Electronic Supporting Information

Cu(I), Ag(I), Ni(II), Cr(III) and Ir(I) Complexes with Tritopic $N^{imine}C^{NHC}N^{amine}$ Pincer Ligands and Catalytic Ethylene Oligomerization

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Contents

1. Synthesis and characterization

1.1. General methods

All manipulations involving organometallics were performed under nitrogen or argon in a Braun glove-box or using standard Schlenk techniques. Solvents were dried using standard methods and distilled under nitrogen prior use or passed through columns of activated alumina and subsequently purged with nitrogen or argon.

1.2 [CuCl{Im[C(Me)=NDipp](C$_2$NMe$_2$)-κ^1C^{NHC}}] (**3**).

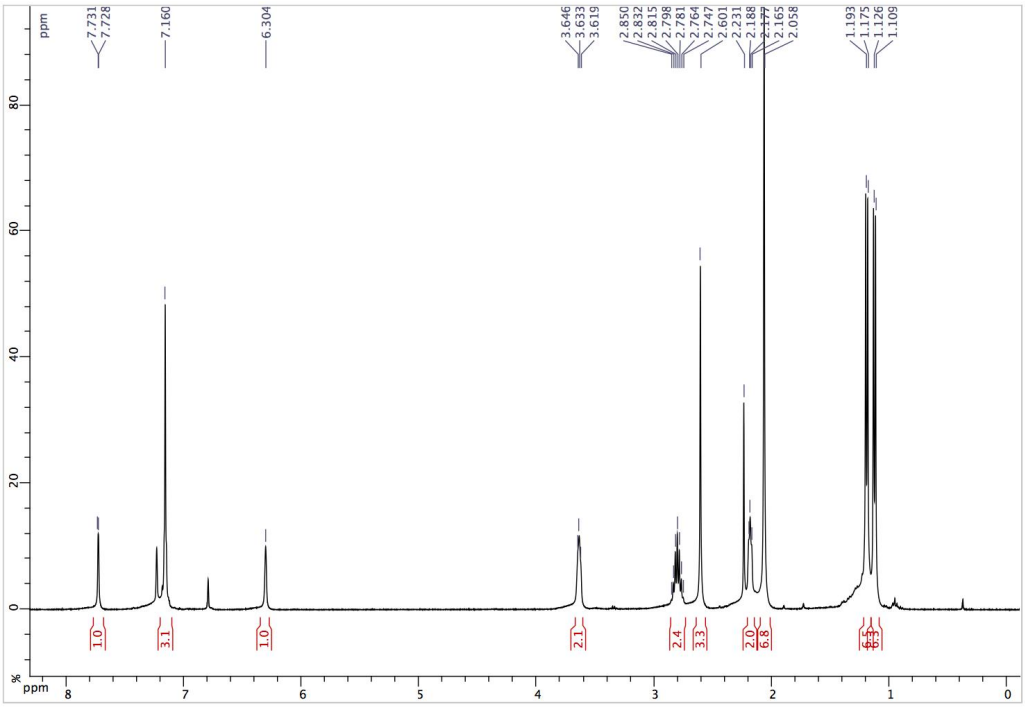

Figure S1. ^{1}H NMR spectrum of **3** in C_6D_6

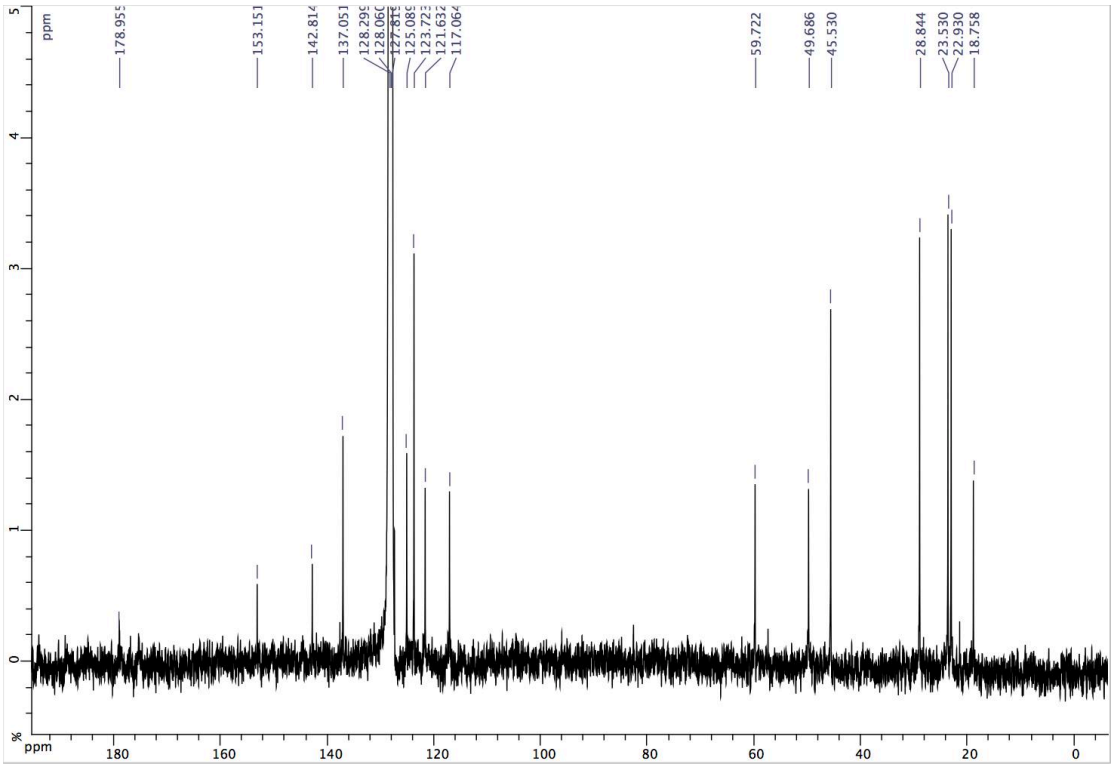

Figure S2. ^{13}C NMR spectrum of **3** in C_6D_6

1.3 [CuCl{Im[C(Me)=NDipp](C$_3$NMe$_2$)-κ^1C^{NHC}}] (**4**).

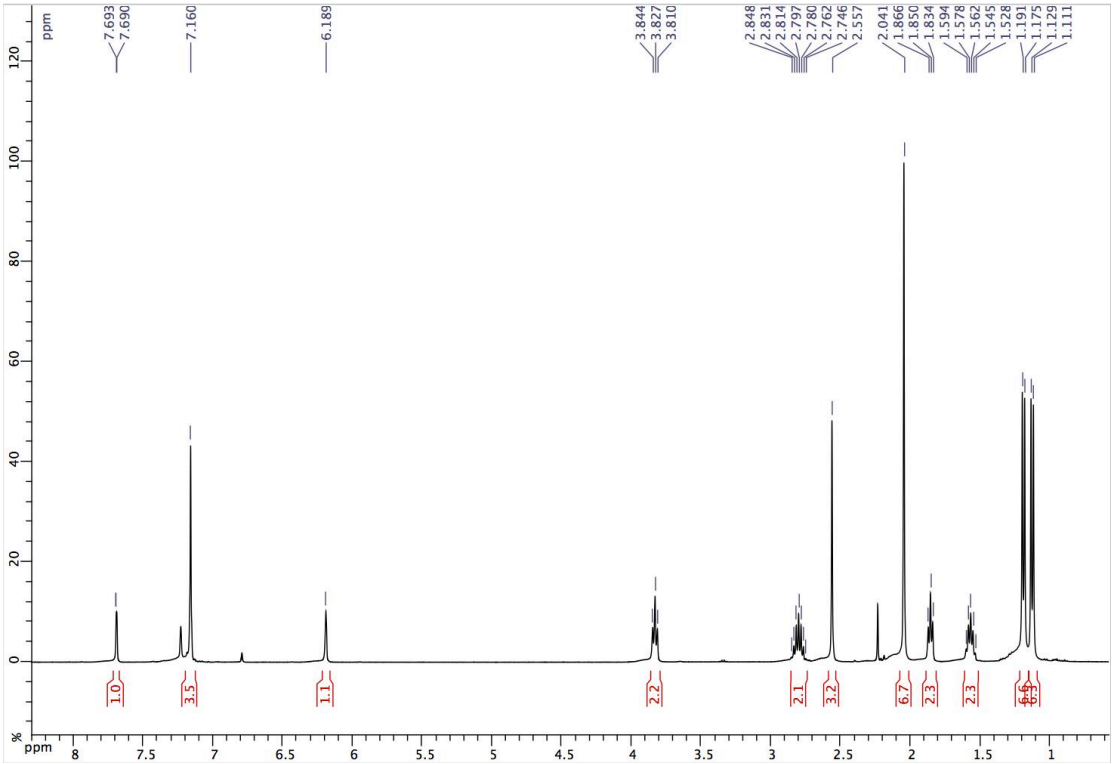

Figure S3. ^1H NMR spectrum of **4** in C_6D_6

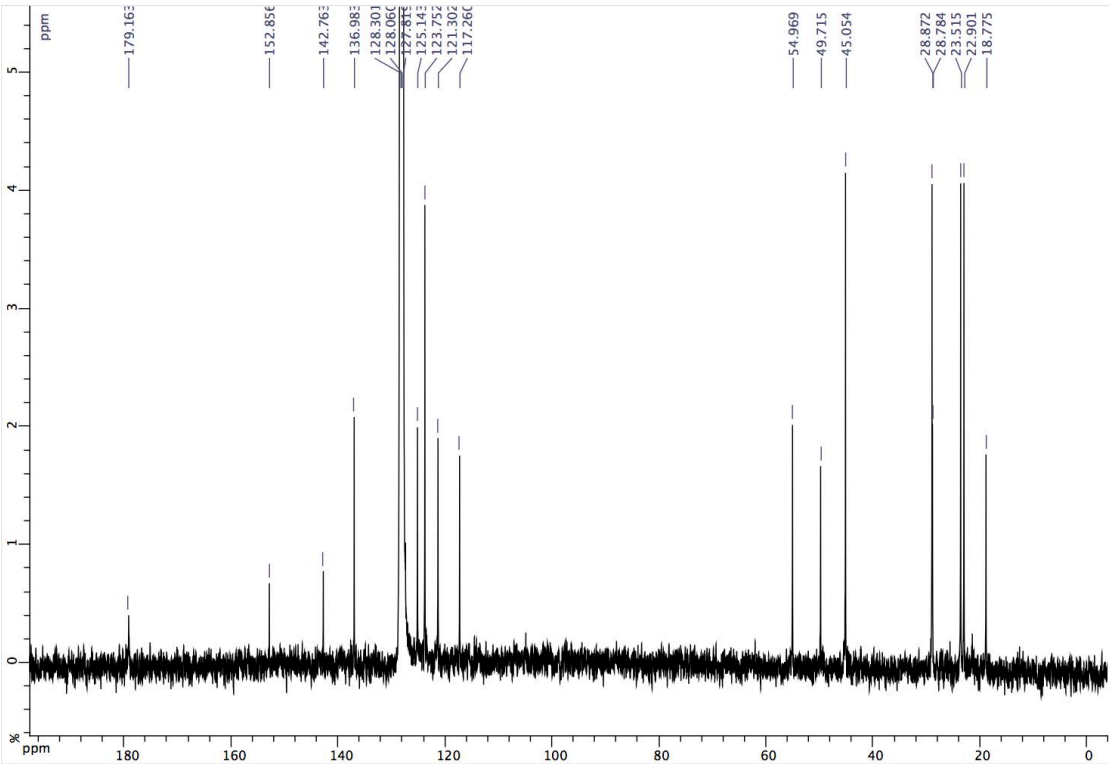

Figure S4. ^{13}C NMR spectrum of **4** in C_6D_6

1.4. $[Cu_4(\mu_2\text{-}I)_2(\mu_3\text{-}I)_2\{\mu\text{-}\kappa^2\text{-}C^{NHC},N^{amine}(Im)\ \{C(Me)=NDipp\}(C_3NMe_2)\}_2]$ (**7**).

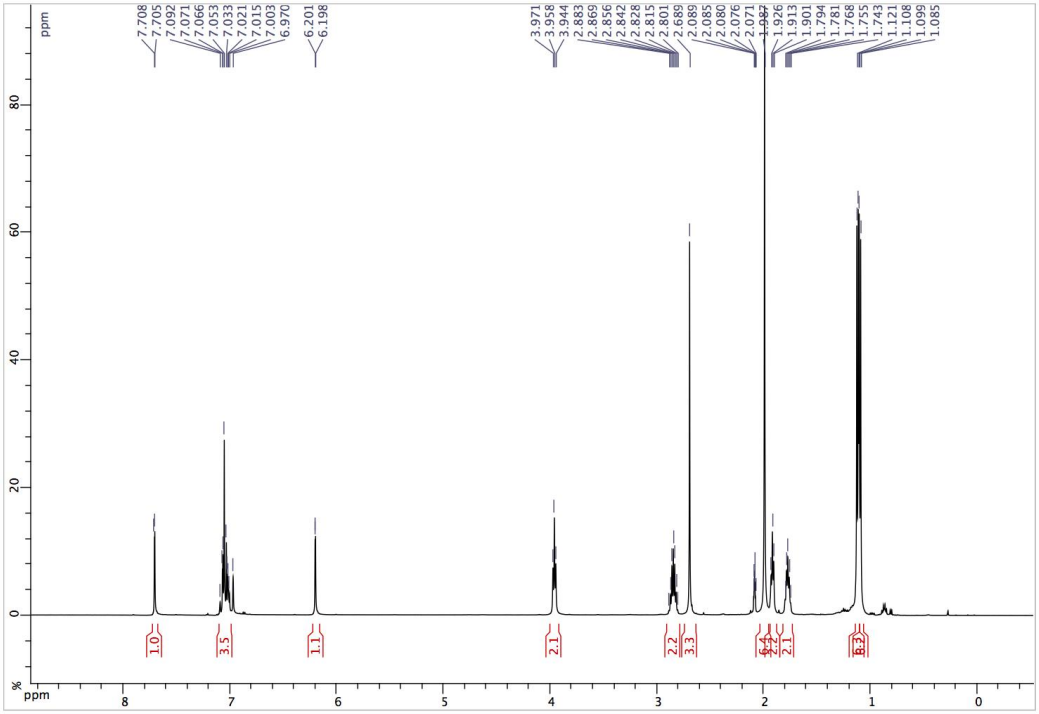

Figure S5. ^{1}H NMR spectrum of **7** in toluene-d_8

1.5. [Ni(NCMe){Im[C(Me)=NDipp](C$_2$NMe$_2$)-κ^3N^{imine},C^{NHC},N^{amine}}][BF$_4$]$_2$ (**9**).

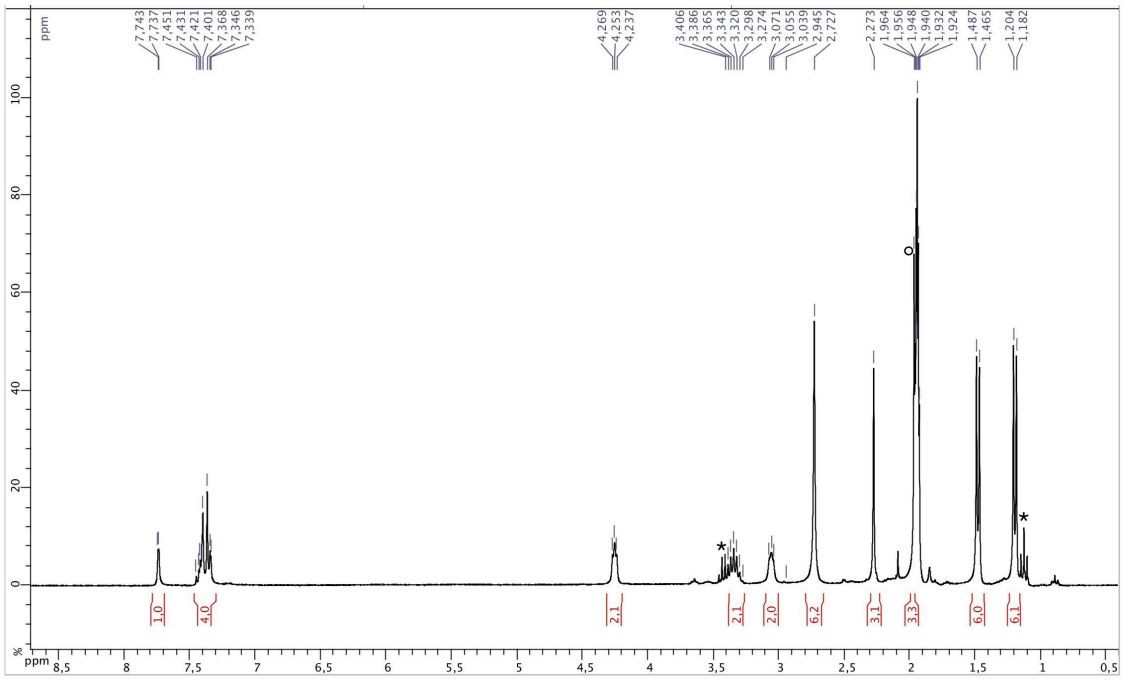

Figure S6. ^{1}H NMR spectrum of **9** in C_6D_6, (*)Et_2O and (°) CH_3CN

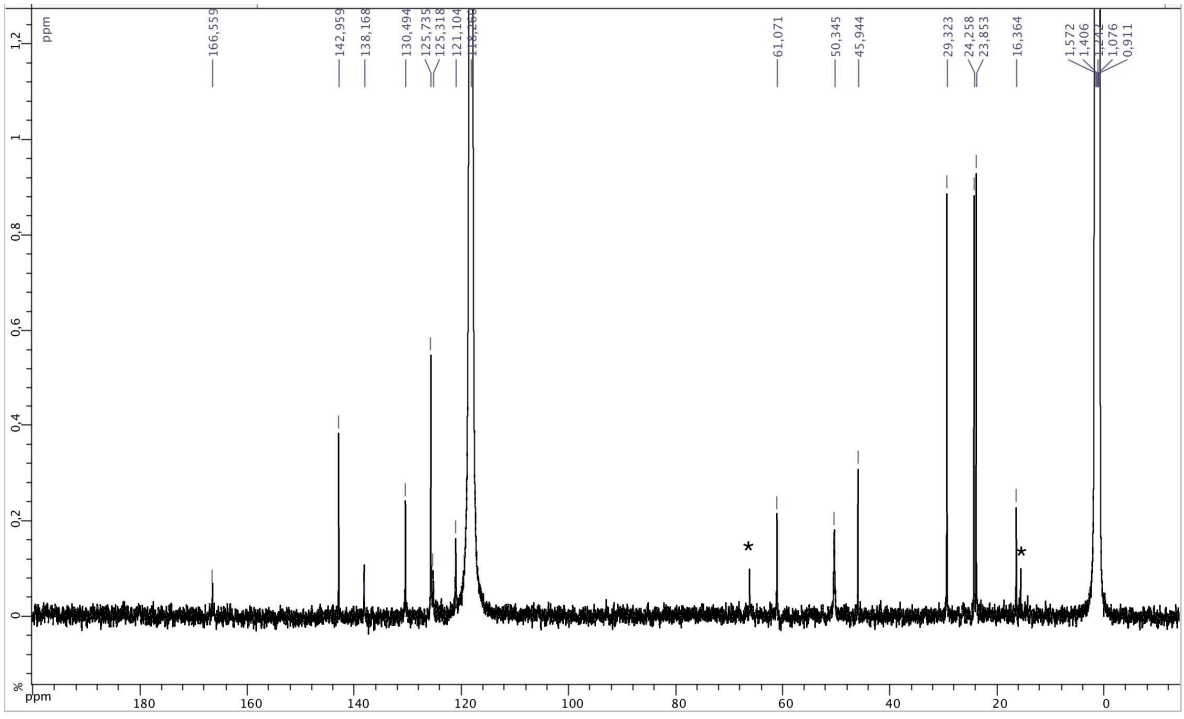

Figure S7. ^{13}C NMR spectrum of **9** in CD_3CN, (*) Et_2O

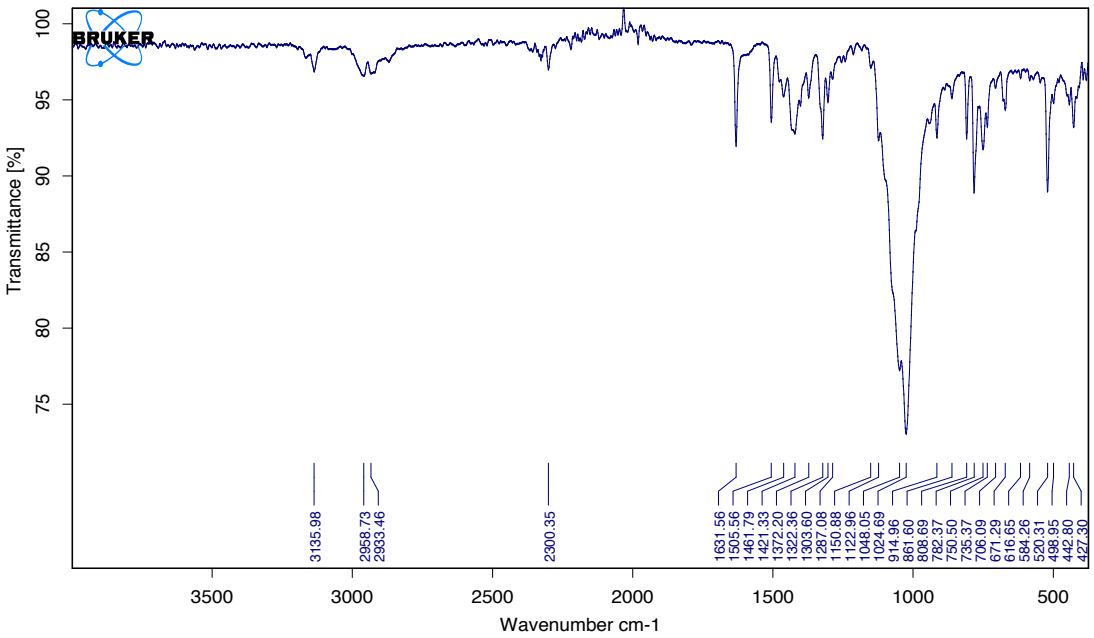

Figure S8. IR spectrum of **9** (ATR platinum Diamond)

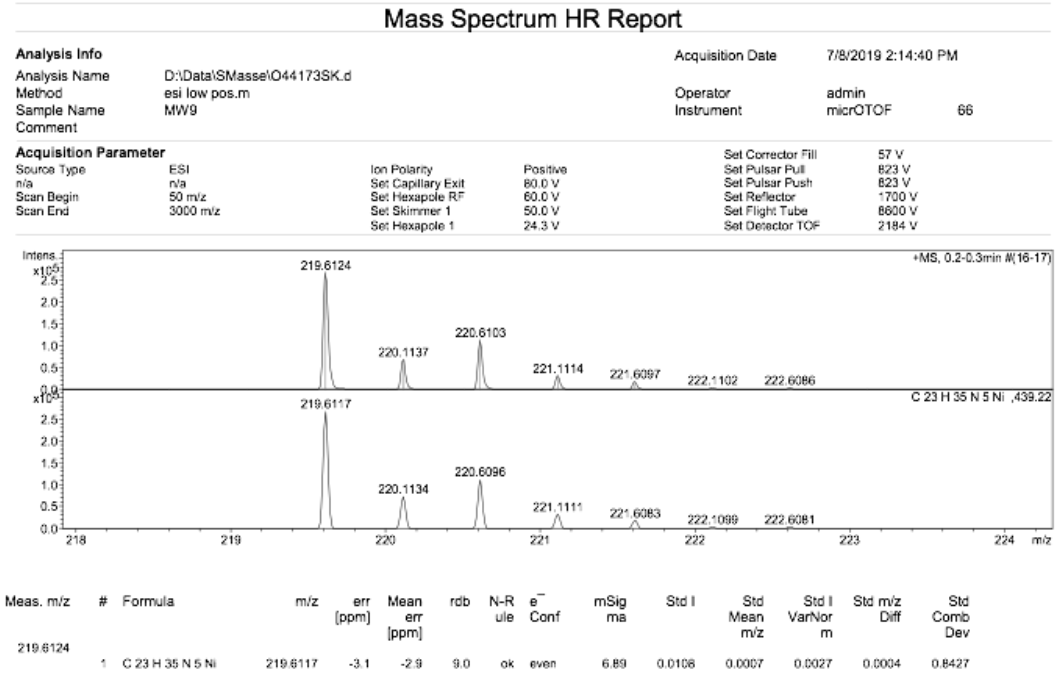

Figure S9. ESI mass spectrum of complex **9**.

1.6. [[IrCl(cod){Im[C(Me)=NDipp](C$_2$NMe$_2$)-κ^1C^{NHC}}] (**13**).

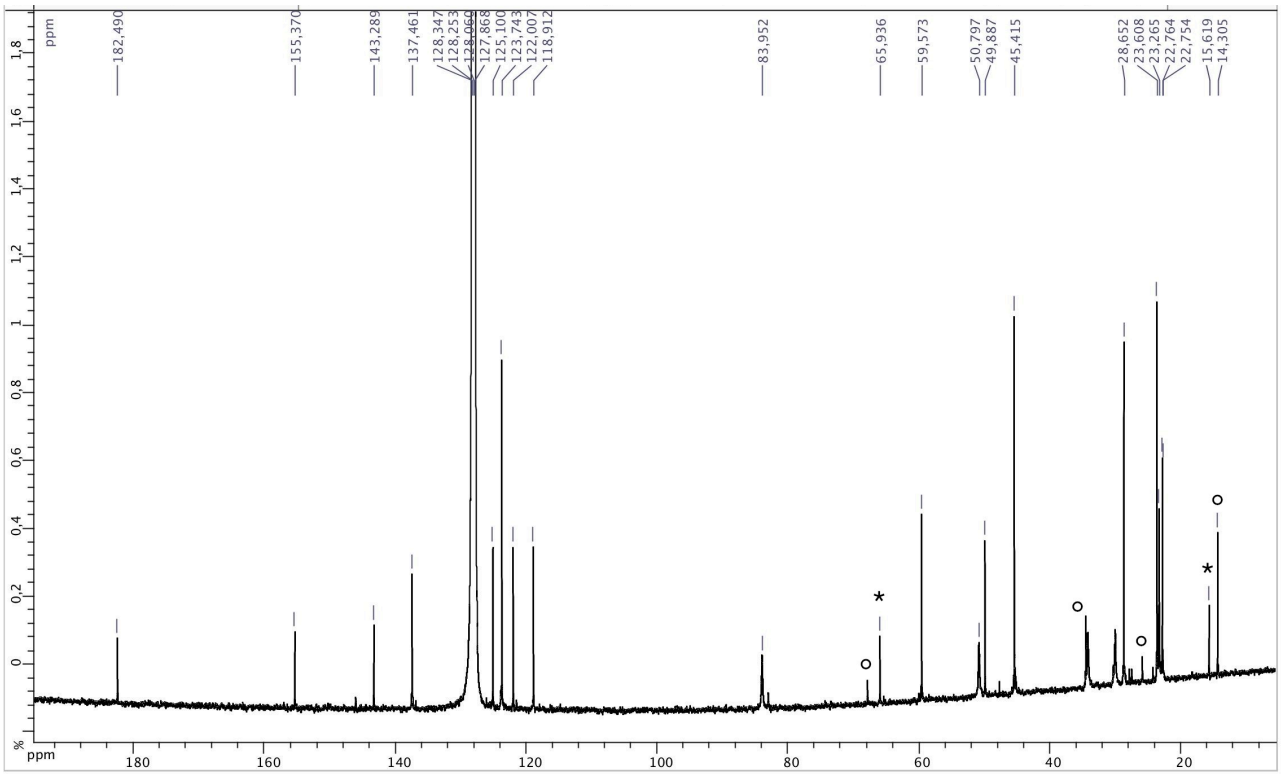

Figure S10. ^{13}C NMR spectrum of **13** in CD_3CN, (*) Et_2O and (°) impurities

1.7. [Ir(cod){Im[C(Me)=NDipp](C$_2$NMe$_2$)-κ^2N^{imine},C^{NHC}}]BF$_4$ (**15**).

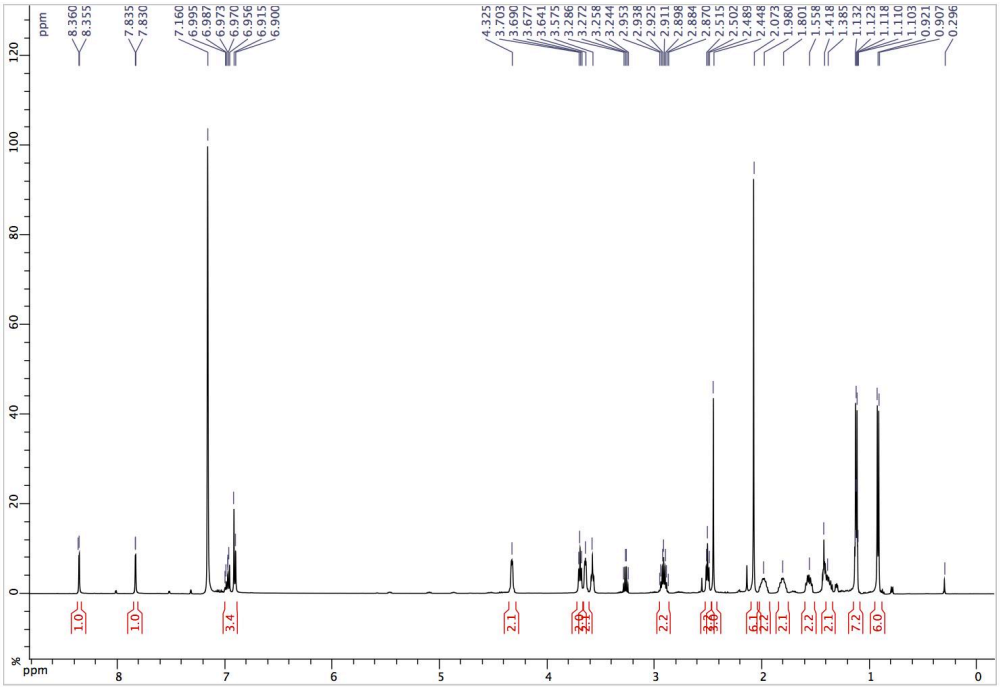

Figure S11. ^{1}H NMR spectrum of **15** in C_6D_6

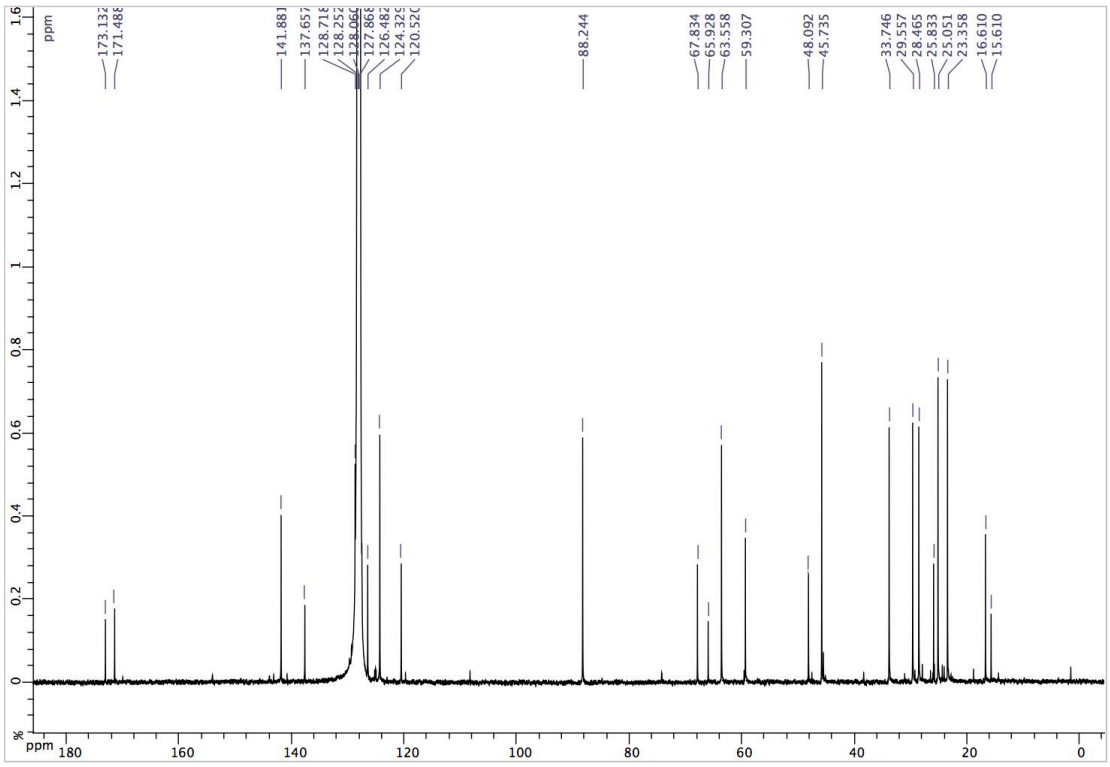

Figure S12. ^{13}C NMR spectrum of **15** in C_6D_6

1.8. [Ir(cod){Im[C(Me)=NDipp](C$_3$NMe$_2$)-κ^2N^{imine},C^{NHC}}]BF$_4$ (**16**).

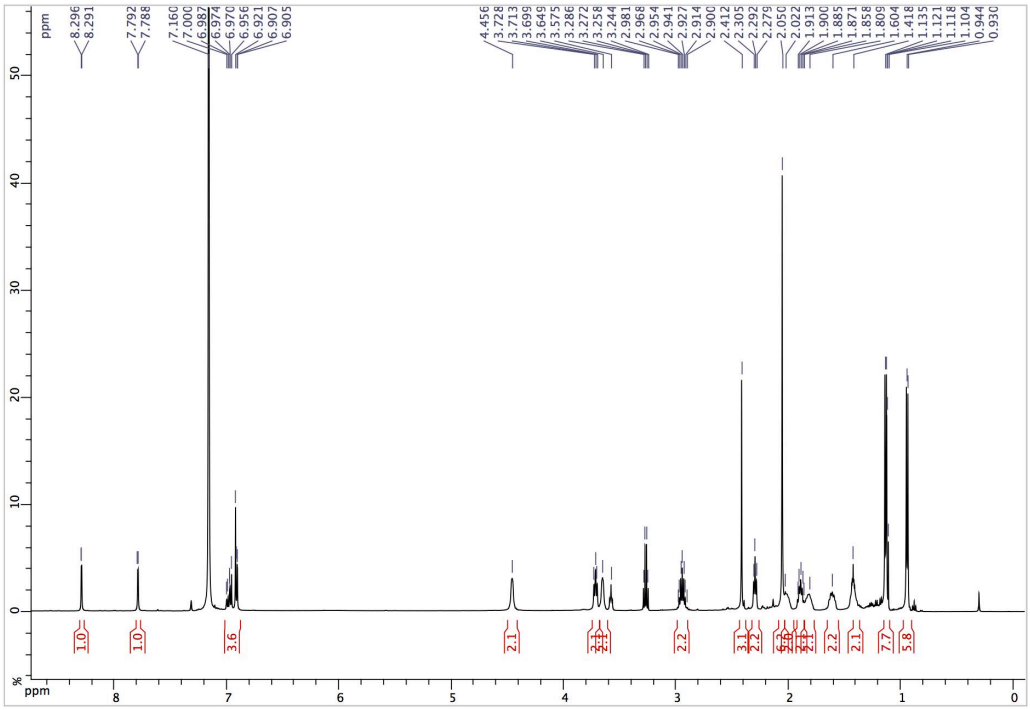

Figure S13. ^{1}H NMR spectrum of **16** in C_6D_6

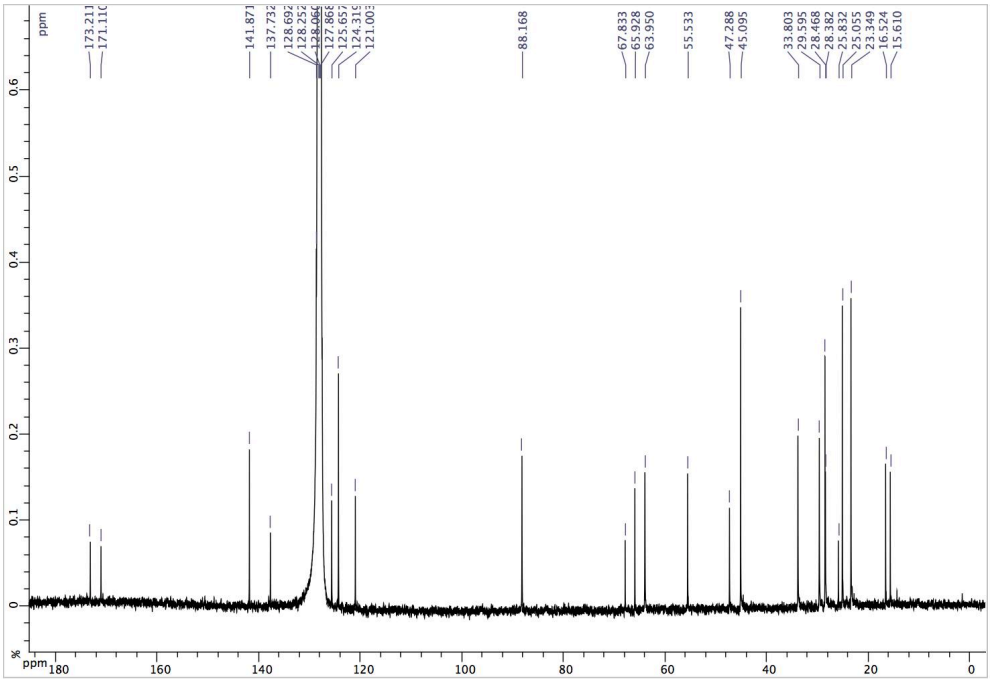

Figure S14. ^{13}C NMR spectrum of **16** in C_6D_6

2. X-Ray diffraction analyses

2.1 General methods

Summary of the crystal data, data collection and refinement for structures of **3**, **6**, **7**, **8**·2Et_2O, **9**-**11**, **12**·2C_7H_8, **14** and **16**·THF are given in Table S1. The crystals were mounted on a glass fibre with grease, from Fomblin vacuum oil. Data sets were collected on a Bruker APEX II DUO diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using Mo-Kα radiation (λ = 0.71073 Å). The crystal-detector distance was 38 mm. The cell parameters were determined (APEX2 software)[1] from reflections taken from three sets of 12 frames, each at 10 s exposure. The structures were solved by direct methods using the program SHELXS-97.[2] The refinement and all further calculations were carried out using SHELXL- 97.[3] The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2.

2.2 Additional details

The following specific comments apply to the models of the structures:

For **3**, the carbon atoms C13, C14 and hydrogen atomss of C12 are disordered on two positions.

For **7**, this complex contains two ligands, four copper and four iodine atoms. Each iodine is coordinated to two copper atoms. The asymmetric unit contains half a molecule of this complex.

For **11**, a squeeze was made. The residual electron density was assigned to one molecule of THF.

For **12**, the chromium is coordinated to one ligand and to three chlorides. The asymmetric unit contains also two molecules of toluene. The methylene carbons C19 and C20 are disordered on two positions. The hydrogens of C18 are also disordered on two position. One toluene (C30, C31, C32, C33, C34, C35, C36) is disordered on two positions.

For **16**, the asymmetric unit also contains a THF molecule.

2.3. Summary of crystal data

Table S1. Summary of the Crystal Data.

	3	**6**	**7**	**8**·2Et_2O
Chemical formula	$C_{21}H_{32}ClCuN_4$	$C_{22}H_{34}AgClN_4$	$C_{44}H_{68}Cu_4I_4N_8$	$C_{84}H_{128}Ag_2Br_4Cl_2N_{16}Ni_2$, 2($C_4H_{10}O$)
CCDC Number	1896575	1590359	1896576	1590360
Formula Mass	439.49	497.85	1470.82	2233.96
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
a/Å	11.5696(5)	8.4886(8)	15.7098(8)	11.6854(9)
b/Å	11.3251(5)	19.7601(19)	8.6227(2)	14.5354(11)
c/Å	17.3683(8)	16.1890(12)	22.1783(10)	16.0920(12)
α/°	90	90	90	90.426(2)
β/°	91.4890(10)	118.595(4)	119.744(3)	95.984(2)
γ/°	90	90	90	99.225(2)
Unit cell volume/Å^3	2274.95(18)	2384.3(4)	2608.5(2)	2682.4(4)
Temperature/K	173(2)	173(2)	173(2)	173(2)
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	P -1
Formula units / cell, *Z*	4	4	2	1
Absorption coefficient, μ/mm^{-1}	1.090	0.971	4.013	2.294
No. of reflections measured	21300	31006	14983	61958
No. of independent reflections	5494	7592	5963	12954
R_{int}	0.0331	0.0333	0.0836	0.0709
Final R_1 values ($I > 2\sigma(I)$)	0.0399	0.0318	0.0555	0.0458
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0903	0.0643	0.1164	0.1021
Final R_1 values (all data)	0.0614	0.0552	0.1020	0.0902
Final $wR(F^2)$ values (all data)	0.0984	0.0734	0.1559	0.1183
Goodness of fit on F^2	1.029	1.010	1.096	1.015

	9	**10**	**11**
Chemical formula	$C_{23}H_{35}N_5Ni$, $2(BF_4)$	$C_{24}H_{37}N_5Ni$, $2(BF_4)$	$C_{21}H_{32}Cl_3CrN_4$
CCDC Number	1590361	1590362	1896577
Formula Mass	613.89	627.91	498.85
Crystal system	monoclinic	monoclinic	triclinic
a/Å	12.8096(5)	12.6898(4)	9.2760(10)
b/Å	13.0115(5)	12.7224(4)	10.6492(12)
c/Å	19.5024(6)	20.9490(6)	15.4308(17)
α/°	90	90	94.943(2)
β/°	119.769(2)	119.931(2)	105.109(2)
γ/°	90	90	96.726(2)
Unit cell volume/Å^3	2821.55(18)	2931.02(16)	1450.6(3)
Temperature/K	173(2)	173(2)	173(2)
Space group	$P2_1/c$	$P2_1/c$	P -1
Formula units / cell, *Z*	4	4	2
Absorption coefficient, μ/mm^{-1}	0.763	0.736	0.683
No. of reflections measured	27535	33303	26545
No. of independent reflections	6826	11084	7041
R_{int}	0.0425	0.0312	0.0619
Final R_1 values ($I > 2\sigma(I)$)	0.0527	0.0437	0.0507
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1262	0.1014	0.1081
Final R_1 values (all data)	0.0929	0.0739	0.0978
Final $wR(F^2)$ values (all data)	0.1451	0.1154	0.1184
Goodness of fit on F^2	1.014	1.015	0.961

	12·2Toluene	**14**	**16**·THF
Chemical formula	$C_{22}H_{34}Cl_3CrN_4$, $2(C_7H_8)$	$C_{30}H_{46}ClIrN_4$	$C_{30}H_{46}IrN_4$, BF_4, C_4H_8O
CCDC Number	1896578	1896579	1896580
Formula Mass	697.15	690.36	813.82
Crystal system	orthorhombic	triclinic	triclinic
a/Å	11.6017(4)	8.4032(4)	10.1636(5)
b/Å	18.8201(7)	11.1493(5)	10.9789(5)
c/Å	32.9818(11)	16.7862(7)	17.0720(9)
α/°	90	105.2100(10)	107.6610(10)
β/°	90	104.4890(10)	92.2080(10)
γ/°	90	96.0040(10)	100.5780(10)
Unit cell volume/Å^3	7201.4(4)	1444.74(11)	1775.30(15)
Temperature/K	173(2)	173(2)	173(2)
Space group	P*bca*	P -1	P -1
Formula units / cell, *Z*	8	2	2
Absorption coefficient, μ/mm^{-1}	0.571	4.739	3.813
No. of reflections measured	82448	41189	57054
No. of independent reflections	8673	10898	12293
R_{int}	0.0795	0.0229	0.0215
Final R_1 values ($I > 2\sigma(I)$)	0.0502	0.0199	0.0257
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1003	0.0424	0.0629
Final R_1 values (all data)	0.0861	0.0254	0.0297
Final $wR(F^2)$ values (all data)	0.1120	0.0441	0.0647
Goodness of fit on F^2	1.022	1.068	1.092

References

1 *APEX2*, *SAINT* and *SADABS*, Bruker AXS Inc.: Madison, Wisconsin, USA, **2006.**

2 G. M. Sheldrick, *Acta Cryst. Section A*, 1990, **46**, 467-473

3 G. M. Sheldrick, *Acta Cryst. Section A*, 2008, **64**, 112-122.

Author Contributions

X. Ren performed the experimental work, analysed the data and wrote the first draft. M. Wesolek and P. Braunstein designed the experiments, contributed to the data analysis and finalized the article. P. Braunstein was in charge of the project administration.