Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
This journal is © The Royal Society of Chemistry 2013

Supporting Information

Modular Synthesis of All-substitued Furans through Oxidative Carbonylation of Cyclopropenes with Tandem Metal Relay Catalysis

Chuanling Song, Shuli Dong, Lei Feng, Xianglong Peng, Mingchao Wang, Jianwu Wang and Zhenghu Xu*

School of chemistry and chemical engineering
Shandong University, 27 South Shanda Road, Jinan, 250100, China

This journal is © The Royal Society of Chemistry 2013

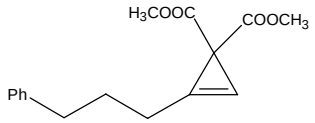
General

All NMR spectra were recorded on Bruker-500 or 300 MHz spectrometer. HRMS were measured on the Q-TOF6510 instruments . Routine monitoring of the reaction was performed by TLC using precoated silica gel plates. All the reagents and Solvents used in this reaction such as CH_3CN were purchased from Acros or local company and used directly. All the reactions don't require inert atmosphere.

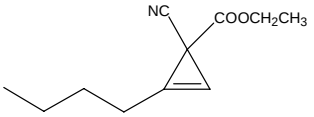
Synthesis of the materials

Diazomalonates and Cyclopropenes

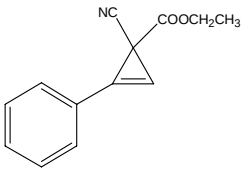
Diazomalonates and cyclopropenes **1a-1m** were synthesized from the procedures reported in the literature[1]



(1d) Yield: 76 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.90-1.98 (m, 2H), 2.55-2.59 (t, *J* =7.24 Hz, 2H), 2.67-2.71 (t, *J* =7.60 Hz, 2H), 3.71 (s, 6H), 6.40(s, 1H), 7.16-7.30 (m, 5H);



(1k) Yield: 70 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, *J* =7.36 Hz, 3H), 1.32 (t, *J* =7.12 Hz, 3H), 1.42-1.46 (m, 2H), 1.62-1.66 (m, 2H), 2.58-2.62(m, 2H), 4.22-4.28 (m, 2H), 6.43 (s, 1H);



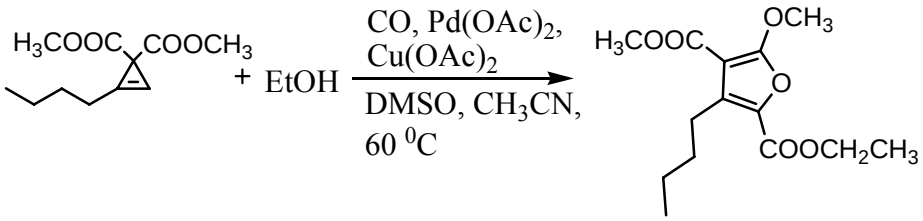
(1l) Yield: 52 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (t, *J* =7.12 Hz, 3H), 4.26-4.32 (q, *J* =7.12 Hz, 2H), 6.93 (s, 1H), 7.50-7.52(m, 3H), 7.60-7.62 (m, 2H);

References

1. C. Song, L.Ju, M. Wang, P. Liu, Y. Zhang, J. Wang, Z. Xu, *Chem. Eur. J.* **2013**, *19*, 3584-3589

This journal is © The Royal Society of Chemistry 2013

Optimization of reaction conditions

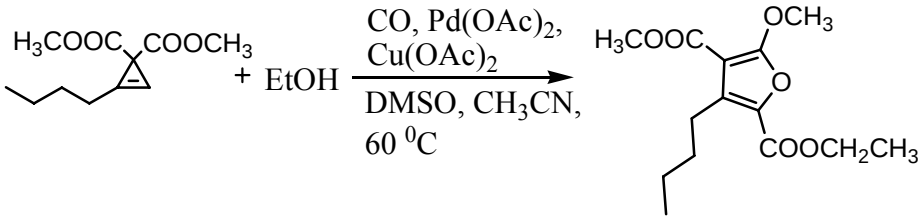


Entry	Catalyst	Oxidant	Additive	Solvent	Yield/%
1[a]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(3 eq.)	CH_3CN	35
2[a,h]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(3 eq.)	CH_3CN	68[g]
3[a,i]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(3 eq.)	CH_3CN	67[g]
4[a]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(3 eq.)	Toluene	0
5[a]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(3 eq.)	DMF	7
6[a]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(3 eq.)	THF	9
7[a]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(3 eq.)	1,2-DCE	<5
8[a]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(3 eq.)	DMSO	17.6
9[b]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(3 eq.)	CH_3CN	62
10[b]	$Pd(OAc)_2$	$Cu(acac)_2$	DMSO(3 eq.)	CH_3CN	3.2
11[b]	$Pd(OAc)_2$	$Cu(Me_3CCOO)_2$	DMSO(3 eq.)	CH_3CN	23
12[b]	$Pd(OAc)_2$	$Cu(OH)_2$	DMSO(3 eq.)	CH_3CN	7
13[b]	$Pd(OAc)_2$	$Cu(OTf)_2$	DMSO(3 eq.)	CH_3CN	N.R.
14[b]	$Pd(OAc)_2$	AgOAc	DMSO(3 eq.)	CH_3CN	48
15[b]	$Pd(OAc)_2$	Ag_2CO_3	DMSO(3 eq.)	CH_3CN	26
16[b]	$PdCl_2$	$Cu(OAc)_2$	DMSO(3 eq.)	CH_3CN	10
17[b]	$Pd(TFA)_2$	$Cu(OAc)_2$	DMSO(3 eq.)	CH_3CN	31
18[b]	$PdCl_2(CH_3CN)_2$	$Cu(OAc)_2$	DMSO(3 eq.)	CH_3CN	67
19[b]	$Pd(PPh_3)_4$	$Cu(OAc)_2$	DMSO(3 eq.)	CH_3CN	65
20[b]	$Pd_2(dba)_3$	$Cu(OAc)_2$	DMSO(3 eq.)	CH_3CN	50
21[b]	$PdCl_2(PPh_3)_2$	$Cu(OAc)_2$	DMSO(3 eq.)	CH_3CN	33
22[b]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(3 eq.)+NaI	CH_3CN	39
23[b]	$Pd(OAc)_2$	$Cu(OAc)_2$	$PhSOCH_3$(3 eq.)	CH_3CN	trace
24[b]	$Pd(OAc)_2$	$Cu(OAc)_2$	PhSOPh(3 eq.)	CH_3CN	trace
25[b]	$Pd(OAc)_2$	$Cu(OAc)_2$	BnSOBn(3 eq.)	CH_3CN	trace
26[b]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(7 eq.)	CH_3CN	84
27[c]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(7 eq.)	CH_3CN	73
28[b,d]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(7 eq.)	CH_3CN	10
29[b,e]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(7 eq.)	CH_3CN	Trace
30[b,f]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(7 eq.)	CH_3CN	Trace
31[a]	$Pd(OAc)_2$	/	DMSO(7 eq.)	CH_3CN	N.R.
32[a]	/	$Cu(OAc)_2$	DMSO(7 eq.)	CH_3CN	42[j]

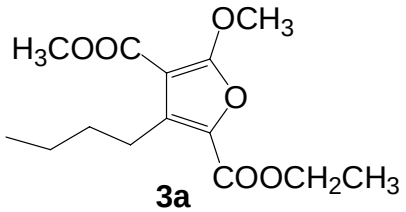
Reaction conditions: [a]1a(0.2 mmol, 42.4 mg), $Pd(OAc)_2$(5 mol%, 0.01 mmol, 2.24 mg), $Cu(OAc)_2$(2 eq. 0.4 mmol, 79.6 mg), 0.2 ml EtOH, DMSO(3 eq. 0.6 mmol, 46.8 mg), 1.0 ml CH_3CN; [b]$Pd(OAc)_2$(5 %, 0.01 mmol, 2.24 mg), $Cu(OAc)_2$(2 eq. 0.4 mmol, 79.6 mg), 0.2 ml EtOH, DMSO, 1.5 ml CH_3CN, 1a(0.2 mmol, 42.4 mg) was slowly injected into the system for 1h; [c]1a(0.2 mmol, 42.4 mg) was slowly injected into the system for 2 hrs; [d]0.5 mL EtOH; [e]0.1 mL EtOH;[f]1.2 eq. $Cu(OAc)_2$; [g]the yield of dimerization product; [h]80℃; [i]100℃; [j]the yield of Isomerization product.

This journal is © The Royal Society of Chemistry 2013

General procedure of Reactions

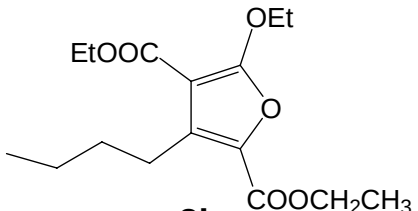


A mixture of $Pd(OAc)_2$ (2.24 mg, 0.01 mmol, 5 mol%) and $Cu(OAc)_2$(79.6 mg, 0.4 mmol, 2 eq.) was dissolved in 0.5 mL CH_3CN, DMSO (106.4 mg, 1.4 mmol, 7 eq.) and 0.2 mL EtOH. The schlenk tube was vacuumed and attached with a CO balloon. Then the solution of **1a** (42.4 mg, 0.2 mmol) in 1 mL CH_3CN was injected into the reaction system by syringe pump in 1 h. The resulting mixture was stirred at 60℃ until the reaction was completed (about 3 h, monitored by TLC). The reaction mixture was filtered and evaporated under reduced pressure and purified by column chromatography (silica gel) to give the pure product **3a**.



3a

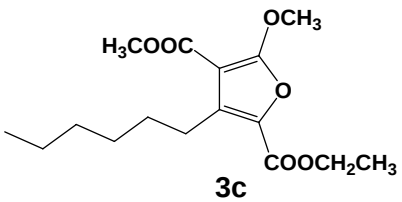
(3a) Yield: 78 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, *J* = 7.28 Hz, 3H), 1.38 (t, *J* = 7.14 Hz, 3H), 1.40-1.44 (m, 2H), 1.51-1.59 (m, 2H), 3.03 (t, *J* = 7.84 Hz, 2H), 3.83 (s, 3H), 4.20 (s, 3H), 4.35 (q, *J* = 7.12 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.79, 14.31, 22.67, 24.59, 32.17, 51.07, 57.79, 60.39, 93.31, 130.87, 139.54, 158.85, 163.02, 163.13; HRMS exact mass calcd for ($C_{14}H_{20}O_6$+H) requires m/z 285.1333, found m/z 285.1354.



3b

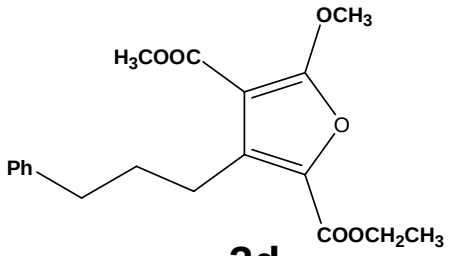
(3b) Yield: 65 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 5.96 Hz, 3H), 1.28-1.72 (m, 13H), 3.03 (t, *J* = 7.84 Hz, 2H), 4.27-4.37 (m, 4H), 4.54-4.59 (q, *J* = 7.08 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.91, 14.26, 14.39, 14.77, 22.82, 24.82, 32.30, 59.94, 60.39, 67.63, 93.97, 130.63, 139.28, 159.04, 162.85, 163.14; HRMS exact mass calcd for ($C_{16}H_{24}O_6$+H) requires m/z 313.1646, found m/z 313.1644.

This journal is © The Royal Society of Chemistry 2013



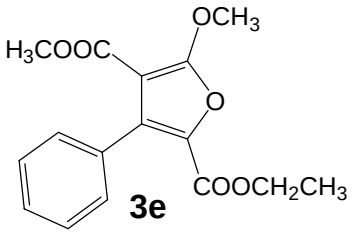
3c

(3c) Yield: 93 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.78-0.80 (m, 3H), 1.25-1.31 (m, 4H), 1.34-1.41 (m, 5H), 1.50-1.57 (m, 2H), 3.00 (t, *J* = 7.92 Hz, 2H), 3.80 (s, 3H), 4.18 (s, 3H), 4.30-4.37 (q, *J* = 7.12 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.05, 14.35, 22.61, 24.91, 29.33, 30.05, 31.57, 51.15, 57.83, 60.44, 93.26, 130.85, 139.59, 158.91, 163.07, 163.16; HRMS exact mass calcd for ($C_{16}H_{24}O_6$+H) requires m/z 313.1646, found m/z 313.1643.



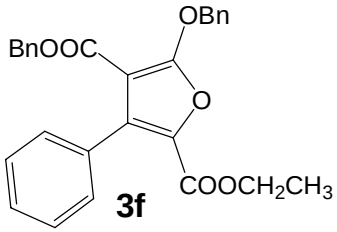
3d

(3d) Yield: 75 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, *J* = 7.10 Hz, 3H), 1.87-1.93 (m, 2H), 2.70 (t, *J* = 7.76 Hz, 2H), 3.06 (t, *J* = 7.78 Hz, 2H), 3.75 (s, 3H), 4.18 (s, 3H), 4.29 (q, *J* = 7.10 Hz, 2H), 7.18-7,25 (m, 5H); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.37, 24.83, 31.61, 35.98, 51.15, 57.88, 60.50, 93.38, 125.69, 128.22, 128.45, 131.01, 138.85, 142.25, 158.84, 163.01, 163.25; HRMS exact mass calcd for ($C_{19}H_{22}O_6$+H) requires m/z 347.1489, found m/z 347.1495.



3e

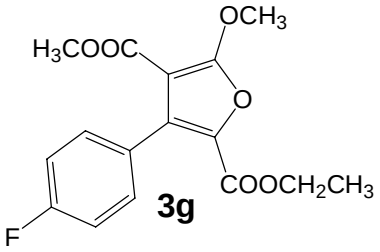
(3e) Yield: 86 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (t, *J* = 7.12 Hz, 3H), 3.64 (s, 3H), 4.14 (q, *J* = 7.12 Hz, 2H), 4.29 (s, 3H), 7.32-7.40 (m, 5H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.88, 51.20, 58.17, 60.57, 94.14, 127.24, 128.04, 129.43, 130.79, 131.21, 136.89, 158.31, 162.52, 162.91; HRMS exact mass calcd for ($C_{16}H_{16}O_6$+H) requires m/z 305.1020, found m/z 305.1027.



3f

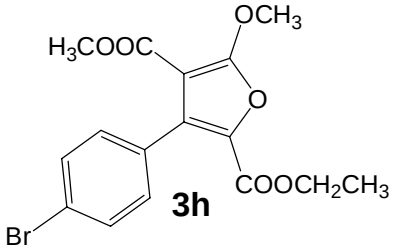
This journal is © The Royal Society of Chemistry 2013

(3f) Yield: 70 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (t, *J* = 7.12 Hz, 3H), 4.15 (q, *J* = 7.16 Hz, 2H), 5.11(s, 2H), 5.59(s, 2H), 7.05-7.52 (m, 15H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.91, 60.58, 65.72, 73.20, 94.95, 127.37, 127.66, 127.73, 128.04, 128.27, 128.53, 128.75, 128.95, 129.47, 130.94, 131.28, 134.32, 135.73, 136.65, 158.30, 161.79, 162.58; HRMS exact mass calcd for ($C_{28}H_{24}O_6$+H) requires m/z 457.1646, found m/z 457.1641.



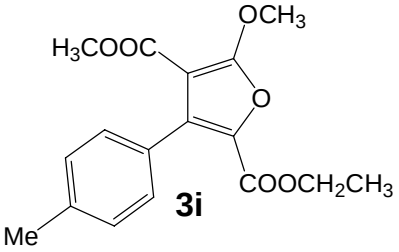
3g

(3g) Yield: 83 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (t, *J* = 6.12 Hz, 3H), 3.65 (s, 3H), 4.15-4.17 (m, 2H), 4.27 (s, 3H), 7.06-7.30 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.94, 51.22, 58.18, 60.66, 94.04, 114.21, 114.42, 127.00, 127.04, 130.87, 131.33, 131.41, 135.87, 158.18, 161.44, 162.45, 162.93, 163.89; HRMS exact mass calcd for ($C_{16}H_{15}O_6F$+H) requires m/z 323.0925, found m/z 323.0933.



3h

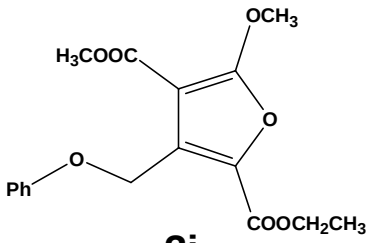
(3h) Yield: 75 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (t, *J* = 6.32 Hz, 3H), 3.66 (s, 3H), 4.16-4.17 (m, 2H), 4.28 (s, 3H), 7.20 (d, *J* = 7.40 Hz, 2H), 7.52 (d, J = 7.40 Hz, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.97, 51.28, 58.24, 60.75, 93.93, 122.40, 130.13, 130.48, 130.72, 131.24, 135.64, 158.09, 162.37, 162.93; HRMS exact mass calcd for ($C_{16}H_{15}O_6Br$+H) requires m/z 383.0125, found m/z 383.0134, 385.0114.



3i

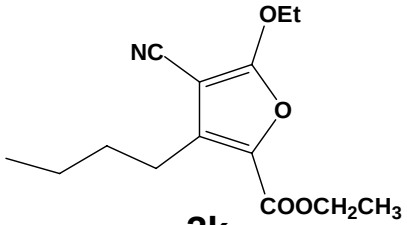
(3i) Yield: 87 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (t, *J* = 7.12 Hz, 3H), 2.34 (s, 3H), 3.64 (s, 3H), 4.14 (q, *J* = 7.12 Hz, 2H), 4.24 (s, 3H), 7.18-7.22 (m, 5H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.99, 21.42, 51.21, 58.12, 60.54, 94.11, 127.96, 128.00, 129.39, 130.72, 137.17, 137.81, 158.32, 162.57, 162.82; HRMS exact mass calcd for ($C_{17}H_{18}O_6$+Na) requires m/z 319.1176, found m/z 319.1173.

This journal is © The Royal Society of Chemistry 2013



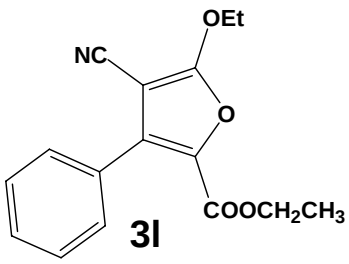
3j

(3j) Yield: 71 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, *J* = 7.12 Hz, 3H), 3.72 (s, 3H), 4.21(s, 3H), 4.31 (q, *J* = 7.12 Hz, 2H), 5.42 (s, 2H), 6.95-6.98 (m, 3H), 7.26-7.28 (m, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.22, 51.46, 58.28, 59.64, 61.13, 93.57, 114.98, 121.03, 129.39, 131.17, 132.62, 158.26, 158.89, 162.55, 162.99; HRMS exact mass calcd for ($C_{17}H_{18}O_7$+H) requires m/z 335.1125, found m/z 335.1132.



3k

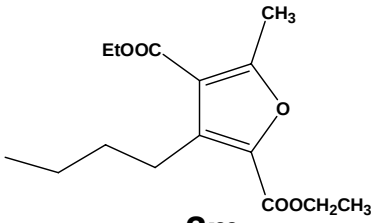
(3k) Yield: 91 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.36 Hz, 3H), 1.34-1.37 (t, *J* = 7.12 Hz, 3H), 1.38-1.42 (m, 2H), 1.47-1.50 (t, *J* = 7.12 Hz, 3H), 1.57-1.63 (m, 2H), 2.78-2.82 (t, *J* = 7.68 Hz, 2H), 4.30-4.35 (q, *J* = 7.08 Hz, 2H), 4.55-4.61 (q, *J* = 7.08 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.72, 14.29, 14.64, 22.36, 24.90, 31.39, 60.83, 68.72, 75.37, 112.35, 130.90, 138.53, 158.09, 164.22; HRMS exact mass calcd for ($C_{14}H_{29}O_4N$+H) requires m/z 266.1387, found m/z 266.1379.



3l

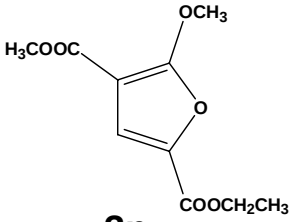
(3l) Yield: 51 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, *J* = 7.12 Hz, 3H), 1.53 (t, *J* = 7.08 Hz, 3H), 4.20-4.26 (q, *J* = 7.12 Hz, 2H), 4.63-4.68 (q, *J* = 7.04 Hz, 2H), 7.43-7.54 (m, 5H); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.04, 14.72, 61.09, 69.06, 75.71, 112.34, 128.15, 128.51, 129.51, 129.55, 130.11, 136.29, 157.69, 164.57; HRMS exact mass calcd for ($C_{16}H_{15}O_4N$+H) requires m/z 286.1074, found m/z 286.1077.

This journal is © The Royal Society of Chemistry 2013



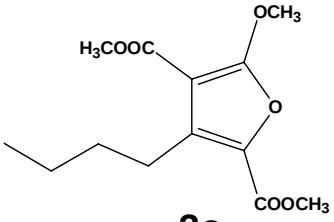
3m

(3m) Yield: 35 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, *J* = 7.28 Hz, 3H), 1.38-1.42 (m, 8H), 1.49-1.54 (m, 2H), 2.61 (s, 3H), 3.00 (t, *J* = 7.76 Hz, 2H), 4.30-4.37 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.89, 14.22, 14.33, 14.82, 22.81, 24.42, 32.53, 60.28, 60.67, 115.28, 136.74, 138.71, 159.26, 162.38, 163.63; HRMS exact mass calcd for ($C_{15}H_{22}O_5$+H) requires m/z 283.1540, found m/z 283.1548.



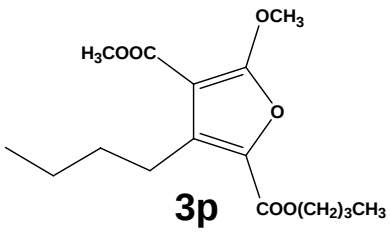
3n

(3n) Yield: 84 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (t, *J* = 7.12 Hz, 3H), 3.81 (s, 3H), 4.22 (s, 3H), 4.31 (q, *J* = 7.12 Hz, 2H), 7.41 (s, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.33, 51.54, 58.40, 60.95, 93.70, 120.79, 134.10, 157.96, 162.44, 163.05; HRMS exact mass calcd for ($C_{10}H_{12}O_6$+H) requires m/z 229.0707, found m/z 229.0702.



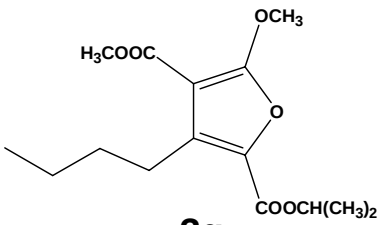
3o

(3o) Yield: 58 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.28 Hz, 3H), 1.35-1.41 (m, 2H), 1.49-1.53 (m, 2H), 3.00 (q, *J* = 7.68 Hz, 2H), 3.80 (s, 3H), 3.84 (s, 3H), 4.17 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.84, 22.65, 24.56, 32.16, 51.18, 51.41, 57.86, 93.43, 130.62, 140.08, 159.22, 163.04, 163.15; HRMS exact mass calcd for ($C_{13}H_{18}O_6$+H) requires m/z 271.1176, found m/z 271.1184.



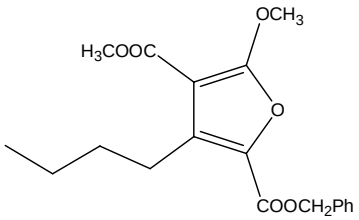
3p

(3p) Yield: 58 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92-0.99 (m, 6H), 1.38-1.56 (m, 6H), 1.70-1.74 (m, 2H), 3.00 (t, *J* = 7.24 Hz, 2H), 3.82 (s, 3H), 4.19 (s, 3H), 4.28 (t, *J* = 6.60 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.68, 13.86, 19.25, 22.79, 24.72, 30.79, 32.30, 51.15, 57.82, 64.35, 93.28, 130.93, 139.43, 159.06, 163.08, 163.19; HRMS exact mass calcd for ($C_{16}H_{24}O_6$+H) requires m/z 313.1646, found m/z 313.1649.



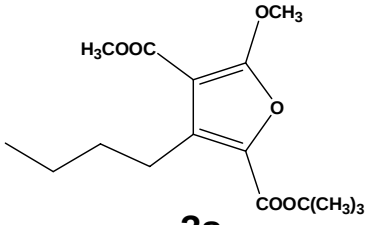
3q

(3q) Yield: 88 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.28 Hz, 3H), 1.32 (d, *J* = 6.24 Hz, 6H), 1.37-1.41 (m, 2H), 1.49-1.53 (m, 2H), 2.97 (t, *J* = 7.92 Hz, 2H), 3.79 (s, 3H), 4.16 (s, 3H), 5.16-5.22 (m, 1H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.90, 22.02, 22.81, 24.72, 32.29, 51.16, 57.83, 68.15, 93.17, 131.18, 139.12, 158.60, 163.14, 163.17; HRMS exact mass calcd for ($C_{15}H_{22}O_6$+Na) requires m/z 299.1489, found m/z 299.1488.



3r

(3r) Yield: 65 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, *J* = 7.32 Hz, 3H), 1.29-1.35 (m, 2H), 1.47-1.51 (m, 2H), 2.98 (t, *J* = 7.92 Hz, 2H), 3.81 (s, 3H), 4.18 (s, 3H), 5.31 (s, 2H), 7.33-7.43 (m, 5H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.82, 22.73, 24.77, 32.30, 51.12, 57.90, 66.20, 93.45, 128.31, 128.59, 130.63, 135.81, 140.23, 158.70, 163.04, 163.33; HRMS exact mass calcd for ($C_{19}H_{22}O_6$+H) requires m/z 347.1489, found m/z 347.1483.

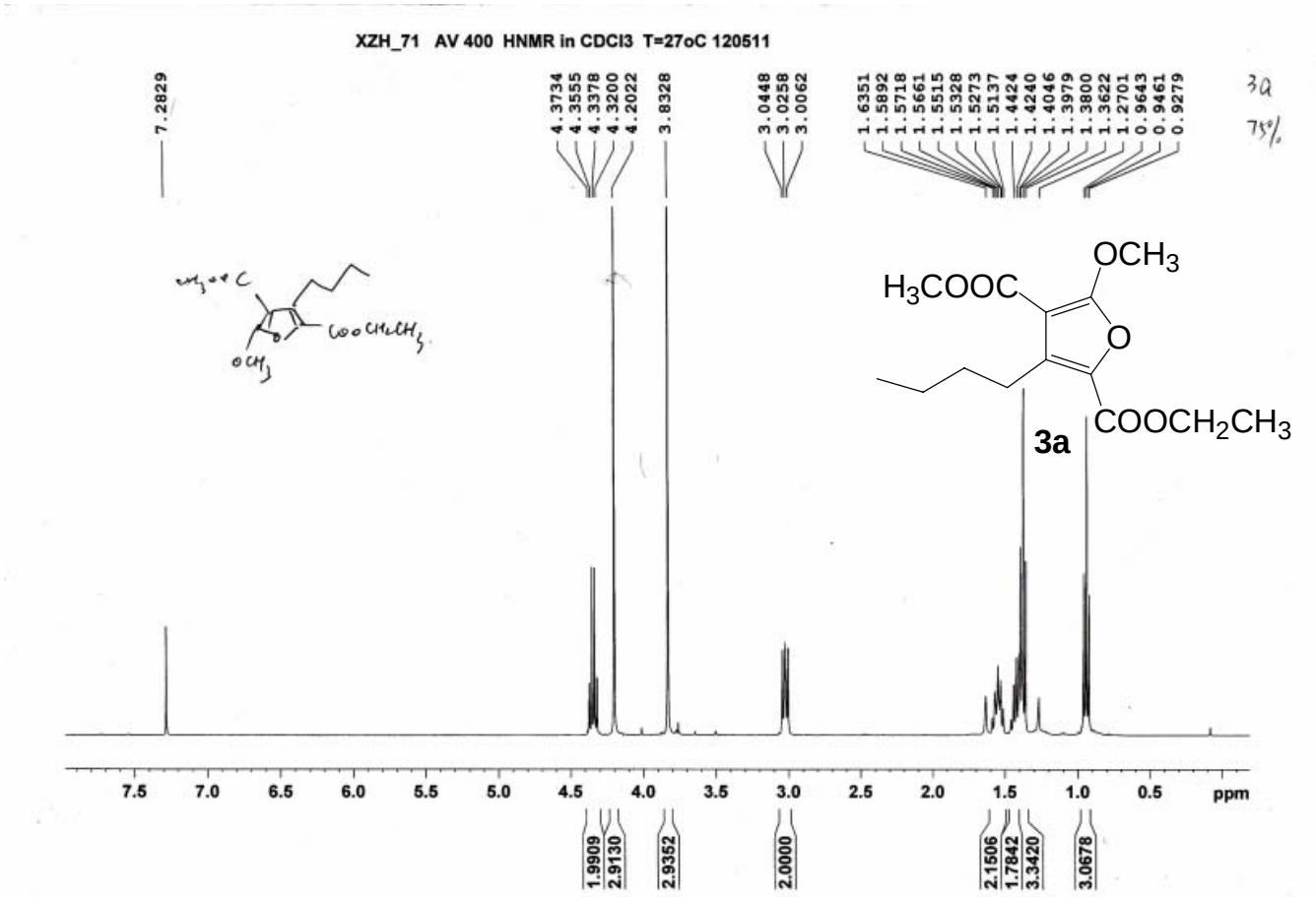


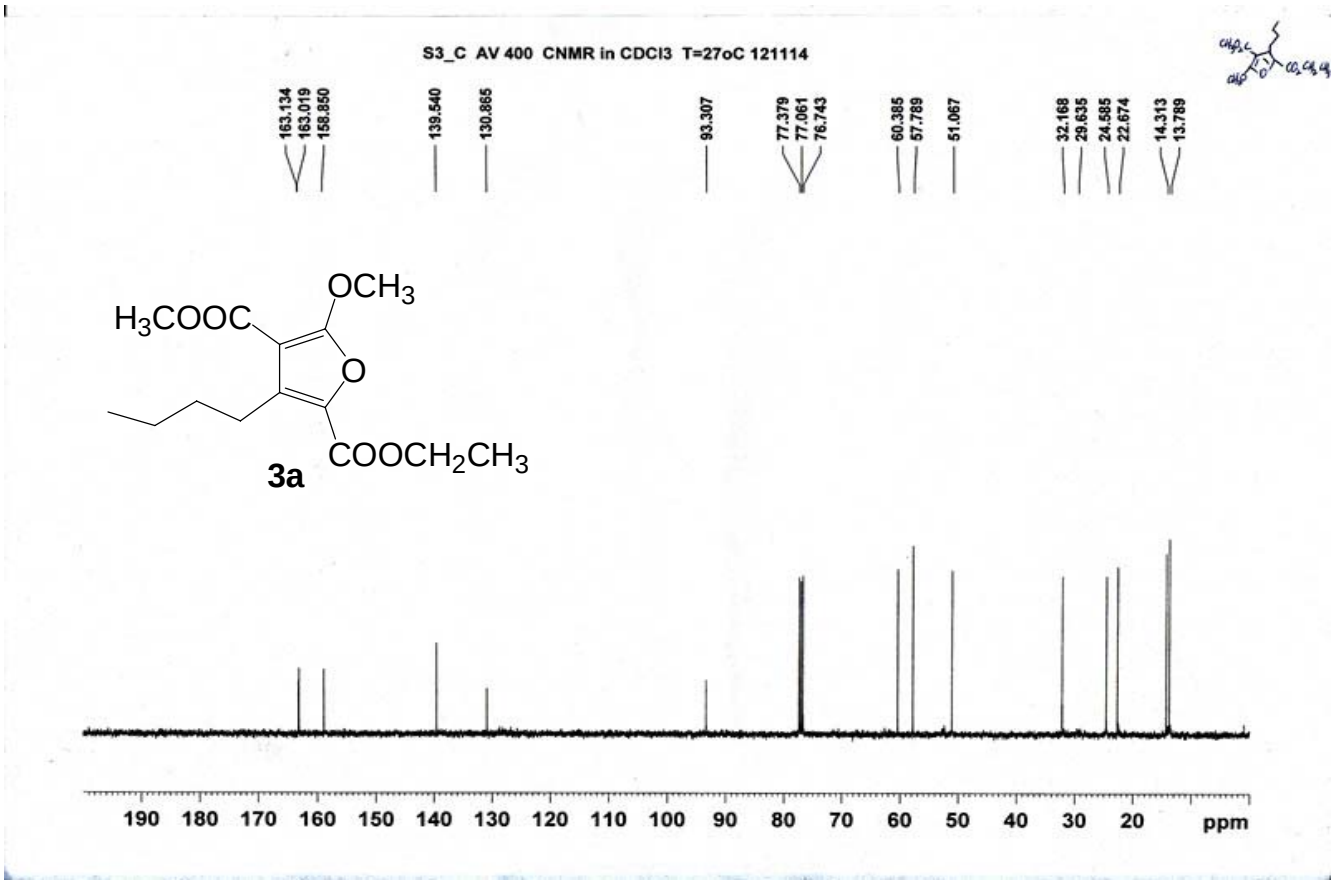
3s

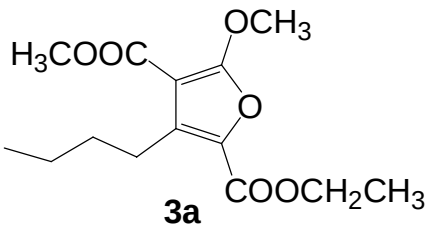
This journal is © The Royal Society of Chemistry 2013

(3s) Yield: 41 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, *J* = 7.24 Hz, 3H), 1.36-1.42 (m, 2H), 1.48-1.50 (m, 2H), 1.57(s, 9H), 2.96 (t, *J* = 7.92 Hz, 2H), 3.81 (s, 3H), 4.17 (s, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.98, 22.85, 24.82, 28.39, 32.39, 51.14, 57.72, 81.78, 92.97, 131.88, 138.06, 158.47, 163.06, 163.25; HRMS exact mass calcd for ($C_{16}H_{24}O_6$+Na) requires m/z 335.1465, found m/z 335.1471.

NMR spectras for products

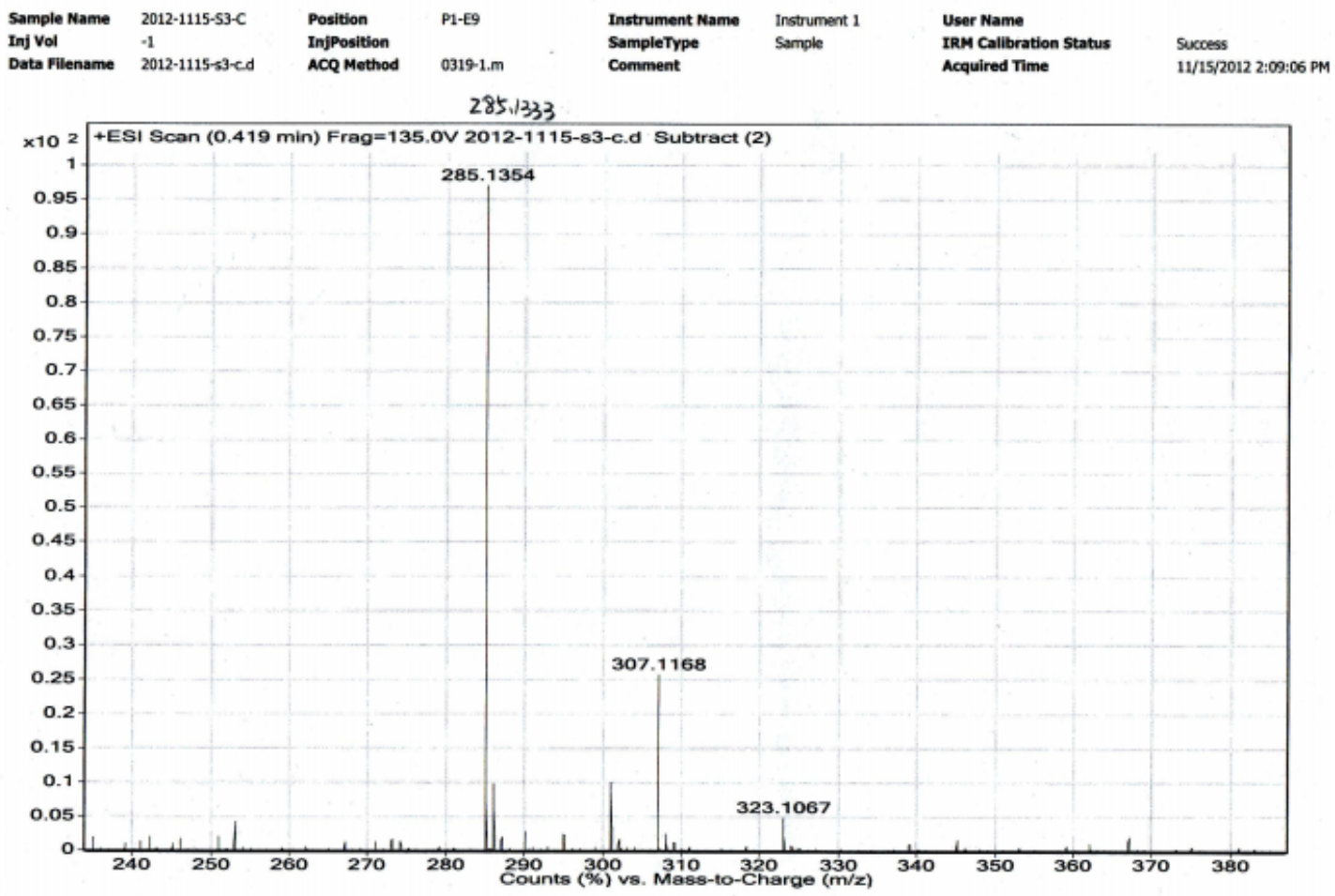




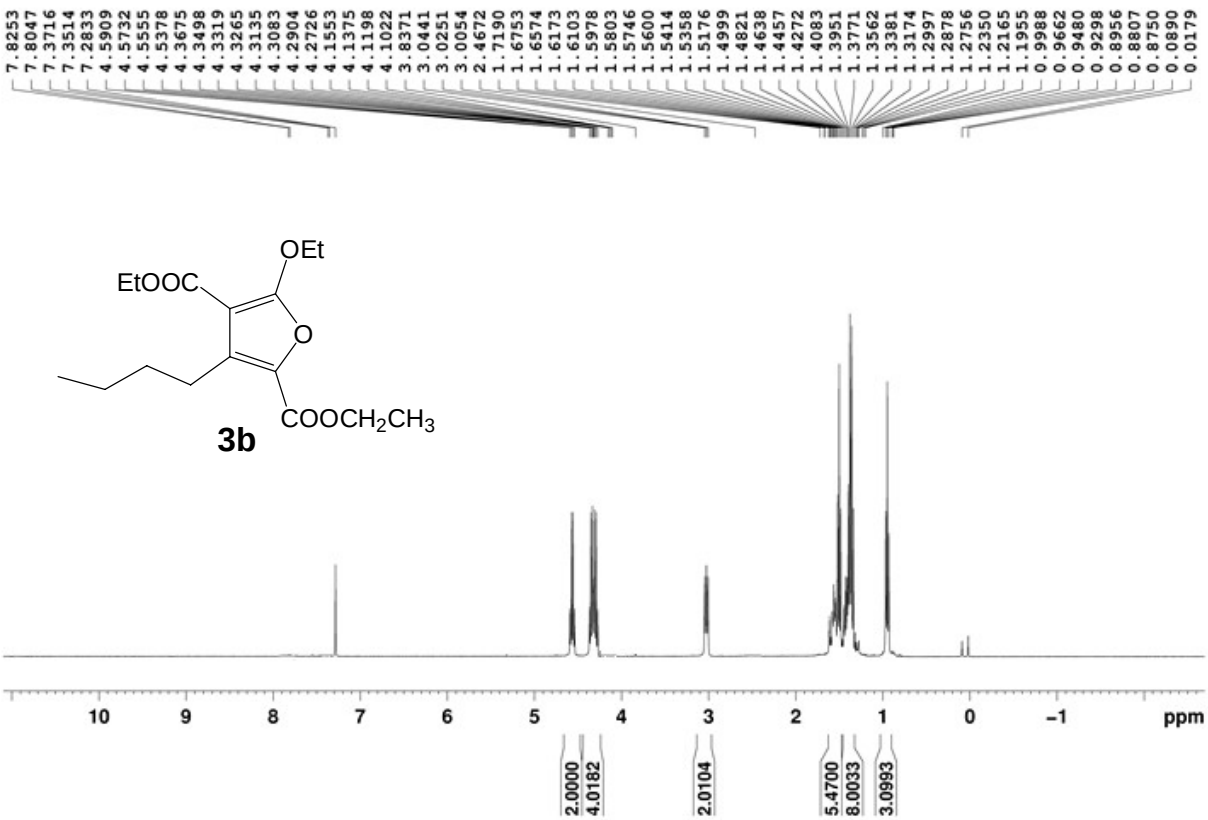


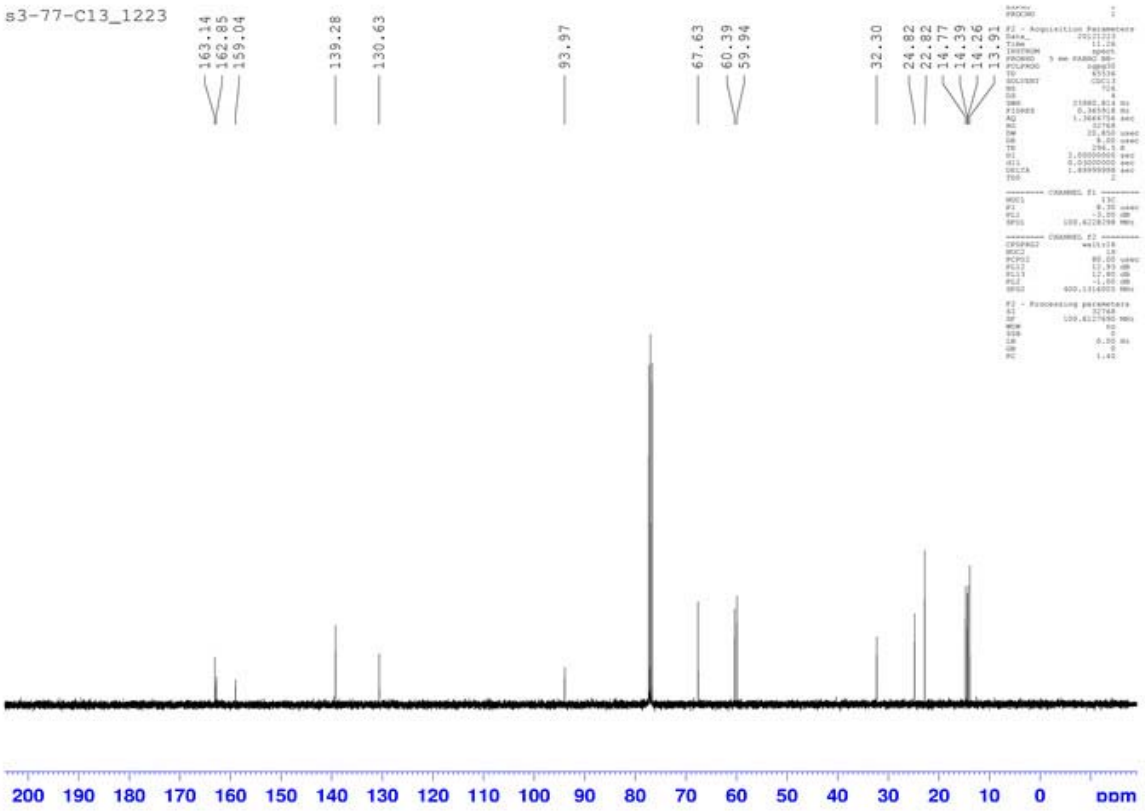
3a

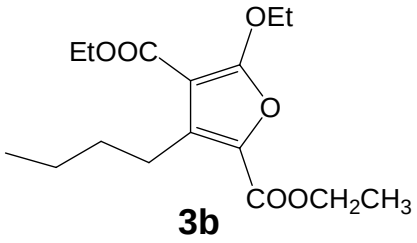
HRMS exact mass calcd for ($C_{14}H_{20}O_6$+H) requires m/z 285.1333, found m/z 285.1354.



This journal is © The Royal Society of Chemistry 2013

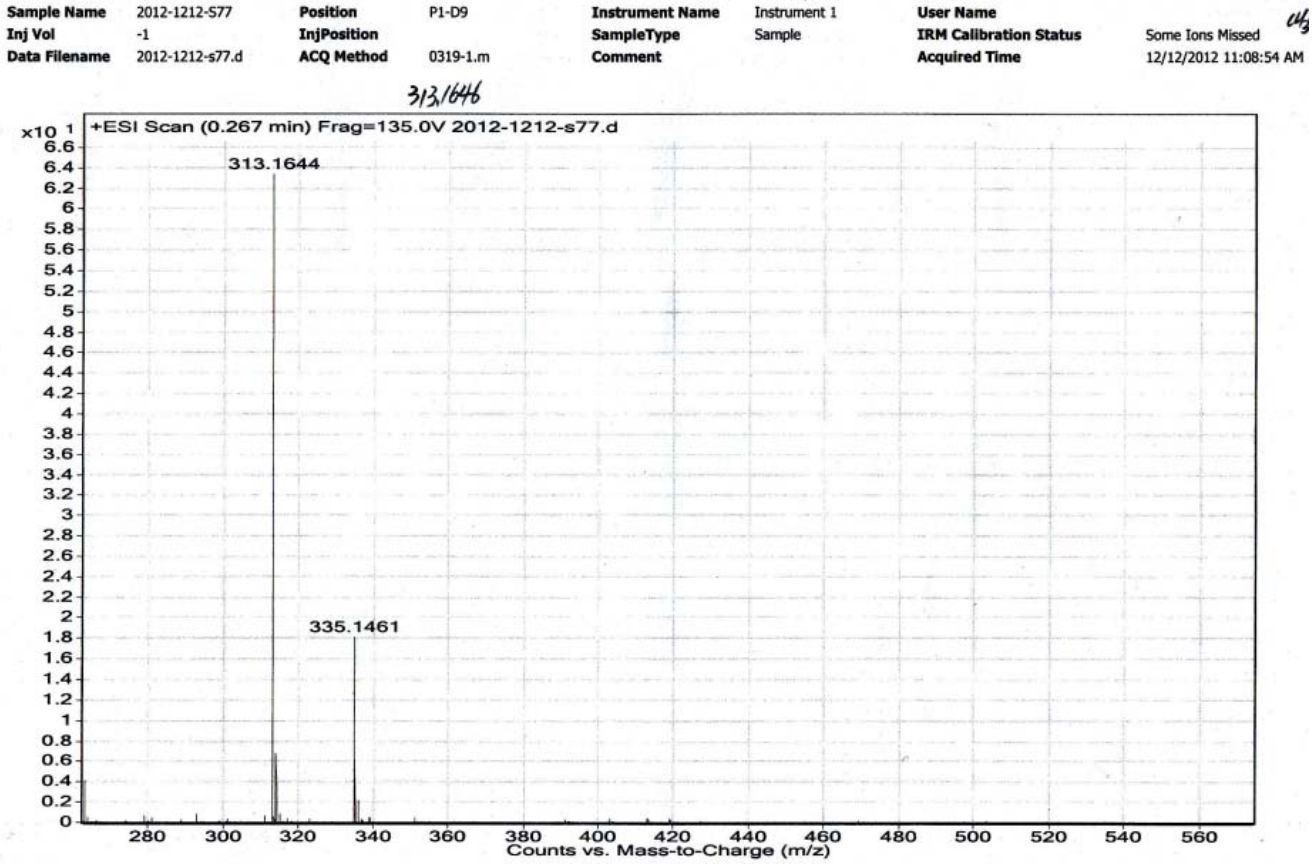


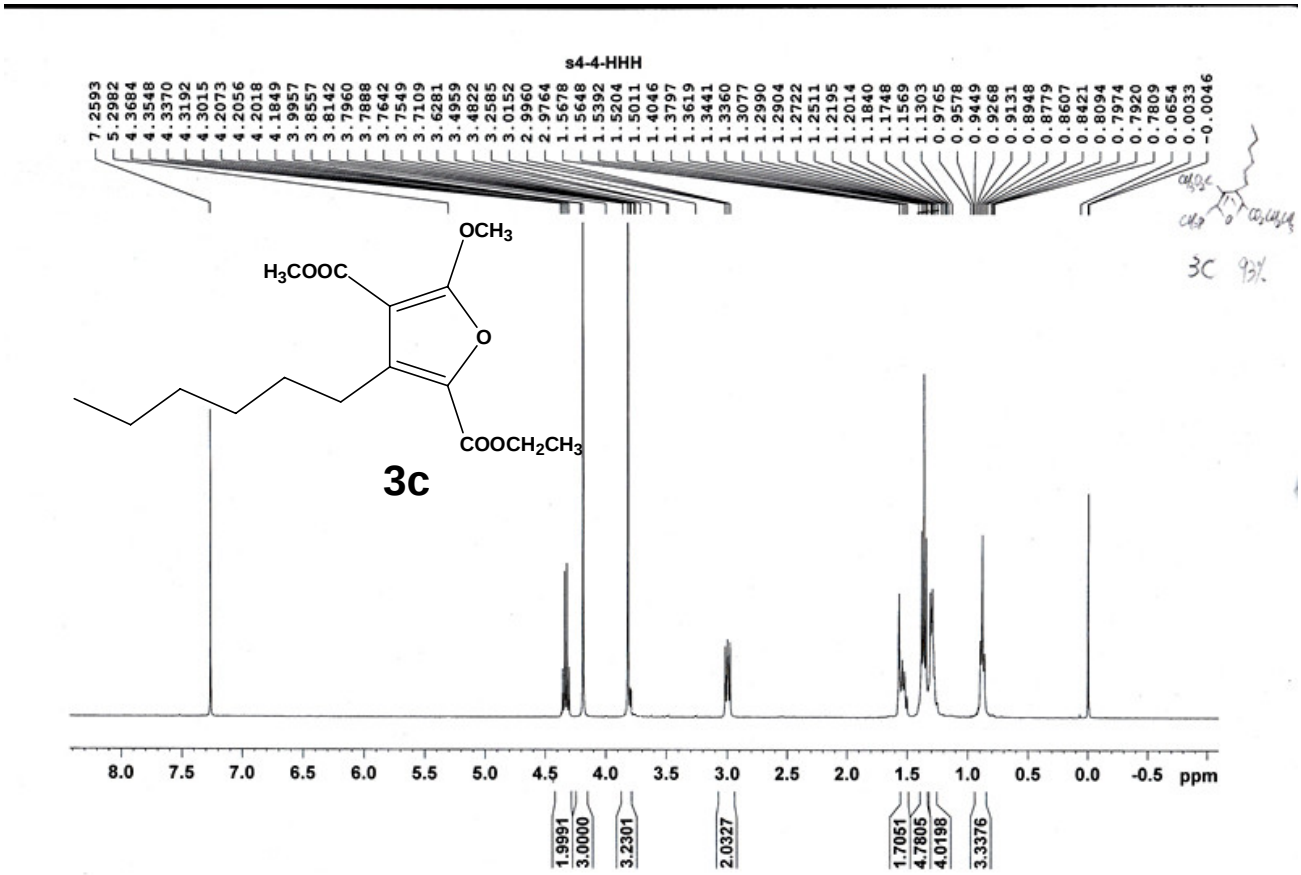


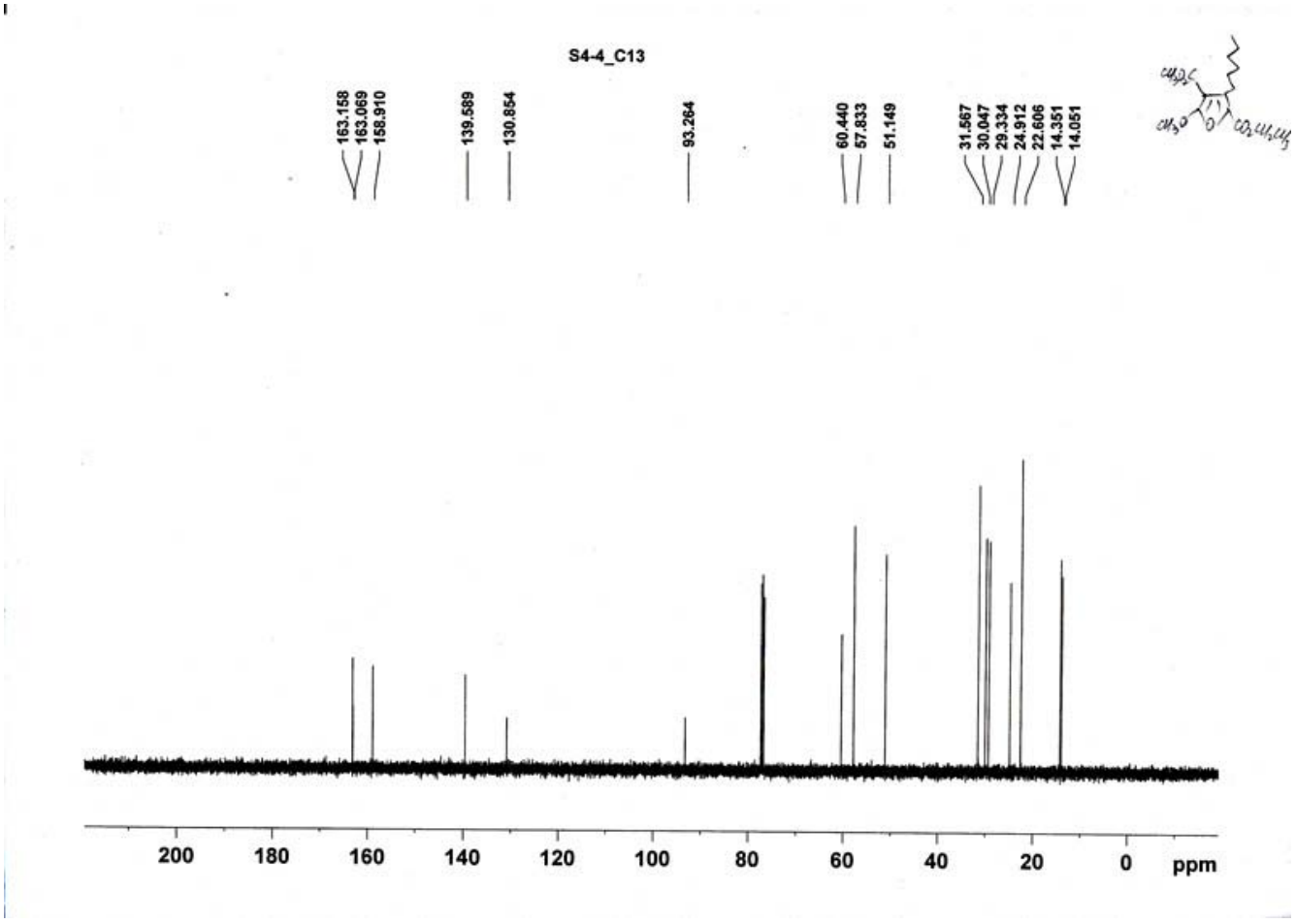


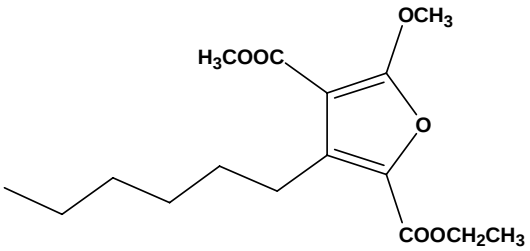
3b

HRMS exact mass calcd for ($C_{16}H_{24}O_6$+H) requires m/z 313.1646, found m/z 313.1644.



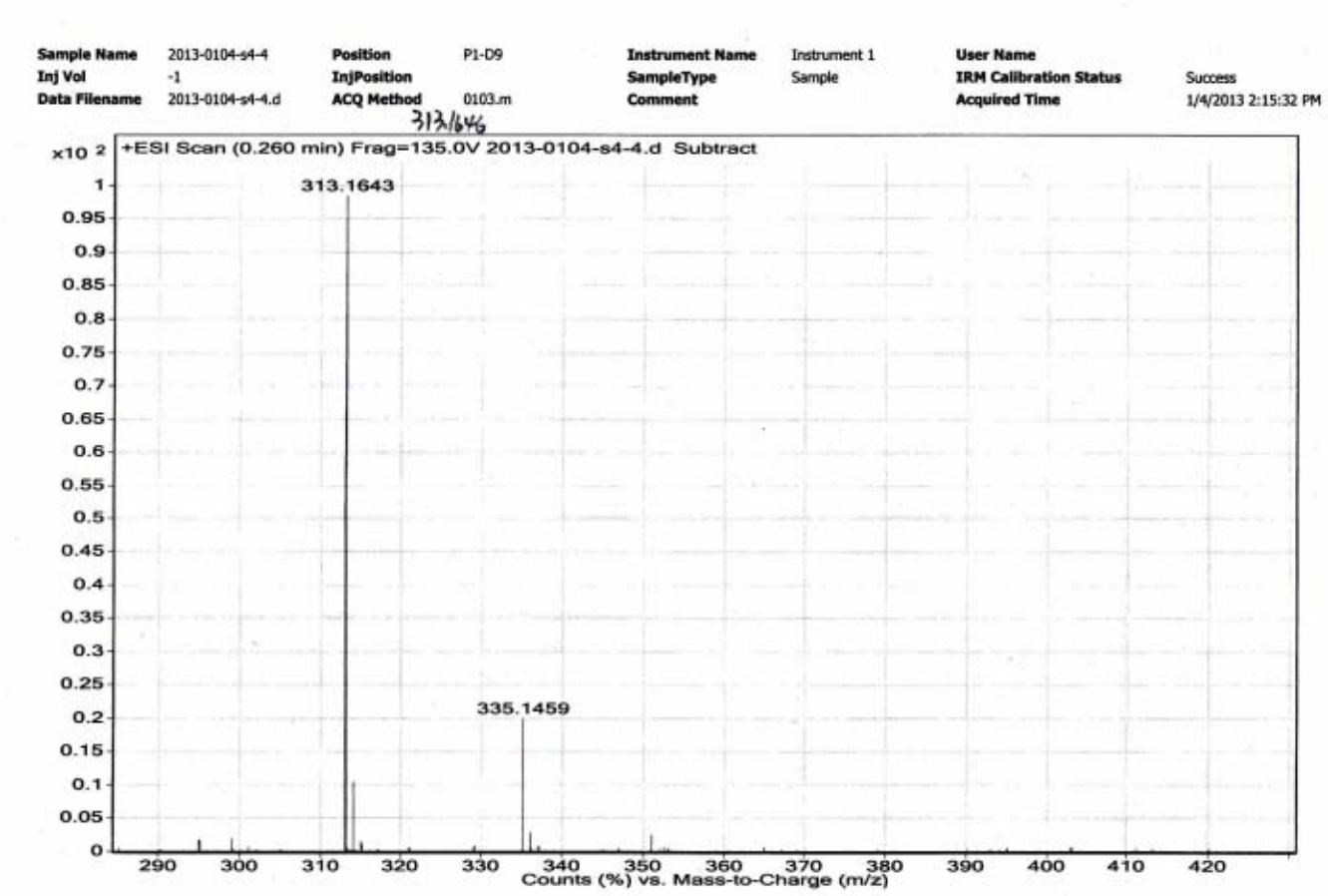

s4-4-HHH
7.2593
5.2982
4.3684
4.3548
4.3370
4.3192
4.3015
4.2073
4.2056
4.2018
4.1849
3.9957
3.8557
3.8142
3.7960
3.7888
3.7642
3.7549
3.7109
3.6281
3.4959
3.4822
3.2585
3.0152
2.9960
2.9764
1.5678
1.5648
1.5392
1.5204
1.5011
1.4046
1.3797
1.3619
1.3441
1.3360
1.3077
1.2990
1.2904
1.2722
1.2511
1.2195
1.2014
1.1840
1.1748
1.1569
1.1303
0.9765
0.9578
0.9449
0.9268
0.9131
0.8948
0.8779
0.8607
0.8421
0.8094
0.7974
0.7920
0.7809
0.0654
0.0033
-0.0046
OCH3
H3COOC
O
COOCH2CH3
3c
3C 93%
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
1.9991
3.0000
3.2301
2.0327
1.7051
4.7805
4.0198
3.3376

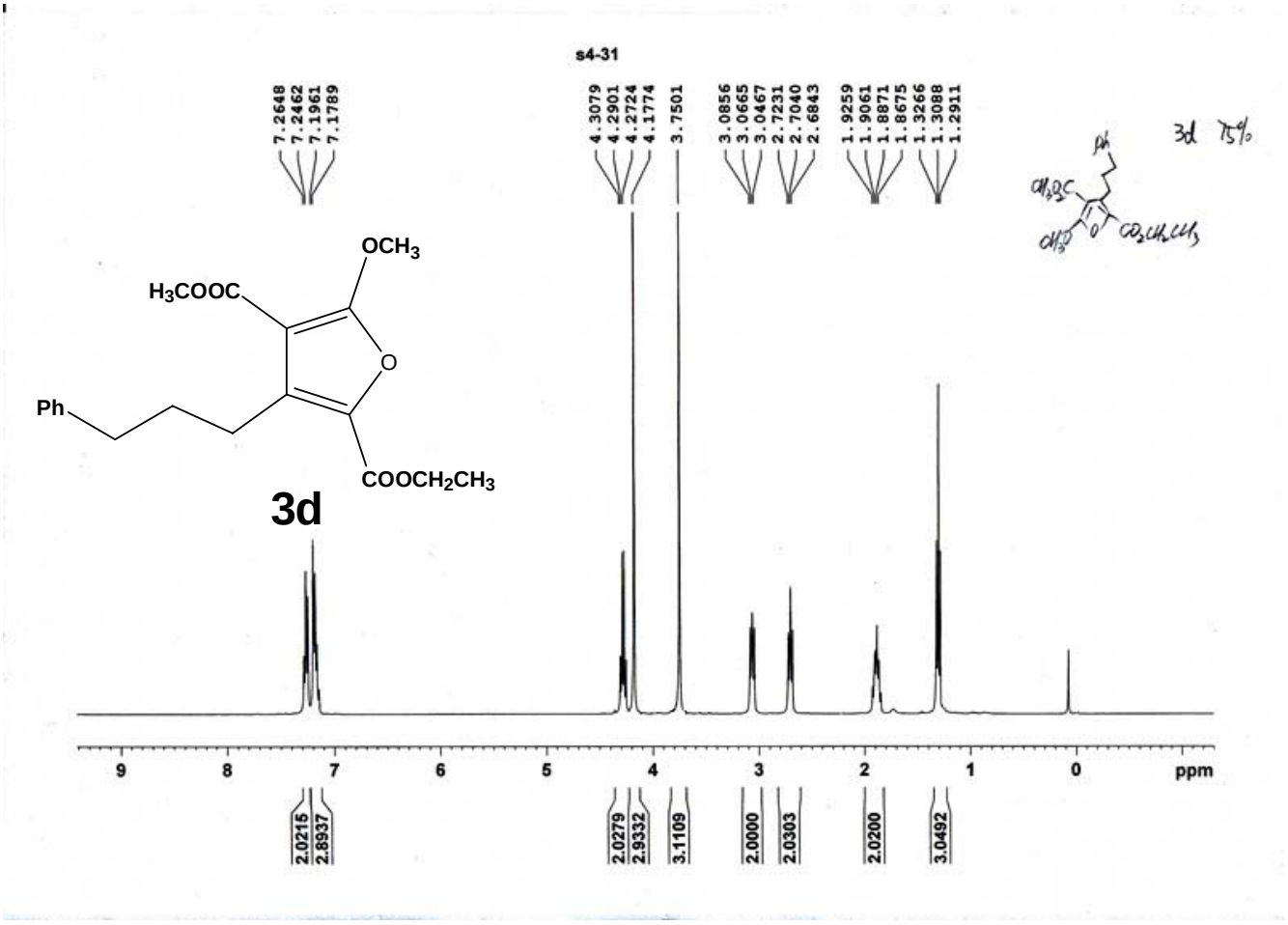

S4-4_C13
163.158
163.069
158.910
139.589
130.854
93.264
60.440
57.833
51.149
31.567
30.047
29.334
24.912
22.606
14.351
14.051
200 180 160 140 120 100 80 60 40 20 0 ppm



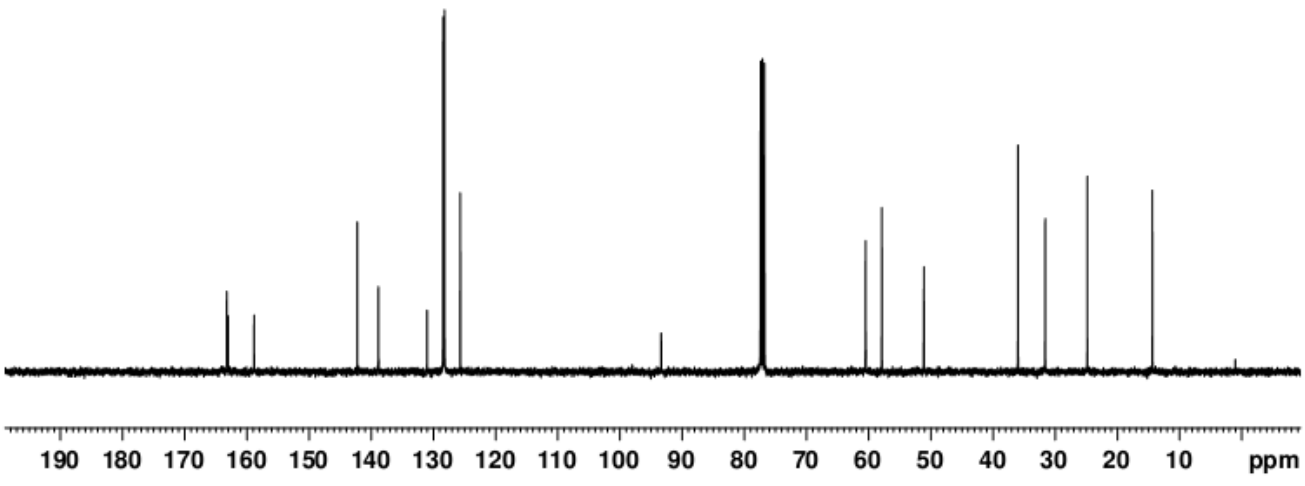
3c

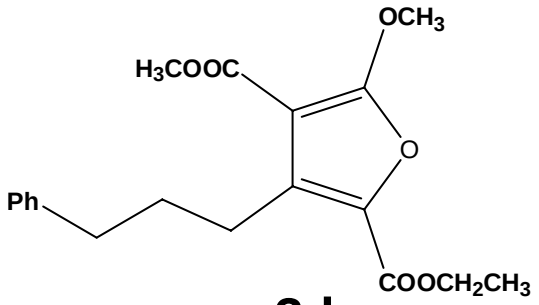
HRMS exact mass calcd for ($C_{16}H_{24}O_6$+H) requires m/z 313.1646, found m/z 313.1643.




s4-31
7.2648
7.2462
7.1961
7.1789
4.3079
4.2901
4.2724
4.1774
3.7501
3.0856
3.0665
3.0467
2.7231
2.7040
2.6843
1.9259
1.9061
1.8871
1.8675
1.3266
1.3088
1.2911
OCH3
H3COOC
O
Ph
COOCH2CH3
3d
3d 75%
9
8
7
6
5
4
3
2
1
0
ppm
2.0215
2.8937
2.0279
2.9332
3.1109
2.0000
2.0303
2.0200
3.0492

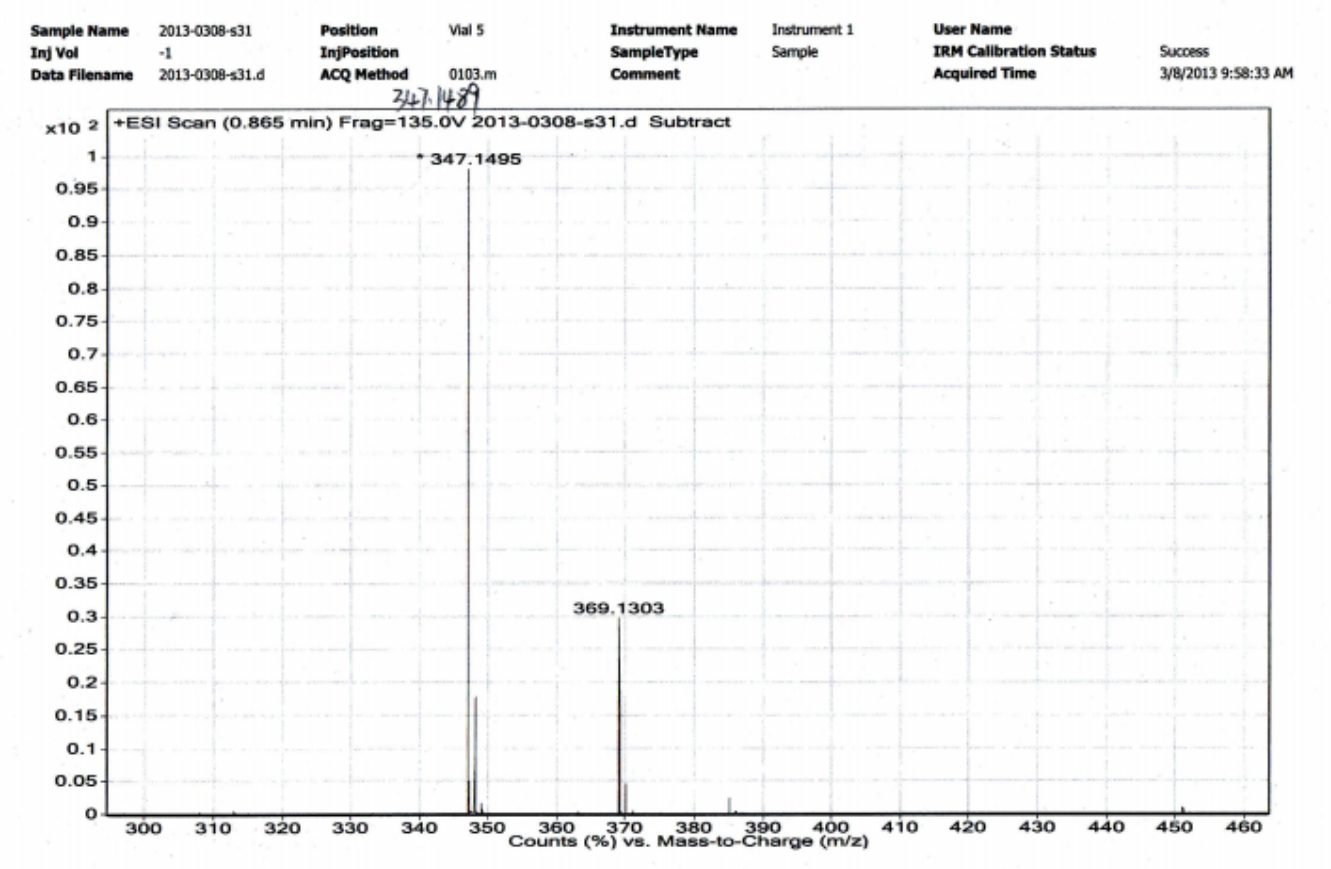

163.246
163.009
158.837
142.254
138.852
131.014
128.454
128.218
125.691
93.377
77.386
77.068
76.750
60.500
60.475
57.879
51.151
51.111
35.975
31.606
24.827
14.369


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

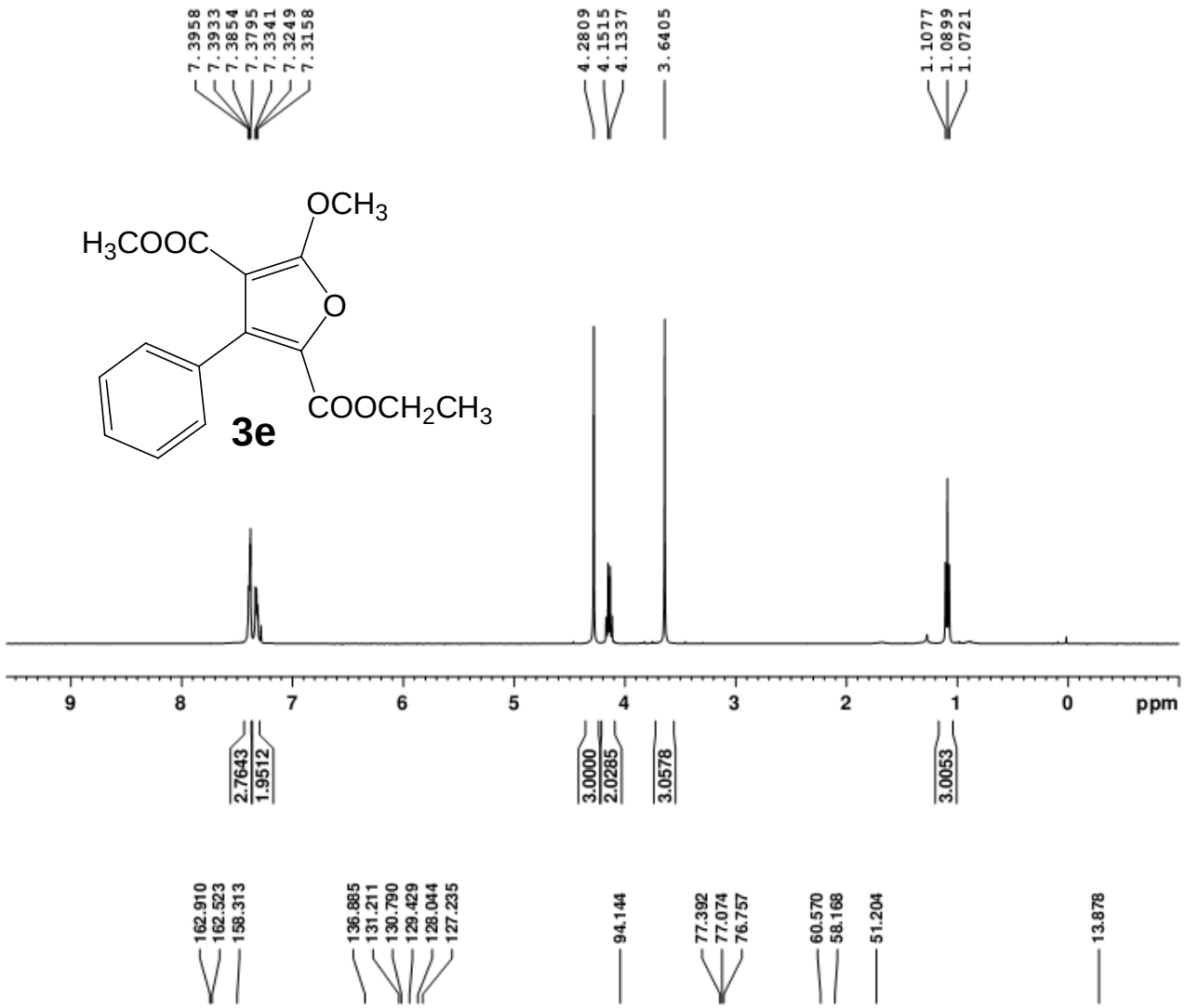


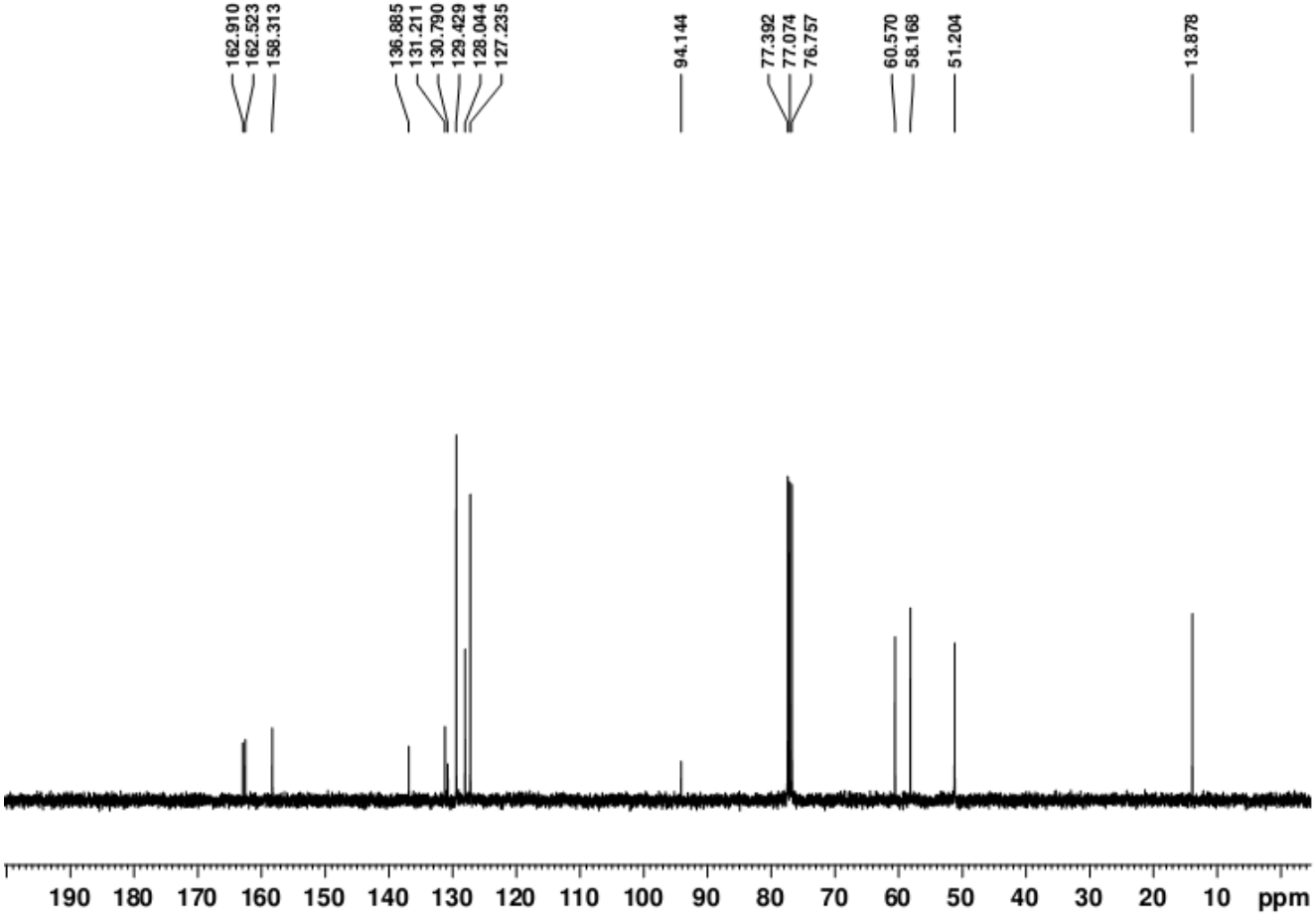
3d

HRMS exact mass calcd for ($C_{19}H_{22}O_6$+H) requires m/z 347.1489, found m/z 347.1495.

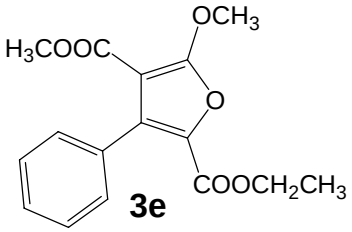


This journal is © The Royal Society of Chemistry 2013



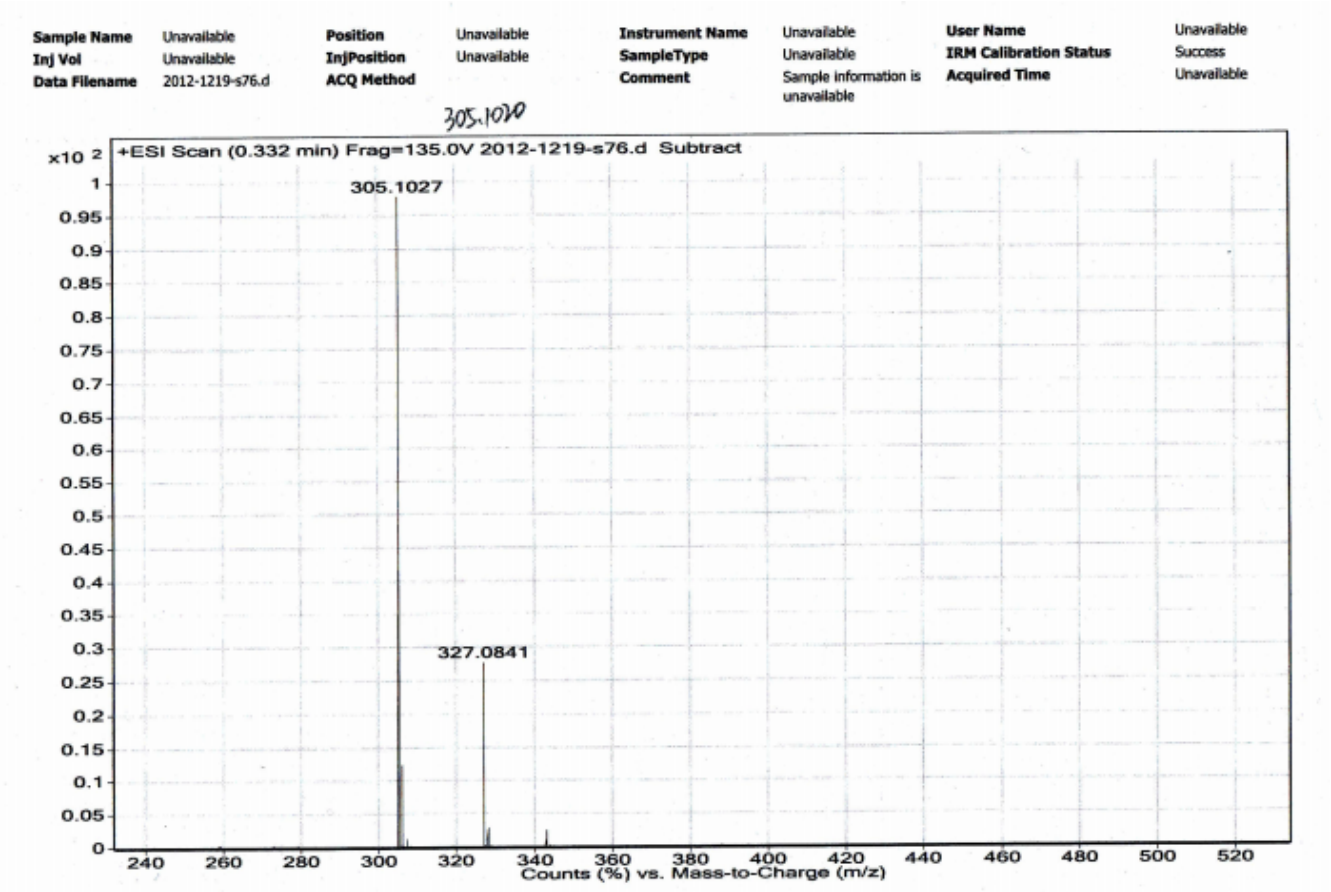


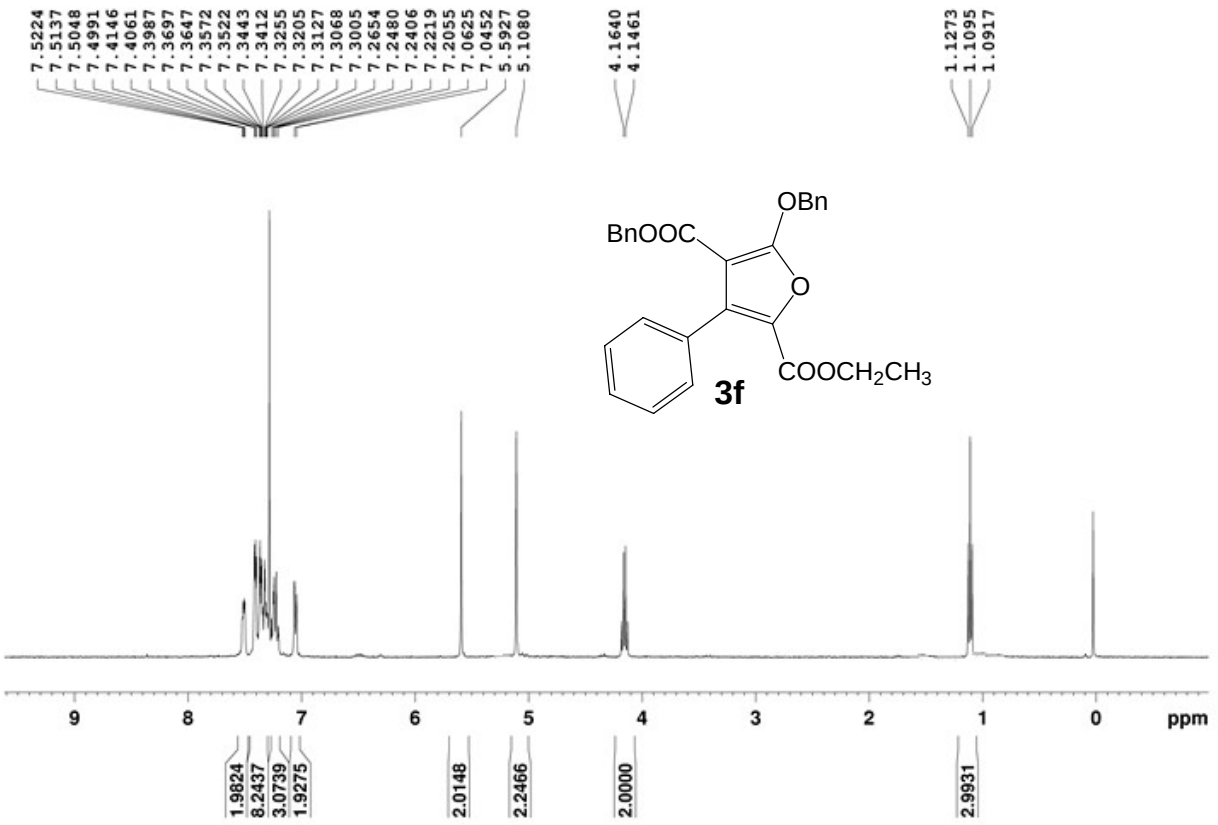
This journal is © The Royal Society of Chemistry 2013

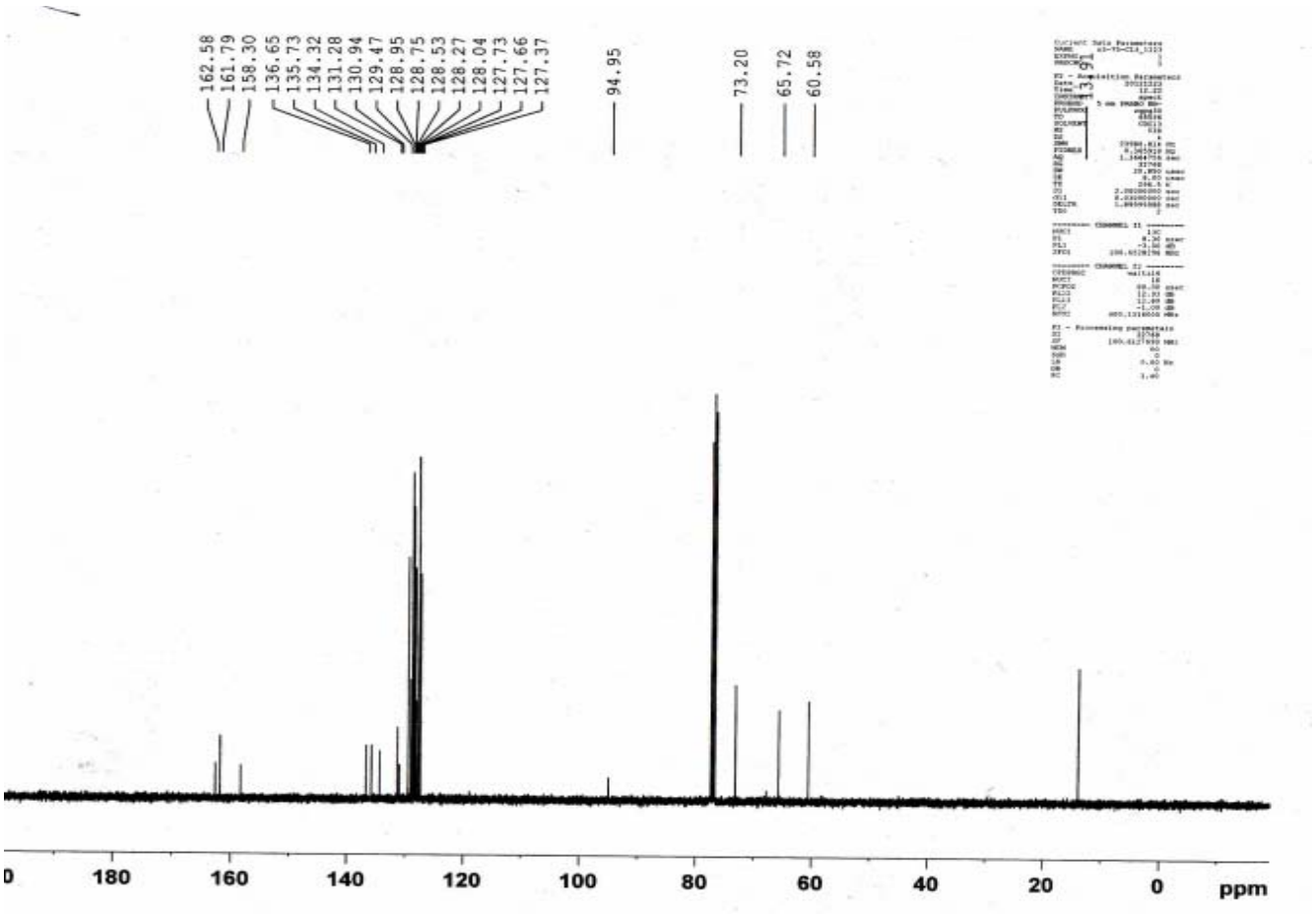


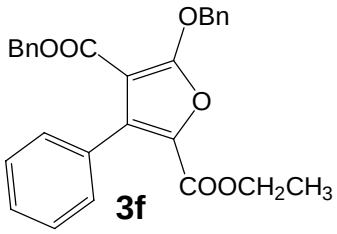
3e

HRMS exact mass calcd for ($C_{16}H_{16}O_6$+H) requires m/z 305.1020, found m/z 305.1027.



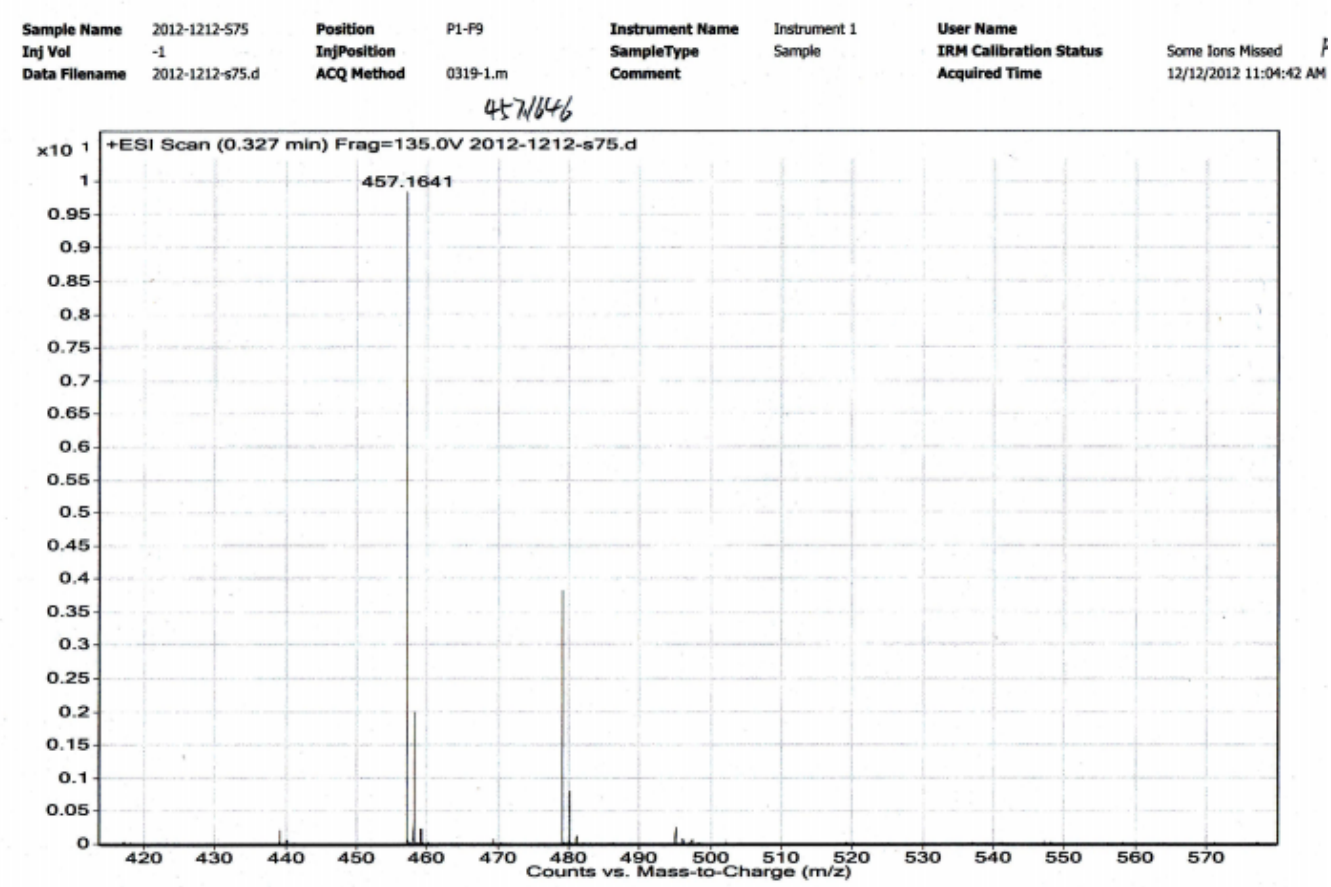

7.5224
7.5137
7.5048
7.4991
7.4146
7.4061
7.3987
7.3697
7.3647
7.3572
7.3522
7.3443
7.3412
7.3255
7.3205
7.3127
7.3068
7.3005
7.2654
7.2480
7.2406
7.2219
7.2055
7.0625
7.0452
5.5927
5.1080
4.1640
4.1461
1.1273
1.1095
1.0917
OBn
BnOOC
O
COOCH2CH3
3f
9
8
7
6
5
4
3
2
1
0
ppm
1.9824
8.2437
3.0739
1.9275
2.0148
2.2466
2.0000
2.9931


162.58
161.79
158.30
136.65
135.73
134.32
131.28
130.94
129.47
128.95
128.75
128.53
128.27
128.04
127.73
127.66
127.37
94.95
73.20
65.72
60.58
180
160
140
120
100
80
60
40
20
0
ppm

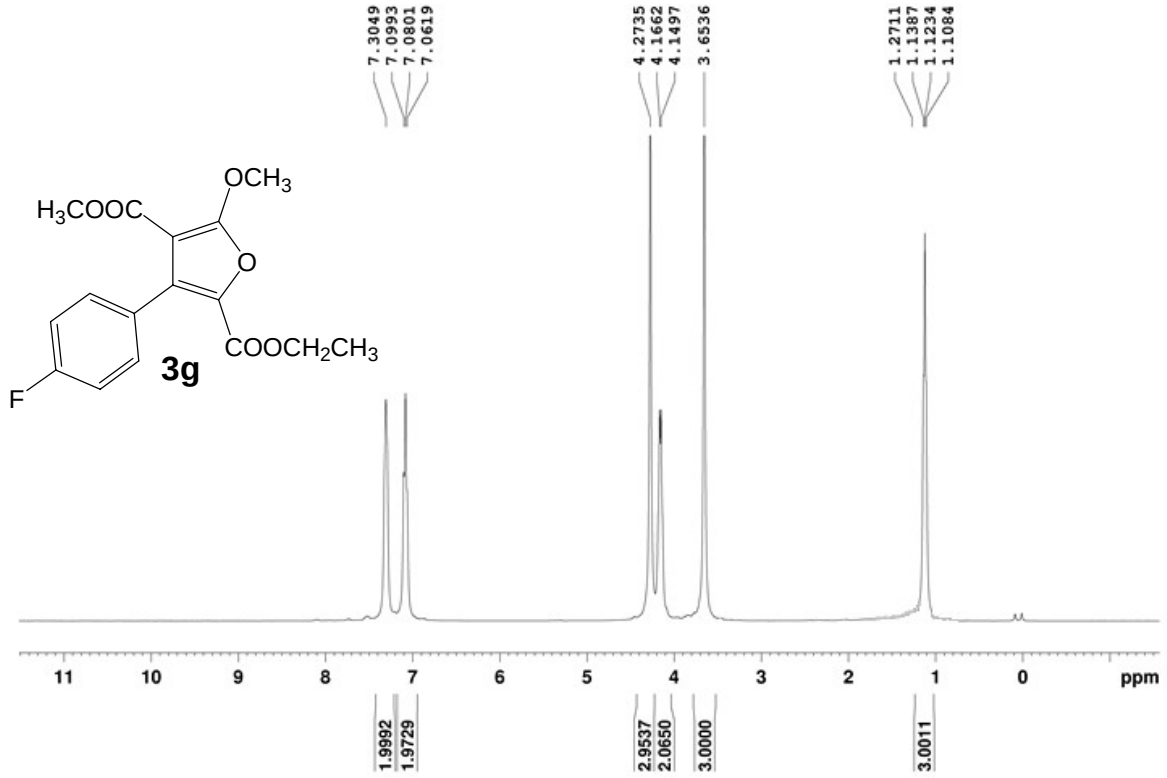


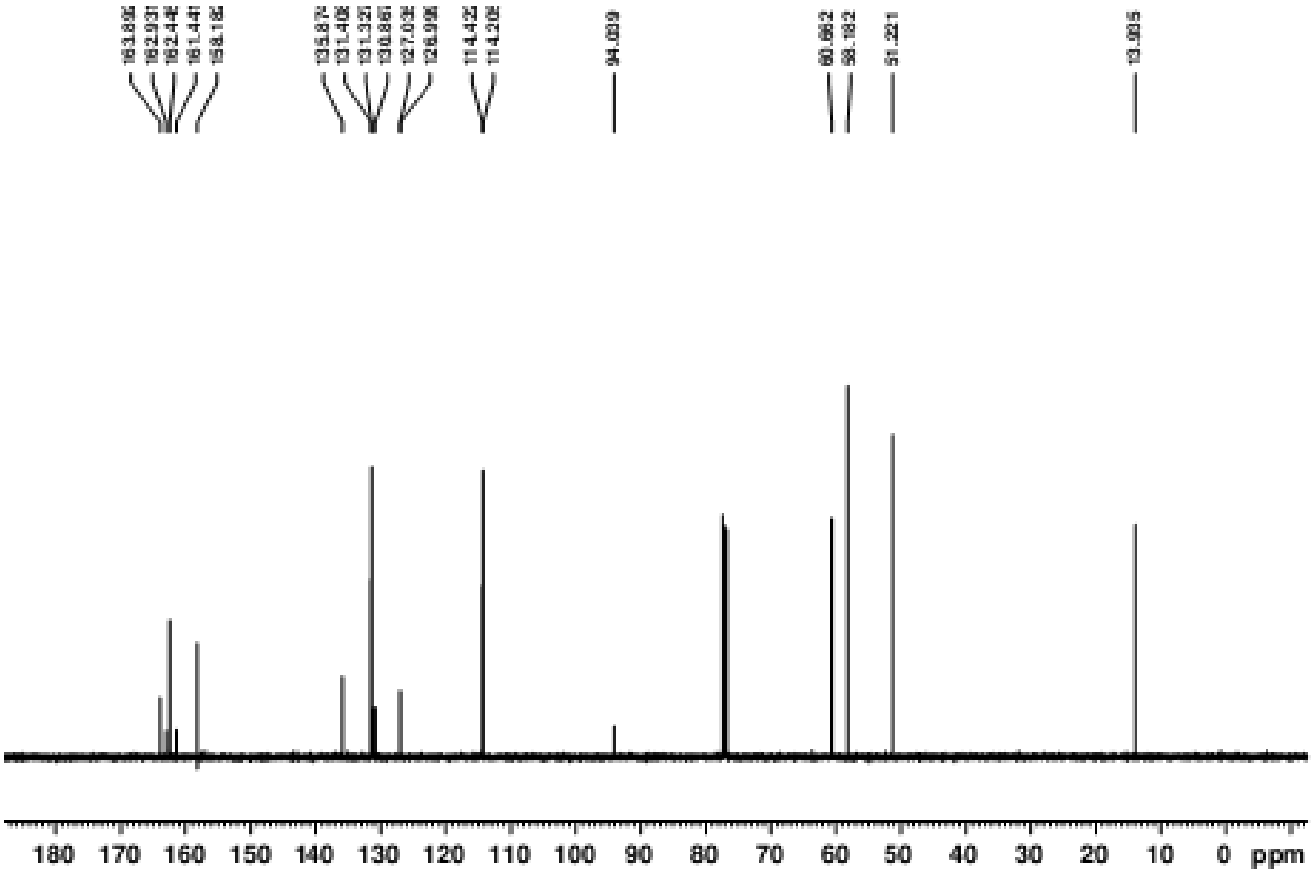
3f

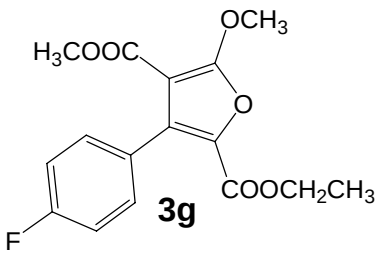
HRMS exact mass calcd for ($C_{28}H_{24}O_6$+H) requires m/z 457.1646, found m/z 457.1641.



This journal is © The Royal Society of Chemistry 2013

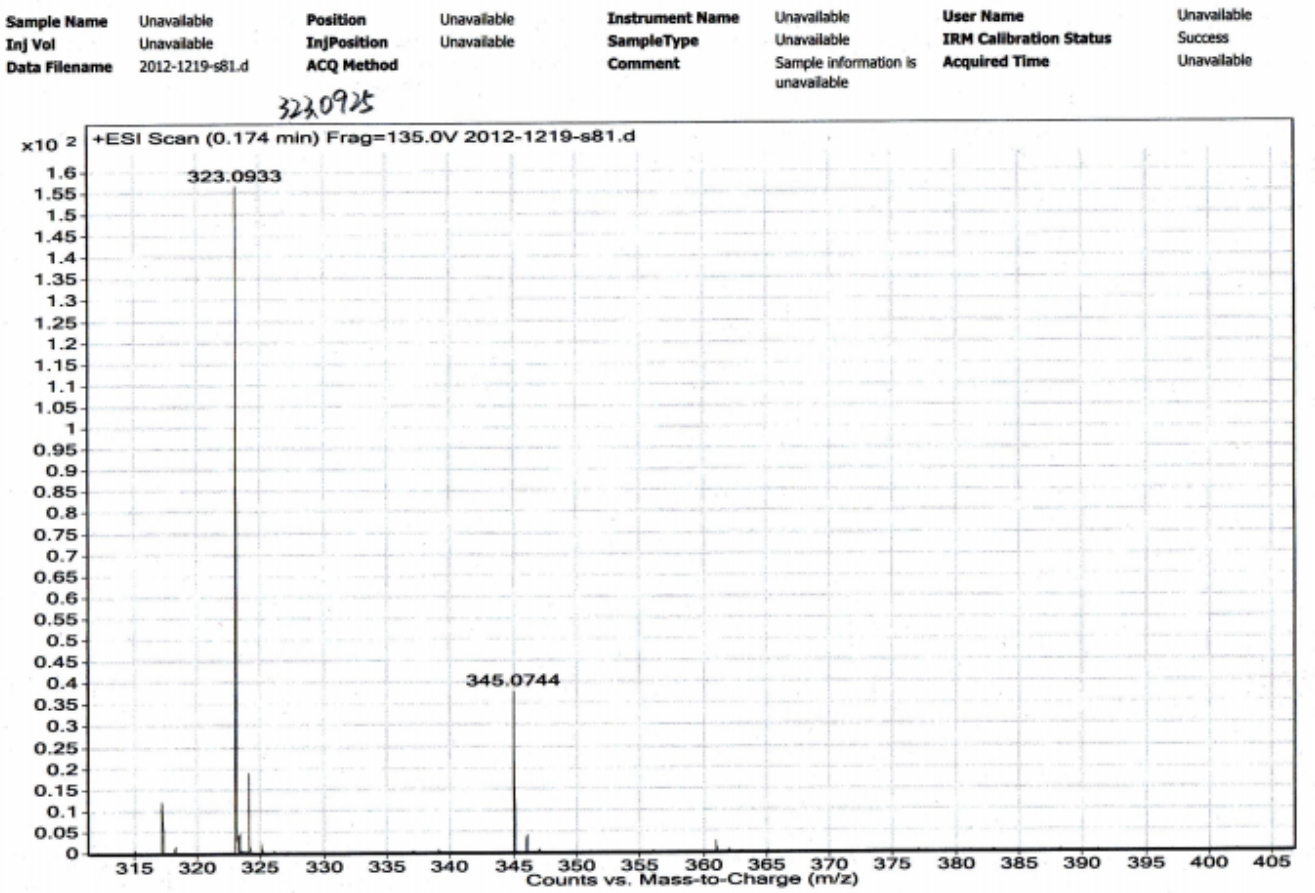




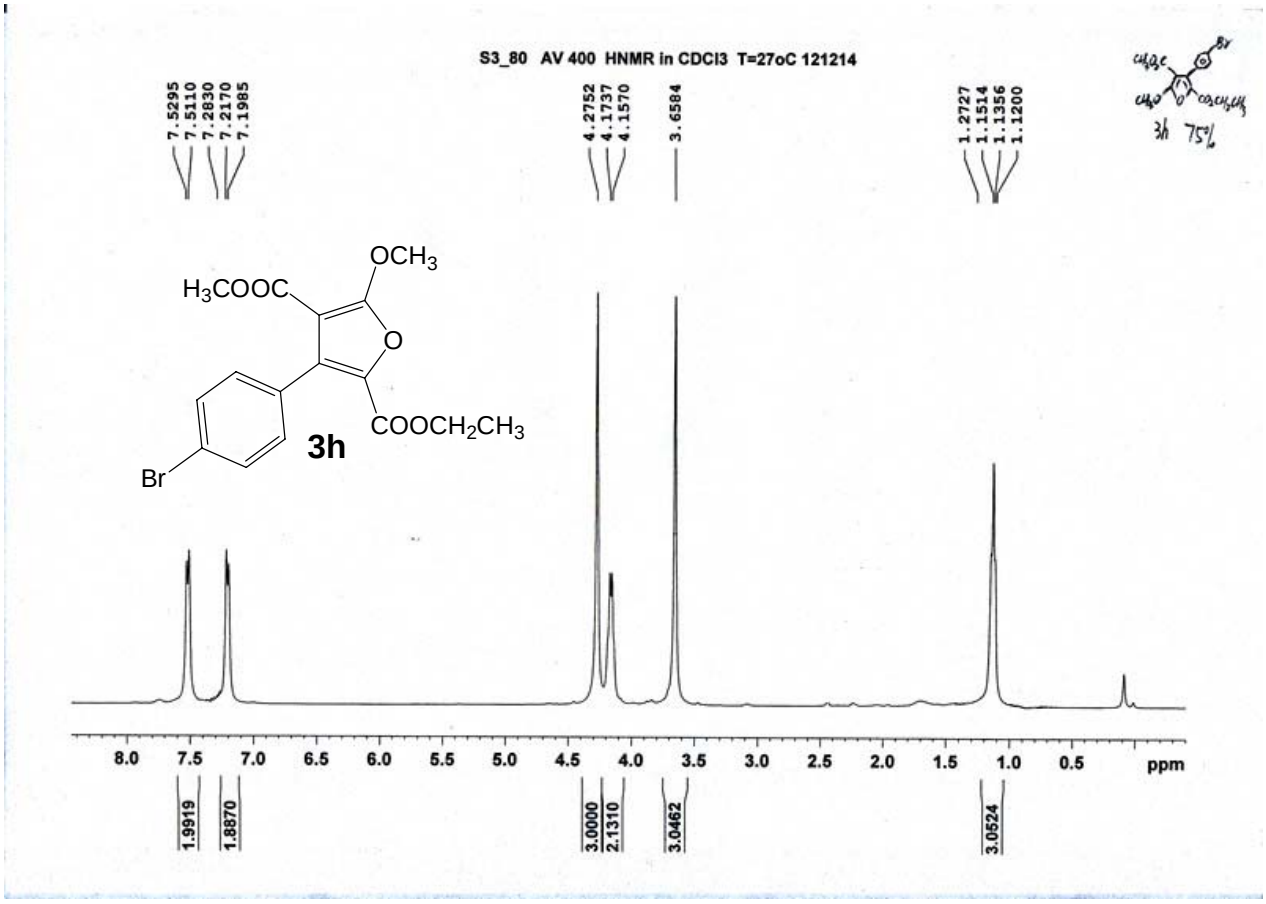


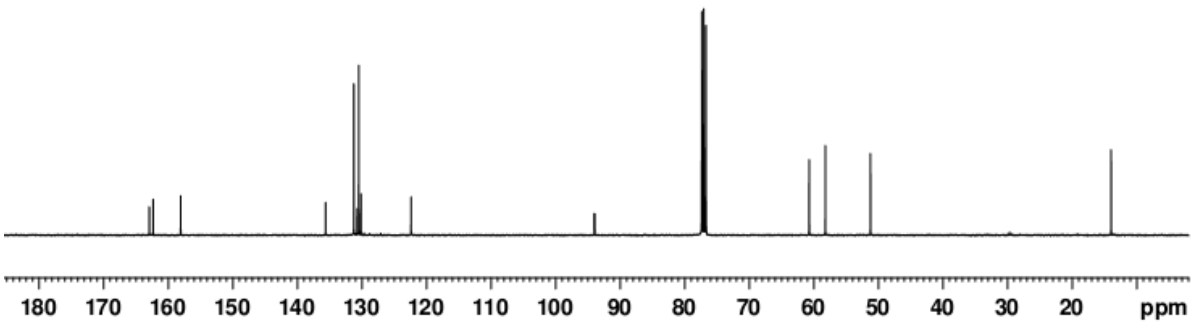
3g

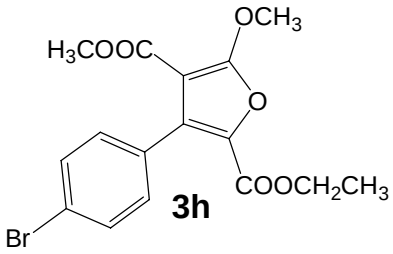
HRMS exact mass calcd for ($C_{16}H_{15}O_6F$+H) requires m/z 323.0925, found m/z 323.0933.



This journal is © The Royal Society of Chemistry 2013

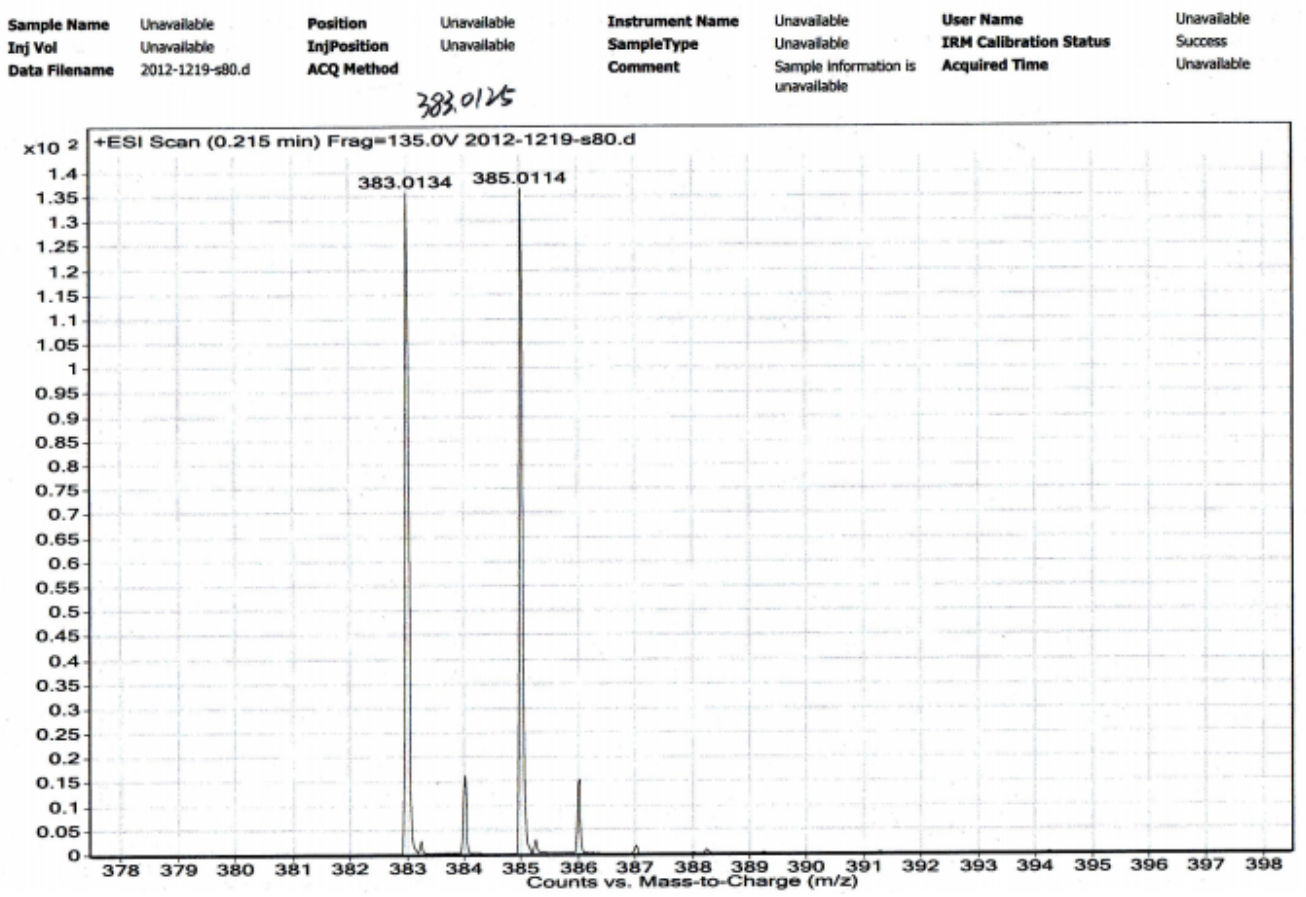




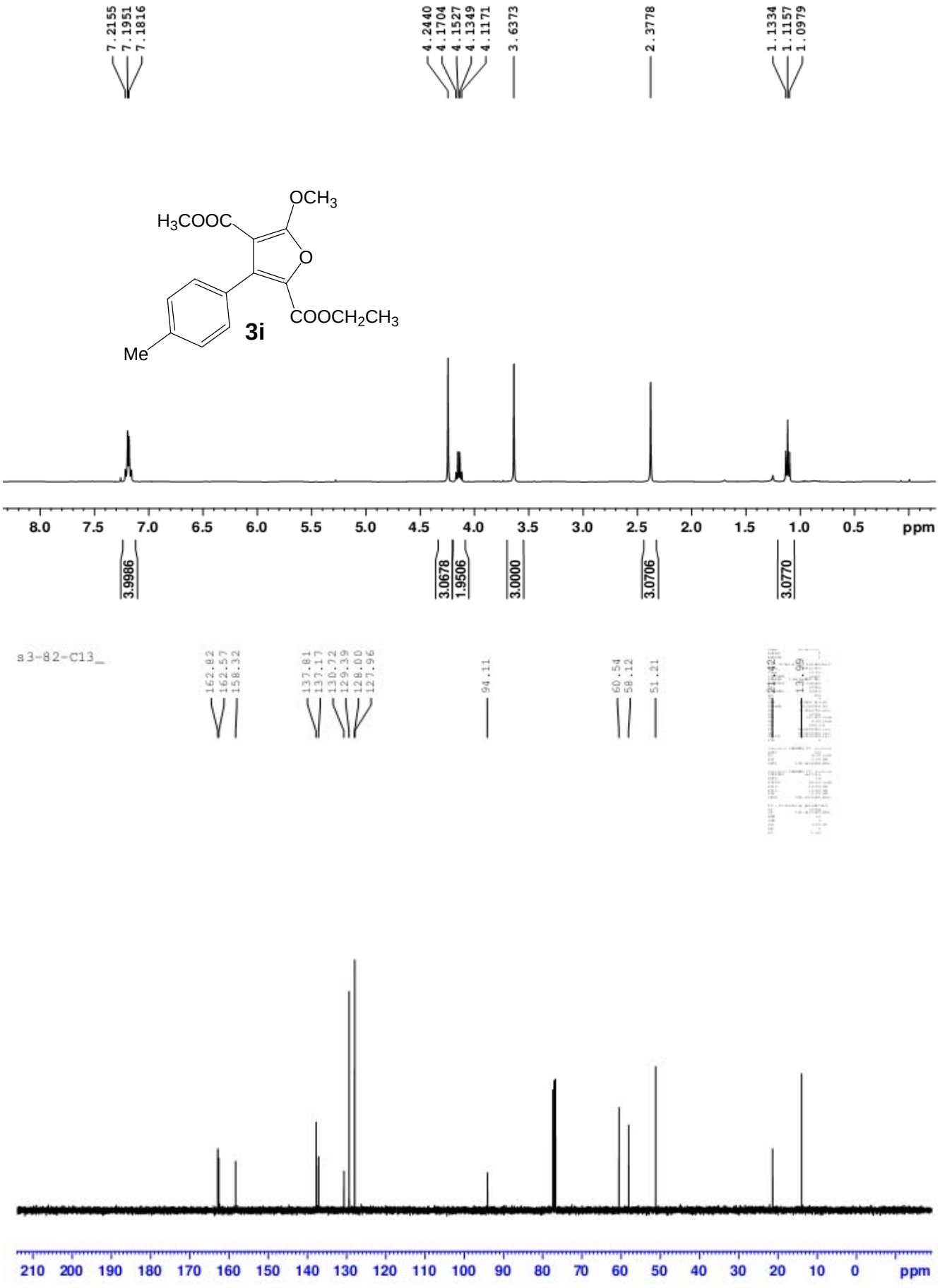


3h

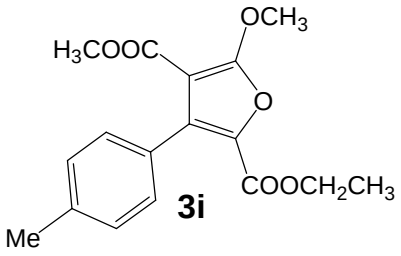
HRMS exact mass calcd for ($C_{16}H_{15}O_6Br$+H) requires m/z 383.0125, found m/z 383.0134, 385.0114.



This journal is © The Royal Society of Chemistry 2013

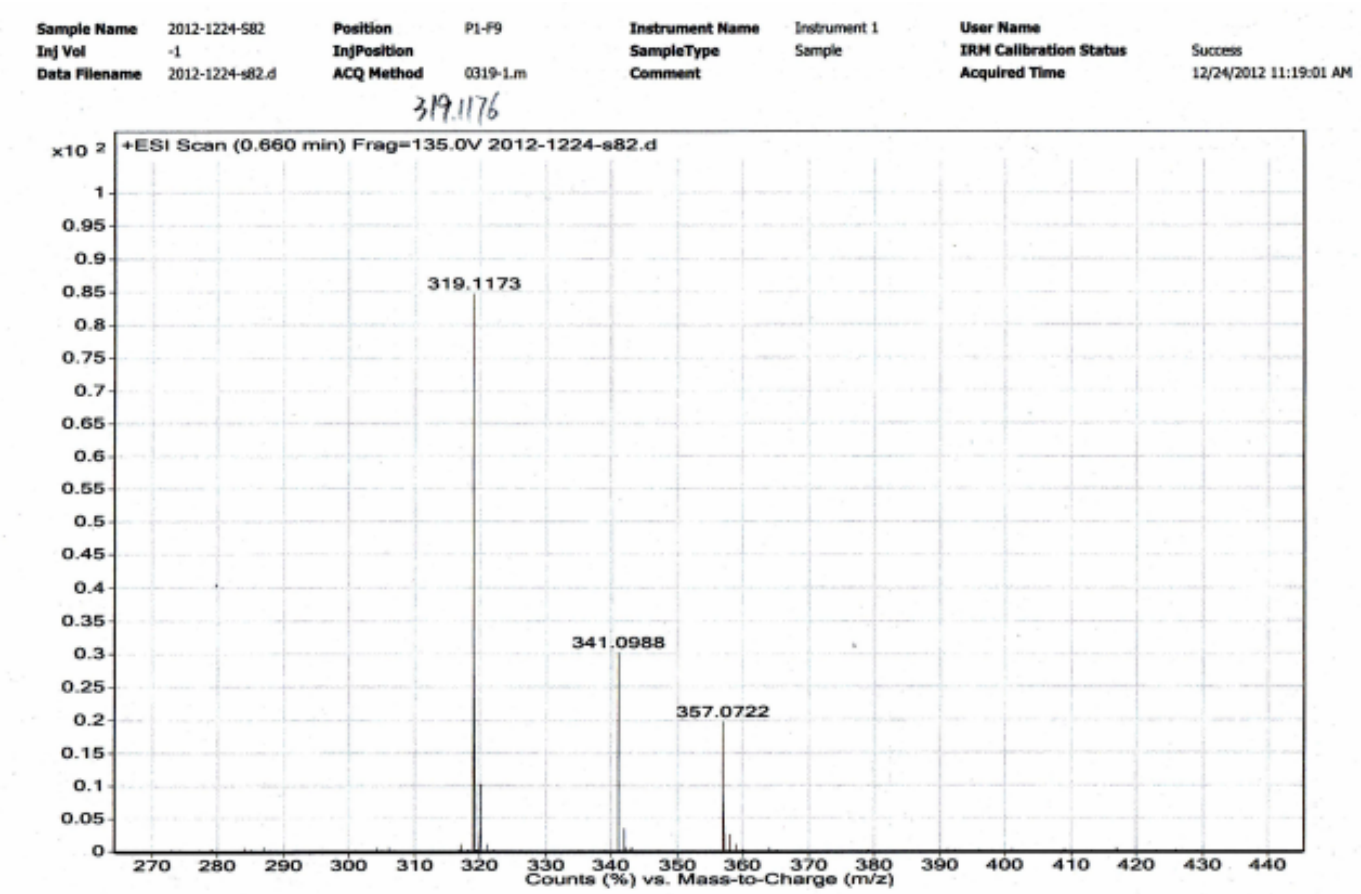


This journal is © The Royal Society of Chemistry 2013

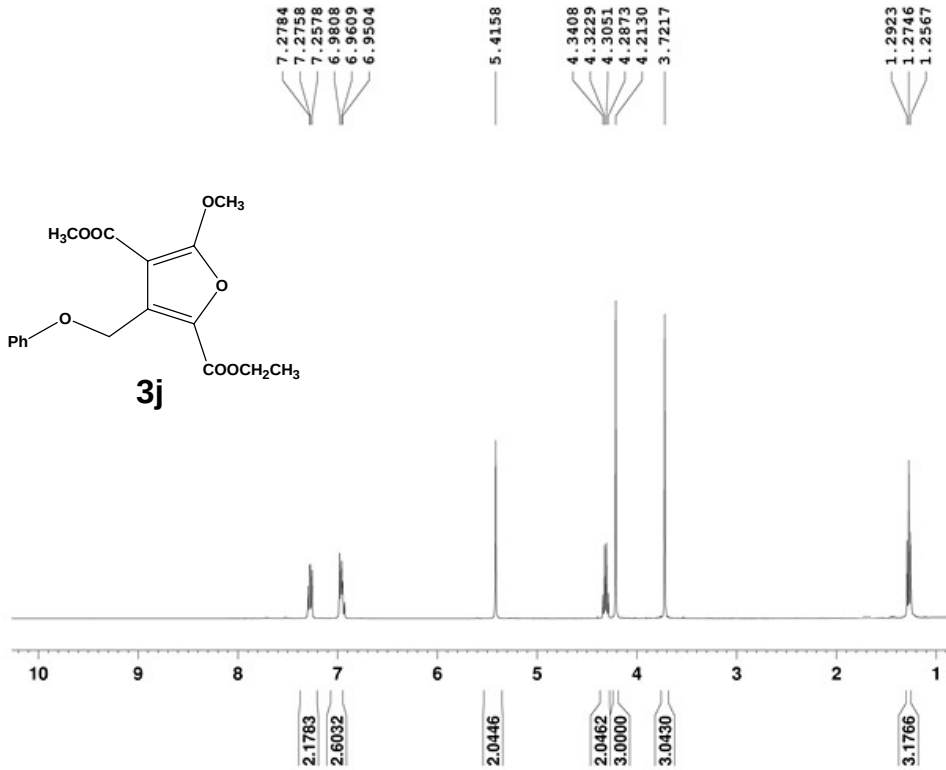


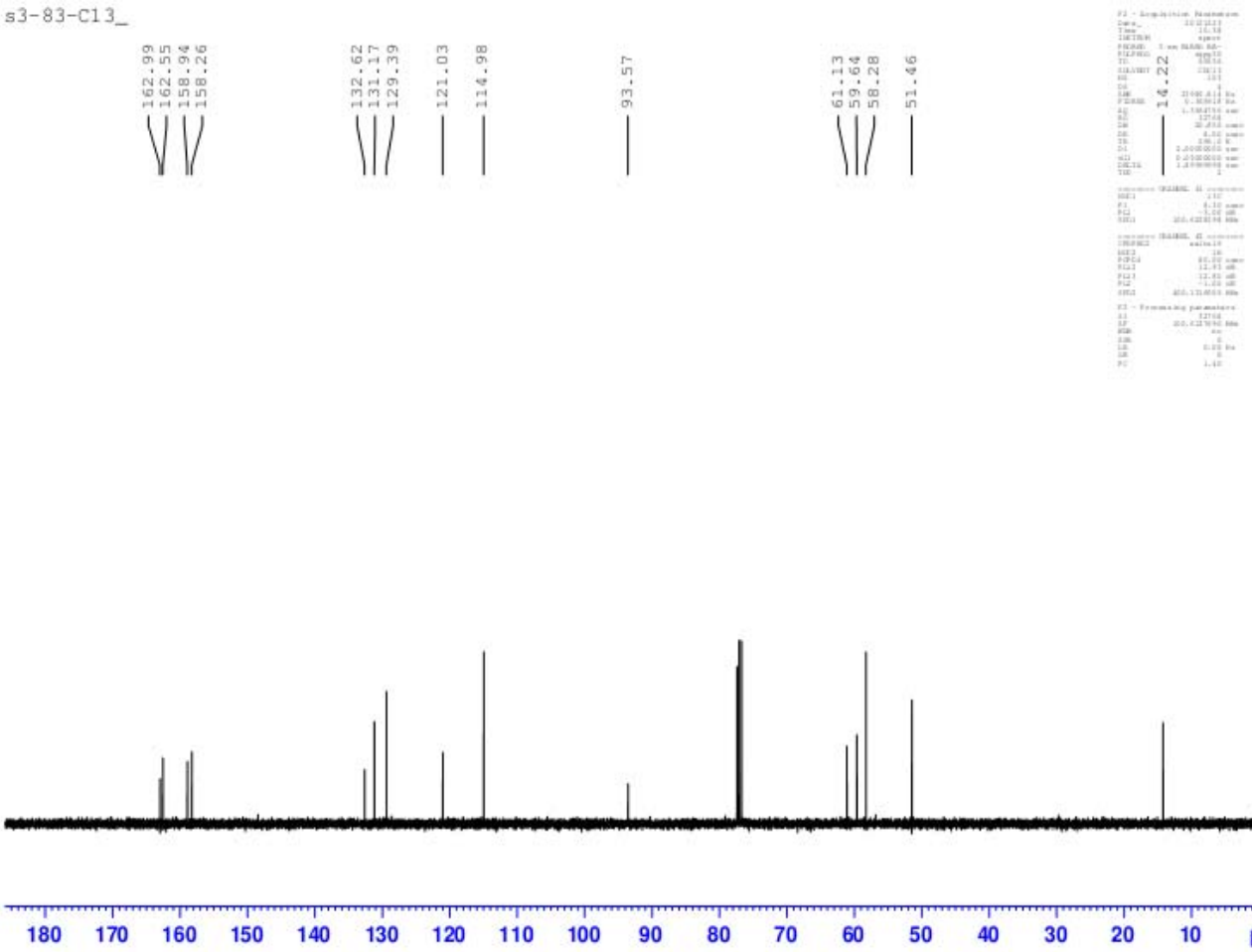
3i

HRMS exact mass calcd for ($C_{17}H_{18}O_6$+Na) requires m/z 319.1176, found m/z 319.1173.

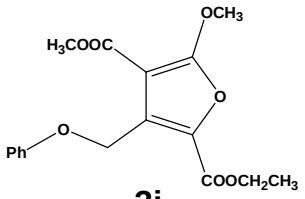


This journal is © The Royal Society of Chemistry 2013



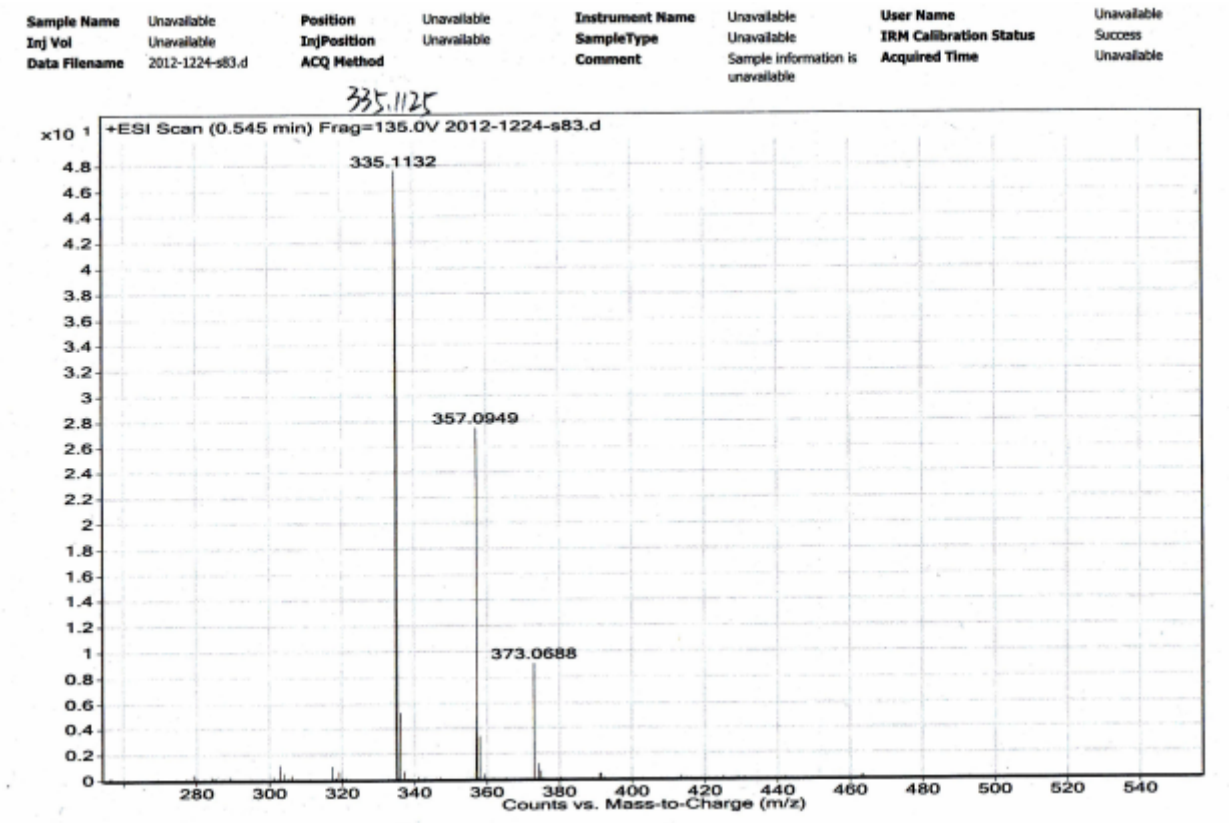


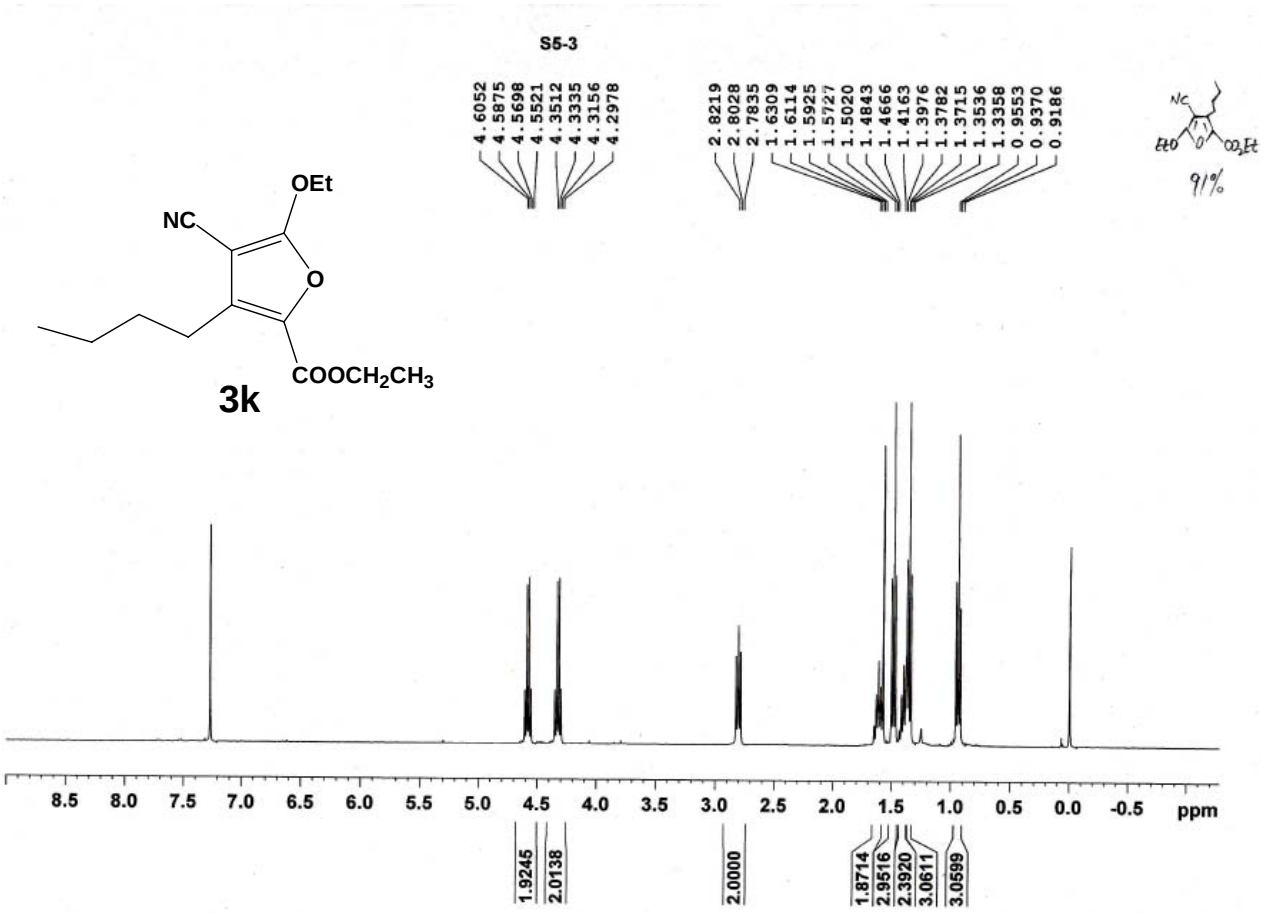
This journal is © The Royal Society of Chemistry 2013

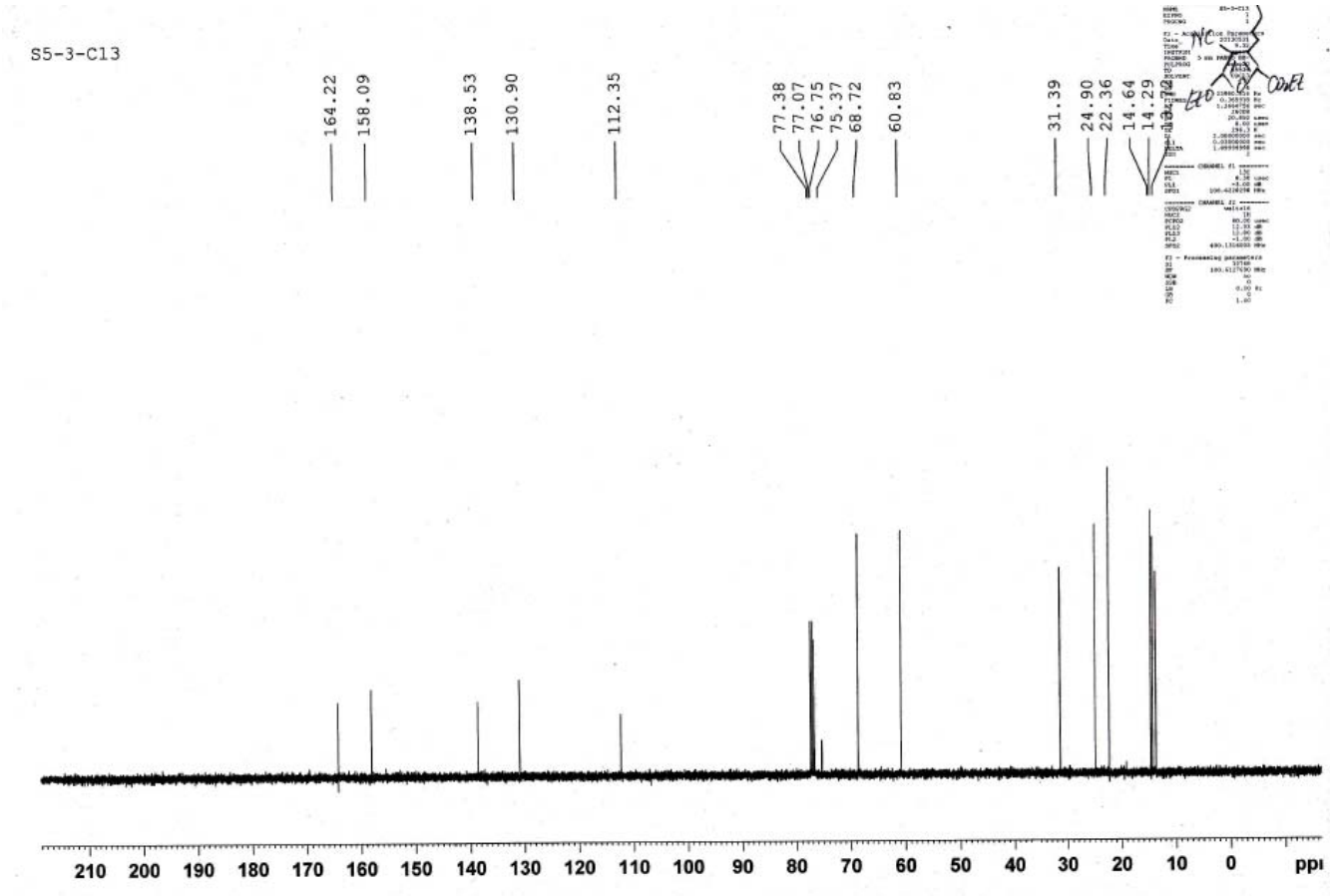


3j

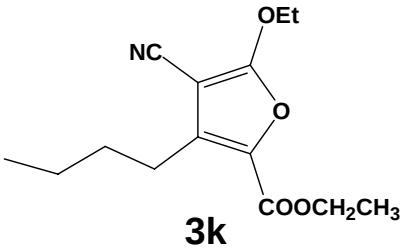
HRMS exact mass calcd for ($C_{17}H_{18}O_7$+H) requires m/z 335.1125, found m/z 335.1132.




S5-3
4.6052
4.5875
4.5698
4.5521
4.3512
4.3335
4.3156
4.2978
2.8219
2.8028
2.7835
1.6309
1.6114
1.5925
1.5727
1.5020
1.4843
1.4666
1.4163
1.3976
1.3782
1.3715
1.3536
1.3358
0.9553
0.9370
0.9186
91%
OEt
NC
O
COOCH2CH3
3k
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
1.9245
2.0138
2.0000
1.8714
2.9516
2.3920
3.0611
3.0599

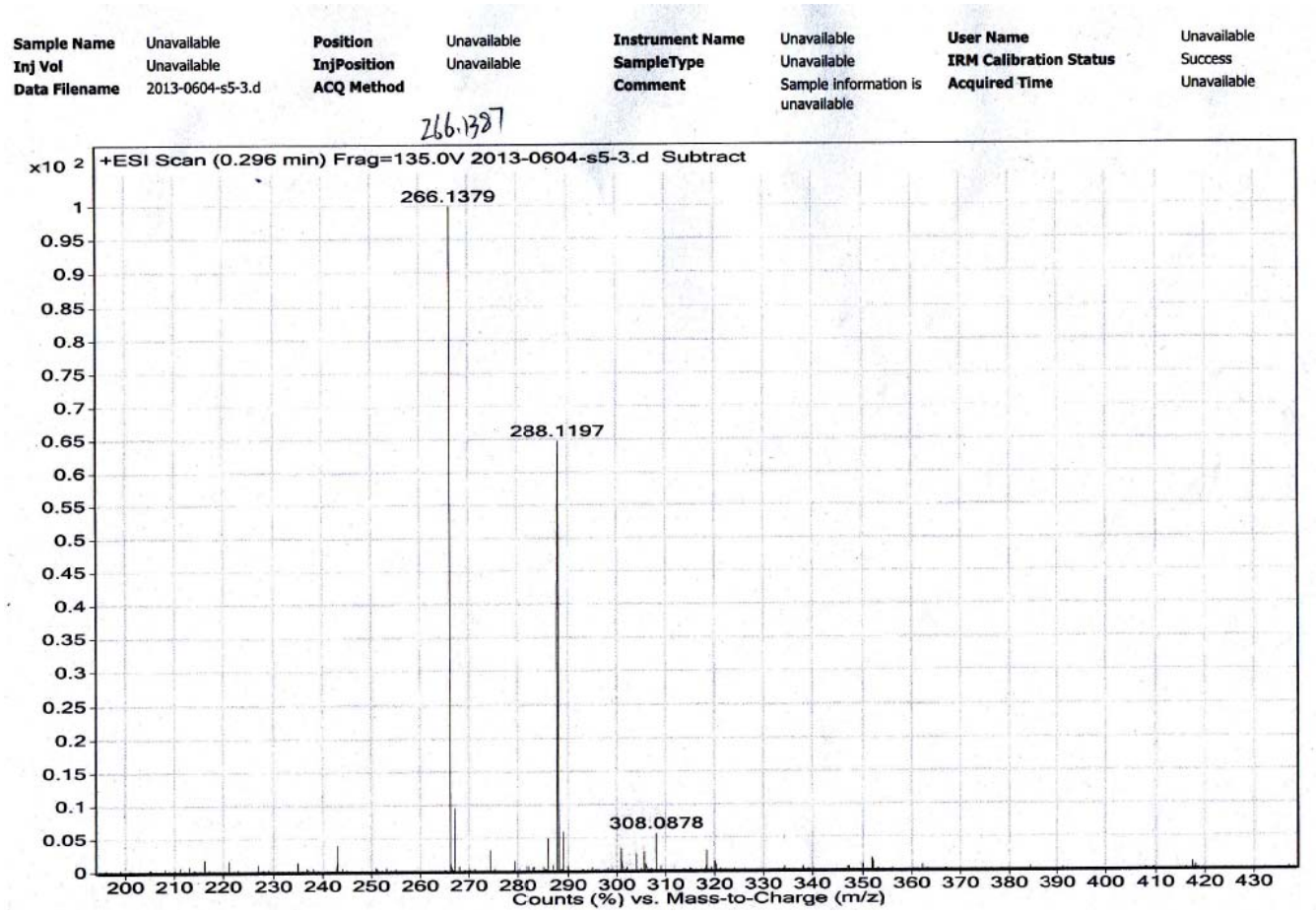

S5-3-C13
164.22
158.09
138.53
130.90
112.35
77.38
77.07
76.75
75.37
68.72
60.83
31.39
24.90
22.36
14.64
14.29
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

This journal is © The Royal Society of Chemistry 2013

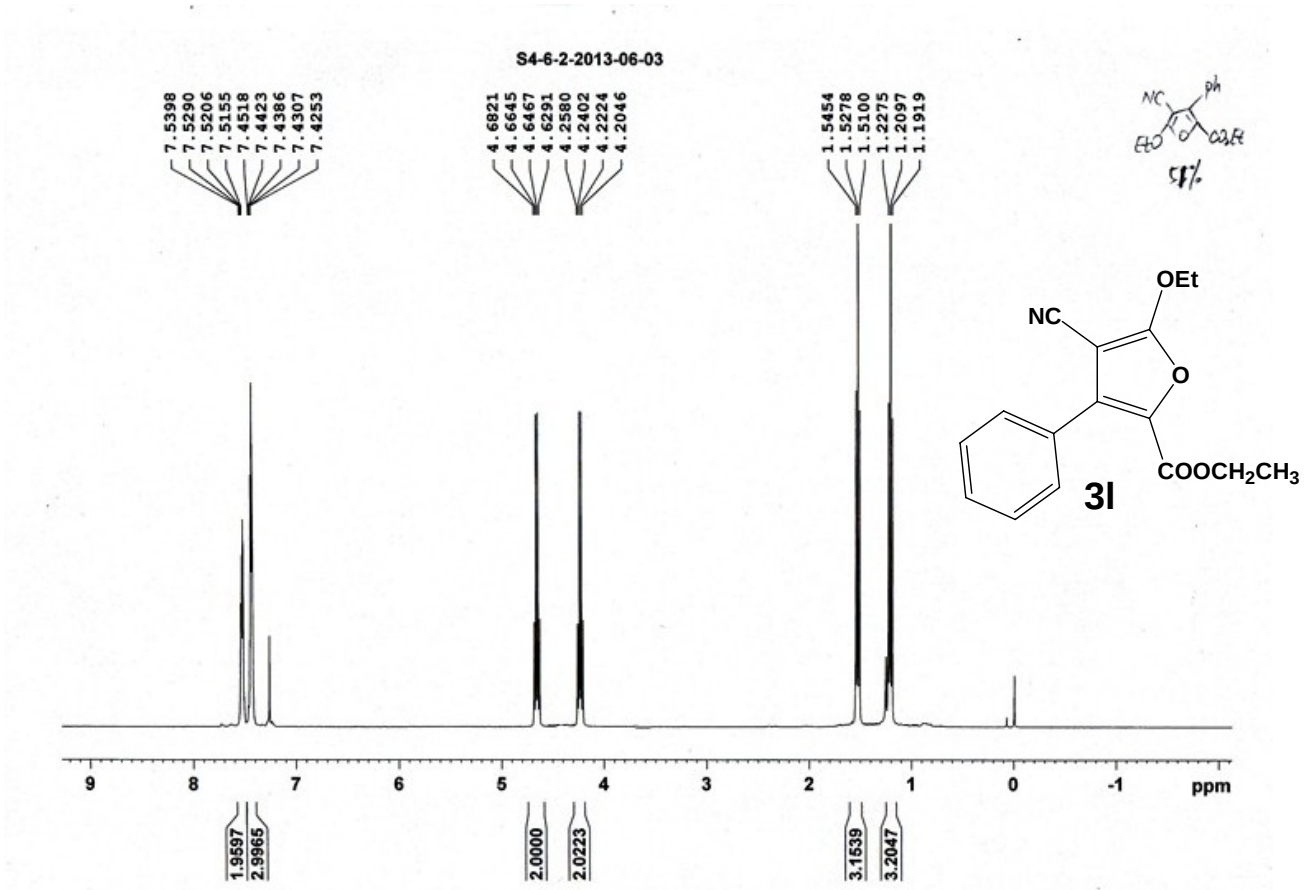


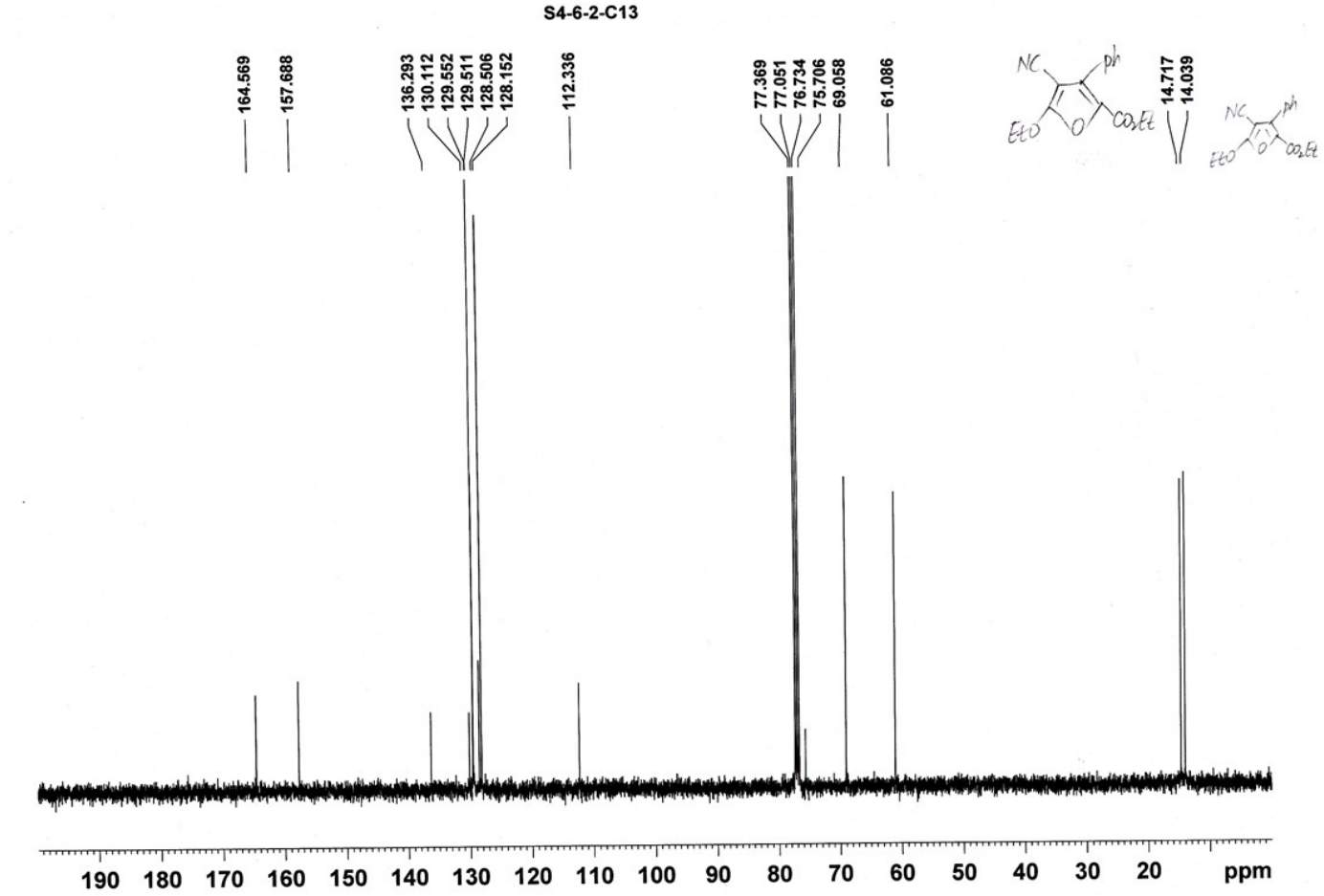
3k

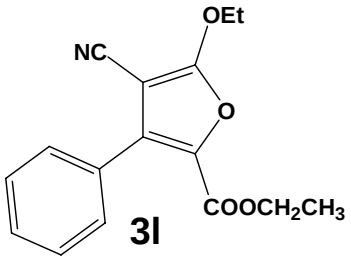
HRMS exact mass calcd for ($C_{14}H_{29}O_4N$+H) requires m/z 266.1387, found m/z 266.1379.



This journal is © The Royal Society of Chemistry 2013

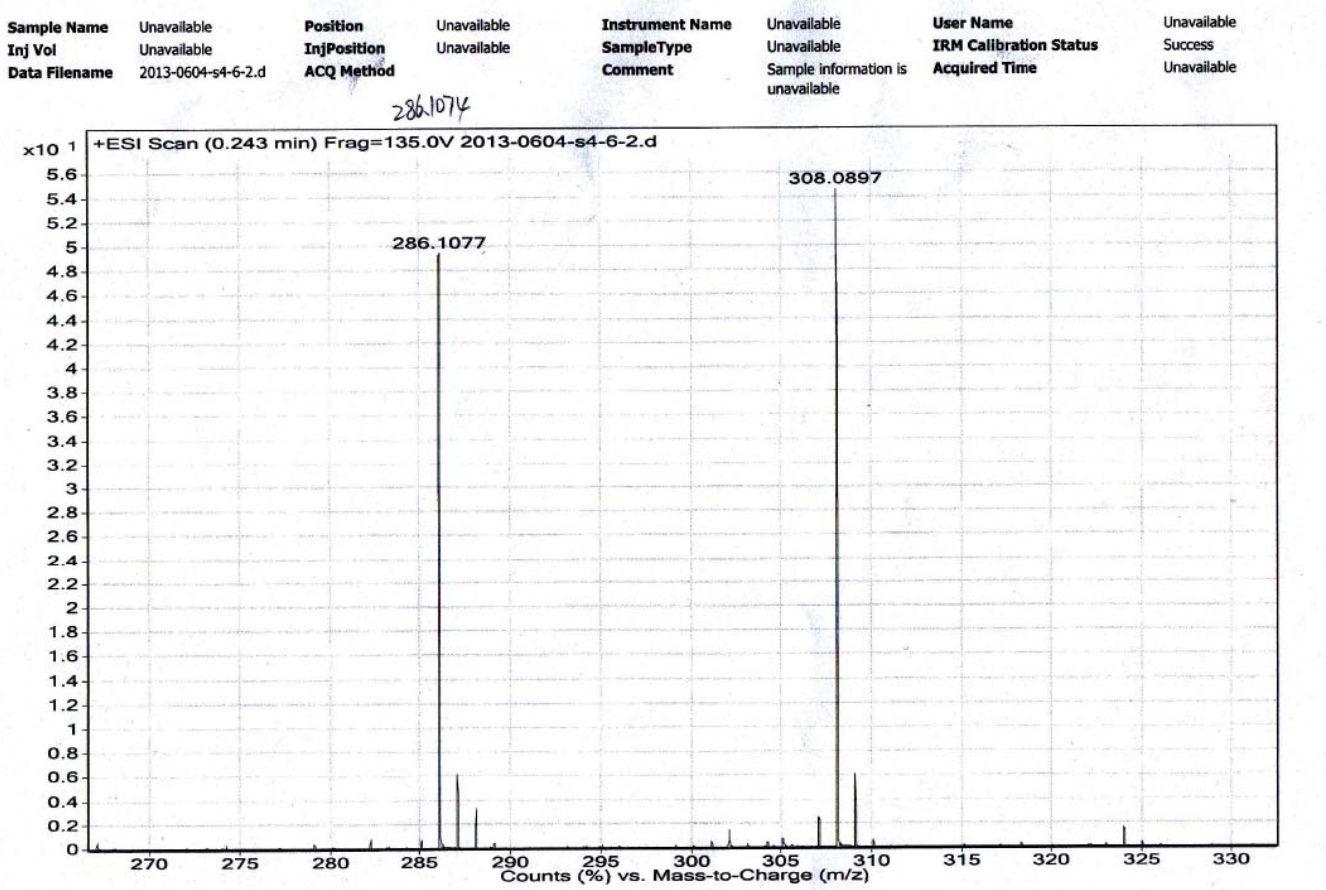




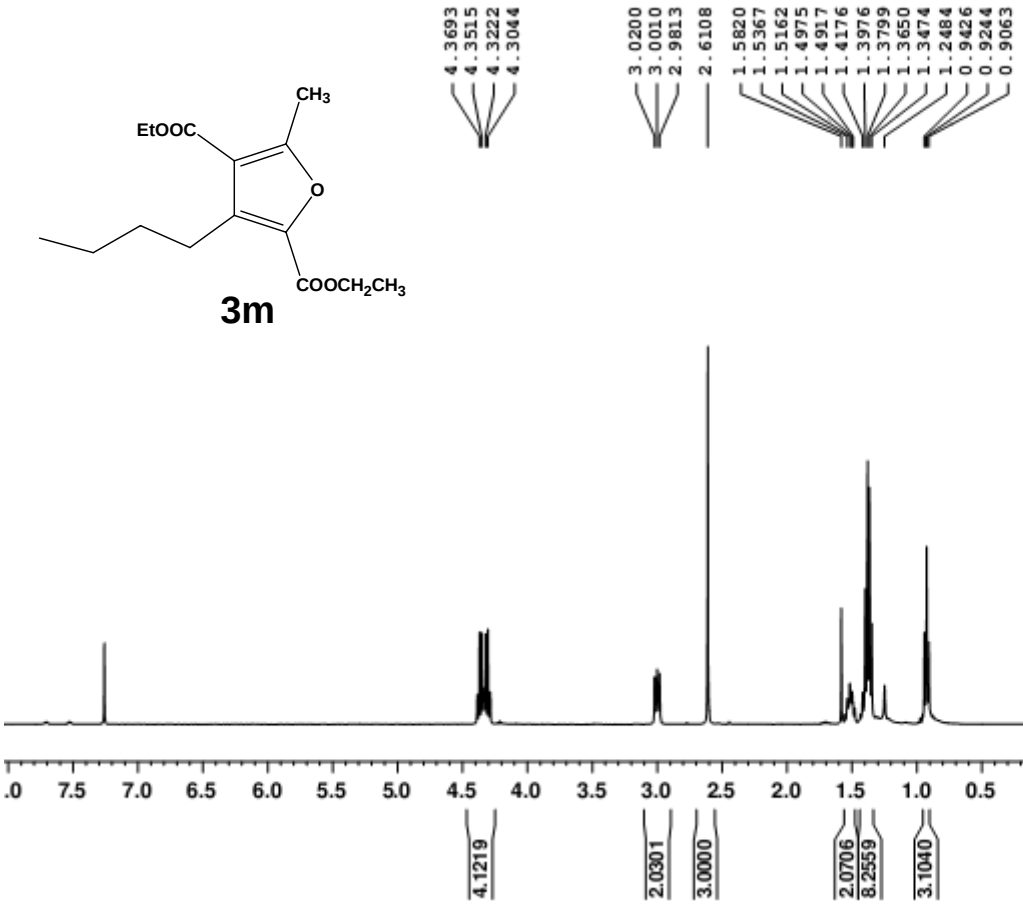


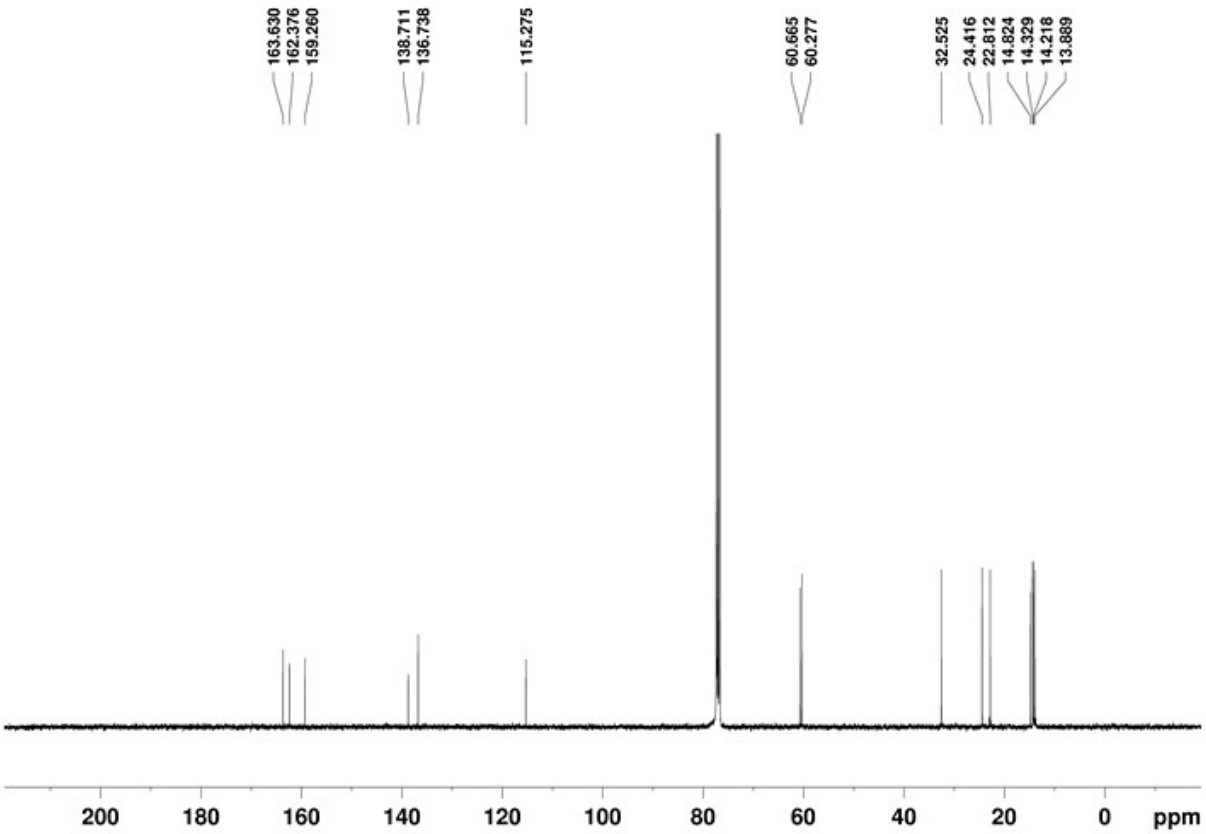
3l

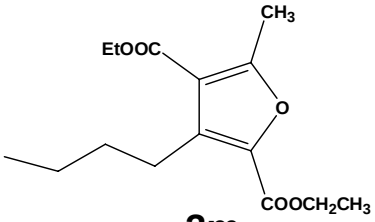
HRMS exact mass calcd for ($C_{16}H_{15}O_4N$+H) requires m/z 286.1074, found m/z 286.1077.



This journal is © The Royal Society of Chemistry 2013

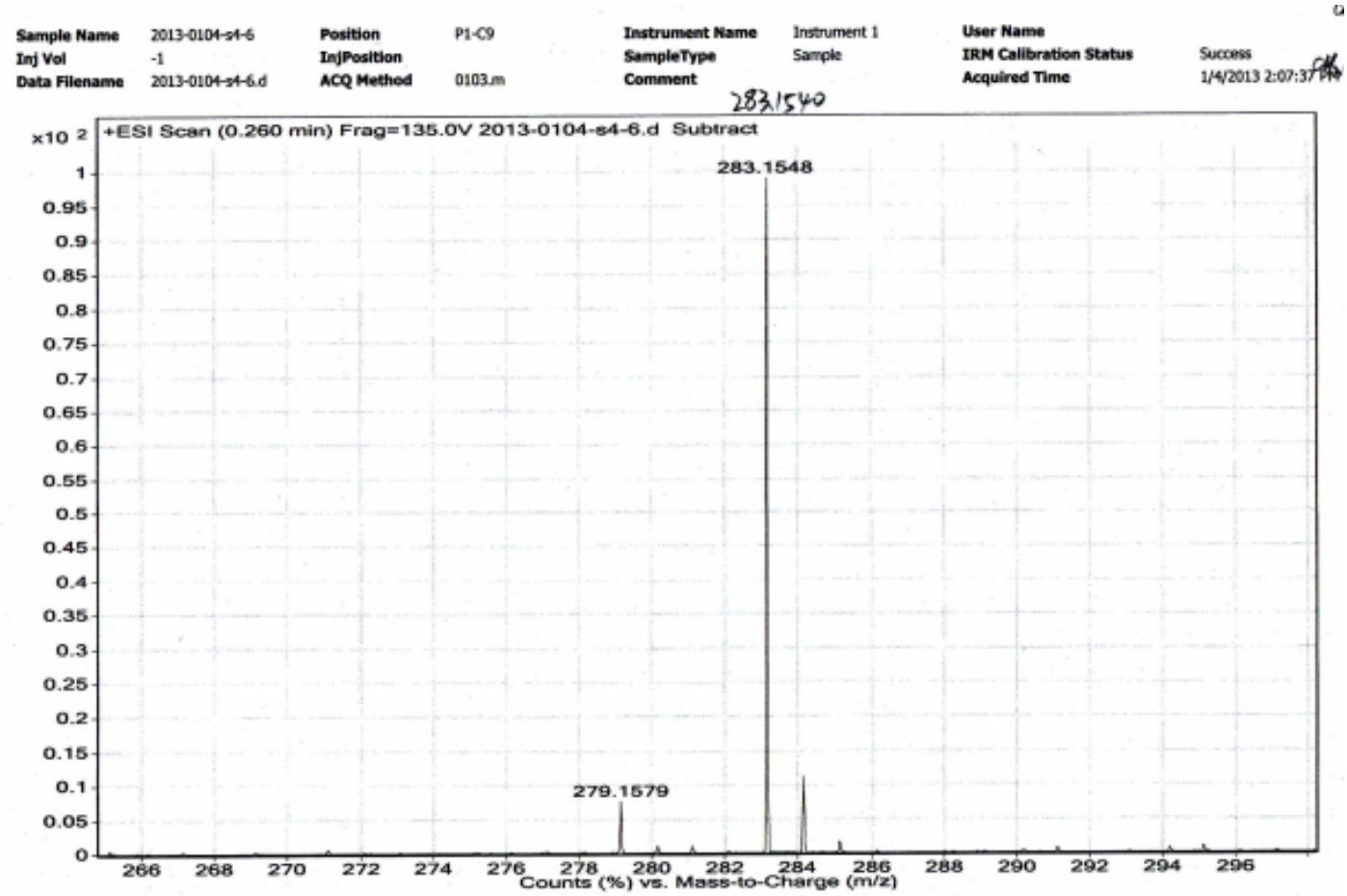




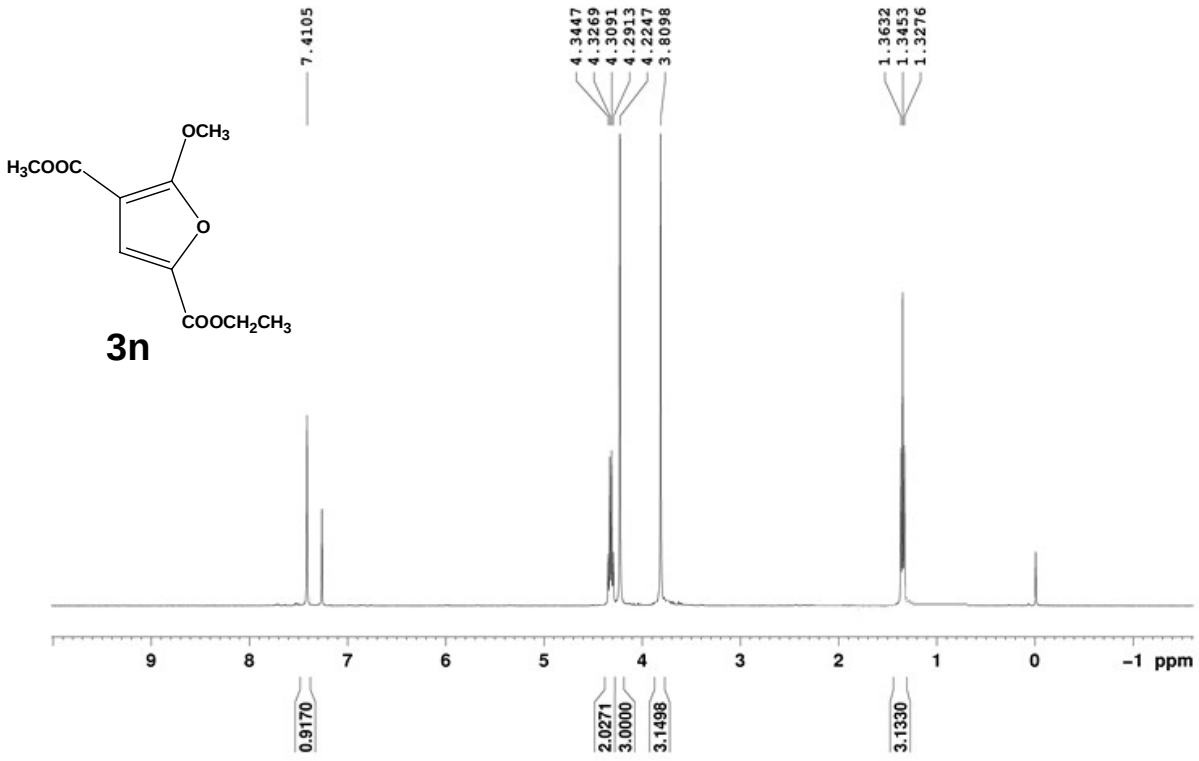


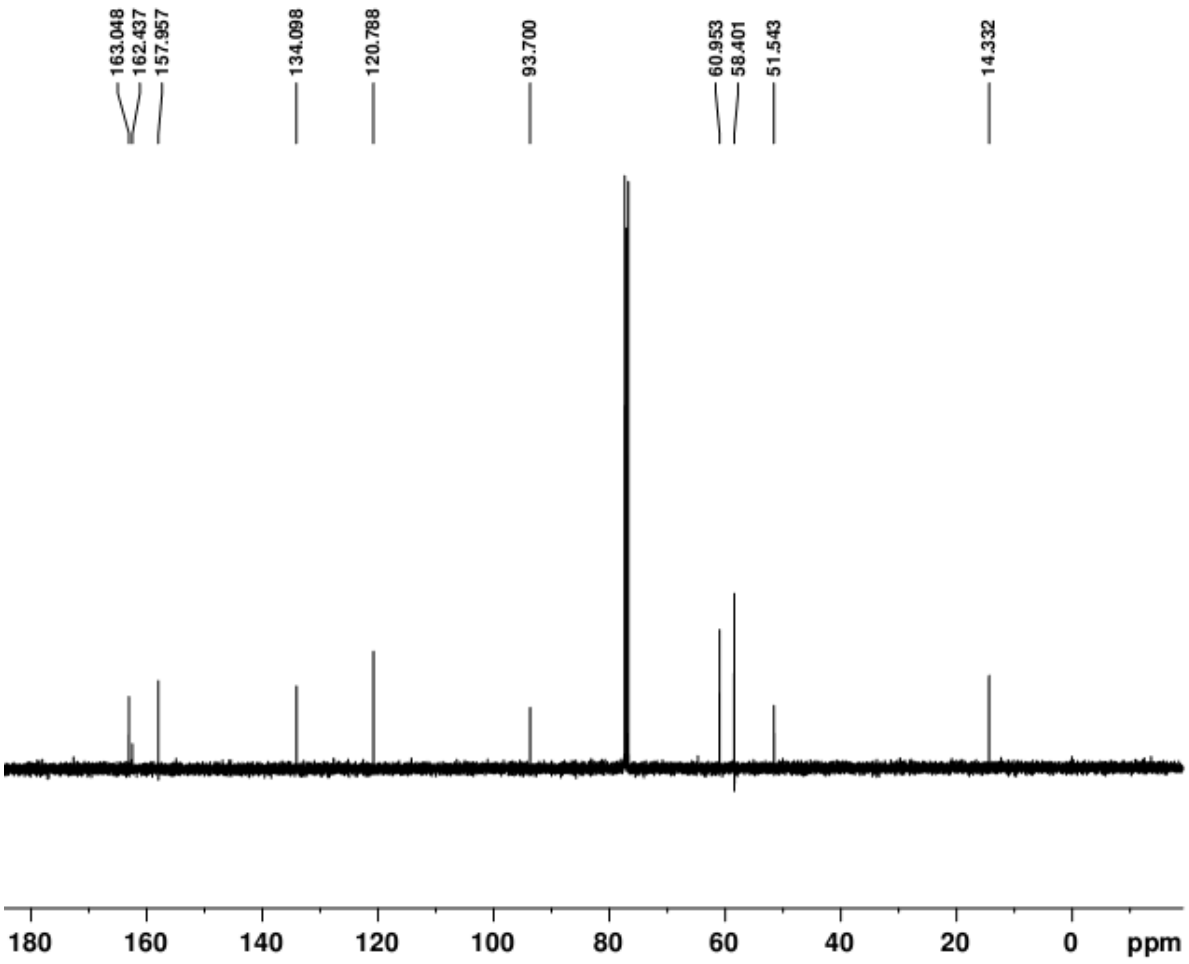
3m

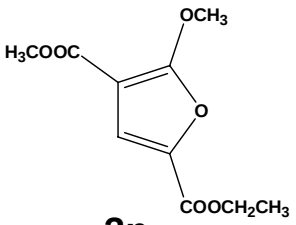
HRMS exact mass calcd for ($C_{15}H_{22}O_5$+H) requires m/z 283.1540, found m/z 283.1548.



This journal is © The Royal Society of Chemistry 2013

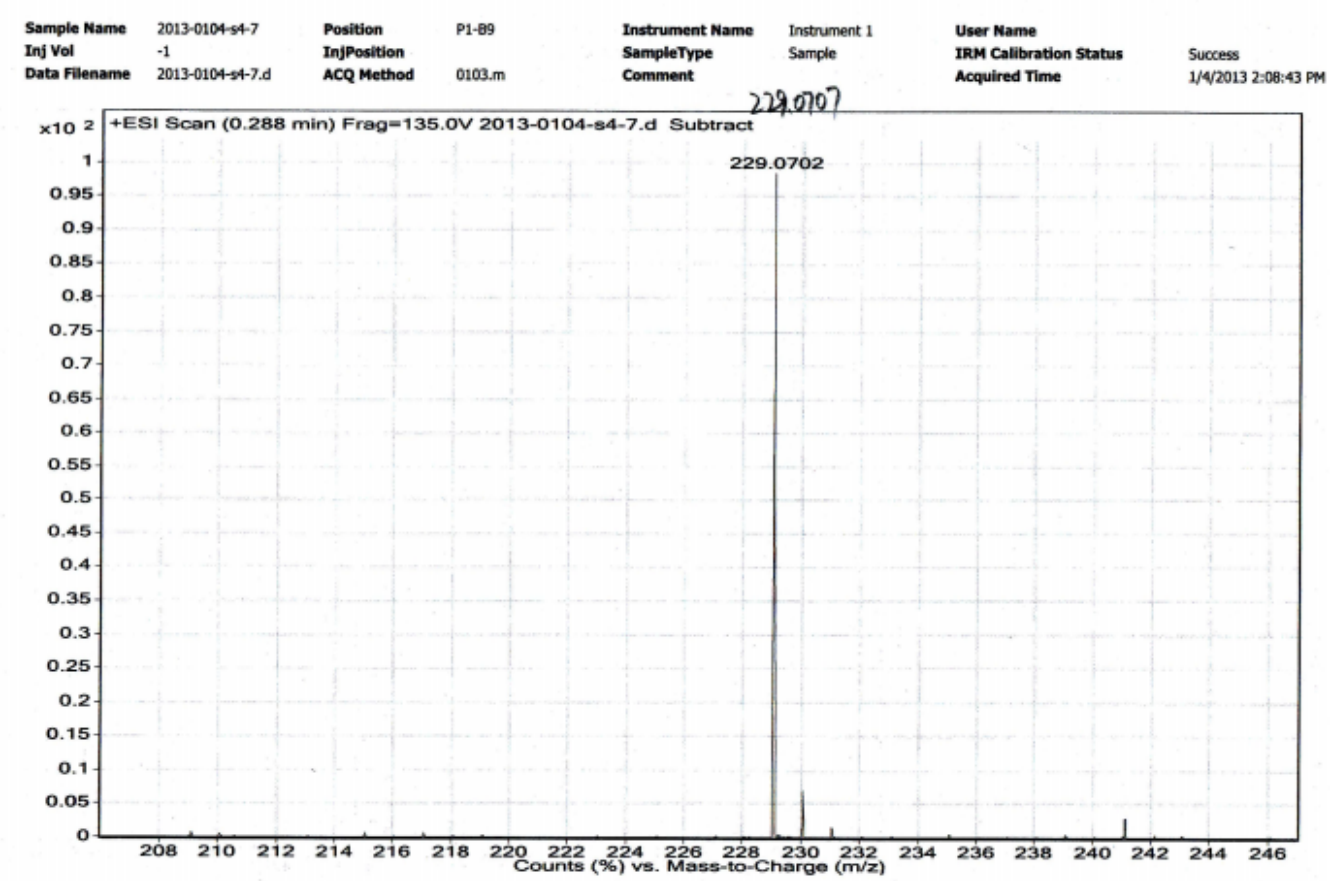




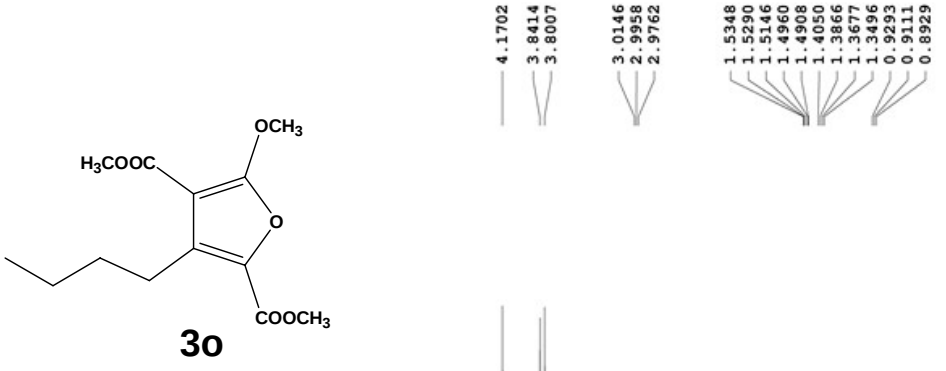


3n

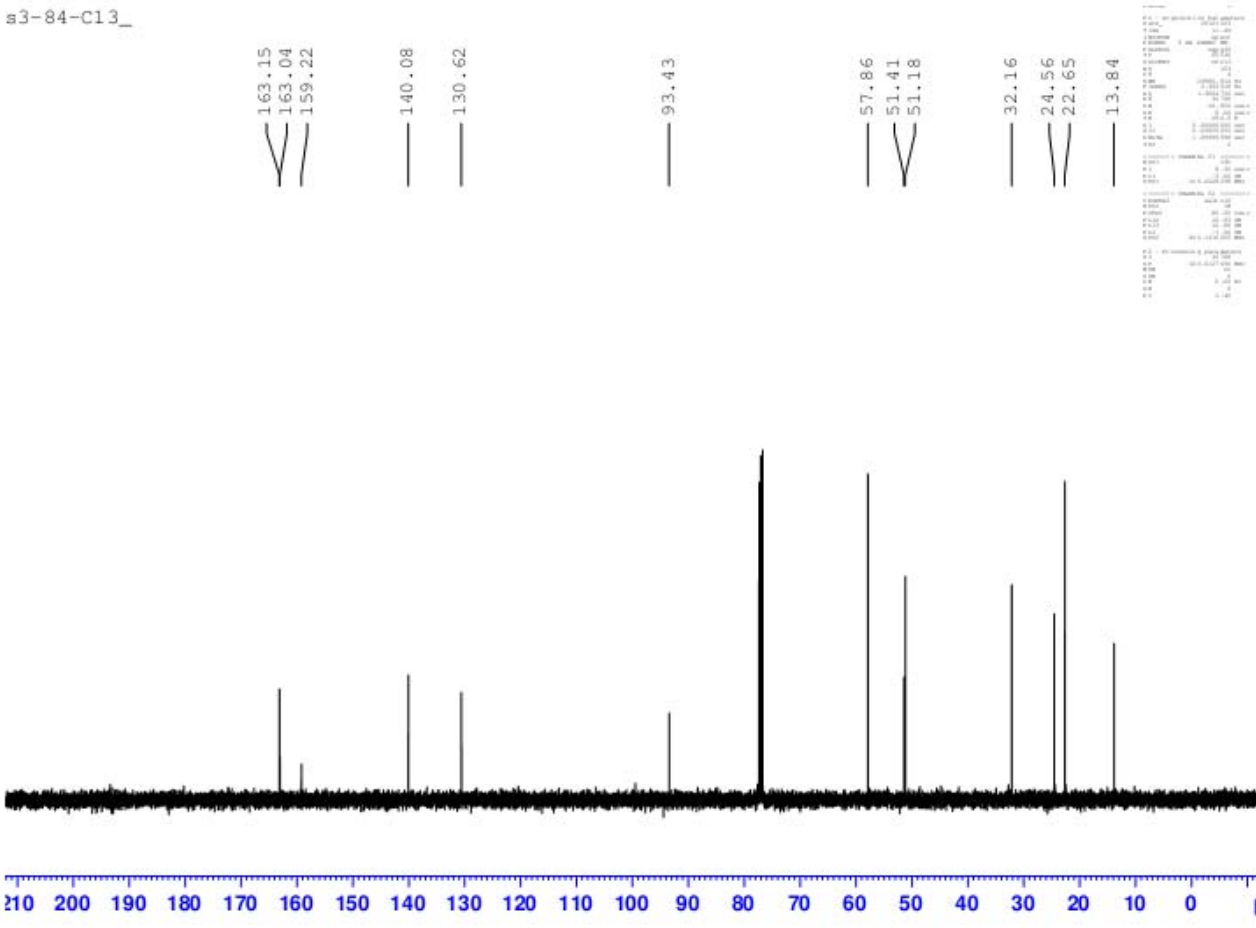
HRMS exact mass calcd for ($C_{10}H_{12}O_6$+H) requires m/z 229.0707, found m/z 229.0702.

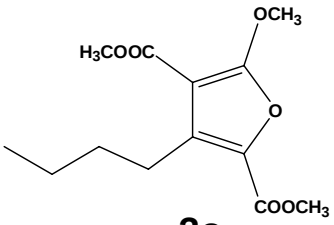


This journal is © The Royal Society of Chemistry 2013



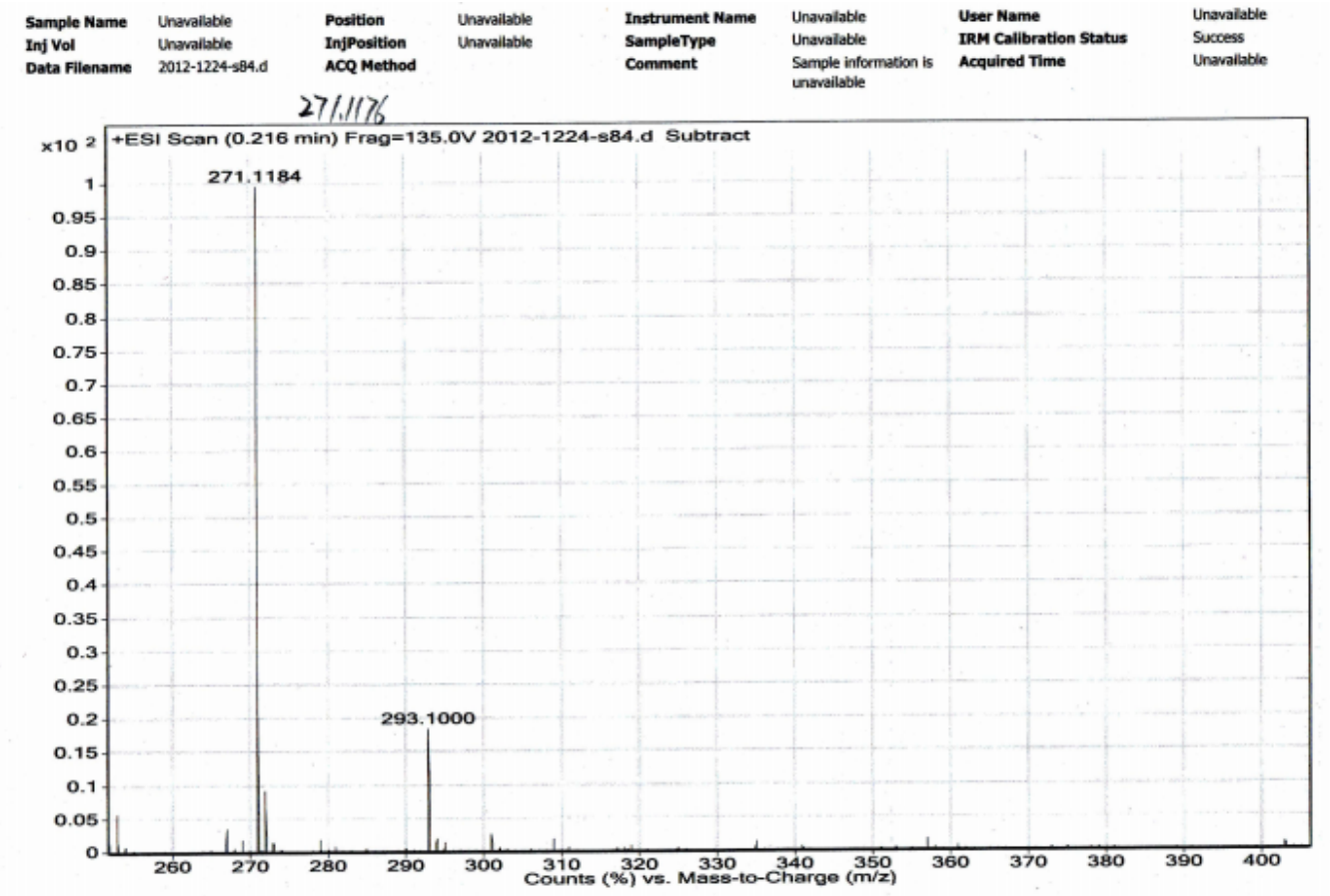
3o



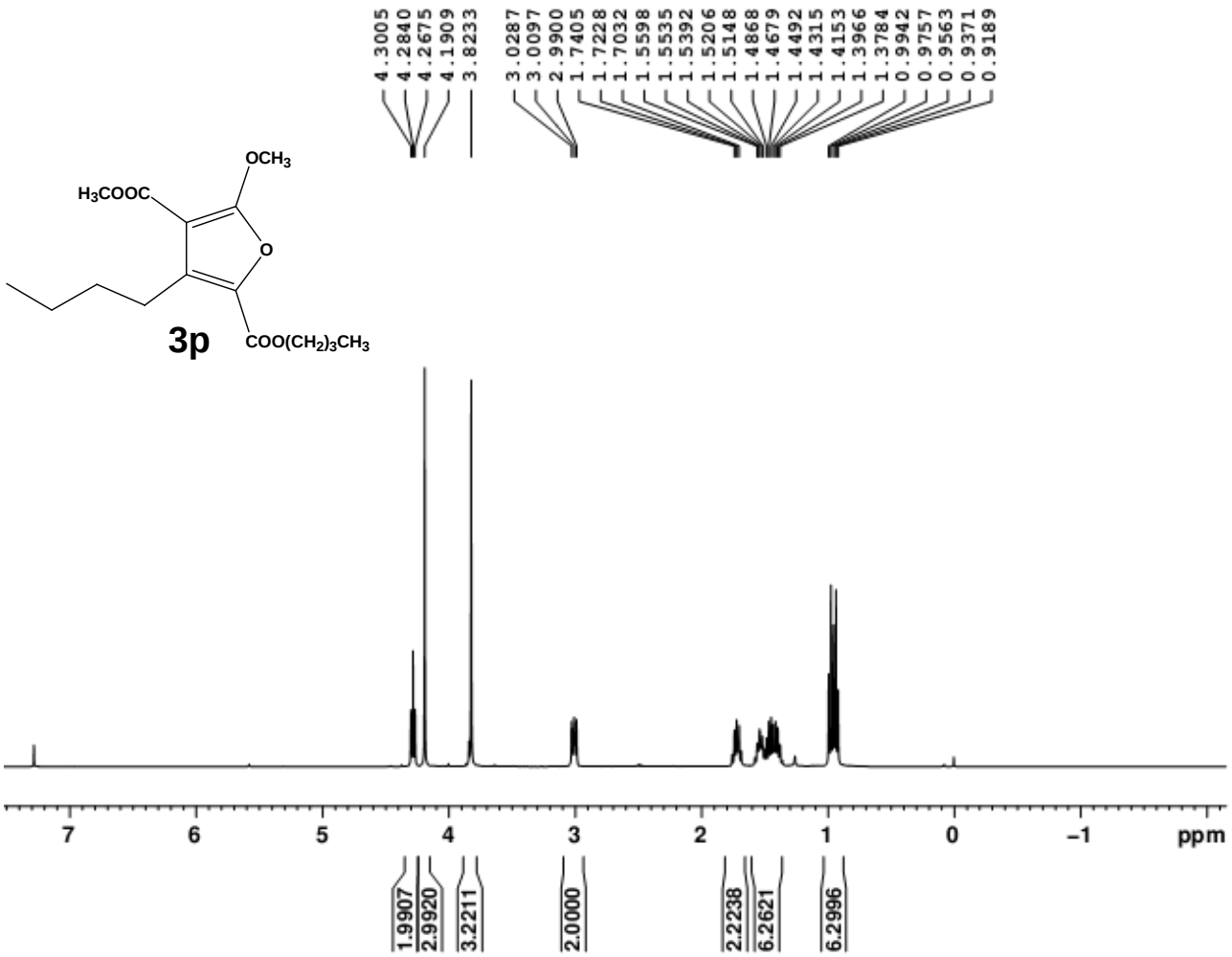


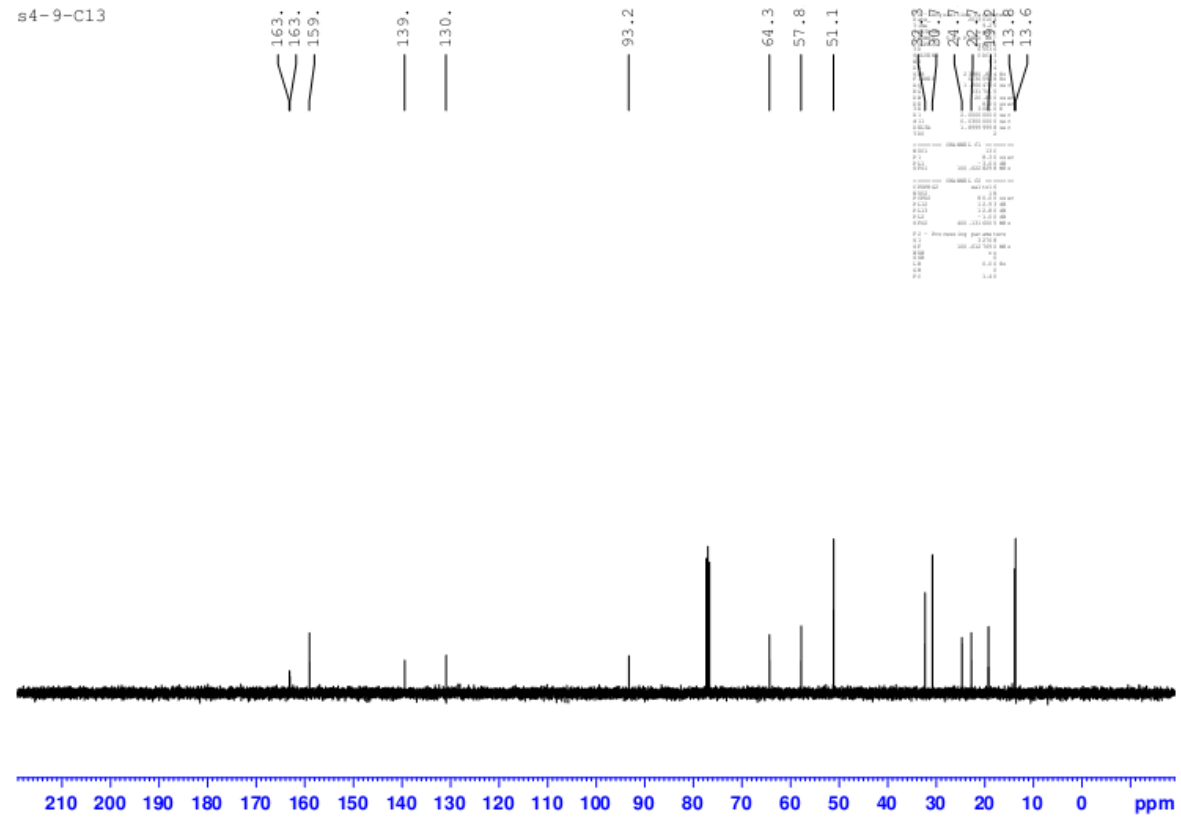
3o

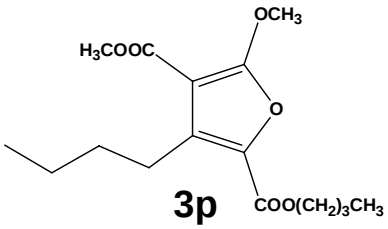
HRMS exact mass calcd for ($C_{13}H_{18}O_6$+H) requires m/z 271.1176, found m/z 271.1184.



This journal is © The Royal Society of Chemistry 2013

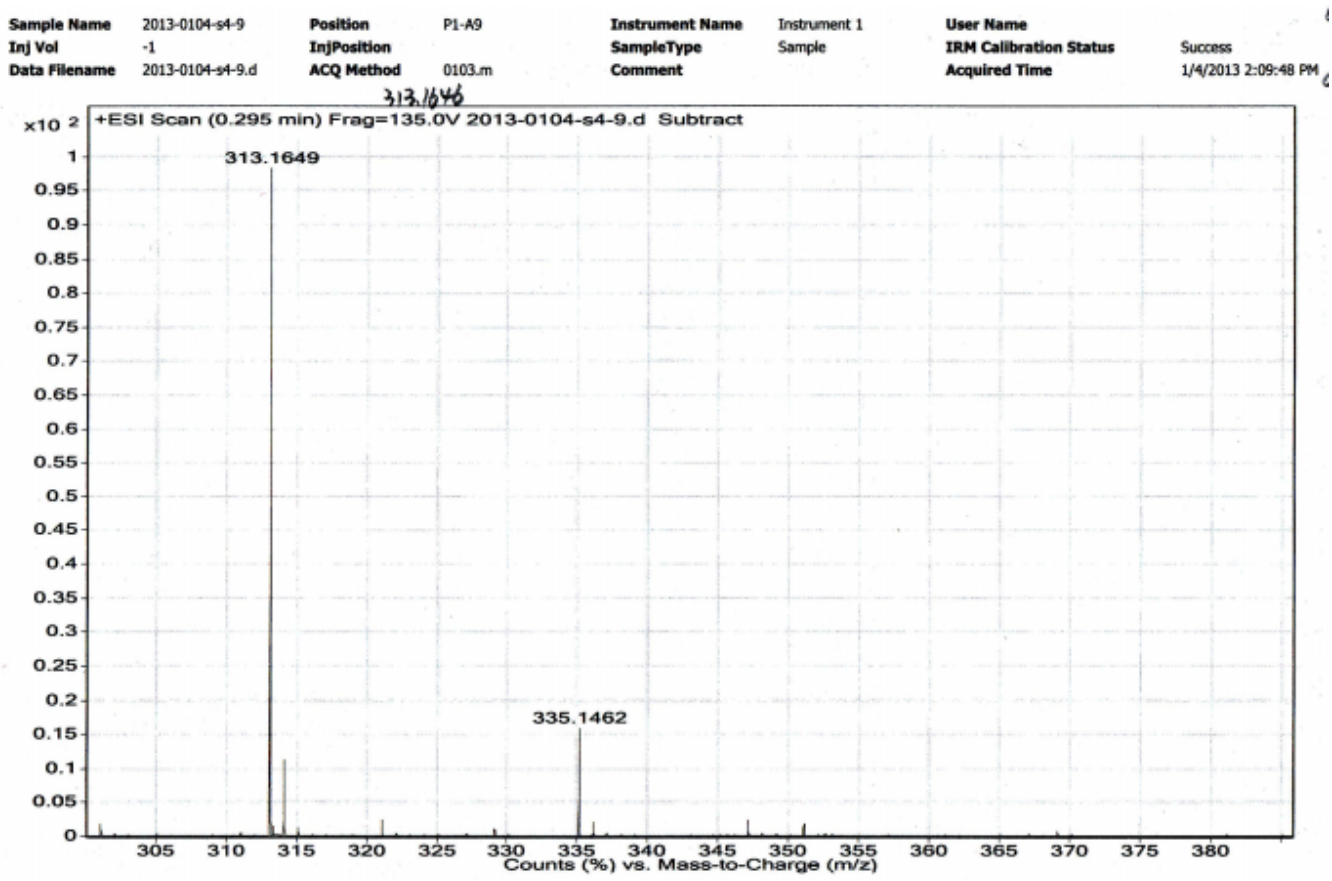




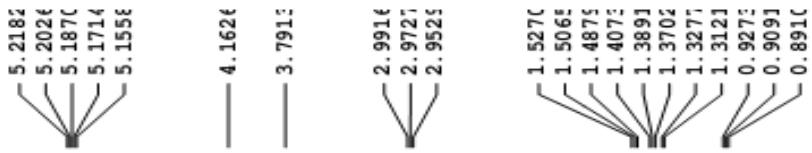


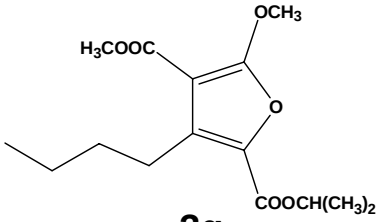
3p

HRMS exact mass calcd for ($C_{16}H_{24}O_6$+H) requires m/z 313.1646, found m/z 313.1649.

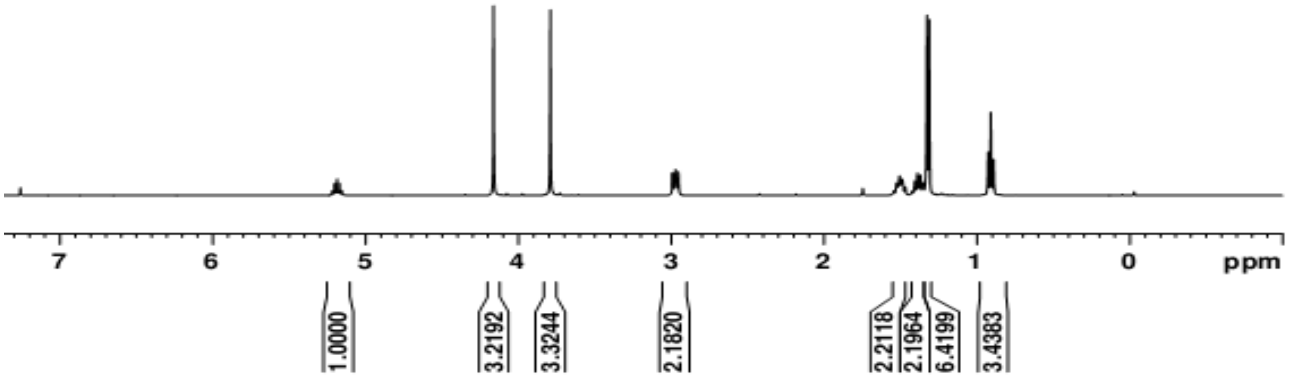


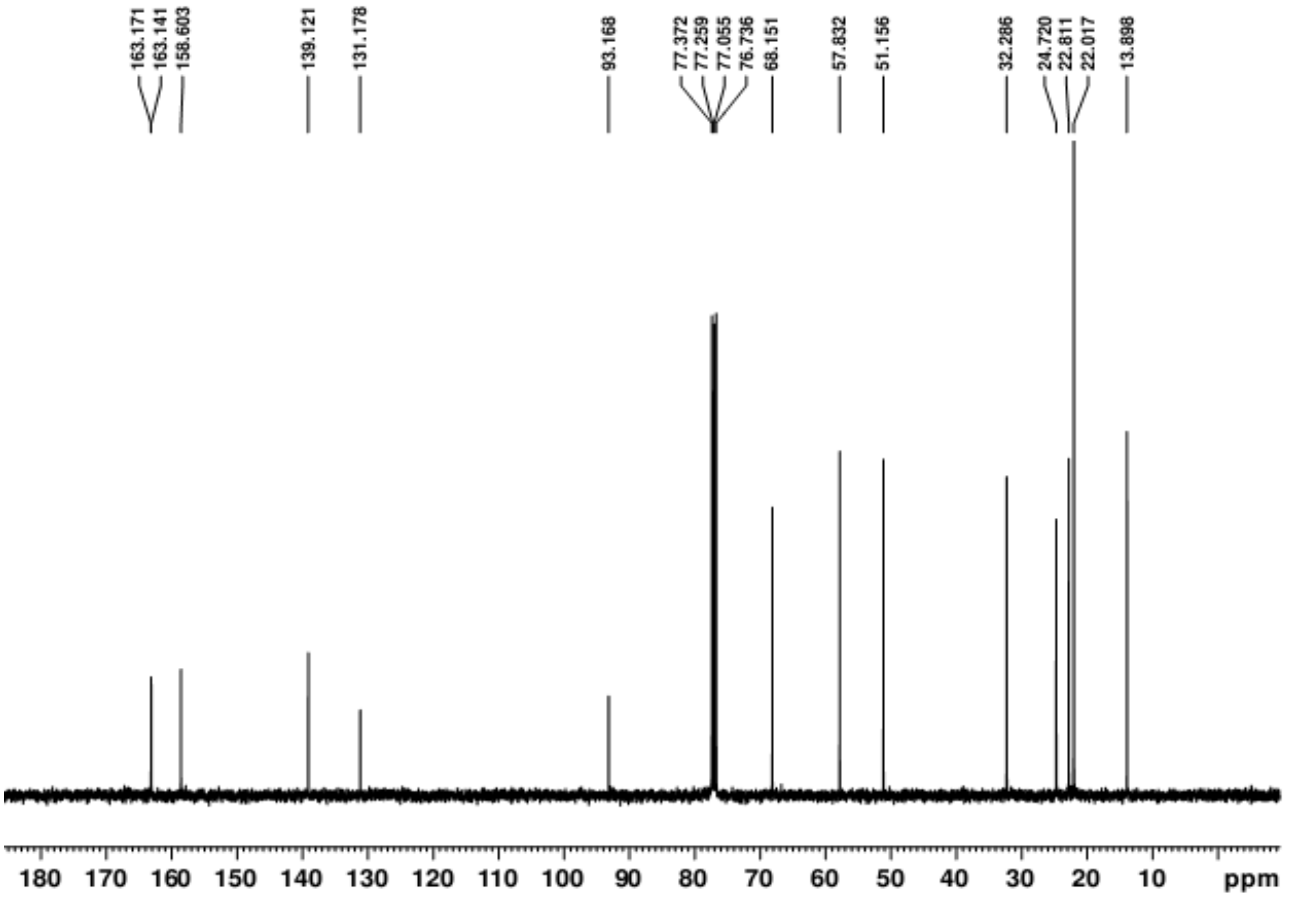
This journal is © The Royal Society of Chemistry 2013

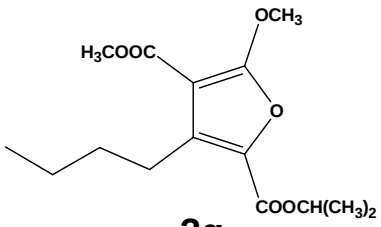




3q

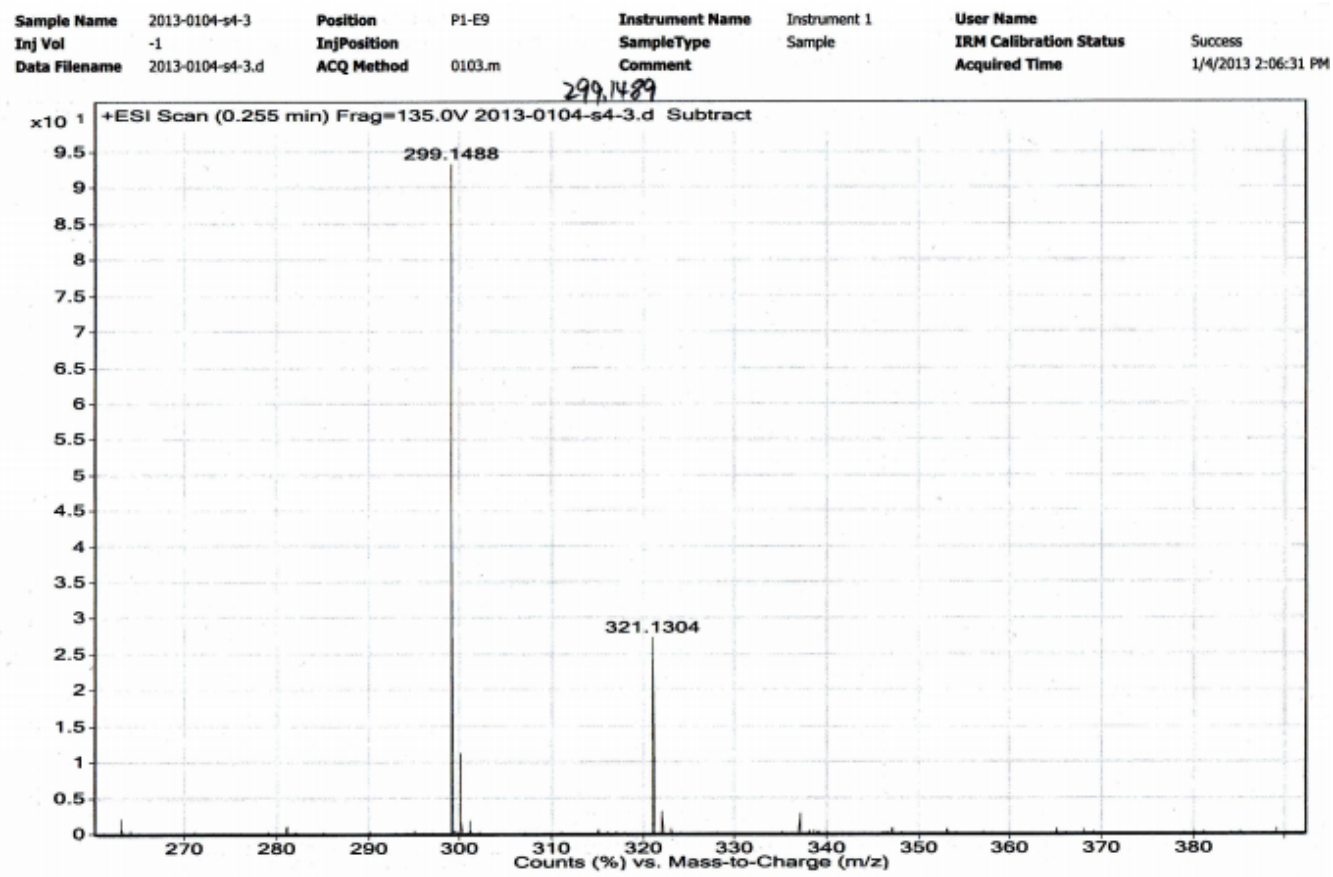




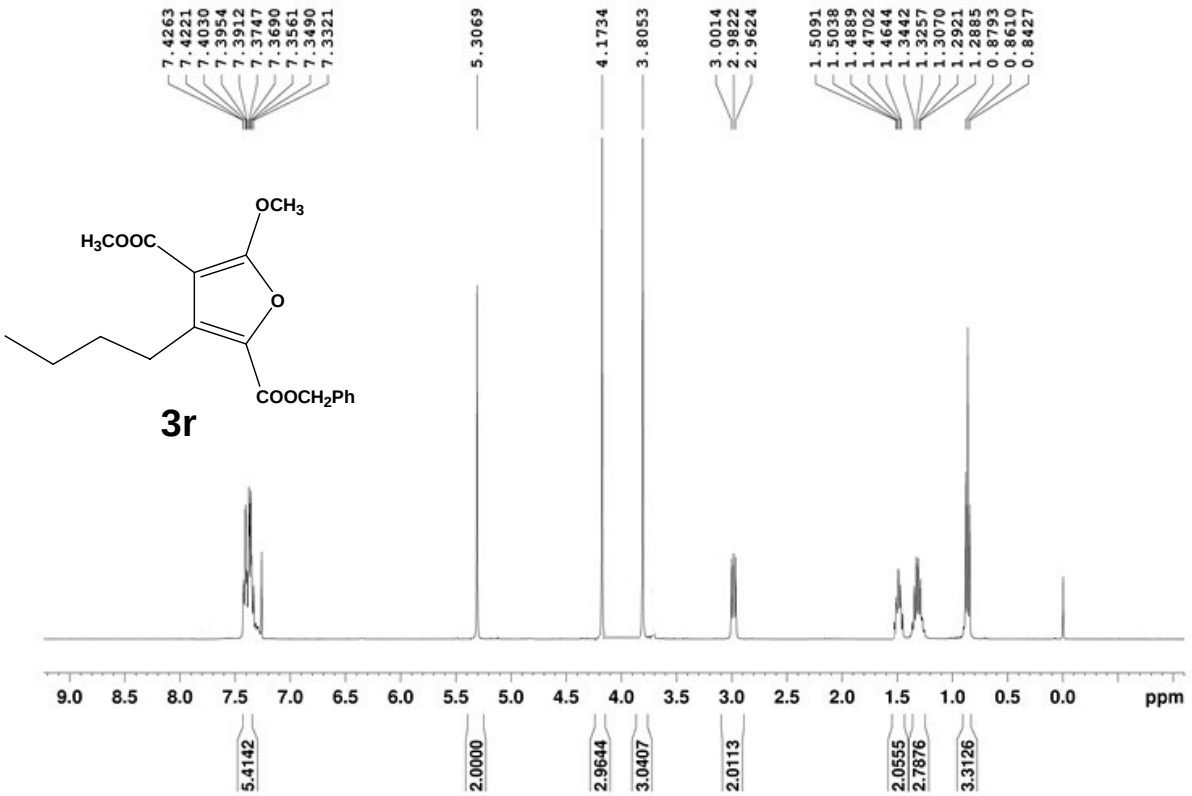


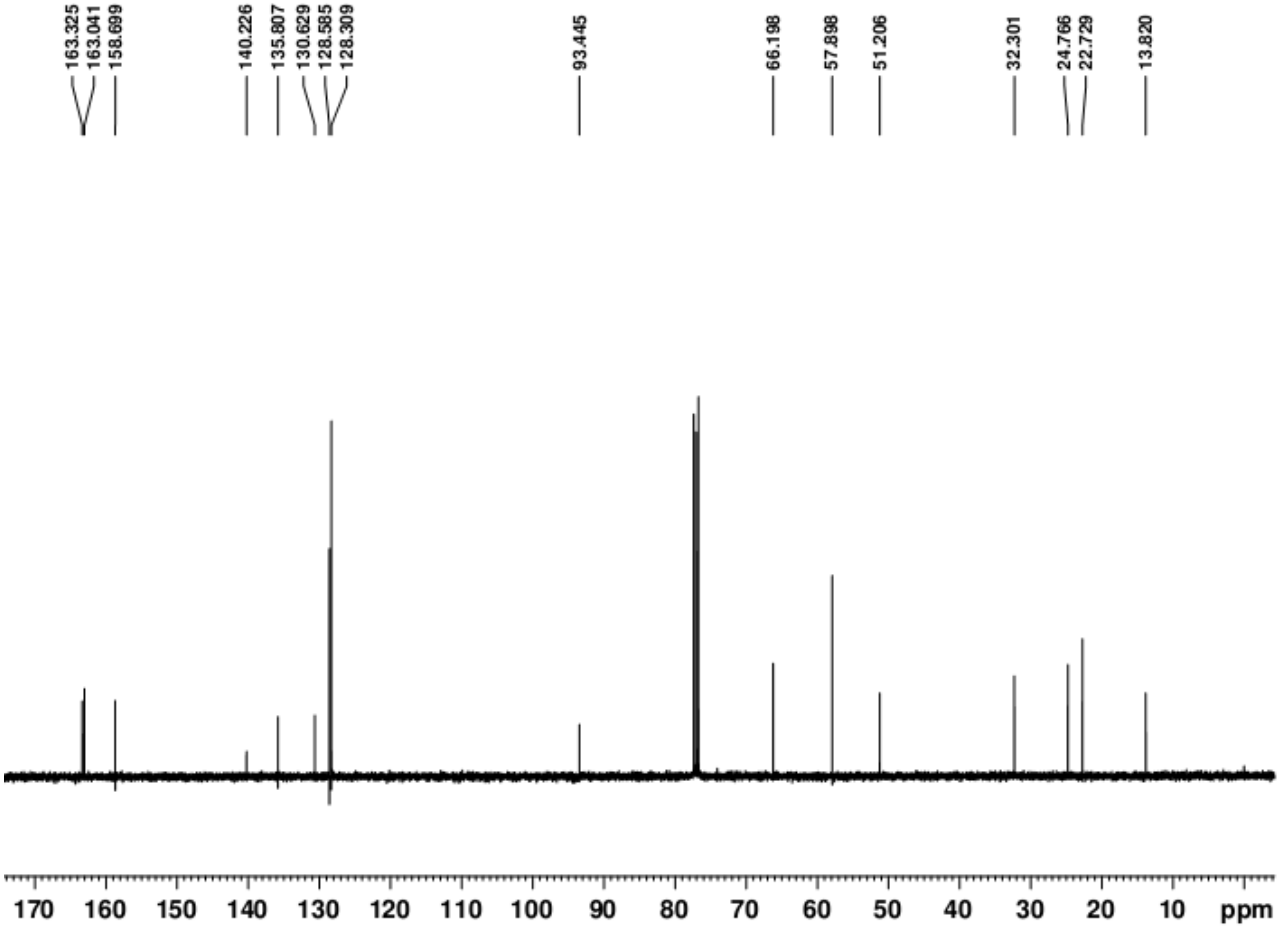
3q

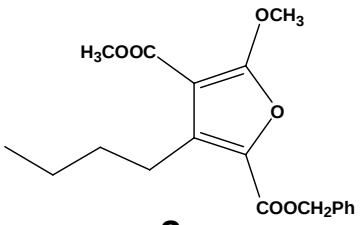
HRMS exact mass calcd for ($C_{15}H_{22}O_6$+Na) requires m/z 299.1489, found m/z 299.1488.



This journal is © The Royal Society of Chemistry 2013

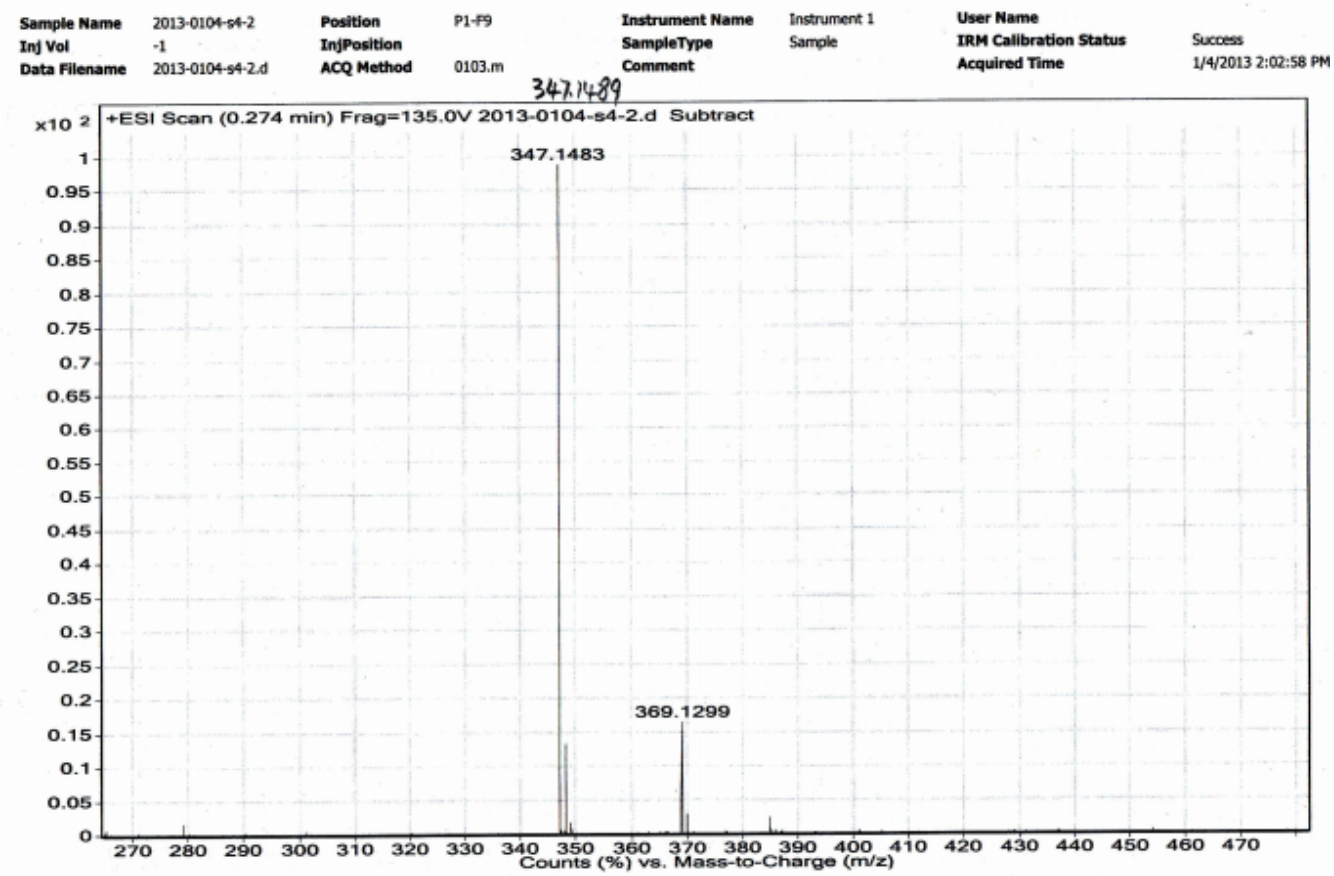




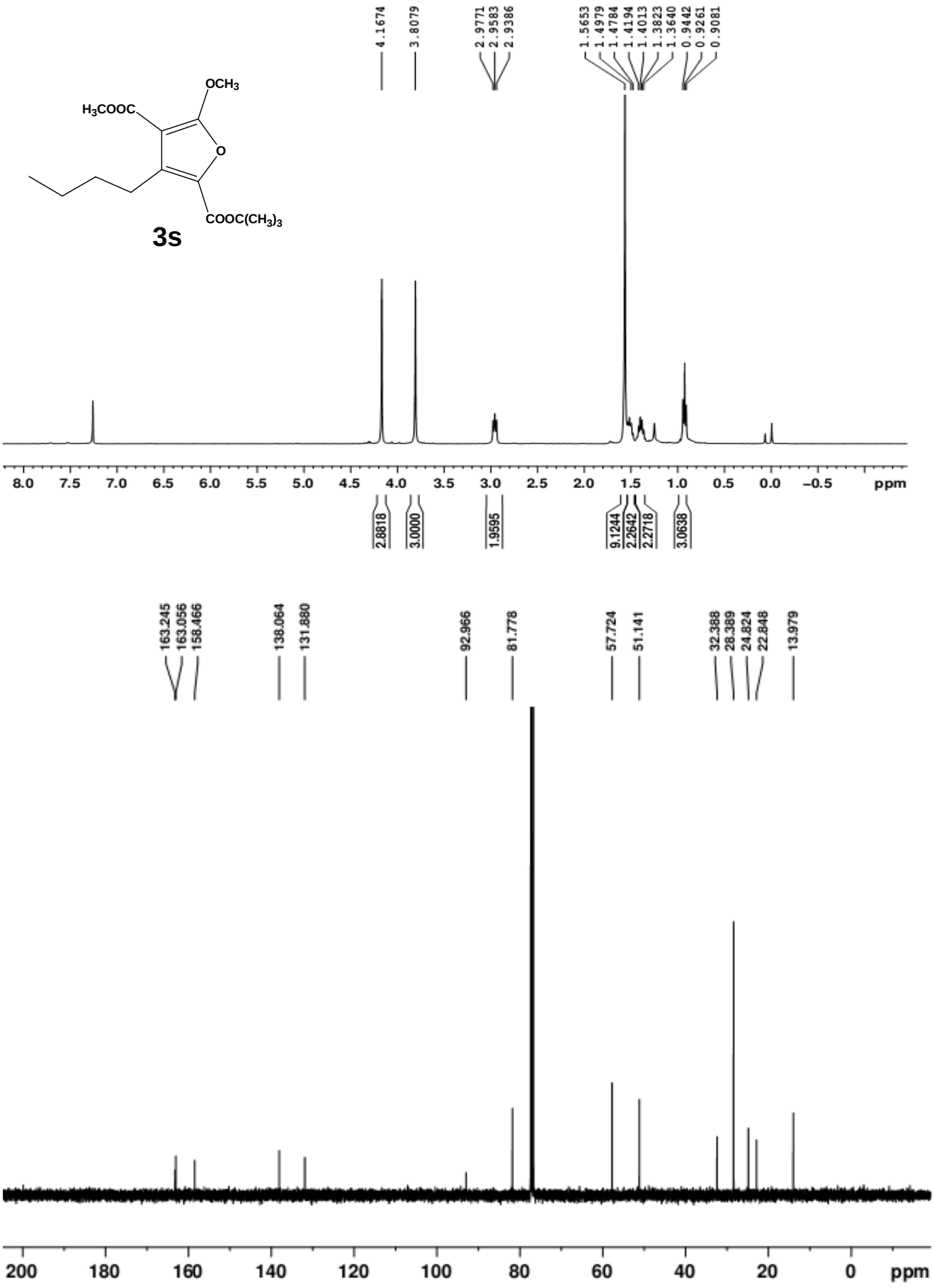


3r

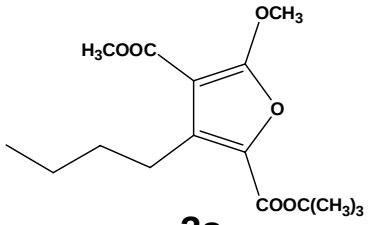
HRMS exact mass calcd for ($C_{19}H_{22}O_6$+H) requires m/z 347.1489, found m/z 347.1483.



This journal is © The Royal Society of Chemistry 2013



This journal is © The Royal Society of Chemistry 2013



3s

HRMS exact mass calcd for ($C_{16}H_{24}O_6$+Na) requires m/z 335.1465, found m/z 335.1471.