Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supplementary materials

Sky-blue thermally activated delayed fluorescence (TADF) based on Ag(I) complexes: strong solvation-induced emission enhancement

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§1. X-Ray crystallography

The X-ray data and the details of the refinement for **1**·$CHCl_3$ and **2** are summarized in Table S1. The data were collected on a Bruker Kappa Apex II CCD diffractometer using ϕ,ω-scans of narrow (0.5°) frames with MoKα radiation (λ = 0.71073 Å) and a graphite monochromator. The structures were solved by direct method and refined by a full matrix least-squares anisotropic-isotropic (for H atoms) procedure using *SHELXL-2014/7* program set.[1] Absorption corrections were applied using the empirical multiscan method with the *SADABS* program.[2] The positions of the hydrogen atoms were calculated with the riding model.

Table S1. Crystal data and structure refinement for **1**·$CHCl_3$ and **2**.

	1·$CHCl_3$	**2**
CCDC	1529534	1529535
Chemical formula	$C_{48}H_{37}Ag_2N_{11}P_3S_2Cl_3$	$C_{46}H_{36}AgN_{10}P_3S$
M_r	1247.01	961.69
Crystal system, space group	Monoclinic, $P2_1/n$	Orthorhombic, $P2_12_12_1$
Temperature (K)	296	200
a, *b*, *c* (Å)	13.3901(4), 16.8437(4), 22.8930(7)	10.8909(2), 15.2773(4), 26.0826(6)
α, β, γ (°)	90, 90.552(1), 90	90, 90, 90
V (Å^3)	5163.0(3)	4339.72(17)
μ (mm^{-1})	1.13	0.67
Crystal size (mm)	0.60 × 0.30 × 0.10	0.50 × 0.30 × 0.10
T_{min}, T_{max}	0.634, 0.746	0.684, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	67667, 11862, 8461	55914, 11712, 10296
R_{int}	0.055	0.045
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.650	0.704
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.047, 0.140, 1.04	0.031, 0.069, 1.01
No. of reflections	11862	11712
No. of parameters	687	550
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.13, −0.89	0.64, −0.58

[1] G. M. Sheldrick, *Acta Crystallogr., Sect. C: Struct. Chem.*, **2015**, *71*, 3–8.
[2] *SADABS*, v. 2008-1, Bruker AXS, Madison, WI, USA, 2008.

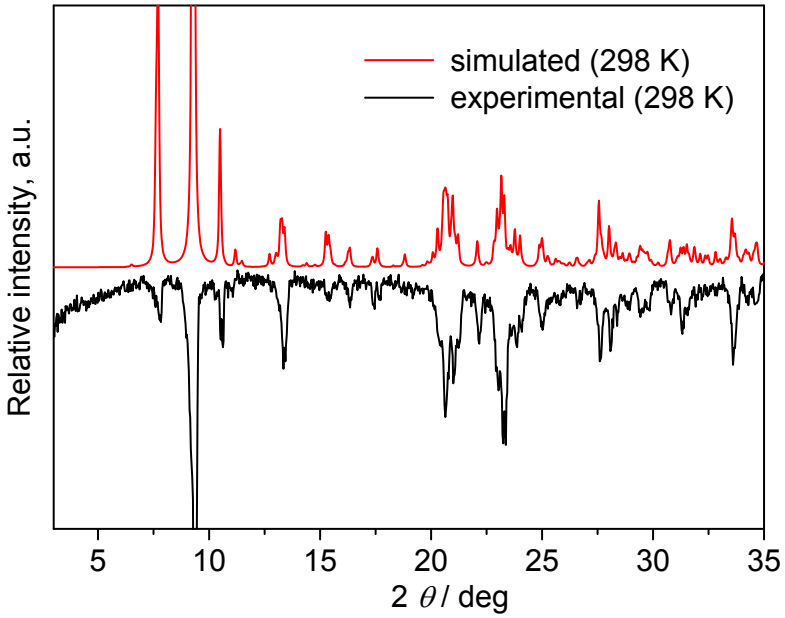


Figure S1. Experimental and simulated X-ray powder patterns for **1**·$CHCl_3$.

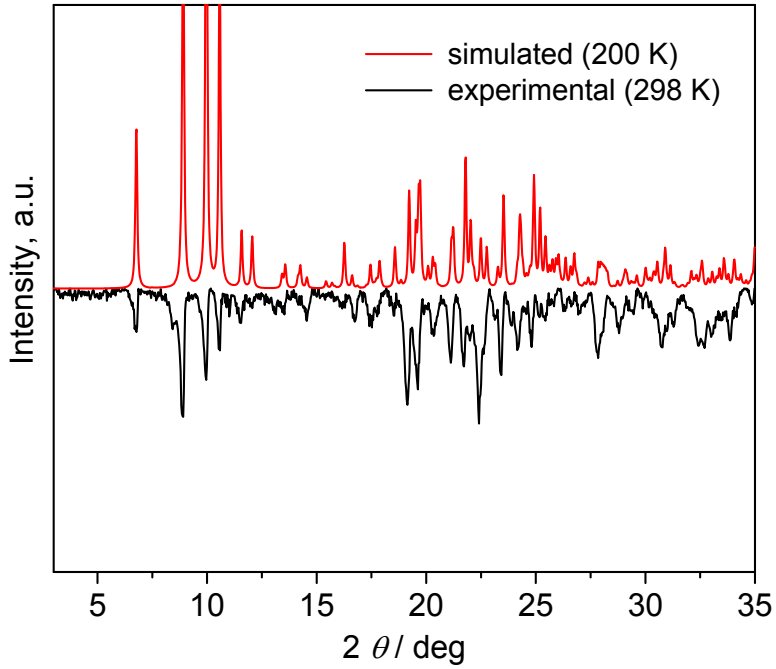


Figure S2. Experimental and simulated X-ray powder patterns for **2**.

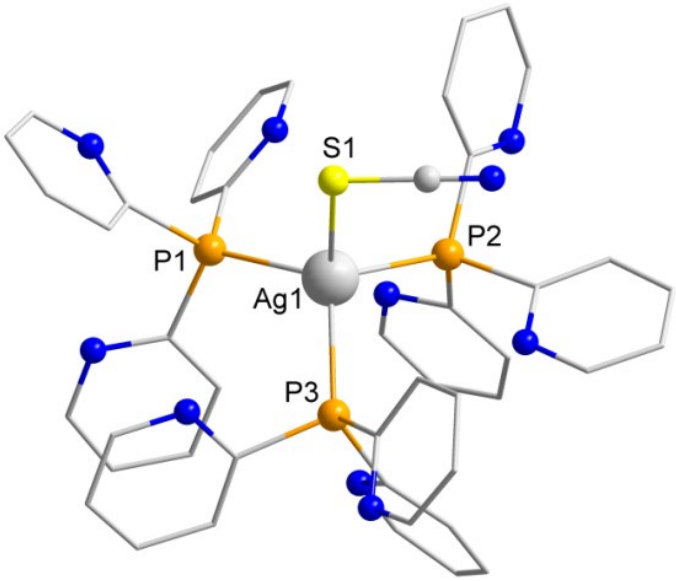


Figure S3. Molecular structure of **2** determined by X-ray diffraction analysis. Selected distances (Å): Ag1–P1 2.4950(5), Ag1–P2 2.5076(5), Ag1–P3 2.5185(5), Ag1–S1 2.6160(5).

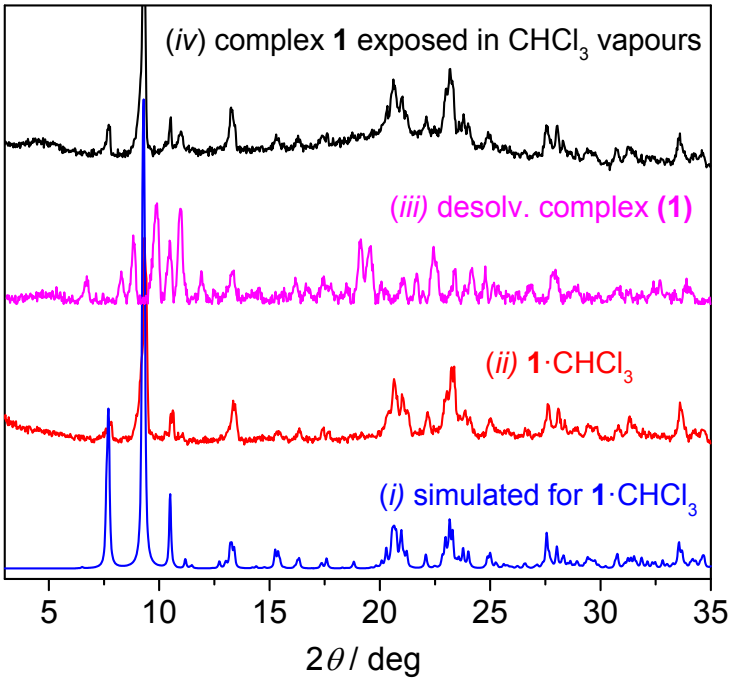


Figure S4. XRPD monitoring of the reversible **1**·$CHCl_3$ ↔ **1** process: (*i*) simulated XRDP pattern for **1**·$CHCl_3$; (*ii*) experimental XRDP pattern for **1**·$CHCl_3$; (*iii*) XRDP pattern for the parent complex **1**,obtained by heating of **1**·$CHCl_3$; (*iv*) XRDP pattern for the **1**·$CHCl_3$, obtained after exposing of the parent complex **1** in $CHCl_3$ vapours (room temperature, a closed vial contacting ~ 0.2–0.3 mL chloroform).

§2. Thermogravimetric data

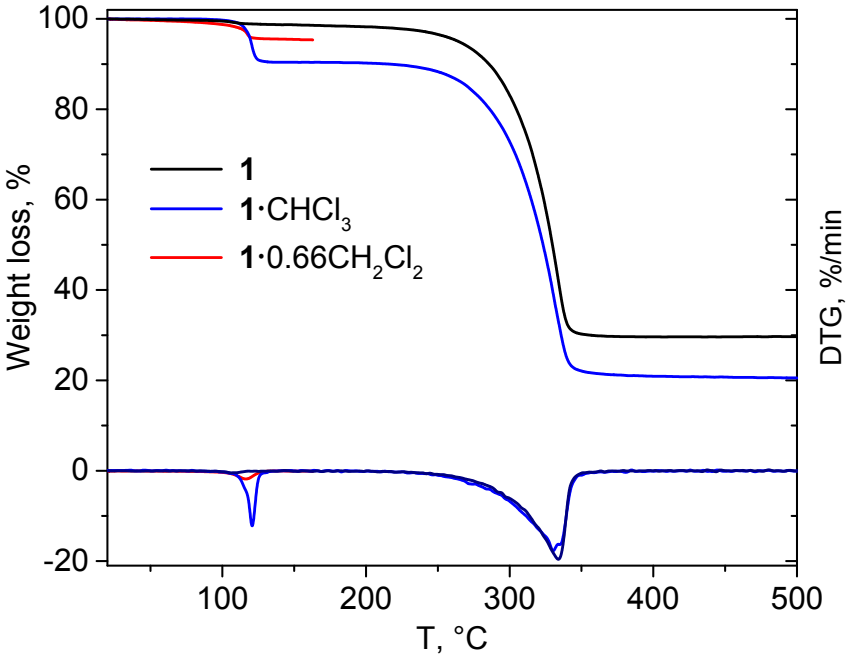


Figure S5. TGA&DTG curves for **1** as well as **1**·$CHCl_3$ and **1**·0.66CH_2Cl_2 in the temperature range of 25–500 °C.

§3. FT-IR spectra

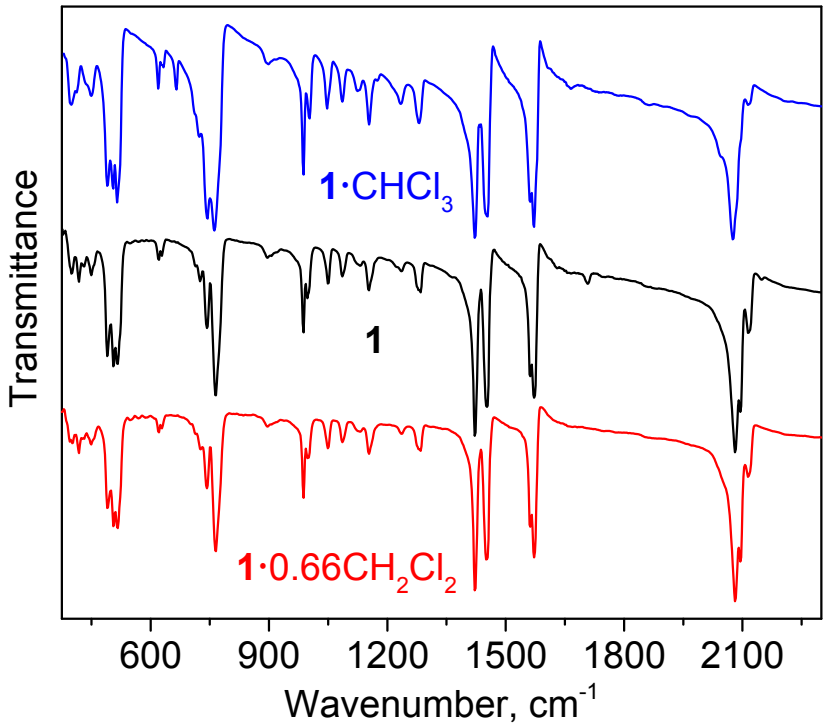


Figure S6. FT-IR spectra of **1** as well as **1**·$CHCl_3$ and **1**·0.66CH_2Cl_2, in the range of 400–2300 cm^{-1}.

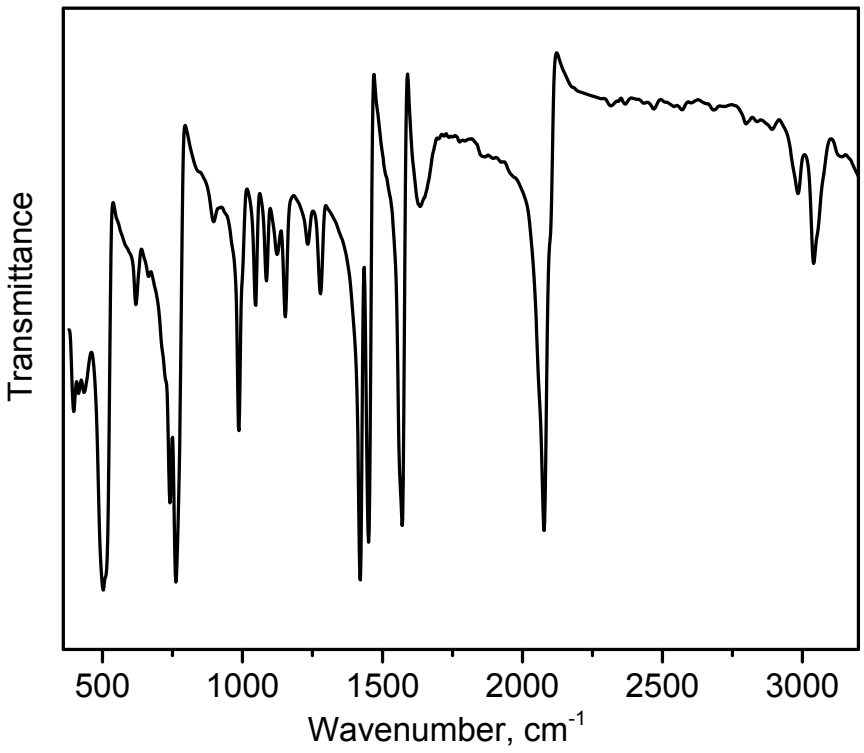


Figure S7. FT-IR spectrum of **1**.

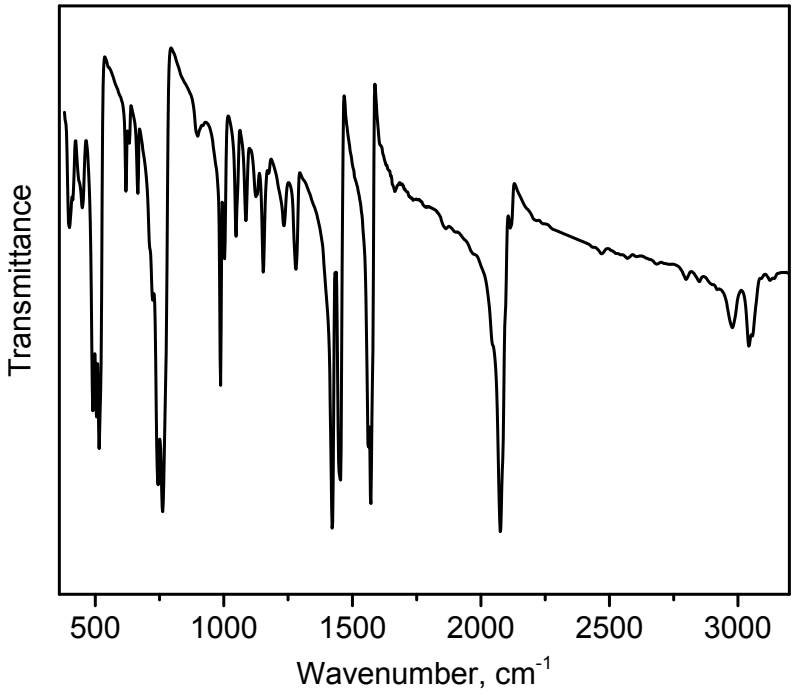


Figure S8. FT-IR spectrum of **1**·$CHCl_3$.

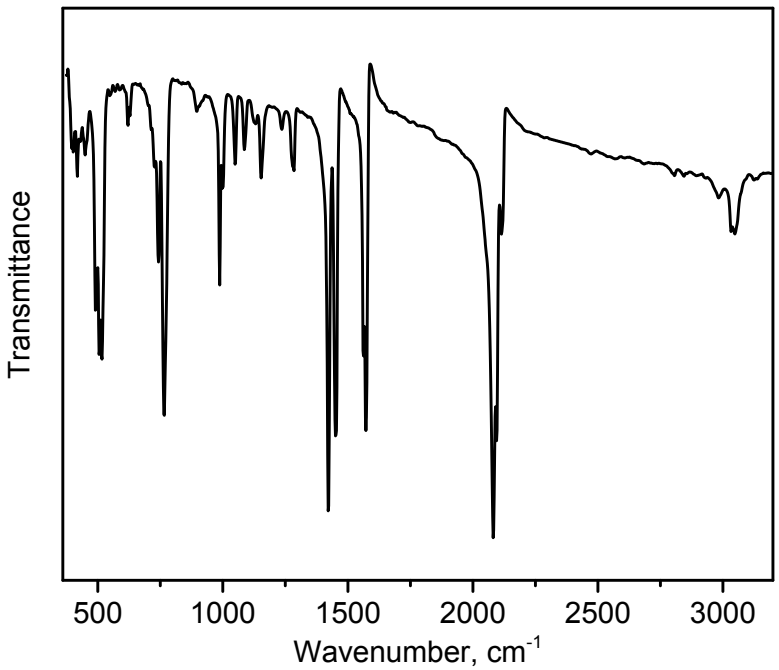


Figure S9. FT-IR spectrum of **1**·0.66CH_2Cl_2.

§4. NMR spectra

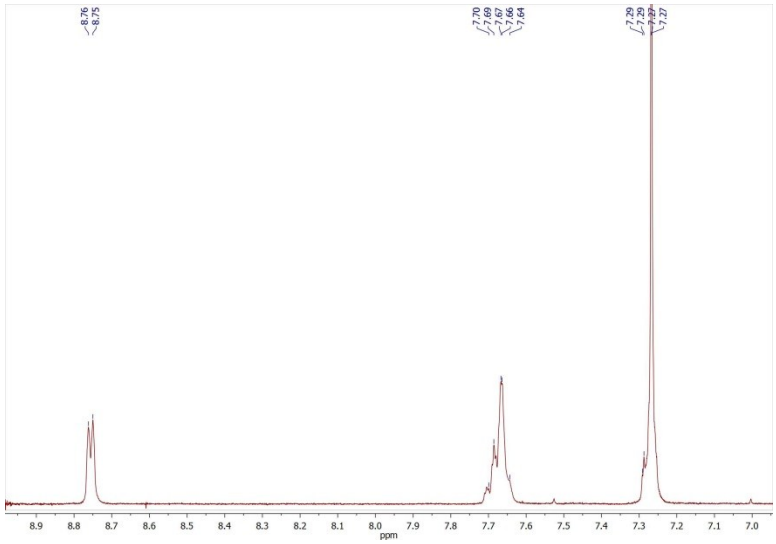


Figure S10. ^1H NMR spectrum of **1** ($CDCl_3$).

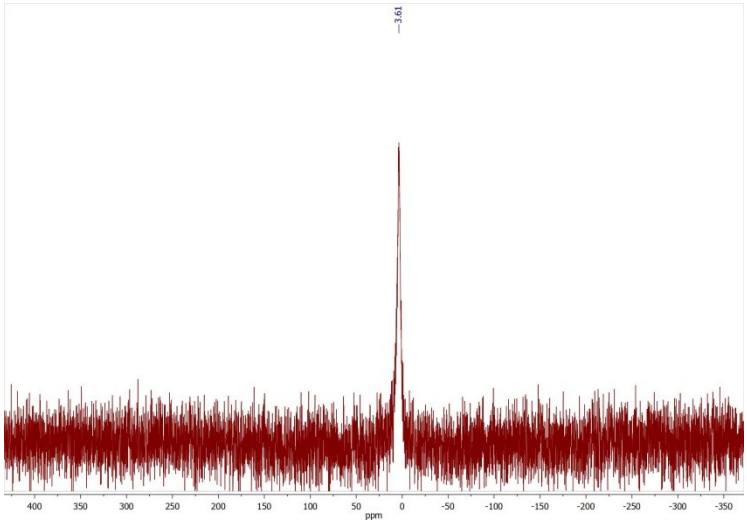


Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum of **1** ($CDCl_3$).

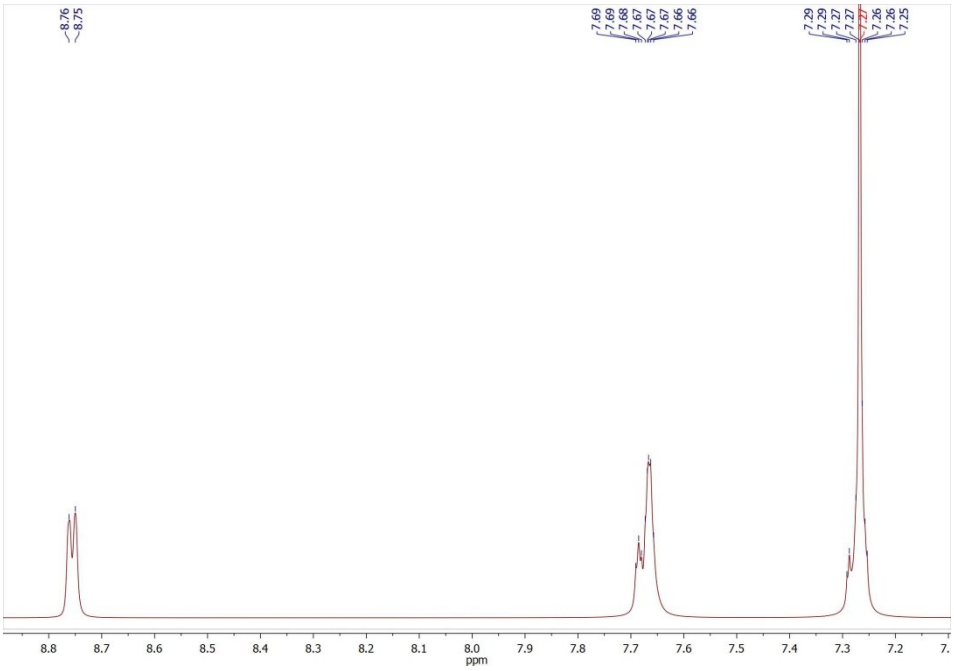


Figure S12. ^{1}H NMR spectrum of **1**·$CHCl_3$ ($CDCl_3$).

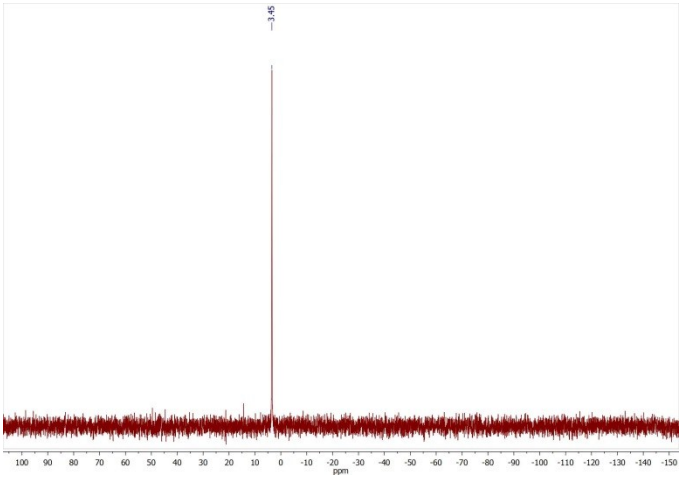


Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of **1**·$CHCl_3$ ($CDCl_3$).

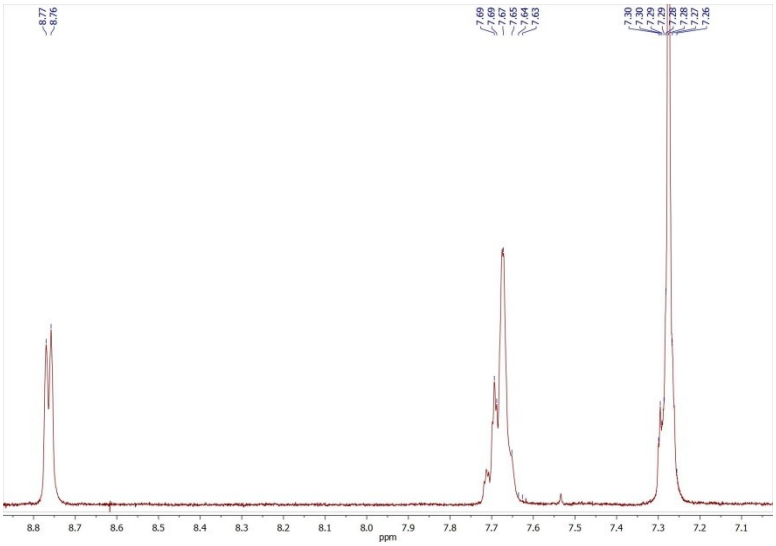


Figure S14. ^{1}H NMR spectrum of **1**·$0.66CH_2Cl_2$ ($CDCl_3$).

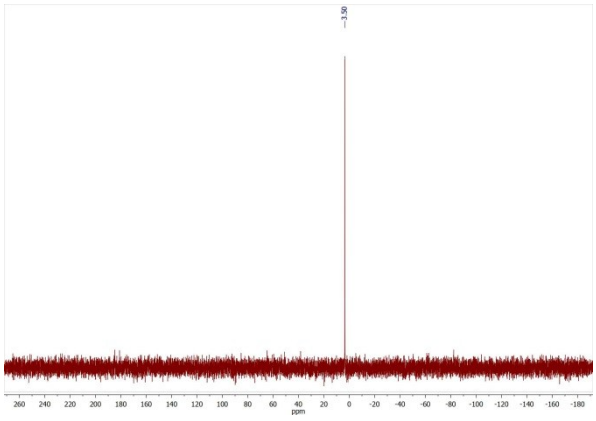


Figure S15. $^{31}P\{^{1}H\}$ NMR spectrum of **1**·$0.66CH_2Cl_2$ ($CDCl_3$).

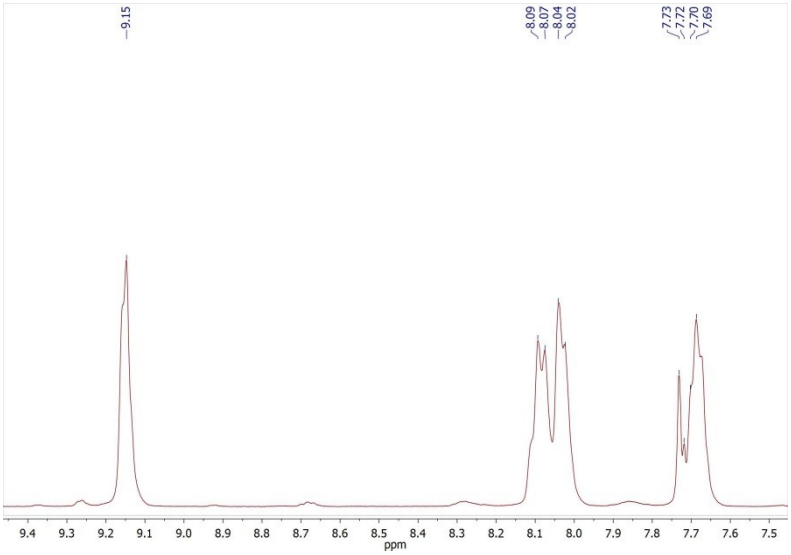


Figure S16. ^{1}H NMR spectrum of **2** (CD_3CN).

§5. Photophysical data

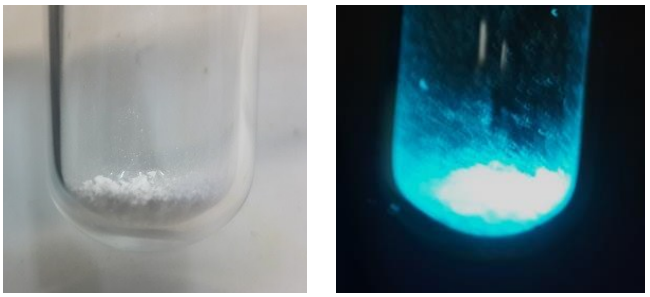


Figure S17. Photographs of the powder **1**·CH_2Cl_2 under ambient light (*left*) and UV-light (*right*).

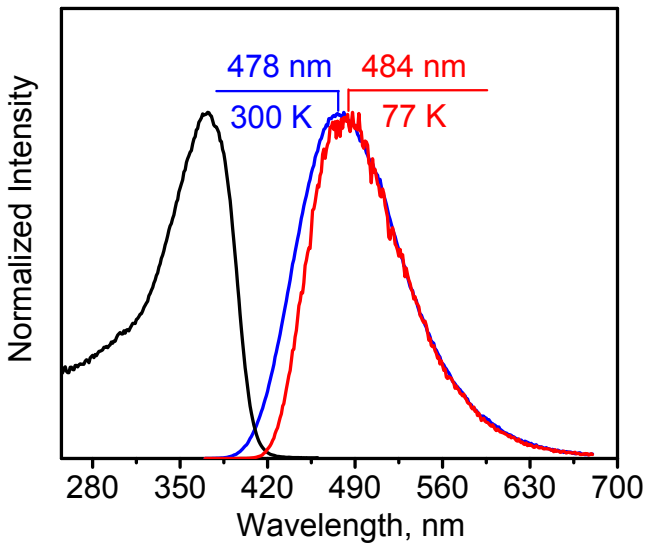


Figure S18. Emission spectra of the powder **1**·$CHCl_3$ recorded at 300 and 77 K (λ_{ex} = 350 nm), and excitation spectrum recorded at 300 K (λ_{det} = 380 nm).

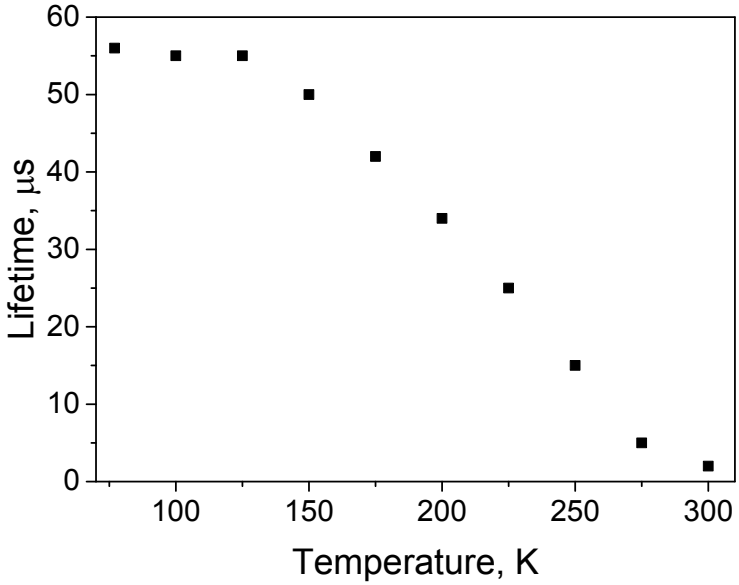


Figure S19. Temperature dependence of the emission lifetimes for the **1** (λ_{ex} = 350 nm and λ_{det} = 470 nm).

§6. Computational details

The DFT (density functional theory) computations of **1** have been performed using Gaussian 09 D01 program.[3] Calculations have been carried out utilizing the def2-SVP[4],[5] basis set combined with the M064[6] functional for geometry optimizations and with the M062X[6] functional for calculations of time-dependent wavefunctions (TD-DFT), all under gas phase conditions. The geometry of the **1** was optimized for the ground state (S_0) and the lowest triplet state (T_1) electronic configurations.

Table S2. Excited state properties of **1** obtained from TD-DFT calculations (M062X/def2-SVP) carried out for the geometry of the lowest excited triplet state (T_1).

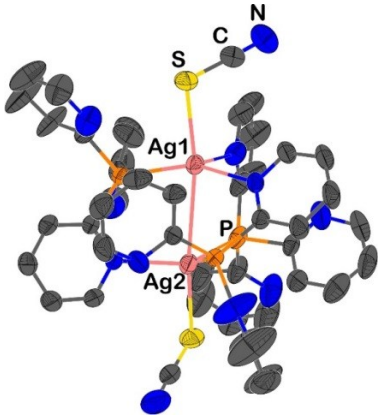
E, eV	*f*	Transition (coefficient)	Character
2.90	(triplet)	HOMO→LUMO (0.65)	$(M_{Ag1}+L_{thcy1})L_{py1}CT$
3.46	(triplet)	HOMO–1→LUMO (0.53) HOMO–4→LUMO (0.24) HOMO→LUMO+1 (-0.19) HOMO–2→LUMO (0.12) HOMO–5→LUMO (0.12)	$L_{thcy1}L_{py1}CT$

[3] M. J. Frisch et al. *Gaussian 09*, Gaussian, Inc.: Wallingford, CT, USA, 2009.
[4] F. Weigend, *Phys. Chem. Chem. Phys.* 2006, **8**, 1057–1065.
[5] F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005**, 7**, 3297–3305.
[6] Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215–241.

3.49	(triplet)	HOMO→LUMO+1 (0.50) HOMO→LUMO+4 (0.20) HOMO→LUMO+3 (-0.16) HOMO–1→LUMO (0.15) HOMO–5→LUMO+1 (0.13) HOMO–4→LUMO+1 (0.12)	$(M_{Ag1}+L_{thcy})L_{py}CT$
3.53	(triplet)	HOMO→LUMO+3 (0.48) HOMO→LUMO+1 (0.24) HOMO→LUMO+4 (-0.22) HOMO→LUMO+2 (0.19) HOMO→LUMO+5 (0.18)	$(M_{Ag1}+L_{thcy1})L_{py}CT$
3.56	(triplet)	HOMO–1→LUMO (0.41) HOMO–4→LUMO (-0.34) HOMO–2→LUMO (-0.18) HOMO–5→LUMO (-0.16) HOMO–7→LUMO (0.15)	$(M_{Ag2}+L_{thcy1})L_{py1}CT$
3.02	0.0165	HOMO→LUMO (0.67)	$(M_{Ag1}+L_{thcy1})L_{py1}CT$
3.51	0.0004	HOMO–1→LUMO (0.68)	$L_{thcy1}L_{py1}CT$
3.63	0.0396	HOMO→LUMO+3 (0.48) HOMO→LUMO+1 (-0.30) HOMO→LUMO+4 (-0.29) HOMO→LUMO+5 (0.20)	$(M_{Ag1}+L_{thcy1})L_{py}CT$
3.71	0.0238	HOMO→LUMO+1 (0.59) HOMO→LUMO+3 (0.30) HOMO→LUMO+2 (0.10)	$(M_{Ag1}+L_{thcy1})L_{py}CT$
3.79	0.0124	HOMO→LUMO+2 (0.66)	$(M_{Ag1}+L_{thcy1})L_{py}CT$

a) thcy1 – thiocyanate anion coordinated to Ag1
b) py1 – pyridine ring coordinated to Ag1
c) py2 – pyridine ring coordinated to Ag2
d) py – not coordinated pyridine rings.

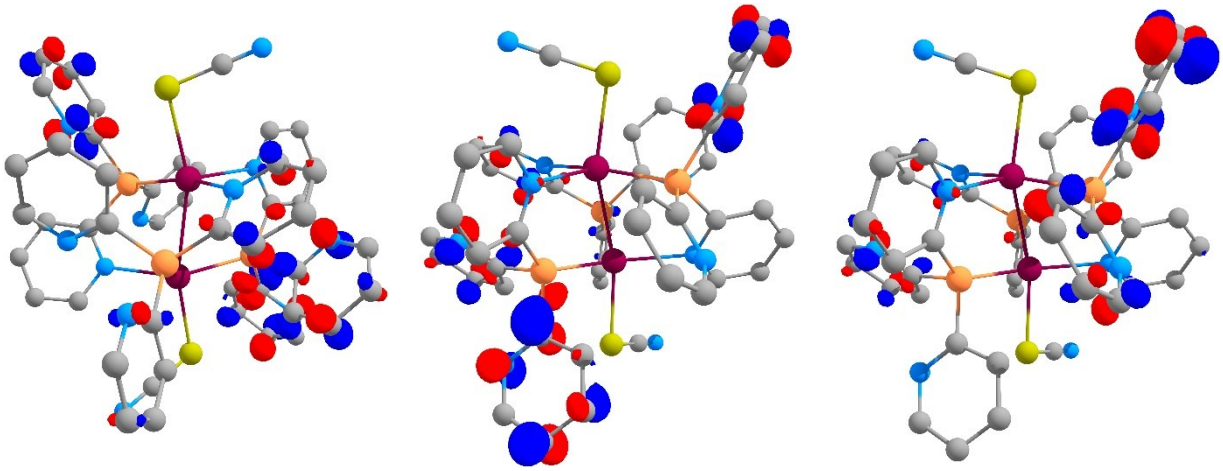
Table S3. Orbital energies and compositions of **1** resulting from Mulliken population analysis in the relaxed geometry of the lowest excited triplet state (T_1) calculated at M062X/def2-SVP level of the theory.



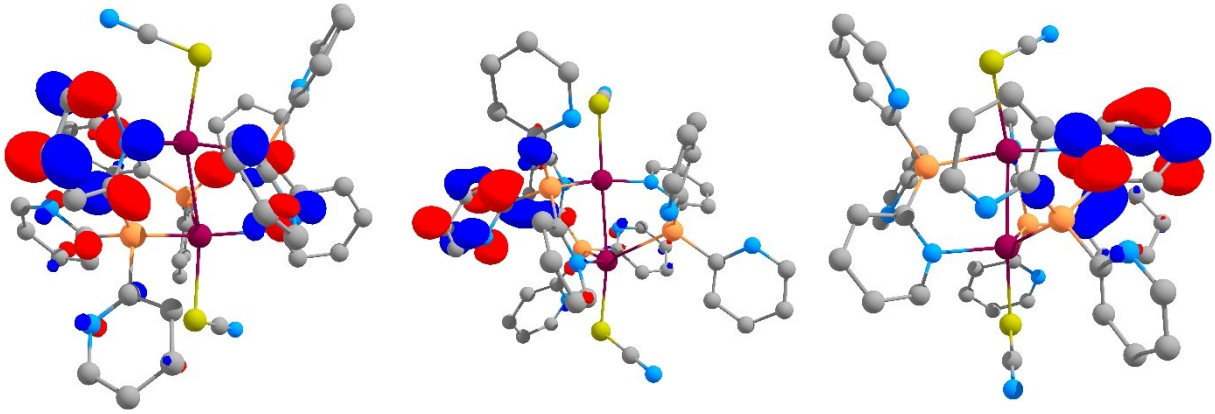
Orbital	Energy, (eV)	Contributions, (%)								
		Ag1	thcy1[a]	py1[c]	py1'[d]	Ag2	thcy2[b]	py2[e]	py[f]	P
LUMO+4	-0.45	0	0	2	17	2	0	1	71	7
LUMO+3	-0.50	8	0	0	7	-1	0	6	74	7
LUMO+2	0.54	0	0	59	4	0	0	0	30	5
LUMO+1	-0.59	1	0	2	0	0	0	9	80	7
LUMO	-1.14	4	0	1	71	-1	0	1	16	7
HOMO	-5.96	12	53	1	4	5	8	2	4	12
HOMO−1	-6.25	4	93	0	0	0	0	0	1	0
HOMO−2	-6.55	0	0	0	0	4	90	1	3	1
HOMO−3	-6.57	3	18	1	0	1	62	1	2	5
HOMO−4	-7.44	2	1	3	7	17	4	2	26	38

e) thcy1 – thiocyanate anion coordinated to Ag1
f) thcy2 – thiocyanate anion coordinated to Ag2
g) py1 – pyridine ring coordinated to Ag1
h) py1' – second pyridine ring coordinated to Ag1
i) py2 – pyridine ring coordinated to Ag2
j) py – not coordinated pyridine rings.

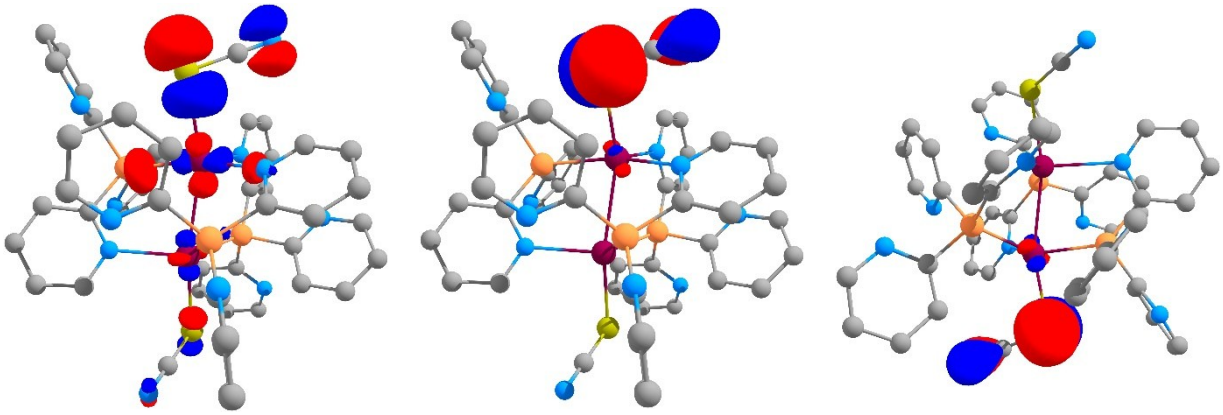
Figure S20. Iso-surface contour plots (iso-value = 0.05) of the selected orbital of **1** in the lowest triplet state (T_1) geometry calculated at M062X/def2-SVP level of the theory.



LUMO+5 **LUMO+4** **LUMO+3**



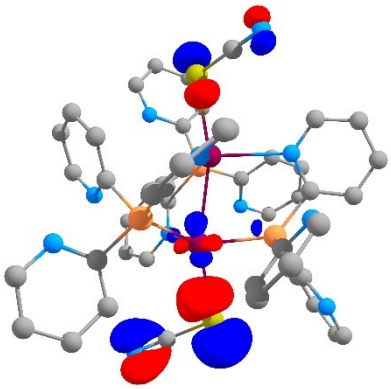
LUMO+2 **LUMO+1** **LUMO**



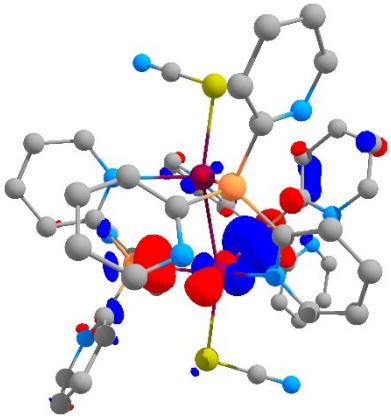
HOMO

HOMO–1

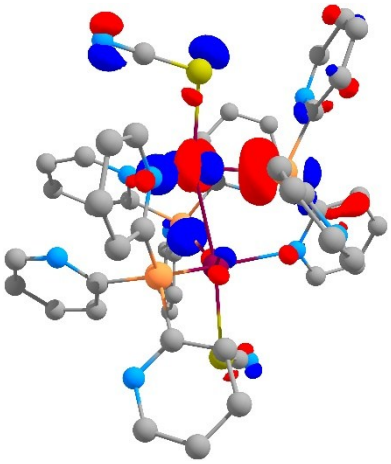
HOMO–2



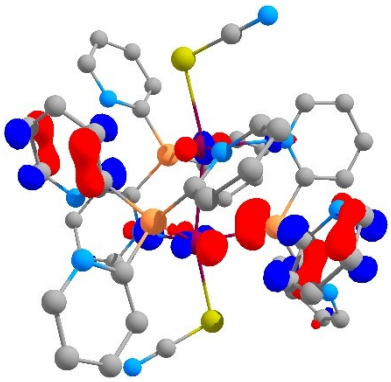
HOMO–3



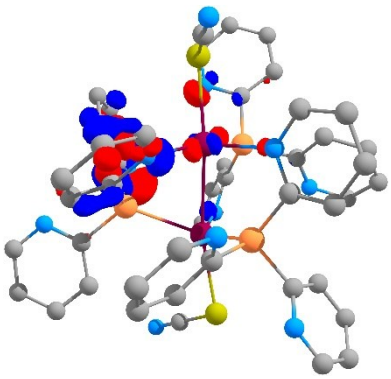
HOMO–4



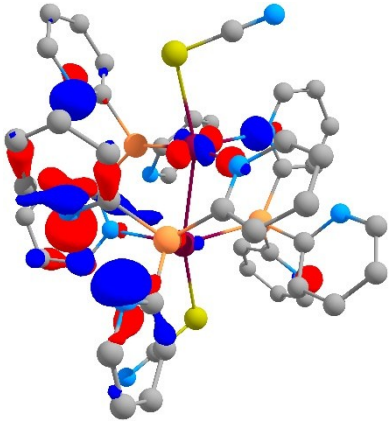
HOMO–5



HOMO–6



HOMO–7



HOMO–8

Table S4. Optimized geometries of **1** calculated at M062X/def2-SVP level of the theory.

Ground state (S_0)				Lowest triplet state (T_1)			
Ag	-1.125957000	0.466809000	1.272622000	Ag	0.934522000	-0.096574000	1.139606000
Ag	0.887053000	-0.485936000	-1.148035000	Ag	-0.893832000	0.252474000	-1.100285000
P	0.457008000	-2.407519000	0.485566000	P	-0.863582000	2.349368000	0.342549000
P	-2.261797000	0.737641000	-0.966675000	P	2.432525000	-0.471012000	-0.827485000
P	1.987133000	1.512860000	0.098341000	P	-1.687336000	-1.851179000	0.082504000
S	-3.238504000	0.762758000	2.790540000	S	3.073628000	0.130064000	2.667550000
S	2.720062000	-0.291028000	-3.049441000	S	-2.791783000	-0.134001000	-2.863339000
C	2.732279000	-1.859267000	-3.625511000	C	-2.893812000	1.370249000	-3.585105000
N	2.718722000	-2.965181000	-4.023274000	N	-2.957680000	2.425216000	-4.096672000
N	-1.774212000	1.488131000	5.122375000	N	2.106657000	-1.157546000	5.005911000

C	-2.392917000	1.180592000	4.171408000	C	2.500895000	-0.606750000	4.045995000
N	0.422247000	-0.792136000	2.600988000	N	-0.500500000	0.831693000	2.513481000
N	-0.976415000	-0.892626000	-2.637749000	N	0.884301000	0.714615000	-2.664574000
N	0.167337000	2.544041000	1.826936000	N	0.292203000	-2.540964000	1.792609000
C	1.227835000	-4.034327000	0.093603000	C	-1.977669000	3.747651000	-0.084032000
N	1.077664000	-5.057508000	0.940013000	N	-1.688992000	4.940043000	0.442384000
C	1.871573000	-4.146916000	-1.136517000	C	-3.053129000	3.525895000	-0.943275000
H	1.975075000	-3.292563000	-1.810733000	H	-3.236255000	2.531222000	-1.359362000
C	1.572542000	-6.235734000	0.578122000	C	-2.475736000	5.962957000	0.126329000
H	1.443200000	-7.061936000	1.289873000	H	-2.223359000	6.933773000	0.573322000
C	2.224285000	-6.457456000	-0.638959000	C	-3.569135000	5.852440000	-0.735437000
H	2.599344000	-7.454353000	-0.885702000	H	-4.170140000	6.733229000	-0.976746000
C	2.376956000	-5.389441000	-1.513747000	C	-3.860044000	4.608272000	-1.284191000
H	2.870607000	-5.487633000	-2.485364000	H	-4.686826000	4.473949000	-1.987071000
C	0.876702000	-2.001019000	2.229336000	C	-1.211493000	1.936267000	2.057498000
C	1.617476000	-2.810805000	3.087706000	C	-2.188300000	2.539953000	2.855910000
H	1.934052000	-3.803538000	2.760961000	H	-2.723815000	3.412353000	2.467718000
C	1.888042000	-2.338203000	4.371256000	C	-2.465604000	2.040616000	4.118749000
H	2.461416000	-2.953335000	5.071293000	H	-3.214336000	2.518202000	4.756174000
C	1.408388000	-1.092553000	4.754028000	C	-1.737553000	0.902084000	4.566835000
H	1.584452000	-0.691256000	5.754508000	H	-1.898993000	0.473962000	5.558984000
C	0.673281000	-0.347154000	3.833479000	C	-0.788007000	0.345414000	3.741787000
H	0.255864000	0.628074000	4.109931000	H	-0.201384000	-0.520775000	4.073516000
C	-1.327850000	-2.878432000	0.573641000	C	0.793056000	3.172274000	0.333163000
N	-1.787972000	-3.319567000	-0.598597000	N	1.277740000	3.414702000	-0.886543000
C	-2.132181000	-2.731082000	1.704956000	C	1.485388000	3.471900000	1.508035000
H	-1.730187000	-2.353523000	2.648748000	H	1.043851000	3.243399000	2.482629000
C	-3.480939000	-3.058432000	1.593433000	C	2.741435000	4.060611000	1.394347000
H	-4.144469000	-2.925121000	2.453009000	H	3.319662000	4.301941000	2.291531000
C	-3.961743000	-3.536157000	0.380513000	C	3.240693000	4.340945000	0.126988000
H	-5.012947000	-3.807588000	0.251973000	H	4.217555000	4.813880000	-0.008180000
C	-3.070895000	-3.651191000	-0.686240000	C	2.467531000	3.997368000	-0.981900000
H	-3.416373000	-4.021735000	-1.660635000	H	2.836259000	4.199605000	-1.996974000
C	-4.059580000	0.907741000	-0.612362000	C	4.192619000	-0.171153000	-0.412418000
N	-4.585540000	-0.228844000	-0.149485000	N	4.404322000	1.103761000	-0.070506000
C	-4.782150000	2.098533000	-0.697166000	C	5.184137000	-1.151799000	-0.353196000
H	-4.324198000	3.008717000	-1.094224000	H	4.976650000	-2.183361000	-0.651405000
C	-6.102717000	2.097099000	-0.253058000	C	6.446782000	-0.776297000	0.098044000
H	-6.698473000	3.013510000	-0.293070000	H	7.250570000	-1.515098000	0.163479000
C	-6.647654000	0.919661000	0.244822000	C	6.669419000	0.547875000	0.464756000
H	-7.674448000	0.881389000	0.616276000	H	7.642869000	0.878040000	0.834944000
C	-5.845437000	-0.222146000	0.263835000	C	5.612232000	1.452088000	0.351828000
H	-6.243293000	-1.172619000	0.644111000	H	5.748791000	2.505888000	0.628560000
C	-1.776257000	2.355544000	-1.713735000	C	2.324968000	-2.218165000	-1.404017000
N	-1.531872000	2.418967000	-3.021313000	N	2.049218000	-2.440026000	-2.687001000
C	-1.604121000	3.448133000	-0.852620000	C	2.457295000	-3.244467000	-0.461023000
H	-1.805914000	3.339740000	0.219441000	H	2.679029000	-3.006918000	0.585238000
C	-1.107172000	3.574949000	-3.526599000	C	1.892183000	-3.699203000	-3.087475000
H	-0.912246000	3.593630000	-4.607151000	H	1.666181000	-3.849852000	-4.151328000
C	-0.905644000	4.720322000	-2.757203000	C	1.995367000	-4.793244000	-2.228662000
H	-0.549727000	5.643260000	-3.222400000	H	1.848787000	-5.808140000	-2.606717000
C	-1.163444000	4.652240000	-1.389624000	C	2.289559000	-4.557429000	-0.887700000
H	-1.013360000	5.523277000	-0.744375000	H	2.380564000	-5.384918000	-0.177734000
C	-2.196865000	-0.403647000	-2.405686000	C	2.166821000	0.512933000	-2.353695000
C	-3.303324000	-0.757536000	-3.174823000	C	3.216228000	1.011903000	-3.122241000
H	-4.288520000	-0.334192000	-2.963695000	H	4.255072000	0.820776000	-2.842354000
C	-3.116767000	-1.664333000	-4.214705000	C	2.903340000	1.762856000	-4.251742000
H	-3.962683000	-1.967504000	-4.838768000	H	3.700424000	2.172946000	-4.878591000
C	-1.845519000	-2.175381000	-4.450157000	C	1.567158000	1.986822000	-4.564986000
H	-1.658330000	-2.894264000	-5.250746000	H	1.275581000	2.581500000	-5.433306000
C	-0.794664000	-1.755055000	-3.637473000	C	0.585168000	1.439098000	-3.743061000
H	0.223274000	-2.137231000	-3.791374000	H	-0.477812000	1.609178000	-3.953555000
C	2.908199000	2.564573000	-1.113135000	C	-2.521118000	-2.958601000	-1.133676000
N	4.141362000	2.977418000	-0.816219000	N	-3.809908000	-3.246655000	-0.968983000
C	2.270114000	2.879777000	-2.315920000	C	-1.771929000	-3.389332000	-2.234188000
H	1.264447000	2.499009000	-2.526422000	H	-0.722396000	-3.089374000	-2.337875000

C	4.793308000	3.706464000	-1.715852000	C	-4.411483000	-3.972229000	-1.907506000
H	5.809817000	4.023084000	-1.448260000	H	-5.477863000	-4.183477000	-1.755641000
C	4.247270000	4.071817000	-2.947000000	C	-3.755486000	-4.458938000	-3.037772000
H	4.830782000	4.666769000	-3.654141000	H	-4.299753000	-5.047384000	-3.780654000
C	2.955840000	3.653607000	-3.247139000	C	-2.403465000	-4.165517000	-3.197870000
H	2.489064000	3.909763000	-4.203018000	H	-1.852891000	-4.519150000	-4.074765000
C	3.335646000	0.706953000	1.067894000	C	-3.017029000	-1.288775000	1.222611000
C	4.230156000	-0.152115000	0.415630000	C	-3.917661000	-0.305166000	0.791232000
H	4.180296000	-0.289236000	-0.672066000	H	-3.904069000	0.049119000	-0.245856000
N	3.332771000	0.894240000	2.384635000	N	-3.004098000	-1.786118000	2.453689000
C	5.166755000	-0.825618000	1.190254000	C	-4.836818000	0.176961000	1.716135000
H	5.884431000	-1.502991000	0.718415000	H	-5.556485000	0.947971000	1.424876000
C	5.173836000	-0.627831000	2.569777000	C	-4.818321000	-0.324697000	3.013923000
H	5.893666000	-1.139915000	3.213615000	H	-5.513691000	0.041282000	3.773651000
C	4.233783000	0.241859000	3.115827000	C	-3.883711000	-1.311604000	3.331252000
H	4.204776000	0.417927000	4.199614000	H	-3.842574000	-1.731501000	4.344467000
C	1.378339000	2.770520000	1.310540000	C	-0.770771000	-3.035383000	1.155168000
C	2.144980000	3.884936000	1.656974000	C	-1.215129000	-4.347573000	1.333263000
H	3.143162000	4.012741000	1.227422000	H	-2.108939000	-4.702774000	0.812714000
C	1.616990000	4.793508000	2.567824000	C	-0.519126000	-5.165833000	2.216059000
H	2.192537000	5.675156000	2.865102000	H	-0.844352000	-6.196129000	2.387834000
C	0.354913000	4.556732000	3.104206000	C	0.578805000	-4.645348000	2.894564000
H	-0.094368000	5.237589000	3.830727000	H	1.142060000	-5.244548000	3.613751000
C	-0.333329000	3.412722000	2.709939000	C	0.945003000	-3.322815000	2.654421000
H	-1.320889000	3.176236000	3.124651000	H	1.791827000	-2.872513000	3.186842000