Electronic Supplementary Material (ESI) for ChemComm.

An extremely electron poor Au(III) trication bearing acetonitrile ligands

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General Procedures

All reactions were performed under N_2 atmosphere in either a glovebox or using Schlenk technique. Glovebox solvents were dried using an Innovative Technologies Solvent Purification System. The dried solvents were stored under N_2 atmosphere over 3 Å molecular sieves in the glovebox. Deuterated solvents for NMR spectroscopy were purchased from Sigma Aldrich and dried by stirring for three days over CaH_2, distilled prior to use, and stored in the glovebox over 3 Å molecular sieves. Synthesis of THT-AuCl from gold powder (obtained from Precious Metals Online) was performed by literature procedure.[1]

All other reagents were purchased from Sigma Aldrich and used as received. Glassware was dried in an oven at 120 °C overnight and transferred to the glovebox port or Schlenk line where it was subjected to three vacuum cycles over 30 minutes prior to use. NMR spectra for all experiments were recorded using Bruker Ultrashield Plus 500 MHz and Ascend 400 MHz spectrometers.

Experimental

Synthesis of $[Au(MeIm)_2]BF_4$

To a solution of THTAuCl (200 mg, 0.63 mmol) in MeCN, 2 equivalents of MeIm (103 mg, 1.26 mmol) was added followed by 0.95 eq of $AgBF_4$ (115 mg, 0.59 mmol). The resulting suspension was pelleted by centrifugation and washed with MeCN twice. The supernatant was reduced under vacuum and Et_2O was added dropwise precipitating a white solid identified as $[Au(MeIm)]_2BF_4$ (Yield 71%). ^{1}H NMR (400 MHz, CD_3CN) δ (ppm): 7.96 (s, 1H), 7.30 (s, 1H), 7.15 (s, 1H) 3.77 (s, 3H), ^{19}F NMR (376 MHz, CD_3CN) δ (ppm): -151.8 (s, BF_4)

Synthesis of $[Au(MeIM)_2F_2]BF_4$

To a solution of $[Au(MeIM)_2]BF_4$ (160 mg, 0.36 mmol) in CH_2Cl_2, 1 equivalent of XeF_2 (60 mg, 0.36 mmol) was added. The solution turned yellow and a yellow precipitate slowly formed. The solid was pelleted by centrifugation and washed with cold $CHCl_3$ three times before being dried under vacuum. (Yield 69%). ^{1}H NMR (400 MHz, CD_3CN) δ (ppm): 8.17 (s, 1H), 7.36 (s, 1H), 7.21 (s, 1H) 3.86 (s, 3H), ^{19}F NMR (376 MHz, CD_3CN) δ (ppm): -151.5 (s, BF_4), -284.1 (s, F-Au-F)

Synthesis of $[Au(MeCN)_2(MeIM)_2][BF_4]_3$

A solution of $[Au(MeIm)_2F_2]BF_4$ (14 mg, 0.028 mmol) suspended in CH_2Cl_2 was frozen in a cold well cooled by N_2(l) along with a CH_2Cl_2 solution of 2 equivalents of BF_3 etherate (4 mg, 0.056 mmol). The solution of BF_3 was added drop wise to the $[Au(MeIM)_2F_2]BF_4$ suspension as they both thawed. Upon thawing MeCN was added (3 drops) dropwise with intermittent shaking. The yellow solid turned orange. The resulting solid was washed once with CH_2Cl_2 before 2 additional washes with n-hexane. The n-hexane washes were carefully decanted, and the orange/yellow powder was dried under vacuum for a few seconds leaving a yellow powder (Yield 67%). The compound should be stored as a solid at -30 °C to avoid decomposition. ^{1}H NMR (400 MHz, CD_3CN) δ (ppm): 8.44 (s, 1H), 7.48 (s, 2H), 3.96 (s, 3H), ^{19}F NMR (376 MHz, CD_3CN) δ (ppm): -150.8 (s, BF_4), ^{13}C{1H} NMR (126 MHz, CD_3CN) δ (ppm): 140.2 (s), 127.5 (s), 125.0 (s), 37.1 (s). A single crystal suitable for x-ray diffraction was grown by vapour diffusion at -40°C in a 1:1 $CD_3CN/CHCl_3$ solution with n-hexane as the antisolvent.

In-situ generation of $[Au(MeCN)_2(MeIM)_2][BF_4]_3$

A solution of $[Au(MeIM)_2F_2]BF_4$ (14 mg, 0.028 mmol) dissolved in CD_3CN was frozen in a cold well, cooled by N_2(l) along with a CD_3CN solution of 2 equivalents of BF_3 etherate (4 mg,

0.056 mmol). The solution of BF_3 was added drop wise to the $[Au(MeIM)_2F_2]BF_4$ solution as they both thawed. ^1H and ^{19}F NMR match as reported earlier.

Generation of $[Au(MeCN)(MeIM)_2(Mes)][BF_4]_2$

To a solution of $[Au(MeCN)_2(MeIM)_2][BF_4]_3$ (30 mg, 0.062 mmol) in CD_3CN, mesitylene (15 mg, 0.123 mmol) was added. The solution turned from a rich orange to yellow over 4 days. The product was identified by NMR and single crystal x-ray diffraction. ^1H NMR (400 MHz, CD_3CN) δ (ppm): 7.95 (s, 2H), 7.30 (t, 2H), 6.95 (t, 2H), 6.79 (m, 4H), 3.77 (s, 6H), 2.45 (s, 6H), 2.28 (s, 3H), 13C{1H} NMR (126 MHz, CD_3CN) δ (ppm): 141.0 (s), 136.3 (s), 131.7 (s), 128.0 (s), 124.4 (q), 36.5 (s), 23.5 (s), 21.3 (s). Yield determined by relative normalisation of the integration from the MeIm CH_3 moiety observed in ^1H NMR to be 62.7%. A single crystal of x-ray diffraction quality was grown in a 1:1 $CD_3CN/CHCl_3$ solution with n-hexane as the antisolvent.

Reaction of $[Au(MeCN)_2(MeIM)_2][BF_4]_3$ with cyclohexene

To a solution of $[Au(MeCN)_2(MeIM)_2][BF_4]_3$ (13 mg, 0.027 mmol) in CD_3CN, cyclohexene (4.5 mg, 0.054 mmol) was added, the reaction turned grey and benzene was identified as the major product of the reaction by ^1H NMR at 7.36 ppm in CD_3CN.

Reaction of $[Au(MeCN)_2(MeIM)_2][BF_4]_3$ with Ferrocene

To a solution of $[Au(MeCN)_2(MeIM)_2][BF_4]_3$ (20 mg, 0.041 mmol) generated *in-situ* in 0.5 mL CD_3CN, 2 equivalent of ferrocene (15.25 mg, 0.082 mol) was added. The reaction mixture instantly turned blue indicative of ferrocenium and $[Au(MeIM)_2]BF_4$ was identified as the major product by ^1H NMR, matching spectral data reported for the synthesis of $[Au(MeIM)_2]BF_4$ above.

Reaction of $[Au(MeCN)_2(MeIM)_2][BF_4]3$ with [Ruthenium(II)trisbipyridine]$[PF_6]_2$

Using 20 mg (0.041 mmol) of $[Au(MeIM)_2F_2]BF_4$, a sample of $[Au(MeCN)_2(MeIM)_2]3BF_4$ was generated *in-situ* in 0.5 mL CD_3CN, 1 eq of $[Ru(bipy)_3][PF_6]_2$ (24 mg, 0.041 mol) was added. The reaction mixture instantly turned green indicative of ruthenium(III)trisbipyridine and $[Au(MeIm)_2]BF_4$ was identified as the major product by ^1H NMR.

X-Ray crystallographic data

Single crystals were selected under n-paratone oil, mounted on a nylon loop, and held under a stream of N_2 at 158 K for $[Au(MeCN)_2(MeIM_2)][BF_4]_3$ and 150 K for $[Au(MeIM)_2(MeCN)(Mes)][BF_4]_2$ on a Rigaku SuperNova CCD diffractometer using Cu Ka radiation. Crystallographic analyses were conducted within OLEX2. The structures were solved with SHELXT (intrinsic phasing) and were refined using a full-matrix least-squares procedure based on F^2 within the program SHELXL. For both crystals, all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed at

geometrically estimated positions. For $[Au(MeCN)_2(MeIM)_2][BF_4]_3$ minor disorder within one of the MeIM ligands was apparent and the atoms were modelled over two sites with reciprocal occupancies. Crystallographic data and structural refinement parameters are presented in Tables S1 and S2 below. Full details of crystal structure refinements in CIF.

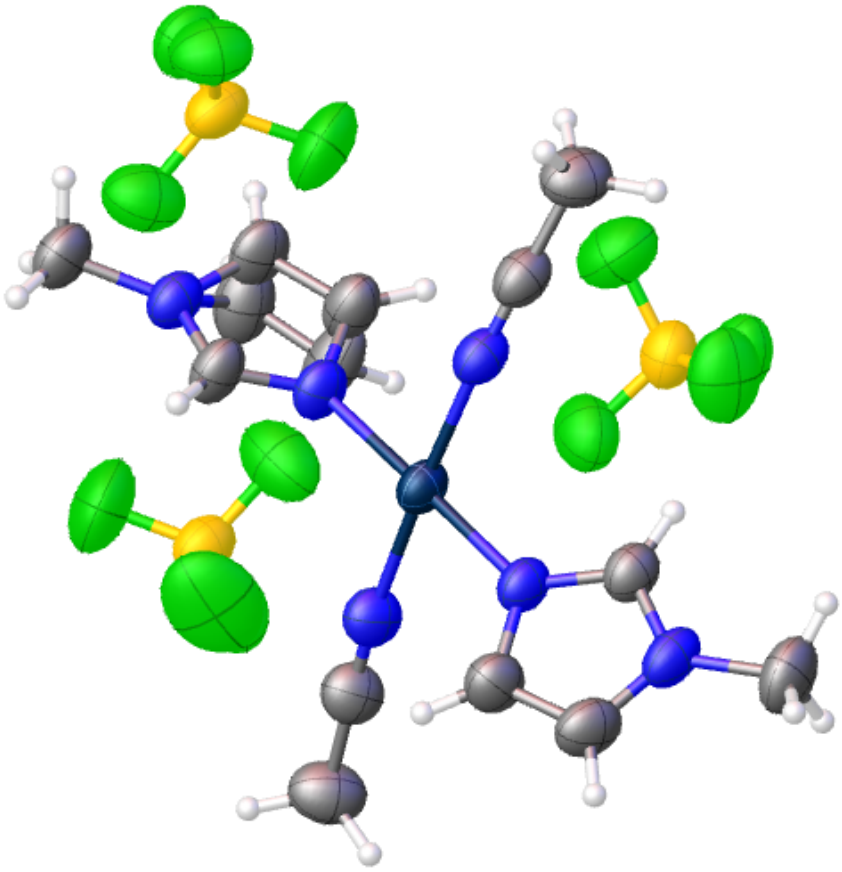

Figure S1: Thermal ellipsoid plot of $[Au(MeCN)_2(MeIM)_2][BF_4]_3$, thermal ellipsoids are drawn at the 50% probability level.

Table S1: Crystallographic information of $[Au(MeCN)_2(MeIM)_2][BF_4]_3$

Compound	**$[Au(MeCN)_2(MeIM)_2][BF_4]_3$**
Empirical Formula	$C_{16}H_{24}AuB_3F_{12}N_8$
FW (g/mol)	703.70
Crystal System	Monoclinic
Space Group	C2/C
α (Å)	15.3073(3)
b (Å)	15.7110(2)
c (Å)	22.0225(4)
α (deg)	90
β (deg)	99.885(2)
γ (deg)	90
V (Å^3)	5217.63(16)
Z	8

R1[I>2σI]	0.0337
wR2(F^2)	0.0856
GOF (S)	1.067

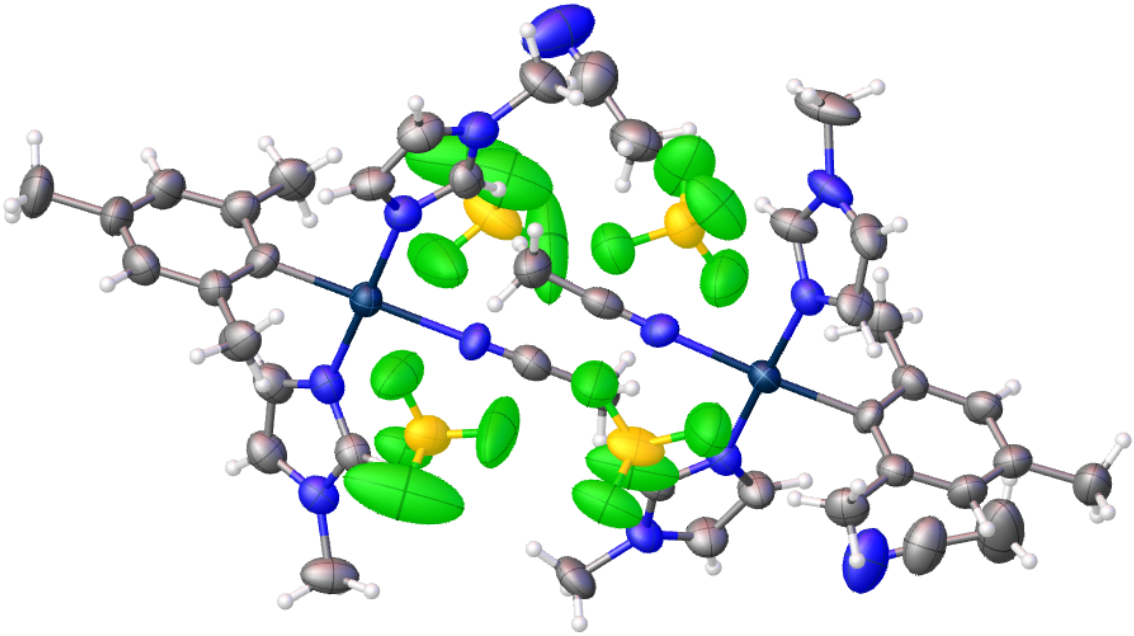

Figure S2: Thermal ellipsoid plot of $[Au(MeIM)_2(MeCN)(Mes)][BF_4]_2$, thermal ellipsoids are drawn at the 50% probability level.

Table S2: Crystallographic information of $[Au(MeIM)_2(MeCN)(Mes)][BF_4]_2$

Compound	**$[Au(MeIM)_2(MeCN)(Mes)][BF_4]_2$**
Empirical Formula	$C_{21}H_{29}AuB_2F_8N_6$
FW (g/mol)	695.03
Crystal System	Monoclinic
Space Group	P2(1)
α (Å)	9.4083(1)
b (Å)	19.4220(2)
c (Å)	15.7483(2)
α (deg)	90
β (deg)	103.473(1)
γ (deg)	90
V ($Å^3$)	2798.46(6)

Z	4
R1[I>2σI]	0.0374
wR2(F^2)	0.0988
GOF (S)	1.042

NMR Spectra

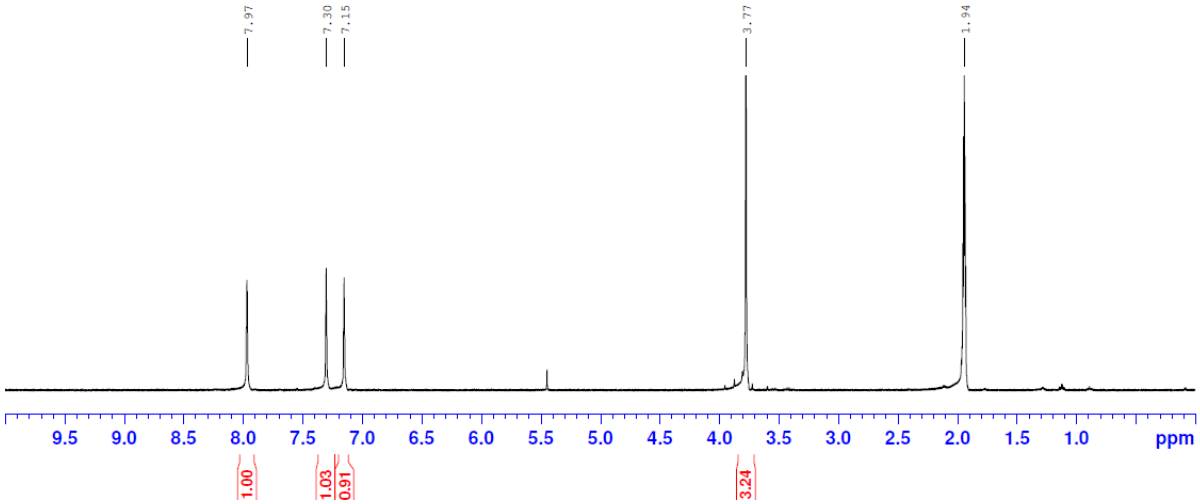

Figure S3: ^{1}H NMR of $[Au(MeIM)_2]BF_4$ starting material

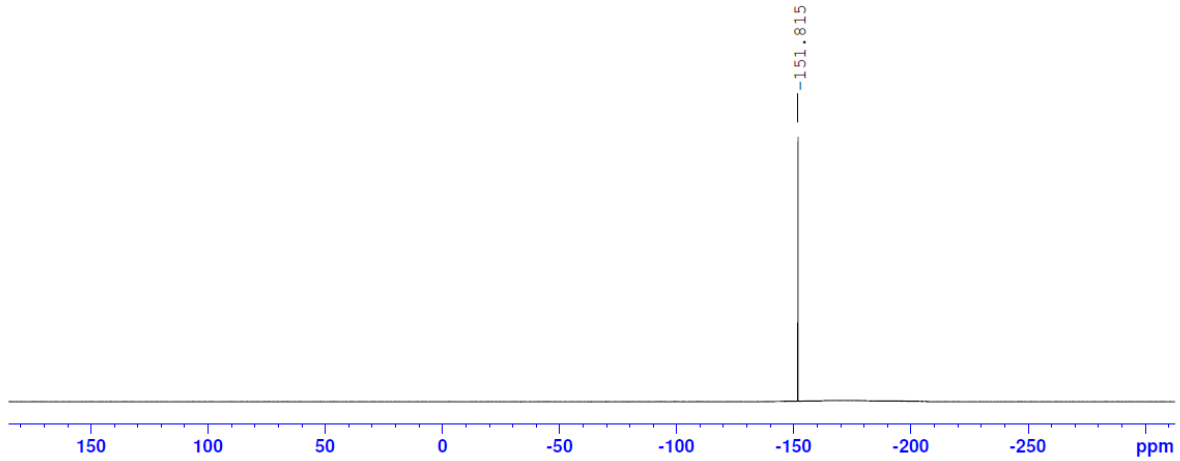

Figure S4: ^{19}F NMR of $[Au(MeIM)_2]BF_4$ starting material

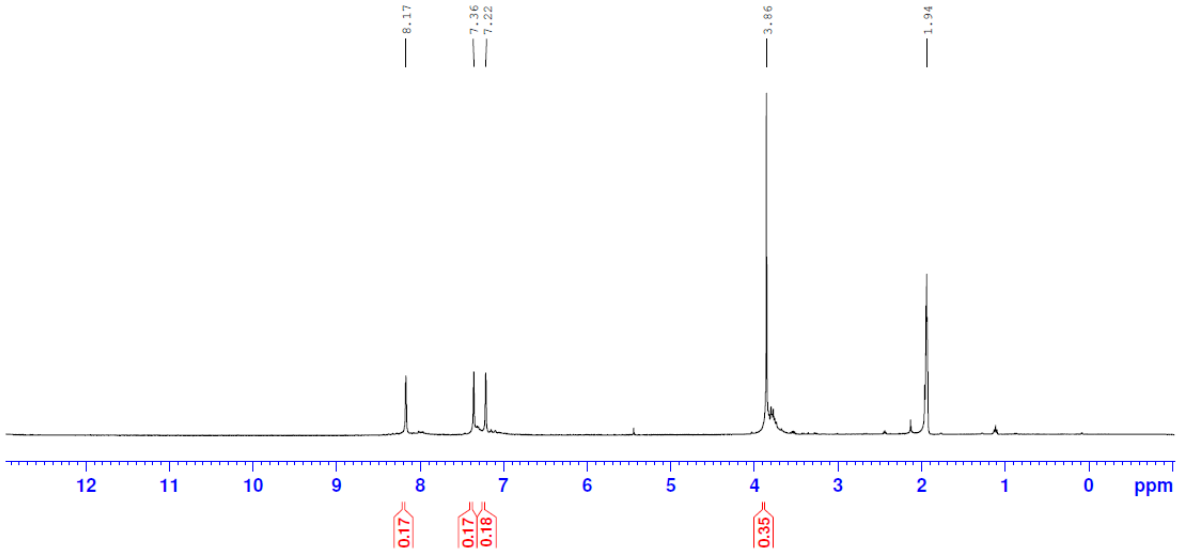

Figure S5: ^{1}H NMR of $[Au(MeIM)_2F_2]BF_4$

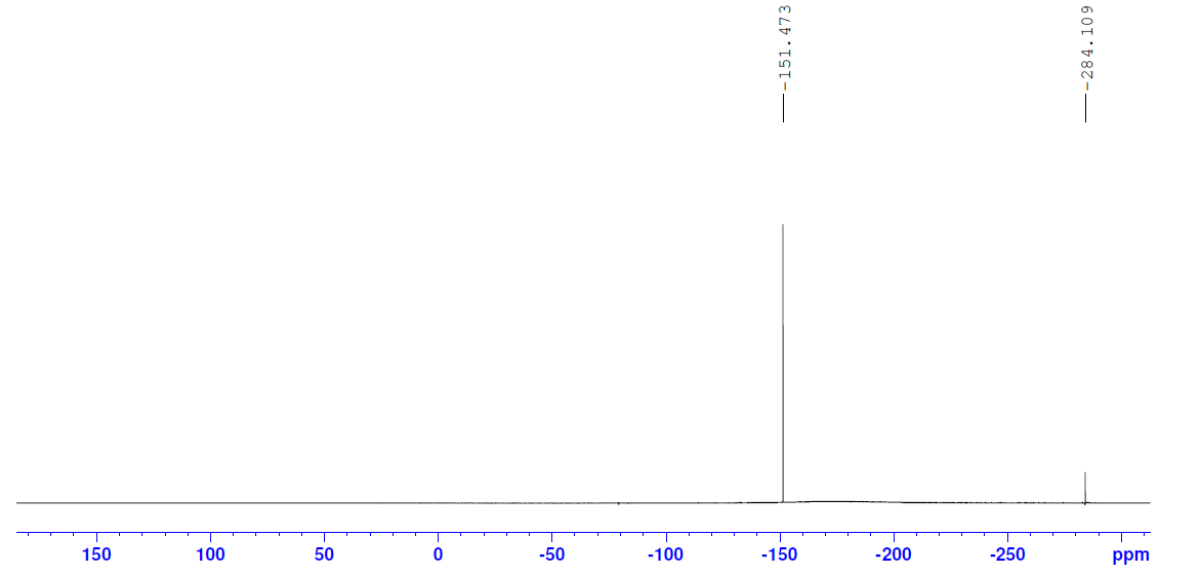

Figure S6: ^{19}F NMR of $[Au(MeIM)_2F_2]BF_4$

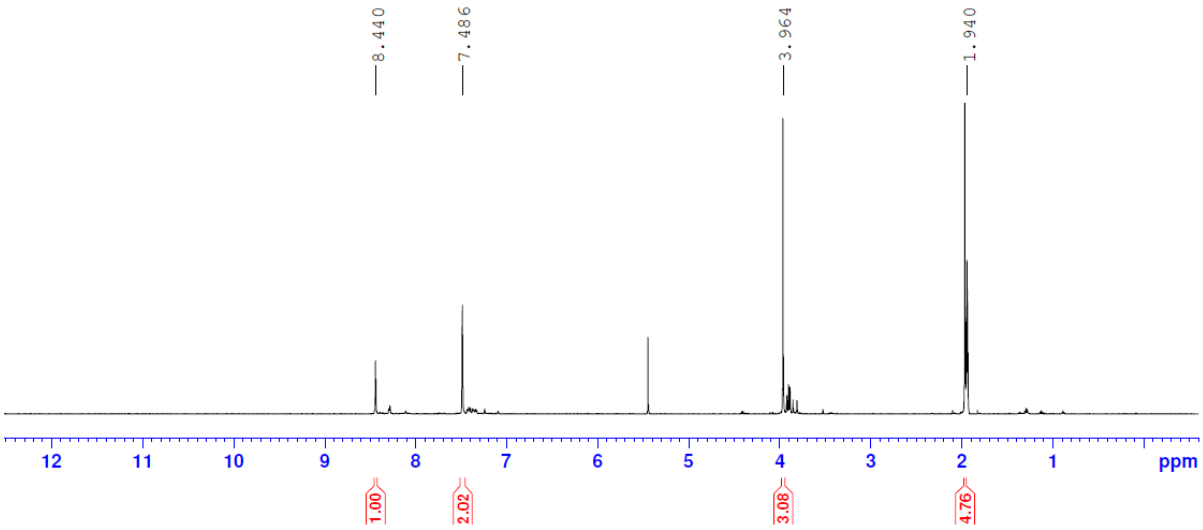

Figure S7: ^{1}H NMR of $[Au(MeCN)_2(MeIM)_2][BF_4]_3$

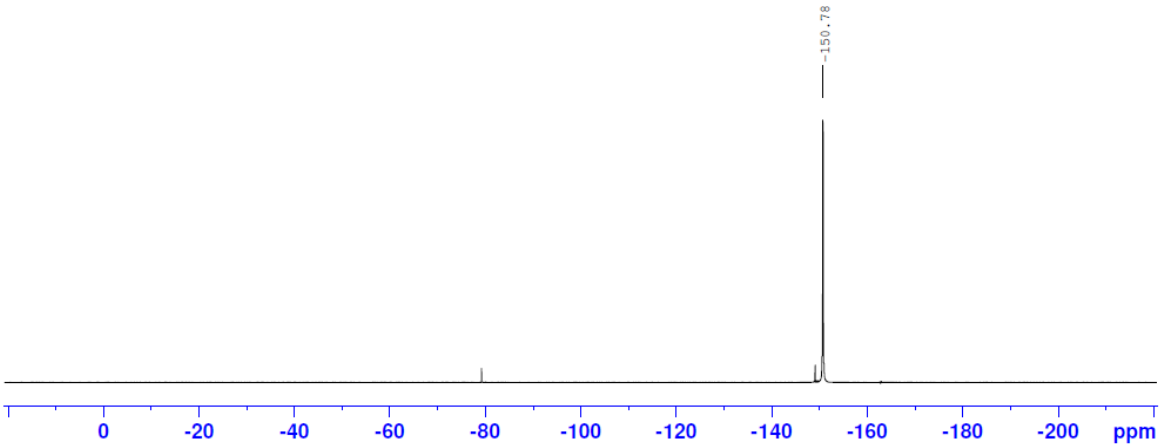

Figure S8: ^{19}F NMR of $[Au(MeCN)_2(MeIM)_2][BF_4]_3$

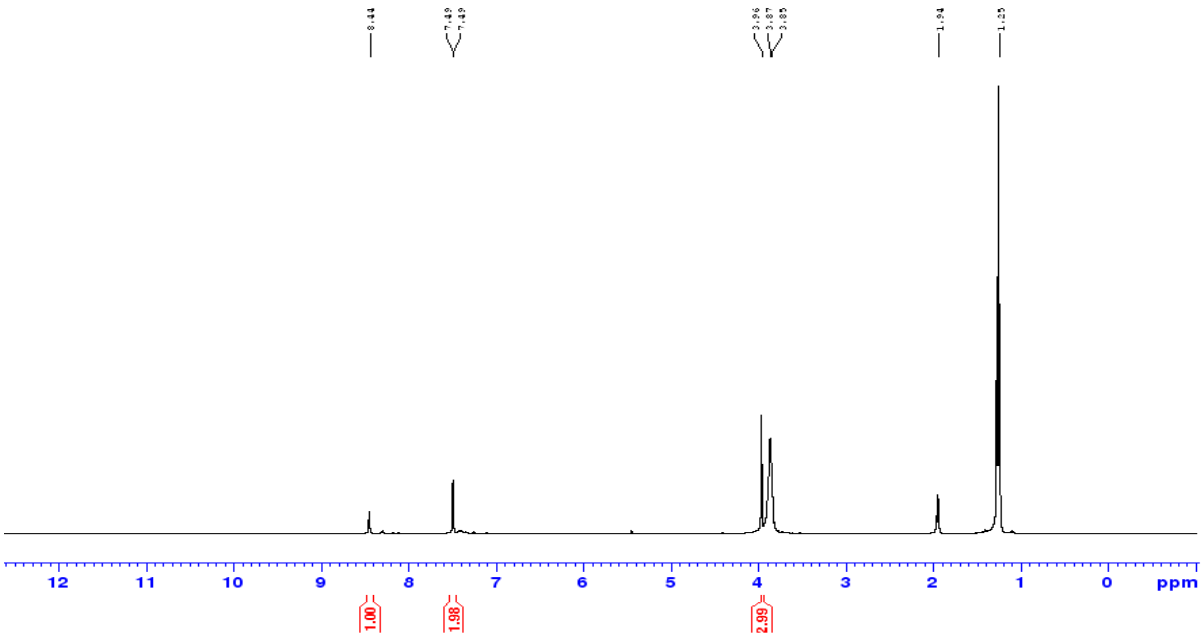

Figure S9: ^{1}H NMR of in-situ generation of $[Au(MeCN)_2(MeIM)_2][BF_4]_3$, multiplets at 3.85 and 1.25 ppm are remaining diethyl ether from BF_3-etherate

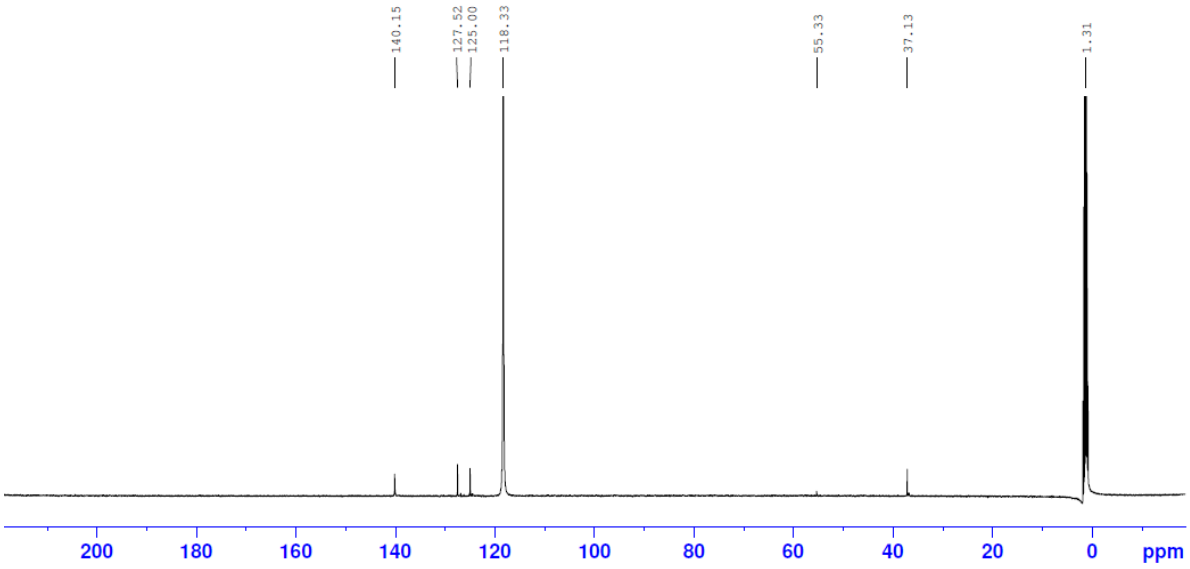

Figure S10: ^{13}C NMR of $[Au(MeCN)_2(MeIM)_2][BF_4]_3$

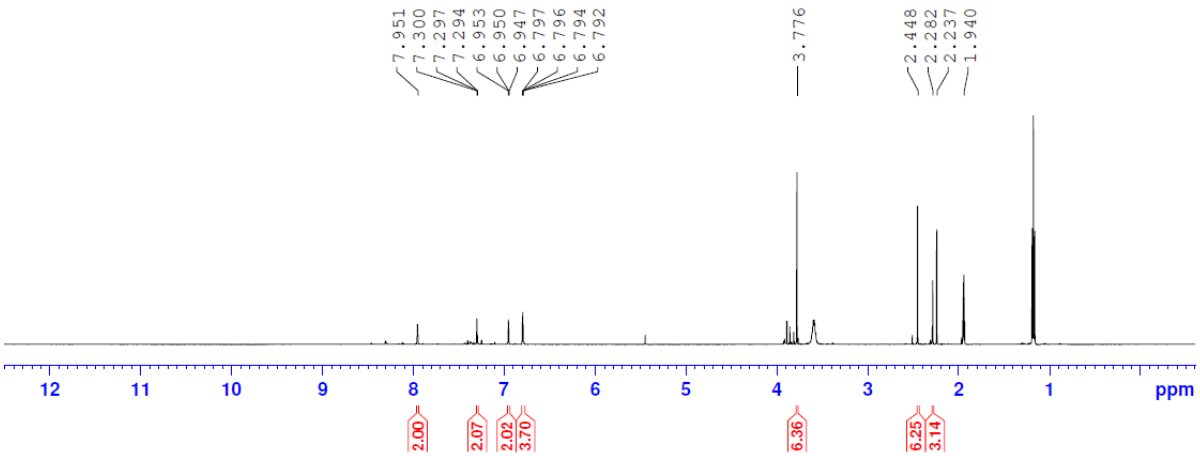

Figure S11: ^{1}H NMR of reaction between $[Au(MeCN)_2(MeIM)_2][BF_4]_3$ and mesitylene, integration of peaks at 6.792 ppm is high due to overlapping of unreacted mesitylene, peak at 2.237 ppm identified as unreacted mesitylene.

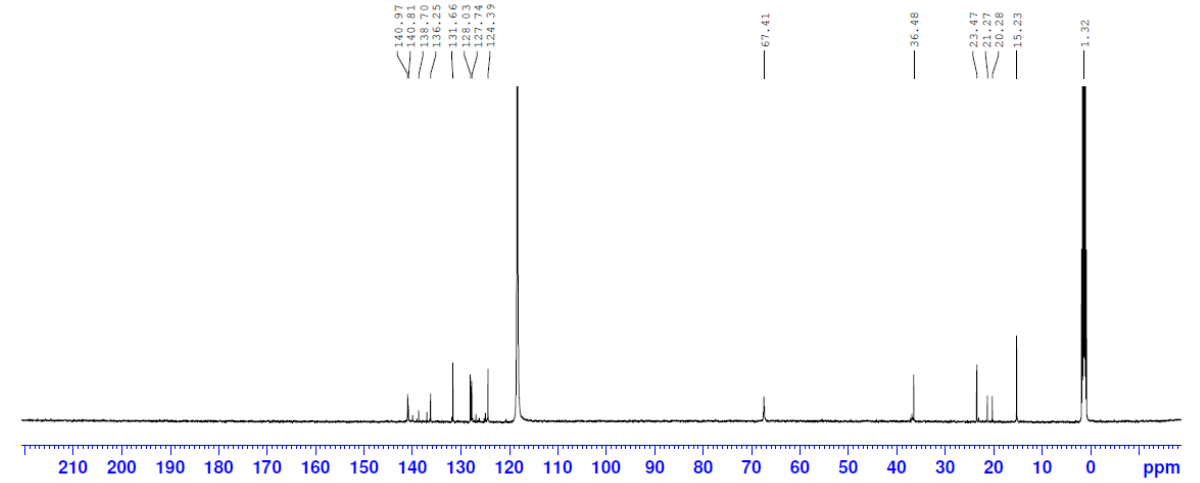

Figure S12: ^{13}C NMR of reaction between $[Au(MeCN)_2(MeIM)_2][BF_4]_3$ and mesitylene, peaks at 127.74, 138.70, and 20.28 ppm were identified as unreacted mesitylene, while peaks at 67.41 and 15.23 ppm were identified as diethyl ether.

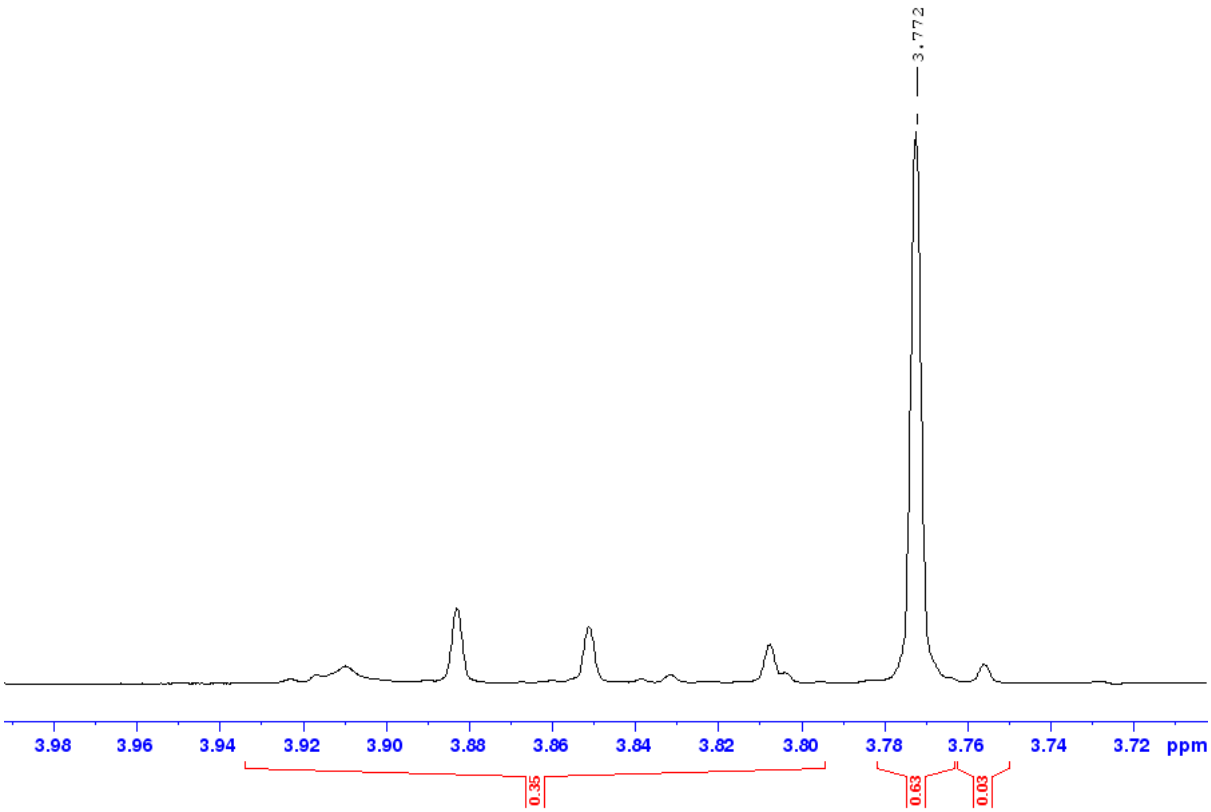

Figure S13: Close-up of methylimidazole methyl resonances with integration normalised to 1, showing NMR conversion of 63%.

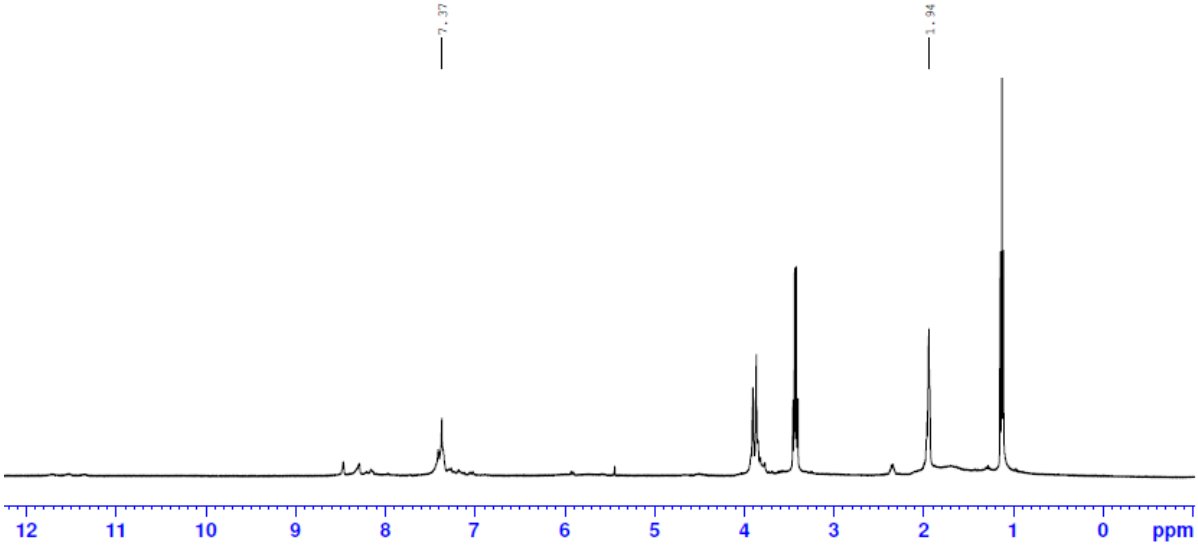

Figure S14: ^{1}H NMR of reaction between $[Au(MeCN)_2(MeIM)_2][BF_4]_3$ and cyclohexene

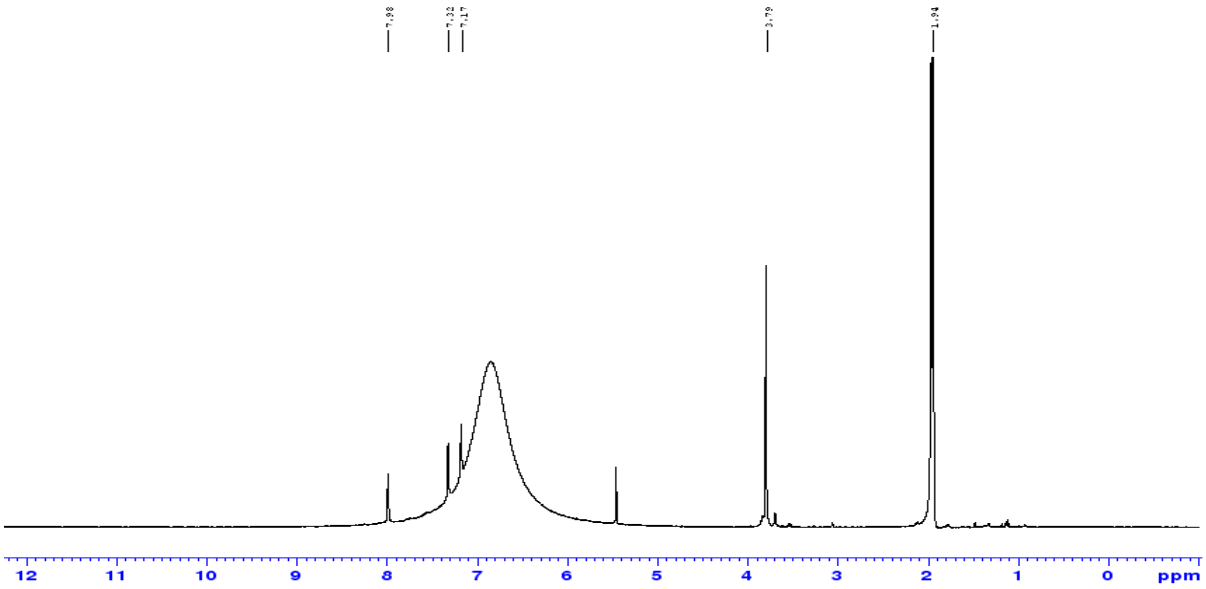

Figure S15: ^{1}H NMR of reaction between $[Au(MeCN)_2(MeIM)_2][BF_4]_3$ and ferrocene

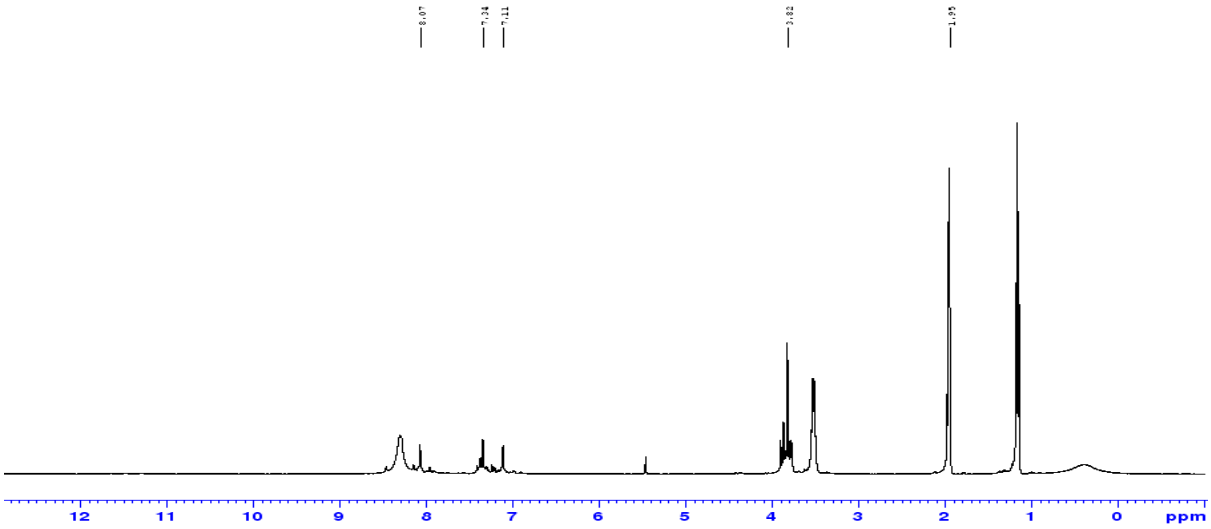

Figure S16: ^{1}H NMR of reaction between $[Au(MeCN)_2(MeIM)_2][BF_4]_3$ and $[Ru(bipy)_3][PF_6]_2$

Figure S17: Photo of reaction between $[Au(MeCN)_2(MeIM)_2][BF_4]_3$ and $[Ru(bipy)_3][PF_6]_2$, top containing $[Ru(bipy)_3][PF_6]_2$ only, bottom containing reaction mixture.

Computational Details:

All geometry optimisation, vibrational frequency were performed using ωPBE/def2-TZVP within Gaussian 16 using the WebMO platform.[5-7] Molecular orbital calculations were performed on the optimized geometries using B3LYP/def2-TZVP.[8, 9]

Cartesian coordinates are in Å and energies are given in Hartree.

Cartesian Coordinates for optimised compound geometries:

$[Au(MeIM)_4]^{3+}$

Electronic Energy: -1196.7017643 Hartree

Au 0.00000000 0.00000000 0.00000000

N 1.39016500 -1.42645400 -0.20105300

C 1.35835300 -2.44716100 -1.12621900

C 2.46405500 -3.19883000 -0.94358400

H 2.81047000 -4.07917000 -1.46261300

N	3.16236700	-2.63969100	0.09331300
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H	2.82471400	-0.94559500	1.33022200
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H	4.74509300	-2.50749200	1.45229100
H	4.27984800	-4.15960000	0.99856300
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H -2.35125200 0.79927900 2.04436300

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H -1.12086600 2.63419600 -1.55265600

$[Au(MeCN)_2(MeIM)_2]^{3+}$

Electronic Energy: -931.121645579 Hartree

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N 0.00008200 1.96191500 0.00009400

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H 1.02243200 4.90367800 0.11002600

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H -0.61896800 -4.89991300 0.82679000

H -0.41141000 -4.89930100 -0.94739300

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