Supplementary Information

Impact of substituents on the crystal structures and anti-leishmanial activity of new homoleptic Bi(III) dithiocarbamates†

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Table S1.a Selected bond lengths (Å) for complexes **1**, **2**, **5**, **6**

Bond lengths	1	2	5	6
Bi(1)–S(11)	2.723(2)	2.790(3)	2.817(2)	2.770(2)
Bi(1)– S(13)	2.780(3)	2.672(3)	2.746(2)	2.725(2)
Bi(1)– S(41)	2.600(2)	2.707(3)	2.687(3)	2.673(2)
Bi(1)– S(43)	2.929(2)	2.819(3)	2.816(3)	2.817(19)
Bi(1)– S(71)	2.830(2)	3.092(3)	3.025(3)	3.014(2)
Bi(1)– S(73)	3.038(3)	3.140(3)	3.006(2)	3.151(2)
Bi(1)–S(71)[a]	3.675(3)	3.061(3)	3.269(3)	3.228(3)
Bi(1)– S(73)[a]	3.215(2)	3.124(3)	3.140(3)	3.076(2)
C(12)–N(14)	1.315(12)	1.311(15)	1.332(11)	1.330(10)
C(42)– N(44)	1.347(11)	1.352(14)	1.328(13)	1.353(9)
C(72)–N(74)	1.330(12)	1.322(16)	1.332(13)	1.333(10)
C(12)–S(11)	1.730(10)	1.711(12)	1.711(9)	1.705(8)
C(12)–S(13)	1.712(9)	1.755(13)	1.734(10)	1.718(8)
C(42)–S(41)	1.726(9)	1.734(13)	1.741(10)	1.725(8)
C(42)–S(43)	1.698(9)	1.717(12)	1.706(10)	1.689(8)
C(72)–S(71)	1.715(10)	1.734(13)	1.715(10)	1.719(8)
C(72)–S(73)	1.726(8)	1.727(13)	1.708(11)	1.719(8)
Bi(1)…Bi(1)[a]	3.8246(8)	3.7258(9)	3.8393(9)	3.7681(5)

Table S1.b Selected bond lengths (Å) for complexes **3** and **4**

Bond lengths	3	Bond lengths	4
Bi(1) – S(11)	2.787(4)	Bi(1) – S(11)	2.975(4)
Bi(1) – S(13)	2.819(4)	Bi(1) –S(13)	2.646(4)
Bi(1) – S(41)	3.038(5)	Bi(1) – S(41)	2.872(4)
Bi(1) – S(43)	2.798(4)	Bi(1) – S(43)	2.674(3)
Bi(1) – S(71)	2.894(3)	Bi(1) – S(71)	3.001(4)
Bi(1) – S(73)	2.669(4)	Bi(1) – S(73)	2.702(3)
Bi(1) – N(84)[a]	2.773(12)	Bi(1) –S(73)[a]	5.341(4)
S(11) – C(12)	1.720(15)	Bi(1) –S(71)[a]	3.355(3)
C(12) – S(13)	1.737(14)	C(12) –N(14)	1.359(18)
C(12) – N(14)	1.33(2)	C(42) – N(44)	1.300(14)
S(41) – C(42)	1.692(16)	C(72) – N(74)	1.365(16)
C(42) – N(44)	1.35(2)	C(12) –S(11)	1.635(18)
C(42) – S(43)	1.704(19)	C(12) –S(13)	1.783(14)
S(71) – C(72)	1.687(15)	C(42) –S(41)	1.715(10)
S(73) – C(72)	1.747(14)	C(42) –S(43)	1.739(12)
C(72) – N(74)	1.346(17)	C(72) –S(71)	1.697(12)
		C(72) –S(73)	1.714(13)
		Bi(1) – Bi(1)[a]	4.0597(11)

Table S1.c Selected angles (°) for complexes **1, 2, 5** and **6**

Bond Angles	**1**	**2**	**5**	**6**
S(13)– Bi(1)–S(11)	65.38(7)	65.59(9)	64.75(7)	64.96(6)
S(41)– Bi(1)– S(43)	64.79(7)	65.32(9)	65.05(7)	65.28(6)
S(71)–Bi(1)– S(73)	60.83(7)	57.63(8)	58.85(7)	57.17(5)
S(71)– Bi(1)– S(73)[a]	87.64(7)	79.44(9)	78.47(7)	82.06(6)
S(41)– Bi(1)– S(11)	85.15(8)	85.76(10)	84.91(8)	84.58(7)
S(11)– Bi(1)– S(43)	132.40(8)	135.81(8)	130.19(7)	137.13(6)
S(11)– Bi(1)– S(71)	74.02(8)	75.61(9)	83.14(7)	75.14(6)
S(11)–Bi(1)– S(71)[a]	127.69(6)	132.02(9)	133.73(7)	133.40(6)
S(11)–Bi(1)– S(73)	134.41(7)	130.16(9)	138.47(7)	130.21(6)
S(11)–Bi(1)– S(73)[a]	78.17(7)	76.22(9)	83.56(7)	78.96(7)
S(13)– Bi(1)– S(41)	89.09(8)	88.37(10)	101.54(8)	87.70(8)
S(13)– Bi(1)– S(43)	77.52(8)	80.22(10)	82.67(7)	83.22(7)
S(13)– Bi(1)– S(71)	139.35(7)	140.82(9)	143.67(7)	139.50(6)
S(13)– Bi(1)– S(71)[a]	76.69(6)	96.80(9)	87.27(7)	96.91(7)
S(13)– Bi(1)– S(73)[a]	82.28(7)	86.18(9)	81.33(7)	83.82(7)
S(13)– Bi(1)– S(73)	159.65(7)	160.93(9)	156.40(7)	162.92(6)
S(41)– Bi(1)– S(71)	89.63(8)	94.14(9)	91.53(8)	95.44(7)
S(41)– Bi(1)–S(71)[a]	144.97(7)	140.37(9)	138.79(7)	139.78(6)
S(41)– Bi(1)–S(73)	88.37(8)	82.91(9)	80.41(7)	86.40(6)
S(41)– Bi(1)– S(73)[a]	163.22(8)	161.85(9)	165.53(7)	163.45(6)
S(43)–Bi(1)– S(71)	136.83(8)	135.72(9)	133.15(7)	134.40(6)
S(43)– Bi(1)– S(71)[a]	81.89(6)	76.86(8)	76.54(7)	75.58(5)
S(43)– Bi(1)– S(73)	83.14(7)	80.73(9)	76.85(7)	79.75(6)
S(43)–Bi(1)–S(73)[a]	126.44(6)	130.38(9)	129.38(7)	127.35(6)
S(71)[a]– Bi(1)– S(73)	76.69(6)	79.65(8)	76.74(7)	77.61(5)
S(71)[a]– Bi(1)– S(71)	109.34(5)	105.47(8)	104.94(7)	105.83(5)
S(73)– Bi(1) –S(73)[a]	104.64(6)	107.00(7)	102.72(6)	105.54(5)
C(12)– S(11)– Bi(1)	88.1(3)	86.7(4)	86.8(3)	87.2(3)
C(12)– S(13)– Bi(1)	86.6(3)	89.6(4)	88.7(3)	88.4(3)
C(42)– S(41)– Bi(1)	91.6(3)	88.9(4)	87.8(3)	89.1(3)
C(42)– S(43)– Bi(1)	81.5(3)	85.6(4)	84.3(4)	85.1(3)
C(72)– S(73)– Bi(1)	85.5(4)	83.7(4)	87.4(3)	84.5(3)
C(72)–S(73)– Bi(1)[a]	84.4(3)	84.5(4)	82.4(4)	86.8(2)
C(72)– S(71)– Bi(1)	92.6(3)	85.1(4)	86.7(4)	88.9(3)
C(72)– S(71)– Bi(1)[a]	70.4(3)	86.4(4)	78.4(3)	81.9(3)

[a]Symmetry element in 1-x, 1-y, -z in **1**; 1-x, 1-y, 1-z in **2**; 2-x, 2-y, 2-z in **5** and 1-x, 2-y, -z in **6**

Table S1.d Selected angles (°) for complexes **3** and **4**

Bond Angles (°)	**3**	**Bond Angles (°)**	**4**
S(73) – Bi(1) – N(84)[a]	154.5(3)	S(13) – Bi(1) – S(11)	63.26(11)
S(73) –Bi(1) – S(11)	77.69(12)	S(41) – Bi(1) – S(43)	64.49(9)
N(84)[a]–Bi(1) – S(11)	76.9(3)	S(71) – Bi(1) – S(73)	62.84(9)
S(73) –Bi(1) – S(43)	87.52(12)	S(41) – Bi(1) –S(11)	128.63(11)
N(84)[a]– Bi(1) – S(43)	85.7(3)	S(11) – Bi(1) – S(43)	142.82(11)
S(11) –Bi(1) – S(43)	76.64(12)	S(11) – Bi(1) – S(71)	127.44(10)
S(73) – Bi(1) – S(13)	85.07(14)	S(11) – Bi(1) – S(71)[a]	71.92(9)
N(84)[a]–Bi(1) – S(13)	84.7(4)	S(11) – Bi(1) – S(73)	83.57(10)
S(11) – Bi(1) – S(13)	64.11(11)	S(13) – Bi(1) – S(41)	96.89(14)
S(43) –Bi(1) – S(13)	140.74(12)	S(13) – Bi(1) – S(43)	81.73(11)
S(73) –Bi(1) – S(71)	64.36(11)	S(13) – Bi(1) – S(71)	107.94(10)
N(84)[a] –Bi(1) – S(71)	137.3(3)	S(13) – Bi(1) –S(71)[a]	151.23(10)
S(11) – Bi(1) –S(71)	132.44(12)	S(13) – Bi(1) – S(73)	95.89(12)
S(43) – Bi(1) – S(71)	126.20(11)	S(41) – Bi(1) – S(71)	93.42(11)
S(13) – Bi(1) –S(71)	84.29(11)	S(41) – Bi(1) – S(71)[a]	70.73(9)
S(73) – Bi(1) – S(41)	110.24(13)	S(41) – Bi(1) – S(73)	147.66(10)
N(84)[a]– Bi(1) – S(41)	87.7(3)	S(43) – Bi(1) –S(71)	135.05(9)
S(11) – Bi(1) – S(41)	135.82(11)	S(43) –Bi(1) – S(71)[a]	78.64(9)
S(43) – Bi(1) – S(41)	60.94(12)	S(43) –Bi(1) –S(73)	88.23(10)
S(13) –Bi(1) – S(41)	155.91(12)	S(71)[a]– Bi(1) – S(73)	132.07(10)
S(71) – Bi(1) – S(41)	85.92(12)	S(71)[a]–Bi(1) –S(71)	100.82(7)
C(12) –S(11) –Bi(1)	89.1(5)	C(12) – S(11) – Bi(1)	84.2(5)
C(12) – S(13) – Bi(1)	87,7(5)	C(12) – S(13) –Bi(1)	92.2(6)
C(42) – S(41) –Bi(1)	84.7(7)	C(42) –S(41) – Bi(1)	84.4(4)
C(42) – S(43) – Bi(1)	92.5(6)	C(42) –S(43) – Bi(1)	90.3(4)
C(72) –S(71) – Bi(1)	84.9(4)	C(72) – S(73) – Bi(1)	92.3(4)
C(72) – S(73) –Bi(1)	91.1(5)	C(72) – S(71) – Bi(1)	82.8(4)
		C(72) – S(71) – Bi(1)[a]	128.5(4)

[a]Symmetry element -1+x, y, z

[a] Symmetry element 1-x,1-y,1-z

Table S2: Weak secondary interactions and their parameters observed in compounds **1**–**6**

Donor (D)-acceptor (A) hydrogen bonds (Å, °)					
Complex	**D–H···A**	**d(H···A)**	**d(D···A)**	**∠D–H···A**	**Symmetry Element**
1	C(21)–H(21A)···O(59)	2.49	3.338(12)	145	½-x, -½+y,½-z
	C(27)–H(27)··· O(89)	2.47	3.314(14)	150	-½-x, ½-y,½+z
	C(87)–H(87)···O(29)	2.45	3.343(14)	158	½+x, 3/2-y,-½-z
	C(21)-H(21B)···O(33)	2.62	3.272(12)	125	x,y,z
	C(94)-H(94)···O(30)	2.57	3.178(16)	123	-x, 2-y,-z
2	C(54)–H(54)···Cl(38)	2.87	3.646(18)	141	2-x,-y,-z
	C(91)–H(91B)···N(56)	2.66	3.391(18)	132	-1+x,y,z
	C(96)-H(96)···Cl(68)	2.94	3.603(15)	129	-1+x,y,z
3	C(26)–H(26)···Br (9B)	2.88	3.52(3)	127	-1+x,y,z
	C(57A)–H(57A)···Br (5A)	2.46	3.00(3)	117	2-x,1-y,1-z
	C(97)–H(97)···N(68)	2.51	3.42(2)	164	x,y,1+z

Complex	**H···H**	**H···H**	**Symmetry element**
1	H(96)···H(26)	2.23	½+x,3/2-y,-1/2+z
4	H(69C)···H(53A)	2.18	2-x,-y,1-z
Complex	**C–H···π**	**C–H···π**	**Symmetry element**
1	C(66)–H(66)··· π (furan ring)	2.65	-x, 1-y, -z
	C(35)–H(35)··· π (furan ring)	2.77	-x, 1-y, -z
2	C(21)–H(21B)··· π(C32–C37)	3.09	1-x,-y, 1-z
	C(31)–H(31B)··· π(C62–C67)	3.43	2-x,1-y,1-z
	C(33)–H(33)··· π(C92–C97)	2.96	1-x,1-y,1-z
3	C(34)–H(34)··· π(C92–C97)	3.23	x,y,z
	C(86)–H(86)··· π(C52A–C57A)	2.48	2-x,1-y,1-z
4	C(34)–H(34)··· π(C92–C97)	3.43	x,y,1+z
	C(39)–H(39A)··· π(C92–C97)	2.97	x,y,1+z
	C(100)–H(10B)··· π(C62–C67)	2.78	1-x,1-y,1-z
5	C(76A)–H(76A)··· π(Pyridine ring)	3.23	
6	C(64)–H(64)··· π(C22–C27)	2.94	
	C(89)–H(89A)··· π(C22–C27)	3.25	

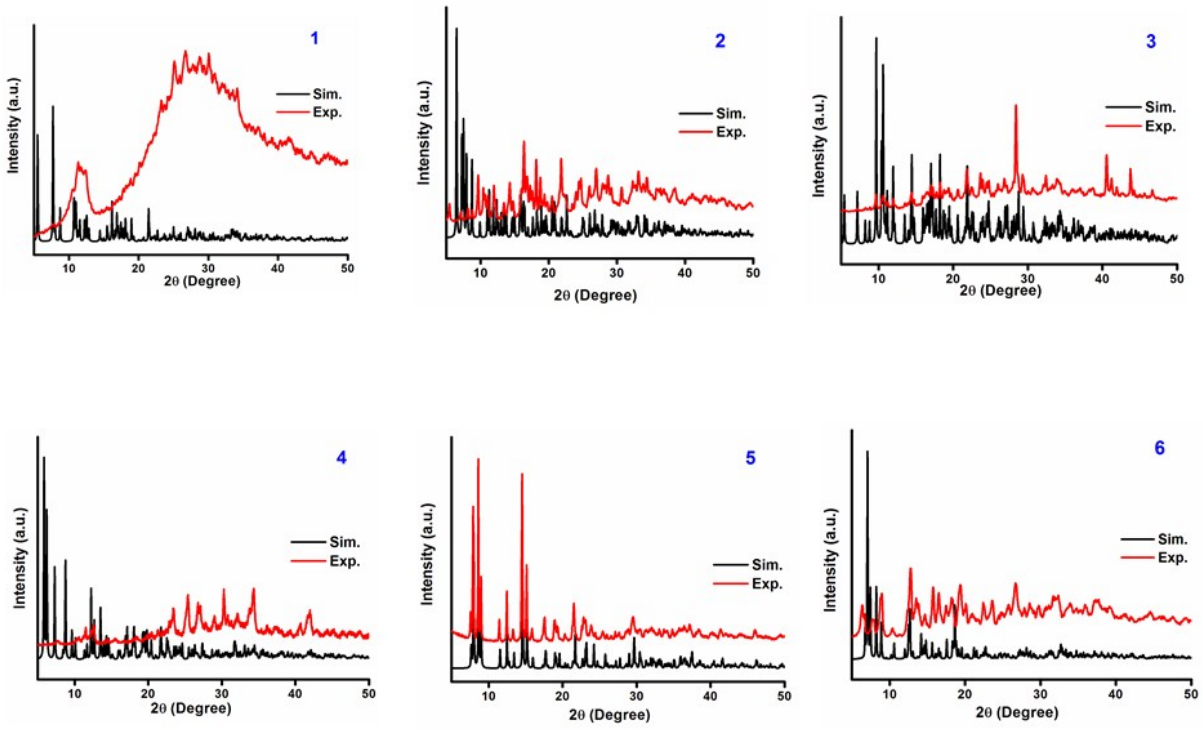


Fig. **S1**. Simulated and experimental PXRD patterns of **1–6**

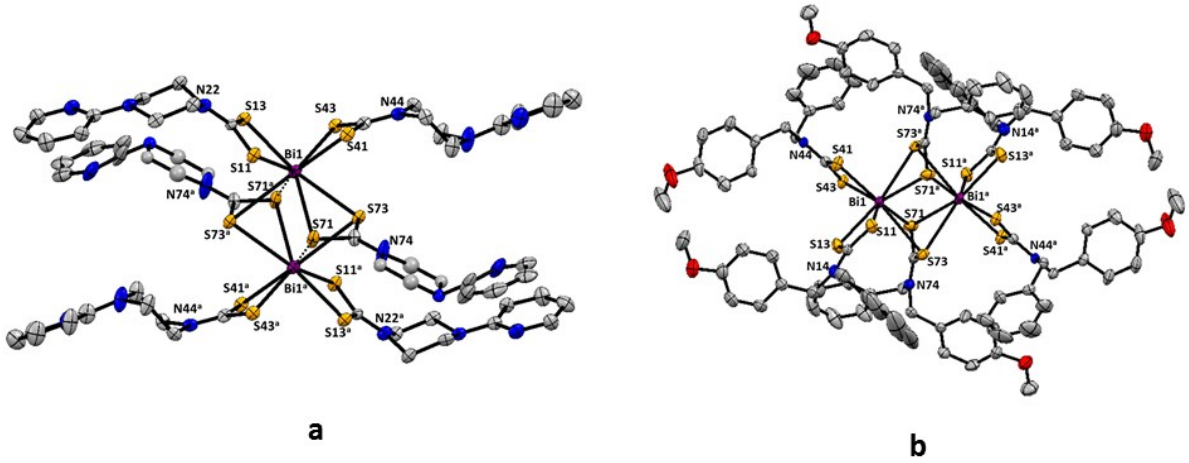


Fig. **S2**. (a) ORTEP representation of **5** and (b) complex **6** with ellipsoids shown at the 30% probability level, Hydrogen atoms are omitted for the sake of clarity.

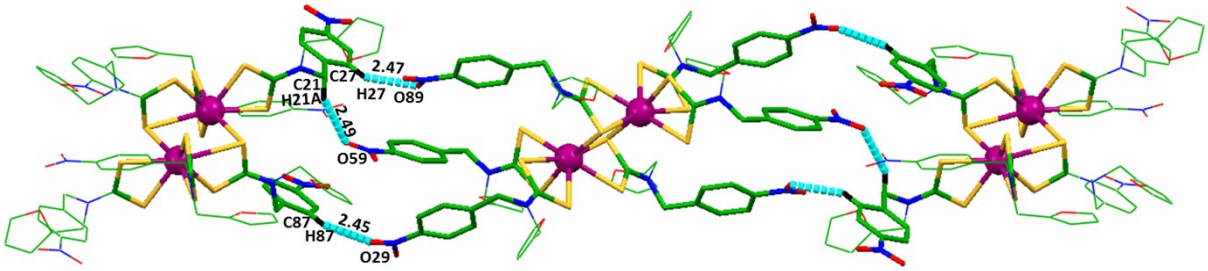


Fig. **S3**. **1** Three type of intermolecular C-H···O interactions generating 1D supramolecular network in **1**.

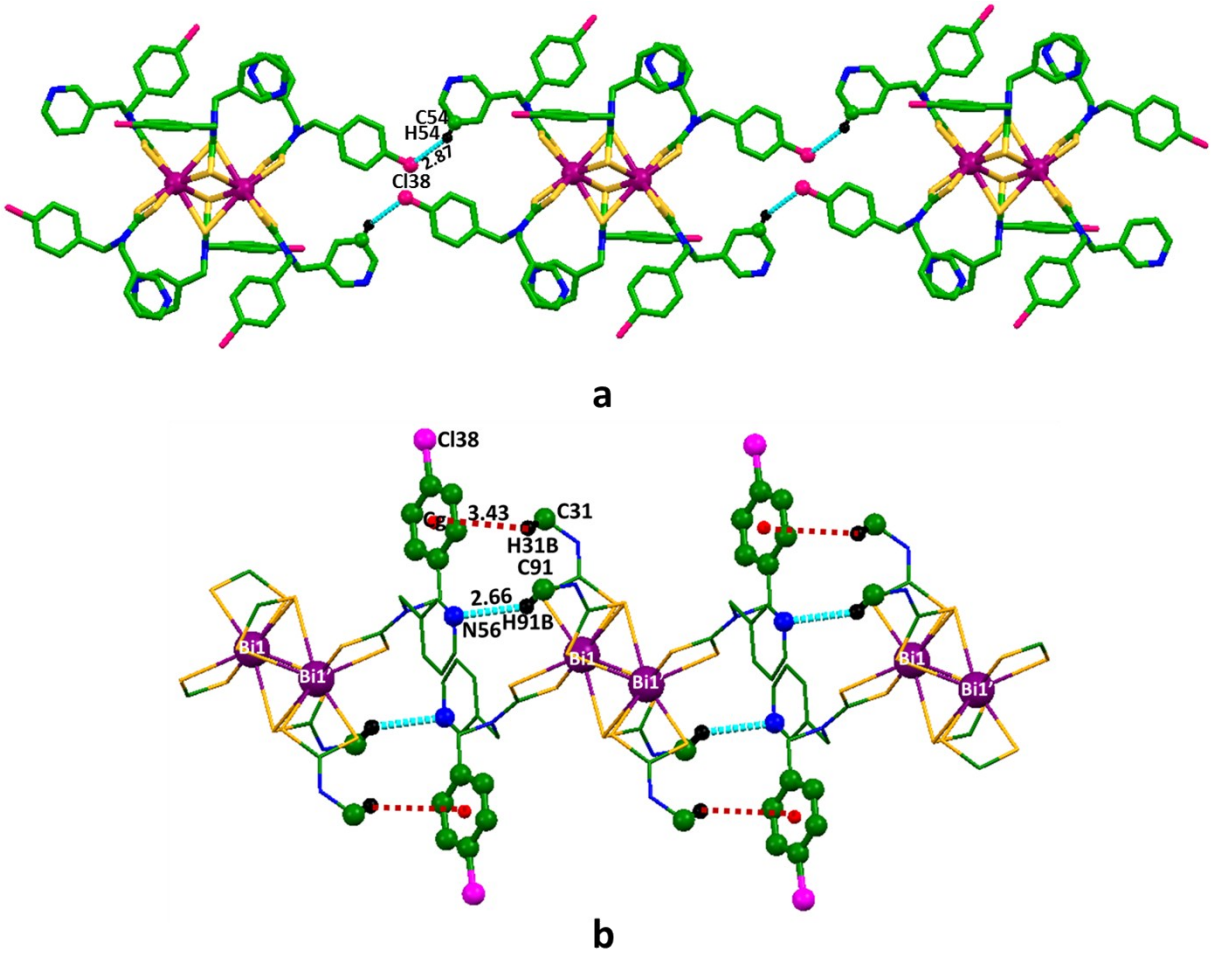


Fig. **S3**. **2** (a) The supramolecular structure sustained by intermolecular C-H···Cl and (b) C-H···N and C-H···π interactions in **2**.

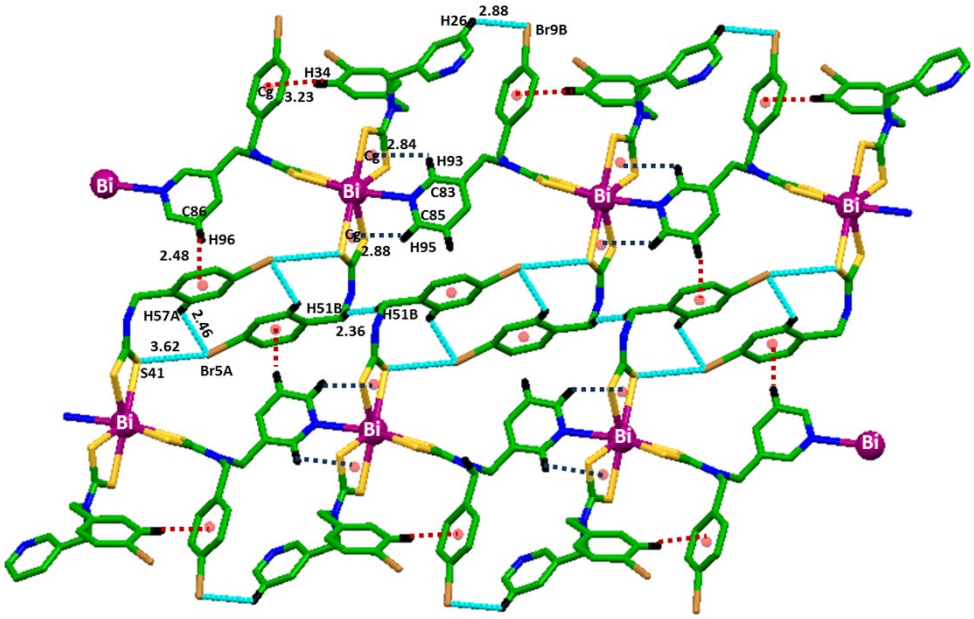


Fig. **S3**. **3** Supramolecular network sustained via C-H···Br, C-H···π and C-H···π (BiS_2C chelate) intermolecular interactions in **3**.

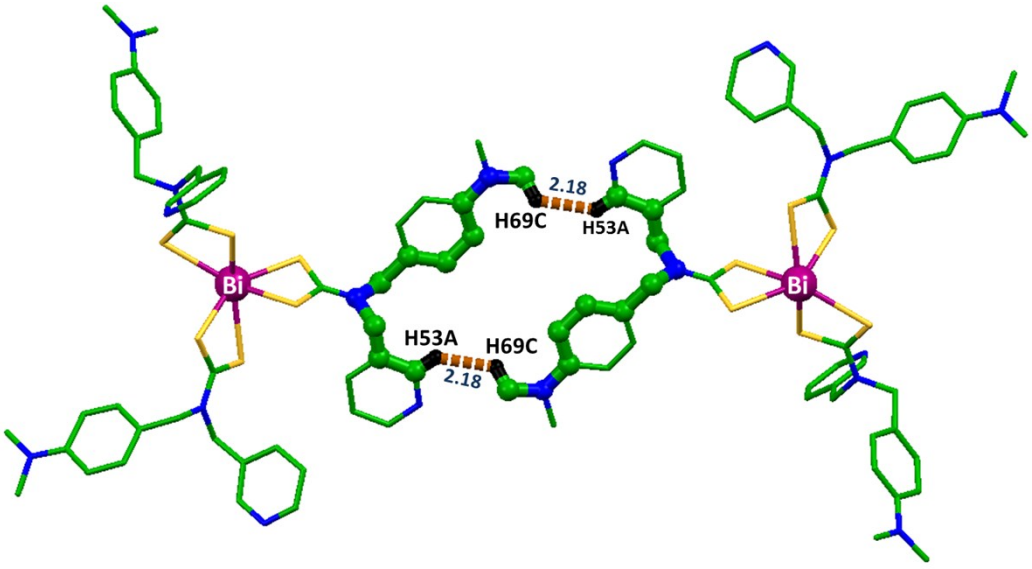


Fig. **S3**. **4** The C–H···H–C intermolecular interactions in complex **4** (Hydrogen atoms are omitted for the sake of clarity).

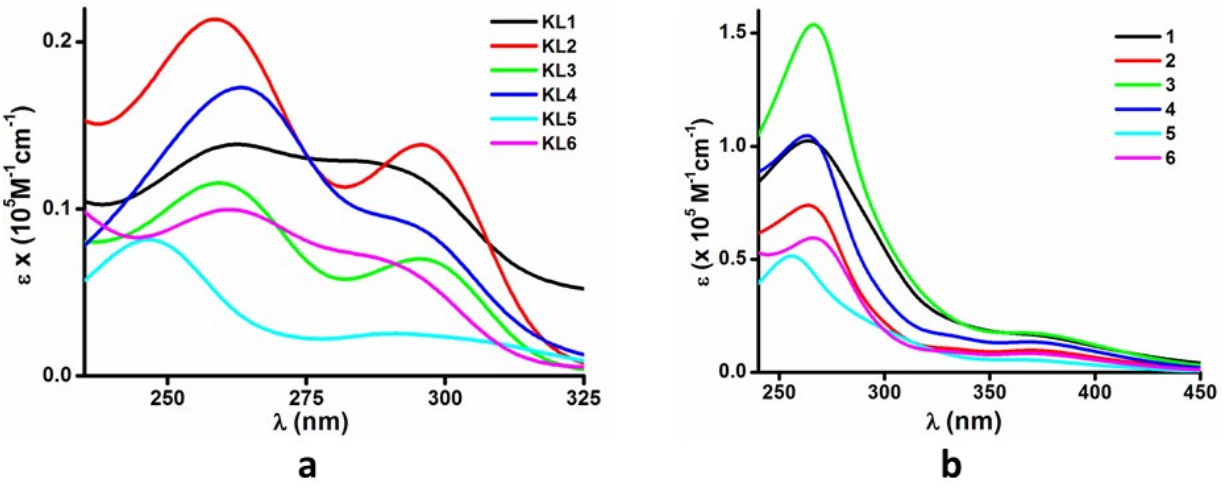
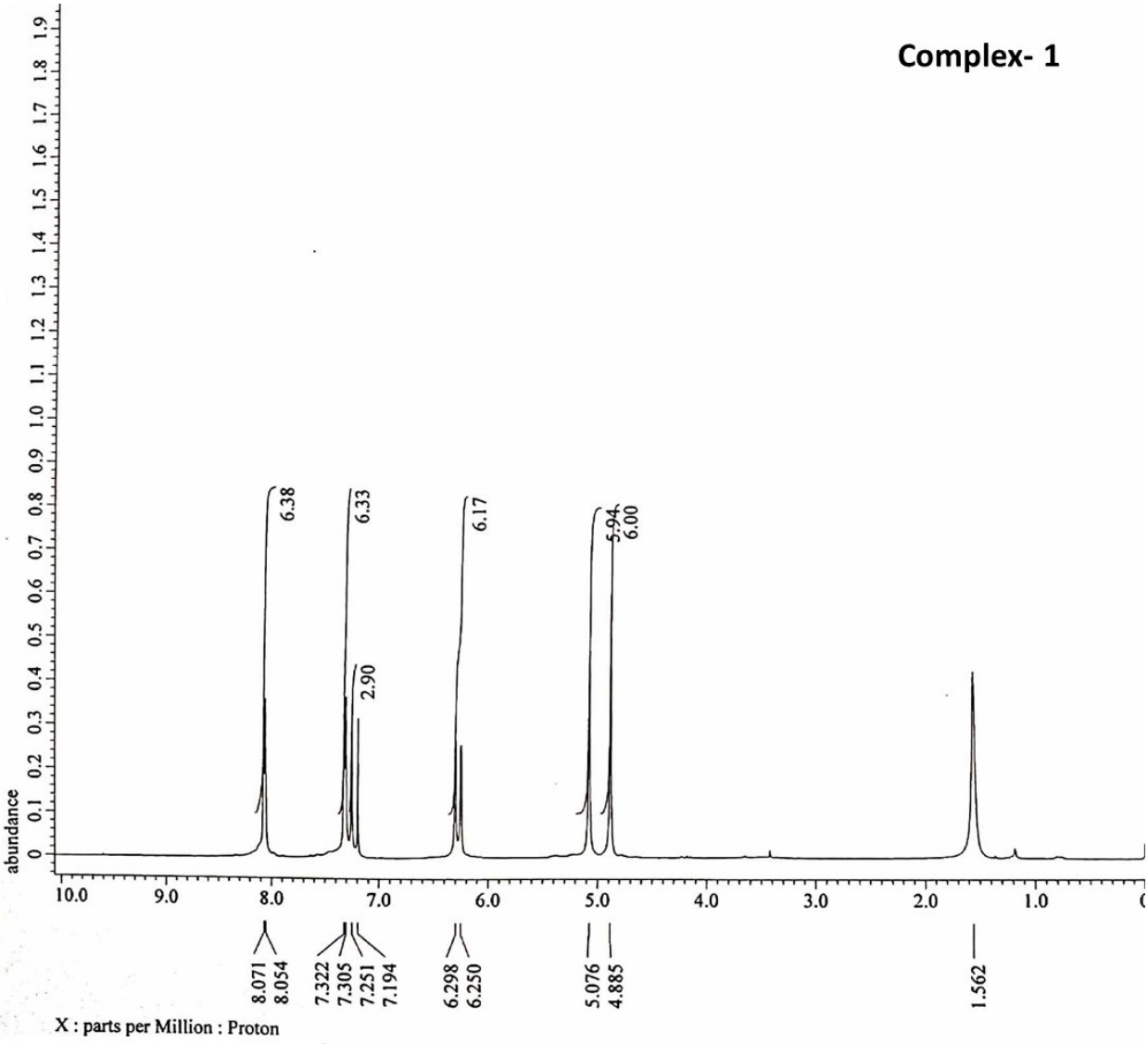
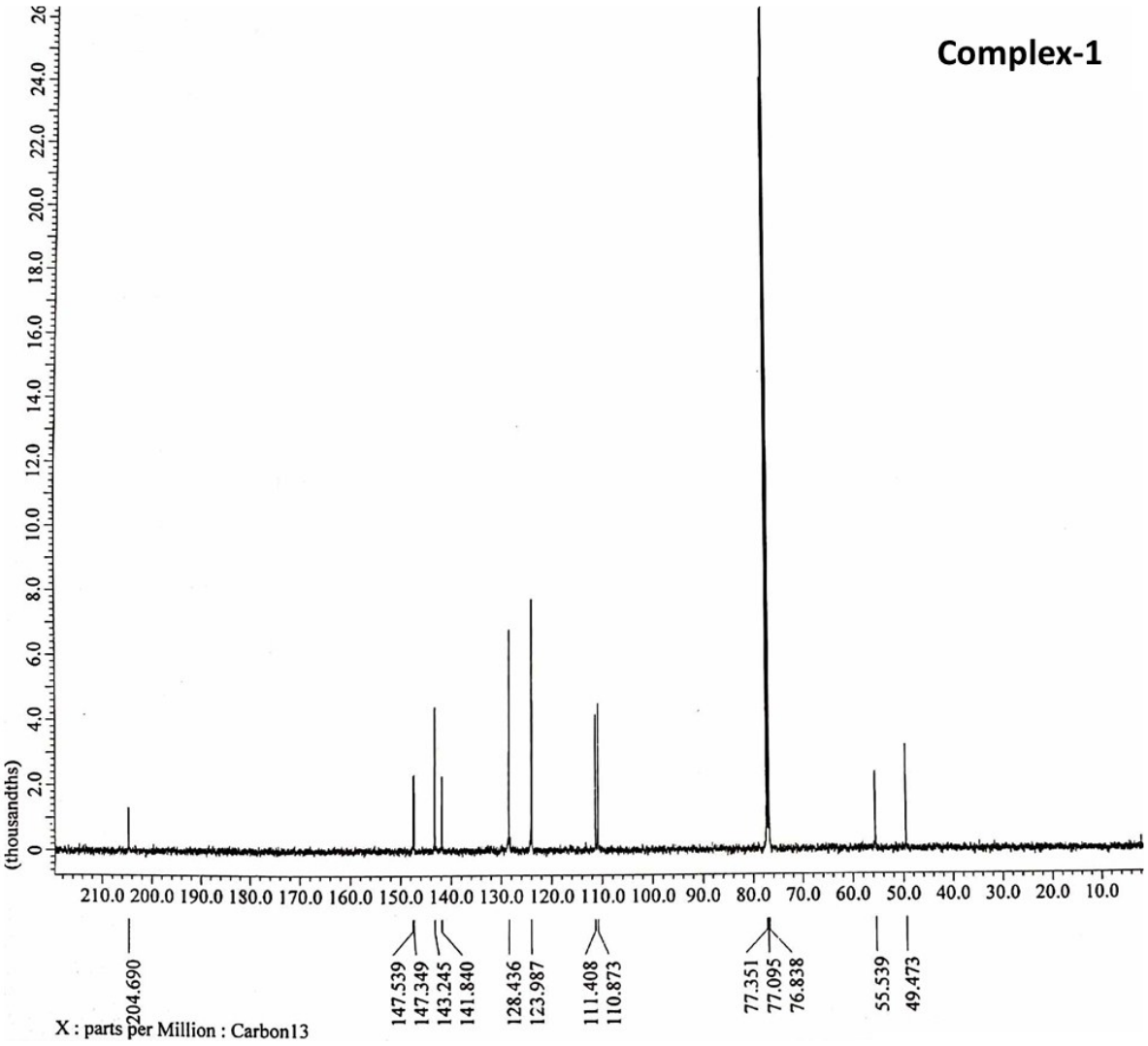


Fig. **S4** (a) UV-Vis spectra of ligands KL1–KL6 in methanol solution and (b) complexes **1-6** in CH_2Cl_2 solution at room temperature.

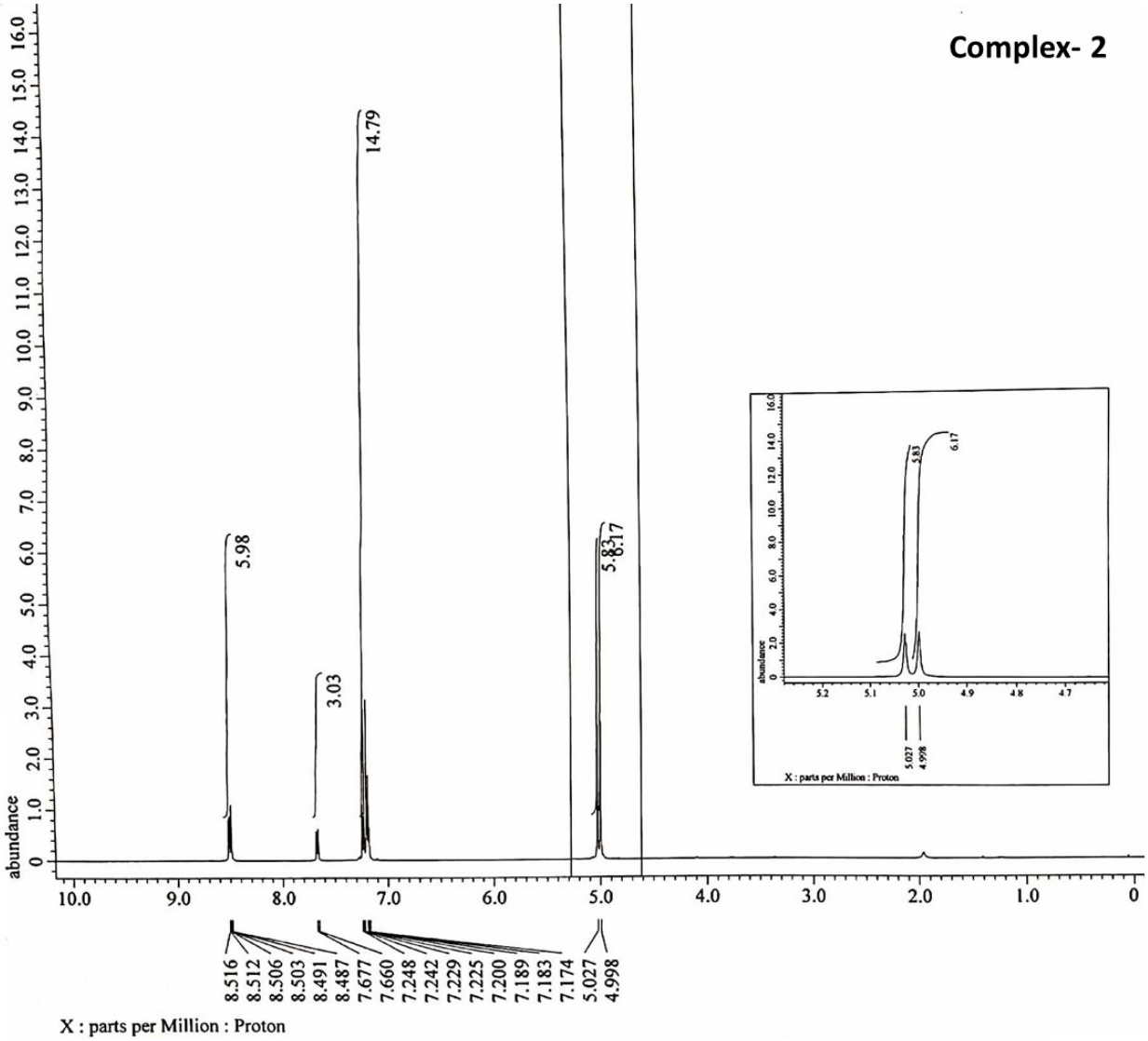
Fig. **S5** ^{1}H and ^{13}C NMR spectra of complexes**1-6**.



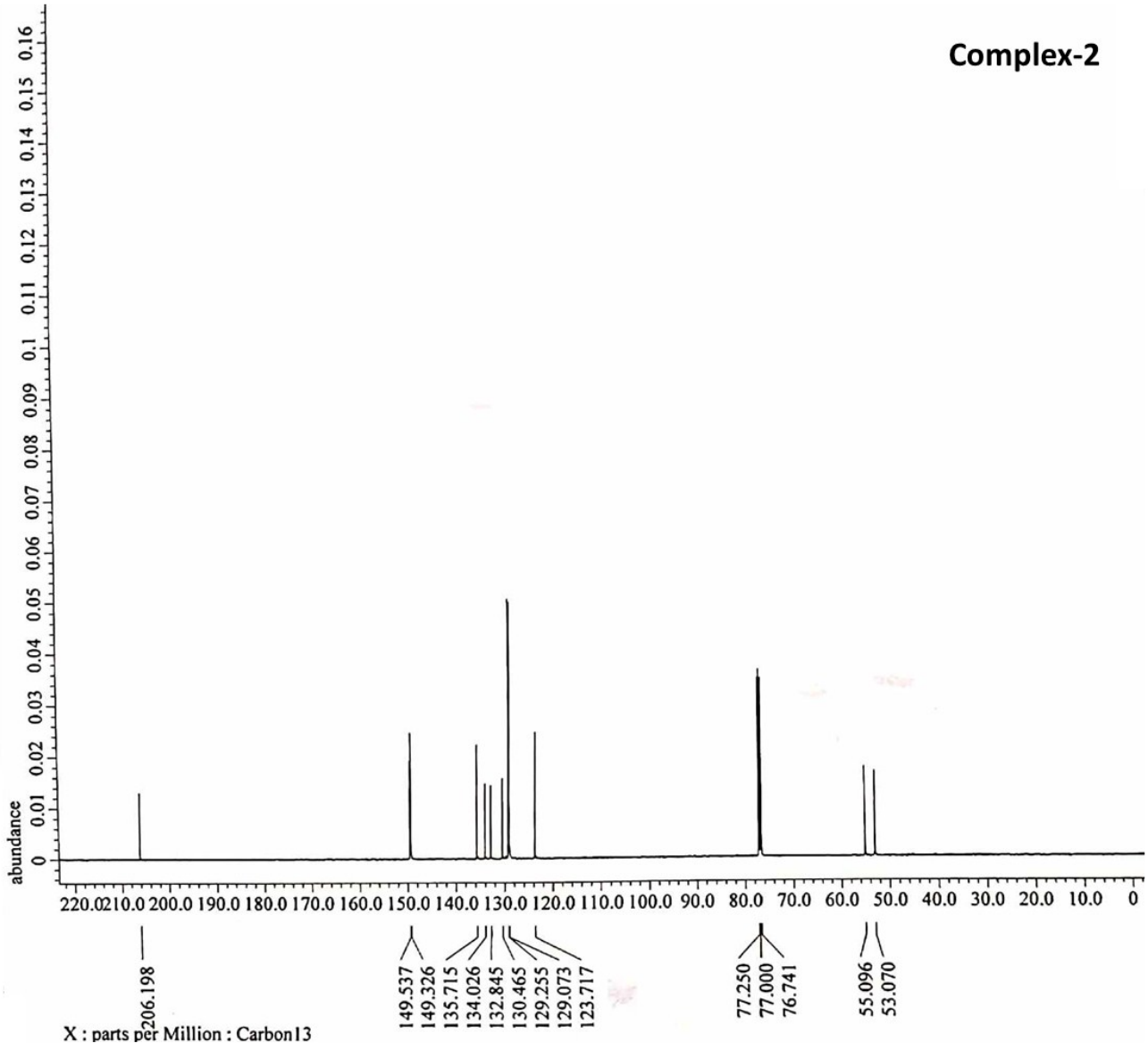
Spectrum 1: ^{1}H NMR (500.15 MHz, $CDCl_3$) of complex **1**



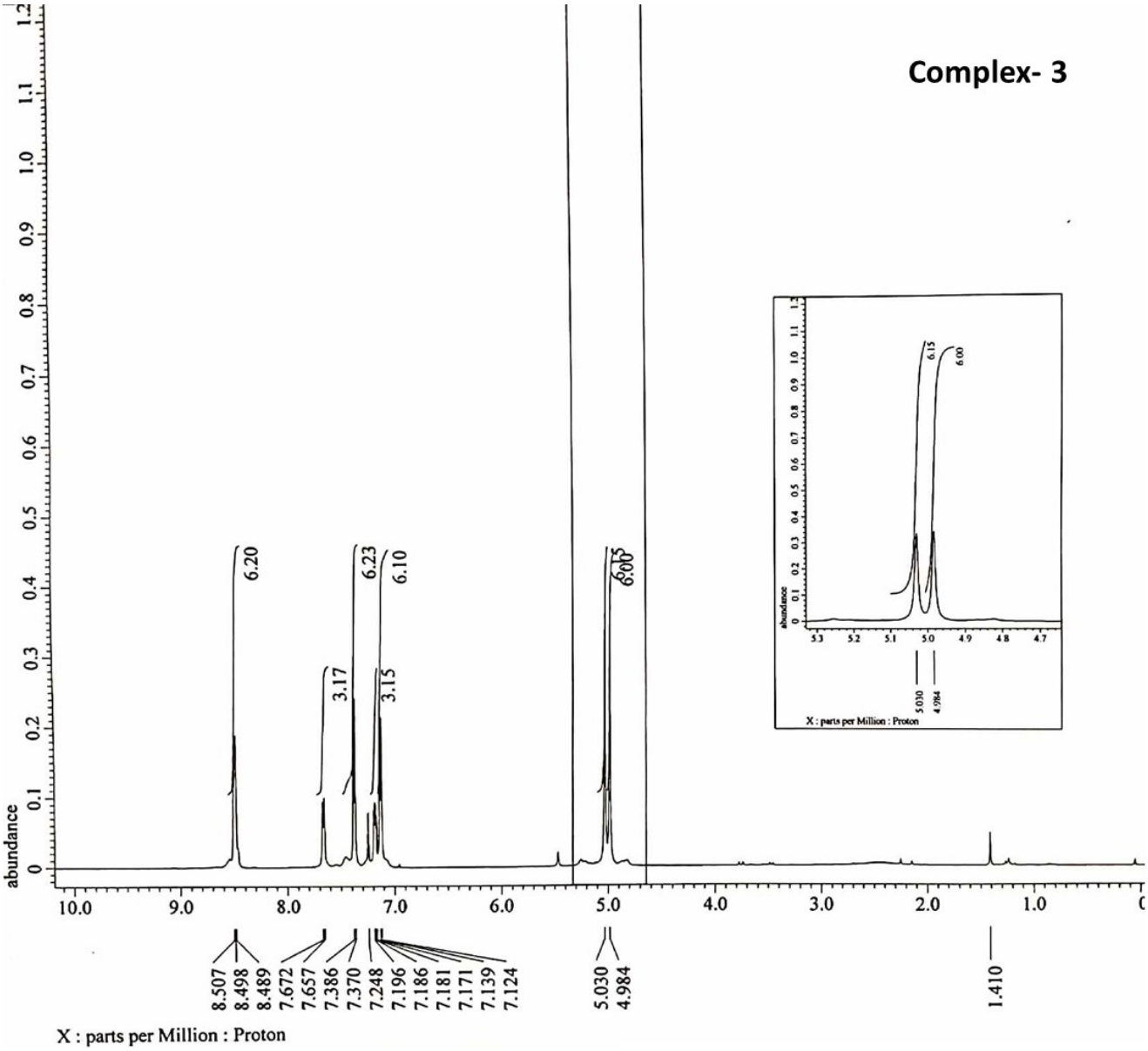
Spectrum 2: ^{13}C NMR (125.76 MHz, $CDCl_3$) of complex **1**



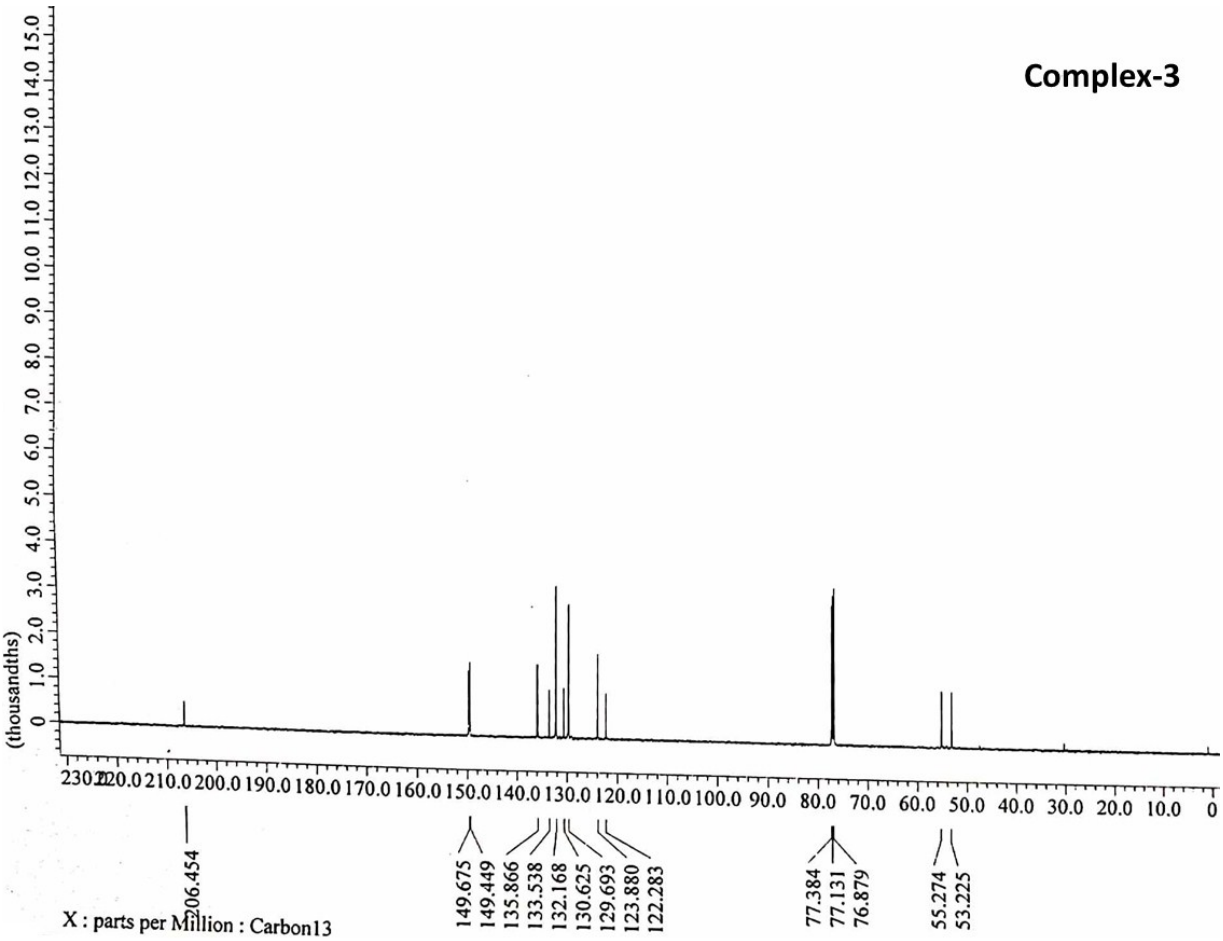
Spectrum 3: ^{1}H NMR (500.15 MHz, $CDCl_3$) of complex **2**.



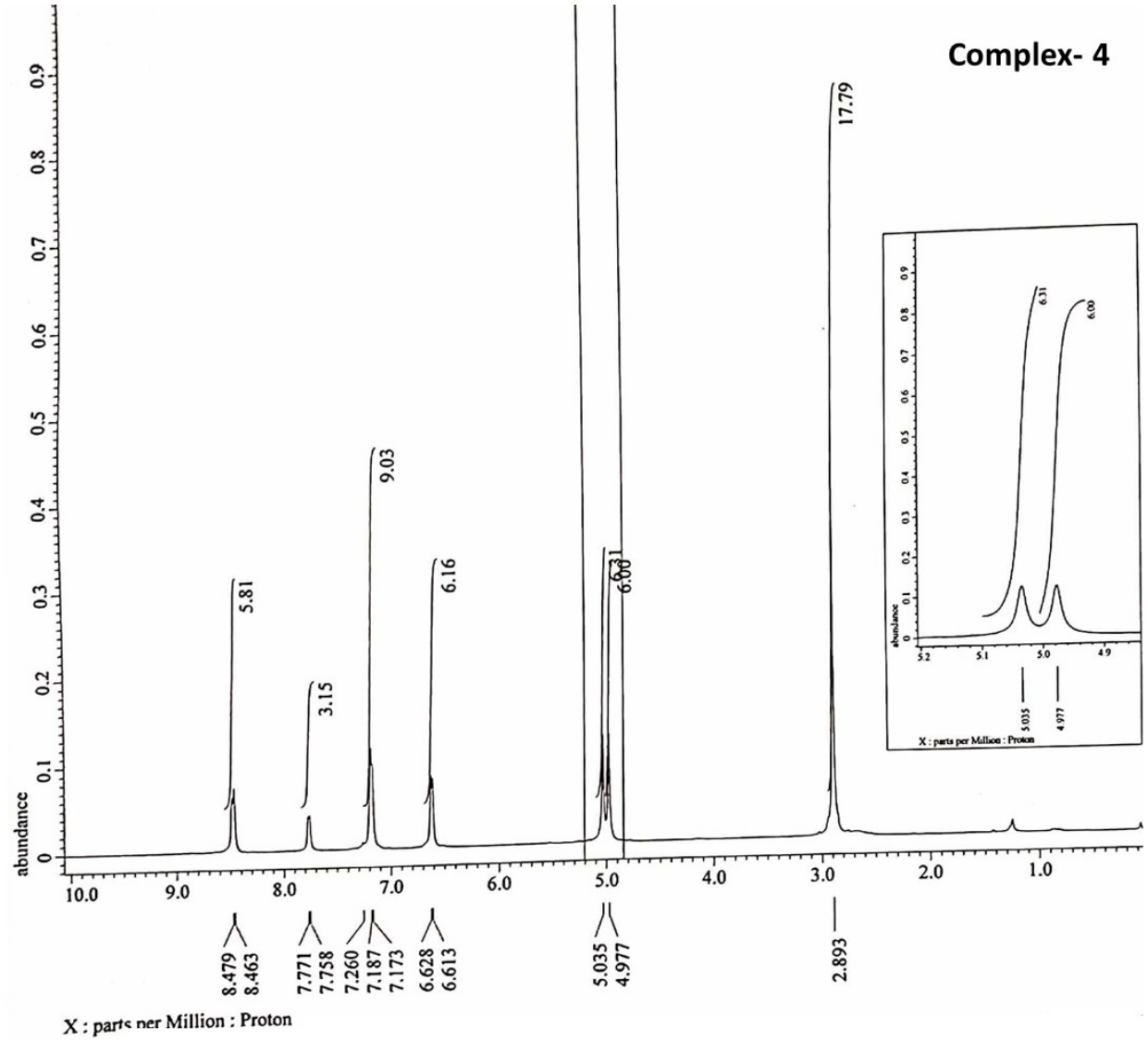
Spectrum 4: ^{13}C NMR (125.76 MHz, $CDCl_3$) of complex **2**



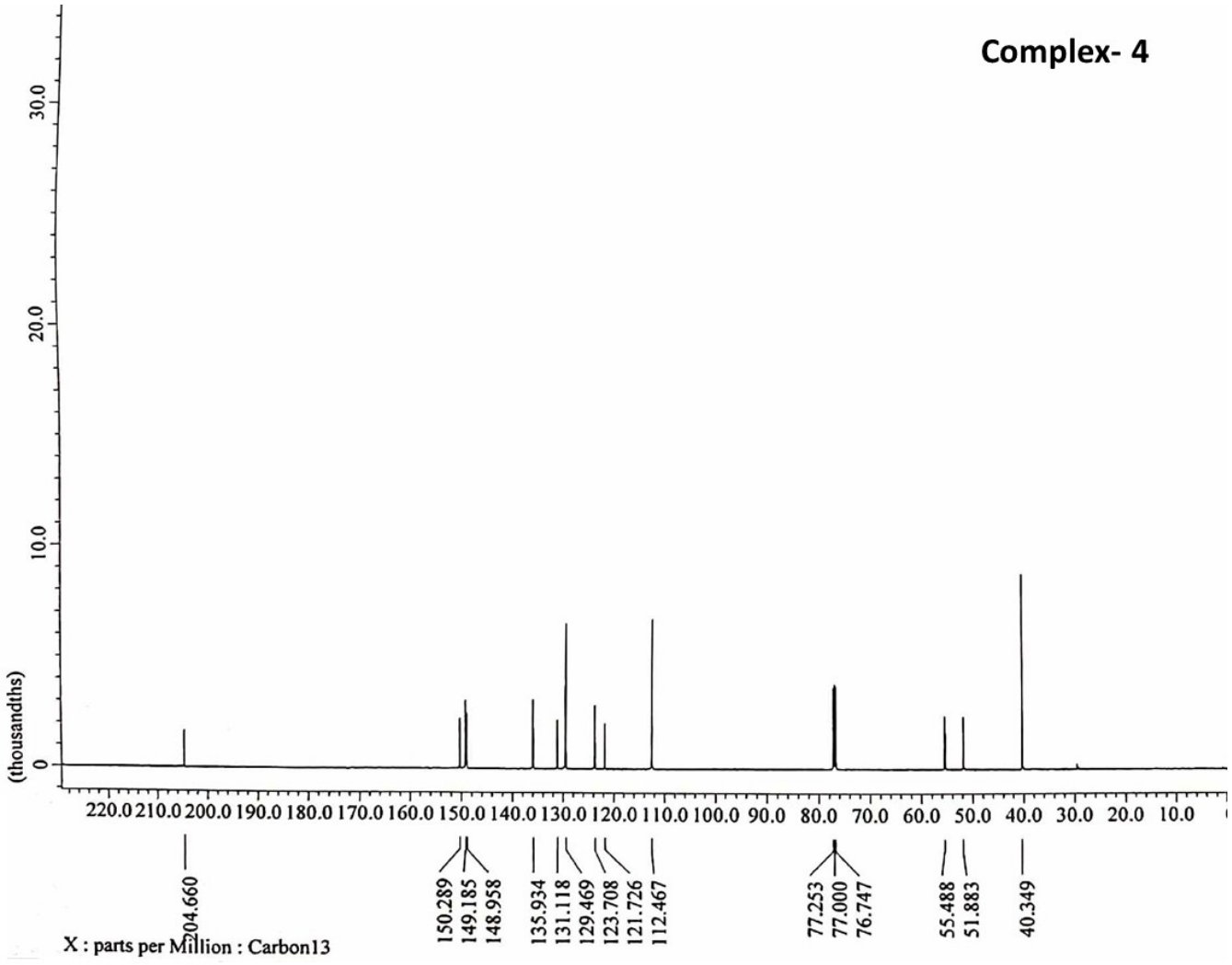
Spectrum 5: ^{1}H NMR (500.15 MHz, $CDCl_3$) of complex **3**.



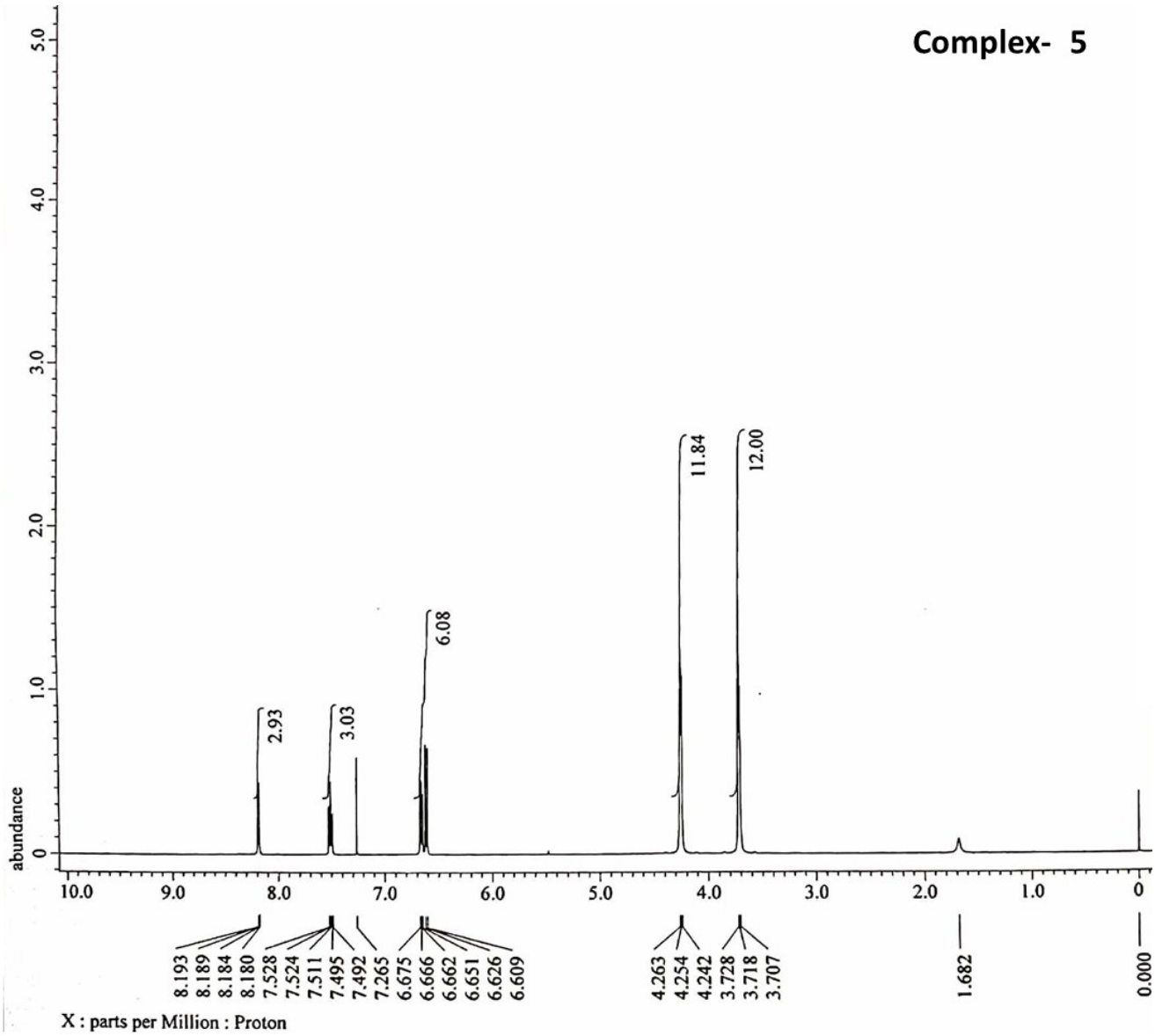
Spectrum 6: ^{13}C NMR (125.76 MHz, $CDCl_3$) of complex **3**



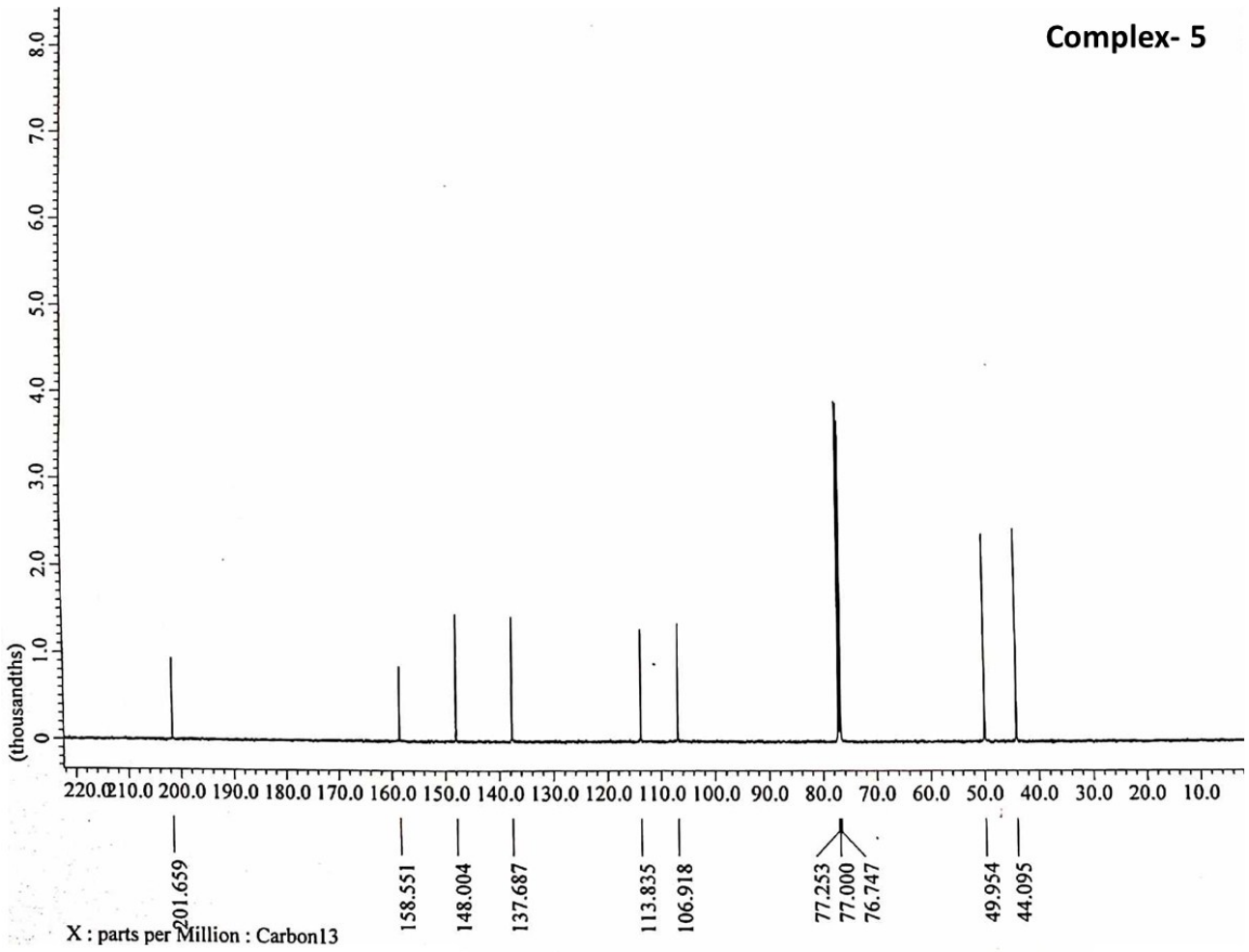
Spectrum 7: ^{1}H NMR (500.15 MHz, $CDCl_3$) of complex **4**.



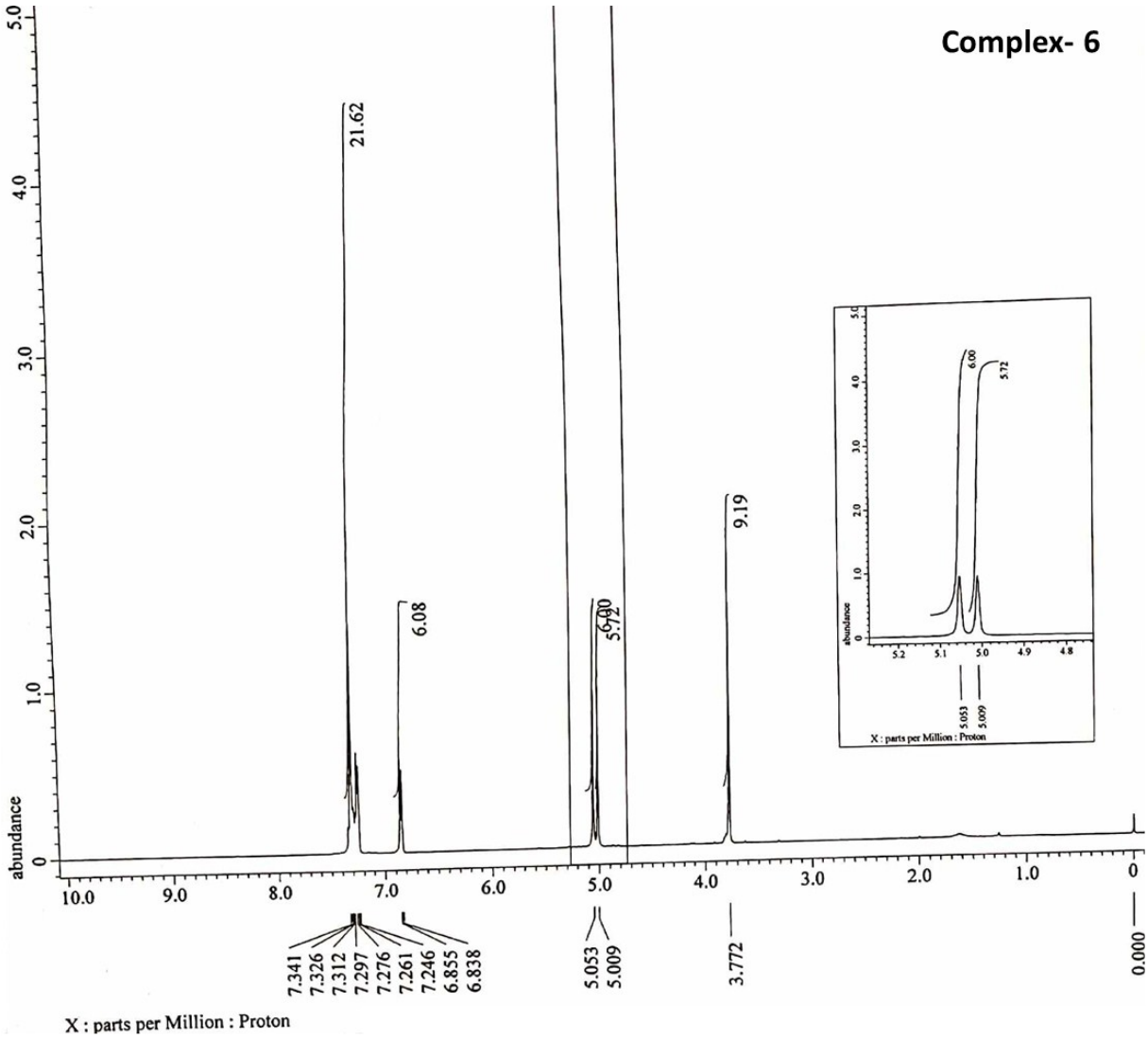
Spectrum 8: ^{13}C NMR (125.76 MHz, $CDCl_3$) of complex **4**



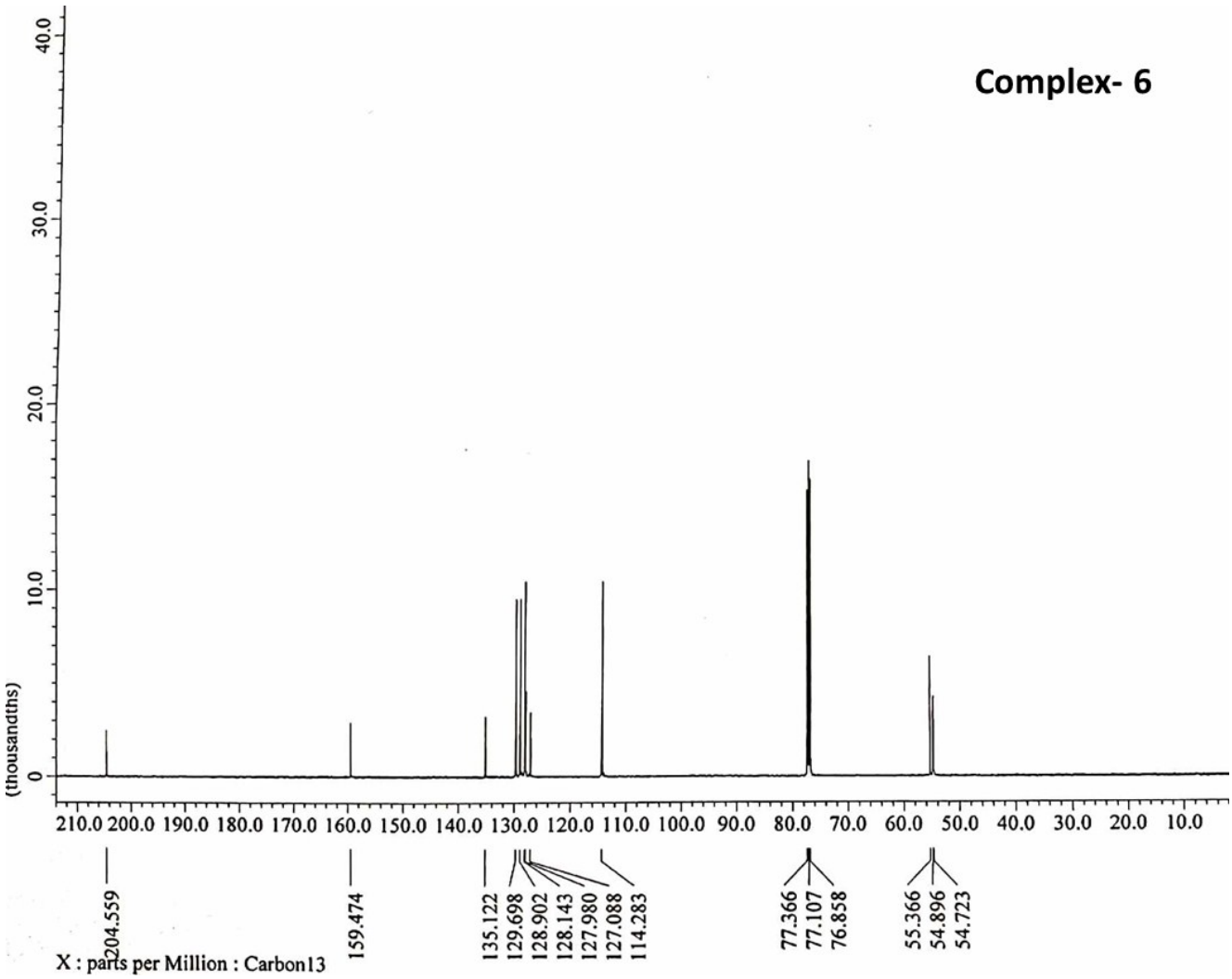
Spectrum 9: ^{1}H NMR (500.15 MHz, $CDCl_3$) of complex **5**.



Spectrum 10: ^{13}C NMR (125.76 MHz, $CDCl_3$) of complex **5**



Spectrum 11: ^{1}H NMR (500.15 MHz, $CDCl_3$) of complex **6**.



Spectrum 12: ^{13}C NMR (125.76 MHz, $CDCl_3$) of complex **6**