Electronic Supplementary Information

Porphyrin(2.1.2.1) Organopalladium Complexes as Efficient Singlet Oxygen Sensitizers

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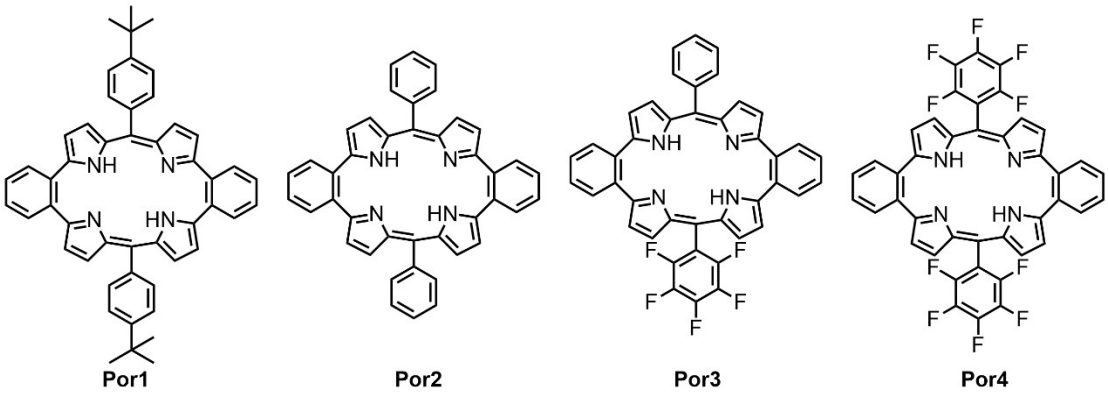

Figure S1. Molecular structures of **Por1**-**Por4**.

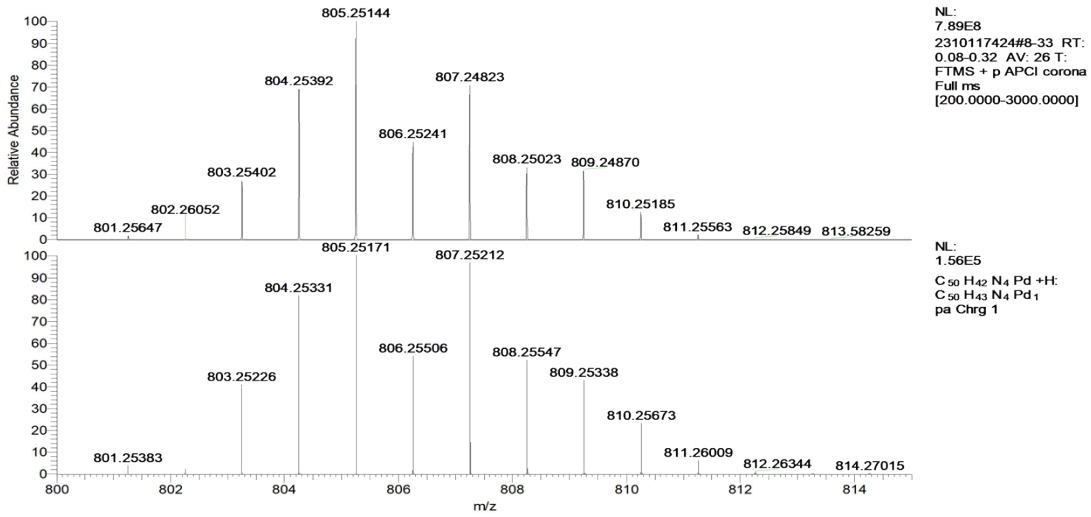

Figure S2. HR-APCI-MS spectrum of **Pd1**.

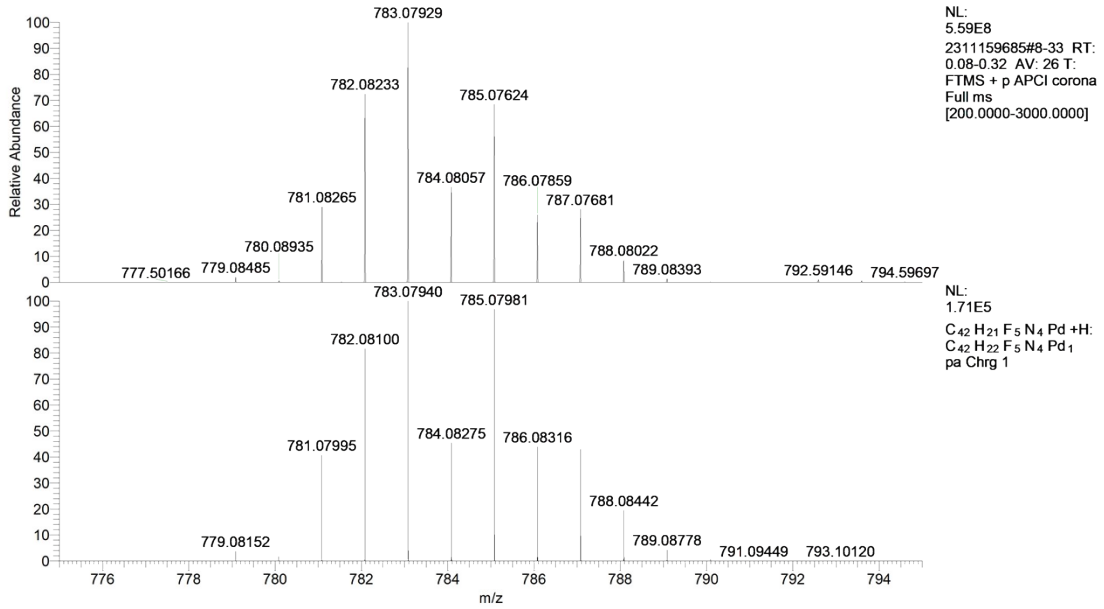

Figure S3. HR-APCI-MS spectrum of **Pd3**.

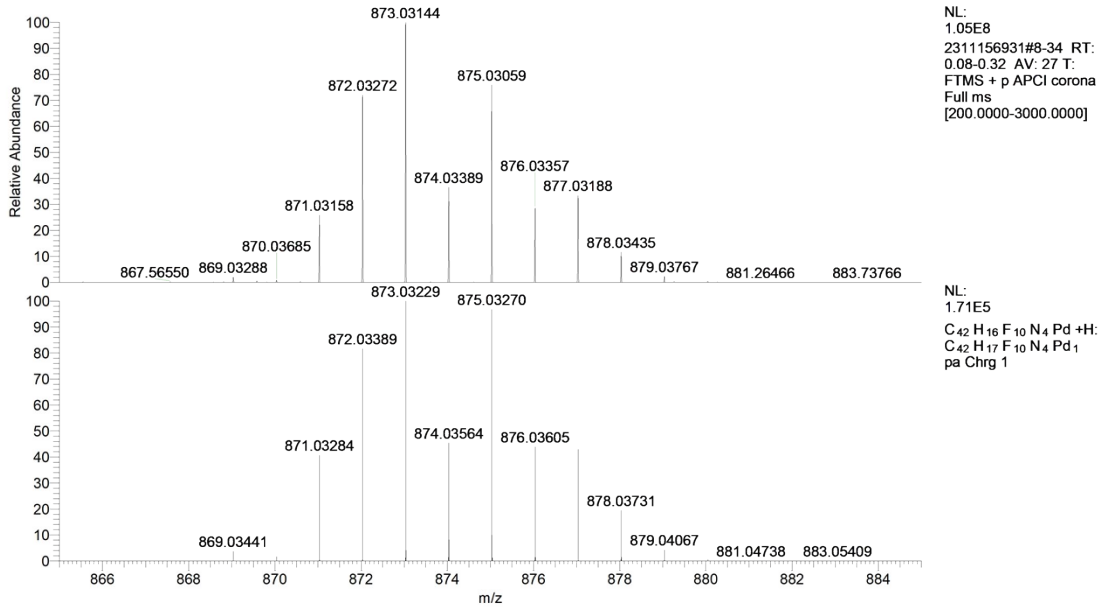

Figure S4. HR-APCI-MS spectrum of **Pd4**.

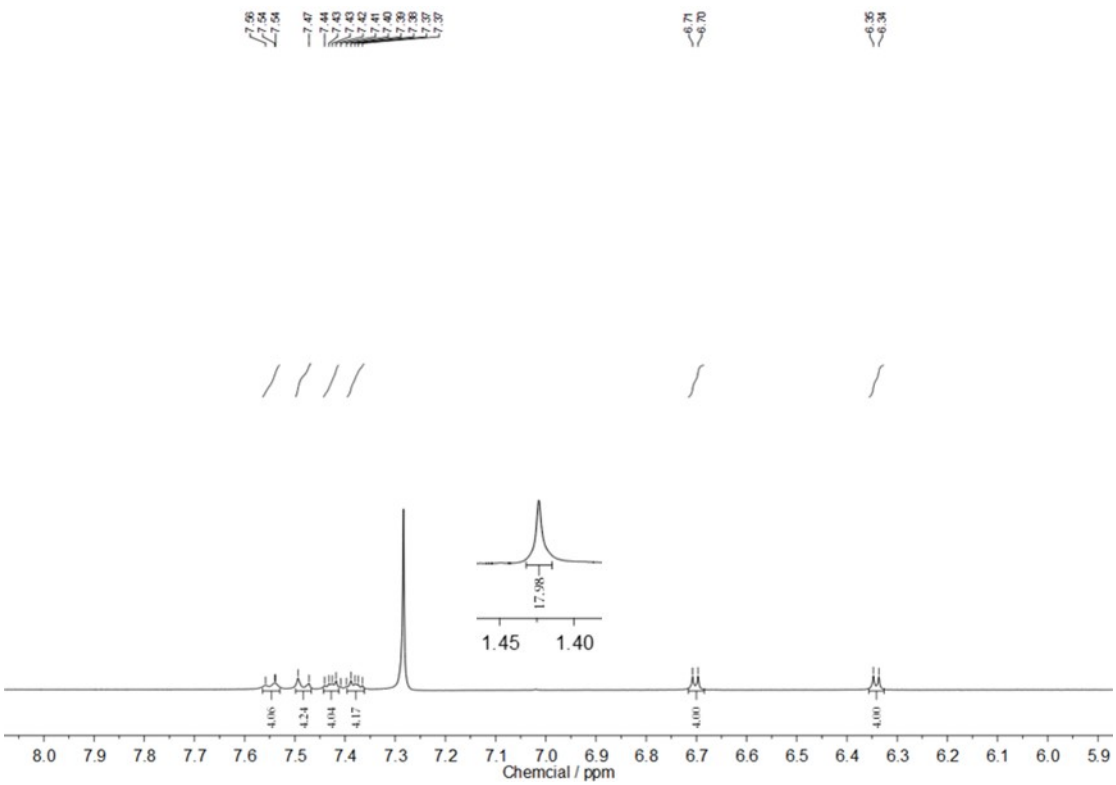

Figure S5. ^{1}H NMR spectrum of **Pd1** recorded at 298 K in $CDCl_3$.

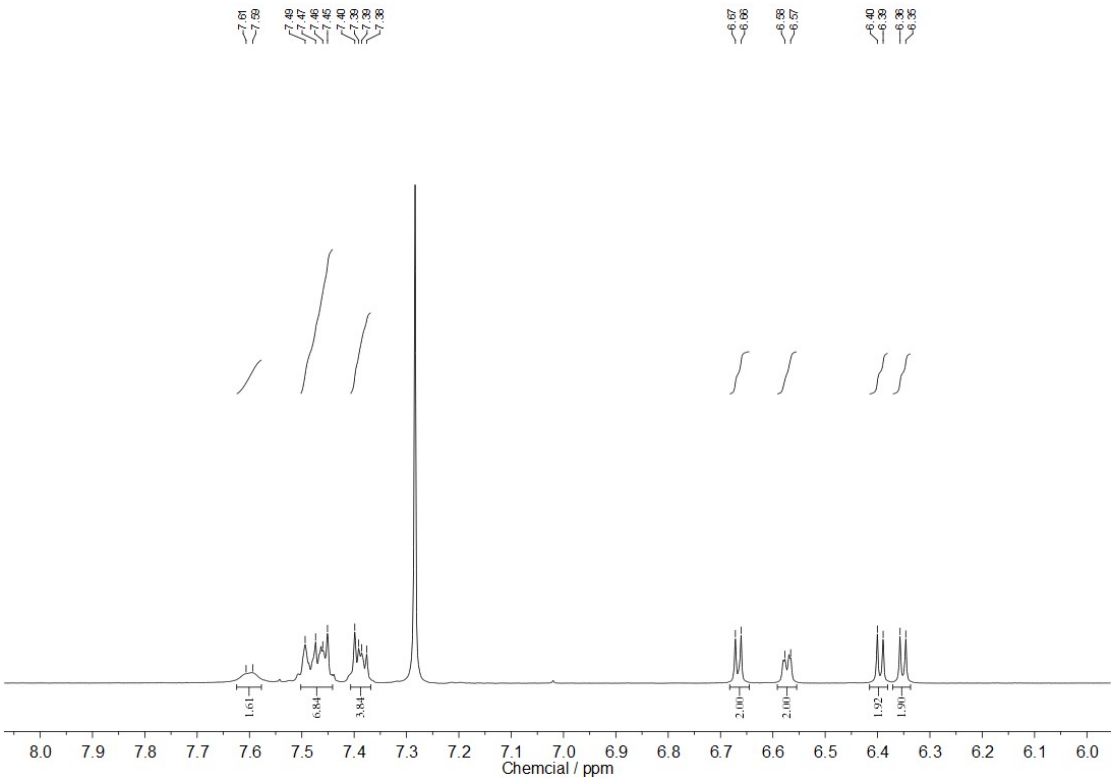

Figure S6. ^{1}H NMR spectrum of **Pd3** recorded at 298 K in $CDCl_3$.

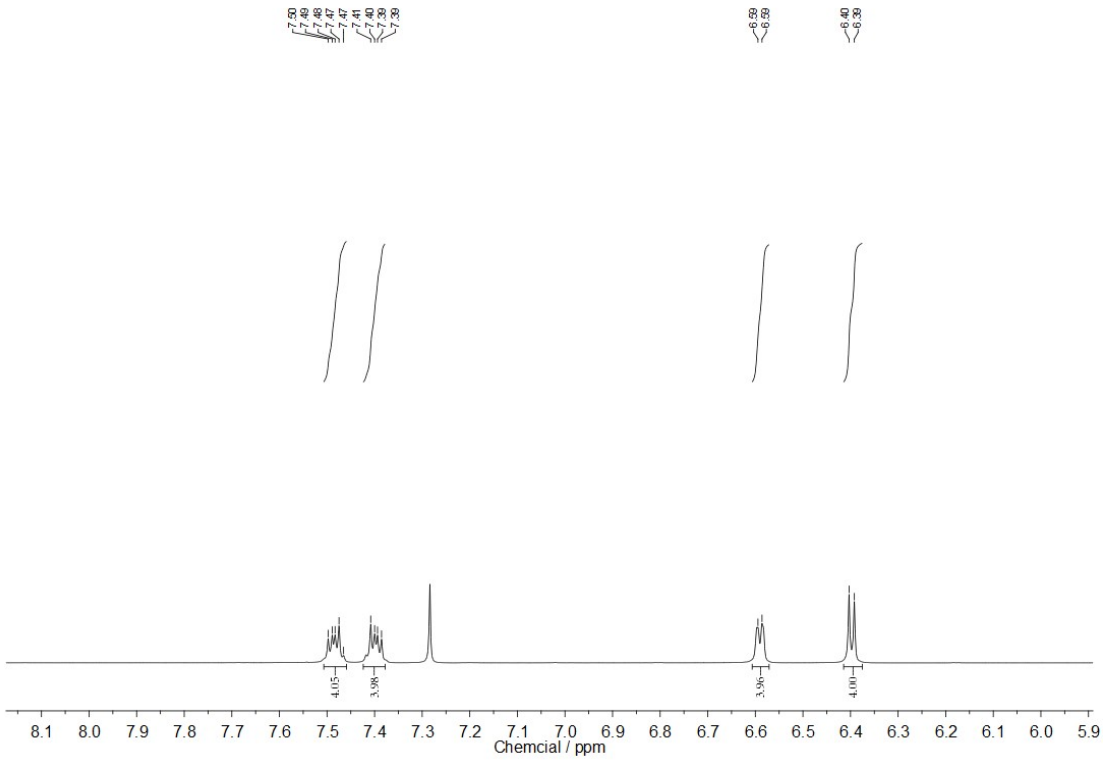

Figure S7. ^{1}H NMR spectrum of **Pd4** recorded at 298 K in $CDCl_3$.

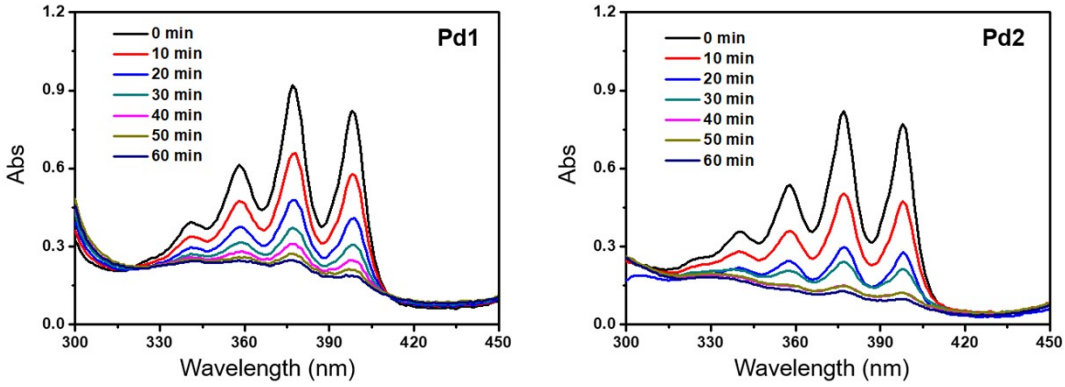

Figure S8. Obtained absorption spectra to calculate singlet oxygen quantum yields of **Pd3** and **Pd4** in acetonitrile.

Table S1. Singlet oxygen quantum yields (Φ) of Pd complexes by comparison with the $[Ru(bpy)_3]Cl_2$ under blue light irradiation.

Complexes	Φ ($^1O_2$)
$[Ru(bpy)_3]^{2+}$	0.57
Pd4	0.54
Pd3	0.56
Pd2	0.42
Pd1	0.41

2. Crystal data

Table S2. Crystal data of **Pd1**.

Empirical formula	$C_{50}H_{42}N_4Pd$
Formula weight	805.27
Temperature/K	300.00
Crystal system	monoclinic
Space group	P21/n
a/Å	15.6620(7)
b/Å	12.2502(5)
c/Å	42.765(2)
α/°	90
β/°	93.497(3)
γ/°	90
Volume/Å^3	8189.7(6)
Z	8
ρcalcg/cm^3	1.306
μ/mm^{-1}	3.948
F(000)	3328.0
Crystal size/mm^3	0.1 × 0.09 × 0.08
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.9 to 127.37
Index ranges	$-18 \leq h \leq 18$, $-14 \leq k \leq 14$, $-49 \leq l \leq 49$
Reflections collected	94131
Independent reflections	13456 [R_{int} = 0.1974, R_{sigma} = 0.1044]
Data/restraints/parameters	13456/1887/1282
Goodness-of-fit on F^2	1.373
Final *R* indexes [$I>=2\sigma(I)$]	R_1 = 0.1578, wR_2 = 0.3885
Final *R* indexes [all data]	R_1 = 0.2393, wR_2 = 0.4709
Largest diff. peak/hole / e Å^{-3}	3.30/-1.01

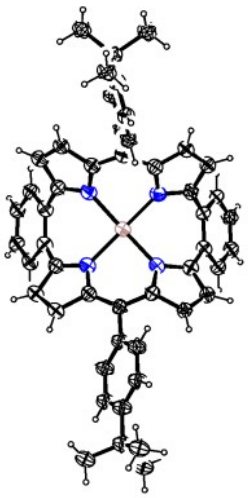

Figure S9 Crystal structure of **Pd1**. The thermal ellipsoids represent for 30% probability.

Table S3. Crystal data of **Pd4**.

Empirical formula	$C_{56}H_{32}F_{10}N_4Pd$

Formula weight	1057.25
Temperature/K	193.00
Crystal system	monoclinic
Space group	C2/c
a/Å	26.8686(7)
b/Å	23.8617(6)
c/Å	14.1565(4)
α/°	90
β/°	103.2470(10)
γ/°	90
Volume/Å^3	8834.7(4)
Z	8
*ρ*calcg/cm^3	1.590
μ/mm^{-1}	0.509
F(000)	4256.0
Crystal size/mm^3	0.12 × 0.1 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.516 to 54.978
Index ranges	$-34 \leq h \leq 34$, $-30 \leq k \leq 30$, $-18 \leq l \leq 18$
Reflections collected	81308
Independent reflections	10138 [R_{int} = 0.1209, R_{sigma} = 0.0611]
Data/restraints/parameters	10138/0/642
Goodness-of-fit on F^2	1.064
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0428, wR_2 = 0.0828
Final *R* indexes [all data]	R_1 = 0.0679, wR_2 = 0.1011
Largest diff. peak/hole / e Å^{-3}	0.50/-0.49

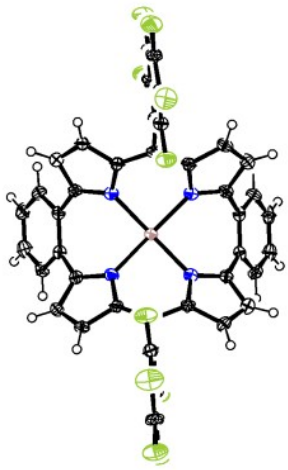

Figure S10. Crystal structure of **Pd4**. The thermal ellipsoids represent for 50% probability.

3. Cartesian coordinates

Pd1 at ground state
Total energy: E = -2275.06544807 a.u.

C	1.42180800	-1.63112400	2.70345100

C	-1.61470300	-1.71244100	2.59507900
N	-1.48898900	-1.21965200	1.35607400
C	-2.50849600	-0.29901600	1.16900800
C	-3.26491600	-0.20630000	2.37117200
C	-2.71954500	-1.10910200	3.25393900
C	2.38881400	-0.91387800	3.45635200
C	2.98053600	-0.01796400	2.59494800
C	2.40991300	-0.24516400	1.31108500
N	1.42510600	-1.21671900	1.43013500
C	0.61335300	-2.73827200	3.22916900
C	-0.79178200	-2.78031800	3.17241600
N	1.48899000	-1.21965900	-1.35607200
C	2.50849700	-0.29902200	-1.16901000
C	3.26491700	-0.20631100	-2.37117400
C	2.71954600	-1.10911600	-3.25393800
C	-2.38881300	-0.91389100	-3.45635100
C	-2.98053500	-0.01797300	-2.59495100
C	-2.40991300	-0.24516900	-1.31108700
N	-1.42510600	-1.21672500	-1.43013300
C	-1.42180800	-1.63113400	-2.70344700
C	1.61470300	-1.71245200	-2.59507500
C	-1.29663200	-3.76436300	-3.89649200
C	-0.61335300	-2.73828500	-3.22916100
C	0.79178200	-2.78033100	-3.17240800
C	1.46310100	-3.85027500	-3.78128900
C	-2.89441900	0.21969100	-0.07833600
C	2.89442000	0.21969000	0.07833200
C	-3.97893800	1.23407300	-0.07323300
C	3.97893900	1.23407200	0.07322600
C	-0.61883700	-4.82571400	-4.48178800
C	0.77174900	-4.86940000	-4.42242700
C	-3.77770300	2.46563500	0.56241800
C	-4.77878500	3.42707700	0.57779400
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C	-6.22463300	1.96129900	-0.63215300
C	-5.22184600	0.99539300	-0.66335600
C	5.22184400	0.99539600	0.66335600
C	6.22463100	1.96130200	0.63215300
C	6.02713400	3.20145500	0.01895400
C	4.77878900	3.42707200	-0.57781200
C	3.77770600	2.46563000	-0.56243200
C	7.10205900	4.28920100	-0.02209400
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C	1.29663200	-3.76434700	3.89650300
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C	-6.57744600	5.54755400	-0.68860900

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C	6.57738600	5.54759700	0.68848500
H	-4.13385300	0.42084000	2.51553500
H	-3.03810000	-1.33122400	4.26400800
H	2.58271200	-1.05223400	4.51198500
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H	2.54842100	-3.87456300	-3.73411600
H	-1.17438000	-5.61462900	-4.98126000
H	1.31698500	-5.69337100	-4.87442500
H	-2.82121600	2.66794500	1.03691400
H	-4.57822300	4.37578200	1.06926800
H	-7.17811700	1.72728200	-1.09414100
H	-5.41334100	0.03458500	-1.13302800
H	5.41333700	0.03459000	1.13303400
H	7.17811400	1.72728800	1.09414500
H	4.57822700	4.37577500	-1.06929000
H	2.82122000	2.66793800	-1.03693200
H	-2.54842200	-3.87454700	3.73412800
H	-1.31698700	-5.69335100	4.87444400
H	1.17437900	-5.61461000	4.98127800
H	2.38152400	-3.72017700	3.94048600
H	-8.19363700	5.41505300	1.52988800
H	-7.81350800	3.74991800	2.01503000
H	-6.54900600	4.98912500	2.02715300
H	-7.33466200	6.34068200	-0.66349400
H	-6.34043000	5.33482500	-1.73710400
H	-5.67079200	5.93616500	-0.21271000
H	-8.23370100	3.62320800	-1.72921900
H	-8.84011100	2.97367500	-0.18985400
H	-9.13133000	4.66435300	-0.61722400
H	9.13131100	4.66437600	0.61726200
H	8.23359800	3.62340900	1.72935400
H	8.84005600	2.97364900	0.19010400
H	8.19375100	5.41495300	-1.52988700
H	6.54915100	4.98901300	-2.02724200
H	7.81363800	3.74979400	-2.01495600
H	6.34031300	5.33493700	1.73698100
H	7.33459000	6.34073400	0.66335700
H	5.67075200	5.93615900	0.21250800

Pd2 at ground state
Total energy: E = -1960.98570657 a.u.

C	1.57191000	-2.62139800	-0.86723000
C	-1.46606900	-2.68062000	-0.78365400
N	-1.44723800	-1.40741700	-0.37001300
C	-2.42941400	-1.27134600	0.60181600
C	-3.02246300	-2.54493600	0.82969400
C	-2.44570200	-3.41669600	-0.06567900
C	2.66506900	-3.29850700	-0.26252800
C	3.22416000	-2.42473800	0.64037500
C	2.48813700	-1.21007200	0.54572800
N	1.46667500	-1.38011200	-0.37583300
C	0.73893700	-3.18661200	-1.93383000
C	-0.66688100	-3.22078200	-1.89054100
N	1.44723000	1.40742100	-0.36999700
C	2.42940800	1.27134700	0.60183000
C	3.02244900	2.54493800	0.82971800
C	2.44568900	3.41670000	-0.06565200
C	-2.66506300	3.29852100	-0.26250000
C	-3.22415600	2.42474400	0.64039300
C	-2.48814300	1.21007400	0.54572700
N	-1.46668400	1.38011900	-0.37583900
C	-1.57191300	2.62141200	-0.86721600
C	1.46605900	2.68062600	-0.78363300
C	-0.73894100	3.18662900	-1.93381600
C	0.66687700	3.22079200	-1.89052300
C	-2.89248600	-0.03038900	1.06557600
C	2.89248200	0.03038800	1.06558300
C	-3.97451300	-0.00613600	2.08435800
C	3.97451500	0.00612600	2.08435700
C	-3.74334300	0.61725200	3.31650300
C	-4.73968200	0.65414300	4.28681200
C	-5.98494800	0.08476700	4.03337800
C	-6.22973200	-0.52107200	2.80361900
C	-5.23170300	-0.56896300	1.83529500
C	3.74336200	-0.61728900	3.31649200
C	4.73971000	-0.65419400	4.28679100
C	5.98497000	-0.08480400	4.03335700
C	6.22973800	0.52106200	2.80360800
C	5.23170000	0.56896600	1.83529400
Pd	-0.00000400	0.00000200	-0.53728800
C	1.36161700	3.87851500	-2.91501800
C	0.69404000	4.47567600	-3.97591800
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C	-1.39960100	3.80777900	-3.00325400
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C	0.69711200	-4.43871200	-4.02080600
C	1.39960100	-3.80775800	-3.00326800
H	-3.79952100	-2.75704900	1.54975300

H	-2.65810800	-4.46808600	-0.20425100
H	2.96671600	-4.31320400	-0.48409200
H	4.08882500	-2.58287200	1.26930600
H	3.79950600	2.75705000	1.54978000
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H	-2.96670300	4.31322400	-0.48405100
H	-4.08881900	2.58287400	1.26932900
H	-2.77236000	1.06437500	3.50870700
H	-4.54210400	1.13107900	5.24250900
H	-6.76411000	0.11809600	4.78942200
H	-7.20381200	-0.95337300	2.59319500
H	-5.42688000	-1.02641000	0.87003000
H	2.77238200	-1.06442100	3.50869700
H	4.54214300	-1.13115000	5.24248100
H	6.76413900	-0.11814500	4.78939300
H	7.20381300	0.95337200	2.59318400
H	5.42686600	1.02643100	0.87003600
H	2.44659000	3.90551700	-2.86925700
H	1.25777700	4.96729200	-4.76331600
H	-1.23397600	4.90055300	-4.84419700
H	-2.48514600	3.77857900	-3.02771200
H	-2.44658700	-3.90551700	-2.86927900
H	-1.25776700	-4.96728500	-4.76333500
H	1.23398700	-4.90053200	-4.84421200
H	2.48514600	-3.77855200	-3.02772500

Pd3 at ground state
Total energy: E = -2456.66911855 a.u.

C	2.76072600	-1.37594300	4.45401000
C	2.40040300	-2.33682600	5.38931100
C	1.06728800	-2.72274700	5.50105800
C	0.11380700	-2.14143100	4.67642300
C	0.09397700	-4.36409300	-2.70993200
C	1.03117400	-5.32960200	-3.05123000
C	2.37586400	-4.97996200	-3.14220200
C	2.76299100	-3.67076500	-2.89107900
Pd	0.77501300	-0.66062400	0.19809200
F	-4.91263800	-1.37989000	-0.11055200
F	-7.29707100	-0.16583900	-0.42865100
F	-7.42538500	2.53426800	-0.67762300
F	-5.15459500	4.02066600	-0.60787300
F	-2.76303600	2.81512700	-0.29561500
C	3.33001800	3.68199700	-1.77777600
C	4.03520100	4.81551400	-2.16964200
C	5.31859200	5.04549100	-1.68063000
C	5.89467200	4.13590000	-0.79741200
C	5.18787400	3.00696900	-0.39525000

C	-3.86068000	2.06588100	-0.32353500
C	-5.08685700	2.69950500	-0.48640600
C	-6.24992100	1.93971700	-0.52286400
C	-6.18251500	0.55716300	-0.39793700
C	-4.94599700	-0.05656600	-0.23669900
C	3.89473600	2.77173500	-0.87646700
C	-3.76442200	0.68101800	-0.20005600
C	3.12340700	1.56587700	-0.47606800
C	-2.43597700	0.03420900	-0.01697500
C	1.83111700	-2.68785100	-2.52807400
C	0.47246300	-3.04234400	-2.43523400
C	2.33429200	-1.31990500	-2.36300700
C	-0.60456700	-2.08882600	-2.14799900
N	-0.66817500	-1.29872300	-1.07056600
C	-1.88976800	-0.64419500	-1.11015600
C	-2.57379200	-1.01780500	-2.30122400
C	-1.78331600	-1.94690800	-2.93334700
C	3.20253000	-0.67275400	-3.28263300
C	3.50743200	0.55627900	-2.74572600
C	2.85098900	0.62780600	-1.48533800
N	2.12119500	-0.53553600	-1.29807800
C	0.46597800	-1.18362700	3.71521100
C	1.81275800	-0.79424900	3.60094000
N	2.13579100	0.27329400	1.37001100
C	2.82460600	1.37598700	0.88173500
C	3.35922500	2.10173400	1.98270900
C	3.05467000	1.38375900	3.11653900
C	-1.82497300	-0.06950000	3.51350700
C	-2.61282600	0.35161300	2.46955600
C	-1.89963700	0.05238700	1.27472200
N	-0.66917600	-0.48998100	1.60964100
C	-0.62300700	-0.57606800	2.94402700
C	2.28565700	0.26486600	2.70069400
H	3.79746900	-1.06454800	4.36426200
H	3.15744000	-2.78099000	6.02885100
H	0.77016900	-3.47246000	6.22836500
H	-0.92909500	-2.43347800	4.75968700
H	-0.95758400	-4.62722100	-2.63962400
H	0.71255200	-6.34947400	-3.24523100
H	3.12125000	-5.72358000	-3.40834100
H	3.80956600	-3.38935700	-2.96344800
H	2.33028400	3.49722800	-2.15995800
H	3.58020900	5.51957000	-2.86034600
H	5.87027800	5.92813200	-1.99105600
H	6.90113500	4.30138400	-0.42382700
H	5.64231500	2.28834900	0.28019500
H	-3.54845200	-0.66290800	-2.60585200
H	-1.98146600	-2.47475400	-3.85610700
H	3.53427400	-1.09122900	-4.22308400
H	4.16086000	1.31502800	-3.15238600

H	3.92240200	3.02124200	1.91521900
H	3.31381700	1.61328200	4.14115400
H	-2.04025100	-0.02524200	4.57232000
H	-3.60586400	0.77669100	2.51947200

Pd4 at ground state
Total energy: E = -2952.35196839 a.u.

C	-1.51644400	1.46773700	2.66048400
C	1.52592400	1.44282000	2.65519400
N	1.45880300	1.00318500	1.39334300
C	2.45739400	0.05421500	1.23345600
C	3.12534600	-0.12484700	2.47738700
C	2.56378500	0.76821800	3.35753600
C	-2.57647100	0.82687800	3.36046700
C	-3.14721900	-0.06743200	2.48688700
C	-2.45734600	0.07418400	1.25048200
N	-1.44452000	1.00657400	1.40594100
C	-0.68949800	2.54287300	3.21861000
C	0.71754000	2.52991300	3.21828500
N	-1.45880300	1.00318700	-1.39334200
C	-2.45739400	0.05421700	-1.23345600
C	-3.12534500	-0.12484500	-2.47738800
C	-2.56378500	0.76822100	-3.35753600
C	2.57647100	0.82688100	-3.36046600
C	3.14721800	-0.06743000	-2.48688700
C	2.45734600	0.07418500	-1.25048200
N	1.44452000	1.00657500	-1.40594000
C	1.51644400	1.46773900	-2.66048200
C	-1.52592400	1.44282300	-2.65519200
C	0.68949800	2.54287700	-3.21860700
C	-0.71754000	2.52991700	-3.21828200
C	2.88269200	-0.41684400	-0.01169400
C	-2.88269200	-0.41684300	0.01169400
C	3.97150000	-1.43182500	-0.03185500
C	-3.97150000	-1.43182400	0.03185400
C	5.30243800	-1.09119800	0.20024200
C	6.31381600	-2.04392200	0.16775900
C	5.99737000	-3.36947700	-0.10537200
C	4.67801900	-3.73559400	-0.34367800
C	3.68195100	-2.76692300	-0.30752400
C	-3.68195100	-2.76692200	0.30752400
C	-4.67801900	-3.73559300	0.34367700
C	-5.99737000	-3.36947700	0.10536900
C	-6.31381600	-2.04392200	-0.16776300
C	-5.30243800	-1.09119800	-0.20024600
F	-6.95544800	-4.28571700	0.13814700
F	2.42802900	-3.14335500	-0.53532600

F	4.37893200	-5.00342500	-0.60250400
F	6.95544800	-4.28571700	-0.13815200
F	7.57689100	-1.69628300	0.38998200
F	5.63455300	0.17116000	0.45440100
F	-4.37893300	-5.00342400	0.60250500
F	-2.42803000	-3.14335400	0.53532800
F	-5.63455300	0.17116000	-0.45440600
F	-7.57689100	-1.69628300	-0.38998900
Pd	0.00000000	1.16787800	0.00000100
C	-1.40609000	3.56577200	-3.86486400
C	-0.73007700	4.60820700	-4.48420900
C	0.66218000	4.62169800	-4.48369100
C	1.35798700	3.59236000	-3.86453200
C	1.40609100	3.56576800	3.86486800
C	0.73007800	4.60820100	4.48421400
C	-0.66217900	4.62169300	4.48369600
C	-1.35798600	3.59235500	3.86453600
H	3.94566400	-0.80489200	2.66010900
H	2.82487800	0.93848900	4.39301000
H	-2.84687100	1.01994100	4.38954400
H	-3.99127300	-0.71948000	2.66464100
H	-3.94566300	-0.80488900	-2.66011100
H	-2.82487700	0.93849300	-4.39301000
H	2.84687100	1.01994500	-4.38954300
H	3.99127200	-0.71947800	-2.66464200
H	-2.49209800	3.54549700	-3.86397800
H	-1.28838000	5.40552400	-4.96567000
H	1.20519900	5.42983500	-4.96462000
H	2.44416400	3.59324200	-3.86325800
H	2.49209800	3.54549200	3.86398200
H	1.28838000	5.40551800	4.96567600
H	-1.20519800	5.42982900	4.96462600
H	-2.44416400	3.59323700	3.86326200