

Supporting Information
For
Rhodium-catalyzed Isomerization and Alkyne Exchange Reactions of
1,4-Dithiins via 1,2-Ethenedithiolato Rhodium Complex

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Supplimentary Materials

^1H - and ^{13}C -NMR spectra were recorded on a Varian Mercury (400 MHz) and tetramethylsilane were used as standard. IR spectra were measured on a JASCO FT/IR-410 spectrophotomer. Melting points were determined with a Yanagimoto micro melting point apparatus without correction. High- and low-resolution mass spectra were measured on a JEOL JMS-DX-303, a JEOL JMS-700, or a JMS-T100GC spectrometer. X-ray diffraction data were recorded on Rigaku R-AXIIS RAPID. Kanto Chemical. CO. INC. silica gel 60 (63-210 μm) was employed for flash column chromatography.

X-ray Crystallographic Data

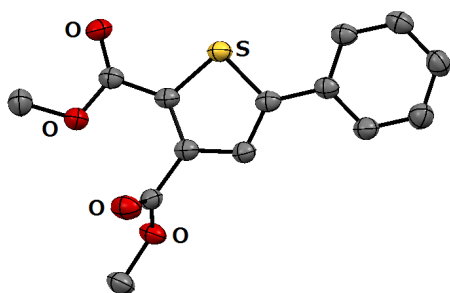


Figure S1. Structure of 13b. Ellipsoids represent 50% probability.

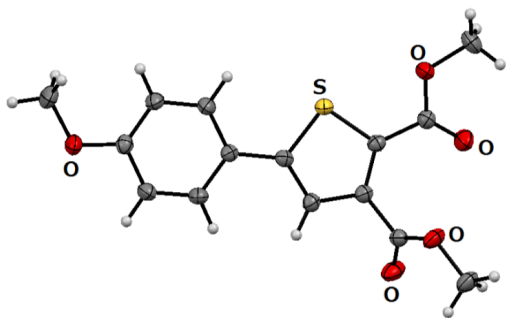


Figure S2. Structure of 13c. Ellipsoids represent 50% probability.

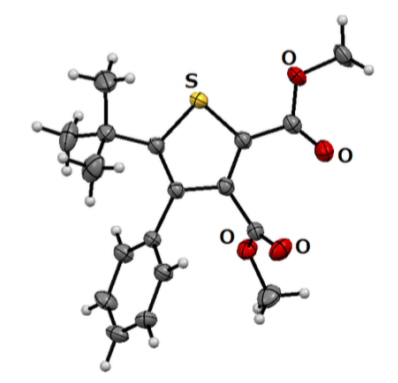


Figure S3. Structure of 17. Ellipsoids represent 50% probability.

Table S1. Crystal data and structure refinement for 13b, 13c, and 17.

Compound	13b	13c	17
CCDC number	1527675	1559628	1560074
Molecular formula	C14 H12 O4 S	C15 H14 O5 S	C18 H20 O4 S
Formula weight	276.30	306.32	332.40
Wave length (Å)	0.71075	0.71075	0.71075
Crystal system	monoclinic	monoclinic	triclinic
Space group	P 21/n	P 21/n	P -1
Color of crystal	Colorless	Yellow	Colorless
Unit cell parameters	a(Å) 8.0558(5) b(Å) 9.0711(5) c(Å) 17.6925(12)	9.4816(3) 7.9918(4) 18.8992(6)	8.014(3) 10.138(3) 12.196(4)
Temperature of data collection	173 (K)	173 (K)	173 (K)
Values of Z	4	4	2
R (reflections)	R = 0.0675	R = 0.0534	R = 0.0757
GOF	wR2 = 0.1688 1.179	wR2 = 0.1346 1.195	wR2 = 0.1728 1.297
Radiation type	Mo K/a	Mo K/a	Mo K/a
Radiation source	sealed X-ray tube	sealed X-ray tube	sealed X-ray tube
Radiation monochromator	graphite	graphite	graphite
Measurement device type	Rigaku R-AXIS RAPID	Rigaku R-AXIS RAPID	Rigaku R-AXIS RAPID
Computing structure solution	SHELXD	SHELXD	SHELXD
Computing structure refinement	SHELXL-97 (Sheldrick, 1997)	SHELXL-97 (Sheldrick, 1997)	SHELXL-97 (Sheldrick, 1997)

```

exp1 proton
=====
NAME: 2
date: Feb 14 2018 temp: not used
solvent: cdcl3 glna: not used
file: /media/raamc/-/n1n 16
263ml461k1n-b-f- hnt 0.008
1d pw90 1d pw90 16.000
=====
ACQUISITION
nu 600.13 mhz 10.000
nu2 300.06 mhz
pb 44872 in n
pb 44872 in x
ds 4 4000 op y
ds 4 4000 op z
dl 1.500 4 hs
dl 1.500 4 hs
nt 16 1b PROCESSING
nt 16 1b not used
=====
PARAMETER 1d 2d
=====
f1 399.351 wd -199.7
f2 399.351 wd -199.7
tad 399.4 xtl 808.4
tper 58 xfo 0
pw 7.500 xp -179.2
=====
DECOUPLER: C13 1b PLOP 0
=====
ch1 131.300 370
ch2 131.300 370
ch3 131.300 370
=====
dum 0
c vs 43
dper 41 th
dnt 29413 at cdc ph 9

```

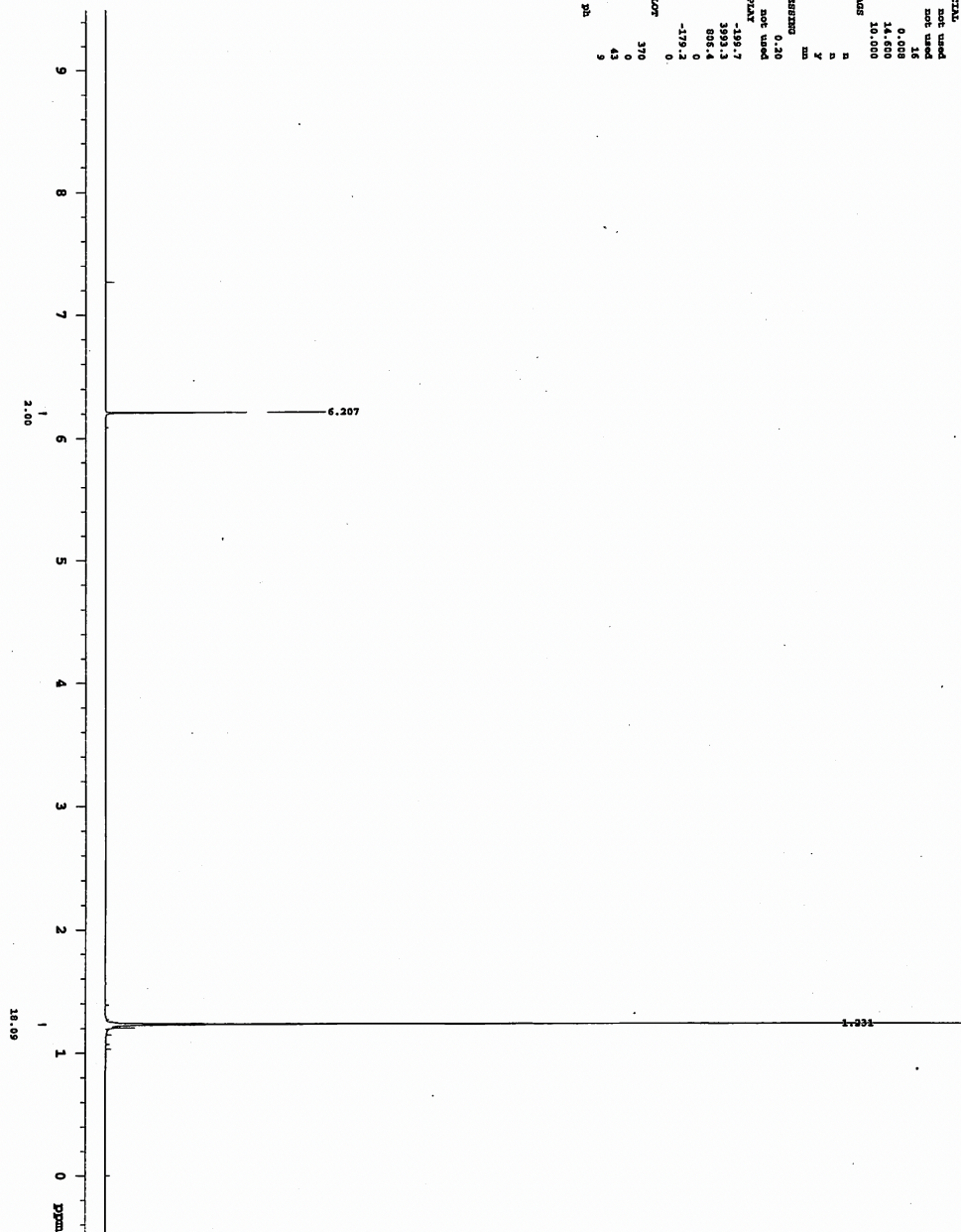
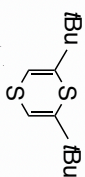
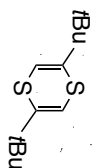


Figure S4. 2,6-Di(1,1-dimethylethyl)-1,4-dithiin (1a) ¹H-NMR

Cc1cc(C)cc(C)c1

Cc1cc(C)cc(C)c1Cc1cc(C)cc(C)c1

Cc1cc(C)sc1

c1ccccc1C2=CC=CC=C2S3C=CC=CC=C3S4C=CC=CC=C4

Figure S8. 2,6-Diphenyl-1,4-dithiin (1b)

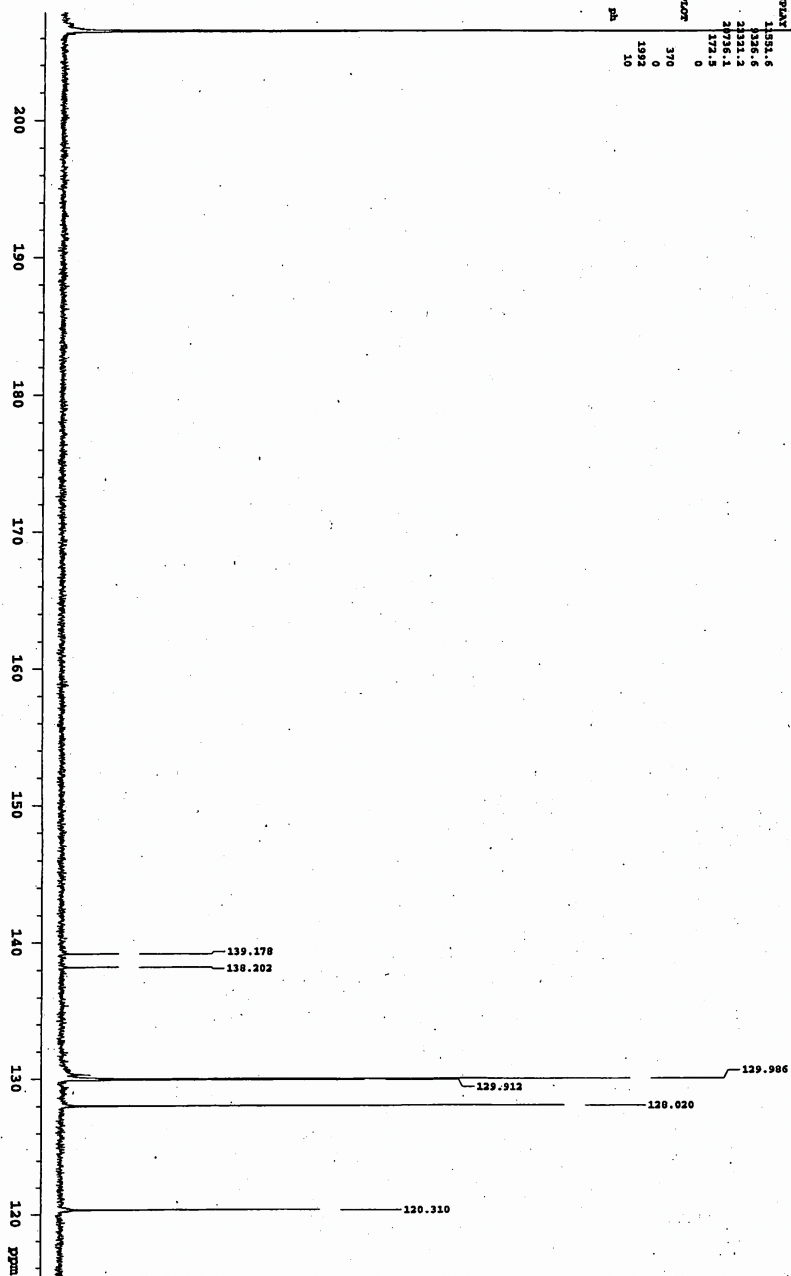
c1ccccc1C2=CC=CC=C2S3C=CC=CC=C3S4C=CC=CC=C4

Figure S9. 2,6-Diphenyl-1,4-dithiin (1b) ¹³C-NMR

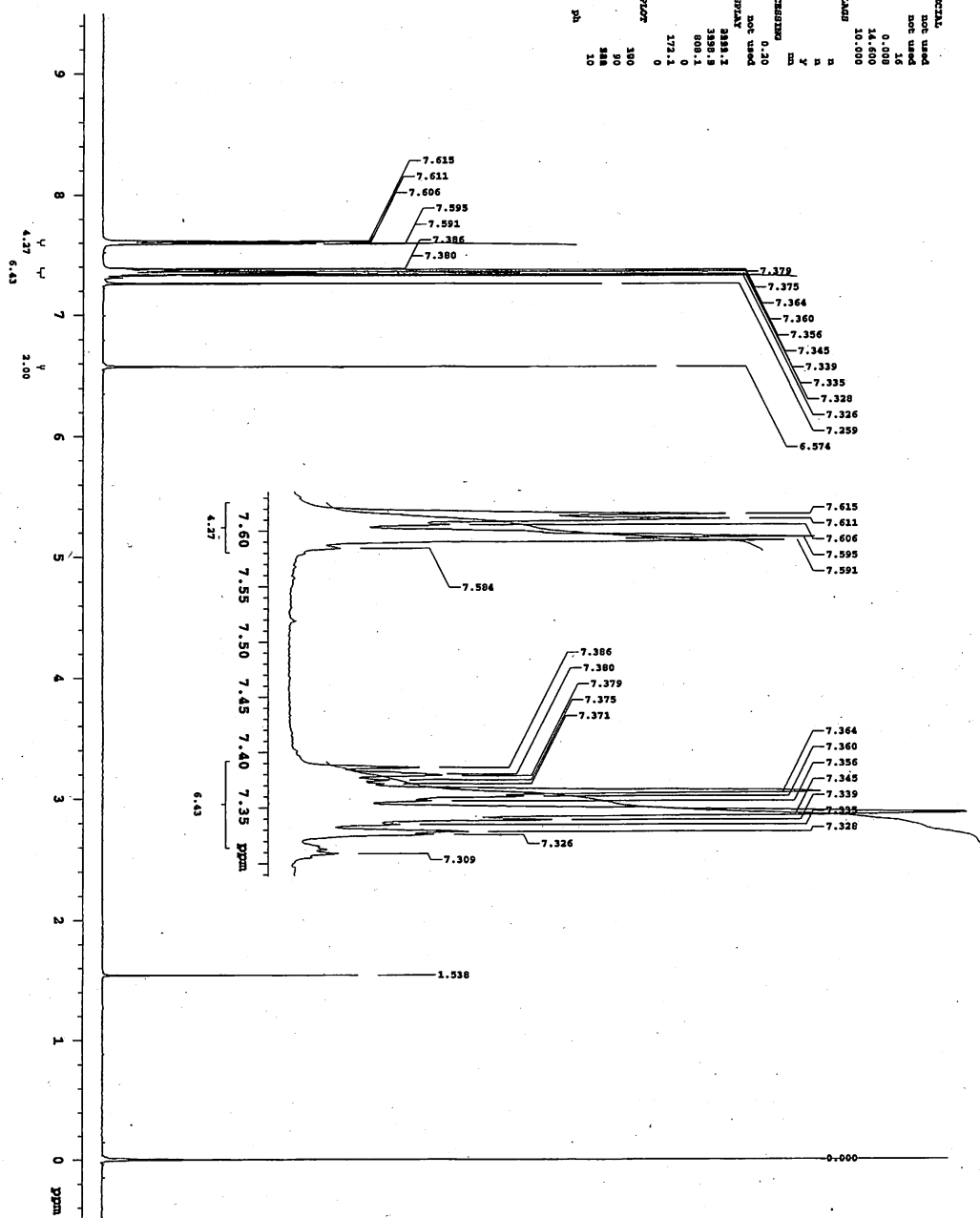
c1ccccc1C2=CC=CC=C2S2

Figure S10. 2,5-Diphenyl-1,4-dithiin (2b) ¹H-NMR

```

exp3 carbon
=====
NAME:
date Feb 15 2018 temp not used
solvent cdcl3 gain not used
file /media/lexar/- apln 16
25diphenyl4dthiin- hnt 0.008
nuc-13C pp90 12.000
=====
ACQUISITION:
24509.8 s18a 10.000
=====
NAME:
at 1.300 f1 FLAG n
mp 53750 f2 n
fb 17000 dp y
ba 4 ha
dl 0.700
=====
PROCESSING:
nuc 10000 f1 1.00
nuc 10000 f2 not used
=====
TRANSMIT:
c13 60 f1
=====
DISPLAY:
ln c13 mp 6975.6
sfreq 100.427 wp 11372.3
cfc 1027.0 f1 9444.7
tprc 60 f2p 7732.1
pw 6.580 rp -34.0
=====
DECODE:
ln 1p
=====
PLOT:
du 300.0 wc 370
dof vvv ac 0
dm vva 6985
dprc 42 ch 26
dnt 9592 at cdc ph

```

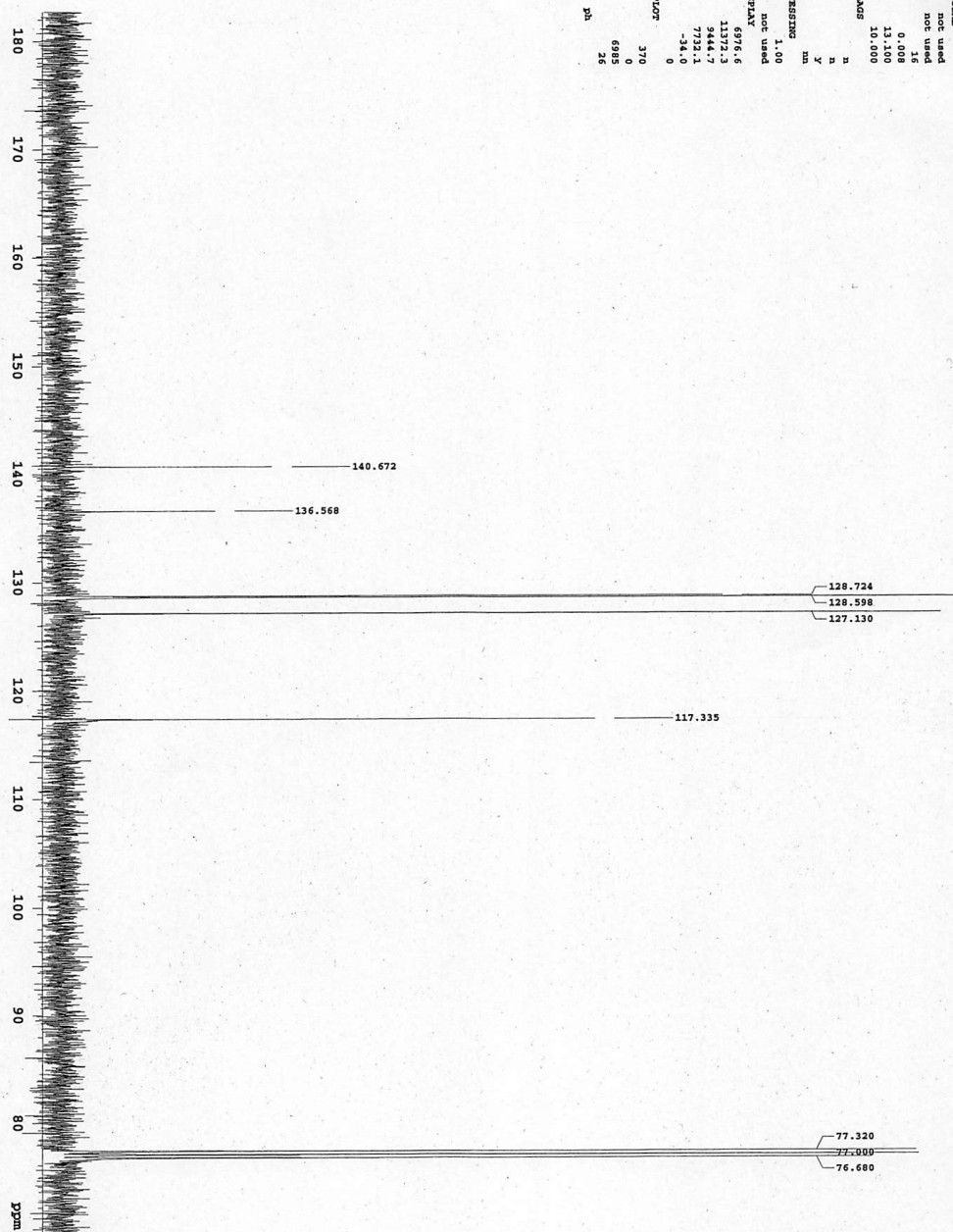
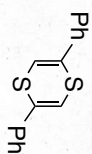


Figure S11. 2,5-Diphenyl-1,4-dithiin (2b) ^{13}C -NMR

COc1ccc(cc1)/C=C2\SCC2/c3ccc(OC)cc3

exp2 Carbon

SAMPLE		SPECIAL	
date	Thu 19 2018	temp	not used
solvent	cdcl3	gain	not used
file	/media/lorenz/-	spin	16
26mls01d4thlm- but		0.008	
-c.fid	pw90	13.100	
ACQUISITION	alpha	PLANS	
nu	26369.8		
at	131300	11	n
mp	63750	1n	n
fb	17000	dp	x
ba	4	ha	m
dl	0.700	PROCESSING	
nt	103400	1b	1.00
ce	4408	fn	not used
TRANSFETTER	C13	SP	DISP1AY
nu	10311.3		
afreq	100.621		15664.8
tof	1036.9	rfl	9443.5
tpor	60	rfd	7731.6
pw	6.550	rp	-122.7
DECOUPLER	1p	PLOT	0
da	HL		
dof	300.0	wc	370
dm	XYX	ac	0
dm	42	na	60432
dpor	42	ls	37
def	9592	nl	cdcl3
		ph	

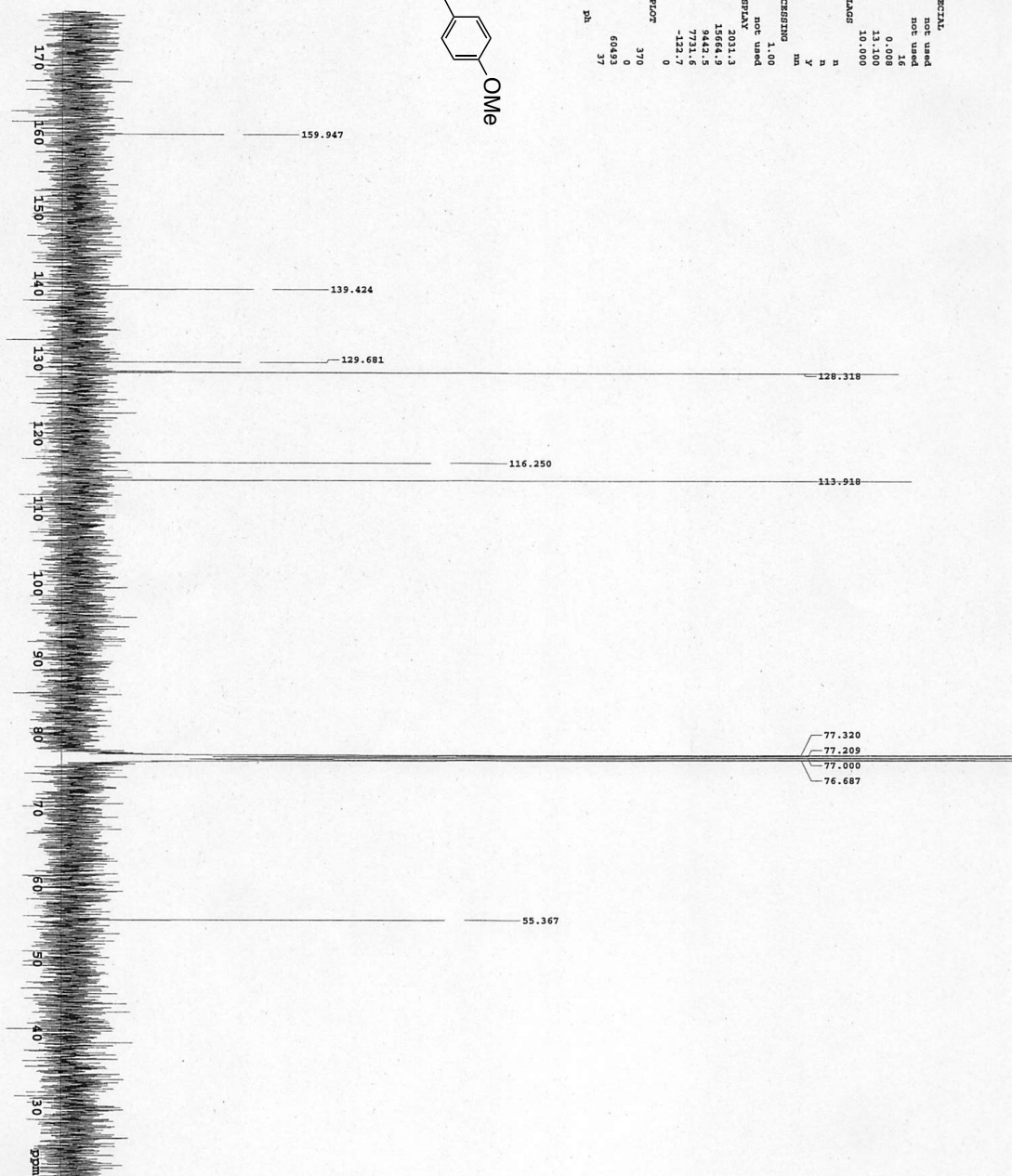
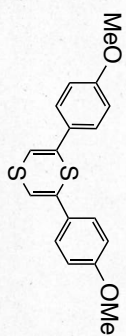


Figure S13. 2,6-Di(4-methoxyphenyl)-1,4-dithiin (1c) ^{13}C -NMR

nhân dân



Figure S14. 2,5-Di(4-methoxyphenyl)-1,4-dithiin (2c) ¹H-NMR

exp2 Carbon

NAME		SPECIAL	
date	2017	temp	not used
solvent	cdcl3	gate	not used
file	/media/roar/- spin	16	
1,4-dithiin nm/25-	hac	0.008	
antioa4dthiin-c-	pw90	13.100	
	.fid a1a	10.000	

ACQUISITION

ac	24390.0	41	h
ac	133900	1	h
np	63750	dp	y
bs	17000	hs	nm
dl	0.700	lb	1.00
nc	3000	fn	not used

PROCESSING

ct	THANNTTTR	912	DISPLAY
un	100.435	sp	0.008.4
sfreq	100.435	rel	9444.7
toct	1027.1	rfb	7732.7
tpwr	60	rp	150.1
pw	6.350	lp	0

DECODE

dn	370	PL0T	0
det	300.0	gc	370
dm	370	gc	370
dmm	370	gc	370
dpr	43	al	cds
dnt	9992	ph	26

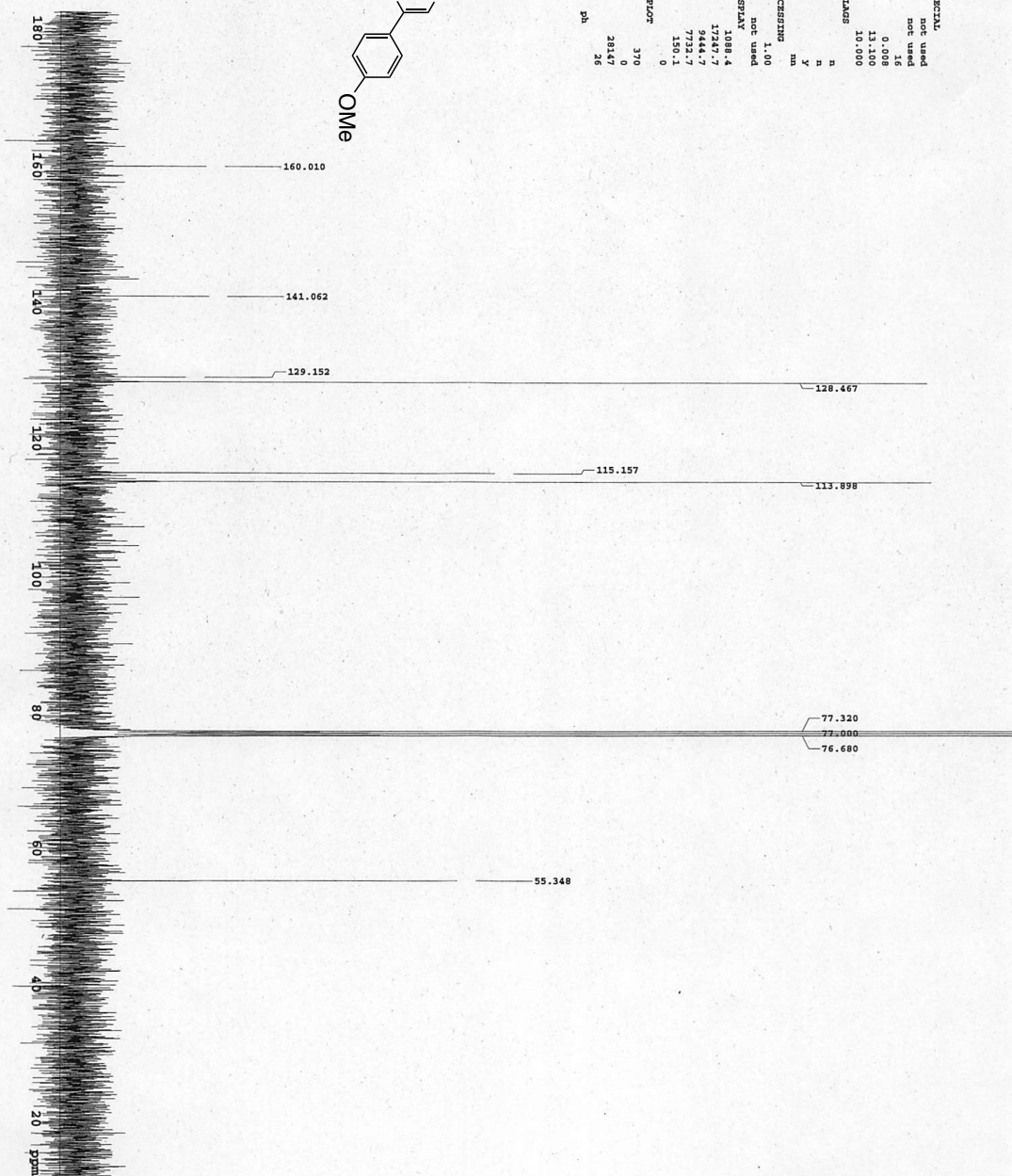
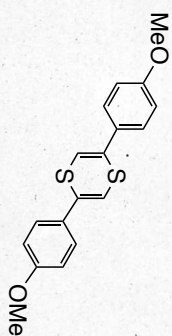


Figure S15. 2,5-Di(4-methoxyphenyl)-1,4-dithiin (2c) ¹³C-NMR

exp3 proton

NAME		SERIAL	
date	Feb 16 2018	temp	not used
solvent	cdcl3	delta	not used
probe	h1h3	delta	not used
2d	h1h3	delta	not used
3d	h1h3	delta	not used
4d	h1h3	delta	not used
5d	h1h3	delta	not used
6d	h1h3	delta	not used
7d	h1h3	delta	not used
8d	h1h3	delta	not used
9d	h1h3	delta	not used
10d	h1h3	delta	not used
11d	h1h3	delta	not used
12d	h1h3	delta	not used
13d	h1h3	delta	not used
14d	h1h3	delta	not used
15d	h1h3	delta	not used
16d	h1h3	delta	not used
17d	h1h3	delta	not used
18d	h1h3	delta	not used
19d	h1h3	delta	not used
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25d	h1h3	delta	not used
26d	h1h3	delta	not used
27d	h1h3	delta	not used
28d	h1h3	delta	not used
29d	h1h3	delta	not used
30d	h1h3	delta	not used
31d	h1h3	delta	not used
32d	h1h3	delta	not used
33d	h1h3	delta	not used
34d	h1h3	delta	not used
35d	h1h3	delta	not used
36d	h1h3	delta	not used
37d	h1h3	delta	not used
38d	h1h3	delta	not used
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40d	h1h3	delta	not used
41d	h1h3	delta	not used
42d	h1h3	delta	not used
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44d	h1h3	delta	not used
45d	h1h3	delta	not used
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61d	h1h3	delta	not used
62d	h1h3	delta	not used
63d	h1h3	delta	not used
64d	h1h3	delta	not used
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67d	h1h3	delta	not used
68d	h1h3	delta	not used
69d	h1h3	delta	not used
70d	h1h3	delta	not used
71d	h1h3	delta	not used
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89d	h1h3	delta	not used
90d	h1h3	delta	not used
91d	h1h3	delta	not used
92d	h1h3	delta	not used
93d	h1h3	delta	not used
94d	h1h3	delta	not used
95d	h1h3	delta	not used
96d	h1h3	delta	not used
97d	h1h3	delta	not used
98d	h1h3	delta	not used
99d	h1h3	delta	not used
100d	h1h3	delta	not used

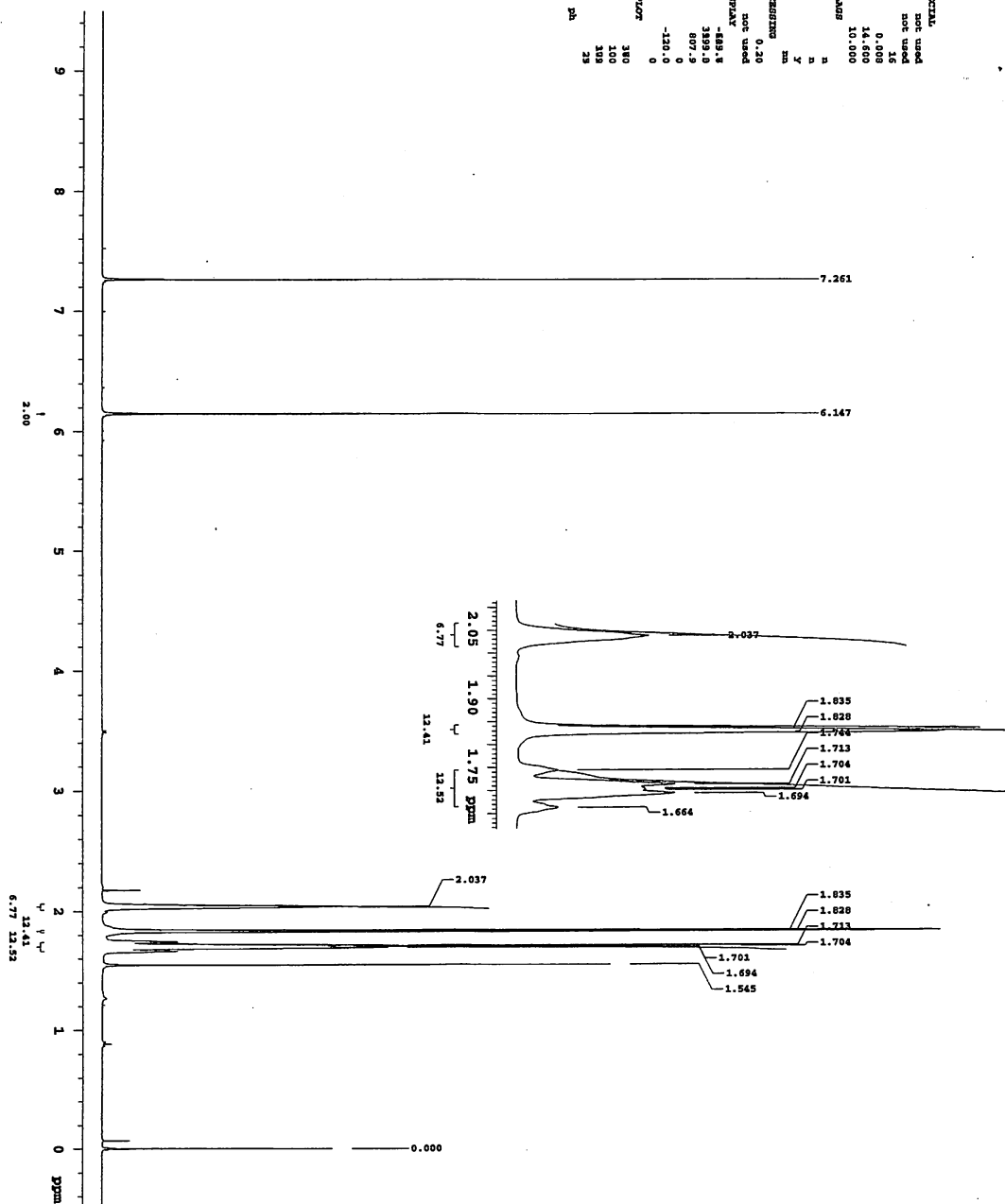
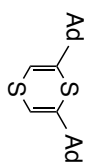


Figure S16. 2,6-Di(1-adamanty)-1,4-dithiin (1d) ¹H-NMR

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C1=CC=C(C=C1)C2=CC=CC=C2

CC1=CC(=S)C(=S)C=C1C

Two ^1H NMR spectra of 2,2,4,4-tetramethyl-5-oxohexanoic acid are shown. The top spectrum is the full spectrum from 0 to 4.25 ppm, with peaks labeled at 1.218, 1.200, 1.935, 1.918, 1.900, 1.884, and 1.867 ppm. The bottom spectrum is an expanded view of the 0.85 to 1.25 ppm region, showing two distinct singlet peaks at 0.894 and 0.877 ppm. Integration values are provided for the peaks in the expanded view.

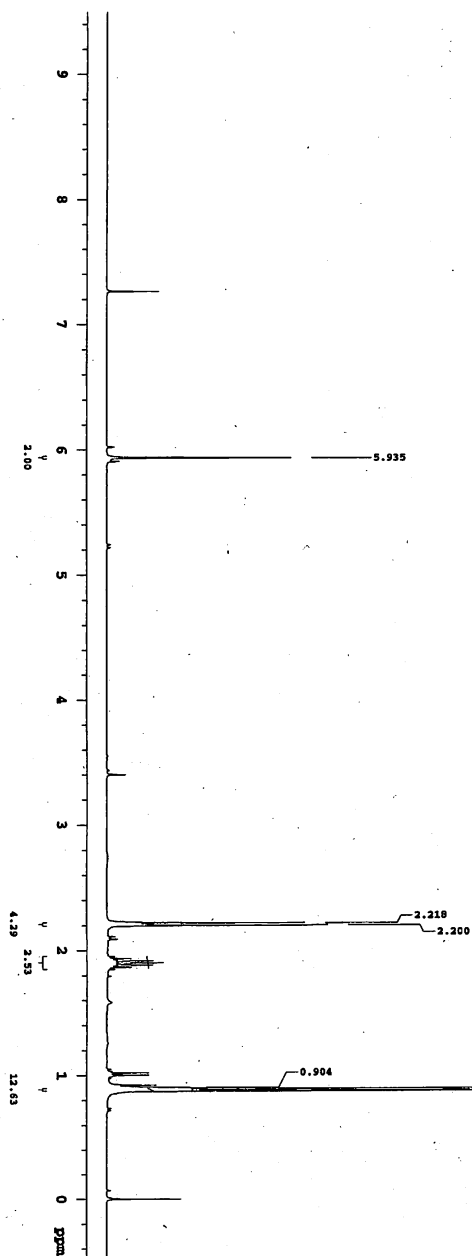
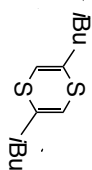


Figure S22. 2,5-Di(2-methylpropyl)-1,4-dithiin (2e) ¹H-NMR

~~7.491~~
~~7.870~~

~~7.880~~

~~7.150~~
~~7.120~~

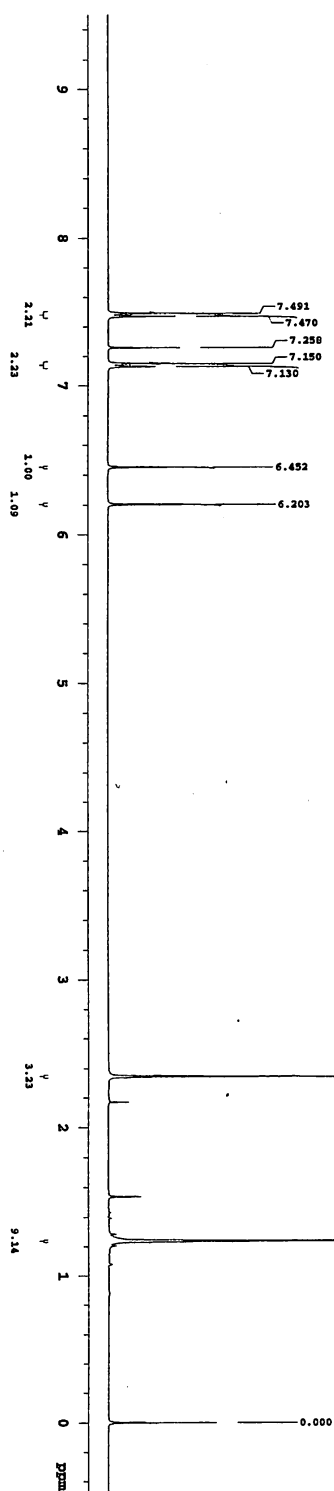
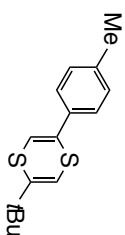


Figure S24. 2-(1,1-Dimethylethyl)-5-(4-tolyl)-1,4-dithiin (5) ¹H-NMR

exp3 Carbon

NAME	DATE	PROB	9	2017	TEMP	NOT USED
solvent	1	cdcl3	gln	not used		
file	/media/lenox/-	apks	16			
1,4-dithia	mm/75-	but	0.058			
library	cd-cl3	pp90	13.100			
acq	14400.8	812	10.000			
NAME	1.300	11	PMAS			
NO	63750	in	n			
FO	17000	cp	y			
HA	4	ha	nm			
CL	0.700	PROCESSED				
HE	2000	12	1.00			
OR	1504	in	not used			
IN	100.440	CD	559.9			
REF	100.440	WD	17738.6			
COF	1027.1	REF	9443.2			
CPW	60	REF	7733.1			
PR	6.550	SP	57.7			
DECOMPOSE	11	12	0			
DEL	300.0	WD	370			
DEL	377	AC	0			
DEL	W	VS	9943			
DEL	42	TH	11			
DEL	9592	AL	cdcl3			

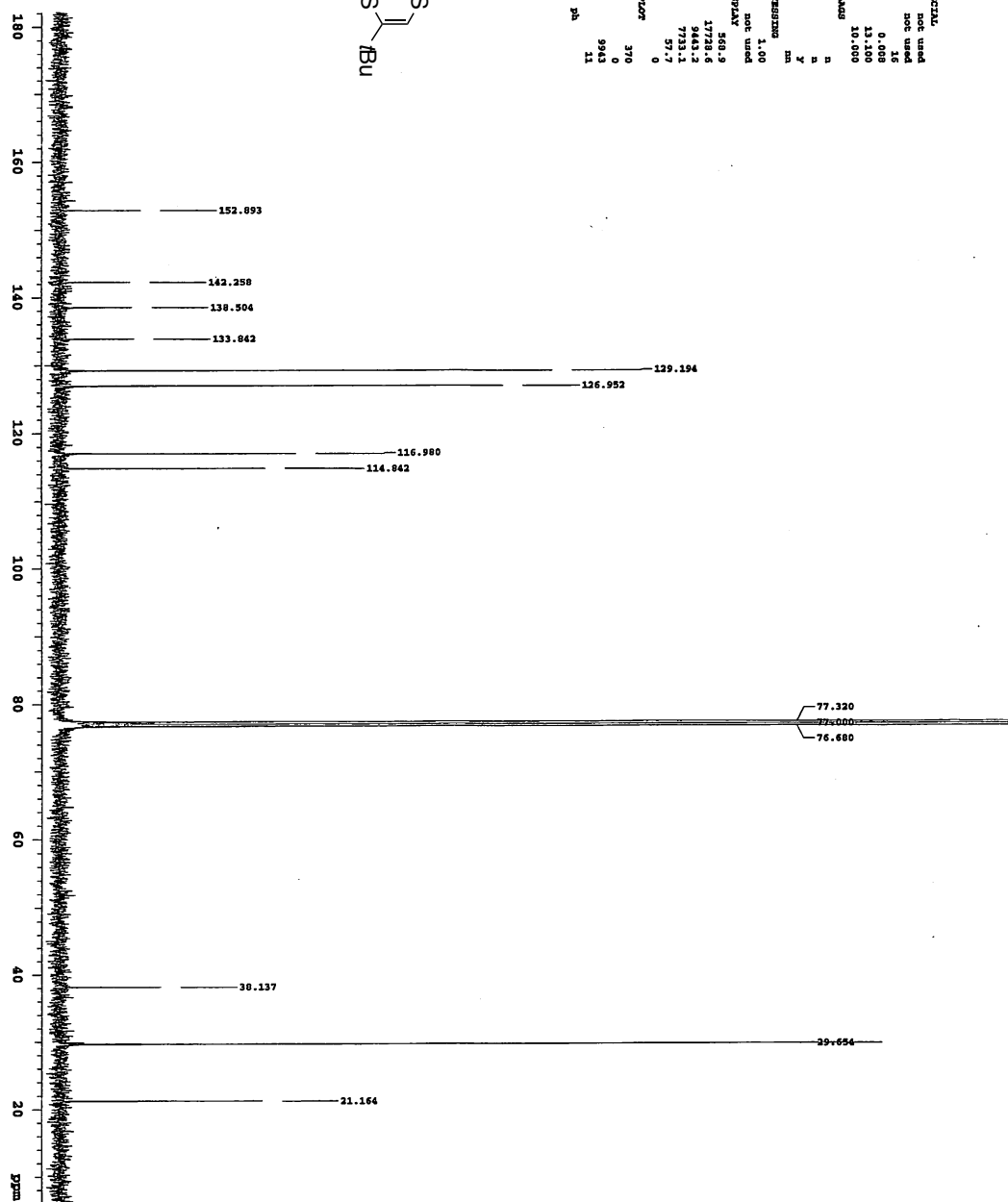
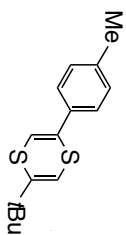


Figure S25. 2-(1,1-Dimethylethyl)-5-(4-tolyl)-1,4-dithiin (5) ¹³C-NMR

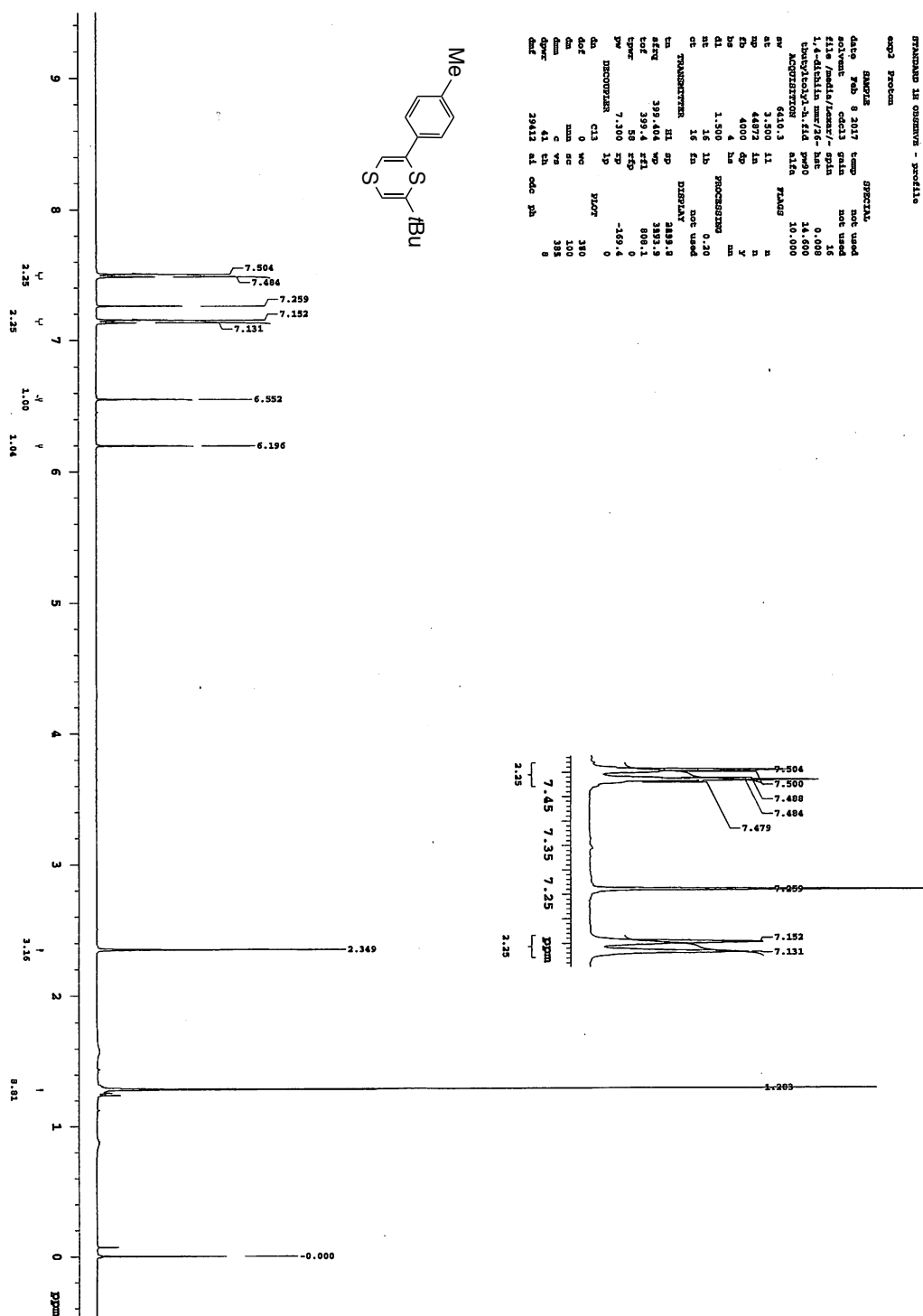
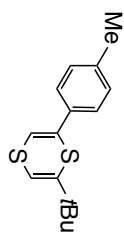
[illegible]

Figure S26. 2-(1,1-Dimethylethyl)-6-(4-tolyl)-1,4-dithiin (6) ¹H-NMR

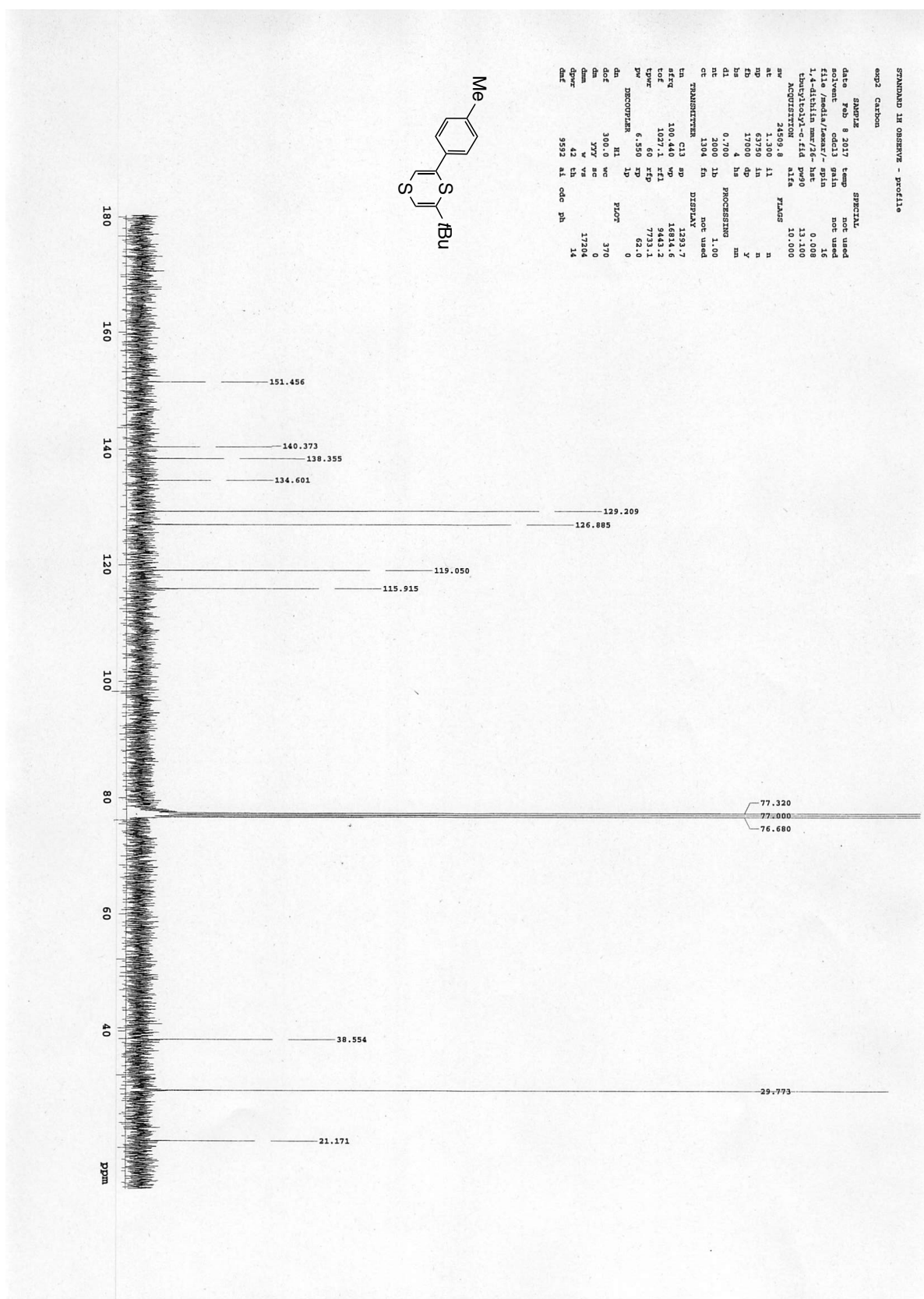


Figure S27. 2-(1,1-Dimethylethyl)-6-(4-tolyl)-1,4-dithiin (6) ^{13}C -NMR

CC(=O)C1=C(C(=O)OC)SC(=C1)C(C)(C)C

CC(=O)OC1C(=S)C(=C(C1)C(=O)OC)C(C)C

CC(=O)Oc1cc(C(=O)OC)c(s1)C(C)(C)C

CC(=O)Oc1cc(C(=O)OC)c(s1)C(C)(C)C

COC(=O)c1cc(C(=O)OC)c(C(=O)OC)s1

exp2 Carbon

SAMPLE		SPECIAL	
date	Jun 30 2018	temp	not used
solvent	cdcl3	gain	not used
file	/media/assess/-	apln	16
label	2,3,4,5-tetra(methoxycarbonyl)thiophene	hnt	0.008
label	2,3,4,5-tetra(methoxycarbonyl)thiophene	hnt	13.100
label	2,3,4,5-tetra(methoxycarbonyl)thiophene	hnt	10.000
ACQUISITION	d	alt	PLACES
sc	24500.8	41	n
at	1.300	41	n
np	63750	dp	y
fb	17000	ha	nm
bs	4	PROCESSED	nm
dl	0.700	1b	1.00
nt	102400	fn	not used
ct	TRANSMITTEN	2764	DEEPAN
tn	1397.1	mp	1397.1
stet	100.421	rel	100.421
loc	1024.9	rel	1024.9
lper	60	rp	118.8
pw	6.350	1p	0
DECODER	11	wg	370
dn	300.0	ag	0
ddc	XXX	ag	15339
dm	XXX	ag	15339
dmu	42	nl	33
dpwr	42	nl	33
date	9592	nl	33

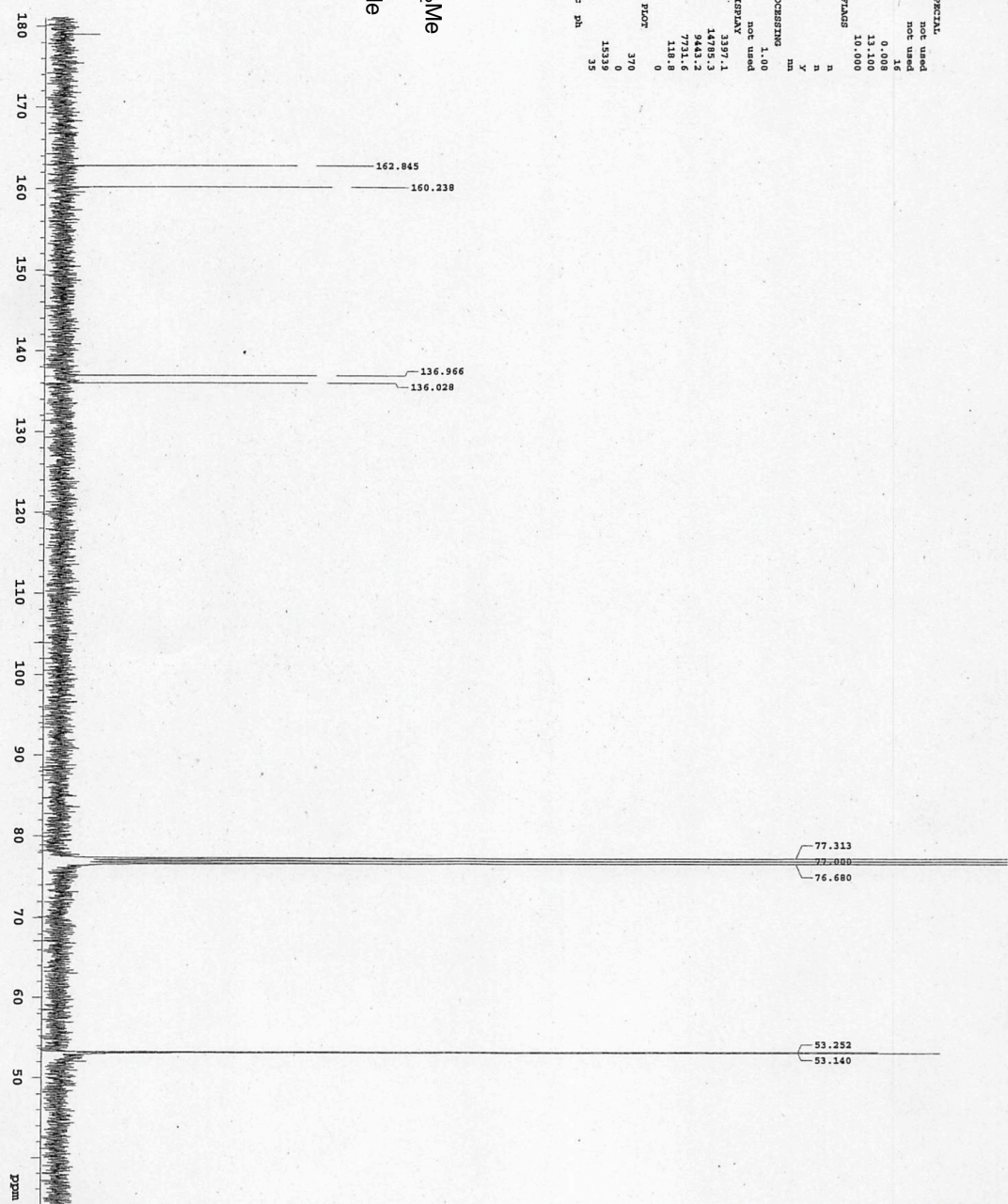
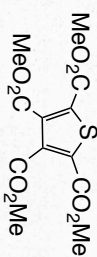


Figure S35. 2,3,4,5-Tetra(methoxycarbonyl)thiophene (10) ¹³C-NMR

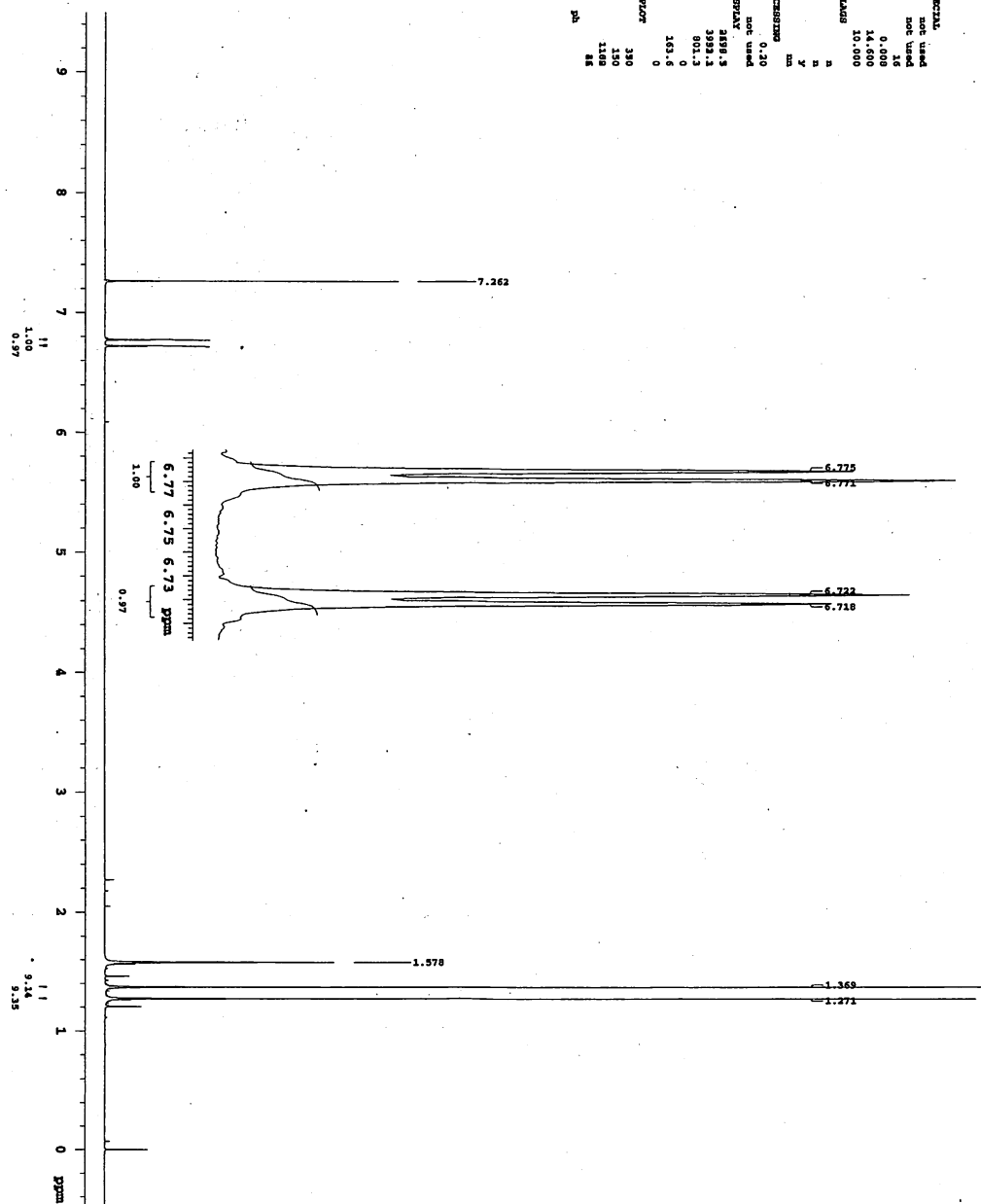
Cc1cc(C)cc1S

Figure S36. 2,4-Di(*t*-butyl)thiophene (12) ¹H-NMR

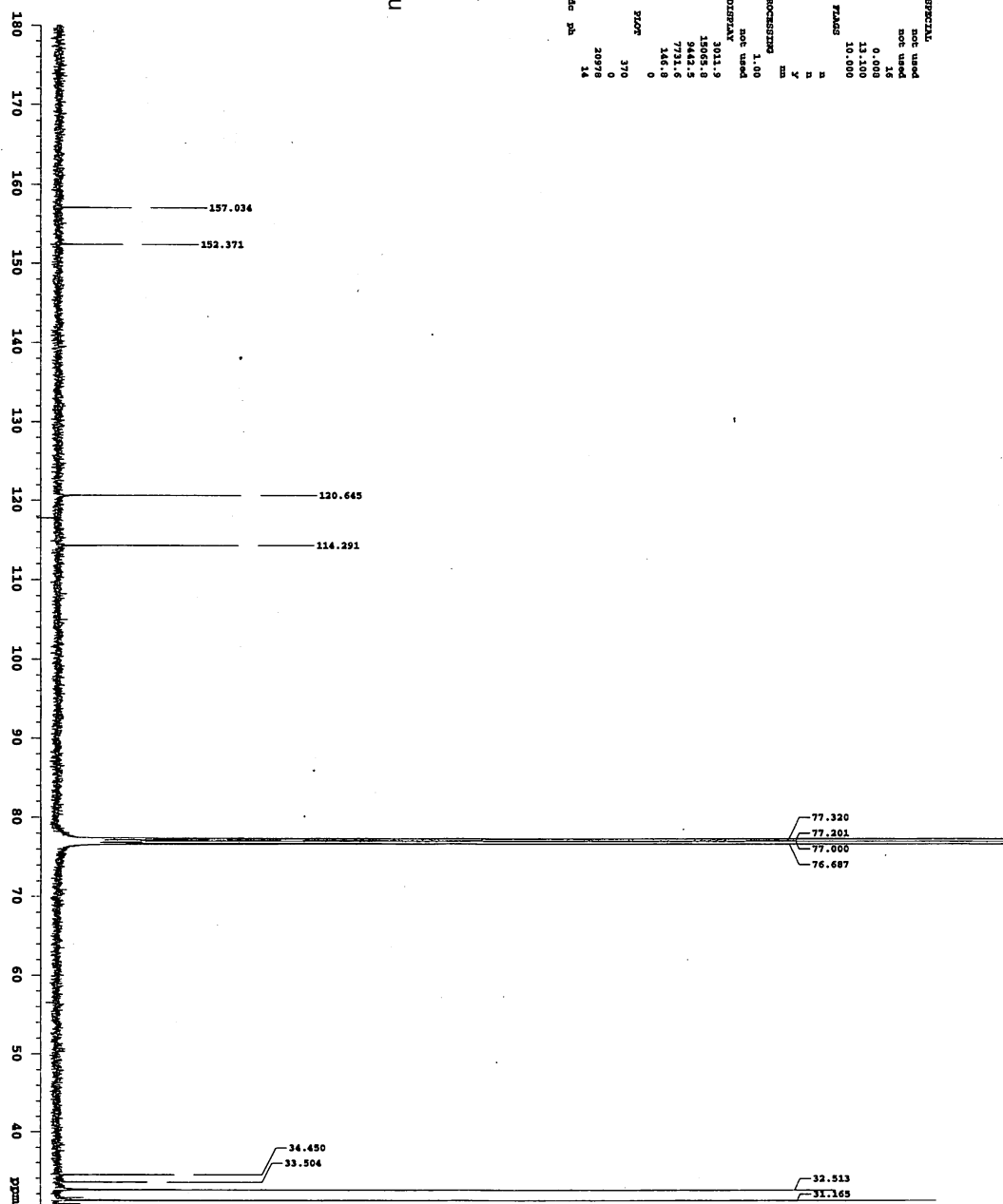
Cc1cc(C)cc1S

Figure S37. 2,4-Di(*t*-butyl)thiophene (12) ¹³C-NMR

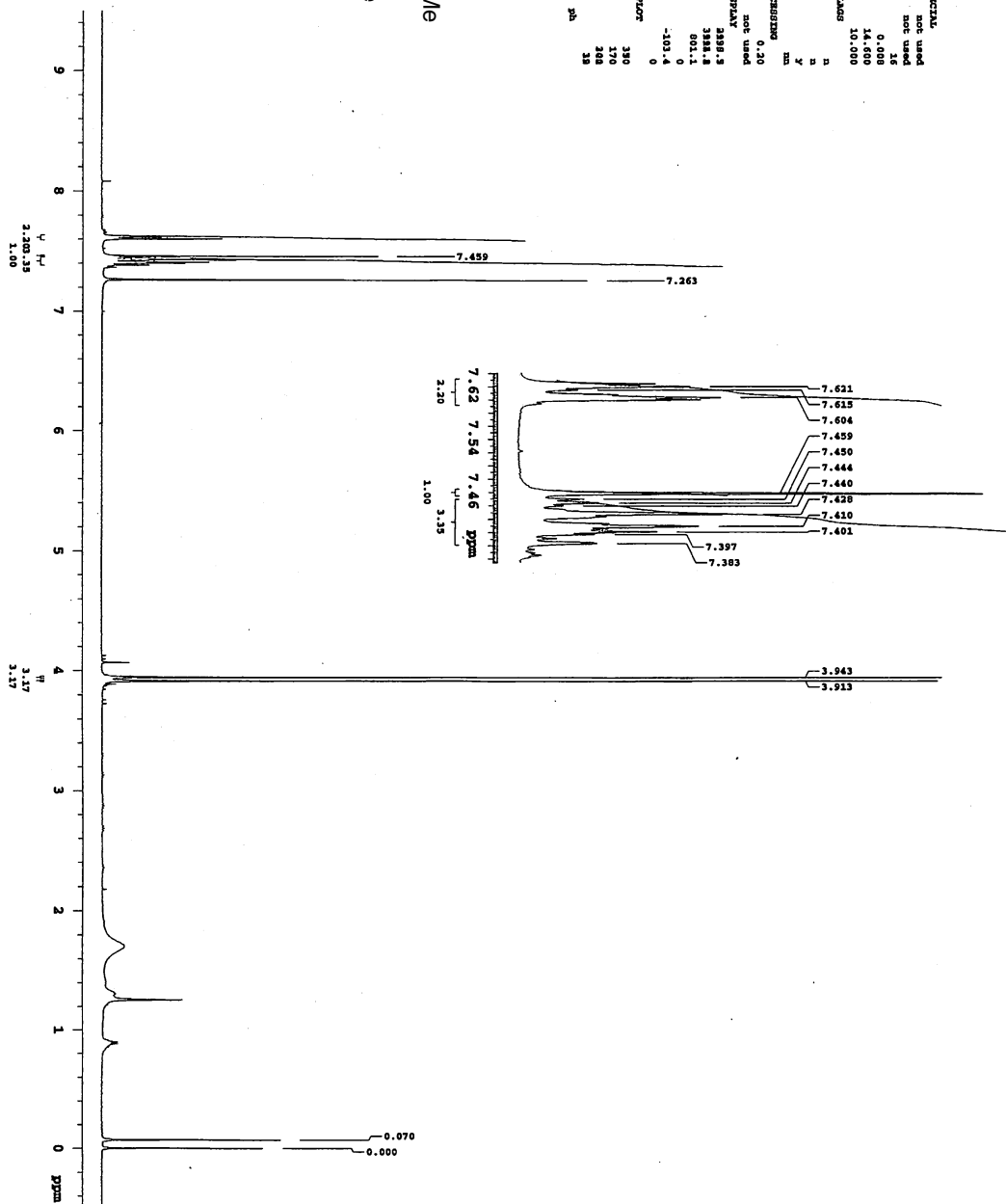
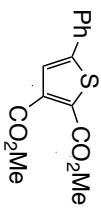
[illegible]

Figure S38. 5-Phenyl-2,3-thiophenedicarboxylic acid 2,3-dimethyl ester (13b) ¹H-NMR

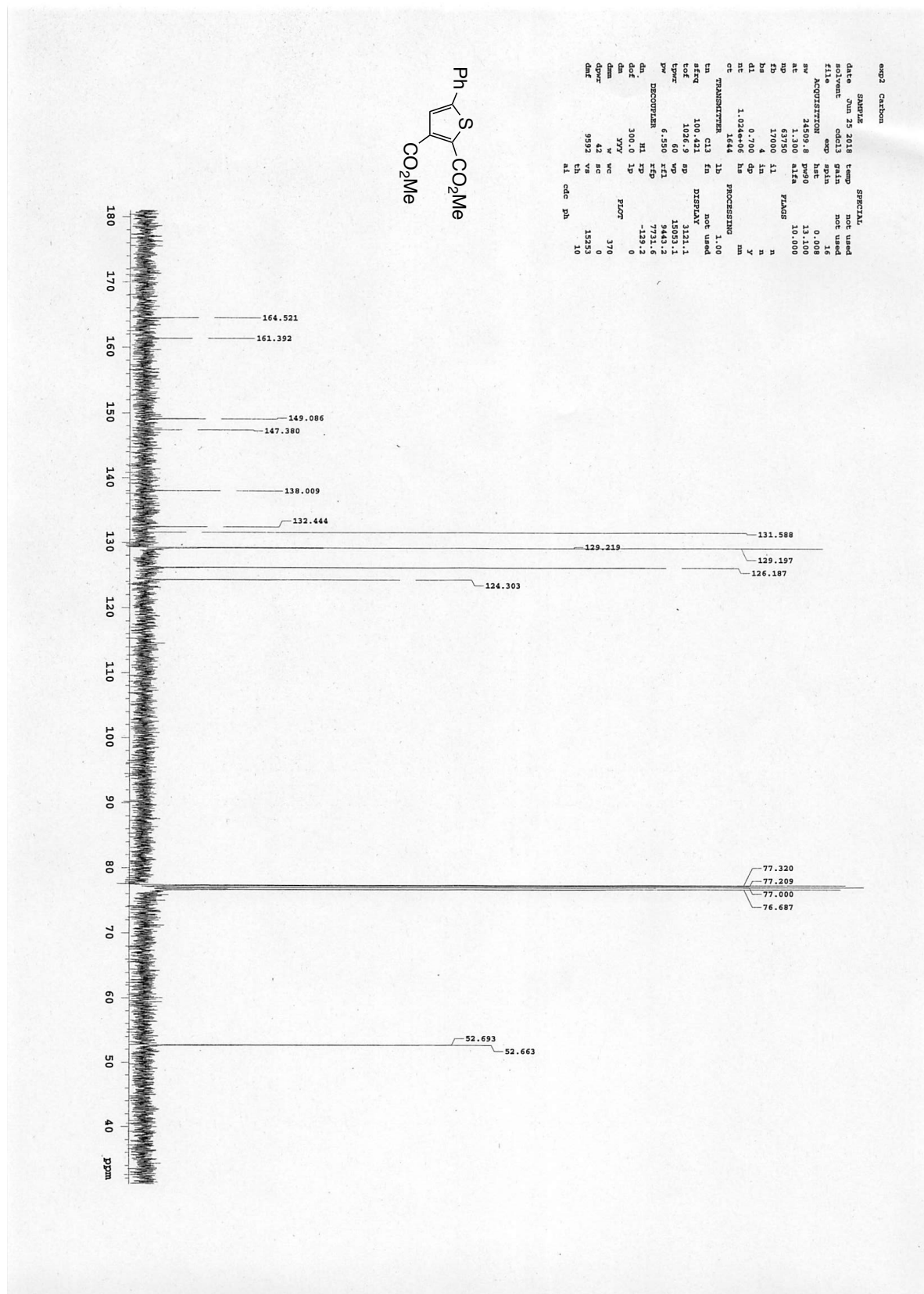
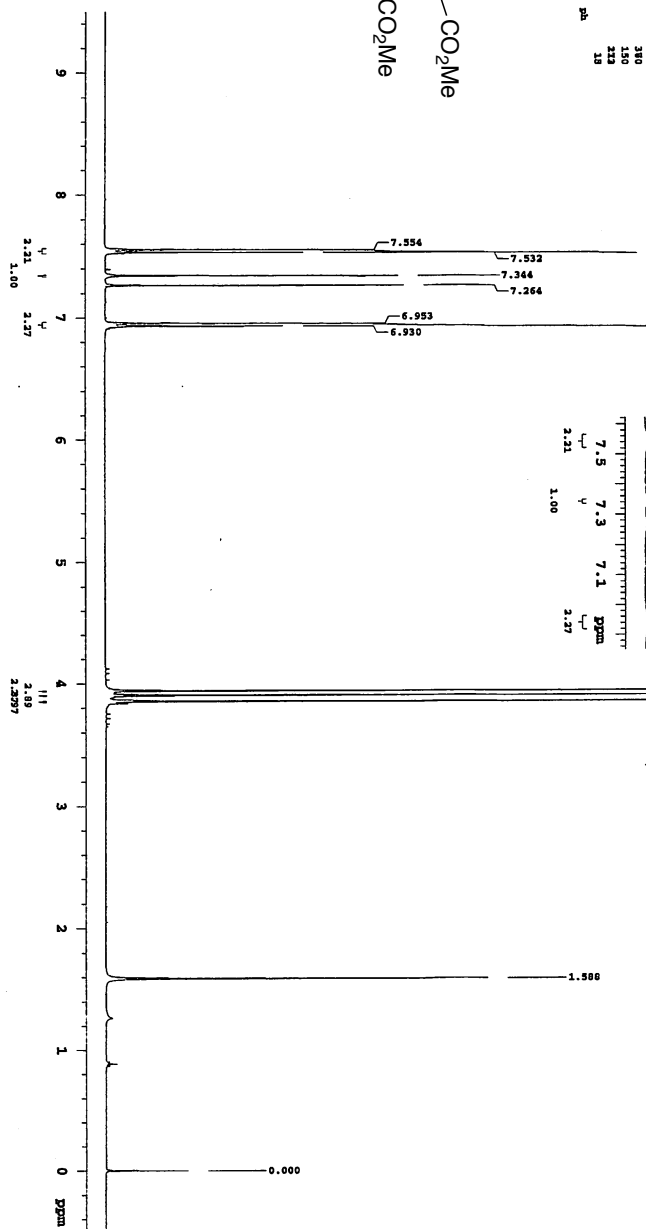


Figure S39. 5-Phenyl-2,3-thiophenedicarboxylic acid 2,3-dimethyl ester (13b) ¹³C-NMR

COC(=O)c1cc(C(=O)c2ccccc2)c(C(=O)c3ccccc3)c1



S42

exp2 Carbon

NAME	DATE	TIME	EXP	PROC	FILE	NAME	DATE	TIME	EXP	PROC	FILE	NAME	DATE	TIME	EXP	PROC
1,4-dithienyl-2,3-dimethyl ester	10/17	10:17	1000	1000	1,4-dithienyl-2,3-dimethyl ester	10/17	10:17	1000	1000	1,4-dithienyl-2,3-dimethyl ester	10/17	10:17	1000	1000	1,4-dithienyl-2,3-dimethyl ester	10/17
1,4-dithienyl-2,3-dimethyl ester	10/17	10:17	1000	1000	1,4-dithienyl-2,3-dimethyl ester	10/17	10:17	1000	1000	1,4-dithienyl-2,3-dimethyl ester	10/17	10:17	1000	1000	1,4-dithienyl-2,3-dimethyl ester	10/17
1,4-dithienyl-2,3-dimethyl ester	10/17	10:17	1000	1000	1,4-dithienyl-2,3-dimethyl ester	10/17	10:17	1000	1000	1,4-dithienyl-2,3-dimethyl ester	10/17	10:17	1000	1000	1,4-dithienyl-2,3-dimethyl ester	10/17
1,4-dithienyl-2,3-dimethyl ester	10/17	10:17	1000	1000	1,4-dithienyl-2,3-dimethyl ester	10/17	10:17	1000	1000	1,4-dithienyl-2,3-dimethyl ester	10/17	10:17	1000	1000	1,4-dithienyl-2,3-dimethyl ester	10/17

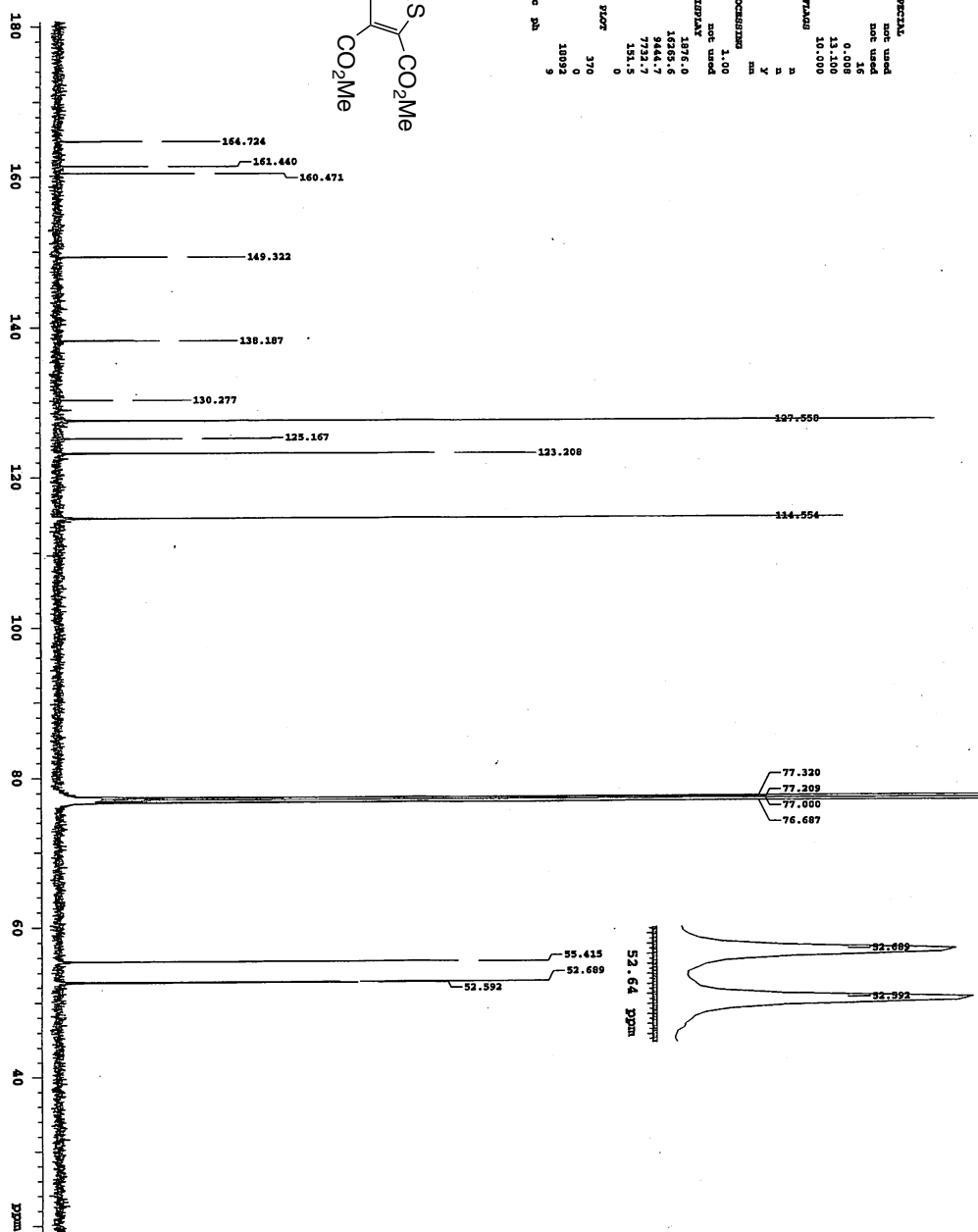
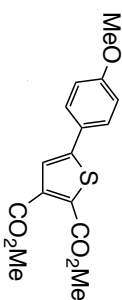


Figure S43. 5-(4-Methoxyphenyl)-2,3-thiophenedicarboxylic acid 2,3-dimethyl ester (13c) ¹³C-NMR

Figure 1 displays two stacked ^{13}C NMR spectra of poly(2-vinylpyridine) in CDCl_3 . The top spectrum shows peaks at 7.364, 7.079, 7.074, 7.063, and 6.796 ppm. The bottom spectrum shows peaks at 7.087, 7.074, 7.063, 7.057, 7.050, 6.803, 6.796, 6.790, 6.774, and 6.766 ppm. A vertical scale bar on the left indicates chemical shift in ppm, with markers at 7.00 and 6.85 ppm.

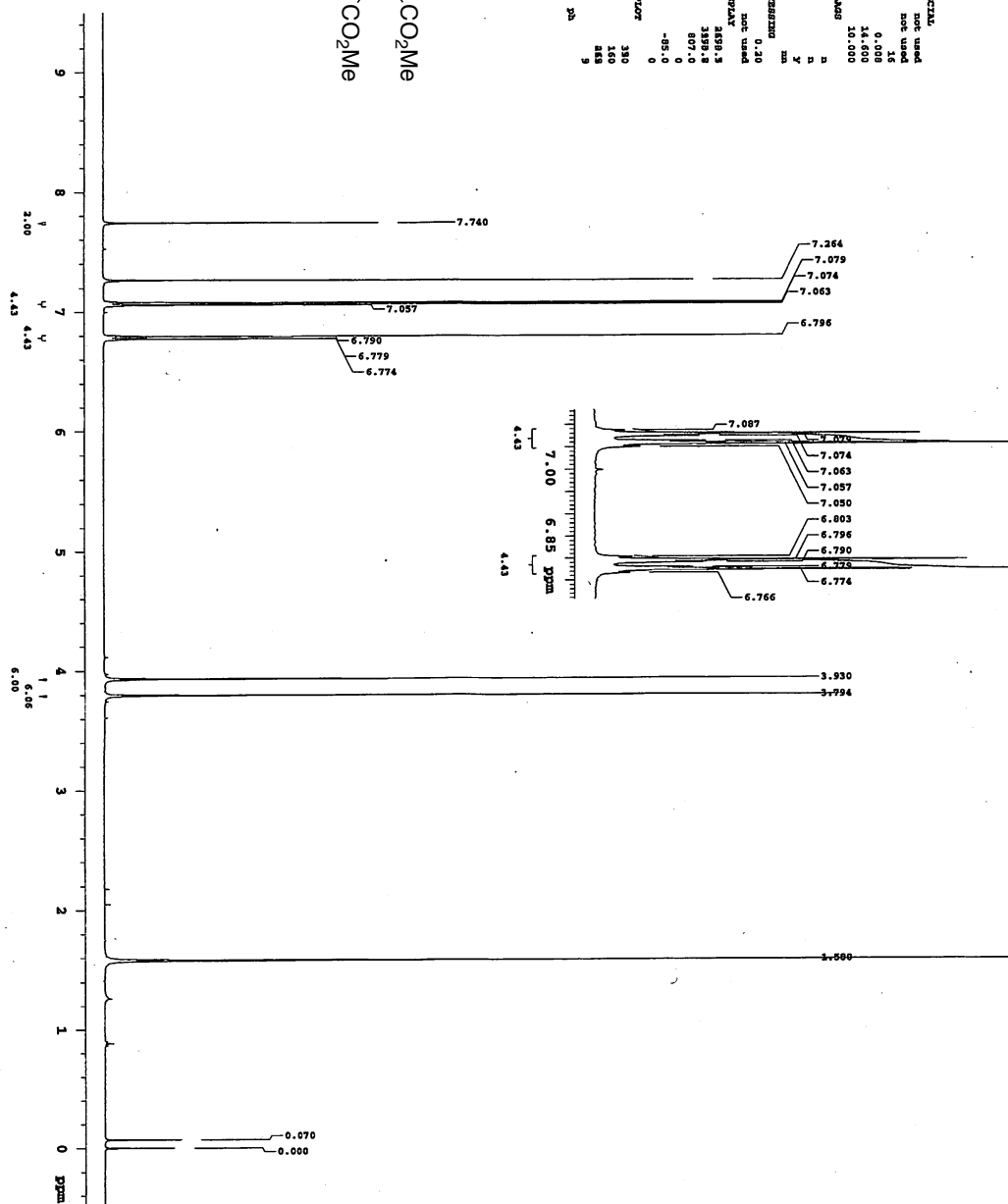
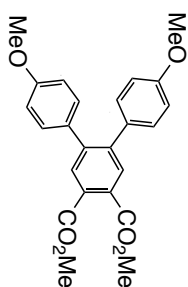


Figure S44. 1,2-Di(4-methoxyphenyl)-4,5-di(methoxycarbonyl)benzene (14c) $^1\text{H-NMR}$

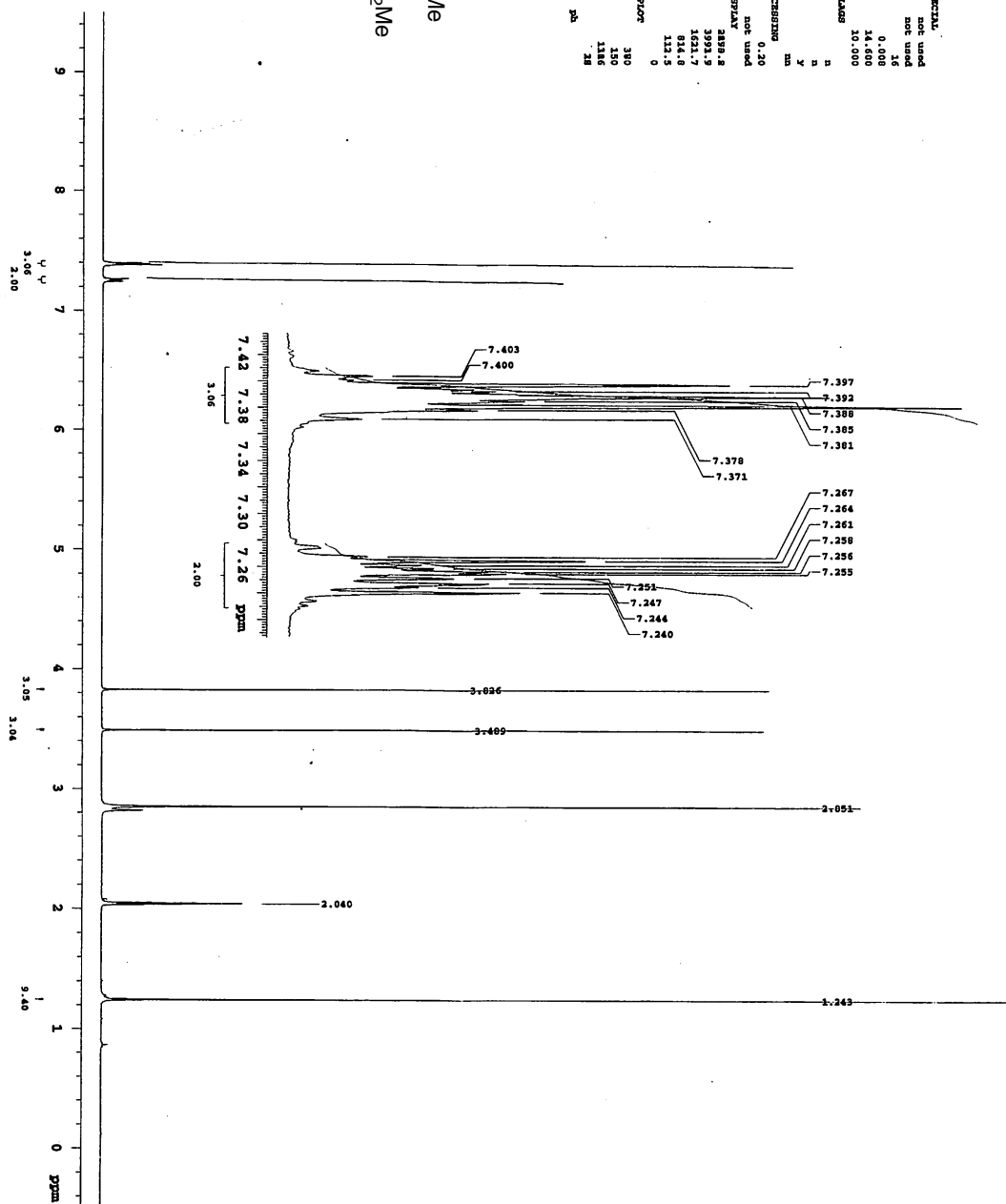
COC(=O)c1cc(C(=O)OC)c(C(=O)OC)c1S

Figure S46. 5-*t*-Butyl-4-phenyl-2,3-thiophenedicarboxylic acid 2,3-dimethyl ester (17) ¹H-NMR

exp3 carbon

NAME	DATE	TIME	TEMP	SPECTRA
exp3	May 10 2017	10:00	125	not used
solvent	acetone	cdcl3		not used
file	/media/lenax/-	exp3		16
1,4-dioxane	mm/2t	not		0.008
butylphenylacetate	ppm			13.100
thoxy/acetophenone	alpha			10.000
-o-acetone	alpha			10.000
NAME <th>DATE</th> <th>TIME</th> <th>TEMP</th> <th>SPECTRA</th>	DATE	TIME	TEMP	SPECTRA
exp3	May 10 2017	10:00	125	not used
solvent	acetone	cdcl3		not used
file	/media/lenax/-	exp3		16
1,4-dioxane	mm/2t	not		0.008
butylphenylacetate	ppm			13.100
thoxy/acetophenone	alpha			10.000
-o-acetone	alpha			10.000
NAME <th>DATE</th> <th>TIME</th> <th>TEMP</th> <th>SPECTRA</th>	DATE	TIME	TEMP	SPECTRA
exp3	May 10 2017	10:00	125	not used
solvent	acetone	cdcl3		not used
file	/media/lenax/-	exp3		16
1,4-dioxane	mm/2t	not		0.008
butylphenylacetate	ppm			13.100
thoxy/acetophenone	alpha			10.000
-o-acetone	alpha			10.000

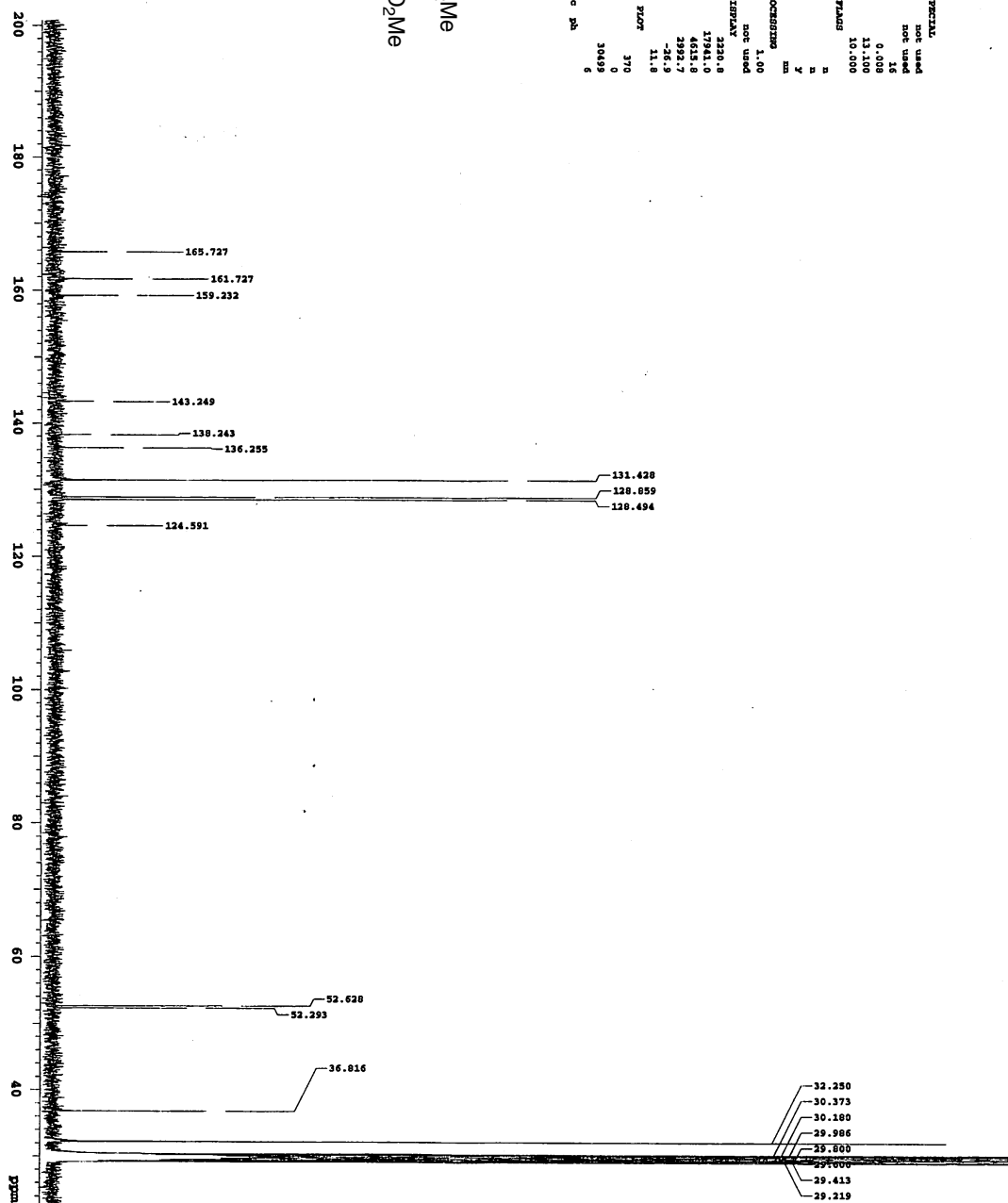
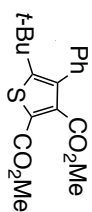


Figure S47. 5-*t*-Butyl-4-phenyl-2,3-thiophenedicarboxylic acid 2,3-dimethyl ester (17) ¹³C-NMR