Supporting Information

Weaving an infinite 3-D supramolecular network *via* $Au^{I}\cdots Au^{III}$ aurophility and C-H···Cl hydrogen bonding

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Contents

General information

All manipulations were performed under a nitrogen atmosphere using standard Schlenk or glovebox techniques. Acetonitrile and dichloromethane were distilled from CaH_2 before use. Diethyl ether was dried by distillation from sodium benzophenone prior to use. All reagents were obtained from commercial sources and used as received without further purification. ^1H NMR and ^{13}C NMR spectra were obtained at room temperature using Bruker Avance 500 and 600 MHz spectrometers. IR data were obtained as KBr on a Bruker Alpha-T FTIR spectrometer. Mass spectra were acquired on a Finnigan TSQ 700 spectrometer. Elemental analyses were performed on a HERAEUS CHN-O-S-Rapid elemental analyzer by Instruments Center, National Chung Hsin University. Solid state emission spectra were recorded on a Variable Temperature Photoluminescence Spectrometer (HORIBA JOBIN YVON Fluorolog-3). Molar conductance was carried out on a JENCO_EC3840

X-ray Crystallographic Analysis of 1-5.

Crystal data collection and processing parameters are given in Table S1. Diffraction data were carried out on a Bruker APEX2 CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.7107 Å). The structures **1-5** were solved by direct methods and refined by full-matrix least-squares procedures using the SHELXL-97 program. All of the non-hydrogen atoms were refined with anisotropic temperature factors. All hydrogen atoms were located geometrically and refined in the riding mode. Note that Checkcif /PLATON report for **5** suggests possible pseudo/new *P*nnm space group. We thus try to transform from $P2_1/n$ to *P*nnm and to solve from beginning but the structure cannot be refined by using the suggested space group. Additional crystallographic data as CIF files are available as Supporting Information.

Table S1 X-ray crystallographic data for complexes **1** – **5**.

	1	**2**	**3**	**4**	**5**
Empirical Formula	$C_6H_{10}N_2AuCl$	$C_{12}H_{20}N_5AuO_3$	$C_{12}H_{20}N_4AuBF_4$	$C_{12}H_{20}N_4AuSbF_6$	$C_{12}H_{20}N_4Au_2Cl_4$
Formula weight	342.58	479.30	504.10	653.04	756.05
T (K)	200(2)	200(2)	200(2)	200(2)	200(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	*Pbca*	$P2_1/m$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a (Å)	7.3641(7)	8.4029(5)	8.5936(14)	7.450(2)	6.6824(4)
b (Å)	13.8244(19)	20.7542(11)	13.854(2)	7.938(2)	8.2695(5)
c (Å)	16.9502(19)	13.5645(8)	14.342(2)	8.481(3)	17.5884(10)
α (°)	90	90	77.941(2)	89.041(7)	90
β (°)	90	99.439(2)	82.224(3)	84.027(7)	90.010(2)
γ (°)	90	90	77.872(3)	68.263(5)	90
V (Å^3)	1725.6(3)	2333.6(2)	1625.0(5)	463.2(2)	971.94(10) Å
Z	8	6	4	1	2
Dcalc (Mg m^{-3})	2.637	2.046	2.060	2.341	2.583
μ (mm^{-1})	17.289	9.474	9.093	9.425	15.627
F(000)	1248	1380	960	304	692
θ range for data collection	2.95–25.00°	2.65–25.05°	1.46–25.00°	2.42–25.10°	2.72– 25.02°
Reflections collected	8170	15858	13731	3791	6807
Independent reflections (R_{int})	1510 (0.0585)	4207 (0.0457)	5656 (0.0295)	1621(0.0532)	1709 (0.0349)
Data / restraints / parameters	1510 / 0 / 91	4207 / 0 / 325	5656 / 0 / 403	1621 / 0 / 112	1709 / 0 / 103
Goodness-of-fit on F^2	1.021	1.117	1.082	1.158	1.037
R_1, wR_2	0.0357, 0.0629	0.0323, 0.0767	0.0314, 0.0768	0.0531, 0.1368	0.0288, 0.0517
CCDC No.	1008362	1427451	1427452	1427453	1427454

1. Synthesis of [Au(L)Cl] (1)

A 4 ml CH_2Cl_2 solution of AuCl (0.146 g, 0.628 mmol) and 1,3,5-trimethyl-1H-pyrazole (0.069 g, 0.628 mmol) was stirred at room temperature for 1 h under N_2. After the addition of 10 ml hexane, the white precipitates formed was filtered and washed by hexane for two times. The resulting white solid was dried under vacuum to yield 0.201 g (93.1 %). Single crystals of **1** were grown from layer CH_2Cl_2/hexane at room temperature. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 5.99 (s, H, C*H*), δ3.79 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.23 (s, 3H, CH_3) ppm. ^{13}C NMR (150.91 MHz, CD_2Cl_2, 300 K): δ 150.42, 143.40, 107.05, 37.51, 14.76, 12.49 ppm. Anal. Calc. for $C_6H_{10}N_2AuCl$ (**1**): C, 21.04; H, 2.99; N, 8.18. Found: C, 20.88; H, 2.80; N, 8.16. Molar conductance, Λ_M (CH_2Cl_2, 298 K) = 6.3 $\Omega^{-1}cm^2mol^{-1}$.

2. Synthesis of [Au(L)$_2$](NO$_3$) (2)

A 10 ml CH_2Cl_2 solution of **1** (0.109 g, 0.318 mmol) and $AgNO_3$ (0.054 g, 0.318 mmol), was stirred for 1h under N_2. The white precipitates formed was filtered off and the resulting solution was dried under vacuum to yield 0.120 g (76.9 %). Single crystals of **2** were grown from layer CH_2Cl_2/hexane at room temperature. Elemental analysis: Anal. Calc. for $C_{12}H_{20}AuO_3N_5$: C, 30.07; H, 4.21; N, 14.61. Found: C, 30.36; H, 4.32; N, 14.88. Positive ESI/MS: 417.14 ([M–NO_3]$^+$, 100%). ^{1}H NMR (600MHz, 300K, CD_2Cl_2): δ 6.12 (s, 2H, 2C*H*), 3.95 (s, 6H, 2CH_3), 2.39 (s, 6H, 2CH_3), 2.36 (s, 6H, 2CH_3) ppm. ^{13}C NMR (150.91MHz, 300K, CD_2Cl_2): δ151.19, 145.26, 107.71, 14.73, 12.53 ppm. Λ_M (CH_2Cl_2, 298 K) = 60.9 $\Omega^{-1}cm^2mol^{-1}$.

3. Synthesis of [Au(L)$_2$](BF$_4$) (3)

A 10 ml CH_2Cl_2 solution of **1** (0.078 g, 0.228 mmol) and $AgBF_4$ (0.044 g, 0.228 mmol), was stirred 1h under N_2. The white precipitates formed was filtered off and the resulting solution was dried under vacuum to yield 0.101 g (87.7 %). Single crystals of **3** were grown from layer CH_2Cl_2/hexane at room temperature. Positive ESI/MS: 417.22 ([M–BF_4]$^+$, 100 %). Elemental analysis: Anal. Calc. for $C_{12}H_{20}N_4AuBF_4$: C, 28.59; H, 4.00; N: 11.11. Found: C, 28.78; H, 3.86; N, 11.32. ^{1}H NMR (600MHz, 300K, CD_2Cl_2): δ 6.12 (s, 2H, 2C*H*), 3.92 (s, 6H, 2CH_3), 2.40 (s, 6H, 2CH_3), 2.36 (s, 6H, 2CH_3) ppm. ^{13}C NMR (150.91MHz, 300K, CD_2Cl_2): δ 151.22, 145.31, 107.73, 14.71, 12.49 ppm. Λ_M (CH_2Cl_2, 298 K) = 69.4 $\Omega^{-1}cm^2mol^{-1}$

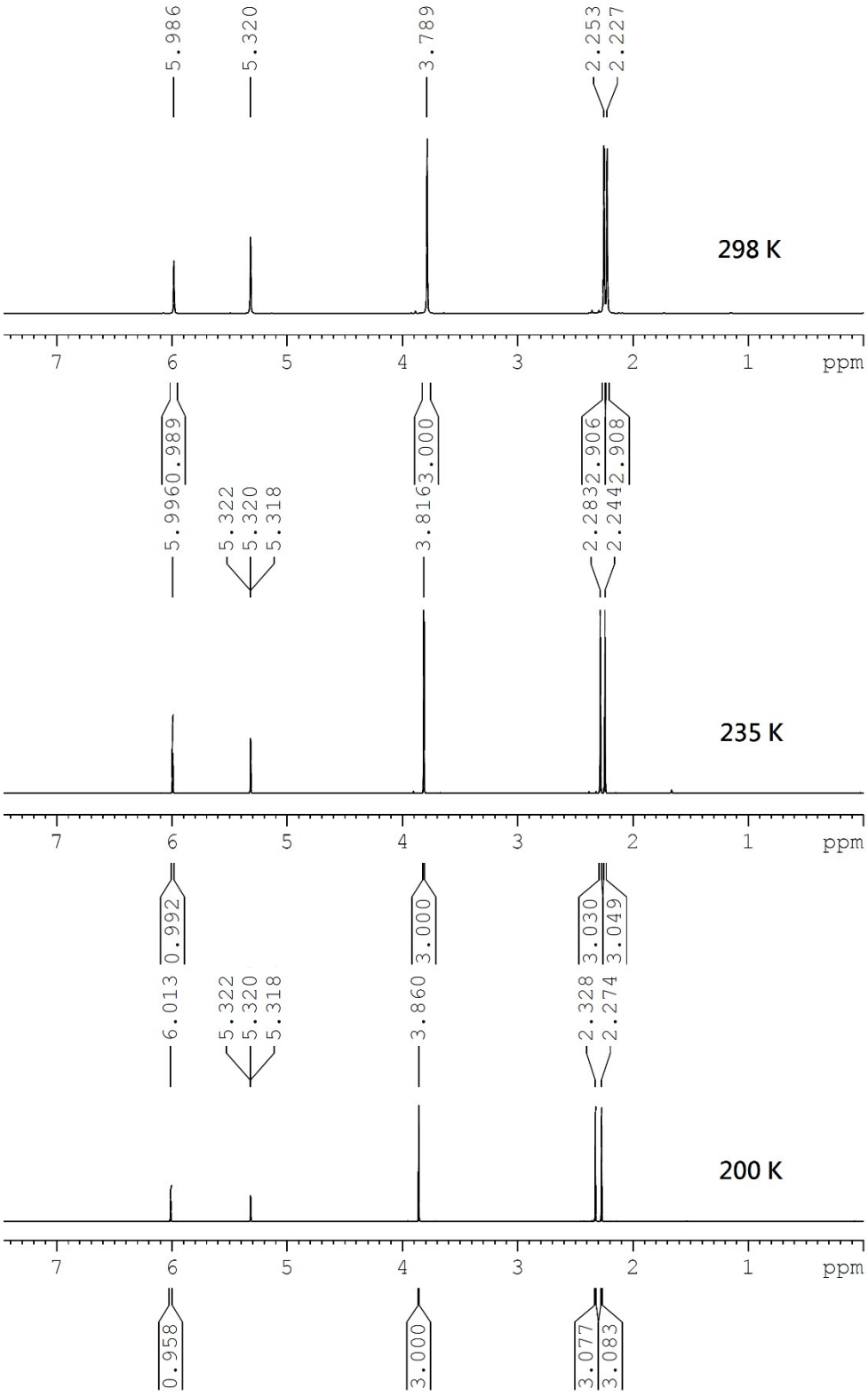
4. Synthesis of [Au(L)$_2$](SbF$_6$) (4)

A 10ml CH_2Cl_2 solution of **1** (0.203 g, 0.593 mmol) and $AgSbF_6$ (0.125 g, 0.593 mmol mol) was stirred for 0.5 h under N_2. The white precipitates formed was filtered off and resulting solution was dried under vacuum to give light yellow solid 0.382 g

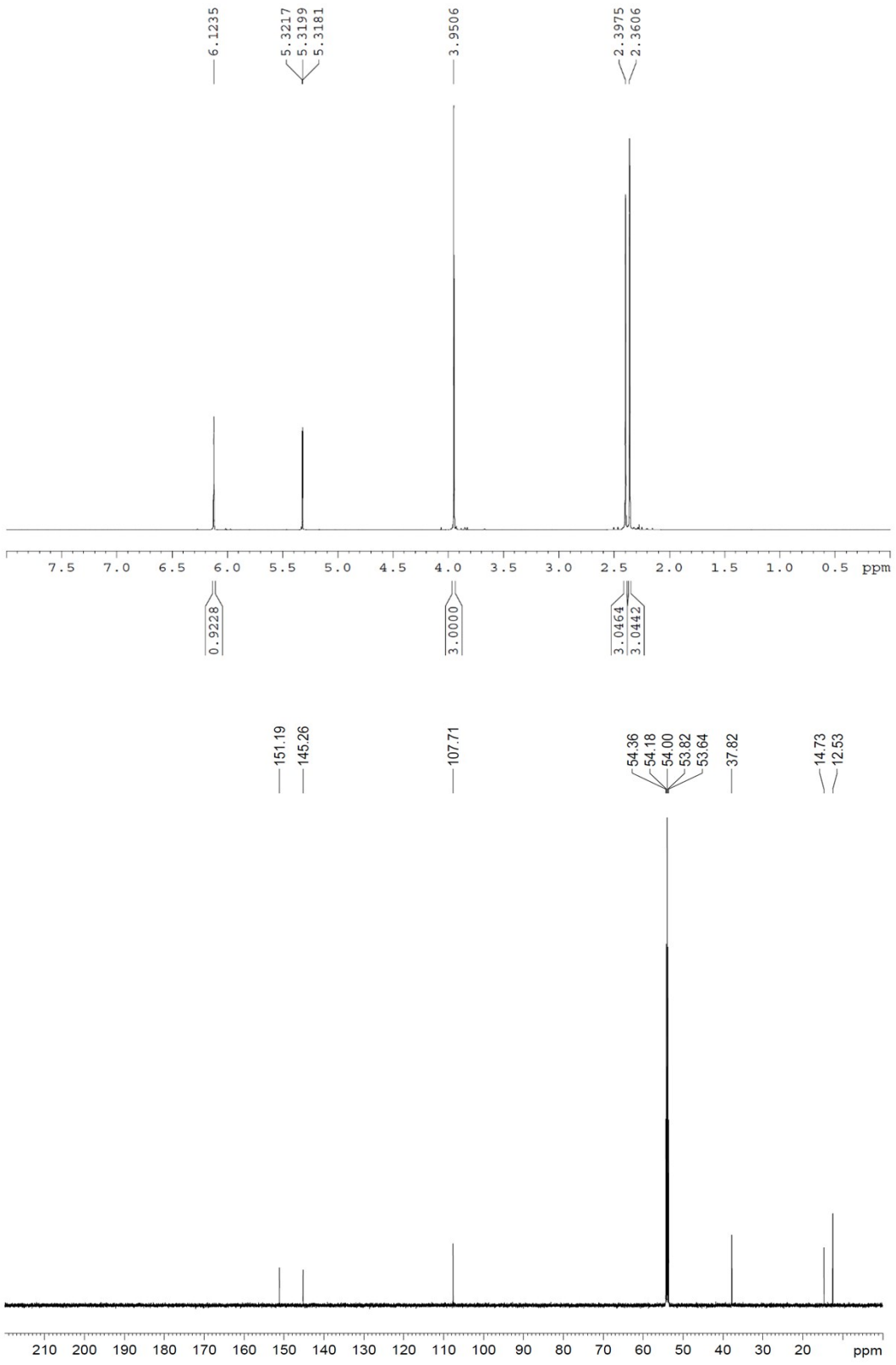
(98.4 %). Single crystals of **4** were grown from layer CH_2Cl_2/hexane at room temperature. ^{1}H NMR (600MHz, 300K, CD_2Cl_2): δ 6.13 (s, 2H, 2C*H*), δ 3.91 (s, 6H, 2CH_3), 2.40 (s, 6H, 2CH_3), 2.36 (s, 6H, 2CH_3) ppm. ^{13}C NMR (150.92MHz, 300K, CD_2Cl_2): δ 151.35, 145.32, 107.8, 37.73, 14.74, 12.53 ppm. Positive ESI/MS: 417.4 ($[M–SbF_6]^+$, 100 %). Elemental analysis: Anal. Calc. for $C_{12}H_{20}N_4AuSbF_6$: C, 22.07; H, 3.09; N, 8.58. Found: C, 22.06; H, 2.67; N, 8.60. Λ_M (CH_2Cl_2, 298 K) = 67.7 $\Omega^{-1}cm^2mol^{-1}$

5. Synthesis of $[Au(L)_2](AuCl_4)$ (5)

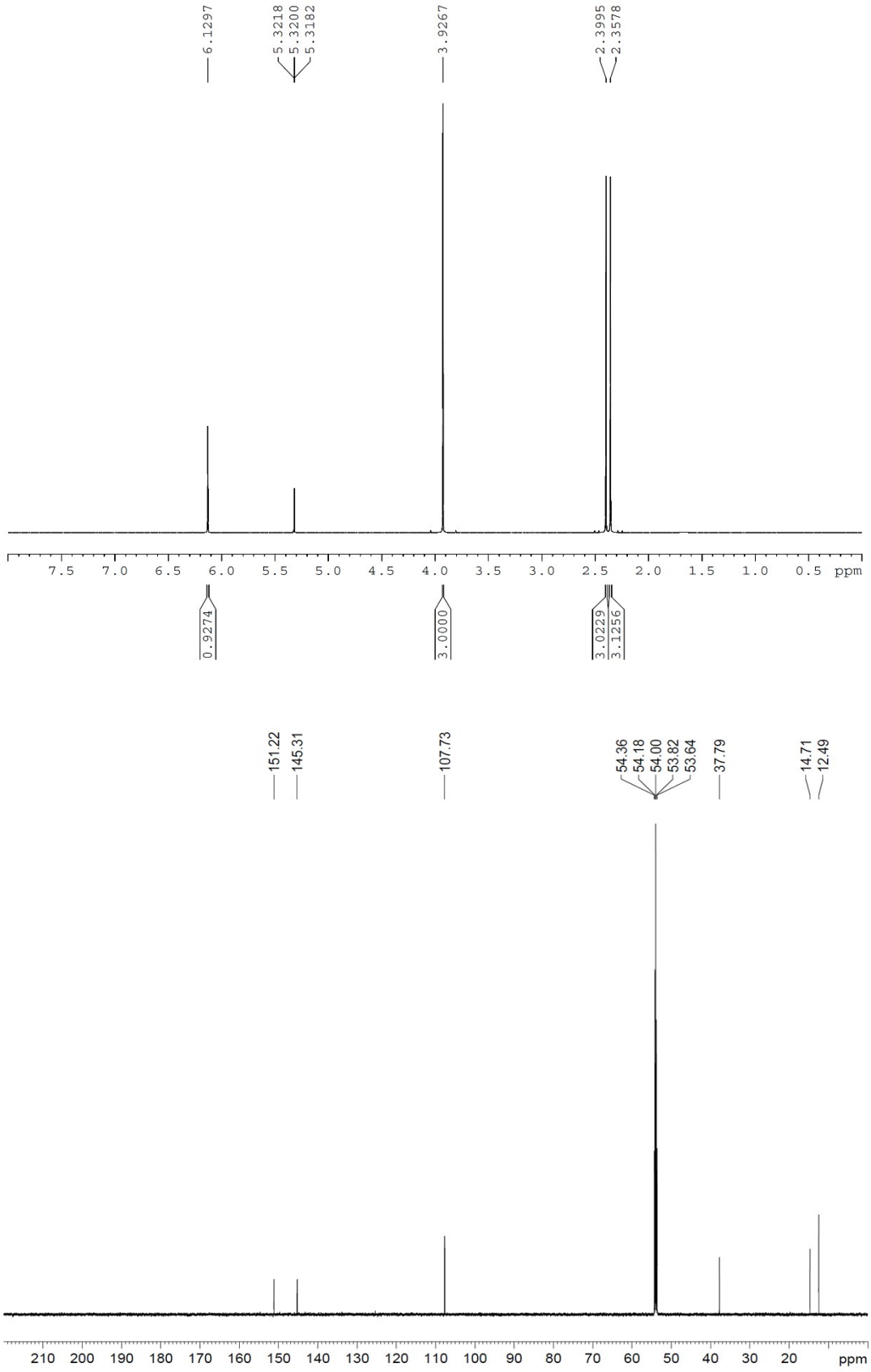
A 5 ml CH_2Cl_2 solution of **1** (0.199 g, 0.580 mmol) and $Na[AuCl_4]•2H_2O$ (0.231 g, 0.580 mmol), was stirred for 2 h under N_2. The precipitates formed was filtered off and the filtrate was added 10 ml hexane to give yellow precipitates. The yellow solid was filtered and dried under vacuum to yield 0.381 g (87.0 %). Single crystals of **5** were grown from layer CH_2Cl_2/hexane at room temperature. ^{1}H NMR (600MHz, 300K, CD_2Cl_2): δ 6.01 (s, 2H, 2C*H*), δ 3.86 (s, 6H, 2CH_3), 2.34 (s, 6H, 2CH_3), 2.27 (s, 6H, 2CH_3) ppm. ^{13}C NMR (150.92MHz, 300K, CD_2Cl_2): δ 150.42, 143.40, 107.05, 37.51, 14.76, 12.50 ppm. Positive ESI-MS: 417.14 ($[M–AuCl_4]^+$, 100 %). Elemental analysis: Anal. Calc. for $C_{12}H_{20}N_4Au_2Cl_4$: C, 19.06; H, 2.67; N, 7.41. Found: C, 18.95; H, 2.60; N, 7.59. Λ_M (CH_2Cl_2, 298 K) = 69.0 $\Omega^{-1}cm^2mol^{-1}$



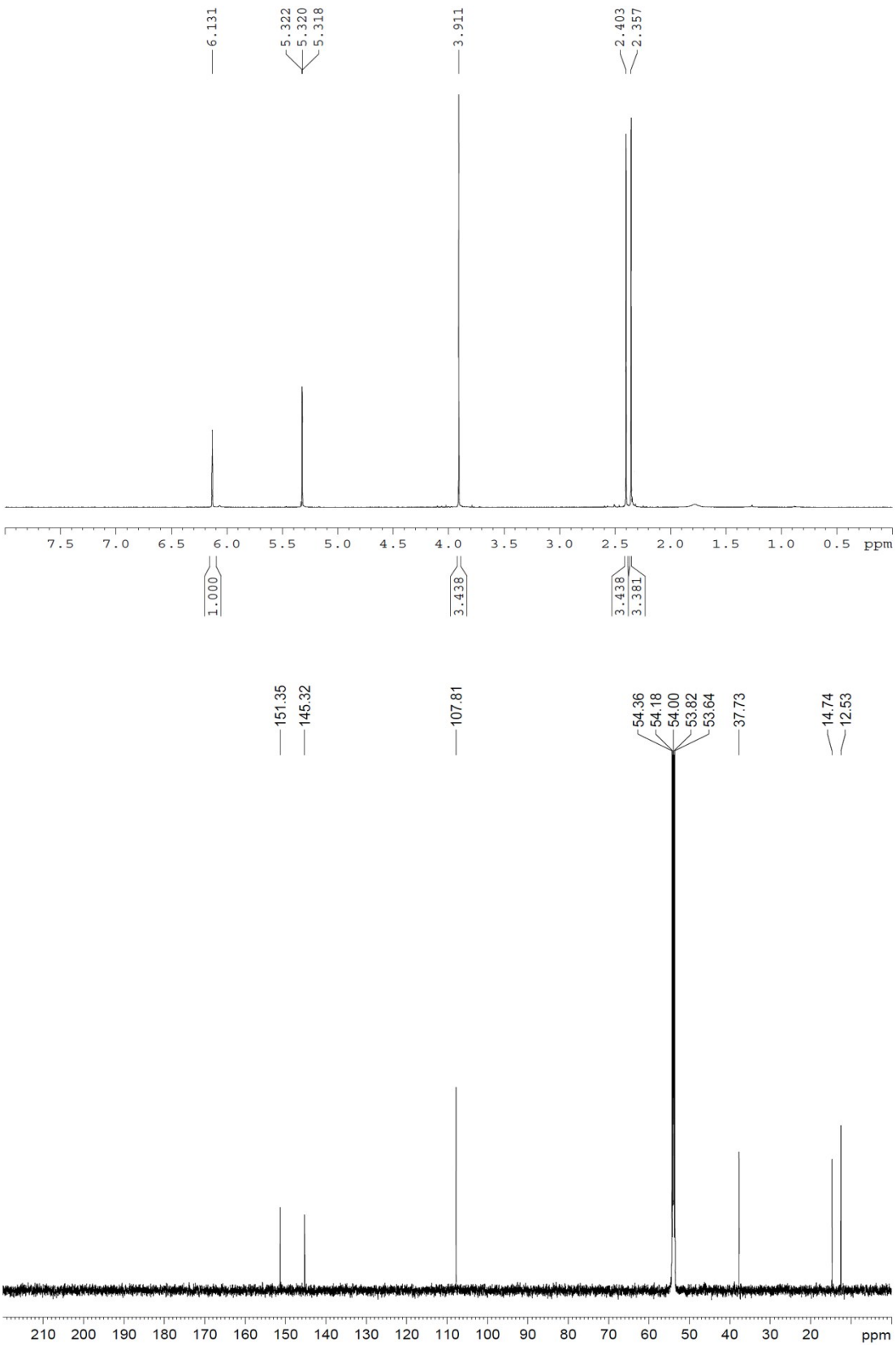
6. Figure S1 Variable-temperature ^{1}H NMR spectra of **1**



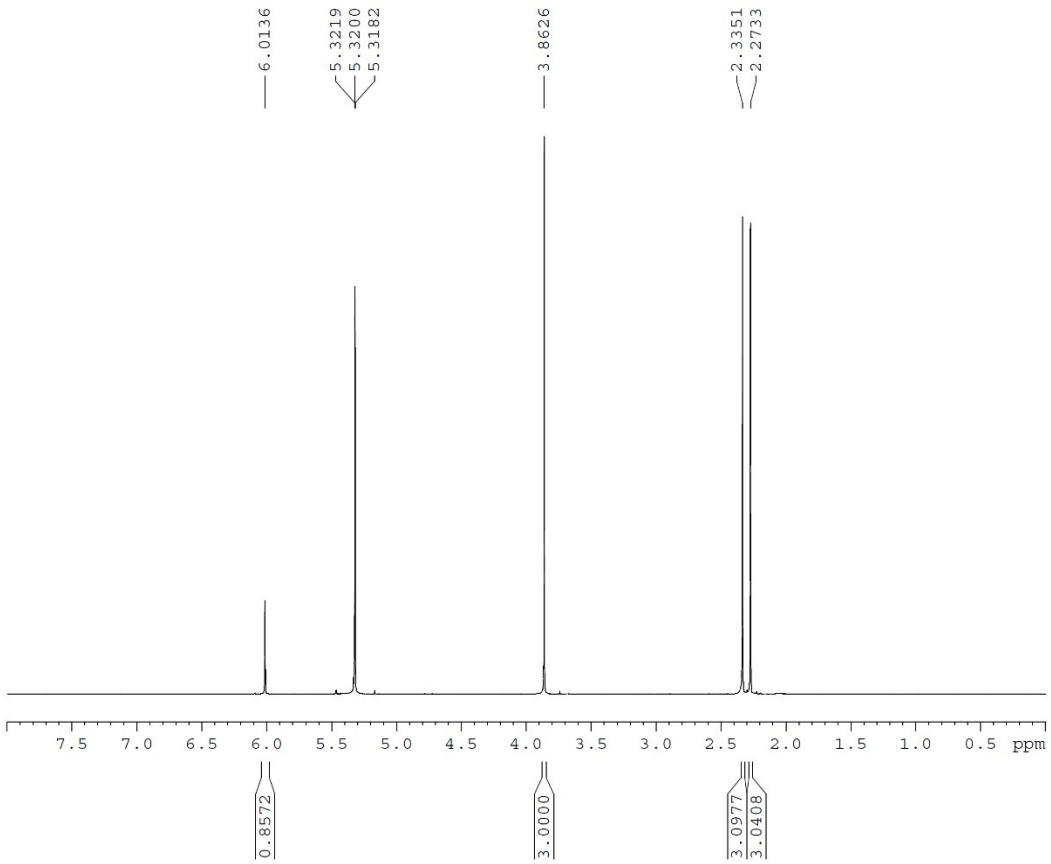
7. Figure S2 ^{1}H & ^{13}C NMR spectra of **2**



8. Figure S3 ^{1}H & ^{13}C NMR spectra of **3**



9. Figure S4 ^{1}H & ^{13}C NMR spectra of **4**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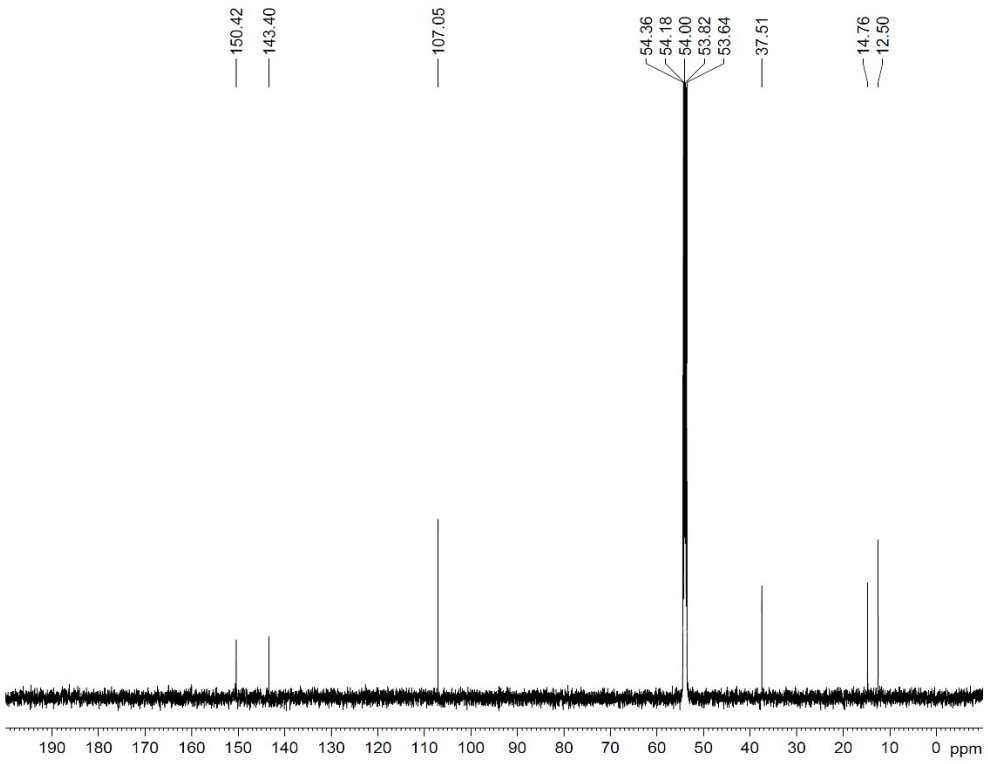
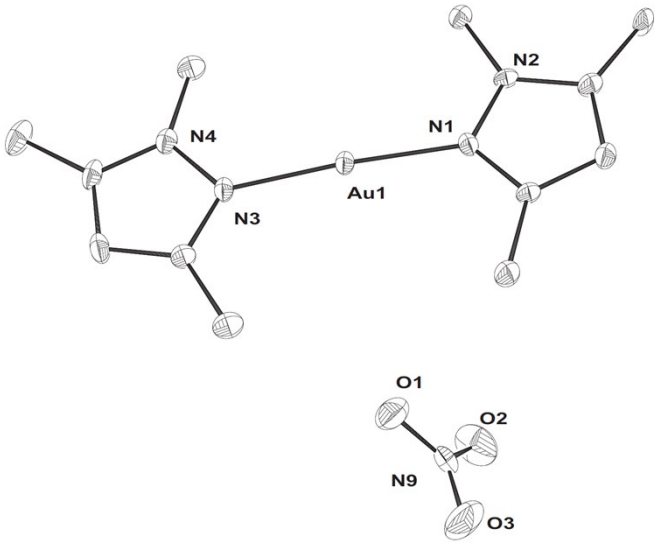
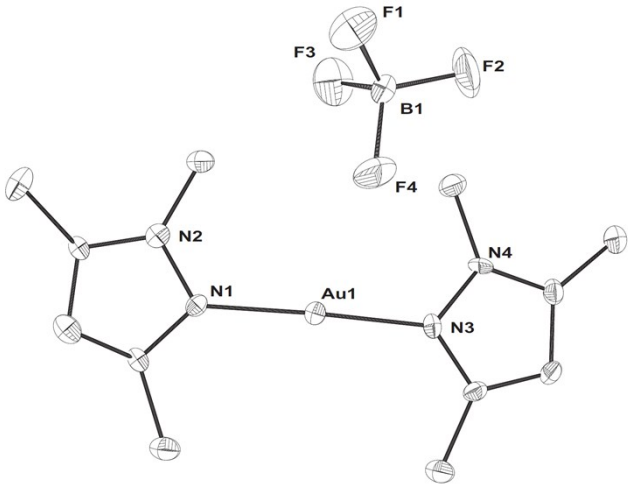
5.3219
5.3200
5.3182
3.8626
2.3351
2.2733
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.8572
3.0000
3.0977
3.0408


150.42
143.40
107.05
54.36
54.18
54.00
53.82
53.64
37.51
14.76
12.50
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

10. Figure S5 ^{1}H & ^{13}C NMR spectra of **5**



11. Figure S6 Molecular structure of **2**



12. Figure S7 Molecular structure of **3**