Supporting Information for:

Synthesis and characterisation of an N-heterocyclic carbene with spatially-defined steric impact

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Contents

Additional Data

Raw Data: (NMR FIDs) http://dx.doi.org/10.15129/ac8aeef2-8109-4c20-bb0d-d8d808e3ceda

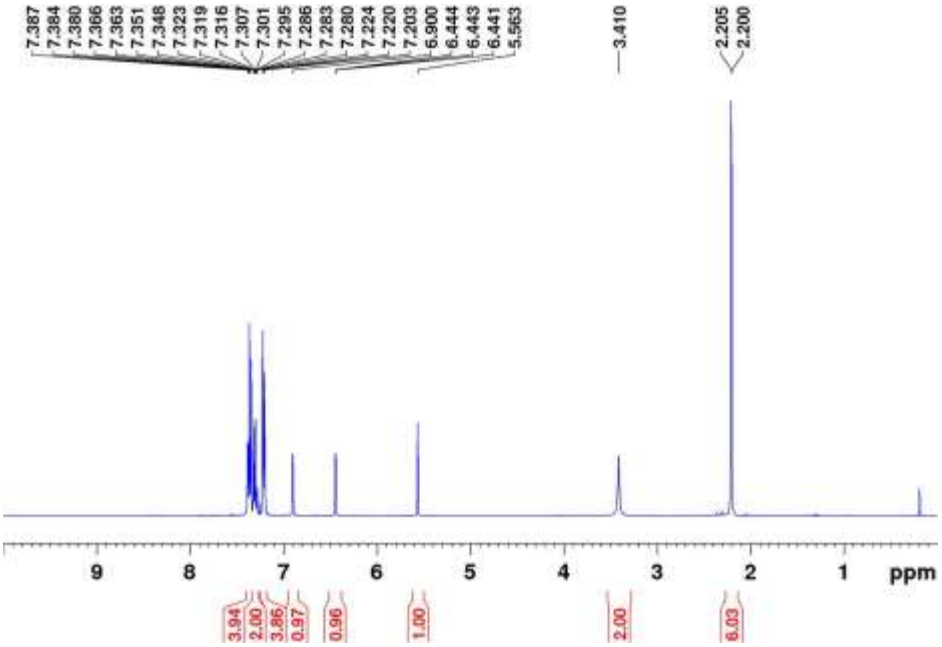
CCDC Data: (XRD data) 1481901 (4), 1481902 (5), 1481903 (6), 1481904 (7), http://www.ccdc.cam.ac.uk/data_request/cif

NMR Spectra

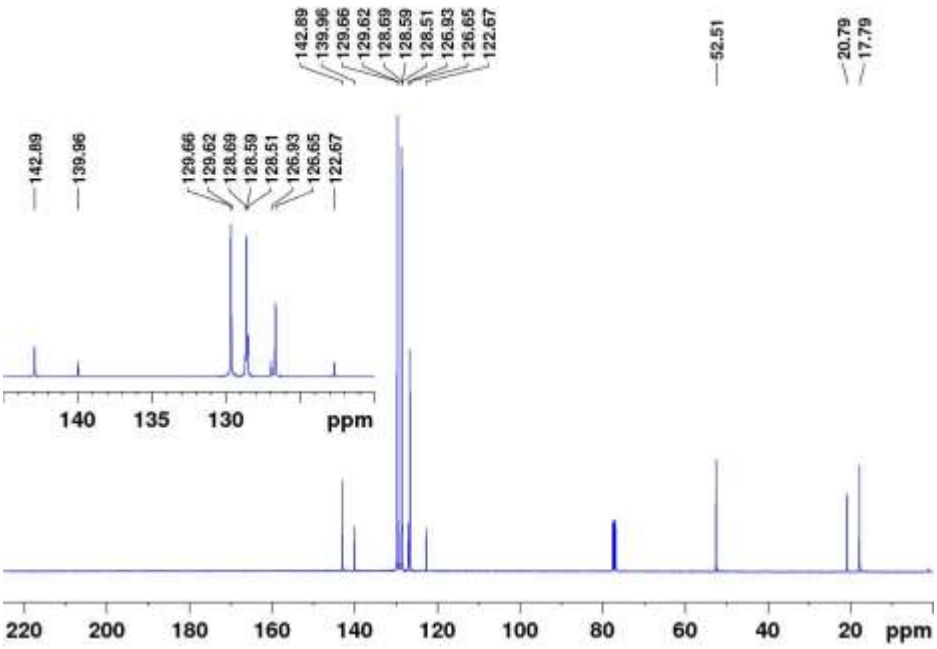
Reference numbers refer to files available in the associated raw data deposit.

2-(Diphenylmethyl)-4,6-dimethylaniline (2) **(D238611)**

^{1}H NMR ($CDCl_3$)

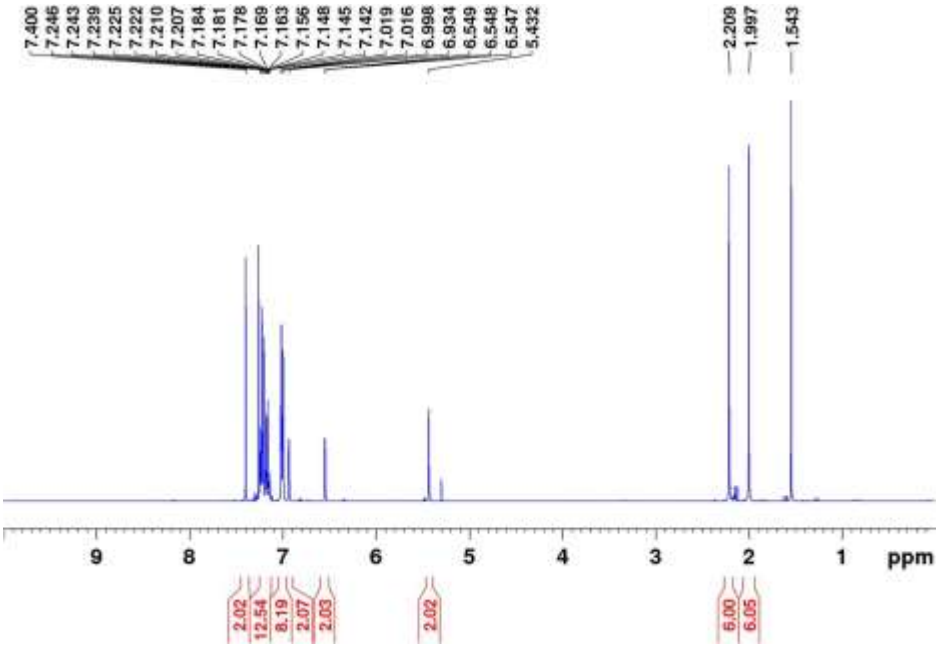


^{13}C{^{1}H} NMR ($CDCl_3$)

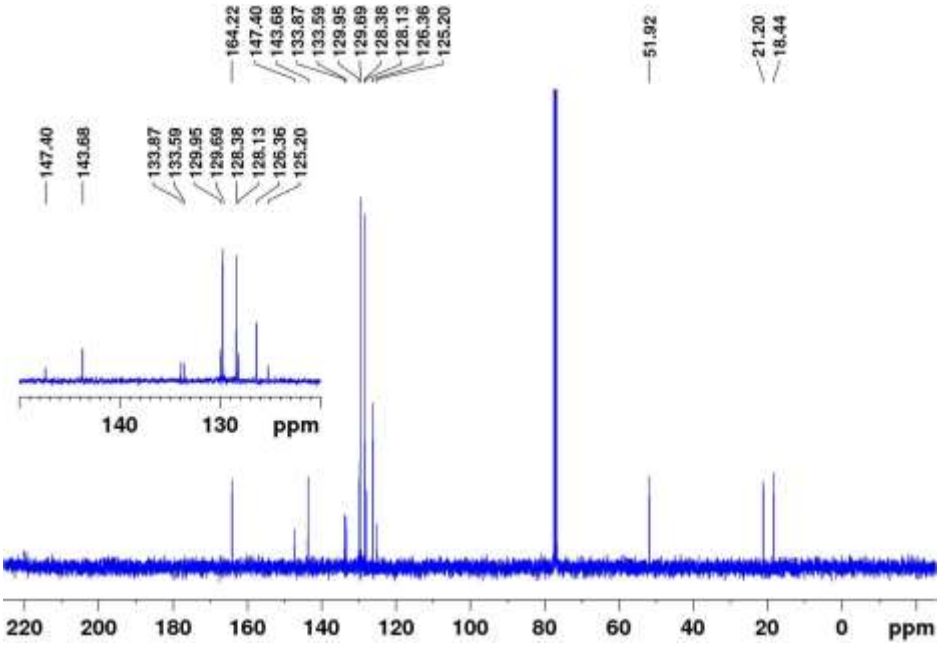


N,N′-bis(2-diphenylmethyl-4,6-dimethylphenyl)-ethane-1,2-diimine (3) **(D243392)**

^{1}H NMR ($CDCl_3$)

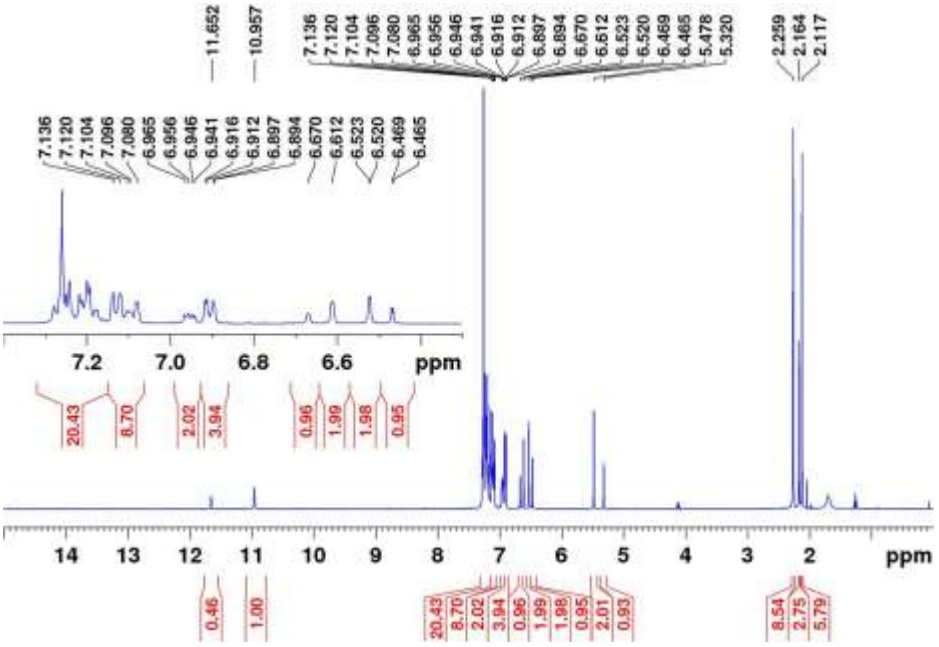


^{13}C{^{1}H} NMR ($CDCl_3$)

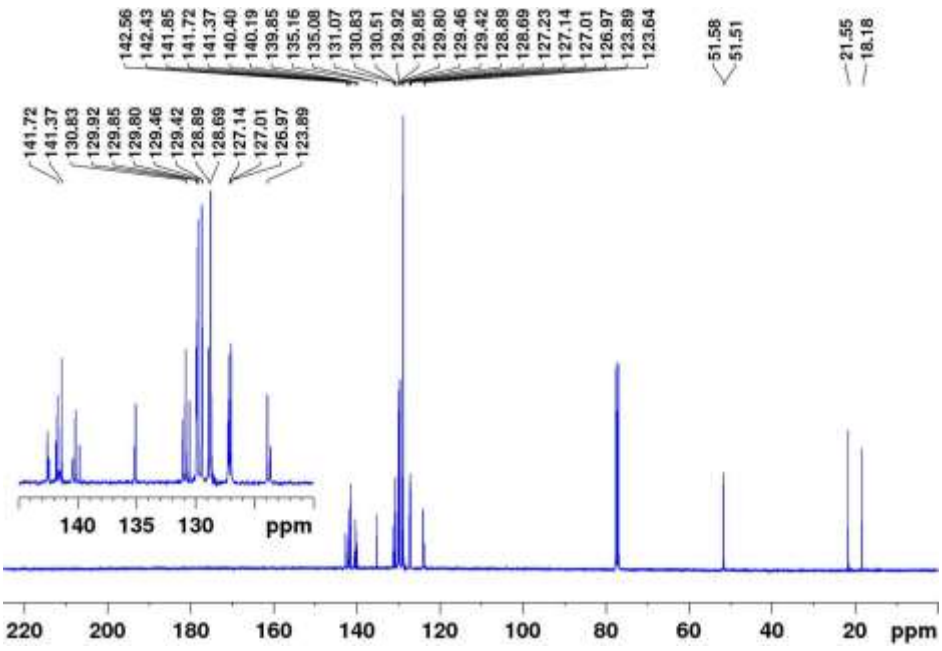


1,3-bis(2-diphenylmethyl-4,6-dimethylphenyl)-imidazolium chloride (1) **(D253527/32)**

^{1}H NMR ($CDCl_3$)

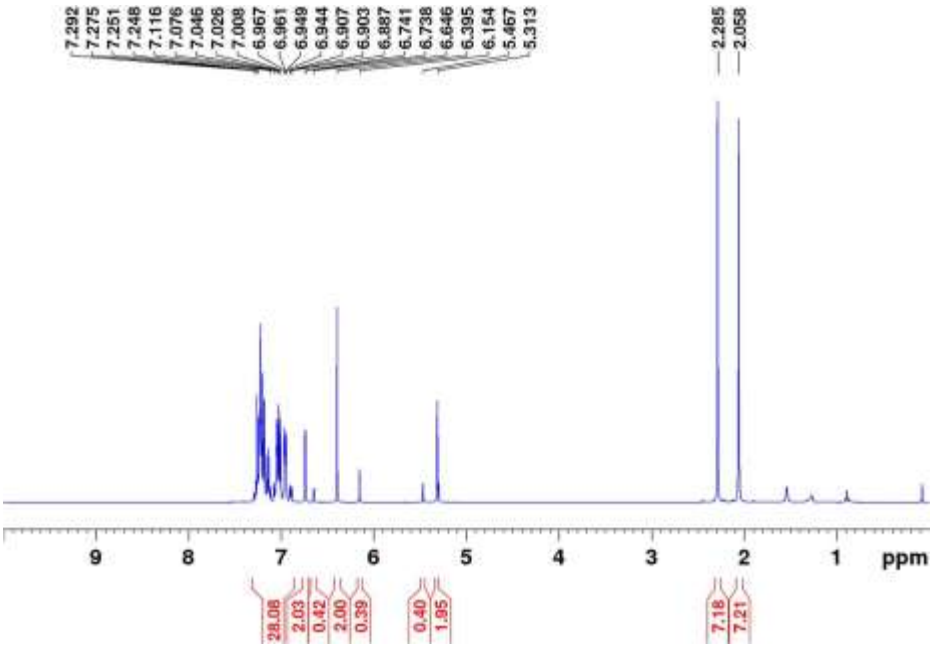


^{13}C{^{1}H} NMR ($CDCl_3$)

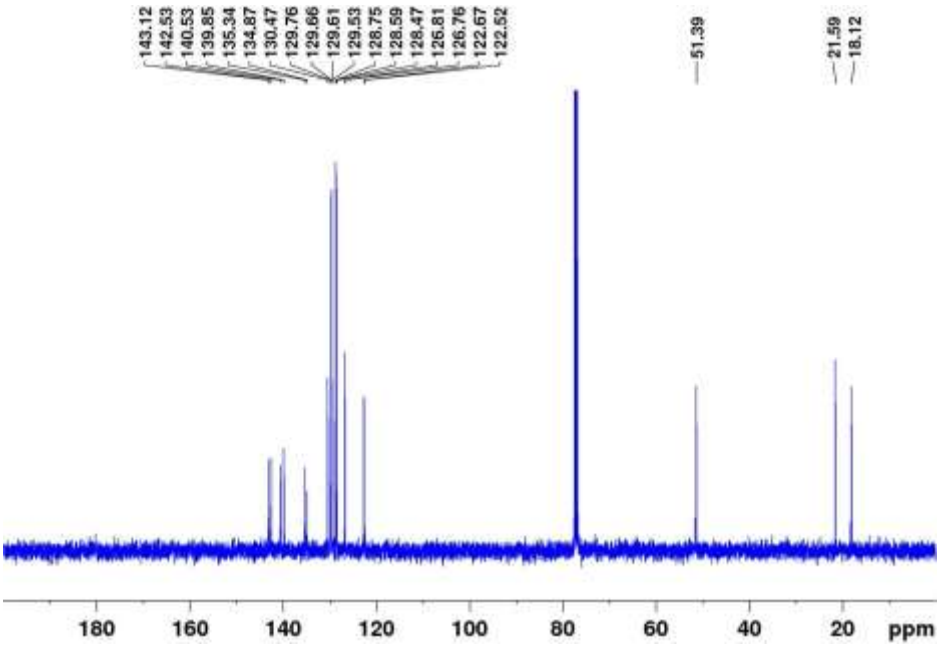


(1,3-bis(2-diphenylmethyl-4,6-dimethylphenyl)-imidazol-2-yl)copper (I) chloride (4) **(D249119)**

^{1}H NMR ($CDCl_3$)

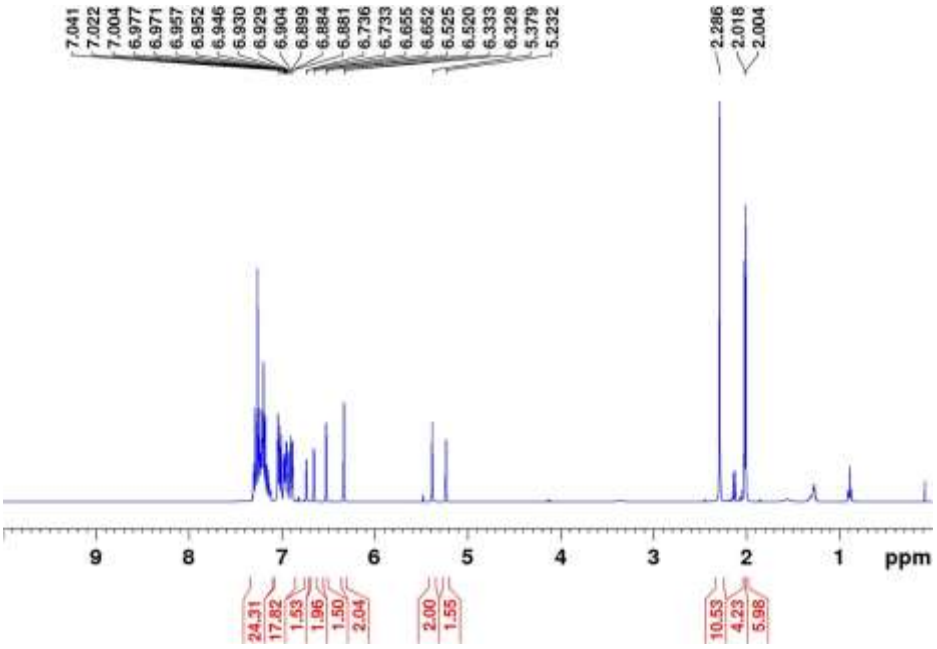


^{13}C{^{1}H} NMR ($CDCl_3$)

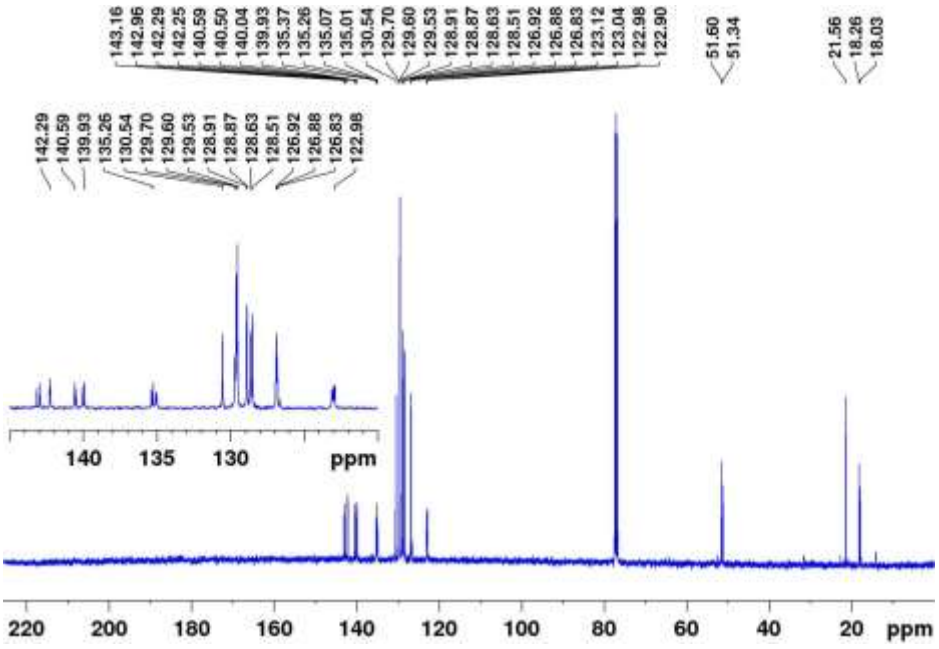


(1,3-bis(2-diphenylmethyl-4,6-dimethylphenyl)-imidazol-2-yl)silver (I) chloride (5) **(D250145)**

^{1}H NMR ($CDCl_3$)

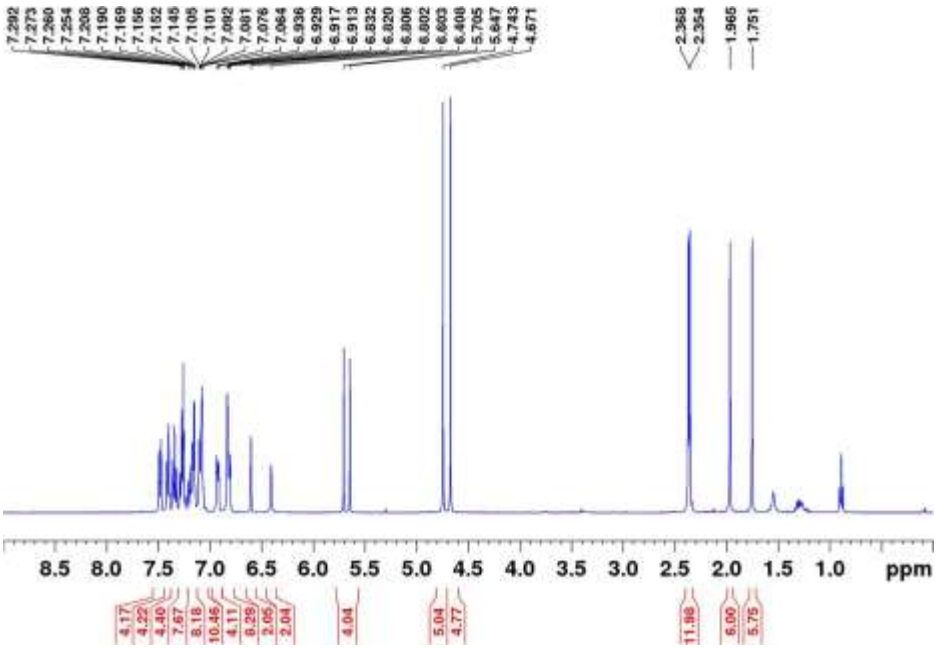


^{13}C{^{1}H} NMR ($CDCl_3$)

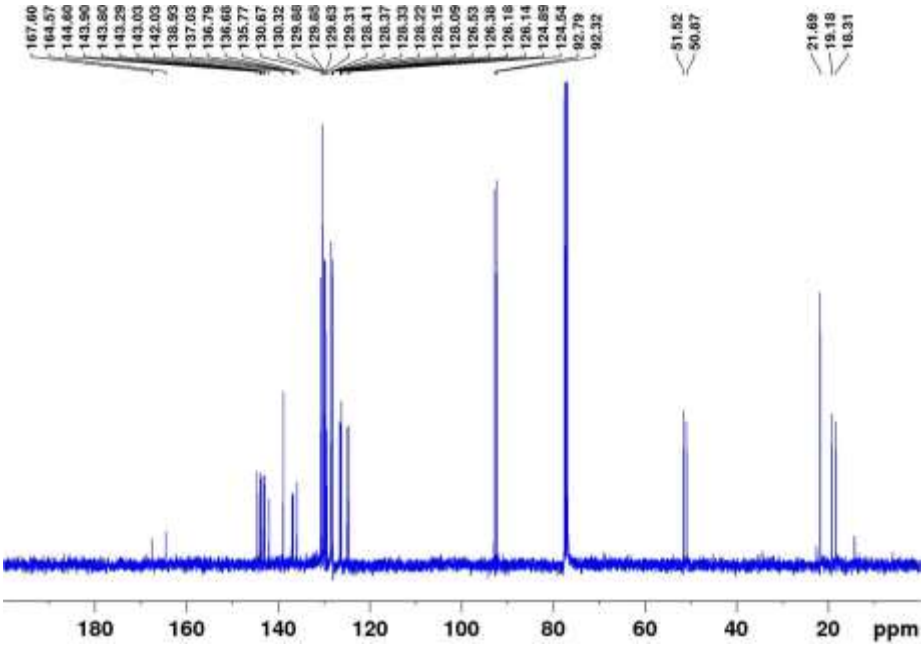


(1,3-bis(2-diphenylmethyl-4,6-dimethylphenyl)-imidazol-2-yl)(η5-cyclopentadienyl)nickel(II) chloride (6) **(D252773)**

^{1}H NMR ($CDCl_3$)

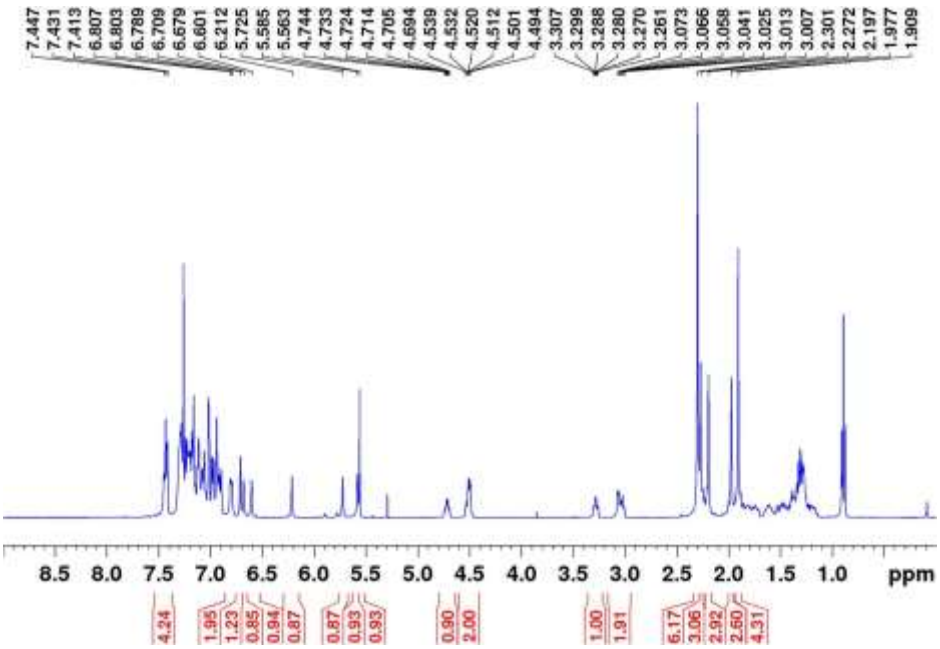


^{13}C{^{1}H} NMR ($CDCl_3$)

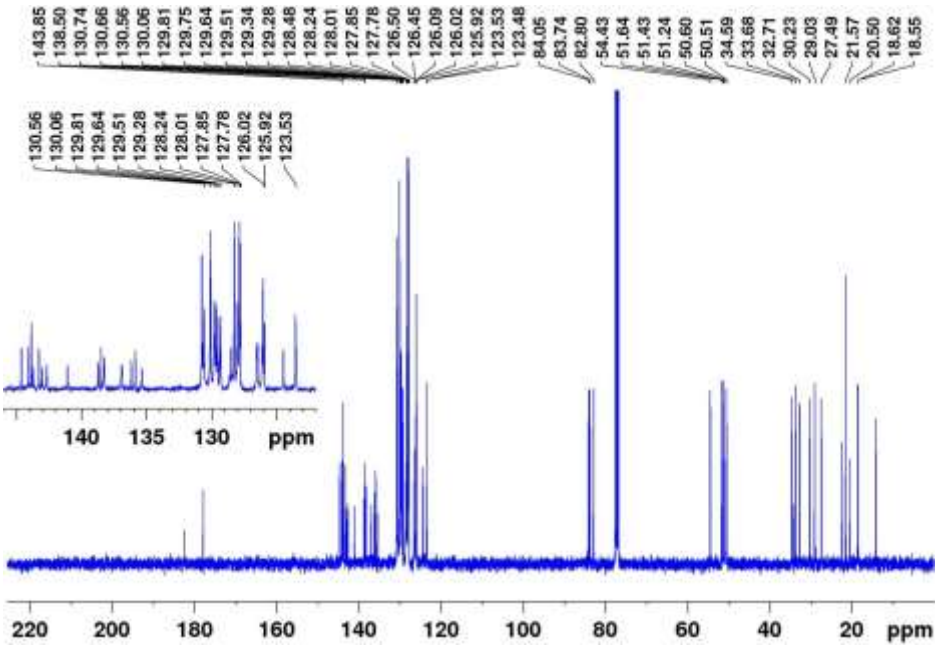


(1,3-bis(2-diphenylmethyl-4,6-dimethylphenyl)-imidazol-2-yl)(η2,η2-1,5-cyclooctadienyl)iridium(I) chloride (7). **(D253696)**

^{1}H NMR ($CDCl_3$)

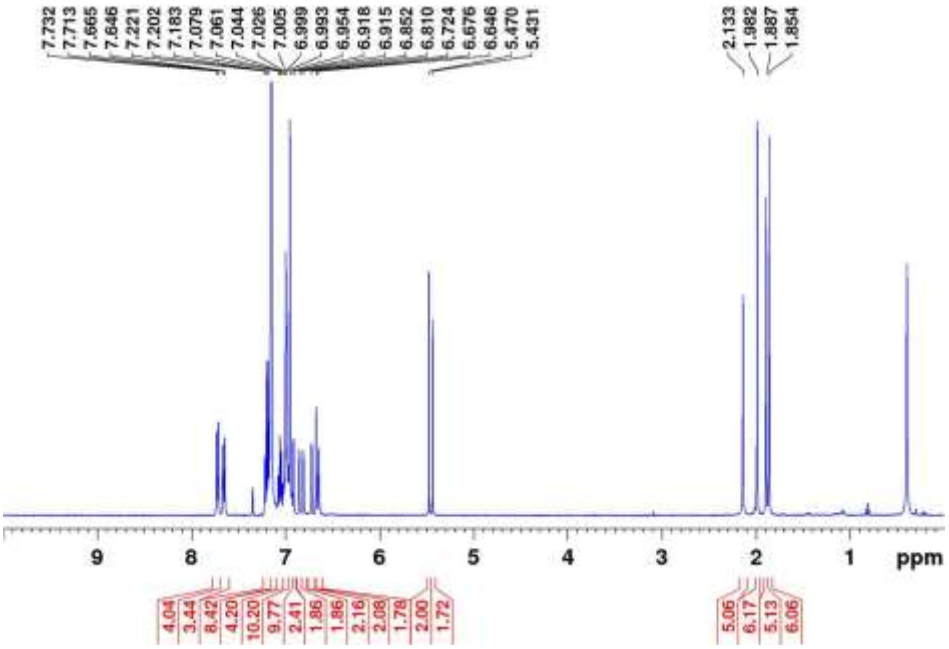


^{13}C{^{1}H} NMR ($CDCl_3$)

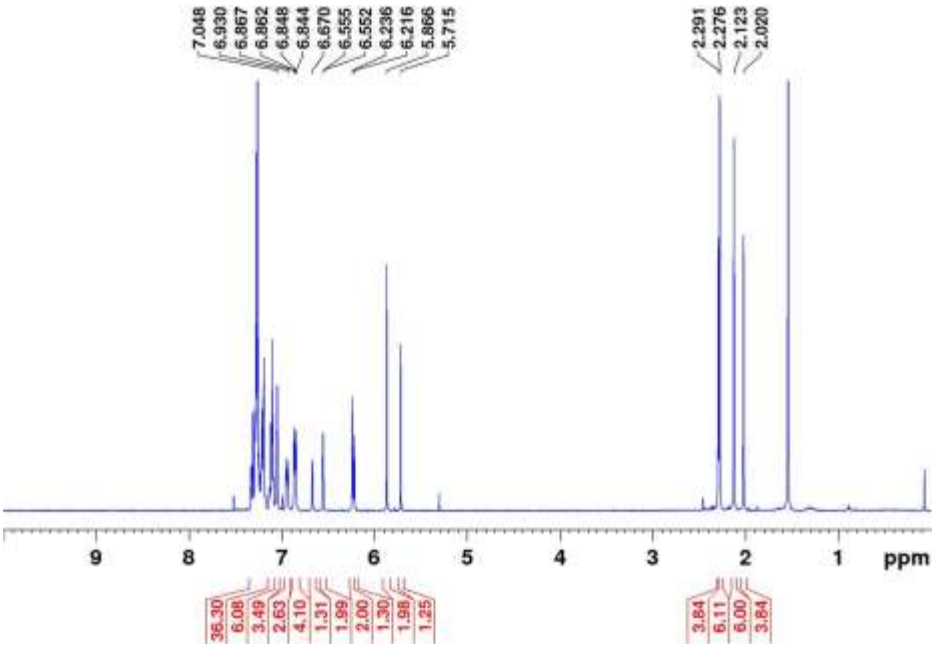


(1,3-bis(2-diphenylmethyl-4,6-dimethylphenyl)-imidazol-2-yl)dicarbonyliridium(I) chloride (8).

^{1}H NMR (C_6D_6) (D254029)

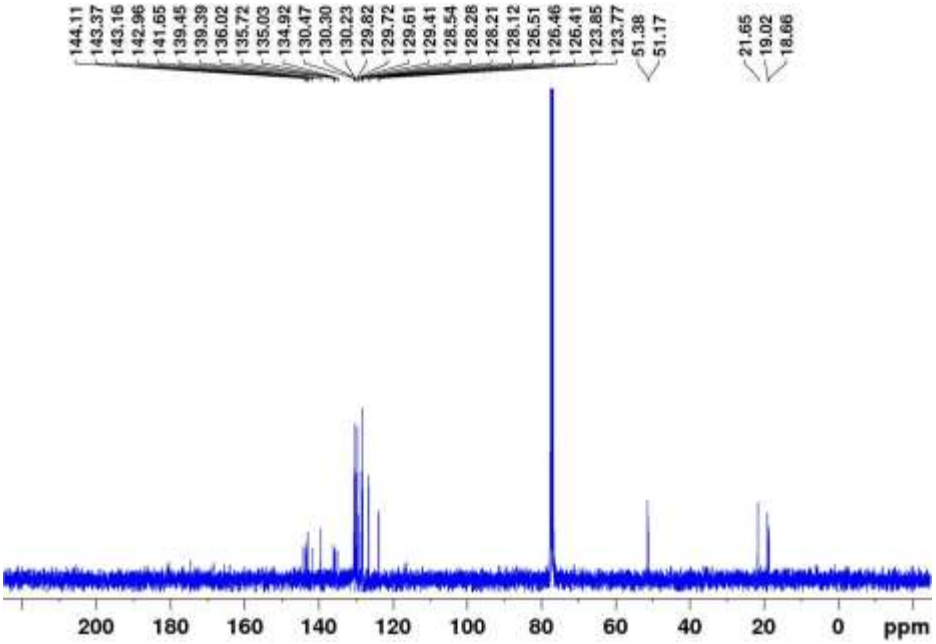


^{1}H NMR ($CDCl_3$) (D254034)



13C{^{1}H} NMR ($CDCl_3$) (D254034)

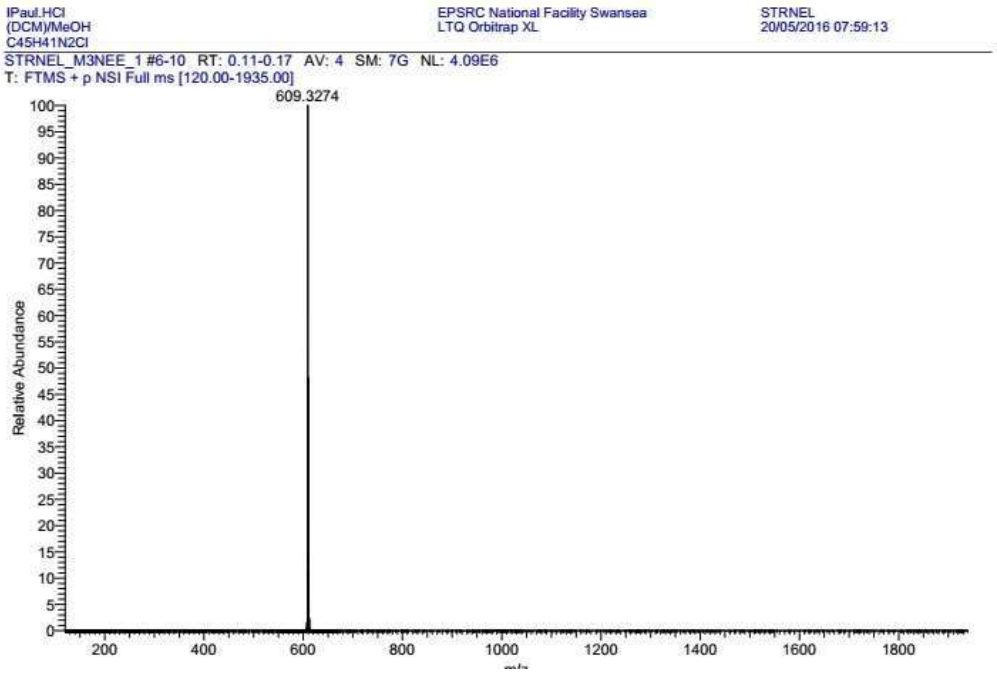
(see note in experimental section)

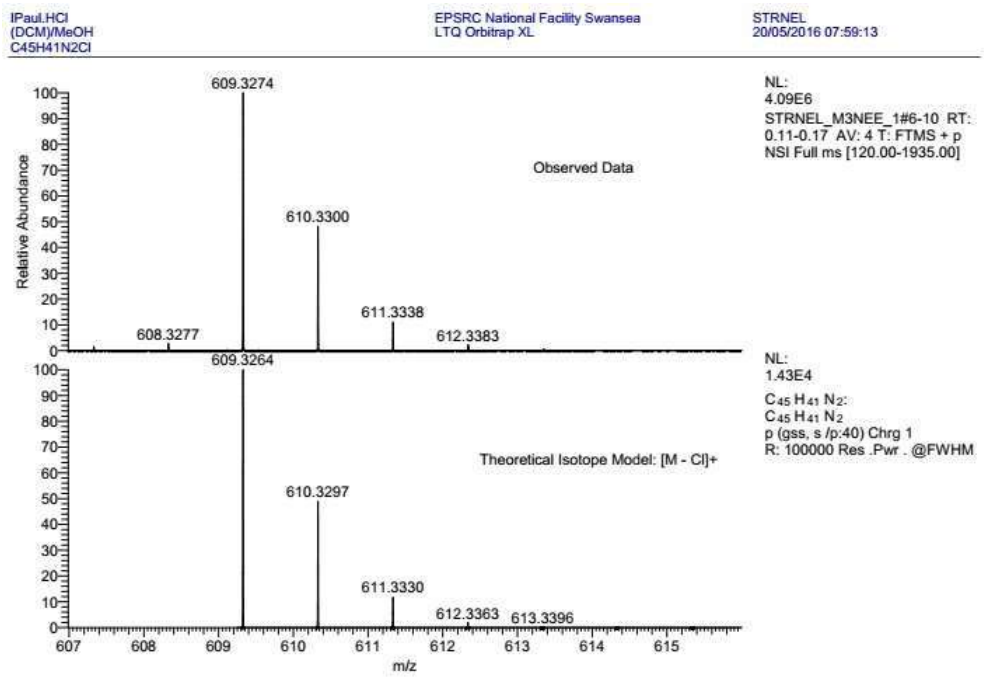


Mass Spectrometry

Accurate mass data collected by the EPSRC UK National Mass Spectrometry Facility at Swansea.

1,3-bis(2-diphenylmethyl-4,6-dimethylphenyl)-imidazolium chloride (1).

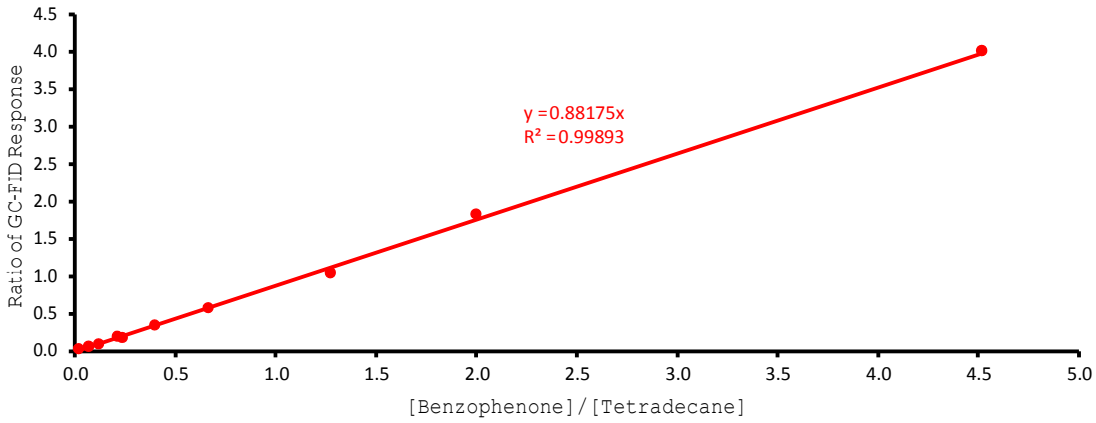




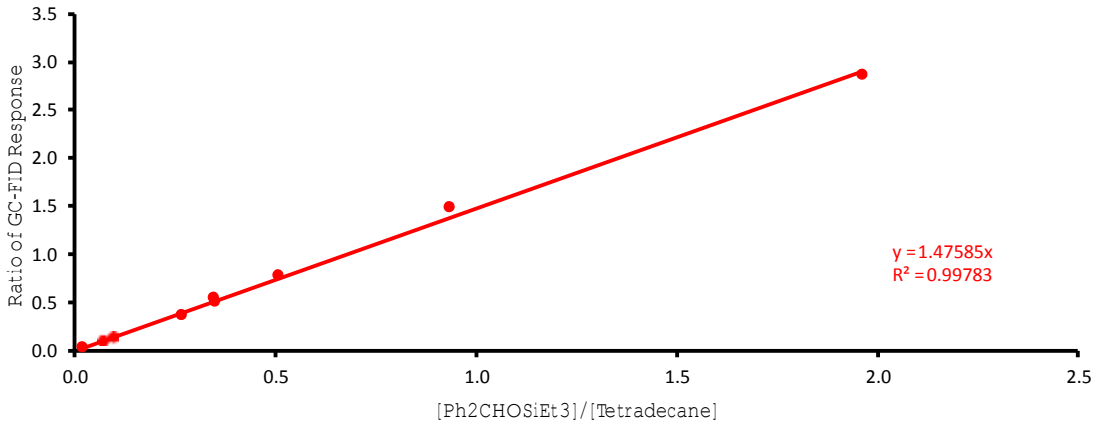
GC-FID Calibration

Each point represents a separate weighing of both analyte and internal standard.

Benzophenone (t_R = 13.40 min)



(Benzhydroyloxy)triethylsilane (t_R = 15.04 min)



X-Ray Diffraction Data

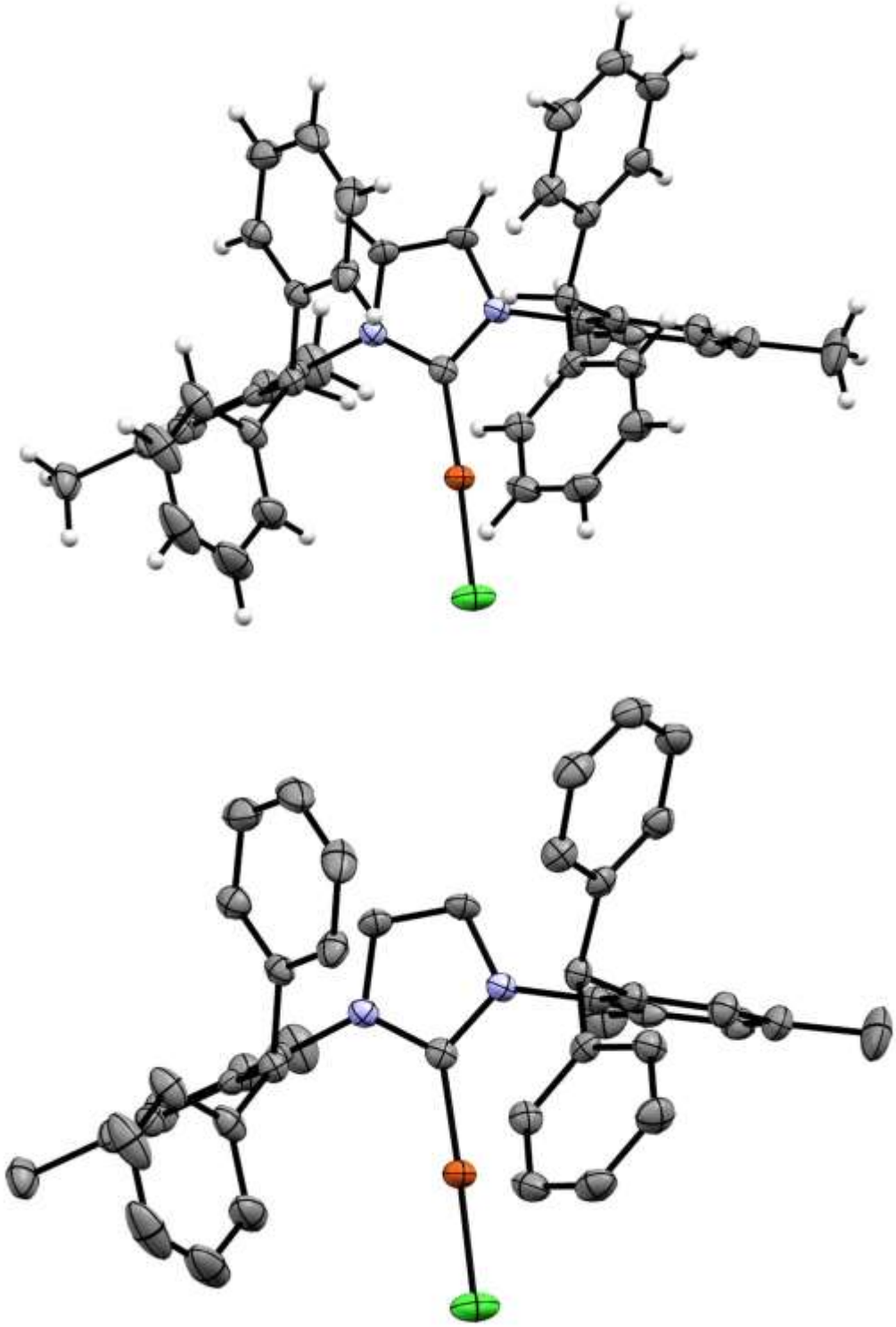
Experimental. Data were measured at low temperature with Oxford Diffraction instrumentation and with monochromated MoKα radiation. All structures were refined to convergence, on F^2 and against all unique reflections with SHELX-97.[1] The structure of [IrCl(cod)(IPaul)] (7) was found to contain disordered solvent molecules. Having failed to model these, the SQUEEZE routine implemented within PLATON was used to remove the solvent from the model.[2] Approximately 38 electron equivalents were removed from 269 $Å^3$ of unit cell volume. In both the [AgCl(IPaul)] (5) and the [IrCl(cod)(IPaul)] (7) structures, one phenyl ring of the carbene ligand was modelled as disordered over two sites. Suitable restraints on displacement parameters and bond lengths were applied in order to ensure that these disordered groups approximated normal behavior. One of the DCM solvent sites in [NiClCp(IPaul)].2CH_2Cl_2 (6) was also disordered and was treated in a similar fashion. Selected crystallographic and geometric parameters are given in the Table on the following page.

1. G. Sheldrick, Acta Crystallogr., Sect. A., 2008, 64, 112-122.
2. A. Spek, Acta Crystallographica Section D, 2009, 65, 148-155.

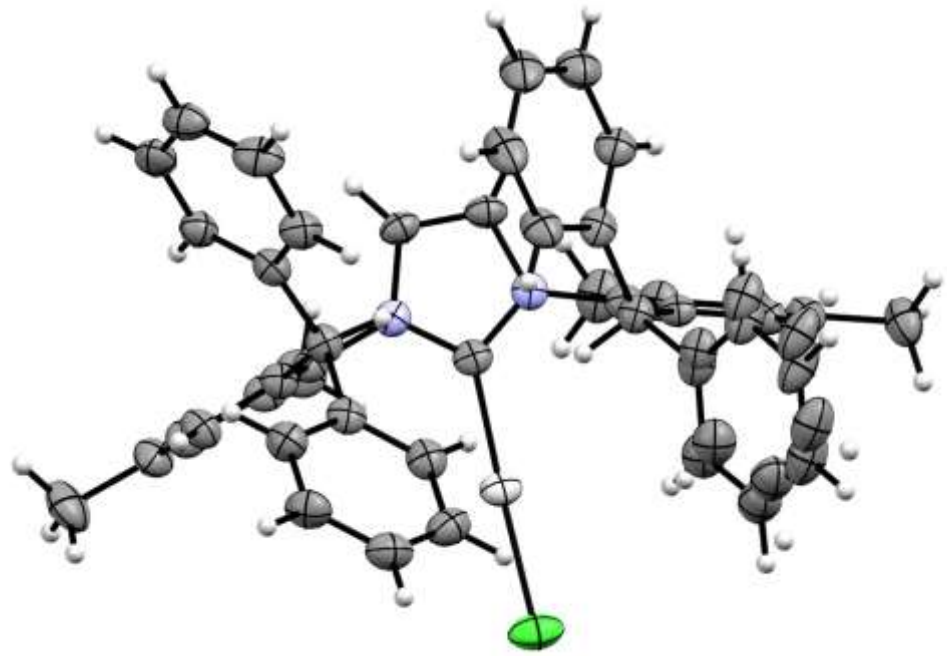
Compound	[CuCl(IPaul)]	[AgCl(IPaul)]	[NiCl(Cp)(IPaul)]	[IrCl(COD)(IPaul)]
M/S Ref.	4	5	6	7
CCDC Ref.	1481901	1481902	1481903	1481904
Formula	$C_{45}H_{40}ClCuN_2$	$C_{45}H_{40}AgClN_2$	$C_{52}H_{49}Cl_5N_2Ni$	$C_{53}H_{52}ClIrN_2$[a]
Formula Weight	707.78	752.11	937.89	944.62
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space Group	P $2_1/c$	P $2_1/c$	P $2_1/n$	P -1
λ Å	0.71073	0.71073	0.71073	0.71073
a Å	18.1556(9)	18.2111(8)	10.8315(4)	9.6593(3)
b Å	9.0431(4)	9.2144(5)	24.7675(6)	12.5384(5)
c Å	22.1244(14)	21.9147(16)	17.4157(5)	21.2099(8)
α°	90	90	90	78.174(3)
β°	96.965(5)	97.416(5)	102.643(3)	77.515(3)
γ°	90	90	90	67.464(3)
Volume $Å^3$	3605.6(3)	3646.6(4)	4558.8(2)	2295.19(14)
Temp. K	123(2)	123(2)	123(2)	123(2)
Z	4	4	4	2
Refls. Collected	17499	34193	20995	12092
2θmax°	59.54	56.00	56.00	54.00
Refls. Unique	8884	8669	10611	9421
Refls. Obs.	6420	6739	7115	8263
Rint	0.0373	0.0665	0.0526	0.0276
Goodness of Fit	1.040	1.067	1.038	1.047
R[I>2s(I)],F	0.0519	0.0581	0.0652	0.0352
Rw, F^2	0.1078	0.1498	0.1854	0.0864
Max/min electron density $eÅ^{-3}$	0.464/-0.533	1.436/-1.869	1.058/-0.591	1.161/-1.014

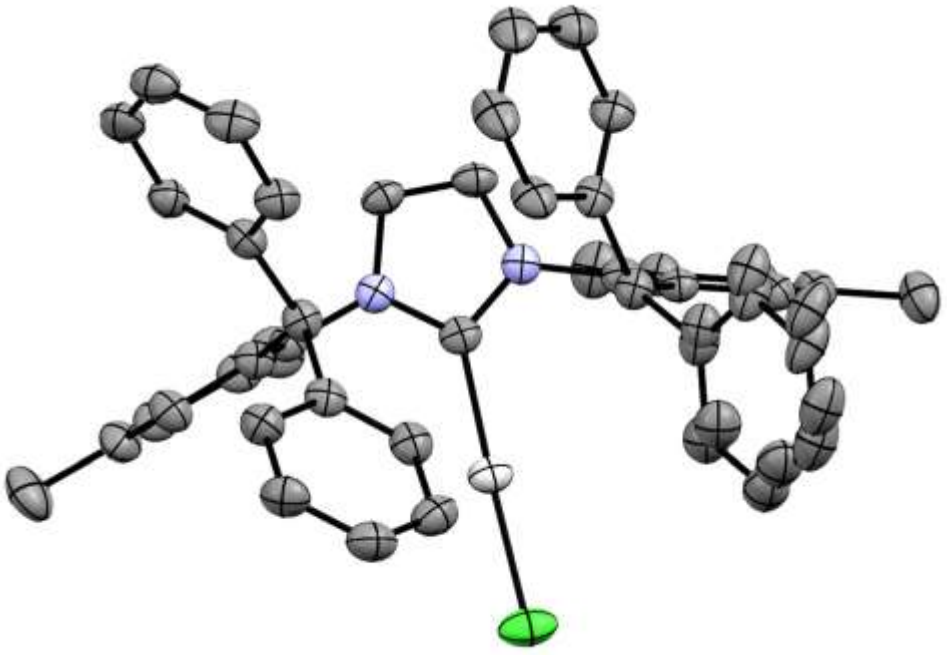
[a] Formula does not include disordered solvent removed by PLATON SQUEEZE.

[CuCl(IPaul)] (4)

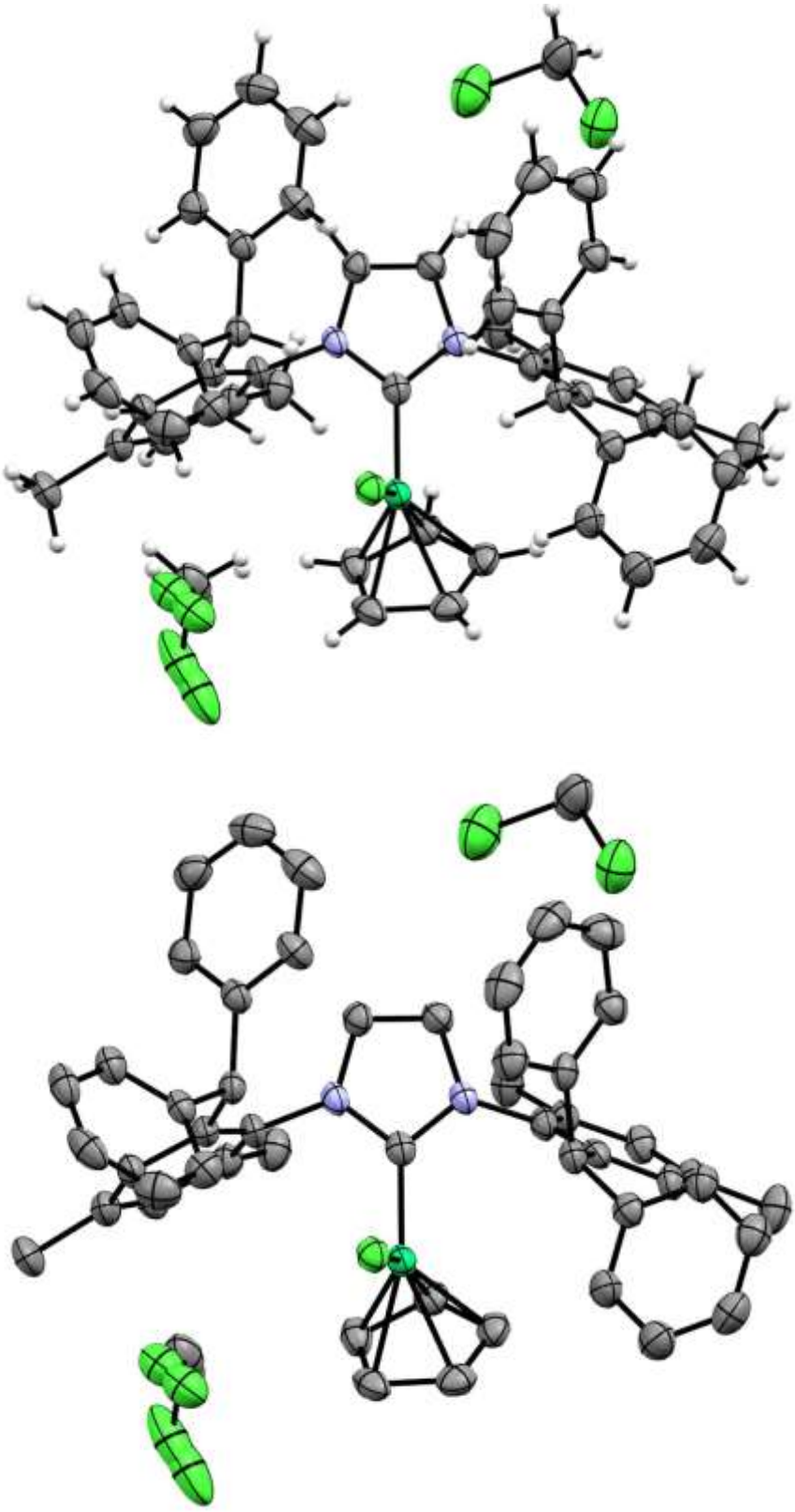


[AgCl(IPaul)] (5)





[NiCl(Cp)(IPaul)] (6)



[IrCl(COD)(IPaul)] (7)