Ruthenium(II) Complexes of N-Heterocyclic Carbenes Derived from Imidazolium-linked Cyclophanes

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Supporting Information

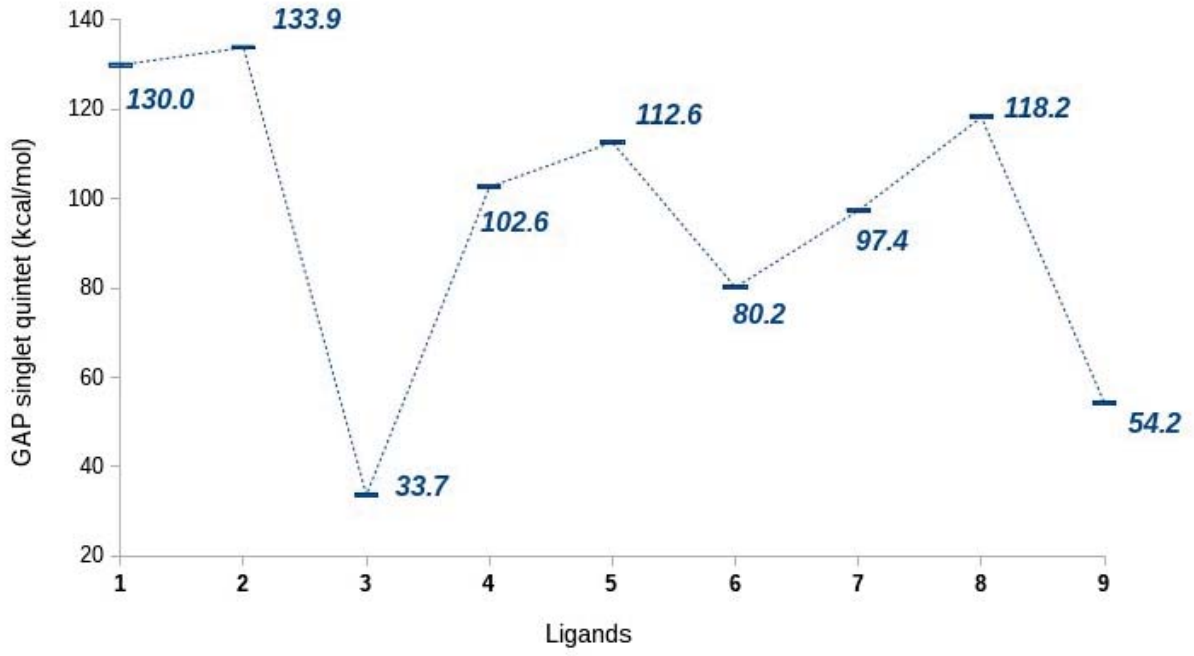
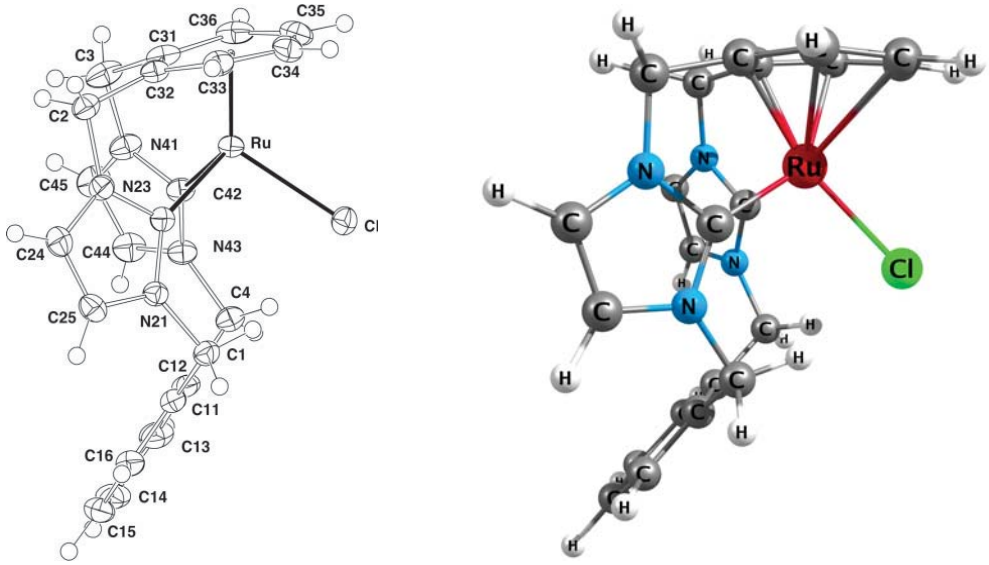


Figure S1. Singlet quintet gaps in kcal/mol for the NHC and PHC-cyclophane ligands 1-9, obtained with BP86/def2-TZVP.



(a) (b)

Figure S2. (a) Crystallographic,[13] and (b) calculated geometric parameters of 1. the geometry optimization was performed by employing BP86-D3/def2-TZVP as level of theory.

Table S1. Selected bond distances (Å) and angles (°) of **1.** Crystallographic[13] and calculated (BP86-D3/def2-TZVP) values are reported.

Parameters	Experimental (x-ray)	Calculated	$\lvert D_i \rvert$
Ru-C(31)	2.091	2.096	0.005
Ru-C(32)	2.094	2.096	0.002
Ru-C(33)	2.274	2.309	0.035
Ru-C(34)	2.330	2.376	0.046
Ru-C(35)	2.333	2.376	0.043
Ru-C(36)	2.271	2.309	0.038
Ru-(X)[a]	1.724	1.756	0.032
Ru-Cl	2.430	2.386	0.044
Ru-C(22)	2.038	2.008	0.030
Ru-C(42)	2.034	2.008	0.026
(X)-Ru-Cl	122.7	125.9	3.2
(X)-Ru-C(22)	122.8	120.7	2.1
(X)-Ru-C(42)	120.9	120.7	0.2
Cl-Ru-C(22)	99.71	98.40	1.31
Cl-Ru-C(42)	99.27	98.40	0.87
C(22)-Ru-C(42)	82.56	82.80	0.24

[a] X, centroid of ring C(31)-C(36), experimental value obtained from the supporting information of ref. [13]).

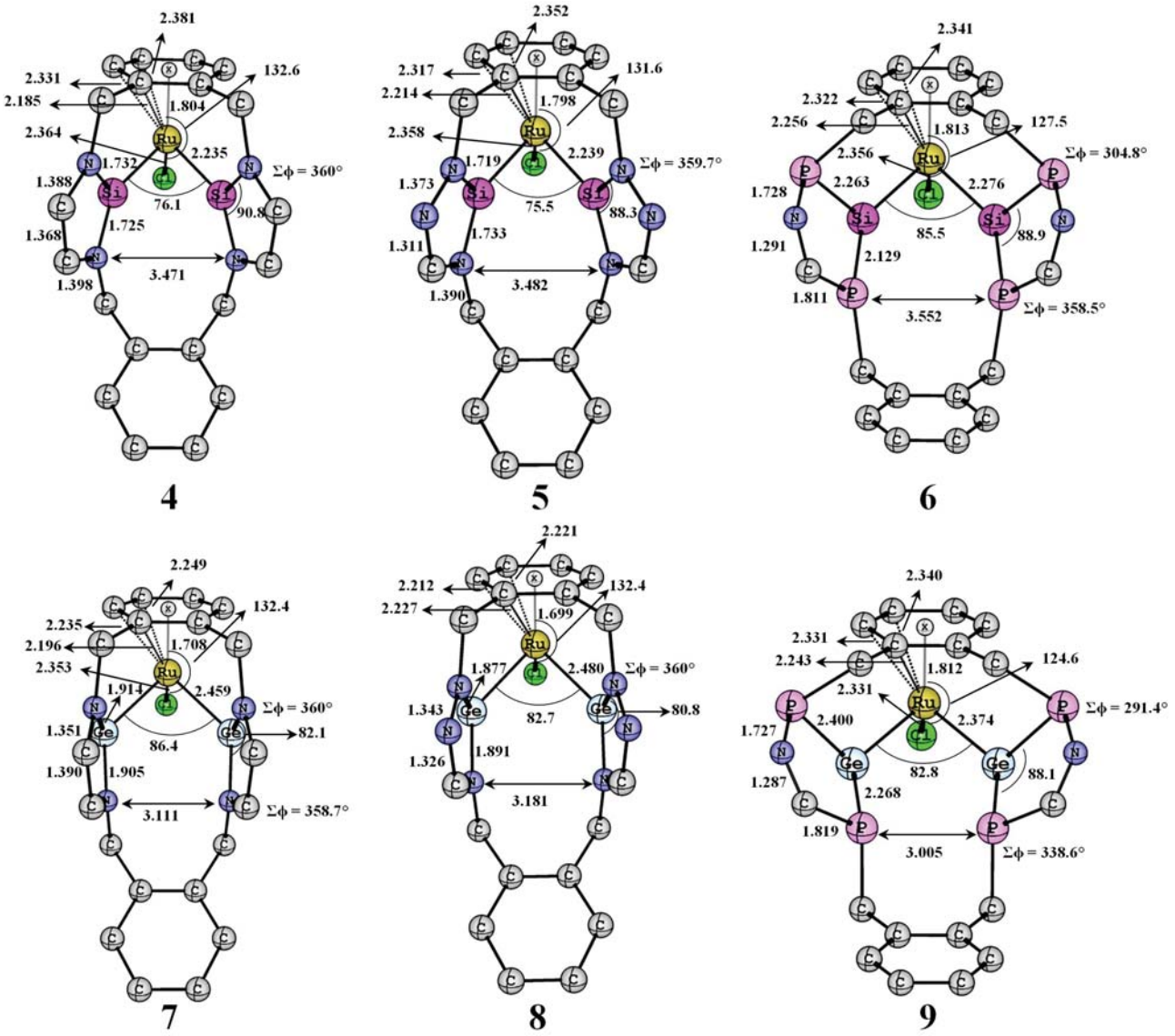


Figure S3. Optimized structures of complexes **4-9**, employing BP86-D3/def2-TZVP as level of theory. .

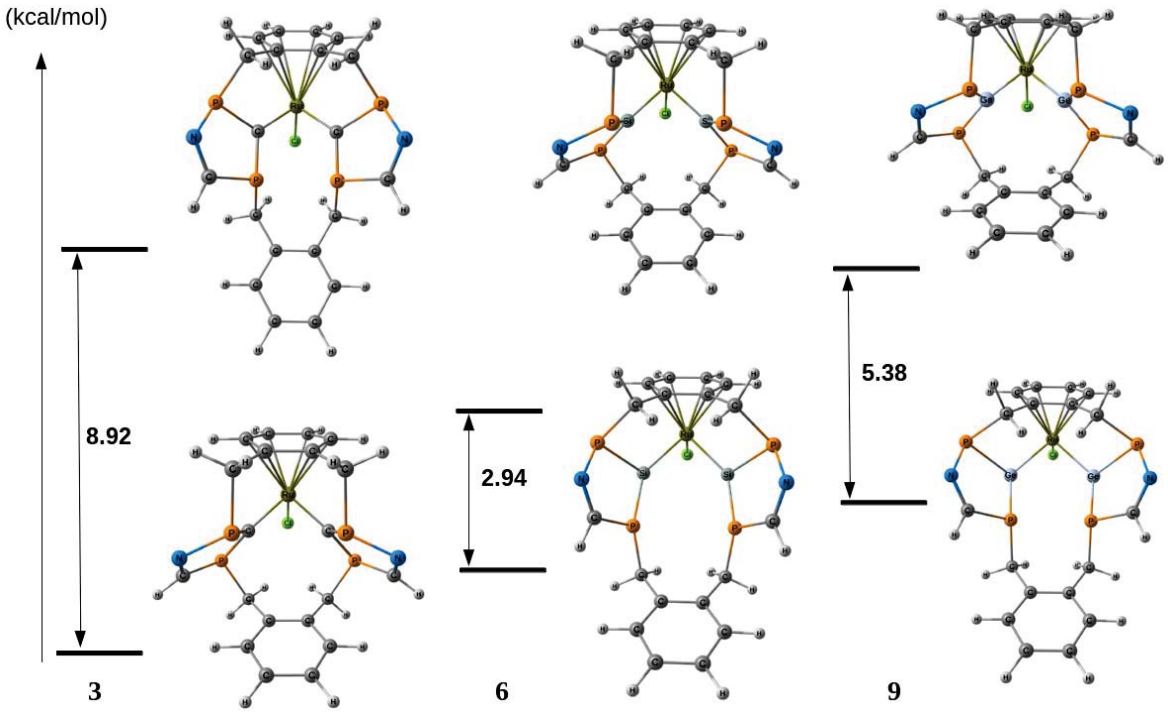


Figure S4. Difference of energy between the conformers of **3**, **6**, and **9**.

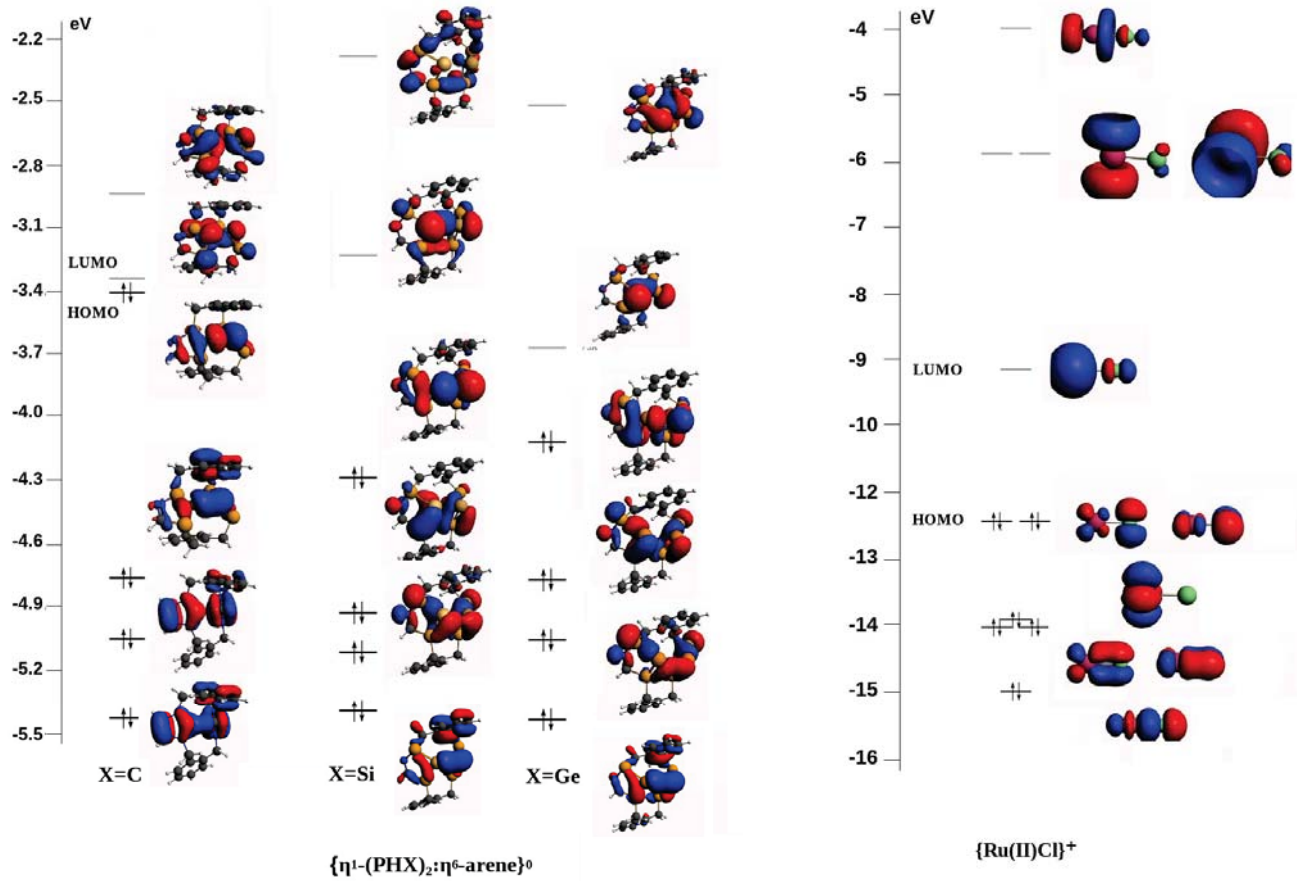


Figure S5. Quantitative diagram of the frontier orbitals for the interacting fragments in **3**, **6**, and **9**.

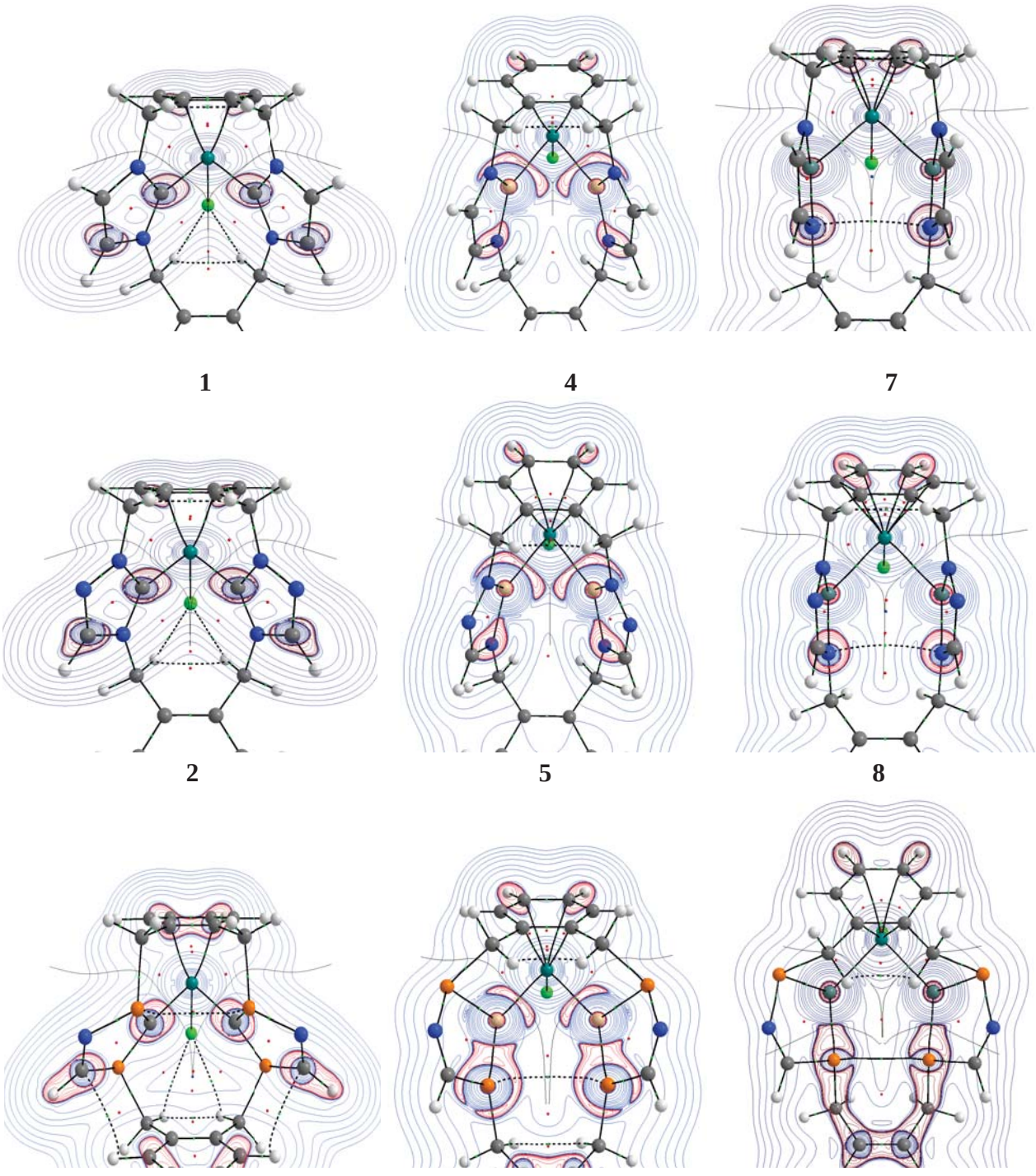


Figure S6. Electron density laplacian plots of complexes **1-9**.

Table S2. Main configurations of the ground state for ligands **1**(big) and **1**(small) at the CASSCF/def2-SVP//BP86-D3/def2-TZVP level of theory.

1(big)		**1**(small)	
CASSCF(8,10)	Coefficient	CASSCF(8,9)	Coefficient
2222000000	0.9240065	222200000	0.9471475
2220200000	-0.1632301	222020000	-0.1002368
0222000200	-0.0830546	202200020	-0.0952048
0222002000	-0.0805434	220202000	-0.0946385
2202020000	-0.0737214	022200200	-0.0835065
22baab0000	-0.0666985	222002000	-0.0830747
22abba0000	-0.0666985	220220000	-0.0825133
ba2200ab00	0.0624262	22ab20000	-0.0730381
ab2200ba00	0.0624262	22ba20000	0.0730381
ba2200ba00	-0.0616595	22ab02000	0.0709064
ab2200ab00	-0.0616595	22ba02000	-0.0709064
2ab2020000	0.0587528	202200002	-0.0624841
2ba2020000	-0.0587528	22abba000	-0.0540015
2a2bba0000	-0.0566260	22baab000	-0.0540015
2b2aab0000	-0.0566260	22abab000	0.0527733
2b2aab0000	-0.0561884	22baba000	0.0527733

Table S3. Main configurations of the ground state for ligands **3**(big) and **3**(small) at the CASSCF/def2-SVP//BP86-D3/def2-TZVP level of theory.

3(big)		**3**(small)	
CASSCF(20,12)	Coefficient	CASSCF(12,8)	Coefficient
222222222200	0.9612948	22222200	0.9620603
222222222020	-0.1012006	22222020	-0.1022103
222222222002	-0.0987634	22222002	-0.1000762
22222222baab	0.0948584	2222baab	-0.0952779
22222222abba	0.0948584	2222abba	-0.0952779
222222220220	-0.0894796	22220220	-0.0890284
22222222abab	-0.0840487	2222baba	0.0846448
22222222baba	-0.0840487	2222abab	0.0846448
222222220202	-0.0707092	22220202	-0.0709982

References

13 . Baker, M. V.; Brown, D. H.; Haque, R. A.; Skelton, B. W.; White, A. H. *Dalton Trans.* **2010**, *39*, 70-72.