Electronic Supporting Information

Platinum(II) and palladium(II) complexes with electron-deficient *meso*-diethoxyphosphorylporphyrins: synthesis, structure and tuning of photophysical properties by varying peripheral substituents

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1. Compound characterization

1.1. NMR spectroscopy

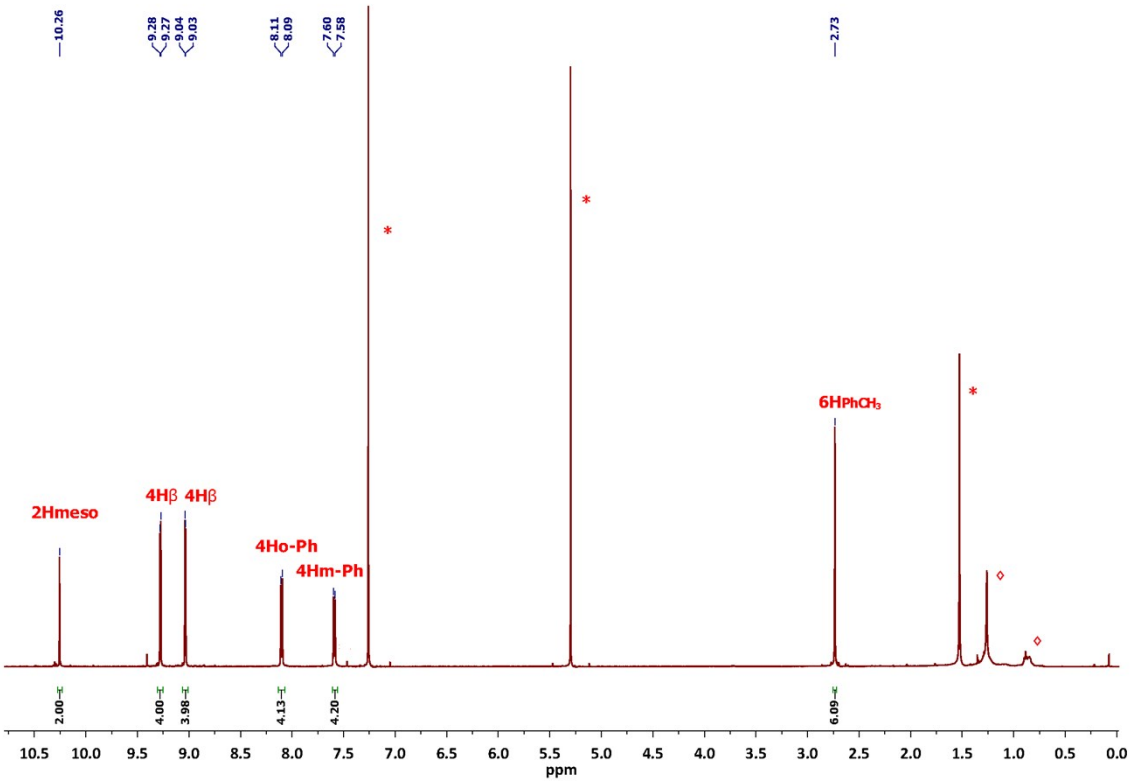


Figure S1. ^{1}H NMR spectrum of **PdDTolP** in $CDCl_3$. Solvent peaks are indicated with * (δ_H 7.38 ppm – $CHCl_3$, δ_H 5.31 ppm – CH_2Cl_2, δ_H 1.56 ppm –DOH and H_2O). Solvent impurity peaks are indicated with ◊.

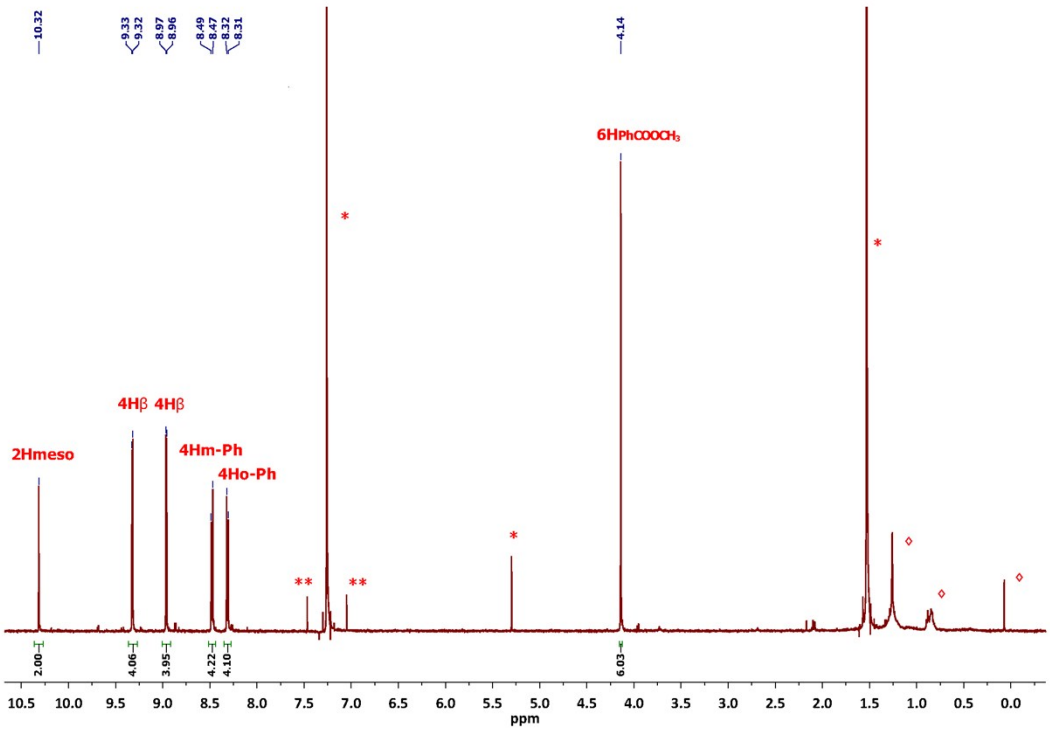


Figure S2. ^{1}H NMR spectrum of **PdD(CMP)P** in $CDCl_3$. Solvent peaks are indicated with * (δ_H 7.38 ppm – $CHCl_3$, δ_H 5.31 ppm – CH_2Cl_2, δ_H 1.56 ppm –DOH and H_2O). Solvent satellite peaks are indicated with **. Solvent impurity peaks are indicated with ◊.

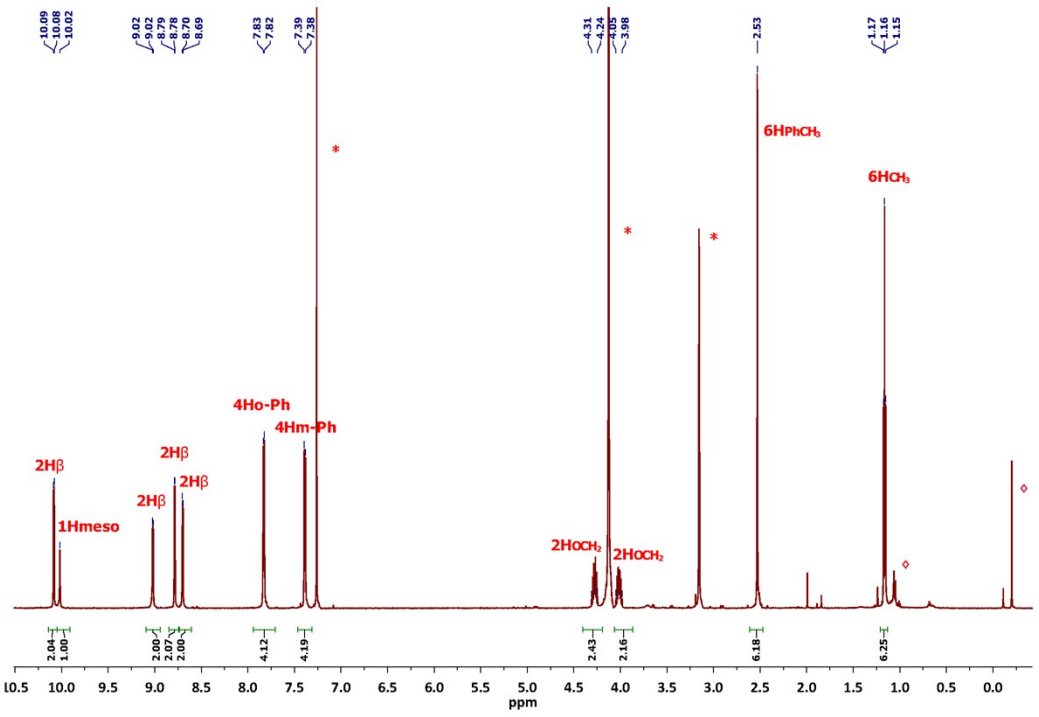


Figure S3. ^{1}H NMR spectrum of **PdDTolPP** in the mixture of $CDCl_3/CD_3OD$ (2:1, v/v). Solvent peaks are indicated with * (δ_H 7.38 ppm – $CHCl_3$, δ_H 4.06 ppm –DOH and H_2O, δ_H 3.33 ppm – CHD_2OD). Solvent impurity peaks are indicated with ◊.

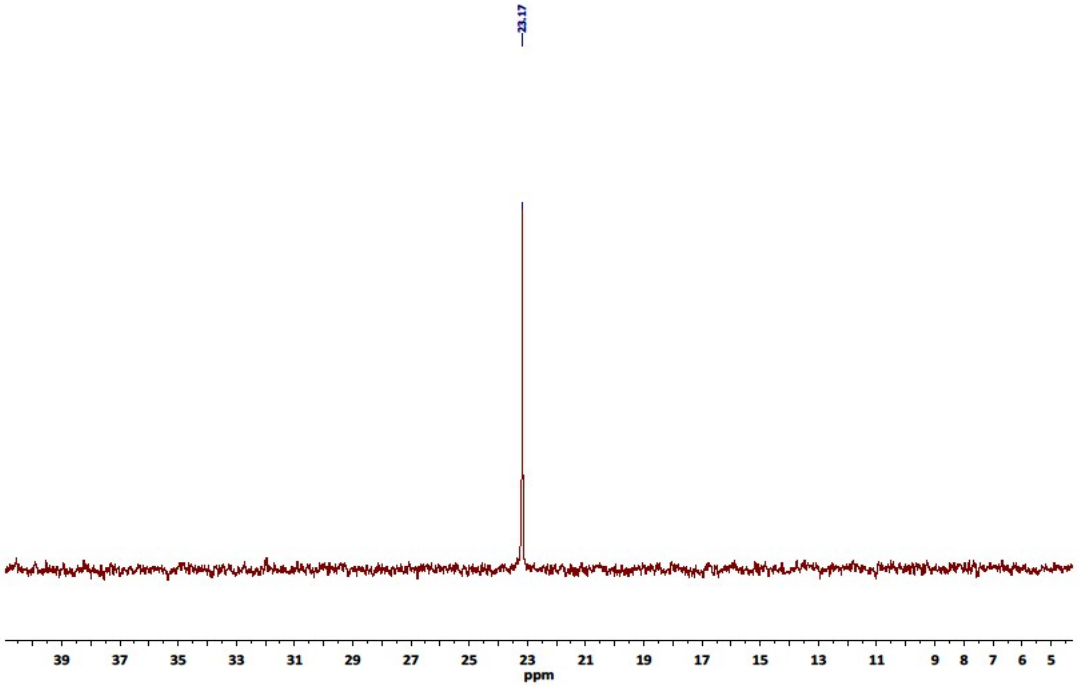


Figure S4. ^{31}P NMR spectrum of **PdDTolPP** in the mixture of $CDCl_3/CD_3OD$ (2:1, v/v).

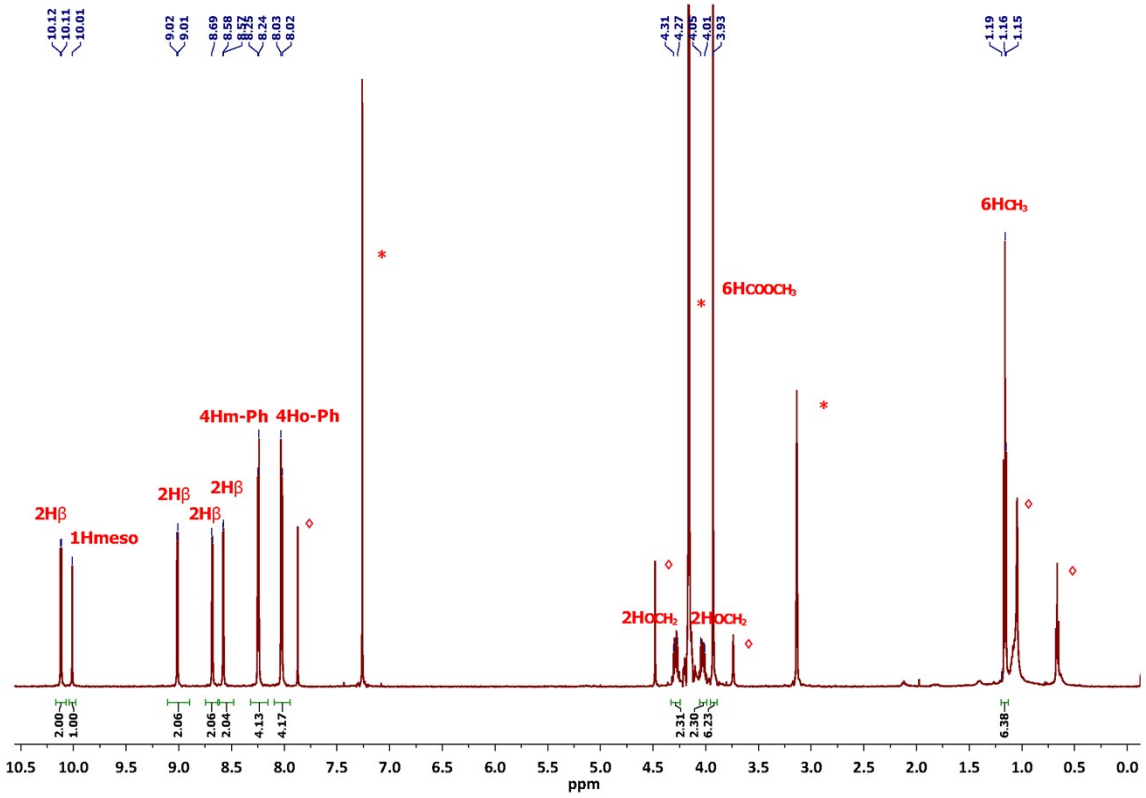


Figure S5. ^{1}H NMR spectrum of **PdD(CMP)PP** in the mixture of $CDCl_3/CD_3OD$ (2:1, v/v). Solvent peaks are indicated with * (δ_H 7.38 ppm – $CHCl_3$, δ_H 4.06 ppm –DOH and H_2O, δ_H 3.33 ppm – CHD_2OD). Solvent impurity peaks are indicated with ◊.

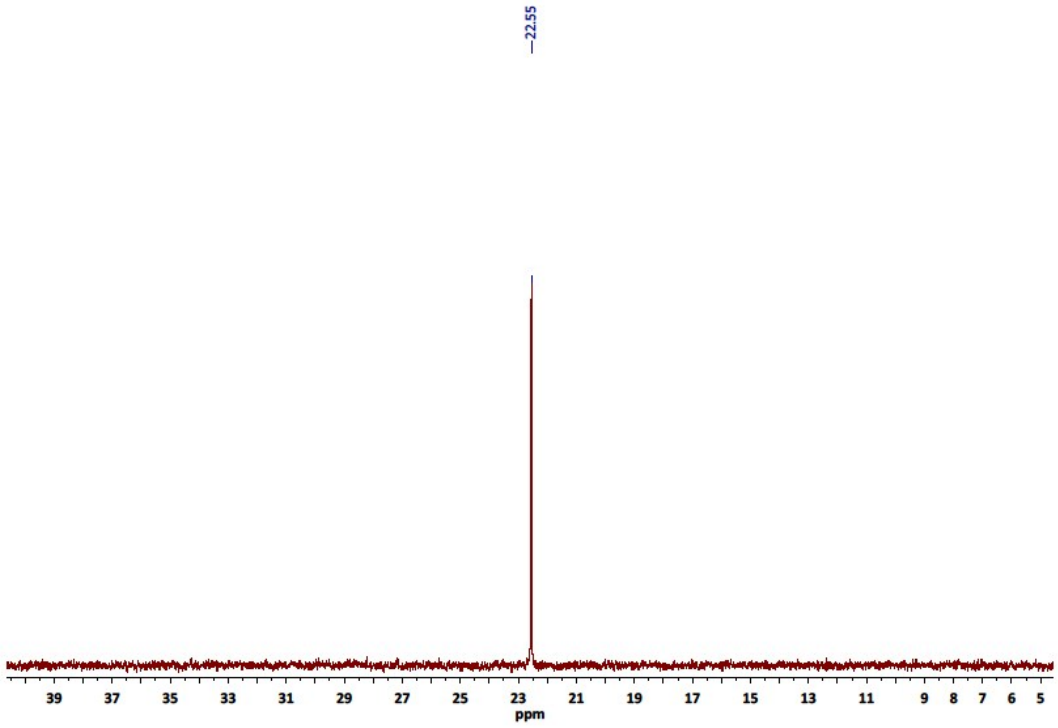


Figure S6. ^{31}P NMR spectrum of **PdD(CMP)PP** in the mixture of $CDCl_3/CD_3OD$ (2:1, v/v).

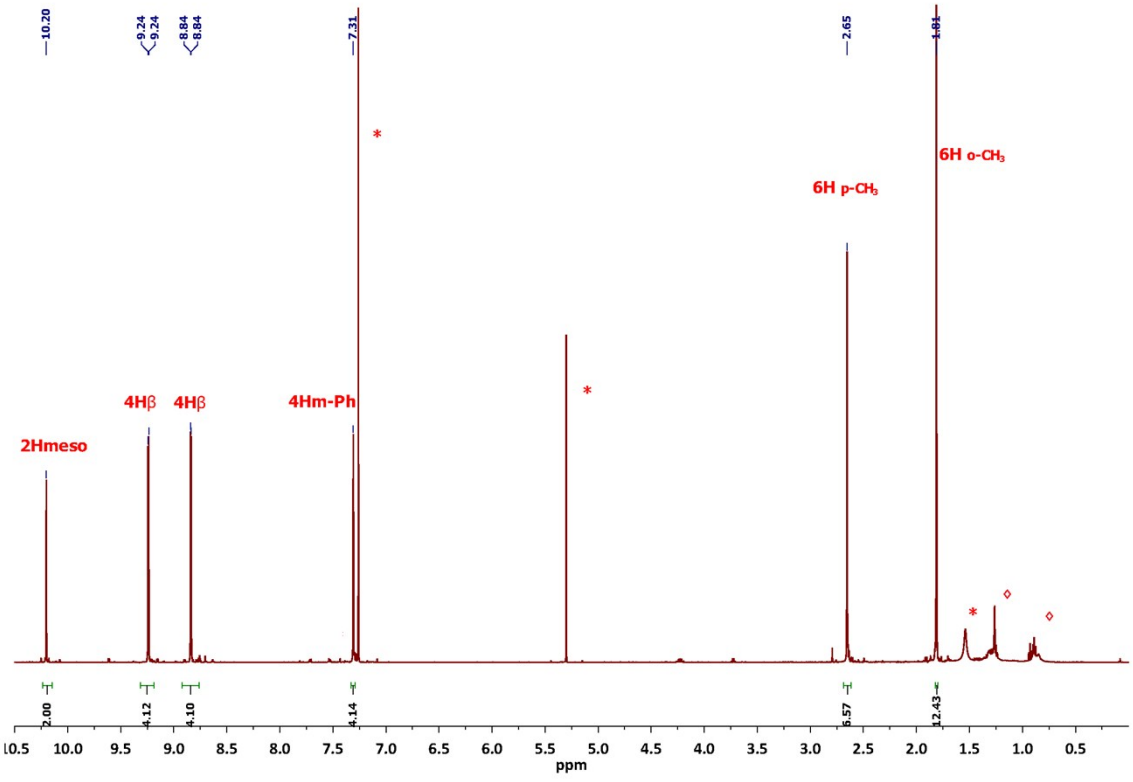


Figure S7. ^{1}H NMR spectrum of **PdDMesP** in $CDCl_3$. Solvent peaks are indicated with * (δ_H 7.38 ppm – $CHCl_3$, δ_H 5.31 ppm – CH_2Cl_2, δ_H 1.56 ppm –DOH and H_2O). Solvent impurity peaks are indicated with ◊.

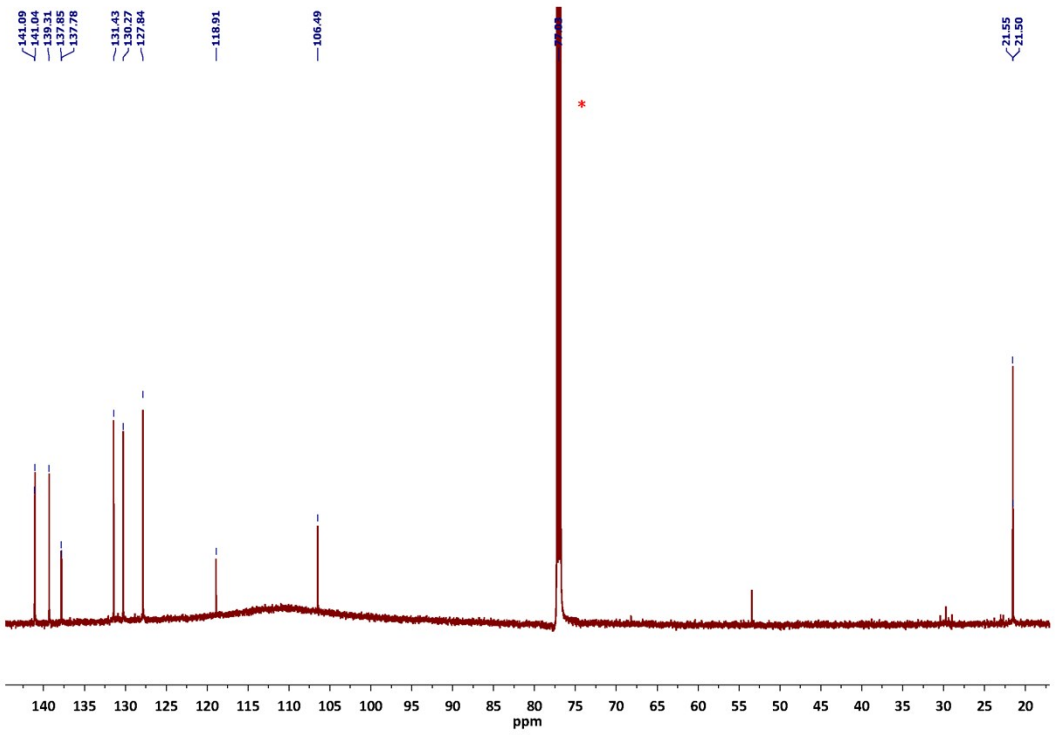


Figure S8. ^{13}C NMR spectrum of **PdDMesP** in $CDCl_3$. Solvent peaks are indicated with * (δ_C 77.21 ppm – $CDCl_3$).

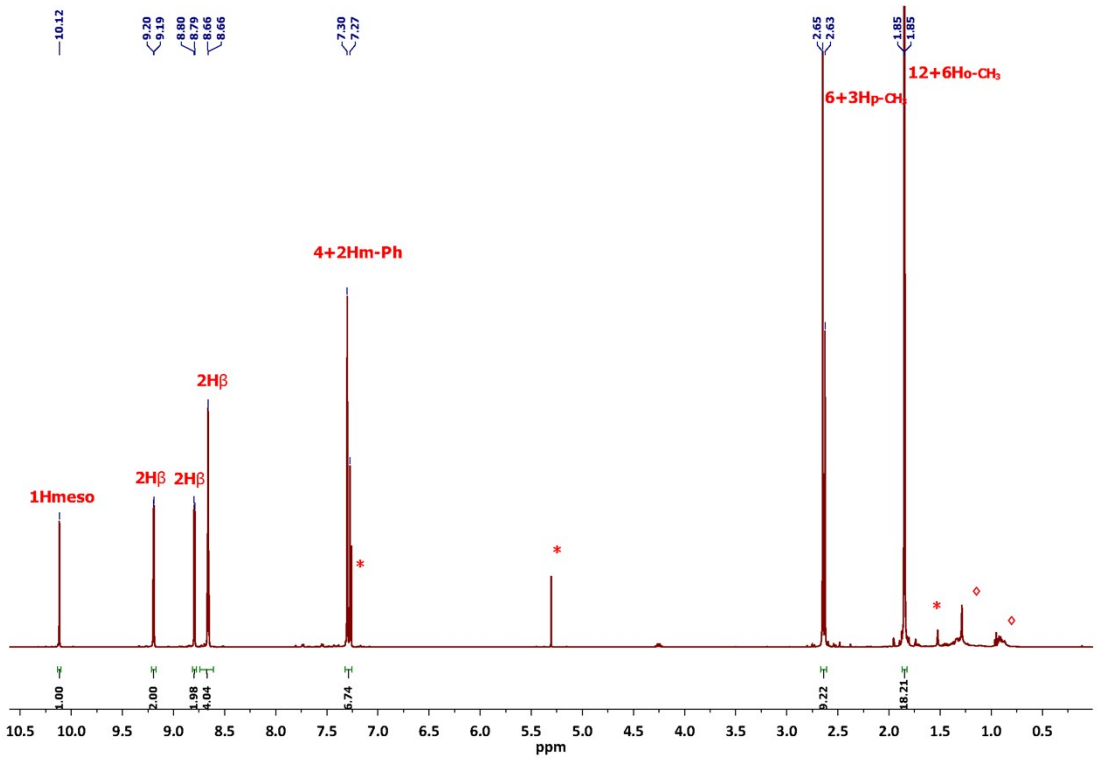


Figure S9. ^{1}H NMR spectrum of **PdTMesP** in $CDCl_3$. Solvent peaks are indicated with * (δ_H 7.38 ppm – $CHCl_3$, δ_H 5.31 ppm – CH_2Cl_2, δ_H 1.56 ppm –DOH and H_2O). Solvent impurity peaks are indicated with ◊.

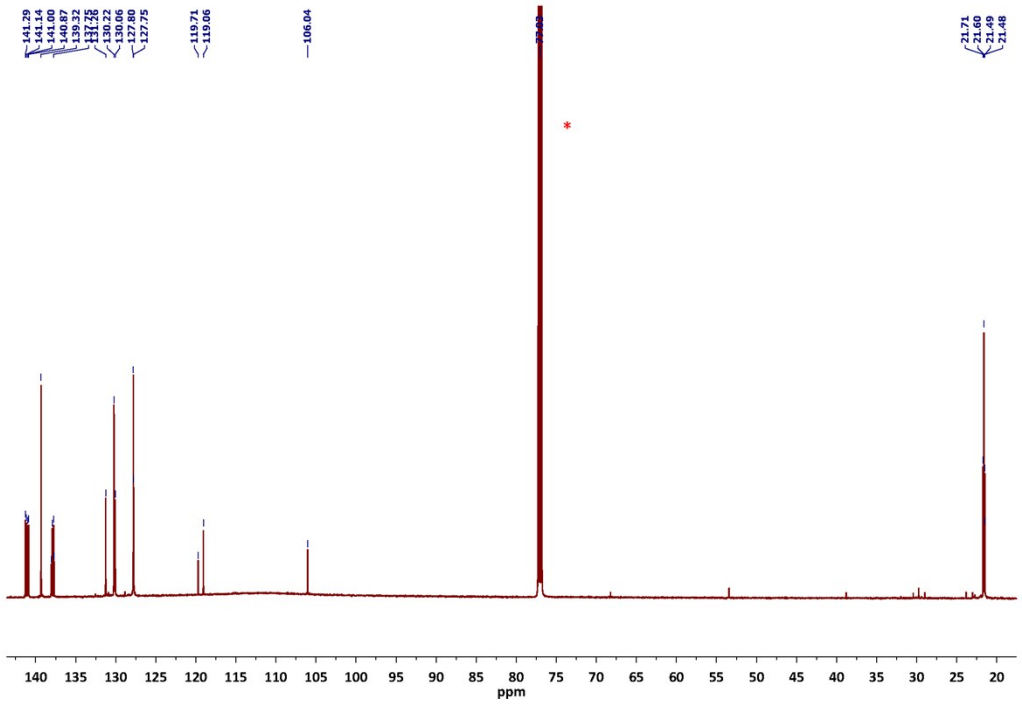


Figure S10. ^{13}C NMR spectrum of **PdTMesP** in $CDCl_3$. Solvent peaks are indicated with * (δ_C 77.21 ppm – $CDCl_3$).

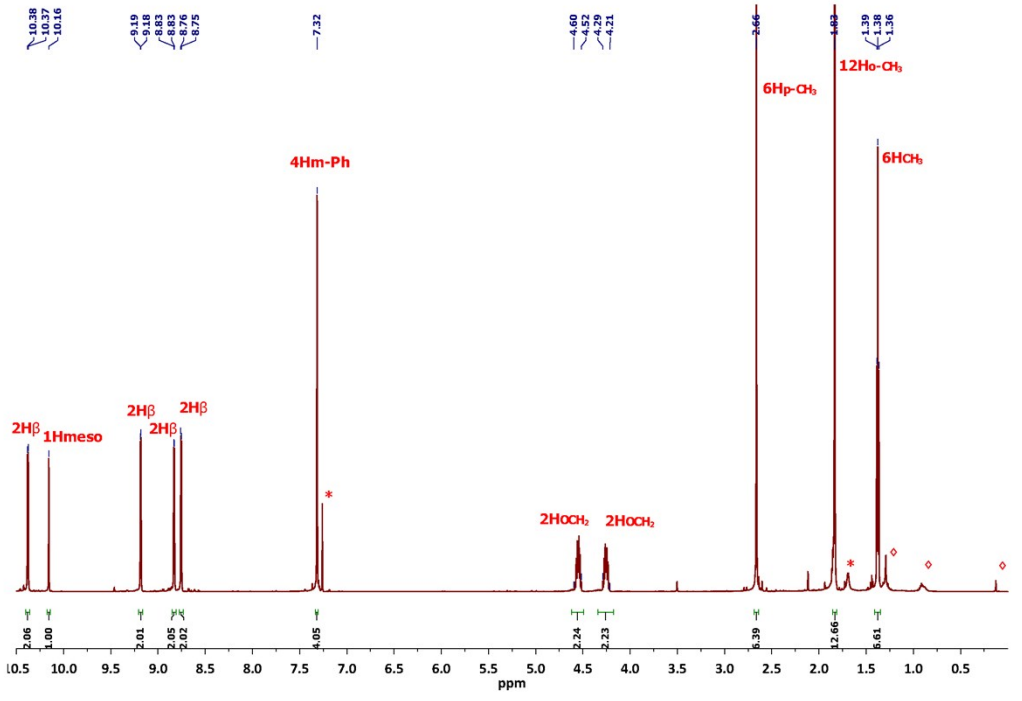


Figure S11. ^{1}H NMR spectrum of **PdDMesPP** in $CDCl_3$. Solvent peaks are indicated with * (δ_H 7.38 ppm – $CHCl_3$, δ_H 5.31 ppm – CH_2Cl_2, δ_H 1.56 ppm –DOH and H_2O). Solvent impurity peaks are indicated with ◊.

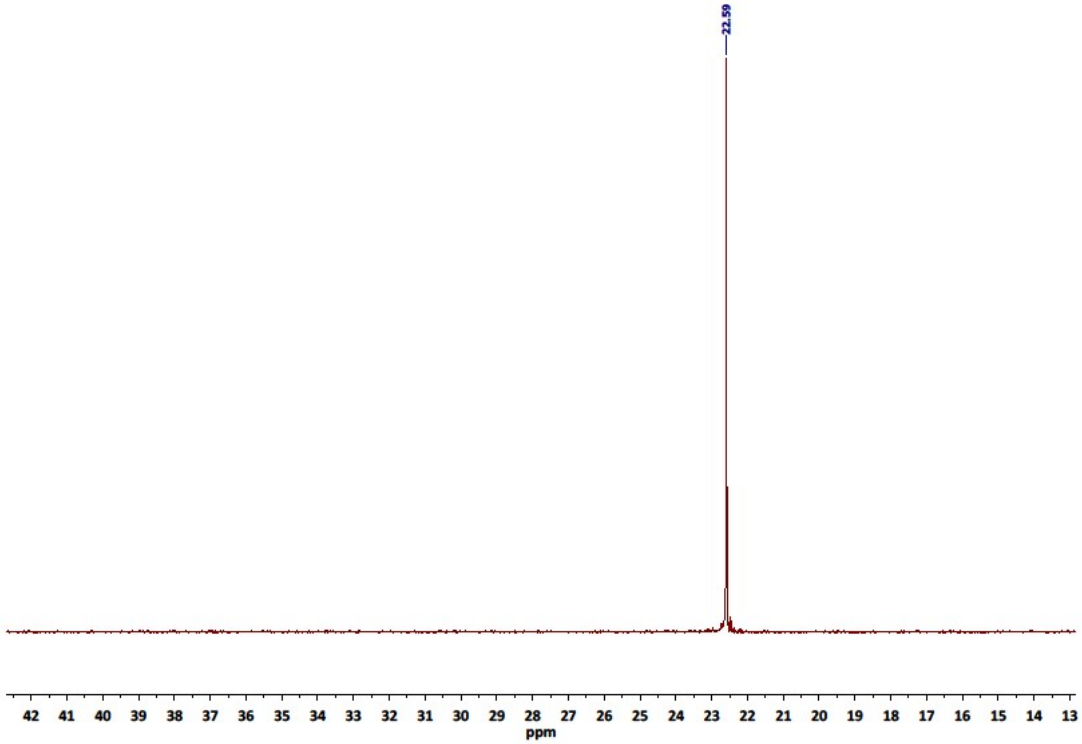


Figure S12. ^{31}P NMR spectrum of **PdDMesPP** in $CDCl_3$.

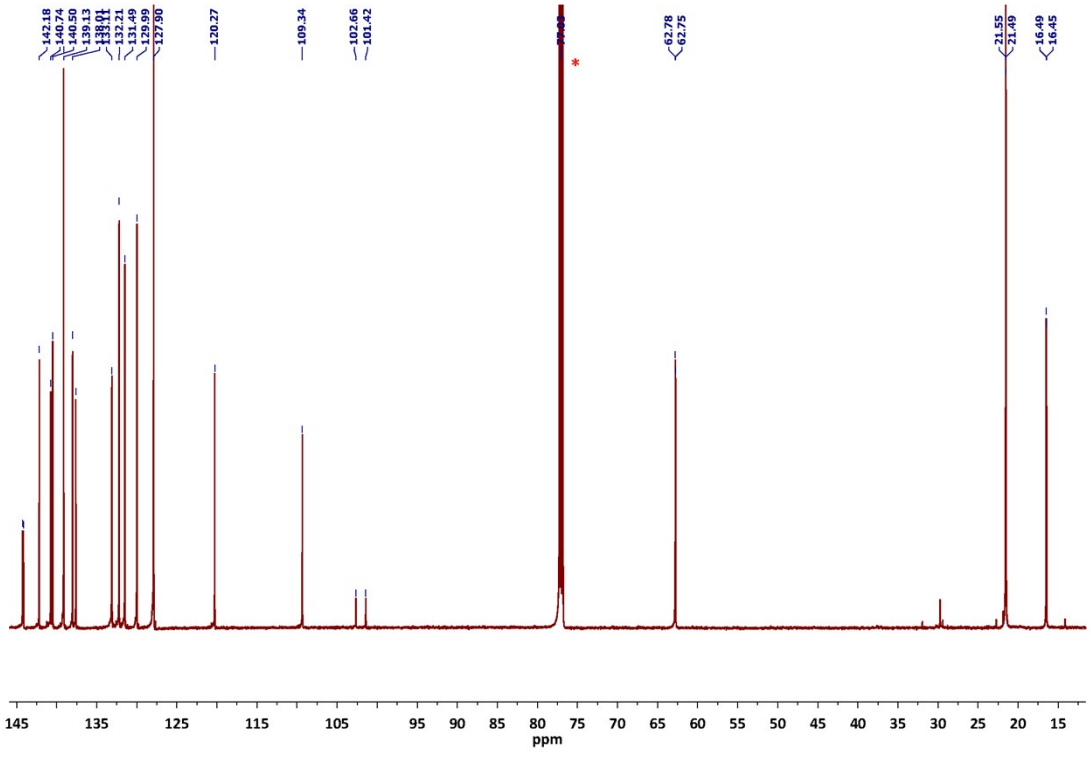


Figure S13. ^{13}C NMR spectrum of **PdDMesPP** in $CDCl_3$. Solvent peaks are indicated with * (δ_C 77.21 ppm – $CDCl_3$).

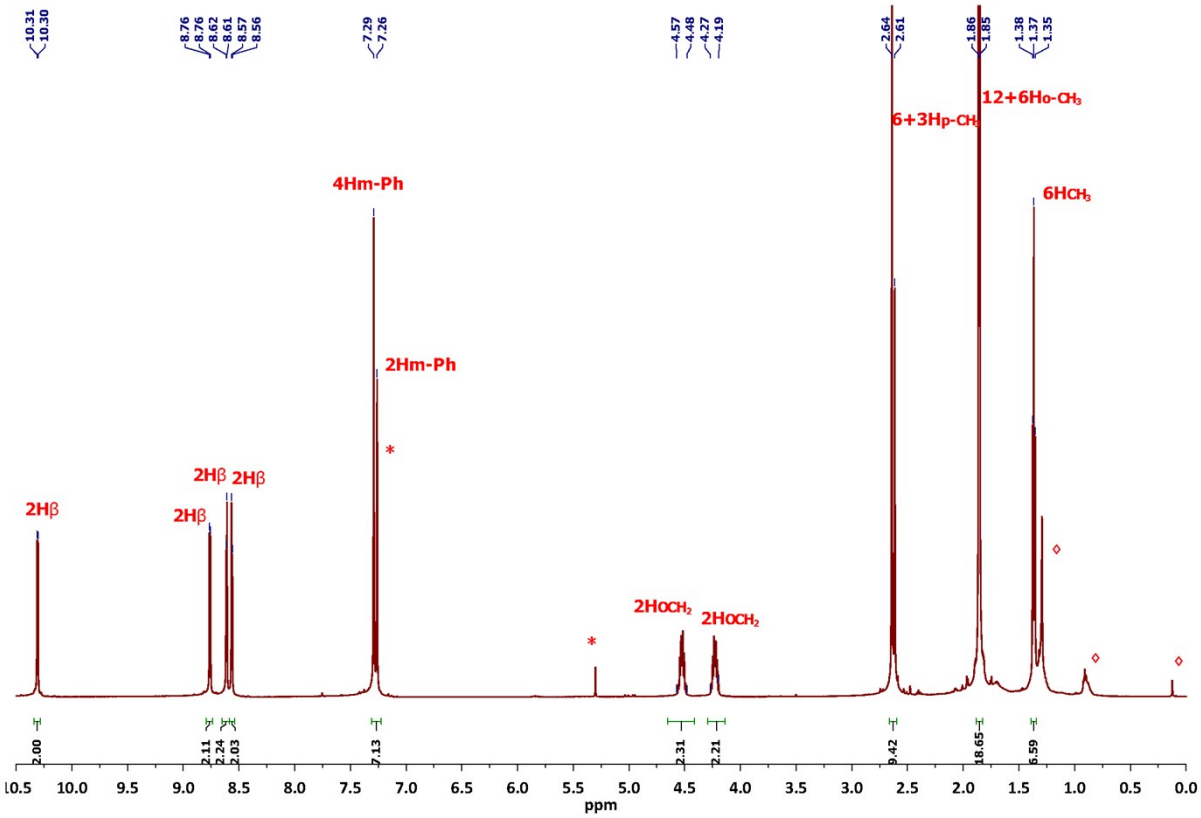


Figure S14. ^{1}H NMR spectrum of **PdTMesPP** in $CDCl_3$. Solvent peaks are indicated with * (δ_H 7.38 ppm – $CHCl_3$, δ_H 5.31 ppm – CH_2Cl_2). Solvent impurity peaks are indicated with ◊.

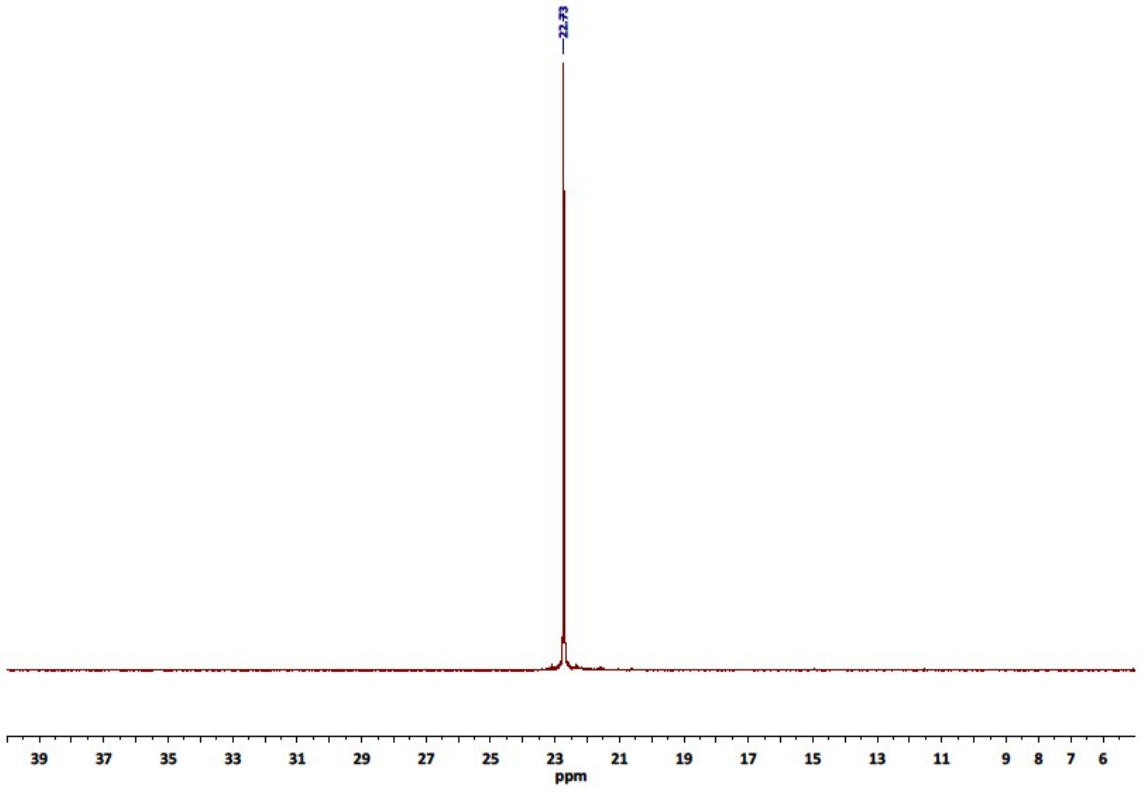


Figure S15. ^{31}P NMR spectrum of **PdTMesPP** in $CDCl_3$.

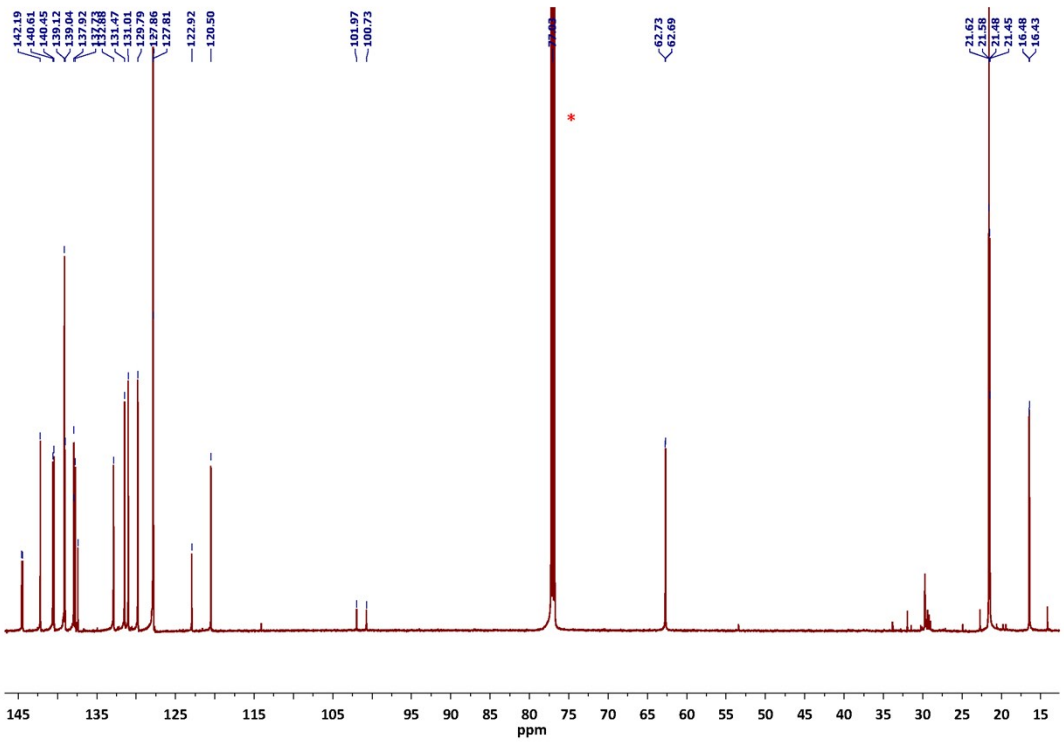


Figure S16. ^{13}C NMR spectrum of **PdTMesPP** in $CDCl_3$. Solvent peaks are indicated with * (δ_C 77.21 ppm – $CDCl_3$).

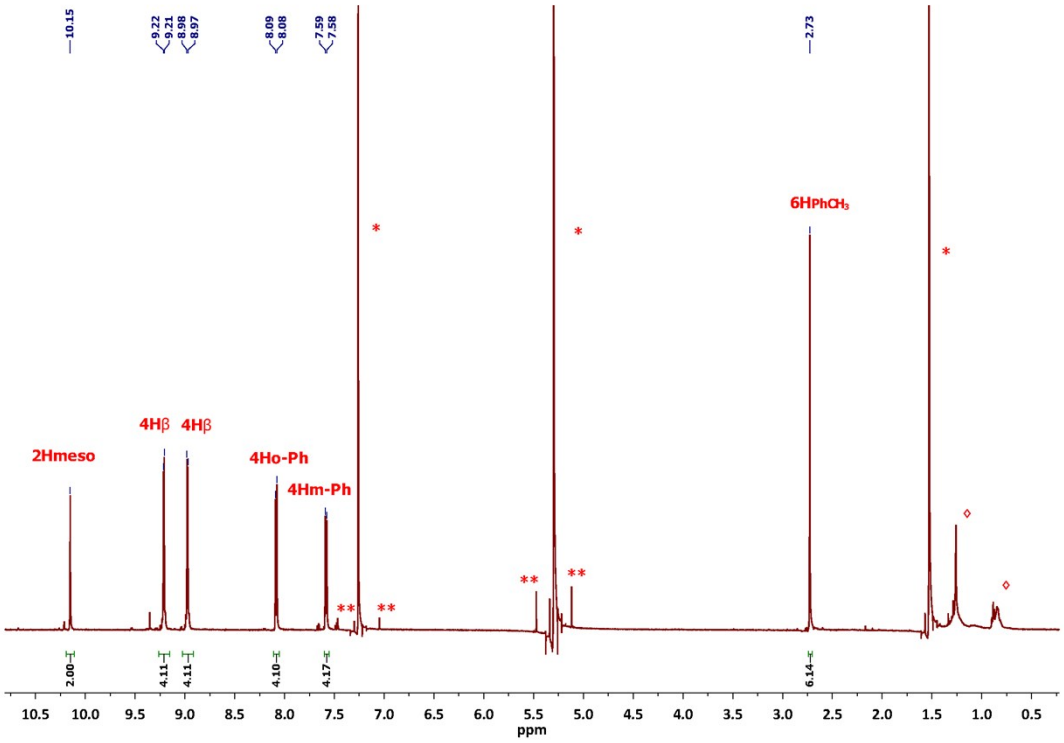


Figure S17. ^1H NMR spectrum of **PtDTolP** in $CDCl_3$. Solvent peaks are indicated with * (δ_H 7.38 ppm – $CHCl_3$, δ_H 5.31 ppm – CH_2Cl_2, δ_H 1.56 ppm –DOH and H_2O). Solvent satellite peaks are indicated with**. Solvent impurity peaks are indicated with ◊.

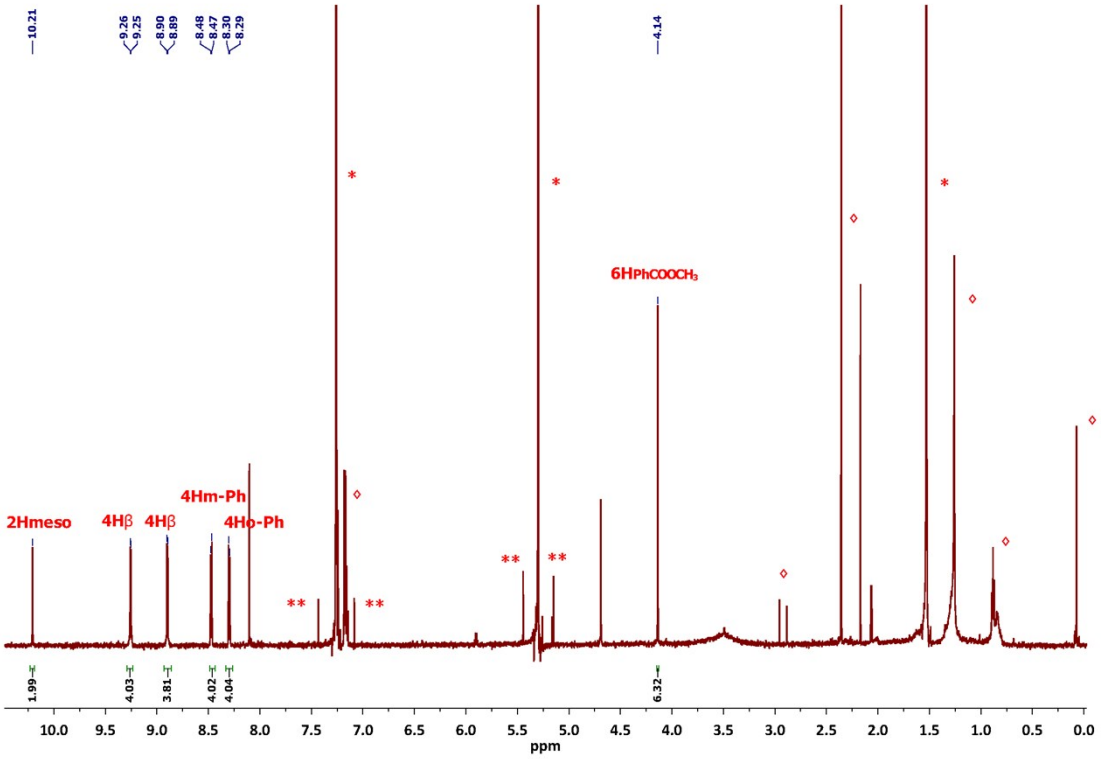


Figure S18. ^{1}H NMR spectrum of **PtD(CMP)P** in $CDCl_3$. Solvent peaks are indicated with * (δ_H 7.38 ppm – $CHCl_3$, δ_H 5.31 ppm – CH_2Cl_2, δ_H 1.56 ppm –DOH and H_2O). Solvent satellite peaks are indicated with**. Solvent impurity peaks are indicated with ◊.

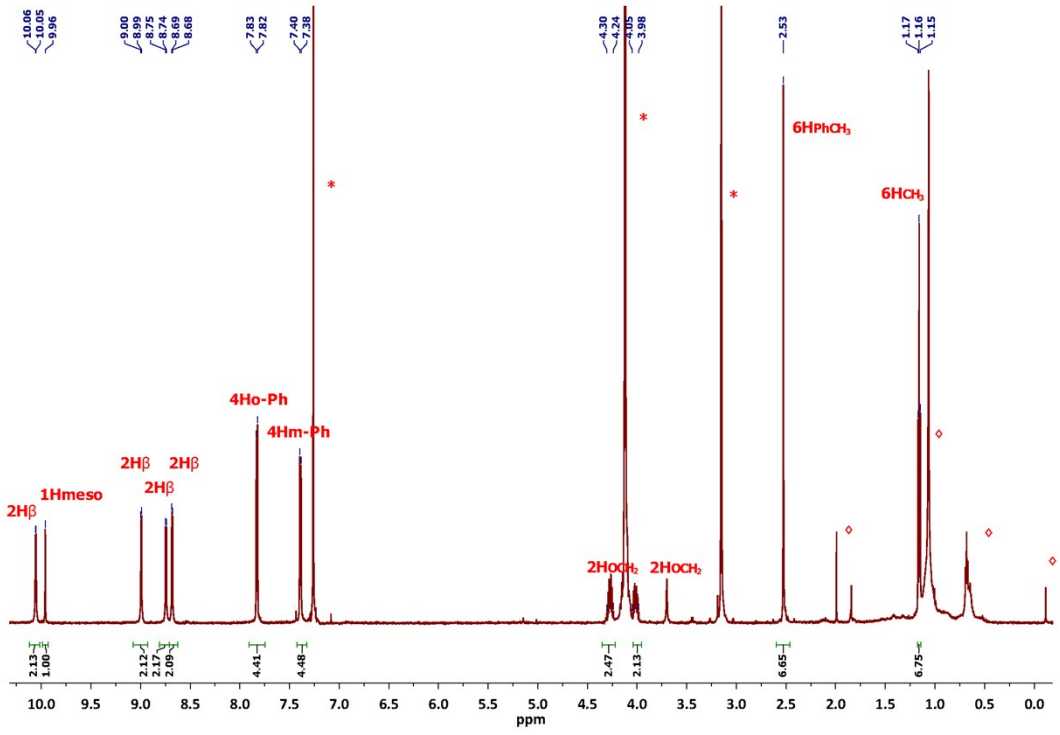


Figure S19. ^{1}H NMR spectrum of **PtDTolPP** in the mixture of $CDCl_3/CD_3OD$ (2:1, v/v). Solvent peaks are indicated with * (δ_H 7.38 ppm – $CHCl_3$, δ_H 4.06 ppm –DOH and H_2O, δ_H 3.33 ppm – CHD_2OD). Solvent impurity peaks are indicated with ◊.

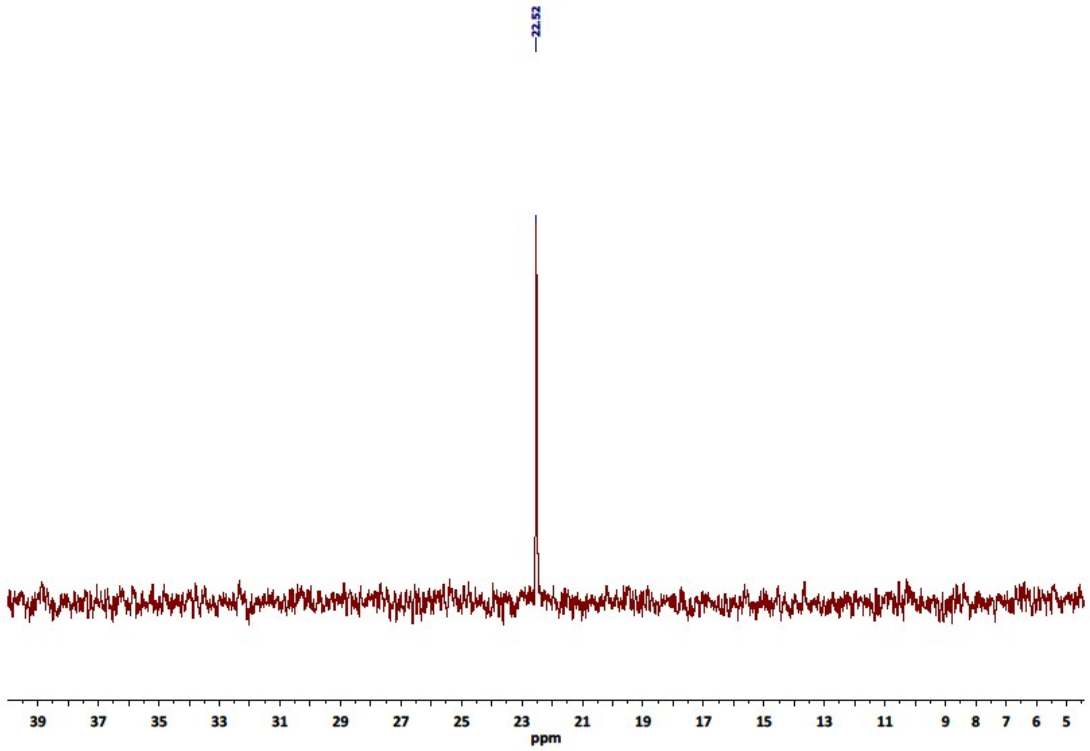


Figure S20. ^{31}P NMR spectrum of **PtDTolPP** in the mixture of $CDCl_3/CD_3OD$ (2:1, v/v).

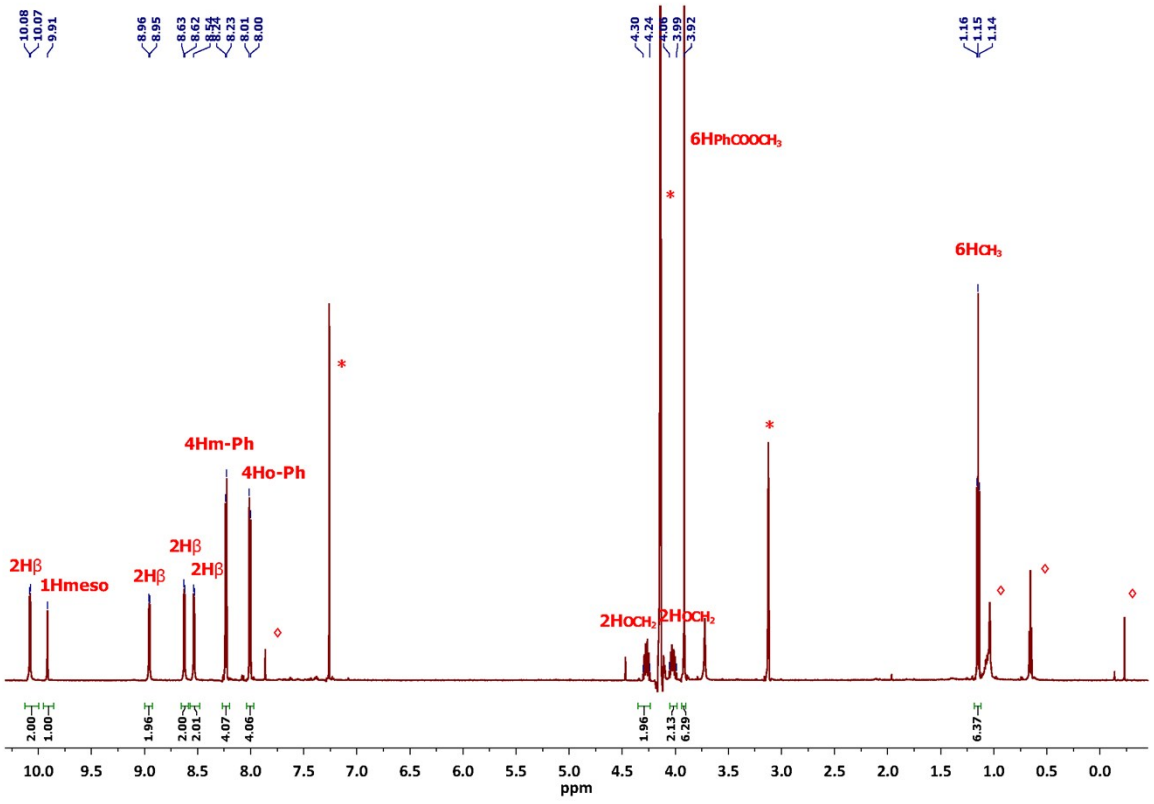


Figure S21. ^{1}H NMR spectrum of **PtD(CMP)PP** in the mixture of $CDCl_3/CD_3OD$ (2:1, v/v). Solvent peaks are indicated with * (δ_H 7.38 ppm – $CHCl_3$, δ_H 4.06 ppm –DOH and H_2O, δ_H 3.33 ppm – CHD_2OD). Solvent impurity peaks are indicated with ◊.

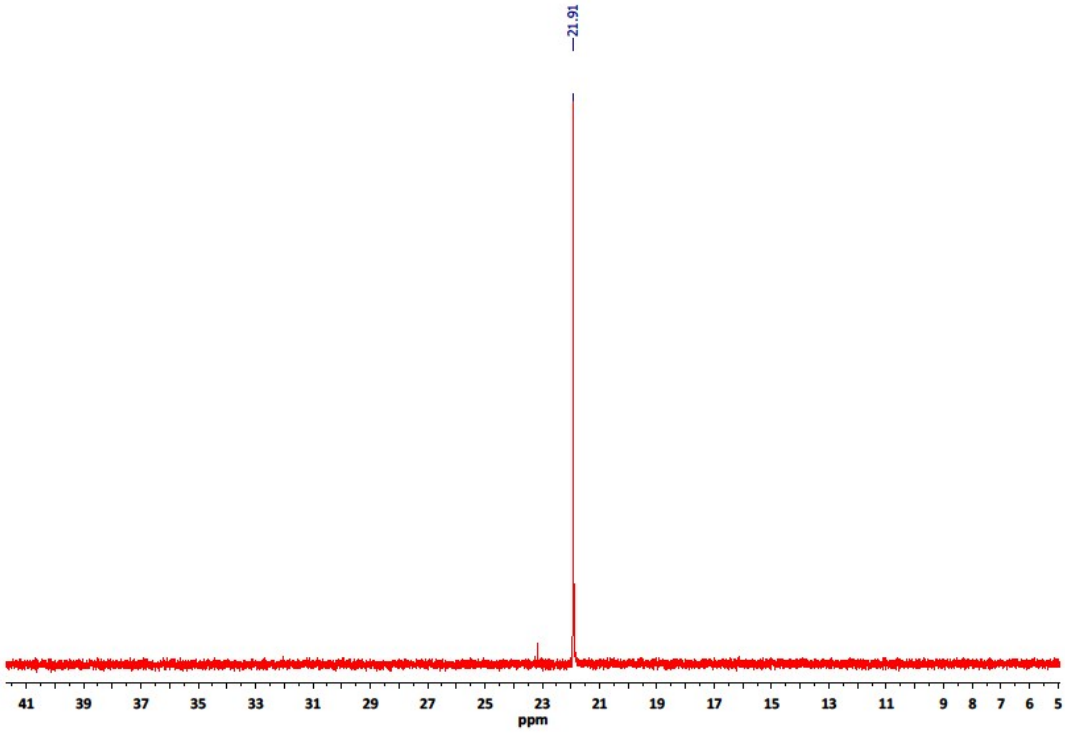


Figure S22. ^{31}P NMR spectrum of **PtD(CMP)PP** in the mixture of $CDCl_3/CD_3OD$ (2:1, v/v).

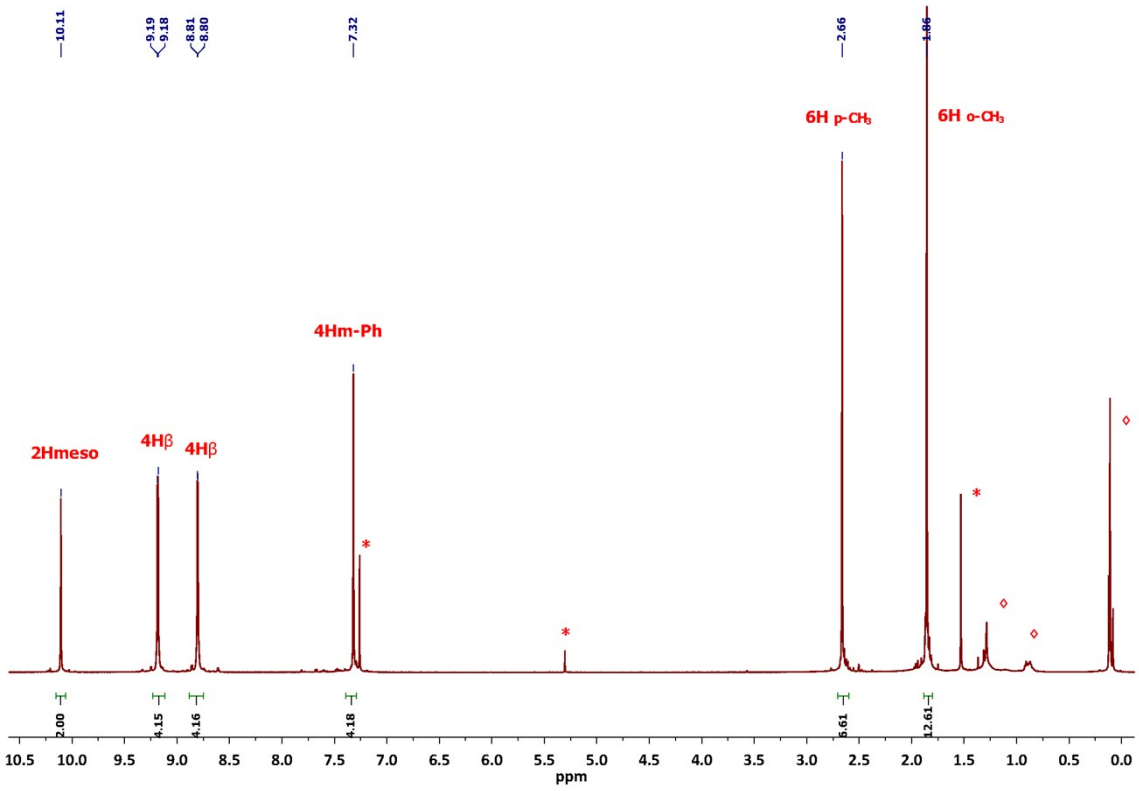


Figure S23. ^{1}H NMR spectrum of **PtDMesP** in $CDCl_3$. Solvent peaks are indicated with * (δ_H 7.38 ppm – $CHCl_3$, δ_H 5.31 ppm – CH_2Cl_2, δ_H 1.56 ppm –DOH and H_2O). Solvent impurity peaks are indicated with ◊.

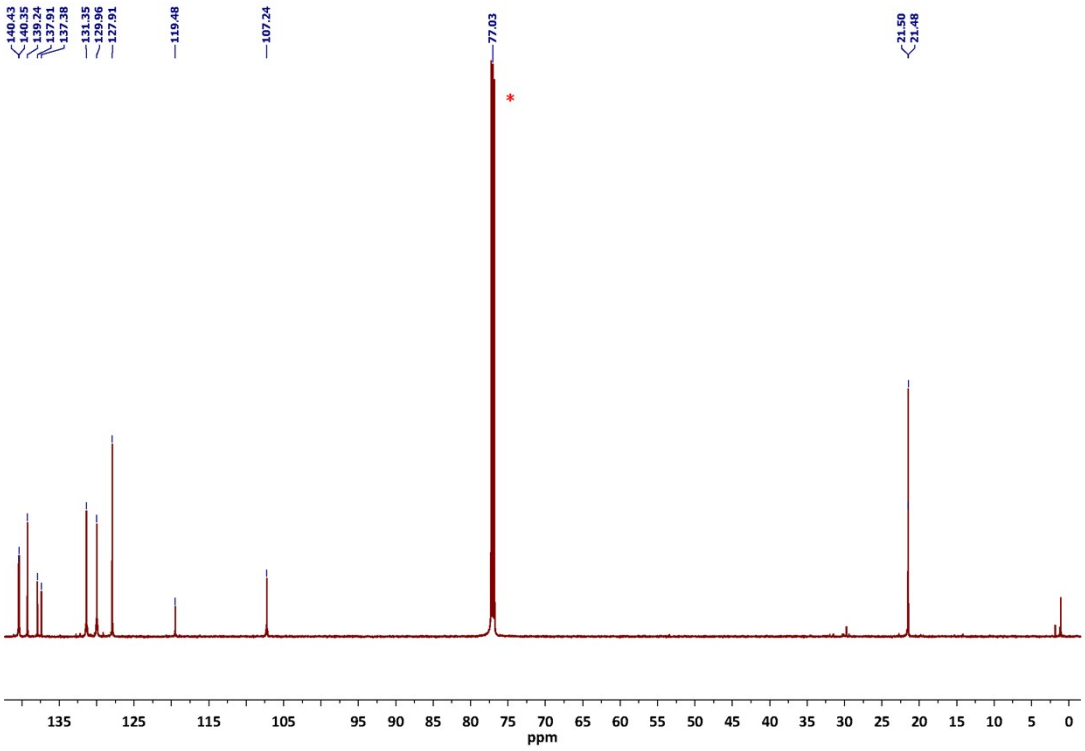


Figure S24. ^{13}C NMR spectrum of **PtDMesP** in $CDCl_3$. Solvent peaks are indicated with * (δ_C 77.21 ppm – $CDCl_3$).

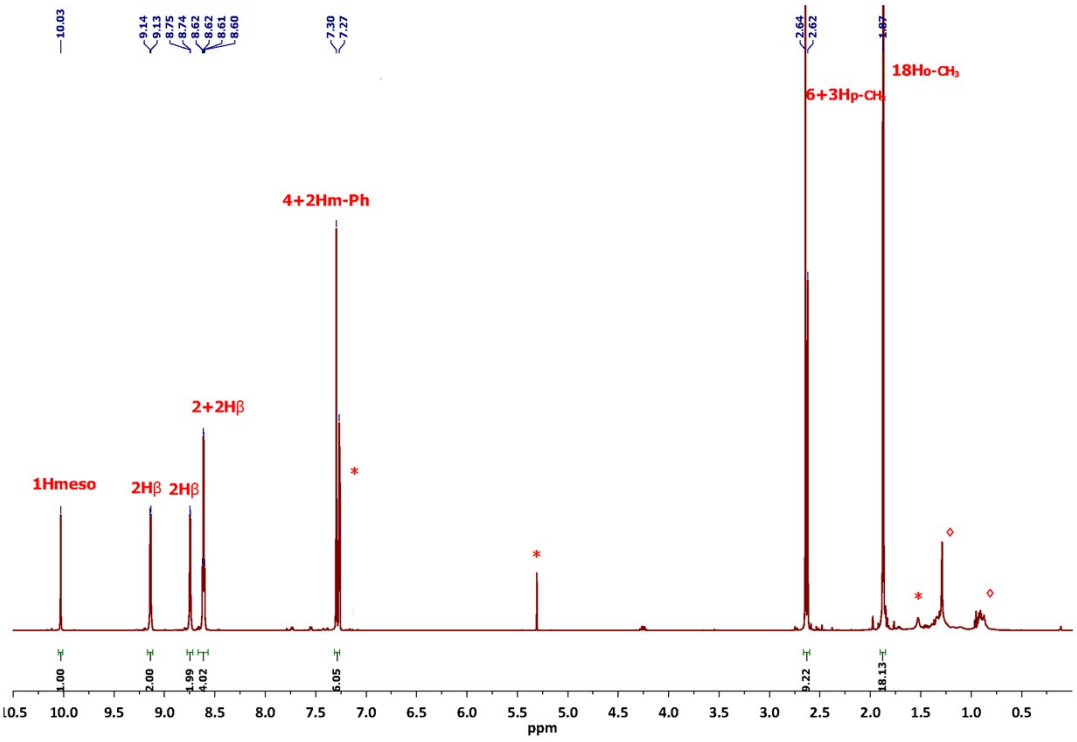


Figure S25. ^1H NMR spectrum of **PtTMesP** in $CDCl_3$. Solvent peaks are indicated with * (δ_H 7.38 ppm – $CHCl_3$, δ_H 5.31 ppm – CH_2Cl_2, δ_H 1.56 ppm –DOH and H_2O). Solvent impurity peaks are indicated with ◊.

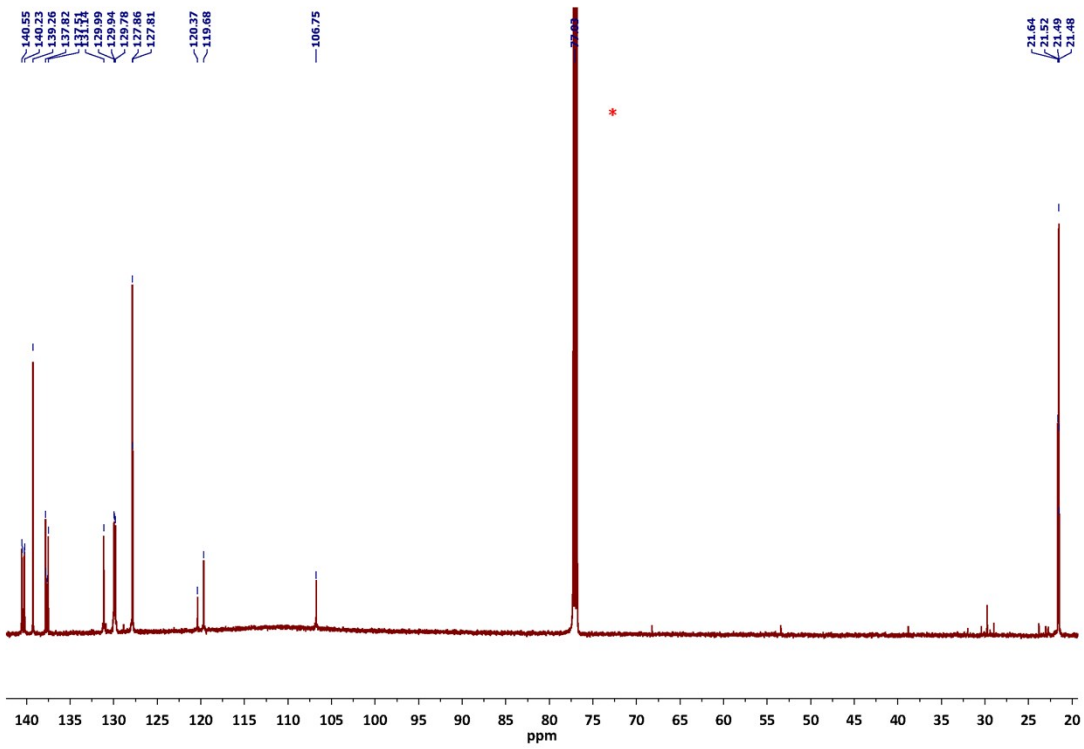


Figure S26. ^{13}C NMR spectrum of **PtTMesP** in $CDCl_3$. Solvent peaks are indicated with * (δ_C 77.21 ppm – $CDCl_3$).

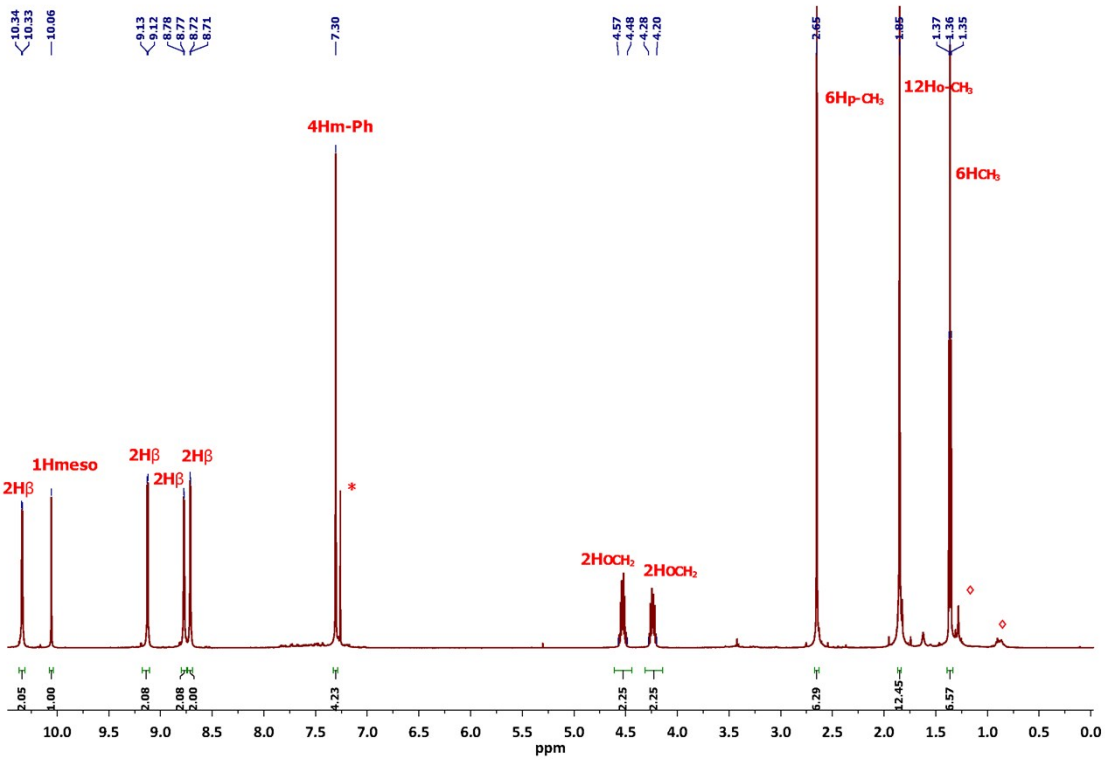


Figure S27. ^{1}H NMR spectrum of **PtDMesPP** in $CDCl_3$. Solvent peaks are indicated with * (δ_H 7.38 ppm – $CHCl_3$). Solvent impurity peaks are indicated with ◊.

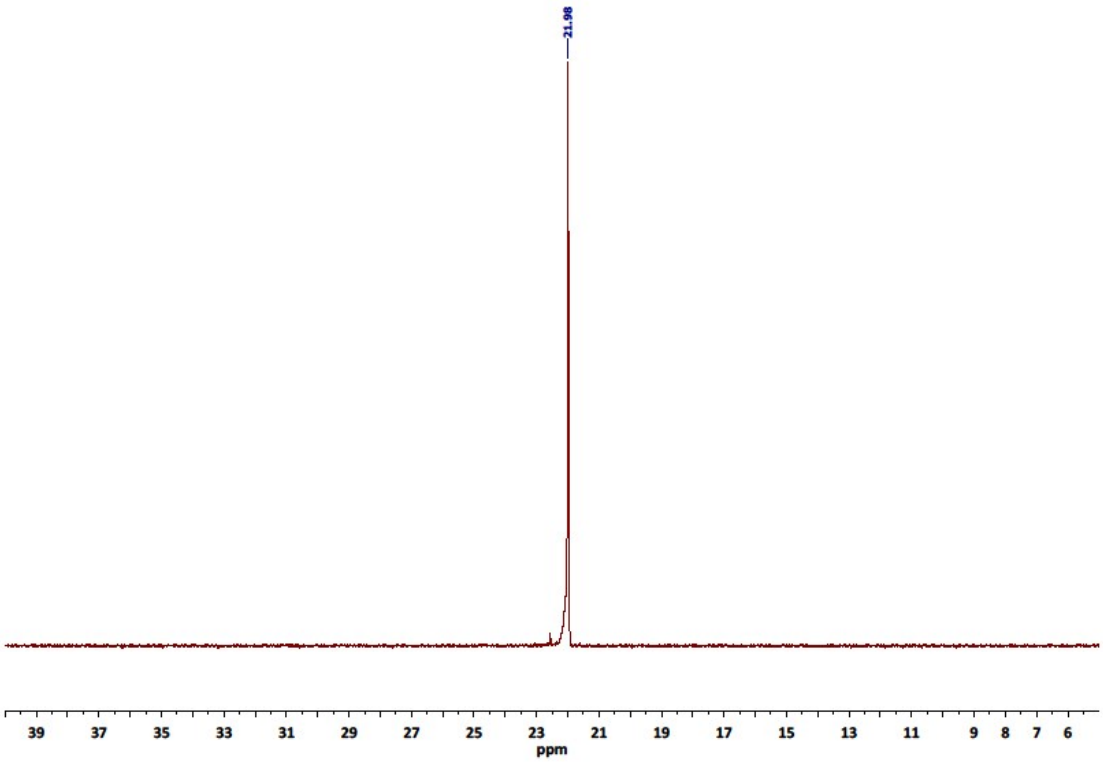


Figure S28. ^{31}P NMR spectrum of **PtDMesPP** in $CDCl_3$.

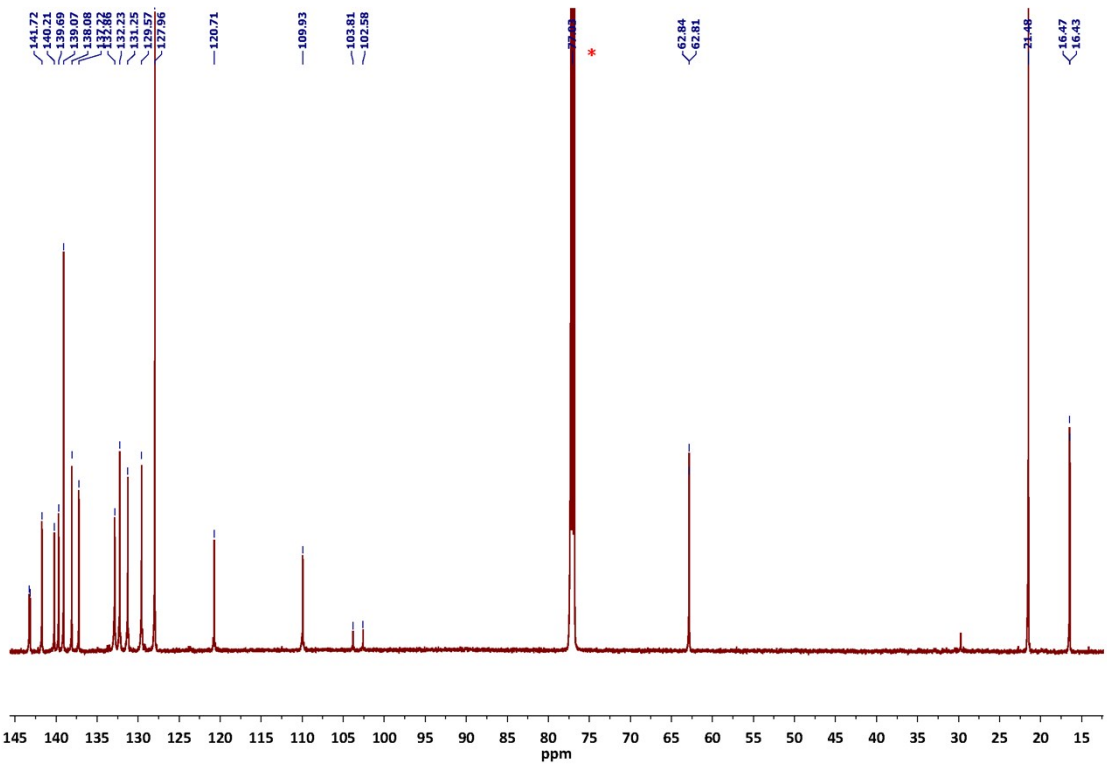


Figure S29. ^{13}C NMR spectrum of **PtDMesPP** in $CDCl_3$. Solvent peaks are indicated with * (δ_C 77.21 ppm – $CDCl_3$).

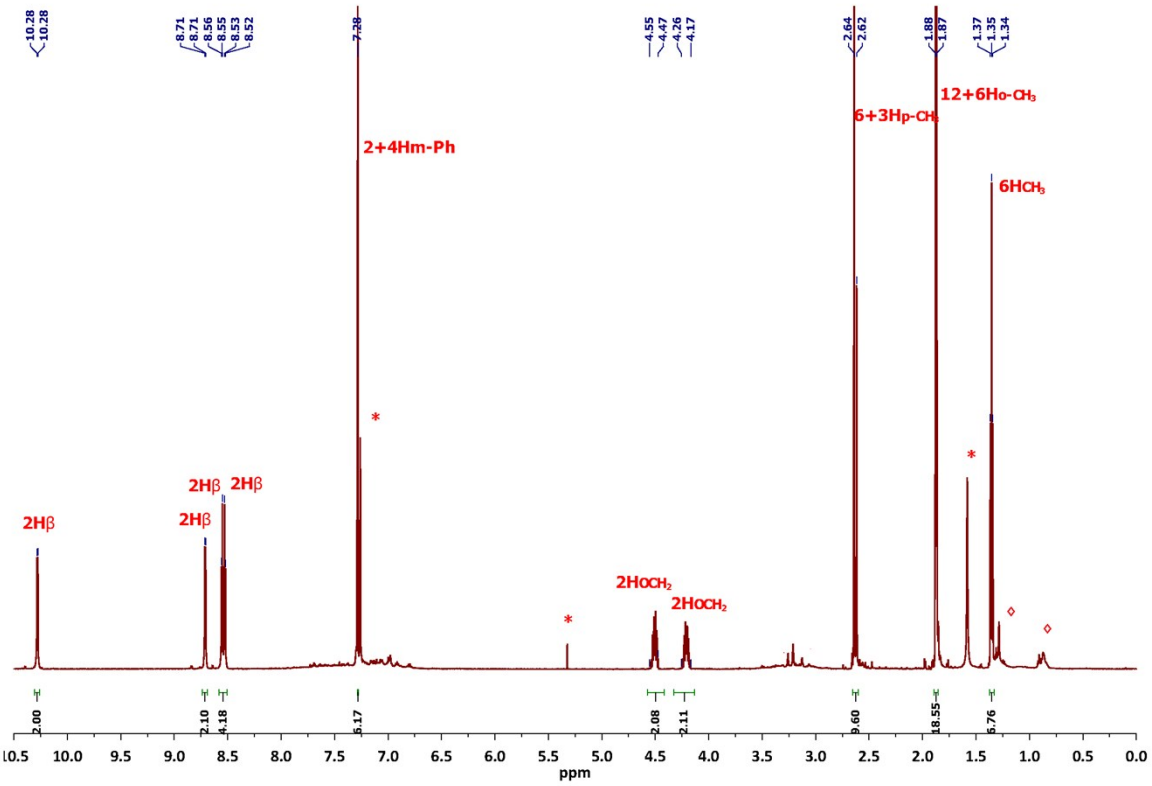


Figure S30. ^{1}H NMR spectrum of **PtTMesPP** in $CDCl_3$. Solvent peaks are indicated with * (δ_H 7.38 ppm – $CHCl_3$, δ_H 5.31 ppm – CH_2Cl_2, δ_H 1.56 ppm –DOH and H_2O). Solvent impurity peaks are indicated with ◊.

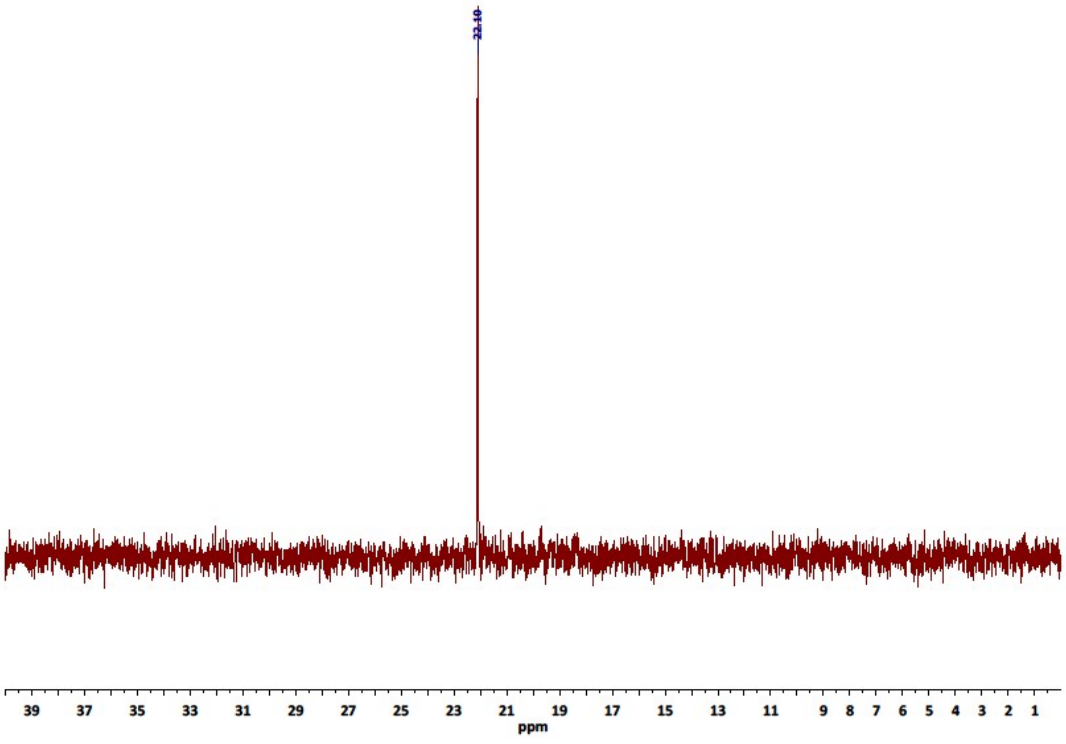


Figure S31. ^{31}P NMR spectrum of **PtTMesPP** in $CDCl_3$.

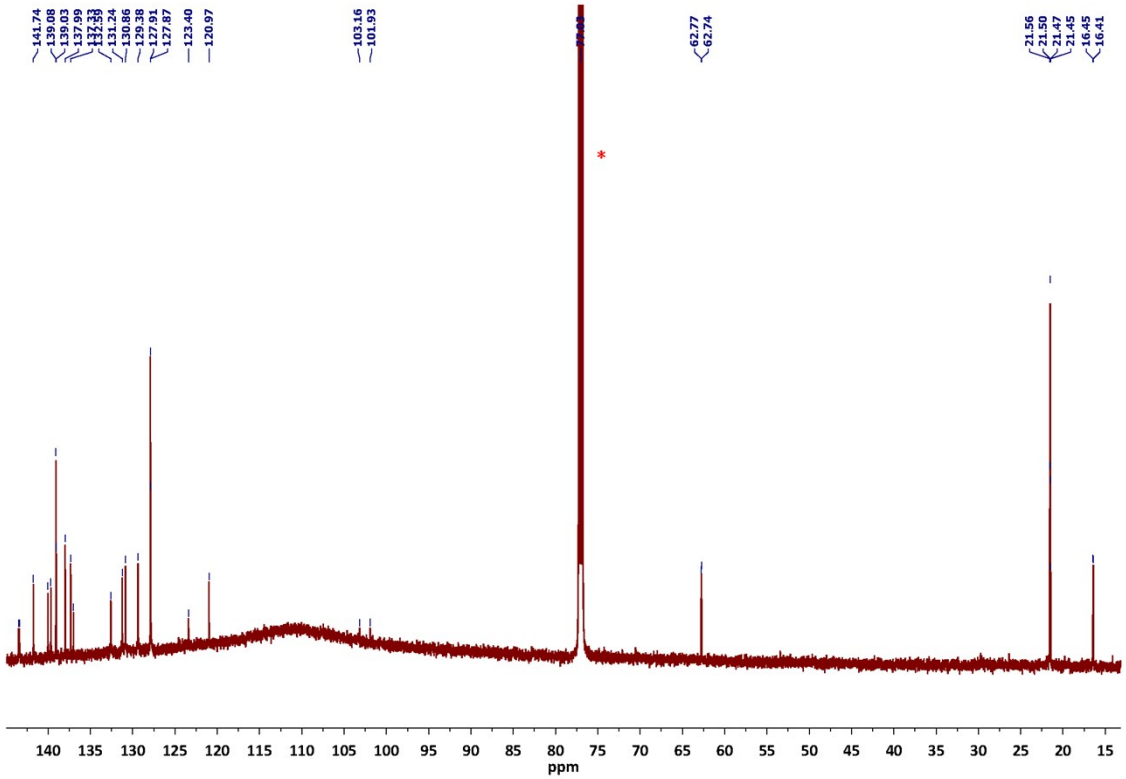


Figure S32. ^{13}C NMR spectrum of **PtTMesPP** in $CDCl_3$. Solvent peaks are indicated with * (δ_C 77.21 ppm – $CDCl_3$).

1.2. MALDI TOF mass spectra

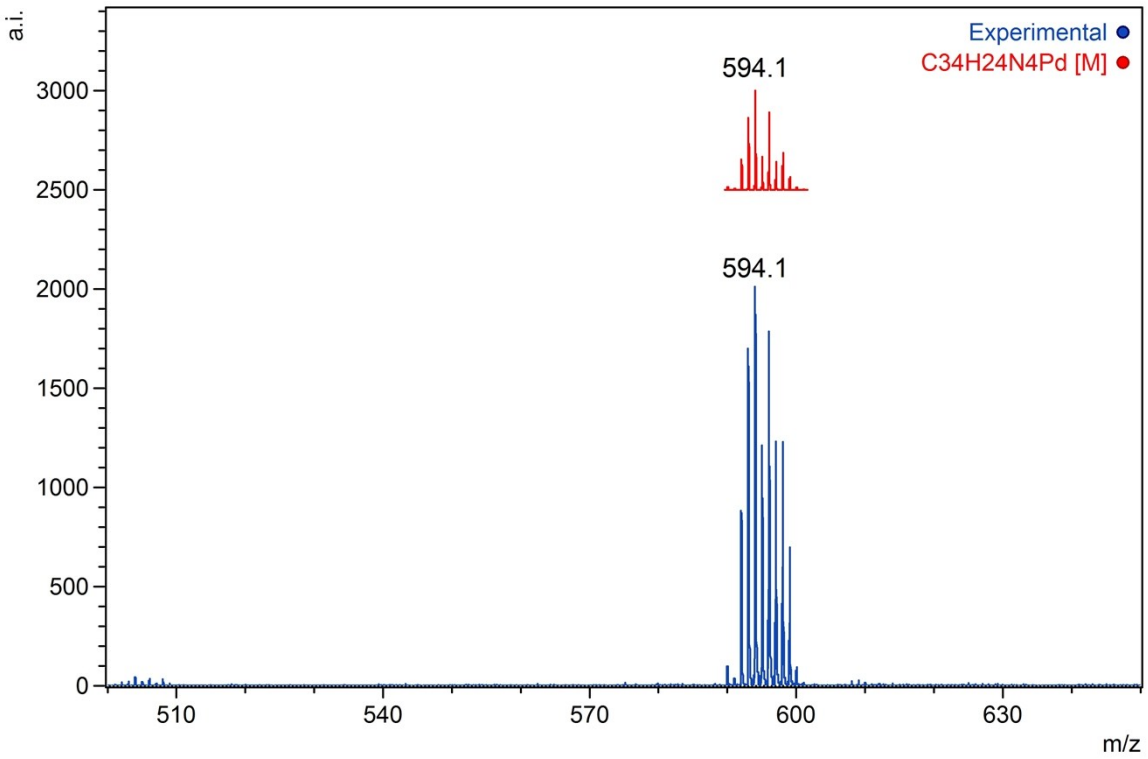


Figure S33. MALDI TOF mass spectrum of **PdDTolP**.

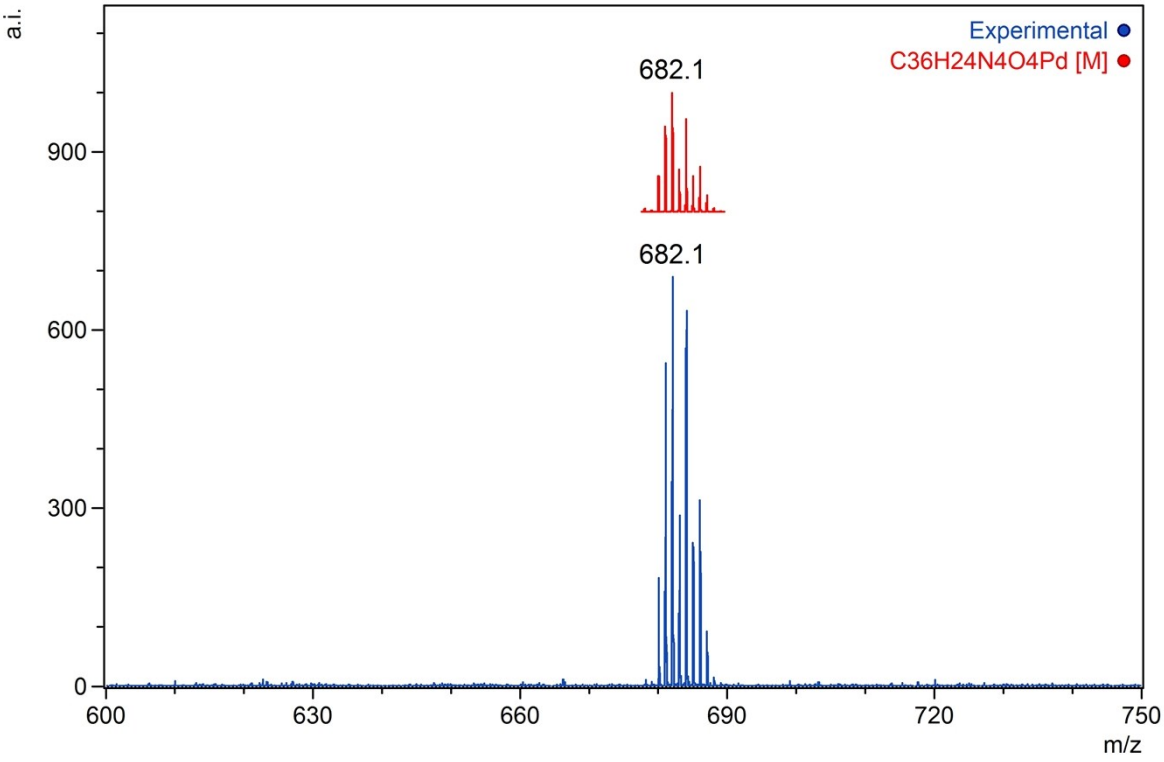


Figure S34. MALDI TOF mass spectrum of **PdD(CMP)P**.

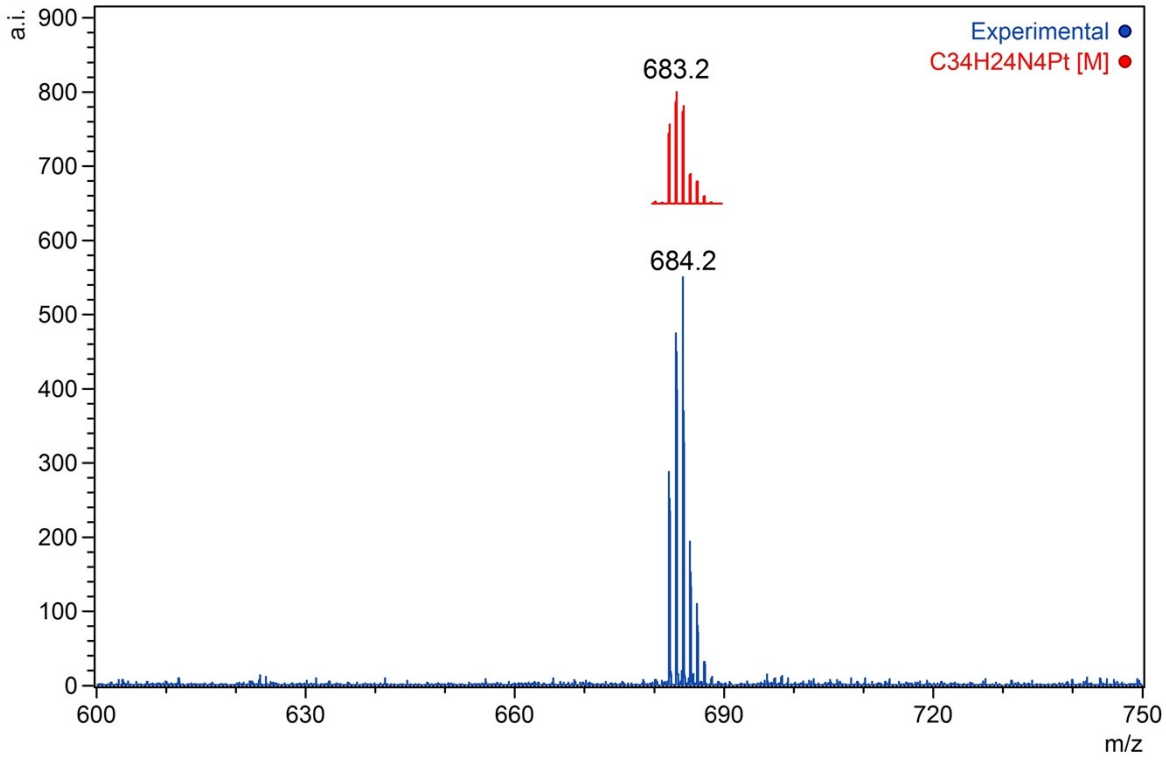


Figure S35. MALDI TOF mass spectrum of **PtDTolP**.

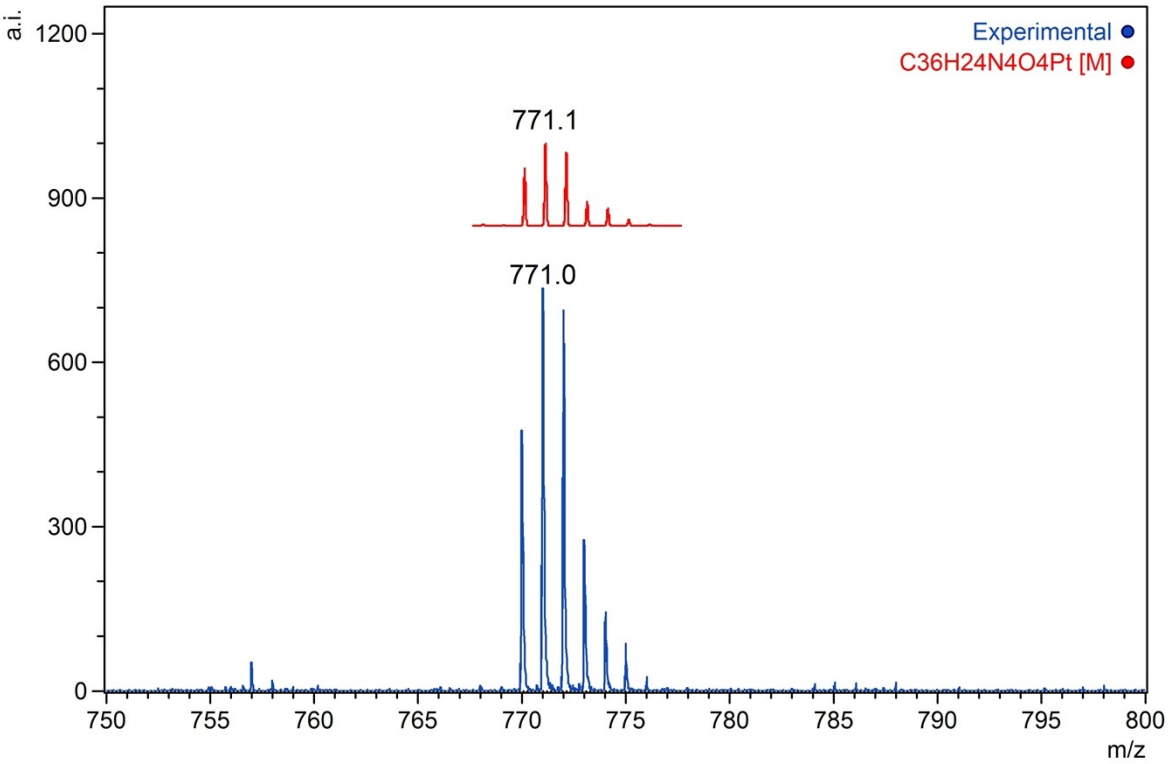


Figure S36. MALDI TOF mass spectrum of **PtD(CMP)P**.

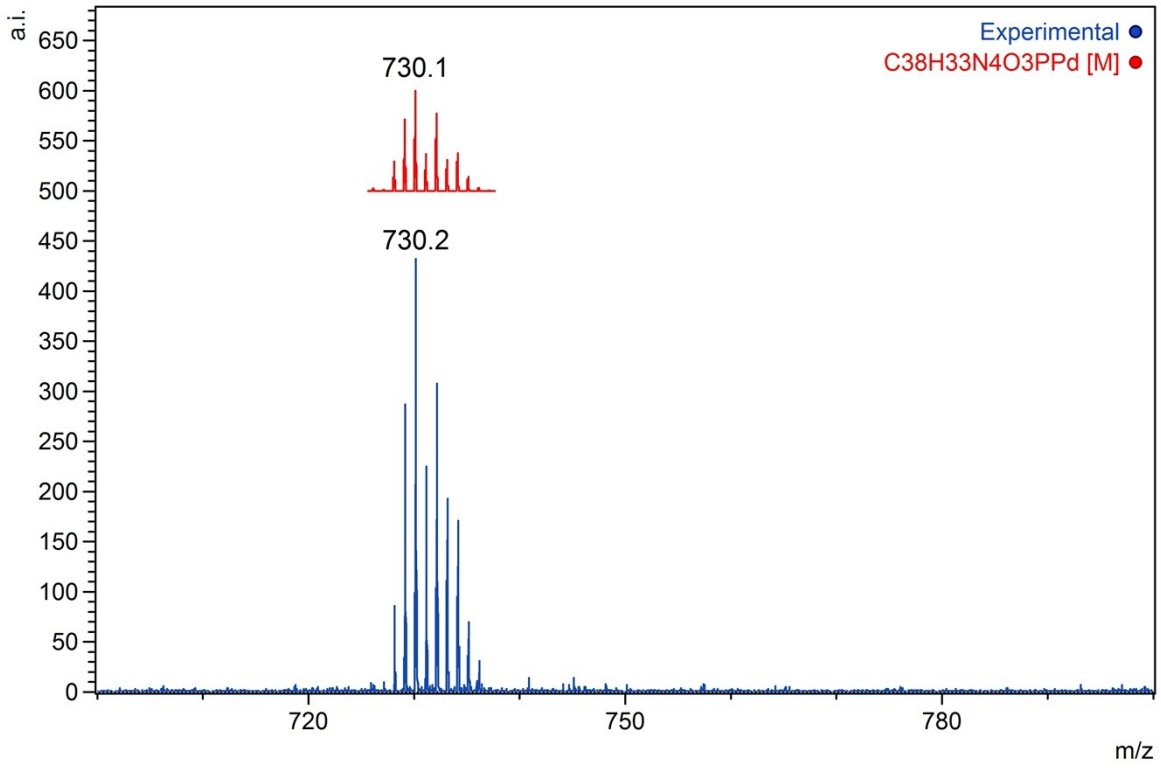


Figure S37. MALDI TOF mass spectrum of **PdDTolPP.**

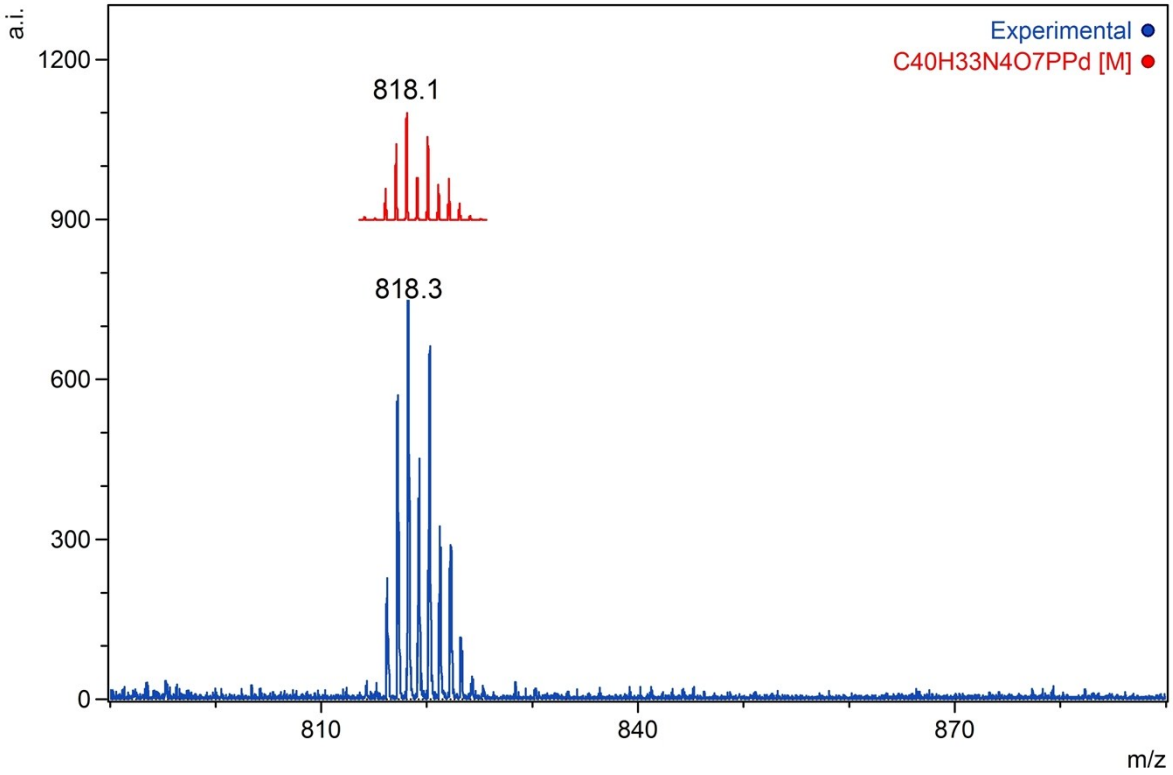


Figure S38. MALDI TOF mass spectrum of **PdD(CMP)PP**.

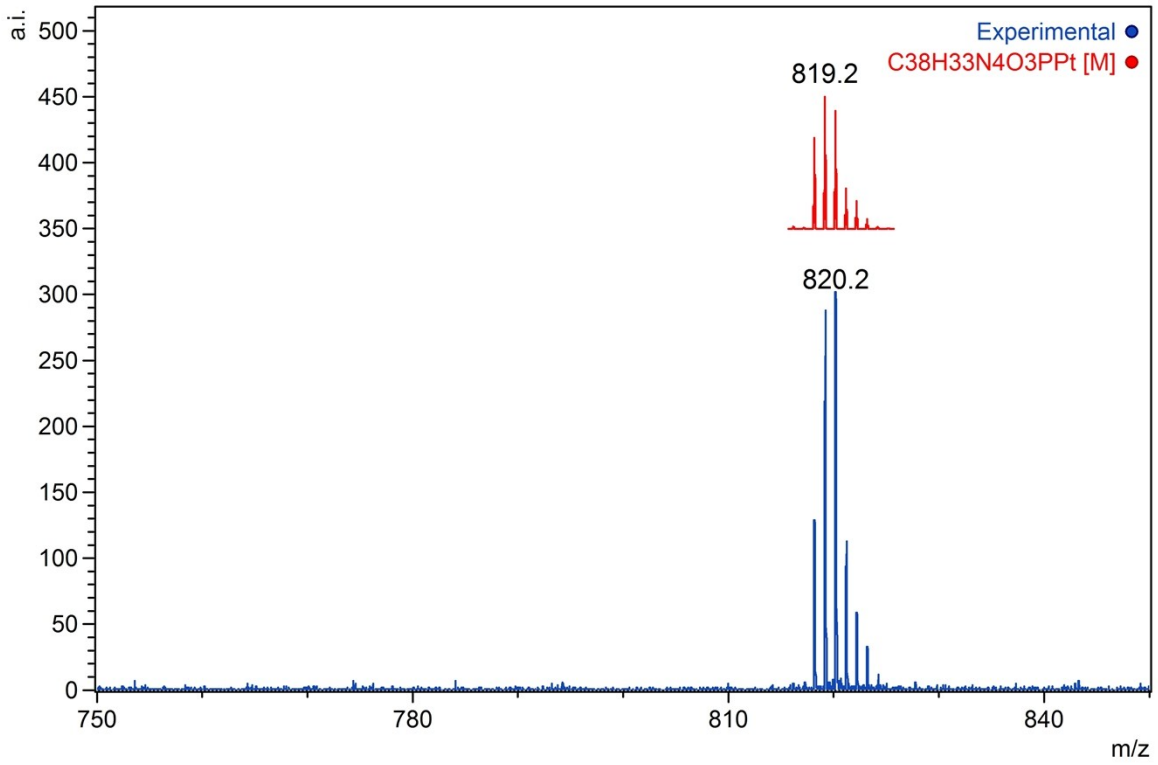


Figure S39. MALDI TOF mass spectrum of **PtDTolPP**.

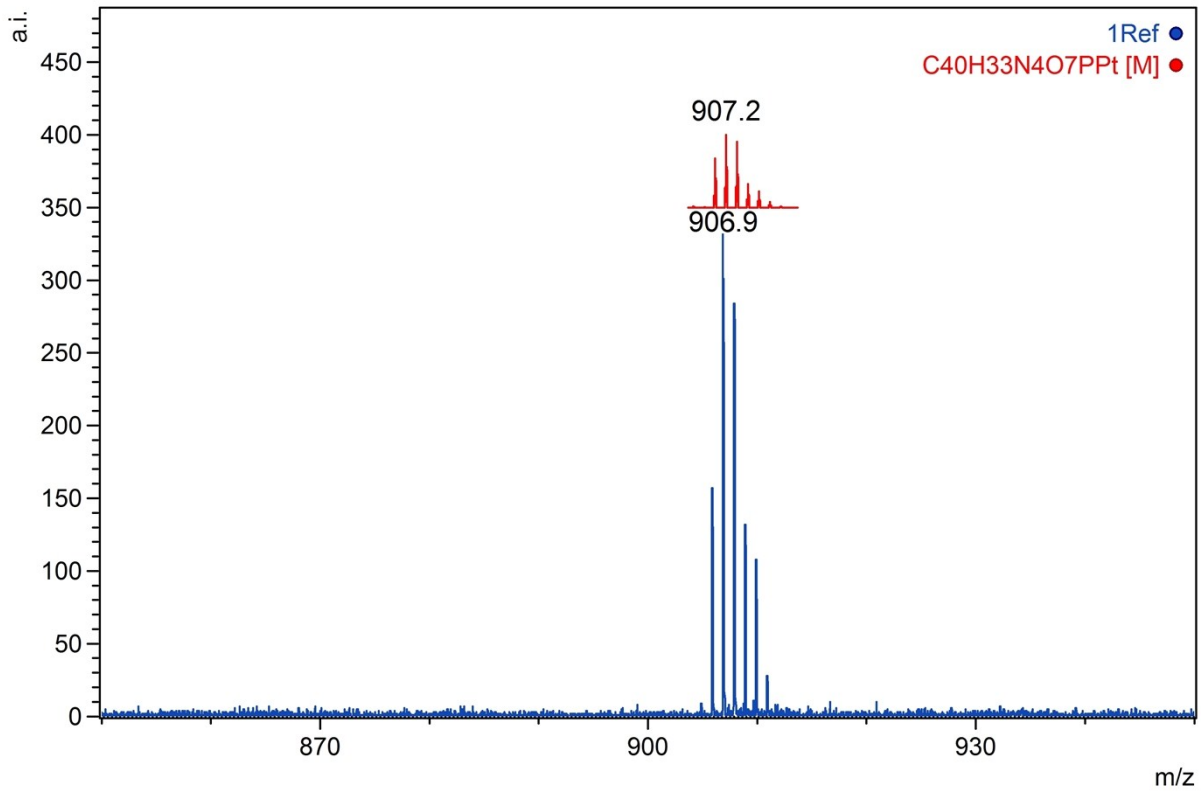


Figure S40. MALDI TOF mass spectrum of **PtD(CMP)PP**.

1.3. HRMS (ESI) spectra

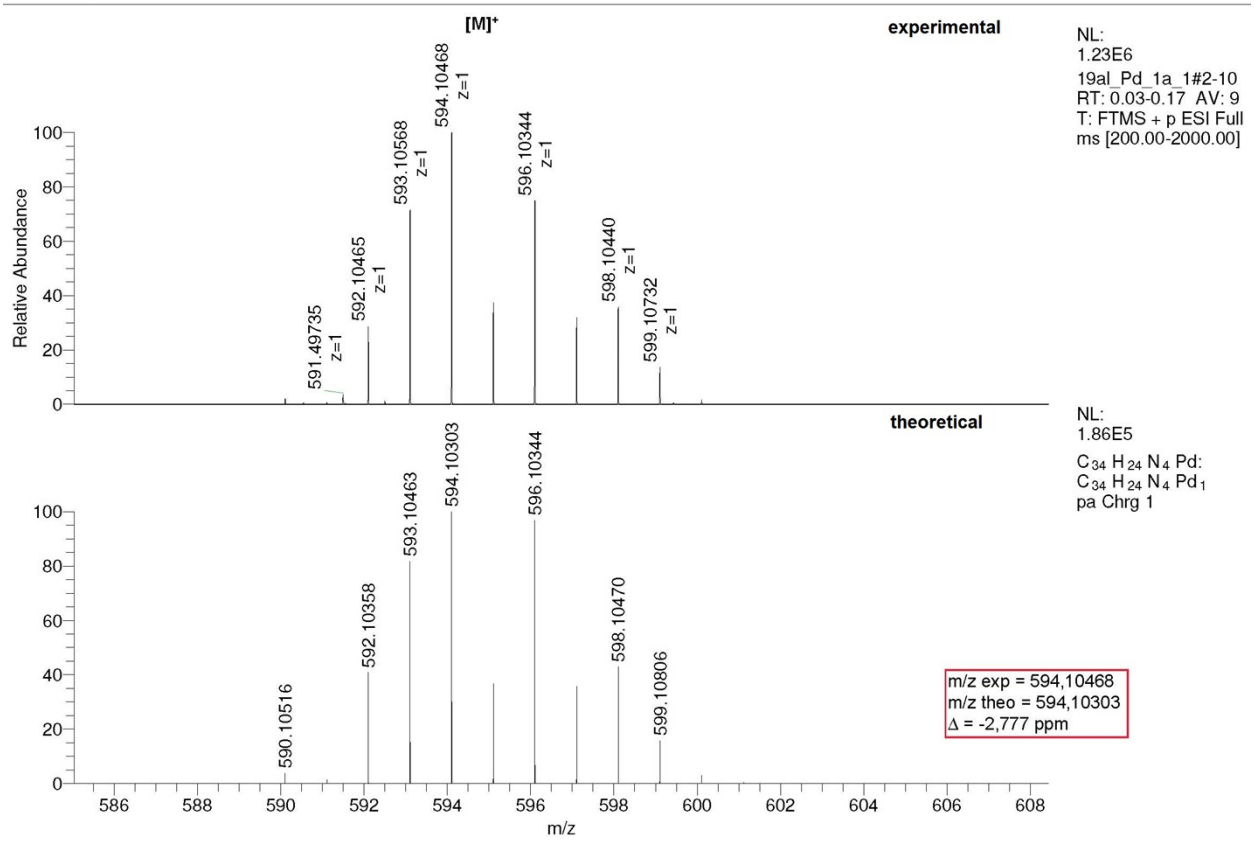


Figure S41. HRMS (ESI) spectrum of **PdDTolP**.

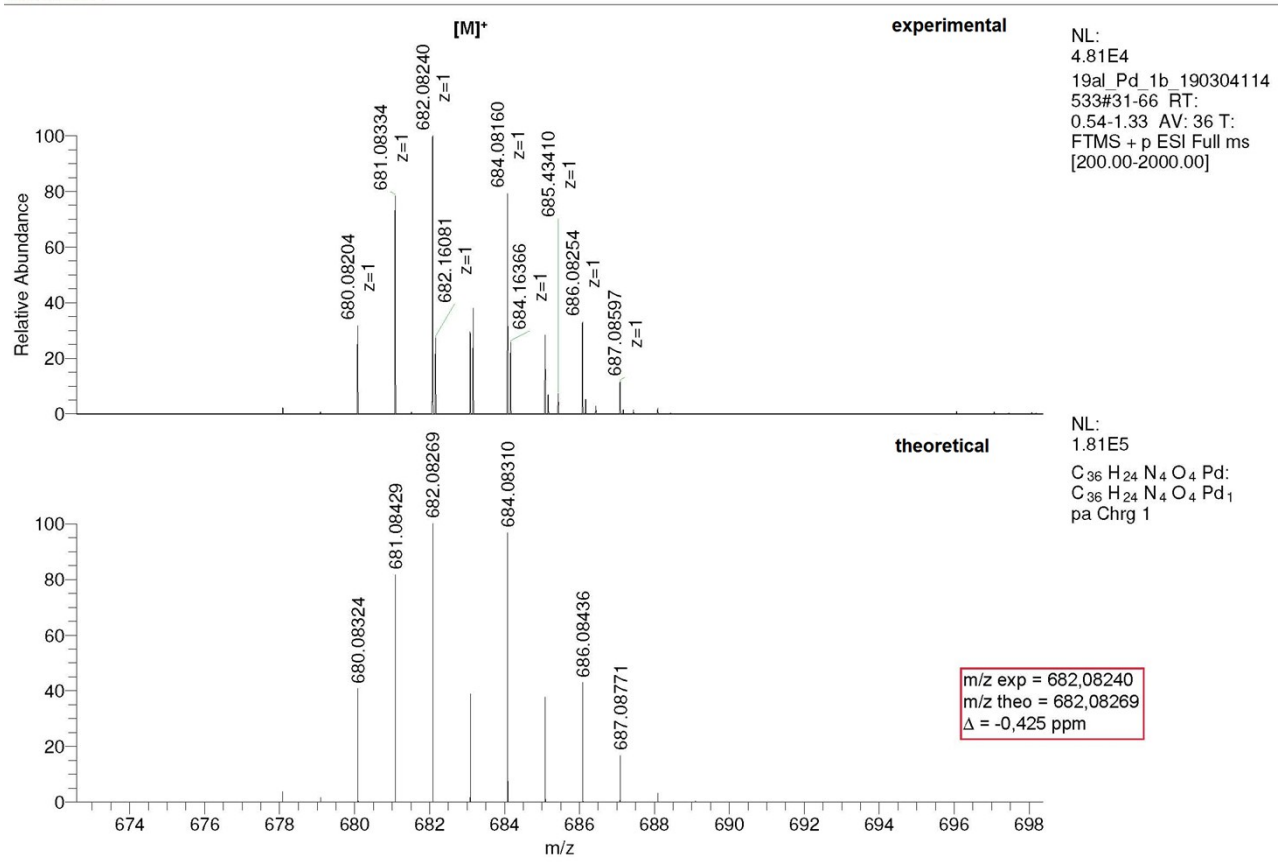


Figure S42. HRMS (ESI) spectrum of **PdD(CMP)P**.

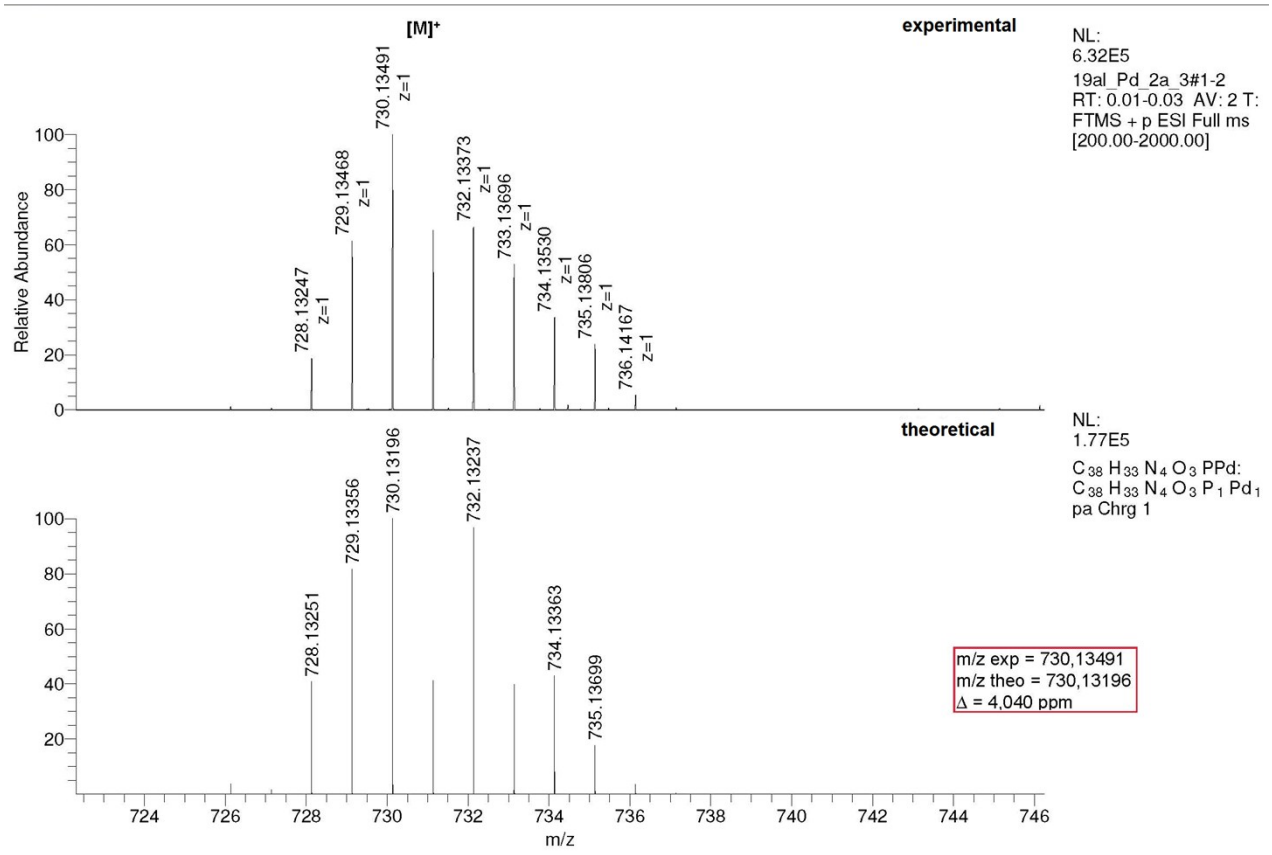


Figure S43. HRMS (ESI) spectrum of **PdDTolPP**.

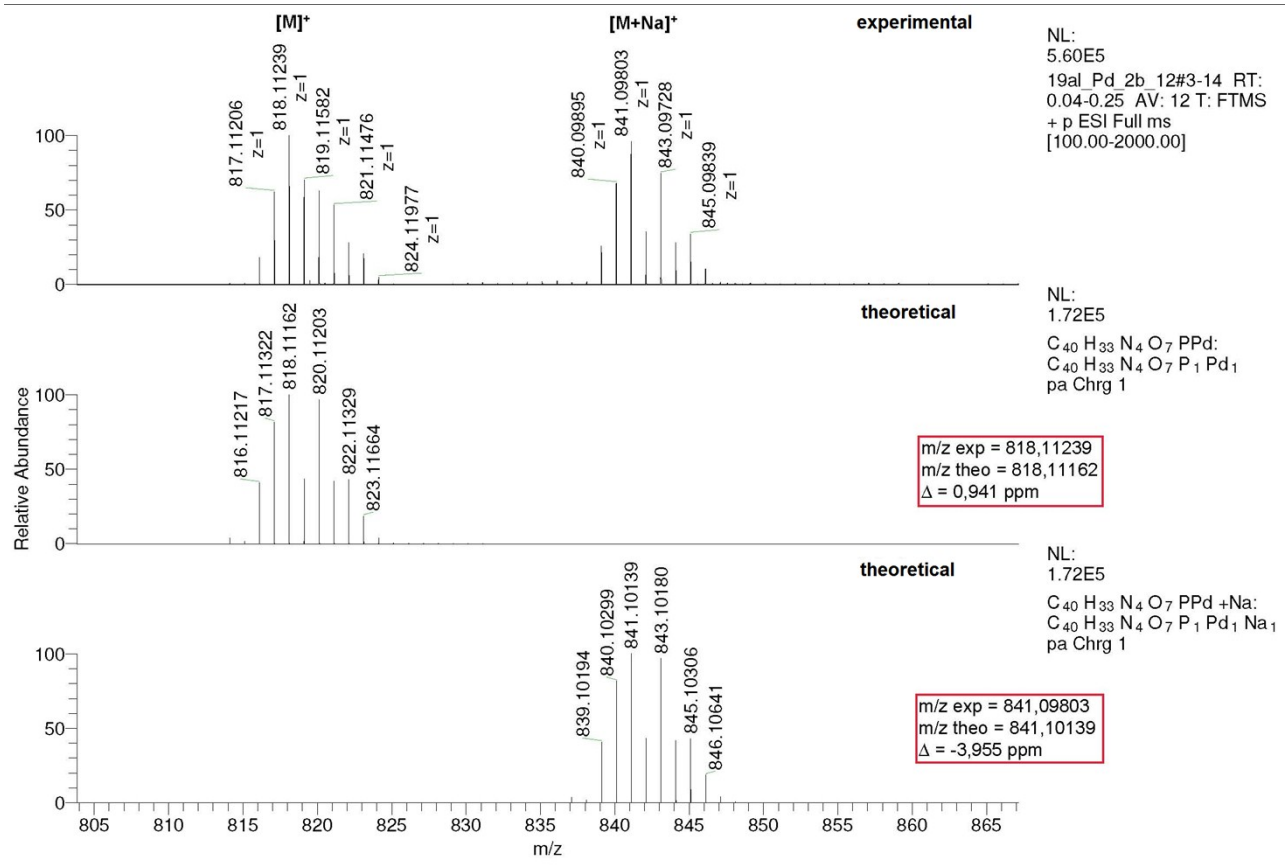


Figure S44. HRMS (ESI) spectrum of **PdD(CMP)PP**.

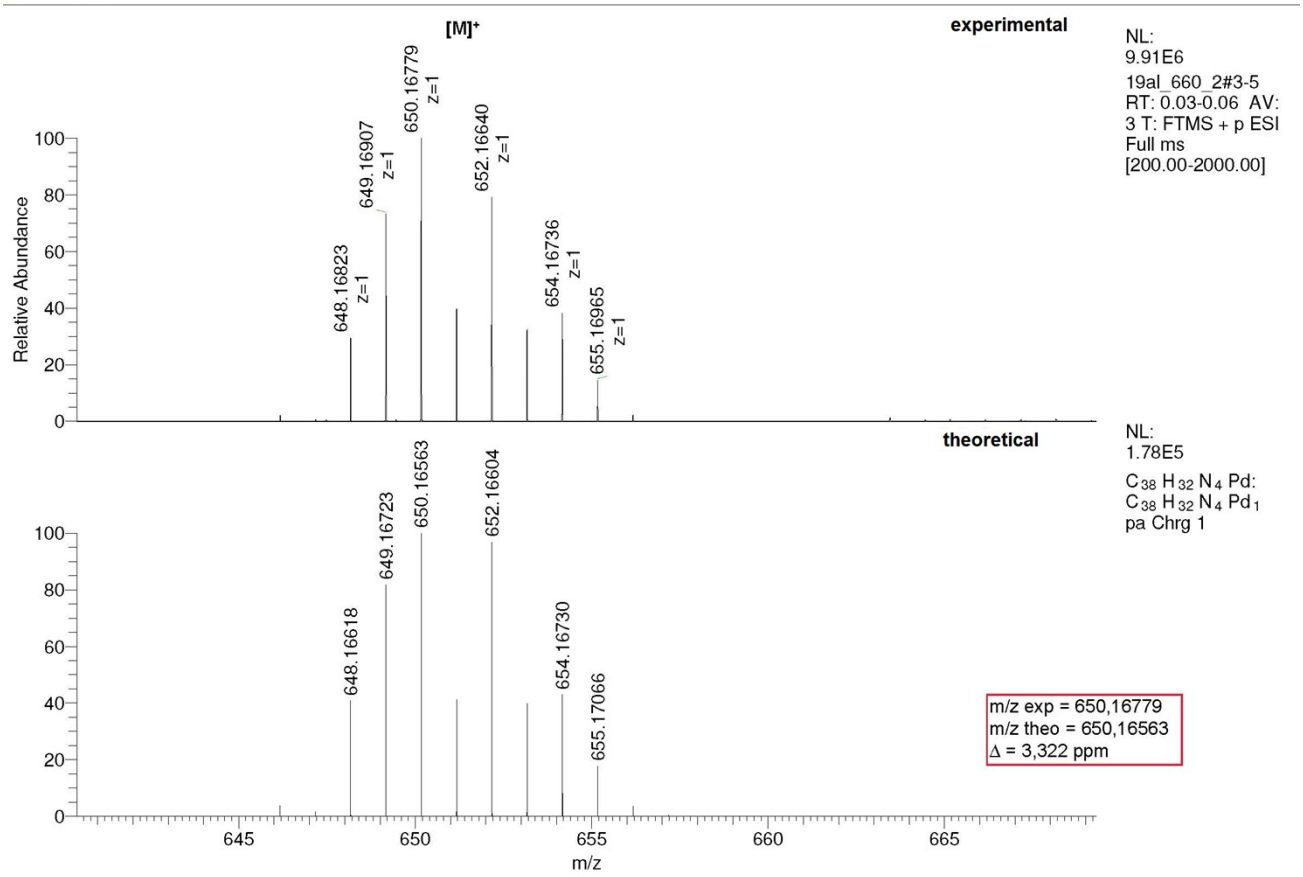


Figure S45. HRMS (ESI) spectrum of **PdDMesP**.

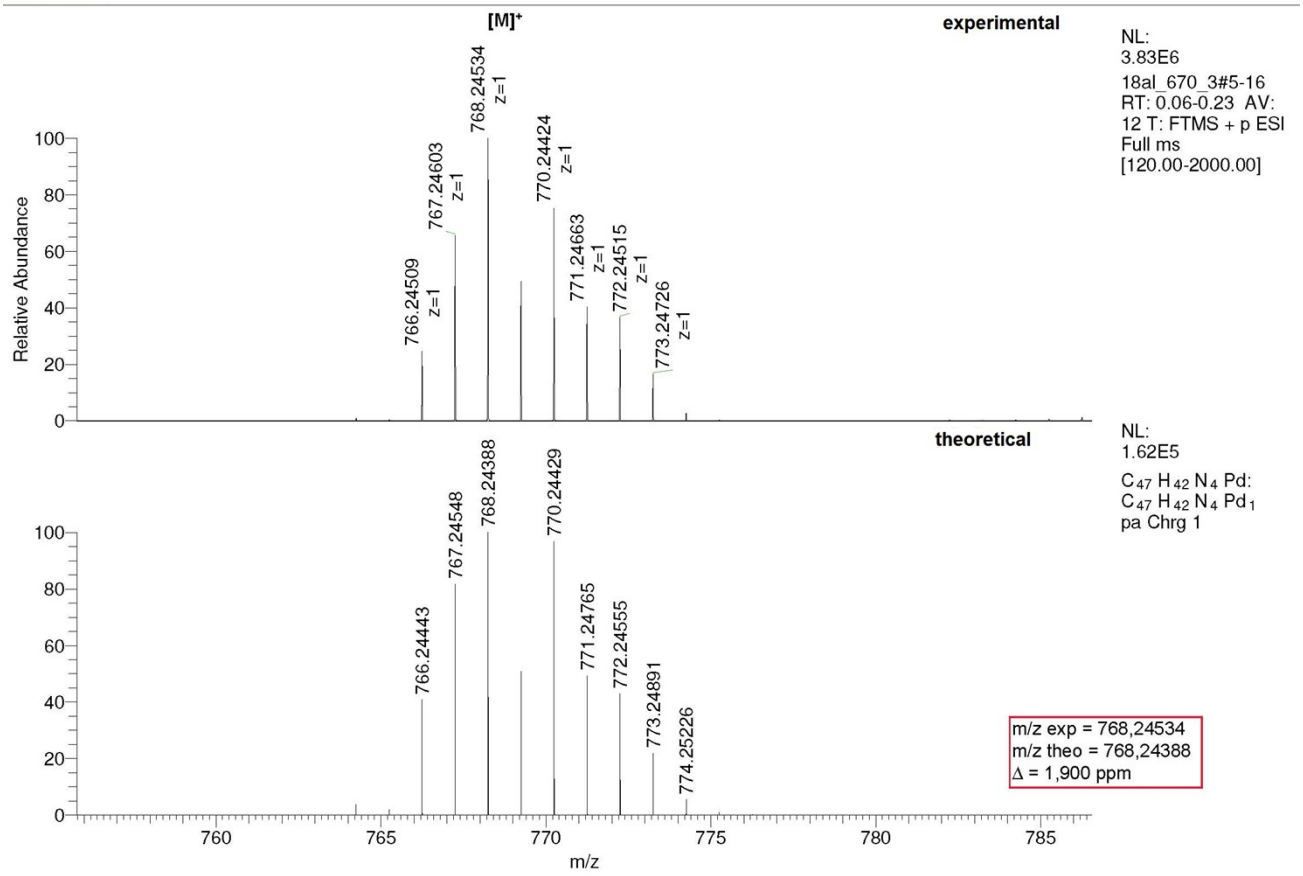


Figure S46. HRMS (ESI) spectrum of **PdTMesP**.

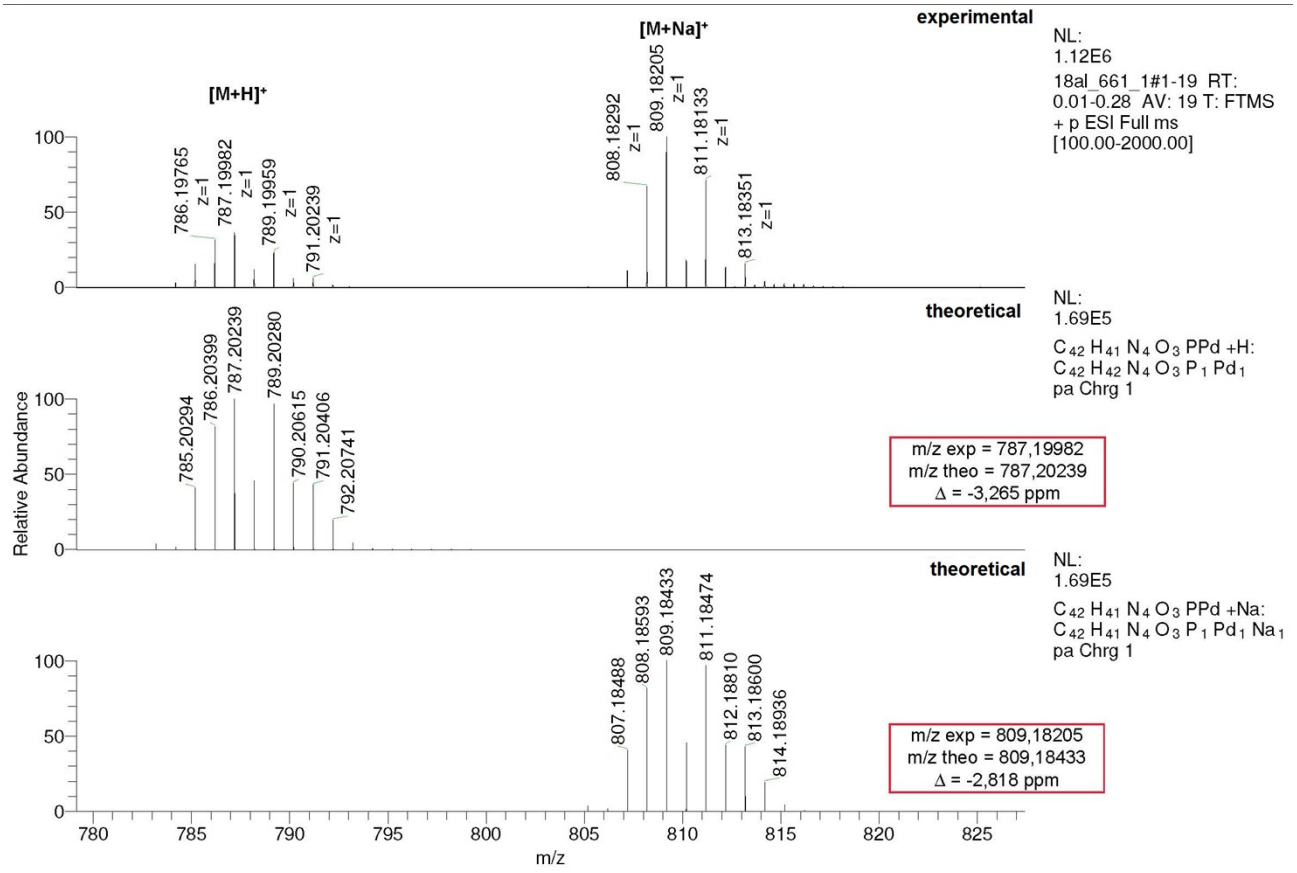


Figure S47. HRMS (ESI) spectrum of **PdDMesPP**.

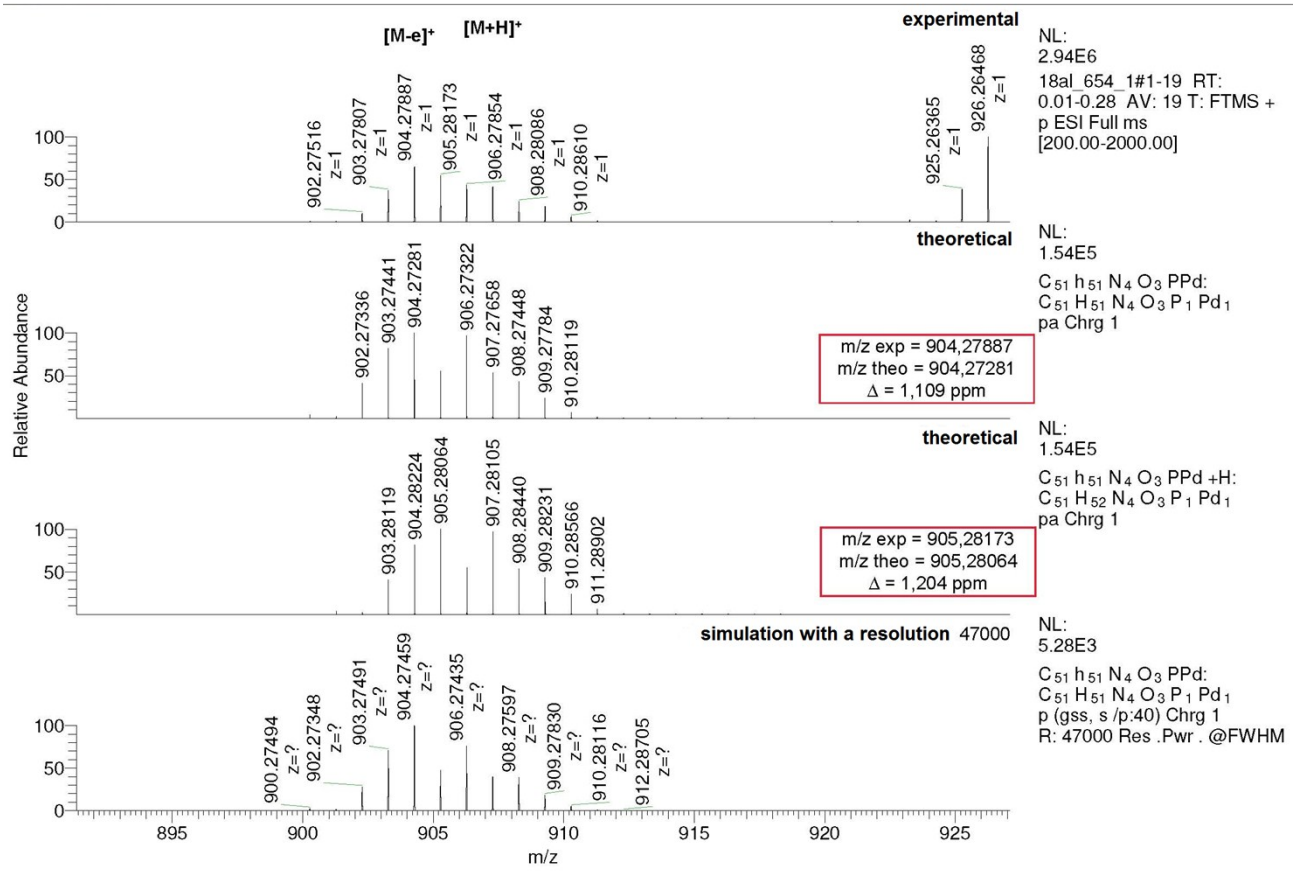


Figure S48. HRMS (ESI) spectrum of **PdTMesPP**.

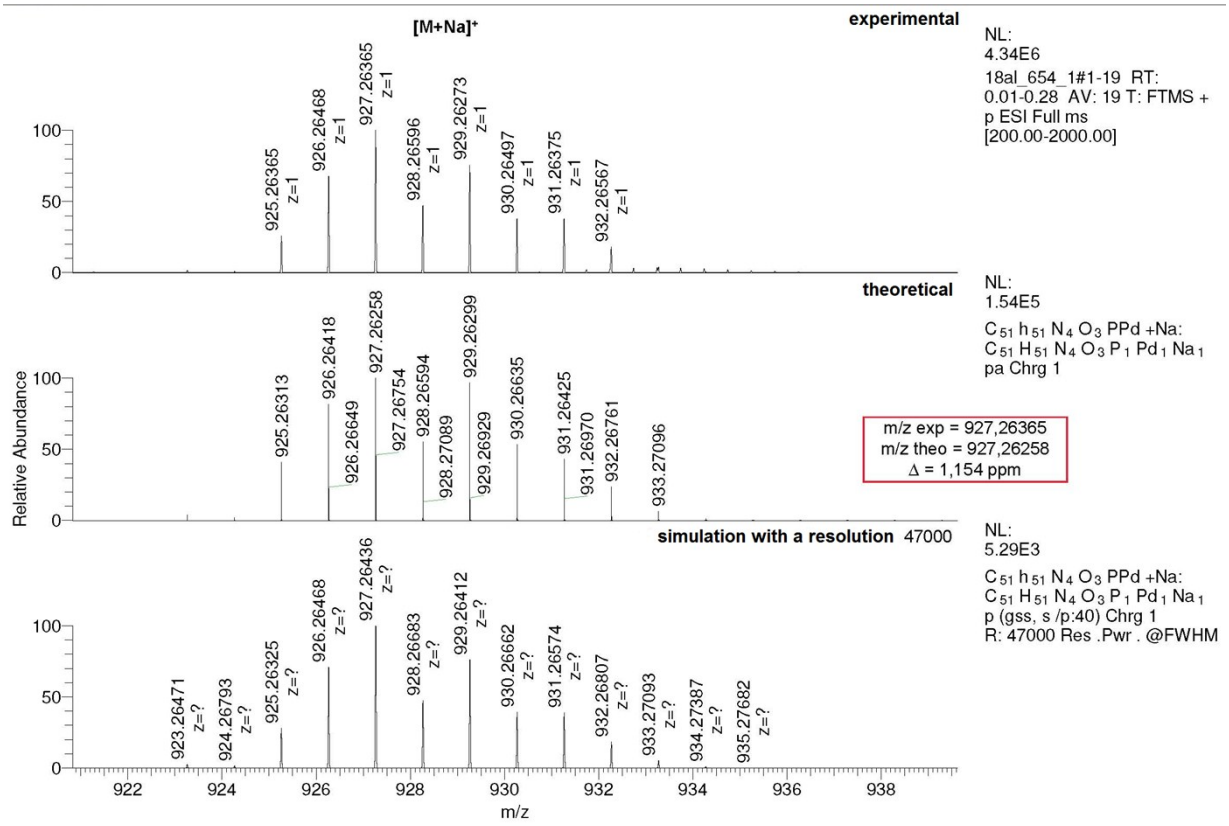


Figure S49. HRMS (ESI) spectrum of **PdTMesPP**.

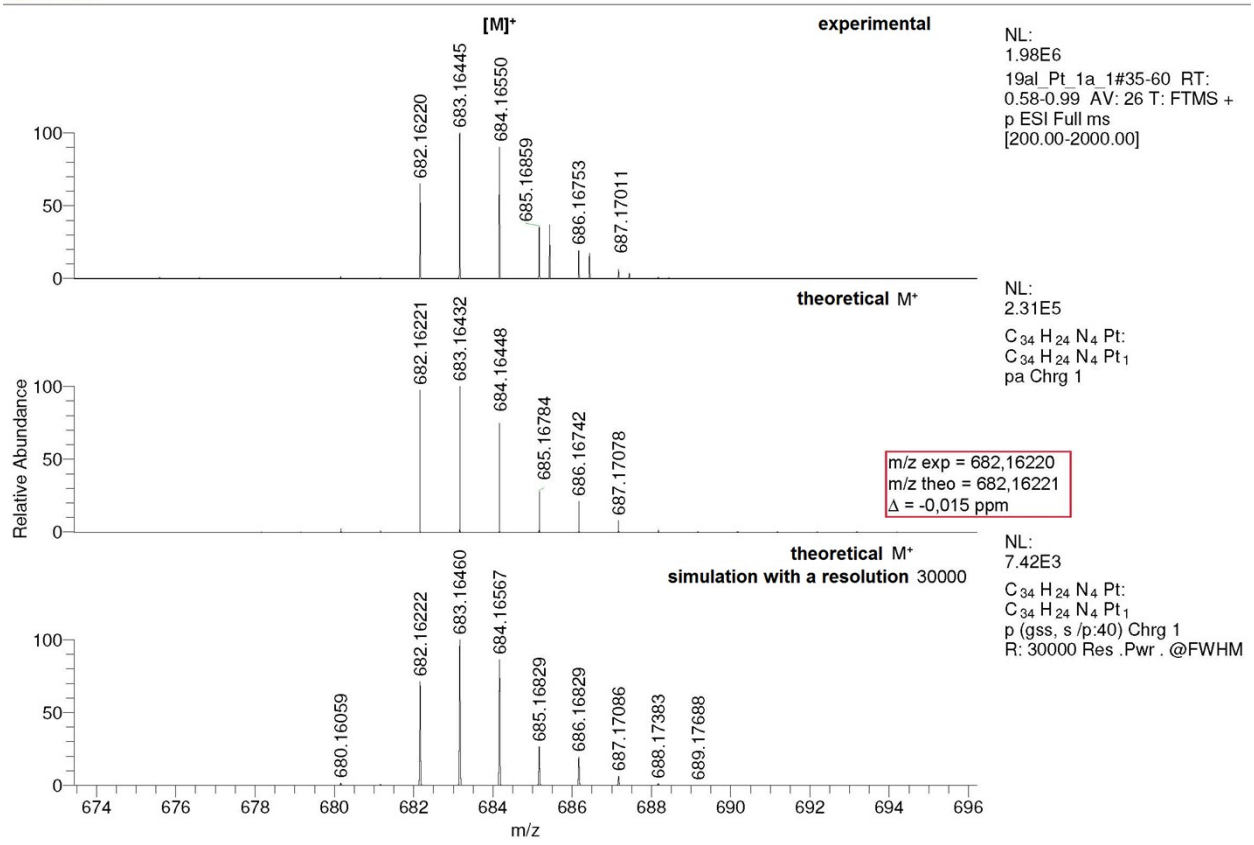


Figure S50. HRMS (ESI) spectrum of **PtDTolP**.

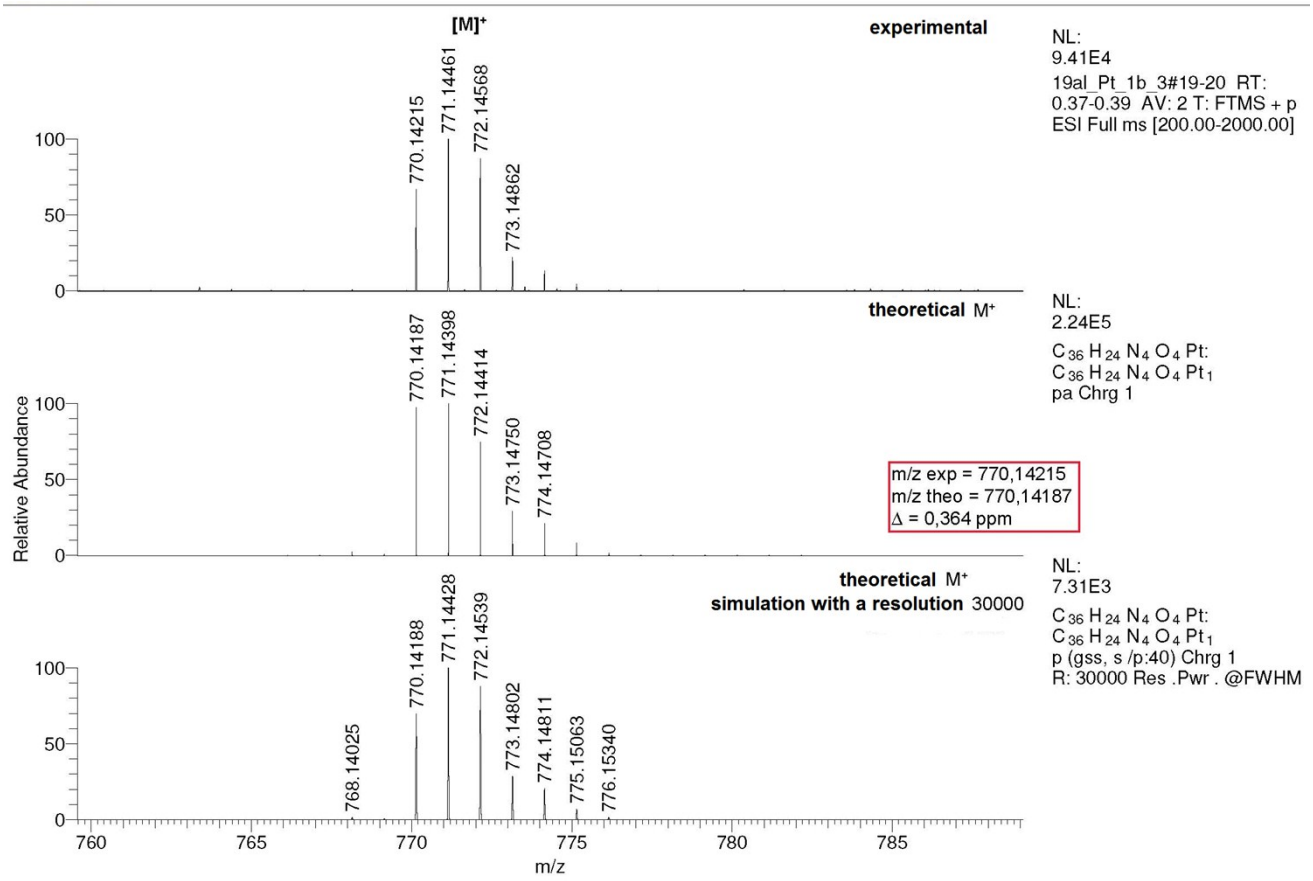


Figure S51. HRMS (ESI) spectrum of **PtD(CMP)P**.

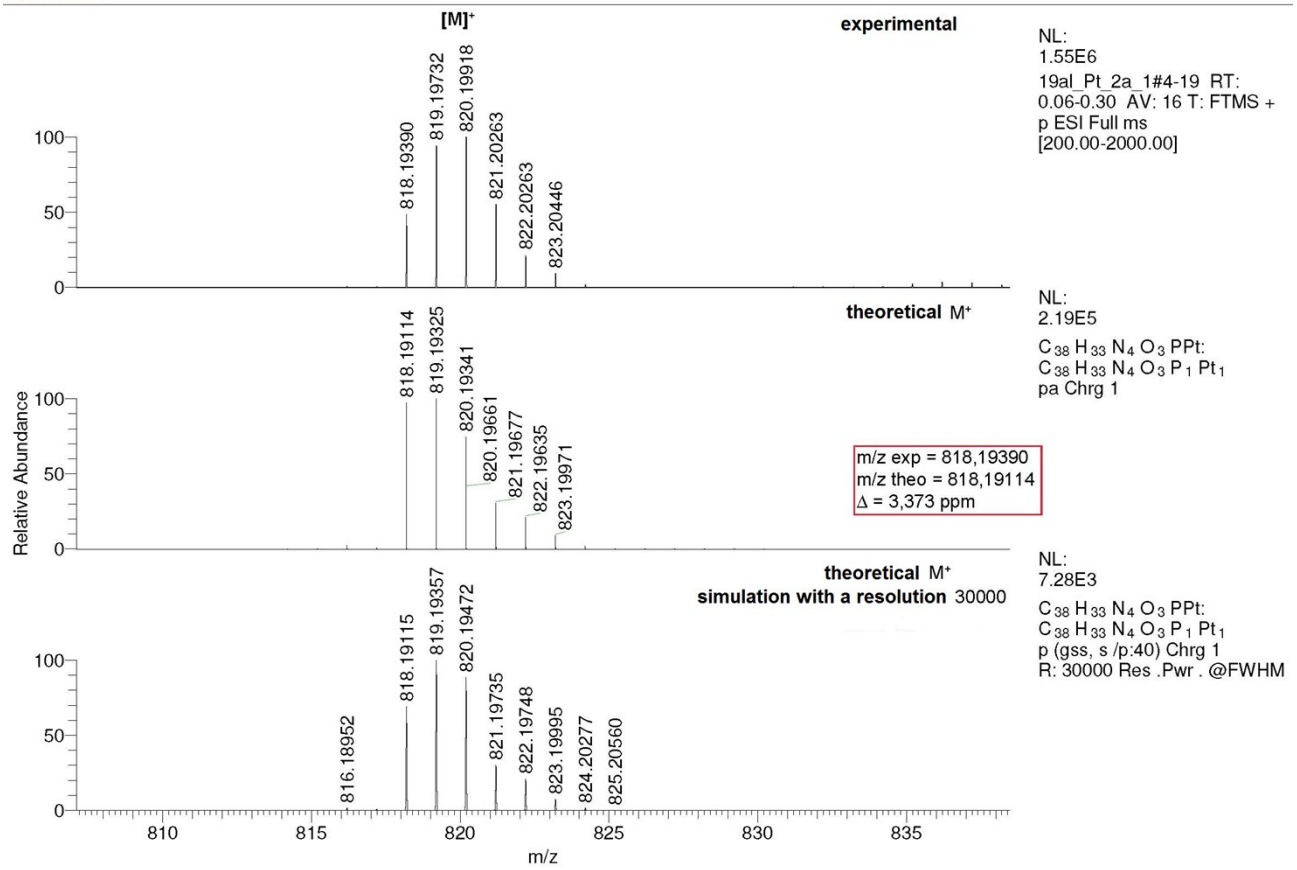


Figure S52. HRMS (ESI) spectrum of **PtDTolPP**.

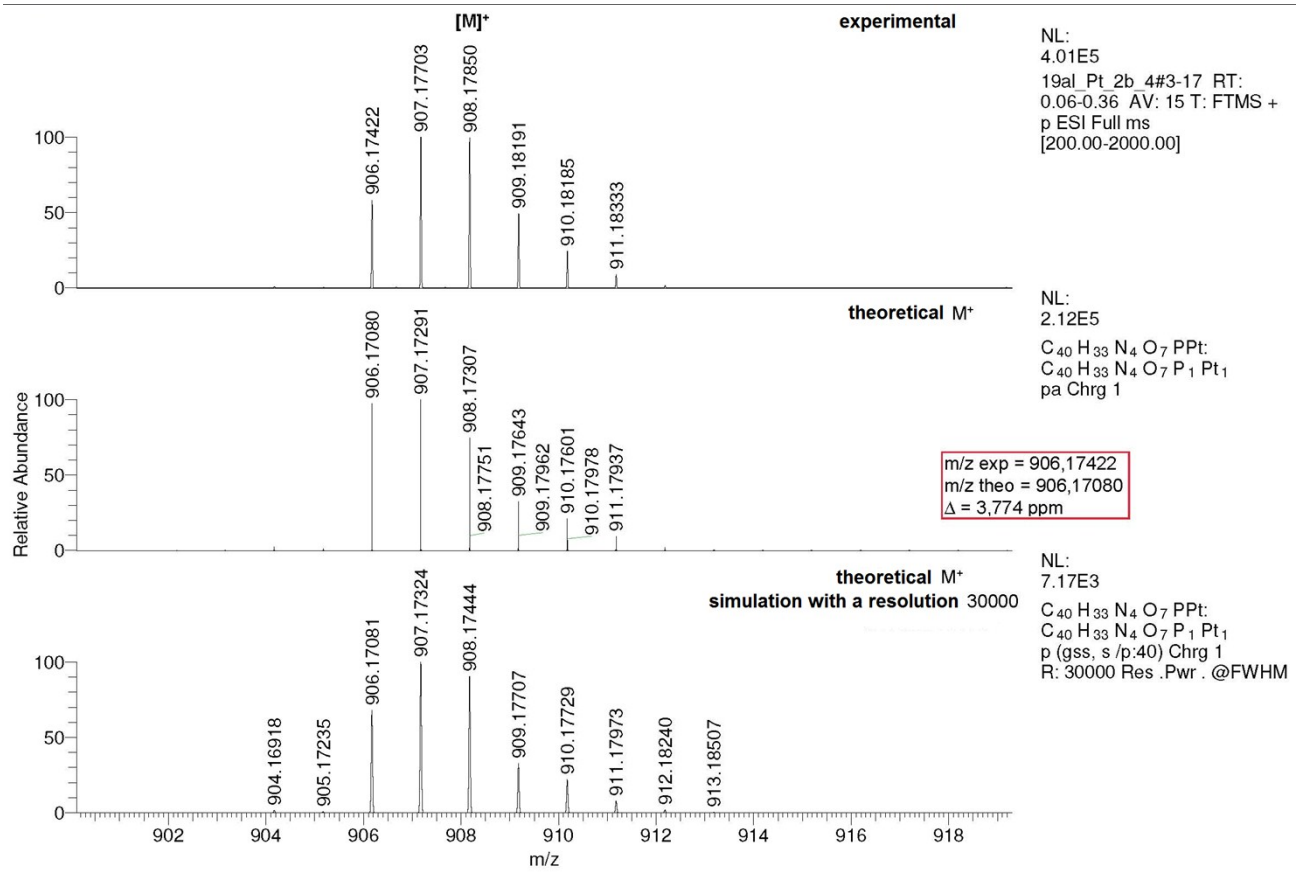


Figure S53. HRMS (ESI) spectrum of **PtD(CMP)PP**.

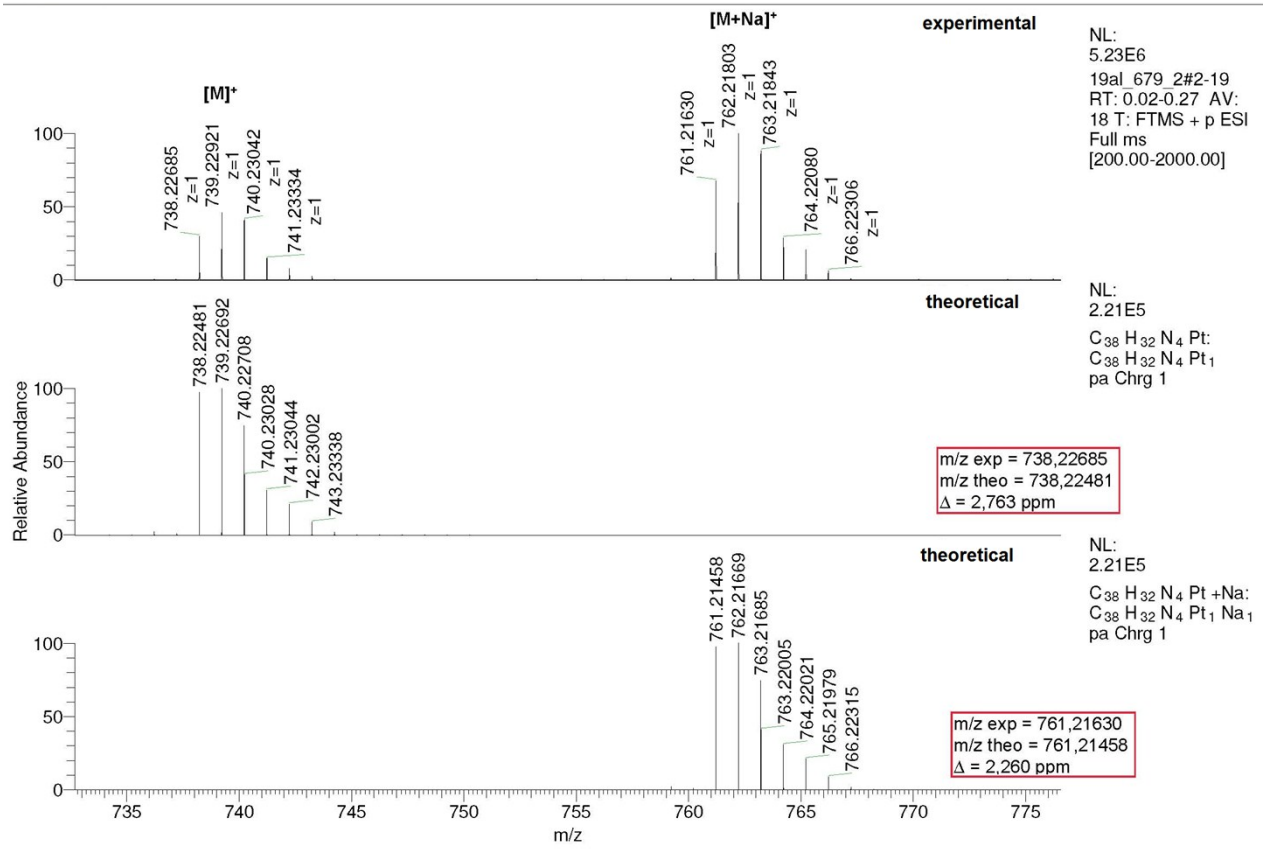


Figure S54. HRMS (ESI) spectrum of **PtDMesP**.

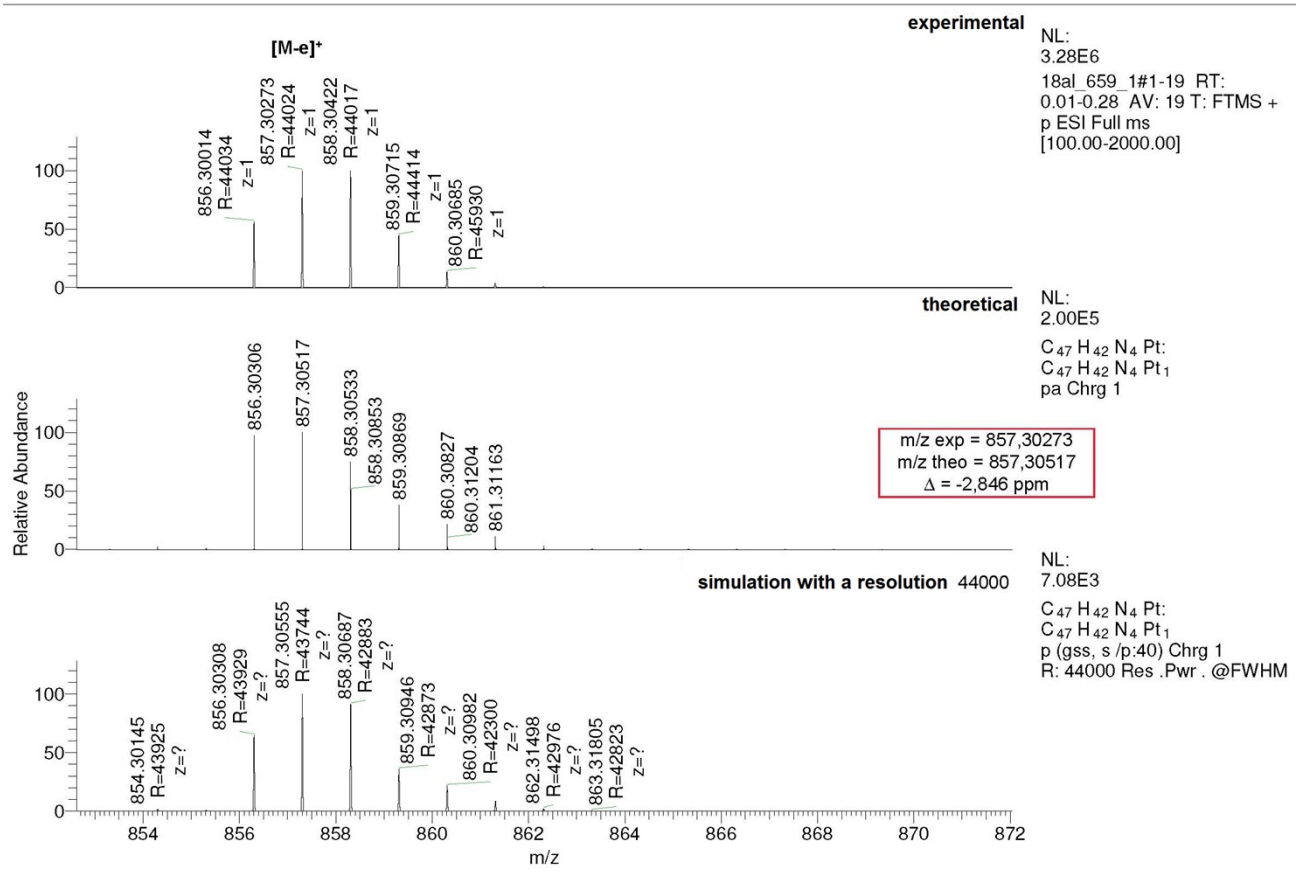


Figure S55. HRMS (ESI) spectrum of **PtTMesP**.

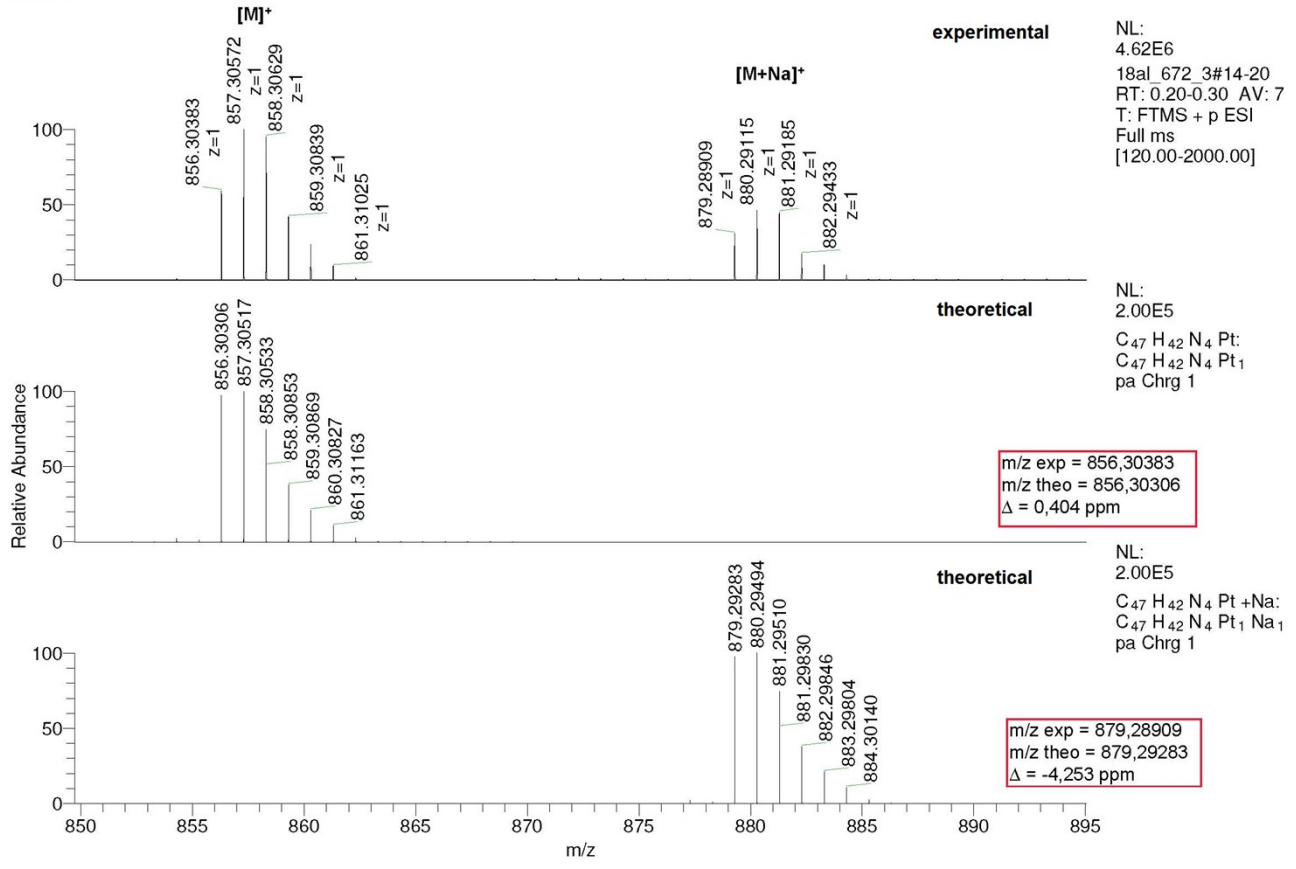


Figure S56. HRMS (ESI) spectrum of **PtTMesP**.

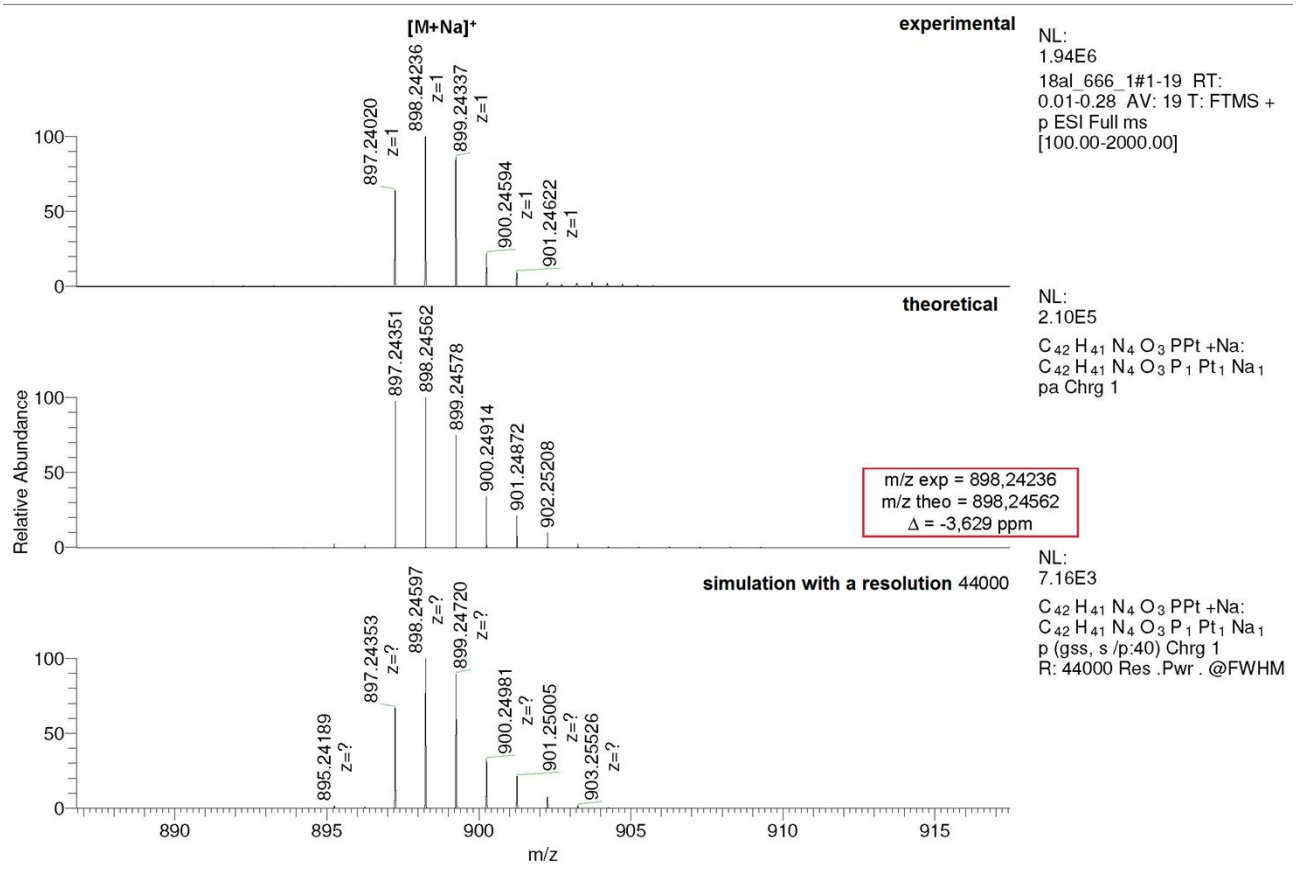


Figure S57. HRMS (ESI) spectrum of **PtDMesPP**.

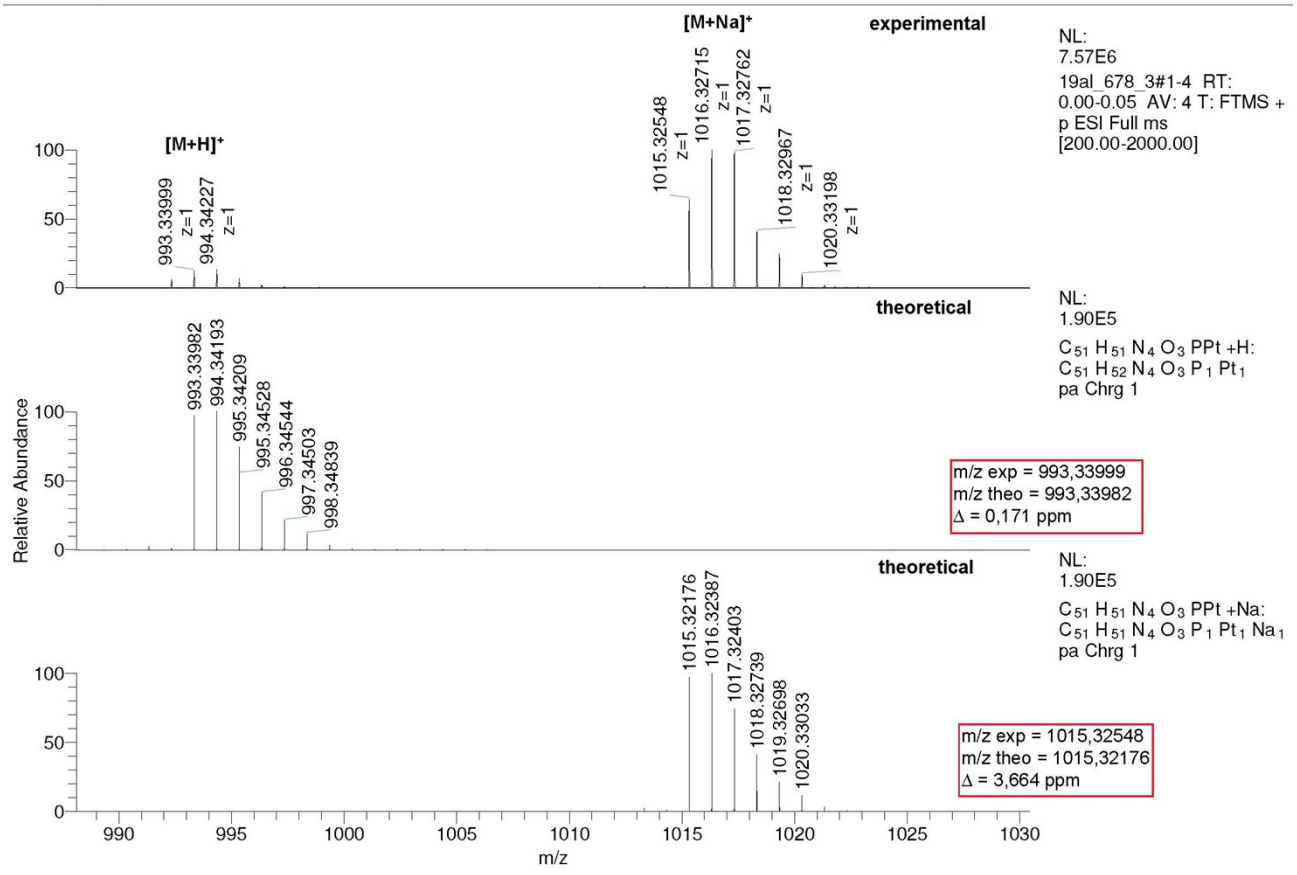


Figure S58. HRMS (ESI) spectrum of **PtTMesPP**.

1.4. IR spectra

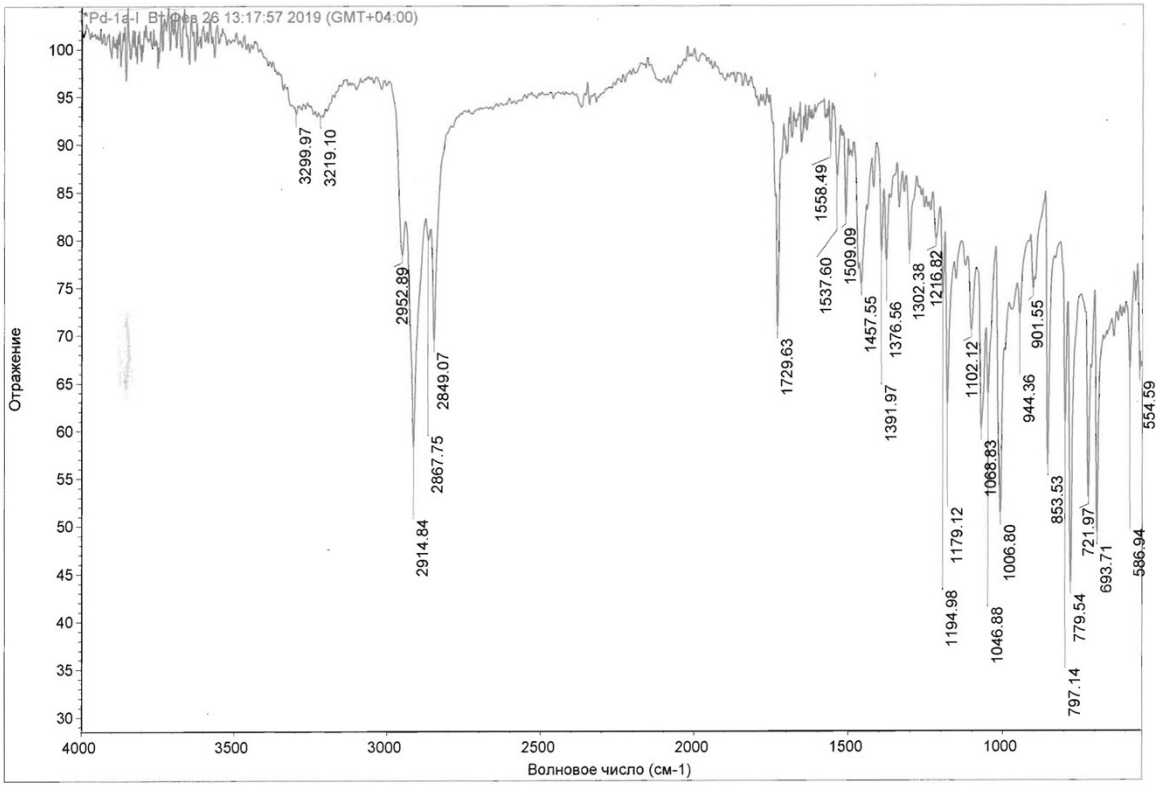


Figure S59. IR spectrum of **PdDTolP**.

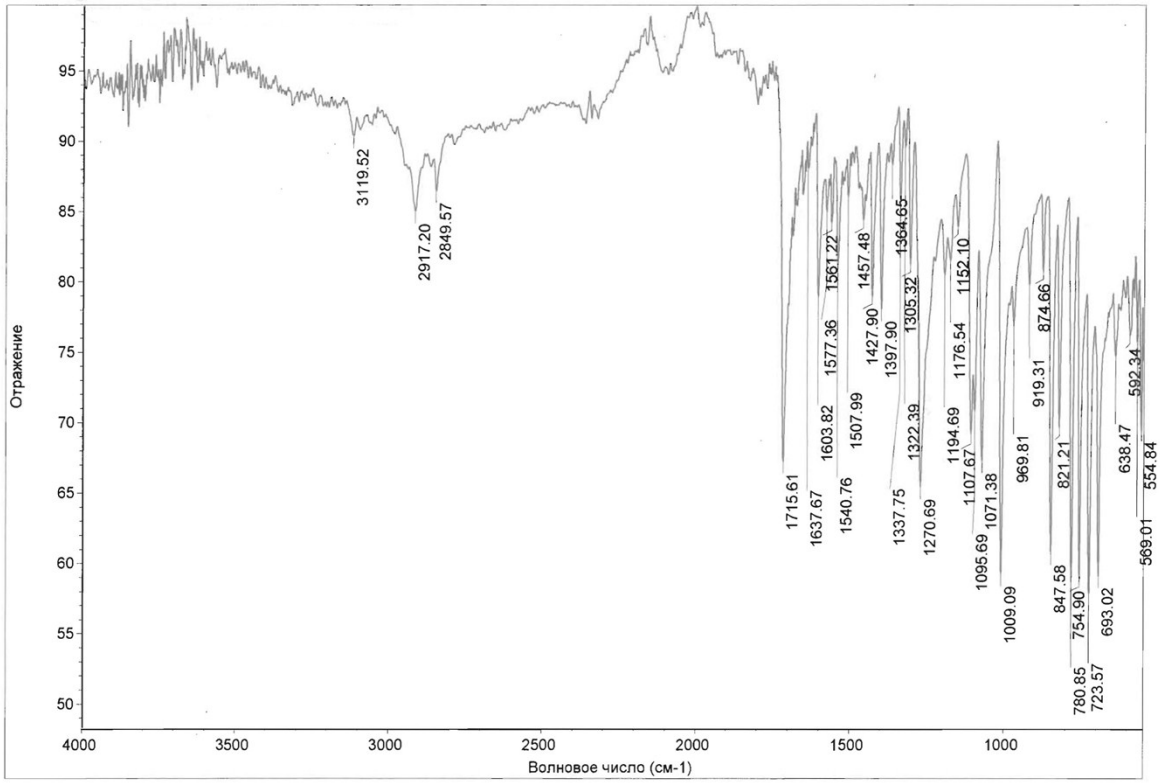


Figure S60. IR spectrum of **PdD(CMP)P**.

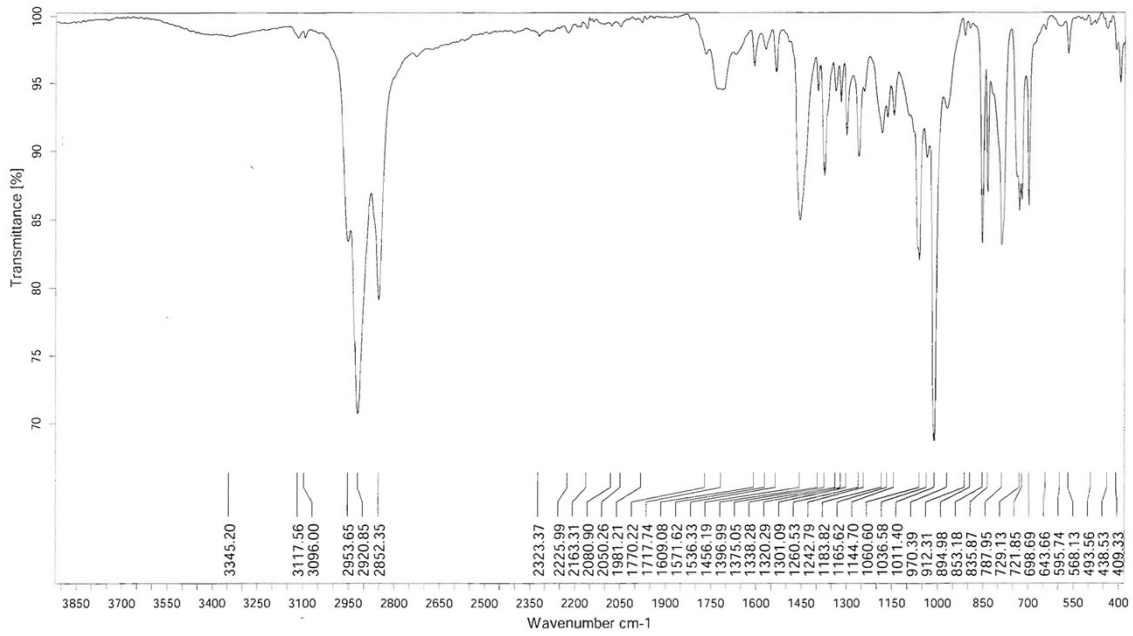


Figure S61. IR spectrum of **PdDMesP**.

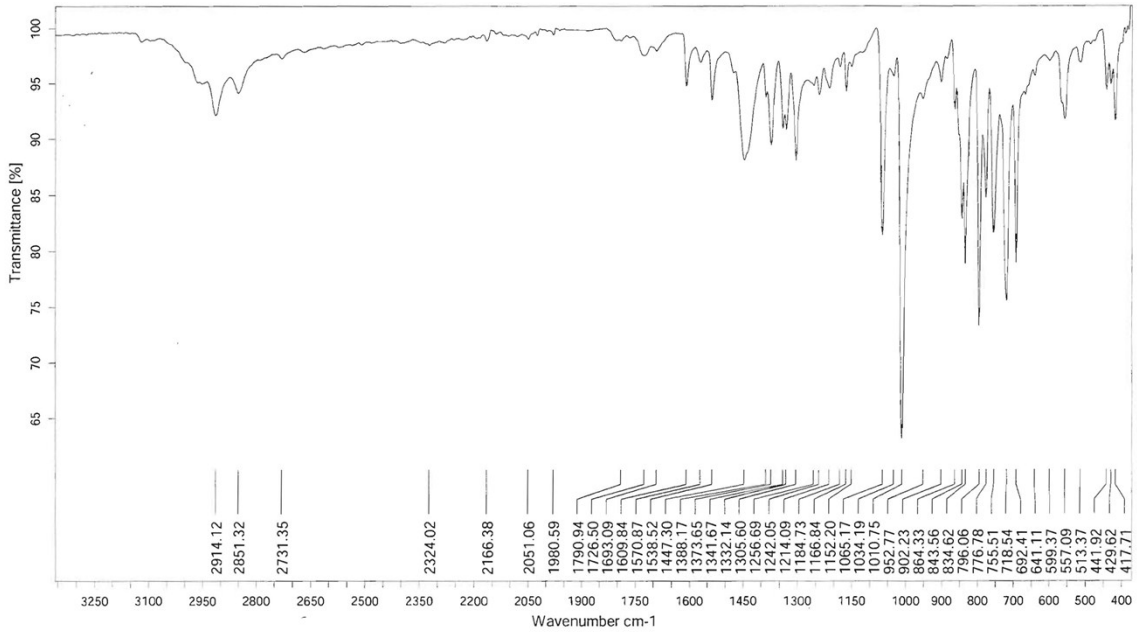


Figure S62. IR spectrum of **PdTMesP**.

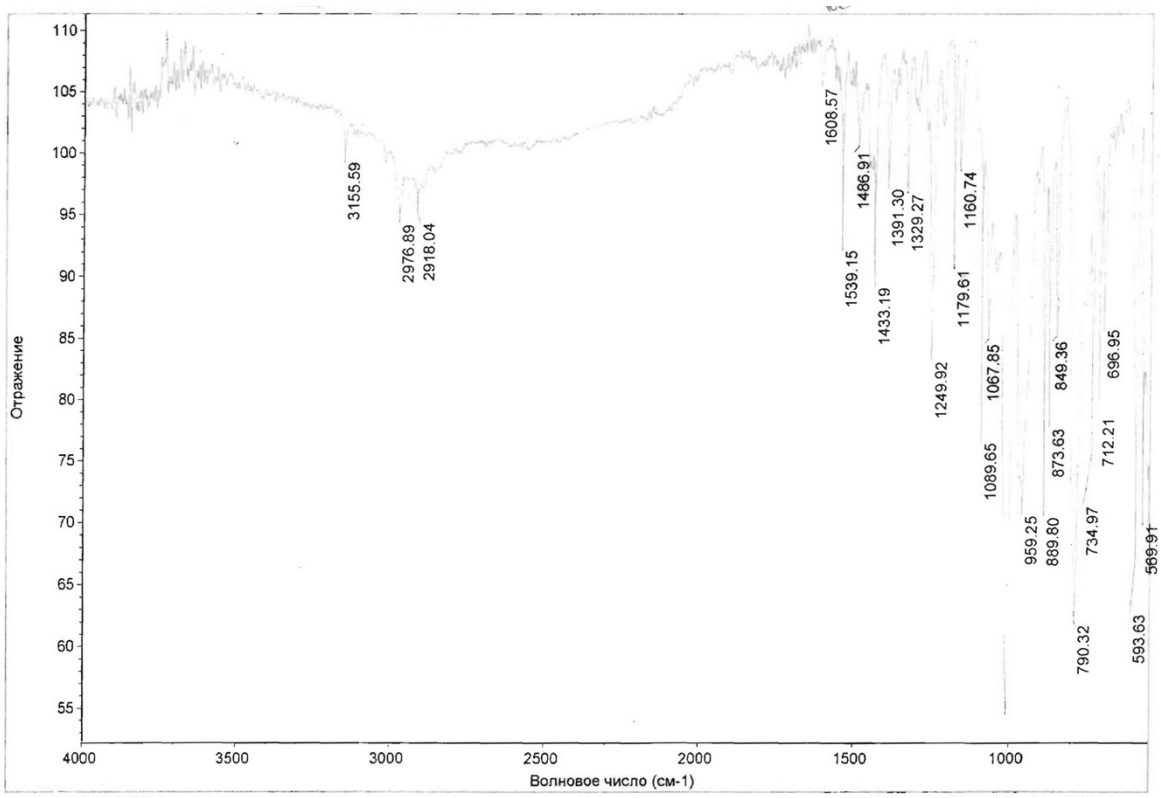


Figure S63. IR spectrum of **PdDTolPP**.

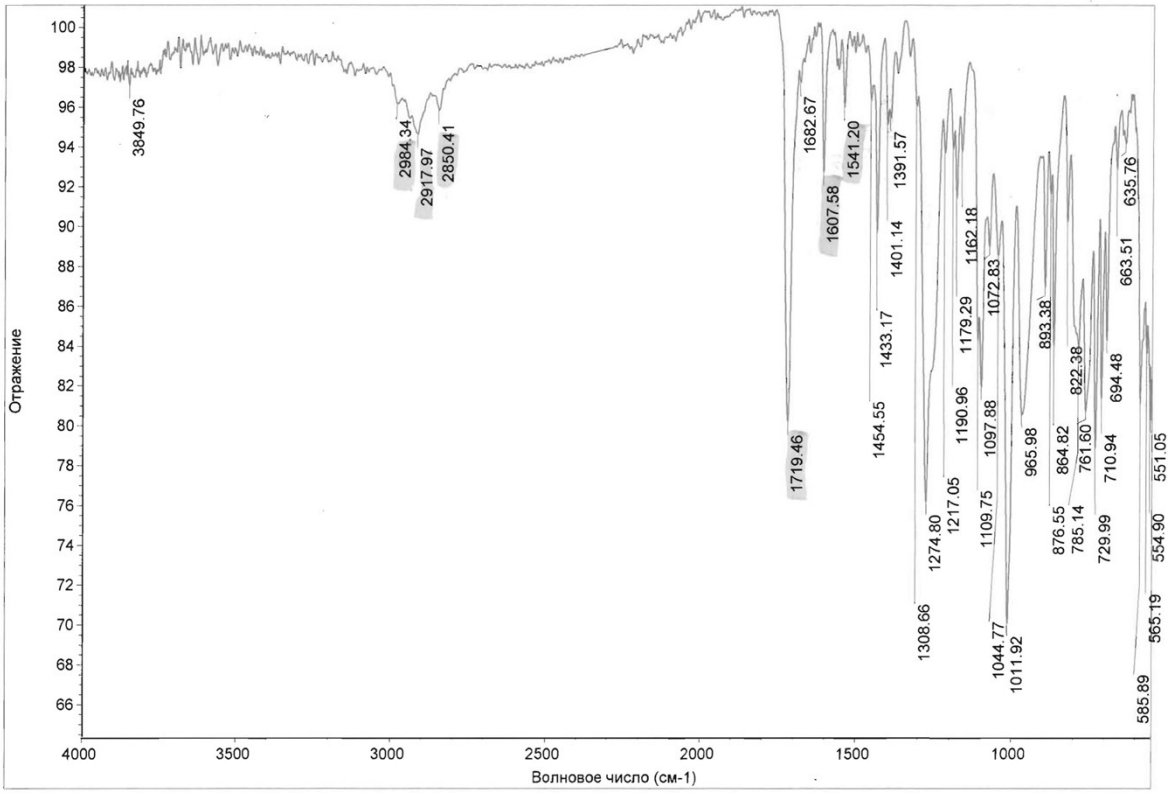


Figure S64. IR spectrum of **PdD(CMP)PP**.

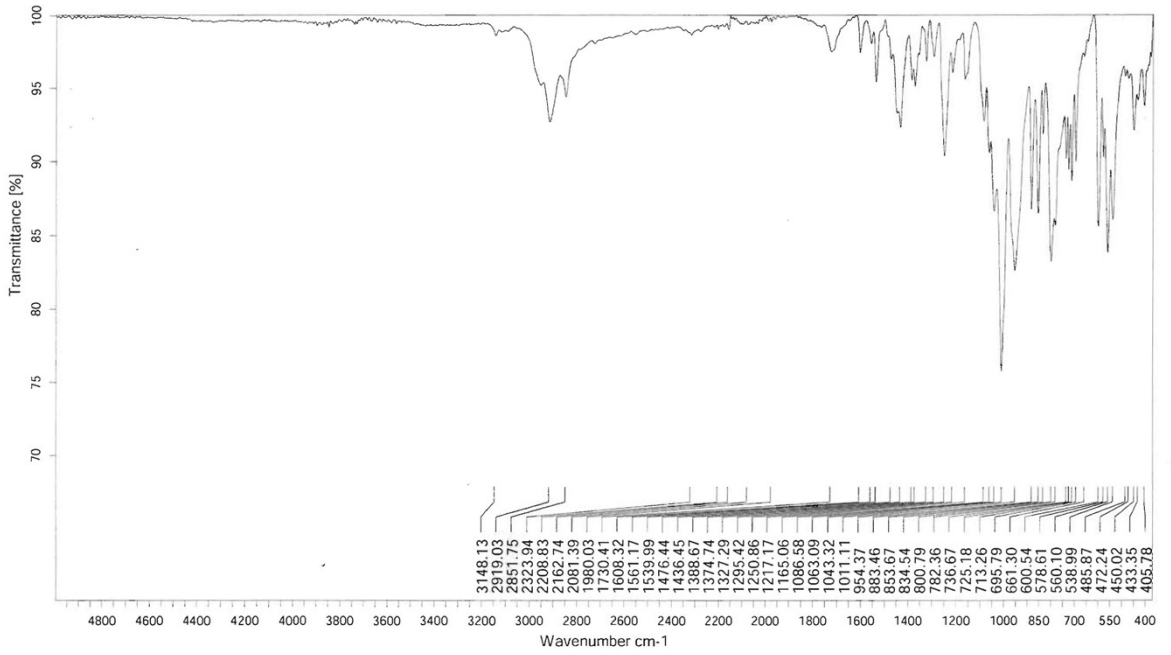


Figure S65. IR spectrum of **PdDMesPP**.

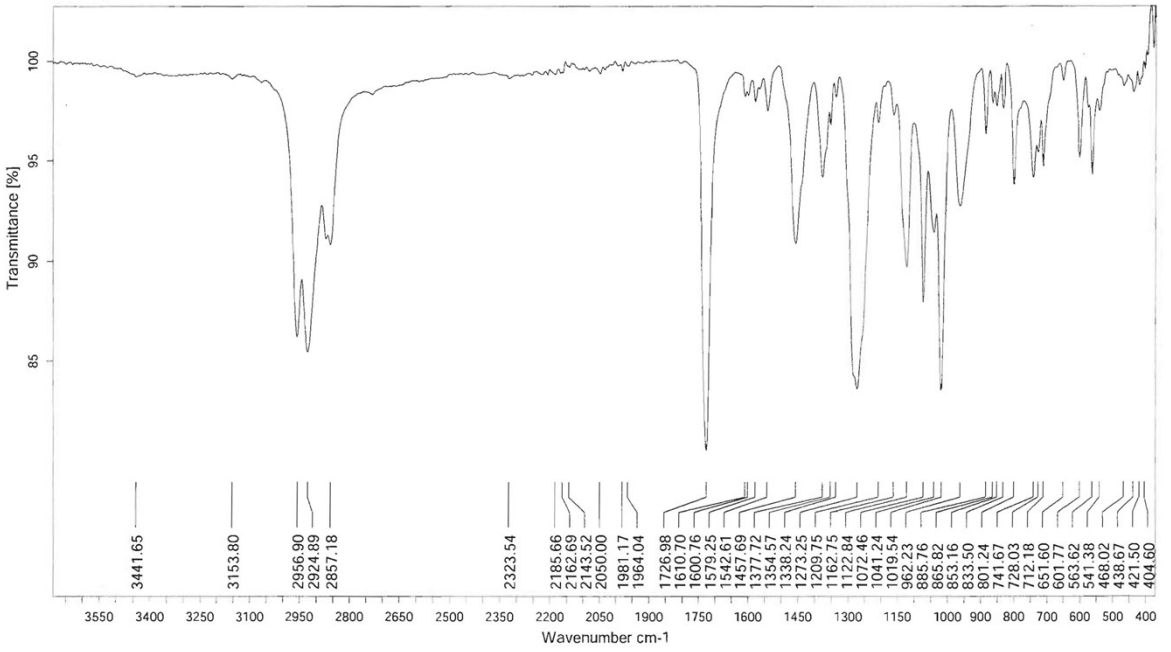


Figure S66. IR spectrum of **PdTMesPP**.

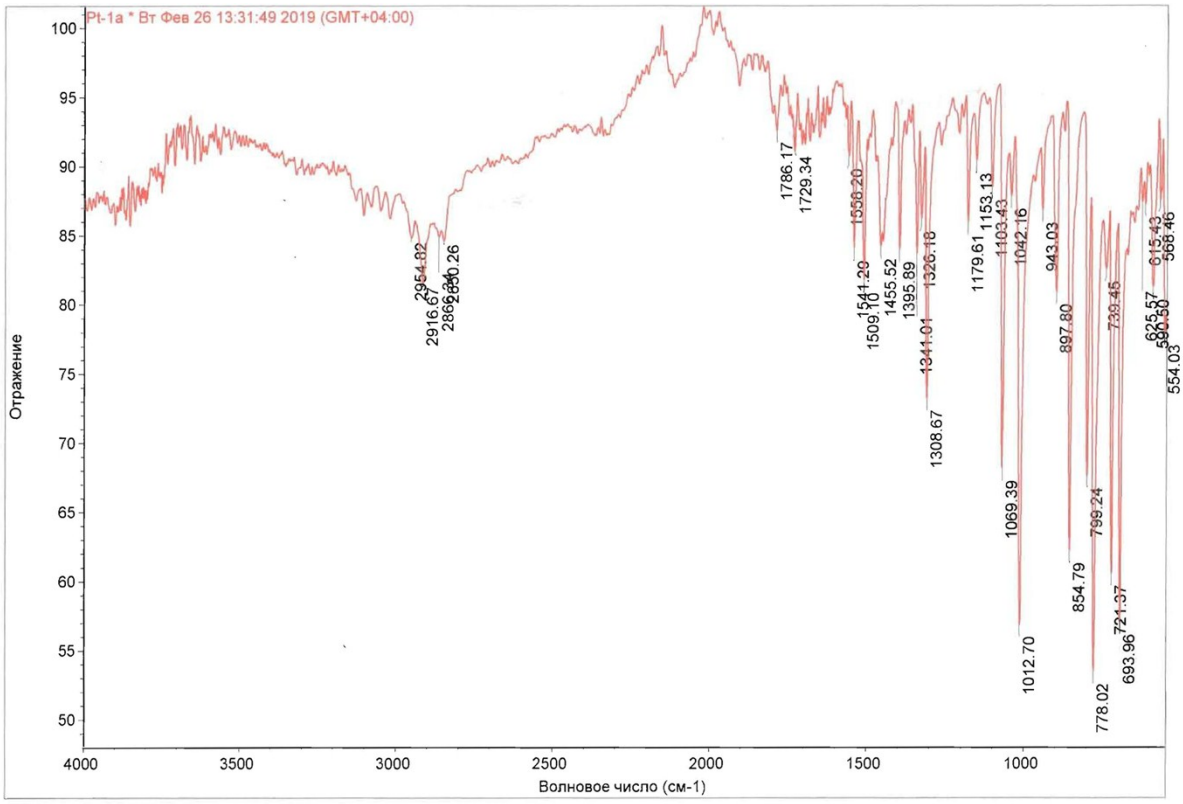


Figure S67. IR spectrum of **PtDTolP**.

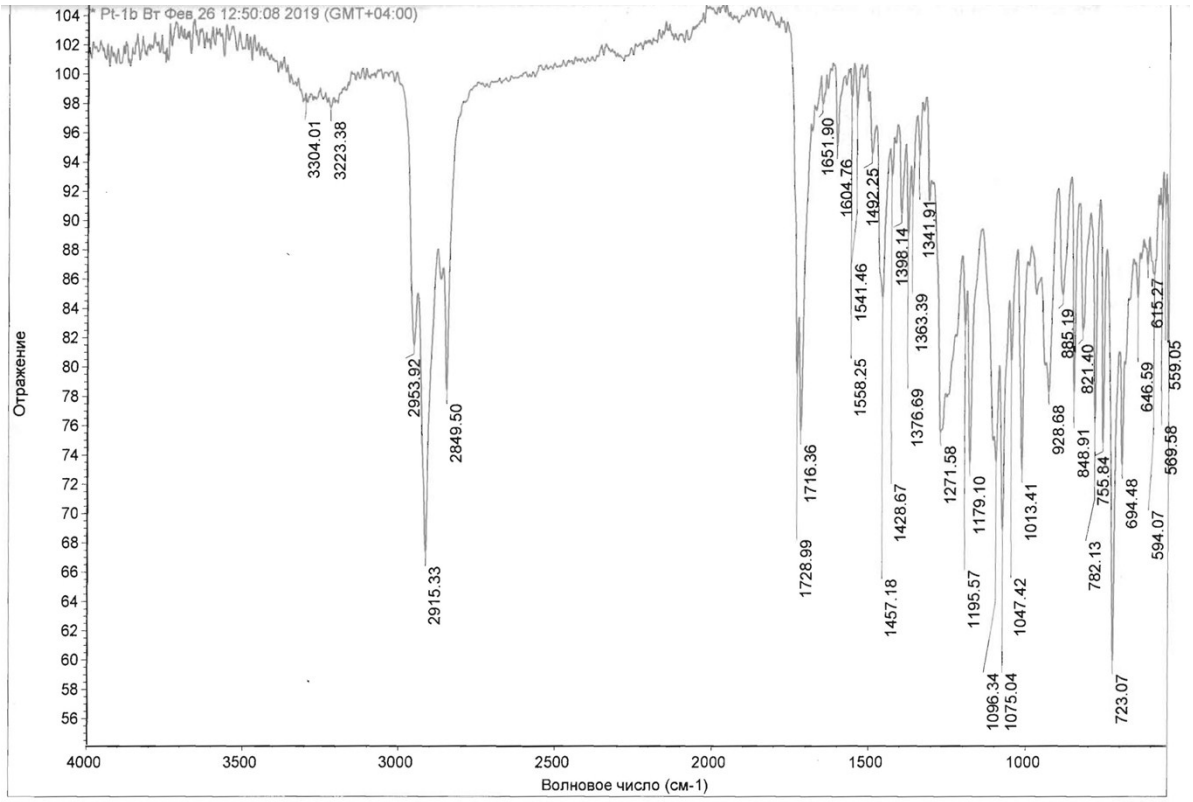


Figure S68. IR spectrum of **PtD(CMP)P**.

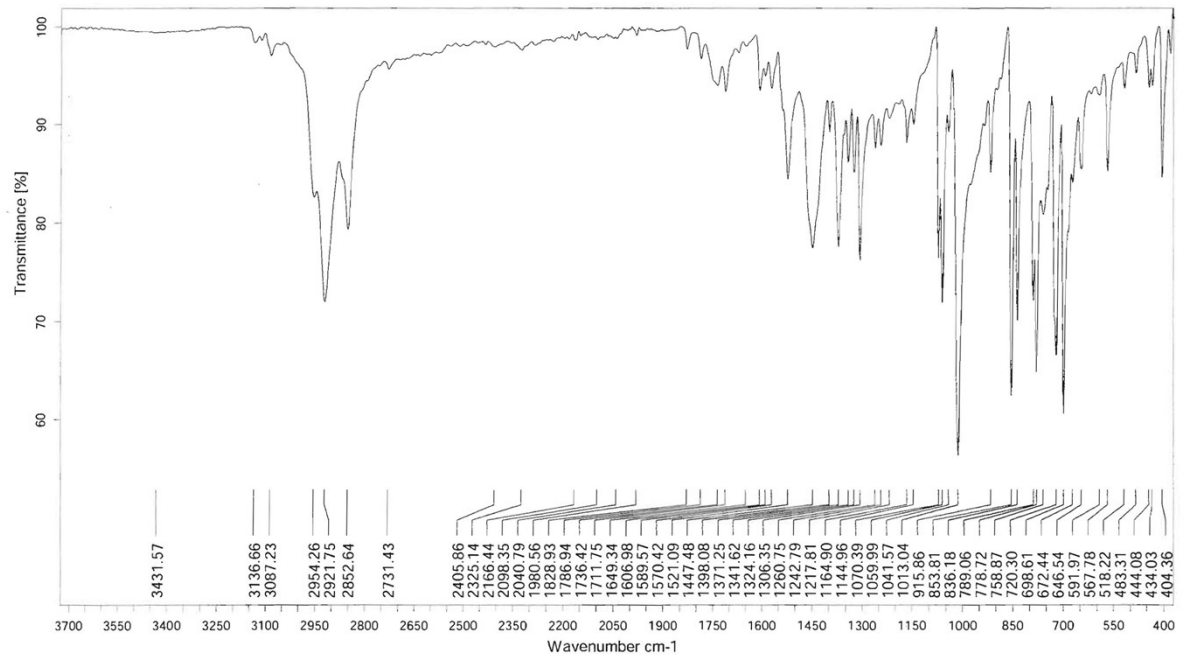


Figure S69. IR spectrum of **PtDMesP**.

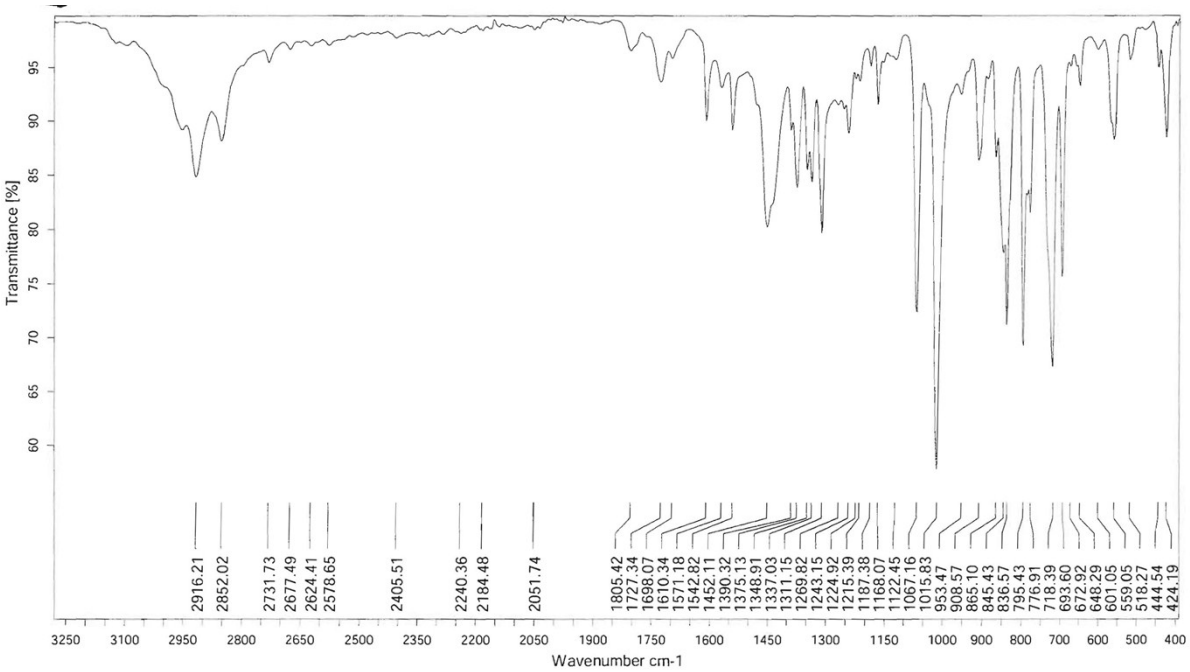


Figure S70. IR spectrum of **PtTMesP**.

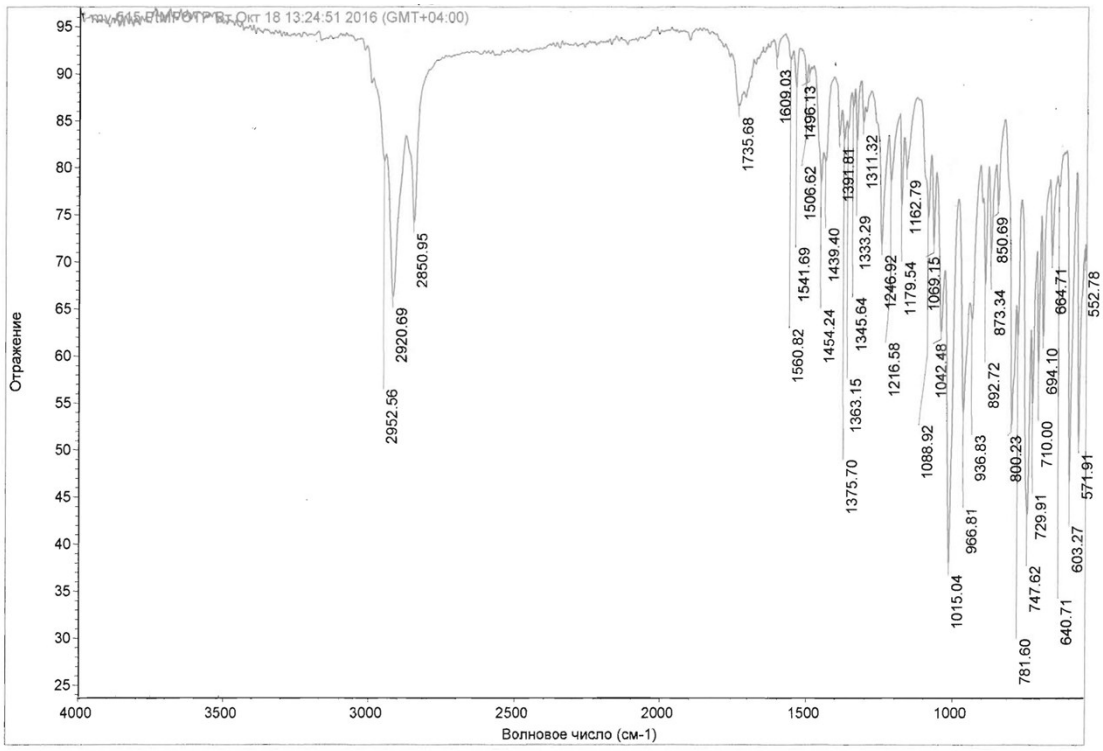


Figure S71. IR spectrum of **PtDTolPP**.

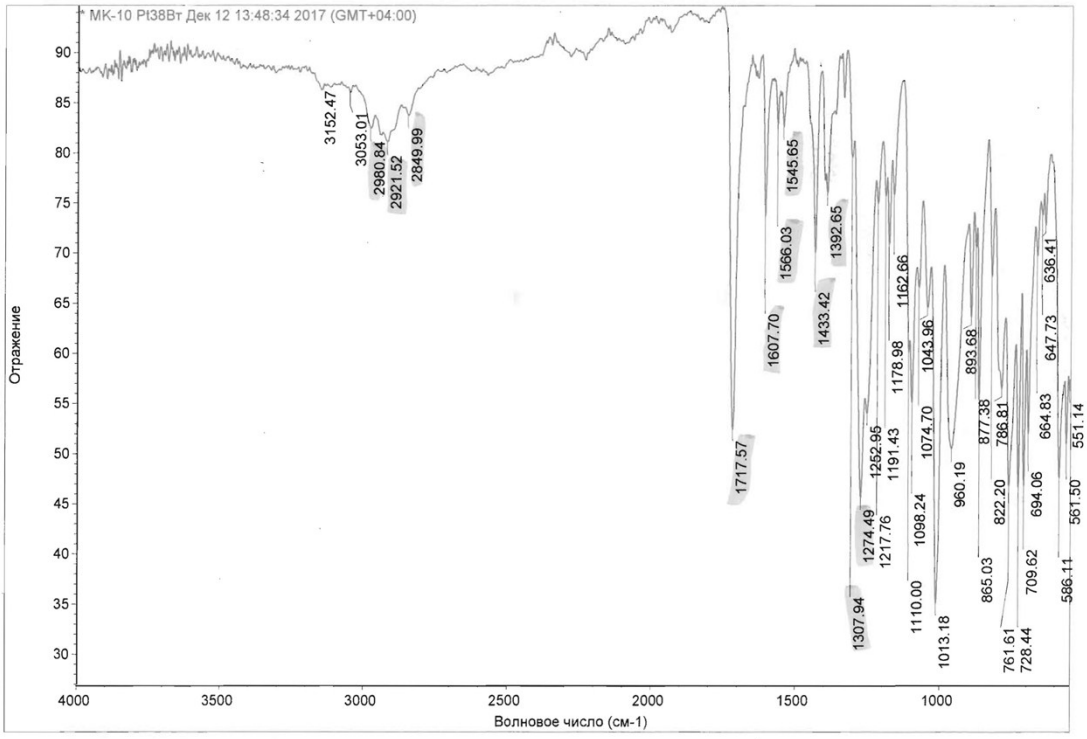


Figure S72. IR spectrum of **PtD(CMP)PP**.

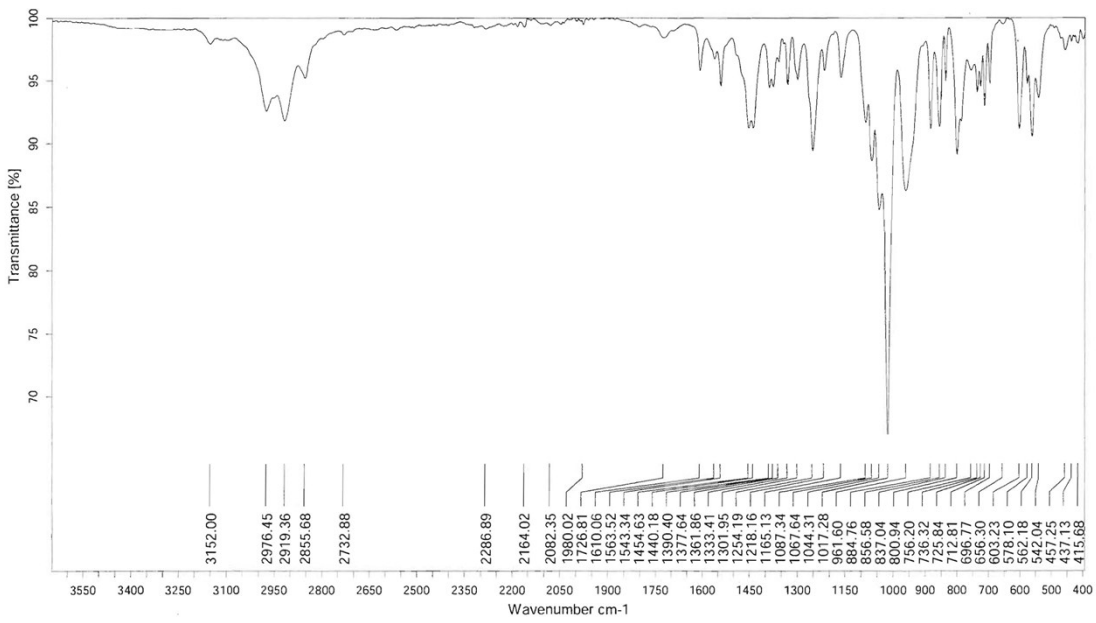


Figure S73. IR spectrum of **PtDMesPP**.

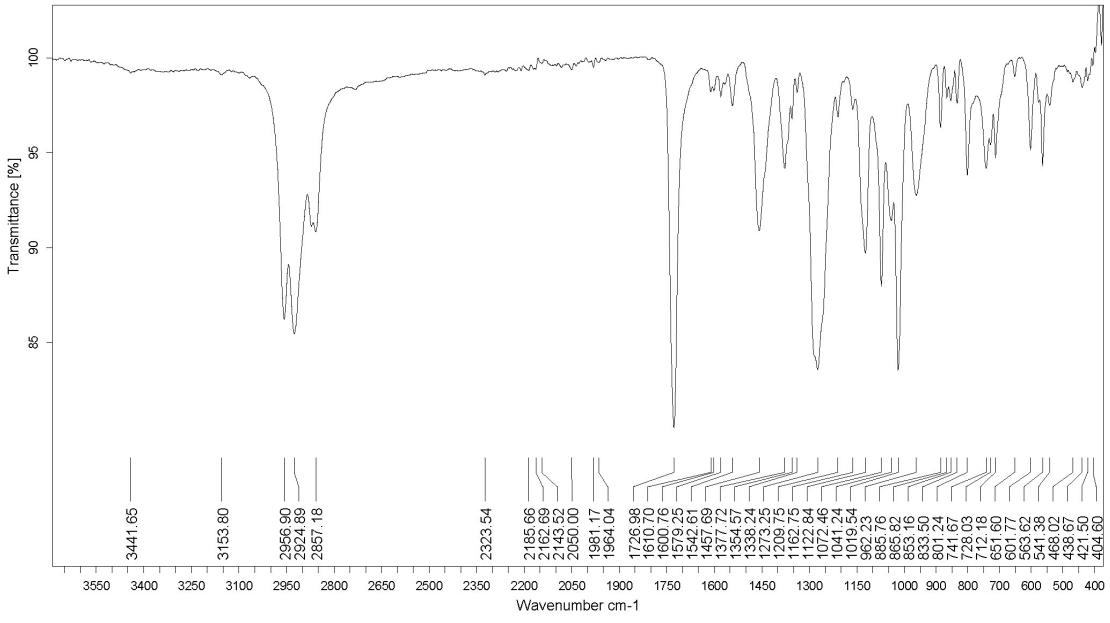


Figure S74. IR spectrum of **PtTMesPP**.

1.5. X-ray structural analysis

Table S1. Crystal data and structure refinement.

Identification code	**PdDTolPP**	**PdD(CMP)PP**	**PtD(CMP)PP**
CCDC number	1904438	1904436	1904437
Chemical formula moiety	$C_{38}H_{33}N_4O_3PPd$, CH_2Cl_2	$C_{40}H_{33}N_4O_7PPd$, $CHCl_3$	$C_{40}H_{33}N_4O_7PPt$, $CHCl_3$
Chemical formula	$C_{39}H_{35}Cl_2N_4O_3PPd$	$C_{41}H_{34}Cl_3N_4O_7PPd$	$C_{41}H_{34}Cl_3N_4O_7PPt$
Formula weight	815.98	938.44	1027.13
Temperature, K	100(2)	100(2)	100(2)
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a, Å	11.8481(7)	10.7842(3)	10.7820(3)
b, Å	12.1054(6)	11.5565(4)	11.5473(4)
c, Å	13.6018(7)	17.0314(6)	17.1136(6)
α, °	64.844(3)	72.119(2)	71.942(2)
β, °	89.227(3)	75.384(2)	75.4160(10)
γ, °	85.015(3)	85.933(2)	85.9580(10)
Volume, Å^3	1758.55(17)	1954.63(11)	1960.41(11)
Z	2	2	2
$\rho_{calc}g$, cm^3	1.541	1.594	1.740
μ, mm^{-1}	0.770	0.778	3.881
F(000)	832.0	952.0	1016.0
Crystal size, mm^3	0.3 × 0.3 × 0.03	0.55 × 0.08 × 0.02	0.5 × 0.16 × 0.14
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection, °	6.622 to 60	6.026 to 59.998	8.254 to 54.998
Index ranges	-16 ≤ h ≤ 16, -17 ≤ k ≤ 17, -19 ≤ l ≤ 19	-15 ≤ h ≤ 13, -16 ≤ k ≤ 16, -23 ≤ l ≤ 23	-14 ≤ h ≤ 13, -14 ≤ k ≤ 15, -22 ≤ l ≤ 22
Reflections collected	32385	24057	26935
Independent reflections	10249 [R_{int} = 0.0776, R_{sigma} = 0.0738]	11378 [R_{int} = 0.0393, R_{sigma} = 0.0638]	8951 [R_{int} = 0.0257, R_{sigma} = 0.0285]
Data,restraints,parameters	10249/0/455	11378/0/518	8951/0/518
Goodness-of-fit on F^2	1.004	1.013	1.046

Final R indexes [I>=2σ (I)]	R_1 = 0.0367, wR_2 = 0.0883	R_1 = 0.0388, wR_2 = 0.0766	R_1 = 0.0231, wR_2 = 0.0580
Final R indexes [all data]	R_1 = 0.0542, wR_2 = 0.0953	R_1 = 0.0615, wR_2 = 0.0844	R_1 = 0.0269, wR_2 = 0.0599
Largest diff. peak/hole, e $Å^{-3}$	1.01/-1.19	0.80/-0.77	1.58/-0.92

Table S2. Bond Lengths for **PdDTolPP**.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Pd1	N2	2.0139(18)		C10	C11	1.452(3)
Pd1	N3	2.0201(18)		C32	C31	1.496(3)
Pd1	N1	2.0123(17)		C32	C38	1.403(3)
Pd1	N4	2.0190(18)		C32	C33	1.387(3)
P1	O3	1.5856(17)		C3	C4	1.447(3)
P1	O2	1.5750(18)		C3	C2	1.347(3)
P1	O1	1.4669(17)		C31	C1	1.395(3)
P1	C5	1.807(2)		C31	C30	1.401(3)
Cl2	C016	1.762(3)		C14	C13	1.390(3)
Cl1	C016	1.763(3)		C25	C26	1.375(3)
O3	C8	1.448(3)		C26	C27	1.382(3)
O2	C6	1.460(3)		C13	C12	1.443(3)
N2	C10	1.379(3)		C20	C21	1.385(3)
N2	C13	1.380(3)		C20	C18	1.385(4)
N3	C22	1.365(3)		C12	C11	1.341(3)
N3	C25	1.376(3)		C1	C2	1.434(3)
N1	C4	1.375(3)		C27	C28	1.430(3)
N1	C1	1.378(3)		C35	C37	1.386(3)
N4	C27	1.375(3)		C35	C36	1.502(3)
N4	C30	1.367(3)		C35	C34	1.386(3)
C23	C24	1.357(3)		C28	C29	1.356(3)
C23	C22	1.440(3)		C29	C30	1.442(3)
C15	C14	1.492(3)		C38	C37	1.389(3)
C15	C21	1.396(3)		C6	C7	1.504(4)
C15	C16	1.385(3)		C16	C17	1.389(3)
C24	C25	1.439(3)		C18	C17	1.387(4)
C22	C14	1.401(3)		C18	C19	1.507(3)
C5	C10	1.403(3)		C33	C34	1.387(3)
C5	C4	1.404(3)		C9	C8	1.491(4)

Table S3. Bond Angles for **PdDTolPP**.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N2	Pd1	N3	90.08(7)		C30	C31	C32	118.30(19)
N2	Pd1	N4	178.76(7)		N1	C4	C5	125.7(2)
N1	Pd1	N2	89.92(7)		N1	C4	C3	109.0(2)
N1	Pd1	N3	179.82(7)		C5	C4	C3	125.2(2)
N1	Pd1	N4	89.94(7)		C22	C14	C15	117.53(18)
N4	Pd1	N3	90.06(7)		C13	C14	C15	118.66(19)
O3	P1	C5	107.43(10)		C13	C14	C22	123.7(2)
O2	P1	O3	101.86(9)		N3	C25	C24	109.6(2)
O2	P1	C5	100.66(10)		C26	C25	N3	125.3(2)
O1	P1	O3	112.83(10)		C26	C25	C24	125.1(2)
O1	P1	O2	114.95(10)		C25	C26	C27	125.6(2)
O1	P1	C5	117.37(10)		N2	C13	C14	126.6(2)
C8	O3	P1	119.37(17)		N2	C13	C12	109.35(18)
C6	O2	P1	120.15(15)		C14	C13	C12	124.0(2)
C10	N2	Pd1	127.25(15)		C21	C20	C18	120.7(2)
C10	N2	C13	106.74(18)		C20	C21	C15	121.0(2)
C13	N2	Pd1	126.00(14)		C11	C12	C13	107.4(2)
C22	N3	Pd1	127.00(14)		C12	C11	C10	107.65(19)
C22	N3	C25	106.45(18)		N1	C1	C31	126.93(19)
C25	N3	Pd1	126.54(15)		N1	C1	C2	109.40(19)
C4	N1	Pd1	127.16(15)		C31	C1	C2	123.7(2)
C4	N1	C1	106.74(17)		C3	C2	C1	107.5(2)
C1	N1	Pd1	125.98(14)		N4	C27	C26	126.0(2)
C27	N4	Pd1	126.01(15)		N4	C27	C28	109.9(2)
C30	N4	Pd1	127.52(14)		C26	C27	C28	124.1(2)
C30	N4	C27	106.47(18)		C37	C35	C36	121.4(2)
C24	C23	C22	106.8(2)		C37	C35	C34	118.3(2)
C21	C15	C14	118.7(2)		C34	C35	C36	120.3(2)
C16	C15	C14	123.3(2)		C29	C28	C27	106.96(19)
C16	C15	C21	118.1(2)		C28	C29	C30	107.1(2)

C23	C24	C25	107.09(19)		N4	C30	C31	125.5(2)
N3	C22	C23	110.04(19)		N4	C30	C29	109.55(18)
N3	C22	C14	125.75(19)		C31	C30	C29	125.0(2)
C14	C22	C23	124.2(2)		C37	C38	C32	120.6(2)
C10	C5	P1	116.97(16)		C35	C37	C38	120.9(2)
C10	C5	C4	123.89(19)		O2	C6	C7	107.1(2)
C4	C5	P1	119.12(16)		C15	C16	C17	120.8(2)
N2	C10	C5	125.4(2)		Cl2	C016	Cl1	111.26(14)
N2	C10	C11	108.78(18)		C20	C18	C17	118.5(2)
C5	C10	C11	125.75(19)		C20	C18	C19	120.1(2)
C38	C32	C31	122.0(2)		C17	C18	C19	121.4(3)
C33	C32	C31	119.94(19)		C34	C33	C32	120.8(2)
C33	C32	C38	118.0(2)		C18	C17	C16	120.9(2)
C2	C3	C4	107.3(2)		C35	C34	C33	121.3(2)
C1	C31	C32	118.06(19)		O3	C8	C9	109.4(2)
C1	C31	C30	123.6(2)					

Table S4. Bond Lengths for **PdD(CMP)PP**.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Pd1	N1	2.0175(18)		C7	C14	1.393(3)
Pd1	N2	2.0182(19)		C8	C9	1.389(3)
Pd1	N3	2.0221(18)		C9	C10	1.392(3)
Pd1	N4	2.0134(19)		C10	C11	1.493(3)
P1	O1	1.4701(16)		C10	C13	1.389(3)
P1	O2	1.5707(17)		C13	C14	1.393(3)
P1	O3	1.5801(18)		C15	C16	1.435(3)
P1	C1	1.813(2)		C16	C17	1.351(3)
O2	C37	1.465(3)		C17	C18	1.431(3)
O3	C39	1.456(3)		C18	C19	1.379(3)
O4	C29	1.195(3)		C19	C20	1.380(3)
O5	C29	1.341(3)		C20	C21	1.439(3)
O5	C30	1.450(3)		C21	C22	1.349(3)
O6	C11	1.206(3)		C22	C23	1.438(3)
O7	C11	1.337(3)		C23	C24	1.392(3)
O7	C12	1.448(3)		C24	C25	1.502(3)
N1	C2	1.378(3)		C24	C33	1.391(3)
N1	C5	1.384(3)		C25	C26	1.395(3)
N2	C15	1.374(3)		C25	C32	1.393(3)
N2	C18	1.377(3)		C26	C27	1.396(3)
N3	C20	1.374(3)		C27	C28	1.391(3)
N3	C23	1.377(3)		C28	C29	1.497(3)
N4	C33	1.384(3)		C28	C31	1.389(3)
N4	C36	1.378(3)		C31	C32	1.392(3)
C1	C2	1.401(3)		C33	C34	1.434(3)
C1	C36	1.414(3)		C34	C35	1.347(3)
C2	C3	1.453(3)		C35	C36	1.442(3)
C3	C4	1.345(3)		C39	C40	1.503(4)
C4	C5	1.441(3)		C37	C38	1.497(4)
C5	C6	1.384(3)		Cl3	C1S	1.754(3)

C6	C7	1.498(3)		Cl1	C1S	1.753(3)
C6	C15	1.393(3)		Cl2	C1S	1.765(3)
C7	C8	1.386(3)				

Table S5. Bond Angles for **PdD(CMP)PP**.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N1	Pd1	N2	90.20(8)		O6	C11	C10	123.6(2)
N1	Pd1	N3	179.55(8)		O7	C11	C10	112.3(2)
N2	Pd1	N3	90.05(8)		C10	C13	C14	119.7(2)
N4	Pd1	N1	89.83(8)		C13	C14	C7	120.6(2)
N4	Pd1	N2	178.33(8)		N2	C15	C6	125.1(2)
N4	Pd1	N3	89.93(7)		N2	C15	C16	109.9(2)
O1	P1	O2	115.64(10)		C6	C15	C16	124.9(2)
O1	P1	O3	111.58(10)		C17	C16	C15	107.3(2)
O1	P1	C1	116.60(10)		C16	C17	C18	106.9(2)
O2	P1	O3	102.41(10)		N2	C18	C17	110.3(2)
O2	P1	C1	101.07(10)		N2	C18	C19	125.2(2)
O3	P1	C1	108.13(10)		C19	C18	C17	124.5(2)
C37	O2	P1	120.60(15)		C18	C19	C20	125.7(2)
C39	O3	P1	120.09(15)		N3	C20	C19	126.0(2)
C29	O5	C30	115.7(2)		N3	C20	C21	110.0(2)
C11	O7	C12	115.29(19)		C19	C20	C21	124.0(2)
C2	N1	Pd1	127.78(15)		C22	C21	C20	106.9(2)
C2	N1	C5	106.70(18)		C21	C22	C23	107.5(2)
C5	N1	Pd1	125.52(16)		N3	C23	C22	109.5(2)
C15	N2	Pd1	127.48(16)		N3	C23	C24	125.0(2)
C15	N2	C18	105.64(19)		C24	C23	C22	125.4(2)
C18	N2	Pd1	126.84(15)		C23	C24	C25	117.30(19)
C20	N3	Pd1	126.19(15)		C33	C24	C23	124.4(2)
C20	N3	C23	106.12(18)		C33	C24	C25	118.3(2)
C23	N3	Pd1	127.70(15)		C26	C25	C24	120.6(2)
C33	N4	Pd1	126.12(15)		C32	C25	C24	120.3(2)
C36	N4	Pd1	127.29(15)		C32	C25	C26	119.0(2)
C36	N4	C33	106.55(18)		C25	C26	C27	120.3(2)
C2	C1	P1	119.29(16)		C28	C27	C26	120.3(2)
C2	C1	C36	124.0(2)		C27	C28	C29	117.9(2)

C36	C1	P1	116.61(17)		C31	C28	C27	119.5(2)
N1	C2	C1	125.4(2)		C31	C28	C29	122.5(2)
N1	C2	C3	108.90(19)		O4	C29	O5	124.1(2)
C1	C2	C3	125.7(2)		O4	C29	C28	123.8(2)
C4	C3	C2	107.6(2)		O5	C29	C28	112.1(2)
C3	C4	C5	107.5(2)		C28	C31	C32	120.2(2)
N1	C5	C4	109.4(2)		C31	C32	C25	120.6(2)
C6	C5	N1	127.2(2)		N4	C33	C24	126.8(2)
C6	C5	C4	123.4(2)		N4	C33	C34	109.38(19)
C5	C6	C7	118.3(2)		C24	C33	C34	123.8(2)
C5	C6	C15	124.4(2)		C35	C34	C33	107.4(2)
C15	C6	C7	117.3(2)		C34	C35	C36	107.7(2)
C8	C7	C6	120.6(2)		N4	C36	C1	125.7(2)
C8	C7	C14	119.3(2)		N4	C36	C35	108.96(19)
C14	C7	C6	120.2(2)		C1	C36	C35	125.3(2)
C7	C8	C9	120.5(2)		O3	C39	C40	109.8(2)
C8	C9	C10	120.0(2)		O2	C37	C38	109.2(2)
C9	C10	C11	117.3(2)		Cl3	C1S	Cl2	109.47(14)
C13	C10	C9	119.9(2)		Cl1	C1S	Cl3	110.82(14)
C13	C10	C11	122.7(2)		Cl1	C1S	Cl2	110.29(15)
O6	C11	O7	124.1(2)					

Table S6. Bond Lengths for **PtD(CMP)PP**.

Atom	Atom	Length/Å		Atom	Atom	Length/Å
Pt1	N1	2.017(2)		C7	C14	1.392(4)
Pt1	N2	2.019(2)		C8	C9	1.398(4)
Pt1	N3	2.024(2)		C9	C10	1.392(4)
Pt1	N4	2.016(2)		C10	C11	1.494(4)
P1	O1	1.472(2)		C10	C13	1.386(4)
P1	O2	1.568(2)		C13	C14	1.387(4)
P1	O3	1.583(2)		C15	C16	1.440(4)
P1	C1	1.816(3)		C16	C17	1.350(4)
O2	C37	1.466(3)		C17	C18	1.436(4)
O3	C39	1.457(4)		C18	C19	1.380(4)
O4	C29	1.196(4)		C19	C20	1.375(4)
O5	C29	1.338(4)		C20	C21	1.423(4)
O5	C30	1.452(3)		C21	C22	1.366(4)
O6	C11	1.208(4)		C22	C23	1.438(4)
O7	C11	1.333(3)		C23	C24	1.397(4)
O7	C12	1.455(3)		C24	C25	1.500(4)
N1	C2	1.386(4)		C24	C33	1.388(4)
N1	C5	1.386(3)		C25	C26	1.403(4)
N2	C15	1.377(4)		C25	C32	1.402(4)
N2	C18	1.384(4)		C26	C27	1.389(4)
N3	C20	1.374(4)		C27	C28	1.393(4)
N3	C23	1.378(3)		C28	C29	1.498(4)
N4	C33	1.389(3)		C28	C31	1.390(4)
N4	C36	1.379(4)		C31	C32	1.394(4)
C1	C2	1.403(4)		C33	C34	1.435(4)
C1	C36	1.408(4)		C34	C35	1.346(4)
C2	C3	1.451(4)		C35	C36	1.453(4)
C3	C4	1.337(4)		C37	C38	1.509(4)
C4	C5	1.435(4)		C39	C40	1.506(5)
C5	C6	1.392(4)		Cl1	C1S	1.756(4)

C6	C7	1.507(4)		Cl2	C1S	1.769(3)
C6	C15	1.389(4)		Cl3	C1S	1.753(3)
C7	C8	1.386(4)				

Table S7. Bond Angles for **PtD(CMP)PP**.

Atom	Atom	Atom	Angle/°		Atom	Atom	Atom	Angle/°
N1	Pt1	N2	90.15(9)		O6	C11	C10	123.2(3)
N1	Pt1	N3	179.58(9)		O7	C11	C10	112.3(2)
N2	Pt1	N3	89.81(9)		C10	C13	C14	120.8(3)
N4	Pt1	N1	89.82(9)		C13	C14	C7	119.8(3)
N4	Pt1	N2	178.33(9)		N2	C15	C6	124.8(3)
N4	Pt1	N3	90.23(9)		N2	C15	C16	110.0(3)
O1	P1	O2	115.63(12)		C6	C15	C16	125.2(3)
O1	P1	O3	111.66(12)		C17	C16	C15	107.3(3)
O1	P1	C1	116.66(13)		C16	C17	C18	107.0(3)
O2	P1	O3	102.39(12)		N2	C18	C17	110.2(3)
O2	P1	C1	101.05(12)		C19	C18	N2	125.0(3)
O3	P1	C1	108.02(12)		C19	C18	C17	124.8(3)
C37	O2	P1	120.78(19)		C20	C19	C18	125.9(3)
C39	O3	P1	120.03(19)		N3	C20	C19	125.8(3)
C29	O5	C30	115.9(2)		N3	C20	C21	110.3(2)
C11	O7	C12	115.2(2)		C19	C20	C21	123.9(3)
C2	N1	Pt1	127.80(18)		C22	C21	C20	107.1(3)
C2	N1	C5	106.3(2)		C21	C22	C23	106.9(2)
C5	N1	Pt1	125.95(19)		N3	C23	C22	109.5(2)
C15	N2	Pt1	127.59(19)		N3	C23	C24	125.3(2)
C15	N2	C18	105.5(2)		C24	C23	C22	125.1(3)
C18	N2	Pt1	126.89(18)		C23	C24	C25	117.5(2)
C20	N3	Pt1	126.54(19)		C33	C24	C23	124.5(3)
C20	N3	C23	106.2(2)		C33	C24	C25	117.9(3)
C23	N3	Pt1	127.24(19)		C26	C25	C24	120.9(2)
C33	N4	Pt1	126.02(19)		C32	C25	C24	120.4(2)
C36	N4	Pt1	127.09(18)		C32	C25	C26	118.7(3)
C36	N4	C33	106.9(2)		C27	C26	C25	120.4(3)
C2	C1	P1	119.1(2)		C26	C27	C28	120.5(3)
C2	C1	C36	123.9(3)		C27	C28	C29	118.0(3)

C36	C1	P1	116.9(2)		C31	C28	C27	119.7(3)
N1	C2	C1	125.2(2)		C31	C28	C29	122.4(3)
N1	C2	C3	108.7(2)		O4	C29	O5	124.1(3)
C1	C2	C3	126.1(3)		O4	C29	C28	123.8(3)
C4	C3	C2	107.8(3)		O5	C29	C28	112.1(2)
C3	C4	C5	107.7(2)		C28	C31	C32	120.1(3)
N1	C5	C4	109.5(2)		C31	C32	C25	120.6(3)
N1	C5	C6	126.3(3)		N4	C33	C34	109.0(2)
C6	C5	C4	124.1(3)		C24	C33	N4	126.7(3)
C5	C6	C7	117.7(2)		C24	C33	C34	124.3(3)
C15	C6	C5	125.1(3)		C35	C34	C33	108.0(2)
C15	C6	C7	117.2(3)		C34	C35	C36	107.3(3)
C8	C7	C6	120.3(2)		N4	C36	C1	126.2(2)
C8	C7	C14	119.7(3)		N4	C36	C35	108.8(2)
C14	C7	C6	120.0(2)		C1	C36	C35	125.0(3)
C7	C8	C9	120.4(3)		O2	C37	C38	108.9(3)
C10	C9	C8	119.7(3)		O3	C39	C40	109.6(3)
C9	C10	C11	122.5(3)		Cl1	C1S	Cl2	110.20(17)
C13	C10	C9	119.5(3)		Cl3	C1S	Cl1	111.05(18)
C13	C10	C11	117.9(2)		Cl3	C1S	Cl2	109.51(18)
O6	C11	O7	124.4(3)					

Table S8. Interactions between solvent and porphyrin molecules in the single crystals.

Crystal name	Atoms	H···O distance, Å	C–H···O angle, °
PdDTolPP·CH_2Cl_2	C(1S)–H(1SB)···O(1)	2.374	164.8
PdD(CMP)PP·$CHCl_3$	C(1S)–H(1S)···O(1)	2.083	165.4
PtD(CMP)PP·$CHCl_3$	C(1S)–H(1S)···O(1)	2.084	165.4
		distance, Å*	
PdD(CMP)PP·$CHCl_3$	Cl(1)…O(4)[1]	3.175	
	Cl(3)…O(2)[2]	3.249	
	Cl(3)…C(3)[2]	3.377	
PtD(CMP)PP·$CHCl_3$	Cl(1)…O(4)[3]	3.186	
	Cl(3)…O(2)[4]	3.247	
	Cl(3)…C(3)[4]	3.379	

[1] 2-x, -y, 2-z. [2] 1-x, 1-y, 2-z. [3] 1-x, -y, 1-z. [4] -x, 1-y, 1-z. * The contacts shorter than sum of Bondi vdW radii (R_{vdW}(Cl) + R_{vdW}(O) = 3.27 Å, R_{vdW}(Cl) + R_{vdW}(C) = 3.45 Å the shortest radii known)

1.5.1. Crystal packing

The crystal packing of **PdDTolPP·CH_2Cl_2**, **PdD(CMP)PP·$CHCl_3$** and **PtD(CMP)PP·$CHCl_3$** is formed by π-π interaction between porphyrin molecules (Figure S59, Table S9). The phosphoryl groups of contacting molecules point out in opposite directions. The N_4 plane–plane distances, centroid–centroid distances and shift distances are presented in the Table S9. The specified interatomic C–C and C–N contacts are listed in the Table S10.

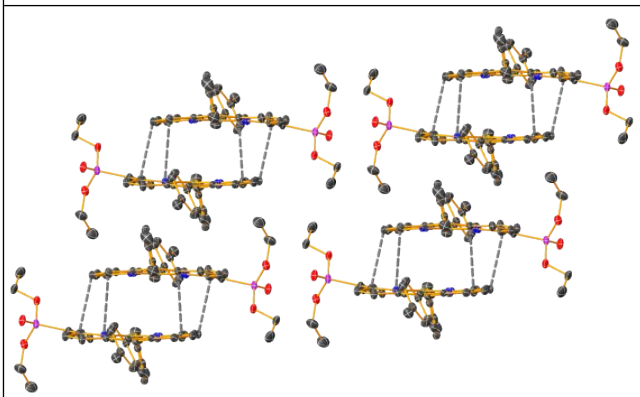
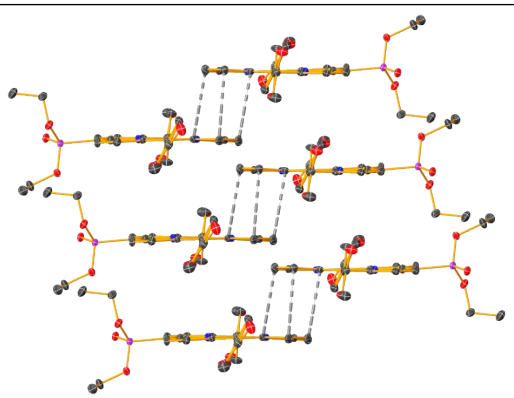
PdDTolPP·CH_2Cl_2	**PdD(CMP)PP·$CHCl_3$** and **PtD(CMP)PP·$CHCl_3$***
	

Figure S75. Crystal packing of complexes **PdDTolPP**, **PdD(CMP)PP** and **PtD(CMP)PP**. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms and solvent molecules are omitted for clarity. * **PdD(CMP)PP·$CHCl_3$** and **PtD(CMP)PP·$CHCl_3$** are isostructural and have the same packing.

Table S9. π–π interaction in single crystals.

$N_4 \ldots N_4^n$	Plane–plane distance, Å	Centroid–centroid distance, Å	Shift distance, Å
PdDTolPP (n=1)	3.409	3.727	1.506
PdD(CMP)PP (n=2)	3.311	6.262	5.315
PtD(CMP)PP (n=3)	3.303	6.297	5.361

[1] 1-x, 1-y, 1-z. [2] 2-x, 1-y, 1-z. [3] 1-x, 1-y, -z

Table S10. C···C, C···N contacts between π–π stacked porphyrins.

	distance Å		distance Å
PdDTolPP			
C2–C20[1]	3.298	C34–C17[1]	3.539
C5–C21[1]	3.579	N4–C17[1]	3.355
N1–C21[1]	3.687	C32–C16[1]	3.526
C3–C20[1]	3.655	C33–C16[1]	3.607
C34–C18[1]	3.253	C31–C16[1]	3.634
PdD(CMP)PP			
C21–C15[2]	3.397	C23–C17[2]	3.514
C20–C18[2]	3.391	N3–C18[2]	3.557
C22–C16[2]	3.438	N3–C17[2]	3.558
C20–N2[2]	3.503		
PtD(CMP)PP			
C21–C15[3]	3.414	C23–C17[2]	3.513
C20–C18[2]	3.380	N3–C18[2]	3.555
C22–C16[2]	3.441	N3–C17[2]	3.560
C20–N2[2]	3.511		

[1] 1-x, 1-y, 1-z. [2] 2-x, 1-y, 1-z. [3] 1-x, 1-y, -z

In the structures of **PdD(CMP)PP·CHCl$_3$** and **PtD(CMP)PP·CHCl$_3$** other short contacts between porphyrin molecules have been found that also can influence the packing. The ethyl group of phosphoryl substituent is oriented toward the ring of adjacent porphyrin like it was observed earlier in the crystal structure of Pt(II) complex with diethoxyphosphorylporphyrin.[1] In [1] it was shown that such orientation of ethoxy group can determine the final supramolecular arrangement in the crystal. In the case of **PdD(CMP)PP·CHCl$_3$** and **PtD(CMP)PP·CHCl$_3$** such orientation gives H···M contacts which are shorter than sum of VDW radii[2]

(**PdD(CMP)PP·CHCl$_3$** H(38C)^{1}···Pd(1) 3.128 Å, **PtD(CMP)PP·CHCl$_3$** H(38C)^{2}···Pt(1) 3.170 Å, ^{1} 2-x, 1-y, 2-z, ^{2} 1-x, 1-y, 1-z). Moreover the presence of phenyl-methoxycarbonyl groups in *meso*-positions leads to the formation of supramolecular dimers due to C_β–H···O hydrogen bonds (**PdD(CMP)PP·CHCl$_3$** O(6)···H(17)^{1} = 2.546 Å, C(17)^{1}–H(17)^{1}···O(6) angle = 127.4º, **PtD(CMP)PP·CHCl$_3$** O(6)···H(17)^{2} 2.539 Å, C(17)^{2}–H(17)^{2}···O(6) angle = 128.1º , ^{1} 1-x, 2-y, 1-z, ^{2} -x, 2-y, -z).

2. Photophysical properties

Table S11. Photophysical properties of the Pd(II) complexes with mono-phosphorylated and corresponding non-phosphorylated porphyrins in toluene.

Dye	λ_{max} abs (ε 10^{-3}), nm (M^{-1} cm^{-1})	λ_{max} em (nm)[a]	ϕ_{em}[b]	τ (μs)	λ_{max} em (77 K) (nm)[c]	τ (77 K) (μs)[c]	E_T[a], (cm^{-1})[d]
PdTMesPP	415 (239), 527 (19), 560 (19)	701	4.1	858	690, 767	1240	14490
PdDMesPP	408 (219), 522 (17), 555 (21)	692	3.4	770	685, 763	1400	14600
PdDTolPP	409 (208); 523 (19); 556 (23)	696, 765(sh.)	4.3	640[e]	684, 762	1465	14620
PdD(CMP)PP	409 (204); 522 (18); 556 (21)	692, 767(sh.)	5.8	633[e]	682, 761	1539	14660
PdTMesP	412 (251), 519 (23), 550 (5)	684	7	675	673,749	1400	14860
PdDMesP	405 (214), 514 (20), 546 (9)	669	4.3	695	663,738	1550	15080
PdDTolP	406 (313); 514 (27); 545 (9)	671, 739(sh.)	5.1	640	664, 738	1632	15060
PdD(CMP)P	407 (94); 514 (9); 546 (3)	664, 738(sh.)	9.1	880	661, 735	1820	15130
$PdF_{20}TPP$[h]	407, 553	670	3	900	-	-	-

[a] Measured using a diluted solutions in toluene at 298 °C, deoxygenated by nitrogen bubbling. [b] The absolute emission quantum yields were determined with an integrating sphere. [c] Measured in frozen glasses (toluene:tetrahydrofuran 4:6, v/v). [d] Calculated from the emission spectra at 77 K. [e] The values might be underestimated. [g] Non mono-exponential signal with much longer component (1.56 ms) present. [h] Data are taken from ref. [3]

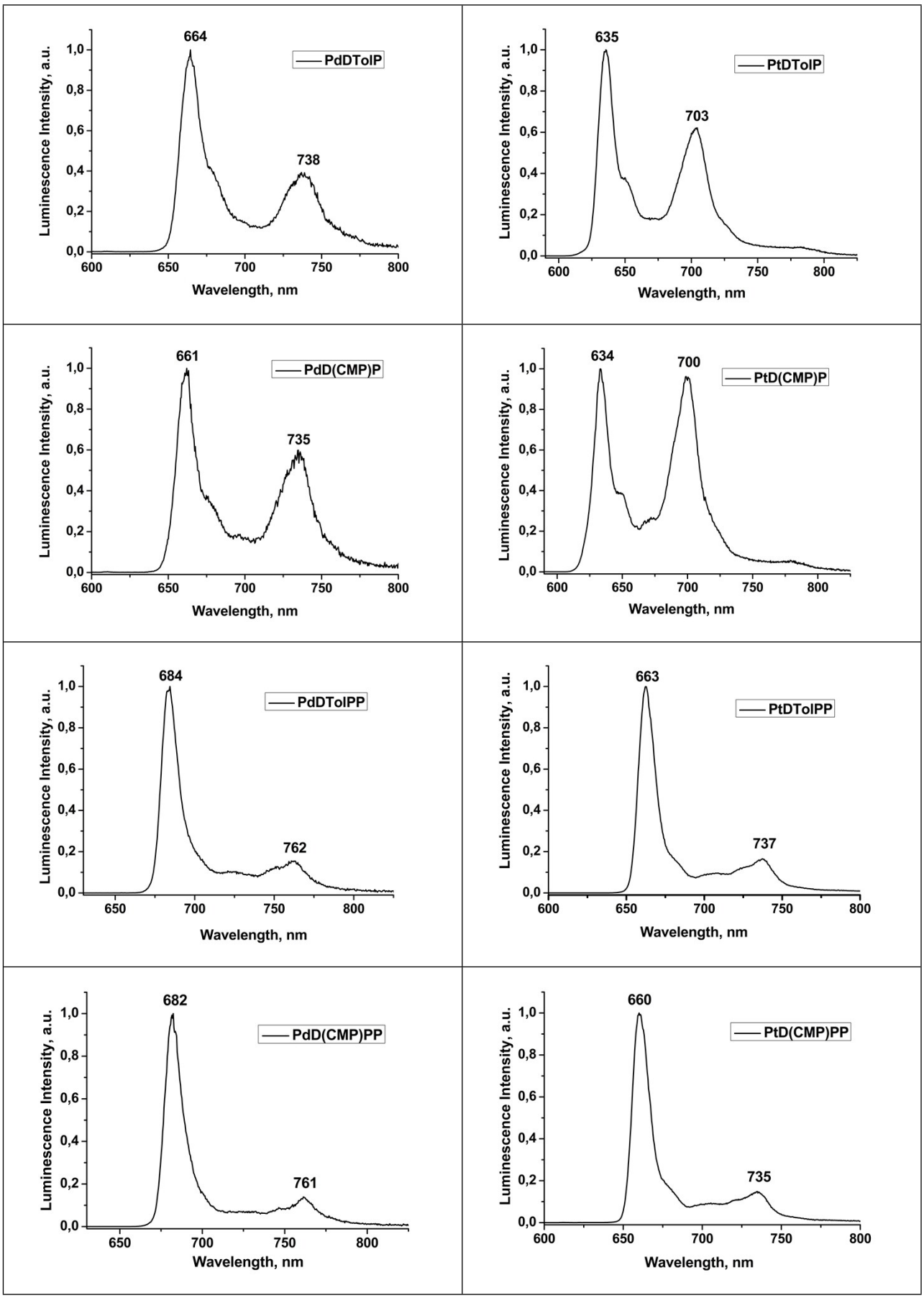


Figure S76. Emission spectra of the investigated Pd(II) and Pt(II) complexes in frozen glasses (toluene/tetrahydrofuran 4:6, v/v) at 77K.

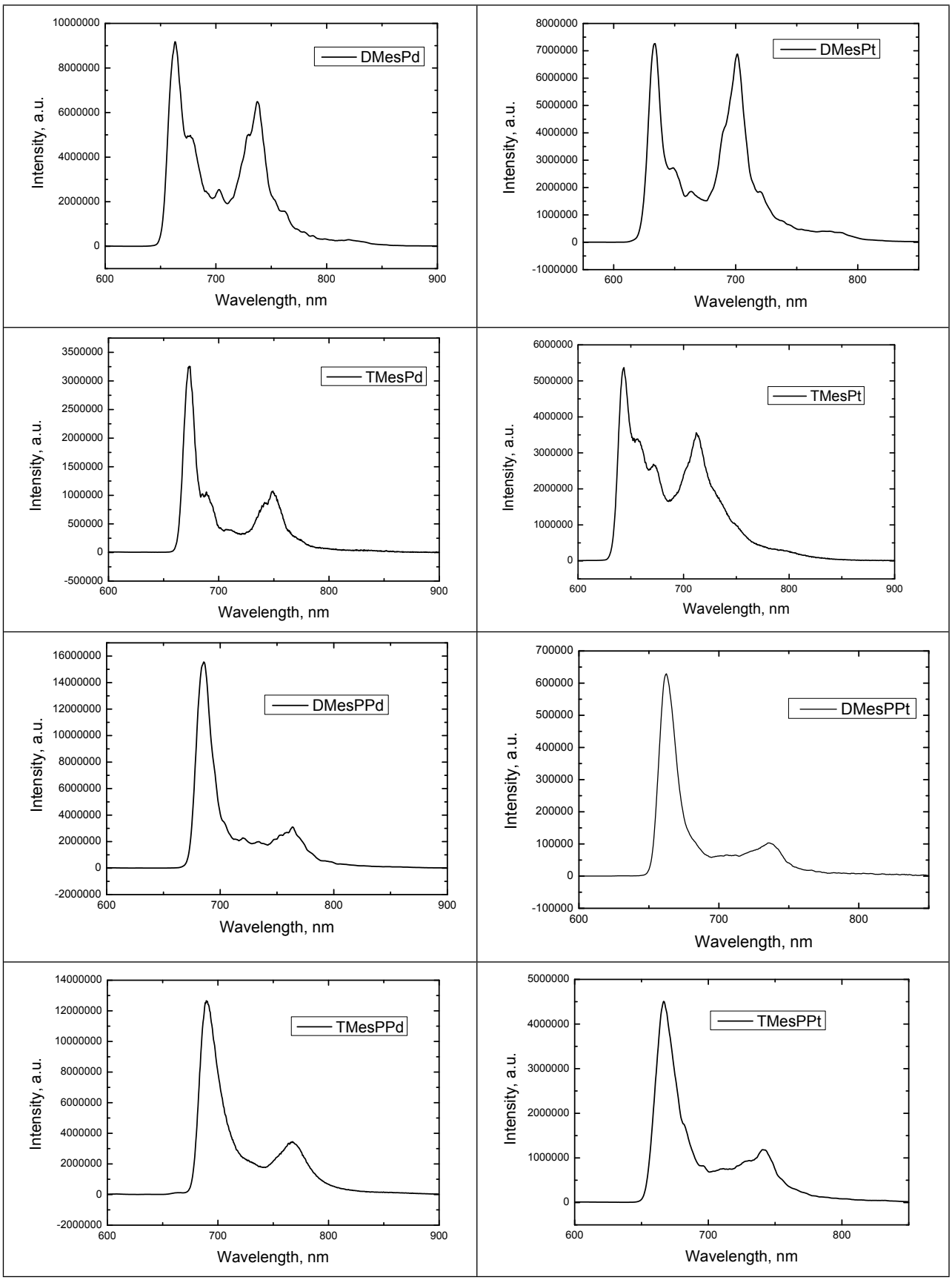


Figure S 77. Emission spectra of the investigated Pd(II) and Pt(II) complexes in frozen glasses (toluene: tetrahydrofuran 4:6, v/v) at 77K.

3. Quenching by Molecular Oxygen

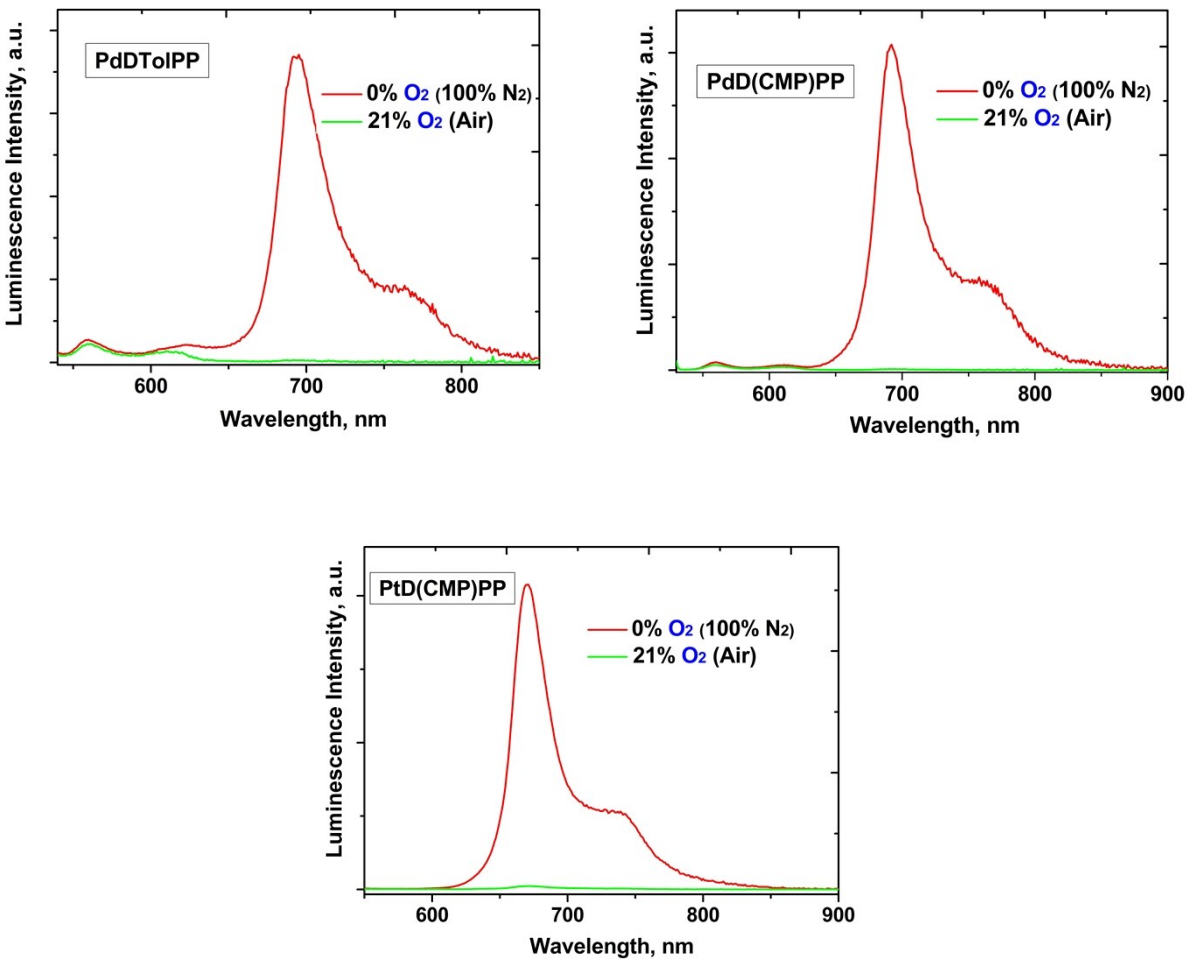


Figure S78. Luminescence spectra of the investigated **PdDTolPP**; **PdD(CMP)PP** and **PtD(CMP)PP** complexes in toluene at 298 K in the absence and in the presence of oxygen.

4. Photodegradation studies

4.1. Optical emission spectrum of the 400 W tungsten lamp

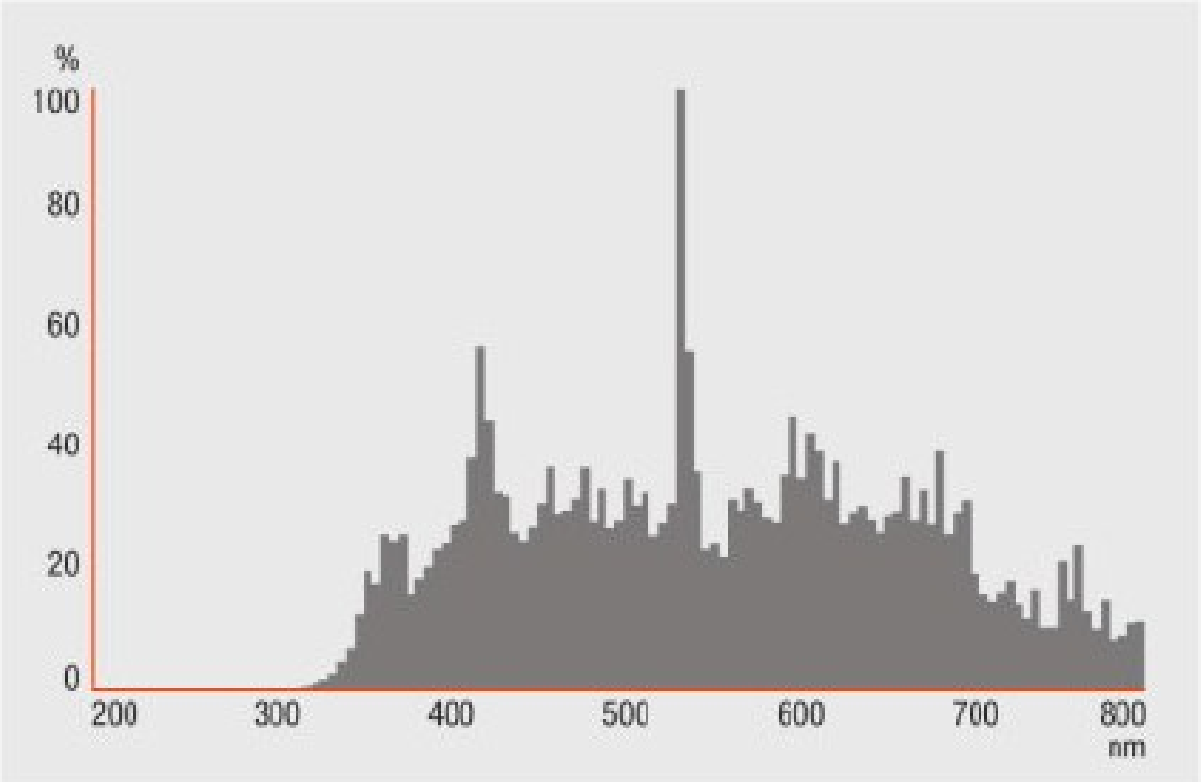


Figure S79. Optical emission spectrum of the 400 W Powerstat HQI BT MM (Osram) tungsten lamp used for the photobleaching studies (picture provided by the courtesy of the manufacturer).

4.2. Photodegradation studies of platinum and palladium porphyrins under vis–NIR irradiation in air

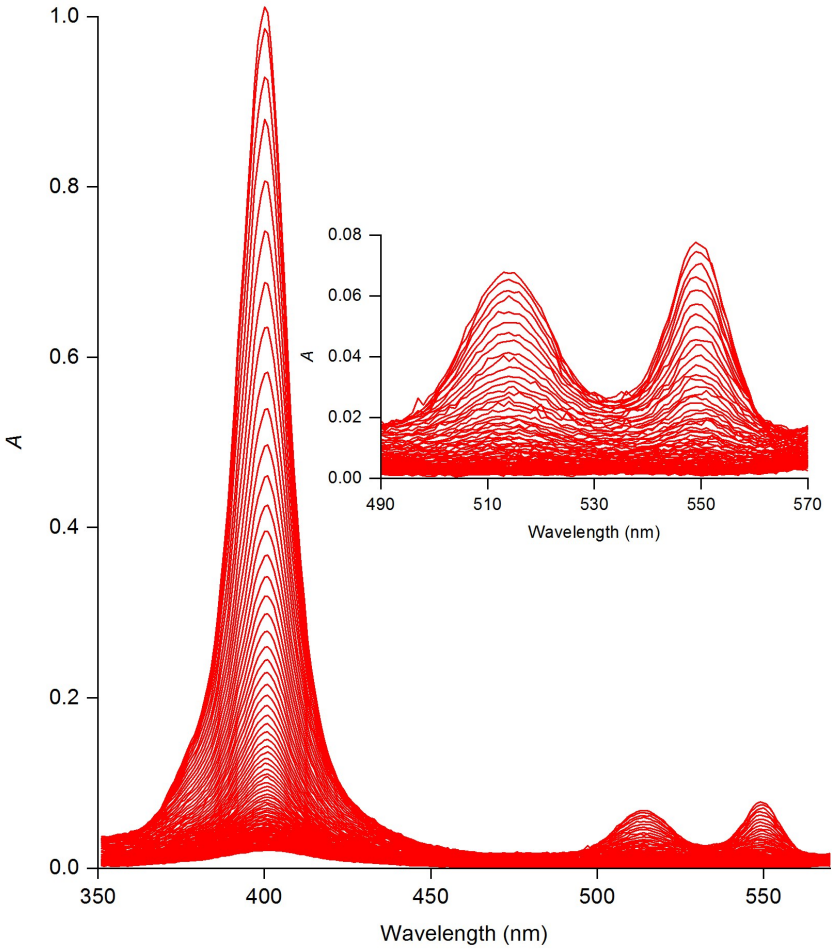


Figure S80. Time-dependent evolution of the electronic absorption spectrum of **PtTMesPP** in DMF (c = 5 μM) recorded at 25.0(5) °C during the vis–NIR irradiation with an Osram Powerstat HQI BT MM 400 W tungsten lamp. Spectra 1–100: t = 0–5940 min with Δt = 60 min.

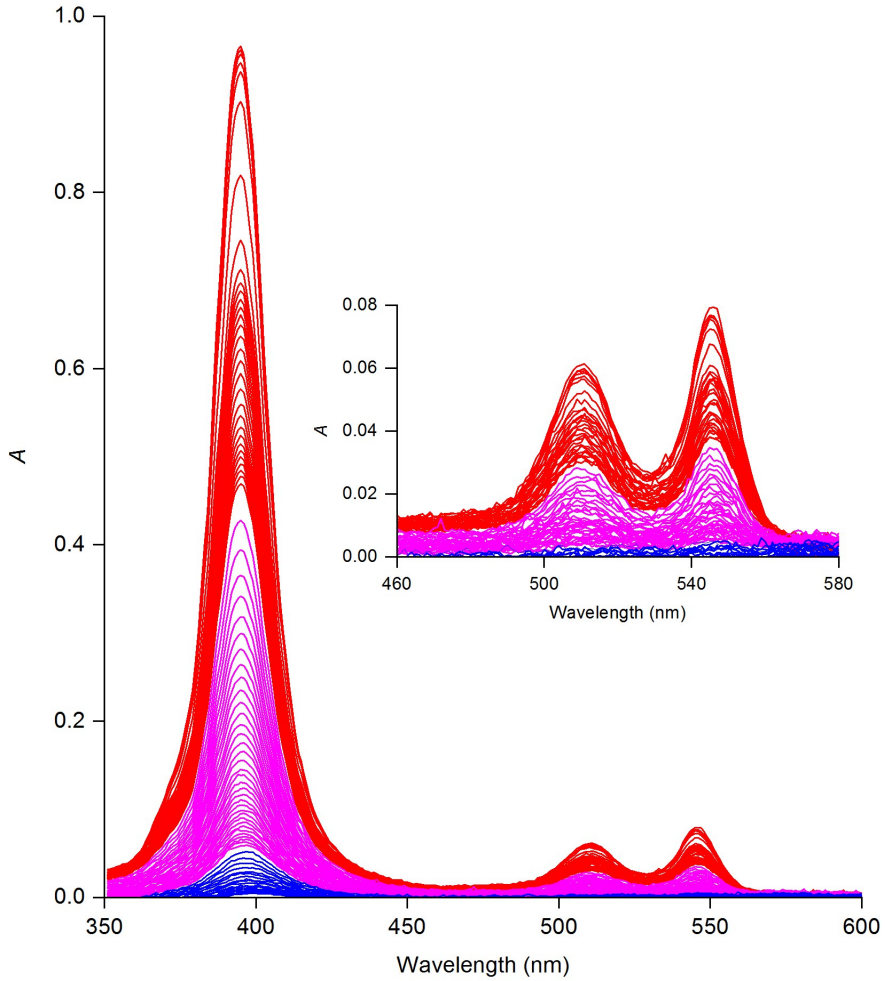


Figure S81. Time-dependent evolution of the electronic absorption spectrum of **PtDTolPP** in DMF (c = 5 μM) recorded at 25.0(5) °C during the vis–NIR irradiation with an Osram Powerstat HQI BT MM 400 W tungsten lamp. Color code: spectra 1–31 (red): t = 0–300 min with Δt = 10 min; spectra 32–66 (magenta): t = 360–2400 min with Δt = 60 min; spectra 67–89 (blue): t = 2400–7000 min with Δt = 200 min.

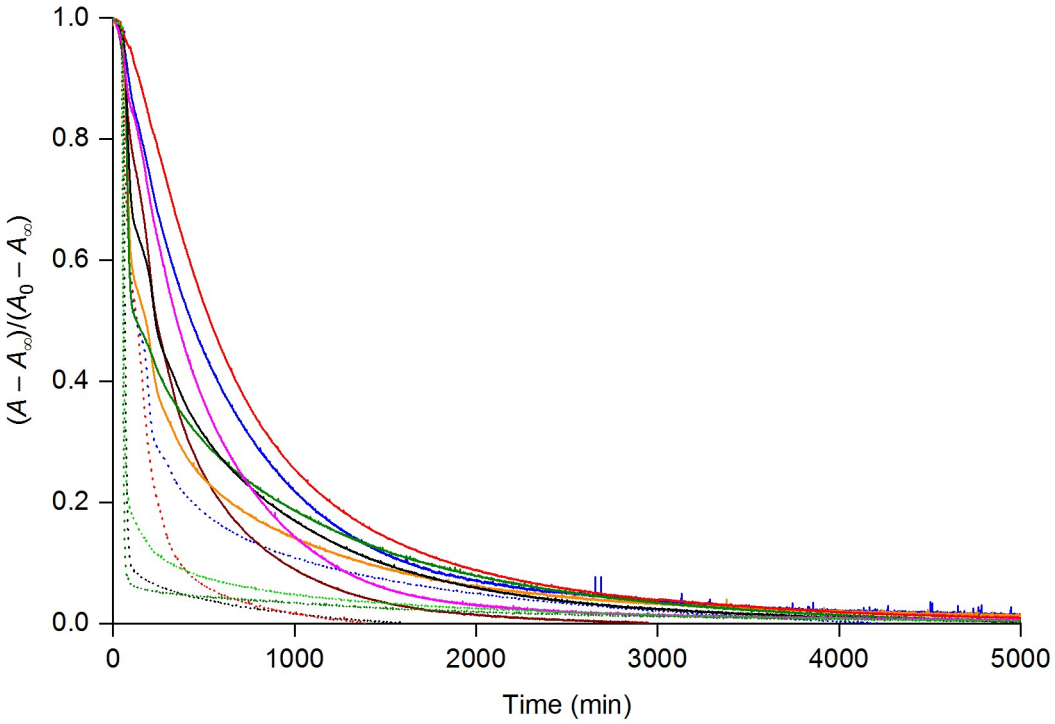


Figure S82. Photodegradation of platinum(II) (solid lines) and palladium(II) (dashed lines) porphyrins (c = 5 μM) in DMF at 25.0(5) °C under vis–NIR irradiation with an Osram Powerstat HQI BT MM 400 W tungsten lamp. Color code: **DTolP** (brown), **DTolPP** (orange), **D(CMP)PP** (dark green), **DMesP** (magenta), **DMesPP** (black), **TMesP** (blue), **TMesPP** (red), **F_{20}TPP** (light green).

4.3. Pseudo-first order rate analysis of the photobleaching data for platinum porphyrins in DMF

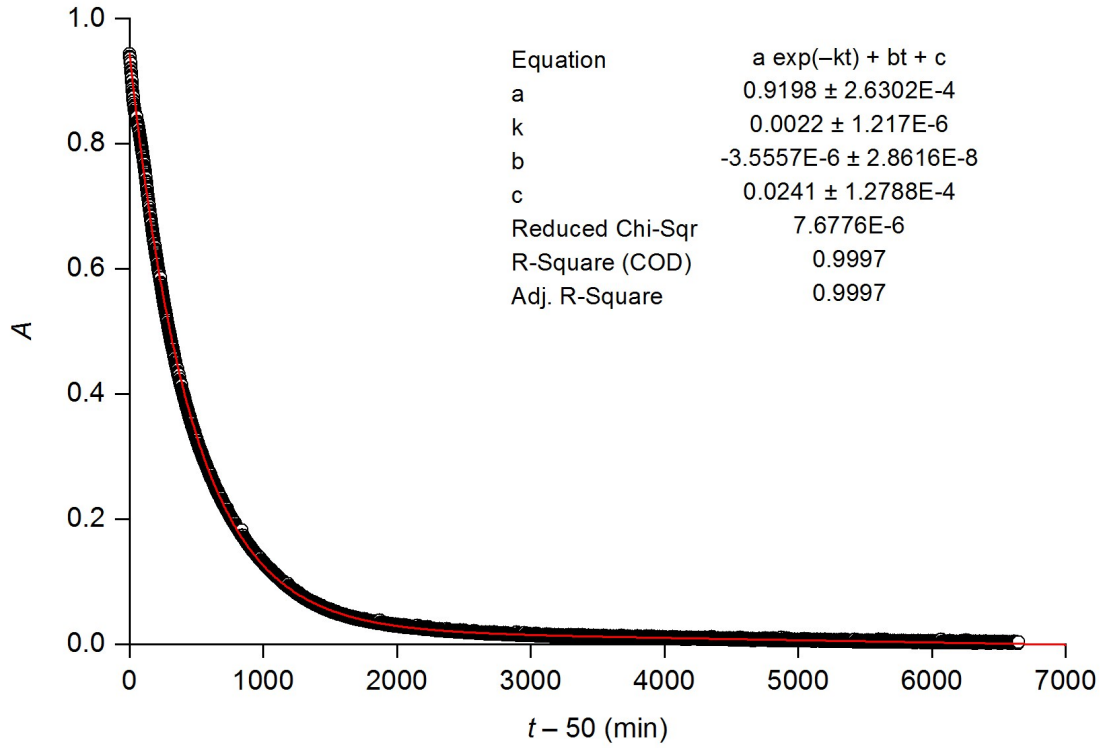


Figure S83. Photodegradation kinetics monitored at λ = 391 nm of **PtDMesP** (c = 5 μM) in DMF at 25.0(5) °C under vis–NIR irradiation with an Osram Powerstat HQI BT MM 400 W tungsten lamp. Experimental points are represented as open circles (1 point/min). The reaction times have been shifted by 50 min to eliminate the first 50 points corresponding to the induction period. The red line corresponds to the best-fitted monoexponential decay curve obtained by unweighted nonlinear least squares.

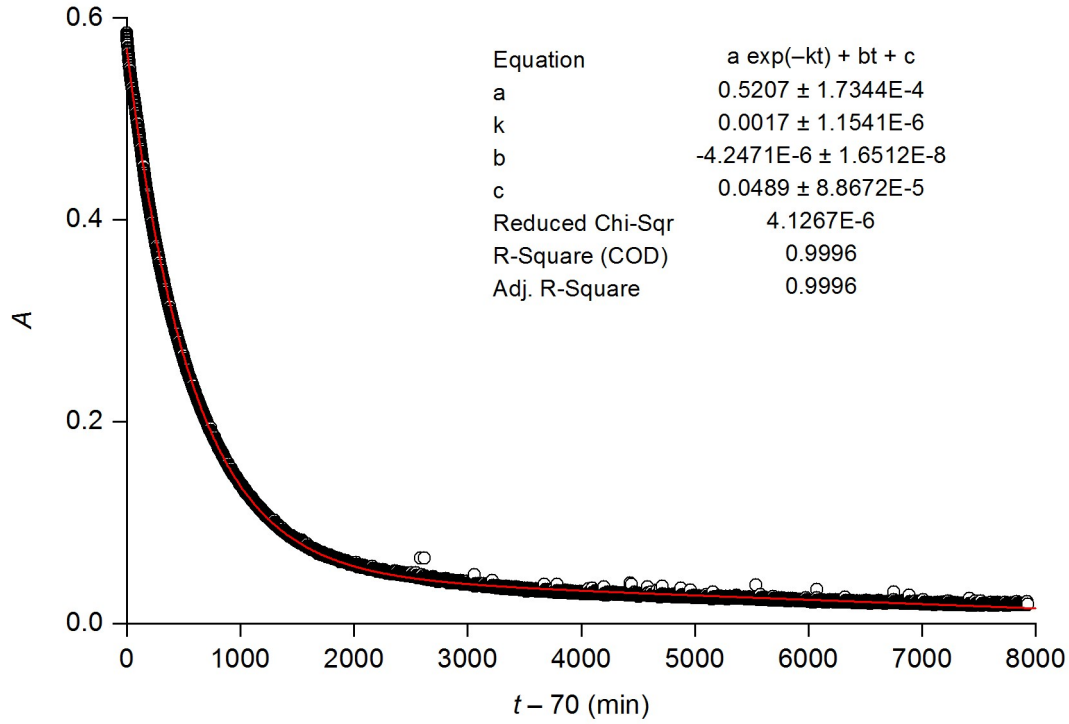


Figure S84. Photodegradation kinetics monitored at λ = 396 nm of **PtTMesP** (c = 5 μM) in DMF at 25.0(5) °C under vis–NIR irradiation with an Osram Powerstat HQI BT MM 400 W tungsten lamp. Experimental points are represented as open circles (1 point/min). The reaction times have been shifted by 70 min to eliminate the first 70 points corresponding to the induction period. The red line corresponds to the best fitted monoexponential decay curve obtained by unweighted nonlinear least squares.

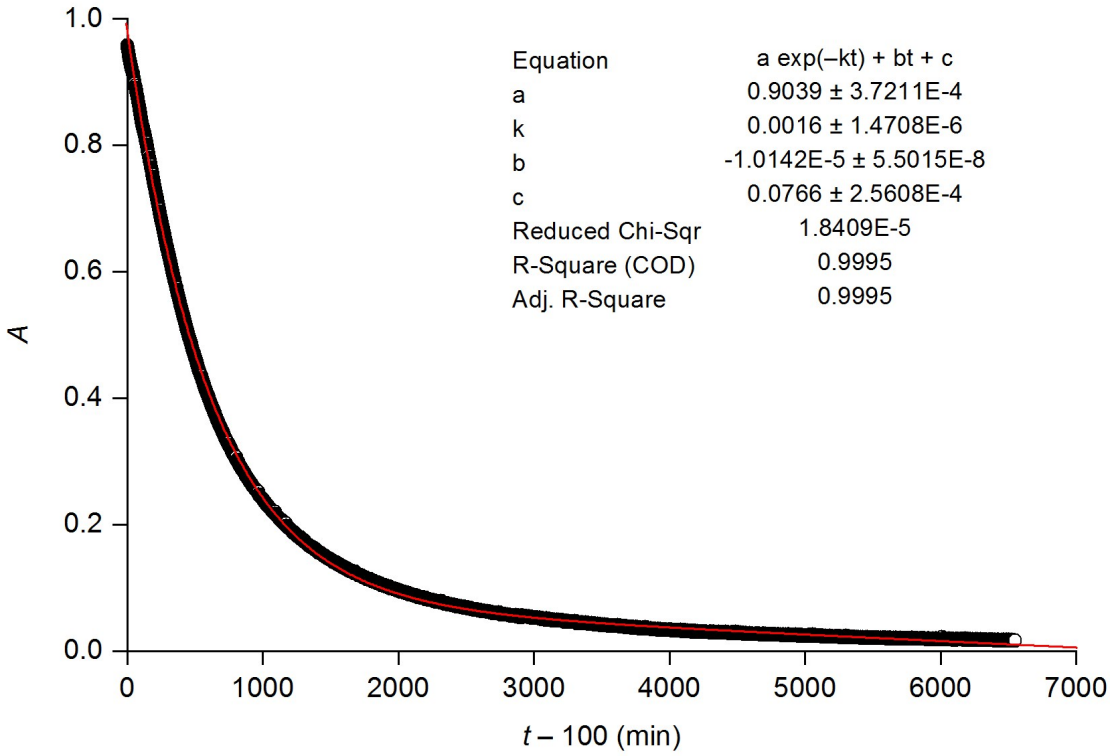


Figure S85. Photodegradation kinetics monitored at λ = 400 nm of **PtTMesPP** (c = 5 μM) in DMF at 25.0(5) °C under vis–NIR irradiation with an Osram Powerstat HQI BT MM 400 W tungsten lamp. Experimental points are represented as open circles (1 point/min). The reaction times have been shifted by 100 min to eliminate the first 100 points corresponding to the induction period. The red line corresponds to the best fitted monoexponential decay curve obtained by unweighted nonlinear least squares.

4.4. Long-Term Photodegradation study under ambient light

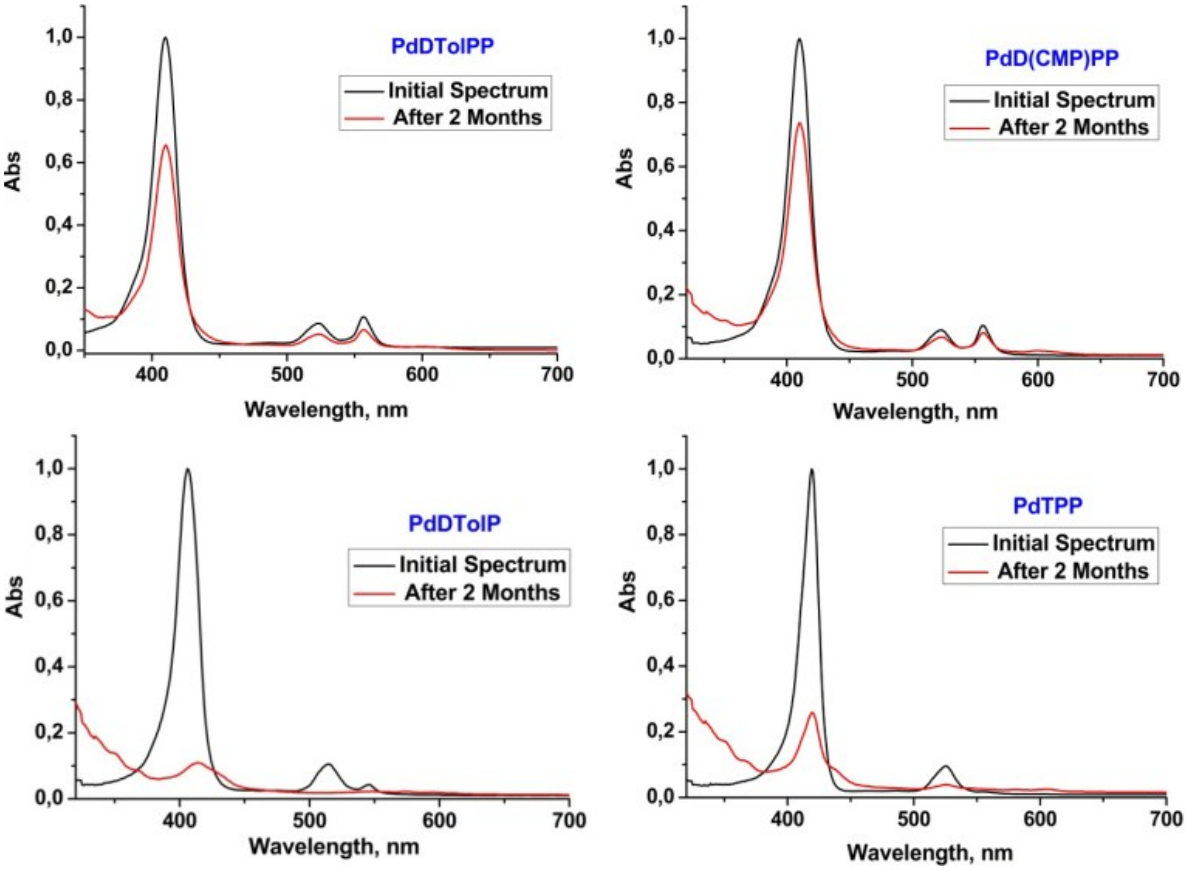


Figure S86. Absorption spectra during photodegradation of Pd(II) porphyrin complexes under ambient light in air-saturated toluene solutions.

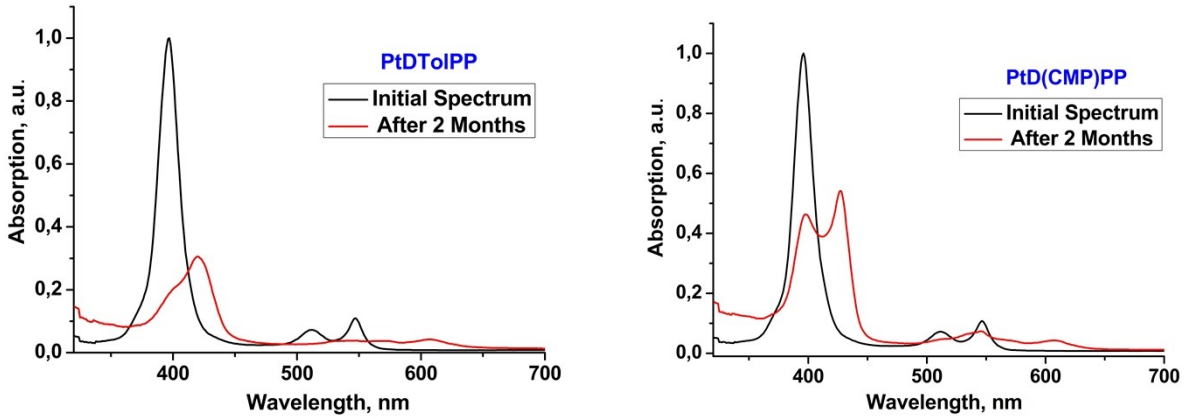


Figure S87. Absorption spectra during photodegradation of of Pt(II) phosphorylporphyrin complexes under ambient light in air-saturated toluene solutions.

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