Supplementary material.

Twisting the arm: Structural Constraints in Bicyclic Expanded-Ring N-Heterocyclic Carbenes

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Crystallographic data.
Crystal structure determination

Single-crystal XRD data were collected on single crystals mounted in paratone. Data were collected using either a Nonius Kappa CCD diffractometer using graphite monochromated Mo Kα radiation or on an Agilent SuperNova Dual Atlas three-circle diffractometer with a mirror monochromator using Mo (λ = 0.7107 Å) radiation. The samples were cooled to 150 K on using an Oxford Cryosystems apparatus. The structures were solved by direct methods using SHELXS[1] and refined using refined against F^2 using SHELXL[2]. The structures deposited with the Cambridge Structural Database (CCDC deposition numbers CCDC 1558895-1558896, 1561527 and 1845379-1845382. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data and structure refinement for **1** (pdn1705b), α-[CgP(O)AmMe]BF_4 (pdn1706) and **2** (pdn1707)

Compound (Identification code)	**1** (kjc1224)	**2** (kjc1221)	**3** (kjc1230)
CCDC reference	1877805	1877806	1877807
Empirical formula	$C_{18}H_{20}N_2ClAu$	$C_{20}H_{24}N_2ClAu$	$C_{10}H_{20}N_2BrAu$
Formula weight	496.78	524.83	445.16
Temperature /K	150(2)	150(2)	150(2)
Wavelength /Å	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$	$P2_1$
a/Å	7.4368(3)	8.1533(2)	9.6232(6)
b/Å	13.2521(4)	17.9539(3)	7.6641(7)
c/Å	17.6939(6)	13.2803(3)	9.7659(7)
α/°	90	90	90
β/°	90	97.812	114.728(4)
γ/°	90	90	90
Volume/$Å^3$	1743.79(11)	1925.98(7)	654.22(9)
Z	4	4	2
Density (calculated)/ Mg m^{-3}	1.892	1.810	2.260
Absorption coefficient/ mm^{-1}	8.59	7.78	14.27
Crystal size/ mm^3	0.25x0.12x0.09	0.20x0.10x0.04	0.10 x 0.06 x 0.03
Reflections collected	3997	4413	2512
Independent reflections	3743	3944	2319
R(int)	0.0001	0.027	0.0001
Data / restraints / parameters	3997 / 312 / 255	4413 / 0 / 221	2512 / 83 / 132
Goodness-of-fit on F^2	1.06	1.06	1.04
R1, wR2 [I>2σ(I)]	0.0382, 0.0793	0.0284, 0.0655	0.0575, 0.1552
R1, wR2 (all data)	0.0436, 0.0813	0.0342, 0.0680	0.0633, 0.1610
Absolute structure parameter	0.49(2)		
Largest diff. peak and hole e.$Å^{-3}$	2.72 and -1.17	0.88 and -1.74	2.00 and -4.76

Compound (Identification code)	**4** (kjc1225)	**5** (kjc1222t)	**6** (kjc1223)
CCDC reference	1877808	1877809	1877810
Empirical formula	$C_{19}H_{22}N_2ClAu$	$C_{21}H_{26}N_2ClAu$	$C_{25}H_{34}N_2ClAu$
Formula weight	510.80	538.85	594.96
Temperature /K	150(2)	150(2)	150(2)
Wavelength /Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/a$	$Pna2_1$	$P2_1/n$
a/Å	14.6513(13)	16.5805(5)	9.5596(2)
b/Å	7.8132(8)	14.6038(6)	18.9069(5)
c/Å	16.1820(13)	8.1861(4)	12.5673(2)
α/°	90	90	90
β/°	97.495(6)	90	90.647(1)
γ/°	90	90	90
Volume/Å^3	1836.6(3)	1982.17(14)	2271.30(8)
Z	4	4	4
Density (calculated)/ Mgm^{-3}	1.847	1.806	1.740
Absorption coefficient/ mm^{-1}	8.16	7.56	6.61
S1Crystal size/ mm^3	0.08x0.08x0.08	0.272x0.183x0.135	0.30 x 0.25 x 0.20
Reflections collected	4138	4350	5216
Independent reflections	2767	3870	4855
R(int)	0.077	0.0001	0.021
Data / restraints / parameters	4138 / 322 / 263	4350 / 7 / 231	5216 / 0 / 266
Goodness-of-fit on F^2	1.16	1.06	1.05
R1, wR2 [I>2σ(I)]	0.0766, 0.1104	0.0336, 0.0802	0.0231, 0.0544
R1, wR2 (all data)	0.1304, 0.1225	0.0397, 0.0829	0.0259, 0.0532
Absolute structure parameter		0.512(16)	
Largest diff. peak and hole e.Å^{-3}	1.24 and -0.95	0.89 and -1.16	0.80 and -1.68

Compound (Identification code)	**7** (kjc1235)	**8** (kjc1233)	**9** (kjc1231)
CCDC reference	1877811	1877812	1877813
Empirical formula	$C_{11}H_{22}N_2ClAu$	$C_{15}H_{30}N_2ClAu$	$C_{11}H_{20}N_2ClAu$
Formula weight	414.72	470.82	412.71
Temperature /K	150(2)	150(2)	150(2)
Wavelength /Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$P2_12_12_1$
a/Å	9.3774(2)	12.3002(3)	6.7532(3)
b/Å	8.3117(2)	9.3860(2)	8.8718(3)
c/Å	17.1446(4)	15.4720(2)	21.8273(9)
α/°	90	90	90
β/°	91.032(2)	101.338(1)	90
γ/°	90	90	90
Volume/Å^3	1336.07(5)	1751.38(6)	1307.74(9)
Z	4	4	4
Density (calculated)/ Mgm^{-3}	2.062	1.786	2.096
Absorption coefficient/ mm^{-1}	11.18	8.54	11.43
S1Crystal size/ mm^3	0.20x0.20x0.04	0.18x0.18x0.18	0.22x0.14x0.08
Reflections collected	3042	4804	2959
Independent reflections	2907	4319	2852
R(int)	0.023	0.022	0.0001
Data / restraints / parameters	3042 / 0 / 140	4804 / 0 / 178	4804 / 0 / 178
Goodness-of-fit on F^2	1.11	1.06	1.06
R1, wR2 [I>2σ(I)]	0.0279, 0.0715	0.0254, 0.0537	0.0293, 0.0643
R1, wR2 (all data)	0.0302, 0.0705	0.0305, 0.0557	0.0319, 0.0654
Absolute structure parameter			0.035(13)
Largest diff. peak and hole e.Å^{-3}	1.30 and -2.50	0.76 and -1.39	2.21 and -1.60

Compound (Identification code)	**10** (kjc1228)	**11** (pdn1807et)	**12** (pdn1806b)
CCDC reference	1877814	1877815	1877816
Empirical formula	$C_{15}H_{28}N_2ClAu$	$C_{23}H_{28.63}N_2Cl_{0.37}B_{0.63}F_{2.63}Au_{0.37}$	$C_{21}H_{25}N_3ClAu$
Formula weight	468.81	474.20	551.86
Temperature /K	150(2)	150(2)	150(2)
Wavelength /Å	0.71073	0.71073	0.71073
Crystal system	Hexagonal	Orthorhombic	Orthorhombic
Space group	$P6_3$	$P2_12_12_1$	$P2_12_12_1$
a/Å	16.1241(3)	10.6937(4)	20.5559(5)
b/Å	16.1241(3)	13.6965(5)	13.8353(4)
c/Å	11.4641(2)	14.7280(5)	14.0400(4)
α/°	90	90	90
β/°	90	90	90
γ/°	90	90	90
Volume/Å^3	2581.20(11)	2157.16(13)	3992.93(19)
Z	6	4	8
Density (calculated)/ Mgm^{-3}	1.810	1.460	1.836
Absorption coefficient/ mm^{-1}	8.70	2.65	7.51
S1Crystal size/ mm^3	0.30x0.10x0.10	0.18x0.18x0.18	0.35x0.20x0.08
Reflections collected	4913	5035	9615
Independent reflections	4490	3824	8196
R(int)	0.103	0.093	0.031
Data / restraints / parameters	4913 / 792 / 345	5035 / 96 / 293	9615 / 0 / 475
Goodness-of-fit on F^2	1.05	1.10	1.02
R1, wR2 [I>2σ(I)]	0.0411, 0.0775	0.0672, 0.1430	0.0285, 0.0456
R1, wR2 (all data)	0.0488, 0.0808	0.0857, 0.1592	0.0384, 0.0498
Absolute structure parameter		0.025(17)	-0.026(5)
Largest diff. peak and hole e.Å^{-3}	1.21 and -2.03	0.75 and -0.60	1.02 and -0.98

Compound (Identification code)	**13** (pdn1704)	**14** (pdn1505)	**15** (pdn1506d)
CCDC reference	1877817	1877818	1877819
Empirical formula	$C_{38}H_{56}N_4I_2Au_2$	$C_{45}H_{58}N_8BF_4OAu$	$C_{191}H_{190}N_8P_{10}F_{12}OAu_2$
Formula weight	1216.60	1010.77	3545.13
Temperature /K	150(2)	150(2)	150(2)
Wavelength /Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1$	$P2_1$	P1
a/Å	7.9564(2)	16.7838(2)	13.3262(2)
b/Å	19.0099(4)	13.0480(1)	14.2393(2)
c/Å	13.4208(3)	20.4063(2)	23.9673(4)
α/°	90	90	73.606(1)
β/°	97.576(2)	91.259(1)	88.232(1)
γ/°	90	90	89.787(1)
Volume/Å^3	2012.18(8)	4467.80(8)	4360.89(12)
Z	2	4	1
Density (calculated)/ Mgm^{-3}	2.008	1.503	1.350
Absorption coefficient/ mm^{-1}	8.85	6.69	1.84
S1Crystal size/ mm^3	0.26x0.19x0.15	0.41x0.23x0.14	0.23x0.10x0.05
Reflections collected	9523	17626	40776
Independent reflections	8835	17021	30195
R(int)	0.030	0.026	0.061
Data / restraints / parameters	9523 / 1 / 429	17626 / 2556 / 1461	40776 / 132 / 2029
Goodness-of-fit on F^2	1.05	1.101	1.01
R1, wR2 [I>2σ(I)]	0.0324, 0.0683	0.0371, 0.0984	0.0550, 0.0869
R1, wR2 (all data)	0.0369, 0.0709	0.0391, 0.1009	0.0892, 0.1022
Absolute structure parameter	-0.001(3)	-0.007(4)	-0.024(2)
Largest diff. peak and hole e.Å^{-3}	1.23 and -1.56	1.03 and -1.33	2.41 and -0.95

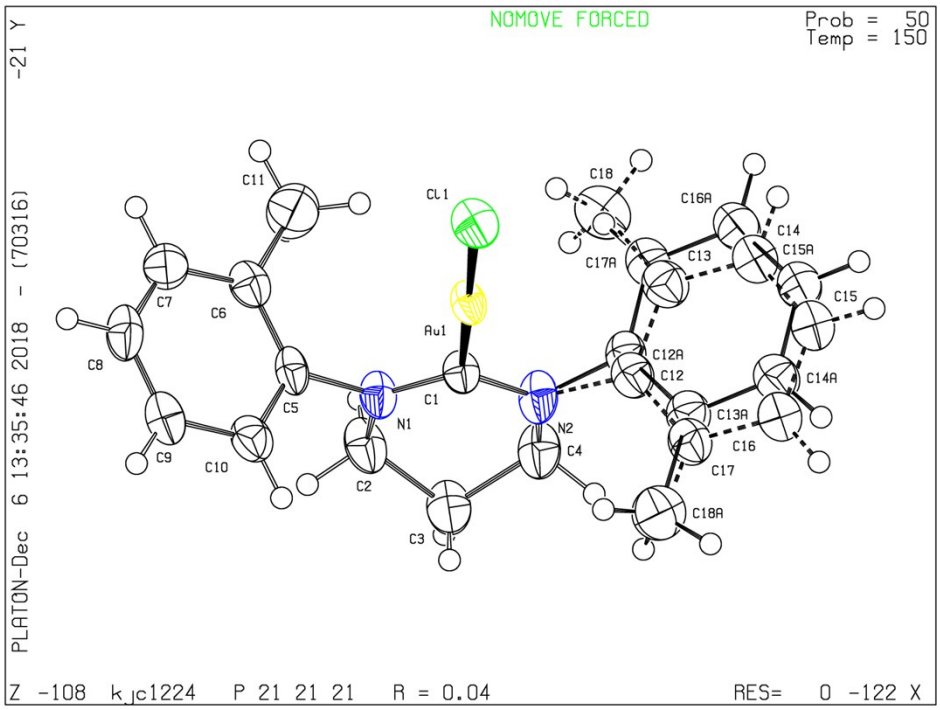

Figure 1: Platon representation of the structure of compound **1**.

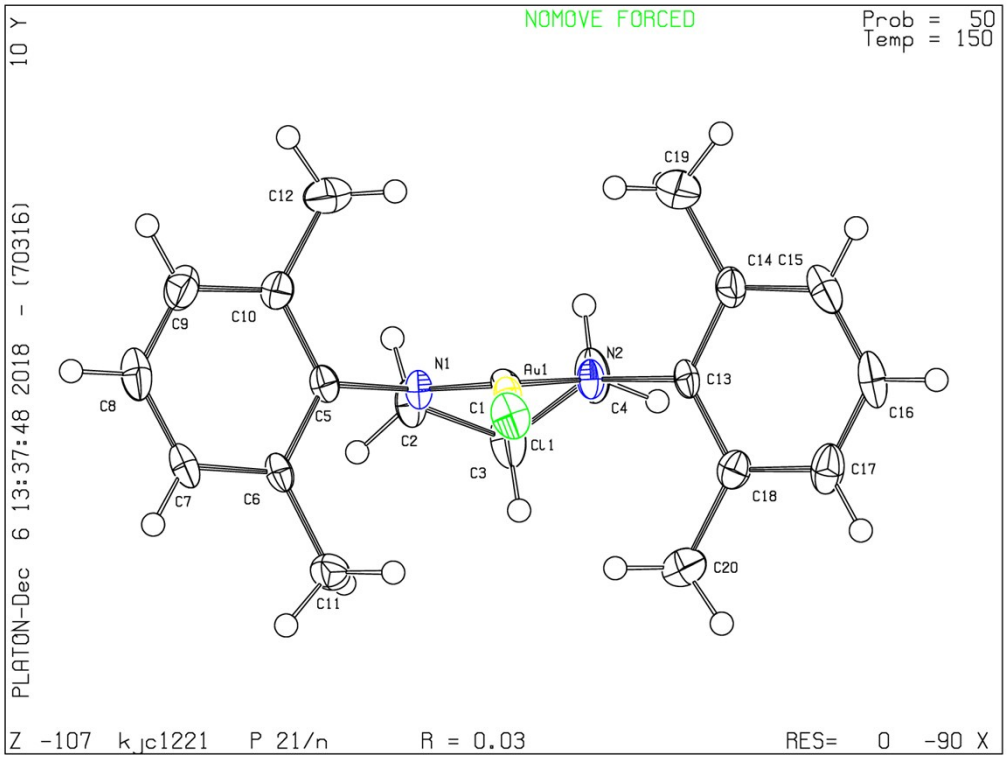

Figure 2: Platon representation of the structure of compound **2**.

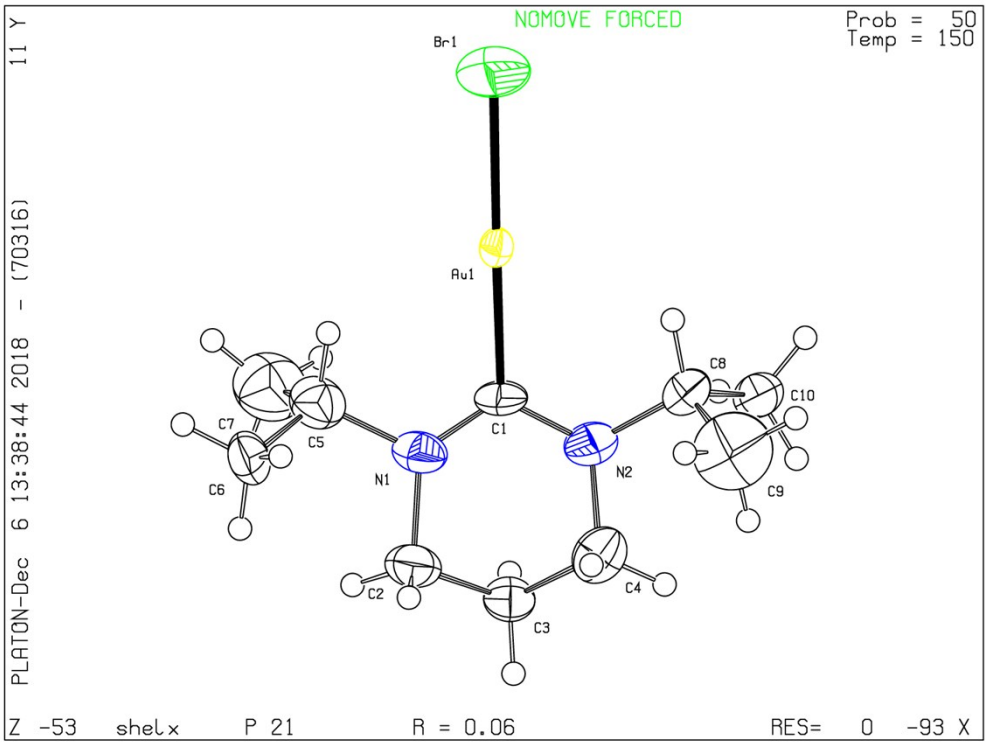

Figure 3: Platon representation of the structure of compound **3**.

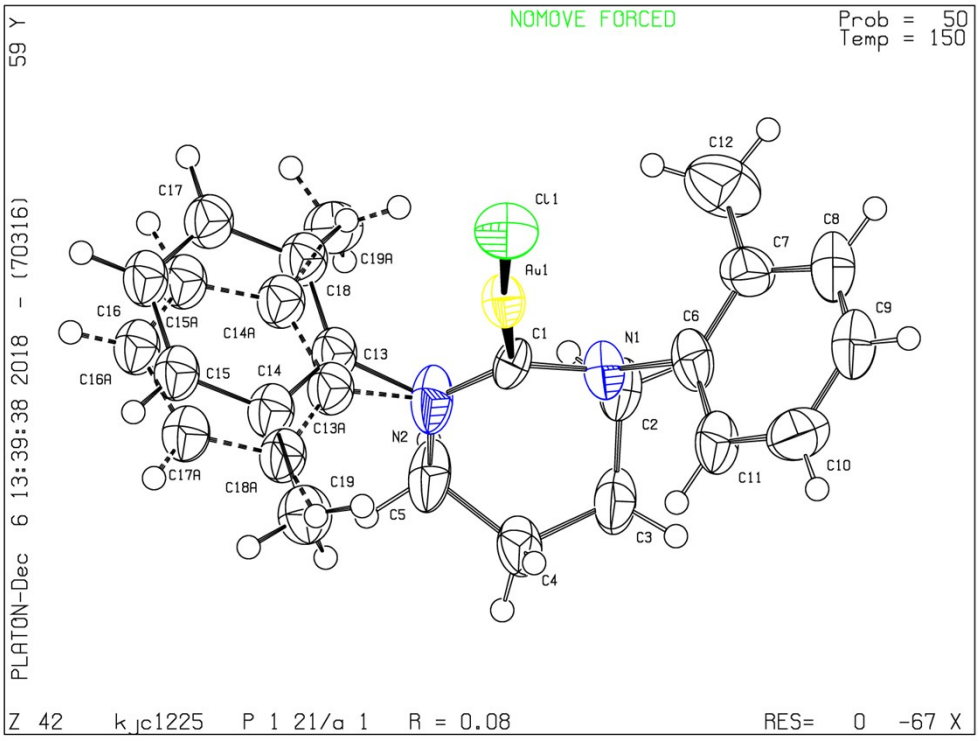

Figure 4: Platon representation of the structure of compound **4**.

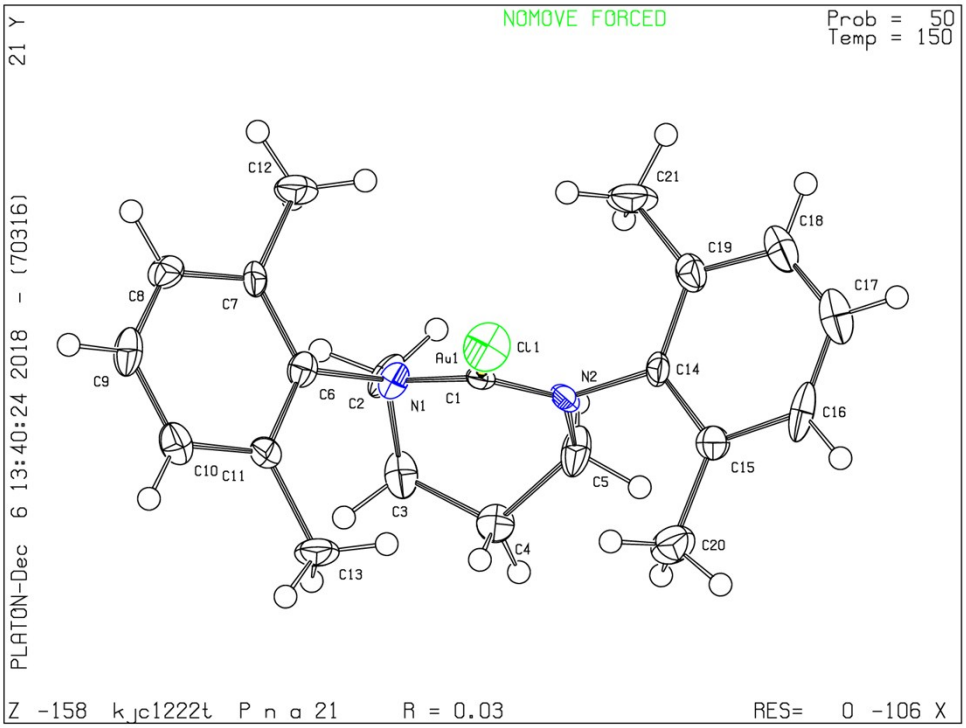

Figure 5: Platon representation of the structure of compound **5**.

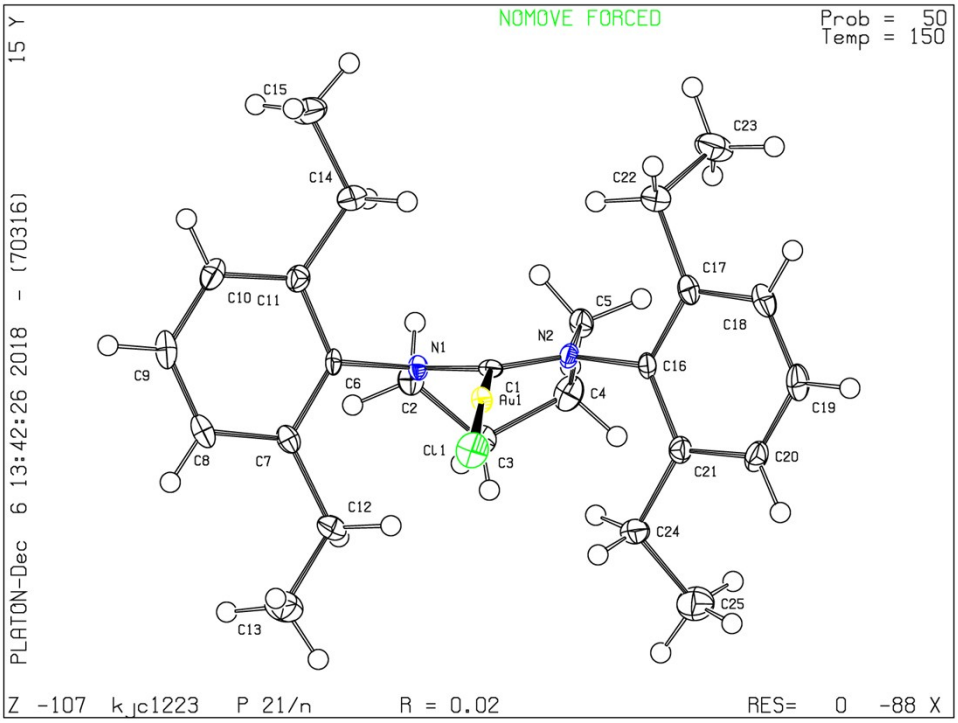

Figure 6: Platon representation of the structure of compound **6**.

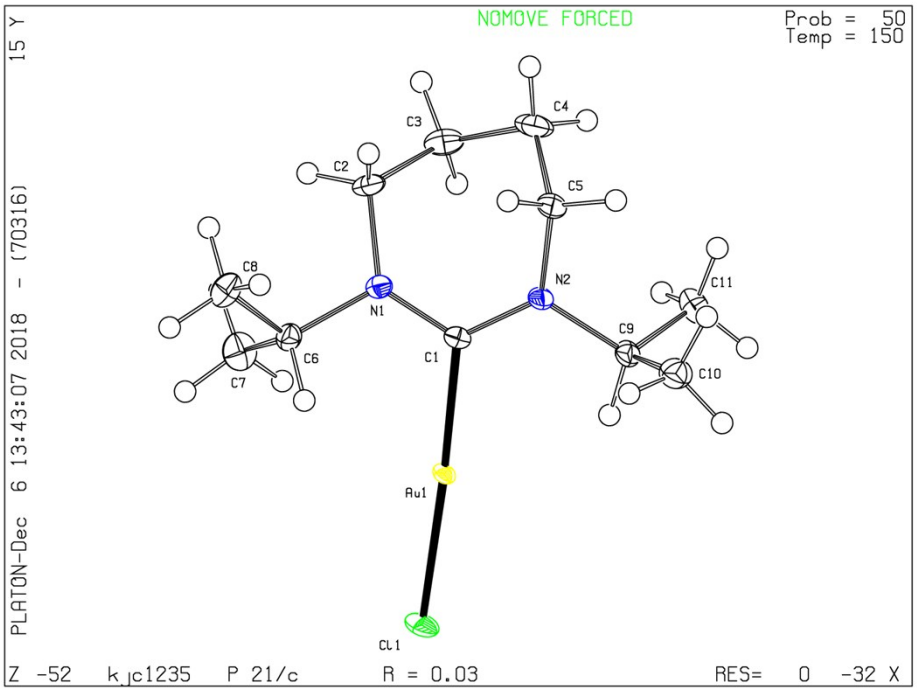

Figure 7: Platon representation of the structure of compound **7**.

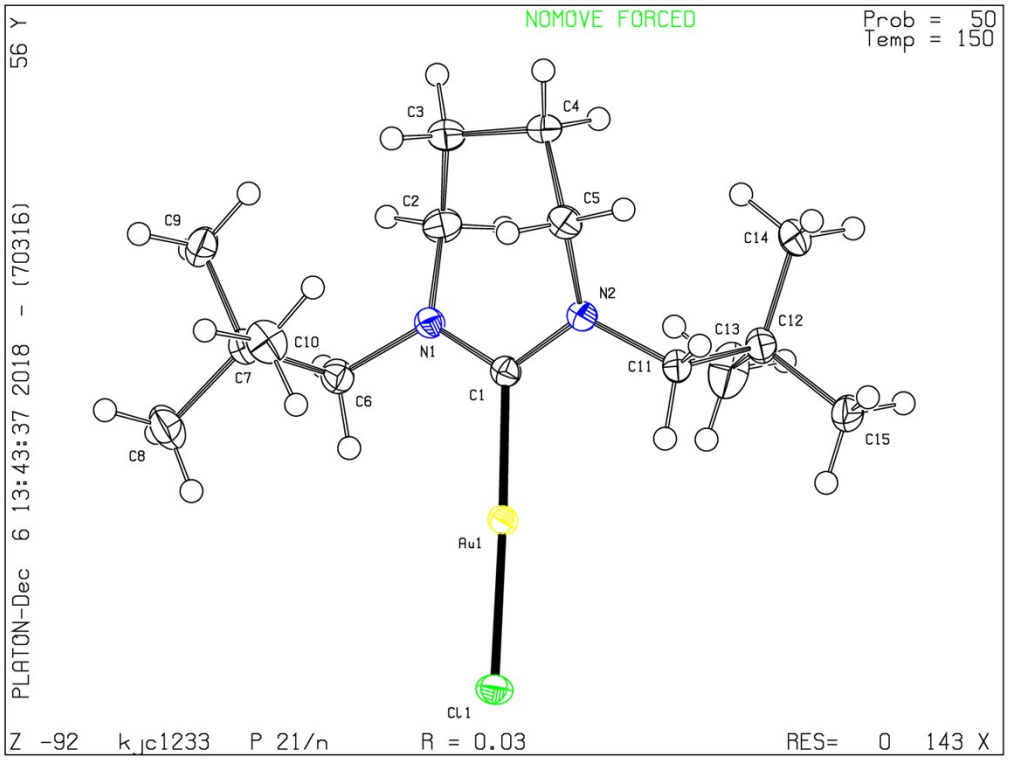

Figure 8: Platon representation of the structure of compound **8**.

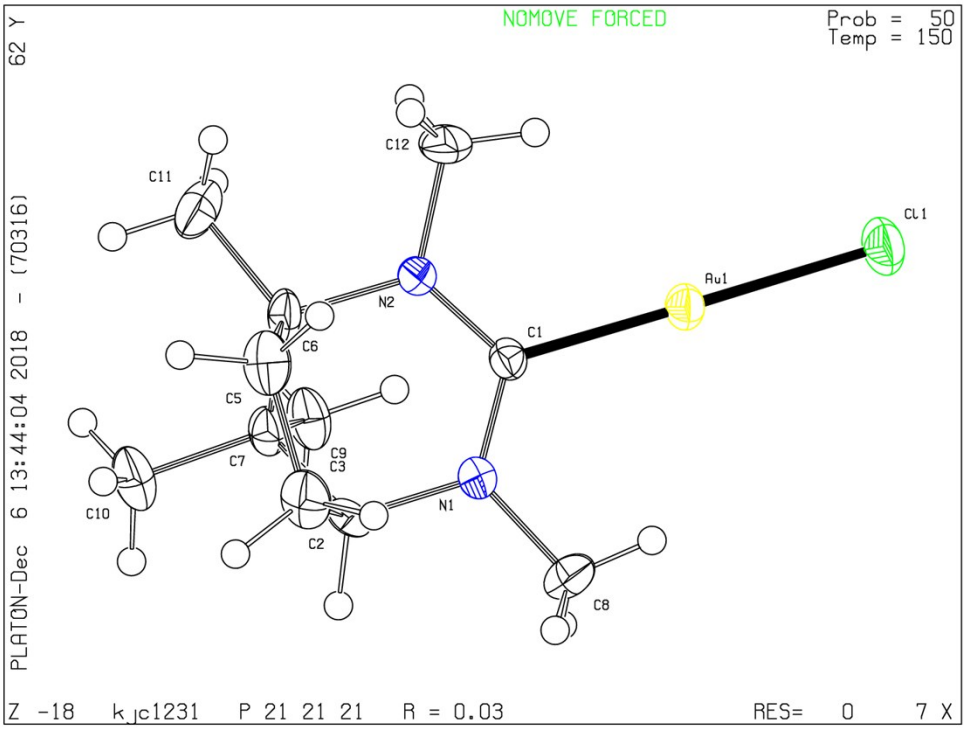

Figure 9: Platon representation of the structure of compound **9**.

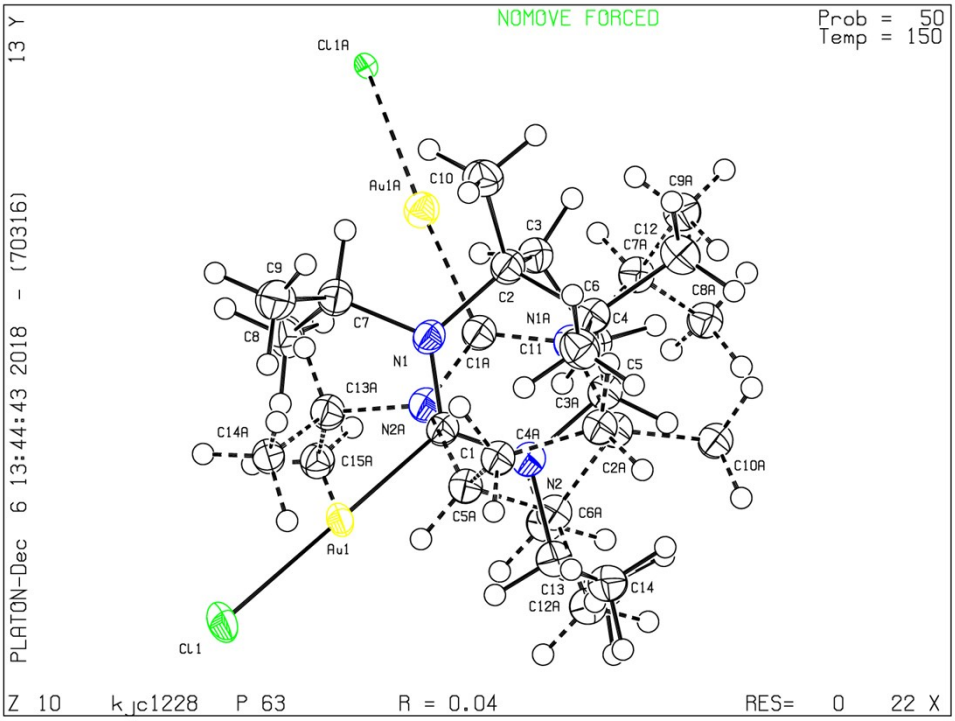

Figure 10: Platon representation of the structure of compound **10**.

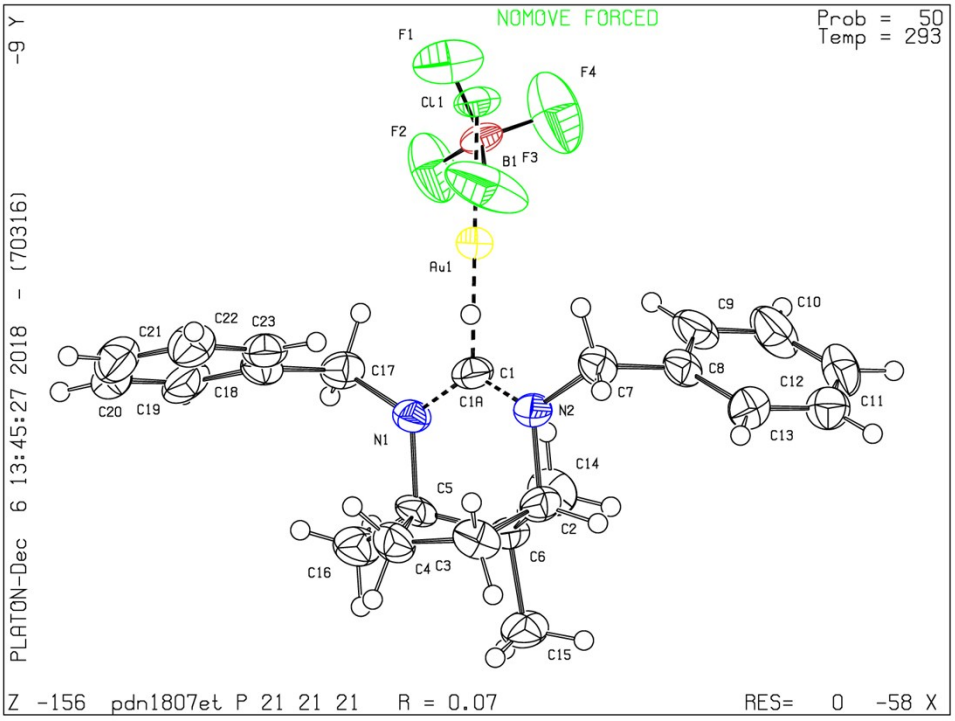

Figure 11: Platon representation of the structure of compound **11**.

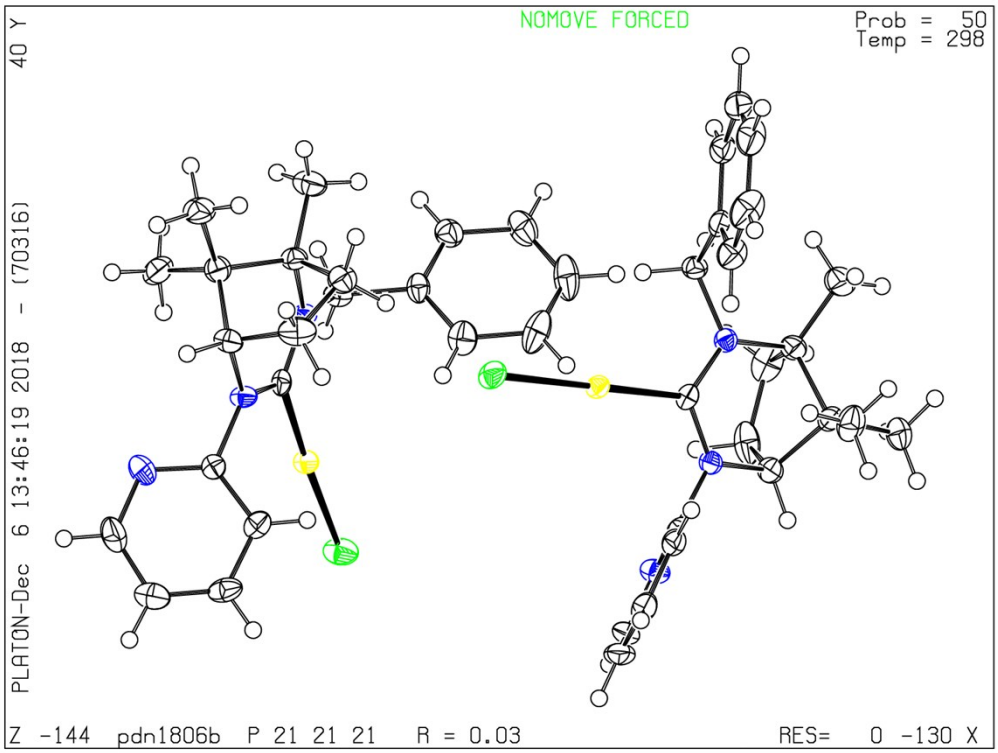

Figure 12: Platon representation of the structure of compound **12**.

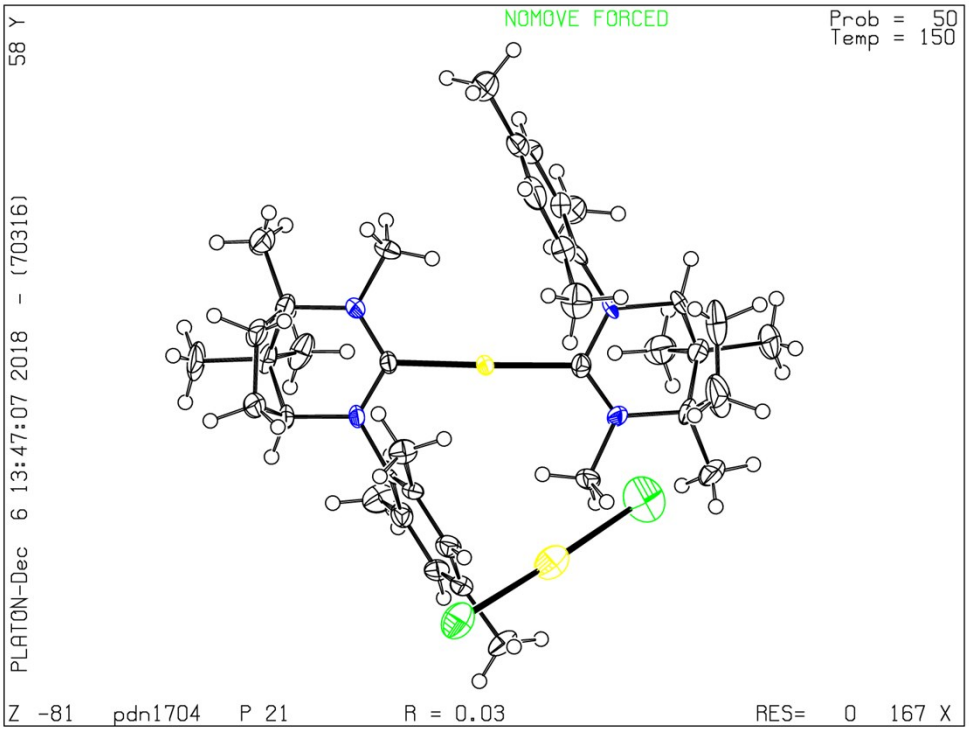

Figure 13: Platon representation of the structure of compound **13**.

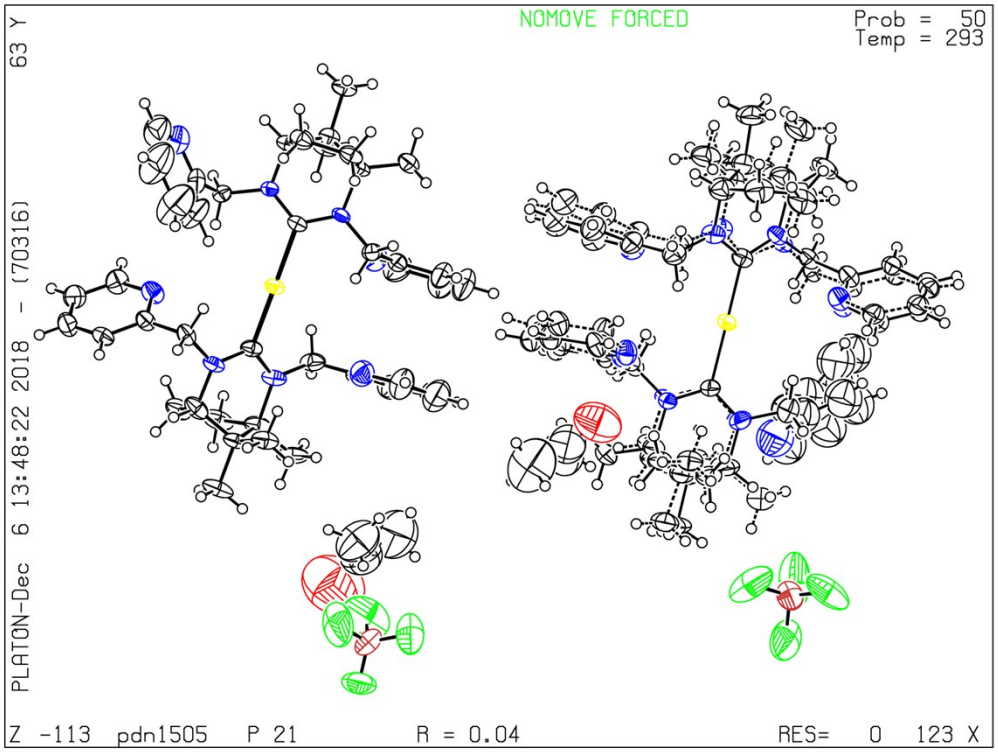

Figure 14:

Platon representation of the structure of compound **14**.

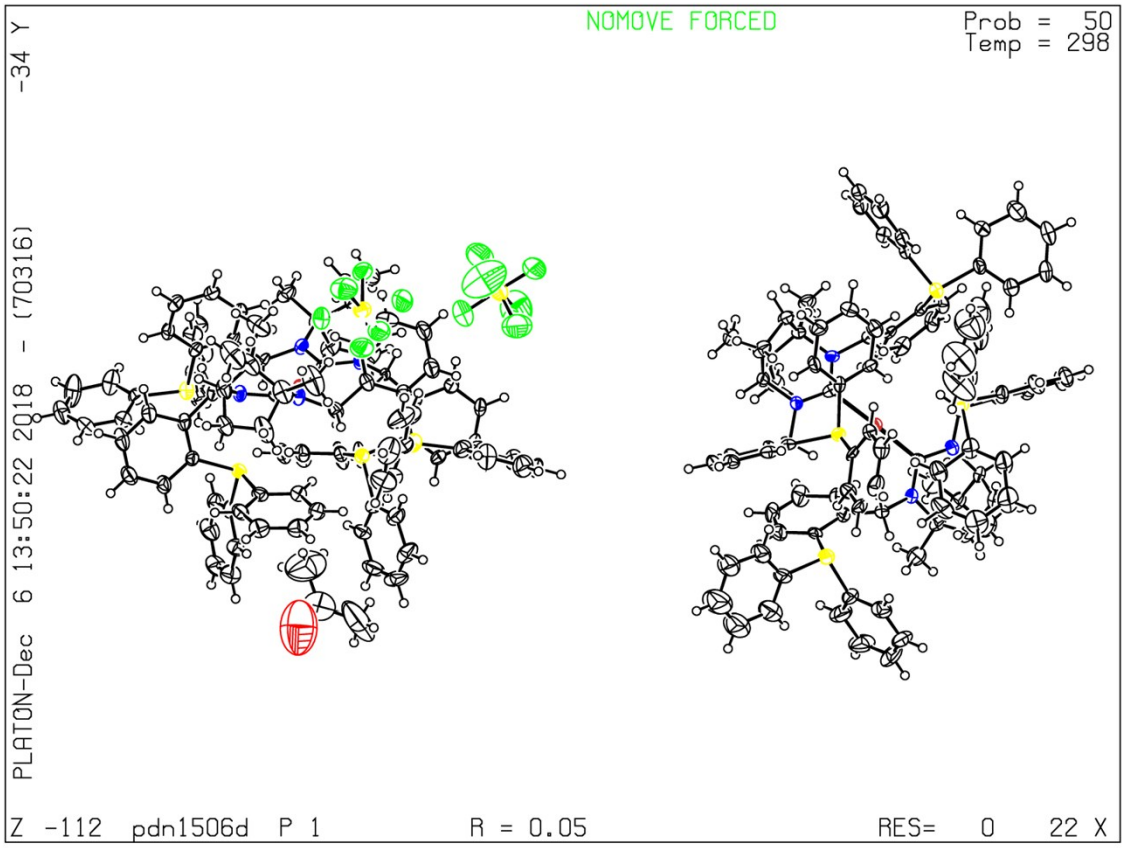

Figure 15: Platon representation of the structure of compound **15**.

(1) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008,** *64*, 112-122.
(2) Sheldrick, G. M. *Acta Crystallogr., Sect. C* **2015,** *71*, 3-8.