Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Synthesis, characterization of chiral aza-macrocycles and study of their enantiomer recognition ability of organo phosphoric acid and phosphonic acid derivatives by ^{31}P NMR and fluorescence spectroscopy

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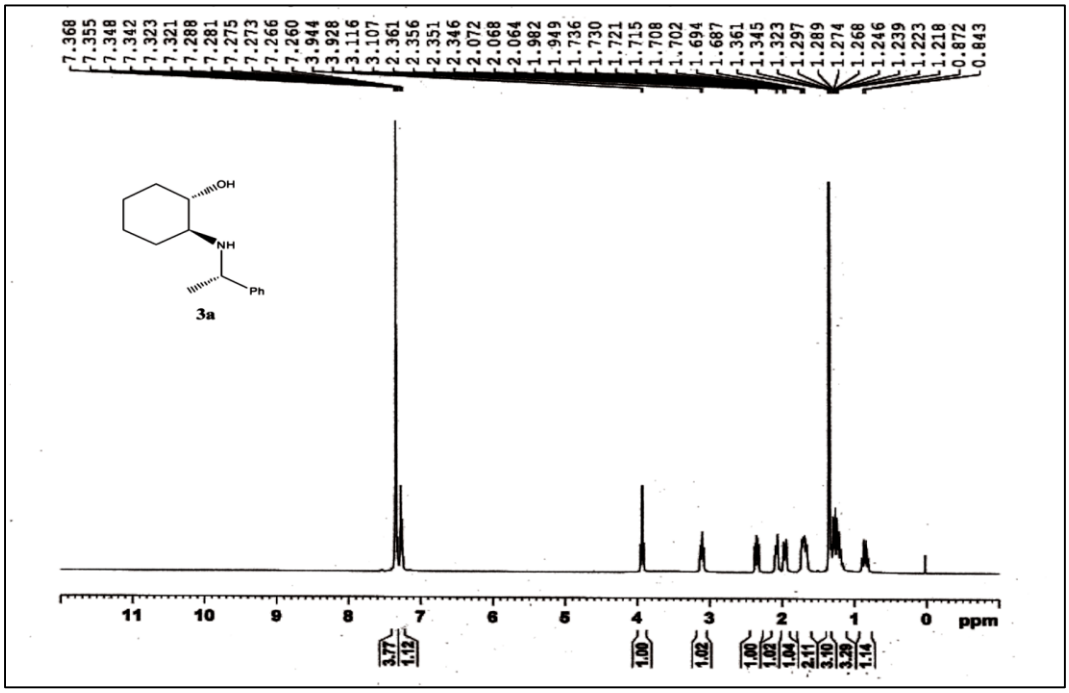
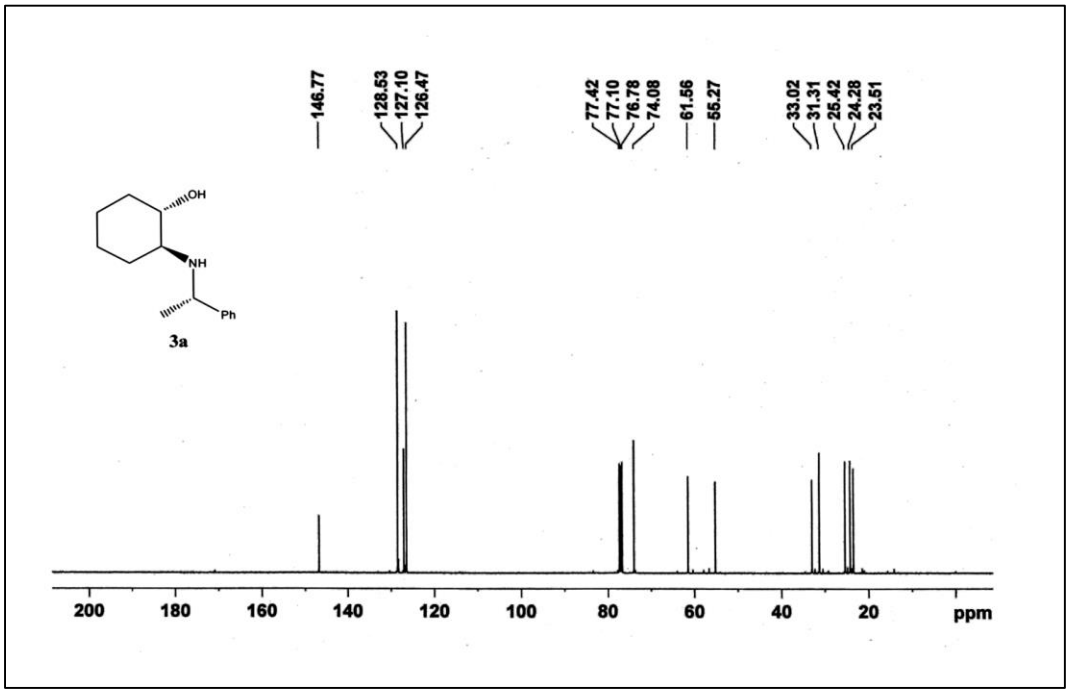


Figure 1: ^{1}H NMR Spectra of **3a**



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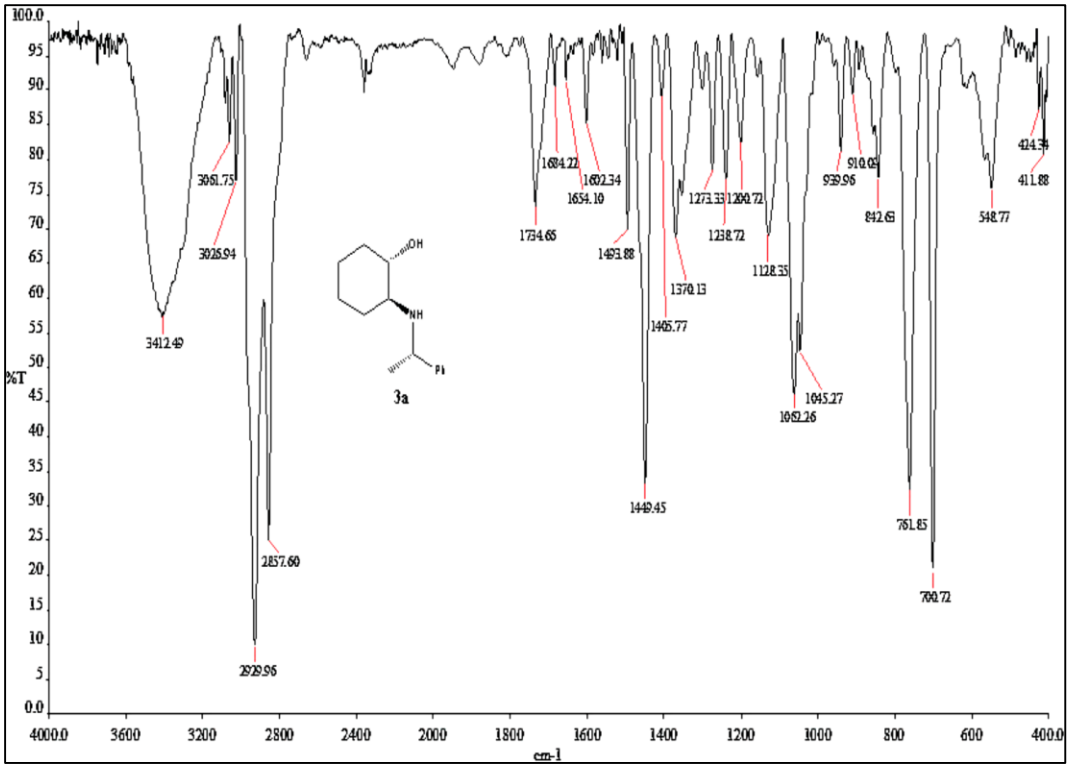

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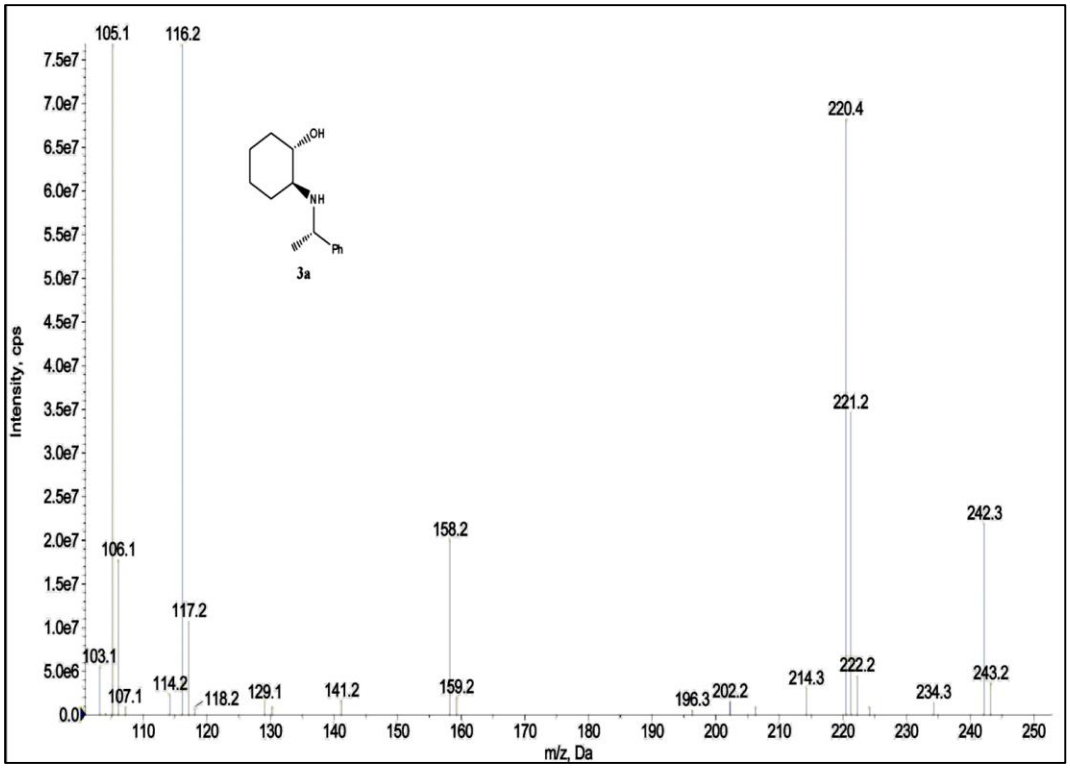

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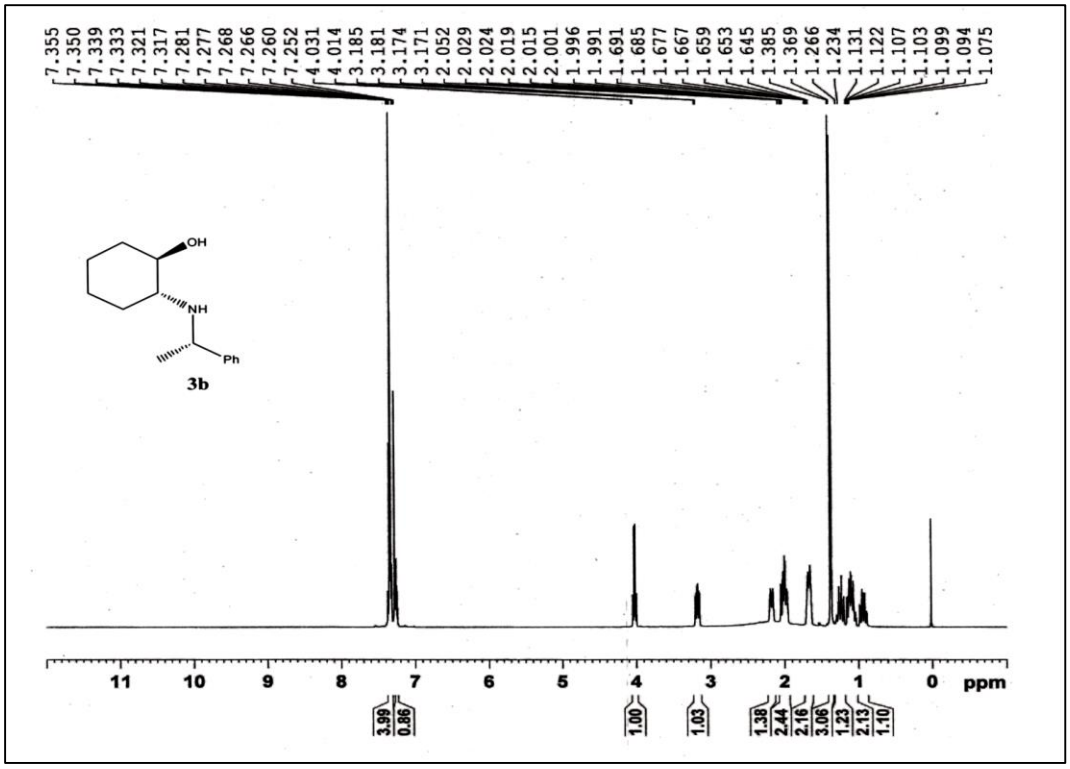

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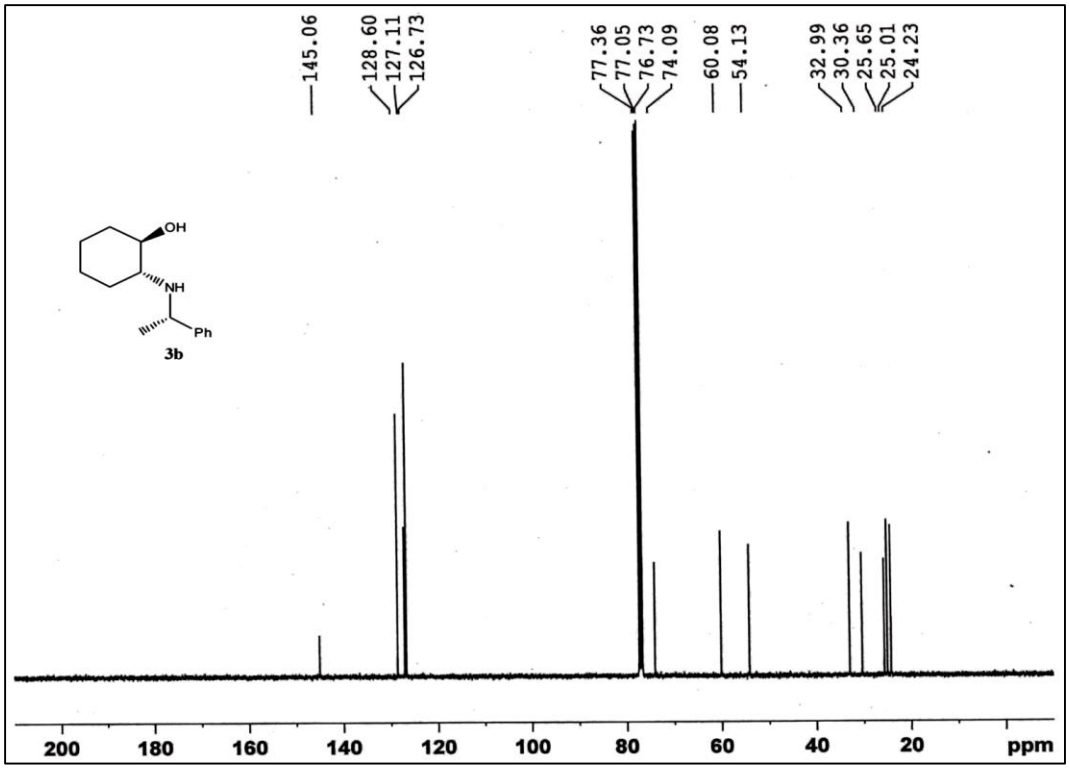

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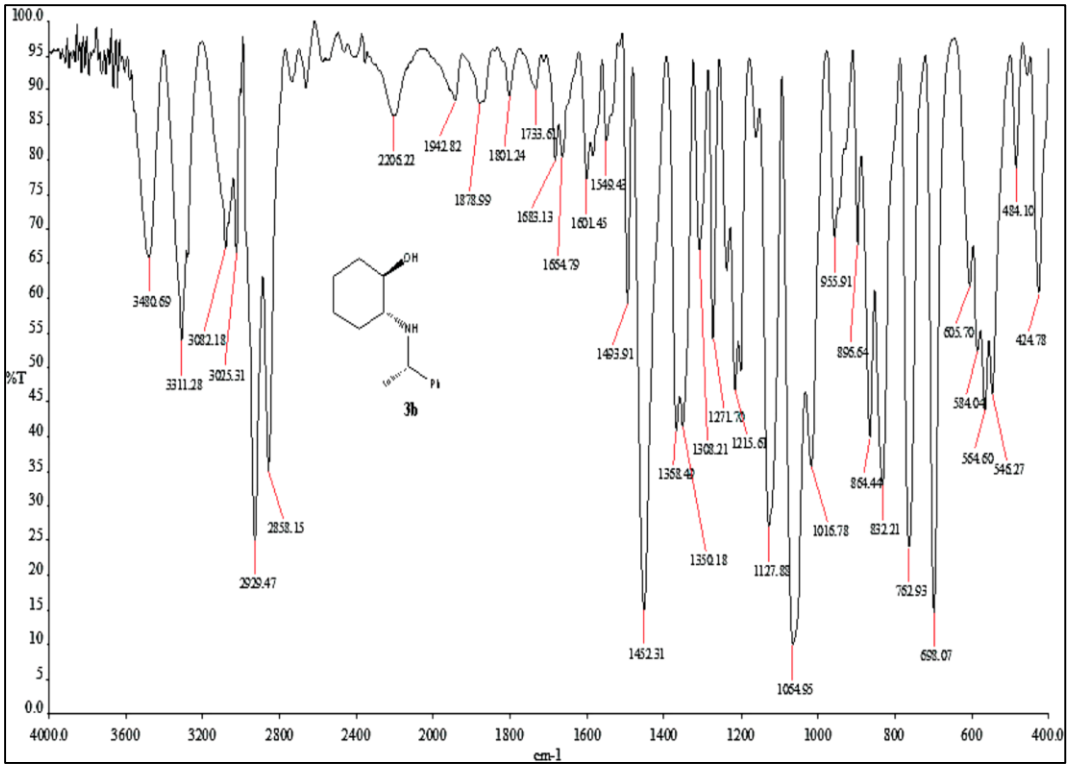

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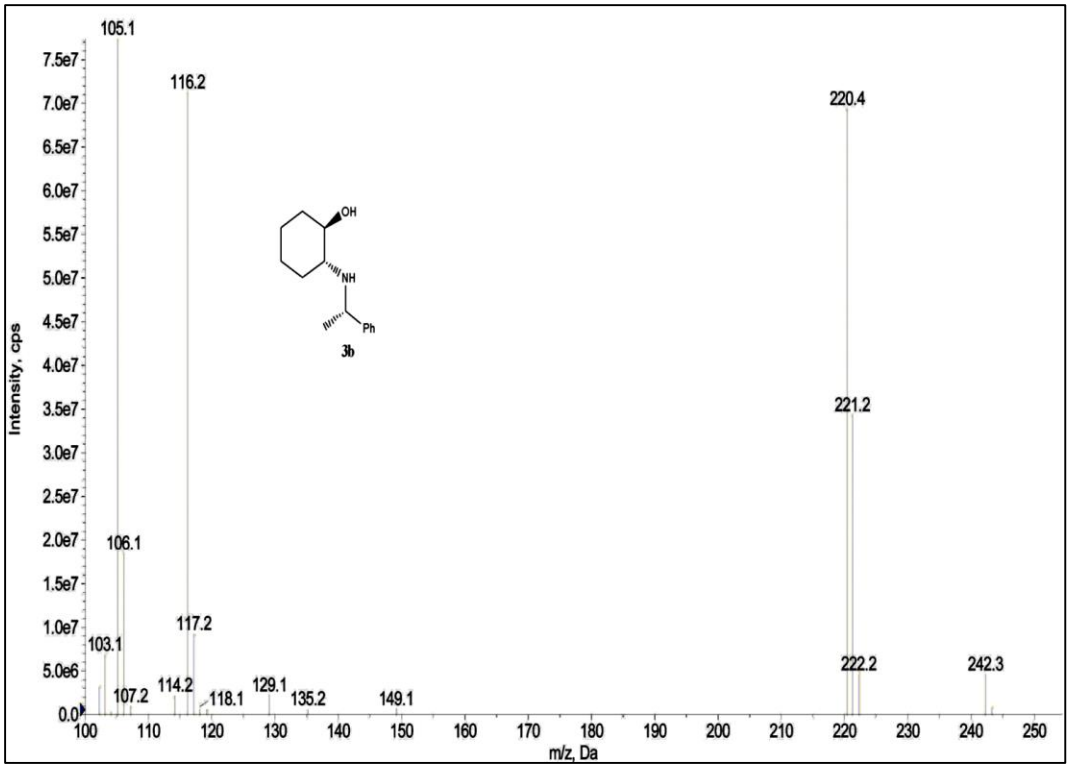

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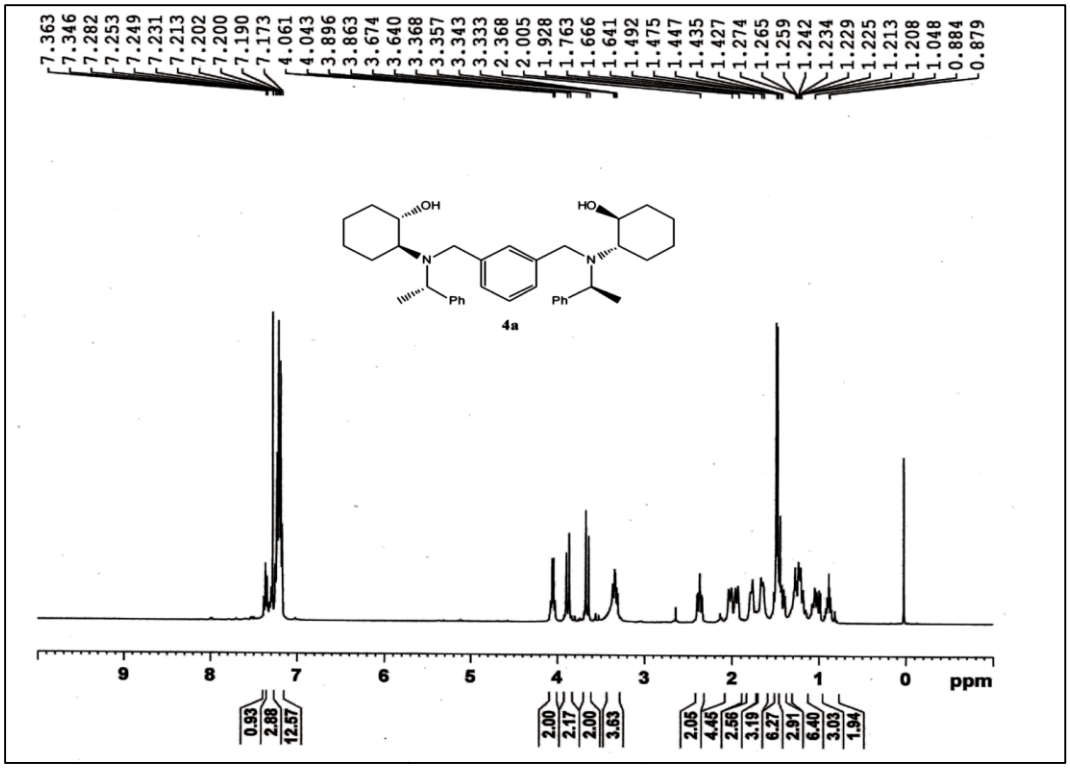

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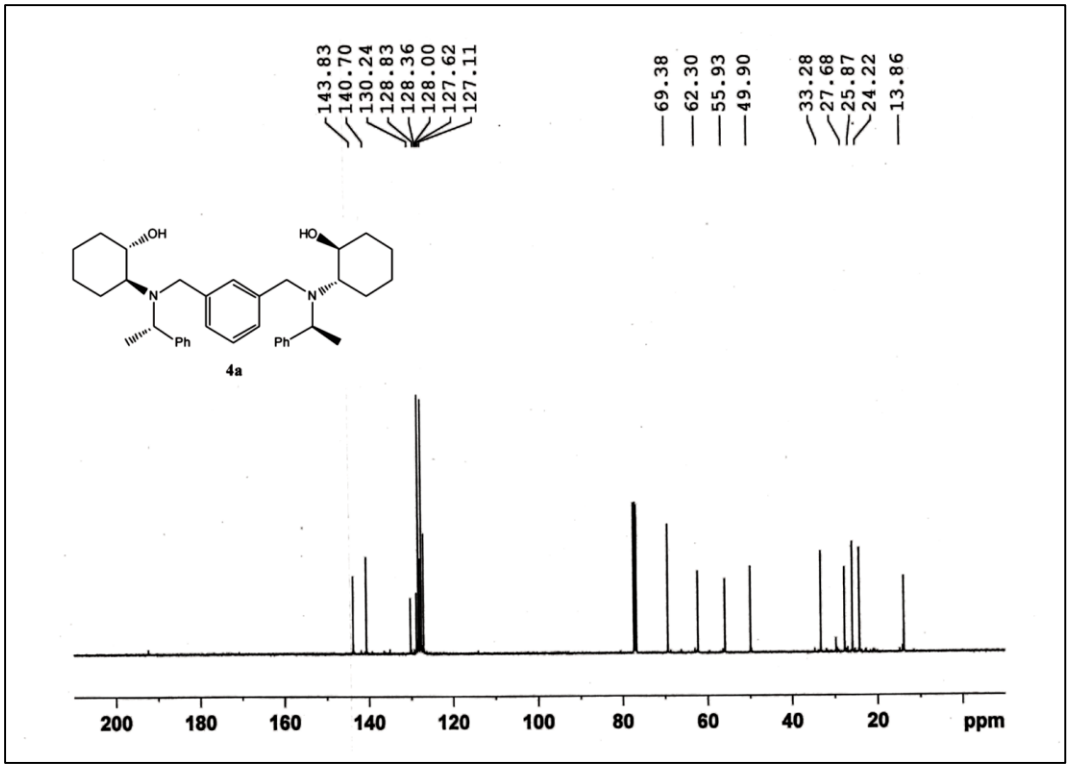

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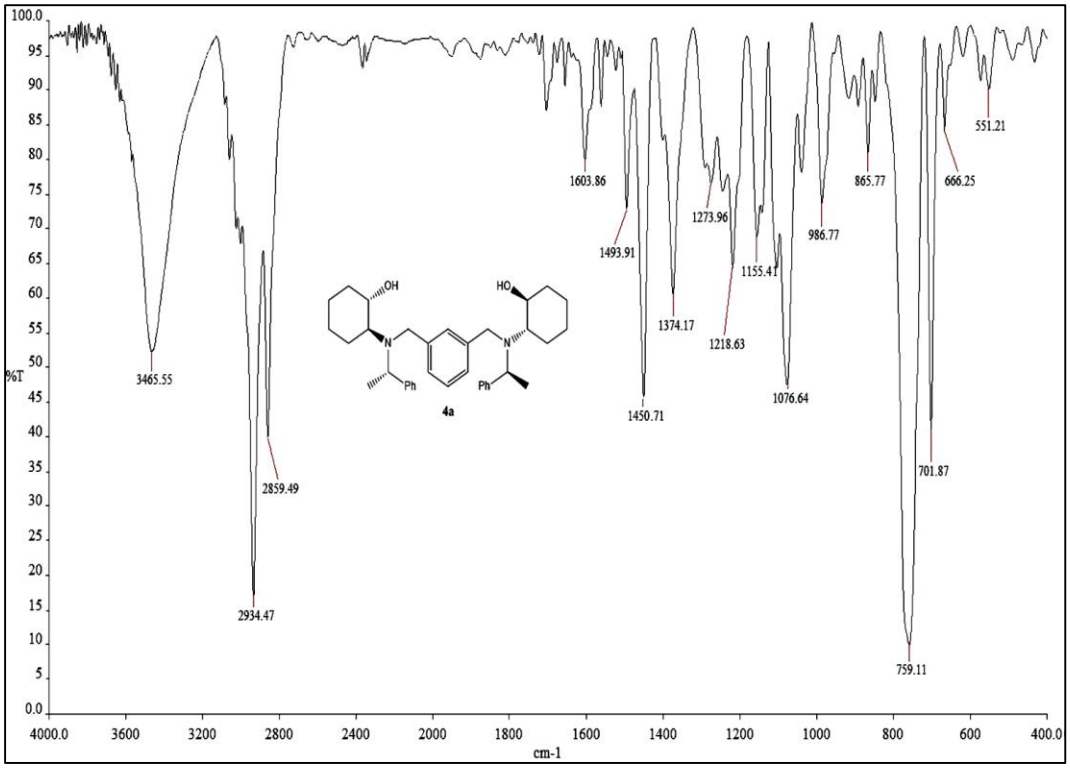

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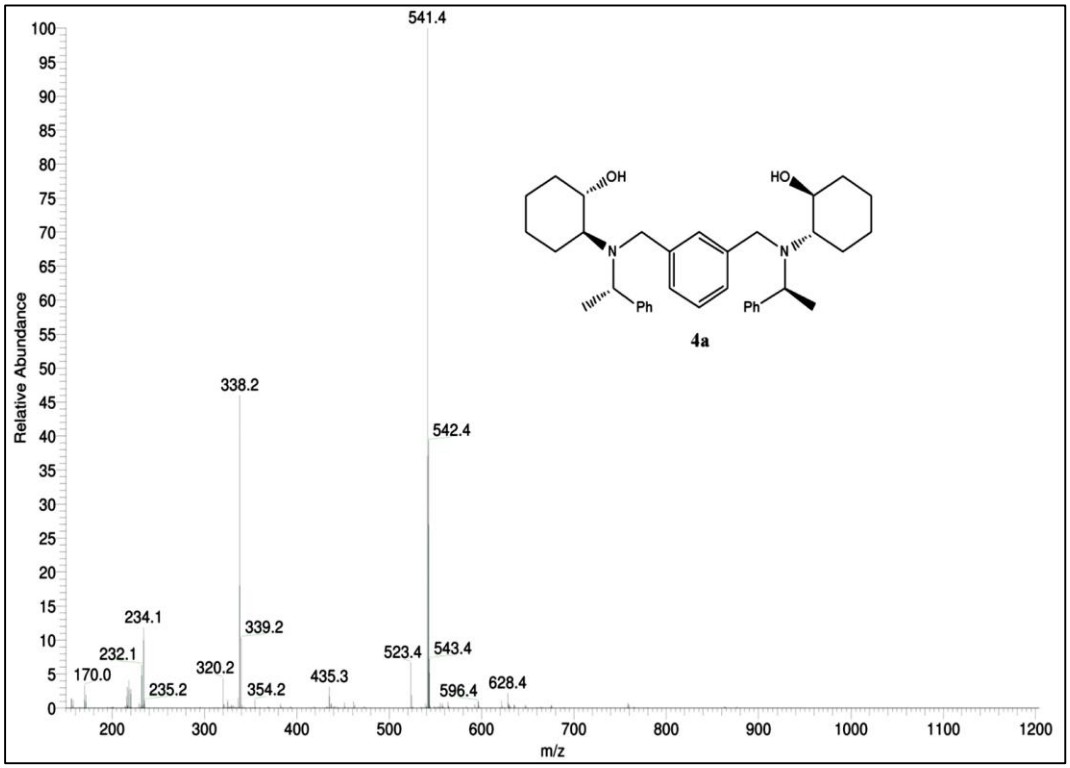

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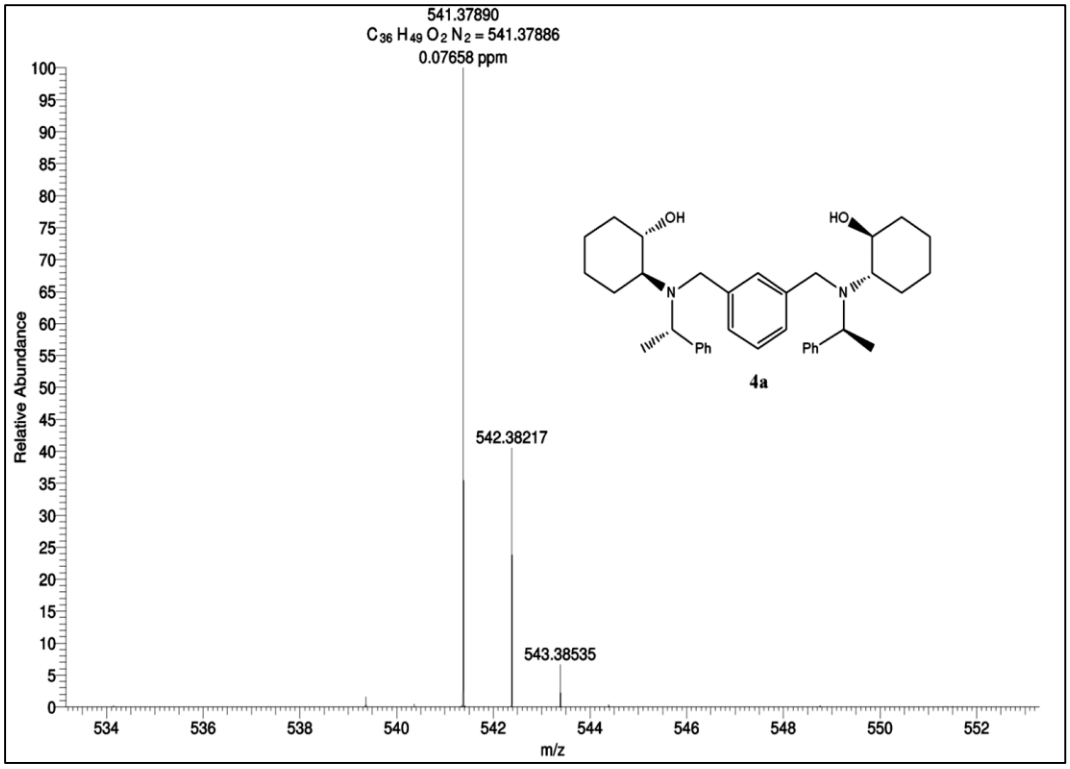

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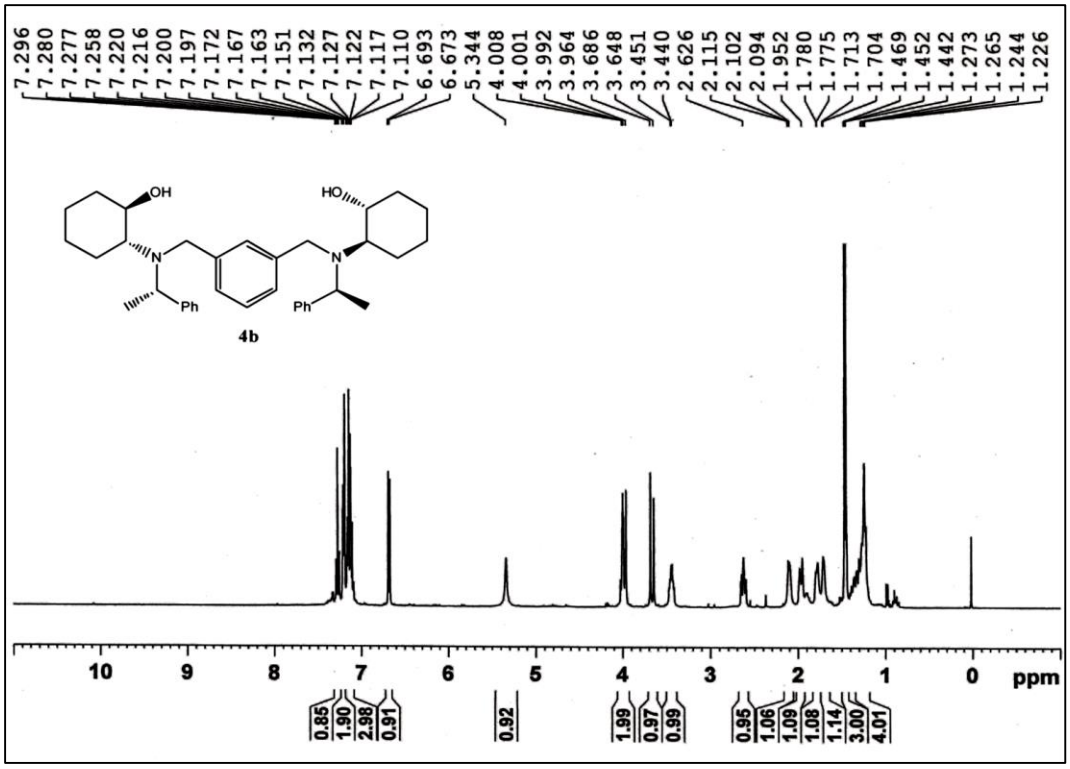

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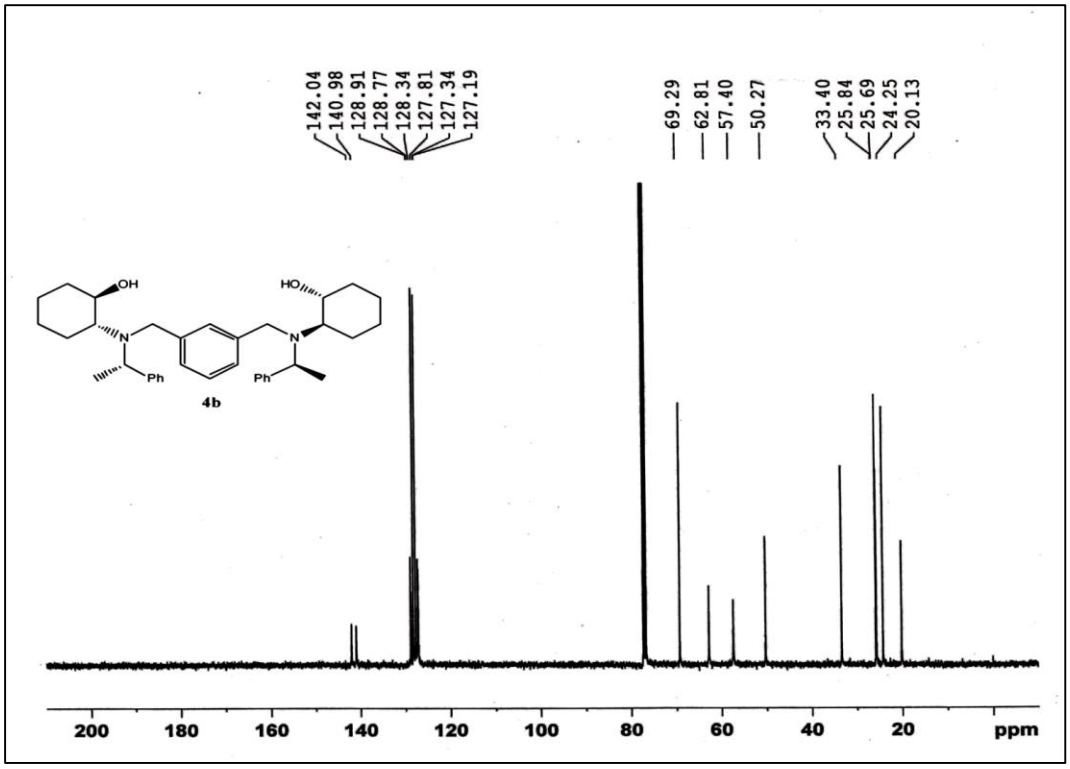

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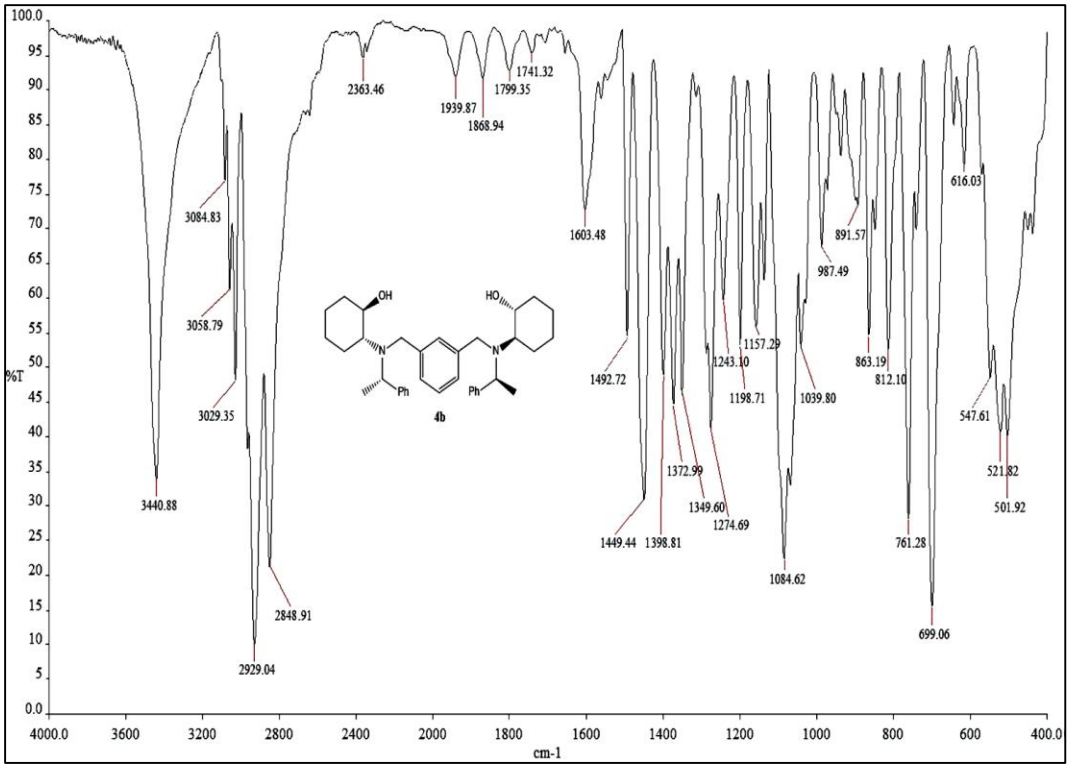

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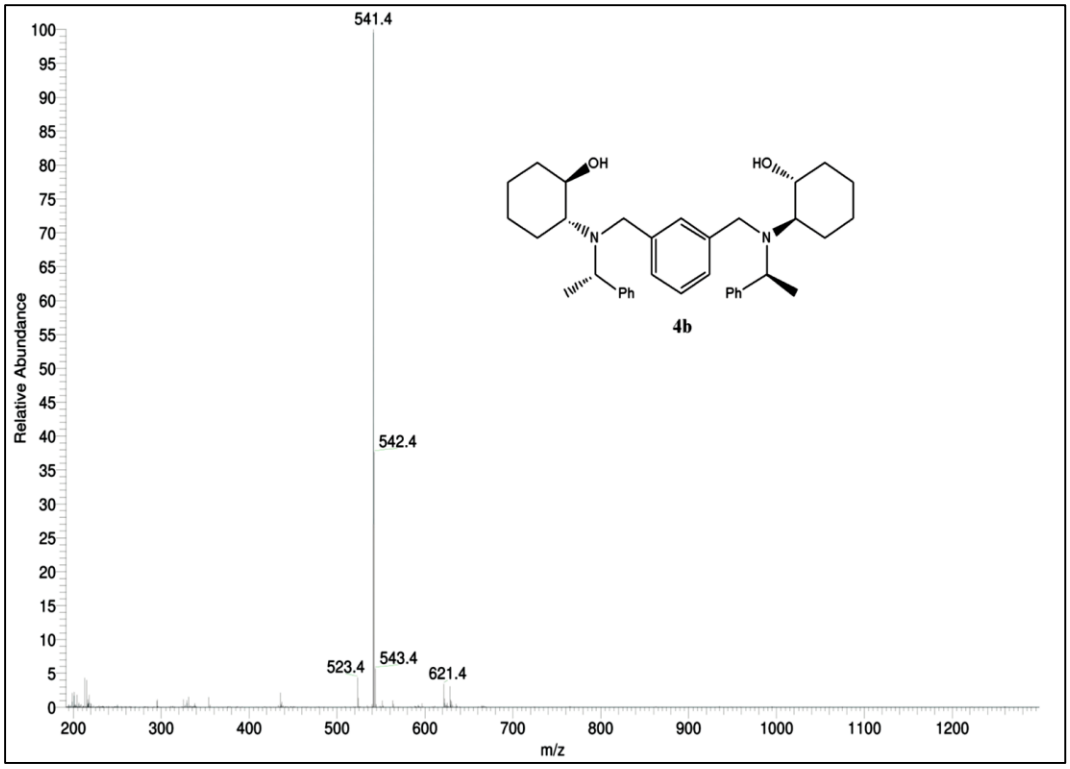

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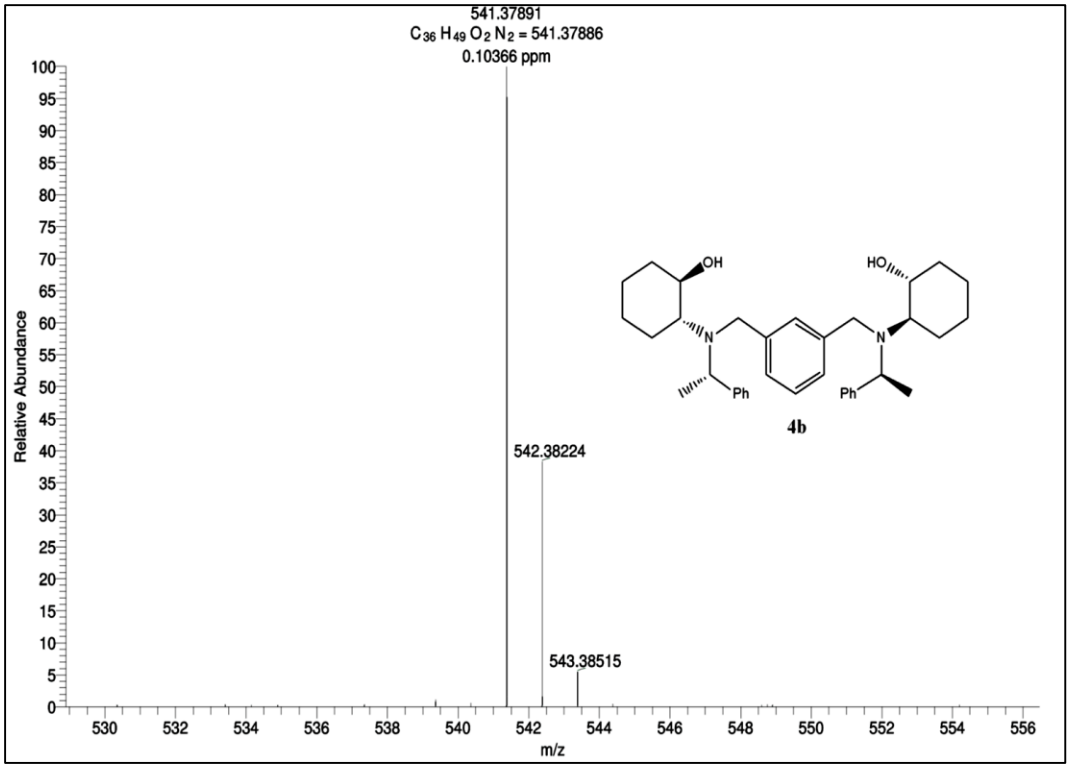

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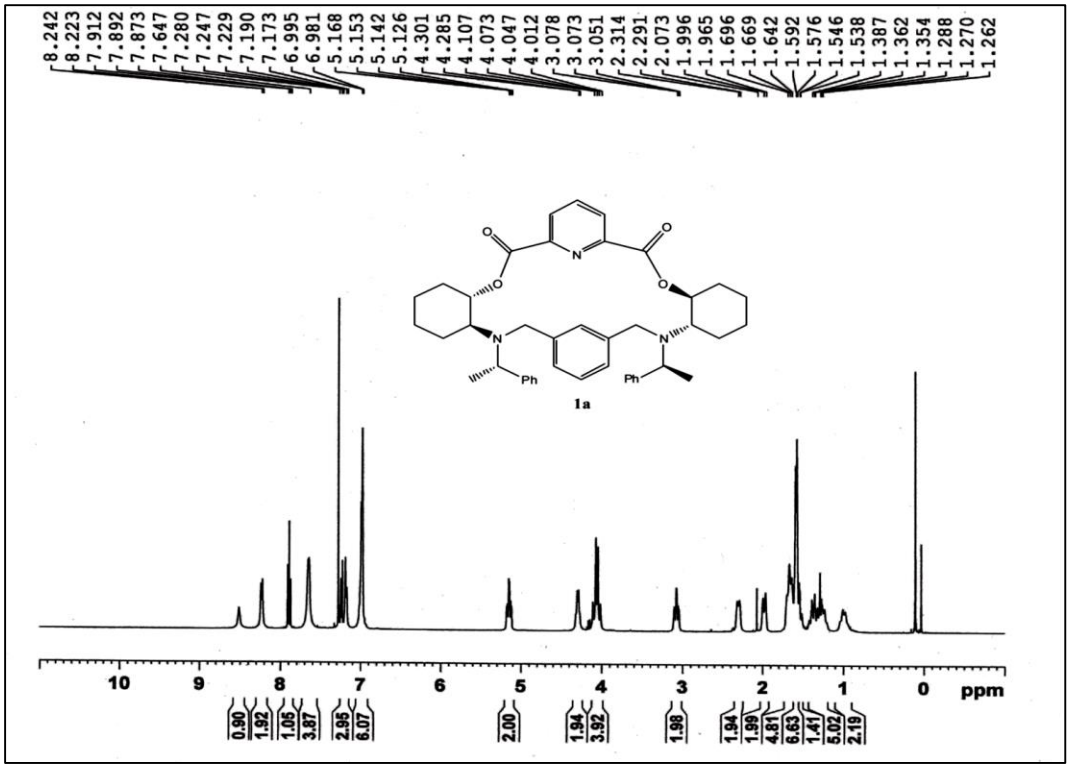

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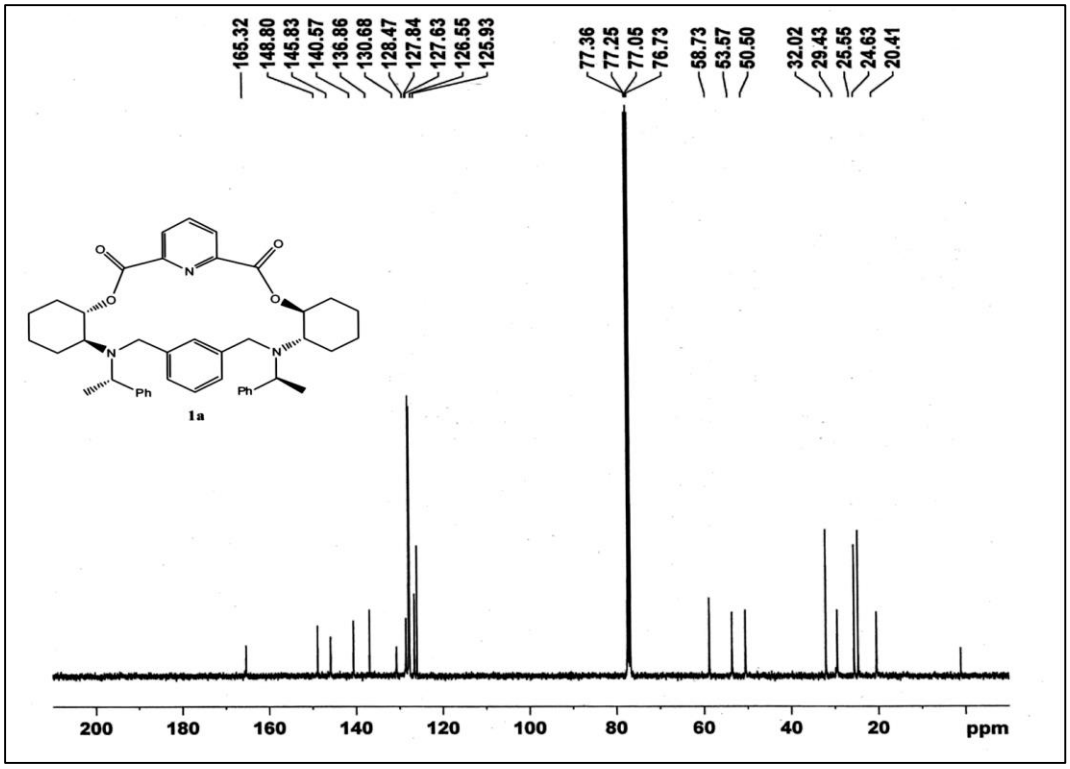

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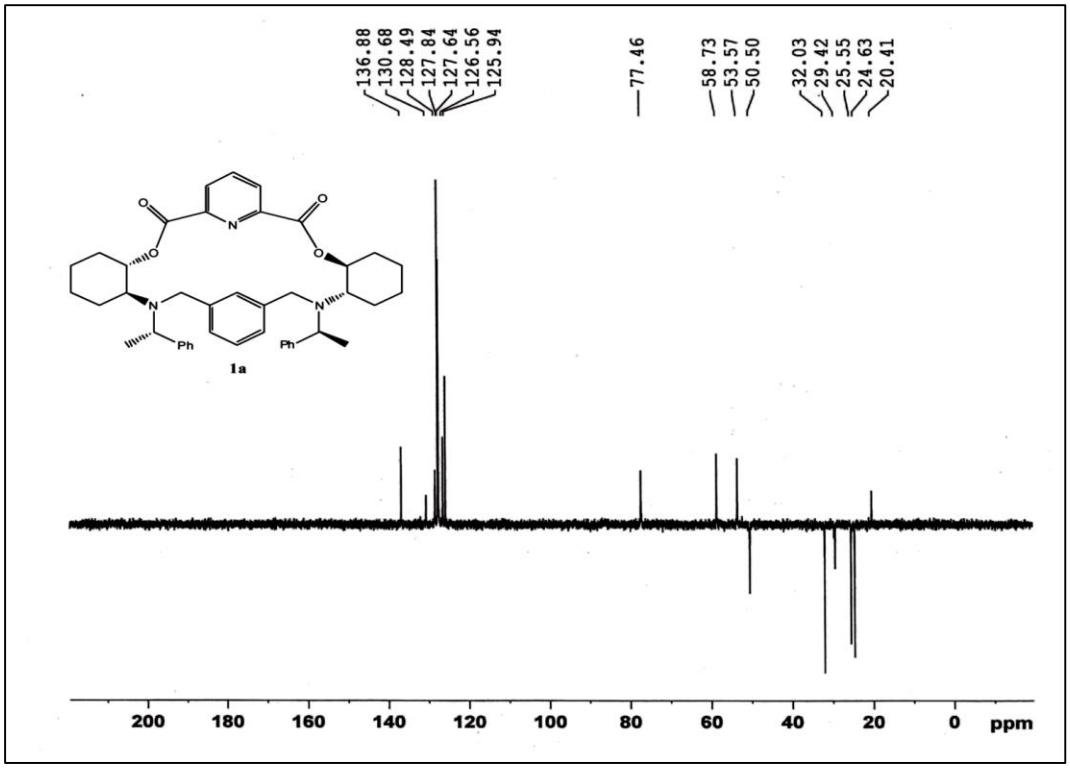

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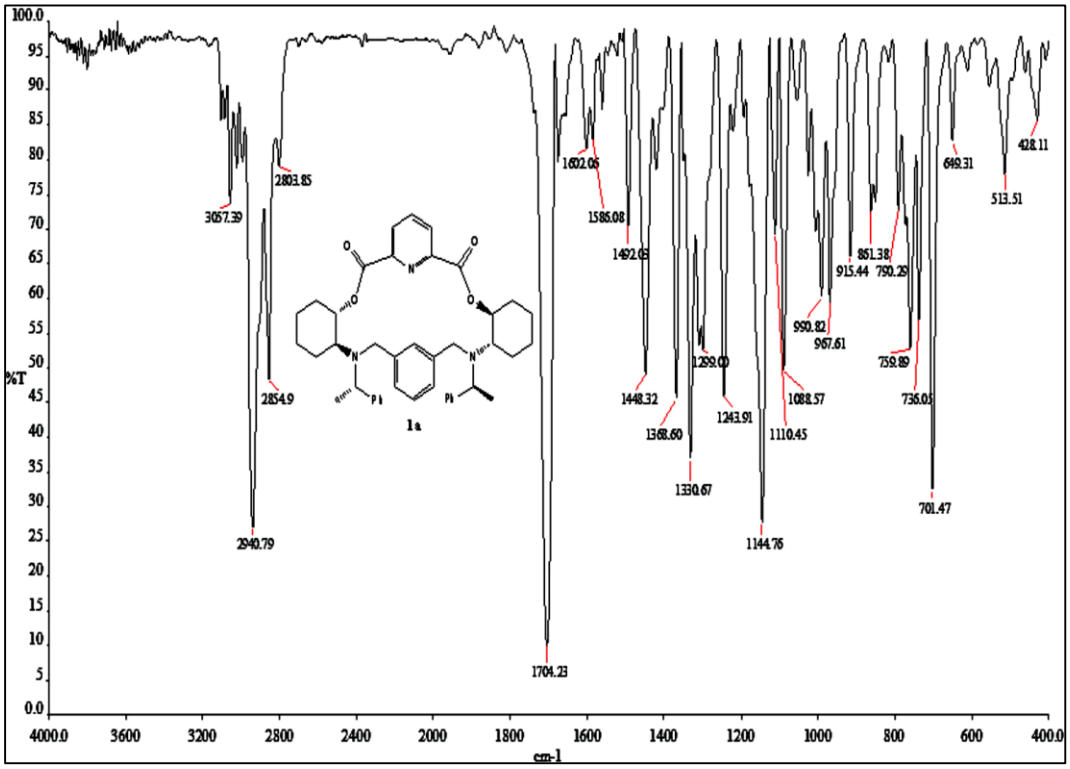

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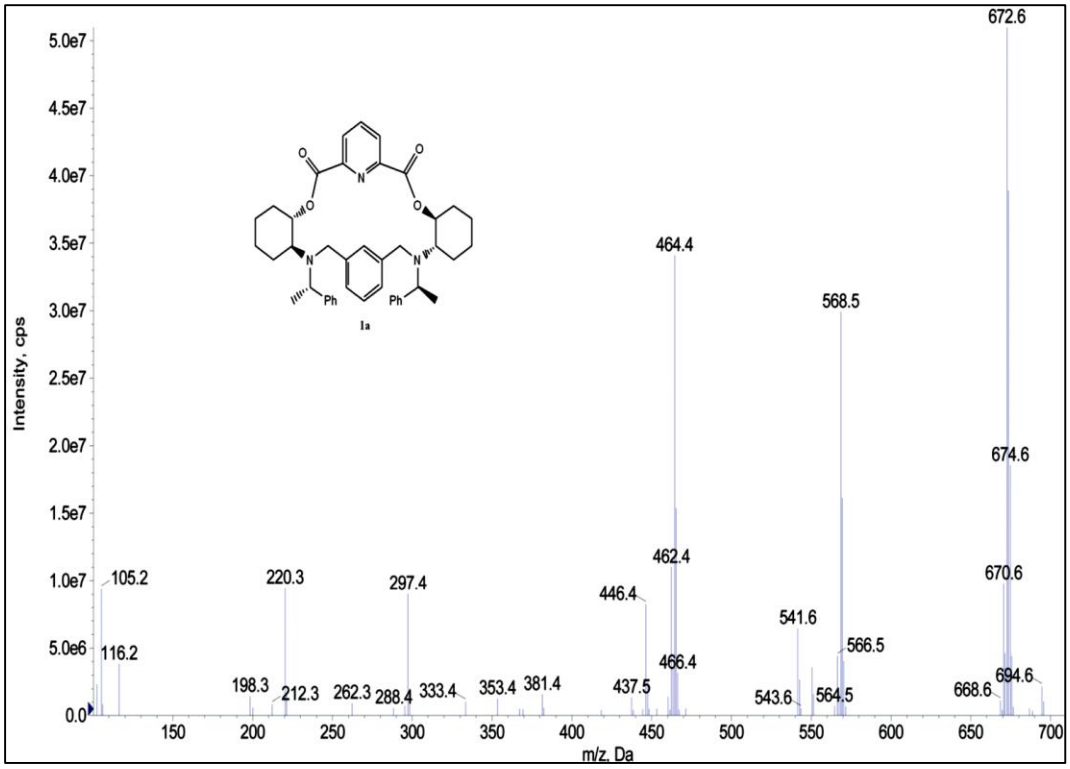

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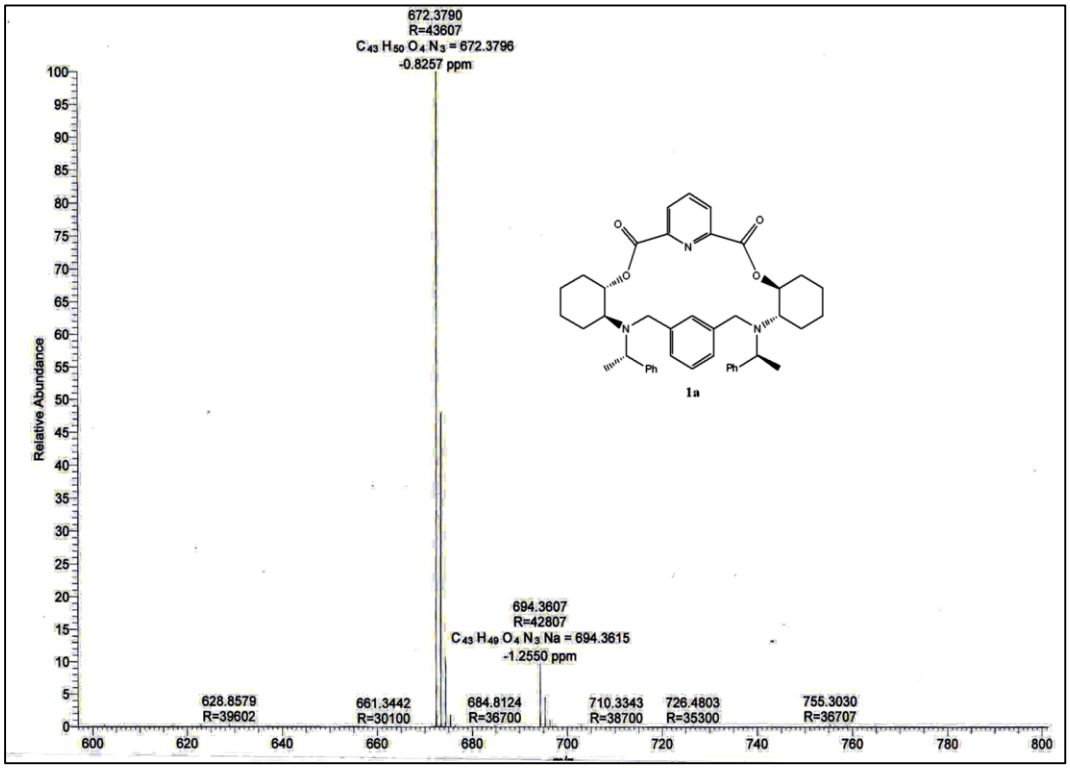

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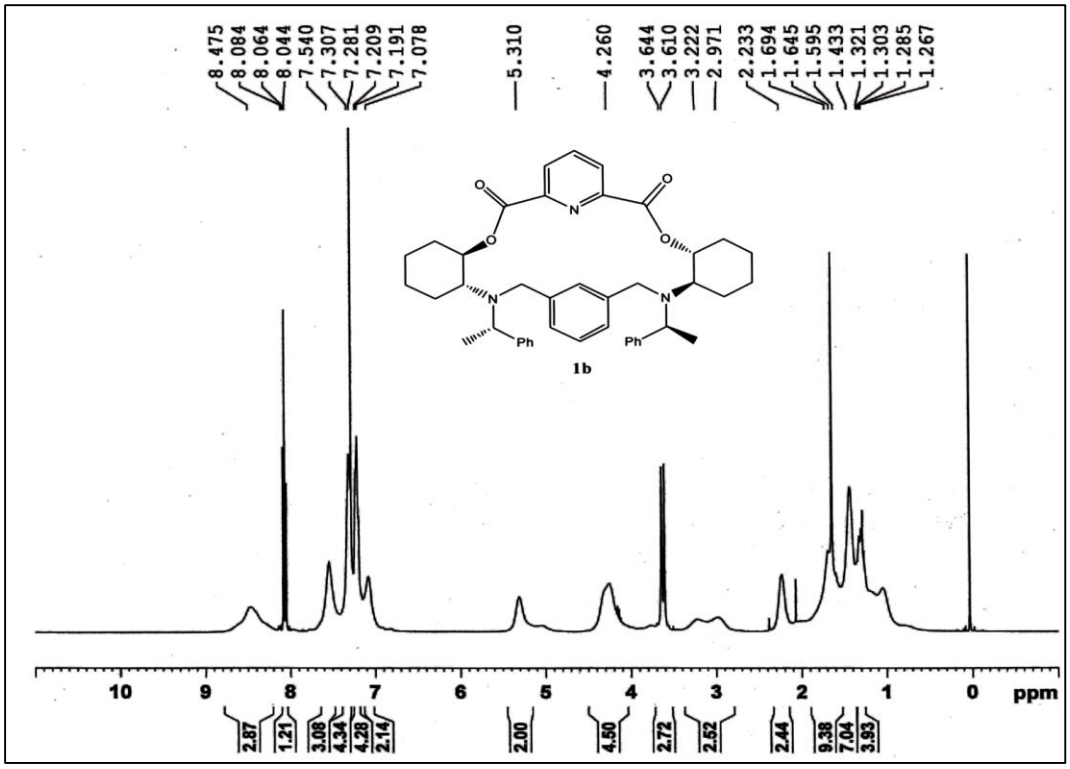

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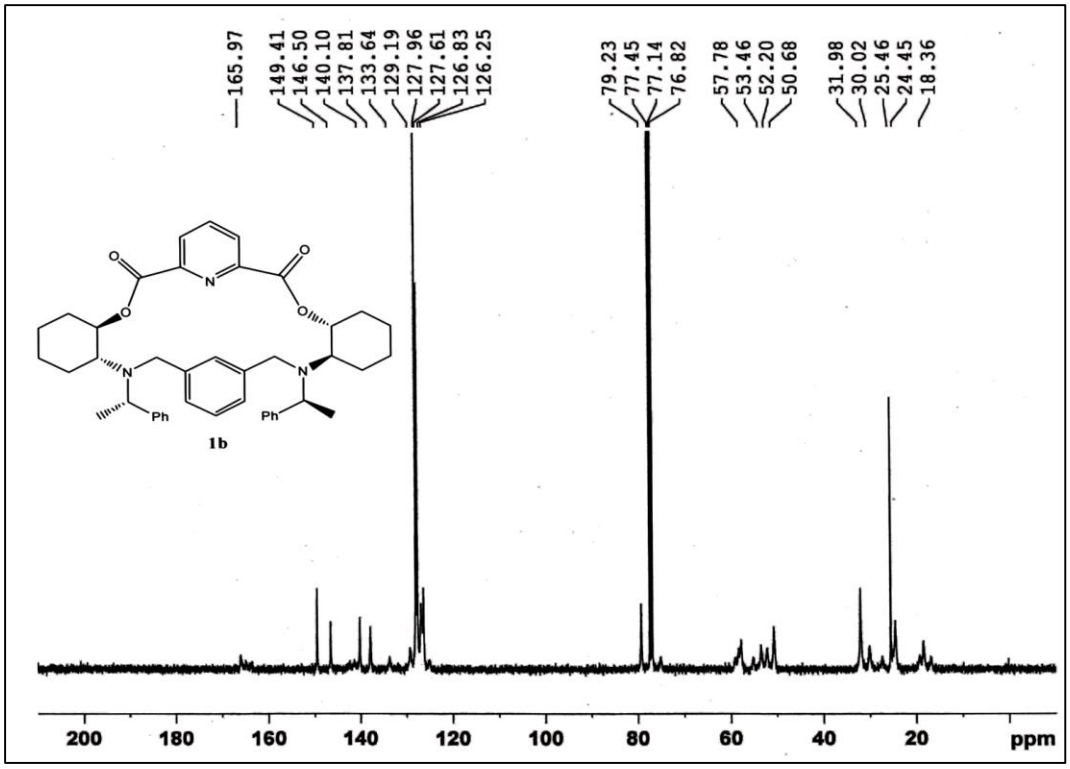

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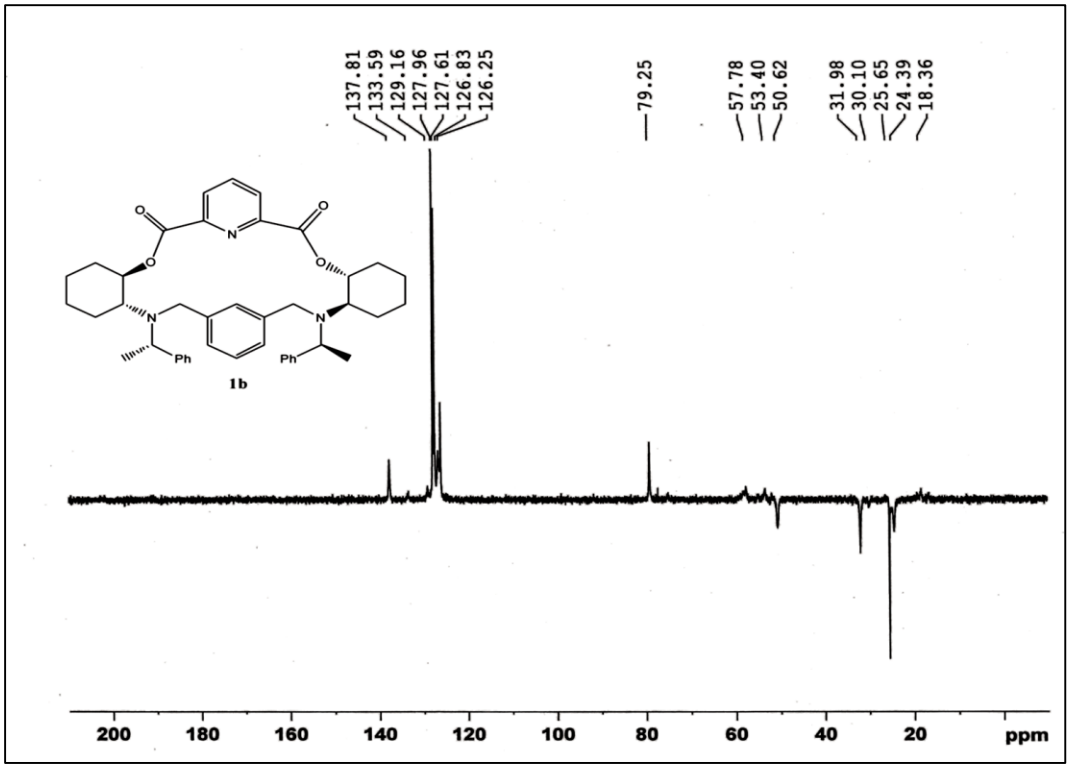

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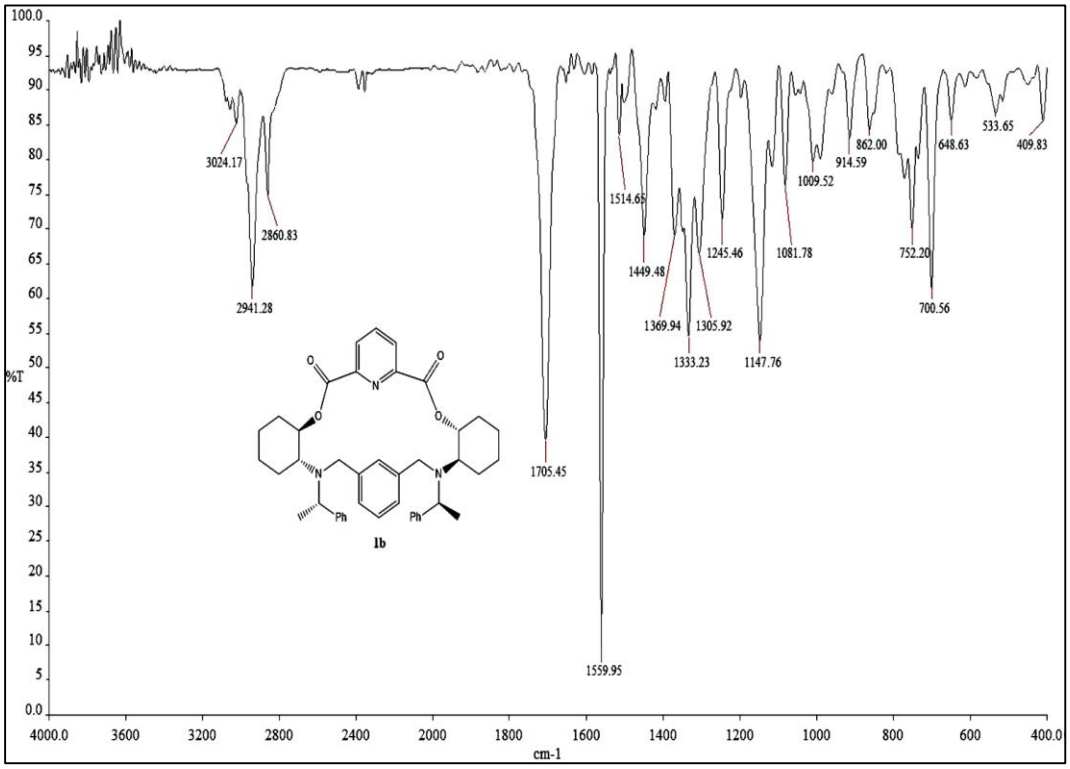

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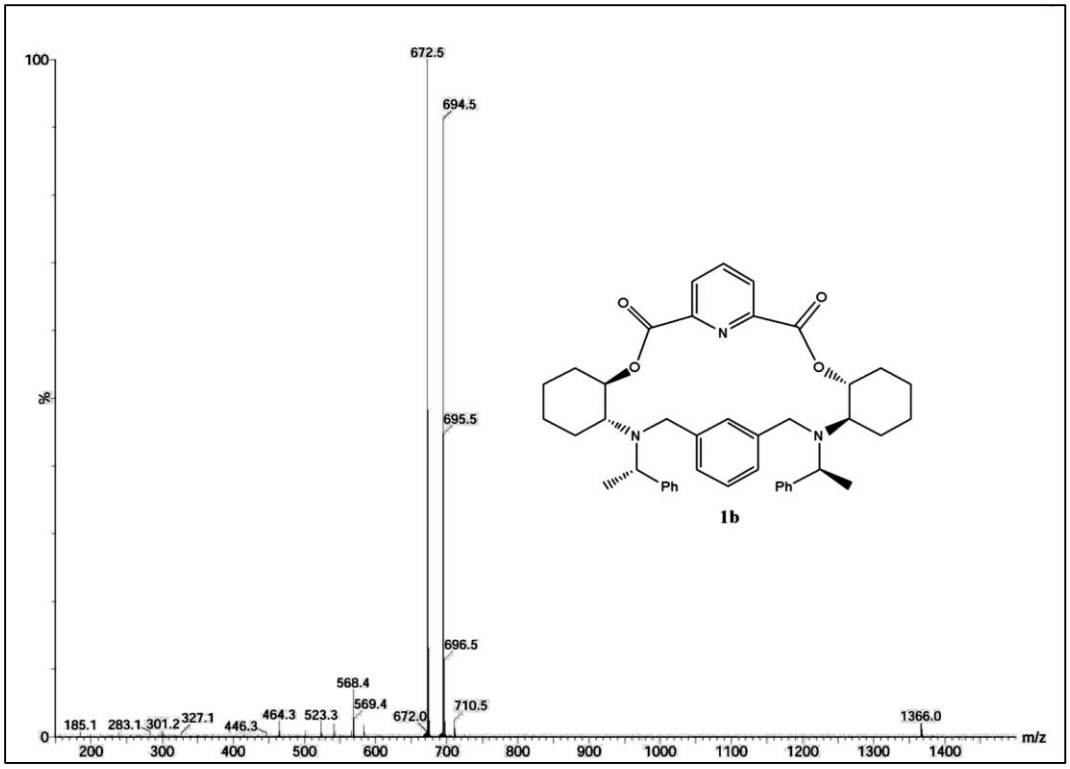

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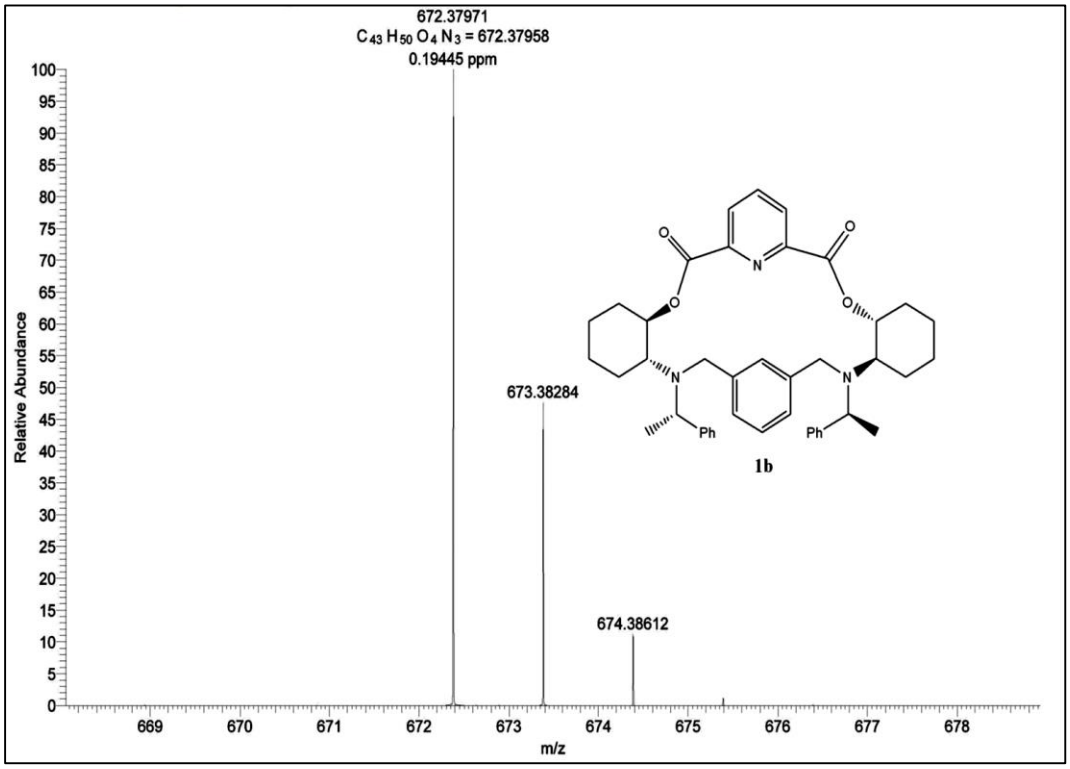


Figure 30: HRMS Spectra of **1b**

X-ray Crystal Data

Crystal data for compound **1a**

Table 1: Crystal data and structure refinement for Compound **1a** CCDC-1004162

Empirical Formula	$C_{43}H_{49}N_3O_4$
Formula Weight	671.85
Temperature	293(2)
Wavelength	0.71073A
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 12.5755(7)Å
	b = 16.6410(10) Å
	c = 17.7068(10) Å
	$\alpha = 90^o$
	$\beta = 90^o$
	$\gamma = 90^o$
Volume	3705.5(4)
Z	4
(Density calculated)	1.206
Absorption coefficient(μ)	0.077
F(000)	1440.0
Crystal size(mm)	0.49x0.28x0.12
θ range for data collection	6.14 to 58^o
Reflections collected	10724
Independent reflections	7779[R(int) = 0.0246]
Refinement method	Least Squares minimization
Data / restraints / Parameters	7779/0/453
Goodness of fit on F^2	0.957
Final R indices [I>2sigma(I)]	R_1 =0.0516, wR_2 = 0.0884
R indices (all data)	R_1 = 0.0897, wR_2 = 0.1001
Largest difference peak and hole	0.19/-0.30

Table 2: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1a**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O23	-1906.1(11)	-3334.3(9)	-2010.1(8)	37.8(4)
N26	-3749.6(14)	-3405.4(11)	-1209.2(9)	37.4(4)
O3	-5194.0(11)	-4601.1(9)	-1422.4(8)	42.3(4)
N16	-870.9(13)	-4821.3(10)	-2177.3(10)	37.2(4)
C13	-2889.3(16)	-5220.4(13)	-2856.6(11)	35.9(5)
C17	-724.7(16)	-4178.9(13)	-2730.9(12)	36.5(5)
C15	-1017.6(18)	-5618.9(13)	-2503.5(14)	43.6(6)
C25	-3020.2(18)	-2859.1(13)	-1017.9(12)	36.4(5)
C32	-2010(2)	-6207.8(15)	-3599.5(13)	50.4(6)
C30	-3808(2)	-5834.8(15)	-3875.0(13)	50.0(6)
C1	-4651.3(18)	-3392.1(14)	-812.8(12)	40.1(5)
C24	-1978(2)	-2833.9(15)	-1430.6(13)	44.8(6)
C12	-3792.9(17)	-5280.2(13)	-3291.6(12)	36.1(5)
C22	-881.2(16)	-3345.6(13)	-2408.4(12)	36.8(5)
C4	-5955.6(18)	-5259.8(14)	-1544.0(12)	41.9(6)
C14	-1990.3(17)	-5680.5(13)	-2999.3(12)	37.3(5)
N10	-5694.8(13)	-5156.4(11)	-2958(1)	39.5(4)
C2	-5509(2)	-4004.5(16)	-970.4(13)	46.8(6)
C39	-963.8(19)	-5237.5(13)	-857.3(12)	42.5(6)
C18	321.5(19)	-4186.7(16)	-3176.8(14)	53.9(7)
C27	-4860(2)	-2855.5(15)	-235.2(14)	52.2(7)
C45	-6730.0(17)	-3921.1(14)	-3312.9(14)	43.2(6)
C40	-548(2)	-5826.7(15)	-386.5(13)	54.2(7)
C35	-6714.0(18)	-4833.8(14)	-3228.7(13)	43.3(6)
C11	-4729.0(17)	-4724.7(14)	-3157.1(12)	41.1(6)
C7	-6223(2)	-6998.8(15)	-1717.5(16)	61.8(8)
O38	-6386.5(14)	-3954.9(12)	-699.1(10)	72.9(6)

O37	-1277.7(16)	-2381.6(13)	-1242.6(11)	84.2(7)
C29	-3153(2)	-2302.6(13)	-439.9(12)	44.2(6)
C9	-5654.4(17)	-5659.1(13)	-2288.9(12)	38.9(5)
C8	-6308.7(19)	-6429.2(14)	-2389.4(15)	52.3(7)
C33	-307.4(17)	-4799.8(15)	-1453.3(12)	44.6(6)
C46	-6780(2)	-3433.4(17)	-2681.7(17)	63.1(7)
C31	-2925(2)	-6292.9(16)	-4028.6(14)	58.7(7)
C44	-2030.1(19)	-5043.6(14)	-772.6(14)	50.4(6)
C5	-5888(2)	-5829.0(16)	-874.1(14)	59.3(7)
C21	-886(2)	-2707.7(14)	-3021.3(14)	52.8(7)
C28	-4088(2)	-2301.6(15)	-46.6(14)	53.9(7)
C42	-2207(3)	-5996(2)	231.7(15)	74.6(10)
C48	-6804(3)	-2239(2)	-3452(3)	87.0(11)
C43	-2643(2)	-5414.7(18)	-228.7(15)	65.5(8)
C6	-6559(2)	-6581.3(16)	-998.7(15)	64.3(8)
C34	854.0(19)	-5087(2)	-1491.4(17)	81.2(10)
C19	311(2)	-3565.8(18)	-3805.4(15)	65.8(8)
C20	133(2)	-2732.4(18)	-3484.8(18)	69.1(9)
C50	-6718(2)	-3541.3(17)	-4010.7(16)	62.2(7)
C41	-1168(3)	-6201.0(17)	148.8(15)	67.6(8)
C36	-7054(2)	-5265.4(16)	-3945.8(14)	73.9(9)
C47	-6814(3)	-2591.1(19)	-2753(2)	81.9(10)
C49	-6756(3)	-2708(2)	-4073(2)	81.9(10)

Table 3: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **1a**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U11+...+2hka \times b \times U_{12}]$

Atom	**U11**	**U22**	**U33**	**U23**	**U13**	**U12**
O23	29.7(8)	39.9(8)	43.9(8)	-7.5(8)	0.6(7)	-2.7(7)
N26	37.1(11)	40.6(10)	34.5(10)	-4.3(9)	-0.3(9)	4.6(10)
O3	35.0(9)	47.9(10)	44.0(9)	-8.5(8)	3.0(7)	-5.7(8)
N16	25.0(9)	41.5(10)	45.2(11)	1.7(10)	0.4(8)	4.7(9)
C13	35.4(13)	36.7(12)	35.7(11)	-3.6(11)	4.8(10)	-1.1(11)
C17	25.7(12)	45.4(13)	38.4(12)	3.7(12)	1(1)	-2.5(11)
C15	37.7(13)	36.9(12)	56.1(15)	-4.0(12)	2.1(12)	5.7(12)
C25	41.8(14)	34.0(12)	33.5(12)	-0.5(11)	-5.6(11)	5.0(11)
C32	45.6(15)	51.7(15)	53.9(15)	-8.9(14)	13.8(13)	7.0(13)
C30	45.2(15)	60.4(16)	44.5(13)	-11.6(14)	-3.5(12)	-4.4(14)
C1	40.0(13)	45.1(13)	35.3(12)	-3.4(12)	-0.7(11)	10.2(12)
C24	43.9(15)	49.4(14)	41.1(13)	-6.9(13)	-4.8(12)	-4.8(13)
C12	32.9(12)	38.6(12)	36.7(11)	2.6(12)	6(1)	-5.3(11)
C22	23.3(11)	45.1(12)	42.1(12)	1.5(12)	1.9(10)	-4.3(11)
C4	32.4(12)	50.8(14)	42.5(13)	1.1(13)	2(1)	-7.4(12)
C14	34.3(13)	36.1(12)	41.4(12)	1.2(12)	6.7(11)	0.8(11)
N10	26.1(10)	48.7(11)	43.7(10)	7.3(10)	0.1(8)	0.8(10)
C2	43.7(15)	58.9(16)	37.7(13)	-6.9(14)	3.0(12)	4.2(14)
C39	47.4(14)	40.0(12)	40.2(12)	-1.9(12)	-4.1(11)	1.9(13)
C18	37.4(14)	64.1(17)	60.3(16)	4.5(15)	13.1(12)	1.0(13)
C27	48.9(17)	59.9(17)	47.6(15)	-10.7(14)	11.3(13)	8.5(15)
C45	29.4(13)	47.2(14)	53.2(15)	-7.0(14)	-6.0(12)	4.0(12)
C40	67.0(19)	48.3(15)	47.2(15)	-1.0(14)	-10.8(14)	5.4(15)
C35	34.2(13)	48.3(13)	47.4(13)	-2.8(13)	-5.5(11)	-0.7(12)
C11	35.5(13)	46.0(13)	42.0(13)	3.4(12)	2.9(10)	-0.5(12)
C7	45.9(16)	50.8(15)	89(2)	14.7(17)	-4.4(16)	-9.2(14)
O38	46.7(11)	96.8(14)	75.2(12)	-30.3(12)	22.2(10)	-5.6(11)

O37	55.6(13)	114.8(17)	82.2(13)	-51.2(13)	6.4(11)	-33.5(12)
C29	51.8(17)	37.4(13)	43.5(13)	-2.1(12)	-8.8(12)	8.3(13)
C9	28.6(12)	45.9(13)	42.2(13)	-0.4(12)	0.6(10)	-3.0(11)
C8	43.9(14)	49.7(15)	63.1(16)	-1.8(14)	-2.2(13)	-9.8(13)
C33	34.5(13)	51.8(15)	47.5(13)	4.8(13)	-6.7(11)	0.2(13)
C46	53.5(17)	64.6(18)	71.0(18)	-12.5(17)	-12.4(15)	10.9(15)
C31	64.3(18)	62.6(17)	49.3(15)	-24.0(15)	2.9(14)	5.0(15)
C44	50.5(16)	48.4(15)	52.3(14)	1.7(14)	2.7(13)	-0.8(13)
C5	60.3(17)	69.5(17)	48.2(14)	9.2(15)	3.0(13)	-5.9(16)
C21	49.7(17)	49.7(14)	58.8(16)	12.4(14)	4.4(13)	1.0(14)
C28	68(2)	47.3(15)	46.4(14)	-14.9(13)	3.5(14)	13.4(15)
C42	102(3)	77(2)	44.3(15)	-0.6(17)	8.4(18)	-40(2)
C48	57(2)	59(2)	145(3)	10(3)	-12(2)	1.5(17)
C43	59.3(18)	76(2)	60.8(16)	-4.8(18)	11.2(15)	-11.9(17)
C6	60.3(18)	62.8(17)	69.9(19)	23.4(17)	9.6(15)	-8.8(16)
C34	37.9(15)	132(3)	73.7(18)	33(2)	-9.4(13)	8.6(19)
C19	46.8(16)	89(2)	61.2(17)	13.9(18)	18.5(14)	2.0(16)
C20	63(2)	71(2)	72.9(19)	24.7(18)	16.1(16)	-10.0(16)
C50	54.3(17)	67.7(19)	64.5(18)	4.1(17)	0.3(14)	10.6(15)
C41	101(3)	54.1(17)	47.8(16)	7.8(15)	-16.5(17)	-14.5(19)
C36	90(2)	59.5(16)	72.2(18)	-16.2(17)	-36.0(17)	10.7(16)
C47	69(2)	68(2)	109(3)	-38(2)	-14(2)	13.4(17)
C49	69(2)	71(2)	106(3)	25(2)	-2(2)	5.2(19)

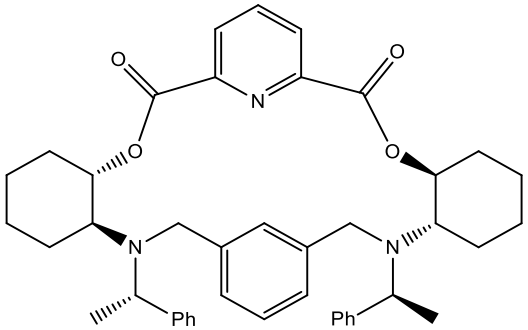
Table 4: Bond Lengths for **1a**

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
O23	C24	1.325(3)	N10	C11	1.455(3)
O23	C22	1.469(2)	N10	C9	1.451(3)
N26	C25	1.335(3)	C2	O38	1.207(3)
N26	C1	1.334(3)	C39	C40	1.389(3)
O3	C4	1.471(3)	C39	C33	1.525(3)
O3	C2	1.335(3)	C39	C44	1.387(3)
N16	C17	1.462(3)	C18	C19	1.519(3)
N16	C15	1.459(3)	C27	C28	1.379(3)
N16	C33	1.465(3)	C45	C35	1.526(3)
C13	C12	1.376(3)	C45	C46	1.383(3)
C13	C14	1.389(3)	C45	C50	1.388(3)
C17	C22	1.512(3)	C40	C41	1.376(4)
C17	C18	1.534(3)	C35	C36	1.520(3)
C15	C14	1.509(3)	C7	C8	1.525(3)
C25	C24	1.501(3)	C7	C6	1.510(4)
C25	C29	1.390(3)	C29	C28	1.368(3)
C32	C14	1.378(3)	C9	C8	1.533(3)
C32	C31	1.386(3)	C33	C34	1.538(3)
C30	C12	1.385(3)	C46	C47	1.408(4)
C30	C31	1.375(3)	C44	C43	1.379(3)
C1	C2	1.510(3)	C5	C6	1.526(4)
C1	C27	1.383(3)	C21	C20	1.522(3)
C24	O37	1.206(3)	C42	C43	1.379(4)
C12	C11	1.516(3)	C42	C41	1.358(4)
C22	C21	1.518(3)	C48	C47	1.369(4)
C4	C9	1.525(3)	C48	C49	1.350(4)
C4	C5	1.520(3)	C19	C20	1.515(4)
N10	C35	1.470(3)	C50	C49	1.392(4)

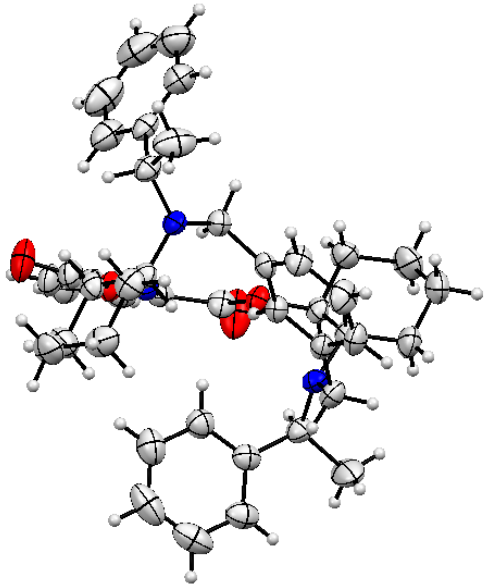
Table 5: Bond Angles for **1a**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C24	O23	C22	116.10(16)	O38	C2	C1	122.2(2)
C1	N26	C25	116.05(19)	C40	C39	C33	123.3(2)
C2	O3	C4	116.67(17)	C44	C39	C40	117.6(2)
C17	N16	C33	120.52(17)	C44	C39	C33	119.1(2)
C15	N16	C17	114.56(17)	C19	C18	C17	111.34(19)
C15	N16	C33	115.45(18)	C28	C27	C1	118.5(2)
C12	C13	C14	122.0(2)	C46	C45	C35	120.4(2)
N16	C17	C22	113.63(17)	C46	C45	C50	116.9(2)
N16	C17	C18	116.52(17)	C50	C45	C35	122.7(2)
C22	C17	C18	108.28(17)	C41	C40	C39	121.3(3)
N16	C15	C14	113.24(17)	N10	C35	C45	114.00(18)
N26	C25	C24	119.7(2)	N10	C35	C36	110.17(19)
N26	C25	C29	123.9(2)	C36	C35	C45	112.6(2)
C29	C25	C24	116.4(2)	N10	C11	C12	112.67(19)
C14	C32	C31	120.2(2)	C6	C7	C8	110.6(2)
C31	C30	C12	120.4(2)	C28	C29	C25	118.6(2)
N26	C1	C2	119.9(2)	C4	C9	C8	109.35(19)
N26	C1	C27	124.1(2)	N10	C9	C4	116.51(18)
C27	C1	C2	115.9(2)	N10	C9	C8	111.61(18)
O23	C24	C25	114.8(2)	C7	C8	C9	113.0(2)
O37	C24	O23	123.8(2)	N16	C33	C39	109.40(18)
O37	C24	C25	121.4(2)	N16	C33	C34	114.4(2)
C13	C12	C30	118.5(2)	C39	C33	C34	113.3(2)
C13	C12	C11	120.6(2)	C45	C46	C47	120.9(3)
C30	C12	C11	120.8(2)	C30	C31	C32	120.4(2)
O23	C22	C17	107.89(16)	C43	C44	C39	120.8(2)
O23	C22	C21	109.32(17)	C4	C5	C6	111.6(2)
C17	C22	C21	111.82(17)	C22	C21	C20	111.31(19)
O3	C4	C9	106.84(16)	C29	C28	C27	118.8(2)

O3	C4	C5	108.27(18)	C41	C42	C43	119.7(3)
C5	C4	C9	112.93(19)	C49	C48	C47	119.4(3)
C13	C14	C15	121.11(19)	C42	C43	C44	120.3(3)
C32	C14	C13	118.5(2)	C7	C6	C5	110.2(2)
C32	C14	C15	120.42(19)	C20	C19	C18	110.5(2)
C11	N10	C35	117.95(18)	C19	C20	C21	110.6(2)
C9	N10	C35	120.48(17)	C45	C50	C49	121.6(3)
C9	N10	C11	116.96(17)	C42	C41	C40	120.4(3)
O3	C2	C1	113.7(2)	C48	C47	C46	120.4(3)
O38	C2	O3	124.1(2)	C48	C49	C50	120.8(3)



1a



ORTEP diagram of the compound **1a**

(50% probability factor for thermal ellipsoids)

Crystal data for compound **1b**

Table 1: Crystal data and structure refinement for Compound **1b** CCDC-1016922

Empirical Formula	$C_{43}H_{49}N_3O_4$
Formula Weight	671.85
Temperature	293(2)
Wavelength	1.54184
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 12.8516(2) Å
	b = 13.9590(3) Å
	c = 21.1978(4) Å
	$\alpha = 90^o$
	$\beta = 90^o$
	$\gamma = 90^o$
Volume	3802.80(14)
Z	4
(Density calculated)	1.170
Absorption coefficient(μ)	0.570
F(000)	1440.0
Crystal size(mm)	0.5x0.3x0.1
θ range for data collection	7.58 to140.06^o
Reflections collected	8447
Independent reflections	5807[R(int) = 0.0235]
Refinement method	Least Squares minimization
Data / restraints / Parameters	5807/0/453
Goodness of fit on F^2	1.054
Final R indices [I>2sigma(I)]	R_1 =0.0512, wR_2 = 0.1531
R indices (all data)	R_1 = 0.0621, wR_2 = 0.1597
Largest difference peak and hole	0.33/-0.35

Table 2: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **1b**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O23	-107.1(14)	-392.9(14)	-1596.3(10)	49.3(4)
N3	-3525.6(13)	610.7(15)	-1155.1(9)	34.0(4)
N26	-1450.2(17)	773.2(17)	-987.4(10)	44.3(5)
N10	-4546.0(16)	183.3(16)	-2400.9(10)	42.1(5)
O37	1232.8(17)	196(2)	-1047.2(14)	78.0(8)
C16	-776.9(17)	-2284.3(17)	-1601.3(11)	35.0(5)
C13	-2565.4(19)	-1453(2)	-2250.5(13)	44.6(6)
C11	-3451(2)	65(2)	-2598.4(13)	45.2(6)
C24	323(2)	185(2)	-1178.5(14)	50.0(6)
O38	-3796.7(18)	1980(2)	-636.4(14)	81.1(8)
C9	-4828.3(19)	-188.5(19)	-1784.1(13)	42.3(6)
C14	-2233.5(19)	-2398(2)	-2343.6(13)	43.1(6)
C22	586.2(19)	-1094(2)	-1888.9(13)	46.8(6)
C25	-431(2)	858(2)	-867.3(13)	47.1(6)
C4	-4653.1(19)	469(2)	-1214.4(13)	45.7(6)
C17	-60(2)	-1948(2)	-2092.1(13)	47.2(6)
C1	-2070(2)	1401(2)	-695.5(12)	46.5(6)
C32	-2508(2)	-2852(2)	-2899.8(14)	49.8(6)
C30	-3444(2)	-1456(2)	-3244.0(13)	49.3(6)
C31	-3115(2)	-2387(2)	-3346.4(14)	54.3(7)
C12	-3157.3(19)	-980(2)	-2692.3(12)	42.0(5)
C33	-5019(2)	1087(2)	-2599.0(13)	48.0(6)
C15	-1593(2)	-2904(2)	-1850.8(14)	51.0(6)
C8	-5978(2)	-510(2)	-1791.5(16)	53.7(7)
C45	-5421(2)	1011(3)	-3279.7(14)	55.2(7)
C2	-3230(2)	1360(2)	-827.7(13)	51.9(7)
C35	-341(2)	-2505(2)	-978.1(13)	53.3(7)

C21	1136(3)	-650(3)	-2452.1(16)	62.9(8)
C5	-5038(2)	42(3)	-600.9(16)	64.2(8)
C6	-6189(2)	-212(3)	-639.6(17)	69.3(9)
C29	-20(2)	1537(3)	-456.6(17)	65.7(9)
C28	-679(3)	2152(3)	-155.1(19)	78.1(11)
C7	-6367(2)	-921(3)	-1169.1(19)	67.9(9)
C27	-1731(3)	2092(3)	-282.2(16)	68.5(9)
C46	-5548(3)	1812(3)	-3655.8(18)	78.5(11)
C19	1225(3)	-2280(3)	-2957.8(16)	71(1)
C18	666(3)	-2688(3)	-2388.9(16)	60.8(8)
C34	-4343(3)	1971(2)	-2494.6(17)	68.3(9)
C20	1819(3)	-1384(3)	-2783.9(19)	77.1(10)
C43	573(7)	-5117(4)	-1012(2)	130(3)
C50	-5732(3)	142(3)	-3519.2(19)	79.0(11)
C39	314(3)	-3413(3)	-932.3(14)	67.4(9)
C36	-1195(3)	-2485(3)	-477.1(16)	73.6(10)
C44	-77(5)	-4306(3)	-1033.7(17)	93.2(15)
C48	-6232(4)	868(6)	-4499(2)	110(2)
C40	1384(3)	-3313(4)	-784.1(18)	93.6(15)
C47	-5950(4)	1735(5)	-4259(2)	108(2)
C49	-6150(4)	53(5)	-4123(2)	104.3(17)
C41	2017(5)	-4105(8)	-754(3)	142(3)
C42	1614(7)	-4989(6)	-877(2)	136(3)

Table 3: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **1b**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U11+...+2hka \times b \times U_{12}]$

Atom	**U11**	**U22**	**U33**	**U23**	**U13**	**U12**
O23	36.8(8)	48.5(10)	62.7(11)	-9.5(9)	-8.1(8)	1.4(8)
N3	19.5(7)	44.6(11)	37.8(9)	-8.7(8)	-0.3(7)	2.0(8)
N26	39.7(10)	48.5(12)	44.5(10)	-2.1(10)	-4.0(9)	-3.3(10)
N10	35.7(10)	41.3(11)	49.3(11)	0.8(9)	-2.8(9)	3.3(9)
O37	39.3(10)	89.2(18)	105.5(19)	-38.4(16)	-15.8(12)	4.2(11)
C16	31.0(9)	34.5(11)	39.4(10)	3.4(10)	-5.3(9)	-0.7(9)
C13	38.0(11)	48.1(14)	47.7(13)	-4.1(12)	0.8(10)	-1.2(12)
C11	37.7(12)	44.9(13)	52.8(13)	2.8(12)	1.2(11)	-0.2(11)
C24	40.8(13)	50.9(15)	58.1(15)	-3.6(13)	-8.3(12)	-1.2(12)
O38	48.1(11)	93.7(18)	101.3(18)	-47.4(17)	2.3(12)	10.9(13)
C9	32.7(11)	40.9(13)	53.3(14)	4.7(11)	-4.9(10)	2(1)
C14	34.1(11)	42.4(13)	52.6(13)	4.6(12)	0.9(10)	-4.8(10)
C22	34.8(11)	50.6(15)	54.8(14)	-4.8(12)	-4.3(11)	3.0(11)
C25	39.8(12)	49.9(15)	51.6(13)	-1.8(12)	-7.4(11)	-3.2(12)
C4	27.8(10)	56.2(16)	53.2(13)	0.2(13)	0.6(10)	4.0(11)
C17	42.3(12)	49.8(14)	49.5(13)	-4.5(12)	-5.0(11)	0.2(12)
C1	42.7(12)	54.6(15)	42.3(12)	-8.3(12)	0.7(10)	-1.3(12)
C32	47.1(13)	41.4(14)	61.0(15)	-4.4(13)	2.9(13)	-2.7(12)
C30	45.1(13)	54.0(15)	48.8(13)	1.3(12)	-2.5(11)	-1.2(13)
C31	57.7(15)	54.6(16)	50.7(14)	-10.1(13)	-7.1(13)	-5.6(14)
C12	34.1(10)	44.5(13)	47.5(12)	0.0(11)	4.1(10)	-0.9(11)
C33	47.8(12)	45.6(14)	50.7(14)	4.6(12)	-1.5(12)	6.2(12)
C15	48.0(14)	43.4(14)	61.5(15)	4.0(13)	-3.3(13)	-4.3(13)
C8	35.9(12)	52.3(16)	72.9(18)	4.0(14)	-5.1(13)	-0.9(12)
C45	42.9(13)	69.1(19)	53.4(15)	6.6(15)	-0.1(12)	14.3(14)
C2	42.0(13)	66.7(18)	47.0(13)	-8.8(14)	6.3(11)	3.5(14)
C35	53.7(14)	55.5(16)	50.6(13)	-0.1(13)	-5.0(12)	4.8(14)

C21	52.6(15)	66(2)	70.3(18)	-1.8(17)	3.0(15)	-16.1(15)
C5	48.5(16)	87(2)	56.6(16)	7.9(17)	2.2(14)	-0.4(17)
C6	46.8(16)	90(3)	71.2(19)	16(2)	13.9(15)	1.0(17)
C29	46.1(14)	74(2)	77(2)	-21.8(18)	-14.0(15)	-5.7(16)
C28	63.7(19)	86(3)	85(2)	-43(2)	-13.0(18)	-7.3(19)
C7	37.0(13)	69(2)	97(2)	20(2)	5.3(15)	-5.4(15)
C27	54.9(16)	85(2)	65.4(18)	-29.0(19)	1.0(15)	3.4(18)
C46	65(2)	97(3)	73(2)	33(2)	-1.0(17)	10(2)
C19	67.8(19)	84(2)	61.0(17)	-20.7(18)	8.9(15)	-2.1(19)
C18	59.8(17)	59.8(18)	62.9(16)	-12.2(15)	2.7(14)	2.9(15)
C34	86(2)	42.0(15)	77(2)	4.2(15)	-6.3(19)	0.2(17)
C20	57.0(17)	99(3)	75(2)	-16(2)	15.2(17)	-15(2)
C43	240(9)	100(4)	51(2)	-12(2)	-28(3)	72(5)
C50	80(2)	86(3)	70(2)	-4(2)	-21.0(19)	9(2)
C39	78(2)	83(2)	40.6(13)	1.7(15)	-5.2(14)	28(2)
C36	75(2)	90(3)	56.1(16)	-2.6(18)	6.4(16)	9(2)
C44	149(4)	75(3)	55.8(18)	0.0(19)	-27(2)	34(3)
C48	75(3)	204(7)	50.7(19)	10(3)	-9.9(18)	21(4)
C40	72(2)	144(4)	65(2)	7(3)	-1.4(18)	37(3)
C47	83(3)	166(6)	74(3)	50(3)	-9(2)	7(4)
C49	89(3)	147(5)	78(3)	-27(3)	-27(2)	7(3)
C41	98(4)	247(9)	81(3)	7(5)	5(3)	93(6)
C42	178(7)	171(7)	60(3)	-12(3)	-4(3)	115(6)

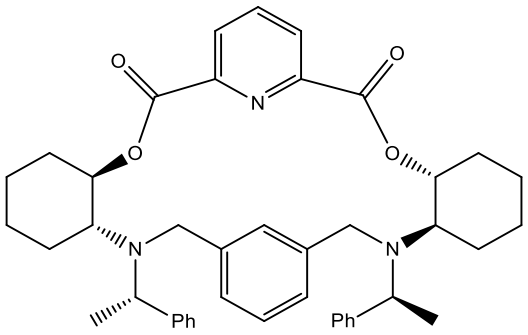
Table 4: Bond Lengths for **1b**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
O23	C24	1.319(3)	C1	C27	1.373(4)
O23	C22	1.461(3)	C32	C31	1.387(4)
N3	C4	1.468(3)	C30	C31	1.384(4)
N3	C2	1.311(4)	C30	C12	1.395(4)
N26	C25	1.339(3)	C33	C45	1.536(4)
N26	C1	1.336(4)	C33	C34	1.526(4)
N10	C11	1.478(3)	C8	C7	1.523(5)
N10	C9	1.453(3)	C45	C46	1.382(5)
N10	C33	1.462(3)	C45	C50	1.375(5)
O37	C24	1.202(4)	C35	C39	1.524(5)
C16	C17	1.467(4)	C35	C36	1.527(5)
C16	C15	1.459(4)	C21	C20	1.522(5)
C16	C35	1.467(4)	C5	C6	1.523(4)
C13	C14	1.400(4)	C6	C7	1.513(6)
C13	C12	1.376(4)	C29	C28	1.365(5)
C11	C12	1.520(4)	C28	C27	1.382(5)
C24	C25	1.503(4)	C46	C47	1.384(6)
O38	C2	1.203(4)	C19	C18	1.515(5)
C9	C4	1.534(4)	C19	C20	1.511(5)
C9	C8	1.544(3)	C43	C44	1.407(7)
C14	C32	1.384(4)	C43	C42	1.379(12)
C14	C15	1.506(4)	C50	C49	1.394(6)
C22	C17	1.516(4)	C39	C44	1.362(6)
C22	C21	1.519(4)	C39	C40	1.418(6)
C25	C29	1.391(4)	C48	C47	1.362(9)
C4	C5	1.514(4)	C48	C49	1.392(8)
C17	C18	1.526(4)	C40	C41	1.374(8)
C1	C2	1.518(4)	C41	C42	1.363(11)

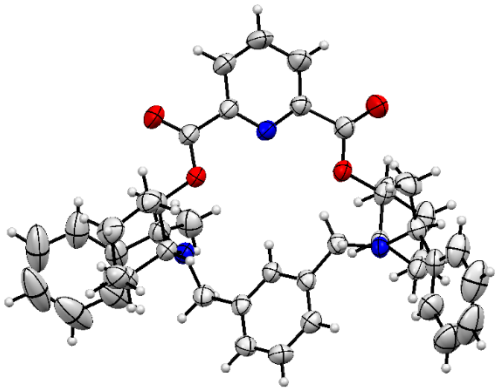
Table 5: Bond Angles for **1b**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C24	O23	C22	116.0(2)	C13	C12	C30	119.2(3)
C2	N3	C4	116.0(2)	C30	C12	C11	120.1(2)
C1	N26	C25	115.9(2)	N10	C33	C45	110.5(2)
C9	N10	C11	116.9(2)	N10	C33	C34	114.8(2)
C9	N10	C33	117.6(2)	C34	C33	C45	112.5(3)
C33	N10	C11	114.3(2)	C16	C15	C14	111.5(2)
C17	C16	C35	117.8(2)	C7	C8	C9	114.5(2)
C15	C16	C17	112.6(2)	C46	C45	C33	121.7(3)
C15	C16	C35	118.4(2)	C50	C45	C33	120.3(3)
C12	C13	C14	121.7(3)	C50	C45	C46	117.8(3)
N10	C11	C12	112.4(2)	N3	C2	C1	114.4(2)
O23	C24	C25	114.0(2)	O38	C2	N3	125.2(3)
O37	C24	O23	124.8(3)	O38	C2	C1	120.4(3)
O37	C24	C25	121.2(3)	C16	C35	C39	116.3(2)
N10	C9	C4	117.3(2)	C16	C35	C36	110.4(3)
N10	C9	C8	109.5(2)	C39	C35	C36	111.6(3)
C4	C9	C8	108.8(2)	C22	C21	C20	110.9(3)
C13	C14	C15	120.7(3)	C4	C5	C6	111.3(3)
C32	C14	C13	118.3(3)	C7	C6	C5	109.8(3)
C32	C14	C15	121.0(3)	C28	C29	C25	119.0(3)
O23	C22	C17	108.3(2)	C29	C28	C27	118.5(3)
O23	C22	C21	110.1(2)	C6	C7	C8	110.3(3)
C17	C22	C21	110.6(2)	C1	C27	C28	118.5(3)
N26	C25	C24	119.4(2)	C45	C46	C47	121.0(5)
N26	C25	C29	123.5(3)	C20	C19	C18	110.9(3)
C29	C25	C24	117.1(2)	C19	C18	C17	111.3(3)
N3	C4	C9	107.0(2)	C19	C20	C21	112.2(3)
N3	C4	C5	107.6(2)	C42	C43	C44	118.6(7)

C5	C4	C9	113.1(3)	C45	C50	C49	122.0(5)
C16	C17	C22	113.2(2)	C44	C39	C35	123.2(4)
C16	C17	C18	117.4(3)	C44	C39	C40	118.9(4)
C22	C17	C18	108.4(2)	C40	C39	C35	117.9(4)
N26	C1	C2	118.3(2)	C39	C44	C43	120.8(6)
N26	C1	C27	124.6(3)	C47	C48	C49	119.5(4)
C27	C1	C2	117.1(3)	C41	C40	C39	120.3(6)
C14	C32	C31	120.7(3)	C48	C47	C46	120.8(5)
C31	C30	C12	119.9(3)	C48	C49	C50	118.8(5)
C30	C31	C32	120.3(3)	C42	C41	C40	119.6(6)
C13	C12	C11	120.6(3)	C41	C42	C43	121.7(6)



1b



ORTEP diagram of the compound **1b**

(50% probability factor for thermal ellipsoids)

CSA Spectras

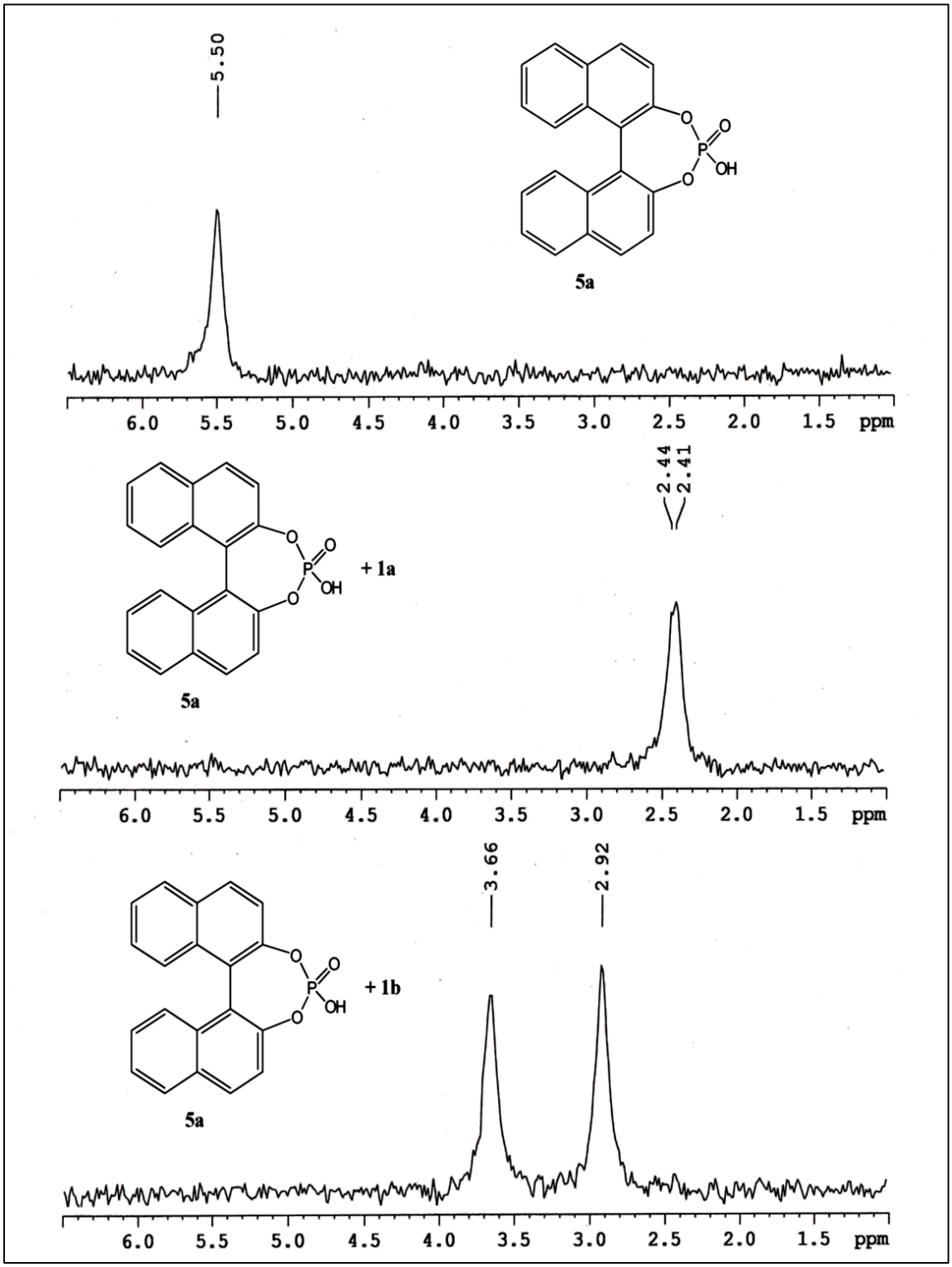
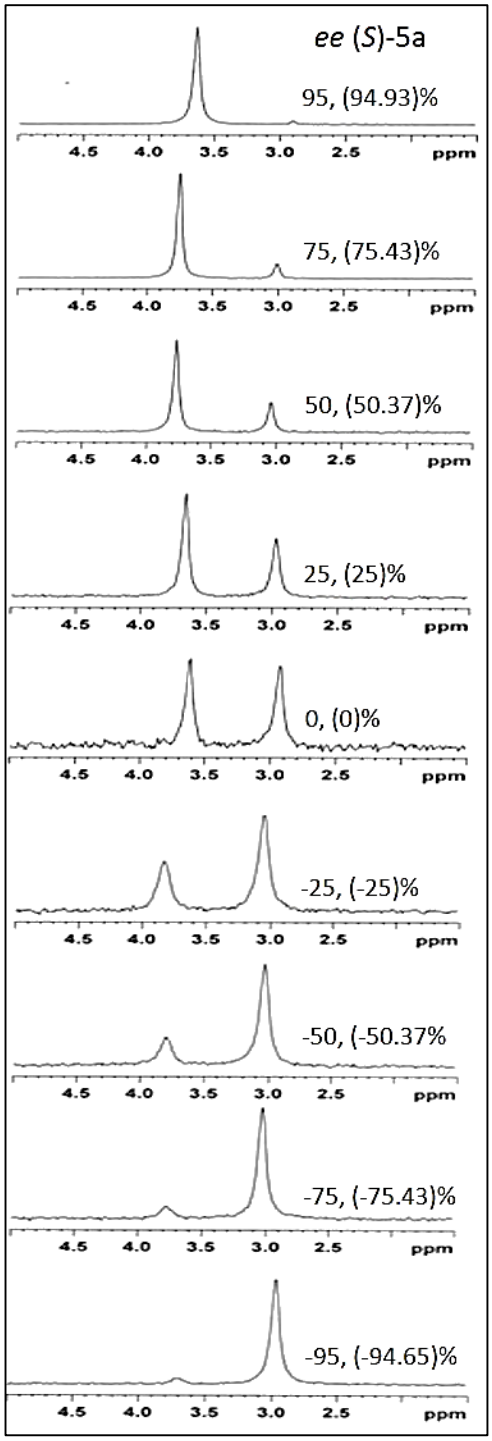


Figure 31: ^{31}P NMR Spectra of **5a** blank (top), **5a** + **1a** (middle) and **5a** + **1b** (bottom)



In order to further establish the practical utility of macrocycle **1b** as CSA for the determination of enantiomeric purity, the optical purity of various scalemic samples of **5a** were determined by integration of ^{31}P signal of **5a** in ^{31}P nmr. Figure 32 indicates that macrocycle **1b** maintains resolution for nonracemic samples of **5a** over a wide range of *ee* values. The plot of *ee* values determined by NMR and by gravimetry shows linear relationship with R^2 = *0.9999*. The scalemic samples of **5a** were prepared by weighing accurate quantities of (*S*) and (*R*)-**5a**.

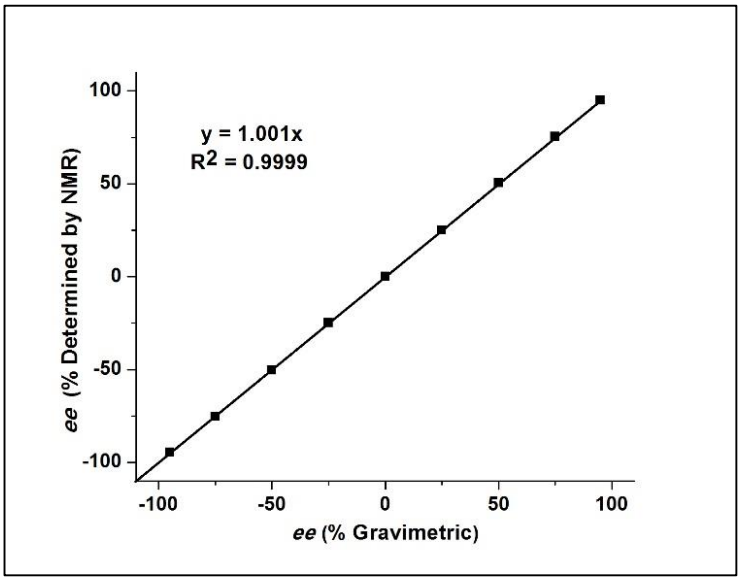


Figure 32. Selected region of ^{31}P NMR spectra of scalemic mixture of **5a** in presence of **1b** (Left) and its correlation between theoretical and observed % *ee* values (Right).

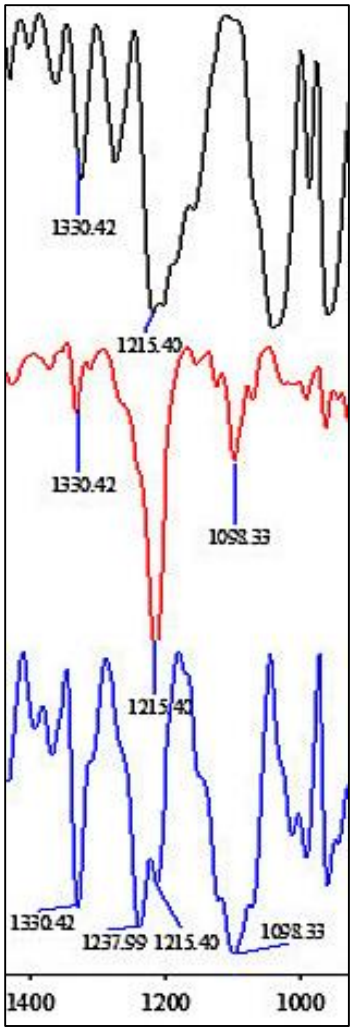


Figure 33: Selected region of IR Spectra of **5a** (top), **5a** + **1a** (middle) and **5a** + **1b** (bottom)

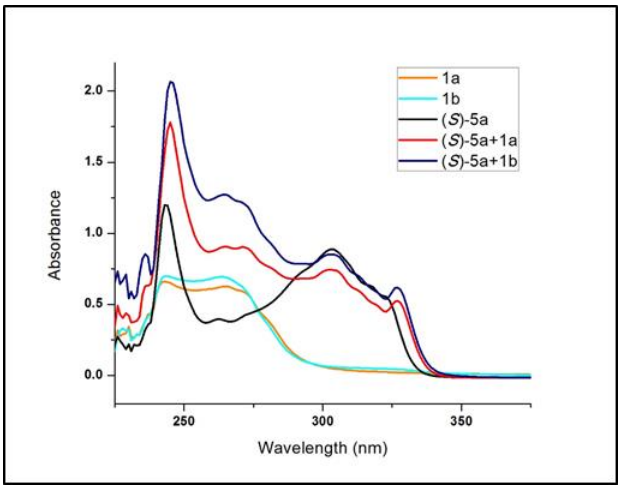


Figure 34: UV-vis Spectra of **5a** blank ($1x10^{-4}$), **5a** + **1a** ($1x10^{-4}$) and **5a** + **1b** ($1x10^{-4}$) in $CHCl_3$

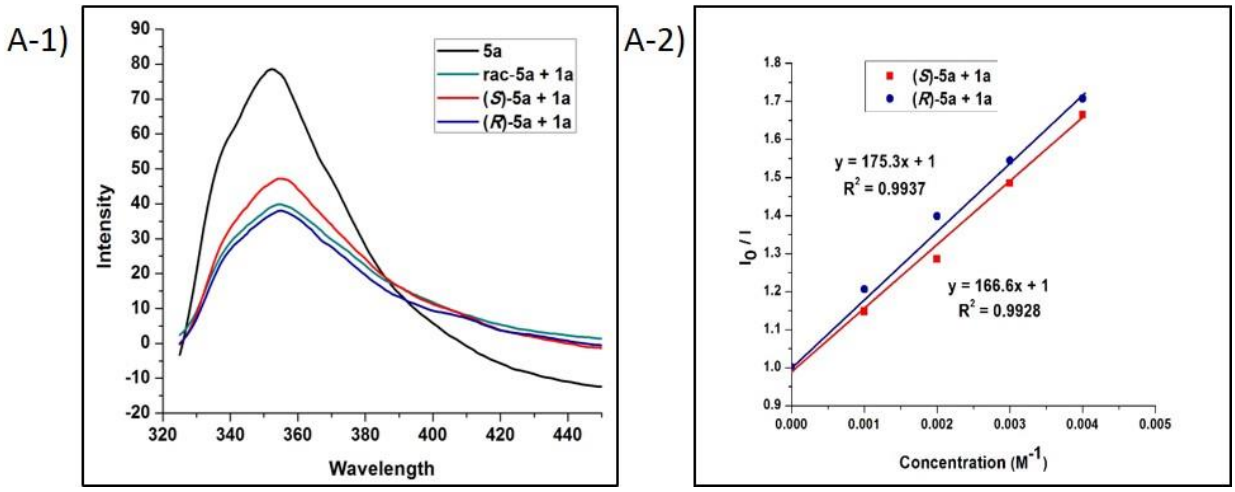


Figure 35: a) Fluorescence Spectra of **5a** blank ($1x10^{-5}$ M); (±)-**5a,** (*S*)-**5a** and (*R*)-**5a** in presence of **1a** in $CHCl_3$ (λ_{ex} = 305nm); b) Stern völmer plot of (*S*)-**5a** and (*R*)-**5a** in presence of **1a**

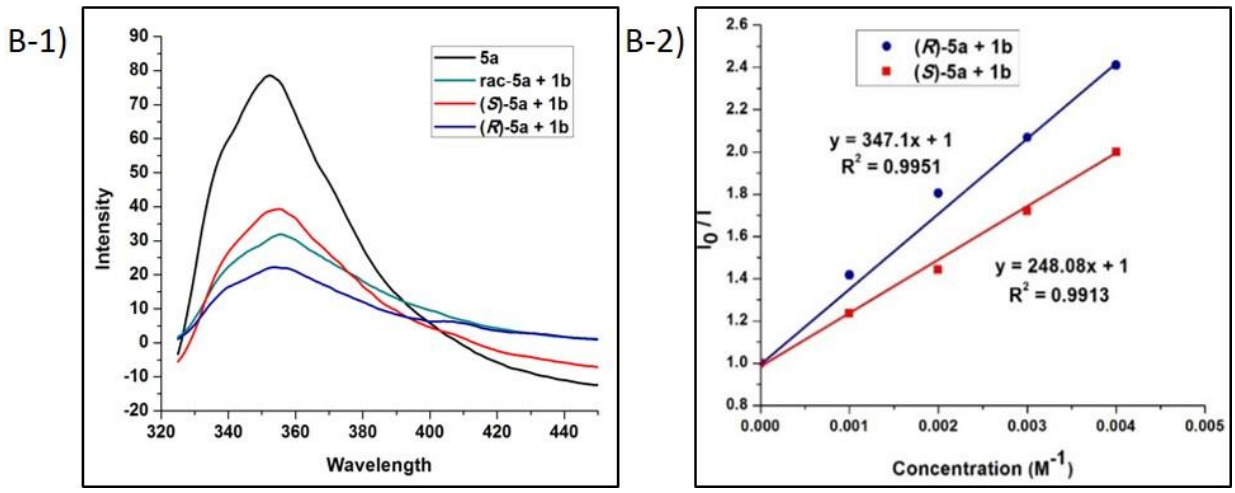


Figure 36: a) Fluorescence Spectra of **5a** blank ($1x10^{-5}$ M); (±)-**5a,** (*S*)-**5a** and (*R*)-**5a** in presence of **1b** in $CHCl_3$ (λ_{ex} = 305nm); b) Stern völmer plot of (*S*)-**5a** and (*R*)-**5a** in presence of **1b**

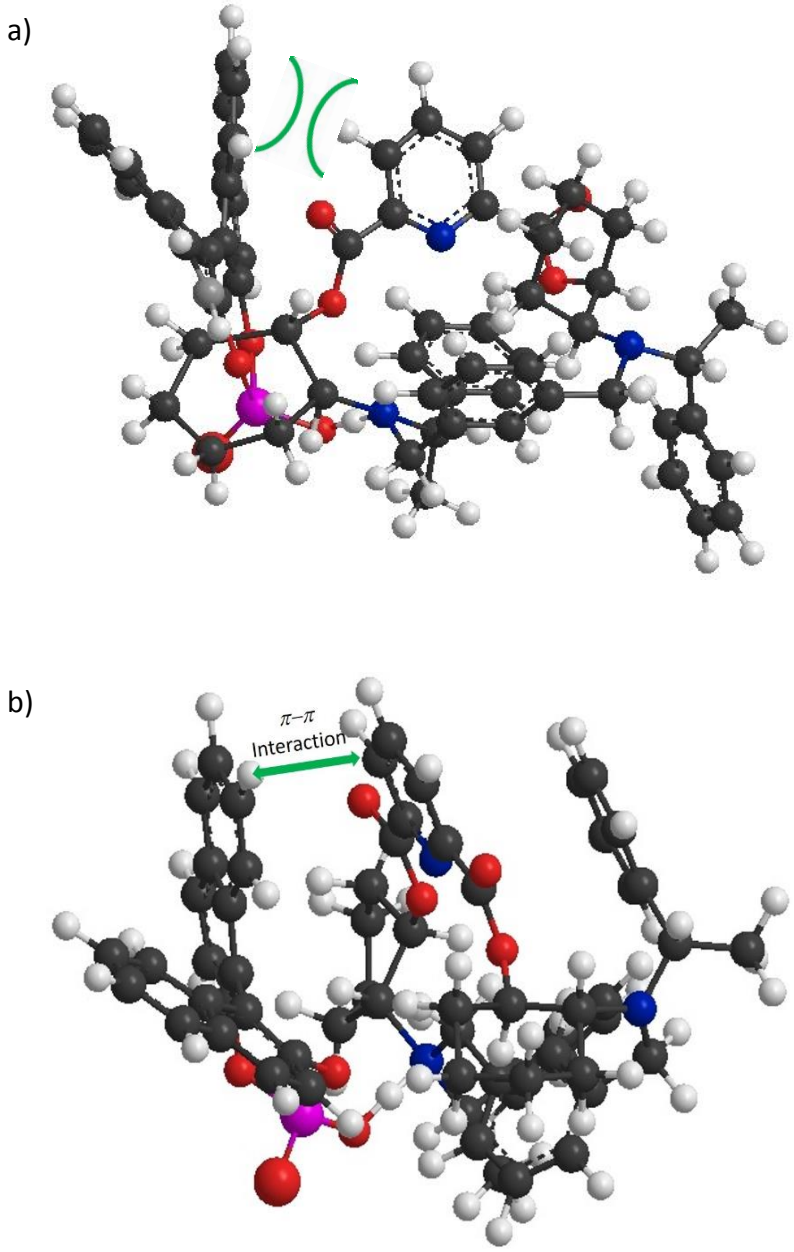


Figure 37: a) Plausible stereochemical representation of Diastereomeric adduct of **5a-1a** b) Plausible stereochemical representation of Diastereomeric adduct of **5a-1b.** (MM2 ChemDraw 3D)

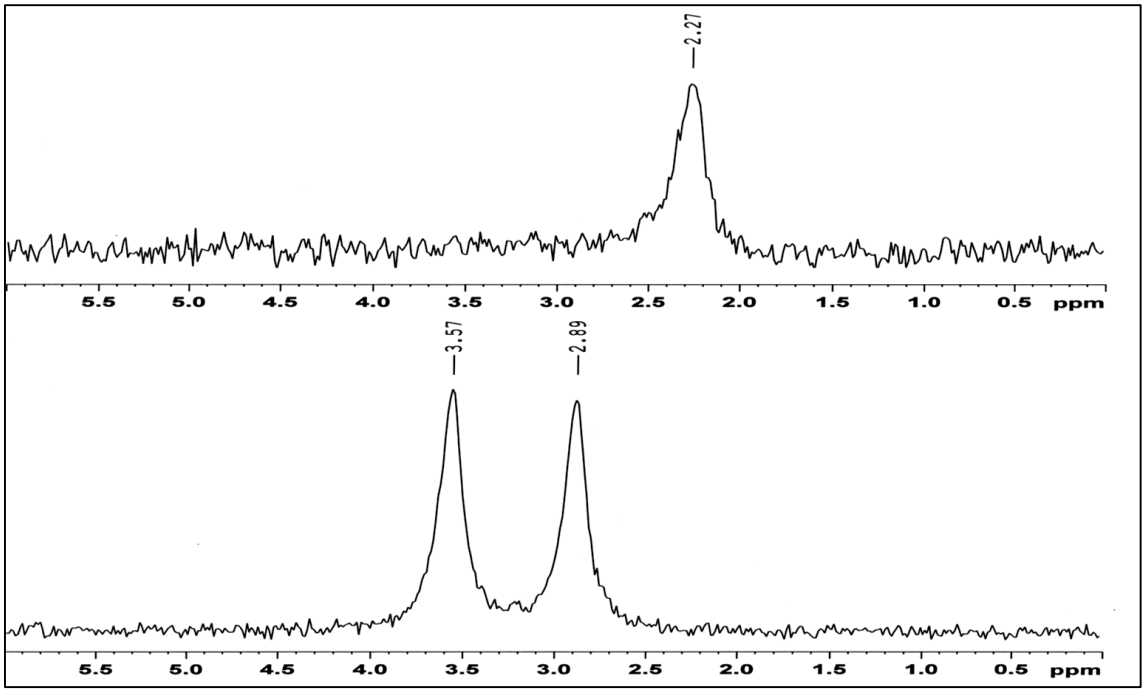


Figure 38: ^{31}P NMR Spectra of **5b** with **1a** (top) and **5b** with **1b** (bottom)

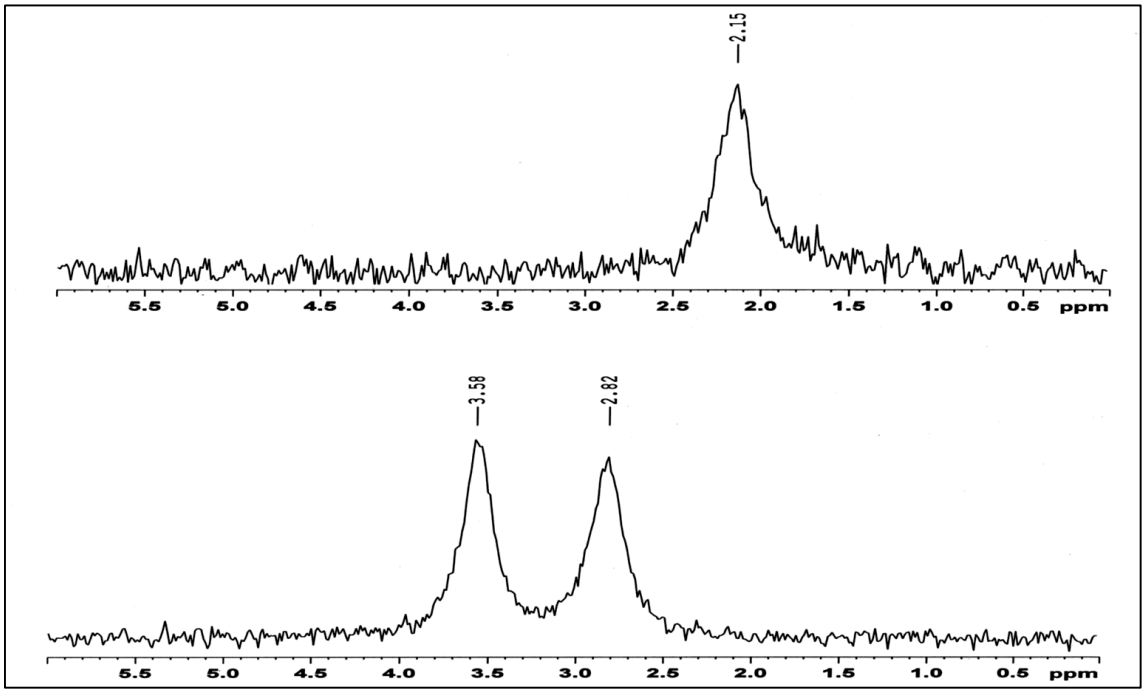


Figure 39: ^{31}P NMR Spectra of **5c** with **1a** (top) and **5c** with **1b** (bottom)

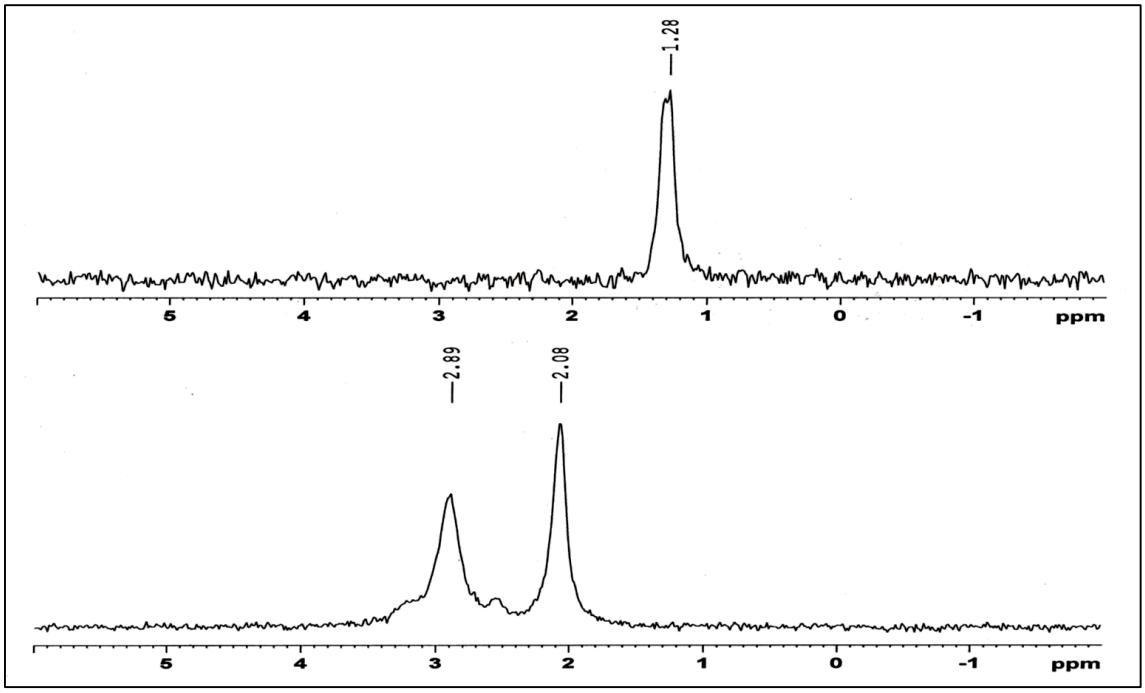


Figure 40: ^{31}P NMR Spectra of **5d** with **1a** (top) and **5d** with **1b** (bottom)

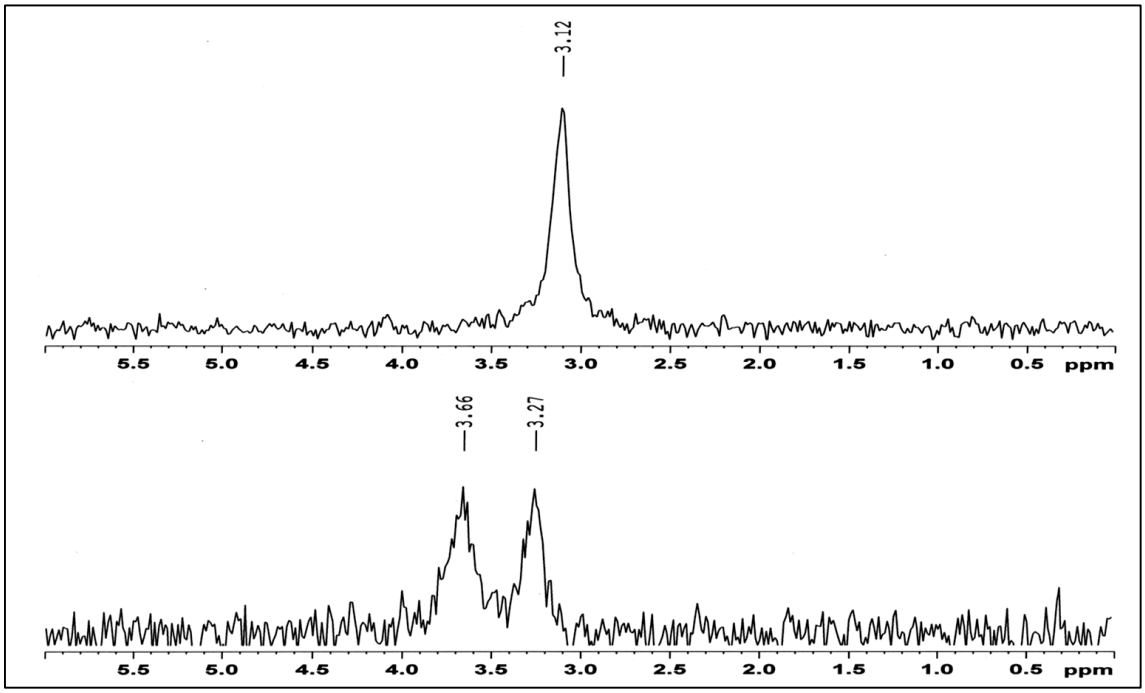


Figure 41: ^{31}P NMR Spectra of **5e** with **1a** (top) and **5e** with **1b** (bottom)

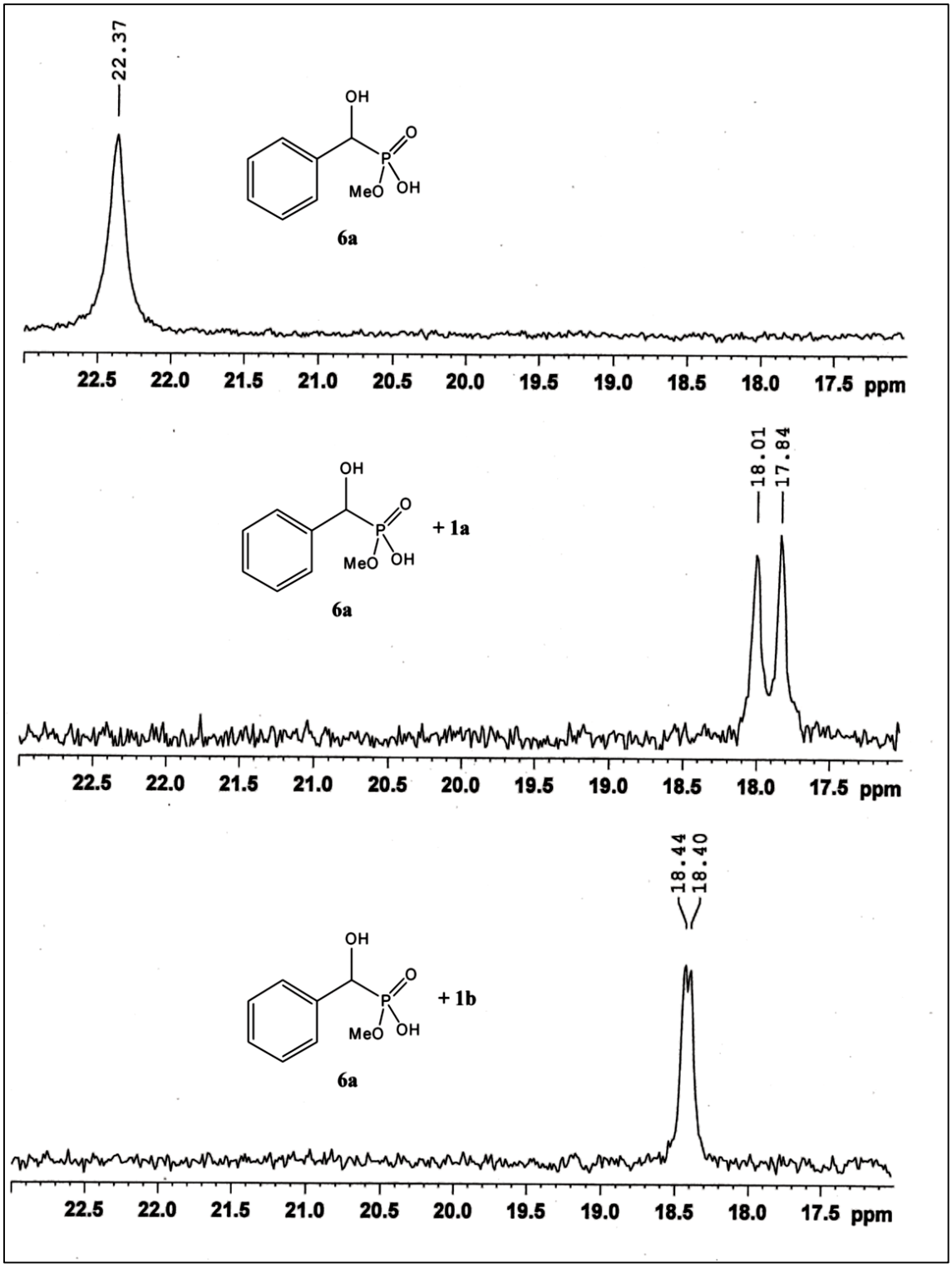


Figure 42: ^{31}P NMR Spectra of **6a** blank (top), **6a** + **1a** (middle) and **6a** + **1b** (bottom)

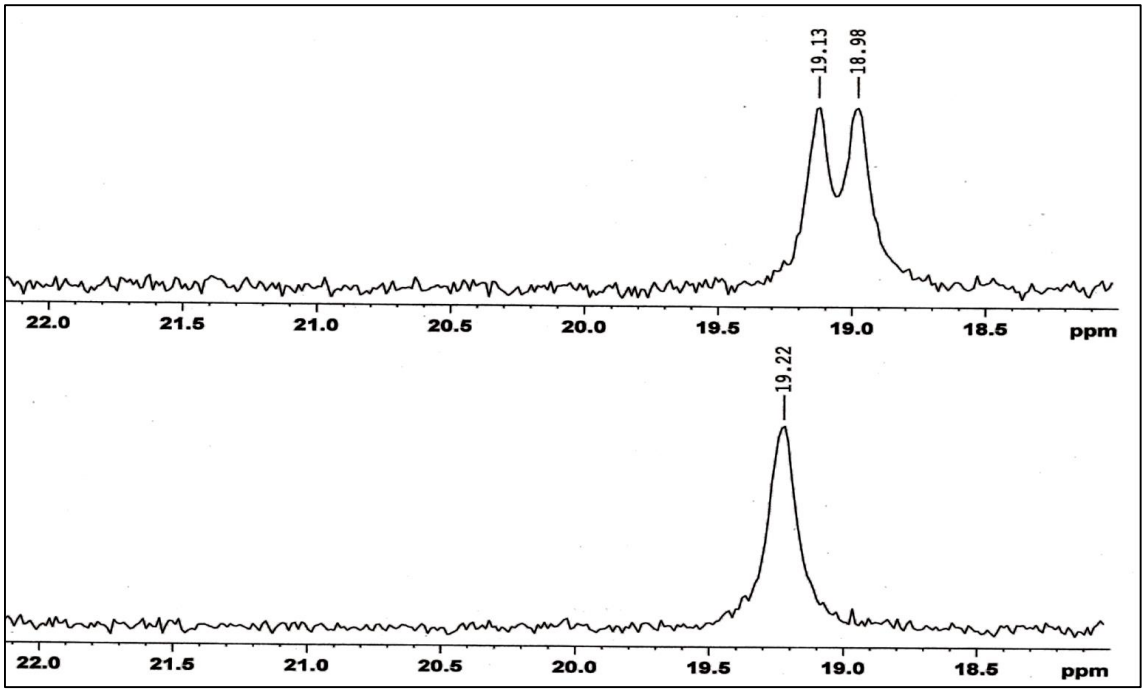


Figure 43: ^{31}P NMR Spectra of **6b** with **1a** (top) and **6b** with **1b** (bottom)

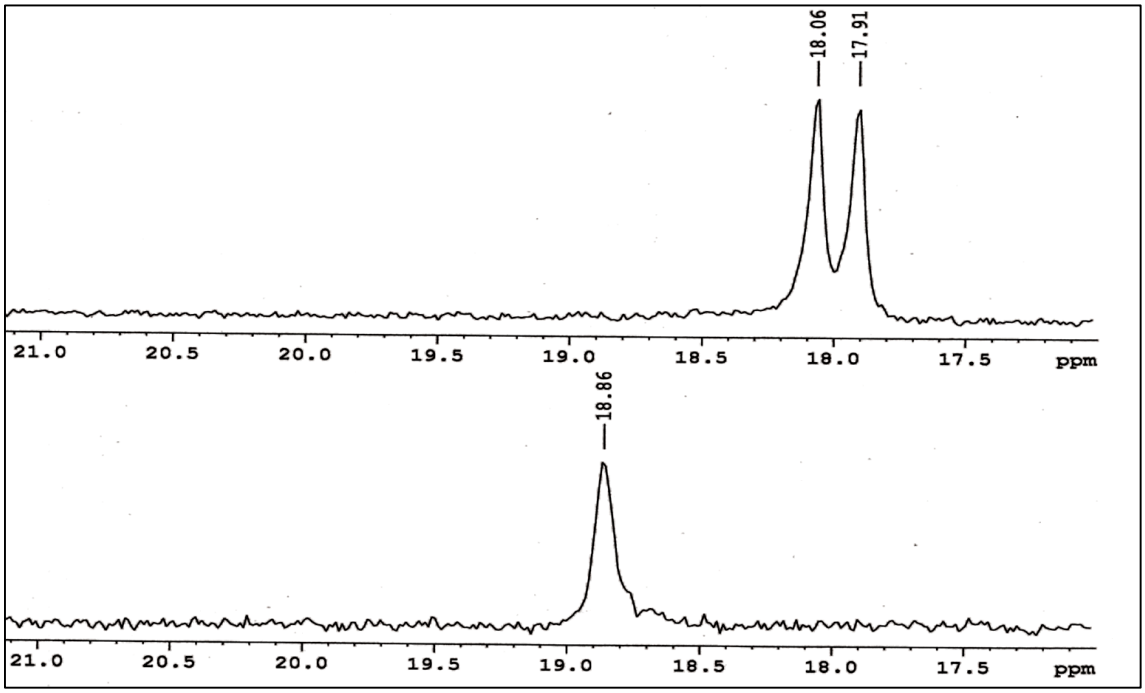


Figure 44: ^{31}P NMR Spectra of **6c** with **1a** (top) and **6c** with **1b** (bottom)

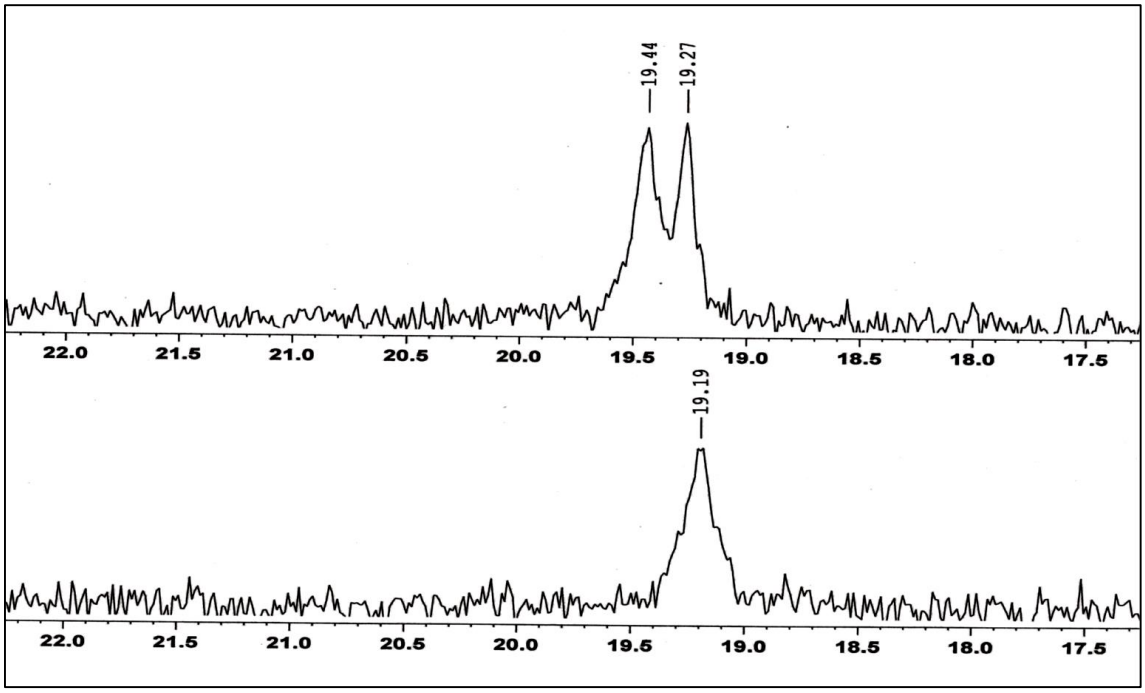


Figure 45: ^{31}P NMR Spectra of **7** with **1a** (top) and **7** with **1b** (bottom)

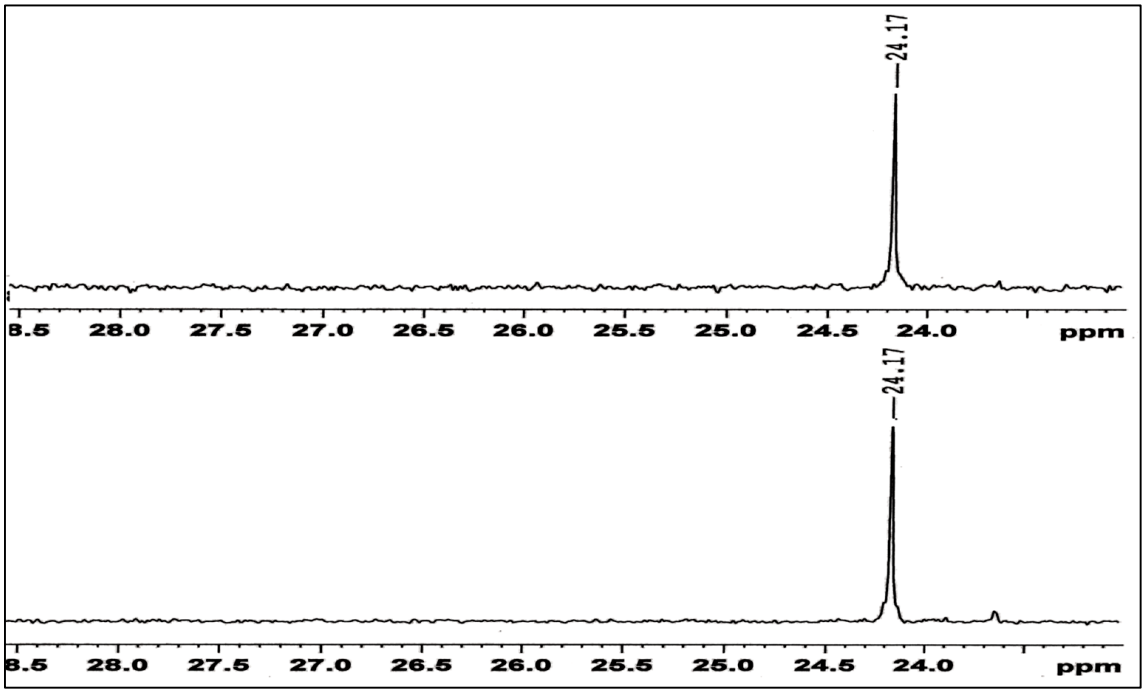


Figure 46: ^{31}P NMR Spectra of **8** with **1a** (top) and **8** with **1b** (bottom)

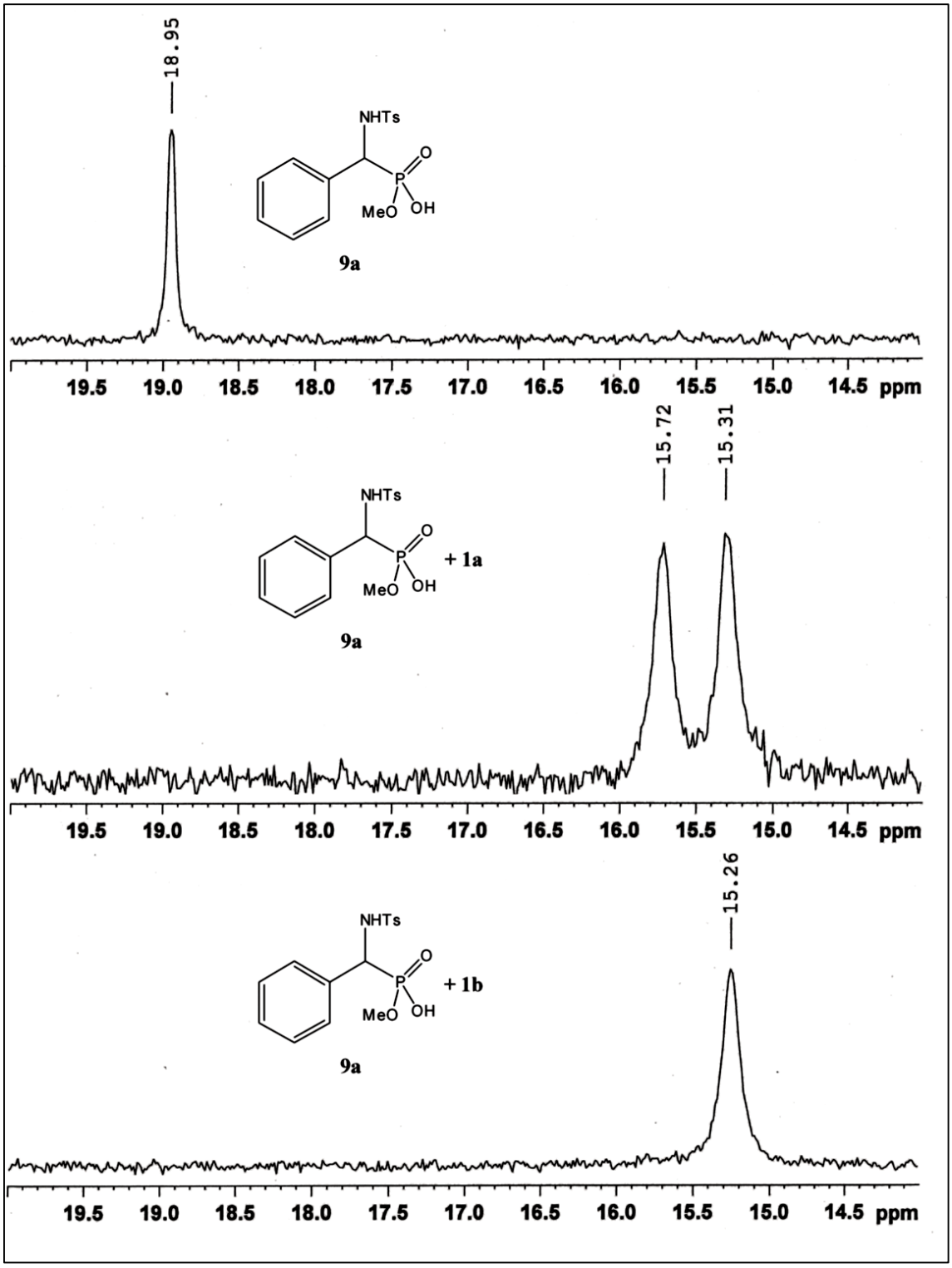


Figure 47: ^{31}P NMR Spectra of **9a** blank (top), **9a + 1a** (middle) and **9a + 1b** (bottom)

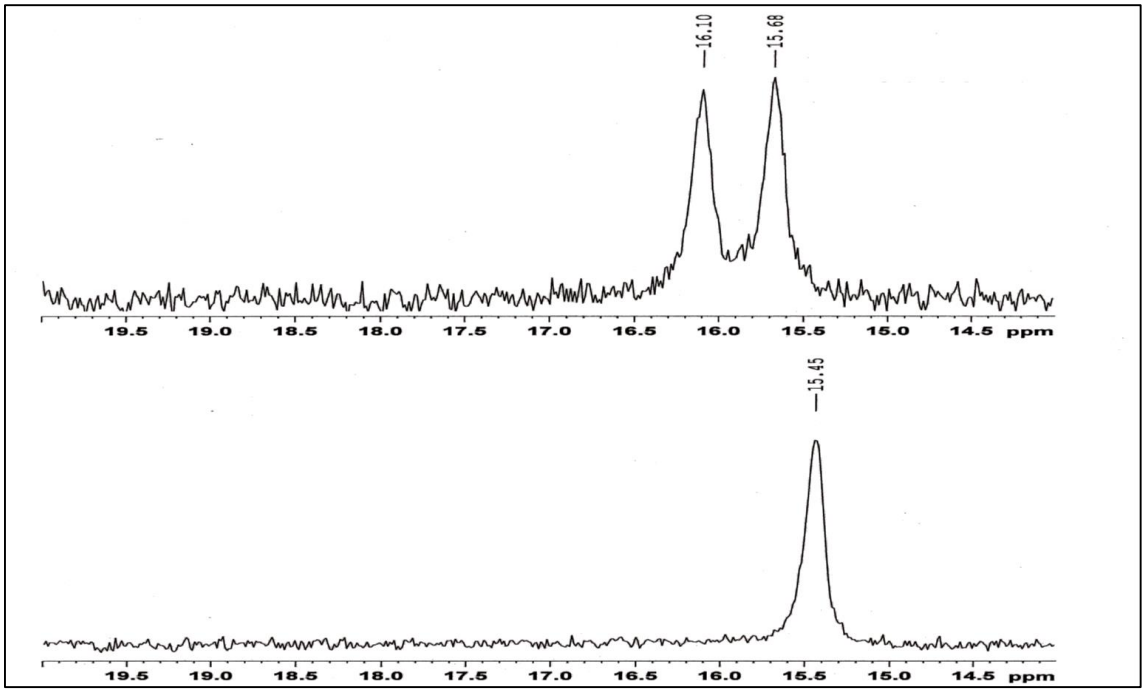


Figure 48: ^{31}P NMR Spectra of **9b** with **1a** (top) and **9b** with **1b** (bottom)

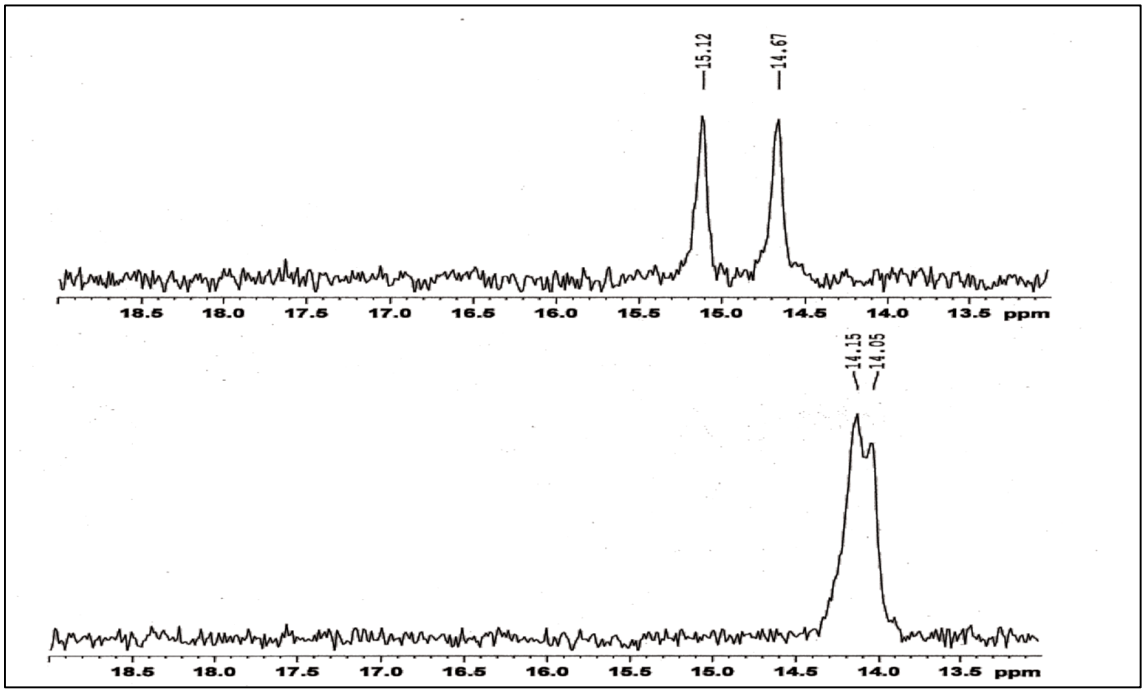


Figure 49: ^{31}P NMR Spectra of **9c** with **1a** (top) and **9c** with **1b** (bottom)

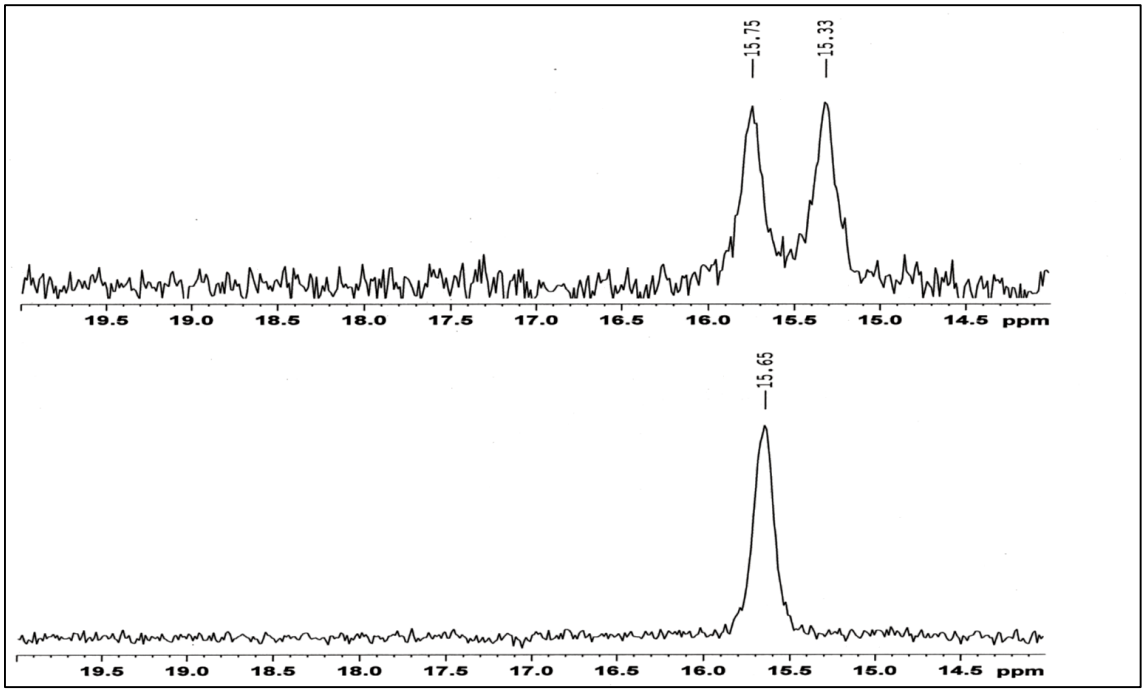


Figure 50: ^{31}P NMR Spectra of **9d** with **1a** (top) and **9d** with **1b** (bottom)

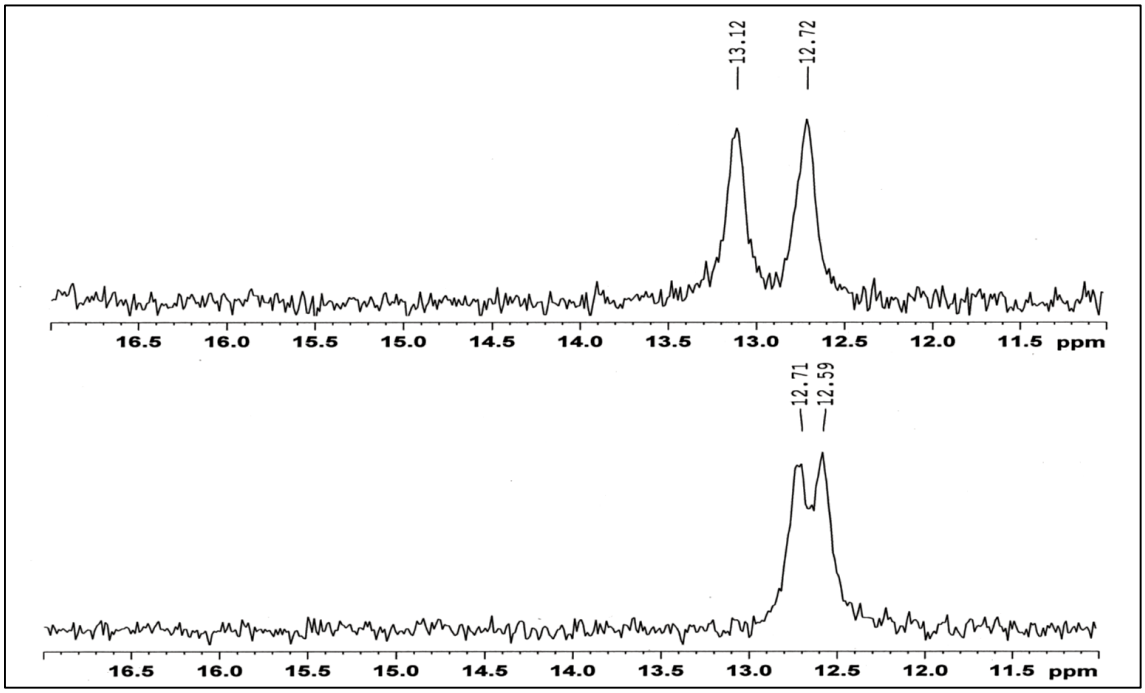


Figure 51: ^{31}P NMR Spectra of **9e** with **1a** (top) and **9e** with **1b** (bottom)

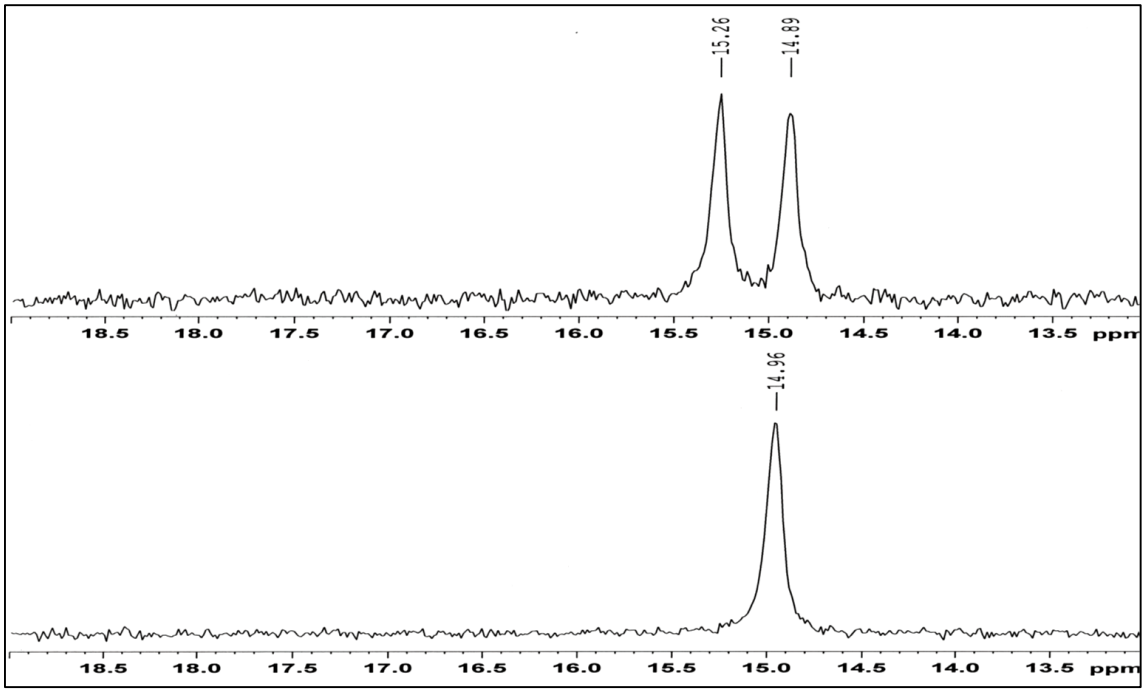


Figure 52: ^{31}P NMR Spectra of **10** with **1a** (top) and **10** with **1b** (bottom)