

**Supplementary Information for**

**Synthesis and Assembling Properties of Bioorganometallic  
Cyclometalated Au(III) Alkynyls Bearing Guanosine Moieties**

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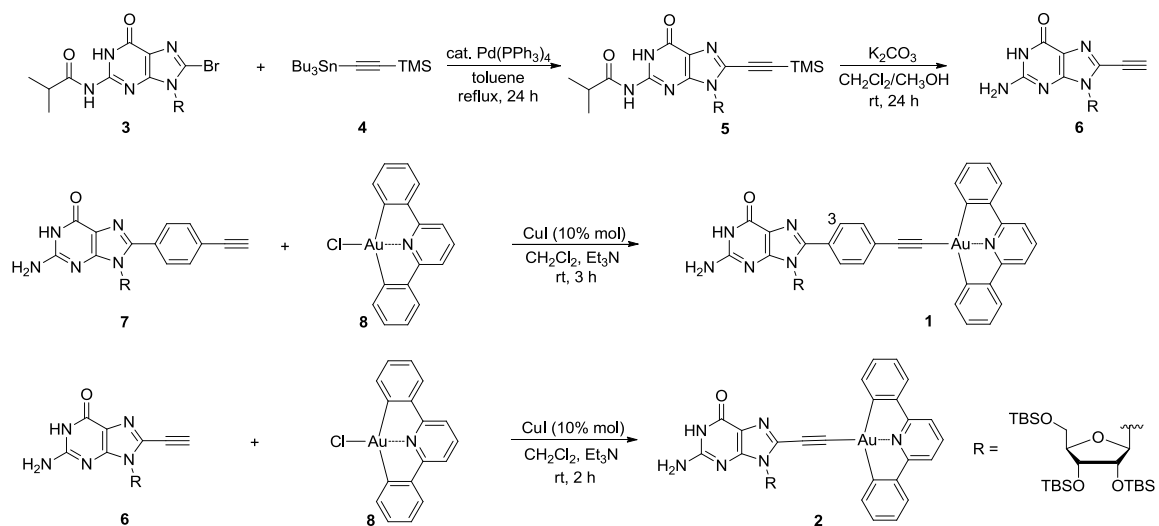
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**General Methods.**

All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary. Solvents employed were dried by refluxing in the presence of appropriate drying reagents and distilled under nitrogen. Analytical thin-layer chromatography (TLC) was performed on Merck TLC plate (silica gel 60 F254, 0.25 mm). Column chromatography was conducted on silica gel (Wakogel C-200). NMR spectra were recorded on a JNM-ECS 400 (400 MHz) and a Varian Unity INOVA 600 (600 MHz) spectrometer. Mass spectra were run on a JEOL JMS-700 or JMS-T100LC equipped with CSI source.

## Physical Measurements.

UV/vis spectra were obtained using a Hitachi U-3500 spectrophotometer in  $\text{CH}_2\text{Cl}_2$  solution with the concentration  $1.0 \times 10^{-4}$  M under argon at 298 K. UV-vis spectra were measured using 1 mm pathlength quartz cuvettes. Emission spectra were collected using a Shimadzu RF-5300PC spectrofluorophotometer in  $\text{CH}_2\text{Cl}_2$  solution with the concentration  $1.0 \times 10^{-4}$  M under argon. Emission spectra were measured using 5 mm pathlength quartz cuvettes. CD spectra of **1** were recorded using a JASCO J-720 spectropolarimeter in  $\text{CH}_2\text{Cl}_2$  solution with the concentration  $1.0 \times 10^{-4}$  M under argon at 298 K. CD spectra were measured using 5 mm pathlength quartz cuvettes.



**Procedure for the synthesis of 5.** A solution of **3** (200 mg, 0.26 mmol) and **4** (300 mg, 0.77 mmol) in dry toluene was purged with nitrogen for 40 min. To this solution was added  $\text{Pd}(\text{PPh}_3)_4$  (30 mg, 0.026 mmol) in one portion and the resulting solution was heated at reflux for 24 h under nitrogen. It was then cooled to room temperature, concentrated under reduced pressure, and then purified by column chromatography (silica gel, gradient eluent 3:1 hexane/ethyl acetate) to afford **5** (100 mg, 49%).  $^1\text{H}$  NMR (400 M,  $\text{CDCl}_3$ ):  $\delta$  11.93 (s, 1H); 7.74 (s, 1H); 6.05 (d,  $J = 6.7$  Hz, 1H); 4.97 (dd,  $J = 4.5, 6.7$  Hz, 1H); 4.39 (dd,  $J = 1.9, 4.4$  Hz, 1H); 4.03 (dd,  $J = 4.4, 10.1$  Hz, 1H); 3.87-3.94 (m, 1H); 3.77 (dd,  $J = 4.6, 10.6$  Hz, 1H); 2.56 (hept,  $J = 7.0$  Hz, 1H); 1.28 (s, 3H); 1.27 (s,

3H); 0.95 (s, 9H); 0.89 (s, 9H); 0.80 (s, 9H); 0.25 (s, 9H); 0.14 (s, 3H); 0.13 (s, 3H); 0.06 (s, 3H); 0.04 (s, 3H); -0.09 (s, 3H); -0.35 (s, 3H).  $^{13}\text{C}$  NMR (100 M,  $\text{CDCl}_3$ ): 177.77, 154.59, 147.34, 147.17, 134.16, 122.43, 102.79, 92.39, 89.07, 85.79, 72.52, 72.36, 62.91, 26.00, 25.96, 25.78, 18.51, 18.14, 17.90, -0.53, -4.34, -4.42ppm.

HRMS (MALDI)  $m/z$  calcd for  $\text{C}_{37}\text{H}_{69}\text{N}_5\text{O}_6\text{Si}_4\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ), 814.4217; found, 814.4207.

**Procedure for the synthesis of 6.** A mixture of **5** (100 mg, 0.13 mmol) and potassium carbonate (88.8 mg, 0.64 mmol) in tetrahydrofuran-dichloromethane (1:1 v/v, 8 ml) was stirred at room temperature for 18 h. The solvent was then removed under reduced pressure and the residue was dissolved in dichloromethane, washed with water, followed by dry over anhydrous  $\text{MgSO}_4$  and filtration. Removal of the solvent under reduced pressure gave a yellow oil, which was purified by column chromatography (silica gel, gradient eluent 20:1 dichloromethane/methanol) to afford **6** (70 mg, yield 85%).  $^1\text{H}$  NMR (400 M,  $\text{CDCl}_3$ ):  $\delta$  12.02 (s, 1H); 6.62 (br, 2H); 5.97 (d,  $J = 6.1$  Hz, 1H); 5.21-5.24 (m, 1H); 4.66 (dd,  $J = 2.3, 4.1$  Hz, 1H); 4.02-4.06 (m, 1H); 3.96-4.00 (m, 1H); 3.76 (dd,  $J = 4.2, 10.4$  Hz, 1H); 3.35 (s, 1H); 0.95 (s, 9H); 0.89 (s, 9H); 0.81 (s, 9H); 0.15 (s, 3H); 0.13 (s, 3H); 0.05 (s, 3H); 0.03 (s, 3H); -0.05 (s, 3H); -0.26 (s, 3H).  $^{13}\text{C}$  NMR (100 M,  $\text{CDCl}_3$ ): 158.53, 153.97, 151.27, 131.17, 117.93, 89.22, 85.65, 82.68, 72.80, 72.54, 71.94, 62.75, 26.02, 25.99, 25.81, 18.52, 18.21, 17.96, -4.38, -4.41, -4.47, -5.05, -5.20, -5.31.

HRMS (FAB)  $m/z$  calcd for  $\text{C}_{30}\text{H}_{55}\text{N}_5\text{O}_5\text{Si}_3\text{Na}$  ( $[\text{M}+\text{Na}]^+$ ), 672.3409; found, 672.3413.

**Procedure for the synthesis of 1.** A mixture of  $[\text{Au}(\text{C}^{\wedge}\text{N}^{\wedge}\text{C})\text{Cl}]$  (40 mg, 0.09 mmol) and **9** (94 mg, 0.13 mmol) in the presence of a catalytic amount of copper(I) iodide (1.8 mg) in triethylamine (0.4 ml) and dichloromethane (7 ml) was stirred at room temperature for 3 h. After removing all of the solvent, the residue was purified by column chromatography (silica gel, gradient eluent 20:1 dichloromethane/methanol) to afford **1** as a yellow solid (90 mg, yield 91%).  $^1\text{H}$  NMR (400 M,  $\text{DMSO-d}_6$ ):  $\delta$  10.78 (s, 1H); 8.11 (t,  $J = 7.9$  Hz, 1H); 7.91 (d,  $J = 8.0$  Hz, 2H); 7.82-7.88 (m, 4H); 7.54-7.62 (m, 4H); 7.35

(t,  $J = 7.2$  Hz, 2H); 7.27 (t,  $J = 7.4$  Hz, 2H); 6.33 (s, 2H); 5.78 (d,  $J = 7.8$  Hz, 1H); 5.46 (s, 1H); 4.16 (d,  $J = 3.8$  Hz, 1H); 3.84 (dt,  $J = 8.1, 12.4$  Hz, 2H); 3.69 (dd,  $J = 4.6, 10.2$  Hz, 1H); 0.84 (s, 9H); 0.83 (s, 9H); 0.68 (s, 9H); 0.05 (s, 3H); 0.04 (s, 3H); 0.03 (s, 6H); -0.11 (s, 3H); -0.33 (s, 3H).  $^{13}\text{C}$  NMR (100 M, DMSO): 166.51, 164.46, 157.15, 153.69, 150.00, 144.36, 136.27, 132.12, 131.79, 129.55, 128.64, 127.65, 126.66, 118.71, 117.88, 100.71, 96.14, 92.65, 87.81, 85.84, 72.94, 70.65, 63.15, 26.33, 26.15, 26.00, 18.50, 18.19, 18.06, -3.98, -4.20, -4.32, -4.77, -4.87, -4.91.

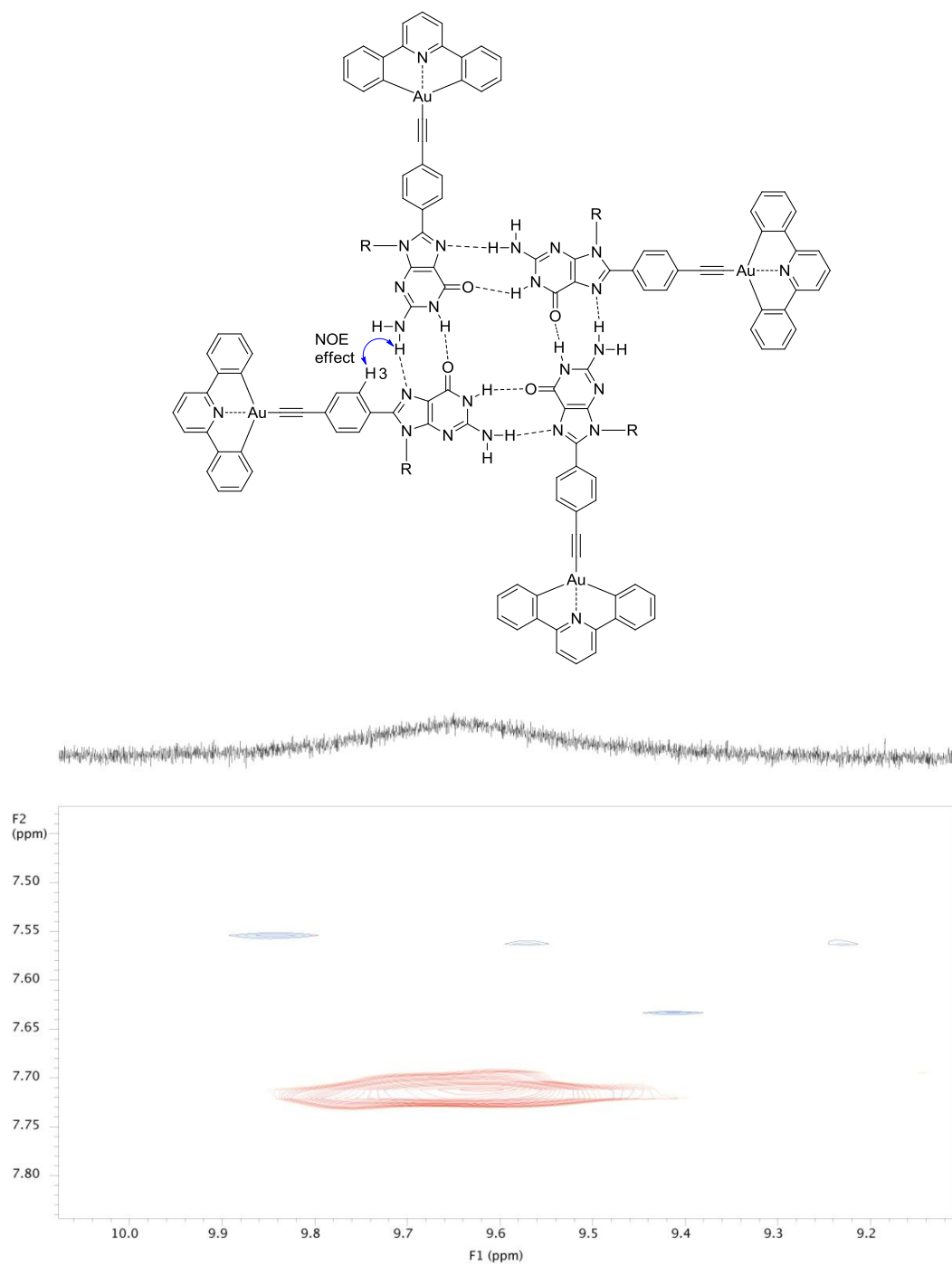
HRMS (FAB)  $m/z$  calcd for  $\text{C}_{53}\text{H}_{69}\text{N}_6\text{O}_5\text{Si}_3\text{NaAu}$  ( $[\text{M}+\text{Na}]^+$ ), 1173.4200; found, 1173.4174.

IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{C}\equiv\text{C})$ , 2152.

**Procedure for the synthesis of 2.** **2** was prepared similarly as mentioned with **1**. (yield 90%)  $^1\text{H}$  NMR (400 M, DMSO- $d_6$ ):  $\delta$  10.74 (s, 1H); 8.13 (t,  $J = 8.0$  Hz, 1H); 7.93 (d,  $J = 8.2$  Hz, 2H); 7.85 (dd,  $J = 1.6, 7.2$  Hz, 2H); 7.78 (dd,  $J = 2.0, 6.4$  Hz, 2H); 7.29 (p,  $J = 7.2$  Hz, 4H); 6.40 (s, 2H); 6.04 (d,  $J = 7.3$  Hz, 1H); 5.48 (br, 1H); 4.18 (d,  $J = 4.6$  Hz, 1H); 3.86 (dt,  $J = 8.3, 12.5$  Hz, 2H); 3.61 (dd,  $J = 4.1, 9.7$  Hz, 1H); 0.76 (s, 9H); 0.73 (s, 9H); 0.68 (s, 9H); 0.02 (s, 3H); 0.01 (s, 3H); -0.07 (s, 3H); -0.18 (s, 6H); -0.23 (s, 3H).

HRMS (FAB)  $m/z$  calcd for  $\text{C}_{53}\text{H}_{69}\text{N}_6\text{O}_5\text{Si}_3\text{NaAu}$  ( $[\text{M}+\text{Na}]^+$ ), 1097.3887; found, 1097.3910.

IR (KBr,  $\text{cm}^{-1}$ ):  $\nu(\text{C}\equiv\text{C})$ , 2156.



**Figure S1.** NOESY of **1** in CD<sub>2</sub>Cl<sub>2</sub> at -25 °C.

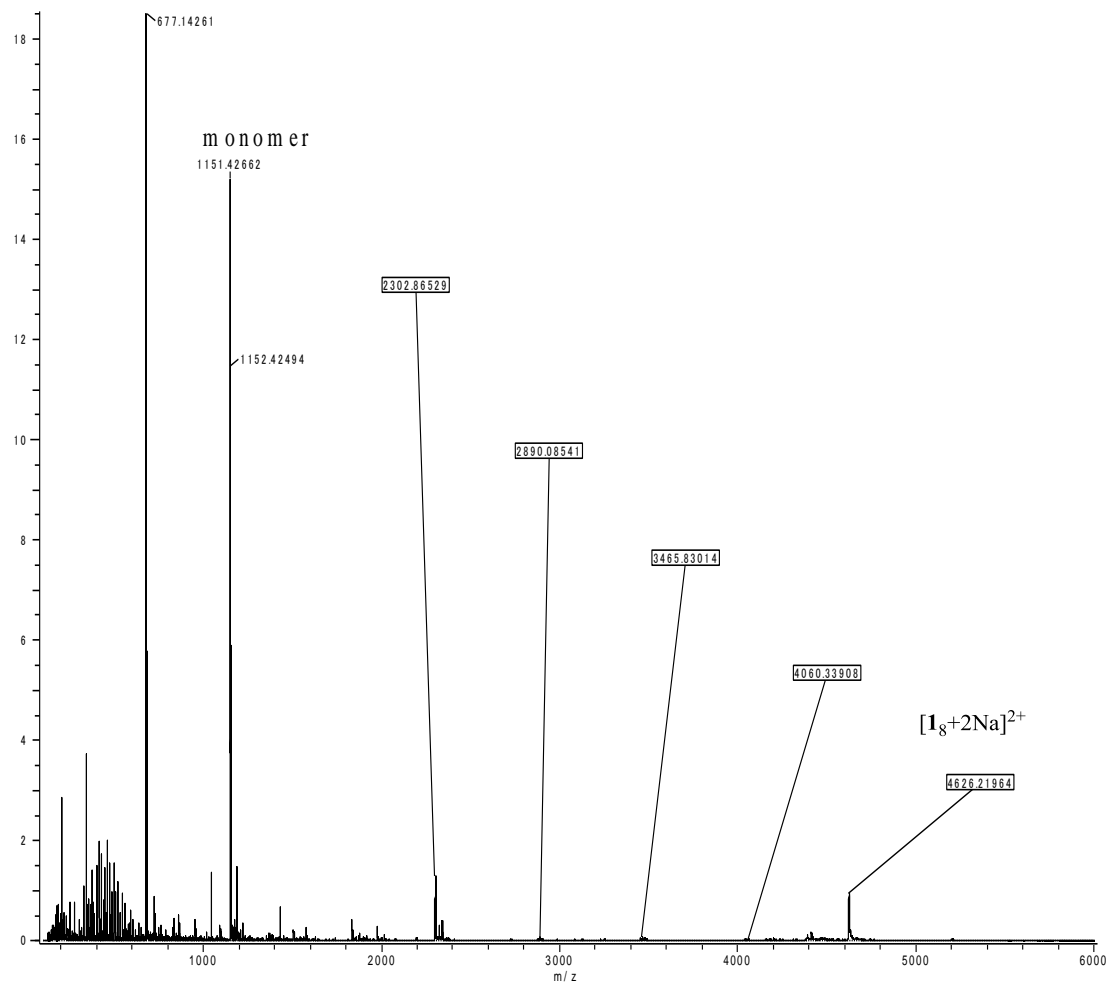


Figure S2. The CSI-TOF mass spectrum of the octamer.

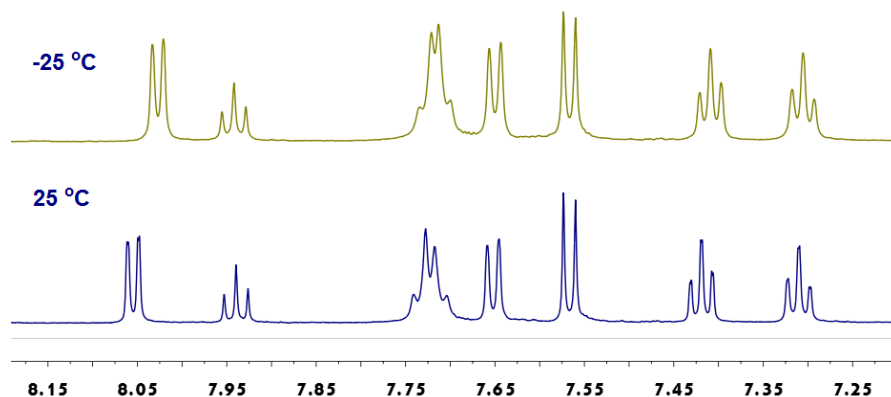


Figure S3. The aromatic part of  $^1\text{H}$  NMR spectrum of **1** in the absence of  $\text{KPF}_6$  in  $\text{CD}_2\text{Cl}_2$ .

**Table S1** Hydrogen Bonds for **5**

crystal	type <sup>a</sup>	donor	acceptor	D···A (Å)	D–H···A (°)
<b>5</b>	intra	N(1)	O(6)	2.651(7)	129(3)
	inter	N(5)	O(5)'	2.946(7)	162(4)

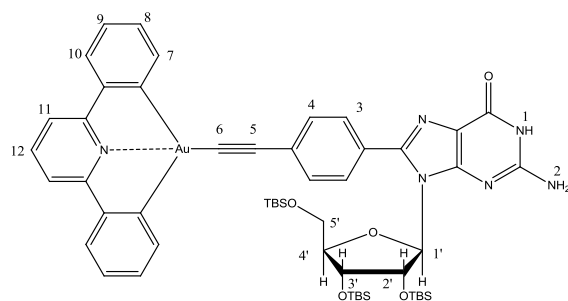
<sup>a</sup> intra: intramolecular; inter: intermolecular

**Table S2** Crystallographic data for **5**

<b>5</b>	
Empirical formula	$\text{C}_{37}\text{H}_{69}\text{N}_5\text{O}_6\text{Si}_4$
Formula weight	792.32
Crystal system	orthrhombic
Space group	$Pca2_1$ (No. 29)
<i>a</i> [Å]	9.8453(2)
<i>b</i> [Å]	13.7667(3)
<i>c</i> [Å]	35.6430(7)
$\beta$ [deg]	
<i>V</i> [Å <sup>3</sup> ]	4831.0(2)
<i>Z</i>	4
<i>D</i> <sub>calcd</sub> [g cm <sup>-3</sup> ]	1.089
$\mu$ (Mo $K\alpha$ ) [cm <sup>-1</sup> ]	
$\mu$ (Cu $K\alpha$ ) [cm <sup>-1</sup> ]	14.865
<i>T</i> [°C]	-70
$\lambda$ (Mo $K\alpha$ ) [Å]	
$\lambda$ (Cu $K\alpha$ ) [Å]	1.54187
<i>R</i> <sub>1</sub> <i>a</i>	0.0718
<i>wR</i> <sub>2</sub> <i>b</i>	0.1962

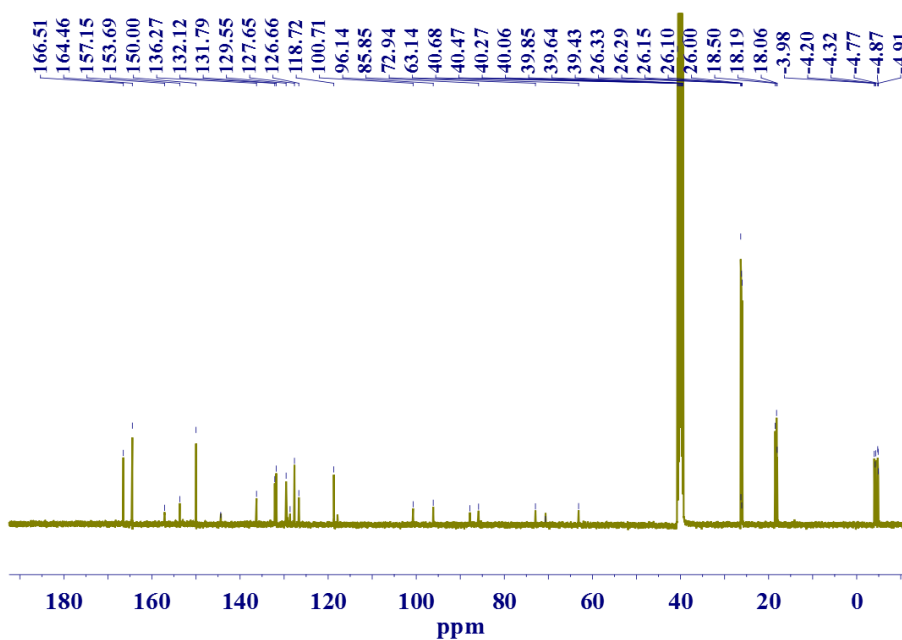
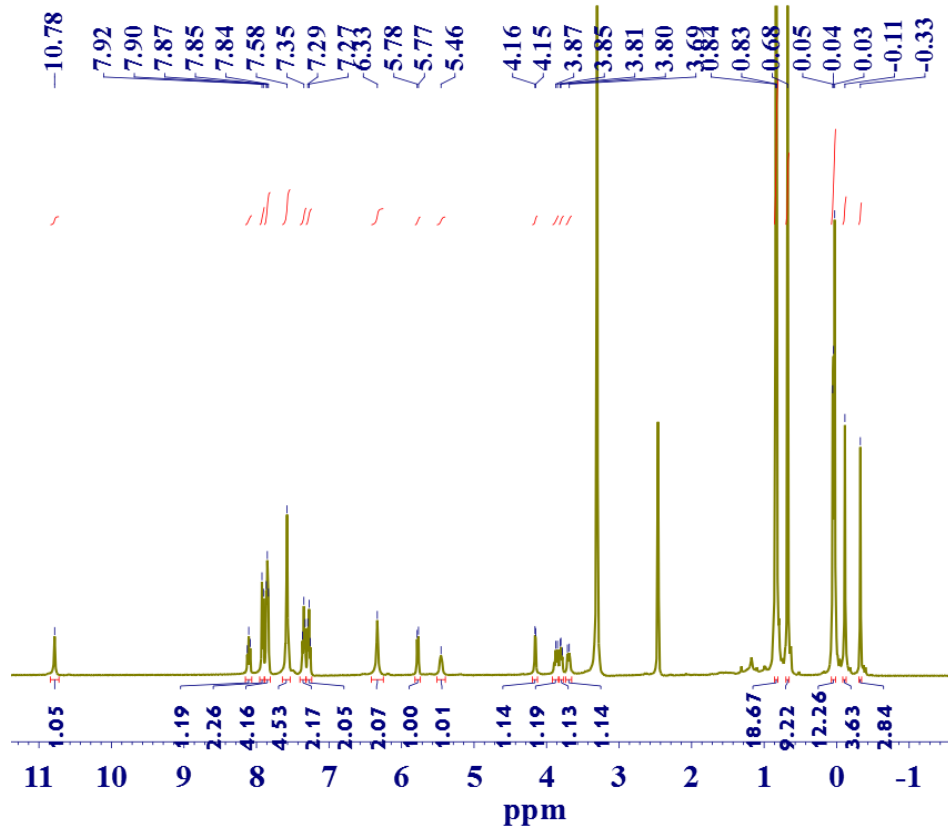
<sup>a</sup>  $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ . <sup>b</sup>  $wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]}{1/2}$ .

**Table S3.** Assignment  $^1\text{H}$  and  $^{13}\text{C}$  NMR of **1** in  $\text{CD}_2\text{Cl}_2$  at room temperature.



proton	$\delta$ (CD <sub>2</sub> Cl <sub>2</sub> , ppm)	
NH	12.45	-
NH <sub>2</sub>	6.6-6.8	-
H1'	5.90	88.78
H2'	5.49	71.52
H3'	4.49	72.40
H4'	3.99	85.24
H5'	3.79, 3.99	62.76
3,4	7.71-7.75	131.85, 129.14
7	7.59	12.26
8	7.27	126.82
9	7.38	131.85
10	7.52	117.01
11	7.89	136.39
12	8.02	142.49
5	-	100.48
6	-	94.84





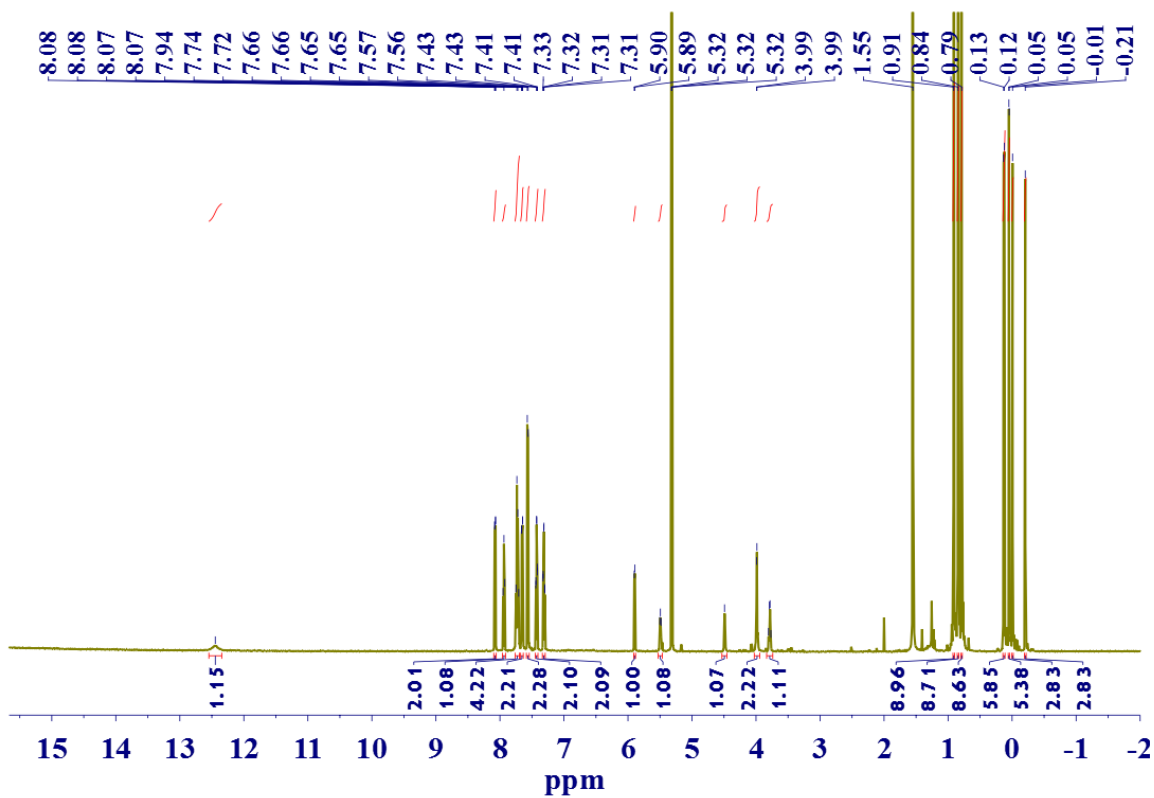


Figure S6. <sup>1</sup>H NMR of 1 in CD<sub>2</sub>Cl<sub>2</sub>.

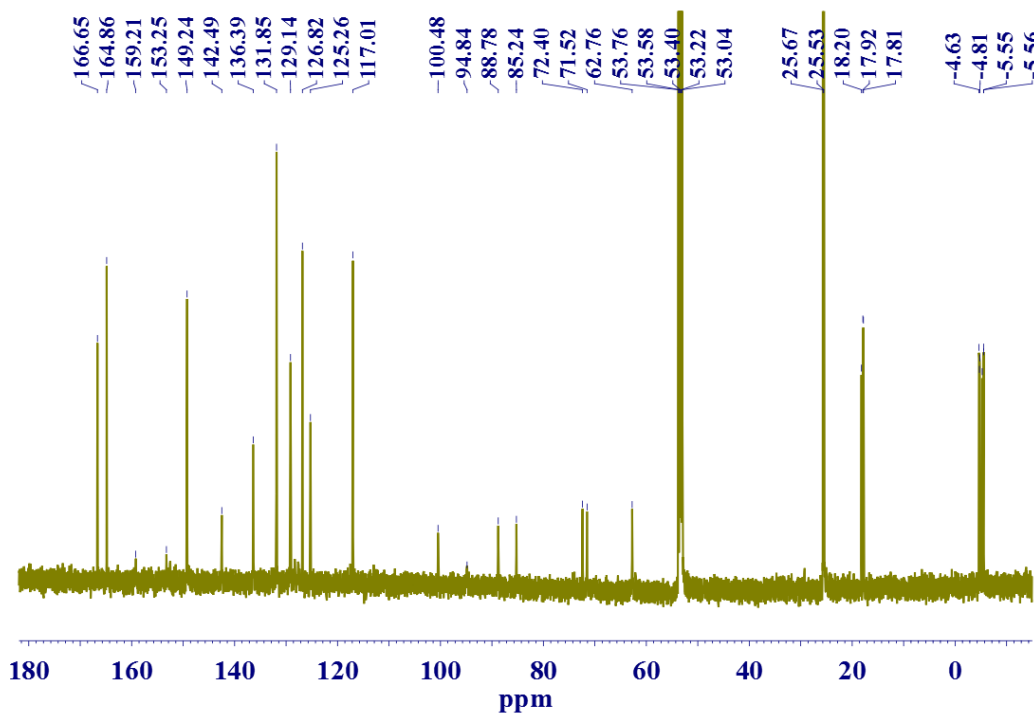
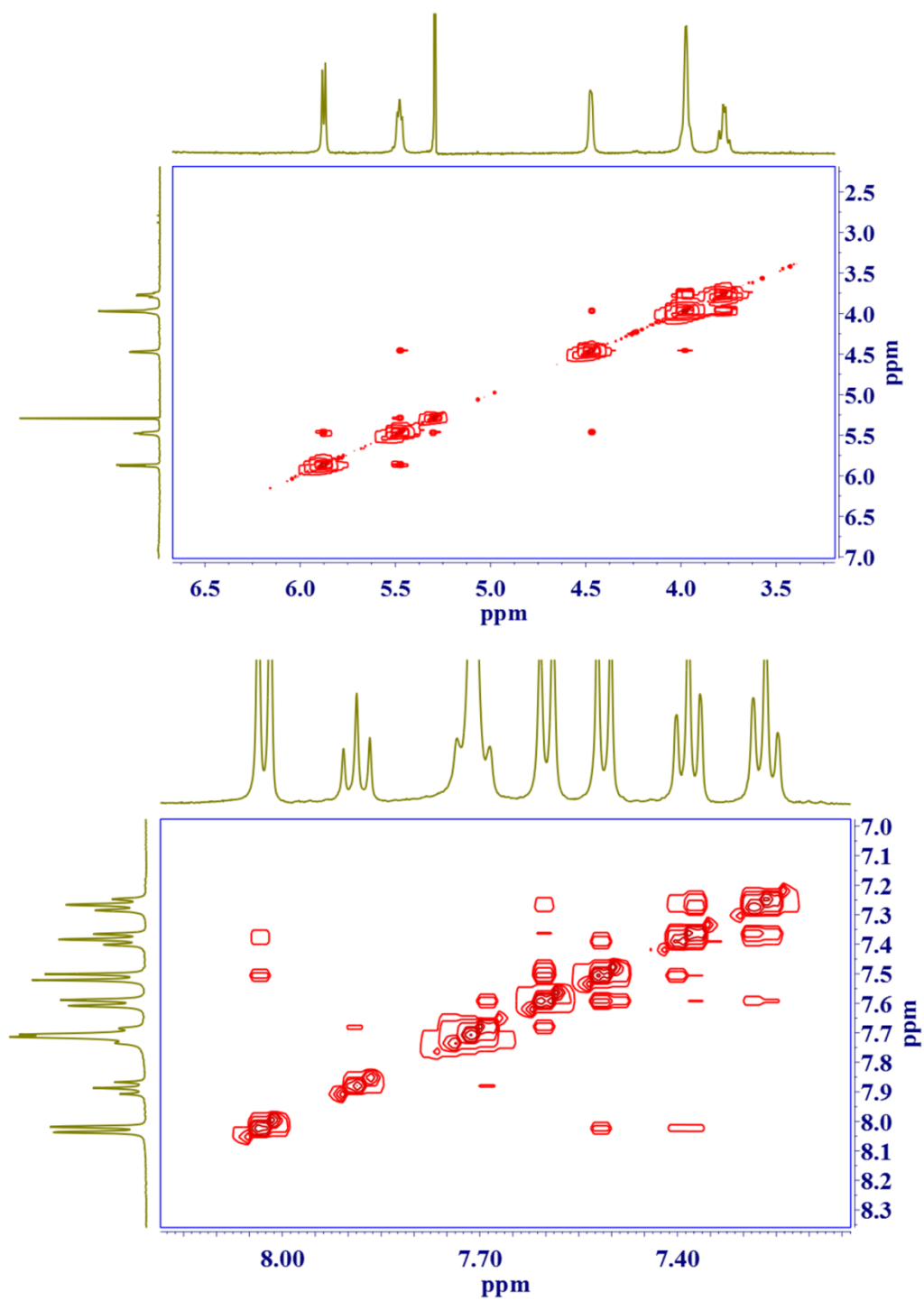
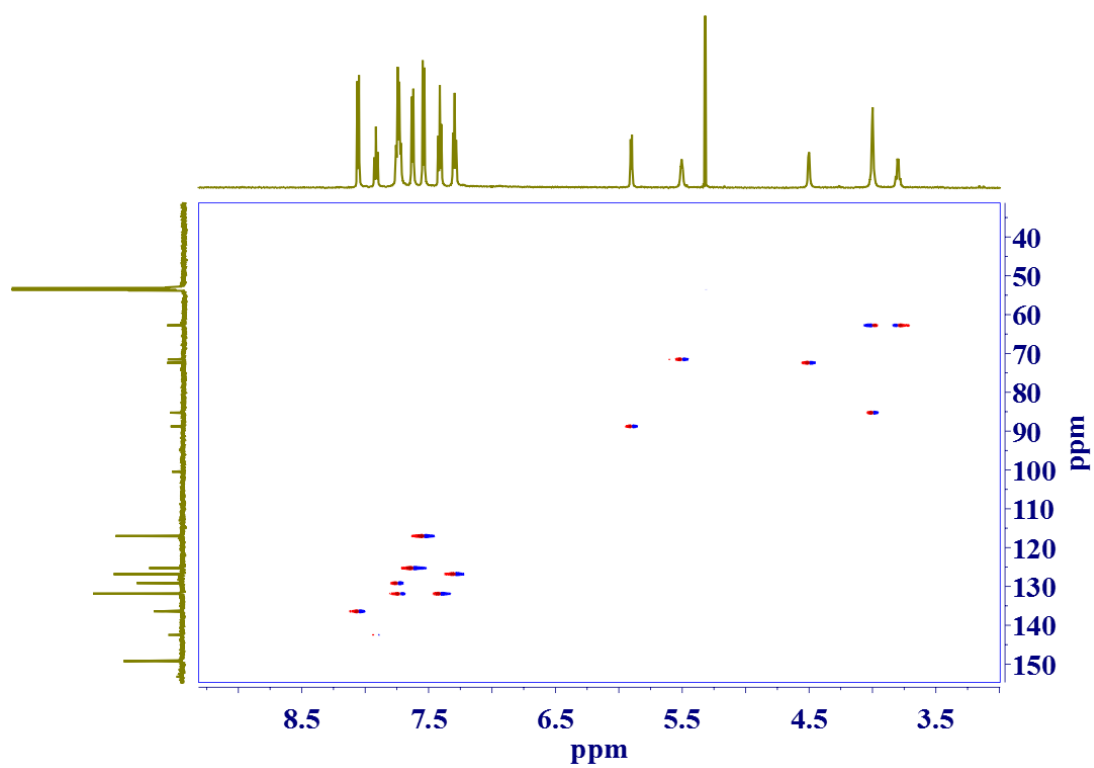


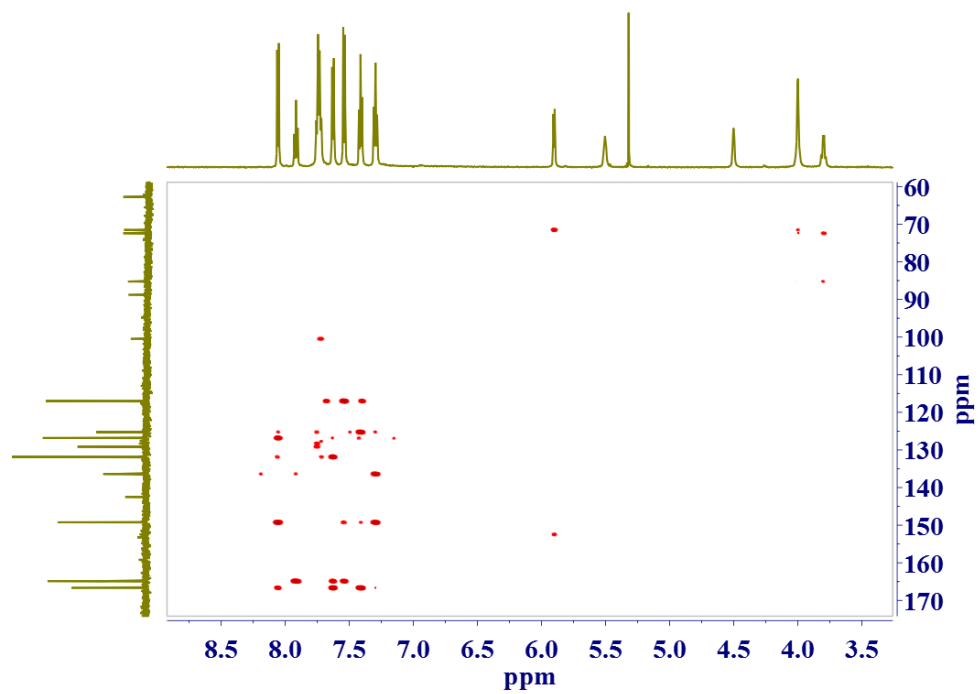
Figure S7. <sup>13</sup>C NMR of 1 in CD<sub>2</sub>Cl<sub>2</sub>.



**Figure S8.**  $^1\text{H}$ - $^1\text{H}$  COSY of **1** in  $\text{CD}_2\text{Cl}_2$ .



**Figure S9.** HSQC of **1** in CD<sub>2</sub>Cl<sub>2</sub>.



**Figure S10.** HMBC of **1** in CD<sub>2</sub>Cl<sub>2</sub>.