Electronic Supplementary Information

Synthesis and Properties of an Au_6 Cluster Supported by a Mixed *N*-Heterocyclic Carbene-Thiolate ligand

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1. General Experimental Considerations

1.1 Materials

Unless otherwise noted, all materials including dry solvents were obtained from commercial suppliers and used without further purification. 1-Isopropylimidazole and chloro(dimethylsulfide)gold(I) were prepared according to a literature procedure.[1]

1.2 Instrumentation and Sample Preparation

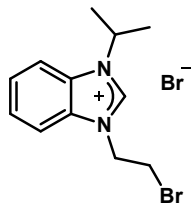
^{1}H and ^{13}C NMR spectra were measured with JEOL ECS 400 MHz, JEOL JNM-ECA600II (600 MHz), or Bruker Avance-300 spectrometers and chemical shifts were calibrated to the residual proton or ^{13}C carbon resonance of the deuterated solvent, which was referenced to tetramethylsilane. All NMR data processing was carried out using either Topspin v.4 or Mestrenova v.12. **HRMS-ESI** spectra were measured using a Thermo Scientific Exactive mass spectrometer. **UV-Vis** spectra were recorded with Agilent Cary 60 UV-vis spectrometer using 1 cm quartz cuvettes. **Single crystal X-ray diffraction** crystals of appropriate quality for X-ray diffraction studies covered with a thin layer of hydrocarbon oil (Paratone-N). A suitable crystal was then selected, attached to a glass fibre or a microsampler, and quickly placed in a low-temperature stream of nitrogen.[2] Data for **4a** were collected at Queen's University using a Bruker AXS D8 Venture Duo diffractometer using Mo K_α radiation (λ = 0.71073 Å), with the crystal cooled to -100 °C. Data for **4a** were solved using intrinsic phasing (SHELXT)[3] and refined using SHELXL-2014.[4] Data for **5a** were collected at Nagoya University on a Rigaku PILATUS diffractometer using Mo K_α radiation (λ = 0.71075 Å) at -150 °C, and refined using the same programs and methods. The assignment of hydrogen atom positions was based on the sp^2 or sp^3 hybridization geometries of their attached carbon atoms and were given thermal parameters 20% greater than those of their parent atoms. **Cyclic Voltammetry** was performed using a CH Instruments electrochemical analyzer and referenced to Ag/AgCl.

1.2 Computational Methods

All calculations have been done by using density-functional theory (DFT) as implemented in the real-space code-package GPAW[5] (Grid-based projector-augmented wave method). Scalar-relativistic corrections for gold are included in GPAW setups. Two exchange-correlation-functionals were used, the Perdew–Burke–Ernzerhof (PBE)[6] and GLLB-SC.[7] The experimental crystal structure was used as a starting point for the calculations. The initial geometry was first relaxed with PBE, 0.2 Å grid spacing and 0.05 eV/Å convergence criterion for the maximum forces acting on atoms in cluster. After relaxation a ground state calculation was done with GLLB-SC functional and 0.25 Å grid spacing, which was used for all further analysis. The electronic density of states was analysed via projections to atomic Au(s), Au(p) and Au(d) symmetries. Optical absorption spectra were calculated by using linear-response time-dependent density functional theory lr-TDDFT,[8] PBE functional in the kernel but with GLLB-SC wave functions and energies. Finally, dipole transition contribution maps (DTCM) were solved for analyzing the peaks in the spectrum by using time-dependent density functional perturbation theory TD-DFPT.[9]

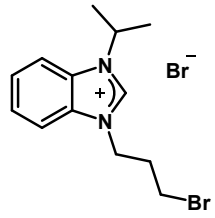
2. Synthetic Procedures

3-(2-bromoethyl)-1-isopropylbenzimidazolium bromide (2a).



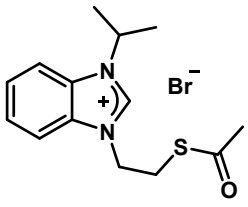
A solution of 1-isopropyl-benzimidazole (1.0 g, 6.6 mmol) and 1,2-dibromoethane (5.4 mL, 62.4 mmol) in acetonitrile (30 mL) was refluxed for 24 hours at 90 °C, and then cooled to room temperature. The white precipitate that formed was removed by filtration through a pad of Celite. The filtrate was collected and solvent was removed by rotary evaporation. Product was purified by silica column chromatography with CH_2Cl_2-MeOH (9:1) affording a sticky white solid after concentration of appropriate fractions and drying in vacuum. Yield 1.3 g (56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.21 (s, 1H), 7.90 (m, 1H), 7.76 (m, 1H), 7.65 (m, 2H), 5.24 (t, J = 5.6 Hz, 2H), 4.99 (sept, J = 6.8 Hz, 1H), 4.08 (t, J = 6.0 Hz, 2H), 1.83 (d, J = 6.8 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 132.1, 130.4, 127.5, 127.3, 113.9, 113.5, 52.1, 48.7, 30.4, 22.4 ppm. HRMS (ESI+) *m/z* calculated for $C_{12}H_{16}Br_2N_2$ $[M]^+$: 267.0491, found: 267.0486. EA: (Calculated) C 41.41, H 4.63, N 8.05. (Observed) C 41.09, H 4.56, N 8.07.

3-(3-bromopropyl)-1-isopropyl-benzimidazolium bromide (2b).



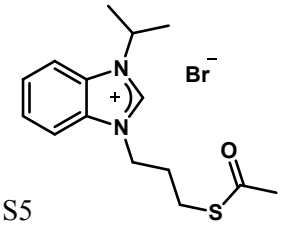
A solution of 1-isopropyl-benzimidazole (0.25 g, 1.6 mmol) and 1,3-dibromopropane (2.0 mL, 19.6 mmol) was heated at 90 °C for 16 hours at ambient conditions. White precipitate that formed was removed by filtration through a pad of Celite. The filtrate was collected and solvent removed by rotary evaporation. The product was purified by silica column chromatography with CH_2Cl_2-MeOH (9:1) to afford a white sticky solid after concentration of appropriate fractions and drying in vacuo. Yield 0.69 (61%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.24 (s, 1H), 7.85 (m, 1H), 7.78 (m, 1H), 7.63 (m, 2H), 4.99 (sept, J = 6.8 Hz, 1H), 4.91 (t, J = 7.2 Hz, 2H), 3.56 (t, J = 6.0 Hz, 2H), 2.67 (m, 2H), 1.79 (d, J = 6.7 Hz, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 131.77, 130.51, 127.42, 127.24, 113.64, 113.29, 77.37, 76.95, 52.00, 45.88, 32.32, 29.92, 22.33 ppm. HRMS (ESI+) *m/z* calculated for $C_{13}H_{18}BrN_2^+$ $[M]^+$: 281.0648, found: 281.0637. EA: (Calculated) C 43.12, H 5.01, N 7.74. (Observed) C 43.10, H 4.97, N 7.40.

3-(2-(acetylthio)ethyl)-1-isopropylbenzimidazolium bromide (3a).



A mixture of **2a** (0.55 g, 1.6 mmol) and potassium thioacetate (0.22 g, 1.9 mmol) was suspended in acetonitrile (20 mL) and stirred overnight at room temperature. The resulting yellow suspension was filtered through a pad of Celite and the solvent was removed by rotary evaporation affording the crude product as viscous yellow oil. The crude product was dissolved in a small amount of CH_2Cl_2 and triturated three times with diethyl ether at cold temperature, which afforded the product as a pale orange solid. Yield 0.43 g (80 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.14 (s, 1H), 7.98 (m, 1H), 7.75 (m, 1H), 7.57 (m, 2H), 4.96 (sept, J = 4.8 Hz, 1H), 4.80 (t, J = 4.8 Hz, 2H), 3.45 (t, J = 4.4 Hz, 2H), 2.19 (s, 3H), 1.72 (d, J = 4.4 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 141.5, 131.7, 130.3, 127.2, 127.0, 113.45, 113.42, 51.7, 46.2, 30.4, 28.5, 22.1 ppm. HRMS (ESI+) *m/z* calculated for $C_{14}H_{19}N_2OS$ $[M]^+$: 263.1213, found: 263.1209. EA: (Calculated) C 48.98, H 5.58, N 8.16. (Observed) C 49.13, H 5.62, N 8.08.

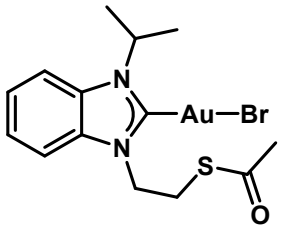
3-(3-(acetylthio)propyl)-1-isopropyl-benzimidazolium bromide (3b).



A mixture of **2b** (0.69 g, 1.91 mmol) and potassium thioacetate (0.26 g, 1.9 mmol) was suspended in acetonitrile (25 mL) and stirred overnight at room temperature. The resulting white suspension was filtered through a pad of Celite, and the solvent was removed by rotary evaporation, affording the crude product as a brown viscous oil. The crude product was dissolved in

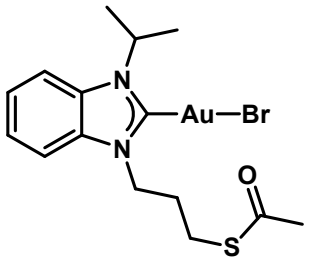
small amount of CH_2Cl_2 and triturated three times with diethyl ether at cold temperature, which afforded the product as a pale orange solid. Yield 0.63 g (96%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 11.13 (s, 1H), 7.78 (m, 1H), 7.74 (m, 1H), 7.60 (m, 2H), 4.99 (sept, *J* = 6.8 Hz, 1H), 4.76 (t, *J* = 7.2 Hz, 2H), 4.76 (t, *J* = 7.2 Hz, 2H), 2.93 (t, *J* = 7.1 Hz, 2H), 2.22 (s, 3H), 1.76 (d, *J* = 6.8 Hz, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.04, 195.54, 131.58, 130.58, 127.25, 127.12, 113.65, 113.24, 51.86, 46.16, 30.89, 30.64, 29.44, 25.64, 22.25 ppm. HRMS (ESI+) *m/z* calculated for $C_{15}H_{21}N_2OS^+$ $[M]^+$: 277.1369, found: 277.1368. EA: (Calculated) C 50.42, H 5.92, N 7.84. (Observed) C 50.18, H 6.01, N 7.63.

(3-(2-(acetylthio)ethyl)-1-isopropylbenzimidazole)gold bromide (4a).



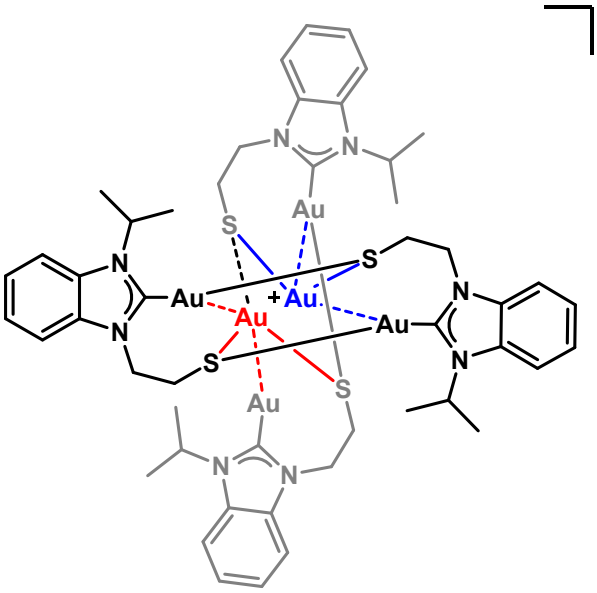
A mixture of **3a** (0.20 g, 0.6 mmol), $Au(SMe_2)Cl$ (0.18 g, 0.6 mmol) and K_2CO_3 (0.26 g, 1.9 mmol) was suspended in acetone and heated at 60 °C for 2 hours. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite. The filtrate was collected and the solvent was removed by rotary evaporation, which afforded the product as a pale orange crystalline solid. Yield 0.29 g (94 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.2 Hz, 1H), 7.62 (d, *J* = 6.0 Hz, 1H), 7.41 (quint-d, *J* = 6.4 and *J* = 0.8 Hz, 2H), 5.41 (sept, *J* = 6.8 Hz, 1H), 4.58 (t, *J* = 7.6 Hz, 2H), 3.30 (t, *J* = 7.6 Hz, 2H), 2.35 (s, 3H), 1.71 (d, *J* = 7.6 Hz, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 180.0, 133.6, 131.6, 124.8, 124.4, 112.9, 112.1, 54.0, 47.7, 30.7, 28.5, 21.9 ppm. HRMS (ESI+) *m/z* calculated for $C_{14}H_{18}AuON_2SBrNa$ $[M+Na]^+$: 560.9881, found: 560.9879. EA: (Calculated) C 31.18, H 3.36, N 5.20. (Observed) C 31.35, H 3.42, N 5.08.

3-(2-(acetylthio)propyl)-1-isopropylbenzimidazole)gold bromide (4b).



A mixture of **3b** (0.28 g, 0.79 mmol), $Au(SMe_2)Cl$ (0.24 g, 0.80 mmol) and K_2CO_3 (0.33 g, 2.4 mmol) was suspended in acetone and heated at 60 °C for 2 hours. After cooling to room temperature, the reaction mixture was filtered through a pad of Celite. The filtrate was collected and volatiles were removed by rotary evaporation. The crude product was purified by silica column chromatography with CH_2Cl_2-MeOH (9:1) which afforded the product as a pale beige solid after concentration of appropriate fractions. Yield 0.28 g (66%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (m, 1H), 7.49 (m, 1H), 7.41 (m, 2H), 5.45 (sept, *J* = 6.8 Hz, 1H), 4.54 (t, *J* = 7.3 Hz, 2H), 2.93 (t, *J* = 6.9 Hz, 2H), 2.34 (s, 3H), 2.27 – 2.20 (m, 2H), 1.73 (d, *J* = 7.0 Hz, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.46, 180.48, 133.69, 131.80, 124.66, 124.37, 113.11, 111.71, 54.15, 47.50, 30.89, 29.84, 26.11, 21.94 ppm. HRMS (ESI+) *m/z* calculated for $C_{15}H_{20}AuBrN_2OSNa^+$ $[M+Na]^+$: 575.0043, found: 575.0048. EA: (Calculated) C 32.56, H 3.64, N 5.06. (Observed) C 33.45, H 3.89, N 4.86.

[(NHC-S)$_4$Au$_6$]Br$_2$ (5a).



To a degassed mixture of **3** (0.16 g, 0.30 mmol) in methanol (8 mL) was added degassed 2 M aqueous HBr solution (3 mL, 6 mmol) with stirring. The reaction mixture was stirred at 65 °C under argon overnight, which resulted in formation of white precipitate. Most of the methanol was removed by rotary evaporation and the aqueous solution was diluted with H_2O and extracted two times with CH_2Cl_2. The combined organic layers were washed with brine and dried with anhydrous Na_2SO_4. The solvent was removed by rotary evaporation and the yellowish solid was washed with a mixture of $CHCl_3$-CCl_4 to remove any impurities. Yield 0.10 g (63% based on NHC, 94% based on Au) as a white powdery solid. ^{1}H NMR (400 MHz, CD_3OD) δ 7.91 (d, *J* = 4.8 Hz, 1H), 7.62 (d, *J* = 5.6 Hz, 1H), 7.43 (quint, J = 4.4 Hz, 2H), 5.55 (sept, *J* = 4.8 Hz, 1H), 5.14 (dd, *J* = 3.6 *and* J = 6.0 Hz, 1H, -NC*H*H-), 5.03 (dd, *J* = 6.8 and *J* = 2.8 Hz, 1H, -NC*H*H-), 3.78 (dd, *J* = 3.6 and *J* = 6.0 Hz, 1H, -C*H*HSH), 3.29 (dd, *J* = 6.8 and *J* = 2.8 Hz, 1H, -C*H*HSH), 1.95 (d, *J* = 4.4 Hz, 3H), 1.77 (d, *J* = 4.8 Hz, 3H) ppm. ^{13}C NMR (100 MHz, CH_3OD) δ 182.4, 134.8, 133.2, 126.1, 126.0, 115.2, 113.2, 56.7, 55.8, 32.6, 22.1, 22.0 ppm. HRMS (ESI+) *m/z* calculated for $C_{48}H_{60}Au_6N_8S_4$ $[M\text{-}2Br]^{2+}$: 1029.0903, found: 1029.0910. EA: (Calculated) C 25.98, H 2.73, N 5.05, S 5.78. (Observed) C 25.87, H 2.84, N 5.86.

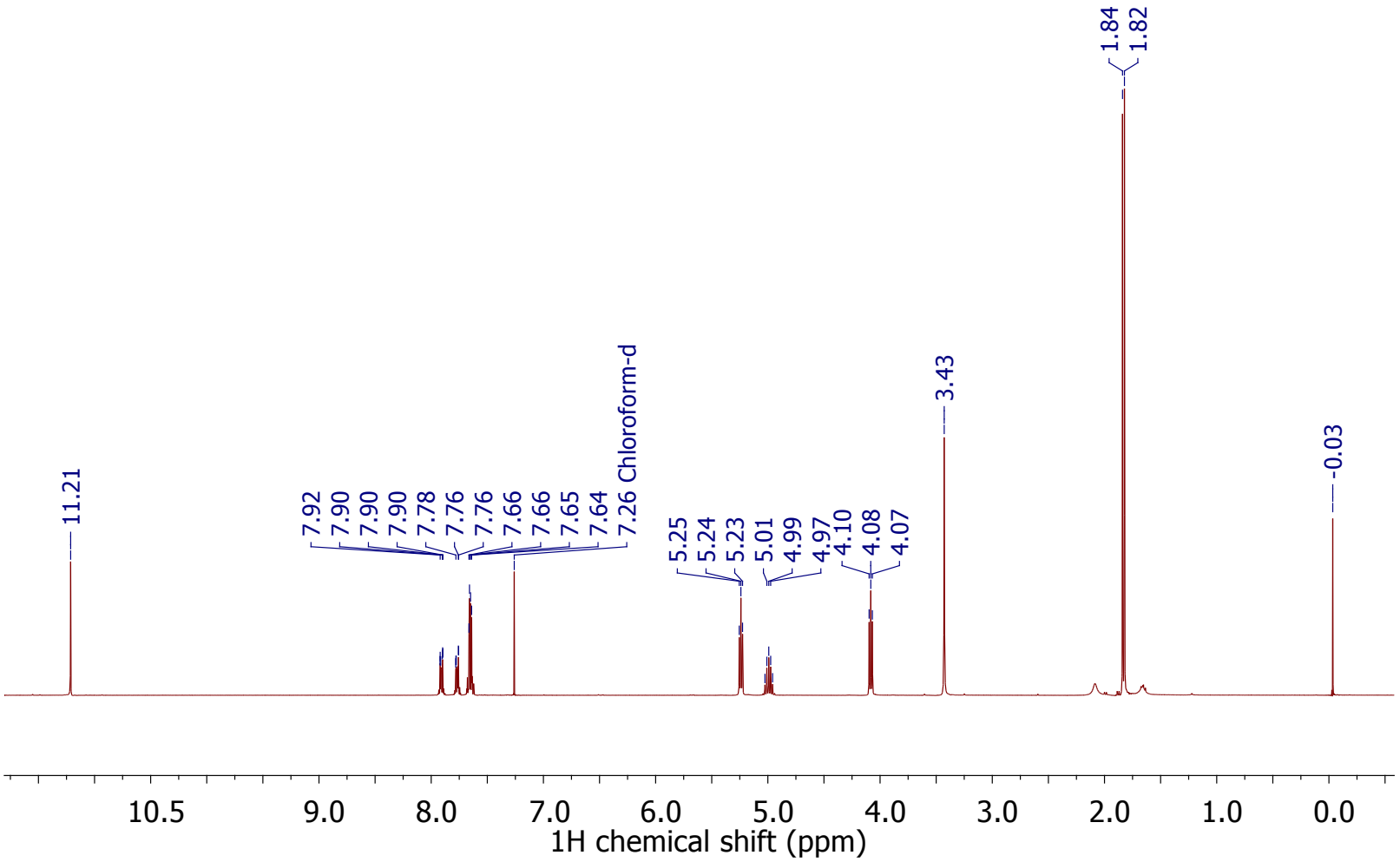
Reaction of compound 4b with HBr.

To a degassed mixture of **4b** (0.16 g, 0.29 mmol) in methanol (8 mL) was added a degassed 2 M aqueous HBr solution (3 mL, 6 mmol) with stirring. The reaction mixture was stirred at 65 °C under argon overnight, which resulted in formation of insoluble white precipitate.

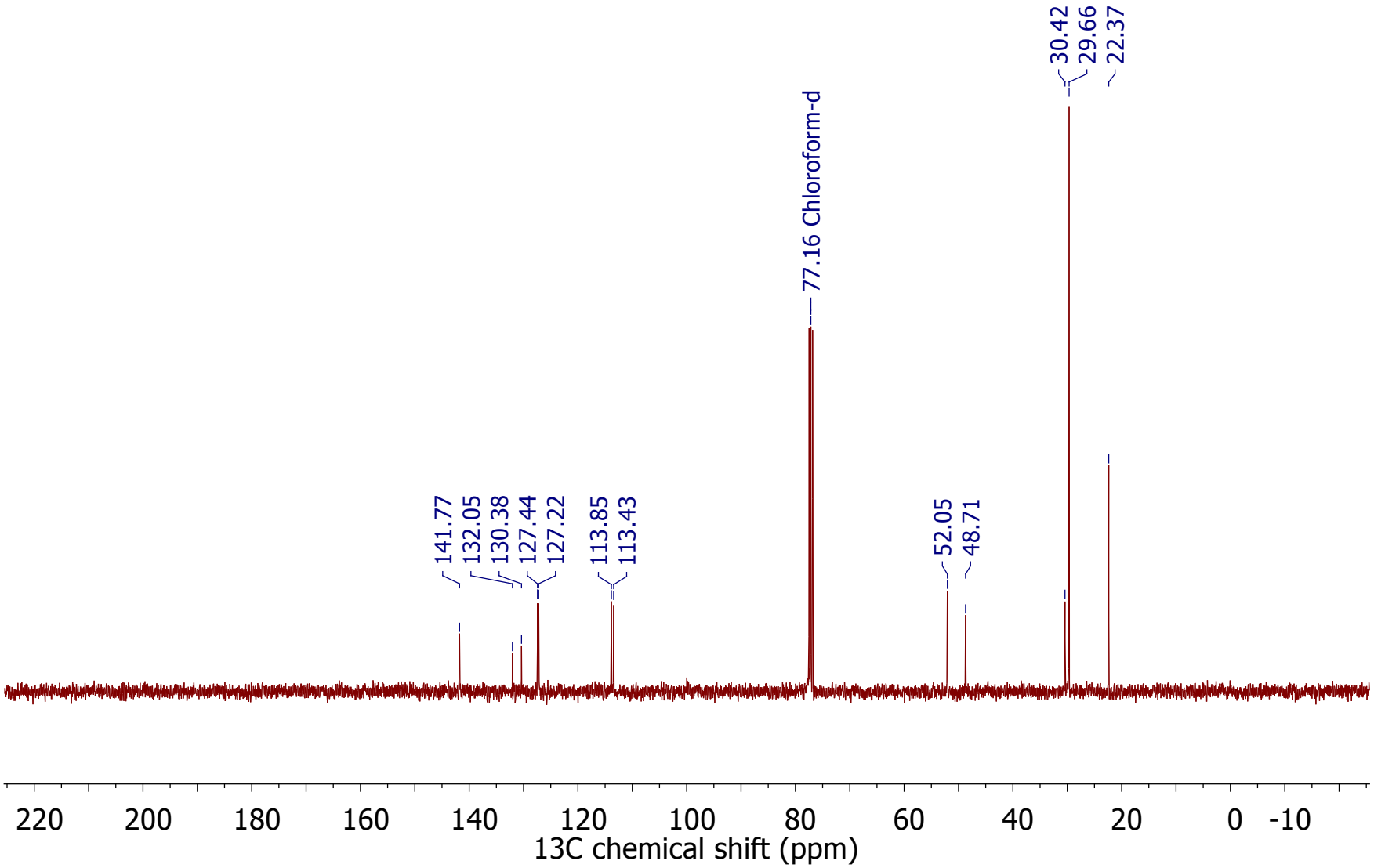
3. Experimental data

3.1 NMR Spectroscopy

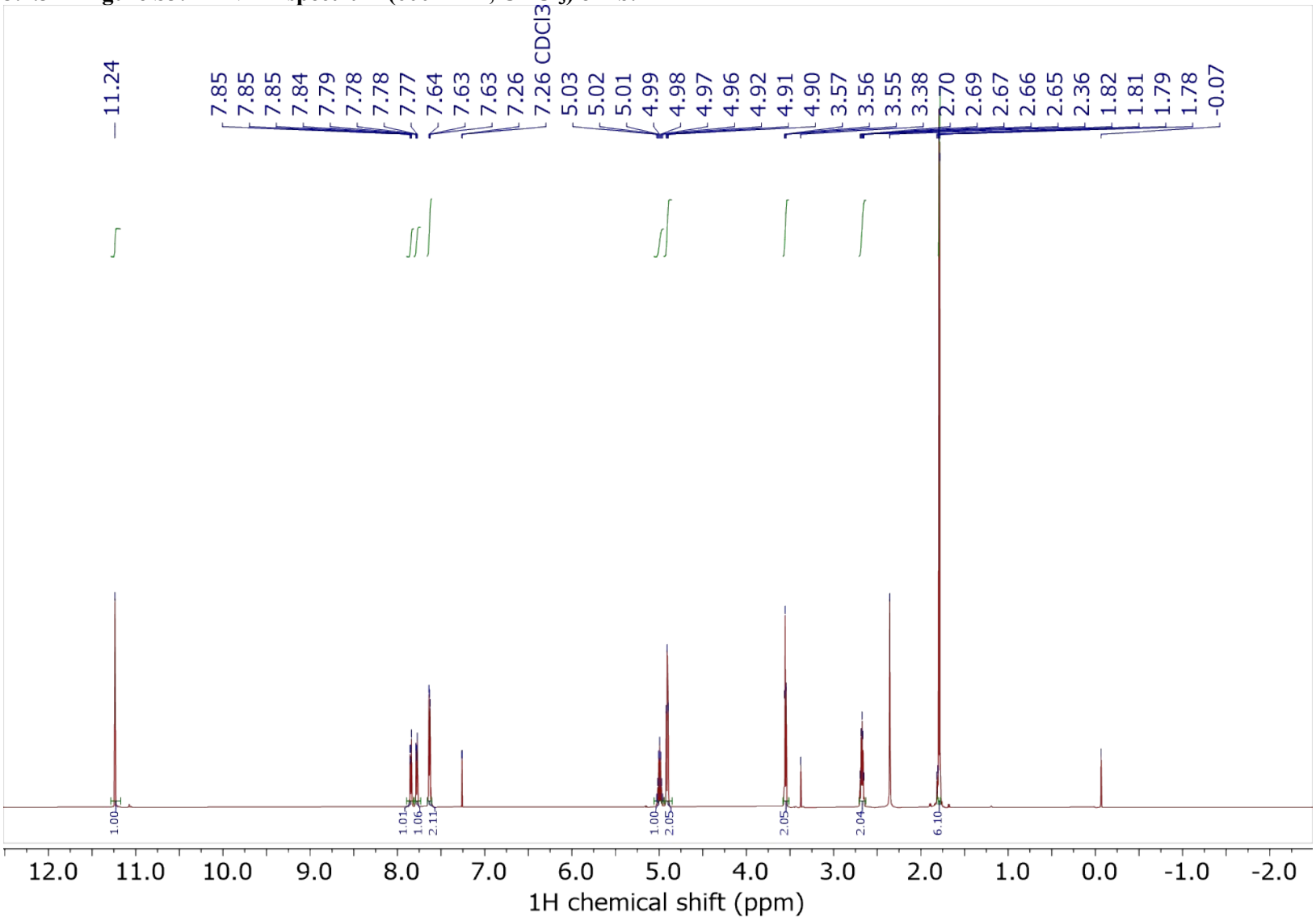
3.1.1 Figure S1: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2a.



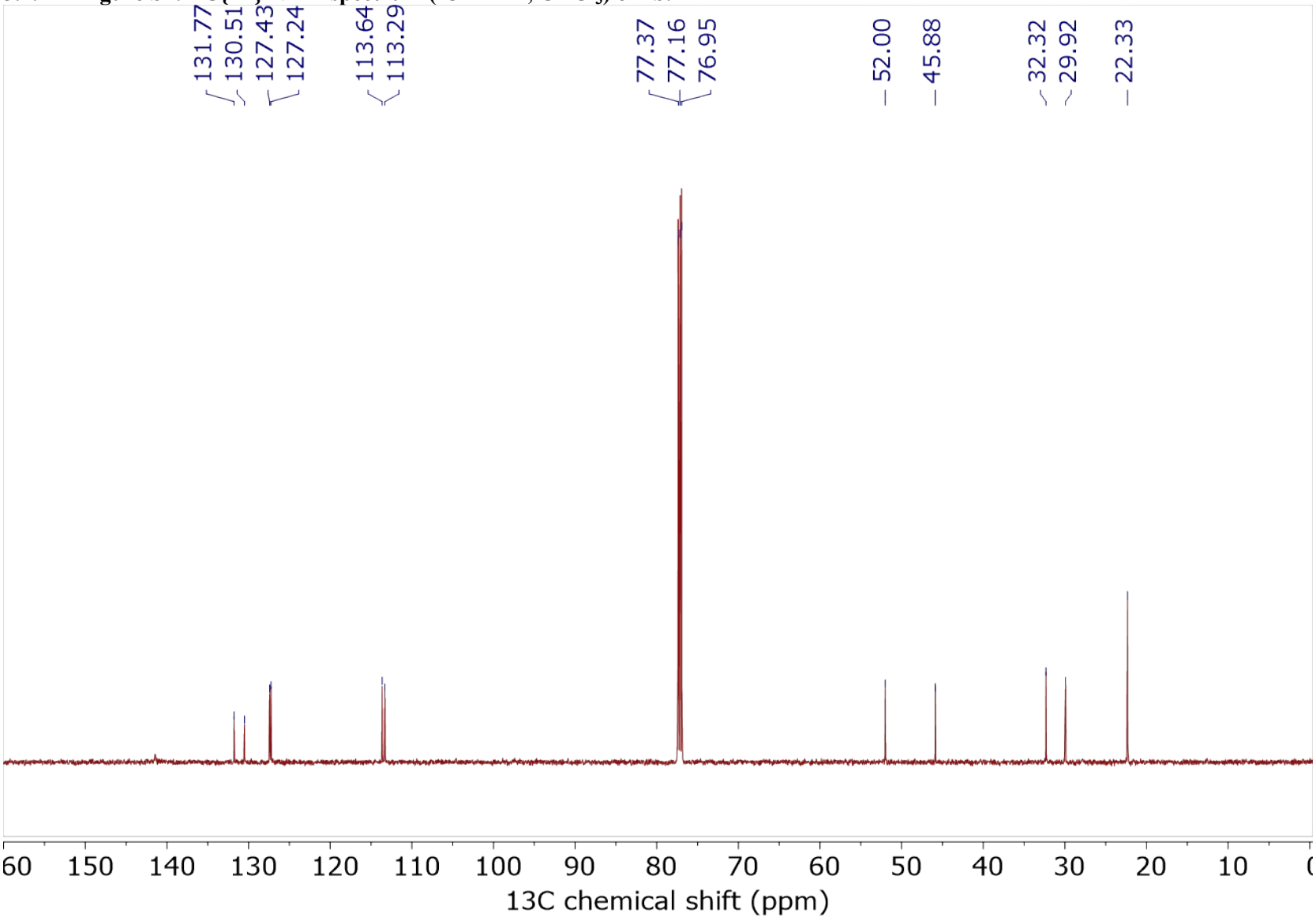
3.1.2 Figure S2: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of 2a.



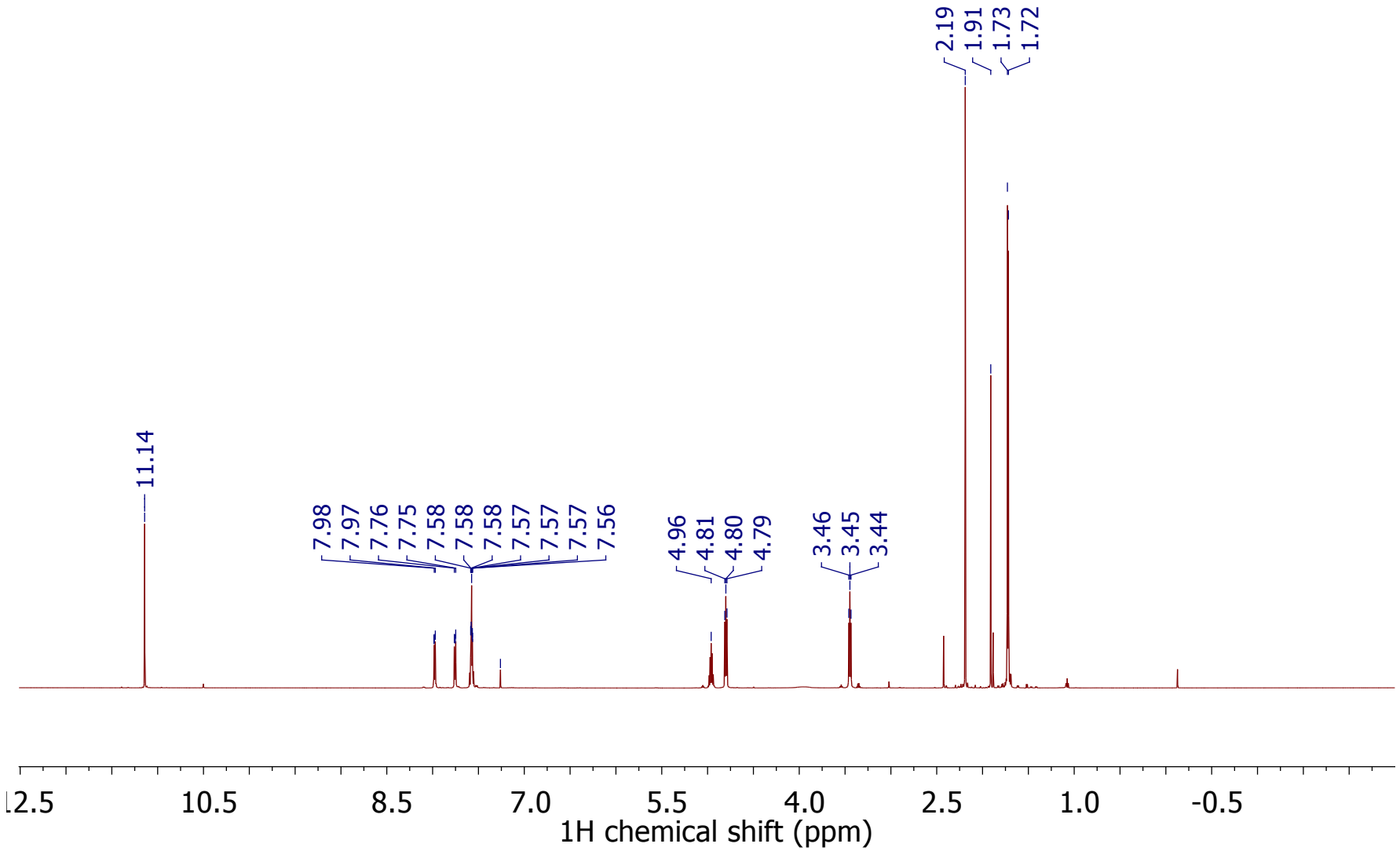
3.1.3 Figure S3: ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 2b.



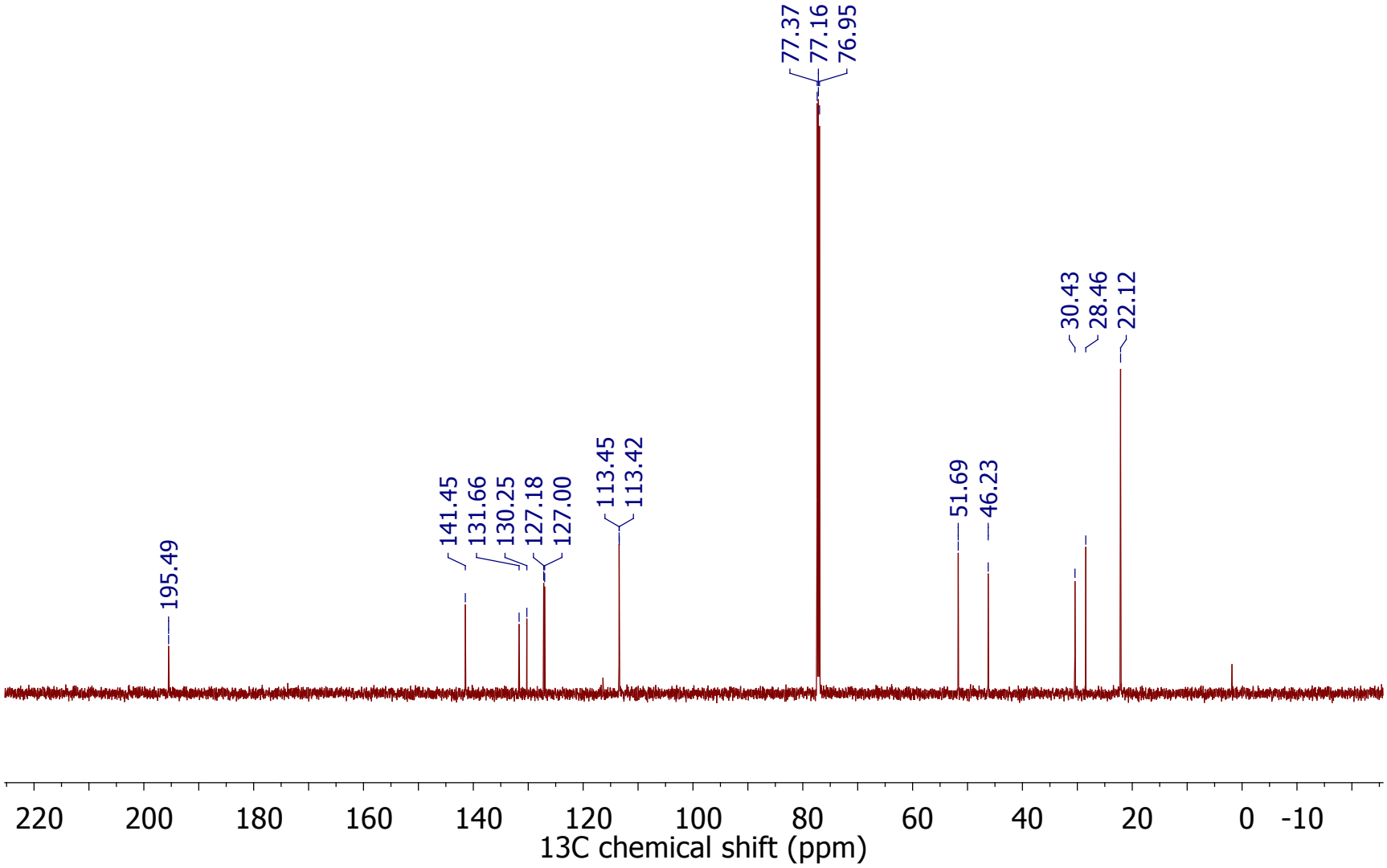
3.1.4 Figure S4: $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of 2b.



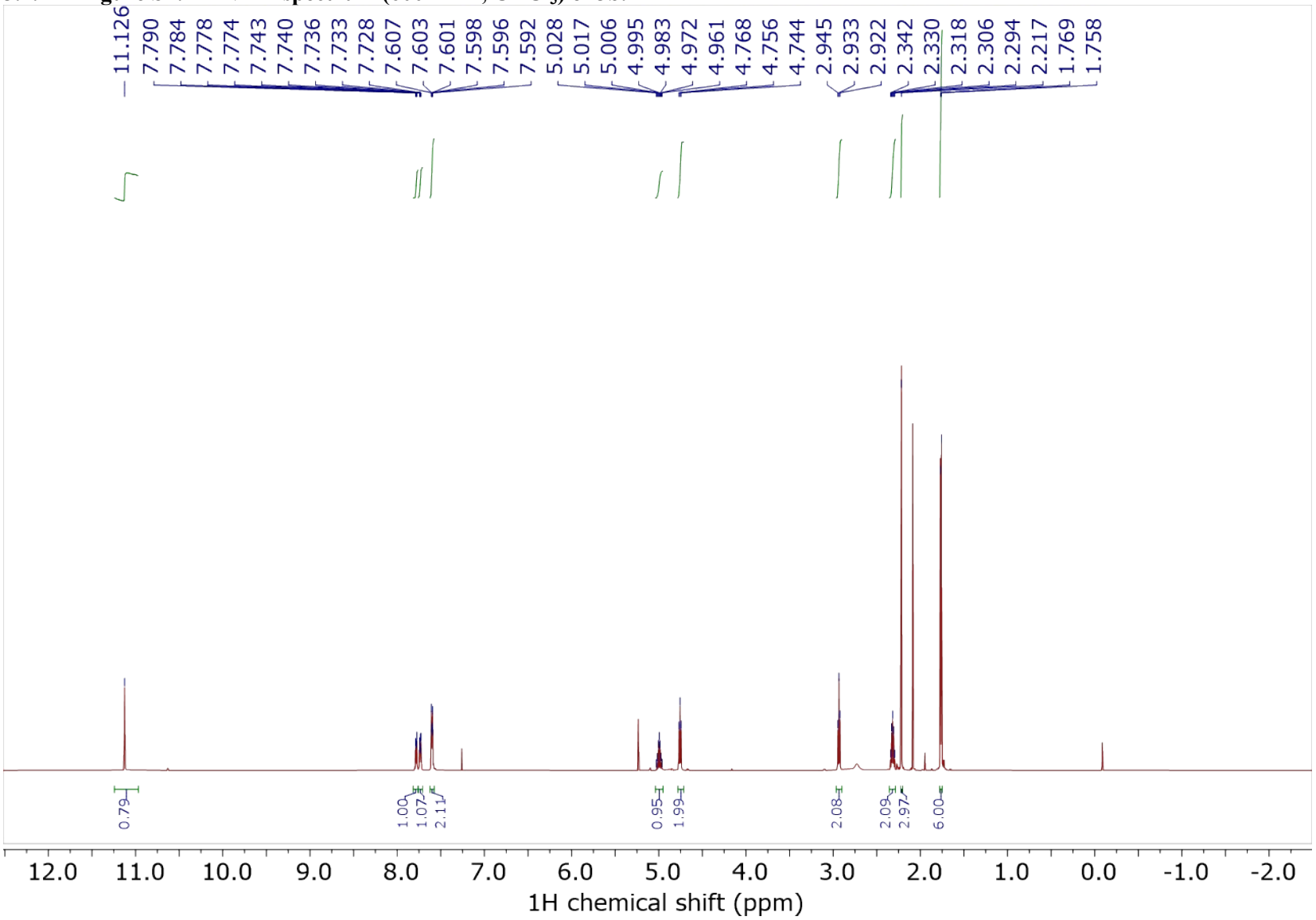
3.1.5 Figure S5: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3a.



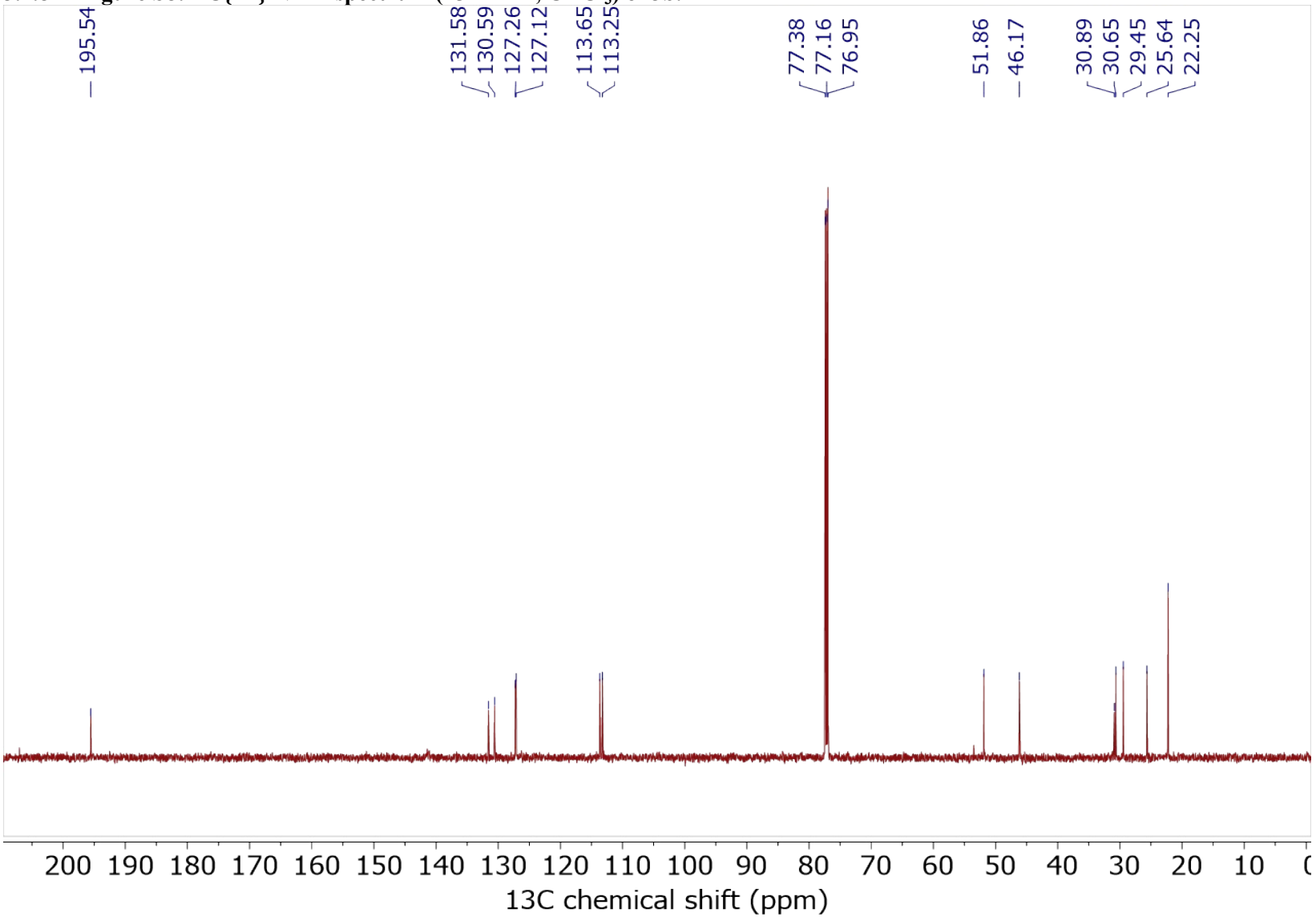
3.1.6 Figure S6: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of 3a.



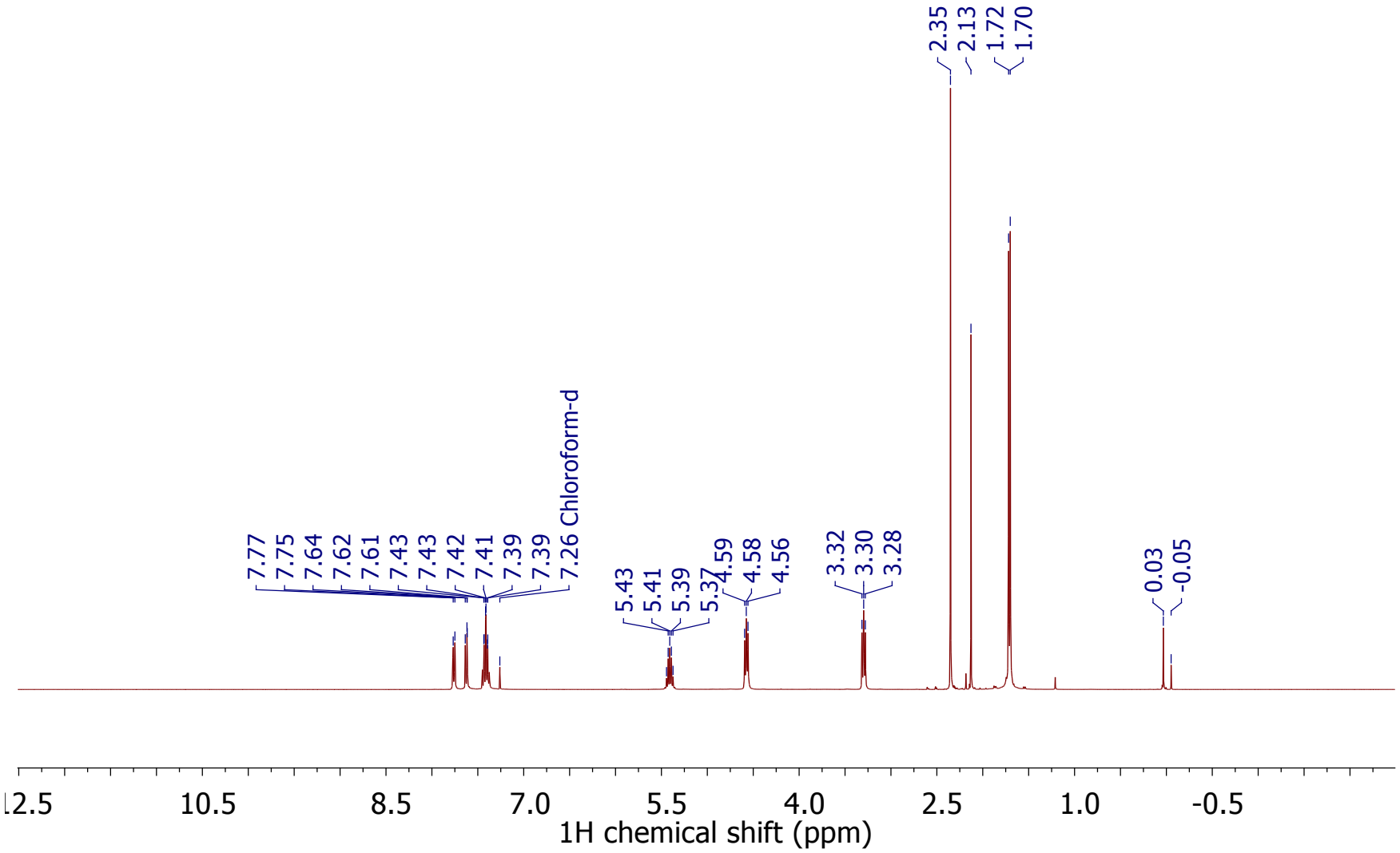
3.1.7 Figure S7: ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3b.



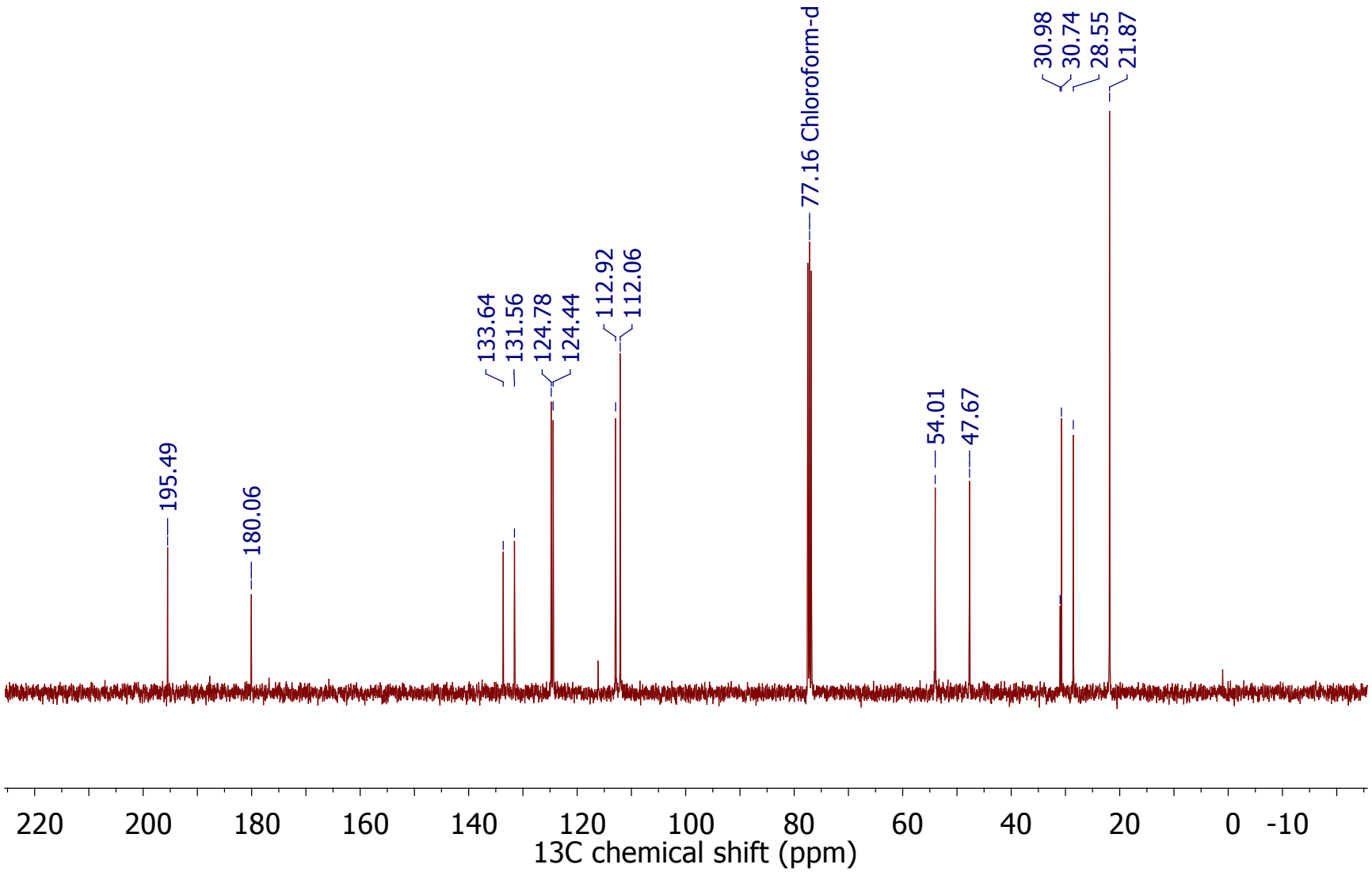
3.1.8 Figure S8: $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of 3b.



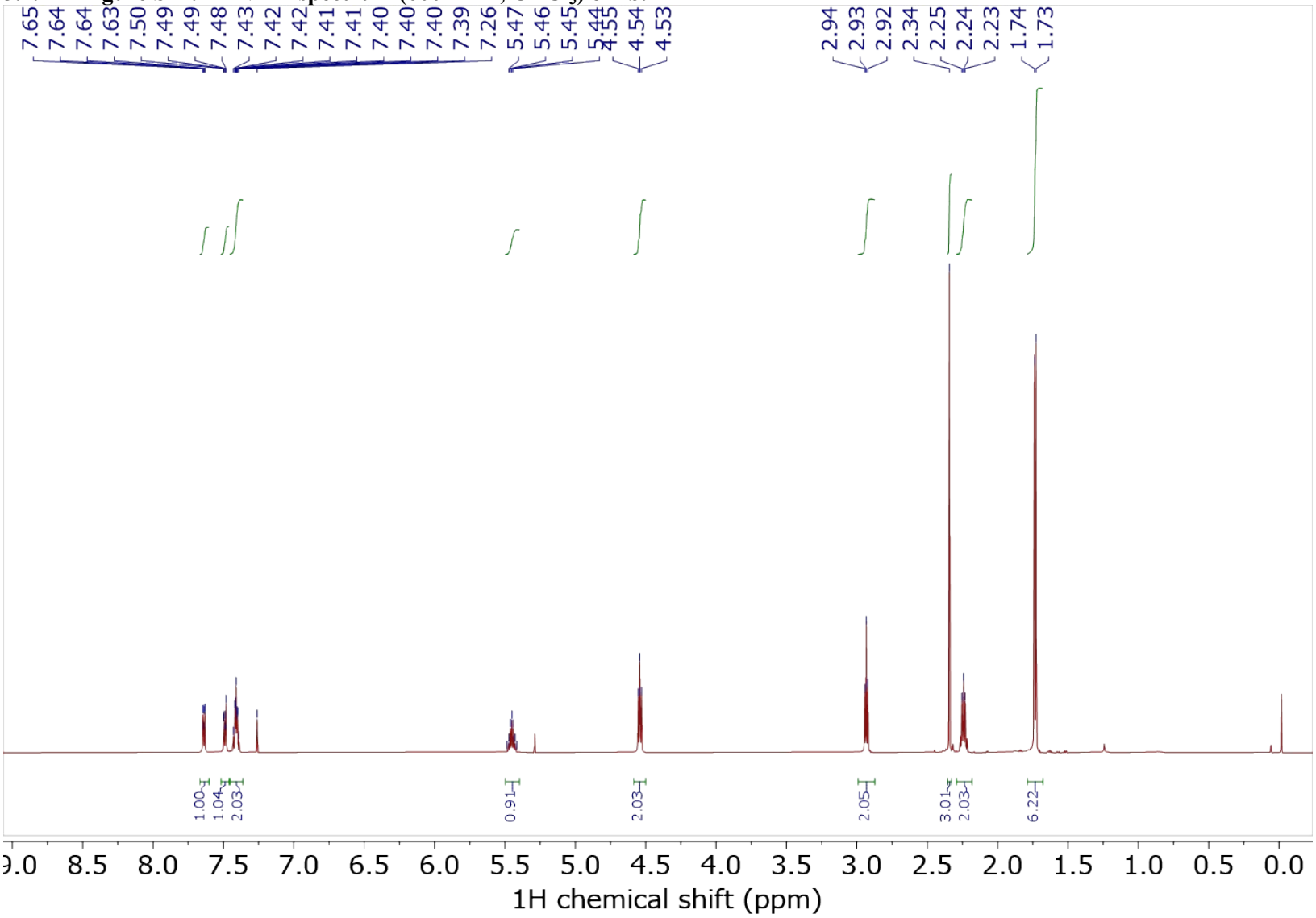
3.1.9 Figure S9: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4a.



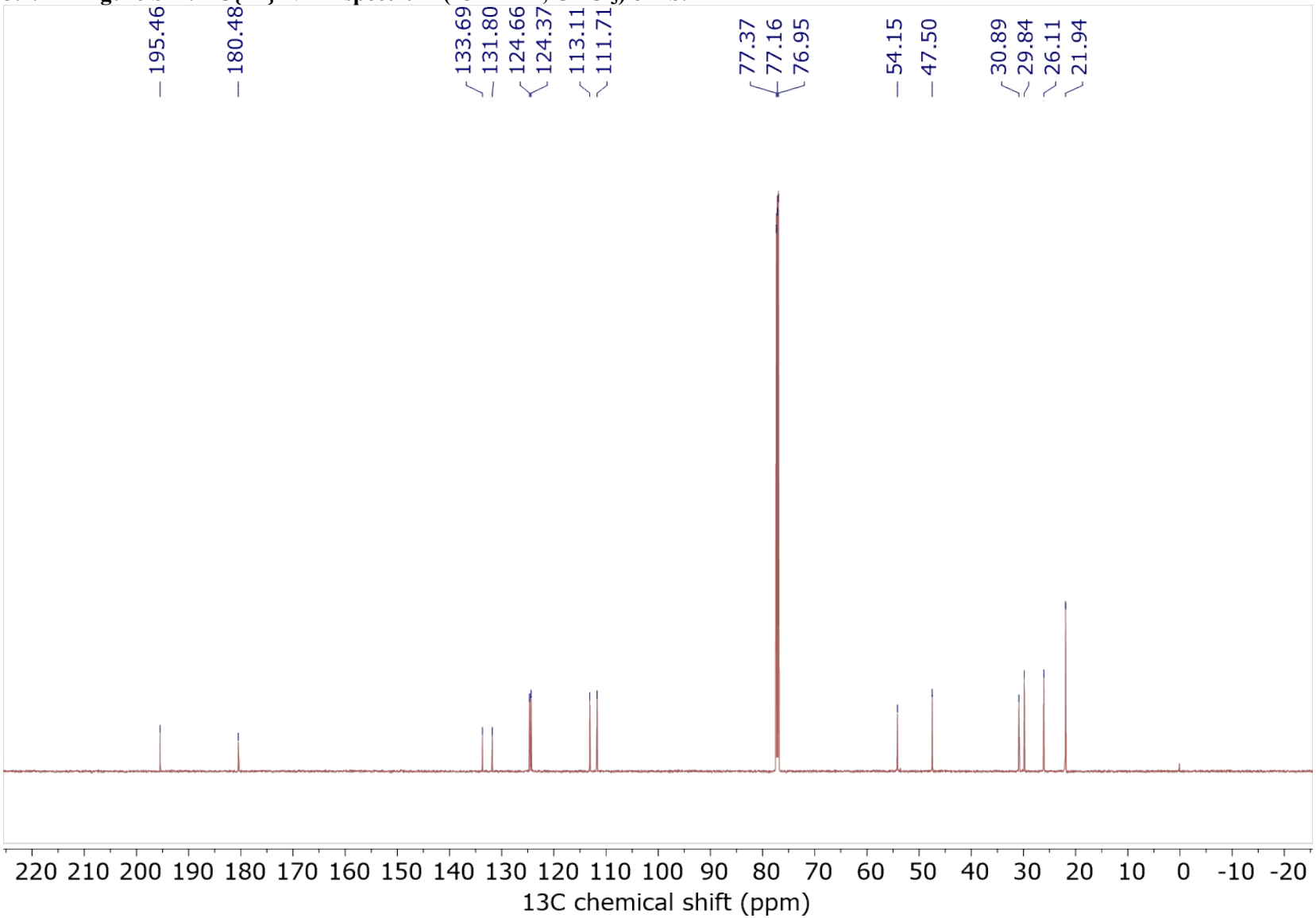
3.1.10 Figure S10: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of 4a.



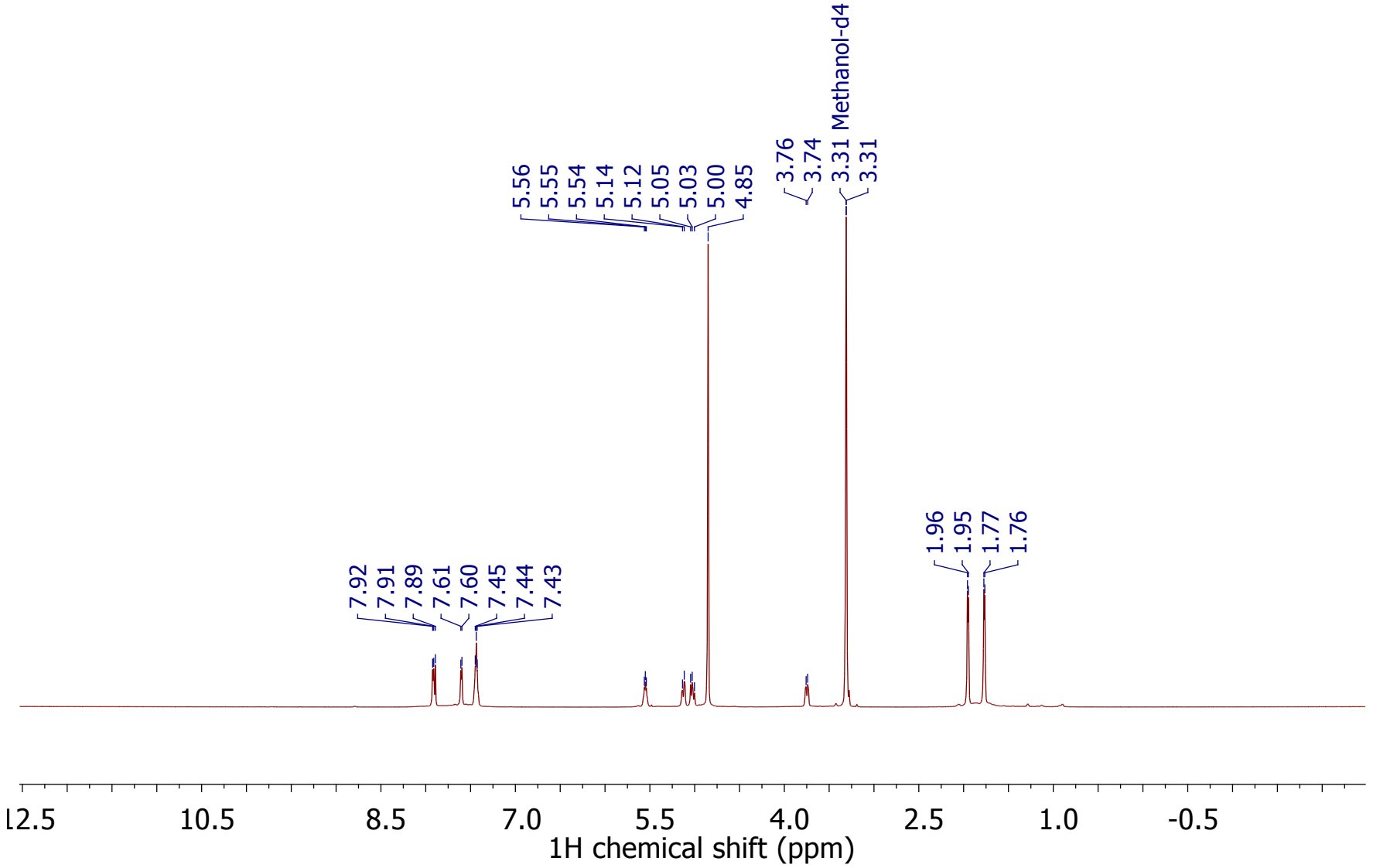
3.1.11 Figure S11: ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 4b.



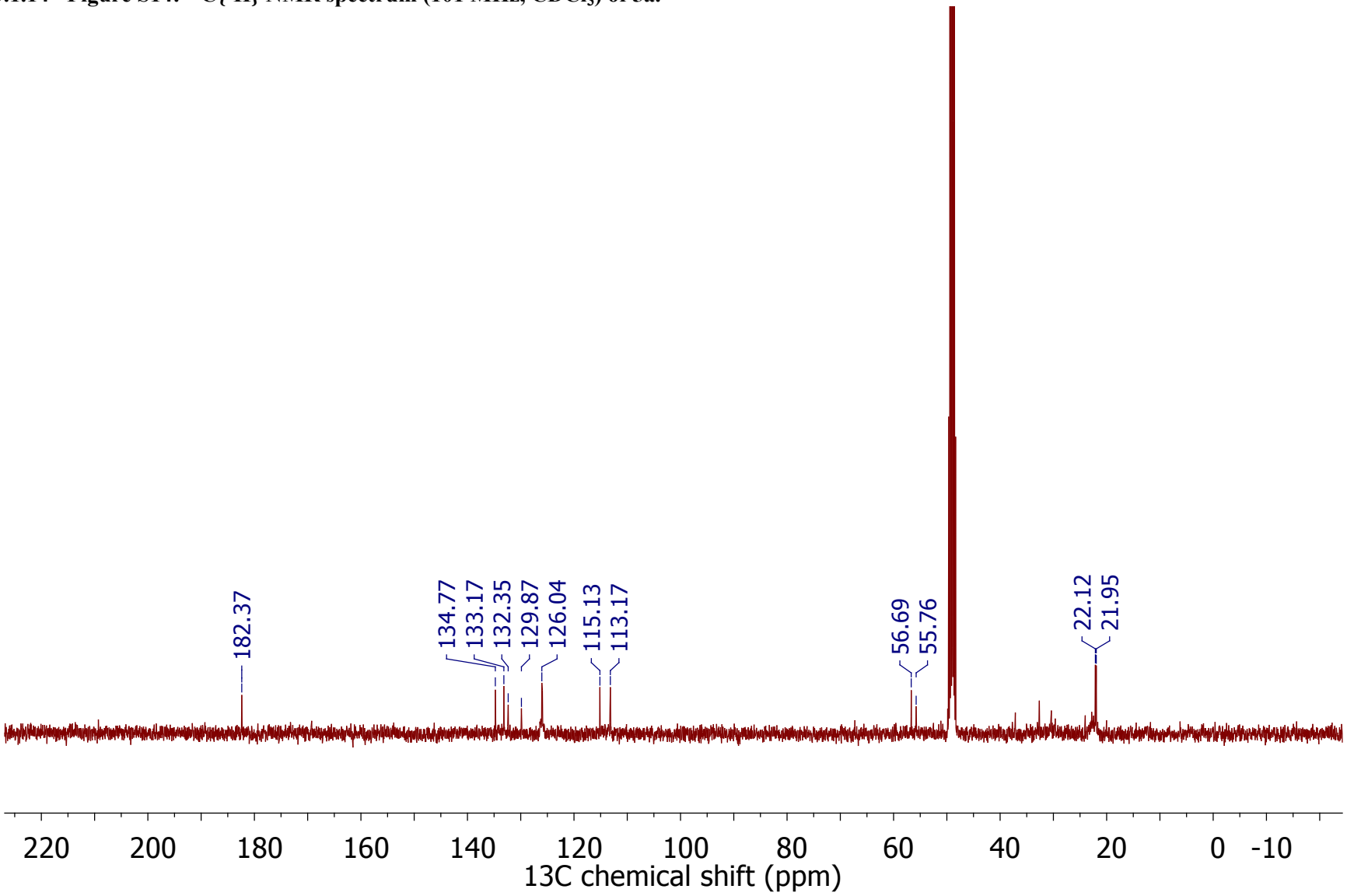
3.1.12 Figure S12: $^{13}C\{^{1}H\}$ NMR spectrum (151 MHz, $CDCl_3$) of 4b.



3.1.13 Figure S13: ^{1}H NMR spectrum (400 MHz, CD_3OD) of 5a.

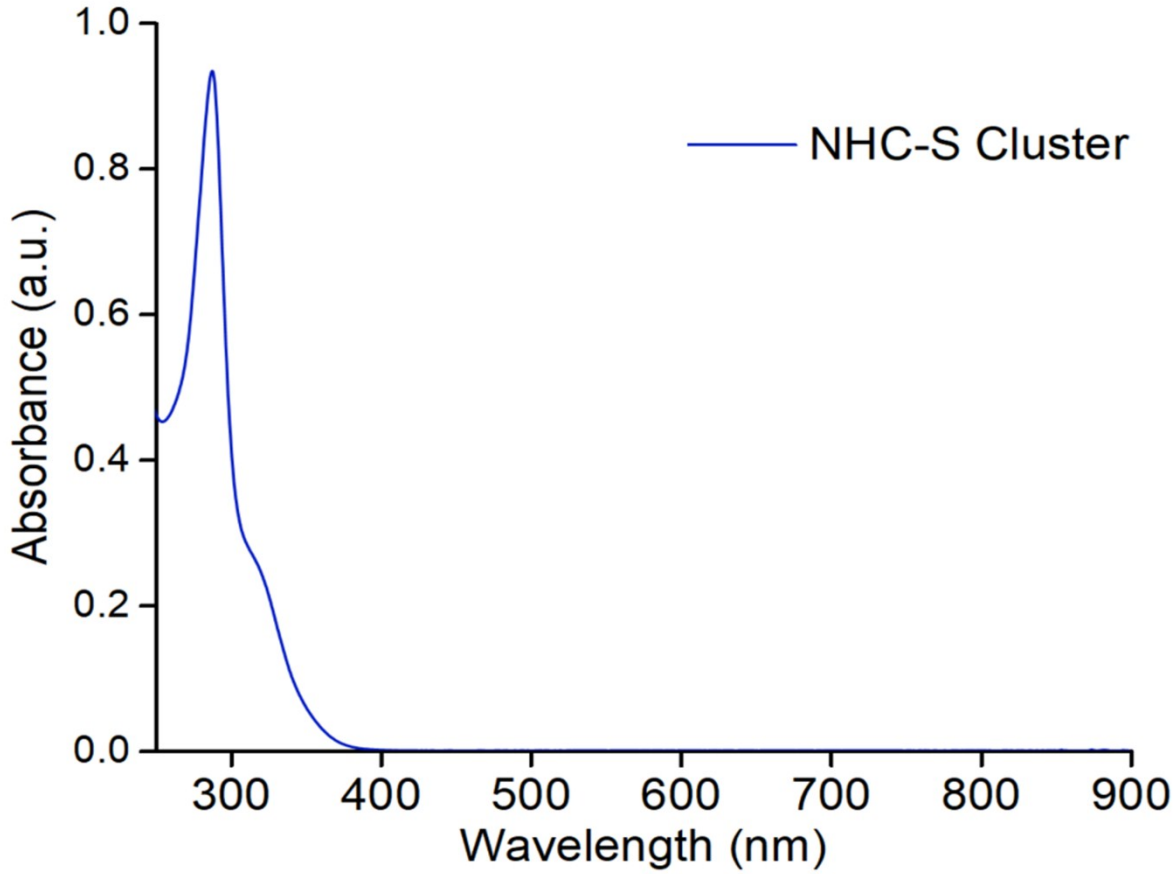


3.1.14 Figure S14: $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of 5a.



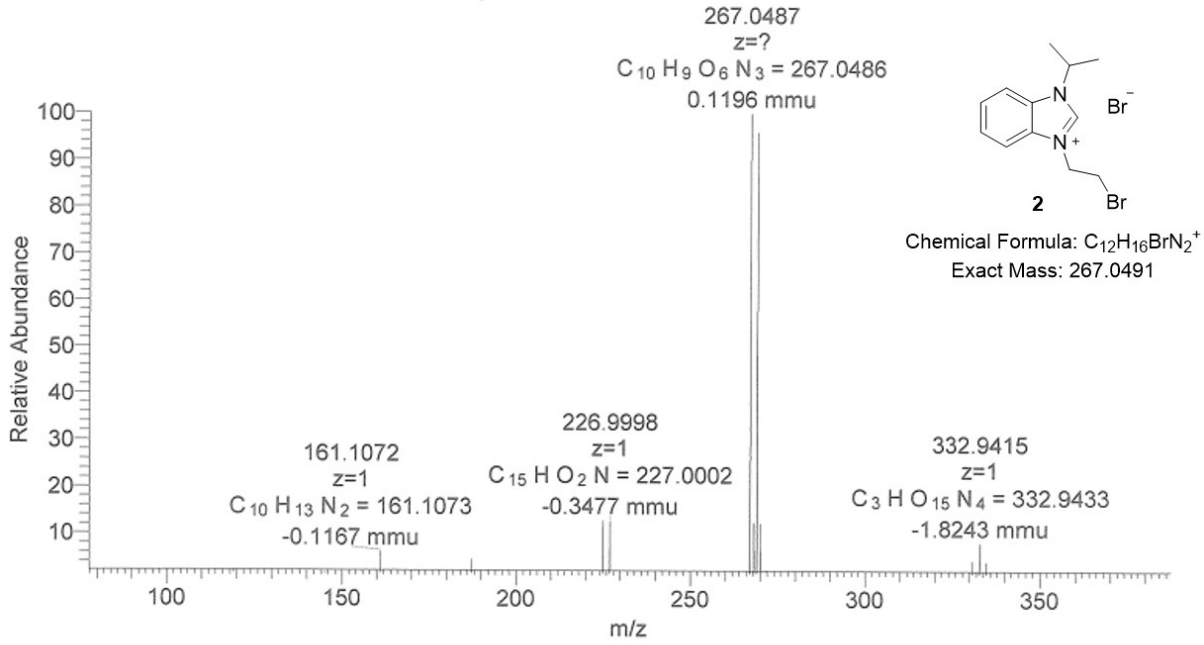
3.2 UV-visible Spectroscopy

3.2.1 Figure S15: UV-Vis Spectrum of 5a in MeOH.

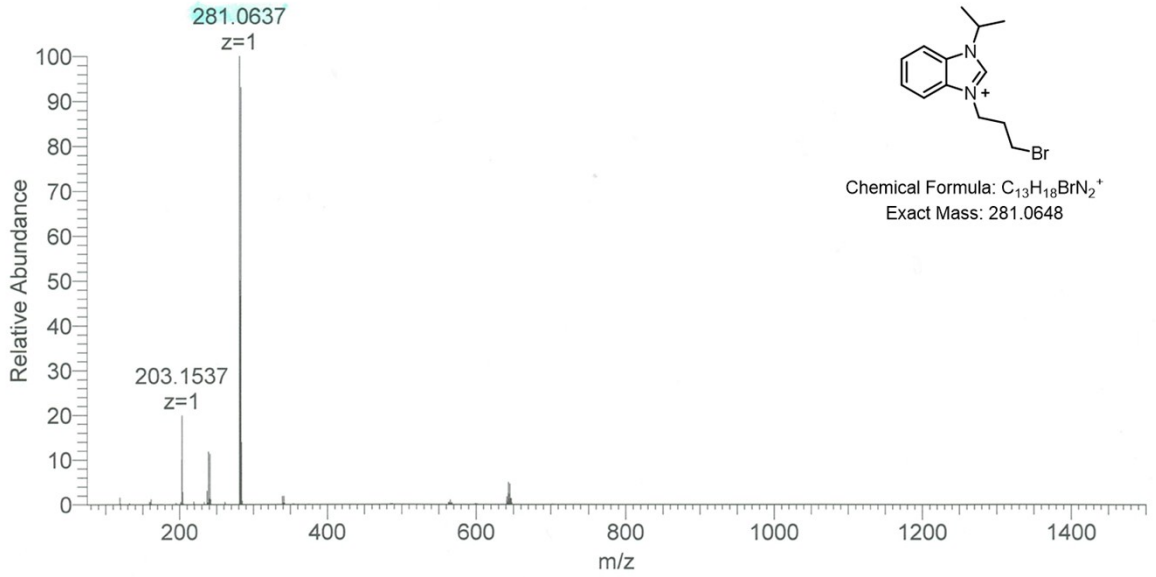


3.3 Mass Spectroscopy

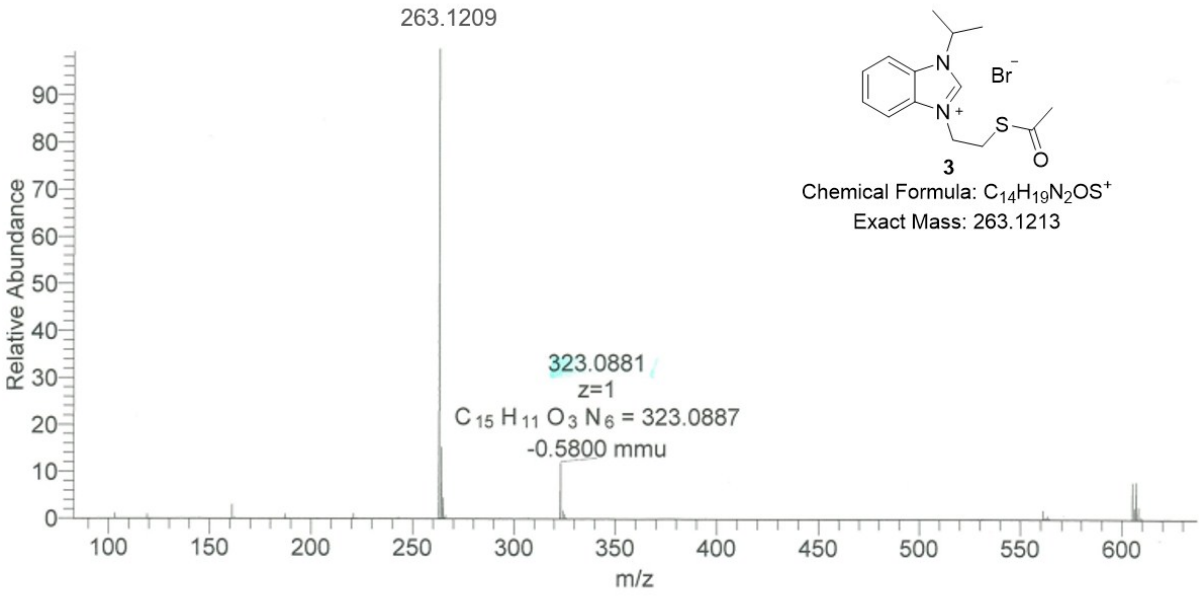
3.3.1 Figure S16: ESI-MS of 2a



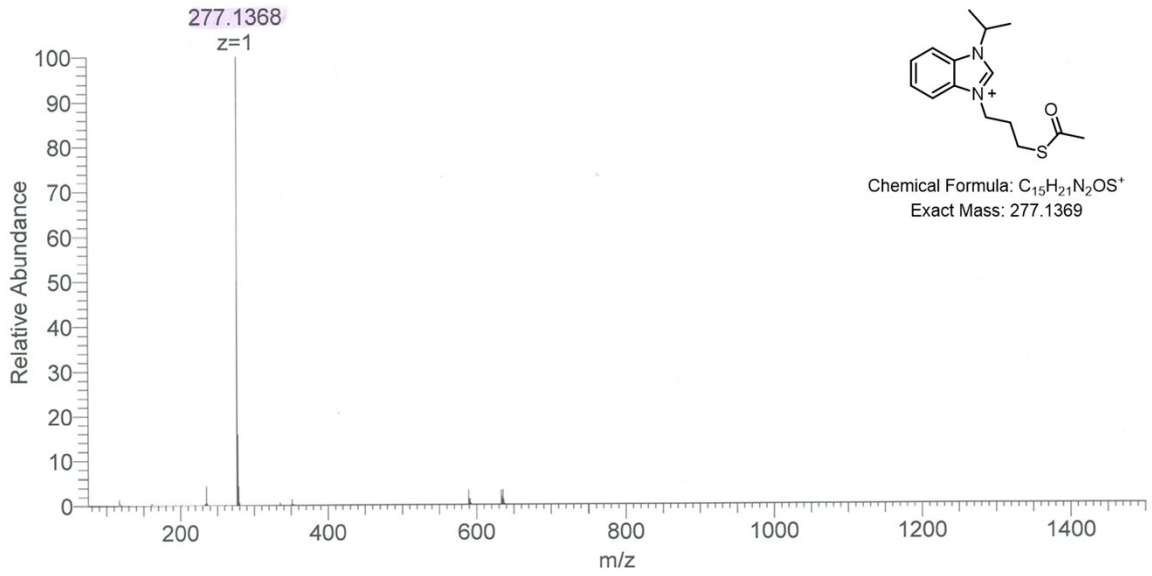
3.3.2 Figure S17: ESI-MS of 2b



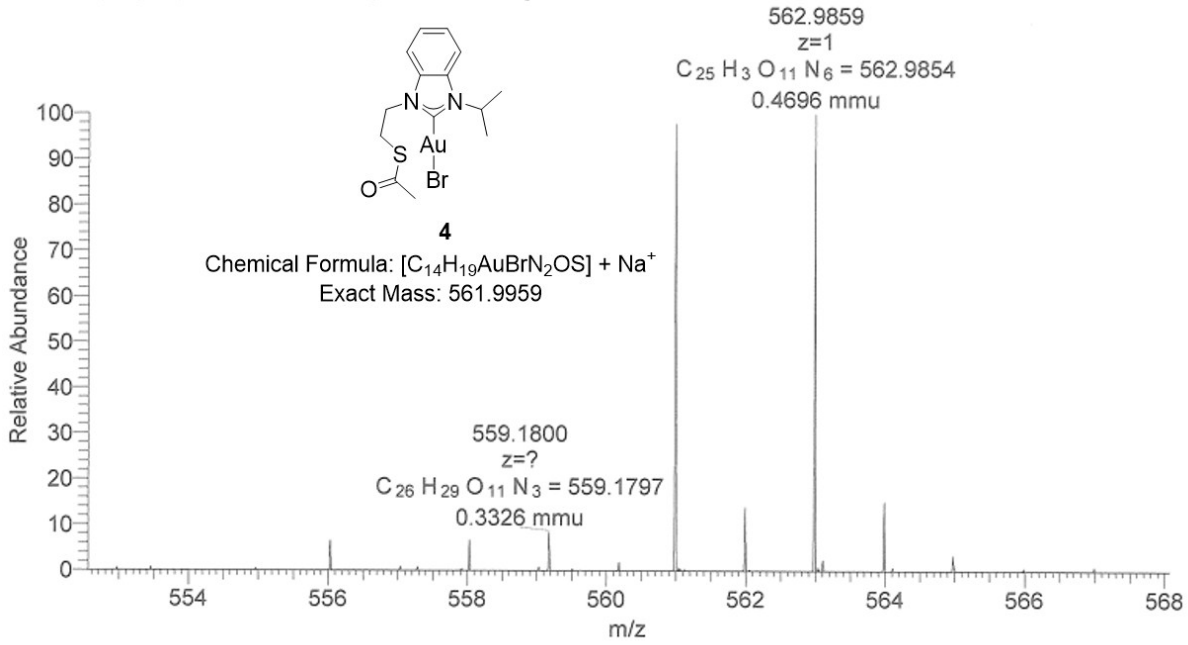
3.3.3 Figure S18: ESI-MS of 3a



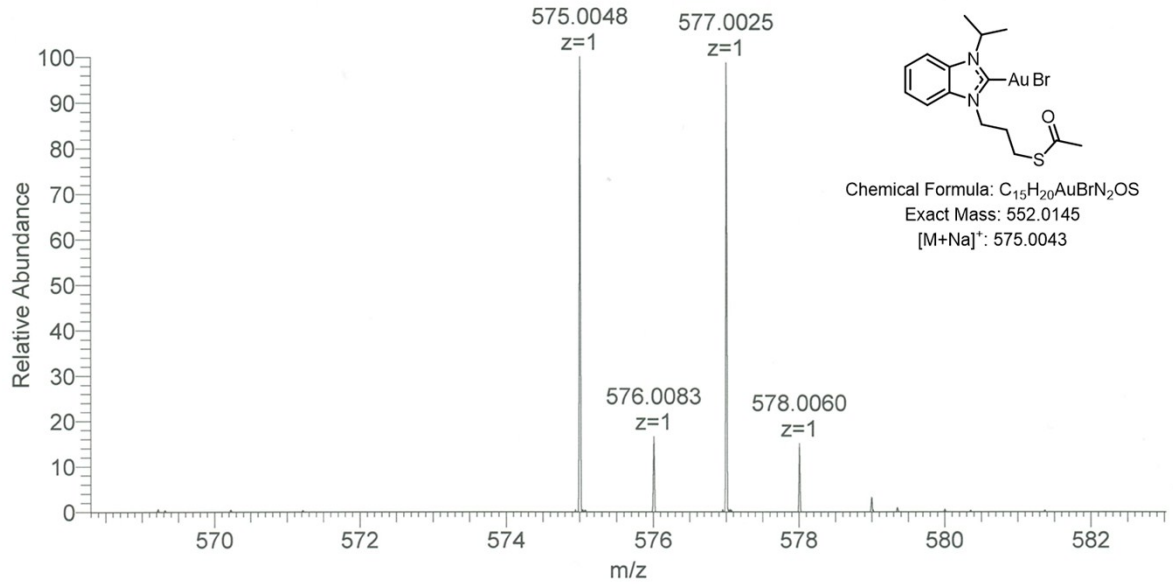
3.3.4 Figure S19: ESI-MS of 3b



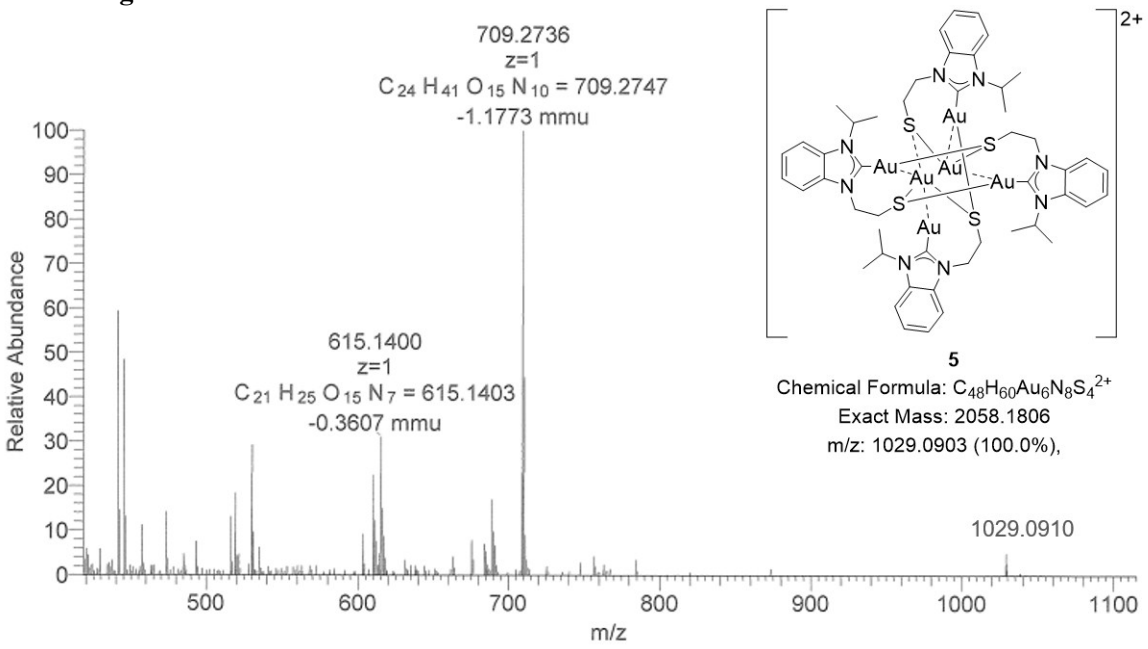
3.3.5 Figure S20: ESI-MS of 4a



3.3.6 Figure S21: ESI-MS of 4b



3.3.7 Figure S22: ESI-MS of 5a



3.4 X-ray Crystallography

3.4.1 Table S1: X-ray data for 4a.

Identification code	**4a**	
Empirical formula	$C_{14}\ H_{18}\ Au\ Br\ N_2\ O\ S$	
Formula weight	539.24	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.2685(3) Å	α= 66.9380(10)°.
	b = 9.2937(3) Å	β= 78.8370(10)°.
	c = 10.4915(3) Å	γ = 79.3620(10)°.
Volume	809.82(4) $Å^3$	
Z	2	
Density (calculated)	2.211 Mg/m^3	
Absorption coefficient	11.676 mm^{-1}	
F(000)	508	
Crystal size	0.151 x 0.122 x 0.102 mm^3	
Theta range for data collection	2.887 to 30.539°.	
Index ranges	-13<=h<=13, -13<=k<=13, -14<=l<=14	
Reflections collected	43744	
Independent reflections	4943 [R(int) = 0.0433]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.4532	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4943 / 0 / 184	
Goodness-of-fit on F^2	1.107	
Final R indices [I>2sigma(I)]	R1 = 0.0193, wR2 = 0.0488	
R indices (all data)	R1 = 0.0215, wR2 = 0.0497	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.984 and -1.543 $e.Å^{-3}$	

3.4.2 Table S2: Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for 4a.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	6389(1)	3828(1)	1012(1)	22(1)
Br(1)	7410(1)	1945(1)	-63(1)	31(1)
S(1)	1070(1)	2434(1)	4096(1)	30(1)
O(1)	1116(3)	3383(3)	6137(2)	40(1)
N(1)	4441(2)	5114(3)	3019(2)	21(1)
N(2)	6123(2)	6662(3)	1831(2)	22(1)
C(1)	5615(3)	5320(3)	1999(3)	21(1)
C(2)	4184(3)	6333(3)	3515(3)	22(1)
C(3)	3150(3)	6623(4)	4562(3)	27(1)
C(4)	3198(3)	7995(4)	4775(3)	30(1)
C(5)	4227(3)	9033(4)	3963(3)	29(1)
C(6)	5279(3)	8735(3)	2935(3)	26(1)
C(7)	5242(3)	7346(3)	2733(3)	21(1)
C(8)	3614(3)	3758(3)	3591(3)	24(1)
C(9)	2036(3)	4159(3)	3229(3)	26(1)
C(10)	793(3)	2363(4)	5844(3)	30(1)
C(11)	143(4)	921(4)	6901(4)	40(1)
C(12)	7387(3)	7386(3)	820(3)	26(1)
C(13)	8763(3)	6214(5)	867(4)	40(1)
C(14)	6923(4)	8217(5)	-622(3)	41(1)

3.4.3 Table S3: Bond lengths [Å] and angles [°] for 4a.

Au(1)-C(1)	1.994(3)
Au(1)-Br(1)	2.3986(3)
S(1)-C(10)	1.779(3)
S(1)-C(9)	1.809(3)
O(1)-C(10)	1.205(4)
N(1)-C(1)	1.354(3)
N(1)-C(2)	1.387(3)
N(1)-C(8)	1.456(3)
N(2)-C(1)	1.349(3)
N(2)-C(7)	1.396(3)
N(2)-C(12)	1.484(3)
C(2)-C(3)	1.388(4)
C(2)-C(7)	1.395(4)
C(3)-C(4)	1.388(4)
C(3)-H(3)	0.9500
C(4)-C(5)	1.396(4)
C(4)-H(4)	0.9500
C(5)-C(6)	1.385(4)
C(5)-H(5)	0.9500
C(6)-C(7)	1.395(4)
C(6)-H(6)	0.9500
C(8)-C(9)	1.524(4)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(11)	1.505(4)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-C(13)	1.511(4)
C(12)-C(14)	1.512(4)
C(12)-H(12)	1.0000
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800

C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800

C(1)-Au(1)-Br(1)	176.54(7)
C(10)-S(1)-C(9)	99.89(14)
C(1)-N(1)-C(2)	110.5(2)
C(1)-N(1)-C(8)	125.3(2)
C(2)-N(1)-C(8)	124.1(2)
C(1)-N(2)-C(7)	109.9(2)
C(1)-N(2)-C(12)	127.0(2)
C(7)-N(2)-C(12)	123.1(2)
N(2)-C(1)-N(1)	107.0(2)
N(2)-C(1)-Au(1)	128.99(19)
N(1)-C(1)-Au(1)	123.96(19)
N(1)-C(2)-C(3)	132.0(3)
N(1)-C(2)-C(7)	106.0(2)
C(3)-C(2)-C(7)	122.0(2)
C(4)-C(3)-C(2)	116.6(3)
C(4)-C(3)-H(3)	121.7
C(2)-C(3)-H(3)	121.7
C(3)-C(4)-C(5)	121.4(3)
C(3)-C(4)-H(4)	119.3
C(5)-C(4)-H(4)	119.3
C(6)-C(5)-C(4)	122.3(3)
C(6)-C(5)-H(5)	118.9
C(4)-C(5)-H(5)	118.9
C(5)-C(6)-C(7)	116.3(3)
C(5)-C(6)-H(6)	121.8
C(7)-C(6)-H(6)	121.8
C(2)-C(7)-C(6)	121.4(2)
C(2)-C(7)-N(2)	106.4(2)
C(6)-C(7)-N(2)	132.1(3)
N(1)-C(8)-C(9)	113.1(2)
N(1)-C(8)-H(8A)	109.0
C(9)-C(8)-H(8A)	109.0
N(1)-C(8)-H(8B)	109.0
C(9)-C(8)-H(8B)	109.0
H(8A)-C(8)-H(8B)	107.8

C(8)-C(9)-S(1)	109.45(19)
C(8)-C(9)-H(9A)	109.8
S(1)-C(9)-H(9A)	109.8
C(8)-C(9)-H(9B)	109.8
S(1)-C(9)-H(9B)	109.8
H(9A)-C(9)-H(9B)	108.2
O(1)-C(10)-C(11)	123.9(3)
O(1)-C(10)-S(1)	122.1(2)
C(11)-C(10)-S(1)	114.0(2)
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
N(2)-C(12)-C(13)	112.2(2)
N(2)-C(12)-C(14)	109.8(2)
C(13)-C(12)-C(14)	113.6(3)
N(2)-C(12)-H(12)	107.0
C(13)-C(12)-H(12)	107.0
C(14)-C(12)-H(12)	107.0
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(12)-C(14)-H(14A)	109.5
C(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(12)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5

Symmetry transformations used to generate equivalent atoms:

3.4.4 Table S4: Anisotropic displacement parameters (Å^2 ×10^3) for 4a.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Au(1)	21(1)	22(1)	23(1)	-10(1)	1(1)	-4(1)
Br(1)	33(1)	28(1)	34(1)	-16(1)	4(1)	-5(1)
S(1)	29(1)	33(1)	32(1)	-14(1)	3(1)	-12(1)
O(1)	42(1)	45(1)	38(1)	-23(1)	7(1)	-14(1)
N(1)	20(1)	20(1)	22(1)	-8(1)	-1(1)	-1(1)
N(2)	20(1)	23(1)	22(1)	-9(1)	-1(1)	-2(1)
C(1)	21(1)	20(1)	20(1)	-6(1)	-3(1)	-2(1)
C(2)	22(1)	21(1)	22(1)	-8(1)	-5(1)	2(1)
C(3)	22(1)	31(1)	27(1)	-13(1)	0(1)	1(1)
C(4)	30(1)	33(2)	29(1)	-18(1)	-3(1)	5(1)
C(5)	31(1)	26(1)	34(1)	-16(1)	-8(1)	4(1)
C(6)	28(1)	22(1)	28(1)	-9(1)	-7(1)	-1(1)
C(7)	22(1)	22(1)	20(1)	-8(1)	-4(1)	1(1)
C(8)	21(1)	21(1)	27(1)	-6(1)	0(1)	-2(1)
C(9)	23(1)	25(1)	27(1)	-7(1)	-1(1)	-5(1)
C(10)	23(1)	32(1)	30(1)	-10(1)	2(1)	-3(1)
C(11)	38(2)	38(2)	36(2)	-5(1)	2(1)	-11(1)
C(12)	24(1)	31(1)	28(1)	-14(1)	4(1)	-11(1)
C(13)	21(1)	51(2)	56(2)	-30(2)	4(1)	-8(1)
C(14)	42(2)	50(2)	29(2)	-7(1)	2(1)	-19(2)

3.4.5 Table S5: Anisotropic Hydrogen coordinates (× 10^4) and isotropic displacement parameters (Å^2 × 10^3) for 4a.

	x	y	z	U(eq)
H(3)	2445	5918	5106	32
H(4)	2517	8232	5489	36
H(5)	4205	9977	4121	35
H(6)	5988	9438	2396	31
H(8A)	3578	3312	4621	29
H(8B)	4145	2940	3229	29
H(9A)	2058	4517	2205	31
H(9B)	1512	5023	3534	31
H(11A)	-308	434	6423	60
H(11B)	-614	1221	7575	60
H(11C)	928	167	7394	60
H(12)	7625	8212	1108	32
H(13A)	8644	5501	421	60
H(13B)	8916	5603	1842	60
H(13C)	9622	6778	369	60
H(14A)	7731	8773	-1268	62
H(14B)	6043	8976	-585	62
H(14C)	6692	7442	-948	62

3.4.6 Table S6: X-ray data for 5a

Identification code	**5a**
Empirical formula	$C_{50}\ H_{60}\ Au_6\ F_{12}\ N_8\ O_2\ P_2\ S_4$
Formula weight	2405.04
Temperature	123(2) K
Wavelength	0.71075 Å
Crystal system	Orthorhombic
Space group	F d d d :2
Unit cell dimensions	a = 12.360(4) Å α= 90°. b = 29.522(9) Å β= 90°. c = 35.0152(10) Å γ = 90°.
Volume	12777(6) $Å^3$
Z	8
Density (calculated)	2.501 Mg/m^3
Absorption coefficient	13.988 mm^{-1}
F(000)	8864
Crystal size	0.150 x 0.150 x 0.150 mm^3
Theta range for data collection	3.170 to 24.997°.
Index ranges	-14<=h<=14, -35<=k<=35, -41<=l<=41
Reflections collected	37240
Independent reflections	2815 [R(int) = 0.0662]
Completeness to theta = 24.997°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.446
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2815 / 83 / 238
Goodness-of-fit on F^2	0.992
Final R indices [I>2sigma(I)]	R1 = 0.0178, wR2 = 0.0413
R indices (all data)	R1 = 0.0227, wR2 = 0.0420
Extinction coefficient	n/a
Largest diff. peak and hole	0.907 and -1.005 $e.Å^{-3}$

3.4.7 Table S7: Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters

($Å^2 \times 10^3$) for a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Au(1)	6183(1)	1859(1)	714(1)	16(1)
Au(2)	8124(1)	1250	1250	17(1)
S(1)	8164(1)	1785(1)	1721(1)	19(1)
C(1)	7760(3)	1966(1)	607(1)	14(1)
N(1)	8412(2)	2243(1)	810(1)	15(1)
C(2)	9415(3)	2281(1)	633(1)	19(1)
C(3)	9366(3)	2010(1)	304(1)	18(1)
N(2)	8327(2)	1819(1)	302(1)	15(1)
C(4)	8112(3)	2490(1)	1154(1)	18(1)
C(5)	8656(3)	2318(1)	1515(1)	18(1)
C(6)	10319(3)	2542(1)	724(1)	23(1)
C(7)	11179(3)	2510(2)	477(1)	32(1)
C(8)	11143(3)	2235(2)	151(1)	33(1)
C(9)	10245(3)	1984(1)	56(1)	27(1)
C(10)	7818(3)	1547(1)	-5(1)	22(1)
C(11)	7404(4)	1858(2)	-316(1)	39(1)
C(12)	8563(4)	1181(2)	-162(1)	33(1)
P(1)	8750	3750	1548(1)	22(1)
F(1)	8750	3750	1097(2)	35(3)
F(2)	8750	3750	2008(2)	44(3)
F(3)	9550(5)	3322(2)	1557(2)	44(3)
F(4)	7723(2)	3420(1)	1550(1)	32(1)
F(5)	9465(7)	3369(3)	1339(3)	30(4)
F(6)	9147(7)	3544(3)	1952(2)	33(4)
F(7)	8421(9)	3949(3)	1142(2)	31(4)
F(8)	8095(10)	4131(3)	1764(3)	37(4)
C(13)	1250	1250	1250	143(6)
O(1)	1250	1250	869(2)	193(5)
C(14)	1110(30)	1705(7)	1449(9)	115(7)

3.4.8 Table S8: Bond lengths [Å] and angles [°] for 5a.

Au(1)-C(1)	2.010(4)
Au(1)-S(1)#1	2.3036(12)
Au(2)-S(1)	2.2855(11)
Au(2)-S(1)#2	2.2855(11)
S(1)-C(5)	1.835(4)
S(1)-Au(1)#1	2.3036(12)
C(1)-N(1)	1.348(5)
C(1)-N(2)	1.349(5)
N(1)-C(2)	1.391(5)
N(1)-C(4)	1.458(5)
C(2)-C(6)	1.395(5)
C(2)-C(3)	1.403(6)
C(3)-C(9)	1.393(5)
C(3)-N(2)	1.401(5)
N(2)-C(10)	1.484(5)
C(4)-C(5)	1.518(5)
C(4)-H(1)	0.9900
C(4)-H(2)	0.9900
C(5)-H(3)	0.9900
C(5)-H(4)	0.9900
C(6)-C(7)	1.373(6)
C(6)-H(5)	0.9500
C(7)-C(8)	1.400(7)
C(7)-H(6)	0.9500
C(8)-C(9)	1.377(6)
C(8)-H(7)	0.9500
C(9)-H(8)	0.9500
C(10)-C(11)	1.514(6)
C(10)-C(12)	1.522(6)
C(10)-H(9)	1.0000
C(11)-H(10)	0.9800
C(11)-H(11)	0.9800
C(11)-H(12)	0.9800
C(12)-H(13)	0.9800
C(12)-H(14)	0.9800
C(12)-H(15)	0.9800
C(1)-Au(1)-S(1)#1	173.66(11)
S(1)-Au(2)-S(1)#2	177.55(5)
C(5)-S(1)-Au(2)	108.38(13)
C(5)-S(1)-Au(1)#1	106.66(12)
Au(2)-S(1)-Au(1)#1	96.60(4)
N(1)-C(1)-N(2)	107.5(3)
N(1)-C(1)-Au(1)	125.2(3)
N(2)-C(1)-Au(1)	126.9(3)
C(1)-N(1)-C(2)	110.3(3)
C(1)-N(1)-C(4)	125.9(3)
C(2)-N(1)-C(4)	123.7(3)
N(1)-C(2)-C(6)	131.1(4)
N(1)-C(2)-C(3)	106.3(3)
C(6)-C(2)-C(3)	122.5(4)
C(9)-C(3)-N(2)	133.6(4)
C(9)-C(3)-C(2)	120.6(4)
N(2)-C(3)-C(2)	105.8(3)

C(1)-N(2)-C(3)	110.1(3)
C(1)-N(2)-C(10)	121.9(3)
C(3)-N(2)-C(10)	127.5(3)
N(1)-C(4)-C(5)	114.1(3)
N(1)-C(4)-H(1)	108.7
C(5)-C(4)-H(1)	108.7
N(1)-C(4)-H(2)	108.7
C(5)-C(4)-H(2)	108.7
H(1)-C(4)-H(2)	107.6
C(4)-C(5)-S(1)	117.8(3)
C(4)-C(5)-H(3)	107.8
S(1)-C(5)-H(3)	107.8
C(4)-C(5)-H(4)	107.8
S(1)-C(5)-H(4)	107.8
H(3)-C(5)-H(4)	107.2
C(7)-C(6)-C(2)	116.0(4)
C(7)-C(6)-H(5)	122.0
C(2)-C(6)-H(5)	122.0
C(6)-C(7)-C(8)	121.9(4)
C(6)-C(7)-H(6)	119.0
C(8)-C(7)-H(6)	119.0
C(9)-C(8)-C(7)	122.3(4)
C(9)-C(8)-H(7)	118.8
C(7)-C(8)-H(7)	118.8
C(8)-C(9)-C(3)	116.6(4)
C(8)-C(9)-H(8)	121.7
C(3)-C(9)-H(8)	121.7
N(2)-C(10)-C(11)	109.7(3)
N(2)-C(10)-C(12)	113.0(3)
C(11)-C(10)-C(12)	112.1(4)
N(2)-C(10)-H(9)	107.3
C(11)-C(10)-H(9)	107.3
C(12)-C(10)-H(9)	107.3
C(10)-C(11)-H(10)	109.5
C(10)-C(11)-H(11)	109.5
H(10)-C(11)-H(11)	109.5
C(10)-C(11)-H(12)	109.5
H(10)-C(11)-H(12)	109.5
H(11)-C(11)-H(12)	109.5
C(10)-C(12)-H(13)	109.5
C(10)-C(12)-H(14)	109.5
H(13)-C(12)-H(14)	109.5
C(10)-C(12)-H(15)	109.5
H(13)-C(12)-H(15)	109.5
H(14)-C(12)-H(15)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x+5/4,y,-z+1/4 #2 x,-y+1/4,-z+1/4 #3 -x+7/4,-y+3/4,z

3.4.9 Table S9: Anisotropic displacement parameters

Anisotropic displacement parameters ($Å^2 \times 10^3$) for a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ \eta^2\ \alpha^{*2} U^{11} + ...\ + 2\ \eta\ \kappa\ \alpha^*\ \beta^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Au(1)	16(1)	15(1)	16(1)	-2(1)	2(1)	-2(1)
Au(2)	14(1)	14(1)	24(1)	4(1)	0	0
S(1)	18(1)	20(1)	19(1)	5(1)	0(1)	2(1)
C(1)	22(2)	8(2)	12(2)	4(2)	3(2)	1(2)
N(1)	16(2)	16(2)	13(2)	0(1)	3(1)	-1(1)
C(2)	19(2)	19(2)	17(2)	5(2)	1(2)	1(2)
C(3)	18(2)	15(2)	20(2)	4(2)	4(2)	0(2)
N(2)	21(2)	11(2)	14(2)	-1(1)	2(1)	2(1)
C(4)	25(2)	11(2)	17(2)	-2(2)	0(2)	-1(2)
C(5)	16(2)	20(2)	17(2)	-3(2)	0(2)	-5(2)
C(6)	22(2)	20(2)	27(3)	8(2)	0(2)	-6(2)
C(7)	20(2)	32(3)	42(3)	9(2)	-2(2)	-9(2)
C(8)	21(2)	40(3)	38(3)	6(2)	13(2)	0(2)
C(9)	25(2)	28(3)	29(3)	0(2)	8(2)	1(2)
C(10)	32(2)	18(2)	17(2)	-7(2)	3(2)	-3(2)
C(11)	59(3)	34(3)	24(3)	-4(2)	-19(2)	5(3)
C(12)	46(3)	22(2)	30(3)	-7(2)	13(2)	0(2)
P(1)	30(1)	16(1)	21(1)	0	0	-7(1)
F(1)	30(5)	57(7)	18(4)	0	0	-1(5)
F(2)	60(7)	50(7)	22(4)	0	0	-24(5)
F(3)	39(4)	20(4)	74(8)	8(5)	-25(6)	0(3)
F(4)	34(1)	23(1)	38(2)	-6(1)	4(1)	-12(1)
F(5)	22(7)	15(7)	54(12)	-12(8)	12(7)	-3(5)
F(6)	35(7)	32(7)	31(6)	19(5)	3(5)	-3(6)
F(7)	36(8)	34(8)	24(6)	-3(5)	-5(5)	-4(6)
F(8)	44(7)	26(7)	40(8)	-16(6)	4(7)	4(5)
C(13)	115(7)	163(8)	150(8)	0	0	0
O(1)	156(7)	224(8)	200(8)	0	0	14(6)
C(14)	103(9)	118(10)	125(10)	3(7)	-8(7)	-3(7)

3.4.10 Table S10: Hydrogen coordinates

Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$)

	x	y	z	U(eq)
H(1)	7318	2470	1188	21
H(2)	8300	2813	1119	21
H(3)	8589	2556	1712	21
H(4)	9437	2282	1460	21
H(5)	10339	2731	943	28
H(6)	11817	2678	529	38
H(7)	11760	2223	-10	40
H(8)	10226	1801	-167	33
H(9)	7176	1391	108	27
H(10)	6884	2073	-207	59
H(11)	7049	1678	-515	59
H(12)	8012	2025	-428	59
H(13)	9105	1319	-330	49
H(14)	8136	961	-307	49
H(15)	8927	1027	50	49

3.4.11 Table S11: Torsion angles [°] for 5a.

N(2)-C(1)-N(1)-C(2)	0.6(4)
Au(1)-C(1)-N(1)-C(2)	-172.9(3)
N(2)-C(1)-N(1)-C(4)	177.5(3)
Au(1)-C(1)-N(1)-C(4)	4.0(5)
C(1)-N(1)-C(2)-C(6)	176.4(4)
C(4)-N(1)-C(2)-C(6)	-0.6(6)
C(1)-N(1)-C(2)-C(3)	-0.1(4)
C(4)-N(1)-C(2)-C(3)	-177.1(3)
N(1)-C(2)-C(3)-C(9)	178.4(4)
C(6)-C(2)-C(3)-C(9)	1.6(6)
N(1)-C(2)-C(3)-N(2)	-0.4(4)
C(6)-C(2)-C(3)-N(2)	-177.3(4)
N(1)-C(1)-N(2)-C(3)	-0.9(4)
Au(1)-C(1)-N(2)-C(3)	172.5(3)
N(1)-C(1)-N(2)-C(10)	-173.3(3)
Au(1)-C(1)-N(2)-C(10)	0.1(5)
C(9)-C(3)-N(2)-C(1)	-177.8(4)
C(2)-C(3)-N(2)-C(1)	0.9(4)
C(9)-C(3)-N(2)-C(10)	-6.0(7)
C(2)-C(3)-N(2)-C(10)	172.7(3)
C(1)-N(1)-C(4)-C(5)	110.7(4)
C(2)-N(1)-C(4)-C(5)	-72.8(4)
N(1)-C(4)-C(5)-S(1)	-74.9(4)
Au(2)-S(1)-C(5)-C(4)	51.1(3)
Au(1)#1-S(1)-C(5)-C(4)	-51.9(3)
N(1)-C(2)-C(6)-C(7)	-177.8(4)
C(3)-C(2)-C(6)-C(7)	-1.8(6)
C(2)-C(6)-C(7)-C(8)	0.8(6)
C(6)-C(7)-C(8)-C(9)	0.4(7)
C(7)-C(8)-C(9)-C(3)	-0.7(7)
N(2)-C(3)-C(9)-C(8)	178.3(4)
C(2)-C(3)-C(9)-C(8)	-0.3(6)
C(1)-N(2)-C(10)-C(11)	91.5(4)
C(3)-N(2)-C(10)-C(11)	-79.5(5)
C(1)-N(2)-C(10)-C(12)	-142.7(4)
C(3)-N(2)-C(10)-C(12)	46.3(5)

Symmetry transformations used to generate equivalent atoms:
#1 -x+5/4,y,-z+1/4 #2 x,-y+1/4,-z+1/4 #3 -x+7/4,-y+3/4,z

3.4.12 Table S12: Hydrogen bonds for 5a [Å and °].

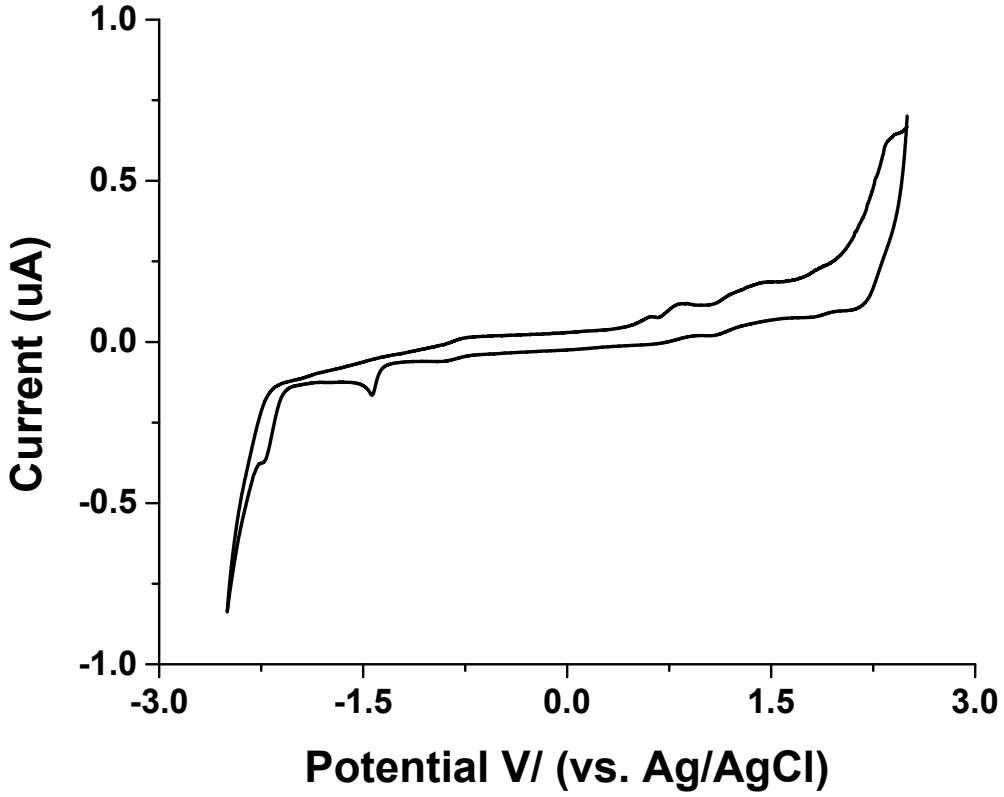
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(4)-H(2)...F(4)	0.99	2.45	3.114(4)	124.1
C(4)-H(2)...F(5)	0.99	2.32	3.155(12)	142.0
C(4)-H(2)...F(7)#3	0.99	2.38	3.353(11)	166.4
C(5)-H(3)...F(3)	0.99	2.61	3.167(8)	115.6
C(5)-H(3)...F(8)#3	0.99	2.61	3.353(11)	132.1
C(6)-H(5)...F(5)	0.95	2.58	3.424(9)	148.7
C(9)-H(8)...F(2)#4	0.95	2.36	3.151(6)	140.9
C(9)-H(8)...F(6)#5	0.95	2.43	3.147(11)	132.2
C(11)-H(11)...F(1)#6	0.98	2.59	3.568(6)	173.4
C(12)-H(13)...F(6)#4	0.98	2.43	3.163(9)	131.0
C(12)-H(15)...S(1)#2	0.98	2.87	3.603(5)	132.1

Symmetry transformations used to generate equivalent atoms:
#1 -x+5/4,y,-z+1/4 #2 x,-y+1/4,-z+1/4 #3 -x+7/4,-y+3/4,z
#4 -x+2,y-1/4,z-1/4 #5 x+1/4,-y+1/2,z-1/4 #6 -x+3/2,-y+1/2,-z

3.5 Cyclic voltammetry

3.5.1 Figure S23: Cyclic voltammogram of 5a.

Scan rate: 50 mV/s; Potential window: -2.5 V to 2.5 V; Electrolyte: 0.10 M $[NH_4][ClO_4]$; Quiet time: 2s; Sample concentration: 0.010 M.

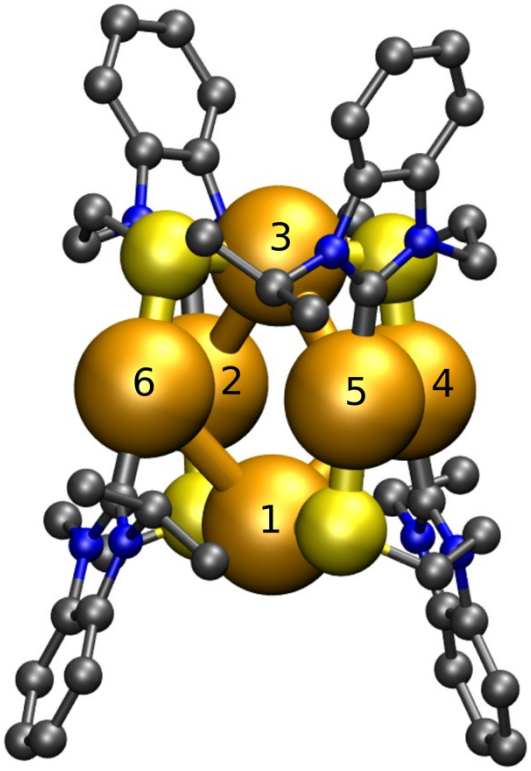


4. Computational data

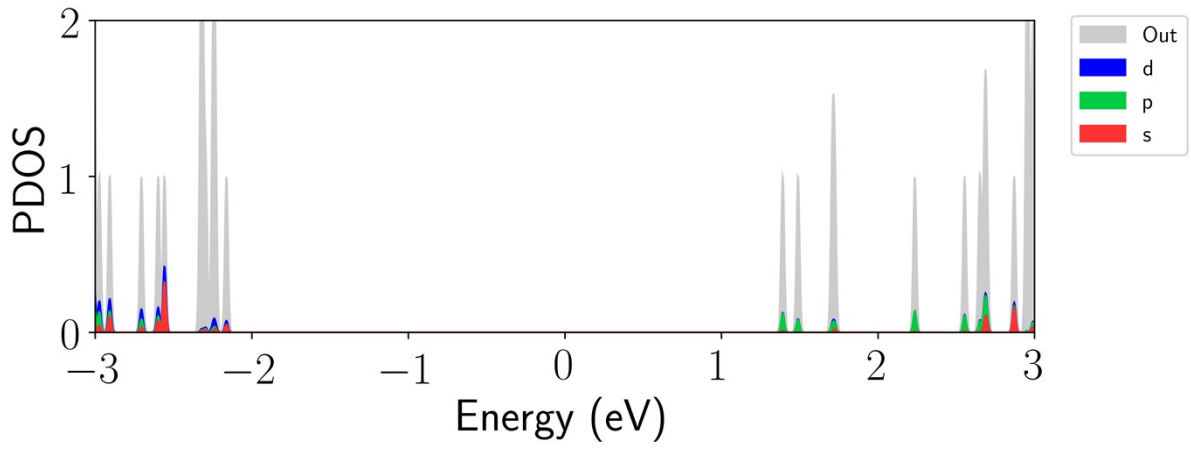
4.1 Computational analysis of cluster 5a.

4.1.1 Figure S24: Relaxed structure of 5a calculated using PBE functional.

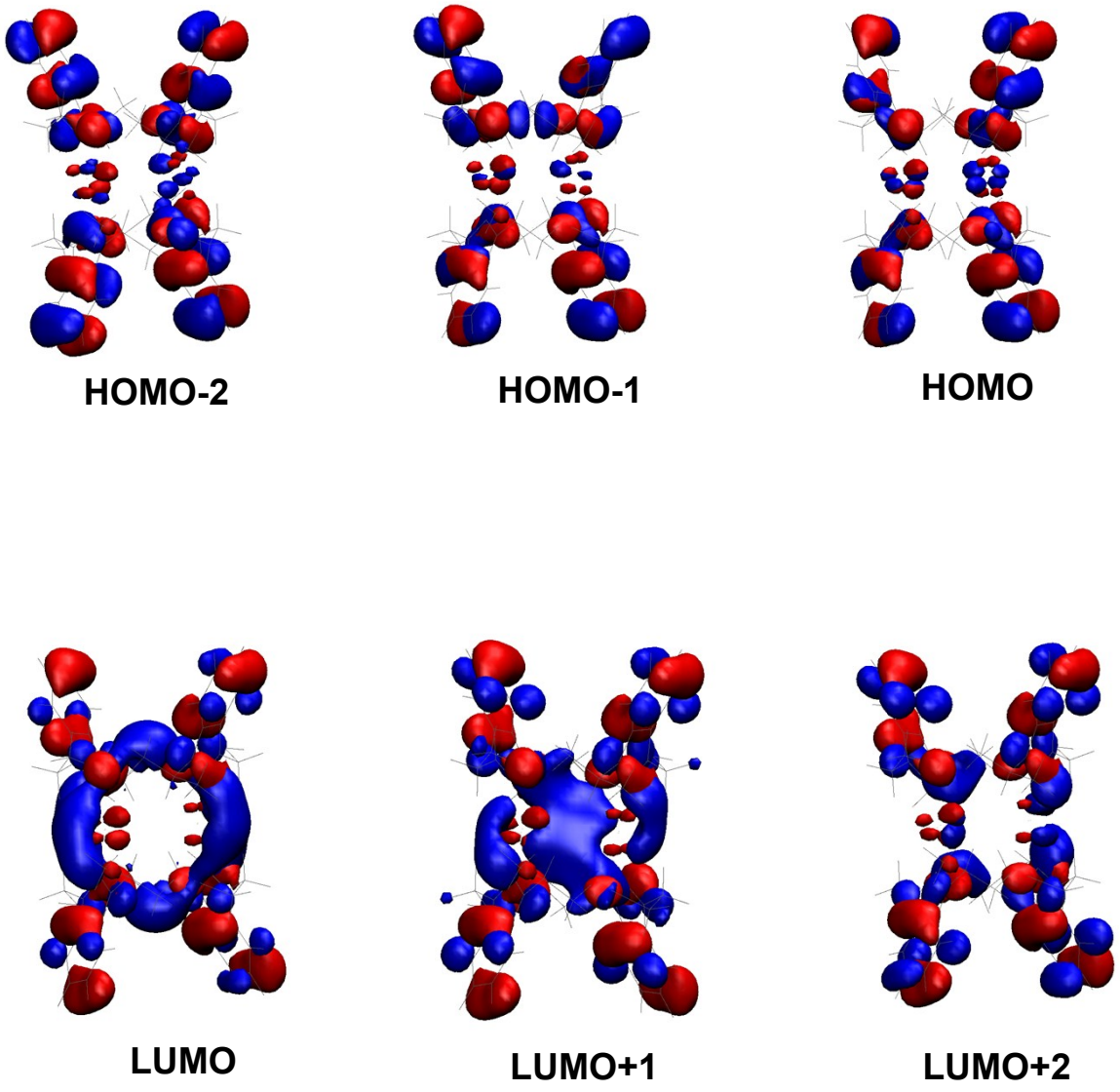
Au atoms are labeled as 1-6 in reference to Table S13.



4.1.2 Figure S25: Gold-projected density of states for 5a.



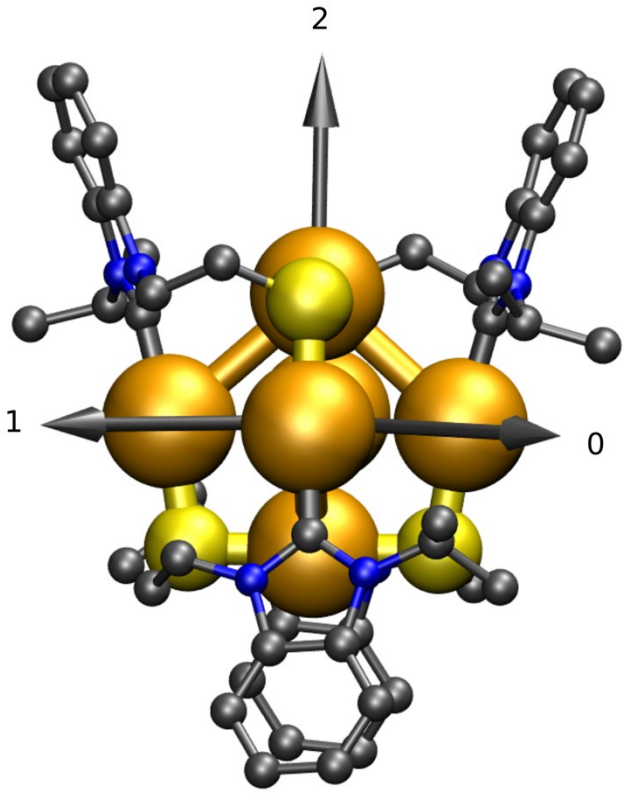
4.1.3 Figure S26: A few frontier orbitals for 5a.



4.1.4 Table S13: Shortest Au-Au distances in 5a.

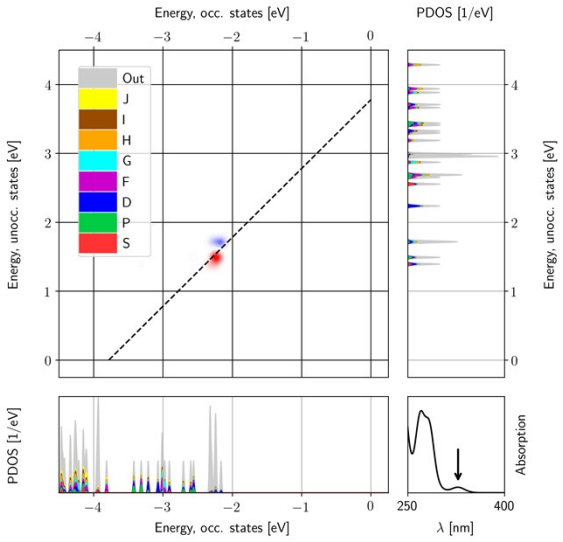
Au-Au	Experimental geometry Distance [**5a**][PF_6]$_2$ (Å)	Optimized geometry distance (Å)
1-6	3.537	3.637
1-5	3.426	3.582
1-3	4.633	4.753
1-4	3.537	3.600
2-3	3.537	3.597
3-4	3.426	3.592
3-5	3.537	3.626

4.1.5 Figure S27: Dipole transition contribution maps (DTCM) analysis for 5a – Principal axes of moments of inertia.

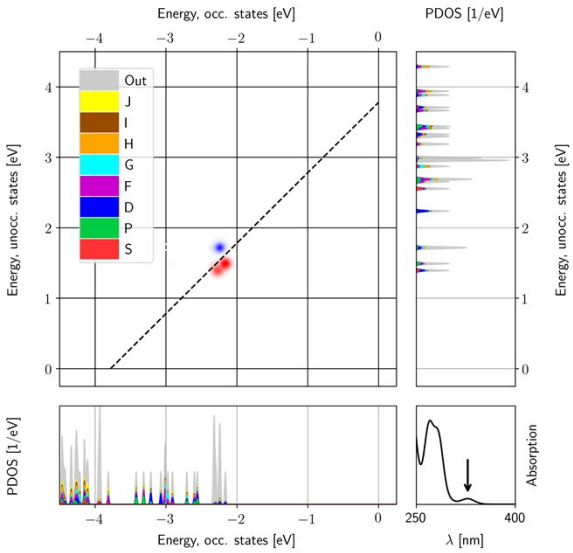


4.1.6 Figure S28: DTCM for peak at E = 3.779 eV.

Red / blue areas indicate constructive / destructive contributions of individual transitions to the total dipole moment. PDOS is analysed as projected to atomic Au s, p, d components. The grey area denotes orbital weights in ligands.

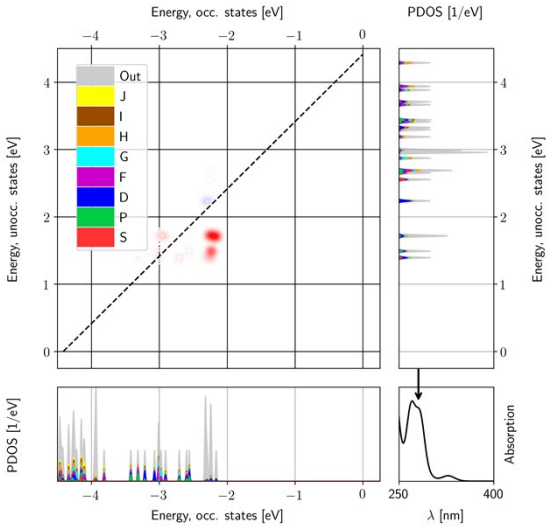


Axis 0

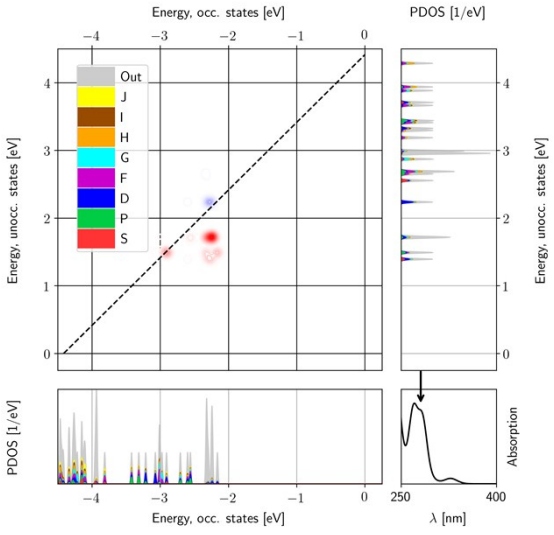


Axis 1

4.1.7 Figure S29: DTCM for peak at E = 4.413 eV.

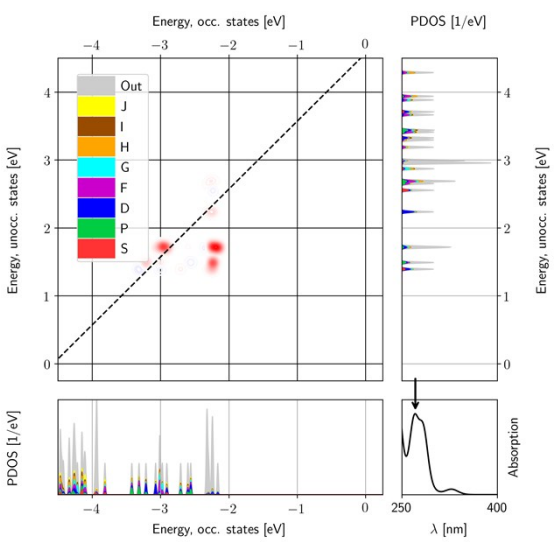


Axis 0

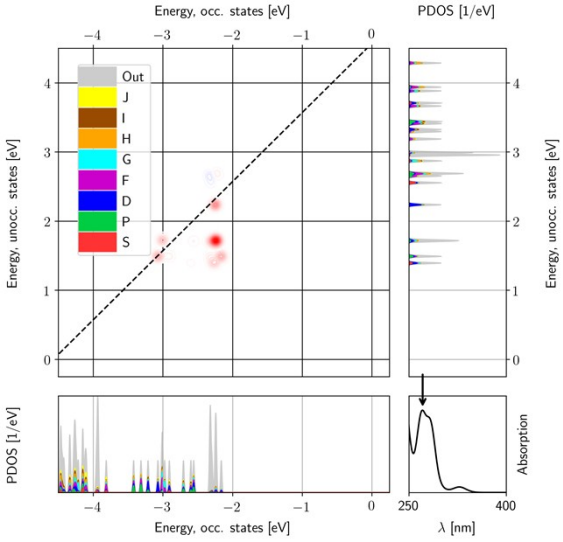


Axis 1

4.1.8 Figure S30: DTCM for peak at E = 4.570 eV.



Axis 0



Axis 1

5. References

1. a) Y. Zhu, C. Cai and G. Lu, *Helv. Chim. Acta*, 2014, **97**, 1666. b) M. -C. Brandy, M. C. Jennings and R. J. Puddephatt, *J. Chem. Soc., Dalton Trans.*, 2000, 4601.
2. H. Hope, *Prog. Inorg. Chem.*, 1993, **41**, 1.
3. G. M. Sheldrick, *Acta. Cryst.*, 2015, **A71**, 3.
4. G. M. Sheldrick, *Acta. Cryst.*, 2015, **C71**, 3.
5. J. Enkovaara, et. al. *J. Phys. Condens. Matter*, 2010, **22**, 253202.
6. J. P. Perdew, K. Burke, and M. Ernzahof, *Phys. Rev. Lett.*, 1996, **78**, 3856.
7. M. Kuisma, J. Ojanen, J. Enkovaara, and T. T. Rantala, *Phys. Rev. B*, **82**, 115106
8. M. Walter, H. Häkkinen, L. Lehtovaara, J. Enkovaara, C. Rostgaard and J. J. Mortensen, *J. Phys. Chem.*, 2008, **128**, 244101.
9. S. Malola, L. Lehtovaara, J. Enkovaara, and H. Häkkinen, *ACS Nano*, 2013, **7**, 10263