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Supplementary Information

Self-Assembly of Arene Ruthenium Acylpyrazolone Fragments to Tetranuclear Metallacycles. Molecular Structures and Solid-State ^{15}N CPMAS NMR Correlations.

Riccardo Pettinari,[a]* Fabio Marchetti,[b] Claudio Pettinari,[a] Francesca Condello,[a] Brian W. Skelton,[c] Allan H. White,[d] Michele Remo Chierotti[e] and Roberto Gobetto.[e]*

[a] School of Pharmacy, University of Camerino, via S. Agostino 1, 62032 Camerino MC, Italy. E-mail: riccardo.pettinari@unicam.it; Tel: +39-0737-632338;
[b] School of Science and Technology, University of Camerino, via S. Agostino 1, 62032 Camerino MC, Italy;
[c] School of Chemistry and Biochemistry M310, The University of Western Australia, Crawley, WA 6009, Australia;
[d] Centre for Microscopy, Characterization and Analysis M010, The University of Western Australia, Crawley, WA 6009, Australia;
[e] Dipartimento di Chimica and NIS Centre, University of Torino, Via P. Giuria 7, 10125 Torino, Italy.

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Crystallographic appendix

Table S1. Crystal/Refinement Data, (**1**), (**2**) and (**4**)

	1	**4**	**2**
formula	$C_{22}H_{24}Cl_2N_2O_2Ru$	$C_{27}H_{35}ClN_2O_2Ru$	$\{[(C_{22}H_{24}ClN_2O_2Ru)]_4(O_3SCF_3)\}(O_3SCF_3)_3CHCl_3\cdot 2H_2O$
M_r (Dal)	520.4	556.1	2691.5
cryst. syst.	Triclinic	Triclinic	Monoclinic
space group	$P\bar{1}$ (No.2)	$P\bar{1}$ (No.2)	$C2$ (No. 5)
a (Å)	7.5449(2)	7.8180(3)	32.1762)
b (Å)	12.0143(4)	11.5430(4)	11.3815(4)
c (Å)	12.9409(5)	14.1909(5)	15.8038(8)
α (deg)	112.841(4)	89.197(3)	
β (deg)	95.867(3)	85.167(3)	116.629(7)
γ (deg)	103.150(3)	77.653(3)	
V (Å^3)	1028.27(7)	1246.55(8)	5173.7(4)
D_c (Z)	1.68_1(2)	1.48_2(2)	1.72_8(2)
μ_{Mo} (mm^{-1})	1.044	0.76	0.93
specimen (mm)	0.25,0.18,0.04	0.62,0.32,0.23	0.13,0.13,0.07
$'T'_{min/max}$	0.86	0.85	0.95
$2\theta_{max}$ (°)	68.6	75	55
N_t	27880	46395	27740
$N(R_{int})$	8240 (0.035)	12528 (0.029)	11356 (0.098)
N_o (I>2σ(I))	7376	11561	6488
R_1 (I>2σ(I))	0.031	0.024	0.074
wR_2 (a,b) (all data)	0.072 (0.032,0.52)	0.060 (0.025,0.35)	0.135 (0.060)
S	1.03	1.08	0.95
$\|\Delta\rho\|_{max}$ (eÅ^{-3})	1.07	0.68	1.49

Table S2. Selected non-hydrogen ruthenium environment geometries, (**1**), (**2**), (**4**). C(0) are the ring centroids, O,N(n2,5,6) the ligating nitrogen or oxygen atoms of segments n = 1,2.

	1	**4**	**2** (components 1; 2)
		Distances (Å)	
Ru-C(Csub6)	2.149(9) –2.201(2)	2.1624(9) –2.1798(9)	2.135(8) 2.146(11) –2.196(8) ; –2.202(10)
Ru-C(0)	1.653	1.640	1.641 ; 1.633
Ru-Cl/*N*	2.4120(4)	2.3968(3)	*2.152(7)* ; *2.137(8)*
Ru-O(n5)	2.0877(11)	2.0835(7)	2.089(6) ; 2.055(6)
Ru-O(n6)	2.108(11)	2.1024(7)	2.099(6) ; 2.089(7)
O(n5)-C(n5)	1.270(2)	1.2732(11)	1.261(11); 1.232(10)
O(n6)-C(n6)	1.258(2)	1.2646(11)	1.235(10); 1.263(11)
C(n5)-C(n4)	1.424(2)	1.4278(11)	1.441(14); 1.491(15)
C(n4)-C(n6)	1.414(2)	1.4166(12)	1.401(13); 1.412(13)
		Angles (degrees)	
C(0)-Ru-O(n5)	127.3	127.0	127.8 ; 127.4
C(0)-Ru-O(n6)	128.2	126.0	127.5 ; 124.3
C(0)-Ru-Cl/N(n2)	129.1	129.9	125.9 ; 130.9
Cl/N(n2)-Ru-O(n5)	84.50(3)	85.07(2)	88.5(3) ; 86.6(3)
Cl/N(n2)-Ru-O(n6)	84.63(3)	85.28(2)	87.8(9) ; 87.2(3)
O(n5)-Ru-O(n6)	88.25(4)	89.23(3)	86.0(2) ; 86.1(3)
Ru-O(n5)-C(n5)	123.07(10)	121.37(6)	123.4(6) ; 127.9(7)
Ru-O(n6)-C(n6)	129.13(10)	129.43(6)	132.7(6) ; 132.0(6)
Ru-N(n2)-N(n1)	-	-	122.5(6) ; 127.7(5)
Ru-N(n2)-C(n3)	-	-	135.1(6) ; 132.8(7)
N(n2)-N(n1)-C(n5)	111.85(14)	112.20(3)	114.0(8) ; 112.0(7)
N(n1)-N(n2)-C(n3)	106.05(11)	105.83(8)	102.4(8) ; 104.4(8)

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC: 945237(**1**); 945230 (**2**); 945238 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

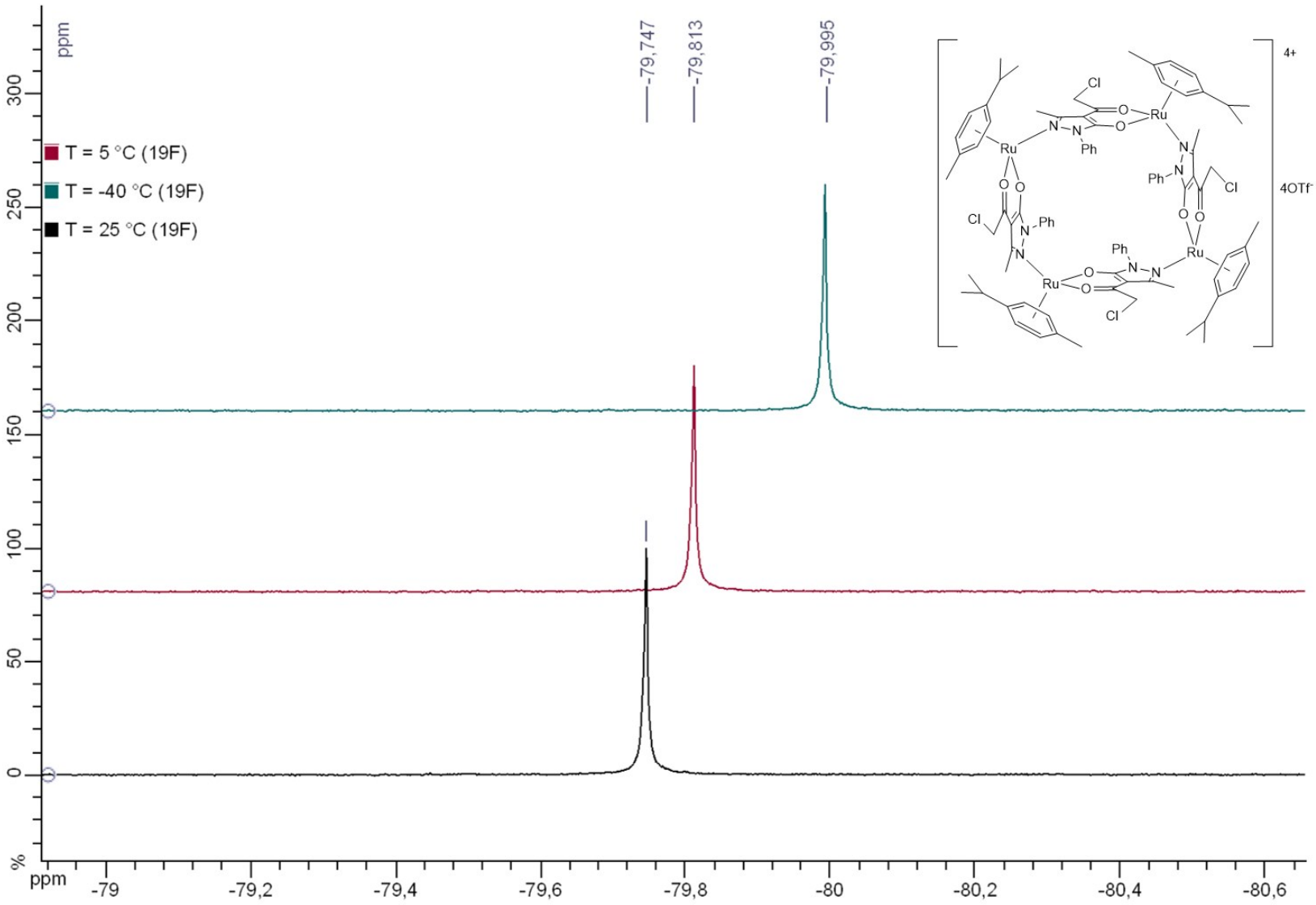
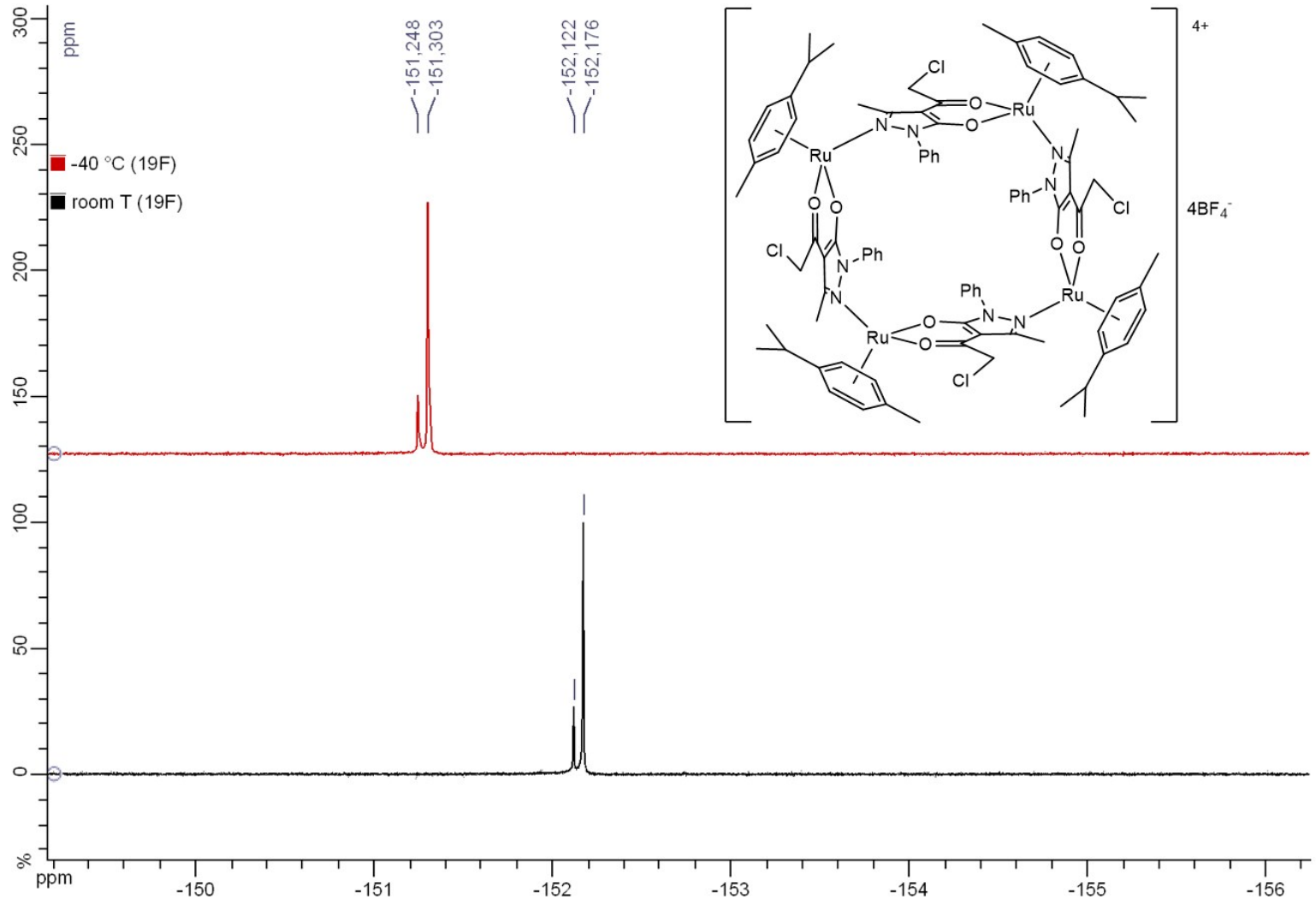


Figure S1. Variable temperature ^{19}F NMR spectra of $[(\eta^6\text{-cym})Ru(Q^{CH2Cl})]_4(SO_3CF_3)_4$ (**4**) carried out in CD_3CN.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-152,122
-152,176
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room T (19F)
4+
4BF4-
Cl
Ru
N
Ph
O
300
250
200
150
100
50
0
%
ppm
-150
-151
-152
-153
-154
-155
-156

Figure S2. Variable temperature ^{19}F NMR spectra of $[(\eta^6\text{-cym})Ru(Q^{CH2Cl})]_4(BF_4)_4$ (**5**) carried out in CD_3CN.

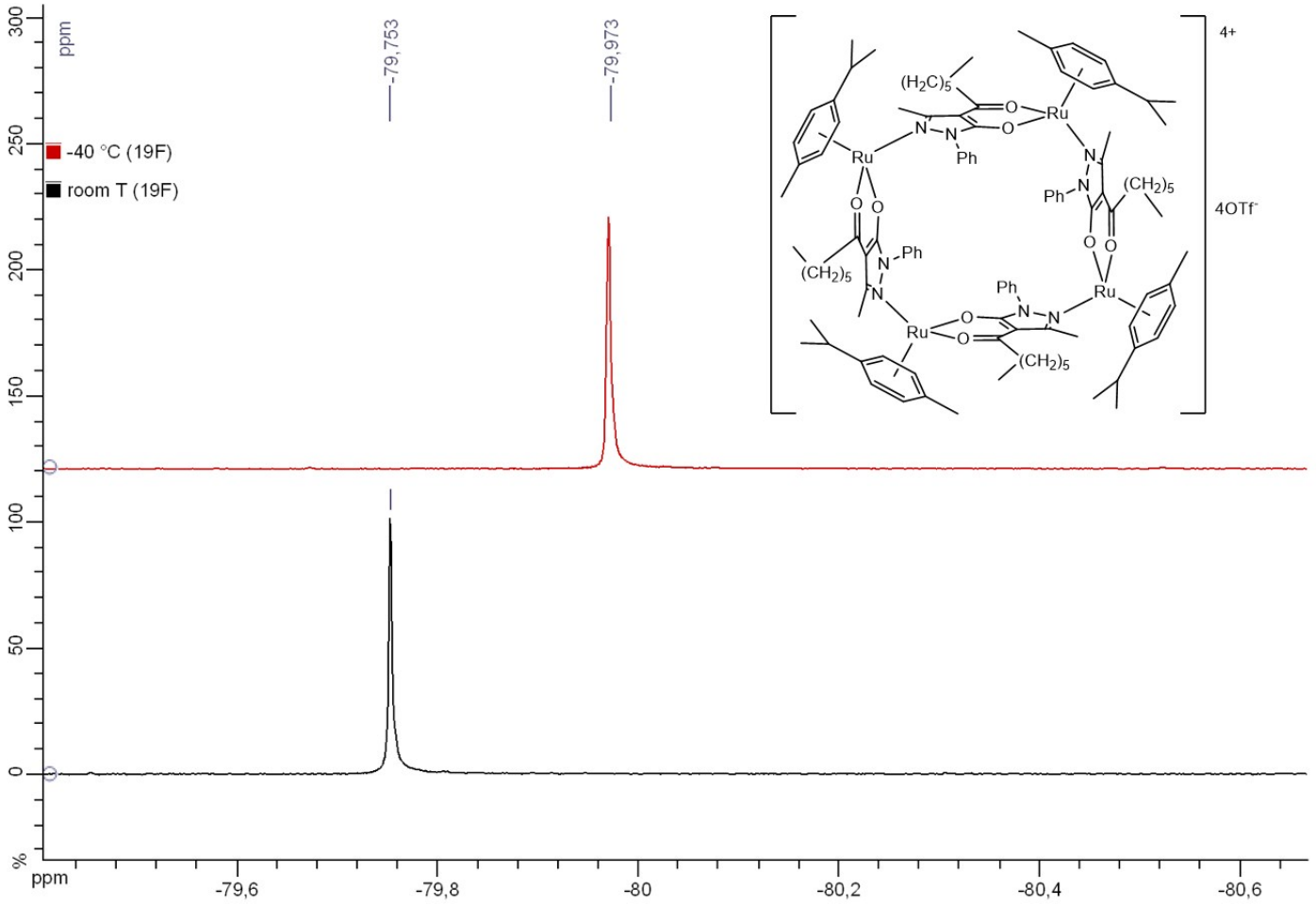

Figure S3. Variable temperature ^{19}F NMR spectra of $[(\eta^6\text{-cym})Ru(Q^{hex})]_4(SO_3CF_3)_4$ (**6**) carried out in CD_3CN.

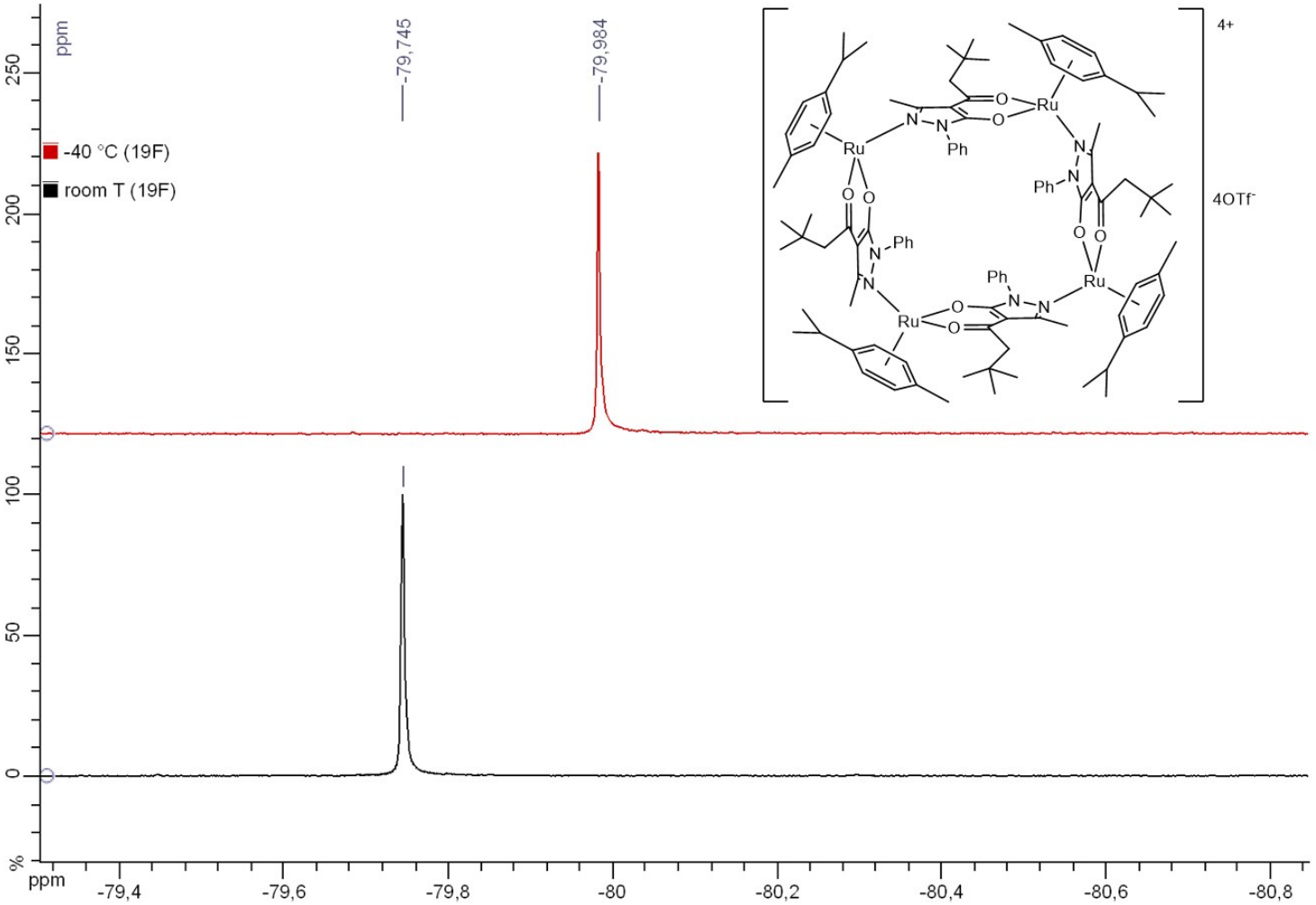

Figure S4. Variable temperature ^{19}F NMR spectra of $[(\eta^6\text{-cym})Ru(Q^{nPe})]_4(SO_3CF_3)_4$ (**7**) carried out in CD_3CN.

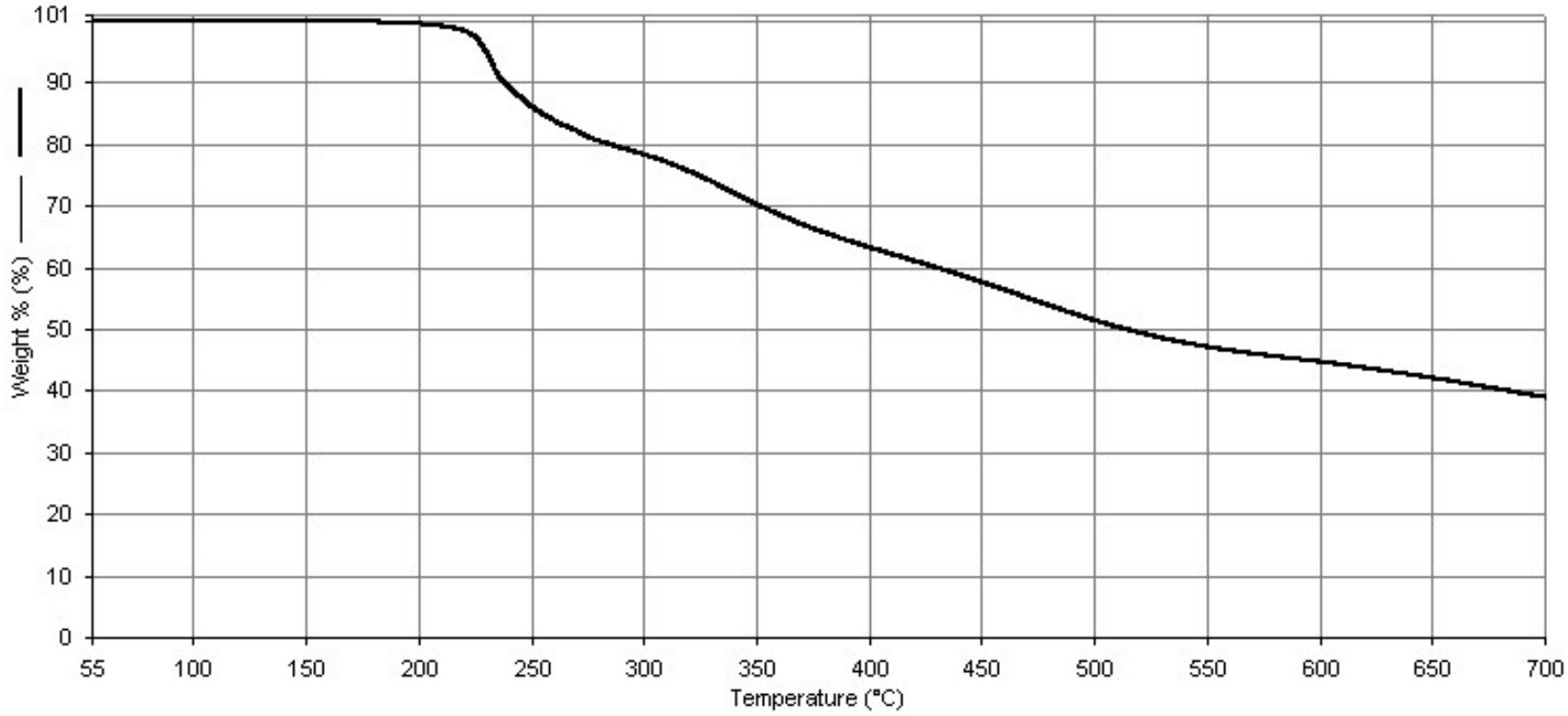

Figure S5. TGA of ligand HQ^{CH2Cl}.

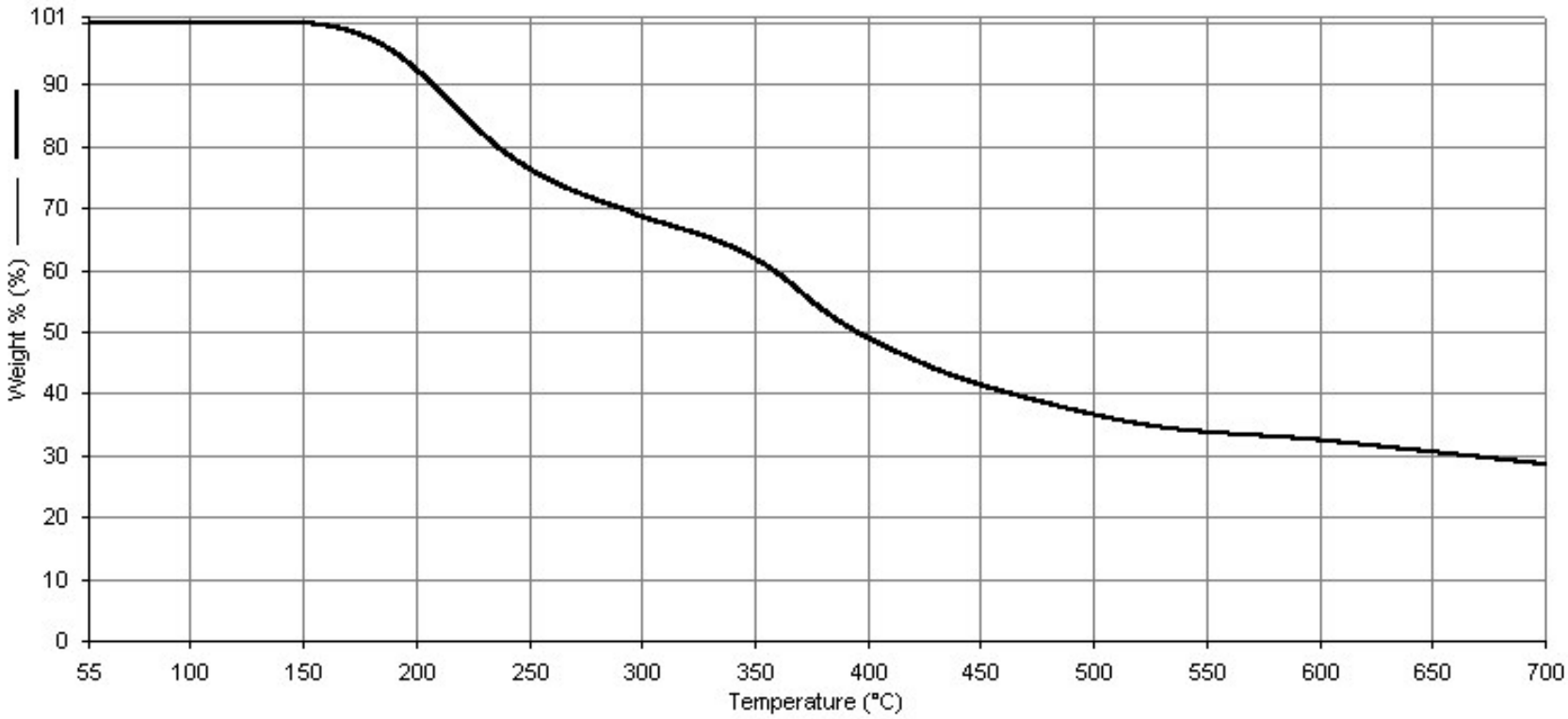

Figure S6. TGA of ligand HQ^{hex}.

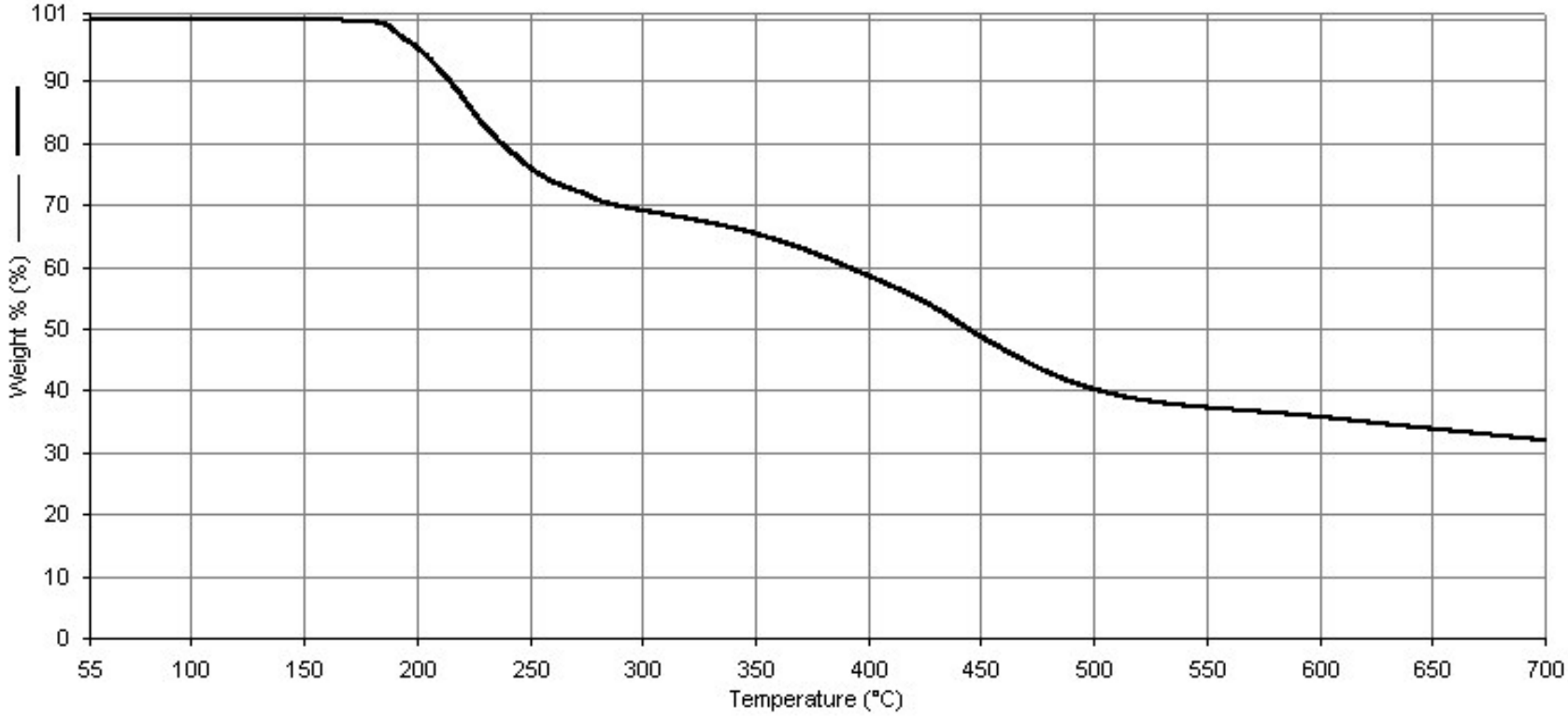

Figure S7. TGA of ligand HQ^{nPe}.

Figure S8. TGA of [(η^6-cym)Ru(Q^{CH2Cl})Cl] (**1**).

Figure S9. TGA of [(η^6-cym)Ru(Q^{hex})Cl] (**2**).

Figure S10. TGA of [(η^6-cym)Ru(Q^{nPe})Cl] (**3**).

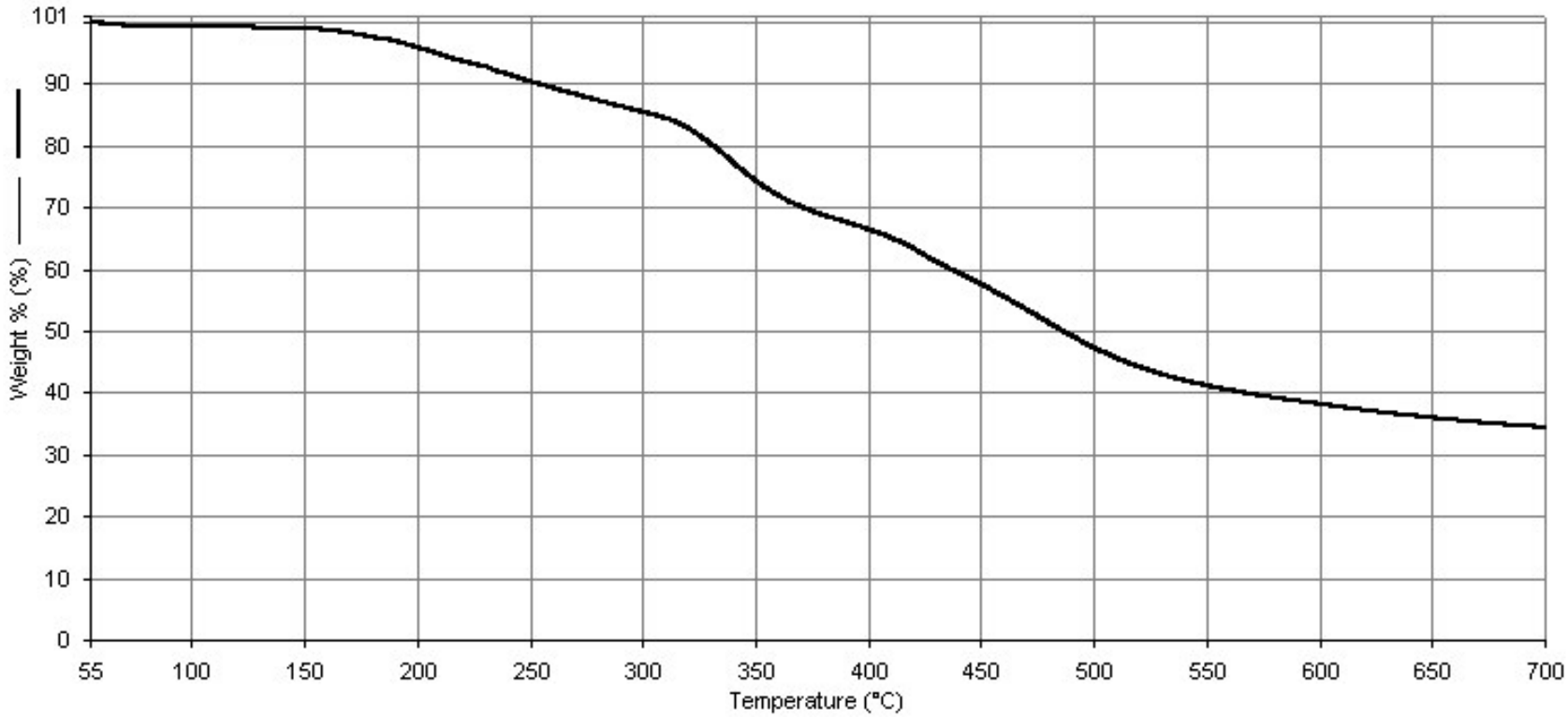

Figure S11. TGA of {[(η^6-cym)Ru(Q^{CH2Cl})]$_4$(OTf)}(OTf)$_3$ (**4**).

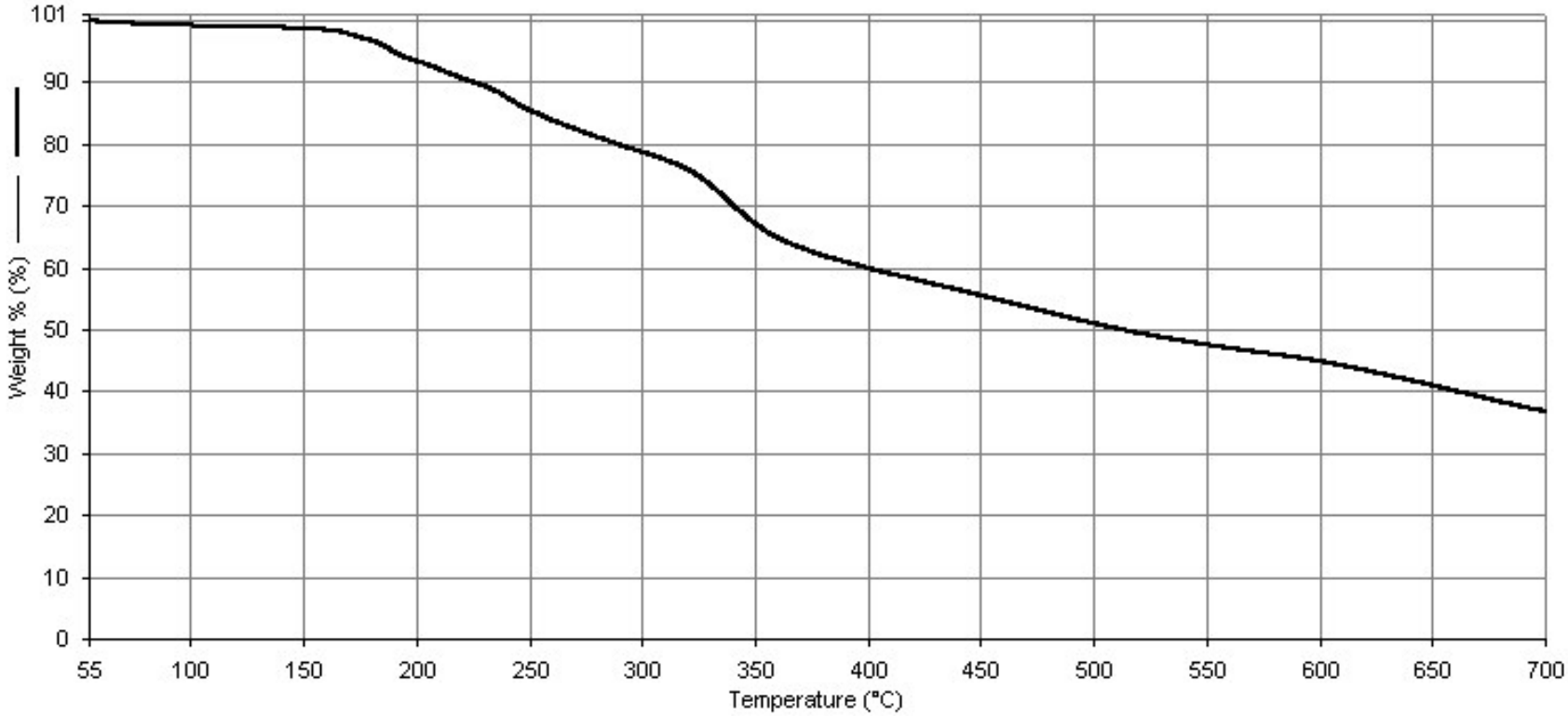

Figure S12. TGA of {[(η^6-cym)Ru(Q^{CH2Cl})]$_4$(BF_4)}(BF_4)$_3$ (**5**).

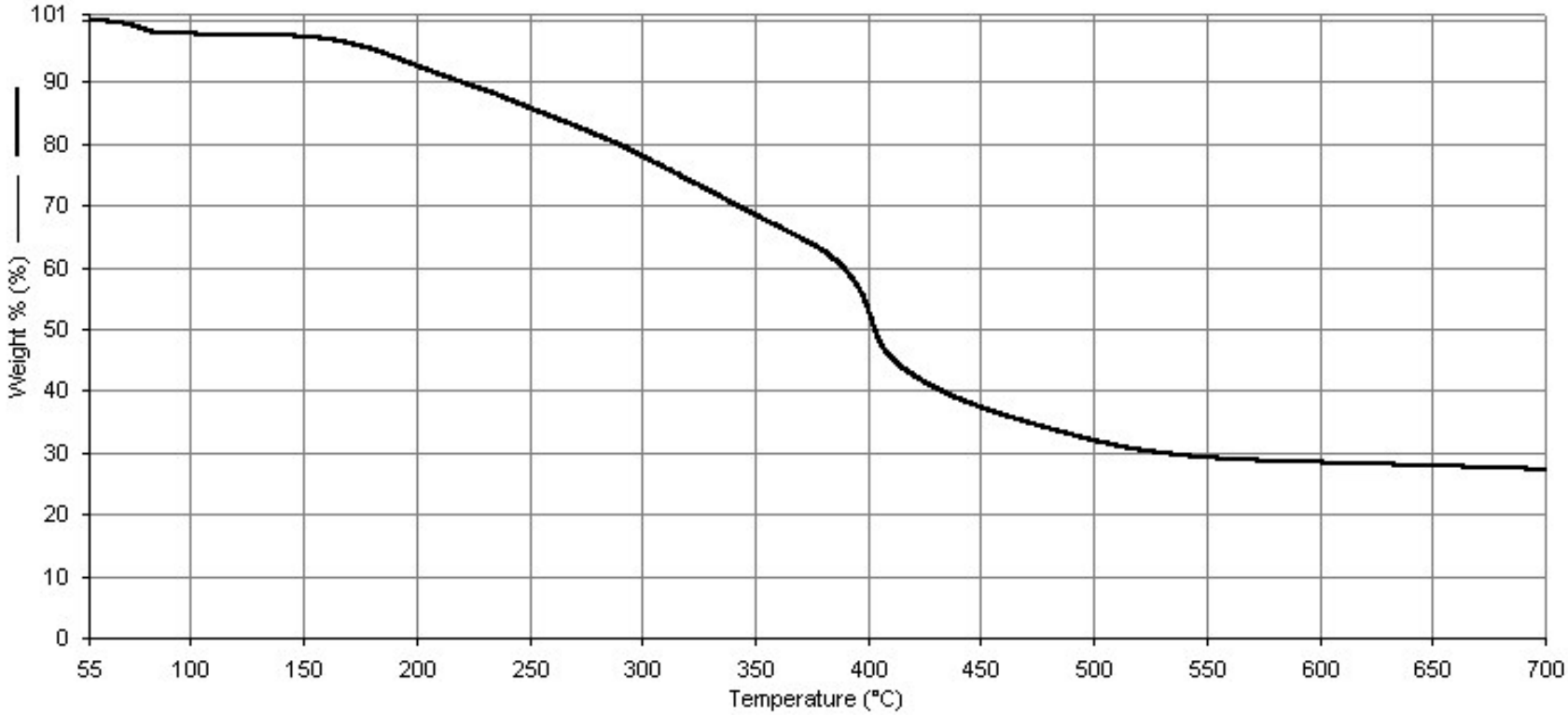

Figure S13. TGA of {[(η^6-cym)Ru(Q^{hex})]$_4$(OTf)}(OTf)$_3$ (**6**).

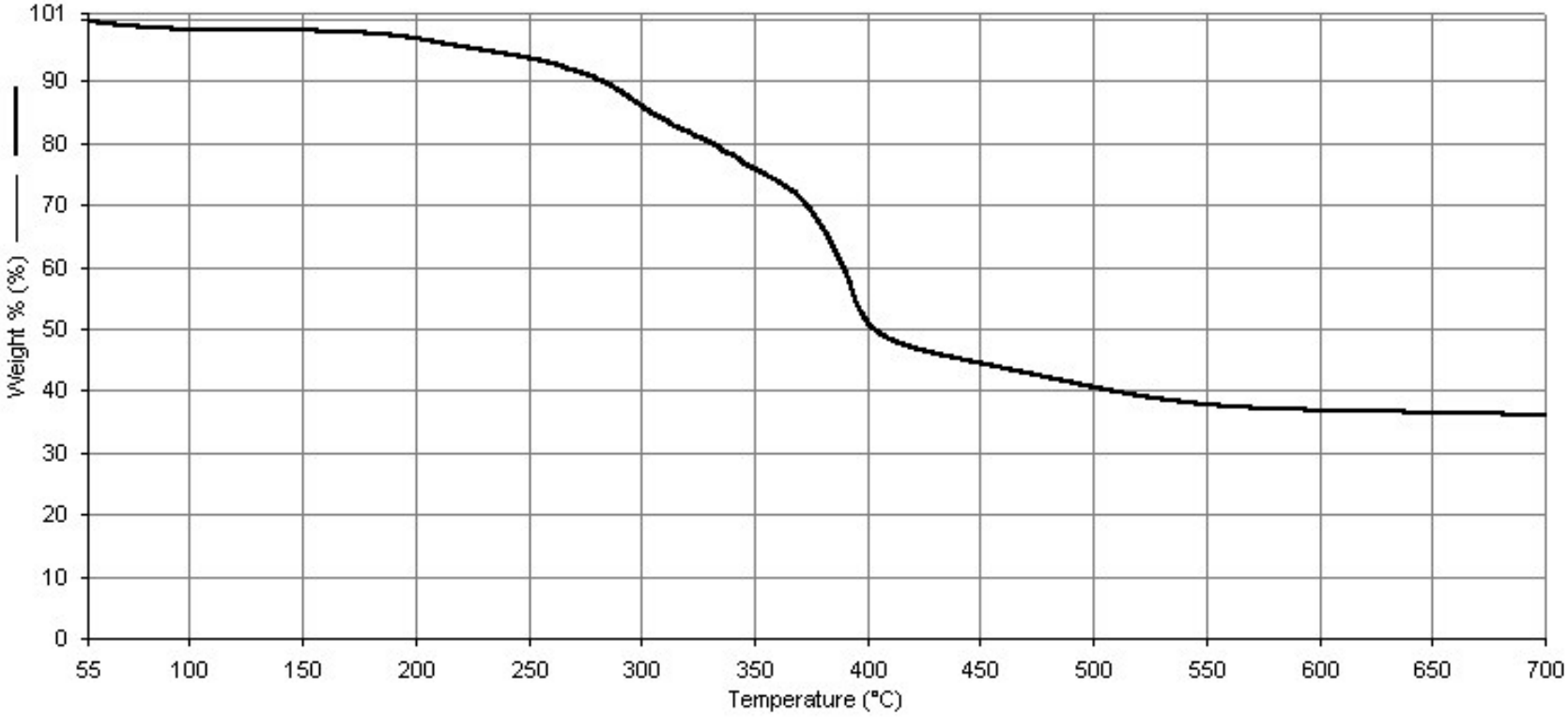

Figure S14. TGA of {[(η^6-cym)Ru(Q^{nPe})]$_4$(OTf)}(OTf)$_3$ (**7**).