Supporting information

Novel Family of Homoleptic Copper(I) Complexes Featuring Disubstituted Cyanamides: Combined Synthetic, Structural, and Theoretical Study

Anna A. Melekhova, Alexander S. Novikov, Taras L. Panikorovskii, Nadezhda A. Bokach,* and Vadim Yu. Kukushkin*

Saint Petersburg State University, 7/9 Universitetskaya Nab., 199034 Saint Petersburg, Russian Federation;

E-mails: n.bokach@spbu.ru and v.kukushkin@spbu.ru

Table of Contents

$[Cu(NCNMe_2)_4](BF_4)$ (**1**)

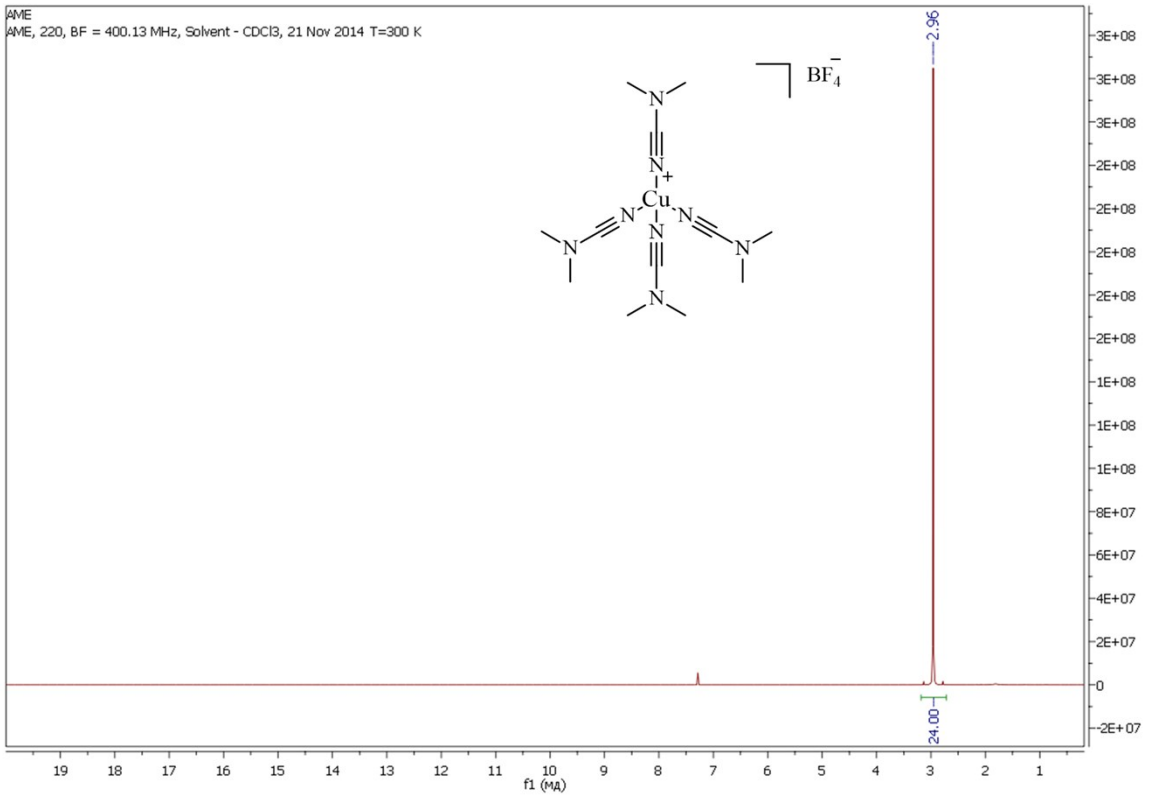


Figure S1. ^{1}H NMR spectrum of **1**, $CDCl_3$, ambient temperature.

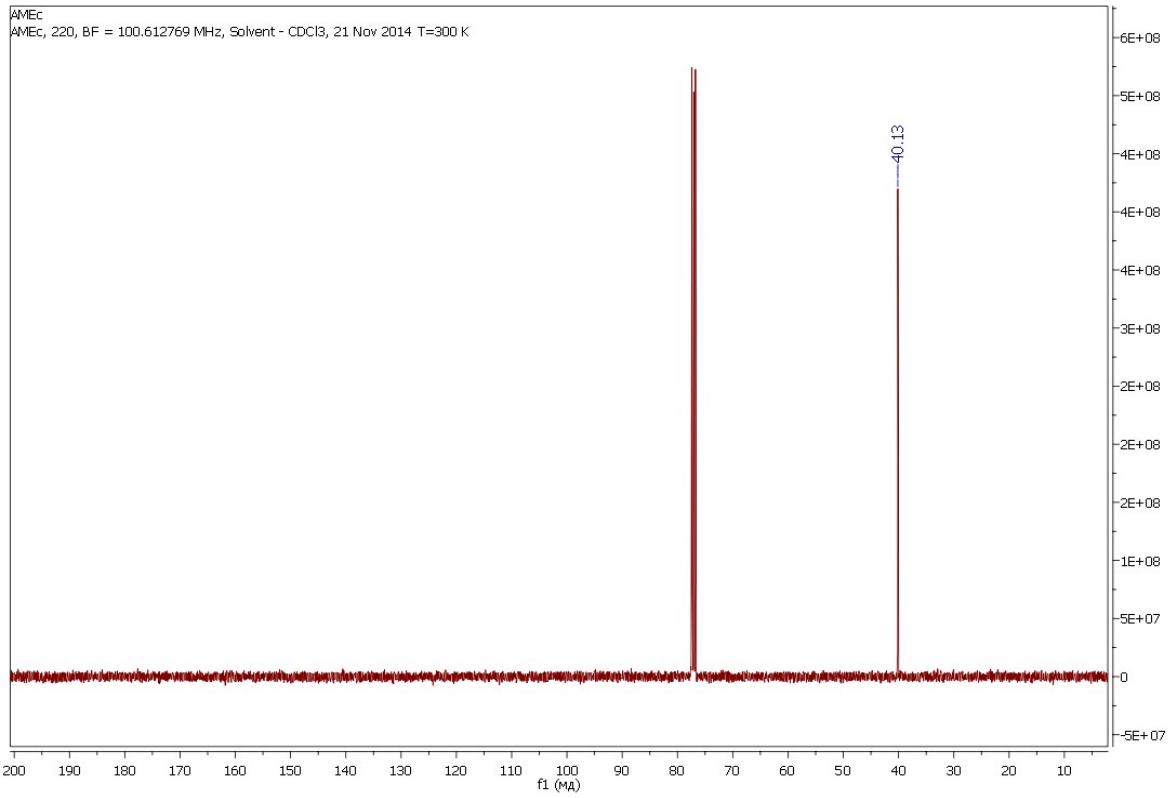


Figure S2. ^{13}C NMR spectrum of **1**, $CDCl_3$, ambient temperature.

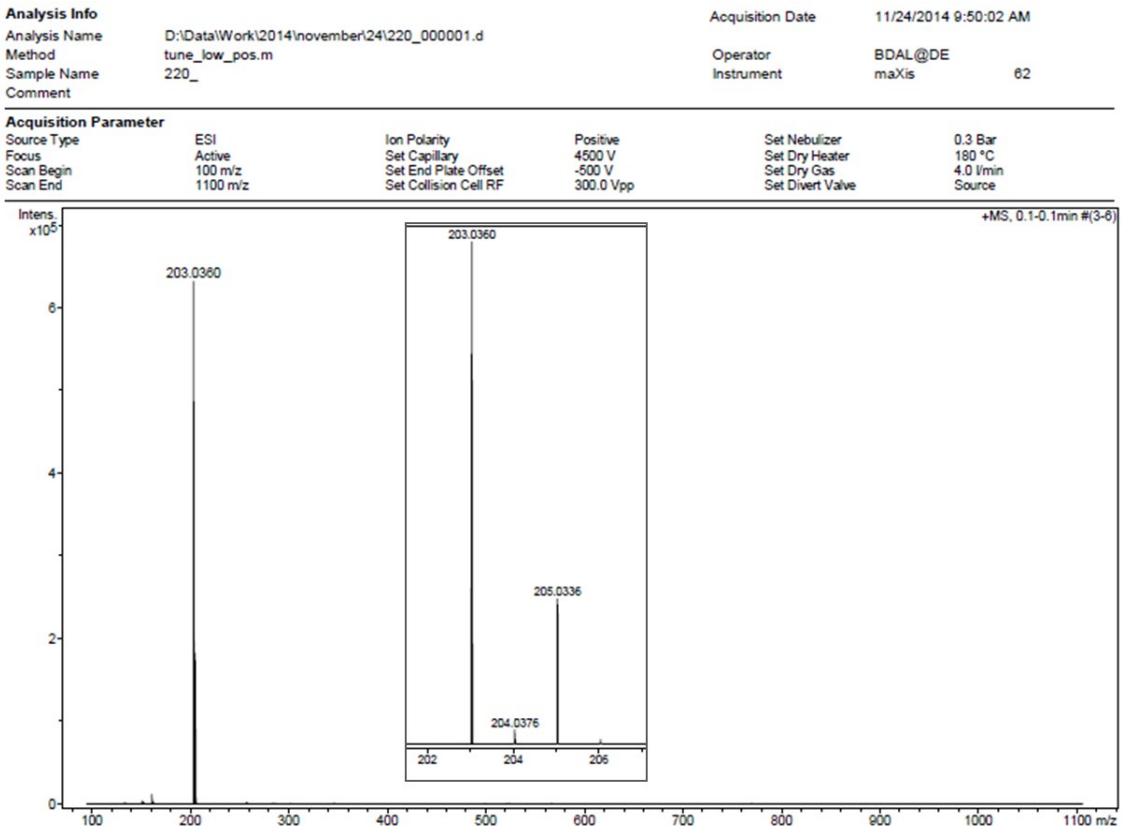


Figure S3. The HR ESI$^+$ mass spectrum of **1**.

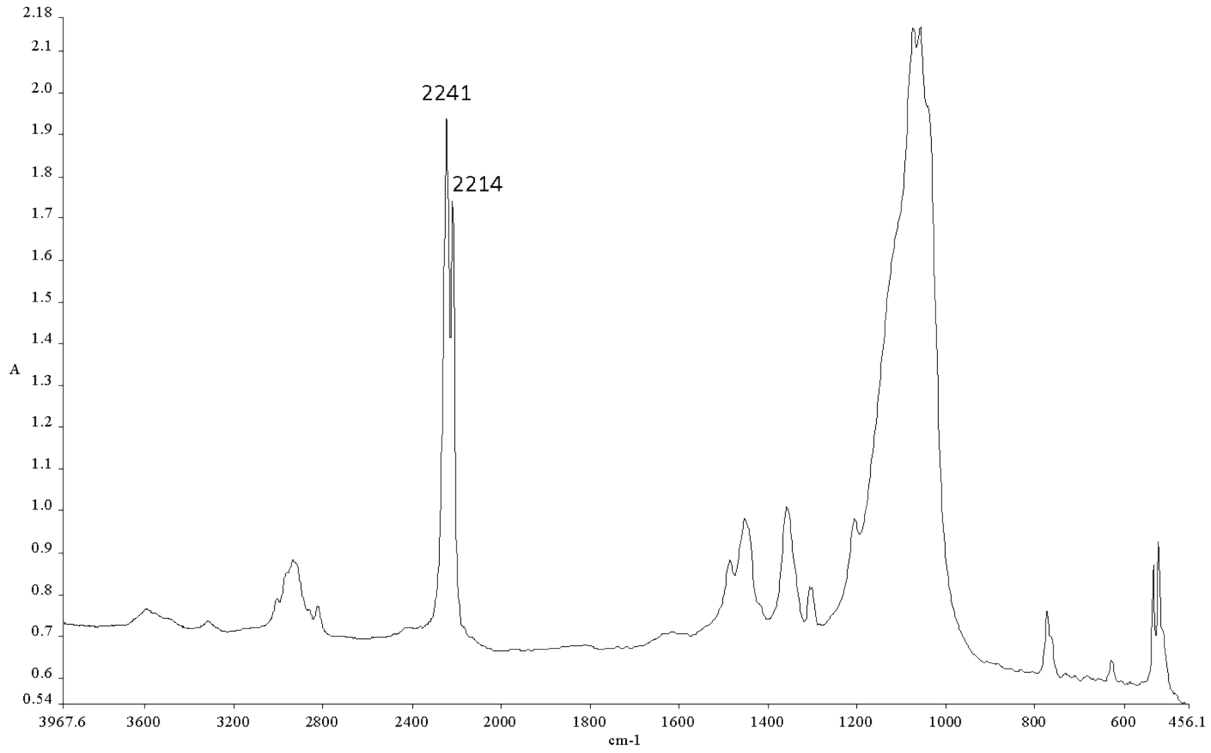


Figure S4. The IR spectrum of **1**.

$[Cu(NCNEt_2)_4]BF_4$ (**2**)

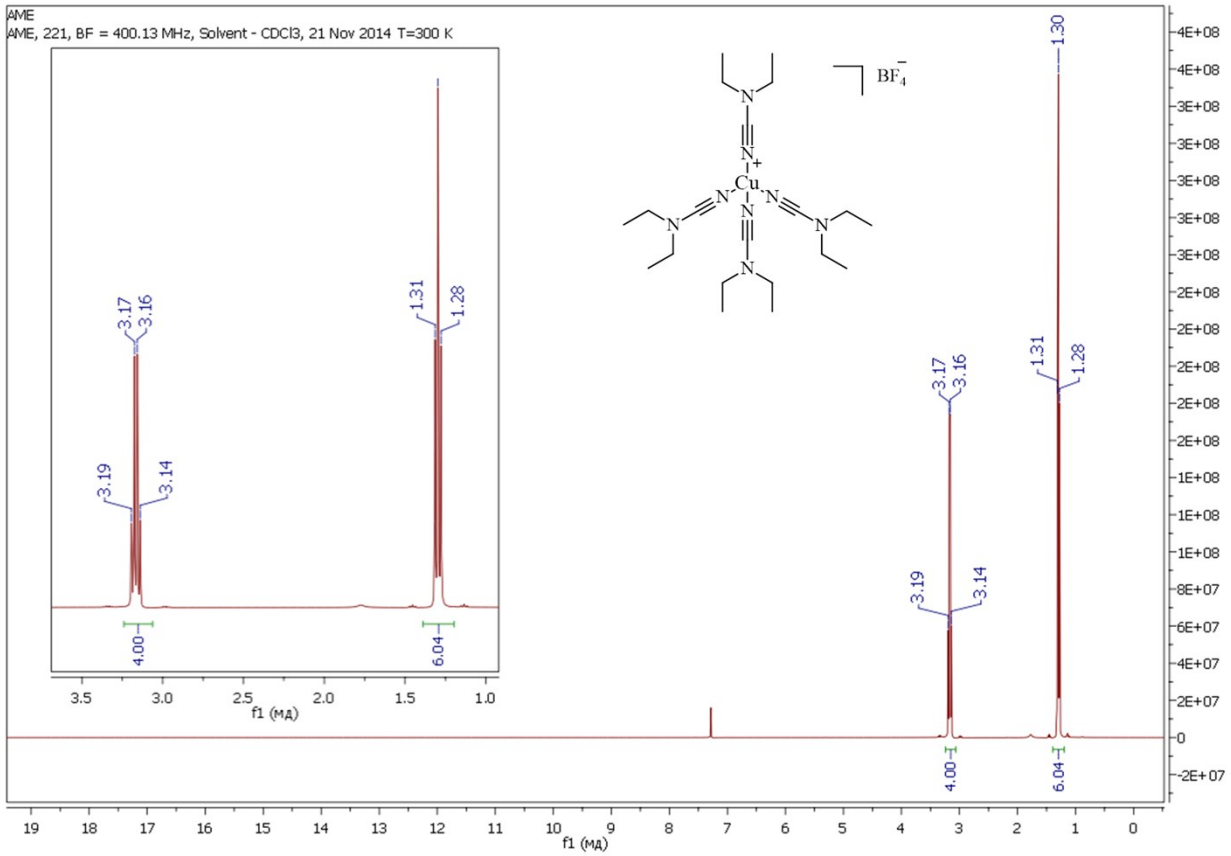


Figure S5. ^{1}H NMR spectrum of **2**, $CDCl_3$, ambient temperature.

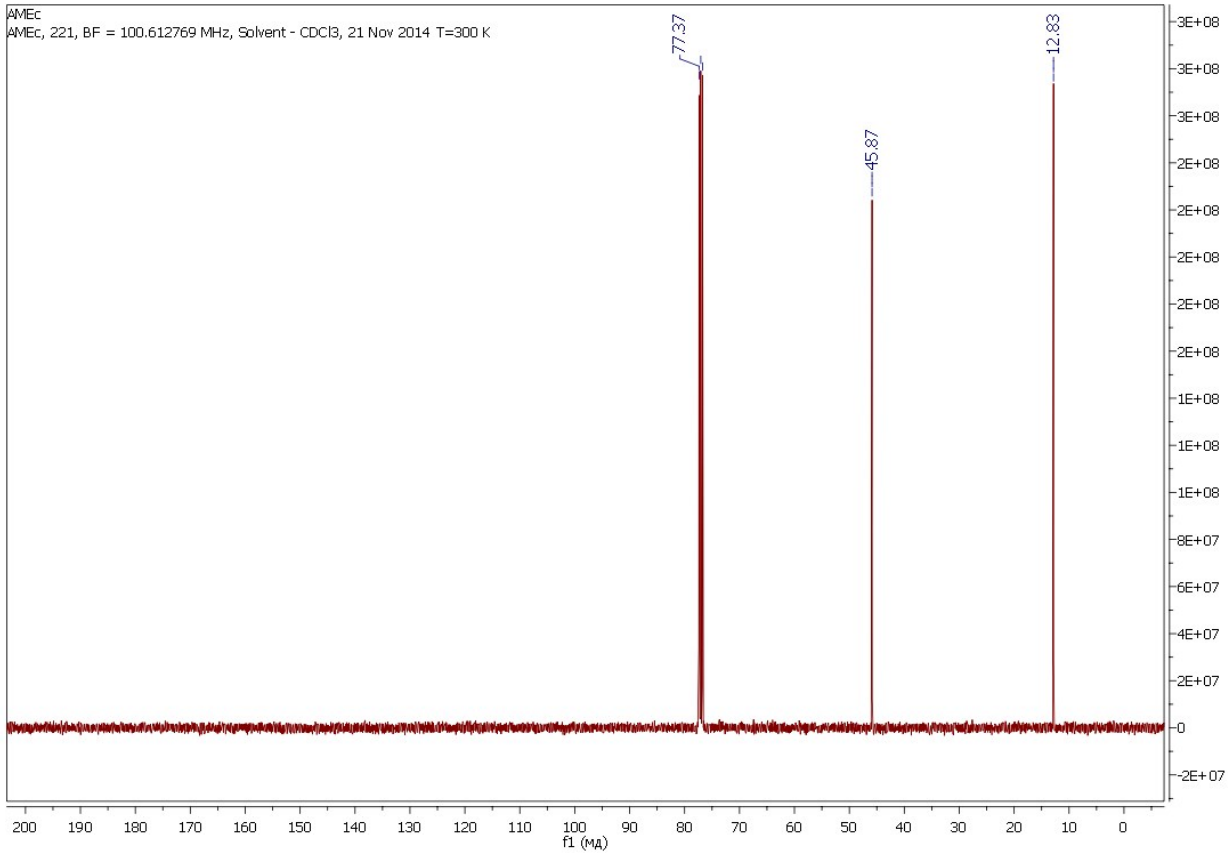


Figure S6. ^{13}C NMR spectrum of **2**, $CDCl_3$, ambient temperature.

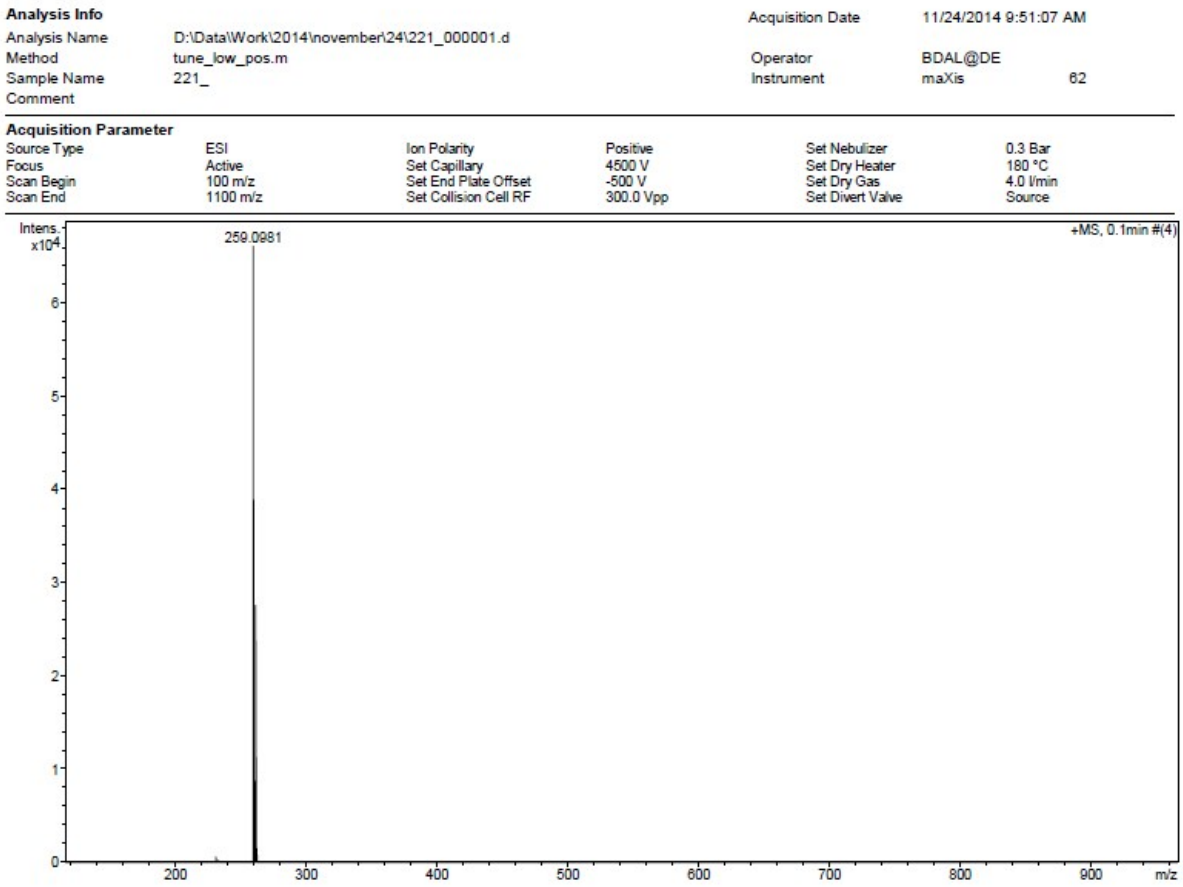


Figure S7. The HR ESI$^+$ mass spectrum of **2.**

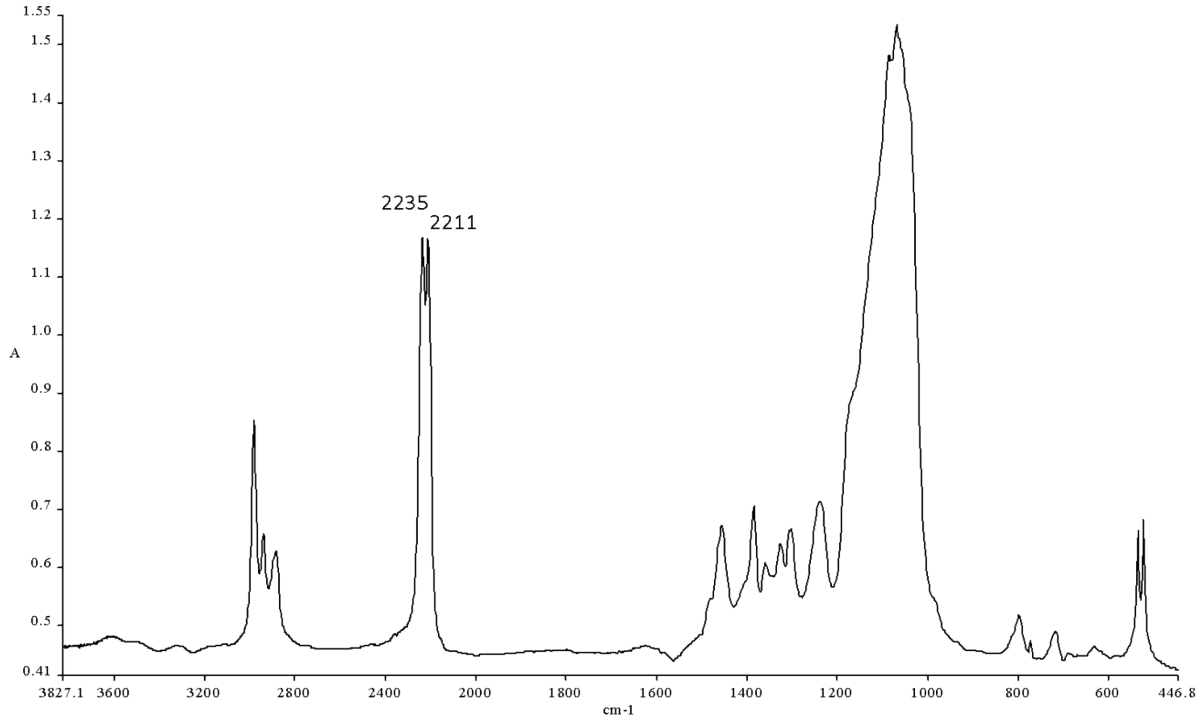


Figure S8. The IR spectrum of **2**.

$[Cu(NCNC_5H_{10})_4]BF_4$ (**3**)

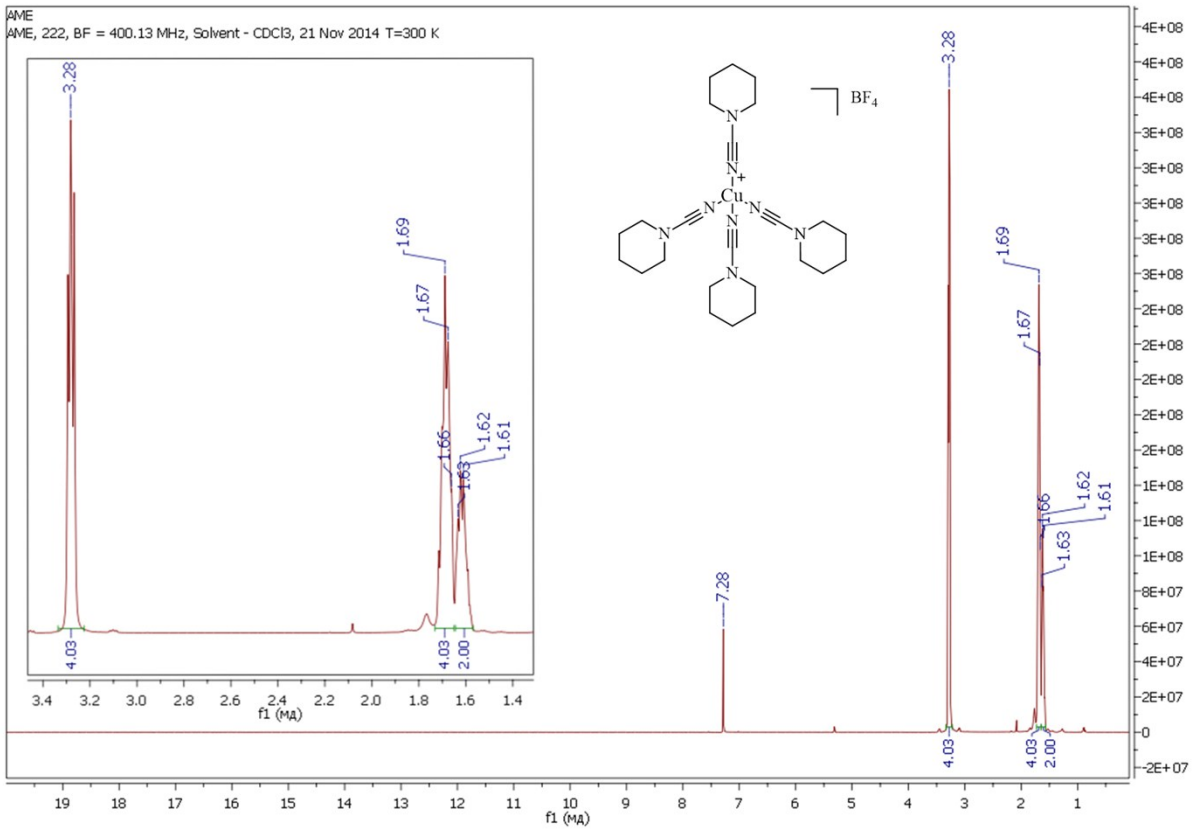


Figure S9. ^{1}H NMR spectrum of **3**, $CDCl_3$, ambient temperature

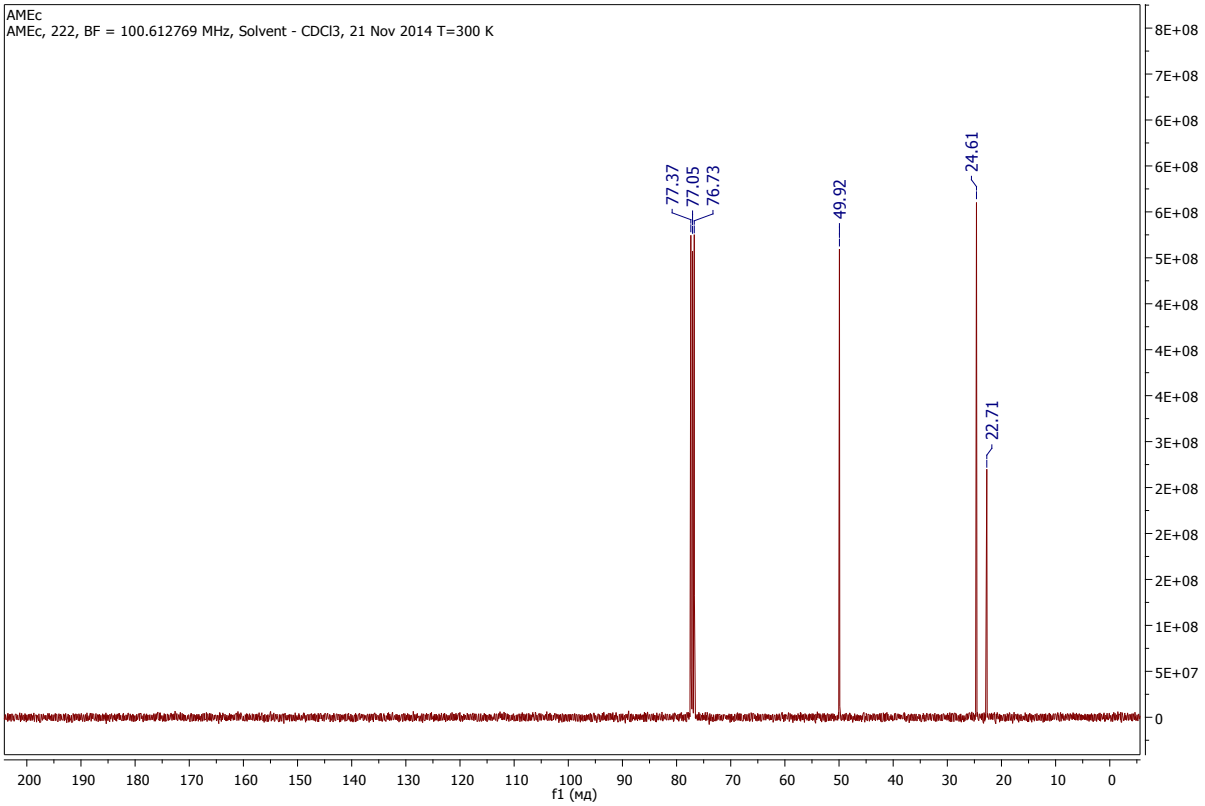


Figure S10. ^{13}C NMR spectrum of **3**, $CDCl_3$, ambient temperature.

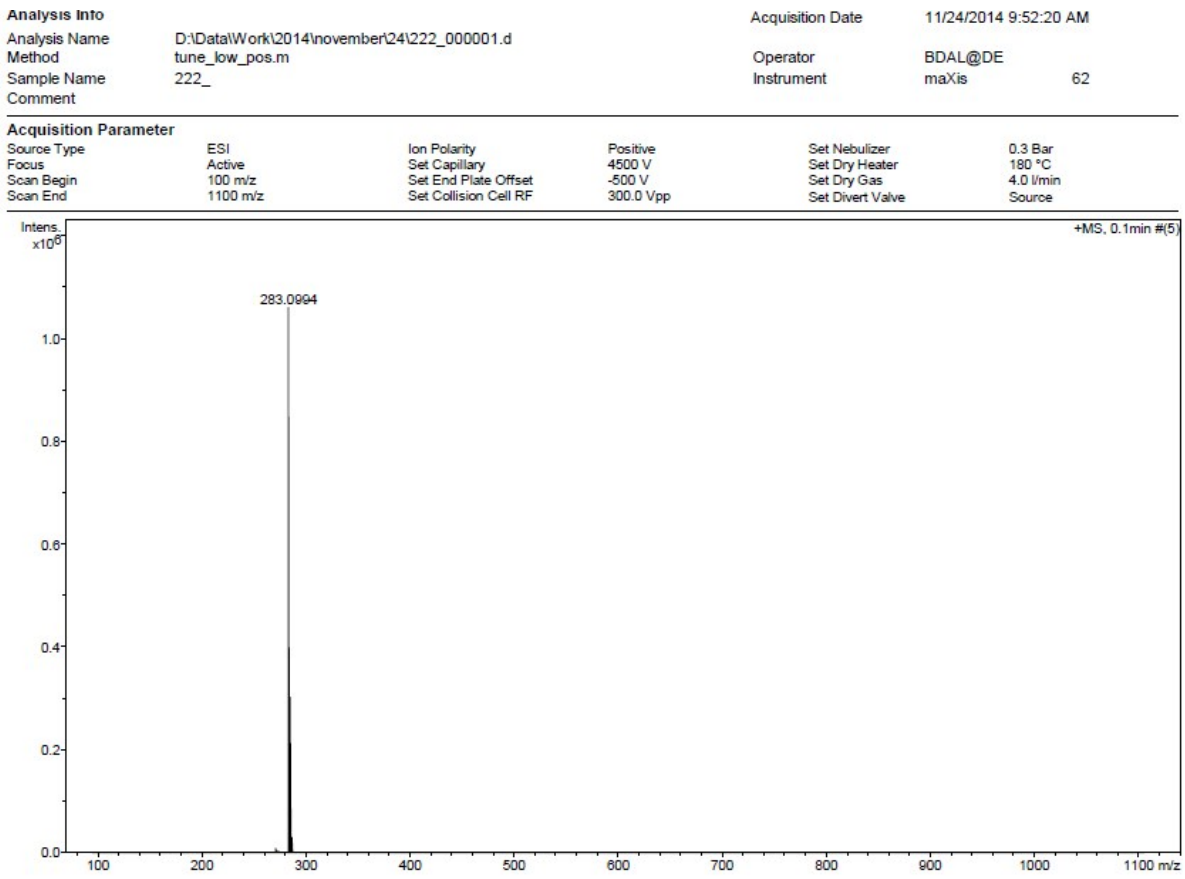


Figure S11. The HR ESI$^+$ mass spectrum of **3**.

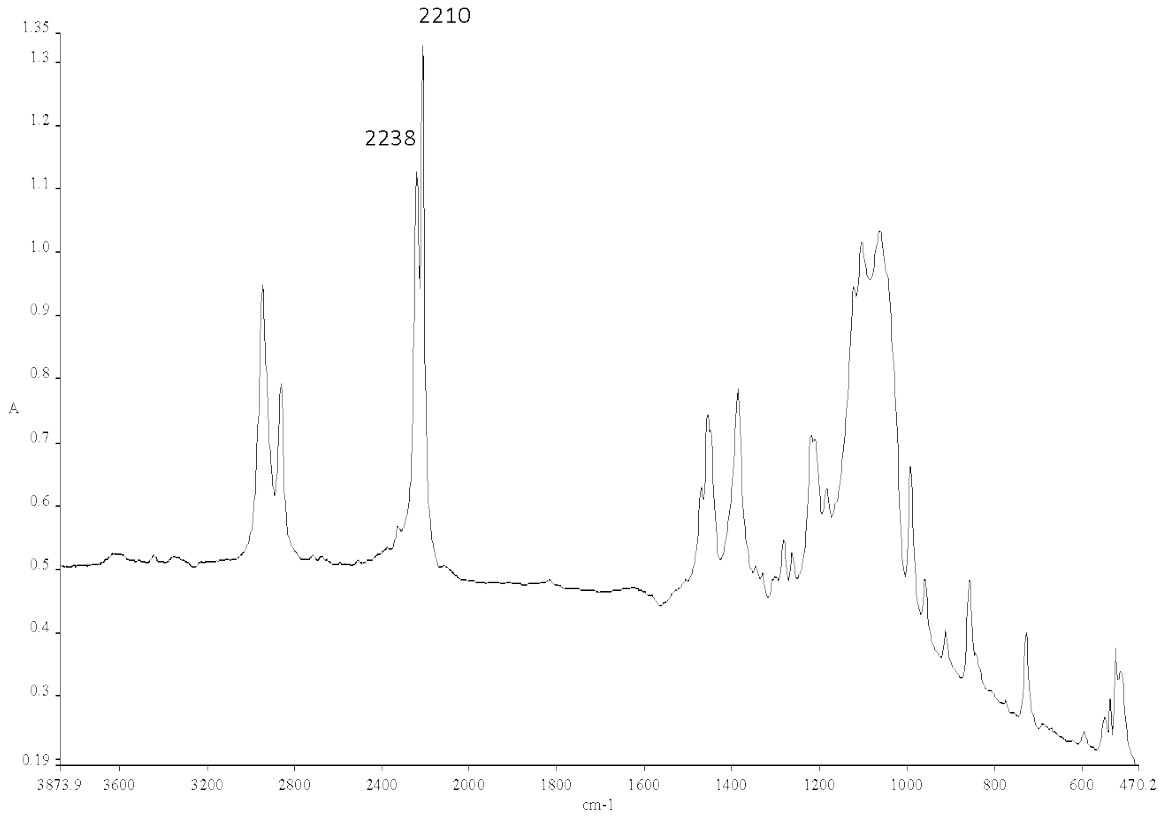


Figure S12. The IR spectrum of **3**.

$[Cu(NCNC_4H_8O)_4]BF_4$ (**4**)

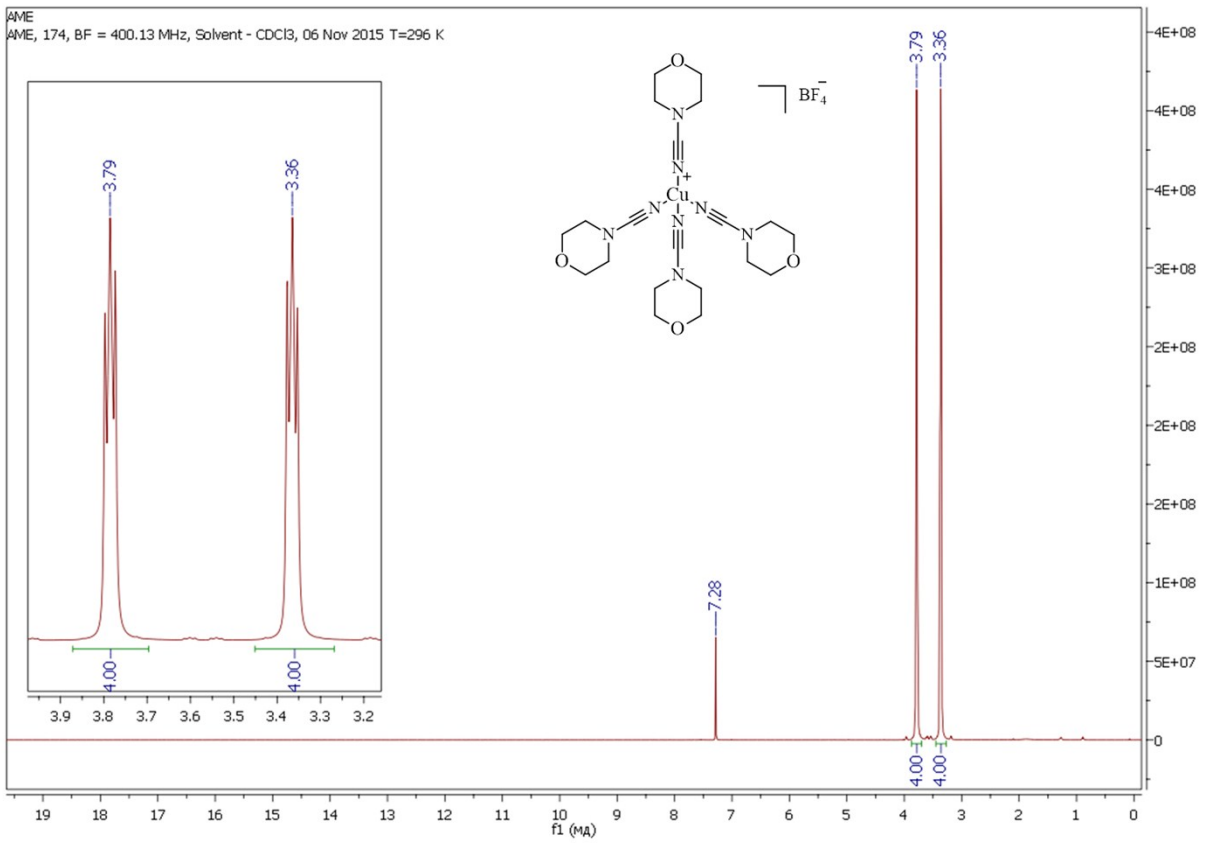


Figure S13. ^{1}H NMR spectrum of **4**, $CDCl_3$, ambient temperature.

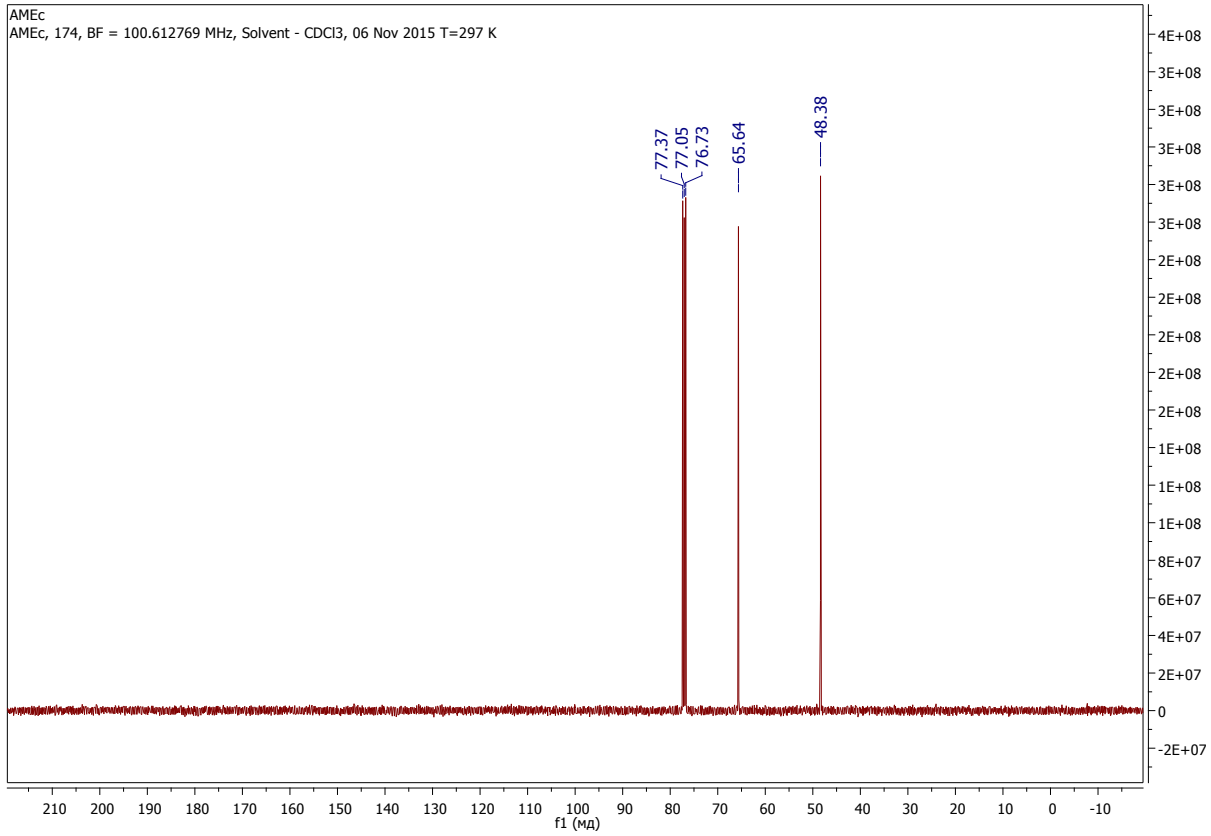


Figure S14. ^{13}C NMR spectrum of **4**, $CDCl_3$, ambient temperature.

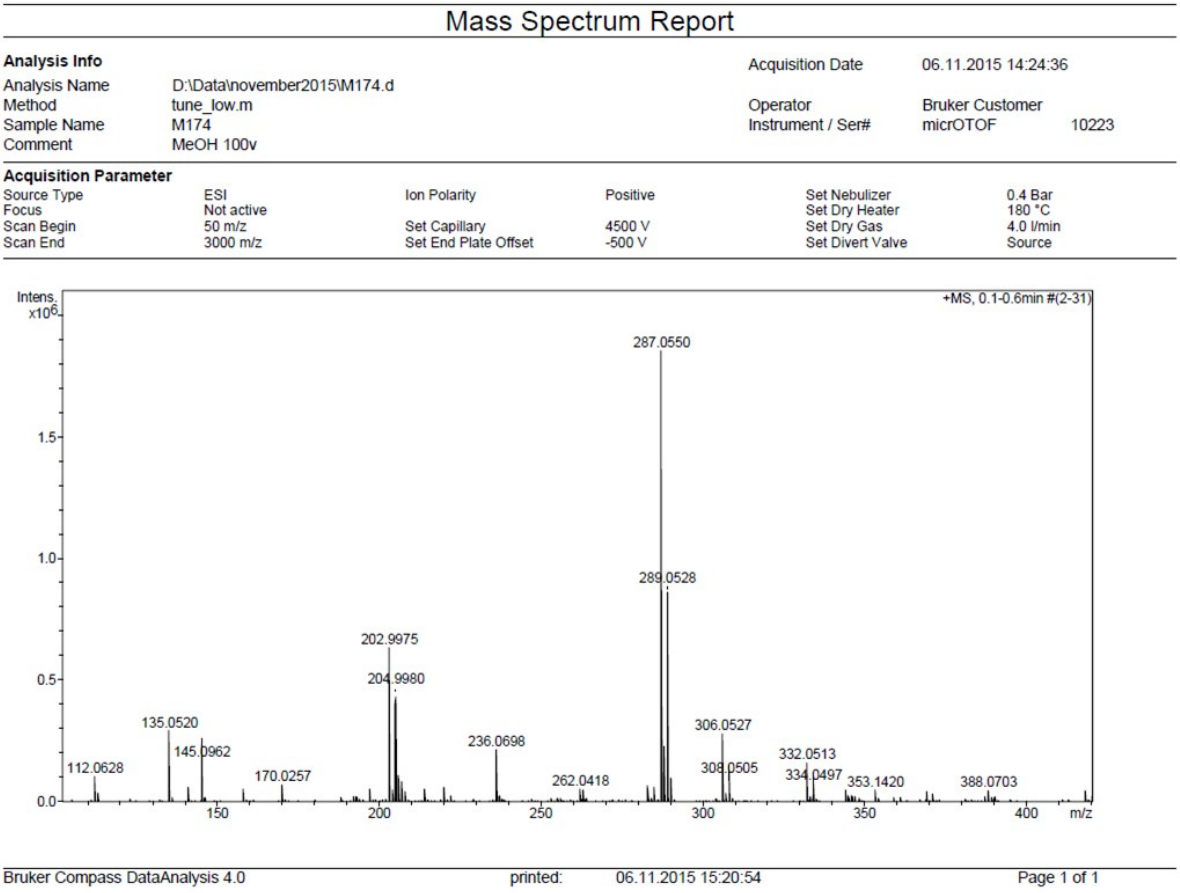


Figure S15. The HR ESI$^+$ mass spectrum of **4**.

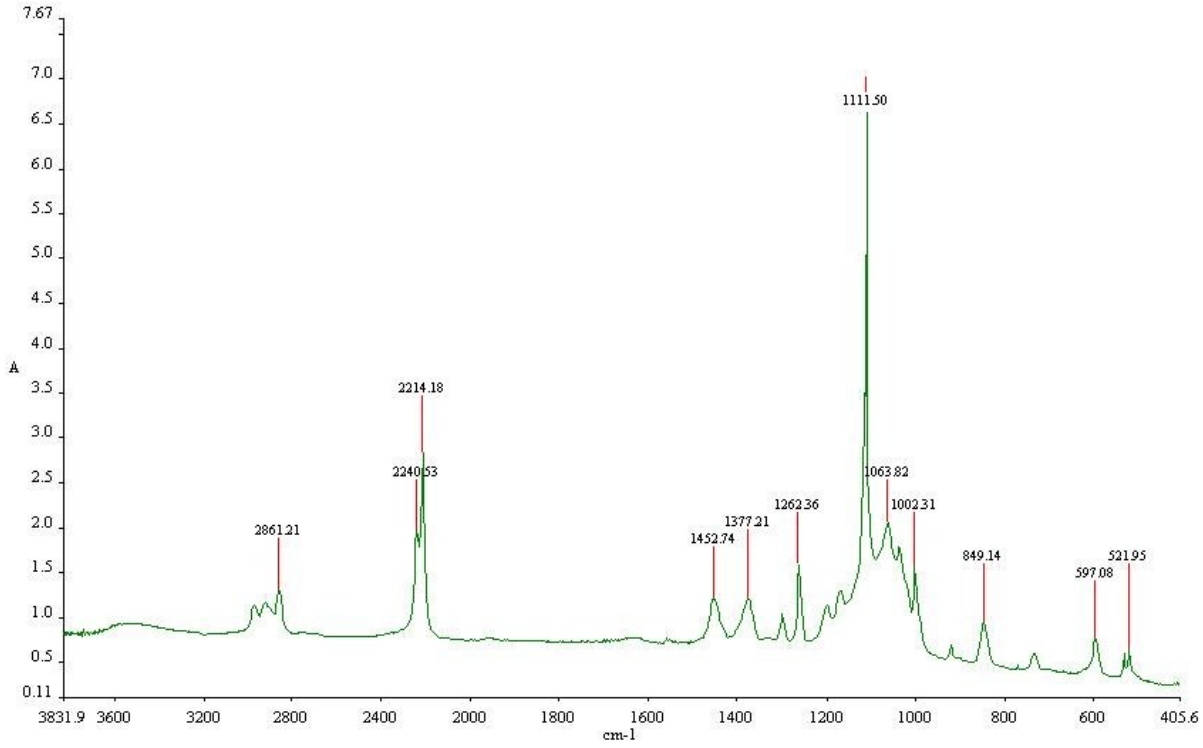


Figure S16. The IR spectrum of **4**.

$[Cu(NCNC_4H_8)_4]BF_4$ (**5**)

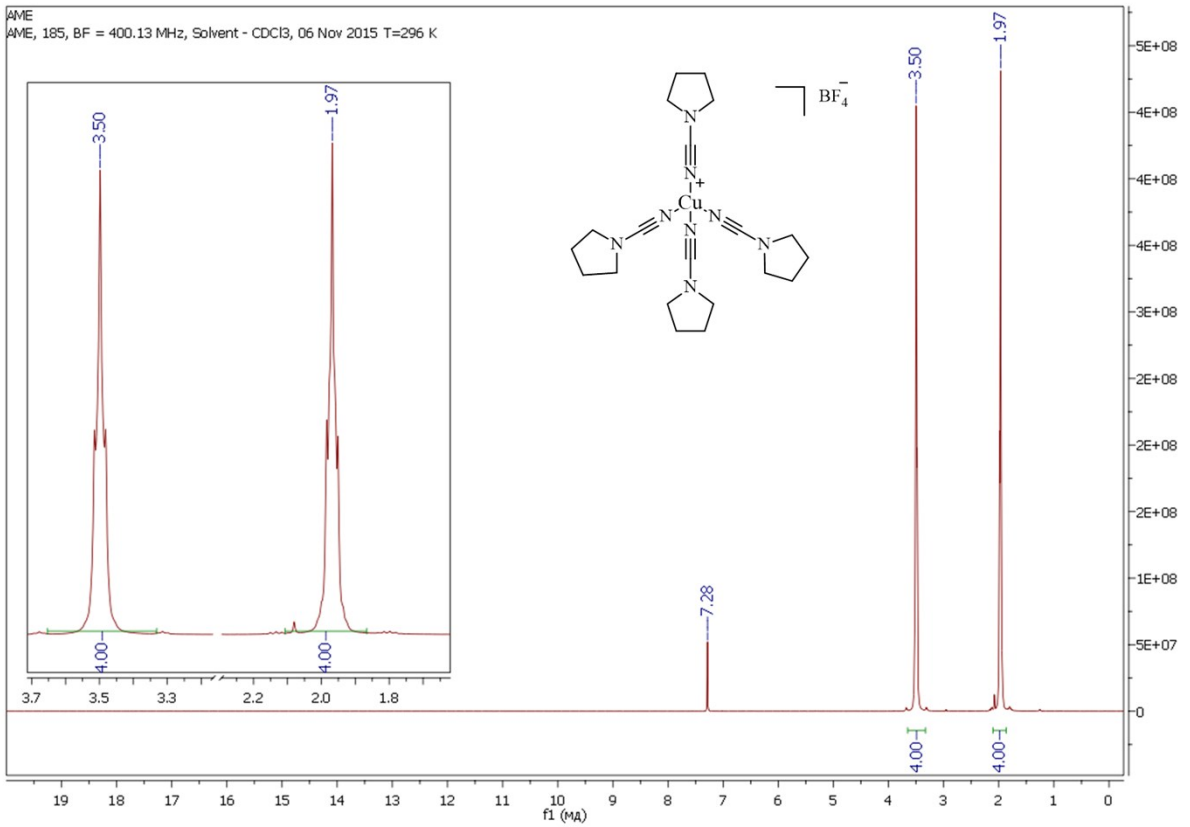


Figure S17. ^{1}H NMR spectrum of **5**, $CDCl_3$, ambient temperature.

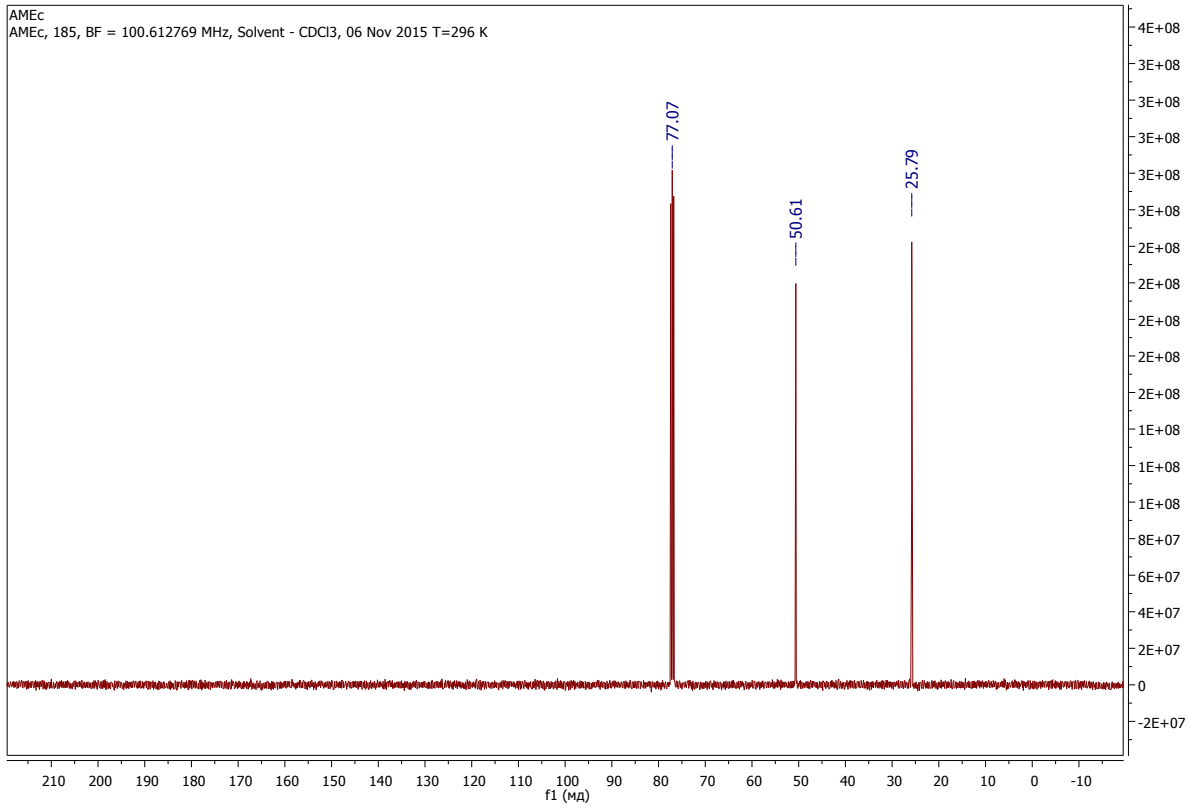


Figure S18. ^{13}C NMR spectrum of **5**, $CDCl_3$, ambient temperature.

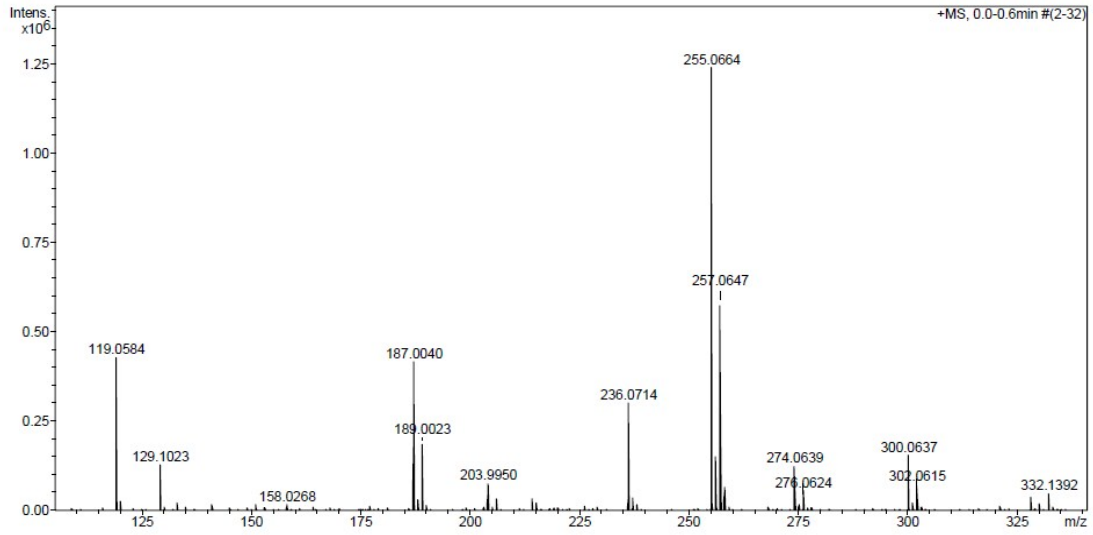
Mass Spectrum Report

Analysis Info

Analysis Name	D:\Data\november2015\M185.d	Acquisition Date	06.11.2015 15:09:32
Method	tune_low.m	Operator	Bruker Customer
Sample Name	M185	Instrument / Ser#	micrOTOF 10223
Comment	MeOH 100v		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



Bruker Compass DataAnalysis 4.0 printed: 06.11.2015 15:12:10 Page 1 of 1

Figure S19. The HR ESI$^+$ mass spectra of **5**.

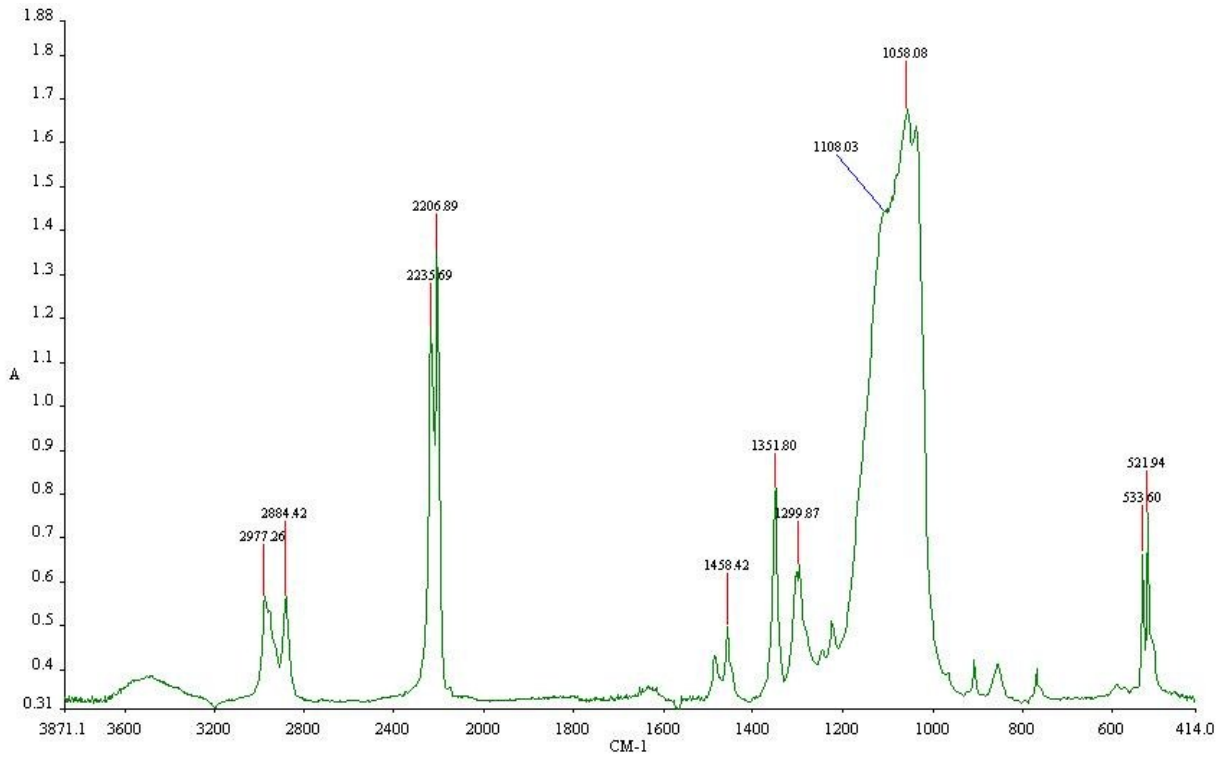


Figure S20. The IR spectrum of **5**.

[Cu(NCNC$_3$H$_6$C$_6$H$_4$)$_4$](BF$_4$) (NCNC$_3$H$_6$C$_6$H$_4$ – 3,4-dihydroisoquinoline-2(1H) carbonitrile)(**6**)

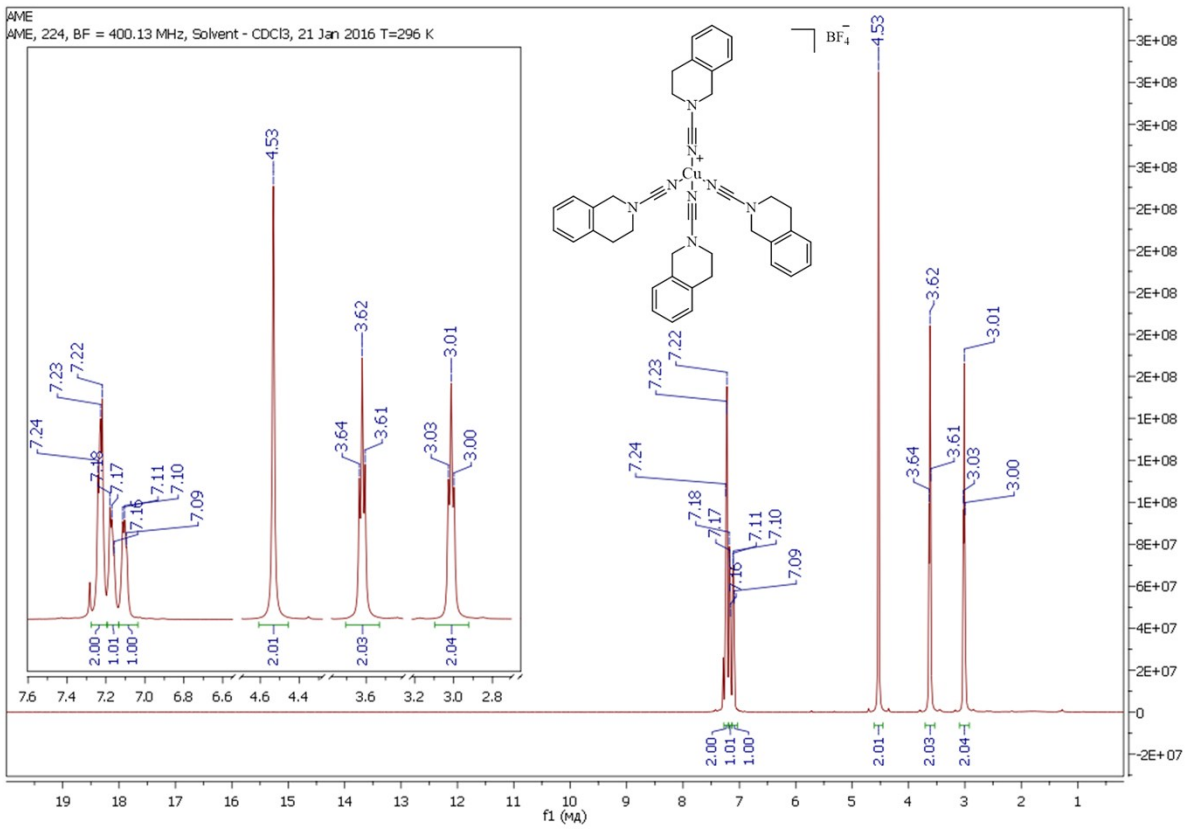


Figure S21. ^{1}H NMR spectrum of **6**, $CDCl_3$, ambient temperature.

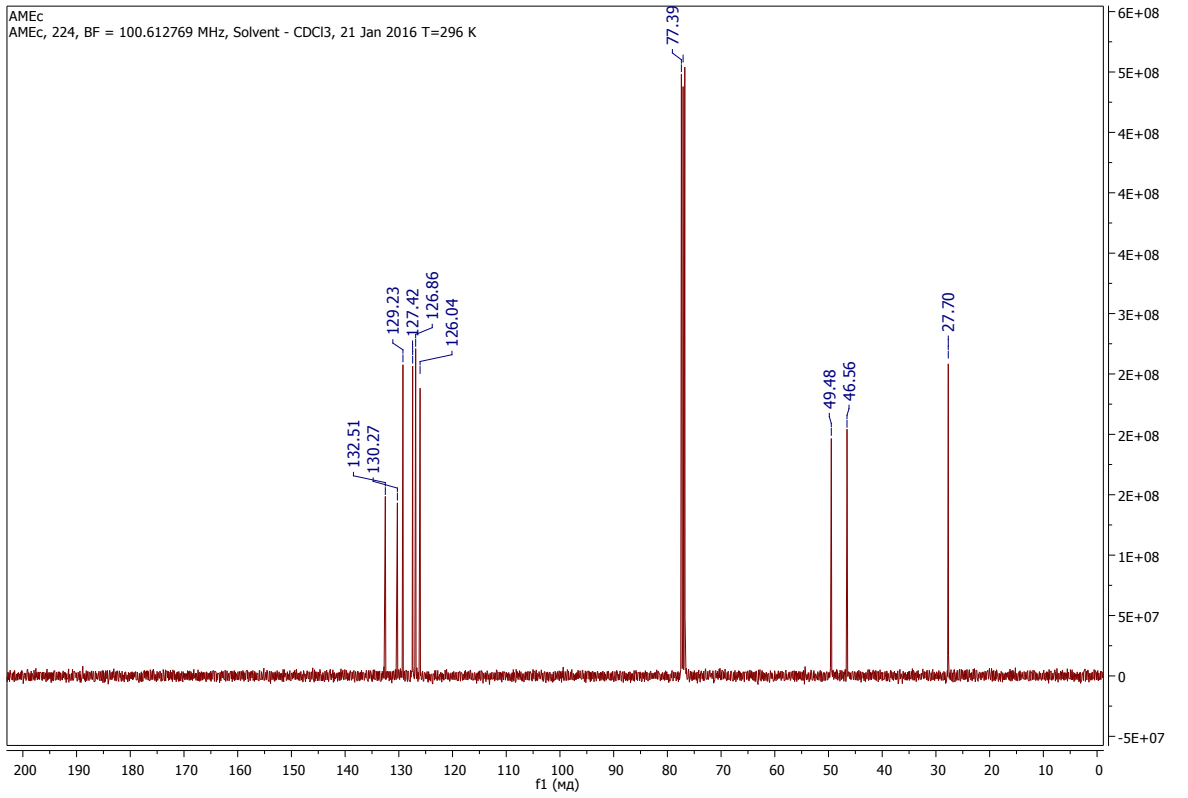


Figure S22. ^{13}C NMR spectrum of **6**, $CDCl_3$, ambient temperature.

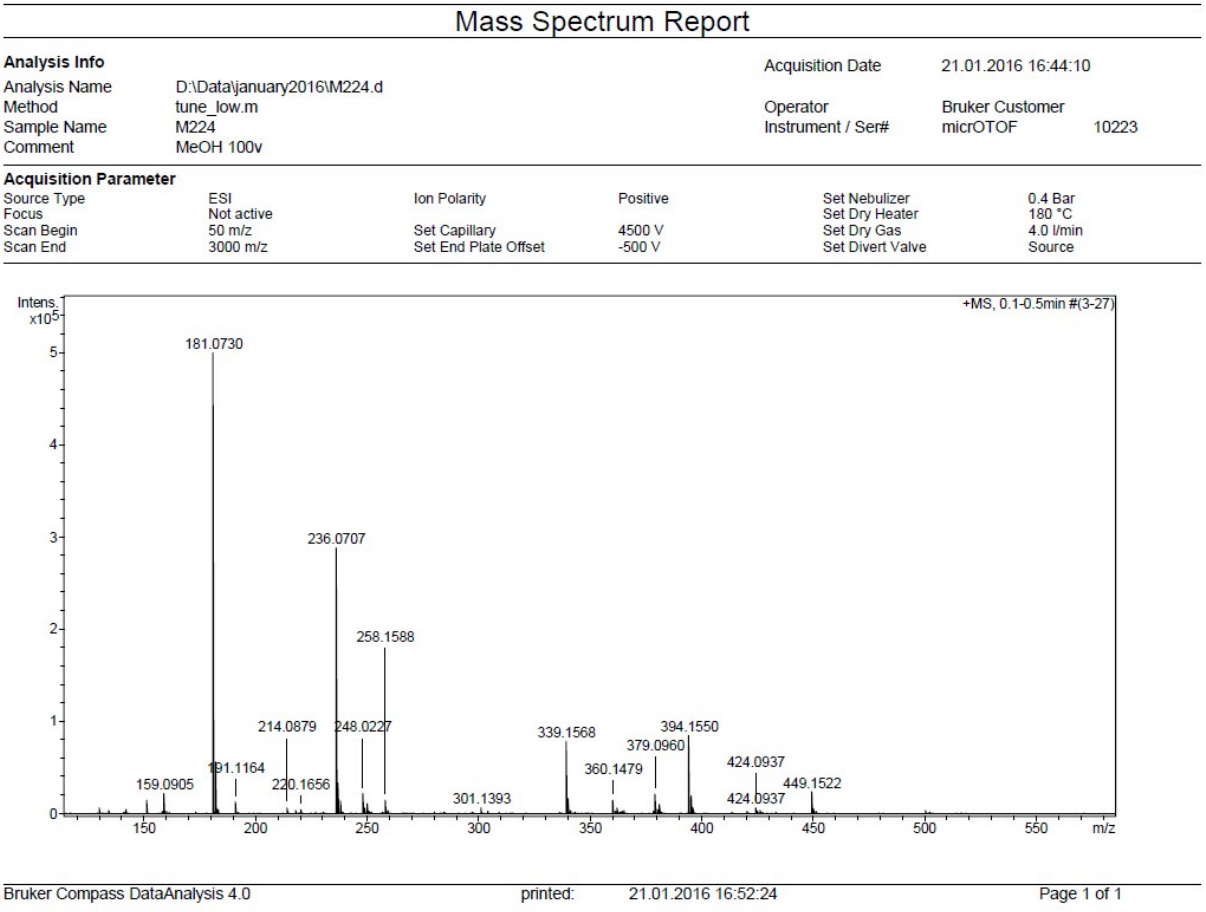


Figure S23. The HR ESI$^+$ mass spectrum of **6**.

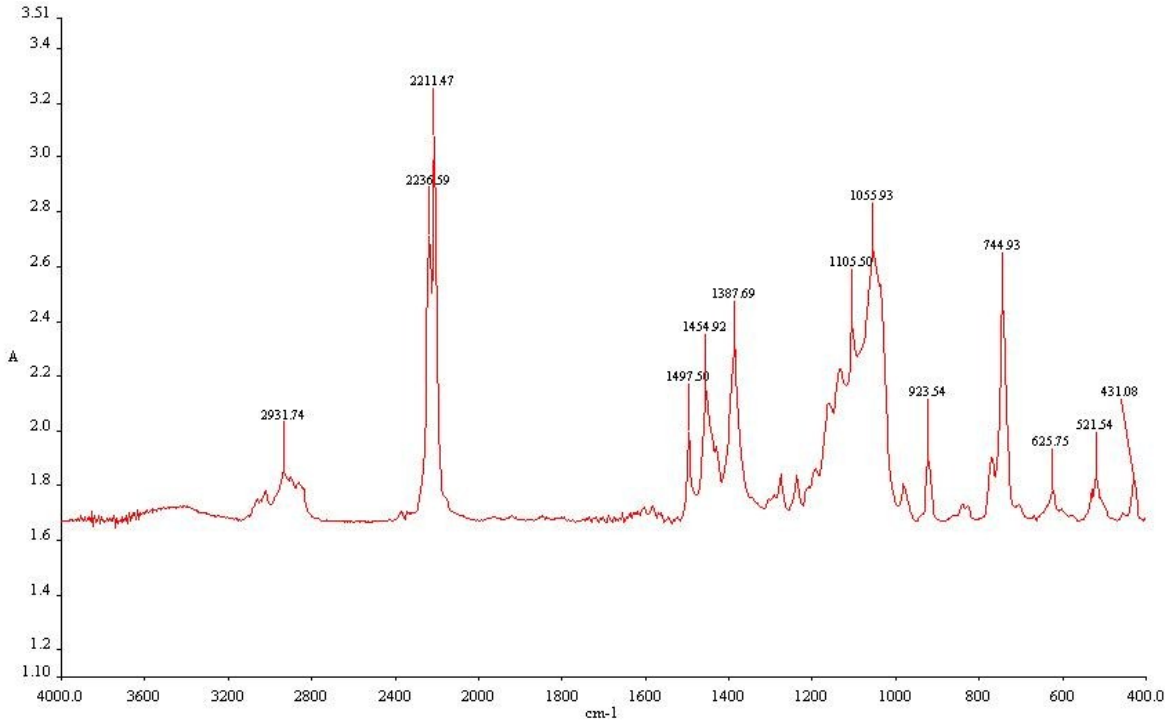


Figure S24. The IR spectrum of **6**.

[Cu(NCN{$(CH_2Ph)_2$}$_4$](BF_4) (**7**).

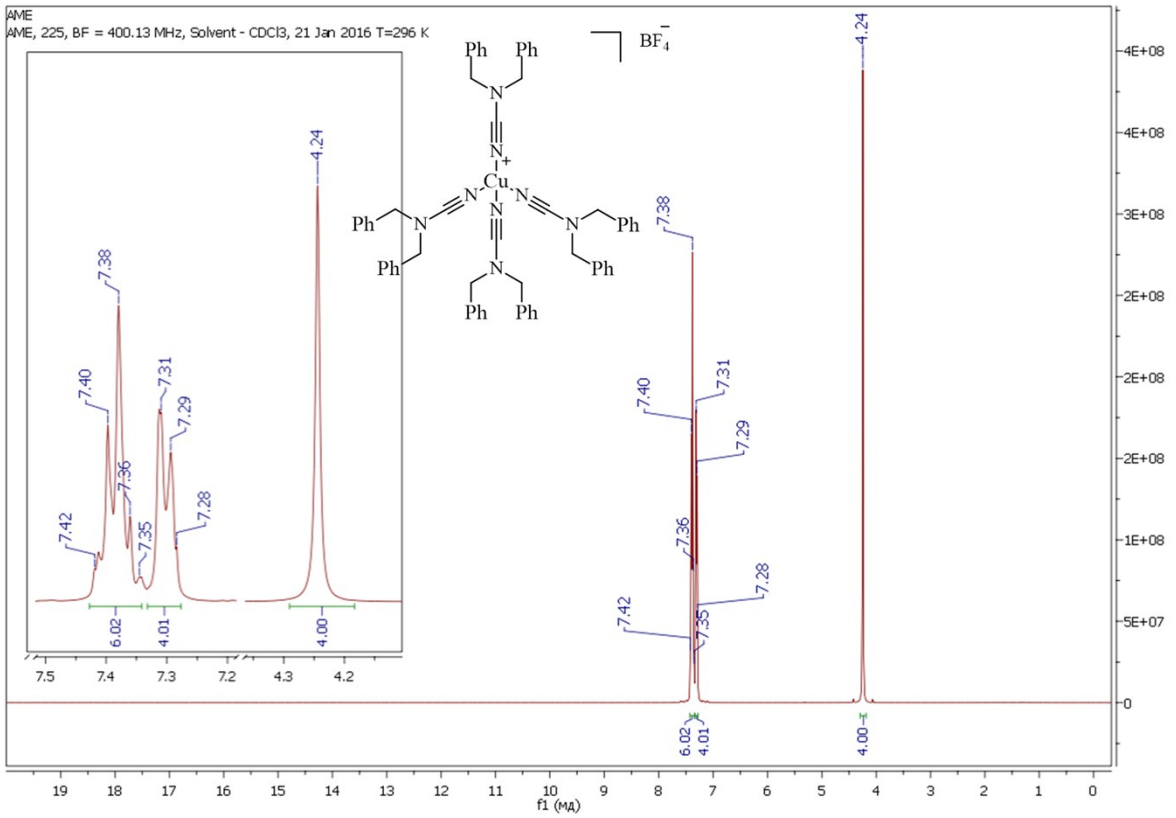


Figure S25. ^{1}H NMR spectrum of **7**, $CDCl_3$, ambient temperature.

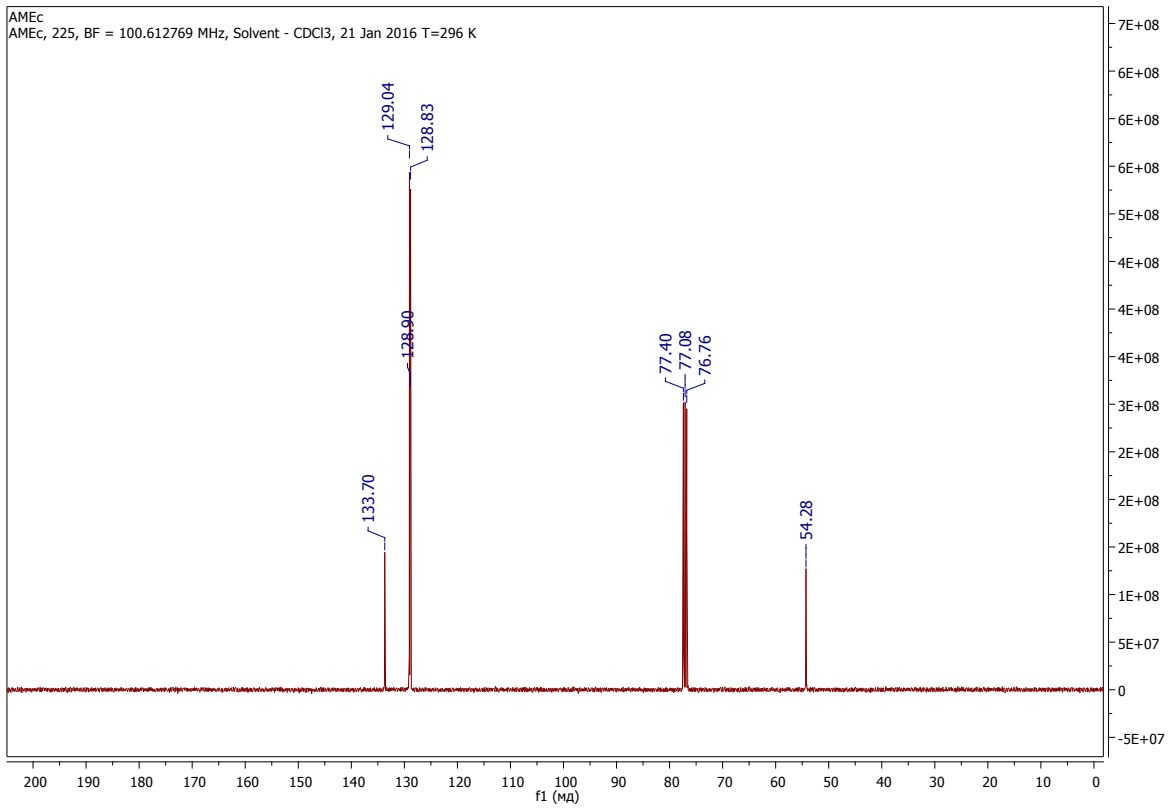


Figure S26. ^{13}C NMR spectrum of **7**, $CDCl_3$, ambient temperature.

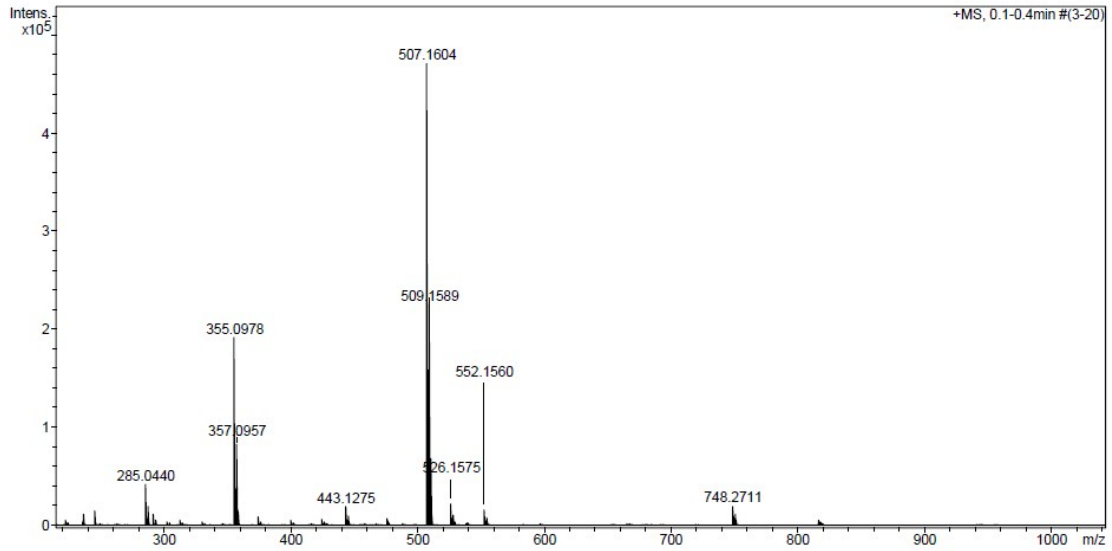
Mass Spectrum Report

Analysis Info

Analysis Name	D:\Data\january2016\M225.d	Acquisition Date	21.01.2016 16:45:28
Method	tune_low.m	Operator	Bruker Customer
Sample Name	M225	Instrument / Ser#	micrOTOF 10223
Comment	MeOH 100v		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



Bruker Compass DataAnalysis 4.0 printed: 21.01.2016 16:54:40 Page 1 of 1

Figure S27. The HR ESI$^+$ mass spectrum of **7**.

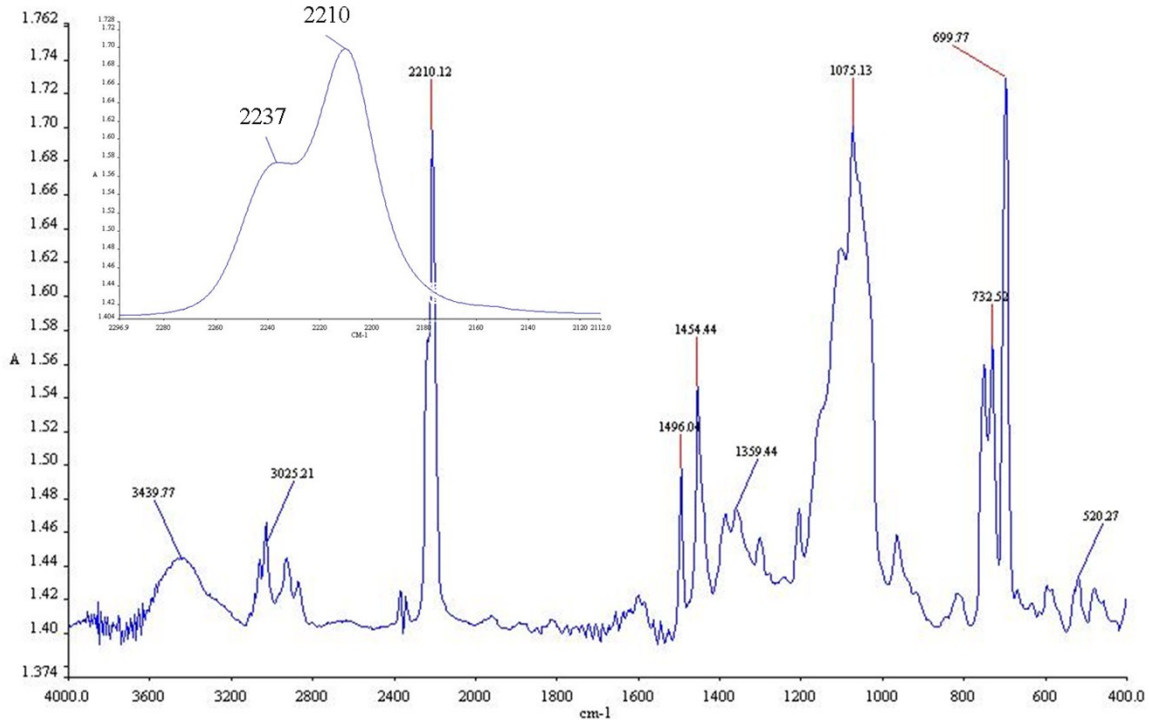


Figure S28. The IR spectrum of **7**.

$Cu(NCNMePh)_4](BF_4)$ (**8**)

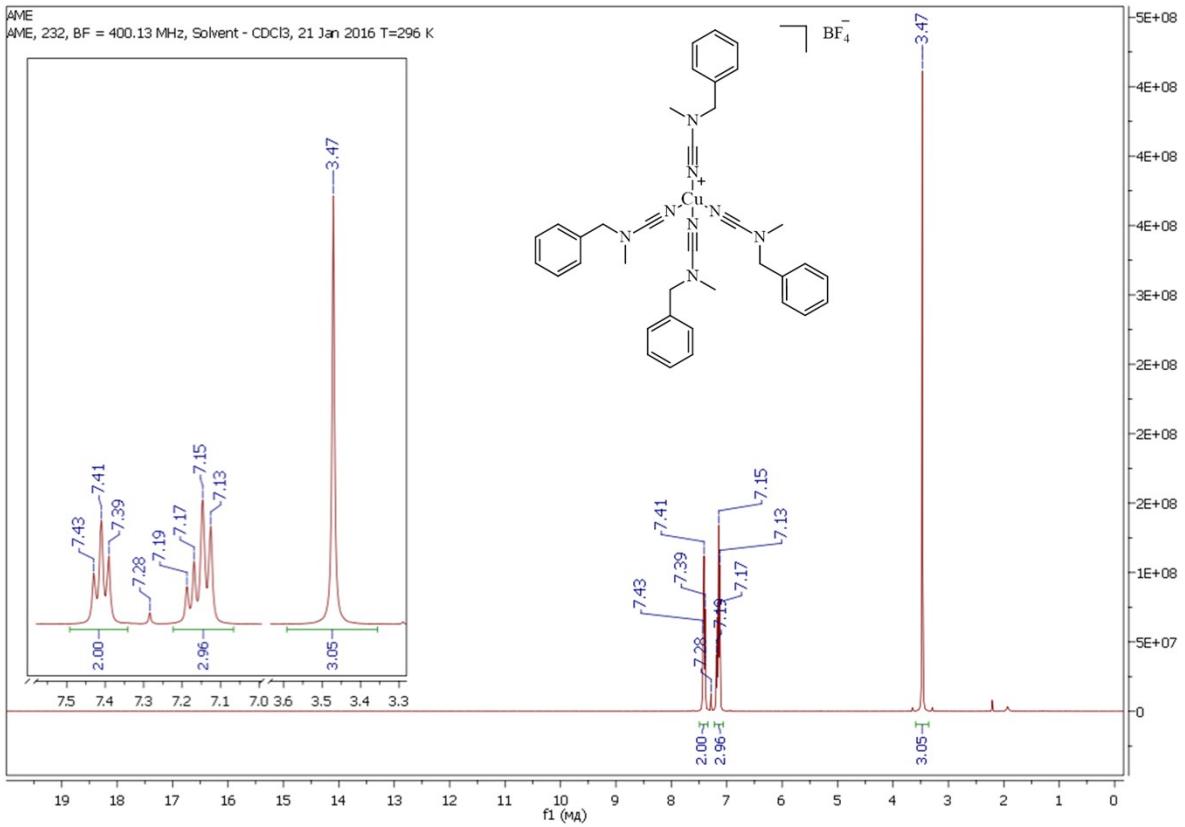


Figure S29. ^{1}H NMR spectrum of **8**, $CDCl_3$, ambient temperature.

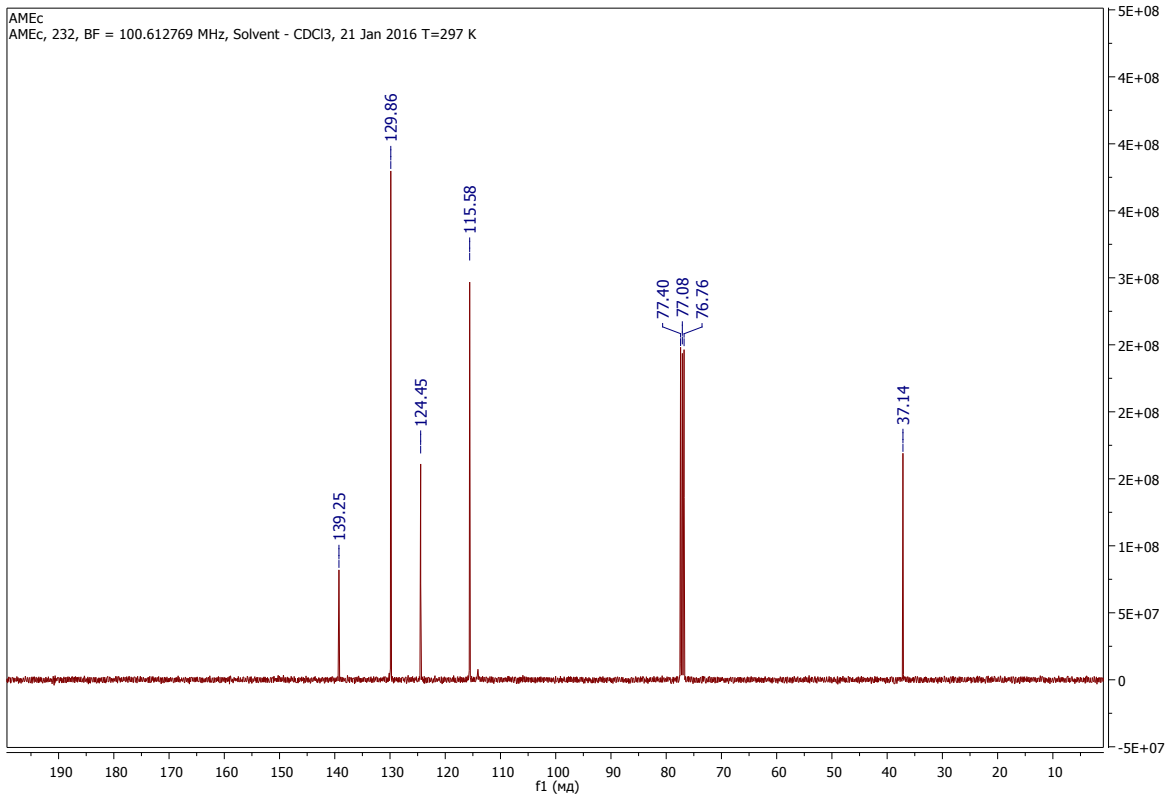


Figure S30. ^{13}C NMR spectrum of **8**, $CDCl_3$, ambient temperature.

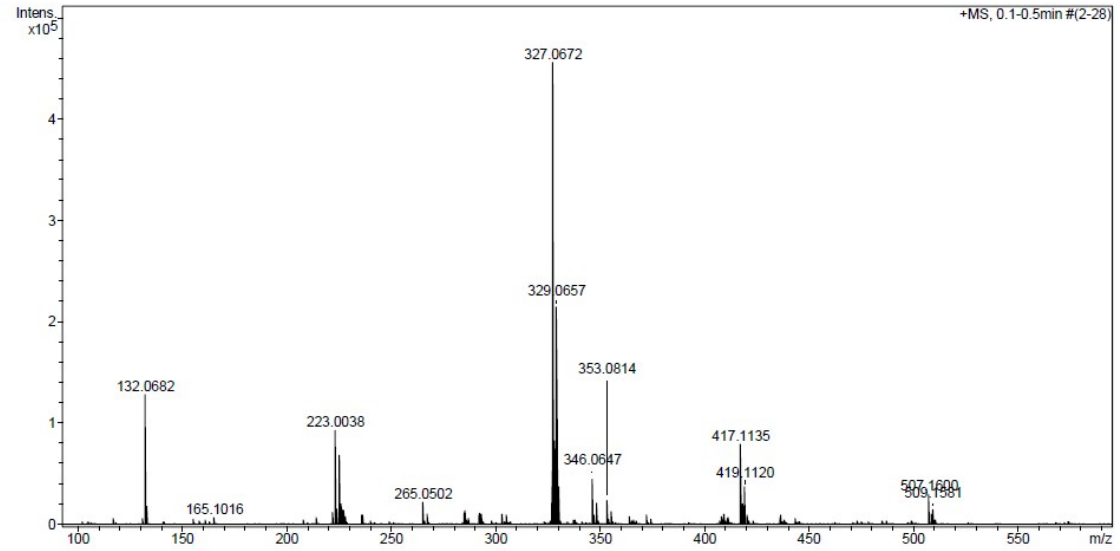
Mass Spectrum Report

Analysis Info

Analysis Name	D:\Data\january2016\M232.d	Acquisition Date	21.01.2016 16:46:50
Method	tune_low.m	Operator	Bruker Customer
Sample Name	M232	Instrument / Ser#	micrOTOF 10223
Comment	MeOH 100v		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Source



Bruker Compass DataAnalysis 4.0 printed: 21.01.2016 16:58:13 Page 1 of 1

Figure S31. The HR ESI$^+$ mass spectrum of **8**.

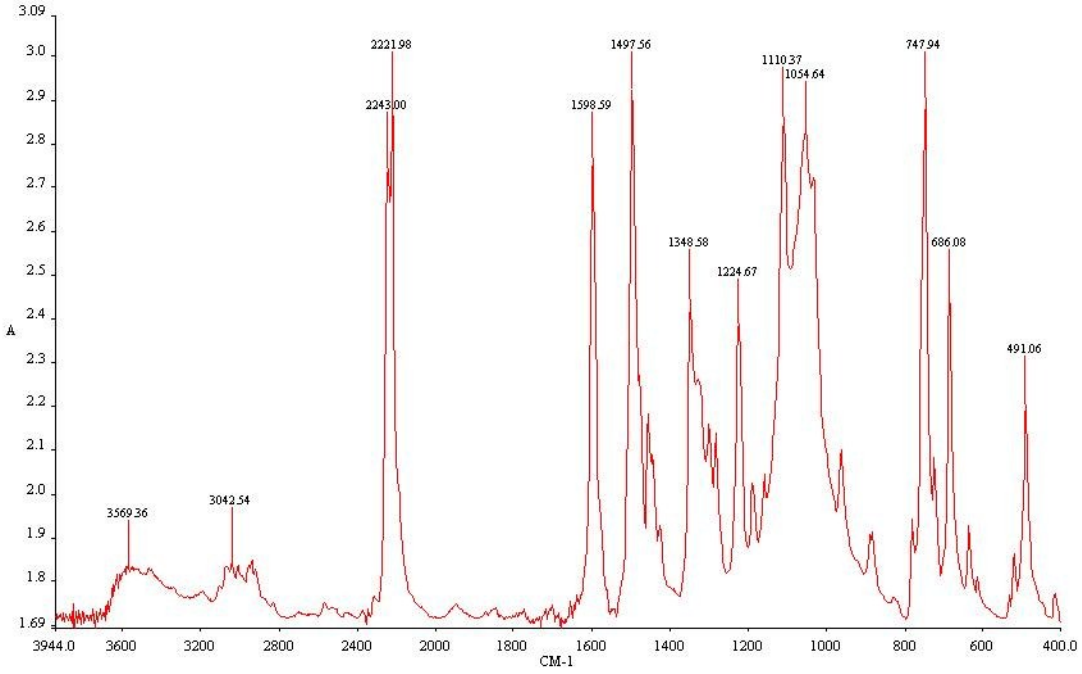


Figure S32. The IR spectrum of **8**.

The TGA data for complexes 1- 8.

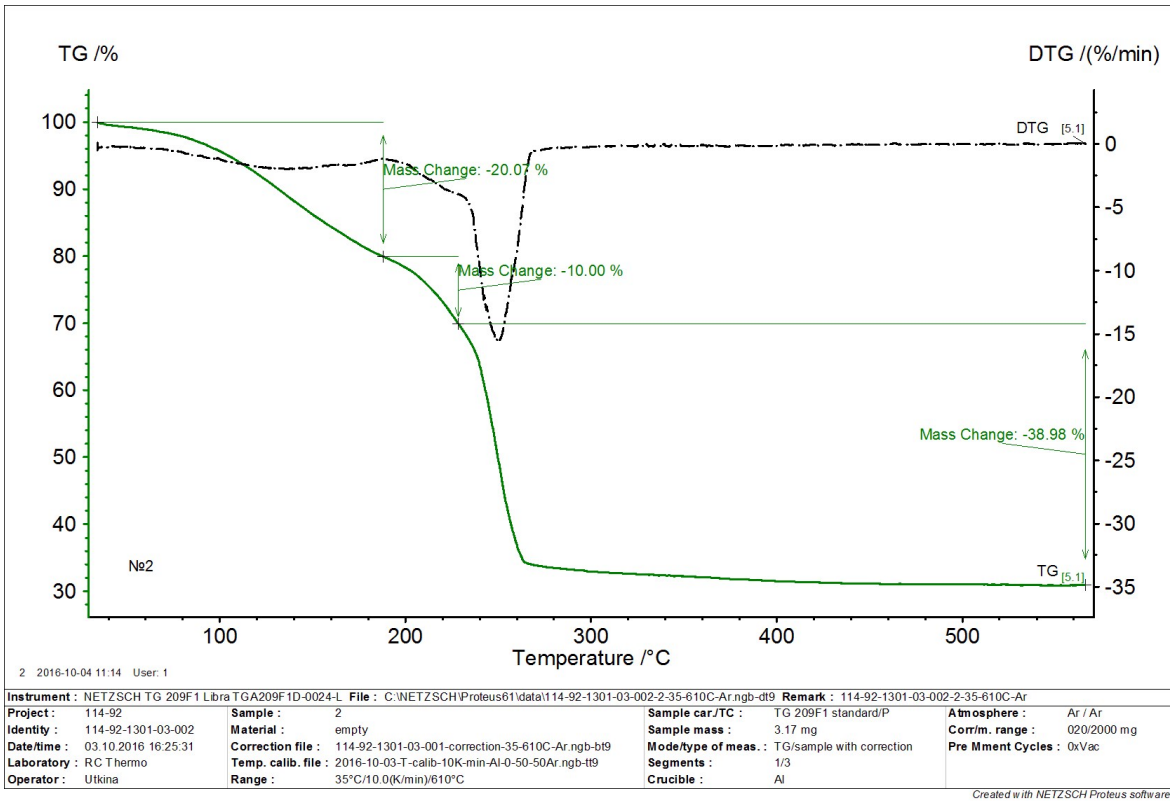


Figure S33. TGA data for **1**.

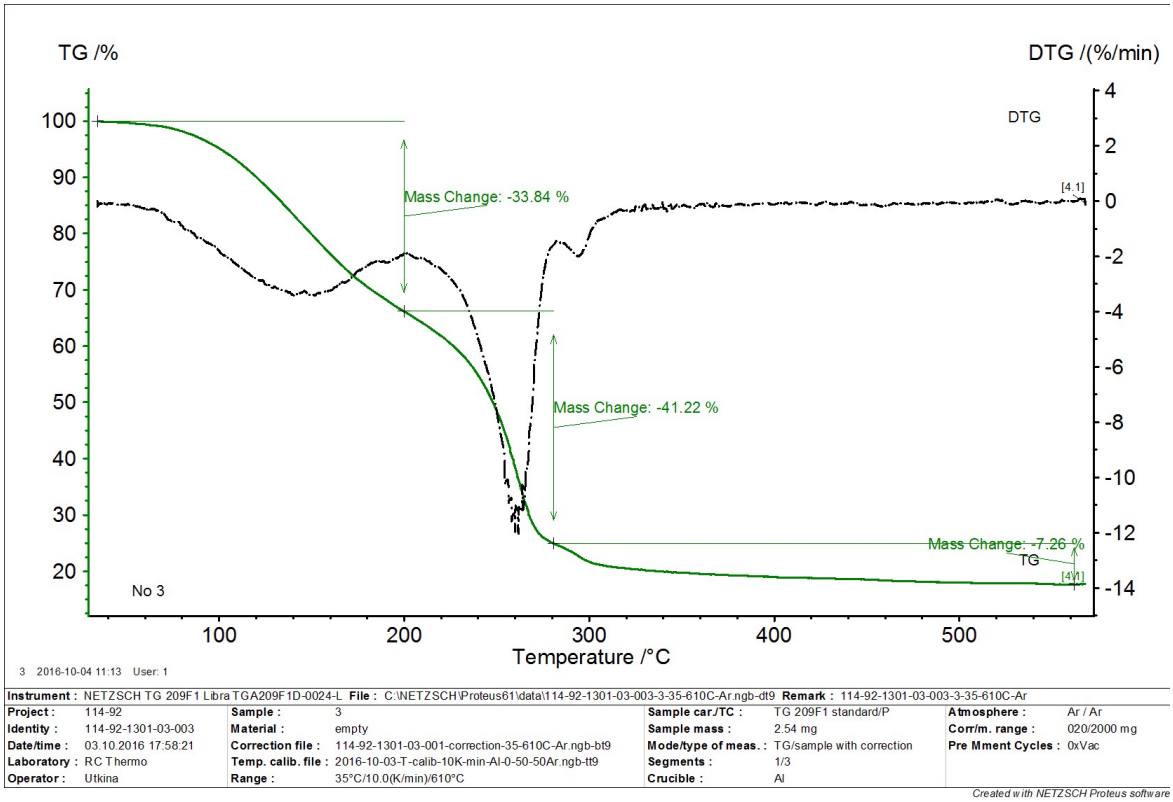


Figure S34. TGA data for **3**.

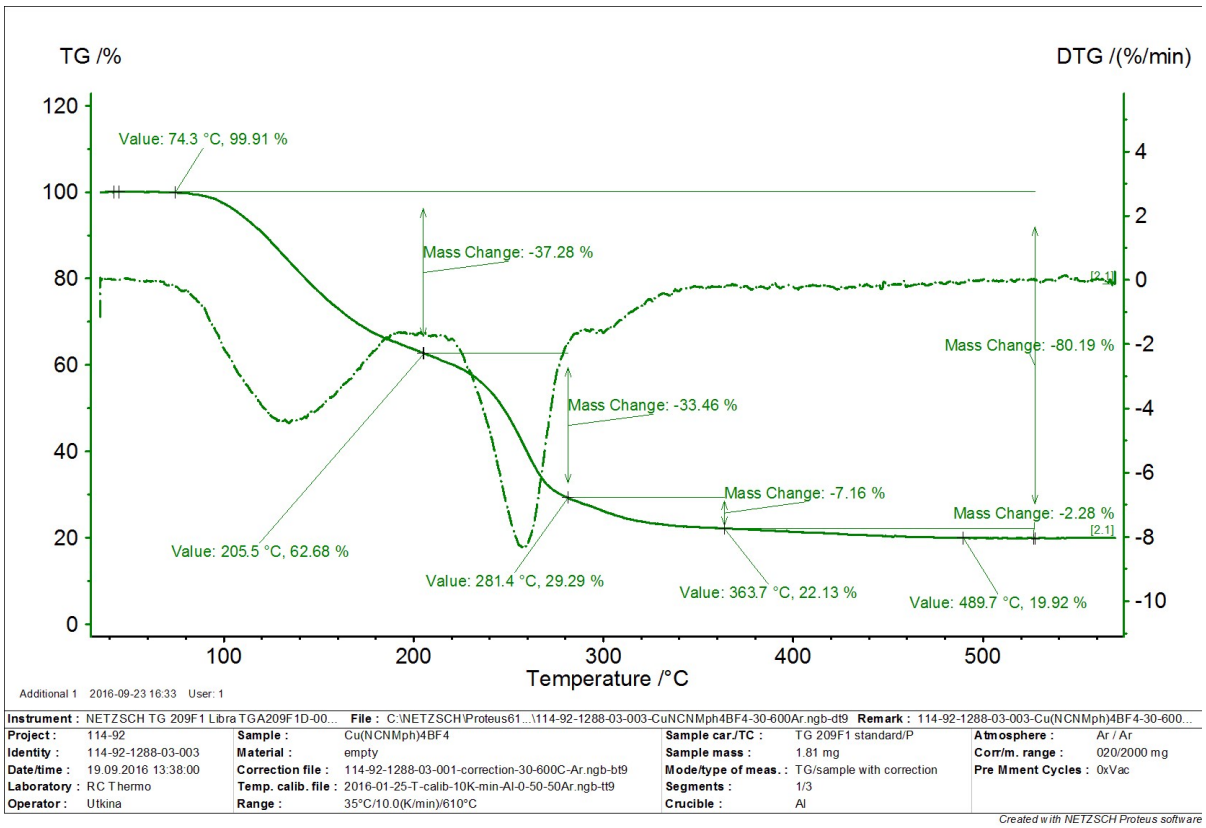


Figure S35. TGA data for **4**.

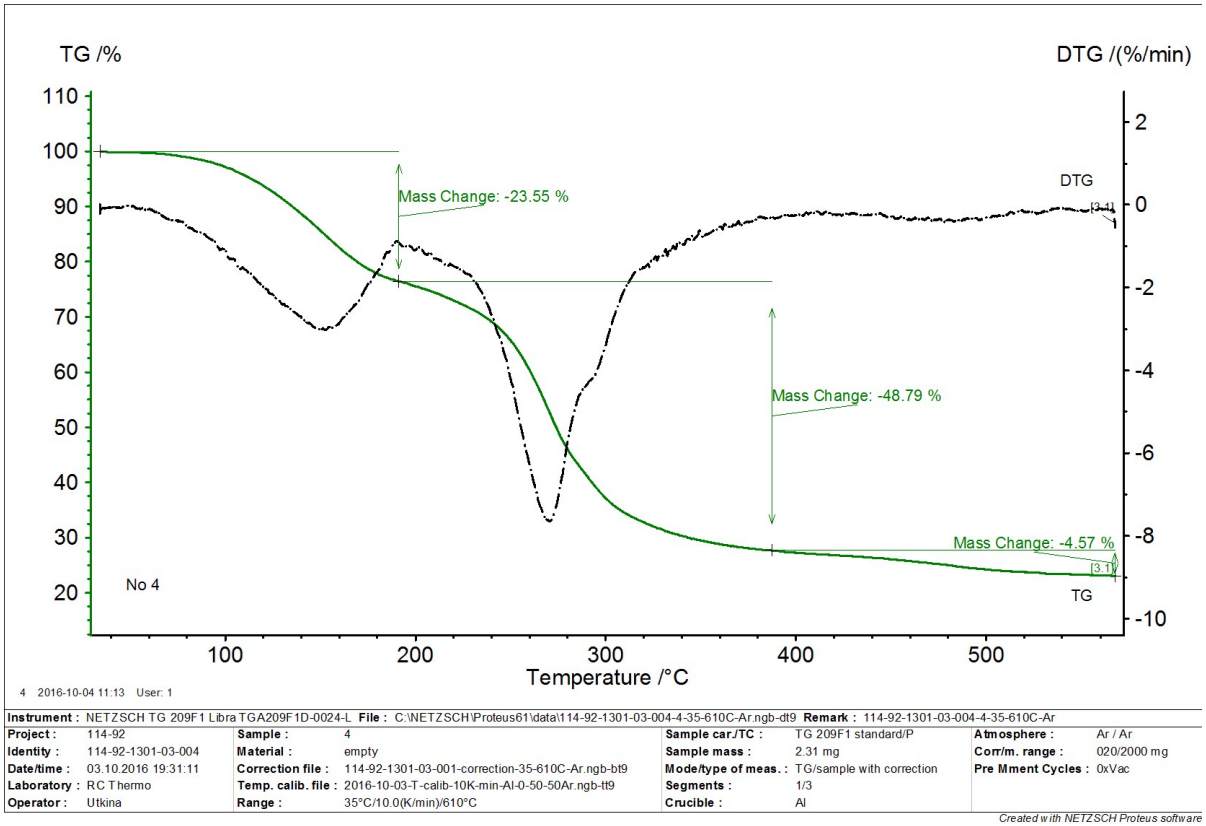


Figure S36. TGA data for **5**.

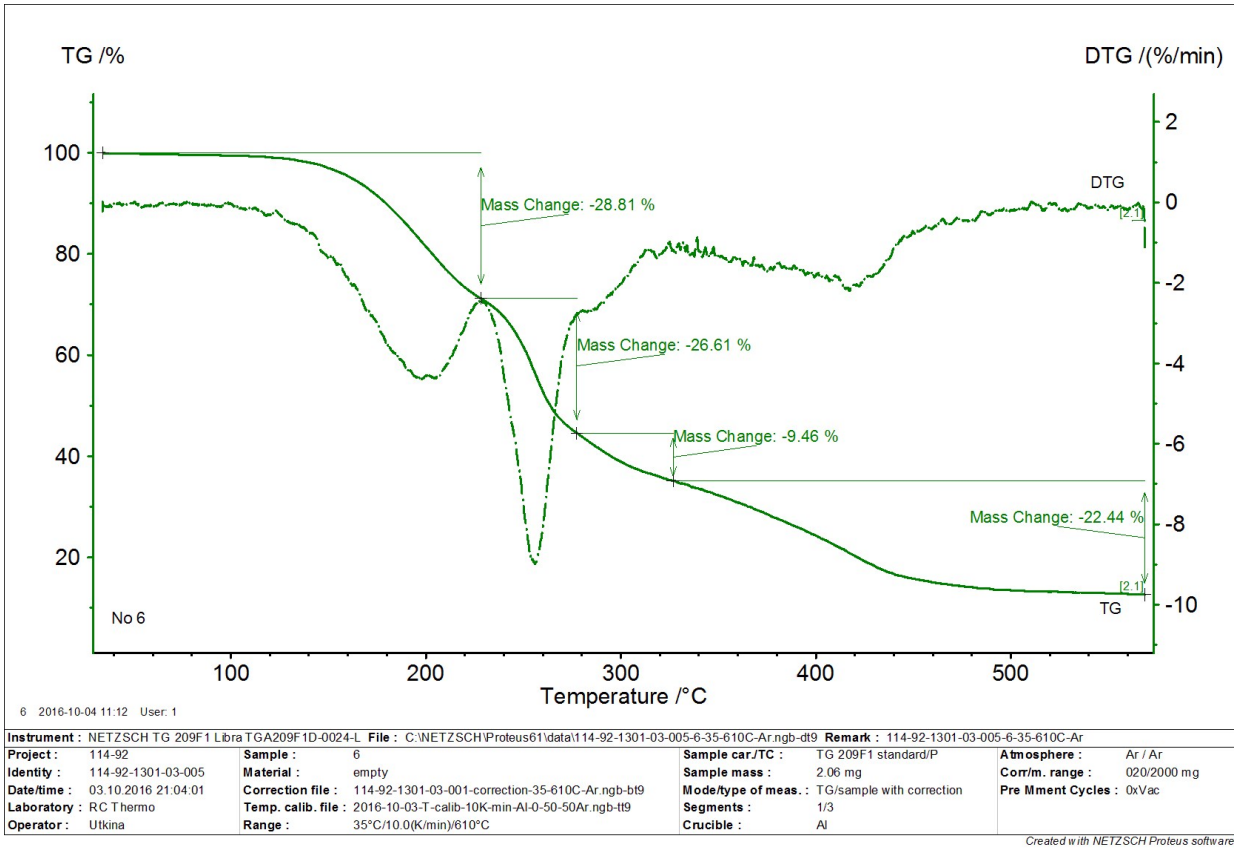


Figure S37. TGA data for **6**.

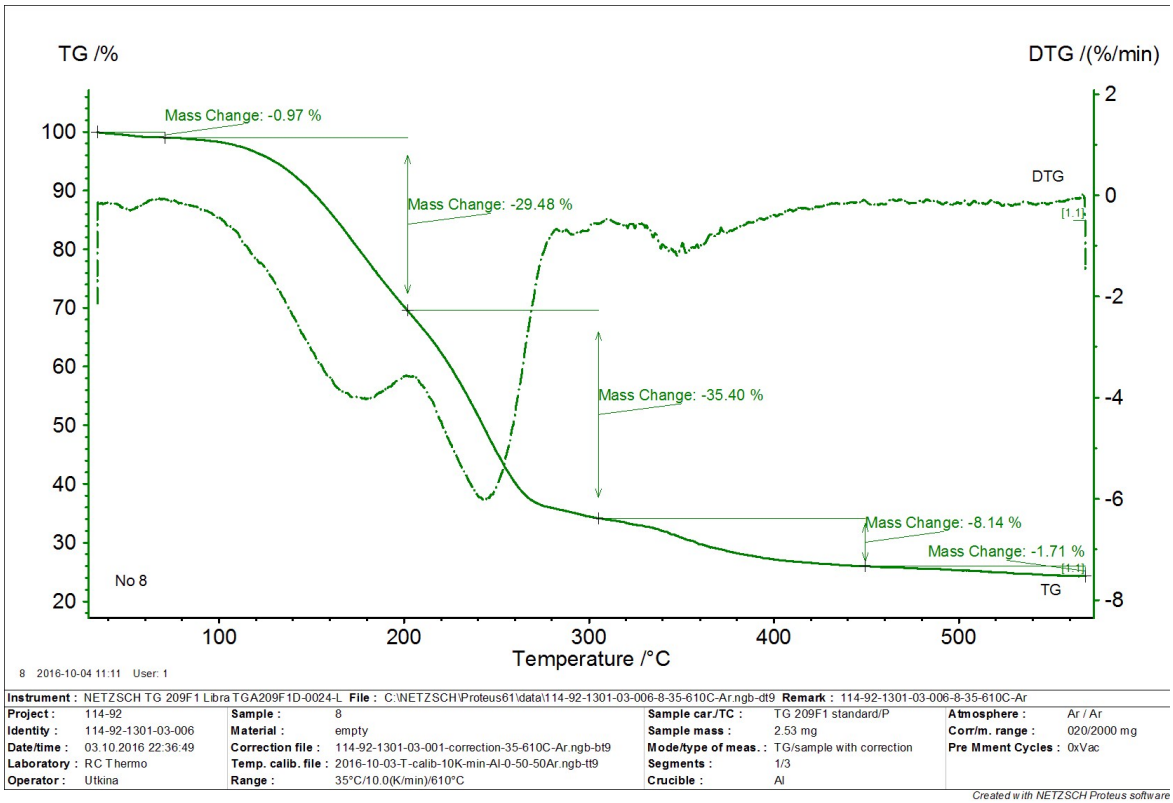


Figure S38. TGA data for **8**.

Table S1 Crystal data and structure refinement for complexes **1**, **3**, **4**.

Identification code	**1**	**3**	**4**
Empirical formula	$C_{12}H_{24}CuN_8 \cdot BF_4$	$C_{24}H_{40}CuN_8 \cdot BF_4$	$C_{20}H_{32}CuN_8O_4 \cdot BF_4$
Formula weight	430.74	591.00	598.90
Temperature/K	100(2)	100(2)	100(2)
Crystal system	tetragonal	monoclinic	monoclinic
Space group	*I*-42*d*	$P2_1/c$	$P2_1$
a/Å	12.4230(4)	8.8710(7)	9.8926(2)
b/Å	12.4230(4)	16.8165(14)	17.9661(3)
c/Å	26.376(2)	21.3749(14)	15.0570(2)
α/°	90.00	90.00	90.00
β/°	90.00	114.521(2)	91.906(2)
γ/°	90.00	90.00	90.00
Volume/Å^3	4070.6(4)	2901.1(4)	2674.62(8)
Z	8	4	4
ρ_{calc}mg/mm^3	1.406	1.353	1.487
m/mm^{-1}	1.121	0.807	0.887
F(000)	1776.0	1240.0	1240.0
Radiation	Mo Kα (λ = 0.7107)	Mo Kα (λ = 0.7107)	Mo Kα (λ = 0.7107)
2Θ range for data collection	5.58 to 54.98°	5.6 to 55	5.5 to 54.98°
Index ranges	-15 ≤ h ≤ 16, -16 ≤ k ≤ 16, -30 ≤ l ≤ 34	-11 ≤ h ≤ 10, -21 ≤ k ≤ 15, -23 ≤ l ≤ 27	-12 ≤ h ≤ 12, -23 ≤ k ≤ 23, -19 ≤ l ≤ 19
Reflections collected	9749	15903	24671
Independent reflections	2340[R_{int} = 0.0246]	6568 [R_{int} = 0.0279]	12292 R_{int} = 0.0190]
Data/restraints/parameters	2340/0/132	6568/0/343	12292/1/686
Goodness-of-fit on F^2	1.135	1.078	1.025
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0218, wR_2 = 0.0528	R_1 = 0.0420, wR_2 = 0.1022	R_1 = 0.0251, wR_2 = 0.0602
Final *R* indexes [all data]	R_1 = 0.0274, wR_2 = 0.0557	R_1 = 0.0524, wR_2 = 0.1079	R_1 = 0.0274, wR_2 = 0.0616
Largest diff. peak/hole / e Å^{-3}	0.19/-0.18	0.82/-0.47	0.46/-0.33
CCDC No	1578478	1578477	1578479

$\boldsymbol{R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|}$; $\boldsymbol{wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}}$;

$w = 1/[\sigma^2(F_o^2)+(aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$; $s = \{\Sigma[w(F_o^2 - F_c^2)]/(n - p)\}^{1/2}$ where n is the number of reflections and p is the number of refinement parameters.

Table S2. Calculated vertical total energies (E_v) for the Cu–N coordination bonds dissociation in $[Cu(NCMe)_4]^+$ and $[Cu(NCNMe_2)_4]^+$ (in kcal/mol).*

Bond (length)	E_v
$[Cu(NCMe)_4]^+$	
Cu–N (2.02 Å)	25
$[Cu(NCNMe_2)_4]^+$	
Cu–N (1.96 and 1.97 Å)	31
Cu–N (2.01 Å)	27
Cu–N (2.25 Å)	15

* $E_v = E(M–L) – E(M) – E(L)$

Table S3. Cartesian atomic coordinates for optimized equilibrium structures of NCMe, $[Cu(NCMe)_4]^+$, $NCNMe_2$, and $[Cu(NCNMe_2)_4]^+$.

Atom	X	Y	Z
NCMe			
C	-1.175110	-0.000210	-0.000066
N	1.437379	-0.000434	-0.000094
C	0.277337	0.001038	0.000227
H	-1.558621	0.031118	1.025401
H	-1.557161	-0.904804	-0.485352
H	-1.559235	0.871753	-0.540357
$[Cu(NCMe)_4]^+$			
C	0.097667	4.029570	2.260948
N	0.052196	1.753319	0.996654
C	0.074341	2.763075	1.558798
H	-0.397195	3.932263	3.233240
H	-0.424507	4.793436	1.675202
H	1.130655	4.355727	2.422750

Cu	0.003742	-0.006188	0.007613
N	1.795692	-0.918601	0.163671
N	-1.439836	-1.181543	0.784039
C	-0.953194	0.778562	-4.449322
C	-3.280508	-2.712458	1.809123
N	-0.400139	0.342300	-1.942329
C	4.119724	-2.076949	0.359603
C	-2.258186	-1.859378	1.238694
C	2.826349	-1.434493	0.249735
C	-0.642836	0.535997	-3.055653
H	-1.345571	-0.133166	-4.912152
H	-0.053908	1.089140	-4.991716
H	-1.706535	1.568779	-4.535022
H	-3.832401	-3.225324	1.014210
H	-3.985212	-2.117456	2.399768
H	-2.822582	-3.464179	2.460903
H	4.017413	-3.057917	0.835716
H	4.794783	-1.462133	0.964172
H	4.561013	-2.211617	-0.633643
$NCNMe_2$			
N	-2.188459	0.000004	0.070407
C	-1.025842	-0.000006	-0.046054
N	0.295875	-0.000002	-0.224918
C	1.014701	-1.233817	0.054854
C	1.014701	1.233819	0.054853
H	1.275353	-1.324402	1.121329
H	1.938307	-1.248134	-0.536333
H	0.399704	-2.090277	-0.235163

H	0.399703	2.090276	-0.235169
H	1.275347	1.324409	1.121329
H	1.938311	1.248142	-0.536327
$[Cu(NCNMe_2)_4]^+$			
N	-1.627968	-1.655616	-0.122567
C	-2.283315	-2.616683	-0.044681
N	-2.998630	-3.711136	0.067534
C	-2.948314	-4.730738	-0.974980
C	-4.119526	-3.758991	1.001060
H	-2.036625	-4.610739	-1.565700
H	-3.820997	-4.655827	-1.638223
H	-2.939166	-5.721505	-0.505868
H	-3.998625	-2.984576	1.762743
H	-4.132496	-4.738919	1.492132
H	-5.072951	-3.607616	0.476461
N	1.139503	-0.060273	-1.258098
C	2.292165	-0.119372	-1.435562
N	3.595015	-0.192709	-1.596358
C	4.406633	1.014392	-1.490806
C	4.190071	-1.352285	-2.252046
H	3.870789	1.766097	-0.904318
H	4.638325	1.425894	-2.482736
H	5.347099	0.767922	-0.981560
H	3.497588	-2.197154	-2.206538
H	5.115701	-1.622799	-1.728538
H	4.425091	-1.135572	-3.302979
C	1.697219	0.013069	1.865687
N	0.533150	-0.045283	1.759630

N	3.017003	0.074856	1.906263
C	3.657275	1.127300	2.689473
C	3.776167	-1.157159	1.719117
H	3.017467	2.013529	2.707491
H	4.612354	1.387899	2.217745
H	3.848940	0.799290	3.720958
H	4.008800	-1.636221	2.680934
H	4.716246	-0.919292	1.204385
H	3.199663	-1.852300	1.101016
Cu	-0.568294	-0.003962	-0.196846
N	-1.500493	1.728779	-0.182317
C	-2.099048	2.729352	-0.174081
N	-2.752522	3.866965	-0.134882
C	-2.472451	4.906425	-1.120002
C	-4.009738	3.960873	0.600683
H	-2.490842	5.883222	-0.622856
H	-3.222532	4.898151	-1.922774
H	-1.481186	4.748308	-1.552362
H	-4.061833	3.162780	1.345552
H	-4.049567	4.927868	1.115291
H	-4.868953	3.880280	-0.079335

Table S4. Calculated total energies, enthalpies, Gibbs free energies (in Hartree) and entropies (in cal/mol•K) in gas phase for the optimized equilibrium structures (E, H, G, S).

Compound	E	H	G	S
$[Cu(NCMe)_4]^+$	-727.935683	-727.726425	-727.802601	160.32
$NCNMe_2$	-227.237256	-227.139222	-227.175092	75.50
$[Cu(NCNMe_2)_4]^+$	-1106.273786	-1105.871930	-1105.976881	220.89
NCMe	-132.656844	-132.606847	-132.635352	59.99

Table S5. Calculated total reaction energy (ΔE), enthalpy and Gibbs free energy of reaction (ΔH and ΔG) (in kcal/mol) in gas phase for ligands substitution process.

Process	ΔE	ΔH	ΔG
$[Cu(NCMe)_4]^+ + 4\ NCNMe_2 \rightarrow [Cu(NCNMe_2)_4]^+ + 4\ NCMe$	-10.3	-10.0	-9.6

Table S6. Geometrical parameters for optimized equilibrium structures of $[Cu(NCMe)_4]^+$ and $[Cu(NCNMe_2)_4]^+$.

$[Cu(NCMe)_4]^+$					
d(Cu–N), Å	d(N≡C), Å	d(C–C), Å	Angle N–Cu–N, °	Angle Cu–N–C, °	Angle N–C–C, °
2.022	1.156	1.449	110.03	179.64	179.81
2.019	1.156	1.448	109.57	179.57	179.81
2.017	1.156	1.448	109.19	179.35	179.80
2.017	1.156	1.448	109.09	179.31	179.75

$[Cu(NCNMe_2)_4]^+$					
d(Cu–N), Å	d(N≡C), Å	d(C–N), Å	Angle N–Cu–N, °	Angle Cu–N–C, °	Angle N–C–N, °
2.246	1.170	1.322	118.99	177.69	178.45
2.011	1.168	1.315	115.52	177.39	178.35
1.968	1.166	1.313	102.49	156.89	178.26
1.964	1.166	1.312	92.45	124.46	176.55