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Supporting Information

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A benzodipyrrole-derived sapphyrin

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Experimental Section

Proton NMR spectra (400 MHz, Bruker DPX-400) were recorded using TMS as the internal standard. High and Low resolution FAB mass spectra were obtained on an AUTO SPEC M-363 high-resolution mass spectrometer. Column chromatography was performed over silica gel (Merck, 230-400 mesh). Pyrrole was distilled at atmospheric pressure from CaH_2. Both CH_2Cl_2 and $CHCl_3$ (reagent grade) were distilled from K_2CO_3 to eliminate traces of acid. All other reagents were obtained from Aldrich and used as received unless noted otherwise.

3,6-Diformylbenzodipyyrole(3)

To the solution of benzodipyrrole **2** (500 mg, 3.2 mmol) dissolved in DMF (750 *m*L, 9.6 mmol) was added 1,2-dichloroethane (5 mL). The mixture was cooled to 0 ^oC in ice-bath under nitrogen atmosphere. Then, $POCl_3$ (900 *m*L, 9.6 mmol) was added dropwise. The whole mixture was heated to reflux for 30 min and then cooled to room temperature. Saturated NaOAc (6mL) was added carefully and the mixture was refluxed for another 30 min and cooled to room temperature. The solvent was removed in vacuo and the residual solid was dissolved in hot water and refrigerated overnight. Pure product was obtained by repeated recrystallization from water. Yield: 407 mg (60 %).^1H NMR (300 MHz, DMSO-d_6, 25 ^oC, TMS): *d*=12.01 (brs, 2H), 10.03 (s, 2H), 8.26 (s, 2H), 7.92 (s, 2H). ^{13}C NMR (300 MHz, DMSO-d_6, 25 ^oC, TMS): *d*= 185.88, 136.73, 123.66, 121.25, 119.86, 116.12. MS (EI) calcd. for $C_{12}H_8N_2O_2$ m/z 212.06; found (m+1)/z 213.02.

3,6-Dimethylbenzodipyrrole (4)

To a mixture of 3,6-diformylbenzodipyrrole **3**(400 mg, 1.9 mmol) and dry THF (20 mL), $LiAlH_4$ (1 M solution in THF, 19.2 mL) was added dropwise under nitrogen atmosphere. After the addition is completed, the reaction mixture was stirred at 40 ^oC for 36 h. Then the mixture was cooled in ice-bath. The mixture was combined with methylene chloride (40 mL) and water was added carefully to quench the reaction. The organic layer was separated, dried over anhd. Na_2SO_4 and excess solvent were removed in vacuo. Column chromatography on silica (CH_2Cl_2/EtOAc = 98/2) afforded pure product. Yield: 146 mg (42 %). ^1H NMR (300 MHz, DMSO-d_6, 25 ^oC, TMS): *d*=10.25 (s, 2H), 7.14 (s, 2H), 6.97 (m, 2H), 2.31 (s, 6H). ^{13}C NMR (300 MHz, DMSO-d_6): δ 123.58, 123.36, 119.24, 111.03, 110.65, 10.54. MS (EI) calcd. for $C_{12}H_{12}N_2$ m/z 184.10; found (m+1)/z 185.06.

2,7-Diformyl-3,6-Dimethylbenzodipyyrole(5)

To the solution of dimethylbenzodipyrrole **2** (130 mg, 0.7 mmol) dissolved in DMF (164 *m*L, 2.1 mmol) was added 1,2-dichloroethane (2 mL). The mixture was cooled to 0 ^oC in ice-bath under nitrogen atmosphere. Then, $POCl_3$ (197 *m*L, 2.1 mmol) was added dropwise. The whole mixture was heated to reflux for 30 min and then cooled to room temperature. Saturated NaOAc (2mL) was added carefully and the mixture was refluxed for another 30 min and cooled to room temperature. The solvent was removed in vacuuo and the residual solid was dissolved in hot water and refrigerated overnight. Pure product was obtained by recrystallization from water. Yield: 122 mg (72 %).^1H NMR (300 MHz, DMSO-d_6, 25 ^oC, TMS): *d*=11.38 (brs, 2H), 10.00 (s, 2H), 7.38 (s, 2H), 2.62 (s, 6H). ^{13}C NMR (300 MHz, DMSO-d_6, 25 ^oC, TMS): *d*=180.97, 131.79, 126.40,

125.64, 125.22, 114.37, 8.87. MS (EI) calcd. for $C_{14}H_{12}N_2O_2$ m/z 240.09; found (m+1)/z 241.09.

Benzosaphhyrin (1)

2,7-Diformyl-3,6-dimethylbenzodipyrrole **5** (68 mg, 0.28 mmol), which was sparingly soluble in absolute ethanol, was mixed with absolute EtOH (280 mL) and refluxed overnight in nitrogen atmosphere to dissolve completely. After cooling to room temperature, tetramethyldiethyltripyromethane dicarboxylic acid **6** (120 mg, 0.28 mmol) was added and followed by addition of *p*-toluenesulfonic acid (215 mg, 1.12 mmol). The mixture was stirred for 18 h while oxygen gas was bubbled through the reaction mixture at a constant speed. The excess solvent was removed in vacuo and the remaining dark solid was purified by chromatography on silica (CH_2Cl_2/ with increasing increment of methanol up to 8 v/v %). The green fraction was collected and repeated column chromatography was necessary in order to obtain reasonably pure product. Analytically pure product was obtained by preparative TLC (silica, CH_2Cl_2/MeOH = 93/7). Yield: 27 mg (18 %).^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): *d*=10.64 (brs, 2H), 10.49 (brs, 2H), 8.86 (s, 2H), 4.42 (m, 4H), 4.32 (s, 6H), 3.80 (s, 6H), 3.77 (s, 6H), 2.03 (t, 6H), -0.87 (brs, 1H), -1.30 (brs, 1H), -2.46 (brs, 1H). MS (FAB) calcd. for $C_{36}H_{37}N_5$ 539.30; found 540.30 (m+1)/z. UV-Vis (1% Et_3N in $CHCl_3$) l_{max}/log ε)=466 (4.92), 618 (3.59), 667 (3.92), 727 nm (4.22).

The disulphonate salt was obtained by washing a chloroform solution of **1** with excess aqueous solution of p-toluenesulphonic acid and than drying the organic layer with anhyds. Na_2SO_4 and by removing the solvent in vacuo. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): *d*=11.28 (s, 2H), 11.23 (s, 2H), 8.63 (s, 2H), 5.44 (brs, 4H), 4.53 (q, 4H), 4.24 (s, 6H), 4.04 (s, 12H), 2.59 (brs, 4H),

2.30 (t, 6H), 1.89 (s, 6H), -3.65 (s, 2H), -3.78 (s, 1H), -4.79 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): *d*=170.63, 167.73, 143.79, 139.61, 137.55, 137.03, 136.57, 136.14, 130.91, 128.84, 125.67, 121.02, 100.79, 92.93, 31.93, 22.70, 20.97, 20.86, 18.47, 14.13, 12.88, 12.84, 12.66. UV-Vis(chloroform) λ_{max}/(log ε)=469 (5.45), 593 (4.03), 638 (4.12), 703 (4.46), 748 nm (4.04).

The dichloride salt was obtained by washing the sapphyrin with aqueous 1N NaOH solution till UV-vis spectra does not change further followed by washing the organic layer a few times with water than with excess aqueous 1 N HCl solution, drying the organic layer with anhyds. Na_2SO_4 and finally evaporating the solvent in vacuo. ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): *d*=11.35 (s, 2H), 11.29 (s, 2H), 8.60 (s, 2H), 4.53 (m, 4H), 4.16 (s, 6H), 4.03 (s, 12H), 4.00 (s, 4H), 2.21 (brt, 6H), -2.50 (brs, 2H), -3.21 (brs, 1H), -4.43 (brs, 2H). ^{13}C NMR (400 MHz, $CDCl_3$, 25 ^{o}C, TMS): *d*=143.28, 137.35, 136.27, 130.14, 121.50, 100.90, 93.03, 29.73, 20.91, 18.51, 12.93, 12.73. UV-Vis ($CHCl_3$) λ_{max}/(log ε)=470 (5.31), 598 (3.59), 637 (3.72), 704 (4.19), 748 nm (3.65).

Figure 1. ^{1}H NMR spectrum of 3,6-diformylbenzodipyrrole **3** in DMSO-d_6.

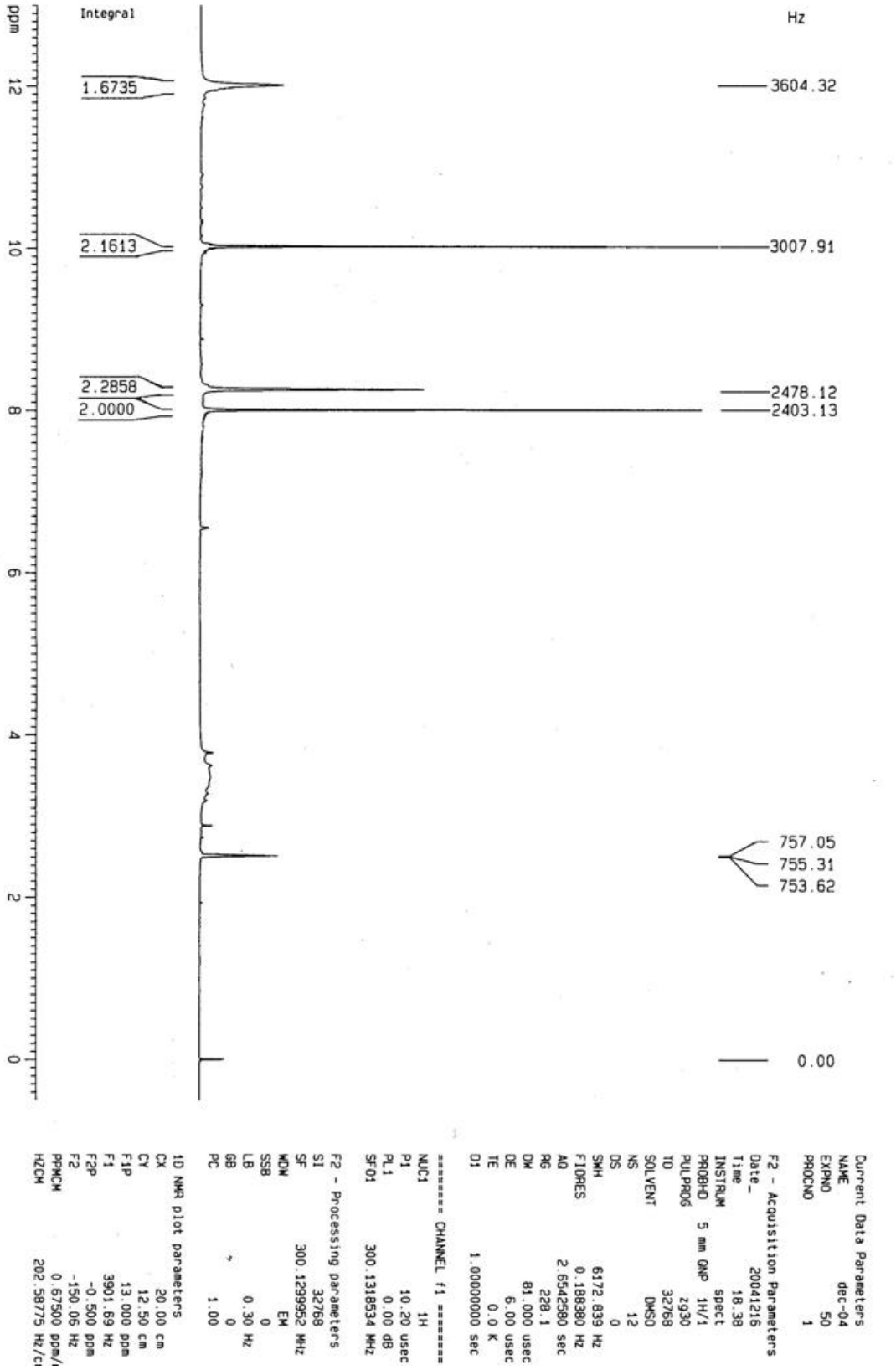


Figure 2. ^{13}C NMR spectrum of 3,6-diformylbenzodipyrrole **3** in DMSO-d_6.

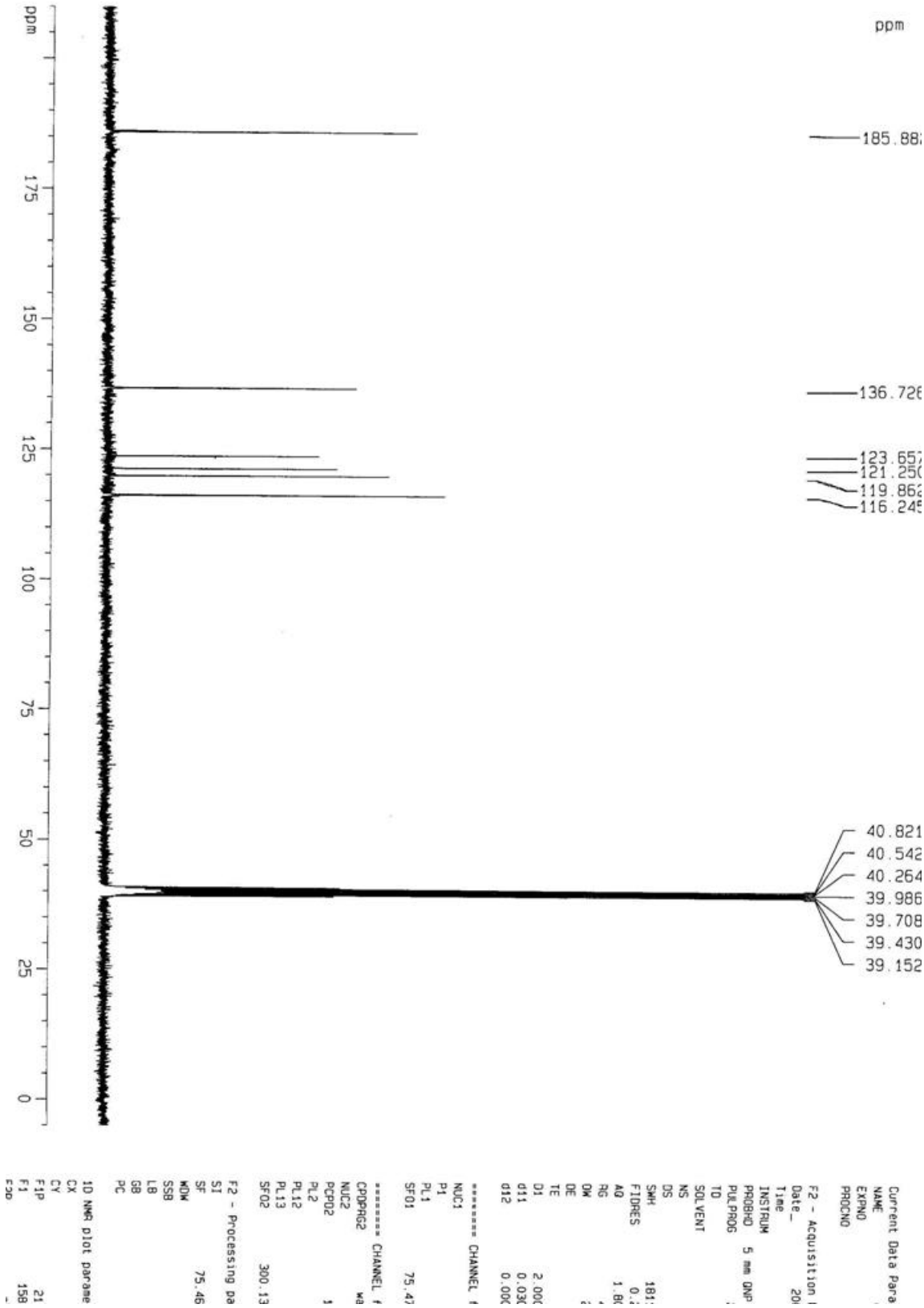


Figure 3. EI mass spectrum of 3,6-diformylbenzodipyrrole **3.**

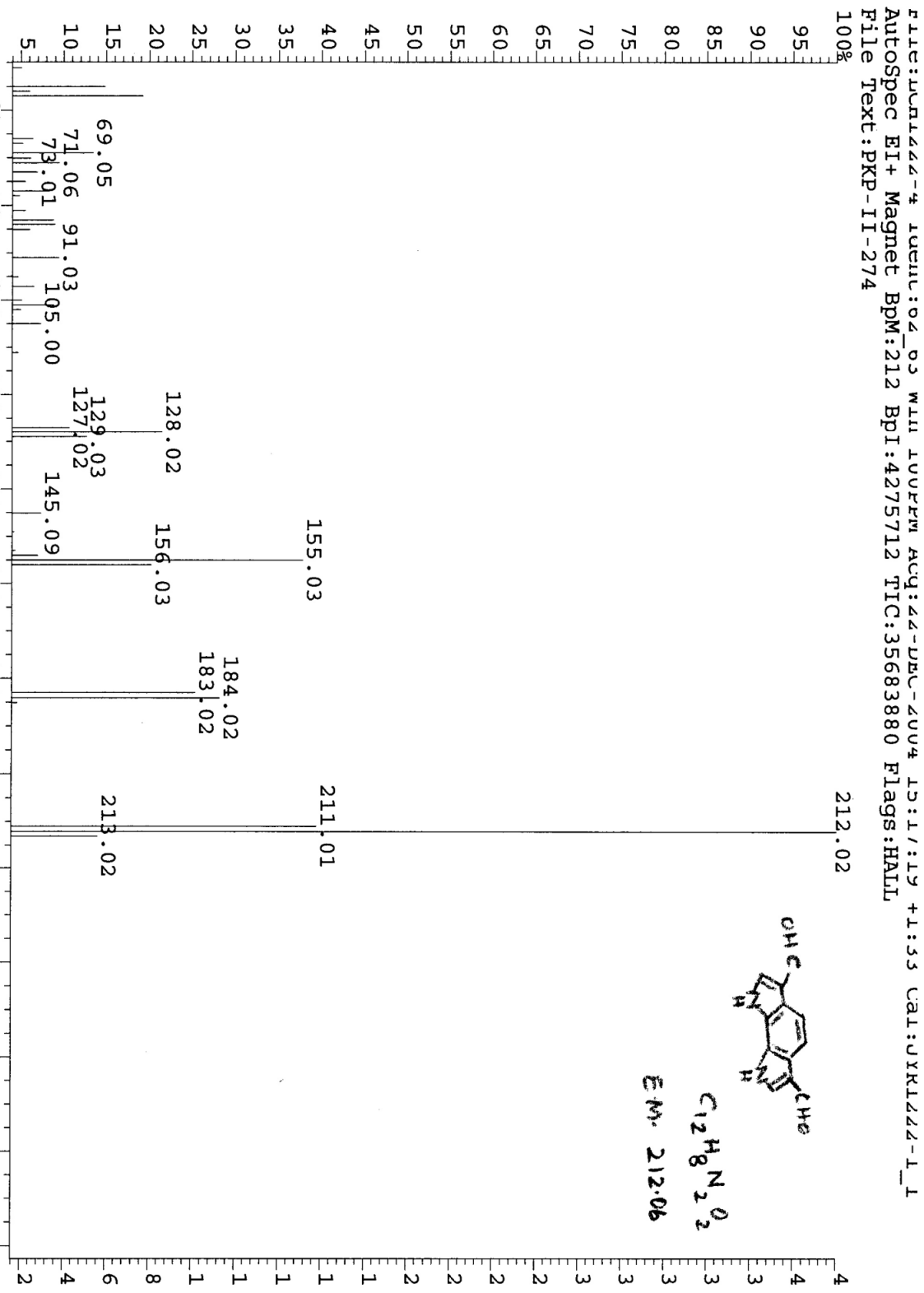


Figure 4. ^{1}H NMR spectrum of 3,6-dimethylbenzodipyrrole **4** in DMSO-d_6.

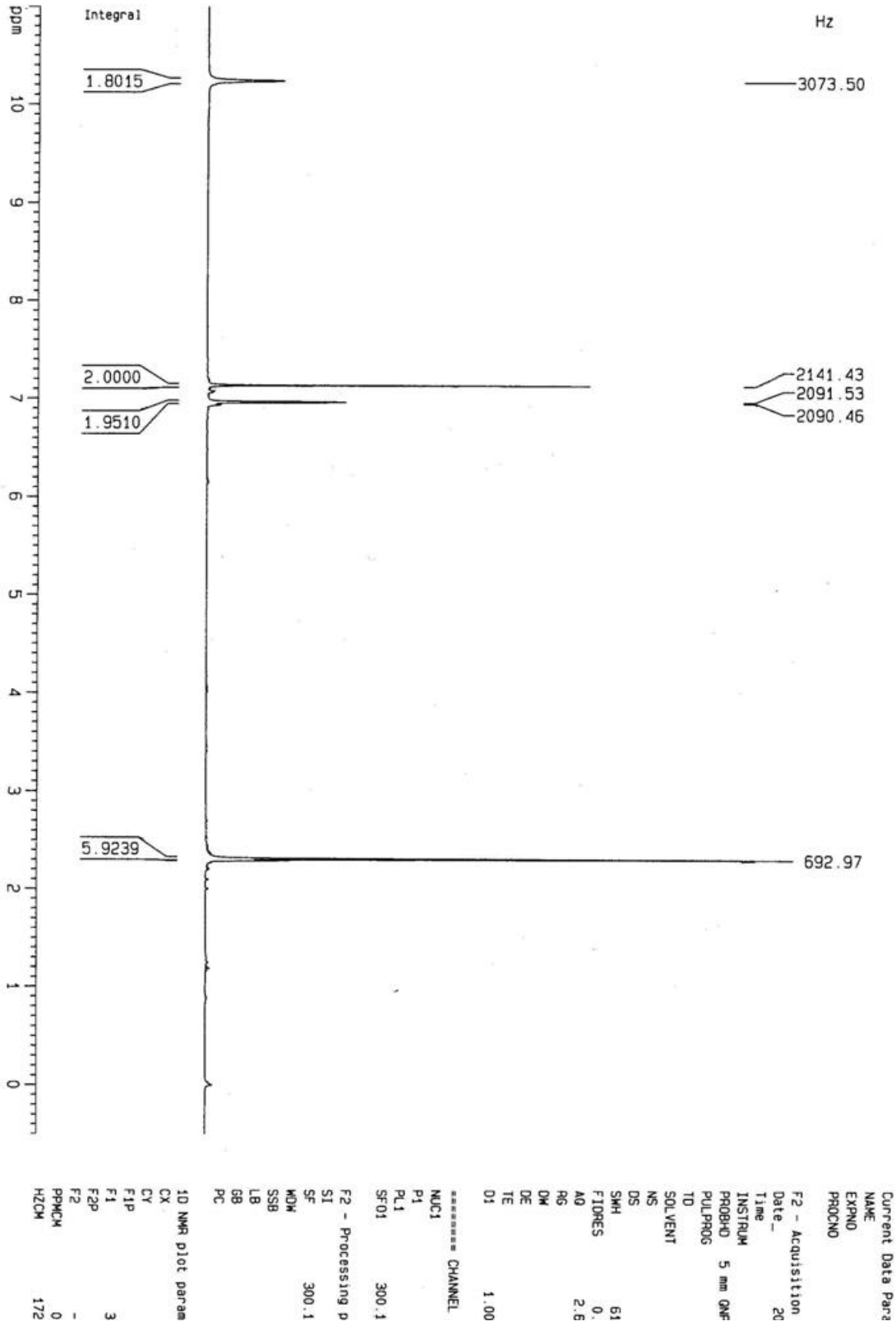


Figure 5. ^{13}C NMR spectrum of 3,6-dimethylbenzodipyrrole **4** in DMSO-d_6.

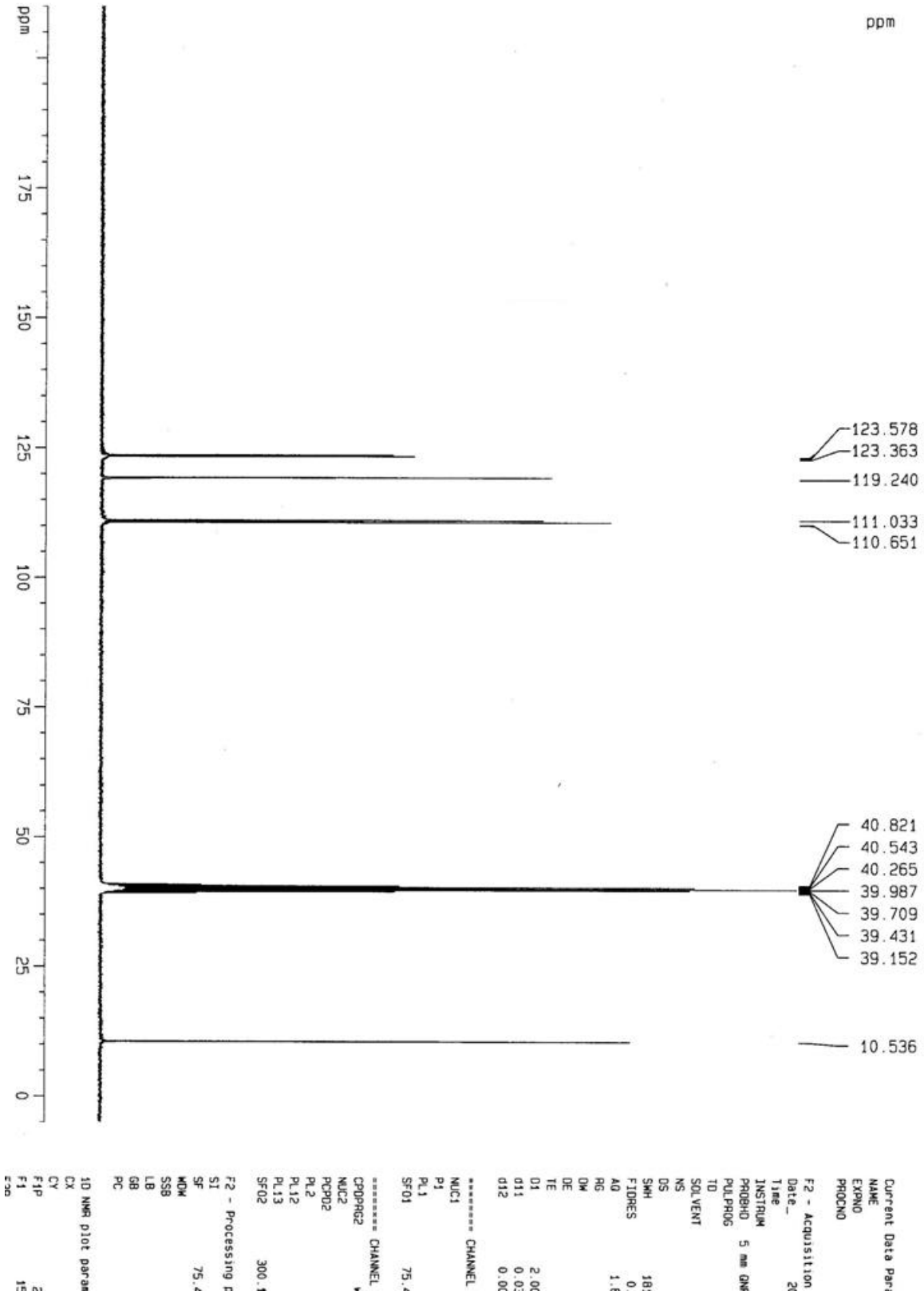


Figure 6. EI mass spectrum of 3,6-dimethylbenzodipyrrole **4.**

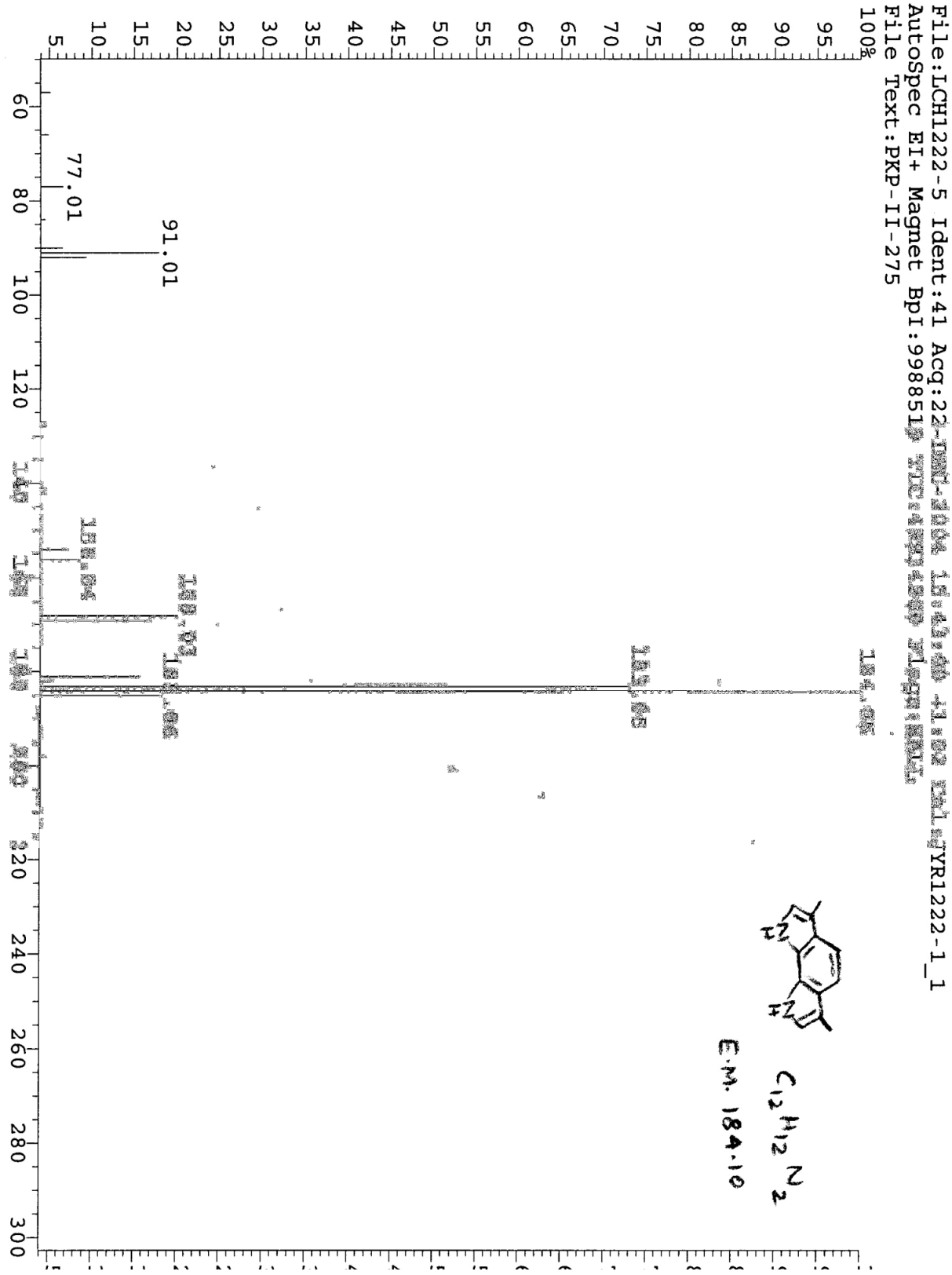


Figure 7. ^{1}H NMR spectrum of 2,7-diformyl-3,6-dimethylbenzodipyrrole **5** in DMSO-d_6.

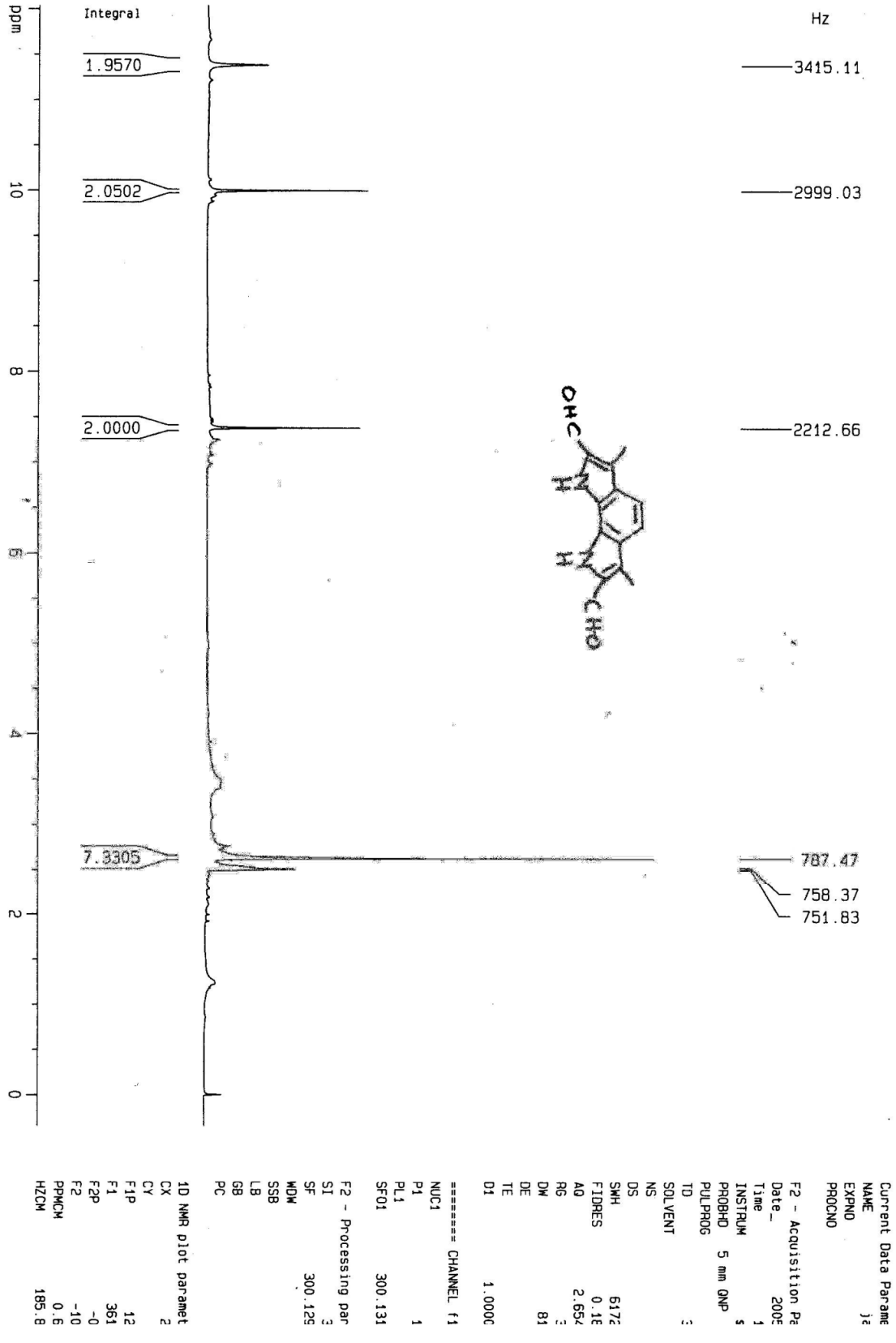


Figure 8. ^{13}C NMR spectrum of 2,7-diformyl-3,6-dimethylbenzodipyrrole **5** in DMSO-d_6.

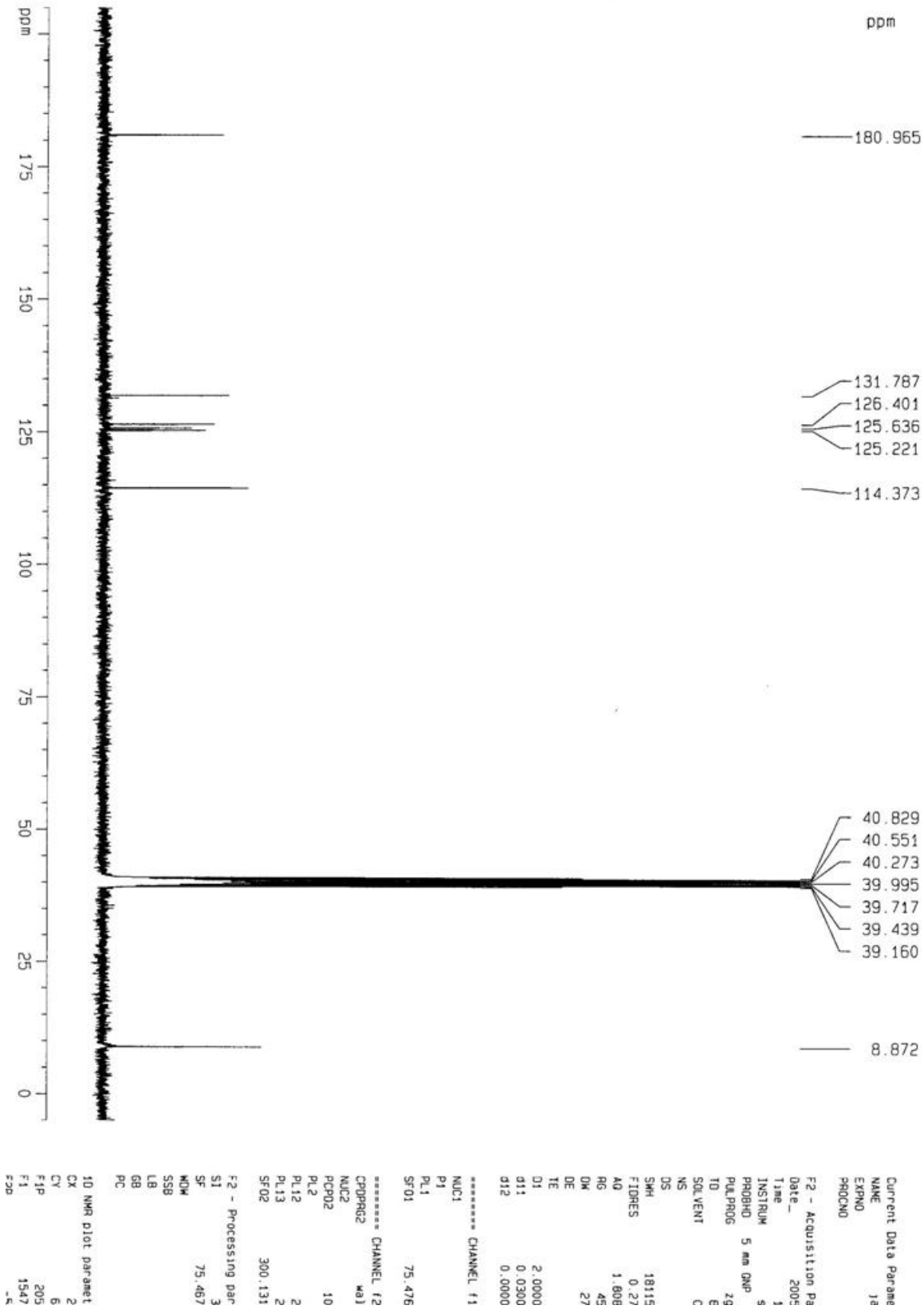


Figure 9. EI mass spectrum of 2,7-diformyl-3,6-dimethylbenzodipyrrole **5.**

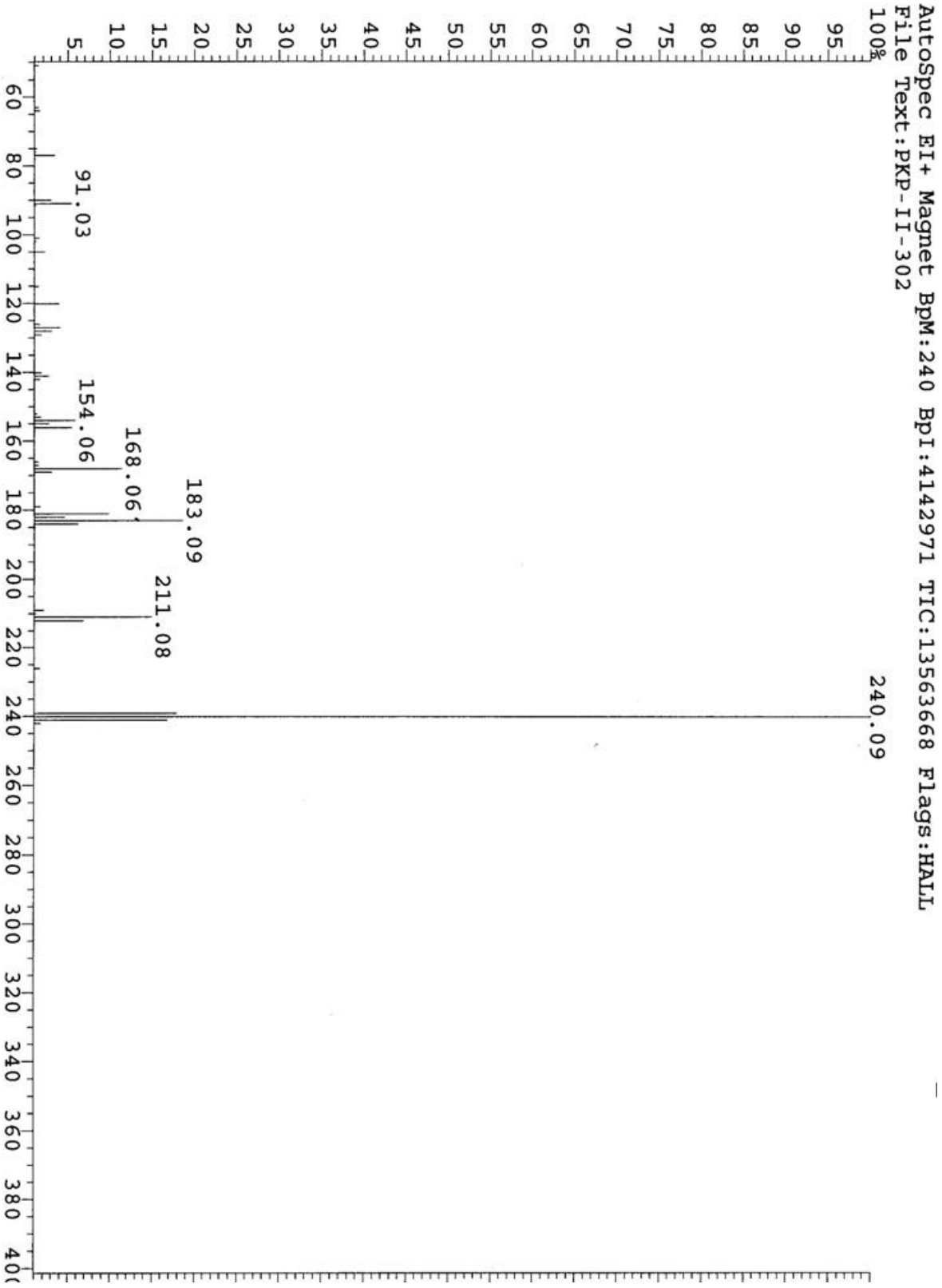


Figure 10. ^{1}H NMR spectrum of benzosapphyrin **1** in $CDCl_3$.

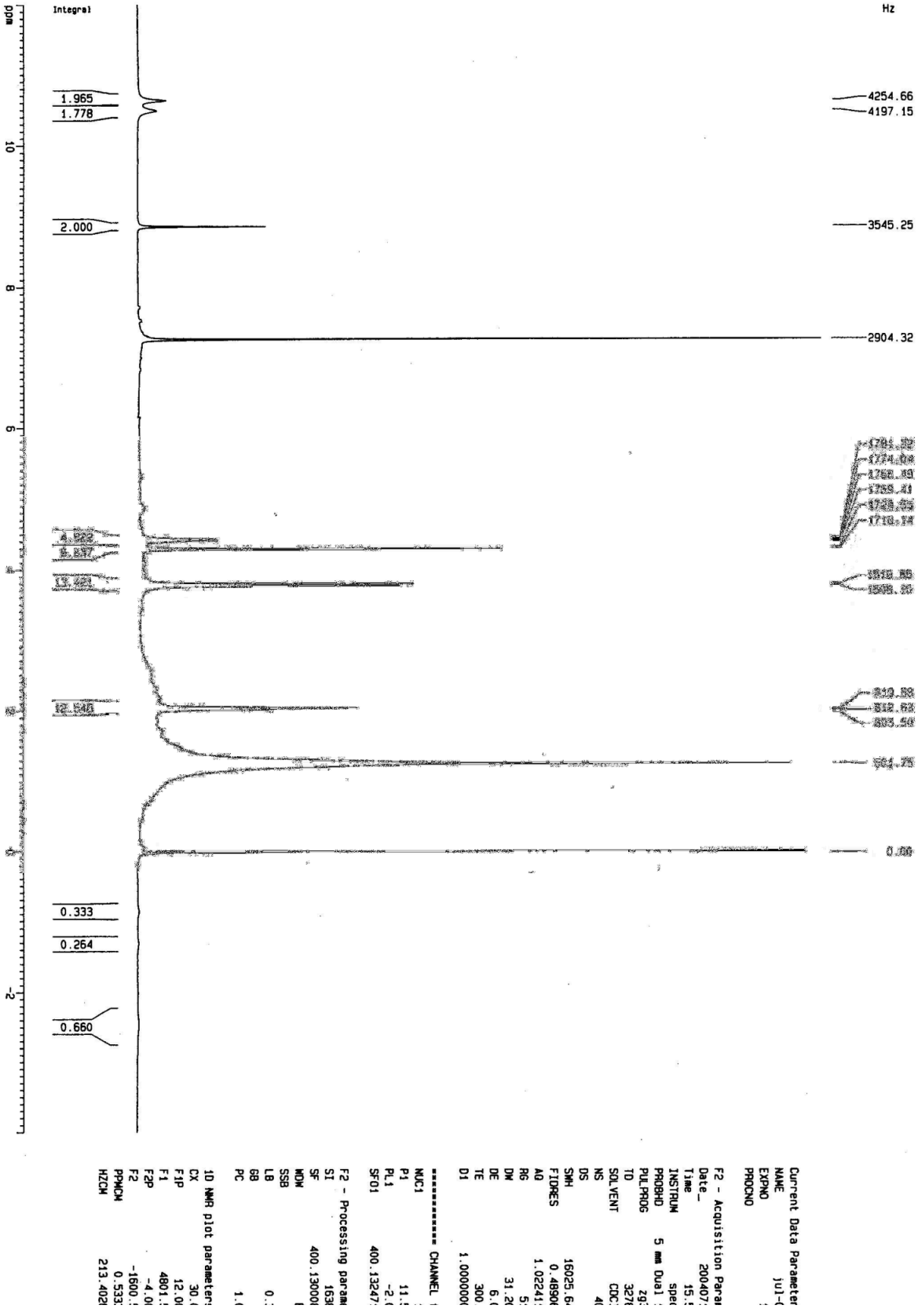
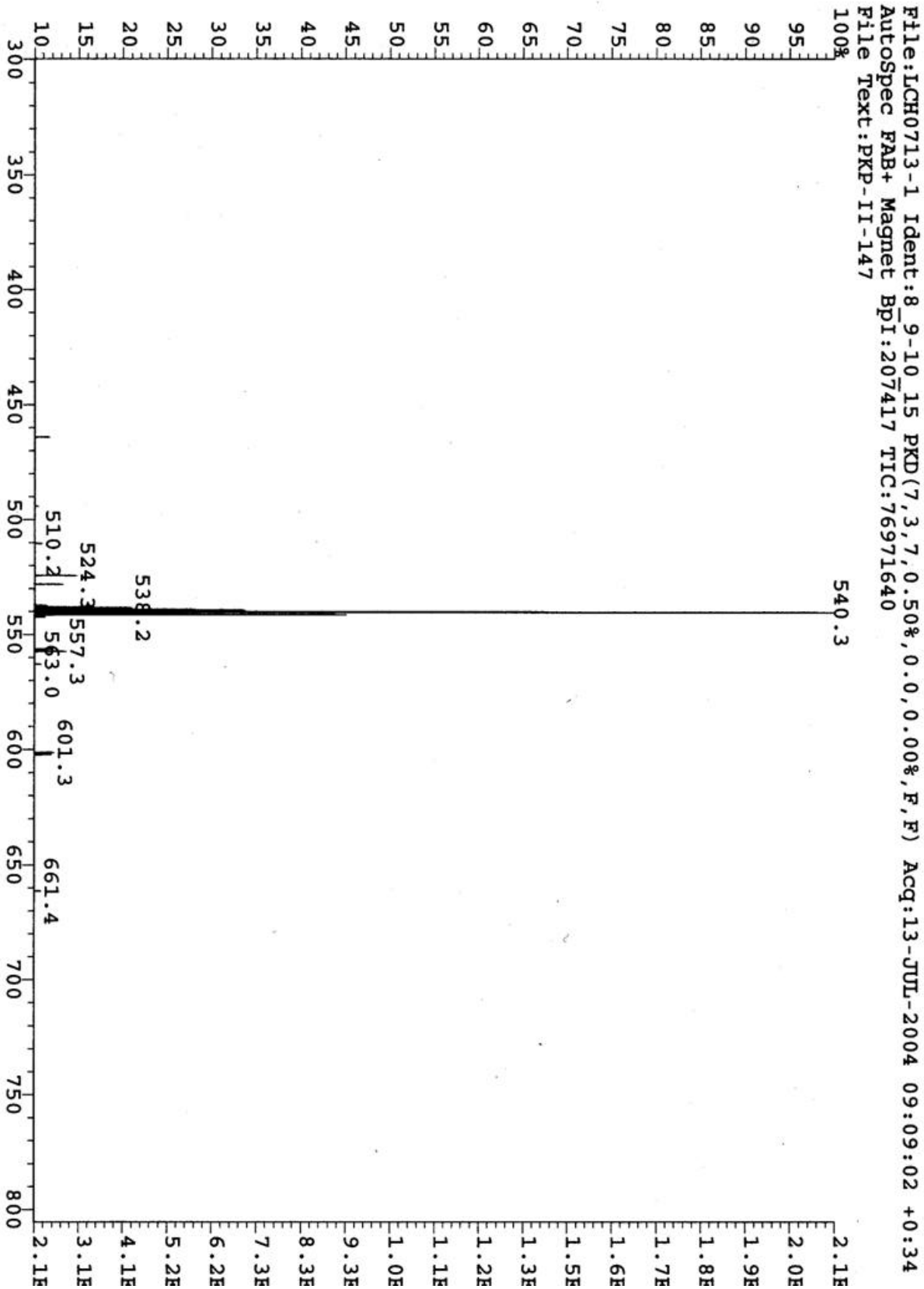


Figure 11. FAB mass spectrum of benzosapphyrin **1**.



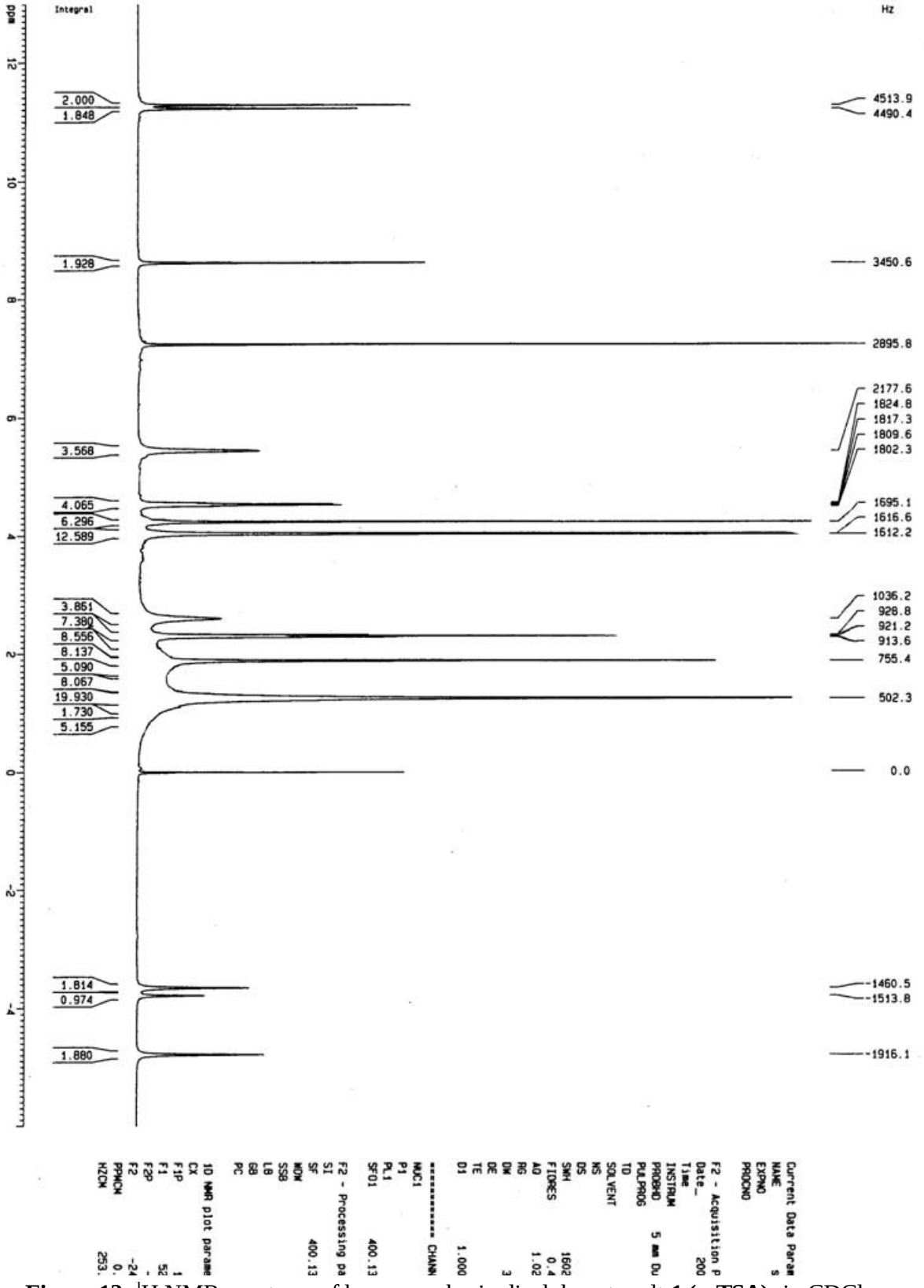


Figure 12. ^{1}H NMR spectrum of benzosapphyrin disulphonate salt **1.(p-TSA)$_2$** in $CDCl_3$.

Figure 13. ^{13}C NMR spectrum of benzosapphyrin disulphonate salt **1.(p-TSA)$_2$** in $CDCl_3$.

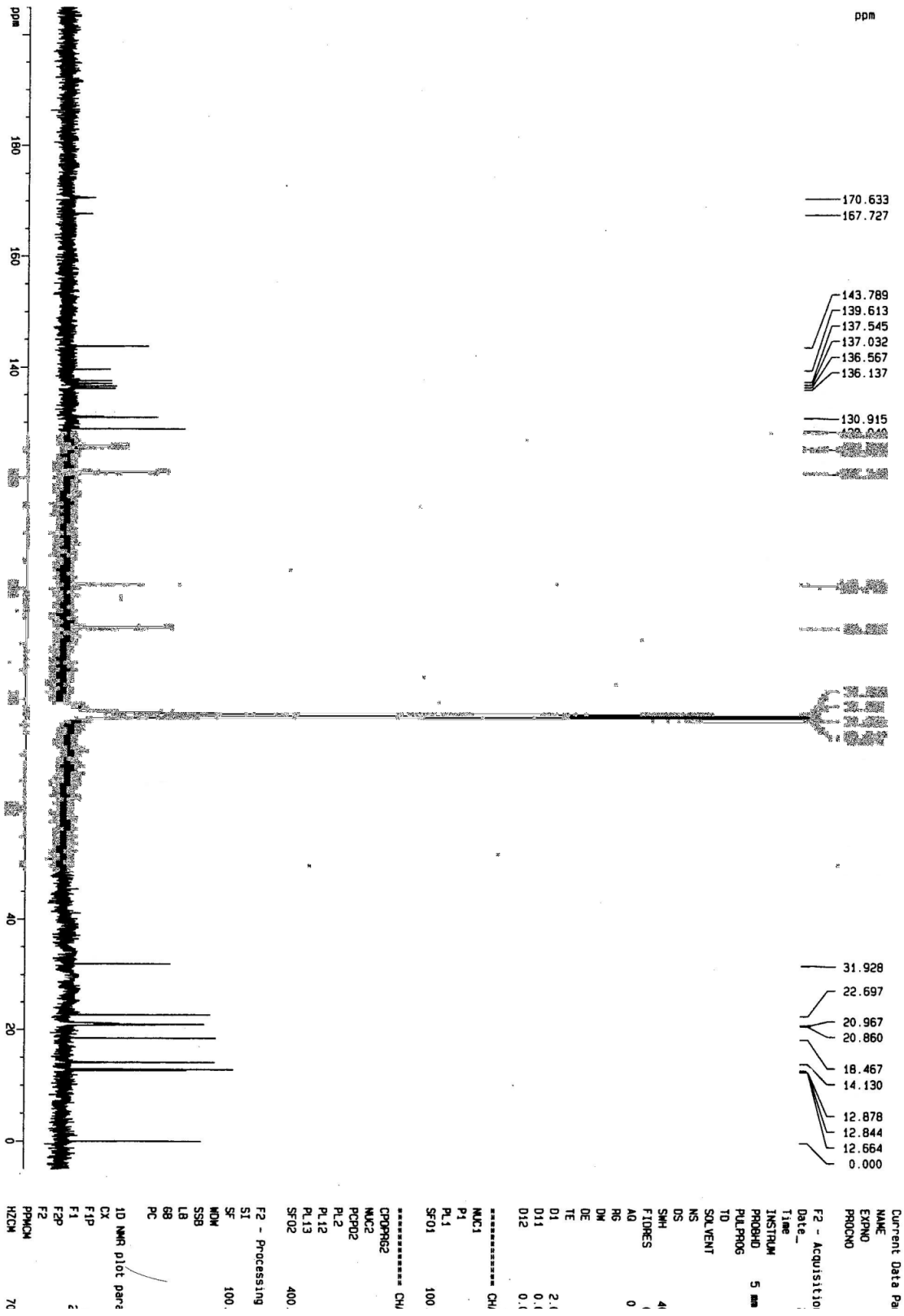


Figure 14. ^{1}H NMR spectrum of benzosapphyrin dichloride salt **1.Cl$_2$** in $CDCl_3$.

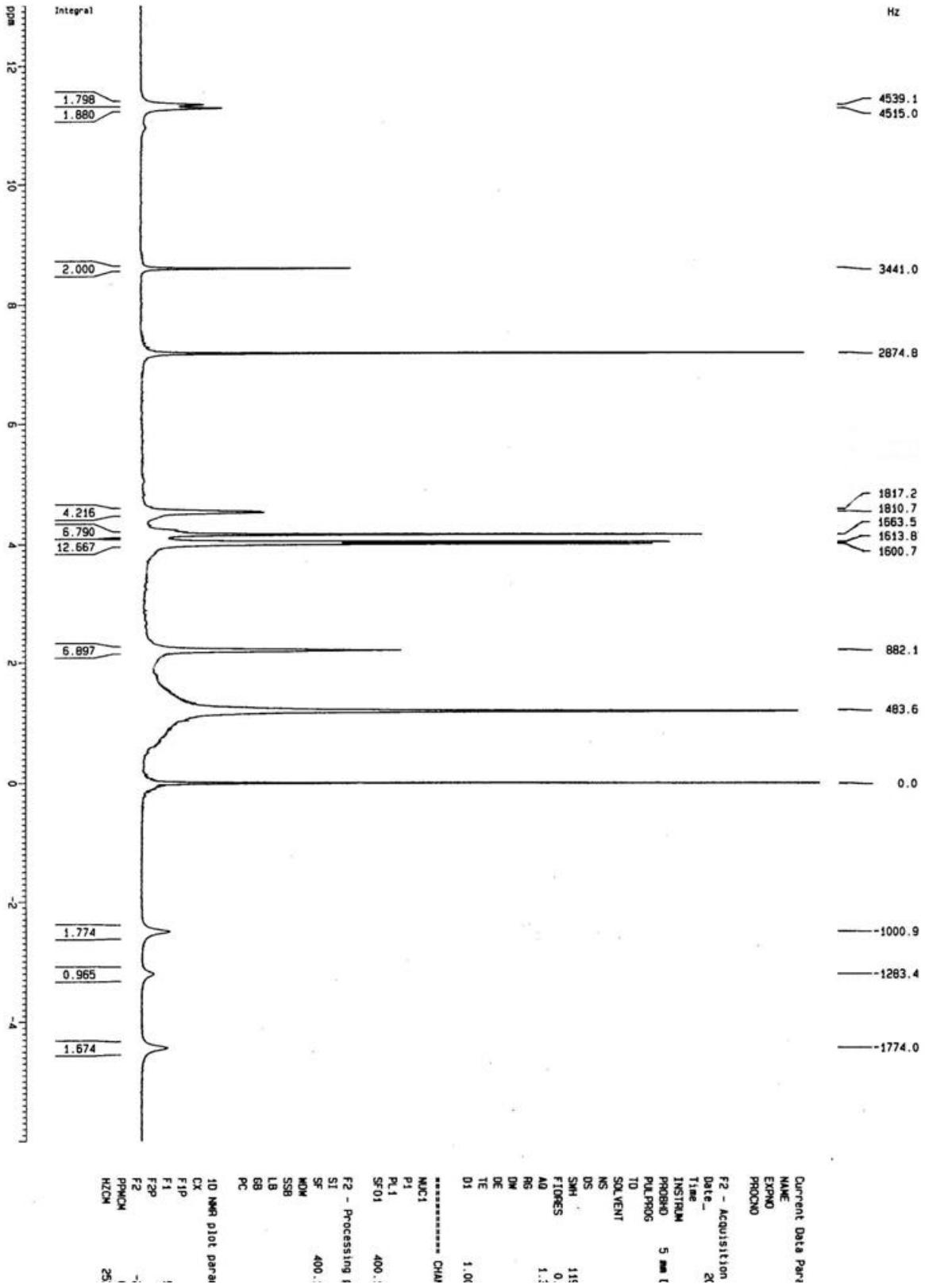
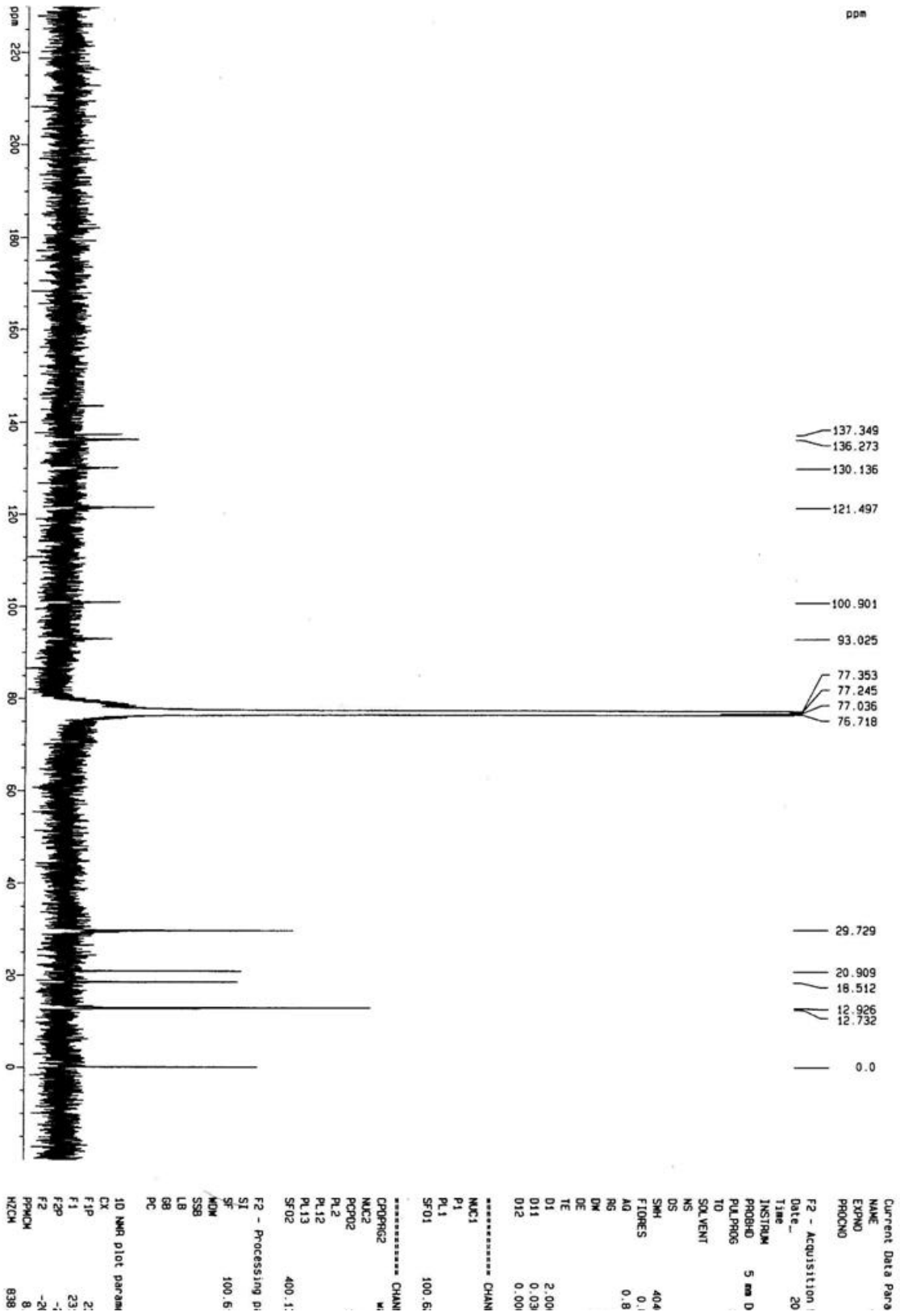
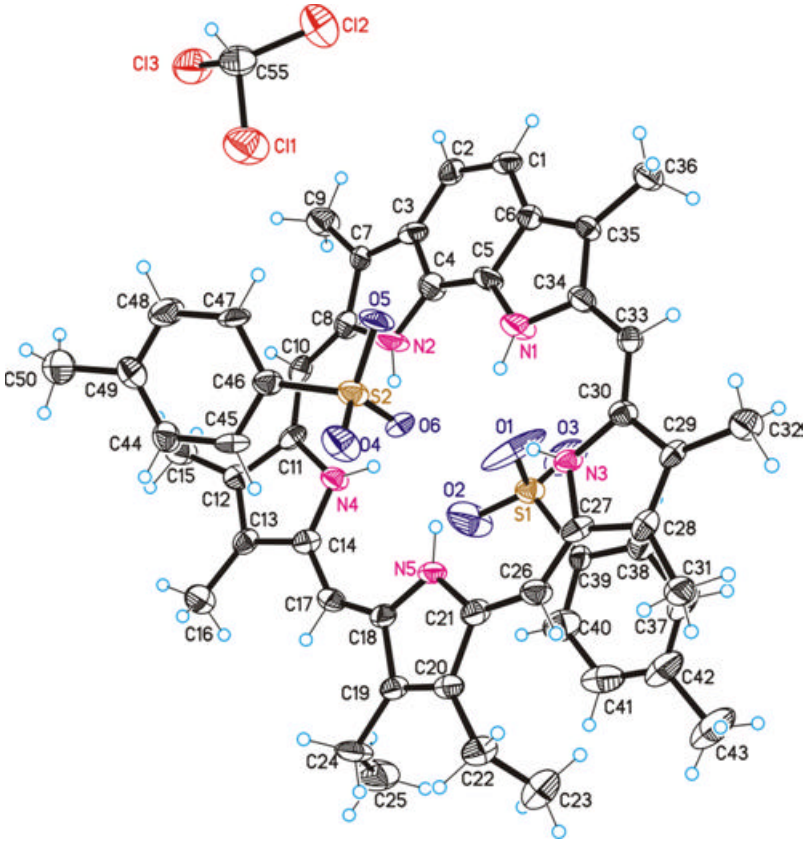


Figure 15. ^{13}C NMR spectrum of benzosapphyrin dichloride salt **1.Cl$_2$** in $CDCl_3$.




Cl2
Cl3
C55
Cl1
C2
C1
C36
C9
C3
C6
C35
C7
C4
C5
C34
C48
C47
O5
C8
N2
N1
C33
C10
C50
C49
C46
S2
C30
O6
O1
O3
C29
C32
C45
C44
O4
C11
N3
C15
N4
O2
S1
C27
C12
C13
C14
C28
N5
C26
C39
C38
C31
C17
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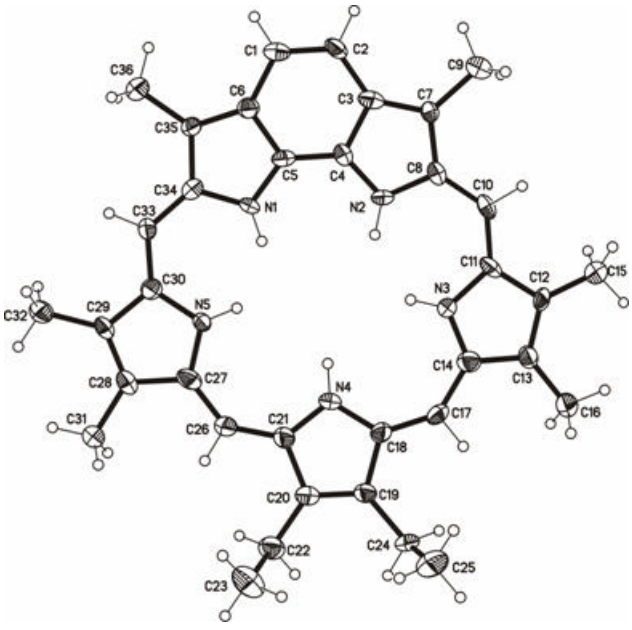
C19
C41
C24
C43
C22
C25
C23


C1
C2
C9
C36
C6
C3
C7
C35
C5
C4
C8
C10
C34
N1
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C33
C11
C12
C15
C30
N3
C32
C29
N5
C14
C13
C28
C27
N4
C16
C31
C26
C21
C17
C18
C20
C19
C22
C24
C25
C23

Table 1. Crystal data and structure refinement for **1**·(***p*-TSA**)$_2$.

Empirical formula	$C_{51}\ H_{54}\ Cl_3\ N_5\ O_6\ S_2$	
Formula weight	1003.46	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.2266(8) Å	α= 108.042(2)°.
	b = 12.7492(10) Å	β= 95.074(2)°.
	c = 19.9972(16) Å	γ = 102.586(2)°.
Volume	2385.1(3) Å^3	
Z	2	
Density (calculated)	1.397 Mg/m^3	
Absorption coefficient	0.336 mm^{-1}	
F(000)	1052	
Crystal size	0.20 x 0.12 x 0.05 mm^3	
Theta range for data collection	1.09 to 26.02°.	
Index ranges	-12<=h<=12, -15<=k<=15, -19<=l<=24	
Reflections collected	13749	
Independent reflections	9229 [R(int) = 0.0927]	
Completeness to theta = 26.02°	98.2 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9229 / 2 / 605	

Goodness-of-fit on F^2	0.853
Final R indices [I>2sigma(I)]	R1 = 0.0646, wR2 = 0.1298
R indices (all data)	R1 = 0.2382, wR2 = 0.1925
Extinction coefficient	0.0013(3)
Largest diff. peak and hole	0.382 and -0.409 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1**·(***p*-TSA**)$_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	7067(2)	3633(2)	3170(1)	66(1)
Cl(2)	9629(2)	3389(2)	2736(1)	64(1)
Cl(3)	9234(2)	3590(2)	4178(1)	58(1)
S(1)	5858(2)	9883(2)	2414(1)	30(1)
S(2)	3083(2)	5290(2)	1999(1)	31(1)
O(1)	5499(6)	8678(4)	2070(3)	88(2)
O(2)	5490(6)	10131(6)	3112(3)	100(3)
O(3)	7220(5)	10423(5)	2434(3)	73(2)
O(4)	1649(4)	4987(4)	1738(2)	43(1)
O(5)	3829(4)	4558(4)	1584(2)	40(1)
O(6)	3732(4)	6507(4)	2122(2)	31(1)
N(1)	5912(6)	6554(5)	1268(3)	49(2)
N(2)	6393(6)	7097(5)	2906(3)	44(2)
N(3)	3688(5)	7318(4)	713(3)	26(1)
N(4)	4561(5)	8306(4)	3718(3)	29(1)
N(5)	2378(5)	8308(4)	2283(3)	26(1)
C(1)	9100(6)	5915(5)	1632(4)	29(2)

C(2)	9293(6)	6138(6)	2350(3)	29(2)
C(3)	8332(6)	6535(6)	2772(4)	29(2)
C(4)	7149(7)	6679(6)	2424(4)	37(2)
C(5)	6937(7)	6434(6)	1691(4)	37(2)
C(6)	7914(6)	6084(5)	1274(3)	25(2)
C(7)	8242(6)	6880(6)	3487(3)	26(2)
C(8)	7026(7)	7236(6)	3572(3)	30(2)
C(9)	9233(6)	6860(6)	4084(3)	41(2)
C(10)	6489(6)	7660(6)	4180(3)	31(2)
C(11)	5339(6)	8085(6)	4239(3)	27(2)
C(12)	4692(7)	8322(5)	4859(3)	26(2)
C(13)	3558(7)	8682(5)	4700(3)	26(2)
C(14)	3492(7)	8655(6)	3984(4)	29(2)
C(15)	5135(7)	8114(6)	5518(3)	39(2)
C(16)	2573(6)	9003(6)	5177(3)	36(2)
C(17)	2407(6)	8886(5)	3607(3)	29(2)
C(18)	1930(6)	8778(6)	2917(3)	27(2)
C(19)	711(6)	9112(5)	2725(3)	26(2)
C(20)	479(6)	8837(6)	2008(4)	31(2)
C(21)	1565(7)	8357(6)	1720(3)	29(2)
C(22)	-700(6)	8970(6)	1559(4)	36(2)
C(23)	-430(7)	10087(6)	1421(4)	54(2)
C(24)	-93(7)	9686(7)	3249(4)	41(2)
C(25)	556(8)	10938(7)	3634(4)	61(2)

C(26)	1648(6)	8035(6)	998(3)	31(2)
C(27)	2507(7)	7590(6)	549(4)	29(2)
C(28)	2313(7)	7367(6)	-217(3)	29(2)
C(29)	3367(6)	6964(5)	-486(3)	23(2)
C(30)	4233(6)	6912(5)	97(3)	24(2)
C(31)	1144(6)	7549(6)	-640(3)	36(2)
C(32)	3582(6)	6653(6)	-1250(3)	33(2)
C(33)	5391(6)	6503(5)	45(3)	26(2)
C(34)	6208(6)	6355(6)	587(3)	30(2)
C(35)	7467(6)	6026(5)	586(3)	23(2)
C(36)	8153(6)	5687(6)	-50(3)	33(2)
C(37)	4036(8)	10583(7)	801(4)	53(2)
C(38)	4867(7)	10187(6)	1198(4)	37(2)
C(39)	4837(6)	10413(5)	1921(3)	24(2)
C(40)	3967(7)	11045(6)	2224(4)	46(2)
C(41)	3157(7)	11434(6)	1818(5)	51(2)
C(42)	3166(8)	11210(7)	1105(5)	50(2)
C(43)	2296(7)	11620(7)	642(5)	79(3)
C(44)	2611(6)	5560(6)	4024(4)	32(2)
C(45)	2606(6)	5739(6)	3380(3)	31(2)
C(46)	3233(6)	5122(6)	2849(3)	28(2)
C(47)	3846(7)	4348(6)	2991(4)	37(2)
C(48)	3822(8)	4144(7)	3633(4)	49(2)
C(49)	3190(7)	4748(6)	4156(4)	36(2)

C(50)	3090(7)	4473(7)	4828(4)	53(2)
C(55)	8453(7)	3048(6)	3275(4)	42(2)

Table 3. Bond lengths [Å] and angles [°] for **1**·(***p*-TSA**)$_2$.

Cl(1)-C(55)	1.765(7)
Cl(2)-C(55)	1.758(7)
Cl(3)-C(55)	1.763(7)
S(1)-O(3)	1.404(5)
S(1)-O(1)	1.421(5)
S(1)-O(2)	1.435(5)
S(1)-C(39)	1.749(6)
S(2)-O(4)	1.438(4)
S(2)-O(5)	1.444(4)
S(2)-O(6)	1.482(4)
S(2)-C(46)	1.774(6)
N(1)-C(5)	1.353(7)
N(1)-C(34)	1.379(8)
N(2)-C(4)	1.344(8)
N(2)-C(8)	1.369(7)
N(3)-C(27)	1.367(7)
N(3)-C(30)	1.396(7)
N(4)-C(14)	1.358(8)
N(4)-C(11)	1.390(7)
N(5)-C(21)	1.365(7)
N(5)-C(18)	1.388(8)
C(1)-C(2)	1.362(8)

C(1)-C(6)	1.444(8)
C(2)-C(3)	1.426(9)
C(3)-C(7)	1.377(8)
C(3)-C(4)	1.418(8)
C(4)-C(5)	1.386(8)
C(5)-C(6)	1.417(9)
C(6)-C(35)	1.386(8)
C(7)-C(8)	1.420(8)
C(7)-C(9)	1.506(8)
C(8)-C(10)	1.384(9)
C(10)-C(11)	1.398(8)
C(11)-C(12)	1.437(8)
C(12)-C(13)	1.383(8)
C(12)-C(15)	1.476(8)
C(13)-C(14)	1.417(8)
C(13)-C(16)	1.484(8)
C(14)-C(17)	1.420(8)
C(17)-C(18)	1.377(8)
C(18)-C(19)	1.459(8)
C(19)-C(20)	1.352(8)
C(19)-C(24)	1.500(9)
C(20)-C(21)	1.460(9)
C(20)-C(22)	1.510(8)
C(21)-C(26)	1.388(8)

C(22)-C(23)	1.506(8)
C(24)-C(25)	1.506(9)
C(26)-C(27)	1.393(9)
C(27)-C(28)	1.456(8)
C(28)-C(29)	1.373(8)
C(28)-C(31)	1.504(8)
C(29)-C(30)	1.427(8)
C(29)-C(32)	1.505(8)
C(30)-C(33)	1.394(8)
C(33)-C(34)	1.394(8)
C(34)-C(35)	1.439(8)
C(35)-C(36)	1.498(8)
C(37)-C(42)	1.380(11)
C(37)-C(38)	1.388(9)
C(38)-C(39)	1.388(8)
C(39)-C(40)	1.384(9)
C(40)-C(41)	1.378(9)
C(41)-C(42)	1.366(10)
C(42)-C(43)	1.511(9)
C(44)-C(45)	1.375(8)
C(44)-C(49)	1.379(9)
C(45)-C(46)	1.407(9)
C(46)-C(47)	1.364(8)
C(47)-C(48)	1.389(8)

C(48)-C(49)	1.394(9)
C(49)-C(50)	1.496(9)

O(3)-S(1)-O(1)	114.4(4)
O(3)-S(1)-O(2)	112.2(4)
O(1)-S(1)-O(2)	108.7(4)
O(3)-S(1)-C(39)	107.7(3)
O(1)-S(1)-C(39)	106.1(3)
O(2)-S(1)-C(39)	107.2(3)
O(4)-S(2)-O(5)	115.1(3)
O(4)-S(2)-O(6)	112.2(3)
O(5)-S(2)-O(6)	111.0(3)
O(4)-S(2)-C(46)	105.7(3)
O(5)-S(2)-C(46)	105.8(3)
O(6)-S(2)-C(46)	106.3(3)
C(5)-N(1)-C(34)	109.5(6)
C(4)-N(2)-C(8)	108.9(6)
C(27)-N(3)-C(30)	110.3(5)
C(14)-N(4)-C(11)	109.1(5)
C(21)-N(5)-C(18)	110.5(5)
C(2)-C(1)-C(6)	120.7(6)
C(1)-C(2)-C(3)	121.5(6)
C(7)-C(3)-C(4)	105.5(6)
C(7)-C(3)-C(2)	136.2(6)

C(4)-C(3)-C(2)	118.2(6)
N(2)-C(4)-C(5)	129.5(6)
N(2)-C(4)-C(3)	109.9(6)
C(5)-C(4)-C(3)	120.6(7)
N(1)-C(5)-C(4)	129.5(6)
N(1)-C(5)-C(6)	109.0(6)
C(4)-C(5)-C(6)	121.3(6)
C(35)-C(6)-C(5)	107.0(5)
C(35)-C(6)-C(1)	135.4(6)
C(5)-C(6)-C(1)	117.6(6)
C(3)-C(7)-C(8)	108.5(5)
C(3)-C(7)-C(9)	126.5(6)
C(8)-C(7)-C(9)	125.0(6)
N(2)-C(8)-C(10)	122.3(6)
N(2)-C(8)-C(7)	107.2(6)
C(10)-C(8)-C(7)	130.6(6)
C(8)-C(10)-C(11)	128.1(6)
N(4)-C(11)-C(10)	128.0(6)
N(4)-C(11)-C(12)	106.6(6)
C(10)-C(11)-C(12)	125.3(6)
C(13)-C(12)-C(11)	108.1(5)
C(13)-C(12)-C(15)	127.6(6)
C(11)-C(12)-C(15)	124.2(6)
C(12)-C(13)-C(14)	106.8(6)

C(12)-C(13)-C(16)	126.9(6)
C(14)-C(13)-C(16)	126.3(6)
N(4)-C(14)-C(13)	109.3(6)
N(4)-C(14)-C(17)	126.8(6)
C(13)-C(14)-C(17)	123.8(6)
C(18)-C(17)-C(14)	138.5(6)
C(17)-C(18)-N(5)	130.8(6)
C(17)-C(18)-C(19)	122.6(6)
N(5)-C(18)-C(19)	106.5(5)
C(20)-C(19)-C(18)	107.8(6)
C(20)-C(19)-C(24)	127.4(6)
C(18)-C(19)-C(24)	124.7(6)
C(19)-C(20)-C(21)	108.5(6)
C(19)-C(20)-C(22)	127.3(6)
C(21)-C(20)-C(22)	124.2(6)
N(5)-C(21)-C(26)	130.9(6)
N(5)-C(21)-C(20)	106.7(5)
C(26)-C(21)-C(20)	122.4(6)
C(23)-C(22)-C(20)	114.0(6)
C(19)-C(24)-C(25)	113.8(6)
C(21)-C(26)-C(27)	138.3(6)
N(3)-C(27)-C(26)	129.4(6)
N(3)-C(27)-C(28)	106.0(6)
C(26)-C(27)-C(28)	124.5(6)

C(29)-C(28)-C(27)	108.9(6)
C(29)-C(28)-C(31)	126.0(6)
C(27)-C(28)-C(31)	125.1(6)
C(28)-C(29)-C(30)	107.3(6)
C(28)-C(29)-C(32)	126.4(5)
C(30)-C(29)-C(32)	126.3(6)
C(33)-C(30)-N(3)	127.1(6)
C(33)-C(30)-C(29)	125.4(6)
N(3)-C(30)-C(29)	107.5(5)
C(30)-C(33)-C(34)	127.5(6)
N(1)-C(34)-C(33)	122.7(6)
N(1)-C(34)-C(35)	106.9(5)
C(33)-C(34)-C(35)	130.4(6)
C(6)-C(35)-C(34)	107.4(6)
C(6)-C(35)-C(36)	127.0(6)
C(34)-C(35)-C(36)	125.5(6)
C(42)-C(37)-C(38)	121.7(8)
C(37)-C(38)-C(39)	120.2(7)
C(40)-C(39)-C(38)	117.8(6)
C(40)-C(39)-S(1)	122.2(5)
C(38)-C(39)-S(1)	120.0(5)
C(41)-C(40)-C(39)	120.8(7)
C(42)-C(41)-C(40)	122.0(8)
C(41)-C(42)-C(37)	117.4(7)

C(41)-C(42)-C(43)	123.7(9)
C(37)-C(42)-C(43)	118.9(8)
C(45)-C(44)-C(49)	121.0(6)
C(44)-C(45)-C(46)	120.7(6)
C(47)-C(46)-C(45)	118.2(6)
C(47)-C(46)-S(2)	122.3(5)
C(45)-C(46)-S(2)	119.3(5)
C(46)-C(47)-C(48)	121.2(6)
C(47)-C(48)-C(49)	120.4(7)
C(44)-C(49)-C(48)	118.4(7)
C(44)-C(49)-C(50)	121.4(6)
C(48)-C(49)-C(50)	120.2(7)
Cl(2)-C(55)-Cl(3)	110.2(4)
Cl(2)-C(55)-Cl(1)	109.8(4)
Cl(3)-C(55)-Cl(1)	109.6(4)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1**·(***p*-TSA**)$_2$. 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}
Cl(1)	55(1)	94(2)	54(1)	22(1)	1(1)	37(1)
Cl(2)	61(2)	76(2)	49(1)	16(1)	16(1)	13(1)
Cl(3)	71(2)	67(2)	40(1)	16(1)	3(1)	33(1)
S(1)	28(1)	34(1)	26(1)	7(1)	0(1)	12(1)
S(2)	28(1)	45(1)	23(1)	10(1)	4(1)	20(1)
O(1)	88(5)	22(4)	128(6)	13(4)	-64(4)	13(3)
O(2)	111(5)	202(8)	30(3)	43(4)	28(4)	114(5)
O(3)	23(3)	84(5)	137(6)	74(4)	6(3)	12(3)
O(4)	23(3)	71(4)	32(3)	13(3)	-1(2)	13(3)
O(5)	51(3)	57(4)	25(3)	10(3)	18(2)	41(3)
O(6)	35(3)	34(3)	36(3)	20(2)	7(2)	20(2)
N(1)	40(4)	100(6)	27(4)	26(4)	9(3)	51(4)
N(2)	40(4)	80(5)	31(4)	21(4)	13(3)	47(4)
N(3)	34(3)	31(4)	17(3)	6(3)	2(3)	20(3)
N(4)	28(3)	43(4)	20(3)	9(3)	6(3)	19(3)
N(5)	22(3)	34(4)	28(3)	12(3)	4(3)	16(3)
C(1)	22(4)	28(5)	39(5)	13(4)	5(3)	12(3)
C(2)	26(4)	39(5)	29(4)	19(4)	0(3)	13(4)

C(3)	23(4)	30(5)	38(5)	12(4)	2(4)	13(3)
C(4)	38(5)	61(6)	23(4)	20(4)	6(4)	27(4)
C(5)	28(4)	61(6)	36(5)	23(4)	14(4)	29(4)
C(6)	24(4)	27(4)	27(4)	11(3)	5(3)	8(3)
C(7)	30(4)	37(5)	19(4)	17(4)	7(3)	16(4)
C(8)	32(4)	40(5)	20(4)	13(4)	1(3)	13(4)
C(9)	32(4)	59(6)	37(5)	16(4)	2(4)	20(4)
C(10)	37(4)	41(5)	21(4)	18(4)	0(3)	14(4)
C(11)	26(4)	29(5)	27(4)	12(4)	-6(3)	10(3)
C(12)	36(4)	22(4)	15(4)	-3(3)	2(3)	11(3)
C(13)	34(4)	24(4)	21(4)	7(3)	0(3)	10(3)
C(14)	30(4)	27(5)	31(4)	10(4)	5(3)	12(4)
C(15)	41(5)	49(5)	30(4)	9(4)	6(4)	24(4)
C(16)	32(4)	48(5)	26(4)	10(4)	3(3)	13(4)
C(17)	34(4)	29(5)	26(4)	5(3)	12(3)	16(4)
C(18)	37(4)	27(5)	25(4)	11(3)	10(4)	18(4)
C(19)	29(4)	24(4)	28(4)	9(4)	4(3)	13(3)
C(20)	29(4)	34(5)	34(4)	13(4)	6(4)	16(4)
C(21)	35(4)	29(5)	24(4)	7(4)	2(3)	15(4)
C(22)	39(5)	32(5)	38(5)	9(4)	2(4)	15(4)
C(23)	59(6)	51(6)	58(6)	29(5)	-3(5)	15(5)
C(24)	38(5)	61(6)	32(4)	9(4)	8(4)	37(4)
C(25)	74(6)	59(7)	50(5)	2(5)	11(5)	43(5)
C(26)	27(4)	39(5)	28(4)	10(4)	2(3)	16(4)

C(27)	33(4)	23(5)	33(4)	10(4)	-2(4)	12(4)
C(28)	34(4)	27(5)	25(4)	12(3)	-2(3)	7(4)
C(29)	31(4)	18(4)	20(4)	7(3)	-3(3)	7(3)
C(30)	28(4)	20(4)	22(4)	2(3)	3(3)	8(3)
C(31)	39(4)	49(5)	29(4)	16(4)	7(4)	23(4)
C(32)	26(4)	43(5)	28(4)	9(4)	-2(3)	11(4)
C(33)	31(4)	31(5)	18(4)	8(3)	4(3)	13(3)
C(34)	30(4)	38(5)	25(4)	9(4)	10(3)	16(4)
C(35)	19(4)	28(4)	21(4)	6(3)	4(3)	7(3)
C(36)	33(4)	40(5)	29(4)	9(4)	9(4)	15(4)
C(37)	56(6)	62(7)	48(5)	36(5)	-8(5)	13(5)
C(38)	36(5)	37(5)	43(5)	20(4)	8(4)	10(4)
C(39)	24(4)	26(4)	27(4)	14(3)	6(3)	6(3)
C(40)	43(5)	45(6)	46(5)	11(4)	-5(4)	14(4)
C(41)	34(5)	40(6)	78(7)	18(5)	4(5)	15(4)
C(42)	33(5)	46(6)	78(7)	39(6)	-9(5)	3(4)
C(43)	42(5)	89(8)	138(9)	87(7)	-1(6)	13(5)
C(44)	35(4)	39(5)	24(4)	11(4)	7(3)	11(4)
C(45)	27(4)	29(5)	38(5)	6(4)	3(4)	18(3)
C(46)	26(4)	32(5)	26(4)	8(4)	2(3)	12(3)
C(47)	54(5)	38(5)	36(5)	16(4)	18(4)	37(4)
C(48)	71(6)	60(6)	35(5)	23(4)	15(4)	45(5)
C(49)	37(5)	41(5)	30(4)	10(4)	10(4)	11(4)
C(50)	64(6)	67(6)	47(5)	30(5)	22(4)	33(5)

C(55)	41(5)	36(5)	43(5)	5(4)	2(4)	13(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **1**·(***p*-TSA**)$_2$.

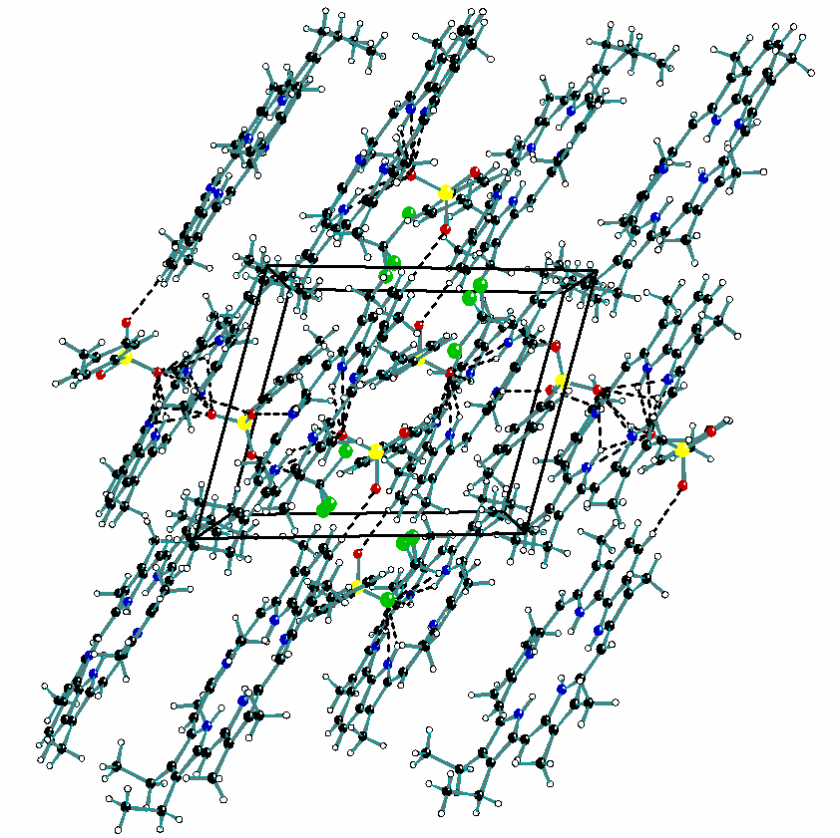
	x	y	z	U(eq)
H(1A)	5170	6731	1405	58
H(2A)	5617	7255	2809	53
H(3A)	4052	7389	1145	31
H(4A)	4734	8232	3284	35
H(5B)	3087	8020	2249	32
H(1B)	9754	5646	1363	34
H(2B)	10084	6025	2574	35
H(9A)	9984	6576	3889	62
H(9B)	8769	6356	4322	62
H(9C)	9589	7634	4429	62
H(10A)	6960	7662	4612	37
H(15A)	4545	8345	5867	58
H(15B)	6076	8559	5717	58
H(15C)	5078	7299	5409	58
H(16A)	2856	8944	5642	54
H(16B)	1668	8488	4965	54

H(16C)	2543	9791	5239	54
H(17A)	1848	9210	3923	35
H(22A)	-929	8337	1096	44
H(22B)	-1501	8902	1802	44
H(23A)	-1235	10114	1128	65
H(23B)	346	10155	1168	65
H(23C)	-225	10720	1875	65
H(24A)	-215	9296	3606	50
H(24B)	-1006	9597	2993	50
H(25A)	-19	11257	3968	73
H(25B)	655	11337	3287	73
H(25C)	1453	11035	3899	73
H(26A)	906	8152	735	37
H(31A)	1247	7339	-1143	43
H(31B)	1134	8354	-458	43
H(31C)	289	7072	-593	43
H(32A)	2838	6771	-1539	40
H(32B)	3599	5849	-1430	40
H(32C)	4448	7136	-1279	40
H(33A)	5653	6302	-412	31
H(36A)	8998	5509	91	40
H(36B)	8360	6317	-238	40
H(36C)	7550	5012	-419	40
H(37A)	4067	10419	306	63

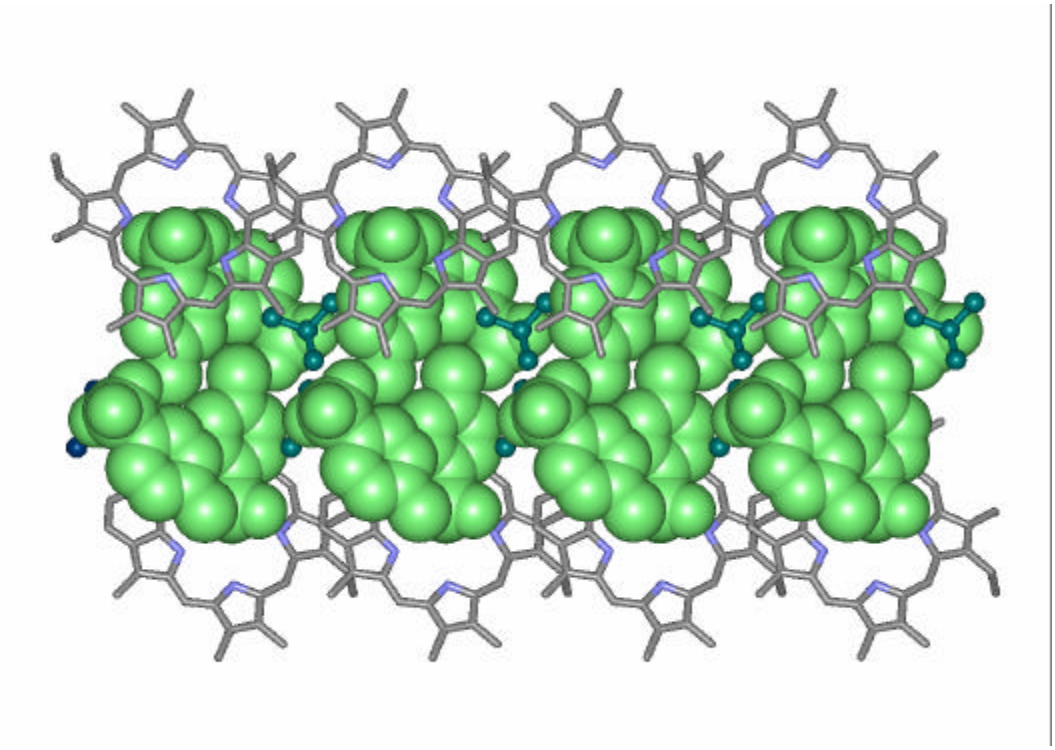
H(38A)	5459	9760	975	44
H(40A)	3927	11213	2718	55
H(41A)	2574	11871	2041	61
H(43A)	1737	12051	931	95
H(43B)	1704	10962	256	95
H(43C)	2881	12115	437	95
H(44A)	2211	6003	4382	38
H(45A)	2175	6284	3293	37
H(47A)	4296	3940	2644	45
H(48A)	4240	3589	3717	58
H(50A)	2621	4976	5135	64
H(50B)	4005	4588	5079	64
H(50C)	2579	3676	4710	64
H(55A)	8113	2199	3126	50

Hydrogen bonding of **1**·(***p*-TSA**)$_2$

D-H	d(H..A)	<DHA	d(D..A)
N1-H1A···O6	2.178	142.80	2.927(7)
N1-H1A···O1	2.358	113.93	2.831(8)
N2-H2A···O6	2.105	140.13	2.837(6)
N5-H5A··· O1	2.210	139.09	2.932(7)
N5-H5A···O6	2.549	142.09	3.288(6)
N3-H3A···O2	2.514	112.14	2.961(8)
N3-H3A···O6	2.592	127.96	3.209(6)
N4-H4A···O6	2.121	144.17	2.881(6)
N4-H4A···O1	2.522	135.48	3.209(7)



Unit cell packing diagram projected down the c axis.



Packing diagram viewing down b axis : The (***p*-TSA**) molecules are highlighted as space-filling models.