Supporting information

Assembly of the Au-diphosphine helical cage molecules via alkynyl–μ_4-methylydine ligand transformation

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Experimental

General comments

Au(tht)Cl (tht = tetrahydrothiophene),[1] $(AuC_2Ph)_n$,[2] 3,6-bis(diphenylphosphino)pyridazine,[3] $PPh_2(C_6H_4)_nPPh_2$ (n = 1–3)[4,5] were synthesized according to published procedures. The complexes $(AuC_2Ph)_2PP$ (*PP* = diphosphine) were obtained as described previously and used without purification.[5,6] Diethyl ether was distilled over Na-benzophenoneketyl under nitrogen atmosphere prior to use. Other reagents and solvents were used as received. The solution 1D ^1H, ^{31}P NMR and ^1H-^1H COSY spectra were recorded on Bruker Avance 400 and Bruker DPX 300 spectrometers. Mass spectra were determined in the ESI^+ mode at St.-Petersburg State University. Microanalyses were carried out in the analytical laboratory of the University of Eastern Finland.

1,3-PPh_2C_2-C_6H_4-C_2PPh_2

1,3-Diethynylbenzene (0.5 g, 3.97 mmol) was dissolved in diethyl ether (60 cm^3) under nitrogen atmosphere, the solution was cooled to -78 ^oC and 1.6 M solution of *n*-BuLi in hexanes (5.5 ml, 8.8 mmol) was added dropwise. The reaction mixture turned into white thick suspension upon slow warming to -20 ^oC (within ca. 2.5 h), then cooled to -78 ^oC again and was treated with neat PPh_2Cl (1.8 g, 8.2 mmol). The resulting suspension was stirred below -60 ^oC for 1 h, then slowly warmed to room temperature (within ca. 2.5 h) and stirring was continued overnight. The brownish reaction mixture was filtered and evaporated. The dark oily residue was dissolved in CH_2Cl_2 (3 cm^3), diluted with hexanes (12 cm^3) and transferred onto a Silica column (2×15 cm, eluent CH_2Cl_2-hexanes 1:4 v/v). Second fraction was collected and passed through a layer of Al_2O_3 (2×5 cm, neutral). The volatiles were removed and pale yellowish oil solidified upon standing at +5 ^oC overnight (1.45 g,

74 %). Analytically pure sample was obtained by washing the solid with hexane (upon cooling to -30 °C, 2×10 cm^3) and methanol (at room temperature, 2×10 cm^3). $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ): -33.6 (s). ^1H NMR ($CDCl_3$; δ): 7.72 (t, 1H, *J* 1.6 Hz), 7.70-7.65 (m, 8H), 7.52 (dd, 2H, *J* 7.8 Hz, *J* 1.6 Hz), 7.41-7.31 (m, 13H). Anal. Calc. for $C_{54}H_{40}P_2$: C, 82.58; H, 4.89. Found: C, 82.54; H 5.17.

General method to generate [{Au(tht)}$_2$*PP*](PF$_6$)$_2$ (*PP* = diphosphine) complexes exemplified by *PP* = PPh$_2$C$_6$H$_4$PPh$_2$

Au(tht)Cl (50 mg, 0.156 mol) was dissolved in CH_2Cl_2 (10 cm^3) and $PPh_2C_6H_4PPh_2$ (35 mg, 0.078 mmol) was added. Colorless solution was stirred for 10 minutes and then treated by a solution of $AgPF_6$ (40 mg, 0.0158 mmol) in acetone. The resulting suspension was stirred in absence of light for 30 min., then filtered to remove precipitate of AgCl and evaporated to give colorless non-crystalline solid, which was used in further reaction without purification.

[Au$_8$(μ$_4$-CCOPh)$_2$(PPh$_2$C$_6$H$_4$PPh$_2$)$_4$](PF$_6$)$_2$ (1)

($AuC_2Ph)_2$*PP* (prepared from 15.5 mg, 0.052 mmol of $(AuC_2Ph)_n$ and *PP* = $PPh_2C_6H_4PPh_2$ 11.8 mg, 0.026 mmol) was suspended in acetone (3 cm^3) and a solution of [{Au(tht)}$_2$*PP*](PF$_6$)$_2$ (prepared from 50 mg, 0.156 mol of Au(tht)Cl, *PP* = $PPh_2C_6H_4PPh_2$ 35 mg, 0.078 mmol and $AgPF_6$ 40 mg, 0.0158 mmol) in acetone (10 cm^3) was added resulting in formation of a yellow-greenish transparent solution. Then H_2O (5 drops) and NEt_3 (2 drops) were added causing color fading and the reaction mixture was stirred overnight in absence of light. Dirty yellow opaque solution was filtered, evaporated, washed with ethanol (2×3 cm^3), diethyl ether (2×3 cm^3) and dried. Recrystallization by slow evaporation of its CH_2Cl_2-ethanol solution at room temperature gave pale-yellow crystalline material (89 mg, 88%). The crystals suitable for X-ray diffraction study were obtained by gas phase diffusion of diethyl ether into concentrated acetonitrile solution of **1**. ES MS (*m*/*z*): $[Au_8(CCOPh)_2(PPh_2C_6H_4PPh_2)_4]^{2+}$ 1798 (calcd 1798). $^{31}P\{^1H\}$ NMR (acetone-d_6; δ): 31.9 (s, 8P), -144.8 (sept, 2PF_6). ^1H NMR (acetone-d_6, -10°C, low temperature limiting spectrum; δ): **diphosphine**: **P-C$_6$H$_4$-P** 6.95 (m, A_2X_2, 16H,), **two sets of inequivalent phenyl rings**: (**A**) 7.77 (t, *para*-H, 8H; J (H–H) 7.6 Hz), 7.71-7.52 (AB system of *ortho*-H+*meta*-H, 32H), (**B**) 7.30 (t, *para*-H, 8H; J (H–H) 7.6 Hz), 7.11 (m, *ortho*-H, 16H, J (H–H) 7.9, J (H–P) 12.2 Hz), 6.75 (dd, *meta*-H, 16H; J (H–H) 7.6, 7.9 Hz); **C-C(O)-Ph:** 8.36 (m, *ortho*-H, 4H, J (H–H) ~7.8 Hz), 7.5-7.41 (m, AB system, *meta*-H and *para*-H, 6H). Anal. Calc. for $Au_8C_{136}H_{106}F_{12}O_2P_{10}$: C, 42.04; H, 2.75. Found: C, 42.04; H, 3.06.

[Au$_8$(μ$_4$-CCOPh)$_2$(PPh$_2$(C$_6$H$_4$)$_2$PPh$_2$)$_4$](PF$_6$)$_2$ (2)

Analogously to **1**, pale yellow crystals, 80%. The crystals suitable for X-ray diffraction study were obtained by gas phase diffusion of diethyl ether into CH_2Cl_2-methanol solution of **2**. ES MS (*m*/*z*): $[Au_8(CCOPh)_2(PPh_2(C_6H_4)_2PPh_2)_4]^{2+}$ 1950 (calcd 1950). $^{31}P\{^1H\}$ NMR (acetone-d_6; δ): 31.9 (s, 8P), -144.8 (sept, $2PF_6$). ^1H NMR (acetone-d_6, -50°C, low temperature limiting spectrum; δ): **diphosphine**: **P-C_6H$_4$- C_6H$_4$-P** 6.97-6.90 (m, ABX, 32H,), **two sets of inequivalent phenyl rings**: (**A**) 7.60-6.80 (broad ABC multiplet, *ortho*-*meta*-*para*-H, 40H, (**B**) 7.38 (m, *ortho*-H, 16H, J (H–H) 8.4, J (H–P) 12 Hz), 7.32 (t, *para*-H, 8H; J (H–H) 8.1 Hz), 6.86 (dd, *meta*-H, 16H; J (H–H) 8.4, 8.1 Hz); **C-C(O)-Ph:** 8.50 (m, *ortho*-H, 4H, J (H–H) ~7 Hz), 7.62-7.48 (m, AB system, *meta*-H and *para*-H, 6H). ^1H NMR (acetone-d_6, +45°C, high temperature limiting spectrum; δ): **diphosphine**: **P-C_6H$_4$-C_6H$_4$-P** 7.26-7.12 (m, ABX, 32H, J (H–H) 8, J (H–P) 14 Hz), **one set of phenyl ring signals**: 7.30 (dd *meta*-H, 32H, J (H–H) 8.2 Hz), 7.56-7.45 (broad AB multiplet, *ortho*-*para*-H, 48H); **C-C(O)-Ph:** 8.45 (m, *ortho*-H, 4H), 7.49-7.45 (m, AB system, *meta*-H and *para*-H, 6H). Anal. Calc. for $Au_8C_{160}H_{122}F_{12}O_2P_{10}$: C, 45.86; H, 2.93. Found: C, 45.84; H, 3.24.

$[Au_8(\mu_4\text{-}CCOPh)_2(PPh_2(C_6H_4)_3PPh_2)_4](PF_6)_2$ (3)

Analogously to **1**, pale yellow crystals, 78%. ES MS (*m*/*z*): $[Au_8(CCOPh)_2(PPh_2(C_6H_4)_3PPh_2)_4]^{2+}$ 2102 (calcd 2102). $^{31}P\{^1H\}$ NMR (acetone-d_6; δ): 31.5 (s, 8P), -144.8 (sept, $2PF_6$). ^1H NMR (acetone-d_6, +45°C, high temperature limiting spectrum; δ): **diphosphine**: **-C_6H$_4$-C_6H$_4$- C_6H$_4$-** 7.21 (s, 16H,), **-C_6H$_4$-C_6H$_4$-P;** 7.37-7.30 (m, ABX system, 32H); **P-Ph** 7.51 (t, *para*-H, 16H; J (H–H) 8 Hz), 7.50 (m, *ortho*-H, 32H, J (H–H) 8, J (H–P) 15 Hz), 7.31 (m, *meta*-H, 32H; J (H–H) 8, J (H–P) 2 Hz); **C-C(O)-Ph:** 8.46 (m, *ortho*-H, 4H, J (H–H) ~8 Hz), 7.50-7.46 (m, AB system, *meta*-H and *para*-H, 6H). Anal. Calc. for $Au_8C_{184}H_{138}F_{12}O_2P_{10}$: C, 49.17; H, 3.09. Found: C, 48.87; H, 3.44.

$[Au_8(\mu_4\text{-}CCOPh)_2(PPh_2C_4N_2H_2PPh_2)_4](PF_6)_2$ (4)

Analogously to **1**, recrystallized by gas phase diffusion of diethyl ether into concentrated acetonitrile-methanol solution of **5** at +5 °C, yellow crystals, 53%. ES MS (*m*/*z*): $[Au_8(CCOPh)_2(PPh_2C_4N_2H_2PPh_2)_4]^{2+}$ 1802 (calcd 1802). $^{31}P\{^1H\}$ NMR (acetone-d_6; δ): 30.5 (s, 8P), -144.8 (sept, $2PF_6$). ^1H NMR (NCMe-d_3, +50°C, high temperature limiting spectrum; δ): **diphosphine**: **P-C_4N_2H$_2$-P** 6.95 (broad multiplet, 8H,), **P-Ph**: 7.45 (t, *para*-H, 8H; J (H–H) 7.4 Hz), 7.51 (m, *ortho*-H, 16H, J (H–H) 7.1, J (H–P) 11.9 Hz), 7.18 (dd, *meta*-H, 16H; J (H–H) 7.1, 7.4 Hz); **C-C(O)-Ph:** 8.17 (m, *ortho*-H, 4H, J (H–H) ~8 Hz), 7.38-7.29 (m, AB system, *meta*-H and *para*-H, 6H). Anal. Calc. for $Au_8C_{128}H_{98}F_{12}N_8O_2P_{10}$: C, 39.48; N, 2.88; H, 2.54. Found: C, 39.74; N, 2.86; H, 3.03.

$[Au_8(\mu_4\text{-}CCOPh)_2(1,3\text{-}PPh_2\text{-}C_2\text{-}C_6H_4\text{-}C_2\text{-}PPh_2)_4](PF_6)_2$ (5)

Analogously to **1**, yellow crystals, 62%. ES MS (*m*/*z*): $[Au_8(CCOPh)_2(PPh_2C_2C_6H_4C_2PPh_2)_4]^{2+}$ 1894 (calcd 1894). $^{31}P\{^1H\}$ NMR (CD_2Cl_2; δ): 6.9 (s, 8P), -143.0 (sept, $2PF_6$). ^1H NMR (CD_2Cl_2, +25°C, high temperature limiting spectrum; δ): **diphosphine**: **1,3(PPh$_2$)-C$_6$H$_4$** 7.13 (t, 4H, H^5 J(H-H) 7.8 Hz), 6.79 (t, 4H, H^2 J(P-H) 1.5 Hz), 6.60 (dd, 8H, $H^{4,6}$ J(H-H) 7.8, J(P-H)1.6 Hz); **P-Ph** 7.78 (dd, *ortho*-H, 32H, J (H–H) 8, J (H–P) 13 Hz), 7.51 (t, *para*-H, 16H; J (H–H) 8 Hz), 7.32 (ddd, *meta*-H, 32H; J (H–H) 8, J (H–P) 2 Hz); **C-C(O)-Ph:** 8.18 (dd, *ortho*-H, 4H, J (H–H) 8.2, 1.4 Hz), 7.39 (tt, *para*-H, 2H; J (H–H) 7.4, 1.4 Hz), 7.27 (dd, *meta*-H, 4H; J (H–H) 8.2, 7.4 Hz). Anal. Calc. for $Au_8C_{152}H_{106}F_{12}O_2P_{10}$: C, 44.77; H, 2.62. Found: C, 44.88; H, 2.92.

X-ray structure determination. The crystals of **1** and **5** were immersed in cryo-oil, mounted in a Nylon loop, and measured at a temperature of 100 K. The X-ray diffraction data were collected on a Nonius KappaCCD diffractometer (**1**) or on a Bruker Kappa Apex II Duo using Mo Kα radiation (λ = 0.710 73 Å). The *Denzo-Scalepack*[7] or *APEX2*[8] program packages were used respectively for cell refinements and data reductions. The structures were solved by direct methods using the *SHELXS-97*[9] program with the *WinGX*[10] graphical user interface. A semi-empirical absorption correction (*SADABS*)[11] was applied to all data. Structural refinements were carried out using *SHELXL-97*.[9] The structure of **1** was refined as a racemic twin in the space group P1. The BASF value was refined to 0.36672. The carbon atoms in one of the phenyl rings (C21 - C26) were restrained so that their U_{ij} components approximate to isotropic behavior. Some of the phenyl rings were slightly dynamically disordered by rotation of the ring. Because of this the $U_{eq(max)}/U_{eq(min)}$ ratio remained relatively large. No satisfactory disorder model could be found to improve this ratio. In **5** dichloromethane of crystallization was partially lost and therefore CH_2Cl_2 molecules, including the guest molecule, were refined with the total occupancies 0.5. Furthermore, one of the chlorine atoms in one of the CH_2Cl_2 molecules was disordered over two sites with occupancies 0.25. The chlorine carbon-distances were restrained in all solvent molecules. Also, all heavy atoms of the solvent molecules were restrained so that their U_{ij} components approximate to isotropic behavior. For both **1** and **5** hydrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with C-H = 0.95-0.99 Å and U_{iso} = 1.2-1.5 U_{eq}(parent atom). The crystallographic details are summarized in Table S1.

Table S1. Crystal data and structure refinement for **1** and **5**.

Identification code	**1**	**5**
Empirical formula	$C_{152}H_{142}Au_8F_{12}N_2O_5P_{10}$	$C_{155}H_{112}Au_8Cl_6F_{12}O_2P_{10}$
Formula weight	4190.11	4332.58
Temperature	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic
Space group	P 1	C2/c
Unit cell dimensions	a = 15.7044(2) Å α= 69.282(7)° b = 15.9465(2) Å β= 75.031(7)° c = 17.4245(2) Å γ = 63.004(6)°	a = 20.8064(4) Å α= 90° b = 20.5555(5) Å β= 91.8480(10)° c = 36.4529(9) Å γ = 90°
Volume	3611.6(2) $Å^3$	15582.3(6) $Å^3$
Z	1	4
Density (calculated)	1.927 Mg/m^3	1.847 Mg/m^3
Absorption coefficient	8.272 mm^{-1}	7.770 mm^{-1}
F(000)	1998	8200
Crystal size	0.44 x 0.34 x 0.30 mm^3	0.34 x 0.32 x 0.18 mm^3
Theta range for data collection	2.38 to 30.05°.	1.77 to 29.62°.
Index ranges	-22<=h<=22, -22<=k<=22, -24<=l<=24	-25<=h<=28, -27<=k<=28, -49<=l<=50
Reflections collected	73258	82208
Independent reflections	38565 [R(int) = 0.0325]	21720 [R(int) = 0.0433]
Completeness to theta = 29.62°	98.7 %	98.9 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.1933 and 0.1230	0.3417 and 0.1793
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	38565 / 39 / 1711	21720 / 42 / 921
Goodness-of-fit on F^2	1.043	1.070
Final R indices [I>2sigma(I)]	R1 = 0.0258, wR2 = 0.0552	R1 = 0.0429, wR2 = 0.0884
R indices (all data)	R1 = 0.0308, wR2 = 0.0575	R1 = 0.0663, wR2 = 0.0955
Largest diff. peak and hole	1.099 and -2.447 $e.Å^{-3}$	3.050 and -1.814 $e.Å^{-3}$

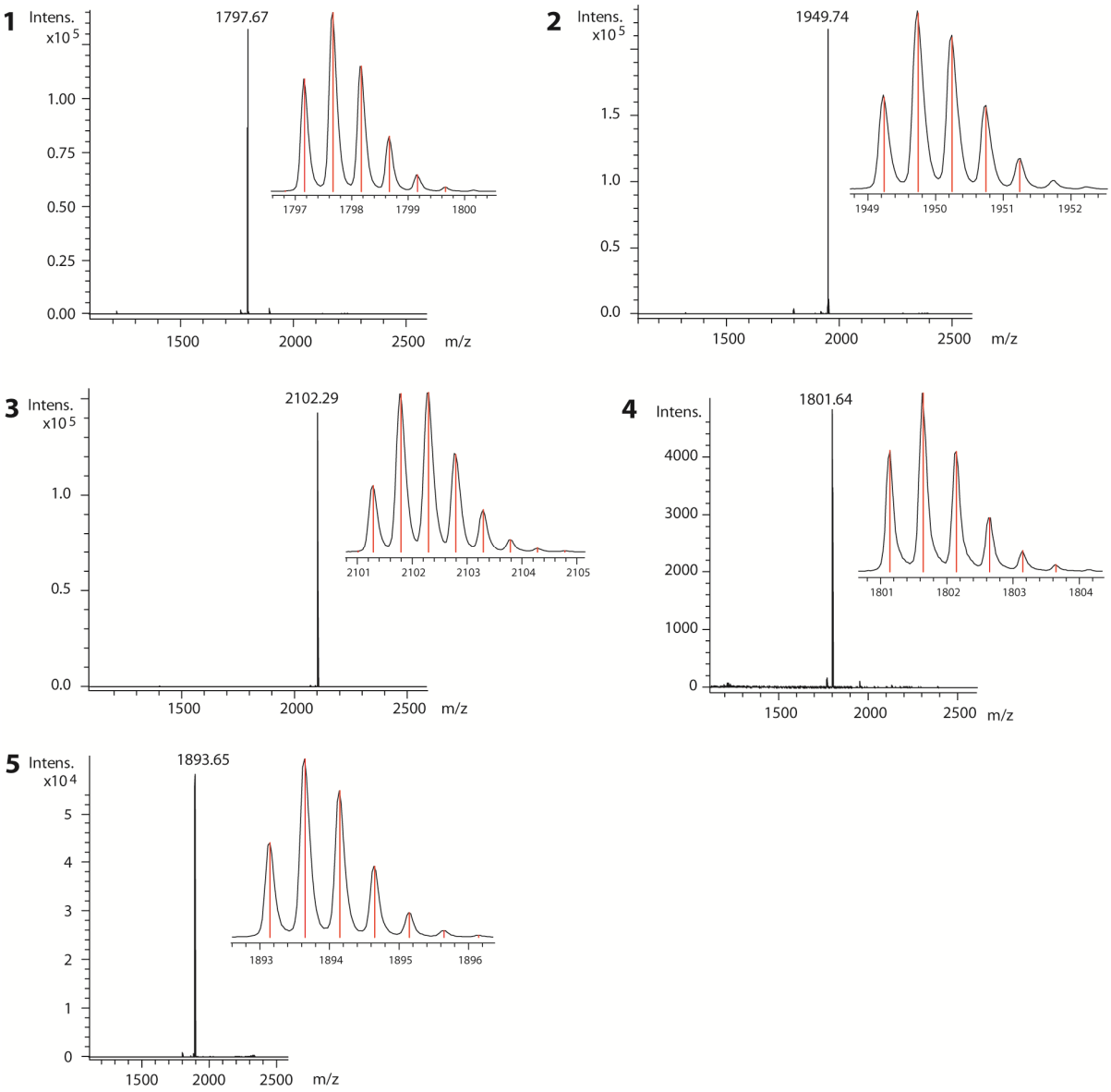

Figure S1. ESI-MS spectra for the dicationic complexes **1**–**5**. Red – calculated pattern.

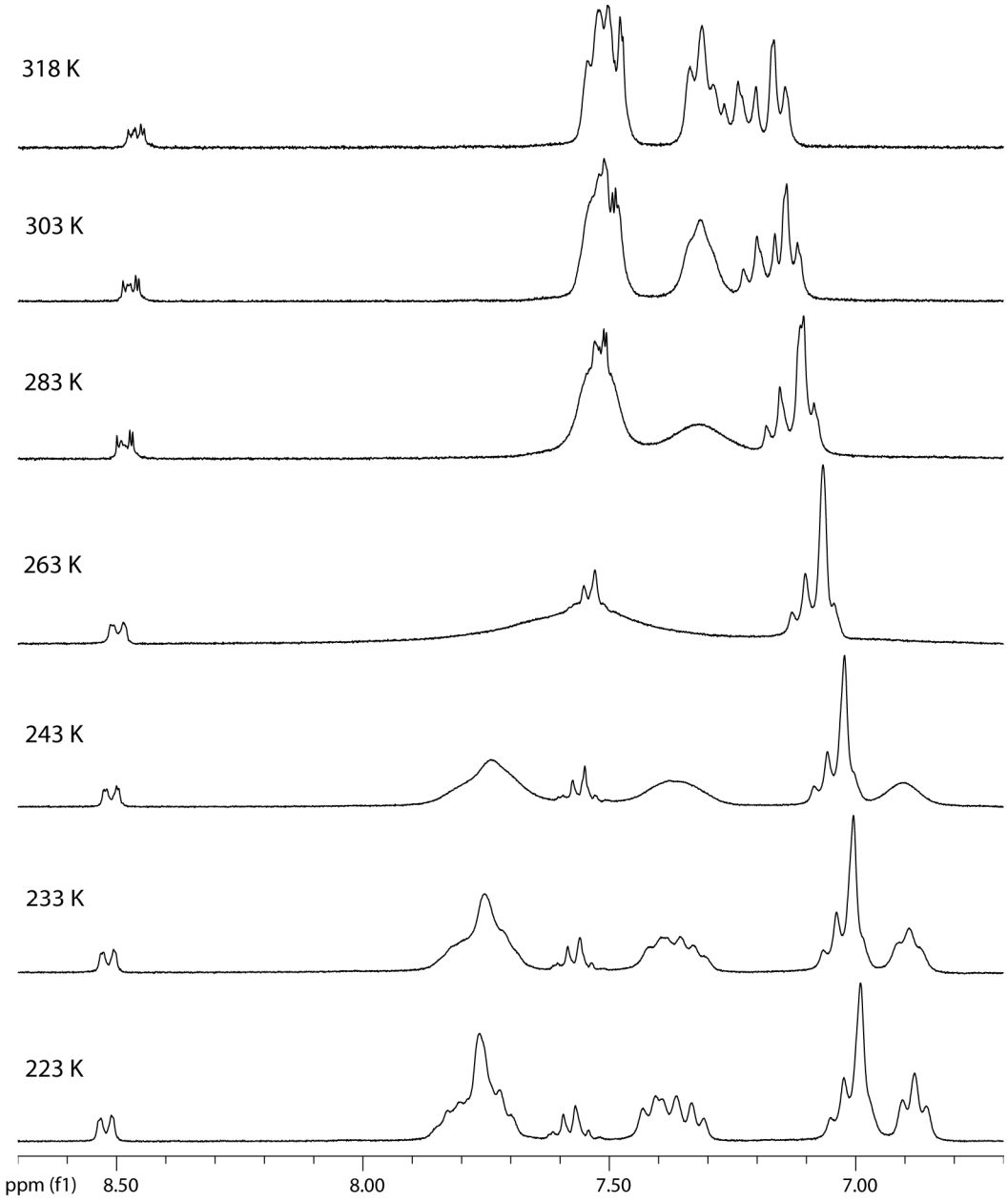

Figure S2. VT ^{1}H NMR spectra of **2**, acetone-d_6, 300 MHz.

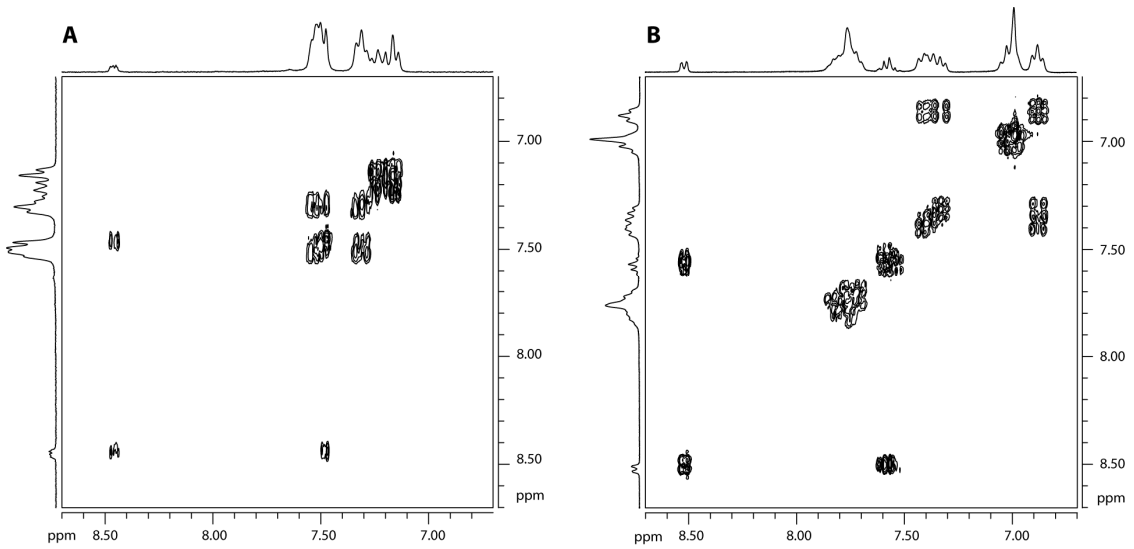

Figure S3. ^{1}H-^{1}H COSY NMR spectra of **2**, **A** 318 K, **B** 223 K, acetone-d_6, 300 MHz.

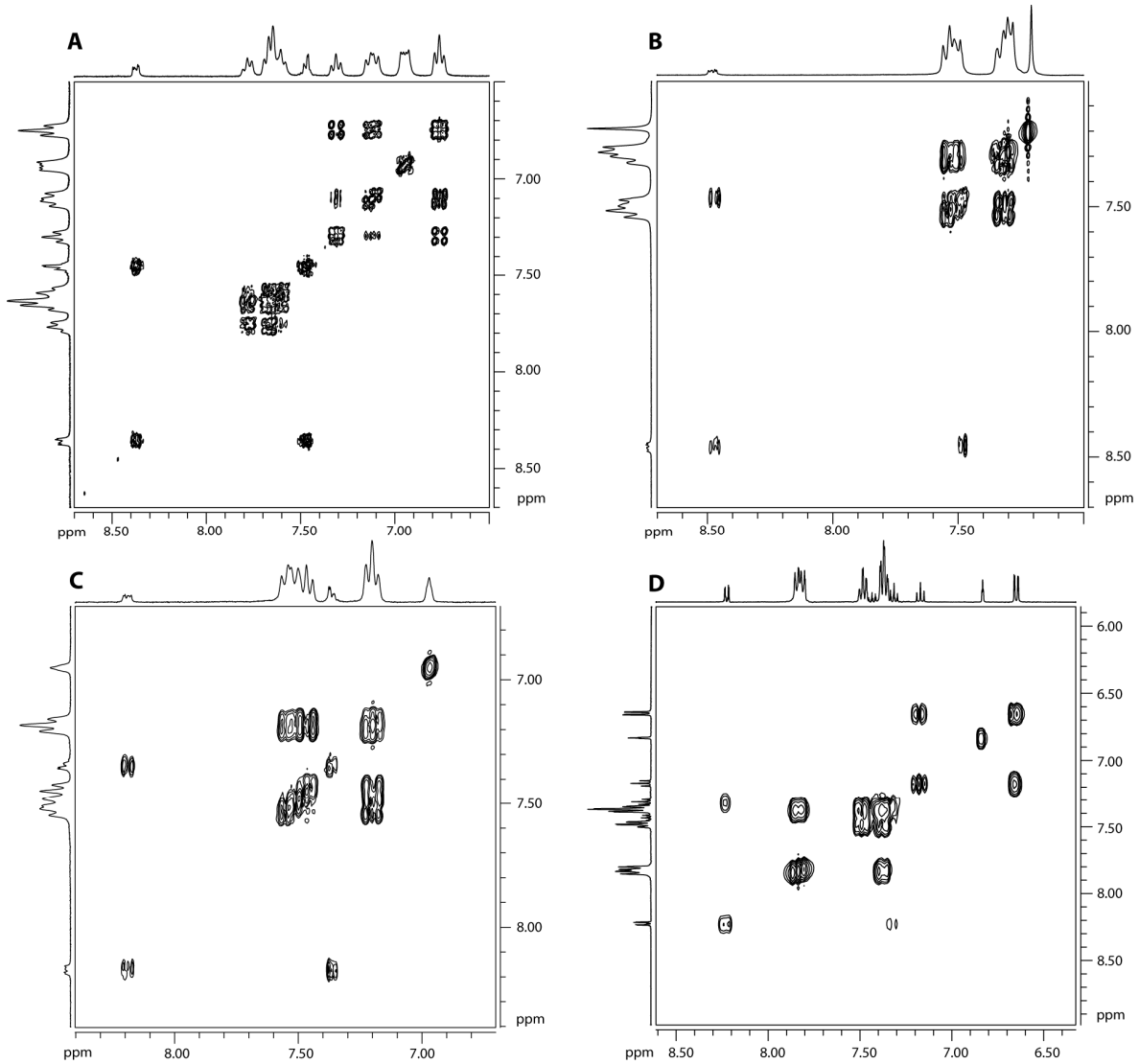

Figure S4. ^{1}H-^{1}H COSY NMR spectra of **1**, **A** 263 K, acetone-d_6; **3**, **B** 318 K, acetone-d_6; **4**, **C** 323 K, acetonitrile-d_3; **5**, **D** 298 K, CD_2Cl_2.

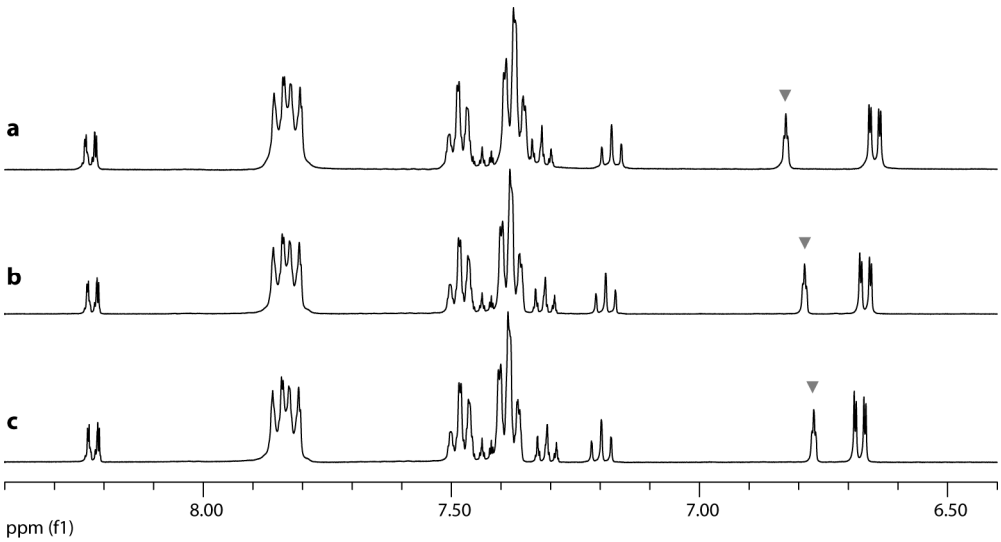

Figure S5. ^{1}H NMR changes of **5** upon increase of CS_2 concentration, acetone-d_6, 400 MHz, 298 K (**a** – solution of **5**, **b** – 3 drops of CS_2, **c** – 6 drops). ▼ denote signals corresponding to H^{i} protons.

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