Supplementary Materials

Noble Metal Complexes of a Bis-Caffeine Containing NHC Ligand

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KEYWORDS caffeine, mesoionic carbene, palladium, platinum, NHC

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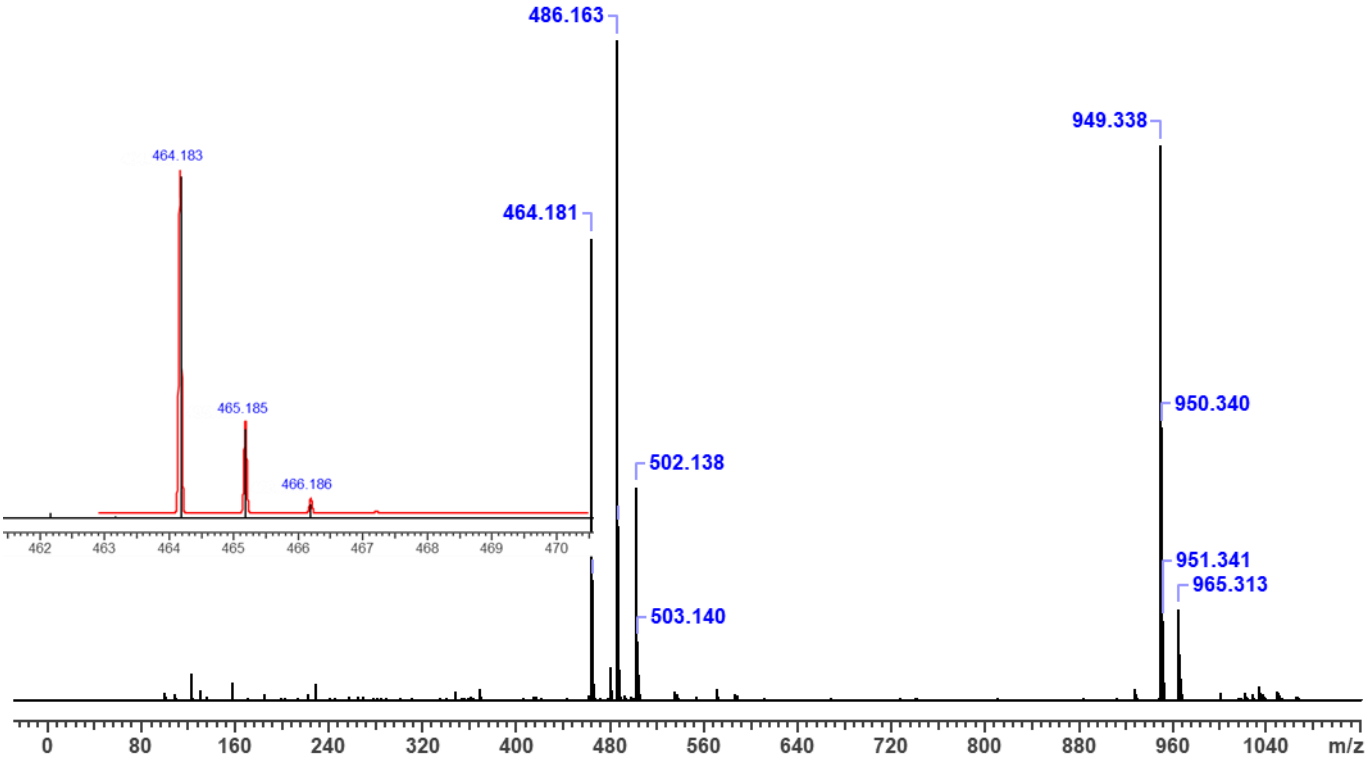

Figure S1: ESI-MS spectrum of **3**.

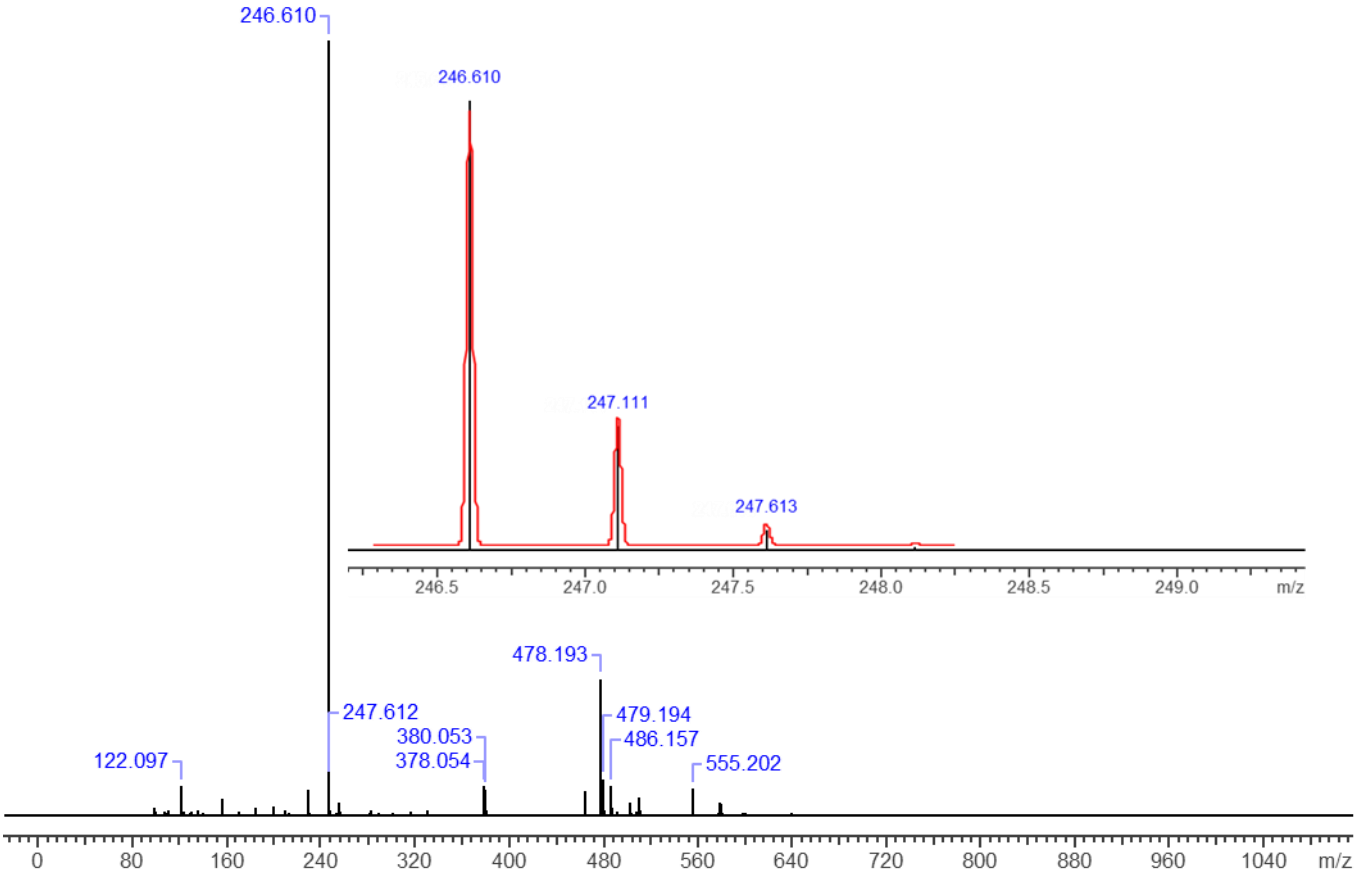

Figure S2: ESI-MS spectrum of **4**.

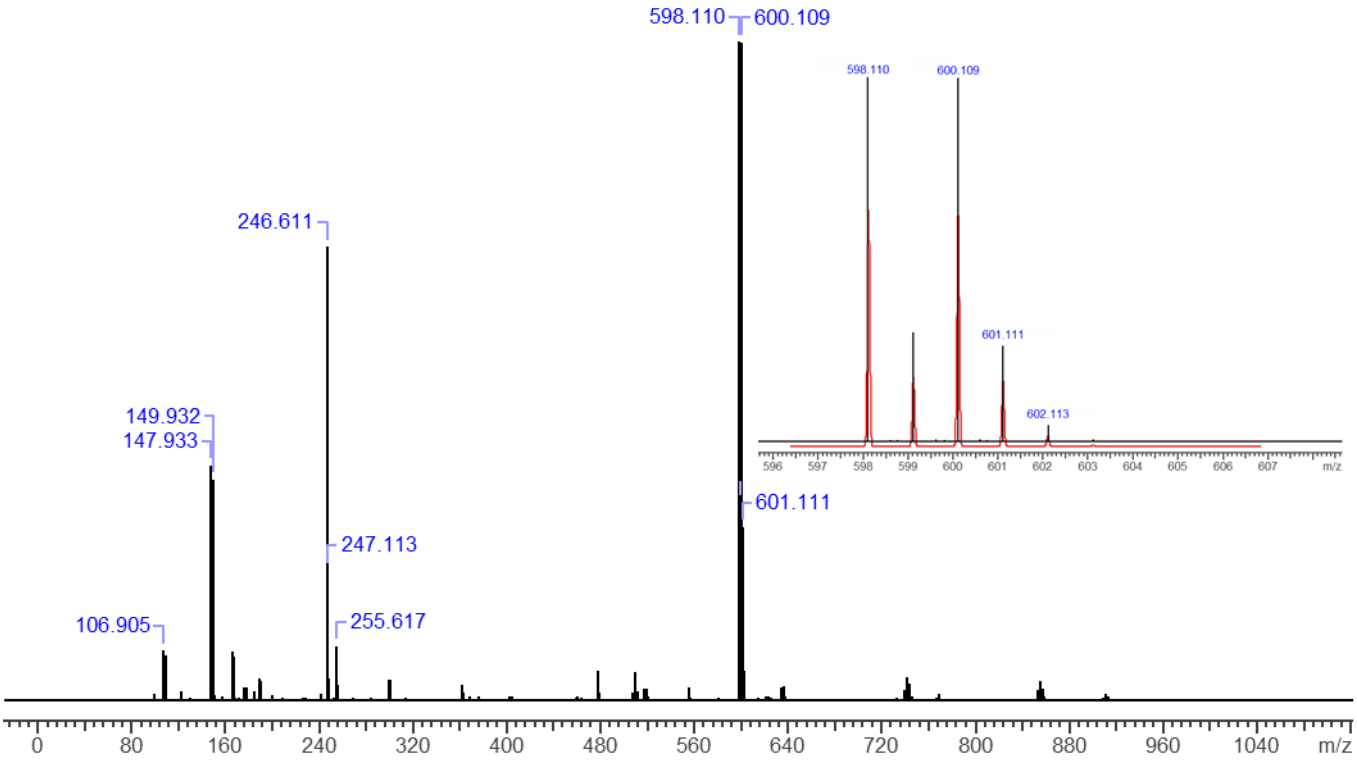

Figure S3: ESI-MS spectrum of **5**.

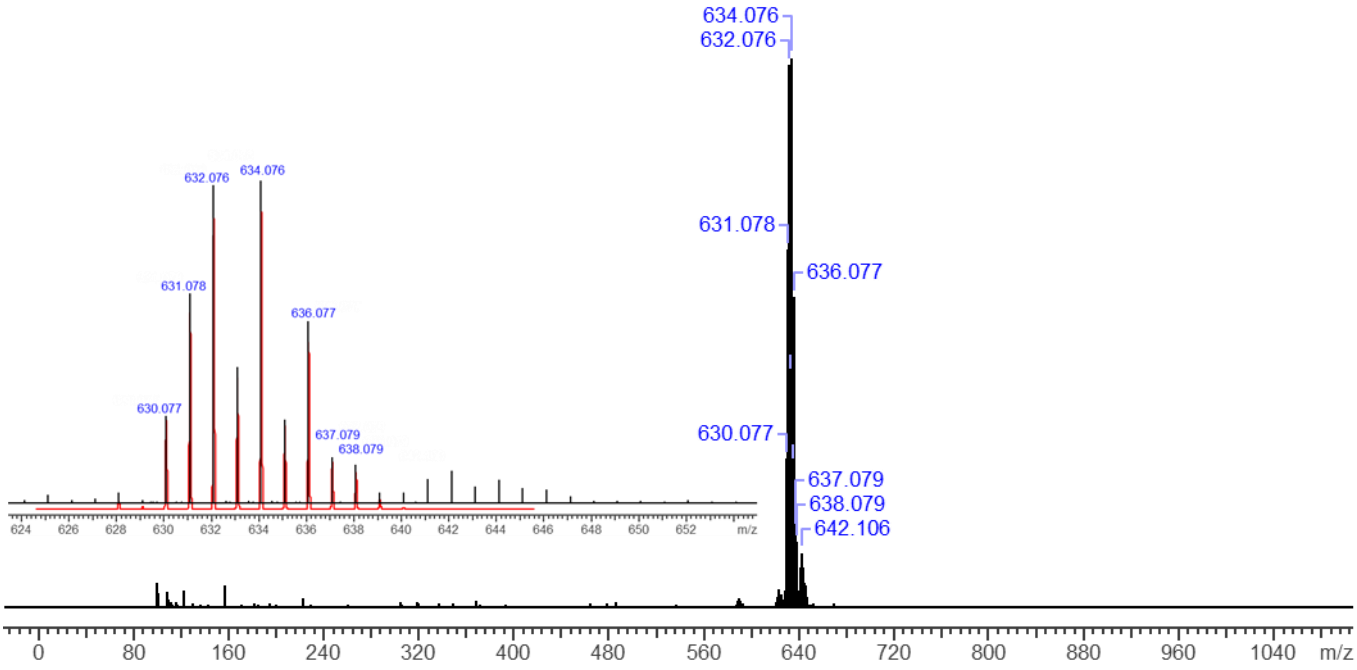

Figure S4: ESI-MS spectrum of **6**.

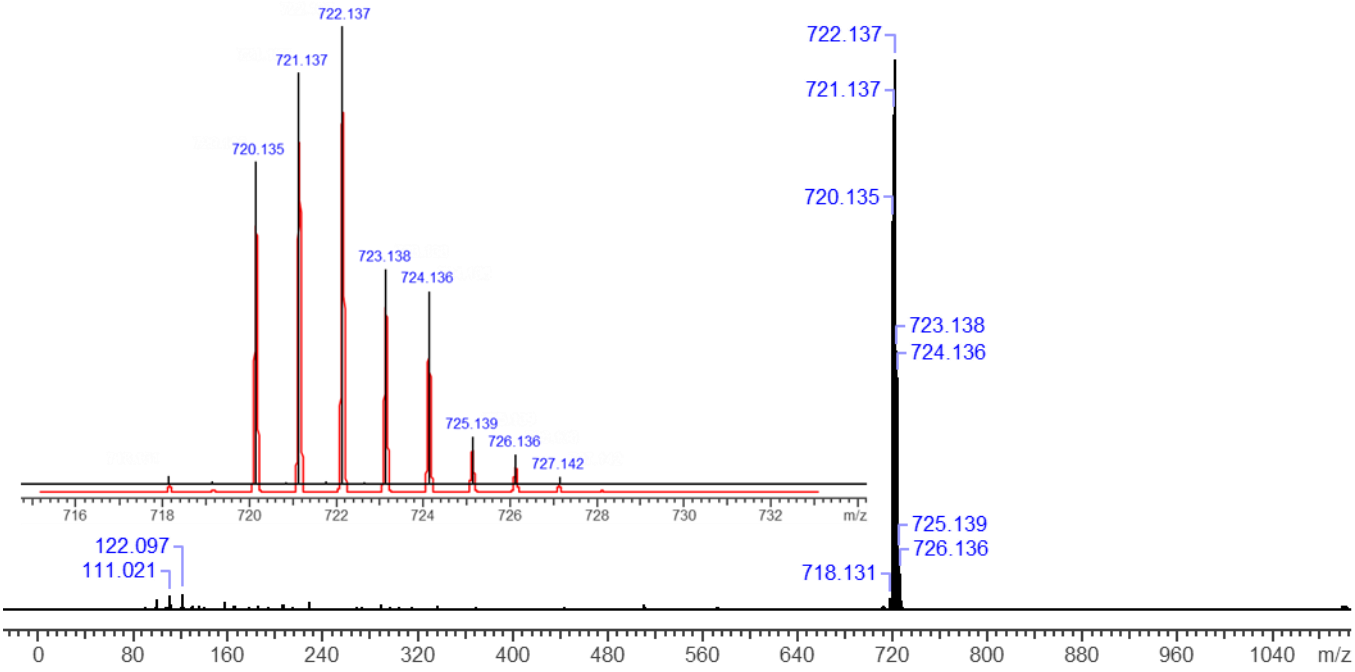

Figure S5: ESI-MS spectrum of **7**.

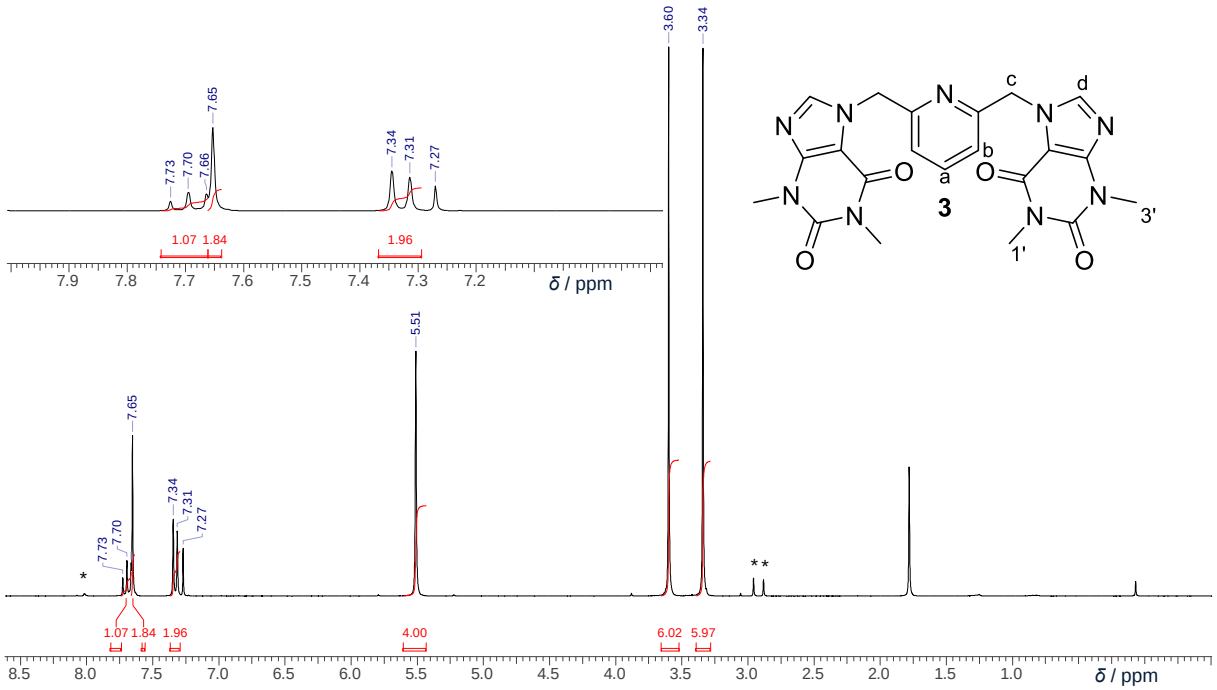

Figure S6: ^{1}H-NMR (300 MHz, $CDCl_3$) spectrum of **3**. Asterisk show residual DMF.

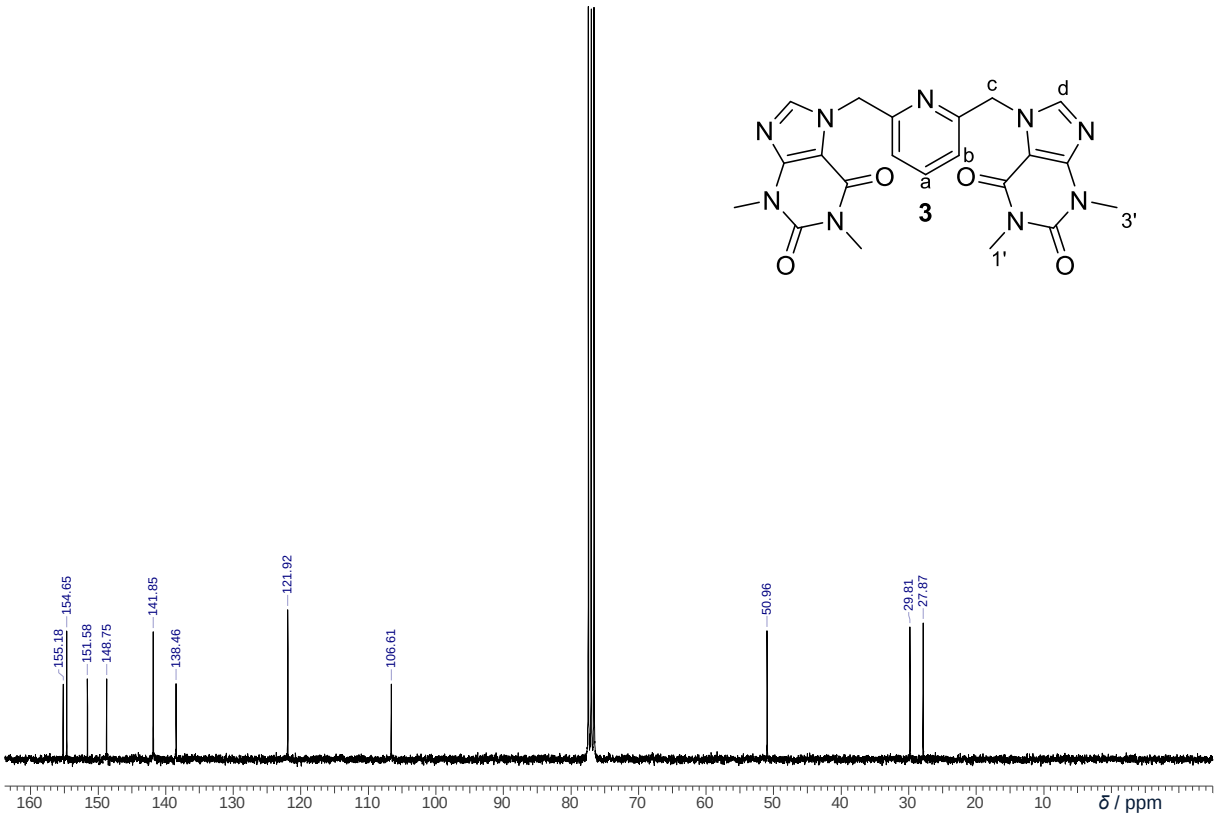

Figure S7: ^{13}C-NMR (75 MHz, $CDCl_3$) spectrum of **3**.

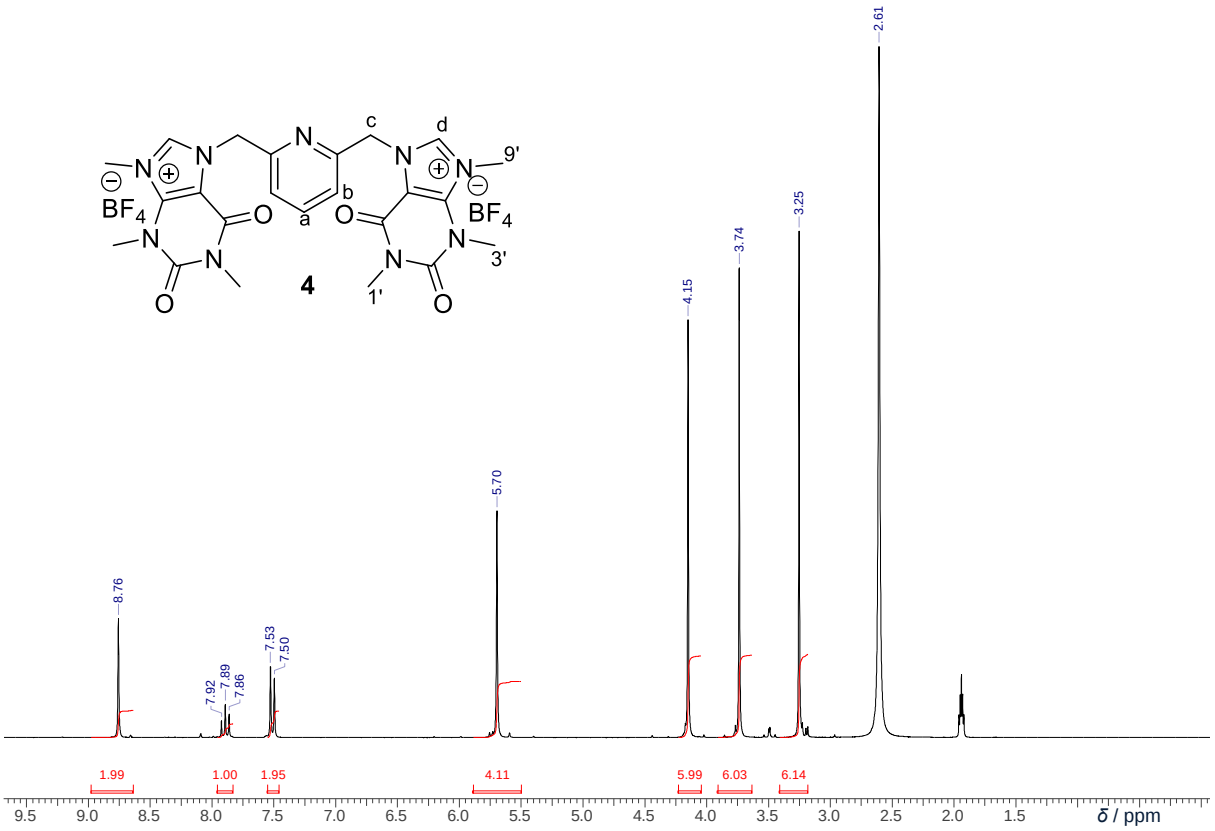

Figure S8: ^{1}H-NMR (300 MHz, CH_3CN) spectrum of **4**.

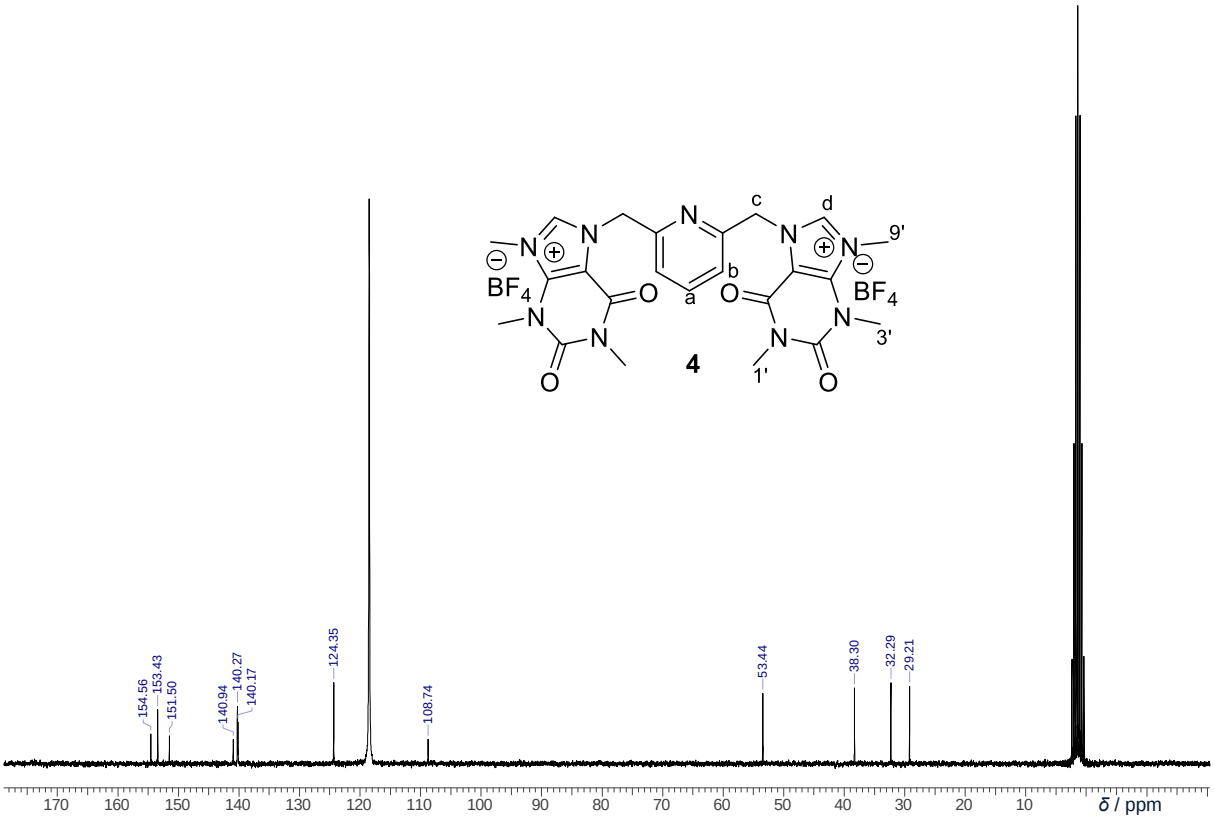

Figure S9: ^{13}C-NMR (75 MHz, CH_3CN) spectrum of **4**.

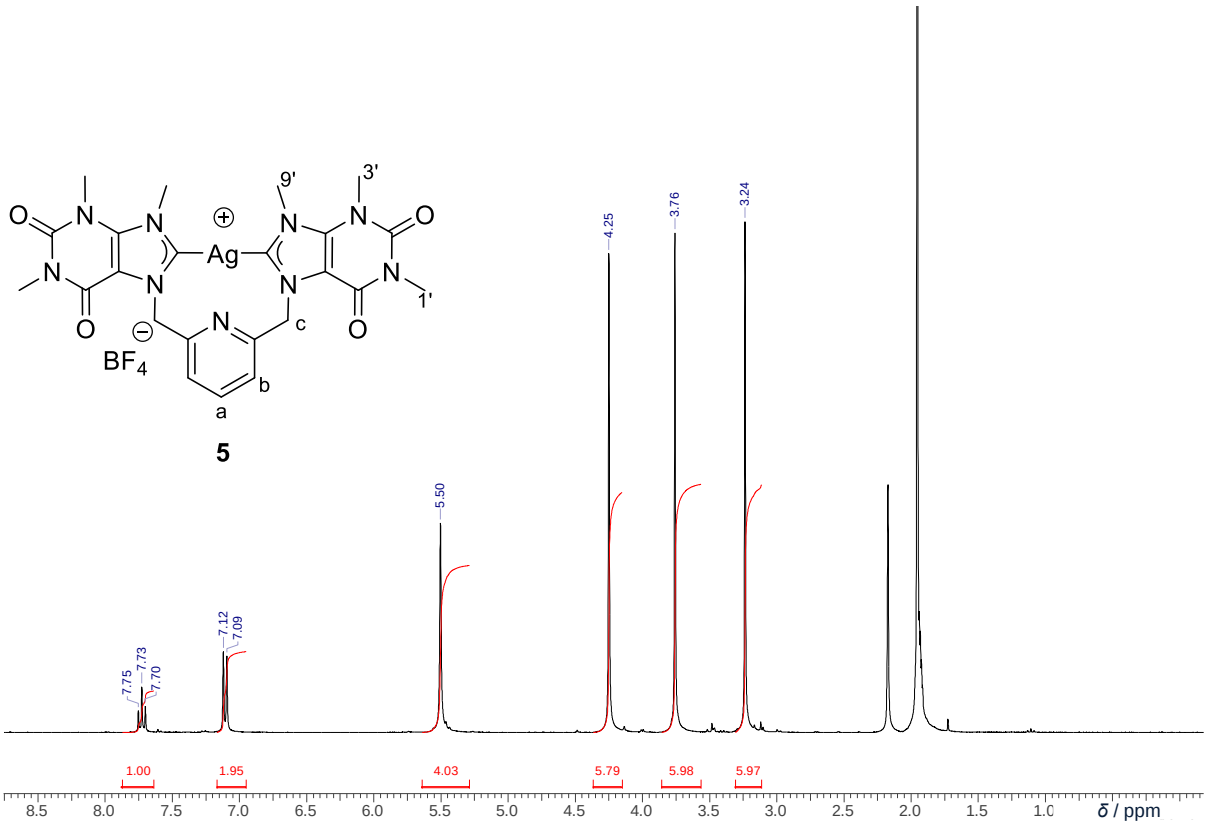

Figure S10: ^{1}H-NMR (300 MHz, CH_3CN) spectrum **5**.

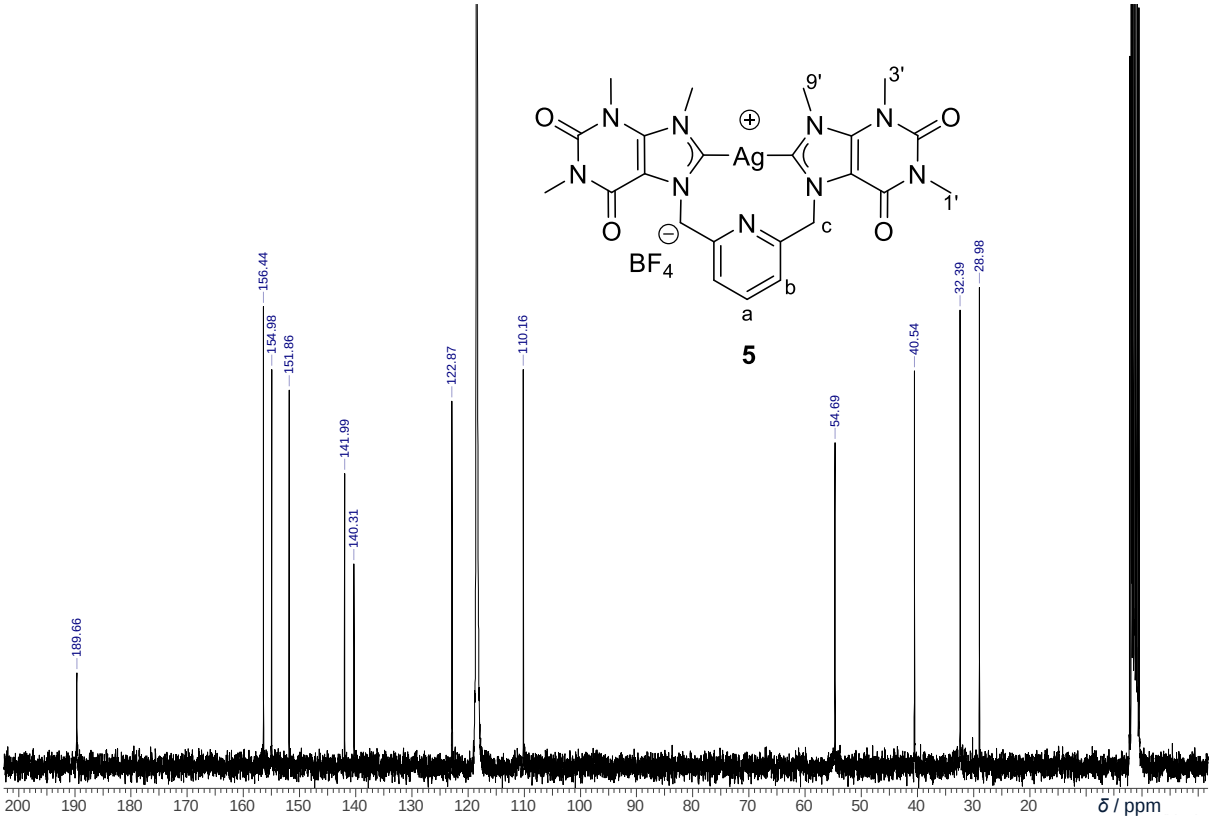

Figure S11: ^{13}C-NMR (75 MHz, CH_3CN) spectrum **5**.

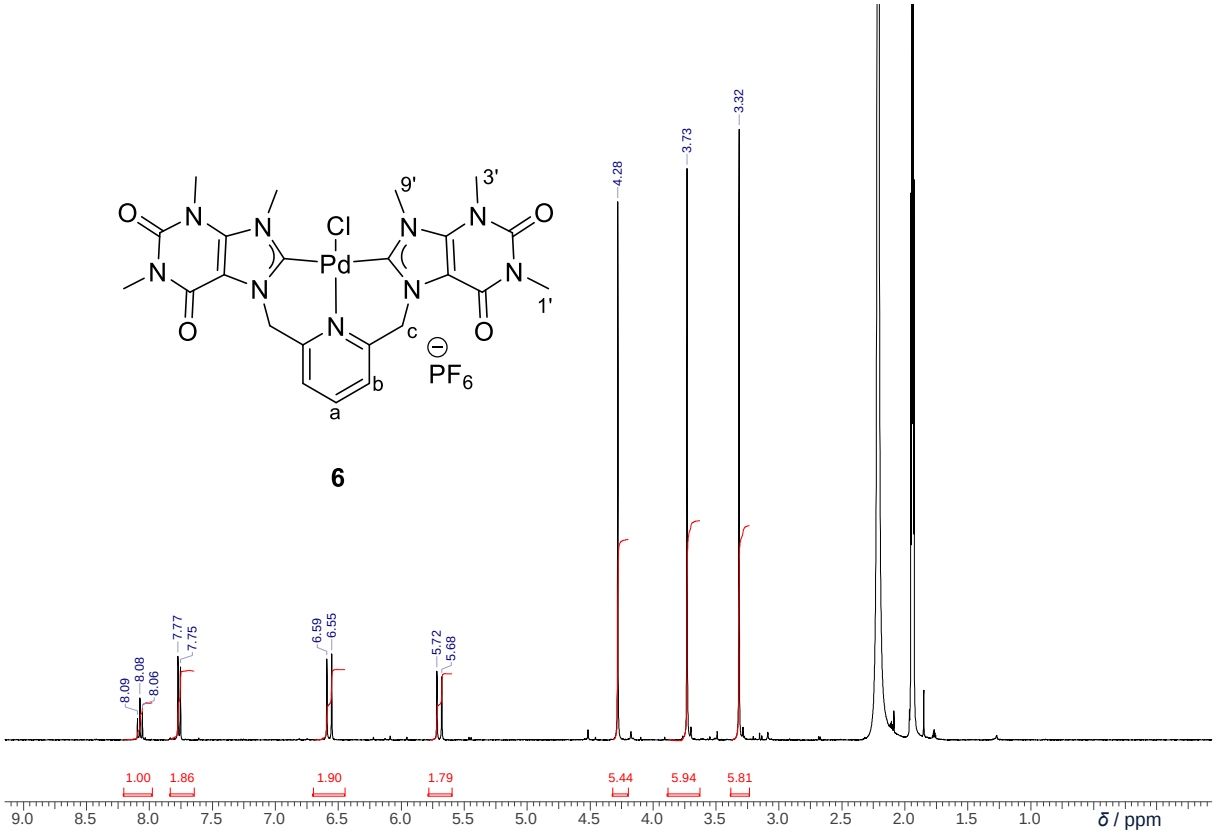

Figure S12: ^{1}H-NMR (300 MHz, CH_3CN) spectrum of **6**.

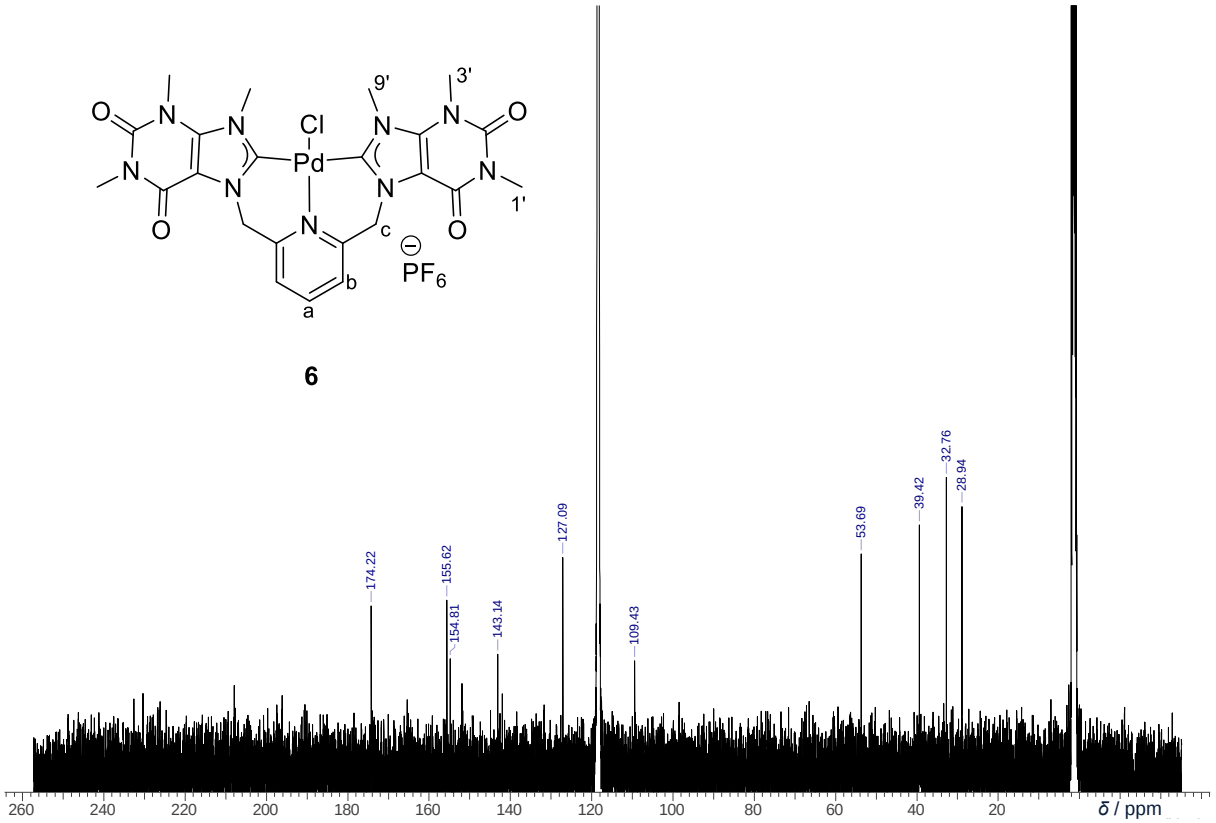

Figure S13: ^{13}C-NMR (75 MHz, CH_3CN) spectrum of **6**.

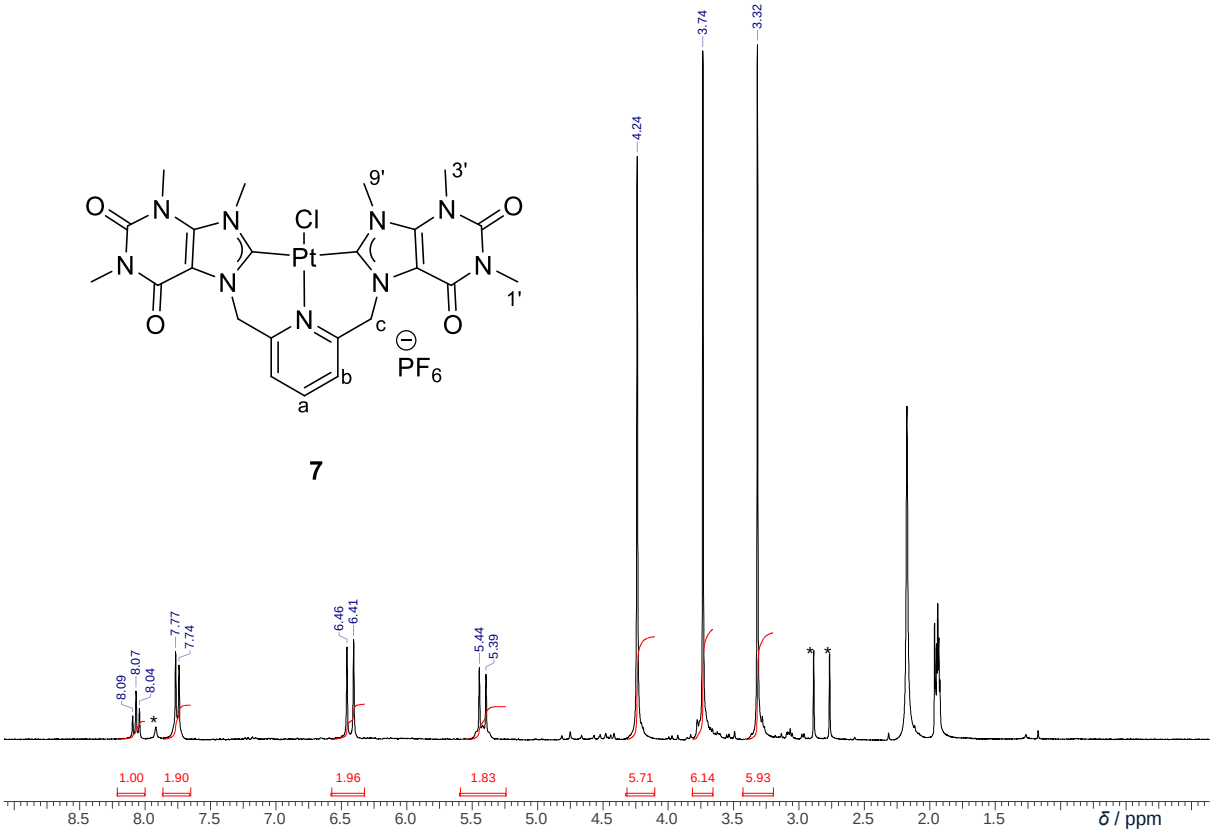

Figure S 14: ^{1}H-NMR (300 MHz, CH_3CN) spectrum of **7**. Asterisk show residual DMF.

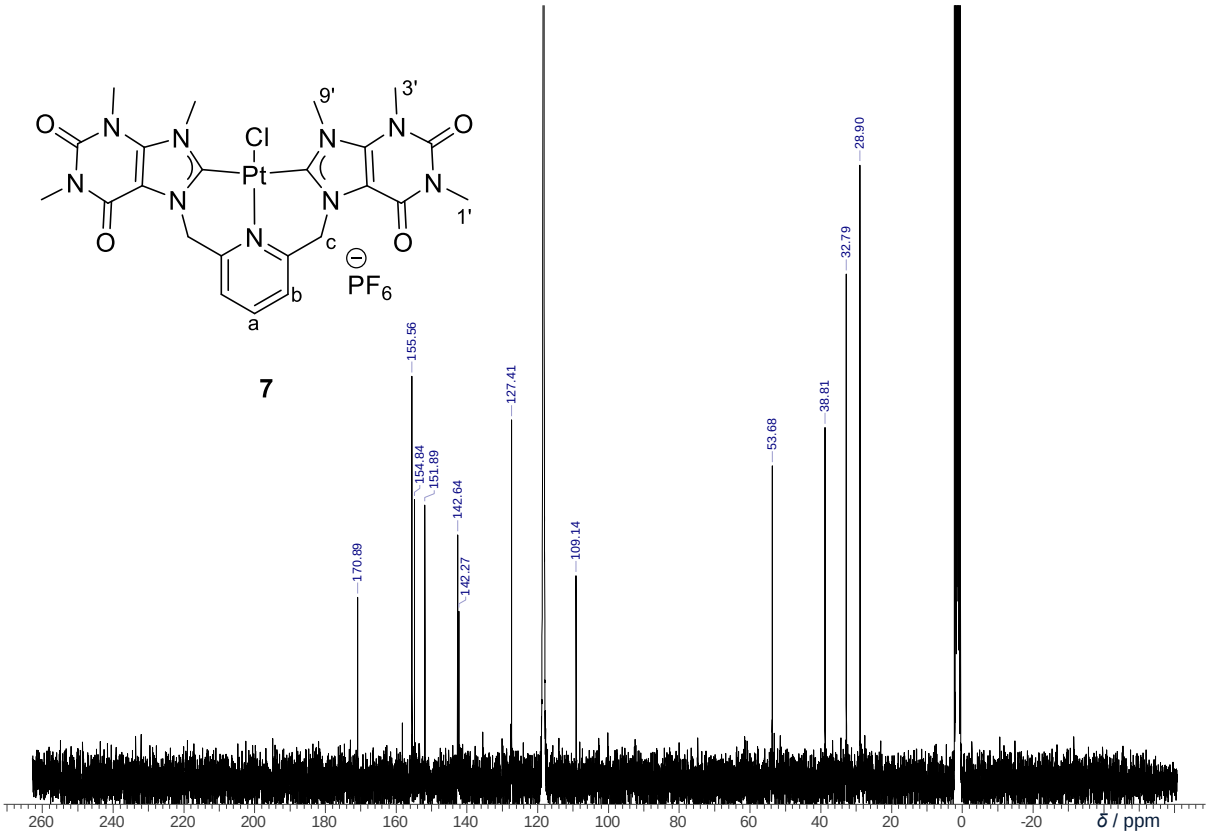

Figure S15: ^{13}C-NMR (75 MHz, CH_3CN) spectrum of **7**.

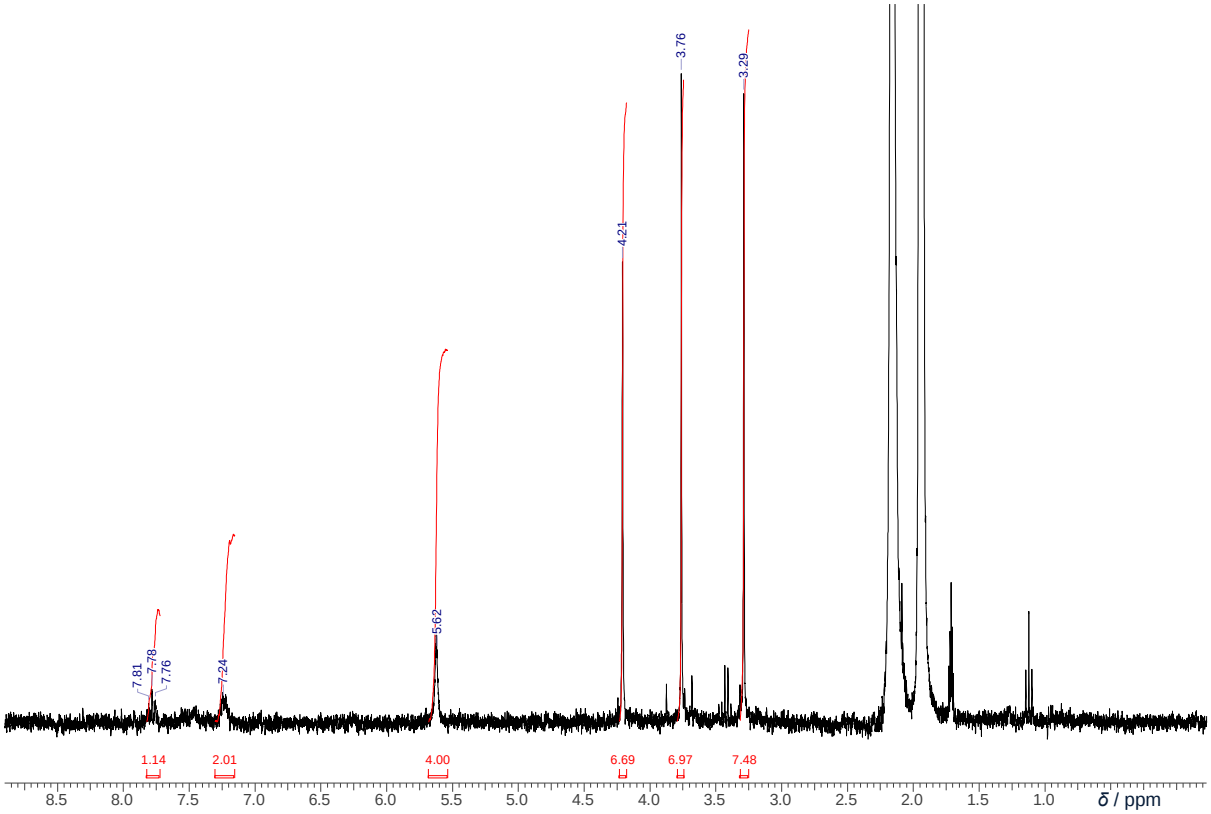

Figure S16: ^{1}H-NMR (300 MHz, CH_3CN) of the nickel complex.

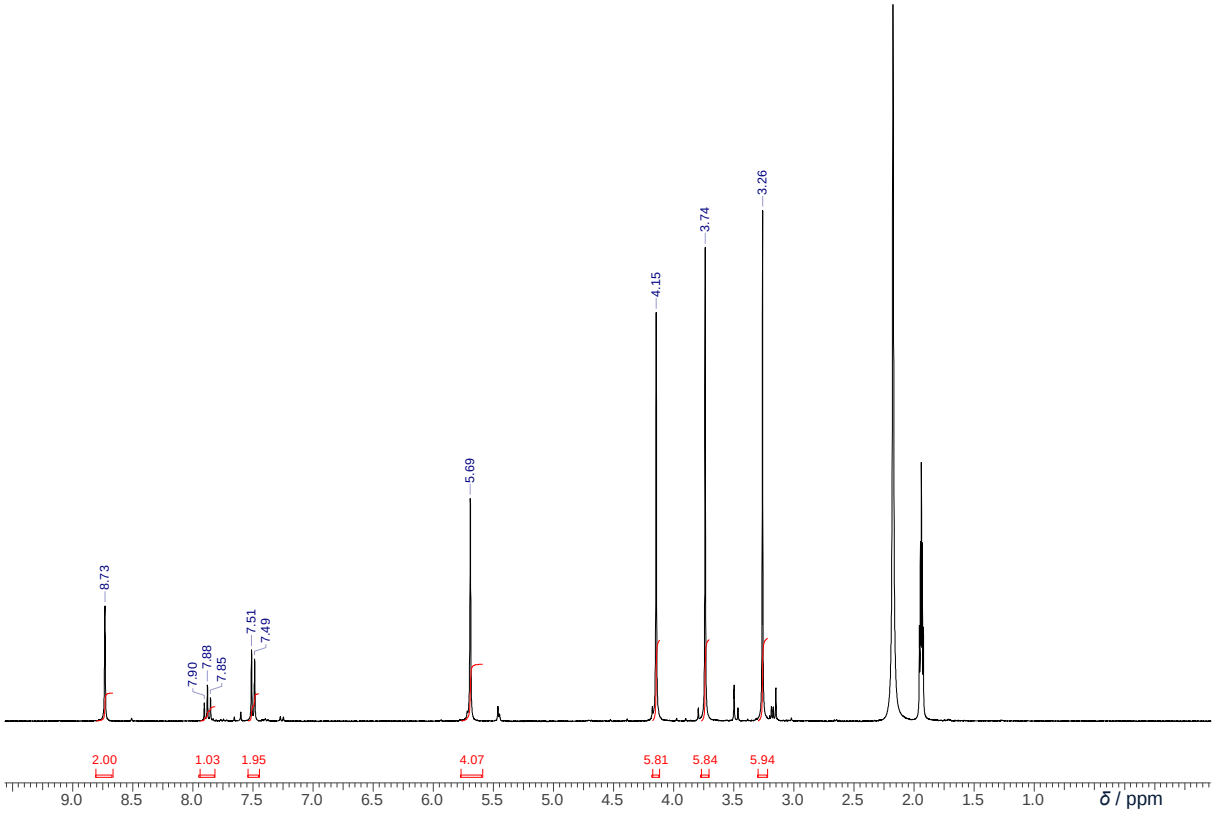

Figure S17: ^{1}H-NMR (300 MHz, CH_3CN) of the ruthenium reaction.

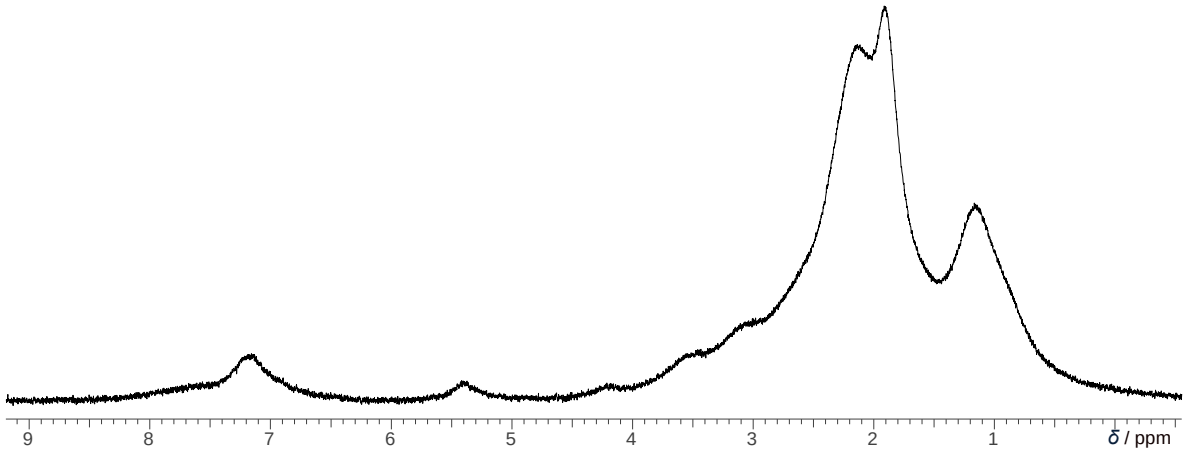

Figure S18: ^{1}H-NMR (300 MHz, CH_3CN) of the iron(II) NHC complex.

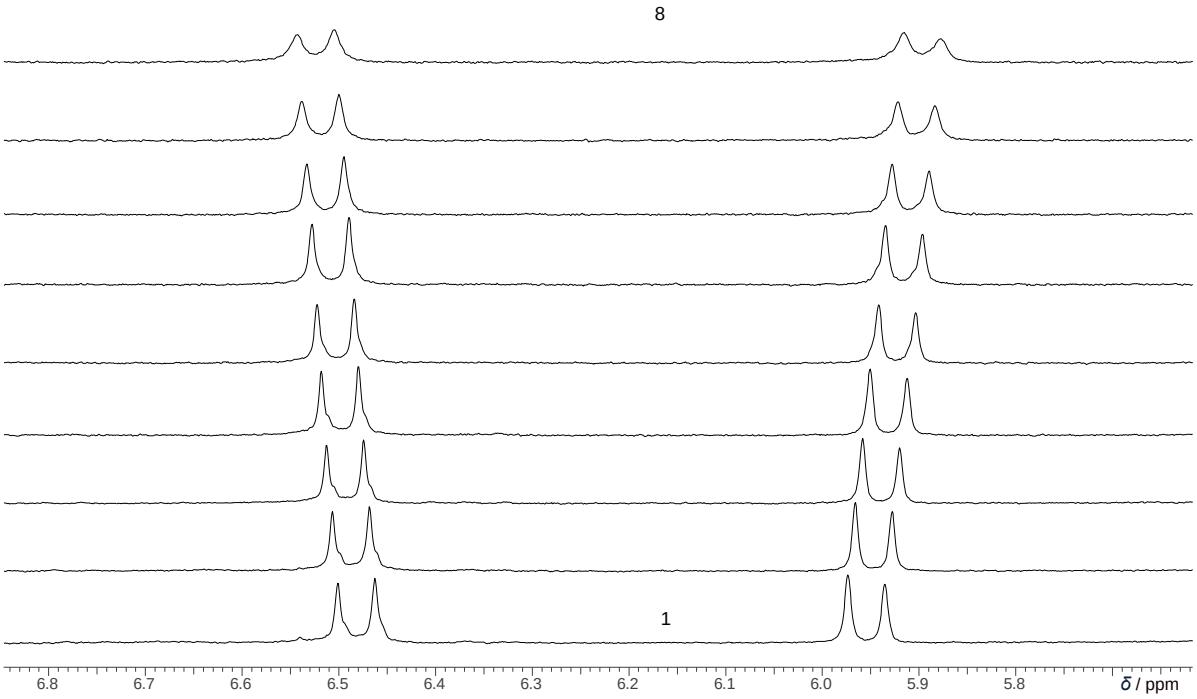

Figure S19: Variable temperature ^{1}H-NMR (300 MHz, DMSO) of **6** from 25 °C (1) to 100 °C (8)

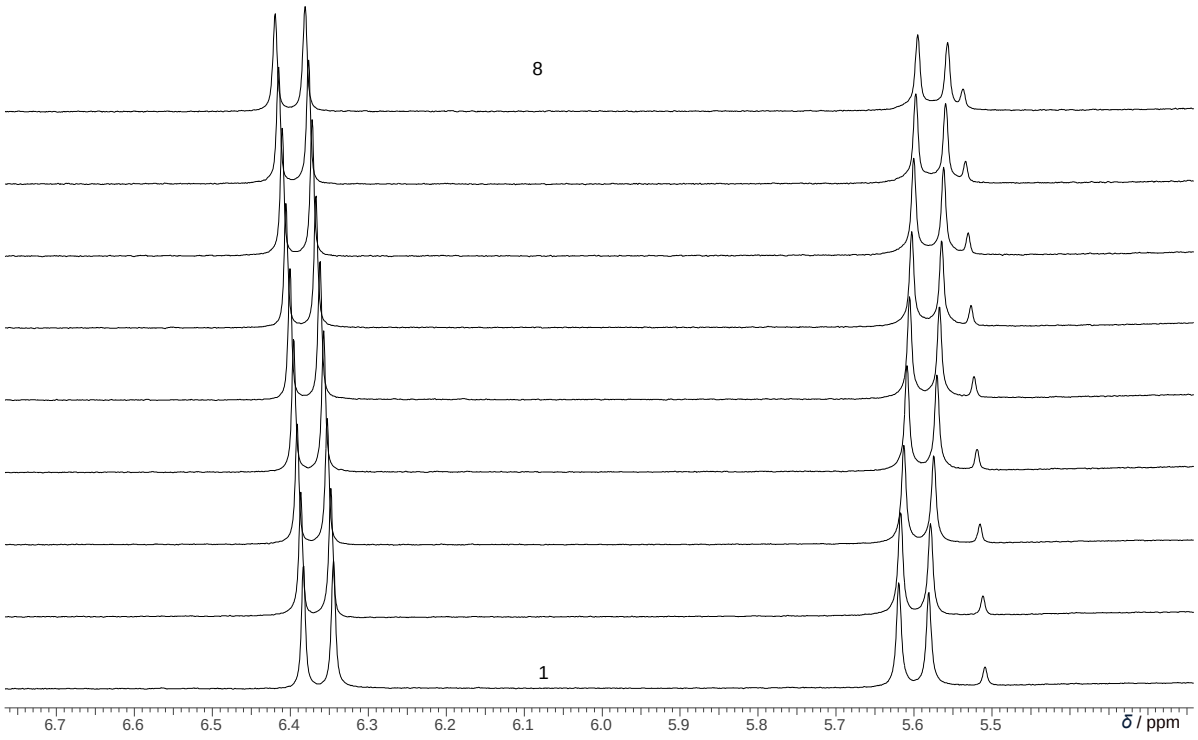

Figure S20: Variable temperature ^{1}H-NMR (300 MHz, DMSO) of **7** from 25 °C (1) to 100 °C (8)

Table S1: Crystal data and details on structure refinement for **7** · CH_3CN.

CSD deposition number	2157149
Internal identification code	bn00083
Empirical formula	$C_{25}H_{28}ClF_6N_{10}O_4PPt$
Formula weight	908.08
Temperature / K	120
Crystal system	triclinic
Space group	$P\bar{1}$
a/Å	10.430(1)
b/Å	12.026(1)
c/Å	13.200(1)
α/°	81.610(2)
β/°	88.365(2)
γ/°	69.819(2)
Cell volume / Å^3	1537.1(2)
Z	2
Calcd. density ρ_{calc} / g/cm^3	1.962
Absorption coefficient μ / mm^{-1}	4.792
F(000)	888.0
Crystal size / mm^3	0.29 × 0.21 × 0.17
Crystal shape and color	colorless prism
Radiation	Mo-Kα (λ = 0.71073)
2Θ range for data collection / °	3.646 to 67.042
Index ranges	$-15 \le h \le 16$, $-16 \le k \le 18$, $-19 \le l \le 20$
Reflections collected	26731
Independent reflections	10968 [R_{int} = 0.0289, R_{sigma} = 0.0353]
Completeness of dataset	100%
Data / restraints / parameters	10968 / 0 / 440
Goodness of fit on F^2	1.038
Final *R* indexes [$I>=2\sigma(I)$]	R_1 = 0.0236, wR_2 = 0.0509
Final *R* indexes [all data]	R_1 = 0.0279, wR_2 = 0.0524
Largest diff. peak and hole / e Å^{-3}	2.29 and –2.30

Table S2: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **7** · CH_3CN. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor.

Atom	***x***	***y***	***z***
Pt1	4790.5(2)	3819.4(2)	2730.2(2)
Cl1	6988.2(5)	3716.0(5)	2348.7(4)
O1	7398.5(18)	-1550.6(14)	7067.0(13)
O2	3577.0(17)	1795.7(15)	6833.3(12)
O3	1446(2)	9681.1(16)	-937.0(15)
O4	471.7(17)	6217.7(15)	-447.0(12)
N1	2806.6(17)	3960.2(14)	3063.2(12)
N2	4634.2(17)	2564.5(15)	4762.4(13)
N3	6412.8(17)	1376.1(15)	4095.5(13)
N4	7081.2(18)	-261.8(15)	5576.1(14)
N5	5465.7(19)	84.7(16)	6917.1(13)
N6	2928.1(18)	5209.9(15)	1030.8(13)
N7	4116.9(17)	6294.6(16)	1351.2(13)
N8	2823.9(19)	8150.3(16)	188.6(14)
N9	955.5(19)	7958.1(17)	-680.5(14)
C1	5392.3(19)	2474.8(18)	3922.1(15)
C2	3975(2)	5198.5(18)	1606.4(15)
C3	3471(2)	3653.1(18)	4873.4(15)
C4	2413(2)	3867.5(17)	4047.6(15)
C5	1090(2)	3948.2(18)	4295.9(16)
C6	135(2)	4140.7(19)	3526.2(17)
C7	535(2)	4249.3(18)	2518.2(17)
C8	1881(2)	4150.9(17)	2305.7(15)
C9	2353(2)	4244.4(19)	1217.0(16)
C10	6277(2)	816.6(18)	5059.2(15)
C11	5139(2)	1545.3(18)	5474.4(15)
C12	6701(2)	-632.4(18)	6551.1(17)
C13	4629(2)	1210.7(18)	6445.5(15)
C14	7452(2)	910(2)	3342.8(17)
C15	8463(2)	-931(2)	5258(2)
C16	5092(3)	-397(2)	7926.2(17)
C17	3115(2)	6987.7(18)	638.2(15)
C18	2364(2)	6315.1(18)	432.8(15)
C19	1721(2)	8661(2)	-502.8(17)
C20	1209(2)	6765.6(19)	-253.3(15)
C21	5063(2)	6663(2)	1915.8(18)
C22	3527(3)	8934(2)	464(2)
C23	-182(2)	8500(2)	-1433.4(19)
P1	1692.4(6)	7596.1(6)	3674.3(5)
F1	3183.3(17)	6701.5(15)	4044.9(13)
F2	1811.2(17)	6976.5(17)	2669.2(13)
F3	1029(2)	6684.4(18)	4263.8(16)
F4	1570.8(16)	8218.4(15)	4682.8(12)
F5	2371.4(18)	8514.2(15)	3087.4(13)
F6	213.3(16)	8512.2(18)	3301.7(14)
N10	2946(2)	2013(2)	-258.2(17)
C24	2115(2)	2216(2)	-868.1(18)
C25	1055(3)	2463(2)	-1649.6(19)

Table S3: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **7** · CH_3CN.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pt1	13.50(3)	15.35(4)	12.34(3)	1.06(2)	0.30(2)	-5.04(3)
Cl1	15.6(2)	30.0(3)	26.7(3)	3.0(2)	4.11(19)	-7.5(2)
O1	29.1(8)	15.3(7)	25.1(8)	4.1(6)	-5.6(7)	-4.9(6)
O2	23.1(8)	24.6(8)	19.3(7)	1.4(6)	4.8(6)	-4.5(6)
O3	38.1(10)	22.5(8)	36.5(10)	12.0(7)	-11.9(8)	-12.6(8)
O4	22.8(7)	26.6(8)	18.7(7)	0.2(6)	-4.5(6)	-12.3(6)
N1	14.2(7)	8.4(6)	12.5(7)	1.2(5)	-1.3(6)	-2.7(5)
N2	14.9(7)	13.3(7)	14.0(7)	0.4(6)	0.3(6)	-3.3(6)
N3	12.6(7)	15.5(7)	14.6(7)	-1.0(6)	-0.5(6)	-4.0(6)
N4	16.9(8)	13.1(7)	17.6(8)	0.0(6)	-1.9(6)	-3.6(6)
N5	21.8(8)	16.2(8)	14.8(8)	1.3(6)	-2.5(6)	-8.4(7)
N6	18.5(8)	14.1(7)	11.9(7)	0.9(6)	-1.3(6)	-7.1(6)
N7	15.7(7)	16.7(8)	14.5(7)	1.6(6)	-0.6(6)	-8.8(6)
N8	22.9(9)	15.9(8)	19.5(8)	5.1(6)	-2.8(7)	-9.7(7)
N9	19.1(8)	18.4(8)	16.3(8)	2.9(6)	-2.4(6)	-5.5(7)
C1	13.6(8)	15.4(8)	12.8(8)	-0.2(7)	-1.6(6)	-4.9(7)
C2	16.2(8)	15.6(8)	12.4(8)	0.3(7)	0.2(7)	-6.8(7)
C3	16.7(8)	13.3(8)	13.7(8)	-1.3(7)	1.4(7)	-2.8(7)
C4	15.6(8)	10.3(8)	15.3(8)	-0.3(6)	0.9(7)	-3.3(7)
C5	17.9(9)	14.9(9)	17.7(9)	-1.6(7)	3.3(7)	-5.7(7)
C6	15.9(9)	18.4(9)	24.9(10)	-1.4(8)	1.6(8)	-6.8(7)
C7	16.9(9)	15.3(9)	21.1(10)	-0.3(7)	-3.0(7)	-6.6(7)
C8	17.7(8)	11.1(8)	16.9(9)	0.4(7)	-0.8(7)	-6.0(7)
C9	22.1(9)	16.2(9)	15.2(9)	-0.9(7)	-1.6(7)	-10.1(8)
C10	14.7(8)	13.7(8)	14.9(8)	0.0(7)	-2.1(7)	-5.7(7)
C11	14.6(8)	14.3(8)	14.4(8)	-0.1(7)	-1.1(7)	-4.6(7)
C12	20.3(9)	14.0(9)	19.9(9)	-0.8(7)	-3.9(7)	-7.6(7)
C13	19.4(9)	16.6(9)	14.2(8)	0.5(7)	-2.1(7)	-8.5(7)
C14	18.1(9)	23.7(10)	18.5(9)	-4.5(8)	5.1(7)	-3.5(8)
C15	18.7(10)	17.0(10)	32.9(12)	2.8(9)	2.3(9)	0.0(8)
C16	32.3(12)	22.6(10)	14.7(9)	3.5(8)	-1.3(8)	-11.2(9)
C17	16.5(8)	16.9(9)	13.4(8)	1.6(7)	0.1(7)	-7.1(7)
C18	19.0(9)	16.5(9)	11.5(8)	0.2(7)	-0.4(7)	-7.7(7)
C19	23.7(10)	20.6(10)	19.1(10)	3.4(8)	-1.9(8)	-7.5(8)
C20	17.9(9)	19.1(9)	11.8(8)	-0.1(7)	0.7(7)	-6.6(7)
C21	23.1(10)	24.2(10)	22.4(10)	3.7(8)	-6.8(8)	-14.9(9)
C22	33.1(13)	20.3(11)	40.9(14)	7.5(10)	-11.1(11)	-16.5(10)
C23	22.3(10)	29.5(12)	25.7(11)	8.1(9)	-8.9(9)	-7.2(9)
P1	19.0(2)	24.4(3)	23.6(3)	-8.8(2)	4.3(2)	-10.9(2)
F1	27.9(8)	34.6(9)	40.1(9)	1.0(7)	-0.3(7)	-2.2(7)
F2	30.2(8)	59.2(11)	40.0(9)	-33.6(9)	10.6(7)	-15.9(8)
F3	60.3(12)	50.1(11)	62.1(12)	-23.5(10)	32.4(10)	-43.4(10)
F4	33.5(8)	42.1(9)	29.0(8)	-17.0(7)	0.7(6)	-16.3(7)
F5	44.9(10)	34.1(9)	39.1(9)	3.3(7)	6.0(7)	-21.6(8)
F6	22.8(7)	62.0(12)	41.5(10)	-26.1(9)	-5.1(7)	2.3(8)
N10	29.2(10)	30.6(11)	29.5(11)	-2.9(9)	1.6(8)	-13.7(9)
C24	24.0(10)	19.3(10)	23.7(10)	-2.8(8)	6.0(8)	-8.7(8)
C25	25.2(11)	28.4(12)	23.9(11)	-2.0(9)	0.8(9)	-6.5(9)

Table S4: Bond lengths for **7** · CH_3CN.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pt1	Cl1	2.2976(6)	N7	C17	1.378(3)
Pt1	N1	2.0571(16)	N7	C21	1.471(3)
Pt1	C1	2.024(2)	N8	C17	1.369(3)
Pt1	C2	2.014(2)	N8	C19	1.393(3)
O1	C12	1.211(3)	N8	C22	1.467(3)
O2	C13	1.226(3)	N9	C19	1.394(3)
O3	C19	1.215(3)	N9	C20	1.398(3)
O4	C20	1.225(3)	N9	C23	1.471(3)
N1	C4	1.352(2)	C3	C4	1.505(3)
N1	C8	1.349(3)	C4	C5	1.382(3)
N2	C1	1.339(2)	C5	C6	1.381(3)
N2	C3	1.469(3)	C6	C7	1.385(3)
N2	C11	1.382(3)	C7	C8	1.391(3)
N3	C1	1.374(3)	C8	C9	1.507(3)
N3	C10	1.377(3)	C10	C11	1.364(3)
N3	C14	1.469(3)	C11	C13	1.431(3)
N4	C10	1.369(3)	C17	C18	1.362(3)
N4	C12	1.392(3)	C18	C20	1.426(3)
N4	C15	1.472(3)	P1	F1	1.5970(17)
N5	C12	1.399(3)	P1	F2	1.5957(16)
N5	C13	1.397(3)	P1	F3	1.5910(18)
N5	C16	1.470(3)	P1	F4	1.6012(15)
N6	C2	1.343(3)	P1	F5	1.6060(17)
N6	C9	1.468(3)	P1	F6	1.5963(18)
N6	C18	1.384(3)	N10	C24	1.139(3)
N7	C2	1.369(3)	C24	C25	1.457(3)

Table S5: Bond Angles for **7** · CH_3CN.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom
N1	Pt1	Cl1	178.50(5)	C6	C7	C8
C1	Pt1	Cl1	93.38(6)	N1	C8	C7
C1	Pt1	N1	87.80(7)	N1	C8	C9
C2	Pt1	Cl1	92.99(6)	C7	C8	C9
C2	Pt1	N1	85.82(7)	N6	C9	C8
C2	Pt1	C1	173.46(8)	N4	C10	N3
C4	N1	Pt1	120.24(13)	C11	C10	N3
C8	N1	Pt1	120.64(13)	C11	C10	N4
C8	N1	C4	119.12(17)	N2	C11	C13
C1	N2	C3	121.68(17)	C10	C11	N2
C1	N2	C11	110.88(16)	C10	C11	C13
C11	N2	C3	127.39(16)	O1	C12	N4
C1	N3	C10	109.02(16)	O1	C12	N5
C1	N3	C14	123.62(17)	N4	C12	N5
C10	N3	C14	127.35(17)	O2	C13	N5
C10	N4	C12	118.40(17)	O2	C13	C11
C10	N4	C15	123.29(18)	N5	C13	C11
C12	N4	C15	117.05(18)	N8	C17	N7
C12	N5	C16	114.73(18)	C18	C17	N7
C13	N5	C12	126.32(18)	C18	C17	N8
C13	N5	C16	118.85(18)	N6	C18	C20
C2	N6	C9	121.18(17)	C17	C18	N6
C2	N6	C18	110.31(17)	C17	C18	C20
C18	N6	C9	127.34(17)	O3	C19	N8
C2	N7	C17	108.94(16)	O3	C19	N9
C2	N7	C21	121.95(17)	N8	C19	N9
C17	N7	C21	128.33(18)	O4	C20	N9
C17	N8	C19	118.79(18)	O4	C20	C18
C17	N8	C22	123.61(19)	N9	C20	C18
C19	N8	C22	117.34(18)	F1	P1	F4
C19	N9	C20	126.24(18)	F1	P1	F5
C19	N9	C23	116.88(19)	F2	P1	F1
C20	N9	C23	116.78(18)	F2	P1	F4
N2	C1	Pt1	118.33(14)	F2	P1	F5
N2	C1	N3	106.17(17)	F2	P1	F6
N3	C1	Pt1	135.39(14)	F3	P1	F1
N6	C2	Pt1	119.40(14)	F3	P1	F2
N6	C2	N7	106.53(17)	F3	P1	F4
N7	C2	Pt1	133.34(15)	F3	P1	F5
N2	C3	C4	109.59(16)	F3	P1	F6
N1	C4	C3	117.74(17)	F4	P1	F5
N1	C4	C5	121.59(19)	F6	P1	F1
C5	C4	C3	120.66(18)	F6	P1	F4
C6	C5	C4	119.76(19)	F6	P1	F5
C5	C6	C7	118.60(19)	N10	C24	C25

Table S6: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **7** · CH_3CN.

Atom	*x*	*y*	*z*	U(eq)
H3A	3786.44	4346.99	4820.38	18
H3B	3067.66	3561.99	5554.87	18
H5	839.05	3871.63	4993.22	20
H6	-777.62	4197.33	3685.22	24
H7	-104.84	4390.12	1974.99	21
H9A	3055.17	3476.72	1101.23	20
H9B	1573.69	4416.76	737.28	20
H14A	7178.3	1403.96	2673.08	32
H14B	7539.21	82.05	3291.34	32
H14C	8331.6	931.75	3562	32
H15A	8397.8	-1359.1	4694.57	38
H15B	8967	-1507.79	5837.87	38
H15C	8944.6	-372.37	5028.12	38
H16A	5829.76	-540.39	8425.56	35
H16B	4947.45	-1151.15	7881.12	35
H16C	4249.61	181.05	8144.54	35
H21A	4538.64	7306.79	2299.39	33
H21B	5647.76	6950.98	1431.05	33
H21C	5631.12	5978.13	2393.13	33
H22A	3393.14	9019.81	1190.29	46
H22B	3152.51	9723.16	46.33	46
H22C	4505.82	8584.04	339.31	46
H23A	96.57	8198.61	-2085.49	41
H23B	-425.86	9372.32	-1535.96	41
H23C	-972.73	8289.27	-1180.45	41
H25A	1457.65	2482.89	-2329.12	40
H25B	347.38	3239.41	-1599.64	40
H25C	647.78	1833.94	-1545.9	40