Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Regioselective phosphorylation and thiophosphorylation of N-confused porphyrin. A route to hybrid carbaporphyrinoids

Norbert Grzegorzek and Lechosław Latos-Grażyński* and Ludmiła Szterenberg

Department of Chemistry, University of Wrocław, 14 F. Joliot-Curie St., 50 383 Wrocław, Poland

Fax: (+)48 71 328 23 48, e-mail: lechoslaw.latos-grazynski@chem.uni.wroc.pl

Supporting Information

1. Instrumentation:

NMR analysis. All NMR spectra were recorded at 300 K on 600 MHz and 500 MHz spectrometers equipped with 5 mm broadband, inverse gradient probeheads. ^{1}H and ^{13}C shifts were referenced to the residual solvent signal. ^{31}P signals were measured in presence of inset with H_3PO_4 as the external reference. The assignment was obtained with a combination of several 2D experiments (COSY, NOESY, ROESY, HSQC and HMBC (^{13}C and ^{31}P)).

Absorption spectra were recorded on spectrophotometer equipped with a Xenon flash lamp.

Mass spectra were recorded on a spectrometer using the electrospray technique.

2. NMR spectra:

Proton and correlation spectra

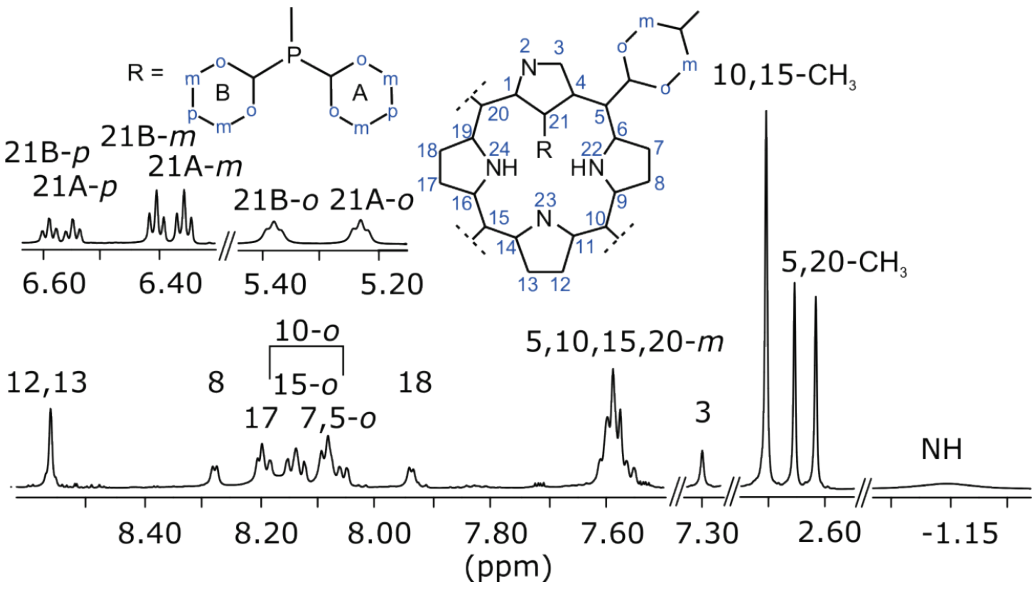

Figure S1. ^{1}H NMR spectrum of **2** (chloroform-*d*, 300 K).

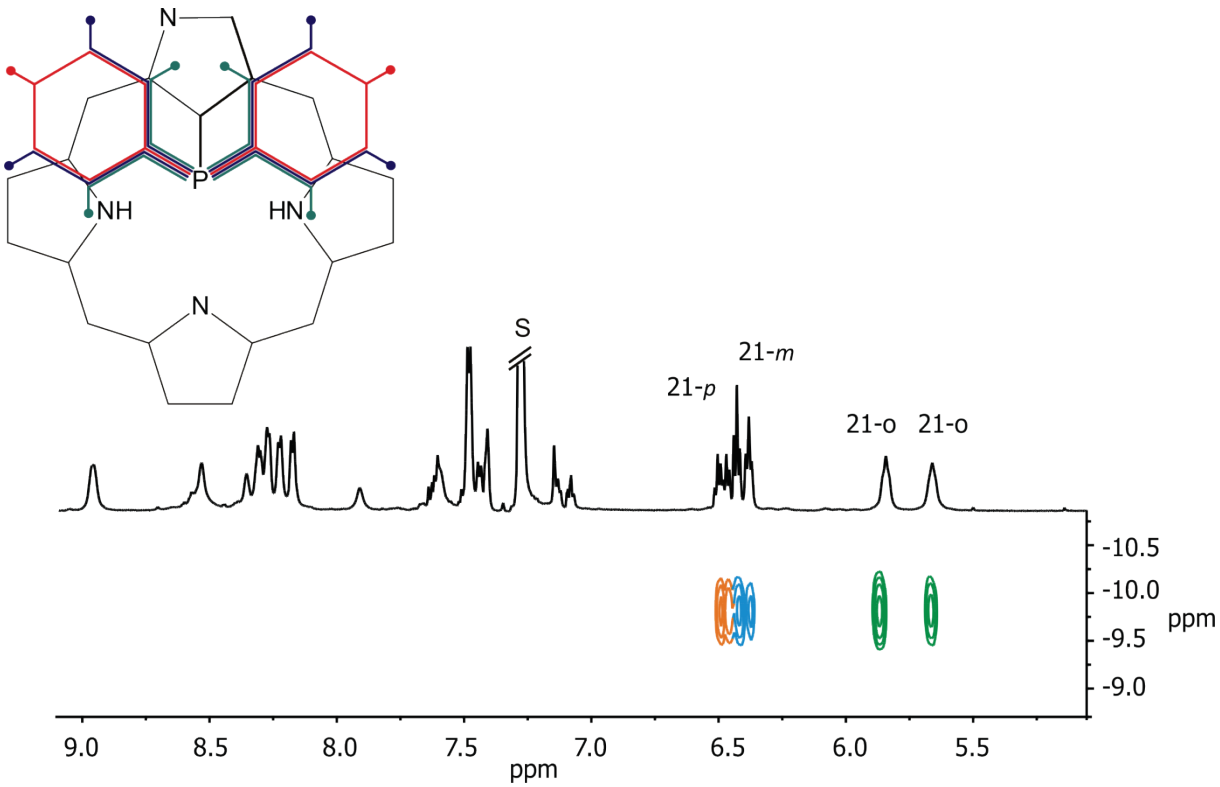

Figure S2. ^{1}H-^{31}P HMBC spectrum of **2** (benzene-d_6, 300 K).

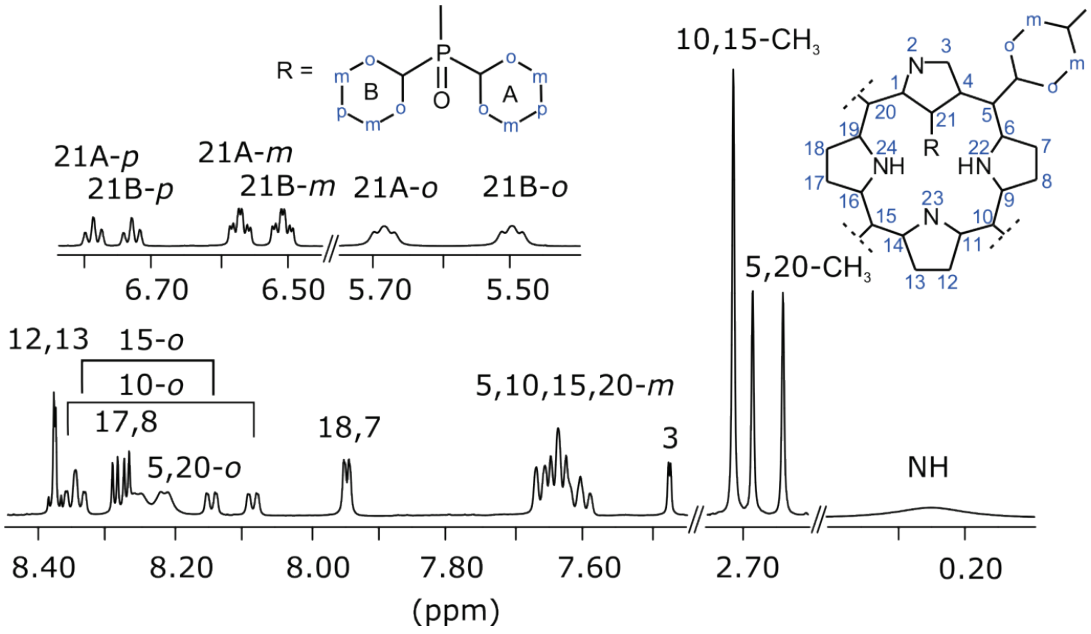

Figure S3. ^{1}H NMR spectrum of **3** (chloroform-*d*, 300 K).

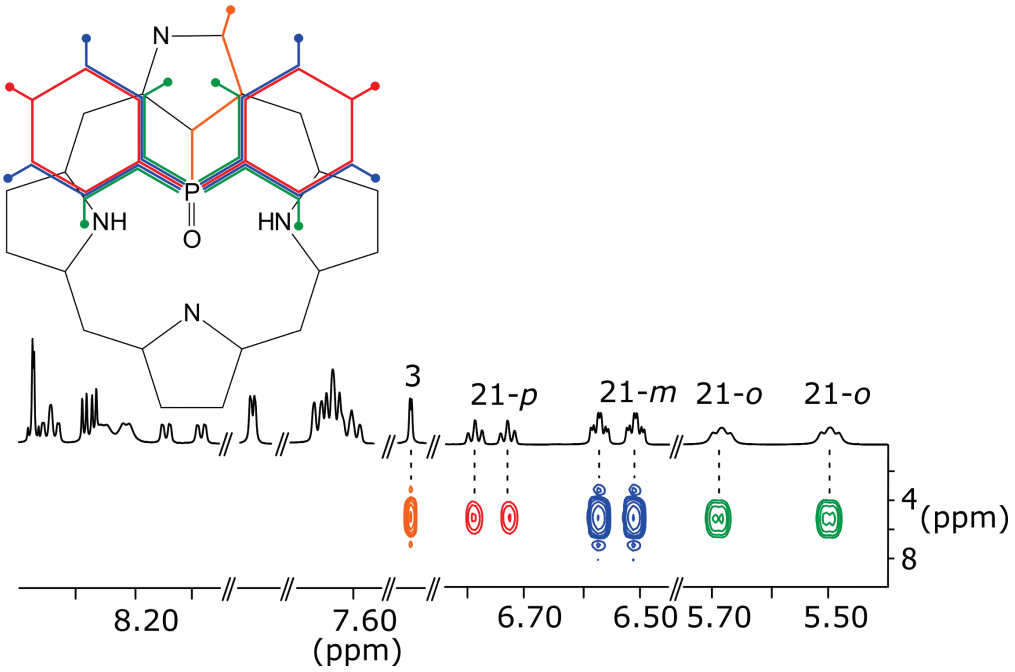

Figure S4. ^{1}H-^{31}P HMBC spectrum of **3** (chloroform-*d*, 300 K).

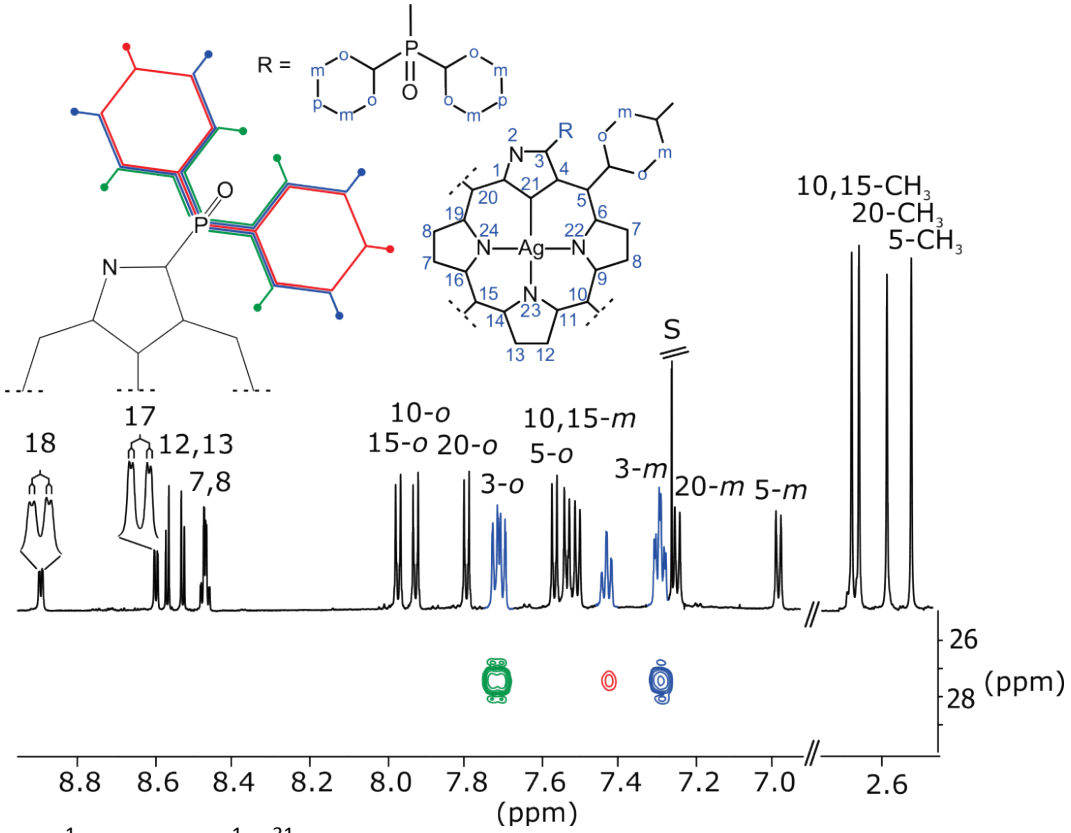

Figure S5. ^{1}H NMR and ^{1}H-^{31}P HMBC spectra of **4(Ag)** (chloroform-*d*, 300 K). The scalar couplings between the β-H resonances and $^{107/109}$Ag are presented.

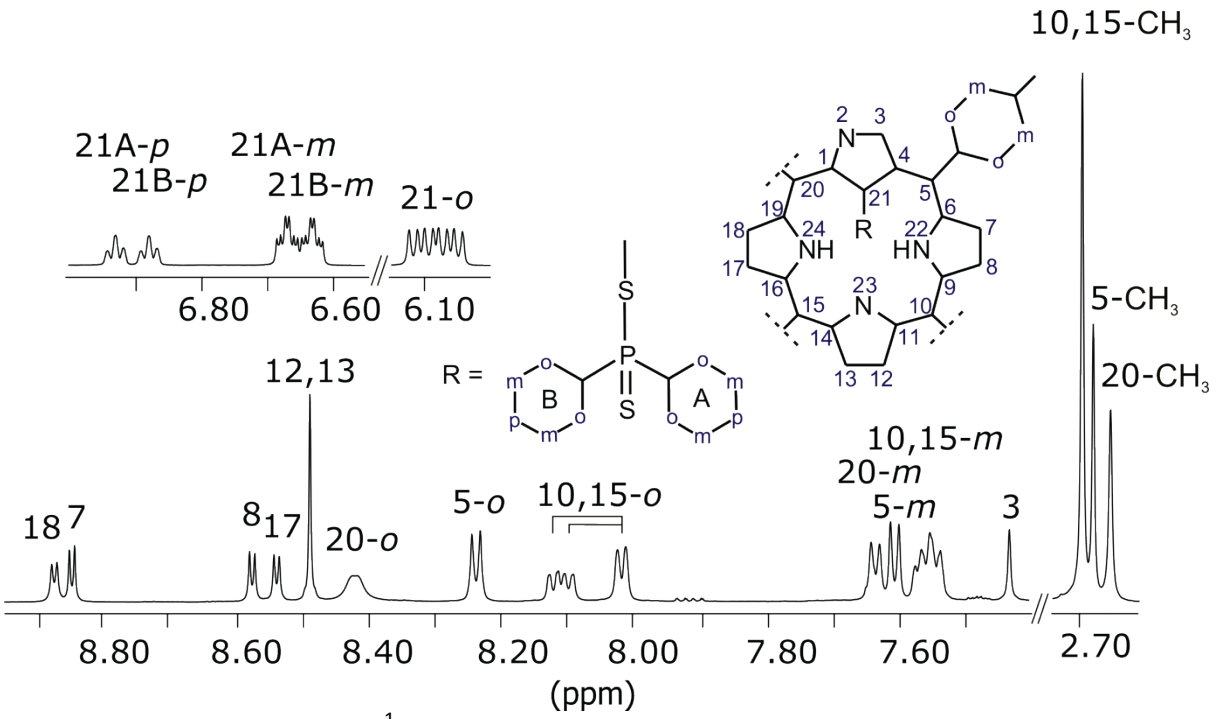

Figure S6. ^{1}H NMR spectrum of **7** (chloroform-*d*, 300 K).

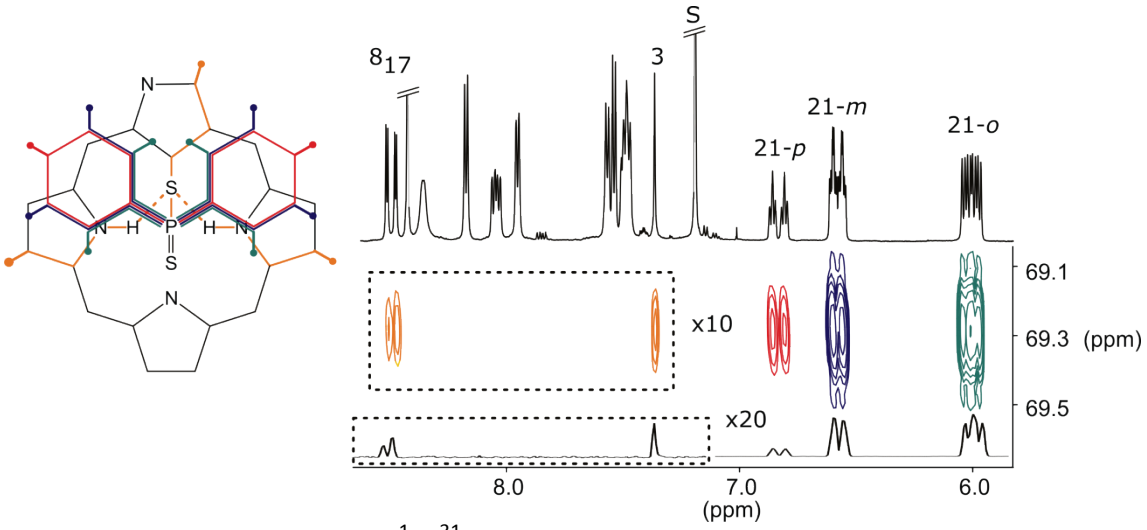

Figure S7. ^{1}H-^{31}P HMBC spectrum of **7** (chloroform-*d*, 300 K).

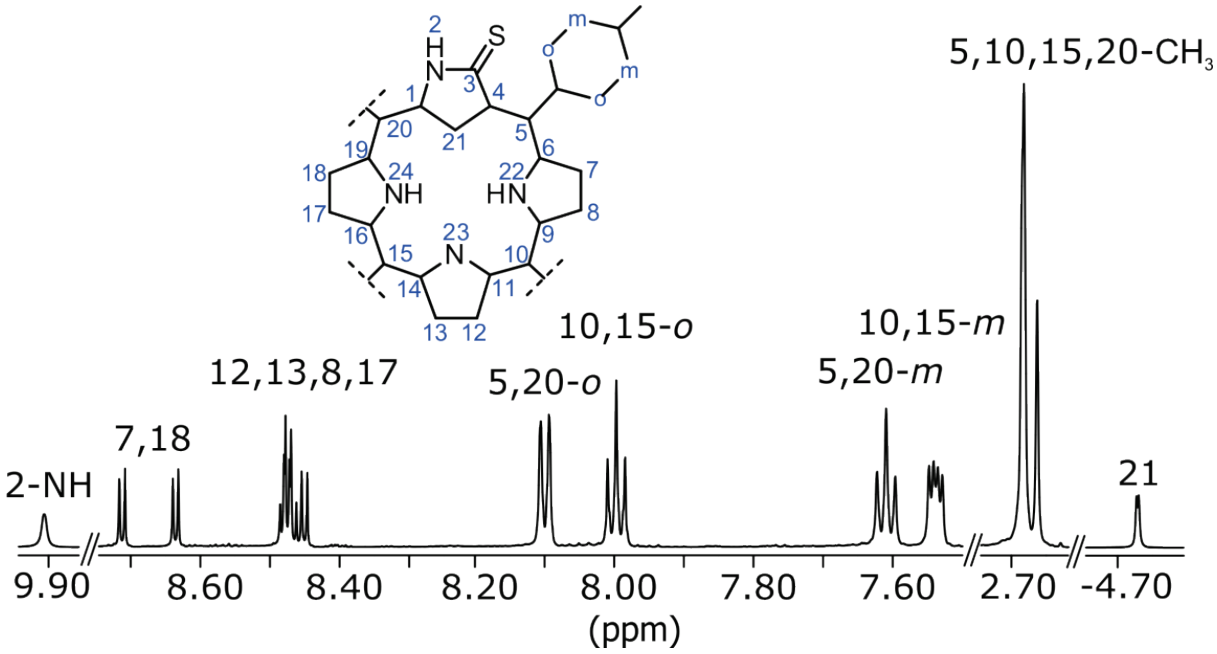

Figure S8. ^{1}H NMR spectrum of **8** (chloroform-*d*, 300 K).

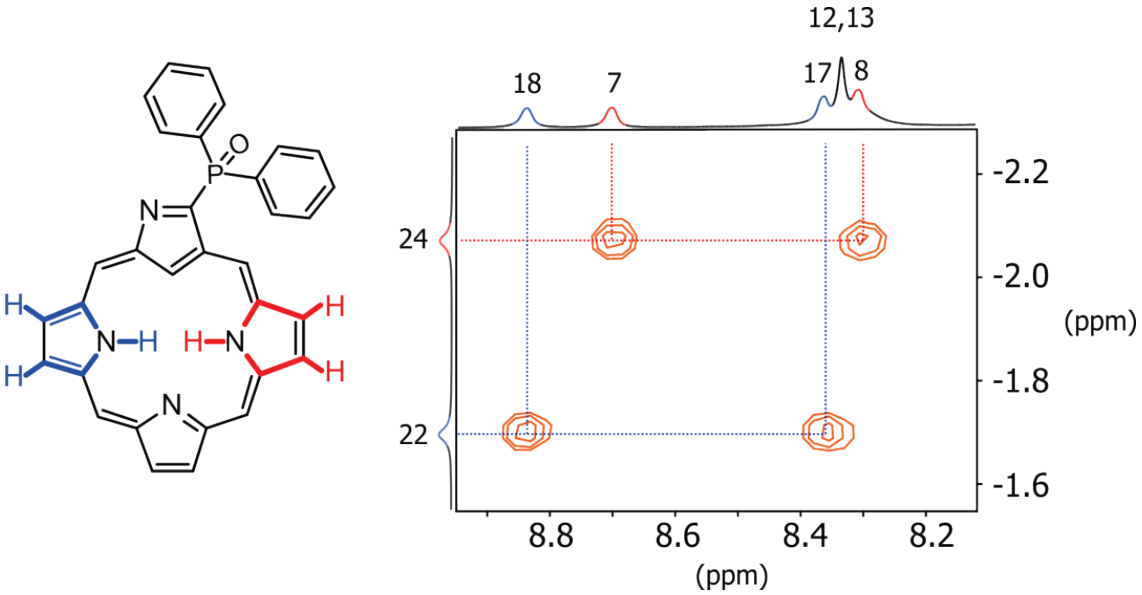

Figure S9. COSY Spectrum of **4** measured in 183 K (dichloromethan-d_2) showing scalar couplings between NH and β protons.

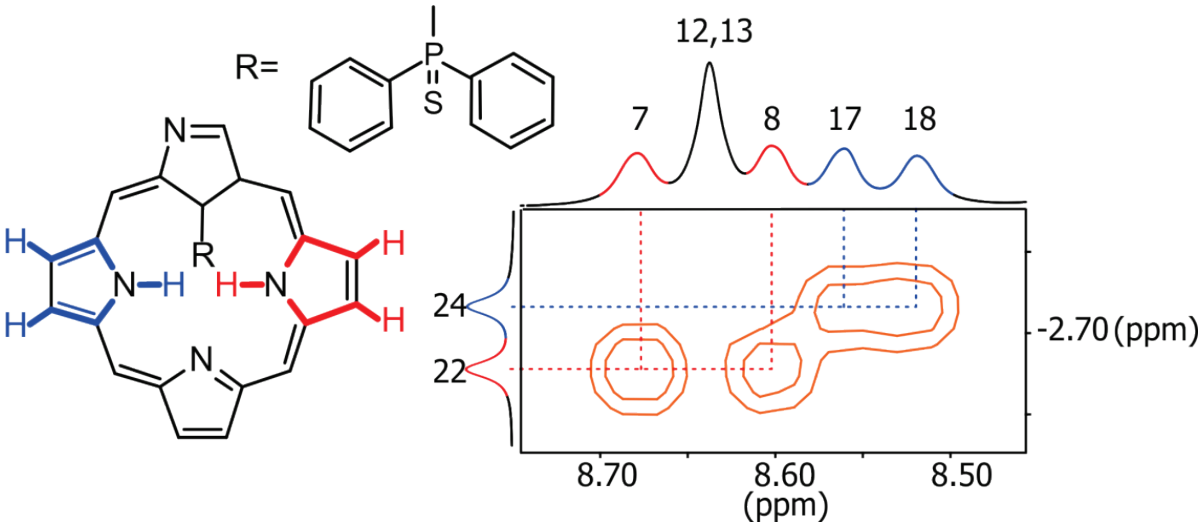

Figure S10. COSY Spectrum of **6** measured in 193 K (dichloromethan-d_2) showing scalar couplings between NH and β protons.

Carbon spectra

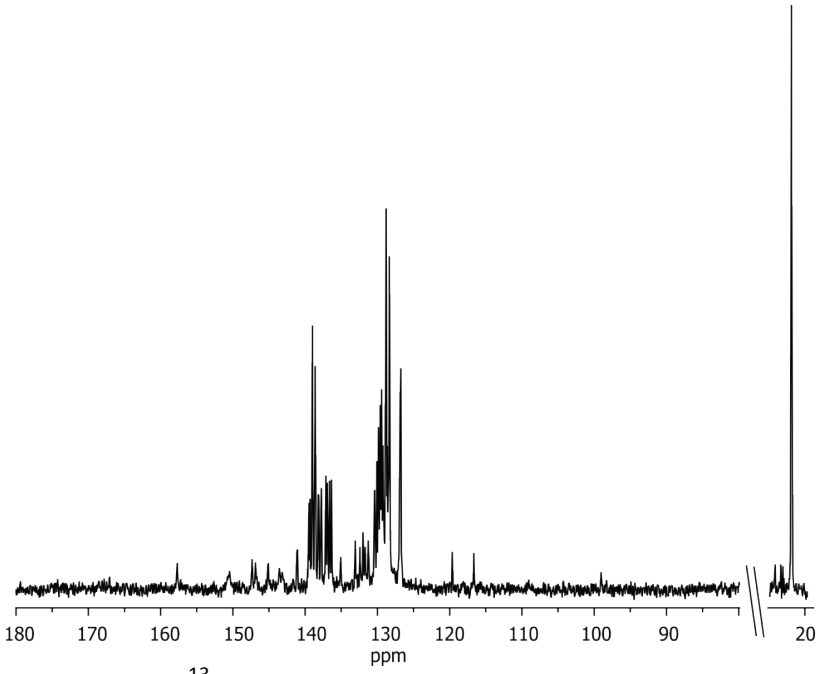

Figure S11. ^{13}C NMR spectrum of **2** (chloroform-*d*, 300 K).

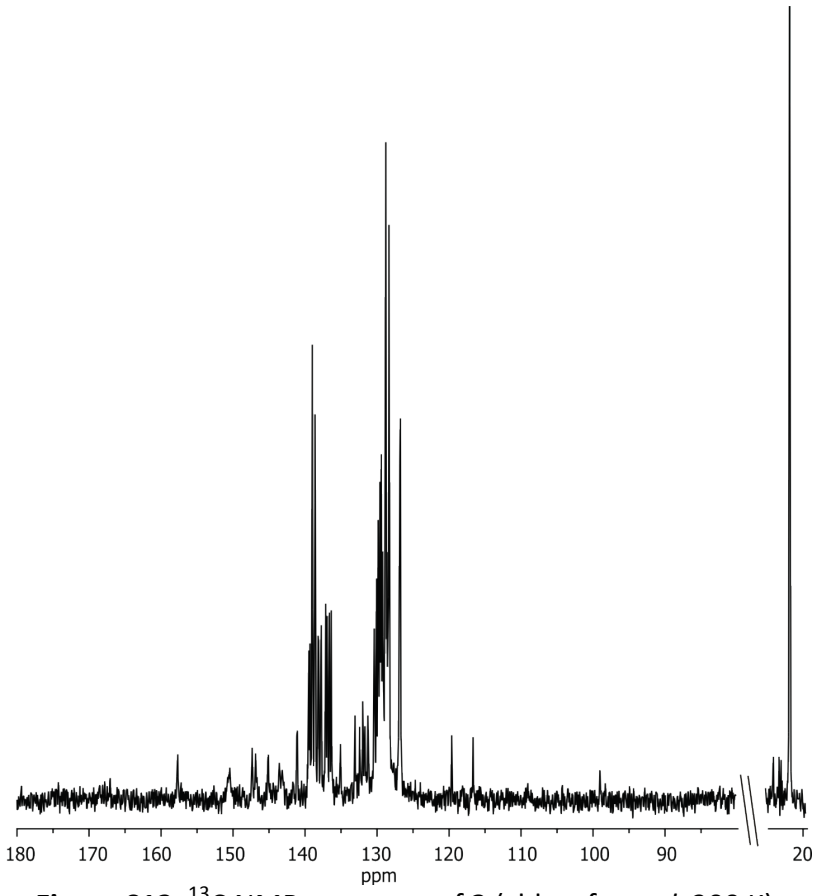

Figure S12. ^{13}C NMR spectrum of **3** (chloroform-*d*, 300 K).

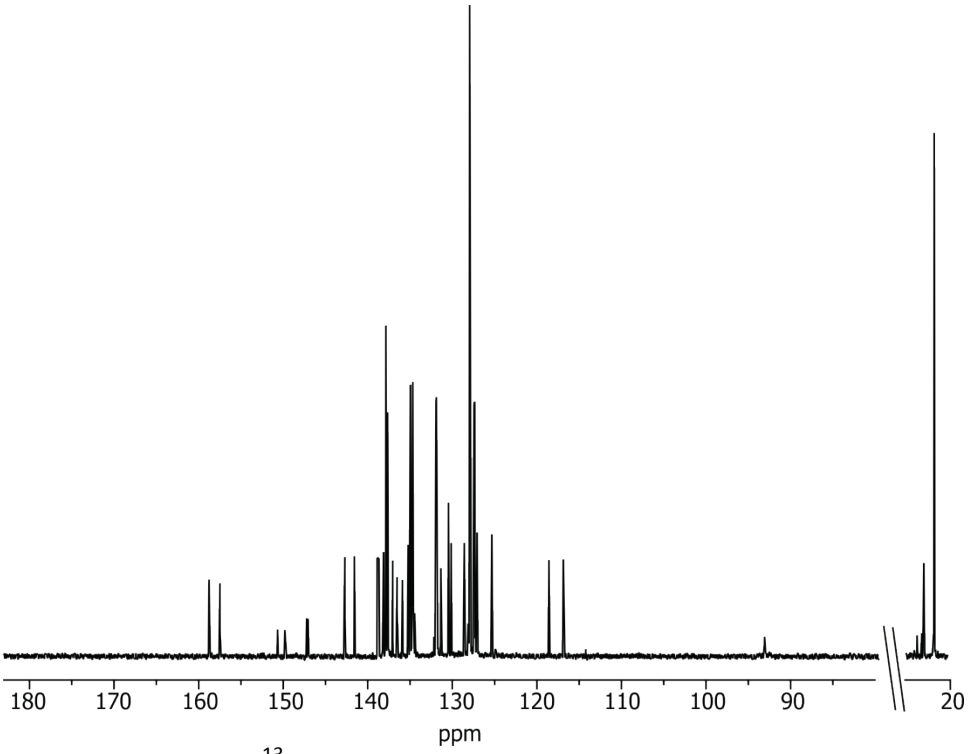

Figure S13. ^{13}C NMR spectrum of **4** (chloroform-*d*, 300 K).

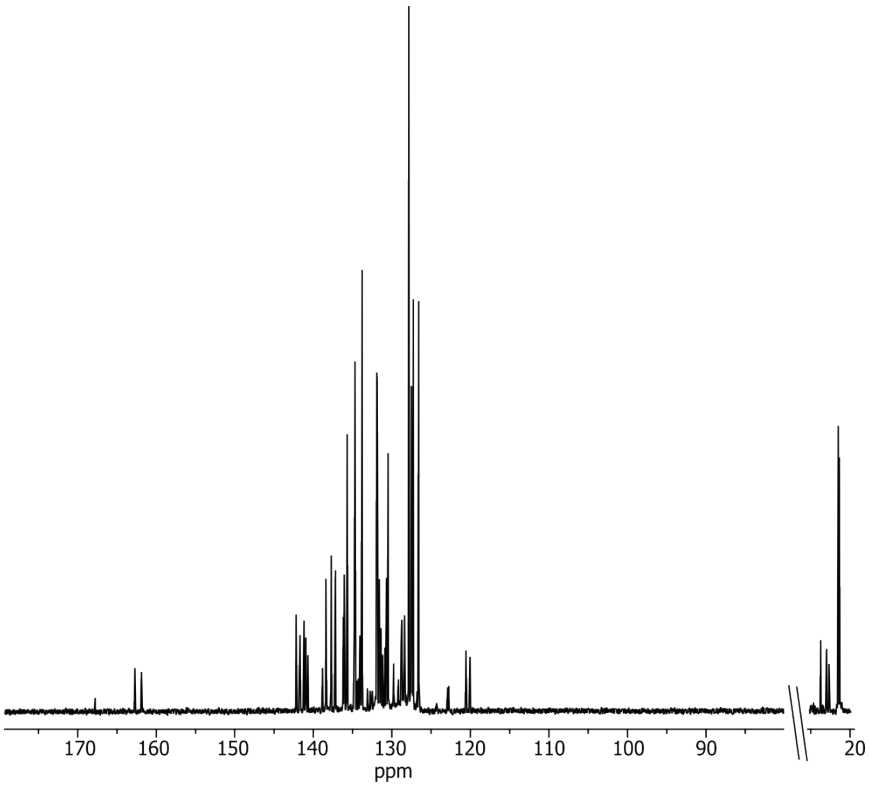

Figure S14. ^{13}C NMR spectrum of **4(Ag)** (chloroform-*d*, 300 K).

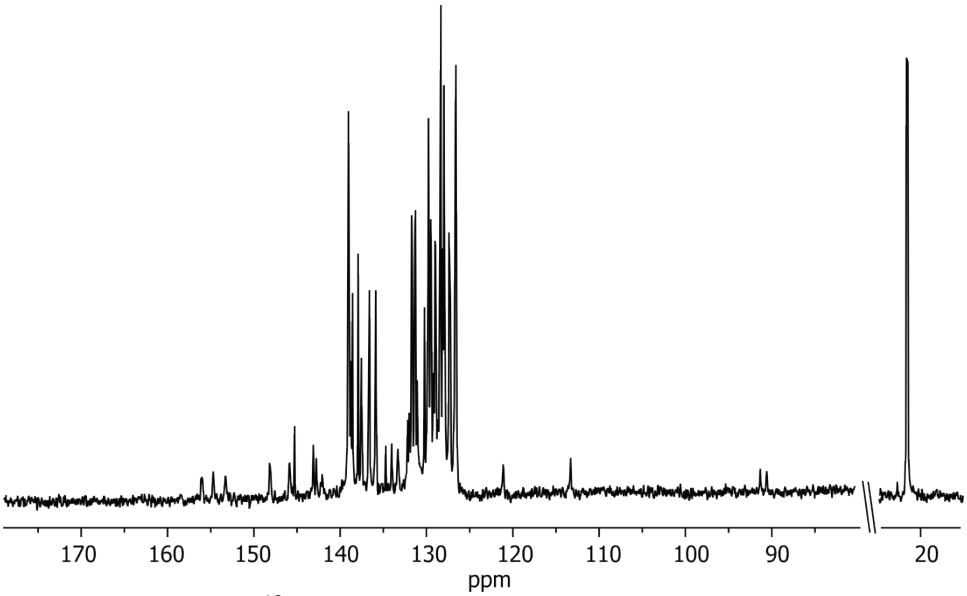

Figure S15. ^{13}C NMR spectrum of **5** (chloroform-*d*, 300 K).

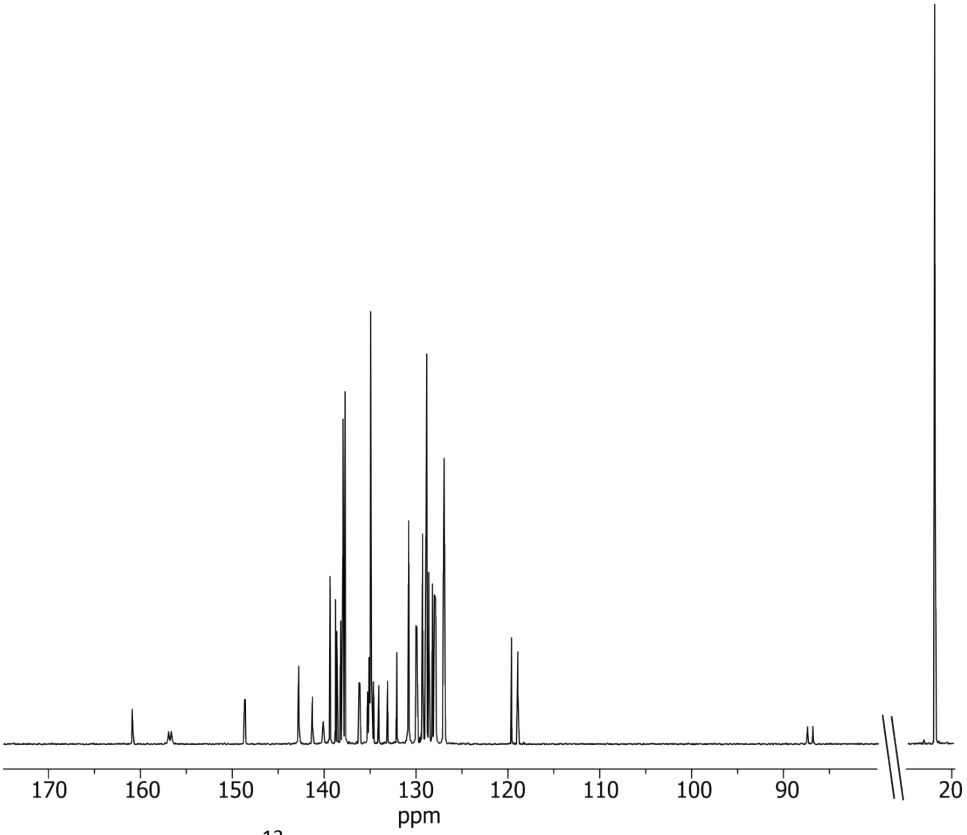

Figure S16. ^{13}C NMR spectrum of **6** (chloroform-*d*, 300 K).

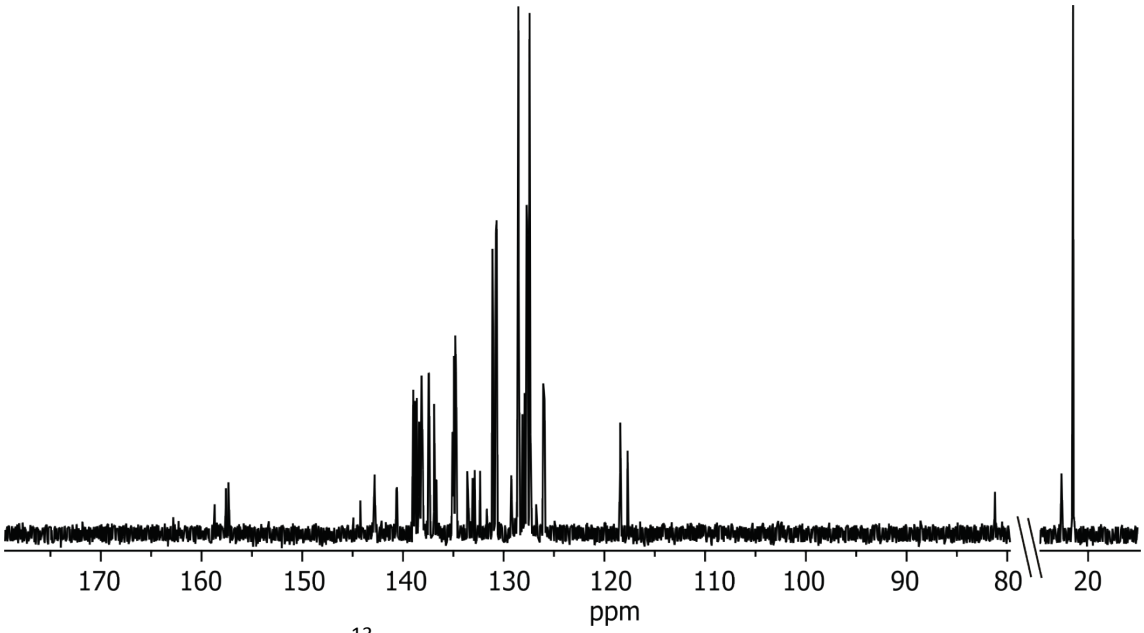

Figure S17. ^{13}C NMR spectrum of **7** (chloroform-*d*, 300 K).

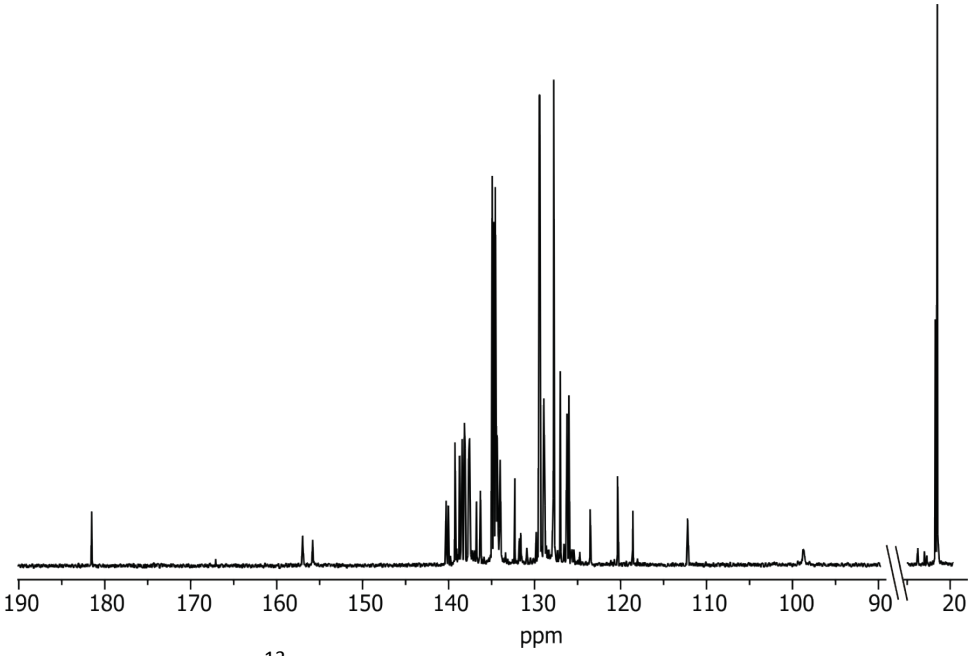

Figure S18. ^{13}C NMR spectrum of **8** (chloroform-*d*, 300 K).

3. X-ray analysis:

X-ray quality crystals of **5**, **6, 7** and **4-Ag** were prepared by diffusion of hexane into a dichloromethane solution(s) contained in a tube stored in a room temperature for **6, 7** and **4-Ag** or in refrigerator for **5**. (Data were collected at 100 K on an Xcalibur PX-k geometry diffractometer, with Mo Kα radiation (λ = 0.71073). Data were corrected for Lorentz and polarization effects. Crystal data are compiled in Table S1 Structure was solved by a heavy metal (**4-Ag**) and direct (**5**, **6, 7**) method(s) with SHELXS-97[1] or Dirdif (**5**)[2] and refined by full-matrix least-squares method by using SHELXL-97[3] with anisotropic thermal parameters for the non-H atoms. Scattering factors were those incorporated in SHELXS-97. NH-protons for **5**, **6** and **7** were initially found on Patterson's map and then introduced with HFIX command. In case of **4-Ag** and **5** SQUEEZE procedure was used with PLATON to remove disordered dichloromethane (**5**) or hexane (**4-Ag**) molecules. Additional details are included in CIF files. Molecule of **4-Ag** has two disordered aryl rings including one of the phenyl rings of diphenylphosphoryl substituent and 5-meso tolyl ring (Figure S19). The less populated conformation has been refined with isotropic thermal parameters.

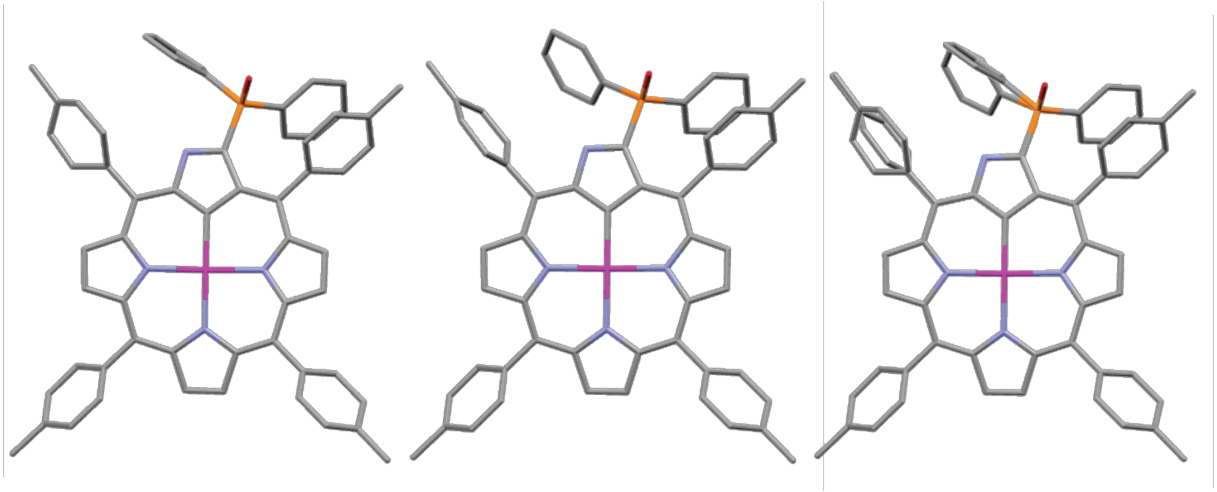

Figure S19. **4-Ag** structures showing different conformations of one of the phenyl and 5-mezo-tolyl rings. From left: less populated species, more populated species, overlayed structures.

Comments to CheckCIF Alerts A:

Alert level A for structure of 5
PLAT051_ALERT_1_A:
Mu(calc) and Mu(CIF) Ratio Differs from 1.0 by . 27.36 Perc.
Comment: This alert arise from the fact that the highly disordered solvents could not be satisfactorily modeled. As a result, the SQUEEZE routine within PLATON was employed to remove the contribution of the solvent to the diffraction pattern. The absence of solvents from the model results in a discrepancy between calculated Mu based on assigned atoms and the actual composition including the solvent molecules.

Alert level A for structure of 4-Ag
PLAT241_ALERT_2_A: Check High Ueq as Compared to Neighbors for C36.
Comment: This alert arise from the fact that the C36 is shared by two rotamers of disordered and differently populated meso-phenyl.

Table S1. Crystal structure data for **7** and **5**.

Compound	**7**	**5***3.25CH_2Cl_2
Crystal obtained by	Slow diffusion of C_6H_{14} into CH_2Cl_2 solution	Slow diffusion of C_6H_{14} into CH_2Cl_2 solution
Crystal habit	Irregular, dark green block	Irregular, dark green block
Crystal dimensions (mm)	0.29 x 0.21 x 0.19	0.18 x 0.16 x 0.08
formula	$C_{60}H_{47}N_4PS_2$	$C_{75.5}H_{62.5}N_4P_2O_2Cl_{6.5}$
mw (Da)	919.1	1347.2
a, Å	14.678(4)	15.207(4)
b, Å	15.687(4)	31.469(6)
c, Å	20.796(6)	15.224(4)
α,°	90	90
β,°	100.53(3)	97.55(3)
γ,°	90	90
V, A^3	4702(3)	7222(3)
Z,	4	4
F(000)	1928	2794
D_{calc},g·cm	1.298	1.239
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Irradiation source	$Mo_{K\alpha}$/0.71073Å	$Mo_{K\alpha}$/0.71073Å
μ, mm	0.19	0.35
Absorotion correction	none	none
T,K	95(2)	100(2)
Θ range	$4.7 \le \theta \le 35.0$	$4.5 \le \theta \le 30.1$
hkl range	$-22 \le h \le 22$ $-22 \le k \le 20$ $-33 \le l \le 26$	$-16 \le h \le 16$ $-38 \le k \le 39$ $-20 \le l \le 17$
Ref. mesoured	57874	47788
Ref. unique, I > 2σ(I)	9965	5305
Parameters /restraints	606/0	781/0
R1	0.055	0.100
wR2	0.117	0.234
S	1.012	1.013
ρ_{max}/ρ_{min}, e·A^{-3}	0.63/-0.60	0.55/-0.57

Table S1 cont. Crystal structure data for **4-Ag 6**.

Compound	**26***2.6CH_2Cl_2	**4-Ag***1.1CH_2Cl_2*C_6H_{14}
Crystal obtained by	Slow diffusion of C_6H_{14} into CH_2Cl_2 solution	Slow diffusion of C_6H_{14} into CH_2Cl_2 solution
Crystal habit	Irregular, dark green block	Irregular, red block
Crystal dimensions (mm)	0.31 x 0.21 x 0.10	0.22 x 0.06 x 0.04
formula	$C_{122.6}H_{99.2}N_8P_2S_2Cl_{5.2}$	$C_{67.1}H_{70.2}Ag_1N_4O_1P_1Cl_{2.2}$
mw (Da)	1993.2	1165.50
a, Å	14.482(3)	22.726(4)
b, Å	13.250(3)	9.750(3)
c, Å	26.632(4)	29.183(4)
α,°	90	90
β,°	92.41(2)	122.45(3)
γ,°	90	90
V, A^3	5106(3)	5456(3)
Z,	2	4
F(000)	2081	2433
D_{calc},g·cm	1.297	1.419
Crystal system	monoclinic	monoclinic
Space group	*Pc*	$P2_1/c$
Irradiation source	$Mo_{K\alpha}$/0.71073Å	$Mo_{K\alpha}$/0.71073Å
μ, mm	0.28	0.56
Absorotion correction	none	analytical
T,K	100(2)	100(2)
Θ range	$3.1 \leq \theta \leq 37.0$	$2.9 \leq \theta \leq 37.0$
hkl range	$-24 \leq h \leq 19$ $-17 \leq k \leq 19$ $-40 \leq l \leq 41$	$-37 \leq h \leq 29$ $-15 \leq k \leq 16$ $-37 \leq l \leq 48$
Ref. mesoured	48890	67866
Ref. unique, I > 2σ(I)	16579	7030
Parameters /restraints	1322/23	717/18
R1	0.063	0.058
wR2	0.161	0.098
S	1.000	1.020
ρ_{max}/ρ_{min}, e·A^{-3}	0.69/-1.02	0.69/-0.64

4. DFT Calculations:

Table S2. Cartesian Coordinates for optimized geometry of **5 I**.

C	2.71886	-0.12907	-0.33709
C	1.68779	-0.76950	0.47691
N	2.52350	1.17603	-0.42495
C	1.38706	1.48033	0.30914
C	0.86933	0.30746	0.94230
C	1.45034	-2.18264	0.56456
C	0.15989	-2.72938	0.43686
C	0.87438	2.81010	0.18924
C	-0.50223	3.09560	0.11144
N	-1.51251	2.19091	-0.17072
C	-2.70959	2.82879	-0.34295
C	-1.13409	4.38320	0.15668
C	-2.46870	4.22366	-0.11190
N	-0.98317	-2.07682	-0.00531
C	-2.02780	-2.95079	-0.14425
C	-0.22466	-4.10205	0.61619
C	-1.53831	-4.23852	0.25847
C	-3.32857	-2.63945	-0.59500
C	-3.82575	-1.34320	-0.85739
C	-3.91965	2.20692	-0.72270
C	-4.09513	0.81821	-0.90539
N	-3.17157	-0.16091	-0.66282
C	-5.19250	-1.10583	-1.33392
C	-5.35991	0.23406	-1.36077
C	1.84511	3.90605	-0.02999
C	1.64627	4.89694	-1.00803
C	3.03688	3.96263	0.71850
C	2.58288	5.90893	-1.20765
C	3.75561	5.97286	-0.44713
C	3.96353	4.97690	0.51938
C	2.59457	-3.10837	0.71483
C	2.72775	-4.27780	-0.06035
C	3.80198	-5.13792	0.12539
C	4.78695	-4.87283	1.08834
C	4.66224	-3.70607	1.84897
C	3.59749	-2.83284	1.65833
C	-4.25612	-3.80383	-0.76435
C	-5.38148	-3.95941	0.05751
C	-4.01932	-4.78090	-1.74541
C	-6.23883	-5.04883	-0.09927
C	-6.00506	-6.02145	-1.07795
C	-4.87880	-5.86601	-1.89861
C	-6.92810	-7.20488	-1.24731
C	-5.09537	3.10966	-0.92932
C	-5.10686	4.06799	-1.95344
C	-6.20379	4.91015	-2.13607
C	-7.32760	4.82769	-1.30577

C	-7.31358	3.87290	-0.27942
C	-6.22101	3.02954	-0.09290
C	-8.52657	5.72139	-1.51662
H	-0.62098	5.30314	0.39053
H	-3.22576	4.99164	-0.14825
H	0.43035	-4.87131	0.99319
H	-2.13307	-5.13837	0.28271
H	-5.90559	-1.86846	-1.60838
H	-6.23690	0.78693	-1.66231
H	0.76688	4.85231	-1.64140
H	3.22351	3.20381	1.46896
H	2.40576	6.65304	-1.98012
H	4.86989	4.99581	1.11962
H	2.00367	-4.48541	-0.84071
H	3.88947	-6.02414	-0.49878
H	5.41825	-3.47117	2.59351
H	3.52378	-1.93291	2.25706
H	-5.58056	-3.22208	0.82933
H	-3.15749	-4.67821	-2.39830
H	-7.10203	-5.14592	0.55456
H	-4.67468	-6.60254	-2.67233
H	-7.78321	-7.14423	-0.56888
H	-6.40853	-8.14880	-1.04479
H	-7.31555	-7.26612	-2.27053
H	-4.25159	4.14612	-2.61816
H	-6.18715	5.64020	-2.94164
H	-8.16832	3.79308	0.38813
H	-6.22841	2.30401	0.71475
H	-8.28619	6.56719	-2.16670
H	-9.35379	5.17250	-1.98335
H	-8.90084	6.11995	-0.56793
H	-1.47613	1.17704	-0.13855
C	4.77587	7.06362	-0.66274
C	5.95368	-5.81128	1.27382
P	3.99959	-0.82725	-1.46216
C	4.88679	0.61410	-2.17176
C	3.03003	-1.56589	-2.83485
C	3.54080	-2.73088	-3.42301
C	2.87069	-3.33039	-4.48992
C	1.68585	-2.77290	-4.97423
C	1.16728	-1.61690	-4.38666
C	1.83464	-1.01581	-3.31909
P	-0.26118	0.28221	2.36351
H	-1.12493	-1.07846	-0.09764
H	4.45451	-3.16051	-3.02433
H	3.27162	-4.23349	-4.94160
H	1.41749	-0.12543	-2.85757
H	1.16387	-3.24051	-5.80440
H	0.24012	-1.18705	-4.75468
C	0.05287	1.81894	3.32127

C	0.24718	-1.06838	3.50211
O	-1.72575	0.15050	2.02673
C	1.50979	-1.16570	4.10302
C	1.77682	-2.17935	5.02212
C	0.78351	-3.10417	5.35245
C	-0.47749	-3.00964	4.76362
C	-0.74731	-1.99383	3.84511
C	-1.07922	2.49913	3.78805
C	1.32748	2.29541	3.65934
C	1.46644	3.43178	4.45488
C	0.33296	4.10416	4.91861
C	-0.93822	3.63853	4.58217
H	2.28882	-0.45003	3.86094
H	2.75900	-2.24735	5.48071
H	0.99338	-3.89299	6.06919
H	-1.25400	-3.72441	5.02058
H	-1.72694	-1.89849	3.38823
H	-2.06035	2.12589	3.51247
H	2.21528	1.79112	3.29019
H	2.45779	3.79624	4.70814
H	0.44307	4.99046	5.53699
H	-1.82156	4.16226	4.93625
O	4.98347	-1.80211	-0.87676
C	4.29172	1.64731	-2.90924
C	6.27629	0.61073	-1.99111
C	5.07727	2.66197	-3.45191
C	7.06039	1.63033	-2.53401
C	6.46205	2.65617	-3.26482
H	3.21781	1.67038	-3.04826
H	6.72555	-0.20176	-1.42922
H	4.60744	3.46191	-4.01687
H	8.13695	1.61956	-2.38821
H	7.07092	3.44893	-3.69107
H	5.74761	6.64580	-0.94998
H	4.93594	7.64624	0.25194
H	4.46338	7.75579	-1.44932
H	6.55754	-5.87261	0.36105
H	5.61777	-6.82866	1.50615
H	6.60926	-5.48057	2.08380

Table S3. Cartesian Coordinates for optimized geometry of **5 II**.

C	-2.47173	0.18839	-0.66191
C	-1.48859	0.91156	0.12916
N	-2.34453	-1.12263	-0.51922
C	-1.27200	-1.34618	0.32645
C	-0.74302	-0.10763	0.80525
C	-1.25389	2.32927	0.09769
C	0.05168	2.84518	0.01977
C	-0.78804	-2.69203	0.41013

C	0.57865	-3.01489	0.37608
N	1.61526	-2.16039	0.03452
C	2.79140	-2.84374	-0.09346
C	1.17339	-4.31647	0.50914
C	2.50913	-4.21516	0.22591
N	1.19571	2.12922	-0.30594
C	2.28355	2.95362	-0.40249
C	0.47830	4.20665	0.17310
C	1.82075	4.27468	-0.08687
C	3.59872	2.57118	-0.74843
C	4.05923	1.24388	-0.89332
C	4.02266	-2.28924	-0.50500
C	4.24922	-0.92308	-0.78160
N	3.35734	0.10186	-0.63167
C	5.42888	0.92592	-1.31183
C	5.54592	-0.41745	-1.24370
C	-1.78724	-3.78354	0.31254
C	-1.64129	-4.85192	-0.58934
C	-2.95305	-3.75251	1.10121
C	-2.60583	-5.85423	-0.67921
C	-3.75359	-5.83161	0.12072
C	-3.90745	-4.75879	1.01238
C	-2.40025	3.25622	0.12372
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C	-3.52930	5.29674	-0.57396
C	-4.62935	5.01623	0.25173
C	-4.60297	3.83150	0.99483
C	-3.51428	2.96619	0.93060
C	4.57584	3.68932	-0.93695
C	5.68609	3.83210	-0.09116
C	4.40622	4.63490	-1.96185
C	6.59190	4.87781	-0.26694
C	6.42361	5.82007	-1.28845
C	5.31466	5.67666	-2.13390
C	7.39078	6.96618	-1.46669
C	5.16697	-3.24538	-0.64453
C	5.15781	-4.24809	-1.62637
C	6.22147	-5.14056	-1.75000
C	7.33326	-5.06595	-0.90120
C	7.33878	-4.06851	0.08230
C	6.27758	-3.17384	0.21033
C	8.49916	-6.01278	-1.05867
H	0.63341	-5.20549	0.79611
H	3.24171	-5.00732	0.23098
H	-0.16597	5.01350	0.48435
H	2.45201	5.14851	-0.04249
H	6.17512	1.64165	-1.62215
H	6.40835	-1.02110	-1.48320
H	-0.78053	-4.87882	-1.24888
H	-3.09058	-2.93819	1.80286

H	-2.46905	-6.66168	-1.39419
H	-4.78857	-4.71511	1.64838
H	-1.64315	4.64508	-1.34523
H	-3.54184	6.18977	-1.19408
H	-5.44602	3.58169	1.63385
H	-3.51573	2.05812	1.52256
H	5.83467	3.11843	0.71349
H	3.56091	4.53948	-2.63694
H	7.44212	4.96451	0.40515
H	5.16359	6.38676	-2.94353
H	8.32021	6.79448	-0.91687
H	6.96241	7.90830	-1.10288
H	7.64441	7.11539	-2.52137
H	4.31129	-4.32102	-2.30283
H	6.18900	-5.90517	-2.52249
H	8.18328	-3.99448	0.76322
H	6.29969	-2.41490	0.98648
H	8.17636	-6.98666	-1.43893
H	9.23836	-5.61711	-1.76656
H	9.01540	-6.17401	-0.10762
H	1.61330	-1.14472	0.05193
C	-4.80372	-6.91128	0.02136
C	-5.80199	5.96338	0.32129
P	-3.63406	0.71817	-1.98479
C	-3.25407	-0.31538	-3.45858
C	-5.28962	0.20367	-1.38034
C	-5.57330	-1.05506	-0.82969
C	-6.87148	-1.35741	-0.41911
C	-7.89091	-0.41106	-0.55043
C	-7.60952	0.84511	-1.08905
C	-6.31254	1.15375	-1.50215
C	-3.10121	-1.71026	-3.46301
C	-2.85741	-2.38039	-4.66147
C	-2.76395	-1.67194	-5.86161
C	-2.91161	-0.28498	-5.86172
C	-3.15677	0.39171	-4.66605
P	0.29383	0.05649	2.28935
H	1.28069	1.12693	-0.42195
O	-3.60688	2.17380	-2.35931
H	-4.77983	-1.78478	-0.70754
H	-7.08701	-2.33374	0.00617
H	-6.07096	2.12862	-1.91359
H	-3.14131	-2.26120	-2.53133
H	-2.73668	-3.46012	-4.65640
H	-2.57346	-2.20008	-6.79194
H	-2.83483	0.27228	-6.79117
H	-3.27136	1.47066	-4.64829
H	-8.90082	-0.65223	-0.23011
H	-8.39883	1.58528	-1.18692
C	-0.27309	-1.23978	3.46415

C	-0.09970	1.63459	3.14373
O	1.78160	-0.04739	2.06244
C	-1.37087	1.99927	3.60742
C	-1.54816	3.18475	4.31880
C	-0.45499	4.01358	4.58216
C	0.81538	3.65163	4.13375
C	0.99421	2.46593	3.41970
C	0.72949	-1.96008	4.12575
C	-1.61673	-1.48704	3.77962
C	-1.95063	-2.43527	4.74592
C	-0.94514	-3.15000	5.40197
C	0.39335	-2.91363	5.08846
H	-2.22814	1.36165	3.42010
H	-2.53878	3.46177	4.66716
H	-0.59510	4.93577	5.13898
H	1.66920	4.29060	4.34015
H	1.97590	2.16424	3.06934
H	1.76553	-1.76423	3.86815
H	-2.40679	-0.95071	3.26237
H	-2.99421	-2.62010	4.98438
H	-1.20705	-3.89013	6.15270
H	1.17750	-3.47127	5.59253
H	-5.74918	-6.51231	-0.36495
H	-5.01862	-7.35015	1.00211
H	-4.48669	-7.71757	-0.64533
H	-6.18826	6.19085	-0.67844
H	-5.51642	6.91860	0.77861
H	-6.62145	5.54442	0.91155

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