Coordination Complexes of Niobium and Tantalum Pentahalides with a Bulky NHC Ligand

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Supporting Information

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Figure S1. DFT C-PCM/ωB97X/BS1 calculated structure of the $[NbCl_4(Ipr)]^+$ cation belonging to $[NbCl_4(Ipr)][NbCl_6]$. Dichloromethane as implicit solvent. Hydrogen atoms have been omitted for clarity.

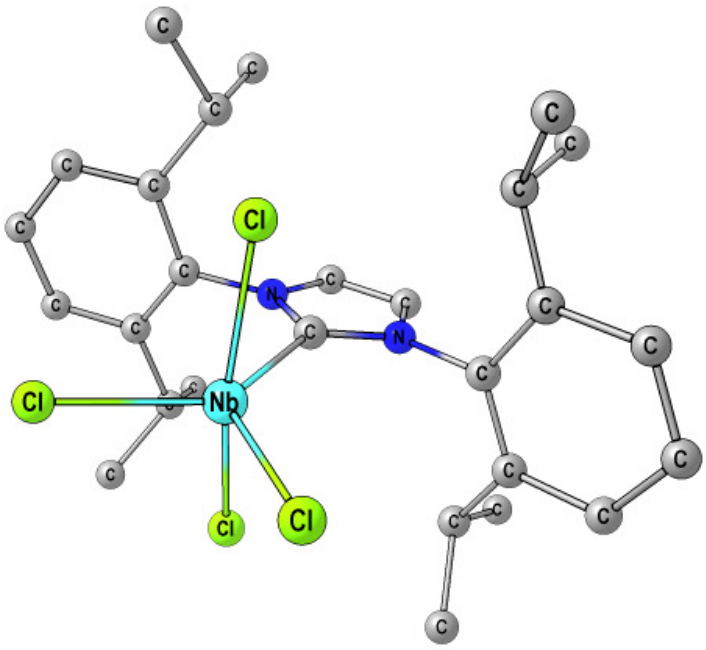

Table S1. Selected computed bond lengths (Å) and angles (°) for the cation $[NbCl_4(Ipr)]^+$ belonging to $[NbCl_4(Ipr)][NbCl_6]$.

Bond		Angle	
Nb–C	2.327	C–Nb–Cl	80.3
Nb–Cl	2.251		82.6
	2.251		127.6
	2.303		127.6
	2.305	N–C–N	106.0
C–N	1.349		
	1.349		

Figure S2. DFT C-PCM/ωB97X/BS2 calculated structure of the $[NbBr_4(Ipr)]^+$ cation belonging to $[NbBr_4(Ipr)][NbBr_6]$. Dichloromethane as implicit solvent. Hydrogen atoms have been omitted for clarity.

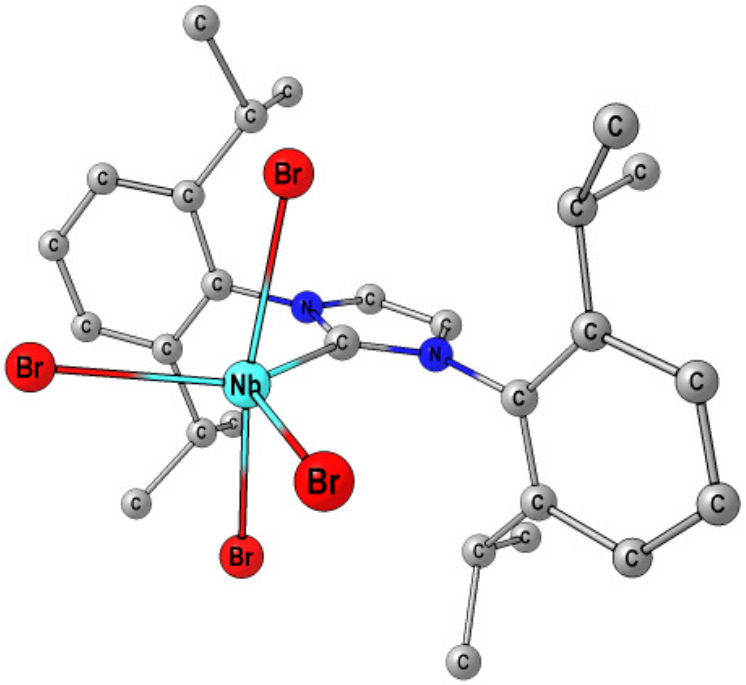

Table S2. Selected computed bond lengths (Å) and angles (°) for the $[NbBr_4(Ipr)]^+$ cation belonging to $[NbBr_4(Ipr)][NbBr_6]$.

Bond		Angle	
Nb–C	2.316	C–Nb–Br	81.4
Nb–Br	2.420		83.0
	2.429		127.2
	2.465		127.7
	2.469	N–C–N	105.7
C–N	1.352		
	1.353		

Figure S3. DFT C-PCM/ωB97X/BS2 calculated structure of the $[TaCl_4(Ipr)]^+$ cation belonging to $[TaCl_4(Ipr)][TaCl_6]$. Dichloromethane as implicit solvent. Hydrogen atoms have been omitted for clarity.

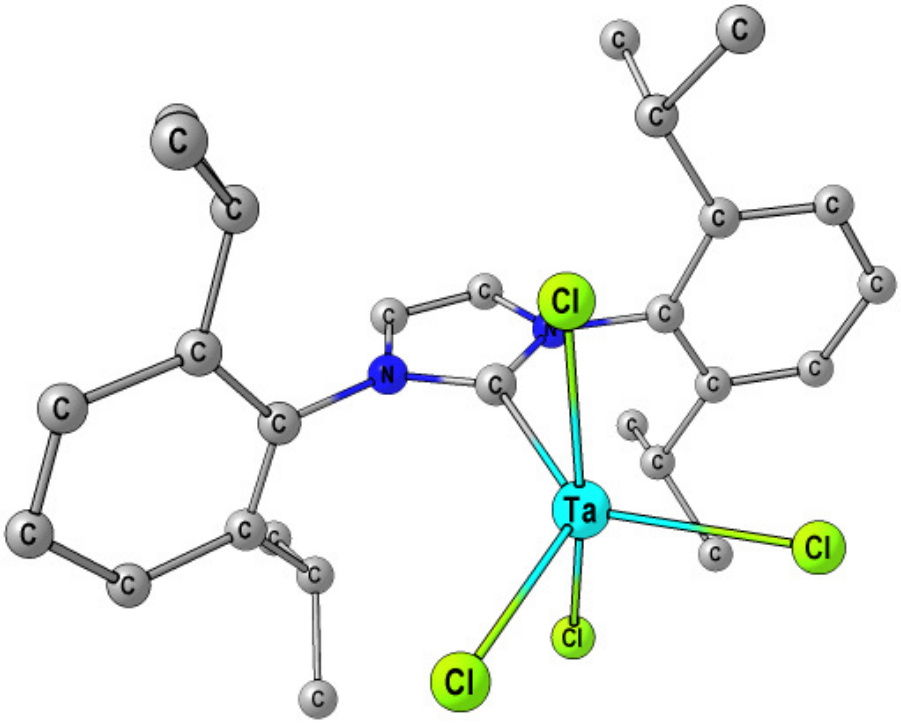

Table S3. Selected computed bond lengths (Å) and angles (°) for the $[TaCl_4(Ipr)]^+$ cation belonging to $[TaCl_4(Ipr)][TaCl_6]$.

Bond		Angle	
Ta–C	2.297	C–Ta–Cl	82.4
Ta–Cl	2.251		84.7
	2.251		127.9
	2.302		127.9
	2.303	N–C–N	105.7
C–N	1.351		
	1.351		

Figure S4. DFT C-PCM/ωB97X/BS2 calculated structure of the $[TaBr_4(Ipr)]^+$ cation belonging to $[TaBr_4(Ipr)][TaBr_6]$. Dichloromethane as implicit solvent. Hydrogen atoms have been omitted for clarity.

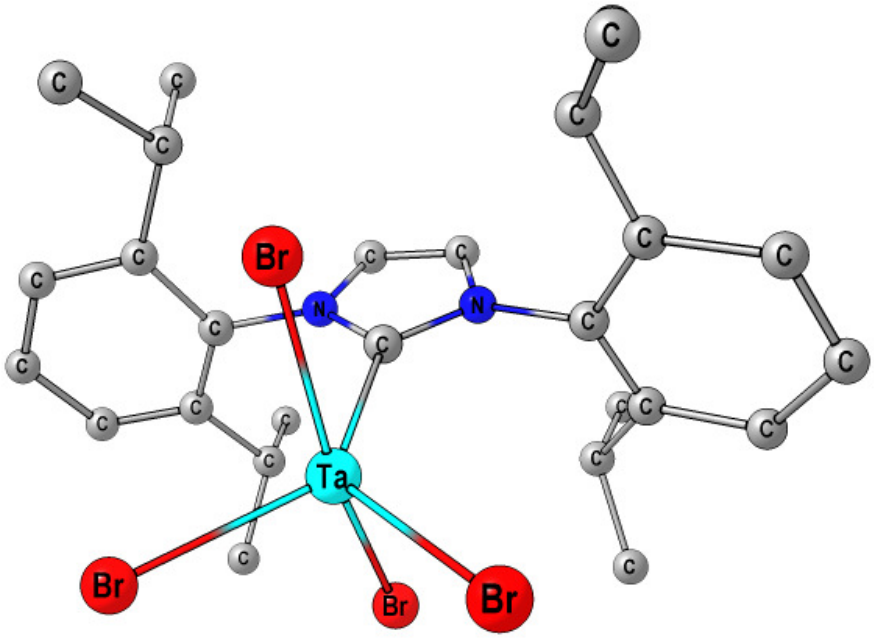

Table S4. Selected computed bond lengths (Å) and angles (°) for the $[TaBr_4(Ipr)]^+$ cation belonging to $[TaBr_4(Ipr)][TaBr_6]$.

Bond		Angle	
Ta–C	2.316	C–Ta–Br	82.0
Ta–Br	2.420		83.2
	2.426		127.3
	2.463		127.7
	2.467	N–C–N	105.6
C–N	1.353		
	1.354		

Figure S5. DFT C-PCM/ωB97X/BS1 calculated structure of the $[NbCl_4(Ipr)_2]^+$ cation belonging to $[NbCl_4(Ipr)_2][NbCl_6]$. Dichloromethane as implicit solvent. Hydrogen atoms have been omitted for clarity.

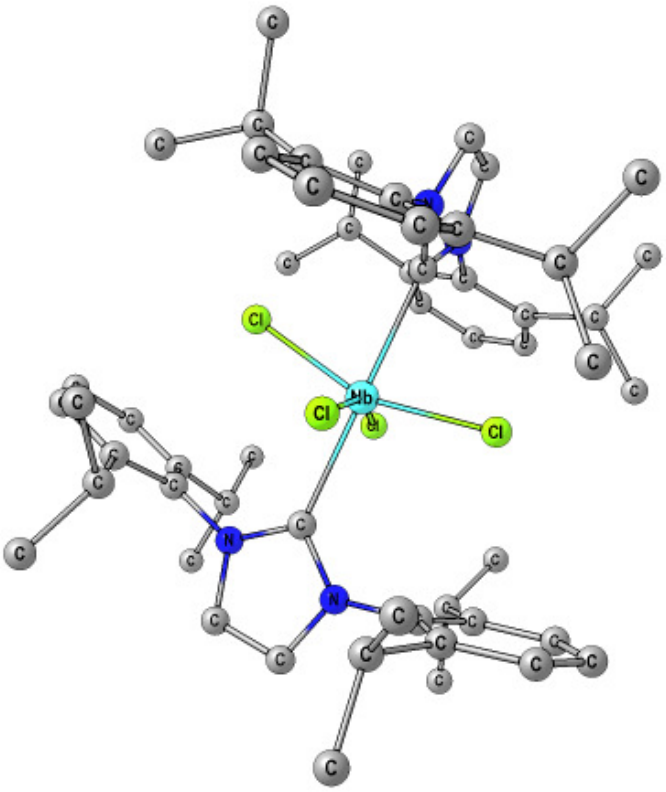

Table S5. Selected computed bond lengths (Å) and angles (°) for the $[NbCl_4(Ipr)_2]^+$ cation belonging to $[NbCl_4(Ipr)_2][NbCl_6]$.

Bond		Angle	
Nb–C	2.387	C–Nb–C	179.9
	2.387	C–Nb–Cl	79.2
Nb–Cl	2.310		79.2
	2.310		100.7
	2.310		100.8
	2.310		79.2
C–N	1.356		79.2
	1.356		100.7
	1.356		100.8
	1.356	N–C–N	104.7
			104.7

Figure S6. DFT C-PCM/ωB97X/BS2 calculated structure of the $[NbBr_4(Ipr)_2]^+$ cation belonging to $[NbBr_4(Ipr)_2][NbBr_6]$. Dichloromethane as implicit solvent. Hydrogen atoms have been omitted for clarity.

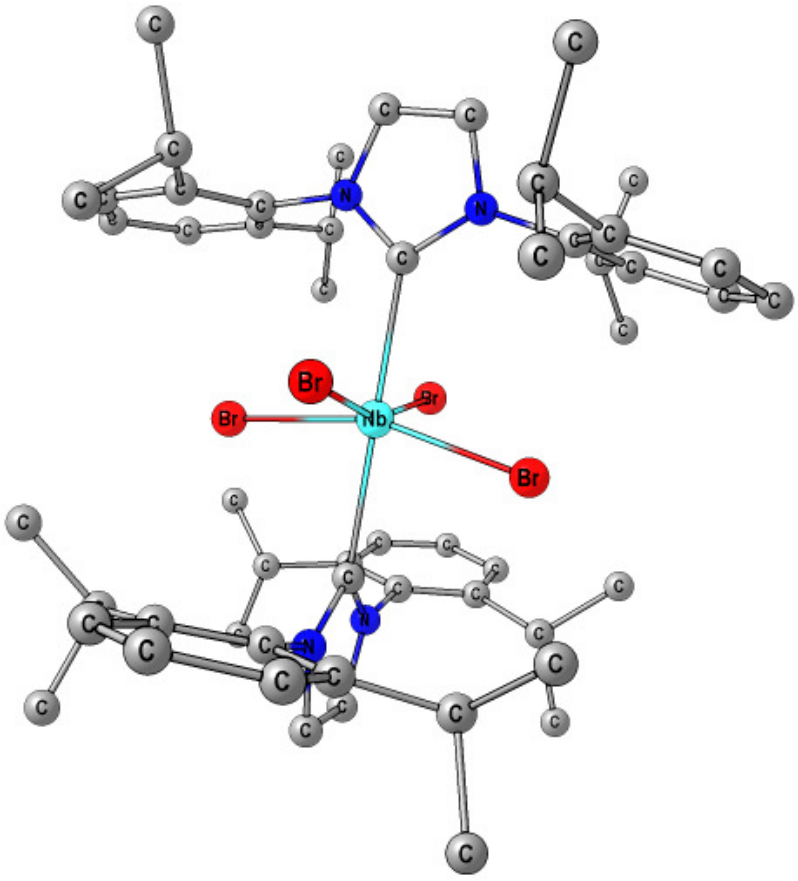

Table S6. Selected computed bond lengths (Å) and angles (°) for the $[NbBr_4(Ipr)_2]^+$ cation belonging to $[NbBr_4(Ipr)_2][NbBr_6]$.

Bond		Angle	
Nb–C	2.419	C–Nb–C	180.0
	2.419	C–Nb–Br	80.2
Nb–Br	2.475		80.3
	2.475		99.6
	2.475		99.8
	2.475		80.3
C–N	1.363		80.3
	1.363		99.7
	1.363		99.8
	1.363	N–C–N	103.9
			103.9

Figure S7. DFT C-PCM/ωB97X/BS2 calculated structure of the $[TaCl_4(Ipr)_2]^+$ cation belonging to $[TaCl_4(Ipr)_2][TaCl_6]$. Dichloromethane as implicit solvent. Hydrogen atoms have been omitted for clarity.

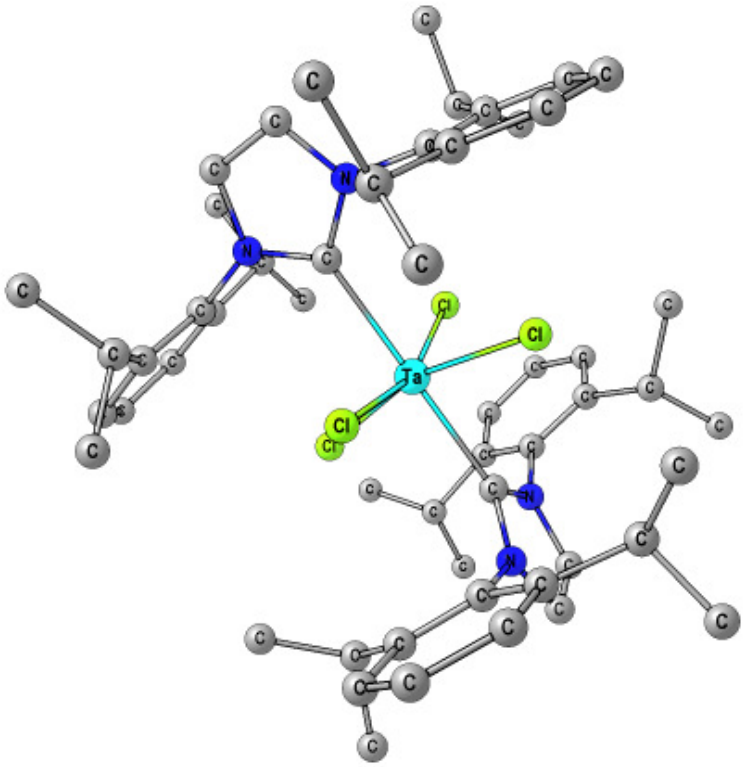

Table S7. Selected computed bond lengths (Å) and angles (°) for the $[TaCl_4(Ipr)_2]^+$ cation belonging to $[TaCl_4(Ipr)_2][TaCl_6]$.

Bond		**Angle**	
Ta–C	2.366	C–Ta–C	180.0
	2.367	C–Ta–Cl	80.9
Ta–Cl	2.304		80.9
	2.304		99.1
	2.304		99.1
	2.304		80.9
C–N	1.359		80.9
	1.359		99.1
	1.359		99.2
	1.360	N–C–N	104.2
			104.2

Figure S8. DFT C-PCM/ωB97X/BS2 calculated structure of the $[TaBr_4(Ipr)_2]^+$ cation belonging to $[TaBr_4(Ipr)_2][TaBr_6]$. Dichloromethane as implicit solvent. Hydrogen atoms have been omitted for clarity.

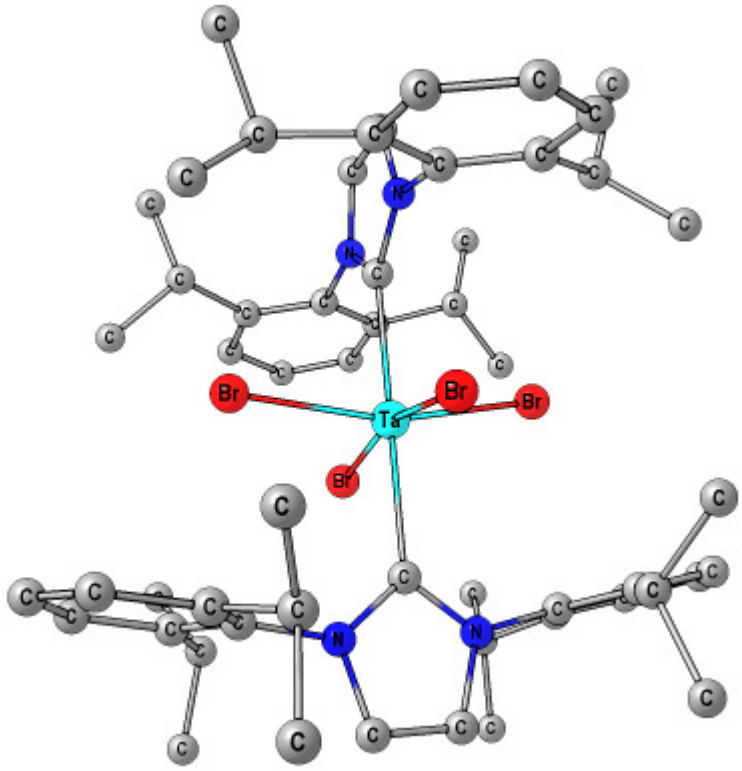

Table S8. Selected computed bond lengths (Å) and angles (°) for the $[TaBr_4(Ipr)_2]^+$ cation belonging to $[TaBr_4(Ipr)_2][TaBr_6]$.

Bond		Angle	
Ta–C	2.393	C–Ta–C	180.0
	2.395	C–Ta–Br	81.8
Ta–Br	2.473		81.9
	2.473		98.1
	2.473		98.2
	2.473		81.8
C–N	1.363		81.9
	1.363		98.1
	1.364		98.2
	1.364	N–C–N	103.9
			104.0

Figure S9. DFT EDF2/BS3 calculated structure of Nb_4F_{10}(Ipr). Dichloromethane as implicit solvent. Hydrogen atoms have been omitted for clarity.

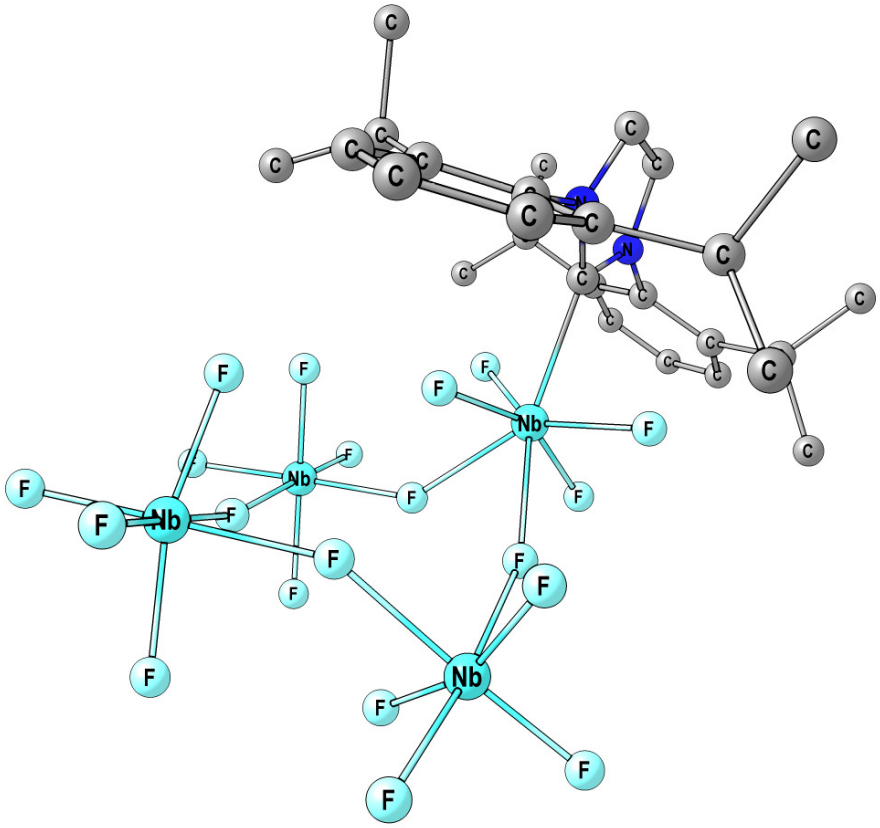

Table S9. Selected computed bond lengths (Å) and angles (°) for Nb_4F_{10}(Ipr).

Bond		**Angle**	
Nb–C	2.273	C–Nb–$F_{terminal}$	73.1 / 74.4 /
Nb–$F_{terminal}$	1.868 / 1.879 /	*(C-bonded fragment)*	86.7 / 119.4 /
(C-bonded fragment)	1.892 / 1.898	C–Nb–$F_{bridging}$	140.9 / 141.4
Nb–$F_{terminal}$	1.849 / 1.857 /	*(C-bonded fragment)*	
(non C-bonded fragment)	1.862 / 1.875 /	Nb–$F_{bridging}$–Nb	141.4 / 155.1
	1.850 / 1.851 /	*(C-bonded–non C-bonded fragments)*	
	1.866 / 1.870 /	Nb–$F_{bridging}$–Nb	149.8 / 163.1
	1.846 / 1.854 /	*(non C-bonded–non C-bonded fragments)*	
	1.864 / 1.876	$F_{bridging}$–Nb–$F_{bridging}$	69.8
Nb–$F_{bridging}$	2.203 / 2.239	*(C-bonded fragment)*	
(C-bonded fragment)		$F_{bridging}$–Nb–$F_{bridging}$	84.5 / 85.5 /
Nb–$F_{bridging}$	1.994 / 2.001 /	*(non C-bonded fragment)*	85.8
(non C-bonded fragment)	2.052 / 2.057 /		
	2.110 / 2.122 /		

Figure S10. ^{1}H NMR spectrum (C_7D_8, 298 K) of $NbF_5(Ipr)$, **2**.

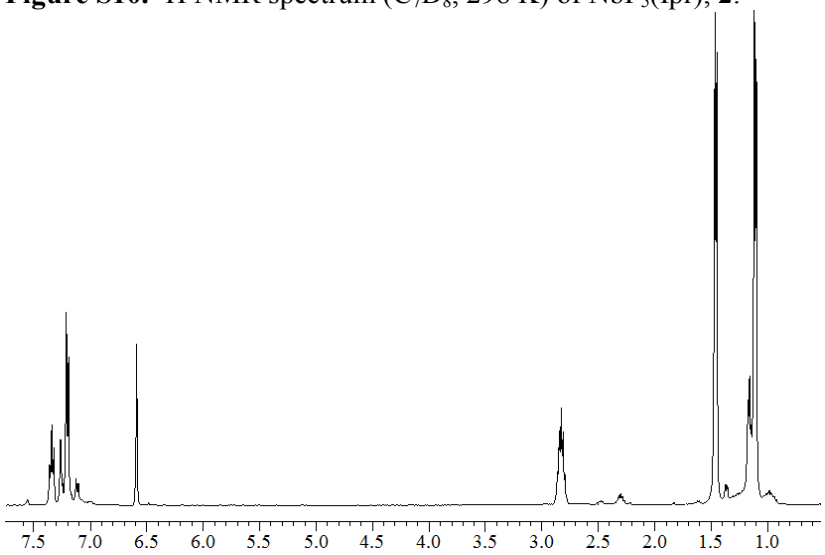

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum (C_7D_8, 298 K) of $NbF_5(Ipr)$, **2**.

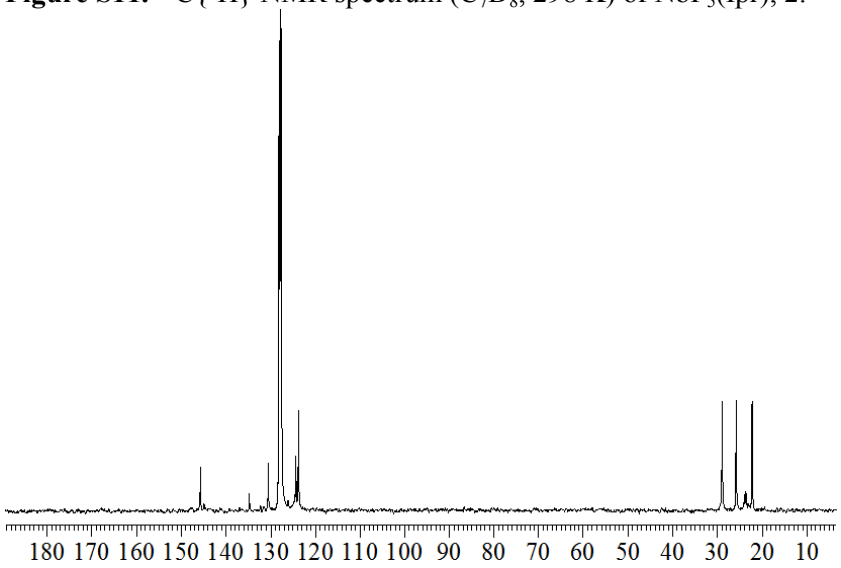

Figure S12. ^{93}Nb NMR spectrum (C_7D_8, 298 K) of $NbF_5(Ipr)$, **2**.

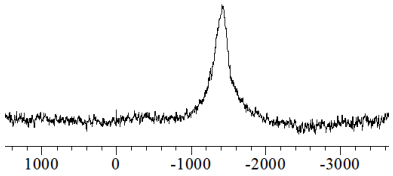

Figure S13. $^{19}F\{^{1}H\}$ NMR spectrum (C_7D_8, 298 K) of $NbF_5(Ipr)$, **2**.

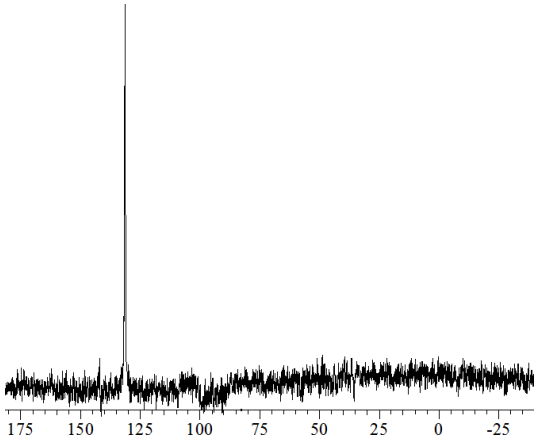

Figure S14. ^{1}H NMR spectrum (C_6D_6, 298 K) of $NbBr_5(Ipr)$, **3**.

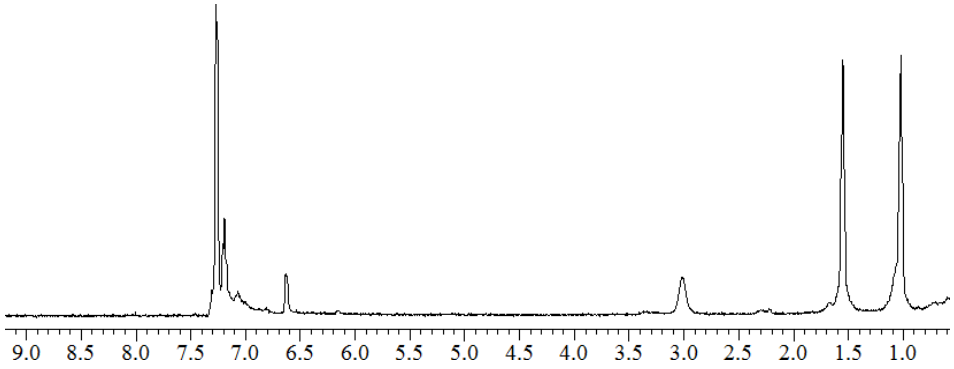

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 298 K) of $NbBr_5(Ipr)$, **3**.

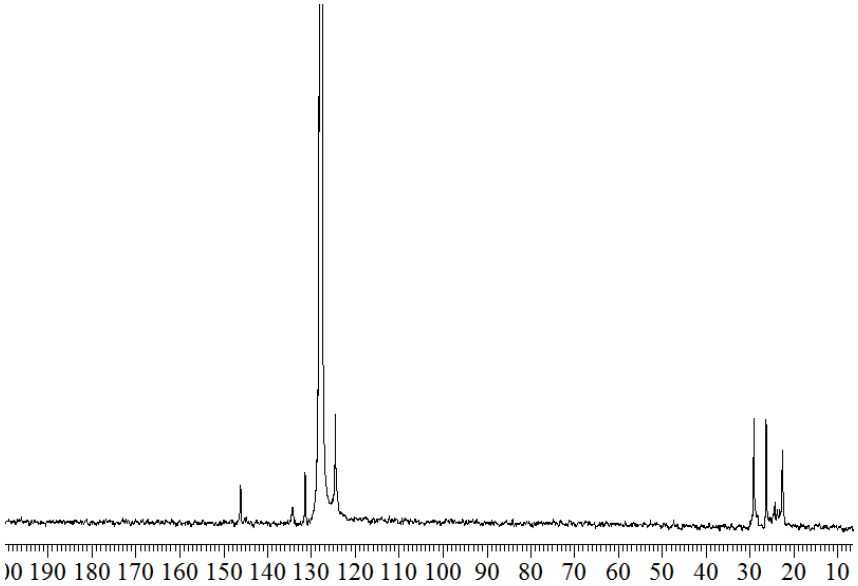

Figure S16. ^{1}H NMR spectrum (C_7D_8, 298 K) of $TaF_5(Ipr)$, **4**.

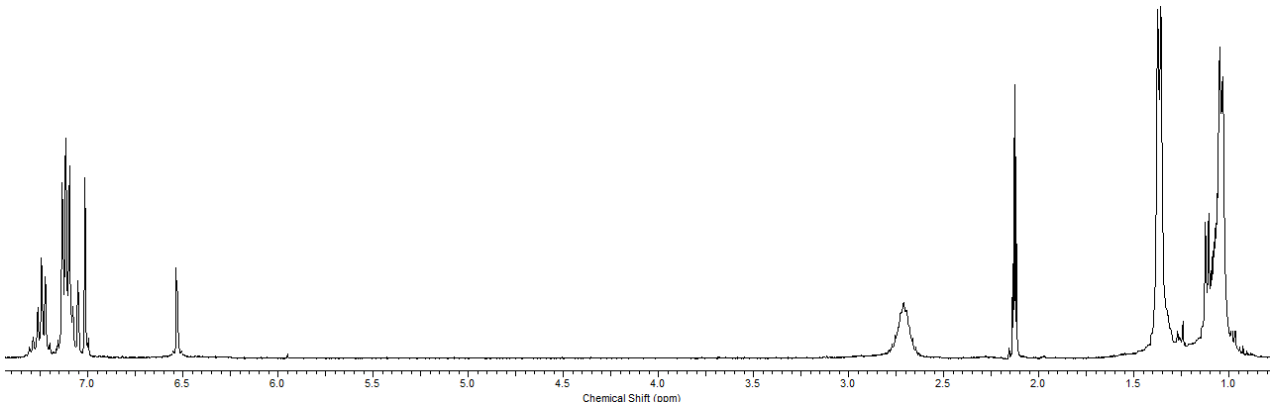

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum (C_7D_8, 298 K) of $TaF_5(Ipr)$, **4**.

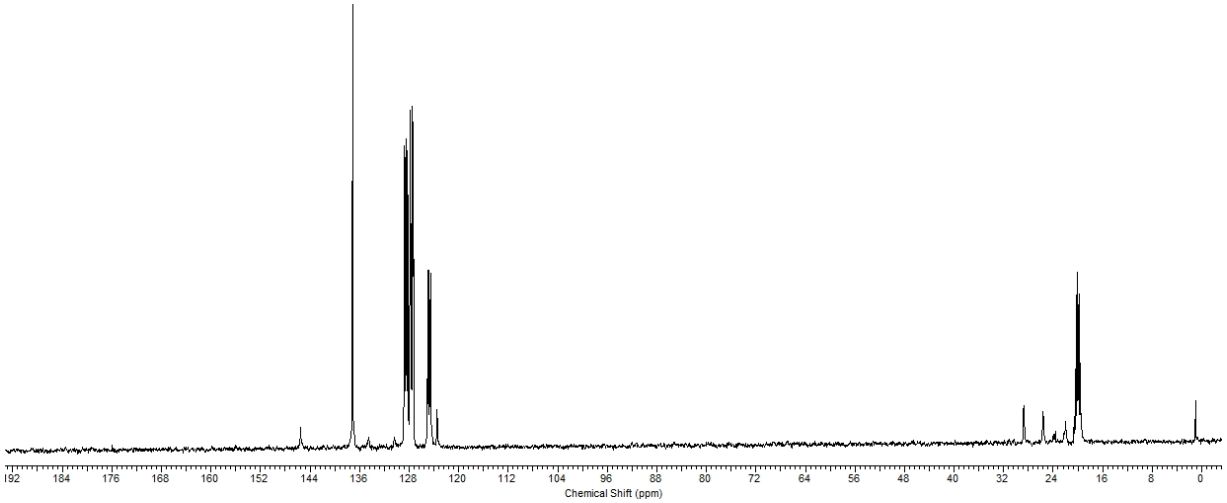

Figure S18. ^{19}F NMR spectrum (C_7D_8, 298 K) of $TaF_5(Ipr)$, **4**.

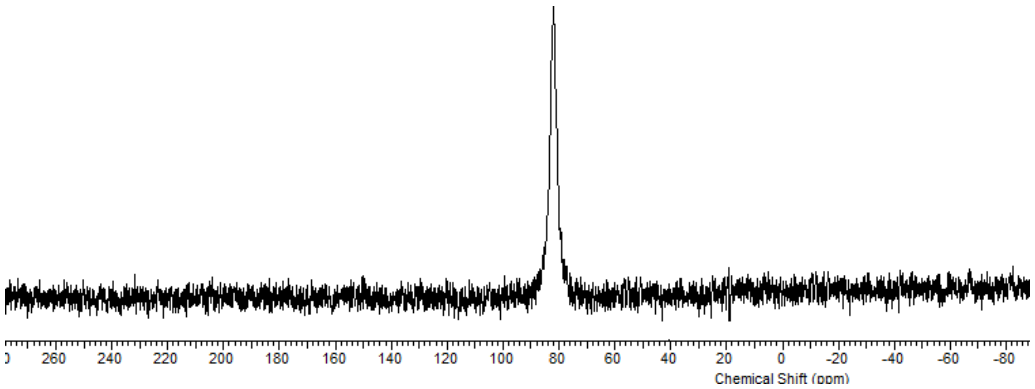

Figure S19. ^{1}H NMR spectrum (C_7D_8, 298 K) of $TaCl_5(Ipr)$, **5**.

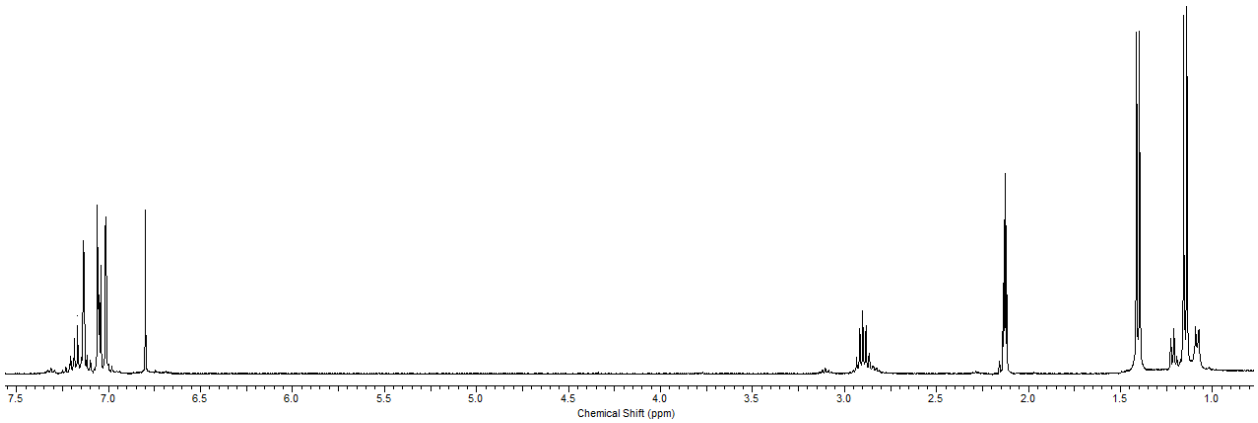

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum (C_7D_8, 298 K) of $TaCl_5(Ipr)$, **5**.

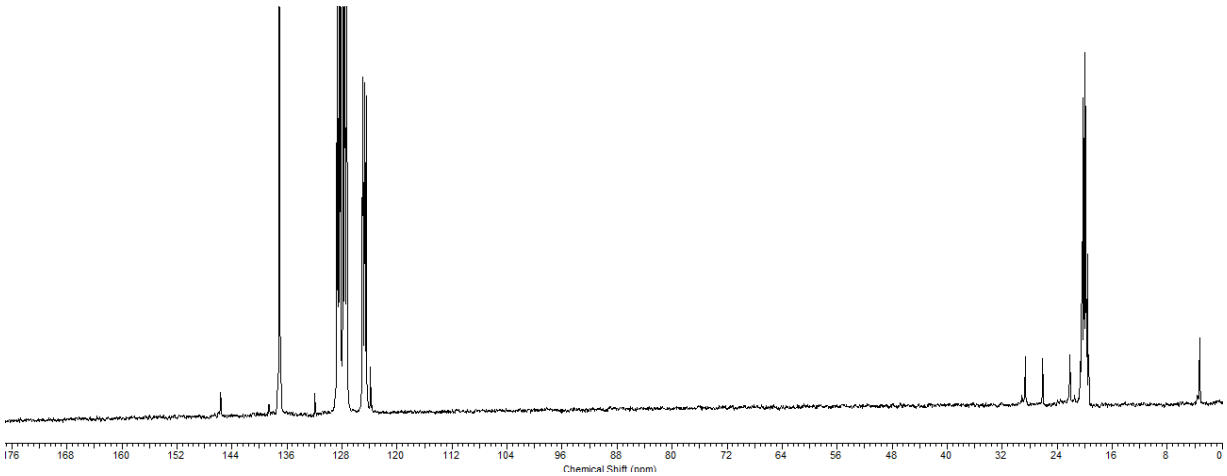

Figure S21. ^{1}H NMR spectrum (C_7D_8, 298 K) of $TaBr_5(Ipr)$, **6**.

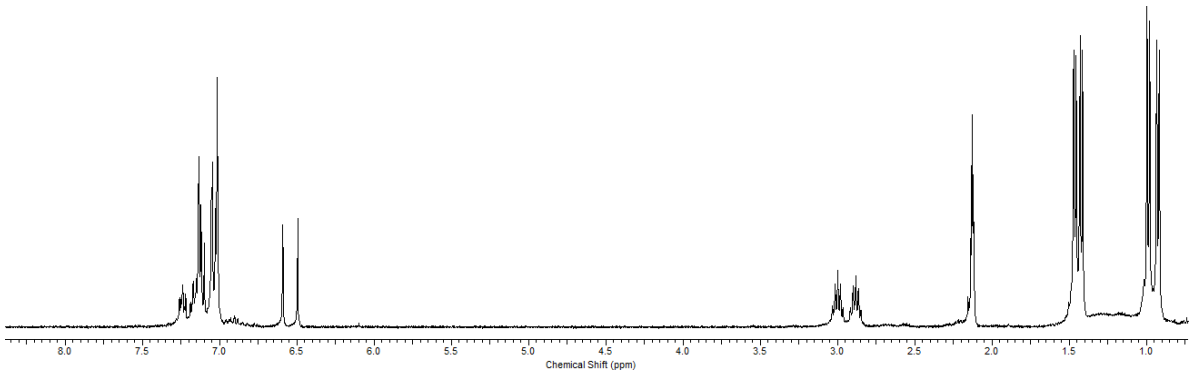

Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum (C_7D_8, 298 K) of $TaBr_5(Ipr)$, **6**.

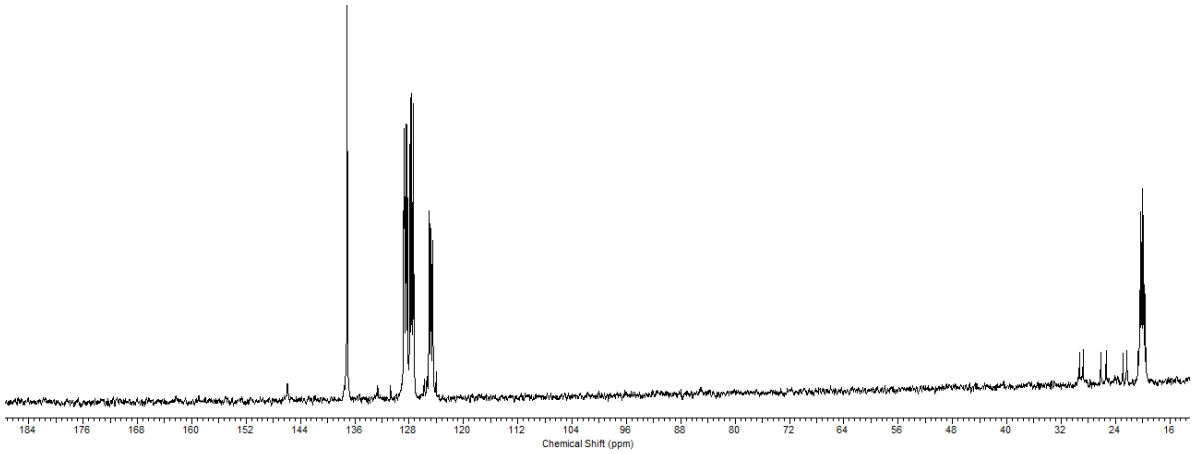

Figure S23. ^{1}H NMR spectrum (CD_2Cl_2, 298 K) of [IxylH][TaF_6], **7**.

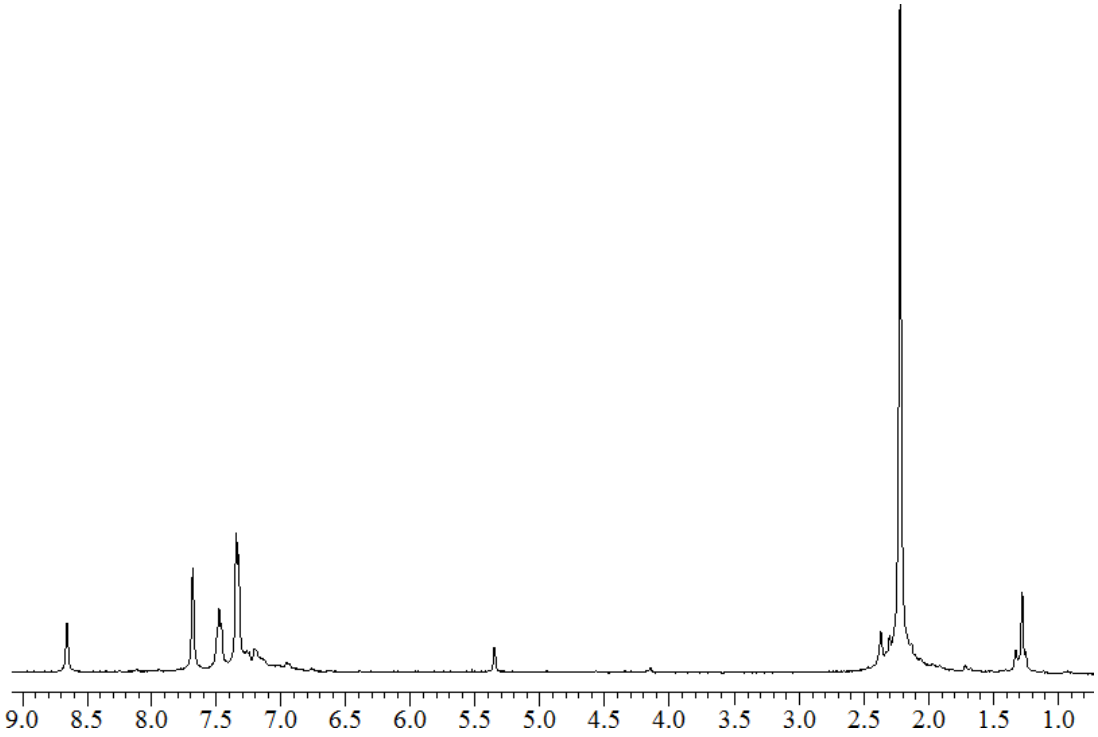

Figure S24. ^{19}F NMR spectrum (CD_2Cl_2, 298 K) of [IxylH][TaF_6], **7**.