Supporting Information

Macrocyclic Aryl-Nickel(II) Complexes: Synthesis, Structure and Reactivity Studies

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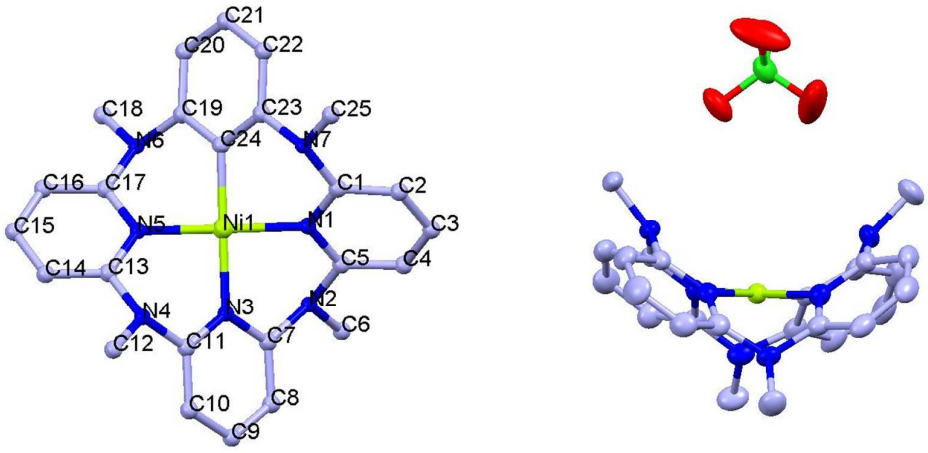


(a) **(b)**

Figure S1 Crystal structure of **2.** Hydrogens are omitted for clarity. (a) top view, (b) side view. Selected bond length (Å): C24-Ni1 1.881, N5-Ni1 1.897, N3-Ni1 1.909, N1-Ni1 1.900. N5-Ni1-C24 90.17, N1-Ni-C24 89.33, N3-Ni1-C24 178.35. The crystal was an orange plate.

Table S1. Bond lengths [Å] and angles [°] for **2**

Ni1-C24	1.881(5)	C8-C9	1.373(9)
Ni1-N5	1.897(4)	C8-H8	0.9500
Ni1-N1	1.900(5)	C9-C10	1.371(9)
Ni1-N3	1.908(5)	C9-H9	0.9500
Cl1-O4	1.372(7)	C10-C11	1.389(8)
Cl1-O1	1.391(6)	C10-H10	0.9500
Cl1-O2	1.405(5)	C12-H12A	0.9800
Cl1-O3	1.424(5)	C12-H12B	0.9800
N1-C5	1.366(7)	C12-H12C	0.9800
N1-C1	1.367(7)	C13-C14	1.400(8)
N2-C5	1.412(7)	C14-C15	1.365(9)
N2-C7	1.415(7)	C14-H14	0.9500
N2-C6	1.469(7)	C15-C16	1.375(9)
N3-C11	1.361(7)	C15-H15	0.9500
N3-C7	1.369(7)	C16-C17	1.390(8)
N4-C11	1.401(7)	C16-H16	0.9500
N4-C13	1.403(7)	C18-H18A	0.9800

N4-C12	1.477(7)	C18-H18B	0.9800
N5-C13	1.360(7)	C18-H18C	0.9800
N5-C17	1.363(7)	C19-C24	1.364(8)
N6-C17	1.401(7)	C19-C20	1.407(8)
N6-C19	1.420(8)	C20-C21	1.383(10)
N6-C18	1.465(7)	C20-H20	0.9500
N7-C1	1.391(7)	C21-C22	1.382(10)
N7-C23	1.418(8)	C21-H21	0.9500
N7-C25	1.471(7)	C22-C23	1.397(8)
C1-C2	1.386(8)	C22-H22	0.9500
C2-C3	1.358(9)	C23-C24	1.360(8)
C2-H2	0.9500	C25-H25A	0.9800
C3-C4	1.374(9)	C25-H25B	0.9800
C3-H3	0.9500	C25-H25C	0.9800
C4-C5	1.393(8)	C24-Ni1-N5	90.2(2)
C4-H4	0.9500	C24-Ni1-N1	89.3(2)
C6-H6A	0.9800	N5-Ni1-N1	178.6(2)
C6-H6B	0.9800	C24-Ni1-N3	178.3(2)
C6-H6C	0.9800	N5-Ni1-N3	90.62(19)
C7-C8	1.380(8)	N1-Ni1-N3	89.93(19)
O4-Cl1-O1	108.3(6)	C3-C4-H4	120.9
O4-Cl1-O2	109.8(5)	C5-C4-H4	120.9
O1-Cl1-O2	108.7(4)	N1-C5-C4	122.2(6)
O4-Cl1-O3	111.0(5)	N1-C5-N2	116.1(5)
O1-Cl1-O3	108.4(4)	C4-C5-N2	121.7(5)
O2-Cl1-O3	110.7(3)	N2-C6-H6A	109.5
C5-N1-C1	117.4(5)	N2-C6-H6B	109.5
C5-N1-Ni1	120.8(4)	H6A-C6-H6B	109.5
C1-N1-Ni1	121.7(4)	N2-C6-H6C	109.5
C5-N2-C7	116.2(5)	H6A-C6-H6C	109.5
C5-N2-C6	116.7(5)	H6B-C6-H6C	109.5
C7-N2-C6	115.9(5)	N3-C7-C8	121.9(5)
C11-N3-C7	118.3(5)	N3-C7-N2	115.5(5)
C11-N3-Ni1	120.8(4)	C8-C7-N2	122.5(5)
C7-N3-Ni1	120.9(4)	C9-C8-C7	118.7(6)
C11-N4-C13	119.7(4)	C9-C8-H8	120.7
C11-N4-C12	117.1(5)	C7-C8-H8	120.7
C13-N4-C12	116.7(5)	C10-C9-C8	120.6(6)

C13-N5-C17	118.4(5)	C10-C9-H9	119.7
C13-N5-Ni1	120.2(4)	C8-C9-H9	119.7
C17-N5-Ni1	121.3(4)	C9-C10-C11	119.0(6)
C17-N6-C19	116.9(5)	C9-C10-H10	120.5
C17-N6-C18	116.8(5)	C11-C10-H10	120.5
C19-N6-C18	117.9(5)	N3-C11-C10	121.4(5)
C1-N7-C23	117.6(5)	N3-C11-N4	116.7(5)
C1-N7-C25	117.2(5)	C10-C11-N4	121.9(5)
C23-N7-C25	117.5(5)	N4-C12-H12A	109.5
N1-C1-C2	121.8(6)	N4-C12-H12B	109.5
N1-C1-N7	116.3(5)	H12A-C12-H12B	109.5
C2-C1-N7	121.8(6)	N4-C12-H12C	109.5
C3-C2-C1	119.1(6)	H12A-C12-H12C	109.5
C3-C2-H2	120.4	H12B-C12-H12C	109.5
C1-C2-H2	120.4	N5-C13-C14	122.1(6)
C2-C3-C4	120.8(6)	N5-C13-N4	117.6(5)
C2-C3-H3	119.6	C14-C13-N4	120.2(5)
C4-C3-H3	119.6	C15-C14-C13	118.2(6)
C3-C4-C5	118.1(6)	C15-C14-H14	120.9
C13-C14-H14	120.9	N7-C25-H25C	109.5
C14-C15-C16	120.8(6)	H25A-C25-H25C	109.5
C14-C15-H15	119.6	H25B-C25-H25C	109.5
C16-C15-H15	119.6	C21-C20-C19	116.9(6)
C15-C16-C17	119.2(6)	C21-C20-H20	121.5
C15-C16-H16	120.4	C19-C20-H20	121.5
C17-C16-H16	120.4	C22-C21-C20	121.7(6)
N5-C17-C16	121.2(6)	C22-C21-H21	119.2
N5-C17-N6	118.1(5)	C20-C21-H21	119.2
C16-C17-N6	120.7(5)	C21-C22-C23	118.1(6)
N6-C18-H18A	109.5	C21-C22-H22	120.9
N6-C18-H18B	109.5	C23-C22-H22	120.9
H18A-C18-H18B	109.5	C24-C23-C22	122.1(6)
N6-C18-H18C	109.5	C24-C23-N7	118.1(5)
H18A-C18-H18C	109.5	C22-C23-N7	119.8(6)
H18B-C18-H18C	109.5	C23-C24-C19	118.3(5)
C24-C19-C20	122.6(6)	C23-C24-Ni1	120.9(4)
C24-C19-N6	118.5(5)	C19-C24-Ni1	120.6(4)
C20-C19-N6	118.8(6)	N7-C25-H25A	109.5

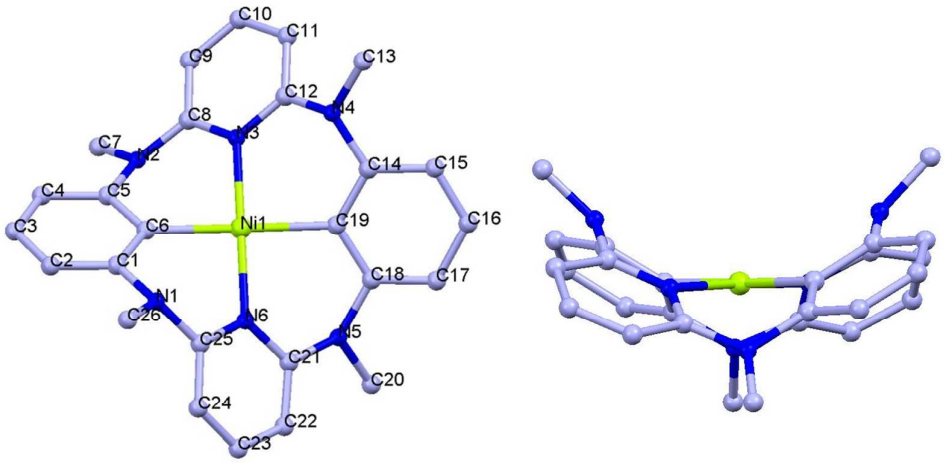
N7-C25-H25B	109.5
H25A-C25-H25B	109.5

Table S2. Torsion angles [°] for **2**

C24-Ni1-N1-C5	-139.7(4)	C6-N2-C5-N1	160.2(5)
N5-Ni1-N1-C5	151(8)	C7-N2-C5-C4	120.8(6)
N3-Ni1-N1-C5	38.8(4)	C6-N2-C5-C4	-21.7(8)
C24-Ni1-N1-C1	44.8(5)	C11-N3-C7-C8	-0.5(8)
N5-Ni1-N1-C1	-24(9)	Ni1-N3-C7-C8	179.3(4)
N3-Ni1-N1-C1	-136.7(5)	C11-N3-C7-N2	-177.7(5)
C24-Ni1-N3-C11	-158(7)	Ni1-N3-C7-N2	2.1(7)
N5-Ni1-N3-C11	-39.2(4)	C5-N2-C7-N3	55.5(7)
N1-Ni1-N3-C11	139.5(4)	C6-N2-C7-N3	-161.7(5)
C24-Ni1-N3-C7	22(7)	C5-N2-C7-C8	-121.7(6)
N5-Ni1-N3-C7	141.0(4)	C6-N2-C7-C8	21.1(8)
N1-Ni1-N3-C7	-40.4(4)	N3-C7-C8-C9	-0.7(9)
C24-Ni1-N5-C13	-140.7(4)	N2-C7-C8-C9	176.3(6)
N1-Ni1-N5-C13	-72(8)	C7-C8-C9-C10	0.7(10)
N3-Ni1-N5-C13	40.8(4)	C8-C9-C10-C11	0.5(11)
C24-Ni1-N5-C17	36.6(4)	C7-N3-C11-C10	1.9(8)
N1-Ni1-N5-C17	106(8)	Ni1-N3-C11-C10	-178.0(4)
N3-Ni1-N5-C17	-141.9(4)	C7-N3-C11-N4	-177.4(5)
C5-N1-C1-C2	-4.3(8)	Ni1-N3-C11-N4	2.8(7)
Ni1-N1-C1-C2	171.4(5)	C9-C10-C11-N3	-1.9(9)
C5-N1-C1-N7	172.9(5)	C9-C10-C11-N4	177.3(6)
Ni1-N1-C1-N7	-11.4(7)	C13-N4-C11-N3	50.1(7)
C23-N7-C1-N1	-45.1(7)	C12-N4-C11-N3	-159.2(5)
C25-N7-C1-N1	166.1(5)	C13-N4-C11-C10	-129.1(6)
C23-N7-C1-C2	132.1(6)	C12-N4-C11-C10	21.6(8)
C25-N7-C1-C2	-16.7(9)	C17-N5-C13-C14	-0.9(8)
N1-C1-C2-C3	5.8(10)	Ni1-N5-C13-C14	176.5(4)
N7-C1-C2-C3	-171.2(6)	C17-N5-C13-N4	176.4(5)
C1-C2-C3-C4	-1.2(10)	Ni1-N5-C13-N4	-6.3(7)
C2-C3-C4-C5	-4.4(9)	C11-N4-C13-N5	-48.4(7)
C1-N1-C5-C4	-1.7(8)	C12-N4-C13-N5	160.7(5)
Ni1-N1-C5-C4	-177.5(4)	C11-N4-C13-C14	128.9(6)
C1-N1-C5-N2	176.4(5)	C12-N4-C13-C14	-22.0(8)

Ni1-N1-C5-N2	0.7(7)	N5-C13-C14-C15	0.7(9)
C3-C4-C5-N1	6.0(9)	N4-C13-C14-C15	-176.5(6)
C3-C4-C5-N2	-172.0(5)	C13-C14-C15-C16	-0.5(10)
C7-N2-C5-N1	-57.3(6)	C14-C15-C16-C17	0.5(10)
C13-N5-C17-C16	0.9(8)	N3-Ni1-C24-C19	76(7)
Ni1-N5-C17-C16	-176.5(5)	N3-Ni1-C24-C23	-99(7)
C13-N5-C17-N6	179.8(5)	N5-Ni1-C24-C19	-42.7(4)
Ni1-N5-C17-N6	2.4(7)	N1-Ni1-C24-C19	138.7(4)
C15-C16-C17-N5	-0.7(9)		
C15-C16-C17-N6	-179.6(6)		
C19-N6-C17-N5	-51.7(7)		
C18-N6-C17-N5	160.7(5)		
C19-N6-C17-C16	127.3(6)		
C18-N6-C17-C16	-20.4(8)		
C17-N6-C19-C24	45.0(7)		
C18-N6-C19-C24	-167.7(5)		
C17-N6-C19-C20	-133.7(5)		
C18-N6-C19-C20	13.6(8)		
C24-C19-C20-C21	-4.9(9)		
N6-C19-C20-C21	173.8(5)		
C19-C20-C21-C22	1.0(9)		
C20-C21-C22-C23	3.2(10)		
C21-C22-C23-C24	-4.0(9)		
C21-C22-C23-N7	174.3(6)		
C1-N7-C23-C24	53.7(7)		
C25-N7-C23-C24	-157.6(6)		
C1-N7-C23-C22	-124.6(6)		
C25-N7-C23-C22	24.0(8)		
C22-C23-C24-C19	0.4(8)		
N7-C23-C24-C19	-177.9(5)		
C22-C23-C24-Ni1	175.9(4)		
N7-C23-C24-Ni1	-2.5(7)		
C20-C19-C24-C23	4.2(8)		
N6-C19-C24-C23	-174.5(5)		
C20-C19-C24-Ni1	-171.3(4)		
N6-C19-C24-Ni1	10.0(7)		
N5-Ni1-C24-C23	142.0(4)		
N1-Ni1-C24-C23	-36.7(4)		

2. X-ray crystallographic data for complex 4



（a） (b)

Figure S2 Crystal structure of **4** Hydrogens are omitted for clarity. (a) top view, (b) side view. Selected bond length (Å): C6-Ni1 2.001, C19-Ni1 2.017, N3-Ni1 2.045, N6-Ni1 2.043. N3-Ni1-C6 90.08, N6-Ni1-C6 90.15, C6-Ni1-C19 178.32. The crystal was a bright yellow plate.

Table S3. Bond lengths [Å] and angles [°] for **4**

Ni1-N3	2.045(5)	C11-H11	0.9300
Ni1-N6	2.043(5)	C11-C12	1.405(9)
Ni1-C6	2.001(7)	C13-H13A	0.9600
Ni1-C19	2.017(7)	C13-H13B	0.9600
N1-C1	1.417(9)	C13-H13C	0.9600
N1-C25	1.409(10)	C14-C15	1.400(10)
N1-C26	1.475(9)	C14-C19	1.392(10)
N2-C5	1.456(8)	C15-H15	0.9300
N2-C7	1.433(9)	C15-C16	1.382(14)
N2-C8	1.391(8)	C16-H16	0.9300
N3-C8	1.361(8)	C16-C17	1.416(13)
N3-C12	1.363(8)	C17-H17	0.9300
N4-C12	1.395(9)	C17-C18	1.371(10)
N4-C13	1.430(9)	C18-C19	1.381(11)
N4-C14	1.434(10)	C20-H20A	0.9600

N5-C18	1.440(10)	C20-H20B	0.9600
N5-C20	1.463(7)	C20-H20C	0.9600
N5-C21	1.393(10)	C21-C22	1.381(10)
N6-C21	1.381(9)	C22-H22	0.9300
N6-C25	1.365(8)	C22-C23	1.380(12)
C1-C2	1.401(10)	C23-H23	0.9300
C1-C6	1.413(9)	C23-C24	1.346(11)
C2-H2	0.9300	C24-H24	0.9300
C2-C3	1.371(12)	C24-C25	1.388(10)
C3-H3	0.9300	C26-H26A	0.9600
C3-C4	1.378(12)	C26-H26B	0.9600
C4-H4	0.9300	C26-H26C	0.9600
C4-C5	1.389(10)	N6-Ni1-N3	177.7(2)
C5-C6	1.378(9)	C6-Ni1-N3	90.1(2)
C7-H7A	0.9600	C6-Ni1-N6	90.2(2)
C7-H7B	0.9600	C6-Ni1-C19	178.3(3)
C7-H7C	0.9600	C19-Ni1-N3	90.0(3)
C8-C9	1.414(9)	C19-Ni1-N6	89.8(3)
C9-H9	0.9300	C1-N1-C26	115.9(6)
C9-C10	1.377(11)	C25-N1-C1	118.5(5)
C10-H10	0.9300	C25-N1-C26	116.6(6)
C10-C11	1.39	C7-N2-C5	116.6(6)
C8-N2-C5	121.3(5)	H7B-C7-H7C	109.5
C8-N2-C7	117.3(6)	N2-C8-C9	118.6(6)
C8-N3-Ni1	120.0(4)	N3-C8-N2	121.1(6)
C8-N3-C12	120.0(5)	N3-C8-C9	120.4(6)
C12-N3-Ni1	119.7(4)	C8-C9-H9	120.3
C12-N4-C13	115.8(6)	C10-C9-C8	119.3(7)
C12-N4-C14	118.8(6)	C10-C9-H9	120.3
C13-N4-C14	117.6(6)	C9-C10-H10	119.7
C18-N5-C20	118.1(8)	C9-C10-C11	120.5(7)
C21-N5-C18	123.5(6)	C11-C10-H10	119.7
C21-N5-C20	114.2(8)	C10-C11-H11	120.9
C21-N6-Ni1	120.6(4)	C10-C11-C12	118.2(7)
C25-N6-Ni1	120.3(5)	C12-C11-H11	120.9
C25-N6-C21	118.6(6)	N3-C12-N4	119.9(6)
C2-C1-N1	122.1(6)	N3-C12-C11	121.5(6)
C2-C1-C6	119.7(6)	N4-C12-C11	118.5(6)

C6-C1-N1	118.2(6)	N4-C13-H13A	109.5
C1-C2-H2	120.2	N4-C13-H13B	109.5
C3-C2-C1	119.6(7)	N4-C13-H13C	109.5
C3-C2-H2	120.2	H13A-C13-H13B	109.5
C2-C3-H3	119.0	H13A-C13-H13C	109.5
C2-C3-C4	122.1(8)	H13B-C13-H13C	109.5
C4-C3-H3	119.0	C15-C14-N4	120.4(7)
C3-C4-H4	121.1	C19-C14-N4	118.9(6)
C3-C4-C5	117.8(7)	C19-C14-C15	120.6(8)
C5-C4-H4	121.1	C14-C15-H15	120.6
C4-C5-N2	119.0(6)	C16-C15-C14	118.7(8)
C6-C5-N2	118.1(6)	C16-C15-H15	120.6
C6-C5-C4	122.8(7)	C15-C16-H16	119.3
C1-C6-Ni1	119.6(5)	C15-C16-C17	121.4(7)
C5-C6-Ni1	122.3(5)	C17-C16-H16	119.3
C5-C6-C1	118.0(6)	C16-C17-H17	121.2
N2-C7-H7A	109.5	C18-C17-C16	117.7(8)
N2-C7-H7B	109.5	C18-C17-H17	121.2
N2-C7-H7C	109.5	C17-C18-N5	118.7(7)
H7A-C7-H7B	109.5	C17-C18-C19	122.5(8)
H7A-C7-H7C	109.5	C19-C18-N5	118.8(6)
C14-C19-Ni1	119.8(6)	C22-C23-H23	119.8
C18-C19-Ni1	120.9(5)	C24-C23-C22	120.5(7)
C18-C19-C14	119.0(6)	C24-C23-H23	119.8
N5-C20-H20A	109.5	C23-C24-H24	120.0
N5-C20-H20B	109.5	C23-C24-C25	120.0(8)
N5-C20-H20C	109.5	C25-C24-H24	120.0
H20A-C20-H20B	109.5	N6-C25-N1	118.2(6)
H20A-C20-H20C	109.5	N6-C25-C24	120.8(7)
H20B-C20-H20C	109.5	C24-C25-N1	121.0(6)
N6-C21-N5	118.4(6)	N1-C26-H26A	109.5
C22-C21-N5	120.9(7)	N1-C26-H26B	109.5
C22-C21-N6	120.7(7)	N1-C26-H26C	109.5
C21-C22-H22	120.4	H26A-C26-H26B	109.5
C23-C22-C21	119.2(8)	H26A-C26-H26C	109.5
C23-C22-H22	120.4	H26B-C26-H26C	109.5

Table S4 Torsion angles [°] for **4**

Ni1-N3-C8-N2	8.1(8)	C7-N2-C8-N3	-162.6(7)
Ni1-N3-C8-C9	-171.3(5)	C7-N2-C8-C9	16.8(10)
Ni1-N3-C12-N4	-10.4(8)	C8-N2-C5-C4	132.6(8)
Ni1-N3-C12-C11	173.4(6)	C8-N2-C5-C6	-50.2(10)
Ni1-N6-C21-N5	13.9(8)	C8-N3-C12-N4	175.5(6)
Ni1-N6-C21-C22	-167.4(5)	C8-N3-C12-C11	-0.7(10)
Ni1-N6-C25-N1	-8.5(8)	C8-C9-C10-C11	-0.9(13)
Ni1-N6-C25-C24	171.9(5)	C9-C10-C11-C12	2.9(13)
N1-C1-C2-C3	-178.9(9)	C10-C11-C12-N3	-2.2(12)
N1-C1-C6-Ni1	-3.5(9)	C10-C11-C12-N4	-178.4(7)
N1-C1-C6-C5	-179.7(6)	C12-N3-C8-N2	-177.8(6)
N2-C5-C6-Ni1	4.4(9)	C12-N3-C8-C9	2.9(10)
N2-C5-C6-C1	-179.5(6)	C12-N4-C14-C15	131.6(7)
N2-C8-C9-C10	178.5(7)	C12-N4-C14-C19	-47.3(8)
N3-C8-C9-C10	-2.1(11)	C13-N4-C12-N3	-153.1(7)
N4-C14-C15-C16	-178.0(6)	C13-N4-C12-C11	23.2(10)
N4-C14-C19-Ni1	-8.0(8)	C13-N4-C14-C15	-16.6(9)
N4-C14-C19-C18	177.7(6)	C13-N4-C14-C19	164.5(6)
N5-C18-C19-Ni1	5.5(8)	C14-N4-C12-N3	58.2(8)
N5-C18-C19-C14	179.8(6)	C14-N4-C12-C11	-125.5(7)
N5-C21-C22-C23	173.8(7)	C14-C15-C16-C17	-0.1(11)
N6-C21-C22-C23	-4.8(11)	C15-C14-C19-Ni1	173.1(5)
C1-N1-C25-N6	59.6(8)	C15-C14-C19-C18	-1.2(9)
C1-N1-C25-C24	-120.8(7)	C15-C16-C17-C18	-0.3(11)
C1-C2-C3-C4	-0.3(17)	C16-C17-C18-N5	-179.1(6)
C2-C1-C6-Ni1	178.7(6)	C16-C17-C18-C19	-0.1(11)
C2-C1-C6-C5	2.5(11)	C17-C18-C19-Ni1	-173.5(5)
C2-C3-C4-C5	0.5(17)	C17-C18-C19-C14	0.8(10)
C3-C4-C5-N2	178.0(9)	C18-N5-C21-N6	39.4(10)
C3-C4-C5-C6	1.0(14)	C18-N5-C21-C22	-139.2(7)
C4-C5-C6-Ni1	-178.5(7)	C19-C14-C15-C16	0.9(10)
C4-C5-C6-C1	-2.4(11)	C20-N5-C18-C17	-27.8(11)
C5-N2-C8-N3	42.8(10)	C20-N5-C18-C19	153.1(8)
C5-N2-C8-C9	-137.8(7)	C20-N5-C21-N6	-164.1(8)
C6-C1-C2-C3	-1.2(14)	C20-N5-C21-C22	17.3(11)
C7-N2-C5-C4	-22.1(11)	C21-N5-C18-C17	127.9(8)
C7-N2-C5-C6	155.1(7)	C21-N5-C18-C19	-51.2(10)

C21-N6-C25-N1	179.4(6)
C21-N6-C25-C24	-0.2(9)
C21-C22-C23-C24	0.3(12)
C22-C23-C24-C25	4.0(13)
C23-C24-C25-N1	176.3(7)
C23-C24-C25-N6	-4.2(11)
C25-N1-C1-C2	125.1(8)
C25-N1-C1-C6	-52.6(9)
C25-N6-C21-N5	-174.0(6)
C25-N6-C21-C22	4.6(9)
C26-N1-C1-C2	-21.0(10)
C26-N1-C1-C6	161.3(7)
C26-N1-C25-N6	-154.5(6)
C26-N1-C25-C24	25.1(9)

3. X-ray Photoelectron Spectroscopy of complexes 2 and 4

X-ray photoelectrons spectroscopic data of **2** and **4** were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W MgKα radiation. The pressure was about 3×10^{-9} mbar. The binding energies are referenced to the C1s line at 284.9 eV from adventitious carbon. The acquisition parameters are as follows.

Table S5 Acquisition parameters

Total acq.	time 8 mins 20.8 secs
No. Scans	10
Lens Mode	LargeArea
Analyser Mode	CAE Pass Energy 30.0 eV
Energy Step Size	0.1 eV
No. of Energy Steps	501

4. Cyclic Voltammetry Experiment Procedure

Experiment procedure: Cyclic voltammetry on complex **2** and **4** was performed in a 3-electrode cell consisting of a glassy carbon working electrode, a Ag/Ag^{+} reference electrode with a Ag wire in a fritted chamber containing a solution of $AgNO_3$ (0.01 M) and NBu_4ClO_4 (0.1 M) in acetonitrile (anhydrous and deoxygenated), and a Pt wire counter electrode. A 3 mL solution of complex **2** and **4** (0.01 M) and NBu_4ClO_4 (0.1 M) in acetonitrile was added to an electrochemical cell. N2 was induced to change air in the flask. Cyclic voltammetry scans were taken at 100 mV/s starting from –
0.5 to -1.4 V in the negative direction. After the measurement, ferrocene was added as internal reference and measurement again. The redox potentials obtained minus the E1/2 of ferrocene gave the relative redox potentials of **2** and **4**.

5. Copies of ^{1}H and ^{13}C NMR Spectra

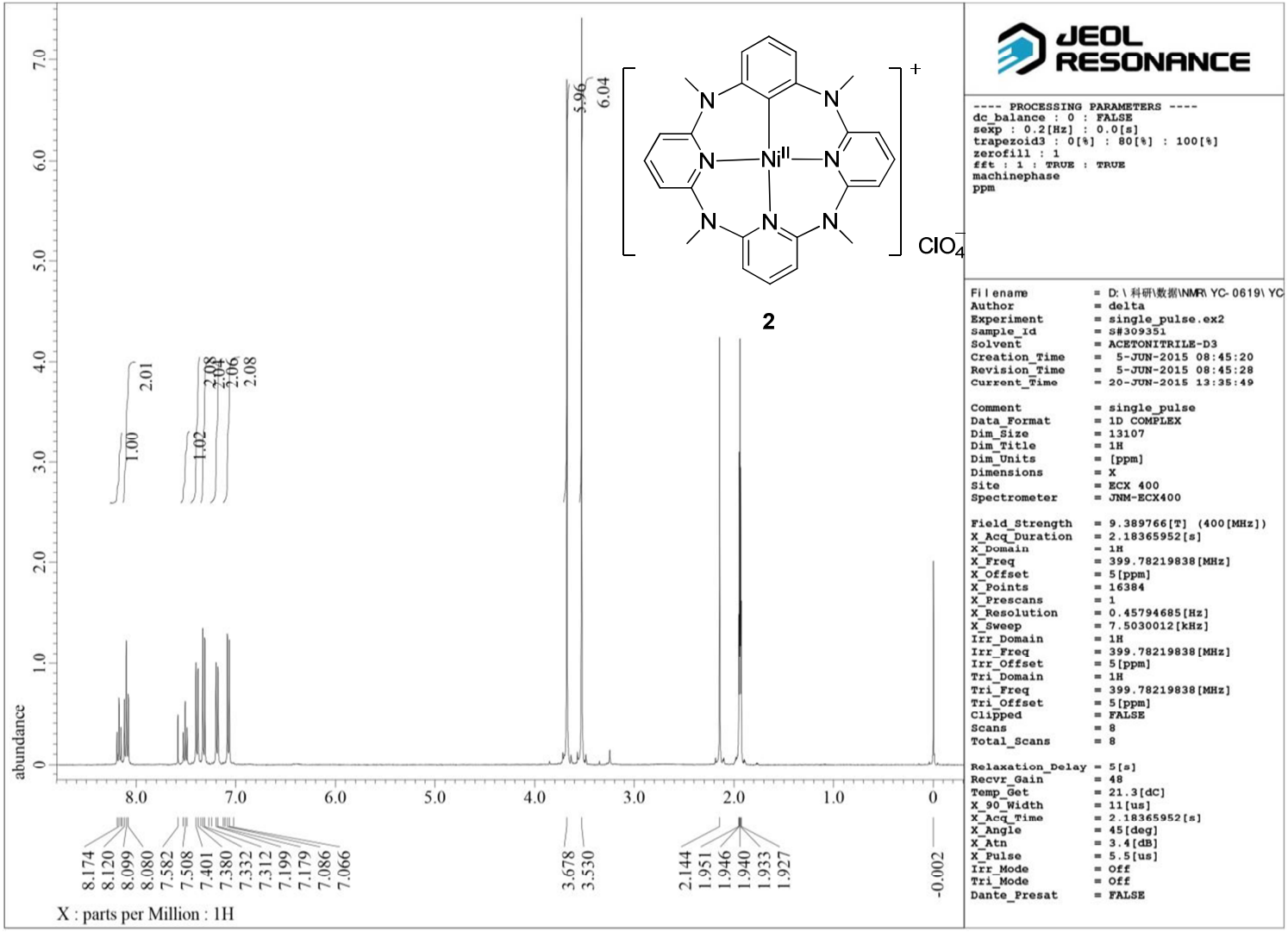


Figure S3 ^{1}H NMR of complex **2** in CD_3CN.

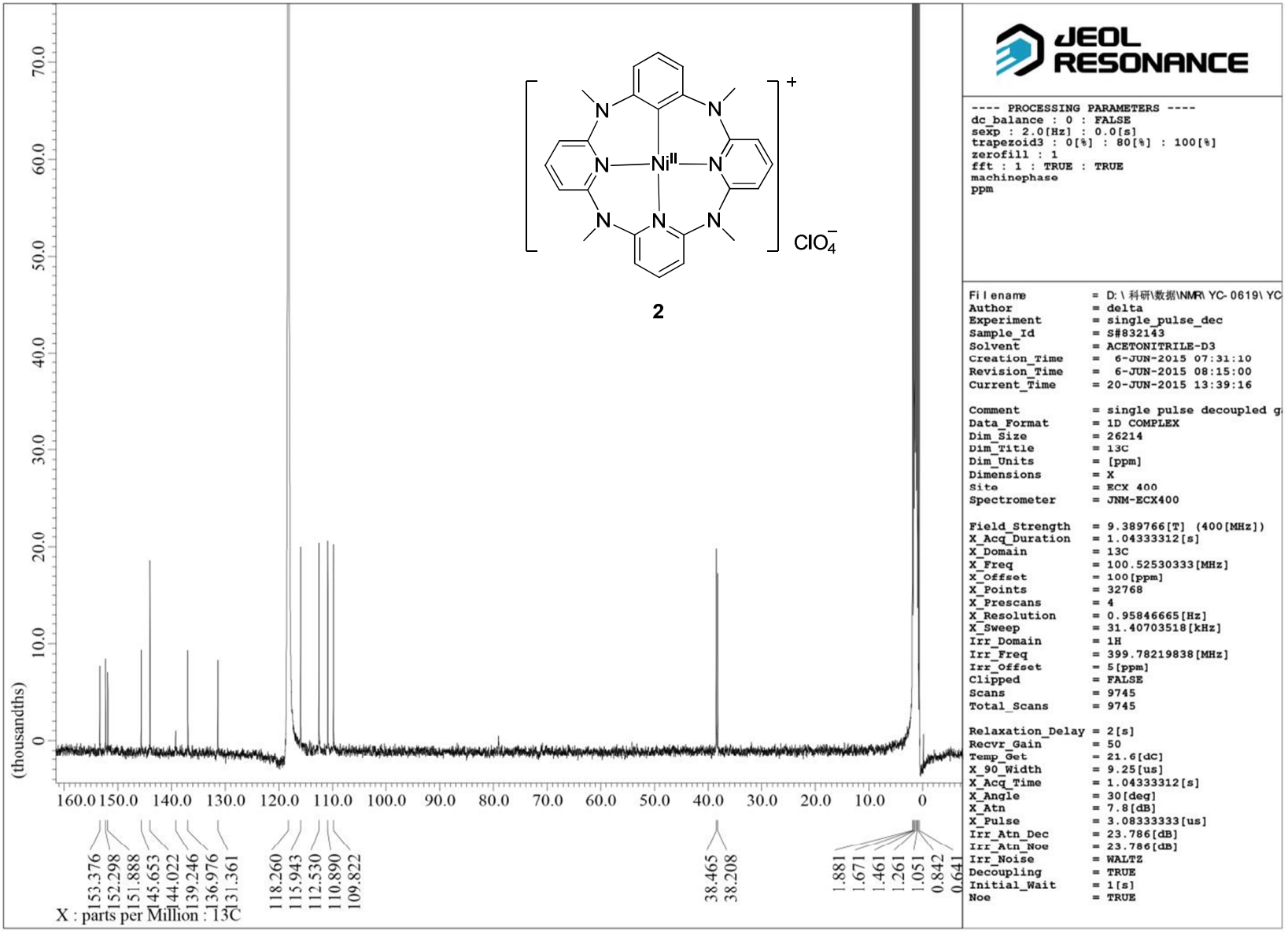


Figure S4 ^{13}C NMR of complex **2** in CD_3CN.

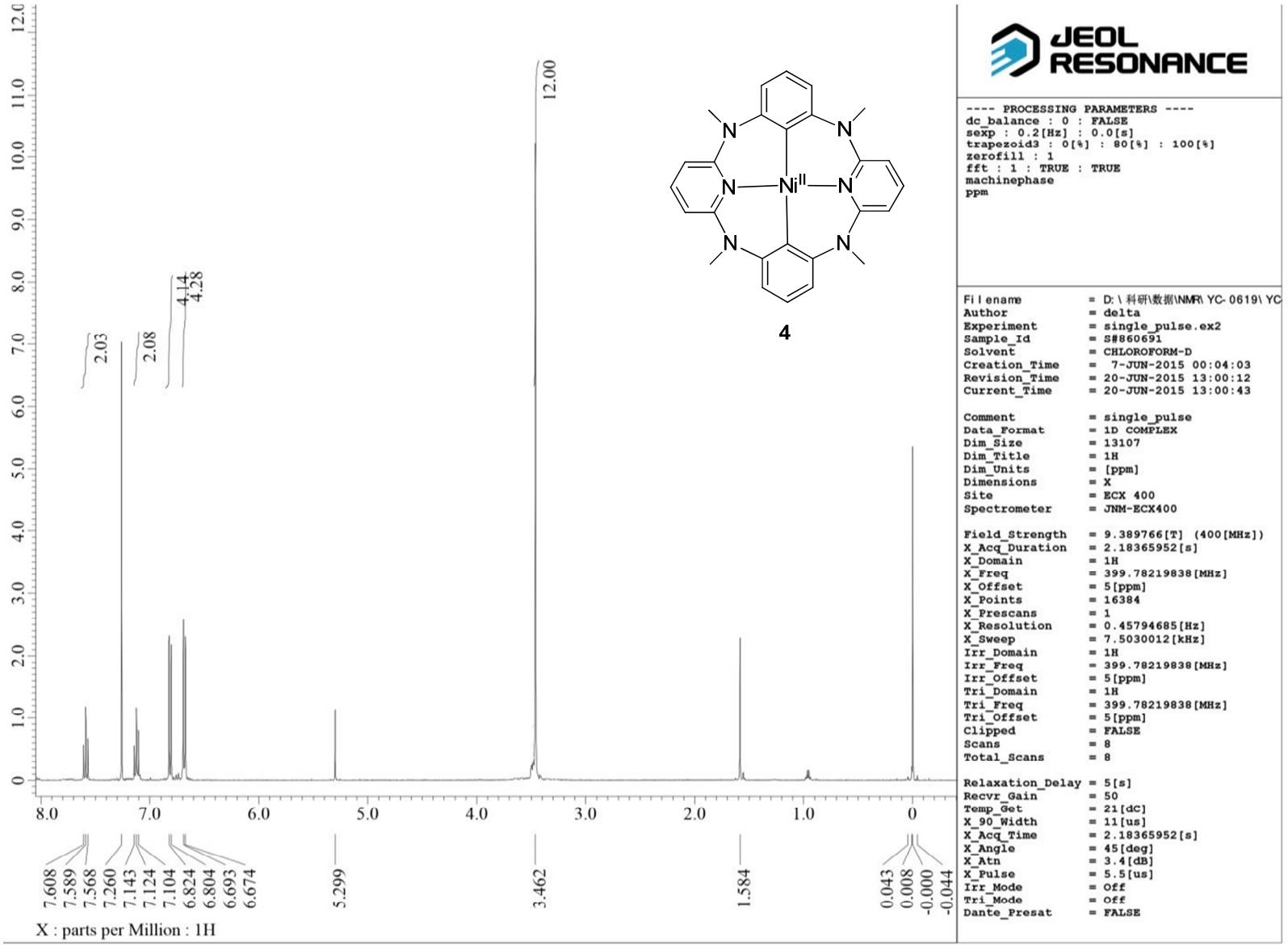


Figure S5 ^{1}H NMR of complex **4** in $CDCl_3$.

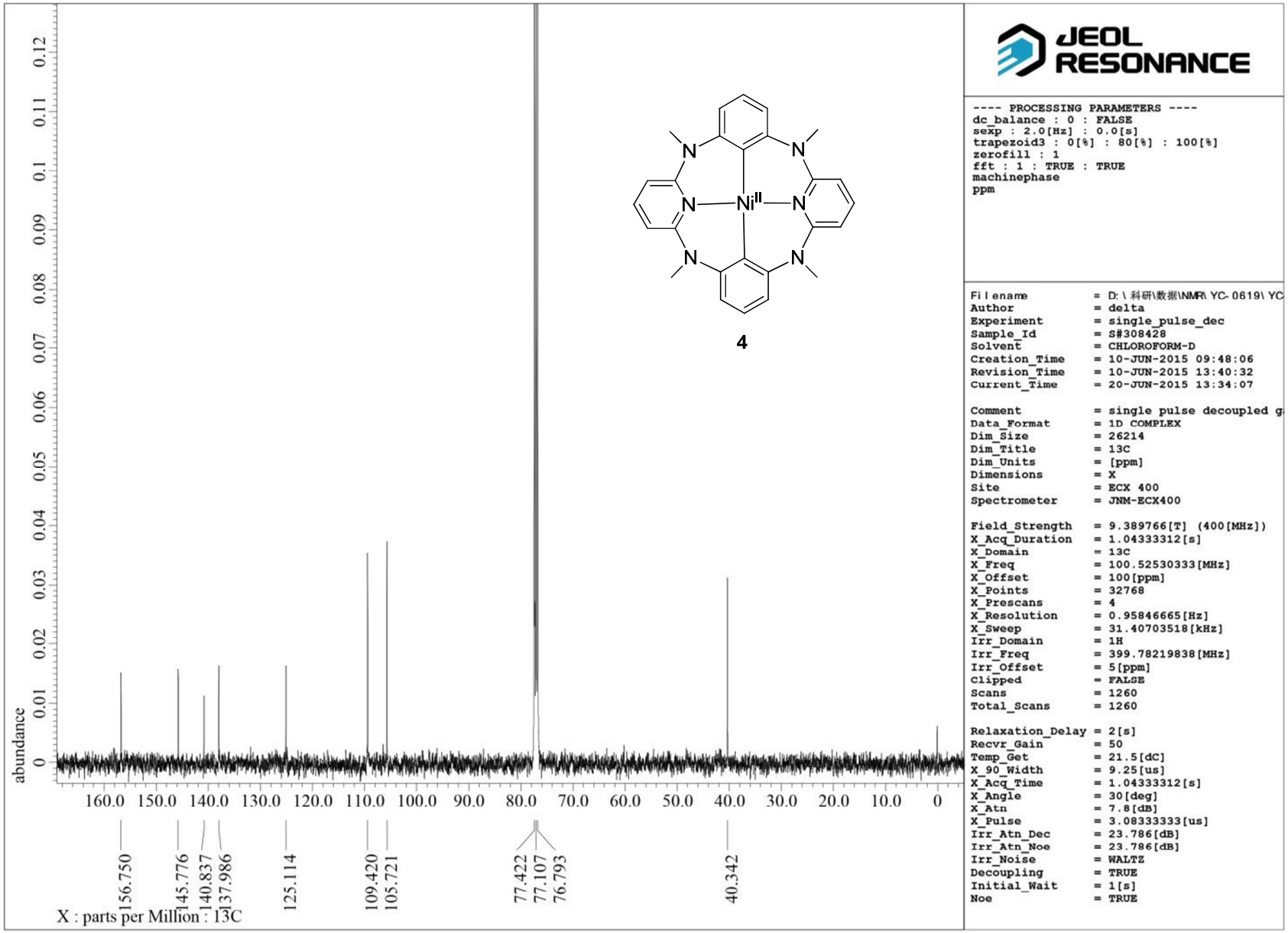


Figure S6 ^{13}C NMR of complex **4** in $CDCl_3$.

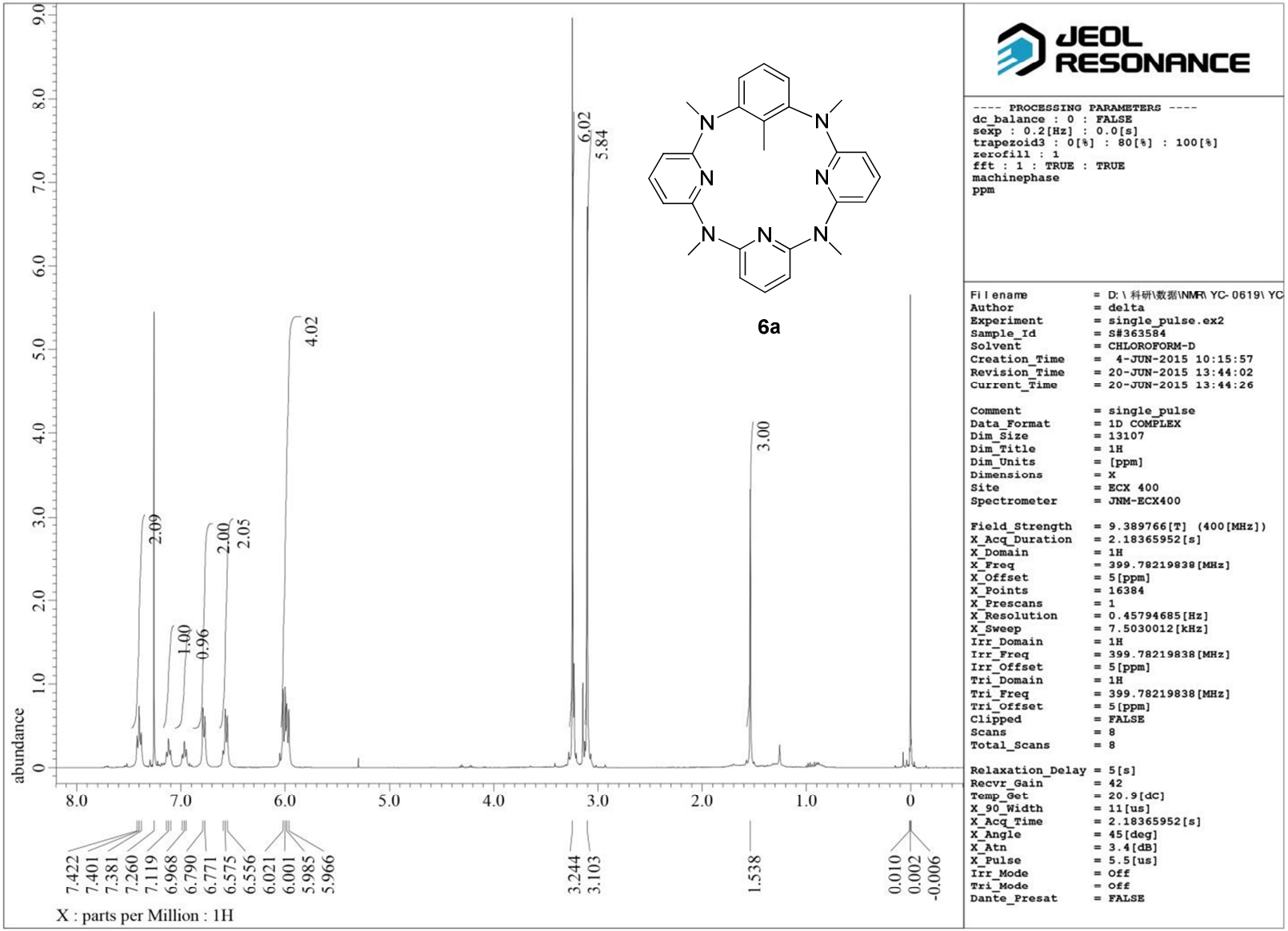


Figure S7 ^{1}H NMR of compound **6a** in $CDCl_3$.

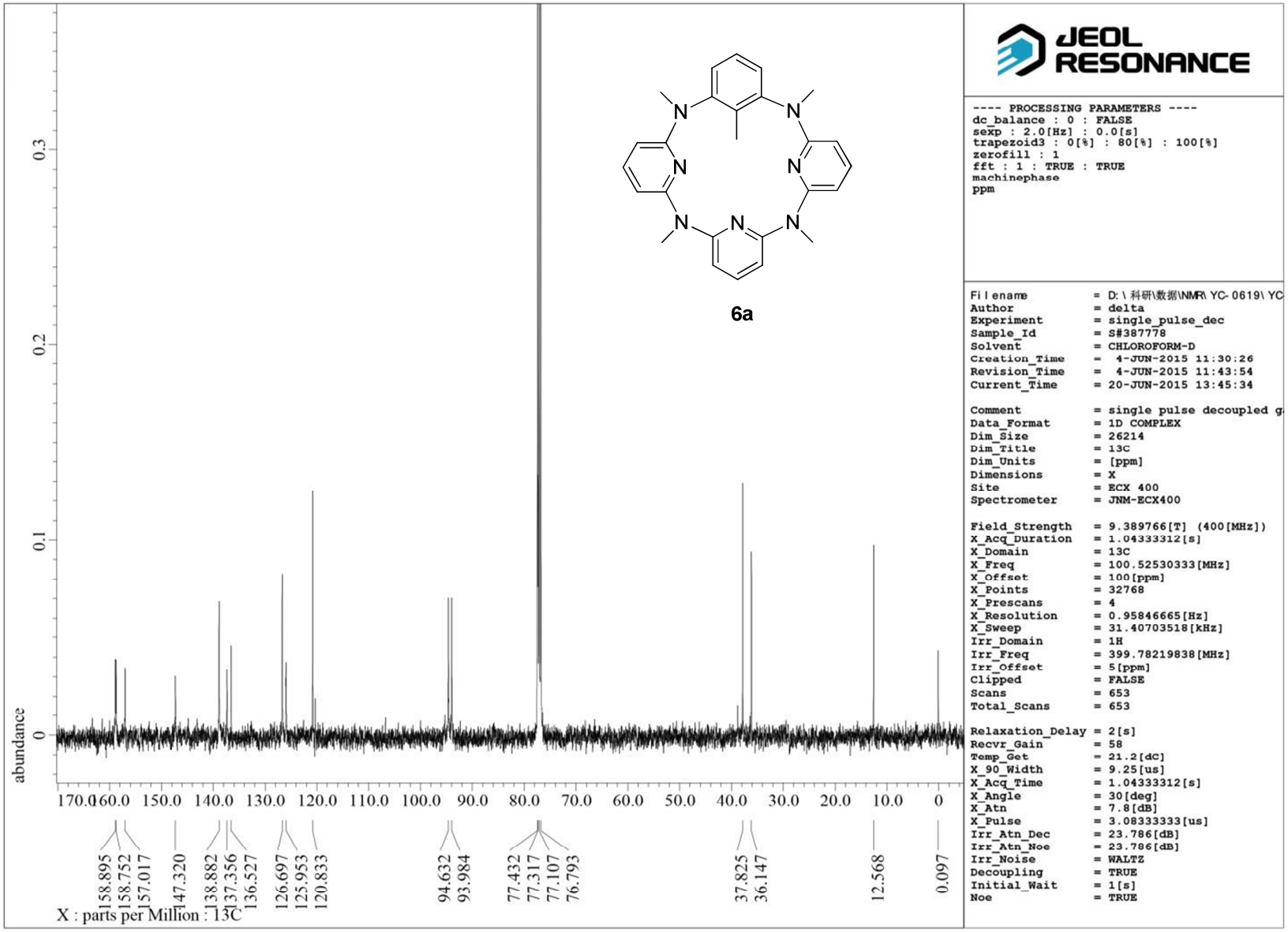


Figure S8 ^{13}C NMR of compound **6a** in $CDCl_3$.

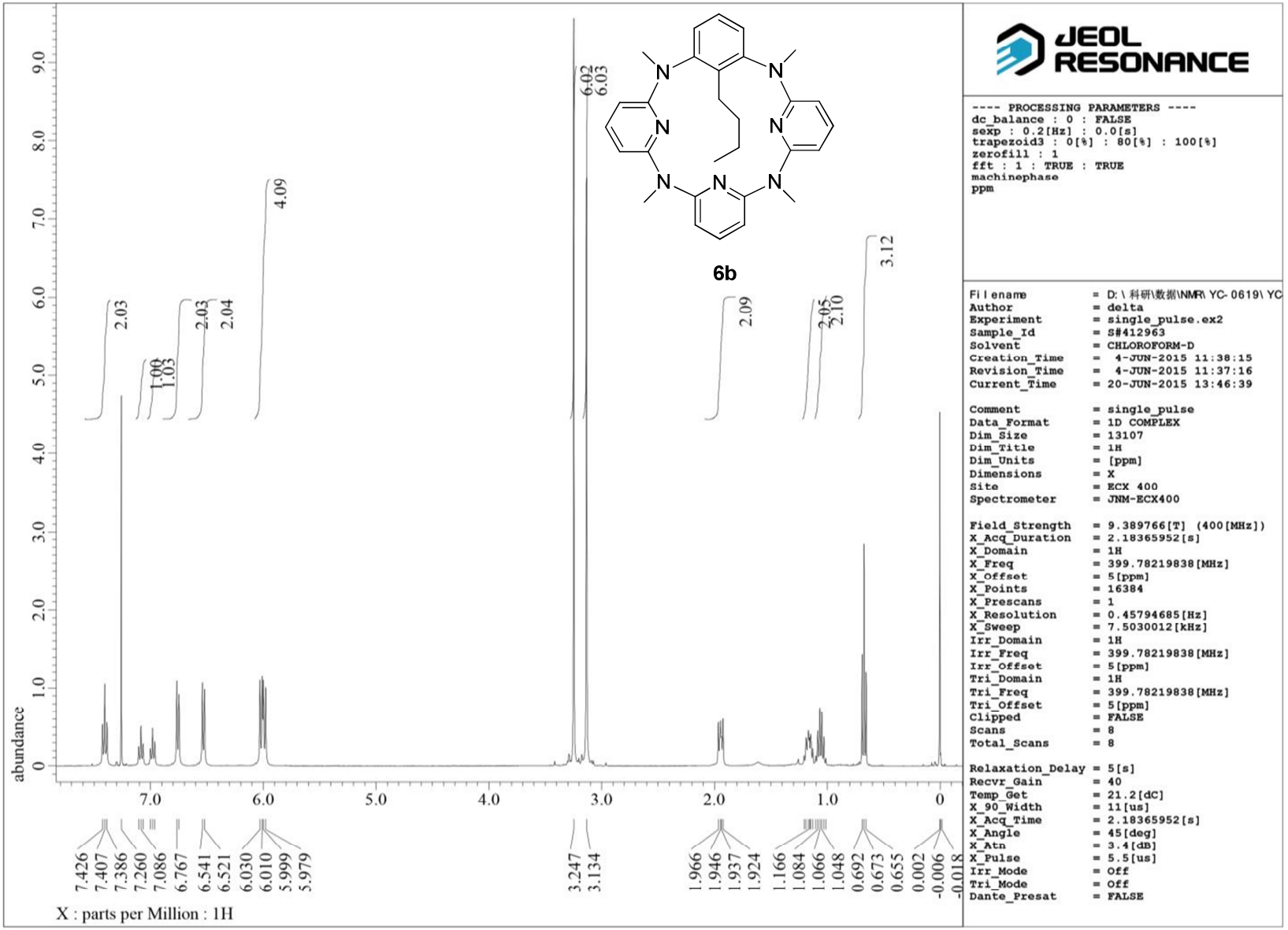


Figure S9 ^{1}H NMR of compound **6b** in $CDCl_3$.

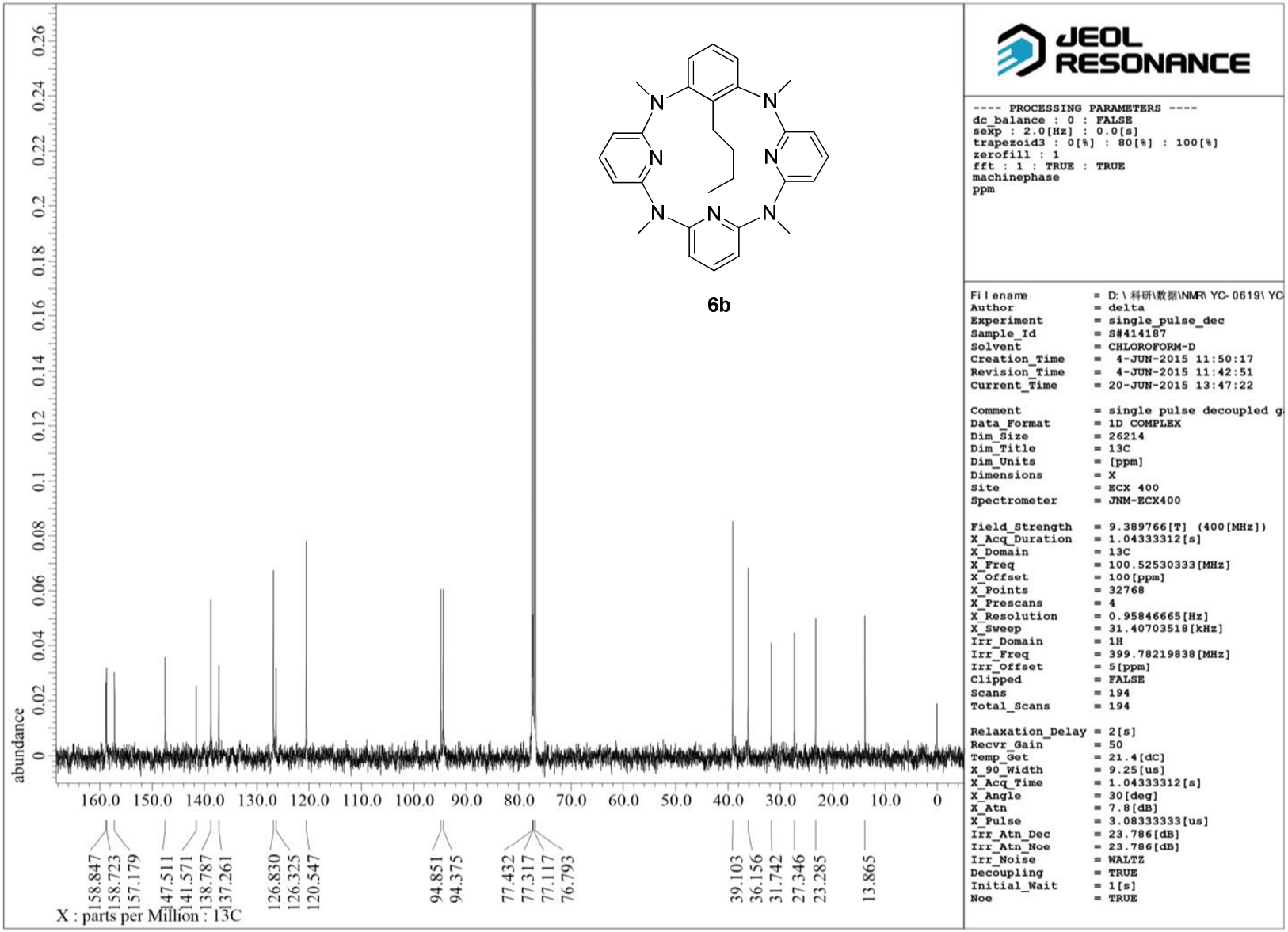


Figure S10 ^{13}C NMR of compound **6b** in $CDCl_3$.

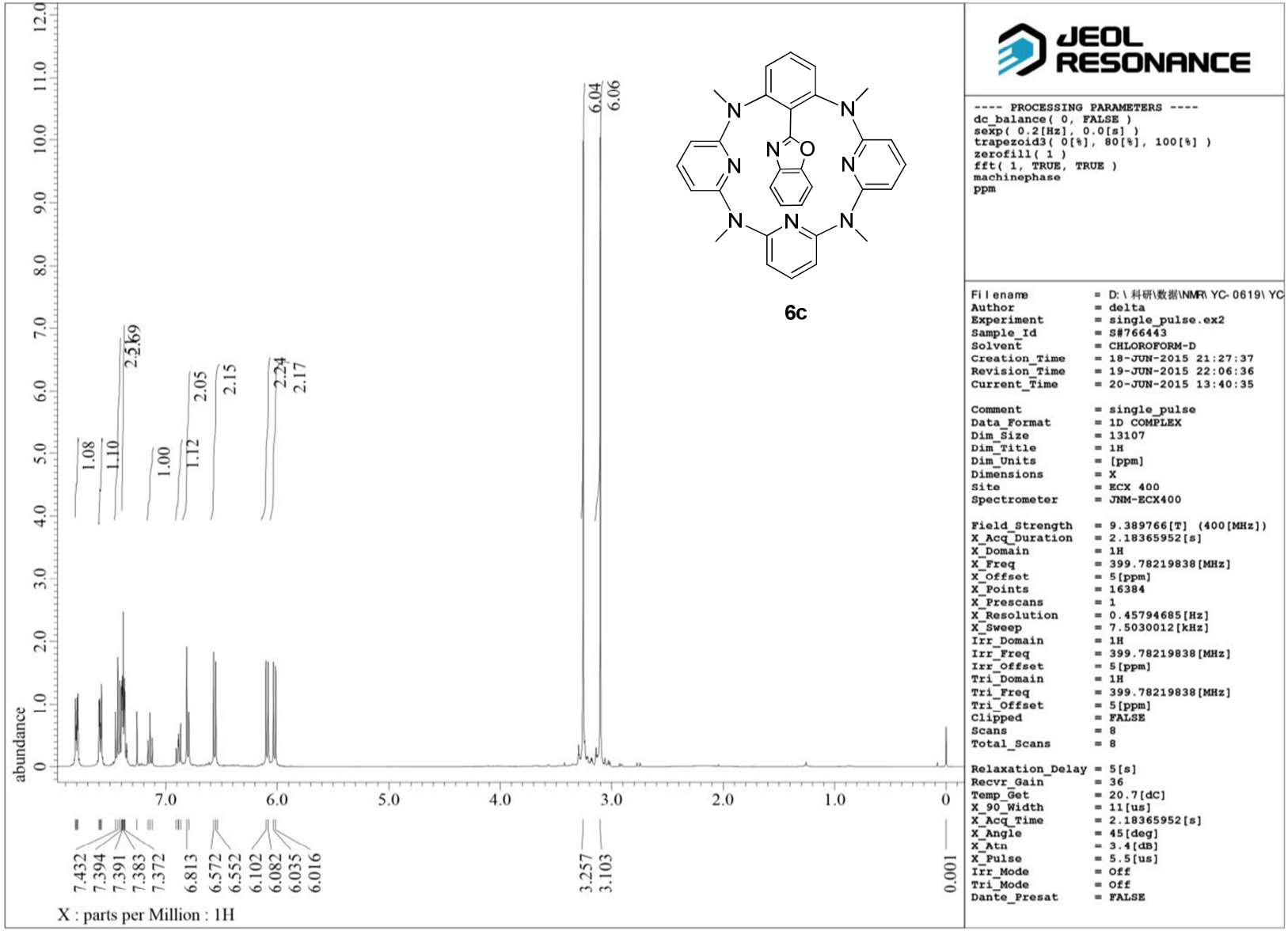


Figure S11 ^{1}H NMR of compound **6c** in $CDCl_3$.

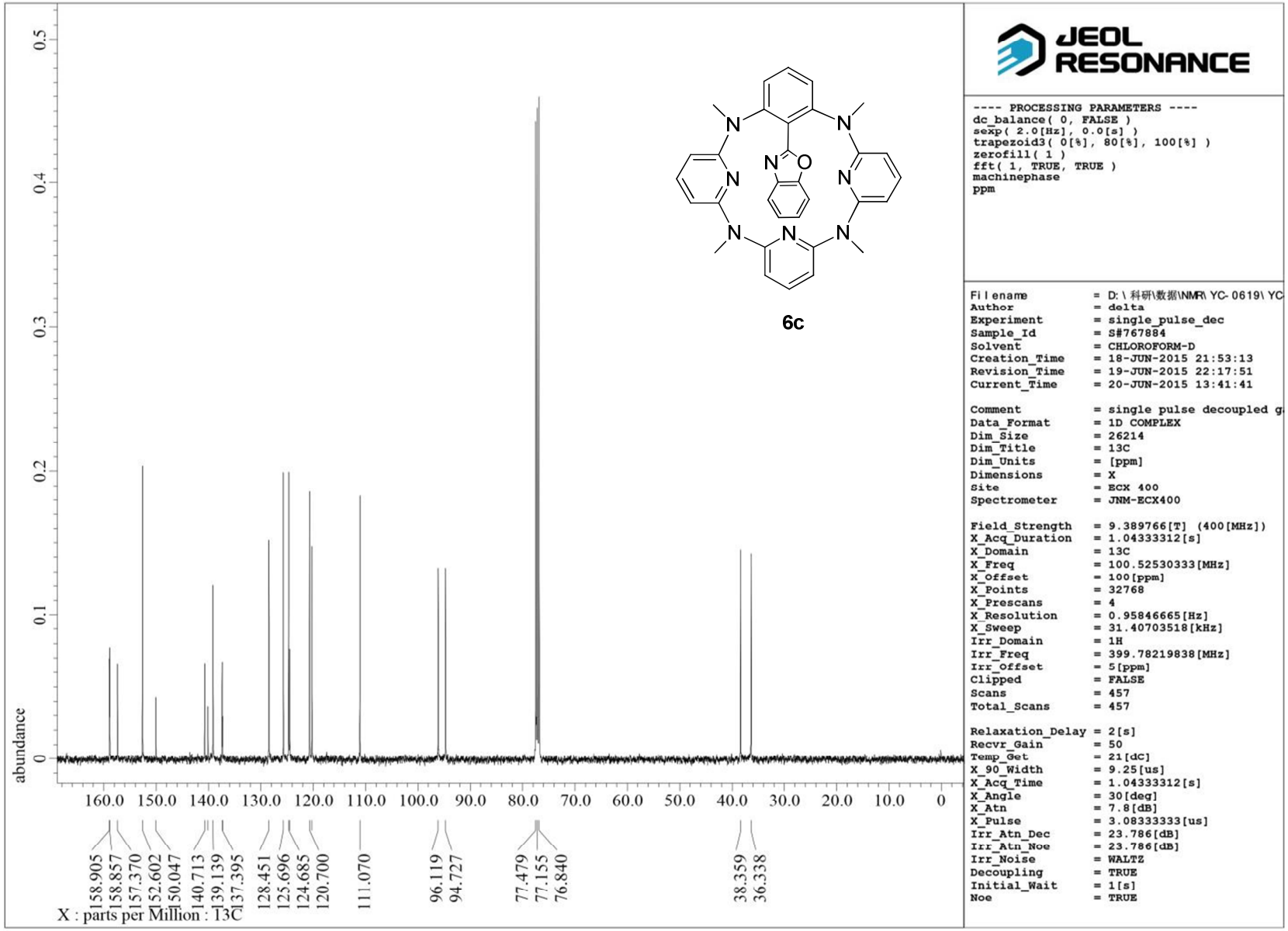


Figure S12 ^{13}C NMR of compound **6c** in $CDCl_3$.

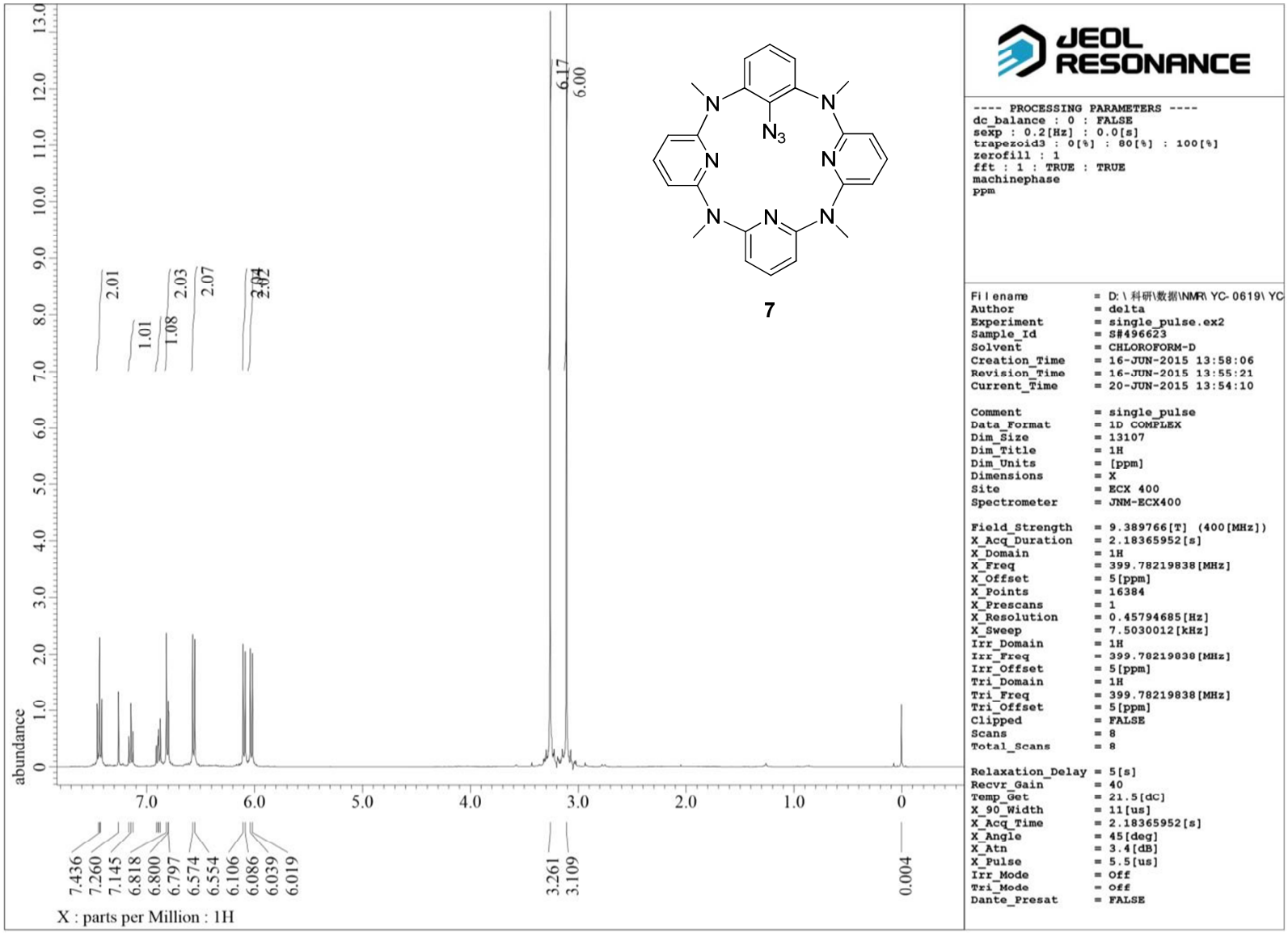


Figure S13 ^{1}H NMR of compound **7** in $CDCl_3$.

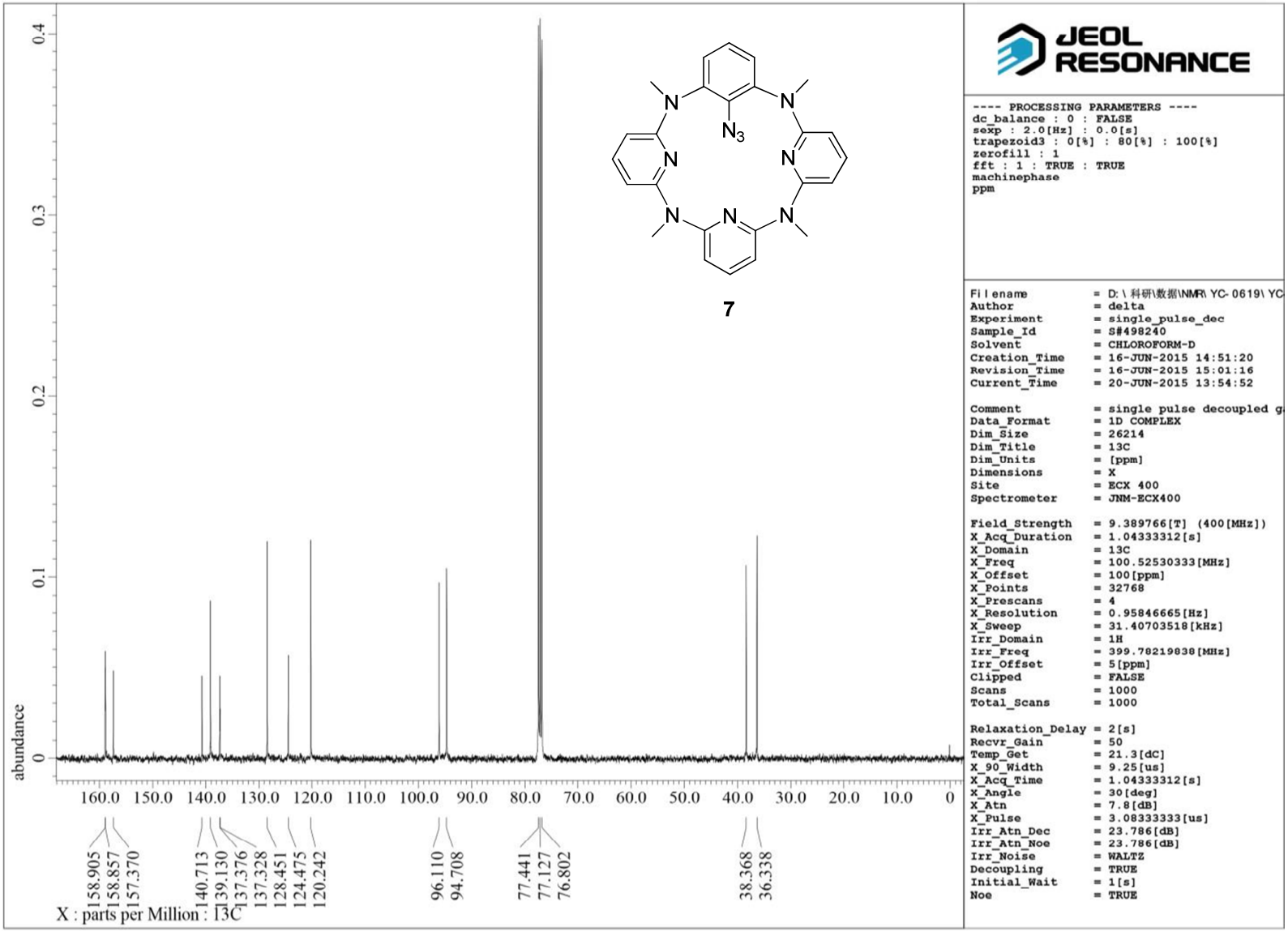


Figure S14 ^{13}C NMR of compound **7** in $CDCl_3$.

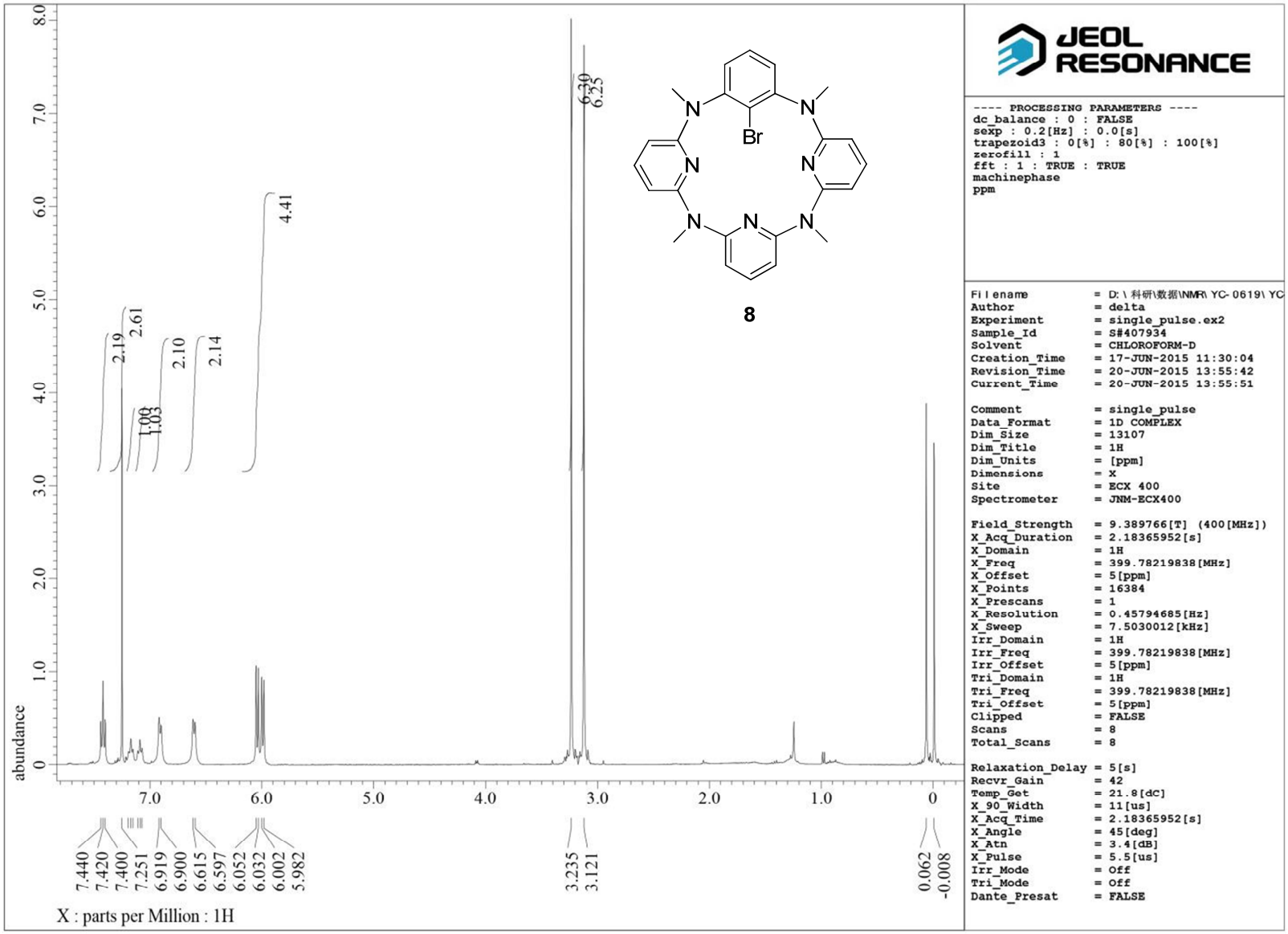


Figure S15 ^{1}H NMR of compound **8** in $CDCl_3$.

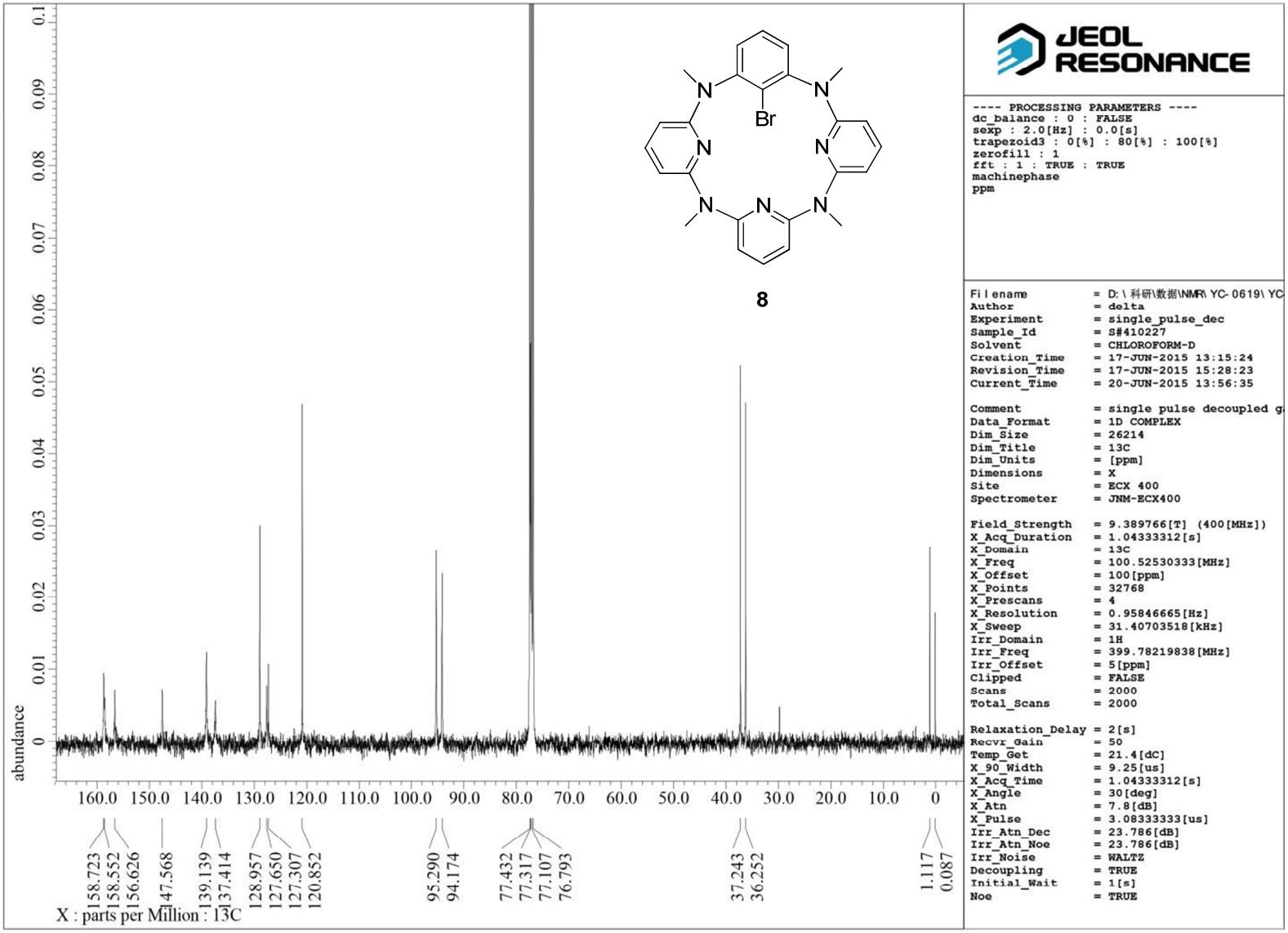


Figure S16 ^{13}C NMR of compound **8** in $CDCl_3$.

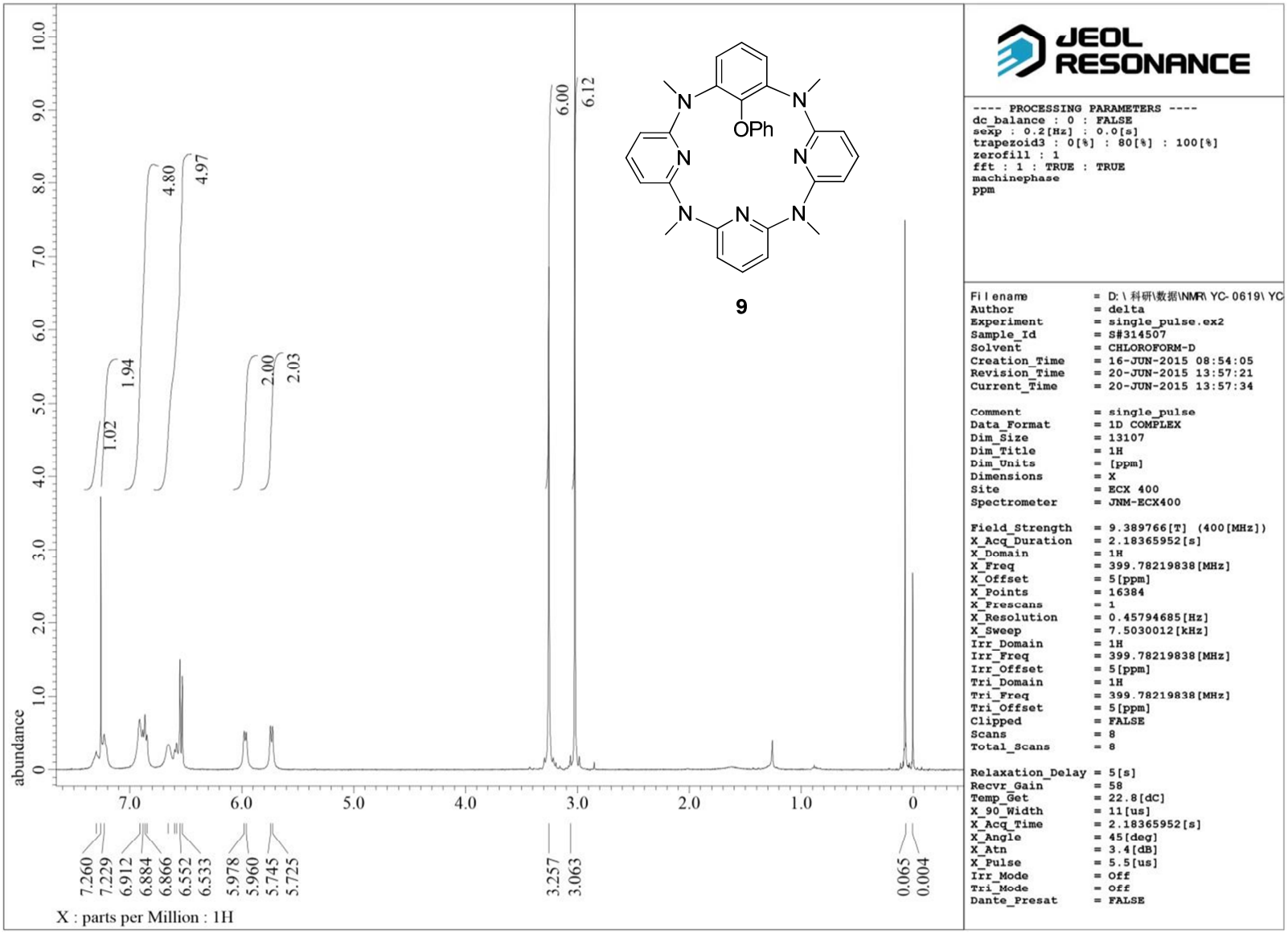


Figure S17 ^{1}H NMR of compound **9** in $CDCl_3$.

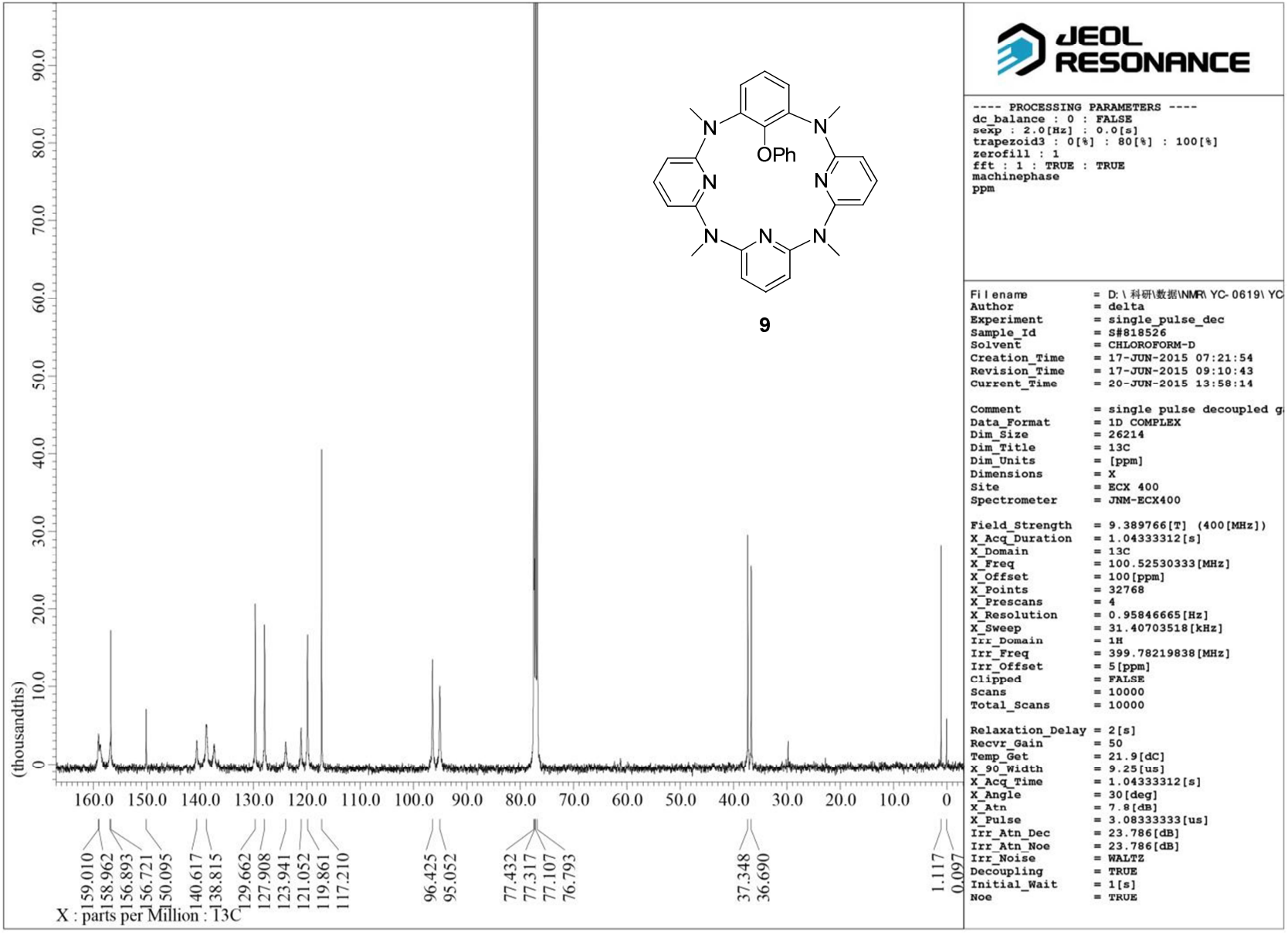


Figure S18 ^{13}C NMR of compound **9** in $CDCl_3$.

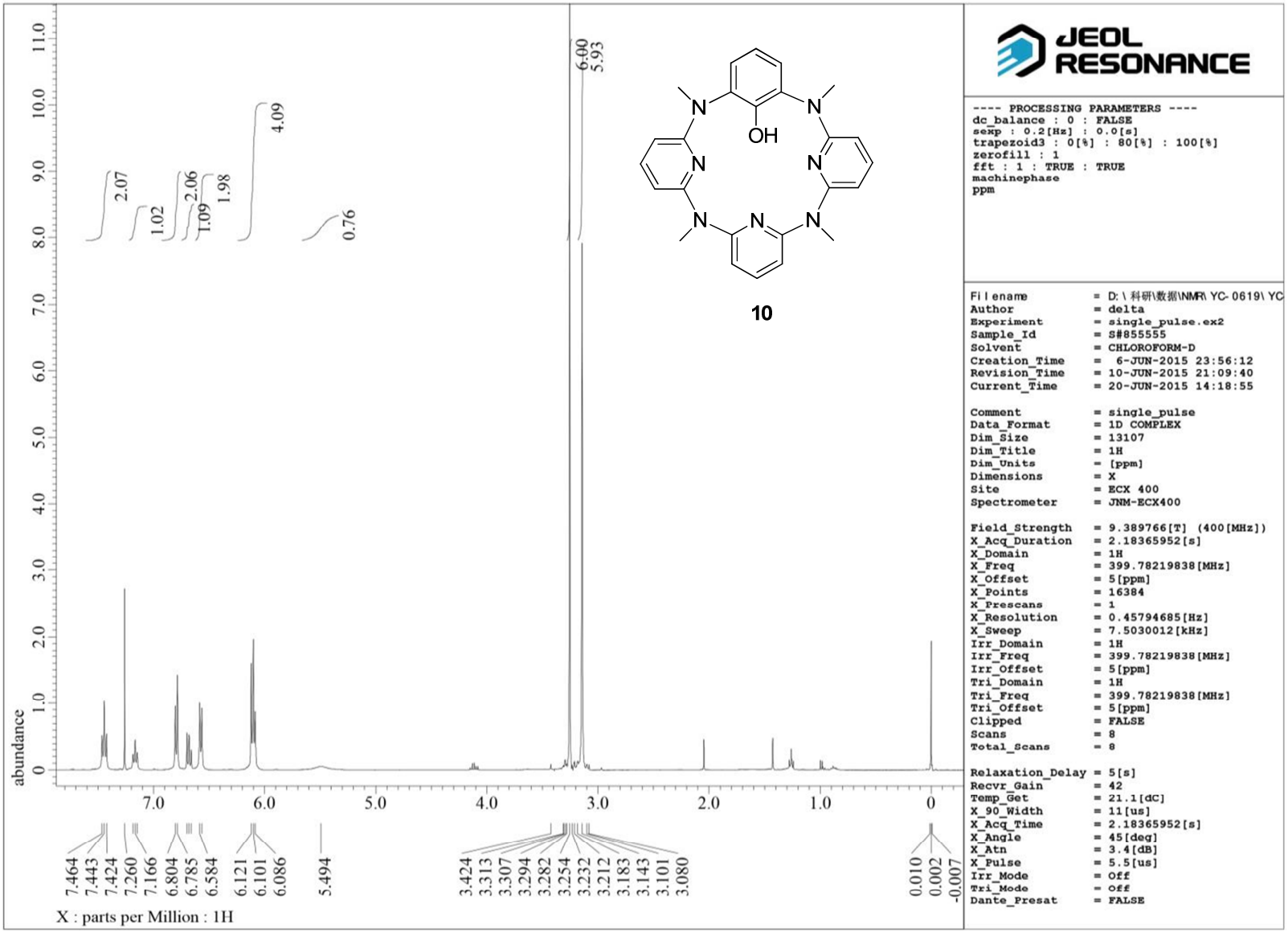


Figure S19 ^{1}H NMR of compound **10** in $CDCl_3$.

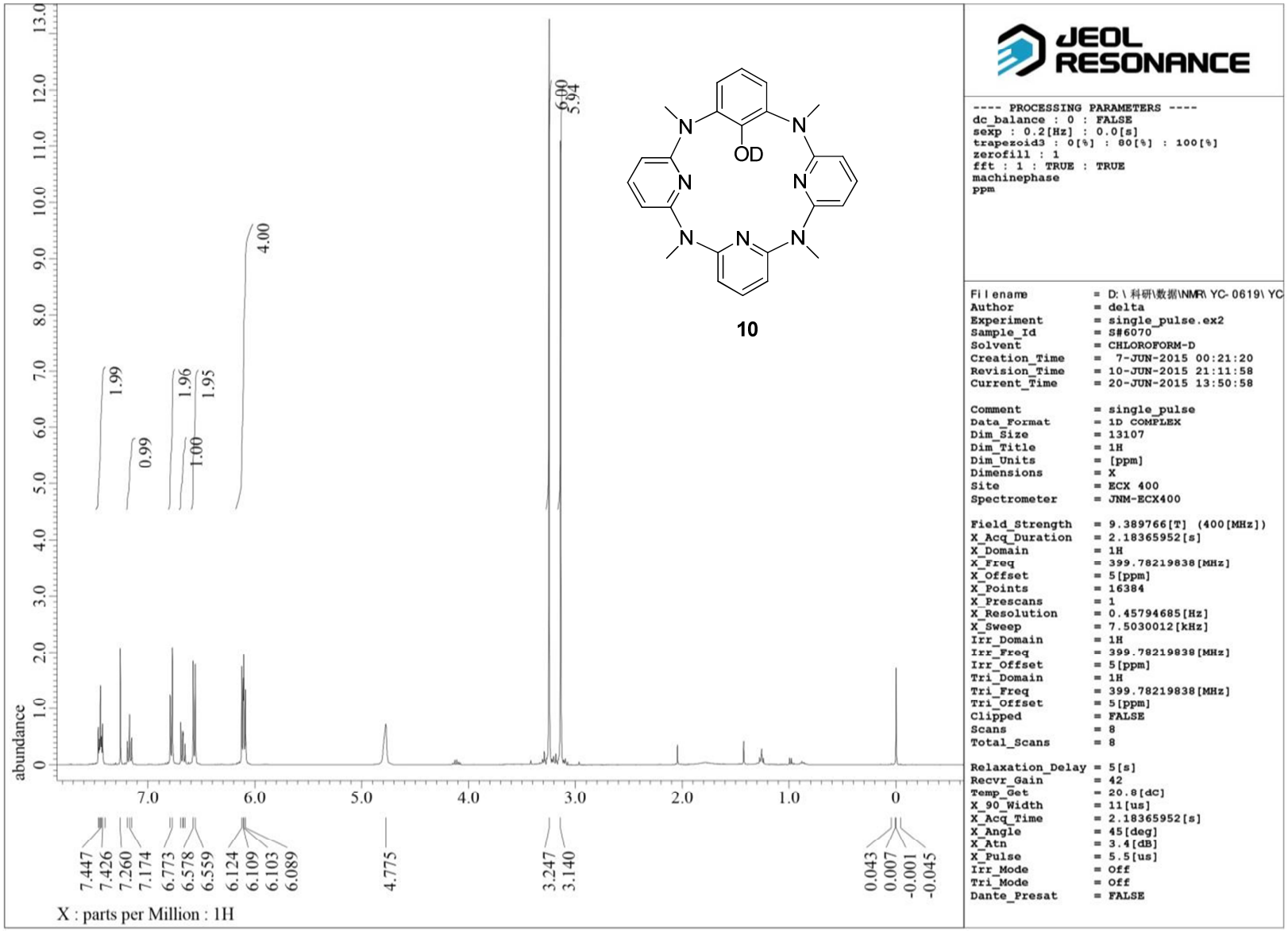


Figure S20 Deuterium experiment using D_2O of compound **10** in $CDCl_3$.

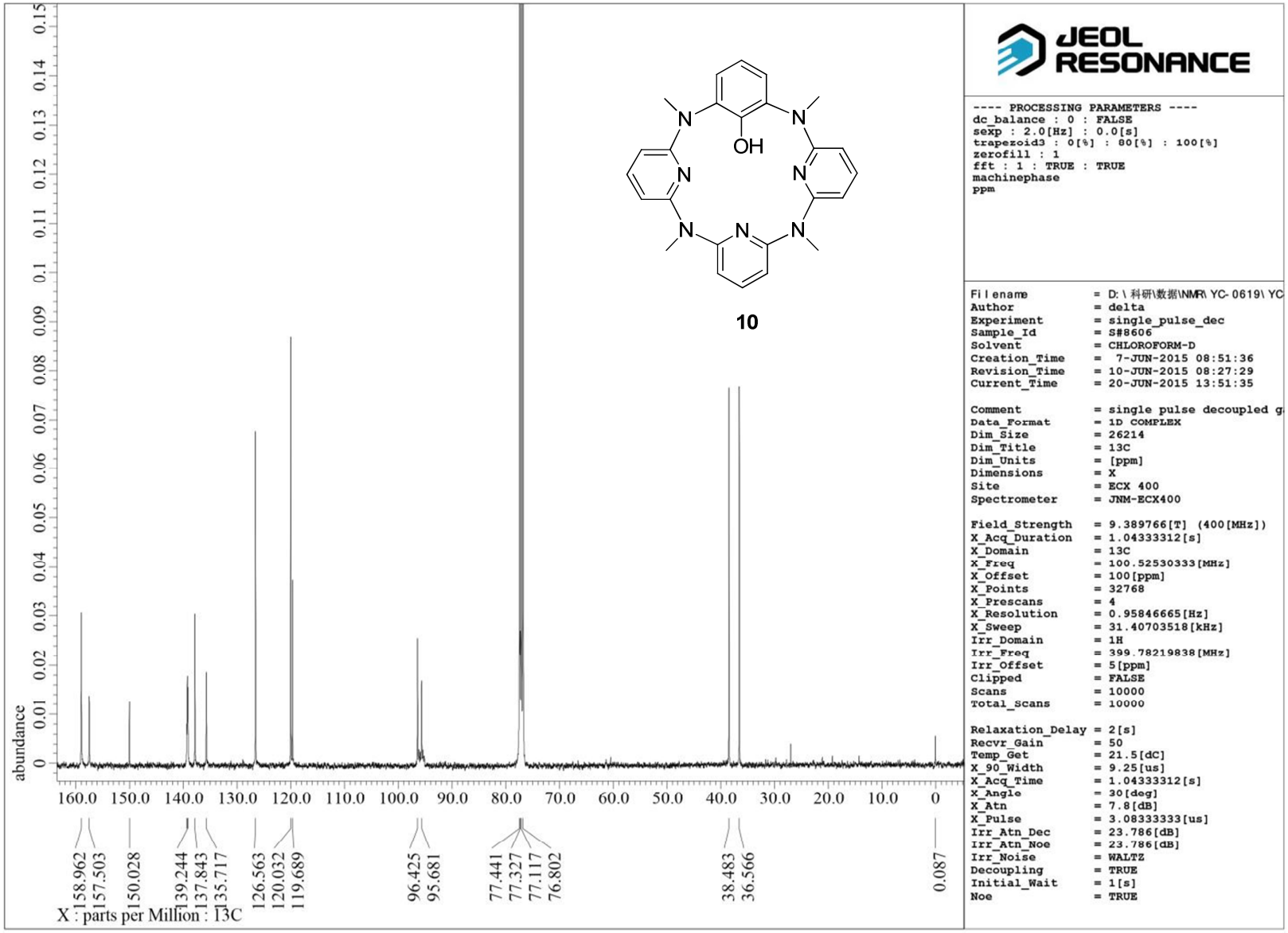


Figure S21 ^{13}C NMR of compound **10** in $CDCl_3$.

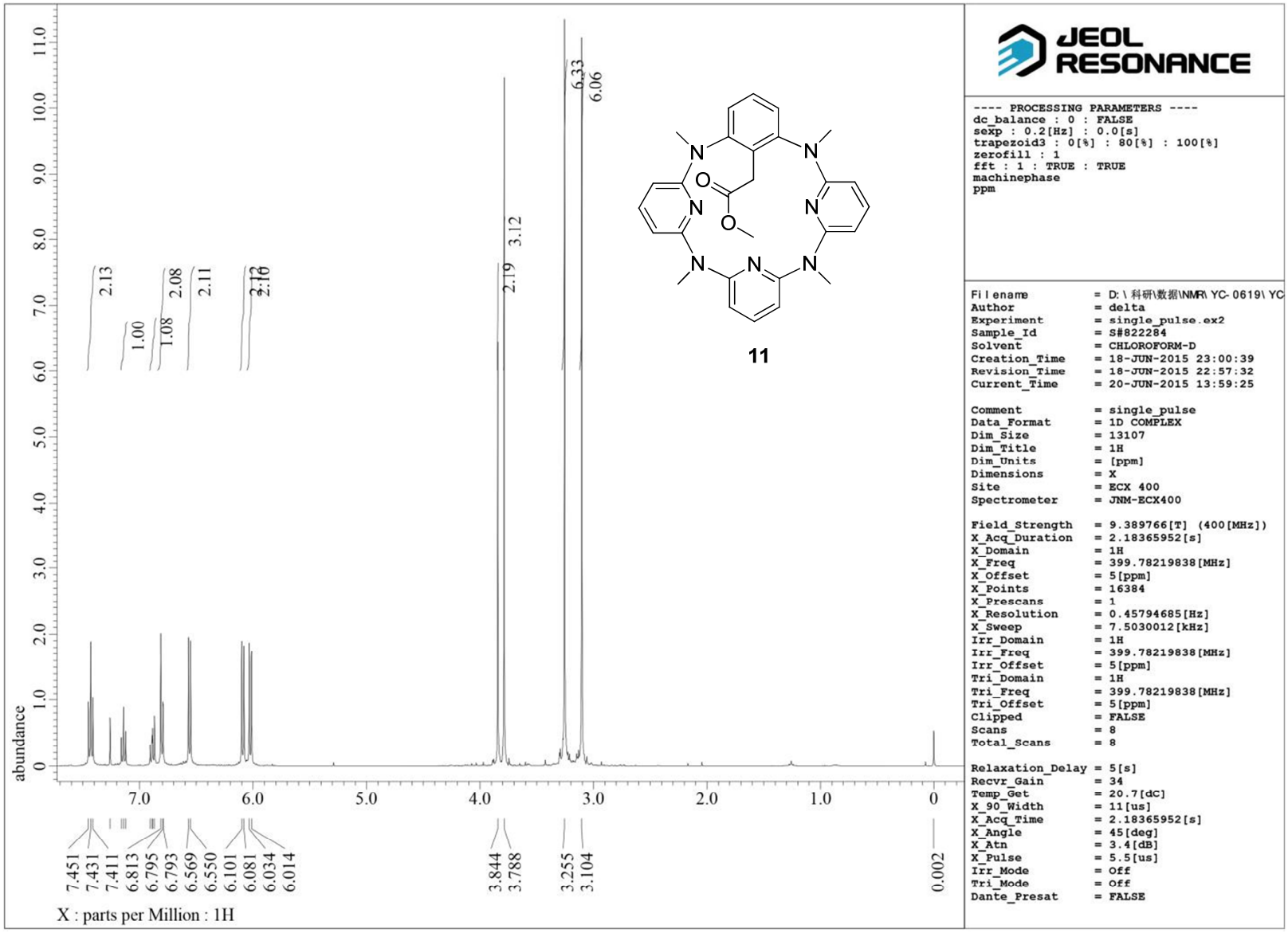


Figure S22 ^{1}H NMR of compound **11** in $CDCl_3$.

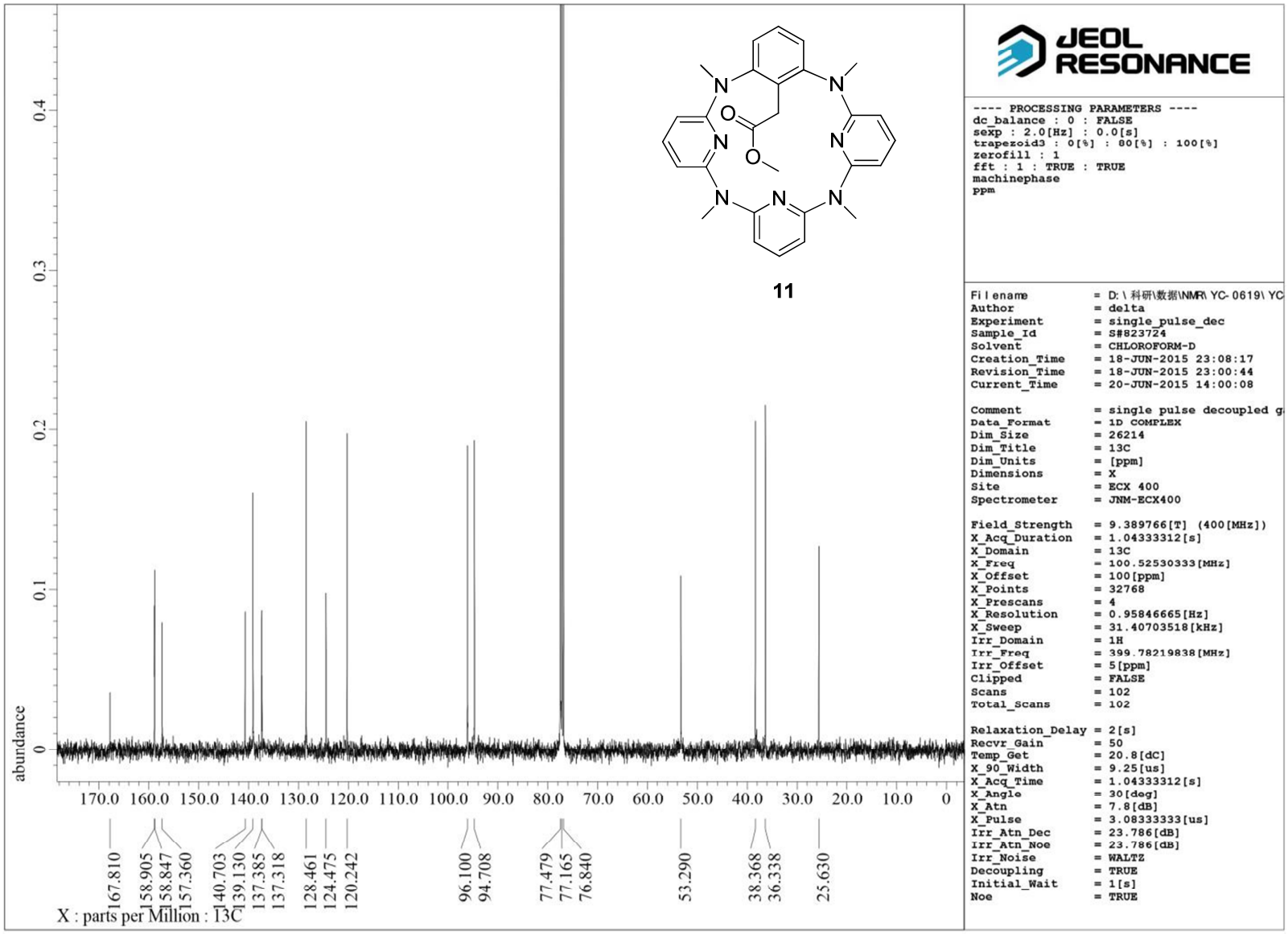


Figure S23 ^{13}C NMR of compound **11** in $CDCl_3$.