Supporting Information

Dimerization of Cyclopropenes to Bifurans with Tandem Metal Relay Catalysis

Chuanling Song, Di Sun, Xianglong Peng, Jing Bai, Rongyi Zhang, Shengzhen Hou, Jianwu Wang and Zhenghu Xu*

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

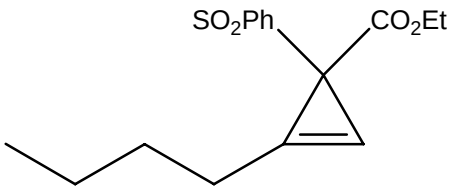
General

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.

Synthesis of the materials

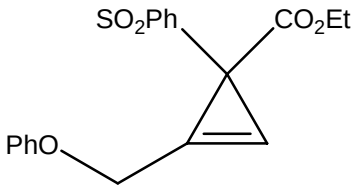
Diazomalonates and Cyclopropenes

Diazomalonates and cyclopropenes **1a-1g, 1j-1k, 1m-1o** were synthesized from the procedures reported in the literature[1]



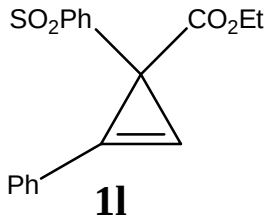
1h

(1h) Yield: 44 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, *J* =7.34 Hz, 2H), 1.17 (t, *J* =7.13 Hz, 3H), 1.41-1.46 (m, 2H), 1.61-1.69 (m, 2H), 2.56-2.74 (m, 2H), 4.05-4.13 (m, 2H), 6.52 (s, 1H), 7.52-7.64 (m, 3H), 7.96 (m, 2H);



1i

(1m) Yield: 54 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (t, *J* =7.13 Hz, 3H), 4.06-4.11 (q, *J* =7.28 Hz, 4H), 5.17-5.30 (m, 2H), 6.79 (s, 1H), 6.96-7.03 (m, 3H), 7.26-7.32(m, 2H), 7.52-7.64 (m, 3H), 7.98-7.99 (m, 2H);



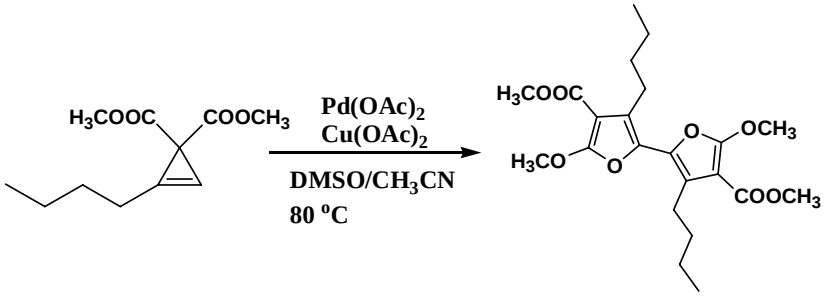
1l

(1l) Yield: 40 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (t, *J* =7.13 Hz, 3H), 4.11-4.17 (q, *J* =7.12 Hz, 2H), 7.01 (s, 1H), 7.42-7.63(m, 8H), 7.96-7.99 (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

Optimization of dimerization[a]



Entry	Catalyst	Oxidant	Additive	Solvent	Yield/%
1[a]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(3 eq.)	CH_3CN	68
2[a,b]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(3 eq.)	CH_3CN	67
3[a,c]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(3 eq.)	CH_3CN	42
4[a]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(3 eq.)	Toluene	N.R.
5[d,e]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(3 eq.)	CH_3CN	73
6[a]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(3 eq.)	CH_3CN	34.
7[a]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(7 eq.)	CH_3CN	86
8[a]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(10 eq.)	CH_3CN	54
9[a]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(14 eq.)	CH_3CN	44
10[a,f]	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(7eq.)	CH_3CN	43
11[a]	$PdCl_2$	$Cu(OAc)_2$	DMSO(7 eq.)	CH_3CN	52
12[a]	$Pd(TFA)_2$	$Cu(OAc)_2$	DMSO(7 eq.)	CH_3CN	67
13[a]	$PdCl_2(CH_3CN)_2$	$Cu(OAc)_2$	DMSO(7 eq.)	CH_3CN	61
14[a]	$PdCl_2(PPh_3)_2$	$Cu(OAc)_2$	DMSO(7 eq.)	CH_3CN	20
15[a]	$Pd(OAc)_2$	/	DMSO(7 eq.)	CH_3CN	N.R.
16[a]	/	$Cu(OAc)_2$	DMSO(7 eq.)	CH_3CN	41[g]

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), 1 mL CH_3CN, 80℃; [b]100℃; [c] $Cu(OAc)_2$(1.2 eq. 0.24 mmol, 47.8 mg); [d]**1**a was slowly injected into the system; [e] KF(1.2 eq., 0.24 mmol, 414 mg) was added into the system; [f] 0.5 ml CH_3CN; [g] the yield of isomerization product.

Table 1. Effects of Solvents and additive

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), 1 mL solvent, 80℃; [b] the yield of isomerization product **4**

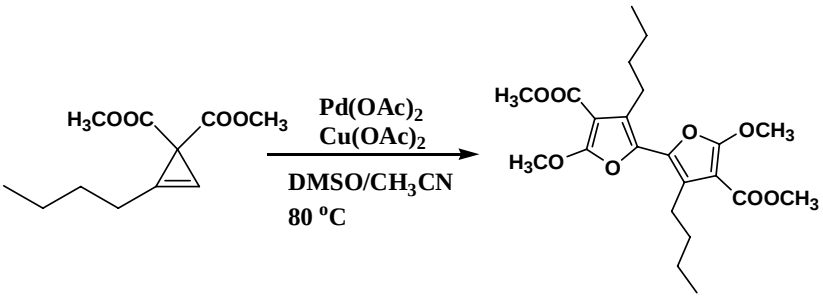
Entry	Catalyst	Oxidant	Additive	Solvent	Yield/%
1	$Pd(OAc)_2$	$Cu(OAc)_2$	/	DMSO	<5
2	$Pd(OAc)_2$	$Cu(OAc)_2$	/	CH_3CN	29
3	$Pd(OAc)_2$	$Cu(OAc)_2$	/	THF	N.D.
4	$Pd(OAc)_2$	$Cu(OAc)_2$	/	DMF	Trace
5	$Pd(OAc)_2$	$Cu(OAc)_2$	/	DCE	50[b]
6	$Pd(OAc)_2$	$Cu(OAc)_2$	/	DCM	N.D.
7	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(7 eq.)	THF	29
8	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(7 eq.)	DMF	14
9	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(7 eq.)	DCE	23
10	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(7 eq.)	DCM	27
11	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(7 eq.)	Toluene	42
12	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(7 eq.)	CH_3CN	86
13	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(3 eq.)	CH_3CN	34
14	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(10 eq.)	CH_3CN	54
15	$Pd(OAc)_2$	$Cu(OAc)_2$	DMSO(14 eq.)	CH_3CN	44

2) Oxidant (**Table 2**)

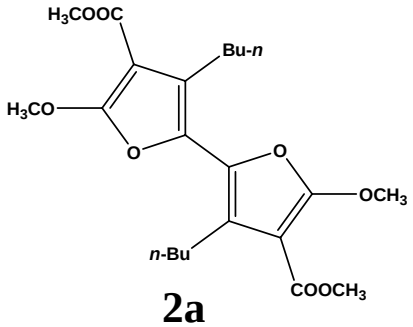
Entry	Catalyst	Oxidant	Additive	Solvent	Yield/%
1	$Pd(OAc)_2$	BQ	DMSO(7 eq.)	CH_3CN	N.R.
2	$Pd(OAc)_2$	DDQ	DMSO(7 eq.)	CH_3CN	N.R.
3	$Pd(OAc)_2$	TBHP	DMSO(7 eq.)	CH_3CN	N.R
4	$Pd(OAc)_2$	$K_2S_2O_8$	DMSO(7 eq.)	CH_3CN	N.R
5	$Pd(OAc)_2$	$FeCl_3$	DMSO(7 eq.)	CH_3CN	N.R
6[a]	$Pd(OAc)_2$	Ag_2O	DMSO(7 eq.)	CH_3CN	N.D.
7[a]	$Pd(OAc)_2$	Ag_2CO_3	DMSO(7 eq.)	CH_3CN	N.D.
8[b]	$Pd(OAc)_2$	$Cu(OAc)_2$+ Ag_2O	DMSO(7 eq.)	CH_3CN	<5
9	$Pd(OAc)_2$	AgOAc	DMSO(7 eq.)	CH_3CN	<5
10[b]	$Pd(OAc)_2$	$Cu(OAc)_2$+BQ	DMSO(7 eq.)	CH_3CN	<5

Reaction conditions: **1a**(0.2 mmol, 42.4 mg), $Pd(OAc)_2$(5 mol%, 0.01 mmol, 2.24 mg), Oxidant(2 eq. 0.4 mmol,), 1 mL CH_3CN, 80℃; [a] another trace amount of unkown product was formed. [b] $Cu(OAc)_2$ (20 mol%), oxidant(2 eq)

General procedure of Reactions

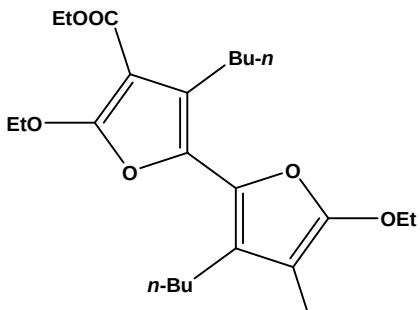


A mixture of $Pd(OAc)_2$ (2.24 mg, 0.01 mmol, 5 mol%) and $Cu(OAc)_2$(79.6 mg, 0.4 mmol, 2 eq.) was dissolved in 1 mL CH_3CN and DMSO (106.4 mg, 1.4 mmol, 7 eq.), **1a** (42.4 mg, 0.2 mmol) was added to the reaction system. The resulting mixture was stirred at 80℃ or room temperature until the reaction was completed (monitored by TLC, < 3h). The reaction mixture was filtered and evaporated under reduced pressure and purified by column chromatography (silica gel) to give the pure product **2a**.



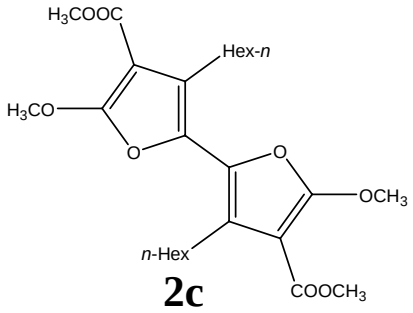
2a

(2a) Yield: 86 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 7.36 Hz, 6H), 1.25-1.36 (m, 4H), 1.48-1.56 (m, 4H), 2.64 (t, J = 7.76 Hz, 4H), 3.82 (s, 6H), 4.10 (s, 6H); ^{13}C NMR (100MHz, $CDCl_3$) δ13.88, 22.68, 24.56, 32.44, 51.02, 57.51, 91.55, 127.47, 130.62, 162.31, 163.69; HRMS exact mass calcd for ($C_{22}H_{30}O_8$+H) requires m/z 423.2013, found m/z 423.2024.



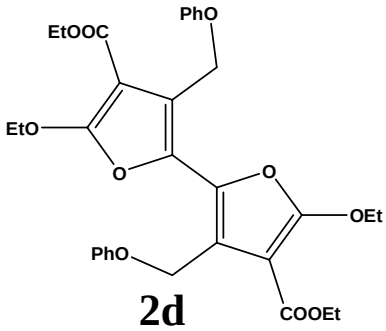
2b

(2b) Yield: 70 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 10.0 Hz, 6H), 1.26-1.38 (m, 10H), 1.44-1.61 (m, 10H), 2.62 (t, *J* = 12.4 Hz, 4H), 4.28 (q, *J* = 9.60 Hz, 4H), 4.43 (q, *J* = 9.60 Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.94, 14.34, 14.98, 22.77, 24.73, 32.61, 59.65, 67.25, 92.51, 126.65, 130.72, 162.16, 163.43; HRMS exact mass calcd for ($C_{26}H_{38}O_8$+H) requires m/z 479.2639, found m/z 479.2639.



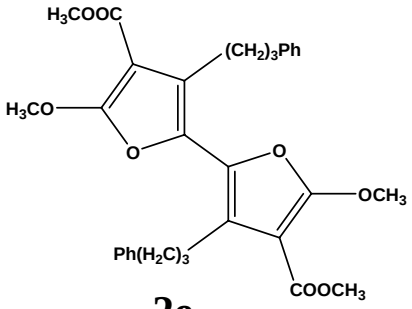
2c

(2c) Yield: 65 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (m, 6H), 1.25 (m, 12H), 1.51 (m, 4H), 2.61 (m, 4H), 3.82 (s, 6H), 4.10 (s, 6H); ^{13}C NMR (100MHz, $CDCl_3$) 14.07, 22.66, 24.90, 29.36, 30.29, 31.68, 51.02, 57.51, 91.56, 127.63, 130.59, 162.33, 163.68; HRMS exact mass calcd for ($C_{26}H_{38}O_8$+H) requires m/z 479.2639, found m/z 479.2642.



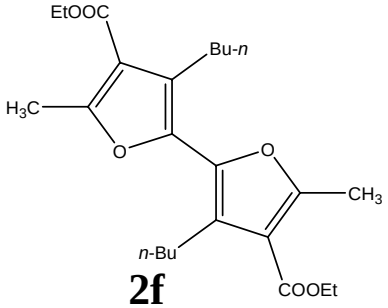
2d

(2d) Yield: 89 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (t, *J* = 7.12 Hz, 6H), 1.33 (t, *J* = 7.04 Hz, 6H), 4.19-4.24 (q, *J* = 7.16 Hz, 4H), 4.25-4.30 (q, *J* = 7.08 Hz, 4H), 6.87-6.96 (m, 6H), 7.23-7.27 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.12, 14.87, 60.01, 60.45, 67.97, 92.54, 114.43, 120.52, 120.74, 129.32, 132.72, 158.75, 162.34, 162.74; HRMS exact mass calcd for ($C_{32}H_{34}O_{10}$+H) requires m/z 601.2044, found m/z 601.2043.



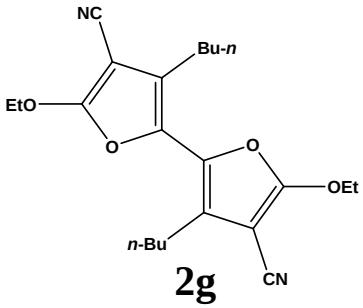
2e

(2e) Yield: 86 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.85-1.91 (m, 4H), 2.63 (t, *J* = 7.58 Hz, 4H), 2.96 (t, *J* = 7.68 Hz, 4H), 3.78 (s, 6H), 3.97 (s, 6H), 7.10-7.25 (m, 10H); ^{13}C NMR (100MHz, $CDCl_3$) δ 24.47, 31.79, 35.84, 51.03, 57.52, 91.58, 125.73, 126.49, 128.26, 128.39, 130.80, 142.17, 162.29, 163.60; HRMS exact mass calcd for ($C_{32}H_{34}O_8$+H) requires m/z 547.2326, found m/z 547.2317.



2f

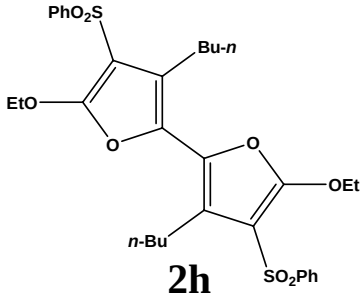
(2f) Yield: 47 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.20 Hz, 6H), 1.25-1.40 (m, 10H), 1.46-1.57 (m, 4H), 2.58 (s, 6H), 2.72 (t, *J* = 7.50 Hz, 4H), 4.28-4.35 (q, *J* = 7.20 Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.88, 14.30, 14.57, 22.66, 24.03, 32.75, 59.97, 114.04, 124.84, 139.81, 159.32, 164.42; HRMS exact mass calcd for ($C_{24}H_{34}O_8$+H) requires m/z 419.2428, found m/z 419.2442.



2g

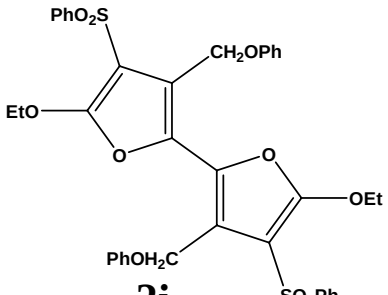
(2g) Yield: 63 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.32 Hz, 6H), 1.31-1.37 (m, 4H), 1.47 (t, *J* = 7.04 Hz, 6H), 1.56-1.60 (m, 4H), 2.48 (t, *J* = 7.31 Hz, 4H), 4.46-4.51 (q, *J* = 7.04 Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.73, 14.79,

22.36, 24.32, 31.44, 68.36, 73.32, 113.29, 126.17, 130.12, 163.73; HRMS exact mass calcd for ($C_{22}H_{28}N_2O_4$+H) requires m/z 385.2122, found m/z 385.2131.



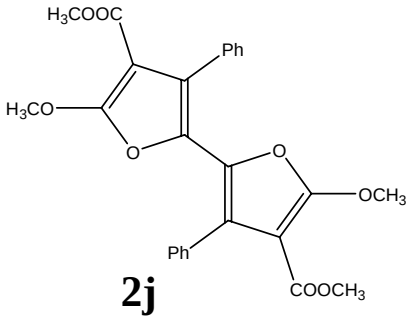
2h

(2h) Yield: 72 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, *J* = 7.28 Hz, 6H), 1.25-1.31 (m, 4H), 1.38-1.44 (m, 10H), 2.59 (t, *J* = 7.06 Hz, 4H), 4.35-4.40 (q, *J* = 7.08 Hz, 4H), 7.48-7.57 (m, 6H), 7.96-7.98 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.77, 14.82, 22.74, 23.85, 32.70, 68.24, 101.21, 125.70, 126.90, 128.86, 130.58, 132.85, 143.30, 159.13; HRMS exact mass calcd for ($C_{32}H_{38}S_2O_8$+H) requires m/z 615.2081, found m/z 615.2078.



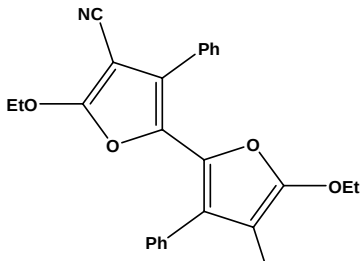
2i

(2i) Yield: 68 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.40 Hz, 6H), 4.18-4.23 (q, *J* = 7.04 Hz, 4H), 5.11(s, 4H), 6.71-7.95 (m, 20H); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.73, 59.06, 68.86, 101.20, 114.34, 120.24, 121.13, 127.15, 128.84, 129.44, 132.10, 133.00, 142.81, 158.06, 159.66; HRMS exact mass calcd for ($C_{38}H_{34}O_{10}S_2$+Na) requires m/z 737.1486, found m/z 737.1481.



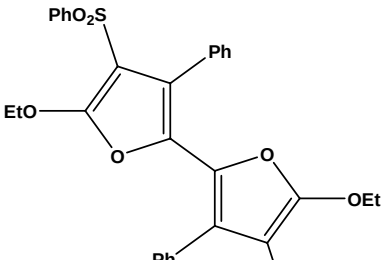
2j

(2j) Yield: 51 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.60 (s, 6H), 3.73 (s, 6H), 7.19-7.29 (m, 10H); ^{13}C NMR (100MHz, $CDCl_3$) δ 51.00, 57.49, 91.90, 125.48, 127.40, 128.42, 130.05, 131.06, 131.91, 161.84, 163.06; HRMS exact mass calcd for ($C_{26}H_{22}O_8$+H) requires m/z 463.1387, found m/z 463.1389.



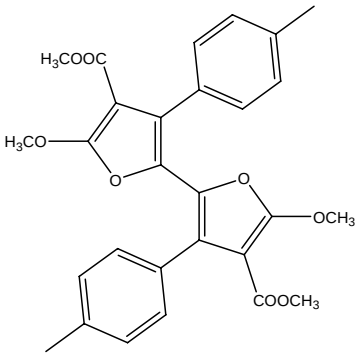
2k

(2k) Yield: 55 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (t, *J* = 7.08 Hz, 6H), 4.38-4.43 (q, *J* = 7.08 Hz, 4H), 7.23-7.29 (m, 10H); ^{13}C NMR (100MHz, $CDCl_3$) δ 14.72, 68.64, 73.29, 113.00, 127.67, 128.23, 128.58, 128.67, 129.12, 129.18, 164.42; HRMS exact mass calcd for ($C_{26}H_{20}N_2O_4$+H) requires m/z 425.1496, found m/z 425.1502.



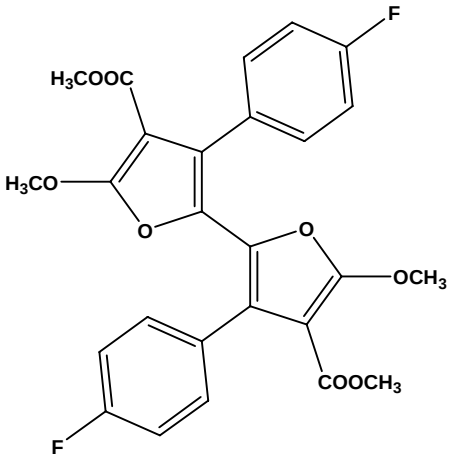
2l

(2l) Yield: 57 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, *J* = 7.00 Hz, 6H), 4.38-4.43 (q, *J* = 7.08 Hz, 4H), 7.25-7.49 (m, 16H), 8.14-8.17 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 13.98, 62.31, 91.60, 112.74, 123.03, 128.28, 128.84, 128.99, 129.77, 131.92, 132.14, 133.48, 139.63, 166.17; HRMS exact mass calcd for ($C_{36}H_{30}S_2O_8$+Na) requires m/z 677.1274, found m/z 677.1279.



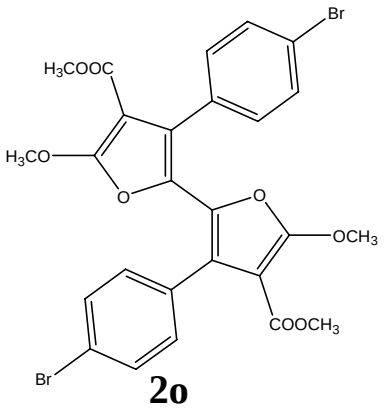
2m

(2m) Yield: 46 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (s, 6H), 3.62 (s, 6H), 3.79 (s, 6H), 7.06-7.26 (m, 8H); ^{13}C NMR (100MHz, $CDCl_3$) δ 21.28, 51.01, 57.48, 91.87, 126.19, 128.05, 128.72, 129.84, 131.03, 136.97, 161.85, 163.14; HRMS exact mass calcd for ($C_{28}H_{26}O_8$+H) requires m/z 491.1700, found m/z 491.1705.



2n

(2n) Yield: 54 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 (s, 6H), 3.90 (s, 6H), 6.93 (d, J = 8.44 Hz, 4H), 7.36 (d, J = 8.36 Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ 51.02, 57.62, 92.02, 114.27, 114.48, 125.31, 127.57, 127.61, 130.88, 131.57, 131.65, 161.03, 162.05, 162.89, 163.48; HRMS exact mass calcd for ($C_{26}H_{20}O_8F_2$+H) requires m/z 499.1199, found m/z 499.1205.

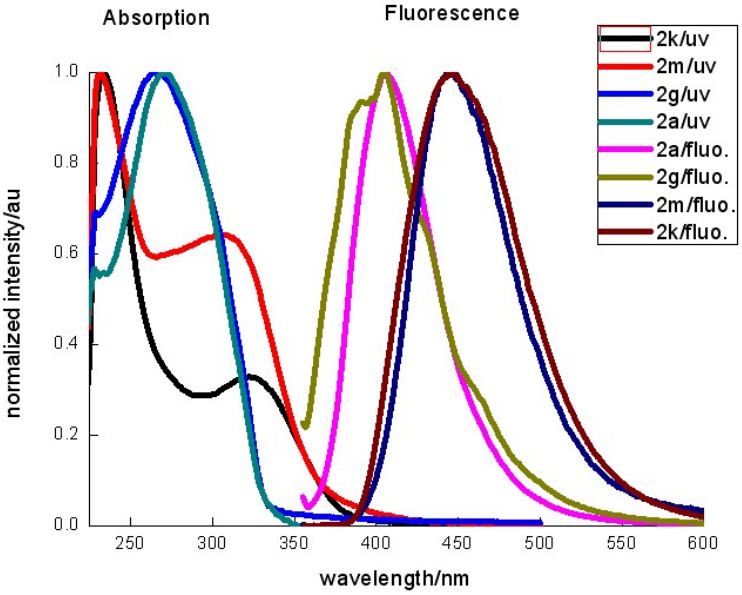


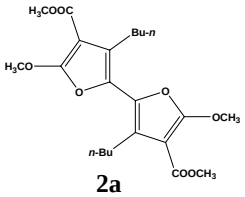
2o

(2o) Yield: 65 % ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62 (s, 6H), 3.86 (s, 6H), 6.93-7.10 (m, 8H); ^{13}C NMR (100MHz, $CDCl_3$) δ 51.12, 57.72, 121.71, 125.38, 128.85, 130.51, 130.59, 130.65, 131.54, 162.18, 162.81; HRMS exact mass calcd for ($C_{26}H_{20}O_8Br_2$+H) requires m/z 618.9598, found m/z 419.2442.

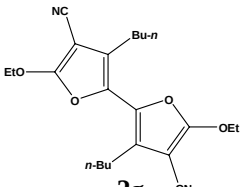
Datas of UV and Fluorescence

Normalized spectra of UV and fluorescence of **2a**, **2g**, **2k**, **2m**

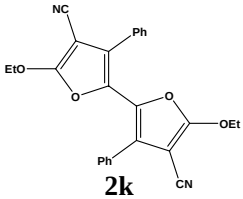




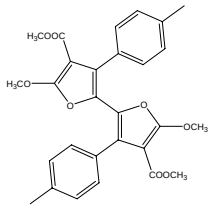
2a



2g

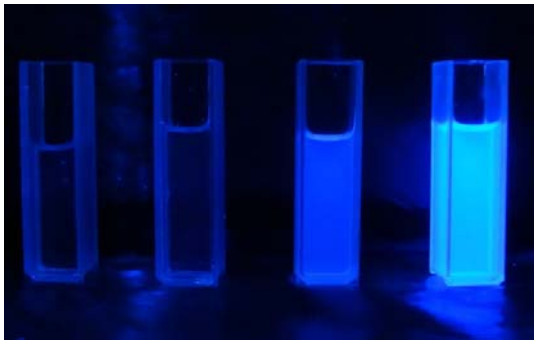


2k



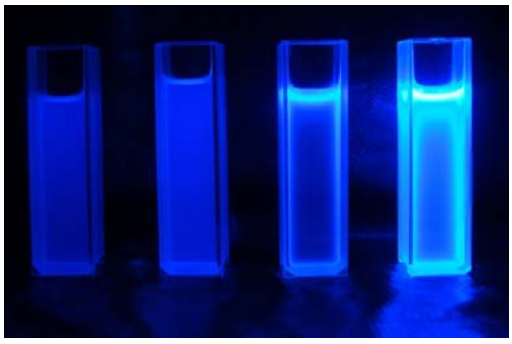
2m

Solution fluorescence in different concentration (in DCM, upon irradiation at 365nm.)



2a **2g** **2k** **2m**

10^{-5} mol/L



2a **2g** **2k** **2m**

10^{-3}mol/L

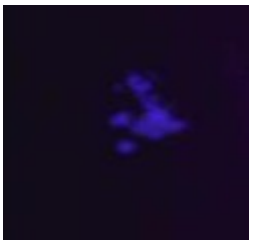
2a $\Phi_f = 0.019$ in DCM (340nm)

2m $\Phi_f = 0.26$ in DCM (300nm)

2k $\Phi_f = 0.97$ in DCM (300nm)

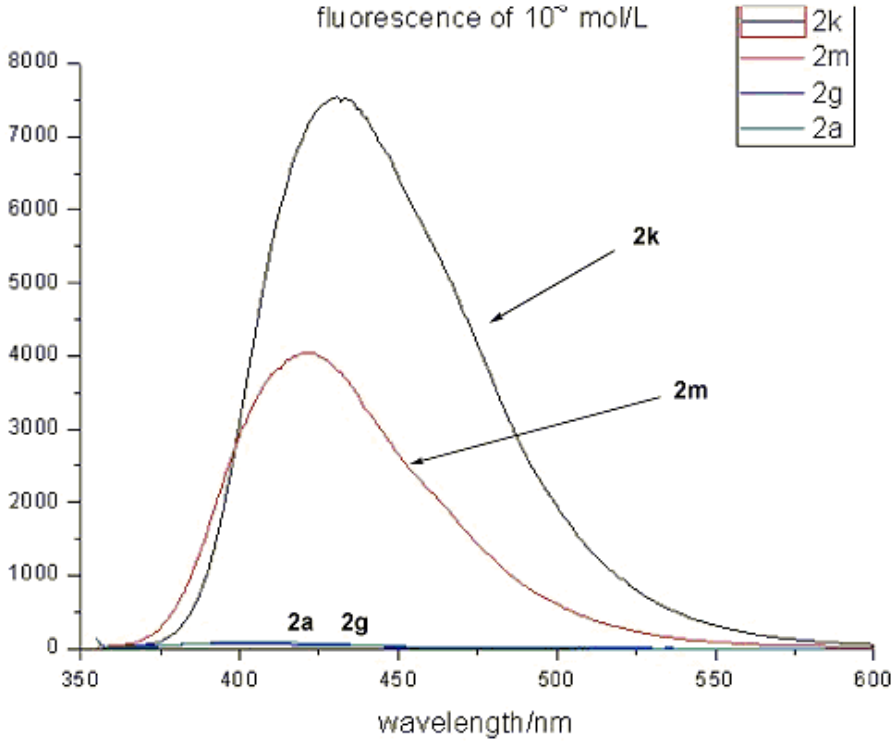
Standard Solution: quinine sulfate in 0.1N sulfuric acid

Solid state fluorescene (**2g**) (upon irradiation at 365nm).

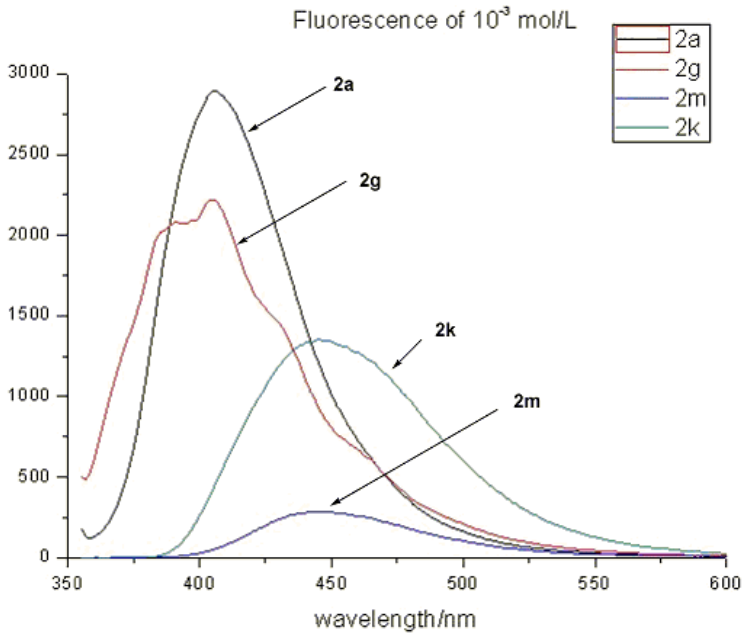


No solid fluorescene for compounds **2k** and **2m**

Solution fluorescence of **2a**, **2g**, **2k** and **2m** in different concentration

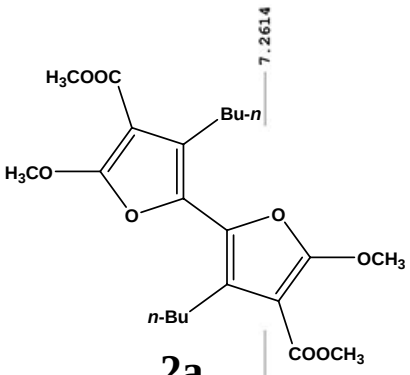


10^{-5}mol/L fluorecense: **2k**,**2m**>>**2a**,**2g**

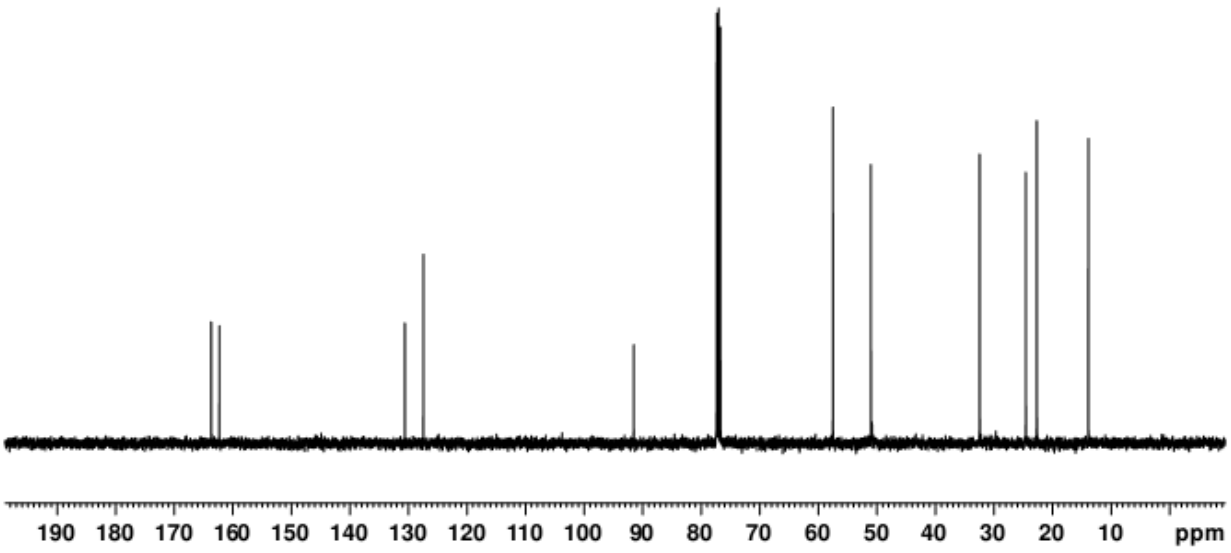


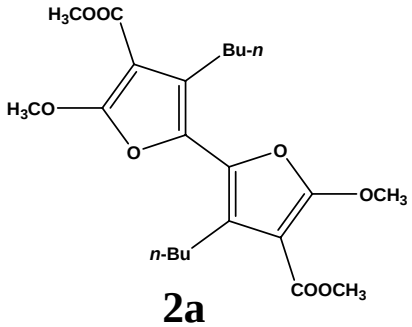
10^{-3}mol/L fluorecense: **2a**,**2g**>**2k**,**2m**

NMR spectra for the products



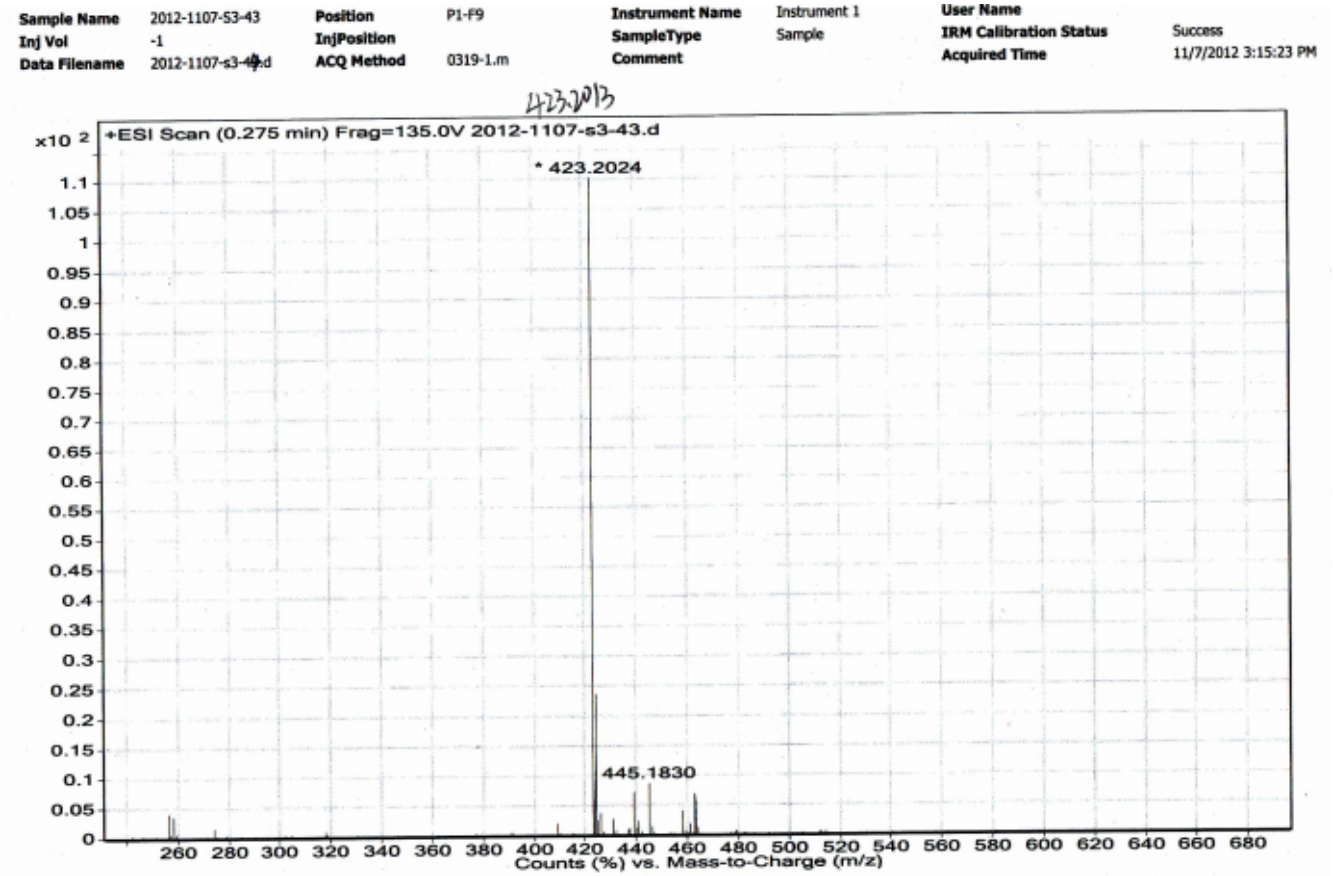
2a





2a

HRMS exact mass calcd for ($C_{22}H_{30}O_8$+H) requires m/z 423.2013, found m/z 423.2024



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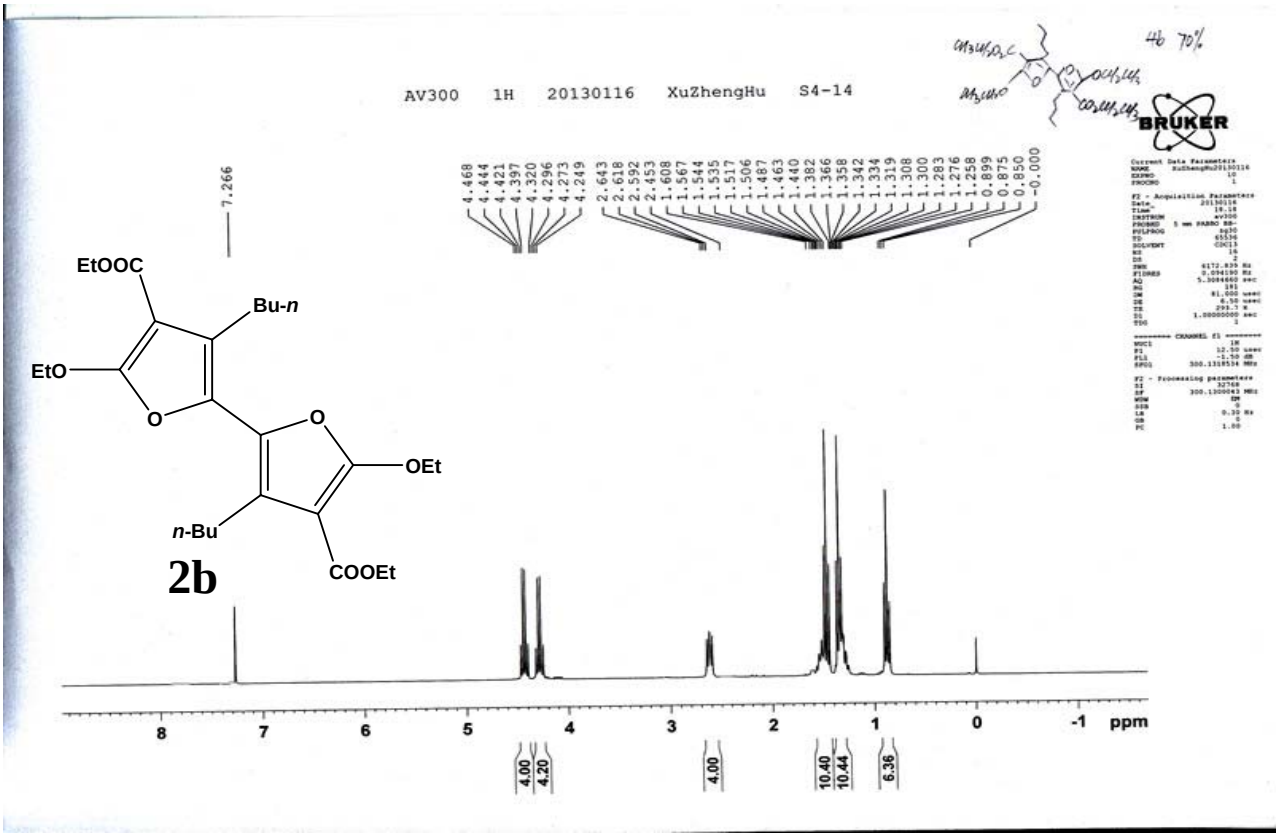
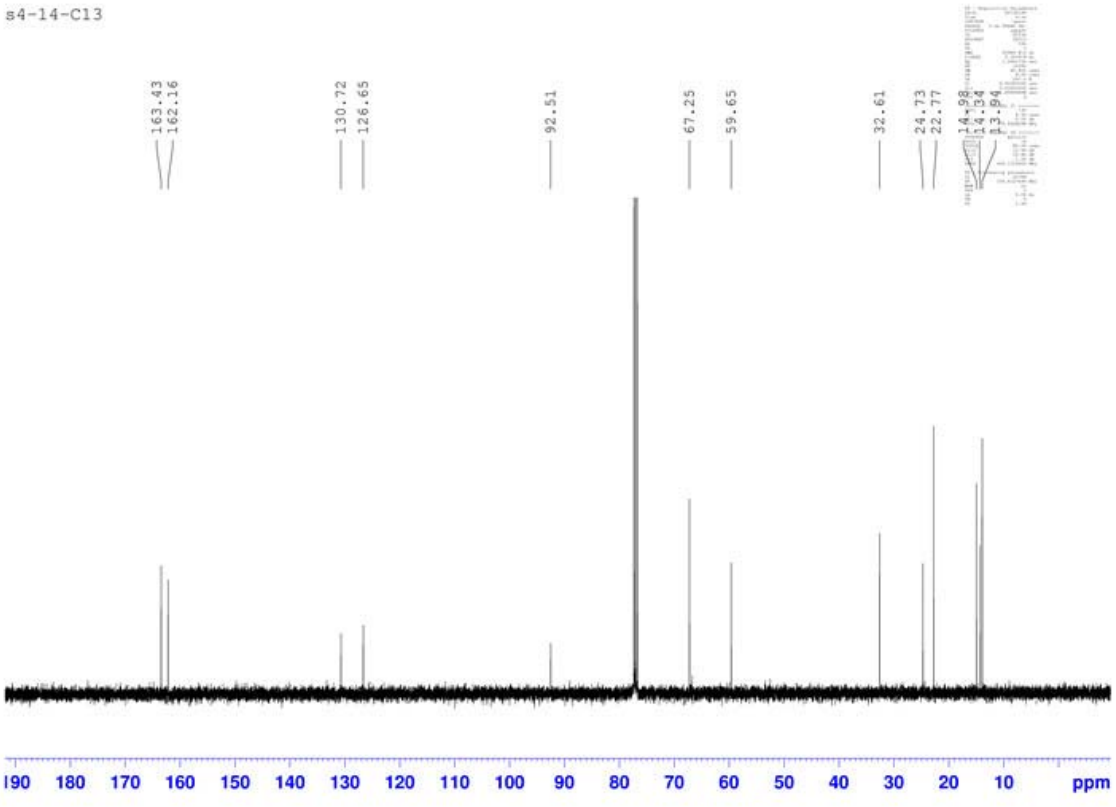
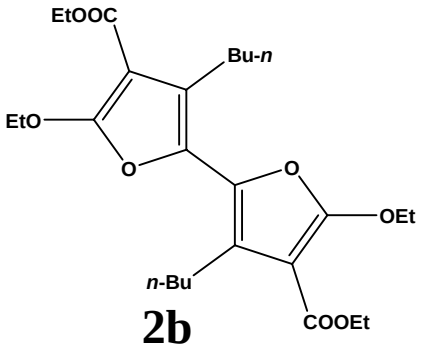
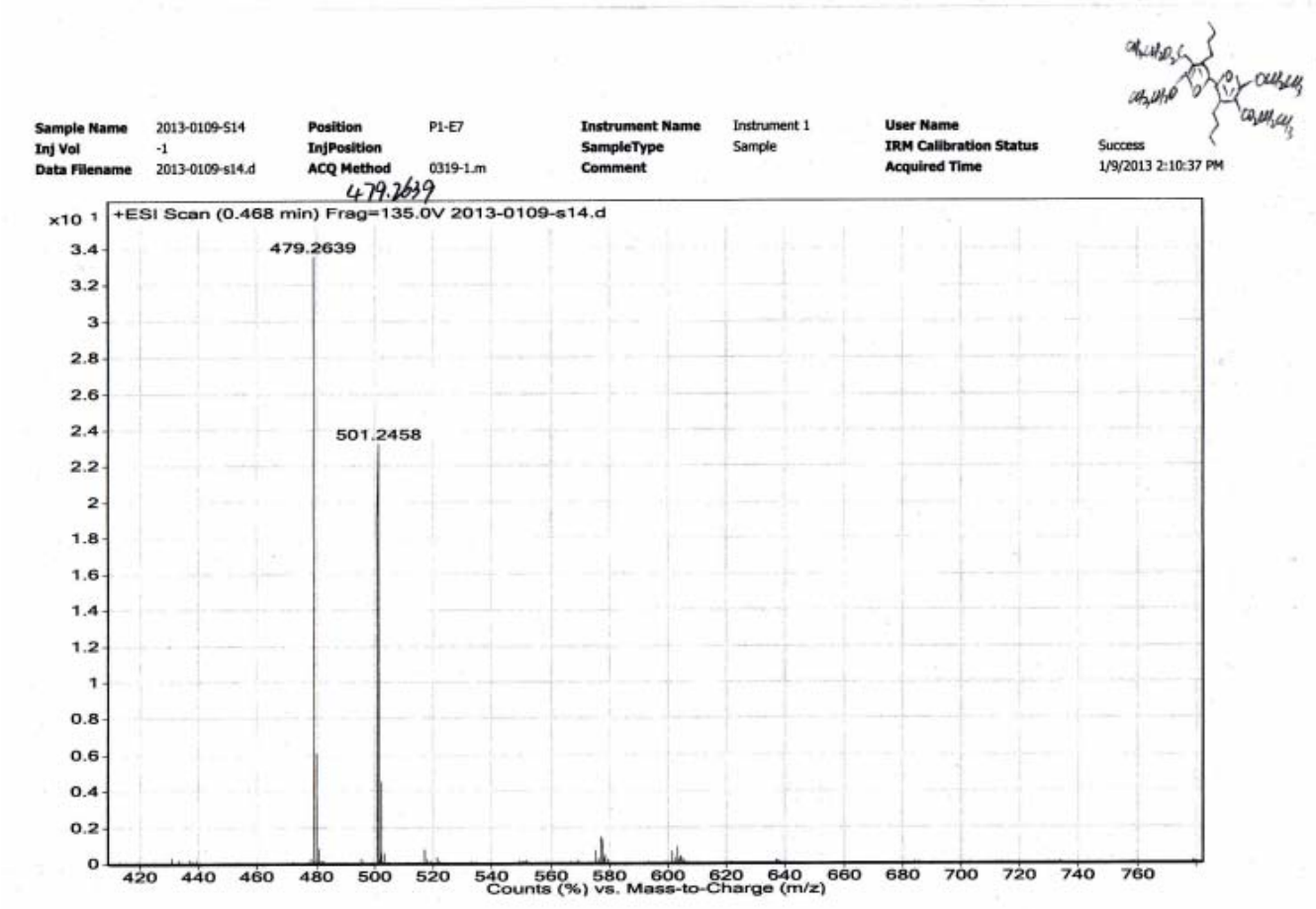

AV300 1H 20130116 XuZhengHu S4-14
46 70%
BRUKER
7.266
4.468
4.444
4.421
4.397
4.320
4.296
4.273
4.249
2.643
2.618
2.592
2.453
1.608
1.567
1.544
1.535
1.517
1.506
1.487
1.463
1.440
1.382
1.366
1.358
1.342
1.334
1.319
1.308
1.300
1.283
1.276
1.258
0.899
0.875
0.850
-0.000
EtOOC
Bu-n
EtO
O
O
OEt
n-Bu
COOEt
2b
8
7
6
5
4
3
2
1
0
-1
ppm
4.00
4.20
4.00
10.40
10.44
6.36

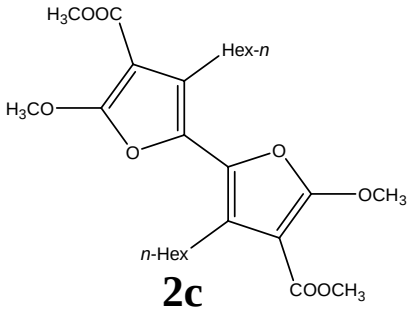

s4-14-C13
163.43
162.16
130.72
126.65
92.51
67.25
59.65
32.61
24.73
22.77
14.98
14.34
13.94
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



2b

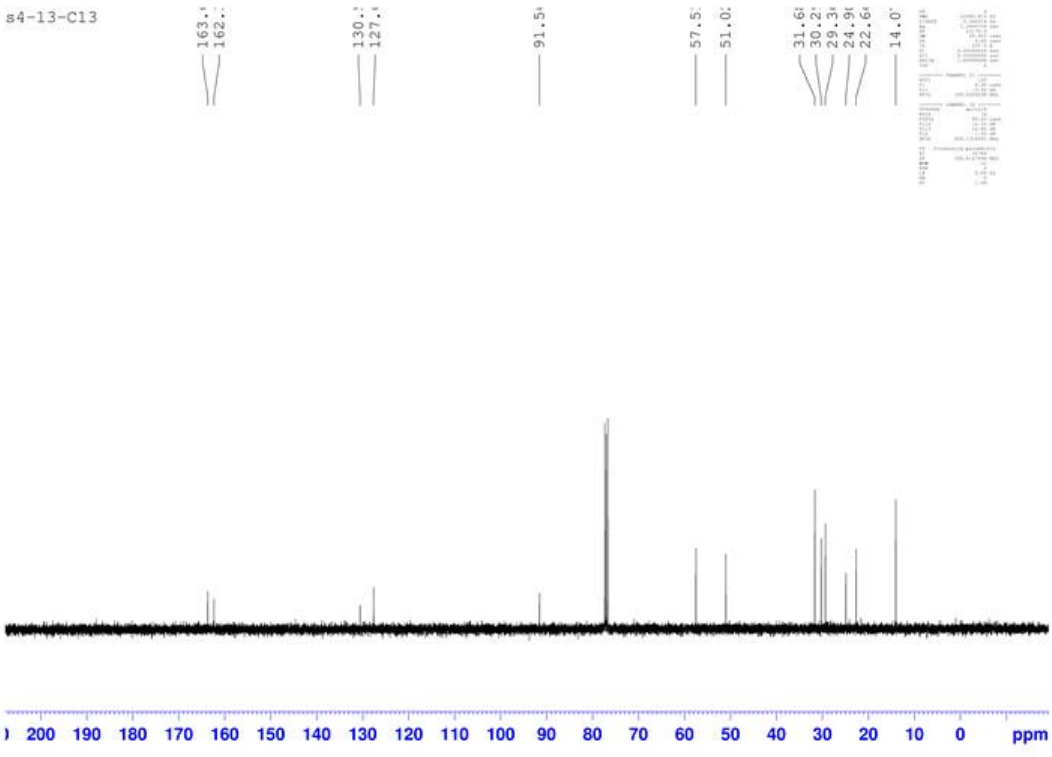
HRMS exact mass calcd for ($C_{24}H_{48}O_8$+H) requires m/z 479.2639, found m/z 479.2639.

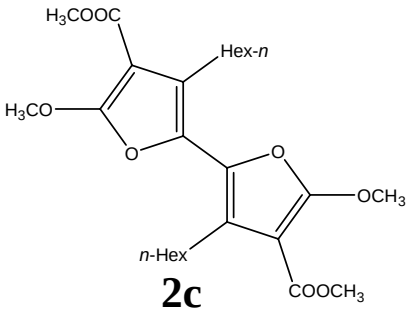



H3COOC
Hex-n
H3CO
O
O
OCH3
n-Hex
COOCH3

2c

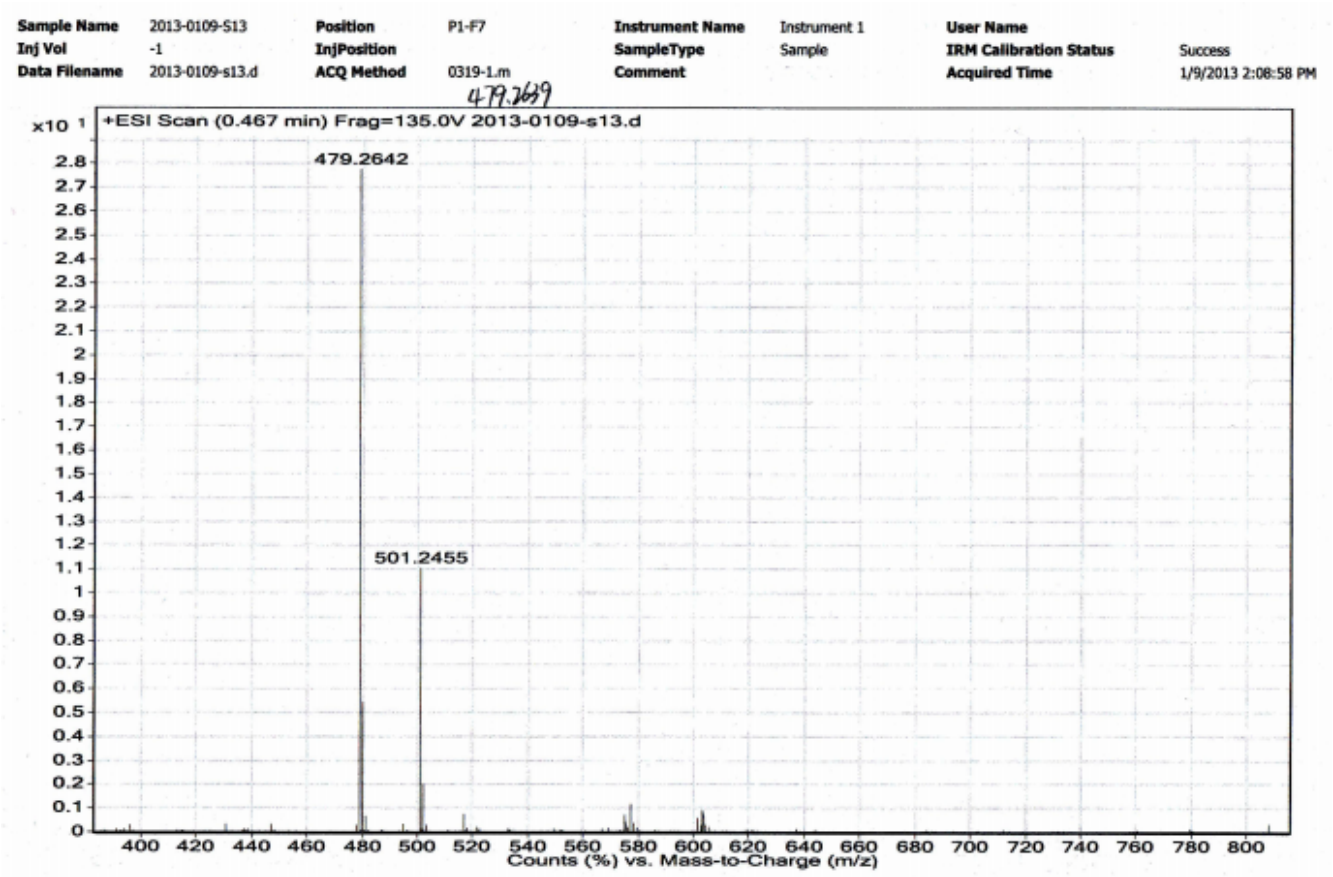
4.0890
3.8113
2.6197
2.6010
2.5813
1.5347
1.5165
1.4981
1.3033
1.2846
1.2670
1.2460
0.8642
0.8480
0.8308
8
7
6
5
4
3
2
1
0
−1
ppm
2.9662
3.0000
1.9773
2.0145
6.3192
3.0621

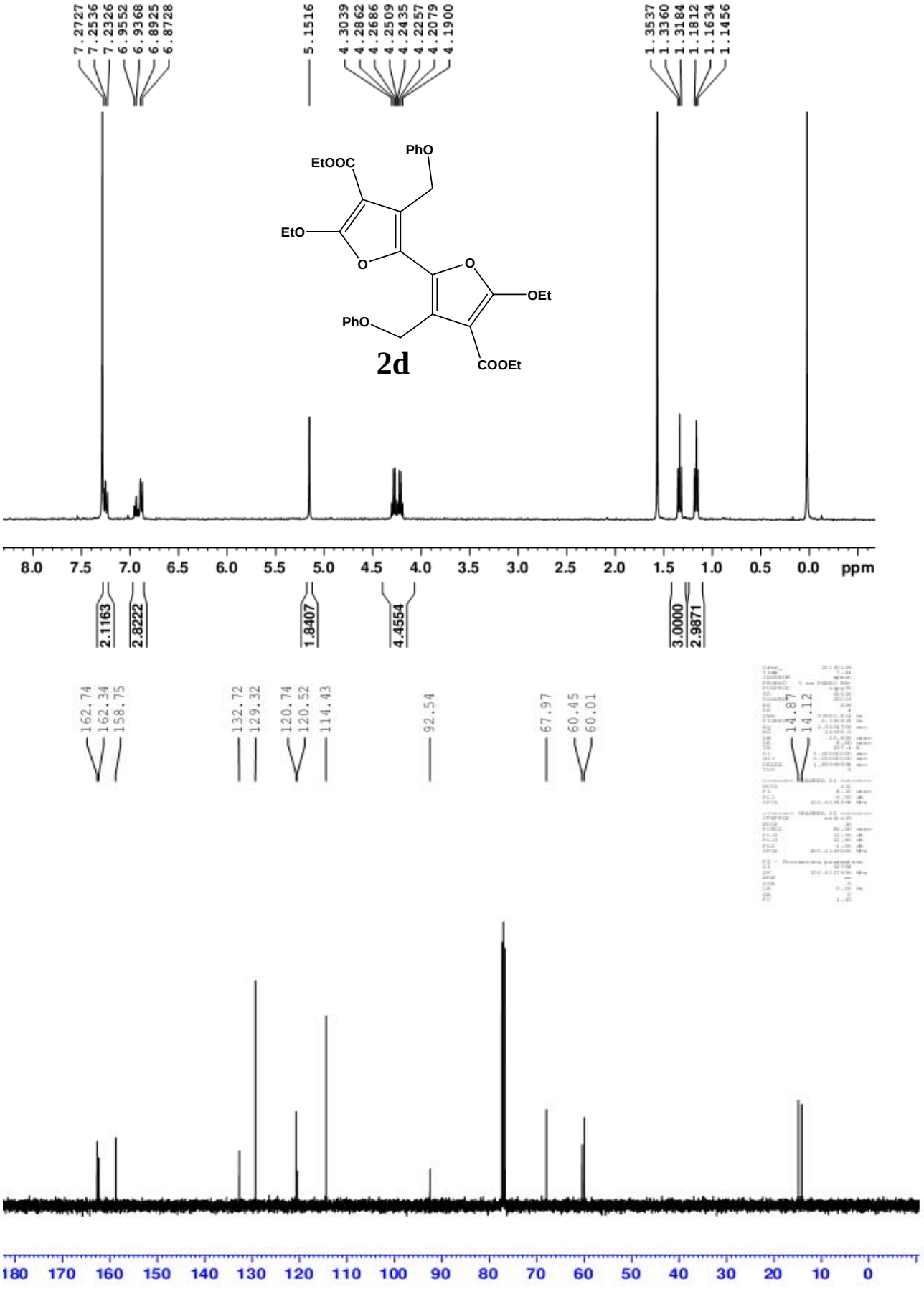

s4-13-C13
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

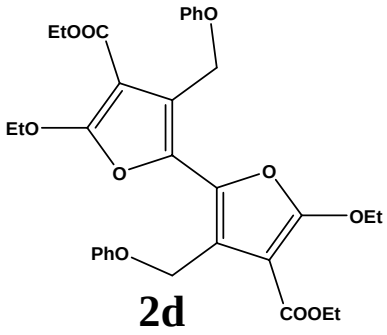


2c

HRMS exact mass calcd for ($C_{26}H_{38}O_8$+H) requires m/z 479.2639, found m/z 479.2642.

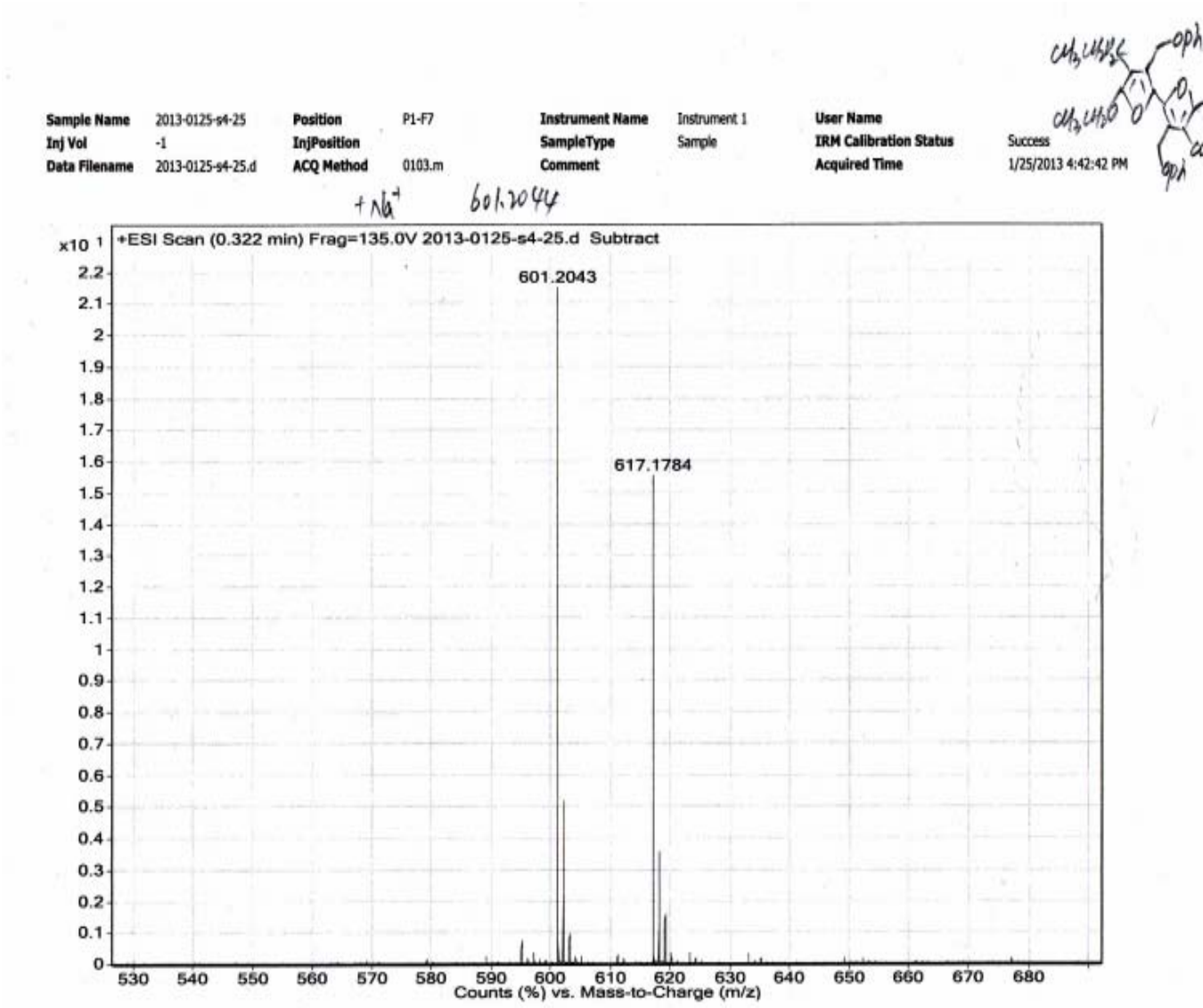


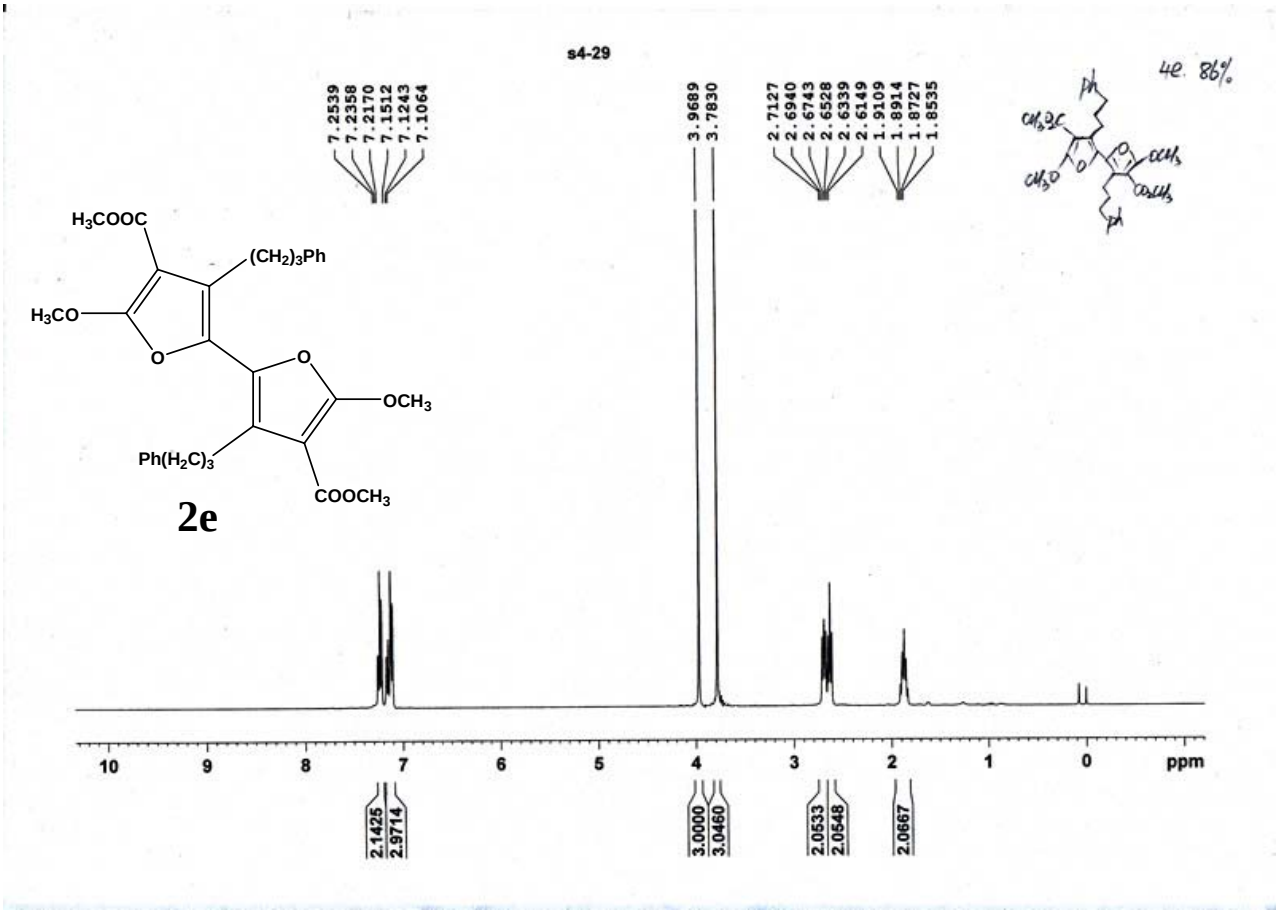

7.2727
7.2536
7.2326
6.9552
6.9368
6.8925
6.8728
5.1516
4.3039
4.2862
4.2686
4.2509
4.2435
4.2257
4.2079
4.1900
1.3537
1.3360
1.3184
1.1812
1.1634
1.1456
EtOOC
PhO
EtO
O
O
OEt
PhO
COOEt
2d
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.1163
2.8222
1.8407
4.4554
3.0000
2.9871
162.74
162.34
158.75
132.72
129.32
120.74
120.52
114.43
92.54
67.97
60.45
60.01
14.87
14.12
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

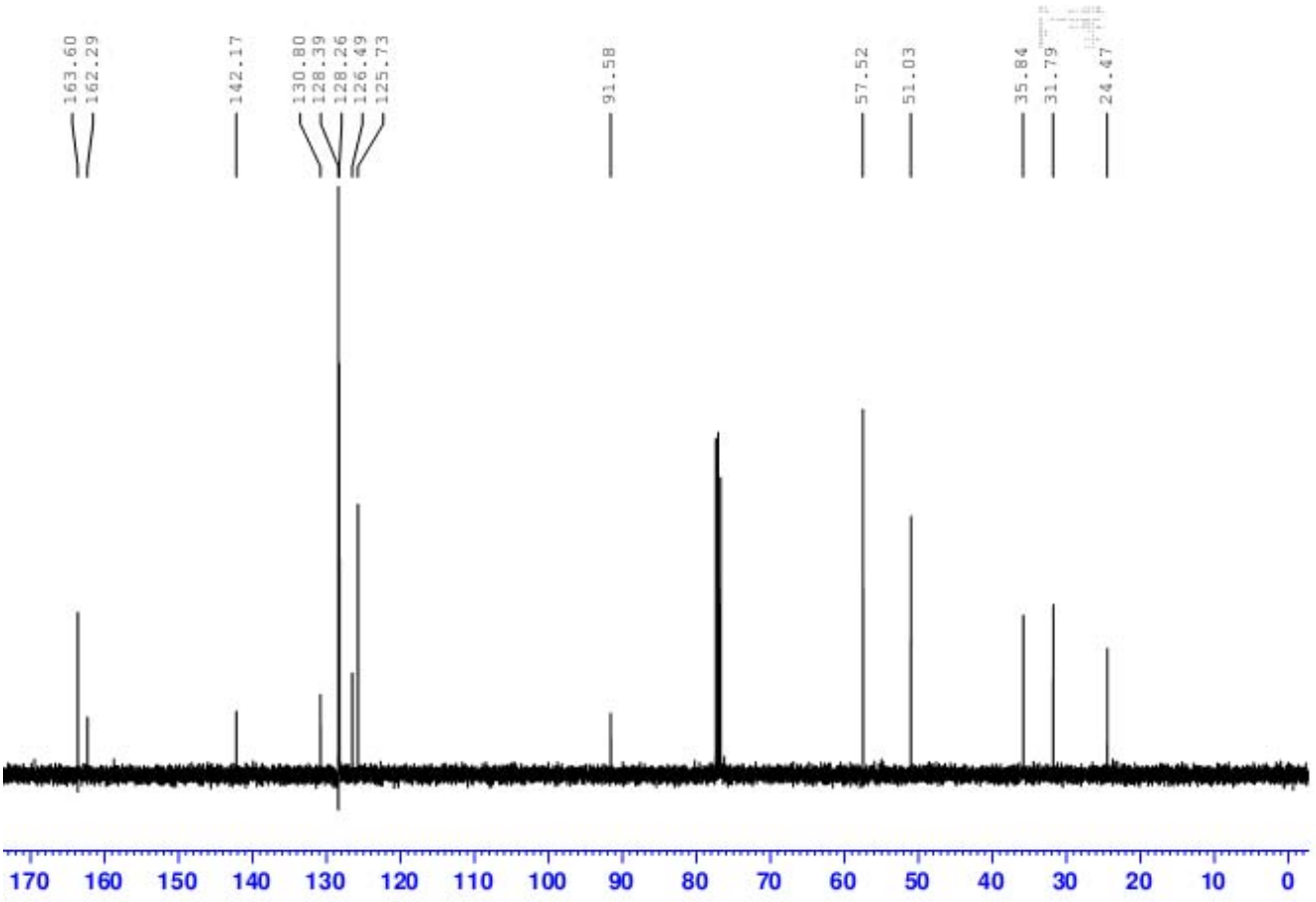


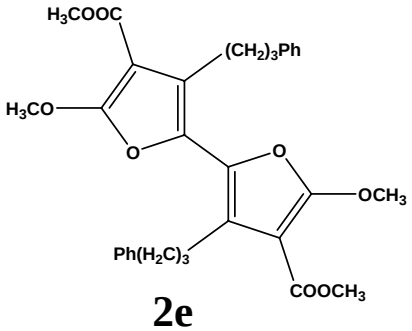
2d

HRMS exact mass calcd for ($C_{26}H_{38}O_8$+H) requires m/z 601.2044, found m/z 601.2043.



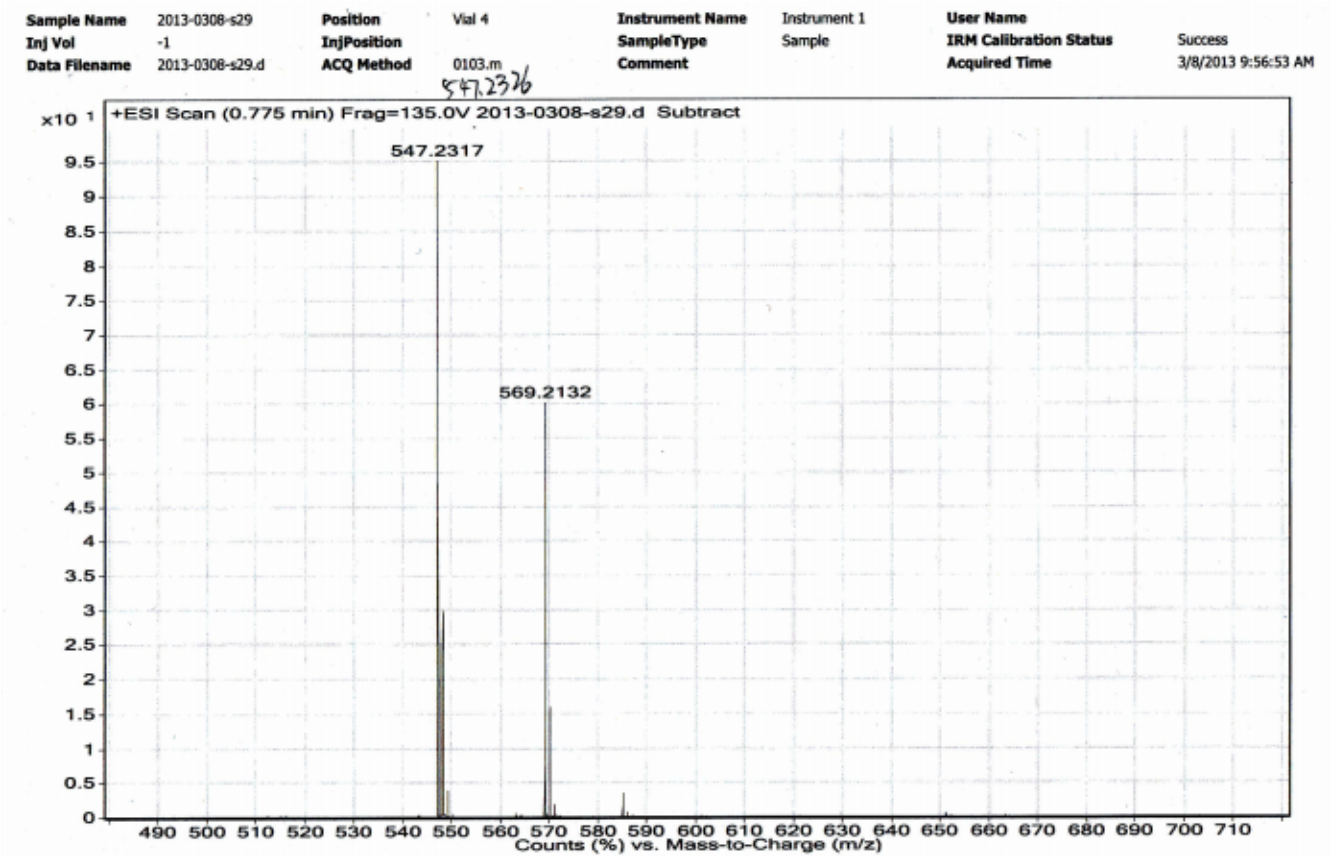

s4-29
4e. 86%
7.2539
7.2358
7.2170
7.1512
7.1243
7.1064
3.9689
3.7830
2.7127
2.6940
2.6743
2.6528
2.6339
2.6149
1.9109
1.8914
1.8727
1.8535
H3COOC
(CH2)3Ph
H3CO
O
O
OCH3
Ph(H2C)3
COOCH3
2e
10
9
8
7
6
5
4
3
2
1
0
ppm
2.1425
2.9714
3.0000
3.0460
2.0533
2.0548
2.0667

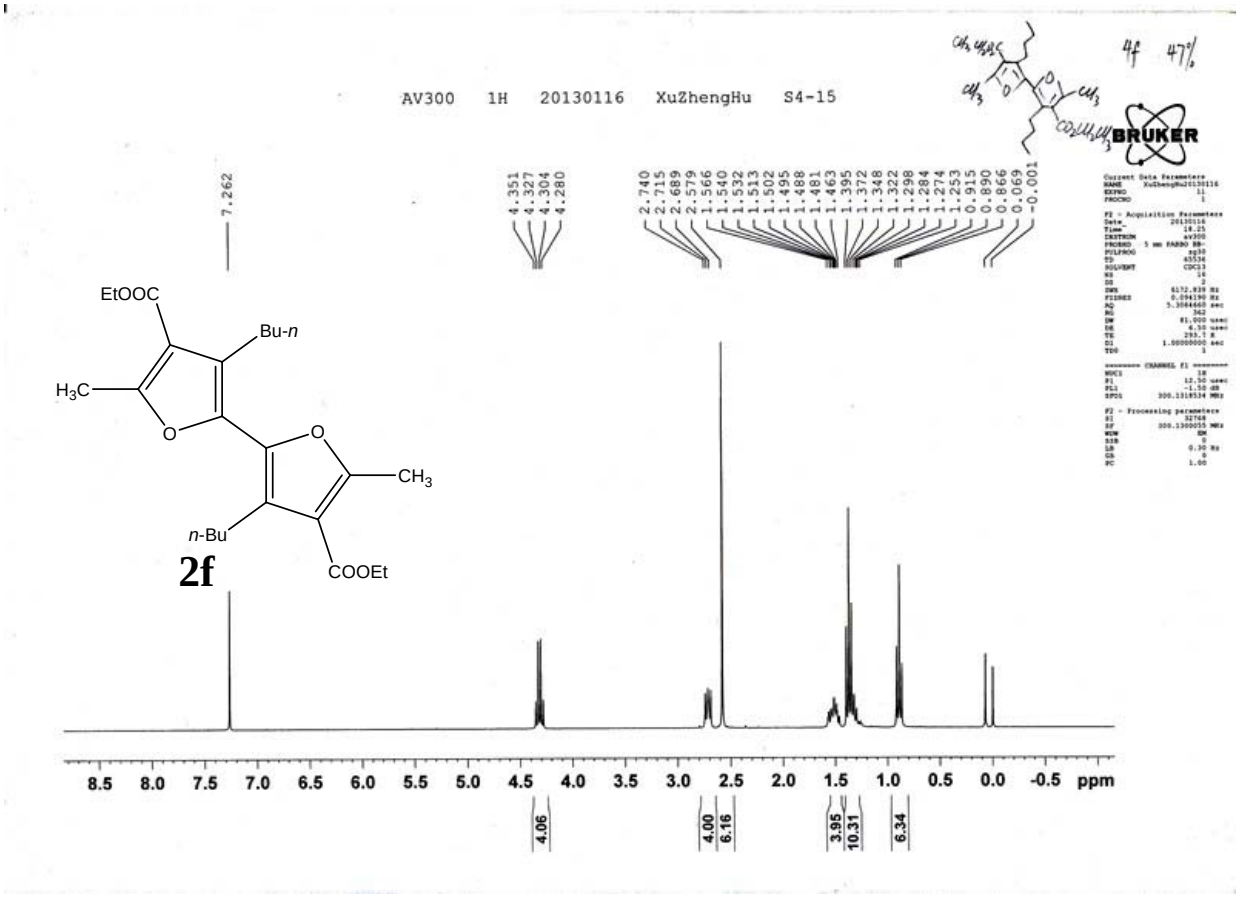

163.60
162.29
142.17
130.80
128.39
128.26
126.49
125.73
91.58
57.52
51.03
35.84
31.79
24.47
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

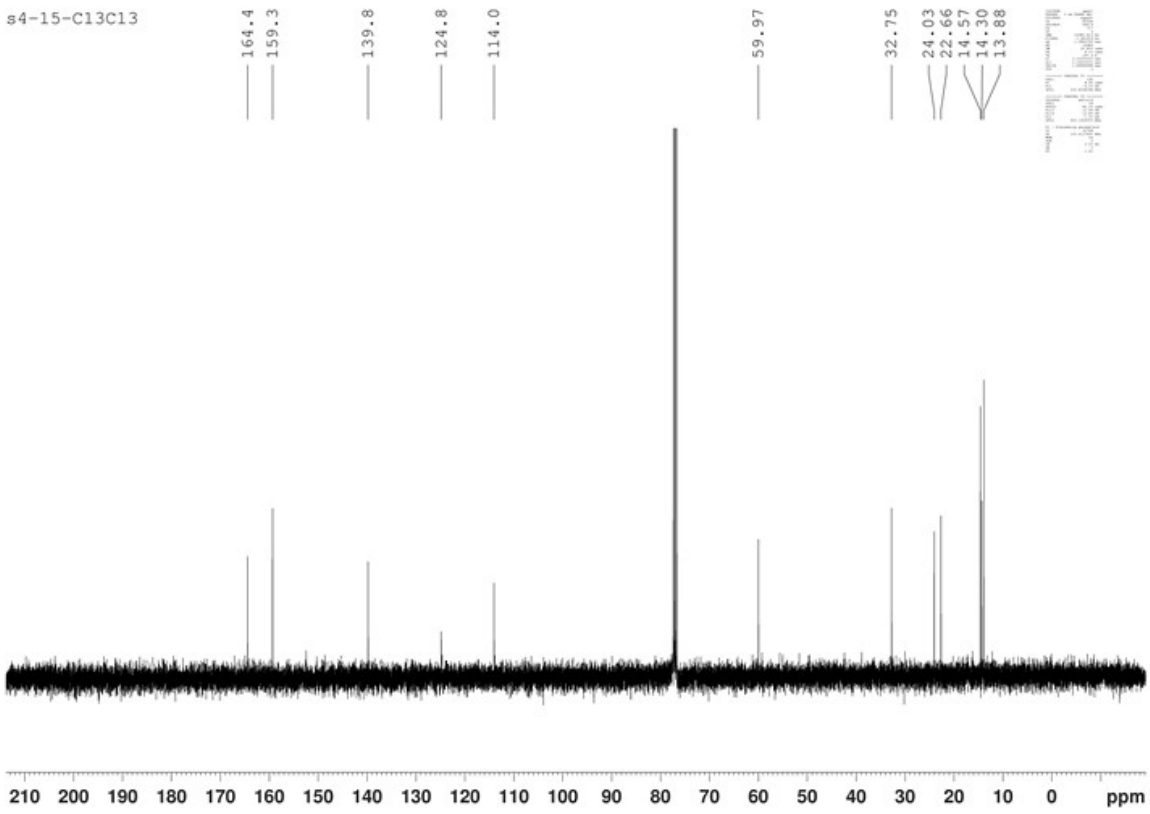


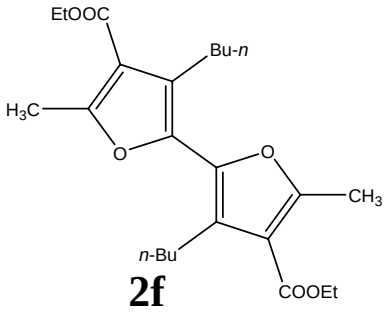
2e

HRMS exact mass calcd for ($C_{32}H_{34}O_8$+H) requires m/z 547.2326, found m/z 547.2317.



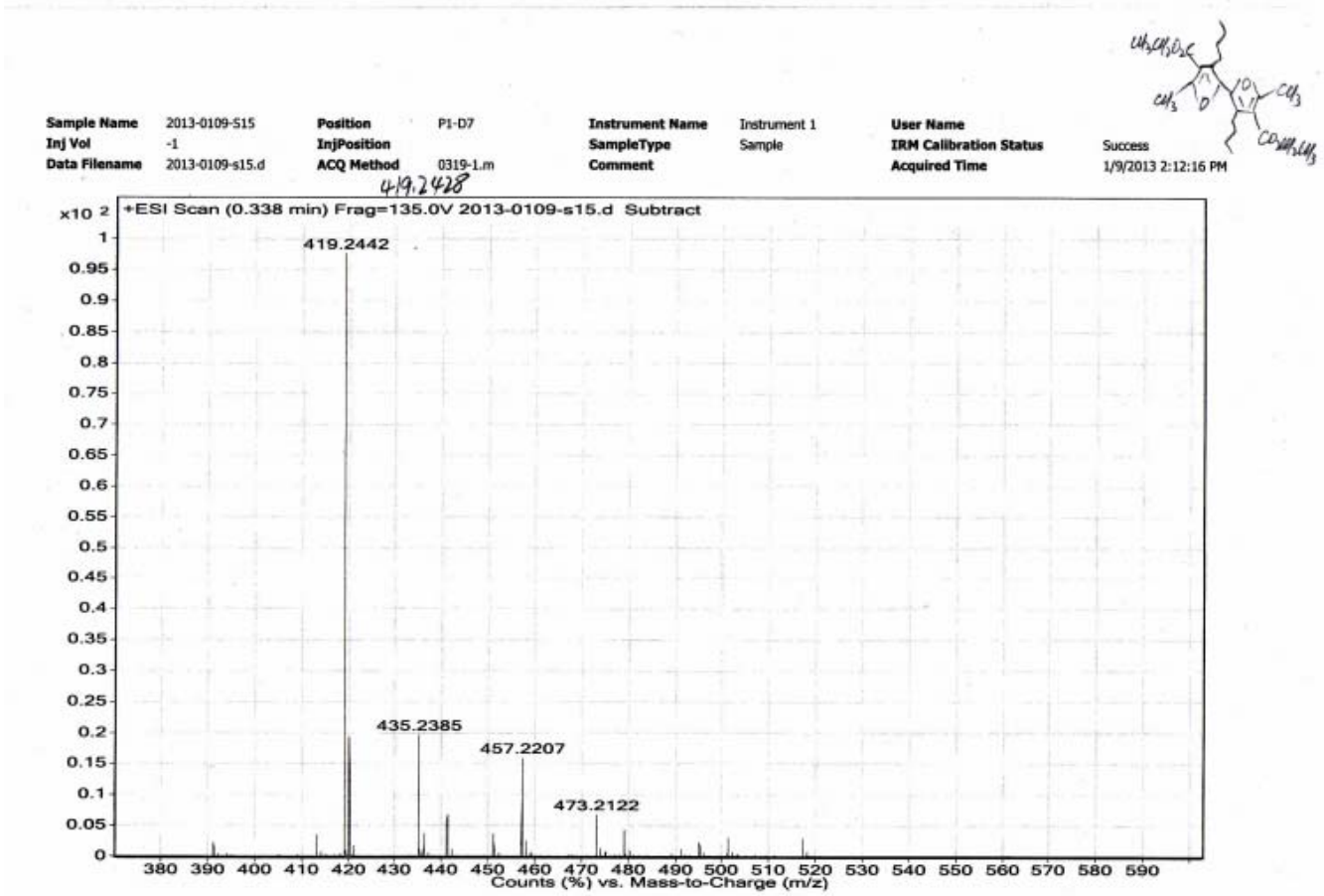

AV300 1H 20130116 XuZhengHu S4-15
4f 47%
BRUKER
7.262
4.351
4.327
4.304
4.280
2.740
2.715
2.689
2.579
1.566
1.540
1.532
1.513
1.502
1.495
1.488
1.481
1.463
1.395
1.372
1.348
1.322
1.298
1.284
1.274
1.253
0.915
0.890
0.866
0.069
-0.001
EtOOC
Bu-n
H3C
O
O
CH3
n-Bu
COOEt
2f
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
4.06
4.00
6.16
3.95
10.31
6.34

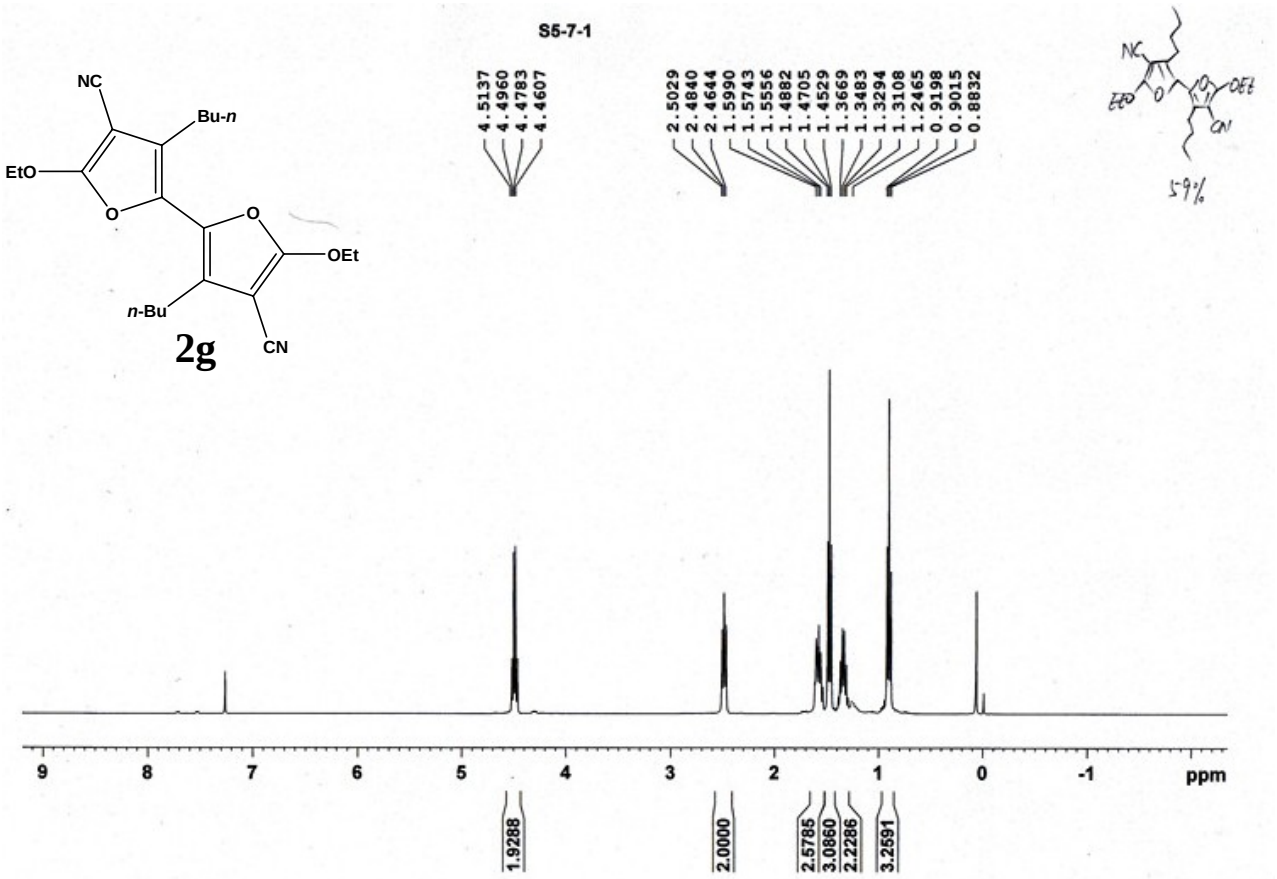

s4-15-C13C13
164.4
159.3
139.8
124.8
114.0
59.97
32.75
24.03
22.66
14.57
14.30
13.88
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

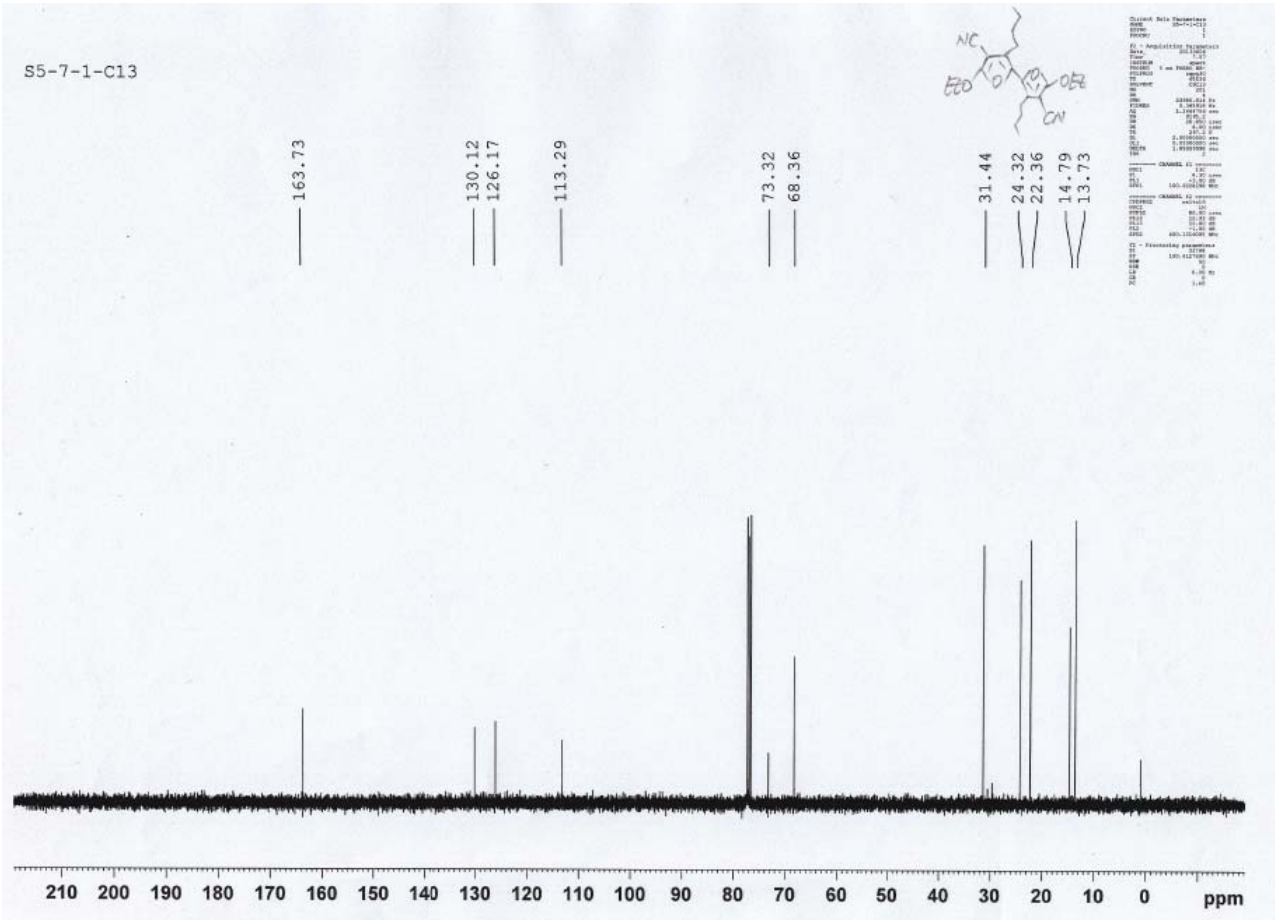


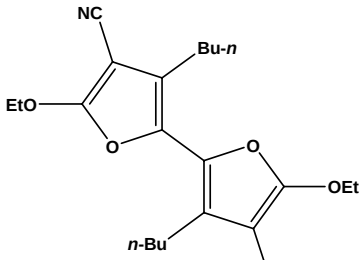
2f

HRMS exact mass calcd for ($C_{24}H_{34}O_8$+H) requires m/z 419.2428, found m/z 419.2442.



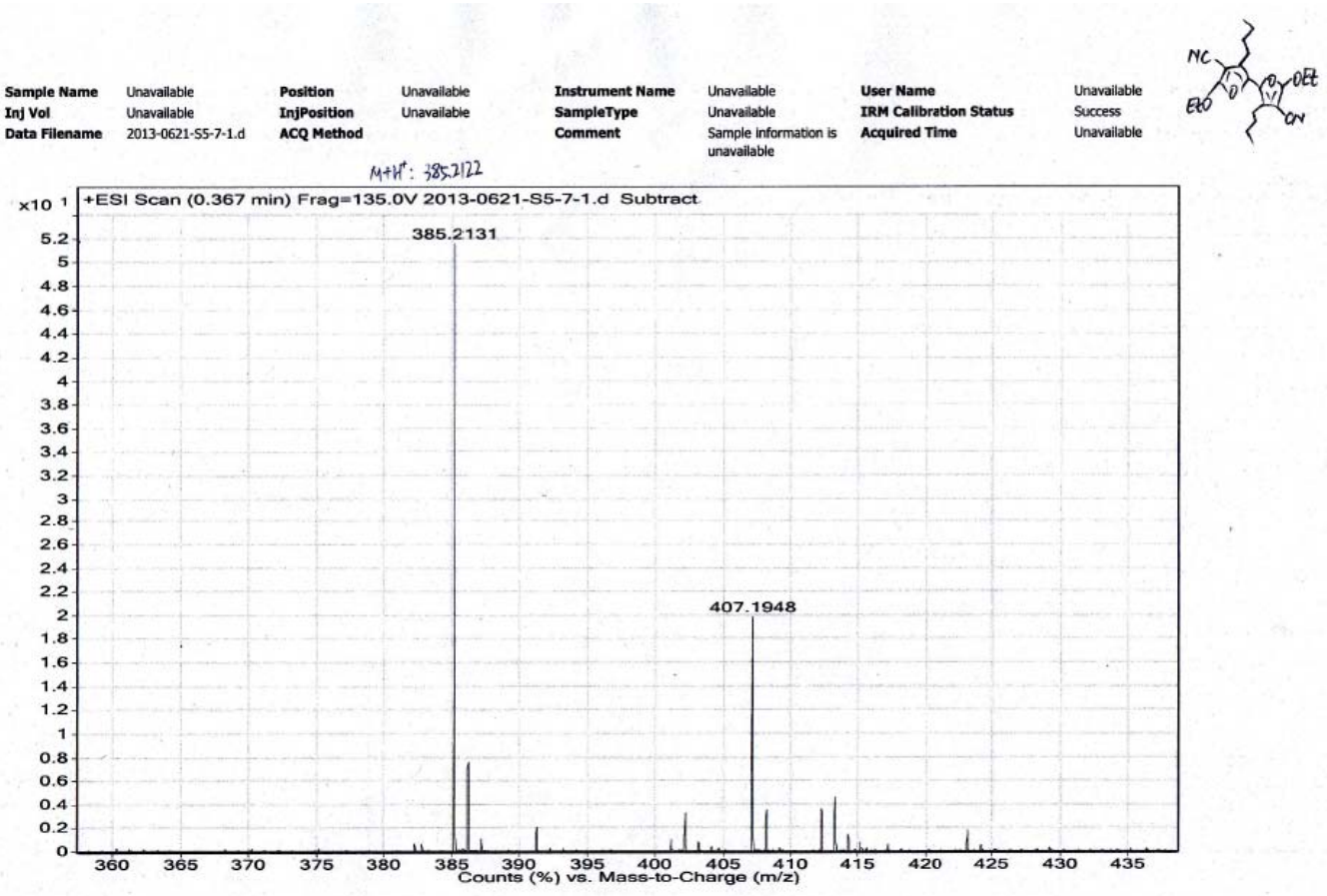

S5-7-1
NC
Bu-n
EtO
O
O
OEt
n-Bu
CN
2g
4.5137
4.4960
4.4783
4.4607
2.5029
2.4840
2.4644
1.5990
1.5743
1.5556
1.4882
1.4705
1.4529
1.3669
1.3483
1.3294
1.3108
1.2465
0.9198
0.9015
0.8832
5-9%
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.9288
2.0000
2.5785
3.0860
2.2286
3.2591

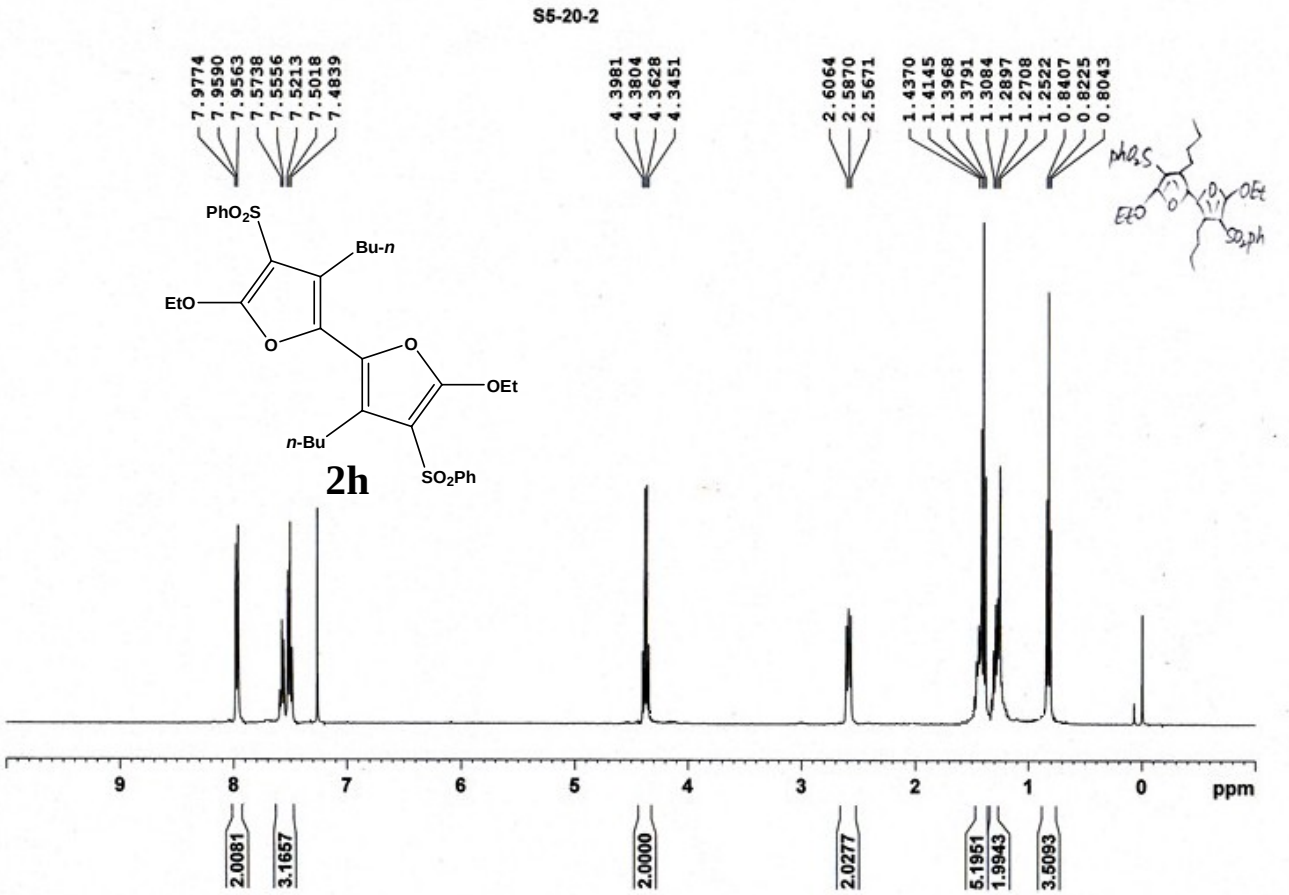

S5-7-1-C13
163.73
130.12
126.17
113.29
73.32
68.36
31.44
24.32
22.36
14.79
13.73
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

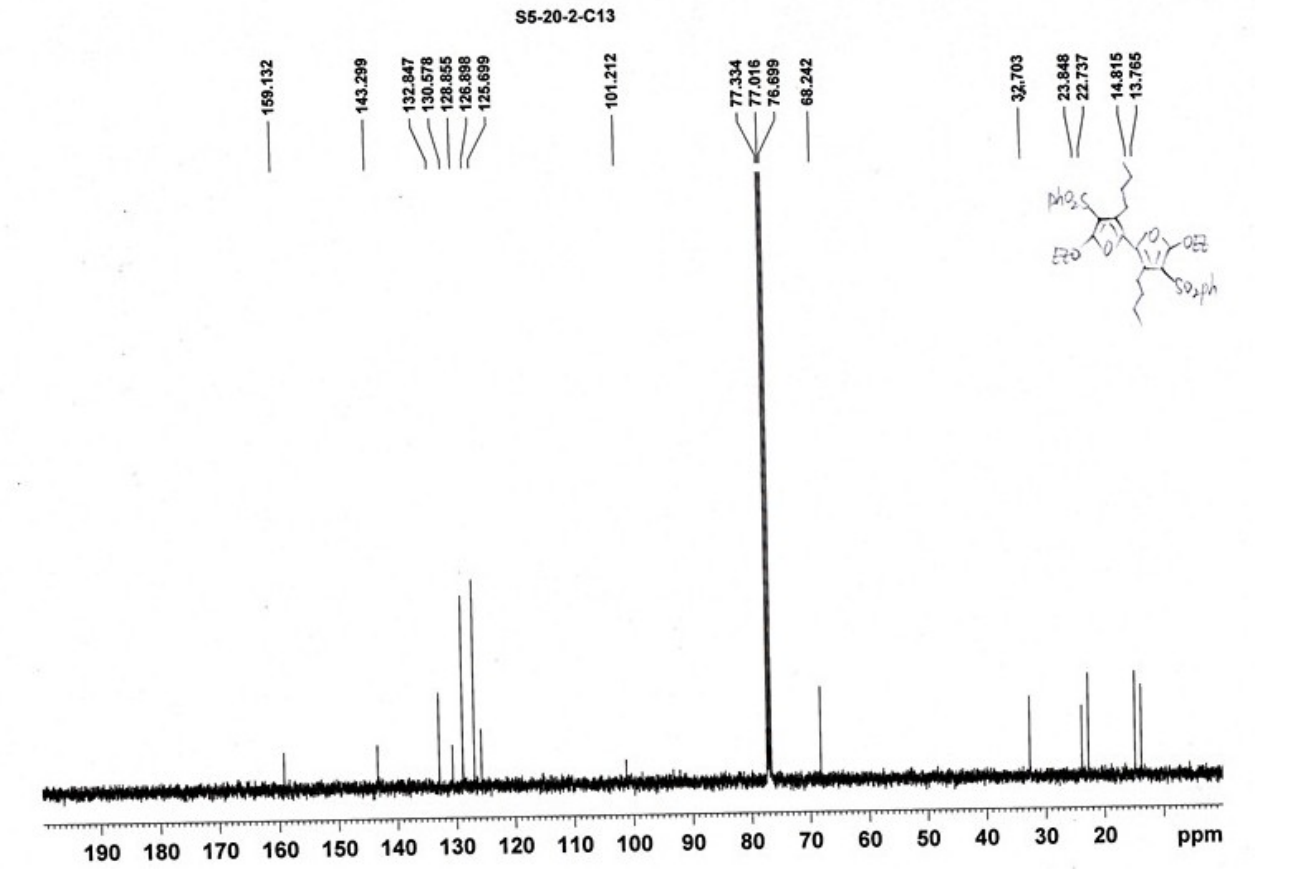


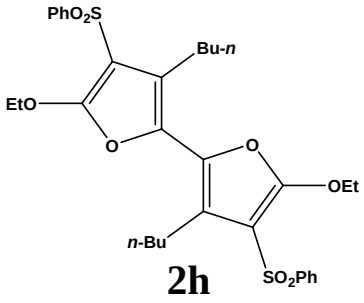
2g

HRMS exact mass calcd for ($C_{22}H_{28}N_2O_4$+H) requires m/z 385.2122, found m/z 385.2131



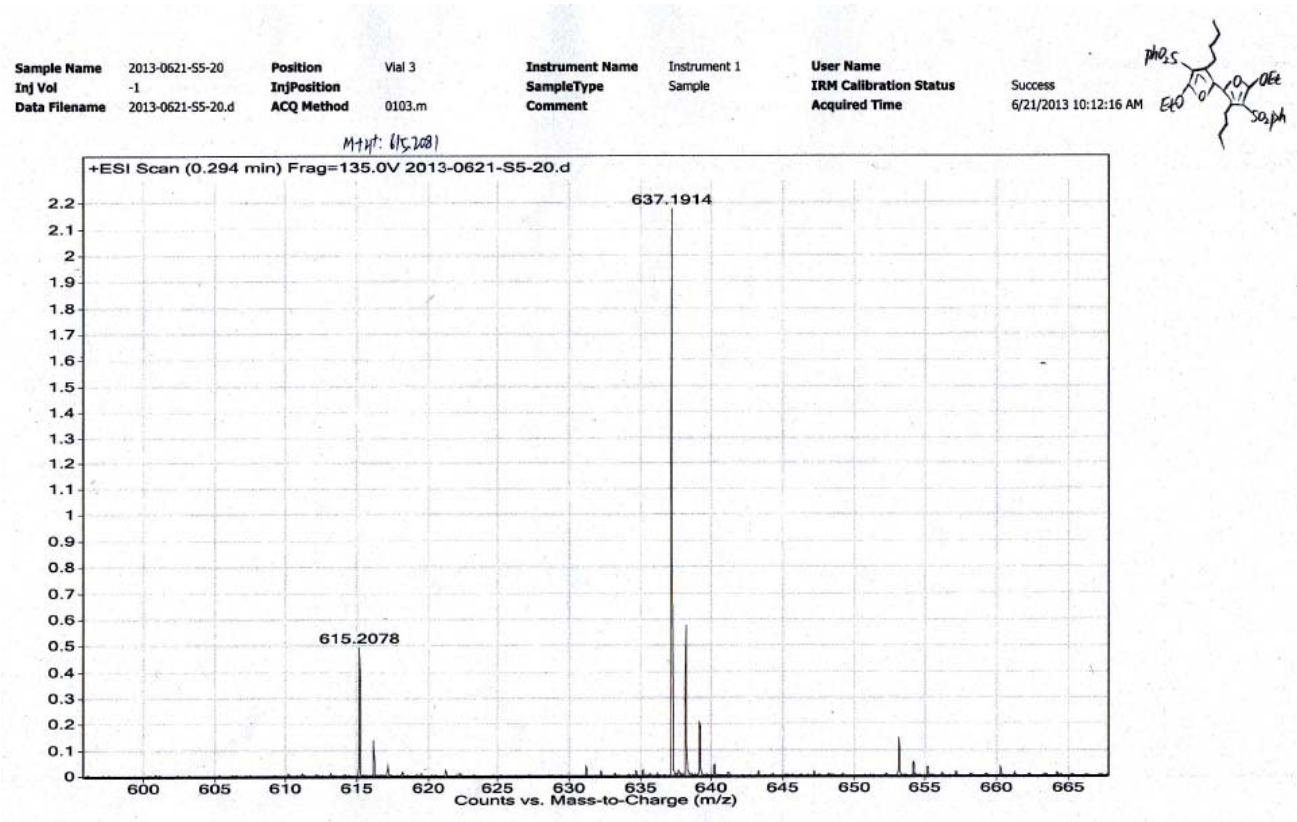

S5-20-2
7.9774
7.9590
7.9563
7.5738
7.5556
7.5213
7.5018
7.4839
4.3981
4.3804
4.3628
4.3451
2.6064
2.5870
2.5671
1.4370
1.4145
1.3968
1.3791
1.3084
1.2897
1.2708
1.2522
0.8407
0.8225
0.8043
PhO2S
Bu-n
EtO
O
O
OEt
n-Bu
SO2Ph
2h
9
8
7
6
5
4
3
2
1
0
ppm
2.0081
3.1657
2.0000
2.0277
6.1951
1.9943
3.5093

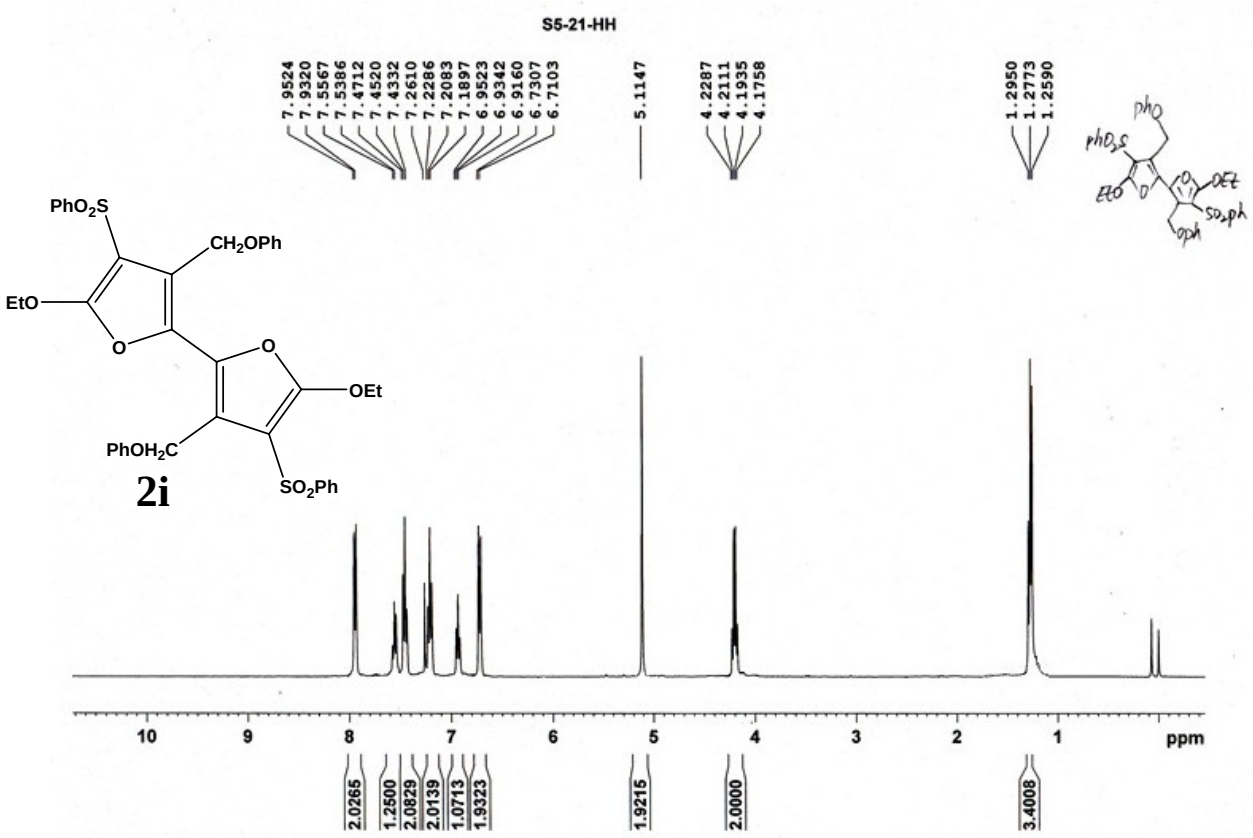

S5-20-2-C13
159.132
143.299
132.847
130.578
128.855
126.898
125.699
101.212
77.334
77.016
76.699
68.242
32.703
23.848
22.737
14.815
13.765
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

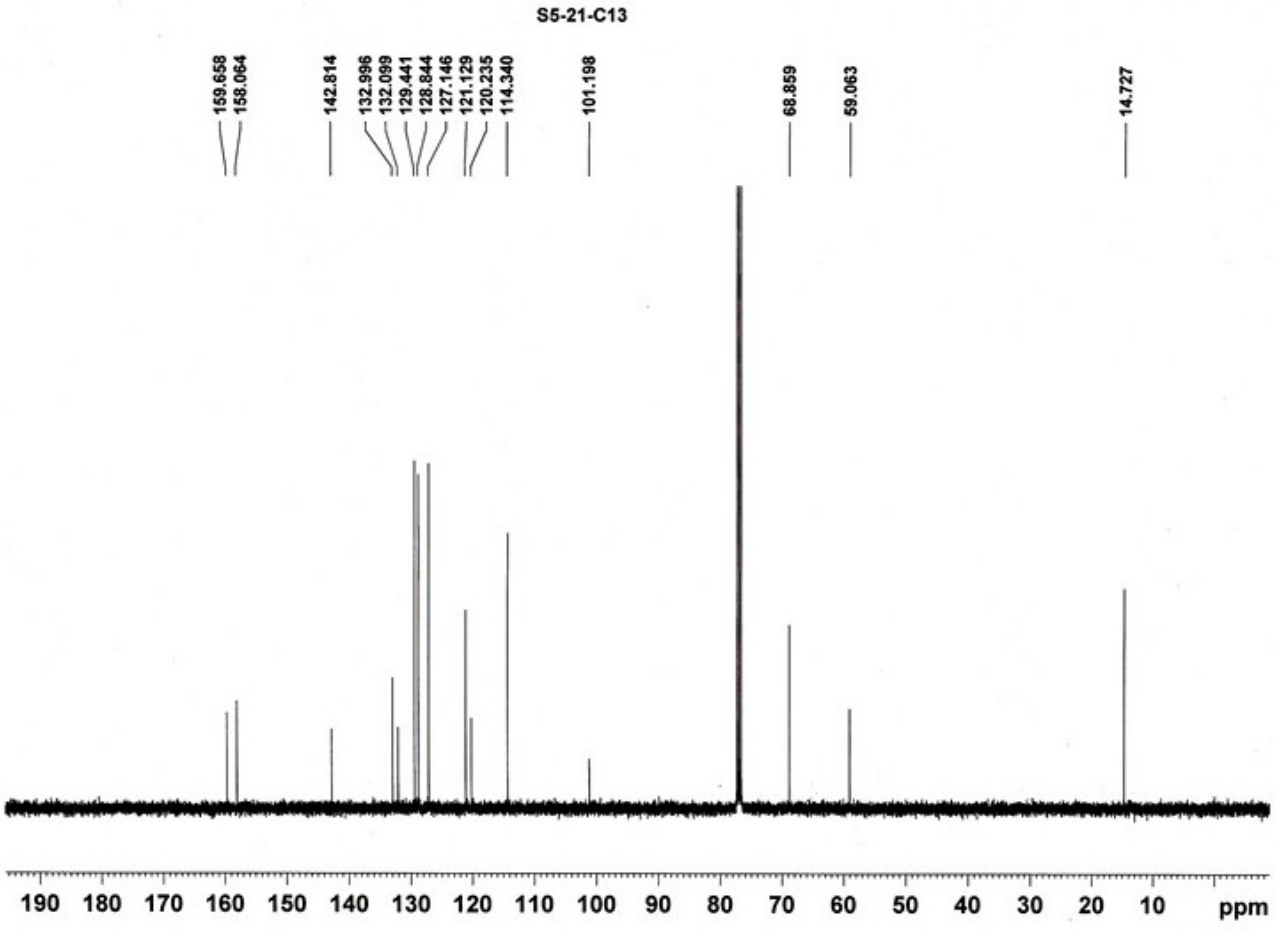


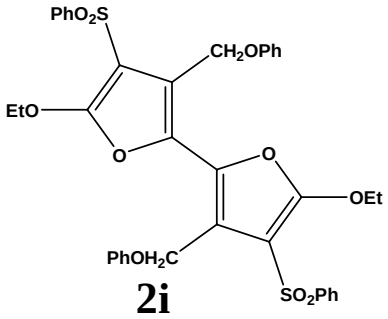
2h

HRMS exact mass calcd for ($C_{32}H_{38}S_2O_8$+H) requires m/z 615.2081, found m/z 615.2078.



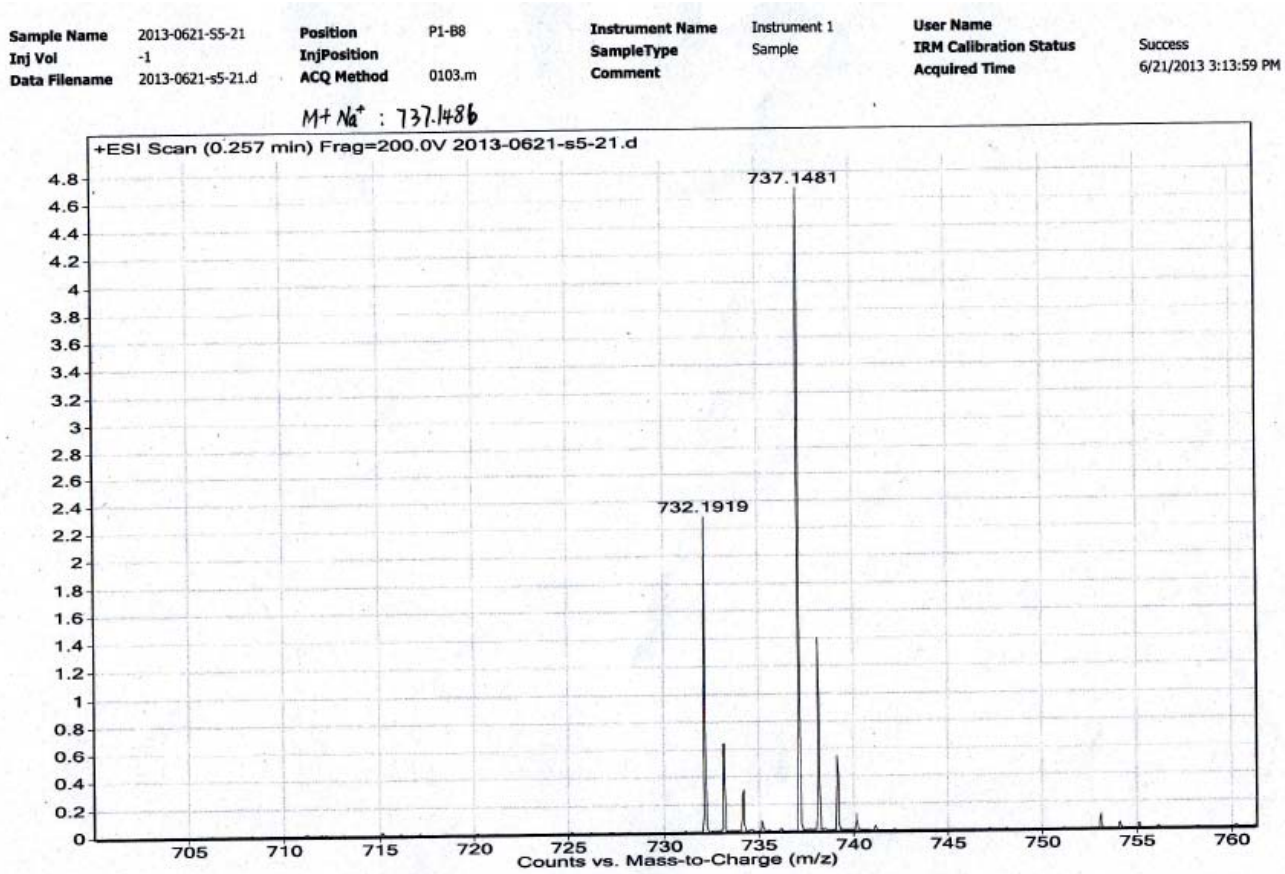

S5-21-HH
7.9524
7.9320
7.5567
7.5386
7.4712
7.4520
7.4332
7.2610
7.2286
7.2083
7.1897
6.9523
6.9342
6.9160
6.7307
6.7103
5.1147
4.2287
4.2111
4.1935
4.1758
1.2950
1.2773
1.2590
PhO2S
CH2OPh
EtO
O
O
OEt
PhOH2C
SO2Ph
2i
10
9
8
7
6
5
4
3
2
1
ppm
2.0265
1.2500
2.0829
2.0139
1.0713
1.9323
1.9215
2.0000
3.4008

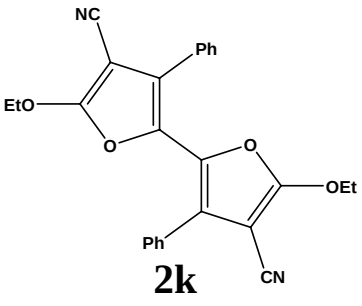

S5-21-C13
159.658
158.064
142.814
132.996
132.099
129.441
128.844
127.146
121.129
120.235
114.340
101.198
68.859
59.063
14.727
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



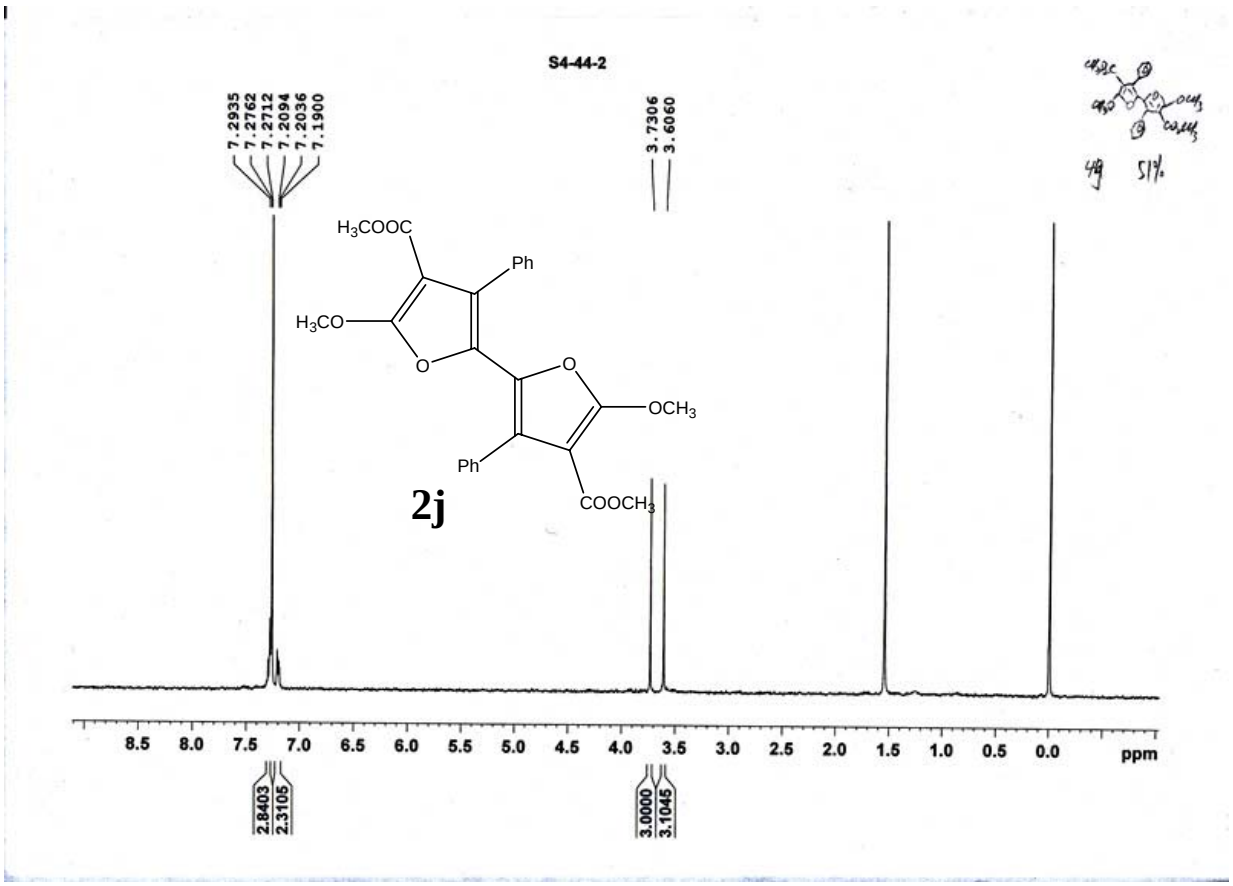
2i

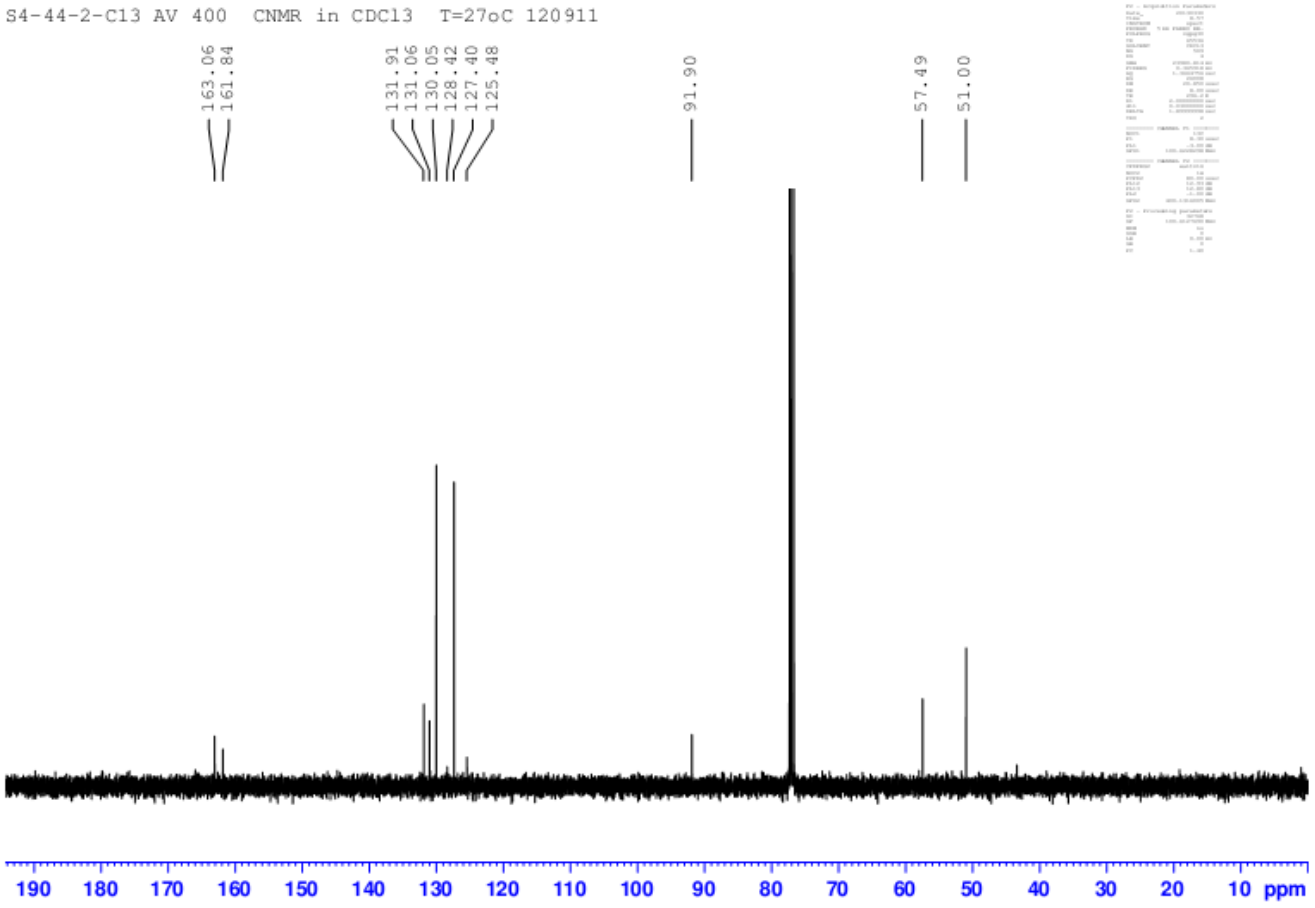
HRMS exact mass calcd for ($C_{38}H_{34}O_{10}S_2$+Na) requires m/z 737.1486, found m/z 737.1481.

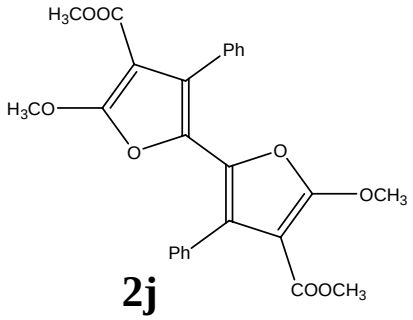




2k

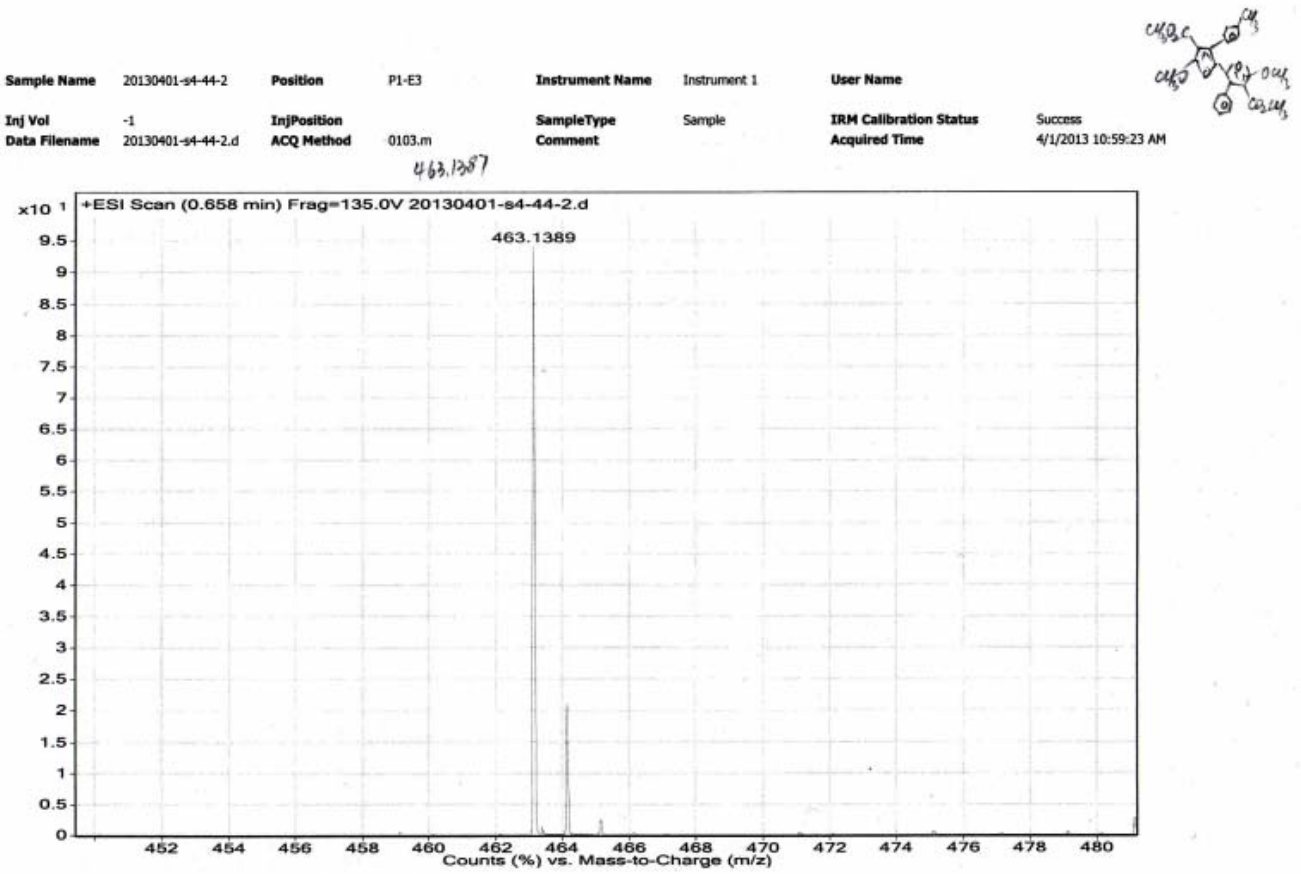

S4-44-2
7.2935
7.2762
7.2712
7.2094
7.2036
7.1900
3.7306
3.6060
H3COOC
Ph
H3CO
O
O
OCH3
Ph
COOCH3
2j
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.8403
2.3105
3.0000
3.1045

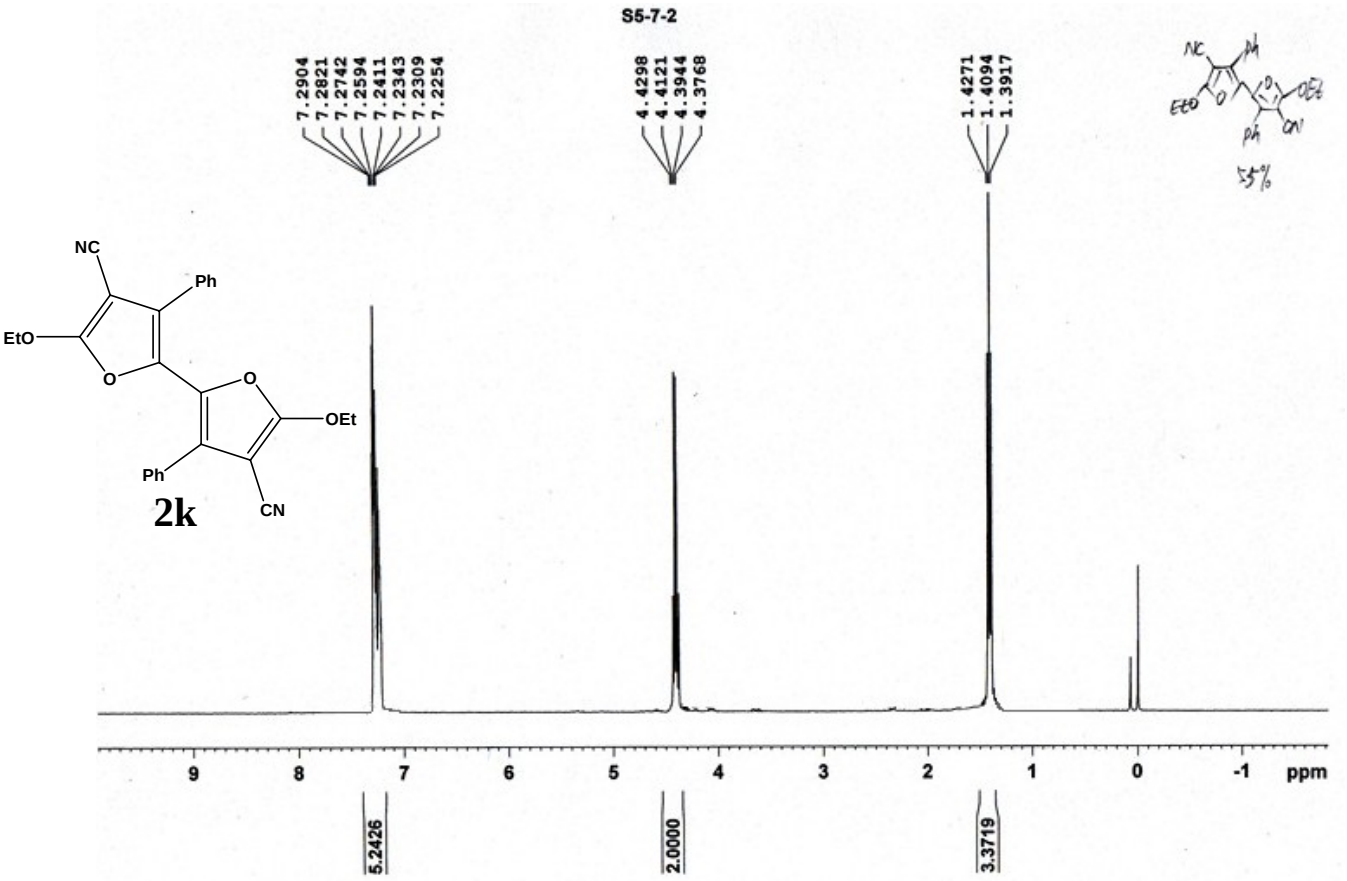

S4-44-2-C13 AV 400 CNMR in CDCl3 T=27oC 120911
163.06
161.84
131.91
131.06
130.05
128.42
127.40
125.48
91.90
57.49
51.00
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

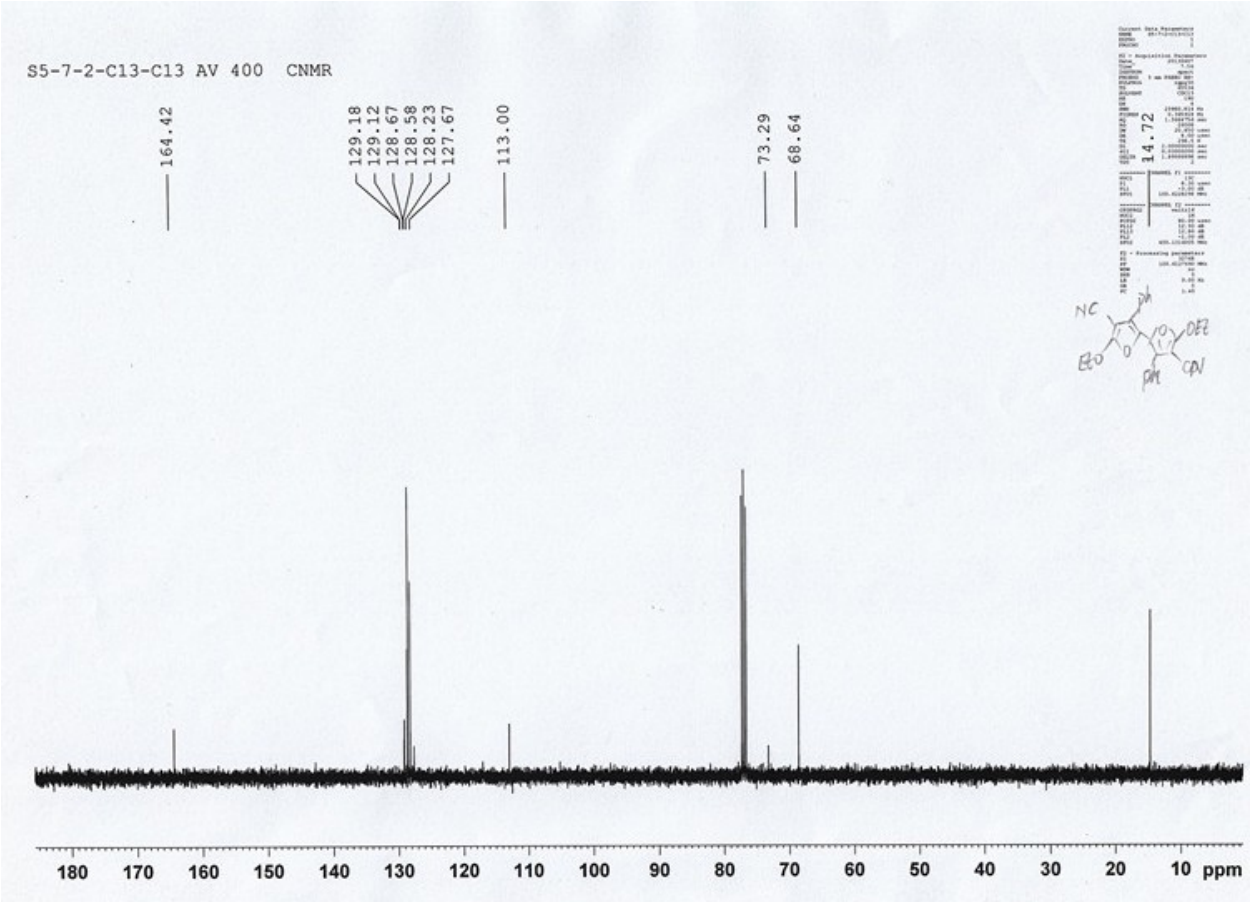


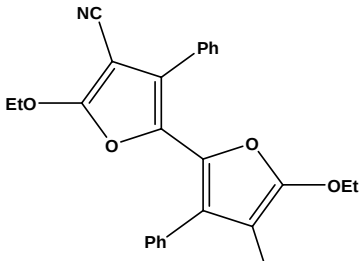
2j

HRMS exact mass calcd for ($C_{26}H_{22}O_8$+H) requires m/z 463.1387, found m/z 463.1389.



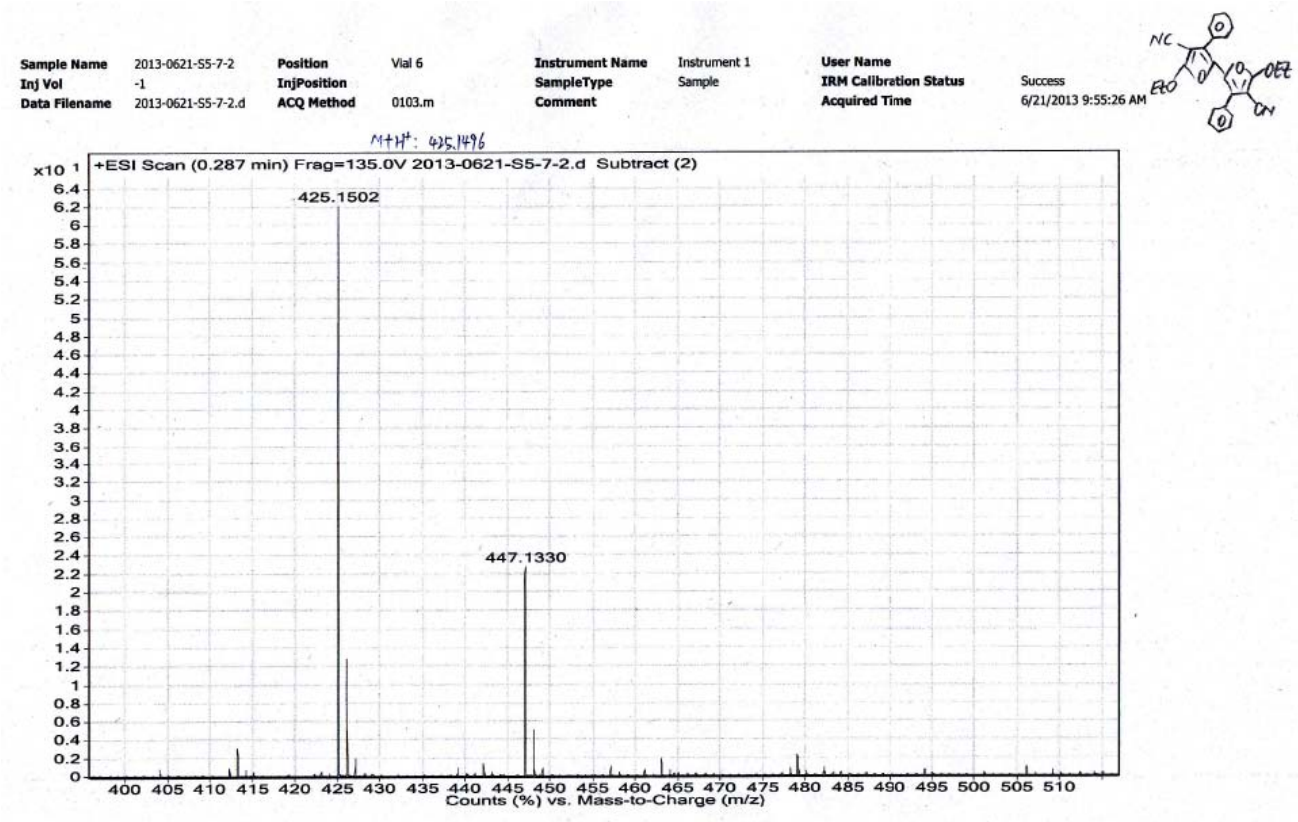

S5-7-2
7.2904
7.2821
7.2742
7.2594
7.2411
7.2343
7.2309
7.2254
4.4298
4.4121
4.3944
4.3768
1.4271
1.4094
1.3917
NC
Ph
EtO
O
O
OEt
Ph
CN
2k
9
8
7
6
5
4
3
2
1
0
-1
ppm
5.2426
2.0000
3.3719

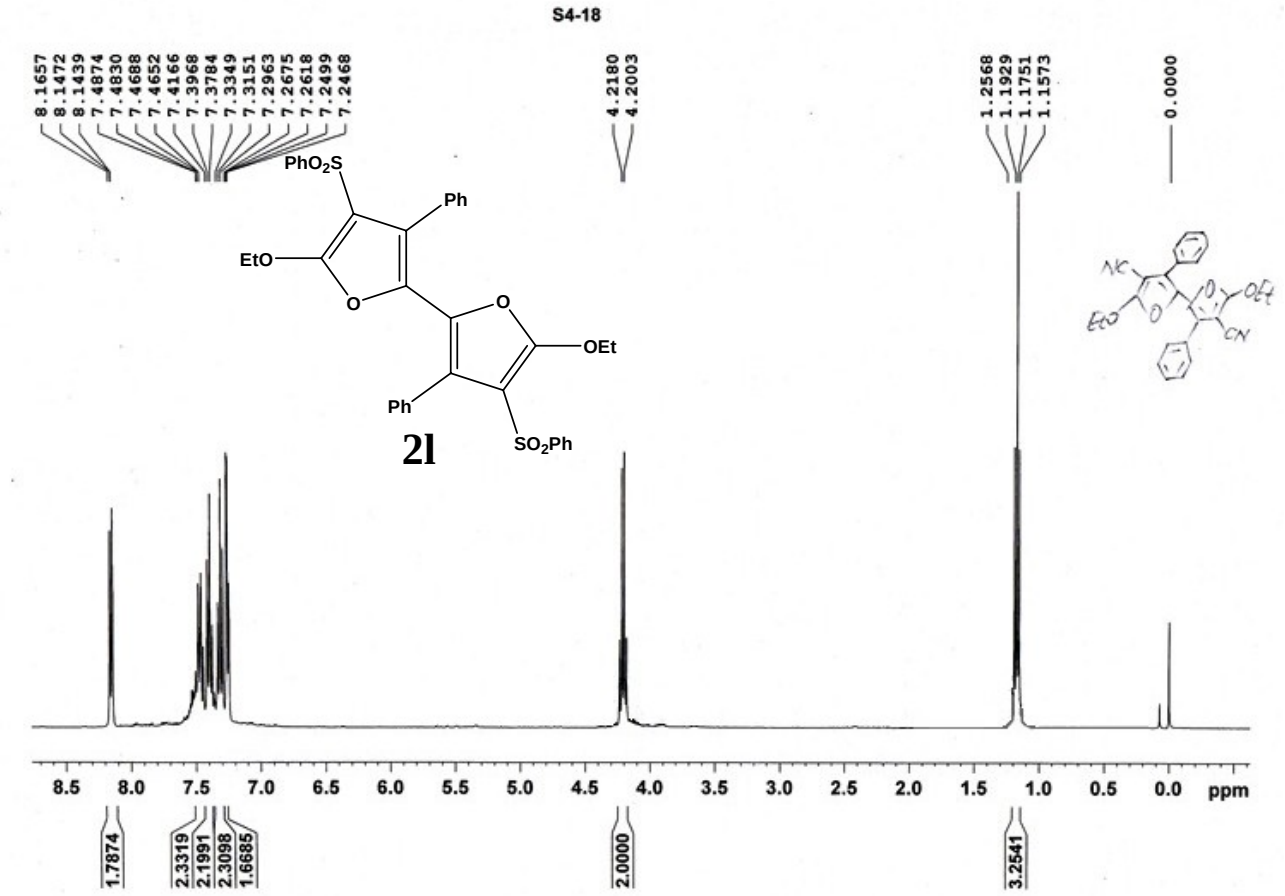

S5-7-2-C13-C13 AV 400 CNMR
164.42
129.18
129.12
128.67
128.58
128.23
127.67
113.00
73.29
68.64
14.72
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

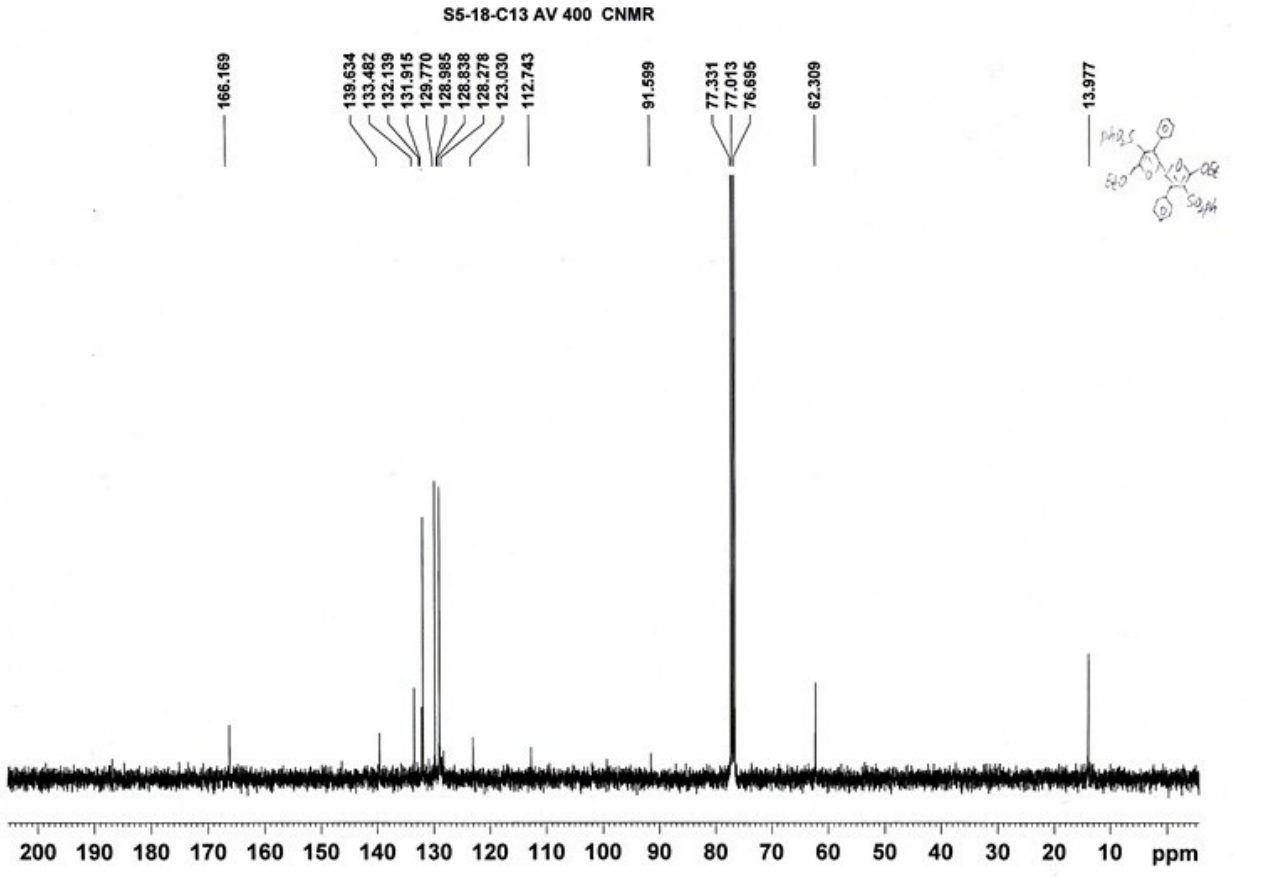


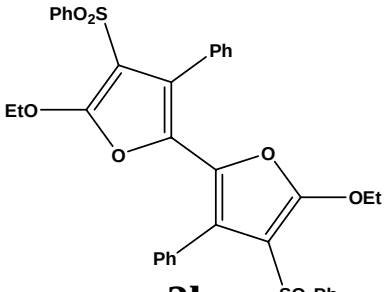
2k

HRMS exact mass calcd for ($C_{26}H_{20}N_2O_4$+H) requires m/z 425.1496, found m/z 425.1502.



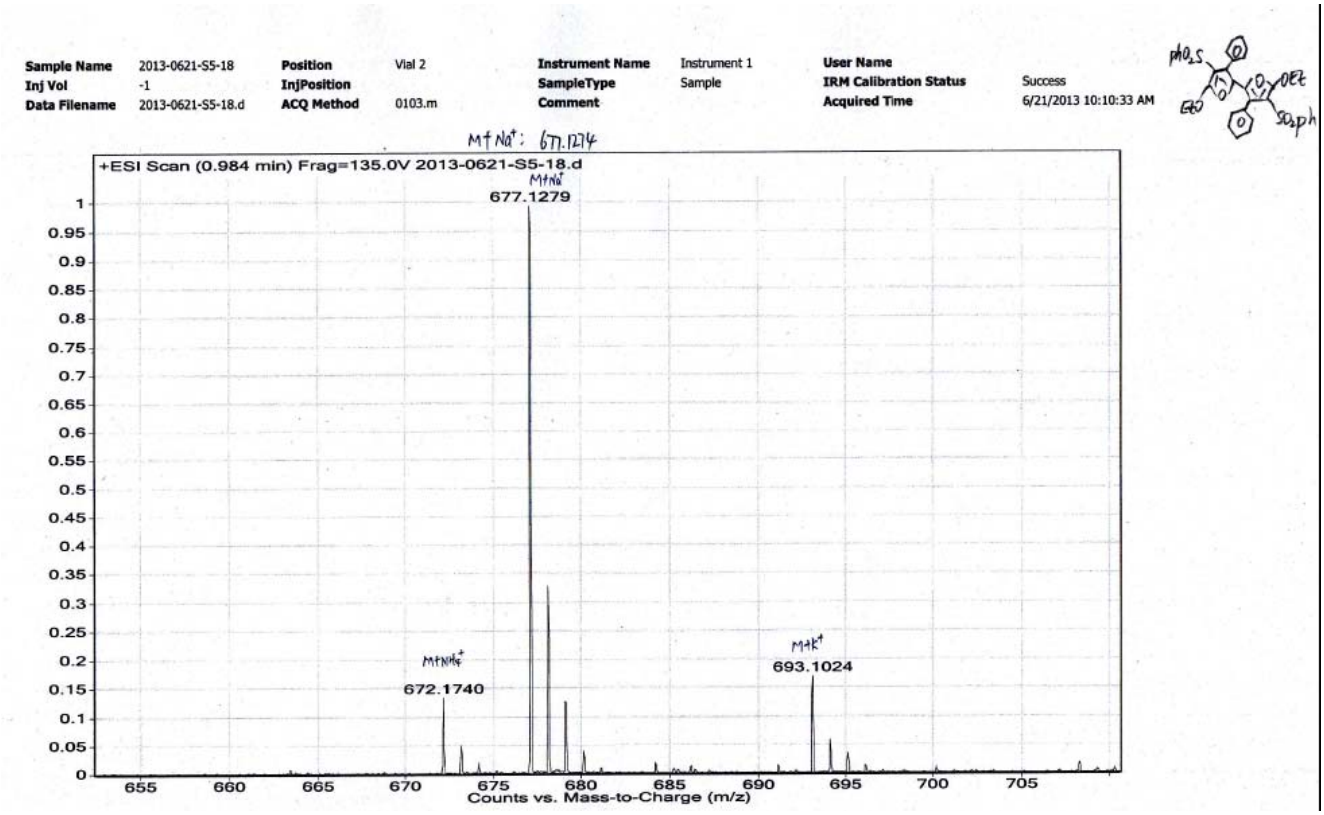

S4-18
8.1657
8.1472
8.1439
7.4874
7.4830
7.4688
7.4652
7.4166
7.3968
7.3784
7.3349
7.3151
7.2963
7.2675
7.2618
7.2499
7.2468
4.2180
4.2003
1.2568
1.1929
1.1751
1.1573
0.0000
PhO2S
Ph
EtO
O
O
OEt
Ph
SO2Ph
21
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.7874
2.3319
2.1991
2.3098
1.6685
2.0000
3.2541

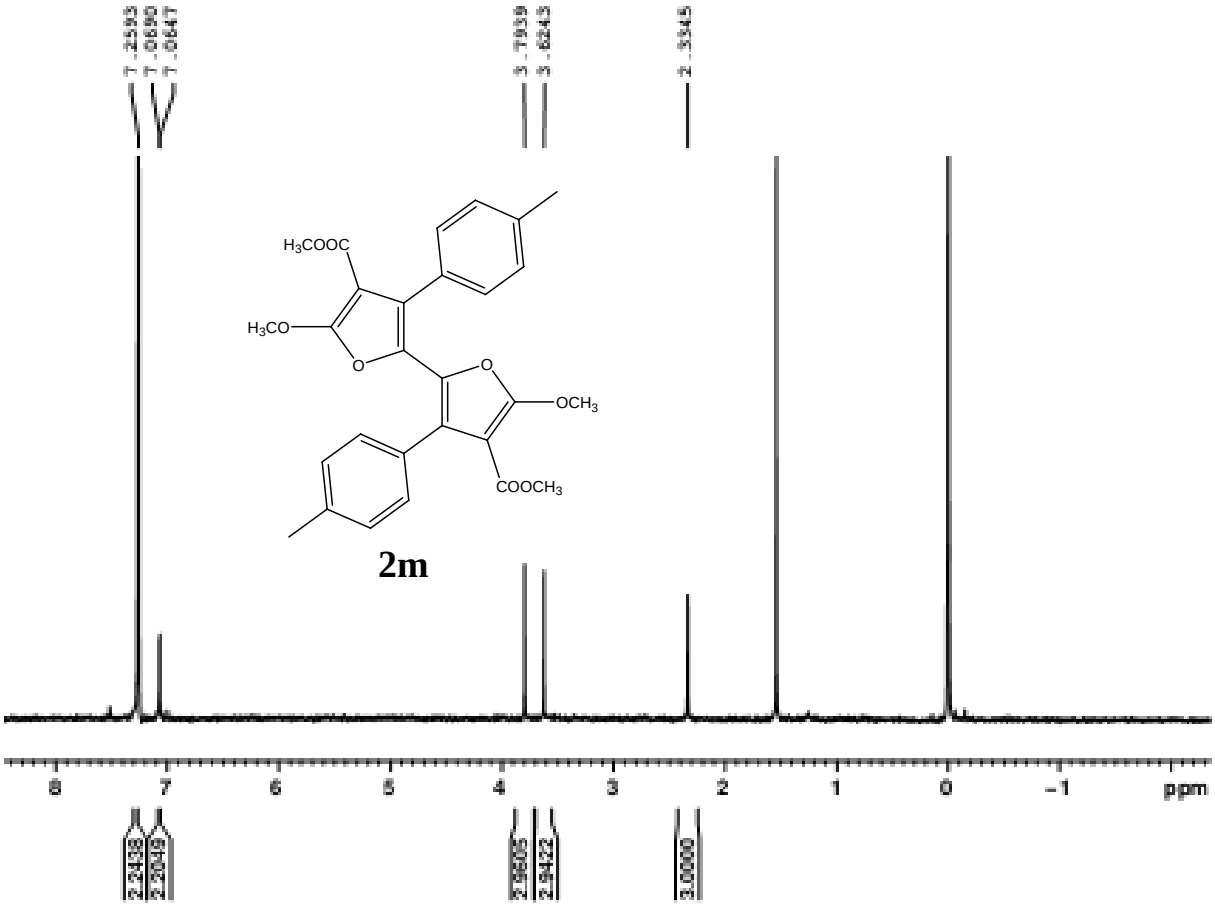

S5-18-C13 AV 400 CNMR
166.169
139.634
133.482
132.139
131.915
129.770
128.985
128.838
128.278
123.030
112.743
91.599
77.331
77.013
76.695
62.309
13.977
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

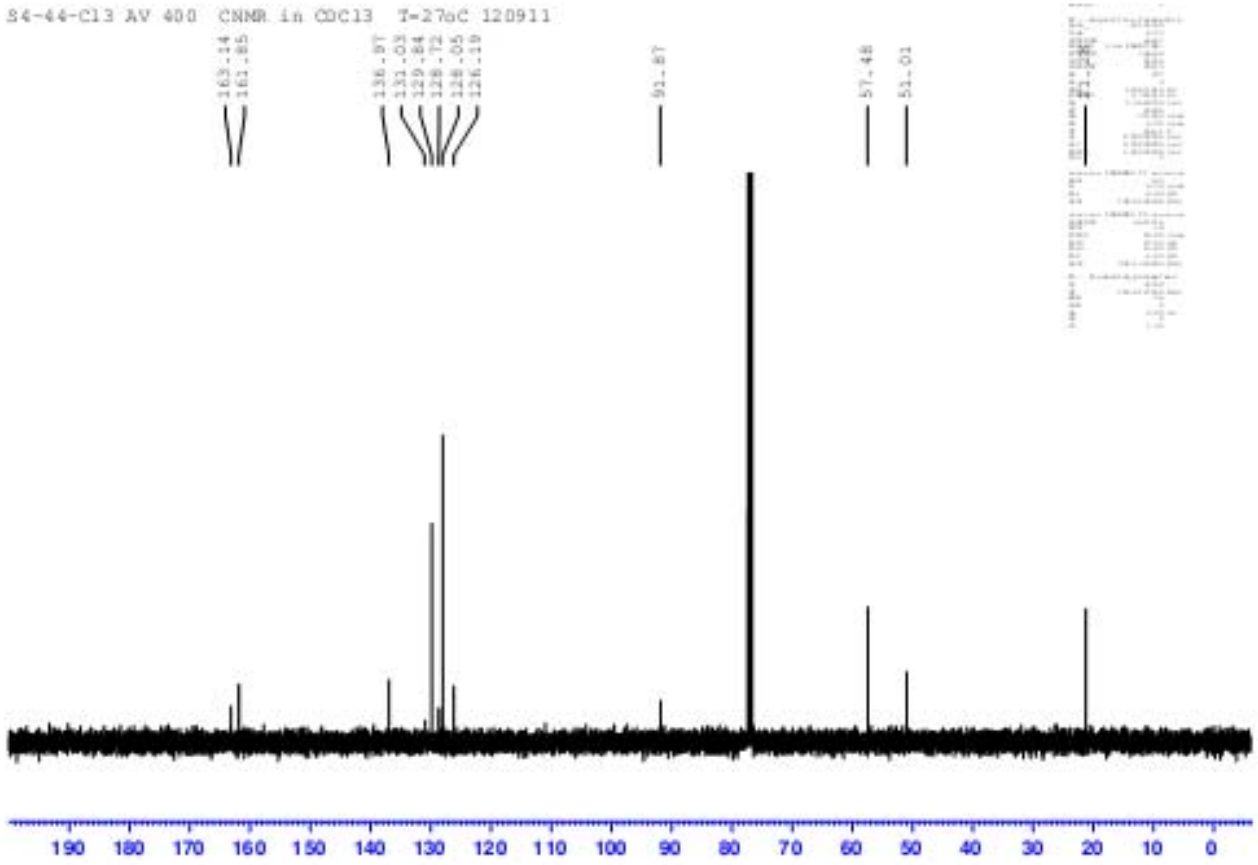


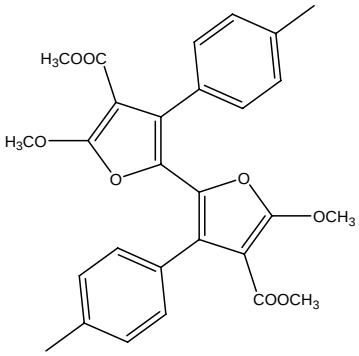
2l

HRMS exact mass calcd for ($C_{36}H_{30}S_2O_8$+Na) requires m/z 677.1274, found m/z 677.1279.



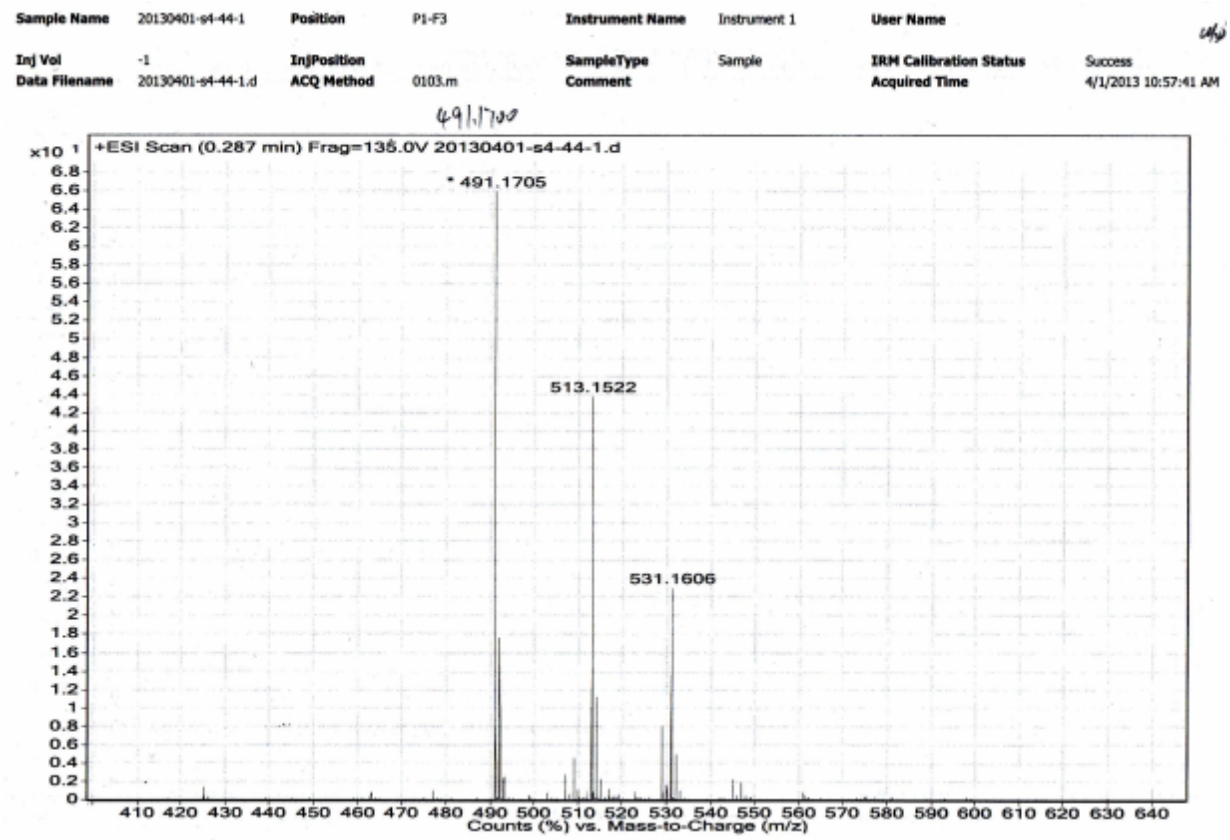

7.2593
7.0690
7.0647
3.7939
3.6243
2.5345
H3COOC
H3CO
O
O
OCH3
COOCH3
2m
8
7
6
5
4
3
2
1
0
−1
ppm
2.2438
2.2049
2.9605
2.9422
3.0000

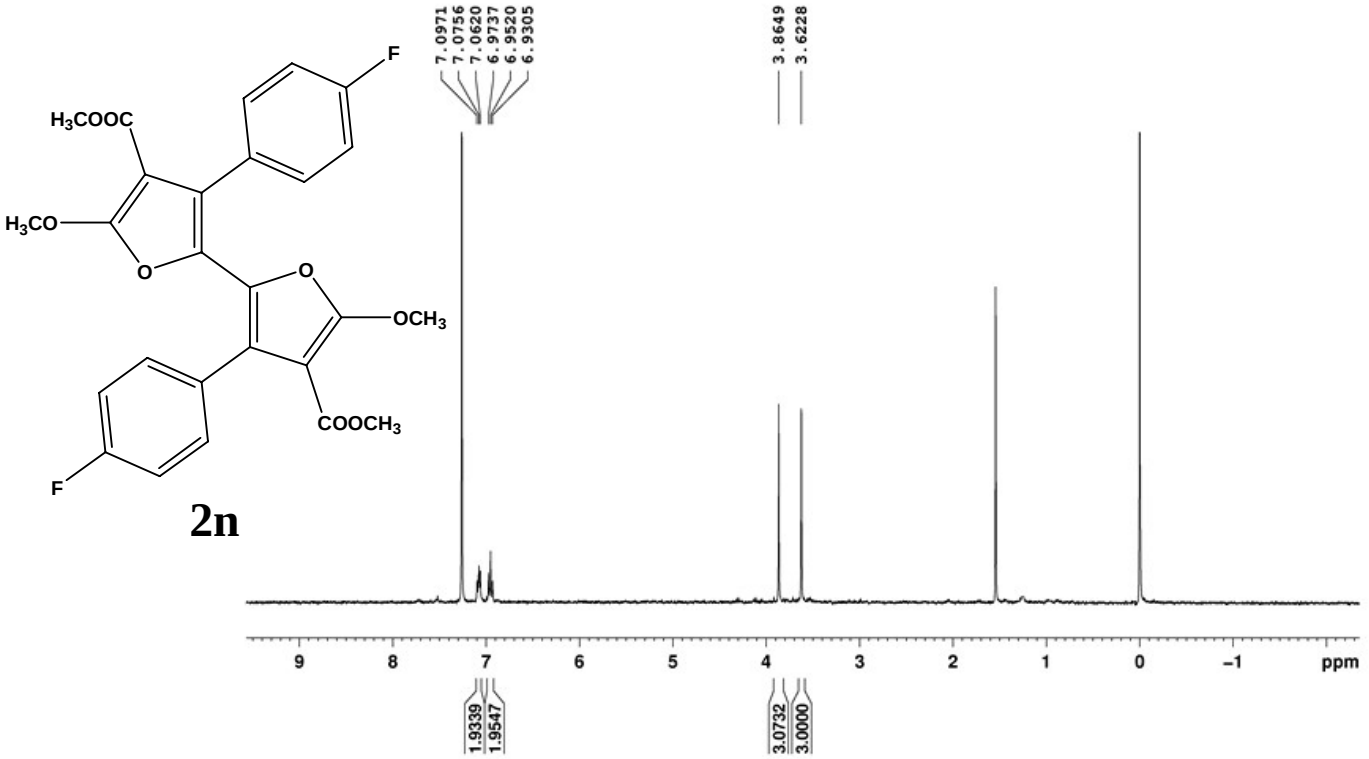

S4-44-C13 AV 400 CNMR in CDCl3 T=27oC 120911
163.14
161.85
136.97
131.03
129.84
128.72
128.05
126.19
91.87
57.48
51.01
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



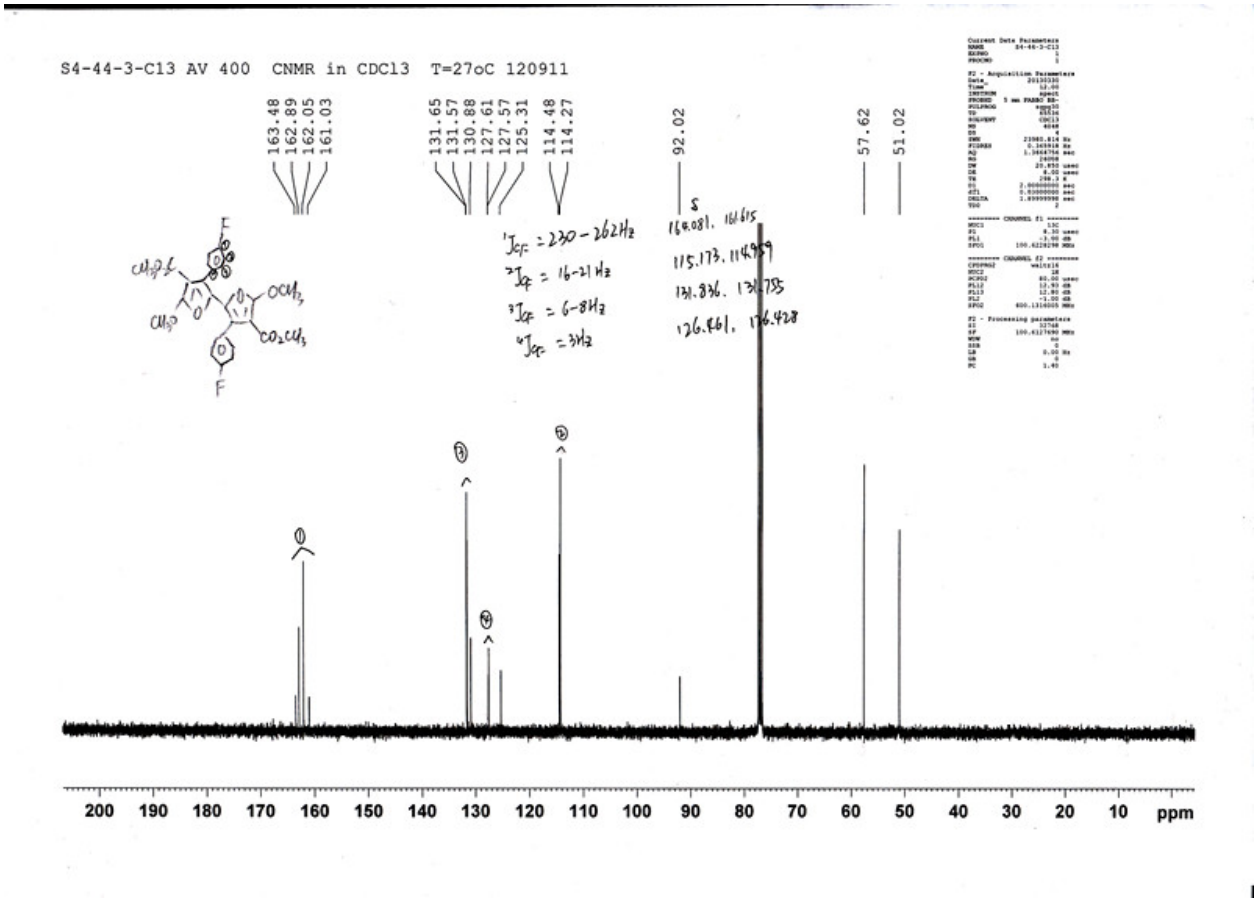
2m

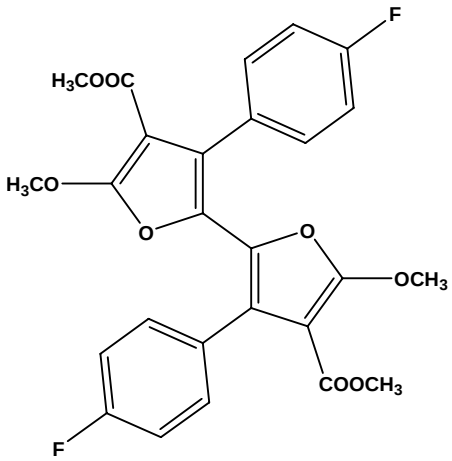
HRMS exact mass calcd for ($C_{28}H_{26}O_8$+H) requires m/z 491.1700, found m/z 491.1705.




F
H3COOC
H3CO
O
O
OCH3
COOCH3
F
7.0971
7.0756
7.0620
6.9737
6.9520
6.9305
3.8649
3.6228
9
8
7
6
5
4
3
2
1
0
−1
ppm
1.9339
1.9547
3.0732
3.0000

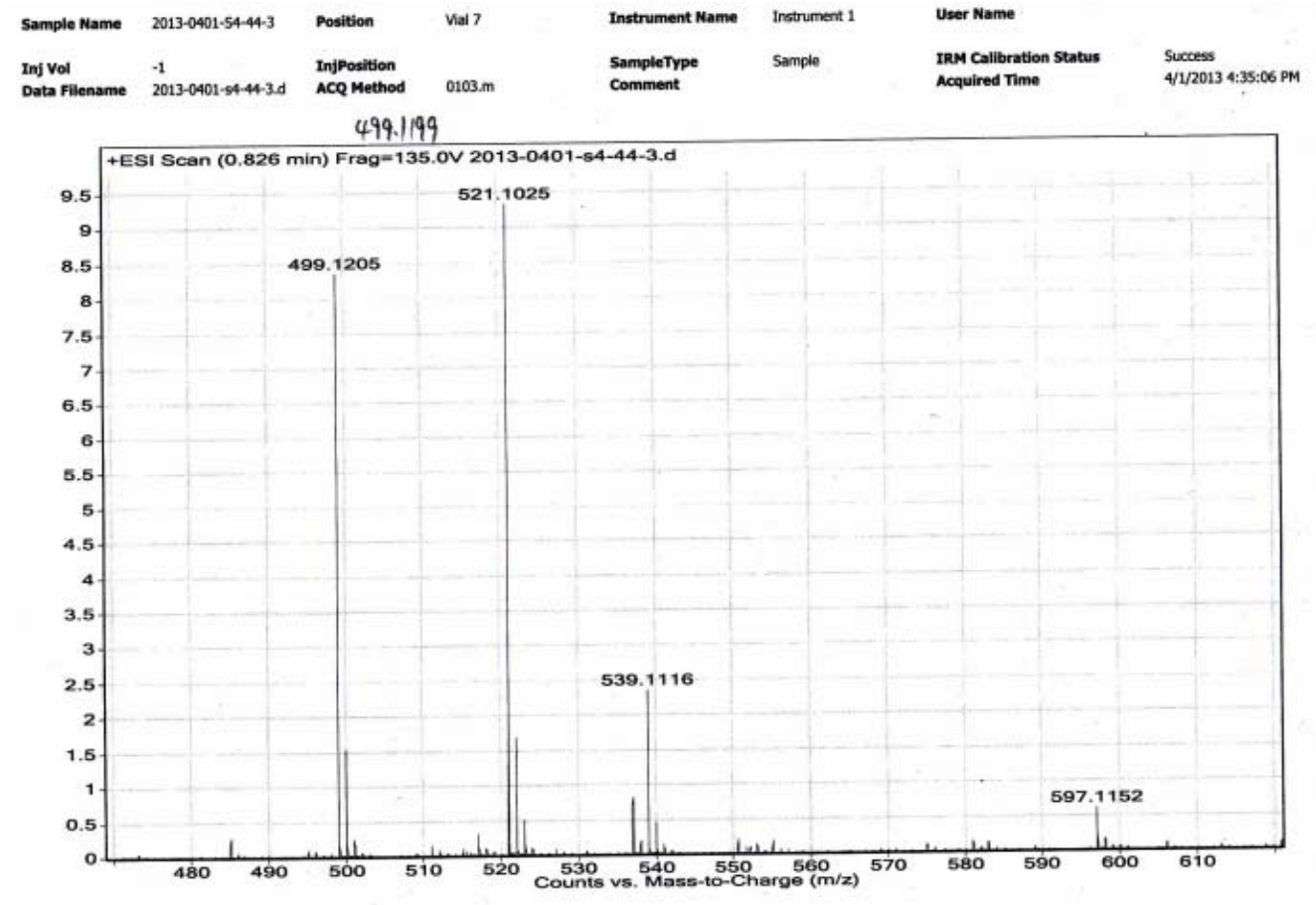
2n

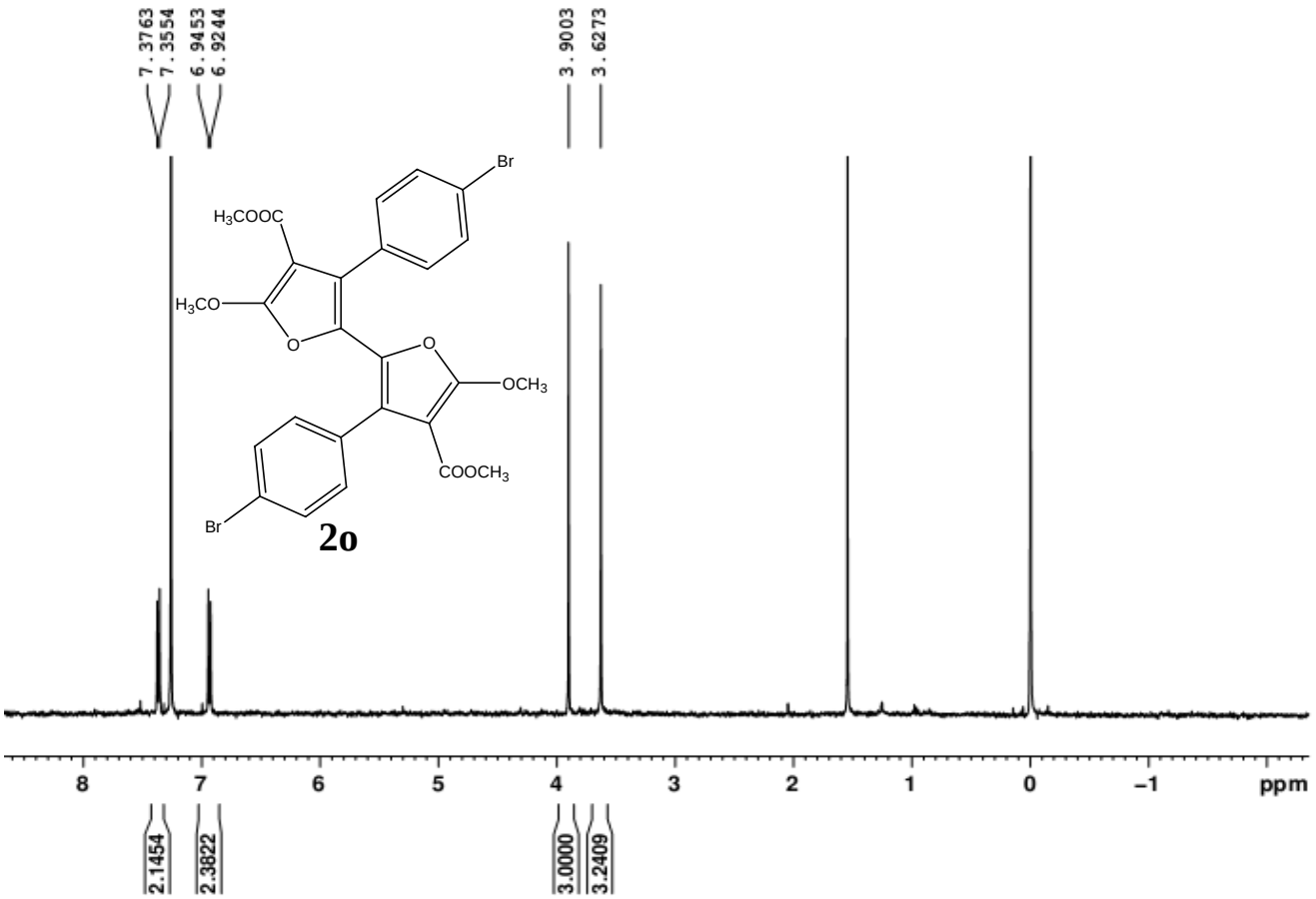

S4-44-3-C13 AV 400 CNMR in CDCl3 T=27oC 120911
163.48
162.89
162.05
161.03
131.65
131.57
130.88
127.61
127.57
125.31
114.48
114.27
92.02
57.62
51.02
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

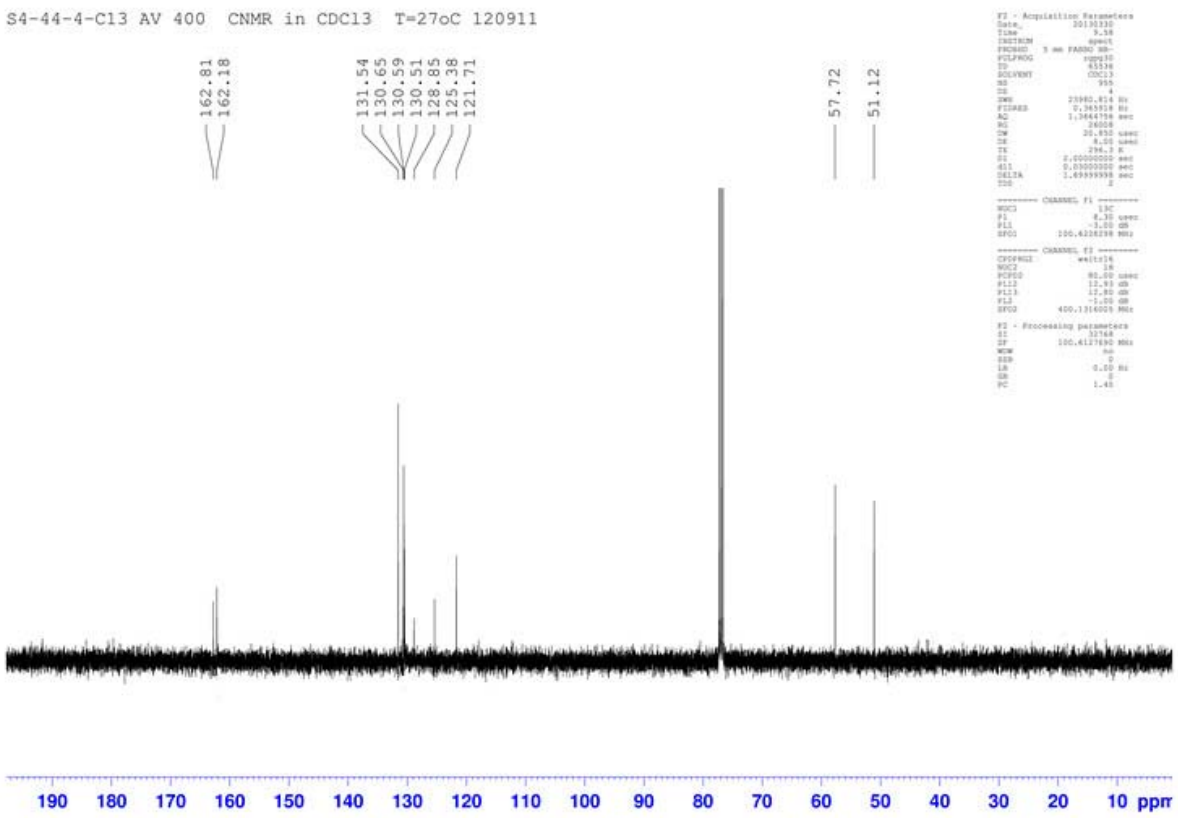


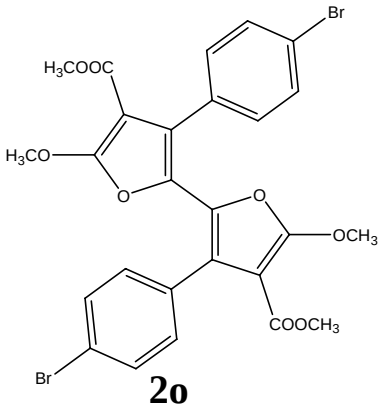
2n

HRMS exact mass calcd for ($C_{26}H_{20}O_8F_2$+H) requires m/z 499.1199, found m/z 499.1205




7.3763
7.3554
6.9453
6.9244
3.9003
3.6273
Br
H3COOC
H3CO
O
O
OCH3
COOCH3
Br
2o
8
7
6
5
4
3
2
1
0
−1
ppm
2.1454
2.3822
3.0000
3.2409


S4-44-4-C13 AV 400 CNMR in CDCl3 T=27oC 120911
162.81
162.18
131.54
130.65
130.59
130.51
128.85
125.38
121.71
57.72
51.12
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm



2o

HRMS exact mass calcd for ($C_{26}H_{20}O_8Br_2$+H) requires m/z 618.9598, found m/z 618.9614.