

SUPPORTING INFORMATION

Title: Synthetic and Mechanistic Investigations on the Rearrangement of 2,3-Unsaturated 1,4-Bis(alkylidene)carbenes to Enediynes

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Experimental Section

General

The melting points are uncorrected. IR spectra were recorded on a Perkin Elmer Spectrum One FT spectrometer. NMR spectra (^1H , ^{13}C , ^{31}P and ^{77}Se) were recorded on an AMX-400 or VXR-300S spectrometer. TMS was the internal standard for ^1H , ^{13}C and ^{77}Se and phosphoric acid was the external standard for ^{31}P . The coupling constants (J values) are given in Hz. While recording ^1H NMR spectra of deuterated compounds **28** and **29**, a pulse delay of 20s was introduced to ensure satisfactory integration for all the protons. High resolution mass spectra were recorded at 60-70 eV on a Waters Micromass Q-TOF spectrometer (ESI, Ar) or on a VG-Fisons "Autospec" spectrometer (DCI, CH_4).

4,5-Bis(4-methoxyphenyl)furan-2,3-dicarbaldehyde (11f). To a stirred solution of MnO_2 (805 mg, 9.4 mmol) in CH_2Cl_2 (15 ml), was added its precursor diol **32** (179 mg, 0.47 mmol) in CH_2Cl_2 (5 ml) at ambient temperature. The resulting mixture was heated to reflux for 5 h, cooled to room temperature, filtered through a pad of celite and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel by eluting with ethyl acetate/pet ether (0-15 %, gradient elution) to afford pure dialdehyde **11f**. Yellow solid. Yield 18 % (0.028 g). m.p. 132 °C. IR (CH_2Cl_2): 3019 (s), 2933 (m), 1695 (s), 1670 (s), 1610 (s), 1520 (m), 1488 (m), 1258 (m), 1216 (s), 1032 (m), 759 (s), 669 (s) cm^{-1} . ^1H NMR (CDCl_3): δ = 3.81 (s, 3H), 3.88 (s, 3H), 6.82 (d, J = 8.9 Hz, 2H), 7.00 (d, J = 8.6 Hz, 2H), 7.30 (d, J = 8.6 Hz, 2H), 7.49 (d, J = 8.9 Hz, 2H), 10.02 (s, 1H), 10.11 (s, 1H) ppm. ^{13}C NMR (CDCl_3): δ = 55.2, 114.1, 114.2, 114.5, 120.9, 121.6, 122.3, 128.4, 131.3, 131.8, 149.9, 154.4, 159.8, 160.7, 178.8, 186.8 ppm. MS (ESI, Ar): m/e (rel intensity) = 337 (MH^+ , 100). HRMS (ESI, Ar): calcd for $\text{C}_{20}\text{H}_{17}\text{O}_5$ (MH^+) 337.1076, found 337.1084.

1-Ethynyl-4-methoxybenzene-d (29, Standard).^[58] To a stirred solution of *p*-methoxyphenylacetylene **25** (132 mg, 1 mmol) in THF (10 ml) was added *n*BuLi (0.6 ml, 1.5 mmol, 2.5 M solution in hexanes) dropwise over a period of 15 min at -78 °C. The low temperature was maintained for 1.5 h and the resulting reddish solution was gradually warmed up to -40 °C. At this temperature, the reaction mixture was quenched with D_2O (2 ml, excess) and stirred for another 3 h at room temperature. The layers were separated and the aqueous layer was further extracted with ether (2 $\times$ 10 ml), the combined organic layers were dried (anhyd. Na_2SO_4) and concentrated in vacuo. The crude residue was further purified by flushing through a pad of silica gel and eluting with pet ether to afford pure *p*-methoxyphenylacetylene-*d* **29**. Light yellow liquid. Yield 70 % (0.093 g). IR (Neat): 3290 (s), 2957 (m), 2931 (m), 2582 (s), 2106 (w), 1607 (s), 1507 (s), 1291 (m), 1251 (s), 1171 (m), 1032 (s), 833 (s) cm^{-1} . ^1H NMR (CDCl_3): δ = 3.79 (s, 3H), 6.83 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H) ppm, D incorporation in **29** is 79.5 % (a singlet at δ 3.0 with an integration value of $\sim$ 0.2 H

corresponds to the acetylenic proton of the minor non-deuterated compound). ^{13}C NMR (CDCl_3 , Major deuterated compound **29**): δ = 55.2 (q), 75.5 (t, $J_{\text{C-D}}$ = 38.1 Hz), 83.2 (t, $J_{\text{C-D}}$ = 7.6 Hz), 113.9 (d), 114.2 (s), 133.5 (d), 159.9 (s) ppm. In agreement with the only available data (^1H NMR) in the literature (Ref. 58). This standard **29** was prepared for comparison with **29** isolated from the D labeling experiment.

Table S1. % Deuterium incorporation in **28** calculated from ^1H NMR integration of the olefinic proton appearing at δ 7.40 in the minor non-deuterated compound **22**.

Integration ^a	δ 3.81 (s)	δ 6.88 (d)	δ 7.50 (d)	Average
1	93.2	91.7	91.7	92.2
2	93.1	92.3	91.7	92.4
3	93.1	92.3	91.8	92.4
				92.3

^a A pulse delay of 20s was introduced to ensure satisfactory integration for all the protons.

Table S2. % Deuterium incorporation in **29** (obtained via D-labeling experiment) calculated from ^1H NMR integration of the acetylenic proton appearing at δ 3.00 in the minor non-deuterated compound **25**.

Integration	δ 3.79 (s)	δ 6.83 (d)	δ 7.42 (d)	Average
1	53.3	51.3	43.0	49.2
2	55.6	52.2	46.0	51.3
3	53.0	52.2	46.0	50.4
				50.3

^a A pulse delay of 20s was introduced to ensure satisfactory integration for all the protons.

Overall retention of D via FBW rearrangement = 54.5%

BS-119
exp2 PROTON

SAMPLE		SPECIAL	
date	Apr 6 2005	temp	not used
solvent	CDCl3	gain	not used
file	/export/home/~	spin	not used
inn1	6thapr11/BS-1	hst	0.008
13-1H.fid	pw90	20.000	
ACQUISITION		alpha	
sw	6389.8	FLAGS	n
at	1.995	il	n
np	25496	in	n
fb	not used	dp	y
bs	2	hs	nn
d1	1.000	fn	not used
nt	400	PROCESSING	not used
ct	70	DISPLAY	-19.9
TRANSMITTER		sp	4827.7
tn	H1	wp	808.9
sfrq	399.863	rfl	0
tof	338.7	rfp	-56.8
tpwr	55	rp	-72.8
pw	4.250	lp	
DECOUPLER		PLOT	
dn	C13	vc	250
dof	0	sc	0
dm	nnn	vs	41
dmm	c	th	6
dpwr	51	ai	ph
dmt	17100		

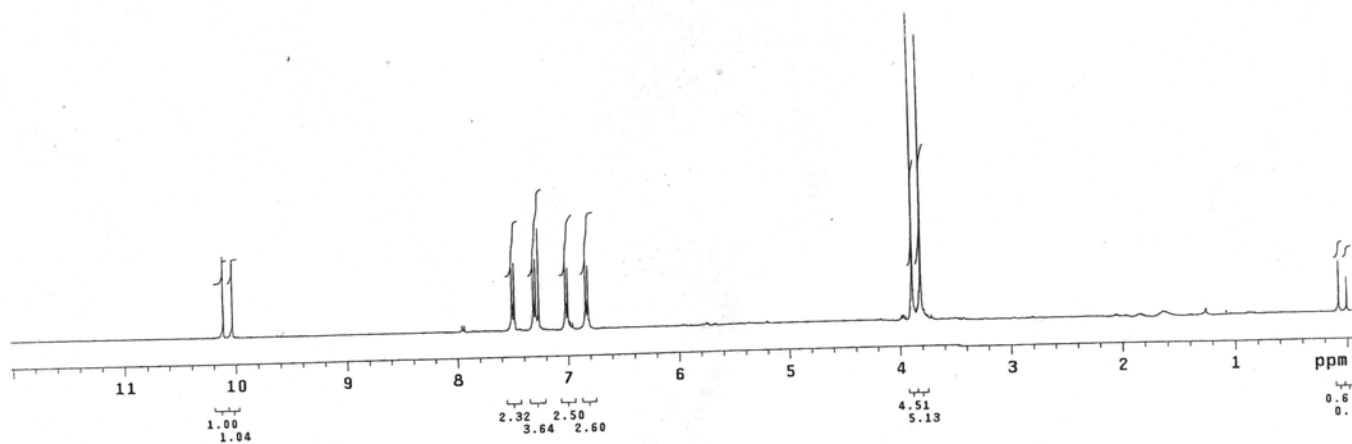
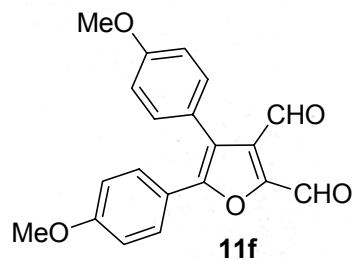


Figure S1. ^1H NMR spectrum (CDCl_3) of 4,5-bis(4-methoxyphenyl)furan-2,3-dicarbaldehyde (**11f**)

```

BS-OMe-DIALD
exp2 CARBON

SAMPLE
date Jun 2 2006 temp not used
solvent CDCL3 gain not used
file /export/home/~ spin not used
inn3/2006/JUNE/2nd~ hst 0.008
/BS-OMe-DIALD-C13.~ pw90 14.000
fid alfa 20.000

ACQUISITION
sw 25125.6 il n
at 1.199 in n
np 60270 dp y
fb 13800 hs nn
bs 4
d1 1.000 lb 1.00
nt 50000 fn not used
ct 1716

TRANSMITTER
tn C13 sp 2.3
sfrq 100.561 wp 20139.9
tof 1554.3 rfp 9258.3
tpwr 56 rp 7742.3
pw 7.000 lp -308.2

DECOUPLER
dn H1 wc 250
dof 0 sc 0
dm yyy vs 37
dmm w th 3
dpwr 41 al ph
dmf 11900

```

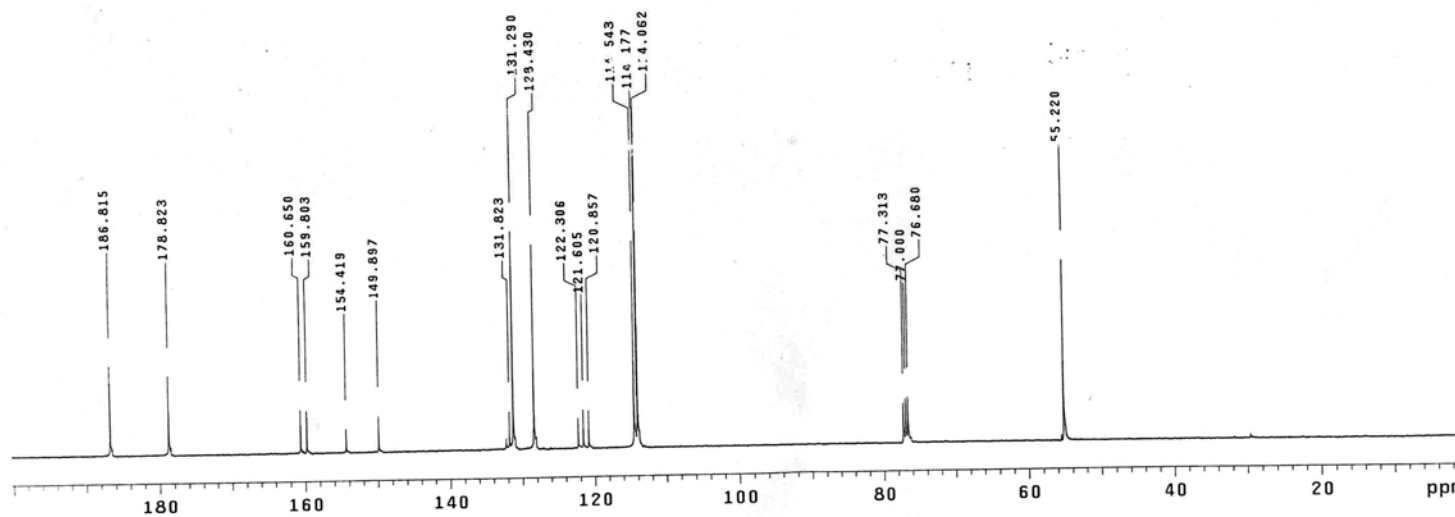
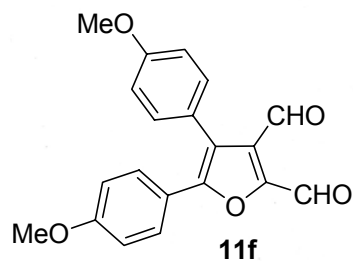


Figure S2. ^{13}C NMR spectrum (CDCl_3) of 4,5-bis(4-methoxyphenyl)furan-2,3-dicarbaldehyde (**11f**)

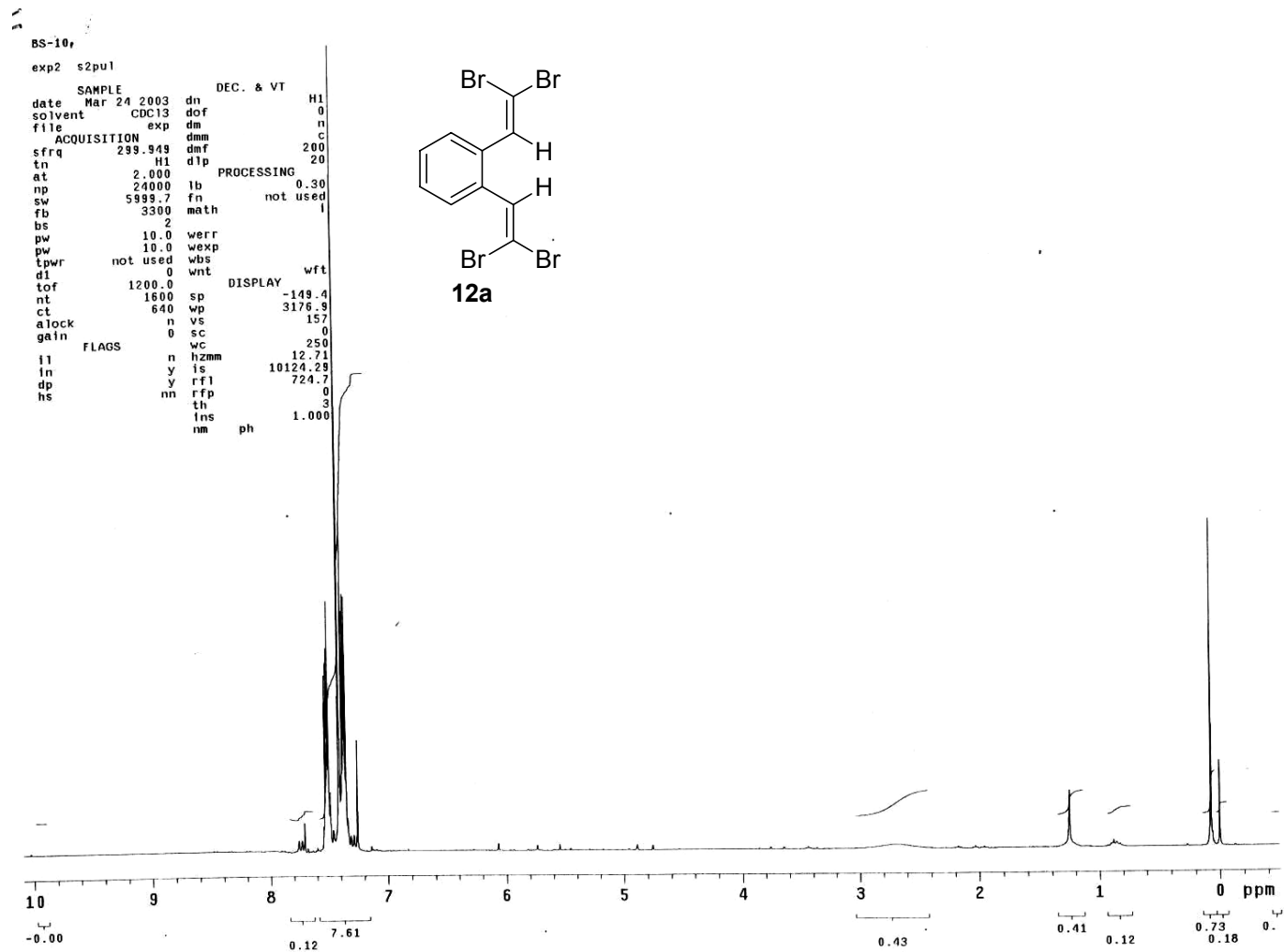


Figure S3. ^1H NMR spectrum (CDCl_3) of 1,2-bis(2,2-dibromovinyl)benzene (**12a**)

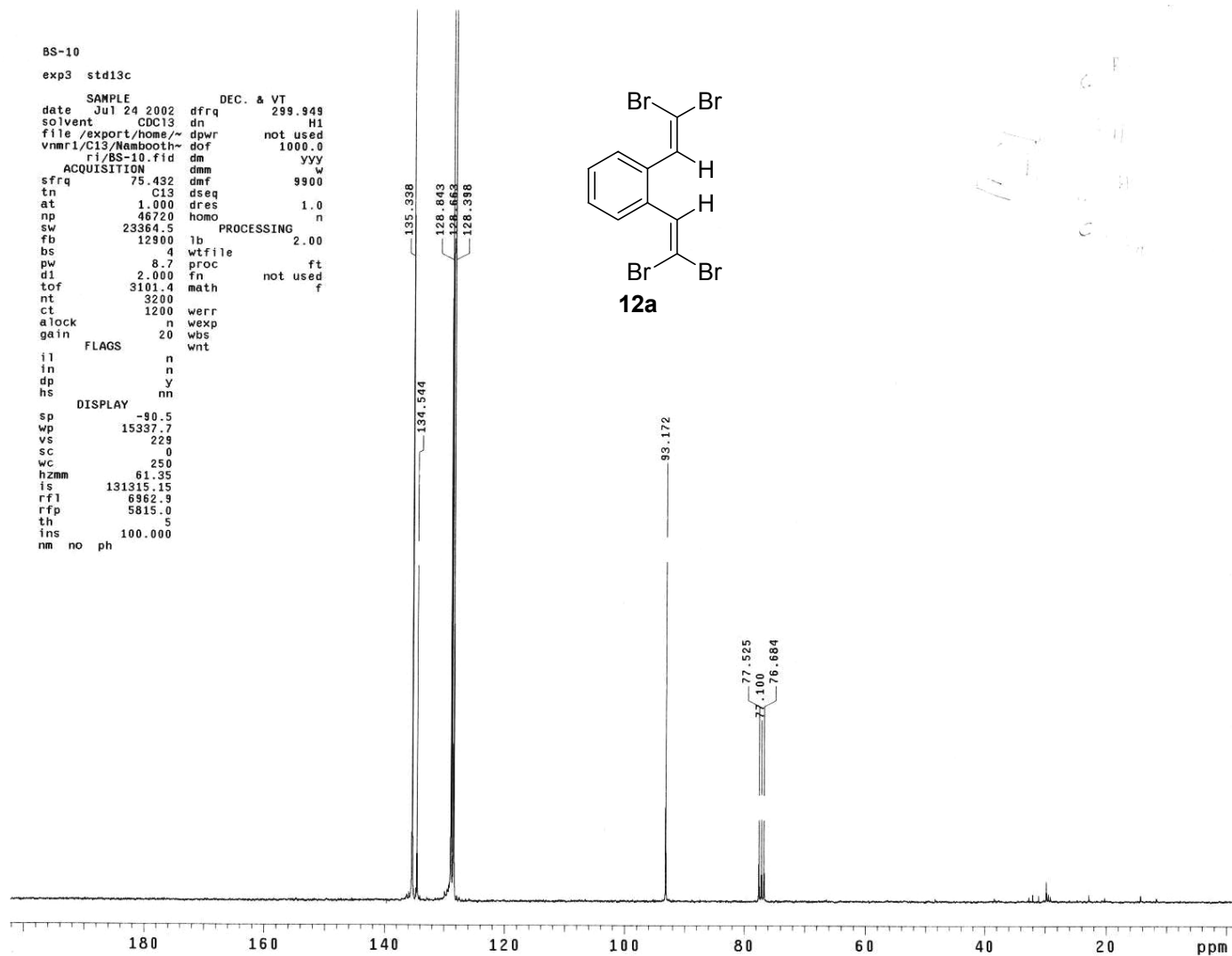


Figure S4. ^{13}C NMR spectrum (CDCl_3) of 1,2-bis(2,2-dibromovinyl)benzene (**12a**)

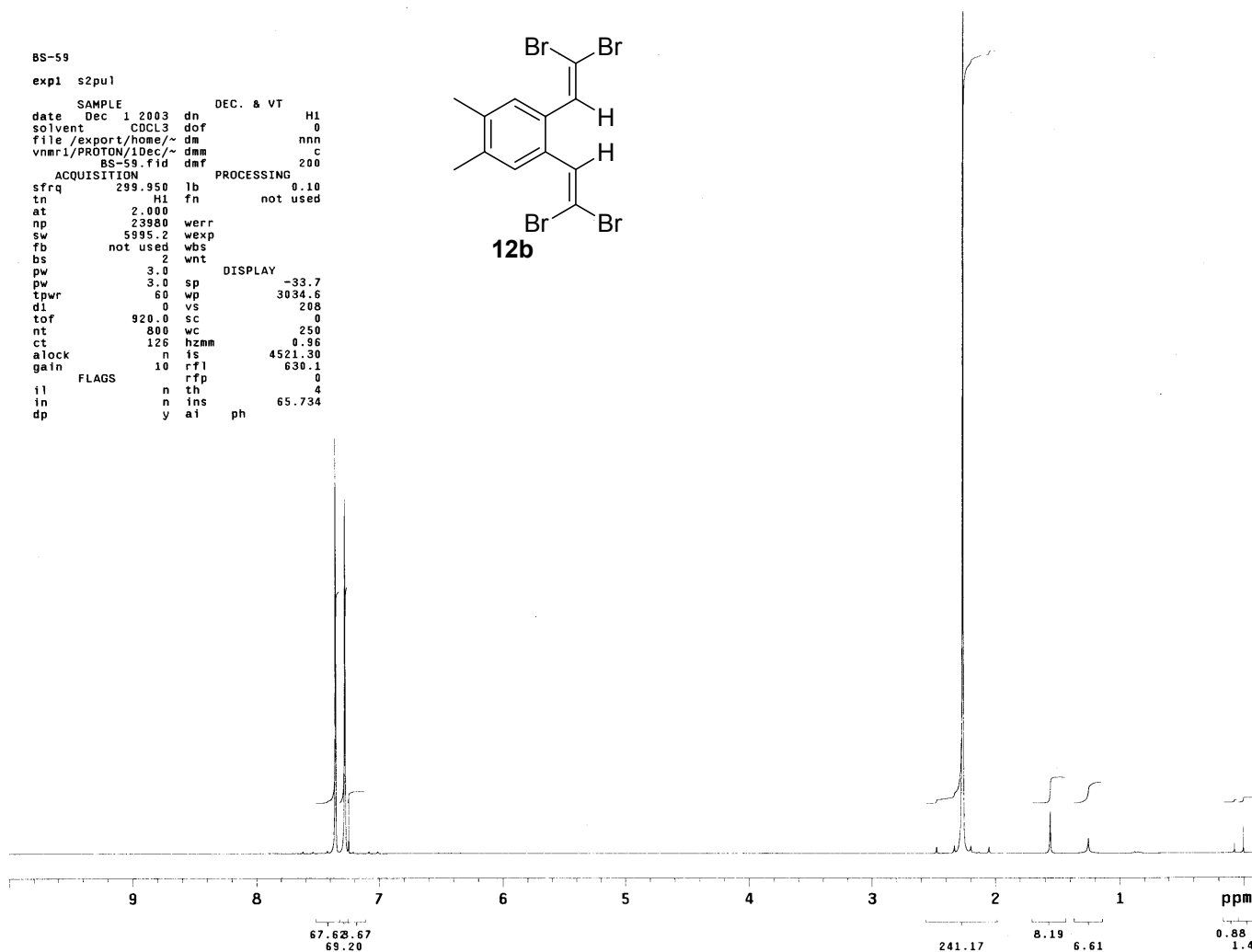


Figure S5. ^1H NMR spectrum (CDCl_3) of 1,2-bis(2,2-dibromovinyl)-4,5-dimethylbenzene (**12b**)

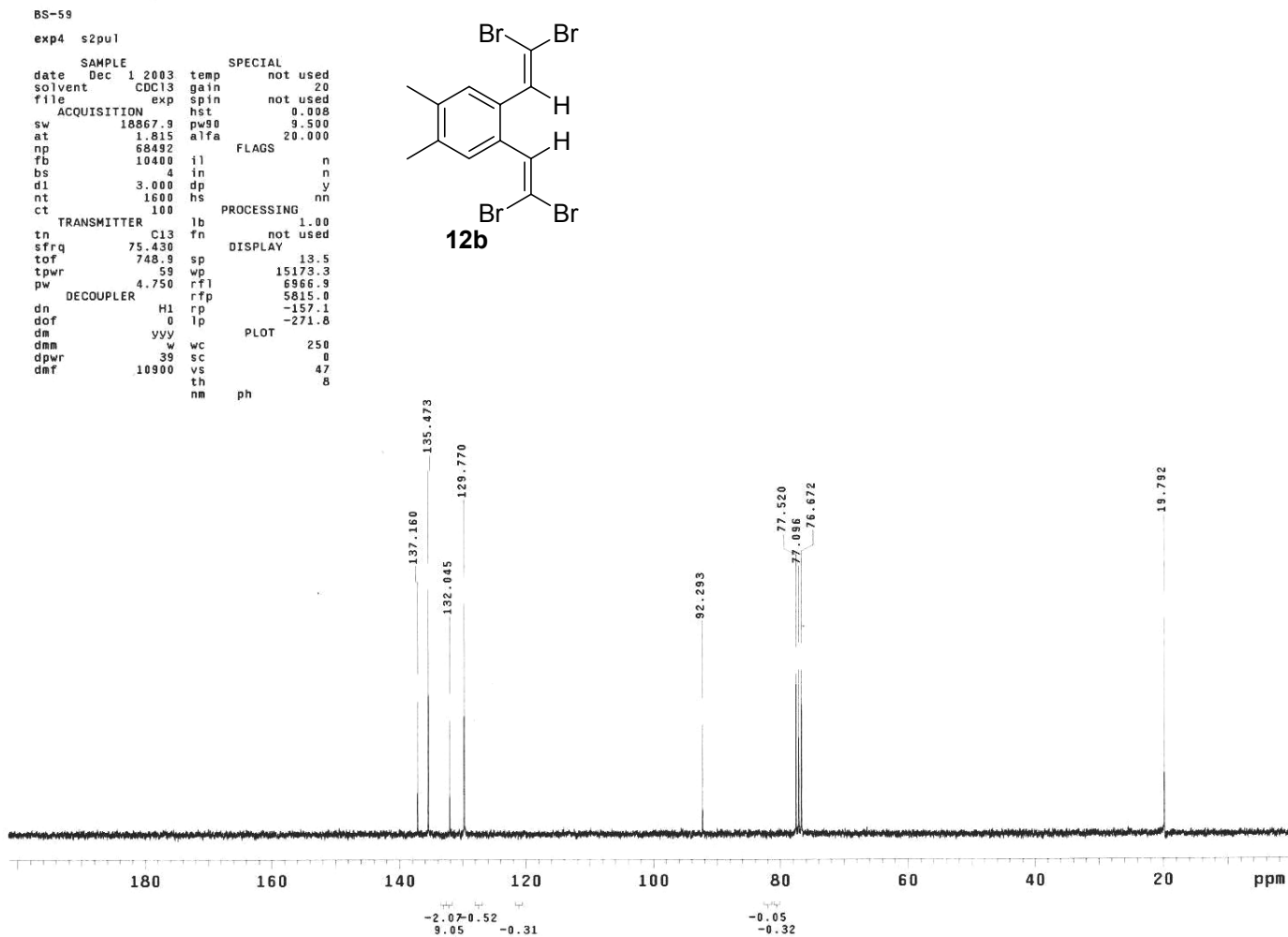


Figure S6. ^{13}C NMR spectrum (CDCl_3) of 1,2-bis(2,2-dibromovinyl)-4,5-dimethylbenzene (**12b**)

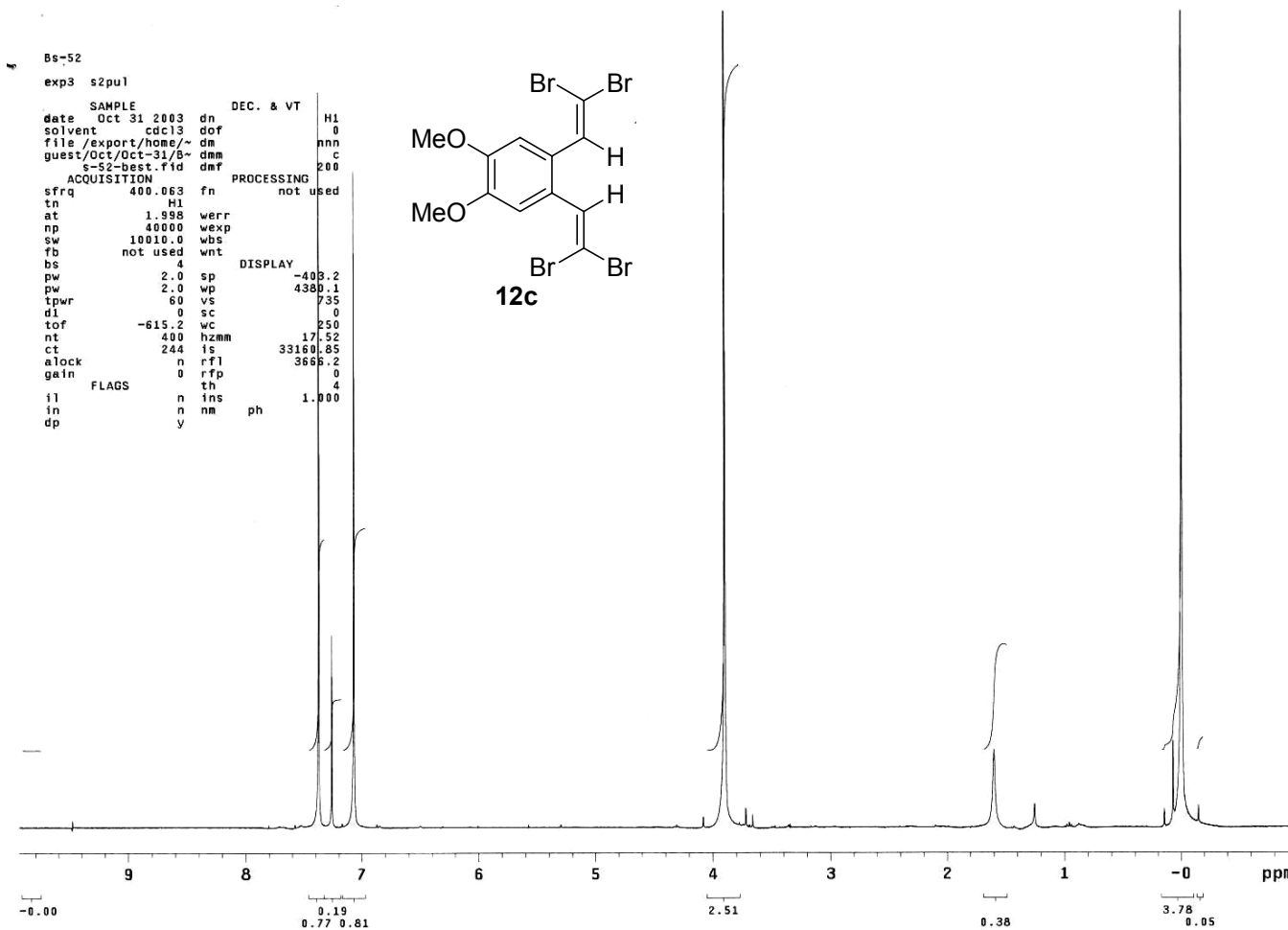


Figure S7. ^1H NMR spectrum (CDCl_3) of 1,2-bis(2,2-dibromovinyl)-4,5-dimethoxybenzene (**12c**)

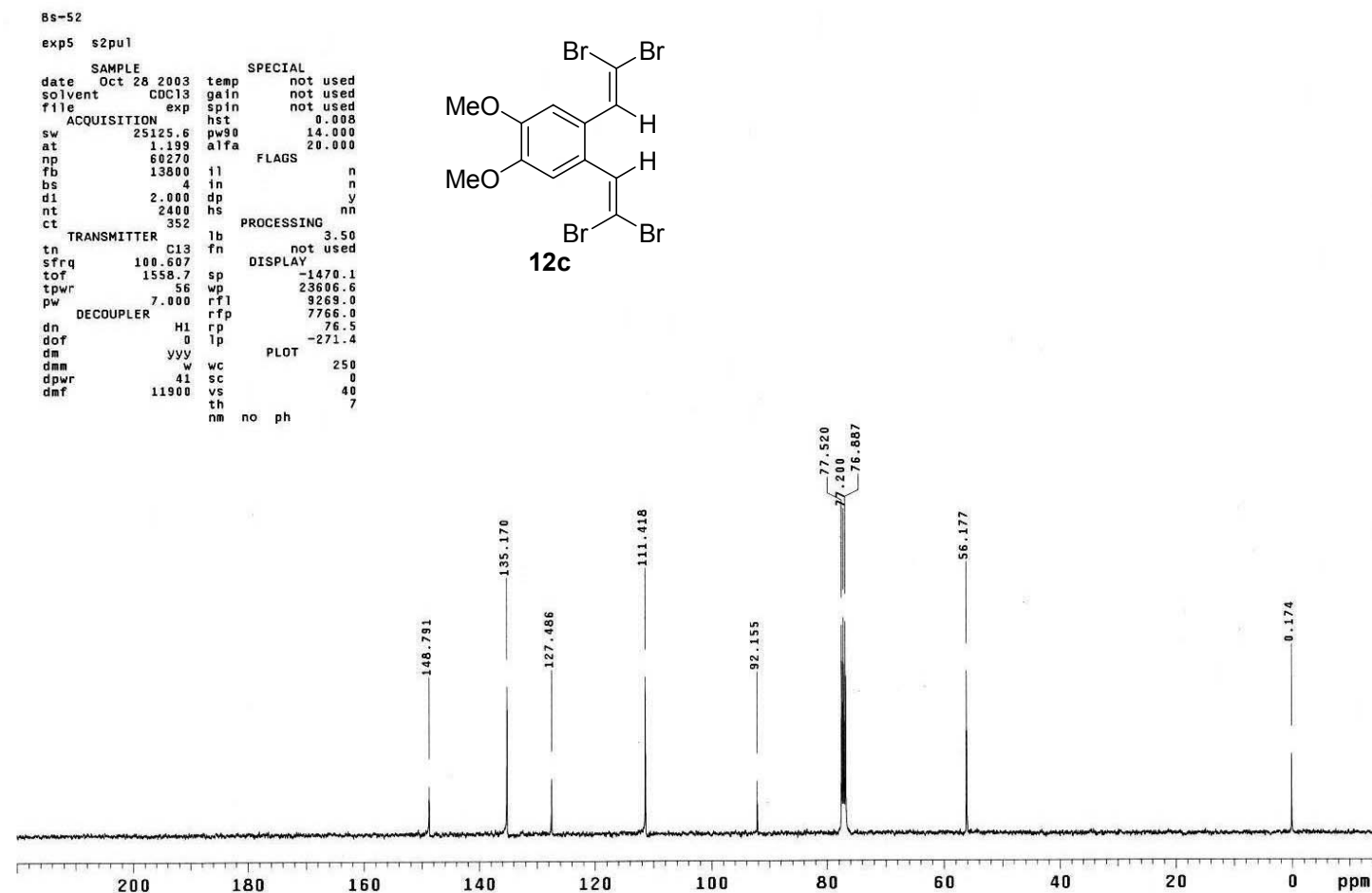


Figure S8. ^{13}C NMR spectrum (CDCl_3) of 1,2-bis(2,2-dibromovinyl)-4,5-dimethoxybenzene (**12c**)

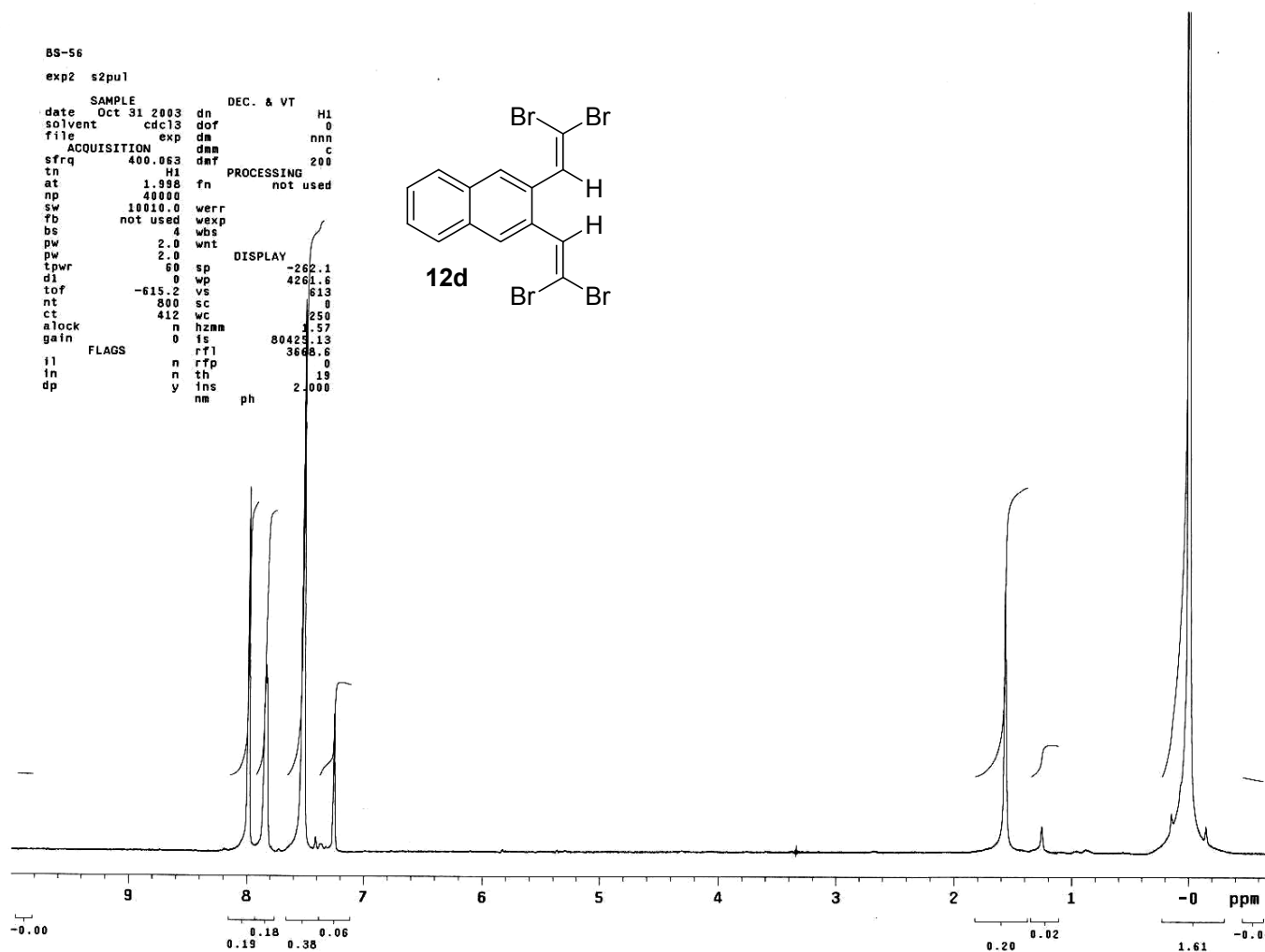


Figure S9. ^1H NMR spectrum (CDCl_3) of 2,3-bis(2,2-dibromovinyl)naphthalene (**12d**)

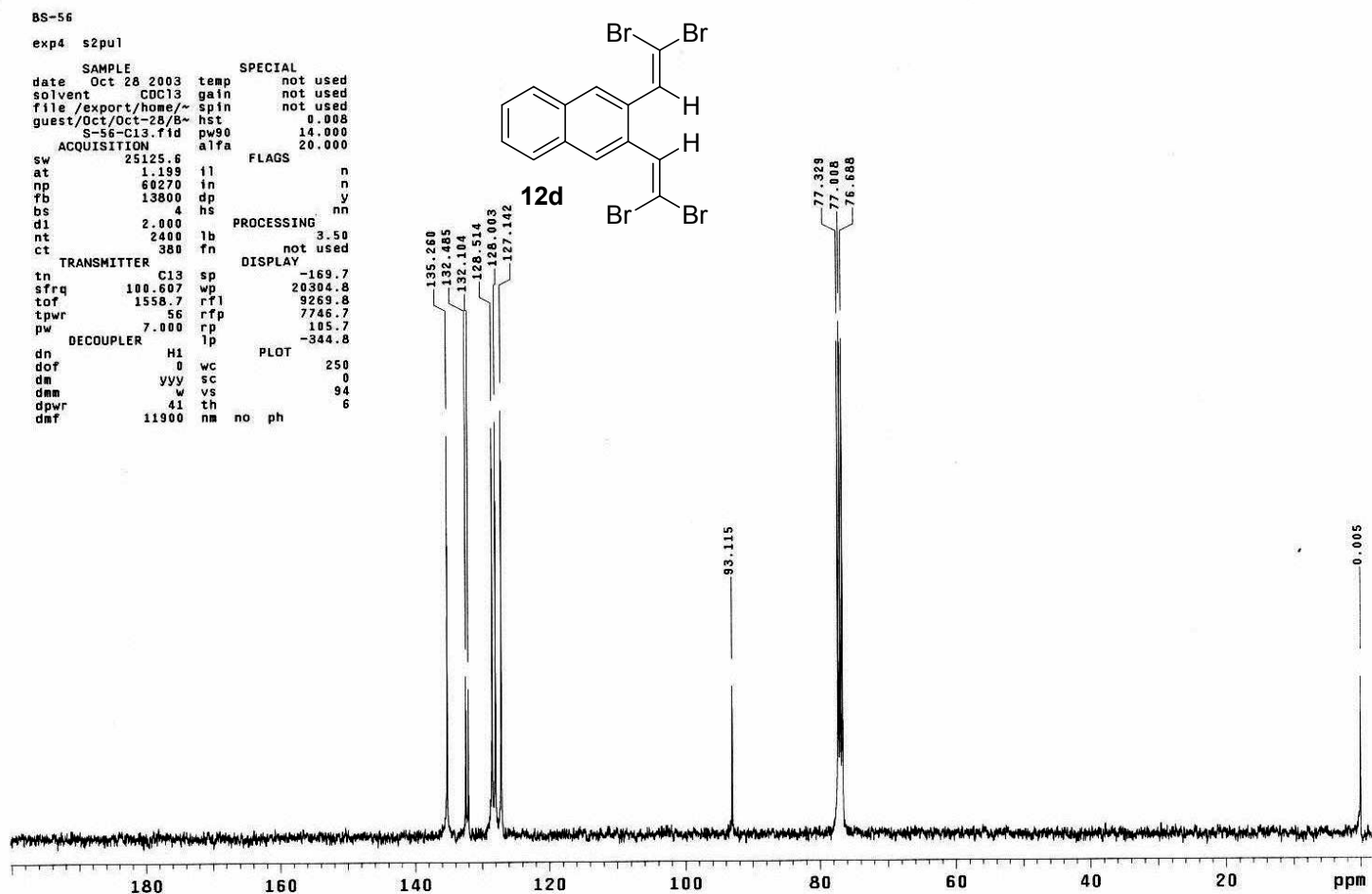


Figure S10. ^{13}C NMR spectrum (CDCl_3) of 2,3-bis(2,2-dibromovinyl)naphthalene (12d)

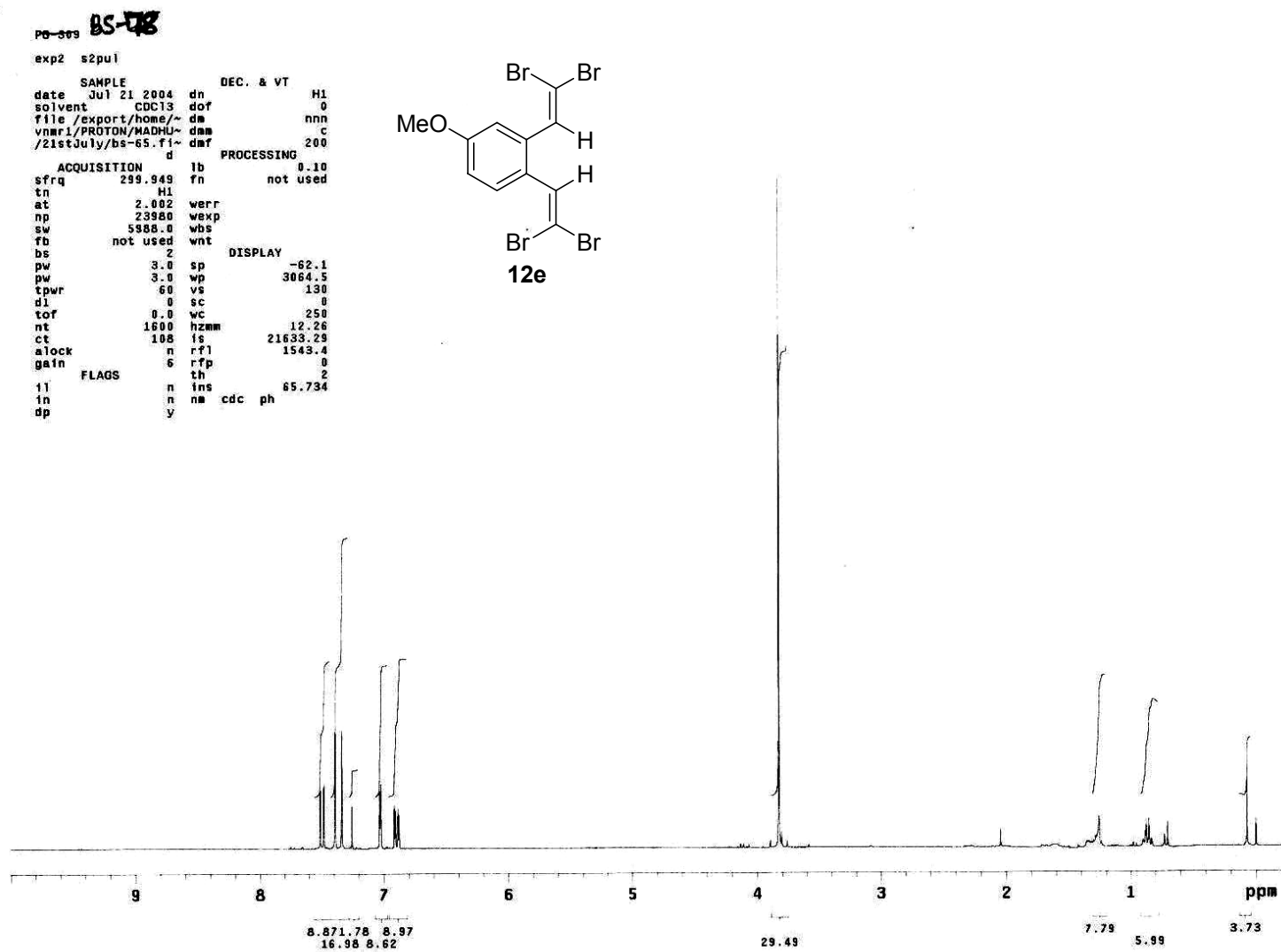


Figure S11. ^1H NMR spectrum (CDCl_3) of 1,2-bis(2,2-dibromovinyl)-4-methoxybenzene (**12e**)

```

BS-78
exp3 s2pul

SAMPLE
date Jul 21 2004
solvent CDCl3
file exp
ACQUISITION
sw 25000.0
st 0.500
np 30000
fb not used
bs 4
di 3.000
nt 3200
ct 268

SPECIAL
temp not used
gain 10
spin not used
hst 0.008
pw90 9.500
alpha 20.000

FLAGS
i1 n
in n
dp y
hs nh

PROCESSING
lb 1.00
fn not used

DISPLAY
sp -175.6
wp 15196.2
rfl 10037.2
rfp 5815.0
rp -118.6
lp -318.3

DECOUPLER
H1
w
39
10900

PLOT
wc 250
sc 0
vs 81
ch 5
nm ph

```

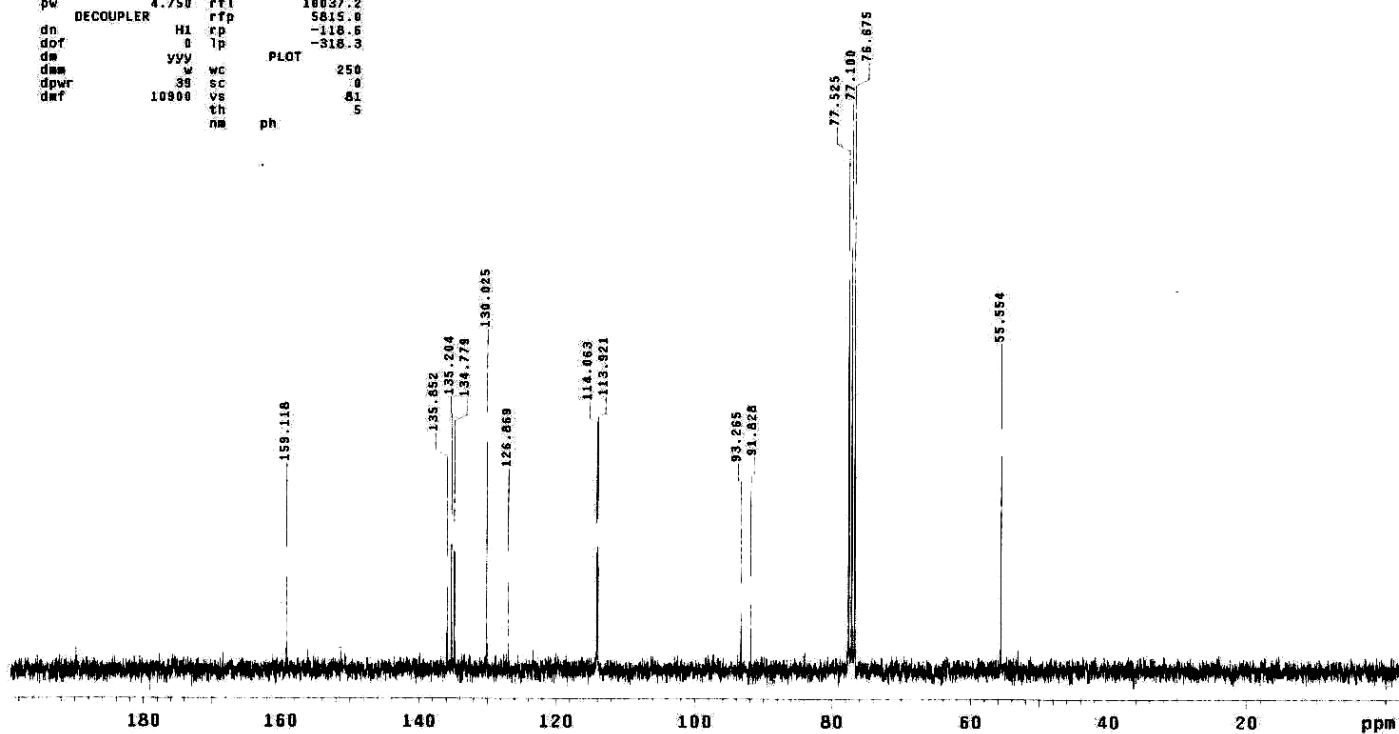
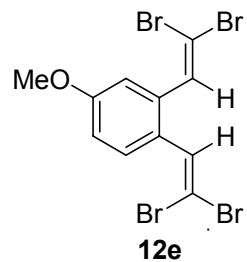


Figure S12. ¹³C NMR spectrum (CDCl₃) of 1,2-bis(2,2-dibromovinyl)-4-methoxybenzene (**12e**)

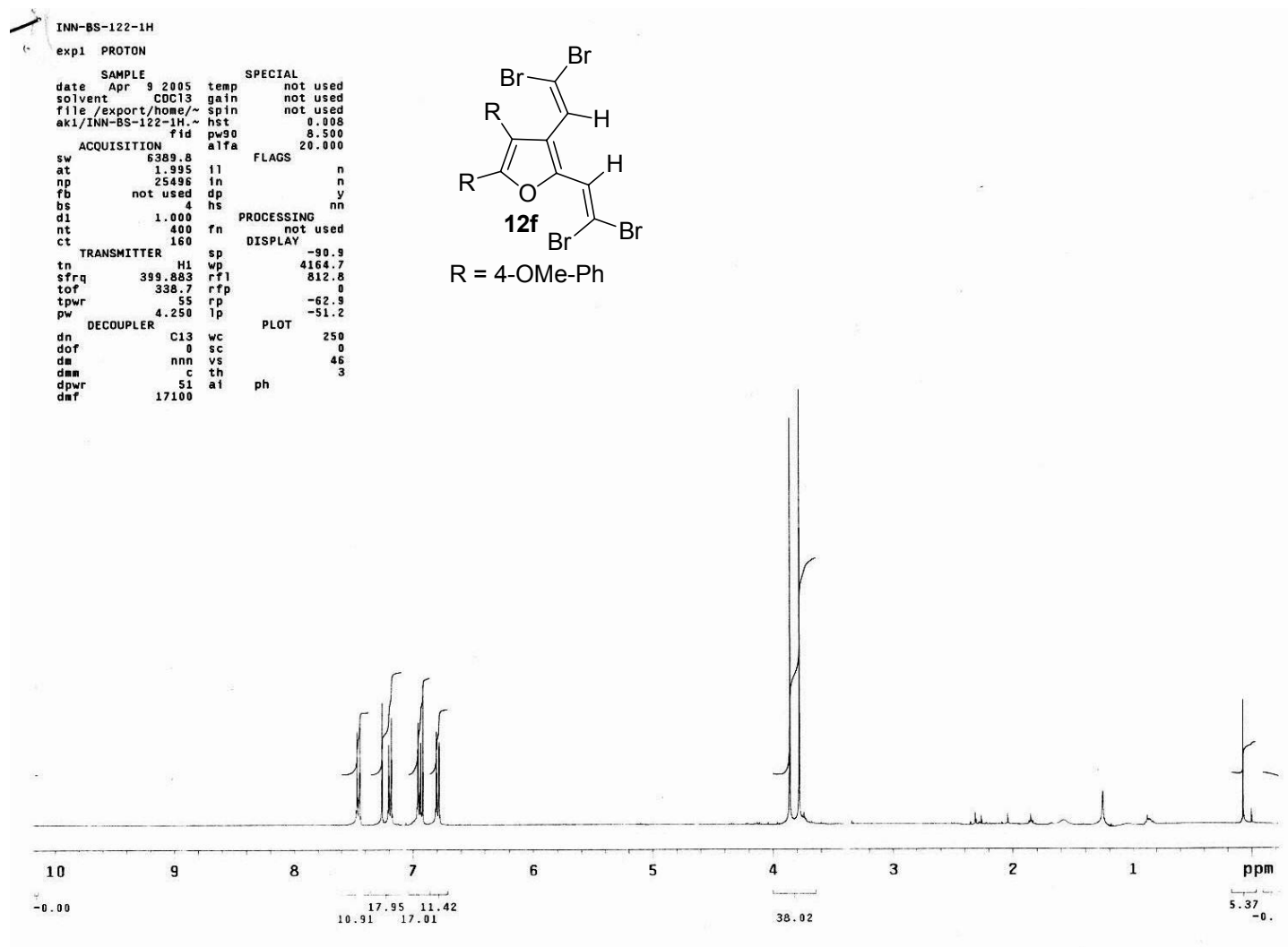
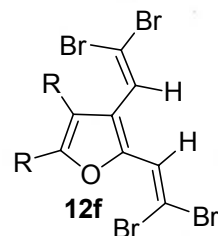


Figure S13. ^1H NMR spectrum (CDCl_3) of 2,3-bis(2,2-dibromovinyl)-4,5-bis(4-methoxyphenyl)furan (**12f**)

```

INN-BS-122-13C
exp5, CARBON
SAMPLE
date Apr 9 2005 temp not used
solvent CDCl3 gain not used
file /export/home/~ spin not used
ak1/INN-BS-122-13C~ hst 0.008
.fid pw90 14.000
ACQUISITION alfa 20.000
sw 25125.6
at 1.199 il
np 60270 in
fb 13800 dp
bs 4 hs
dl 1.000
nt 5000 lb
ct 2568 fn
PROCESSING
tn C13 sp
sfrq 100.561 wp
tof 1554.3 rfl
tpwr 56 rfp
pw 7.000 rp
DECOUPLER lp
dn H1
dof 0 wc
dm yyy sc
dmm w vs
dpwr 41 th
dmf 11900 ai no ph
PLOT
-69.8
20172.9
9248.3
7742.3
45.7
-344.1
250
0
178
3

```



R = 4-Me-Ph

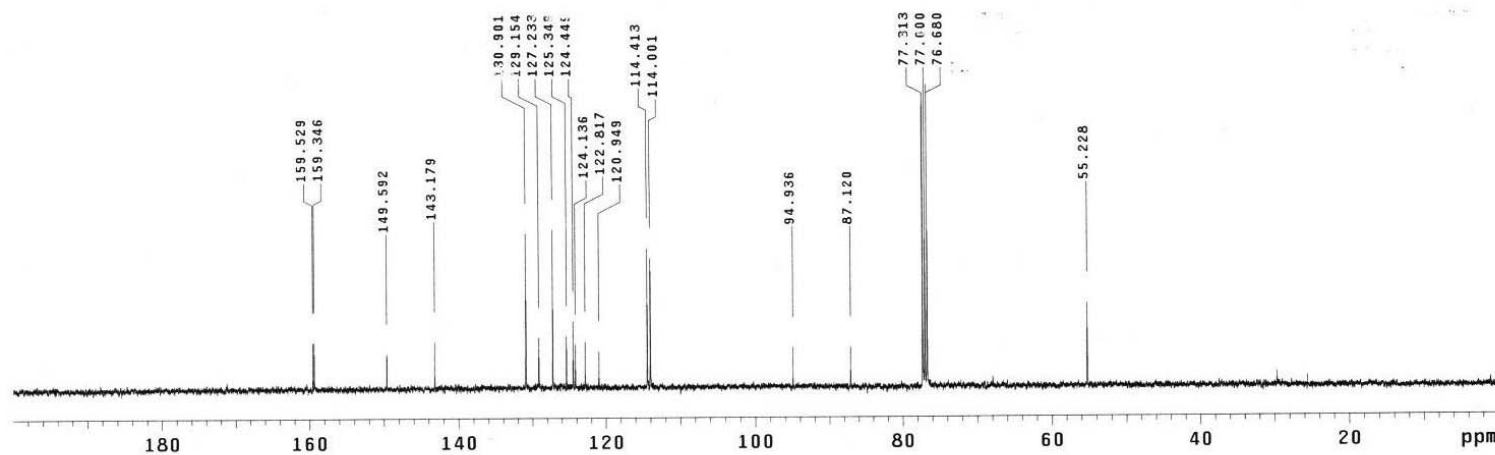


Figure S14. ^{13}C NMR spectrum (CDCl_3) of 2,3-bis(2,2-dibromovinyl)-4,5-bis(4-methoxyphenyl)furan (**12f**)

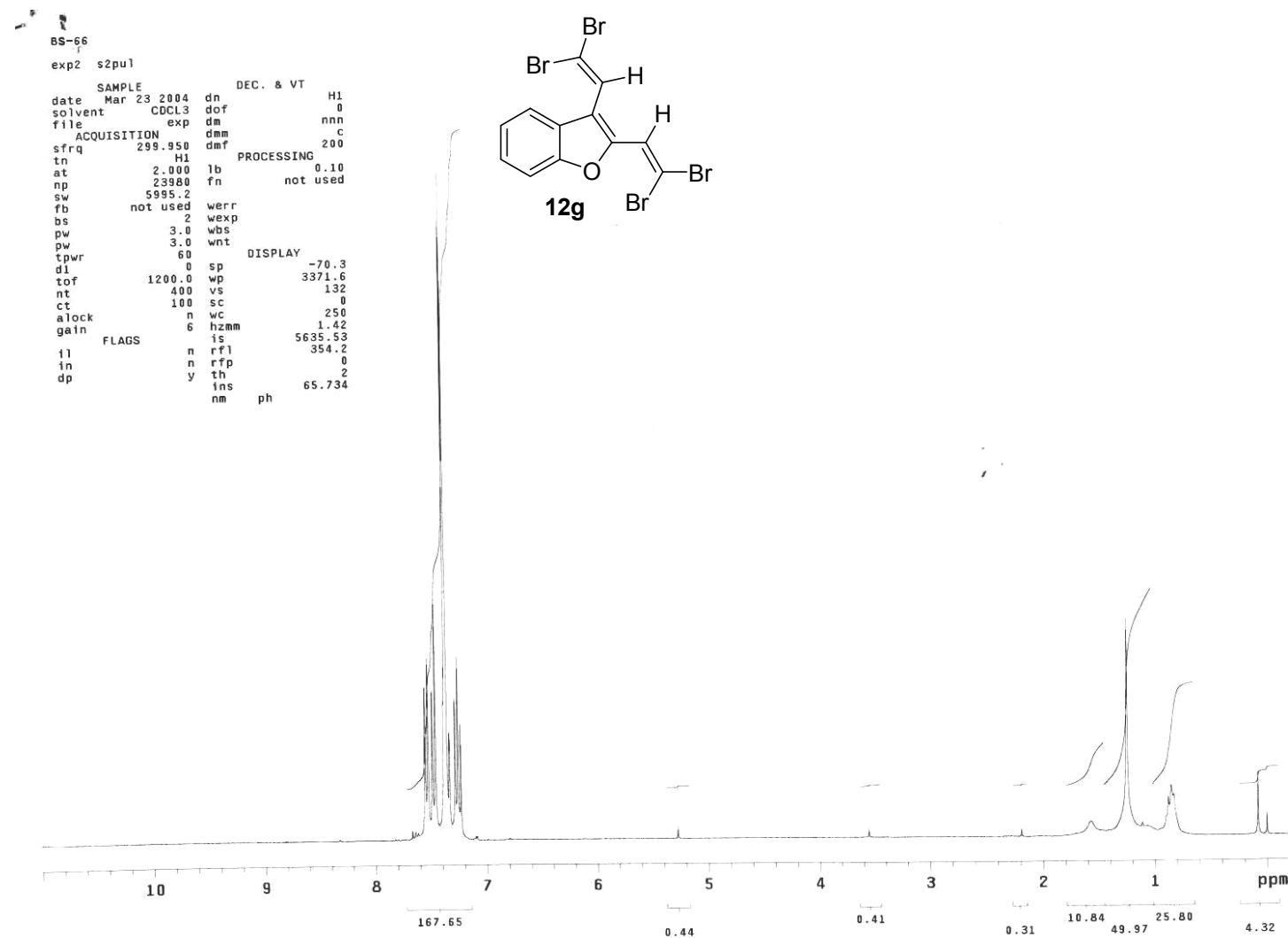


Figure S15. ^1H NMR spectrum (CDCl_3) of 2,3-bis(2,2-dibromovinyl)benzofuran (**12g**)

BS-66

expl s2pu1

SAMPLE		SPECIAL	
date	Mar 23 2004	temp	not used
solvent	CDCl3	gain	10
file	/export/home/~	spin	not used
vnar1	2004/March-2~	hst	0.008
004/23Mar/BS-66-C1~		pw90	9.500
	3.fid	alfa	20.000
ACQUISITION		FLAGS	
sw	25000.0	f1	n
at	1.280	fn	n
np	64000	dp	y
fb	13800	hs	nn
bs	4	PROCESSING	
d1	3.000	lb	1.00
nt	3200	fn	not used
ct	204	DISPLAY	
TRANSMITTER		sp	-47.4
tn	C13	wp	15143.6
sfrq	75.430	rfl	10034.9
tof	748.9	rpf	5815.0
tpwr	59	rp	-151.0
pw	4.750	lp	-315.9
DECOUPLER		PLOT	
dn	H1	wc	250
dof	0	sc	0
dm	yyy	vs	48
dmm	w	th	8
dpwr	39	nm	ph
dmf	10900		

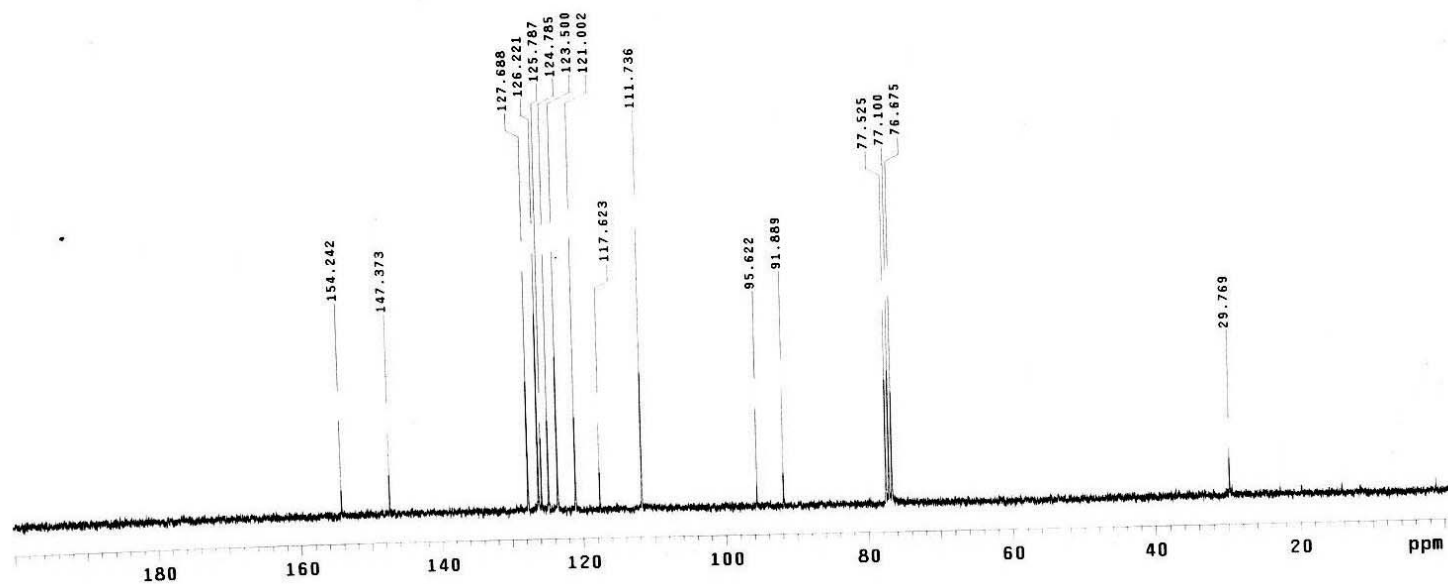
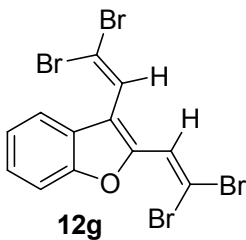


Figure S16. ^{13}C NMR spectrum (CDCl_3) of 2,3-bis(2,2-dibromovinyl)benzofuran (**12g**)

BS-67

exp1 s2pul

SAMPLE
date Mar 23 2004 temp not used
solvent CDCl3 gain 10
file /export/home/~ spin not used
vnmr1/2004/March-2~ hst 0.008
004/23Mar/BS-67-Cl~ pw90 9.500
3.fid alfa 20.000

ACQUISITION
sw 25000.0 f1 n
at 1.200 in n
np 64000 dp y
fb 13800 hs nn
bs 4
dl 3.000 lb PROCESSING 1.00
nt 3200 fn not used
ct 100 DISPLAY 15.9

TRANSMITTER
tn C13 wp 13550.6
sfrq 75.430 rfi 10036.9
tof 748.9 rfp 5815.9
tpwr 59 fp -116.8
pw 4.750 tp -395.1

DECOUPLER
dn H1 wc PLOT 250
dof 0 sc 0
dm yyy vs 56
dmm w th 7
dpwr 39 nm ph
dof 10900

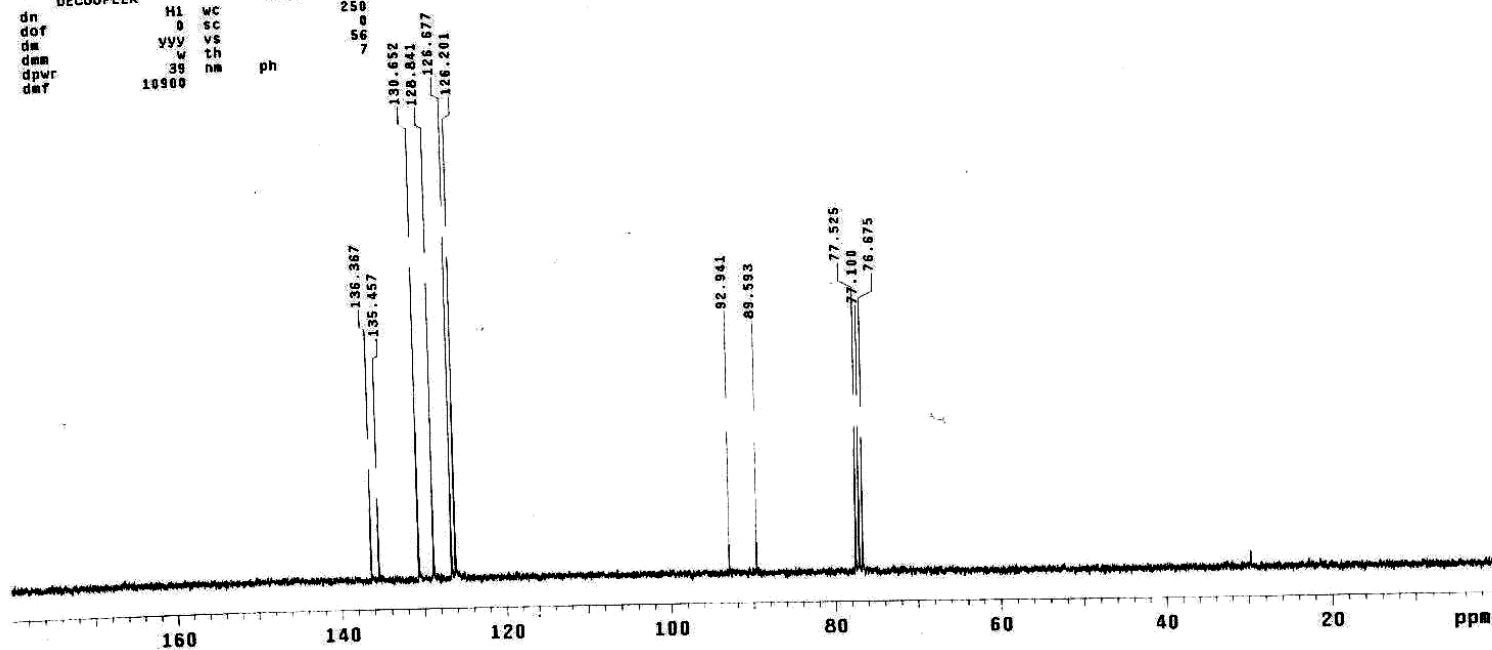
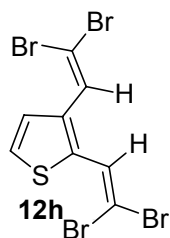


Figure S18. ^{13}C NMR spectrum (CDCl_3) of 2,3-bis(2,2-dibromovinyl)thiophene (12h)

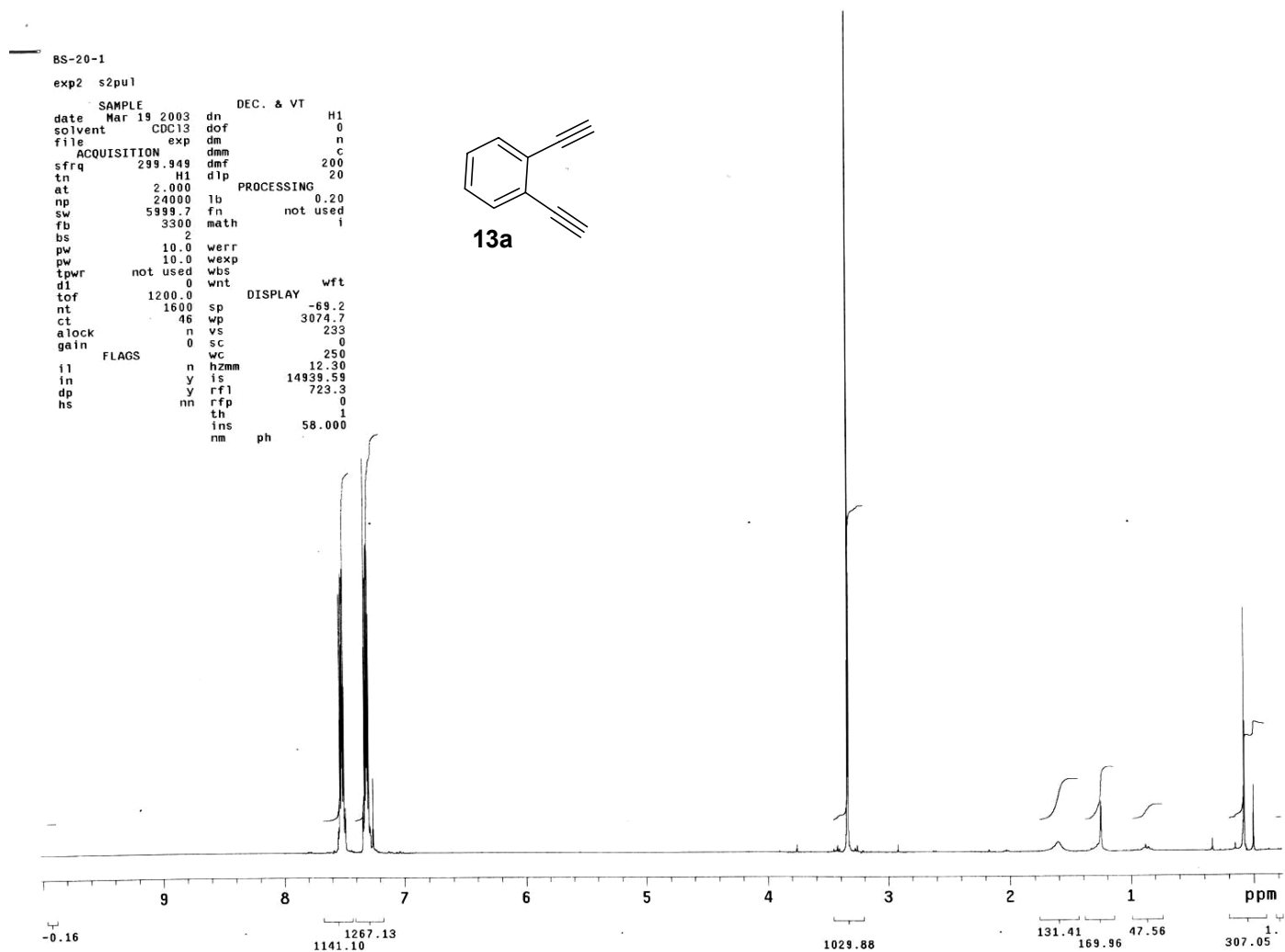


Figure S19. ^1H NMR spectrum (CDCl_3) of 1,2-diethynylbenzene (**13a**)

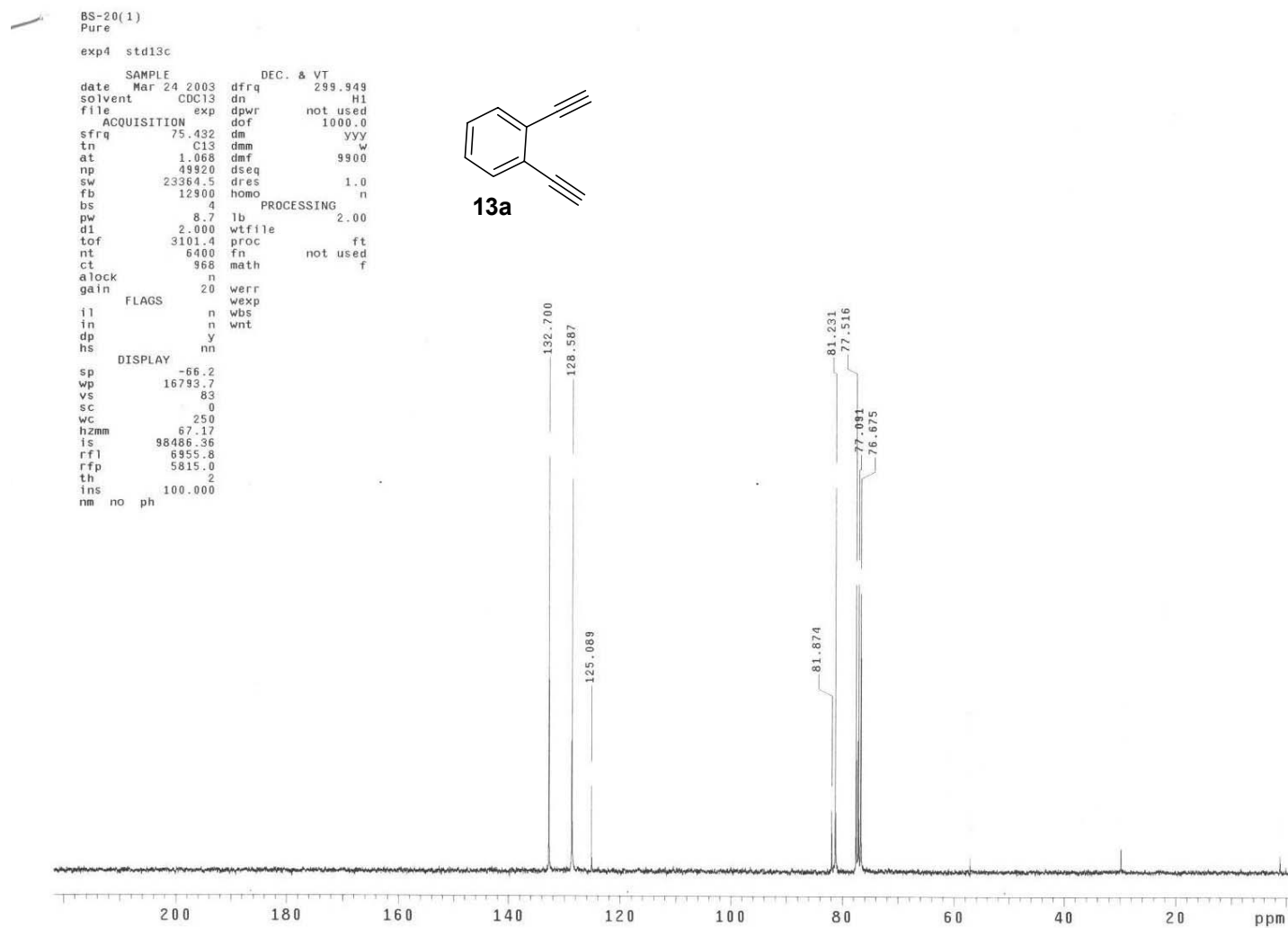


Figure S20. ^{13}C NMR spectrum (CDCl_3) of 1,2diethynylbenzene (**13a**)

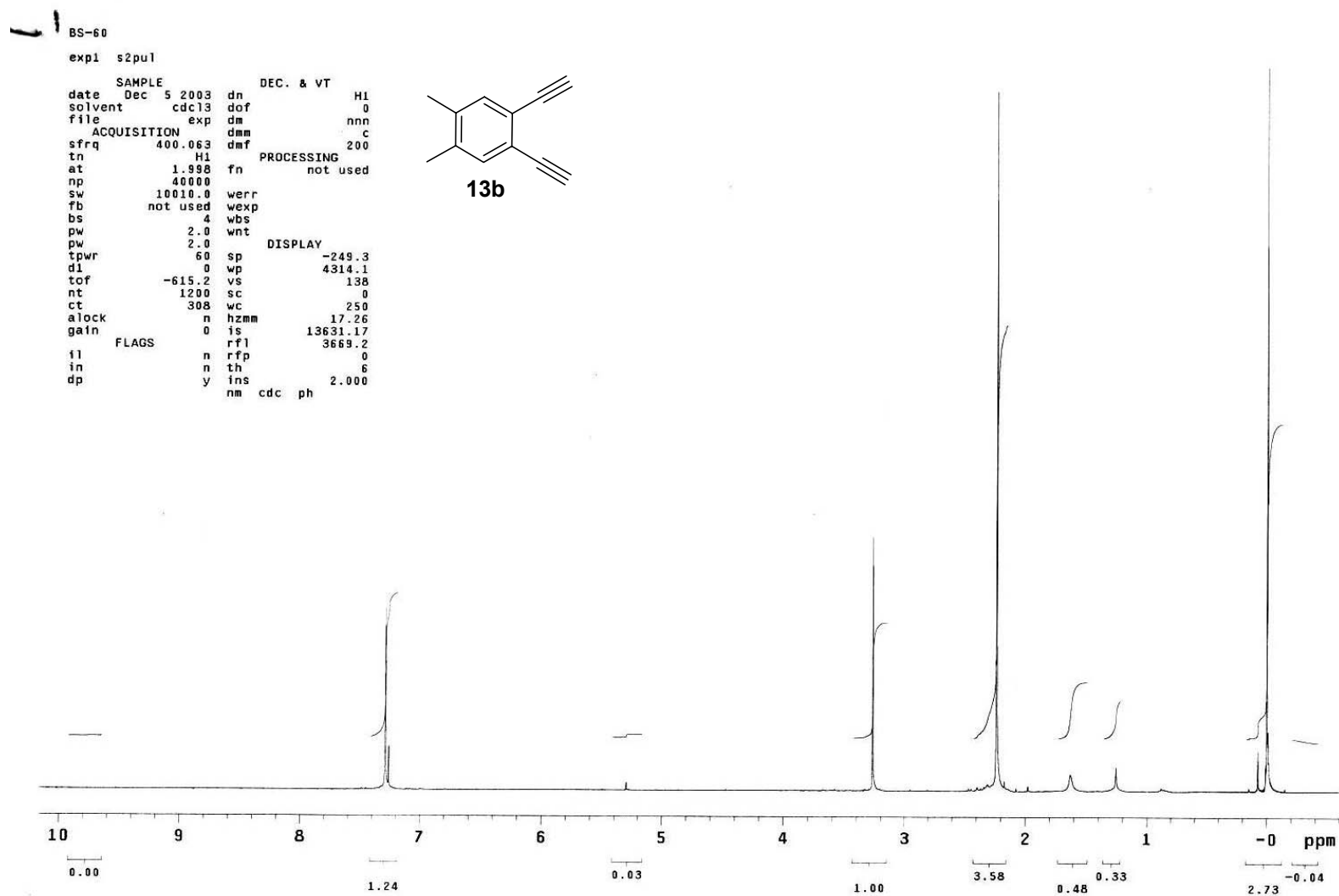


Figure S21. ^1H NMR spectrum (CDCl_3) of 1,2-diethynyl-4,5-dimethylbenzene (**13b**)

```

BS-60-c13
exp1 s2pu1
SAMPLE
date Dec 5 2003 temp not used
solvent CDC13 gain not used
file exp spin not used
ACQUISITION hst 0.008
sw 25125.6 pw90 14.000
at 1.199 alfa 20.000
np 60270
fb 13800
bs 4 in n
dl 2.000 dp y
nt 1600 hs nn
ct 464
TRANSMITTER lb 3.50
tn C13 fn not used
sfrq 100.607 DISPLAY
tof 1558.7 sp -1502.3
tpwr 56 wp 25125.6
pw 7.000 rfl 9268.3
DECOUPLER H1 rfp 7766.0
dn 0 rp 74.5
dof 0 lp -303.5
dm yyy PLOT
dmm w wc 250
dpwr 41 sc 0
dmf 11900 vs 149
th 6
al no ph

```

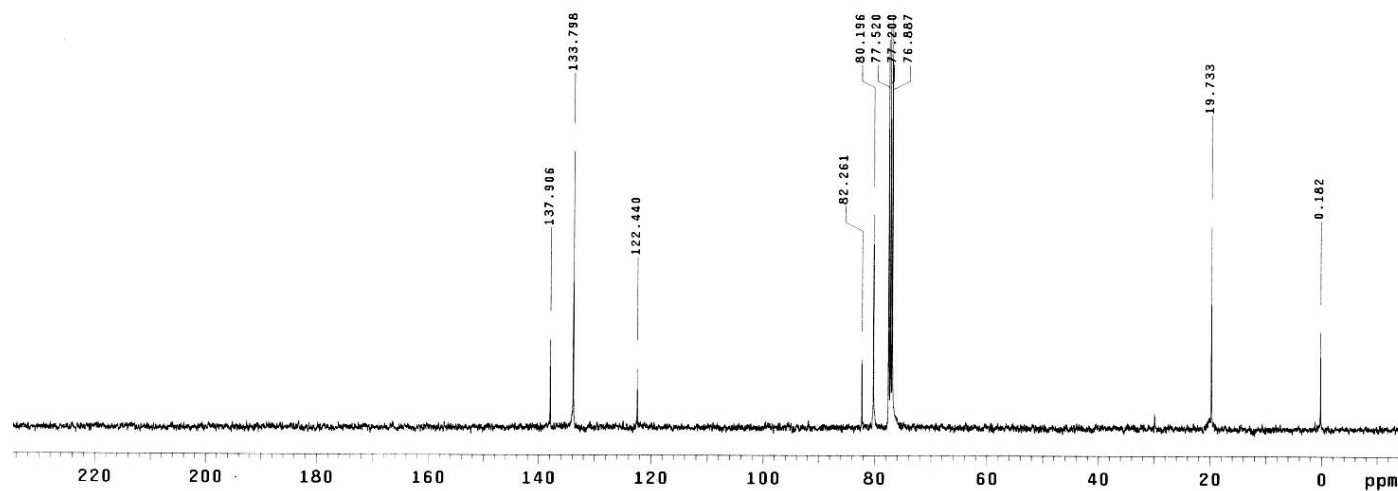
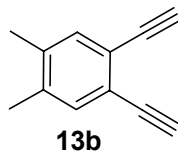


Figure S22. ^{13}C NMR spectrum (CDCl_3) of 1,2-diethynyl-4,5-dimethylbenzene (**13b**)

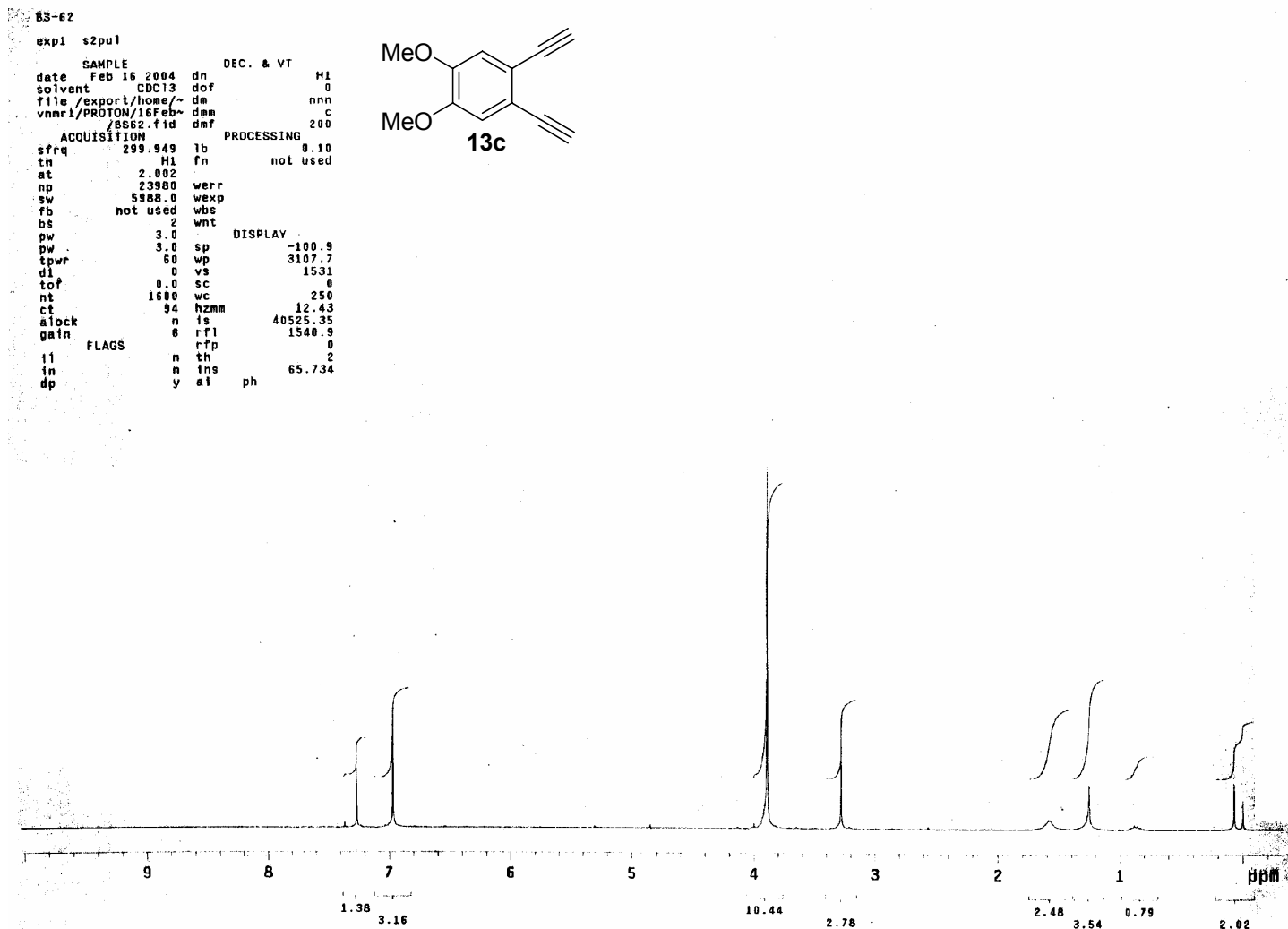


Figure S23. ^1H NMR spectrum (CDCl_3) of 1,2-diethynyl-4,5-dimethoxybenzene (13c)

```

BS-62
exp3 s2pu1

SAMPLE
date Feb 16 2004 temp not used
solvent CDCl3 gain not used
file exp spin not used
ACQUISITION hst 0.008
sw 25000.0 pw90 9.500
at 1.280 alfa 20.000
np 64000
fb 13800
bs 4
dl 3.000 dp y
nt 3200 hs nn
ct 500

TRANSMITTER
tn C13 fb 1.00
sfrq 75.430 fn not used
tof 748.9 sp -75.6
tpwr 59 wp 15242.0
pw 4.750 rfl 10030.4
DECOUPLER H1 rfp 5815.0
dn 0 rp -133.6
dof 0 lp -342.2
dm yvy wc 250
dmm w sc 0
dpwr 39 vs 96
dmf 10900 th 5
nm ph

```

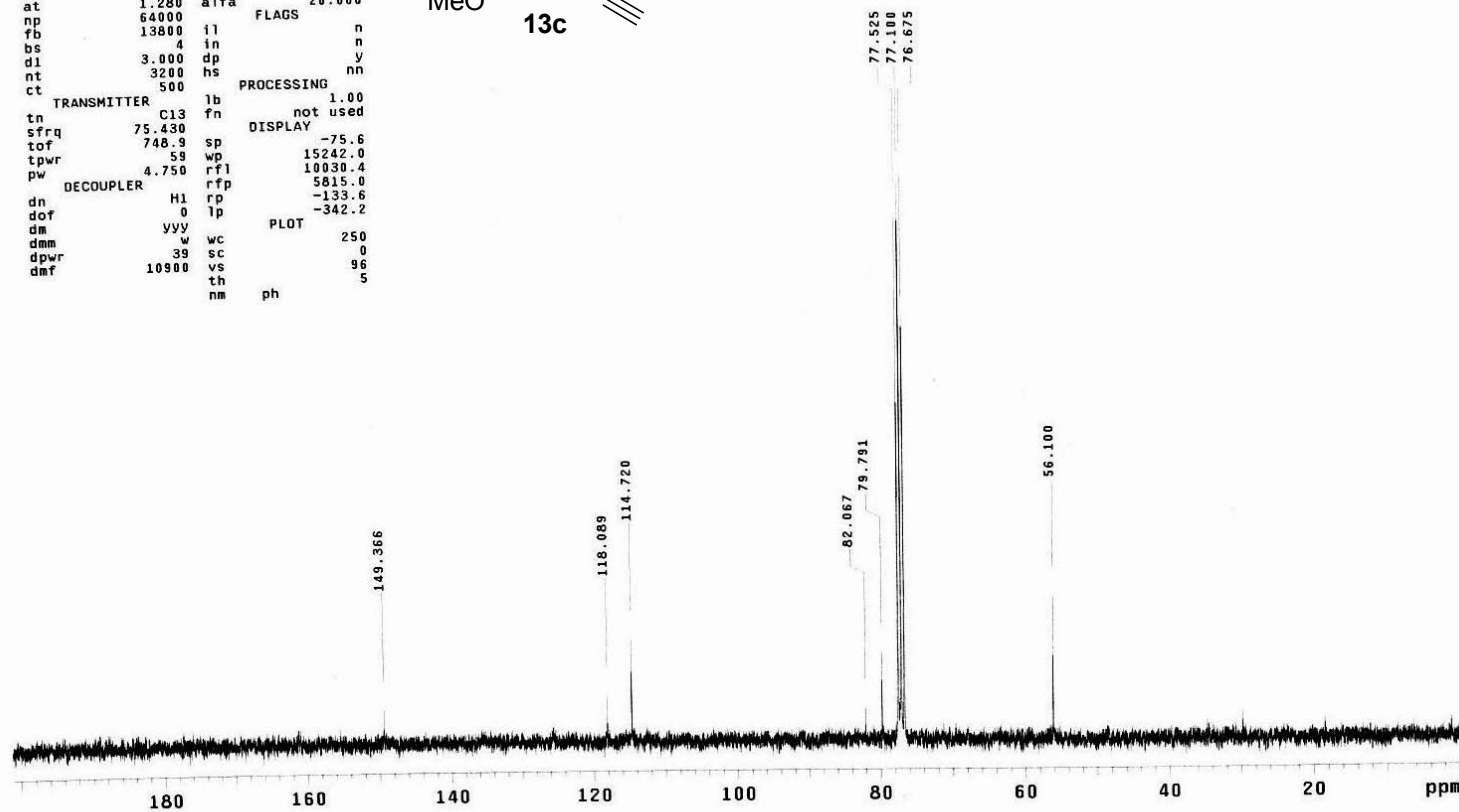
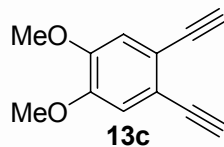


Figure S24. ^{13}C NMR spectrum (CDCl_3) of 1,2-diethynyl-4,5-dimethoxybenzene (**13c**)

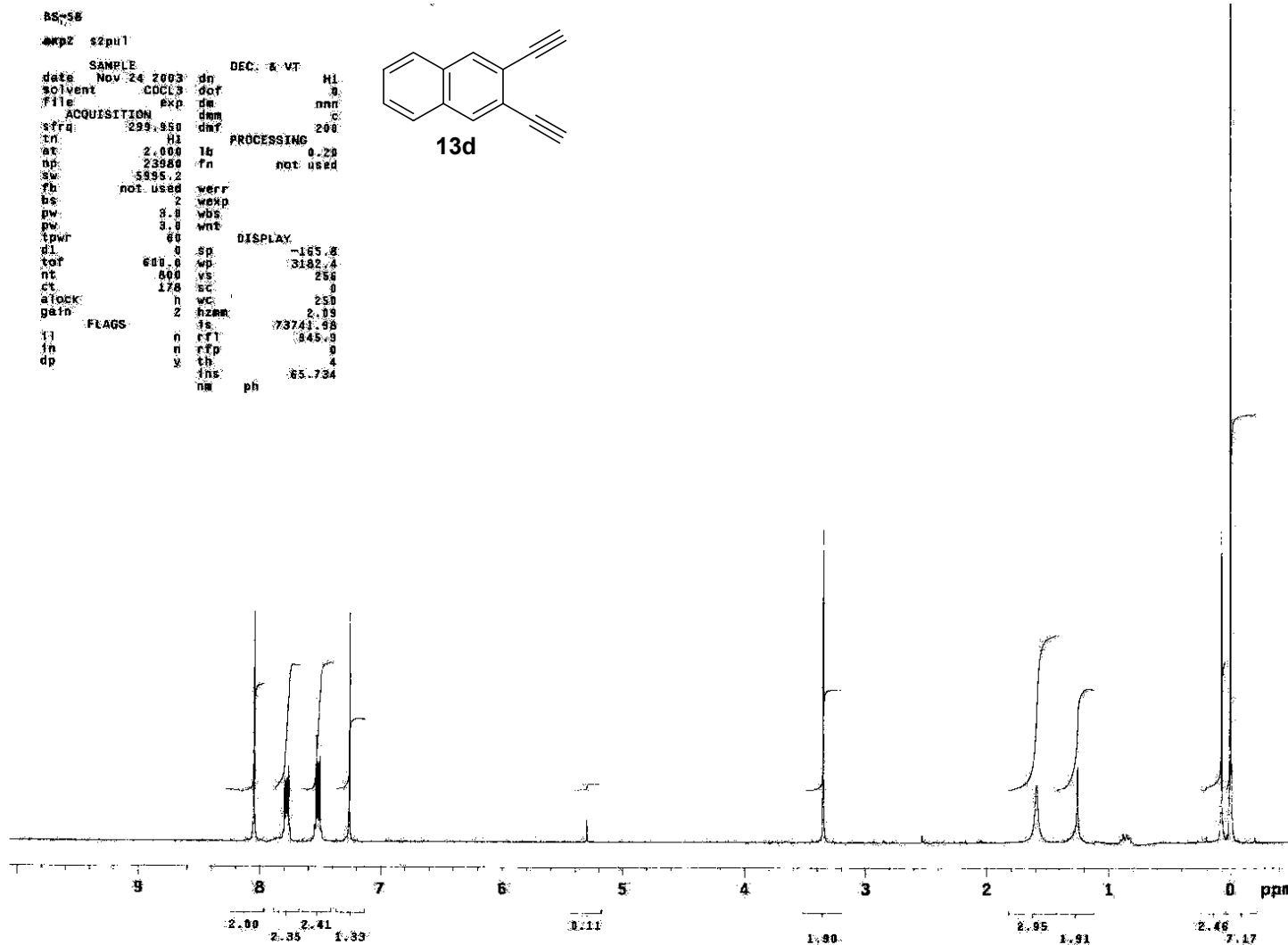


Figure S25. ^1H NMR spectrum (CDCl_3) of 2,3-diethynynaphthalene (**13d**)

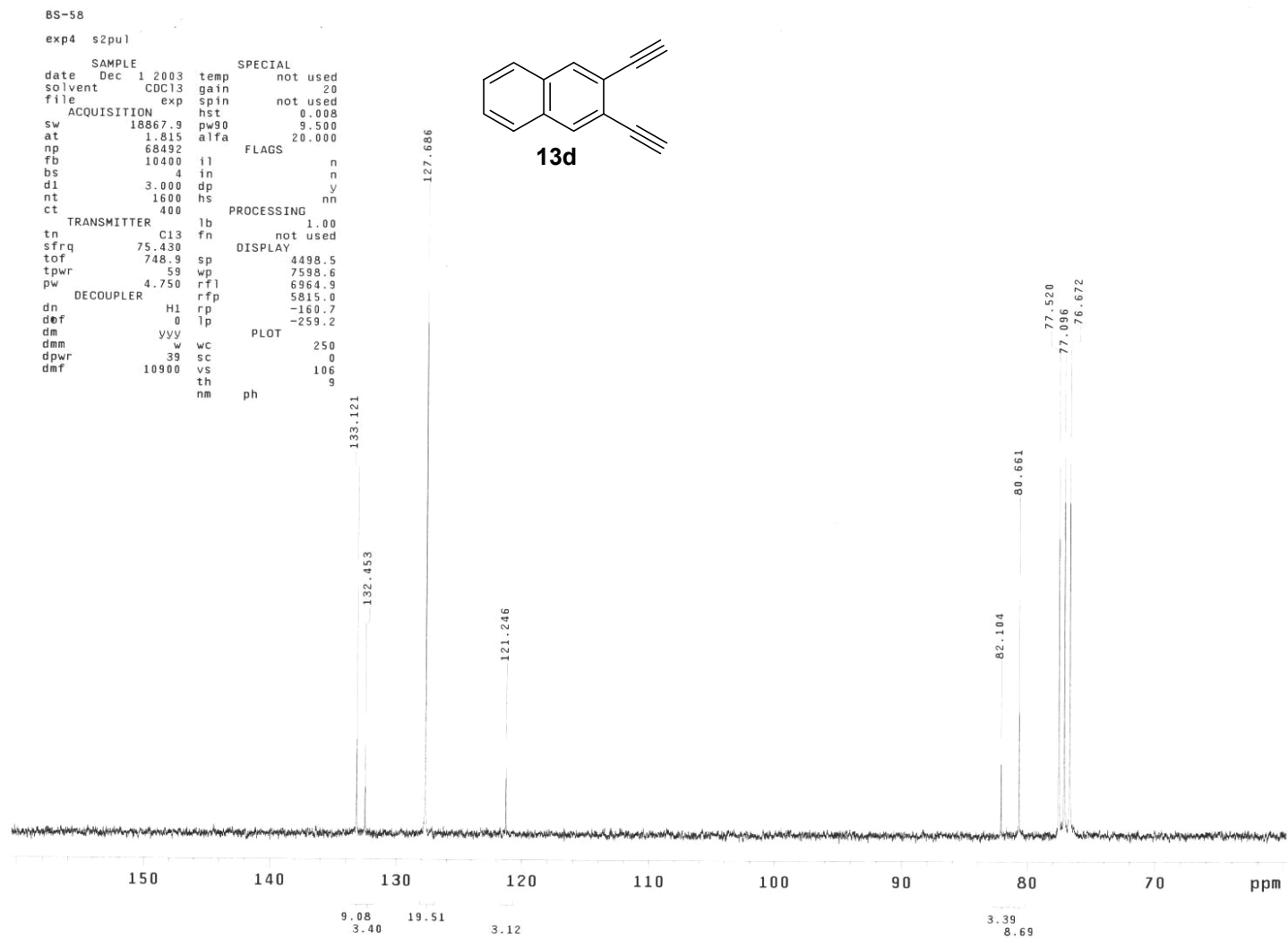


Figure S26. ¹³C NMR spectrum (CDCl₃) of 2,3-diethynynaphthalene (**13d**)

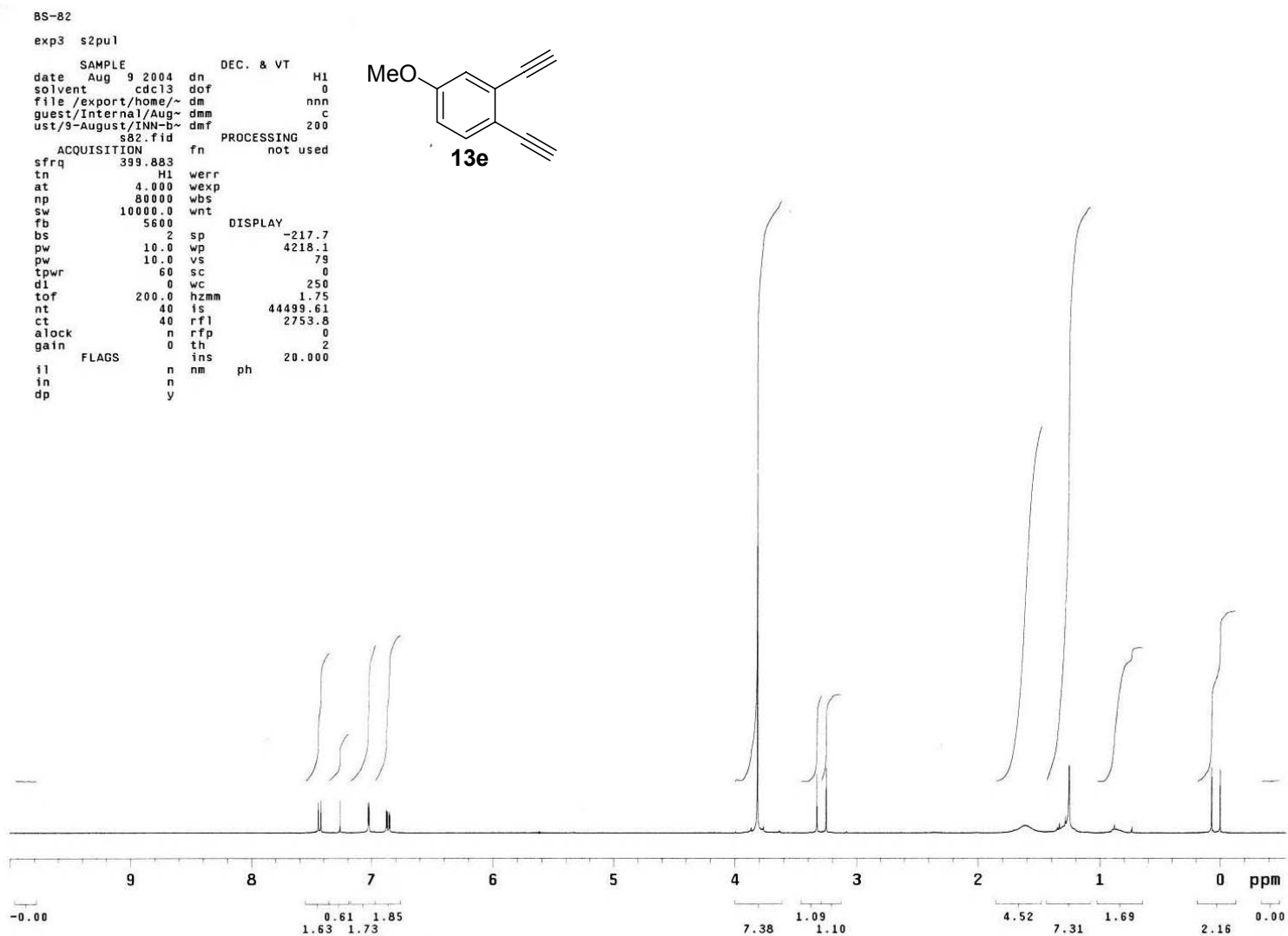


Figure S27. ^1H NMR spectrum (CDCl_3) of 1,2-diethynyl-4-methoxybenzene (**13e**)

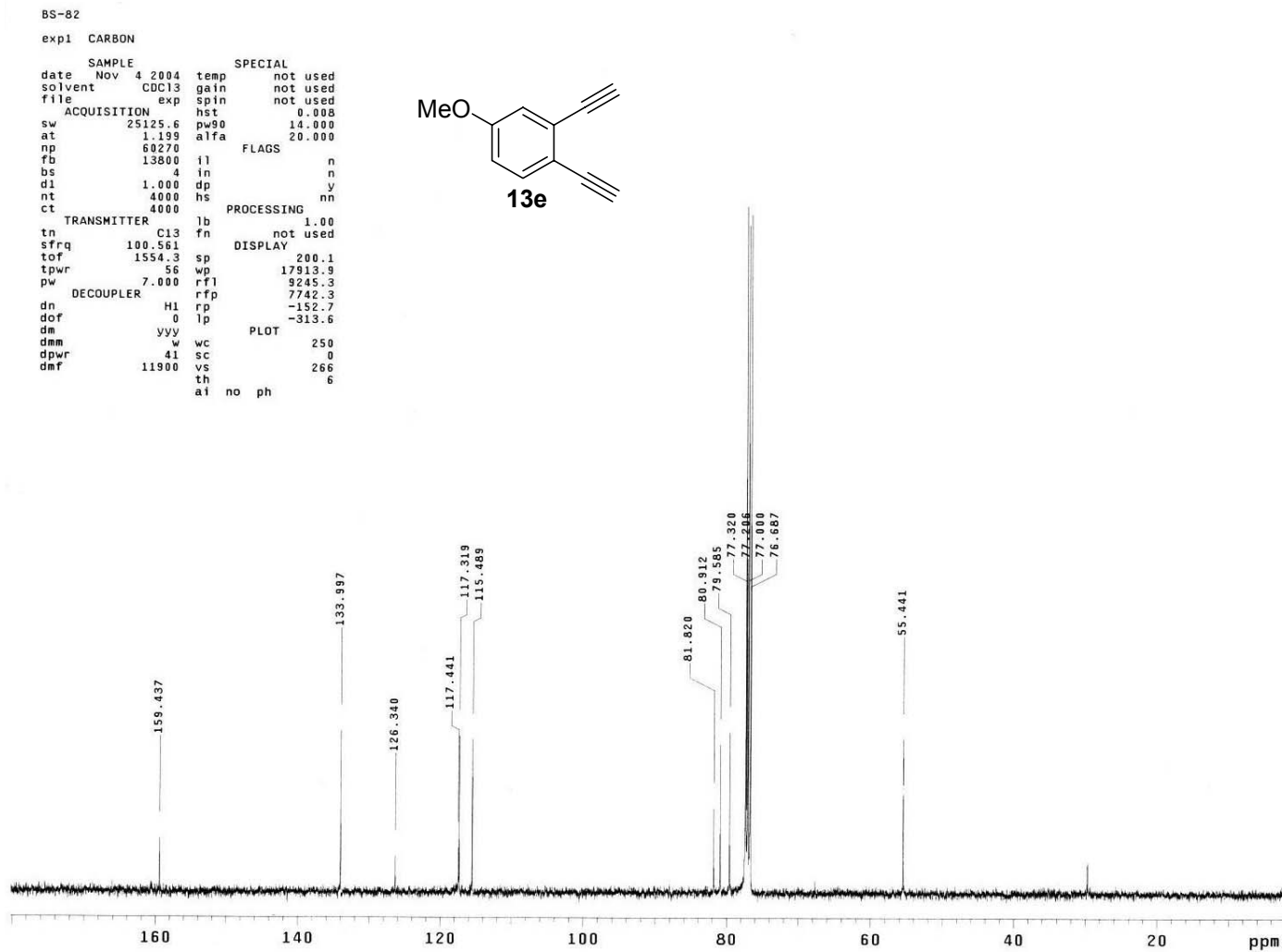
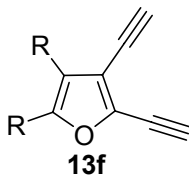


Figure S28. ¹³C NMR spectrum (CDCl₃) of 1,2-diethynyl-4-methoxybenzene (13e)

BS-125

exp4 PROTON

SAMPLE		SPECIAL	
date	Apr 11 2006	temp	not used
solvent	CDCl3	gain	not used
file	/export/home/~	spin	not used
inn3/2006/apr/11/11~	hst	0.008	
th/BS-125-1H.fid	pw90	8.500	
ACQUISITION	alfa	20.000	
sw	10010.0	FLAGS	n
at	1.990	fl	n
np	39846	in	n
fb	not used	dp	y
bs	4	hs	nn
d1	1.000	PROCESSING	
nt	400	lb	0.10
ct	0	fn	not used
TRANSMITTER		DISPLAY	
tn	H1	sp	-17.1
sfrq	399.883	wp	3215.6
tof	338.7	rfl	2647.7
tpwr	55	rfp	0
pw	2.000	rp	101.3
DECOUPLER		lp	-144.4
dn	C13	PLOT	
dof	338.7	wc	250
dm	nnn	sc	0
dma	c	vs	40
dpwr	51	th	8
dmf	17100	ai	ph



R = 4-OMe-Ph

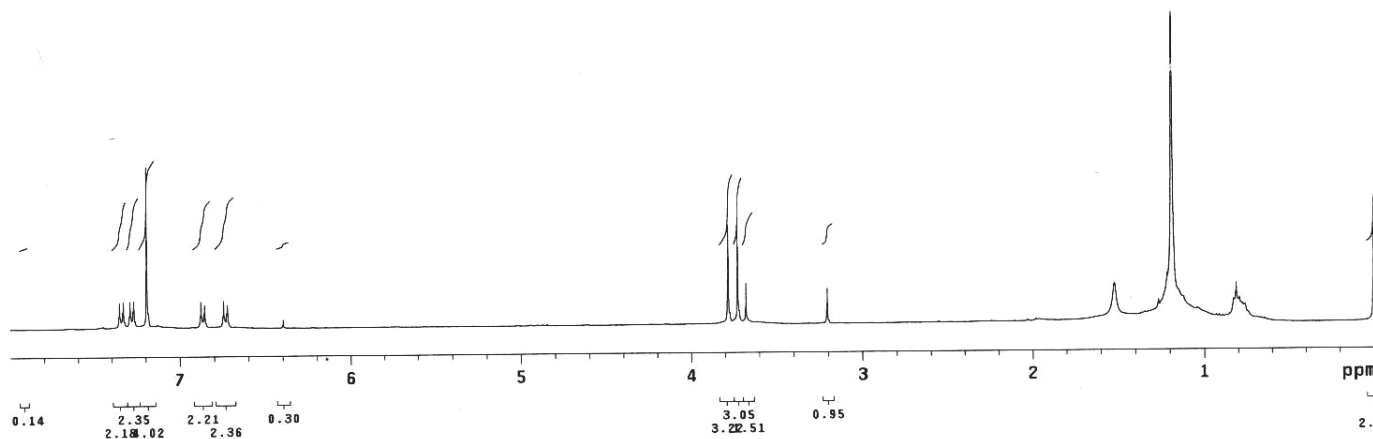


Figure S29. ^1H NMR spectrum (CDCl_3) of 2,3-diethynyl-4,5-bis(4-methoxyphenyl)furan (**13f**)

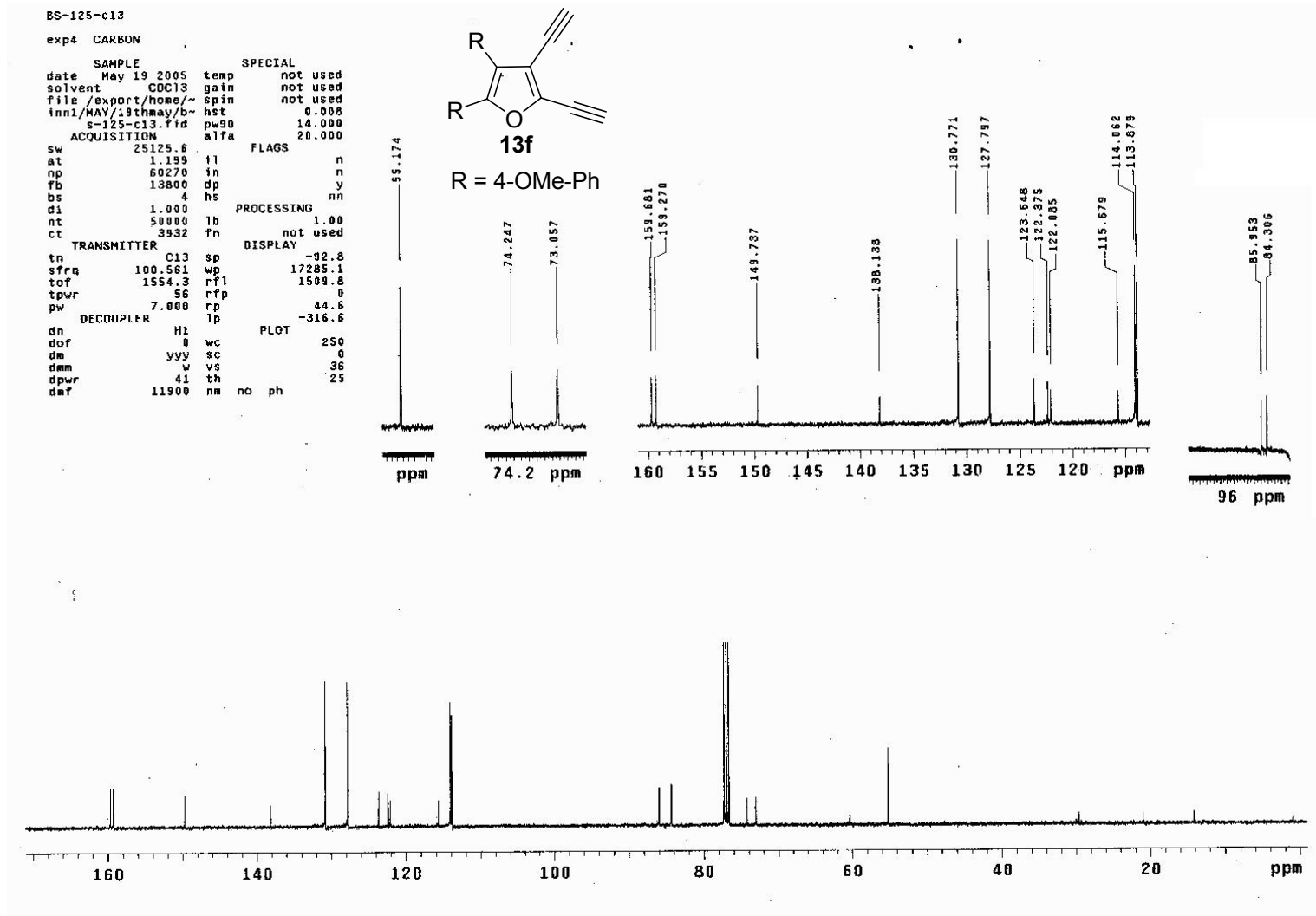


Figure S30. ^{13}C NMR spectrum (CDCl_3) of 2,3-diethynyl-4,5-bis(4-methoxyphenyl)furan (**13f**)

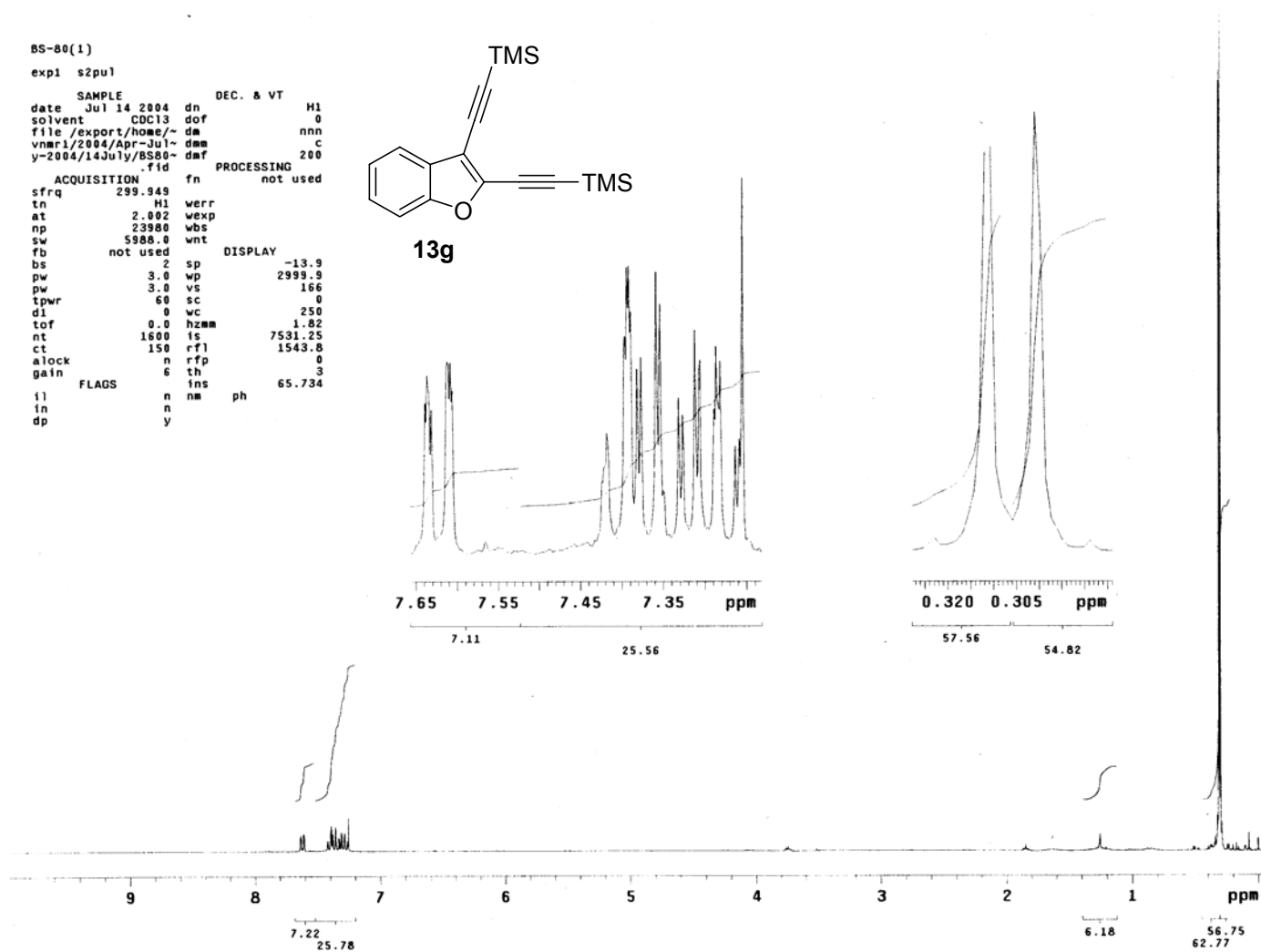


Figure S31. ^1H NMR spectrum (CDCl_3) of 2,3-bis(2-(trimethylsilyl)ethynyl)benzofuran (**13g**)

BS-80(1)

expl s2pul

SAMPLE		SPECIAL	
date	Jul 14 2004	temp	not used
solvent	CDCL3	gain	10
file	/export/home/~	spin	not used
nmr1	2004/Apr~Jul~	hst	0.008
y-2004/14Jul	BS-8~	pw90	9.500
q-C13.fid	alfa	20.000	

ACQUISITION		FLAGS	
sw	25000.0	il	n
at	0.600	in	n
np	30000	dp	y
fb	13800	hs	nn
bs	4		
dl	3.000	lb	4.00
nt	3200	fn	not used
ct	524	DISPLAY	-436.5

TRANSMITTER		PLOT	
tn	C13	sp	250
sfrq	75.430	wp	0
tof	748.9	rfl	134
tpwr	59	rfp	5
pw	4.750	rp	
		lp	

DECOUPLER		PLOT	
dn	H1	wc	250
dof	0	sc	0
dm	yv	vs	134
dmm	w	th	5
dpwr	39	nm	
dmf	10900	cdc	ph

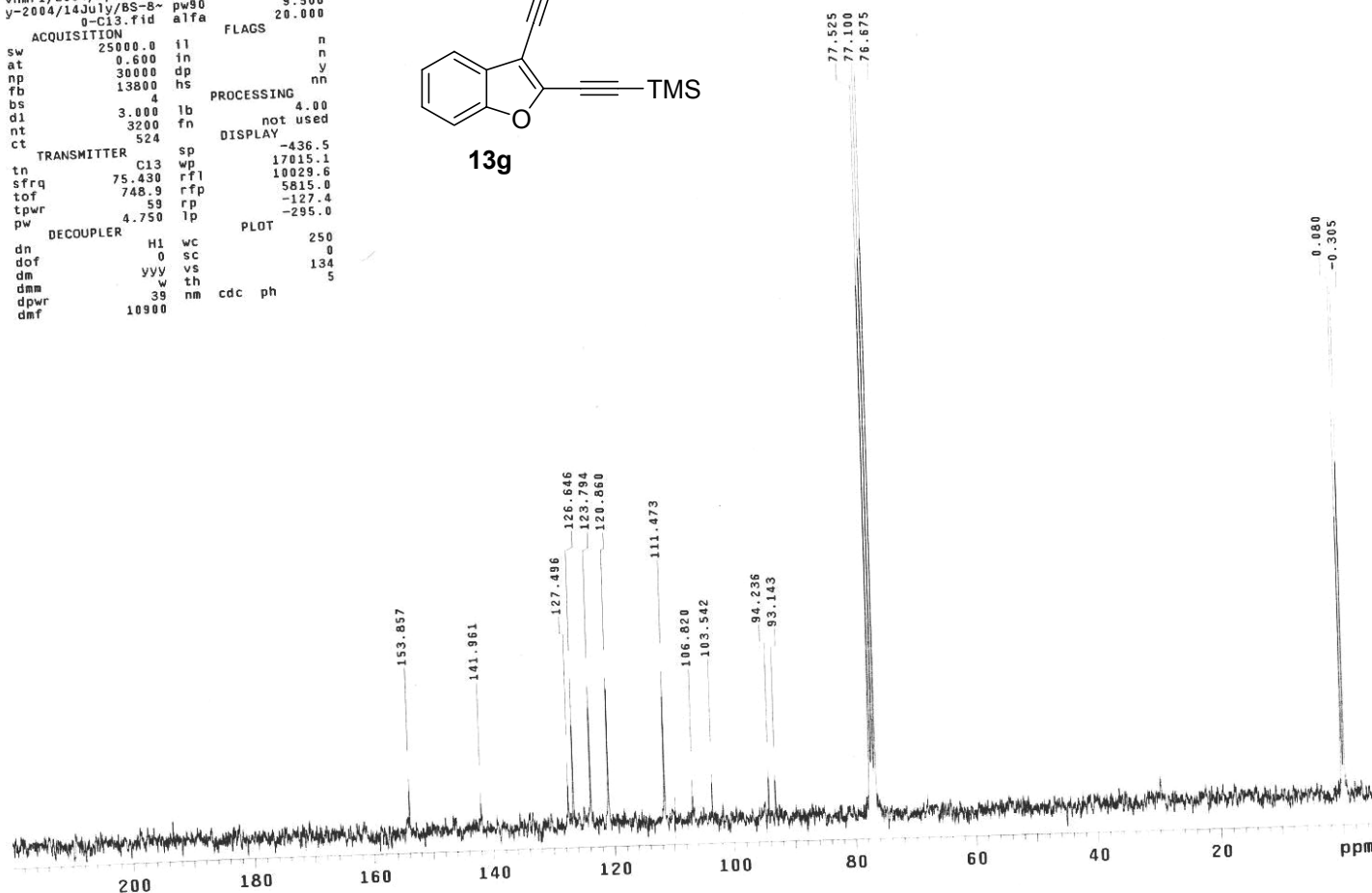
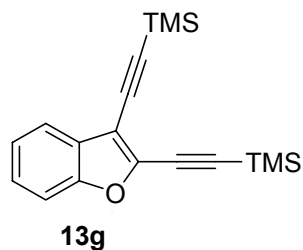


Figure S32. ¹³C NMR spectrum (CDCl₃) of 2,3-bis(2-(trimethylsilyl)ethynyl)benzofuran (**13g**)

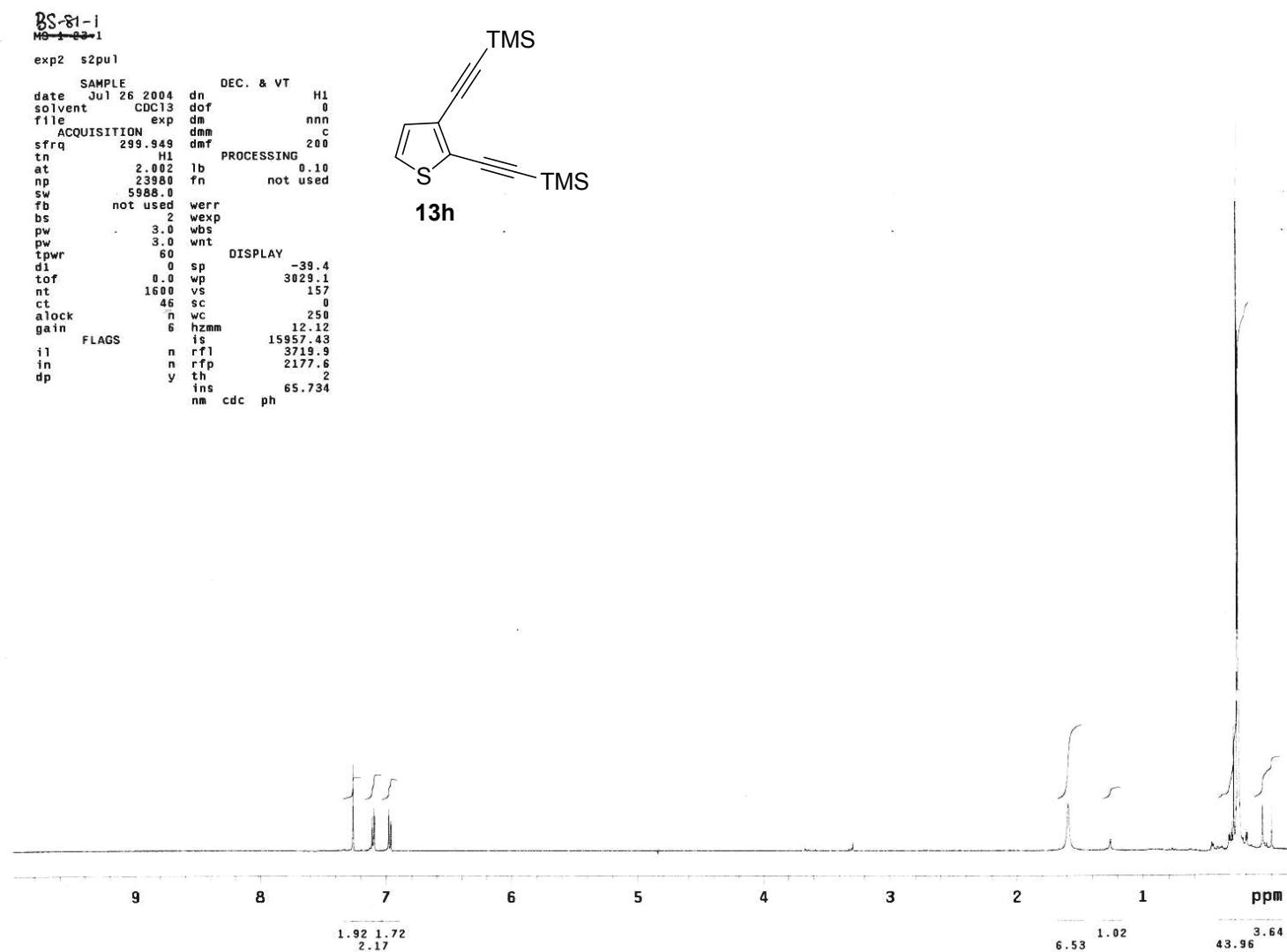


Figure S33. ^1H NMR spectrum (CDCl_3) of 2,3-bis(2-(trimethylsilyl)ethynyl)thiophene (**13h**)

```

BS-81
exp4 CARBON
SAMPLE
date Nov 12 2004 temp not used
solvent CDCl3 gain not used
file /export/home/~ spin not used
inn1/12thNov/BS-81~ hst 0.008
.fid pw90 14.000
ACQUISITION alfa 20.000
sw 25125.6
at 1.199 il FLAGS n
np 60270 in n
fb 13800 dp y
bs 4 hs nn
dl 1.000
nt 1800 lb PROCESSING 1.00
ct 564 fn not used
TRANSMITTER C13 sp DISPLAY -157.2
sfrq 100.561 wp 13652.0
tof 1554.3 rfl 9250.6
tpwr 56 rfp 7742.3
pw 7.000 rp -155.3
DECOUPLER H1 lp -300.7
dn H1 PLOT
dof 0 wc 250
dm yyy sc 0
dmm w vs 103
dpwr 41 th
dmf 11900 ai no ph 5

```

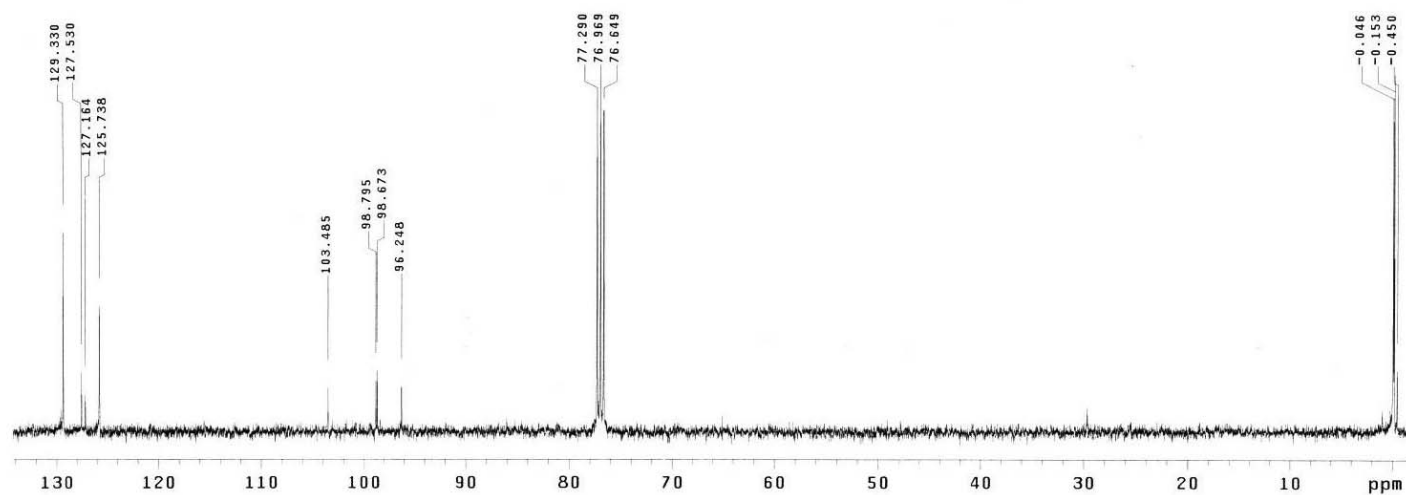
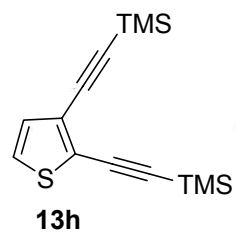


Figure S34. ¹³C NMR spectrum (CDCl₃) of 2,3-bis(2-(trimethylsilyl)ethynyl)thiophene (**13h**)

RM-123

exp2 PROTON

SAMPLE		SPECIAL	
date	Jun 6 2006	temp	not used
solvent	CDCl3	gain	not used
file	/export/home/~	spin	not used
inn3/2006/JUNE/6th~		hst	0.008
/RM-123.fid		pw90	8.500
ACQUISITION		alfa	20.000
sw	10010.0	FLAGS	n
at	1.990	il	n
np	39846	in	n
fb	not used	dp	y
bs	4	hs	nn
dl	1.000	PROCESSING	
nt	400	lb	0.10
ct	44	fn	not used
TRANSMITTER		DISPLAY	
tn	H1	sp	-29.3
sfrq	399.883	wp	3643.6
tof	338.7	rfl	2620.5
tpwr	55	rflp	0
pw	2.000	rp	7.8
DECOUPLER		lp	-114.7
dn	C13	PLOT	
dof	338.7	wc	250
dm	nnn	sc	0
dmm	c	vs	13
dpwr	51	th	2
dmf	17100	ai	ph

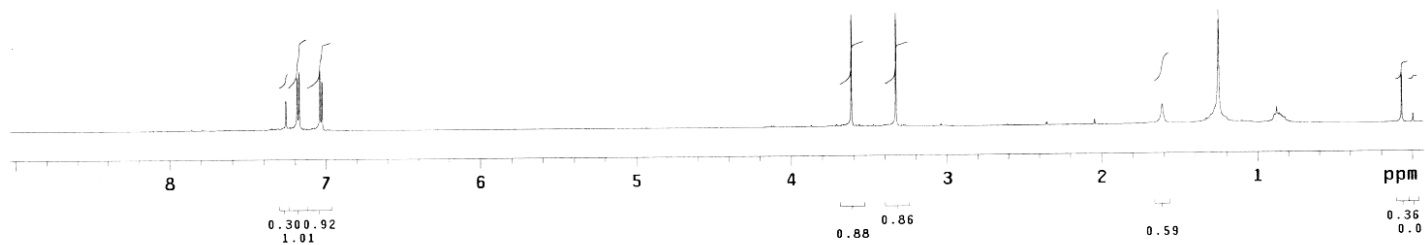
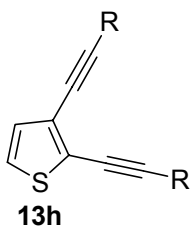


Figure S35. ^1H NMR spectrum (CDCl_3) of 2,3-diethynylthiophene (**13h**, $\text{R} = \text{H}$)

RM-123

exp1 CARBON

SAMPLE		SPECIAL	
date:	Jun 6 2006	temp	not used
solvent	CDCl3	gain	not used
file	/export/home/~	spin	not used
aks2/2006/June/6th	hst	0.008	
RM-123-Cl3.fid	pw90	14.000	
ACQUISITION	aifa	20.000	
sw	25125.6	FLAGS	
at	1.199	il	n
np	60270	in	n
fb	13800	dp	y
bs	4	hs	nn
d1	1.000	PROCESSING	
nt	6000	lb	1.00
ct	6000	fn	not used
TRANSMITTER		DISPLAY	
tn	C13	sp	30.1
sfrq	100.561	wp	16046.0
tof	1554.3	rfl	9250.6
tpwr	56	rtp	7762.5
pw	7.000	rp	111.7
DECOUPLER		lp	-370.4
dn	H1	PLOT	
dof	0	wc	250
dm	yyy	sc	0
dmm	w	vs	72
dpwr	41	th	13
dmt	11900	ai	ph

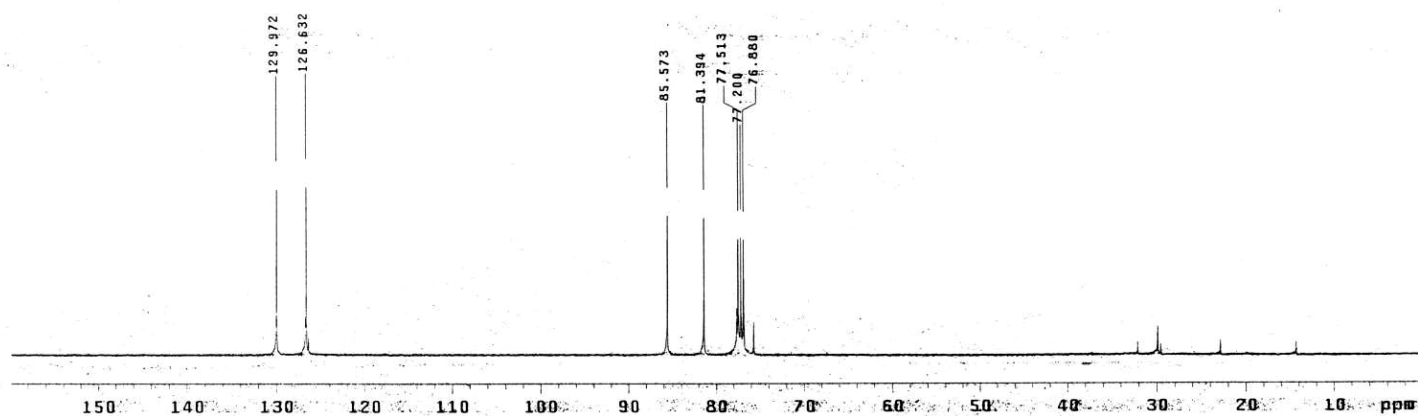
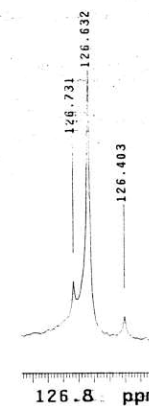
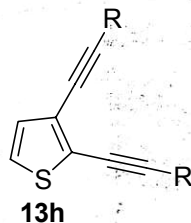


Figure S36. ^{13}C NMR spectrum (CDCl_3) of 2,3-diethynylthiophene (**13h**, R = H)

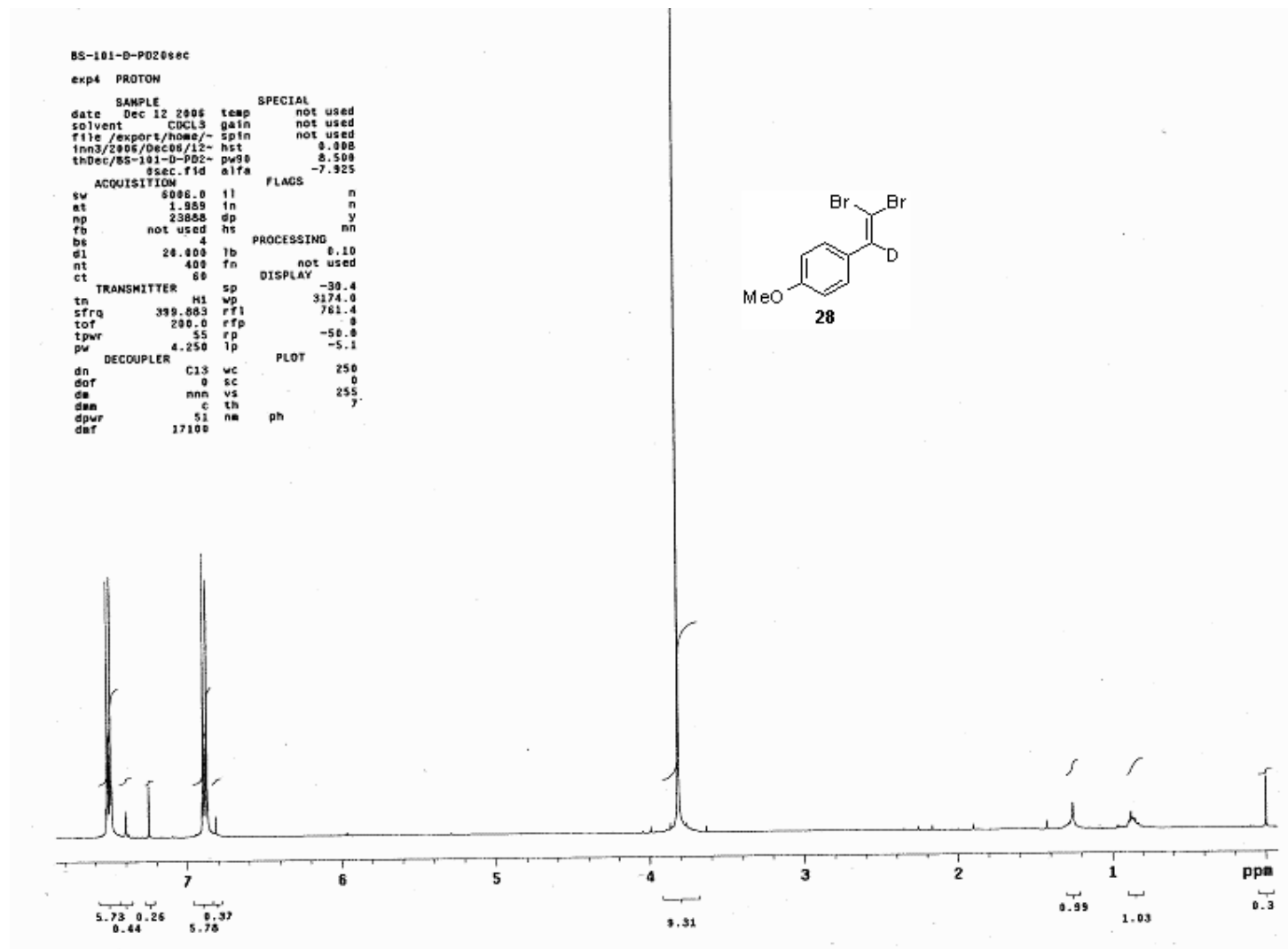


Figure S37a. ^1H NMR spectrum (CDCl_3) of 1-(2,2-dibromovinyl)-4-methoxybenzene-*d* (**28**)

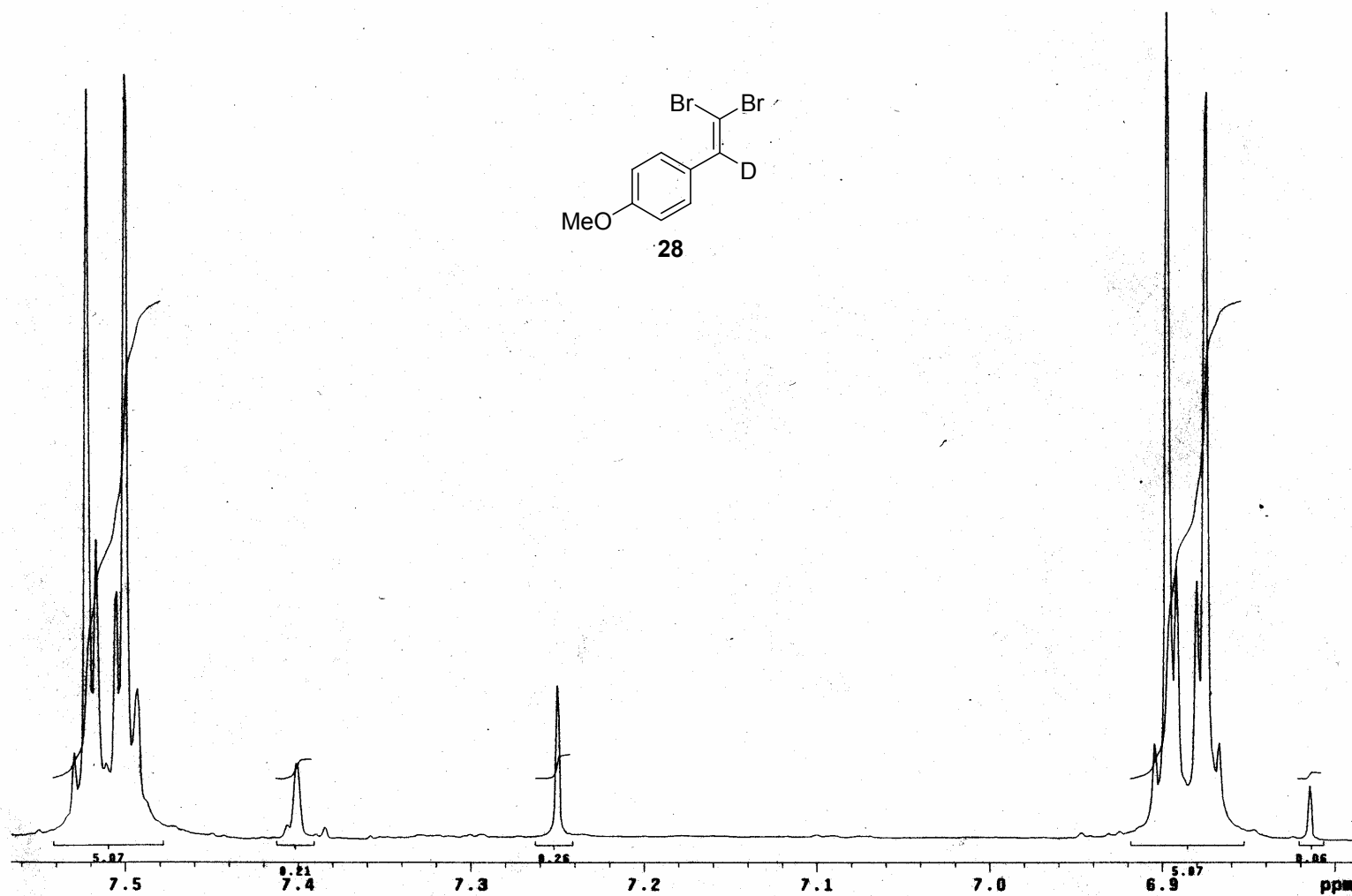


Figure S37b. ¹H NMR (expansion of aromatic region) spectrum (CDCl₃) of 1-(2,2-dibromovinyl)-4-methoxybenzene-*d* (28)

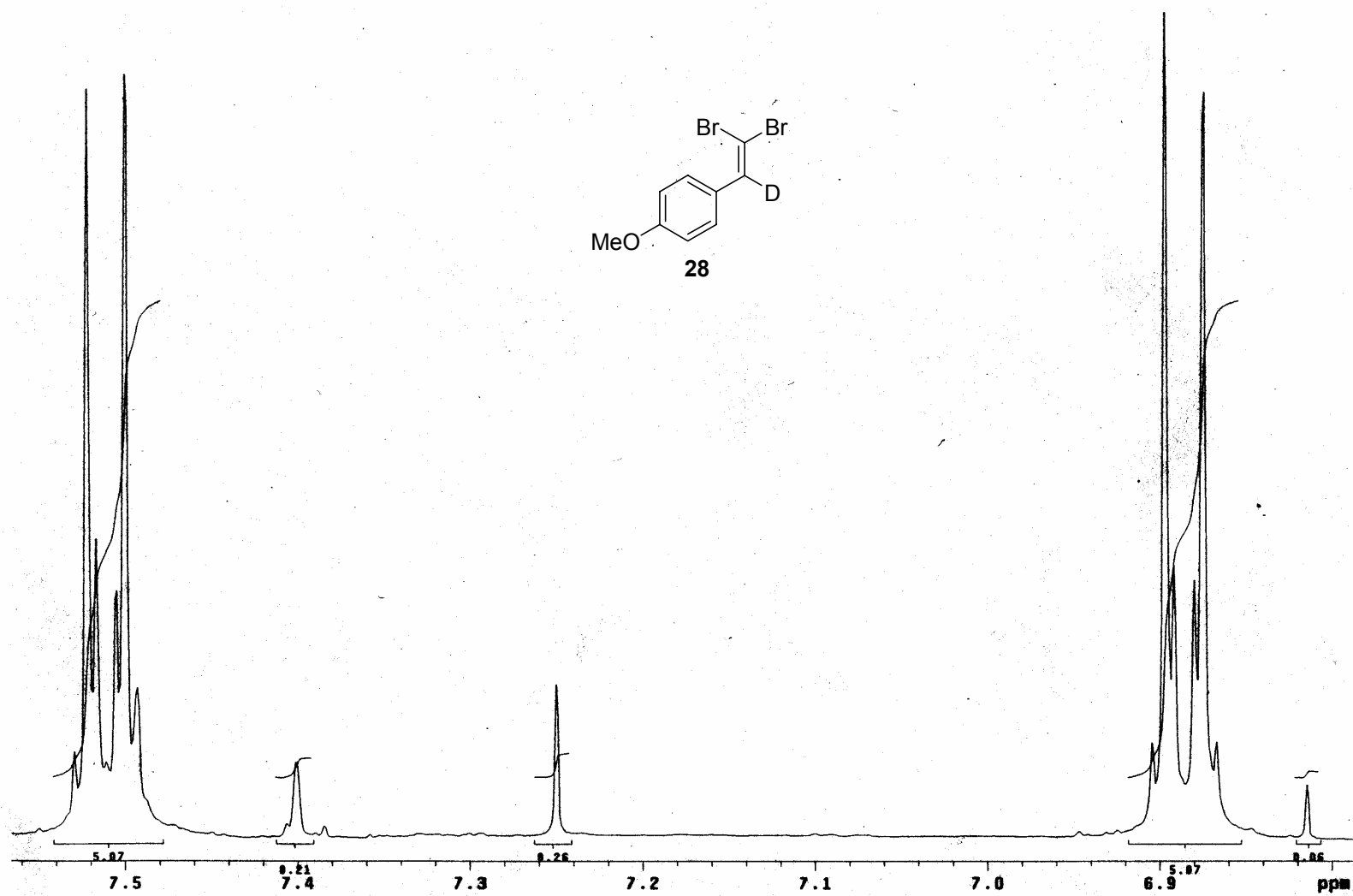


Figure S37c. ^1H NMR (expansion of aromatic region) spectrum (CDCl_3) of 1-(2,2-dibromovinyl)-4-methoxybenzene-*d* (**28**)

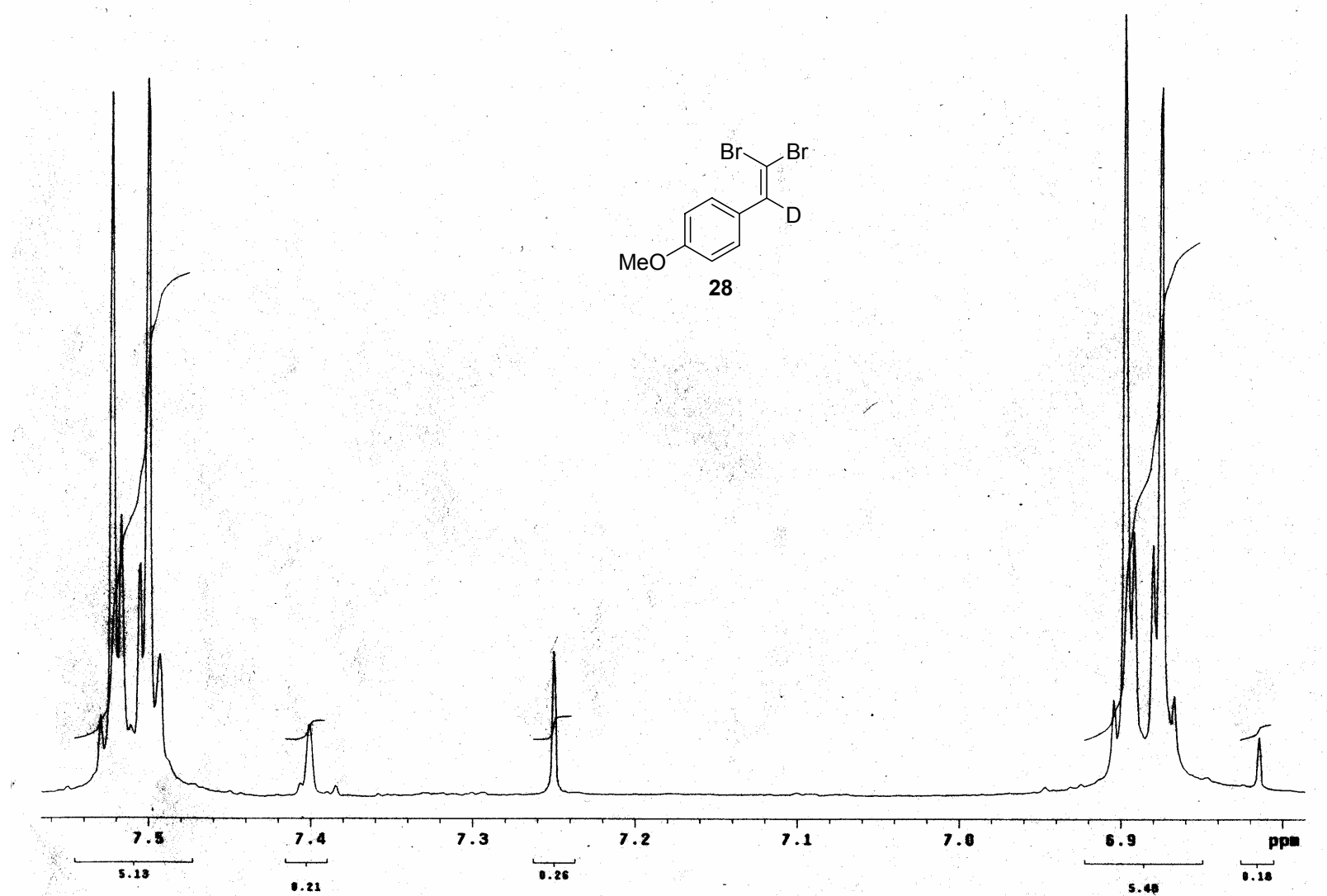


Figure S37d. ¹H NMR (expansion of aromatic region) spectrum (CDCl₃) of 1-(2,2-dibromovinyl)-4-methoxybenzene-*d* (**28**)

BS-102

exp1 CARBON

SAMPLE		SPECIAL	
date	Mar 28 2005	temp	not used
solvent	CDCl3	gain	not used
file	/export/home/~	spin	not used
ak1/INN-BS-102-13C~		hst	0.008
	.fid	pw90	14.000
ACQUISITION	alfa		20.000
sw	25125.6	FLAGS	
at	1.199	il	n
np	60270	in	n
fb	13800	dp	y
bs	4	hs	nn
d1	1.000	PROCESSING	
nt	5000	lb	5.00
ct	1096	fn	not used
TRANSMITTER		DISPLAY	
tn	C13	sp	40.6
sfrq	100.561	wp	20041.0
tof	1554.3	rfl	9252.9
tpwr	56	rfp	7742.3
pw	7.000	rp	52.4
DECOUPLER		lp	-359.0
dn	H1	PLOT	
dof	0	wc	250
dm	yyy	sc	0
dmm	w	vs	134
dpwr	41	th	2
dmf	11900	ai	no ph

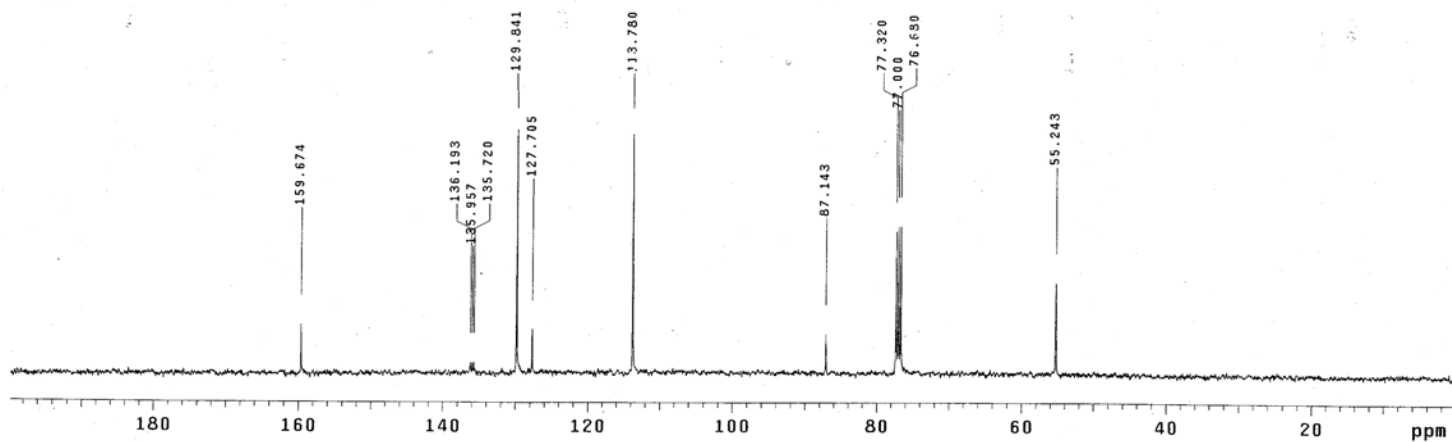
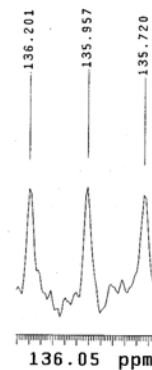
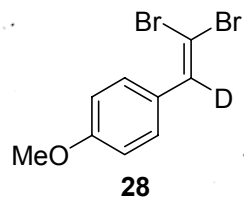


Figure S38. ^{13}C NMR spectrum (CDCl_3) of 1-(2,2-dibromovinyl)-4-methoxybenzene-*d* (**28**)

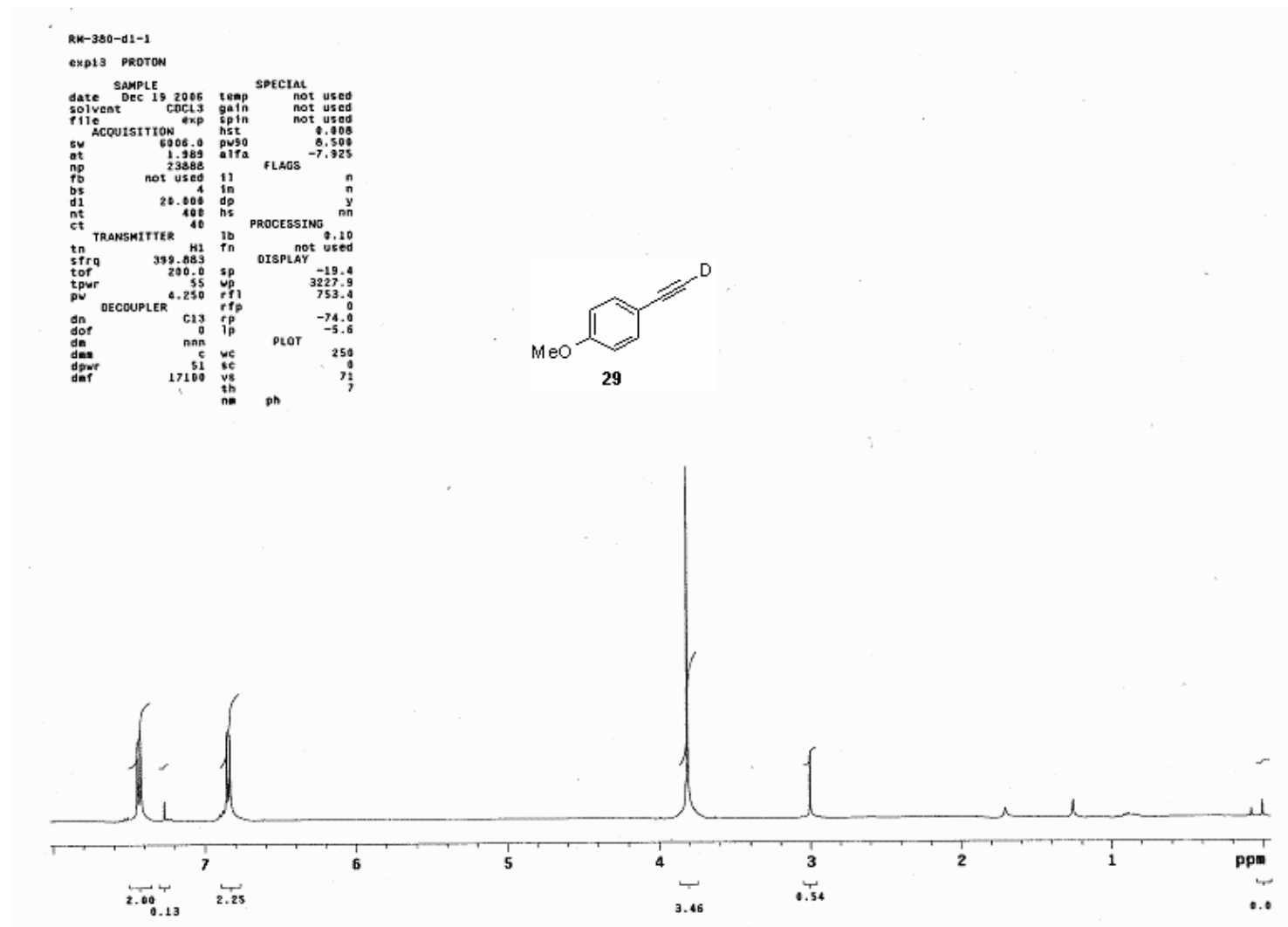


Figure S39a. ^1H NMR (CDCl_3) spectrum of 1-ethynyl-4-methoxybenzene-*d* (**29**) from deuterium labeling experiment (Integration 1)

```

RM-380-di-1
exp13 PROTON

SAMPLE
date Dec 19 2006 temp not used
solvent CDCl3 gain not used
file exp spin not used
ACQUISITION hst 8.008
sw 6006.0 pw90 8.508
at 1.989 alfa -7.925
np 23888
fb not used ll
bs 4 tn n
dl 20.000 dp y
nt 408 hs mn
ct 40
TRANSMITTER lb 0.10
tn H1 fn not used
sfrq 399.863 DISPLAY
tof 200.0 sp -11.6
tpwr 55 wp 3891.9
pw 4.250 rfl 753.4
DECOUPLER C13 rfp 0
dn 0 lp -74.0
dof 0 lp -5.6
dm mnm
dmc c wc 250
dpwr 51 sc 0
dmf 17100 vs 69
na th 7
ph

```

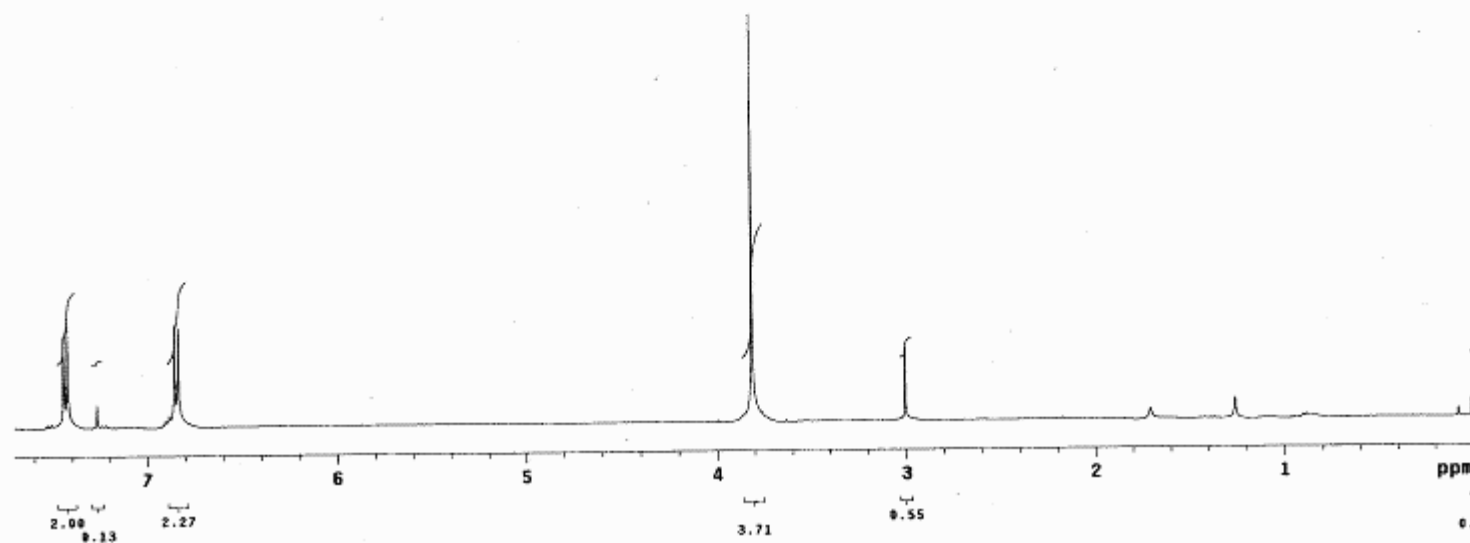
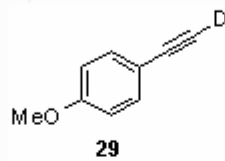


Figure S39b. ^1H NMR (CDCl_3) spectrum of 1-ethynyl-4-methoxybenzene-*d* (**29**) from deuterium labeling experiment (Integration 2)

```

RM-380-d1-1
exp13  PROTON

SAMPLE
date   Dec 19 2008   temp   not used
solvent CDCl3       gain   not used
file   exp          spin   not used
ACQUISITION
sw      6006.0      pw90    8.500
at      1.989      alfa    -7.925
mp      23888
fb      not used   fl      n
bs      4          fm      n
d1      20.000     dp      y
st      400       hs      nn
ct      40
TRANSMITTER
tn      H1         fn      not used
sfrq    399.883    sp      -19.4
tof      200.0     wp      3227.9
tpwr     55        rf1     753.4
pw      4.250     rfp     0
DECOUPLER
dn      C13       rp      -74.0
dof      0         lp      -5.6
dm      nnn
dmc      c        wc      250
dpwr     51       sc      0
dmf      17100    vs      71
                   th      7
                   ne      ph

```

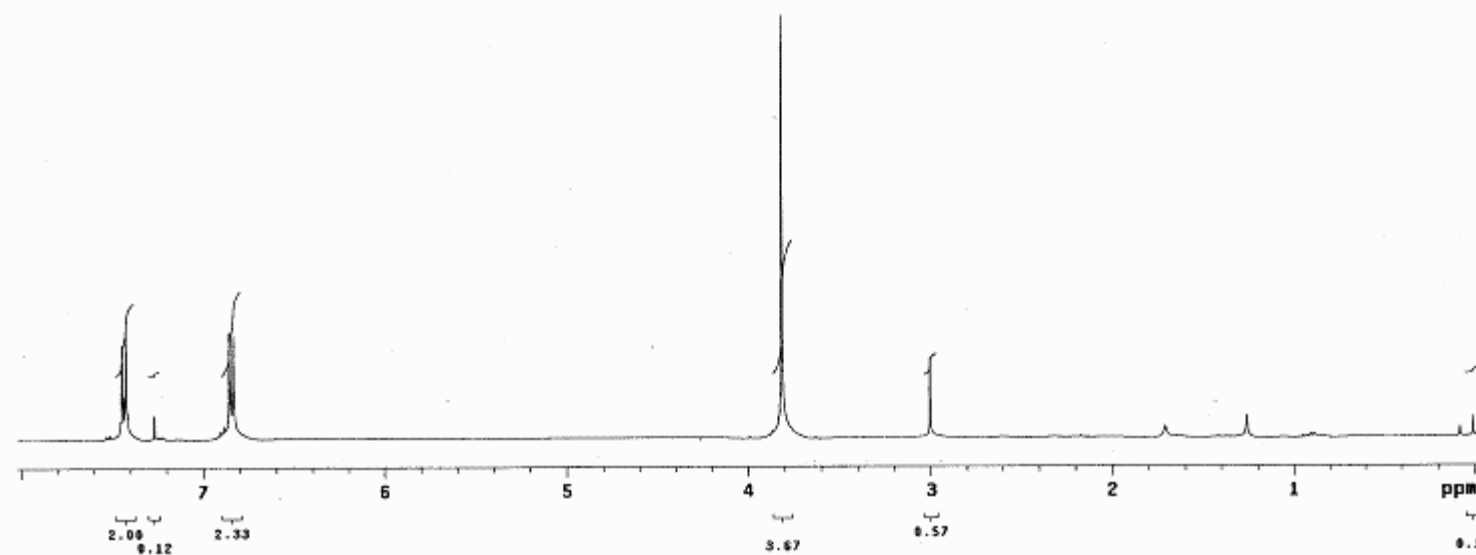
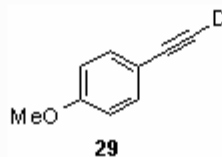


Figure S39c. ^1H NMR (CDCl_3) spectrum of 1-ethynyl-4-methoxybenzene-*d* (**29**) from deuterium labeling experiment (Integration 3)

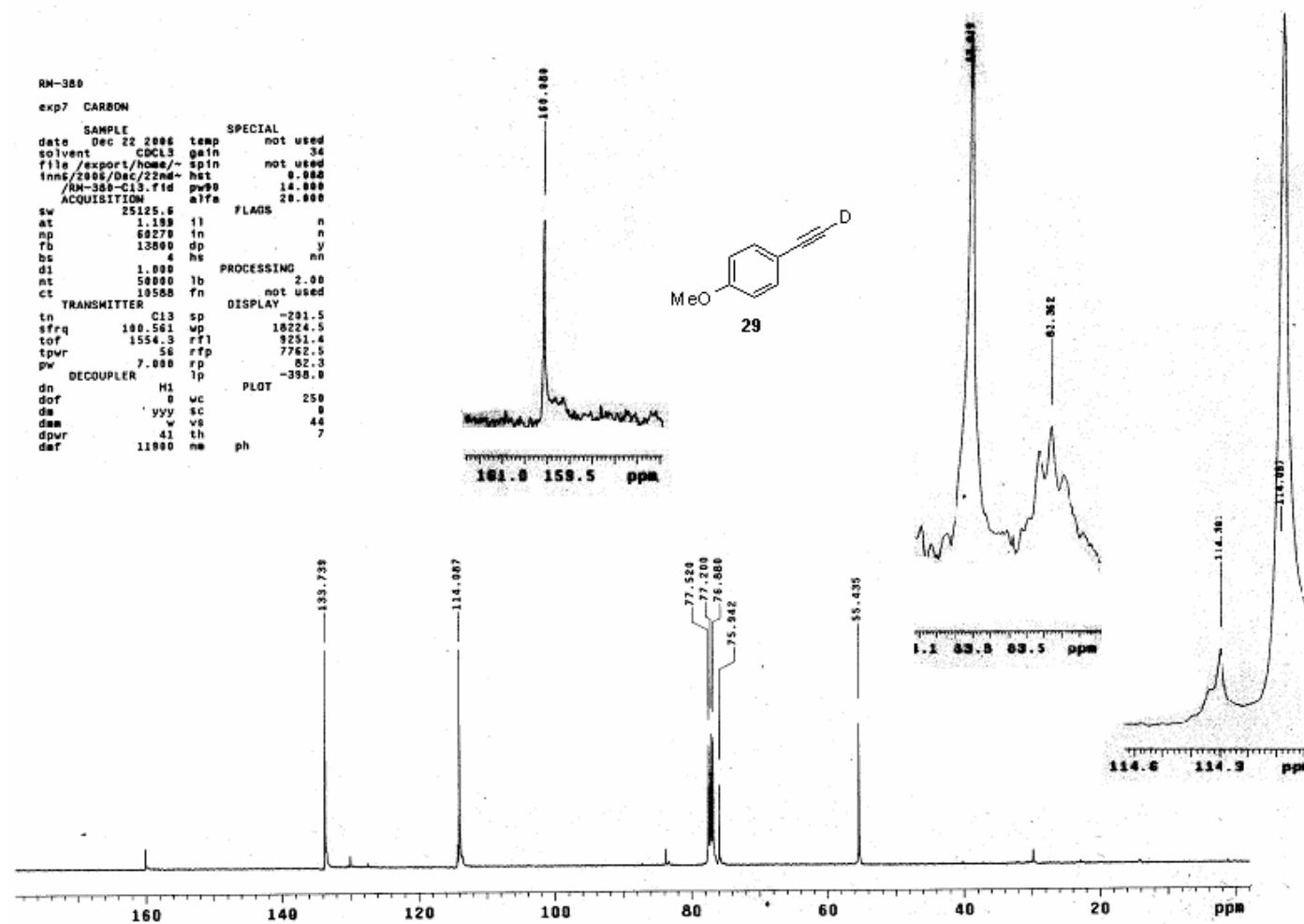


Figure S40. ^{13}C NMR (CDCl_3) spectrum of 1-ethynyl-4-methoxybenzene- d (29) from deuterium labeling experiment

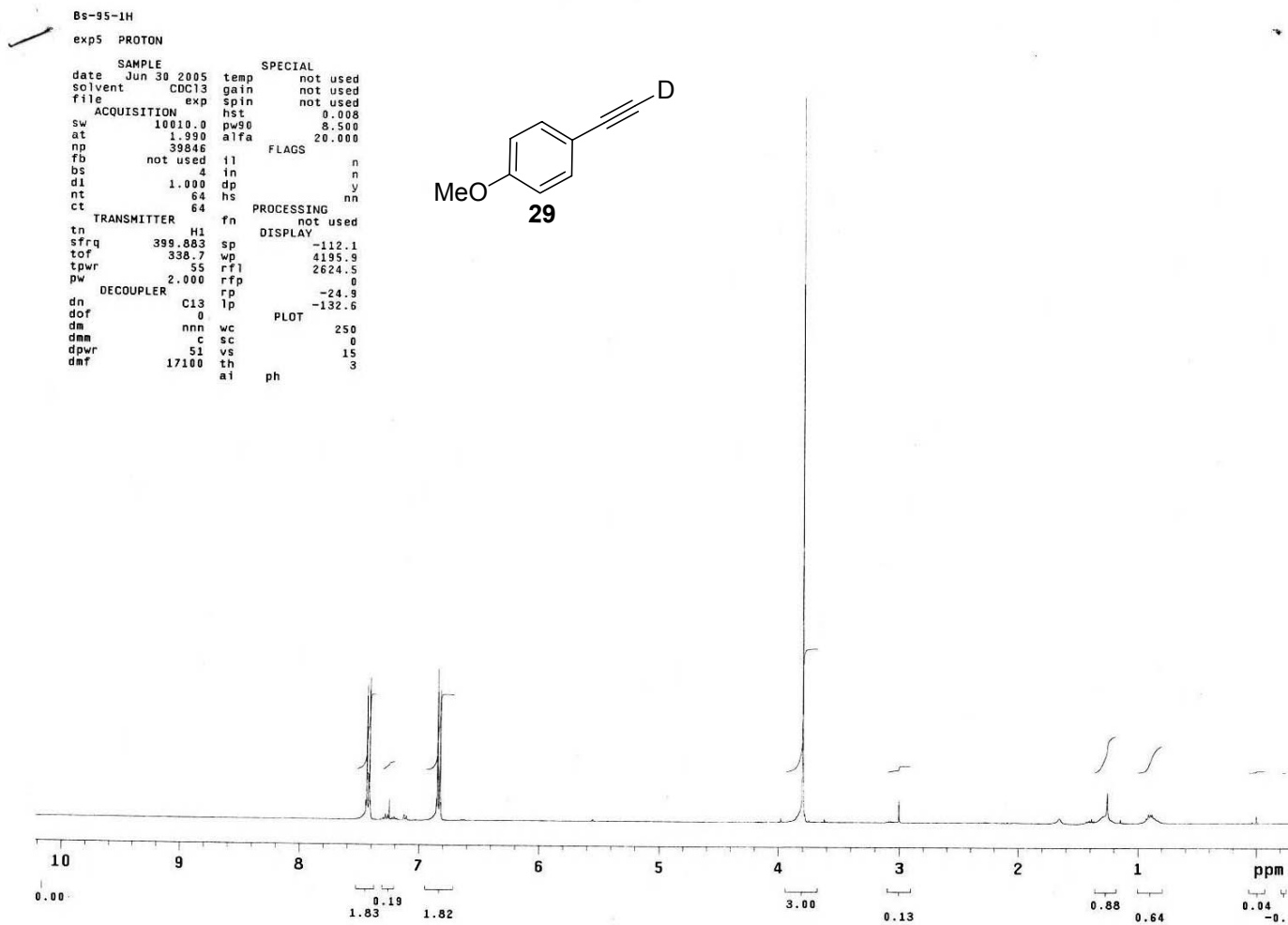


Figure S41. ^1H NMR spectrum (CDCl_3) of *standard* 1-ethynyl-4-methoxybenzene-*d* (**29**)

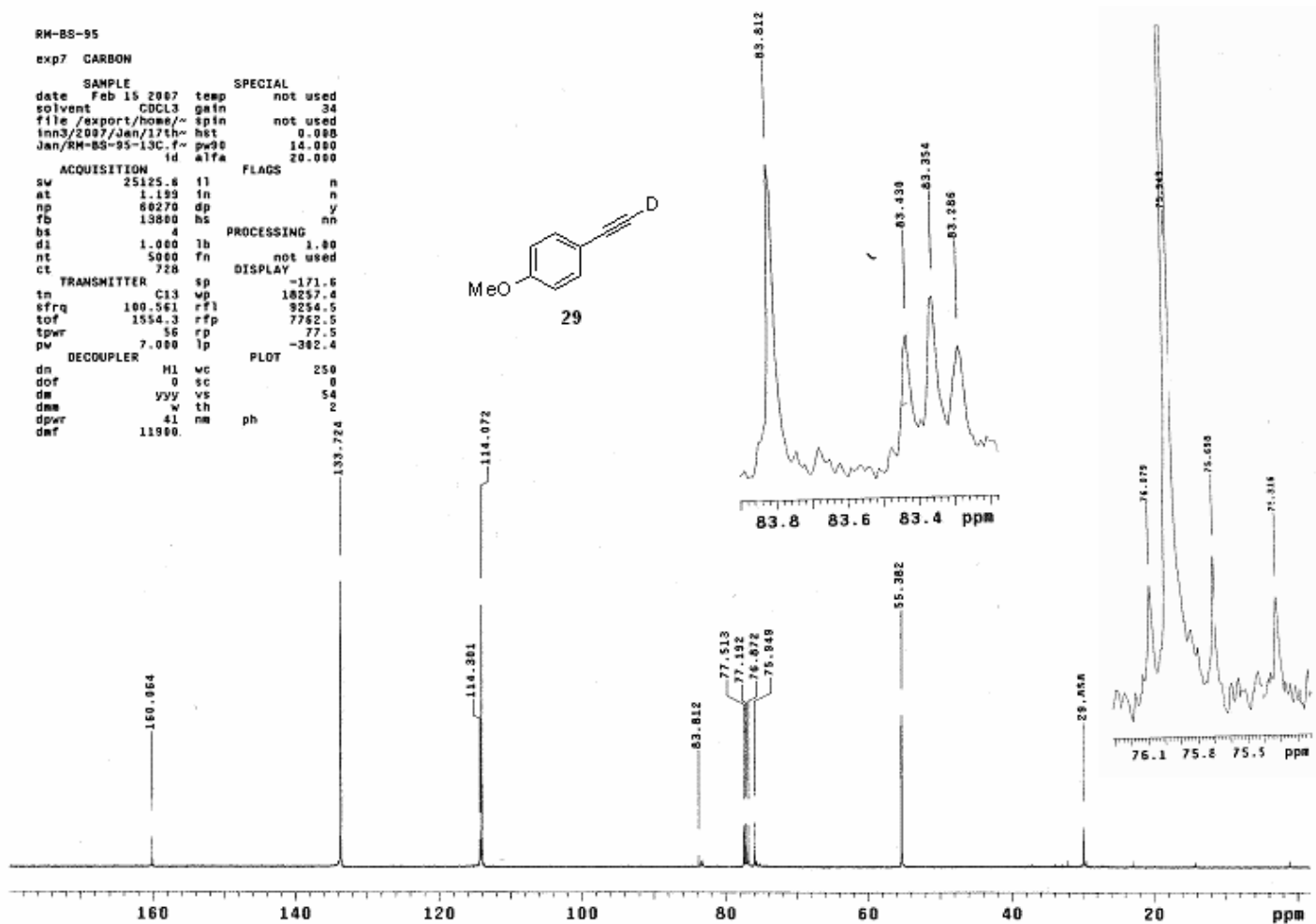


Figure S42. ^{13}C NMR spectrum (CDCl_3) of *standard* 1-ethynyl-4-methoxybenzene-*d* (29)

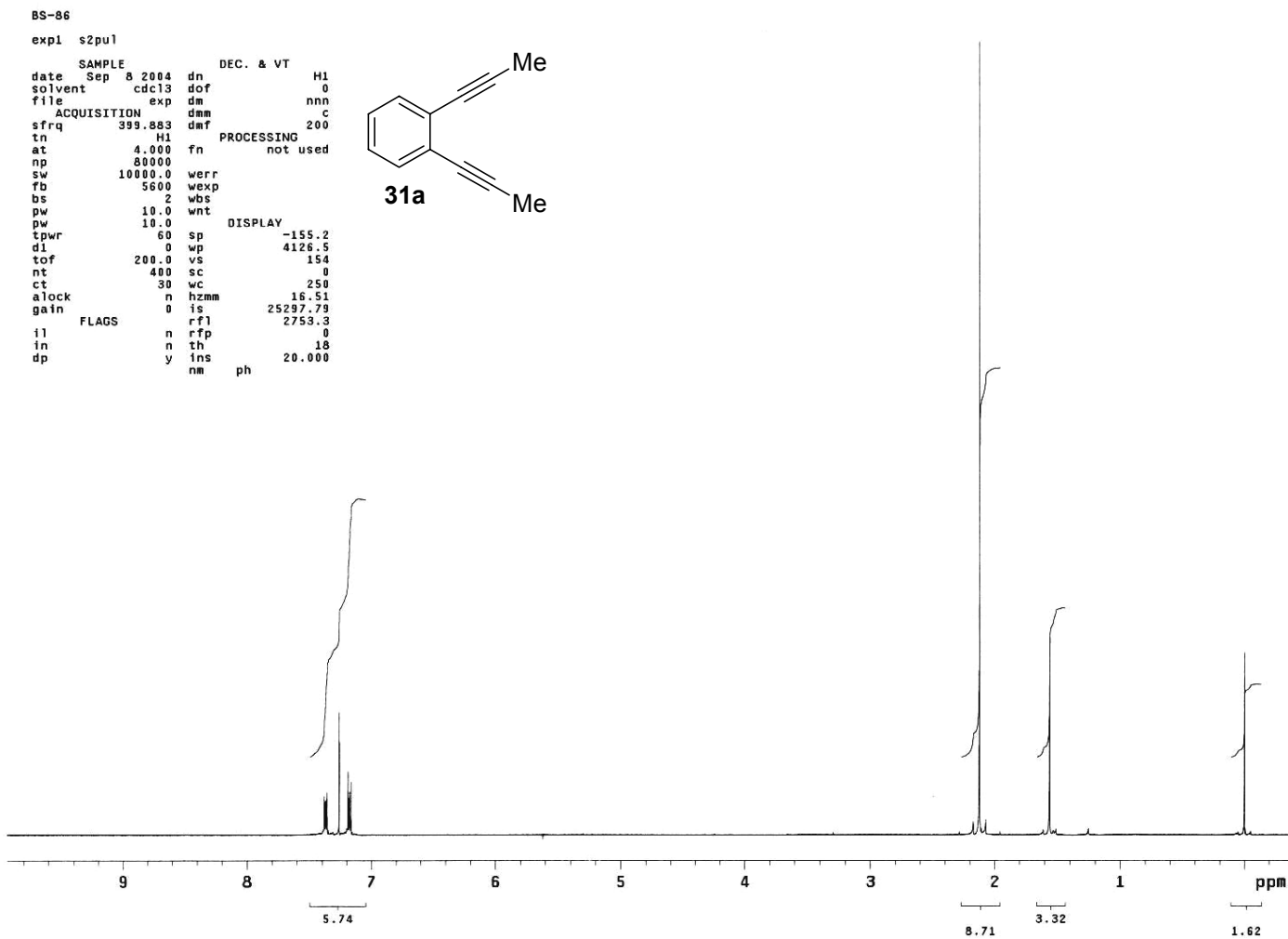


Figure S43. ^1H NMR spectrum (CDCl_3) of 1,2-di(prop-1-ynyl)benzene (**31a**)

```

BS-86
exp1 CARBON
SAMPLE
date Sep 8 2004 temp not used
solvent CDC13 gain not used
file exp hst not used
ACQUISITION sw 25125.6 pw90 14.000
at 1.199 alfa 20.000
np 60270
fb 13800
bs 1.4 in n
dl 1.000 dp y
nt 1800 hs nn
ct 112
TRANSMITTER tn C13 lb 1.00
sfrq 100.561 fn not used
tof 1554.3 sp DISPLAY -430.2
tpwr 56 wp 20469.6
pw 7.000 rfl 9252.2
DECOUPLER dn H1 rfp 7742.3
dof 0 rp 83.2
dm VVY PLOT 307.1
dmm w wc 200
dpwr 41 sc 0
dmf 11900 vs 55
th 7
al no ph

```

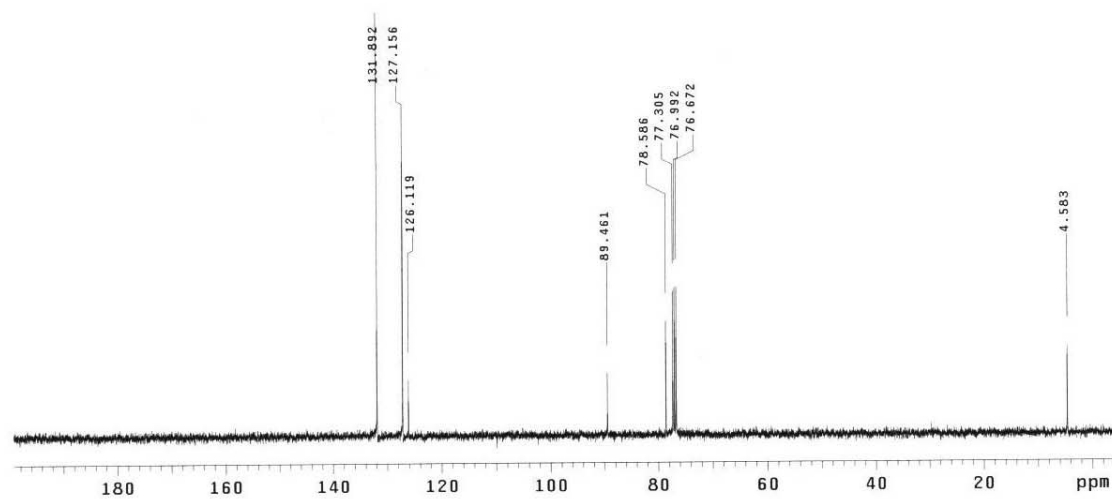
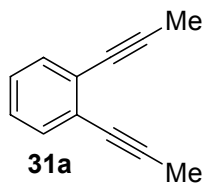


Figure S44. ¹³C NMR spectrum (CDCl₃) of 1,2-di(prop-1-ynyl)benzene (**31a**)

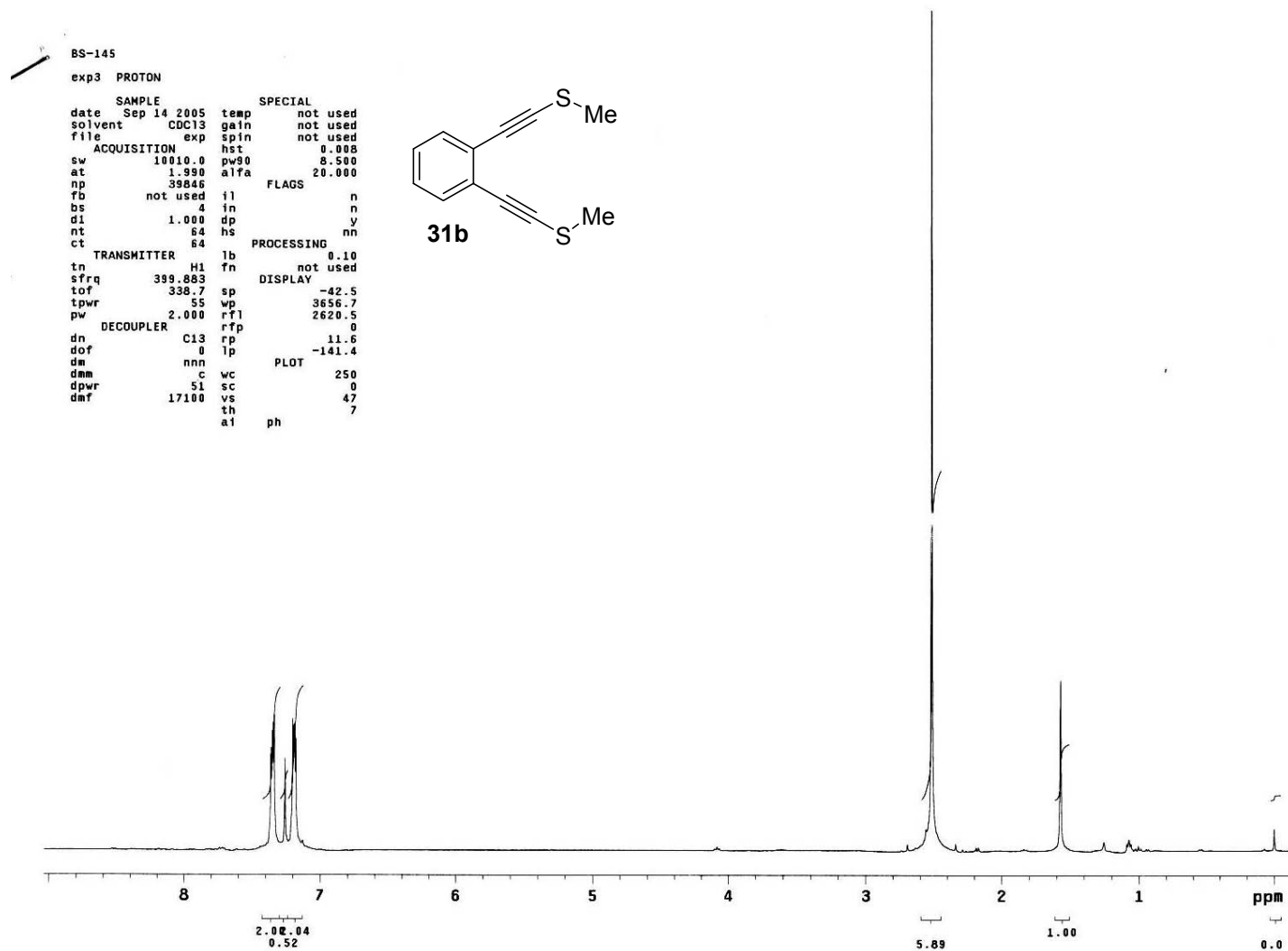


Figure S45. ^1H NMR spectrum (CDCl_3) of 1,2-bis(2-(methylthio)ethynyl)benzene (**31b**)

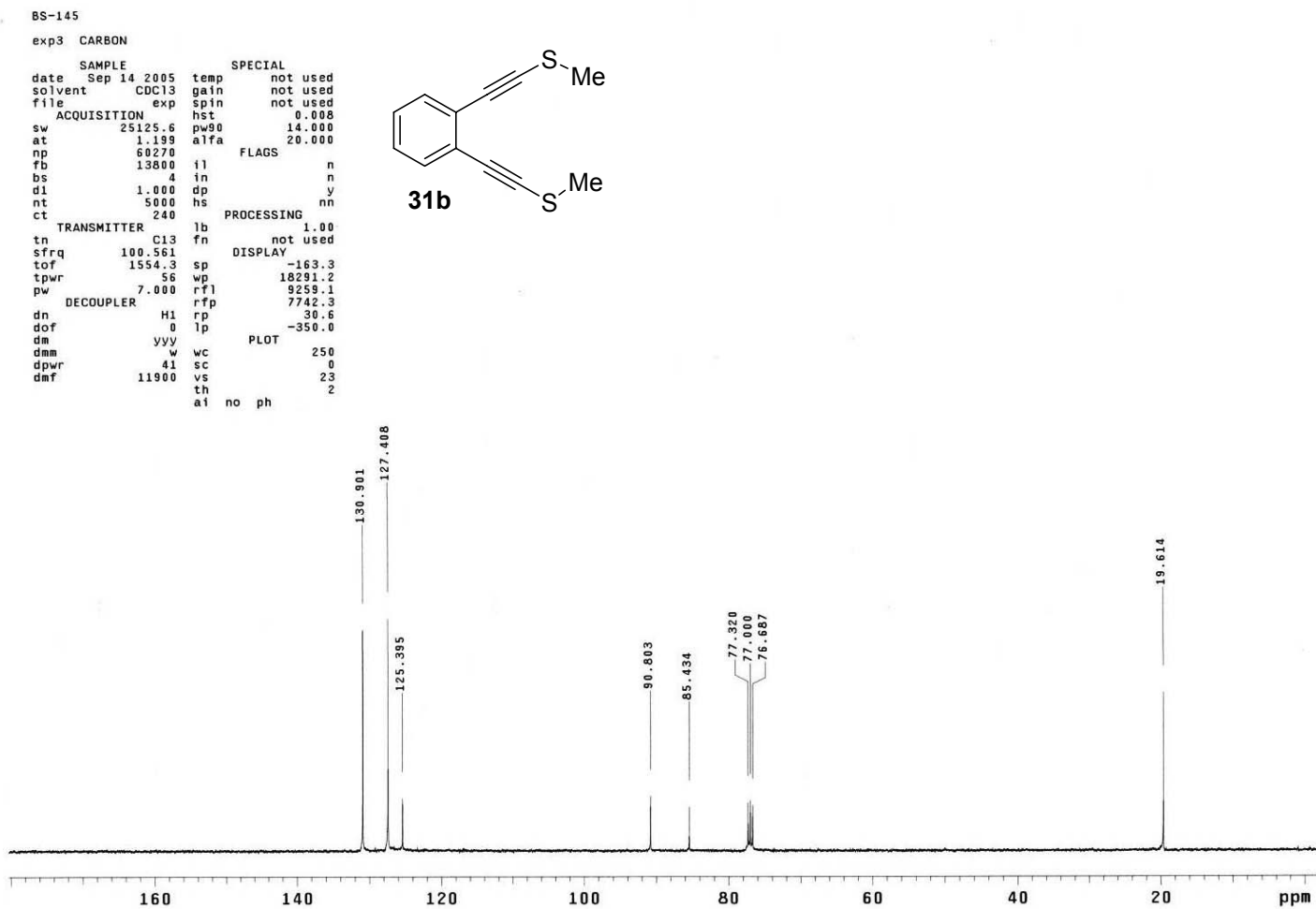


Figure S46. ¹³C NMR spectrum (CDCl₃) of 1,2-bis(2-(methylthio)ethynyl)benzene (**31b**)

BS-150

exp7 PROTON

SAMPLE		SPECIAL	
date	Apr 11 2006	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		hst	0.008
sw	10010.0	pw90	8.500
at	1.990	alfa	20.000
np	39846	FLAGS	
fb	not used	il	n
bs	4	in	n
dl	1.000	dp	y
nt	400	hs	nn
ct	0	PROCESSING	
TRANSMITTER	lb	0.10	
tn	H1	fn	not used
sfrq	399.883	DISPLAY	
tof	338.7	sp	-45.8
tpwr	55	wp	4051.1
pw	2.000	rfl	2623.9
DECOUPLER	C13	rfl	0
dn	C13	rp	101.3
dof	338.7	lp	-144.4
dm	nnn	PLOT	
dmm	c	wc	250
dpwr	51	sc	0
dmt	17100	vs	28
	th	8	
	ai	ph	

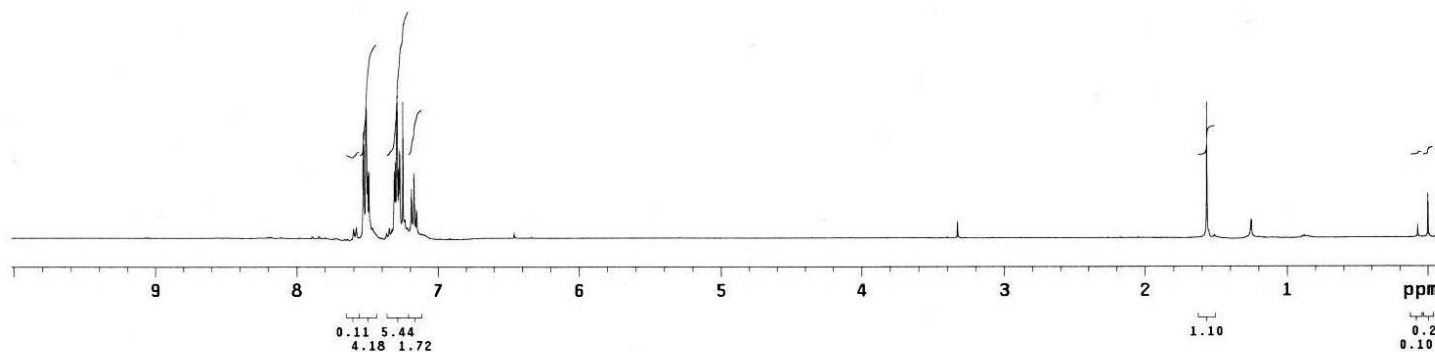
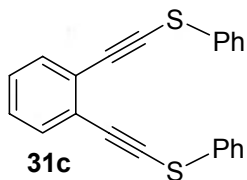


Figure S47. ^1H NMR spectrum (CDCl_3) of 1,2-bis(2-(phenylthio)ethynyl)benzene (**31c**)

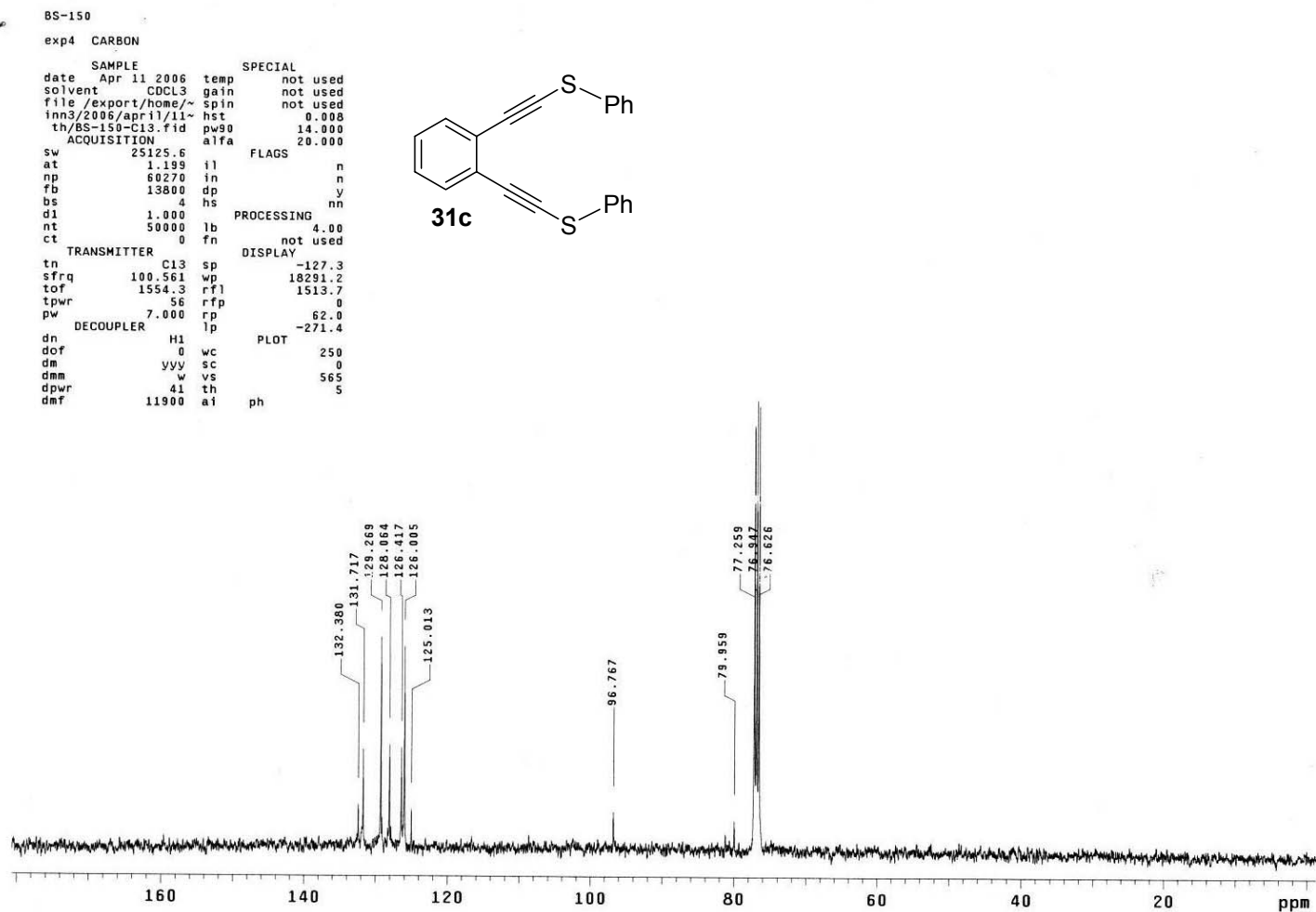


Figure S48. ¹³C NMR spectrum (CDCl₃) of 1,2-bis(2-(phenylthio)ethynyl)benzene (**31c**)

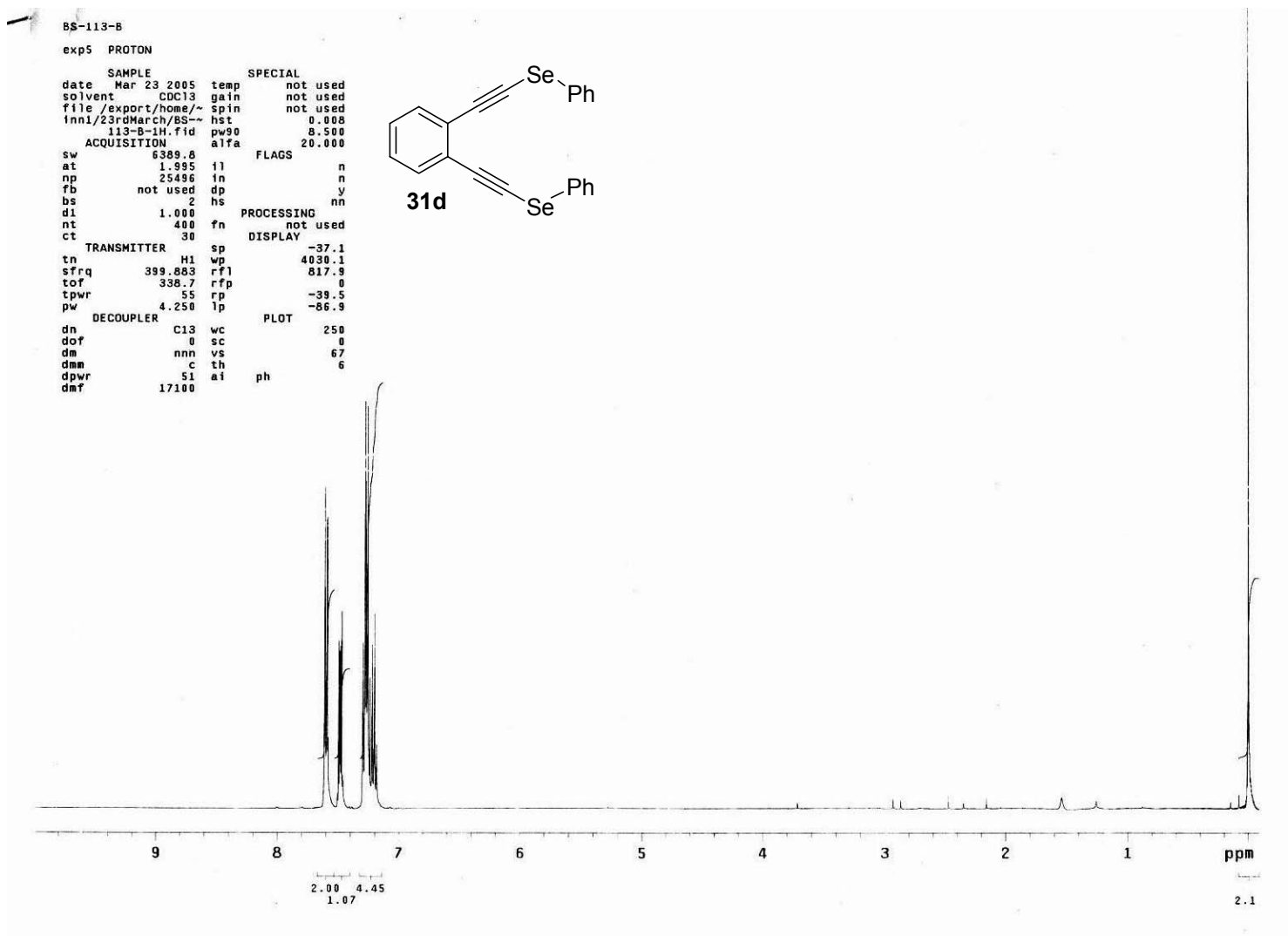


Figure S49. ^1H NMR spectrum (CDCl_3) of 1,2-bis(2-(phenylselanyl)ethynyl)benzene (**31d**)

BS-113-8

exp4 CARBON

SAMPLE		SPECIAL	
date	Mar 23 2005	temp	not used
solvent	CDCl ₃	gain	not used
file	/export/home/~	spin	not used
inn1/23rdMarch/BS~		hst	0.008
113-8-C13.fid		pw90	14.000
ACQUISITION		alfa	20.000
sw	25125.6	FLAGS	
at	1.199	il	n
np	60270	in	n
fb	13800	dp	y
bs	4	hs	nn
dl	1.000	PROCESSING	
nt	1800	lb	1.00
ct	480	fn	not used
TRANSMITTER		DISPLAY	
tn	C13	sp	6.1
sfrq	100.561	wp	18191.5
tof	1554.3	rfl	9254.5
tpwr	56	rfp	7742.3
pw	7.000	rp	40.2
DECOUPLER		lp	-320.0
dn	H1	PLOT	
dof	0	wc	250
dm	yyy	sc	0
dmm	w	vs	69
dpwr	41	th	2
dmf	11900	ai	no ph

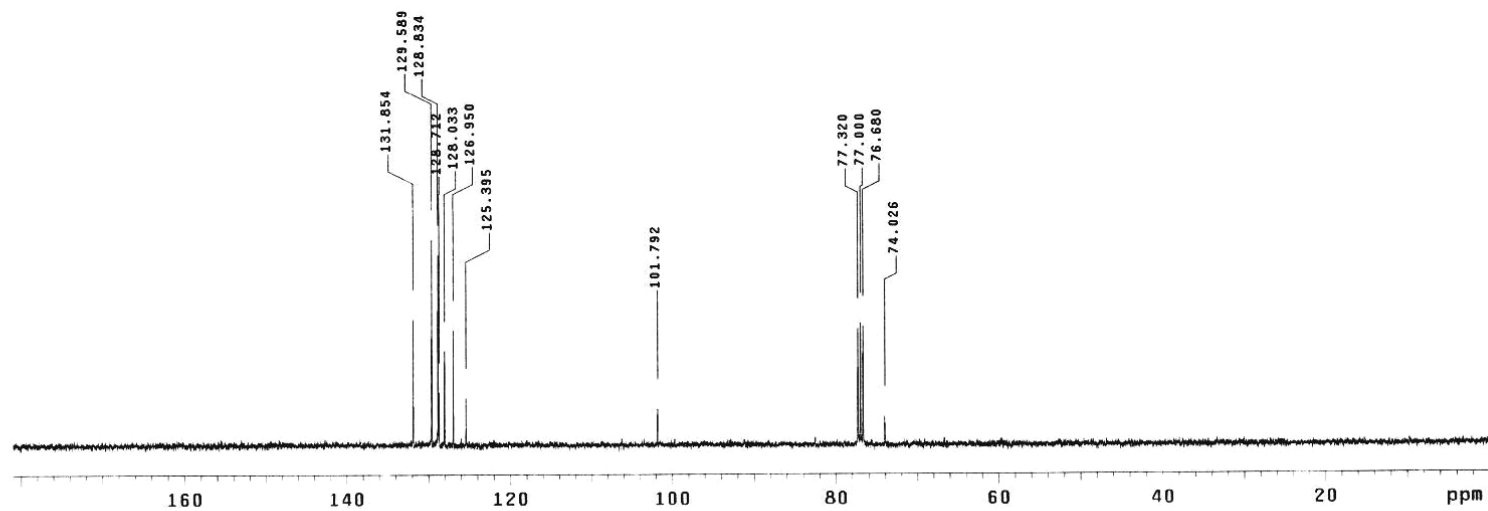
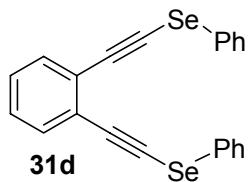


Figure S50. ¹³C NMR spectrum (CDCl₃) of 1,2-bis(2-(phenylselanyl)ethynyl)benzene (**31d**)

```

BS-113
exp9 s2pul

SAMPLE
date Apr 1 2005 dn
solvent CDCl3 dof
file exp dm
ACQUISITION dmm
sfrq 57.221 dmf
in Se77
at 0.640 lb
np 128000 fn
sw 100000.0 werr
fb 55000 wexp
bs 16 wbs
pw 3.0 wnt
tpwr 58
d1 0 sp
tof 900.0 wp
nt 32000 vs
ct 2848 sc
alock n wc
gain 6 hzmm
          3.44329e+06
          33654.6
          0
          8
          45.000
          ph
          nm
  
```

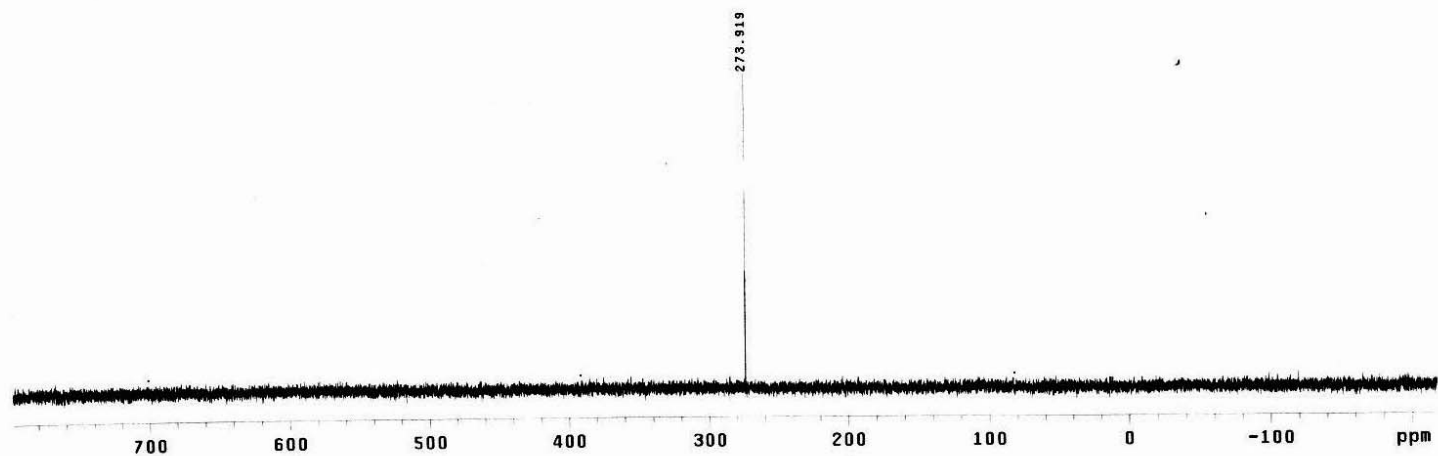
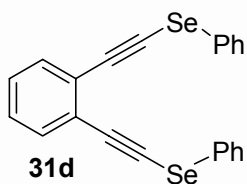


Figure S51. ^{77}Se NMR spectrum (CDCl_3) of 1,2-bis(2-(phenylselanyl)ethynyl)benzene (**31d**)

BS-126

exp2 PROTON

SAMPLE		SPECIAL	
date	May 2 2005	temp	not used
solvent	CDCl3	gain	not used
file	/export/home/~	spin	not used
inn1	MAY/2ndmay/BS-	hst	0.008
	-126-1H.fid	pw90	8.500
ACQUISITION		alfa	20.000
sw	6389.8	FLAGS	
at	1.995	il	n
np	25496	in	n
fb	not used	dp	y
bs	2	hs	nn
d1	1.000	PROCESSING	
nt	400	fn	not used
ct	56	DISPLAY	
TRANSMITTER		sp	-34.3
tn	H1	wp	4063.7
sfrq	399.883	rfl	815.2
tof	338.7	rpf	0
tpwr	55	rp	-46.1
pw	4.250	lp	-82.5
DECOUPLER		PLOT	
dn	C13	wc	250
dof	0	sc	0
dm	nnn	vs	63
dmm	c	th	3
dpwr	51	ai	ph
dmt	17100		

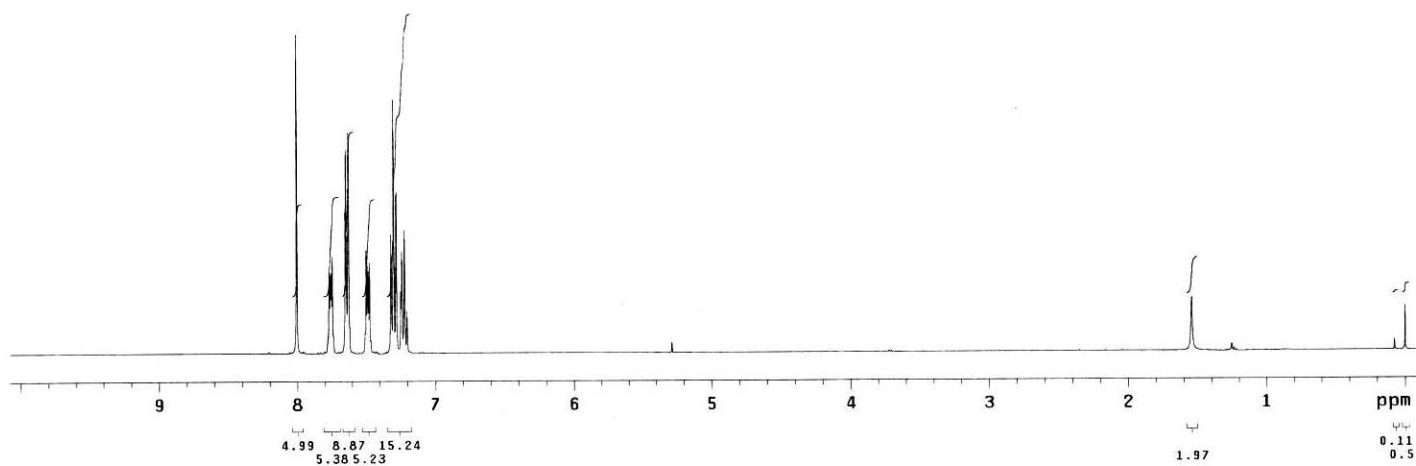
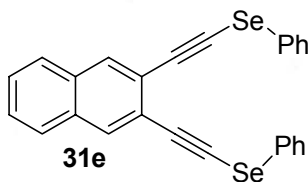


Figure S52. ^1H NMR spectrum (CDCl_3) of 2,3-bis(2-(phenylselanyl)ethynyl)naphthalene (**31e**)

BS-126-c13

exp6 CARBON

SAMPLE		SPECIAL	
date	May 2 2005	temp	not used
solvent	CDCl ₃	gain	not used
file	exp	spin	not used
ACQUISITION		SPECIAL	
sw	25125.6	hst	0.008
at	1.199	pw90	14.000
np	60270	alpha	20.000
fb	13800	fl	n
bs	4	in	n
dl	1.000	dp	y
nt	50000	hs	nn
ct	1848	hs	nn
TRANSMITTER		PROCESSING	
tn	C13	lb	1.00
sfrq	100.561	fn	not used
tof	1554.3	sp	-19.9
tpwr	56	wp	20238.8
pw	7.000	rfl	9247.6
DECOUPLER		PLOT	
dn	H1	rtp	7742.3
dof	0	rp	41.7
dm	yyy	lp	-327.4
dmm	w	wc	250
dpwr	41	sc	0
dmf	11900	vs	59
		th	2
		af	no ph

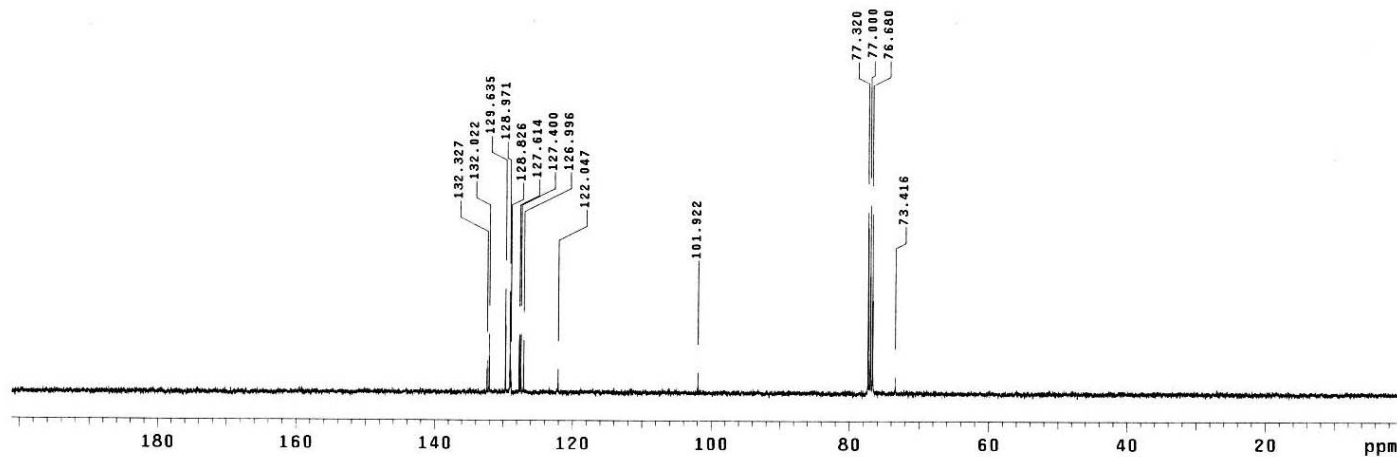
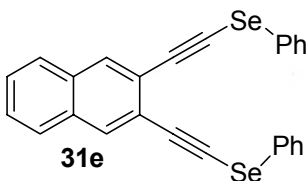


Figure S53. ¹³C NMR spectrum (CDCl₃) of 2,3-bis(2-(phenylselanyl)ethynyl)naphthalene (**31e**)

```

BS-126
exp1 s2pul
SAMPLE
date May 11 2005 dn H1
solvent CDCl3 dof 0
file exp dm nnn
ACQUISITION dnm c
sfrq 57.260 dmf 200
tn Se77 PROCESSING
at 0.640 lb 14.00
np 128000 fn not used
sw 100000.0
fb 55000 werr
bs 8 wexp
pw 3.0 wbs
pw 3.0 wnt
tpwr 58
d1 0 sp 8022.6
tof 40000.0 wp 48848.0
nt 32000 vs 27
ct 10048 sc 0
alock n wc 250
gain 6 hzmm 195.39
FLAGS n is 436896.63
il n rfl -5445.4
in n rfp 0
dp y th 3
ins 65.734
nm ph

```

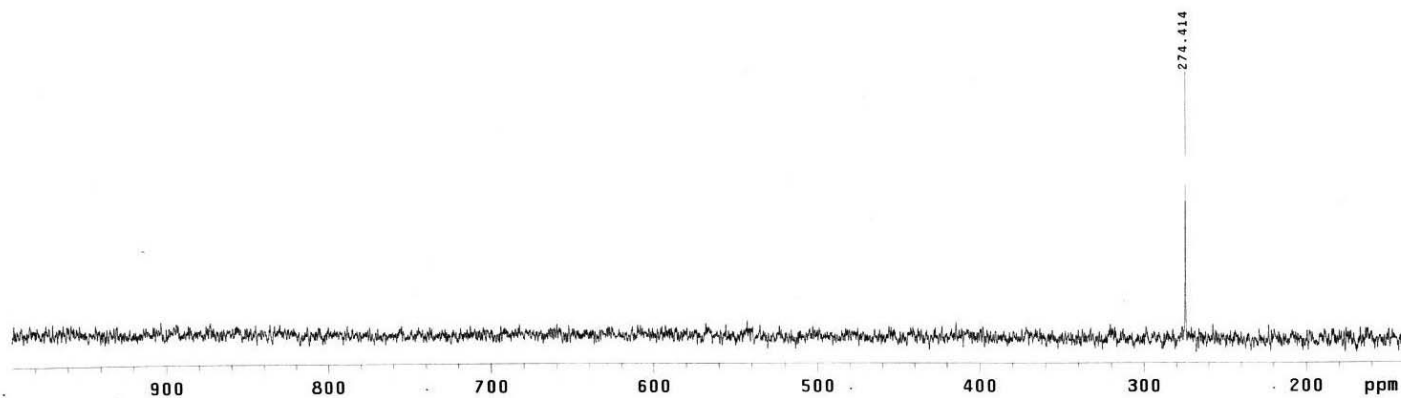
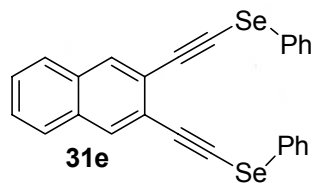


Figure S54. ^{77}Se NMR spectrum (CDCl_3) of 2,3-bis(2-(phenylselanyl)ethynyl)naphthalene (**31e**)

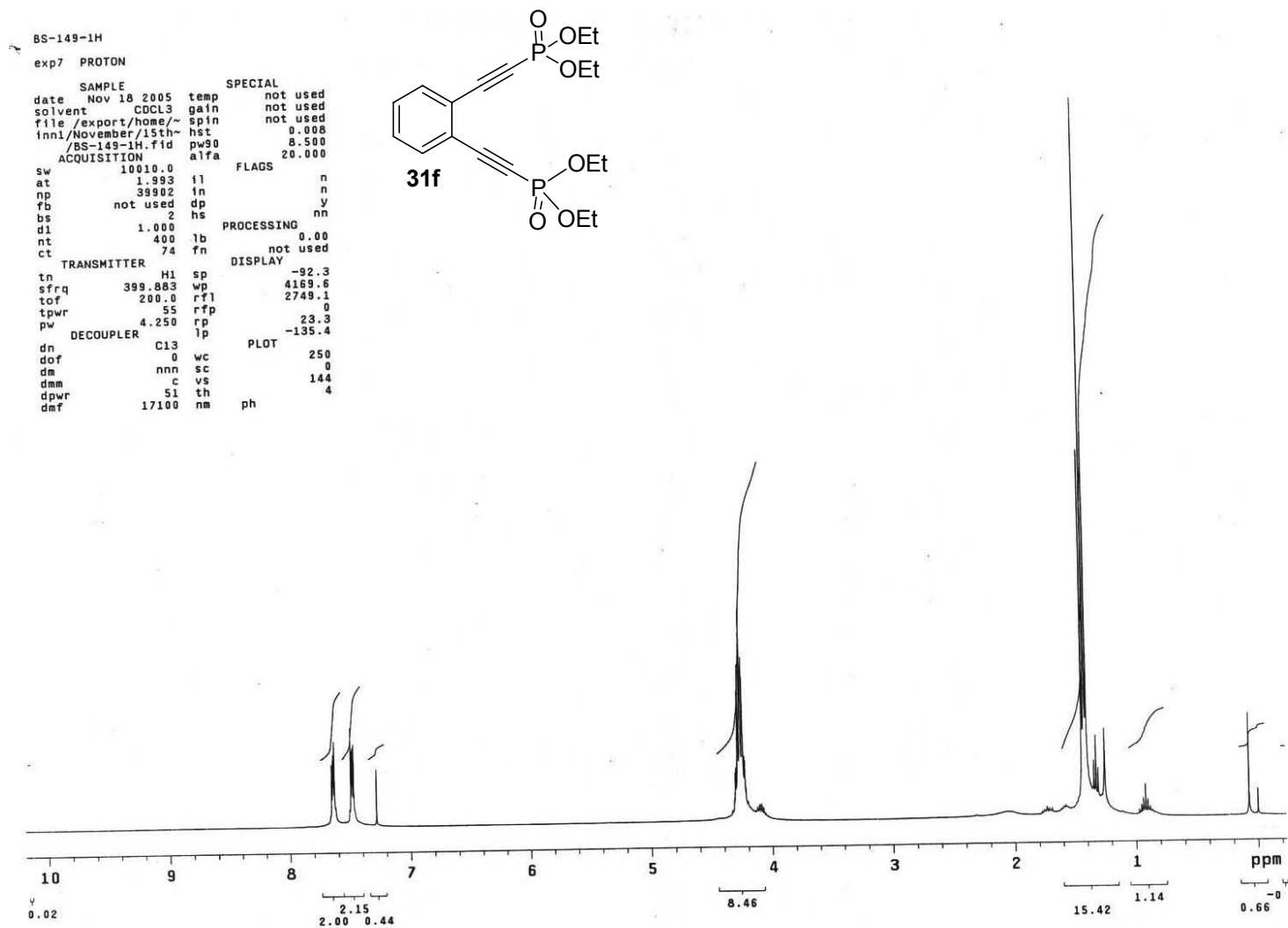


Figure S55. ^1H NMR spectrum (CDCl_3) of 1,2-bis(diethyl 2-phenylethynyl)phosphonate (**31f**)

IBD-BH-3-165-c13

exp7 CARBON

SAMPLE		SPECIAL	
date	Nov 19 2005	temp	not used
solvent	CDCl3	gain	not used
file	/export/home/~	spin	not used
inn1	19-NOV05/IBD~	hst	0.008
BS-149-c13.fid		pw90	14.000
ACQUISITION	alpha	20.000	
sw	25125.6	FLAGS	n
at	1.199	il	n
np	60270	in	n
fb	13800	dp	y
bs	4	hs	nn
d1	1.000	PROCESSING	0.50
nt	50000	lb	not used
ct	3112	fn	
TRANSMITTER	C13	sp	42.2
sfrq	100.561	wp	20139.9
tof	1554.3	rfl	9251.4
tpwr	56	rpf	7742.3
pw	7.000	rp	145.0
DECOUPLER	H1	lp	-299.1
dn	0	wc	250
dof	0	sc	0
dm	yyy	vs	66
dmm	41	th	4
dpwr	11900	ai	ph

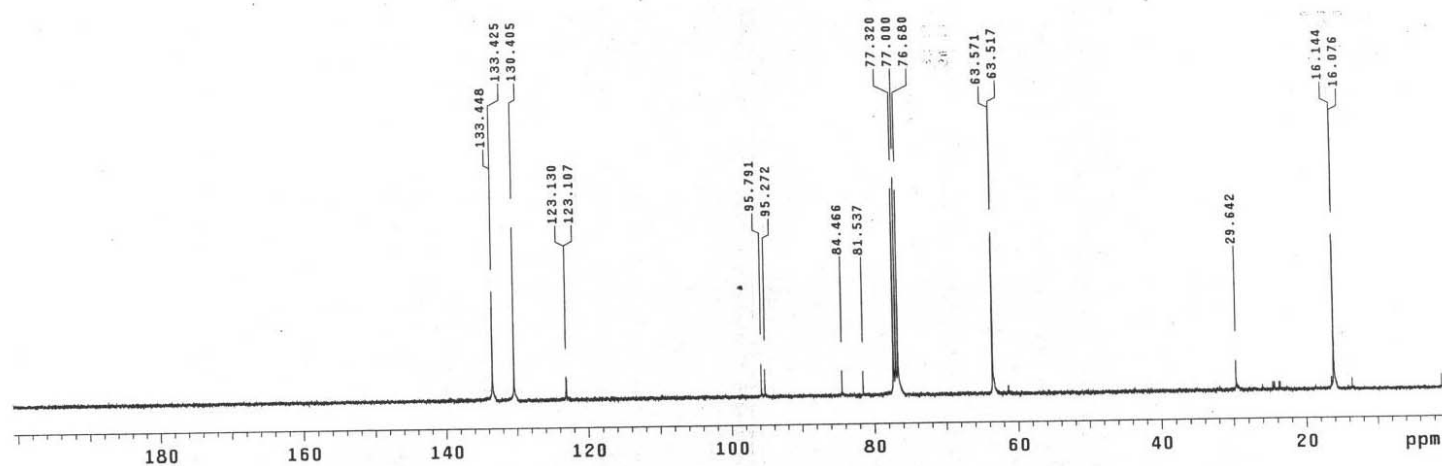
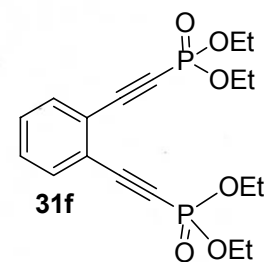
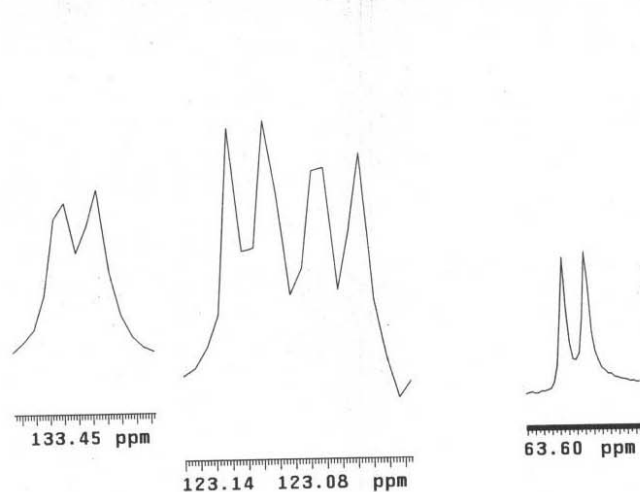


Figure S56. ^{13}C NMR spectrum (CDCl_3) of 1,2-bis(diethyl 2-phenylethynyl)phosphonate (**31f**)

```

BS-149
exp5 s2pu1
SAMPLE 13 2005 DEC. & VT 299.949
date Dec 13 2005 dfrq dn H1
solvent CDC13 exp dpwr 39
file ACQUISITION dof 0
sfrq 121.421 dm nny
tn P31 dmm w
at 1.280 dmf 9900
np 50000.0 lb PROCESSING 2.00
sw 27600 wtfile
fb 4 proc ft
bs 55 fn not used
tpwr 10.0
pw 0 verr
d1 0.0 wexp
tof 32000 wbs
nt 120 wnt
ct
alock n
gain 6
FLAGS
il n
in n
dp y
DISPLAY
sp -12087.1
wp 21825.4
vs 63
sc 0
wc 250
hzmm 0.82
is 41097.77
rfl 25028.1
rtp 0
th 4
ins 100.000
nm cdc ph

```

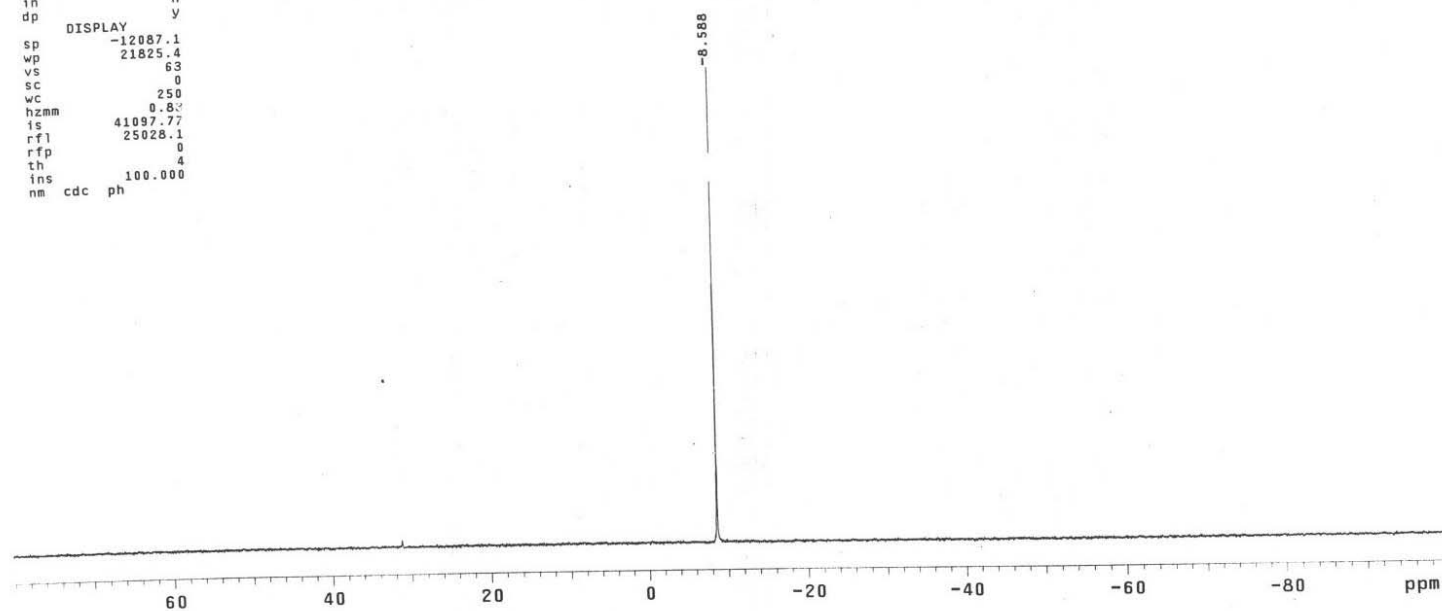
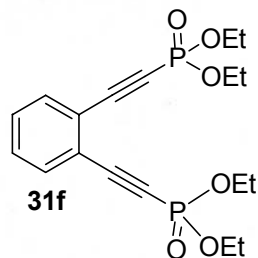


Figure S57. ^{31}P NMR spectrum (CDCl_3) of 1,2-bis(diethyl 2-phenylethynyl)phosphonate (**31f**)