Supporting Information

Reactivity of a New Aryl Cycloplatinated(II) Complex Containing Rollover 2,2´-Bipyridine *N*-Oxide toward a Series of Diphosphine Ligands

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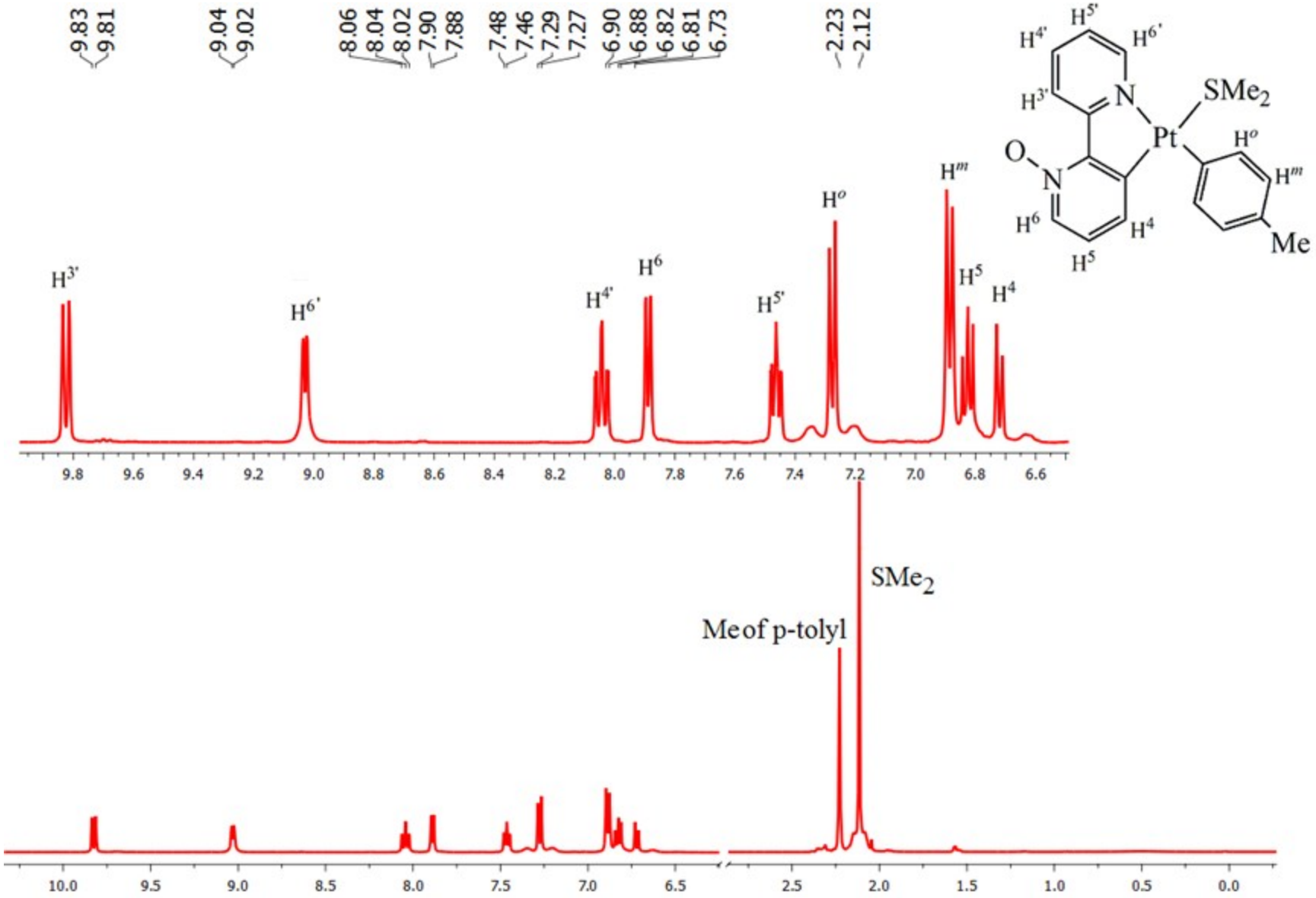

Figure S1. ^{1}H NMR spectrum of the complex **1** in CD_2Cl_2.

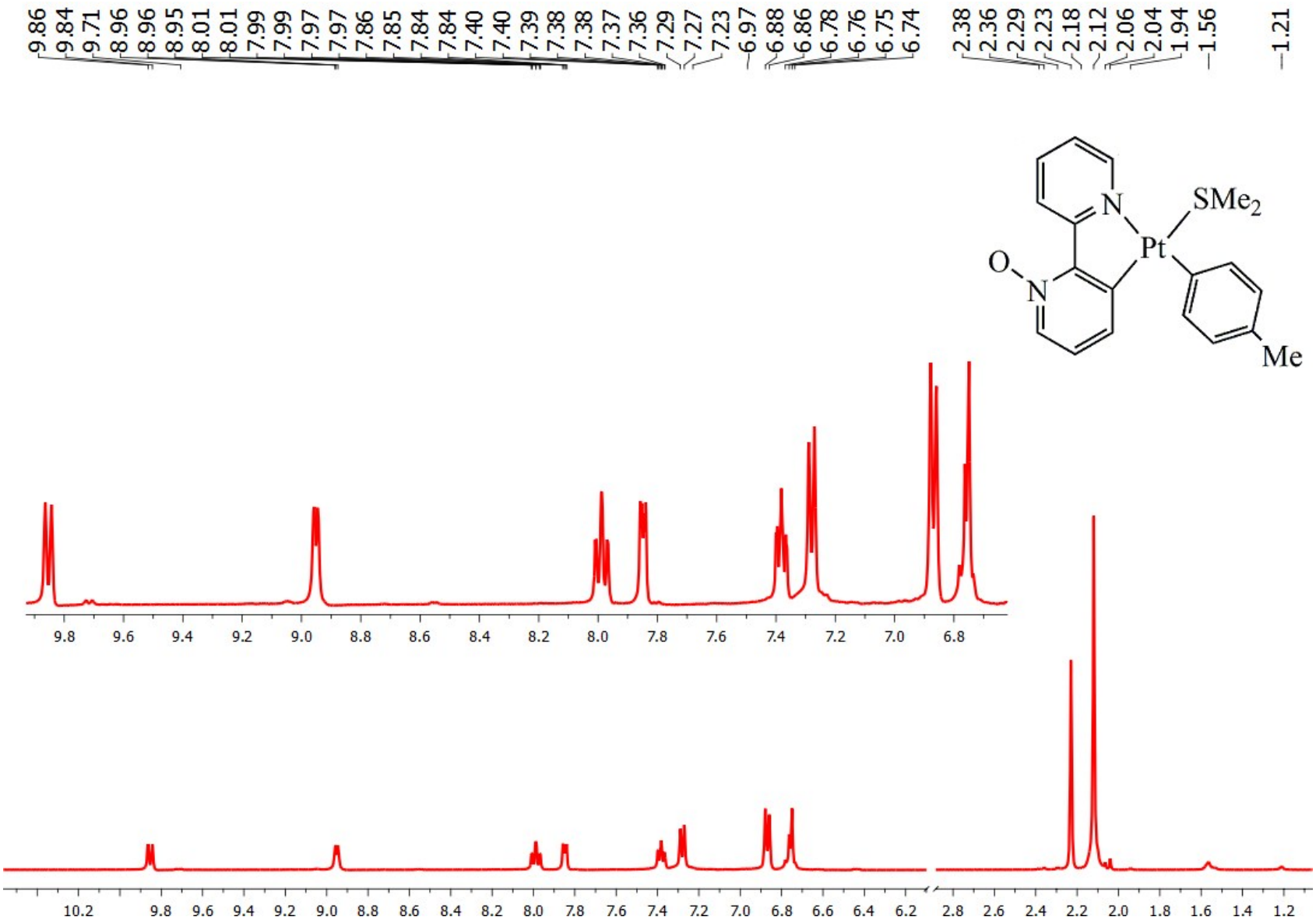

Figure S2. $^{1}H\{Pt\}$ NMR spectrum of the complex **1** in CD_2Cl_2.

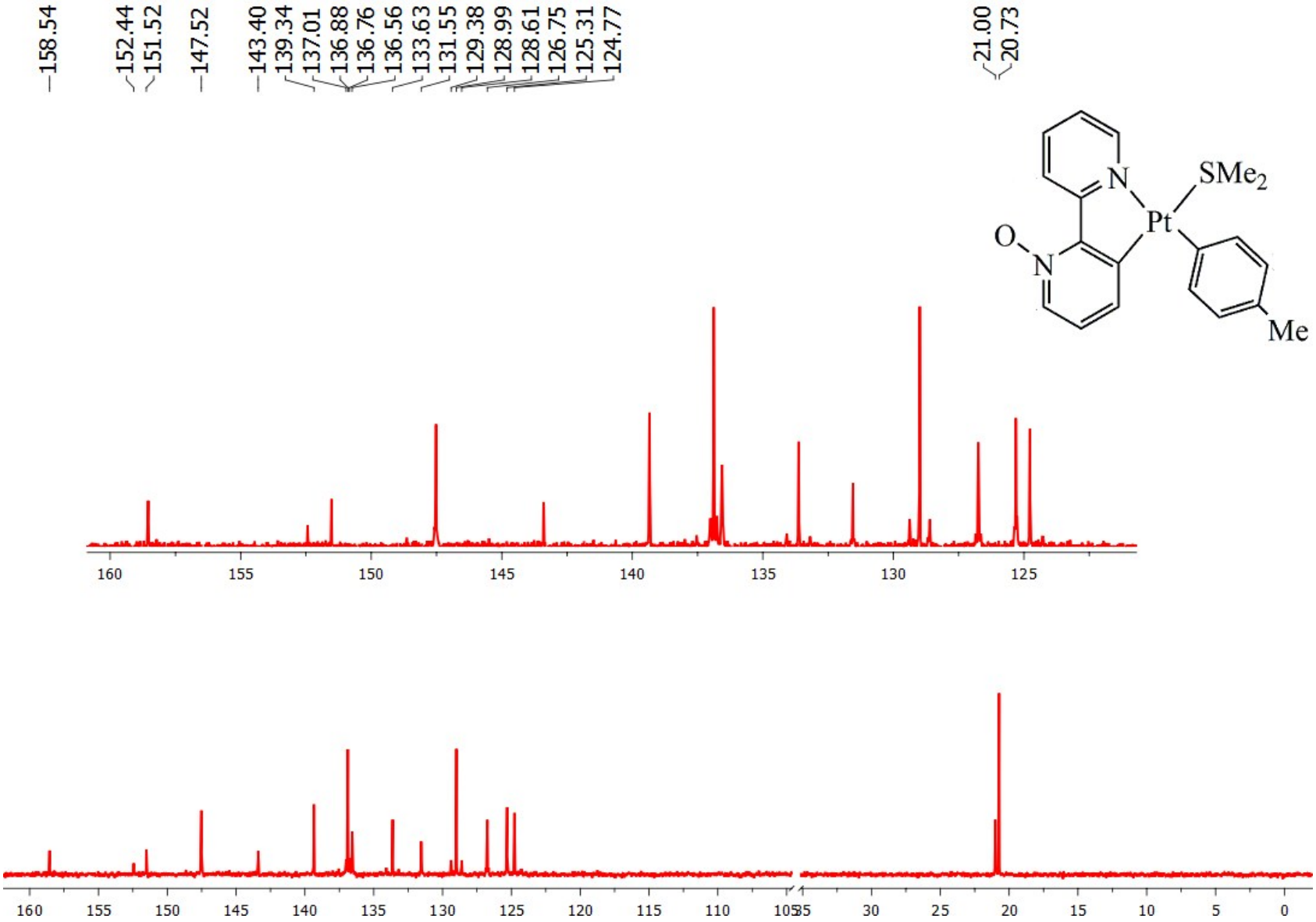

Figure S3. $^{13}C\{H\}$ NMR spectrum of the complex **1** in CD_2Cl_2.

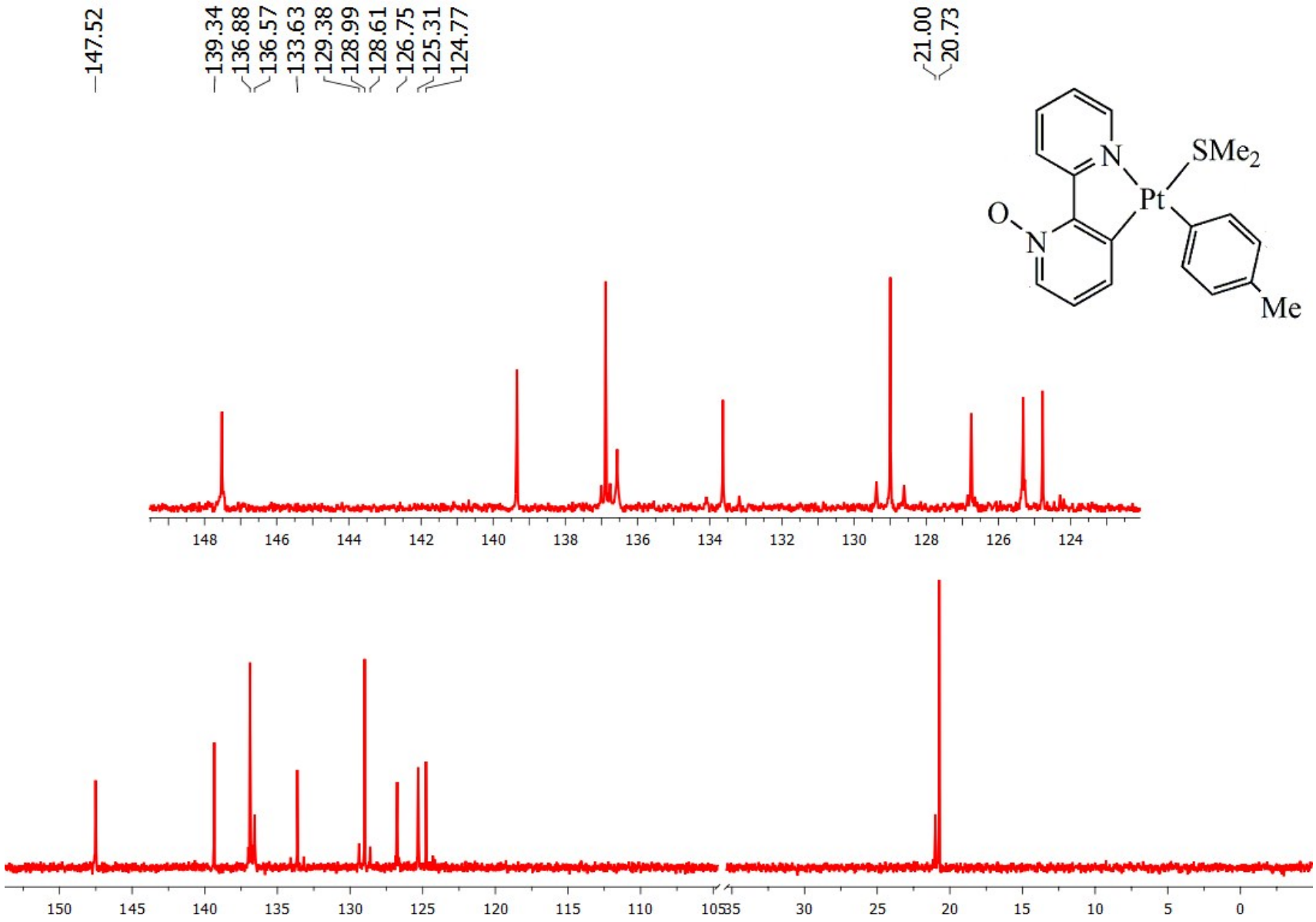

Figure S4. DEPT 135° spectrum of the complex **1** in CD_2Cl_2.

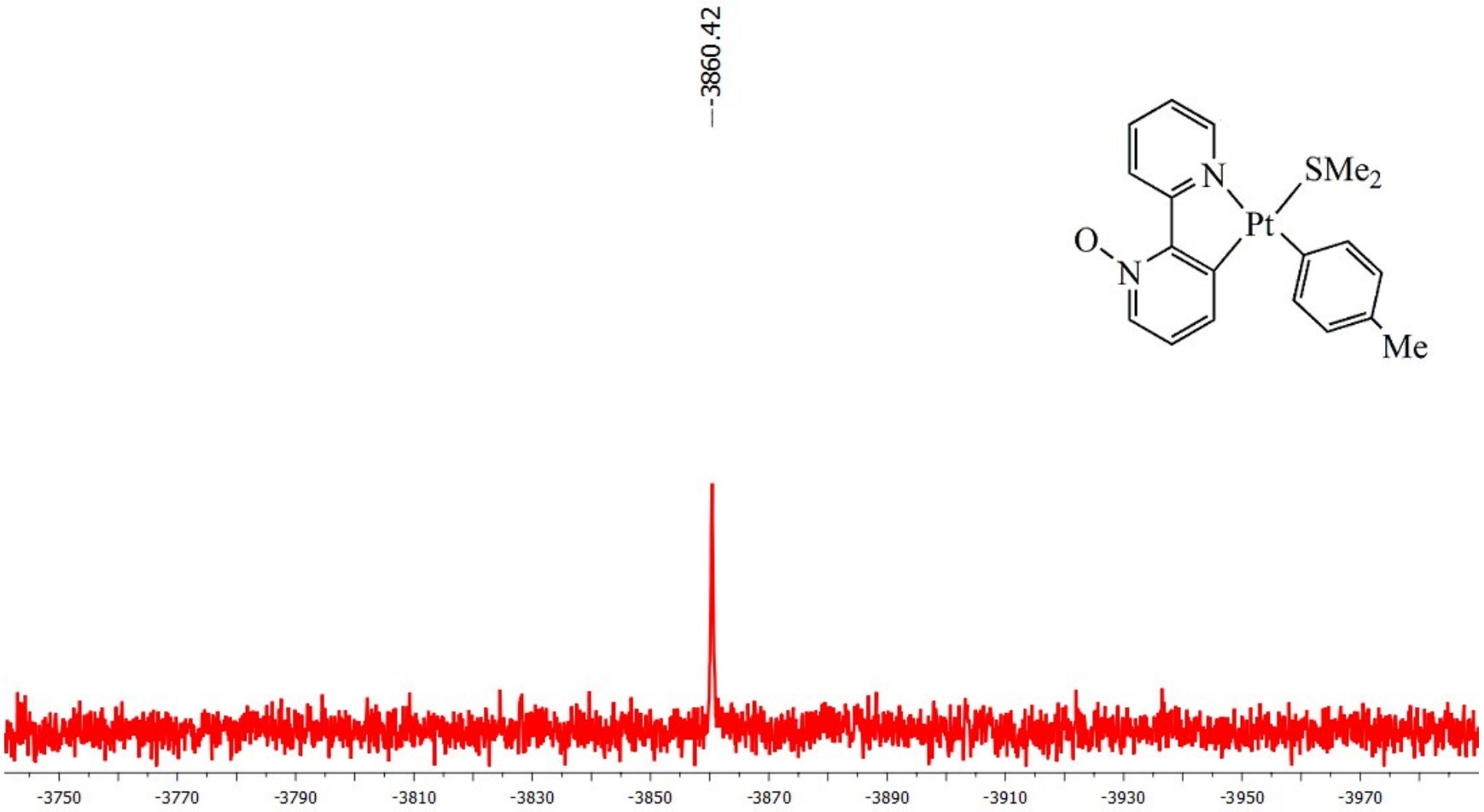

Figure S5. $^{195}Pt\{H\}$ NMR spectrum of the complex **1** in CD_2Cl_2.

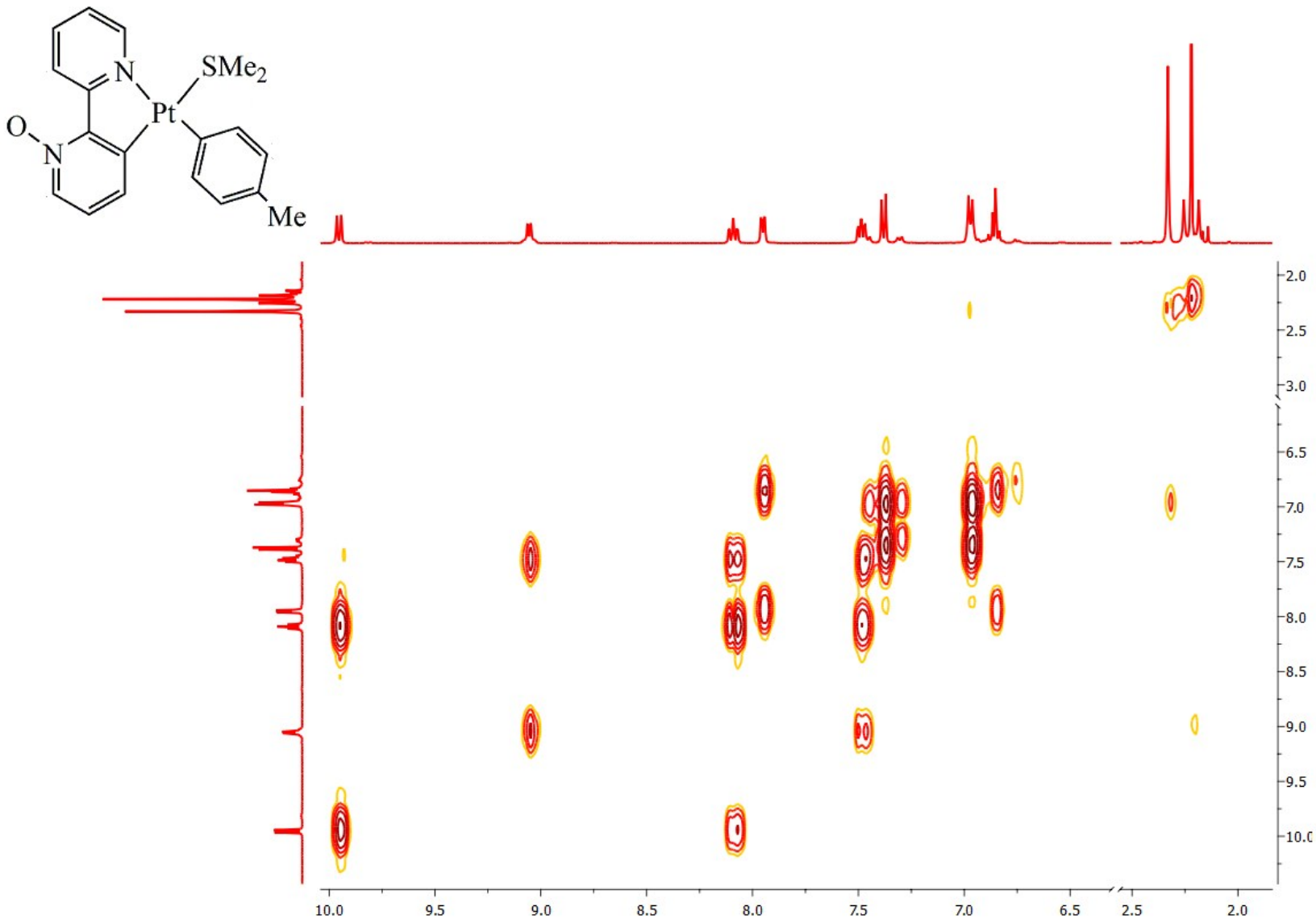

Figure S6. HHCOSY spectrum of the complex **1** in CD_2Cl_2.

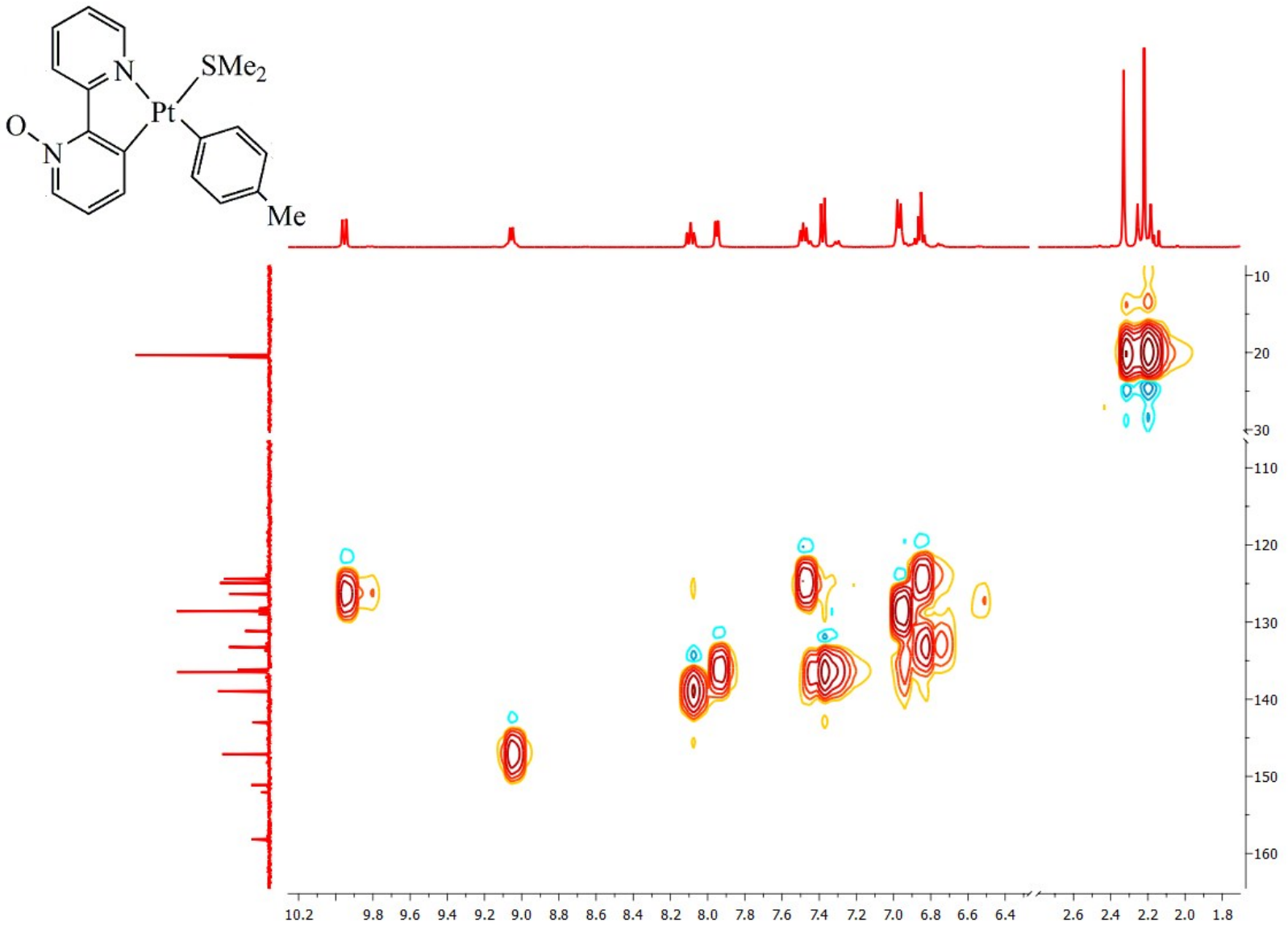

Figure S7. HSQC spectrum of the complex **1** in CD_2Cl_2.

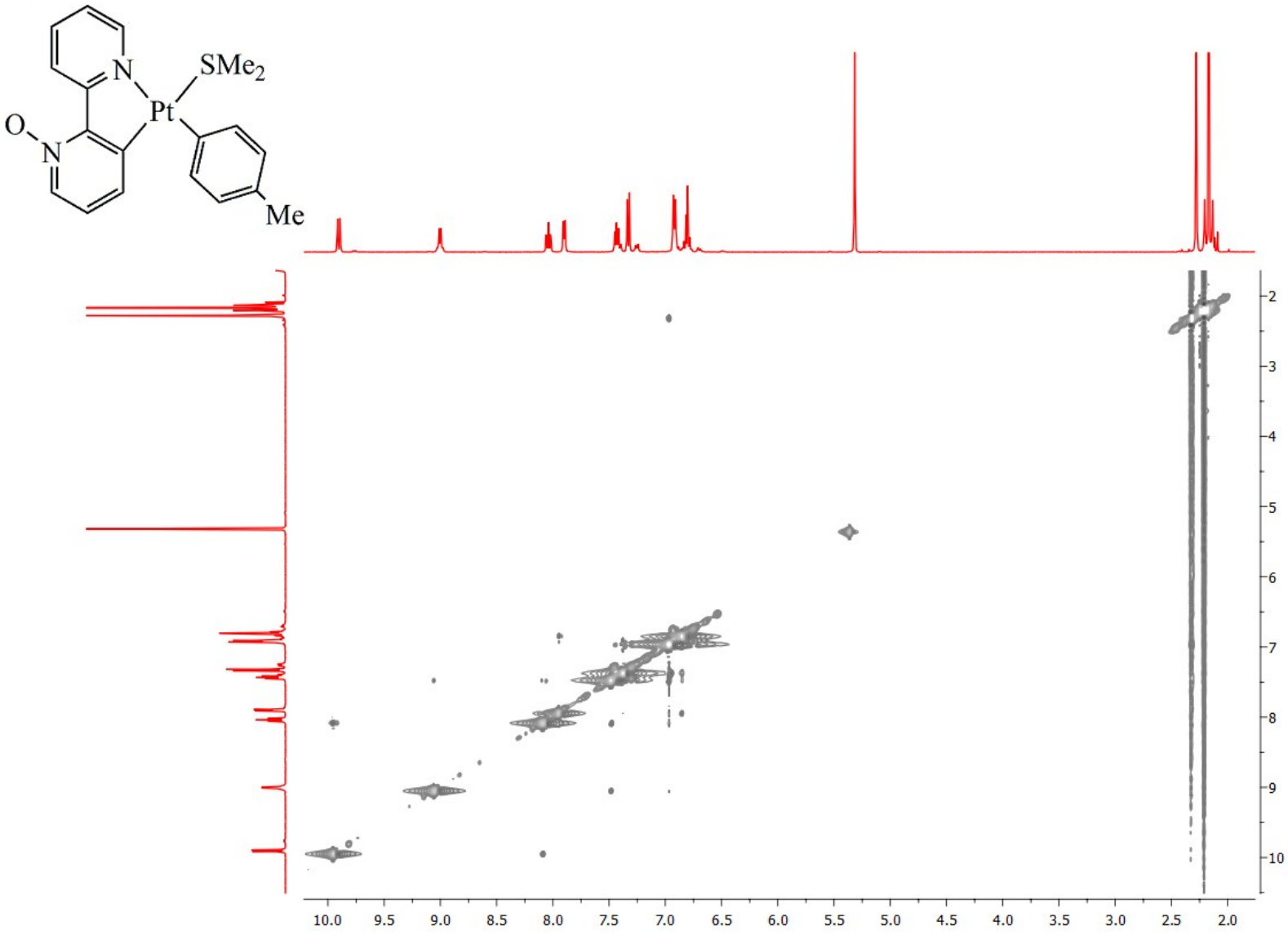

Figure S8. NOESY spectrum of the complex **1** in CD_2Cl_2.

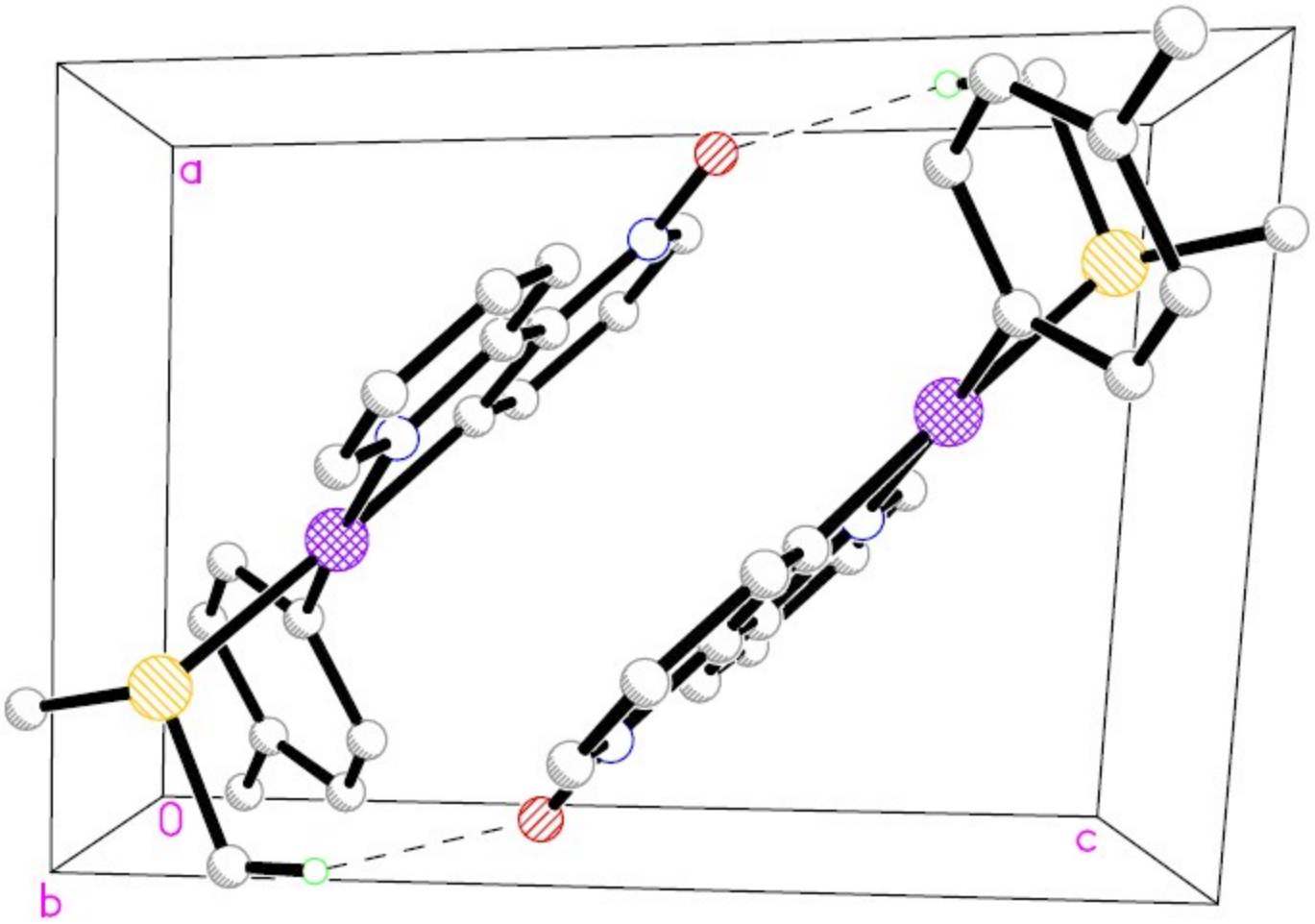

Figure S9. Crystal packing of the complex **1** shows the formation of centrosymmetric head-to-tail dimer through the intermolecular C–H···O interaction.

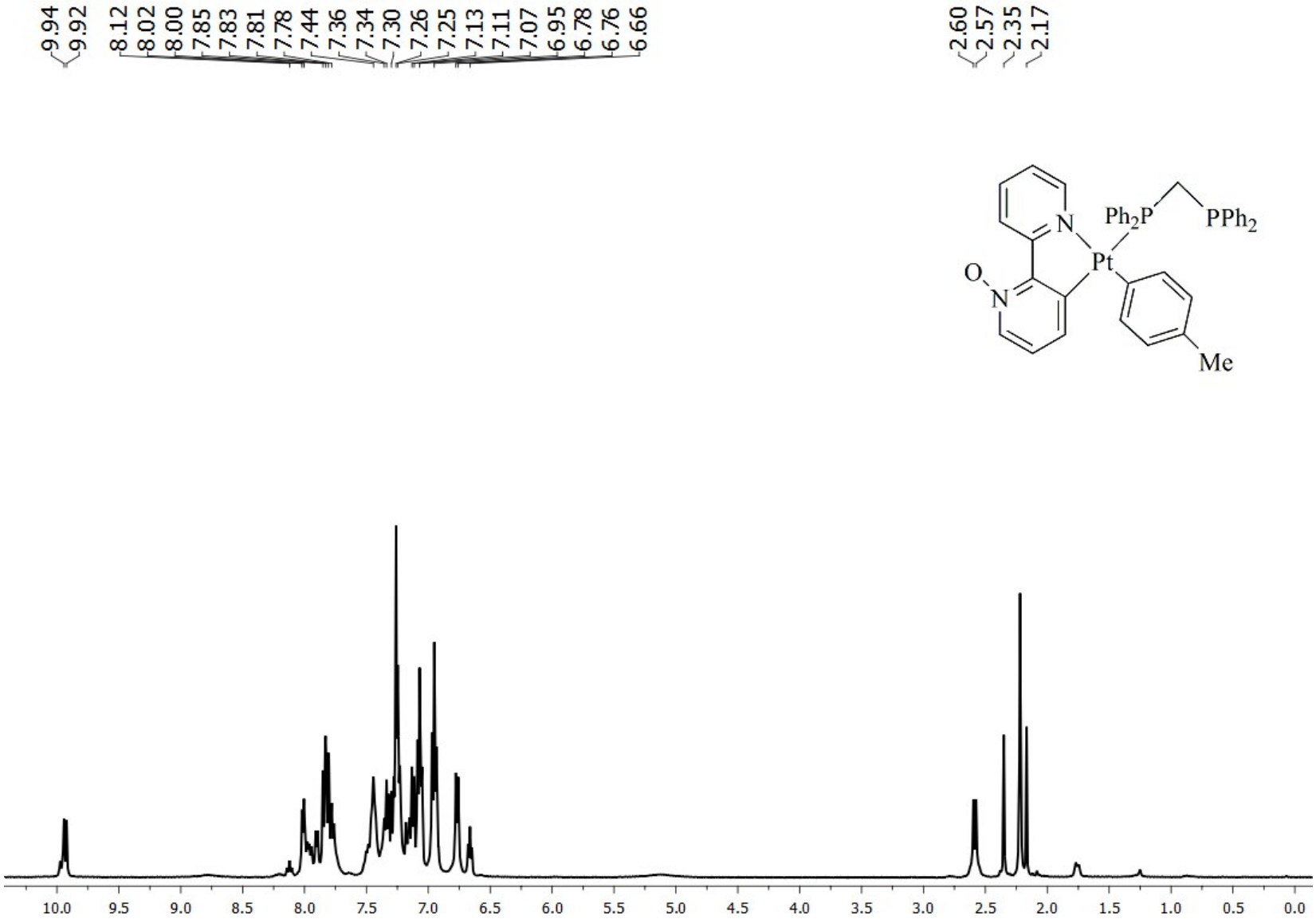

Figure S10. ^{1}H NMR spectrum of the complex **2a** in $CDCl_3$**.**

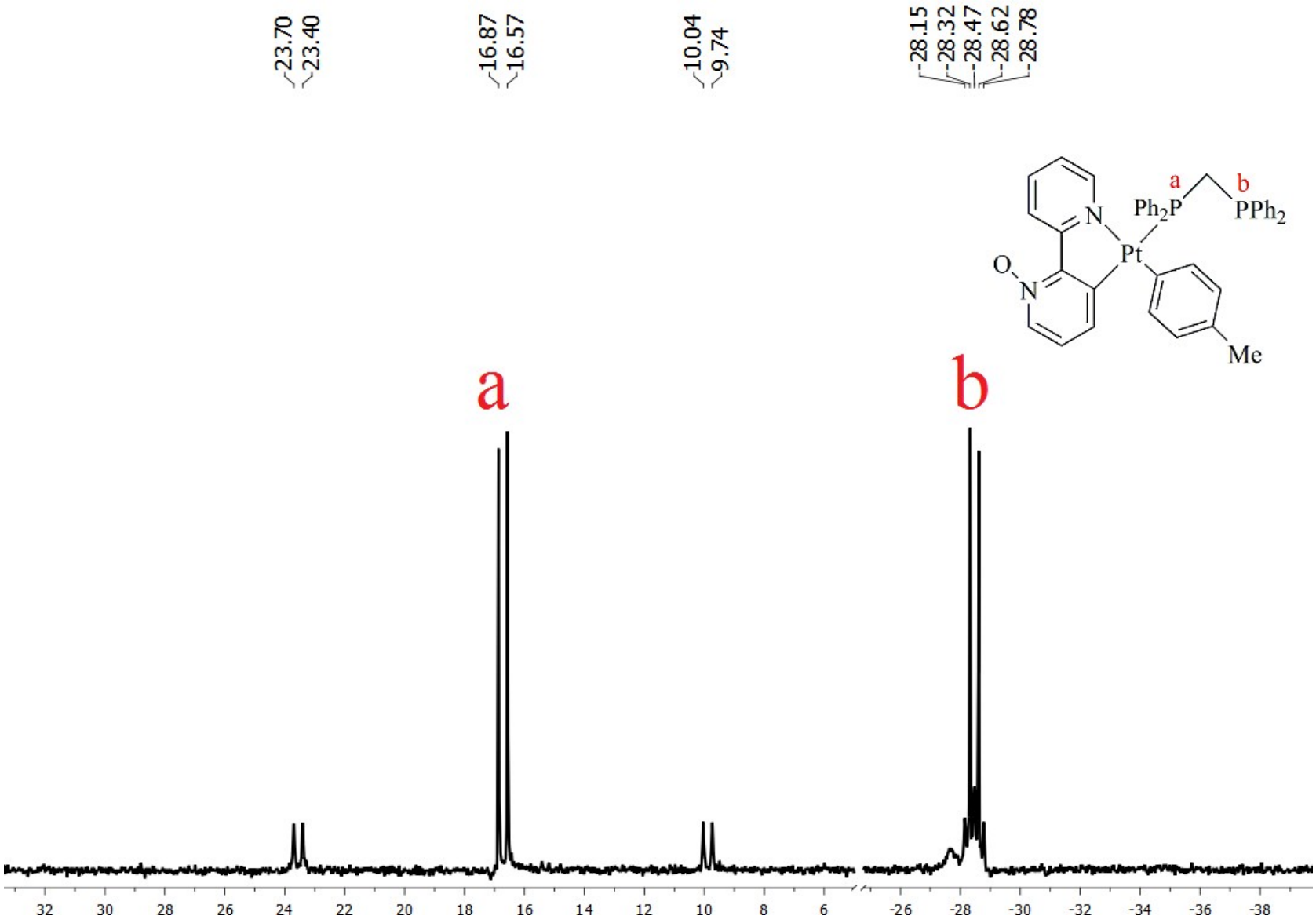

Figure S11. $^{31}P\{H\}$ NMR spectrum of the complex **2a** in $CDCl_3$.

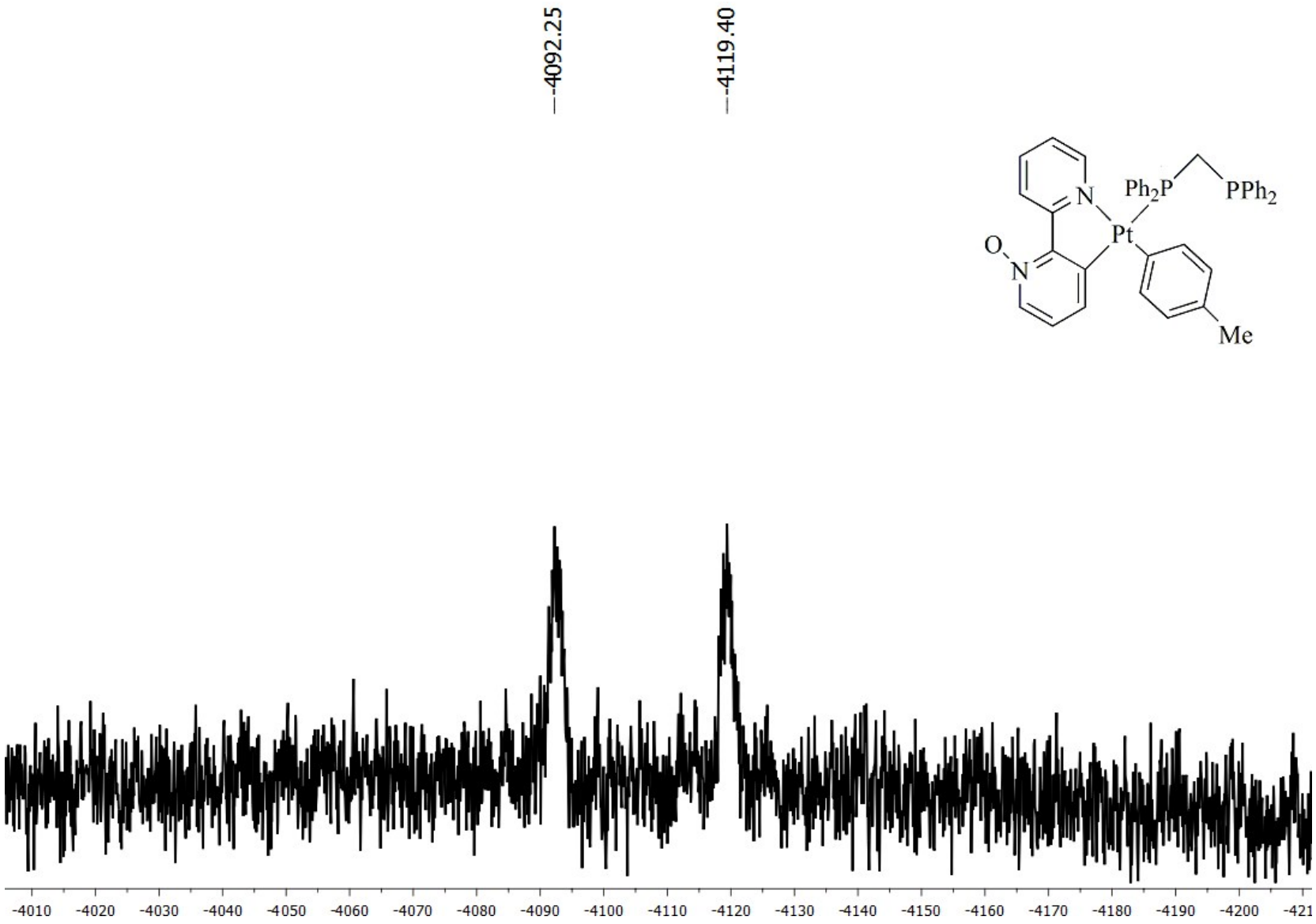

Figure S12. ^{195}Pt NMR spectrum of the complex **2a** in $CDCl_3$.

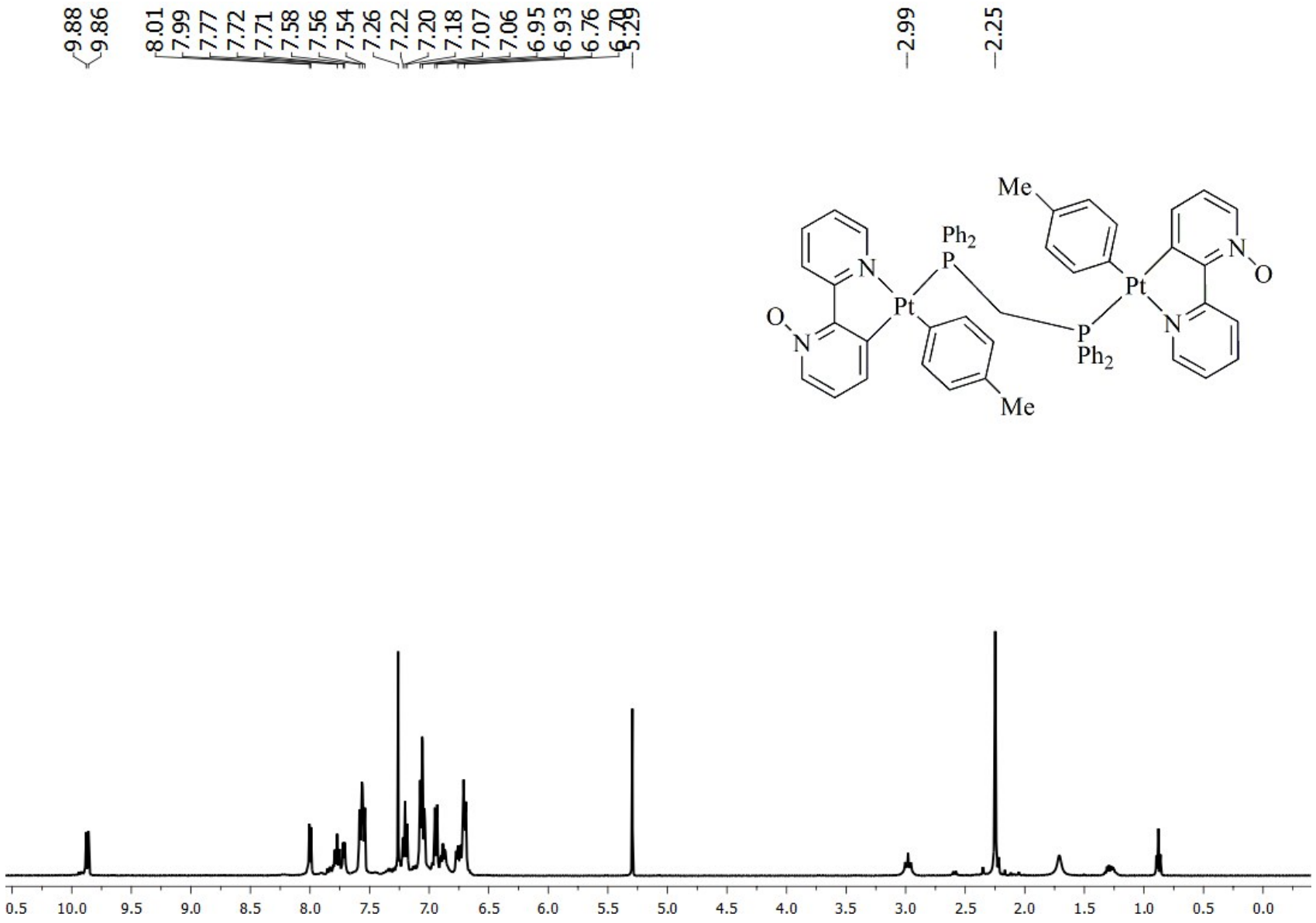

Figure S13. ^{1}H NMR spectrum of the complex **2b** in $CDCl_3$**.**

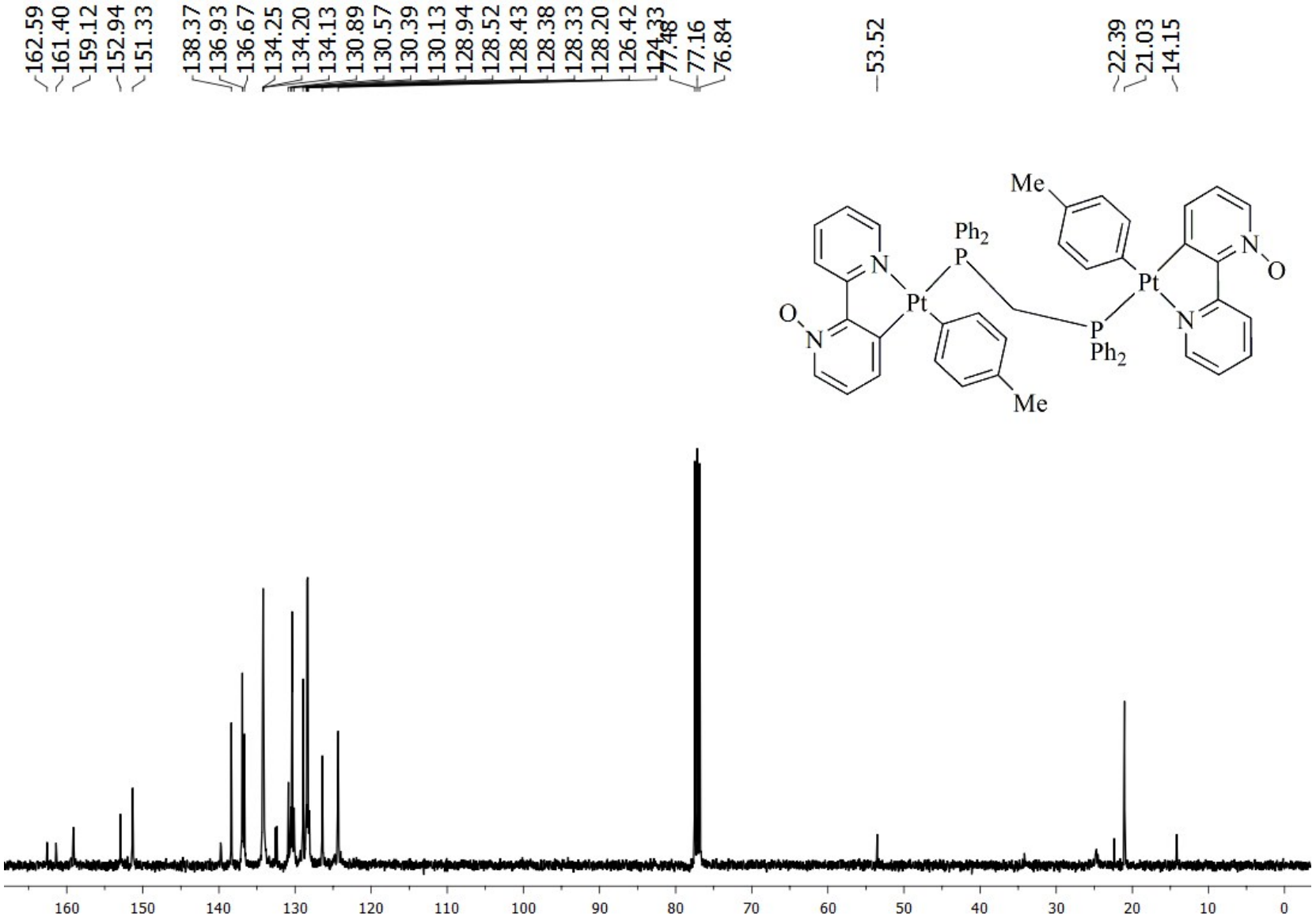

Figure S14. ^{13}C NMR spectrum of the complex **2b** in $CDCl_3$**.**

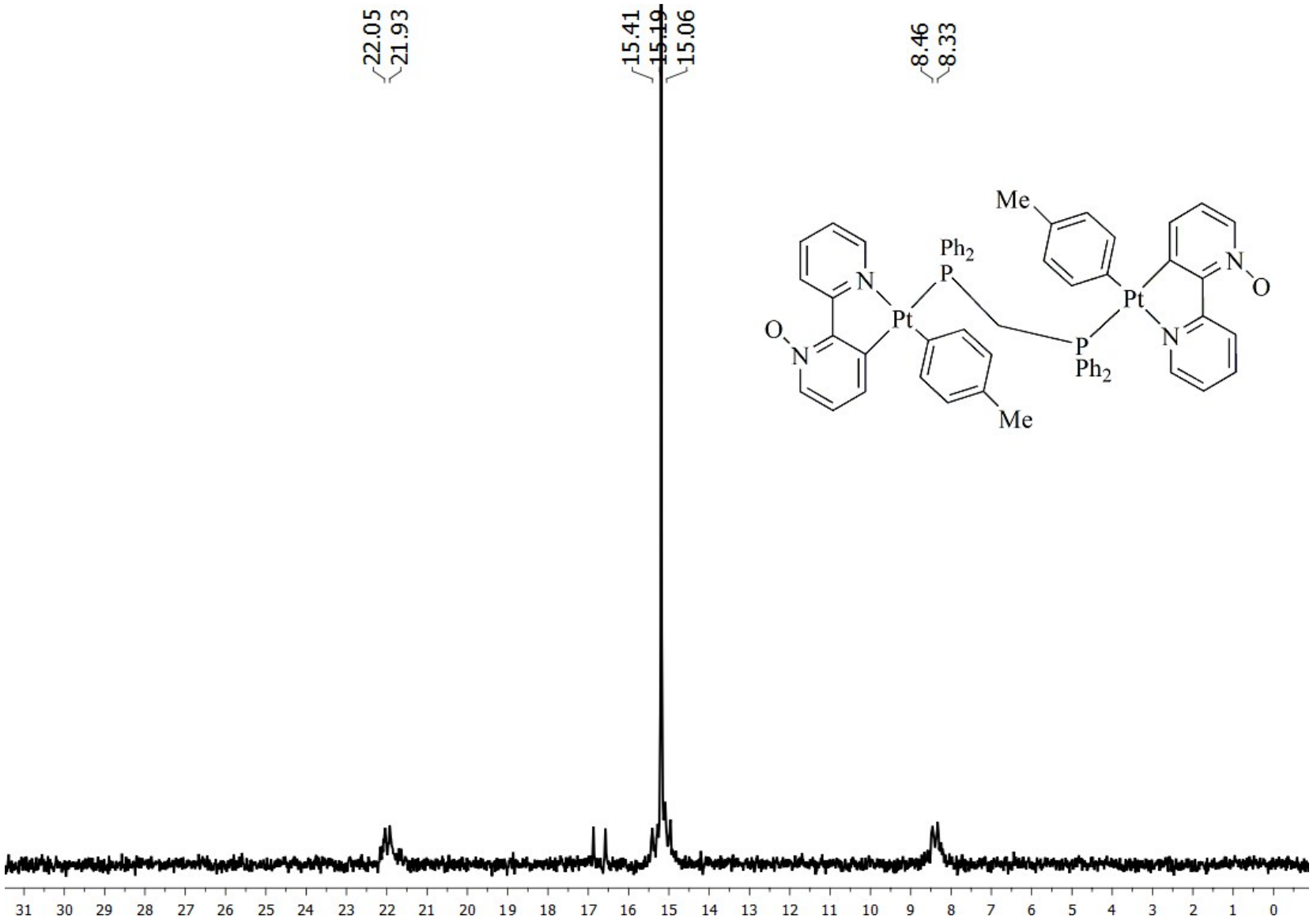

Figure S15. $^{31}P\{H\}$ NMR spectrum of the complex **2b** in $CDCl_3$**.**

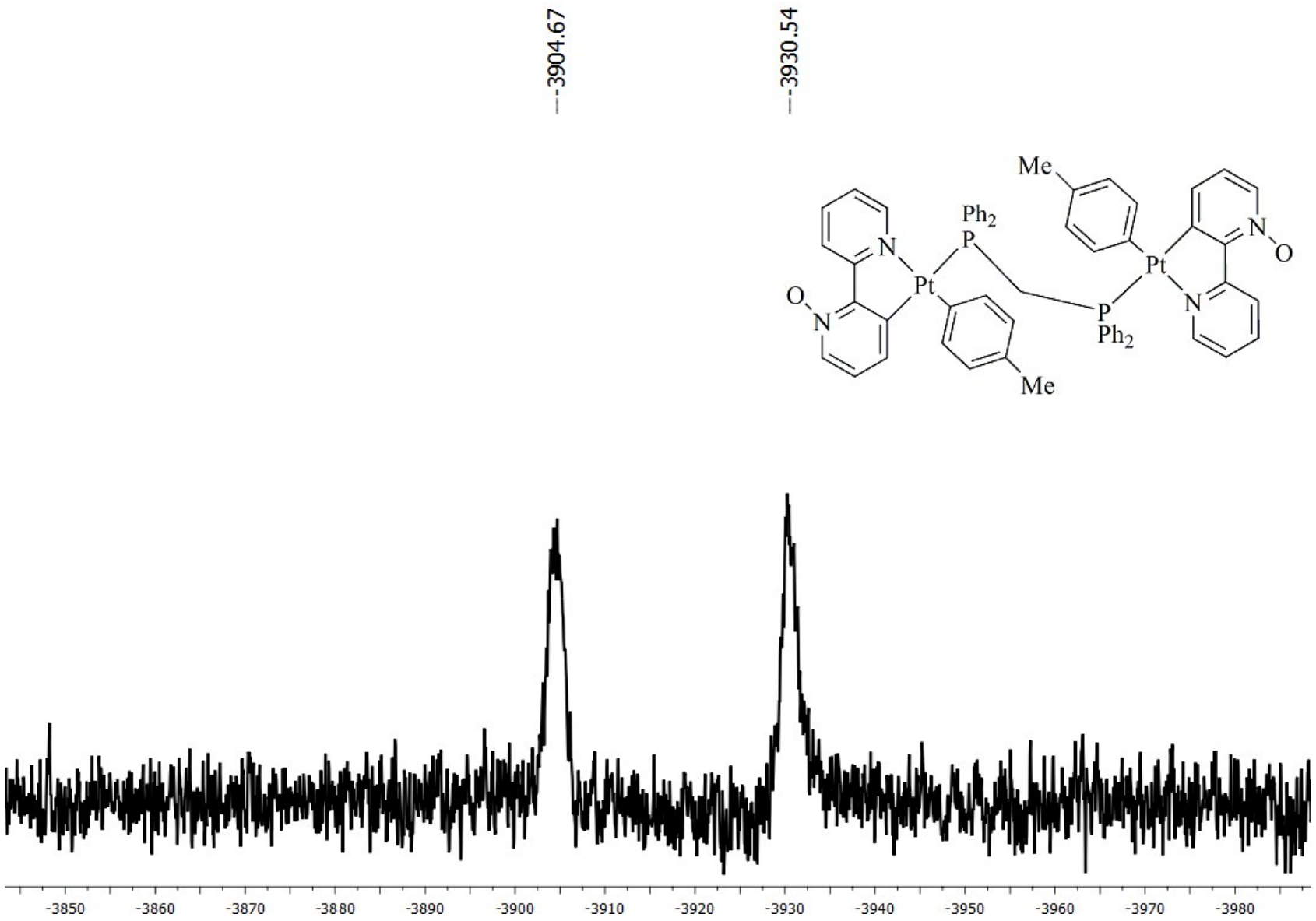

Figure S16. ^{195}Pt NMR spectrum of the complex **2b** in $CDCl_3$**.**

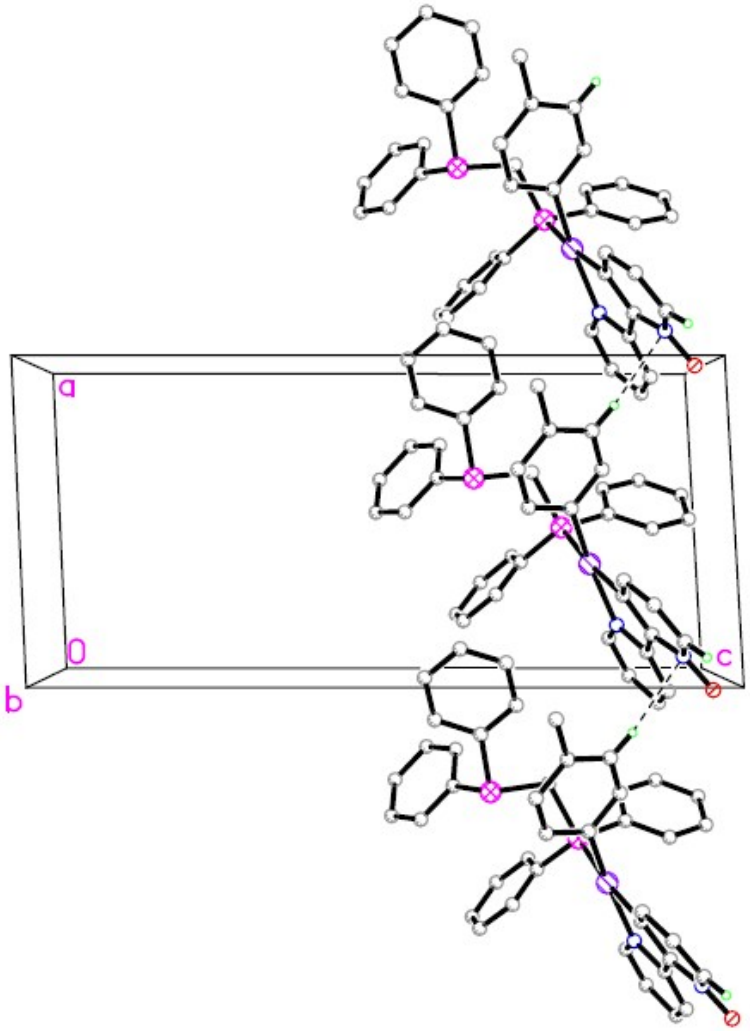

Figure S17. Crystal packing of the complex **2a** showing one-dimensional extended chain along the *a*-axis through intermolecular C–H···N interactions.

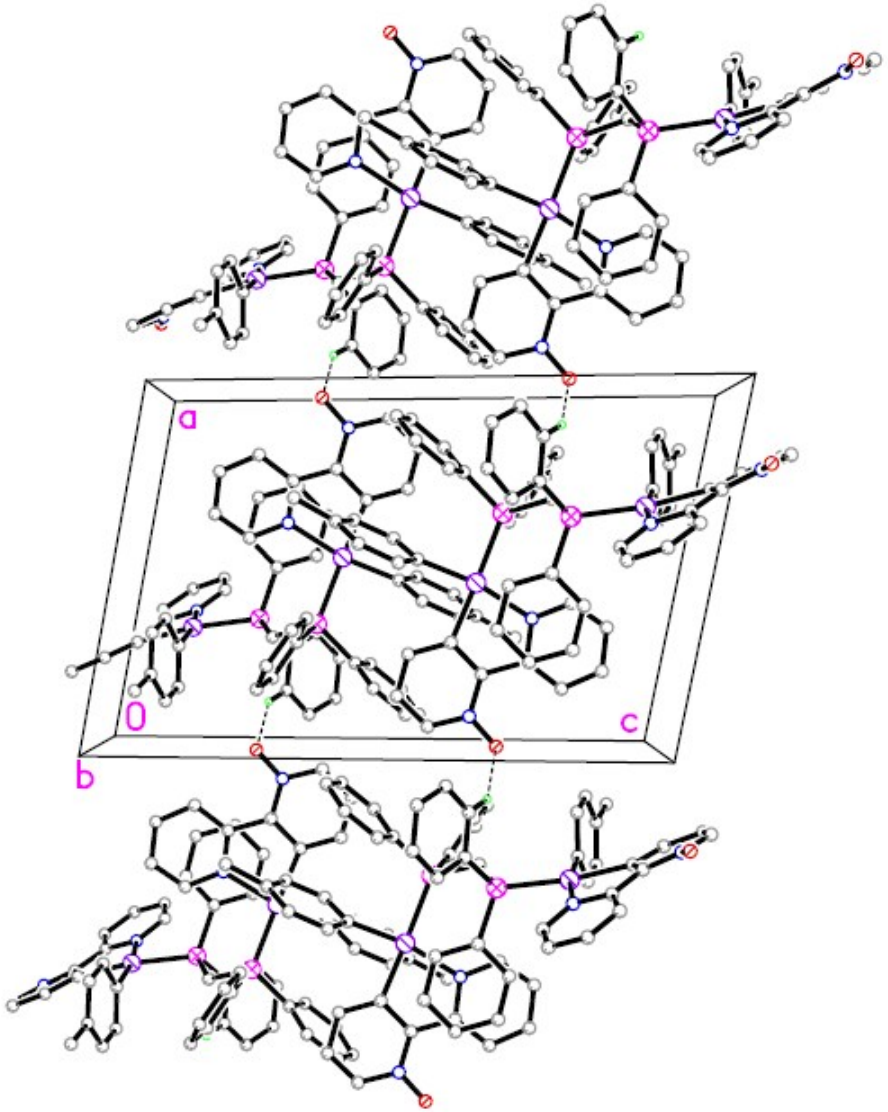

Figure S18. Crystal packing of the complex **2b** showing one-dimensional extended chain along the *a*-axis through intermolecular C–H···O interactions.

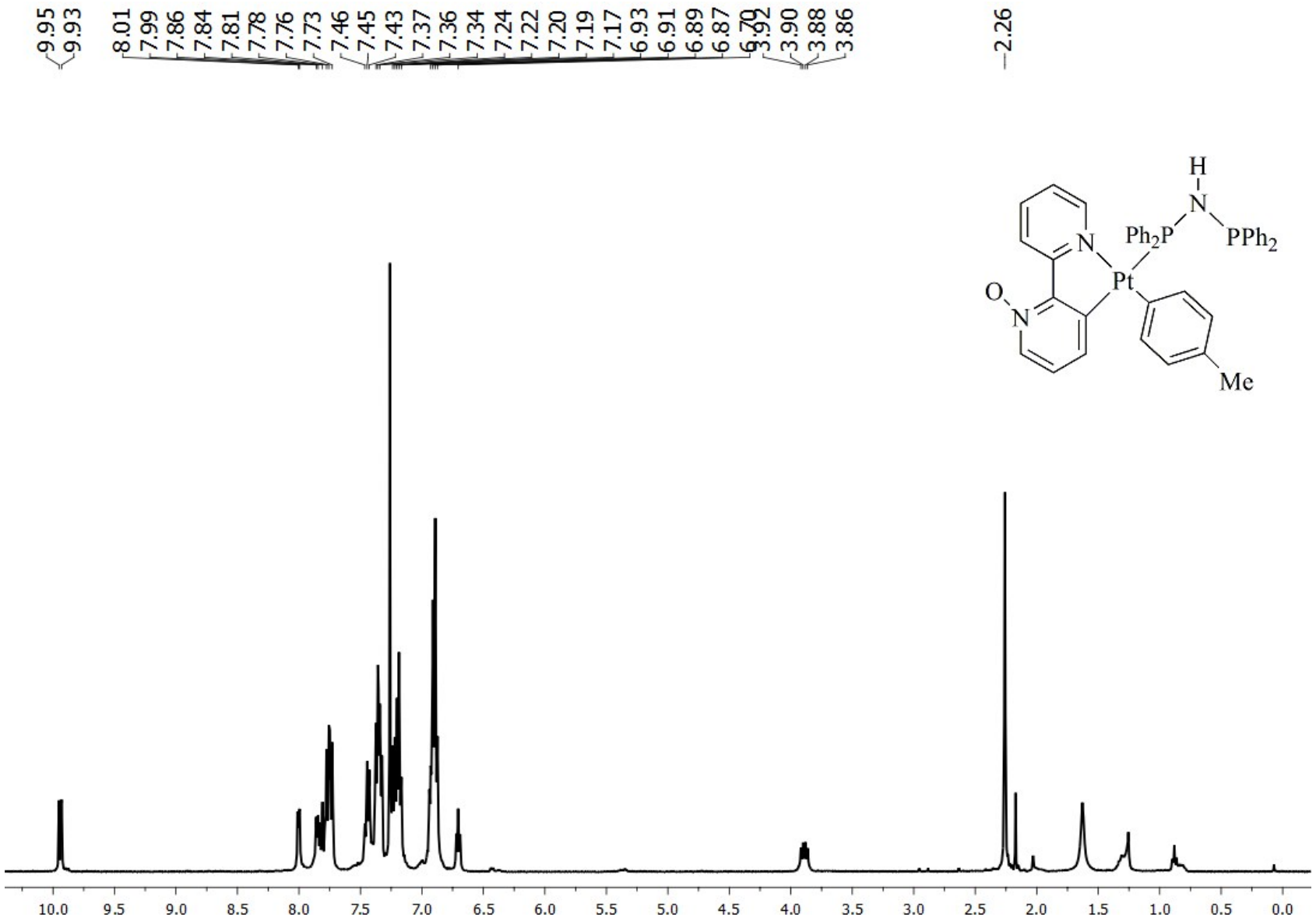

Figure S19. ^{1}H NMR spectrum of the complex **3a** in $CDCl_3$**.**

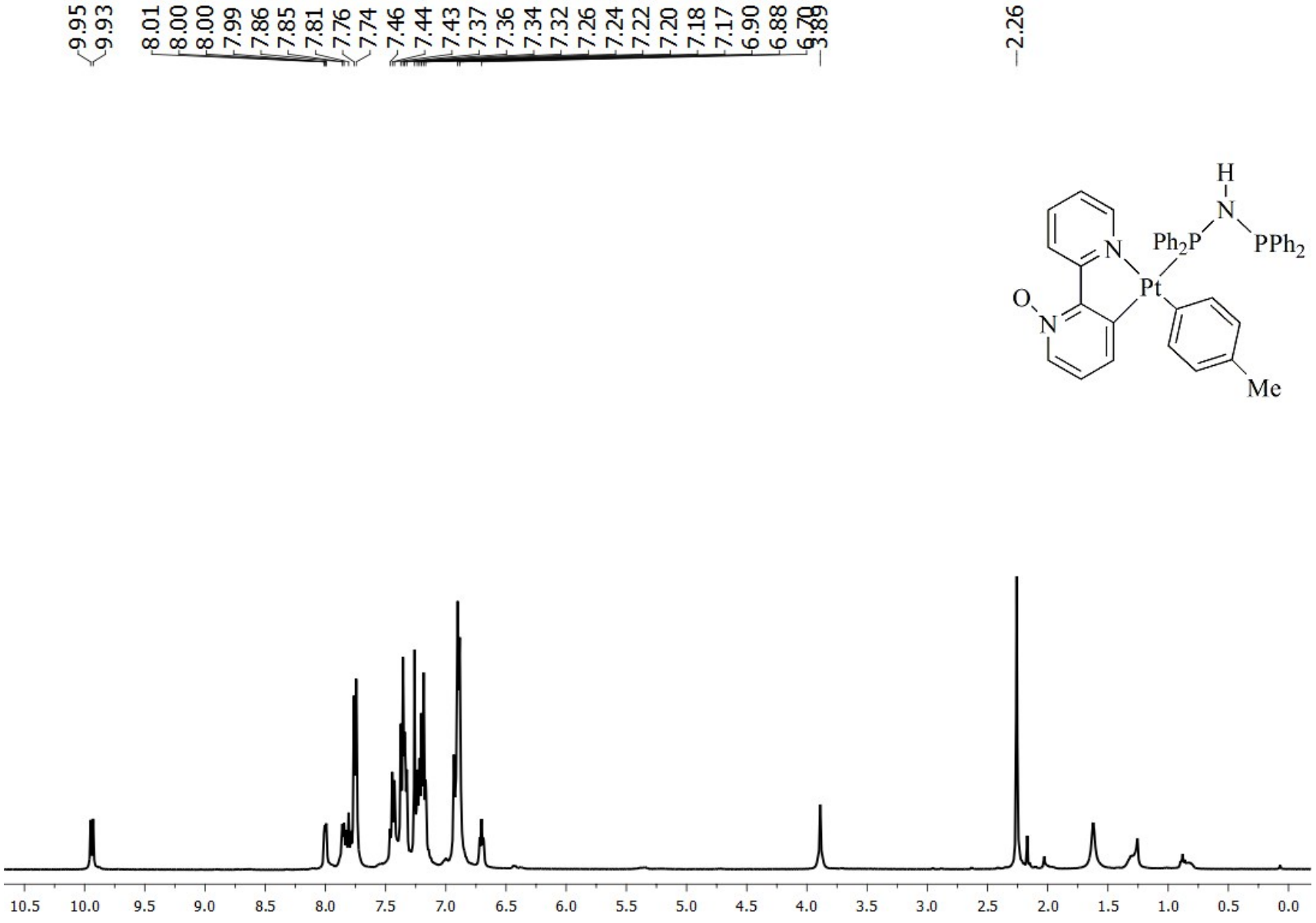

Figure S20. $^{1}H\{P\}$ NMR spectrum of the complex **3a** in $CDCl_3$.

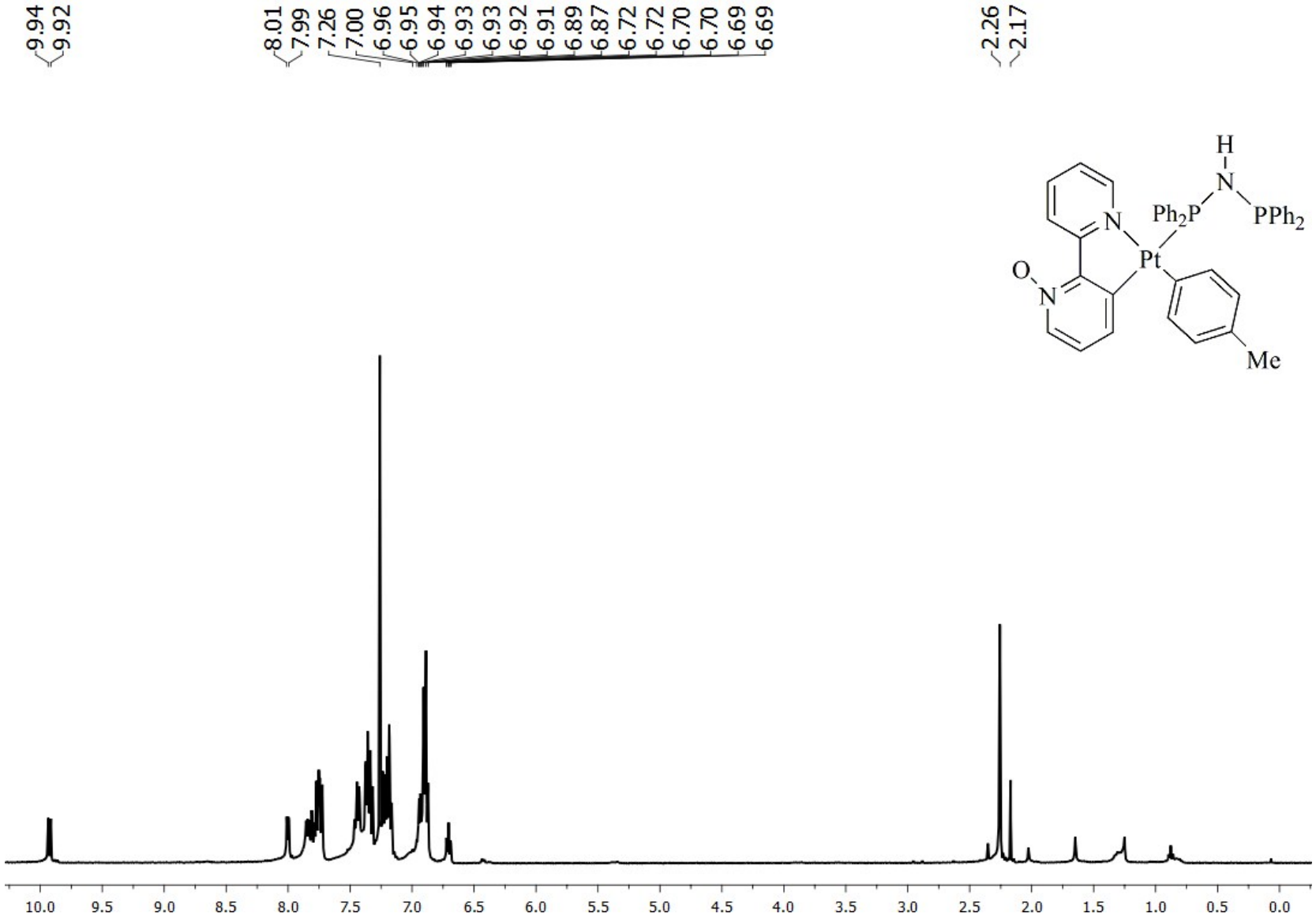

Figure S21. ^{1}H NMR spectrum of the complex **3a** + **D_2O** in $CDCl_3$**.**

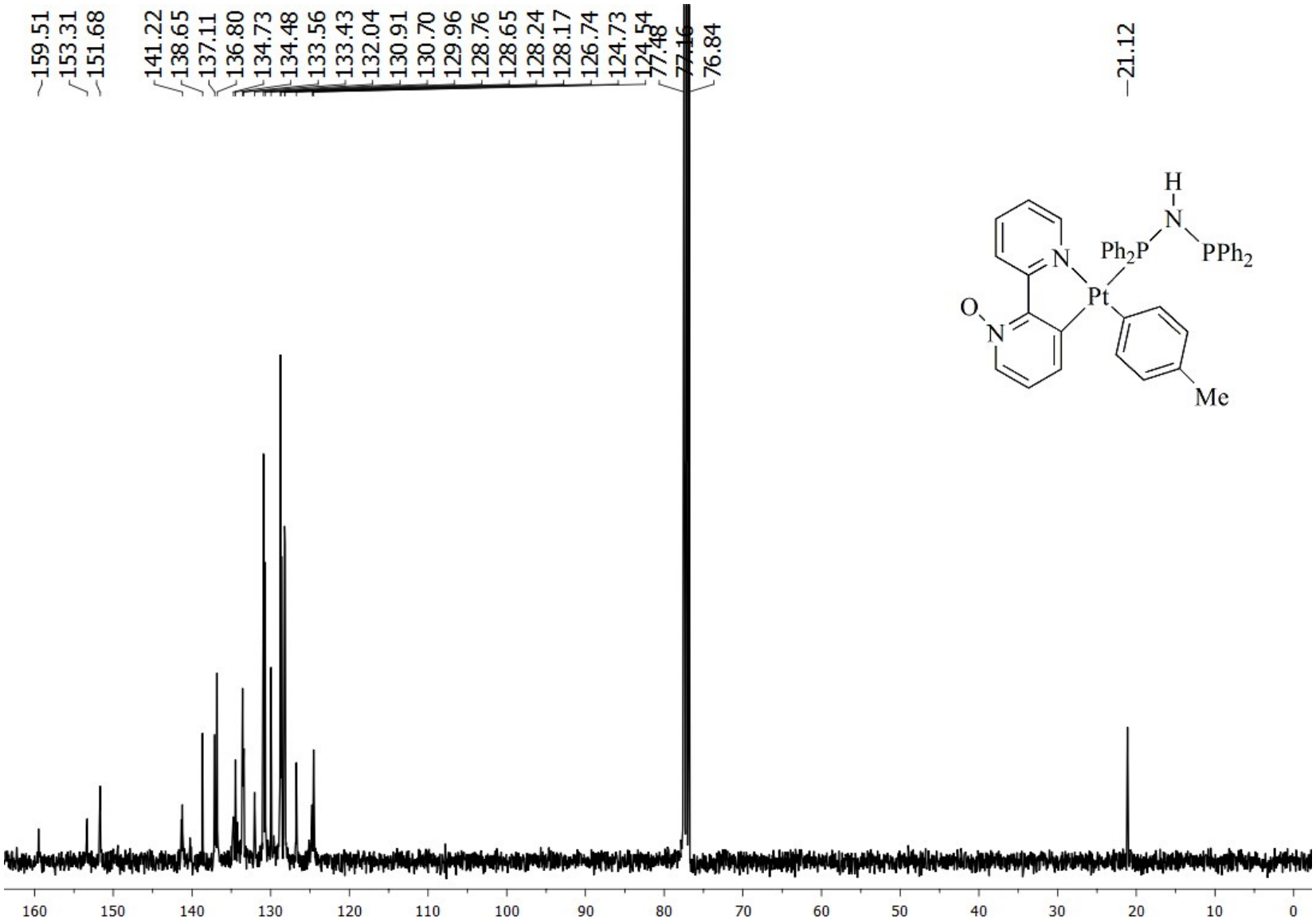

Figure S22. ^{13}C NMR spectrum of the complex **3a** in $CDCl_3$**.**

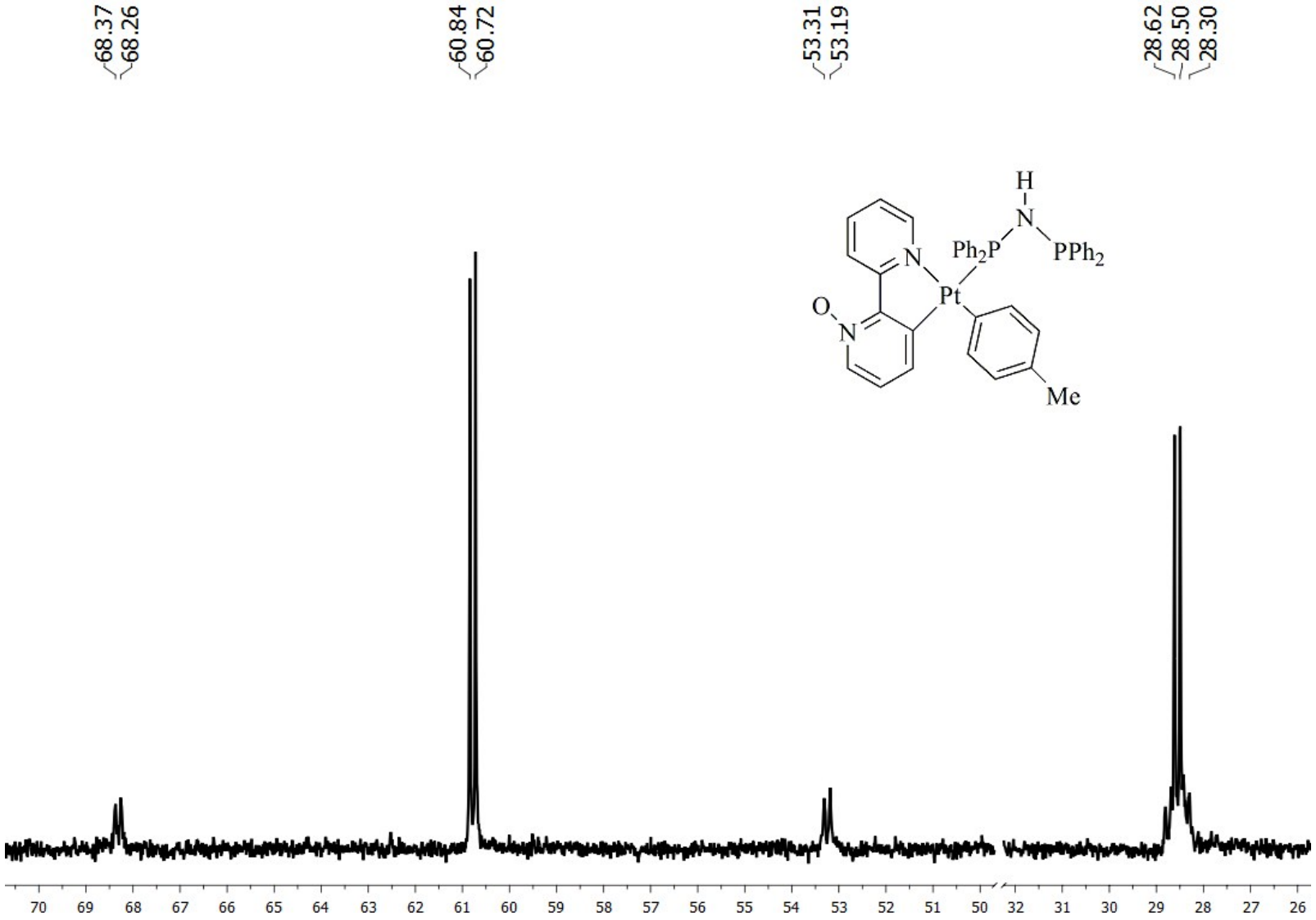

Figure S23. $^{31}P\{H\}$ NMR spectrum of the complex **3a** in $CDCl_3$.

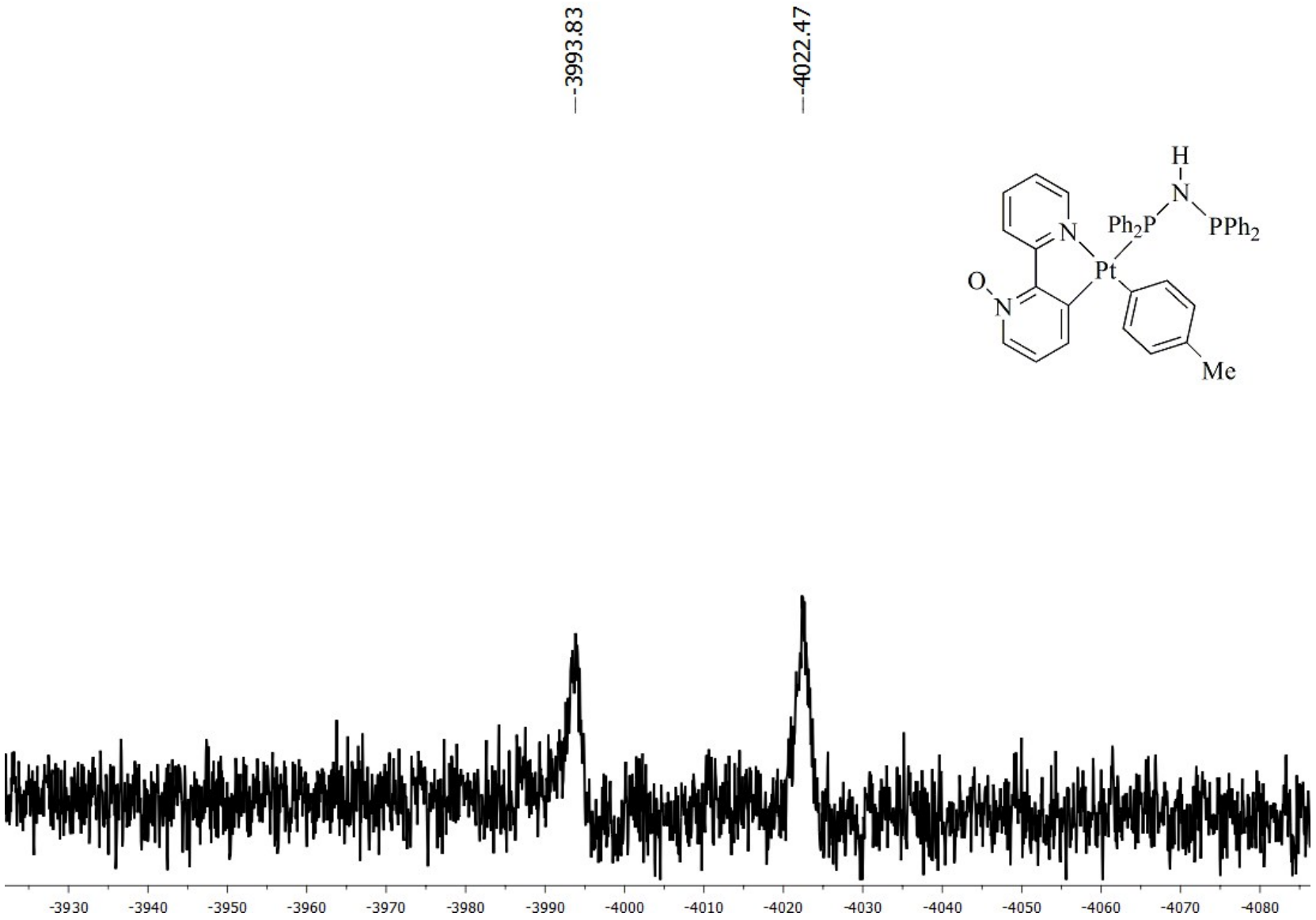

Figure S24. ^{195}Pt NMR spectrum of the complex **3a** in $CDCl_3$.

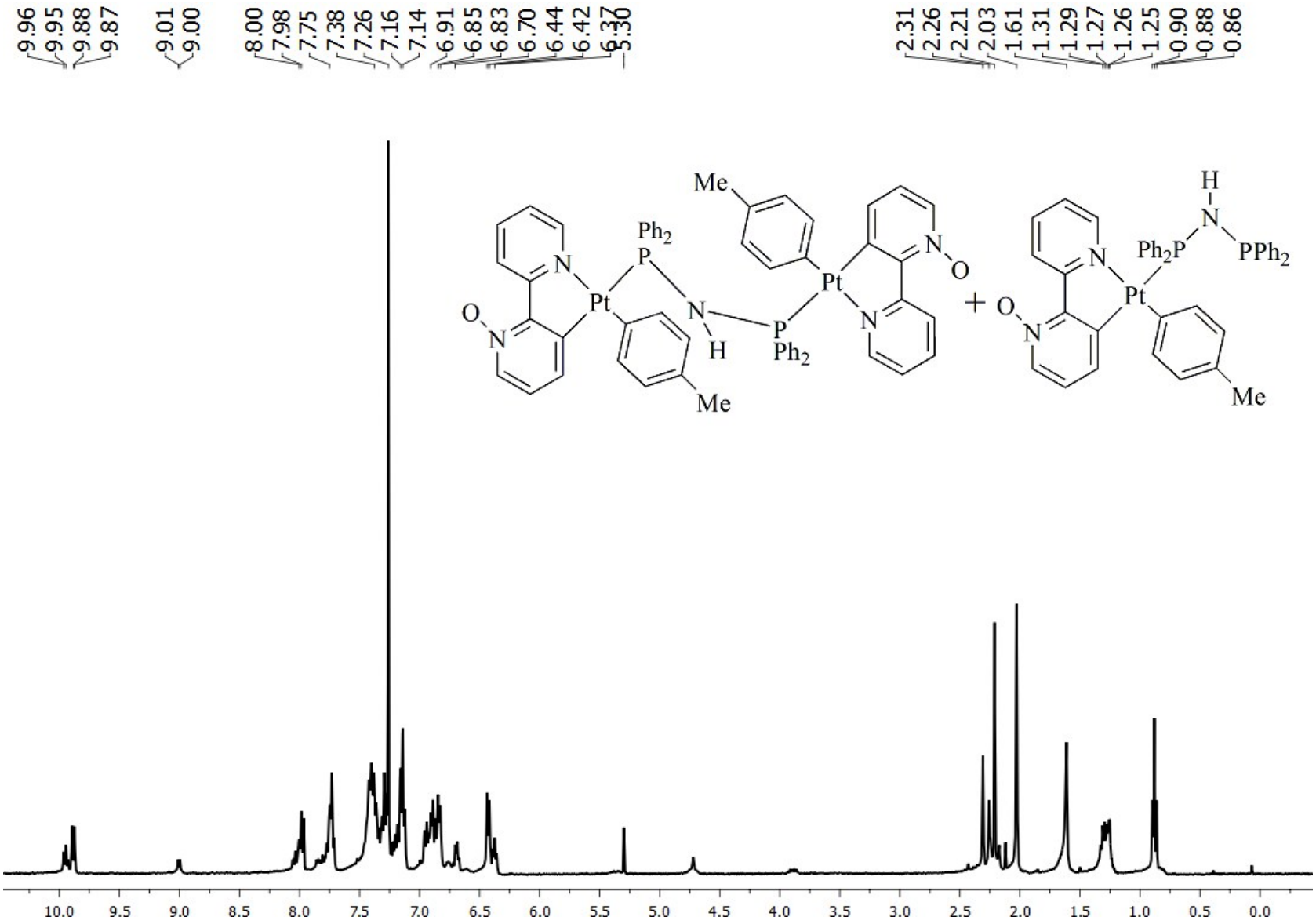

Figure S25. ^{1}H NMR spectrum of the mixture of the complexes **3a** and **3b** in $CDCl_3$**.**

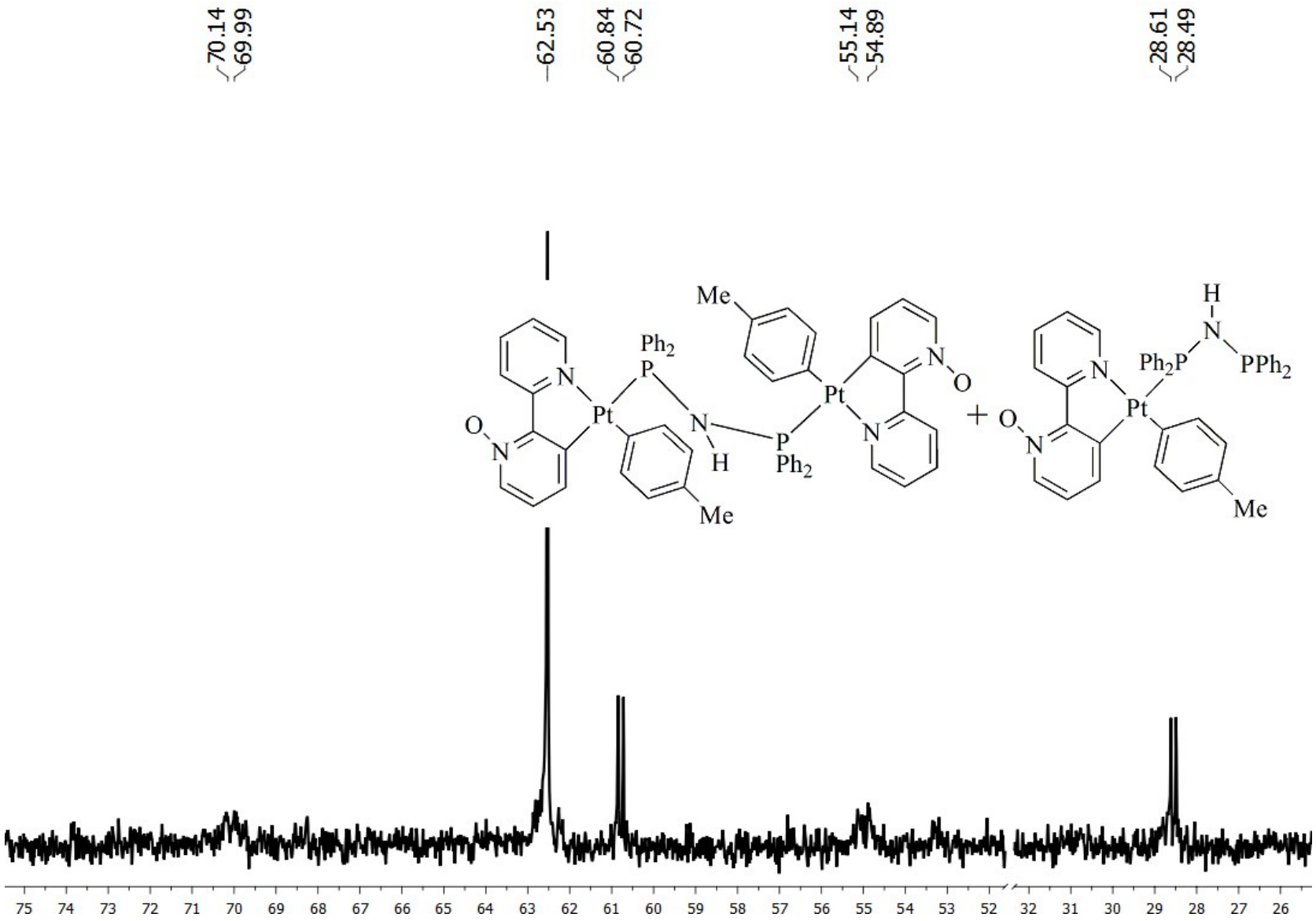

Figure S26. $^{31}P\{H\}$ NMR spectrum of the mixture of the complexes **3a** and **3b** in $CDCl_3$**.**

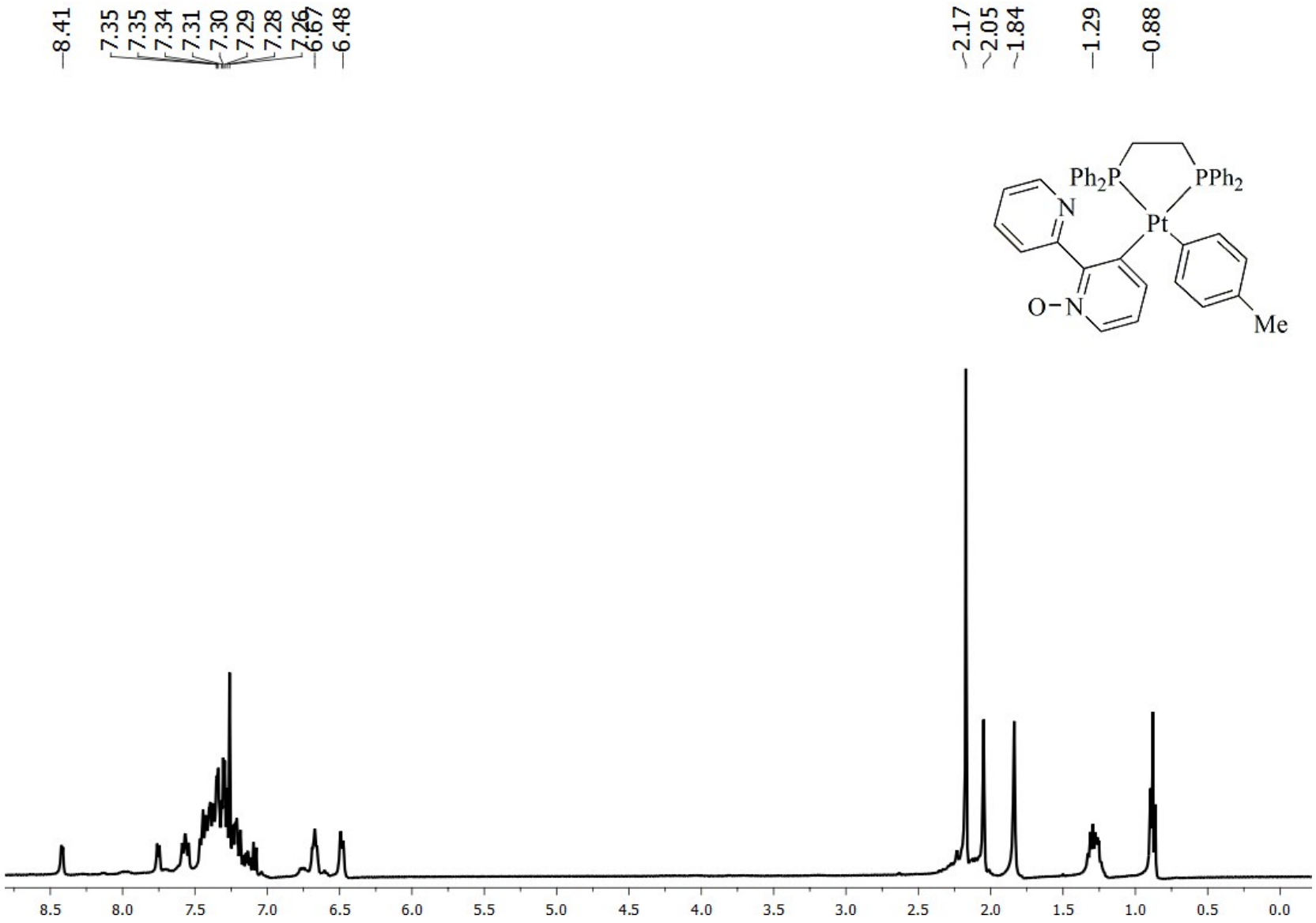

Figure S27. ^{1}H NMR spectrum of the complex **4a** in $CDCl_3$.

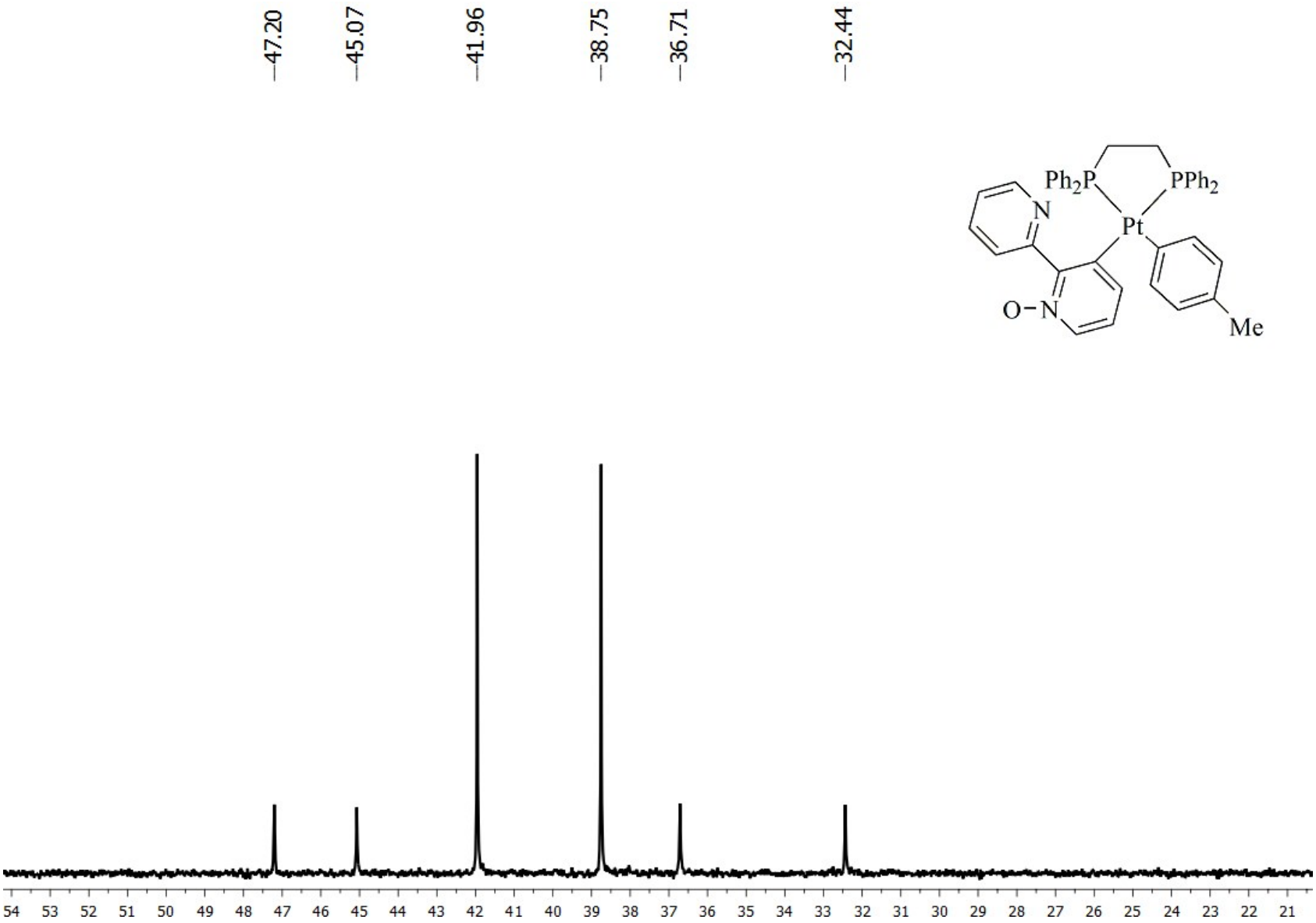

Figure S28. $^{31}P\{H\}$ NMR spectrum of the complex **4a** in $CDCl_3$.

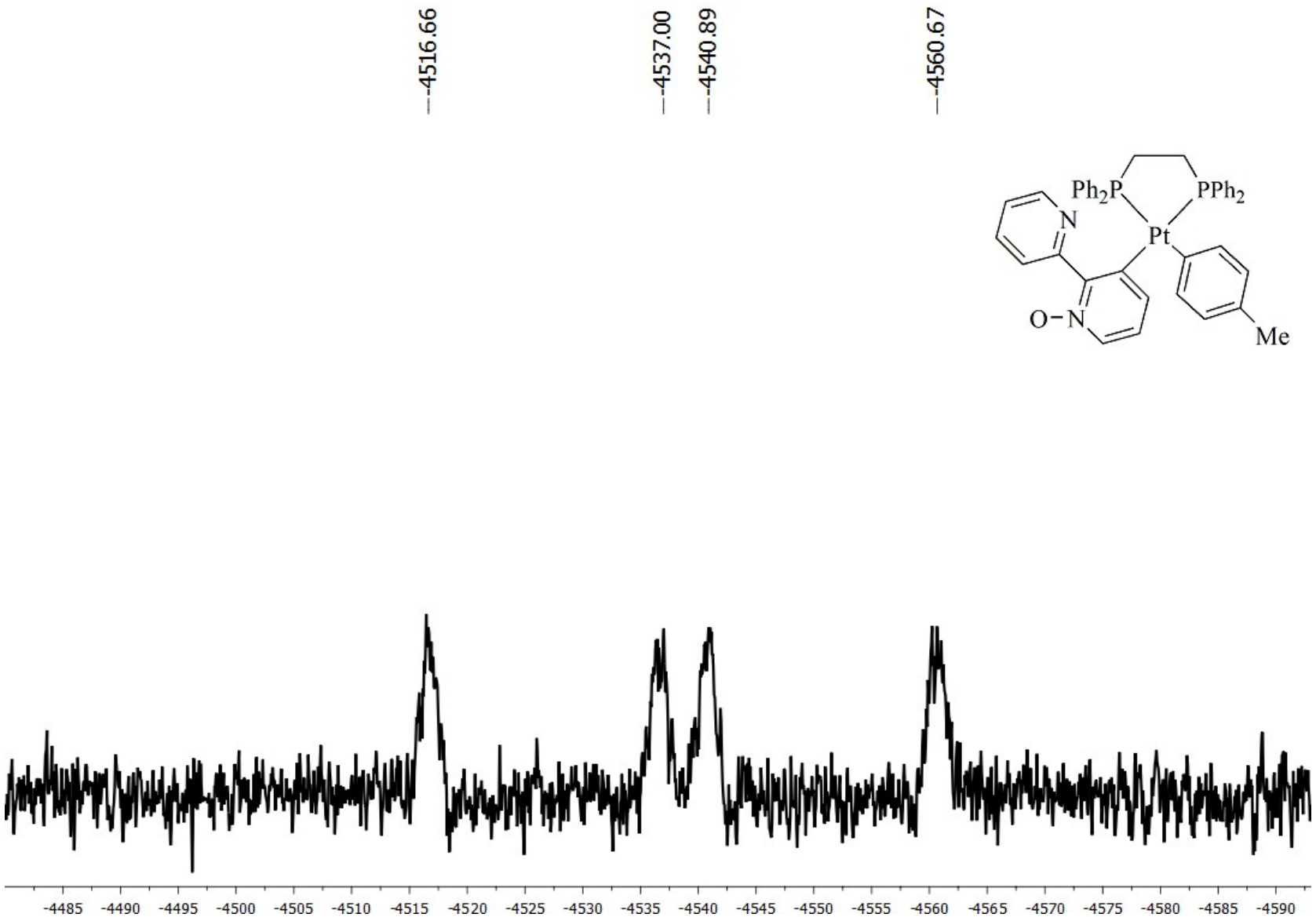

Figure S29. ^{195}Pt NMR spectrum of the complex **4a** in $CDCl_3$.

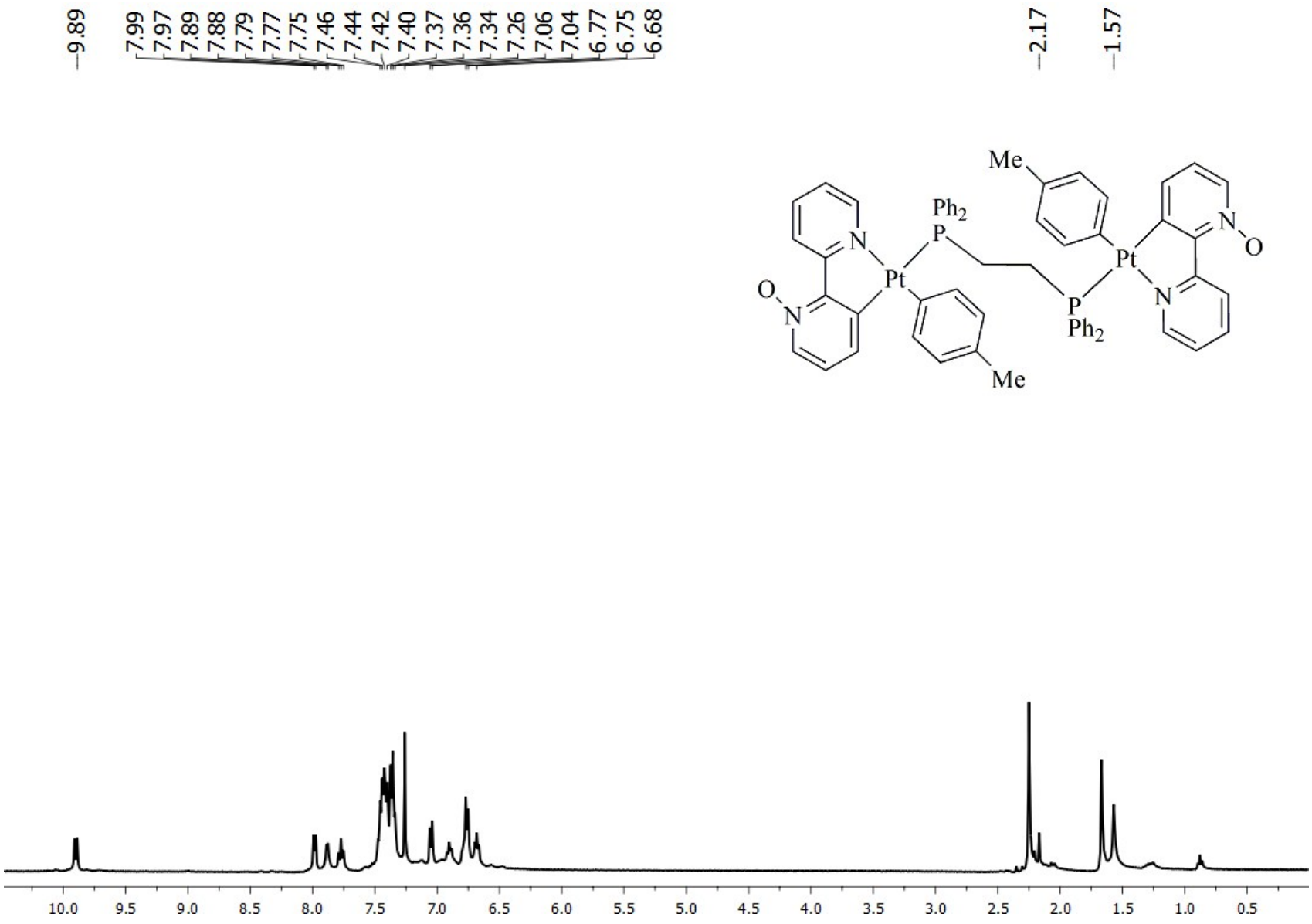

Figure S30. ^{1}H NMR spectrum of the complex **4b** in $CDCl_3$**.**

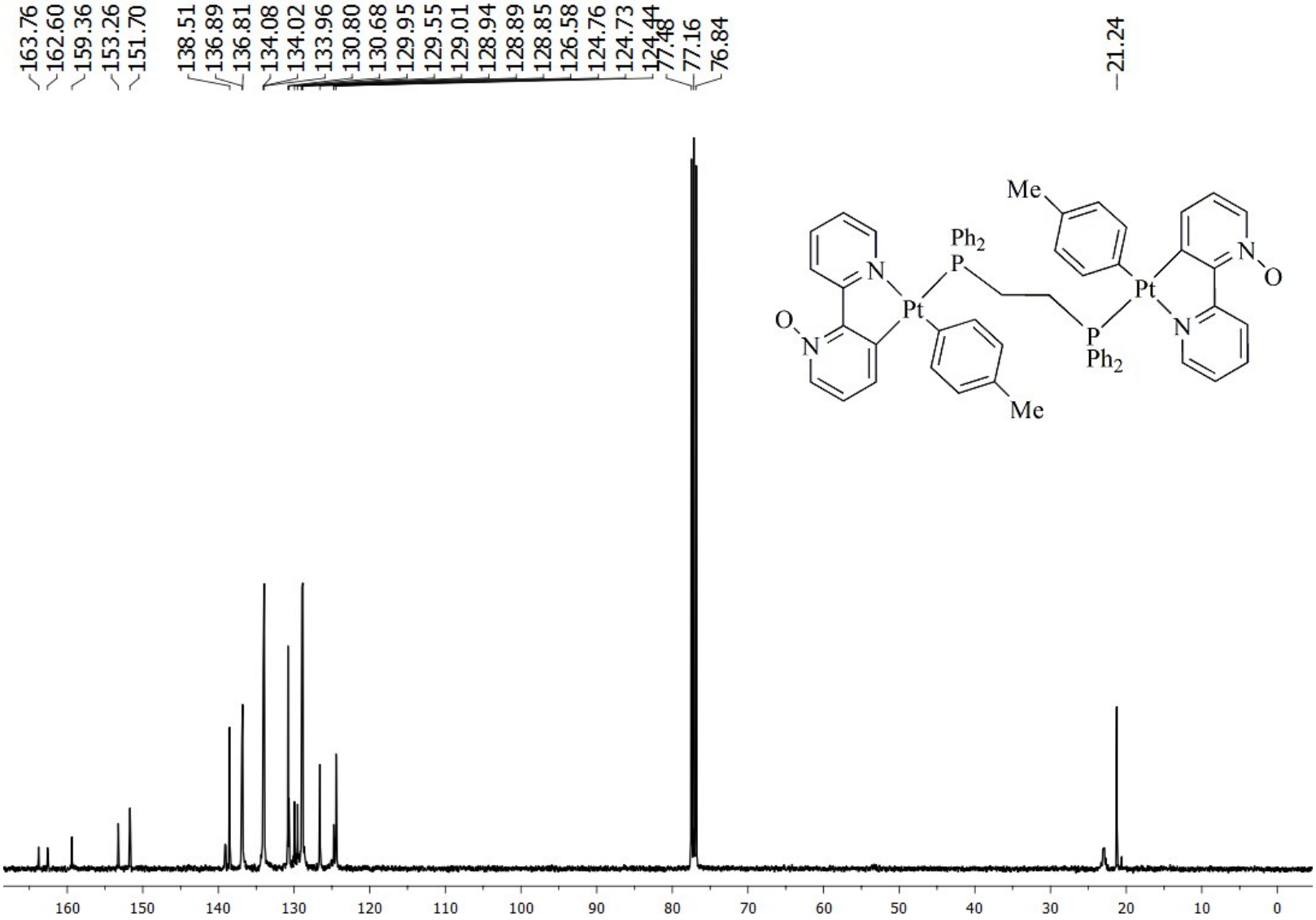

Figure S31. ^{13}C NMR spectrum of the complex **4b** in $CDCl_3$.

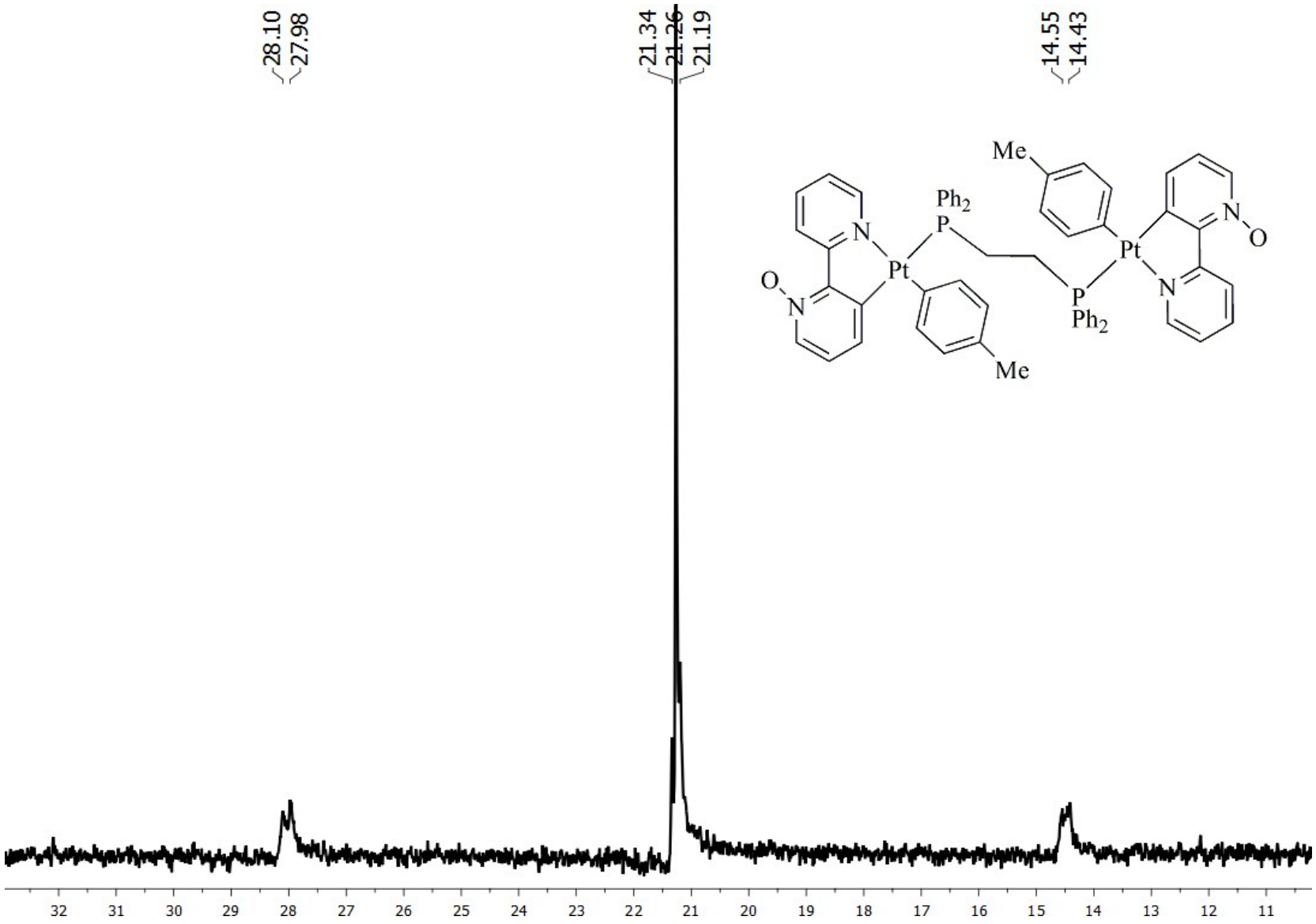

Figure S32. $^{31}P\{H\}$ NMR spectrum of the complex **4b** in $CDCl_3$**.**

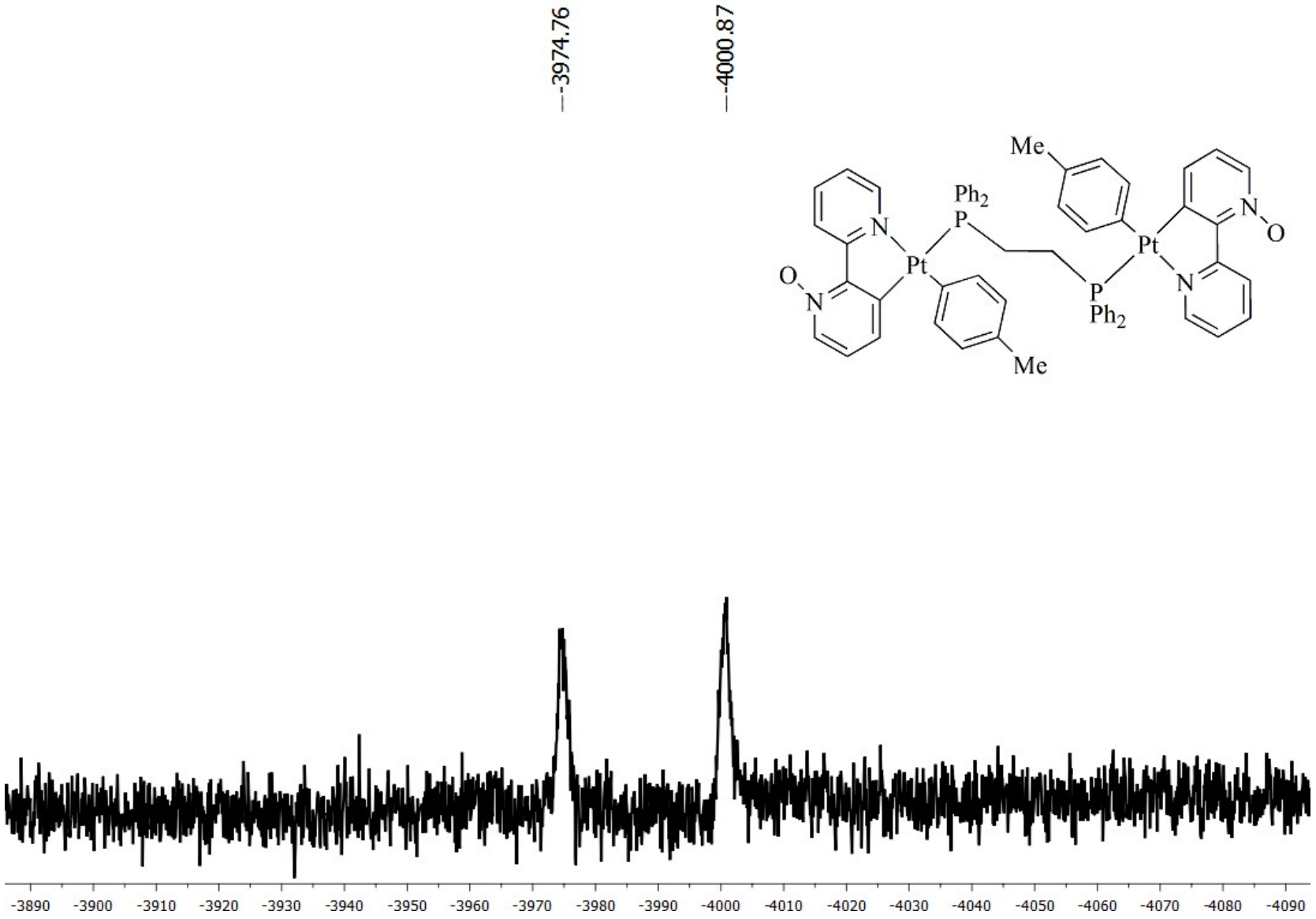

Figure S33. ^{195}Pt NMR spectrum of the complex **4b** in $CDCl_3$**.**

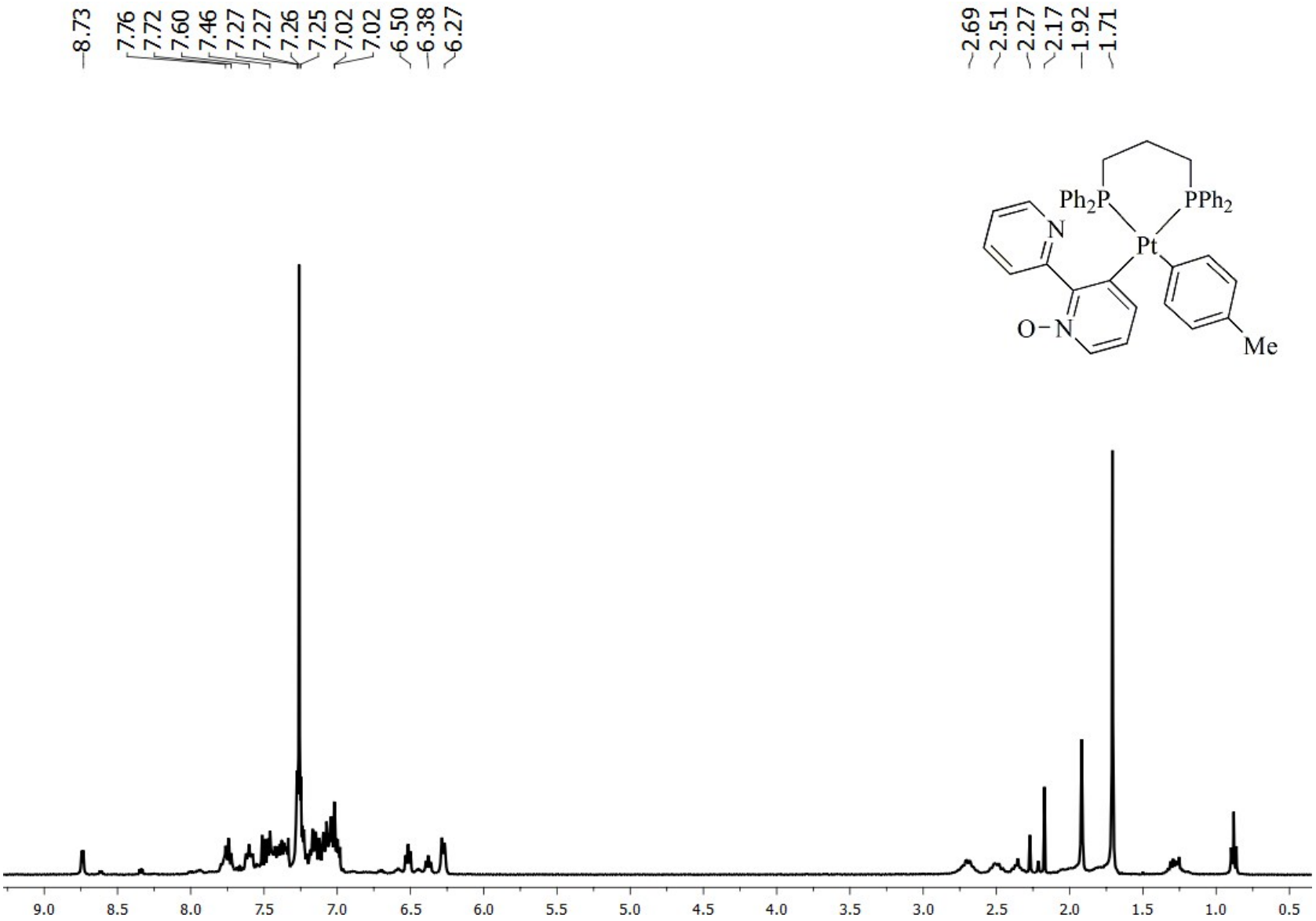

Figure S34. ^{1}H NMR spectrum of the complex **5a** in $CDCl_3$**.**

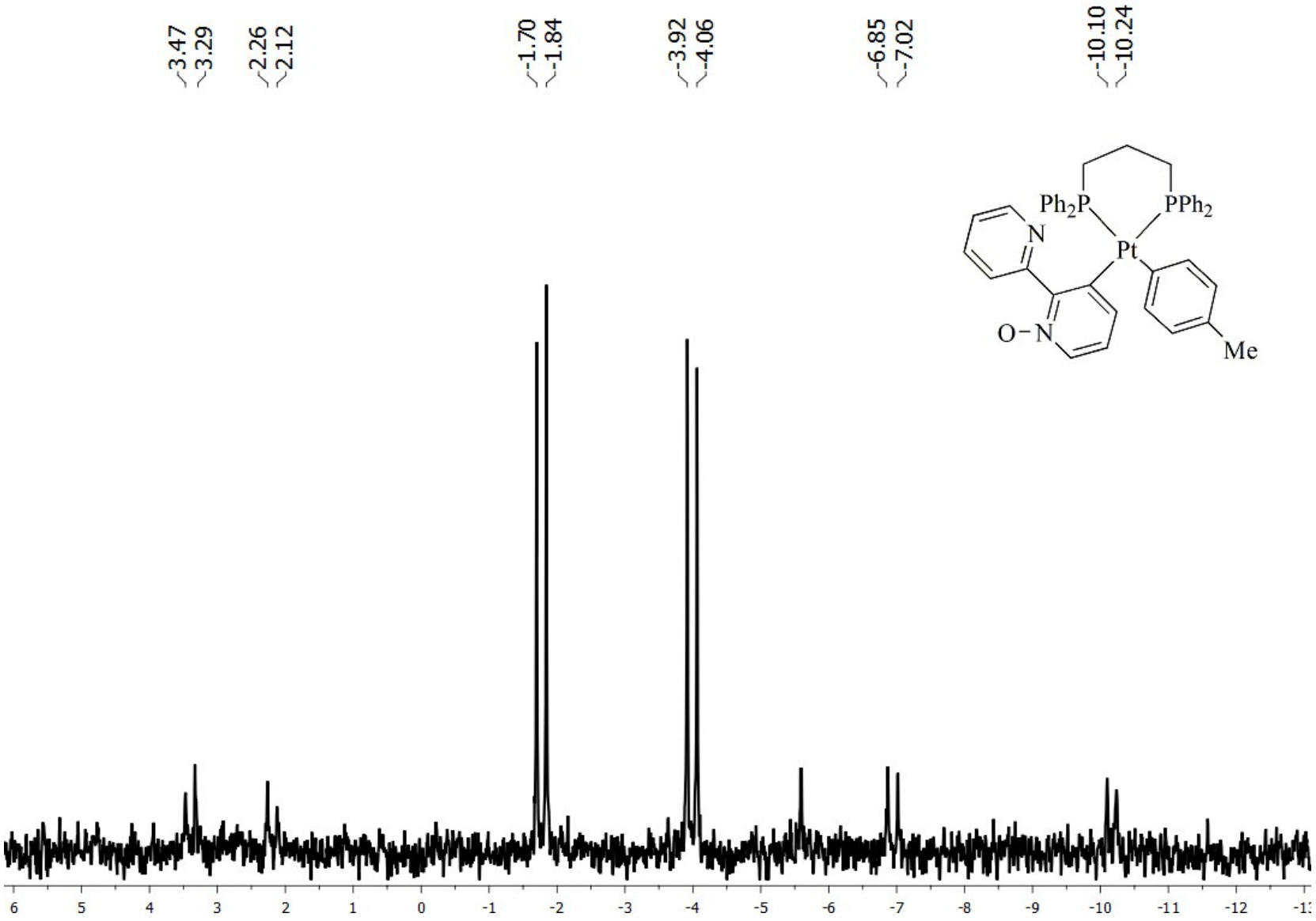

Figure S35. $^{31}P\{H\}$ NMR spectrum of the complex **5a** in $CDCl_3$.

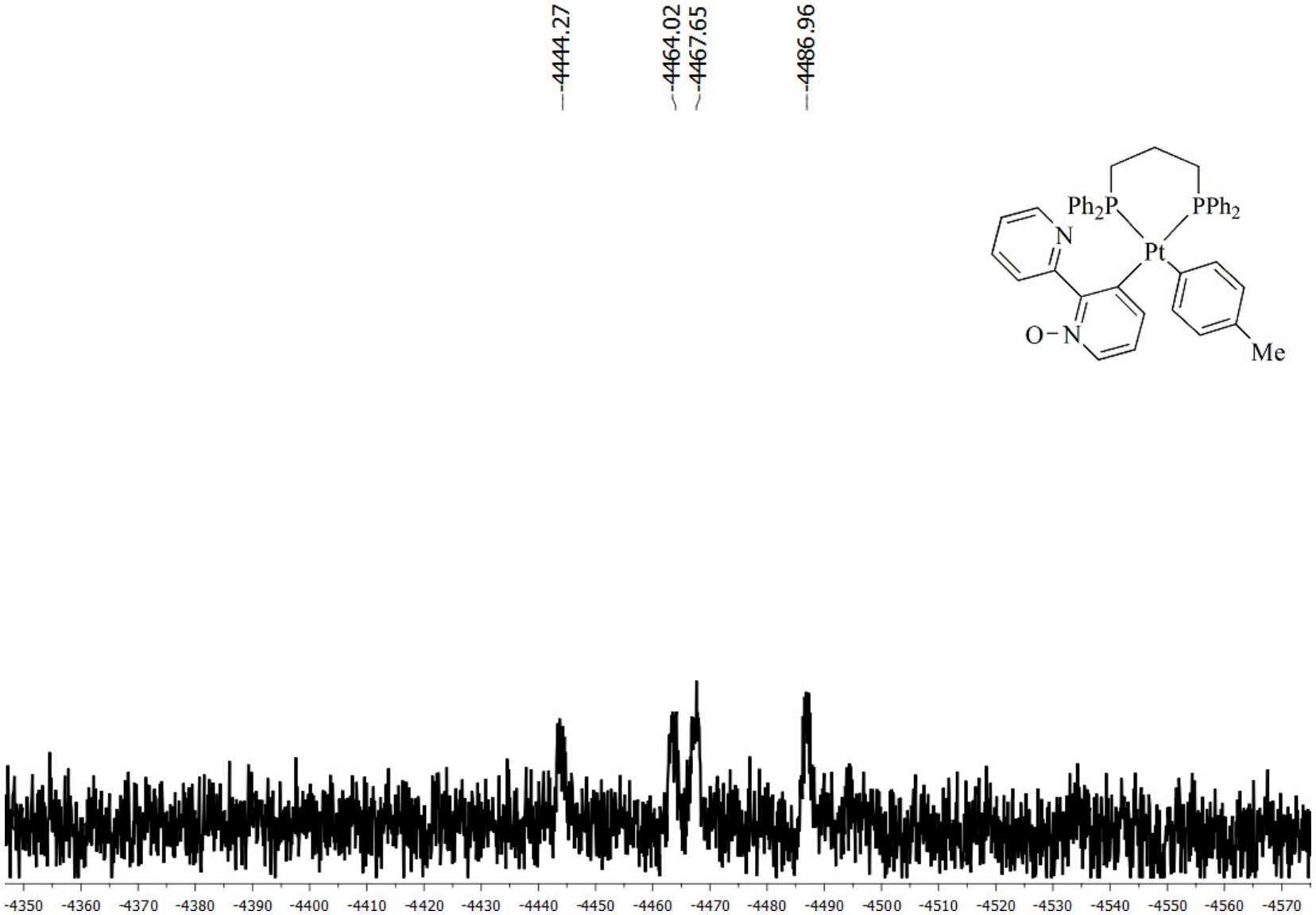

Figure S36. ^{195}Pt NMR spectrum of the complex **5a** in $CDCl_3$.

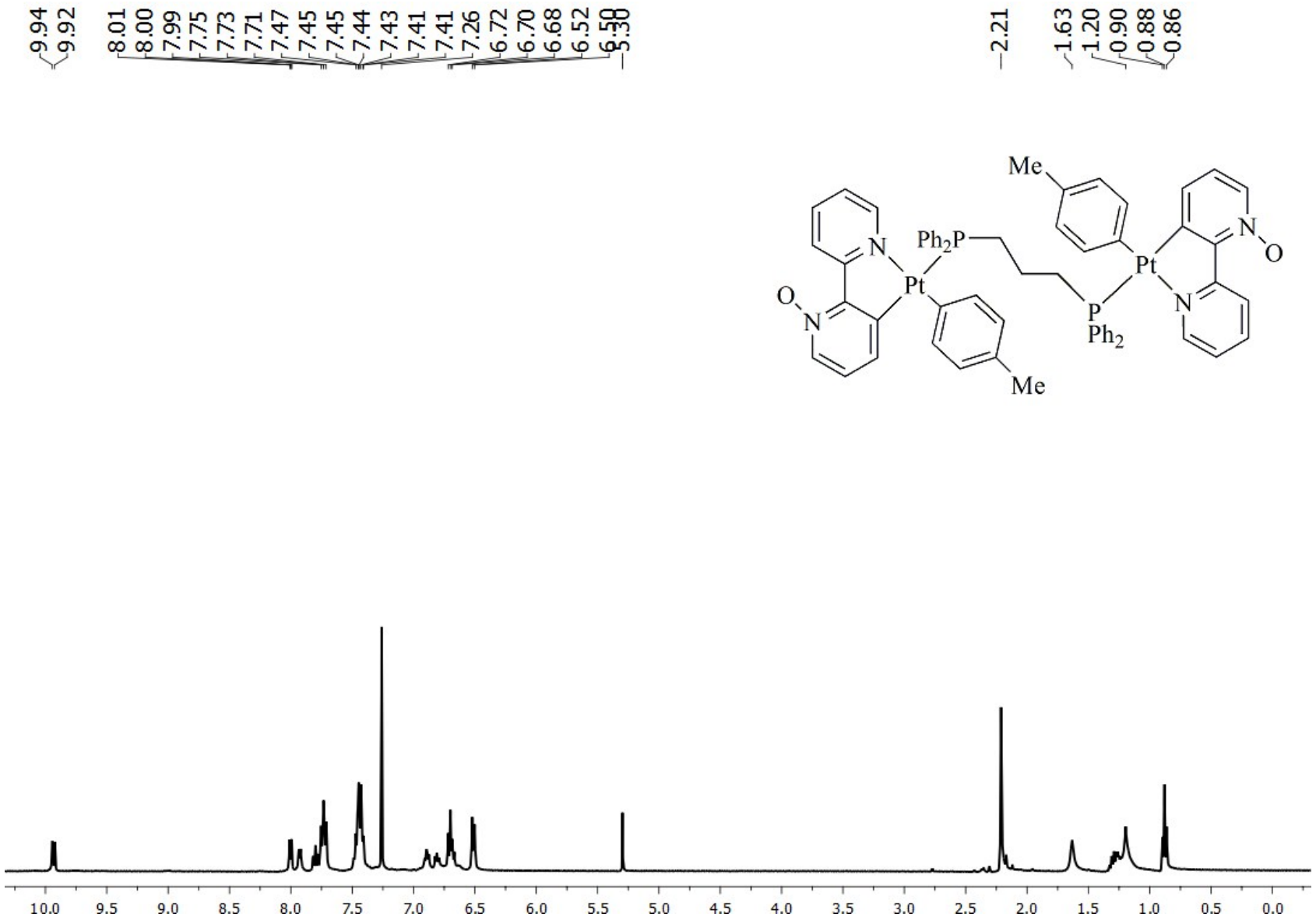

Figure S37. ^{1}H NMR spectrum of the complex **5b** in $CDCl_3$.

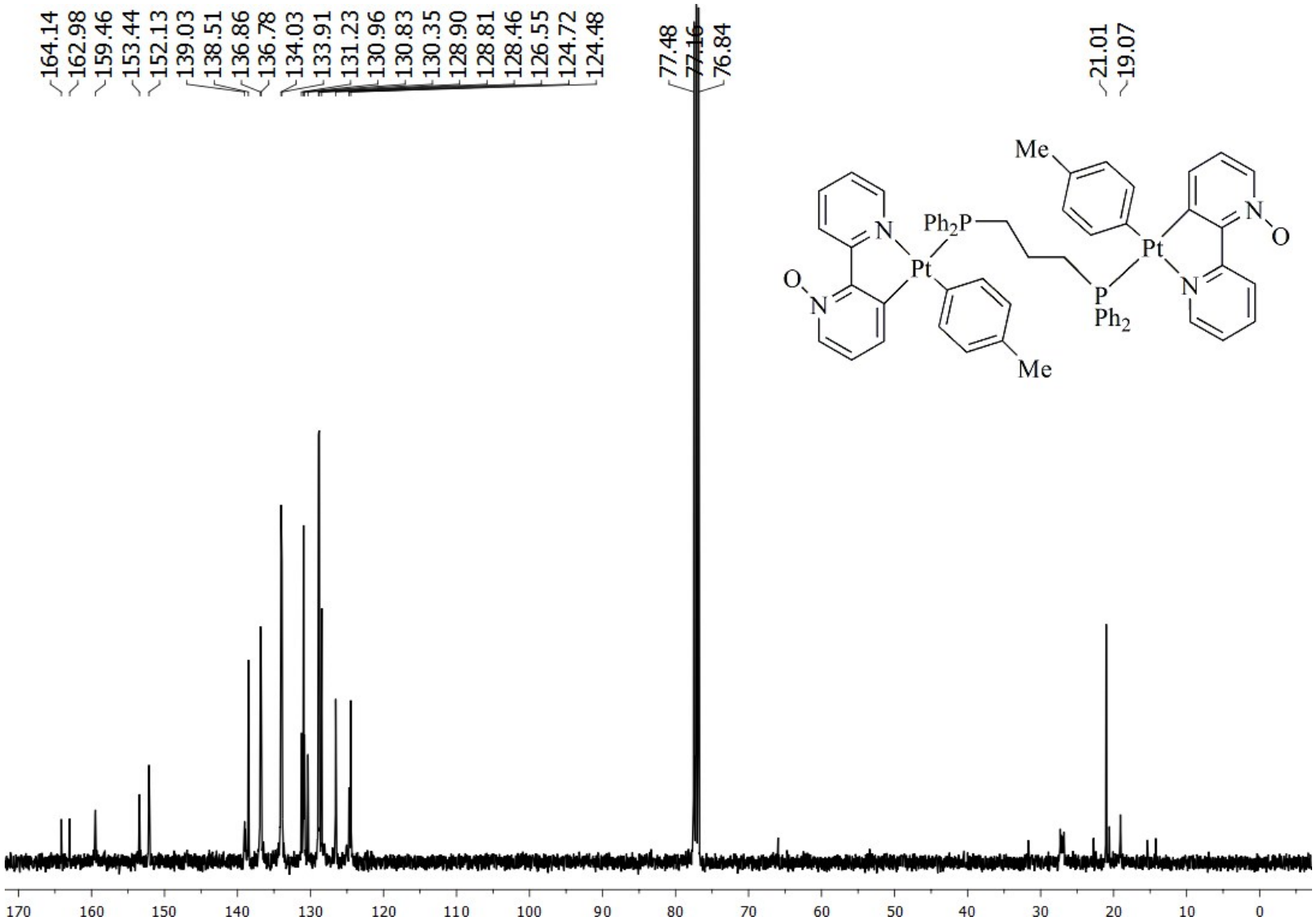

Figure S38. ^{13}C NMR spectrum of the complex **5b** in $CDCl_3$.

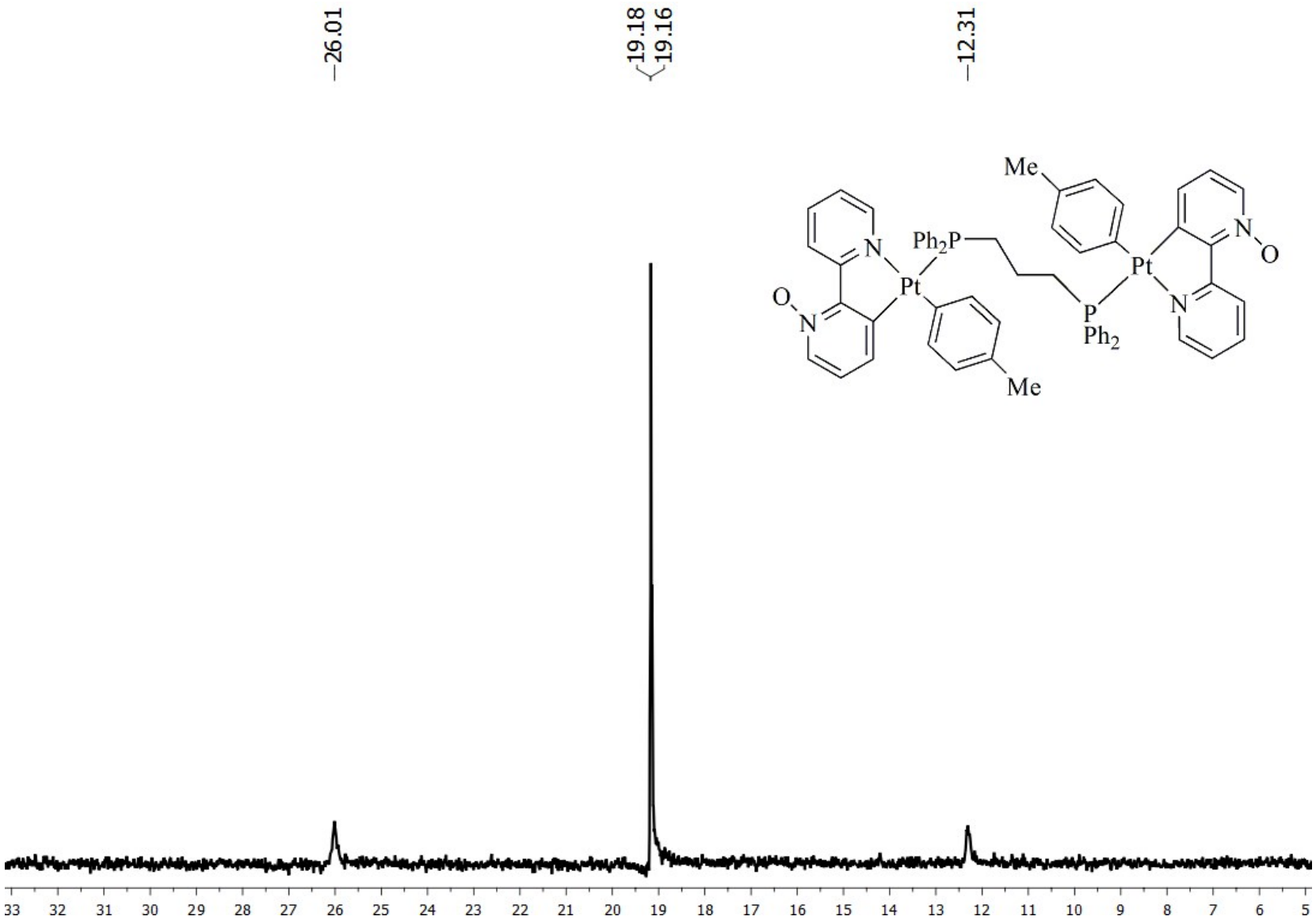

Figure S39. $^{31}P\{H\}$ NMR spectrum of the complex **5b** in $CDCl_3$**.**

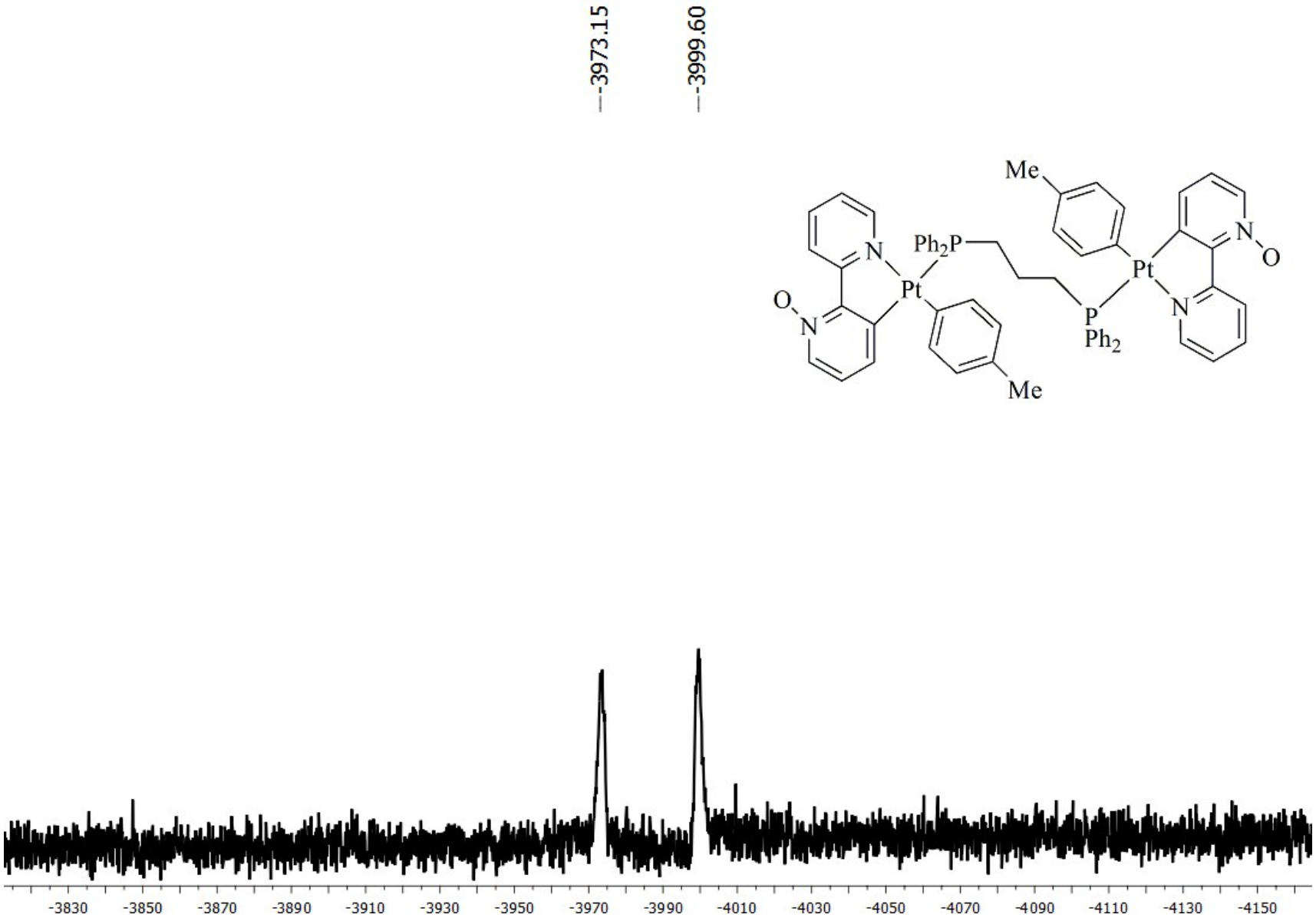

Figure S40. ^{195}Pt NMR spectrum of the complex **5b** in $CDCl_3$**.**

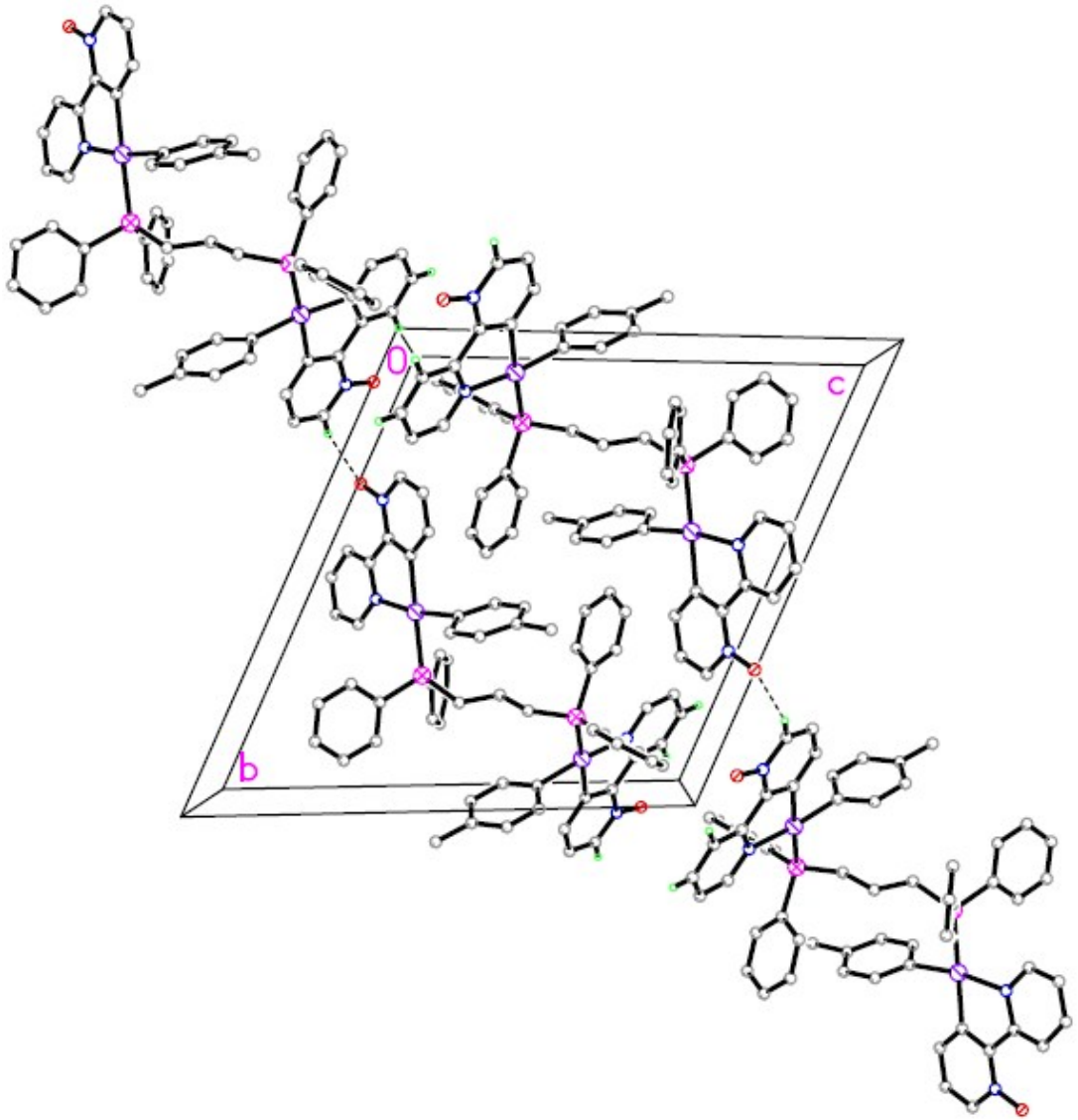

Figure S41. Crystal packing of the complex **5b** showing one-dimensional extended chain along the [011] direction through intermolecular C–H···O interactions.

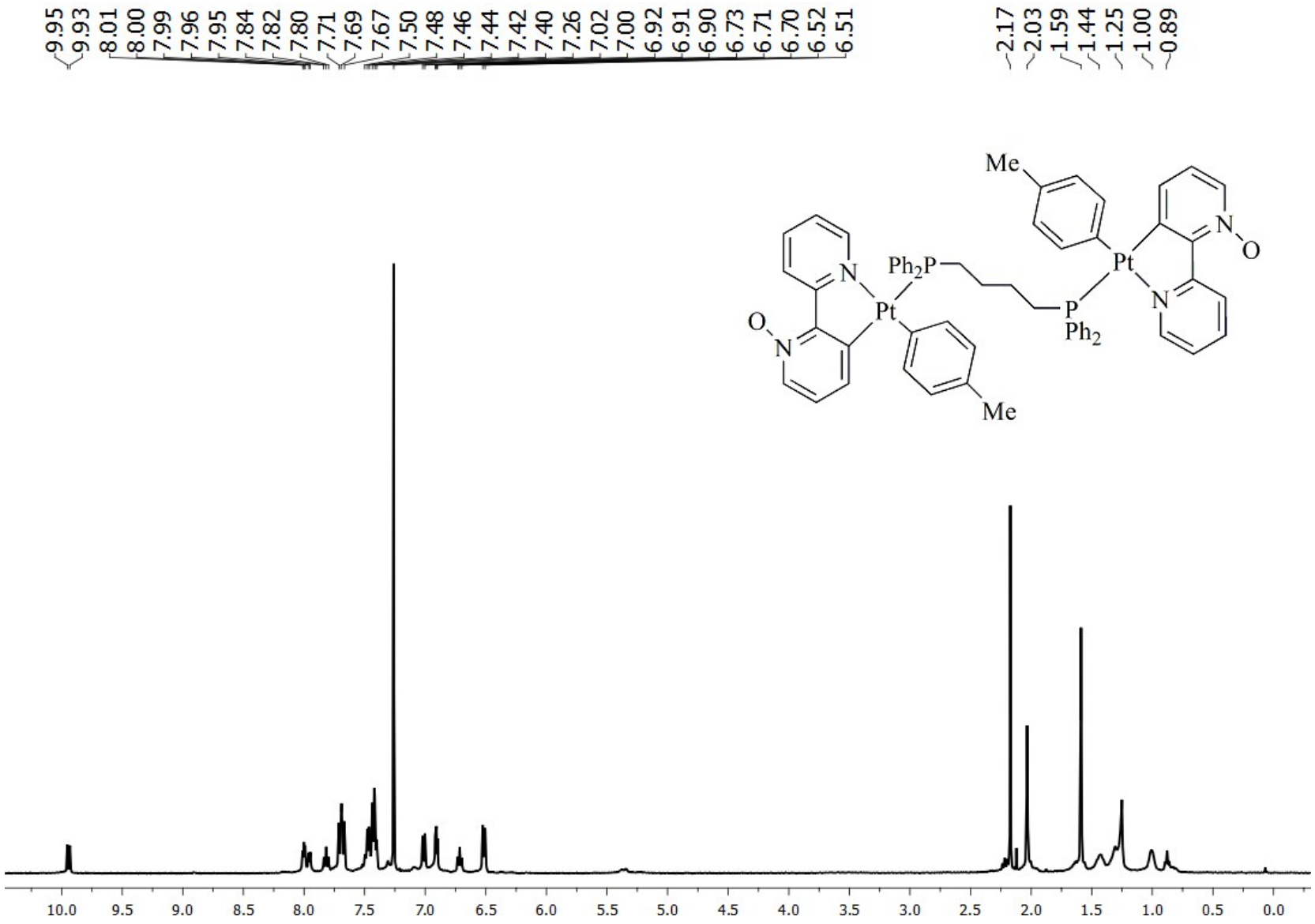

Figure S42. ^{1}H NMR spectrum of the complex **6b** in $CDCl_3$**.**

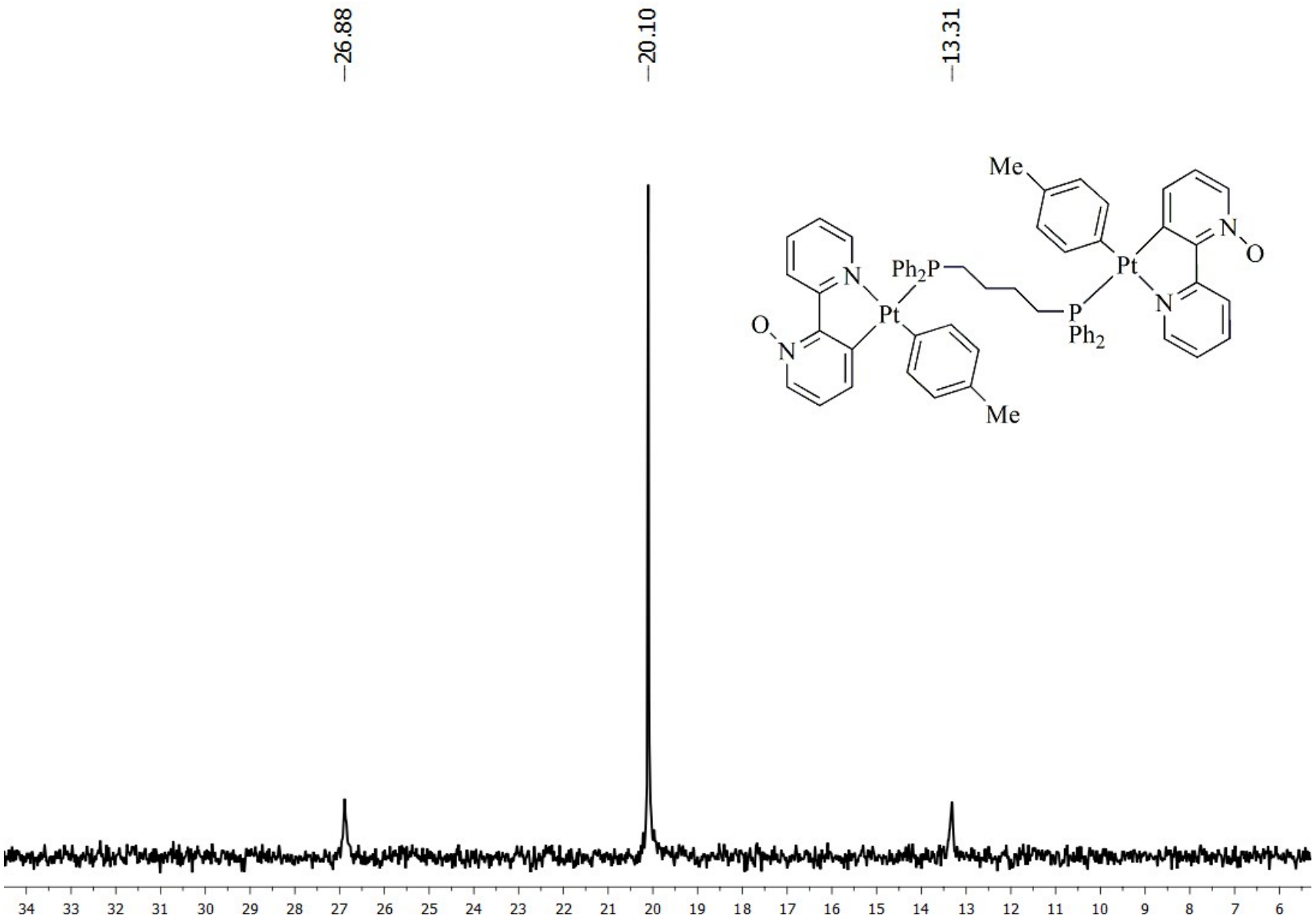

Figure S43. $^{31}P\{H\}$ NMR spectrum of the complex **6b** in $CDCl_3$**.**

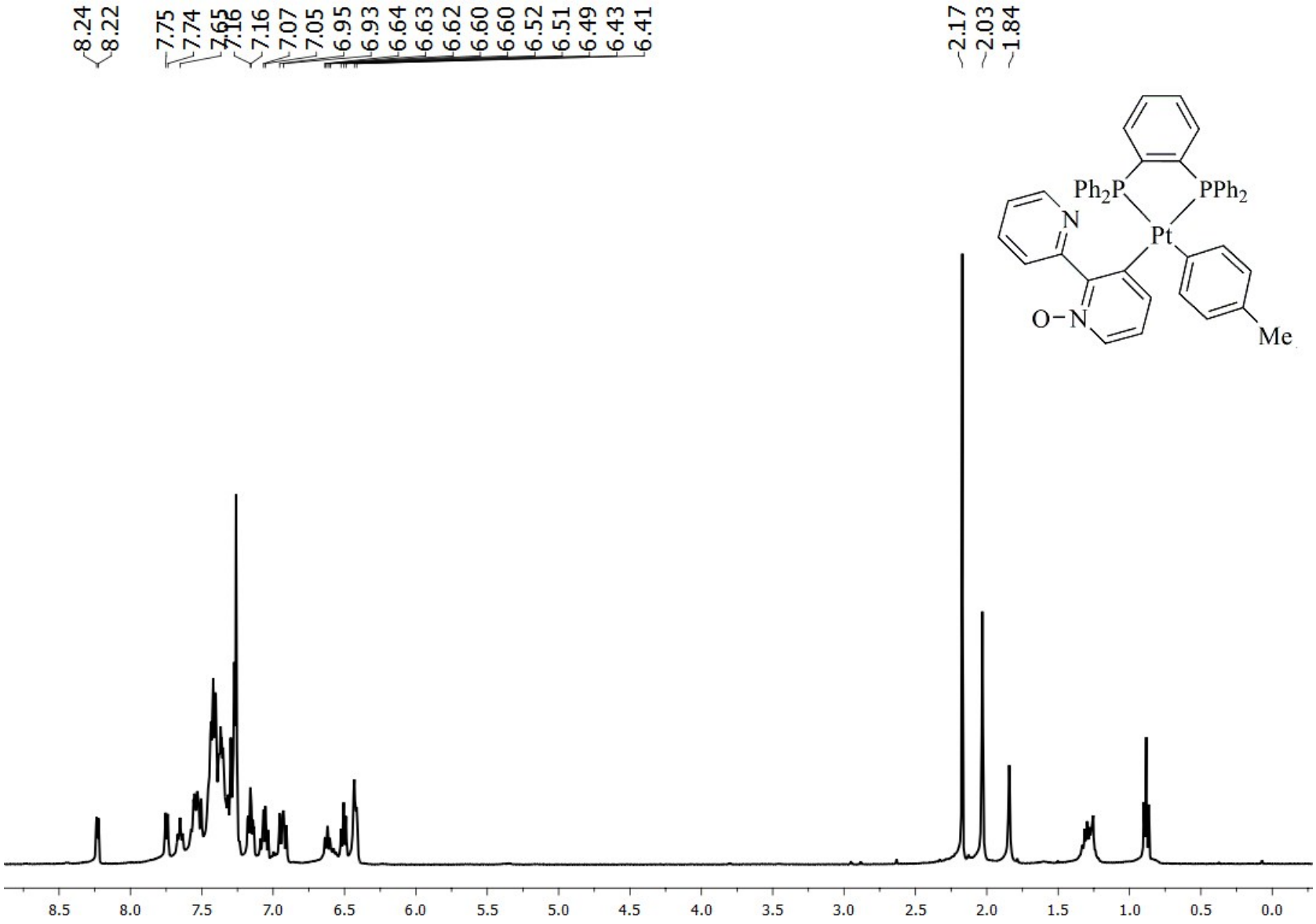

Figure S44. ^{1}H NMR spectrum of the complex **7a** in $CDCl_3$**.**

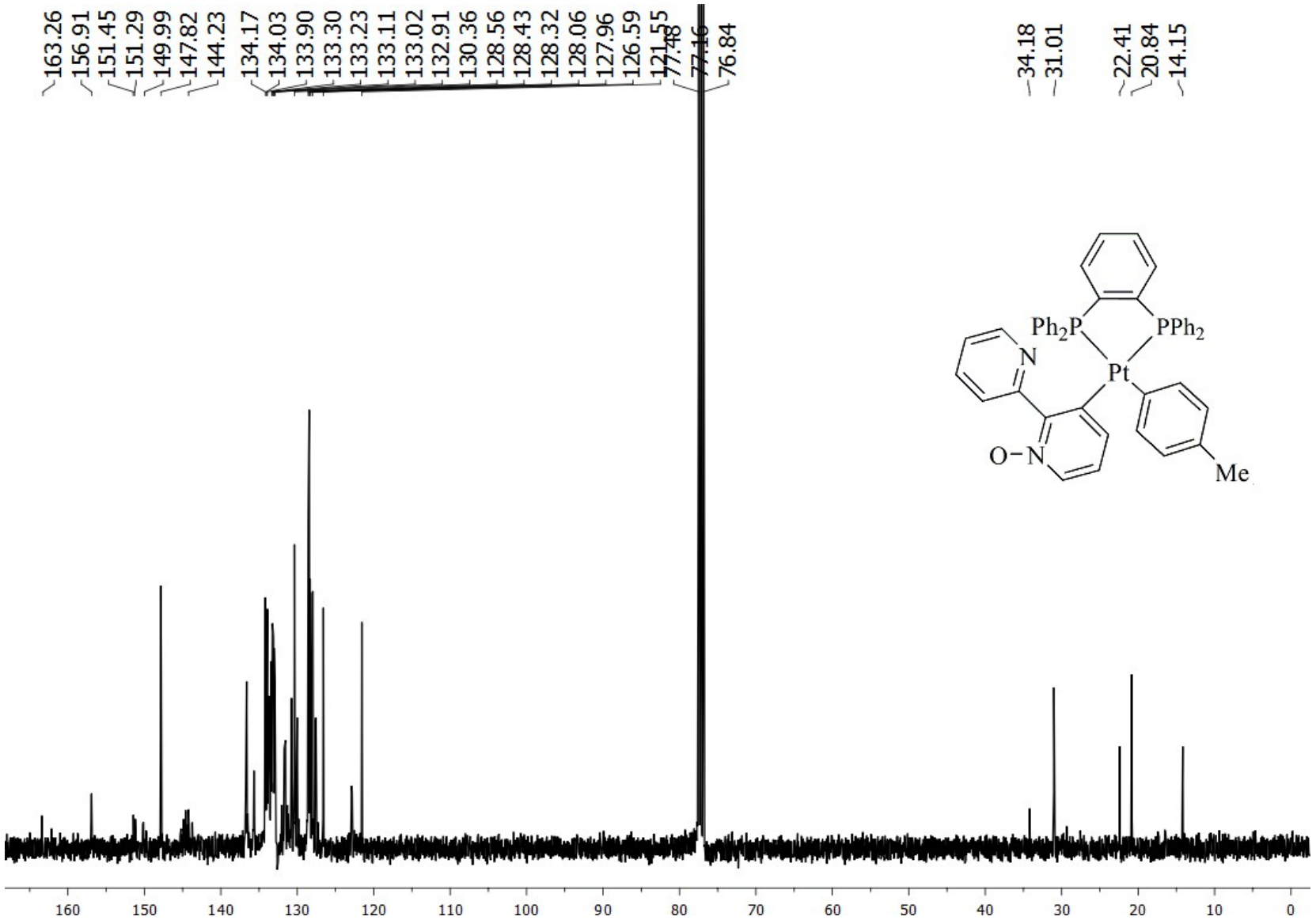

Figure S45. ^{13}C NMR spectrum of the complex **7a** in $CDCl_3$.

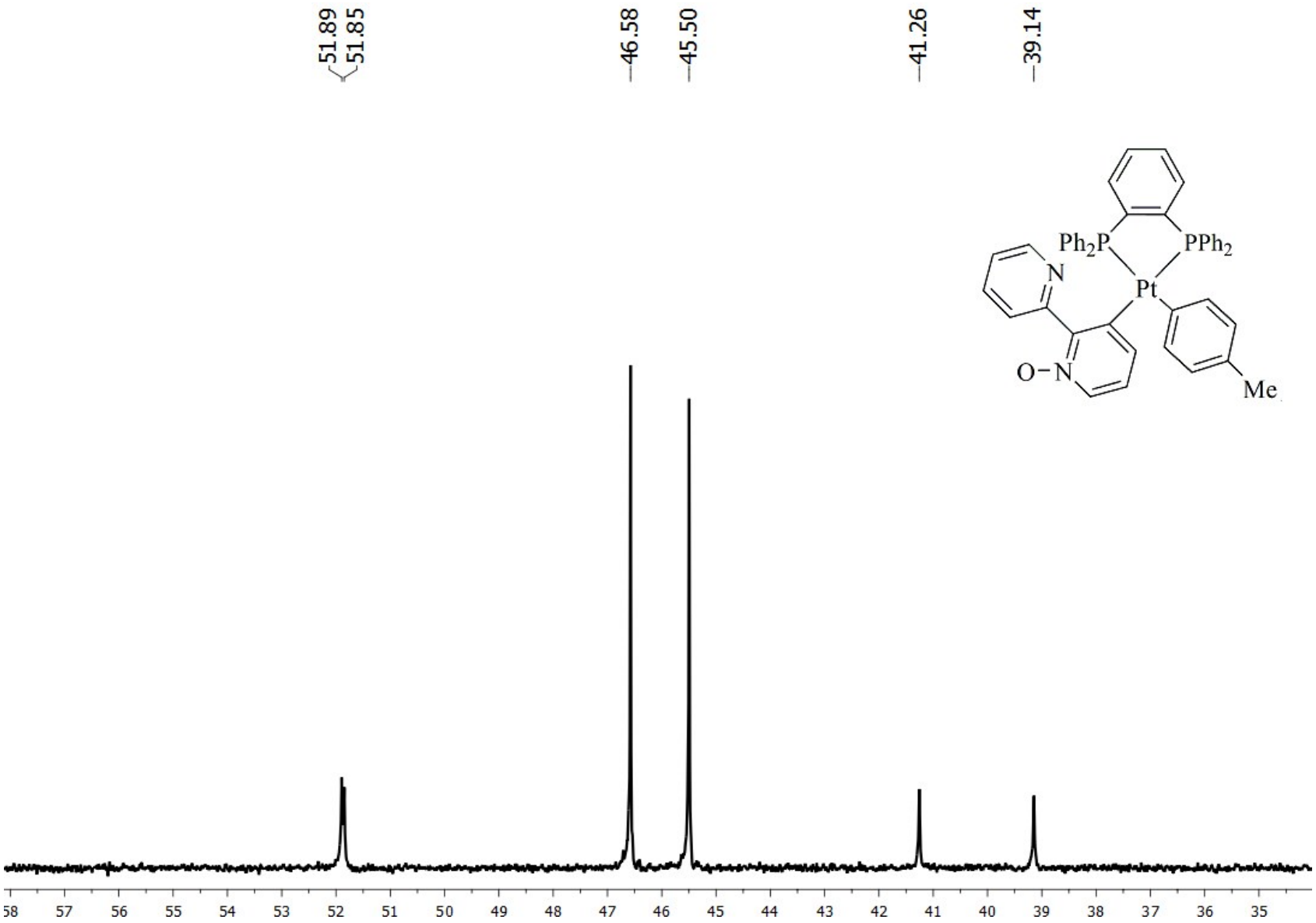

Figure S46. $^{31}P\{H\}$ NMR spectrum of the complex **7a** in $CDCl_3$**.**

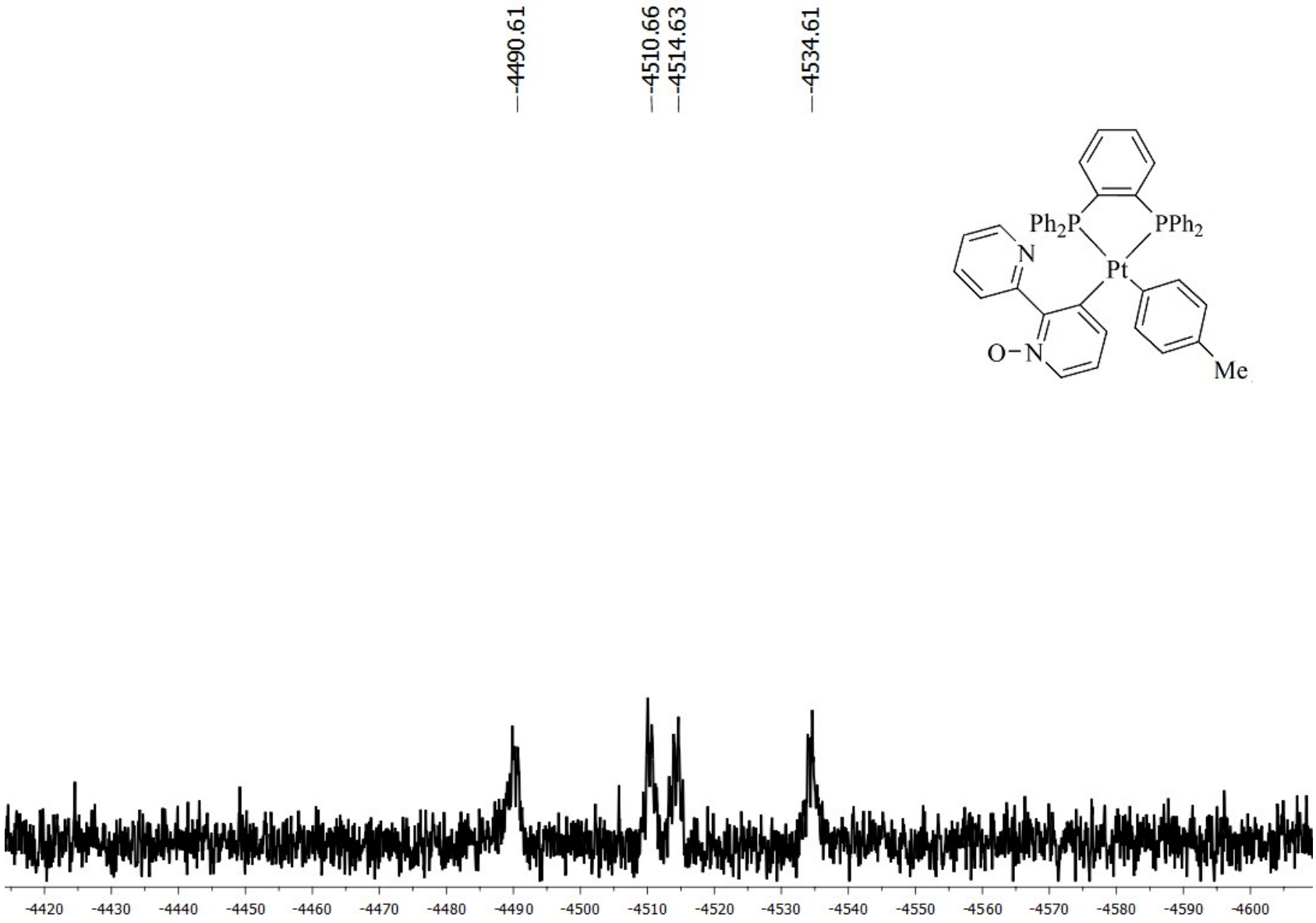

Figure S47. ^{195}Pt NMR spectrum of the complex **7a** in $CDCl_3$**.**

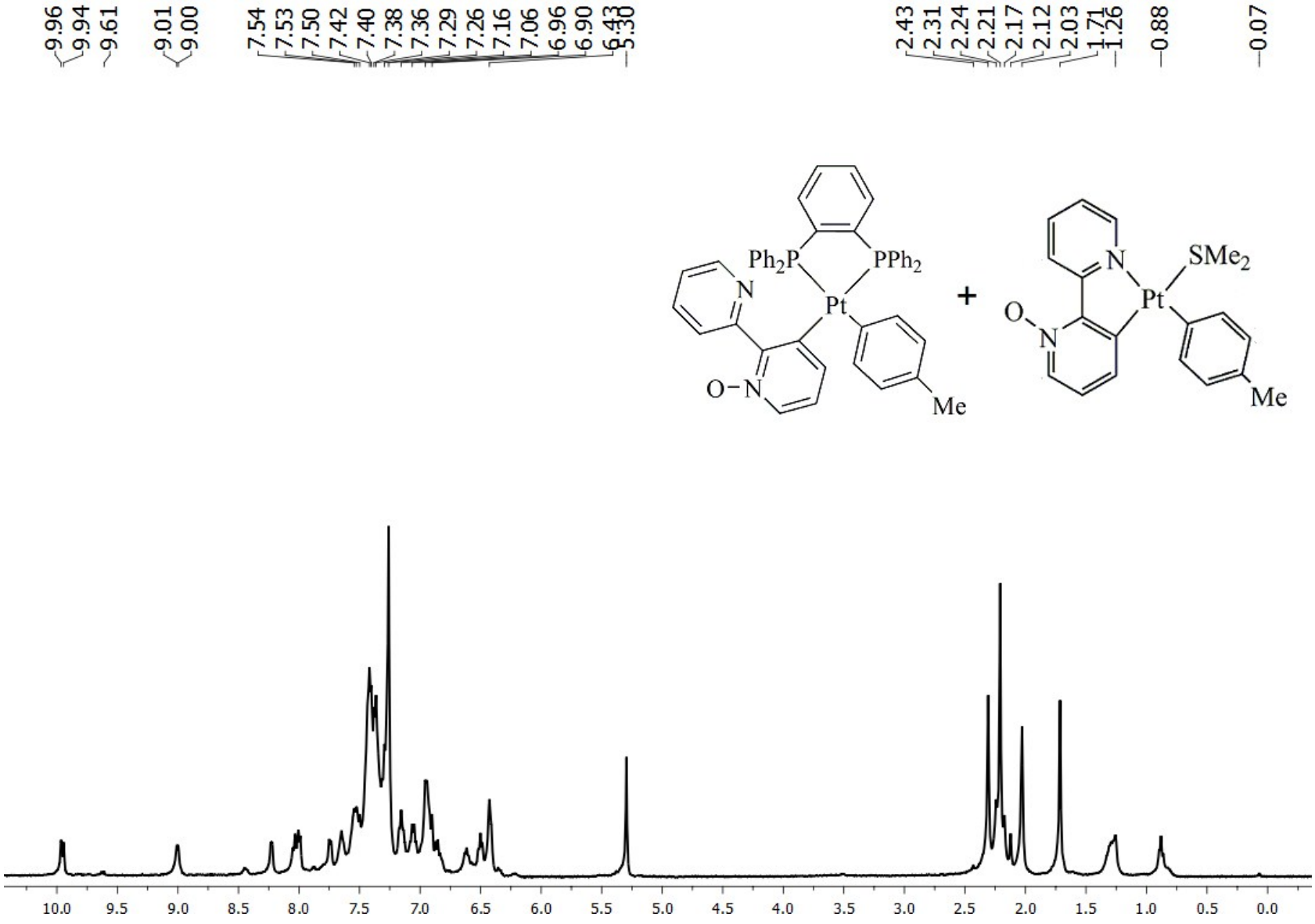

Figure S48. ^{1}H NMR spectrum of the complexes **7a + 1** in $CDCl_3$.

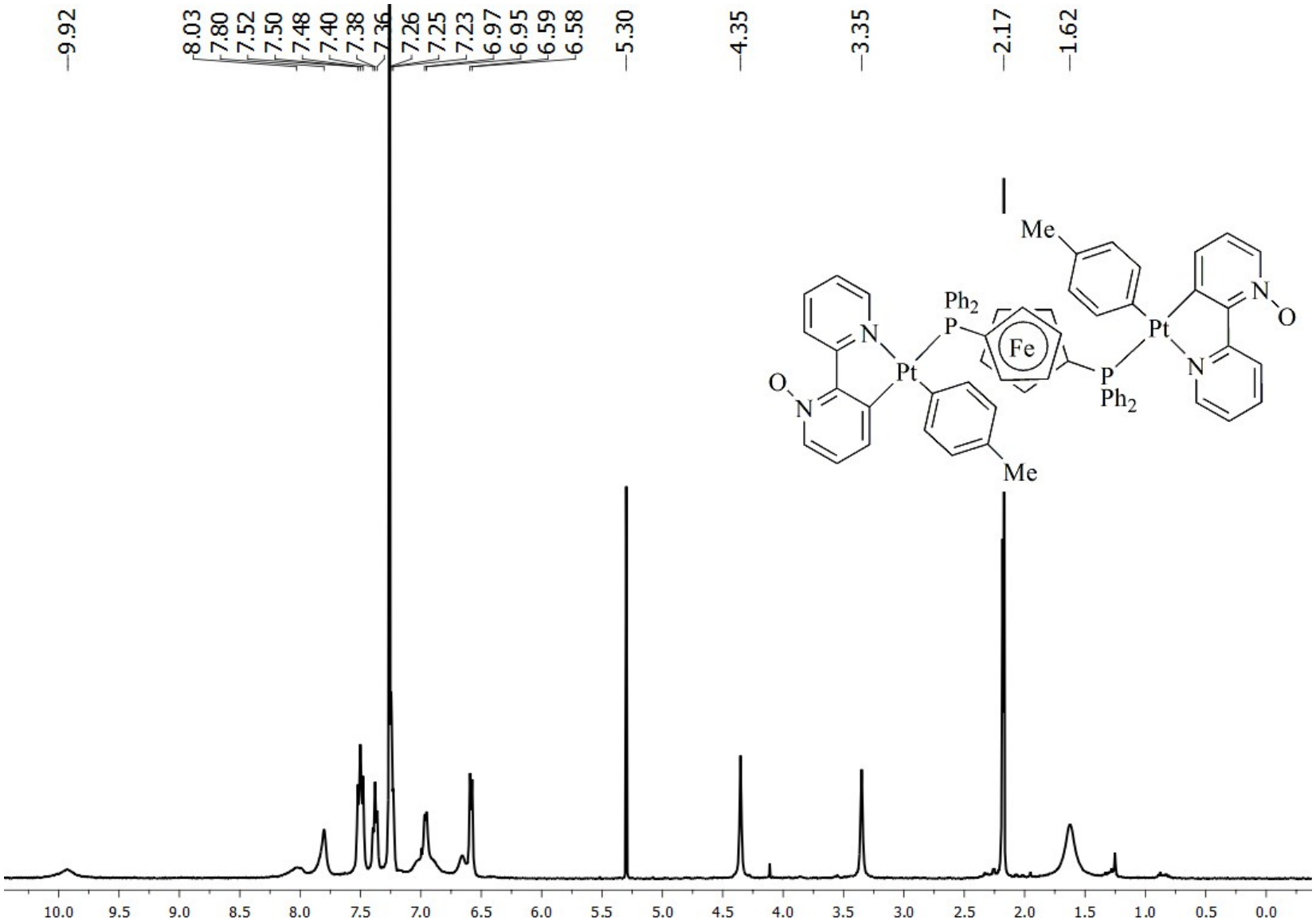

Figure S49. ^{1}H NMR spectrum of the complex **8b** in $CDCl_3$.

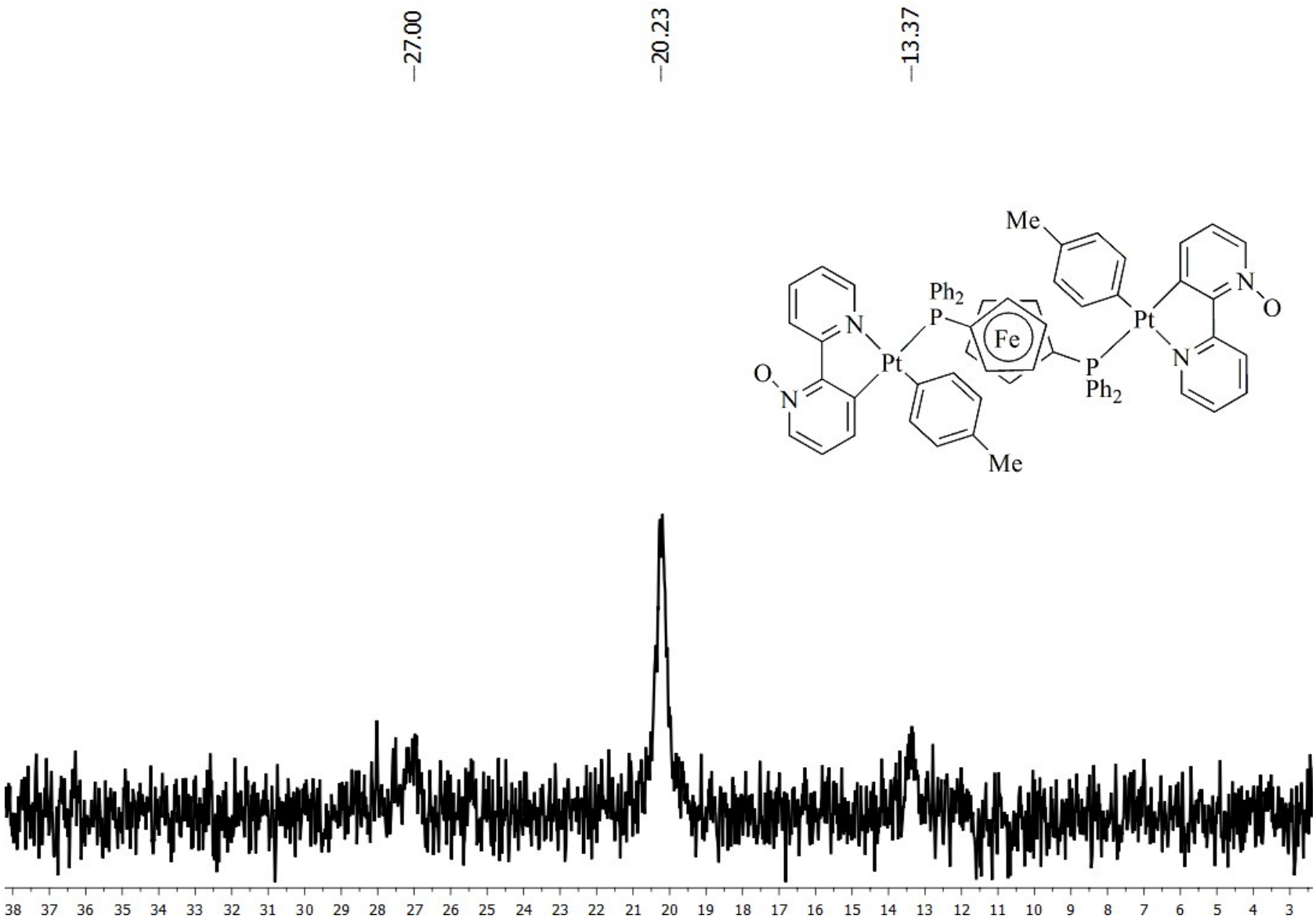

Figure S50. $^{31}P\{H\}$ NMR spectrum of the complex **8b** in $CDCl_3$**.**

Table S1. Crystal data and refinement parameters of the complexes **1**, **2a**, **2b** and **5b**.

Complex	**1**	**2a**	**2b**	**5b**
Empirical formula	$C_{19}H_{20}N_2OPtS$	$C_{42}H_{36}N_2OP_2Pt$	$C_{60}H_{52}Cl_2N_4O_2P_2Pt_2$	$C_{67}H_{68}N_4O_2P_2Pt_2$
Formula mass	519.52	841.76	1384.07	1413.37
Crystal size (mm)	0.05 × 0.103 × 0.14	0.06 × 0.09 × 0.12	0.05 × 0.11 × 0.14	0.10 × 0.18 × 0.35
Colour	Yellow	Pale-yellow	Pale-yellow	Pale-yellow
Crystal system	triclinic	triclinic	triclinic	triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
θ_{max} (°)	25.0	72.4	32	73.1
a (Å)	8.1277(16)	9.0415(3)	11.856(9)	12.7963(4)
b (Å)	10.499(2)	9.8123(3)	12.742(3)	16.9607(5)
c (Å)	11.580(2)	19.3945(6)	18.406(4)	17.2418(5)
α (°)	73.55(3)	90.271(3)	78.96(2)	112.543(3)
β (°)	82.97(3)	92.925(3)	77.62(4)	106.309(3)
γ (°)	73.60(3)	92.873(3)	80.60(4)	91.346(2)
V (Å³)	908.2(4)	1716.19(9)	2644(2)	3280.56(19)
Z	2	2	2	2
D_{calc} *(Mg/m³)*	1.900	1.629	1.739	1.431
μ (mm⁻¹)	7.847	8.811	5.495	8.653
F (000)	500	836	1352	1400
Index ranges	-9 ≤ h ≤9	-10 ≤ h ≤11	-16 ≤ h ≤17	-10 ≤ h ≤15
	-11 ≤ k ≤12	-11 ≤ k ≤8	-15 ≤ k ≤17	-20 ≤ k ≤20
	-13 ≤ l ≤13	-23 ≤ l ≤23	-27 ≤ l ≤24	-21 ≤ l ≤21
No. of meas. reflns.	6439	12582	30406	27596
No. of independent reflns./R_{int}	3157/0.078	6653/0.058	16055/0.0628	12729/0.039
No. of observed reflns. I > 2σ(I)	3112	6418	10688	11425
No. of parameters	220	434	651	739
Goodness-of-fit	0.873	1.114	1.005	1.021
R_1 (observed data)	0.0475	0.0392	0.0604	0.0317
wR_2 (all data)	0.0971	0.1043	0.0828	0.0849
CCDC No.	1818536	1818535	1818538	1818537

Table S2. Selected bond lengths (Å) and angles (°) of the complexes **1**, **2a**, **2b** and **5b**.

Bond lengths (Å)	**1**	**2a**	**2b**	**5b**
Pt(1)–N(1)	2.151(9)	2.125(4)	2.111(6)	2.108(3)
Pt(1)–C(1)	1.918(15)	2.036(5)	2.040(6)	2.043(3)
Pt(1)–C(11)	2.017(11)	2.001(4)	2.005(7)	2.018(3)
Pt(1)–P(1)	–	2.3089(10)	2.3043(17)	2.3109(8)
Pt(2)–P(2)	–	–	2.330(2)	2.3061(8)
Pt(1)–N(1)	2.151(9)	2.125(4)	2.111(6)	2.108(3)
Pt(2)–N(1A)	–	–	2.127(5)	2.110(3)
N(2)–O(1)	1.309(12)	1.302(5)	1.301(8)	1.309(5)
Bond angles (°)				
C(1)–Pt(1)–N(1)	80.5(5)	79.71(16)	79.6(2)	79.27(14)
C(11)–Pt(1)–P(1)	–	90.85(12)	91.55(17)	85.69(10)
C(1)–Pt(1)–P(1)	–	173.77(12)	171.81(18)	176.08(11)
N(1)–Pt(1)–C(11)	173.7(5)	169.59(15)	169.6(2)	170.08(13)
C(1)–Pt(1)–S(1)	175.9(4)	–	175.9(4)	–
N(1)–Pt(1)–P(1)	–	99.16(10)	98.83(15)	104.18(9)
C(1)–Pt(1)–C(11)	93.4(5)	86.9(9)	90.1(3)	90.90(15)
C(11)–Pt(1)–S(1)	90.6(3)	–	–	–

Table S3. Hydrogen bonding interactions parameters in the complexes **1**, **2a**, **2b** and **5b**.

	D–H···A	H···A (Å)	D···A (Å)	D–H···A (°)
2b	C(1S)–H(1S1)···O(1)	2.27	3.235(10)	173
	C(1S)–H(1S2)···O(1)^{i}	2.58	3.518(11)	163
	C(7)–H(7)···O(1)	2.17	2.762(9)	120
	C(7)–H(7A)···O(1A)	2.15	2.761(9)	122
	C(19)–H(19)···O(1A)^{ii}	2.57	3.397(8)	148
2a	C(4)–H(4)···O(1)^{iii}	2.24	3.153(5)	166
	C(7)–H(7)···O(1)	2.13	3.742(6)	122
	C(15)–H(15)···N(2)^{iv}	2.56	3.462(6)	164
5b	C(4)–H(4)···O(1A)^{v}	2.39	3.255(6)	155
	C(7)–H(7)···O(1)	2.14	2.767(6)	123
	C(7)–H(7)···O(1)^{vi}	2.55	3.250(5)	132
	C(7A)–H(7A)···O(1A)	2.12	2.729(5)	122
	C(8)–H(8)···O(1A)^{vii}	2.33	3.179(6)	152
1	C(18)–H(18B)···O(1)^{viii}	2.44	3.380(17)	166
	C(12)–H(10)···S(1)	2.73	3.356(13)	126
	C(7)–H(7)···O(1)	2.15	2.763(17)	122

*Symmetry codes: (i) 1 - x, - y, - z (ii) -1 + x, y, z (iii) -x, 2 - y, 2 - z (iv) 1 + x, y, z (v) x, -1 + y, -1 + z (vi) 2 - x, 2 - y, -z (vii) 2 - x, 3 - y, 1 - z (vii) 1 - x, -y, 1 - z