 min, 33 Scans) Frag=200.0V YRF-1015.015.d Subtract
x10 5
939.4511
459.2379
([C26 H34 O7]+H)+
319.1544
141.0910
663.2904
1413.6465

3i.

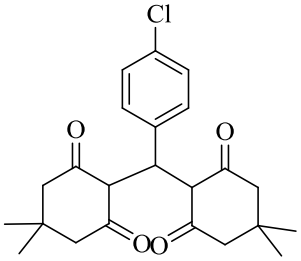

OH
OCH3
O
O
O
O

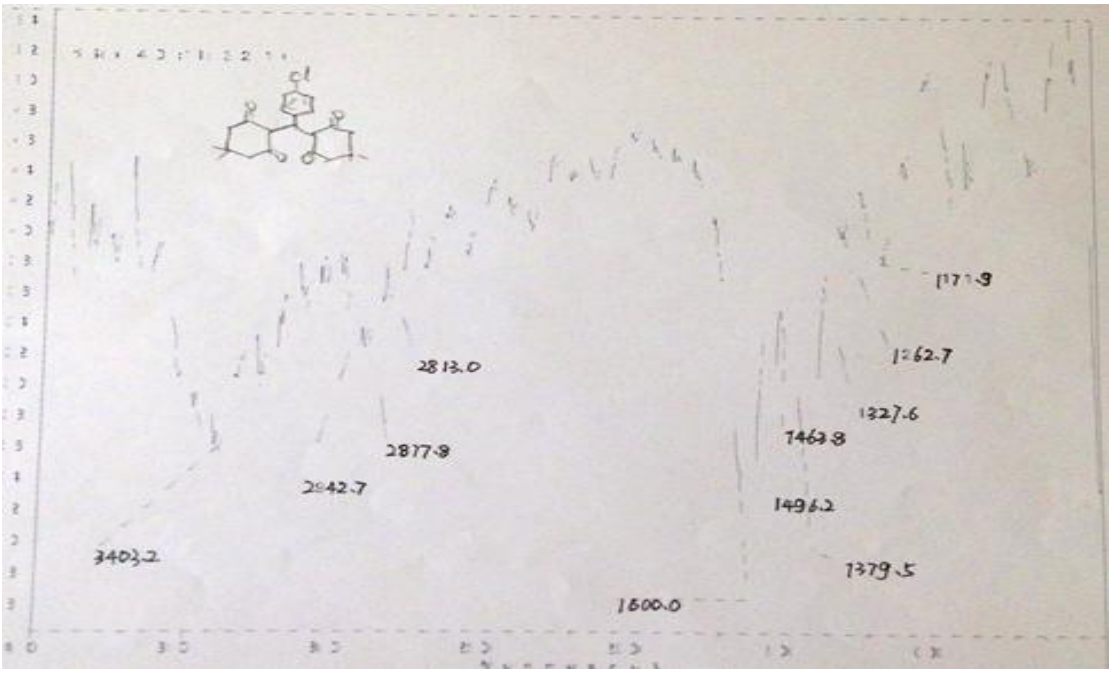

Fri Sep 24 22:00:26 2010
3520.0
3442.2
2968.6
2936.2
2877.8
2067.0
1613.0
1522.2
1470.3
1431.4
1373.0
1321.1
1275.7
Wavenumbers (cm-1)

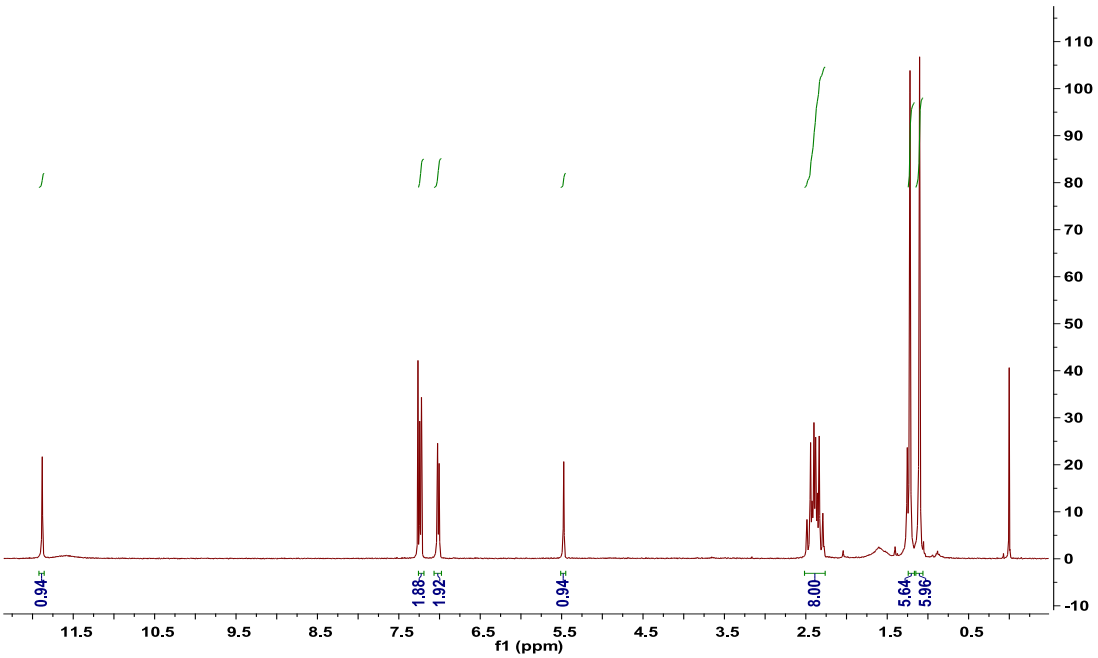

0.83
0.81
2.03
1.93
2.98
8.43
6.16
6.16
f1 (ppm)

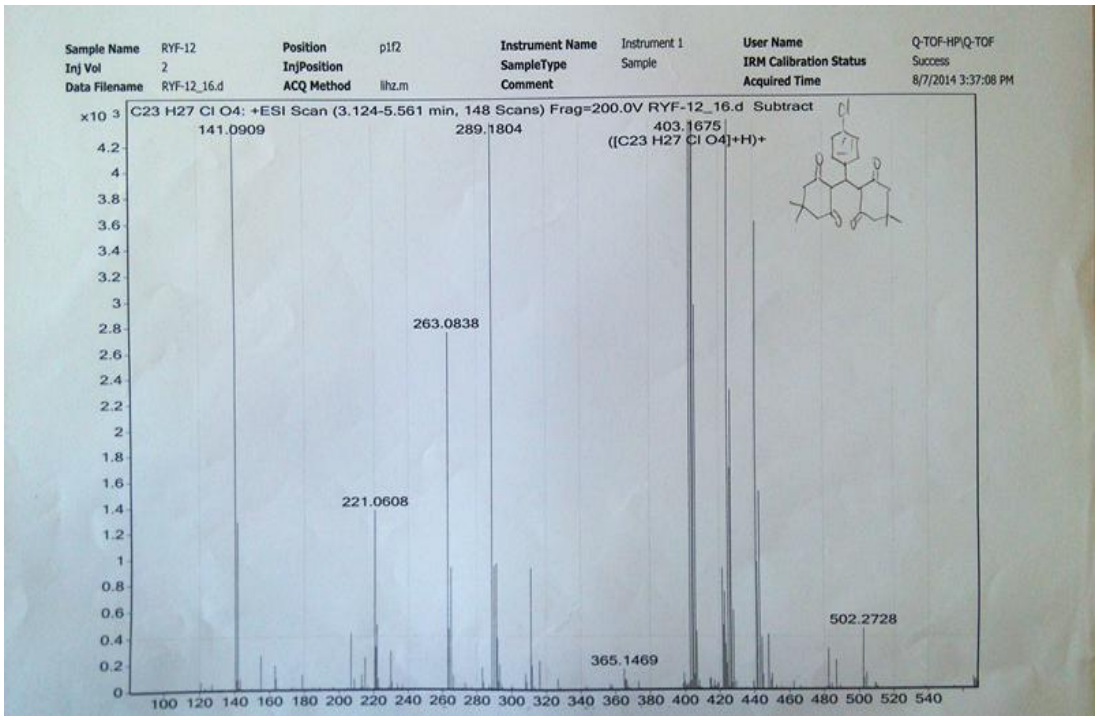

Sample Name RYF-1016
Position p1e7
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 2
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename YRF-1016.016.d
ACQ Method lihz.m
Comment
Acquired Time 10/14/2014 1:07:28 PM
C24 H30 O6: +ESI Scan (1.126-1.657 min, 33 Scans) Frag=200.0V YRF-1016.016.d Subtract
x10 4
437.1938
([C24 H30 O6]+Na)+
275.1283
327.1570
141.0911
219.0653
514.3165
631.3242
699.3150
741.3578

3j.

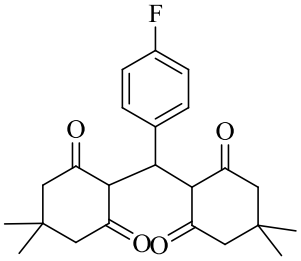

Cl
O
O
O
O

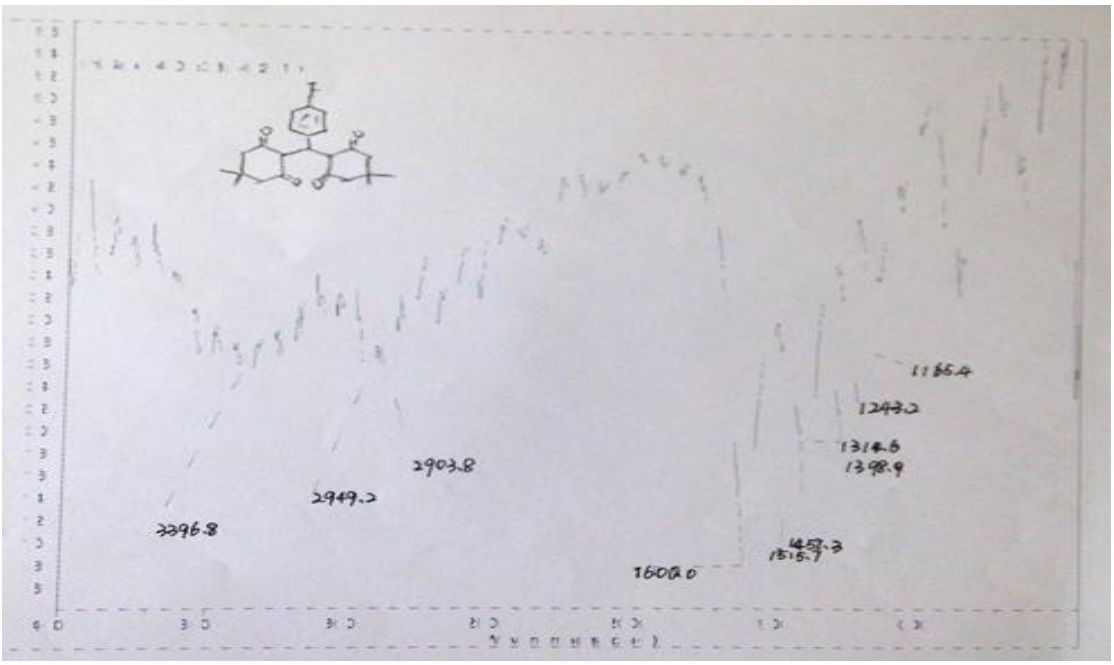

2813.0
2877.8
2942.7
3403.2
1600.0
1496.2
1379.5
1327.6
1746.8
1162.7

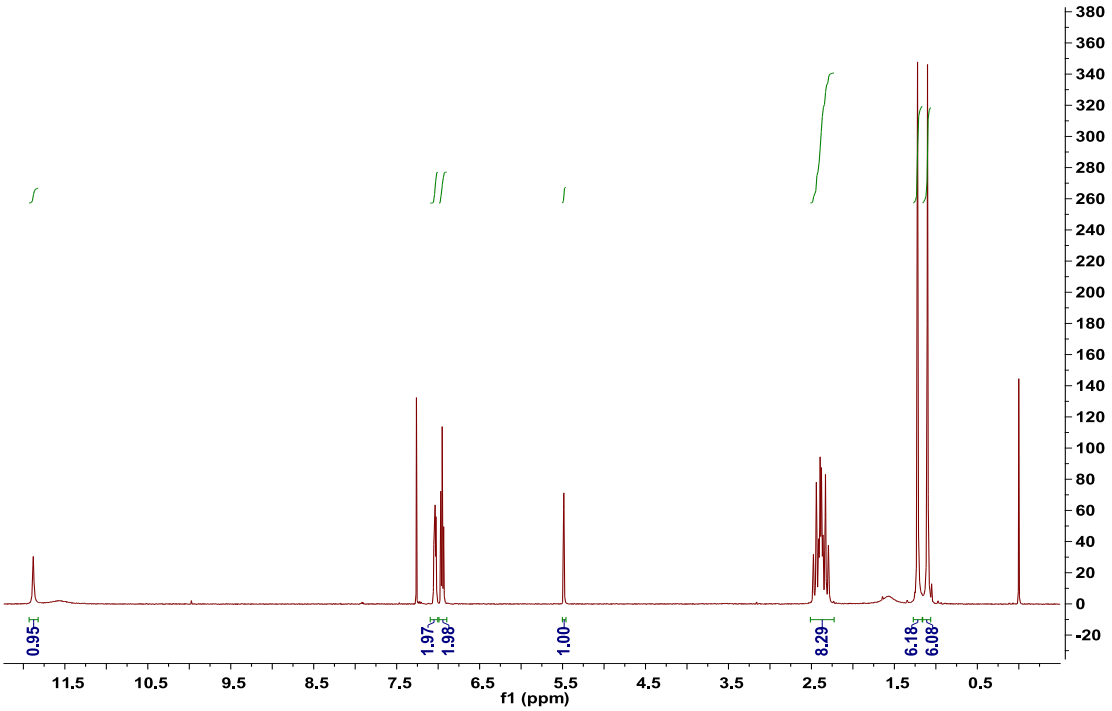

110
100
90
80
70
60
50
40
30
20
10
0
-10
0.94
1.88
1.92
0.94
8.00
5.64
5.96
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

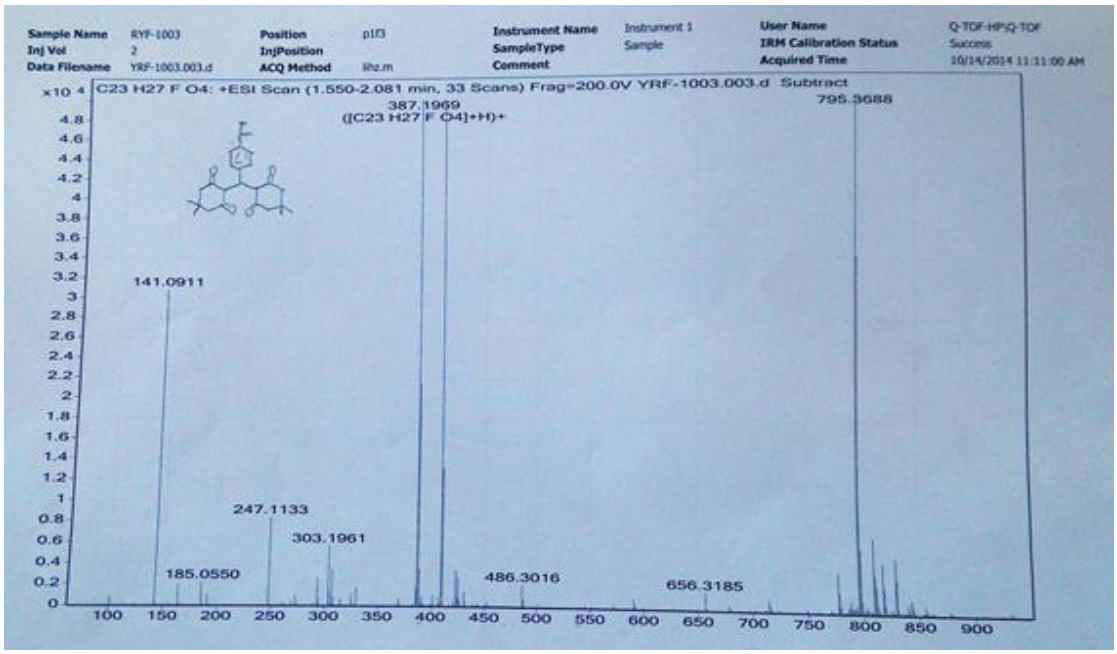

Sample Name RYF-12
Position p1f2
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 2
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename RYF-12_16.d
ACQ Method lihz.m
Comment
Acquired Time 8/7/2014 3:37:08 PM
C23 H27 Cl O4: +ESI Scan (3.124-5.561 min, 148 Scans) Frag=200.0V RYF-12_16.d Subtract
x10 3
141.0909
289.1804
403.1675
([C23 H27 Cl O4]+H)+
263.0838
221.0608
502.2728
365.1469
4.2
4
3.8
3.6
3.4
3.2
3
2.8
2.6
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540

3k.

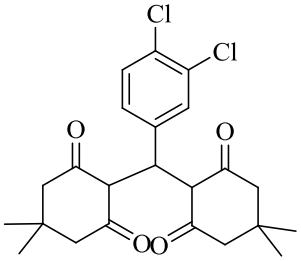

F
O
O
O
O

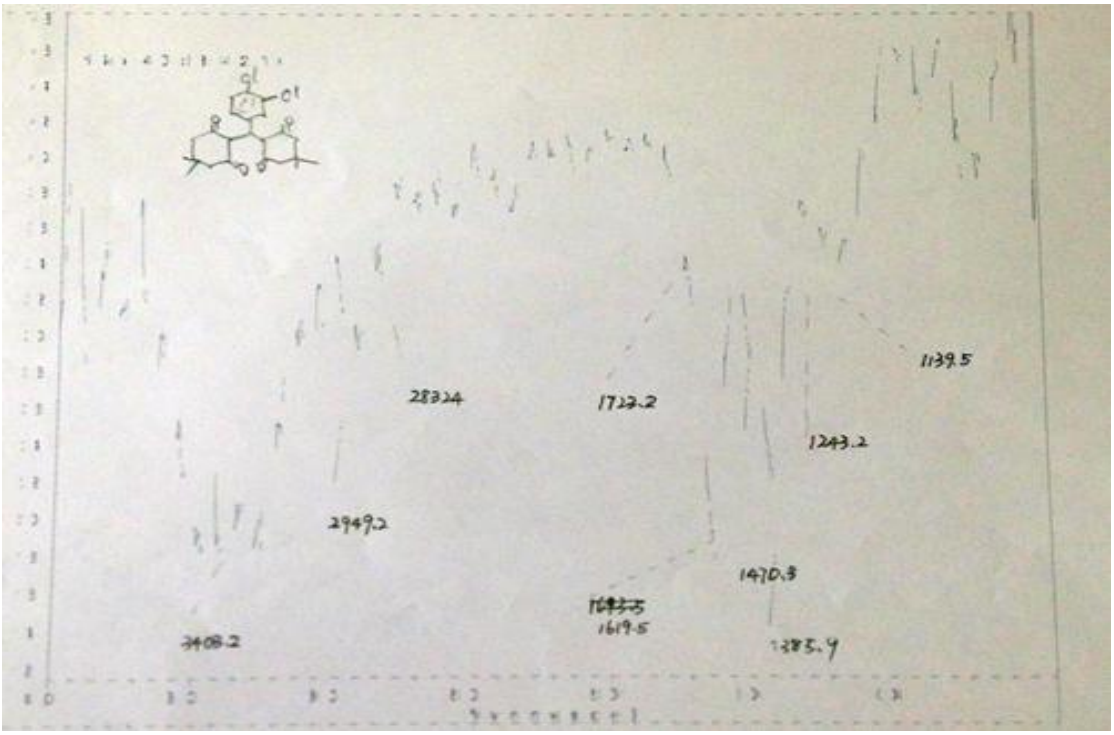

3396.8
2949.2
2903.8
1600.0
1515.7
1398.9
1243.2
1186.4

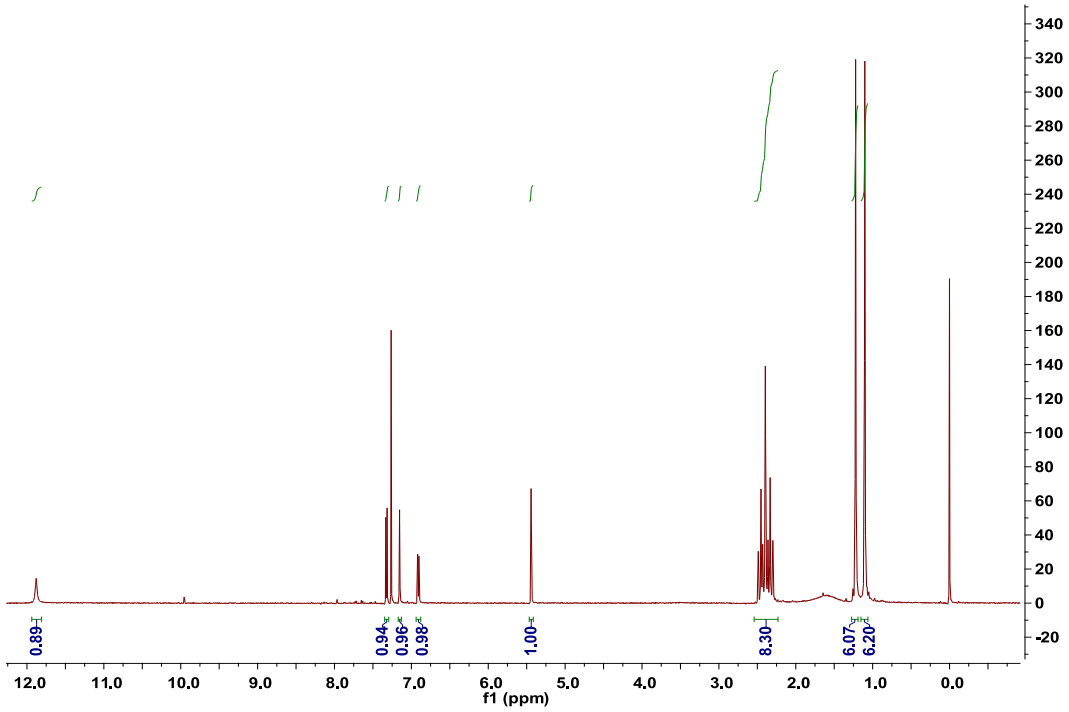

0.95
1.97
1.98
1.00
8.29
6.18
6.08
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)
380
360
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20

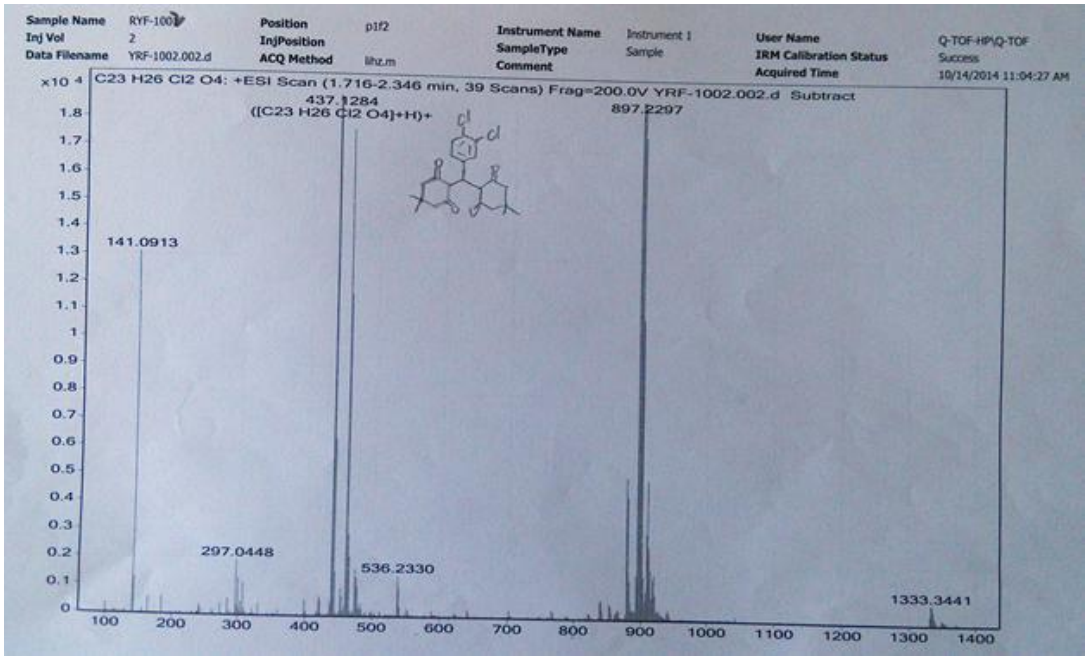

Sample Name RYF-1003
Inj Vol 2
Data Filename YRF-1003.003.d
Position p1f3
InjPosition
ACQ Method lhz.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status
Acquired Time
Q-TOF-HP/Q-TOF
Success
10/14/2014 11:11:00 AM
C23 H27 F O4: +ESI Scan (1.550-2.081 min, 33 Scans) Frag=200.0V YRF-1003.003.d Subtract
387.1969
([C23 H27 F O4]+H)+
795.3688
141.0911
247.1133
303.1961
185.0550
486.3016
656.3185
x10 4

3l.

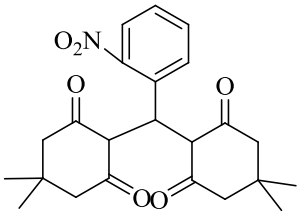

Cl
Cl
O
O
O
O

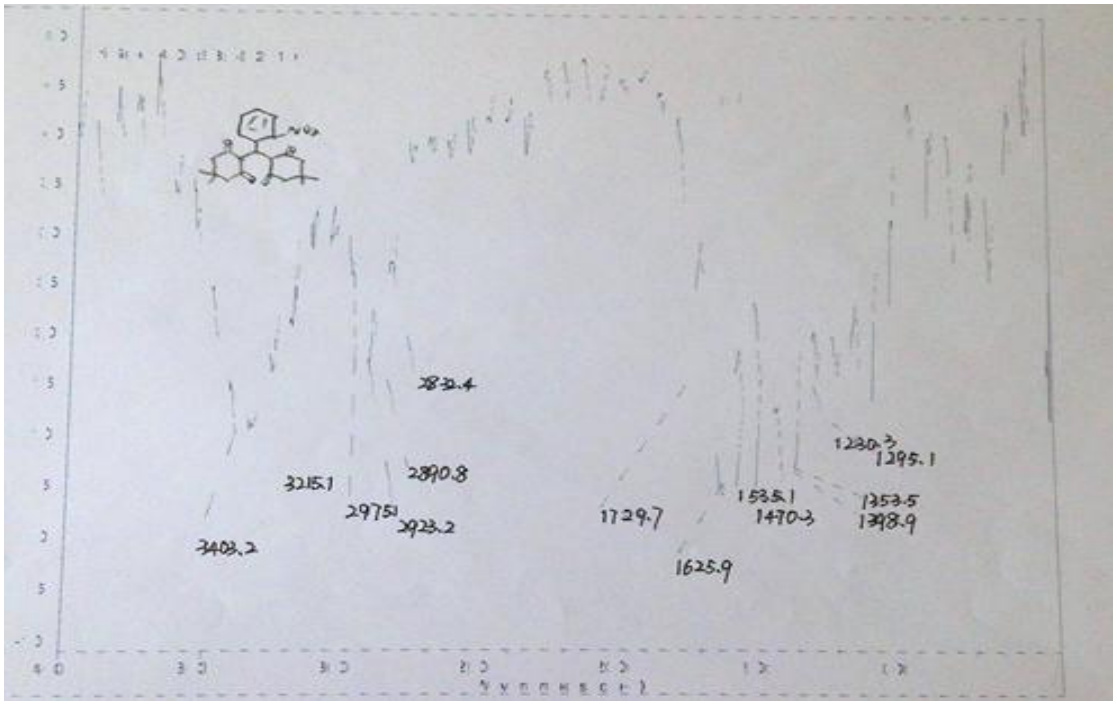

2834
1722.2
1139.5
1243.2
2949.2
1470.3
1619.5
3408.2

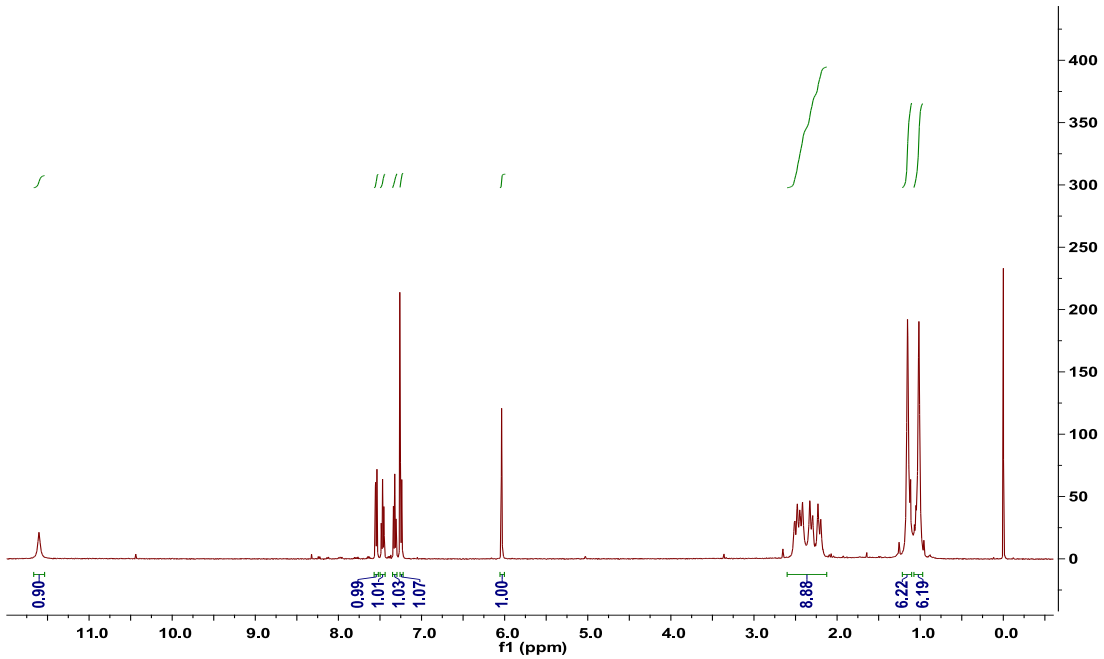

0.89
0.94
0.96
0.98
1.00
8.30
6.07
6.20
f1 (ppm)

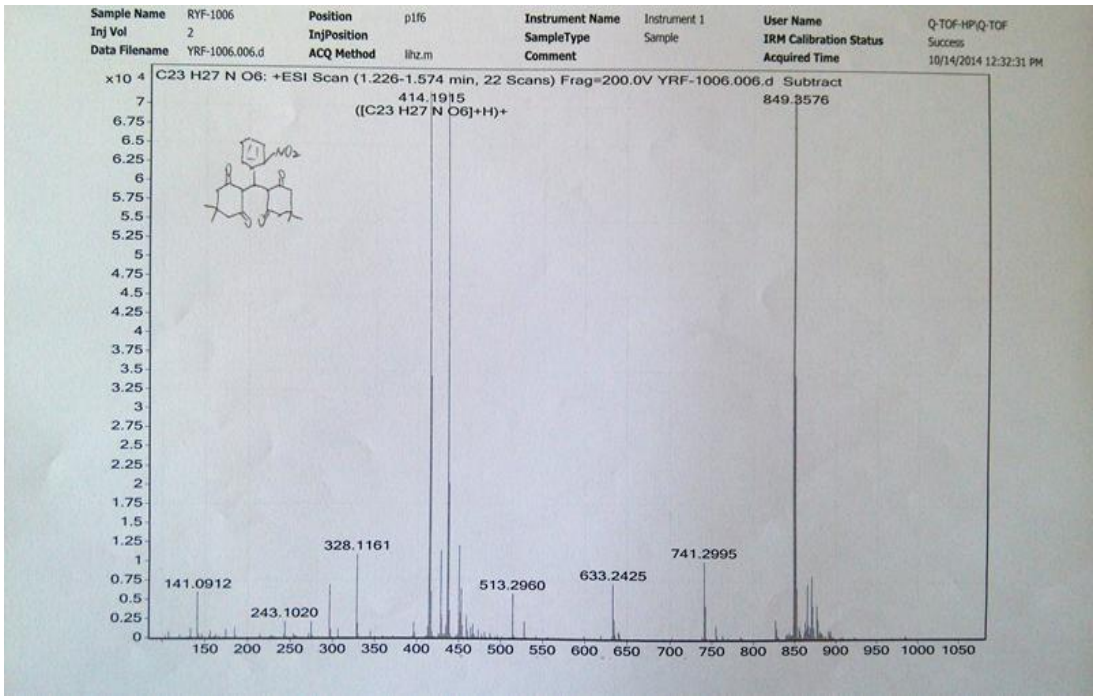

Sample Name RYF-100
Inj Vol 2
Data Filename YRF-1002.002.d
Position p1f2
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 10/14/2014 11:04:27 AM
C23 H26 Cl2 O4: +ESI Scan (1.716-2.346 min, 39 Scans) Frag=200.0V YRF-1002.002.d Subtract
437.1284
([C23 H26 Cl2 O4]+H)+
897.2297
141.0913
297.0448
536.2330
1333.3441
x10 4

3m.

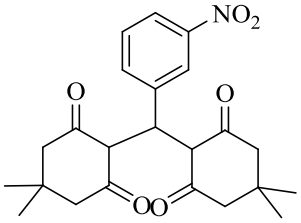


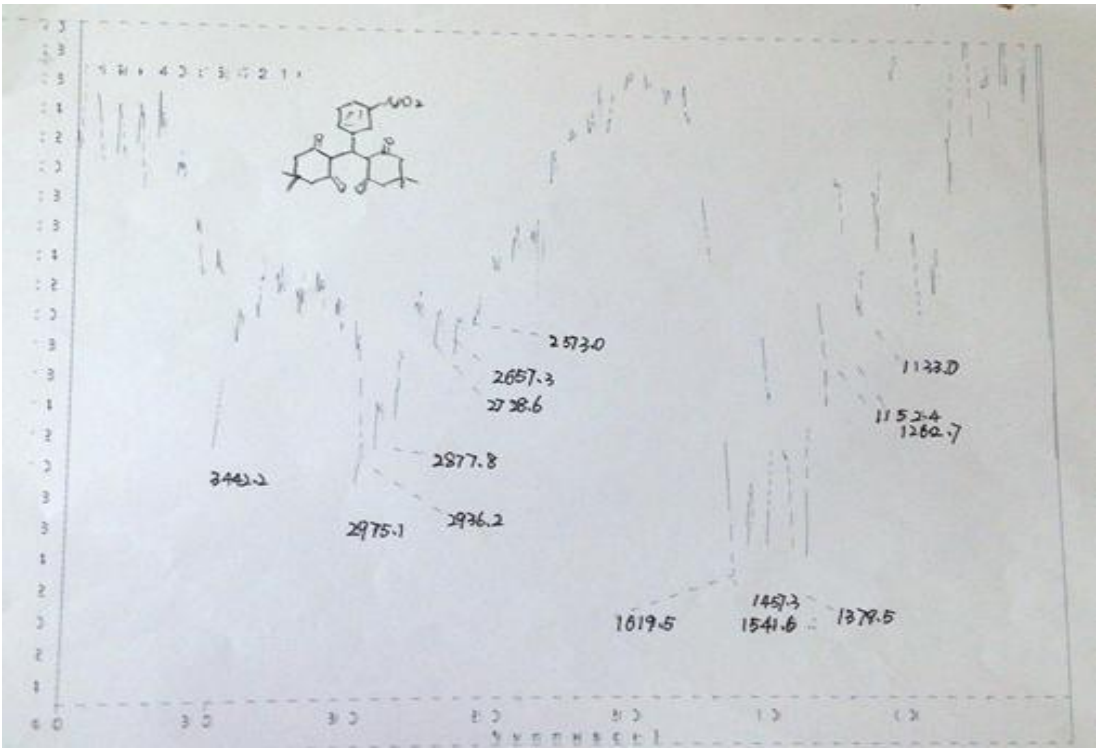

2832.4
3215.1
2890.8
2975.1
2923.2
3403.2
1729.7
1625.9
1535.1
1470.3
1230.3
1295.1
1353.5
1398.9

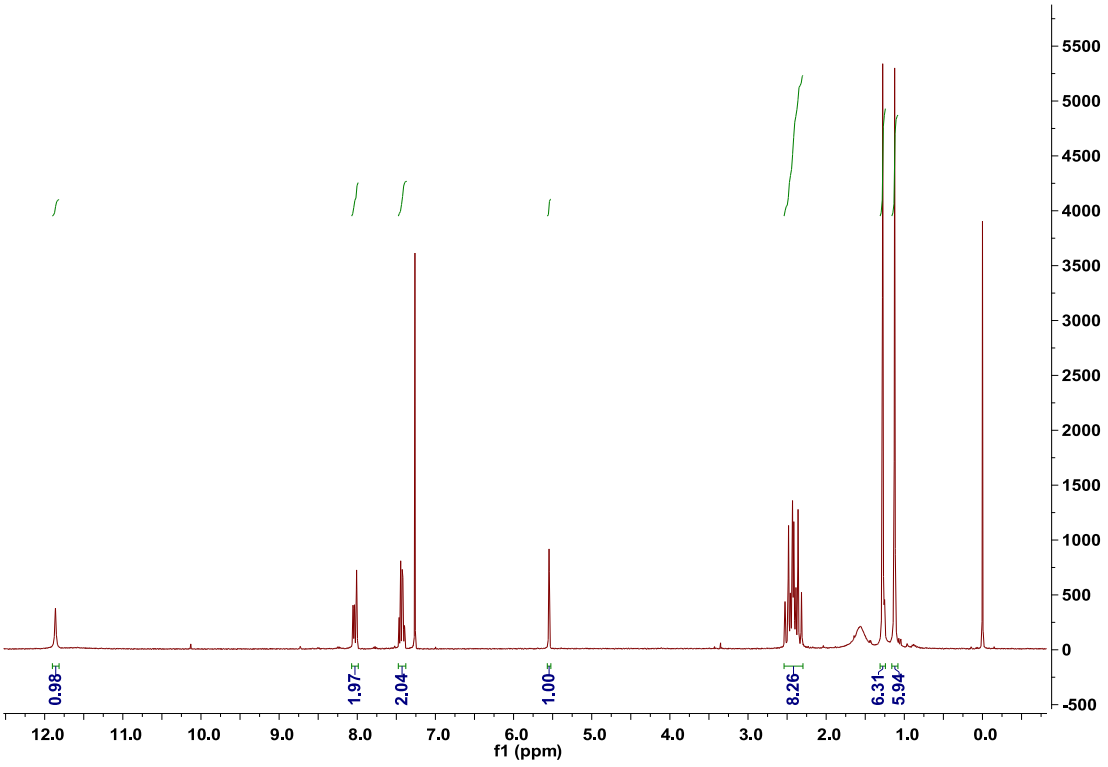

0.90
0.99
1.01
1.03
1.07
1.00
8.88
6.22
6.19
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)
400
350
300
250
200
150
100
50
0

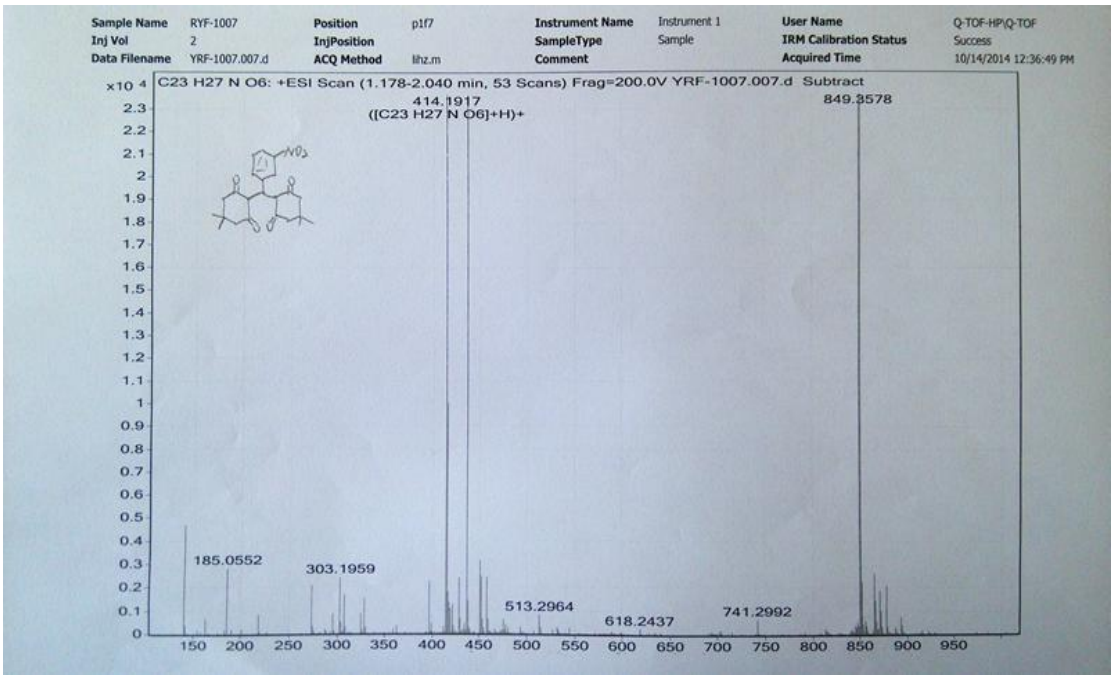

Sample Name RYF-1006
Inj Vol 2
Data Filename YRF-1006.006.d
Position p1f6
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 10/14/2014 12:32:31 PM
C23 H27 N O6: +ESI Scan (1.226-1.574 min, 22 Scans) Frag=200.0V YRF-1006.006.d Subtract
414.1915
([C23 H27 N O6]+H)+
849.3576
328.1161
741.2995
633.2425
513.2960
141.0912
243.1020
x10 4

3n.

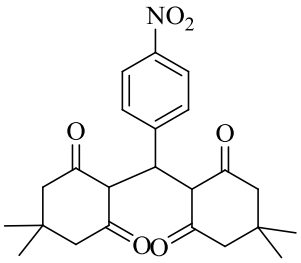

NO2
O
O
O
O

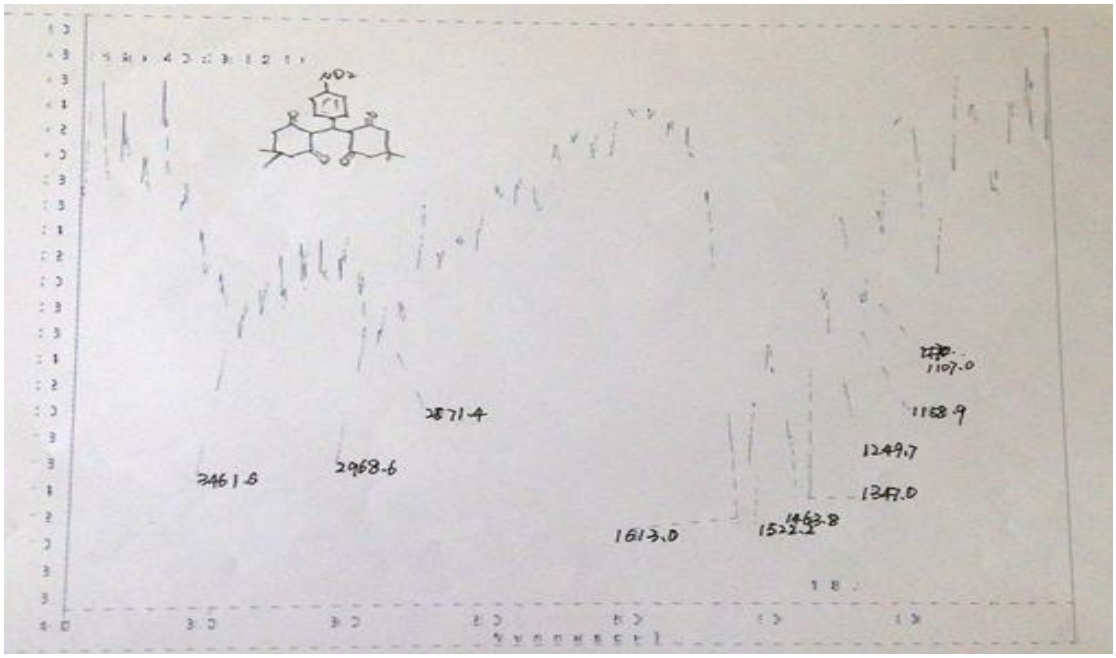

2573.0
2657.3
2738.6
1133.0
1152.4
1262.7
2877.8
3441.2
2975.1
2936.2
1619.5
1457.3
1541.6
1379.5

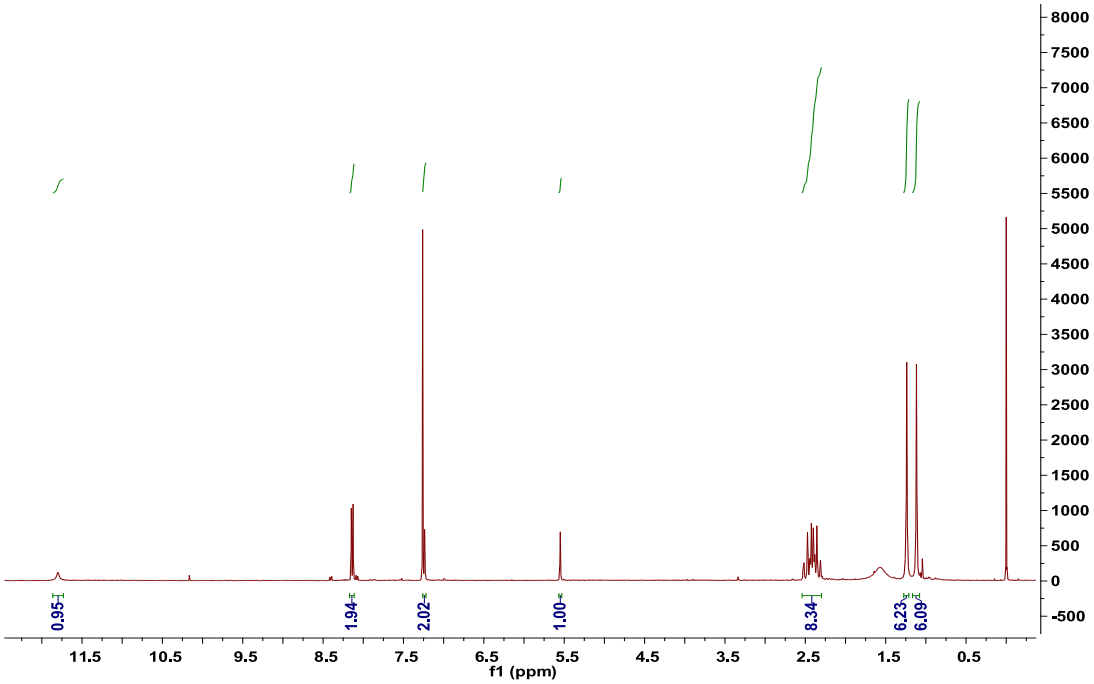

5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
0.98
1.97
2.04
1.00
8.26
6.31
5.94
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

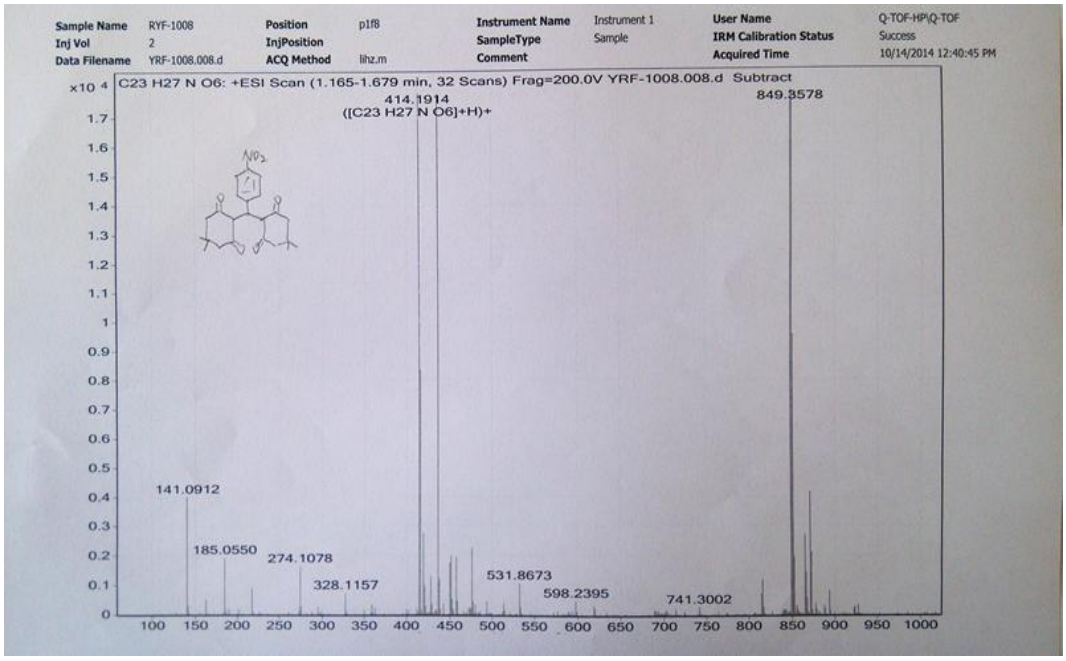

Sample Name RYF-1007
Position p1f7
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 2
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename YRF-1007.007.d
ACQ Method lihz.m
Comment
Acquired Time 10/14/2014 12:36:49 PM
C23 H27 N O6: +ESI Scan (1.178-2.040 min, 53 Scans) Frag=200.0V YRF-1007.007.d Subtract
414.1917
([C23 H27 N O6]+H)+
849.3578
185.0552
303.1959
513.2964
618.2437
741.2992
x10 4

3o.

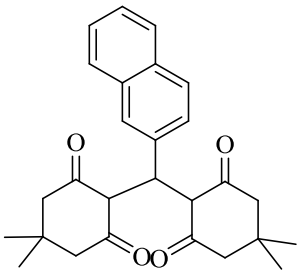

NO2
O
O
O
O

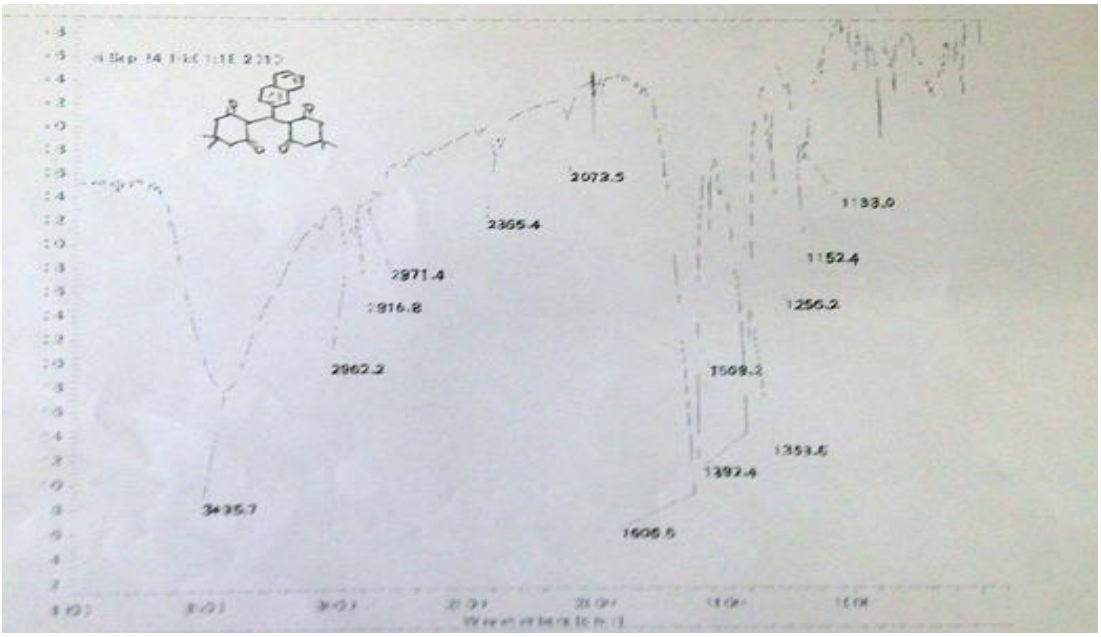

2871.4
2961.6
2968.6
1613.0
1463.8
1249.7
1347.0
1158.9
1107.0

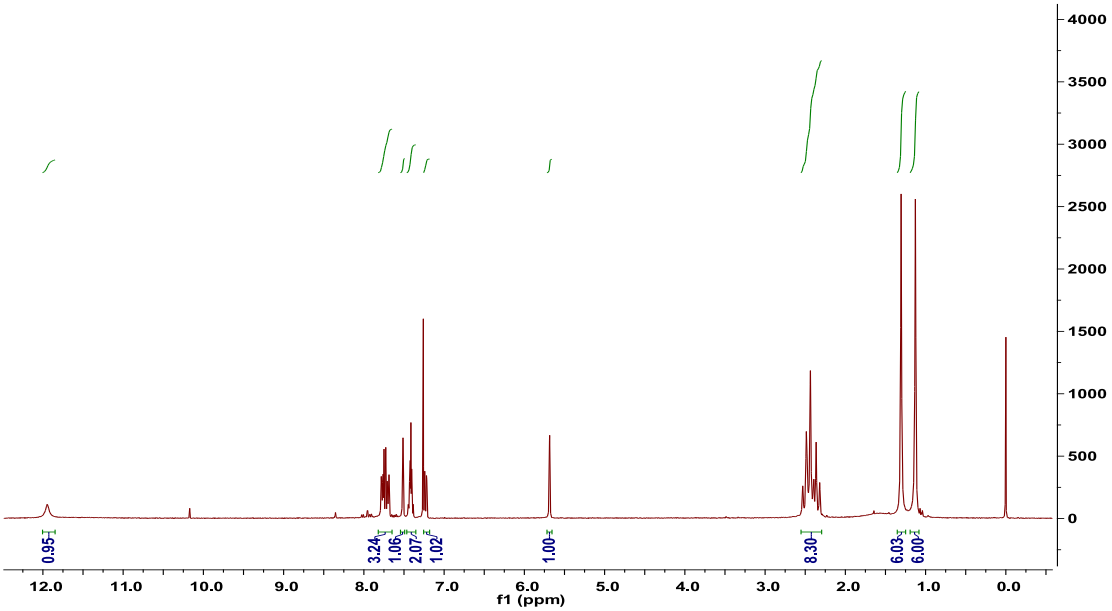

8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
0.95
1.94
2.02
1.00
8.34
6.23
6.09
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

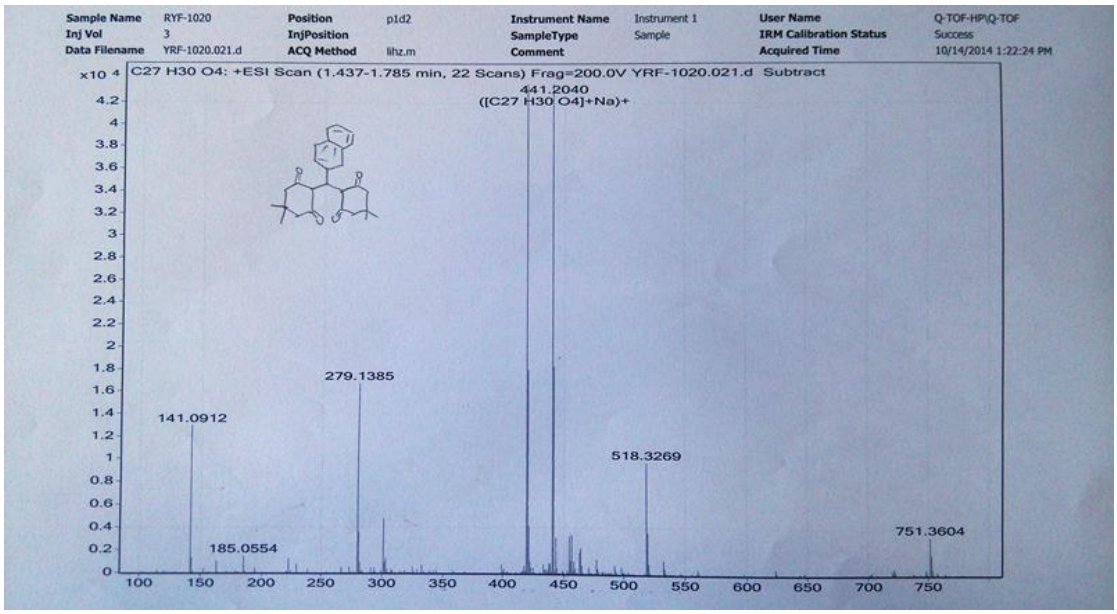

Sample Name RYF-1008
Inj Vol 2
Data Filename YRF-1008.008.d
Position p1f8
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 10/14/2014 12:40:45 PM
C23 H27 N O6: +ESI Scan (1.165-1.679 min, 32 Scans) Frag=200.0V YRF-1008.008.d Subtract
414.1914
([C23 H27 N O6]+H)+
849.3578
141.0912
185.0550
274.1078
328.1157
531.8673
598.2395
741.3002
×10 4

3p.

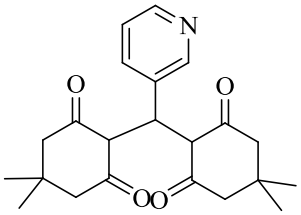

O
O
O
O

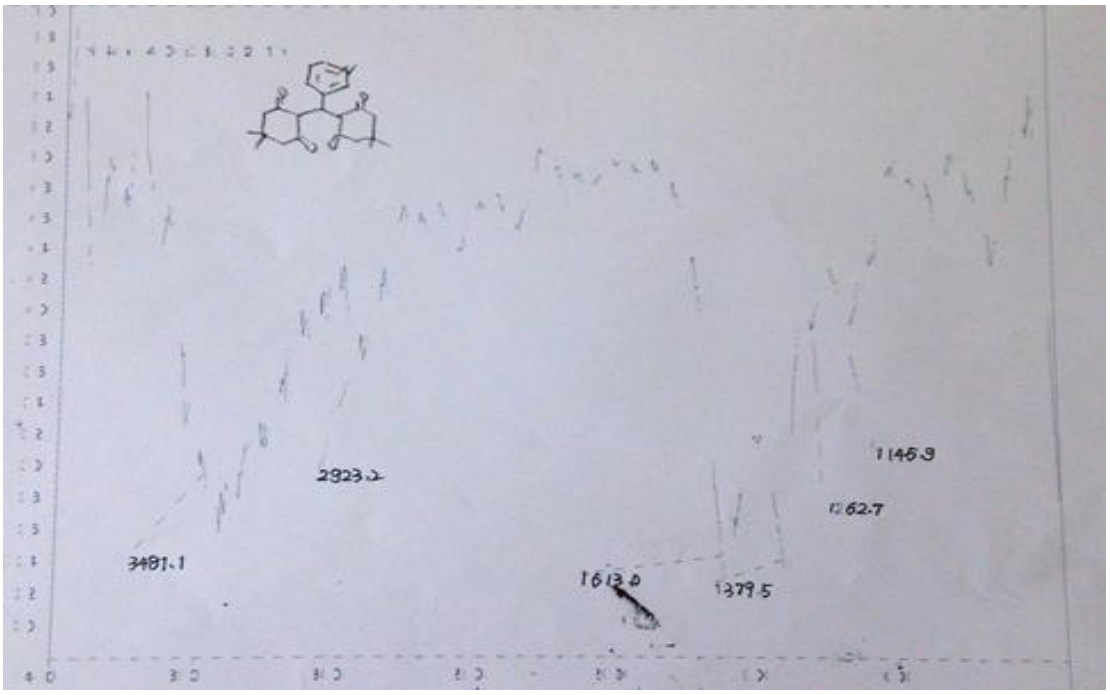

2073.5
2365.4
2971.4
2916.8
2962.2
1509.2
1392.4
1606.5
3435.7
1256.2
1152.4
1353.6

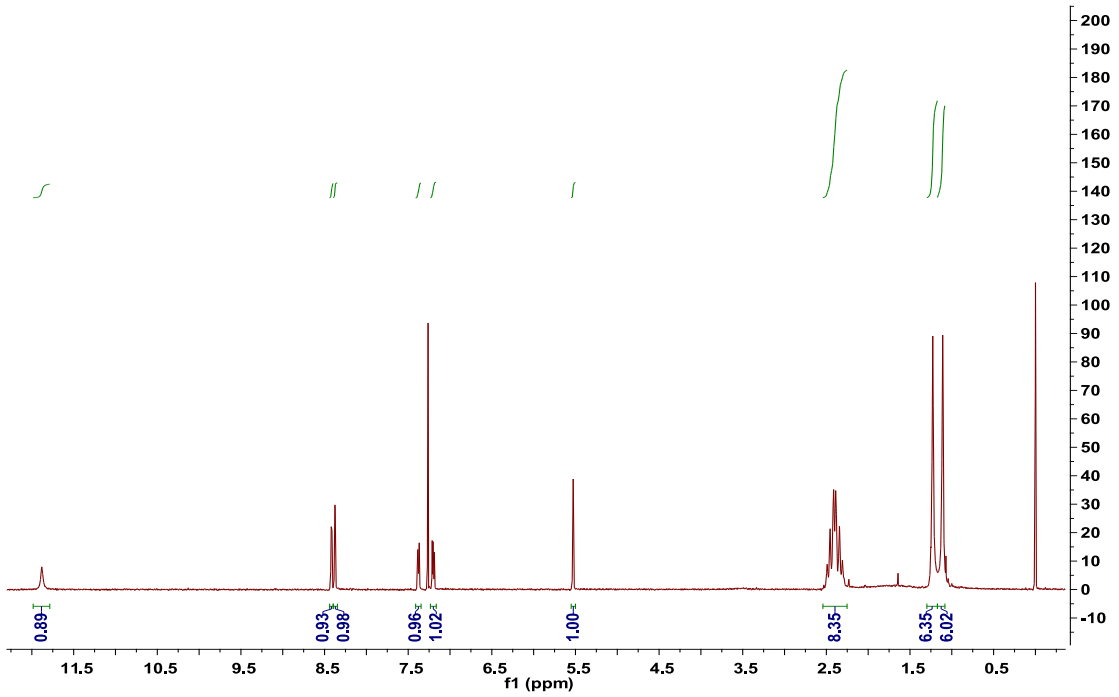

4000
3500
3000
2500
2000
1500
1000
500
0
0.95
3.24
1.06
2.07
1.02
1.00
8.30
6.03
6.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

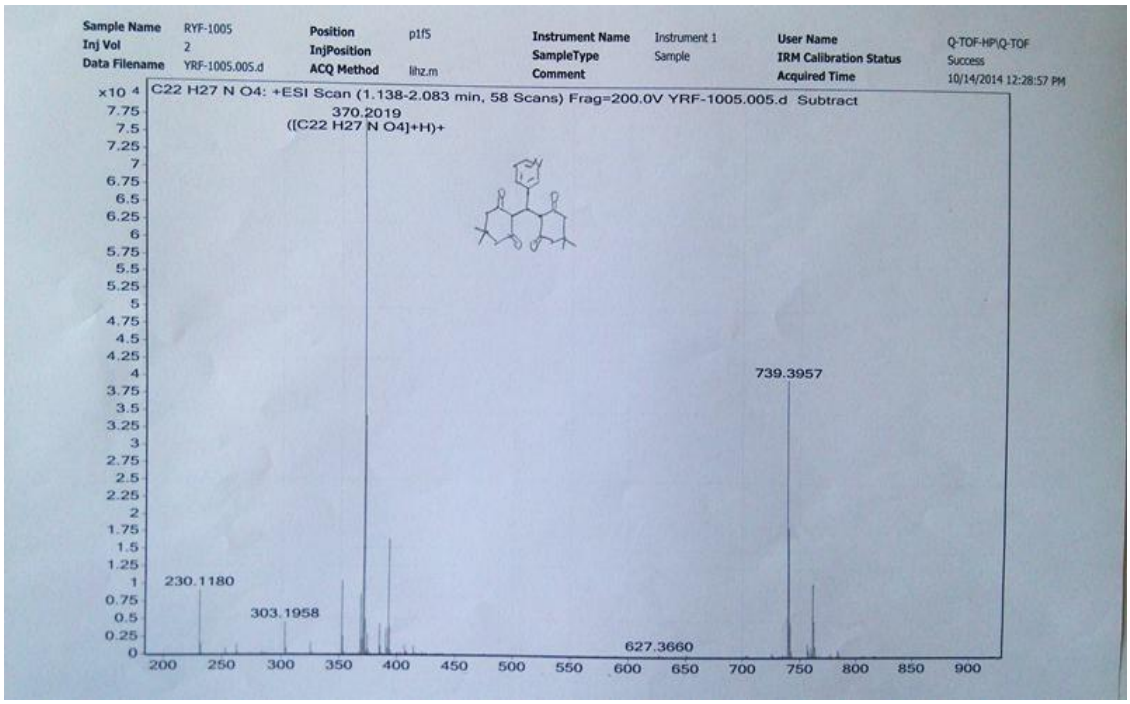

Sample Name RYF-1020
Position p1d2
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 3
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename YRF-1020.021.d
ACQ Method lihz.m
Comment
Acquired Time 10/14/2014 1:22:24 PM
C27 H30 O4: +ESI Scan (1.437-1.785 min, 22 Scans) Frag=200.0V YRF-1020.021.d Subtract
x10 4
441.2040
([C27 H30 O4]+Na)+
279.1385
141.0912
518.3269
751.3604
185.0554

3q.

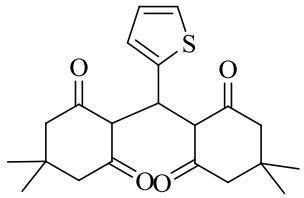

N
O
O
O
O

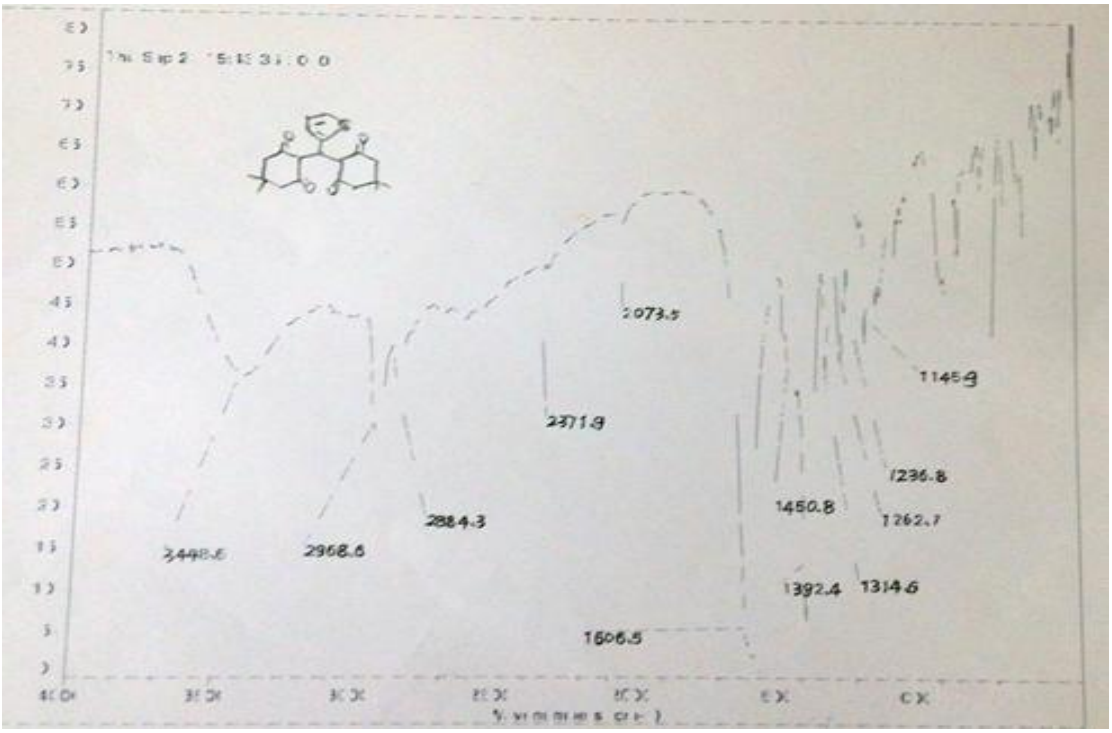

2923.2
1145.9
1062.7
3481.1
1613.0
1379.5

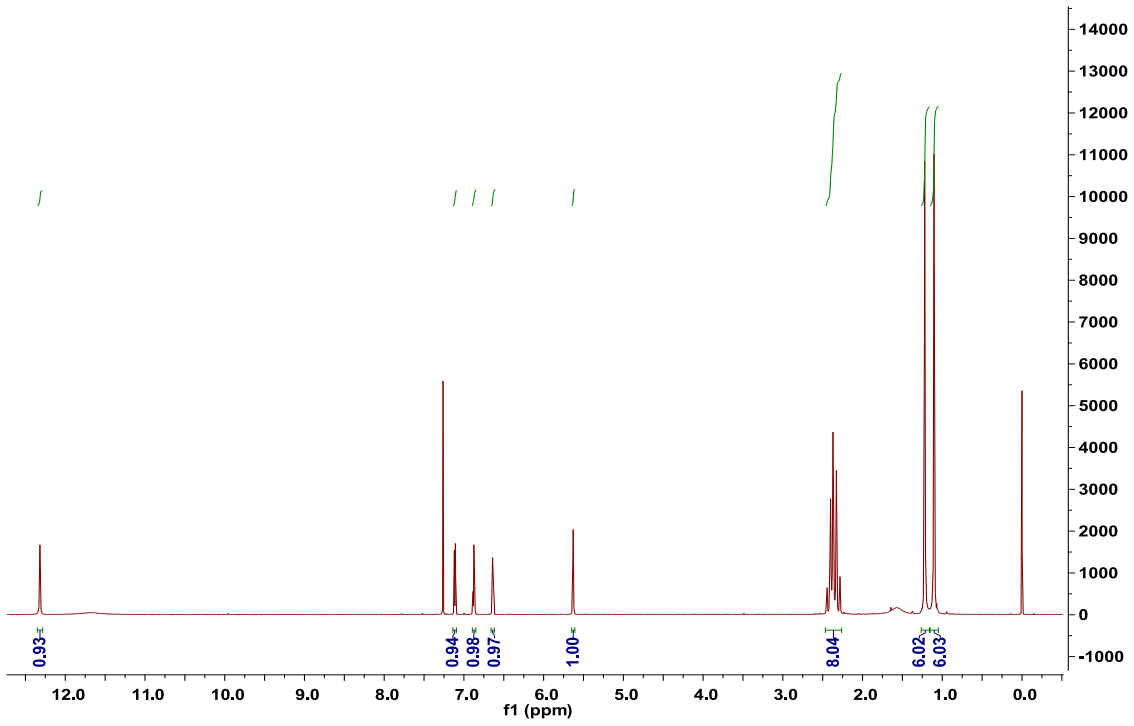

0.89
0.93
0.98
0.96
1.02
1.00
8.35
6.35
6.02
f1 (ppm)

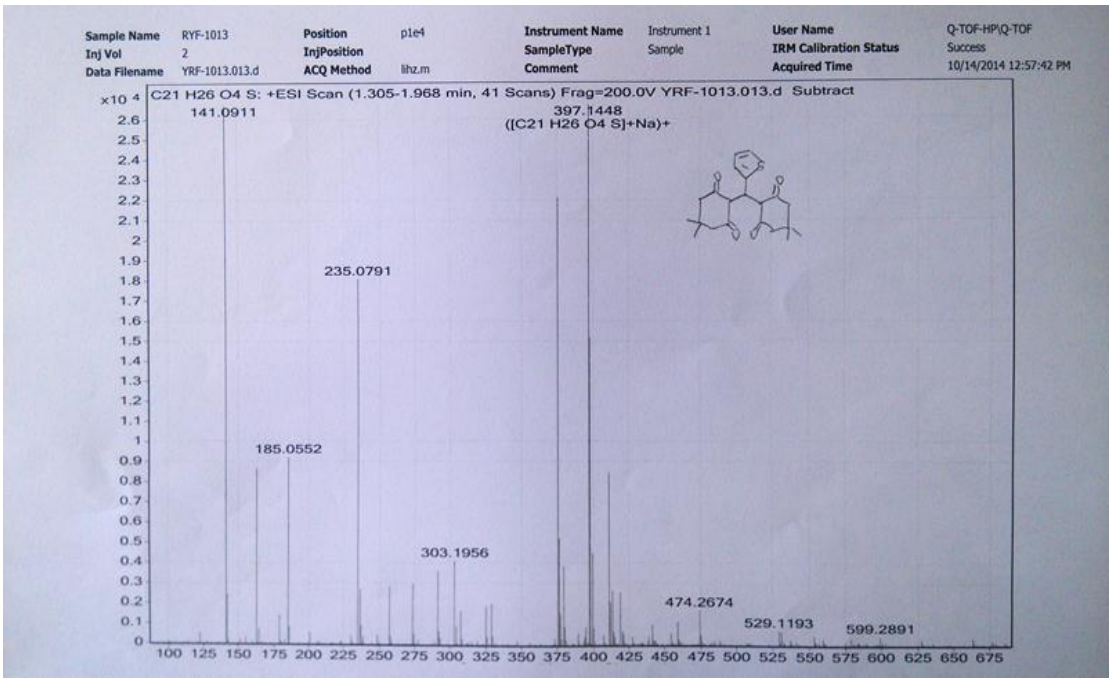

Sample Name RYF-1005
Inj Vol 2
Data Filename YRF-1005.005.d
Position p1f5
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 10/14/2014 12:28:57 PM
C22 H27 N O4: +ESI Scan (1.138-2.083 min, 58 Scans) Frag=200.0V YRF-1005.005.d Subtract
370.2019
([C22 H27 N O4]+H)+
739.3957
230.1180
303.1958
627.3660
x10 4

3r.

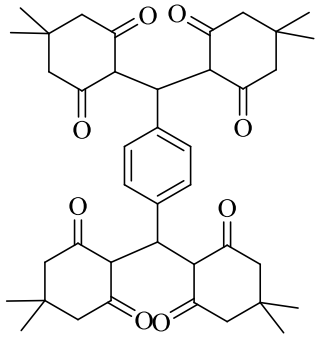

S
O
O
O
O

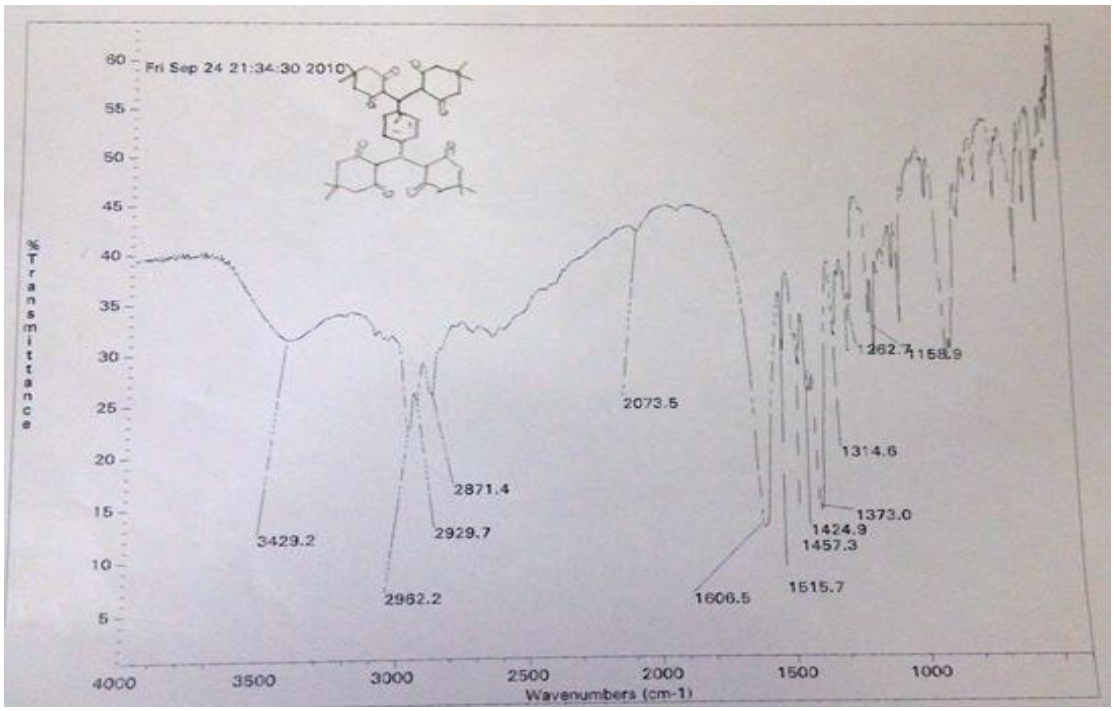

2073.5
1145.9
2871.9
1236.8
1450.8
1262.7
2884.3
3448.6
2968.6
1392.4
1314.6
1606.5

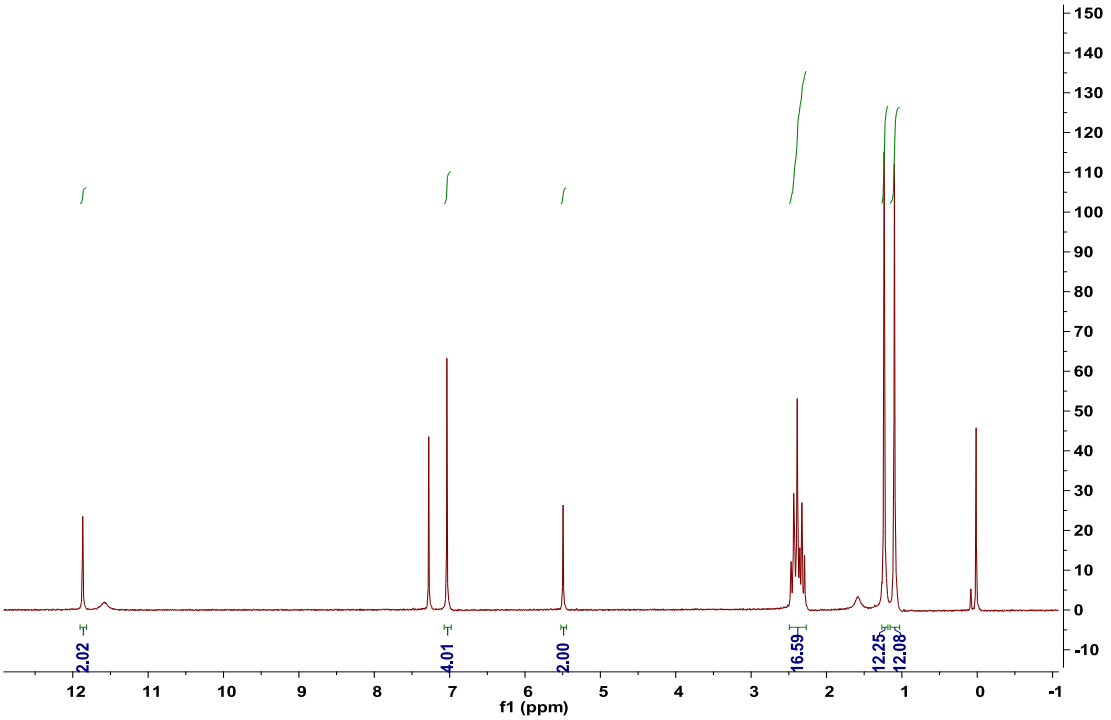

14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
0.93
0.94
0.98
0.97
1.00
8.04
6.02
6.03
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

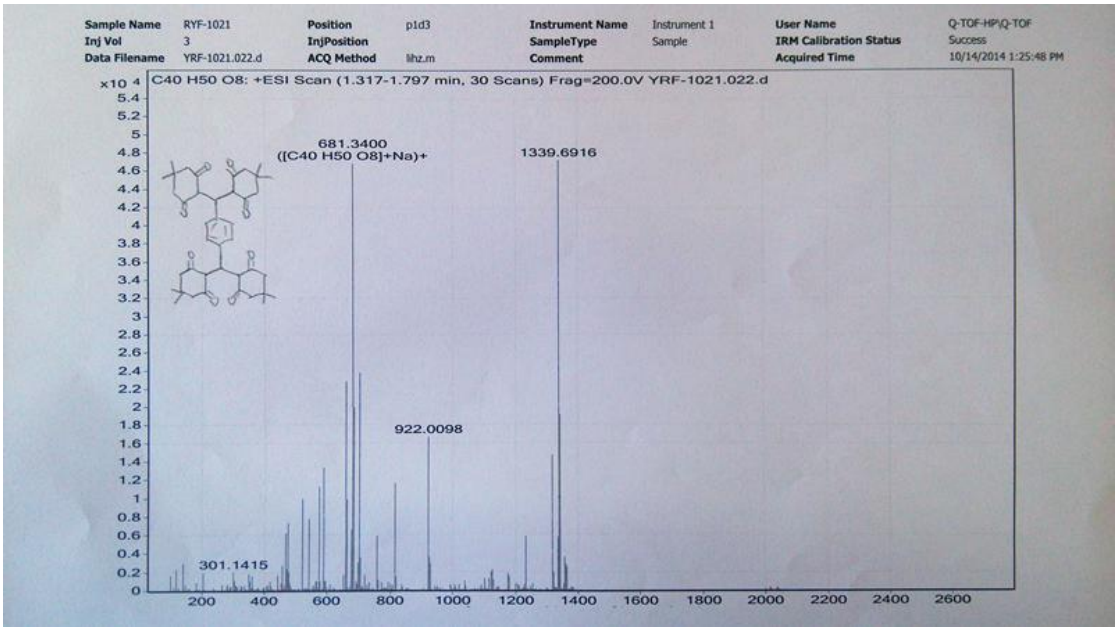

Sample Name RYF-1013
Inj Vol 2
Data Filename YRF-1013.013.d
Position p1e4
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 10/14/2014 12:57:42 PM
C21 H26 O4 S: +ESI Scan (1.305-1.968 min, 41 Scans) Frag=200.0V YRF-1013.013.d Subtract
x10 4
141.0911
397.1448
([C21 H26 O4 S]+Na)+
235.0791
185.0552
303.1956
474.2674
529.1193
599.2891

3s.

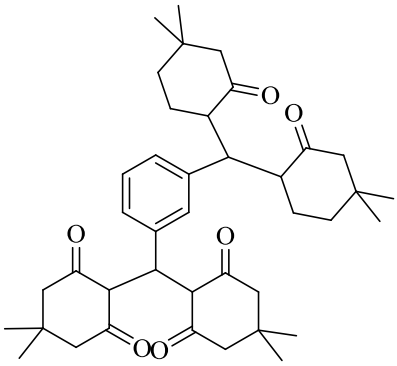


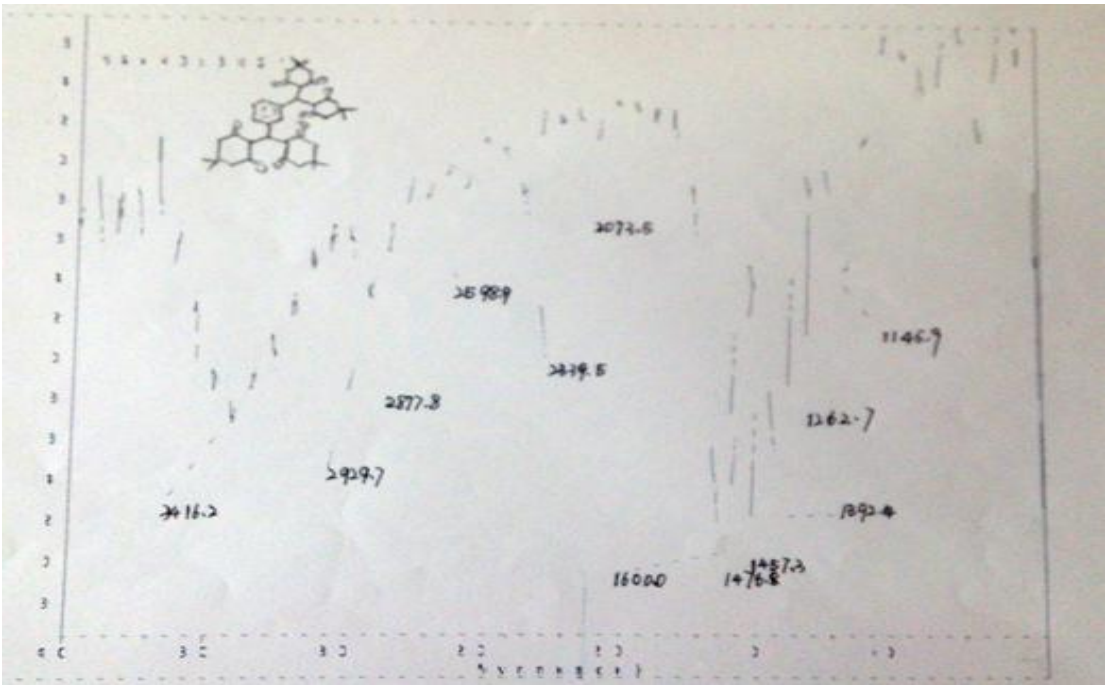

Fri Sep 24 21:34:30 2010
%Transmittance
60
55
50
45
40
35
30
25
20
15
10
5
4000
3500
3000
2500
2000
1500
1000
Wavenumbers (cm-1)
3429.2
2962.2
2929.7
2871.4
2073.5
1606.5
1515.7
1457.3
1424.9
1373.0
1314.6
1262.7
1158.9

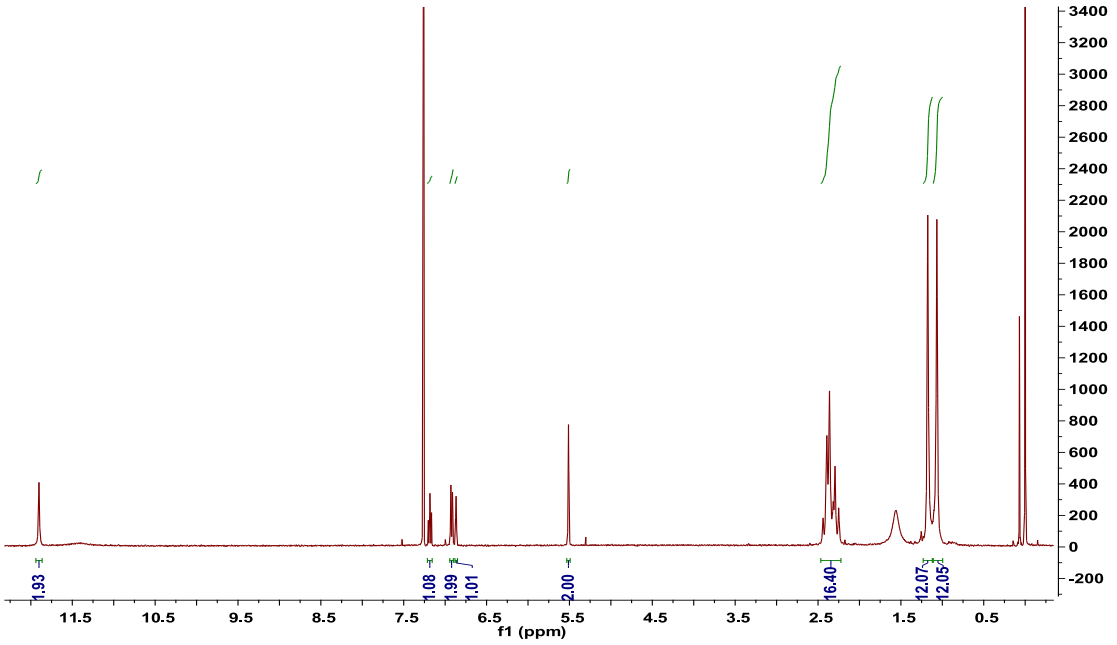

2.02
4.01
2.00
16.59
12.25
12.08
f1 (ppm)

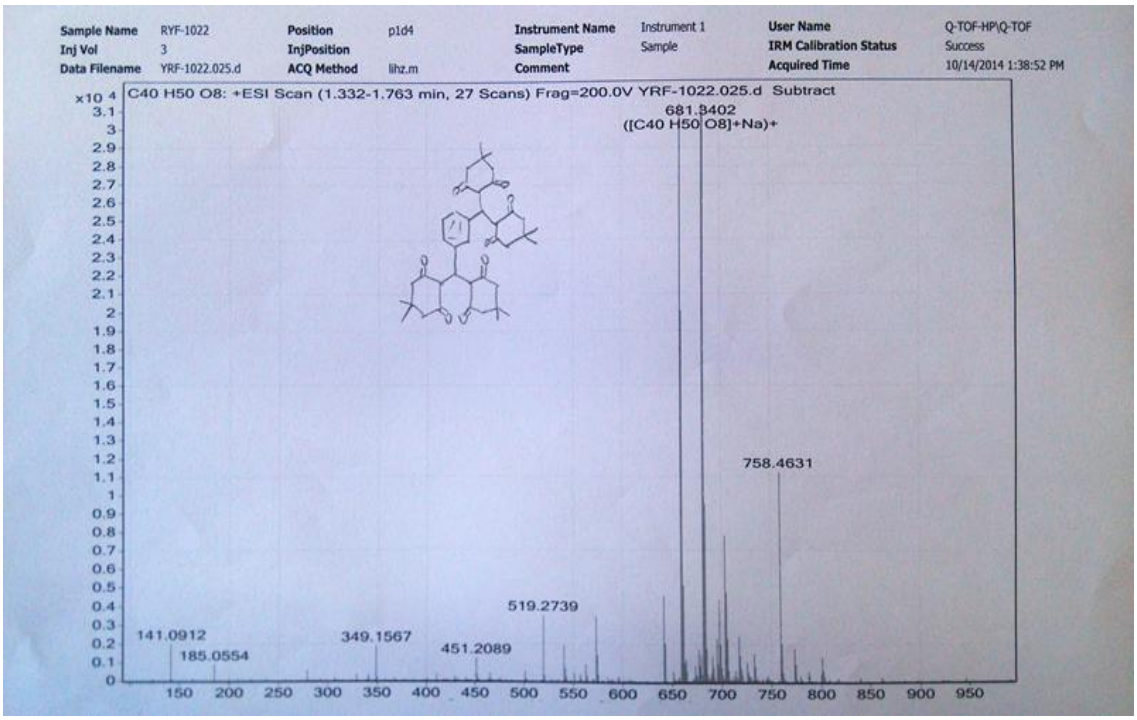

Sample Name RYF-1021
Inj Vol 3
Data Filename YRF-1021.022.d
Position p1d3
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name
IRM Calibration Status Success
Acquired Time 10/14/2014 1:25:48 PM
C40 H50 O8: +ESI Scan (1.317-1.797 min, 30 Scans) Frag=200.0V YRF-1021.022.d
681.3400
([C40 H50 O8]+Na)+
1339.6916
922.0098
301.1415

3t.

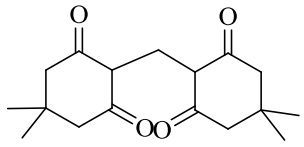


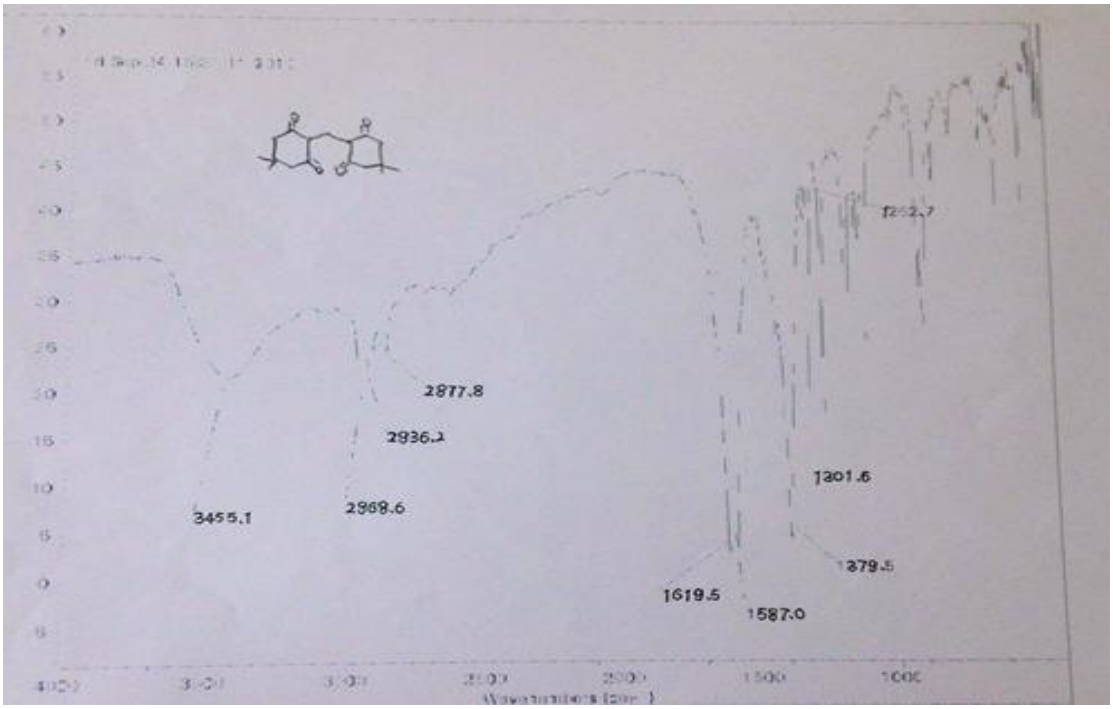


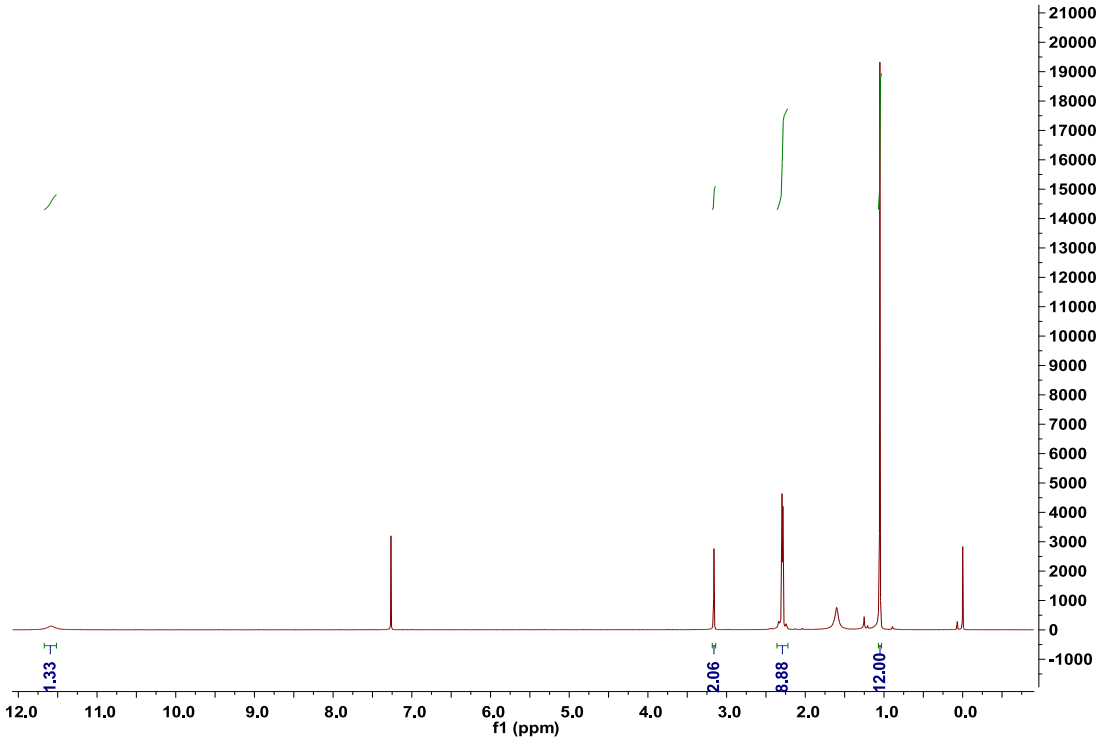

1.93
1.08
1.99
1.01
2.00
16.40
12.07
12.05
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

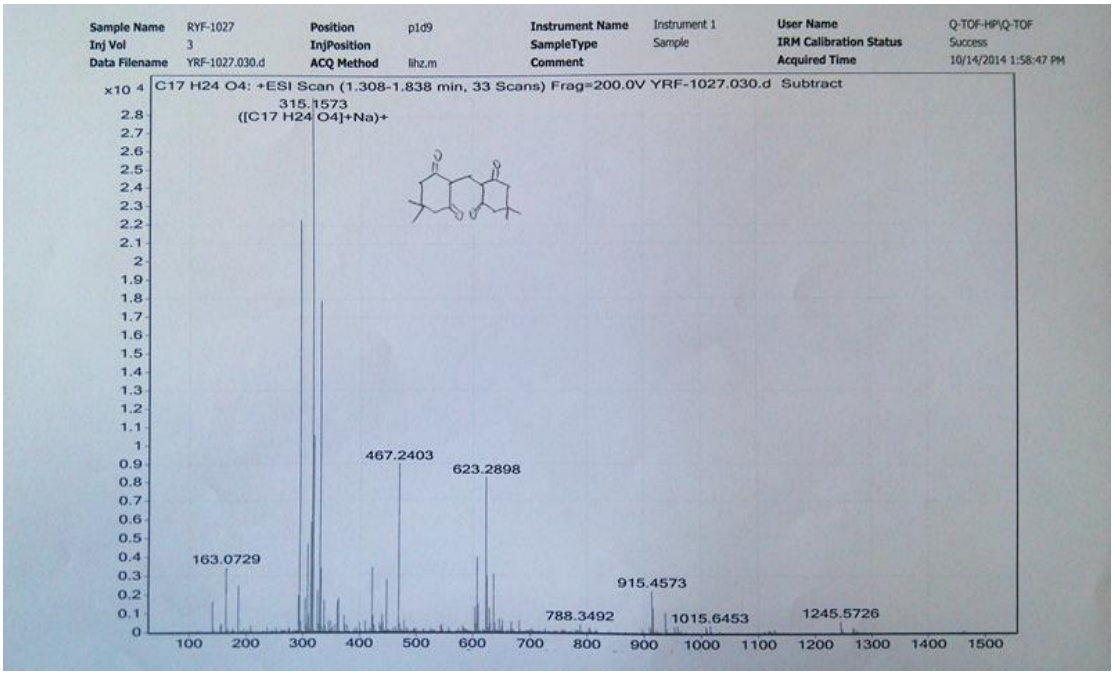

Sample Name RYF-1022
Position p1d4
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 3
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename YRF-1022.025.d
ACQ Method lihz.m
Comment
Acquired Time 10/14/2014 1:38:52 PM
C40 H50 O8: +ESI Scan (1.332-1.763 min, 27 Scans) Frag=200.0V YRF-1022.025.d Subtract
x10 4
681.3402
([C40 H50 O8]+Na)+
758.4631
519.2739
141.0912
185.0554
349.1567
451.2089

3u.

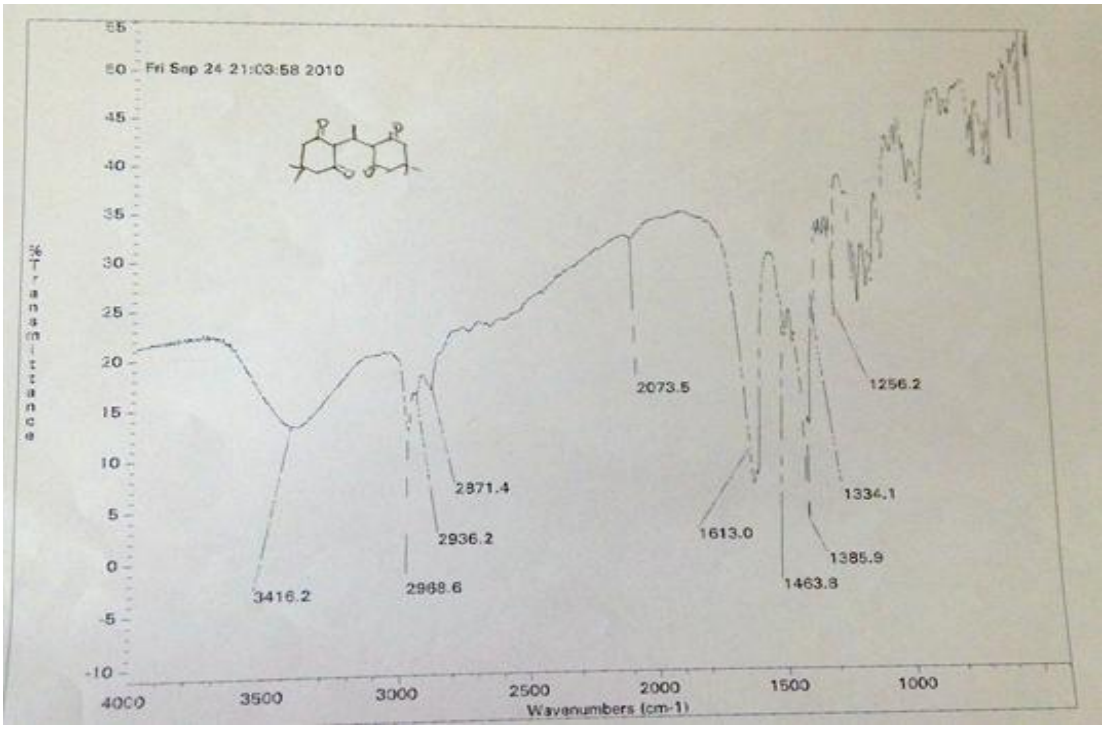


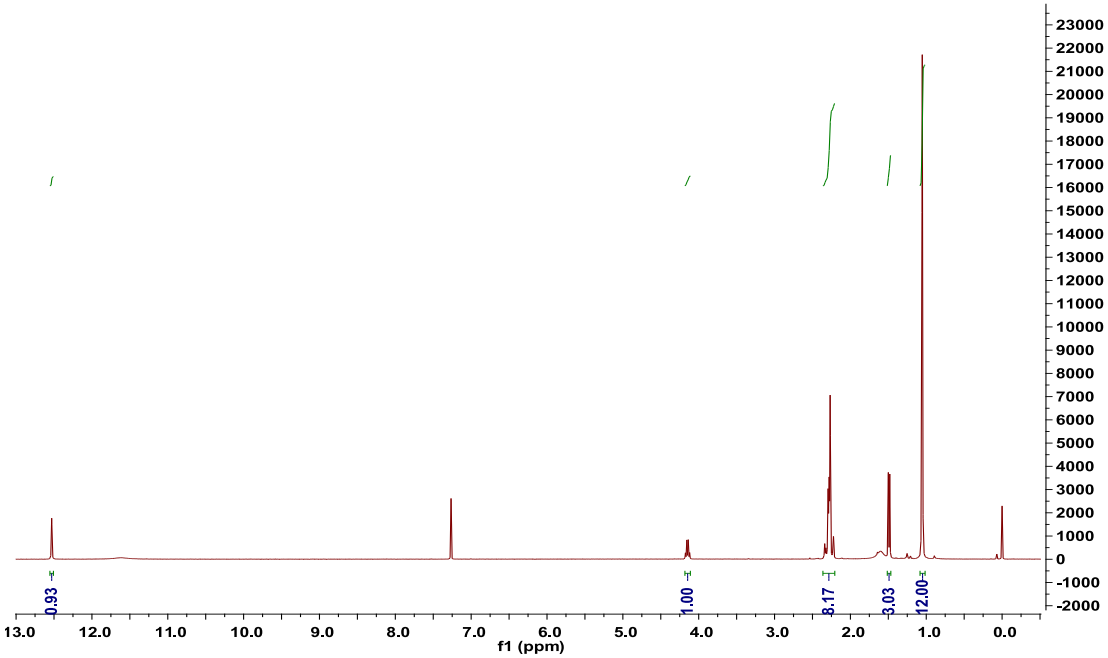

2877.8
2936.2
3455.1
2968.6
1619.5
1587.0
1379.5

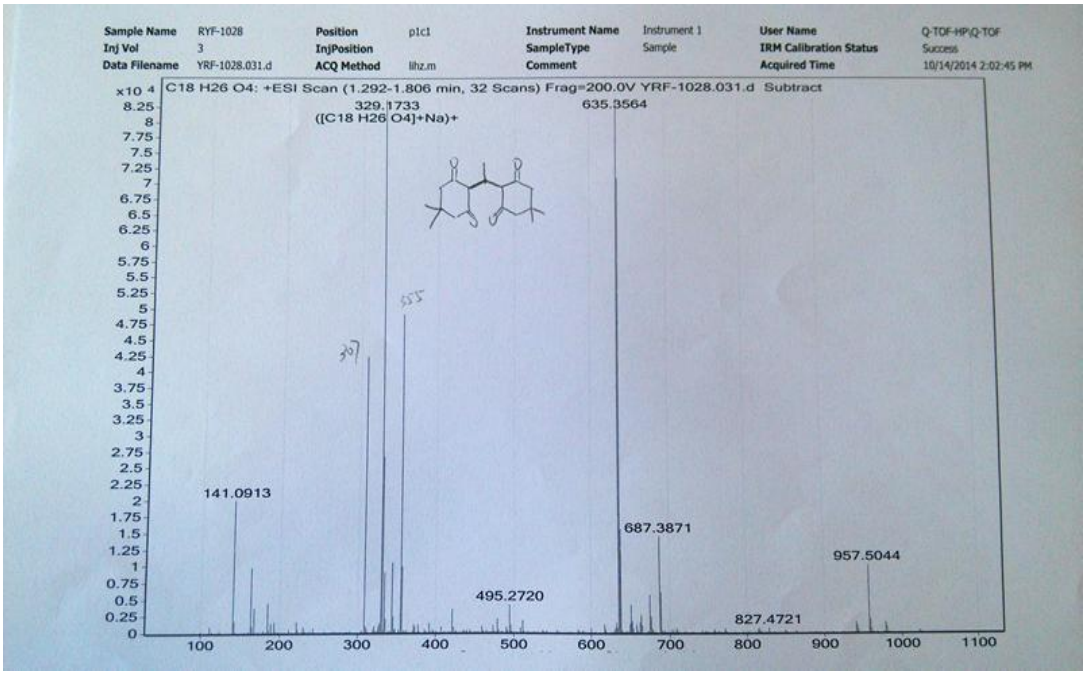

1.33
2.06
8.88
12.00
f1 (ppm)


Sample Name RYF-1027
Position p1d9
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 3
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename YRF-1027.030.d
ACQ Method lihz.m
Comment
Acquired Time 10/14/2014 1:58:47 PM
C17 H24 O4: +ESI Scan (1.308-1.838 min, 33 Scans) Frag=200.0V YRF-1027.030.d Subtract
x10 4
315.1573
([C17 H24 O4]+Na)+
467.2403
623.2898
163.0729
915.4573
788.3492
1015.6453
1245.5726

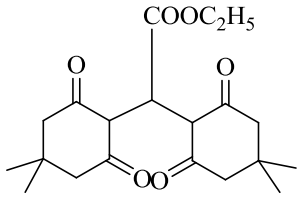
3v.

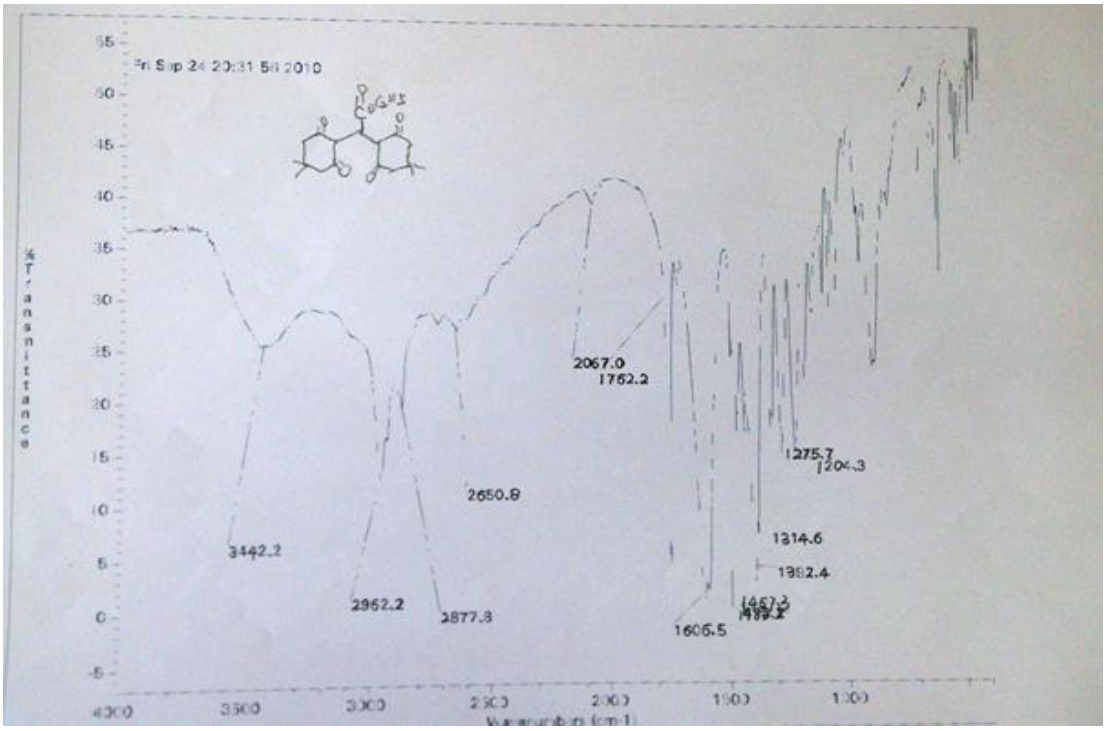

Fri Sep 24 21:03:58 2010
%Transmittance
3416.2
2968.6
2936.2
2871.4
2073.5
1613.0
1463.8
1385.9
1334.1
1256.2
Wavenumbers (cm-1)

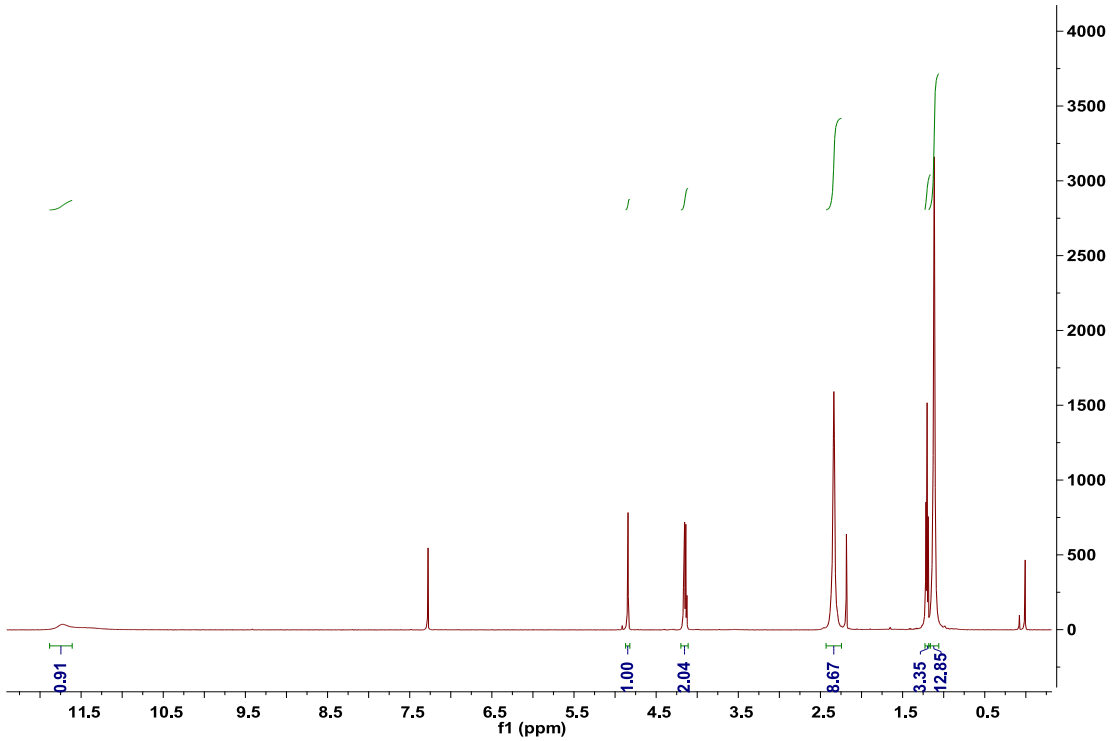

0.93
1.00
8.17
3.03
12.00
f1 (ppm)

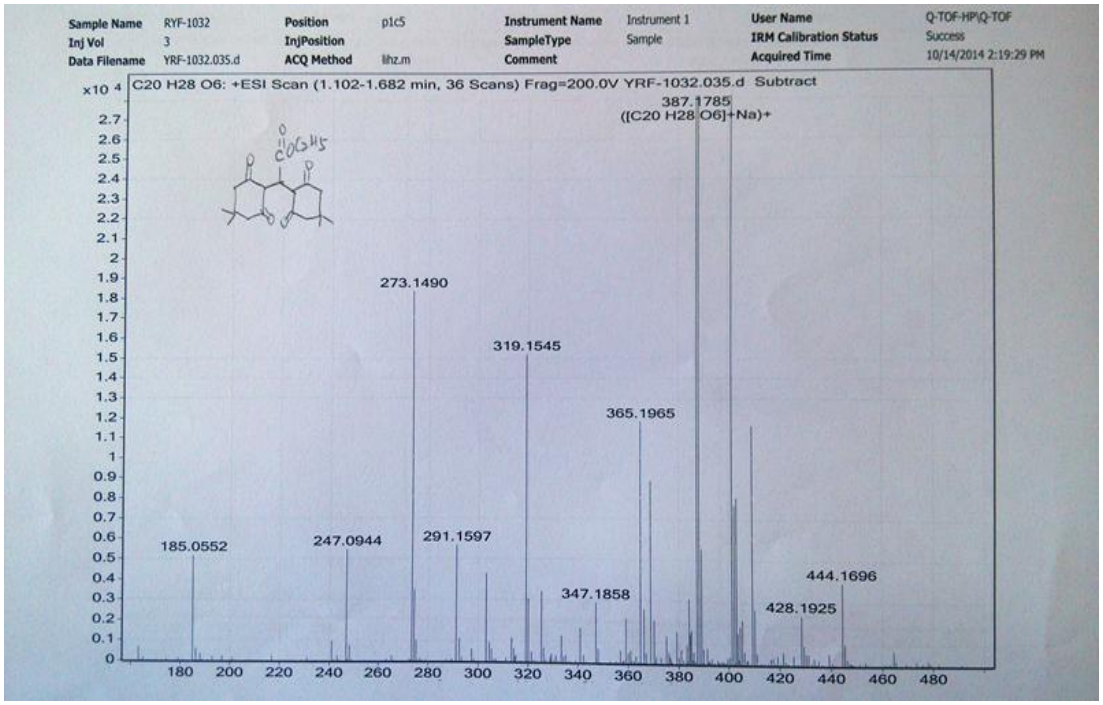

Sample Name RYF-1028
Position p1c1
Instrument Name Instrument 1
User Name Q-TOF-HP/Q-TOF
Inj Vol 3
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename YRF-1028.031.d
ACQ Method lihz.m
Comment
Acquired Time 10/14/2014 2:02:45 PM
C18 H26 O4: +ESI Scan (1.292-1.806 min, 32 Scans) Frag=200.0V YRF-1028.031.d Subtract
x10 4
329.1733
([C18 H26 O4]+Na)+
635.3564
141.0913
687.3871
957.5044
495.2720
827.4721

3w.

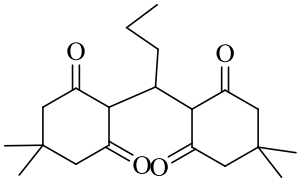

COOC2H5
O
O
O
O

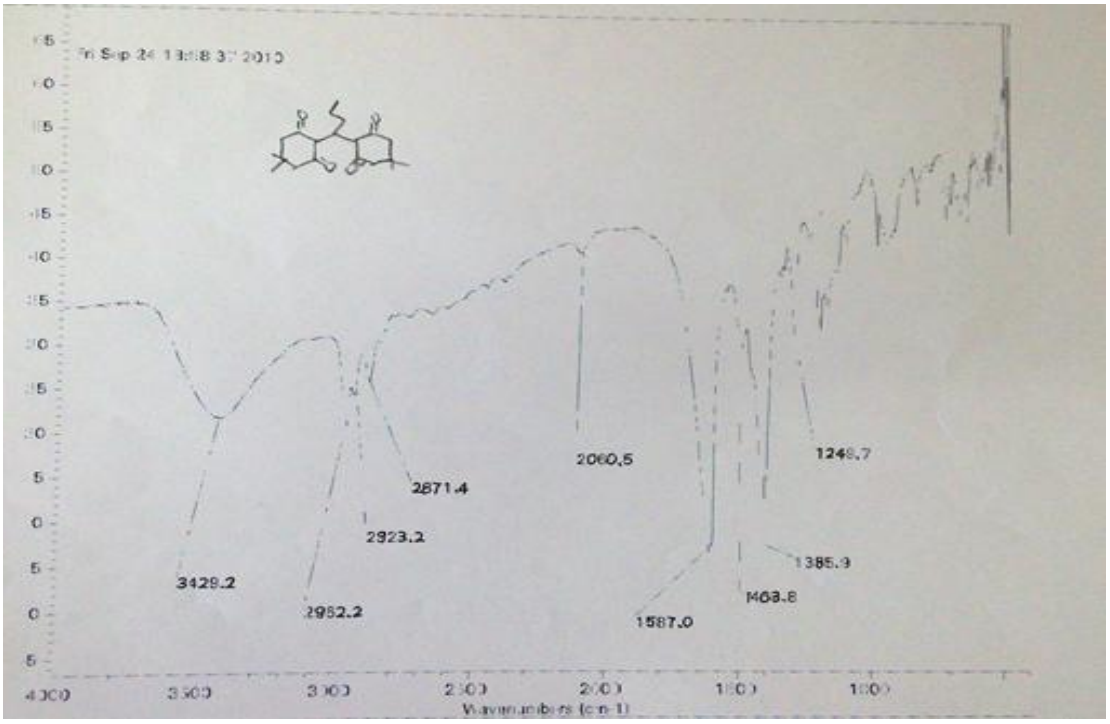

Fri Sep 24 20:31:58 2010
%Transmittance
3442.2
2962.2
2877.3
2650.8
2067.0
1762.2
1606.5
1314.6
1382.4
1275.7
1204.3

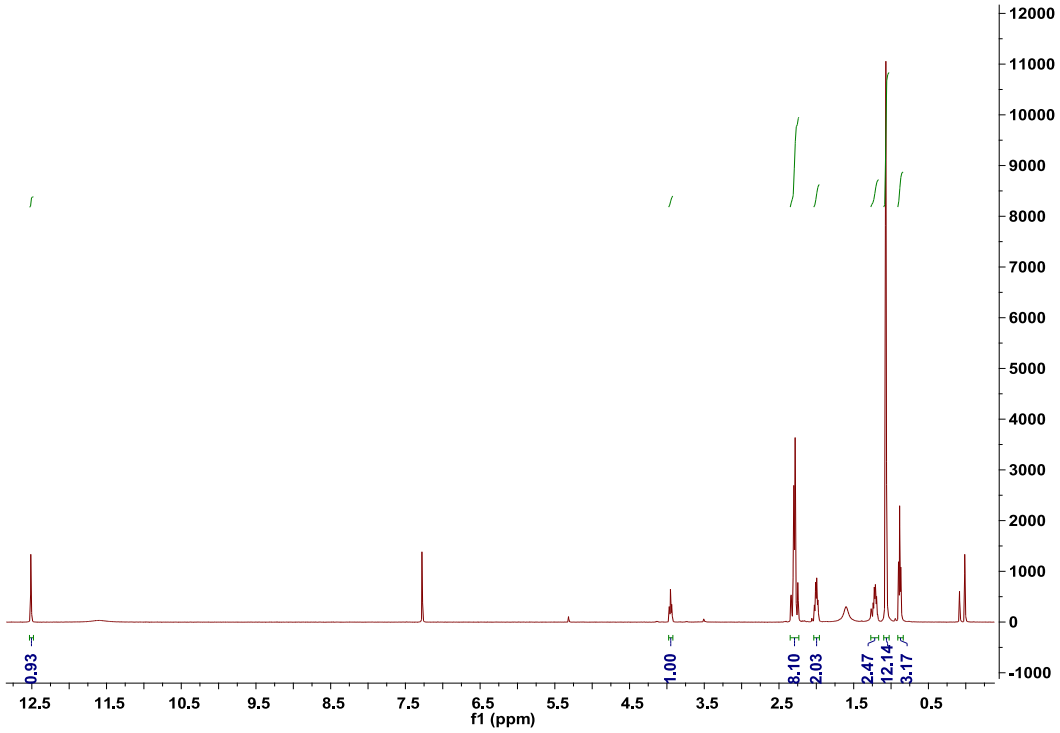

4000
3500
3000
2500
2000
1500
1000
500
0
0.91
1.00
2.04
8.67
3.35
12.85
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

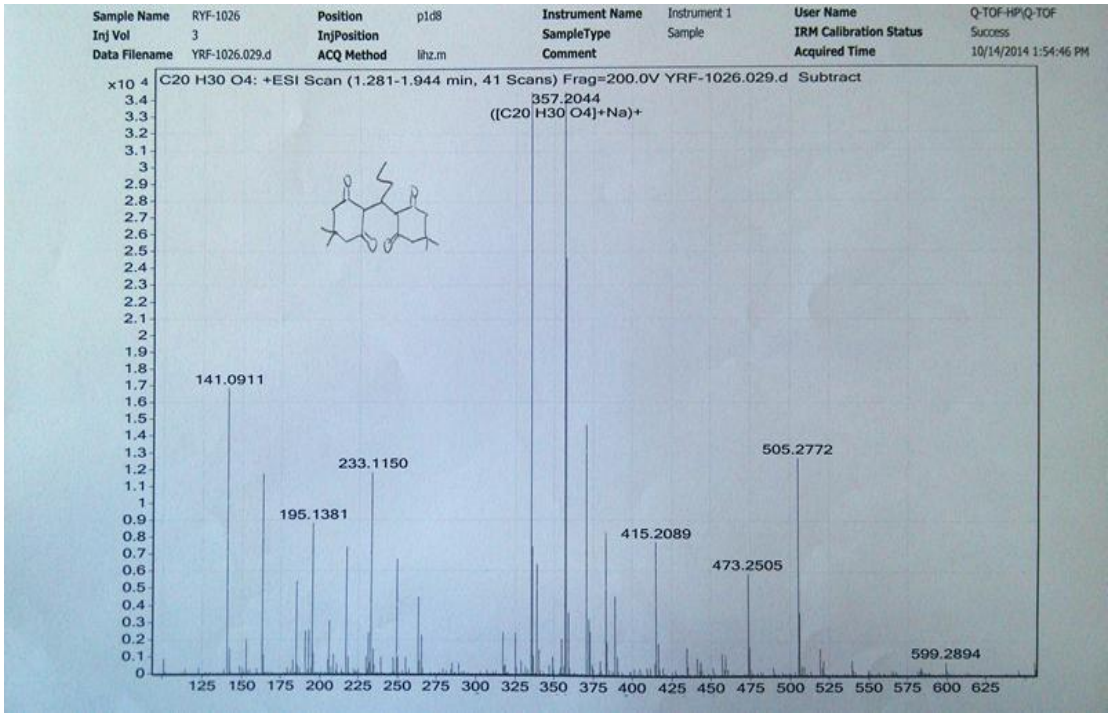

Sample Name RYF-1032
Position p1c5
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 3
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename YRF-1032.035.d
ACQ Method lihz.m
Comment
Acquired Time 10/14/2014 2:19:29 PM
C20 H28 O6: +ESI Scan (1.102-1.682 min, 36 Scans) Frag=200.0V YRF-1032.035.d Subtract
x10 4
387.1785
([C20 H28 O6]+Na)+
273.1490
319.1545
365.1965
185.0552
247.0944
291.1597
347.1858
428.1925
444.1696

3x.

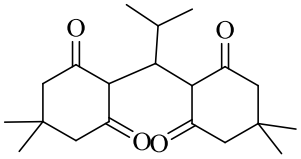

O
O
O
O

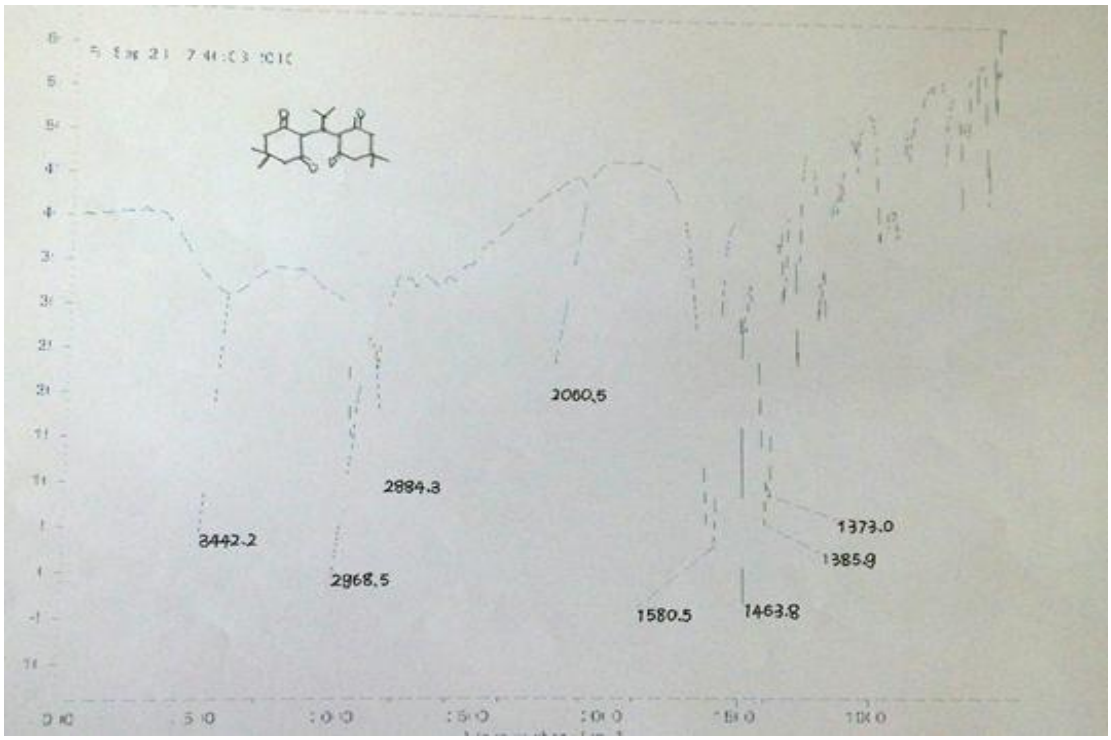

3429.2
2952.2
2923.2
2871.4
2060.5
1587.0
1463.8
1385.9
1248.7

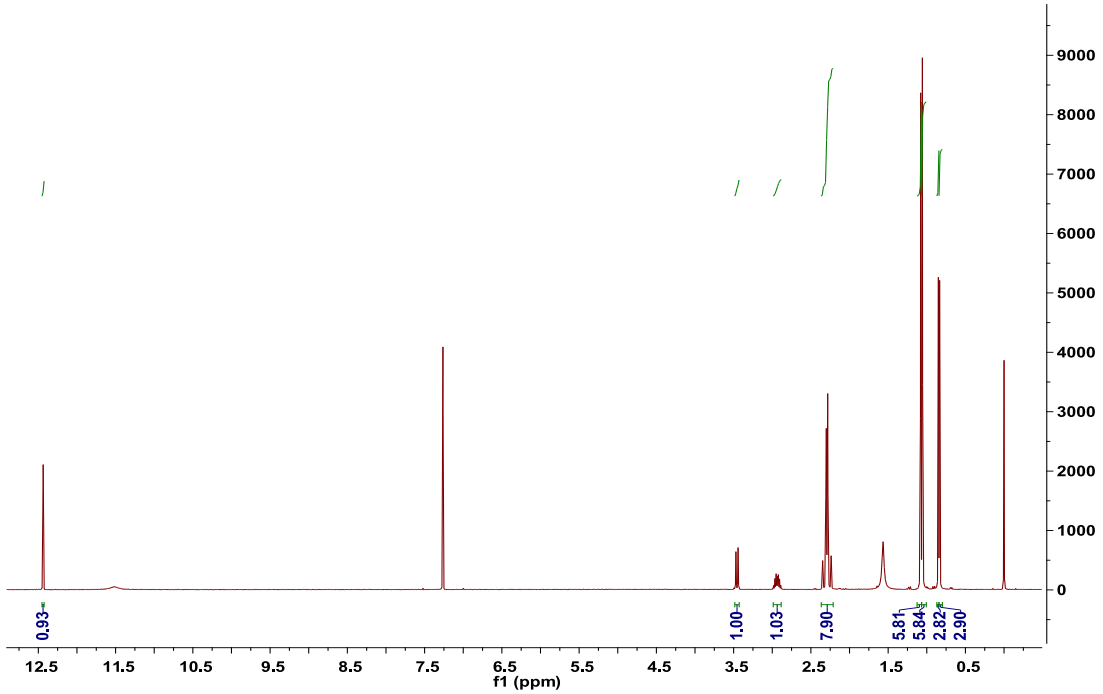

0.93
1.00
8.10
2.03
2.47
12.14
3.17
f1 (ppm)

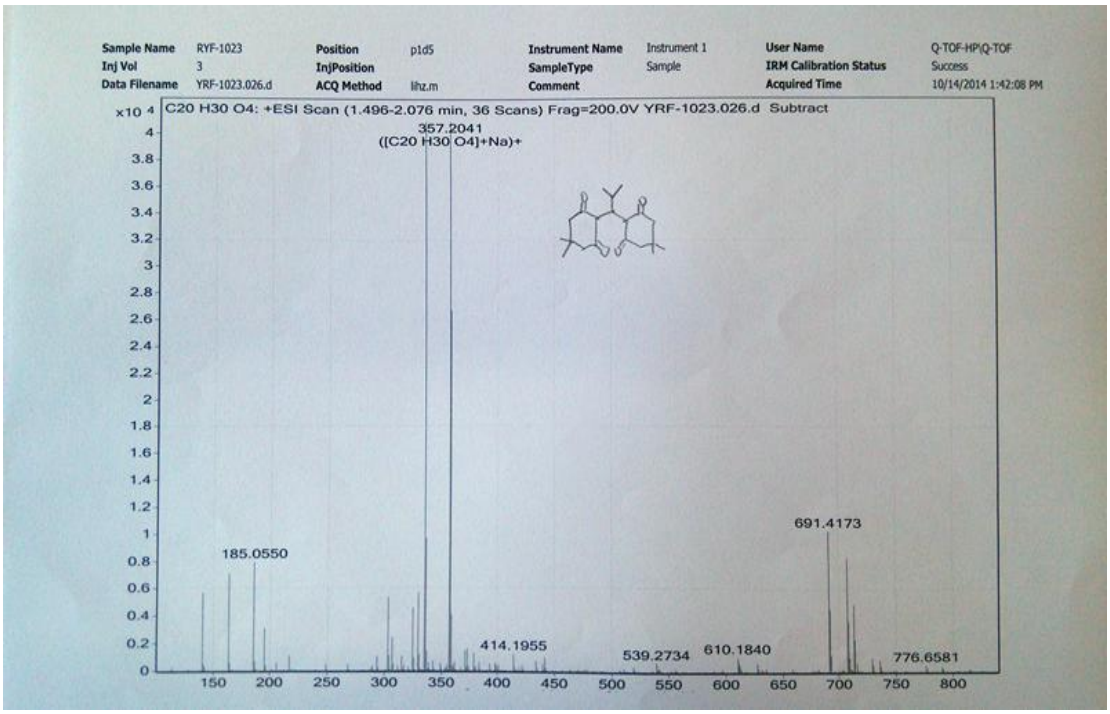

Sample Name RYF-1026
Position p1d8
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 3
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename YRF-1026.029.d
ACQ Method lihz.m
Comment
Acquired Time 10/14/2014 1:54:46 PM
C20 H30 O4: +ESI Scan (1.281-1.944 min, 41 Scans) Frag=200.0V YRF-1026.029.d Subtract
x10 4
357.2044
([C20 H30 O4]+Na)+
141.0911
233.1150
195.1381
415.2089
473.2505
505.2772
599.2894

3y.

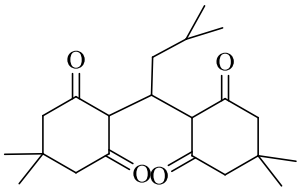

O
O
O
O

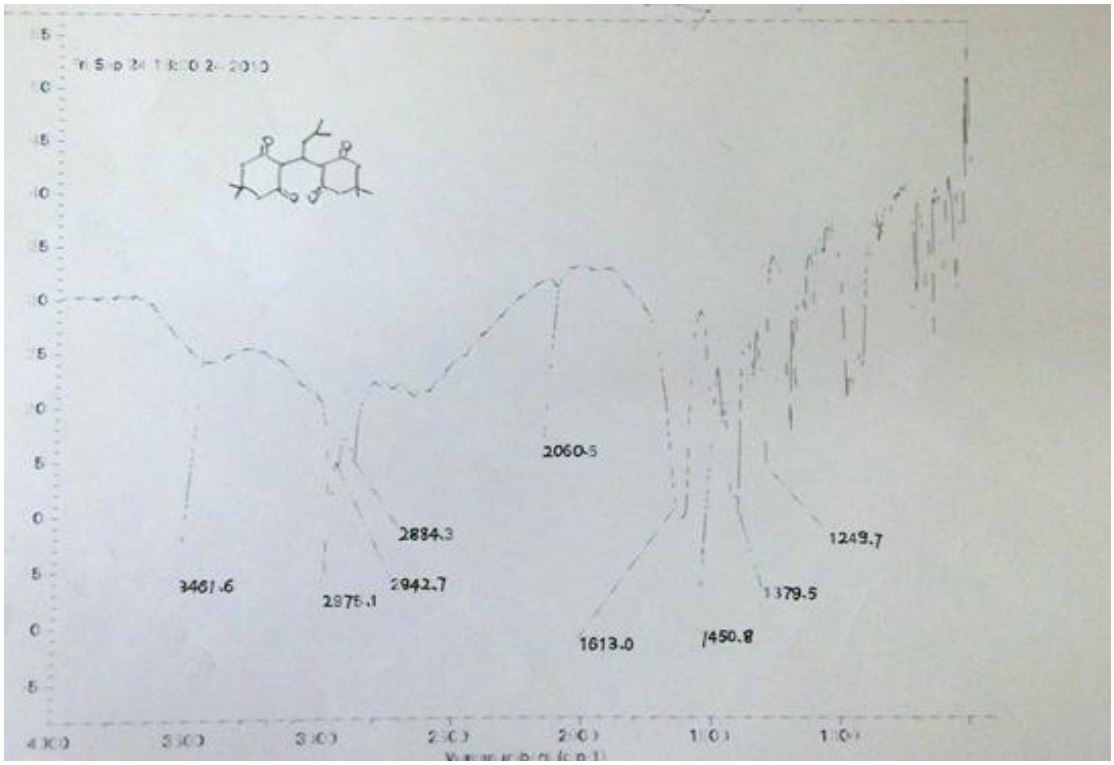

2060.5
2884.3
3442.2
2968.5
1373.0
1385.9
1580.5
1463.8

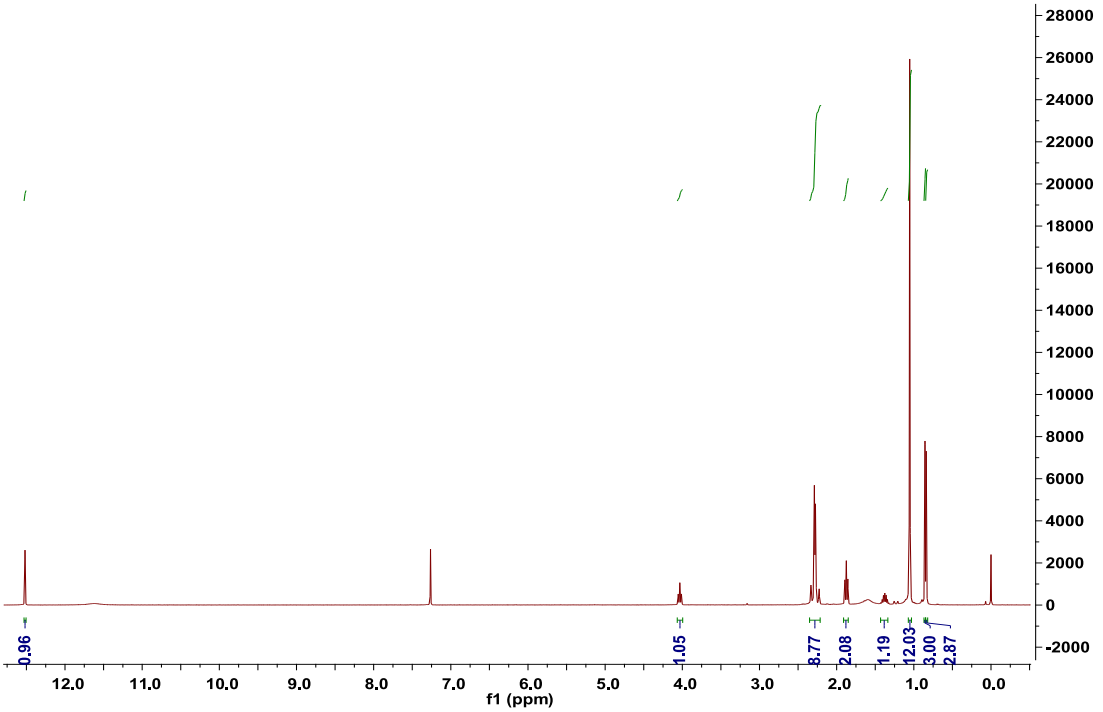

9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0.93
1.00
1.03
7.90
5.81
5.84
2.82
2.90
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

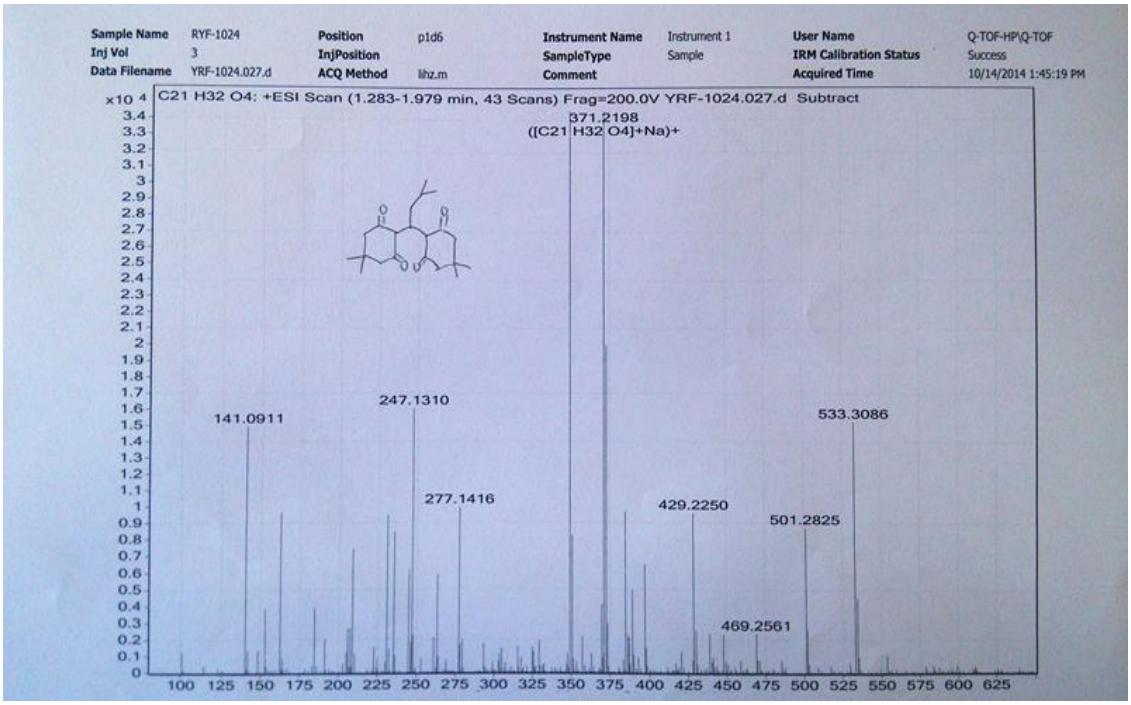

Sample Name RYF-1023
Position p1d5
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 3
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename YRF-1023.026.d
ACQ Method lihz.m
Comment
Acquired Time 10/14/2014 1:42:08 PM
C20 H30 O4: +ESI Scan (1.496-2.076 min, 36 Scans) Frag=200.0V YRF-1023.026.d Subtract
x10 4
357.2041
([C20 H30 O4]+Na)+
185.0550
414.1955
539.2734
610.1840
691.4173
776.6581

3z.

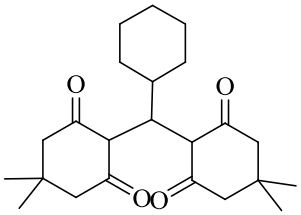


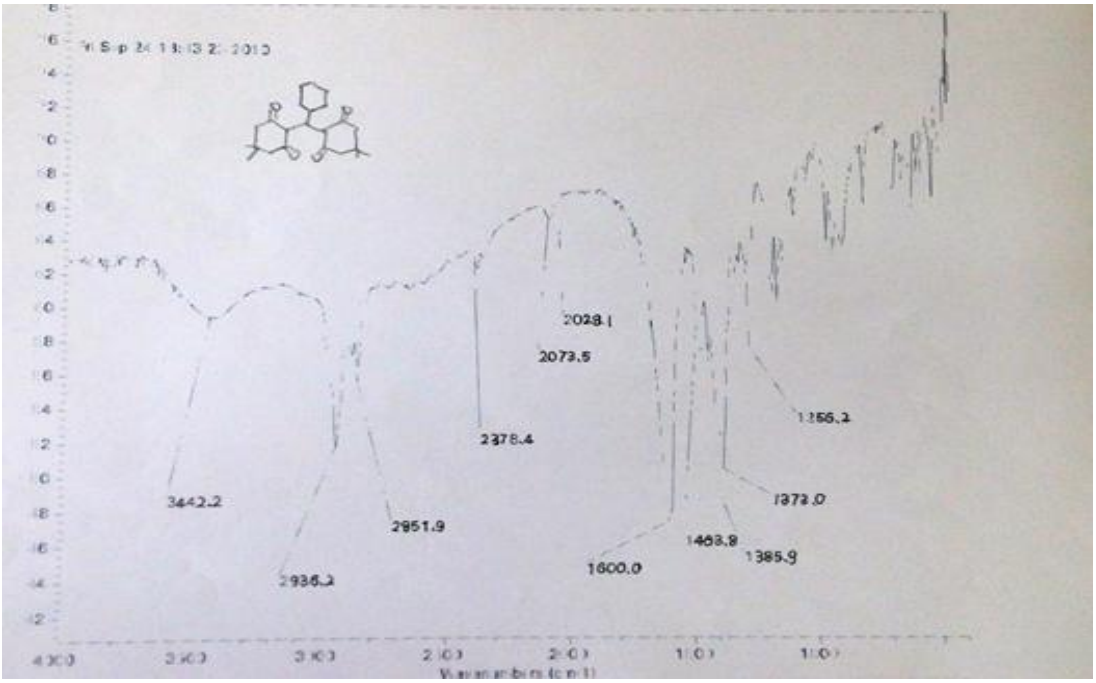

2884.3
2060.5
1249.7
3461.6
2875.1
2942.7
1379.5
1613.0
1450.8

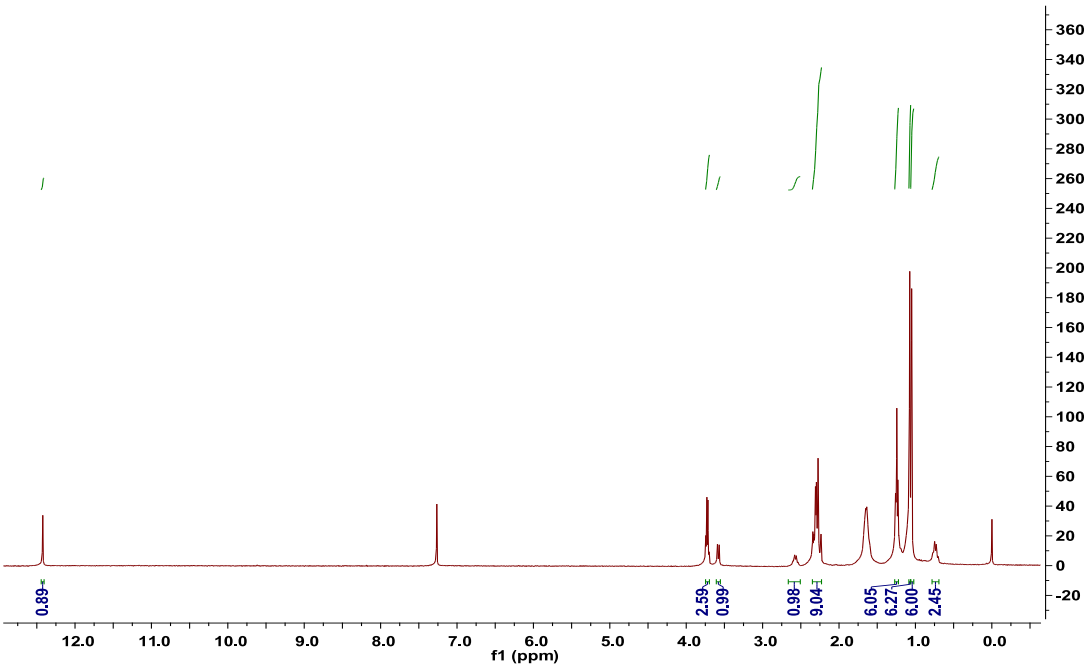

0.96
1.05
8.77
2.08
1.19
12.03
3.00
2.87
f1 (ppm)

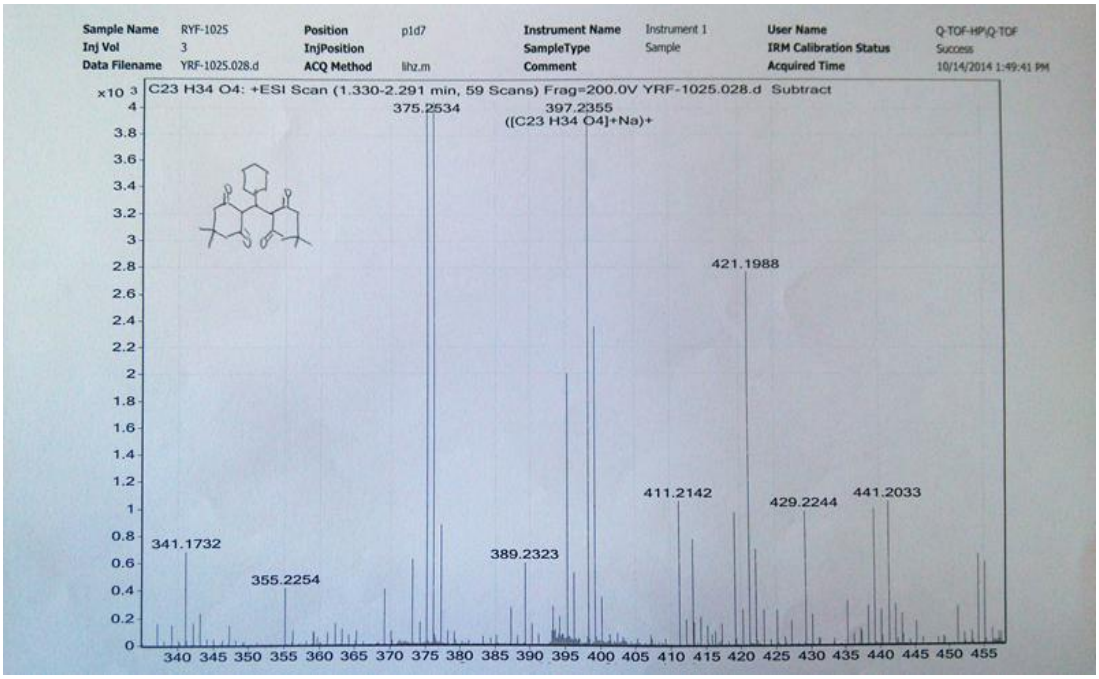

Sample Name RYF-1024
Position p1d6
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 3
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename YRF-1024.027.d
ACQ Method lihz.m
Comment
Acquired Time 10/14/2014 1:45:19 PM
C21 H32 O4: +ESI Scan (1.283-1.979 min, 43 Scans) Frag=200.0V YRF-1024.027.d Subtract
x10 4
371.2198
([C21 H32 O4]+Na)+
247.1310
141.0911
533.3086
277.1416
429.2250
501.2825
469.2561

3aa.

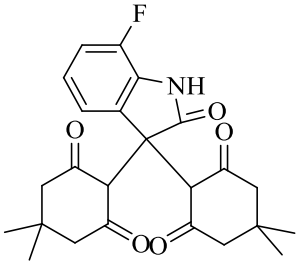


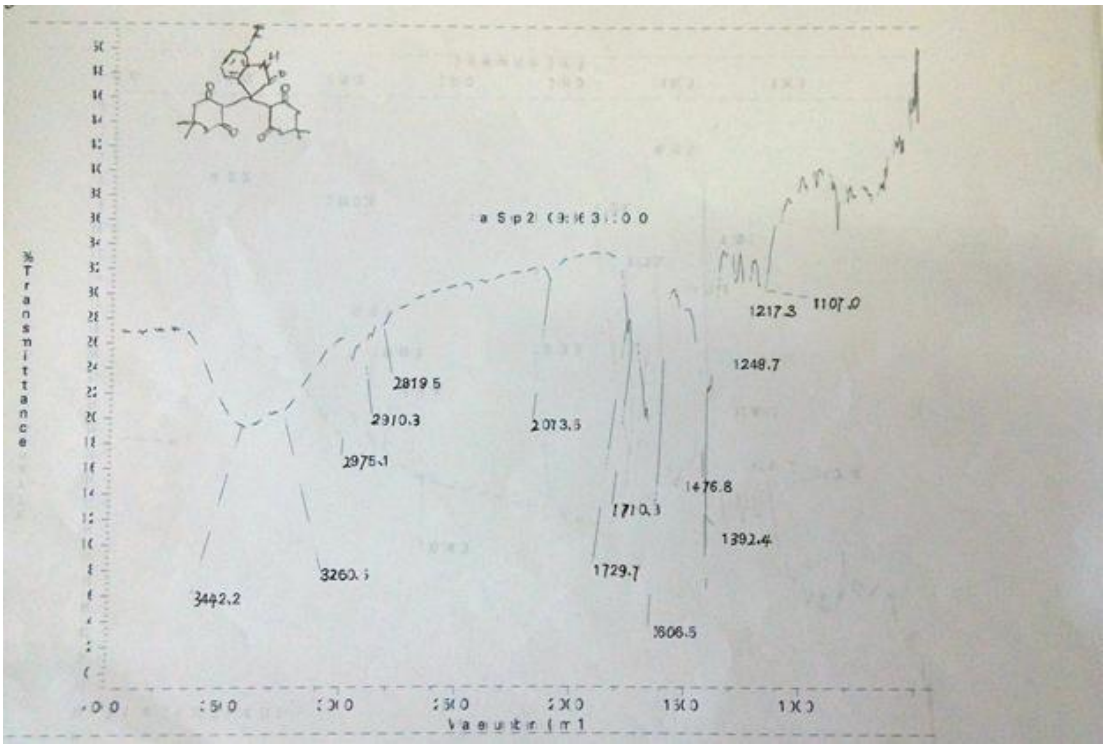

3442.2
2936.2
2951.9
2378.4
2028.1
2073.5
1600.0
1468.8
1385.9
1372.0
1355.2

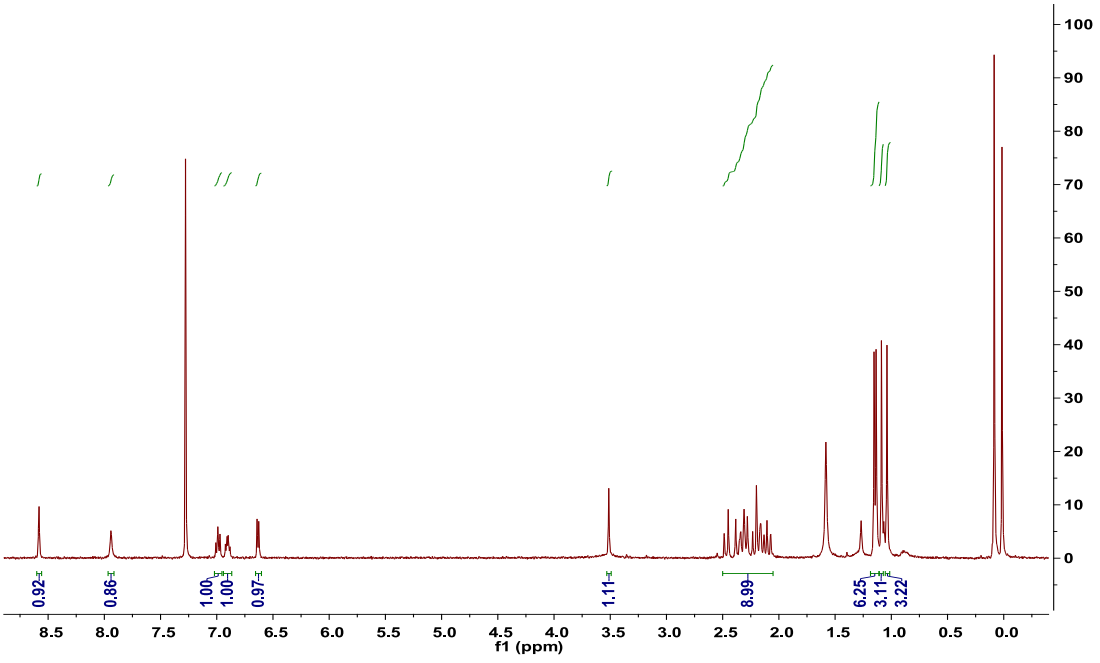

0.89
2.59
0.99
0.98
9.04
6.05
6.27
6.00
2.45
f1 (ppm)

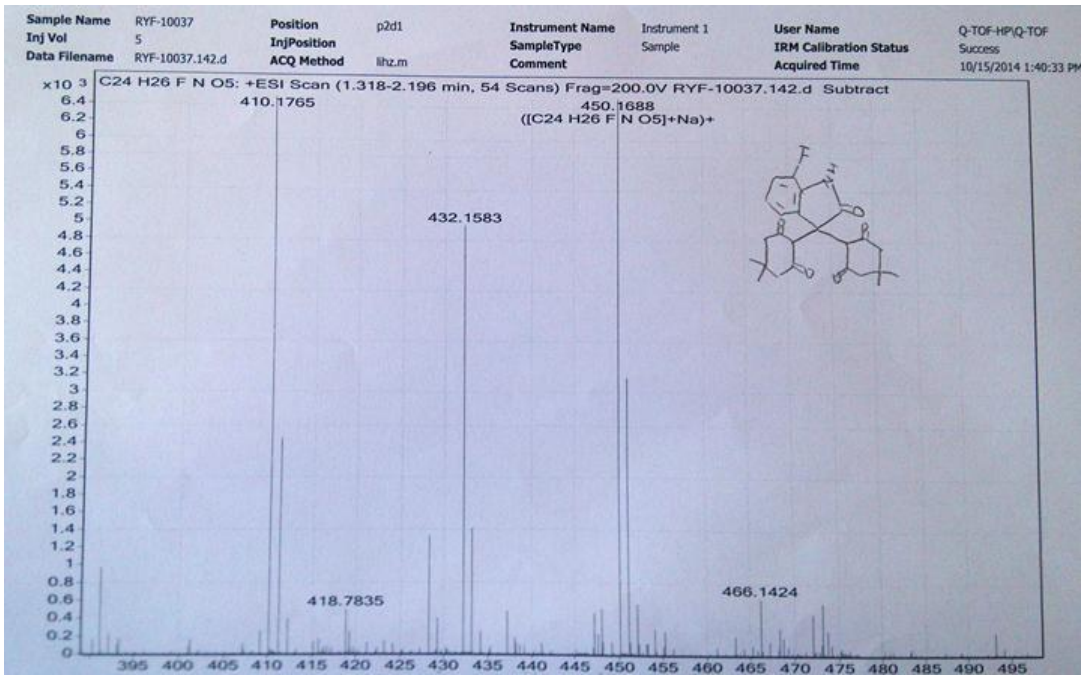

Sample Name RYF-1025
Inj Vol 3
Data Filename YRF-1025.028.d
Position p1d7
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 10/14/2014 1:49:41 PM
C23 H34 O4: +ESI Scan (1.330-2.291 min, 59 Scans) Frag=200.0V YRF-1025.028.d Subtract
x10 3
375.2534
397.2355
([C23 H34 O4]+Na)+
421.1988
411.2142
429.2244
441.2033
341.1732
389.2323
355.2254

3bb.

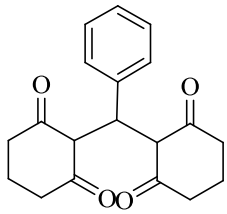

F
NH
O
O
O
O
O

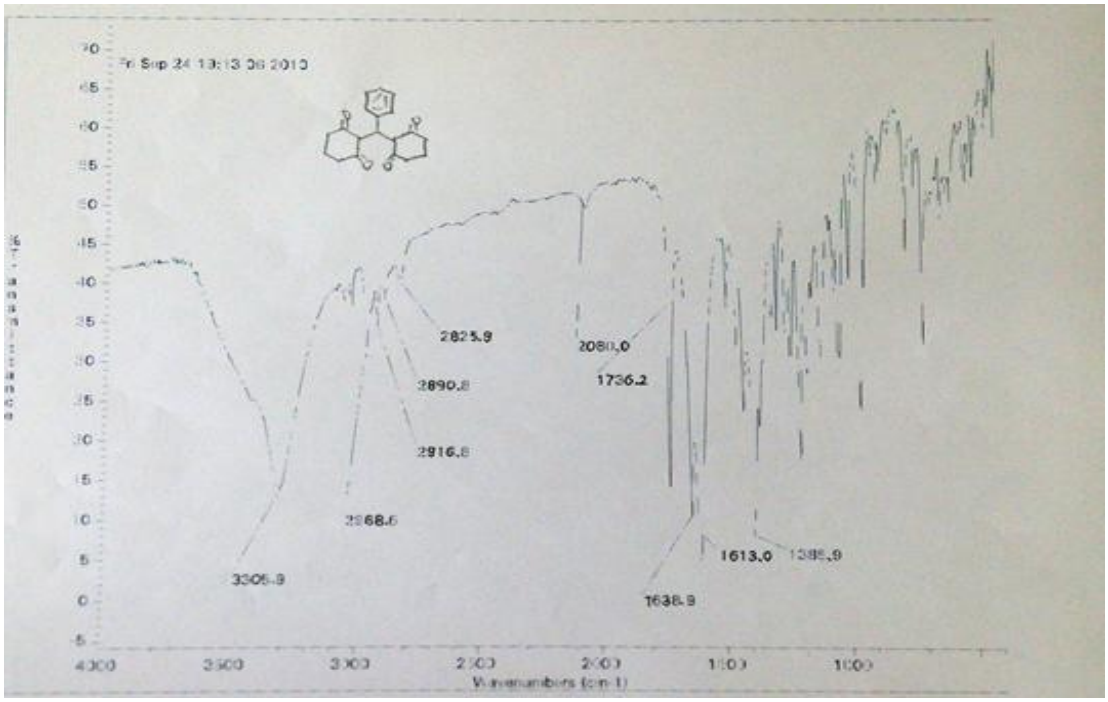

%Transmittance
3442.2
2819.5
2910.3
2975.1
2013.5
1729.7
1710.3
1476.8
1392.4
1248.7
1217.3
1107.0
3606.5

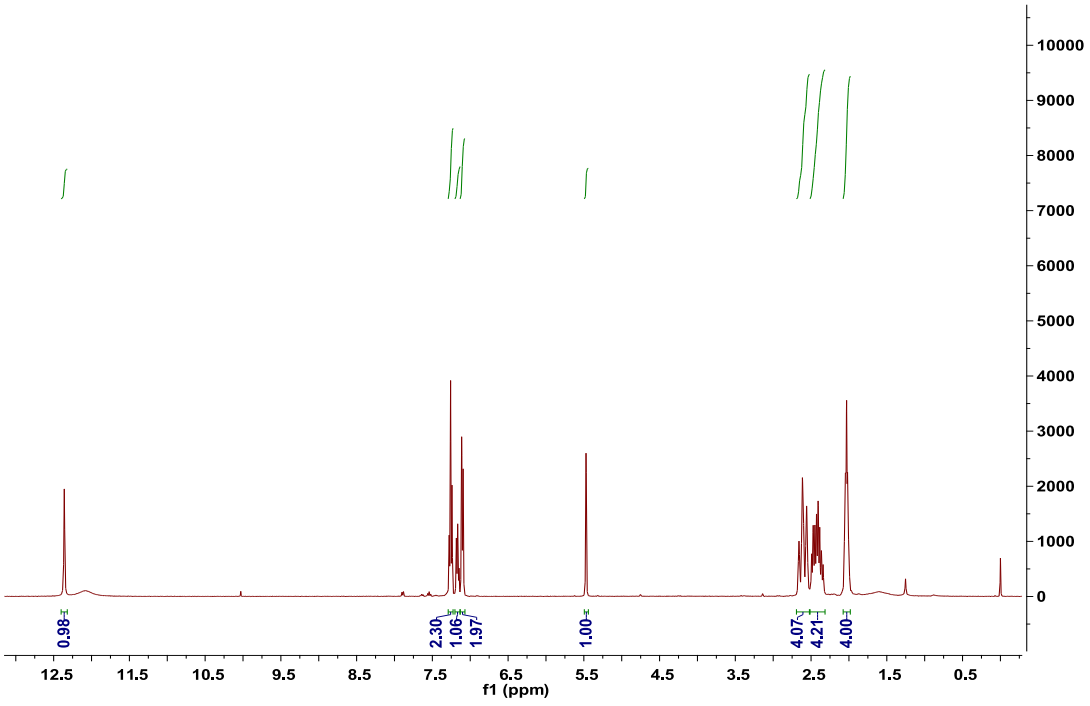

0.92
0.86
1.00
1.00
0.97
1.11
8.99
6.25
3.11
3.22
f1 (ppm)

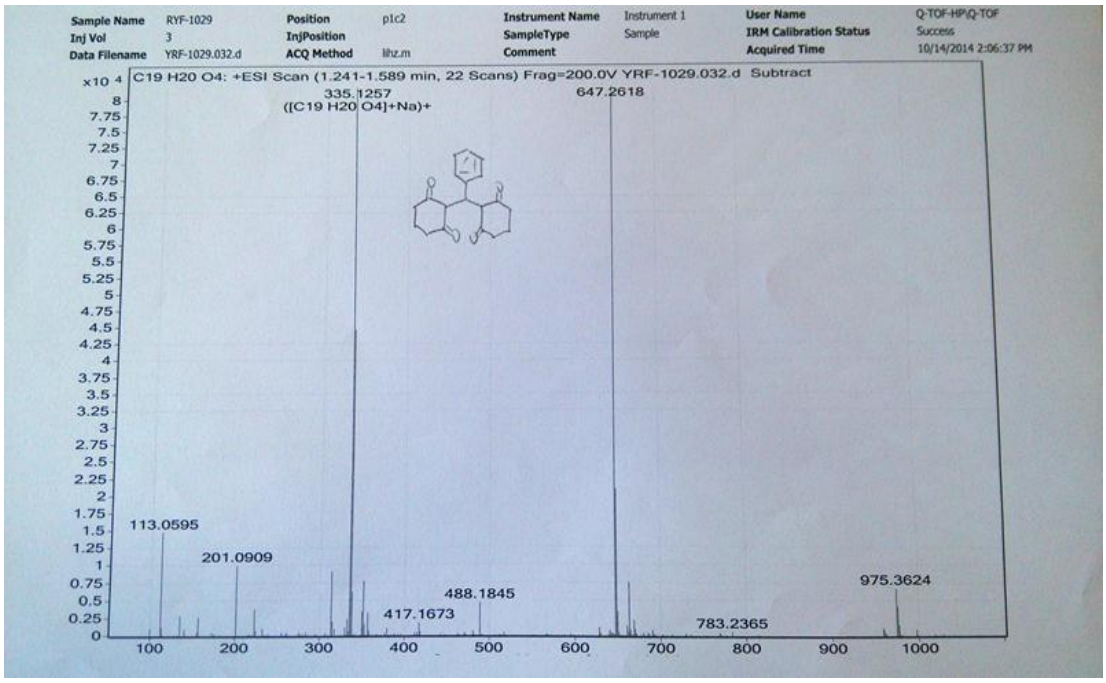

Sample Name RYF-10037
Inj Vol 5
Data Filename RYF-10037.142.d
Position p2d1
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 10/15/2014 1:40:33 PM
C24 H26 F N O5: +ESI Scan (1.318-2.196 min, 54 Scans) Frag=200.0V RYF-10037.142.d Subtract
x10 3
410.1765
450.1688
([C24 H26 F N O5]+Na)+
432.1583
418.7835
466.1424

3cc.

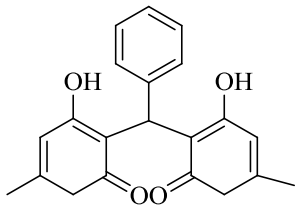


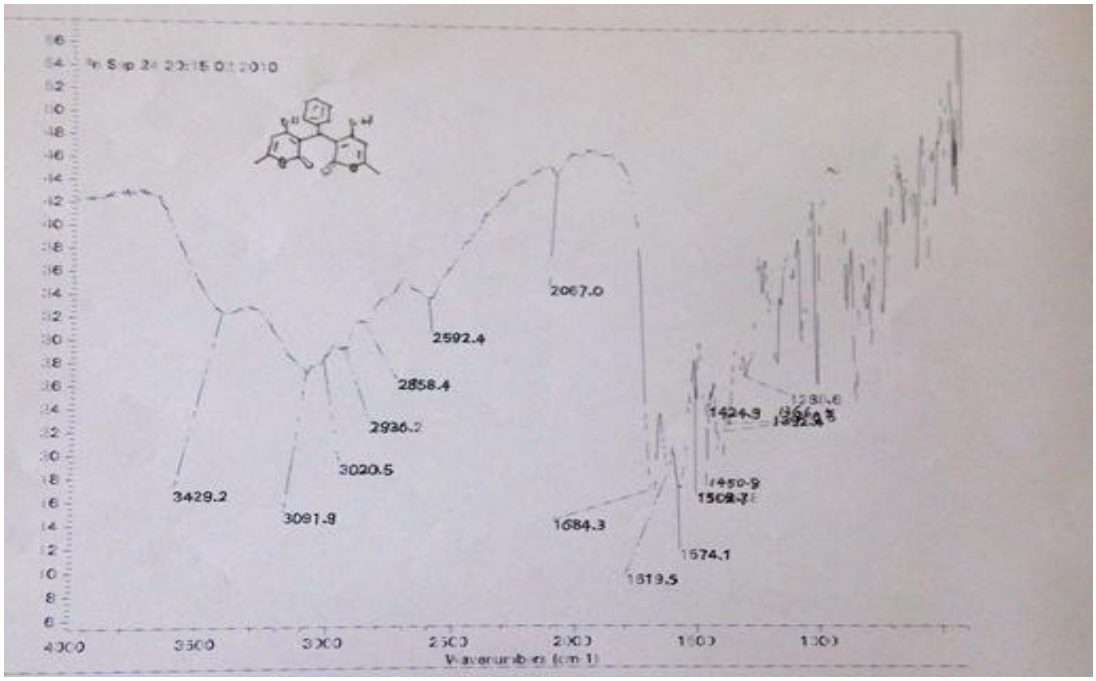

2825.9
2890.8
2916.8
2968.6
3305.9
2080.0
1736.2
1638.9
1613.0
1385.9

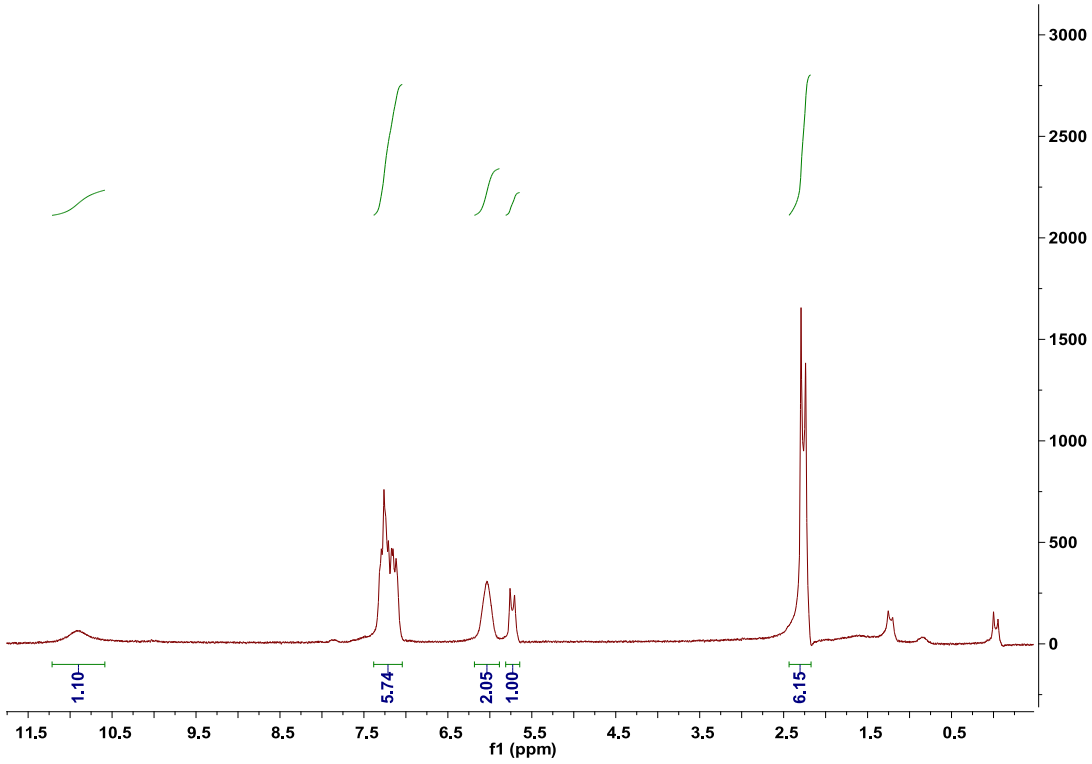

0.98
2.30
1.06
1.97
1.00
4.07
4.21
4.00
f1 (ppm)

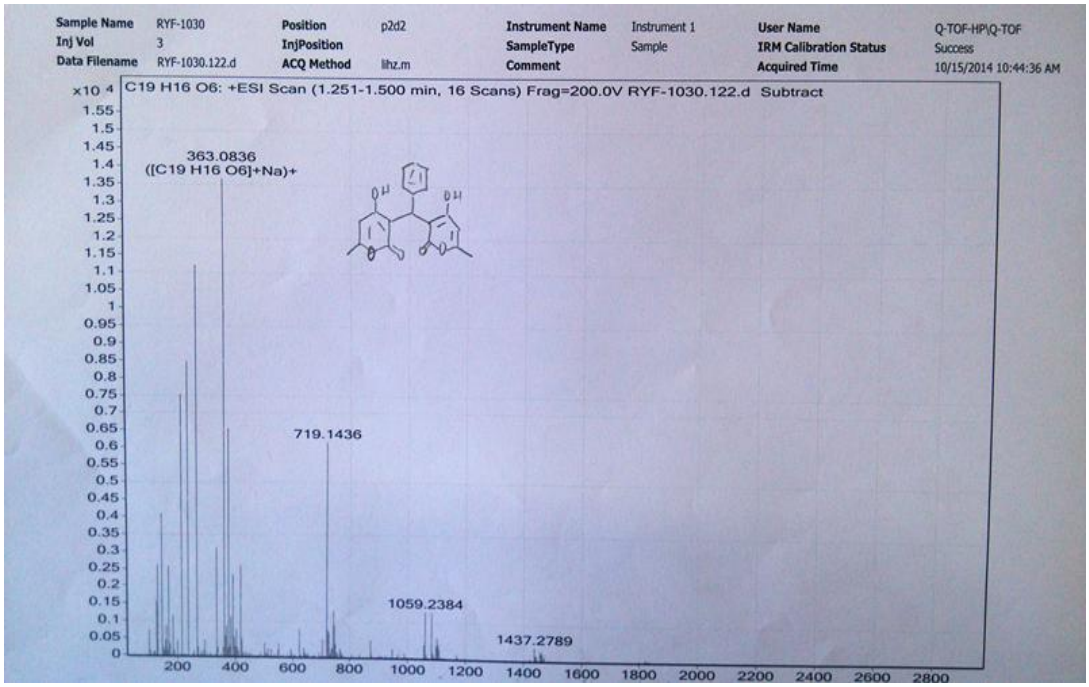

Sample Name RYF-1029
Position p1c2
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 3
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename YRF-1029.032.d
ACQ Method lihz.m
Comment
Acquired Time 10/14/2014 2:06:37 PM
C19 H20 O4: +ESI Scan (1.241-1.589 min, 22 Scans) Frag=200.0V YRF-1029.032.d Subtract
x10 4
335.1257
([C19 H20 O4]+Na)+
647.2618
113.0595
201.0909
417.1673
488.1845
783.2365
975.3624

3dd.


OH
OH
O
O

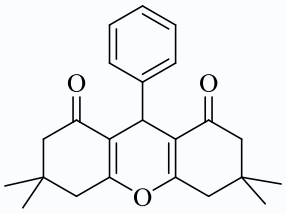

3429.2
3091.9
3020.5
2936.2
2858.4
2592.4
2067.0
1684.3
1619.5
1574.1
1424.9
4000
3500
3000
2500
2000
1500
1000

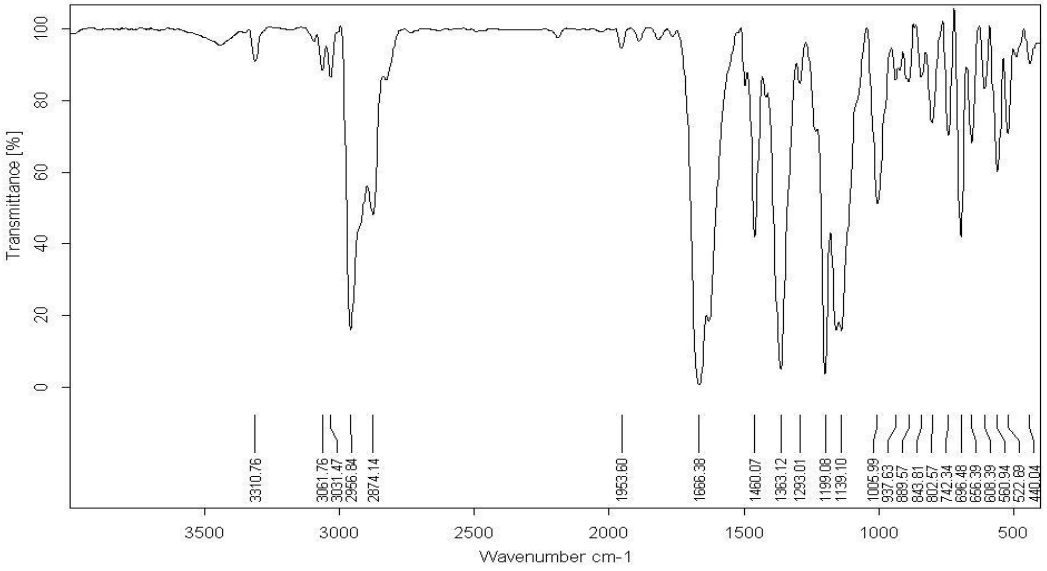

3000
2500
2000
1500
1000
500
0
1.10
5.74
2.05
1.00
6.15
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


Sample Name RYF-1030
Position p2d2
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 3
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename RYF-1030.122.d
ACQ Method lihz.m
Comment
Acquired Time 10/15/2014 10:44:36 AM
C19 H16 O6: +ESI Scan (1.251-1.500 min, 16 Scans) Frag=200.0V RYF-1030.122.d Subtract
x10 4
363.0836
([C19 H16 O6]+Na)+
719.1436
1059.2384
1437.2789

5. IR, ^{1}H NMR and ESI-MS copies of xanthenedione 4a and acridinedione 4b

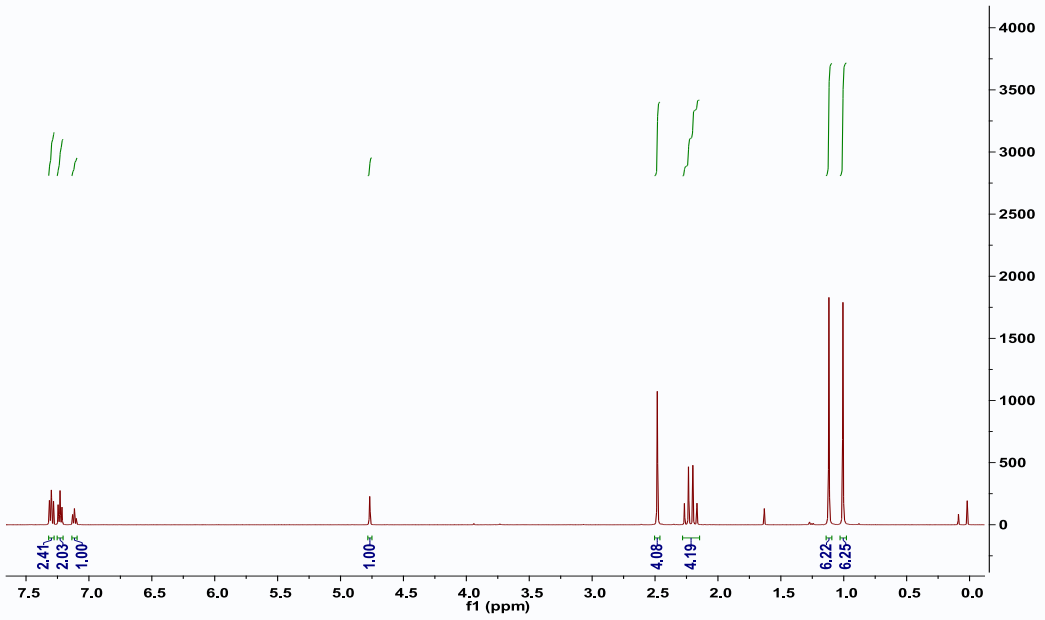
4a.

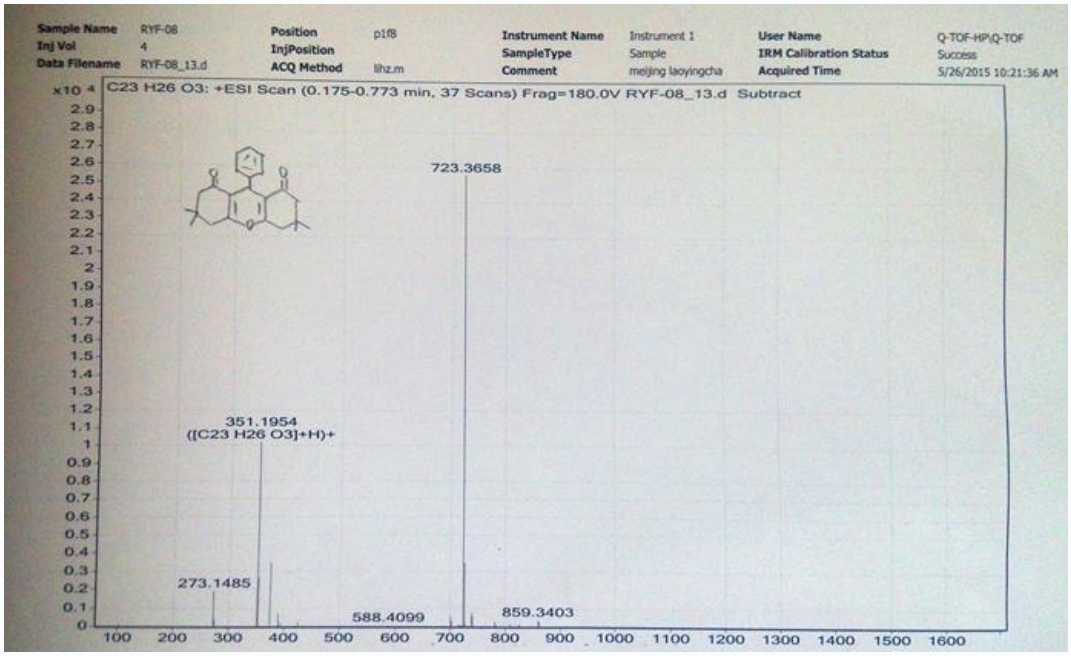




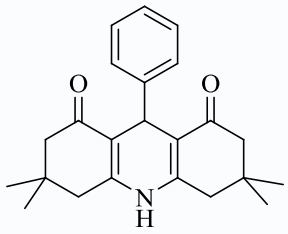
D:\? ? ? ? \.18440	Instrument type and / or accessory	09/04/2015

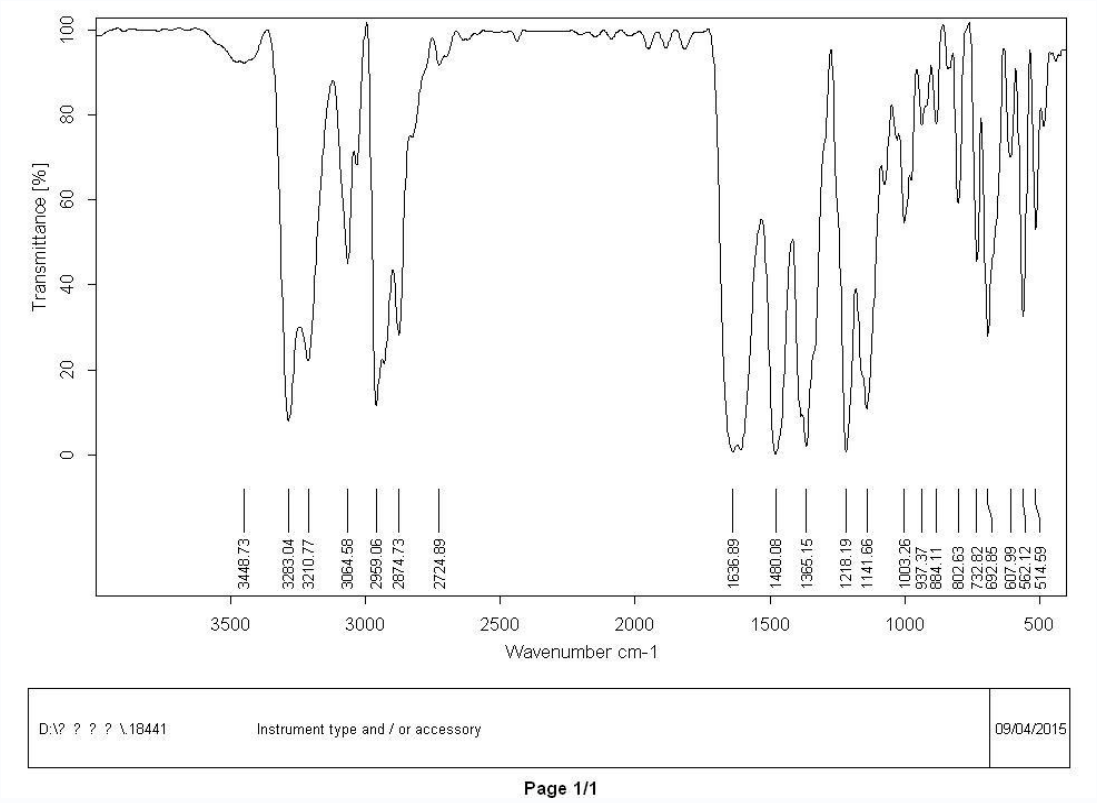
Page 1/1

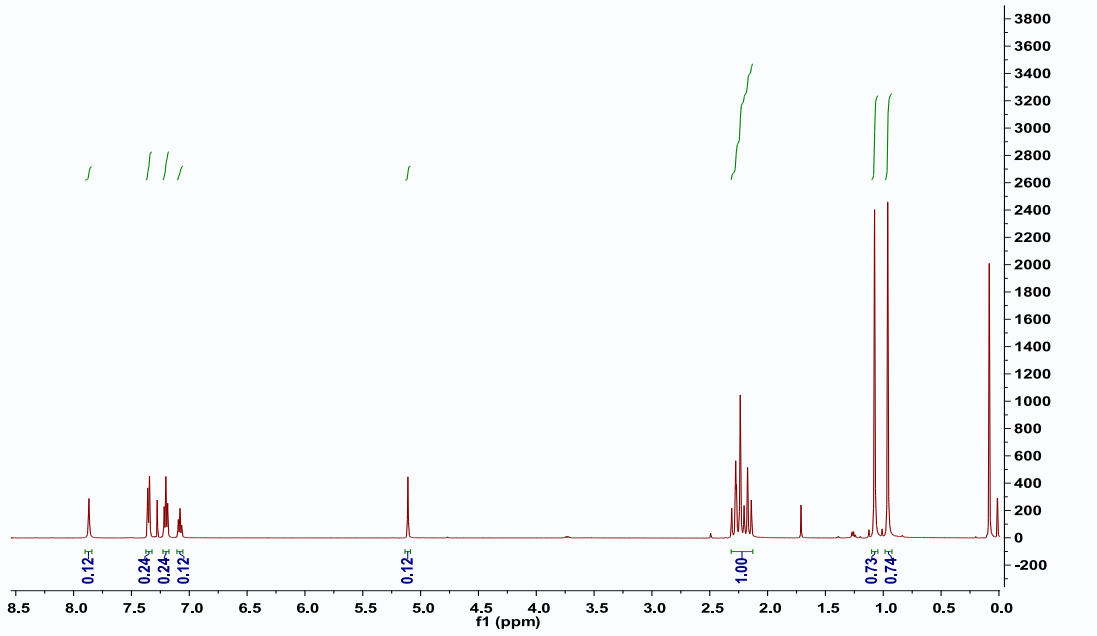


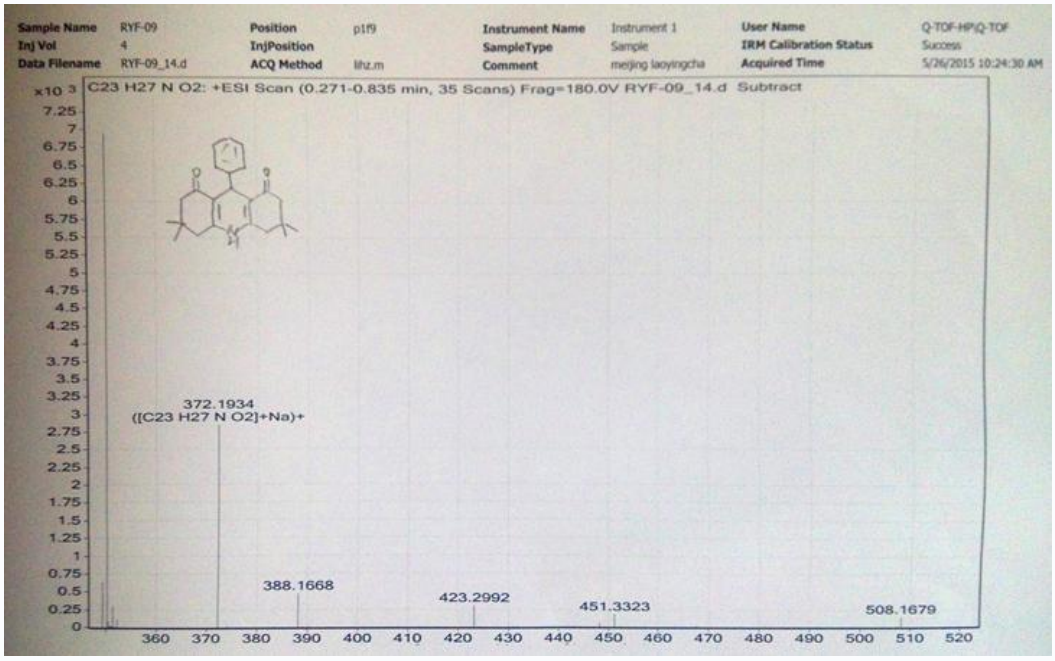

Sample Name RYF-08
Inj Vol 4
Data Filename RYF-08_13.d
Position p1f8
InjPosition
ACQ Method lihz.m
Instrument Name Instrument 1
SampleType Sample
Comment meijing laoyingcha
User Name Q-TOF-HP\Q-TOF
IRM Calibration Status Success
Acquired Time 5/26/2015 10:21:36 AM
C23 H26 O3: +ESI Scan (0.175-0.773 min, 37 Scans) Frag=180.0V RYF-08_13.d Subtract
x10 4
723.3658
351.1954
([C23 H26 O3]+H)+
273.1485
588.4099
859.3403

4b.


O
O
N
H


Transmittance [%]
100
80
60
40
20
0
3448.73
3283.04
3210.77
3064.58
2959.06
2874.73
2724.89
1636.89
1480.08
1365.15
1218.19
1141.66
1003.26
937.37
884.11
802.63
732.82
692.85
607.99
562.12
514.59
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
D:\? ? ? ? \.18441
Instrument type and / or accessory
09/04/2015
Page 1/1


0.12
0.24
0.24
0.12
0.12
1.00
0.73
0.74
f1 (ppm)


Sample Name RYF-09
Position p1f9
Instrument Name Instrument 1
User Name Q-TOF-HP\Q-TOF
Inj Vol 4
InjPosition
SampleType Sample
IRM Calibration Status Success
Data Filename RYF-09_14.d
ACQ Method lihz.m
Comment meijing laoyingcha
Acquired Time 5/26/2015 10:24:30 AM
C23 H27 N O2: +ESI Scan (0.271-0.835 min, 35 Scans) Frag=180.0V RYF-09_14.d Subtract
x10 3
372.1934
([C23 H27 N O2]+Na)+
388.1668
423.2992
451.3323
508.1679