Electronic supplementary information

New Insight into Solid-State Molecular Dynamics: Mechanochemical Synthesis of Azobenzene/Triphenylphosphine Palladacycles

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Experimental Section

General measurements

All chemicals were obtained commercially and used as supplied. The reactions were done under normal atmosphere. Complexes **1-4** were prepared as described previously.[1]

Elemental analyses were carried out with a Perkin-Elmer Series II 2400 CHNS/O analyzer.

X-ray measurements. The powder X-ray diffraction (PXRD) experiments of the samples were performed on a PHILIPS PW 1840 X-ray diffractometer with Cu$K_{\alpha 1}$ (1.54056 Å) radiation at 40 mA and 40 kV. The scattered intensities were measured with a scintillation counter. The angular range was from 3 to 50° (2θ) with steps of 0.02°, and the measuring time was 1 s per step. The data collection and analysis was performed using the program package *Philips X'Pert*.[2]

Single crystal measurements were performed on an Oxford Diffraction Xcalibur Nova R (microfocus Cu tube) at room temperature. Program package CrysAlisPRO[3] was used for data reduction. The structures were solved using SHELXS97[4] and refined with SHELXL97.[4] The models were refined using the full-matrix least squares refinement; all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were treated as riding entities using the command AFIX in SHELXL-97.[4]

Crystals of all compounds diffracted relatively weakly due to large asymmetric units (Table S1). A special problem in refinement was large thermal motion of triphenylphosphine moieties; in **1a**, **3a** and **4a** isotropic restraints had to be used for some atoms to prevent unrealistically elongated displacement ellipsoids. In addition, solvent water and ethanol molecules in **4a** were refined isotropically with fixed atomic positions. In **3a** large voids ($V \approx$ 140 Å^3) are present; however no meaningful electron density was found in them. It is possible that they contained partially occupied and disordered acetone molecules (the compound was crystallized from acetone), which evaporated. Due to a poor crystallinity of the sample, additional measurements (including low temperature) would not improve data quality.

Molecular geometry calculations were performed by PLATON[5] and molecular graphics were prepared using ORTEP-3[6] and CCDC-Mercury.[7] Crystallographic and refinement data for the structures reported in this paper are shown in Table S1.

CCDC 831717-831720 contain the supplementary crystallographic data for this paper. They can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the

Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

NMR measurements. The ^{1}H and ^{31}P NMR spectra were recorded at 25 °C in $CDCl_3$ with Bruker AV-600 spectrometer operating at 600.13 MHz for the ^{1}H and 242.92 MHz for the ^{31}P resonances. The ^{31}P NMR spectra were externally referenced using 85 % H_3PO_4, Table S2. ^{1}H NMR spectra of **2a** complex were recorded at 50, 25, 0 −25 and −50 °C in $CDCl_3$ with the same instrument. The signal assignment was based on the chemical shifts and quantum chemical calculations of the chemical shifts.

^{31}P MAS NMR spectra of solid samples were recorded on Varian Unity Inova 300 MHz NMR spectrometer equipped with 5 mm Magic Angle Probe, Table S2. Larmor frequency of phosphorus nuclei was 122.65 MHz. The ^{31}P MAS NMR spectra were externally referenced using $AlPO_4$, which was set to −29.5 ppm corresponding to 85 % H_3PO_4 (δ 0.0 ppm). All samples were spun at the magic angle with ca. 5 kHz spinning frequency. Repetition delay in all experiments was 30 s, the number of scans was between 168 and 3760.

Computational methods. Electronic structure was calculated by DFT method, with the B3LYP functional[8] and 6-31G(d,p) basis set on nonmetal atoms. For the Pd atoms Stuttgart-Dresden pseudopotential and the accompanying basis set (SDD) were used.[9] Calculations were performed with the program package Gaussian03.[10]

Molecular geometries were optimized with tight convergence criteria in the gas phase only. Harmonic frequency calculations were performed to confirm stationary points as minima on the potential energy surfaces and to estimate vibrational contributions to the free energy. NMR shifts were calculated by the GIAO method with the basis set including diffuse functions on the hydrogen atoms (6-311++G(d,p)). The solvation effect ($CHCl_3$) on the NMR shifts was accounted by the PCM model with UA0 atomic radii.[10]

Synthesis of complexes

Solid-phase reactions

Grinding experiments were performed at room temperature in a 10 mL stainless steel jar using two 7 mm stainless steel grinding balls. A Retsch MM200 grinder mill operating at 25 Hz frequency was used for the synthesis.

Compound **1a** was synthesized by liquid-assisted grinding 80.3 mg (0.13 mmol) of **1** and 69.1 mg (0.26 mmol) of PPh_3 in the presence of 30 μL of nitromethane. Compounds **2a**, **3a**, and **4a** were obtained by the same procedure. Analysis of the products using PXRD revealed

complete conversion of reactants into the products after 30 (**1a** and **4a**) or 45 (**2a** and **3a**) minutes of grinding. Analogous NG reactions were performed with the same amounts of reactants as LAG reactions. The mixtures of solid reactants were ground 65-80 min.

Solvent-based reactions

A mixture of **1** or **2** or **3** (70 mg, 0.11 mmol) and PPh_3 (57.70 mg, 0.22 mmol) in acetone (5 mL) was heated under reflux for 2 h. After cooling, the orange (**1a** and **2a**) or red (**3a**) crystals were filtered off and dried under vacuum. **1a**: 98.33 mg, 77%; **2a**: 94.50 mg, 74%; **3a**: 90.67 mg, 71%.

1a found: C 58.64, H 3.82, N 2.63; calcd. for $C_{48}H_{38}N_2P_2Pd_2Cl_2$: C 58.32, H 3.87, N 2.83.

2a found: C 59.10, H 4.17, N 2.43; calcd. for $C_{49}H_{40}N_2P_2Pd_2Cl_2$: C 58.70, H 4.02, N 2.79.

3a found: C 57.50, H 3.80, N 4.07; calcd. for $C_{48}H_{39}N_3P_2Pd_2Cl_2$: C 57.45, H 3.92, N 4.19.

A mixture of **4** (70 mg, 0.10 mmol) and PPh_3 (52.45 mg, 0.20 mmol) in acetone (4 mL) was heated under reflux for 2 h. After cooling, the dark violet (**4a**) crystals were filtered off and dried under vacuum. **4a**: 90.62 mg, 74%.

4a found: C 56.01, H 4.11, N 4.91; calcd. for $C_{50}H_{42}N_4O_2P_2Pd_2Cl_2$: C 55.78, H 3.93, N 5.20.

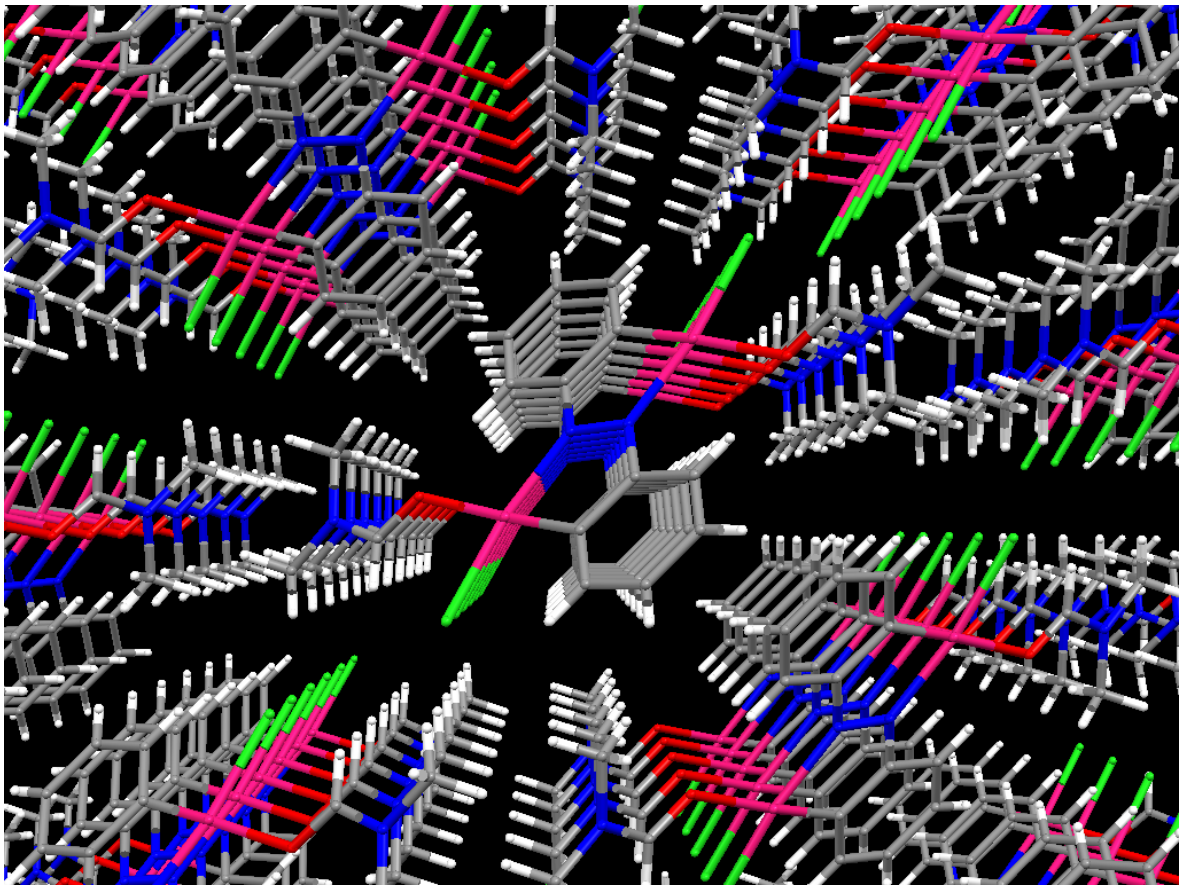

Figure S1. Crystal packing of initial complex **1**.

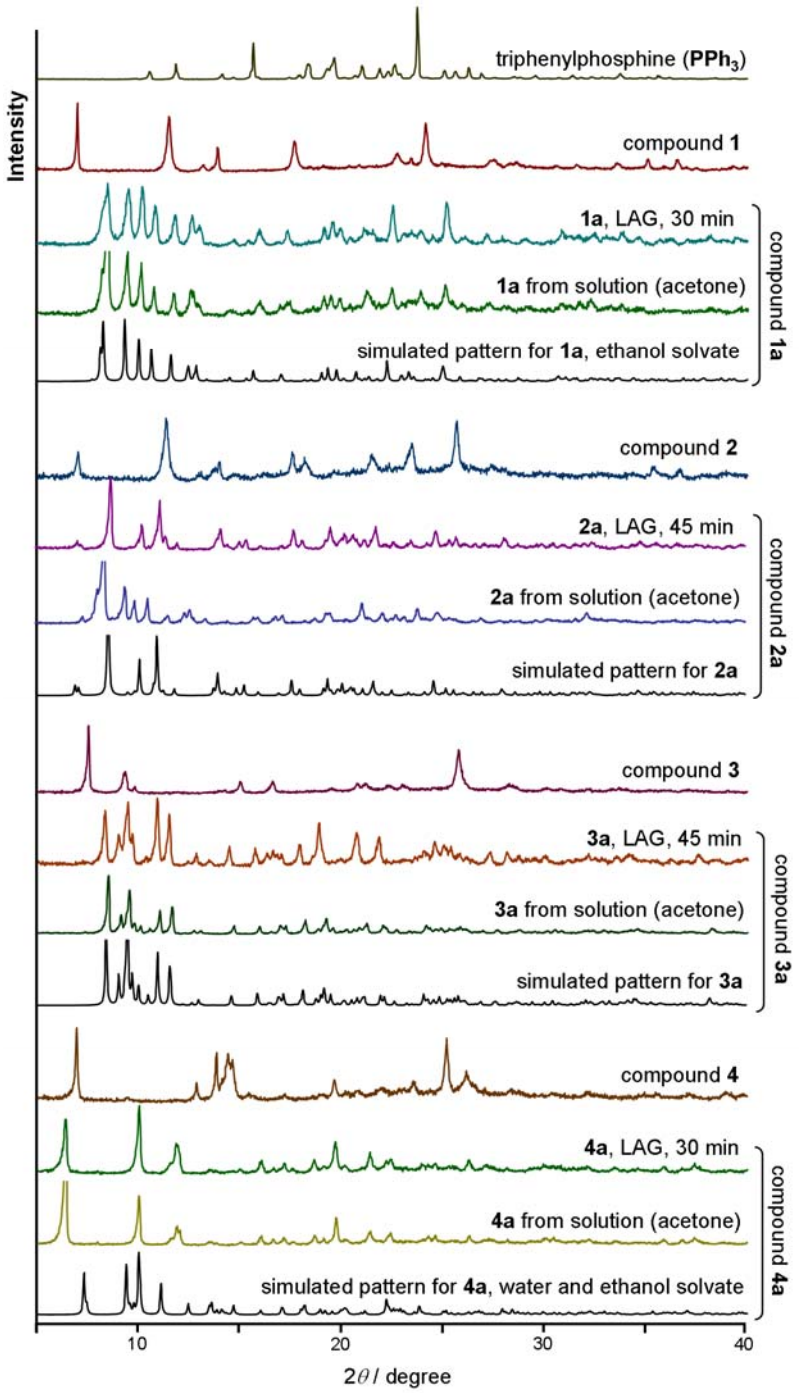

Figure S2. Comparison of PXRD patterns between initial compounds, products obtained by grinding and from solution and simulated from the single crystals. PXRD experiments have also confirmed that the structures of ground samples are identical to those generated from acetone for all complexes except for **2a**, Figure 1. Since the results of X-ray single-crystal and powder experiments strongly indicated that solid-state reactions of initial complex **2** with PPh_3 lead to beta isomers of **2a**, we assumed that the analogous solvent-based reactions can lead to alpha isomer, or a mixture of alpha and beta isomers or to a different solid phase of beta isomer of **2a**.

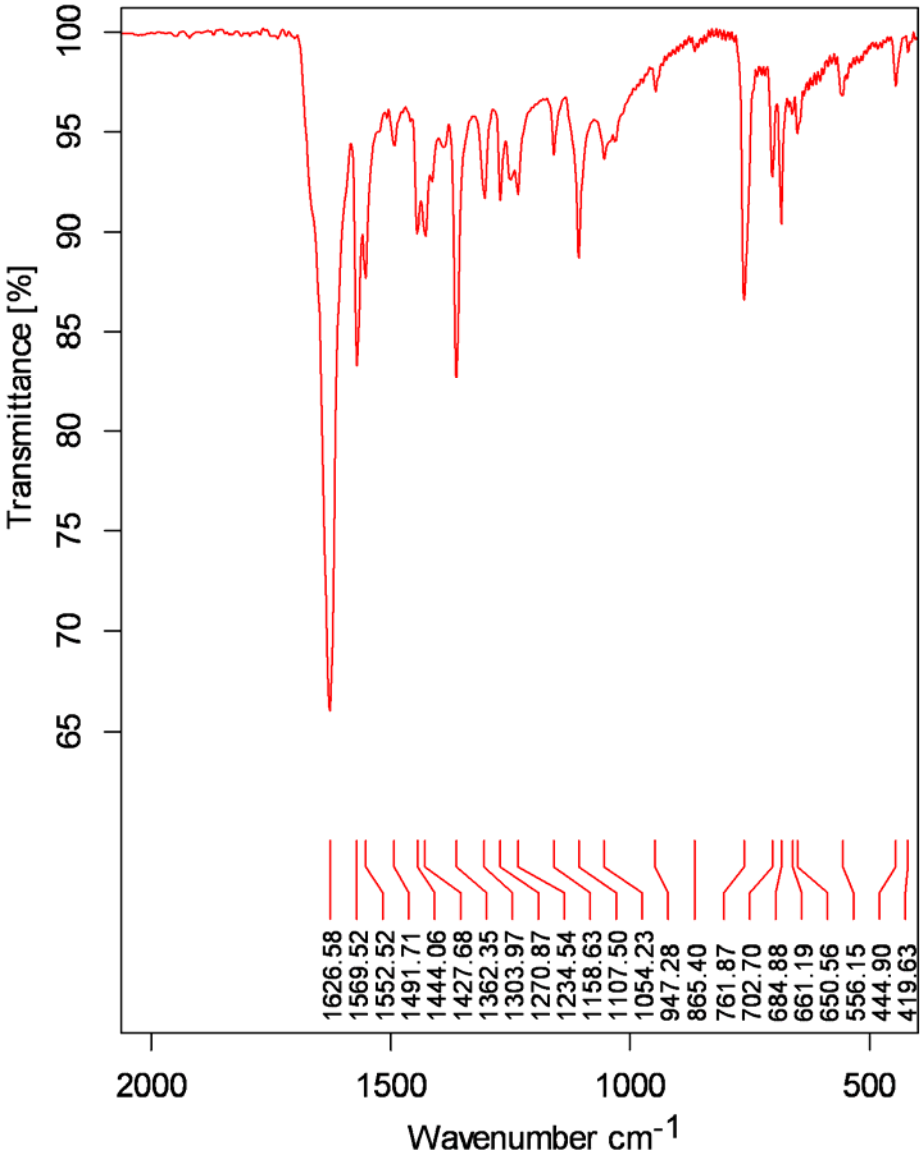

Figure S2. IR spectrum of complex **1a** after grinding. It is identical to IR spectrum of initial complex **1a** before grinding.

Table S1. ^{31}P NMR data of complexes **1a**-**4a** in the solid state and in $CDCl_3$ at room temperature (δ / ppm).

Phosphorus	**1a**	**2a** (**alpha** and **beta**)	**3a**	**4a**	Method
P1	28.89	31.45	34.44	31.34	Solid-state
	32.69	32.36, 32.84	32.79	33.28	$CDCl_3$
P2	43.40	37.98	39.61	39.89	Solid-state
	41.20	41.22, 41.65	40.69	41.79	$CDCl_3$

Table S2. Crystallographic, data collection and structure refinement details.

Compound	**1a**	**2a**	**3a**	**4a**
Empirical formula	$C_{50}H_{44}Cl_2N_2OP_2Pd_2$	$C_{49}H_{40}Cl_2N_2P_2Pd_2$	$C_{48}H_{39}Cl_0N_3P_2Pd_2$	$C_{102}H_{92}C_{l4}N_8O_6P_4Pd_4$
Formula wt. / g mol^{-1}	1034.51	1002.47	1003.46	2217.12
Crystal dimensions/ mm	0.23 x 0.16 x 0.04	0.15 x 0.12 x 0.10	0.25 x 0.04 x 0.03	0.21 x 0.07 x 0.06
Space group	$P\,2_1/n$	$P\,2_1/n$	$C\,2/c$	$P\,\bar{1}$
a / Å	11.62710(10)	13.36700(10)	19.6854(4)	10.0943(3)
b / Å	9.02440(10)	18.4303(2)	10.8731(3)	20.0688(7)
c / Å	43.0468(4)	18.4227(2)	42.8266(13)	25.3224(6)
α / °	90	90	90	110.178(3)
β / °	95.9830(10)	109.3200(10)	96.989(2)	90.883(2)
γ / °	90	90	90	90.024(3)
Z	4	4	8	2
V / Å^3	736.69(6)	4282.99(7)	9098.5(4)	4814.3(2)
D_{calc} / g cm^{-3}	1.530	1.555	1.465	1.529
μ / mm^{-1}	8.532	8.911	8.397	8.048
Θ range / °	3.85 – 76.21	3.49 – 76.10	4.16 – 76.39	3.46 – 76.14
T / K	293(2)	293(2)	293(2)	293(2)
Radiation vawelength	1.54179 (CuK_α)	1.54179 (CuK_α)	1.54179 (CuK_α)	1.54179 (CuK_α)
Diffractometer type	Xcalibur Nova	Xcalibur Nova	Xcalibur Nova	Xcalibur Nova
Range of h, k, l	$-14 \le h \le 14$; $-10 \le k \le 11$; $-54 \le l \le 50$	$-10 \le h \le 16$; $-23 \le k \le 22$; $-22 \le l \le 23$	$-24 \le h \le 23$; $-9 \le k \le 13$; $-53 \le l \le 49$	$-12 \le h \le 12$; $-25 \le k \le 25$; $-27 \le l \le 31$
Reflections collected	22989	23737	19815	43140
Independent reflections	9219	8856	9302	19491
Observed reflections ($I \ge 2\sigma$)	8513	7544	8720	9835
Absorption correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan
R_{int}	0.0461	0.0308	0.0402	0.0509
R (F)	0.0640	0.0543	0.1036	0.0905
R_w (F^2)	0.1804	0.1369	0.2611	0.2358
Goodness of fit	1.201	1.026	1.119	1.203
H atom treatment	Constrained	Constrained	Constrained	Constrained
No. of parameters	561	514	514	987
No. of restraints	7	0	12	86
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	1.271; –0.996	2.274; –2.388	2.609; –2.247	1.224; –0.910

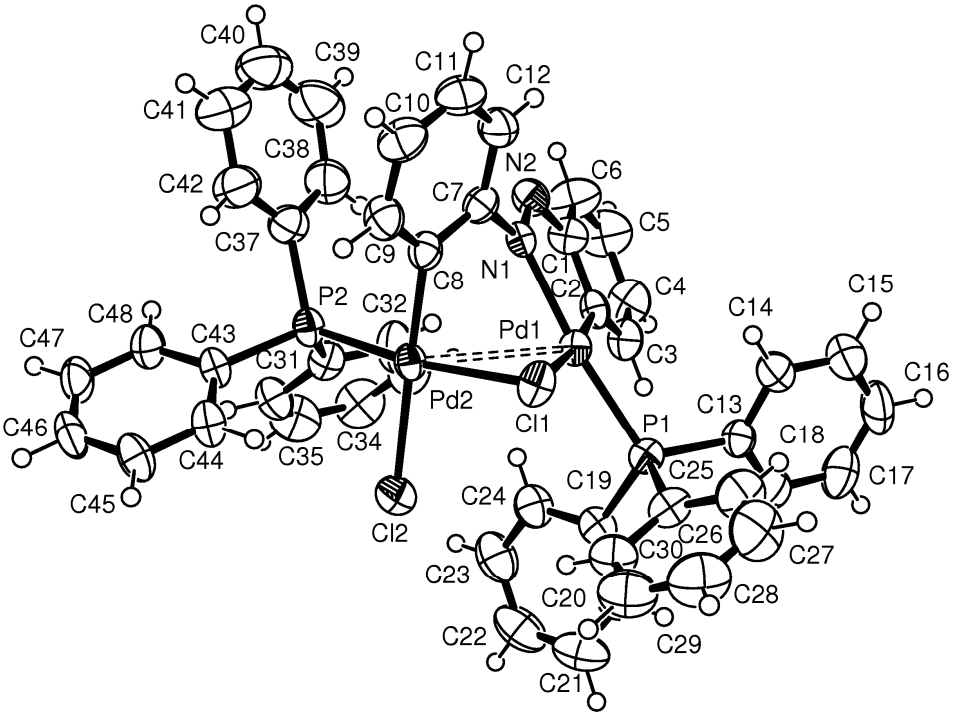

Figure S4. Molecular structure of **1a**. Displacement ellipsoids are drawn at the 50 % probability level and hydrogen atoms are depicted as spheres of arbitrary radii.

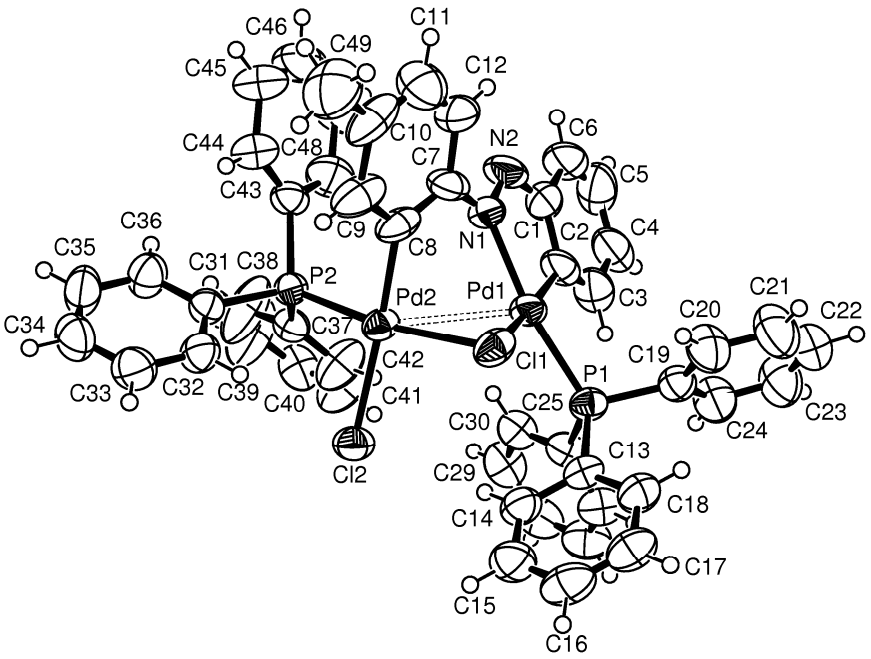

Figure S5. Molecular structure of **2a**. Displacement ellipsoids are drawn at the 50 % probability level and hydrogen atoms are depicted as spheres of arbitrary radii.

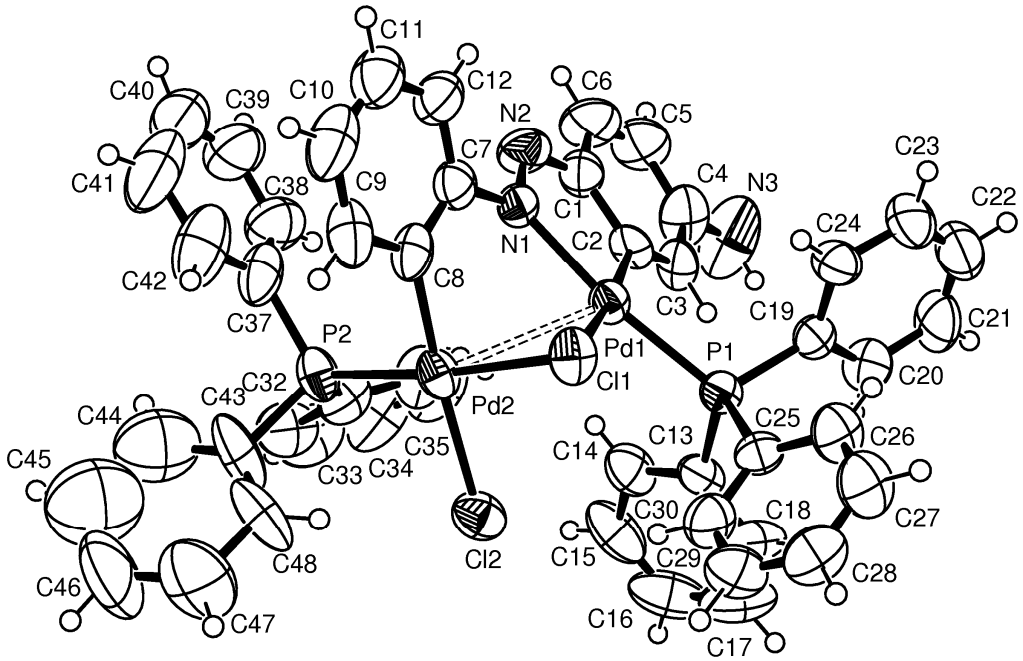

Figure S6. Molecular structure of **3a**. Displacement ellipsoids are drawn at the 50 % probability level and hydrogen atoms are depicted as spheres of arbitrary radii.

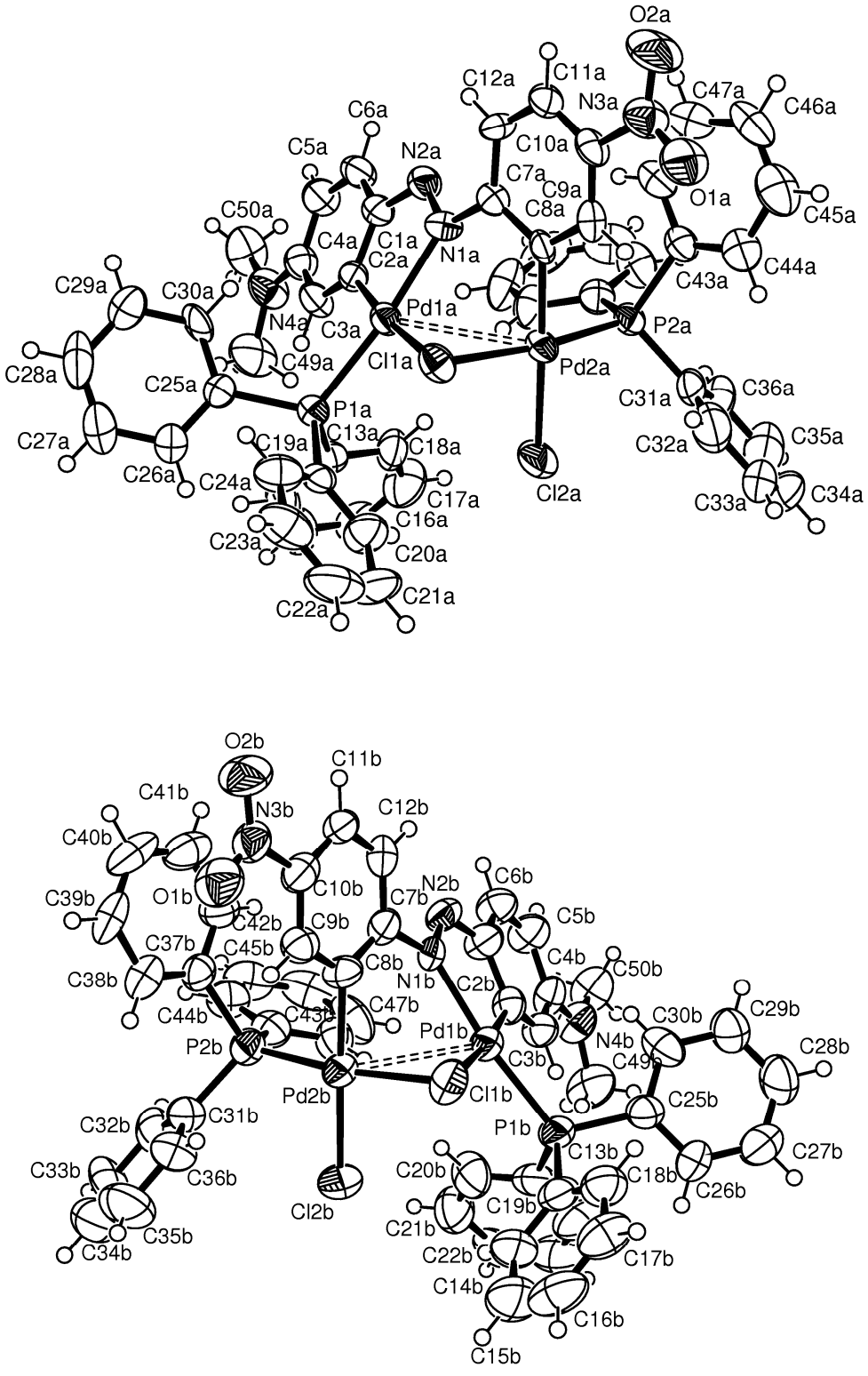

Figure S7. Molecular structures of two symmetry independent molecules of **4a**. The molecules are related by a pseudo-inversion centre and are therefore approximately enantiomeric. Displacement ellipsoids are drawn at the 50 % probability level and hydrogen atoms are depicted as spheres of arbitrary radii.

Table S3. Bond distances (in Ångströms) and bond angles (in degrees) around Pd atoms from X-ray diffraction and gas phase DFT calculations.

	1a		**2a**		**3a**		**4a***	
	exp	calc	exp	calc	exp	calc	exp	calc
Pd1–C2	1.993(8)	2.017	2.058(8)	2.017	1.967(9)	2.018	2.010(13) 1.998(16)	2.021
Pd1–N1	2.113(6)	2.137	2.097(5)	2.137	2.096(8)	2.130	2.124(11) 2.116(12)	2.127
Pd1–Cl1	2.411(2)	2.460	2.4348(17)	2.461	2.414(3)	2.459	2.434(3) 2.424(4)	2.455
Pd1–P1	2.281(2)	2.344	2.2670(15)	2.345	2.283(3)	2.348	2.285(3) 2.285(4)	2.345
Pd2–C8	1.992(8)	2.013	2.011(6)	2.013	2.000(13)	2.013	1.999(13) 2.000(15)	2.013
Pd2–Cl2	2.397(2)	2.440	2.3967(14)	2.441	2.418(3)	2.445	2.388(4) 2.378(5)	2.436
Pd2–P2	2.240(2)	2.307	2.2488(14)	2.307	2.255(3)	2.306	2.251(4) 2.245(4)	2.308
Pd2–Cl1	2.397(2)	2.452	2.4059(15)	2.452	2.391(3)	2.453	2.390(4) 2.389(4)	2.453
C2–Pd1–N1	79.0(3)	78.2	79.2(3)	78.3	79.1(4)	78.4	79.3(5) 78.6(6)	78.5
N1–Pd1–Cl1	93.58(18)	93.3	95.1(2)	93.3	93.9(3)	93.2	94.6(3) 94.7(4)	92.6
Cl1–Pd1–P1	92.75(7)	92.4	93.58(5)	92.4	93.42(10)	92.2	92.48(12) 92.88(16)	92.4
P1–Pd1–C2	94.8(2)	95.8	91.4(2)	95.8	93.2(3)	96.1	93.6(4) 93.8(5)	96.4
N1–Pd1–P1	172.05(17)	172.4	169.11(18)	172.5	171.0(3)	173.3	172.1(3) 171.2(4)	173.6
C2–Pd1–Cl1	172.3(2)	171.3	171.4(2)	171.2	172.2(4)	171.2	173.9(4) 173.3(5)	170.8
C8–Pd2–Cl2	176.3(2)	175.7	170.8(2)	175.8	175.9(3)	175.8	177.5(4) 176.5(5)	175.9
Cl2–Pd2–P2	91.81(8)	89.6	93.56(5)	89.6	93.48(12)	89.7	90.23(14) 90.44(18)	89.4
P2–Pd2–Cl1	169.76(8)	174.7	167.49(6)	174.8	173.57(13)	174.4	94.31(14) 172.28(18)	176.1
Cl1–Pd2–C8	83.5(2)	83.2	84.99(17)	83.2	84.4(3)	83.2	85.7(3) 85.3(5)	83.4
Cl2–Pd2–Cl1	93.65(8)	92.6	94.13(5)	92.6	91.62(11)	92.6	94.31(14) 94.88(19)	92.6
P2–Pd2–C8	91.3(2)	94.7	88.96(17)	94.6	90.4(3)	94.5	89.6(3) 89.1(5)	94.6

* Two symmetry independent molecules are present.

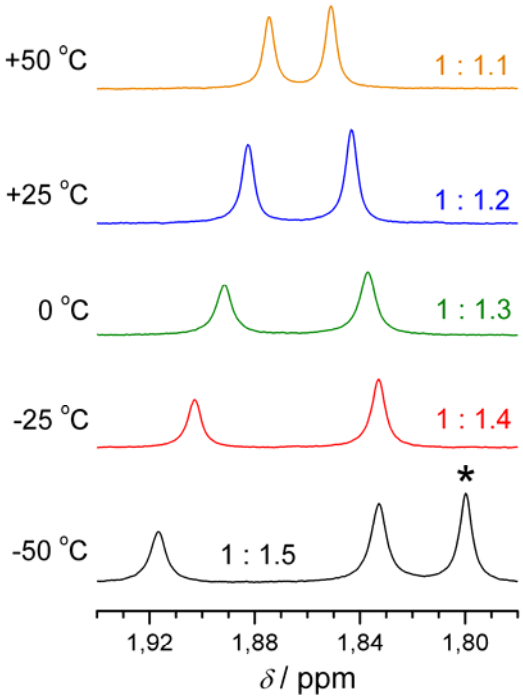

Figure S8. Aliphatic part of ^{1}H NMR spectra of complex **2a** at different temperatures. The ratios of two isomers, **2a**-alpha and **2a**-beta, is given using integration of methyl group signals. Signal at the higher field is used as a unit measure. Water signal is designated with an asterisk (*).

Table S4. The calculated atomic coordinates for isomers of **1a-bridge, 1a-cis, 1a-trans** in the gas phase (E: single-point energy, G: Gibbs energy).

1a-bridge

	x/Å	y/Å	z/Å
C	-0.959	3.283	1.038
C	-1.069	4.341	1.954
C	1.165	2.371	-1.650
C	1.197	-0.028	3.881
C	1.431	3.578	-2.320
C	1.594	0.026	2.545
C	-1.818	2.145	1.074
C	1.845	1.179	-1.964
C	1.886	-0.842	4.784
C	-2.033	4.284	2.955
C	-2.092	-2.202	3.410
C	-2.165	-1.385	2.280
C	2.365	3.602	-3.347
C	2.702	-0.713	2.101
C	-2.767	2.121	2.100
C	-2.772	-2.802	-1.622
C	2.788	1.238	-2.999
C	-2.871	3.169	3.027
C	2.973	-1.598	4.344
C	-3.033	-3.764	-2.595
C	3.038	2.425	-3.693
C	-3.068	-3.172	3.636
C	-3.217	-1.531	1.366
C	3.384	-1.531	3.011
C	-3.646	-1.712	-1.465
C	4.057	-2.998	-0.747
C	-4.110	-3.340	2.720
C	-4.151	-3.648	-3.425
C	-4.179	-2.534	1.585
C	4.185	1.949	1.366
C	4.292	0.977	0.361
C	4.438	-1.882	0.013
C	-4.766	-1.596	-2.300
C	5.749	-1.812	0.517
C	-4.804	0.547	-0.053
C	-4.898	1.645	-0.925
C	4.972	-4.023	-0.996
C	4.974	3.101	1.327
C	-5.014	-2.563	-3.277
C	5.207	1.187	-0.685
C	5.997	2.334	-0.718
C	-5.868	0.281	0.821
C	5.882	3.296	0.287
C	-6.038	2.447	-0.934
C	6.270	-3.948	-0.491
C	6.657	-2.842	0.269
C	-7.004	1.095	0.818
C	-7.093	2.175	-0.061
Cl	-0.651	-0.388	-2.411
Cl	0.669	-2.660	-0.045
H	0.346	0.560	4.212
H	-0.389	5.182	1.863
H	0.882	4.470	-2.037
H	1.035	0.636	1.842

(continued)

	x/Å	y/Å	z/Å
H	-1.386	-0.655	2.091
H	1.574	-0.890	5.823
H	-1.882	-2.891	-1.005
H	-2.129	5.093	3.672
H	-2.350	-4.601	-2.710
H	2.559	4.525	-3.884
H	-3.008	-3.811	4.512
H	3.040	-3.072	-1.117
H	3.325	0.338	-3.285
H	-3.451	1.287	2.200
H	3.493	1.810	2.189
H	3.506	-2.242	5.037
H	-3.623	3.108	3.810
H	3.757	2.431	-4.508
H	-4.068	1.878	-1.587
H	4.230	-2.126	2.683
H	-4.346	-4.399	-4.185
H	4.664	-4.881	-1.586
H	-4.859	-4.109	2.880
H	4.879	3.841	2.116
H	-4.969	-2.699	0.859
H	5.312	0.446	-1.471
H	-5.450	-0.762	-2.190
H	-5.812	-0.551	1.513
H	-5.886	-2.465	-3.918
H	6.066	-0.951	1.096
H	-6.096	3.291	-1.616
H	6.497	4.191	0.259
H	6.702	2.476	-1.532
H	6.980	-4.747	-0.689
H	7.666	-2.776	0.665
H	-7.817	0.882	1.505
H	-7.978	2.805	-0.061
H	-1.258	-2.089	4.095
N	0.066	3.364	0.099
N	0.156	2.341	-0.641
P	3.223	-0.533	0.341
P	-3.275	-0.483	-0.143
Pd	1.380	-0.552	-1.047
Pd	-1.391	0.881	-0.438

E: -3820.599778 H
G: -3819.966824 H

1a-cis

	x/Å	y/Å	z/Å
C	0.087	-2.948	0.429
C	-0.087	2.948	0.429
C	0.509	1.683	0.287
C	-0.509	-1.683	0.287
C	0.713	4.055	0.687
C	-0.713	-4.055	0.687
C	1.918	1.486	0.414
C	-1.918	-1.486	0.414
C	2.094	3.895	0.796
C	-2.094	-3.895	0.796
C	2.682	2.630	0.657
C	-2.682	-2.630	0.657
C	4.478	0.533	2.815
C	-4.478	-0.533	2.815
C	4.646	1.531	-2.158
C	-4.646	-1.531	-2.158
C	4.829	1.129	4.027
C	-4.829	-1.129	4.027
C	5.180	2.254	-3.226
C	-5.180	-2.254	-3.226
C	5.236	0.771	1.657
C	-5.236	-0.771	1.658
C	5.489	0.814	-1.296
C	-5.489	-0.814	-1.296
C	5.773	-1.654	0.203
C	-5.773	1.654	0.203
C	-5.930	-1.984	4.093
C	5.931	1.984	4.093
C	-6.076	2.361	-0.972
C	6.076	-2.361	-0.973
C	-6.230	2.149	1.433
C	6.231	-2.149	1.433
C	6.341	1.631	1.733
C	-6.341	-1.631	1.733
C	6.557	2.265	-3.447
C	-6.557	-2.265	-3.447
C	6.681	2.237	2.944
C	-6.681	-2.237	2.944
C	6.835	-3.528	-0.915
C	-6.835	3.528	-0.915
C	-6.874	-0.816	-1.536
C	6.874	0.816	-1.537
C	6.981	-3.325	1.486
C	-6.981	3.325	1.486
C	7.287	-4.015	0.313
C	-7.287	4.015	0.313
C	7.403	1.542	-2.603
C	-7.403	-1.542	-2.603
Cl	2.830	-2.423	-1.340
Cl	-2.830	2.423	-1.340
H	0.259	5.035	0.795
H	-0.259	-5.035	0.795
H	1.157	-3.048	0.310
H	-1.157	3.048	0.310
H	2.729	4.755	0.997

(continued)

	x/Å	y/Å	z/Å
H	-2.729	-4.755	0.997
H	3.573	1.513	-1.999
H	-3.573	-1.513	-1.999
H	3.601	-0.106	2.760
H	-3.601	0.106	2.760
H	3.757	2.560	0.763
H	-3.757	-2.560	0.763
H	4.233	0.935	4.914
H	-4.233	-0.935	4.914
H	4.515	2.800	-3.889
H	-4.515	-2.800	-3.889
H	5.711	-2.007	-1.929
H	-5.711	2.007	-1.929
H	-6.012	1.619	2.353
H	6.013	-1.619	2.353
H	6.198	2.457	5.034
H	-6.198	-2.457	5.034
H	6.930	1.843	0.848
H	-6.930	-1.843	0.848
H	6.970	2.825	-4.281
H	-6.971	-2.825	-4.281
H	7.061	-4.063	-1.832
H	-7.061	4.063	-1.832
H	7.330	-3.695	2.446
H	-7.330	3.695	2.446
H	7.534	2.909	2.987
H	-7.534	-2.909	2.987
H	7.537	0.234	-0.904
H	-7.537	-0.234	-0.904
H	7.874	-4.928	0.355
H	-7.874	4.928	0.355
H	8.475	1.535	-2.779
H	-8.475	-1.535	-2.779
N	0.311	-0.562	0.119
N	-0.311	0.562	0.119
P	4.753	-0.118	0.109
P	-4.753	0.118	0.109
Pd	2.446	-0.400	-0.070
Pd	-2.446	0.400	-0.070

E: -3820.594183 H
G: -3819.962856 H

1a-trans

	x/Å	y/Å	z/Å
C	0.500	3.742	-0.104
C	-0.500	-3.742	0.104
C	0.539	2.349	-0.170
C	-0.539	-2.349	0.170
C	0.595	-1.633	-0.289
C	-0.595	1.633	0.289
C	0.612	-4.396	-0.440
C	-0.613	4.396	0.441
C	1.693	-2.285	-0.872
C	-1.694	2.285	0.872
C	1.694	-3.671	-0.952
C	-1.694	3.671	0.952
C	3.177	-1.473	2.154
C	-3.177	1.473	-2.154
C	3.195	-2.326	3.260
C	-3.195	2.326	-3.260
C	4.344	-1.234	1.416
C	-4.344	1.234	-1.416
C	4.381	-2.951	3.641
C	-4.382	2.951	-3.641
C	4.997	-0.918	-1.457
C	-4.998	0.918	1.457
C	5.131	-0.175	-2.645
C	-5.131	0.175	2.645
C	5.315	-2.284	-1.468
C	-5.316	2.284	1.468
C	5.368	2.075	1.506
C	-5.368	-2.075	-1.506
C	5.540	-1.851	1.824
C	-5.541	1.851	-1.824
C	5.556	-2.710	2.922
C	-5.556	2.710	-2.922
C	5.595	-0.787	-3.809
C	-5.595	0.787	3.809
C	5.661	1.117	0.523
C	-5.661	-1.117	-0.523
C	5.771	-2.893	-2.641
C	-5.771	2.893	2.641
C	5.915	-2.147	-3.811
C	-5.915	2.148	3.811
C	6.364	2.924	1.983
C	-6.364	-2.924	-1.983
C	-6.965	-1.033	-0.019
C	6.965	1.033	0.020
C	7.663	2.834	1.477
C	-7.664	-2.835	-1.477
C	-7.960	-1.891	-0.494
C	7.960	1.891	0.495
Cl	3.425	2.923	-1.281
Cl	-3.425	-2.923	1.282
H	0.624	-5.482	-0.479
H	-0.624	5.483	0.479
H	1.346	4.315	-0.465
H	-1.346	-4.315	0.466
H	2.250	-0.986	1.872

(continued)

	x/Å	y/Å	z/Å
H	-2.250	0.986	-1.872
H	2.280	-2.498	3.820
H	-2.281	2.498	-3.820
H	2.512	-1.707	-1.280
H	-2.512	1.707	1.280
H	2.536	-4.182	-1.409
H	-2.536	4.182	1.409
H	4.355	2.168	1.887
H	-4.355	-2.168	-1.887
H	4.396	-3.617	4.499
H	-4.397	3.617	-4.499
H	4.869	0.879	-2.653
H	-4.869	-0.879	2.654
H	5.206	-2.878	-0.567
H	-5.207	2.878	0.567
H	5.699	-0.201	-4.717
H	-5.699	0.201	4.717
H	6.015	-3.952	-2.635
H	-6.015	3.952	2.635
H	-6.123	-3.664	-2.740
H	6.123	3.664	2.741
H	6.271	-2.623	-4.720
H	-6.271	2.623	4.720
H	6.465	-1.648	1.292
H	-6.465	1.648	-1.292
H	6.487	-3.182	3.223
H	-6.487	3.182	-3.223
H	7.208	0.306	-0.748
H	-7.208	-0.306	0.748
H	8.438	3.502	1.844
H	-8.438	-3.502	-1.844
H	8.967	1.818	0.093
H	-8.967	-1.819	-0.092
N	0.581	-0.241	-0.148
N	-0.582	0.241	0.148
P	-4.311	0.034	-0.010
P	4.311	-0.034	0.011
Pd	2.133	1.163	-0.434
Pd	-2.133	-1.163	0.434

E: -3820.576714 H
G: -3819.946568 H

Table S5. The calculated atomic coordinates for **2a-alpha-bridge**, **2a-beta-bridge**, **2a-cis** and **2a-trans** in the gas phase (E: single-point energy, G: Gibbs energy).

2a-alpha-bridge

	x/Å	y/Å	z/Å
C	-0.953	3.289	1.042
C	-1.077	4.345	1.956
C	1.173	2.372	-1.639
C	1.211	-0.062	3.886
C	1.442	3.580	-2.307
C	1.602	-0.002	2.548
C	-1.817	2.153	1.079
C	1.851	1.180	-1.957
C	1.910	-0.871	4.785
C	-2.055	4.290	2.943
C	-2.108	-2.194	3.418
C	-2.176	-1.377	2.288
C	2.377	3.604	-3.334
C	2.715	-0.731	2.099
C	-2.767	-2.794	-1.617
C	-2.773	2.135	2.092
C	2.793	1.239	-2.993
C	-2.906	3.182	3.029
C	3.002	-1.616	4.339
C	-3.025	-3.760	-2.587
C	3.047	2.427	-3.683
C	-3.086	-3.163	3.641
C	-3.225	-1.522	1.371
C	3.408	-1.543	3.004
C	-3.645	-1.708	-1.460
C	-3.956	3.089	4.110
C	4.057	-3.002	-0.761
C	-4.125	-3.329	2.722
C	-4.146	-3.650	-3.414
C	4.183	1.940	1.371
C	-4.189	-2.523	1.587
C	4.296	0.971	0.364
C	4.443	-1.887	-0.001
C	-4.767	-1.599	-2.292
C	-4.804	0.556	-0.055
C	-4.899	1.645	-0.937
C	4.969	3.094	1.337
C	4.970	-4.026	-1.018
C	-5.013	-2.568	-3.267
C	5.213	1.186	-0.679
C	5.757	-1.820	0.495
C	-5.864	0.302	0.827
C	5.878	3.296	0.299
C	5.999	2.336	-0.708
C	-6.037	2.451	-0.948
C	6.271	-3.953	-0.521
C	6.663	-2.849	0.239
C	-6.997	1.119	0.823
C	-7.088	2.191	-0.066
Cl	-0.649	-0.381	-2.408
Cl	0.669	-2.663	-0.048

(continued)

	x/Å	y/Å	z/Å
H	0.355	0.518	4.221
H	-0.401	5.190	1.873
H	0.896	4.473	-2.022
H	1.034	0.604	1.848
H	-1.275	-2.083	4.106
H	-1.396	-0.647	2.103
H	1.603	-0.924	5.825
H	-1.875	-2.879	-1.002
H	-2.158	5.107	3.653
H	-2.339	-4.594	-2.702
H	2.573	4.529	-3.868
H	-3.029	-3.803	4.518
H	3.038	-3.075	-1.126
H	3.327	0.338	-3.282
H	-3.460	1.301	2.182
H	3.489	1.796	2.192
H	3.544	-2.257	5.029
H	-3.677	2.346	4.868
H	3.766	2.433	-4.499
H	-4.073	1.870	-1.606
H	-4.094	4.046	4.619
H	4.257	-2.129	2.672
H	-4.340	-4.404	-4.172
H	4.658	-4.883	-1.608
H	4.869	3.832	2.127
H	-4.876	-4.097	2.879
H	-4.921	2.777	3.698
H	-4.977	-2.687	0.858
H	5.321	0.448	-1.467
H	-5.455	-0.767	-2.183
H	-5.806	-0.525	1.526
H	-5.887	-2.476	-3.906
H	6.078	-0.959	1.074
H	-6.097	3.288	-1.638
H	6.491	4.193	0.275
H	6.705	2.483	-1.520
H	6.980	-4.752	-0.725
H	7.675	-2.784	0.629
H	-7.808	0.914	1.516
H	-7.971	2.824	-0.067
N	0.074	3.365	0.110
N	0.163	2.342	-0.632
P	3.229	-0.540	0.337
P	-3.274	-0.476	-0.141
Pd	1.382	-0.552	-1.046
Pd	-1.388	0.887	-0.432

E: -3859.920436 H
G: -3859.263170 H

2a-beta-bridge

	x/Å	y/Å	z/Å
C	-0.966	3.286	1.045
C	-1.085	4.345	1.959
C	1.166	2.375	-1.633
C	1.187	-0.020	3.864
C	1.450	3.584	-2.294
C	1.588	0.029	2.528
C	-1.817	2.142	1.086
C	1.843	1.185	-1.961
C	1.873	-0.830	4.772
C	-2.048	4.284	2.960
C	-2.094	-2.212	3.411
C	-2.165	-1.392	2.283
C	2.386	3.607	-3.316
C	2.697	-0.712	2.091
C	-2.764	2.112	2.112
C	-2.768	-2.797	-1.623
C	2.788	1.250	-2.993
C	-2.876	3.162	3.037
C	2.961	-1.587	4.338
C	-3.029	-3.759	-2.597
C	3.061	2.433	-3.692
C	-3.070	-3.182	3.634
C	-3.217	-1.534	1.369
C	3.377	-1.526	3.006
C	-3.644	-1.709	-1.462
C	4.039	2.445	-4.842
C	4.060	-3.004	-0.752
C	-4.113	-3.346	2.717
C	-4.150	-3.644	-3.423
C	4.175	1.952	1.344
C	-4.181	-2.536	1.585
C	4.294	0.971	0.350
C	4.438	-1.889	0.011
C	-4.766	-1.595	-2.293
C	-4.800	0.549	-0.048
C	-4.892	1.647	-0.920
C	4.965	3.103	1.303
C	4.976	-4.030	-0.995
C	-5.015	-2.561	-3.272
C	5.221	1.170	-0.688
C	5.745	-1.823	0.526
C	-5.865	0.284	0.824
C	5.886	3.289	0.272
C	6.012	2.317	-0.723
C	-6.032	2.450	-0.930
C	6.270	-3.959	-0.480
C	6.653	-2.854	0.284
C	-7.000	1.098	0.820
C	-7.088	2.179	-0.058
Cl	-0.654	-0.378	-2.414
Cl	0.674	-2.670	-0.070

(continued)

	x/Å	y/Å	z/Å
H	0.334	0.569	4.189
H	-0.411	5.192	1.865
H	0.914	4.482	-2.005
H	1.031	0.636	1.821
H	-1.259	-2.103	4.096
H	-1.386	-0.662	2.098
H	1.558	-0.874	5.811
H	-1.876	-2.886	-1.009
H	-2.150	5.094	3.675
H	-2.344	-4.594	-2.715
H	2.588	4.538	-3.841
H	-3.011	-3.824	4.508
H	3.046	-3.076	-1.131
H	3.321	0.346	-3.280
H	-3.441	1.273	2.215
H	3.474	1.821	2.160
H	3.492	-2.229	5.035
H	3.514	2.436	-5.806
H	-3.627	3.097	3.821
H	-4.062	1.880	-1.581
H	4.223	-2.122	2.683
H	-4.346	-4.394	-4.184
H	4.665	3.344	-4.826
H	4.670	-4.888	-1.588
H	4.695	1.571	-4.820
H	4.861	3.851	2.083
H	-4.863	-4.115	2.875
H	-4.970	-2.698	0.857
H	5.335	0.422	-1.465
H	-5.452	-0.763	-2.181
H	-5.810	-0.549	1.517
H	-5.889	-2.464	-3.910
H	6.060	-0.962	1.107
H	-6.088	3.294	-1.611
H	6.502	4.183	0.243
H	6.728	2.450	-1.529
H	6.979	-4.759	-0.672
H	7.659	-2.790	0.688
H	-7.814	0.886	1.507
H	-7.972	2.810	-0.059
N	0.061	3.370	0.109
N	0.159	2.344	-0.628
P	3.223	-0.538	0.331
P	-3.272	-0.482	-0.139
Pd	1.380	-0.553	-1.058
Pd	-1.387	0.881	-0.428

E: -3859.920151 H

G: -3859.262962 H

2a-cis

	x/Å	y/Å	z/Å
C	-0.168	2.946	0.093
C	0.173	-2.957	0.035
C	0.455	1.692	-0.021
C	-0.456	-1.703	-0.048
C	-0.595	-4.093	0.264
C	0.601	4.075	0.338
C	-1.866	-1.548	0.111
C	1.868	1.541	0.129
C	-1.977	-3.974	0.403
C	1.992	3.976	0.463
C	2.596	2.709	0.354
C	-2.598	-2.719	0.323
C	2.841	5.202	0.692
C	4.308	0.755	2.661
C	-4.312	-0.784	2.646
C	4.576	1.412	3.862
C	-4.590	-1.442	3.844
C	-4.764	-1.542	-2.342
C	4.780	1.547	-2.327
C	5.131	0.955	1.540
C	-5.136	-0.967	1.523
C	-5.353	-2.222	-3.410
C	5.374	2.233	-3.388
C	-5.561	-0.867	-1.406
C	5.572	0.873	-1.386
C	5.657	2.290	3.955
C	-5.684	-2.306	3.931
C	-5.769	1.525	0.233
C	5.771	-1.530	0.237
C	6.125	-1.978	1.518
C	-6.130	1.963	1.515
C	-6.166	2.280	-0.883
C	6.176	-2.276	-0.883
C	6.215	1.838	1.642
C	-6.231	-1.837	1.619
C	6.471	2.505	2.842
C	-6.499	-2.505	2.816
C	-6.740	-2.231	-3.556
C	6.762	2.248	-3.524
C	6.873	-3.147	1.677
C	-6.879	3.131	1.678
C	-6.922	3.438	-0.715
C	6.931	-3.435	-0.718
C	-6.958	-0.867	-1.570
C	6.970	0.879	-1.540
C	-7.279	3.868	0.565
C	7.280	-3.876	0.560
C	-7.542	-1.550	-2.637
C	7.559	1.568	-2.600
Cl	-2.970	2.338	-1.572
Cl	2.988	-2.317	-1.607

(continued)

	x/Å	y/Å	z/Å
H	-0.114	-5.064	0.326
H	0.116	5.043	0.426
H	-1.240	3.022	-0.037
H	1.243	-3.026	-0.109
H	2.276	5.993	1.195
H	-2.586	-4.857	0.581
H	3.198	5.614	-0.261
H	-3.441	-0.139	2.572
H	3.446	0.099	2.583
H	3.672	2.665	0.475
H	-3.672	-2.681	0.449
H	-3.684	-1.524	-2.241
H	3.699	1.523	-2.234
H	3.724	4.971	1.296
H	3.931	1.246	4.720
H	-3.944	-1.290	4.703
H	-4.723	-2.736	-4.130
H	4.747	2.746	-4.112
H	5.829	-1.417	2.397
H	-5.839	1.395	2.392
H	5.859	2.810	4.887
H	-5.875	1.971	-1.880
H	5.891	-1.960	-1.878
H	-5.894	-2.827	4.860
H	6.854	2.021	0.785
H	-6.871	-2.008	0.760
H	7.140	-3.479	2.676
H	-7.152	3.456	2.678
H	-7.197	-2.757	-4.390
H	7.223	2.778	-4.352
H	-7.223	4.011	-1.588
H	7.237	-4.001	-1.593
H	7.309	3.194	2.904
H	-7.346	-3.183	2.873
H	-7.588	-0.317	-0.878
H	7.597	0.330	-0.844
H	-7.864	4.774	0.692
H	7.864	-4.783	0.684
H	-8.621	-1.541	-2.754
H	8.640	1.564	-2.709
N	-0.328	0.549	-0.191
N	0.331	-0.555	-0.204
P	-4.749	0.003	-0.003
P	4.753	-0.007	0.006
Pd	-2.463	0.329	-0.314
Pd	2.467	-0.329	-0.321

E: -3859.915048 H
G: -3859.259981 H

2a-trans

	x/Å	y/Å	z/Å
C	0.508	-3.732	0.013
C	-0.525	3.748	-0.040
C	0.542	-2.340	0.106
C	-0.558	2.359	-0.133
C	0.587	1.637	0.291
C	0.589	4.424	0.492
C	-0.597	-1.620	-0.332
C	-0.604	-4.381	-0.538
C	0.612	5.931	0.538
C	1.678	3.675	0.969
C	1.687	2.292	0.865
C	-1.691	-3.650	-1.029
C	-1.695	-2.265	-0.922
C	-3.129	-2.418	3.232
C	-3.134	-1.537	2.147
C	3.167	1.524	-2.166
C	3.183	2.390	-3.262
C	-4.305	-3.061	3.614
C	-4.314	-1.290	1.433
C	4.339	1.271	-1.438
C	4.369	3.015	-3.642
C	4.997	0.921	1.429
C	-5.016	-0.907	-1.421
C	5.126	0.166	2.610
C	-5.174	-0.135	-2.588
C	5.322	2.285	1.454
C	-5.325	-2.274	-1.462
C	-5.360	2.005	1.625
C	5.369	-2.030	-1.576
C	-5.492	-2.811	2.919
C	-5.499	-1.926	1.843
C	5.535	1.888	-1.846
C	5.547	2.760	-2.933
C	5.592	0.764	3.780
C	-5.653	-0.721	-3.759
C	5.660	-1.088	-0.577
C	-5.661	1.072	0.621
C	5.779	2.881	2.633
C	-5.796	-2.857	-2.642
C	5.919	2.123	3.796
C	-5.964	-2.083	-3.790
C	-6.355	2.833	2.140
C	6.366	-2.871	-2.064
C	6.963	-1.013	-0.069
C	-6.972	0.993	0.134
C	-7.661	2.749	1.651
C	7.664	-2.791	-1.554
C	7.959	-1.864	-0.555
C	-7.966	1.831	0.647
Cl	3.432	-2.923	1.204
Cl	-3.472	2.942	-1.173

(continued)

	x/Å	y/Å	z/Å
H	-0.393	6.341	0.677
H	-0.612	-5.466	-0.598
H	1.002	6.343	-0.401
H	1.251	6.299	1.346
H	1.359	-4.308	0.359
H	-1.386	4.318	-0.373
H	-2.205	-2.596	3.773
H	-2.216	-1.036	1.863
H	2.241	1.037	-1.884
H	2.265	2.572	-3.814
H	2.517	1.718	1.255
H	-2.519	-1.683	-1.314
H	2.525	4.180	1.424
H	-2.534	-4.155	-1.490
H	-4.302	-3.748	4.456
H	-4.343	2.094	1.994
H	4.357	-2.116	-1.961
H	4.382	3.691	-4.493
H	4.859	-0.888	2.608
H	-4.918	0.921	-2.574
H	-5.197	-2.889	-0.578
H	5.217	2.888	0.559
H	5.692	0.168	4.683
H	-5.775	-0.113	-4.650
H	6.028	3.938	2.638
H	-6.032	-3.917	-2.659
H	-6.107	3.553	2.915
H	6.126	-3.599	-2.834
H	6.276	2.588	4.710
H	-6.331	-2.538	-4.705
H	-6.414	-3.298	3.222
H	-6.433	-1.717	1.330
H	6.462	1.675	-1.323
H	6.478	3.232	-3.235
H	7.205	-0.300	0.712
H	-7.222	0.286	-0.650
H	-8.435	3.400	2.048
H	8.439	-3.453	-1.930
H	8.964	-1.799	-0.150
H	-8.978	1.763	0.258
N	0.576	0.252	0.129
N	-0.588	-0.231	-0.166
P	4.308	0.053	-0.047
P	-4.311	-0.054	0.057
Pd	2.134	-1.154	0.384
Pd	-2.151	1.170	-0.394

E: -3859.897831 H
G: -3859.243195 H

Table S6. The calculated atomic coordinates for **3a-alpha-bridge**, **3a-beta-bridge**, **3a-cis** and **3a-trans** in the gas phase (E: single-point energy, G: Gibbs energy).

3a-alpha-bridge

	x/Å	y/Å	z/Å
C	-0.939	3.286	1.065
C	-1.061	4.332	1.997
C	1.169	2.383	-1.629
C	1.194	0.015	3.860
C	1.435	3.594	-2.292
C	1.597	0.057	2.525
C	-1.819	2.156	1.091
C	1.851	1.196	-1.957
C	1.869	-0.802	4.770
C	-2.037	4.287	2.977
C	-2.085	-2.196	3.420
C	-2.163	-1.375	2.293
C	2.371	3.627	-3.319
C	2.698	-0.698	2.089
C	-2.757	-2.788	-1.639
C	-2.778	2.130	2.092
C	2.790	1.262	-2.995
C	-2.906	3.178	3.038
C	2.949	-1.572	4.338
C	-3.016	-3.744	-2.619
C	-3.038	-3.192	3.629
C	3.043	2.455	-3.677
C	-3.199	-1.544	1.365
C	3.367	-1.518	3.007
C	-3.640	-1.708	-1.466
C	4.043	-3.009	-0.748
C	-4.064	-3.381	2.700
C	-4.139	-2.571	1.568
C	-4.141	-3.632	-3.439
C	4.212	1.943	1.344
C	4.311	0.964	0.344
C	4.428	-1.896	0.014
C	-4.767	-1.596	-2.291
C	-4.809	0.525	-0.027
C	-4.919	1.637	-0.878
C	4.951	-4.043	-0.989
C	-5.013	-2.556	-3.276
C	5.015	3.085	1.300
C	5.230	1.157	-0.700
C	5.736	-1.838	0.528
C	-5.868	0.232	0.844
C	5.928	3.264	0.261
C	6.034	2.295	-0.738
C	-6.068	2.428	-0.870
C	6.245	-3.980	-0.474
C	6.636	-2.876	0.288
C	-7.013	1.033	0.861
C	-7.117	2.129	0.002
Cl	-0.655	-0.355	-2.412
Cl	0.660	-2.657	-0.064

(continued)

	x/Å	y/Å	z/Å
H	0.348	0.615	4.183
H	-0.376	5.171	1.928
H	0.887	4.484	-2.002
H	1.048	0.669	1.816
H	-1.262	-2.065	4.116
H	-1.402	-0.624	2.120
H	1.553	-0.839	5.809
H	-1.861	-2.874	-1.030
H	-2.134	5.092	3.699
H	-2.326	-4.573	-2.746
H	2.566	4.556	-3.845
H	-2.972	-3.834	4.503
H	3.029	-3.074	-1.126
H	3.325	0.362	-3.289
H	-3.472	1.302	2.178
H	3.472	-2.219	5.037
H	3.516	1.816	2.165
H	3.762	2.467	-4.492
H	-4.094	1.892	-1.538
H	-4.114	3.936	4.510
H	4.206	-2.125	2.685
H	-4.335	-4.378	-4.204
H	-4.625	2.452	3.876
H	4.639	-4.899	-1.581
H	-4.795	-4.170	2.846
H	-4.915	-2.752	0.830
H	4.926	3.831	2.085
H	5.327	0.412	-1.482
H	-5.458	-0.769	-2.170
H	-5.802	-0.615	1.518
H	-5.891	-2.460	-3.909
H	6.057	-0.979	1.108
H	-6.137	3.282	-1.536
H	6.553	4.152	0.230
H	6.742	2.425	-1.552
H	6.949	-4.786	-0.665
H	7.643	-2.819	0.692
H	-7.824	0.796	1.543
H	-8.009	2.748	0.015
N	0.080	3.360	0.141
N	0.160	2.345	-0.620
N	-3.854	3.083	4.038
P	3.224	-0.534	0.329
P	-3.266	-0.486	-0.138
Pd	1.381	-0.541	-1.056
Pd	-1.393	0.899	-0.429

E: -3875.962354 H

G: -3875.314400 H

3a-beta-bridge

	x/Å	y/Å	z/Å
C	-1.051	3.322	0.230
C	1.129	0.702	3.762
C	1.224	1.961	-2.111
C	-1.263	4.545	0.886
C	1.519	3.025	-2.987
C	1.570	0.511	2.452
C	1.823	0.120	4.826
C	-1.839	2.165	0.507
C	1.937	0.744	-2.191
C	-2.053	-1.640	3.673
C	-2.109	-1.068	2.401
C	-2.252	4.643	1.859
C	2.481	2.879	-3.969
C	-2.528	-3.259	-1.147
C	-2.725	-4.410	-1.907
C	2.726	-0.243	2.193
C	-2.815	2.300	1.497
C	2.906	0.620	-3.185
C	2.959	-0.649	4.573
C	-3.007	-2.580	4.061
C	-3.017	3.516	2.168
C	-3.124	-1.431	1.505
C	3.183	1.662	-4.091
C	3.414	-0.826	3.265
C	-3.443	-2.195	-1.238
C	-3.820	-4.511	-2.769
C	-4.011	-2.964	3.168
C	-4.064	-2.403	1.893
C	4.111	2.295	0.999
C	4.284	1.161	0.192
C	4.298	-2.972	-0.068
C	-4.539	-2.298	-2.105
C	4.599	-1.696	0.433
C	-4.720	0.258	-0.354
C	-4.724	-3.453	-2.868
C	-4.815	1.150	-1.434
C	4.836	3.462	0.747
C	5.199	1.225	-0.873
C	5.275	-3.971	-0.077
C	5.743	3.513	-0.310
C	-5.807	0.135	0.523
C	5.892	-1.442	0.924
C	5.923	2.389	-1.119
C	-5.979	1.889	-1.644
C	6.555	-3.711	0.413
C	6.861	-2.444	0.917
C	-6.967	0.886	0.318
C	-7.058	1.759	-0.766
Cl	-0.475	-0.979	-2.372
Cl	0.865	-2.692	0.425

(continued)

	x/Å	y/Å	z/Å
H	0.240	1.298	3.947
H	-0.637	5.392	0.622
H	0.959	3.949	-2.896
H	1.009	0.940	1.628
H	-1.247	-1.363	4.345
H	-1.347	-0.361	2.093
H	1.477	0.263	5.846
H	-1.654	-3.185	-0.505
H	-2.011	-5.224	-1.831
H	-2.422	5.582	2.376
H	2.687	3.694	-4.659
H	-2.959	-3.029	5.049
H	3.296	-3.186	-0.424
H	3.417	2.272	1.831
H	-3.446	1.462	1.770
H	3.464	-0.309	-3.280
H	3.497	-1.114	5.395
H	-3.785	3.576	2.934
H	-3.966	-5.409	-3.362
H	-3.968	1.276	-2.104
H	4.099	2.122	-5.858
H	4.298	-1.427	3.083
H	4.387	0.558	-5.315
H	4.690	4.329	1.385
H	-4.743	-3.712	3.457
H	-4.822	-2.738	1.192
H	5.028	-4.954	-0.467
H	-5.255	-1.487	-2.185
H	5.354	0.359	-1.508
H	-5.578	-3.524	-3.535
H	-5.750	-0.535	1.373
H	-6.037	2.573	-2.485
H	6.146	-0.458	1.305
H	6.306	4.422	-0.504
H	6.624	2.419	-1.949
H	7.312	-4.490	0.404
H	-7.798	0.786	1.010
H	7.855	-2.234	1.300
H	-7.961	2.342	-0.922
N	0.004	3.261	-0.674
N	0.193	2.100	-1.154
N	4.170	1.511	-5.057
P	-3.155	-0.709	-0.186
P	3.301	-0.385	0.447
Pd	-1.304	0.638	-0.695
Pd	1.512	-0.787	-0.958

E: -3875.960862 H
G: -3875.312799 H

3a-cis

	x/Å	y/Å	z/Å
C	-0.166	2.960	0.027
C	0.168	-2.952	0.059
C	-0.449	-1.688	-0.035
C	0.454	1.702	-0.061
C	-0.587	-4.080	0.310
C	0.607	4.094	0.254
C	1.865	1.546	0.092
C	-1.866	-1.540	0.136
C	-1.982	-3.970	0.469
C	1.989	3.971	0.388
C	-2.594	-2.696	0.371
C	2.602	2.713	0.304
C	4.296	0.781	2.637
C	-4.339	-0.769	2.653
C	4.572	1.434	3.838
C	-4.613	-1.437	3.846
C	4.770	1.547	-2.343
C	-4.774	-1.548	-2.332
C	5.129	0.959	1.521
C	-5.150	-0.963	1.523
C	-5.362	-2.234	-3.396
C	5.363	2.230	-3.407
C	5.563	0.867	-1.407
C	-5.571	-0.865	-1.401
C	5.673	2.288	3.934
C	-5.690	-2.323	3.921
C	5.767	-1.527	0.226
C	-5.782	1.529	0.234
C	6.127	-1.966	1.508
C	-6.143	1.969	1.516
C	6.168	-2.280	-0.890
C	-6.182	2.282	-0.883
C	-6.229	-1.854	1.607
C	6.232	1.819	1.626
C	-6.493	-2.534	2.799
C	6.498	2.482	2.825
C	-6.749	-2.241	-3.545
C	6.750	2.237	-3.550
C	6.879	-3.132	1.671
C	-6.893	3.135	1.679
C	6.928	-3.436	-0.722
C	-6.941	3.439	-0.715
C	6.960	0.865	-1.569
C	-6.967	-0.864	-1.568
C	7.283	-3.867	0.558
C	-7.296	3.871	0.565
C	7.548	1.550	-2.632
C	-7.551	-1.552	-2.632
Cl	2.977	-2.355	-1.578
Cl	-2.998	2.317	-1.597

(continued)

	x/Å	y/Å	z/Å
H	-0.107	-5.052	0.377
H	0.128	5.066	0.318
H	1.237	-3.030	-0.093
H	-1.237	3.034	-0.110
H	-2.299	-5.926	1.002
H	2.602	4.851	0.563
H	3.419	0.145	2.555
H	-3.479	-0.108	2.588
H	-3.668	-2.657	0.509
H	3.677	2.670	0.427
H	-3.689	-4.949	1.048
H	3.690	1.532	-2.244
H	-3.694	-1.531	-2.228
H	3.919	1.286	4.693
H	-3.978	-1.274	4.712
H	-4.732	-2.753	-4.112
H	4.736	2.748	-4.126
H	5.833	-1.400	2.385
H	-5.850	1.404	2.394
H	5.878	-1.971	-1.887
H	5.882	2.805	4.866
H	-5.891	1.973	-1.879
H	-5.898	-2.851	4.848
H	-6.860	-2.031	0.743
H	6.878	1.986	0.771
H	7.151	-3.457	2.671
H	-7.165	3.461	2.678
H	-7.205	-2.770	-4.377
H	7.210	2.765	-4.381
H	7.231	-4.007	-1.595
H	-7.243	4.010	-1.588
H	-7.329	-3.225	2.848
H	7.350	3.153	2.890
H	7.588	0.312	-0.877
H	-7.597	-0.309	-0.880
H	7.872	-4.771	0.685
H	-7.883	4.776	0.692
H	8.628	1.540	-2.747
H	-8.630	-1.542	-2.752
N	0.322	-0.553	-0.208
N	-0.337	0.557	-0.221
N	-2.758	-5.087	0.684
P	4.744	-0.007	-0.010
P	-4.758	0.011	-0.003
Pd	2.459	-0.333	-0.330
Pd	-2.468	0.330	-0.315

E: -3875.957683 H
G: -3875.311752 H

3a-trans

	x/Å	y/Å	z/Å
C	0.480	-3.685	0.001
C	0.511	-2.293	0.088
C	-0.559	3.788	-0.093
C	0.574	1.681	0.231
C	0.576	4.470	0.409
C	-0.587	2.408	-0.167
C	-0.616	-1.572	-0.375
C	-0.621	-4.337	-0.569
C	1.689	2.352	0.769
C	1.690	3.728	0.867
C	-1.696	-3.607	-1.085
C	-1.700	-2.220	-0.986
C	-3.059	-2.455	3.171
C	-3.089	-1.551	2.106
C	3.215	1.512	-2.197
C	3.259	2.352	-3.312
C	-4.218	-3.135	3.543
C	-4.278	-1.316	1.402
C	4.377	1.237	-1.463
C	4.465	2.927	-3.707
C	4.982	0.962	1.422
C	-5.029	-0.867	-1.432
C	5.057	0.248	2.633
C	-5.220	-0.064	-2.572
C	-5.318	-2.237	-1.508
C	5.351	2.315	1.406
C	-5.365	1.948	1.704
C	5.365	-2.080	-1.488
C	-5.414	-2.897	2.859
C	-5.447	-1.988	1.803
C	5.512	0.875	3.792
C	5.593	1.805	-1.885
C	5.634	2.650	-2.992
C	5.650	-1.114	-0.510
C	-5.667	1.044	0.674
C	-5.711	-0.622	-3.752
C	5.799	2.939	2.574
C	-5.802	-2.792	-2.697
C	5.884	2.222	3.767
C	-6.003	-1.987	-3.818
C	6.358	-2.949	-1.933
C	-6.363	2.744	2.260
C	6.944	-1.044	0.021
C	-6.984	0.962	0.205
C	7.648	-2.873	-1.399
C	-7.675	2.658	1.788
C	7.936	-1.922	-0.421
C	-7.982	1.768	0.760
Cl	3.368	-2.873	1.281
Cl	-3.542	3.001	-1.090

(continued)

	x/Å	y/Å	z/Å
H	-0.273	6.335	0.302
H	-0.628	-5.423	-0.625
H	1.288	6.311	0.993
H	1.323	-4.259	0.367
H	-1.428	4.357	-0.409
H	-2.128	-2.625	3.703
H	-2.184	-1.025	1.828
H	2.273	1.063	-1.903
H	2.348	2.551	-3.869
H	-2.513	-1.639	-1.400
H	-2.529	-4.112	-1.563
H	2.531	1.785	1.142
H	2.549	4.240	1.290
H	-4.195	-3.840	4.369
H	-4.343	2.039	2.061
H	4.359	-2.163	-1.890
H	4.500	3.581	-4.574
H	4.755	-0.796	2.662
H	-4.979	0.996	-2.531
H	-5.163	-2.877	-0.646
H	5.291	2.886	0.485
H	5.570	0.310	4.718
H	-5.859	0.011	-4.622
H	-6.022	-3.855	-2.741
H	6.084	3.987	2.546
H	-6.113	3.442	3.055
H	6.123	-3.694	-2.687
H	6.233	2.708	4.673
H	-6.323	-3.412	3.155
H	-6.380	-2.420	-4.740
H	-6.388	-1.790	1.299
H	6.512	1.572	-1.356
H	6.580	3.083	-3.305
H	7.181	-0.312	0.786
H	-7.237	0.276	-0.597
H	8.420	-3.556	-1.741
H	-8.451	3.284	2.218
H	8.935	-1.860	0.003
H	-8.999	1.698	0.383
N	0.556	0.307	0.084
N	0.597	5.842	0.429
N	-0.611	-0.181	-0.214
P	4.304	0.058	-0.039
P	-4.310	-0.048	0.057
Pd	2.103	-1.113	0.383
Pd	-2.180	1.214	-0.400

E: -3875.941575 H
G: -3875.296037 H

Table S7. Calculated atomic coordinates for **4a-alpha-bridge**, **4a-beta-bridge**, **4a-cis** and **4a-trans** in the gas phase, and calculated energies (E: single-point energy, G: Gibbs energy).

4a-alpha-bridge

	x/Å	y/Å	z/Å
C	-1.010	3.312	1.046
C	1.129	2.413	-1.613
C	-1.144	4.358	1.978
C	1.257	0.136	3.859
C	1.397	3.631	-2.266
C	1.649	0.140	2.520
C	1.839	1.233	-1.916
C	-1.880	2.173	1.085
C	1.927	-0.669	4.783
C	-2.101	4.303	2.970
C	-2.104	-2.143	3.446
C	-2.191	-1.338	2.309
C	2.374	3.695	-3.247
C	2.734	-0.644	2.094
C	-2.740	-2.809	-1.623
C	2.820	1.316	-2.908
C	-2.829	2.134	2.093
C	-2.963	3.176	3.061
C	-2.974	-3.767	-2.607
C	2.992	-1.466	4.361
C	-3.031	-3.166	3.652
C	3.074	2.527	-3.553
C	-3.209	-1.546	1.368
C	3.398	-1.452	3.025
C	-3.629	-1.731	-1.470
C	3.983	-3.046	-0.742
C	-4.036	-3.395	2.709
C	-4.040	4.163	5.031
C	-4.081	-3.657	-3.453
C	-4.119	-2.599	1.568
C	4.302	1.949	1.226
C	4.369	0.925	0.271
C	4.398	-1.941	0.016
C	-4.736	-1.621	-2.322
C	-4.771	1.922	4.160
C	-4.850	0.484	-0.054
C	4.863	-4.105	-0.980
C	-4.947	1.625	-0.867
C	-4.958	-2.582	-3.311
C	5.126	3.071	1.121
C	5.279	1.052	-0.793
C	5.708	-1.916	0.529
C	-5.943	0.130	0.750
C	6.026	3.187	0.062
C	6.101	2.173	-0.895
C	-6.115	2.387	-0.885
C	6.158	-4.075	-0.463
C	6.579	-2.979	0.294
C	-7.108	0.901	0.739
C	-7.198	2.028	-0.080
Cl	0.639	-2.602	-0.010
Cl	-0.659	-0.339	-2.395

(continued)

	x/Å	y/Å	z/Å
H	0.423	0.757	4.174
H	-0.472	5.207	1.904
H	0.826	4.512	-1.995
H	1.103	0.742	1.800
H	-1.294	-1.984	4.150
H	-1.448	-0.568	2.136
H	1.619	-0.677	5.825
H	-1.857	-2.892	-0.994
H	-2.181	5.118	3.677
H	-2.280	-4.594	-2.718
H	2.600	4.613	-3.774
H	-2.958	-3.797	4.533
H	2.968	-3.086	-1.123
H	-3.118	4.311	5.607
H	3.401	0.449	-3.197
H	-3.505	1.294	2.157
H	3.510	-2.104	5.072
H	3.613	1.873	2.061
H	-4.098	1.924	-1.477
H	-4.192	0.997	4.277
H	4.224	-2.080	2.712
H	-4.255	-4.404	-4.222
H	-4.297	5.116	4.550
H	4.529	-4.953	-1.570
H	-4.744	-4.206	2.853
H	-4.838	3.913	5.730
H	-4.877	-2.814	0.821
H	5.064	3.853	1.873
H	5.356	0.271	-1.543
H	-5.412	2.032	5.035
H	-5.413	1.813	3.277
H	-5.431	-0.795	-2.219
H	-5.820	-2.489	-3.966
H	-5.888	-0.742	1.392
H	6.053	-1.061	1.101
H	-6.175	3.265	-1.522
H	6.666	4.061	-0.019
H	6.795	2.253	-1.727
H	6.840	-4.899	-0.652
H	7.587	-2.947	0.696
H	-7.946	0.615	1.368
H	-8.106	2.624	-0.089
N	0.004	3.391	0.129
N	0.102	2.367	-0.626
N	-3.903	3.089	4.058
N	4.132	2.582	-4.568
O	4.285	3.639	-5.184
O	4.821	1.574	-4.741
P	3.242	-0.539	0.324
P	-3.288	-0.499	-0.144
Pd	1.371	-0.512	-1.028
Pd	-1.435	0.910	-0.428

E: -4159.077359 H
G: -4158.378627 H

4a-beta-bridge

	x/Å	y/Å	z/Å
C	-0.343	-0.614	4.024
C	-0.870	-0.107	5.215
C	-1.020	-0.418	2.820
C	1.256	-3.110	-0.022
C	-1.484	-1.767	-1.793
C	1.660	-4.353	0.495
C	-1.920	-2.817	-2.631
C	2.009	-1.915	0.196
C	-2.077	0.593	5.194
C	2.214	3.562	-1.301
C	-2.236	-0.571	-1.704
C	2.241	4.766	-2.002
C	-2.247	0.265	2.797
C	2.521	1.286	2.124
C	2.715	1.803	3.406
C	-2.767	0.774	3.993
C	2.805	-4.444	1.274
C	-3.042	-2.675	-3.418
C	3.138	2.549	-1.614
C	3.142	-2.028	0.997
C	3.175	4.971	-3.021
C	-3.371	-0.446	-2.496
C	3.395	1.629	1.084
C	3.520	-3.271	1.520
C	-3.666	-2.327	1.756
C	3.780	2.665	3.659
C	-3.797	-1.470	-3.382
C	-4.070	-1.176	1.065
C	4.073	2.757	-2.636
C	4.088	3.966	-3.337
C	-4.323	2.956	0.922
C	-4.366	-3.526	1.608
C	4.450	2.523	1.340
C	-4.469	1.660	1.440
C	4.503	-0.634	-2.372
C	4.584	0.060	-1.152
C	4.646	3.028	2.624
C	-5.189	-1.256	0.219
C	-5.276	-2.333	-5.143
C	-5.327	3.907	1.116
C	-5.478	-3.594	0.770
C	-5.563	-0.007	-4.257
C	5.589	-1.372	-2.840
C	-5.636	1.337	2.155
C	5.765	-0.019	-0.402
C	-5.889	-2.453	0.077
C	-6.482	3.579	1.826
C	-6.634	2.293	2.348
C	6.764	-1.444	-2.087
C	6.846	-0.772	-0.867
Cl	0.038	1.260	-2.250
Cl	-0.844	2.826	0.802

(continued)

	x/Å	y/Å	z/Å
H	-0.340	-0.253	6.151
H	-0.590	-0.787	1.894
H	0.600	-1.153	4.028
H	1.056	-5.228	0.281
H	-1.334	-3.728	-2.675
H	1.464	3.409	-0.530
H	1.521	5.540	-1.754
H	1.674	0.640	1.925
H	2.018	1.541	4.196
H	-2.487	1.000	6.114
H	-2.811	-2.292	2.422
H	3.147	-5.381	1.693
H	3.189	5.910	-3.566
H	-3.322	-3.483	-4.083
H	-3.413	3.223	0.395
H	3.584	-0.605	-2.951
H	-3.702	1.322	3.993
H	3.766	-1.180	1.240
H	3.929	3.069	4.657
H	-3.941	0.473	-2.438
H	-4.040	-4.406	2.155
H	-4.506	-2.484	-5.913
H	4.796	1.989	-2.886
H	4.819	4.118	-4.126
H	-4.876	0.784	-4.588
H	5.107	2.837	0.535
H	-5.200	4.907	0.711
H	-5.453	-3.294	-4.646
H	5.467	3.713	2.813
H	5.513	-1.900	-3.786
H	-5.524	-0.377	-0.321
H	-5.772	0.337	2.555
H	5.843	0.485	0.554
H	-5.976	0.291	-3.285
H	-6.024	-4.526	0.659
H	-6.201	-2.042	-5.640
H	-6.389	-0.064	-4.966
H	-6.757	-2.493	-0.575
H	-7.261	4.322	1.974
H	-7.530	2.030	2.904
H	7.606	-2.029	-2.445
H	7.749	-0.837	-0.268
N	0.053	-3.074	-0.716
N	-0.296	-1.896	-1.060
N	4.726	-3.345	2.355
N	-4.906	-1.304	-4.182
O	5.052	-4.449	2.796
O	5.347	-2.302	2.567
P	3.092	1.001	-0.616
P	-3.131	0.416	1.186
Pd	1.201	-0.371	-0.810
Pd	-1.649	0.937	-0.508

E: -4159.072979 H
G: -4158.375114 H

4a-cis

	x/Å	y/Å	z/Å
C	-0.125	2.907	0.317
C	0.128	-2.987	0.432
C	-0.467	-1.719	0.251
C	0.486	1.647	0.187
C	-0.647	-4.098	0.677
C	0.648	4.029	0.578
C	-1.892	-1.556	0.344
C	1.897	1.472	0.323
C	2.025	3.867	0.701
C	-2.061	-3.986	0.744
C	-2.234	-6.396	1.157
C	2.646	2.620	0.574
C	-2.646	-2.694	0.576
C	-4.299	-4.974	0.978
C	-4.487	-0.623	2.682
C	4.526	1.597	-2.265
C	4.528	0.492	2.733
C	-4.625	-1.669	-2.259
C	4.856	1.090	3.949
C	-4.856	-1.198	3.898
C	5.006	2.354	-3.335
C	-5.148	-2.412	-3.318
C	5.219	0.837	1.559
C	-5.254	-0.843	1.526
C	5.417	0.942	-1.403
C	-5.475	-0.926	-1.425
C	-5.774	1.563	0.041
C	5.859	-1.527	0.035
C	5.864	2.055	4.004
C	-5.988	-2.012	3.974
C	-6.077	2.253	-1.145
C	6.138	-2.206	-1.163
C	6.228	1.808	1.624
C	-6.228	2.077	1.264
C	6.379	2.462	-3.556
C	-6.389	-1.662	1.611
C	6.412	-2.003	1.232
C	-6.522	-2.419	-3.560
C	6.543	2.416	2.841
C	-6.750	-2.246	2.827
C	6.799	1.041	-1.644
C	-6.833	3.422	-1.103
C	-6.857	-0.924	-1.688
C	6.965	-3.327	-1.159
C	-6.975	3.256	1.301
C	7.232	-3.133	1.231
C	7.275	1.802	-2.711
C	-7.282	3.929	0.119
C	-7.375	-1.671	-2.745
C	7.512	-3.795	0.037
Cl	-2.828	2.304	-1.493
Cl	2.885	-2.503	-1.267

(continued)

	x/Å	y/Å	z/Å
H	-0.159	-5.055	0.804
H	0.205	5.011	0.683
H	-1.196	2.996	0.188
H	1.203	-3.082	0.346
H	-1.543	-6.399	2.009
H	-1.680	-6.719	0.266
H	-3.015	-7.130	1.355
H	3.457	1.505	-2.105
H	-3.554	-1.651	-2.085
H	-3.589	-0.014	2.621
H	3.719	2.592	0.696
H	-3.719	-2.611	0.661
H	3.720	-0.234	2.687
H	-4.254	-1.016	4.784
H	4.305	2.854	-3.996
H	4.315	0.812	4.849
H	-4.476	-2.975	-3.960
H	-4.655	-4.329	1.790
H	-4.676	-4.569	0.031
H	-4.731	-5.965	1.117
H	5.703	-1.865	-2.095
H	-5.712	1.885	-2.096
H	-6.008	1.562	2.193
H	6.110	2.533	4.948
H	6.215	-1.492	2.168
H	-6.273	-2.464	4.919
H	6.752	3.052	-4.389
H	6.756	2.110	0.726
H	-6.926	-2.993	-4.389
H	-6.990	-1.856	0.729
H	-7.059	3.945	-2.027
H	7.172	-3.841	-2.093
H	7.314	3.180	2.873
H	-7.320	3.642	2.256
H	7.502	0.510	-1.010
H	-7.525	-0.322	-1.081
H	-7.631	-2.880	2.878
H	7.655	-3.488	2.167
H	-7.866	4.844	0.147
H	8.154	-4.672	0.037
H	8.344	1.873	-2.886
H	-8.444	-1.659	-2.939
N	-0.321	0.516	0.018
N	0.321	-0.609	0.075
N	-2.845	-5.086	0.970
N	2.857	5.044	0.977
O	2.289	6.128	1.123
O	4.079	4.887	1.047
P	-4.750	0.029	-0.028
P	4.759	-0.045	0.003
Pd	-2.440	0.314	-0.183
Pd	2.461	-0.415	-0.122

E: -4159.072143 H
G: -4158.374960 H

4a-trans

	x/Å	y/Å	z/Å
C	0.458	-3.670	-0.006
C	0.495	-2.280	0.074
C	0.570	1.686	0.225
C	-0.573	3.798	-0.060
C	0.576	4.496	0.417
C	-0.584	6.628	0.063
C	-0.599	2.421	-0.144
C	-0.628	-1.553	-0.392
C	-0.656	-4.293	-0.577
C	1.693	2.361	0.746
C	1.699	3.733	0.853
C	-1.713	-2.193	-1.011
C	-1.729	-3.576	-1.108
C	1.760	6.570	0.974
C	-3.008	-2.450	3.168
C	-3.060	-1.535	2.114
C	3.221	1.497	-2.204
C	3.273	2.334	-3.321
C	-4.148	-3.167	3.529
C	-4.253	-1.325	1.409
C	4.377	1.230	-1.457
C	4.481	2.915	-3.705
C	4.963	0.947	1.434
C	-5.024	-0.859	-1.419
C	5.026	0.229	2.643
C	-5.228	-0.046	-2.550
C	-5.293	-2.234	-1.512
C	5.337	2.299	1.425
C	-5.348	-2.953	2.845
C	5.364	-2.093	-1.476
C	-5.390	1.913	1.753
C	-5.404	-2.033	1.800
C	5.474	0.851	3.808
C	5.595	1.803	-1.867
C	5.643	2.645	-2.976
C	5.644	-1.124	-0.500
C	-5.682	1.022	0.709
C	-5.710	-0.598	-3.736
C	-5.767	-2.782	-2.707
C	5.776	2.918	2.598
C	5.849	2.196	3.790
C	-5.980	-1.967	-3.818
C	6.360	-2.962	-1.914
C	-6.397	2.691	2.320
C	6.936	-1.049	0.036
C	-6.998	0.933	0.237
C	7.647	-2.882	-1.376
C	-7.707	2.598	1.844
C	7.931	-1.927	-0.400
C	-8.004	1.721	0.802
Cl	3.340	-2.878	1.251
Cl	-3.568	3.026	-1.022

(continued)

	x/Å	y/Å	z/Å
H	-0.360	7.692	0.146
H	-0.863	6.416	-0.975
H	1.282	-4.271	0.356
H	-1.449	6.407	0.699
H	-1.459	4.343	-0.356
H	1.597	7.643	0.880
H	1.945	6.345	2.033
H	-2.074	-2.601	3.702
H	-2.170	-0.978	1.847
H	2.278	1.044	-1.920
H	2.368	2.526	-3.890
H	-2.520	-1.609	-1.432
H	2.542	1.795	1.106
H	-2.548	-4.102	-1.581
H	2.569	4.217	1.277
H	2.661	6.313	0.406
H	-4.107	-3.883	4.344
H	4.360	-2.181	-1.881
H	-4.370	2.009	2.114
H	4.522	3.565	-4.574
H	4.722	-0.814	2.665
H	-5.004	1.016	-2.497
H	-5.128	-2.881	-0.658
H	5.286	2.873	0.505
H	5.523	0.282	4.732
H	-5.868	0.042	-4.599
H	-5.968	-3.848	-2.764
H	6.066	3.965	2.576
H	6.128	-3.711	-2.665
H	-6.156	3.379	3.125
H	6.193	2.679	4.700
H	-6.244	-3.498	3.131
H	-6.349	-1.855	1.295
H	-6.349	-2.395	-4.746
H	6.510	1.575	-1.329
H	6.591	3.081	-3.280
H	7.169	-0.315	0.800
H	-7.242	0.257	-0.576
H	8.421	-3.566	-1.711
H	-8.491	3.210	2.282
H	8.928	-1.863	0.028
H	-9.020	1.646	0.424
N	0.551	0.323	0.071
N	0.592	5.862	0.464
N	-0.624	-0.165	-0.226
N	-0.692	-5.762	-0.650
O	0.260	-6.386	-0.184
O	-1.680	-6.284	-1.174
P	4.297	0.049	-0.036
P	-4.314	-0.046	0.077
Pd	2.094	-1.106	0.369
Pd	-2.196	1.231	-0.375

E: -4159.053811 H
G: -4158.357718 H

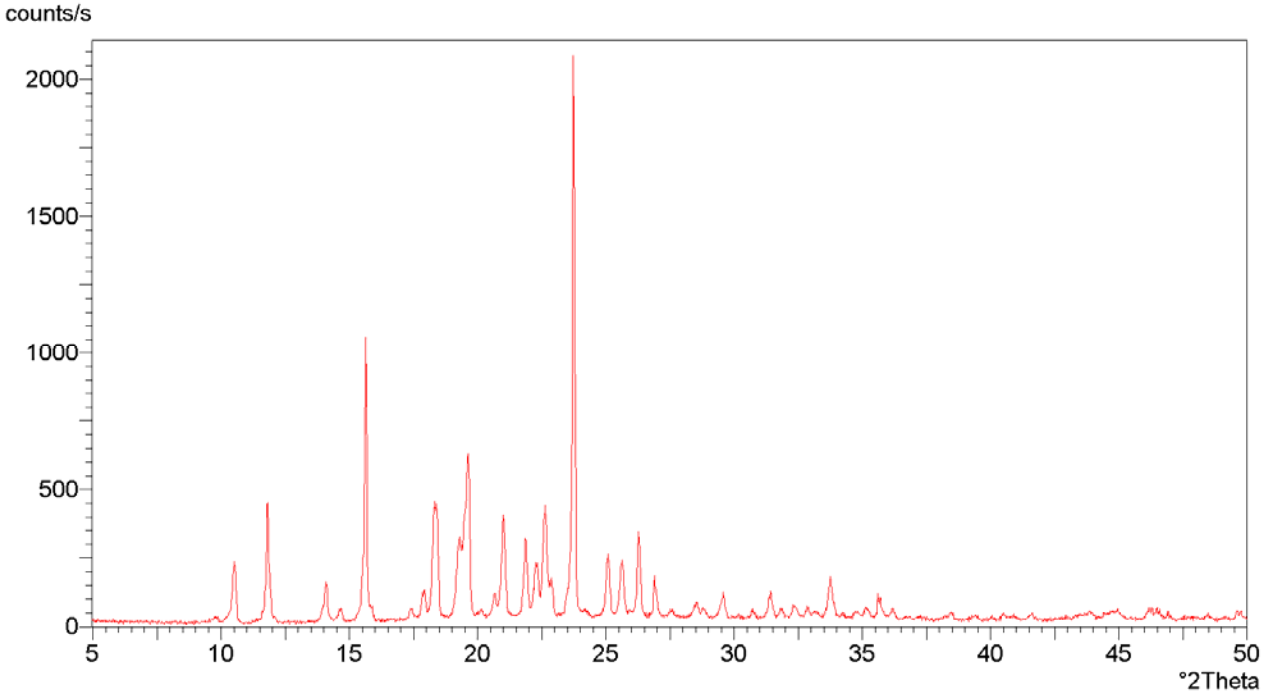

Figure S9. X-ray powder diffraction pattern of **PPh_3**.

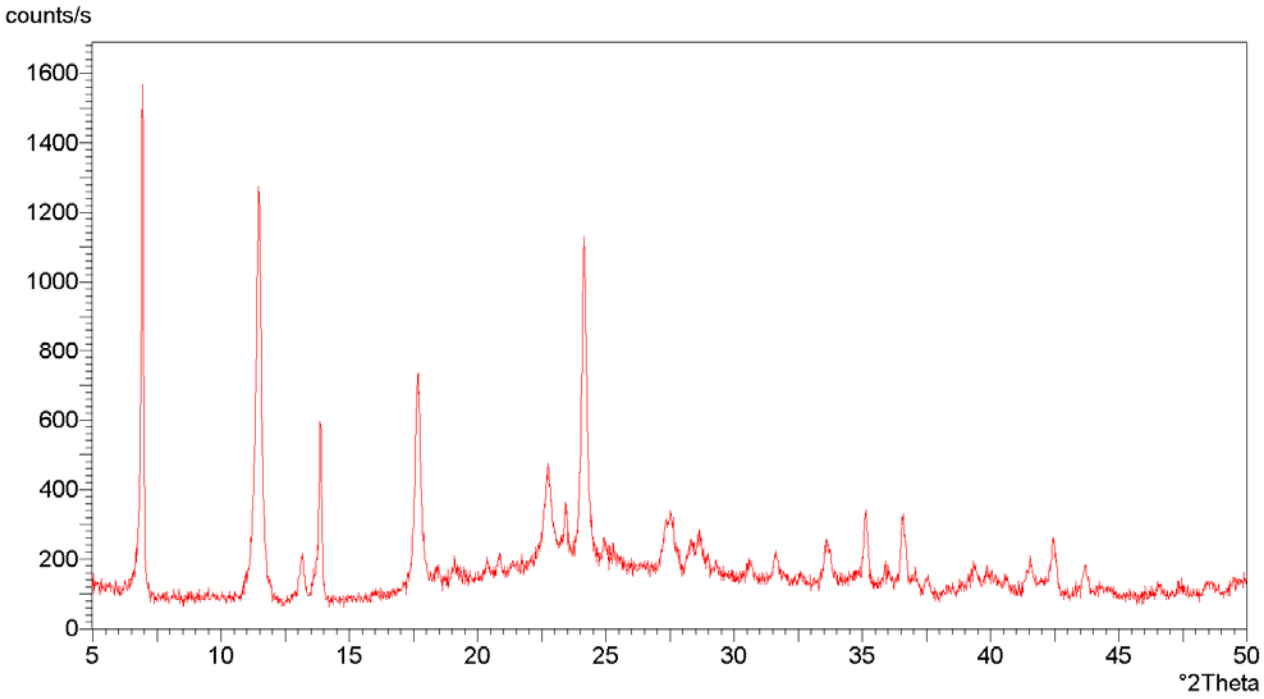

Figure S10. X-ray powder diffraction pattern of **1**.

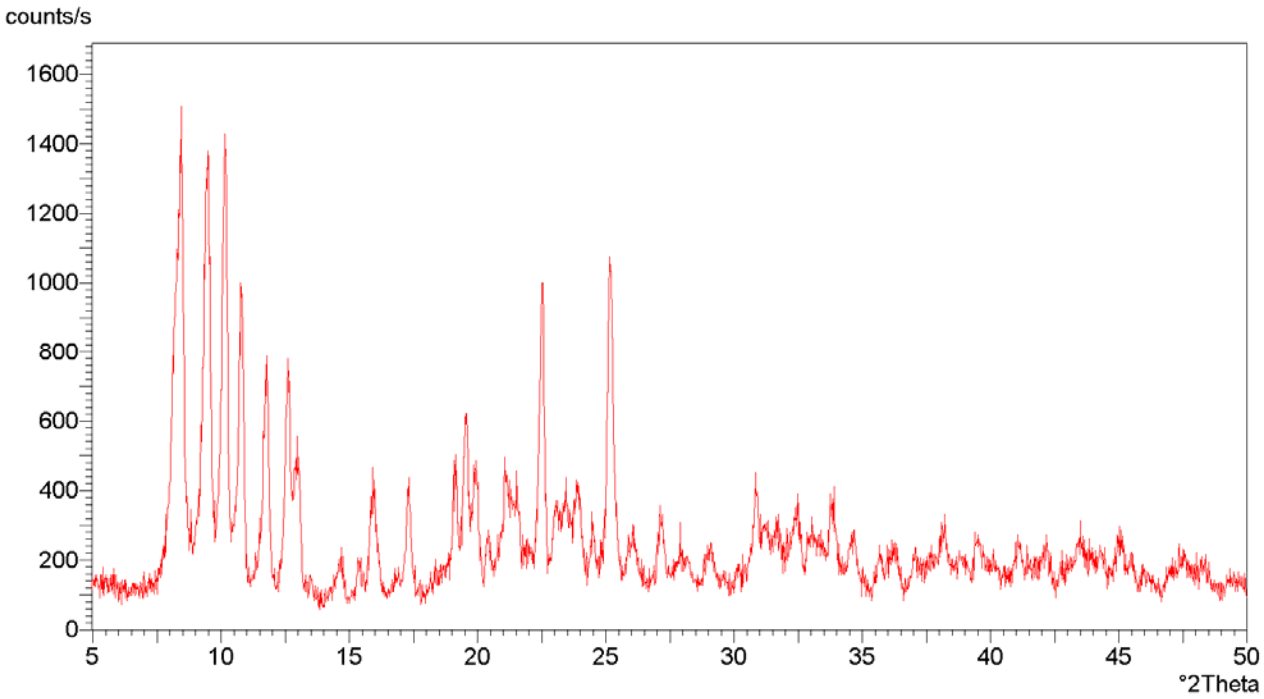

Figure S11. X-ray powder diffraction pattern of **1a** obtained by liquid-assisted grinding.

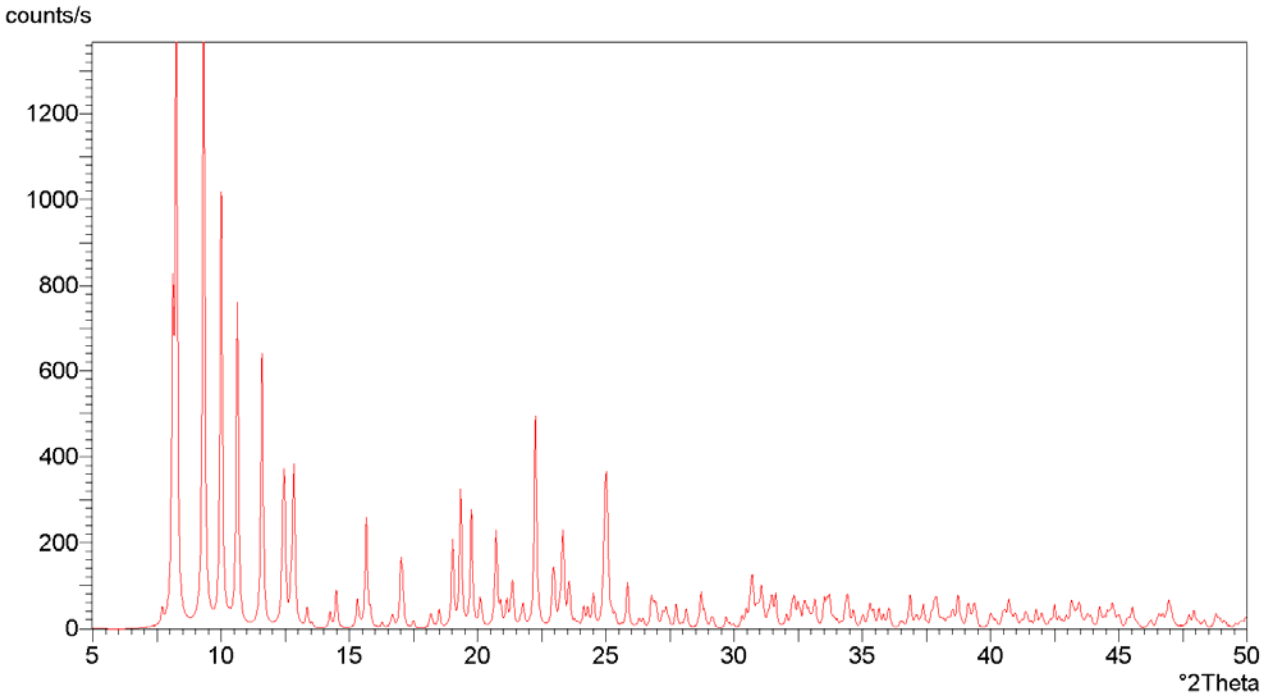

Figure S13. Simulated X-ray powder diffraction pattern for ethanol solvate of **1a.**

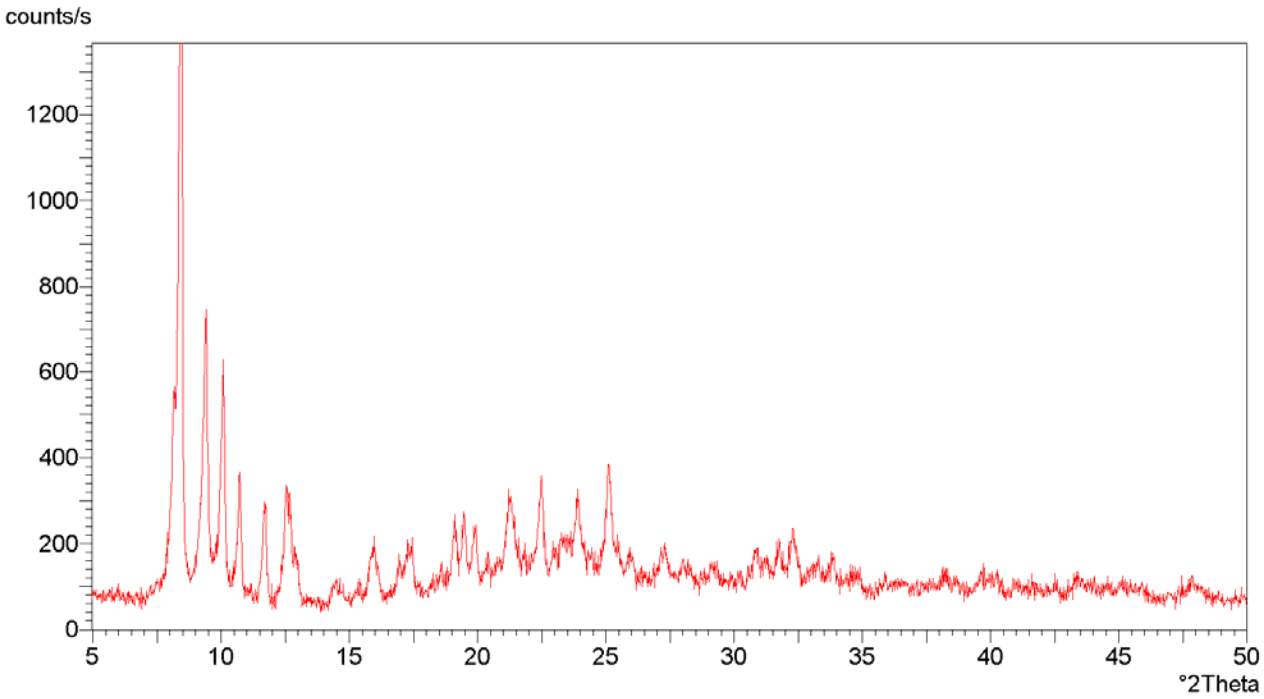

Figure S12. X-ray powder diffraction pattern of **1a** obtained from solution (acetone).

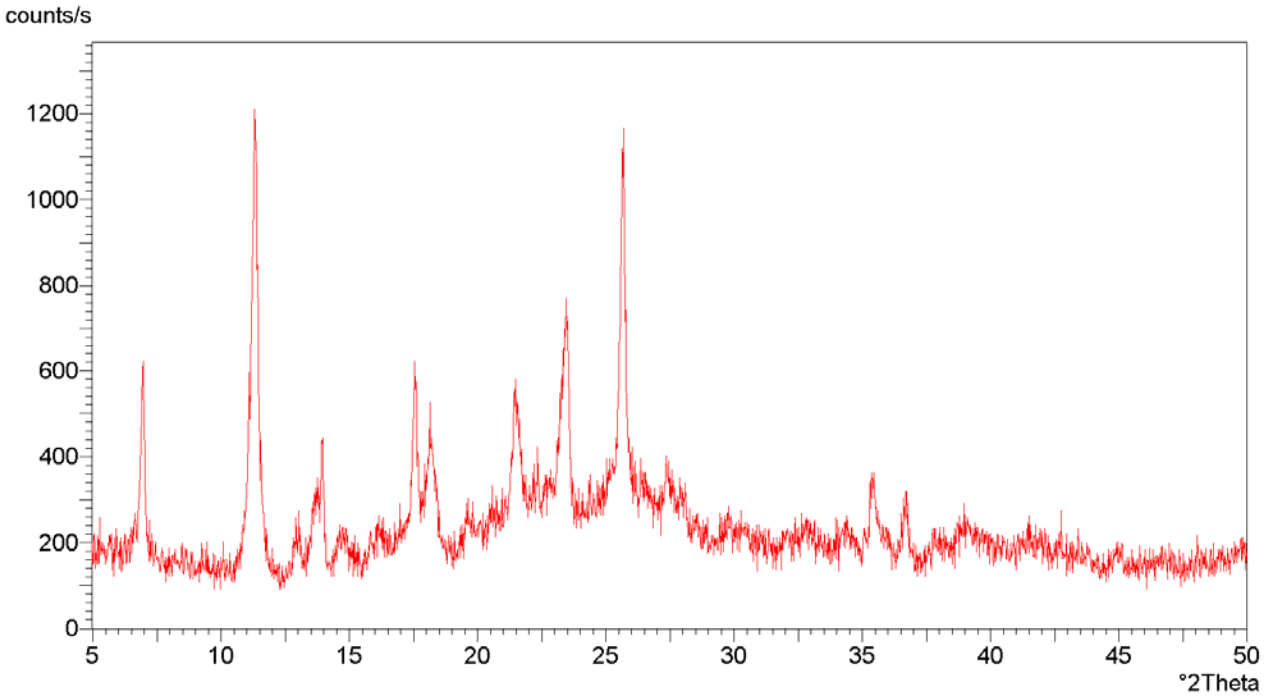

Figure S14. X-ray powder diffraction pattern of **2**.

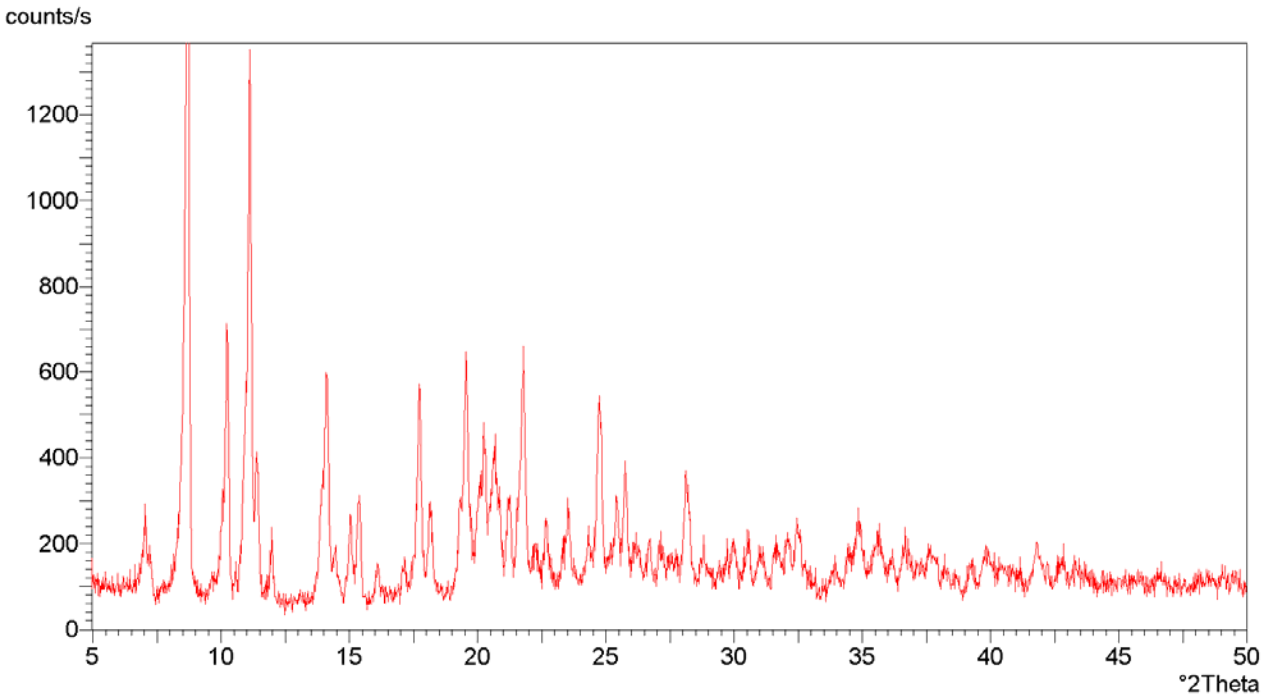

Figure S15. X-ray powder diffraction pattern of **2a** obtained by liquid-assisted grinding.

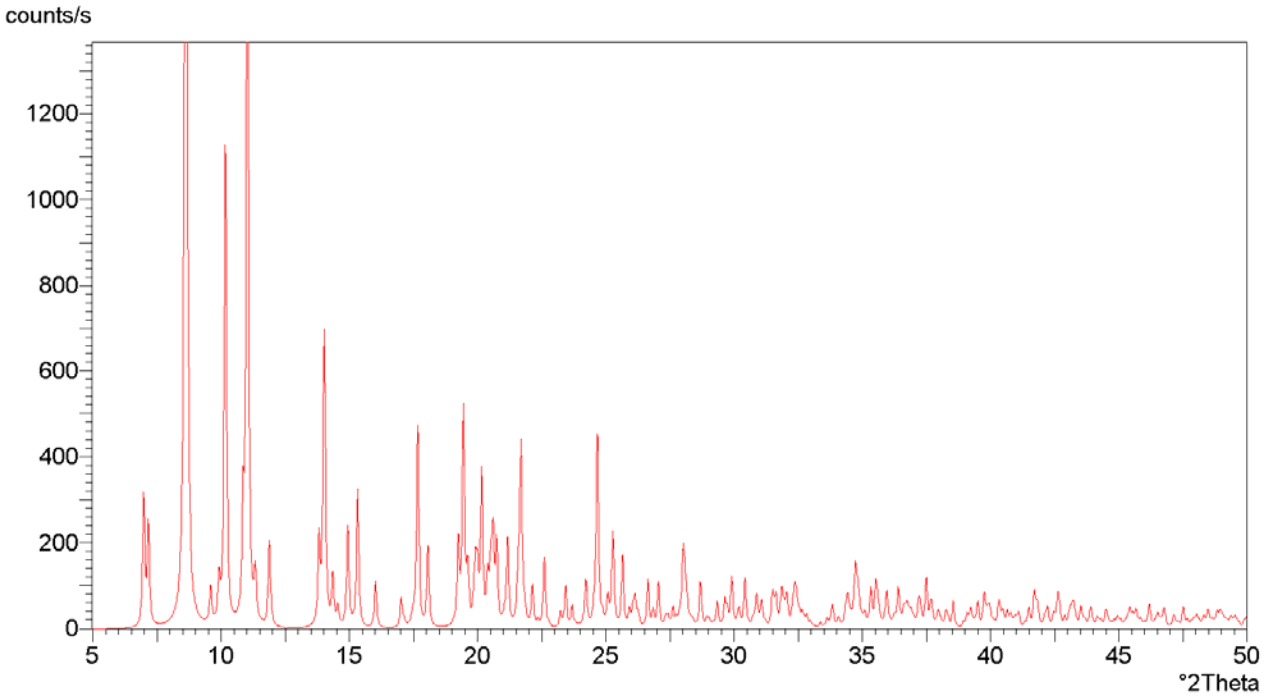

Figure S16. Simulated X-ray powder diffraction pattern for **2a.**

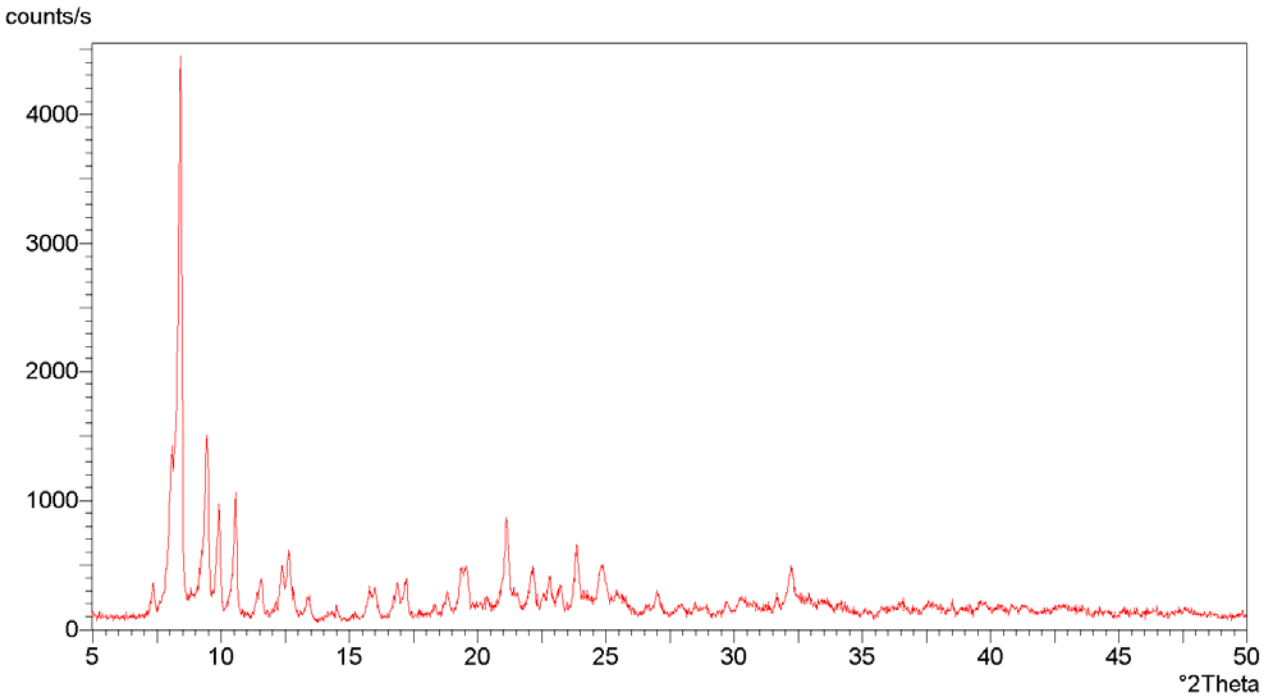

Figure S17. X-ray powder diffraction pattern of **2a** obtained from solution (acetone).

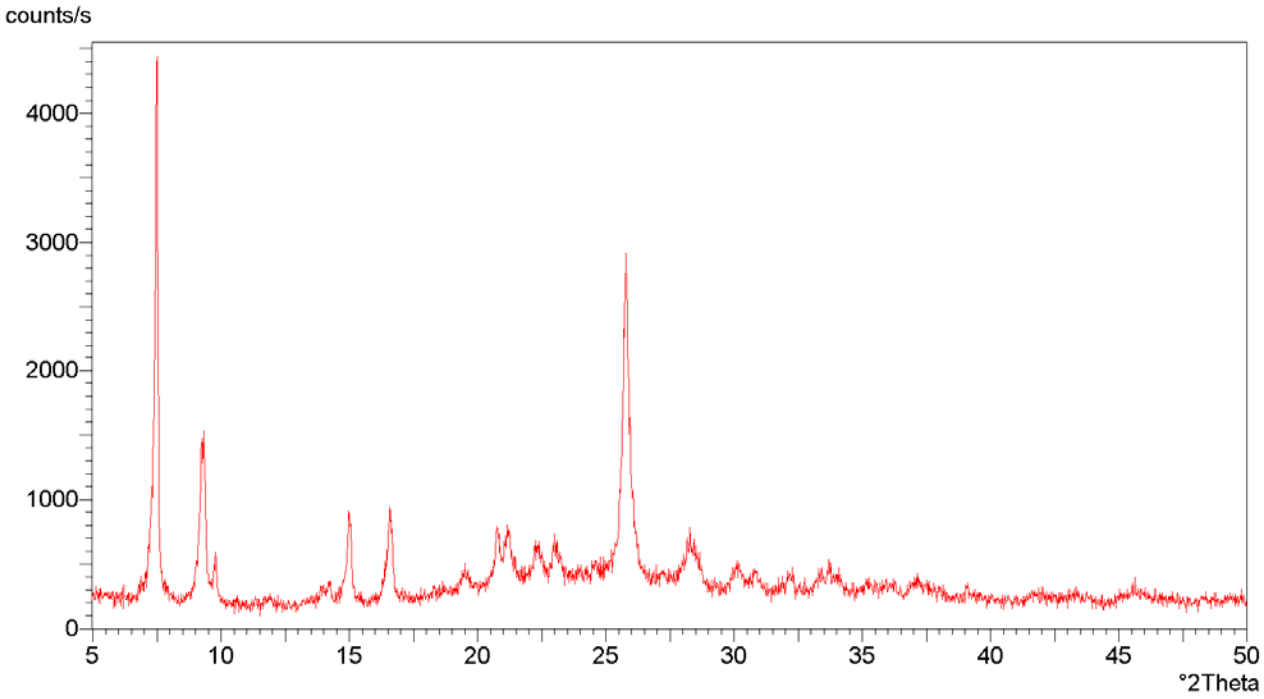

Figure S18. X-ray powder diffraction pattern of **3**.

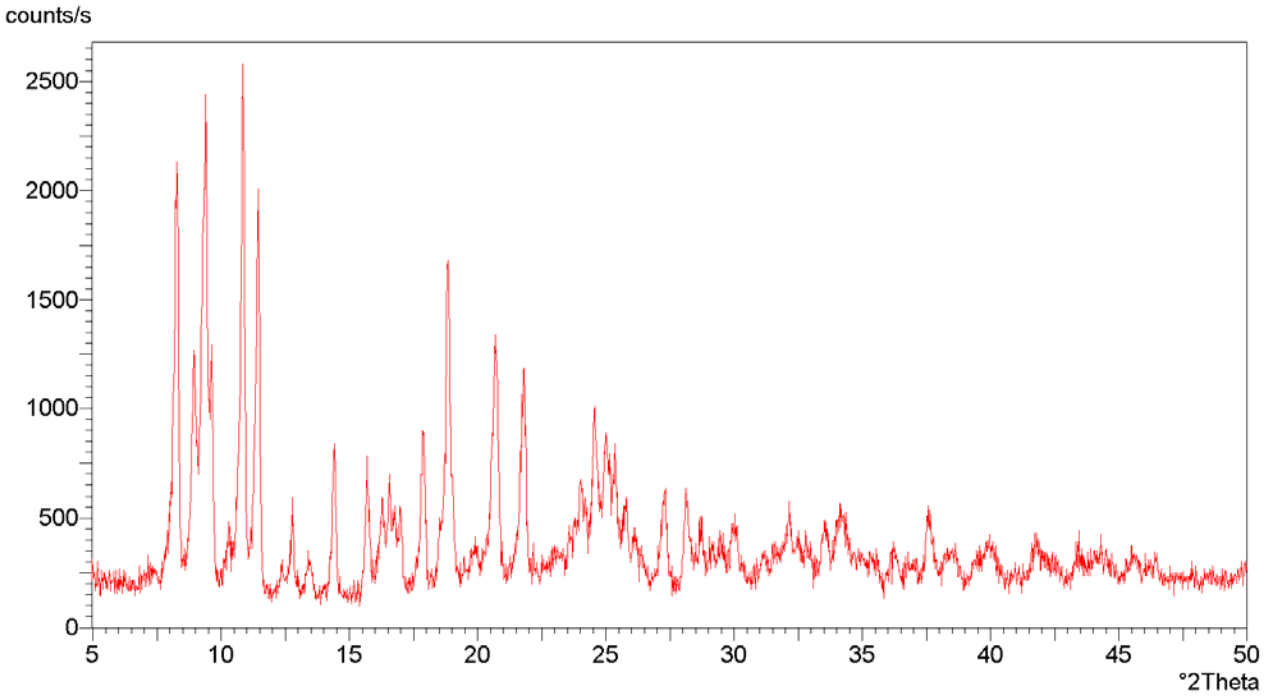

Figure S19. X-ray powder diffraction pattern of **3a** obtained by liquid-assisted grinding.

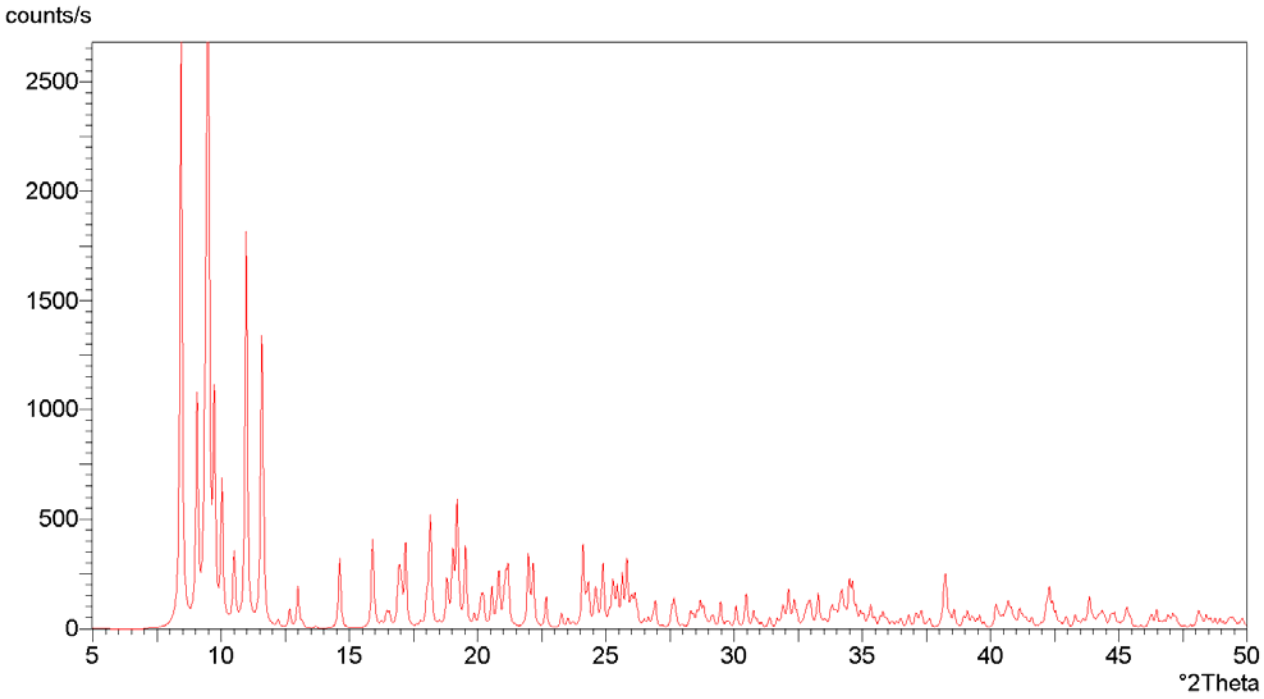

Figure S20. Simulated X-ray powder diffraction pattern for **3a.**

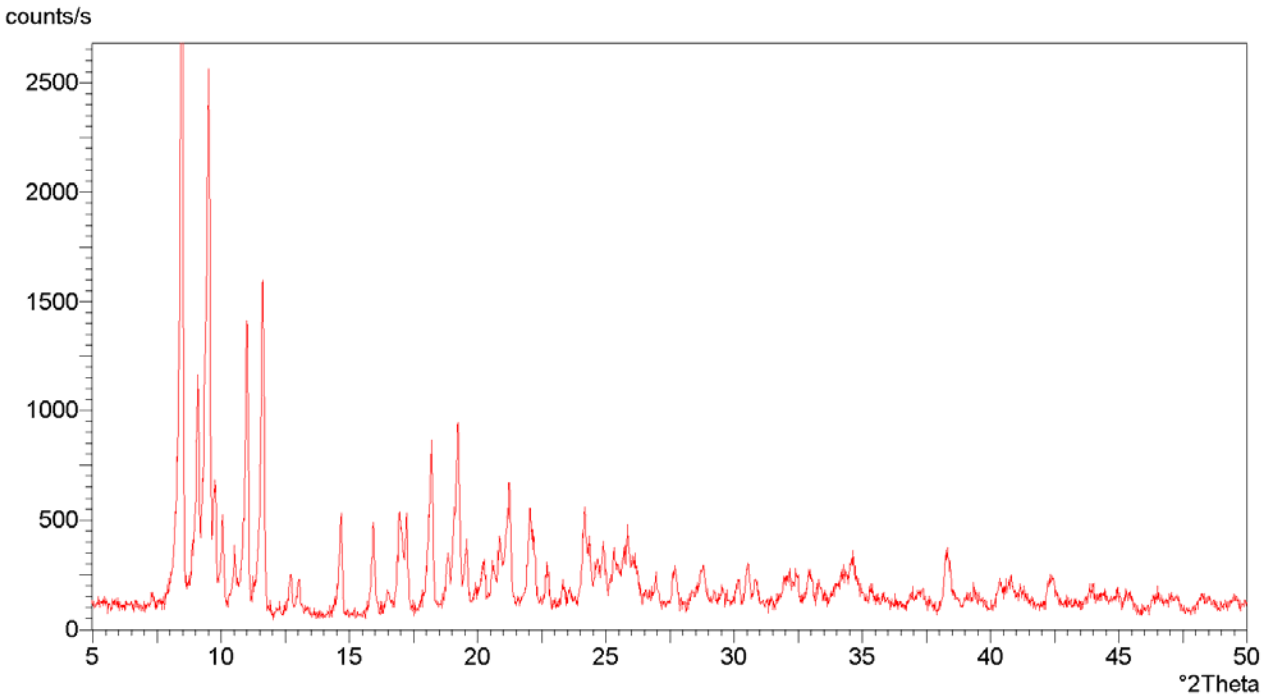

Figure S21. X-ray powder diffraction pattern of **3a** obtained from solution (acetone).

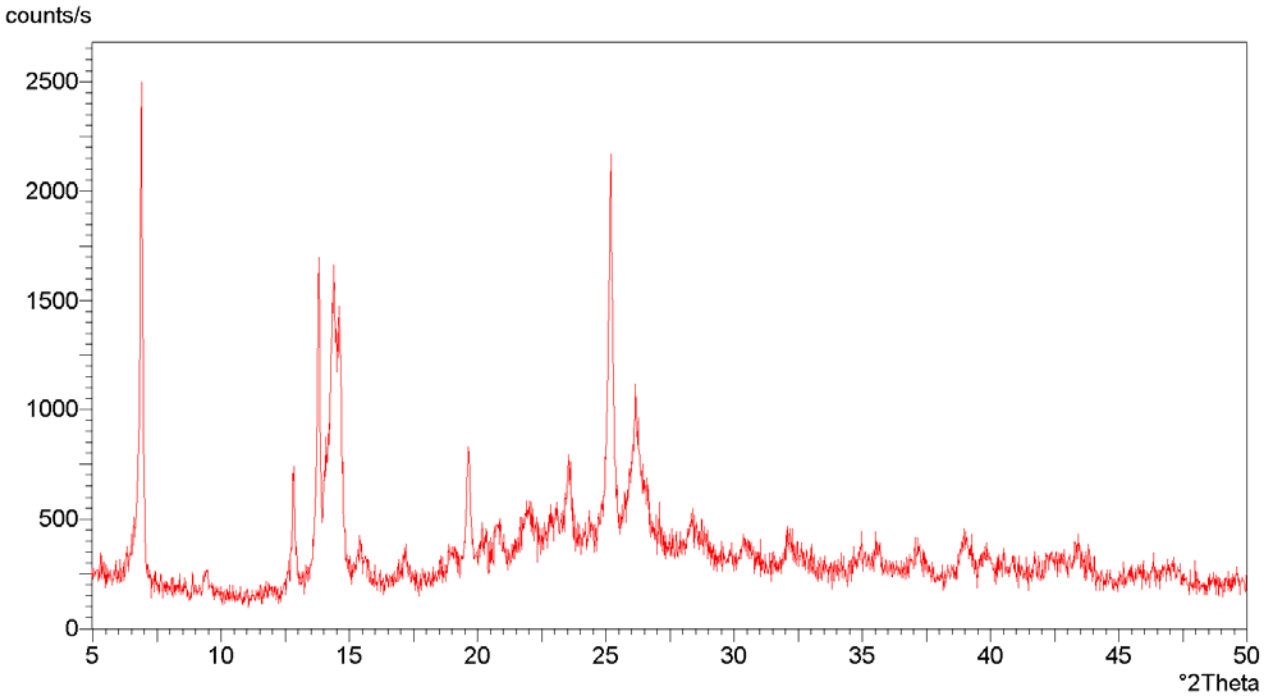

Figure S22. X-ray powder diffraction pattern of **4**.

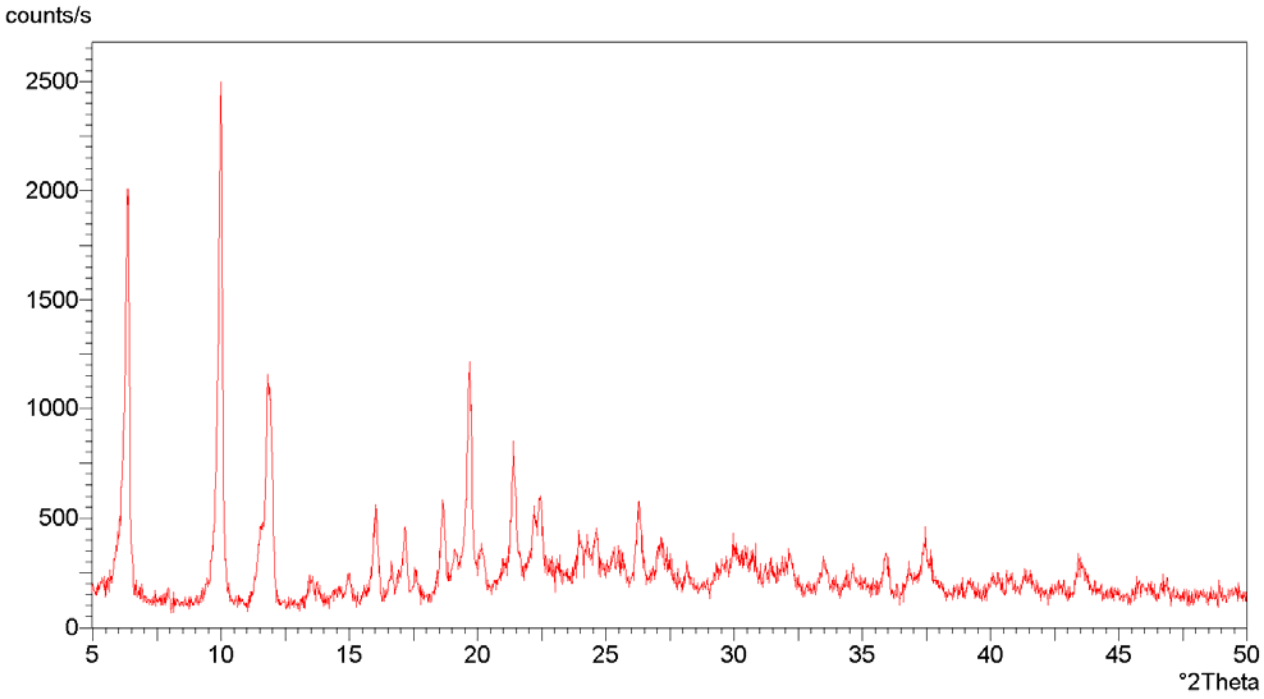

Figure S23. X-ray powder diffraction pattern of **4a** obtained by liquid-assisted grinding.

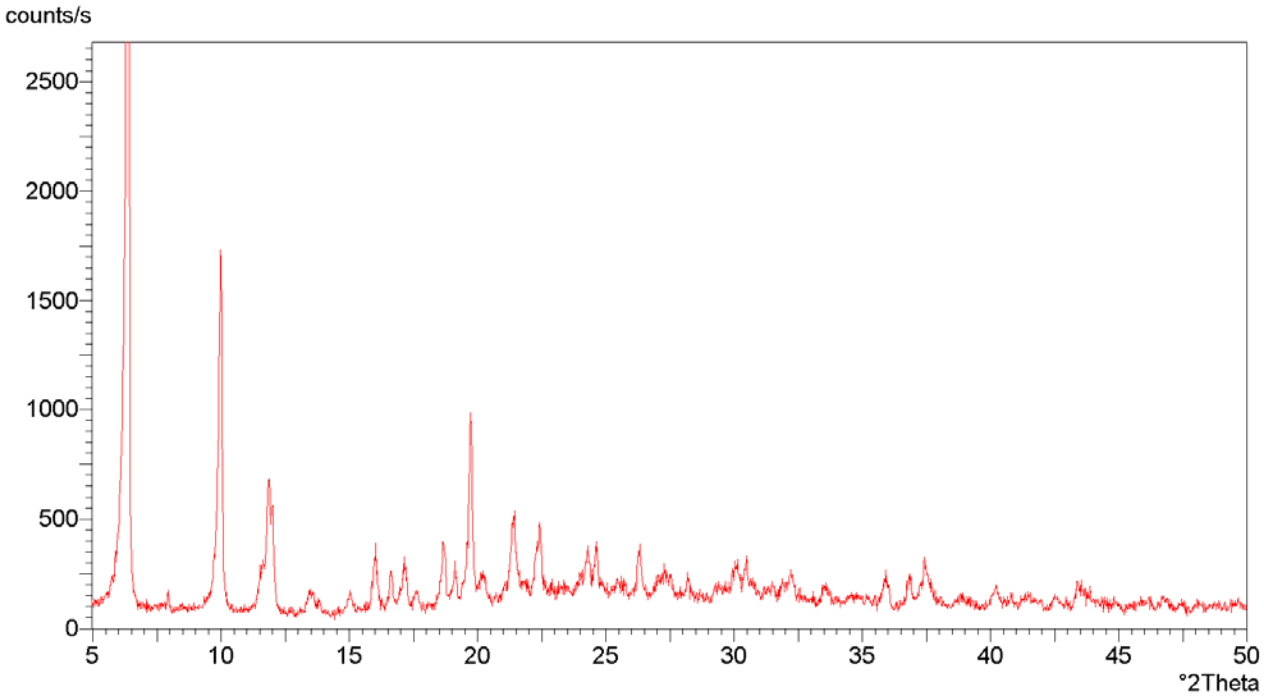

Figure S24. X-ray powder diffraction pattern of **4a** obtained from solution (acetone).

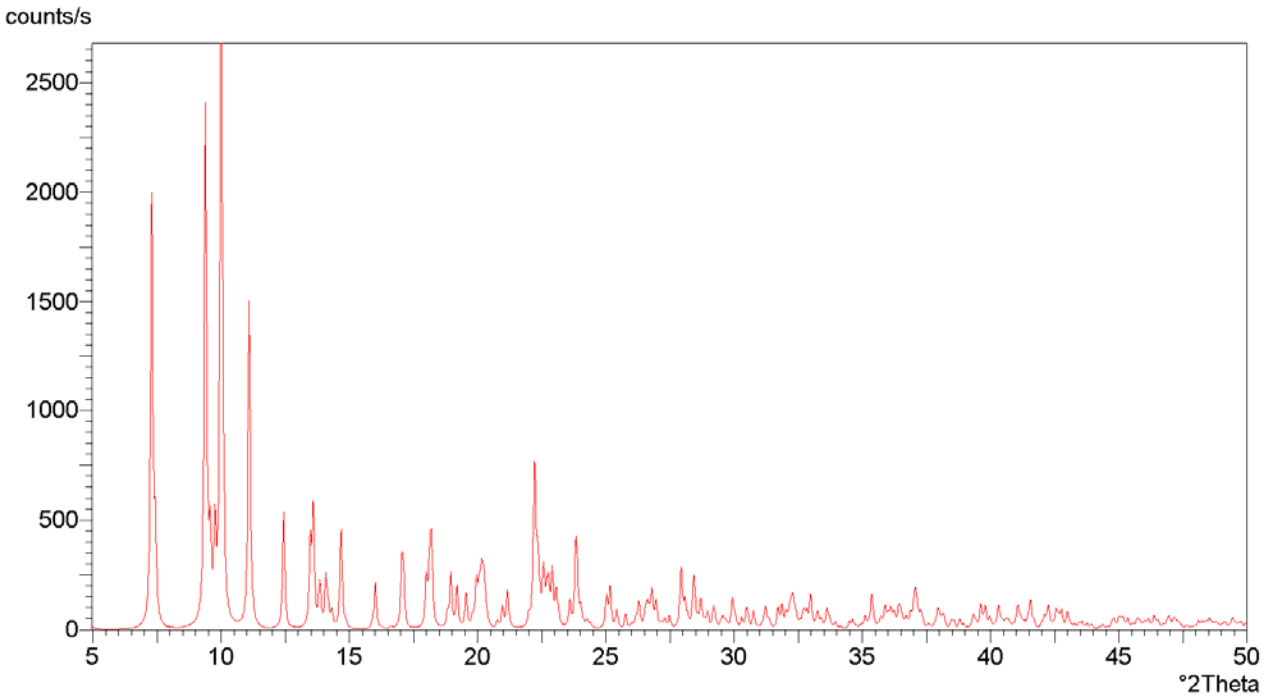

Figure S25. Simulated X-ray powder diffraction pattern for water and ethanol solvate of **4a.**

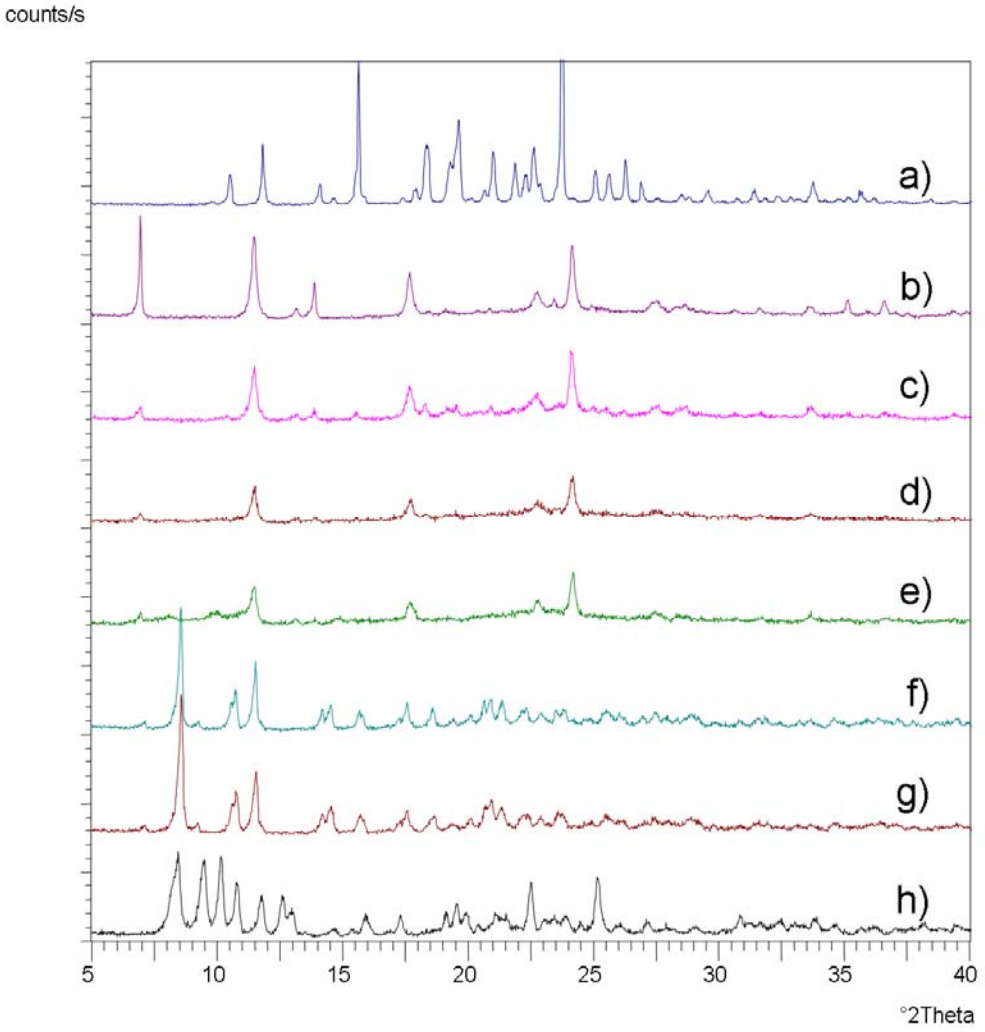

Figure S26. PXRD patterns of NG reaction of complex **1** and PPh_3: a) PPh_3, b) complex **1**, c) 5 min grinding, d) 10 min grinding, e) 20 min grinding, f) 45 min grinding, g) 65 min grinding and h) **1a** obtained by liquid-assisted grinding.

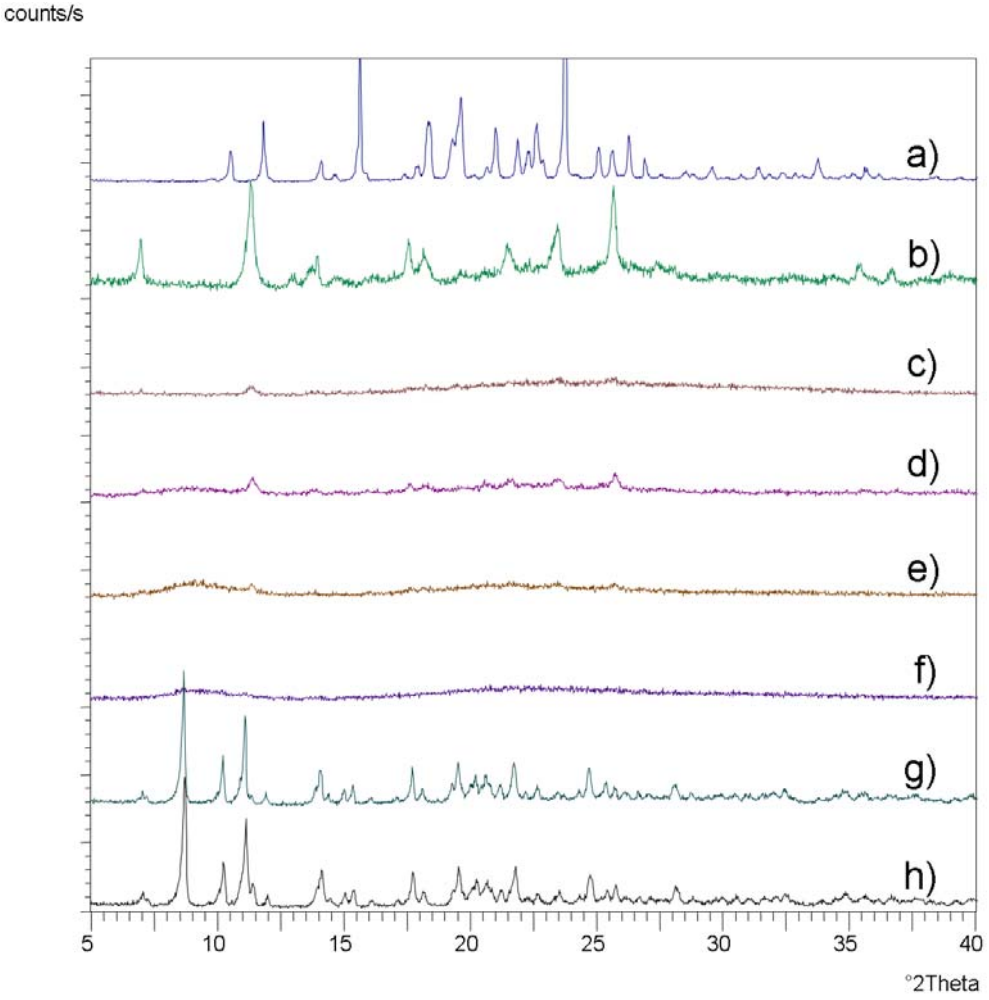

Figure S27. PXRD patterns of NG reaction of complex **2** and PPh_3: a) PPh_3, b) complex **2**, c) 10 min grinding, d) 25 min grinding, e) 45 min grinding, f) 65 min grinding, g) 80 min grinding and h) **2a** obtained by liquid-assisted grinding.

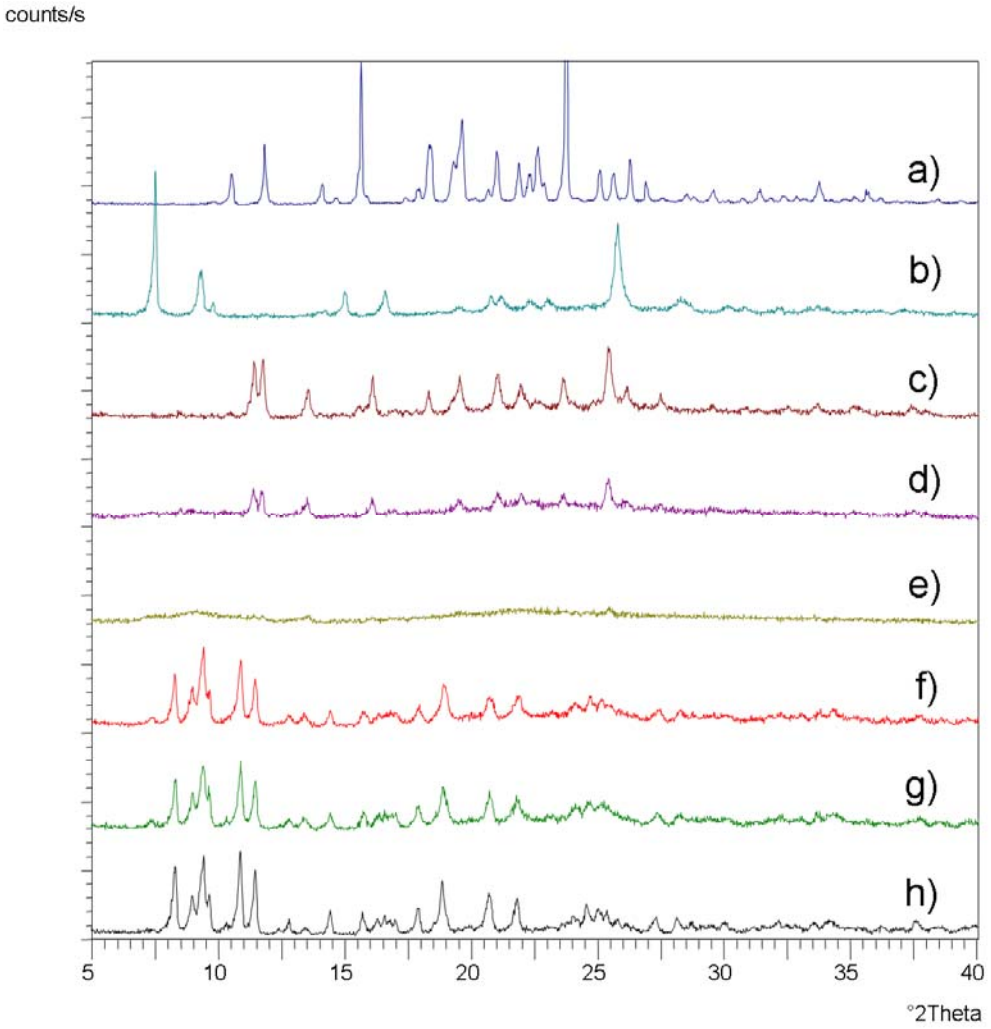

Figure S28. PXRD patterns of NG reaction of complex **3** and PPh_3: a) PPh_3, b) complex **3**, c) 5 min grinding, d) 15 min grinding, e) 30 min grinding, f) 60 min grinding, g) 75 min grinding and h) **3a** obtained by liquid-assisted grinding.

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