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Supplementary Information

Alkynyl Fischer Carbene Complex as a Traceless Directing Group for the Regioselective Cycloaddition of Dithiolethiones to Arylacetylene: Synthesis of *E*-Dithiafulvene Thione and Dithioesters.

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General: In ^{1}H NMR, chemical shifts are reported in ppm from tetramethylsilane with the residual solvent resonance as the internal standard (TMS: δ 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet), integration and assignment coupling constants (*J* in Hz). ^{13}C NMR spectra were recorded with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$: δ 77.00 ppm). High-resolution mass spectrometry analyses (HRMS) were made in UCR Mass Spectrometry (Universidad de California, Deparment of Chemistry) Riverside C.A. 92521, USA and in the in SCAI of the University of Burgos, Spain; elemental analyses were made in Galbraith Laboratories, INC., Knoxville, TN 37921-1700, USA and X ray diffraction analyses were made in SCAI of the University of Burgos, Spain.

All reactions were carried out under nitrogen atmosphere. Ethyl ether, dichoromethane and hexane were analytical grade used without further purification.

Synthesis of starting materials:

[Pentacarbonyl(phenylethynyl-methoxy)chromium(0)] (2): Fischer carbene was prepared according to literature procedures.[1]

5-Cyclopenthylthio-3*H*-1,2-dithiole-3-one*:* This substrate was obtained from the transformation of the corresponding 5-cyclopenthylthio-3*H*-1,2-dithiole-3-thione **1a** in 70% yield, according to the method described recently in our laboratory.[2] ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.73 (m, 4H); 2.17 (m, 4H); 3.75 (m, 1H); 6.37 (s, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 24.77; 33.66; 47.54; 116.70; 171.17; 192.03. IR (KBr, cm^{-1}): 611.4; 790.5; 930.6; 1105.8; 1226.4; 1448.3; 1506.7; 1646.8; 1658.5; 2861.2; 2954.6; 3075.3. HRMS calculated for $C_8H_{10}OS_3$: 217.9894 found 217.9890.

Synthesis of [pentacarbonyl(5-methyl-3*H*-1,2-dithiole-3-thione)chromium(0)]: Obtained by reaction of 5-methyl-3*H*-1,2-dithiole-3-thione (**1d**) with [(hexacarbonyl)chromium(0)]: 5-methyl-3*H*-1,2-dithiole-3-thione (1 mmol) and 1.2 mmol of [(hexacarbonyl)chromium(0)] (1 mmol) were added to benzene (50 mL). The solution was stirred under N_2 and irradiated with UV light (257 nm) for two hours. The reaction was monitored by TLC until no remaining substrate was observed. The solvent was removed under vacuum, and the resulting solid was then dried with a vacuum pump. The crude product was purified by column chromatography using silica gel and a mixture of hexane/dichoromethane 70/30 V/V as solvent. The product was obtained as a blue solid, 70%. m.p. decomposed at 280 °C (1 atm). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.55 (s, 3H); 7.28 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 18.37; 137.65; 169.93; 215.04; 216.93; 222.74.

X-Ray Diffraction Structure Report for [pentacarbonyl(5-methyl-3*H*-1,2-dithiole-3-thione)chromium(0)]: Crystallographic data are presented in Tables 1-5. A single crystal of [pentacarbonyl(5-methyl-3*H*-1,2-dithiole-3-thione)cromium(0)] was mounted on a glass fibre. X-ray measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo-K$_\alpha$ radiation (λ = 0.71073 Å).[3] Intensities were integrated[4] from several series of exposures, each exposure covering 0.3° in ω, and the total data set being a sphere. Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.[5] The structure was solved by direct methods and refined by least squares on weighted F^2 values for all reflections (see Table 1).[6] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. Refinement proceeded smoothly to give the residuals shown in Table 1. Complex neutral-atom scattering factors were used.[7]

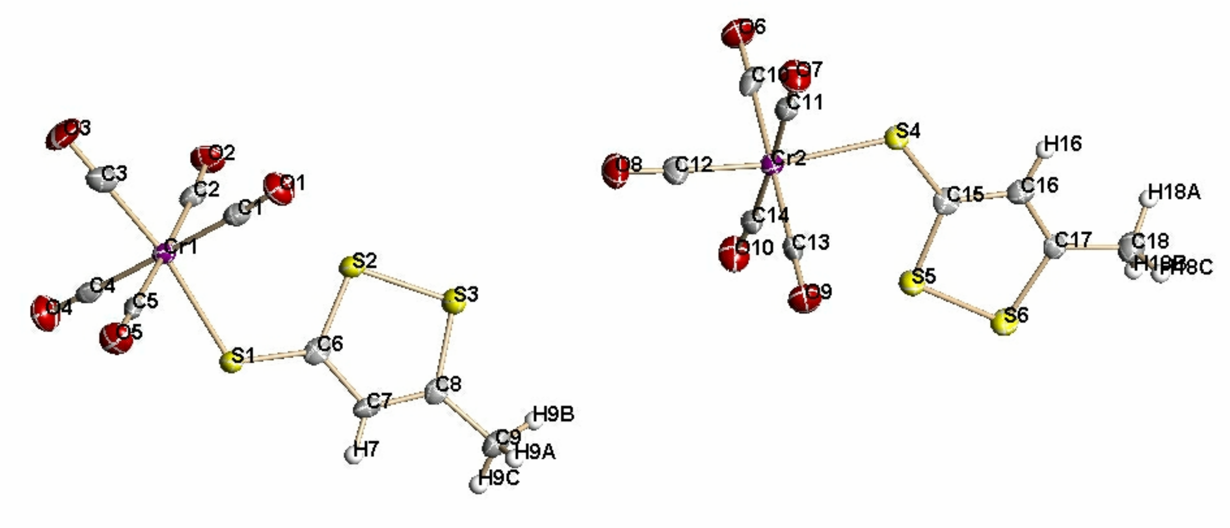


Table 1. Crystal data and structure refinement for [pentacarbonyl(5-methyl-3H-1,2-dithiole-3-thione)chromium(0)].

Identification code	datosm	
Empirical formula	C9 H4 Cr O5 S3	
Formula weight	340.30	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 23.944(3) Å	α = 90°
	b = 7.6413(10) Å	β = 105.663(2)°
	c = 28.506(4) Å	γ = 90°
Volume	5022.0(11) $Å^3$	
Z	16	
Density (calculated)	1.800 Mg/m^3	
Absorption coefficient	1.416 mm^{-1}	
F(000)	2720	
Crystal size	0.60 x 0.30 x 0.02 mm	
θ range for data collection	1.48 to 25.00°	
Index ranges	-28<=h<=28, -9<=k<=9, -33<=l<=33	
Reflections collected	23664	
Independent reflections	4407 [R_{int} = 0.1013]	
Completeness to θ = 25.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.972 and 0.508	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4407 / 0 / 327	
Goodness-of-fit on F^2	S = 1.007	
R indices [for 3066 reflections with $I>2\sigma(I)$]	R_1 = 0.0507, wR_2 = 0.1284	
R indices (for all 4407 data)	R_1 = 0.0840, wR_2 = 0.1679	
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + (bP)$,	
	where $P = [\max(F_o^2, 0) + 2F_c^2]/3$	
	a = 0.0919, b = 0.0000	
Largest diff. peak and hole	0.534 and -0.533 $eÅ^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [pentacarbonyl(5-methyl-3H-1,2-dithiole-3-thione)chromium(0)]. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cr(1)	6269(1)	10121(1)	5678(1)	20(1)
S(1)	5653(1)	9972(2)	4849(1)	24(1)
S(2)	6725(1)	10395(2)	4525(1)	25(1)
S(3)	6766(1)	10191(2)	3814(1)	29(1)
O(1)	7096(2)	7254(5)	5550(2)	37(1)
O(2)	7102(2)	12998(5)	5574(2)	36(1)
O(3)	6863(2)	10135(6)	6756(2)	47(1)
O(4)	5466(2)	13020(6)	5845(2)	39(1)
O(5)	5492(2)	7159(6)	5856(2)	37(1)
C(1)	6780(2)	8351(7)	5583(2)	23(1)
C(2)	6783(2)	11902(8)	5597(2)	25(1)
C(3)	6639(3)	10126(7)	6345(2)	30(2)
C(4)	5754(2)	11927(8)	5781(2)	24(1)
C(5)	5770(2)	8290(8)	5788(2)	23(1)
C(6)	5992(3)	9993(7)	4403(2)	24(1)
C(7)	5714(3)	9697(7)	3904(2)	22(1)
C(8)	6041(3)	9752(7)	3575(2)	22(1)
C(9)	5828(3)	9439(7)	3040(2)	29(1)
Cr(2)	8735(1)	9524(1)	2638(1)	21(1)
S(4)	9307(1)	9236(2)	2064(1)	25(1)
S(5)	8261(1)	10194(2)	1277(1)	30(1)
S(6)	8240(1)	10489(2)	555(1)	31(1)
O(6)	9616(2)	12284(6)	3138(2)	43(1)
O(7)	9470(2)	6477(6)	3146(2)	39(1)
O(8)	8224(2)	9641(6)	3492(2)	42(1)
O(9)	7830(2)	6852(6)	2118(2)	40(1)
O(10)	7950(2)	12577(6)	2202(2)	40(1)
C(10)	9296(3)	11223(8)	2955(2)	28(1)
C(11)	9196(2)	7638(8)	2954(2)	25(1)
C(12)	8405(3)	9589(8)	3155(2)	29(2)

C(13)	8164(2)	7860(8)	2308(2)	24(1)
C(14)	8244(2)	11410(8)	2342(2)	23(1)
C(15)	8978(3)	9624(6)	1476(2)	22(1)
C(16)	9267(3)	9536(7)	1099(2)	26(1)
C(17)	8956(2)	9933(7)	638(2)	21(1)
C(18)	9178(3)	9982(8)	194(2)	33(2)

Table 3. Bond lengths [Å] and angles [°] for [pentacarbonyl(5-methyl-3H-1,2-dithiole-3-thione)chromium(0)].

Cr(1)-C(3)	1.871(6)
Cr(1)-C(2)	1.890(6)
Cr(1)-C(1)	1.893(6)
Cr(1)-C(5)	1.920(6)
Cr(1)-C(4)	1.925(6)
Cr(1)-S(1)	2.4261(16)
S(1)-C(6)	1.683(6)
S(2)-C(6)	1.722(6)
S(2)-S(3)	2.059(2)
S(3)-C(8)	1.718(6)
O(1)-C(1)	1.149(6)
O(2)-C(2)	1.148(6)
O(3)-C(3)	1.147(7)
O(4)-C(4)	1.129(7)
O(5)-C(5)	1.139(7)
C(6)-C(7)	1.416(8)
C(7)-C(8)	1.375(8)
C(7)-H(7)	0.9300
C(8)-C(9)	1.493(7)
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
Cr(2)-C(12)	1.853(6)
Cr(2)-C(11)	1.889(6)
Cr(2)-C(14)	1.907(6)
Cr(2)-C(10)	1.912(7)

Cr(2)-C(13)	1.917(6)
Cr(2)-S(4)	2.4091(17)
S(4)-C(15)	1.675(6)
S(5)-C(15)	1.712(6)
S(5)-S(6)	2.058(2)
S(6)-C(17)	1.722(6)
O(6)-C(10)	1.140(7)
O(7)-C(11)	1.150(7)
O(8)-C(12)	1.157(7)
O(9)-C(13)	1.138(6)
O(10)-C(14)	1.140(6)
C(15)-C(16)	1.428(8)
C(16)-C(17)	1.359(8)
C(16)-H(16)	0.9300
C(17)-C(18)	1.498(8)
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600
C(3)-Cr(1)-C(2)	88.7(2)
C(3)-Cr(1)-C(1)	90.0(2)
C(2)-Cr(1)-C(1)	91.7(3)
C(3)-Cr(1)-C(5)	88.8(2)
C(2)-Cr(1)-C(5)	177.4(2)
C(1)-Cr(1)-C(5)	87.6(2)
C(3)-Cr(1)-C(4)	89.4(2)
C(2)-Cr(1)-C(4)	88.1(2)
C(1)-Cr(1)-C(4)	179.4(2)
C(5)-Cr(1)-C(4)	92.6(2)
C(3)-Cr(1)-S(1)	170.9(2)
C(2)-Cr(1)-S(1)	99.23(17)
C(1)-Cr(1)-S(1)	94.25(16)
C(5)-Cr(1)-S(1)	83.35(16)
C(4)-Cr(1)-S(1)	86.38(16)
C(6)-S(1)-Cr(1)	116.4(2)
C(6)-S(2)-S(3)	96.1(2)
C(8)-S(3)-S(2)	95.4(2)

O(1)-C(1)-Cr(1)	176.4(5)
O(2)-C(2)-Cr(1)	176.5(5)
O(3)-C(3)-Cr(1)	179.6(6)
O(4)-C(4)-Cr(1)	178.0(5)
O(5)-C(5)-Cr(1)	177.3(5)
C(7)-C(6)-S(1)	124.4(5)
C(7)-C(6)-S(2)	114.0(4)
S(1)-C(6)-S(2)	121.5(3)
C(8)-C(7)-C(6)	118.7(5)
C(8)-C(7)-H(7)	120.6
C(6)-C(7)-H(7)	120.6
C(7)-C(8)-C(9)	126.3(5)
C(7)-C(8)-S(3)	115.8(4)
C(9)-C(8)-S(3)	117.9(4)
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(12)-Cr(2)-C(11)	87.8(2)
C(12)-Cr(2)-C(14)	89.2(2)
C(11)-Cr(2)-C(14)	176.9(2)
C(12)-Cr(2)-C(10)	90.1(3)
C(11)-Cr(2)-C(10)	92.7(3)
C(14)-Cr(2)-C(10)	88.0(2)
C(12)-Cr(2)-C(13)	90.4(3)
C(11)-Cr(2)-C(13)	88.6(2)
C(14)-Cr(2)-C(13)	90.7(3)
C(10)-Cr(2)-C(13)	178.6(3)
C(12)-Cr(2)-S(4)	170.21(19)
C(11)-Cr(2)-S(4)	83.57(17)
C(14)-Cr(2)-S(4)	99.48(16)
C(10)-Cr(2)-S(4)	85.80(17)
C(13)-Cr(2)-S(4)	93.88(17)
C(15)-S(4)-Cr(2)	117.5(2)

C(15)-S(5)-S(6)	96.4(2)
C(17)-S(6)-S(5)	94.7(2)
O(6)-C(10)-Cr(2)	177.5(6)
O(7)-C(11)-Cr(2)	179.0(5)
O(8)-C(12)-Cr(2)	176.9(6)
O(9)-C(13)-Cr(2)	178.9(6)
O(10)-C(14)-Cr(2)	174.5(5)
C(16)-C(15)-S(4)	123.5(4)
C(16)-C(15)-S(5)	114.2(4)
S(4)-C(15)-S(5)	122.4(3)
C(17)-C(16)-C(15)	117.9(5)
C(17)-C(16)-H(16)	121.0
C(15)-C(16)-H(16)	121.0
C(16)-C(17)-C(18)	126.6(5)
C(16)-C(17)-S(6)	116.9(5)
C(18)-C(17)-S(6)	116.5(4)
C(17)-C(18)-H(18A)	109.5
C(17)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(17)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for [pentacarbonyl(5-methyl-3H-1,2-dithiole-3-thione)chromium(0)].
The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cr(1)	18(1)	22(1)	18(1)	0(1)	3(1)	-3(1)
S(1)	17(1)	35(1)	19(1)	-1(1)	4(1)	-1(1)
S(2)	20(1)	35(1)	20(1)	-1(1)	3(1)	-4(1)
S(3)	24(1)	40(1)	22(1)	0(1)	8(1)	-4(1)

O(1)	34(3)	34(3)	45(3)	3(2)	14(2)	8(2)
O(2)	28(3)	35(3)	44(3)	0(2)	9(2)	-14(2)
O(3)	53(3)	62(3)	21(3)	-2(2)	-1(2)	-11(3)
O(4)	42(3)	33(3)	47(3)	-3(2)	18(2)	10(2)
O(5)	37(3)	34(3)	41(3)	3(2)	13(2)	-12(2)
C(1)	23(3)	25(3)	20(3)	3(2)	2(3)	-5(3)
C(2)	26(3)	26(3)	19(3)	-5(2)	0(3)	-2(3)
C(3)	24(3)	29(4)	35(4)	1(3)	4(3)	-2(3)
C(4)	23(3)	31(4)	18(3)	1(3)	2(2)	-11(3)
C(5)	20(3)	35(4)	13(3)	-5(3)	5(2)	4(3)
C(6)	32(4)	18(3)	20(3)	5(2)	4(3)	1(3)
C(7)	22(3)	21(3)	20(3)	-2(2)	-2(2)	-3(2)
C(8)	29(3)	19(3)	19(3)	1(2)	5(3)	1(3)
C(9)	36(4)	27(3)	20(3)	-3(3)	3(3)	-3(3)
Cr(2)	19(1)	25(1)	19(1)	1(1)	5(1)	1(1)
S(4)	22(1)	33(1)	20(1)	2(1)	5(1)	4(1)
S(5)	24(1)	42(1)	23(1)	2(1)	6(1)	5(1)
S(6)	28(1)	41(1)	24(1)	2(1)	4(1)	9(1)
O(6)	37(3)	48(3)	41(3)	-15(2)	6(2)	-11(2)
O(7)	38(3)	43(3)	36(3)	8(2)	10(2)	15(2)
O(8)	44(3)	57(3)	30(3)	3(2)	17(2)	7(2)
O(9)	34(3)	42(3)	40(3)	-8(2)	6(2)	-8(2)
O(10)	47(3)	37(3)	37(3)	7(2)	14(2)	12(2)
C(10)	37(4)	31(4)	17(3)	0(3)	6(3)	8(3)
C(11)	23(3)	35(4)	19(3)	-2(3)	6(3)	-1(3)
C(12)	29(4)	35(4)	25(3)	3(3)	9(3)	4(3)
C(13)	19(3)	33(3)	24(3)	-5(3)	12(3)	-2(3)
C(14)	20(3)	31(3)	18(3)	0(3)	8(2)	-2(3)
C(15)	29(3)	11(3)	25(3)	4(2)	7(3)	1(2)
C(16)	26(3)	26(3)	23(3)	2(3)	2(3)	0(3)
C(17)	23(3)	19(3)	22(3)	-4(2)	7(2)	0(2)
C(18)	37(4)	37(4)	26(3)	1(3)	8(3)	5(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for [pentacarbonyl(5-methyl-3H-1,2-dithiole-3-thione)chromium(0)].

	x	y	z	U(eq)
H(7)	5318	9471	3801	27
H(9A)	5770	8207	2979	43
H(9B)	6109	9862	2882	43
H(9C)	5467	10045	2913	43
H(16)	9655	9216	1168	31
H(18A)	9593	10082	292	50
H(18B)	9015	10970	-3	50
H(18C)	9069	8925	11	50

1,2-Dithiole-3-thione derivatives (1a-e): were synthesized according to literature procedures.[8]

Synthesis of compounds 3a-e:

Synthesis of compound 3a: Reaction of 5-cyclopenthylthio-3*H*-1,2-dithiole-3-thione (**1a**) with [pentacarbonyl(phenylethynylmethoxy)chromium(0)] (**2**): Fischer carbene complex **2** (1 mmol) was added to diethyl ether (100 mL). The solution was stirred under N_2 and cooled to –40 ºC. Compound **1a** (1 mmol) was added to the previous solution and the reaction was monitored by TLC until no remaining substrate was observed (30 minutes). The solvent was removed under vacuum, and the resulting solid was then dried with a vacuum pump. The crude product was purified by column chromatography using silica gel and a mixture of hexane/dichoromethane 80/20 V/V as solvent. The product **1a** was obtained as a black solid, 92%, m.p. decomposed at 115 °C (1 atm). ^{1}H NMR ($CDCl_3$, 200 MHz two isomers) δ: 1.69 (m, 6H); 2.24 (m, 2H); 4.10 (m, 1H); 4.44 (s, 3H, very minor) and 4.49 (s, 3H, predominant isomer); 7.23 (m, 2H), 7.39 (m, 3H); 7.43 (s, 1H, predominant isomer) and 7.49 (s, 1H, very minor). ^{13}C NMR ($CDCl_3$, 50 MHz, two isomers) δ: 25.09; 32.66; 47.50; 66.57; 115.71; 116.54; 125.47; 128.76; 128.96; 129.10; 129.44; 129.69; 130.80; 157.19; 206.77; 214.98; 223.61;

334.95 (minor) and 337.77 (predominant isomer). Elemental analysis, calculated for $C_{23}H_{18}CrO_6S_4$: C: 48.41%; H: 3.18%; S: 22.48%. Found: C: 48.27%; H: 3.17%; S: 22.69%.

X-Ray Diffraction Structure Report for **3a**: Crystallographic data are presented in Tables 6-11. A single crystal of **3a** was mounted on a glass fibre. X-ray measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo-K_α radiation (λ = 0.71073 Å).[3] Intensities were integrated[4] from several series of exposures, each exposure covering 0.3° in ω, and the total data set being a sphere. Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.[5] The structure was solved by direct methods and refined by least squares on weighted F^2 values for all reflections (see Table 6).[6] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. Refinement proceeded smoothly to give the residuals shown in Table 1. Complex neutral-atom scattering factors were used.[7]

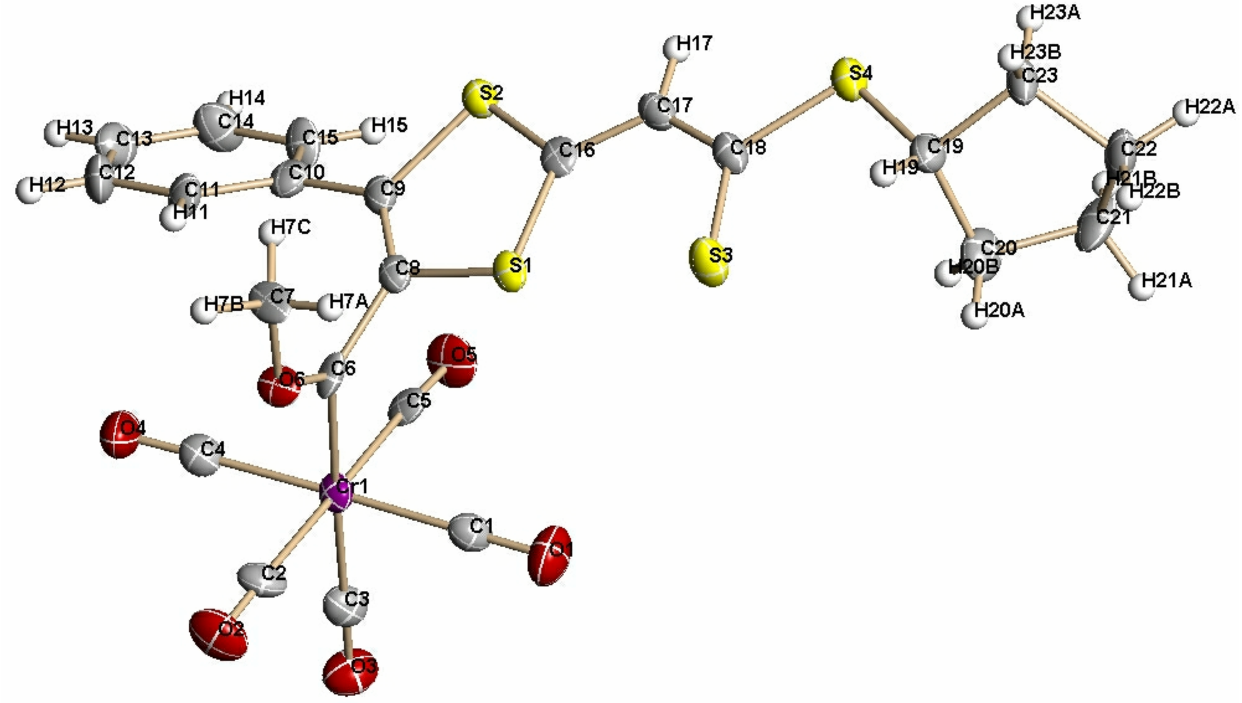


Table 6. Crystal data and structure refinement for **3a**.

Identification code	datosm	
Empirical formula	C23 H18 Cr O6 S4	
Formula weight	570.61	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.668(3) Å	α = 100.190(8)°
	b = 9.884(3) Å	β = 90.645(7)°
	c = 19.498(7) Å	γ = 97.238(8)°
Volume	1254.0(8) Å^3	
Z	2	
Density (calculated)	1.511 Mg/m^3	
Absorption coefficient	0.826 mm^{-1}	
F(000)	584	
Crystal size	0.15 x 0.10 x 0.02 mm	
θ range for data collection	2.53 to 25.00°	
Index ranges	-7<=h<=7, -11<=k<=11, -23<=l<=23	
Reflections collected	12132	
Independent reflections	4368 [R_{int} = 0.1389]	
Completeness to θ = 25.00°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.980 and 0.868	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4368 / 0 / 308	
Goodness-of-fit on F^2	S = 0.968	
R indices [for 2358 reflections with $I>2\sigma(I)$]	R_1 = 0.0798, wR_2 = 0.1382	
R indices (for all 4368 data)	R_1 = 0.1575, wR_2 = 0.1650	
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + (bP)$,	
	where $P = [\max(F_o^2, 0) + 2F_c^2]/3$	
	a = 0.0442, b = 0.0000	
Largest diff. peak and hole	0.471 and -0.472 eÅ^{-3}	

Table 7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **3a**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cr(1)	2661(2)	5271(1)	6414(1)	23(1)
S(1)	3548(3)	7223(2)	8507(1)	24(1)
S(2)	5265(3)	9915(2)	8181(1)	26(1)
S(3)	5197(3)	6652(2)	9783(1)	37(1)
S(4)	8367(3)	8886(2)	10535(1)	29(1)
O(1)	4560(9)	3796(6)	7465(3)	50(2)
O(2)	-1228(8)	3221(6)	6302(3)	47(2)
O(3)	4465(8)	3457(6)	5200(3)	41(2)
O(4)	673(9)	6671(6)	5358(3)	45(2)
O(5)	6608(8)	7218(6)	6446(3)	43(2)
O(6)	-325(7)	6136(5)	7424(2)	27(1)
C(1)	3861(12)	4344(8)	7072(4)	29(2)
C(2)	198(12)	4004(8)	6357(4)	31(2)
C(3)	3772(12)	4119(8)	5658(4)	31(2)
C(4)	1405(12)	6161(8)	5756(4)	29(2)
C(5)	5089(10)	6529(7)	6448(4)	24(2)
C(6)	1553(10)	6454(7)	7219(4)	24(2)
C(7)	-1259(10)	6970(8)	8005(4)	33(2)
C(8)	2812(10)	7644(8)	7701(4)	22(2)
C(9)	3587(10)	8879(7)	7546(4)	24(2)
C(10)	3126(11)	9464(7)	6919(4)	27(2)
C(11)	1096(11)	9328(7)	6662(4)	28(2)
C(12)	676(12)	9901(8)	6079(4)	36(2)
C(13)	2206(13)	10601(8)	5761(4)	39(2)
C(14)	4216(13)	10749(8)	6013(4)	41(2)
C(15)	4631(11)	10187(8)	6589(4)	31(2)
C(16)	5165(10)	8747(7)	8761(4)	24(2)
C(17)	6436(10)	9072(8)	9354(4)	26(2)
C(18)	6539(10)	8190(8)	9854(4)	26(2)
C(19)	8275(12)	7533(8)	11049(4)	29(2)
C(20)	9454(12)	6296(9)	10727(4)	40(2)

C(21)	11393(12)	6523(9)	11170(4)	44(2)
C(22)	10771(11)	7071(8)	11895(4)	36(2)
C(23)	9353(11)	8151(8)	11778(4)	32(2)

Table 8. Bond lengths [Å] and angles [°] for **3a**.

Cr(1)-C(5)	1.906(7)
Cr(1)-C(3)	1.914(9)
Cr(1)-C(4)	1.917(9)
Cr(1)-C(2)	1.926(8)
Cr(1)-C(1)	1.926(9)
Cr(1)-C(6)	1.993(7)
S(1)-C(16)	1.729(7)
S(1)-C(8)	1.774(7)
S(2)-C(16)	1.749(7)
S(2)-C(9)	1.750(7)
S(3)-C(18)	1.646(8)
S(4)-C(18)	1.776(7)
S(4)-C(19)	1.802(8)
O(1)-C(1)	1.140(8)
O(2)-C(2)	1.139(8)
O(3)-C(3)	1.147(9)
O(4)-C(4)	1.136(8)
O(5)-C(5)	1.147(8)
O(6)-C(6)	1.335(8)
O(6)-C(7)	1.472(8)
C(6)-C(8)	1.522(10)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-C(9)	1.350(9)
C(9)-C(10)	1.487(10)
C(10)-C(15)	1.388(9)
C(10)-C(11)	1.420(9)
C(11)-C(12)	1.397(10)

C(11)-H(11)	0.9500
C(12)-C(13)	1.375(10)
C(12)-H(12)	0.9500
C(13)-C(14)	1.404(11)
C(13)-H(13)	0.9500
C(14)-C(15)	1.378(10)
C(14)-H(14)	0.9500
C(15)-H(15)	0.9500
C(16)-C(17)	1.393(9)
C(17)-C(18)	1.423(10)
C(17)-H(17)	0.9500
C(19)-C(23)	1.571(10)
C(19)-C(20)	1.578(10)
C(19)-H(19)	1.0000
C(20)-C(21)	1.517(10)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-C(22)	1.504(10)
C(21)-H(21A)	0.9900
C(21)-H(21B)	0.9900
C(22)-C(23)	1.556(10)
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(5)-Cr(1)-C(3)	87.4(3)
C(5)-Cr(1)-C(4)	91.6(3)
C(3)-Cr(1)-C(4)	89.5(3)
C(5)-Cr(1)-C(2)	178.7(3)
C(3)-Cr(1)-C(2)	91.9(3)
C(4)-Cr(1)-C(2)	87.3(3)
C(5)-Cr(1)-C(1)	89.9(3)
C(3)-Cr(1)-C(1)	90.5(3)
C(4)-Cr(1)-C(1)	178.6(3)
C(2)-Cr(1)-C(1)	91.2(3)
C(5)-Cr(1)-C(6)	92.3(3)

C(3)-Cr(1)-C(6)	178.4(3)
C(4)-Cr(1)-C(6)	92.0(3)
C(2)-Cr(1)-C(6)	88.5(3)
C(1)-Cr(1)-C(6)	88.0(3)
C(16)-S(1)-C(8)	94.5(4)
C(16)-S(2)-C(9)	96.5(4)
C(18)-S(4)-C(19)	103.1(4)
C(6)-O(6)-C(7)	124.1(5)
O(1)-C(1)-Cr(1)	179.5(7)
O(2)-C(2)-Cr(1)	177.2(7)
O(3)-C(3)-Cr(1)	178.3(7)
O(4)-C(4)-Cr(1)	178.8(7)
O(5)-C(5)-Cr(1)	175.7(6)
O(6)-C(6)-C(8)	114.6(6)
O(6)-C(6)-Cr(1)	121.0(5)
C(8)-C(6)-Cr(1)	123.8(5)
O(6)-C(7)-H(7A)	109.5
O(6)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
O(6)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(9)-C(8)-C(6)	127.0(7)
C(9)-C(8)-S(1)	118.6(6)
C(6)-C(8)-S(1)	113.9(5)
C(8)-C(9)-C(10)	127.6(7)
C(8)-C(9)-S(2)	115.0(6)
C(10)-C(9)-S(2)	117.3(5)
C(15)-C(10)-C(11)	118.8(7)
C(15)-C(10)-C(9)	121.5(7)
C(11)-C(10)-C(9)	119.7(7)
C(12)-C(11)-C(10)	119.2(7)
C(12)-C(11)-H(11)	120.4
C(10)-C(11)-H(11)	120.4
C(13)-C(12)-C(11)	120.5(7)
C(13)-C(12)-H(12)	119.8

C(11)-C(12)-H(12)	119.8
C(12)-C(13)-C(14)	120.8(8)
C(12)-C(13)-H(13)	119.6
C(14)-C(13)-H(13)	119.6
C(15)-C(14)-C(13)	118.8(8)
C(15)-C(14)-H(14)	120.6
C(13)-C(14)-H(14)	120.6
C(14)-C(15)-C(10)	121.9(7)
C(14)-C(15)-H(15)	119.0
C(10)-C(15)-H(15)	119.0
C(17)-C(16)-S(1)	125.9(6)
C(17)-C(16)-S(2)	118.7(6)
S(1)-C(16)-S(2)	115.3(4)
C(16)-C(17)-C(18)	124.0(7)
C(16)-C(17)-H(17)	118.0
C(18)-C(17)-H(17)	118.0
C(17)-C(18)-S(3)	123.6(6)
C(17)-C(18)-S(4)	112.7(5)
S(3)-C(18)-S(4)	123.6(5)
C(23)-C(19)-C(20)	105.3(6)
C(23)-C(19)-S(4)	108.8(5)
C(20)-C(19)-S(4)	113.6(5)
C(23)-C(19)-H(19)	109.7
C(20)-C(19)-H(19)	109.7
S(4)-C(19)-H(19)	109.7
C(21)-C(20)-C(19)	104.3(6)
C(21)-C(20)-H(20A)	110.9
C(19)-C(20)-H(20A)	110.9
C(21)-C(20)-H(20B)	110.9
C(19)-C(20)-H(20B)	110.9
H(20A)-C(20)-H(20B)	108.9
C(22)-C(21)-C(20)	104.6(6)
C(22)-C(21)-H(21A)	110.8
C(20)-C(21)-H(21A)	110.8
C(22)-C(21)-H(21B)	110.8
C(20)-C(21)-H(21B)	110.8

H(21A)-C(21)-H(21B)	108.9
C(21)-C(22)-C(23)	103.2(6)
C(21)-C(22)-H(22A)	111.1
C(23)-C(22)-H(22A)	111.1
C(21)-C(22)-H(22B)	111.1
C(23)-C(22)-H(22B)	111.1
H(22A)-C(22)-H(22B)	109.1
C(22)-C(23)-C(19)	104.3(6)
C(22)-C(23)-H(23A)	110.9
C(19)-C(23)-H(23A)	110.9
C(22)-C(23)-H(23B)	110.9
C(19)-C(23)-H(23B)	110.9
H(23A)-C(23)-H(23B)	108.9

Table 9. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **3a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cr(1)	15(1)	29(1)	25(1)	3(1)	2(1)	3(1)
S(1)	16(1)	30(1)	25(1)	5(1)	0(1)	1(1)
S(2)	24(1)	26(1)	27(1)	5(1)	-3(1)	1(1)
S(3)	31(1)	38(1)	41(1)	14(1)	-10(1)	-7(1)
S(4)	24(1)	34(1)	29(1)	5(1)	-3(1)	3(1)
O(1)	50(4)	61(4)	47(4)	20(4)	-2(3)	23(3)
O(2)	38(4)	48(4)	47(4)	4(3)	6(3)	-15(3)
O(3)	49(4)	40(4)	37(4)	7(3)	14(3)	11(3)
O(4)	53(4)	43(4)	40(4)	3(3)	-14(3)	17(3)
O(5)	18(3)	49(4)	57(4)	7(3)	5(3)	-4(3)
O(6)	15(3)	32(3)	32(3)	1(3)	11(2)	4(2)
C(1)	33(5)	27(5)	24(5)	4(4)	2(4)	-1(4)
C(2)	39(5)	25(5)	23(5)	-4(4)	4(4)	-1(4)
C(3)	39(5)	27(5)	27(5)	10(4)	0(4)	-1(4)
C(4)	27(5)	32(5)	27(5)	4(4)	5(4)	2(4)

C(5)	14(4)	22(4)	38(5)	7(4)	7(4)	7(3)
C(6)	13(4)	32(5)	32(5)	16(4)	3(3)	10(3)
C(7)	13(4)	42(5)	38(5)	-13(4)	7(4)	11(4)
C(8)	16(4)	27(5)	23(5)	2(4)	2(3)	6(3)
C(9)	18(4)	27(5)	26(5)	3(4)	-1(3)	6(3)
C(10)	26(5)	27(5)	29(5)	2(4)	5(4)	11(4)
C(11)	17(4)	31(5)	39(5)	12(4)	-3(4)	4(3)
C(12)	28(5)	41(5)	40(6)	8(4)	-14(4)	8(4)
C(13)	57(6)	35(5)	24(5)	6(4)	-12(4)	7(5)
C(14)	42(6)	40(6)	40(6)	12(5)	-2(4)	-9(4)
C(15)	14(4)	48(6)	33(5)	10(4)	2(4)	5(4)
C(16)	15(4)	32(5)	25(5)	0(4)	8(3)	9(3)
C(17)	20(4)	27(5)	29(5)	-1(4)	-2(4)	-1(3)
C(18)	19(4)	33(5)	24(5)	1(4)	-1(3)	1(3)
C(19)	32(5)	31(5)	23(5)	1(4)	-5(4)	8(4)
C(20)	44(6)	56(6)	22(5)	6(4)	-2(4)	16(5)
C(21)	36(5)	54(6)	47(6)	11(5)	7(5)	30(5)
C(22)	21(4)	41(5)	49(6)	15(5)	-9(4)	5(4)
C(23)	24(5)	44(5)	28(5)	-1(4)	-6(4)	14(4)

Table 10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **3a**.

	x	y	z	U(eq)
H(7A)	-981	6648	8440	49
H(7B)	-2724	6872	7916	49
H(7C)	-693	7947	8047	49
H(11)	36	8854	6884	34
H(12)	-676	9806	5901	43
H(13)	1898	10988	5366	47
H(14)	5271	11227	5791	49
H(15)	5987	10298	6766	37
H(17)	7286	9935	9431	32
H(19)	6835	7171	11115	35

H(20A)	8661	5393	10756	48
H(20B)	9749	6325	10233	48
H(21A)	11965	5642	11154	52
H(21B)	12413	7202	11007	52
H(22A)	11960	7516	12198	43
H(22B)	10043	6321	12108	43
H(23A)	10141	9067	11771	39
H(23B)	8354	8254	12149	39

Synthesis of compound 3b: Reaction of 5-buthylthio-3*H*-1,2-dithiole-3-thione (**1b**) with [pentacarbonyl(phenylethynylmethoxy)chromium(0)] (**2**): Fischer carbene complex **2** (1 mmol) was added to diethyl ether (100 mL). The solution was stirred under N_2 and cooled to –42 ºC. Compound **1b** (1 mmol) was added to solution and the reaction was monitored by TLC until no remaining substrate was observed (25 minutes). The solvent was removed under vacuum, and the resulting solid was then dried with a vacuum pump. The crude product was purified by column chromatography using silica gel and a mixture of hexane/dichoromethane 80/20 V/V as solvent. The product **3b** was obtained as a black solid, 75%. m.p. decomposed at 92 °C (1 atm). ^1H NMR ($CDCl_3$, 200 MHz two isomers) δ: 0.94 (t, 3H); 1.43 (m, 2H); 1.68 (m, 2H); 3.27 (t, 2H); 4,44 (s, 3H, very minor) and 4.48 (s, 3H, predominant isomer); 7.30 (m, 5H), 7.45 (s, 1H, predominant isomer) and 7.51 (s, 1H, very minor). ^{13}C NMR ($CDCl_3$, 50 MHz) δ: 13.69; 22.18; 30.43; 34.36; 66.62; 115.96; 116.73; 125.61; 128.76; 128.96; 129.06; 129.42; 130.75; 141.48; 157.49; 206.05; 214.93; 223.56; 337.47. HRMS calculated for $C_{22}H_{18}O_6S_4Cr$: 557.9391; found 557.9332. Elemental analysis, calculated for $C_{22}H_{18}CrO_6S_4$: C: 47.30%; H: 3.25%; S: 22.96%. Found: C: 47.19%; H: 3.15%; S: 23.07%.

Synthesis of compound 3c: Reaction of 5-ehylthio-4-phenyl-3*H*-1,2-dithiole-3-thione (**1c**) with [pentacarbonyl(phenylethynylmethoxy)chromium(0)] (**2**): The procedure was the same that for the synthesis of compound **3a**, but the reaction time was 6 hours. The mixture was stirred under N_2 from -40º C to room temperature and the reaction was monitored by TLC until no remaining substrate was observed. The crude product was purified by column chromatography using the same procedure that was used for **3a**. The product **3c** was obtained as black oil, 35%. ^1H NMR ($CDCl_3$, 400 MHz two isomers): δ 1.24 (t, 3H); 2.76 (m, 2H); 4.42 (s, 3H, very minor) and 4.52 (s, 3H, predominant isomer);

7.40 (m, 10H). ^{13}C NMR (CDCl$_3$, 100 MHz two isomers): δ 14.13; 31.60; 31.93; 66.77; 128.39; 128.79; 129.01; 129.10; 129.69; 129.77; 129.84; 130.02; 130.09; 130.95; 137.66; 137.79; 162.50; 203.03; 214.75; 214.97; 223.65; 329.02 (minor) and 330.57 (predominant isomer). HRMS calculated for $C_{26}H_{18}O_6S_4Cr$: 605.9391; found 605.9387. Elemental analysis, calculated for $C_{26}H_{18}CrO_6S_4$: C: 51.47%; H: 2.99%; S: 21.14%. Found: C: 51.32%; H: 2.85%; S: 21.08%.

Synthesis of compound 3d: Reaction of 5-methyl-3*H*-1,2-dithiole-3-thione (**1d**) with [pentacarbonyl(phenylethynylmethoxy)chromium(0)] (**2**): The procedure was the same that for the synthesis of compound **3a**. The mixture was stirred under these conditions and the reaction was monitored by TLC until no remaining substrate was observed (2 hours). The crude product was purified by column chromatography following the same procedure used for **3a.** The product **3d** was obtained as a black solid, 83%, m.p. decomposed at 94 °C (1 atm). ^{1}H NMR (CDCl$_3$, 200 MHz two isomers) δ: 2.80 (s, 3H); 4.48 (s, 3H, very minor) and 4.53 (s, 3H, predominant isomer); 7.24 (m, 2H), 7.40 (m, 3H); 7.64 (s, 1H, predominant isomer) and 7.70 (s, 1H, very minor). ^{13}C NMR (CDCl$_3$, 50 MHz two isomers) δ: 38.19; 38.67; 66.71; 66.81; 119.01; 119.89; 128.91; 129.01; 129.15; 129.54; 129.83; 162.14; 212.50; 213.71; 214.83; 223.61; 335.44 (minor) and 338.44 (predominant isomer). HRMS calculated for $C_{19}H_{12}O_6S_3Cr$: 483.9201; found 483.9211. Elemental analysis, calculated for $C_{19}H_{12}CrO_6S_3$: C: 47.10%; H: 2.50%; S: 19.86%. Found: C: 46.92%; H: 2.39%; S: 19.91%.

Synthesis of compound 3e: Reaction of 4-ethyl-3-thioxo-3*H*,4*H*,5*H*-bis[1,2]dithiolo[3,4-*b*:4',3'-*e*]-[1,4]thiazin-5-one (**1e**) with [pentacarbonyl(phenylethynylmethoxy)chromium(0)] (**2**): The procedure was the same that for the synthesis of compound **3a**. The mixture was stirred under N_2 from –40º C to reflux of the solvent and the reaction was monitored by TLC until no remaining substrate was observed (7 hours). The crude product was purified by column chromatography of the same form that the compuond **3a.** The product **3e** was obtained as a black solid, 23%, m.p. decomposed at 103°C (1 atm). ^{1}H NMR (CDCl$_3$, 400 MHz two isomers) δ: 0.88 (m, 3H); 3.35 (m, 1H); 3.54 (m, 1H); 3.78 (d, 1H); 3.88 (d, 1H); 4.53 (s, 3H, minor) and 4.58 (s, 3H, predominant isomer); 7.24 (m, 2H); 7.42 (m, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz two isomers) δ:14.08; 47.99; 66.81; 67.01; 128.23; 128.52; 129.06; 129.15; 129.34; 129.88; 130.03; 131.24; 167.19; 209.01; 214.64; 214.73; 223.22; 224.63; 242.43; 336.16 (minor) and 336.36 (predominant isomer). HRMS calculated for ion M+1 of $C_{23}H_{13}CrNO_7S_6$:

659.8500; found 659.8489. Elemental analysis, calculated for $C_{23}H_{13}CrNO_7S_6$: C: 41.87%; H: 1.99%; N: 2.12%; S: 29.16%. Found: C: 41.76%; H: 1.86%; N: 1.90%; S: 29.05%.

Synthesis of compounds 4a-d:

Synthesis of compound 4a: Compound **3a** (0.25 mmol) dissolved in dichloromethane (50 mL), was added to a two necked flask with neutral aluminum oxide (1 g). The solvent was removed under vacuum, and the resulting solid was purified by column chromatography using neutral aluminum oxide and a mixture of hexane/dichoromethane 80/20 V/V as solvent. The product **4a** was obtained in quantitative yield, m.p. 122.5 – 123.5 ºC (1 atm). ^{1}H NMR ($CDCl_3$, 400 MHz two isomers) δ: 1.67 (m, 6H); 2.24 (m, 2H); 4.13 (m, 1H); 6.86 (d, 1H, ^5J = 1.00 Hz, predominant isomer) and 6.93 (s, 1H, minor); 7.45 (m, 5H); 7.55 (s, 1H, minor) and 7.61 (d, 1H ^5J = 1.00 Hz, predominant isomer). ^{13}C NMR ($CDCl_3$, 100 MHz, two isomers) δ: 25.09; 32.70; 47.18; 47.28; 112.09; 115.20; 116.79; 117.67; 126.62; 127.01; 128.31; 129.11; 129.19; 131.22; 132.32; 135.93; 137.47; 162.31; 162.33; 205.93; 206.07. HRMS calculated for $C_{12}H_{10}S_3$: 336.0135; found 336.0125. Elemental analysis, calculated for $C_{16}H_{16}S_4$: C: 57.10%; H: 4.79%. Found: C: 56.87%; H: 4.72 %.

X-Ray Diffraction Structure Report for **4a**: Crystallographic data are presented in Tables 11-15. A single crystal of **4a** was mounted on a glass fibre. X-ray measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo-K_α radiation (λ = 0.71073 Å).[3] Intensities were integrated[4] from several series of exposures, each exposure covering 0.3° in ω, and the total data set being a sphere. Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.[5] The structure was solved by direct methods and refined by least squares on weighted F^2 values for all reflections (see Table 11).[6] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. Refinement proceeded smoothly to give the residuals shown in Table 11. Complex neutral-atom scattering factors were used.[7]

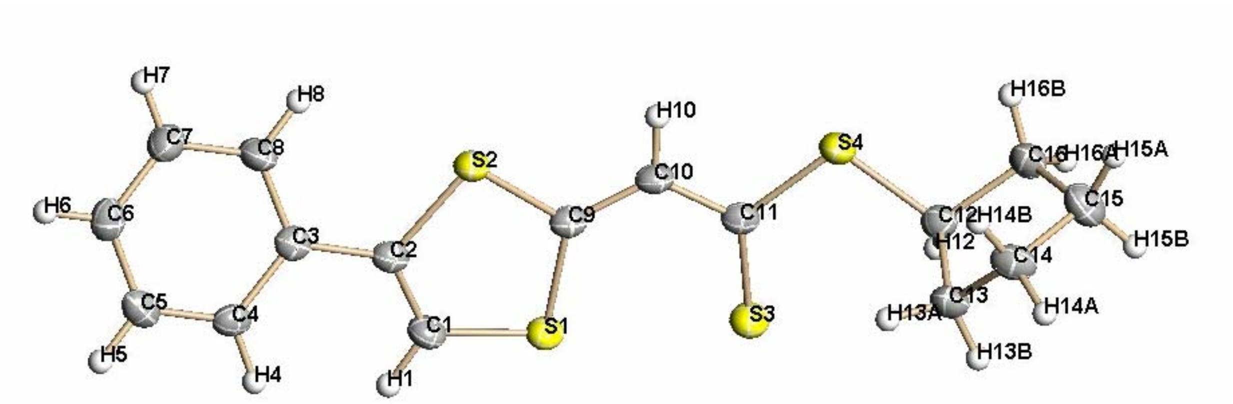


Table 11. Crystal data and structure refinement for **4a**.

Identification code	datosm	
Empirical formula	C16 H16 S4	
Formula weight	336.53	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 15.354(6) Å	α = 90°
	b = 11.400(3) Å	β = 98.52(2)°
	c = 8.9237(17) Å	γ = 90°
Volume	1544.8(8) $Å^3$	
Z	4	
Density (calculated)	1.447 Mg/m^3	
Absorption coefficient	0.601 mm^{-1}	
F(000)	704	
Crystal size	0.50 x 0.30 x 0.02 mm	
θ range for data collection	2.23 to 25.00°	
Index ranges	-18<=h<=18, -13<=k<=13, -10<=l<=10	
Reflections collected	14425	
Independent reflections	2717 [R_{int} = 0.0518]	
Completeness to θ = 25.00°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.990 and 0.842	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2717 / 0 / 181	
Goodness-of-fit on F^2	S = 1.096	

R indices [for 2280 reflections with I>2σ(I)]	R_1 = 0.0372, wR_2 = 0.0862
R indices (for all 2717 data)	R_1 = 0.0466, wR_2 = 0.0896
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + (bP)$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$ a = 0.0398, b = 0.2986
Largest diff. peak and hole	0.281 and -0.221 eÅ^{-3}

Table 12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **4a**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1)	9368(1)	299(1)	3341(1)	28(1)
S(2)	9573(1)	2108(1)	1124(1)	28(1)
S(3)	7675(1)	479(1)	4571(1)	31(1)
S(4)	6464(1)	2285(1)	2898(1)	33(1)
C(1)	10315(2)	276(2)	2487(3)	29(1)
C(2)	10433(2)	1092(2)	1466(3)	24(1)
C(3)	11189(2)	1214(2)	640(2)	25(1)
C(4)	11777(2)	283(2)	593(3)	27(1)
C(5)	12484(2)	386(2)	-184(3)	32(1)
C(6)	12619(2)	1418(2)	-935(3)	32(1)
C(7)	12054(2)	2347(2)	-887(3)	33(1)
C(8)	11341(2)	2245(2)	-110(3)	31(1)
C(9)	8920(2)	1524(2)	2367(3)	24(1)
C(10)	8108(2)	2001(2)	2448(3)	27(1)
C(11)	7484(2)	1563(2)	3321(3)	25(1)
C(12)	5711(2)	1412(2)	3820(3)	27(1)
C(13)	5483(2)	240(2)	3007(3)	32(1)
C(14)	4656(2)	486(2)	1911(3)	35(1)
C(15)	4137(2)	1304(2)	2803(3)	39(1)
C(16)	4831(2)	2084(2)	3705(3)	33(1)

Table 13. Bond lengths [Å] and angles [°] for **4a**.

S(1)-C(9)	1.733(2)
S(1)-C(1)	1.739(3)
S(2)-C(9)	1.734(2)
S(2)-C(2)	1.750(2)
S(3)-C(11)	1.661(2)
S(4)-C(11)	1.761(2)
S(4)-C(12)	1.813(2)
C(1)-C(2)	1.333(3)
C(1)-H(1)	0.9500
C(2)-C(3)	1.470(3)
C(3)-C(8)	1.389(3)
C(3)-C(4)	1.399(3)
C(4)-C(5)	1.376(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.385(3)
C(5)-H(5)	0.9500
C(6)-C(7)	1.374(3)
C(6)-H(6)	0.9500
C(7)-C(8)	1.385(3)
C(7)-H(7)	0.9500
C(8)-H(8)	0.9500
C(9)-C(10)	1.372(3)
C(10)-C(11)	1.413(3)
C(10)-H(10)	0.9500
C(12)-C(13)	1.537(3)
C(12)-C(16)	1.543(3)
C(12)-H(12)	1.0000
C(13)-C(14)	1.509(3)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.525(3)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.523(3)

C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(9)-S(1)-C(1)	95.05(11)
C(9)-S(2)-C(2)	97.31(11)
C(11)-S(4)-C(12)	104.66(11)
C(2)-C(1)-S(1)	119.73(19)
C(2)-C(1)-H(1)	120.1
S(1)-C(1)-H(1)	120.1
C(1)-C(2)-C(3)	127.3(2)
C(1)-C(2)-S(2)	113.94(18)
C(3)-C(2)-S(2)	118.79(17)
C(8)-C(3)-C(4)	118.2(2)
C(8)-C(3)-C(2)	121.5(2)
C(4)-C(3)-C(2)	120.3(2)
C(5)-C(4)-C(3)	120.8(2)
C(5)-C(4)-H(4)	119.6
C(3)-C(4)-H(4)	119.6
C(4)-C(5)-C(6)	120.2(2)
C(4)-C(5)-H(5)	119.9
C(6)-C(5)-H(5)	119.9
C(7)-C(6)-C(5)	119.9(2)
C(7)-C(6)-H(6)	120.0
C(5)-C(6)-H(6)	120.0
C(6)-C(7)-C(8)	120.1(2)
C(6)-C(7)-H(7)	120.0
C(8)-C(7)-H(7)	120.0
C(7)-C(8)-C(3)	120.9(2)
C(7)-C(8)-H(8)	119.5
C(3)-C(8)-H(8)	119.5
C(10)-C(9)-S(1)	126.15(18)
C(10)-C(9)-S(2)	119.79(18)
S(1)-C(9)-S(2)	113.98(13)
C(9)-C(10)-C(11)	125.7(2)
C(9)-C(10)-H(10)	117.1

C(11)-C(10)-H(10)	117.1
C(10)-C(11)-S(3)	124.56(18)
C(10)-C(11)-S(4)	111.74(17)
S(3)-C(11)-S(4)	123.69(14)
C(13)-C(12)-C(16)	105.31(19)
C(13)-C(12)-S(4)	112.30(16)
C(16)-C(12)-S(4)	107.95(16)
C(13)-C(12)-H(12)	110.4
C(16)-C(12)-H(12)	110.4
S(4)-C(12)-H(12)	110.4
C(14)-C(13)-C(12)	104.79(19)
C(14)-C(13)-H(13A)	110.8
C(12)-C(13)-H(13A)	110.8
C(14)-C(13)-H(13B)	110.8
C(12)-C(13)-H(13B)	110.8
H(13A)-C(13)-H(13B)	108.9
C(13)-C(14)-C(15)	103.3(2)
C(13)-C(14)-H(14A)	111.1
C(15)-C(14)-H(14A)	111.1
C(13)-C(14)-H(14B)	111.1
C(15)-C(14)-H(14B)	111.1
H(14A)-C(14)-H(14B)	109.1
C(16)-C(15)-C(14)	104.7(2)
C(16)-C(15)-H(15A)	110.8
C(14)-C(15)-H(15A)	110.8
C(16)-C(15)-H(15B)	110.8
C(14)-C(15)-H(15B)	110.8
H(15A)-C(15)-H(15B)	108.9
C(15)-C(16)-C(12)	106.43(19)
C(15)-C(16)-H(16A)	110.4
C(12)-C(16)-H(16A)	110.4
C(15)-C(16)-H(16B)	110.4
C(12)-C(16)-H(16B)	110.4
H(16A)-C(16)-H(16B)	108.6

Table 14. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **4a**.

The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	29(1)	28(1)	26(1)	8(1)	0(1)	3(1)
S(2)	29(1)	24(1)	32(1)	7(1)	5(1)	3(1)
S(3)	33(1)	32(1)	29(1)	6(1)	3(1)	2(1)
S(4)	30(1)	26(1)	45(1)	8(1)	8(1)	4(1)
C(1)	28(1)	27(1)	31(1)	3(1)	0(1)	5(1)
C(2)	26(1)	22(1)	23(1)	-2(1)	-2(1)	0(1)
C(3)	25(1)	25(1)	22(1)	-4(1)	-3(1)	-2(1)
C(4)	29(1)	21(1)	29(1)	-1(1)	-3(1)	-4(1)
C(5)	25(1)	28(1)	40(2)	-10(1)	-3(1)	1(1)
C(6)	27(1)	37(2)	32(1)	-7(1)	5(1)	-5(1)
C(7)	32(1)	34(1)	34(2)	5(1)	6(1)	-2(1)
C(8)	33(1)	26(1)	35(2)	4(1)	5(1)	7(1)
C(9)	28(1)	22(1)	22(1)	-1(1)	-2(1)	-2(1)
C(10)	31(1)	21(1)	27(1)	4(1)	1(1)	0(1)
C(11)	30(1)	21(1)	22(1)	-3(1)	-1(1)	-1(1)
C(12)	30(1)	25(1)	28(1)	-1(1)	6(1)	1(1)
C(13)	33(2)	23(1)	39(2)	-1(1)	6(1)	3(1)
C(14)	44(2)	27(1)	32(2)	-5(1)	1(1)	5(1)
C(15)	32(2)	40(2)	44(2)	-7(1)	0(1)	7(1)
C(16)	32(1)	26(1)	42(2)	-4(1)	10(1)	3(1)

Table 15. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **4a**.

	x	y	z	U(eq)
H(1)	10747	-315	2747	35
H(4)	11688	-429	1102	33
H(5)	12879	-253	-205	38

H(6)	13102	1483	-1483	39
H(7)	12152	3060	-1387	40
H(8)	10950	2889	-89	37
H(10)	7951	2687	1865	32
H(12)	5960	1274	4906	33
H(13A)	5965	-17	2460	38
H(13B)	5376	-378	3739	38
H(14A)	4324	-245	1627	42
H(14B)	4795	872	981	42
H(15A)	3713	1779	2110	47
H(15B)	3811	853	3488	47
H(16A)	4680	2238	4727	40
H(16B)	4872	2843	3181	40

Synthesis of compound 4b: Compound **3b** (0.30 mmol) dissolved in dichloromethane (50 mL), was added to a two necked flask with neutral aluminum oxide (1 g). The solvent was removed under vacuum, and the resulting solid was then dried with a vacuum pump. The crude product was purified by column chromatography using neutral aluminum oxide and a mixture of hexane/dichoromethane 80/20 V/V as solvent. The product **4b** was obtained as an orange solid, 80%, m.p. 99.4 – 100.4 °C (1 atm).^{1}H NMR (CDCl$_3$, 200 MHz two isomers): δ 0.95 (t, 3H); 1.48 (m, 2H); 1.69 (m, 2H); 3.29 (t, 2H); 6.86 (d, 1H, ^5J = 1.46 Hz, predominant isomer) and 6.94 (s, 1H, very minor); 7.42 (m, 5H), 7.57 (s, 1H, very minor) and 7.63 (d, 1H, ^5J = 1.46 Hz, predominant isomer). ^{13}C NMR (CDCl$_3$, 50 MHz two isomers) δ: 13.72; 22.21; 30.56; 34.15; 34.25; 112.15; 115.22; 117.02; 117.89; 126.62; 127.00; 129.13; 129.21; 129.29; 162.60; 205.64. HRMS calculated for $C_{15}H_{16}S_4$: 324.0135, found 324.0140. Elemental analysis, calculated for $C_{15}H_{16}S_4$: C: 55.51%; H: 4.97%. Found: C: 55.46%; H: 5.02 %.

Synthesis of compound 4c: Compound **3c** (0.30 mmol) dissolved in dichloromethane (50 mL), was added to a two necked flask with neutral aluminum oxide (1 g). The solvent was removed under vacuum, and the resulting solid was then dried with a vacuum pump. The crude product was purified by column chromatography using neutral aluminum oxide and a mixture of hexane/dichoromethane 80/20 V/V as solvent. Product **4c** was obtained as an orange solid, 72%, m.p. 112º C (1 atm). ^{1}H NMR (CDCl$_3$, 400 MHz two isomers) δ: 1.23 (t, 3H); 2.75 (m, 2H); 6.69 (s, 1H) and 7.01 (s, 1H); 7.39 (m, 6H); 7.57 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz two isomers) δ: 14.06; 31.97; 31.99; 115.16; 116.25; 126.63; 127.13; 129.09; 129.17; 129.32; 129.55; 129.95; 130.00; 130.84; 130.94; 131.10; 131.39; 132.25; 138.51; 138.64; 139.07: 139.12; 167.87; 169.00; 201.73; 210.81. HRMS calculated for $C_{19}H_{16}S_4$: 372.5903; found 372.5916. Elemental analysis, calculated for $C_{19}H_{16}S_4$: C: 61.25%; H: 4.33%. Found: C: 61.16%; H: 4.25%.

Synthesis of compound 4d: Compound **3d** (0.30 mmol) dissolved in dichloromethane (50 mL), was added to a two necked flask with neutral aluminum oxide (1 g). The solvent was removed under vacuum, and the resulting solid was then dried with a vacuum pump. The crude product was purified by column chromatography using neutral aluminum oxide and a mixture of hexane/dichoromethane 80/20 V/V as solvent. Product **4d** was obtained as an orange solid, m.p. decomposed at 180 °C (1 atm), in quantitative yield. ^{1}H NMR ($CDCl_3$, 200 MHz two isomers) δ: 2.78 (s, 3H); 2.79 (s, 3H); 6.97 (d, 1H, ^{5}J = 1.08 Hz, predominant isomer); 7.11 (s, 1H, minor); 7.56 (m, 5H), 7.73 (s, 1H, minor); 7.77 (d, 1H, ^{5}J = 1.08 Hz, predominant isomer). ^{13}C NMR ($CDCl_3$, 50 MHz two isomers) δ: 38.70; 113.12; 120.04; 121.04; 126.78; 127.21; 128.37; 128.94; 129.05; 129.18; 129.29; 129.50; 179.53; 204.16. HRMS calculated for $C_{12}H_{10}S_3$: 249.9945; found 249.9942. Elemental analysis, calculated for $C_{12}H_{10}S_3$: C: 57.56%; H: 4.03%. Found: C: 57.49%; H: 3.95%.

X-Ray Diffraction Structure Report for **4d**: Crystallographic data are presented in Tables 16-20. A single crystal of **4d** was mounted on a glass fibre. X-ray measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo-K_α radiation (λ = 0.71073 Å).[3] Intensities were integrated[4] from several series of exposures, each exposure covering 0.3° in ω, and the total data set being a sphere. Absorption corrections were applied, based on multiple and symmetry-equivalent measurements.[5] The structure was solved by direct methods and refined by least squares on weighted F^2 values for all reflections (see Table 16).[6] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters. Refinement proceeded smoothly to give the residuals shown in Table 16. Complex neutral-atom scattering factors were used.[7]

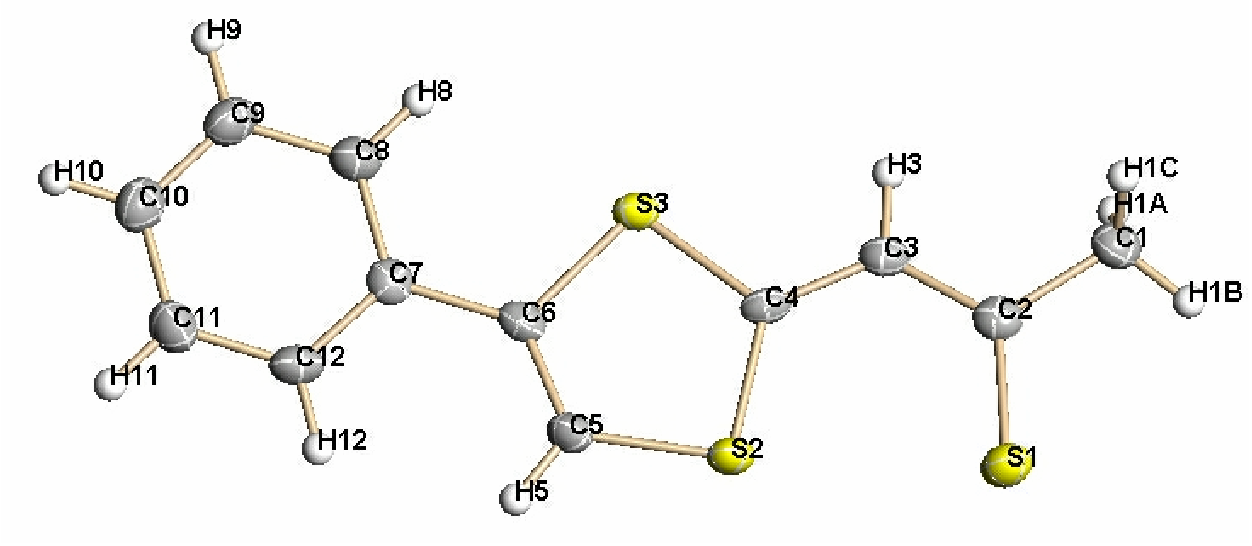


Table 16. Crystal data and structure refinement for **4d**.

Identification code	datosm	
Empirical formula	C12 H10 S3	
Formula weight	250.38	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 14.836(2) Å	α = 90°
	b = 5.6318(9) Å	β = 90°
	c = 26.458(4) Å	γ = 90°
Volume	2210.7(6) $Å^3$	
Z	8	
Density (calculated)	1.505 Mg/m^3	
Absorption coefficient	0.630 mm^{-1}	
F(000)	1040	
Crystal size	0.50 x 0.20 x 0.07 mm	
θ range for data collection	1.54 to 25.00°	
Index ranges	-17<=h<=17, -6<=k<=6, -31<=l<=31	
Reflections collected	19688	
Independent reflections	1946 [R_{int} = 0.0965]	

Completeness to θ = 25.00°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.957 and 0.853
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1946 / 0 / 137
Goodness-of-fit on F^2	S = 1.071
R indices [for 1474 reflections with $I>2\sigma(I)$]	$R_1 = 0.0394$, $wR_2 = 0.1086$
R indices (for all 1946 data)	$R_1 = 0.0603$, $wR_2 = 0.1282$
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (aP)^2 + (bP)$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$ a = 0.0728, b = 0.0000
Largest diff. peak and hole	0.364 and -0.411 eÅ^{-3}

Table 17. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **4d**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1)	9230(1)	1802(2)	6284(1)	30(1)
S(2)	9202(1)	1378(2)	7391(1)	24(1)
S(3)	8319(1)	5381(2)	7873(1)	24(1)
C(1)	8336(2)	5751(6)	5935(1)	30(1)
C(2)	8631(2)	4273(6)	6378(1)	25(1)
C(3)	8395(2)	5083(6)	6859(1)	23(1)
C(4)	8621(2)	4008(5)	7314(1)	21(1)
C(5)	9207(2)	1491(6)	8046(1)	24(1)
C(6)	8817(2)	3311(5)	8284(1)	21(1)
C(7)	8781(2)	3783(6)	8829(1)	22(1)
C(8)	8377(2)	5837(6)	9018(1)	28(1)
C(9)	8366(2)	6282(7)	9536(1)	33(1)
C(10)	8764(2)	4713(6)	9865(1)	35(1)
C(11)	9162(2)	2669(7)	9681(1)	33(1)
C(12)	9171(2)	2204(6)	9169(1)	28(1)

Table 18. Bond lengths [Å] and angles [°] for **4d**.

S(1)-C(2)	1.670(3)
S(2)-C(4)	1.726(3)
S(2)-C(5)	1.736(3)
S(3)-C(4)	1.727(3)
S(3)-C(6)	1.758(3)
C(1)-C(2)	1.503(4)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.396(4)
C(3)-C(4)	1.389(4)
C(3)-H(3)	0.9500
C(5)-C(6)	1.335(4)
C(5)-H(5)	0.9500
C(6)-C(7)	1.467(4)
C(7)-C(12)	1.391(4)
C(7)-C(8)	1.395(4)
C(8)-C(9)	1.393(5)
C(8)-H(8)	0.9500
C(9)-C(10)	1.374(5)
C(9)-H(9)	0.9500
C(10)-C(11)	1.382(5)
C(10)-H(10)	0.9500
C(11)-C(12)	1.380(5)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(4)-S(2)-C(5)	95.06(15)
C(4)-S(3)-C(6)	97.14(15)
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5

H(1B)-C(1)-H(1C)	109.5
C(3)-C(2)-C(1)	117.1(3)
C(3)-C(2)-S(1)	122.9(3)
C(1)-C(2)-S(1)	120.0(2)
C(4)-C(3)-C(2)	125.9(3)
C(4)-C(3)-H(3)	117.1
C(2)-C(3)-H(3)	117.1
C(3)-C(4)-S(2)	126.7(2)
C(3)-C(4)-S(3)	118.9(2)
S(2)-C(4)-S(3)	114.39(18)
C(6)-C(5)-S(2)	119.9(3)
C(6)-C(5)-H(5)	120.1
S(2)-C(5)-H(5)	120.1
C(5)-C(6)-C(7)	128.2(3)
C(5)-C(6)-S(3)	113.5(2)
C(7)-C(6)-S(3)	118.2(2)
C(12)-C(7)-C(8)	118.5(3)
C(12)-C(7)-C(6)	120.3(3)
C(8)-C(7)-C(6)	121.2(3)
C(9)-C(8)-C(7)	120.4(3)
C(9)-C(8)-H(8)	119.8
C(7)-C(8)-H(8)	119.8
C(10)-C(9)-C(8)	120.1(3)
C(10)-C(9)-H(9)	119.9
C(8)-C(9)-H(9)	119.9
C(9)-C(10)-C(11)	119.8(3)
C(9)-C(10)-H(10)	120.1
C(11)-C(10)-H(10)	120.1
C(12)-C(11)-C(10)	120.5(3)
C(12)-C(11)-H(11)	119.8
C(10)-C(11)-H(11)	119.8
C(11)-C(12)-C(7)	120.6(3)
C(11)-C(12)-H(12)	119.7
C(7)-C(12)-H(12)	119.7

Table 19. Anisotropic displacement parameters (Å^2 x 10^3) for **4d**.

The anisotropic displacement factor exponent takes the form:
$-2\pi^2$ [h^2 a^{*2} U_{11} + ... + 2 h k a* b* U_{12}]

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	32(1)	27(1)	31(1)	-5(1)	-3(1)	7(1)
S(2)	26(1)	19(1)	28(1)	-2(1)	-1(1)	6(1)
S(3)	26(1)	19(1)	27(1)	-1(1)	2(1)	5(1)
C(1)	32(2)	26(2)	32(2)	4(2)	2(2)	0(2)
C(2)	20(2)	23(2)	31(2)	-1(1)	-2(1)	-4(2)
C(3)	20(2)	19(2)	31(2)	-1(1)	-1(1)	0(1)
C(4)	15(2)	16(2)	30(2)	-4(1)	2(1)	1(1)
C(5)	26(2)	20(2)	26(2)	1(1)	-4(1)	3(1)
C(6)	15(2)	20(2)	29(2)	4(1)	-2(1)	-1(1)
C(7)	16(2)	25(2)	26(2)	2(1)	2(1)	-4(1)
C(8)	26(2)	25(2)	34(2)	1(2)	1(2)	2(2)
C(9)	36(2)	30(2)	35(2)	-6(2)	8(2)	1(2)
C(10)	36(2)	37(2)	30(2)	-2(2)	5(2)	-1(2)
C(11)	35(2)	34(2)	30(2)	5(2)	-1(2)	3(2)
C(12)	26(2)	20(2)	37(2)	-2(2)	3(2)	3(2)

Table 20. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **4d**.

	x	y	z	U(eq)
H(1A)	7685	6030	5956	44
H(1B)	8476	4910	5621	44
H(1C)	8654	7275	5941	44
H(3)	8048	6499	6876	28
H(5)	9486	260	8235	29
H(8)	8107	6938	8792	34
H(9)	8082	7674	9662	40
H(10)	8765	5031	10217	41

H(11)	9432	1577	9909	40
H(12)	9446	791	9048	33

References:

(1) (a) R. Aumann and H. Nienaber, *Advances in Organometallic Chemistry* 1997, **41**, 163. (b) H. K. Dötz and W. Khun, *J. Organomet. Chem* 1985, **286**, C23.

(2) A. M. Fracaroli, J. Kreiker, R. H. de Rossi and A. Granados, *ARKIVOC* 2007, **IV**, 279.

(3) SMART diffractometer control software, Bruker Analytical X-ray Instruments Inc., Madison, WI, 2000.

(4) SAINT integration software, Siemens Analytical X-ray Instruments Inc., Madison, WI, 2000.

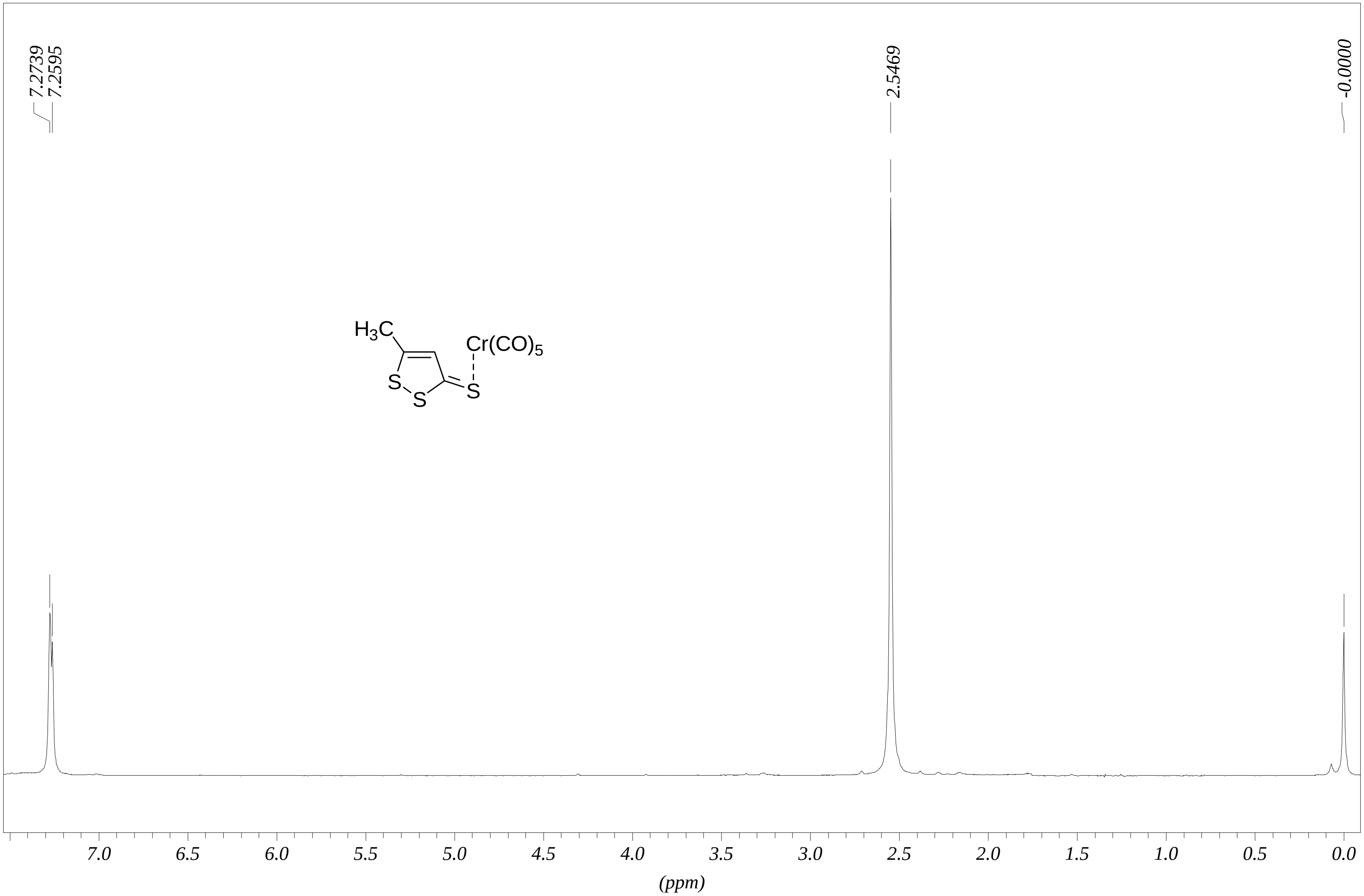
(5) G. M. Sheldrick. *SADABS: A program for absorption correction with the Siemens SMART system;* University of Göttingen: Germany, 2001.

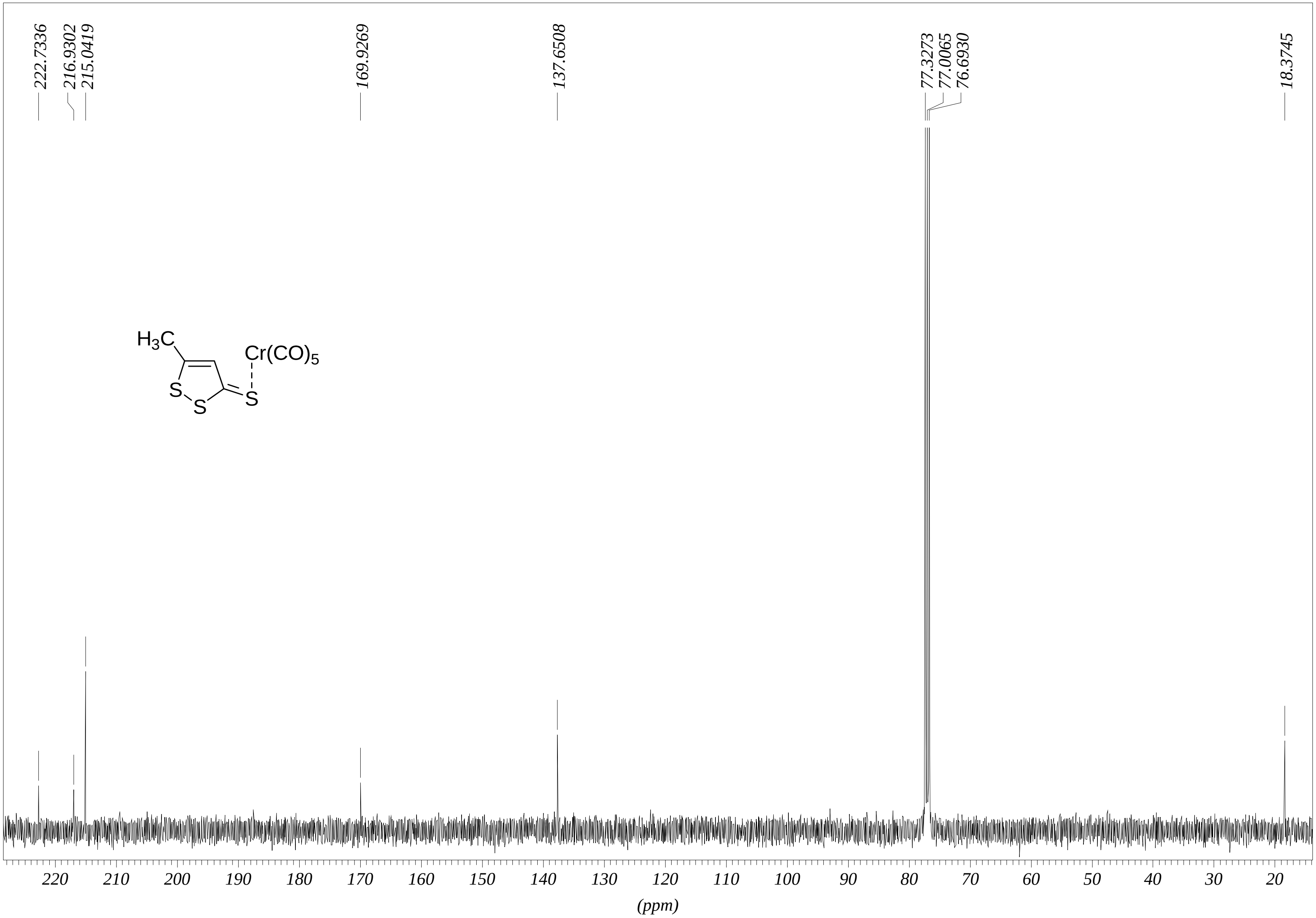
(6) *SHELXTL program system version 6.1;* Bruker Analytical X-ray Instruments Inc., Madison, WI, 1998.

(7) *International Tables for Crystallography*, Kluwer, Dordrecht, 1992, vol. C.

(8) (a) C. W. Rees, A. J. P. White, D. J. Williams, O. A. Rakitin, C. F. Marcos, C. Polo and T. Torroba, *J. Org. Chem.* 1998, **63**, 2189. (b) M. L. Aimar, J. Kreiker and R. H. de Rossi, *Tetrahedron Lett* 2002, **43**, 1947.

NMR Spectra of [pentacarbonyl(5-methyl-3*H*-1,2-dithiole-3-thione)chromium(0)]

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S
S
220
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200
190
180
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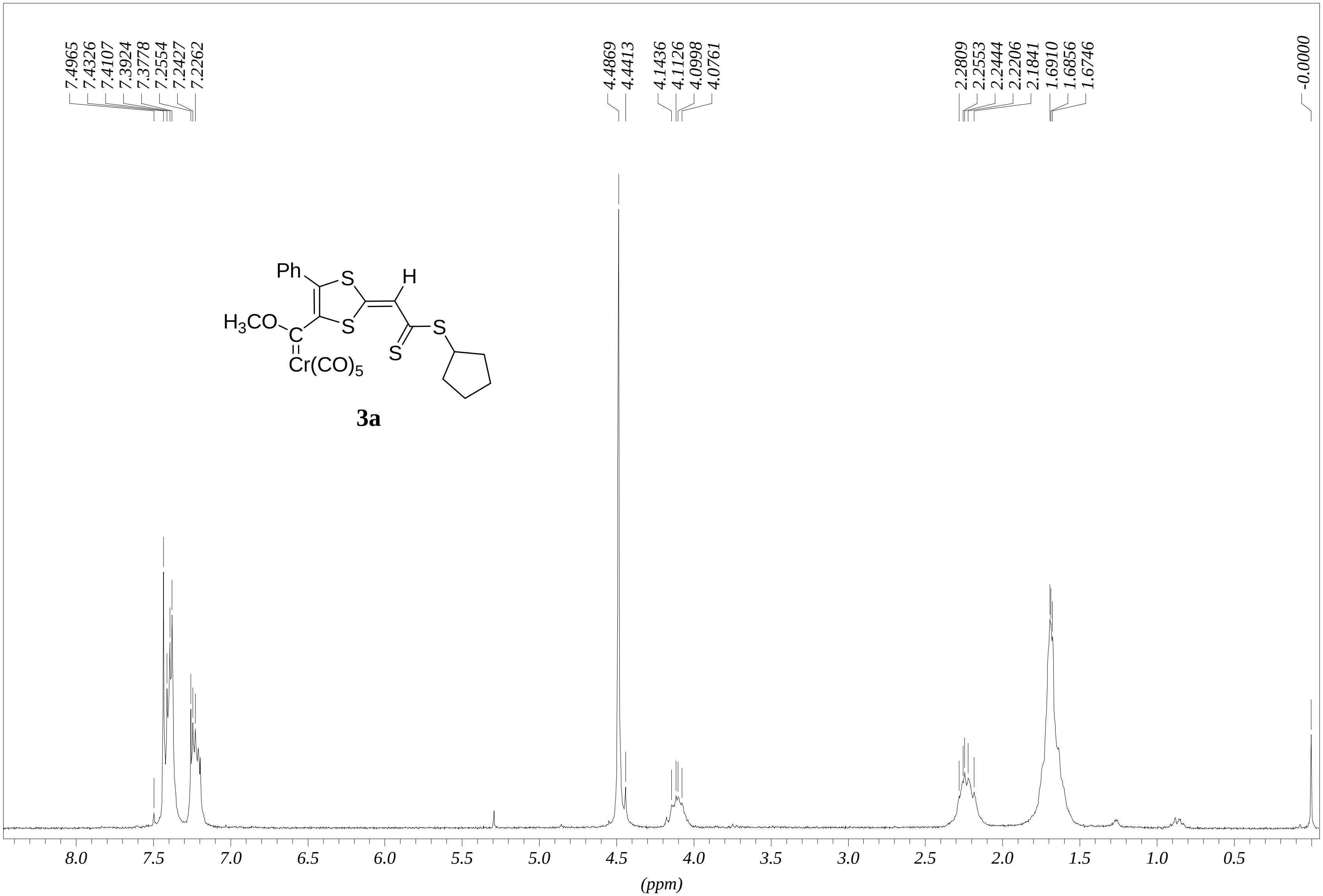
50
40
30
20
(ppm)

NMR Spectra of compounds 3a-e



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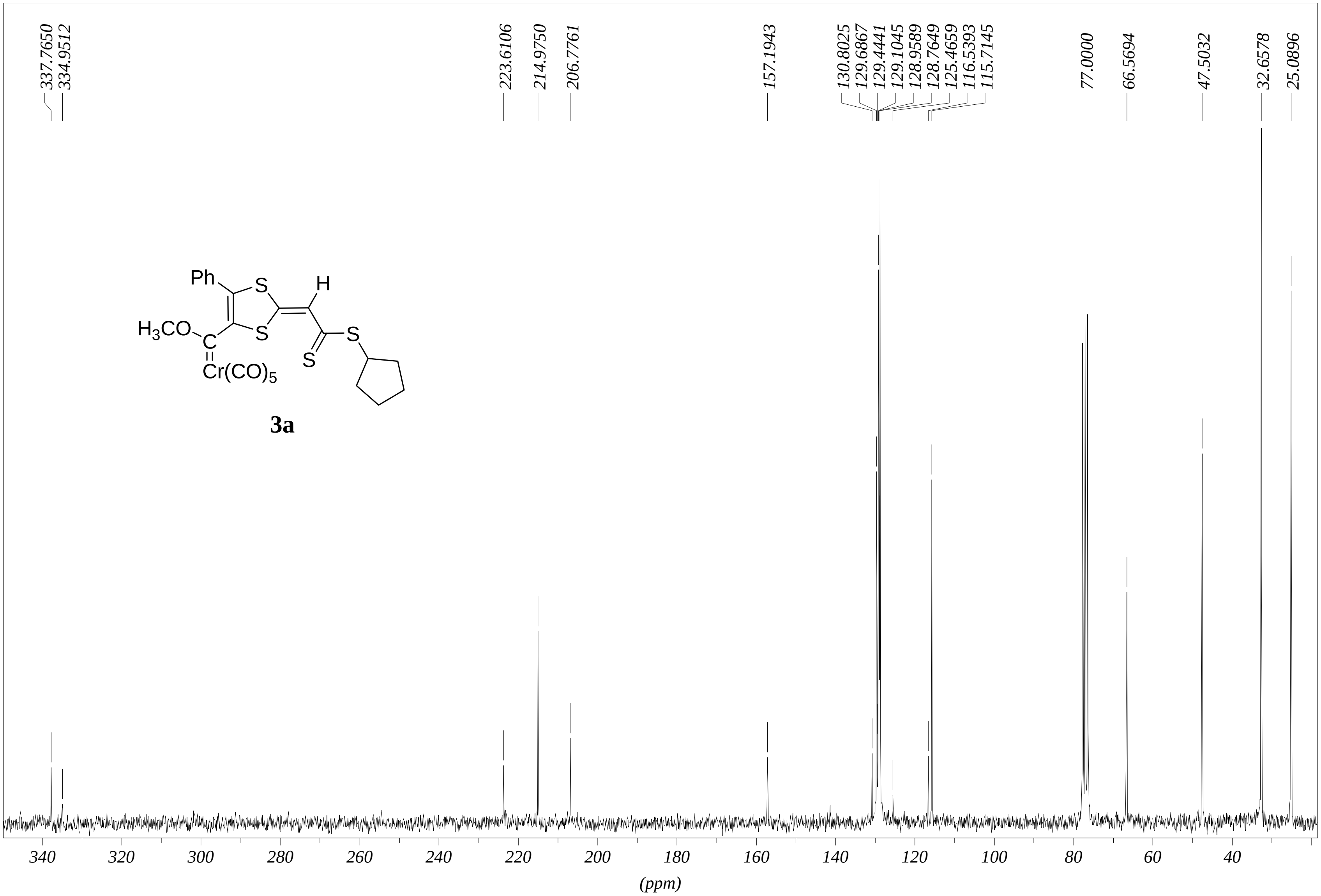

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C
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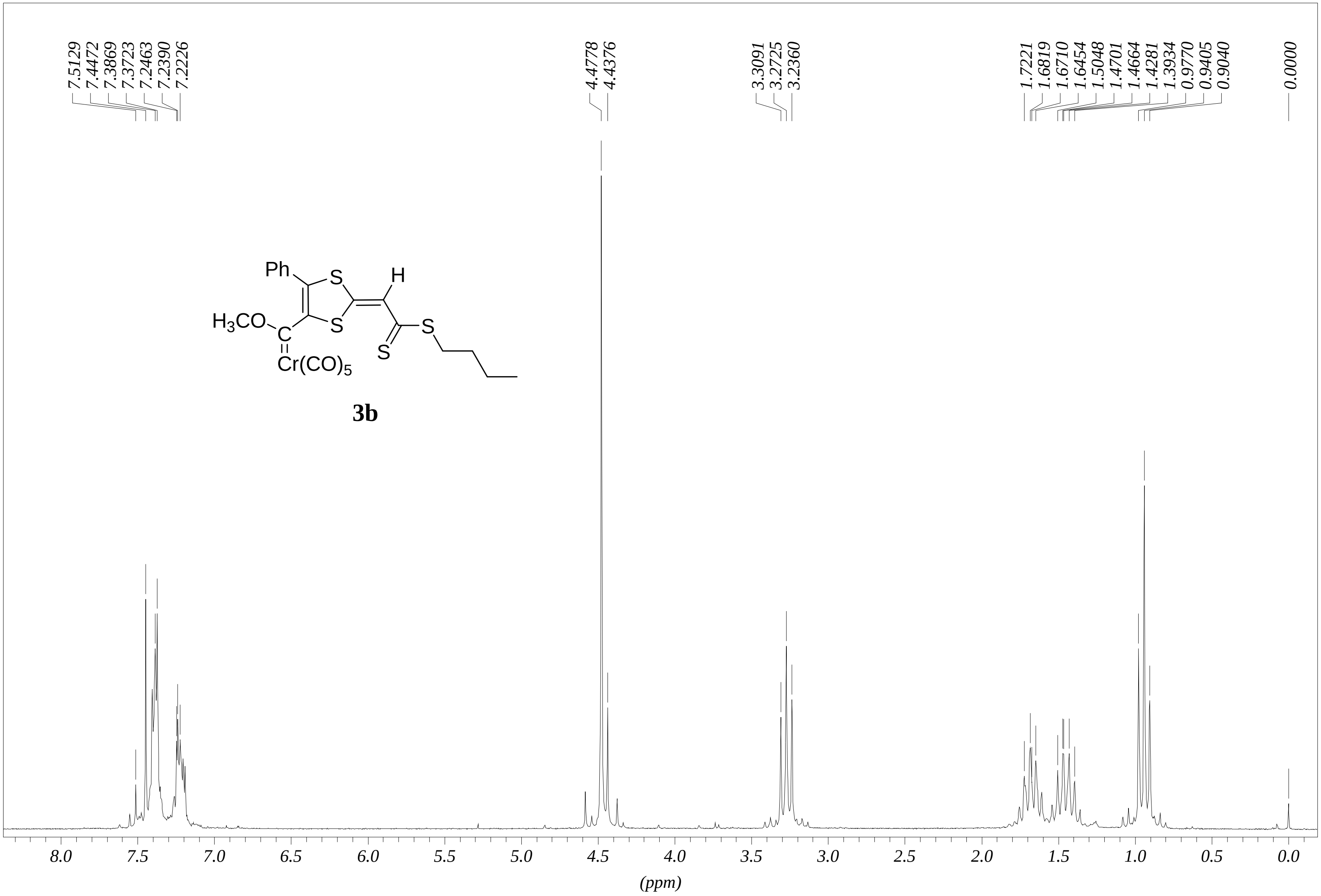
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S
S
S
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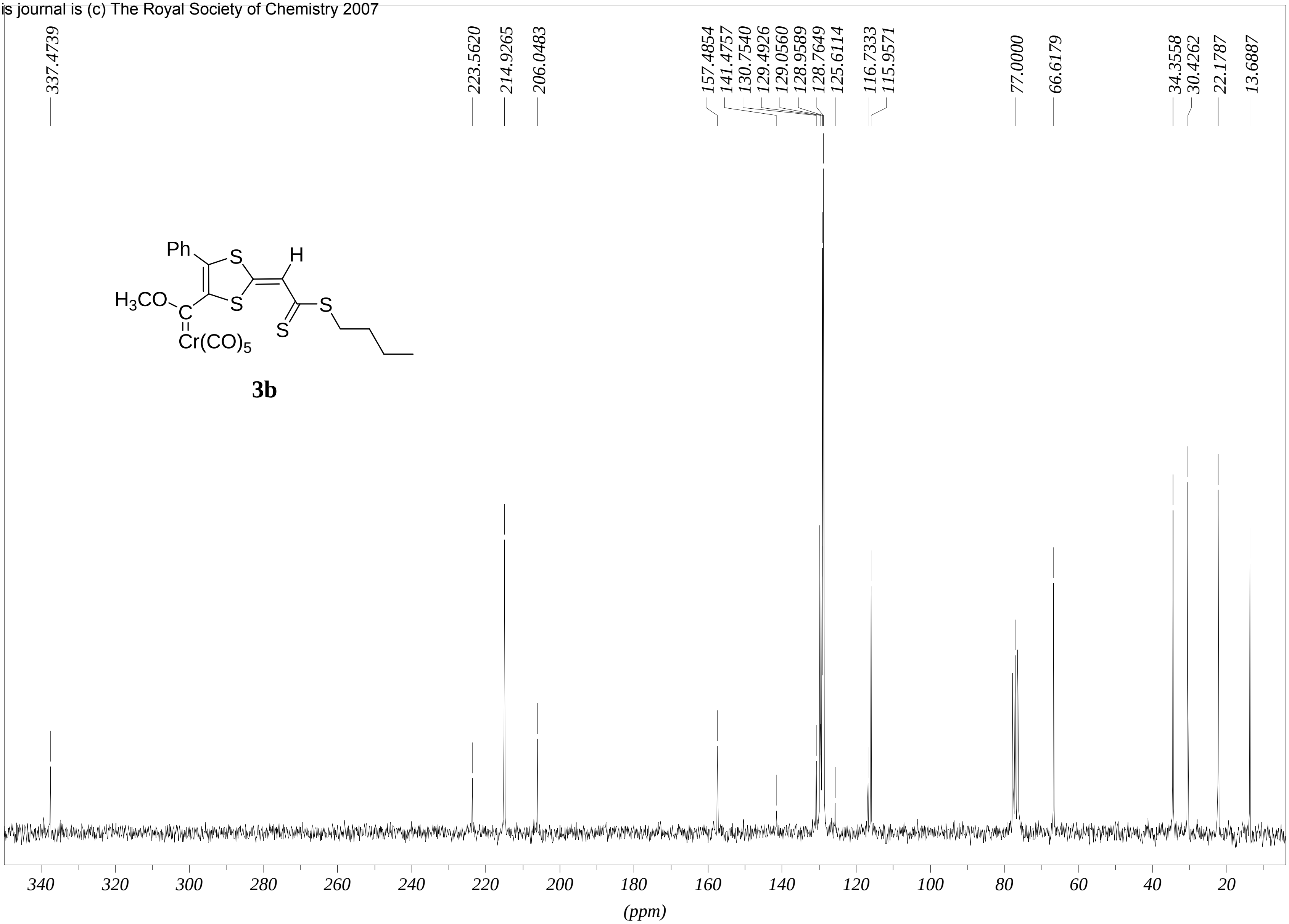
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S
S
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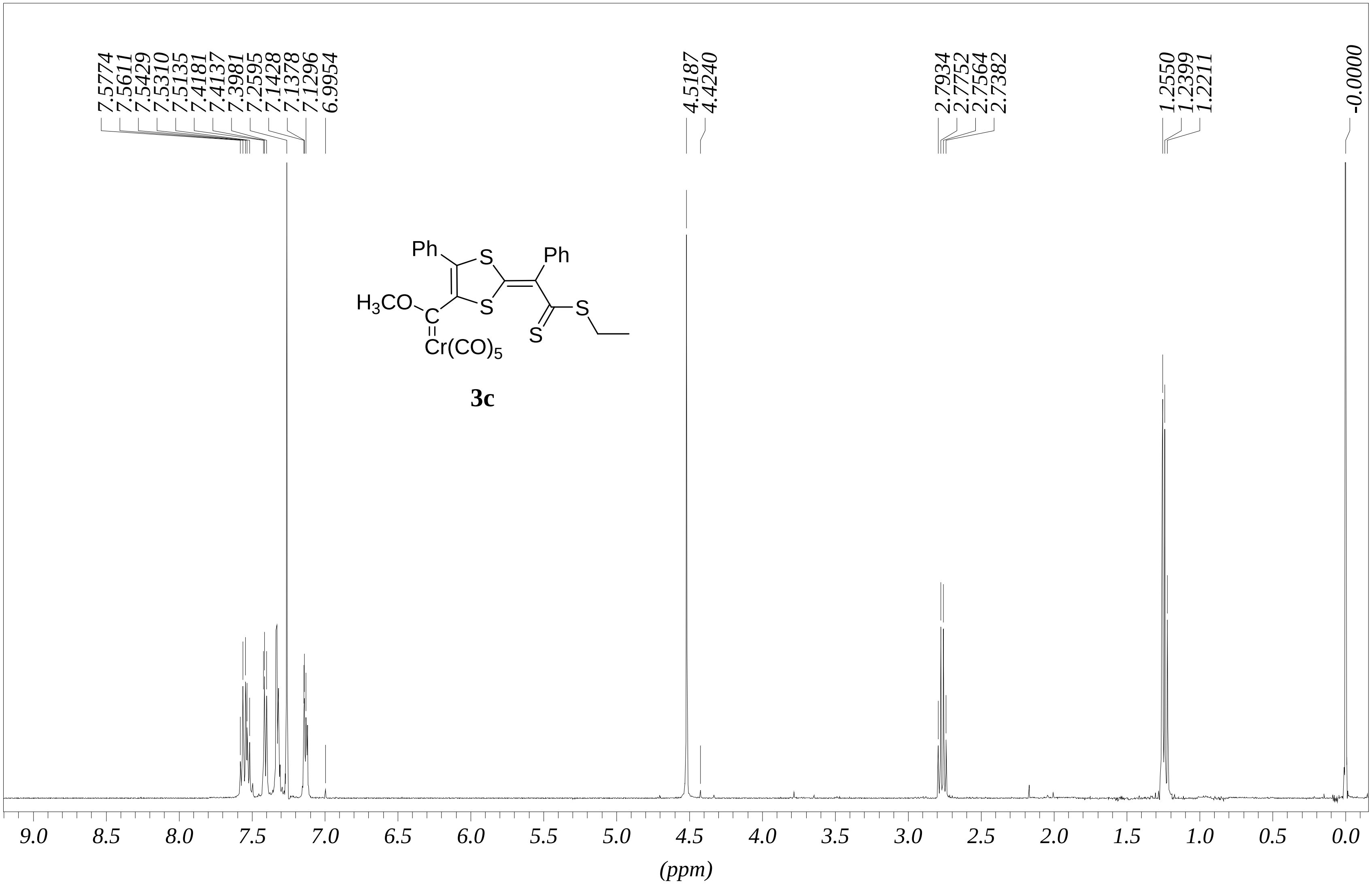
(ppm)



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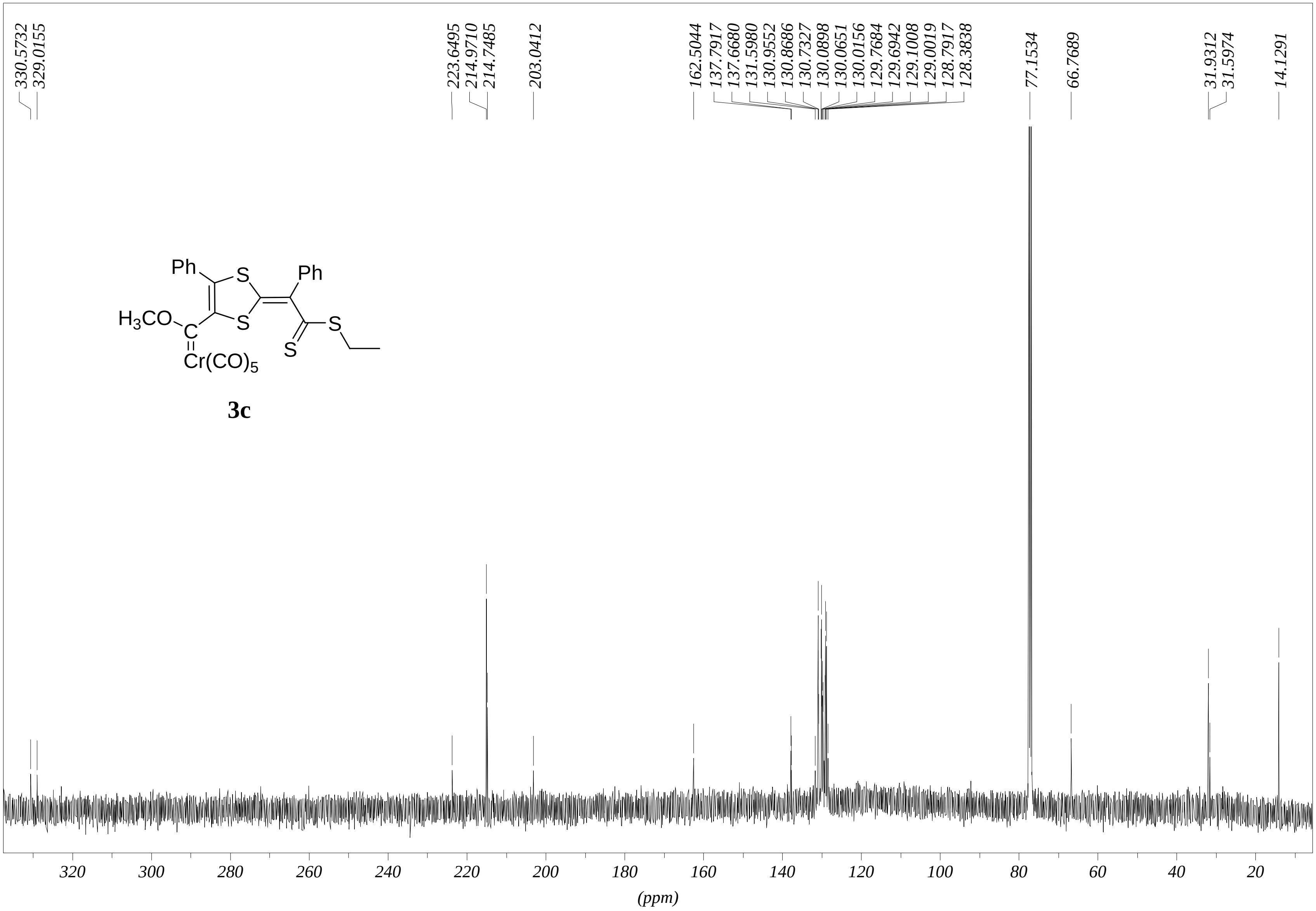
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S
S
S
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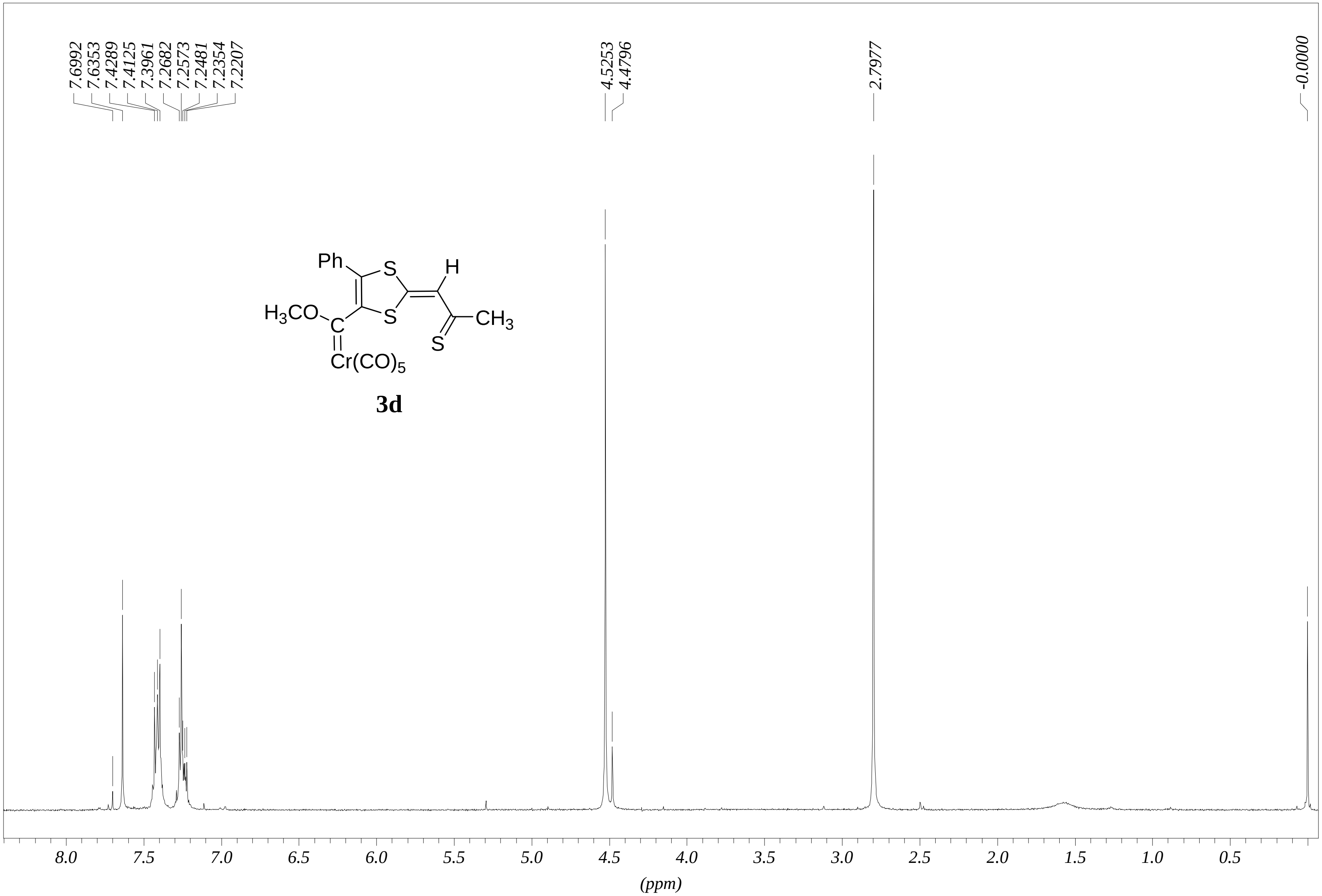
3c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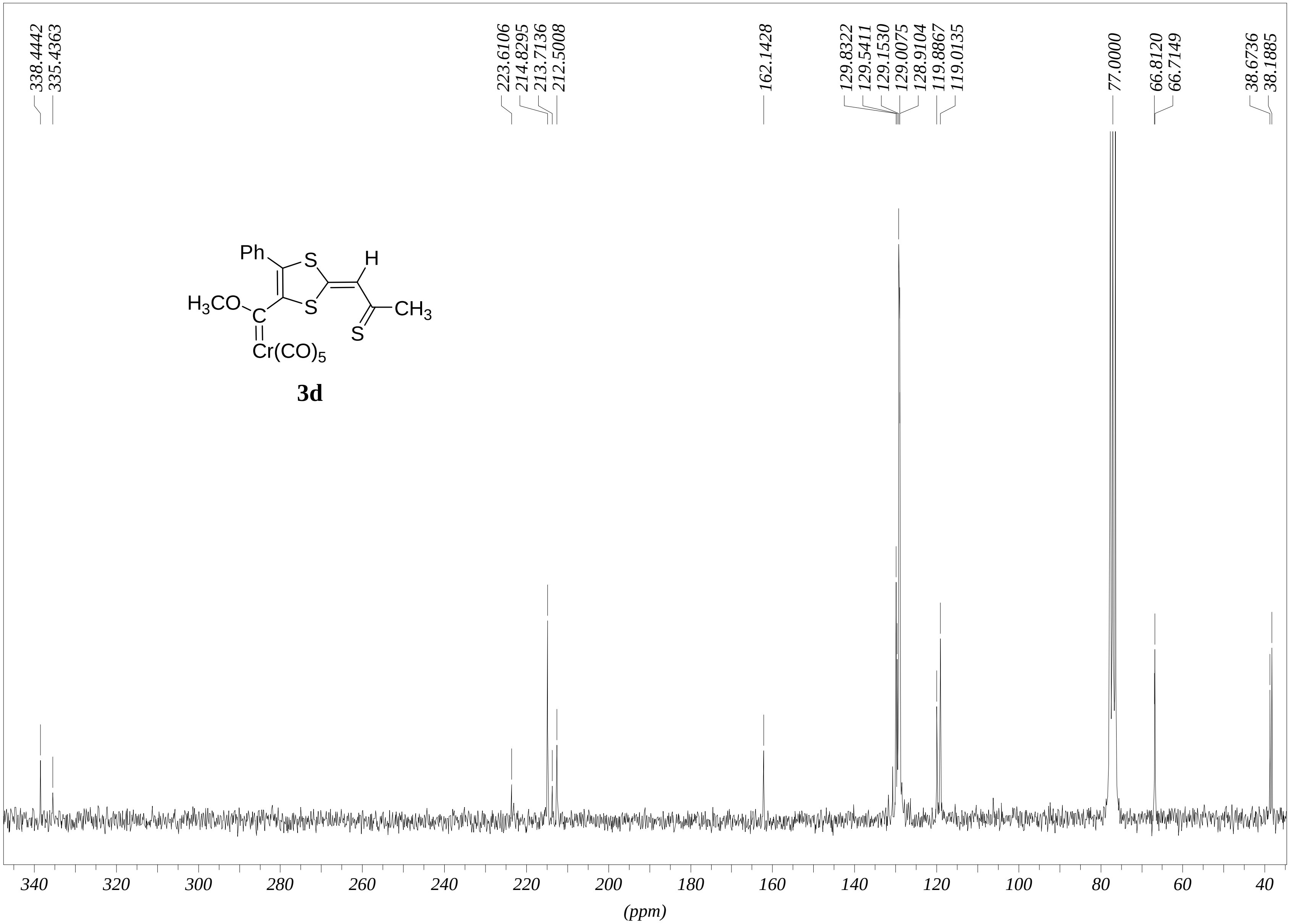
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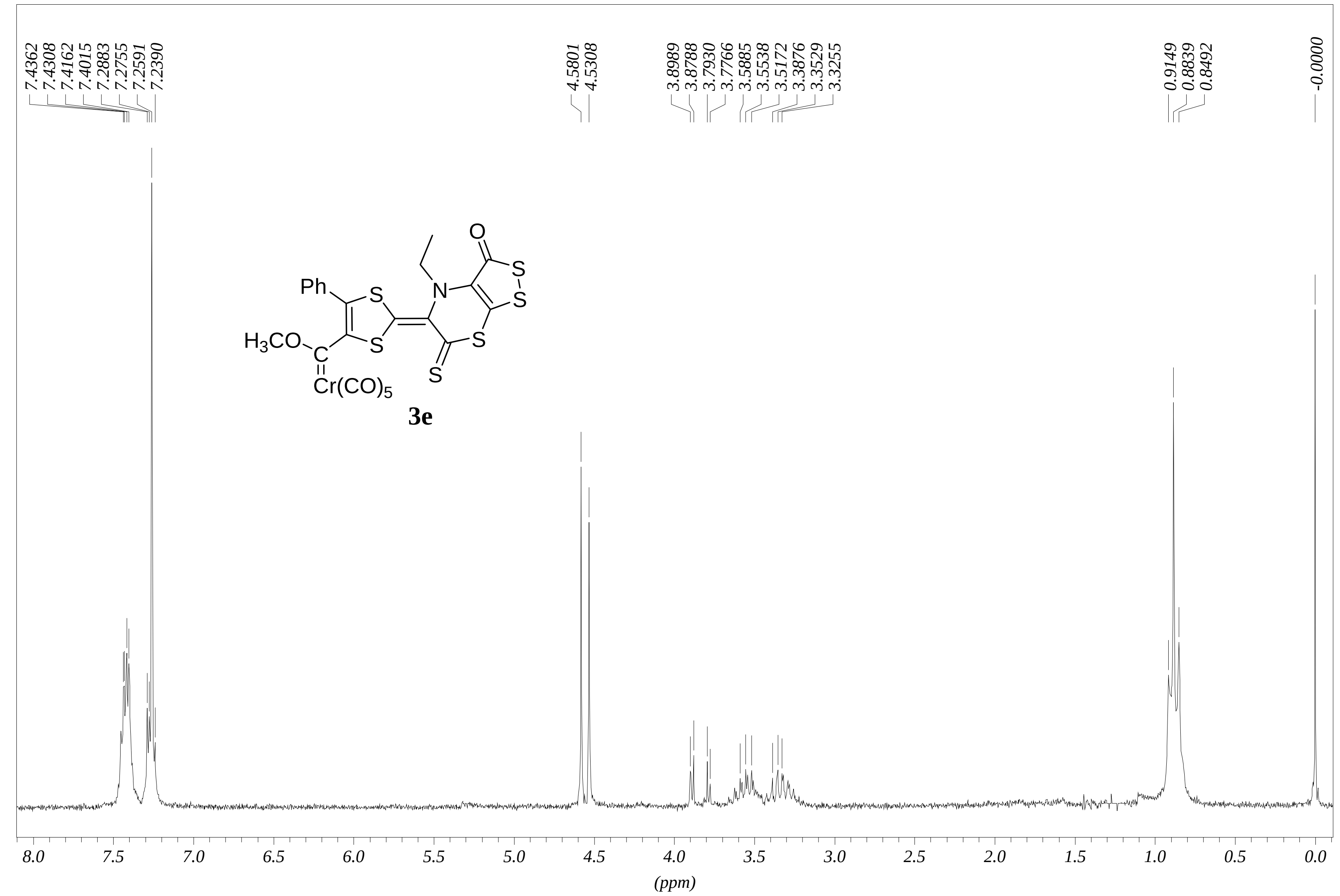
3d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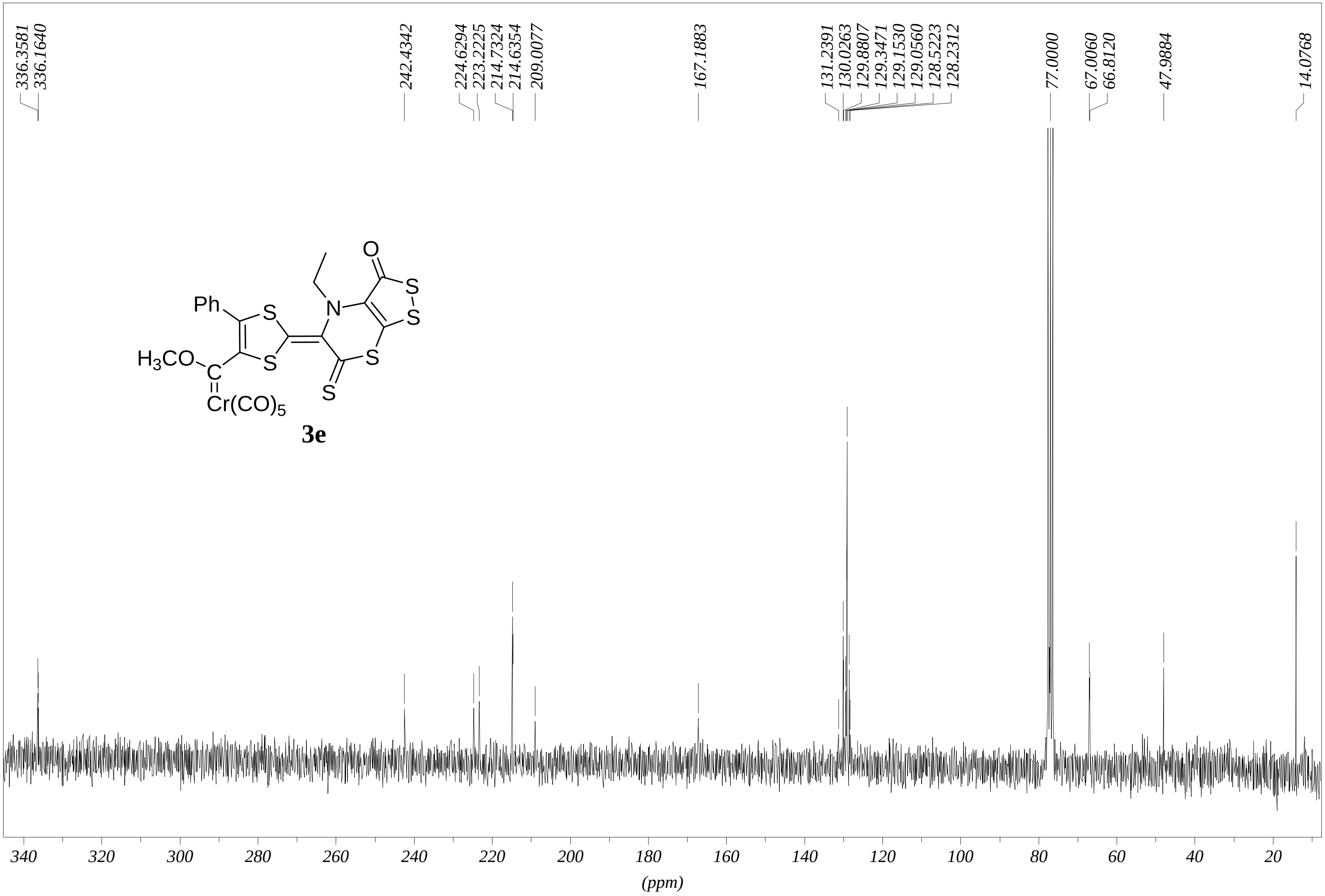
(ppm)

3e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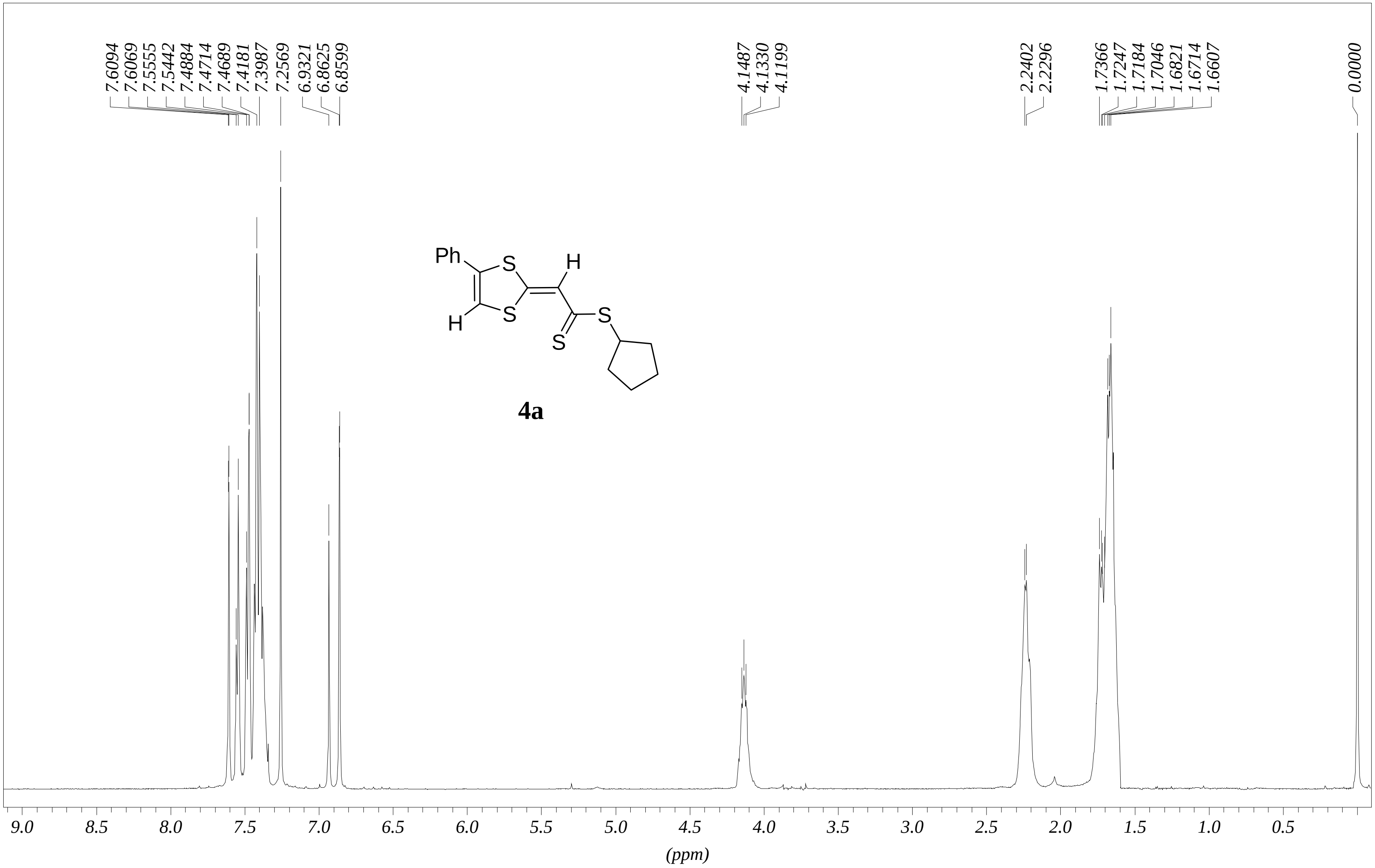
(ppm)

NMR Spectra of compounds 4a-d



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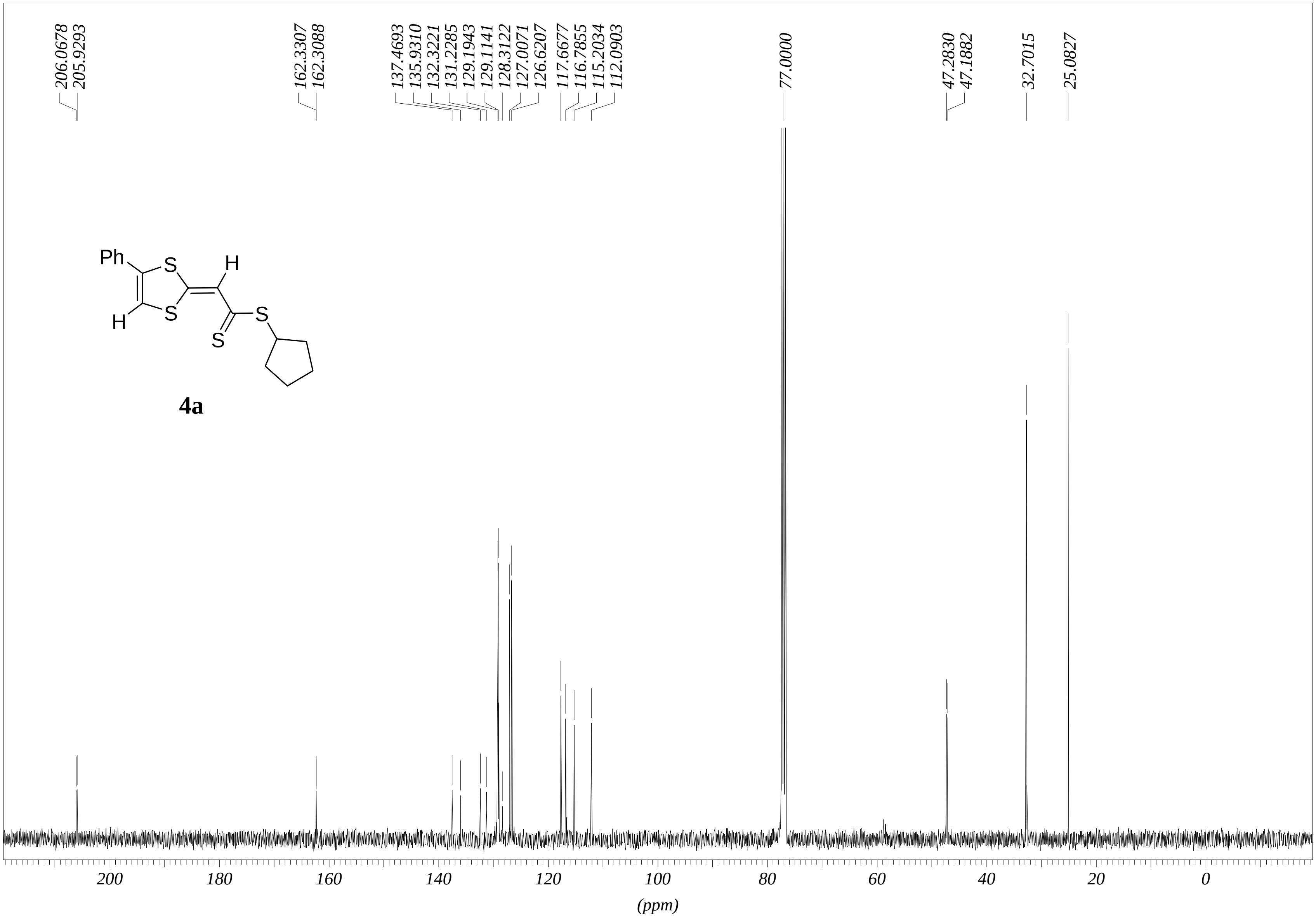
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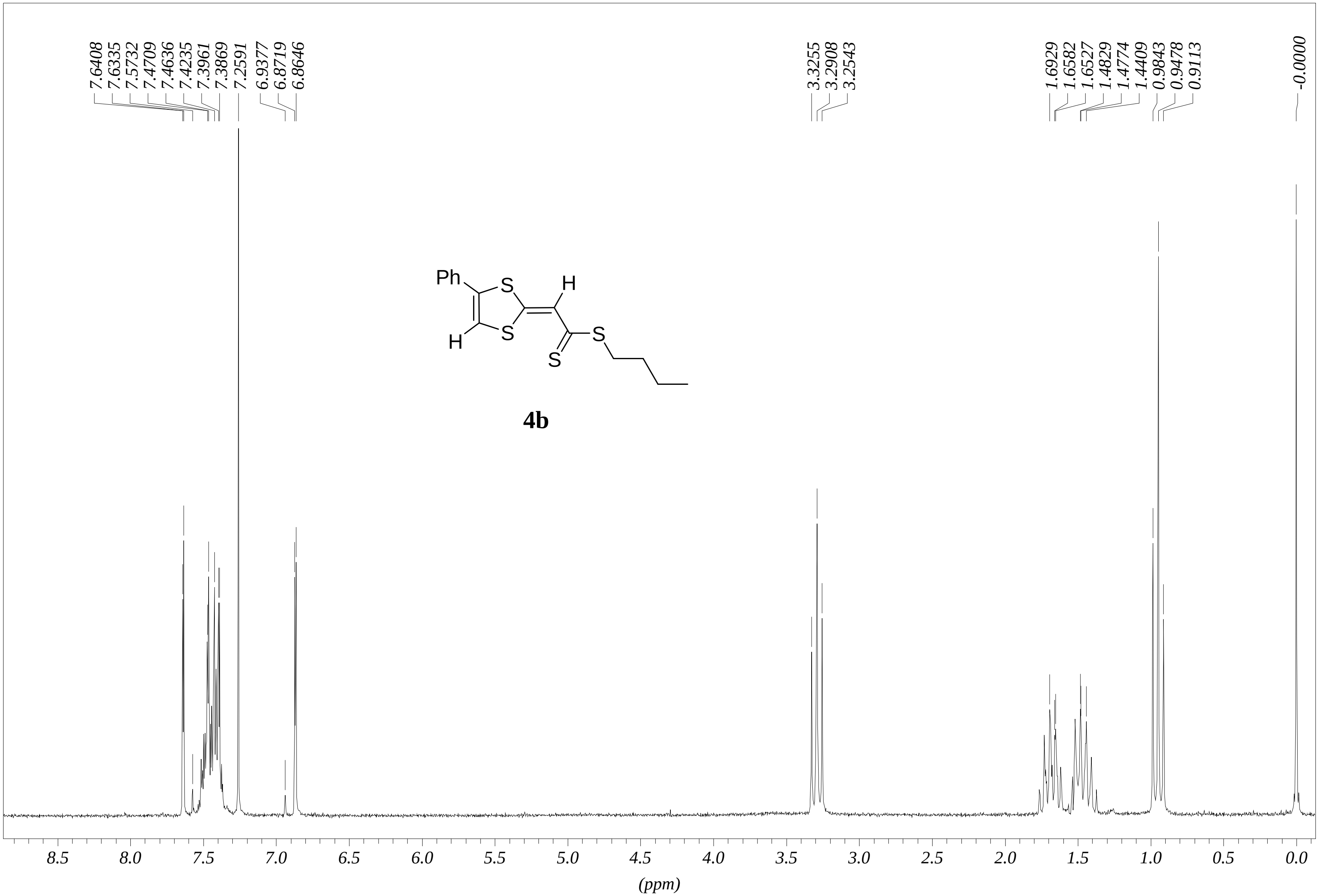
4a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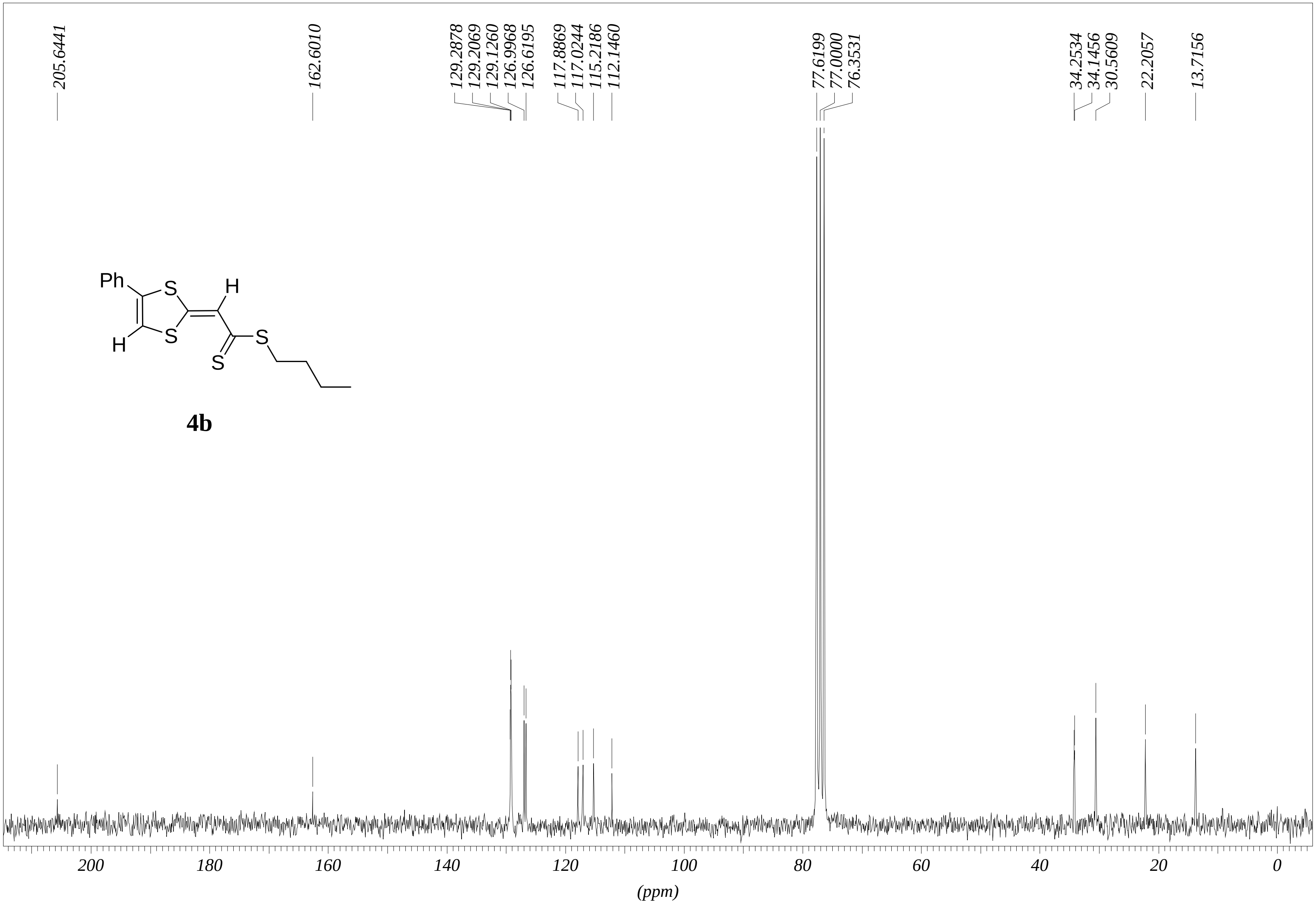
(ppm)

4b



4b

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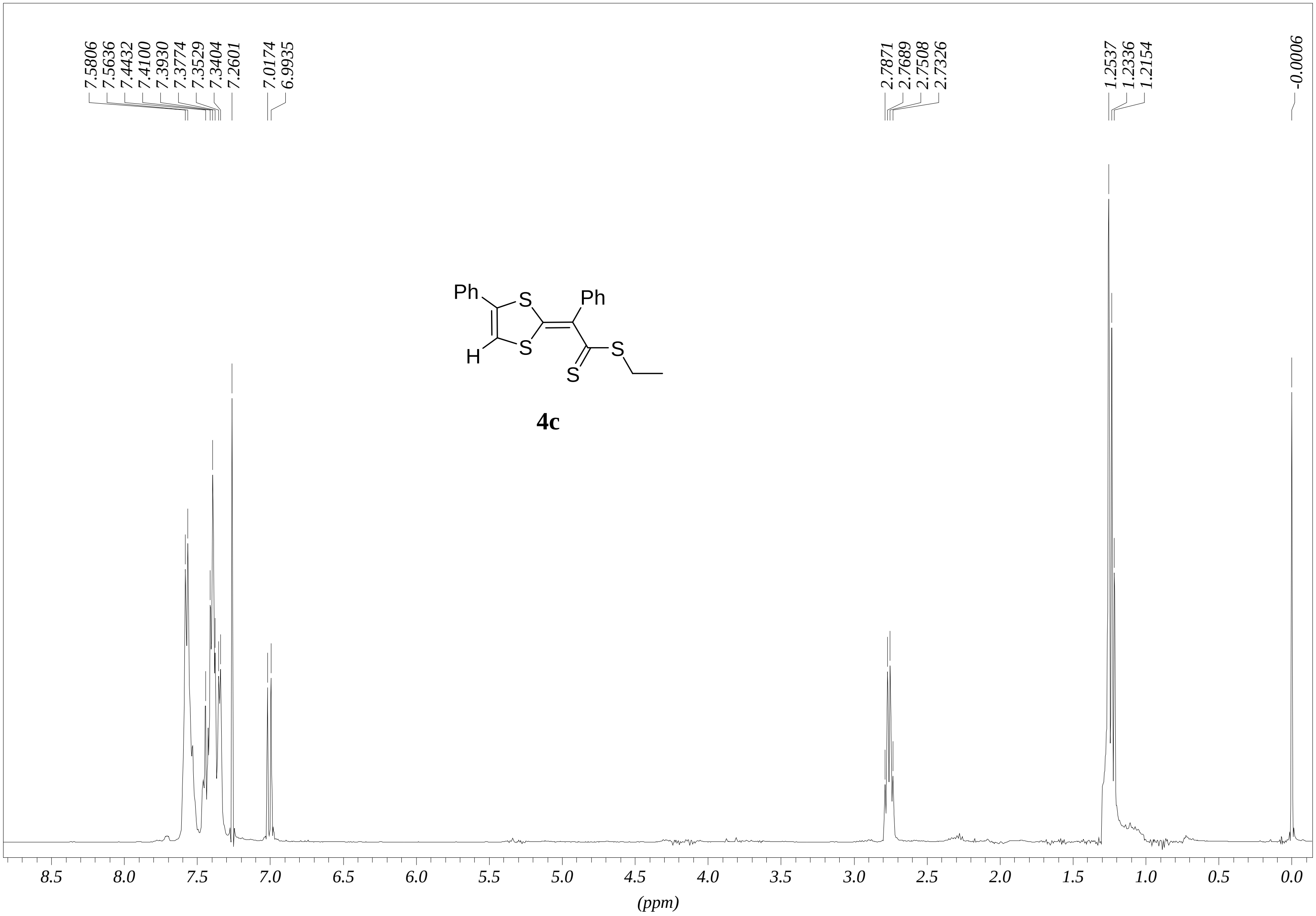
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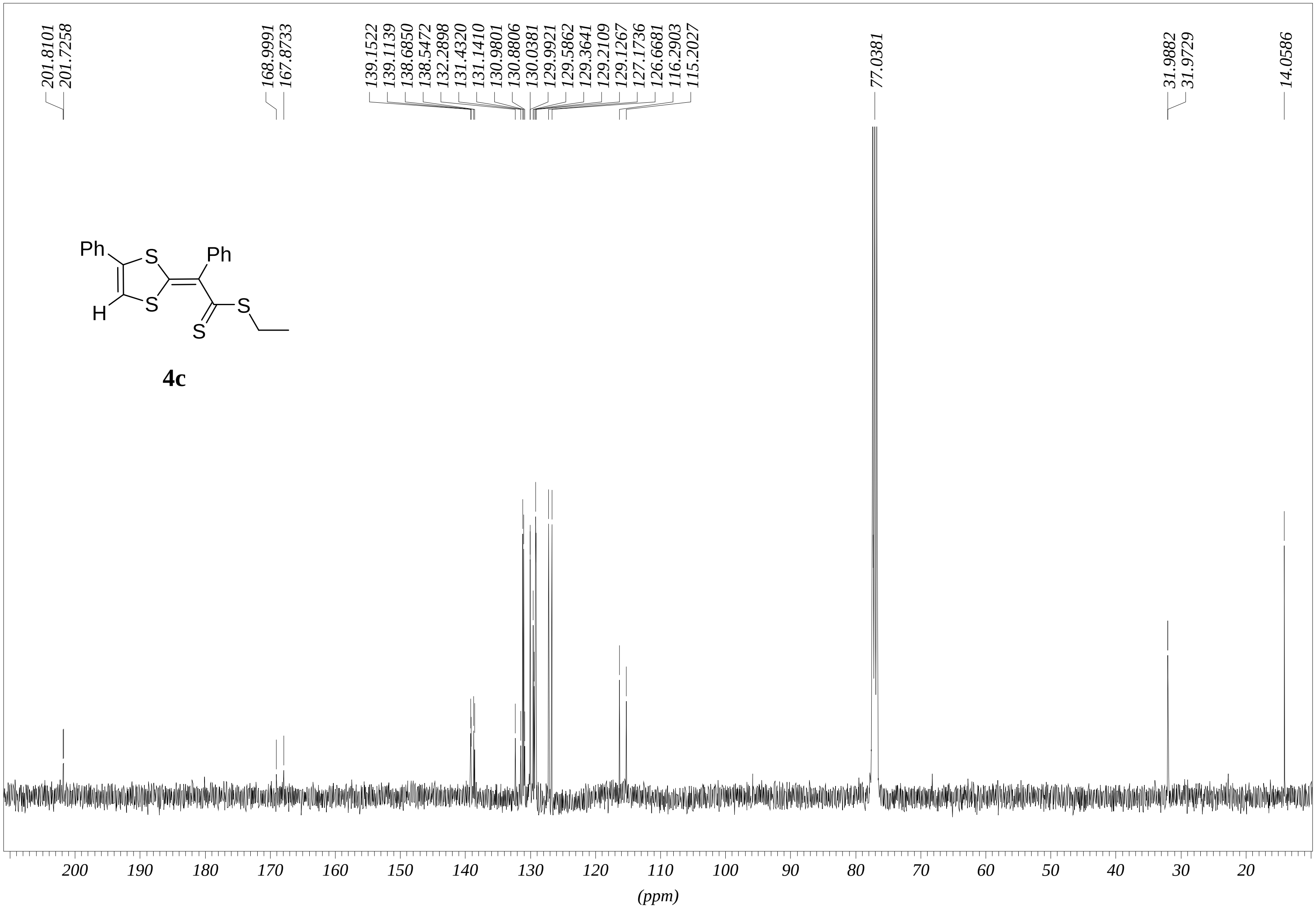
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

4c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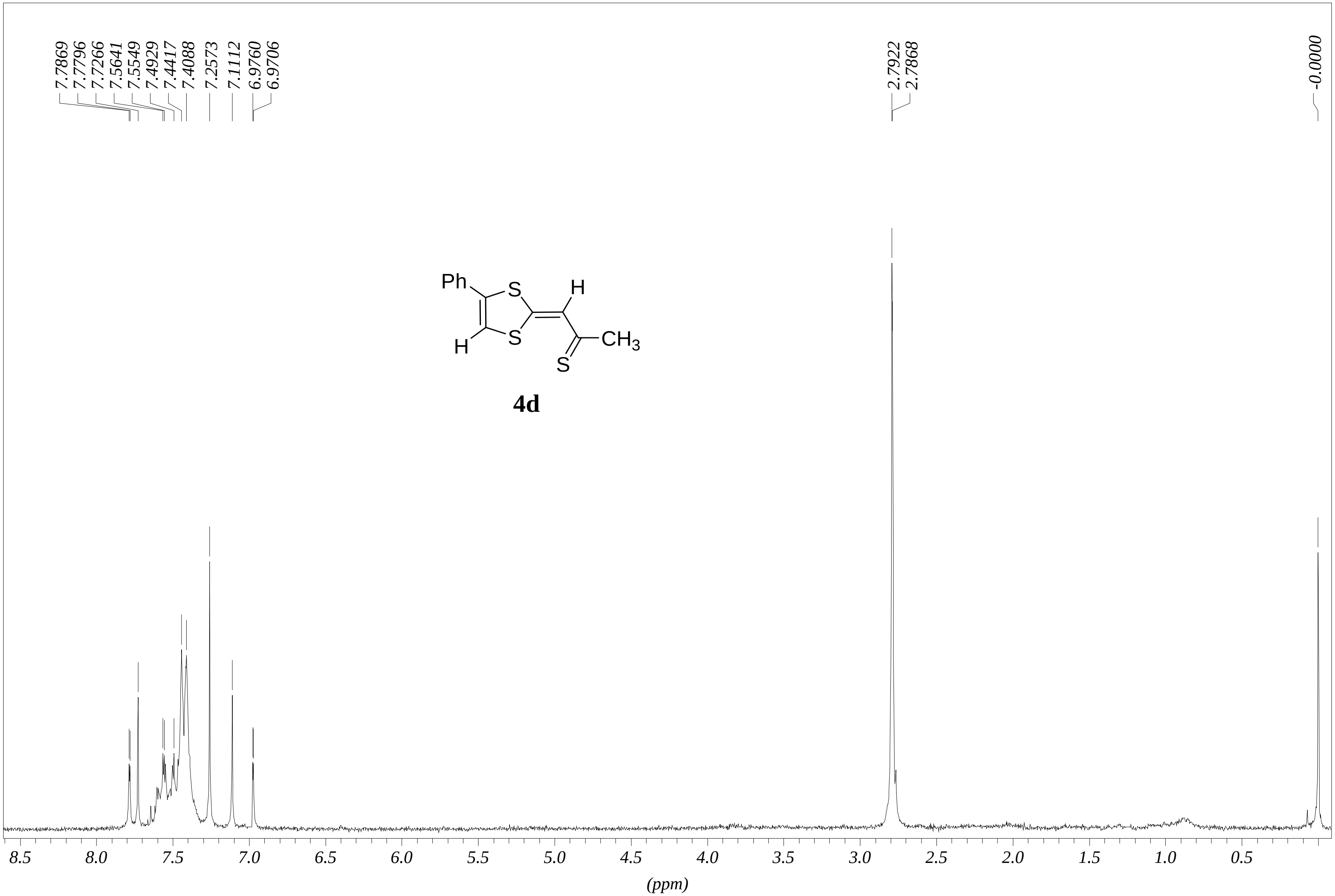
130.9801
130.8806
130.0381
129.9921
129.5862
129.3641
129.2109
129.1267
127.1736
126.6681
116.2903
115.2027
77.0381
31.9882
31.9729
14.0586
Ph
S
Ph
S
H
S
S
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
(ppm)

4c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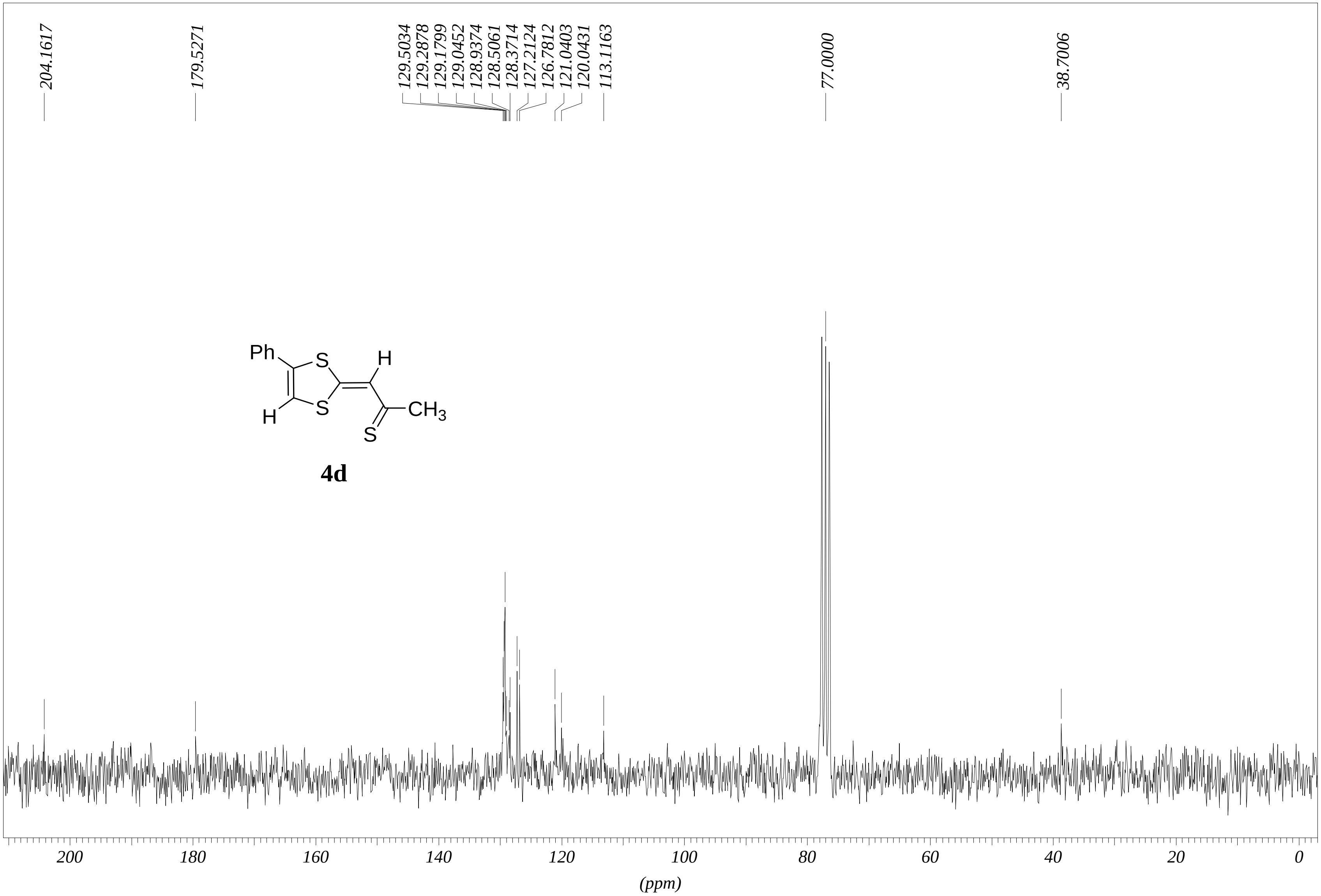
6.9760
6.9706
2.7922
2.7868
-0.0000
Ph
S
S
H
H
CH3
S
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

4d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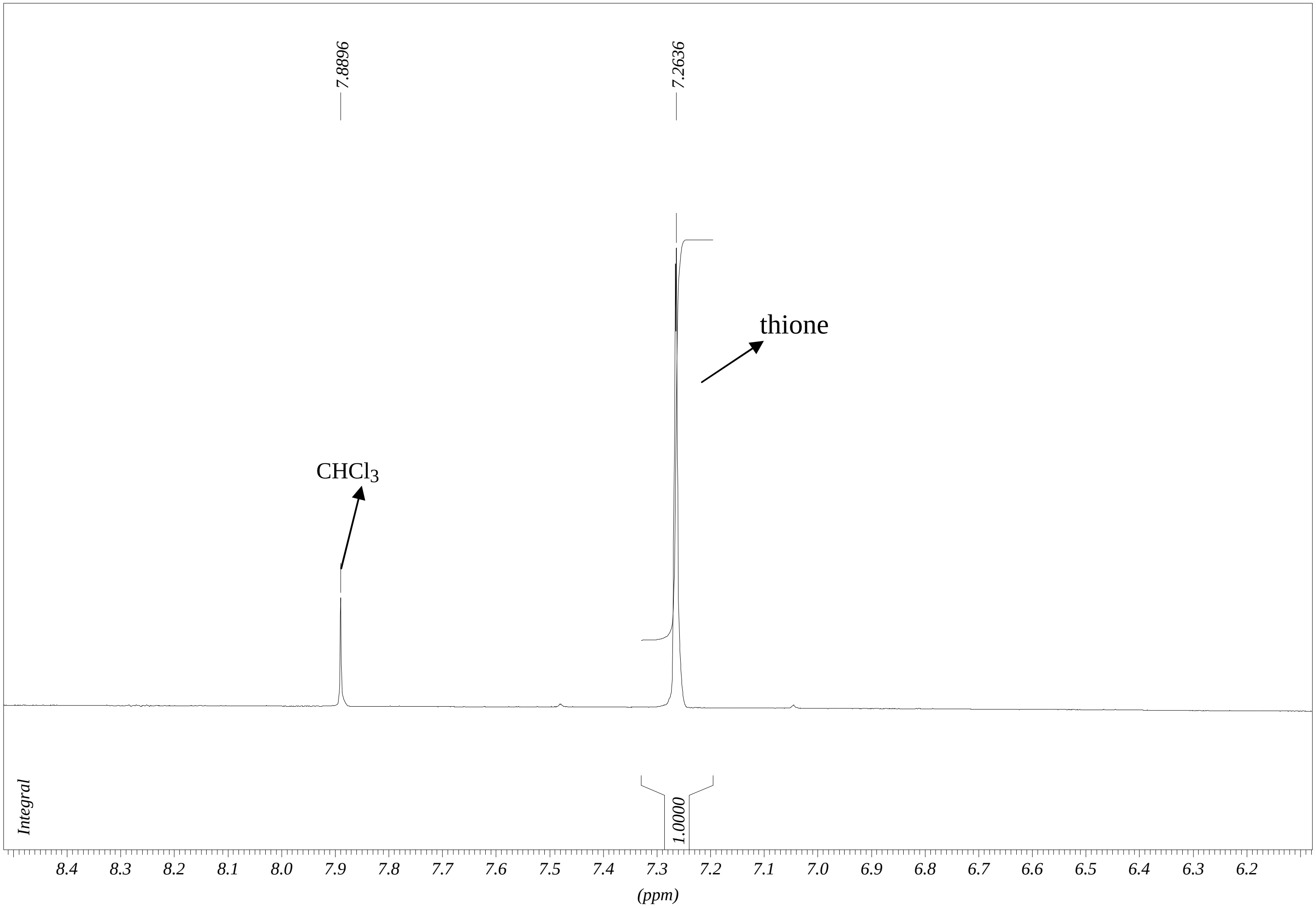
126.7812
121.0403
120.0431
113.1163
77.0000
38.7006
Ph
S
H
S
H
CH3
S
200
180
160
140
120
100
80
60
40
20
0
(ppm)

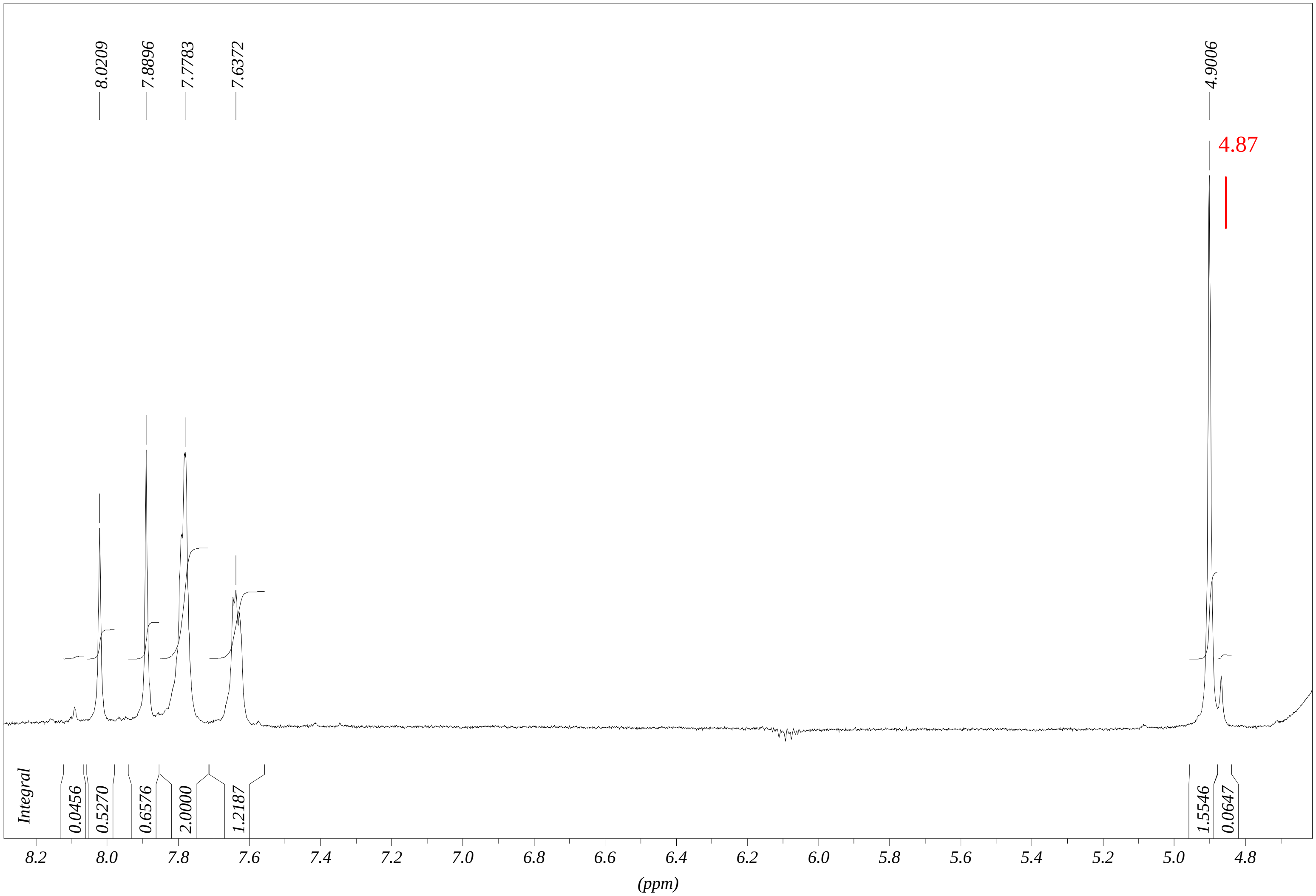
4d

EXPERIMENTS TO ASSESS THE STERESOSELECTIVITY OF THE REACTION

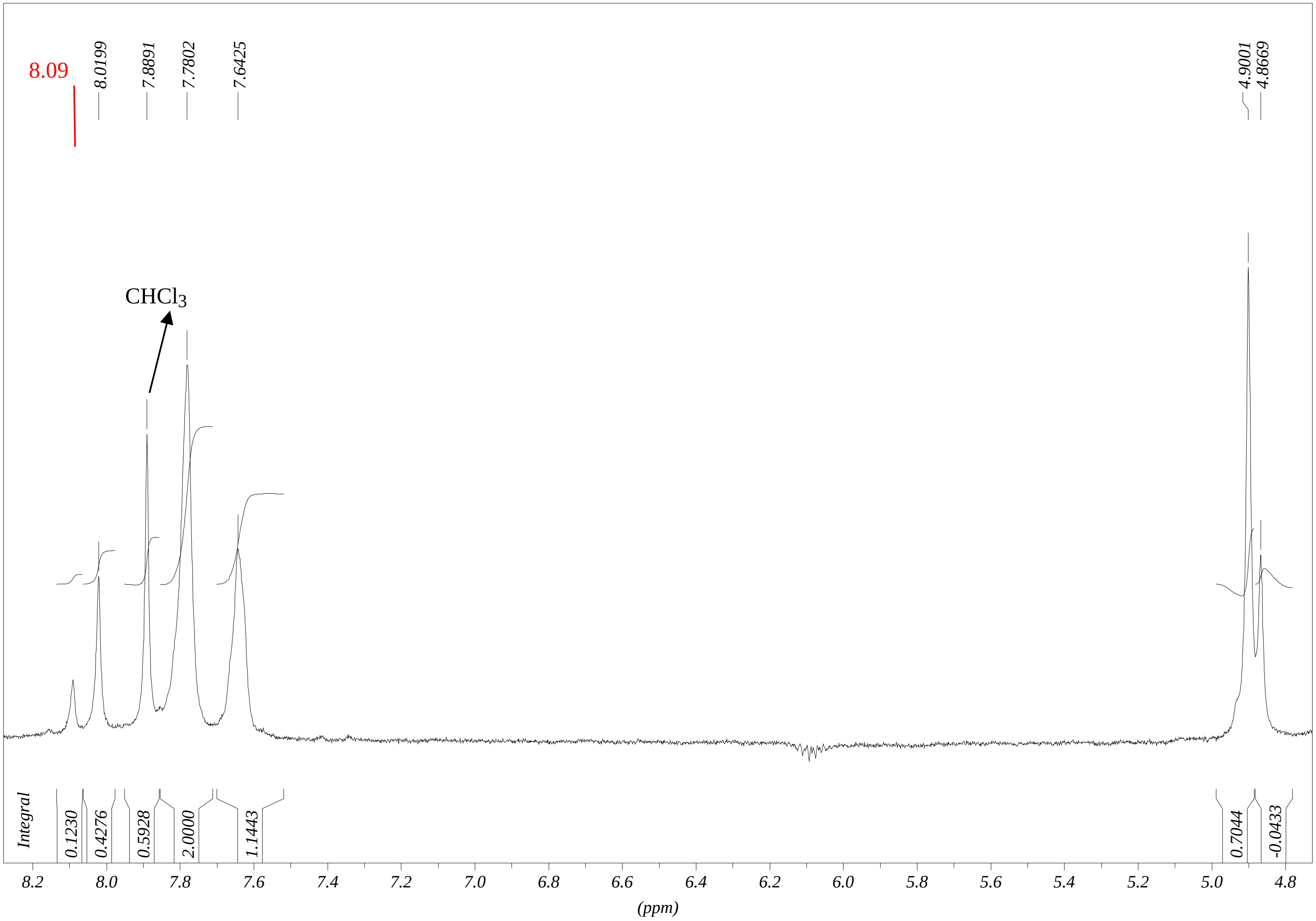
Spectrum 1: ^{1}H RMN of 5-methyl-3*H*-1,2-dithiole-3-thione **1d** (T = 300ºK, solvent: Ethyl ether/$CDCl_3$ 50:50)



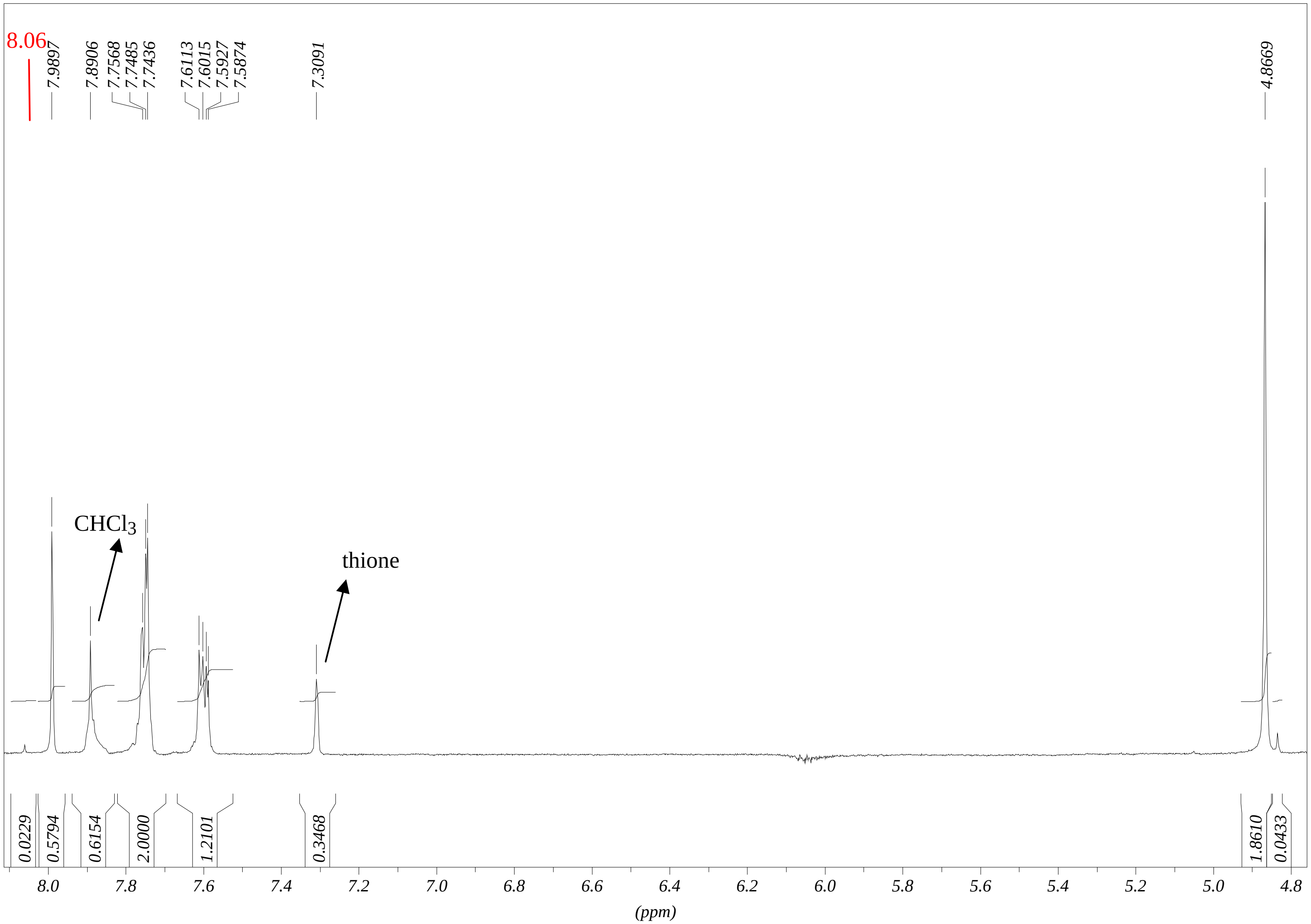
Spectrum 2A: ^{1}H RMN of Carbene **3d** obtained from 5-methyl-3*H*-1,2-dithiole-3-thione (T = 300 ºK, solvent: Ethyl ether/$CDCl_3$ 50:50, **18 minutes after preparing the solution**)



Spectrum 2B: ^{1}H RMN of Carbene **3d** obtained from 5-methyl-3*H*-1,2-dithiole-3-thione (T = 300ºK, solvent: Ethyl ether/$CDCl_3$ 50:50, **3.75 hours after preparing the solution**)



Spectrum 3A: ^{1}H RMN of **crude reaction mixture** obtained from 5-methyl-3*H*-1,2-dithiole-3-thione **1d** and **2** (T = 300 ºK, solvent: Ethyl ether/$CDCl_3$ 50:50, **20 minutes after preparing the solution**)



Spectrum 3B: ^{1}H RMN of **crude reaction mixture** obtained from 5-methyl-3*H*-1,2-dithiole-3-thione **1d** and **2** (T = 300 ºK, solvent: Ethyl ether/$CDCl_3$ 50:50, **1.4 hours after preparing the solution**)