Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Synthesis and NMR study of Trimethylphosphine Gold(I)-appended Calix[8]arenes as precursors of Gold nanoparticles

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I. Materials and experimental methods

Materials

All reactions were carried out under argon atmosphere. THF was dried and distilled over sodium/benzophenone, Methanol (MeOH) was distilled over magnesium. Extra dry dimethylformamide (DMF) was purchased from Alfa Aesar. Sodium hydride (NaH) was purchased from Aldrich. All commercially available reagents were used as received.

NMR experiments

1D and 2D ^{1}H, ^{31}P and ^{13}C NMR experiments in liquid state were recorded on either a Bruker DPX 250, Brucker 300 MHz, Bruker Avance 400 or 500 spectrometer. For 2D diffusion ordered spectroscopy (DOSY), after Fourier transformation and baseline correction, the diffusion dimension was processed with the Bruker Topspin software package DOSY (Contin protocole). All diffusion measurements were made using the stimulated echo pulse sequence. The recycle delay was adjusted to 3s. ^{31}P EXSY experiment was acquired with a mixing time of 150 ms. All chemical shifts for ^{1}H and ^{13}C are relative to TMS. ^{31}P chemical shifts were referenced to an external 85% H_3PO_4 sample. Data are reported in ppm with the solvent signal as reference.

Solid-state NMR experiments were recorded on a Bruker Avance III HD 400 spectrometer equipped with a 3.2 mm probe. Samples were spun at 16 kHz at the magic angle using ZrO_2 rotors. ^{31}P-CP/MAS spectra were recorded with a recycle delay of 2 s and contact times of 1 ms. $^{31}P/^{1}H$ HETCOR experiment was realized with a contact time of 1 ms and with frequency switched Lee-Goldburg homonuclear decoupling during ^{1}H evolution. The ^{1}H-^{31}P FBCP NMR method were performed with a first CP transfer of 2 ms and a second CP contact of 0.05 ms or 2 ms.

Instrumentation and analysis

Elemental analyses were performed by the microanalysis service of the Institut de Chimie des Substances Naturelles in Gif-Sur-Yvette(France).

Fourier transform infrared spectra were recorded on a Perkin Elmer Spectrum 100 spectrometer. Organic compounds pellets were prepared using oven dried KBr powder.

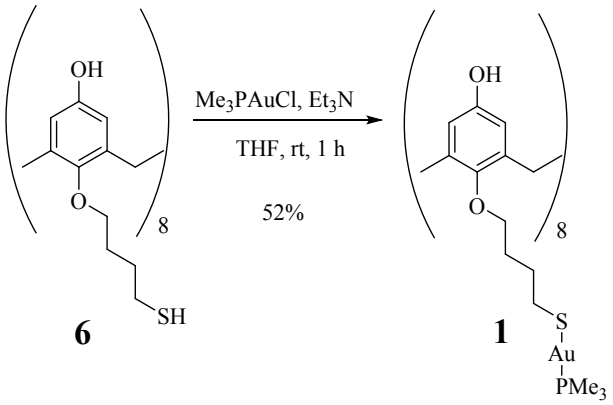
X-ray photoelectron (XPS) measurements were performed on a K alpha (Thermo Fisher) spectrometer equipped with a monochromatic Aluminium source (Al, Ka = 1486.6 eV, beam size: 200 µm). A spot size of 400 µm was used. The hemispherical analyzer was operated in CAE (Constant Analyzer Energy) mode, with a pass energy of 200 eV and a step of 1 eV for the acquisition of surveys spectra, and a pass energy of 50 eV and a step of 0.1 eV for the acquisition of high resolution spectra. A “dual beam” flood gun was used to neutralize the charge build-up. The recorded spectra were processed by means of the Avantage software, using a peak-fitting routine with Shirley background and symmetrical 70%-30% mixed Gaussian-Lorentzian peak shapes. The atomic ratios were evaluated following normalizations of the peak areas with the Scofield sensitivity factors, after a Shirley type background subtraction. The C1s component at 284.8 eV was used as binding energy reference.

The gamma irradiations were performed using a ^{60}Co source with a dose rate of 1.8 or 3.7 kGy h^{-1}. The total dose received by the samples was adjusted to totally reduce the gold(I) complexes in ethanolic solution (576 Gy). Metallic-calixarene complex solution (0.4 mM metal) was prepared in dry EtOH (6 mL). The solution was kept under stirring at rt for 15 min. The solution was flushed with nitrogen for 15 min before irradiation and kept under nitrogen when irradiated.

Transmission electron microscopy (TEM) images were obtained with a JEOL JEM 100CX or a JEOL1400 operating at 100 and 120 kV, respectively. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were acquired with a JEOL JEM-ARM200F operating at 200 kV. Immediately after irradiation, drops of irradiated solutions were deposited and dried on copper grids coated by amorphous carbon membrane for TEM analysis.

II. Synthetic procedure for complexes 1 and 1'

Synthesis of compounds (**3**, **4**, **5** and **6**) were described previously.[1] Only the last step between compound **6** and complex **1** (Scheme S1) is detailed here.



Scheme S1 Last step of the synthetic route of complex **1**

p-octa(hydroxyl)-octa[mercaptobutoxy-gold(I)-trimethylphosphine] calix[8]arene, Complex 1:

To a degassed solution of **6** (0.150 g, 0.089 mmol, 1 equiv.) in dry THF (17 mL) was added chloro(trimethylphosphine)gold(I) (0.221 g, 0.715 mmol, 8 equiv.). To the mixture was added dry Et_3N (109 µL, 0.804 mmol, 9 equiv.). The mixture was stirred at rt for 30 min. The mixture was then filtered and the solid washed with THF and was dried under vacuum. The residue was washed under stirring with EtOH (50 mL), then filtered and the residue was dried under vacuum. The product **1** was obtained as a white powder in 52% yield (0.180 g, 0.047 mmol).
^{1}H NMR (400 MHz, DMSO-d_6, ppm): δ 8.77 (s, 8H), 6.25 (m, 16H), 3.81 (s, 16H), 3.61 (m, 16H), 2.87 (m, 16H), 1.77 (m, 32H), 1.55 (m, 52).

[1] P. Ray, M. Clément, C. Martini, I. Abdellah, P. Beaunier, J. L. Rodriguez-Lopez, V. Huc, H. Remita, I. Lampre*, New. J. Chem.* 2018, **42**, 14128-14137.

^{13}C NMR (100 MHz, DMSO-d_6, ppm): δ 153.2, 148.2, 134.7, 115.4, 73.5, 34.2, 29.8, 15.8.
^{31}P NMR (162 MHz, DMSO-d_6, ppm): δ –1.01.
Elemental Analysis: $C_{112}H_{176}Au_8O_{16}P_8S_8$. Theoretical: C 34.86%, H 4.60%, S 6.65%. Measured: C 35.40%, H 4.39%, S 6.87%.
IR (KBr, cm^{-1}): 3198 (*vs*, O-H stretching), 2906 (*s*, C-H stretching), 1595, 1454 (*vs*, aromatic breathing), 1202 (*vs*, C-O stretching), 960 (*vs*, aromatic C-H stretching).
UV-vis spectroscopy (DMSO/EtOH – 20/80) λ_{max} (nm) [ε ($M^{-1}.cm^{-1}$)]: 286 [37000].
XPS (eV): 533.03 (O1s), 284.9 (C1s), 163.19 (S2p), 131.9 (P2p), 84.94 (Au4f).

Complex 1'

From complex 1. In NMR tube, to a solution of **1** (16 mg, 4.15 µmol, 1 equiv.) in DMSO-d_6 (0.4 mL), Cl-Au-PMe_3 (10.23 mg, 0.033 mmol, 8 equiv.) was added under argon.

From compound 6. In a NMR tube, to a solution of **6** (8.4 mg, 5 µmol, 1 equiv.) in DMSO-d_6 (0.3 mL), Cl-Au-PMe3 (25 mg, 81 µmol, 16 équiv.) was added under argon. To the mixture was added dry Et3N (8 µL, 59.3 µmol, 12 equiv.). The mixture was sonicated for 2 minutes and heated with a gun for 30 seconds. With this synthetic route a mixture of complexes **1** and **1'** is obtained in the tube as deduced from ^{1}H NMR spectra (Fig. S7)

III. Supplementary characterizations of complex 1

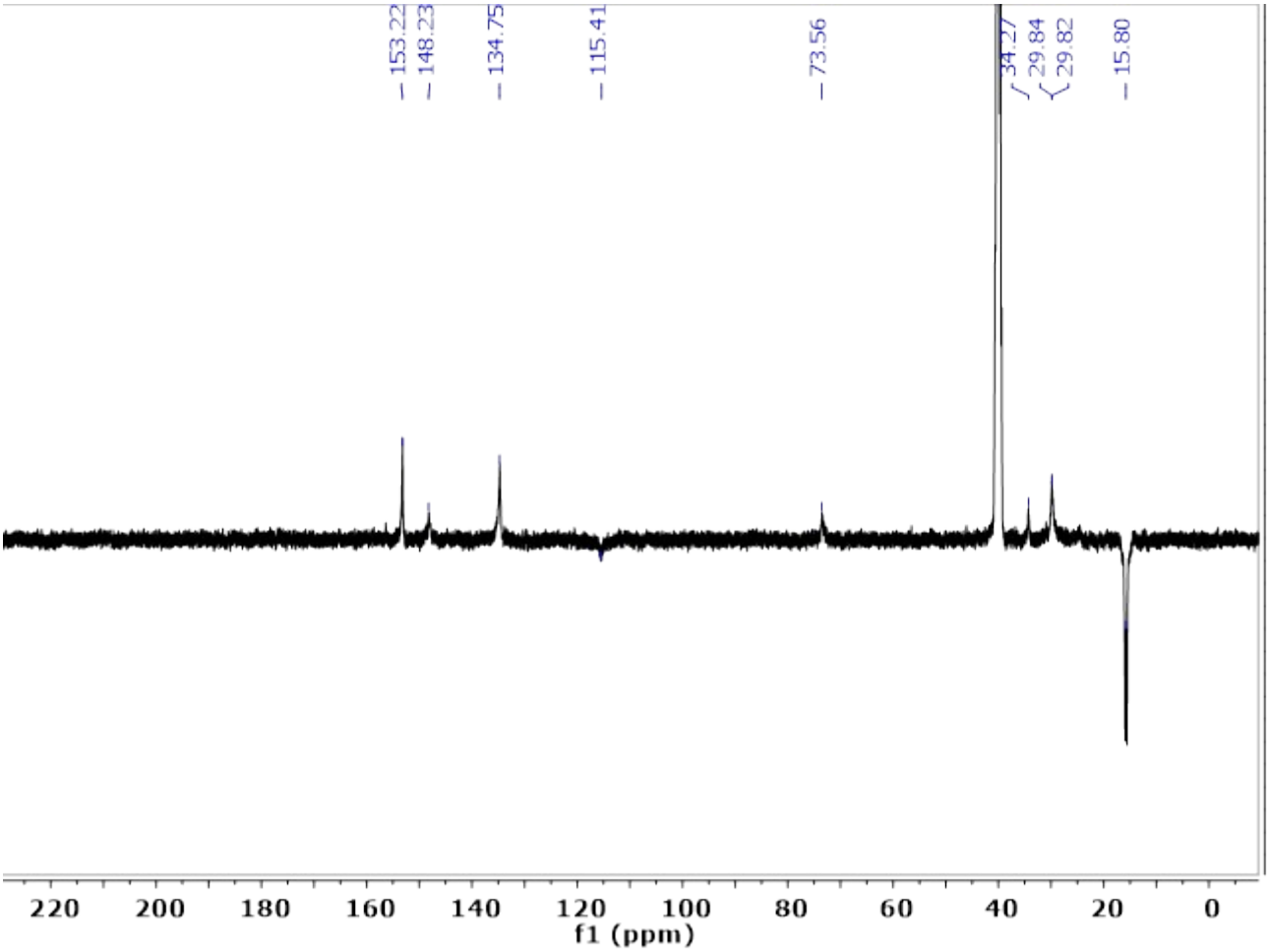


Fig. S1 ^{13}C NMR spectrum of complex **1**

Effect of temperature on ^{1}H and ^{31}P NMR spectra

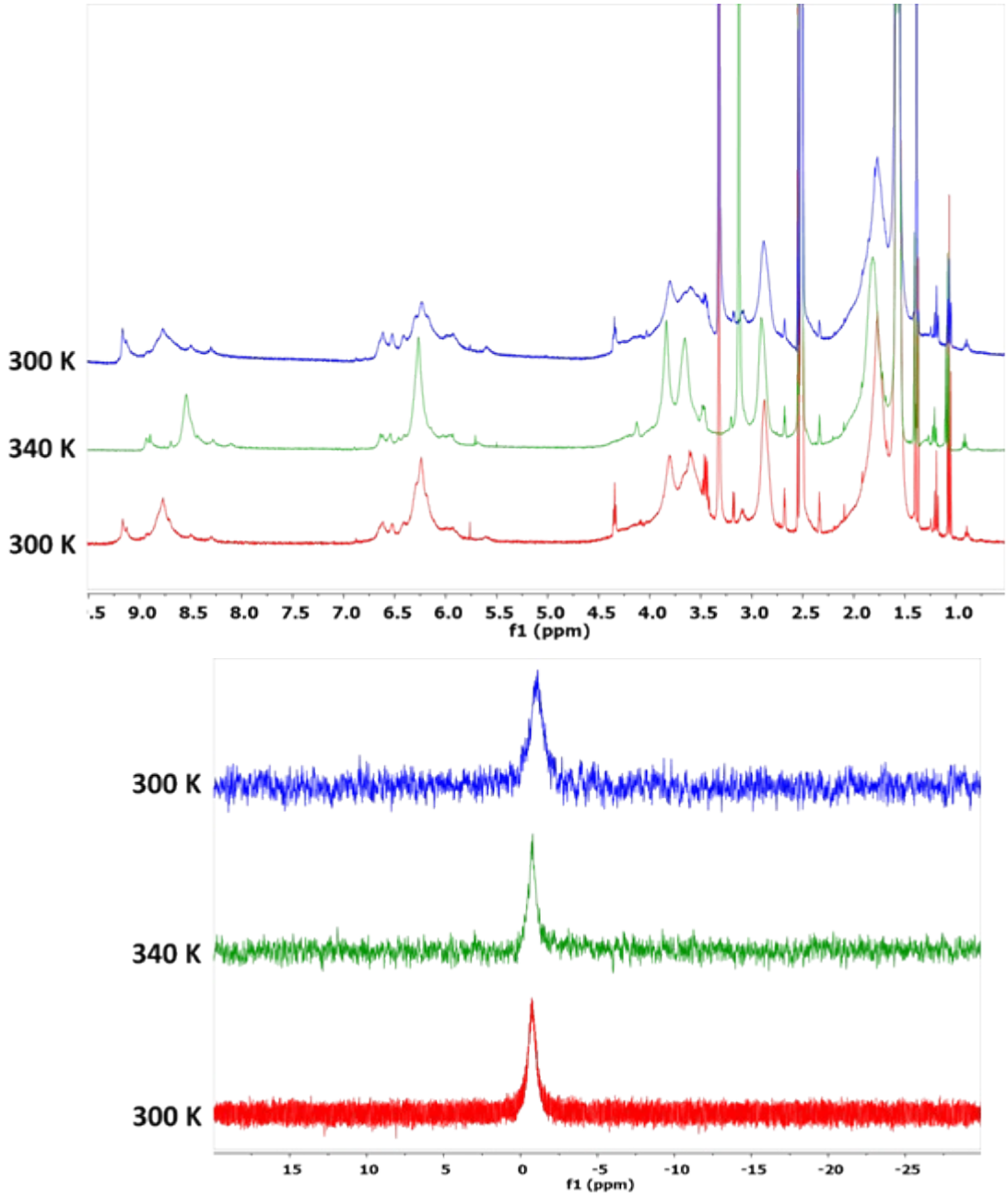


Fig. S2 ^{1}H **(top)** and ^{31}P **(bottom)** NMR spectra of complex **1** in DMSO-d_6 as a function of temperature: initially 300 K (red), then 340 K (green) and back to 300 K (blue)

We observe a slight sharpening of the peaks when the temperature increases and also some differences between the ^{1}H NMR spectra at 300 K corroborating the existence of equilibria between at least two adducts for complex **1**. No major temperature effect is detected on the ^{31}P spectra indicating a similar environment for Au-P-Me_3.

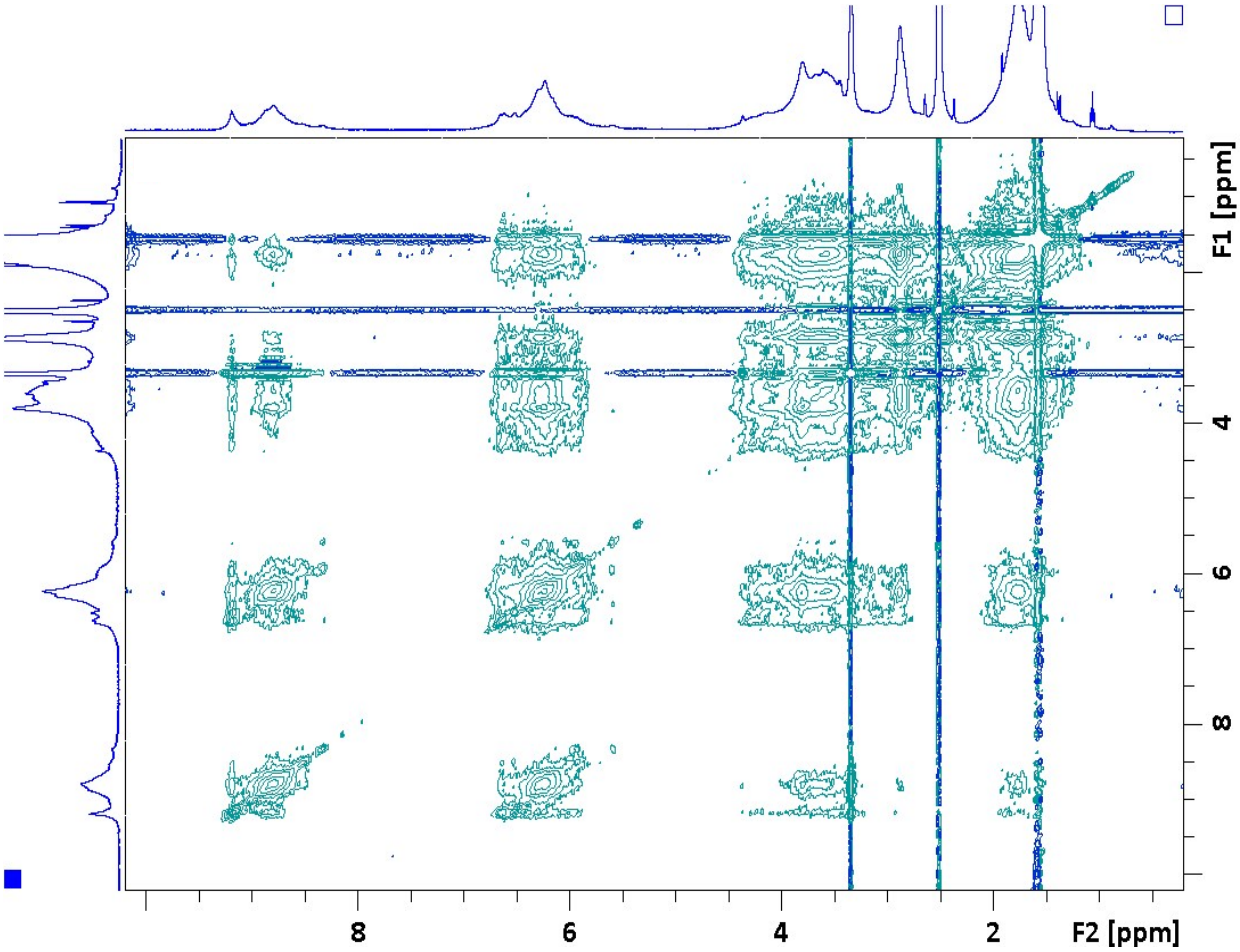


Fig. S3 2D NOESY NMR spectrum of complex **1** in DMSO-d_6 registered at 500 MHz and 298 K

The high intensity of the off-diagonal signals indicates low changes in conformations due to the presence of the Au-PMe3 groups reducing the molecular flexibility of the calixarene ring.

NMR in solid phase

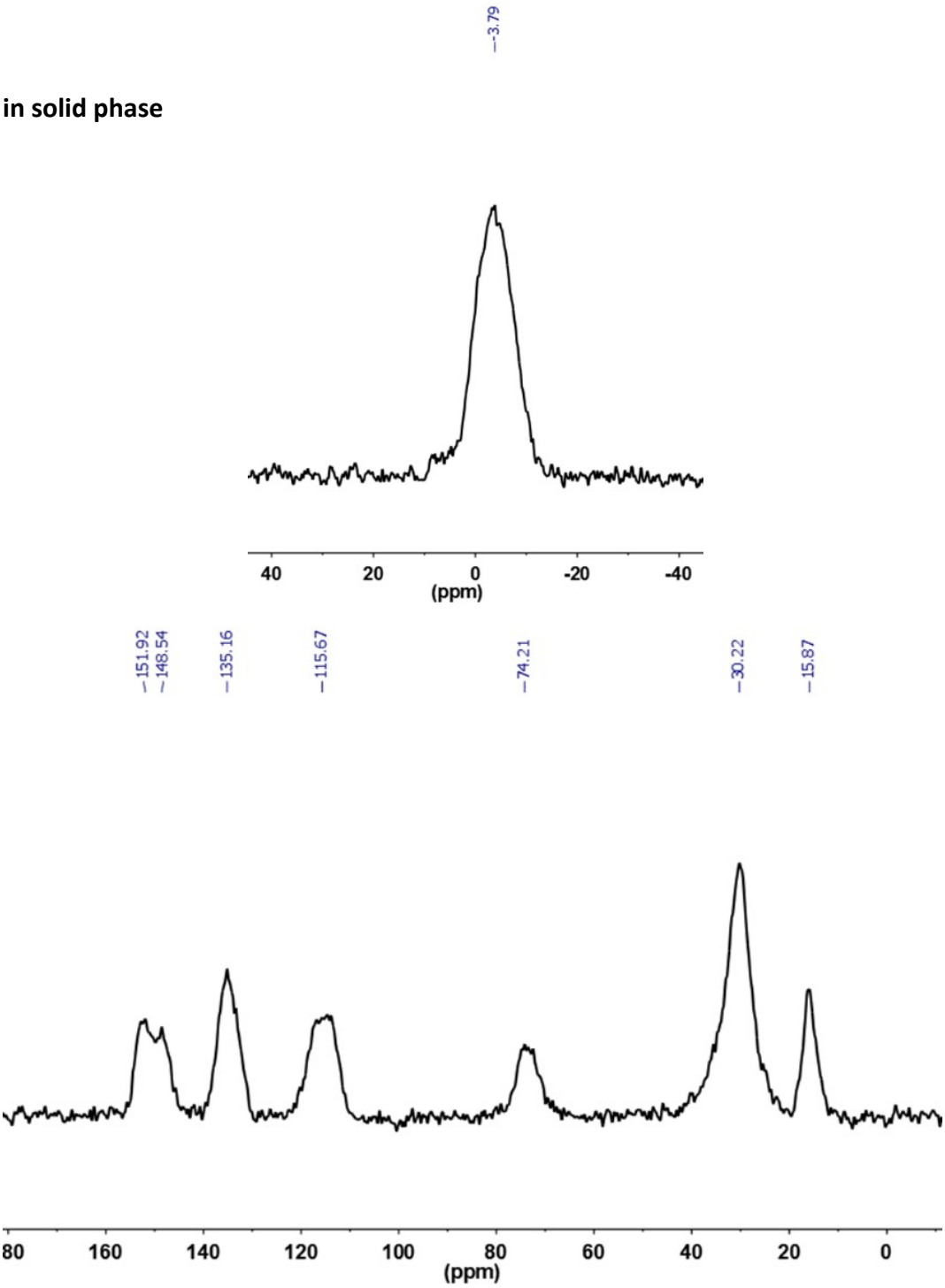


Fig. S4 ^{31}P **(top)** and ^{13}C **(bottom)** CP-MAS NMR spectra of complex **1**

The CP-MAS spectra present broad, not-well resolved signals suggesting the presence of different conformations. The ^{31}P CP-MAS NMR spectrum of 1 displayed a single signal at –3.6 ppm, downfield shifted from that of Me_3PAuCl (–9.6 ppm[2]), confirming the coordination of the Me_3PAu units to the calix[8]arene core.

[2] (a) M. Okumura, T. Akita, M.Haruta, *Catal. Today,* 2002**, 74**, 265-269; (b) P. A. Sermon, G. C. Bond, P. B. Wells, *J. Chem. Soc., FaradayTrans.* 1979, **75,** 385.

UV-visible and XPS analysis

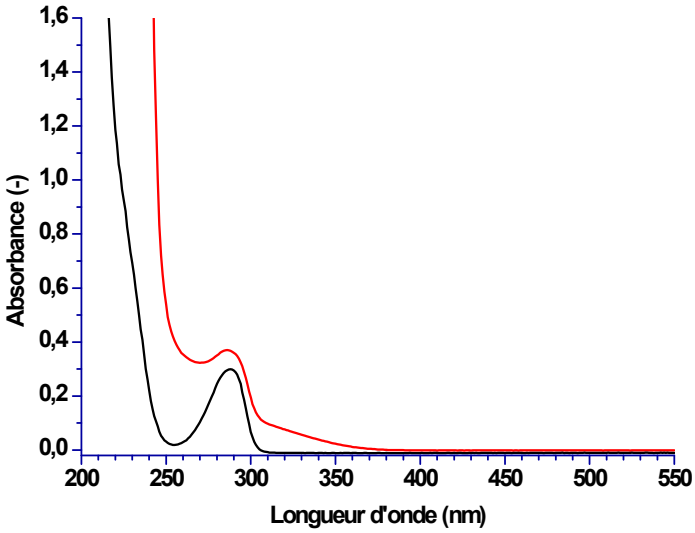


Fig. S5 UV-visible absorption spectra of ethanolic solutions containing compound 6 (black) or complex 1 (red) at a concentration of 5×10^{-5} M.

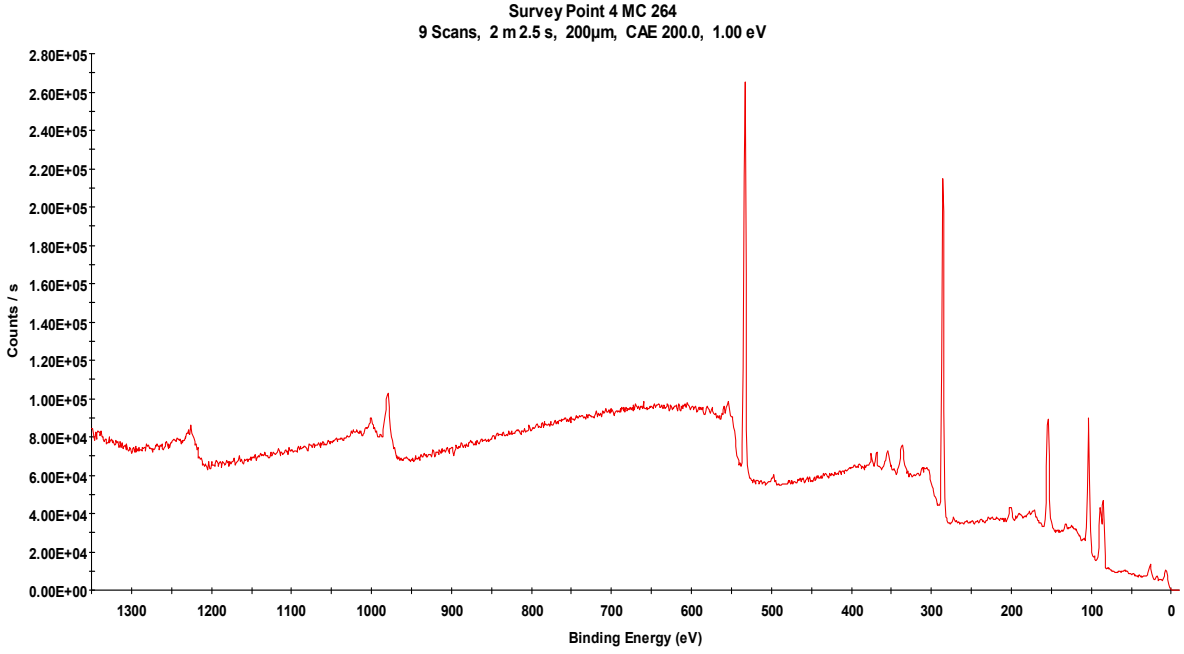


Fig. S6. XPS wide-scan spectrum of complex **1**

IV. NMR characterizations of complex 1'

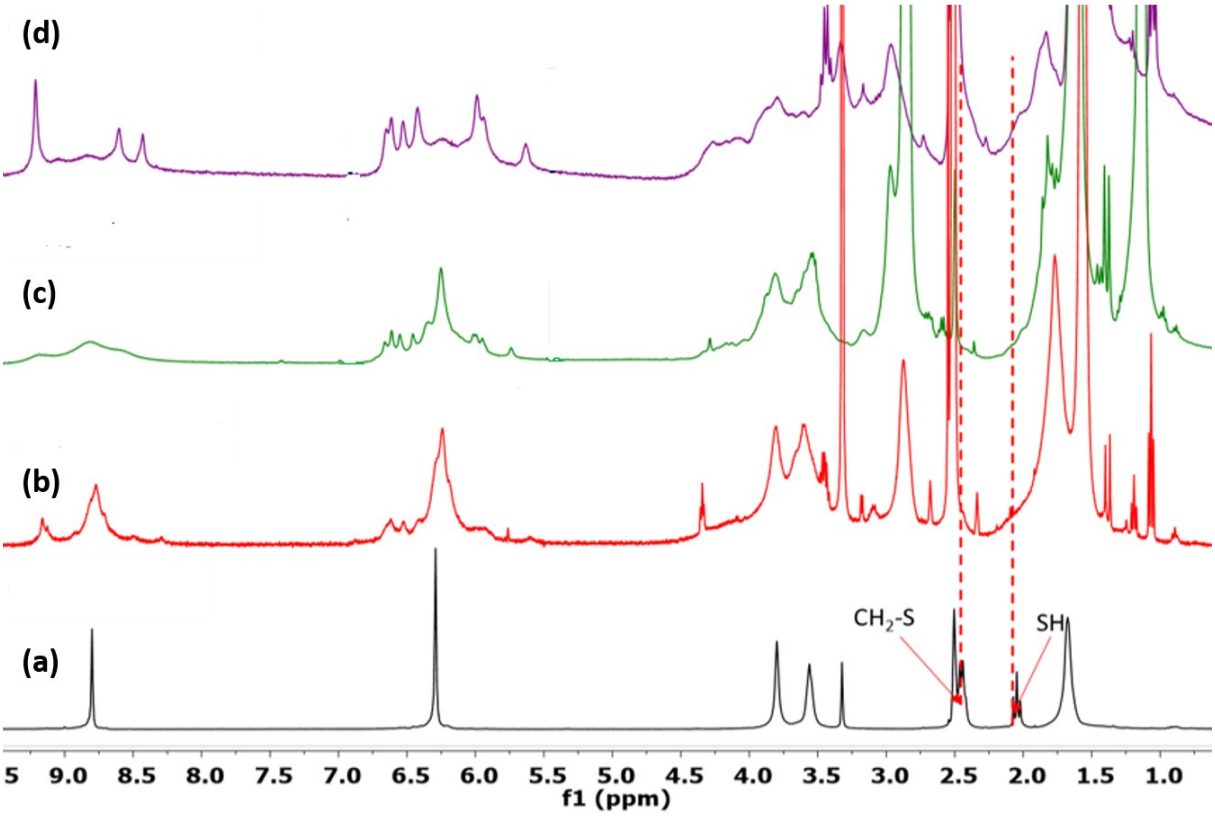
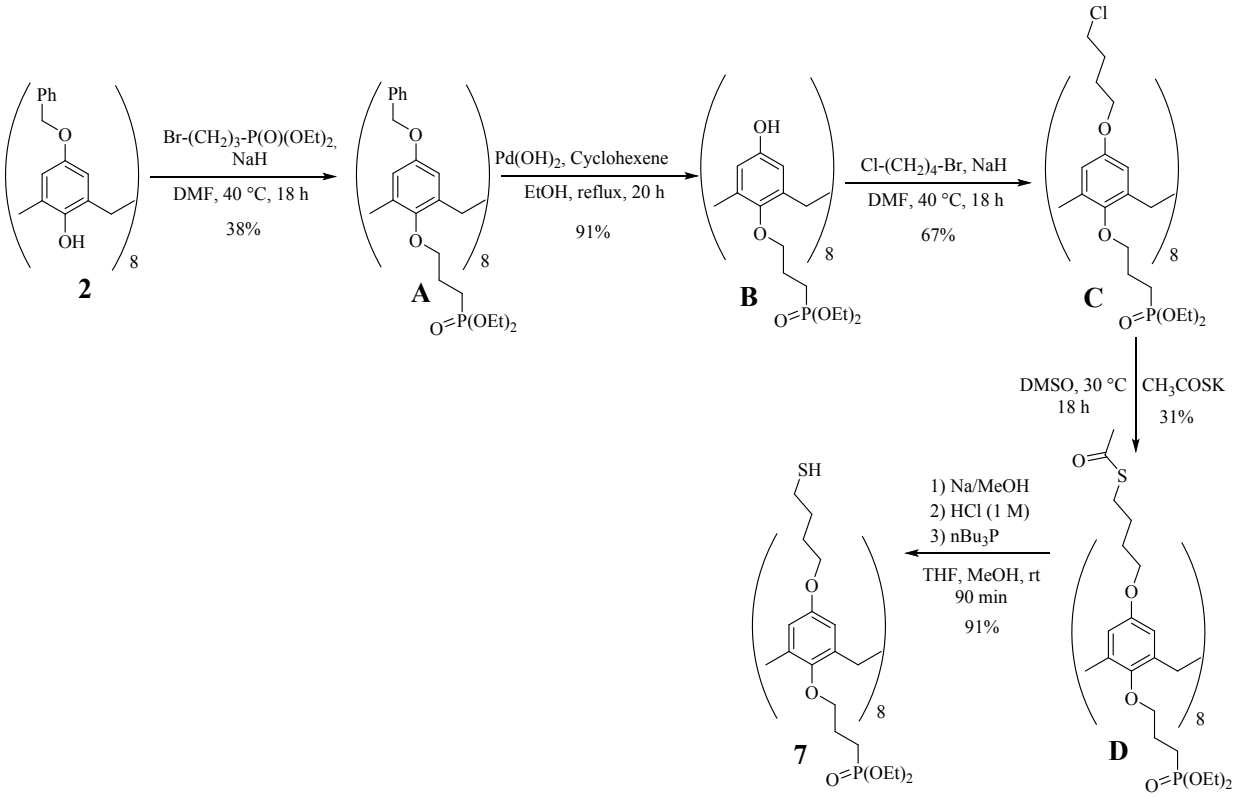


Fig. S7. 1H NMR spectra in DMSO-d_6 at 298K of **(a)** compound 6, **(b)** complex **1**, **(c)** compound **6** after addition of 16 equivalents of Me_3PAuCl, and **(d)** complex **1** with addition of eight equivalent of Me_3PAuCl

After addition of eight equivalents of Me_3PAuCl in an NMR tube containing a solution of complex **1** in DMSO-d_6, a global modification of the ^1H spectrum **(d**) is observed, indicating the formation of complex **1'**. The ^1H NMR spectrum **(**c) obtained after addition of sixteen equivalents of Me_3PAuCl in an NMR tube containing a solution of compound **6** in DMSO-d_6 presents the features of both spectra **(b)** and **(d)** indicating the formation of a mixture of complex **1** and complex **1'**.

V. Synthetic procedure for compound 7



Scheme S2. Synthetic route of compound **7**

Compound A:

To a solution of **2** (1 g, 3.85 mmol) in dry DMF (3 mL) was added to diethyl 3-bromopropy-lphosphonate (0.410 g, 0.241 mmol, 1 equiv.). The mixture was heated to 40 °C under stirring and under argon. To the mixture was added *carefully* NaH (0.154 g, 3.859 mmol, 16 equiv.) over 6 h. The mixture was allowed to stand under stirring at 40 °C overnight under argon. The mixture reaction was cooled down and filtered through celite and washed with CH_2Cl_2. The solvent was removed from the filtrate at 60 °C under reduced pressure. The solid residue was dried under vacuum. The product was extracted with CH_2Cl_2 (3 x 100 mL). The organic layer was dried over $MgSO_4$, filtered with CH_2Cl_2 and dried at 40 °C under reduced pressure. The solid residue was washed with pentane (50 mL) under stirring for 1 h, filtered and dried under vacuum. The solid residue was purified by column chromatography (SiO_2, EtOH/$CHCl_3$ – 10/90). The product **A** was obtained as orange powder in 38 % yield (288 mg, 0.092 mmol).

^{1}H NMR (360 MHz, DMSO-d_6, ppm): δ 7.07 (*s*, 40H), 6.48 (s, 16H), 4.63 (*s*, 16H), 3.87-3.95 (m, 48H), 3.71 (br*s*, 16H), 1.82-1.86 (m, 32H), 1.12-1.16 (m, 48H).

^{13}C NMR (90 MHz, DMSO-d_6, ppm): δ 155.0, 149.1, 137.8, 135.5, 128.9, 128.2, 115.3, 73.7 (d, $J_{C\text{-}P}$ = 15.3 Hz), 69.8, 61.7 (d, $J_{C\text{-}P}$ = 6.3 Hz), 30.5, 22.9, 21.4, 17.1 (d, $J_{C\text{-}P}$ = 5.4 Hz).

^{31}P NMR (121 MHz, DMSO-d_6, ppm): δ 31.9.

HRMS (ESI, positive mode) : calcd. For $C_{168}H_{216}Na_2O_{40}P_8$ $[M+2Na]^{2+}/2$ 1583.6277. Found 1583.6445.

Compound B:

Compound A (1.78 g, 0.57 mmol) was introduced in a two-necked flask equipped with a reflux condenser. Cyclohexene 16 mL and Pearlman's catalyst $Pd(OH)_2/C$ (20 % Pd, 1.71 g) were added at rt under argon. To the mixture were added dry EtOH (45 mL). The mixture was stirred and heated to 75 °C overnight. The mixture was cooled down, filtered through celite and washed with DCM. The filtrate was evaporated under reduced pressure. The residue was dissolved in DCM and precipitated with Pentane. The mixture was filtered and washed with petane. The solvent was removed under vacuum. The product **B** was obtained as a white powder in 91 % yield (1.25 g).

^{1}H NMR (360 MHz, DMSO-d6, ppm): δ 8.88 (*s*, 8H), 6.28 (s, 16H), 3.91-3.99 (m, 32H), 3.79 (br*s*, 16H), 3.64 (brs, 16H), 1.87-1.90 (m, 32H), 1.16-1.20 (m, 48H).

^{13}C NMR (90 MHz, DMSO-d_6, ppm): δ 153.8, 147.9, 135.4, 115.9, 73.7 (d, $J_{C\text{-}P}$ = 16.2 Hz), 61.9 (d, $J_{C\text{-}P}$ = 6.3 Hz), 29.8, 23.9, 17.7 (d, $J_{C\text{-}P}$ = 5.4 Hz).

^{31}P NMR (121 MHz, DMSO-d_6, ppm): δ 31.9.

Compound C:

To a solution of **B** (2 g, 0.832 mmol, 1 equiv.) in anhydrous DMF (10 mL) was added 1-bromo-4-chlorobutane (10 mL, 86.8 mmol, 100 equiv.). The mixture was stirred and heated to 40 °C under argon. NaH (400 mg, 1 mmol, 12 equiv.) was <u>*carefully*</u> introduced in 3 times over 6 h and the reaction mixture was stirred for 18 h under argon at 40 °C. Then the mixture was cooled down and toluene was added to the mixture (around 20 mL). The suspension was filtered through celite with toluene. The solvent was removed from the filtrate at 30°C under reduced pressure. The solid residue was dried under vacuum. The product was extracted with CH_2Cl_2 (3 x 100 mL). The organic layer was dried over $MgSO_4$, filtered with CH_2Cl_2 and the solvent was removed at 60 °C under reduced pressure. The crude residue was purified by column chromatography (SiO_2, $CHCl_3$/EtOH, 95/5). The compound **C** was obtained as a white powder in 67 % yield (1.73 g).

^{1}H NMR (360 MHz, $CDCl_3$, ppm): δ 6.36 (s, 16H), 4.05-4.13 (m, 32H), 3.85-3.88 (m, 32H), 3.52 (br*s*, 16H), 3.20-3.25 (m, 16H), 2.14 (m, 16H), 1.91-2.02 (m, 16H), 1.49-1.61 (m, 32H), 1.16-1.20 (*m*, 48H).

^{13}C NMR (90 MHz, $CDCl_3$, ppm): δ 155.4, 148.7, 135.2, 114.7, 74.0 (d, $J_{C\text{-}P}$ = 16.2 Hz), 67, 61.8 (d, $J_{C\text{-}P}$ = 6.3 Hz), 45.1, 29.4, 26.8, 24.0, 23.7, 22.1, 16.8 (d, $J_{C\text{-}P}$ = 5.4 Hz).

^{31}P NMR (121 MHz, DMSO-d_6, ppm): δ 31.7.

Compound D:

To a solution of C (1.73 g, 0.55 mmoll) in DMSO 8 mL was added potassium thioacetate (885 mg, 7.75 mmol) at rt. The mixture was stirred 18 h at rt under argon. The solution was diluted

with CH_2Cl_2 (35 mL) and placed for 1 h at rt. The suspension was filtered through celite with CH_2Cl_2. The product was extracted with CH_2Cl_2 (3 x 100 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent was removed at 50 °C under reduced pressure. The crude residue was purified by column chromatography (SiO_2, $CHCl_3$/EtOH, 94/6). The product D is obtained as white powder in 31 % yield (559 mg).

^{1}H NMR (360 MHz, $CDCl_3$, ppm): δ 6.32 (s, 16H), 4.00-4.09 (m, 32H), 3.79-3.86 (m, 32H), 3.46 (br*s*, 16H), 2.61-2.65 (m, 16H), 2.25 (s, 24H), 2.03-2.12 (m, 16H), 1.86-1.96 (m, 16H), 1.39-1.43 (m, 32H), 1.24-1.28 (m, 48H).

^{13}C NMR (90 MHz, $CDCl_3$, ppm): δ 196.6, 155.3, 148.7, 135.1, 114.8, 73.9 (d, $J_{C\text{-}P}$ = 16.2 Hz), 67.3, 61.8 (d, $J_{C\text{-}P}$ = 6.3 Hz), 30.4, 29.0, 28.4, 26.4, 23.8, 23.5, 22.0, 16.8 (d, $J_{C\text{-}P}$ = 6.3 Hz).

^{31}P NMR (121 MHz, $CDCl_3$,ppm): δ 31.7.

HRMS (ESI, positive mode) : calcd. For $C_{160}H_{248}NaO_{48}P_8S_8$ $[M+Na]^+$ 3464.25. Found 3464.26.

Compound 7:

To a degassed solution of compound D (559 mg, 0.165 mmol) in dry THF (5 mL) was added a degassed solution of Na (0.224 g, 9.75 mmol) in dry EtOH 5 mL. The mixture was stirred for 1 h at rt. To the mixture was added dropwise an aqueous solution of HCl (1 M) until a pH of 1 was reached. The residue was extracted with CH_2Cl_2 (3 x 100 mL). The organic layer was dried over $MgSO_4$ and filtered with CH_2Cl_2. The solvent was removed under vacuum. The solid residue was diluted in CH_2Cl_2 and precipitate with pentane. The suspension was filtered with pentane and the solid residue was dried under vacuum. The residue was resolubilized under argon in a mixture of $CHCl_3$/MeOH/H_2O (30/4/0.5 mL) and tri-*n*-butylphosphine (587 µL, 2.38 mmol.) was added. The mixture was stirred for 30 min at rt. Pentane (200 mL) was fed upon stirring for 15 min. The mixture was filtered and the solid was dried under vacuum. The product 7 was obtained as a white powder in 63 % yield (328 mg).

^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.36 (s, 16H), 4.04-4.13 (m, 32H), 3.83-3.88 (m, 32H), 3.45-3.58 (m, 16H), 2.20-2.28 (m, 16H), 1.91-2.03 (m, 16H), 1.41-1.52 (m, 32H), 1.27-1.32 (m, 48H), 1.18-1.23 (m, 8H).

^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 155.4, 148.6, 135.2, 114.7, 74.0 (d, $J_{C\text{-}P}$ = 17.2 Hz), 67.4, 61.9 (d, $J_{C\text{-}P}$ = 6.7 Hz), 30.7, 30.2, 28.1, 24.6, 24.0, 23.8, 21.9, 16.9 (d, $J_{C\text{-}P}$ = 6.0 Hz).

^{31}P NMR (121 MHz, $CDCl_3$, ppm): δ 31.7.

VI. NMR characterizations of compound 7

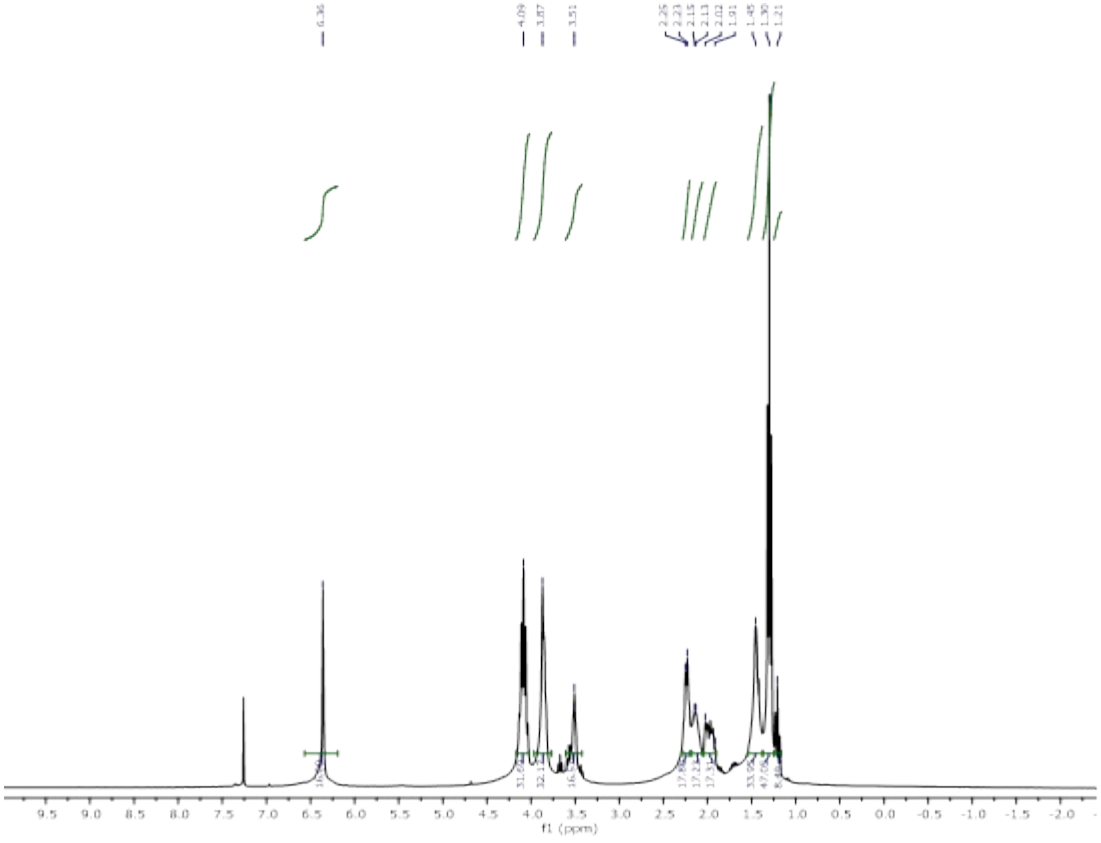


Fig. S8 ^{1}H NMR spectrum of compound 7 in DMSO-d_6

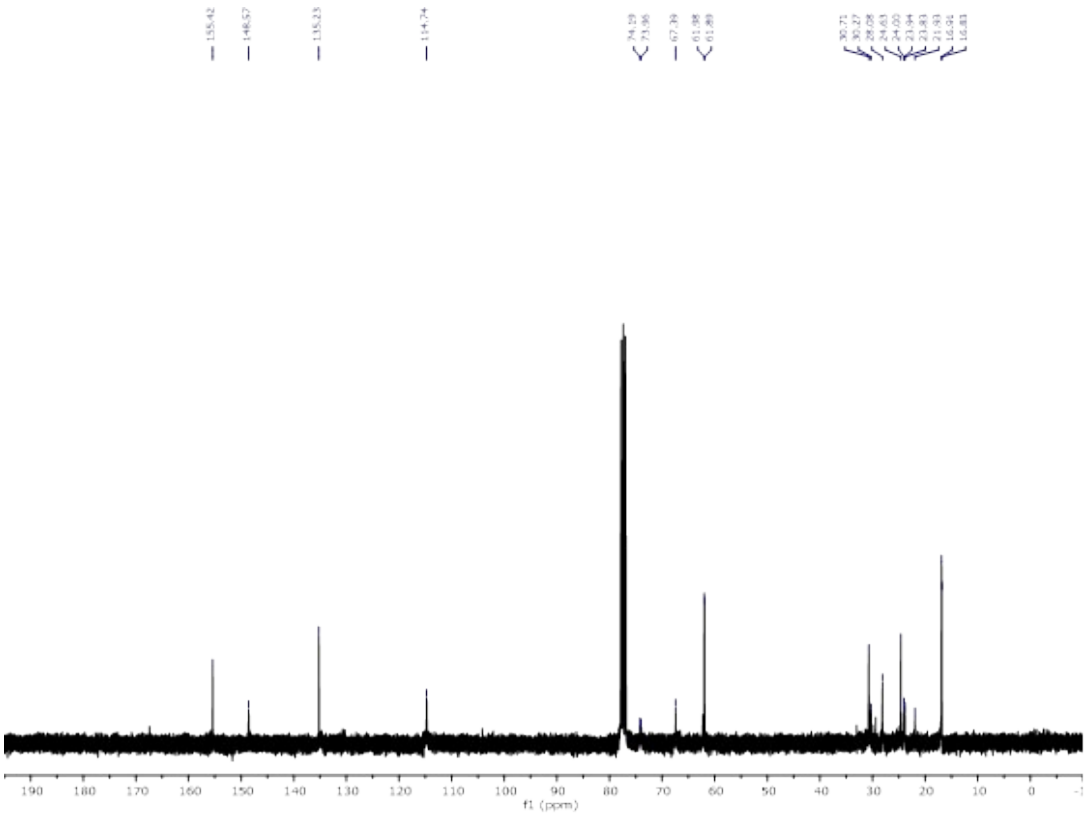


Fig. S9 ^{13}C NMR spectrum of compound 7 in DMSO-d_6

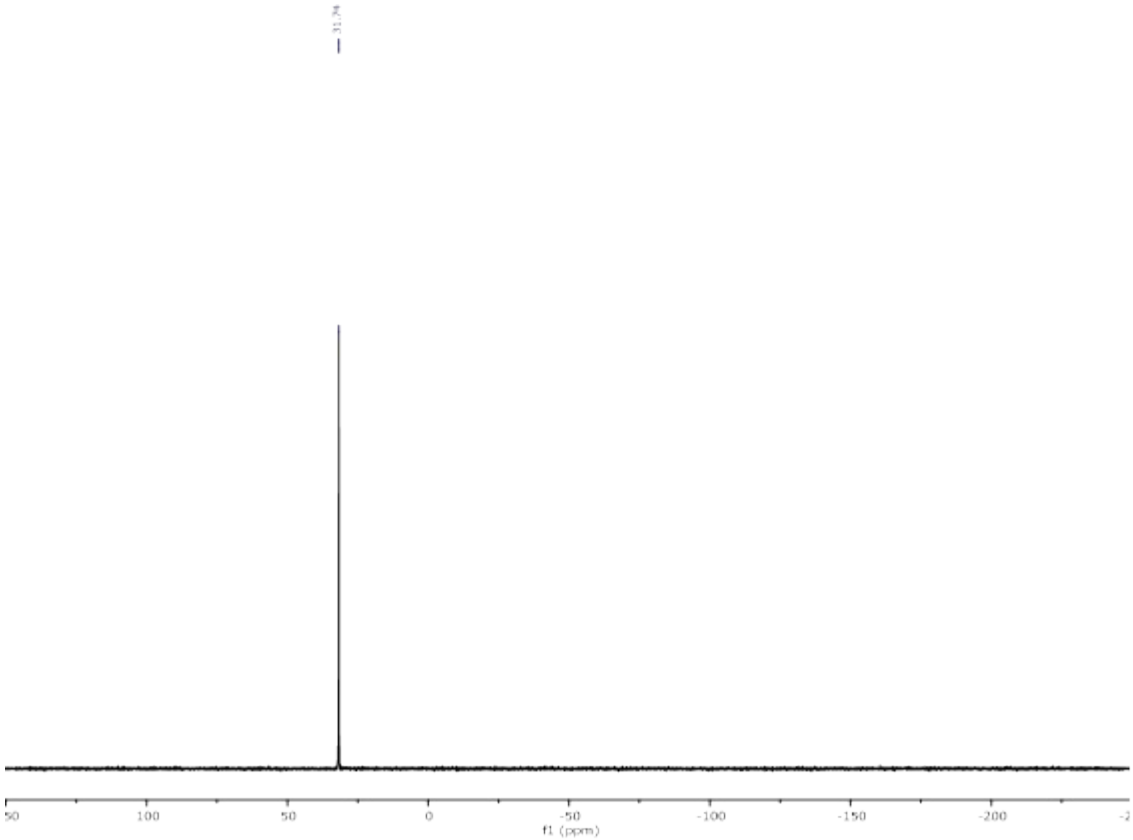


Fig. S10 ^{31}P NMR spectrum of compound **7** in DMSO-d_6

2D NMR

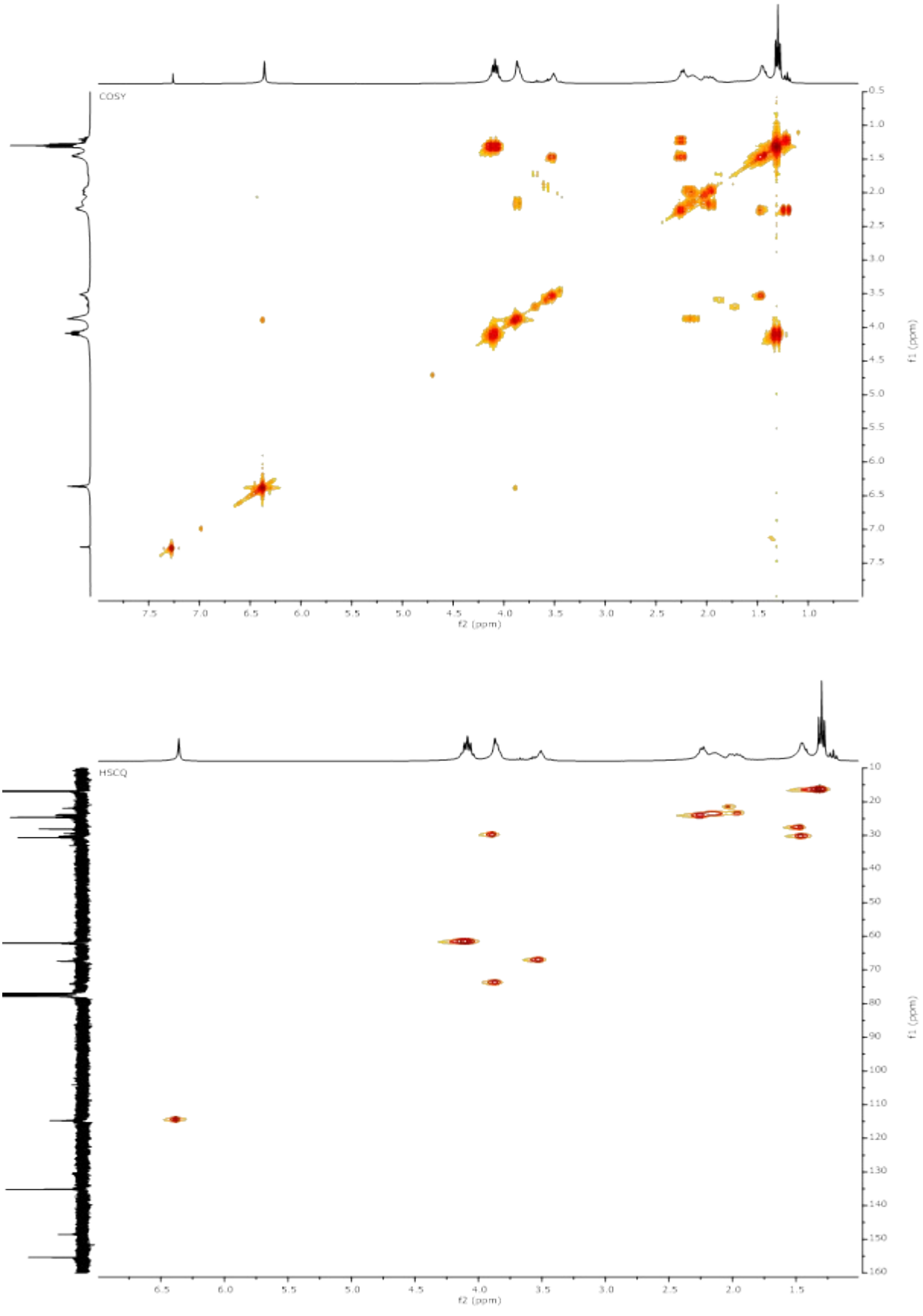


Fig. S11 2D COSY and HSQC NMR spectrum of compound 7 in DMSO-d_6

VII. ^{1}H NMR characterization of complexes 9 and 9’

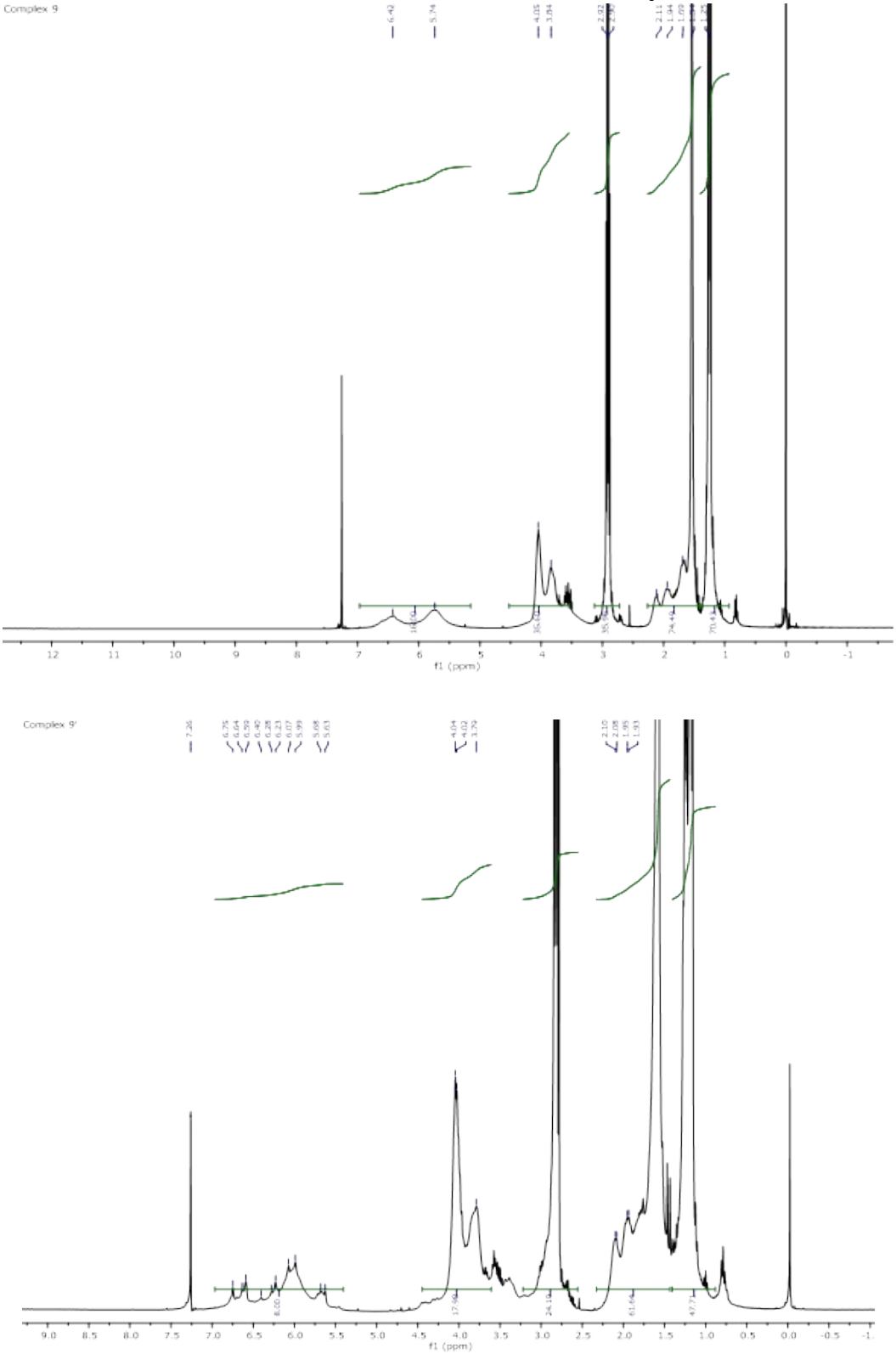


Fig. S12 ^{1}H NMR spectra of complexes 9 (top) and 9’ (bottom) in DMSO-d_6

VIII. Possible conformations for complex 1’

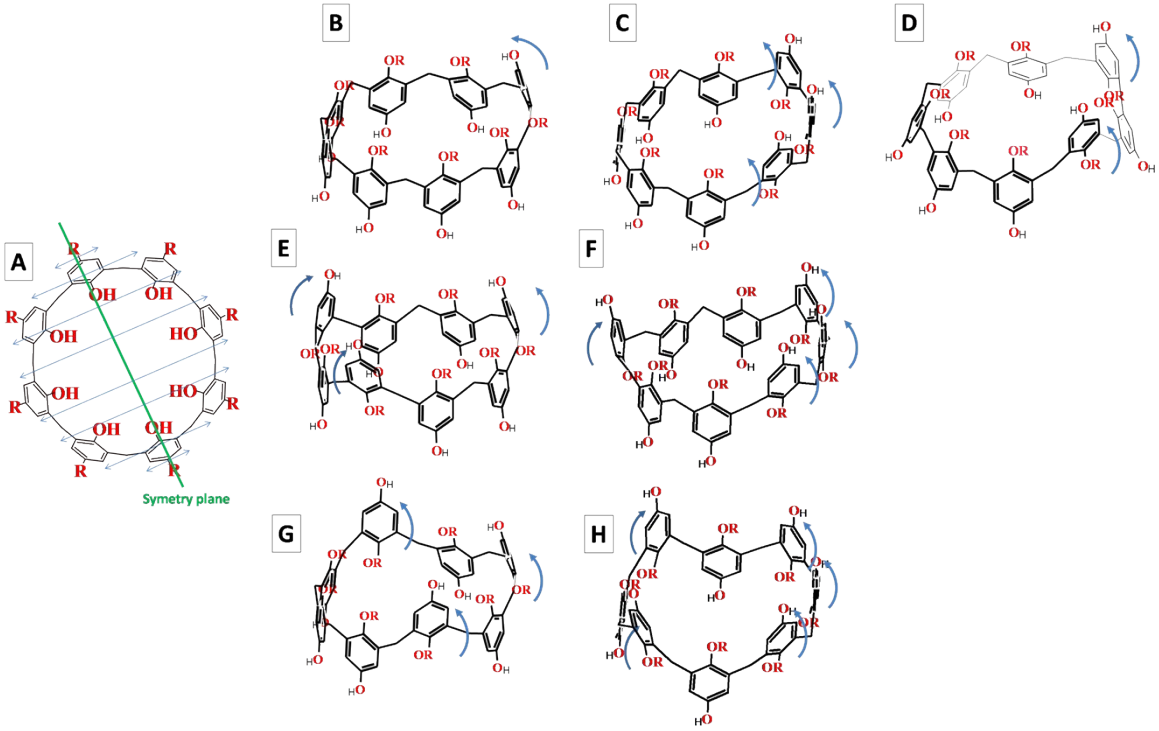


Fig. S13 Molecular schemes of possible conformations of complex 1’ with symmetry plane