The Chemistry of High Valent Tungsten Chlorides with *N*-Substituted Ureas, Including Urea Self-Protonation Reactions Triggered by WCl_6

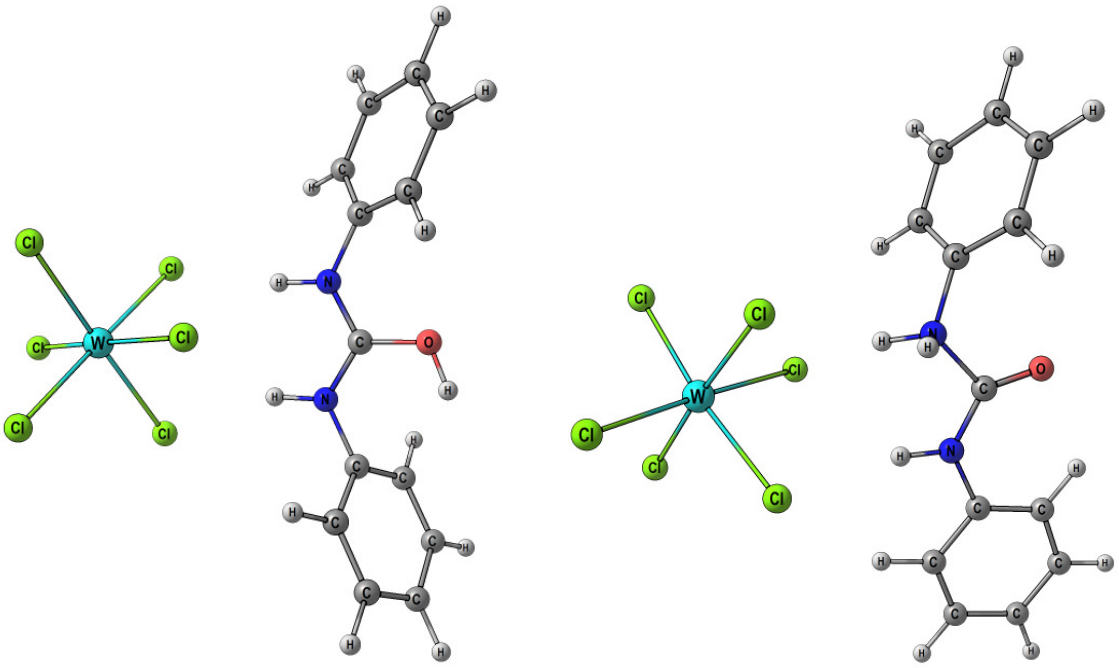
Marco Bortoluzzi, Fabio Marchetti, Guido Pampaloni, Stefano Zacchini

New Journal of Chemistry

Supporting Information

Table of contents *Page*

Figure S1. DFT-optimized geometries of the *O*- and *N-protonated* isomers of **2** and relative Gibbs energies. ωB97X DFT functional, C-PCM solvation model for dichloromethane.



O-protonated (0 kcal mol^{-1}) ***N-protonated*** (+4.4 kcal mol^{-1})

Table S1. Selected computed bond lengths (Å) and angles (°) for the *O*- and *N-protonated* isomers of **2**.

2 (*O-protonated*)		**2 (*N-protonated*)**	
C–O	1.309	C–O	1.200
C–N	1.323	C–NH	1.337
	1.330	C–NH_2	1.537
N–H	1.019	N–H (*NH*)	1.012
	1.019	N–H (NH_2)	1.028
O–H	0.971		1.036
W–Cl	2.272	W–Cl	2.256
	2.309		2.294
	2.311		2.309
	2.315		2.351
	2.391		2.371
	2.399		2.422
H---$Cl_{shortest}$	2.292	H---$Cl_{shortest}$	2.212
	2.342		2.527
N–C–O	117.5	HN–C–O	131.8
	121.3	H_2N–C–O	118.7
N–C–N	121.2	N–C–N	109.5

Figure S2. DFT-optimized geometry of $[dpu]^{2+}$ (triplet state) and spin density surface (isovalue = 0.01 a.u.). ωB97X DFT functional, C-PCM solvation model for dichloromethane.

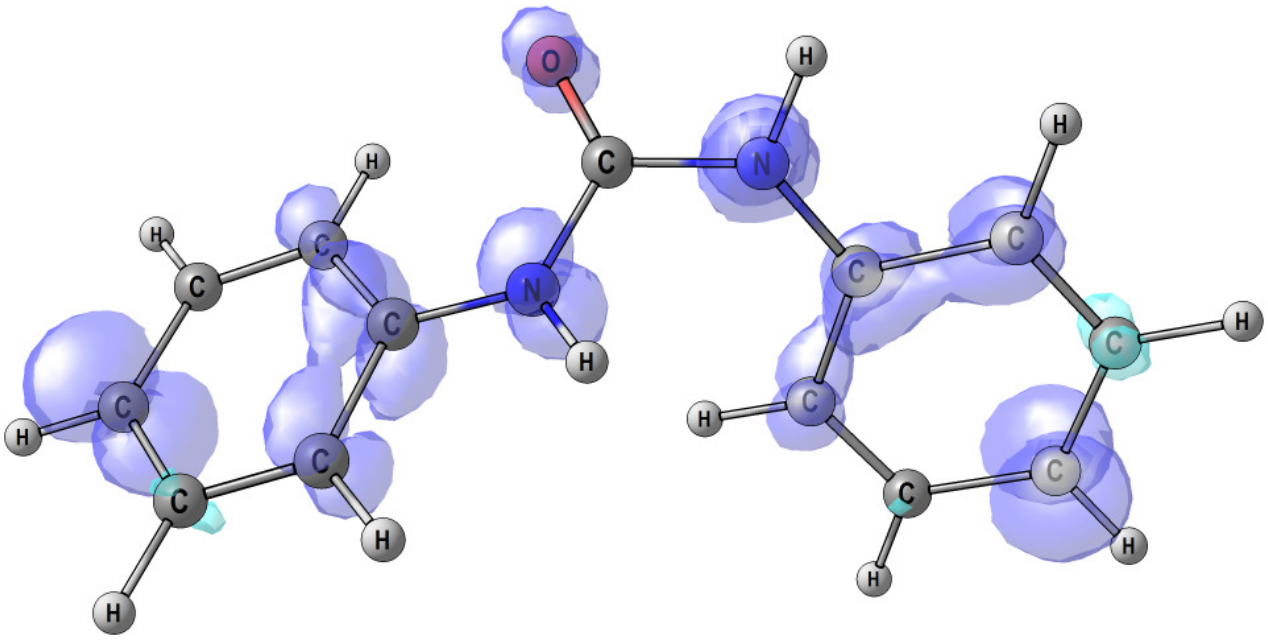


Table S2. Selected computed bond lengths (Å) and angles (°) for $[dpu]^{2+}$ (triplet state).

	$[dpu]^{2+}$
C–O	1.197
C–N	1.403
	1.421
N–H	1.017
	1.018
N–C–O	120.4
	125.1
N–C–N	114.4

Figure S3. DFT-optimized geometry of PhNC(O)NHPh and spin density surface (isovalue = 0.01 a.u.). ωB97X DFT functional, C-PCM solvation model for dichloromethane.

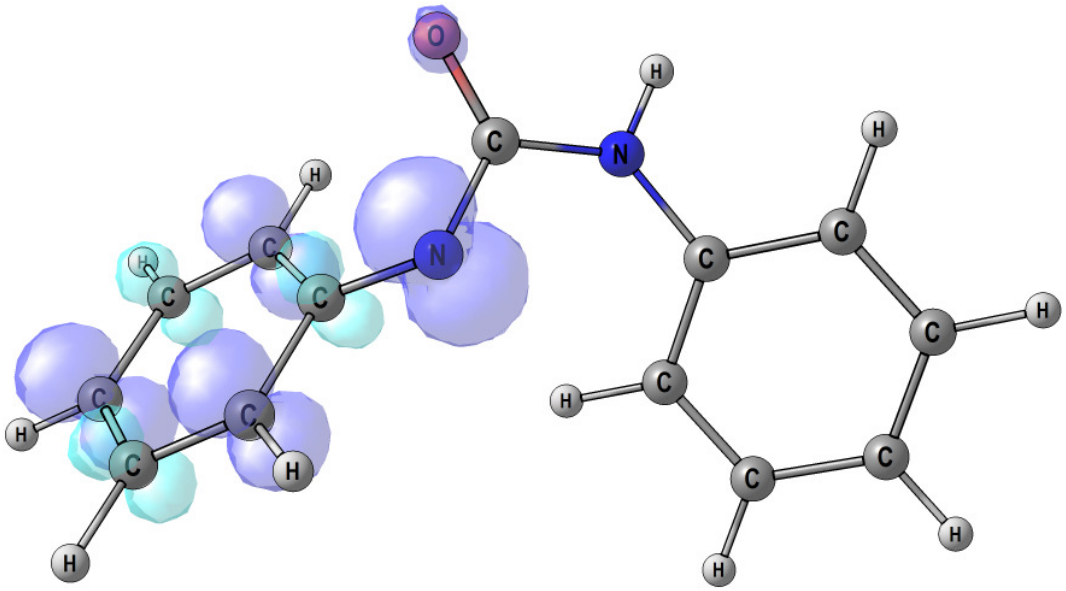


Table S3. Selected computed bond lengths (Å) and angles (°) for PhNC(O)NHPh.

PhNC(O)NHPh	
C–O	1.227
C–N	1.397
C–NH	1.368
N–H	1.011
N–C–O	123.5
HN–C–O	120.8
N–C–N	115.6

Figure S4. IR spectrum (solid state) of **1a**.

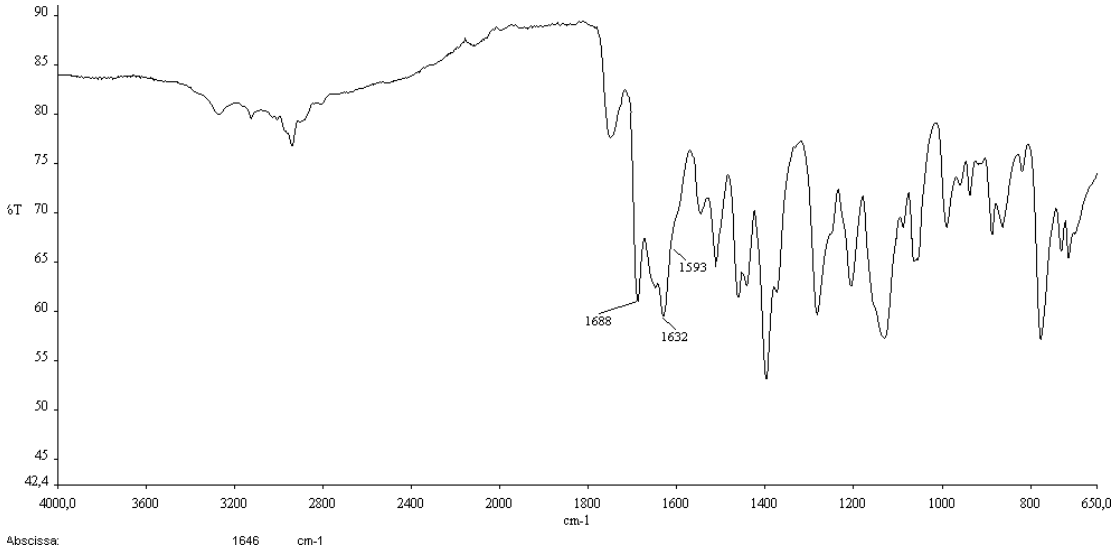


Figure S5. IR spectrum (solid state) of **1b**.

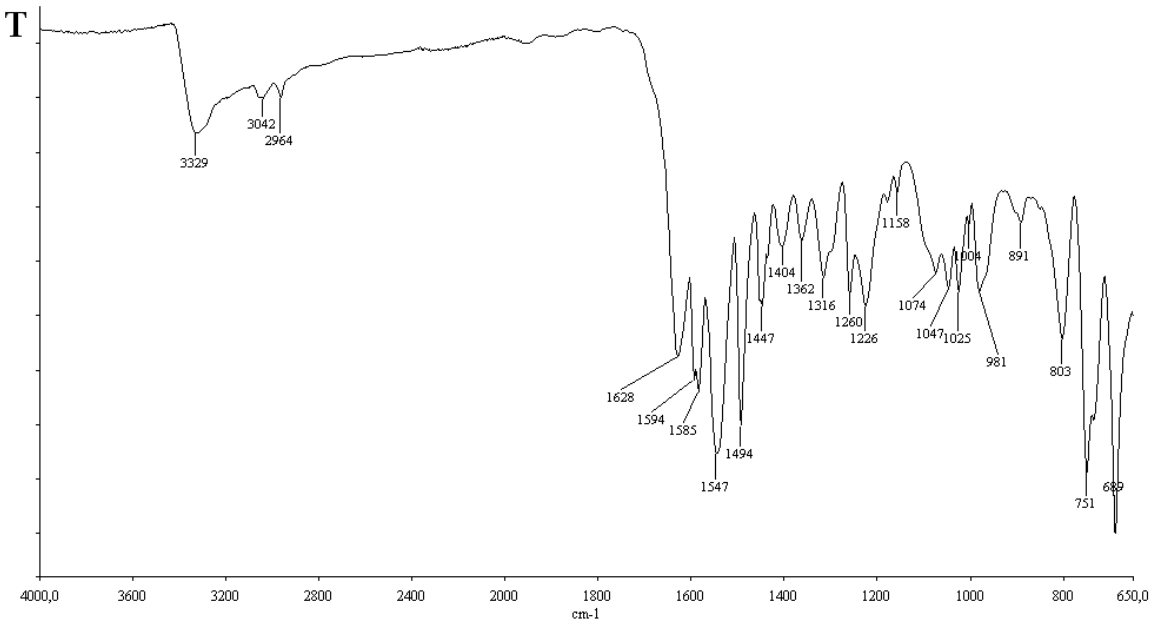


Figure S6. Comparative view of the IR spectra of **1b** (black) and 1,3-diphenylurea (dpu, red).

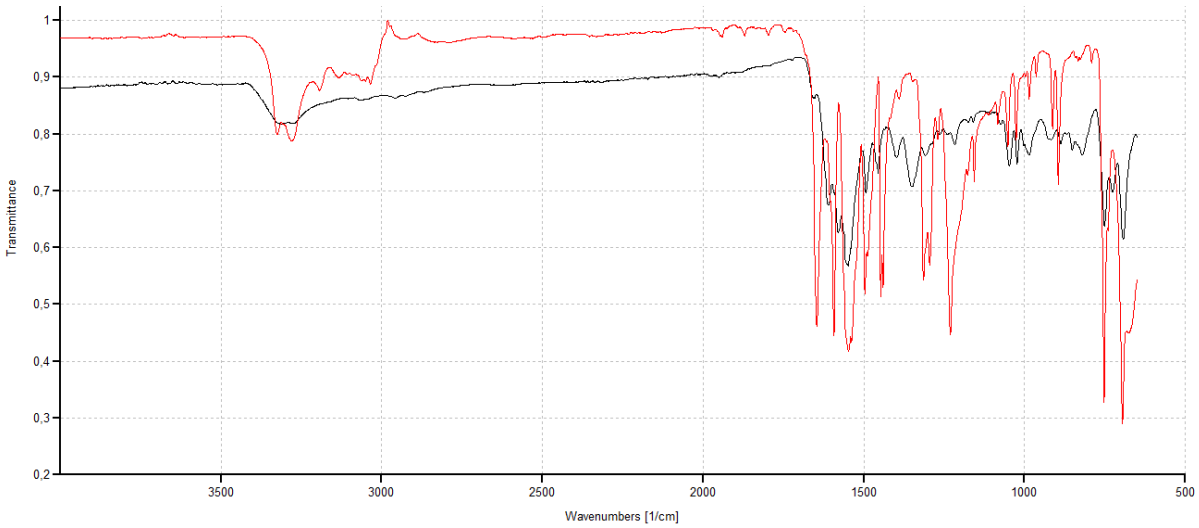


Figure S7. IR spectrum (solid state) of **2**.

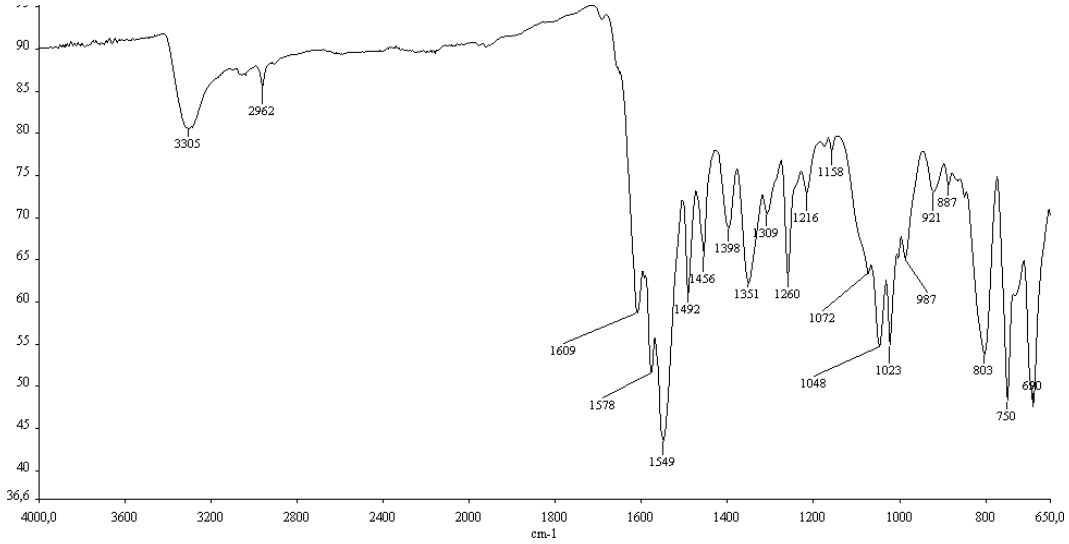


Figure S8. Comparative view of the IR spectra of **2** (black) and 1,3-diphenylurea (dpu, red).

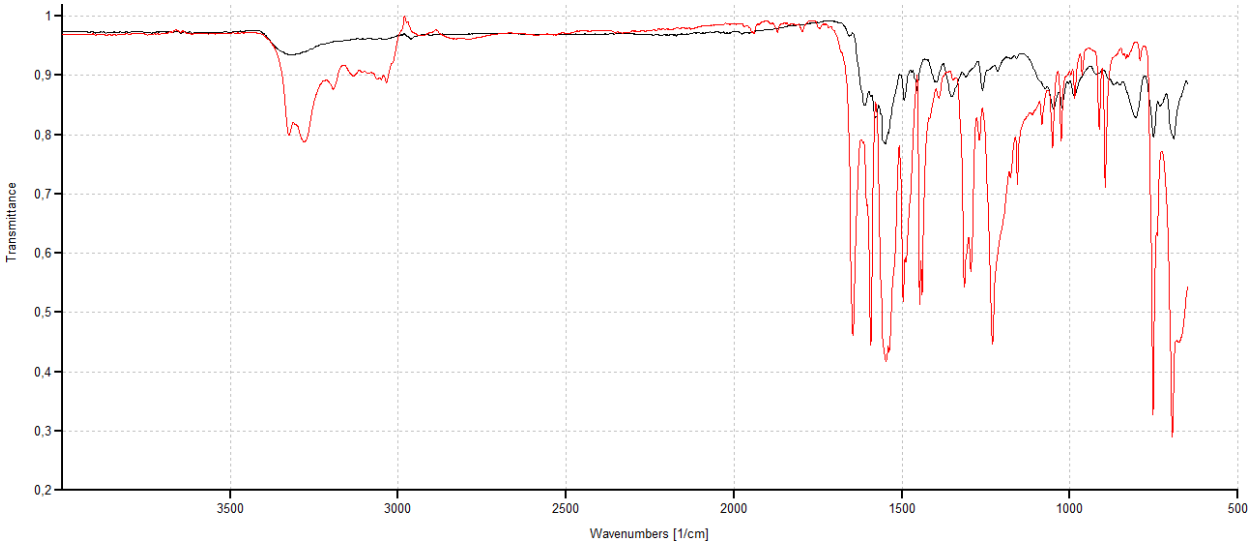


Figure S9. IR spectra (solid state) of **3a** (top) and 1,3-dimethylurea (bottom).

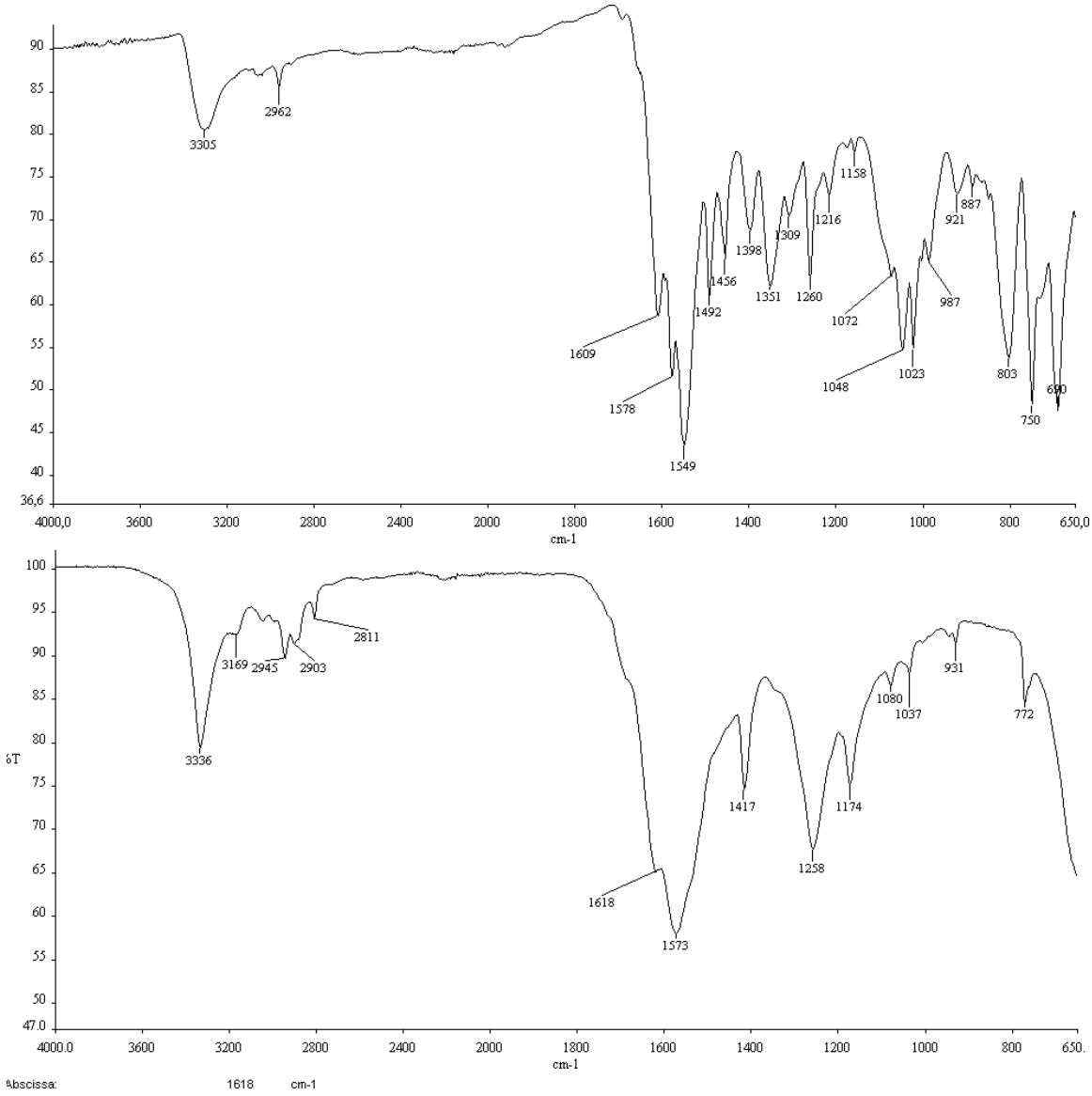


Figure S10. IR spectrum (solid state) of **3c**.

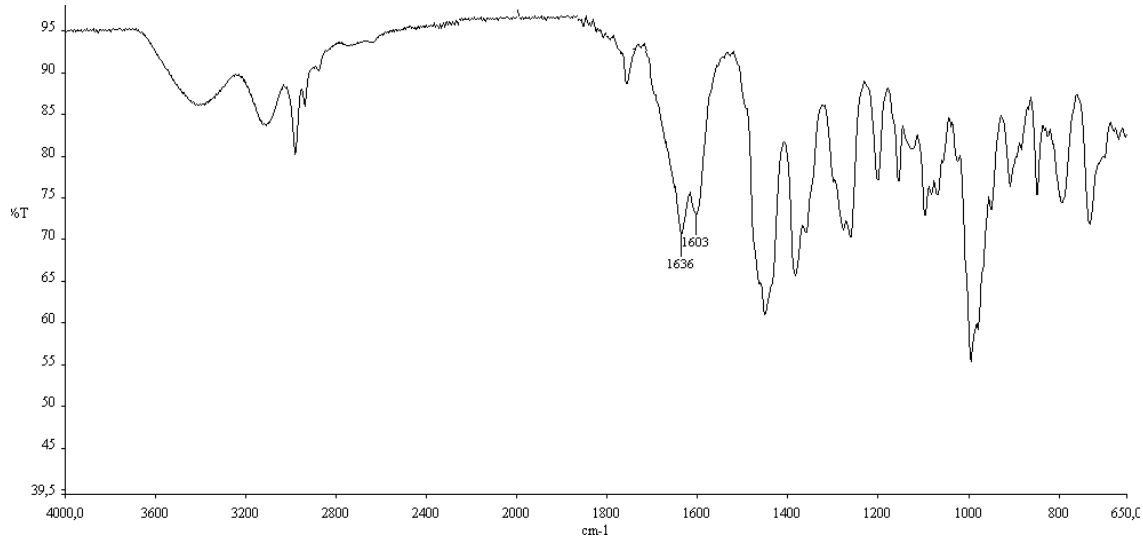


Figure S11. IR spectrum (solid state) of **4**.

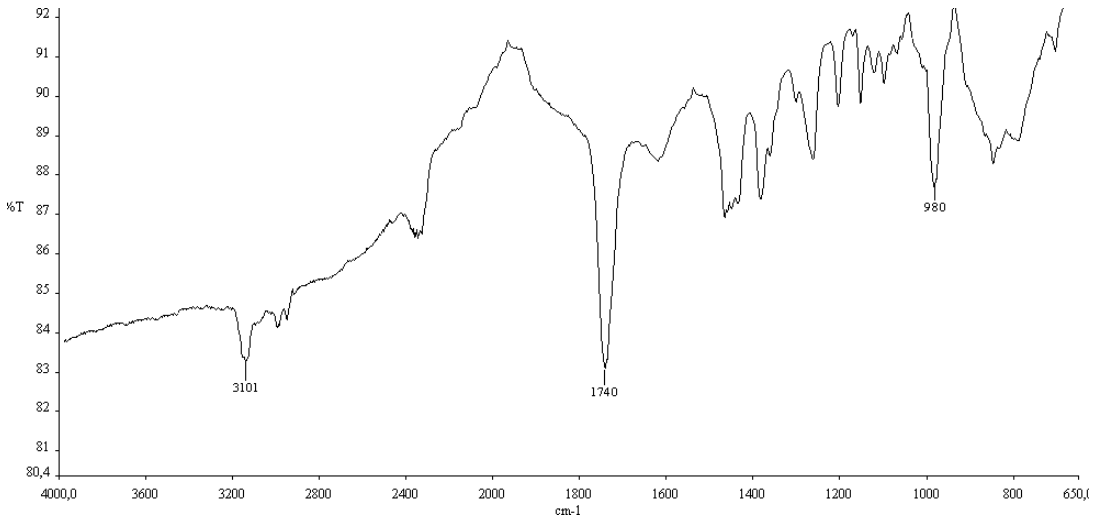


Figure S12. IR spectrum (solid state) of **5**.

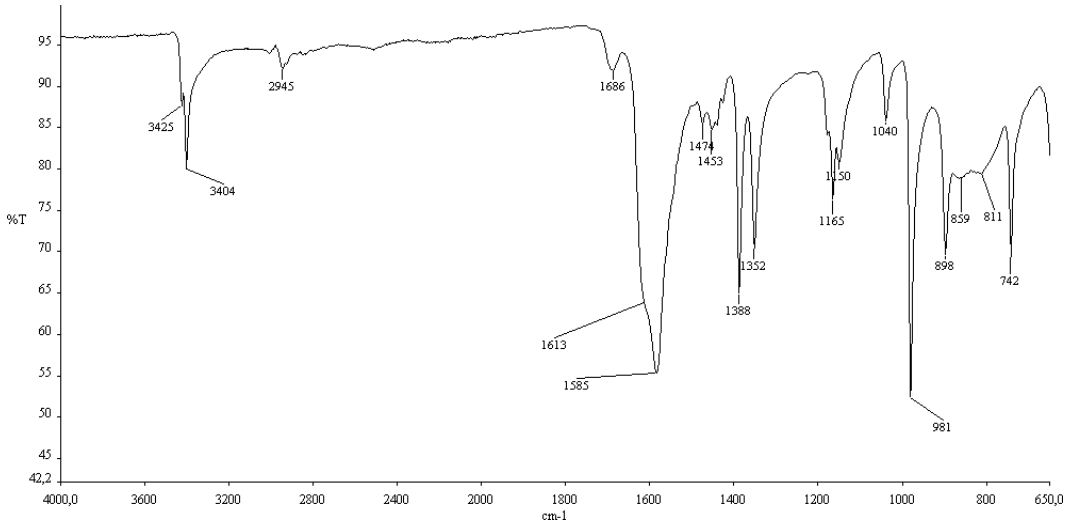


Figure S13. Comparative view of the IR spectra of **5** (black) and 1,3-dimethylurea (dmu, red).

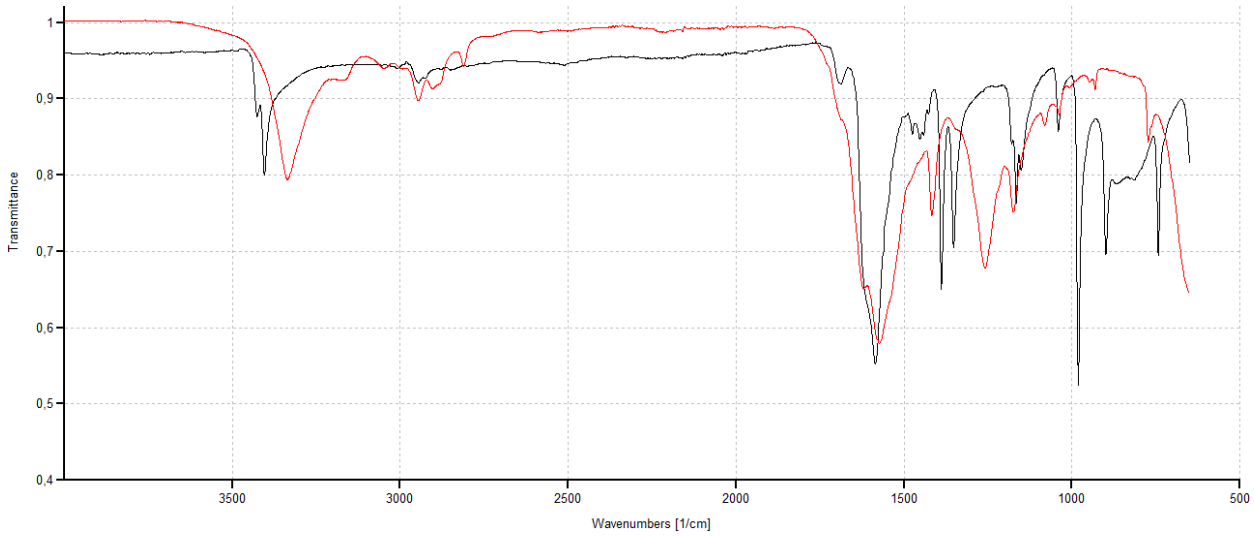


Figure S14. IR spectrum of the reaction mixture $WOCl_4$/dpu.