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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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Ref. No.: O200601137

Experimental Section

General

The melting points are uncorrected. IR spectra were recorded on a Perkin Elmer Spectrum One FT spectrometer. NMR spectra (^{1}H, ^{13}C, ^{31}P and ^{77}Se) were recorded on an AMX-400 or VXR-300S spectrometer. TMS was the internal standard for ^{1}H, ^{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 ^{1}H 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}. ^{1}H 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 $C_{20}H_{17}O_5$ (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 × 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}. ^{1}H 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 ~ 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, $J_{C\text{-}D}$ = 38.1 Hz), 83.2 (t, $J_{C\text{-}D}$ = 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%

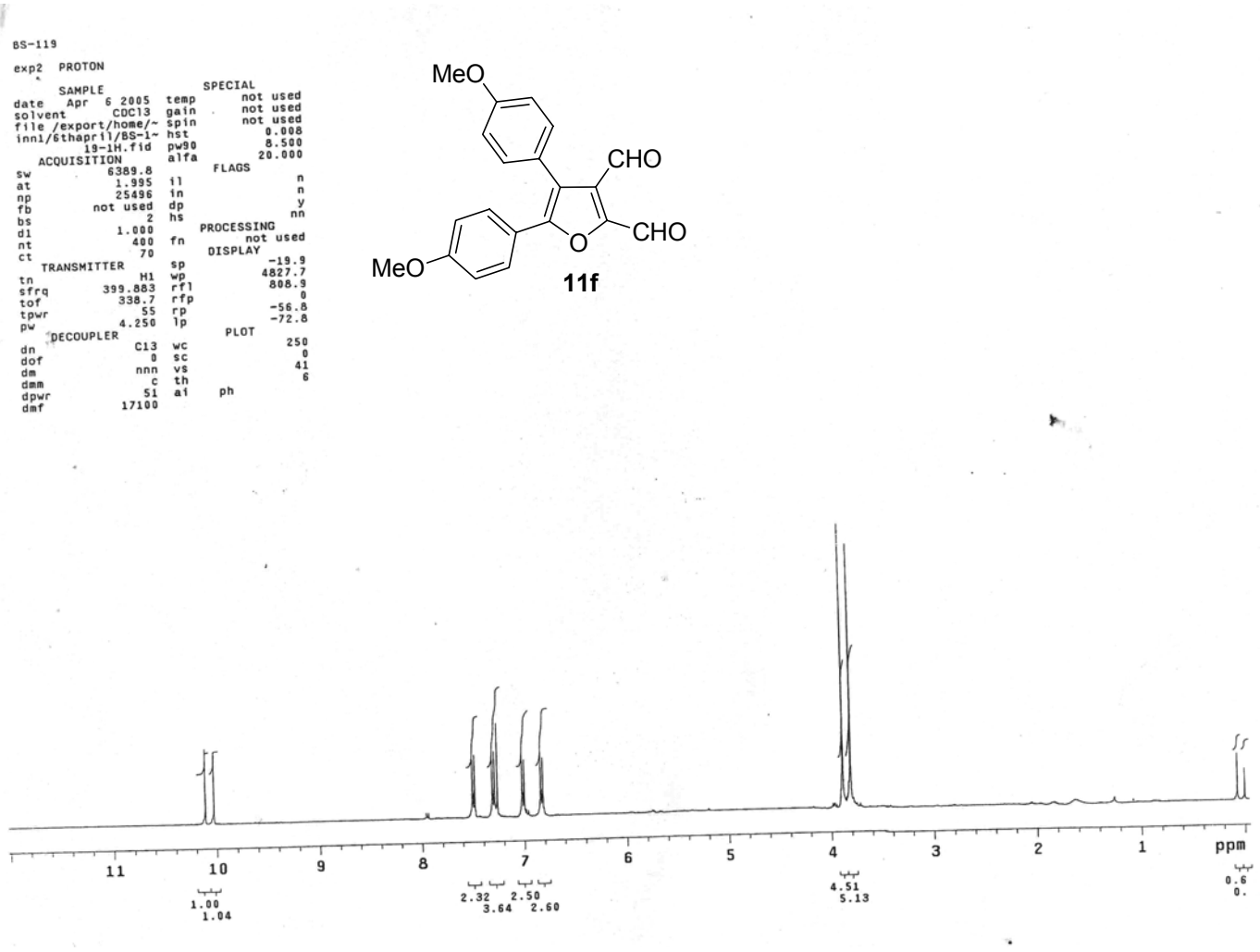

Figure S1. ^{1}H NMR spectrum ($CDCl_3$) of 4,5-bis(4-methoxyphenyl)furan-2,3-dicarbaldehyde **(11f)**

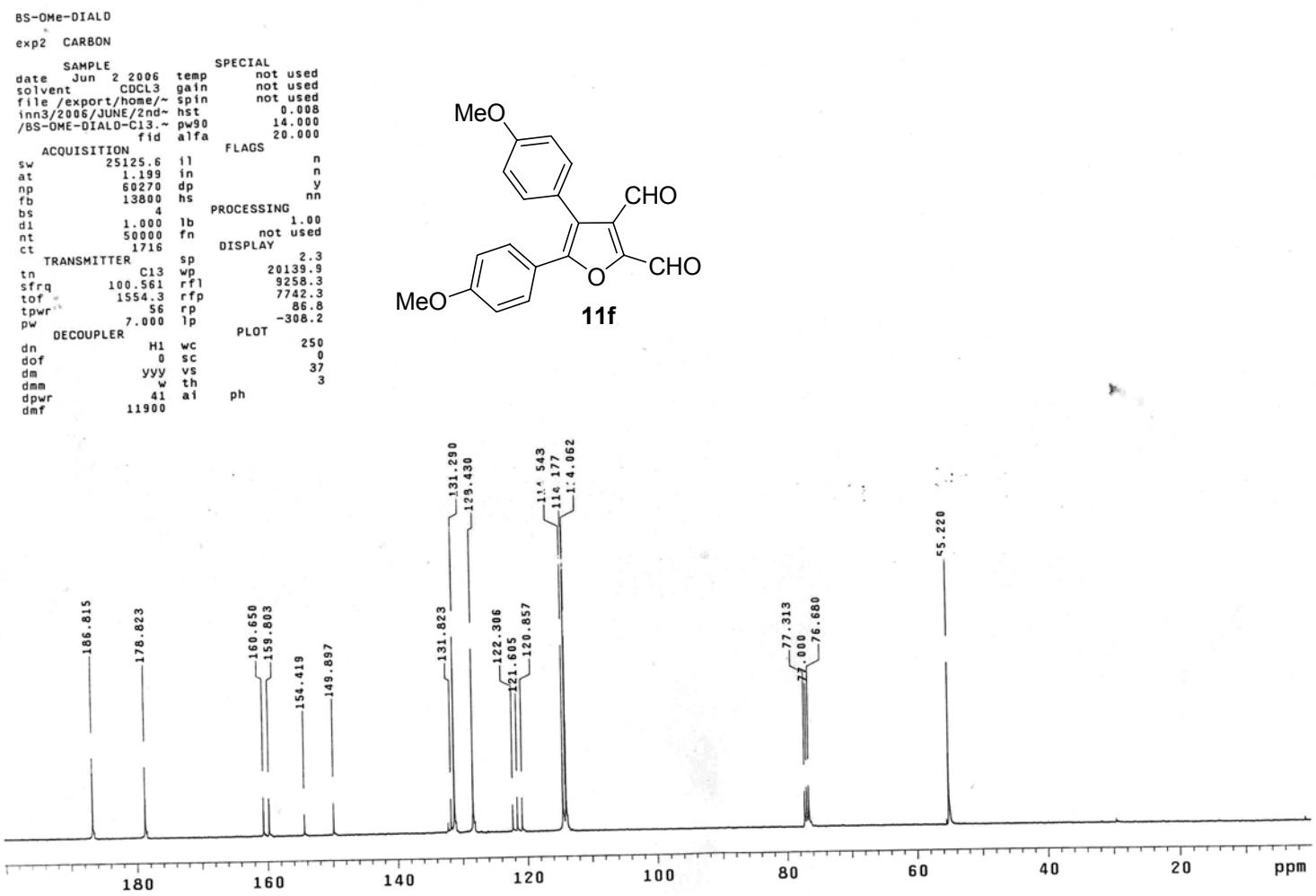

Figure S2. ^{13}C NMR spectrum ($CDCl_3$) of 4,5-bis(4-methoxyphenyl)furan-2,3-dicarbaldehyde **(11f)**

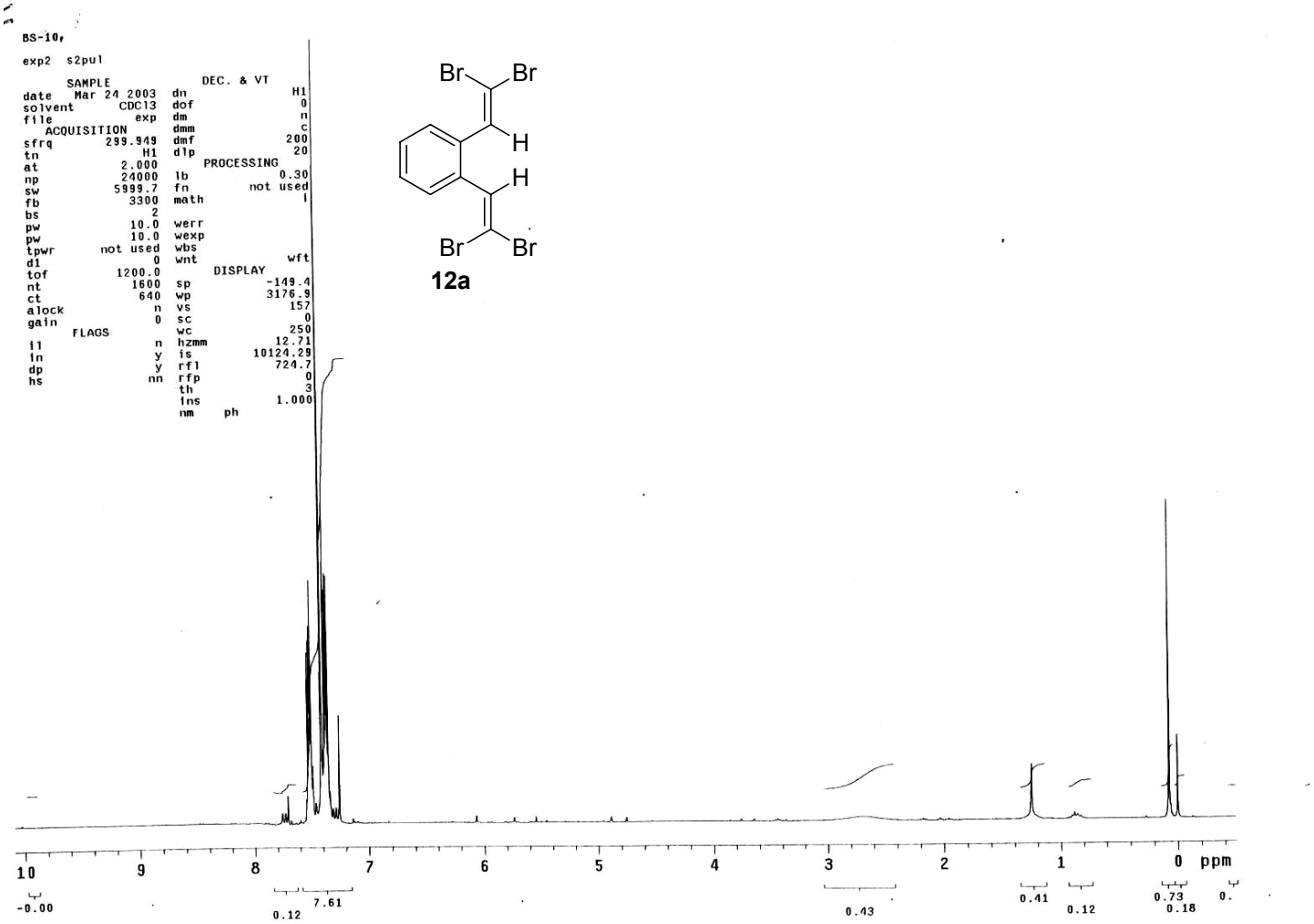

Figure S3. ^{1}H NMR spectrum ($CDCl_3$) of 1,2-bis(2,2-dibromovinyl)benzene **(12a)**

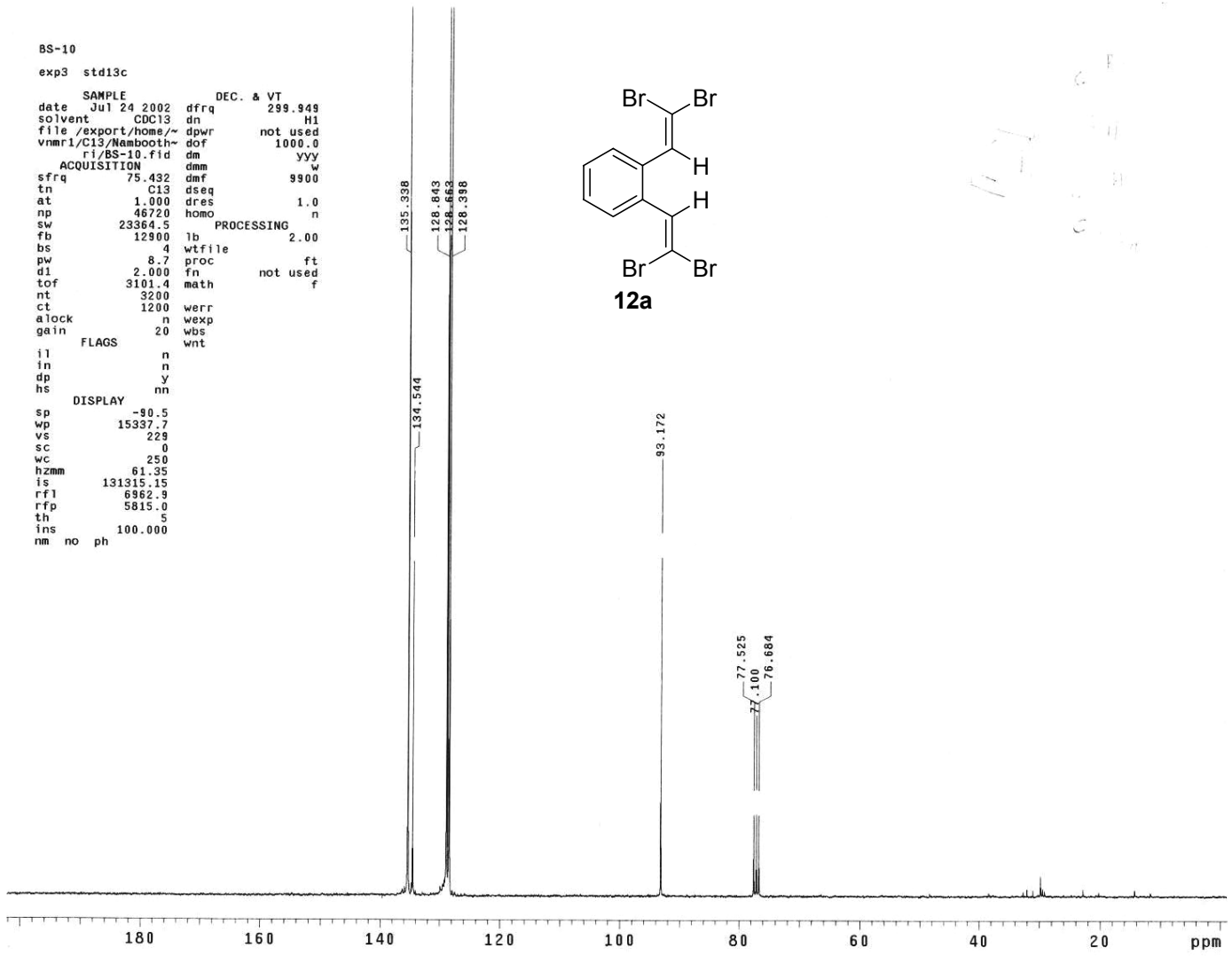

Figure S4. ^{13}C NMR spectrum ($CDCl_3$) of 1,2-bis(2,2-dibromovinyl)benzene **(12a)**

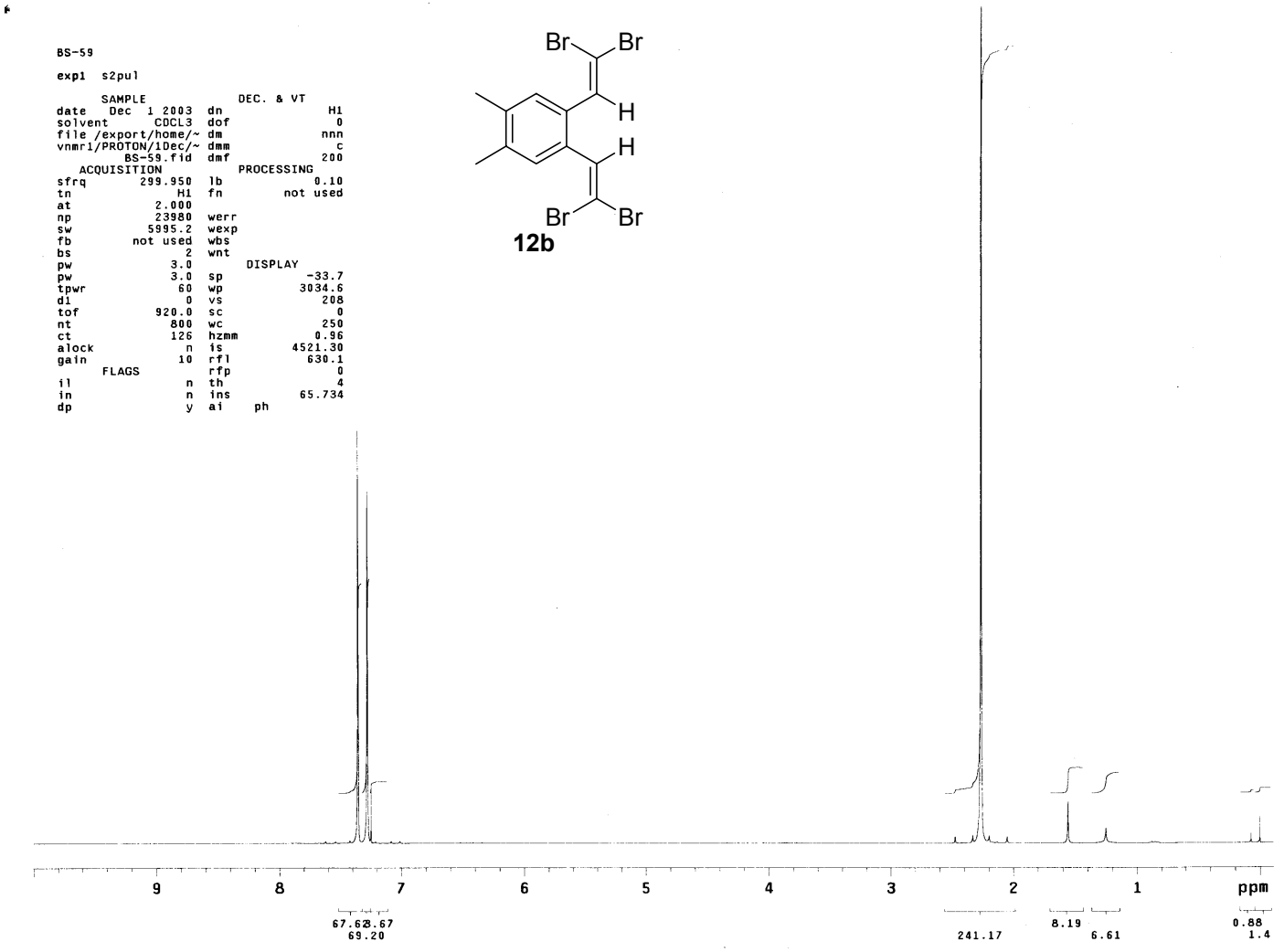

Figure S5. ^{1}H NMR spectrum ($CDCl_3$) of 1,2-bis(2,2-dibromovinyl)-4,5-dimethylbenzene **(12b)**

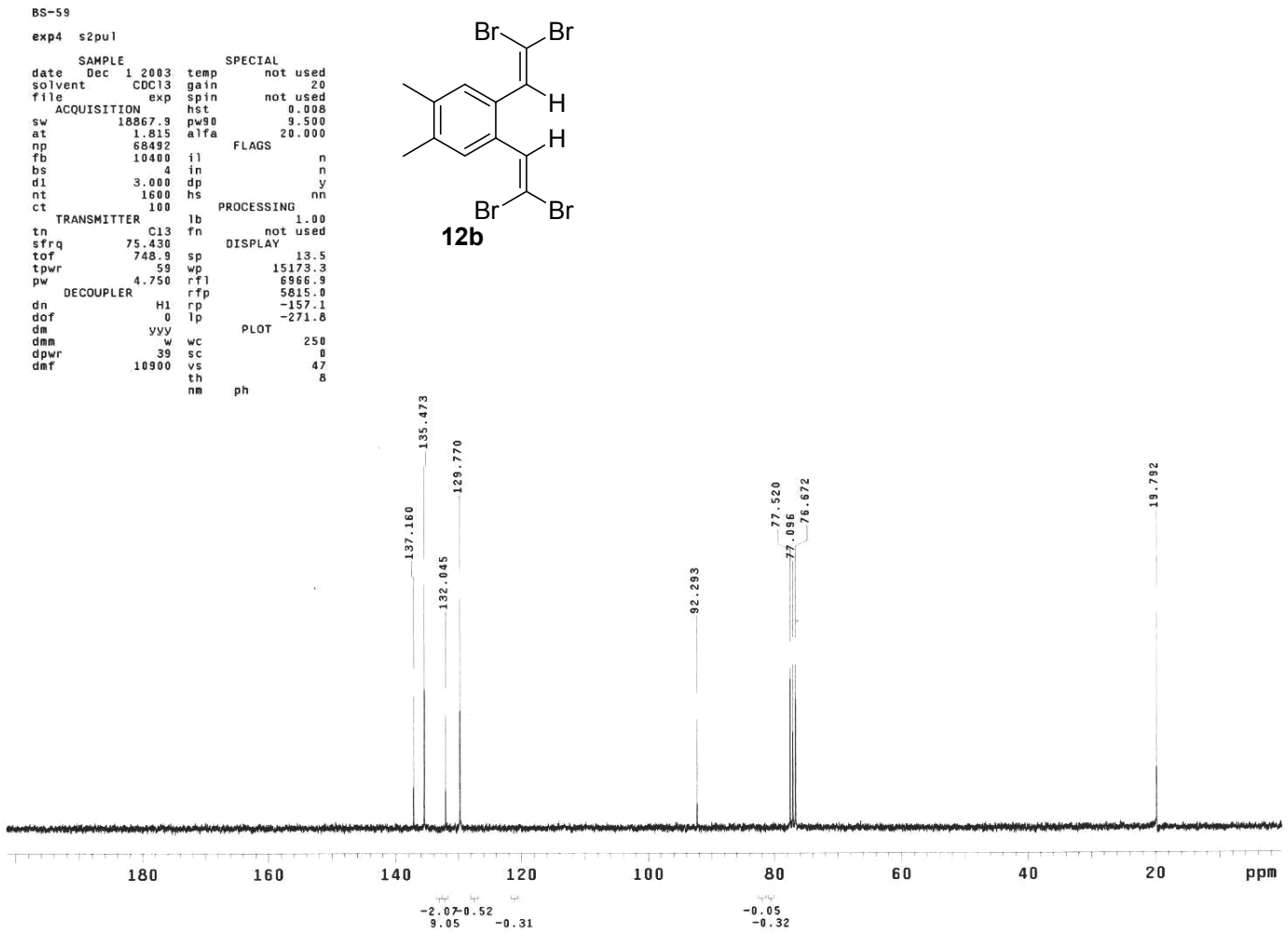

Figure S6. ^{13}C NMR spectrum ($CDCl_3$) of 1,2-bis(2,2-dibromovinyl)-4,5-dimethylbenzene **(12b)**

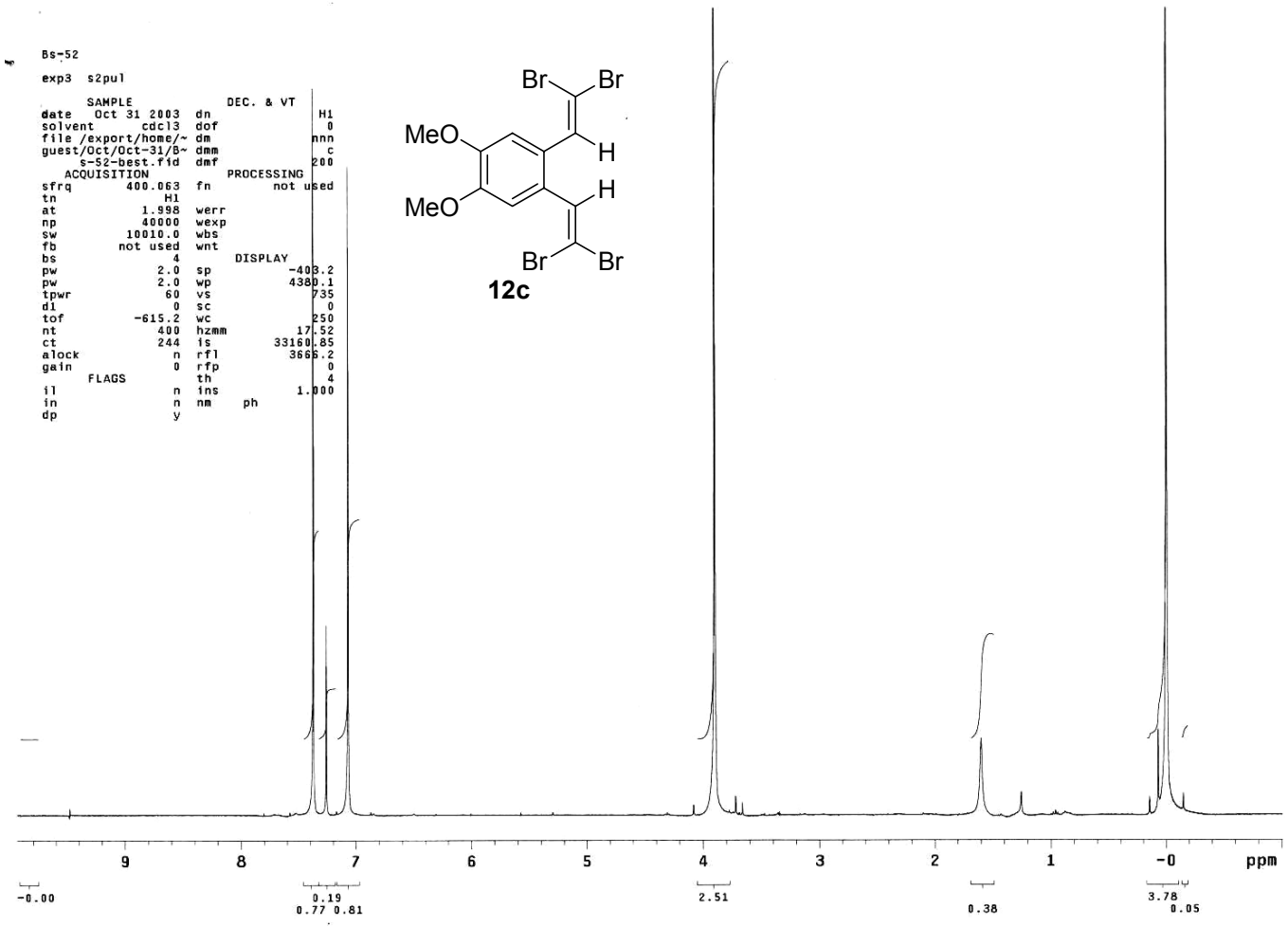

Figure S7. ^{1}H NMR spectrum ($CDCl_3$) of 1,2-bis(2,2-dibromovinyl)-4,5-dimethoxybenzene **(12c)**

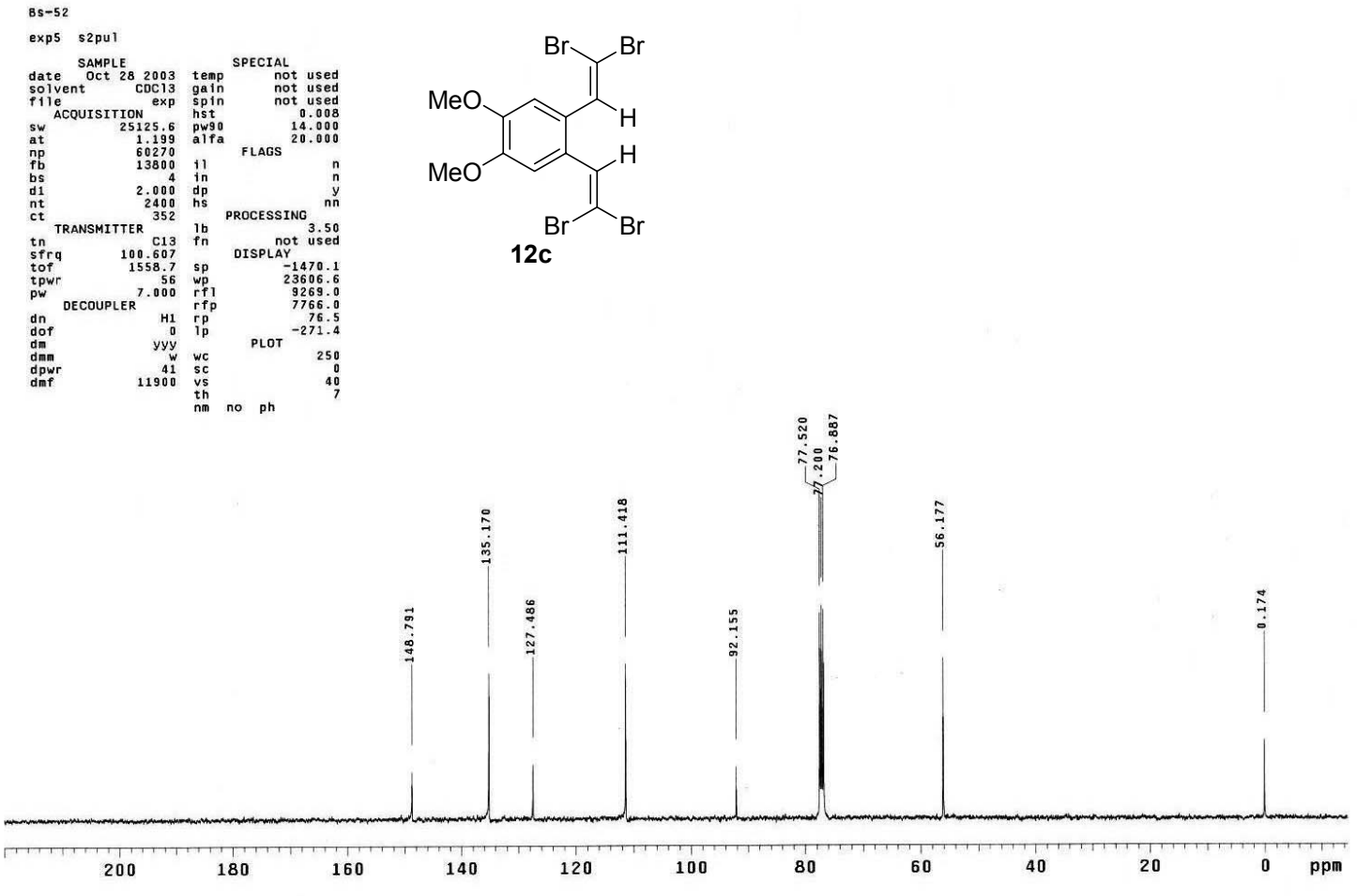

Figure S8. ^{13}C NMR spectrum ($CDCl_3$) of 1,2-bis(2,2-dibromovinyl)-4,5-dimethoxybenzene **(12c)**

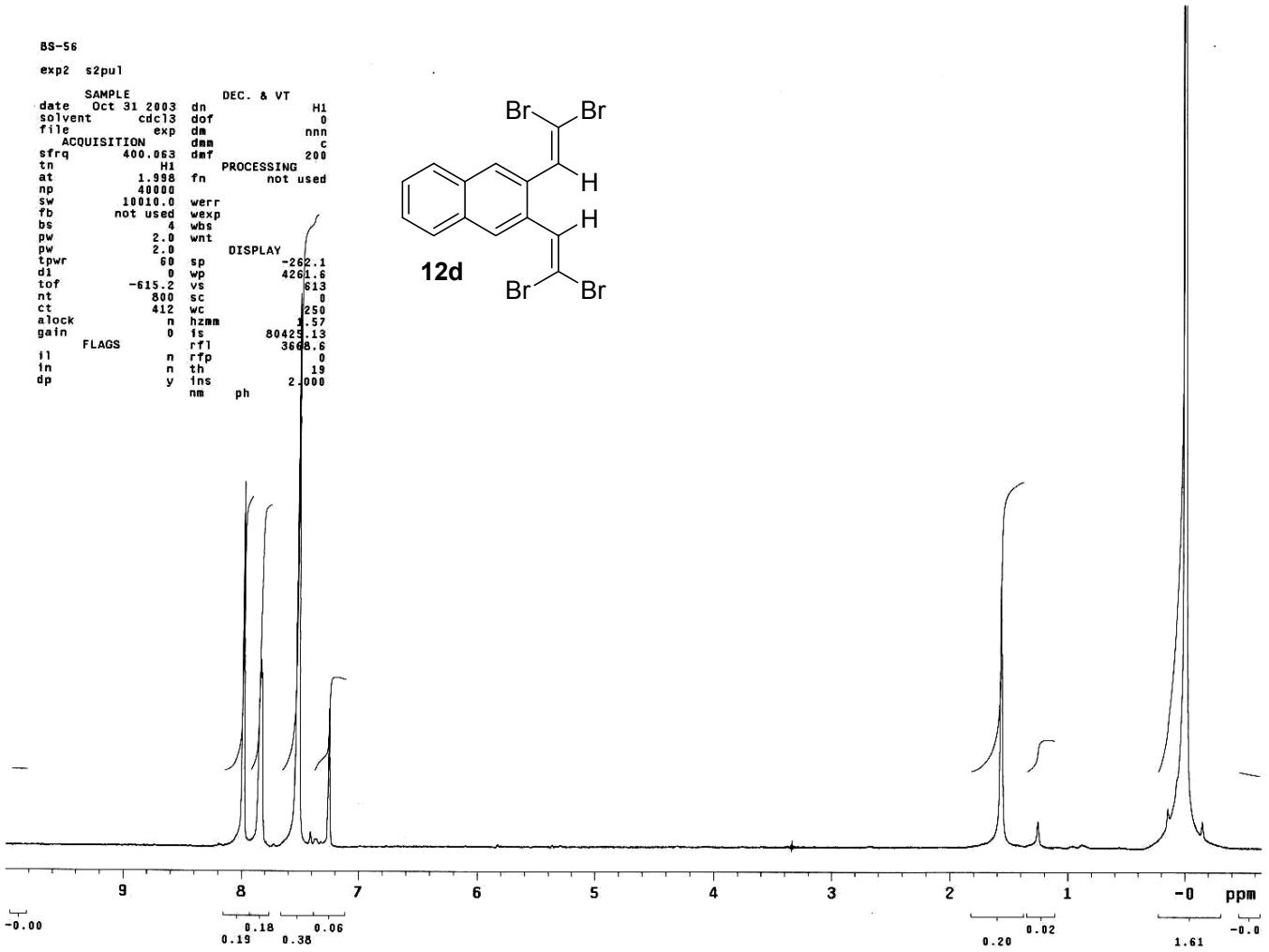

Figure S9. ^{1}H NMR spectrum ($CDCl_3$) of 2,3-bis(2,2-dibromovinyl)naphthalene **(12d)**

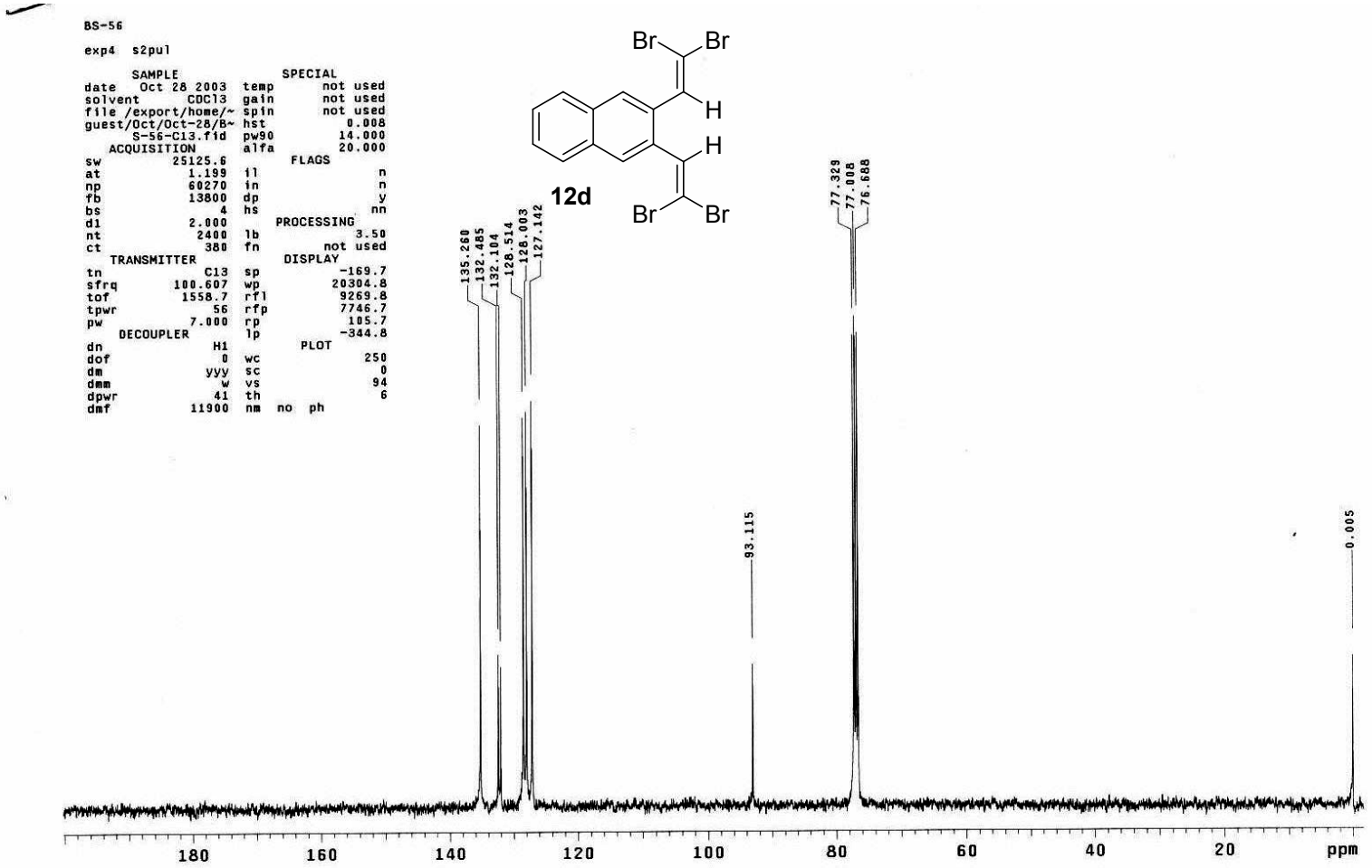

Figure S10. ^{13}C NMR spectrum ($CDCl_3$) of 2,3-bis(2,2-dibromovinyl)naphthalene **(12d)**

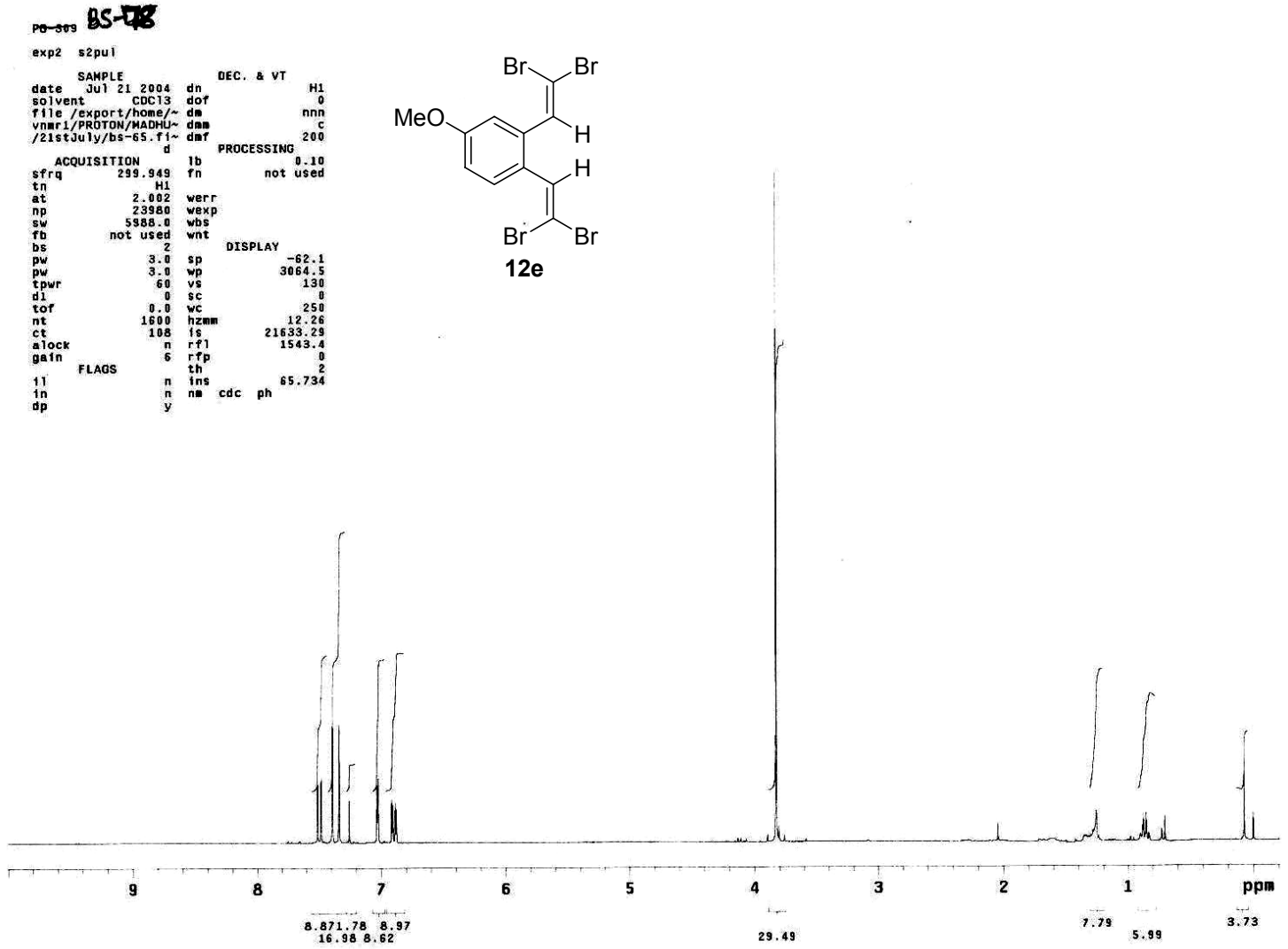

Figure S11. ^{1}H NMR spectrum ($CDCl_3$) of 1,2-bis(2,2-dibromovinyl)-4-methoxybenzene **(12e)**

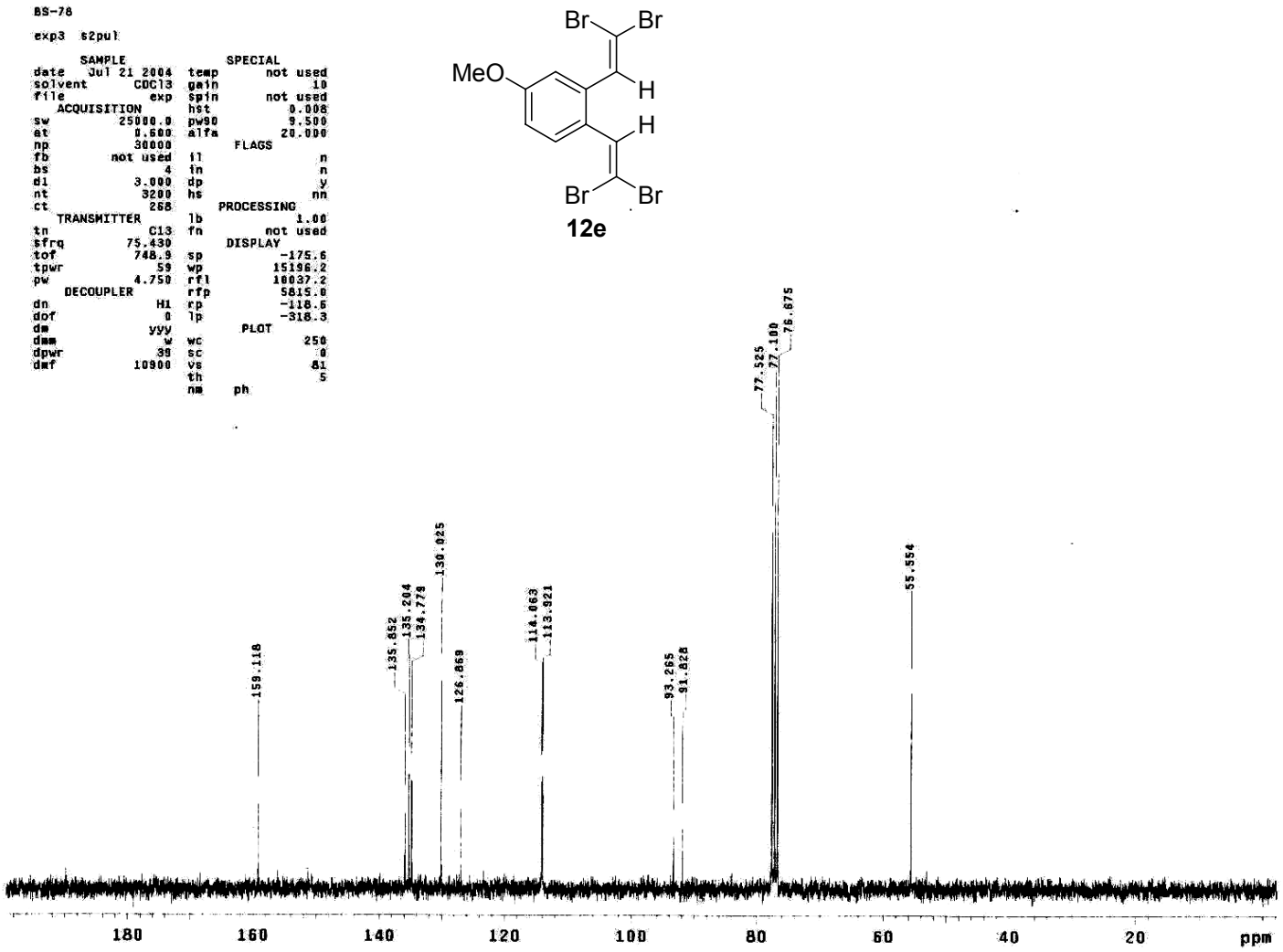

Figure S12. ^{13}C NMR spectrum ($CDCl_3$) of 1,2-bis(2,2-dibromovinyl)-4-methoxybenzene **(12e)**

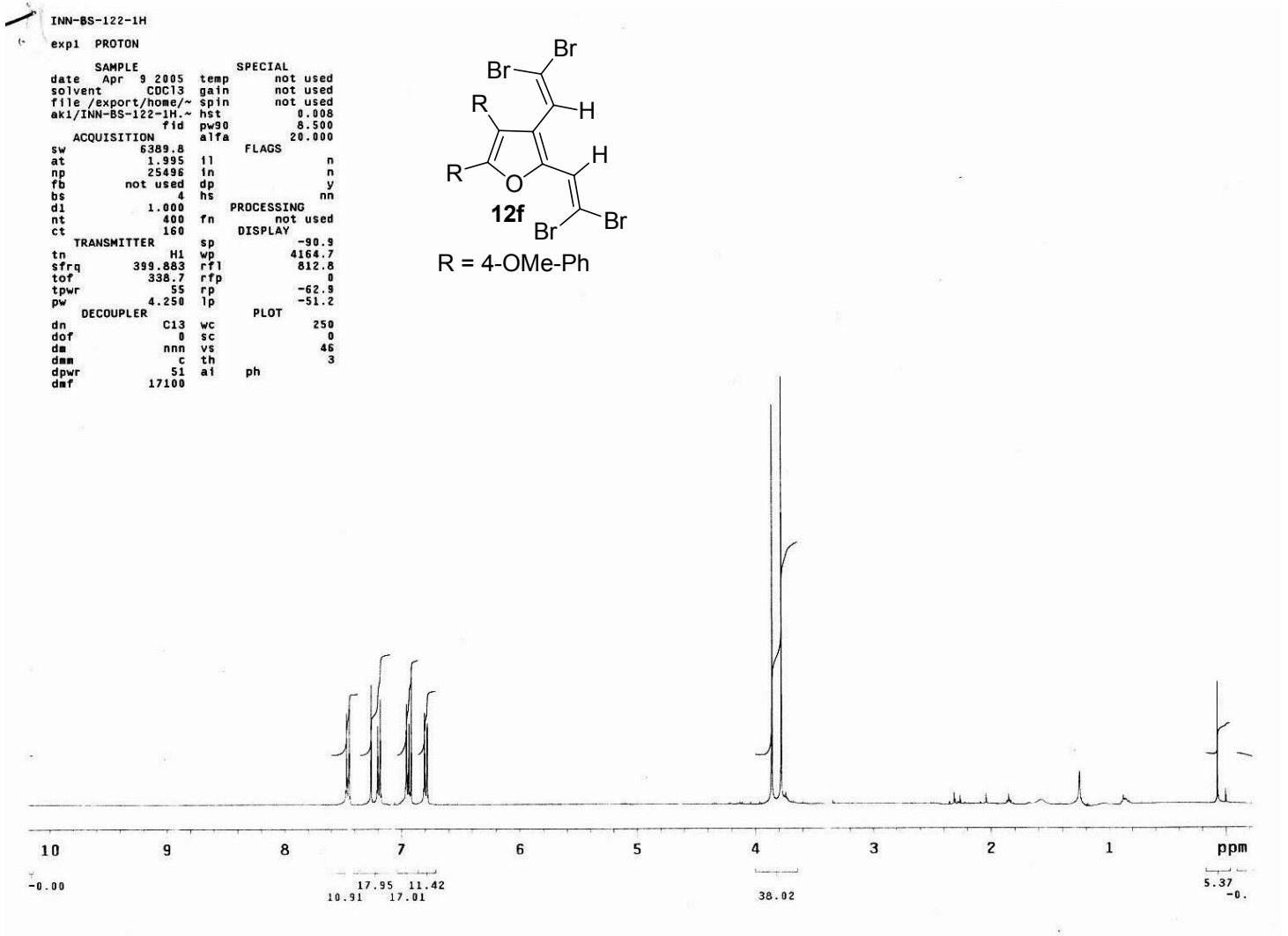

Figure S13. ^{1}H NMR spectrum ($CDCl_3$) of 2,3-bis(2,2-dibromovinyl)-4,5-bis(4-methoxyphenyl)furan **(12f)**

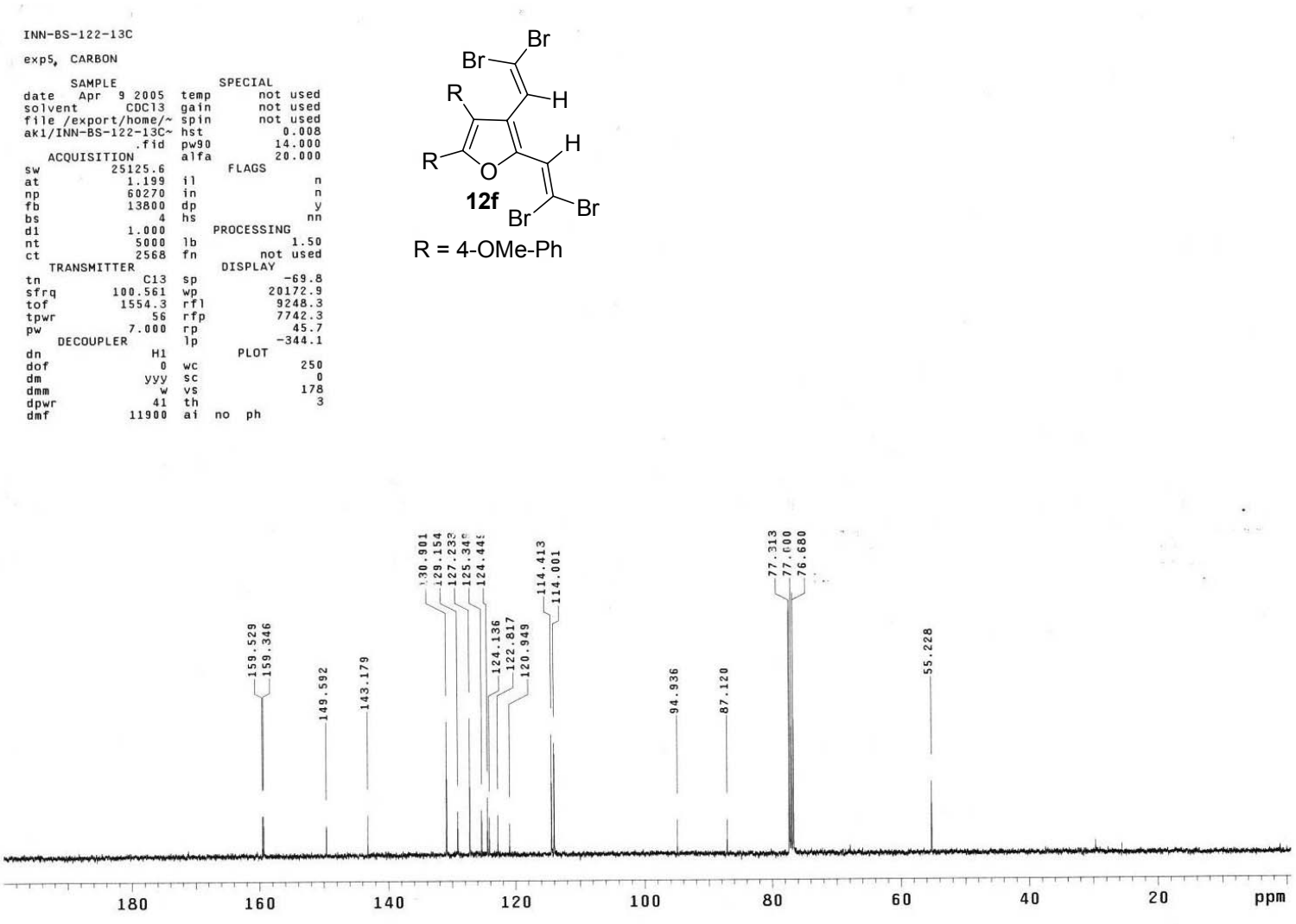

Figure S14. ^{13}C NMR spectrum ($CDCl_3$) of 2,3-bis(2,2-dibromovinyl)-4,5-bis(4-methoxyphenyl)furan **(12f)**

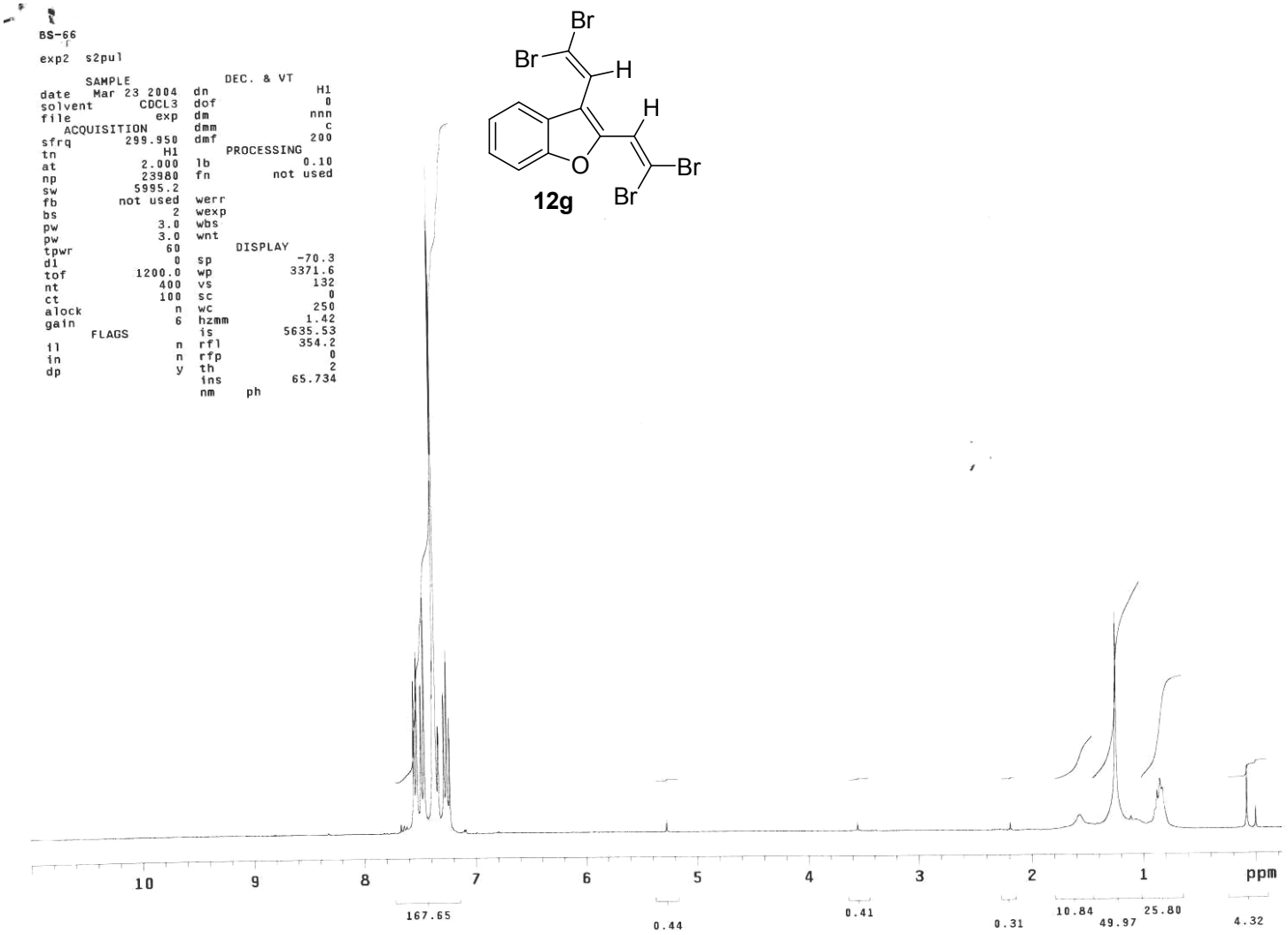

Figure S15. ^{1}H NMR spectrum ($CDCl_3$) of 2,3-bis(2,2-dibromovinyl)benzofuran **(12g)**

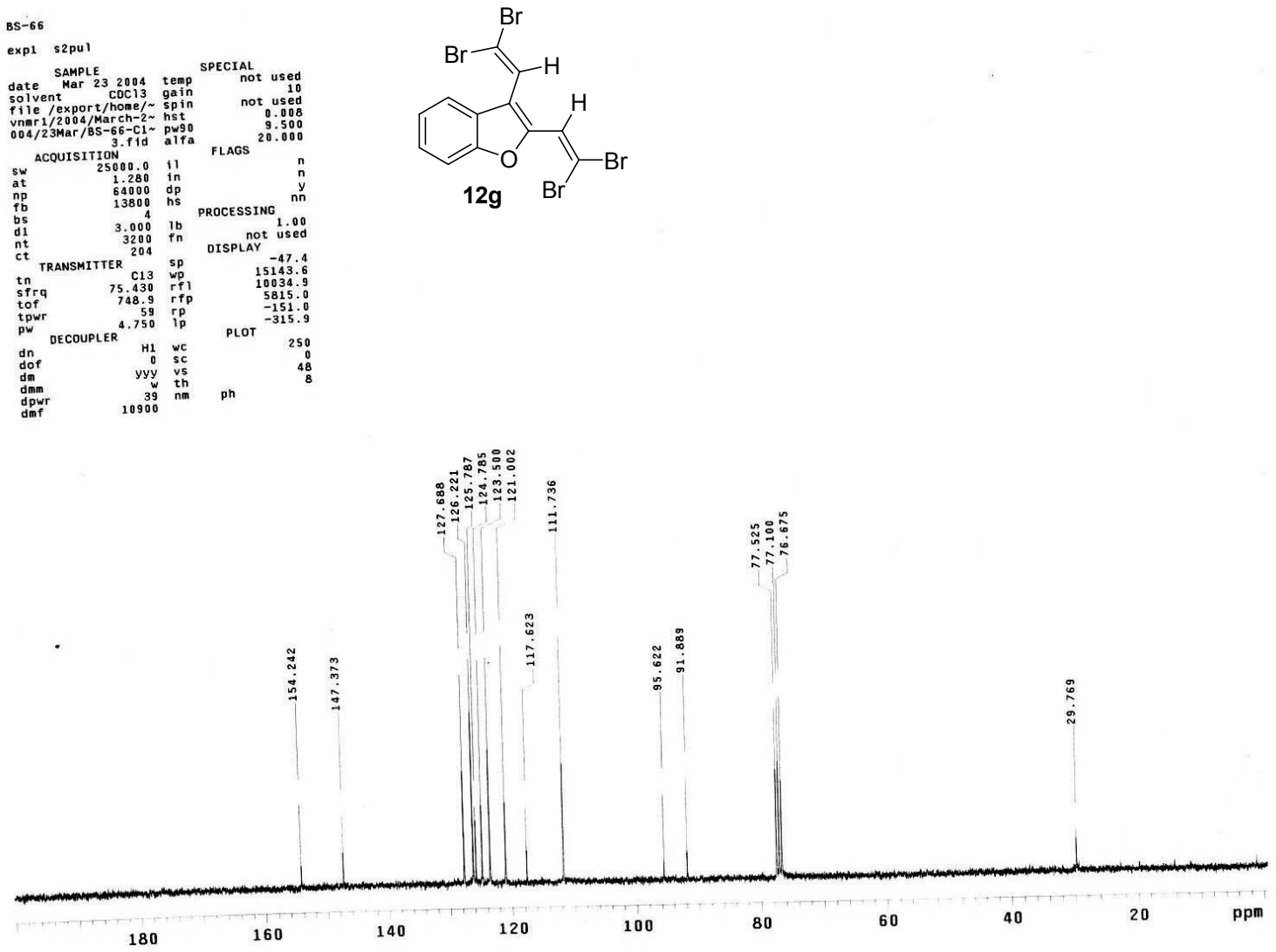

Figure S16. ^{13}C NMR spectrum ($CDCl_3$) of 2,3-bis(2,2-dibromovinyl)benzofuran **(12g)**

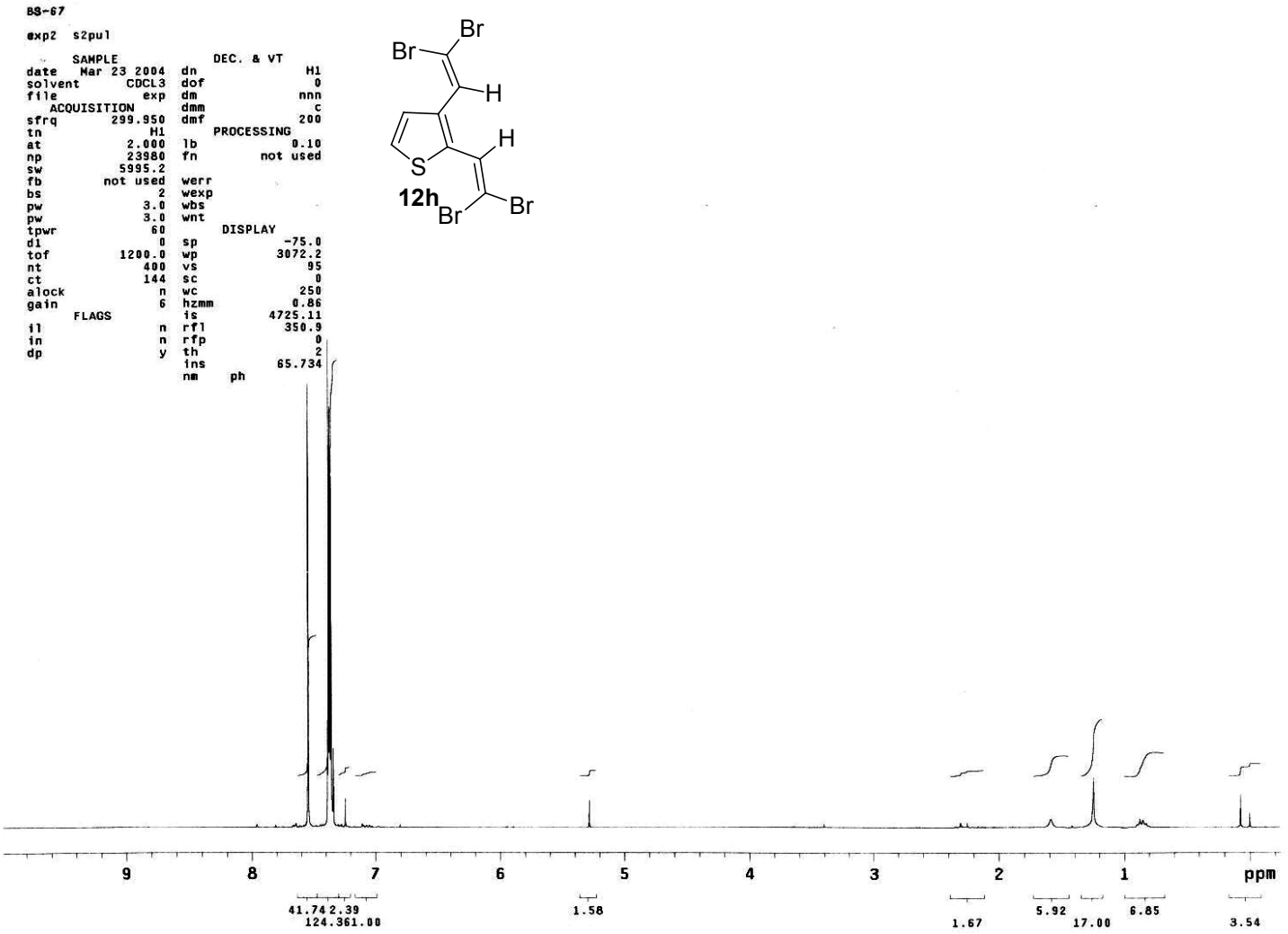

Figure S17. ^{1}H NMR spectrum ($CDCl_3$) of 2,3-bis(2,2-dibromovinyl)thiophene **(12h)**

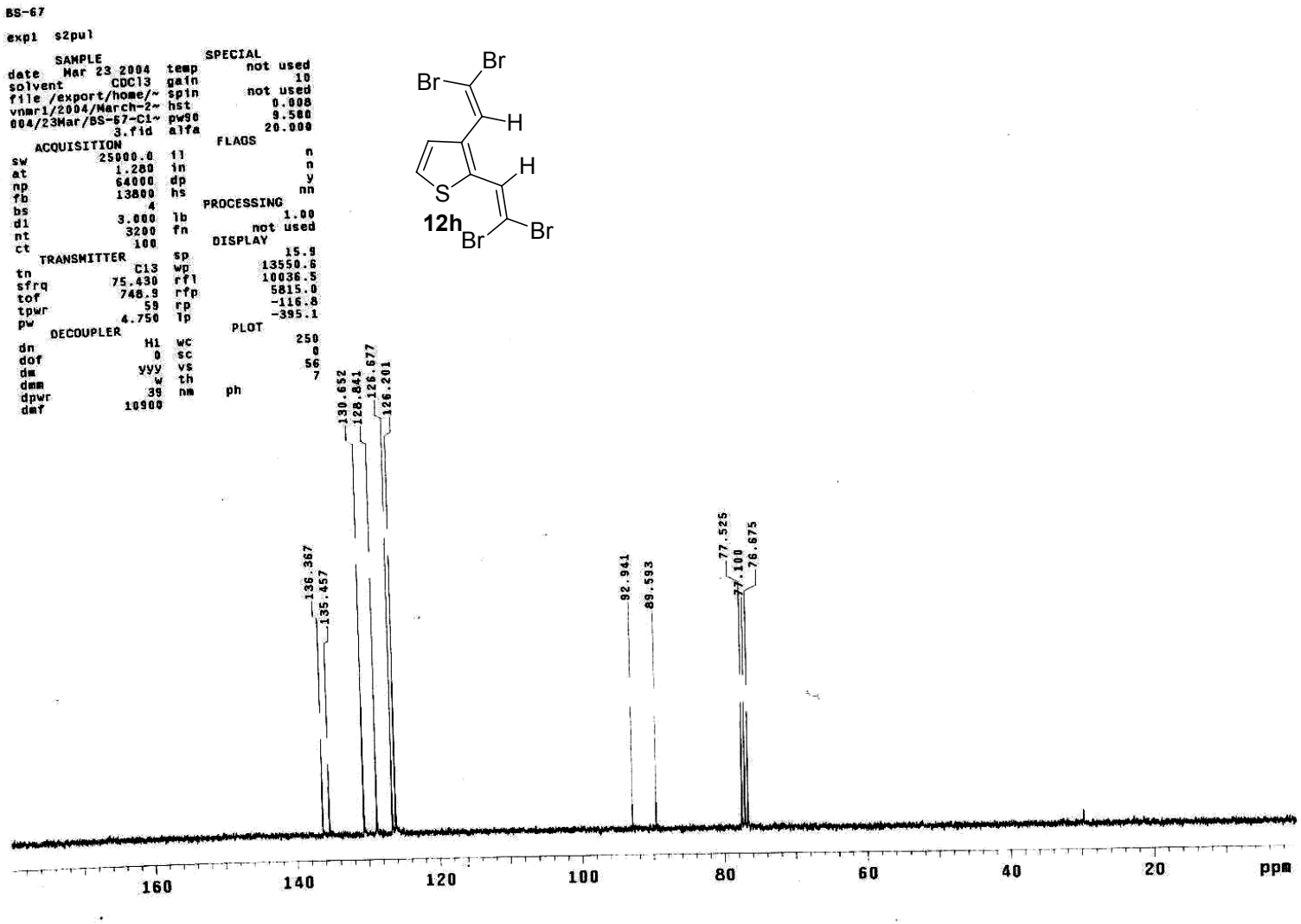

Figure S18. ^{13}C NMR spectrum ($CDCl_3$) of 2,3-bis(2,2-dibromovinyl)thiophene **(12h)**

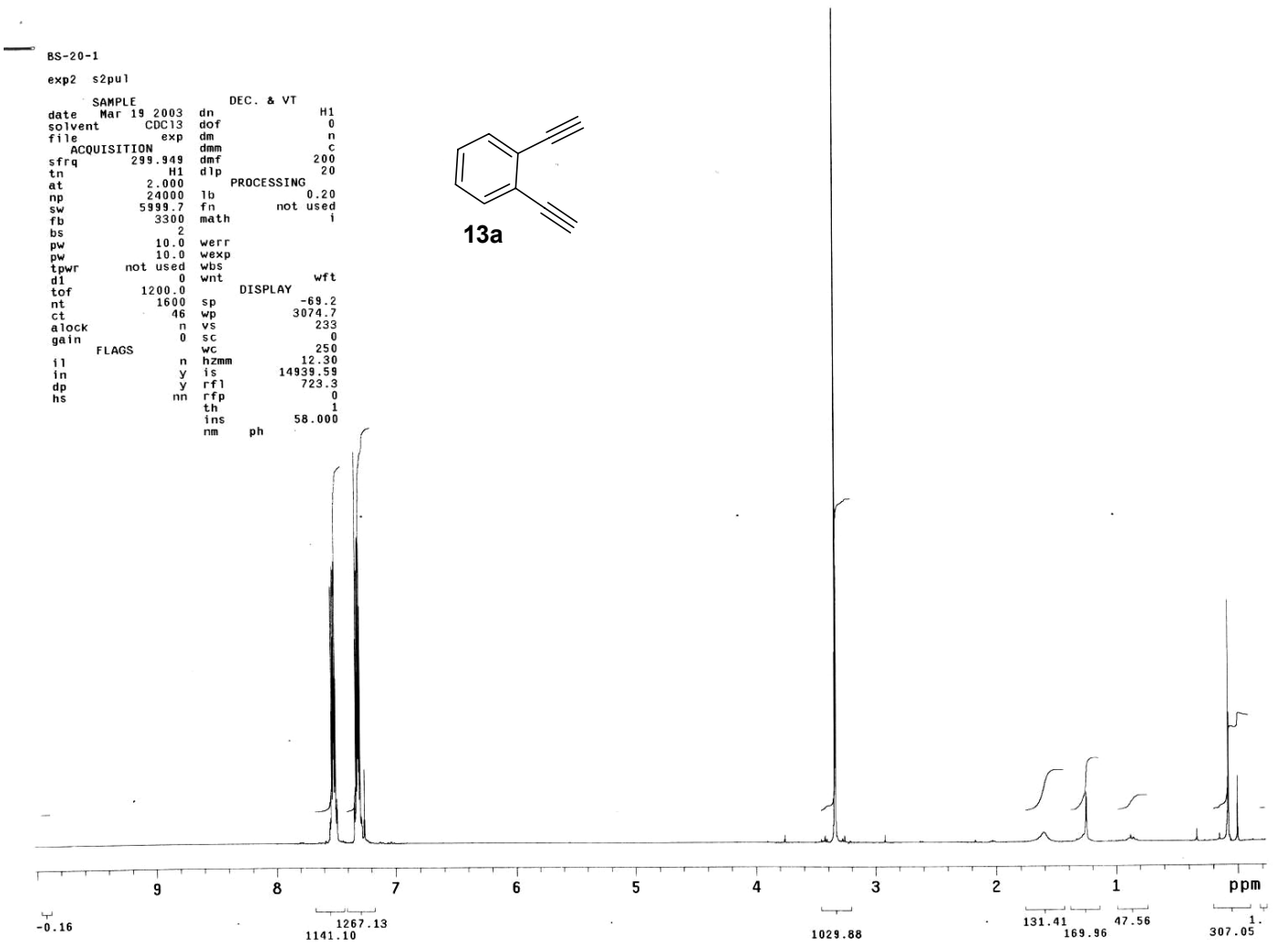

Figure S19. ^{1}H NMR spectrum ($CDCl_3$) of 1,2diethynylbenzene **(13a)**

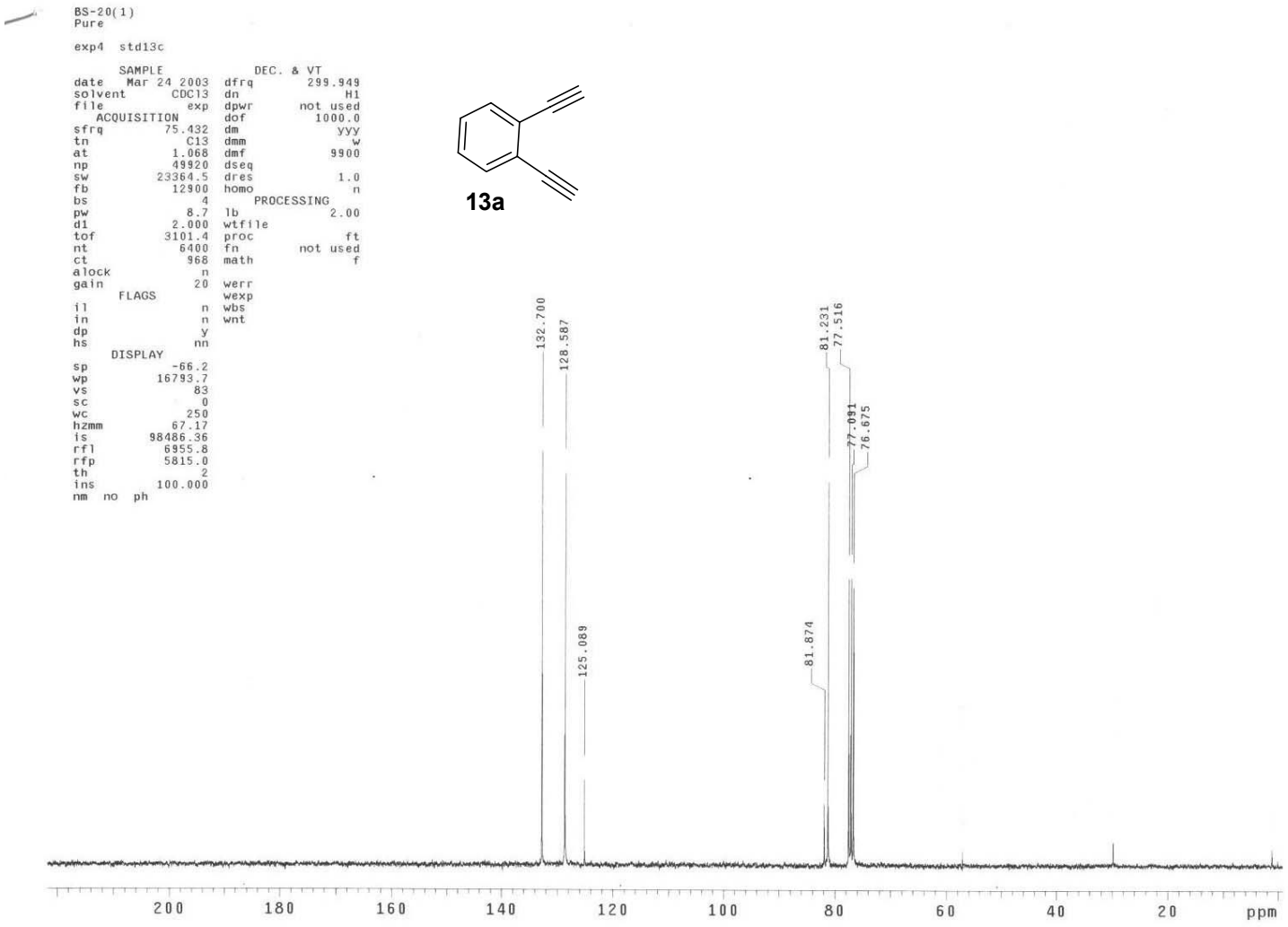

Figure S20. ^{13}C NMR spectrum ($CDCl_3$) of 1,2diethynylbenzene **(13a)**

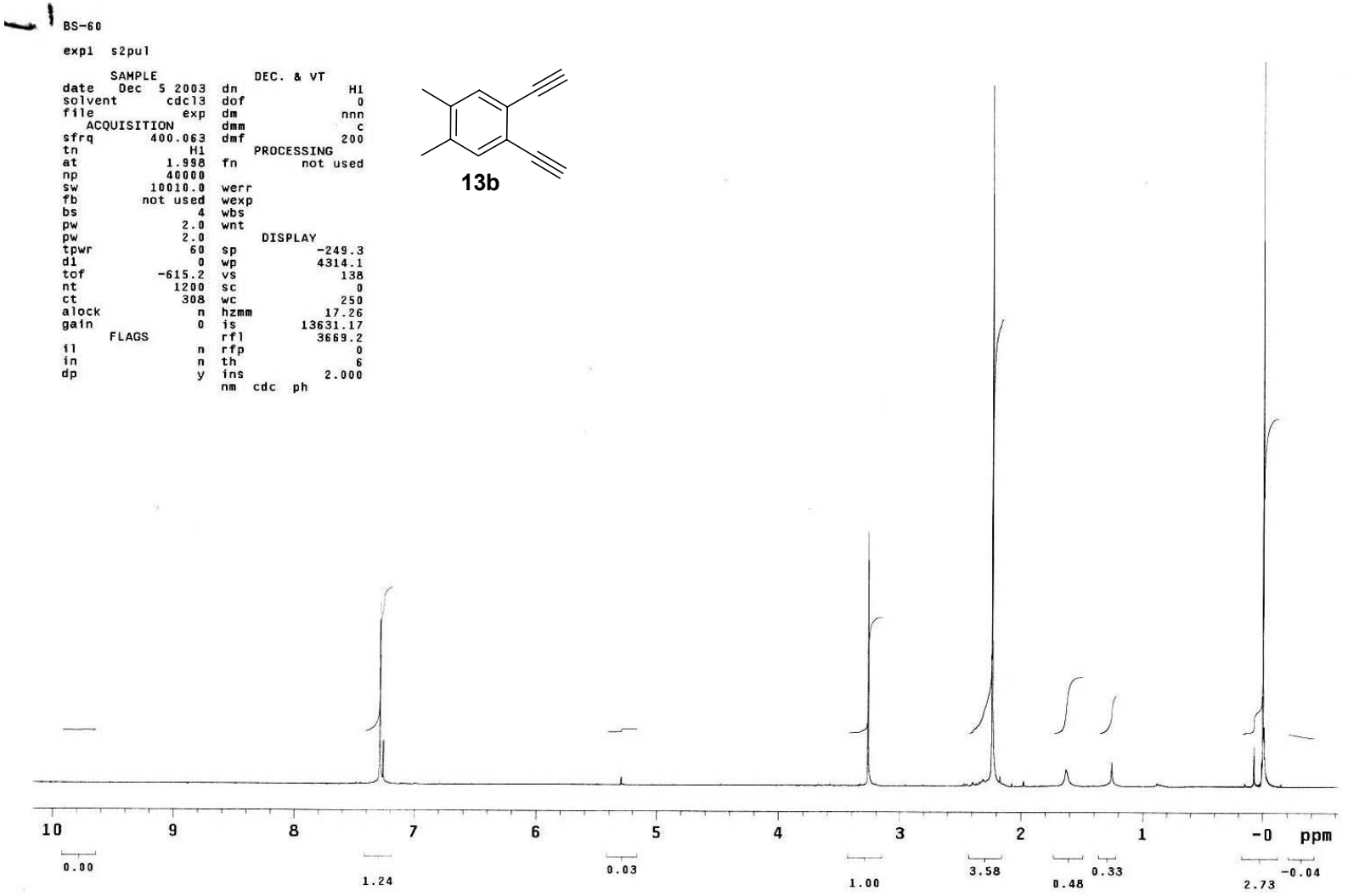

Figure S21. ^{1}H NMR spectrum ($CDCl_3$) of 1,2-diethynyl-4,5-dimethylbenzene **(13b)**

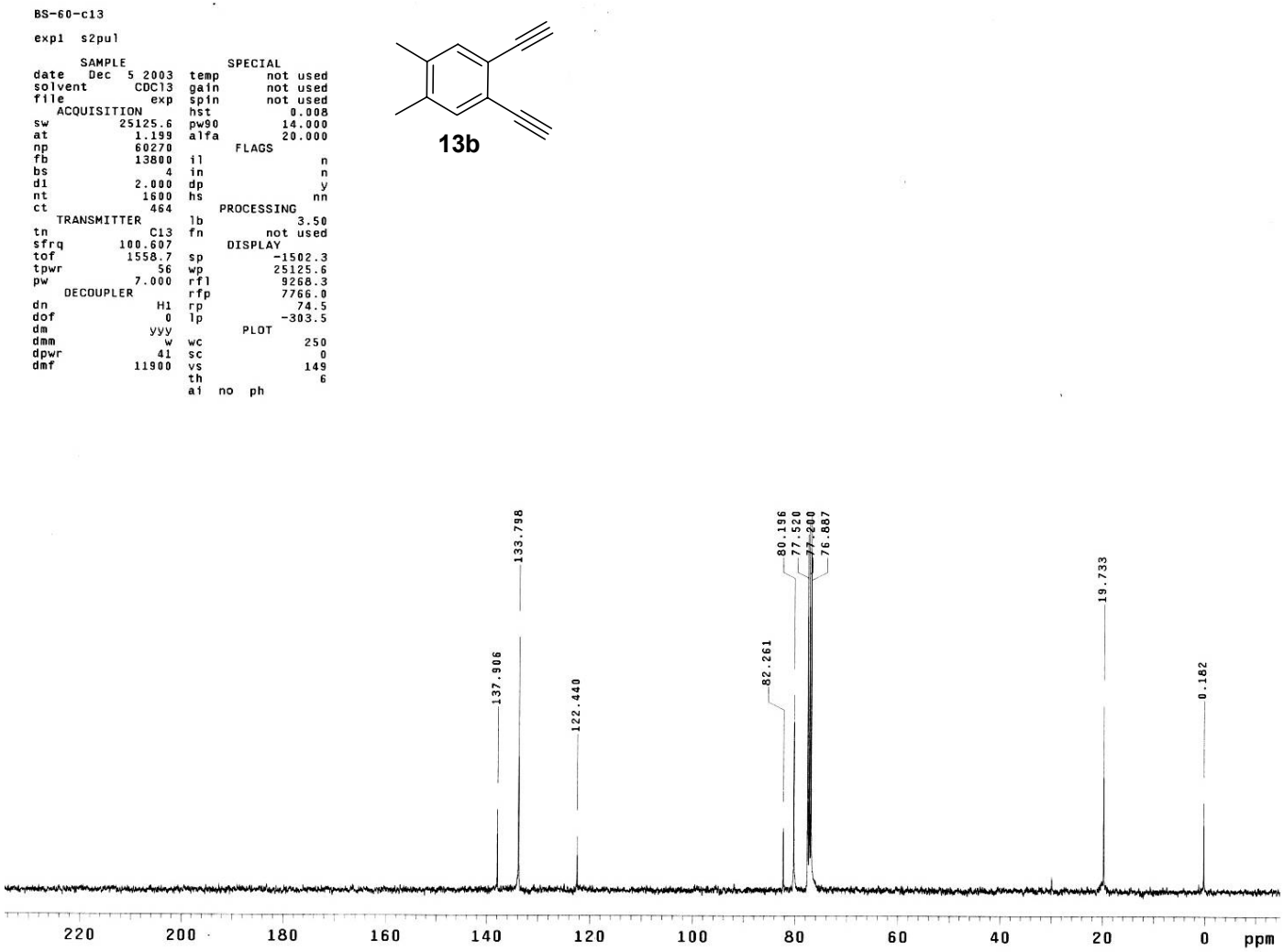

Figure S22. ^{13}C NMR spectrum ($CDCl_3$) of 1,2-diethynyl-4,5-dimethylbenzene **(13b)**

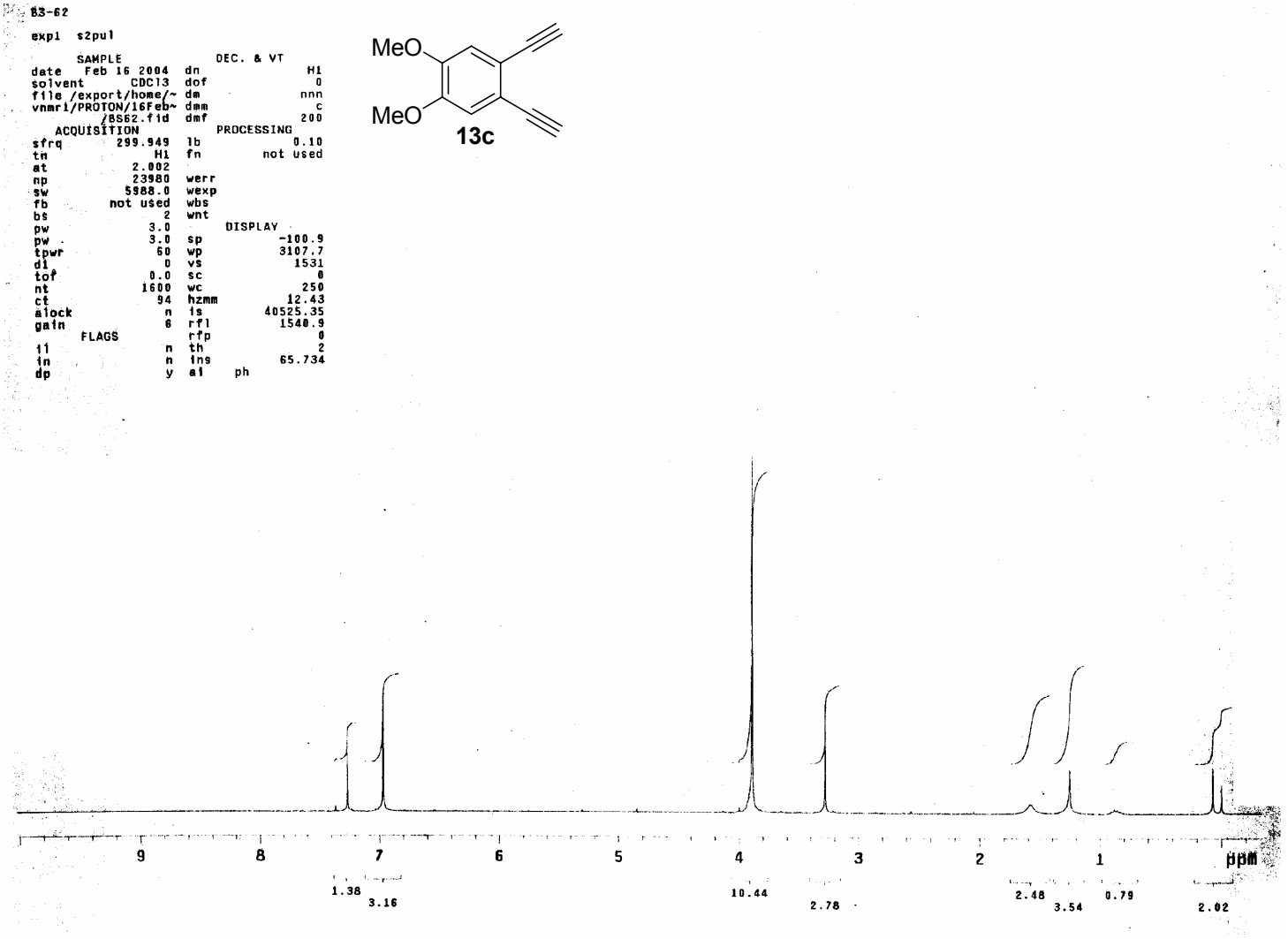

Figure S23. ^{1}H NMR spectrum ($CDCl_3$) of 1,2-diethynyl-4,5-dimethoxylbenzene **(13c)**

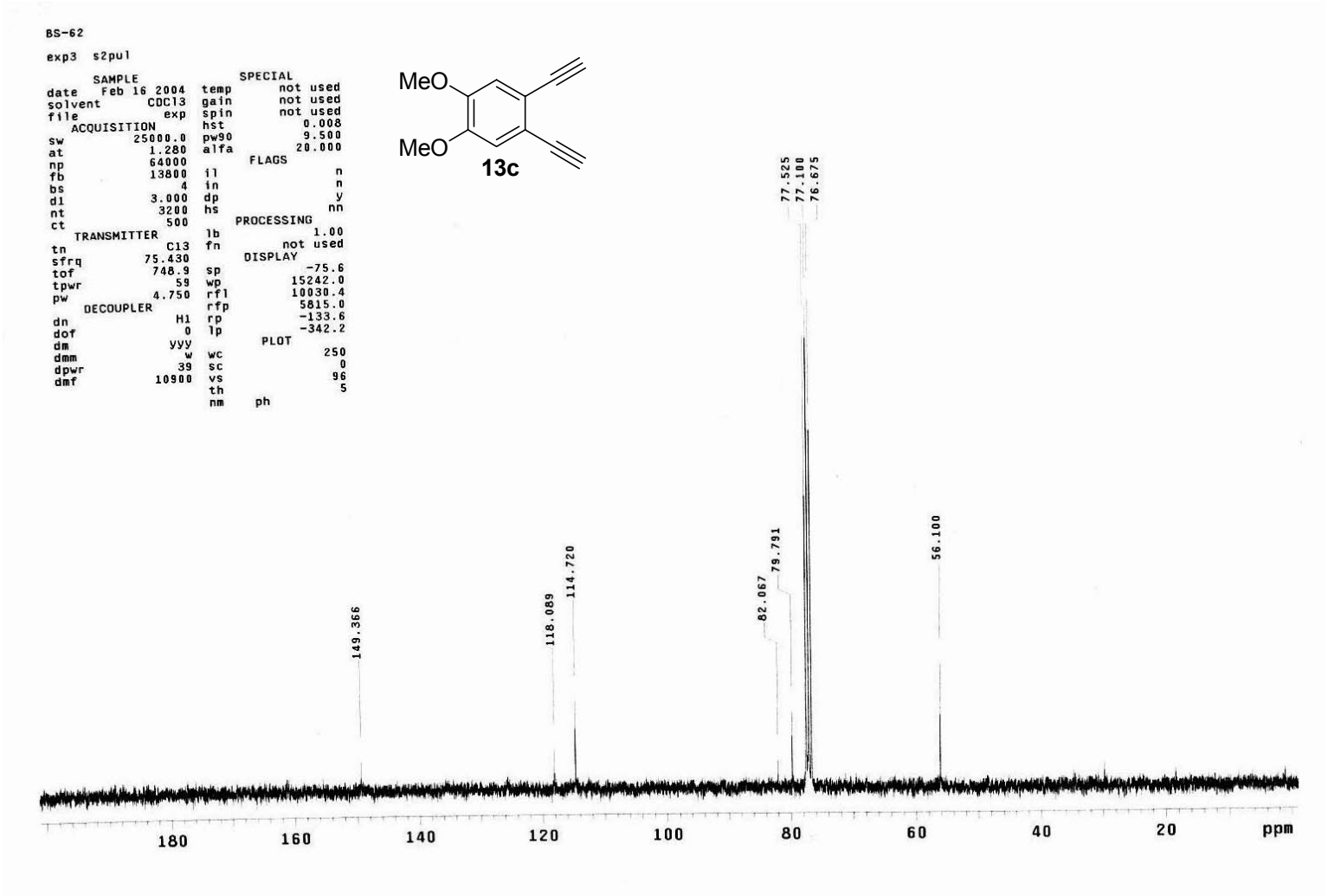

Figure S24. ^{13}C NMR spectrum ($CDCl_3$) of 1,2-diethynyl-4,5-dimethoxylbenzene **(13c)**

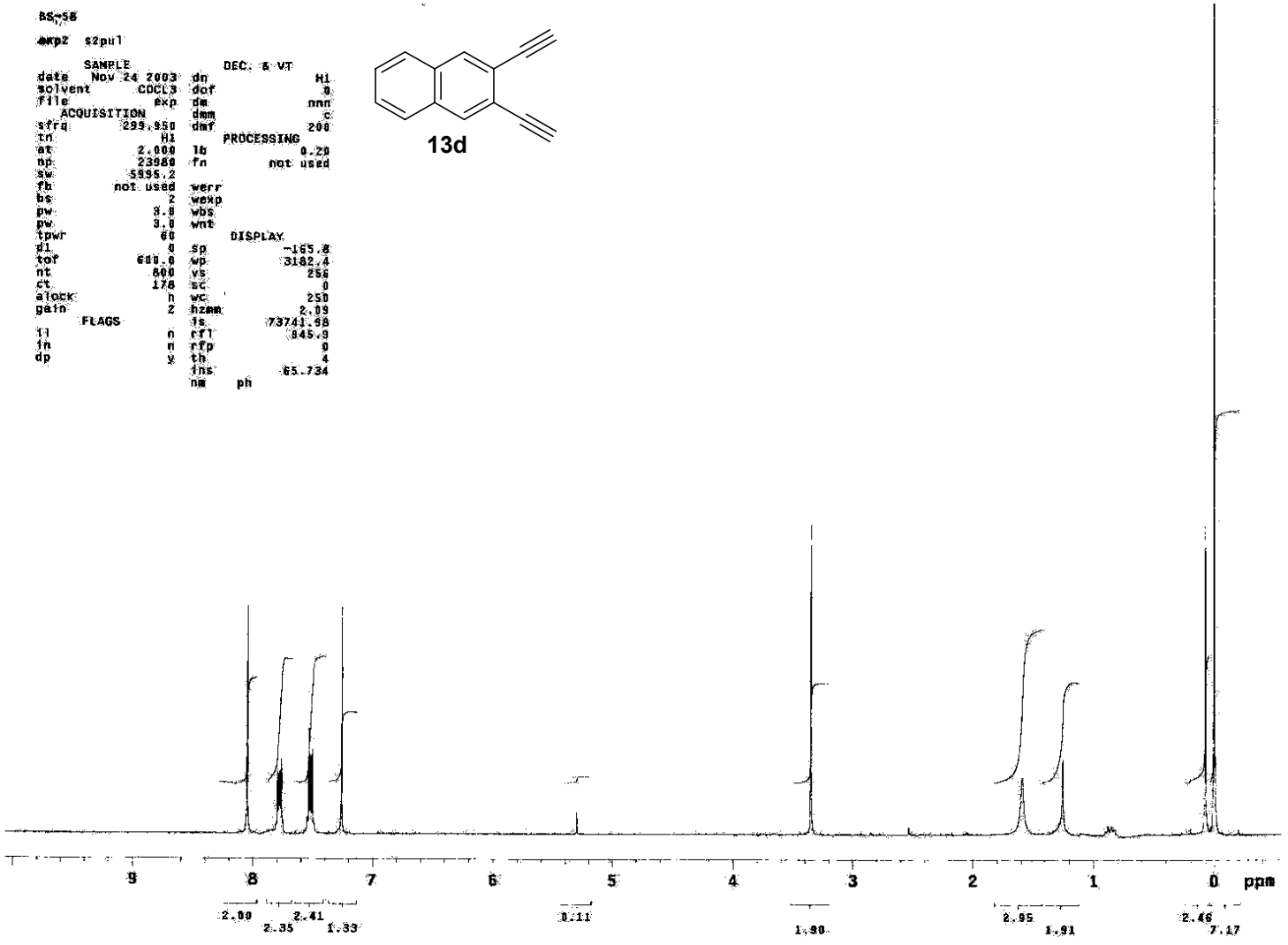

Figure S25. ^{1}H NMR spectrum ($CDCl_3$) of 2,3-diethynylnaphthalene **(13d)**

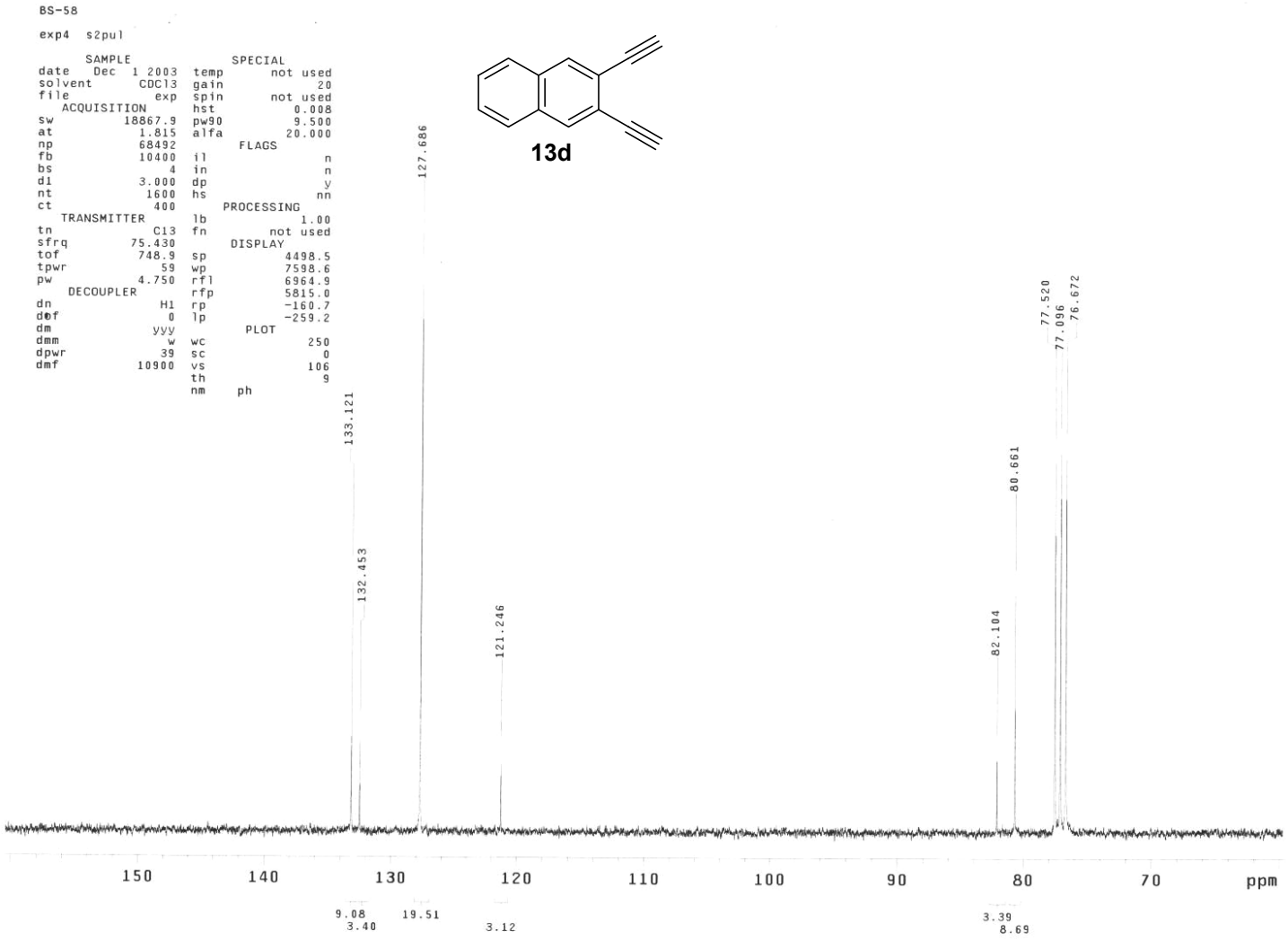

Figure S26. ^{13}C NMR spectrum ($CDCl_3$) of 2,3-diethynylnaphthalene **(13d)**

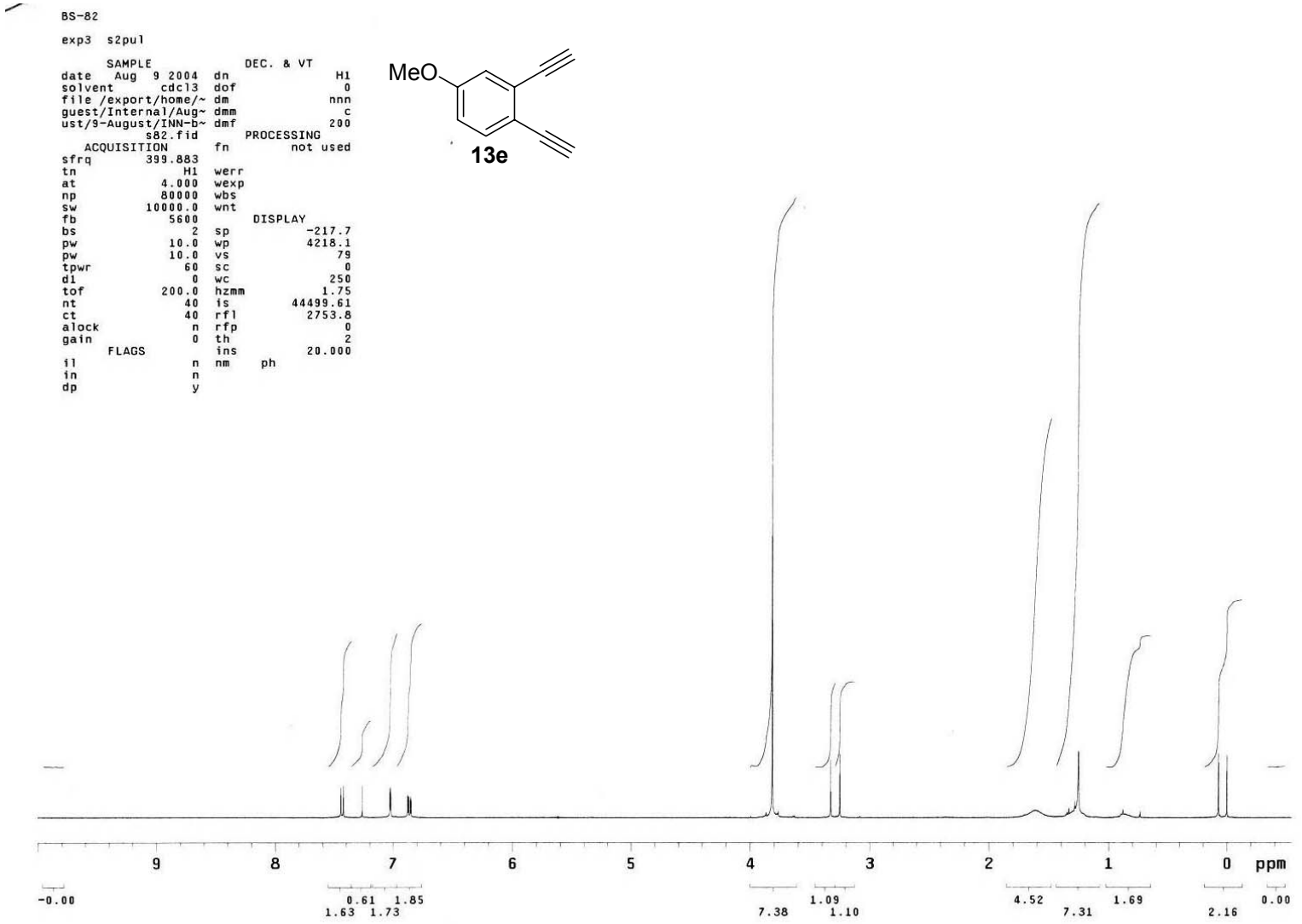

Figure S27. ^{1}H NMR spectrum ($CDCl_3$) of 1,2-diethynyl-4-methoxybenzene **(13e)**

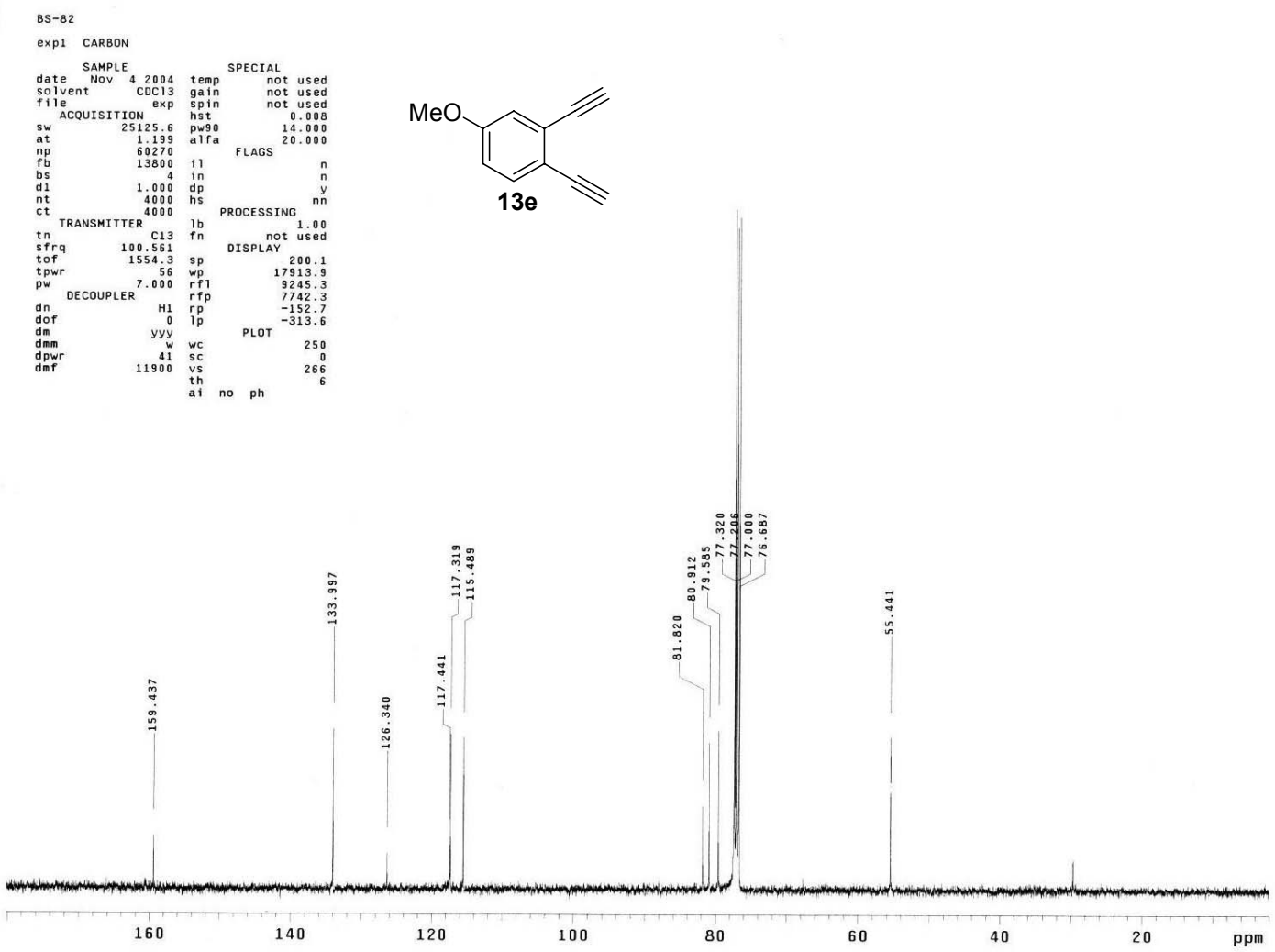

Figure S28. ^{13}C NMR spectrum ($CDCl_3$) of 1,2-diethynyl-4-methoxybenzene **(13e)**

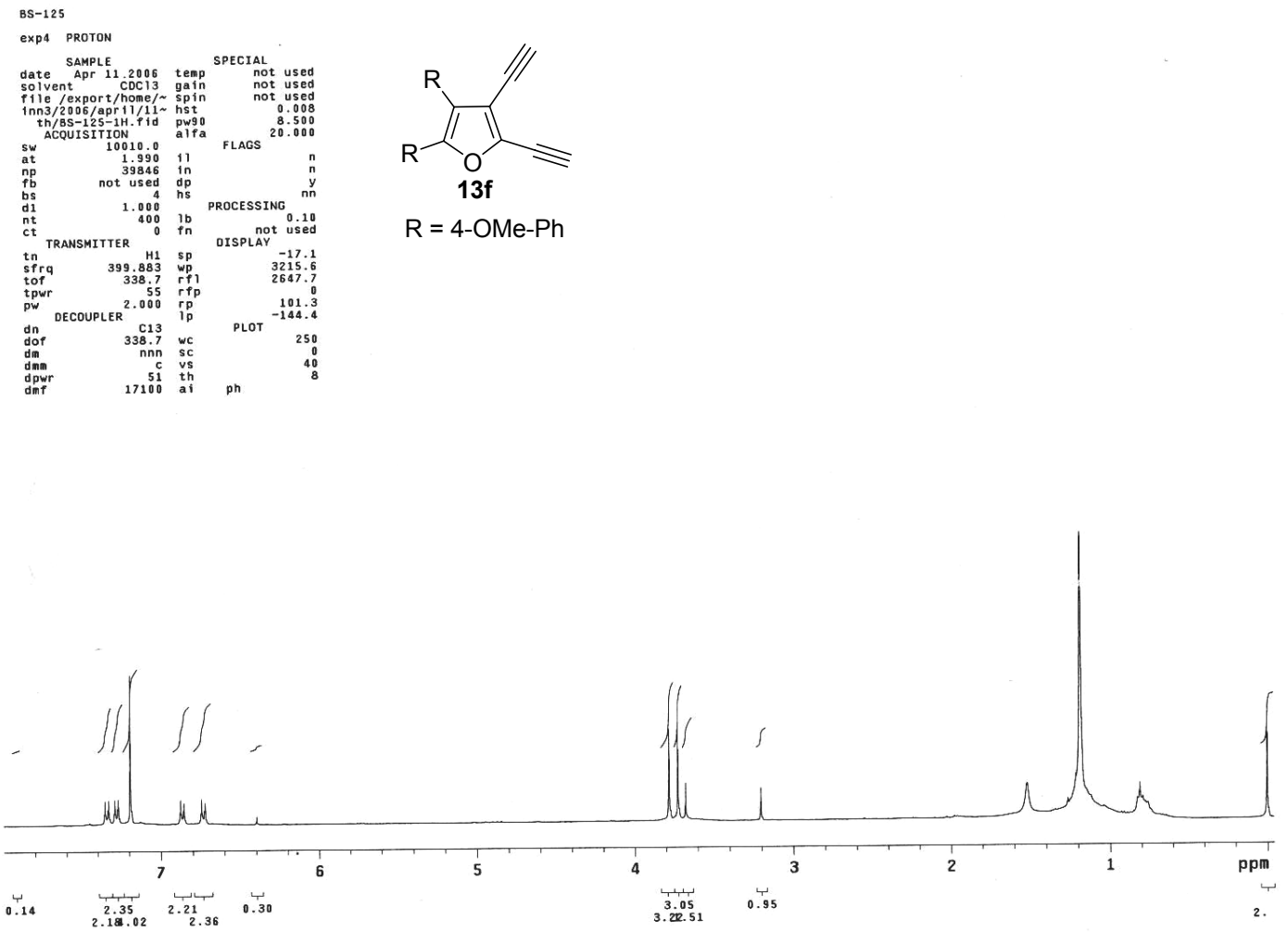

Figure S29. ^{1}H NMR spectrum ($CDCl_3$) of 2,3-diethynyl-4,5-bis(4-methoxyphenyl)furan **(13f)**

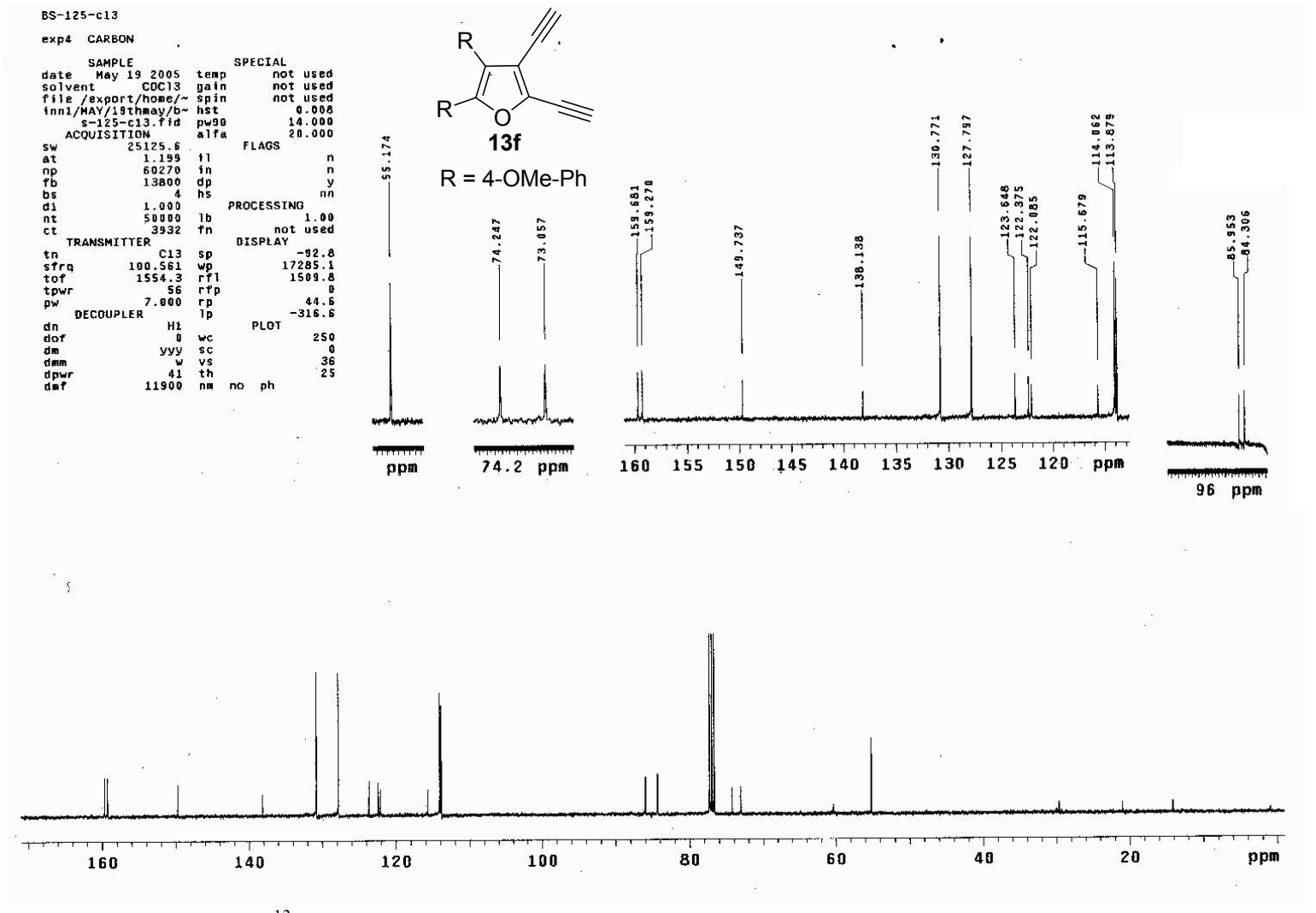

Figure S30. ^{13}C NMR spectrum ($CDCl_3$) of 2,3-diethynyl-4,5-bis(4-methoxyphenyl)furan **(13f)**

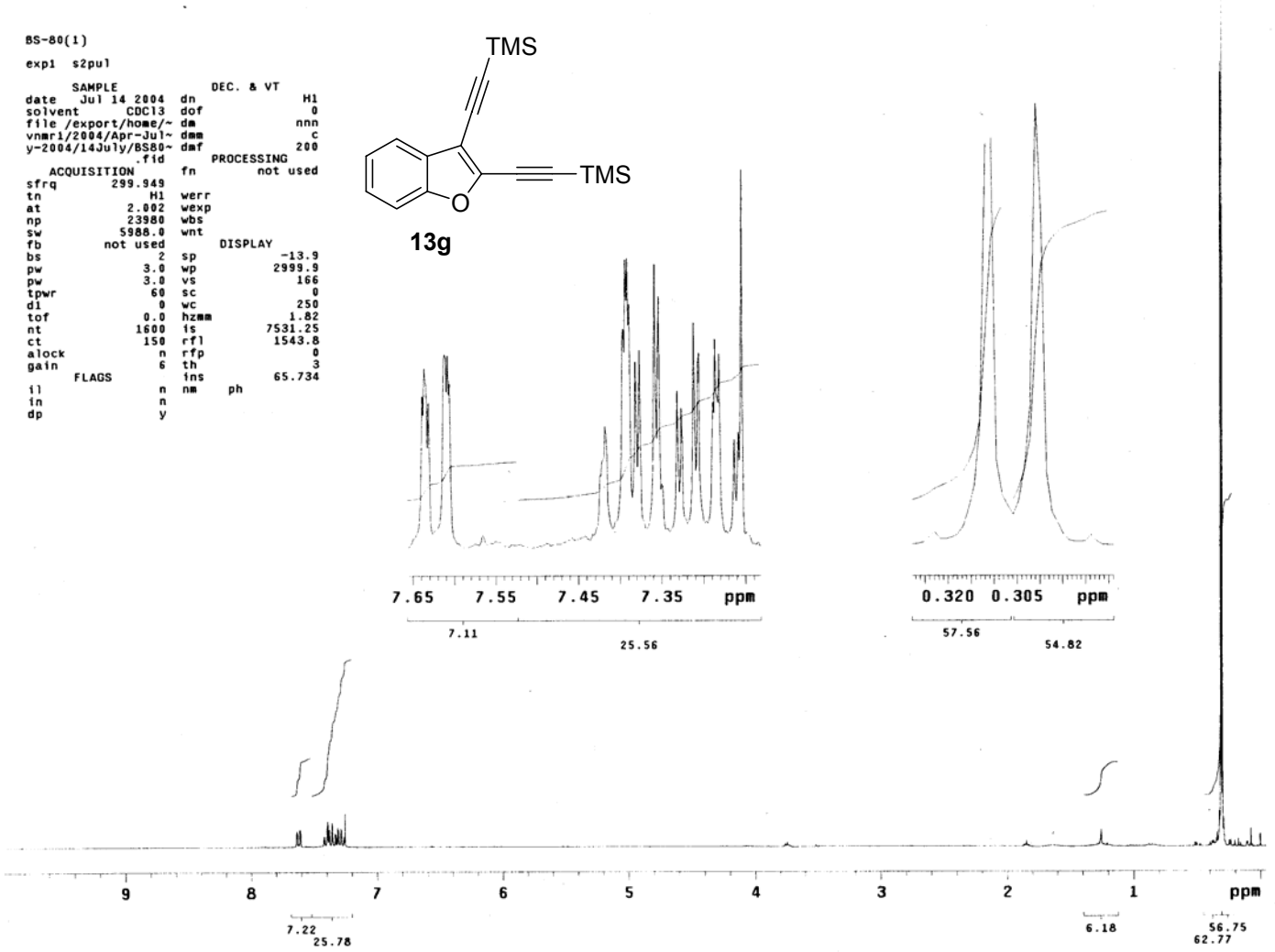

Figure S31. ^{1}H NMR spectrum ($CDCl_3$) of 2,3-bis(2-(trimethylsilyl)ethynyl)benzofuran **(13g)**

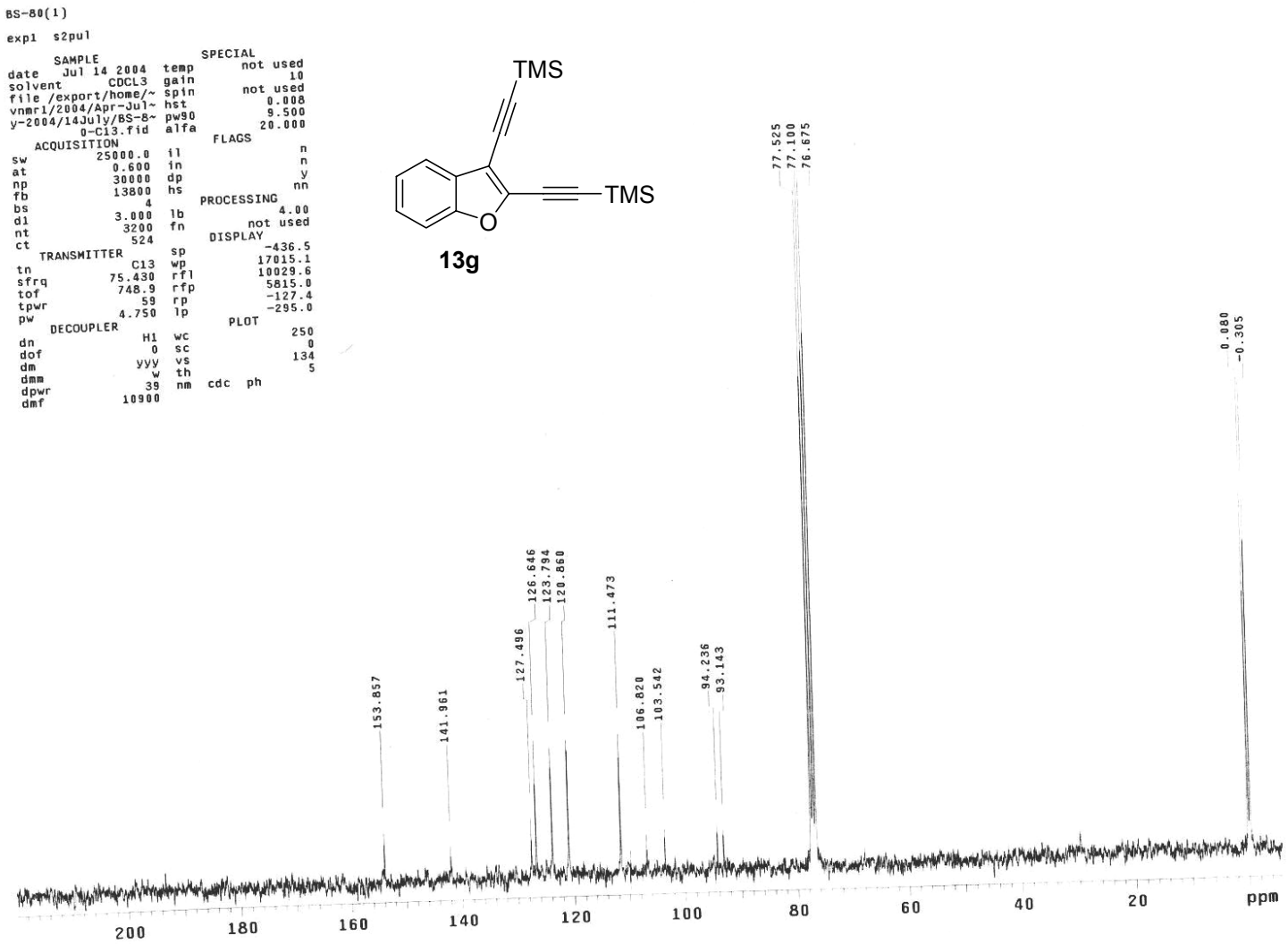

Figure S32. ^{13}C NMR spectrum ($CDCl_3$) of 2,3-bis(2-(trimethylsilyl)ethynyl)benzofuran **(13g)**

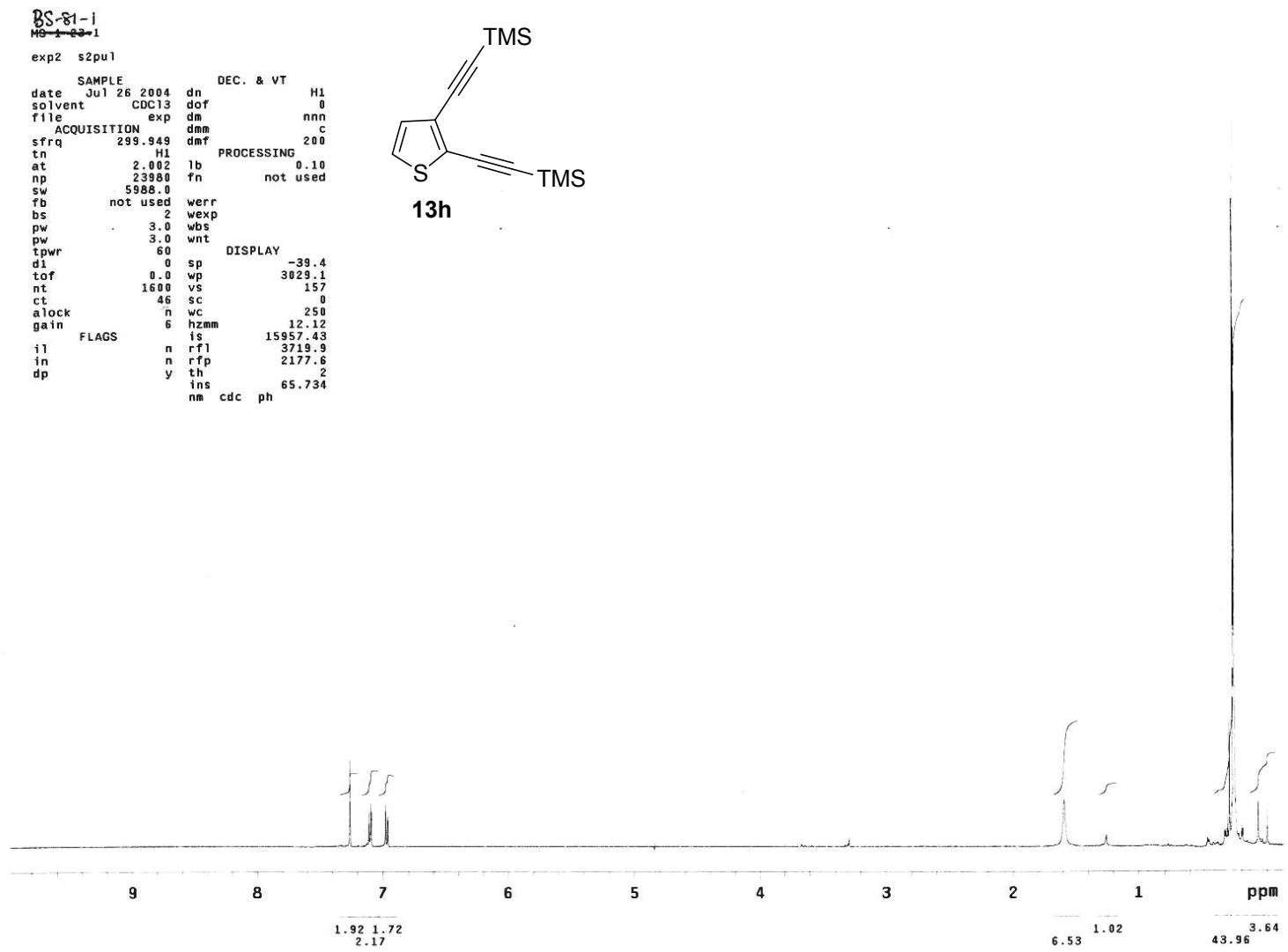

Figure S33. ^{1}H NMR spectrum ($CDCl_3$) of 2,3-bis(2-(trimethylsilyl)ethynyl)thiophene **(13h)**

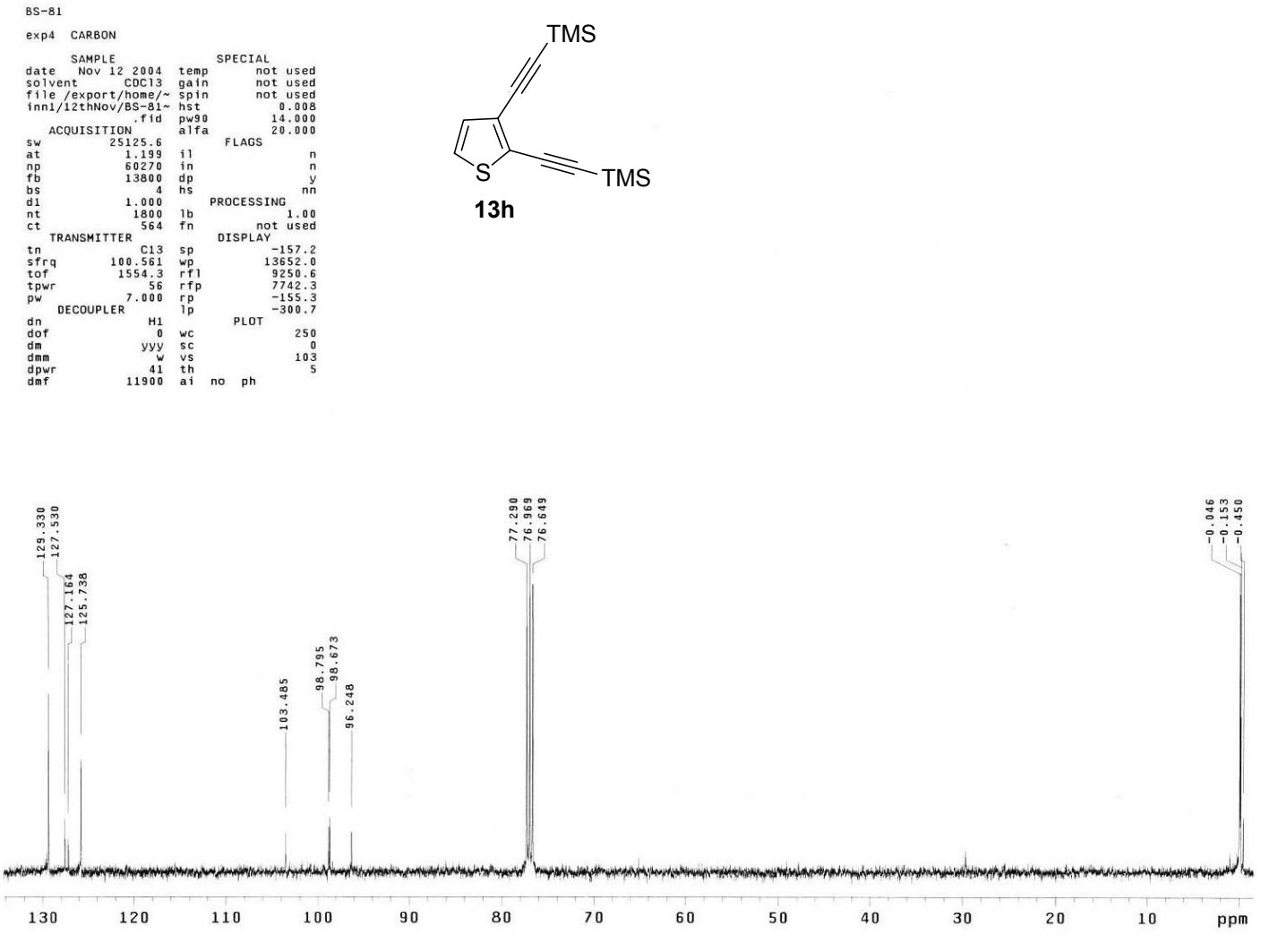

Figure S34. ^{13}C NMR spectrum ($CDCl_3$) of 2,3-bis(2-(trimethylsilyl)ethynyl)thiophene **(13h)**

RM-123

exp2 PROTON

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bs	4	hs	nn
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ct	44	fn	not used
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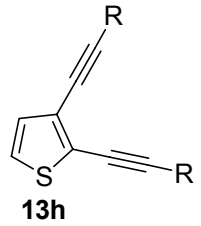
tof	338.7	rfl	2620.5
tpwr	55	rfp	0
pw	2.000	rp	7.8
DECOUPLER		lp	-114.7
dn	C13	PLOT	
dof	338.7	wc	250
dm	nnn	sc	0
dmm	c	vs	13
dpwr	51	th	2
dmf	17100	ai	ph



13h

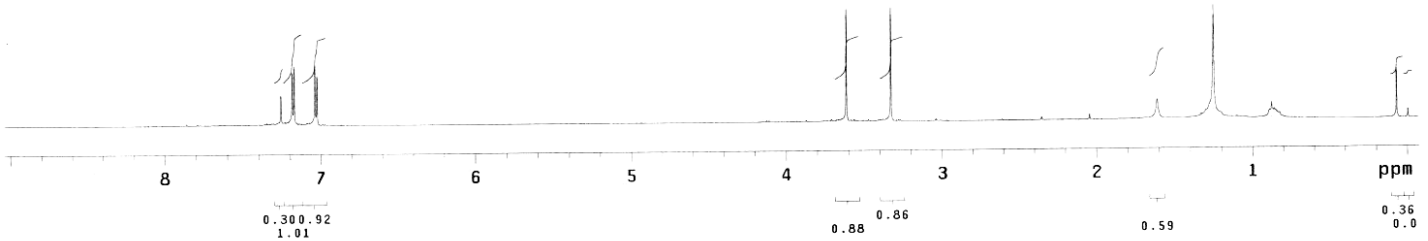


Figure S35. ^{1}H NMR spectrum ($CDCl_3$) of 2,3-diethynylthiophene **(13h,** R = H**)**

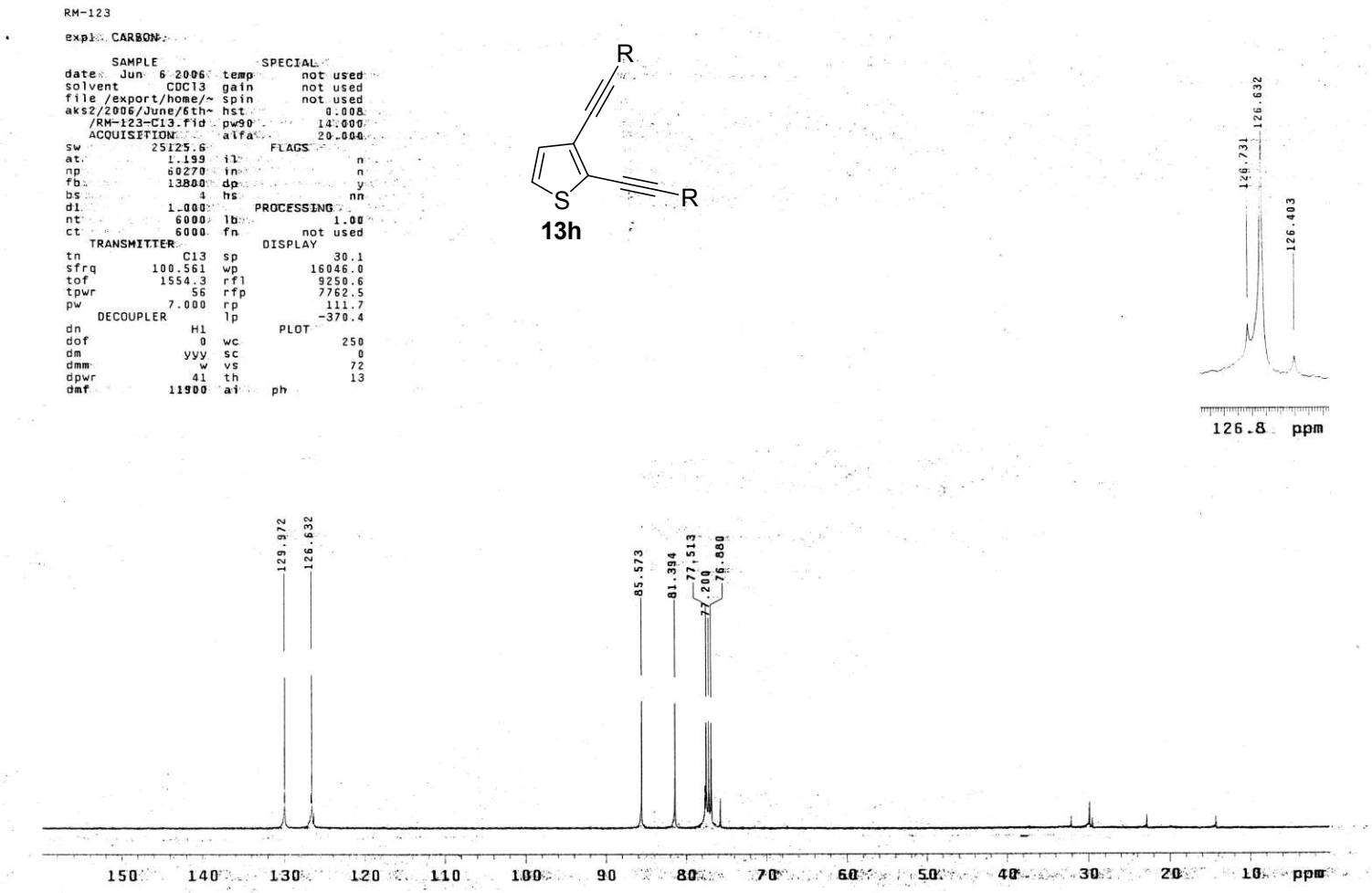


Figure S36. ^{13}C NMR spectrum ($CDCl_3$) of 2,3-diethynylthiophene **(13h,** R = H**)**

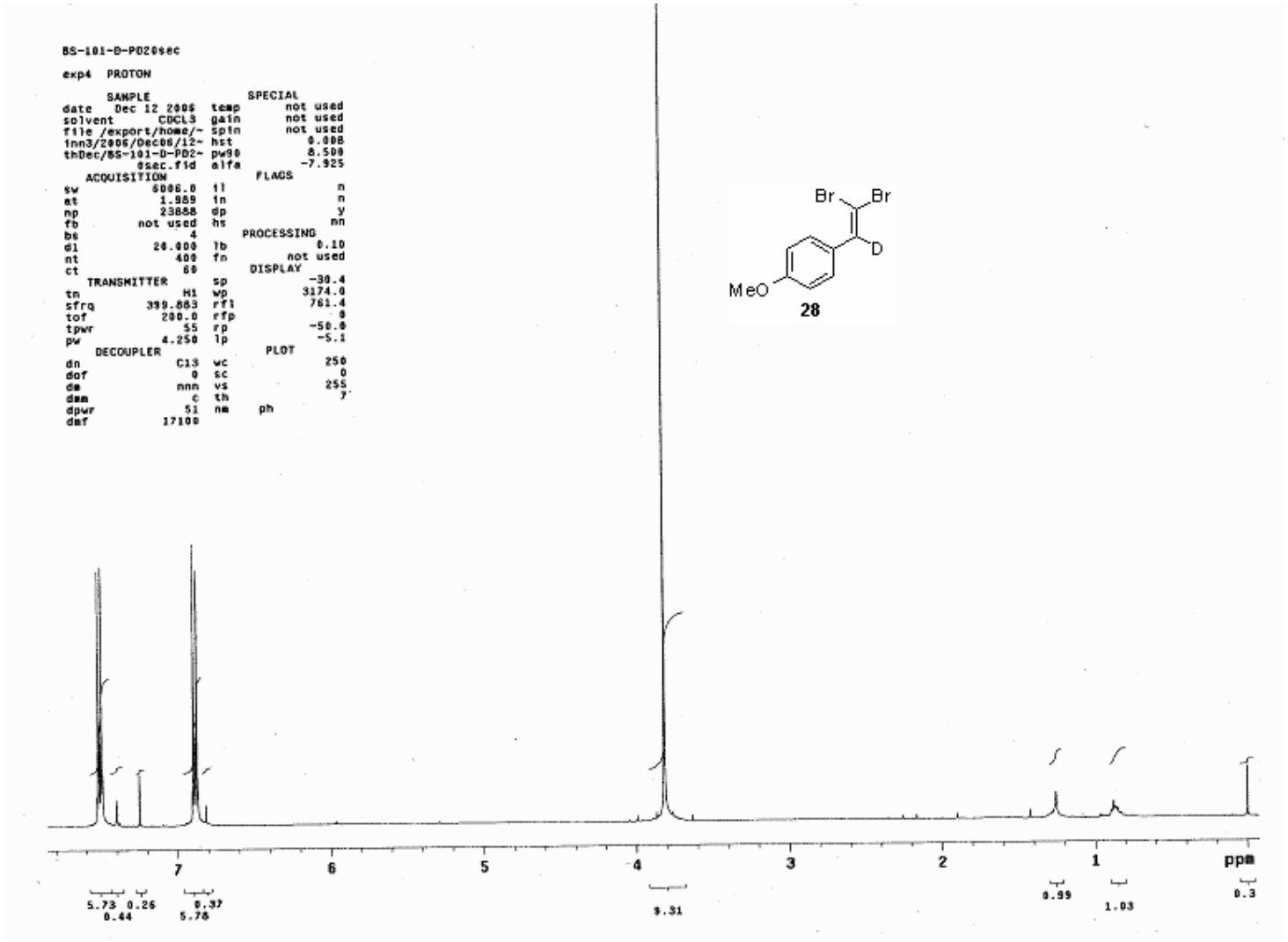


Figure S37a. ^{1}H NMR spectrum ($CDCl_3$) of 1-(2,2-dibromovinyl)-4-methoxybenzene-*d* **(28)**

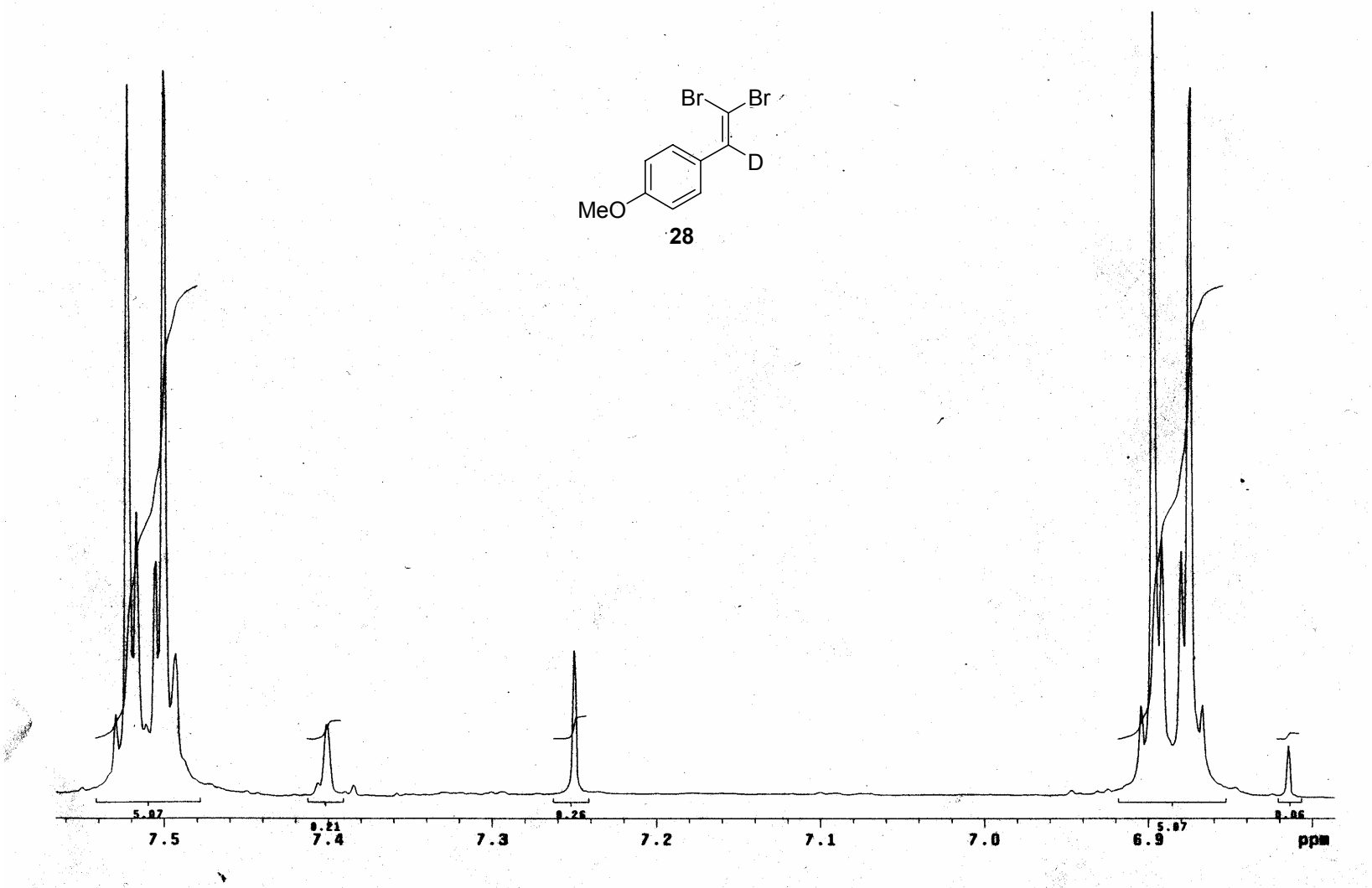


Figure S37b. ^{1}H NMR (expansion of aromatic region) spectrum ($CDCl_3$) of 1-(2,2-dibromovinyl)-4-methoxybenzene-*d* **(28)**

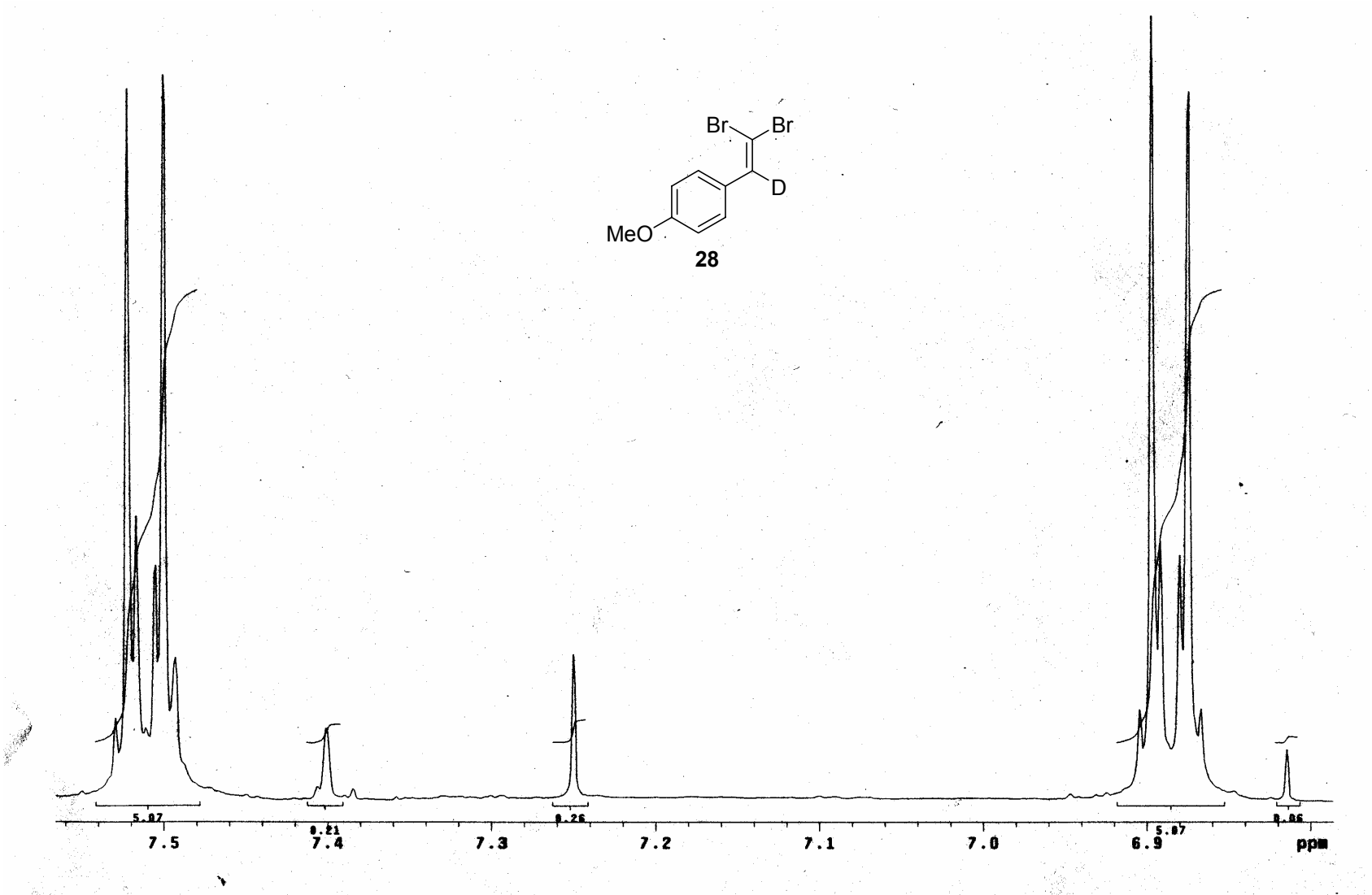


Figure S37c. ^{1}H NMR (expansion of aromatic region) spectrum ($CDCl_3$) of 1-(2,2-dibromovinyl)-4-methoxybenzene-*d* **(28)**

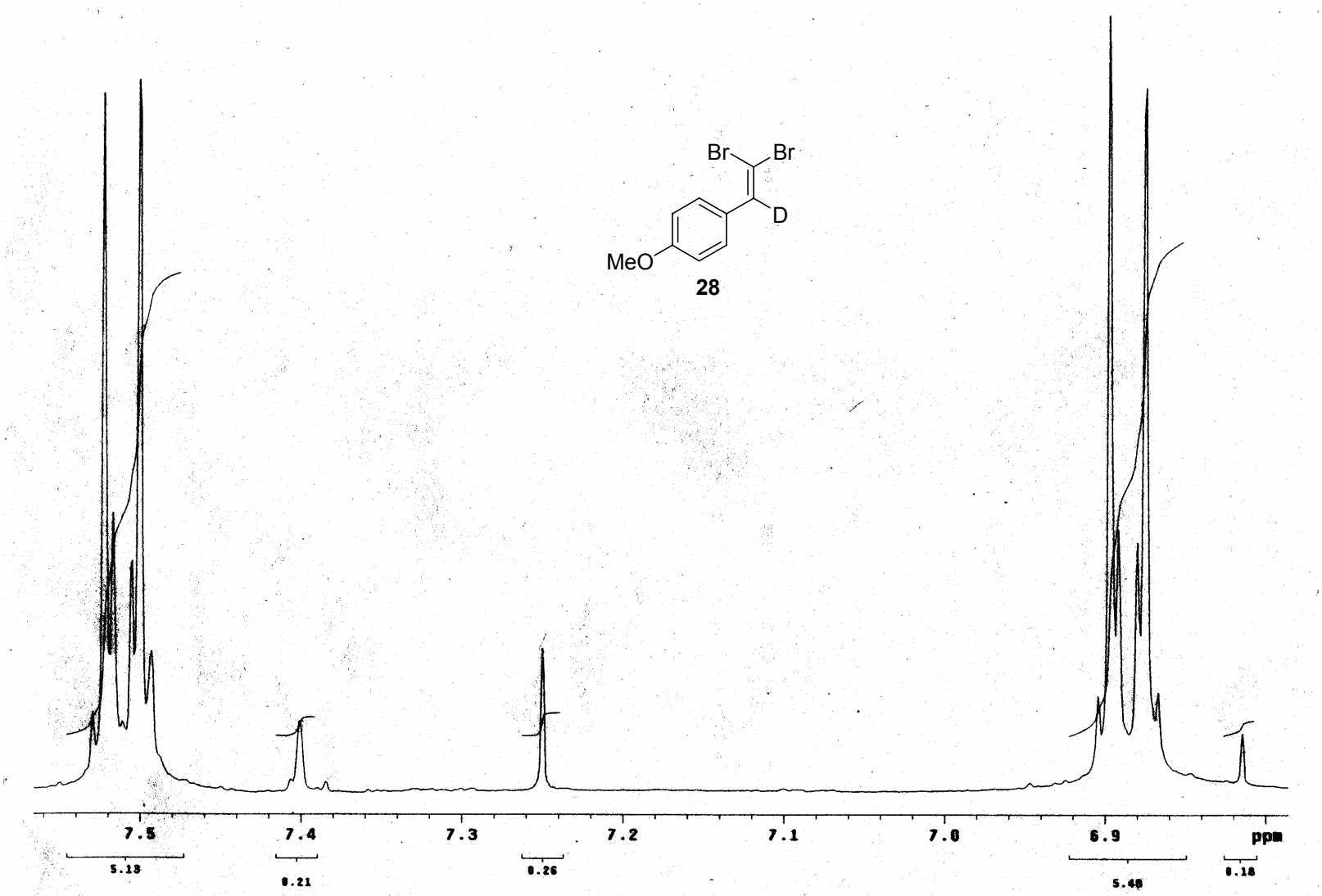


Figure S37d. ^{1}H NMR (expansion of aromatic region) spectrum ($CDCl_3$) of 1-(2,2-dibromovinyl)-4-methoxybenzene-*d* **(28)**

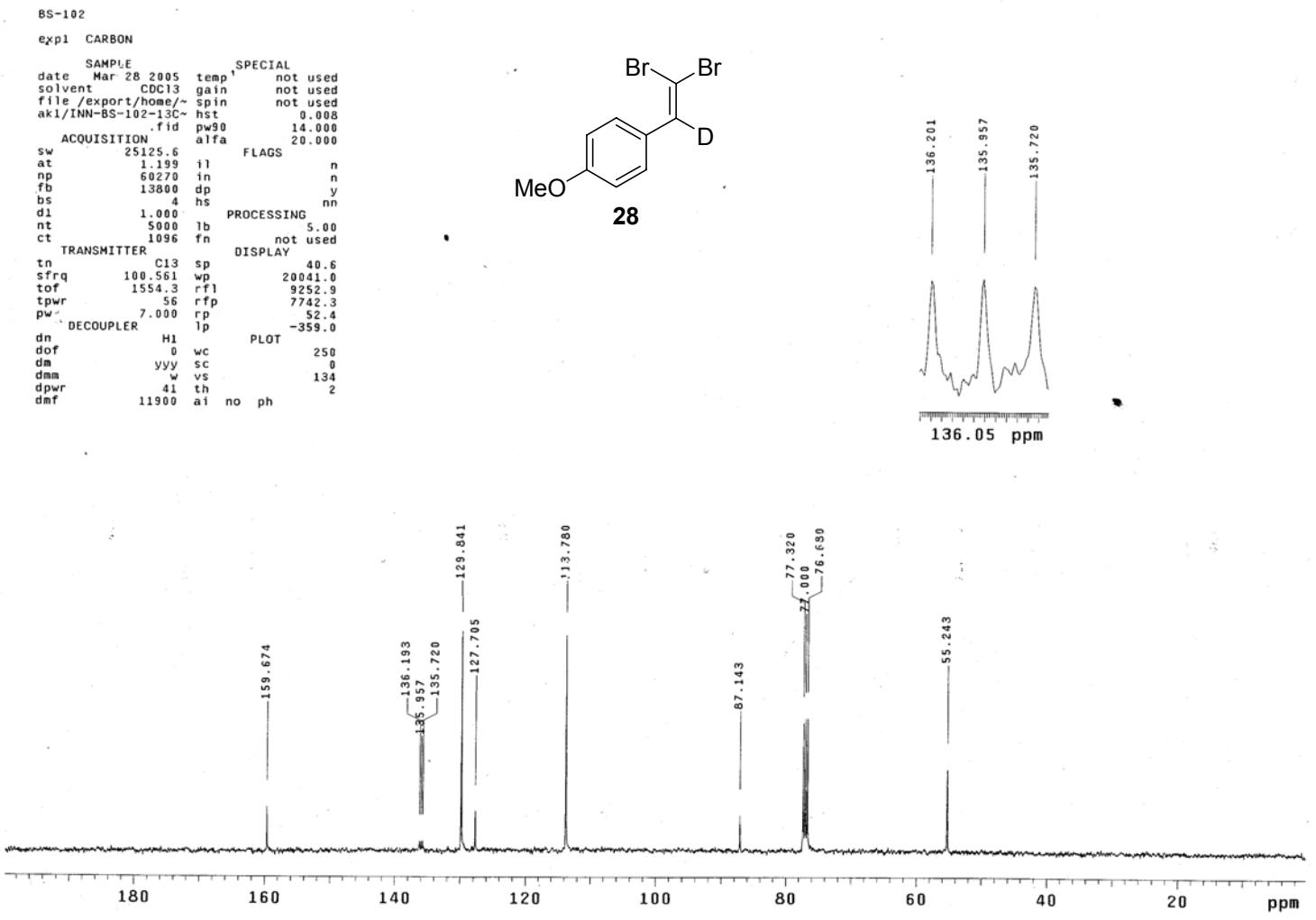


Figure S38. ^{13}C NMR spectrum ($CDCl_3$) of 1-(2,2-dibromovinyl)-4-methoxybenzene-*d* **(28)**

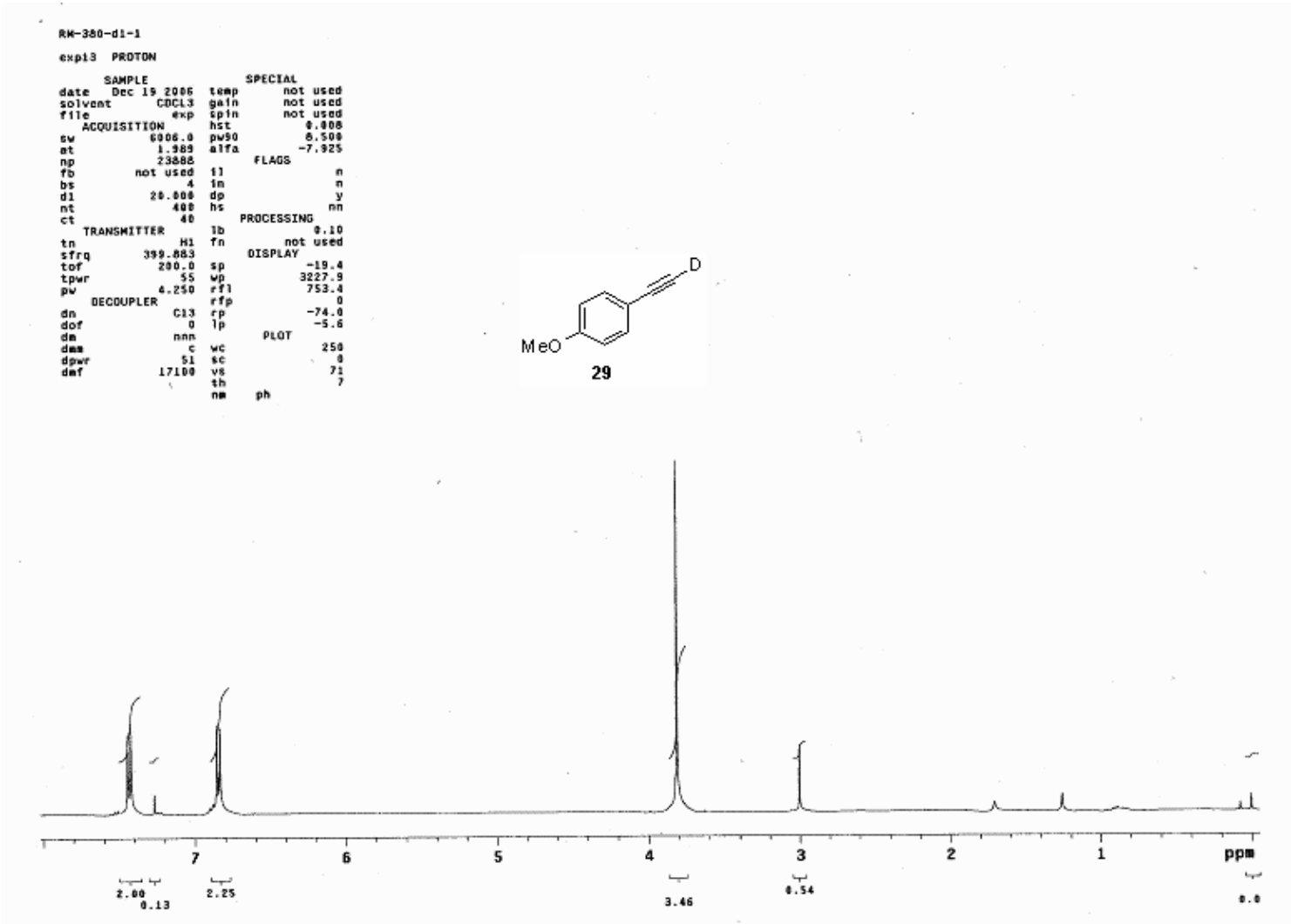


Figure S39a. ^{1}H NMR ($CDCl_3$) spectrum of 1-ethynyl-4-methoxybenzene-*d* (**29**) from deuterium labeling experiment (Integration 1)

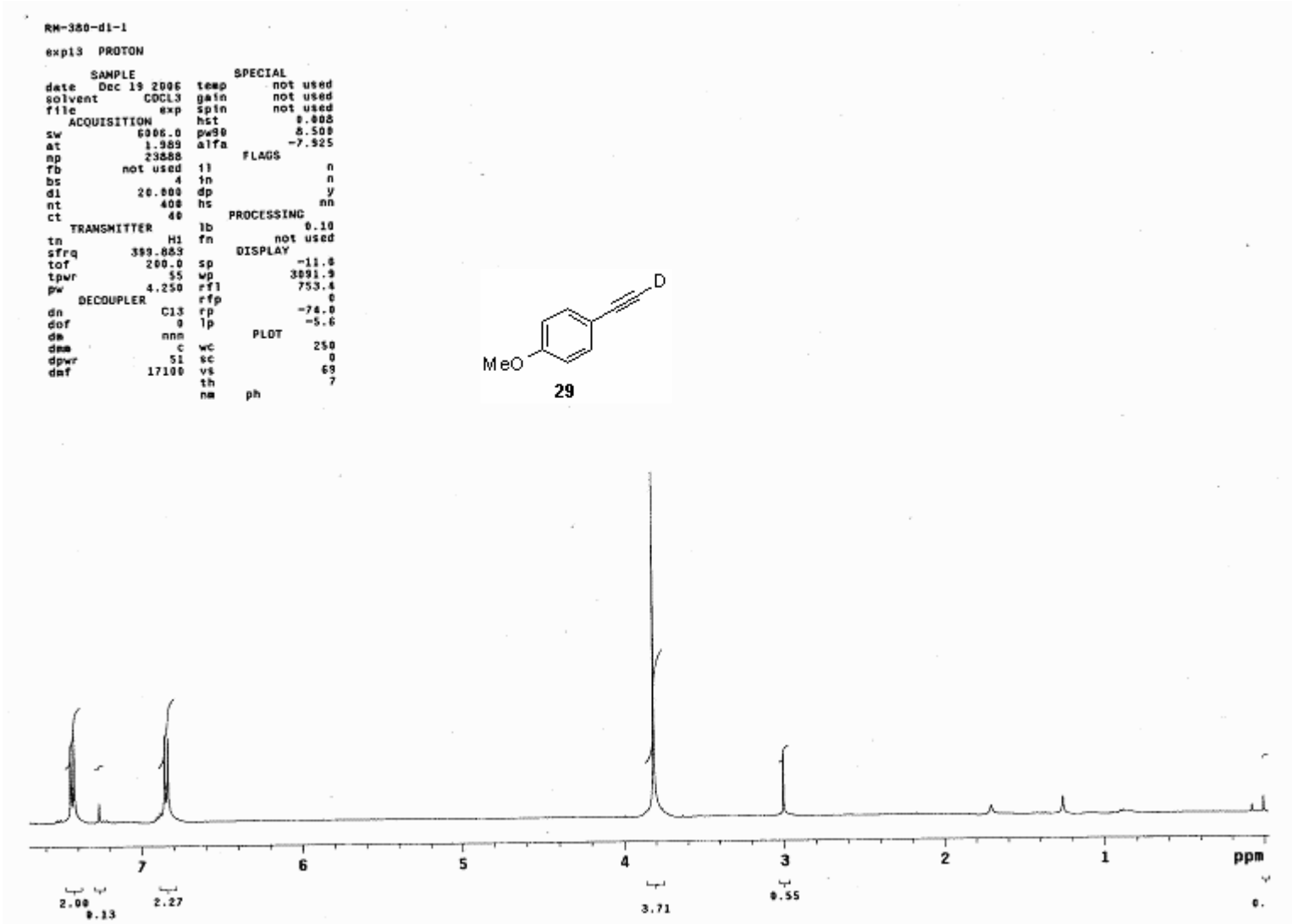


Figure S39b. ^{1}H NMR ($CDCl_3$) spectrum of 1-ethynyl-4-methoxybenzene-*d* (**29**) from deuterium labeling experiment (Integration 2)

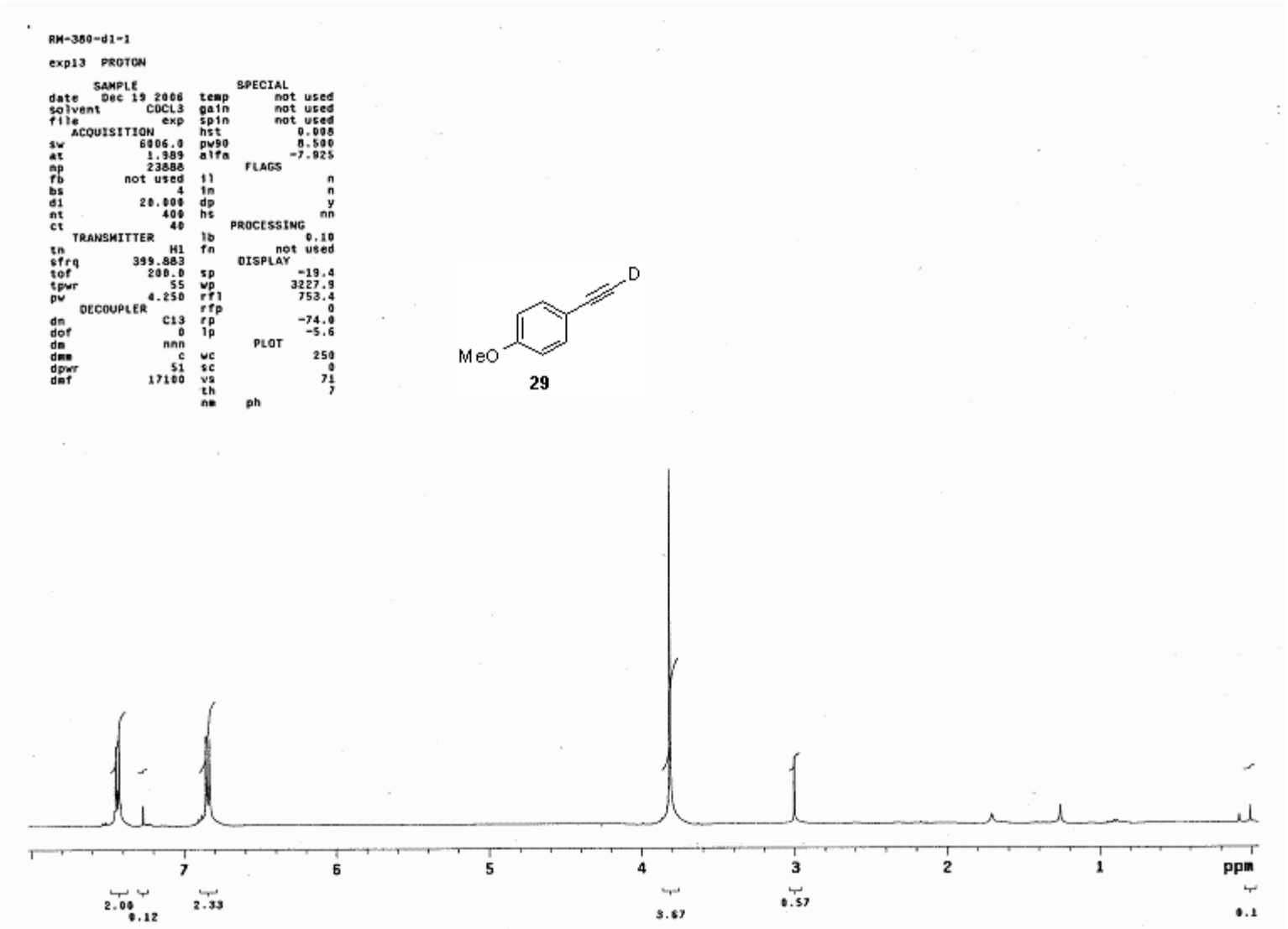


Figure S39c. ^{1}H NMR ($CDCl_3$) spectrum of 1-ethynyl-4-methoxybenzene-*d* (**29**) from deuterium labeling experiment (Integration 3)

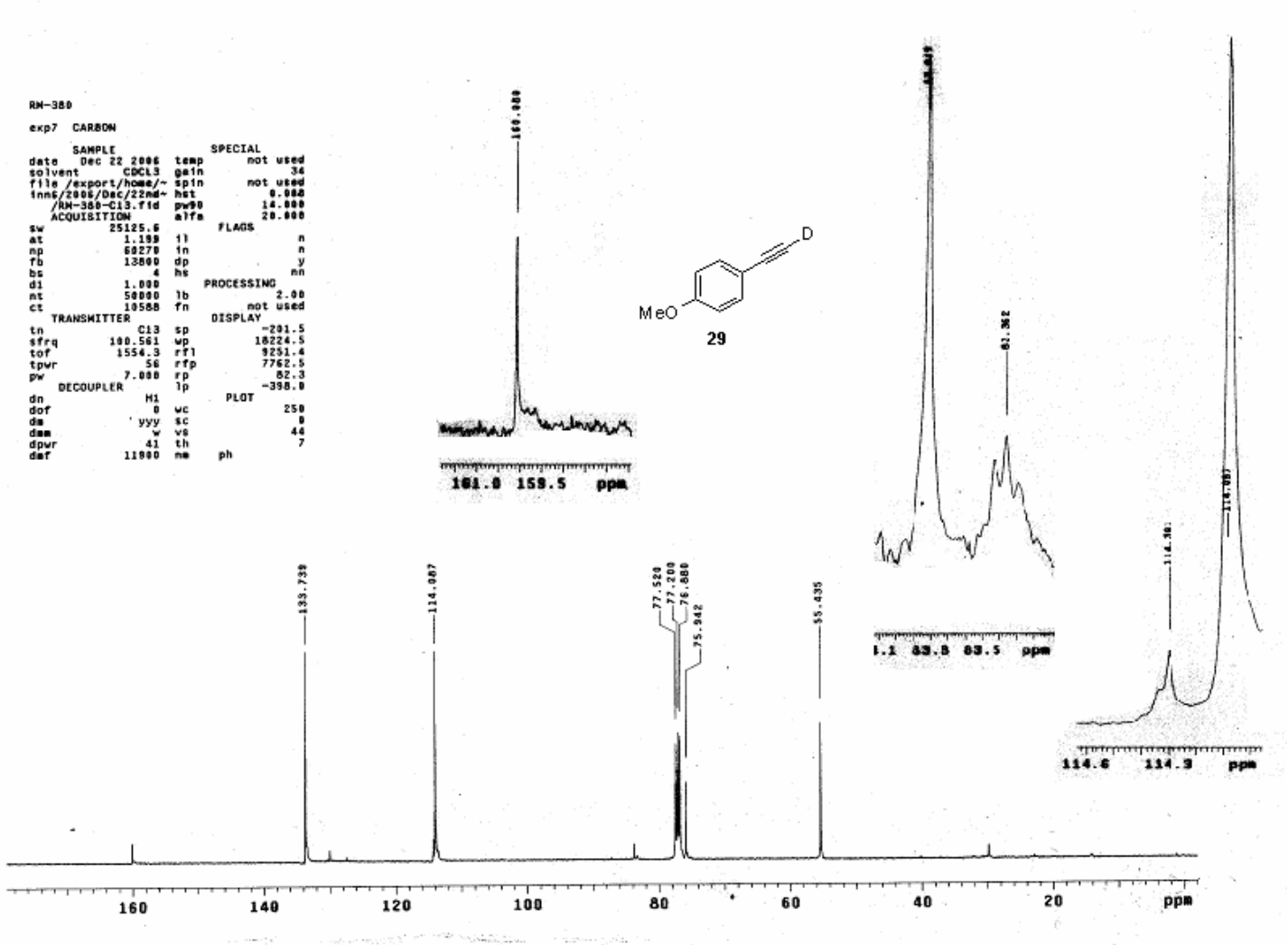


Figure S40. ^{13}C NMR ($CDCl_3$) spectrum of 1-ethynyl-4-methoxybenzene-*d* (**29**) from deuterium labeling experiment

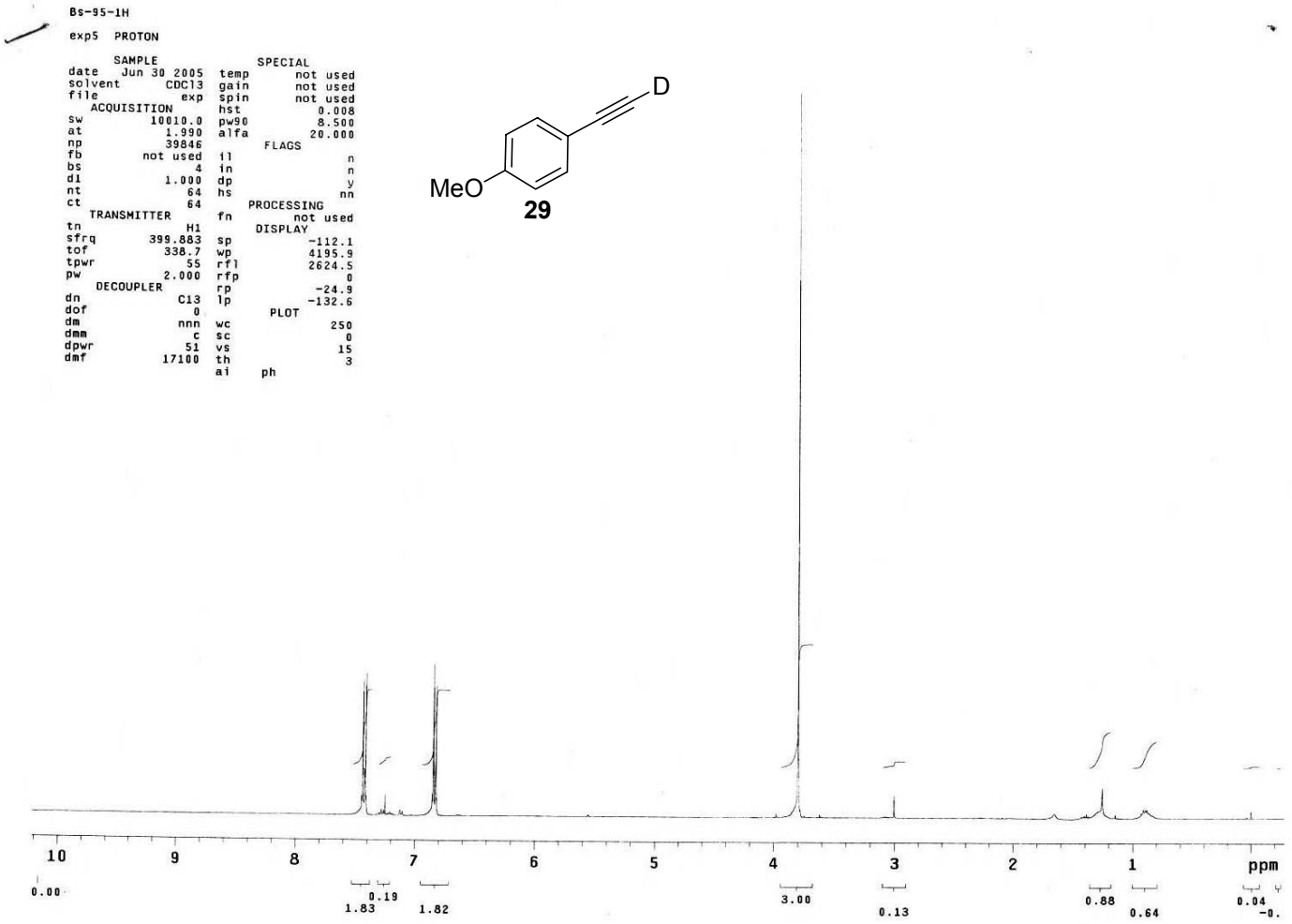


Figure S41. ^{1}H NMR spectrum ($CDCl_3$) of *standard* 1-ethynyl-4-methoxybenzene-*d* **(29)**

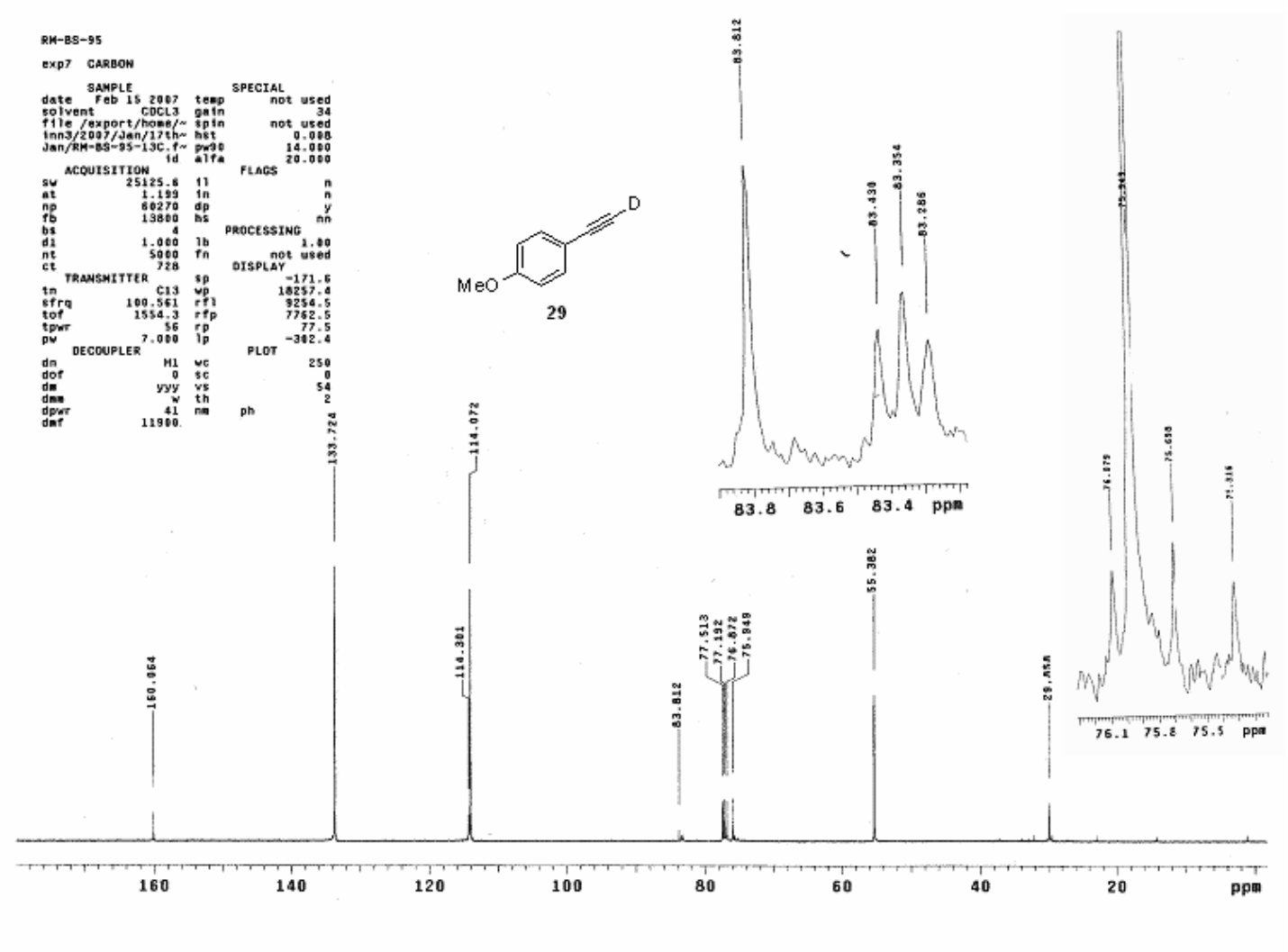


Figure S42. ^{13}C NMR spectrum ($CDCl_3$) of *standard* 1-ethynyl-4-methoxybenzene-*d* **(29)**

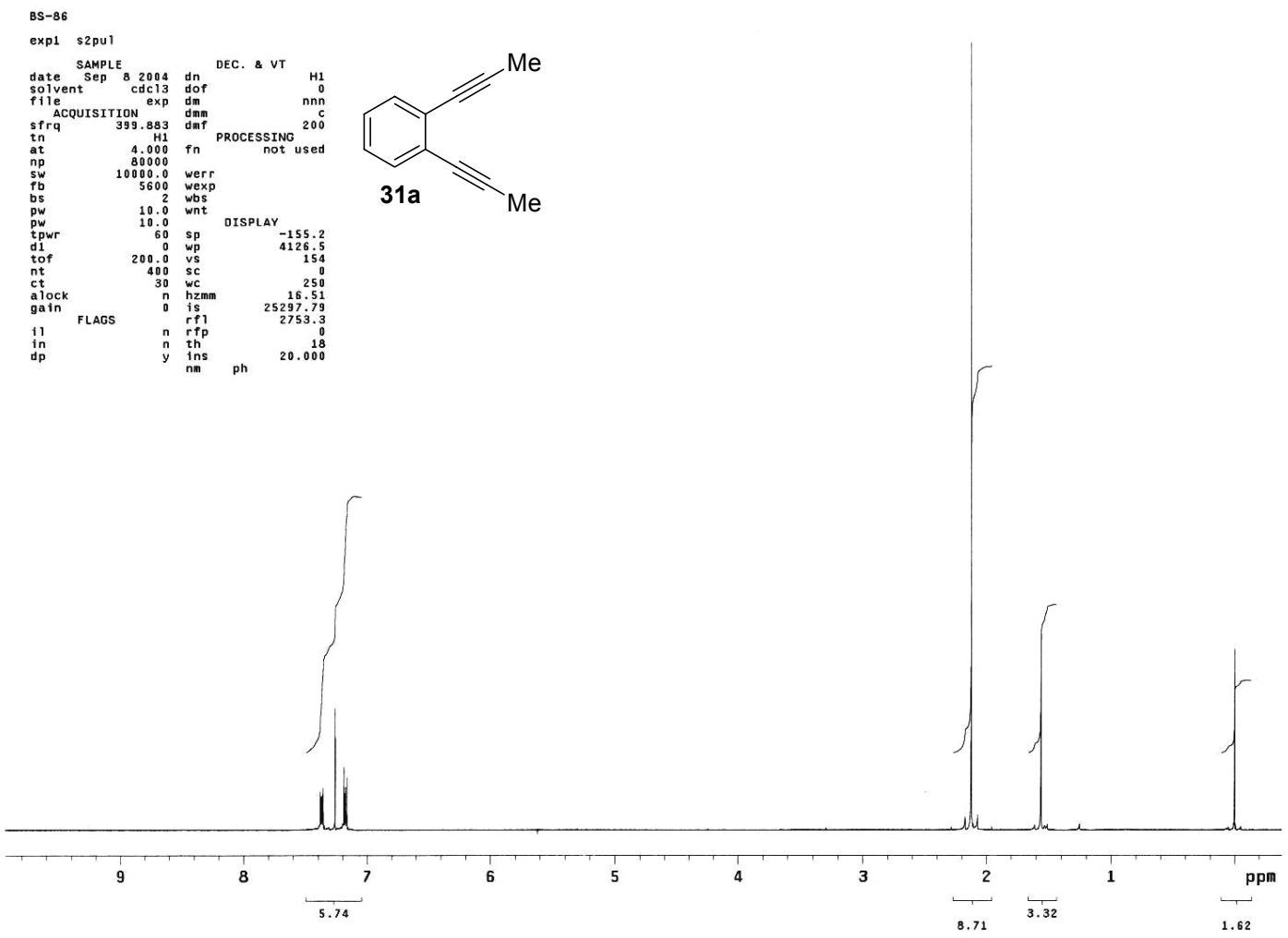


Figure S43. ^{1}H NMR spectrum ($CDCl_3$) of 1,2-di(prop-1-ynyl)benzene **(31a)**

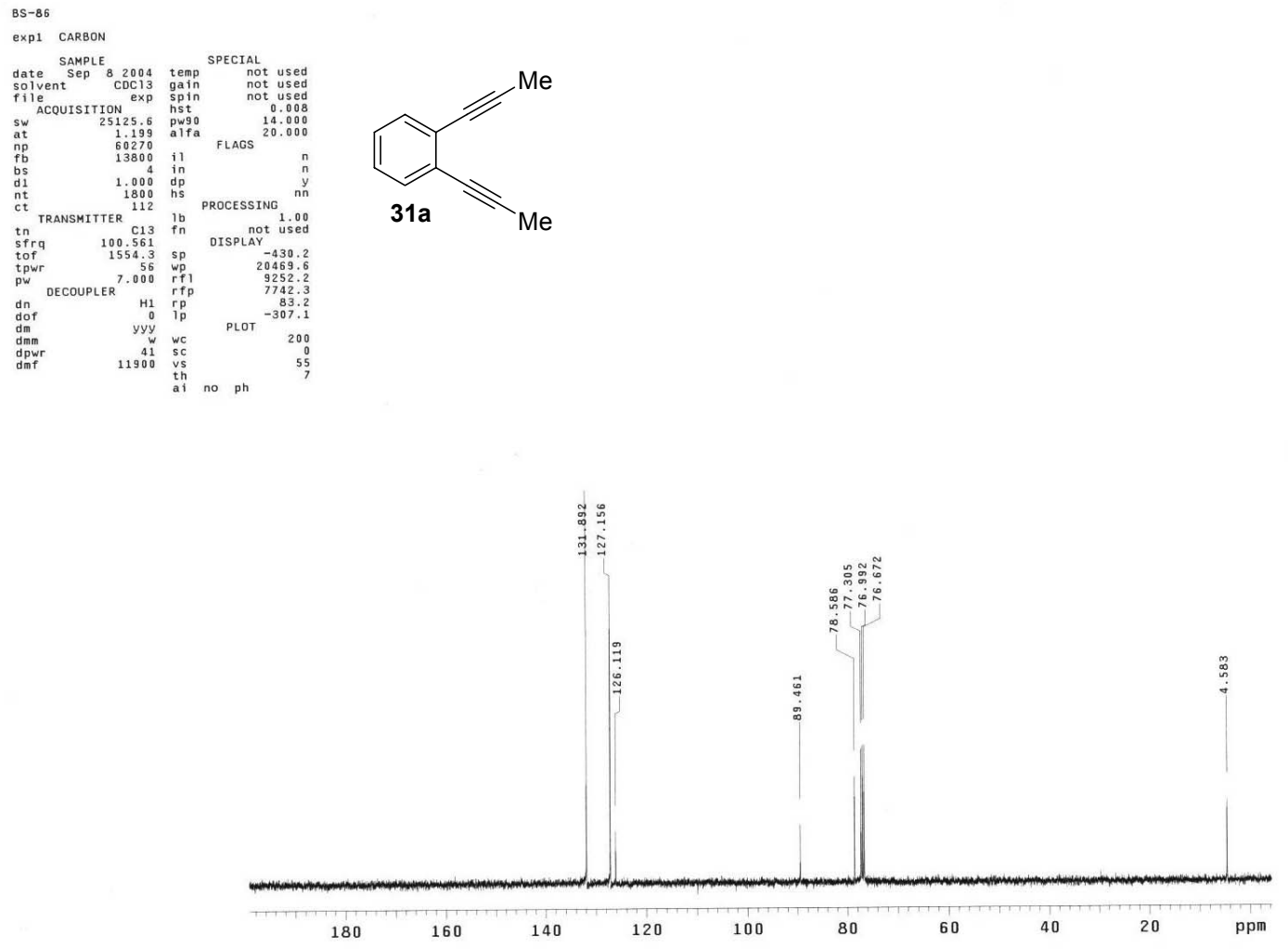


Figure S44. ^{13}C NMR spectrum ($CDCl_3$) of 1,2-di(prop-1-ynyl)benzene **(31a)**

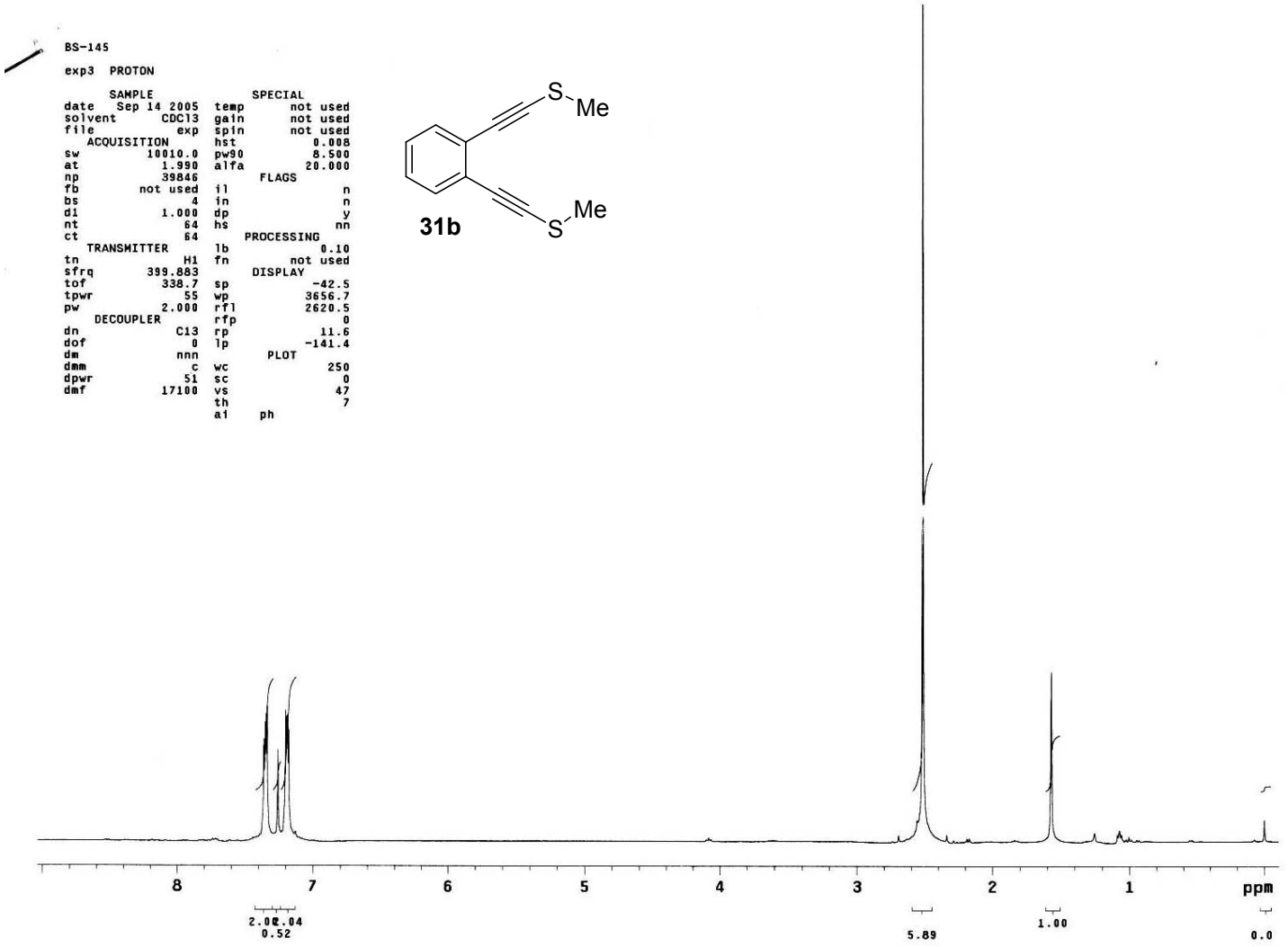


Figure S45. ^{1}H NMR spectrum ($CDCl_3$) of 1,2-bis(2-(methylthio)ethynyl)benzene **(31b)**

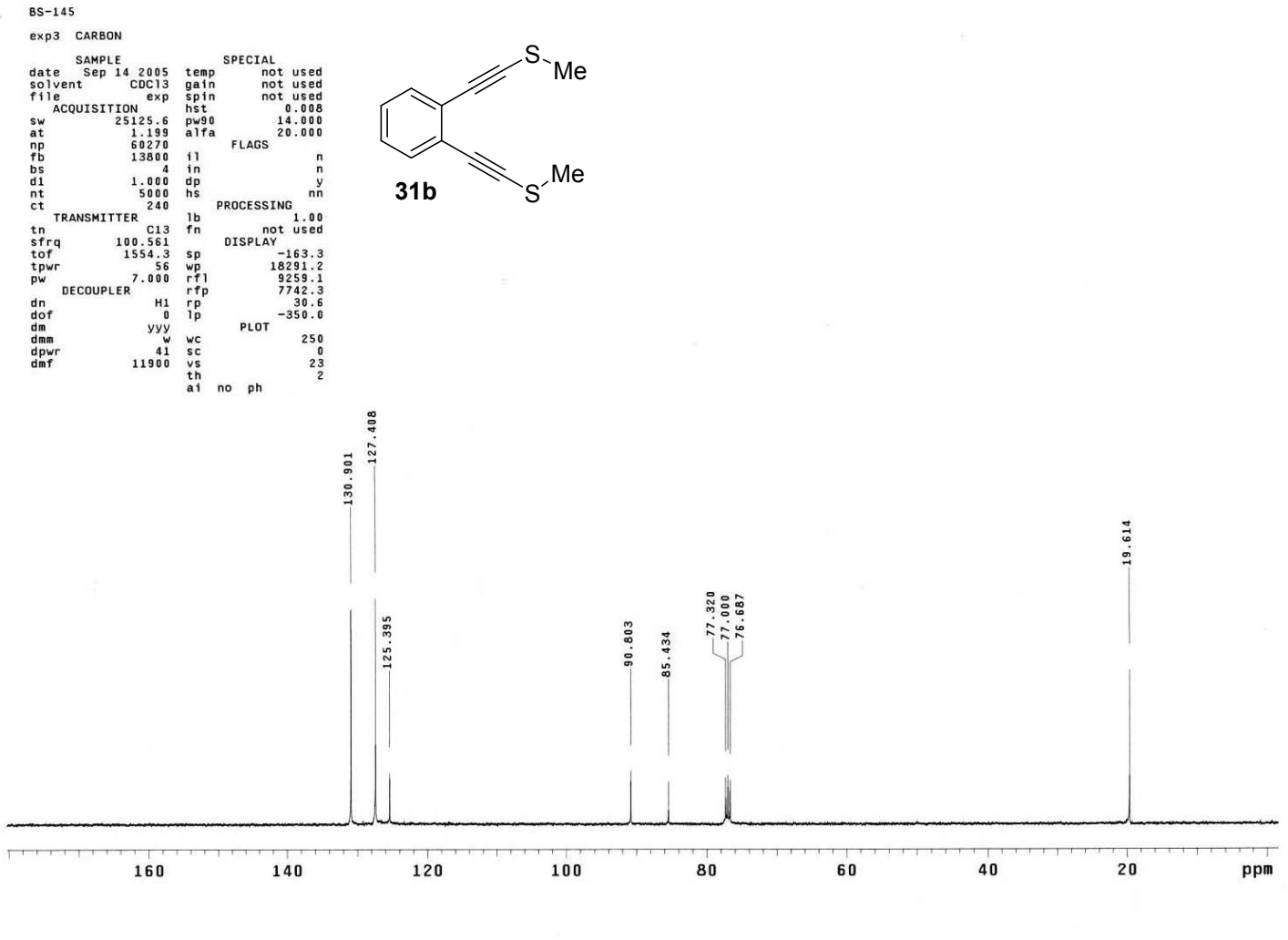


Figure S46. ^{13}C NMR spectrum ($CDCl_3$) of 1,2-bis(2-(methylthio)ethynyl)benzene **(31b)**

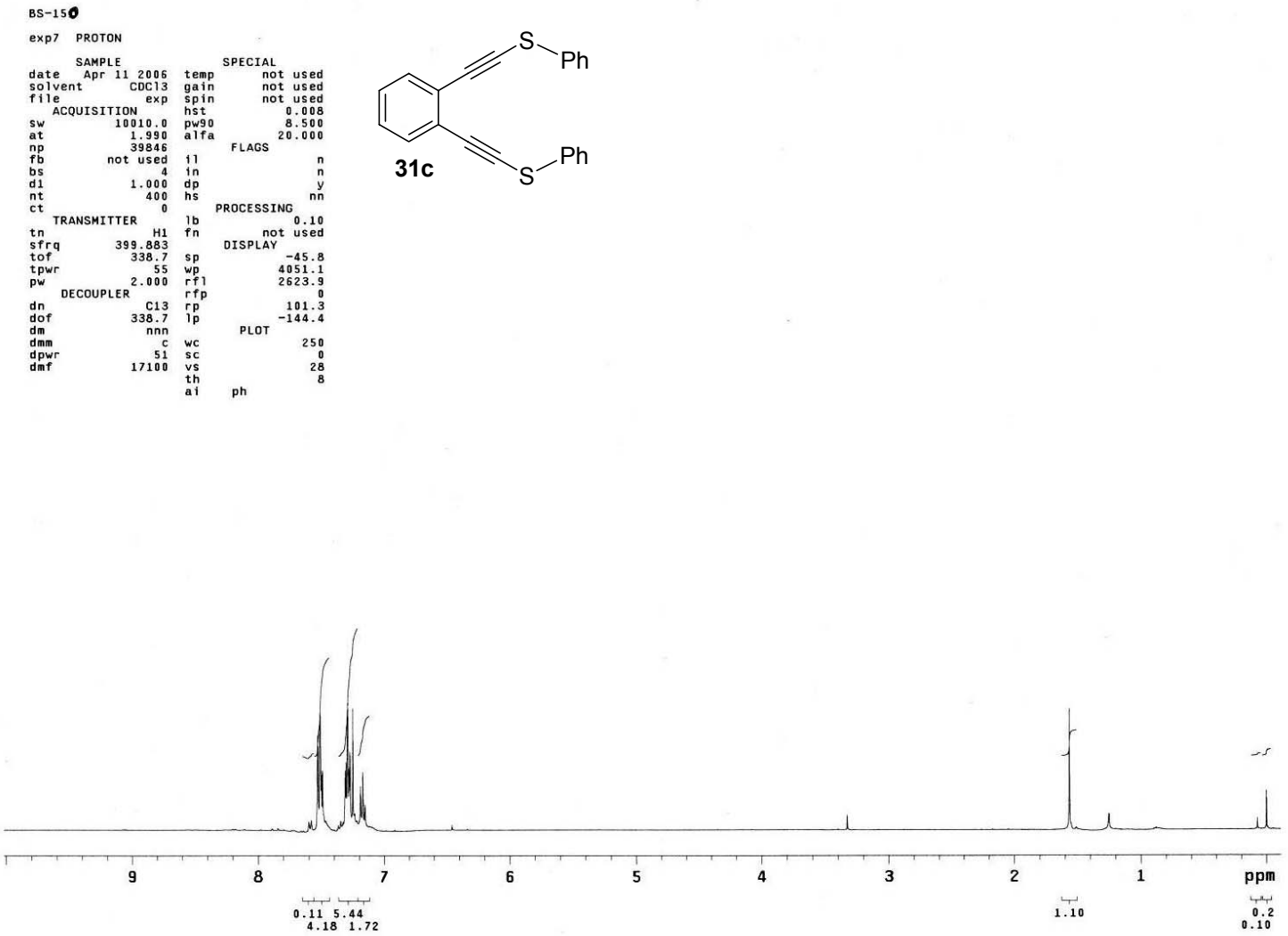


Figure S47. ^{1}H NMR spectrum ($CDCl_3$) of 1,2-bis(2-(phenylthio)ethynyl)benzene **(31c)**

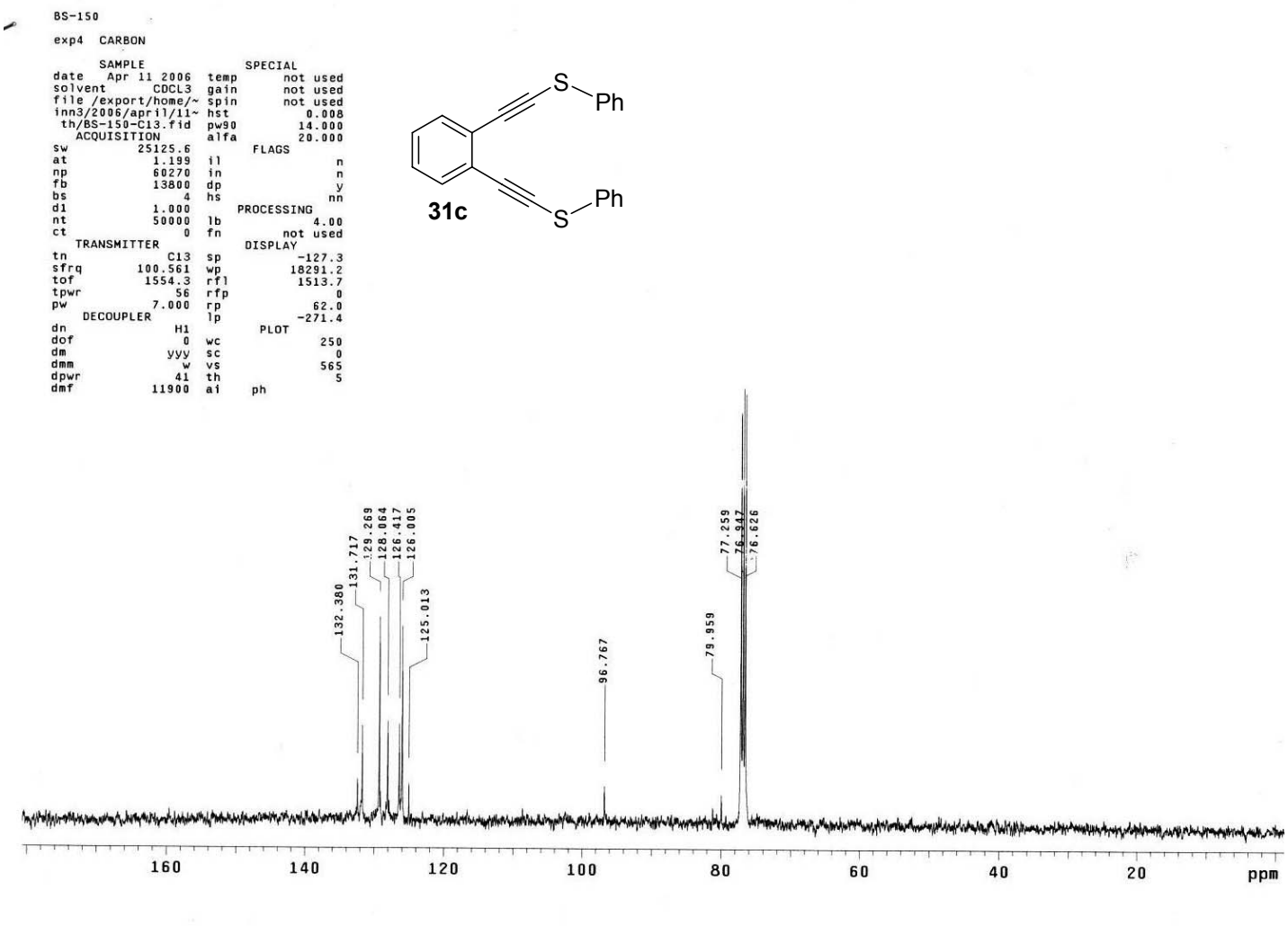


Figure S48. ^{13}C NMR spectrum ($CDCl_3$) of 1,2-bis(2-(phenylthio)ethynyl)benzene **(31c)**

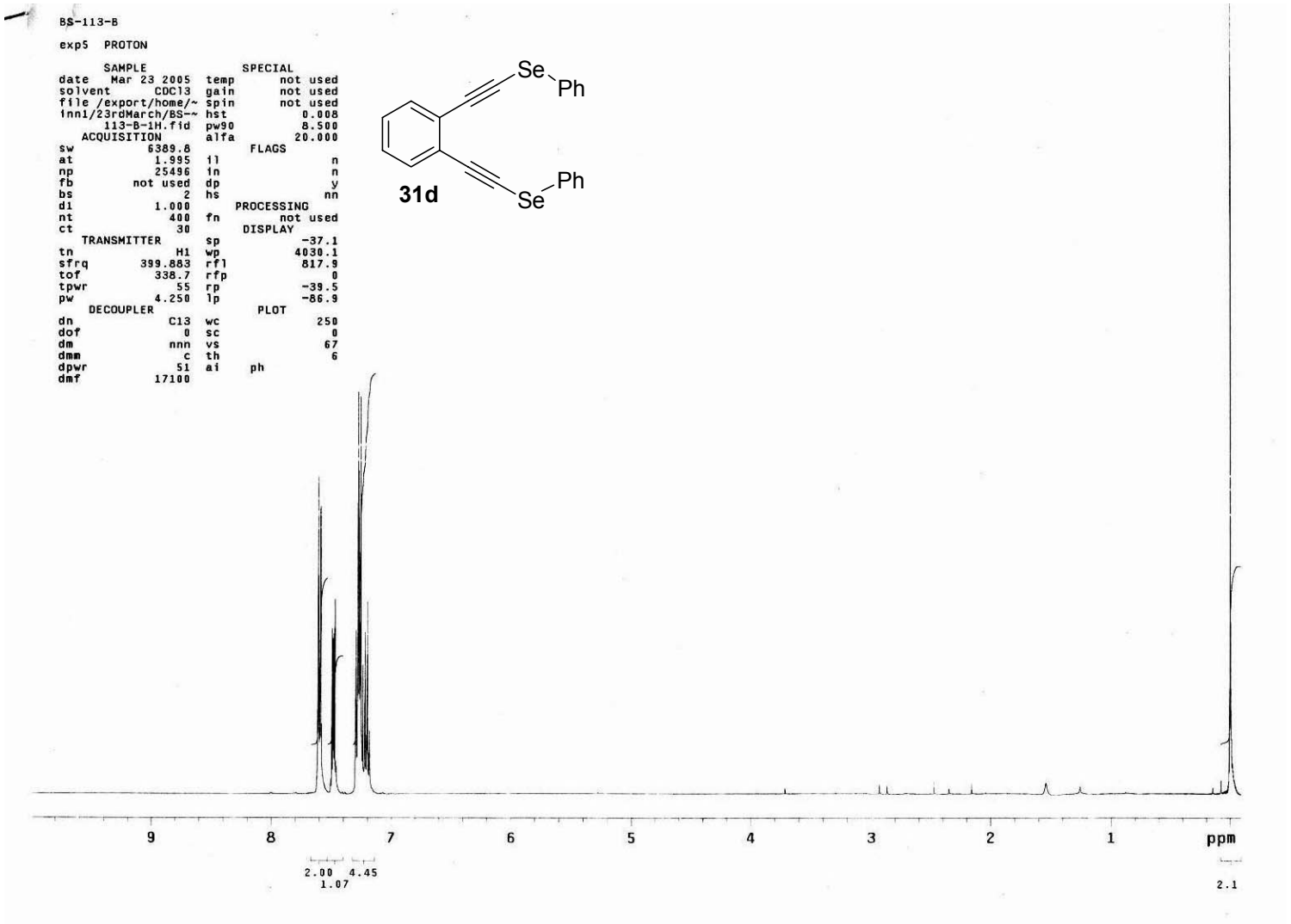


Figure S49. ^{1}H NMR spectrum ($CDCl_3$) of 1,2-bis(2-(phenylselanyl)ethynyl)benzene **(31d)**

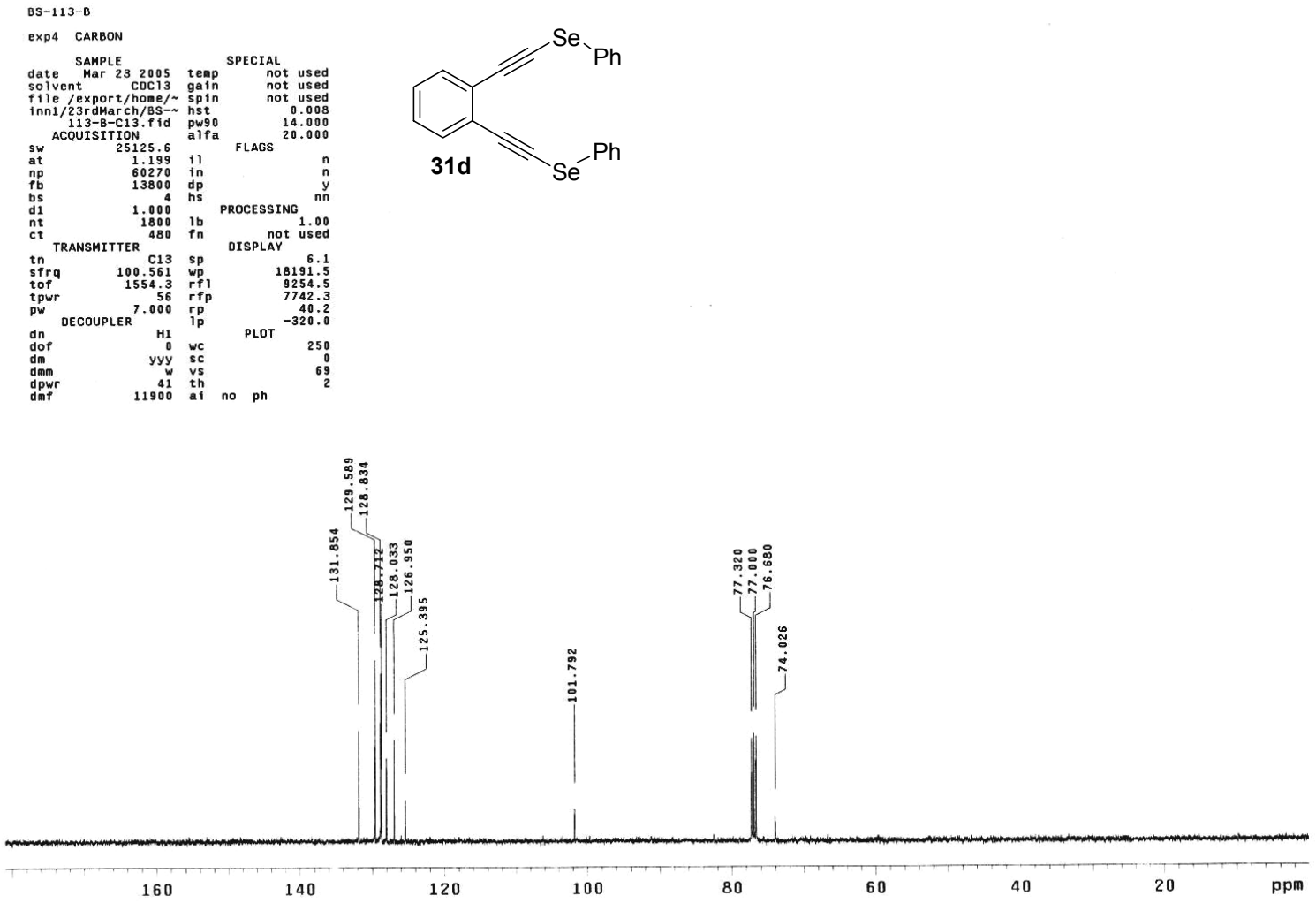


Figure S50. ^{13}C NMR spectrum ($CDCl_3$) of 1,2-bis(2-(phenylselanyl)ethynyl)benzene **(31d)**

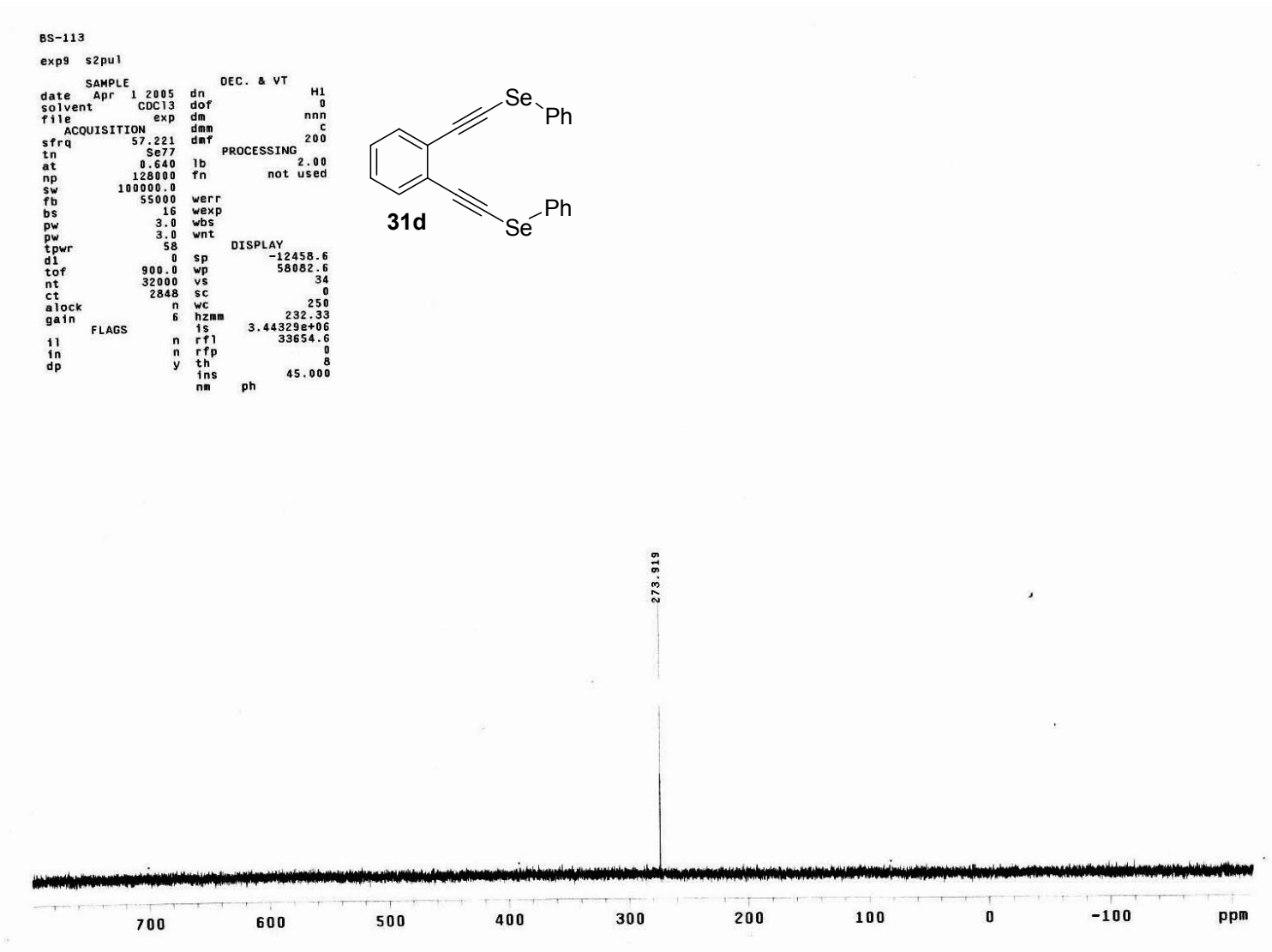


Figure S51. ^{77}Se NMR spectrum ($CDCl_3$) of 1,2-bis(2-(phenylselanyl)ethynyl)benzene **(31d)**

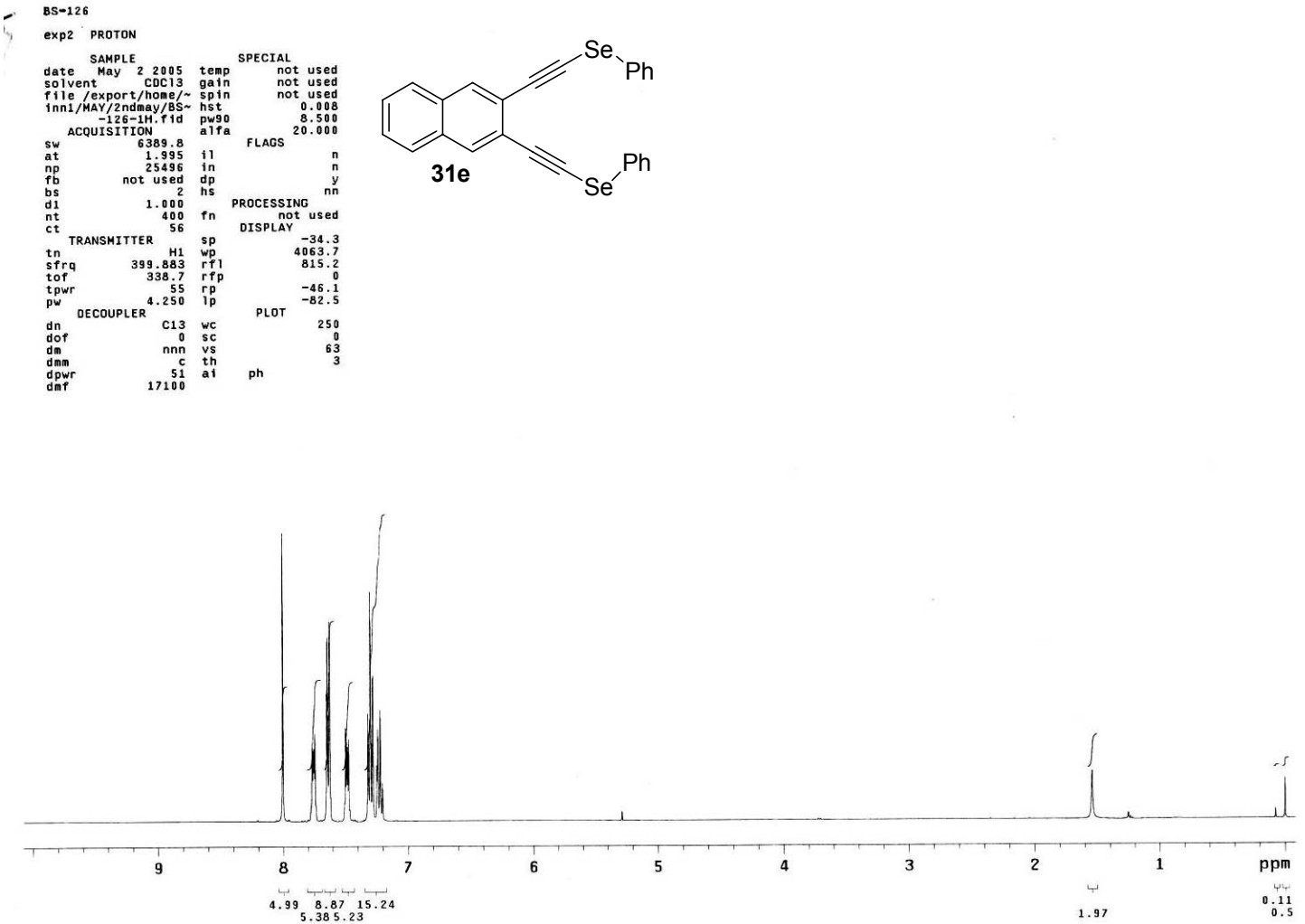


Figure S52. ^{1}H NMR spectrum ($CDCl_3$) of 2,3-bis(2-(phenylselanyl)ethynyl)naphthalene **(31e)**

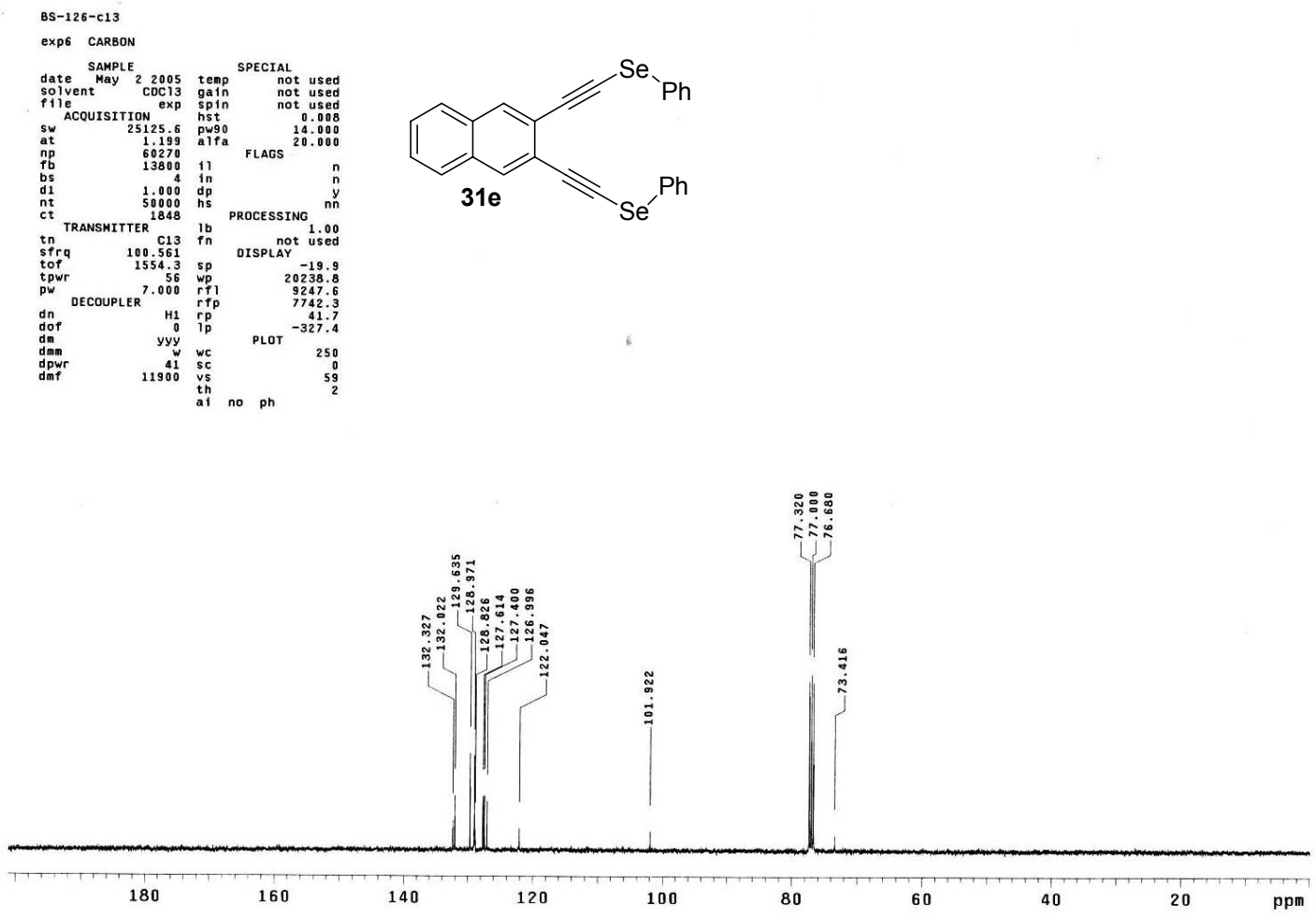


Figure S53. ^{13}C NMR spectrum ($CDCl_3$) of 2,3-bis(2-(phenylselanyl)ethynyl)naphthalene **(31e)**

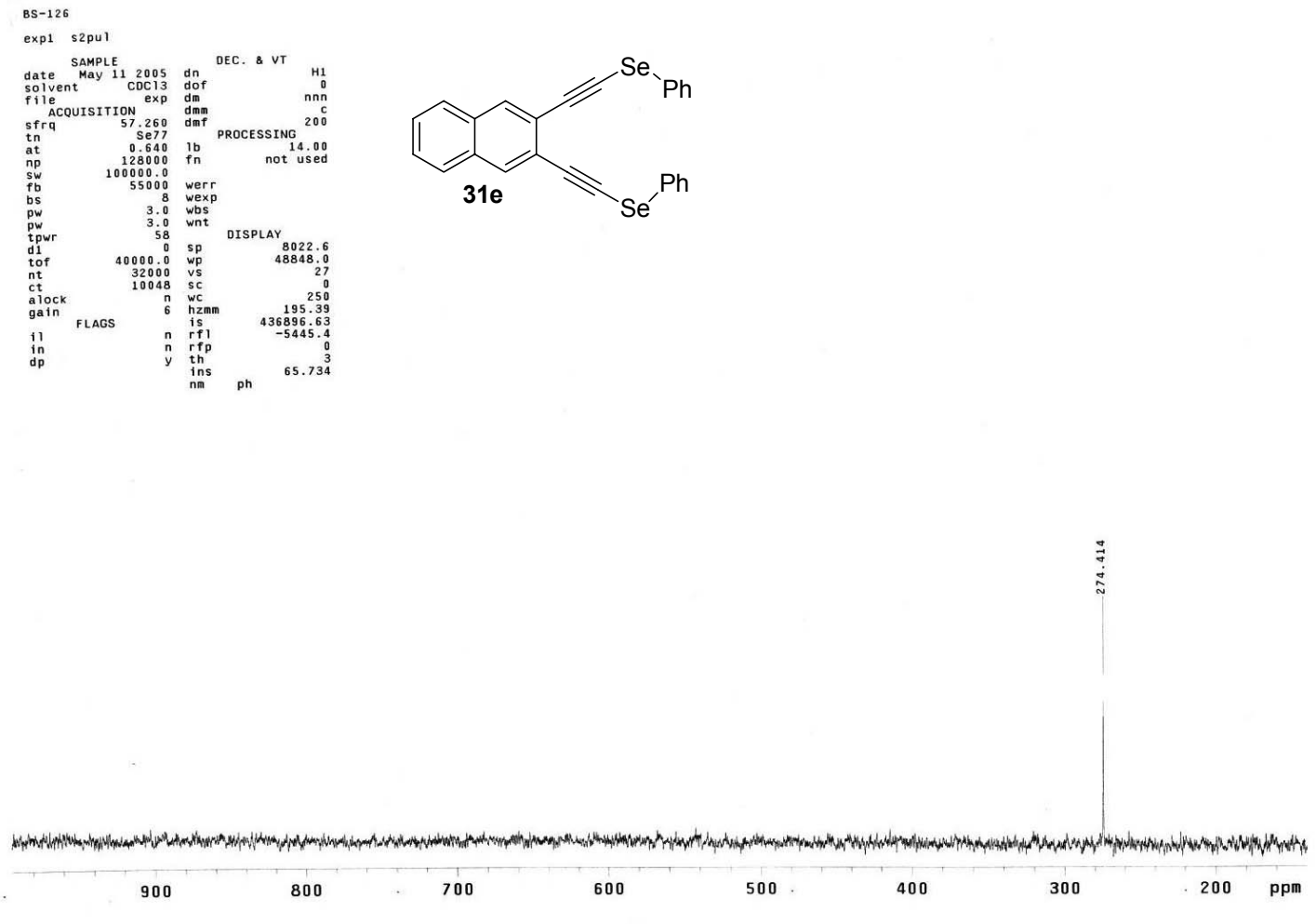


Figure S54. ^{77}Se NMR spectrum ($CDCl_3$) of 2,3-bis(2-(phenylselanyl)ethynyl)naphthalene **(31e)**

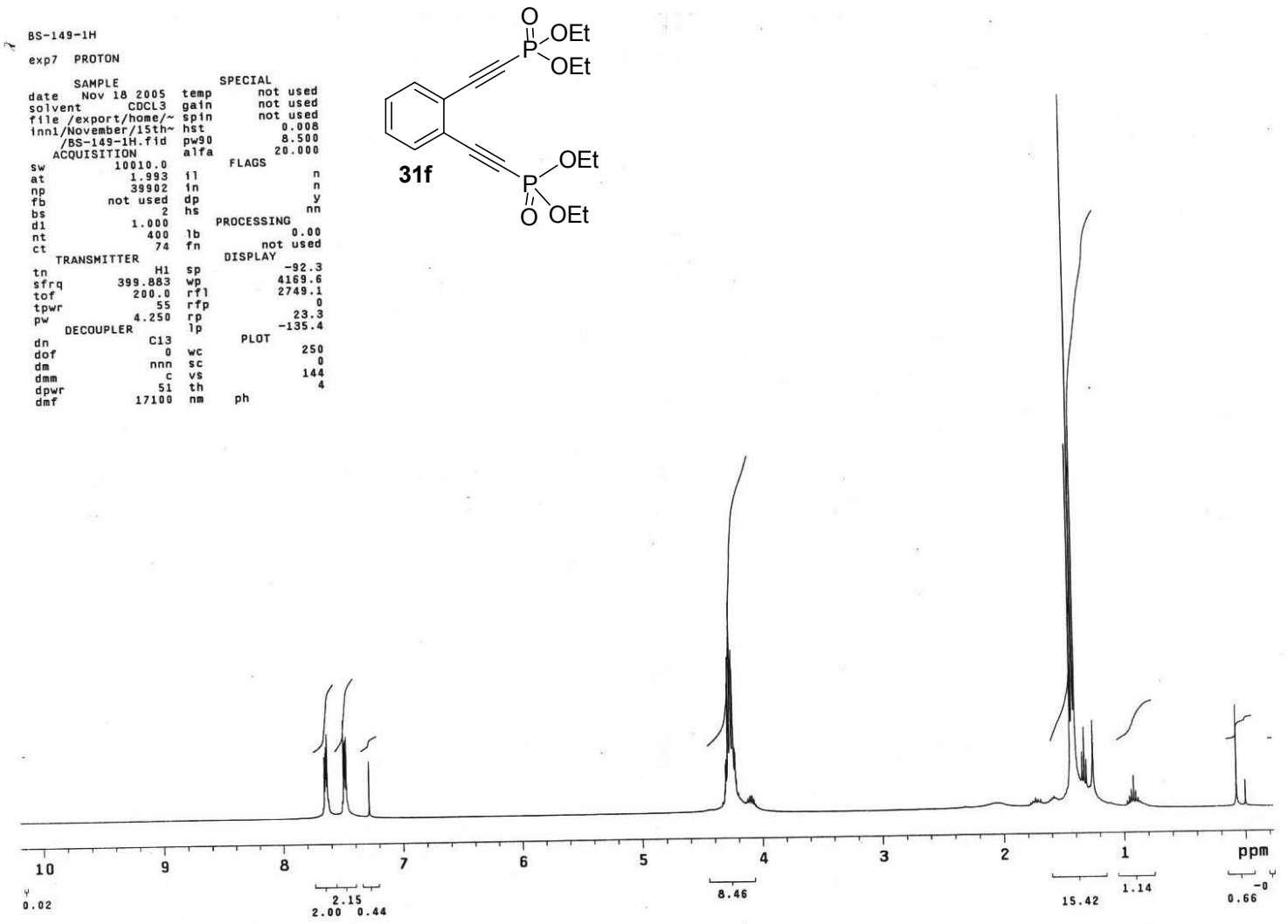


Figure S55. ^{1}H NMR spectrum ($CDCl_3$) of 1,2-bis(diethyl 2-phenylethynyl)phosphonate **(31f)**

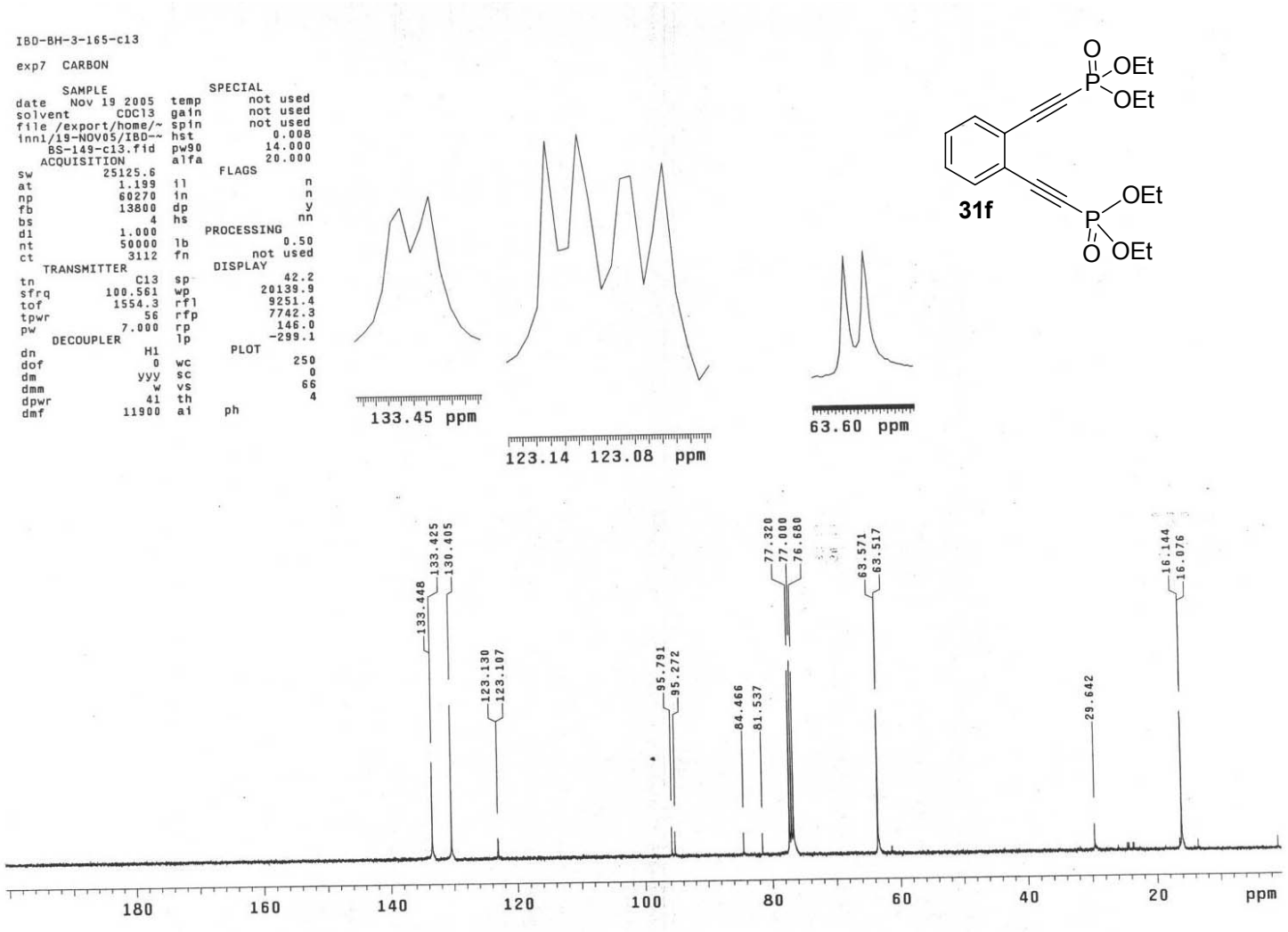


Figure S56. ^{13}C NMR spectrum ($CDCl_3$) of 1,2-bis(diethyl 2-phenylethynyl)phosphonate **(31f)**

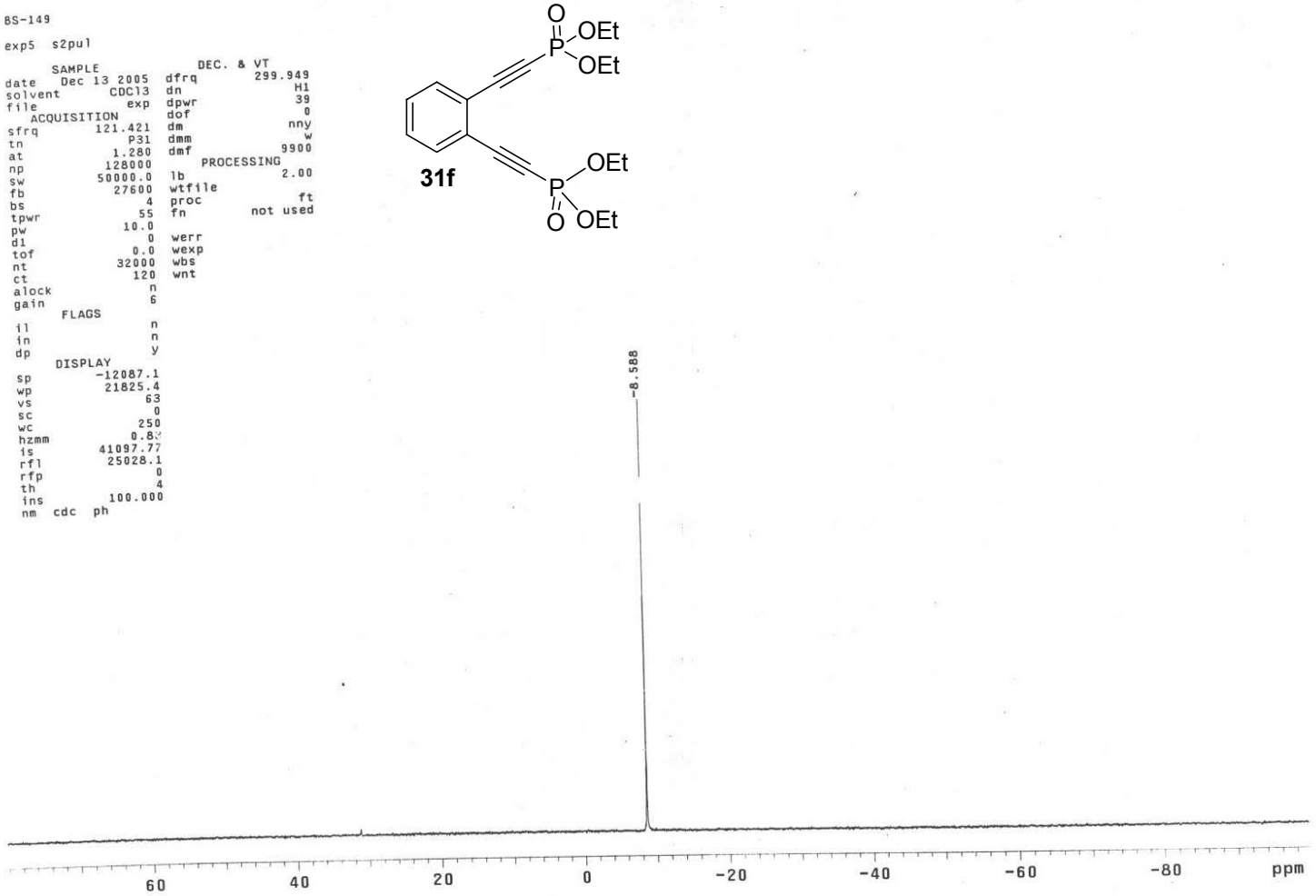


Figure S57. ^{31}P NMR spectrum ($CDCl_3$) of 1,2-bis(diethyl 2-phenylethynyl)phosphonate **(31f)**