Supporting Information

A Polymorphic Pentiptycene-Containing Gold(I) Isocyanide Complex: Solvent- and Conformation-Dependent Supramolecular Luminescence

Ying-Feng Hsu, Ssu-Ying Chen, Subhendu Maity, Yi-Hung Liu, Shie-Ming Peng, and Jye-Shane Yang*

Department of Chemistry, National Taiwan University, Taipei, Taiwan 10617

jsyang@ntu.edu.tw

Contents:

General Methods. The ^{1}H NMR spectra and ^{13}C-NMR spectra were recorded by Bruker AVIII-400 MHz. High-resolution mass data were determined by using fast-atom-bombardment (FAB) ionization with a JEOL JMS-700 spectrometer or electrospray ionization (ESI) with a Bruker microTOF-QII spectrometer. UV/visible spectra were recorded using a Cary300 double-beam spectrophotometer. Emission spectra were recorded using an Edinburgh FLS920 spectrometer at ambient temperature and corrected for the R928P detector. A solution of quinine bisulfate [Φ_f = 0.546 in 1N H_2SO_4 (aq)] was used as the standard for the phosphorescence quantum yield determination, corrected with a solvent refractive index, of compounds in a solution under purging with nitrogen for 20 min. The optical density of all solutions was about 0.1 at the wavelength of excitation, and an error of 5% was estimated for emission quantum yields. The absolute quantum yields for powders of solid samples were determined using an integrating sphere (150 mm diameter, $BaSO_4$ coating) by Edinburgh FLS920 spectrometer. Luminescence lifetimes were measured by Edinburgh FLS920 spectrometer apparatus with nF900, a gated hydrogen arc lamp, and the range of measured decay was from 0.3 ns to 1 μs. The goodness of the nonlinear least-squares fit for phosphorescence was judged by the reduced χ^2 value < 1.2, the randomness of the residuals, and the autocorrelation function. The luminescence sample photographs were taken using an Olympus IX73 inverted microscope equipped with a DP73 color camera. The light source of the microscope is a halogen lamp equipped with an Olympus U-FUW filter, which passed light in the range of 340–390 nm. Powder X-ray diffraction (PXRD) were measured by Bruker D2 Phaser diffractometer using nickel-filtered Cu Kα radiation (λ = 1.5413 A) at a voltage of 30 kV and a current of 10 mA. The hydrodynamic size measurement was performed using dynamic light scattering (DLS) on a Zetasizer Nano ZS (Malvern Panalytical, Malvern, U.K.). For the AIE

experiment, the THF/water and hexane/THF mixtures with various water fractions were prepared by slowly adding water or hexane into the THF solution of sample. The mechanochromism tests were carried out by gentle hand grinding of the sample with a spatula until the luminescence colour was uniform and no longer changed. For vapochromism tests, the sample were placed in a 20 mL vial bottle that contains a piece of cotton soaked with about 0.5 mL of target solvent (hexane for 60 min or DCM for 5 min). The solvents used for crystal growth are DCM/hexane (1: 3) for **1B**, DCM/MeOH (1: 1) for **1C**, DCM/MeOH (2: 1) for **1G**, and DCM/MeOH (4: 1) for **1BG**. The crystal structures were determined using a Rigaku Oxford Diffraction diffractometer (Xcalibur, Atlas, Gemini). The simulated XRD of the crystals were provided by the Mercury program.

Computational Method: The density functional theory (DFT) and time dependent density functional theory (TD-DFT) calculations were performed using the Gaussian 16, Reversion A. 03 program package.[1] For all of calculation, the M06-2X functional[2] is employed for energy and orbital in singlet and triplet excited state. In addition, the effective core potential (ECP) SDD[3] basis set is used for Au atoms and the 6-311+G (d,p) basis set for other ligand atoms. TDDFT-derived state energy, oscillator strength, configuration interactions, and electronic character of the low-lying singlet excited states (S_1) and the lowest triplet excited state (T_1) are used in the same method as DFT. The electron density of relative orbital was calculated with Mulliken population analysis (MPA) by Multiwfn program.[4]

Materials and Synthesis. All commercial reagents, catalysts, solvents (HPLC grade for photophysical measurements) were used as received. Column chromatography was carried out on silica gel (Geduran® SI 60).

Synthesis of Compound 3: Compound **2** (1.35 g, 2.92 mmol) was taken in 20 mL

of anhydrous DMF at 0°C, and then sodium hydride (0.15 g, 3.75 mmol) was added into DMF solution to react for 30 min. Then 1-bromooctane (0.60 mL, 3.50 mmol) was added dropwise to the reaction mixture at 0°C, and the resulting mixture was stirred for overnight. After removal of the volatile solvent under reduced pressure, the residue was extracted by CH_2Cl_2 and water. The organic layer was dried over anhydrous $MgSO_4$ and the filtrate was concentrated under reduced pressure. The crude was purified by silica gel column chromatography with CH_2Cl_2 /hexane (2:1) eluent to produce white solid compound **3** (1.53 g, 92%); m.p.: 285°C; ^{1}H-NMR (400 MHz, $CDCl_3$), δ: 7.33-7.39 (m, 8H), 6.96-7.00 (m, 8H), 5.71 (s, 2H), 5.44 (s, 2H), 3.93 (t, *J*= 6.8 Hz, 2H), 3.85 (s, 2H), 2.02-2.09 (m, 2H), 1.69 - 1.76 (m, 2H), 1.44-1.58 (m, 8H), 1.01 (t, *J*= 6.8 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$), δ:14.2, 22.7, 26.5, 29.4, 29.6, 30.5, 31.9, 48.3, 48.6, 76.3, 123.3, 123.5, 125.0, 125.1, 130.2, 132.1, 135.4, 143.4, 145.3, 145.4; IR(KBr): 3381, 3066, 3040, 3018, 2927, 2854, 1621, 1478, 1459, 1298, 1262, 1197, 1197, 1110, 1086, 1021; Calculated m/z for $C_{42}H_{40}NO^+$ (ESI^+-TOF): 574.3104. Found: 573.3105.

Synthesis of Compound 4: A mixture solution of formic acid (0.53 mL, 14 mmol) and acetic anhydride (0.53, 5.6mmol) firstly react 1hr at 60°C. The reacted mixture solution was added dropwise at 0 °C to a tetrahydrofuran solution (20 mL) of compound **3** (0.8g, 1.4 mmol), and the mixture solution was stirred for 2 h at room temperature. After removal of the volatile solvent under reduced pressure, the residue was washed with hexane to produce white solid intermediate in a quantitative yield. A CH_2Cl_2 solution (20 mL) of acquired intermediate and Et_3N (1.17 mL, 8.40 mmol) was cooled at 0 °C, then $POCl_3$ (0.19 mL, 2.1 mmol) was added dropwise. After the reaction was completed, an aqueous saturated Na_2CO_3 solution was added at 0 °C to quench the reaction and the mixture was extracted with CH_2Cl_2. After removal of the volatile

solvent under reduced pressure, the residue was extracted by CH_2Cl_2 and water. The organic layer was dried over anhydrous $MgSO_4$ and the filtrate was concentrated under reduced pressure. The crude was purified by silica gel column chromatography with CH_2Cl_2 /hexane (3:1) eluent to produce white solid compound **4** (0.81 g, 82%); m.p.: 290°C; ^{1}H-NMR (400 MHz, $CDCl_3$), δ:7.43-7.48 (m, 4H), 7.35-7.40 (m, 4H), 6.99-7.05 (m, 8H), 5.79 (s, 2H), 5.73 (s, 2H), 4.01 (t, *J*= 6.8 Hz, 2H), 2.01-2.09 (m, 2H), 1.64-1.74 (m, 2H), 1.41-1.59 (m, 8H), 1.01 (t, *J*= 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$), δ:14.1, 22.7, 26.3, 29.3, 29.5, 30.5, 31.9, 48.2, 50.2, 76.2, 114.5, 123.6, 124.1, 125.5, 125.6, 137.1, 140.5, 144.1, 144.5, 149.9, 166.9; IR (KBr): 3067, 3042, 3022, 2926, 2852, 2118, 1479, 1458, 1403, 1326, 1302, 1253, 1198, 1183, 1150, 1107, 1078, 1023;. Calculated m/z for $C_{43}H_{38}NO^+$ (ESI^+-TOF): 583.2948. Found: 584.2944.

Synthesis of Complex 5: Compound **4** (0.40 g, 0.69 mmol) and chloro (dimethyl sulfide) gold(I) (0.20 g, 0.68 mmol) was taken in dry CH_2Cl_2 under nitrogen atmosphere to react at room temperature for overnight. After removal of the volatile solvent under reduced pressure, the residue was extracted by CH_2Cl_2 and water. The organic layer was dried over anhydrous $MgSO_4$ and the filtrate was concentrated under reduced pressure to produce white solid Complex **5** (0.51 g, 91%); m.p.: 230°C (decomposed) ; ^{1}H-NMR (400 MHz, $CDCl_3$), δ:7.45 - 7.47 (m, 4H), 7.35-7.37 (m, 4H), 6.99 - 7.05 (m, 8H), 5.73 (s, 2H), 5.66 (s, 2H), 4.02 (t, *J*= 6.7 Hz, 2H), 1.99-2.06 (m, 2H), 1.64-1.70 (m, 2H), 1.39-1.54 (m, 8H), 0.97 (t, *J*= 6.8 Hz, 3H) ; ^{13}C-NMR (100 MHz, $CDCl_3$), δ:151.43, 146.17, 144.04, 143.35, 141.75, 138.23, 125.92, 125.79, 124.27, 123.75, 112.03, 76.38, 50.14, 48.19, 31.87, 30.47, 29.48, 29.31, 26.24, 22.67, 14.13; IR (KBr): 3068, 3040, 3020, 2925, 2853, 2205, 1636, 1570, 1478, 1458, 1325, 1303, 1291, 1252, 1197, 1109, 1082; Calculated m/z for $C_{43}H_{37}AuClNO^+$ (FAB^+-TOF): 815.2224. Found: 815.2231.

Synthesis of 1: $ZnBr_2$ (0.31 g, 1.36 mmol) was taken in dry THF (6 mL) under nitrogen atmosphere. After it cool down to -78°C, a dibutyl ether solution of phenyllithium (0.92 mL, 9.06 mmol) was added to react for 30 min at -78°C. Then, compound **4** (0.52 g, 0.64 mmol) in dry THF (20 mL) was added dropwise to the mixture solution to react 1 hr at 0°C, and then allowed to room temperature for overnight. The crude solid was washed by hexane and methanol to produce white solid complex **1** (0.38 g, 70%); m.p.: 170-220°C (decomposed); ^{1}H-NMR (400 MHz, CDCl3), δ:7.63-7.65 (m, 2H), 7.44-7.46 (m, 4H), 7.33 - 7.38 (m, 6H), 7.15 - 7.20 (m, 1H), 6.97-7.04 (m, 8H), 5.71 (s, 2H), 5.67 (s, 2H), 3.99 (t, *J*= 6.8 Hz, 2H), 1.97 - 2.05 (m, 2H), 1.62-1.70 (m, 2H), 1.38 - 1.55 (m, 8H), 0.95 (t, *J*= 6.9 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$), δ:14.13, 22.68, 26.25, 29.31, 29.49, 30.46, 31.88, 48.19, 50.56, 76.32, 112.44, 123.68, 124.30, 125.71, 125.82, 126.44, 127.68, 138.07, 140.53, 141.54, 143.47, 144.08, 151.16, 162.51, 164.52; IR(KBr): 3052, 2925, 2853, 2187, 1634, 1572, 1474, 1458, 1421, 1326, 1303, 1291, 1252, 1197, 1184, 1151, 1109, 1081, 1024 ; Calculated m/z for $C_{49}H_{43}AuNO^+$ (FAB^+-TOF): 858.3005. Found: 858.3007.

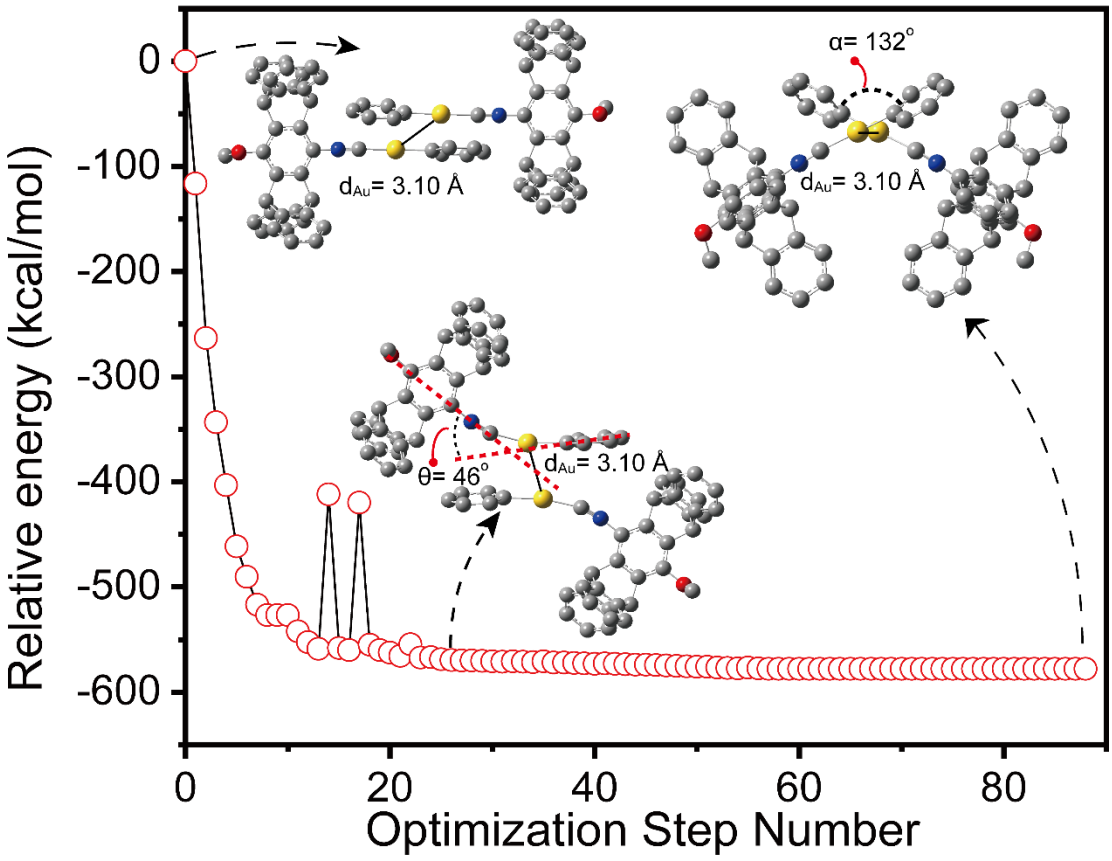

Fig. S1 A DFT-derived structure-energy plot for a molecular pair of **1**. The molecular pair was initially set antiparallel with a planar π-backbone for both molecules. The Au···Au distance was fixed at 3.10 Å and the energy was calculated (step number = 0). Then the molecular was subjected to energy optimization. Each red dot represents the energy after every 128 cycles of self-consistent field calculation (one loop), corresponding to one optimization step. The structure at the 26th step gave a bending angle of 46^{o} for the π-backbone (called **1G**-like), which is similar to the molecular pair in **1G** (53^{o}). The calculation converged at the 88th step, which afforded a linear crossed geometry (crossing angle = 132^{o}, called **1C**-like) similar to the molecular pair in **1C**.

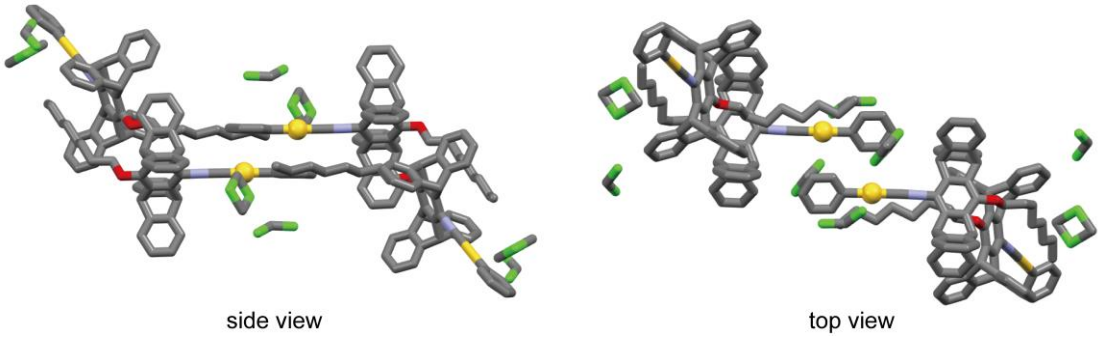

Fig. S2. Side view (left) and top view (right) of **1BG** crystal packaging**.**

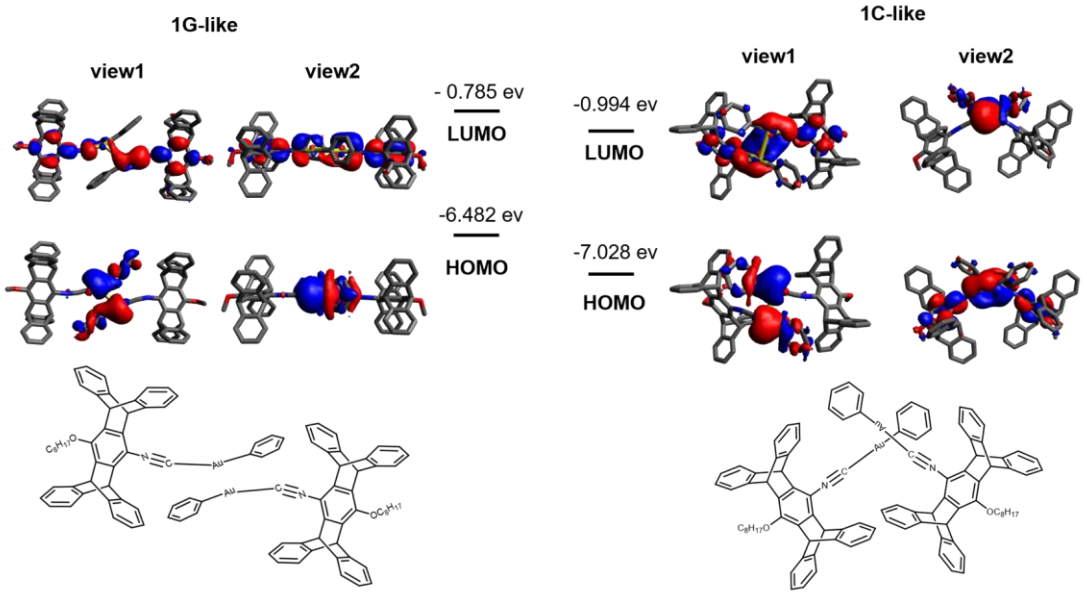

Fig S3. Frontier molecular orbitals and energies of the **1G**-like (left) and **1C**-like (right) molecular pair derived from the optimization shown in Figure S1.

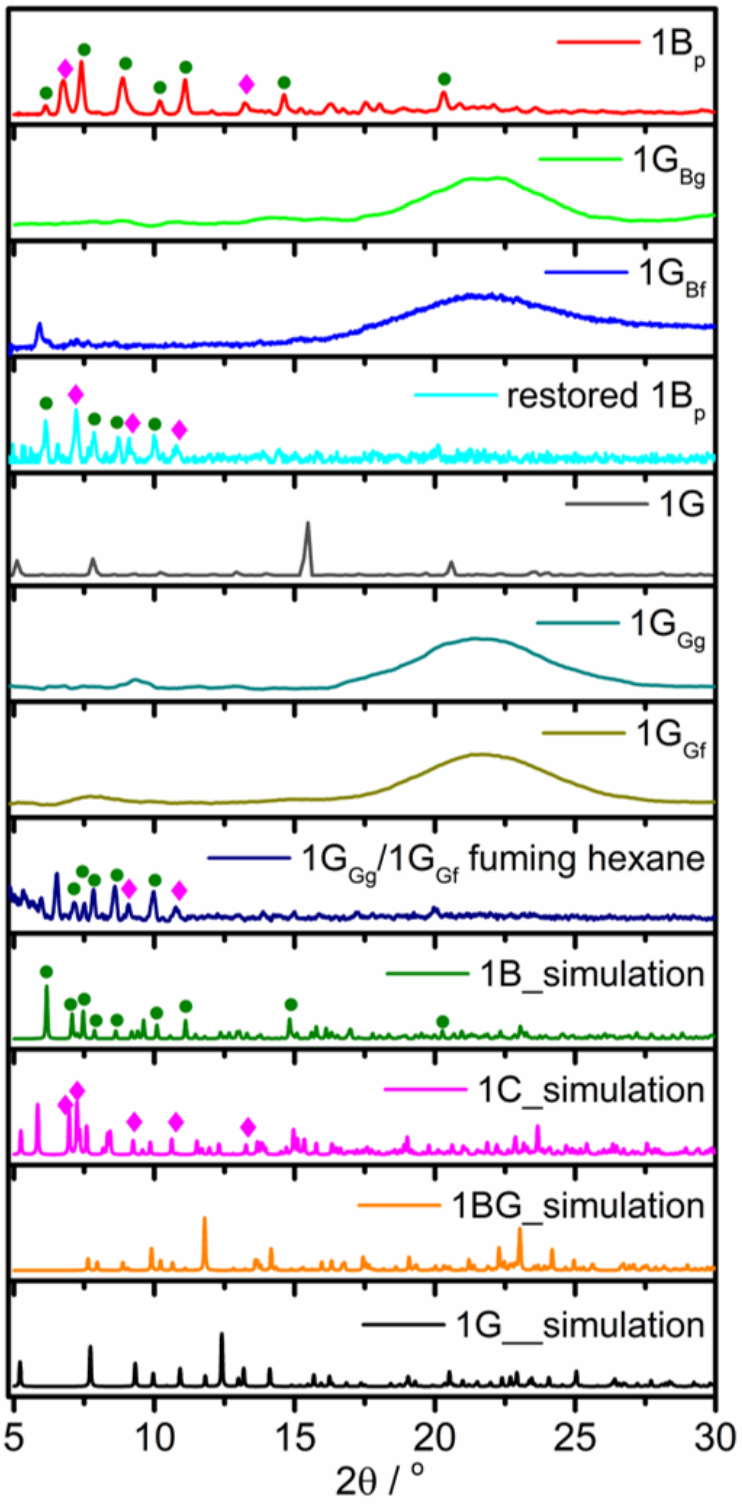

Fig. S4. Powder X-ray diffraction (XRD) patterns of both experimental and simulated systems. The notations on the peaks of **1B$_p$**, restored **1B$_p$**, **1G$_{Gg}$/1G$_{Gf}$** are to correlate with the peaks of **1B** (solid circle) and **1C** (diamond).

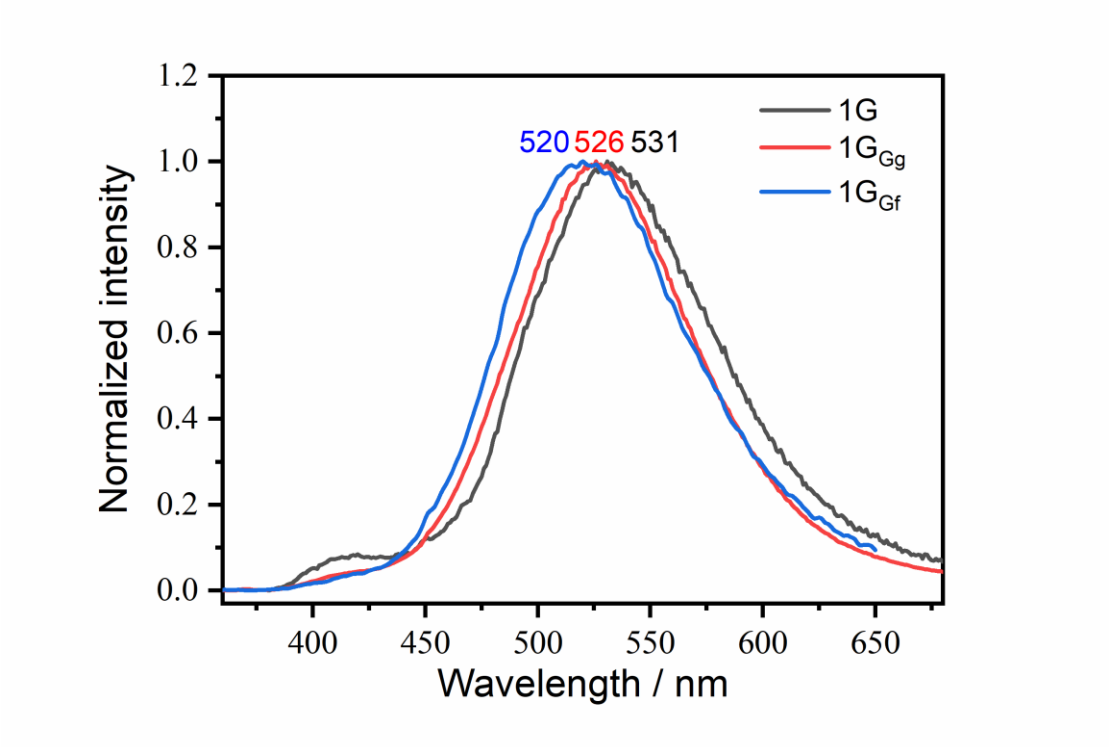

Fig. S5. Luminescence spectra of the luminescence of **1G** (black line) and its ground **1G**$_{Gg}$ (red line) form and DCM-fumed **1G**$_{Gf}$ form (blue line).

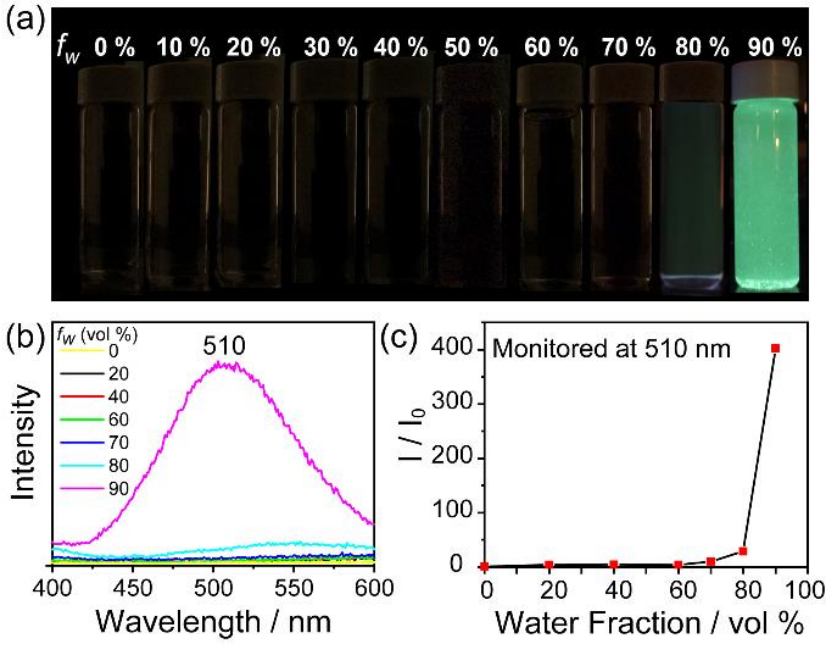

Fig. S6. The AIE behaviour of **1** in mixed water/THF (v/v) from 0% to 90% water at 10% interval: (a) photographic images of luminescence (λ_{ex} = 365 nm); (b) emission spectra (λ_{ex} = 315 nm); (c) emission Intensity ratio of each solution vs 0% water at 510 nm.

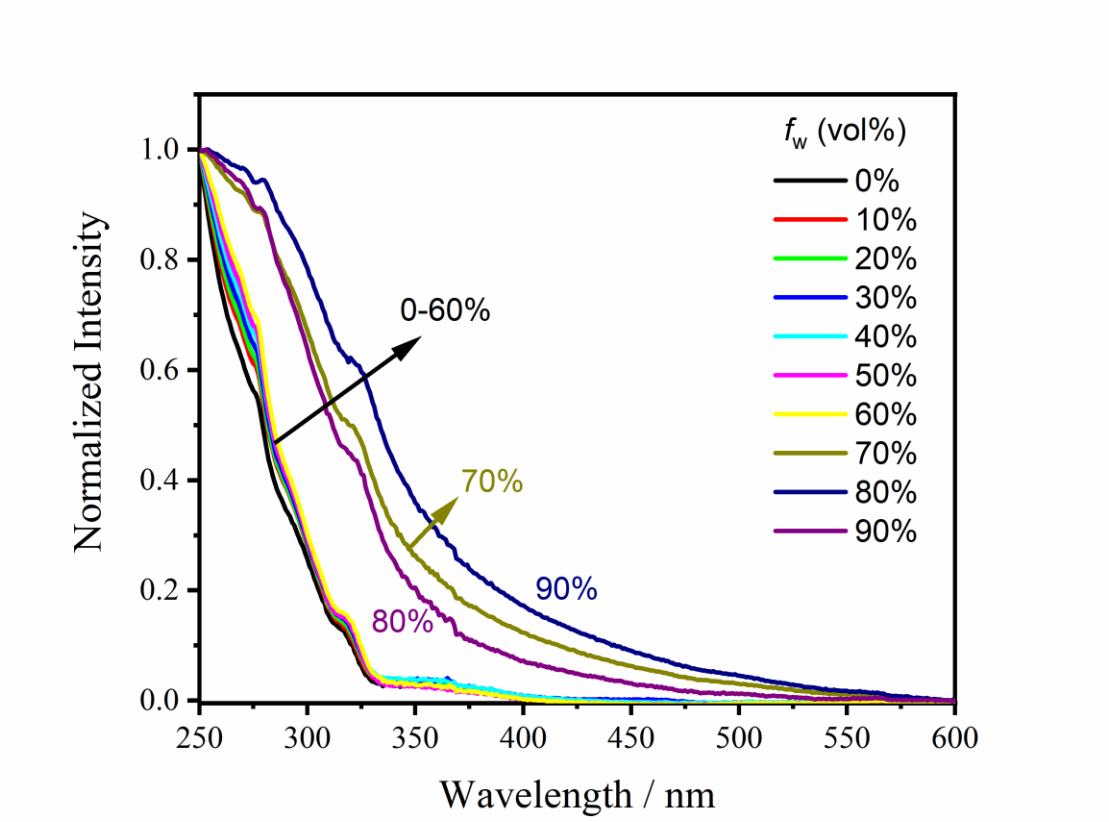

Fig. S7. Absorption spectra for complex 1 in mixed water/THF (v/v) solutions from 0% to 90% water fraction at 10% interval at 1×10^{-5} M.

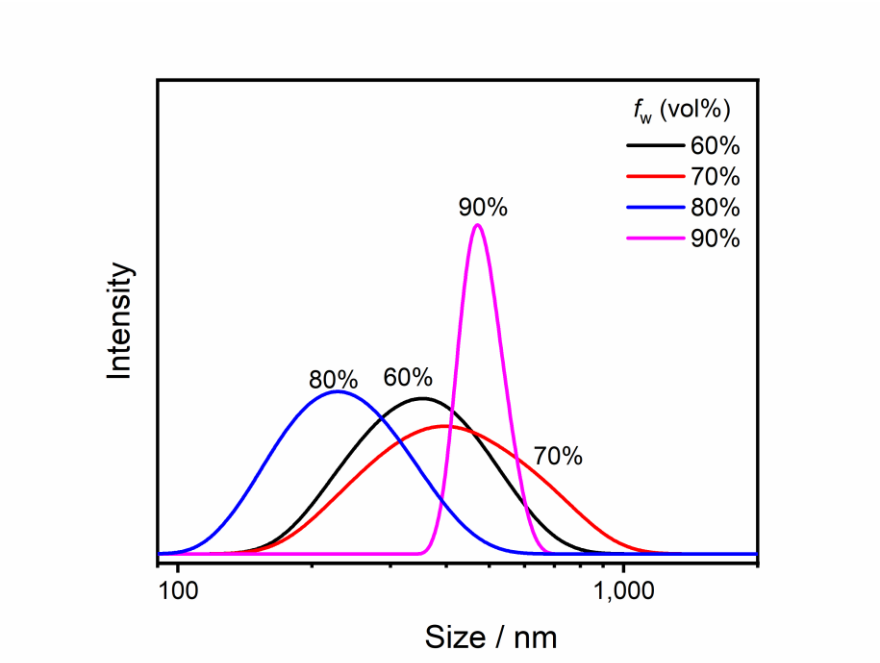

Fig. S8. Dynamic Light Scattering (DLS) derived aggregate sizes distribution of complex **1** in selected water/THF (v/v) solutions at $1x10^{-5}$ M.

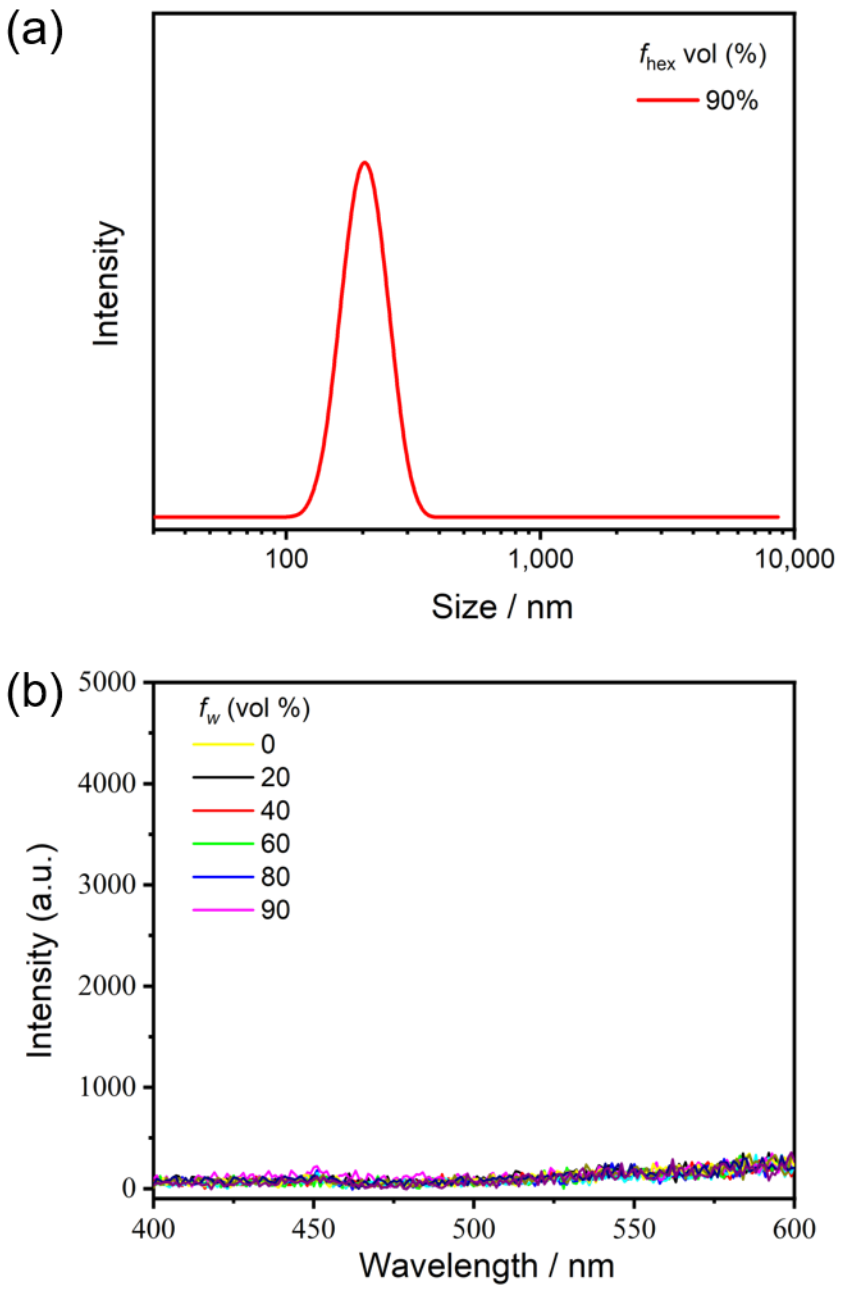

Fig. S9. Complex **1** dissolved in mixed hexane/THF (v/v) from 0% to 90% hexane at $1x10^{-5}$ M. (a) DLS derived aggregate sizes in 90% hexane solution (b) emission spectra in selected solutions

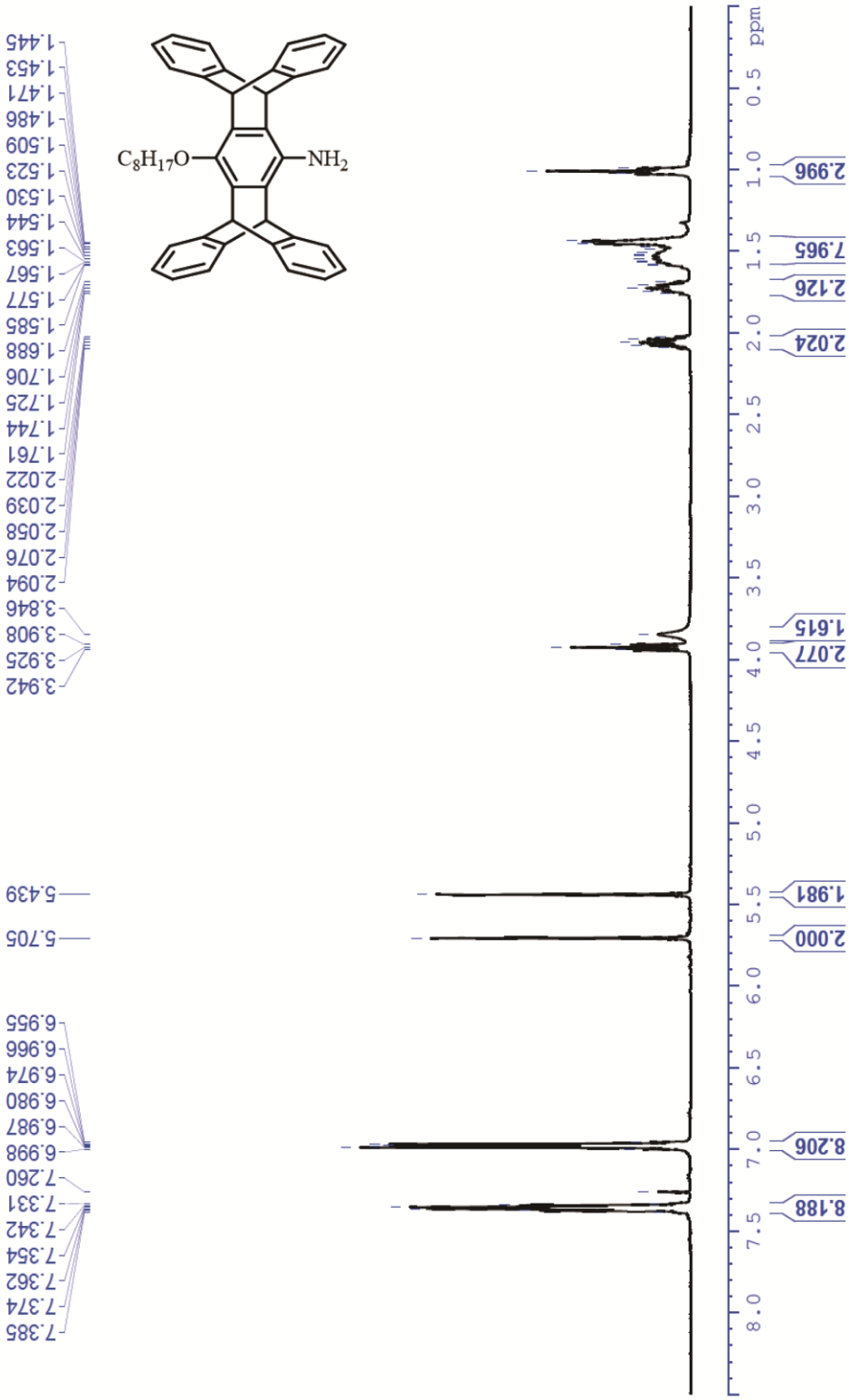

Fig. S10. [1]H-NMR spectrum of compound **3** (400 MHz, CDCl3).

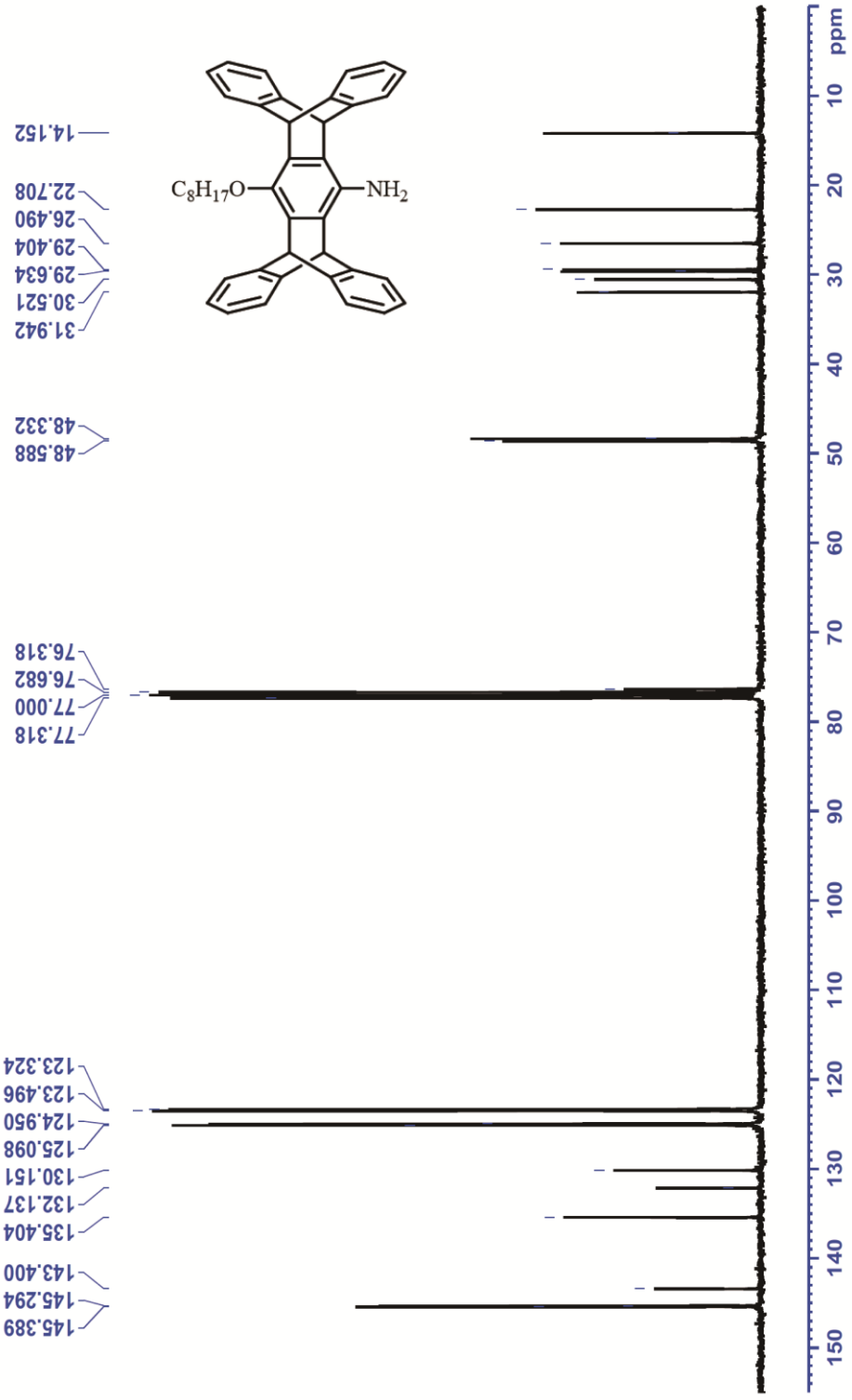

Fig. S11. ^{13}C-NMR spectrum of compound **3** (400 MHz, CDCl3).

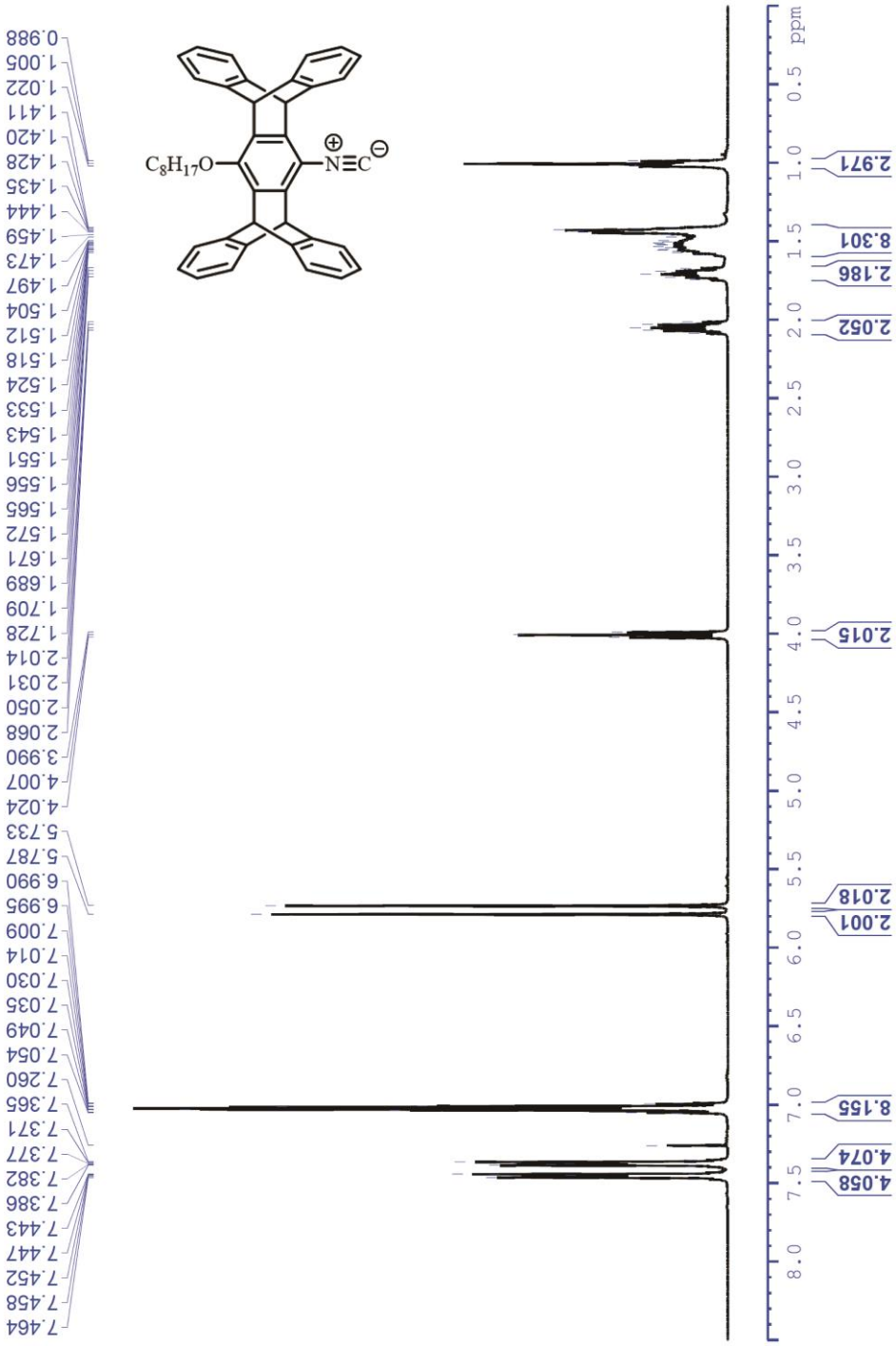

Fig. S12. [1]H-NMR spectrum of compound **4** (400 MHz, CDCl3).

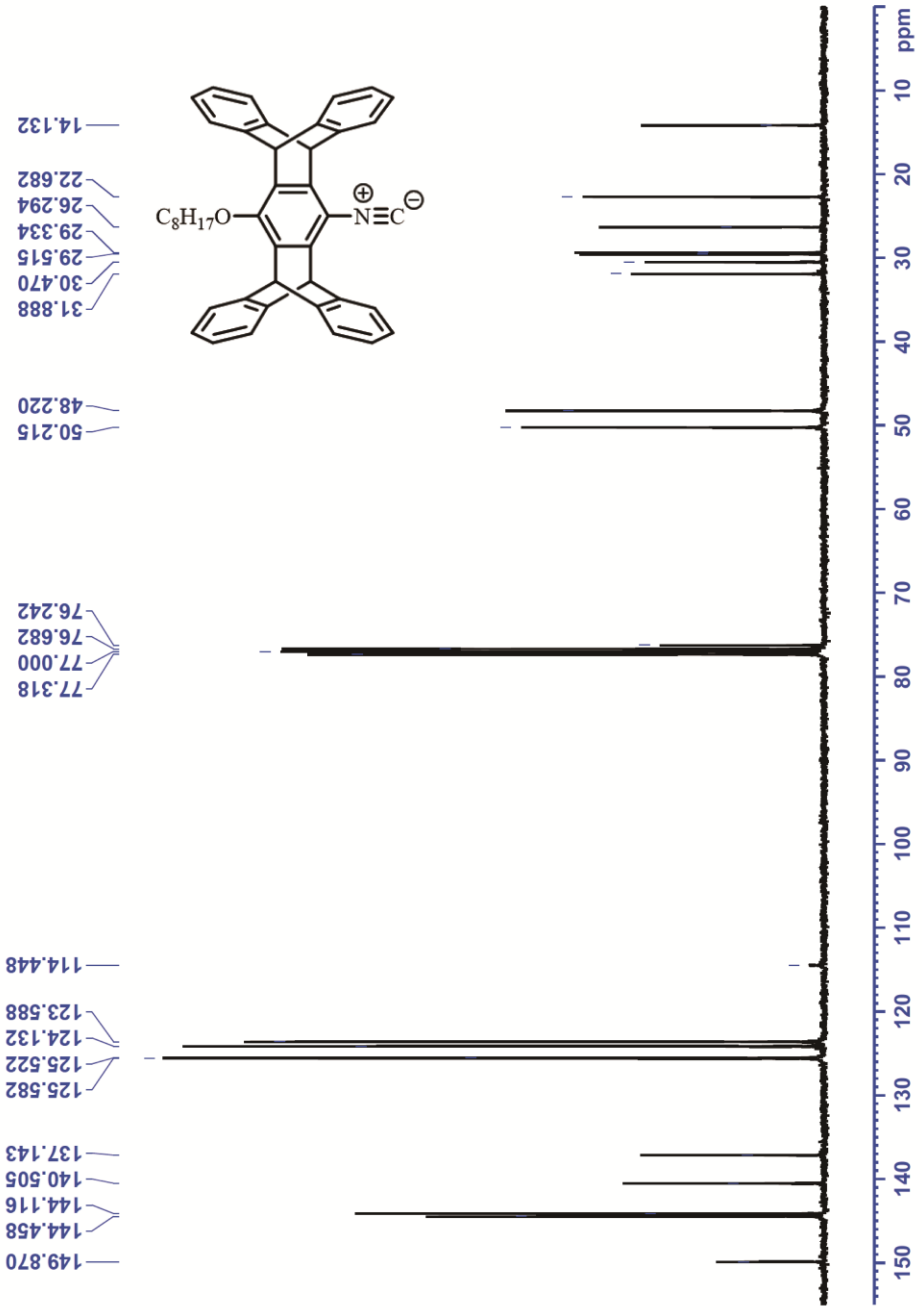

Fig. S13. ^{13}C-NMR spectrum of compound **4** (400 MHz, CDCl3).

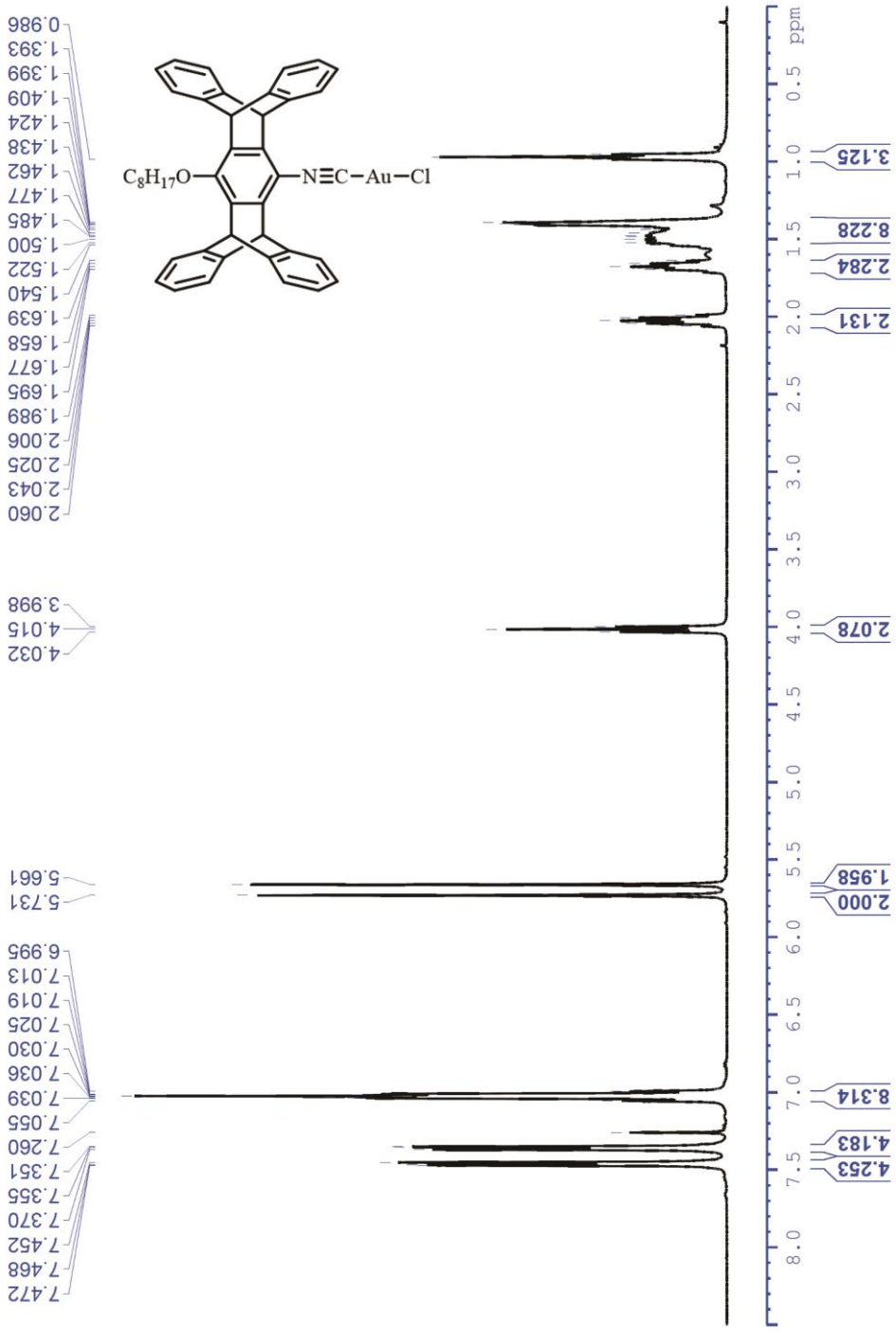

Fig. S14. [1]H-NMR spectrum of complex **5** (400 MHz, CDCl3).

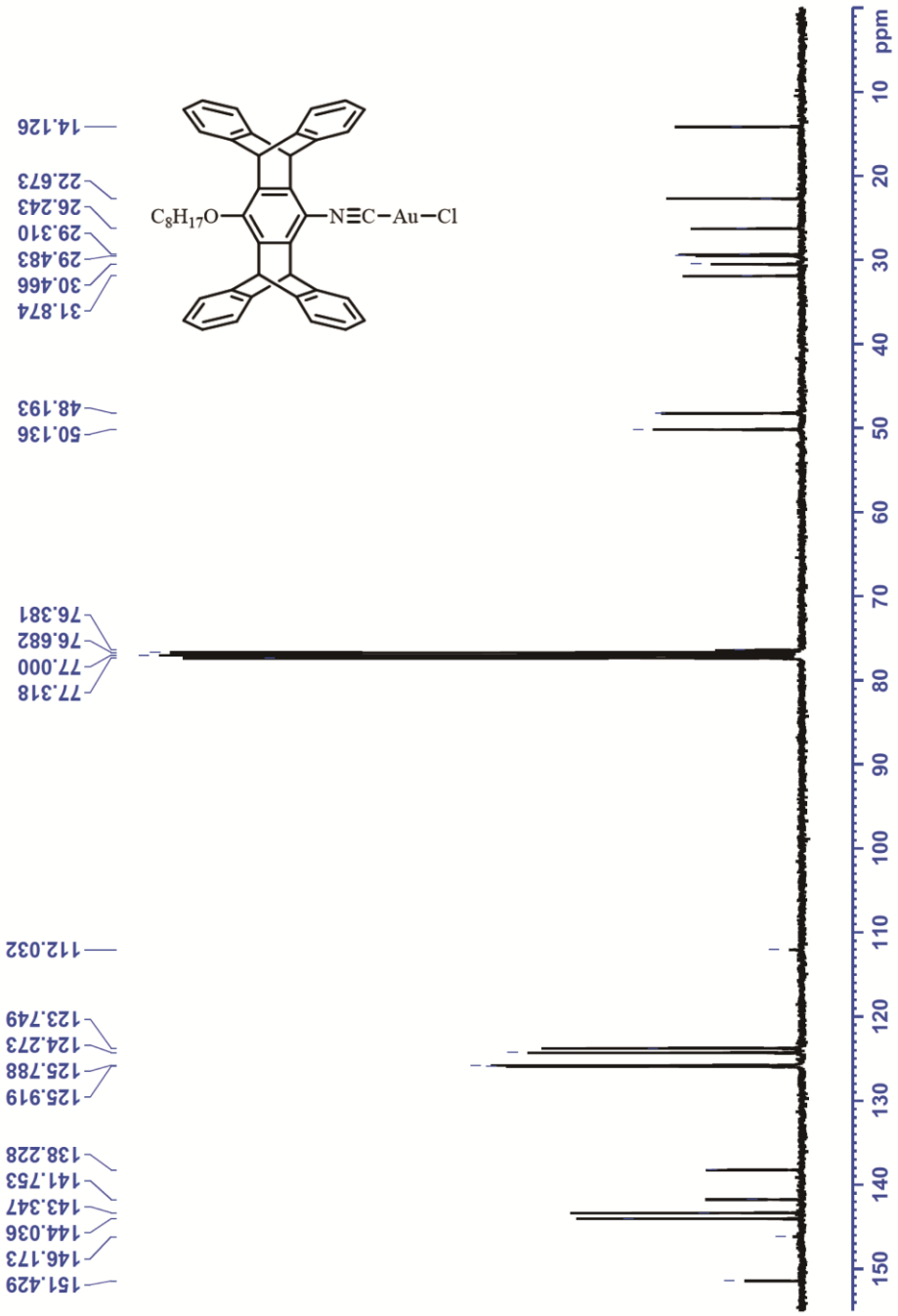

Fig. S15. ^{13}C-NMR spectrum of complex **5** (400 MHz, CDCl3).

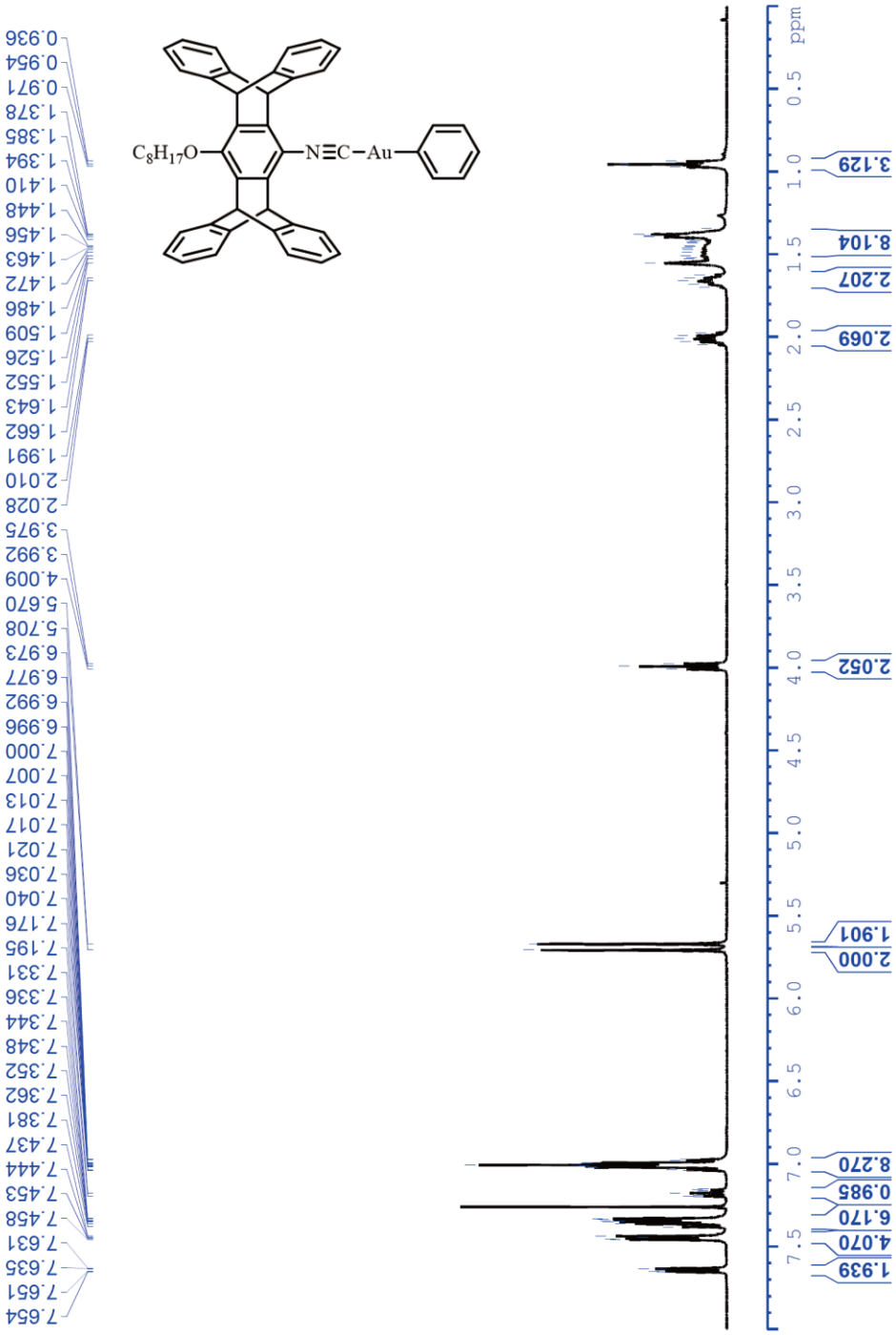

Fig. S16. ^{1}H-NMR spectrum of complex **1** (400 MHz, CDCl3).

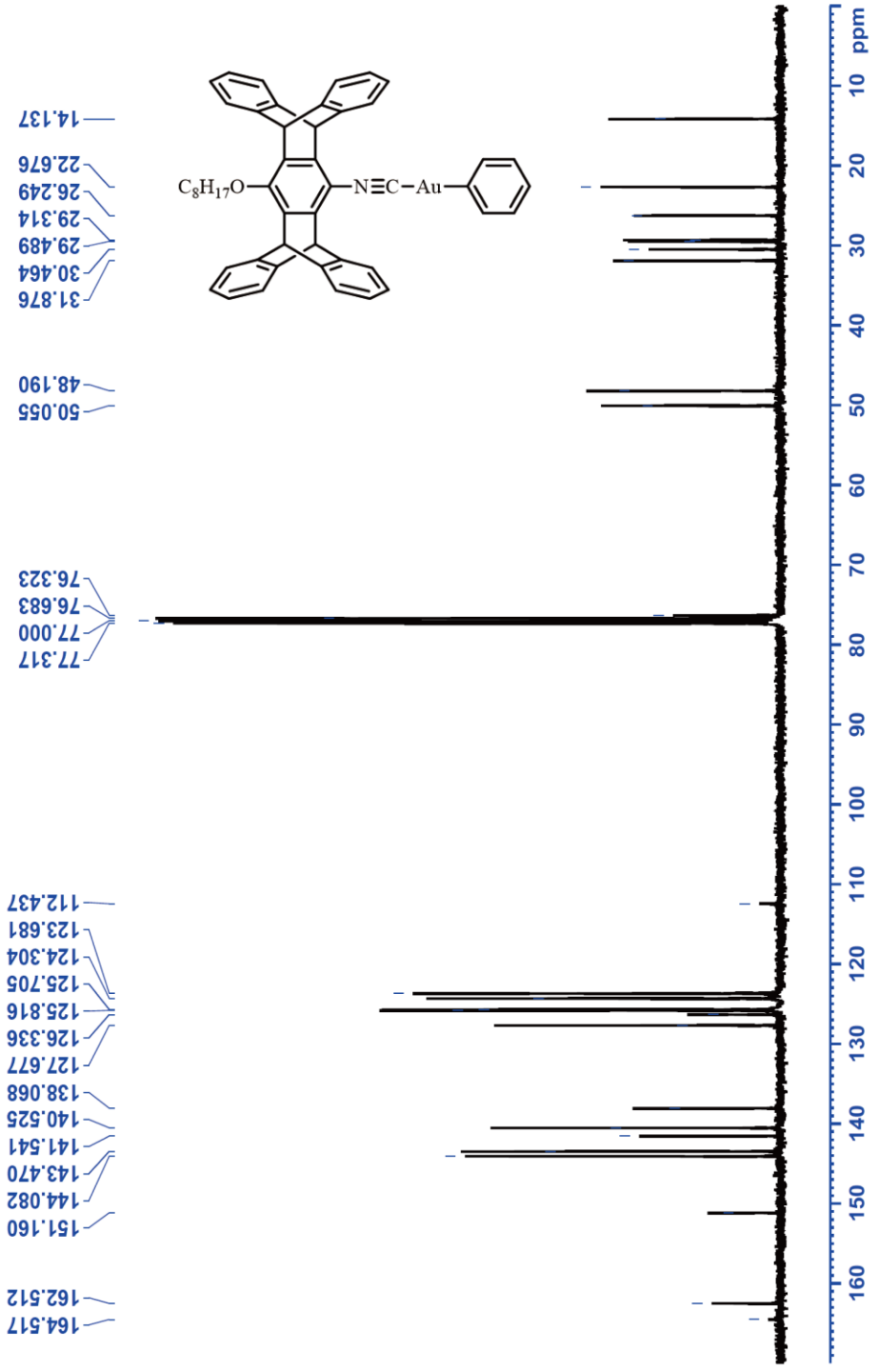

Fig. S17. ^{13}C-NMR spectrum of complex **1** (400 MHz, CDCl3).

Table S1. X-ray crystallographic data for **1B**, **1C**, **1BG**, and **1G**.

	1B	**1C**	**1BG**	**1G**
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$	P(1)/c
empirical formula	$C_{98}H_{84}Au_2N_2O_2 \cdot 1.5C_6H_{14}$	$C_{98}H_{84}Au_2N_2O_2 \cdot 4CH_2Cl_2$	$C_{49}H_{42}AuNO \cdot 2CH_2Cl_2$	$C_{98}H_{84}Au_2N_2O_2$
Crystal System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Z value	4	4	4	2
a/ Å	23.9280(12)	15.3831(4)	11.8776(3)	11.8805(5)
b/ Å	14.4942(5)	23.2901(4)	39.0337(7)	33.876(3)
c/ Å	26.2838(15)	24.8211(5)	9.4164(2)	9.5447(4)
α/ deg	90°	90°	90°	90°
β/ deg	110.163(6)°	100.617(2)°	103.027(2)°	105.559(5)°
γ/ deg	90°	90°	90°	90°
D_{calc} (Mg/m^3)	1.432	1.562	1.543	1.540
Volume ($Å^3$)	8557.0(8)	8740.5(3)	4253.34(16)	3700.6(4)
residuals: R_1	0.0877	0.0877	0.0525	0.1049
residuals: wR_2	0.1453	0.2523	0.1329	0.2535
goodness of fit	1.025	1.566	1.080	1.177

Table S2. Selected structural parameters of **1C**-like and **1G**-like molecular pairs derived from the DFT optimization shown in Figure S1.

	d_{au} (Å)	φ (°)	χ_{Au} (°)	χ_{ip} (°)
1C-like	3.10	12, 12	59, 59	48, 48
1G-like	3.10	79, 79	5, 5	82, 82

Table S3. TDDFT-derived electronic characters for the lowest singlet ($S_0 \rightarrow S_1$) and triplet excited state ($S_0 \rightarrow T_1$) for the **1C**-like and **1G**-like molecular pairs.

Compd.	State	λ_{max} (nm)	***f***	configuration	Character
1C-like	$S_0 \rightarrow S_1$	307	0.05	HOMO → LUMO (89%)	MMLCT
	$S_0 \rightarrow T_1$	343	0	HOMO → LUMO (72%)	MMLCT
1G-like	$S_0 \rightarrow S_1$	327	0.006	HOMO → LUMO (84%)	MMLCT
	$S_0 \rightarrow T_1$	350	0	HOMO → LUMO (68%)	MMLCT

Table S4. Coordinates for DFT-derived **1C**-like molecular pair.

Center Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	Au	-0.479730	-3.094690	-1.476220
2	O	-7.697320	1.631685	-0.387720
3	N	-3.209730	-1.619040	-0.664460
4	C	-4.351650	-0.833530	-0.576920
5	C	-4.565670	0.130083	-1.567510
6	C	-5.704530	0.926879	-1.516870
7	C	-6.617800	0.792036	-0.472510
8	C	-6.396270	-0.174300	0.503528
9	C	-5.264100	-0.992370	0.464871
10	C	-5.171920	-1.947430	1.650761
11	H	-4.283820	-2.587560	1.637727
12	C	-6.481020	-2.734410	1.626064
13	C	-6.607900	-4.112260	1.556621
14	H	-5.720360	-4.734860	1.518922
15	C	-7.885730	-4.678500	1.538304
16	H	-7.994580	-5.757060	1.485431
17	C	-9.015900	-3.869690	1.584152
18	H	-10.004200	-4.317920	1.568340
19	C	-8.886500	-2.479500	1.643079
20	H	-9.766570	-1.843300	1.668397
21	C	-7.619610	-1.919340	1.662030

22	C	-7.288310	-0.433230	1.708000
23	H	-8.171320	0.208284	1.711183
24	C	-6.383770	-0.235780	2.916752
25	C	-6.593810	0.648671	3.961608
26	H	-7.485360	1.269871	3.981386
27	C	-5.646510	0.729543	4.986324
28	H	-5.801020	1.419247	5.809936
29	C	-4.507470	-0.067000	4.950948
30	H	-3.773840	0.004547	5.747681
31	C	-4.295790	-0.960260	3.895478
32	H	-3.408540	-1.584740	3.861592
33	C	-5.239040	-1.043510	2.883841
34	C	-3.648940	0.471242	-2.735210
35	H	-2.745450	-0.140910	-2.770160
36	C	-3.351470	1.962108	-2.586640
37	C	-2.099800	2.545343	-2.482090
38	H	-1.203700	1.931526	-2.510300
39	C	-2.004620	3.933105	-2.334430
40	H	-1.027630	4.397507	-2.248510
41	C	-3.151530	4.717835	-2.294550
42	H	-3.068900	5.794185	-2.180140
43	C	-4.415240	4.128018	-2.403670
44	H	-5.314080	4.739249	-2.375930
45	C	-4.508220	2.753419	-2.549810

46	C	-5.789350	1.933507	-2.656790
47	H	-6.699640	2.535374	-2.614330
48	C	-5.668510	1.120061	-3.941470
49	C	-6.564210	1.102923	-4.997950
50	H	-7.463310	1.711429	-4.964620
51	C	-6.297770	0.290474	-6.104150
52	H	-6.994680	0.269216	-6.935640
53	C	-5.148370	-0.491250	-6.144240
54	H	-4.950290	-1.119930	-7.006200
55	C	-4.245140	-0.473920	-5.077990
56	H	-3.346810	-1.084510	-5.103710
57	C	-4.511520	0.331811	-3.983630
58	C	-2.230610	-2.203940	-0.891240
59	C	1.243454	-3.930630	-2.179350
60	C	2.001917	-4.835600	-1.413130
61	H	1.679564	-5.088870	-0.404210
62	C	3.155553	-5.439670	-1.913390
63	H	3.704359	-6.146720	-1.295600
64	C	3.600575	-5.147230	-3.201760
65	H	4.501137	-5.611330	-3.593320
66	C	2.874456	-4.252750	-3.982730
67	H	3.209016	-4.014990	-4.989170
68	C	1.715770	-3.661580	-3.476580
69	H	1.163143	-2.976160	-4.115590

70	C	-7.340550	2.890156	0.192789
71	H	-6.450490	3.281455	-0.319900
72	H	-7.072870	2.741255	1.250789
73	C	-8.516460	3.834837	0.048960
74	H	-8.774610	3.903884	-1.015140
75	H	-9.381520	3.396355	0.557590
76	C	-8.216570	5.229453	0.603203
77	H	-7.972920	5.159707	1.671735
78	H	-9.125380	5.838860	0.535642
79	C	-7.081160	5.945991	-0.129650
80	H	-6.132850	5.415000	0.025808
81	H	-7.277980	5.914963	-1.211790
82	C	-6.898930	7.397944	0.304011
83	H	-7.820380	7.959680	0.099525
84	H	-6.749050	7.437620	1.391538
85	C	-5.721510	8.074921	-0.393490
86	H	-5.861340	8.016732	-1.482390
87	H	-4.801440	7.515320	-0.173070
88	C	-5.532970	9.534392	0.013482
89	H	-6.449830	10.092700	-0.212890
90	H	-5.400140	9.590109	1.101159
91	C	-4.344410	10.188580	-0.685280
92	H	-4.222800	11.231750	-0.382840
93	H	-4.470970	10.166740	-1.772250

94	H	-3.415070	9.660411	-0.449480
95	H	-4.501200	-5.611170	3.593658
96	C	-3.600630	-5.147070	3.202091
97	H	-3.209210	-4.014640	4.989413
98	C	-2.874580	-4.252500	3.983011
99	H	-3.704330	-6.146710	1.296009
100	C	-3.155560	-5.439600	1.913765
101	C	-1.715880	-3.661340	3.476867
102	C	-2.001930	-4.835530	1.413497
103	H	-1.163300	-2.975840	4.115837
104	C	-1.243520	-3.930470	2.179685
105	H	-1.679550	-5.088850	0.404598
106	Au	0.479496	-3.094480	1.476255
107	H	3.346457	-1.084090	5.103706
108	H	1.203584	1.931620	2.509880
109	C	2.230437	-2.203850	0.891119
110	H	4.949759	-1.119240	7.006357
111	C	4.244797	-0.473510	5.077984
112	H	2.745278	-0.140760	2.769993
113	C	2.099682	2.545444	2.481655
114	H	1.027524	4.397601	2.247907
115	C	5.147929	-0.490700	6.144322
116	C	2.004507	3.933195	2.333900
117	N	3.209565	-1.618960	0.664361

118	C	3.648785	0.471367	2.735029
119	C	4.511275	0.332069	3.983535
120	C	3.351345	1.962226	2.586298
121	C	6.297337	0.291020	6.104230
122	C	3.151423	4.717916	2.294010
123	C	4.351590	-0.833600	0.576888
124	C	4.565582	0.130083	1.567430
125	H	6.994158	0.269878	6.935790
126	C	5.668271	1.120306	3.941373
127	C	4.508106	2.753523	2.549459
128	H	3.068793	5.794260	2.179531
129	H	4.283830	-2.587780	-1.637610
130	C	6.563883	1.103310	4.997933
131	C	4.415134	4.128110	2.403211
132	H	3.408714	-1.585040	-3.861580
133	H	5.720295	-4.735140	-1.518580
134	C	5.264111	-0.992560	-0.464810
135	C	5.789217	1.933597	2.656607
136	C	5.171965	-1.947700	-1.650640
137	C	5.704473	0.926840	1.516807
138	C	4.296000	-0.960610	-3.895460
139	C	6.607866	-4.112580	-1.556270
140	H	7.462988	1.711804	4.964602
141	H	5.313957	4.739356	2.375463

142	C	5.239190	-1.043850	-2.883770
143	C	6.481034	-2.734730	-1.625820
144	C	6.396313	-0.174540	-0.503450
145	H	3.415814	9.660183	0.449748
146	H	6.699527	2.535447	2.614144
147	C	6.617812	0.791867	0.472523
148	C	4.507772	-0.067420	-4.950970
149	H	3.774186	0.004119	-5.747740
150	C	7.885673	-4.678860	-1.537820
151	H	7.994475	-5.757420	-1.484860
152	H	4.471833	10.166410	1.772458
153	C	4.345176	10.188320	0.685504
154	H	4.802083	7.515101	0.173055
155	C	6.383969	-0.236170	-2.916670
156	C	7.619657	-1.919710	-1.661760
157	H	6.450715	3.281364	0.319626
158	C	7.288429	-0.433590	-1.707850
159	H	4.223553	11.231520	0.383148
160	H	5.862121	8.016389	1.482311
161	O	7.697369	1.631467	0.387734
162	C	5.722197	8.074660	0.393430
163	H	6.133272	5.414811	-0.026090
164	C	5.646854	0.729070	-4.986330
165	C	9.015870	-3.870090	-1.583640

166	C	7.340699	2.889844	-0.193030
167	C	5.533663	9.534167	-0.013420
168	C	6.594096	0.648212	-3.961560
169	C	8.886523	-2.479900	-1.642680
170	H	7.072923	2.740723	-1.250980
171	H	7.278592	5.914553	1.211429
172	C	7.081661	5.945680	0.129303
173	H	5.400735	9.589971	-1.101080
174	H	8.171455	0.207893	-1.711020
175	H	5.801445	1.418718	-5.809970
176	H	10.004150	-4.318370	-1.567710
177	C	6.899524	7.397678	-0.304230
178	C	8.516744	3.834406	-0.049500
179	H	8.775118	3.903441	1.014546
180	H	6.450559	10.092430	0.212916
181	H	7.485677	1.269373	-3.981320
182	H	9.766618	-1.843740	-1.667980
183	H	6.749558	7.437455	-1.391740
184	C	8.216892	5.229038	-0.603720
185	H	7.821021	7.959339	-0.099770
186	H	7.973065	5.159292	-1.672210
187	H	9.381642	3.395823	-0.558310
188	H	9.125772	5.838351	-0.536320

Table S5. Coordinates for DFT-derived **1G-**like molecular pair.

Center Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	Au	-1.282880	0.694340	-0.921990
2	O	-9.837710	-0.565900	-0.472800
3	N	-4.299260	-0.366240	-0.753870
4	C	-5.686760	-0.413570	-0.701490
5	C	-6.420100	0.761510	-0.487240
6	C	-7.810830	0.700120	-0.440620
7	C	-8.474460	-0.515600	-0.577230
8	C	-7.734160	-1.673180	-0.798930
9	C	-6.342050	-1.627900	-0.864610
10	C	-5.699430	-2.991100	-1.080830
11	H	-4.612830	-2.953630	-1.129820
12	C	-6.337860	-3.539440	-2.353050
13	C	-5.670510	-3.969330	-3.488220
14	H	-4.585740	-3.928170	-3.532400
15	C	-6.411870	-4.452390	-4.570660
16	H	-5.898680	-4.792240	-5.464390
17	C	-7.800130	-4.497670	-4.509530
18	H	-8.366870	-4.872110	-5.355860
19	C	-8.471740	-4.063920	-3.362560
20	H	-9.556350	-4.096260	-3.311390
21	C	-7.736580	-3.589000	-2.289460

22	C	-8.293770	-3.079310	-0.964710
23	H	-9.383820	-3.101820	-0.917660
24	C	-7.620050	-3.911360	0.119970
25	C	-8.254760	-4.657330	1.099490
26	H	-9.340090	-4.693390	1.143840
27	C	-7.481810	-5.364380	2.026020
28	H	-7.969960	-5.951370	2.797300
29	C	-6.094000	-5.319700	1.962720
30	H	-5.501480	-5.873650	2.683580
31	C	-5.453740	-4.563470	0.975010
32	H	-4.369470	-4.523300	0.921920
33	C	-6.220640	-3.861110	0.060690
34	C	-5.880850	2.167700	-0.258870
35	H	-4.791490	2.228470	-0.282530
36	C	-6.471750	2.611200	1.078410
37	C	-5.758710	3.041250	2.184910
38	H	-4.673780	3.092380	2.149600
39	C	-6.454250	3.408240	3.341720
40	H	-5.905420	3.745270	4.215180
41	C	-7.842520	3.343500	3.378280
42	H	-8.375410	3.630760	4.279660
43	C	-8.561380	2.914280	2.257910
44	H	-9.647600	2.871260	2.283900
45	C	-7.871650	2.550700	1.112570

46	C	-8.471020	2.049780	-0.196610
47	H	-9.561690	1.984030	-0.182560
48	C	-7.942350	2.973120	-1.289060
49	C	-8.698520	3.707610	-2.187970
50	H	-9.783300	3.655660	-2.163380
51	C	-8.047060	4.512760	-3.126910
52	H	-8.631250	5.088910	-3.837070
53	C	-6.658440	4.577810	-3.157440
54	H	-6.161760	5.204770	-3.890970
55	C	-5.895720	3.836930	-2.249910
56	H	-4.810570	3.885630	-2.267060
57	C	-6.544320	3.037330	-1.322460
58	C	-3.163670	-0.106860	-0.786100
59	C	0.270600	2.042540	-1.082400
60	C	0.769950	2.467990	-2.326290
61	H	0.413850	1.990330	-3.236010
62	C	1.711960	3.492870	-2.436870
63	H	2.060600	3.798160	-3.420930
64	C	2.204660	4.122840	-1.294830
65	H	2.922640	4.936870	-1.386920
66	C	1.743740	3.711020	-0.043700
67	H	2.113090	4.188290	0.860840
68	C	0.799290	2.687570	0.054680
69	H	0.468780	2.378870	1.043670

70	C	-10.272600	-0.554810	0.889790
71	H	-9.736330	0.234610	1.435920
72	H	-10.015200	-1.517600	1.359870
73	C	-11.768000	-0.311700	0.903220
74	H	-11.967500	0.626240	0.369690
75	H	-12.259700	-1.109870	0.336660
76	C	-12.339800	-0.242150	2.320460
77	H	-12.157300	-1.193870	2.837720
78	H	-13.428900	-0.135140	2.252940
79	C	-11.776700	0.904760	3.164360
80	H	-10.708100	0.743370	3.358400
81	H	-11.848500	1.844940	2.596260
82	C	-12.496200	1.069670	4.500470
83	H	-13.558300	1.283670	4.319900
84	H	-12.463900	0.118110	5.049300
85	C	-11.891400	2.173070	5.367310
86	H	-11.899500	3.122620	4.812340
87	H	-10.834700	1.941000	5.560590
88	C	-12.619700	2.359880	6.696660
89	H	-13.672900	2.595700	6.499790
90	H	-12.615300	1.409440	7.245530
91	C	-11.997200	3.456160	7.557520
92	H	-12.532700	3.577760	8.502950
93	H	-12.012900	4.419180	7.036320

94	H	-10.953400	3.223110	7.790370
95	H	-3.128730	-4.913900	-0.923700
96	C	-2.349440	-4.155350	-0.899230
97	H	-2.207840	-4.135450	1.250300
98	C	-1.820950	-3.730240	0.318380
99	H	-2.277210	-3.906630	-3.038660
100	C	-1.857740	-3.603760	-2.082270
101	C	-0.805930	-2.773160	0.346430
102	C	-0.841780	-2.646830	-2.040050
103	H	-0.425250	-2.449060	1.312500
104	C	-0.267010	-2.215840	-0.828720
105	H	-0.489600	-2.221260	-2.977130
106	Au	1.353400	-0.938110	-0.772350
107	H	4.826610	-3.883310	-2.180390
108	H	4.780500	-3.036550	2.274070
109	C	3.180020	-0.014700	-0.724270
110	H	6.164360	-5.201470	-3.806940
111	C	5.910390	-3.819580	-2.175440
112	H	4.816900	-2.185600	-0.197450
113	C	5.864450	-2.969920	2.267660
114	H	6.079260	-3.635470	4.303730
115	C	6.665640	-4.559610	-3.089870
116	C	6.598640	-3.306110	3.409580
117	N	4.283450	0.353730	-0.719070

118	C	5.907340	-2.127170	-0.198520
119	C	6.561120	-3.001410	-1.267140
120	C	6.535130	-2.546200	1.132460
121	C	8.053420	-4.474910	-3.086100
122	C	7.985990	-3.216890	3.407670
123	C	5.663810	0.435640	-0.672380
124	C	6.422650	-0.717870	-0.455520
125	H	8.632370	-5.051370	-3.800310
126	C	7.959510	-2.915270	-1.264020
127	C	7.934770	-2.460710	1.130400
128	H	8.547640	-3.477080	4.299260
129	H	4.537280	2.977730	-1.058430
130	C	8.709100	-3.647960	-2.169660
131	C	8.663480	-2.792580	2.260610
132	H	4.350300	4.509570	1.000820
133	H	4.412910	3.932210	-3.437480
134	C	6.294290	1.666600	-0.855230
135	C	8.498130	-1.968200	-0.197030
136	C	5.626090	3.019620	-1.047620
137	C	7.811810	-0.633180	-0.442300
138	C	5.433020	4.582320	1.017530
139	C	5.497200	3.997480	-3.444910
140	H	9.792960	-3.576210	-2.167940
141	H	9.748620	-2.723210	2.253030

142	C	6.179420	3.896230	0.074950
143	C	6.215040	3.576700	-2.338540
144	C	7.687250	1.733400	-0.828290
145	H	11.030990	-3.169670	7.648550
146	H	9.587330	-1.885800	-0.205940
147	C	8.451890	0.590010	-0.615870
148	C	6.093240	5.351590	1.981480
149	H	5.517120	5.894530	2.723800
150	C	6.189100	4.492080	-4.554560
151	H	5.638210	4.823410	-5.428990
152	H	12.226260	-4.263580	6.944190
153	C	12.101260	-3.307470	7.462080
154	H	10.891560	-1.885580	5.423740
155	C	7.578680	3.970410	0.086060
156	C	7.614060	3.645450	-2.326010
157	H	9.764270	-0.160770	1.358000
158	C	8.223950	3.144370	-1.021050
159	H	12.603450	-3.382350	8.430530
160	H	12.079700	-2.969310	4.716060
161	O	9.816710	0.661170	-0.536280
162	C	11.971190	-2.026990	5.271310
163	H	10.742840	-0.655780	3.240240
164	C	7.481370	5.423280	1.994210
165	C	7.578170	4.557700	-4.545250

166	C	10.263210	0.660720	0.822580
167	C	12.659900	-2.157460	6.628380
168	C	8.234070	4.728760	1.041310
169	C	8.300420	4.132580	-3.425790
170	H	9.964910	1.602630	1.309930
171	H	11.970260	-1.677350	2.504300
172	C	11.825000	-0.748440	3.075140
173	H	12.550610	-1.214220	7.177980
174	H	9.315210	3.178470	-1.013590
175	H	7.985530	6.022690	2.745600
176	H	8.106750	4.941700	-5.412050
177	C	12.516620	-0.874560	4.430470
178	C	11.768310	0.485530	0.832730
179	H	12.012950	-0.440800	0.298150
180	H	13.737350	-2.299510	6.474120
181	H	9.319550	4.784910	1.046290
182	H	9.385710	4.181580	-3.418000
183	H	12.398600	0.066660	4.984540
184	C	12.337000	0.434830	2.251280
185	H	13.596820	-1.008690	4.279660
186	H	12.102620	1.370580	2.776300
187	H	12.219590	1.307680	0.266500
188	H	13.430950	0.382540	2.191990

Reference

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford, CT, 2016.

2. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc*. 2008, **120**, 215−241.

3. D. Andrae, U. Häußermann, M. Dolg, H. Stoll and H. Preuss, *Theor. Chim. Acta*, 1990, **77**, 123

4. T. Lu and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580-592.