Catalysis Science & Technology

Electronic Supporting Information

Catalytic hydration of cyanamides with phosphinous acid-based ruthenium(II) and osmium(II) complexes: Scope and mechanistic insights

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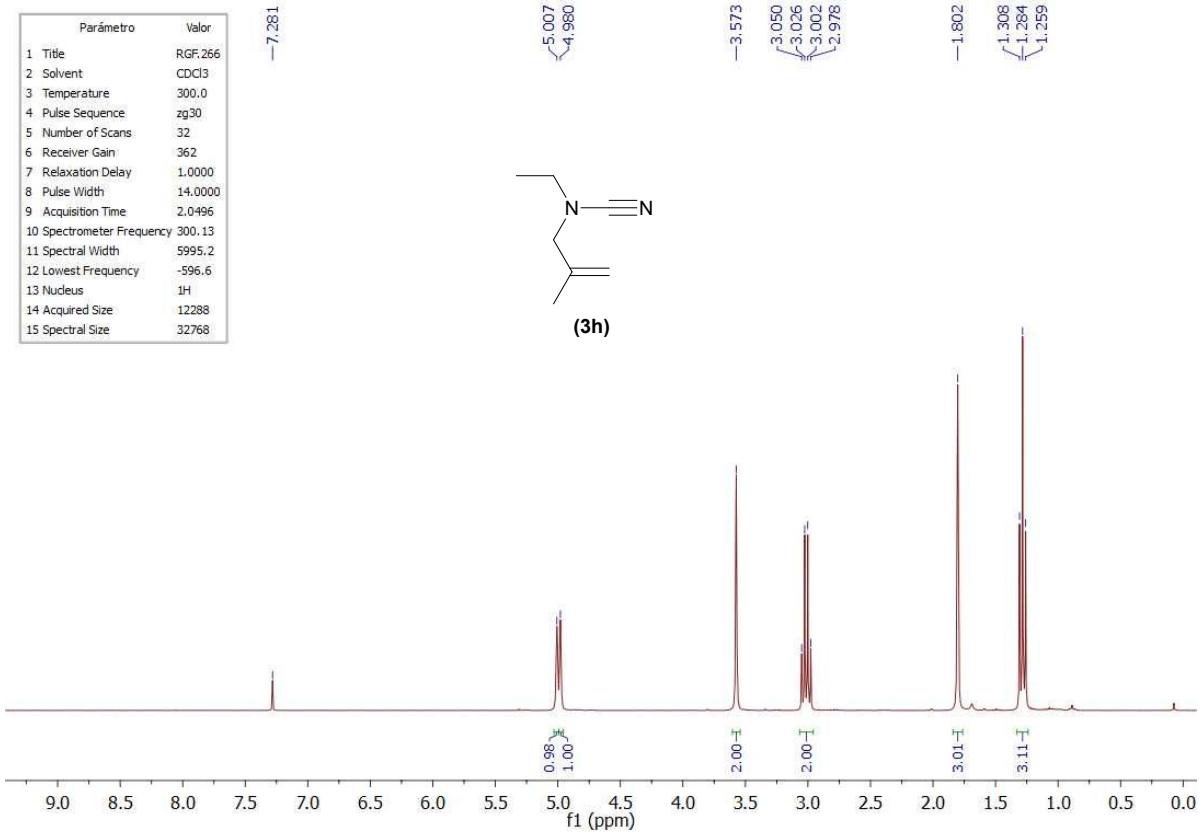

Figure S1. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of cyanamide **3h**.

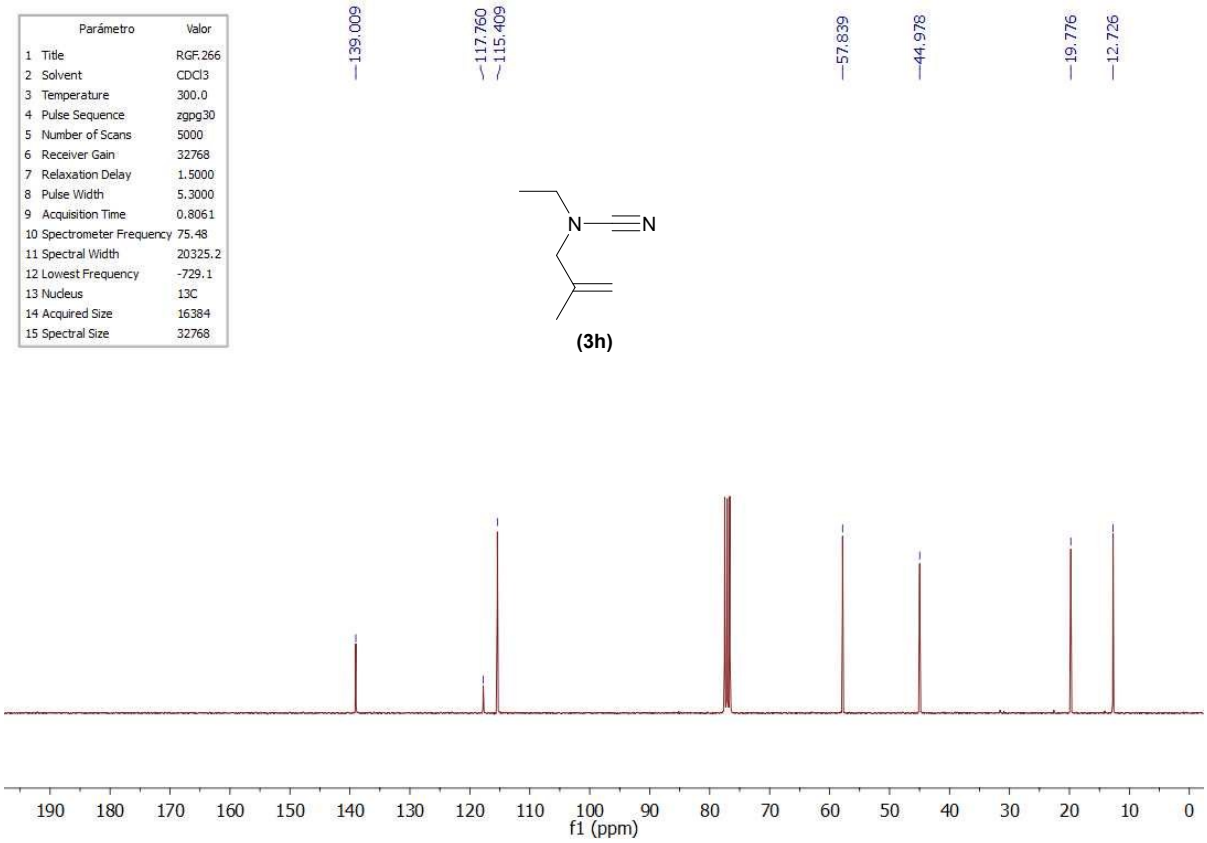

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 75 MHz) of cyanamide **3h**.

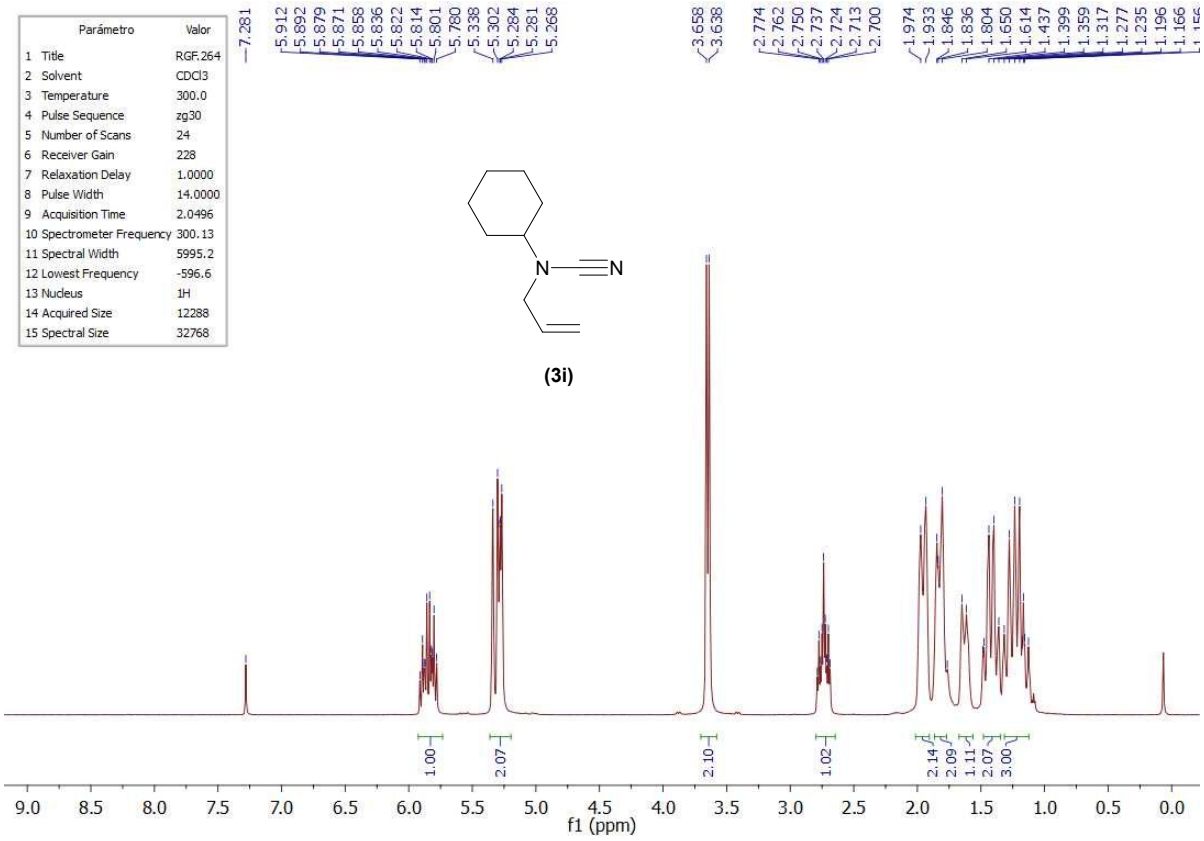

Figure S3. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of cyanamide **3i**.

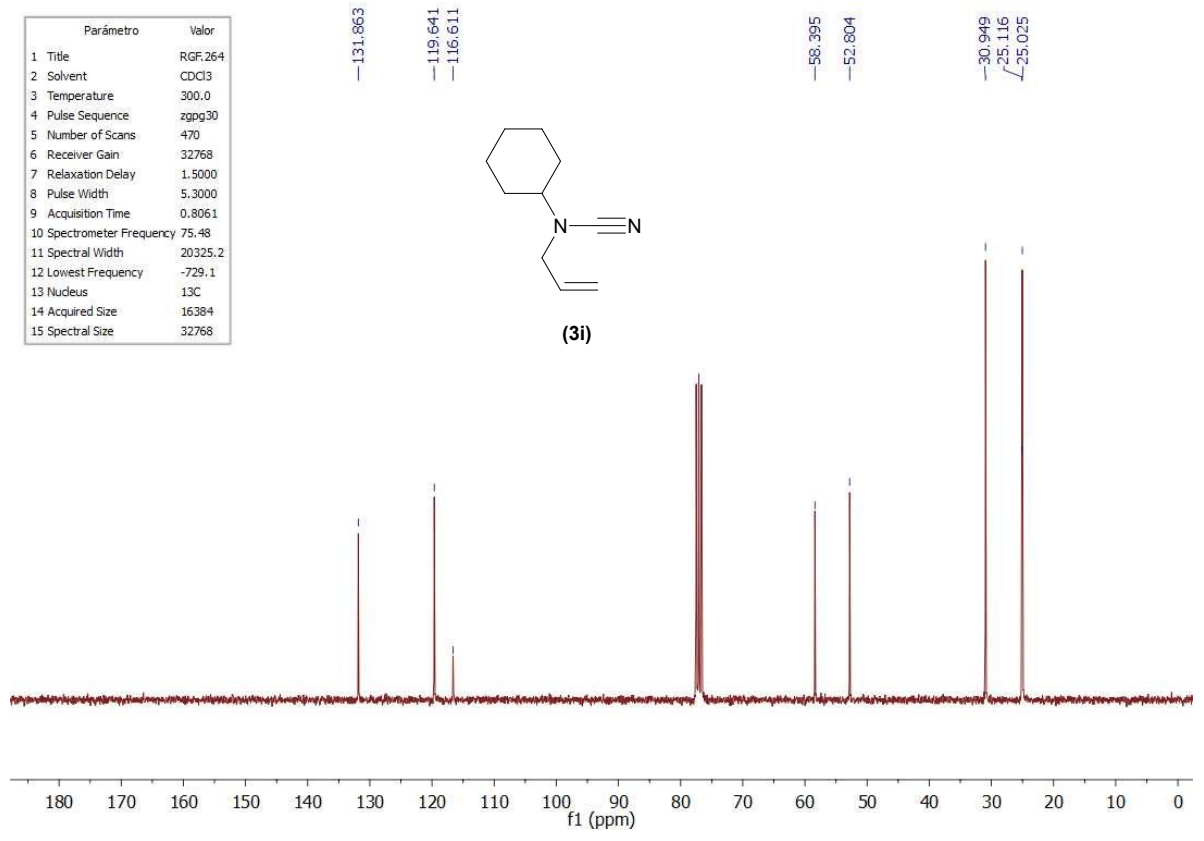

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 75 MHz) of cyanamide **3i**.

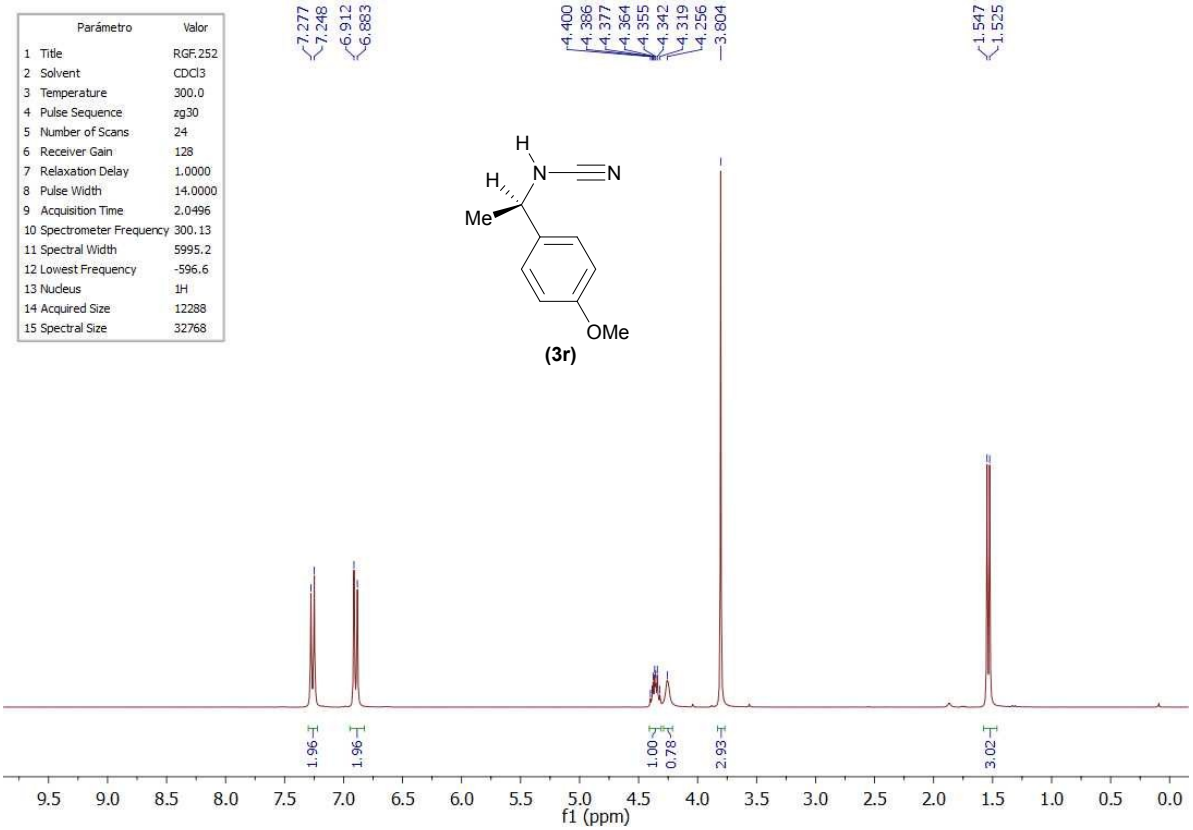

Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of cyanamide **3r**.

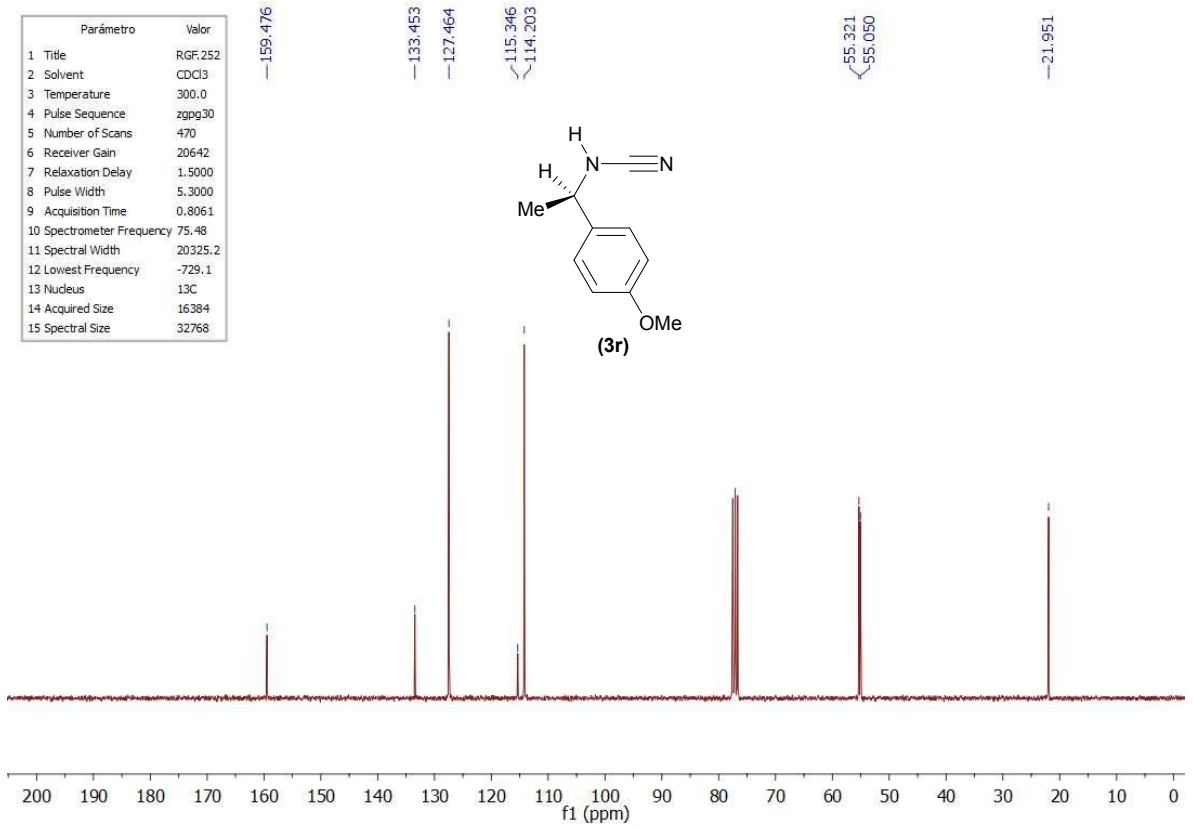

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 75 MHz) of cyanamide **3r**.

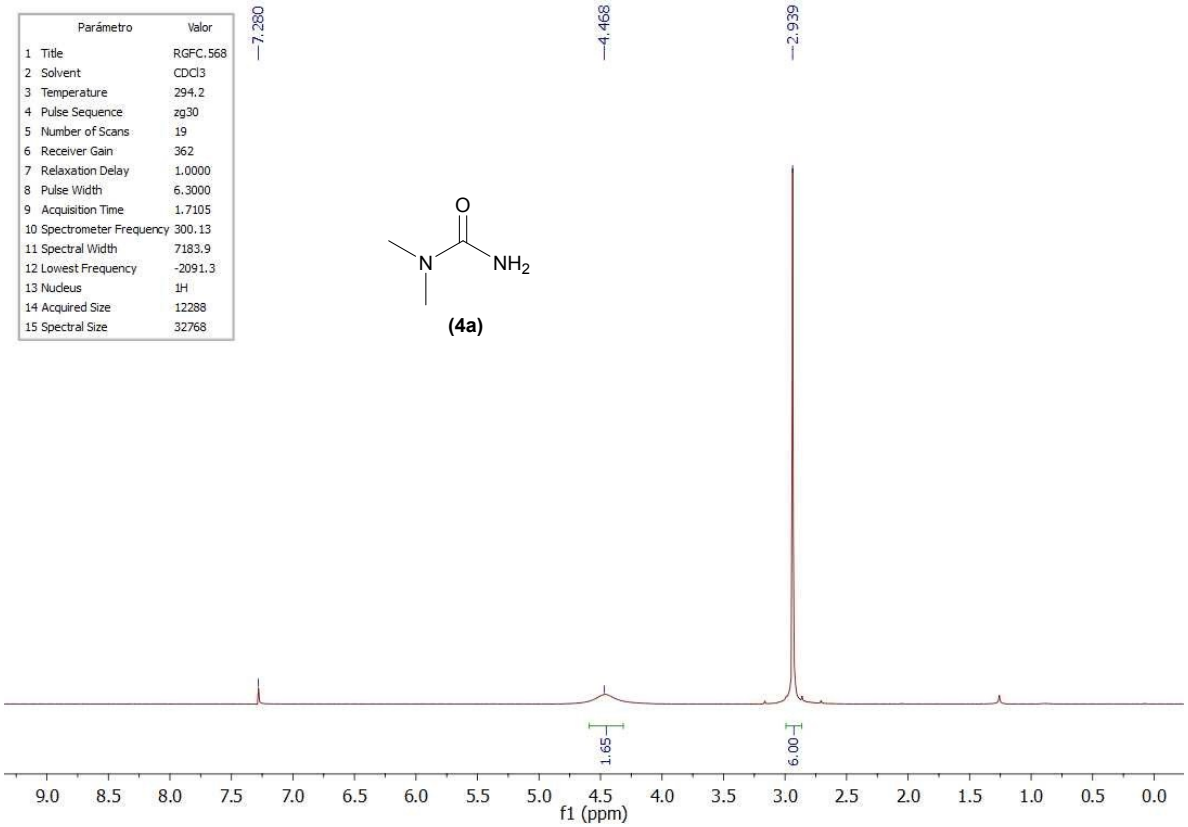

Figure S7. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of urea **4a**.

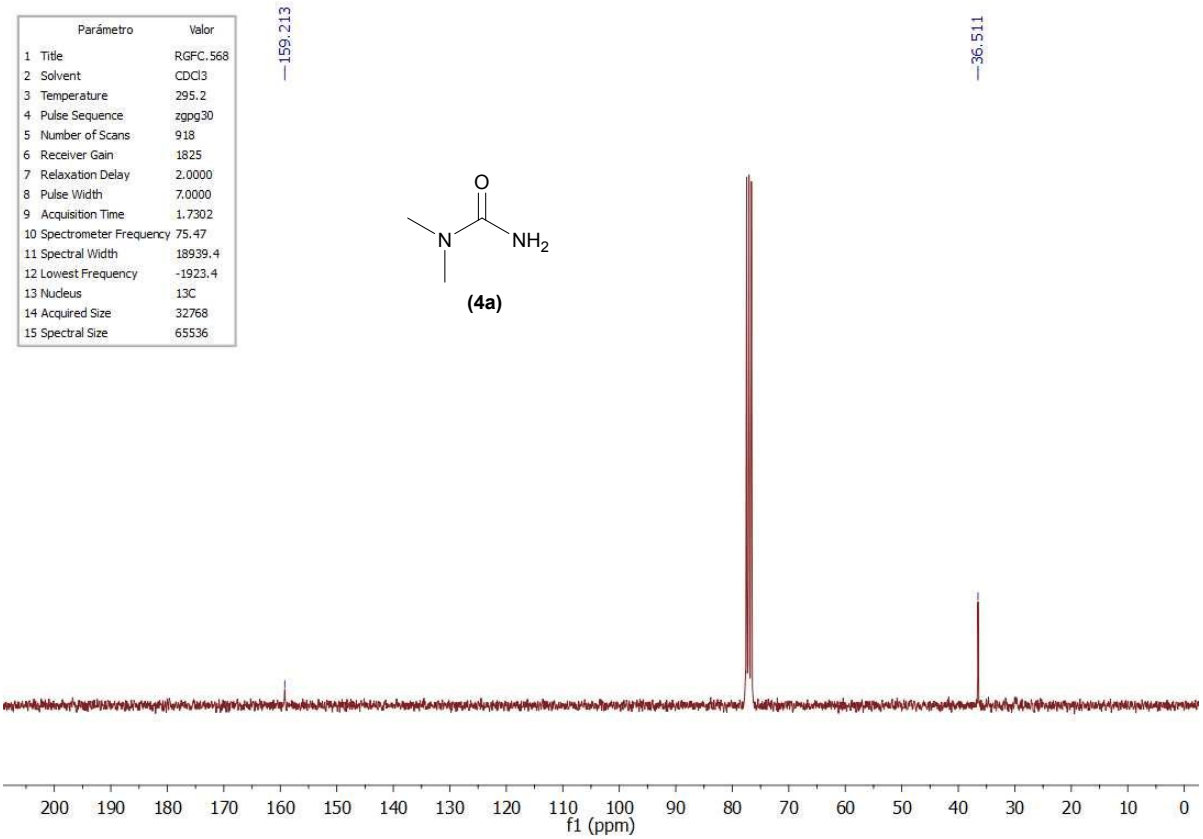

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 75 MHz) of urea **4a**.

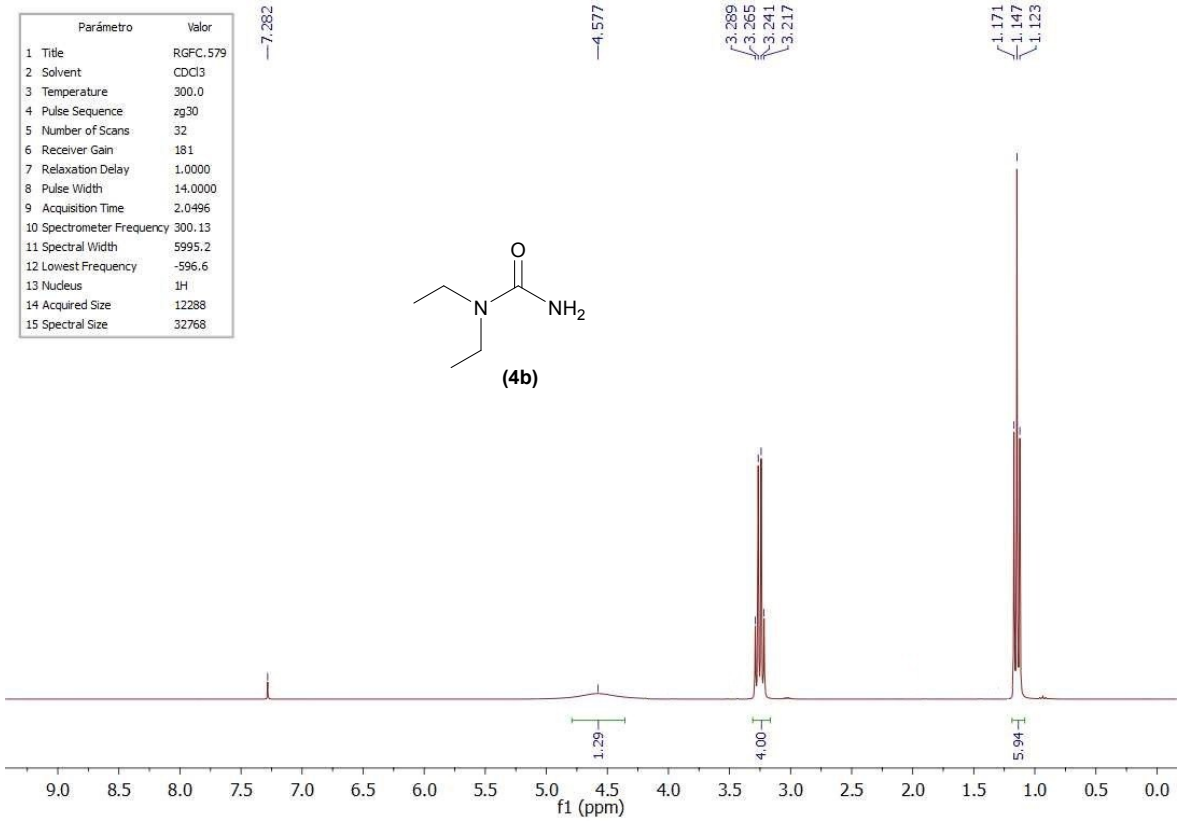

Figure S9. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of urea **4b**.

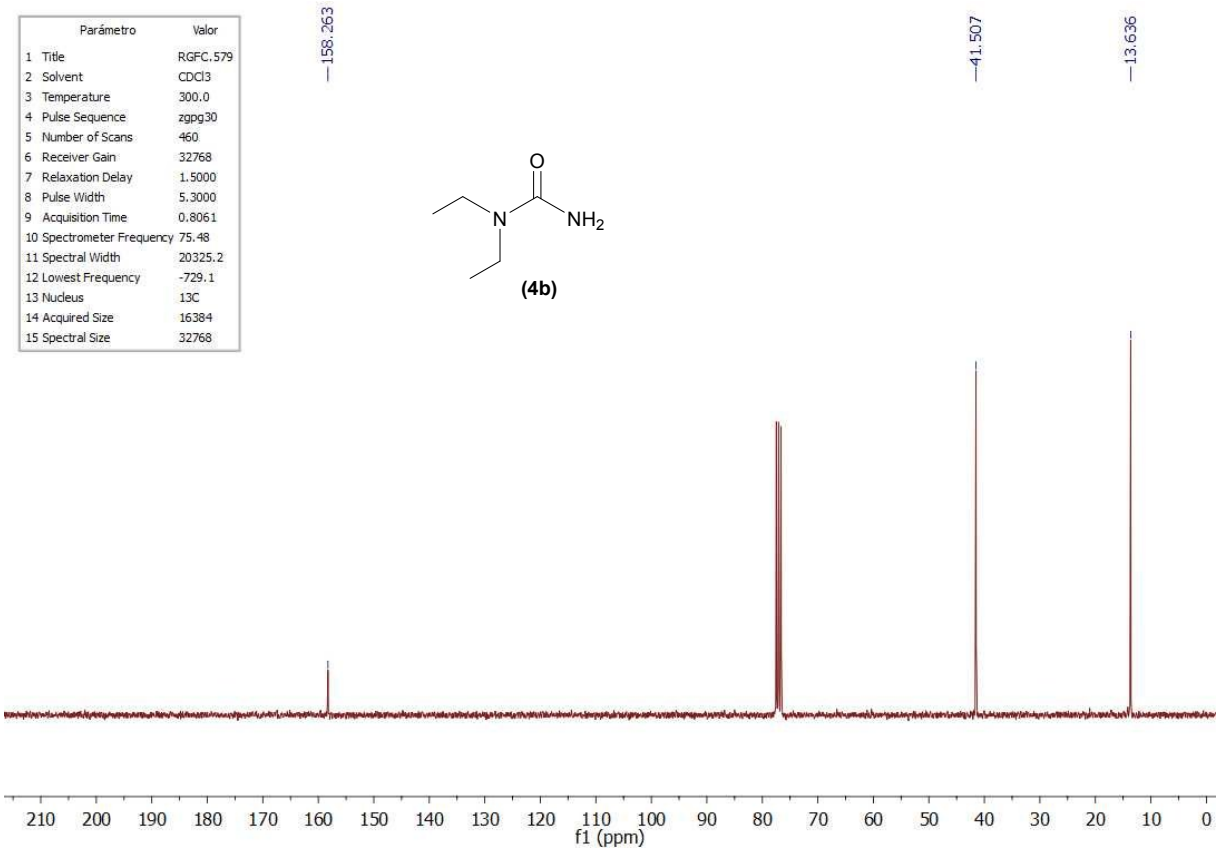

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 75 MHz) of urea **4b**.

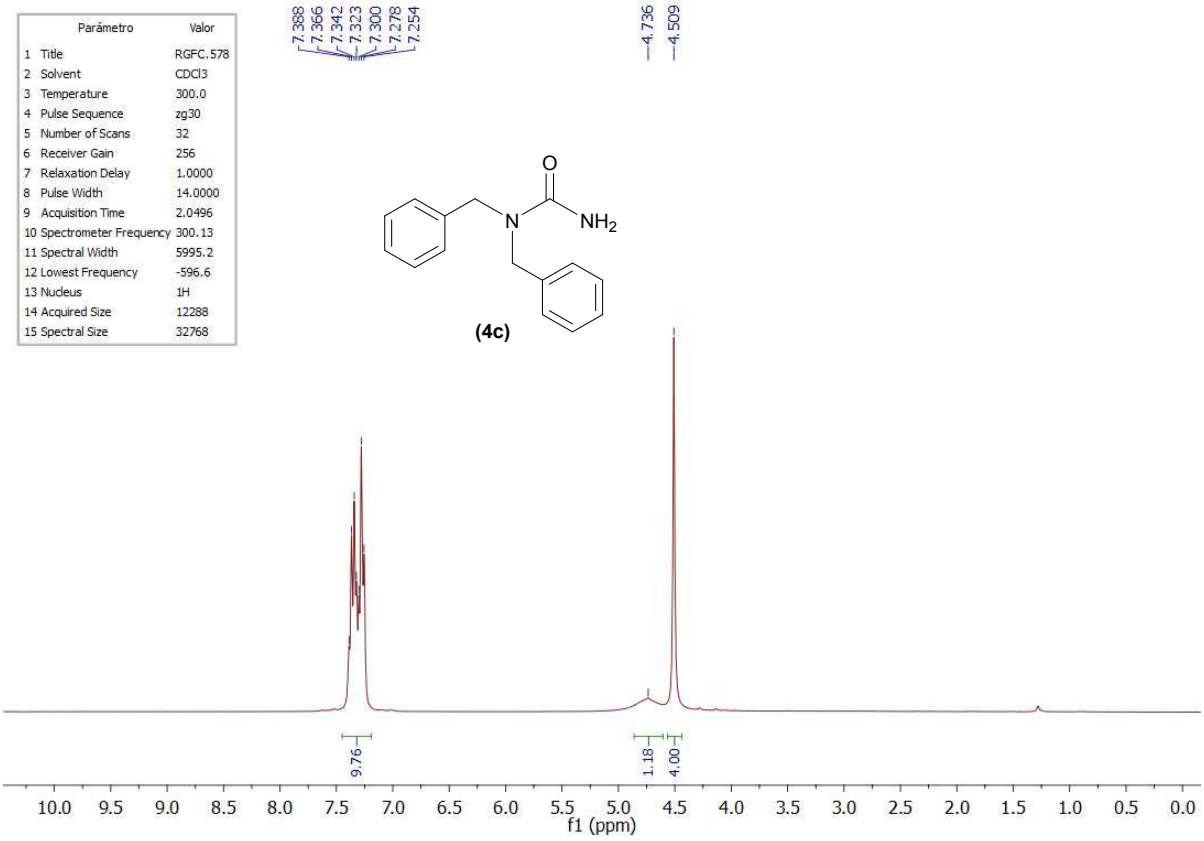

Figure S11. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of urea **4c**.

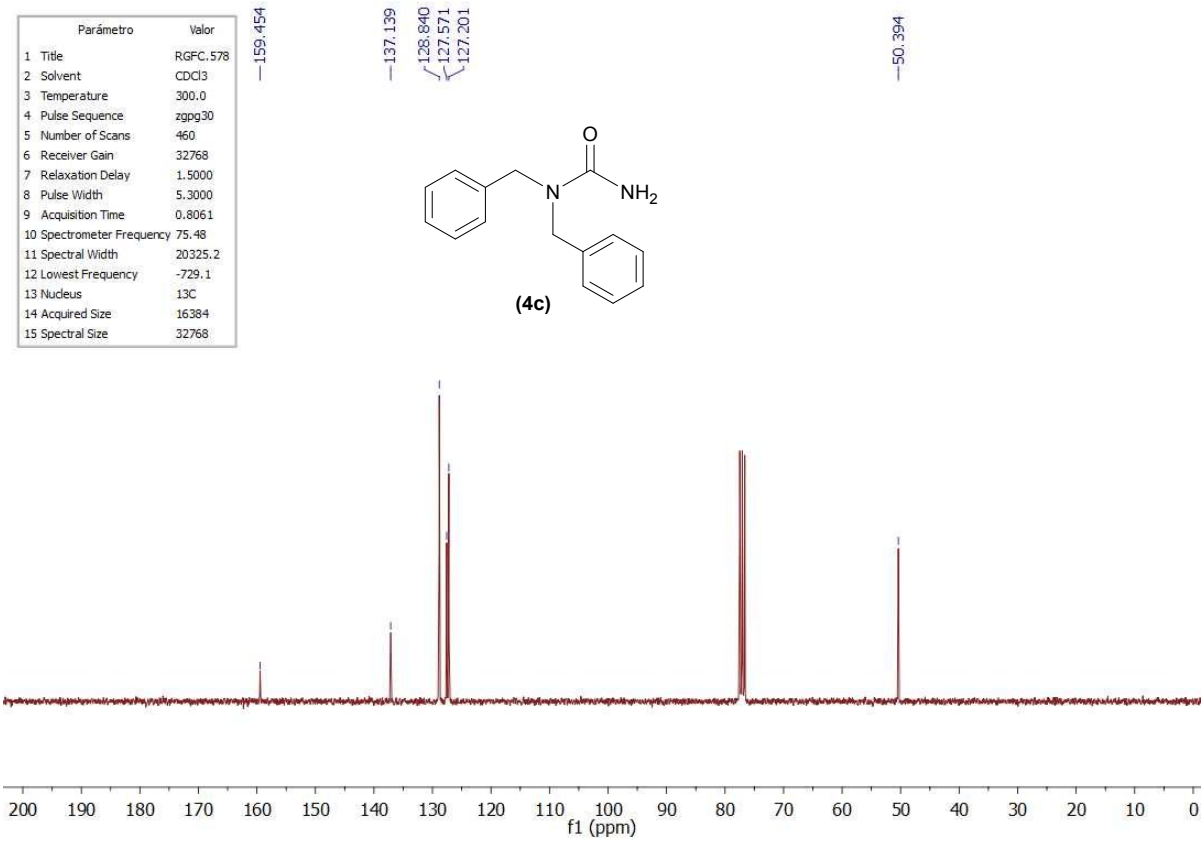

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 75 MHz) of urea **4c**.

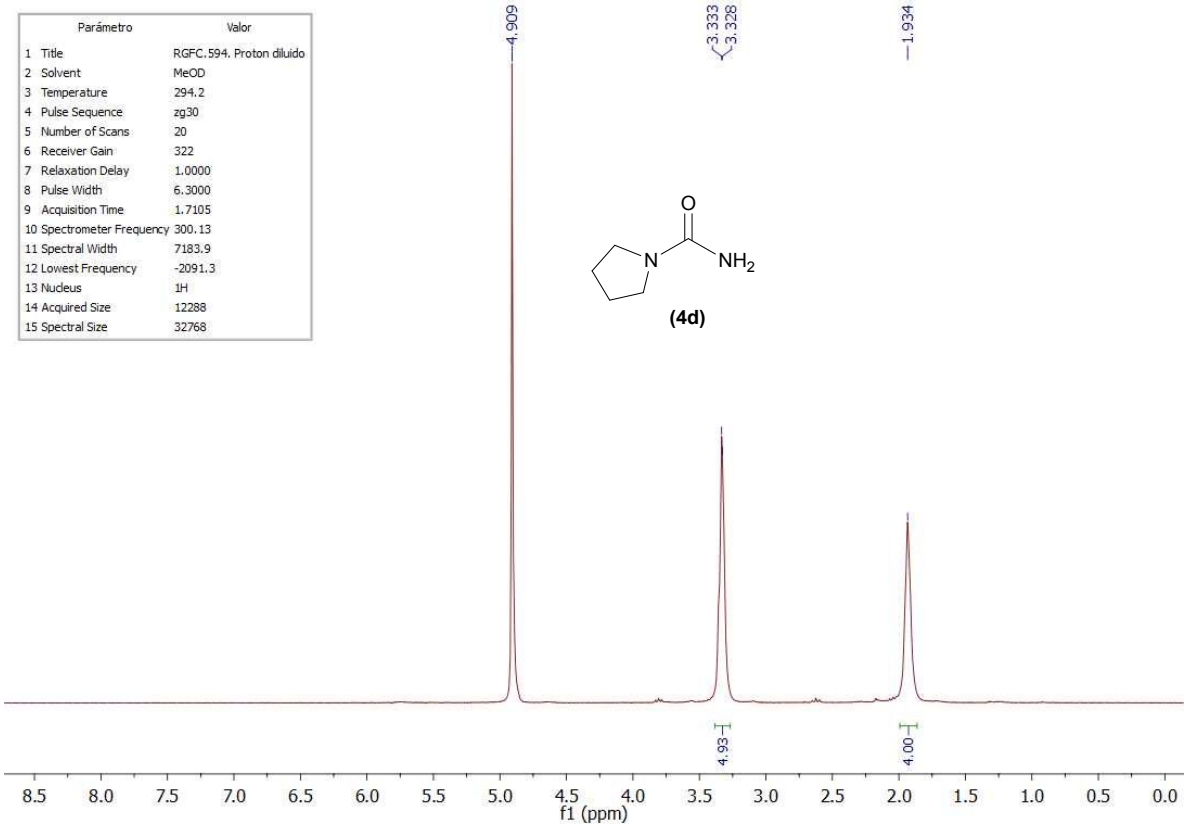

Figure S13. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of urea **4d**.

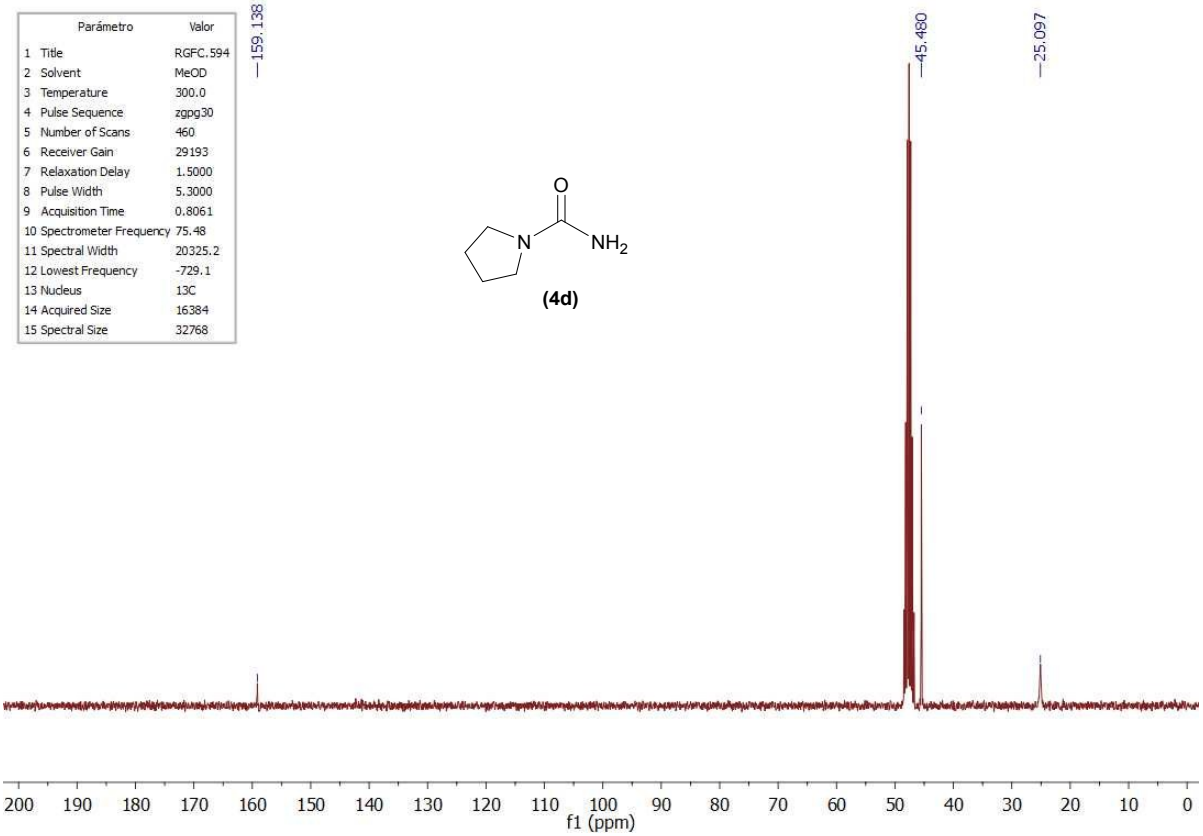

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD, 75 MHz) of urea **4d**.

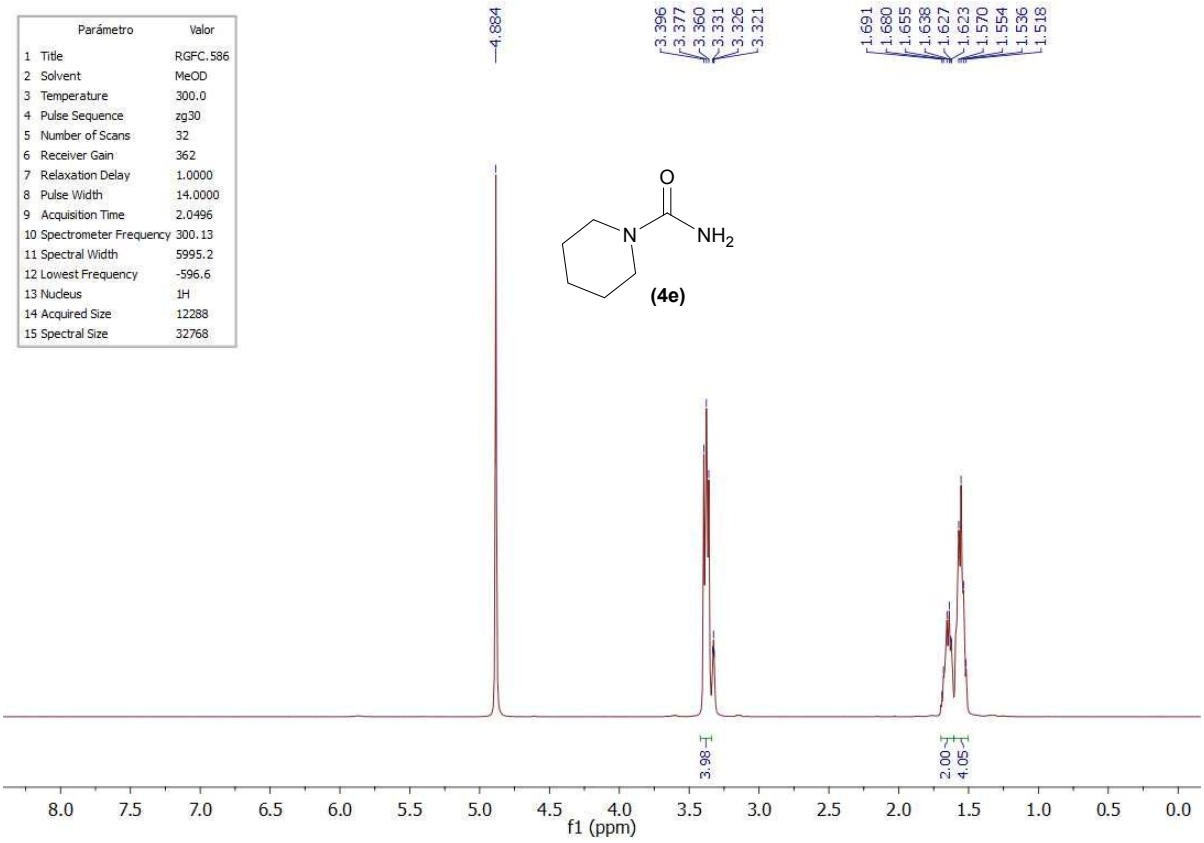

Figure S15. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of urea **4e**.

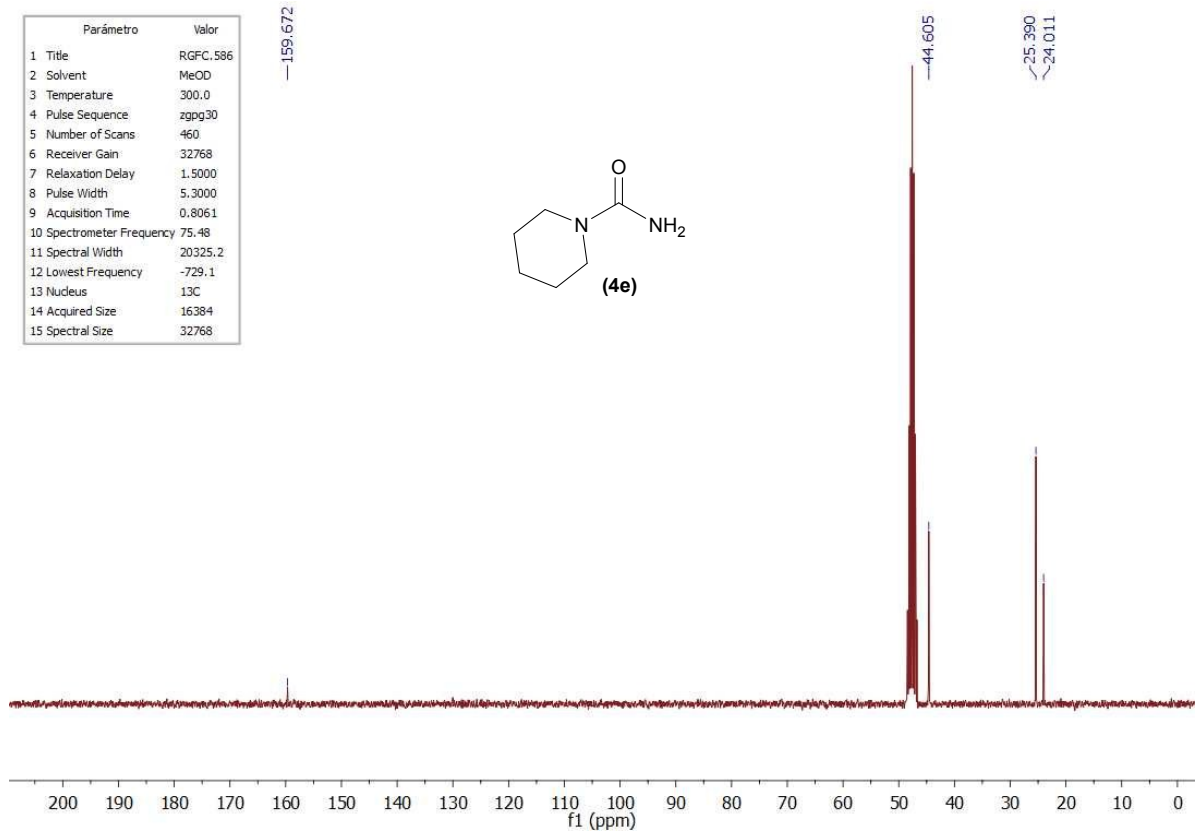

Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD, 75 MHz) of urea **4e**.

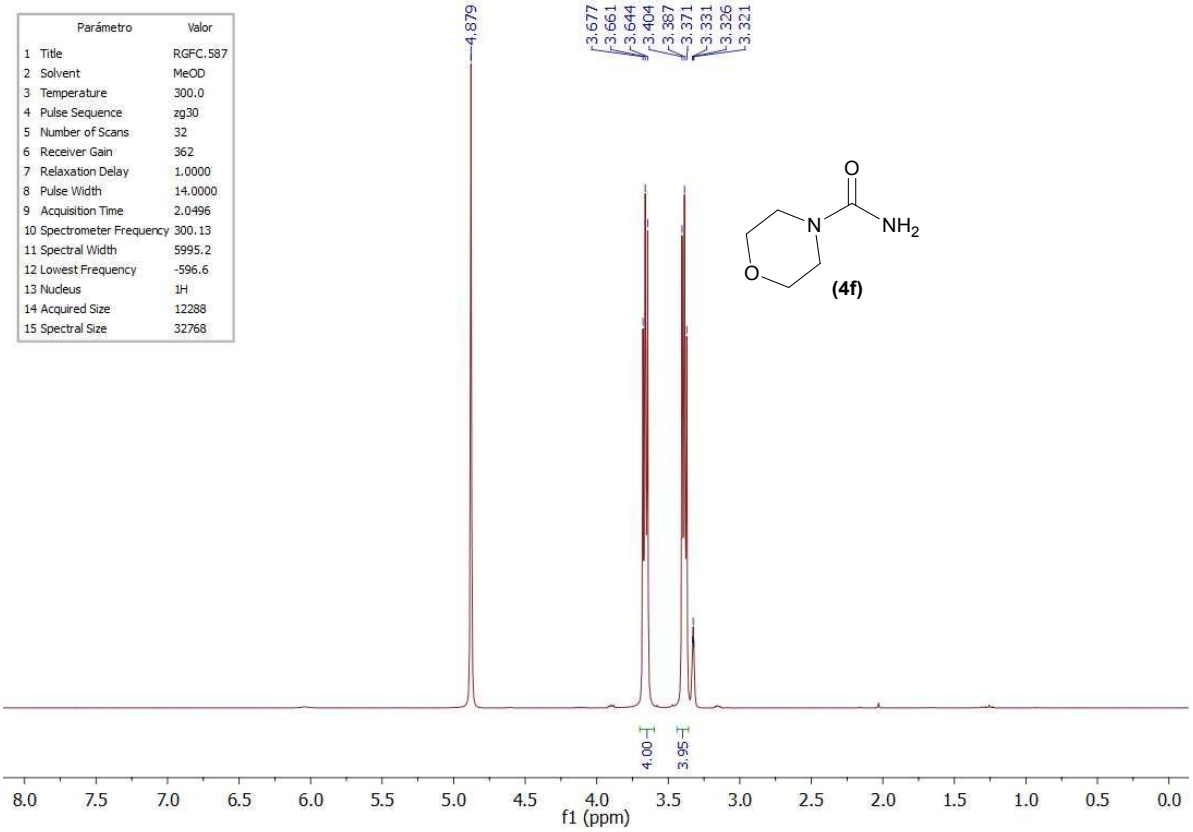

Figure S17. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of urea **4f**.

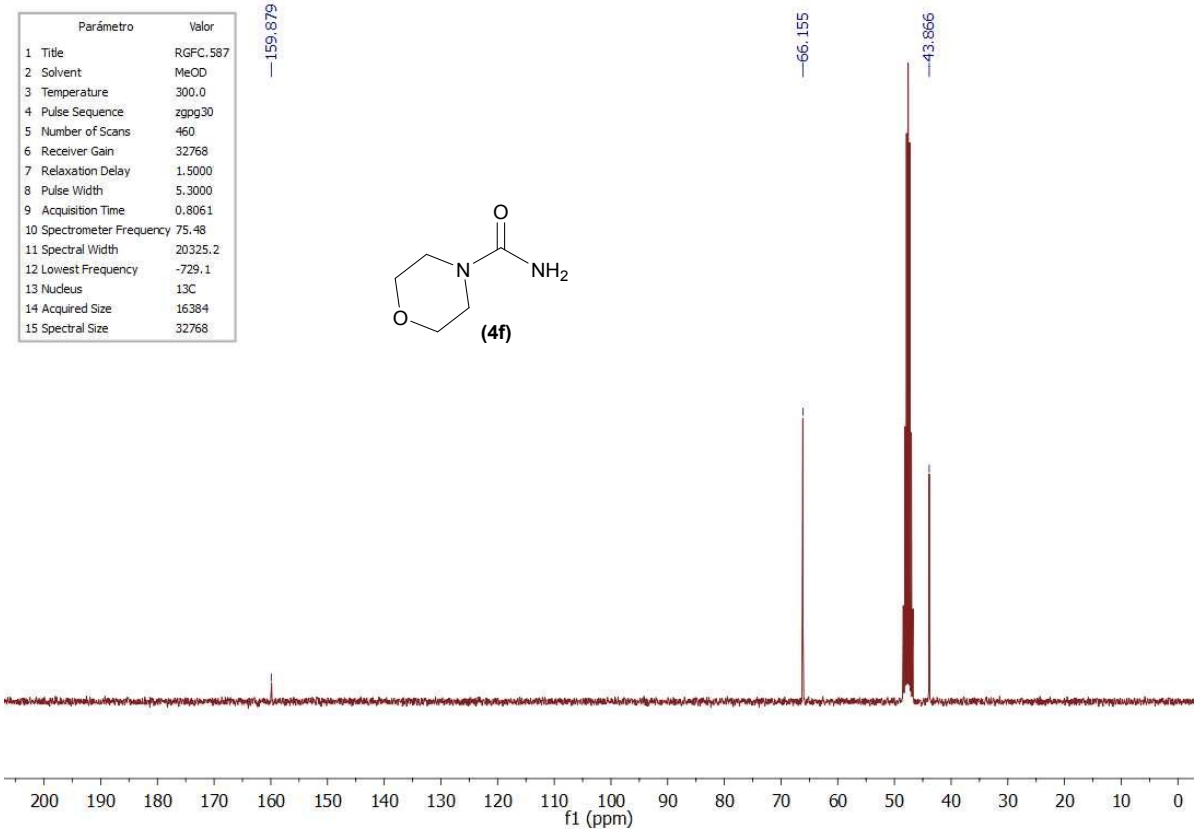

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD, 75 MHz) of urea **4f**.

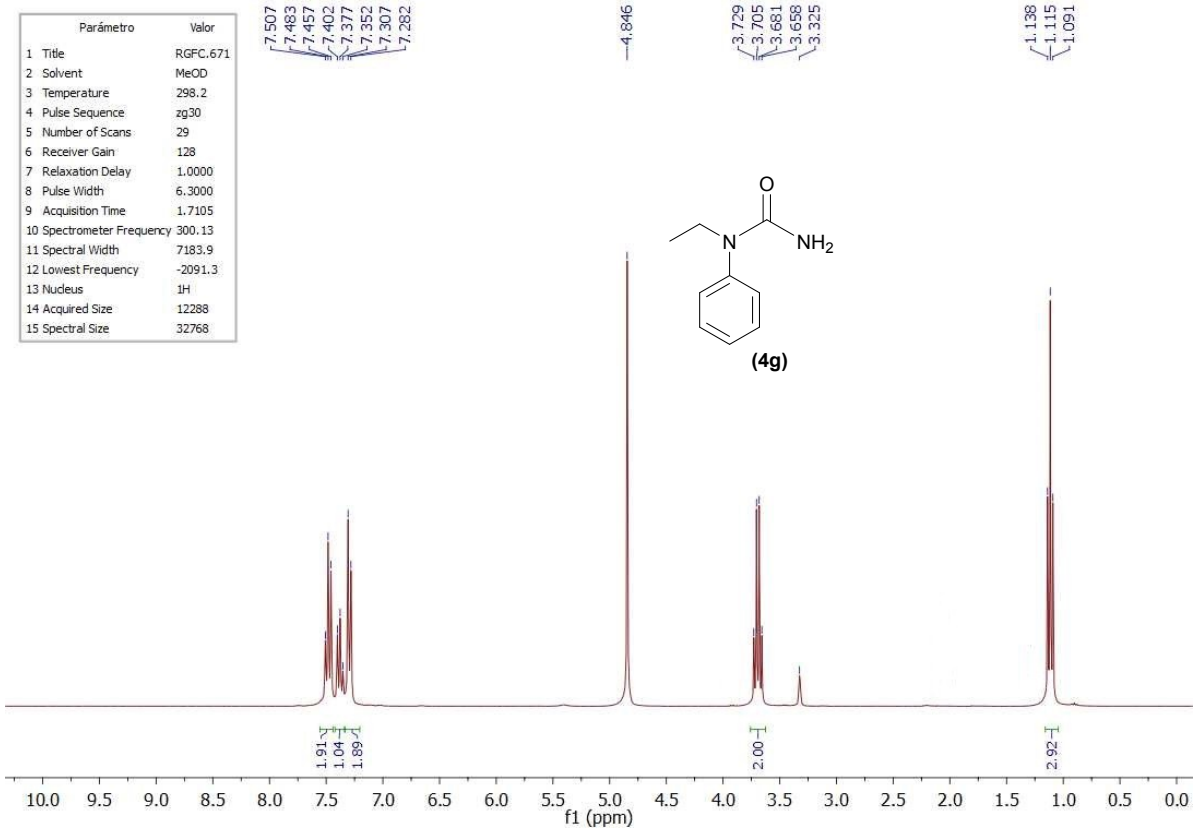

Figure S19. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of urea **4g**.

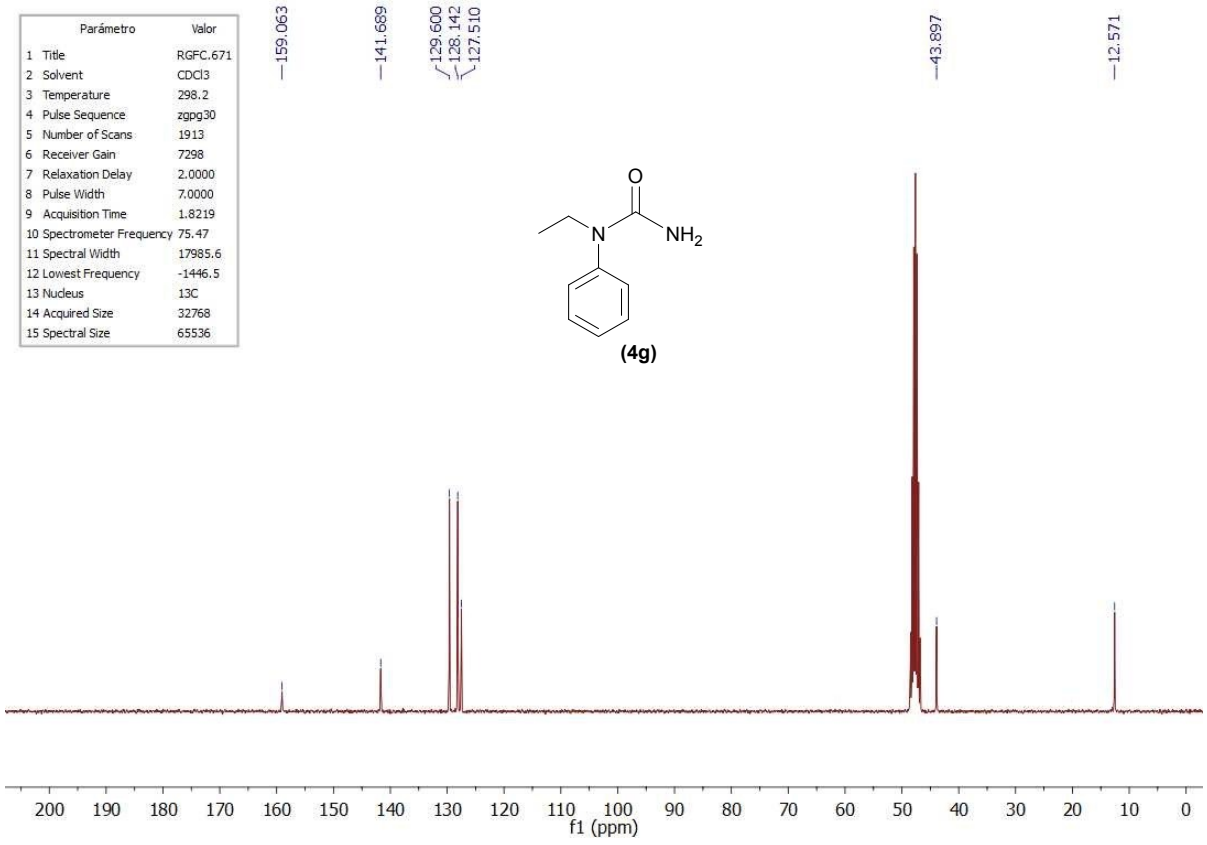

Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD, 75 MHz) of urea **4g**.

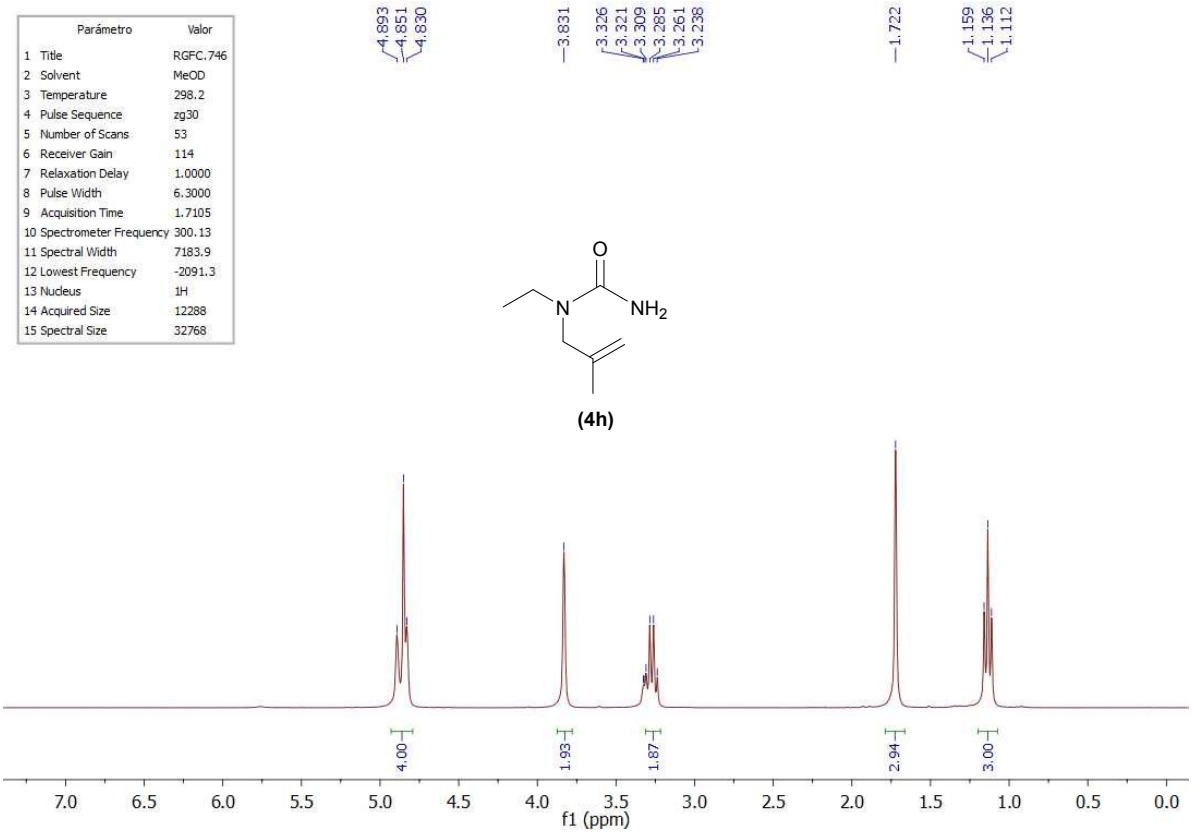

Figure S21. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of urea **4h**.

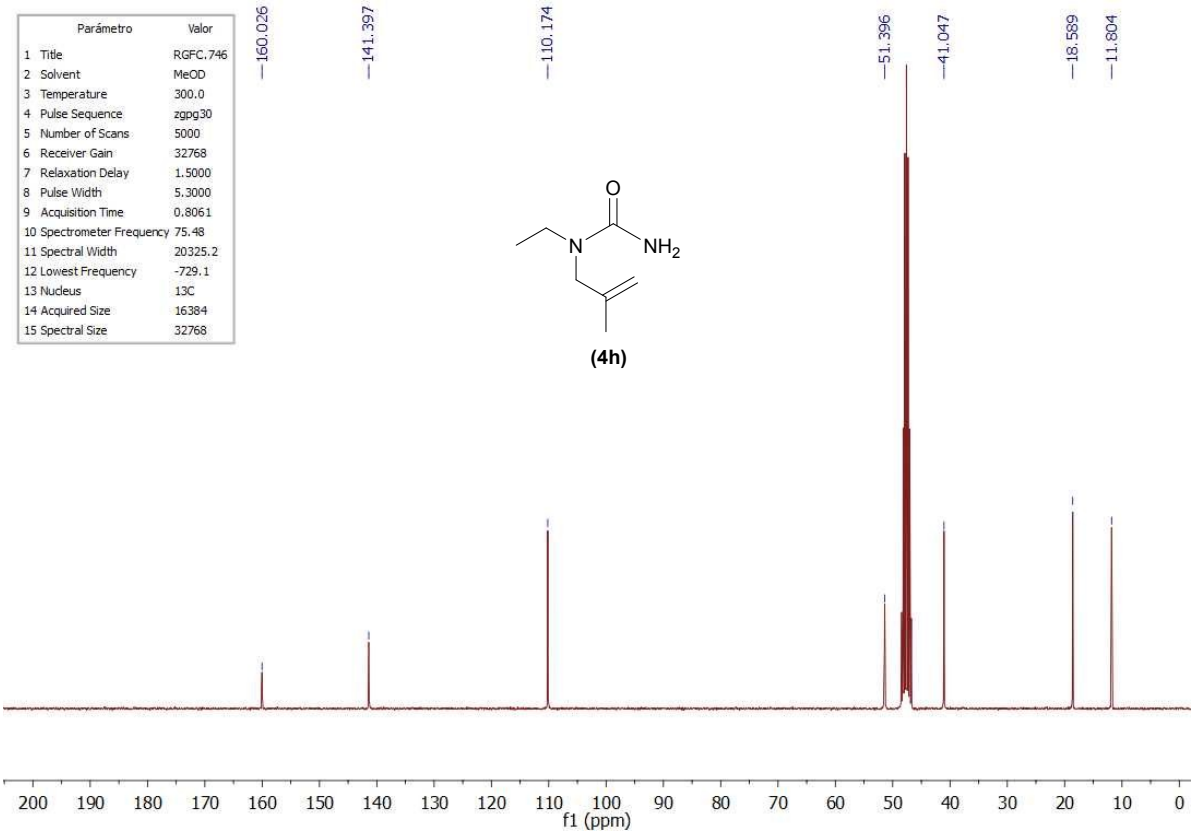

Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD, 75 MHz) of urea **4h**.

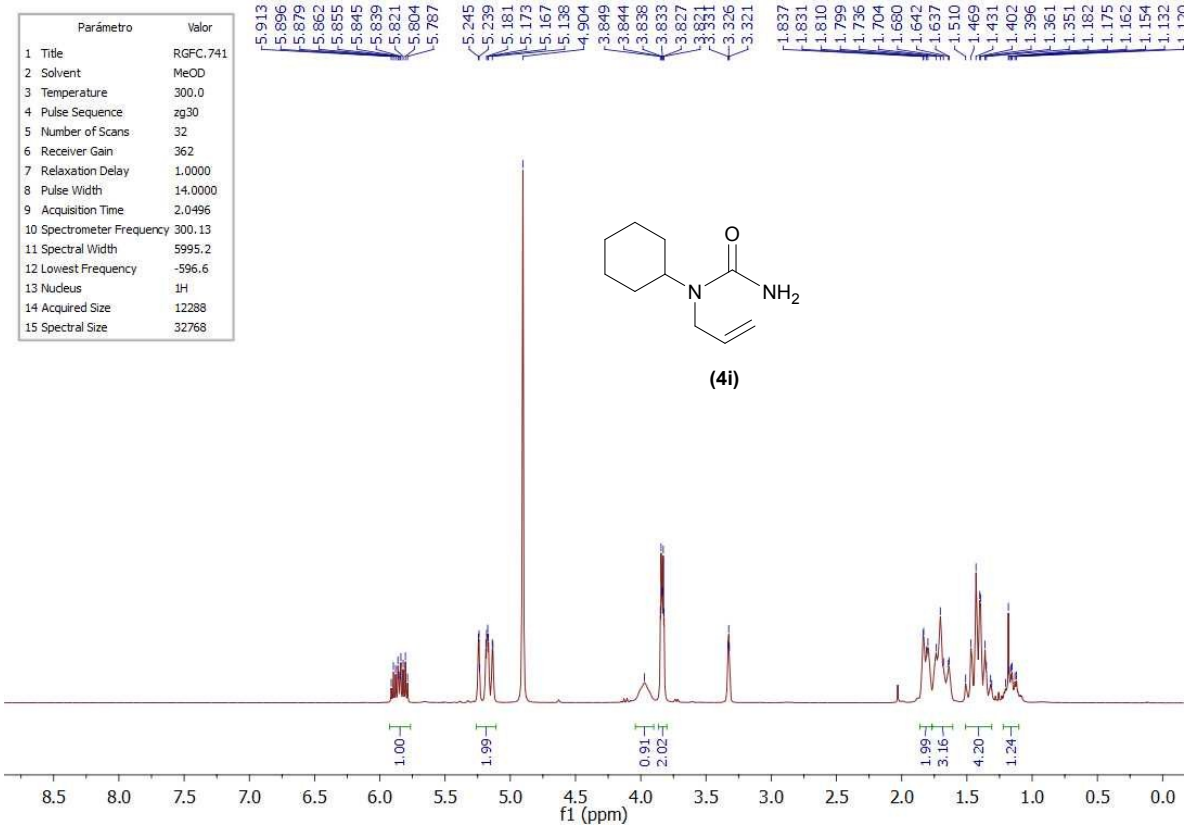

Figure S23. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of urea **4i**.

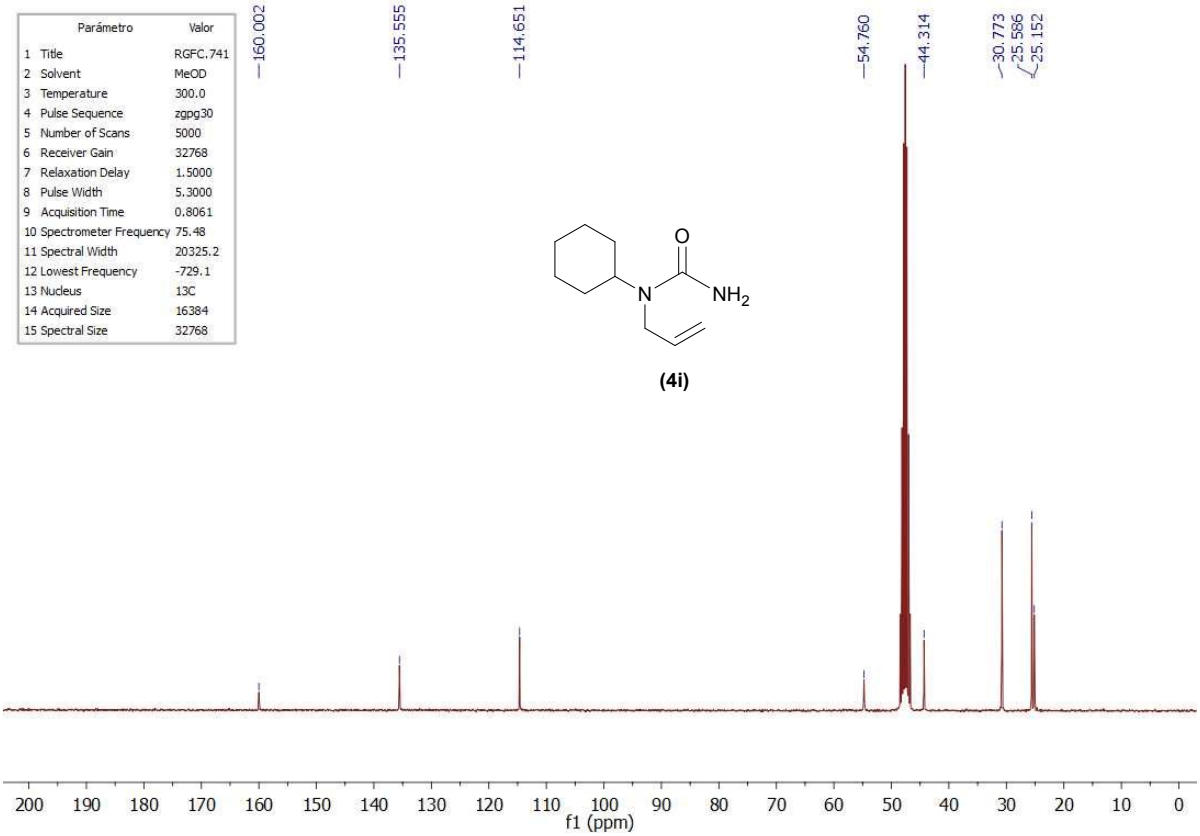

Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD, 75 MHz) of urea **4i**.

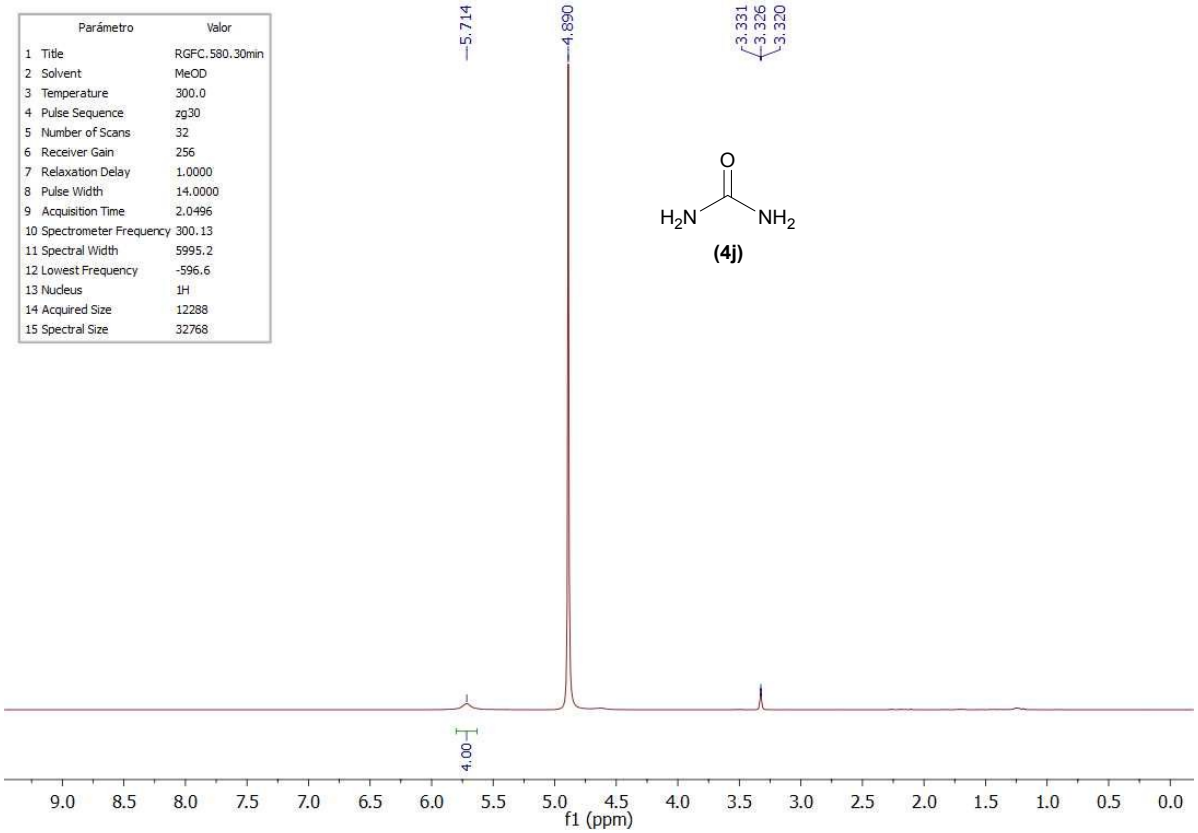

Figure S25. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of urea **4j**.

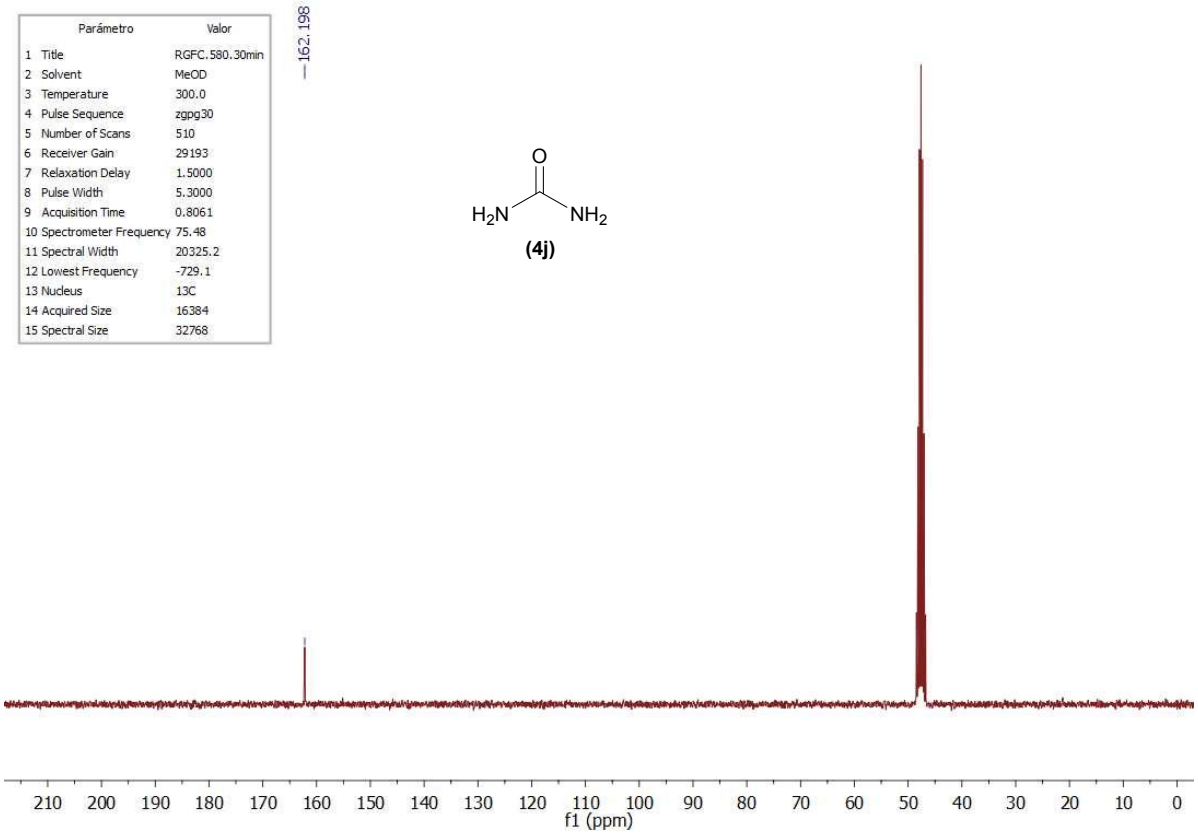

Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD, 75 MHz) of urea **4j**.

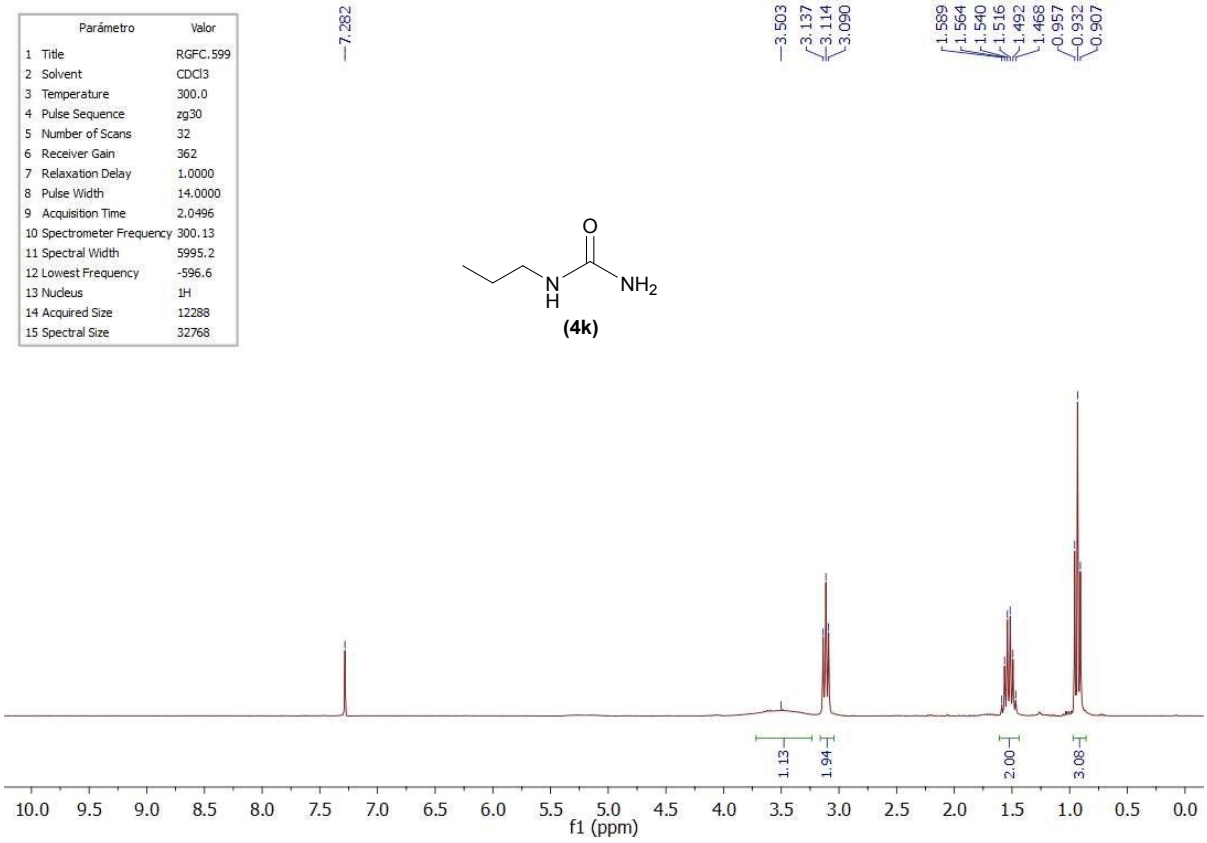

Figure S27. ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of urea **4k**.

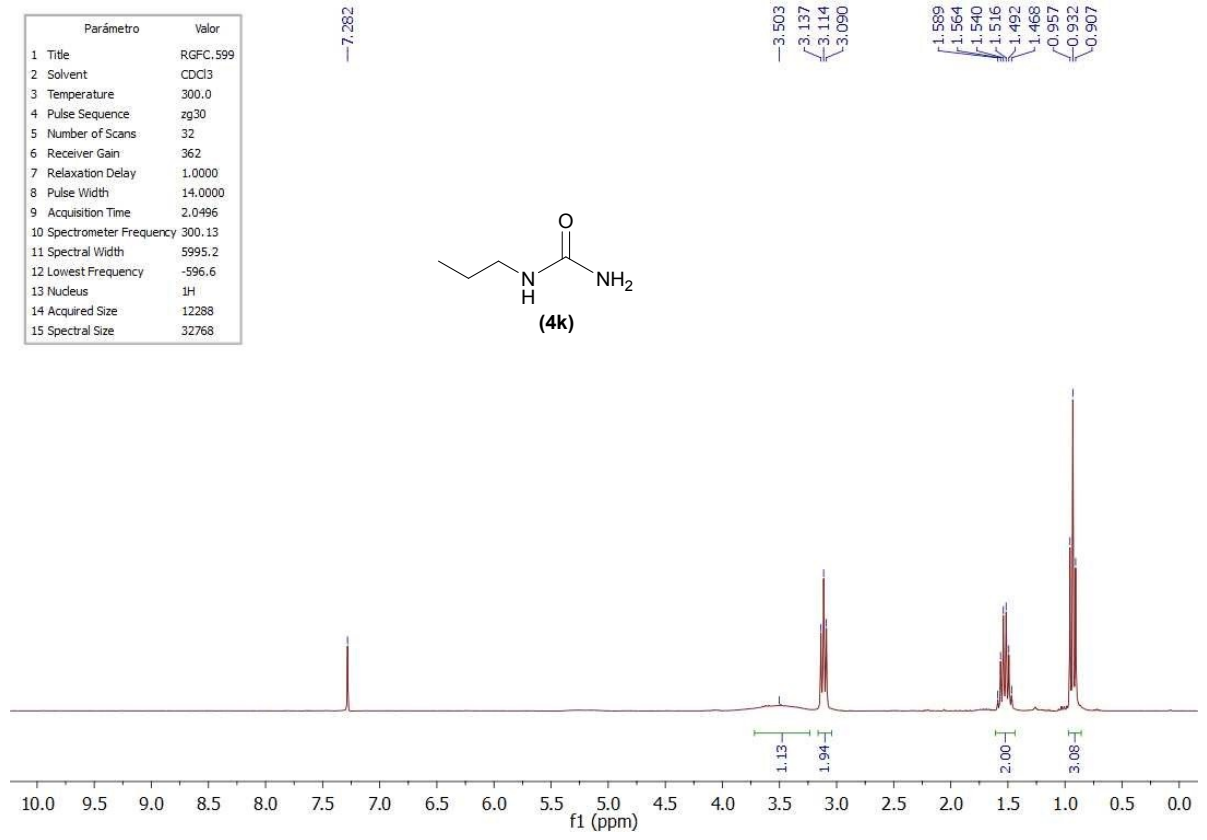

Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 75 MHz) of urea **4k**.

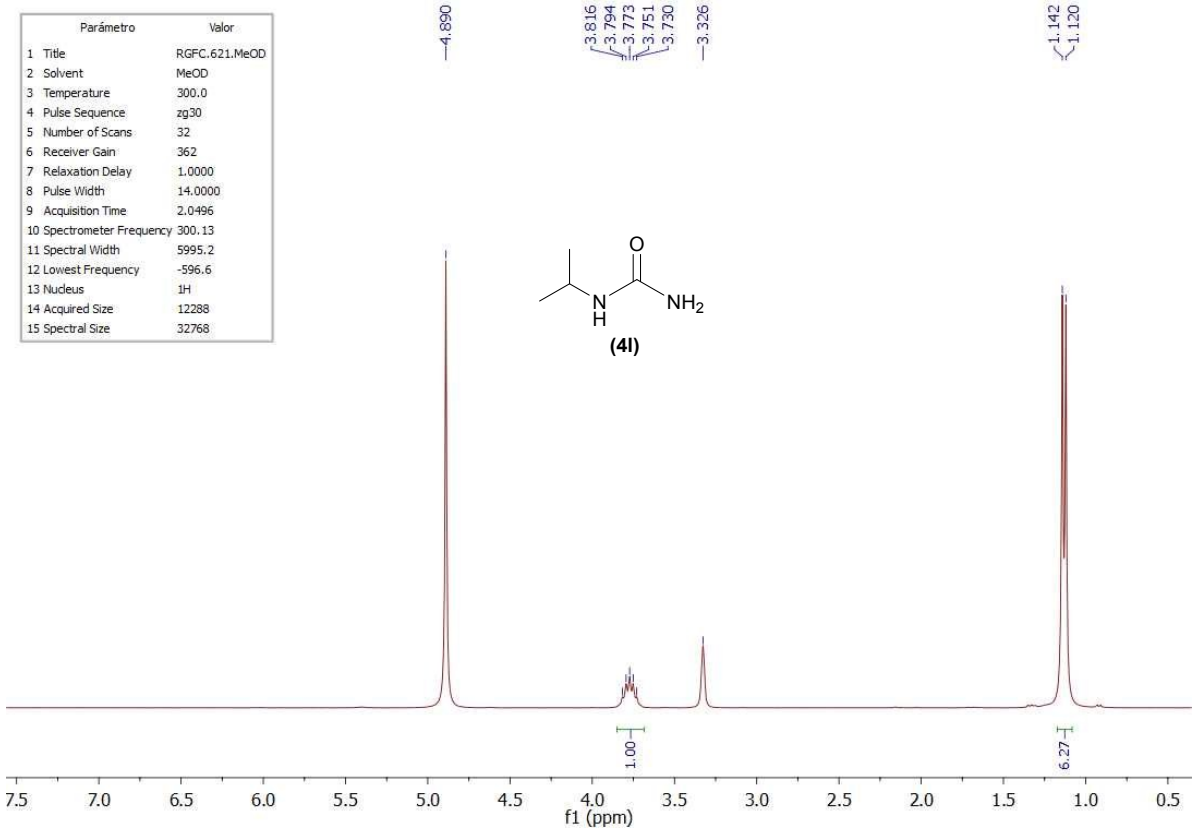

Figure S29. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of urea **4l**.

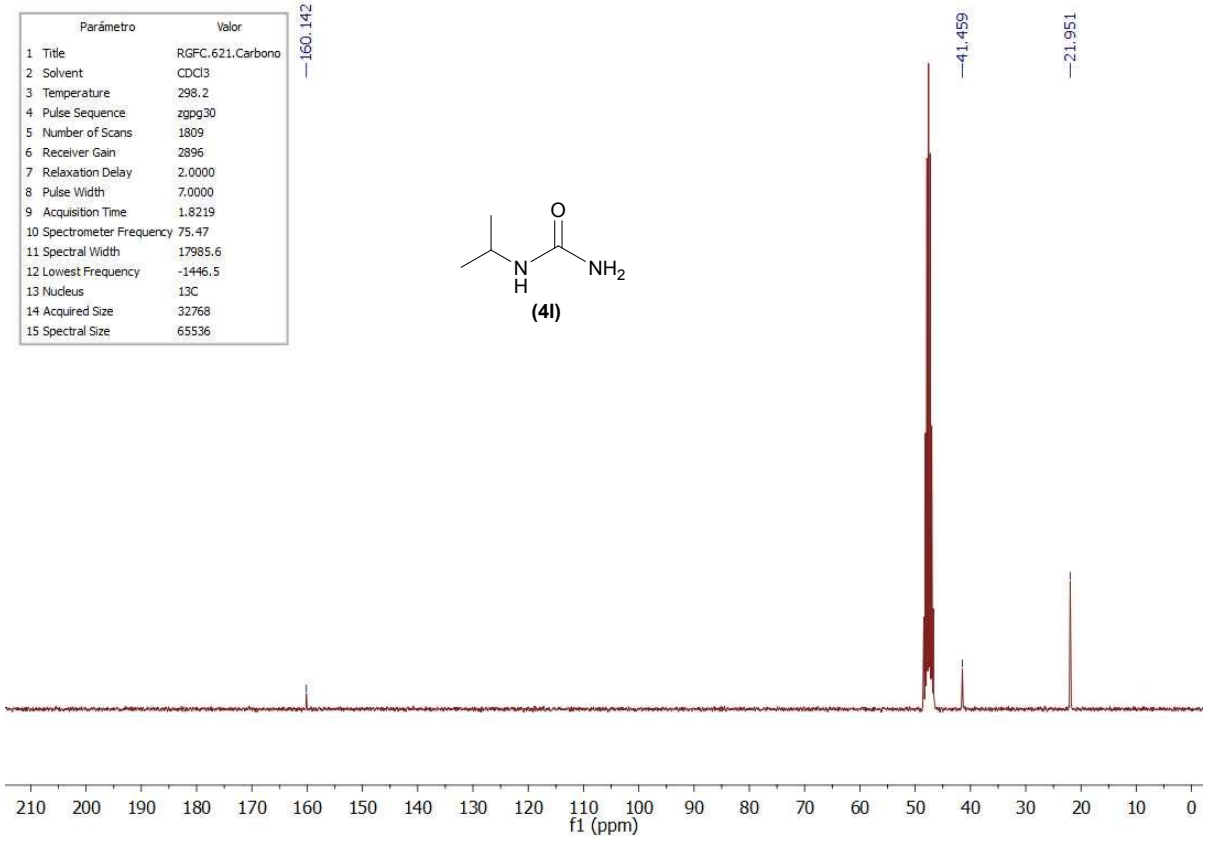

Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD, 75 MHz) of urea **4l**.

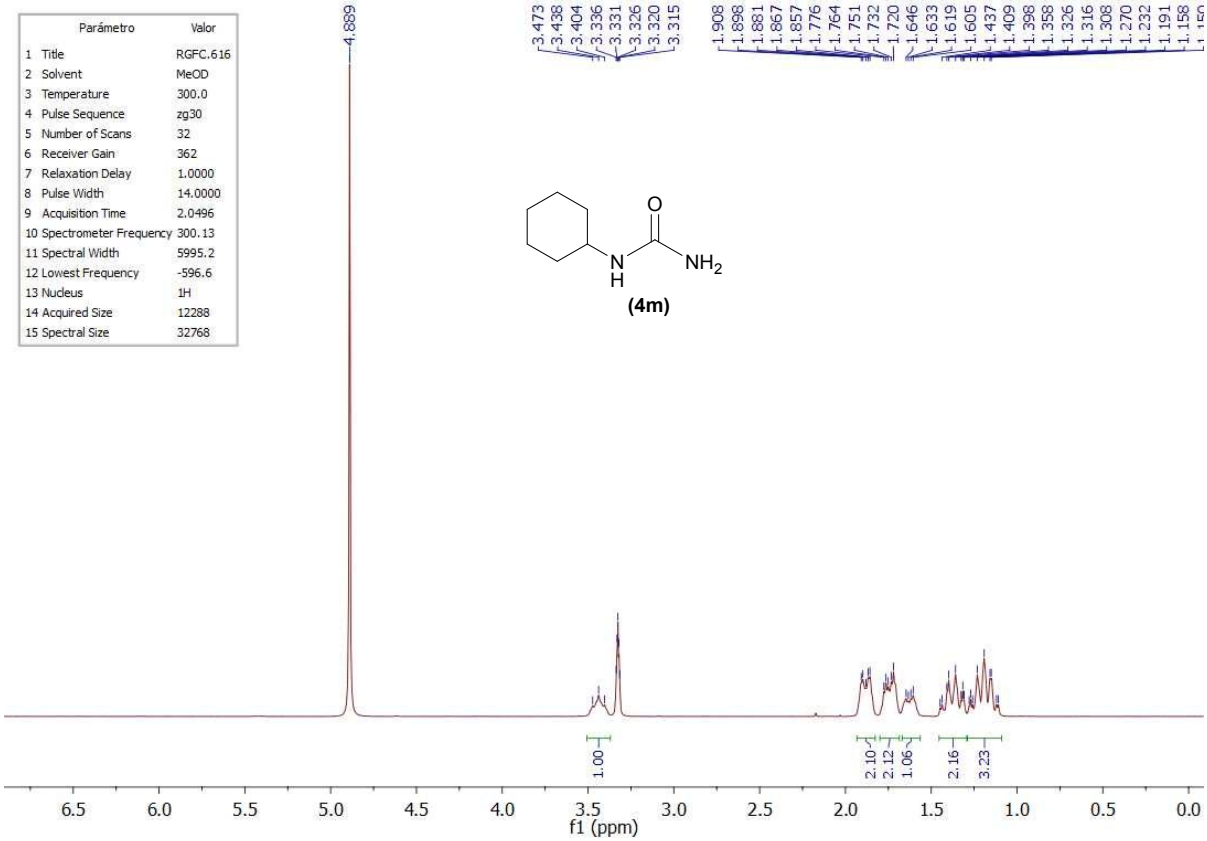

Figure S31. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of urea **4m**.

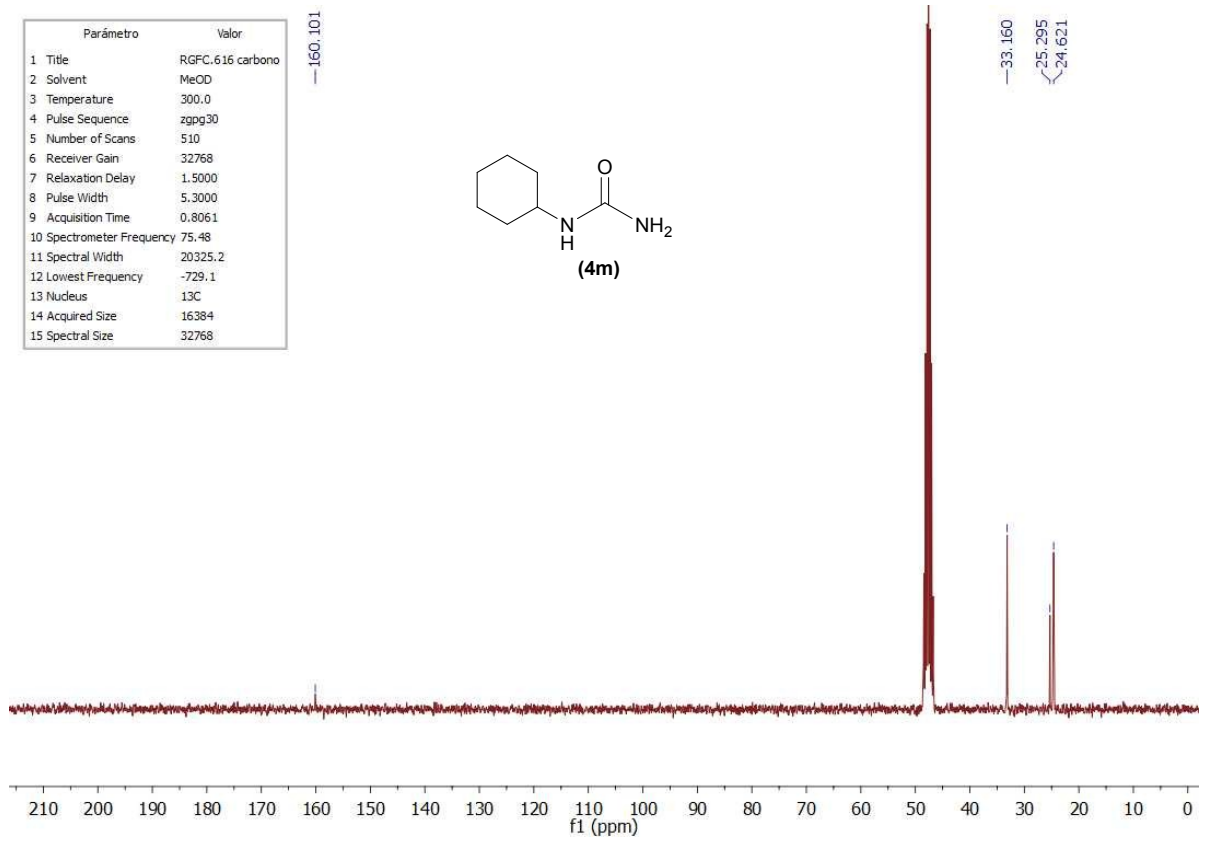

Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD, 75 MHz) of urea **4m**.

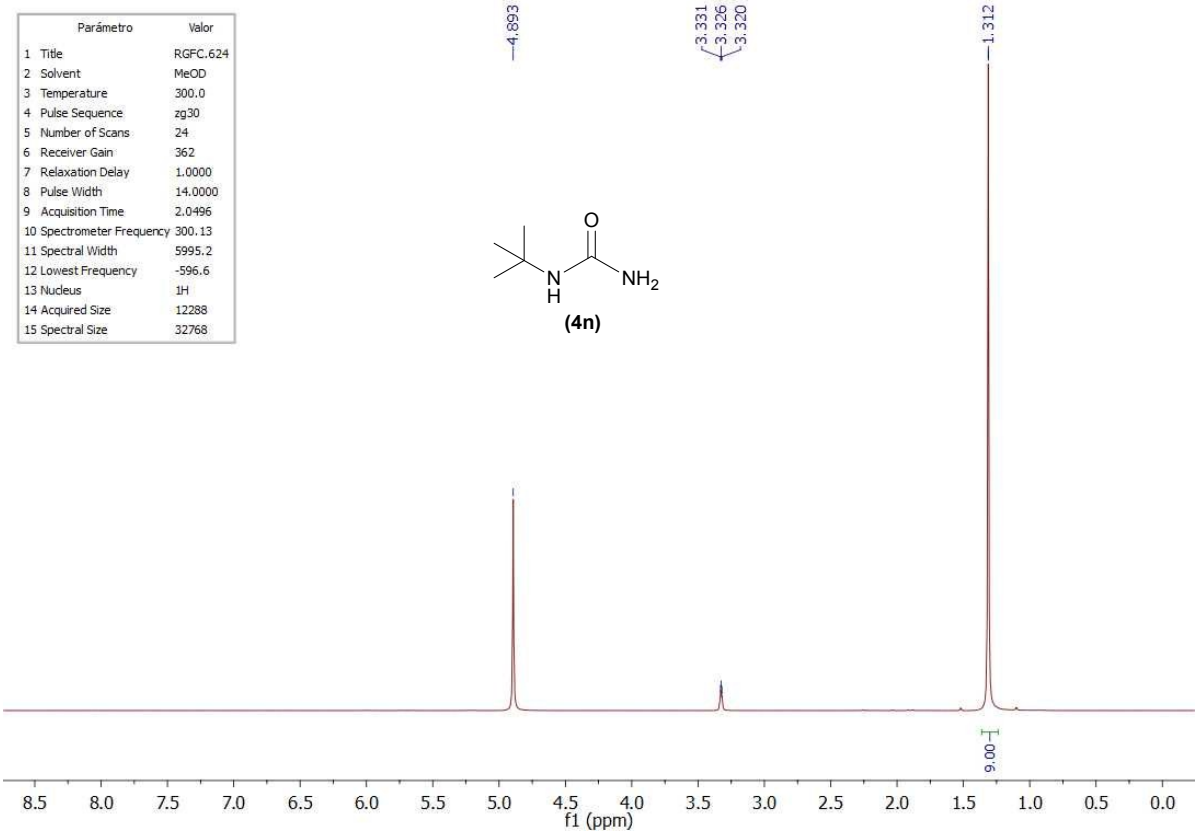

Figure S33. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of urea **4n**.

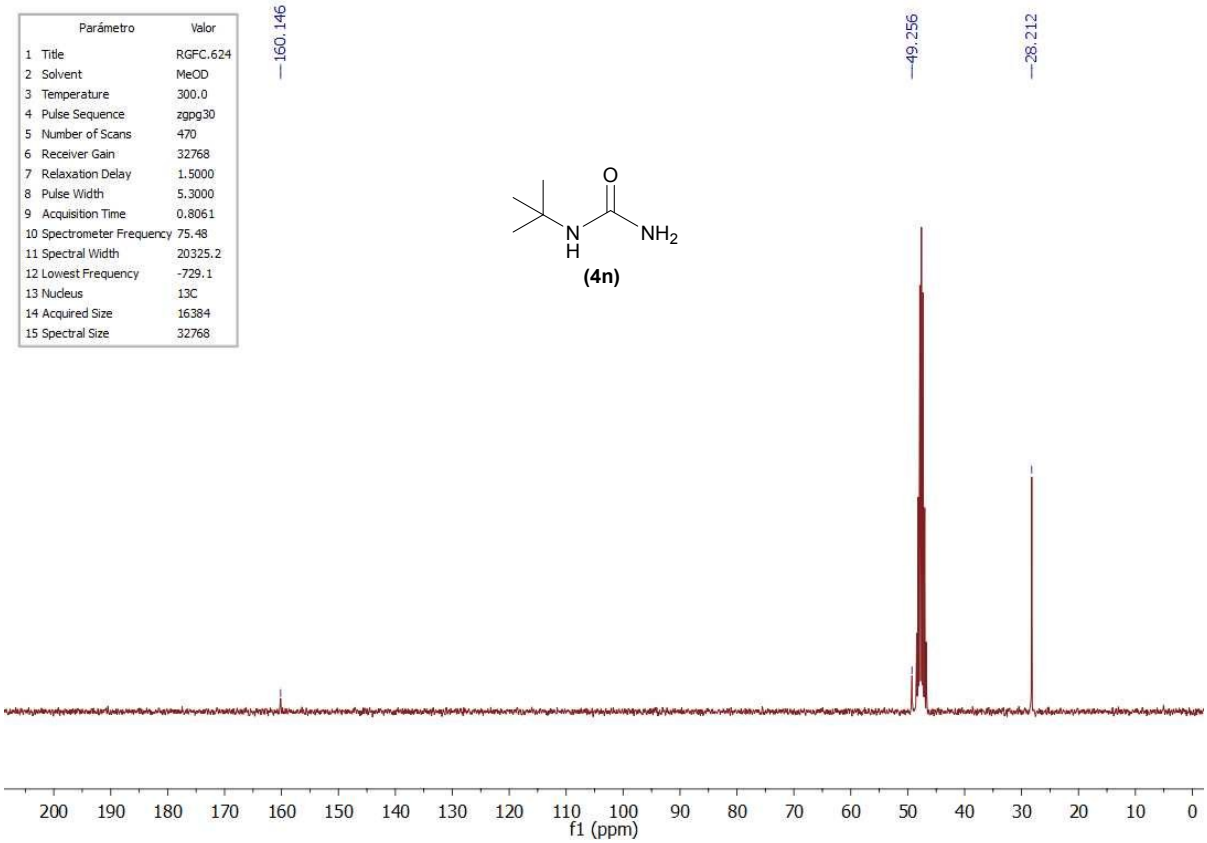

Figure S34. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD, 75 MHz) of urea **4n**.

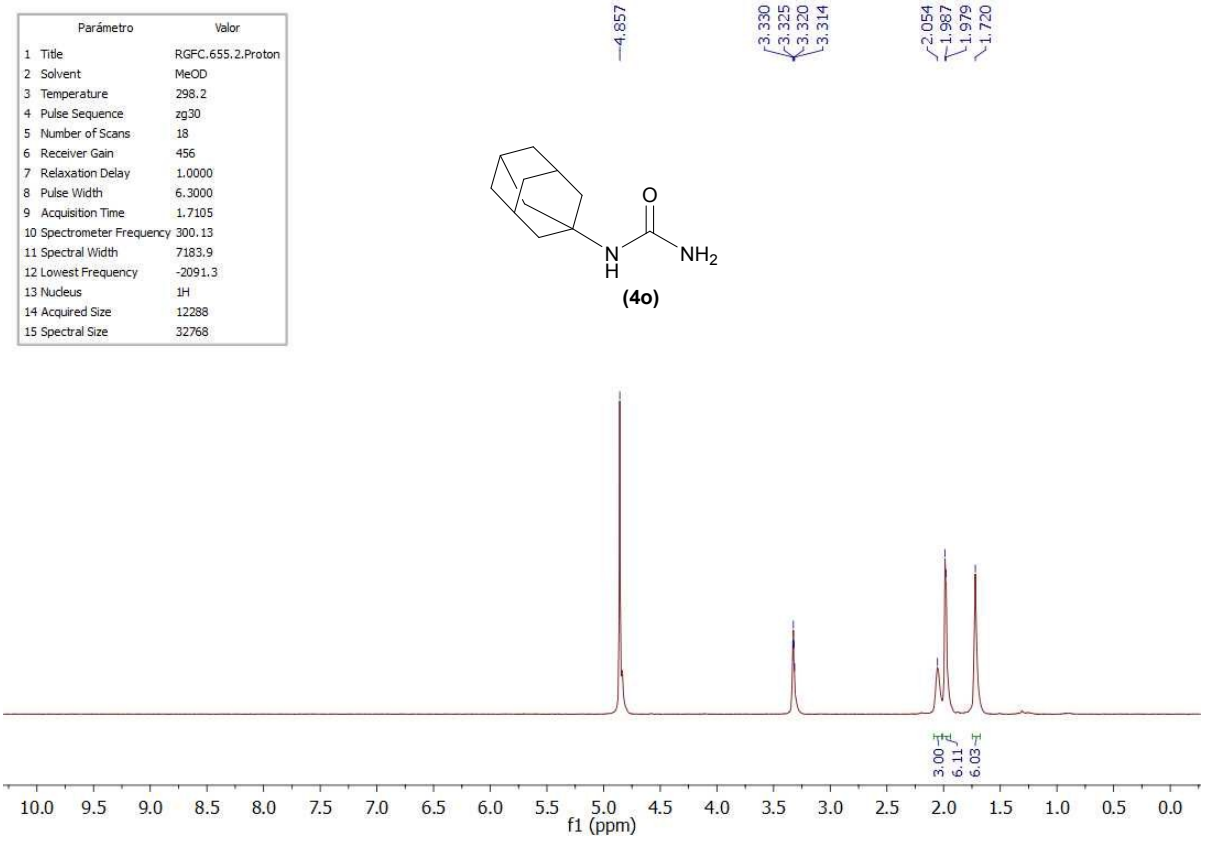

Figure S35. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of urea **4o**.

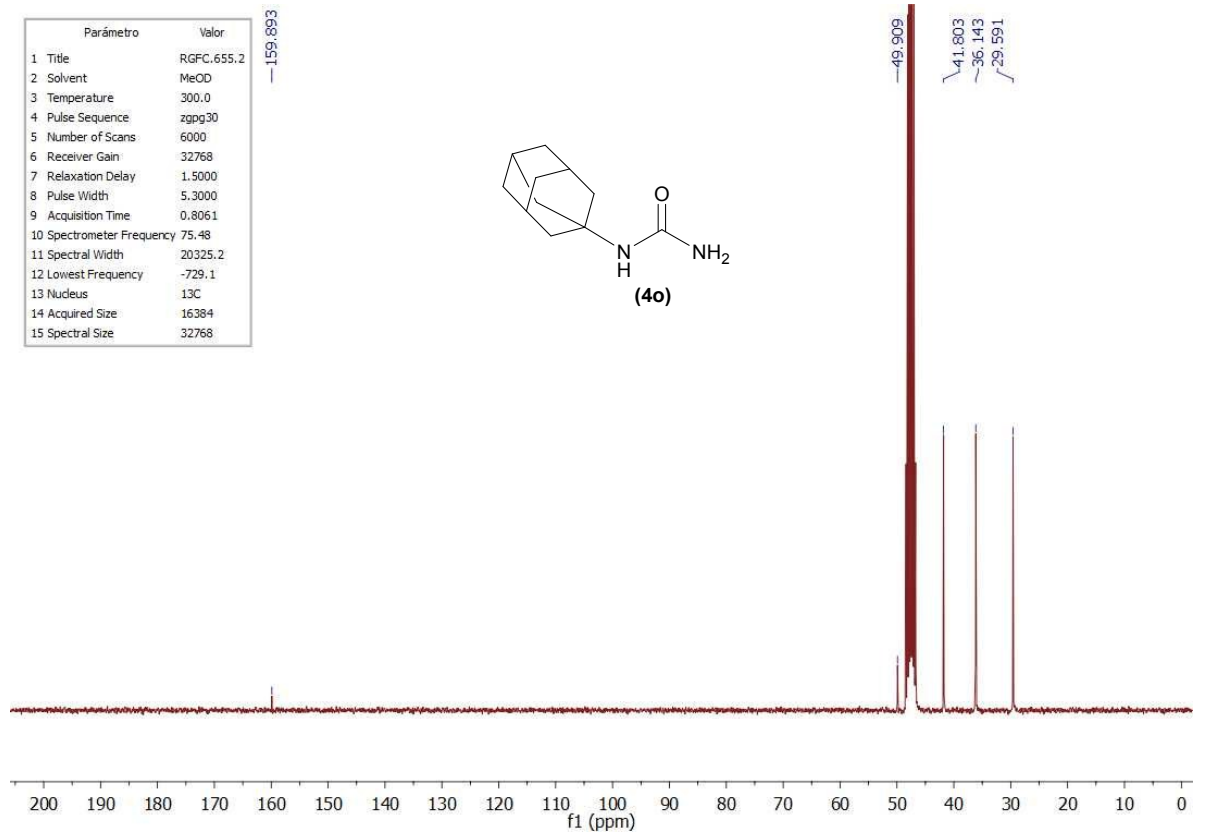

Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD, 75 MHz) of urea **4o**.

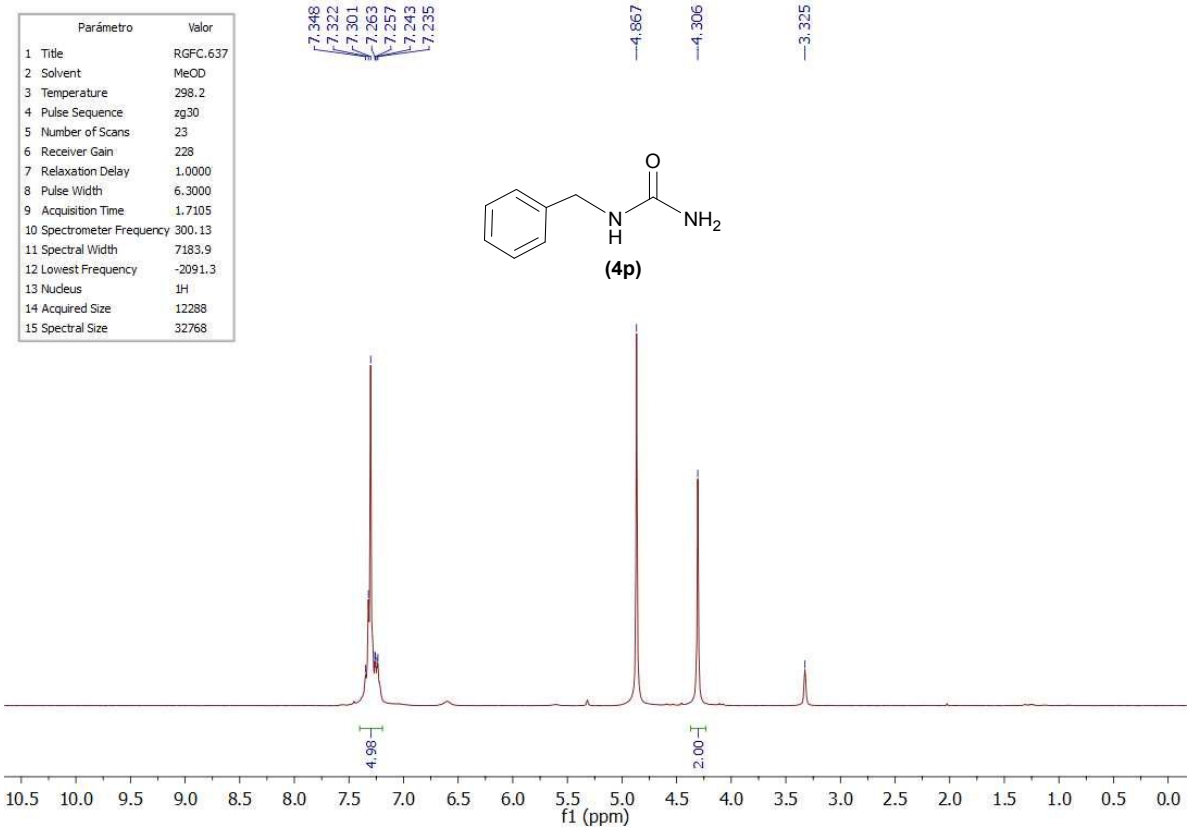

Figure S37. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of urea **4p**.

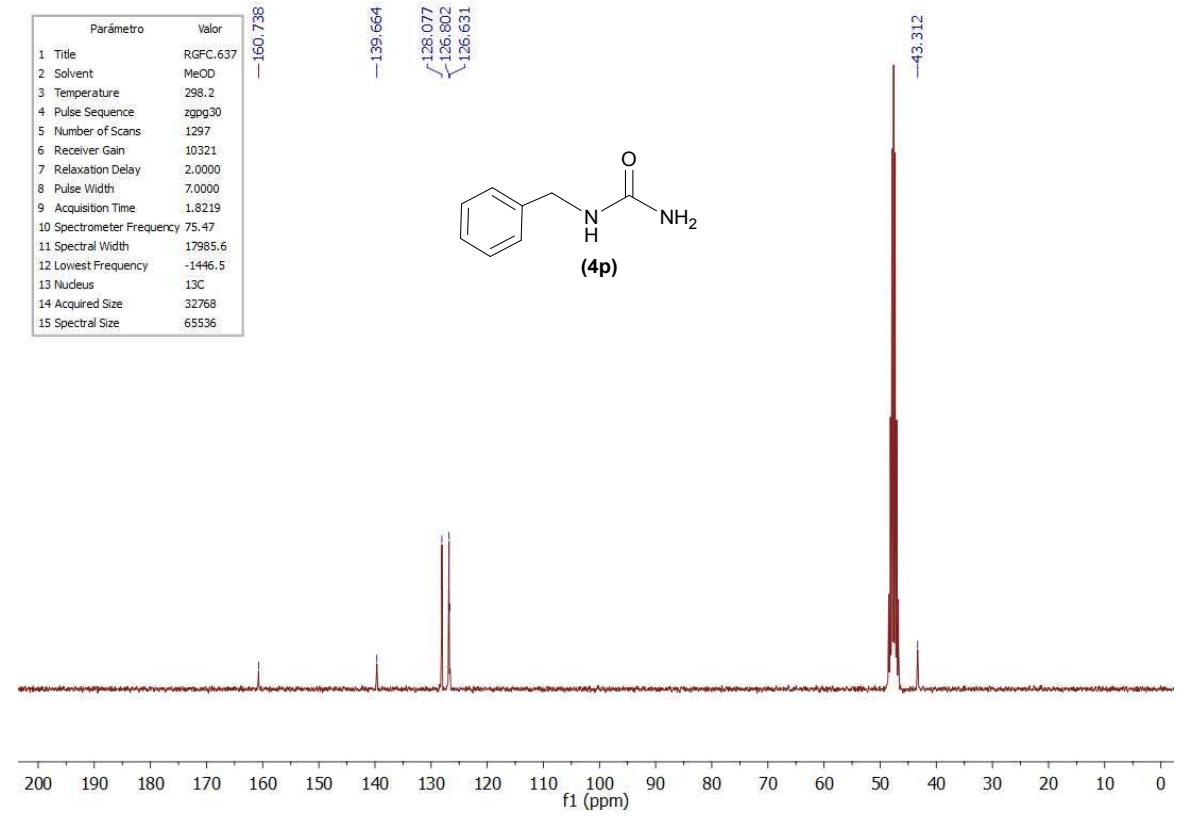

Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD, 75 MHz) of urea **4p**.

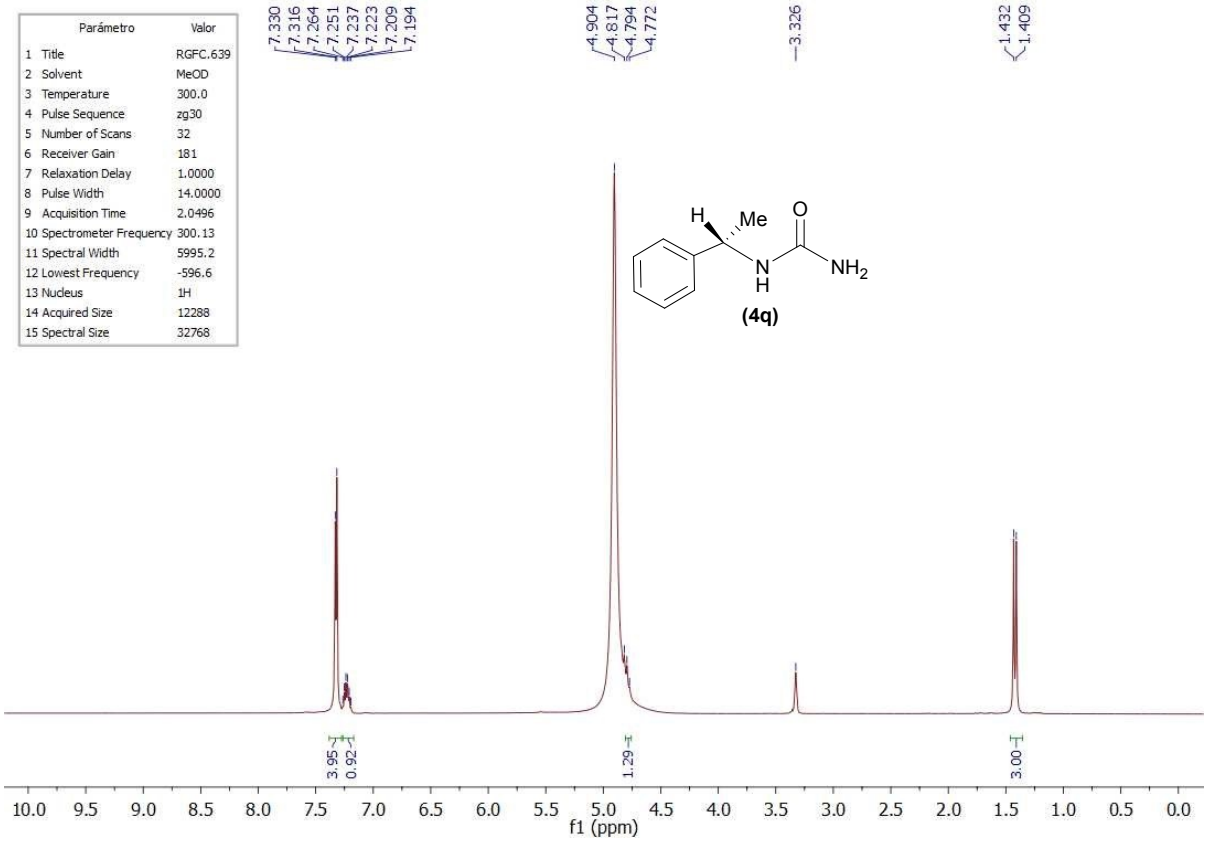

Figure S39. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of urea **4q**.

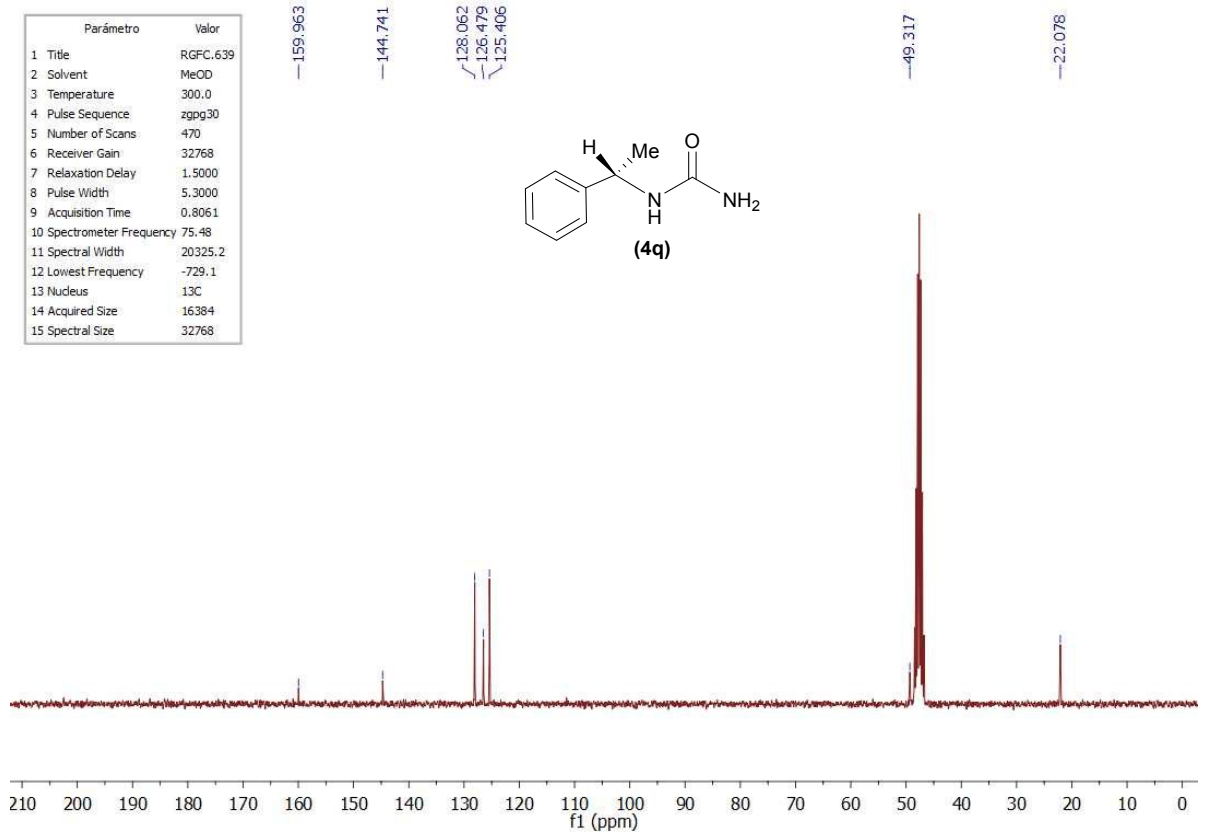

Figure S40. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD, 75 MHz) of urea **4q**.

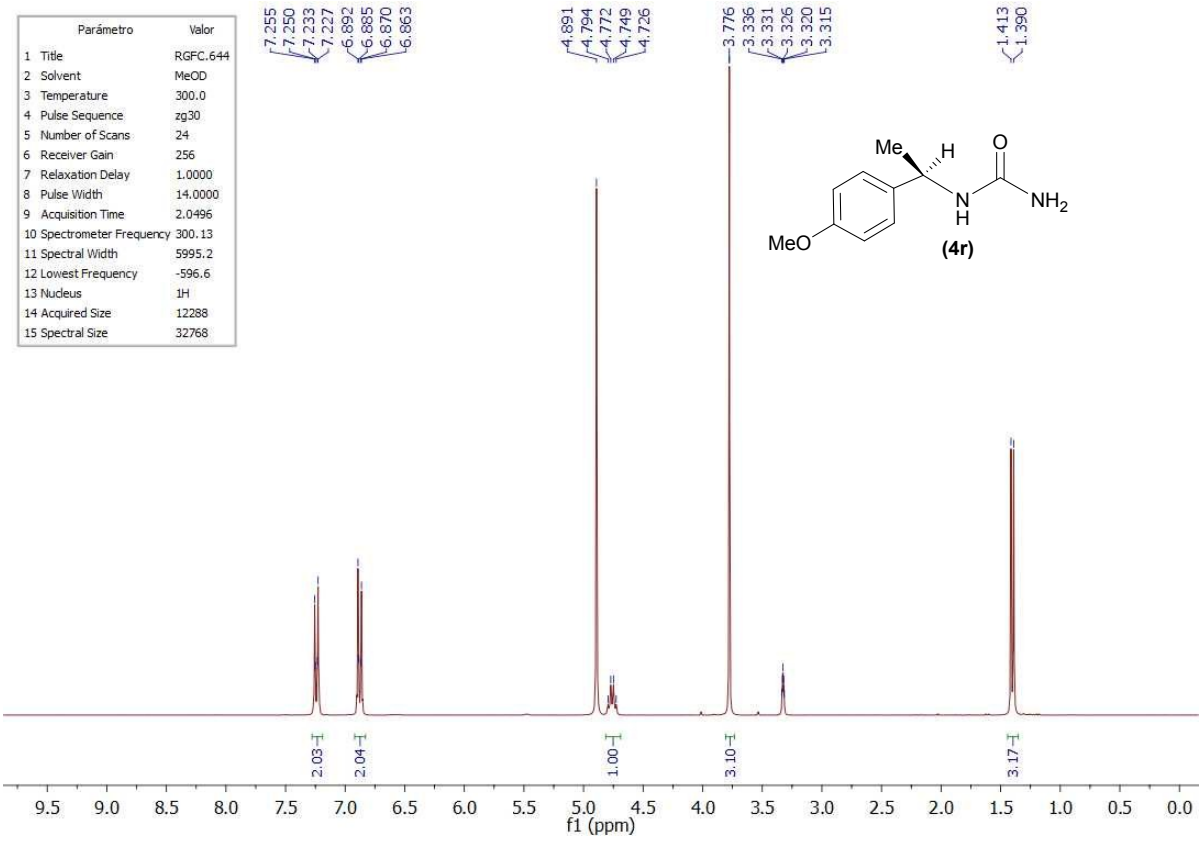

Figure S41. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of urea **4r**.

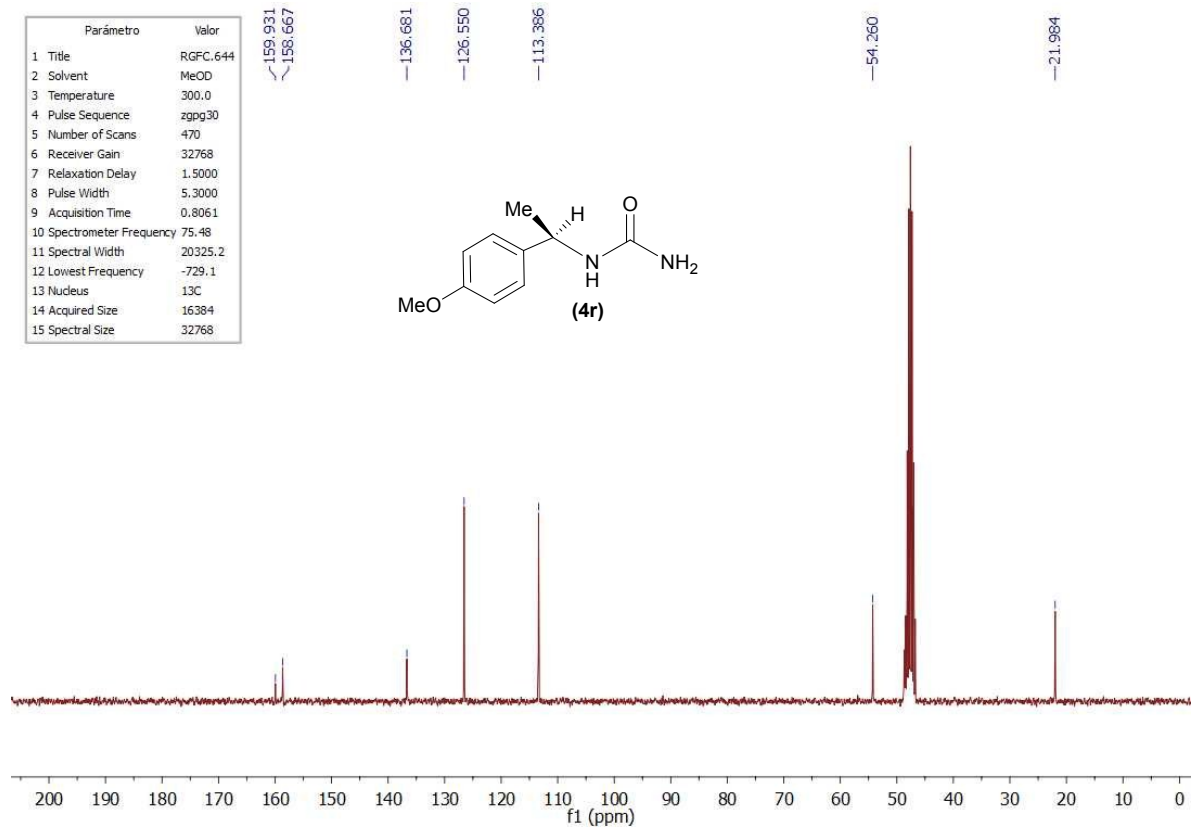

Figure S42. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD, 75 MHz) of urea **4r**.

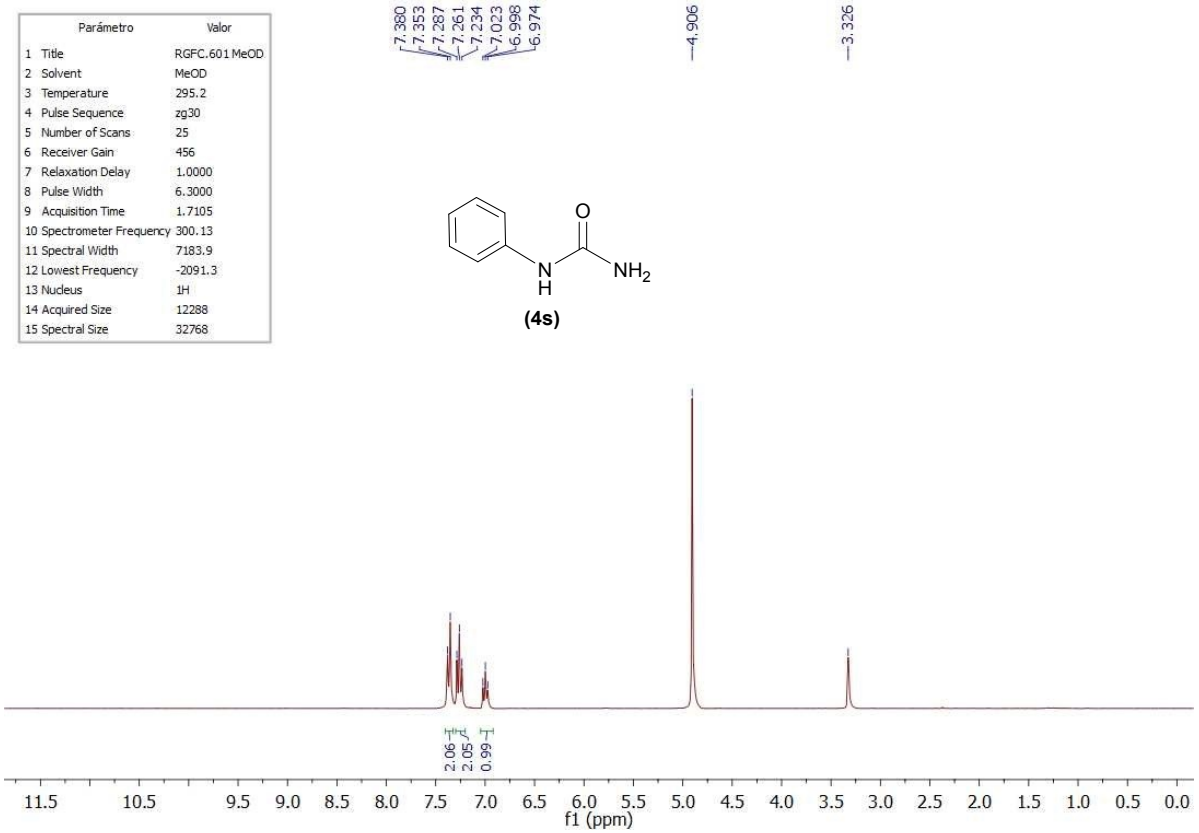

Figure S43. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of urea **4s**.

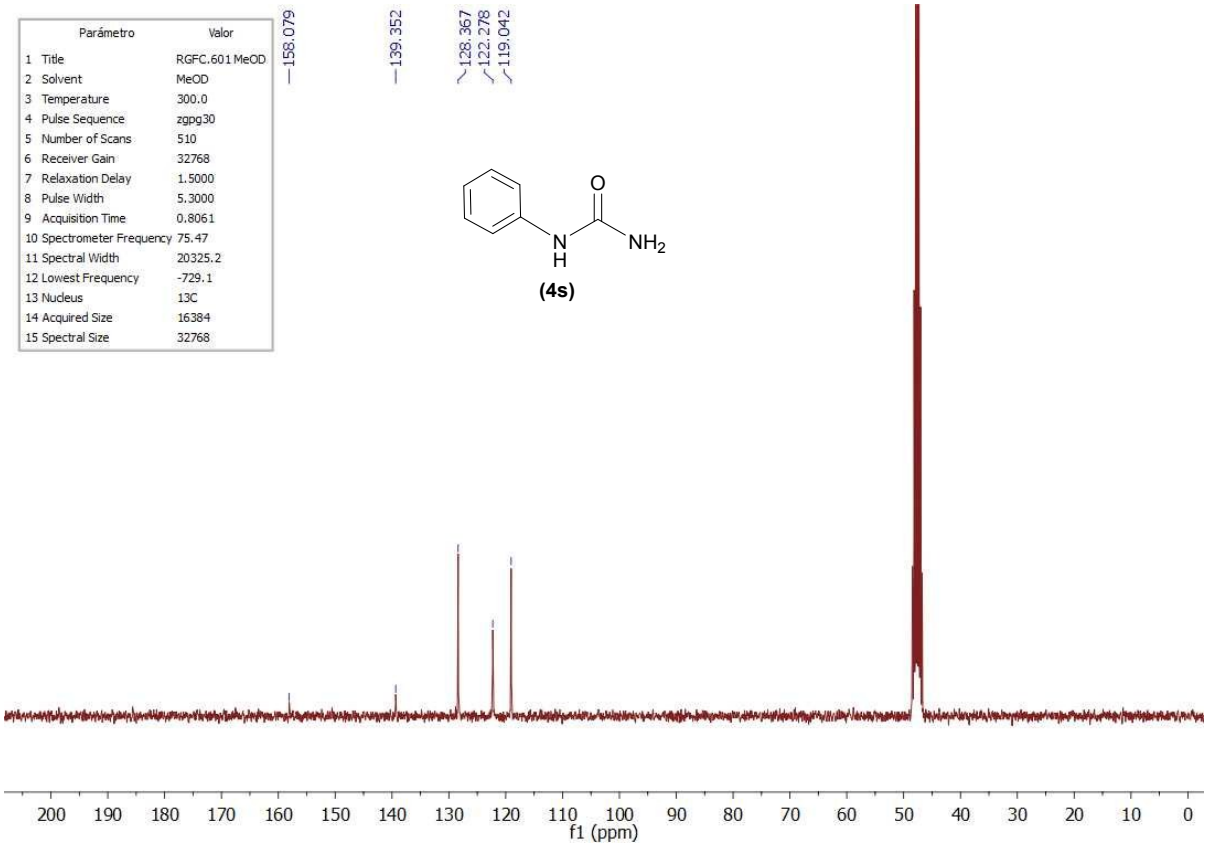

Figure S44. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD, 75 MHz) of urea **4s**.

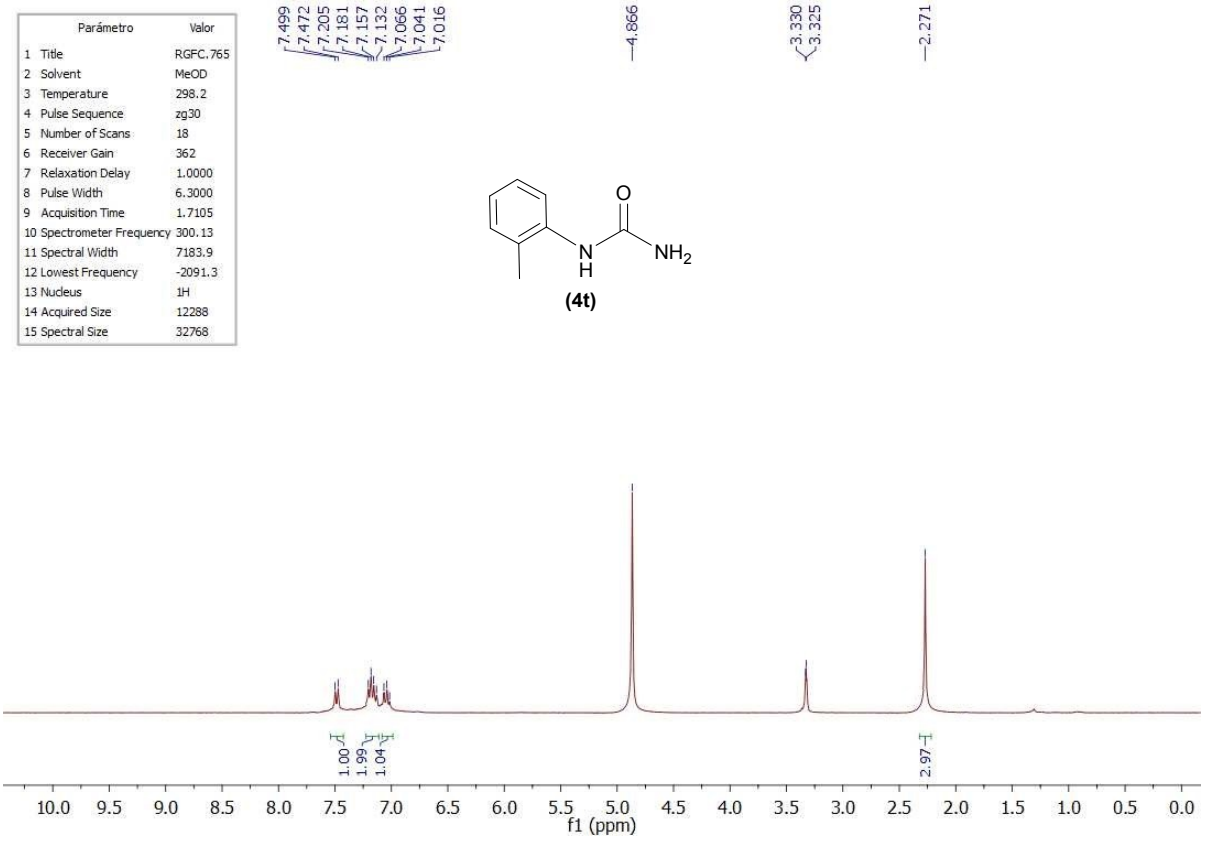

Figure S45. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of urea **4t**.

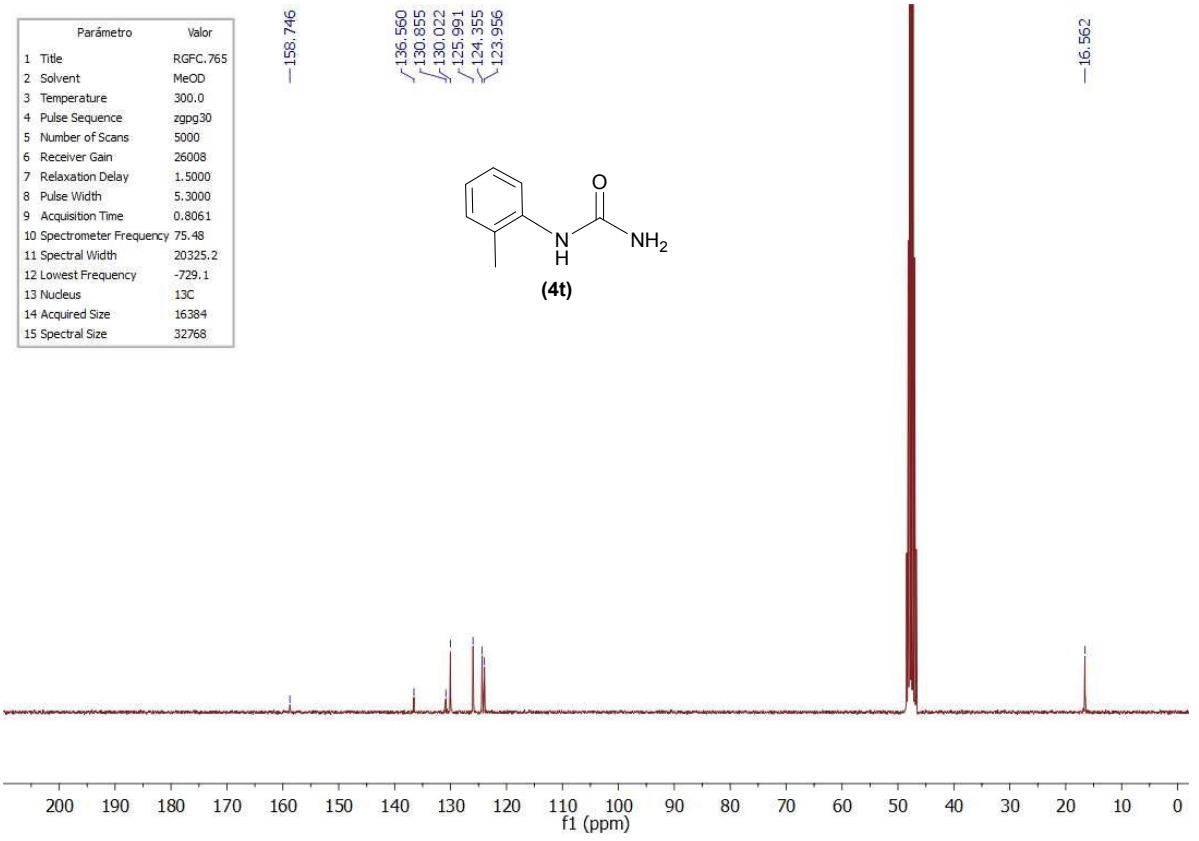

Figure S46. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD, 75 MHz) of urea **4t**.

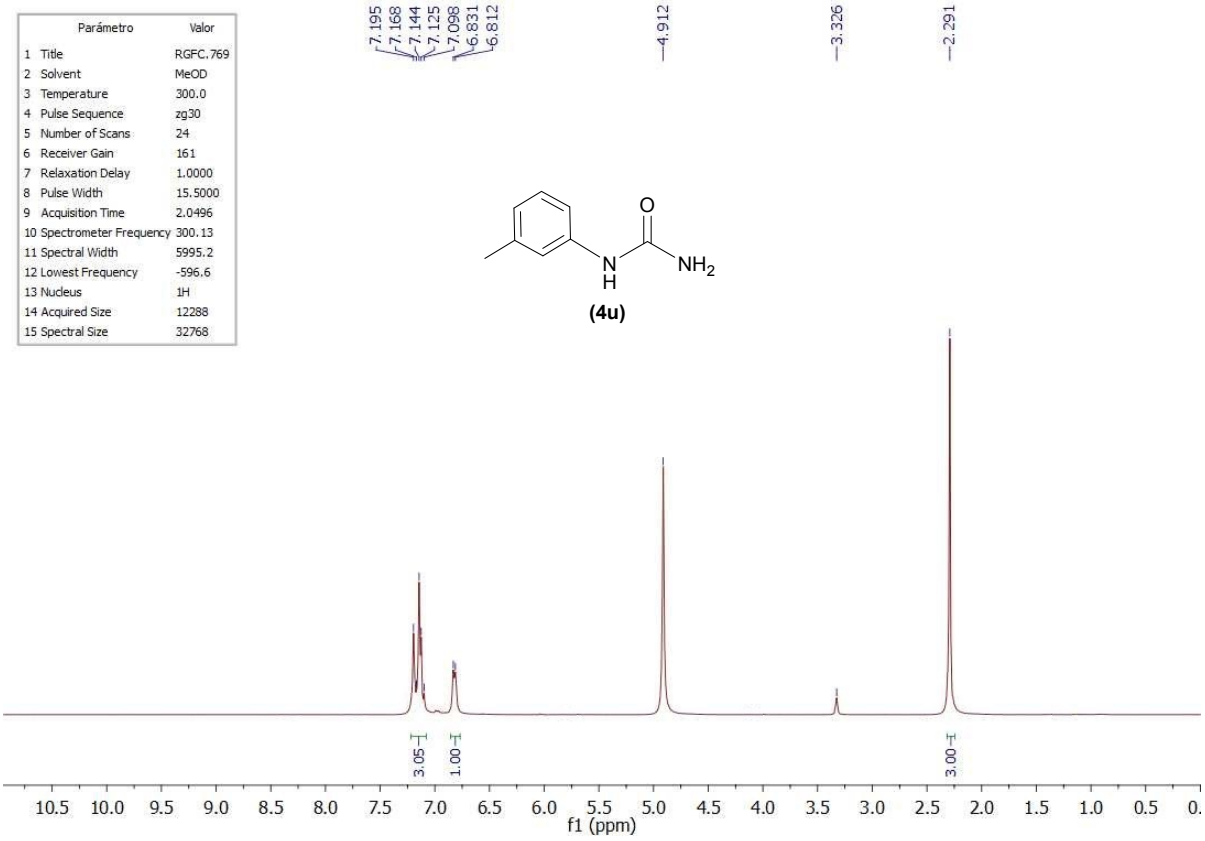

Figure S47. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of urea **4u**.

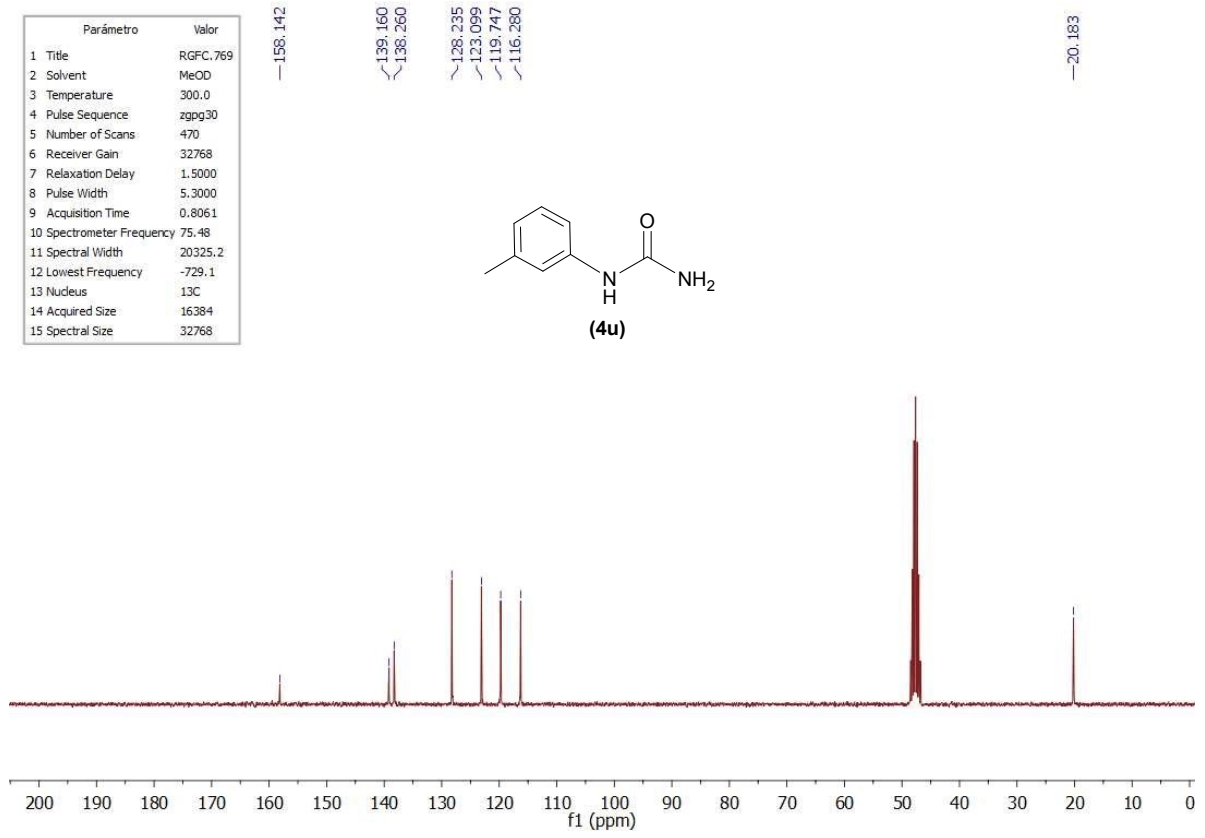

Figure S48. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD, 75 MHz) of urea **4u**.

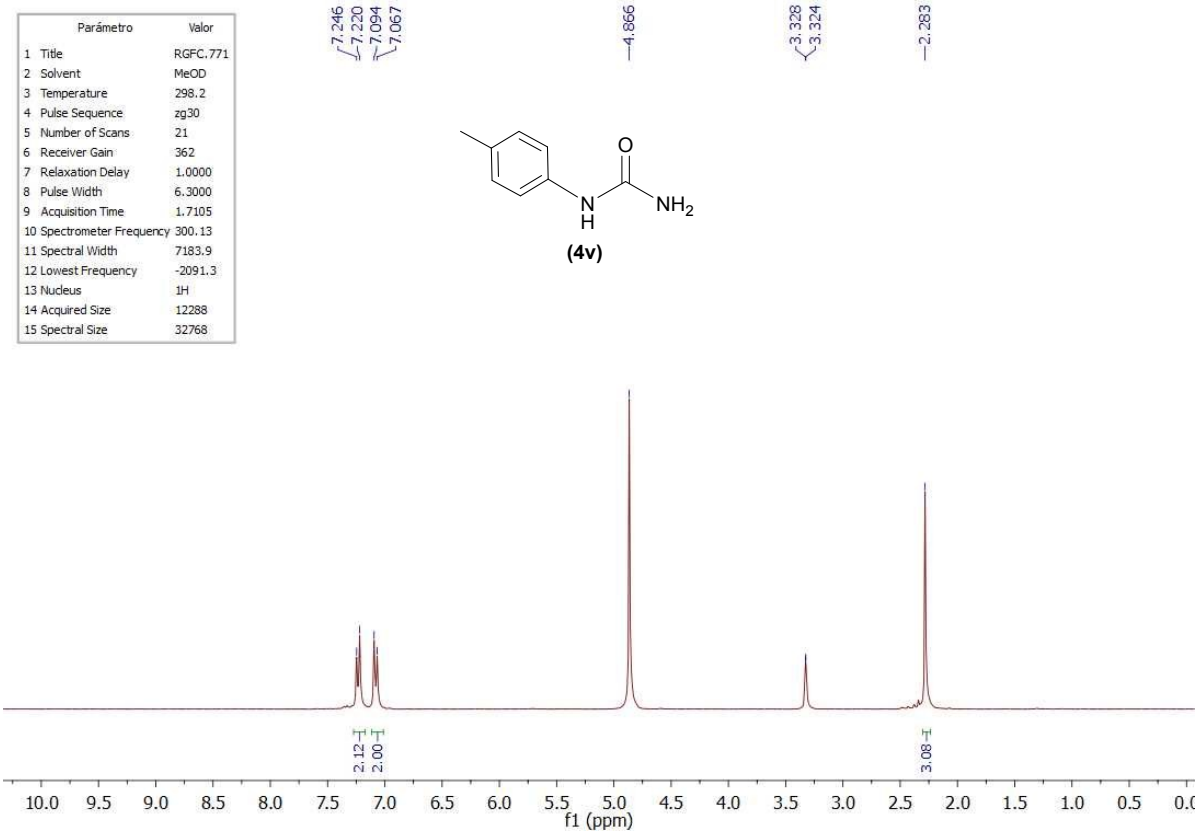

Figure S49. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of urea **4v**.

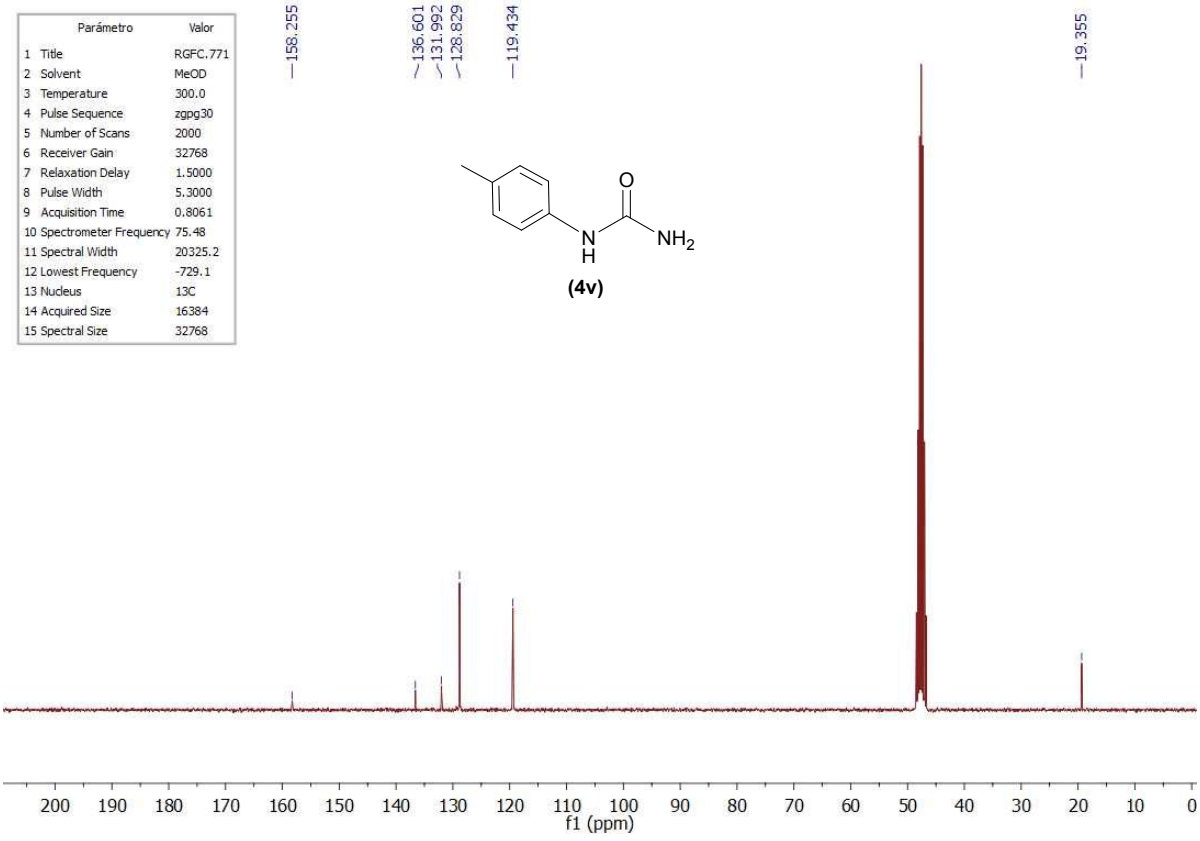

Figure S50. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD, 75 MHz) of urea **4v**.

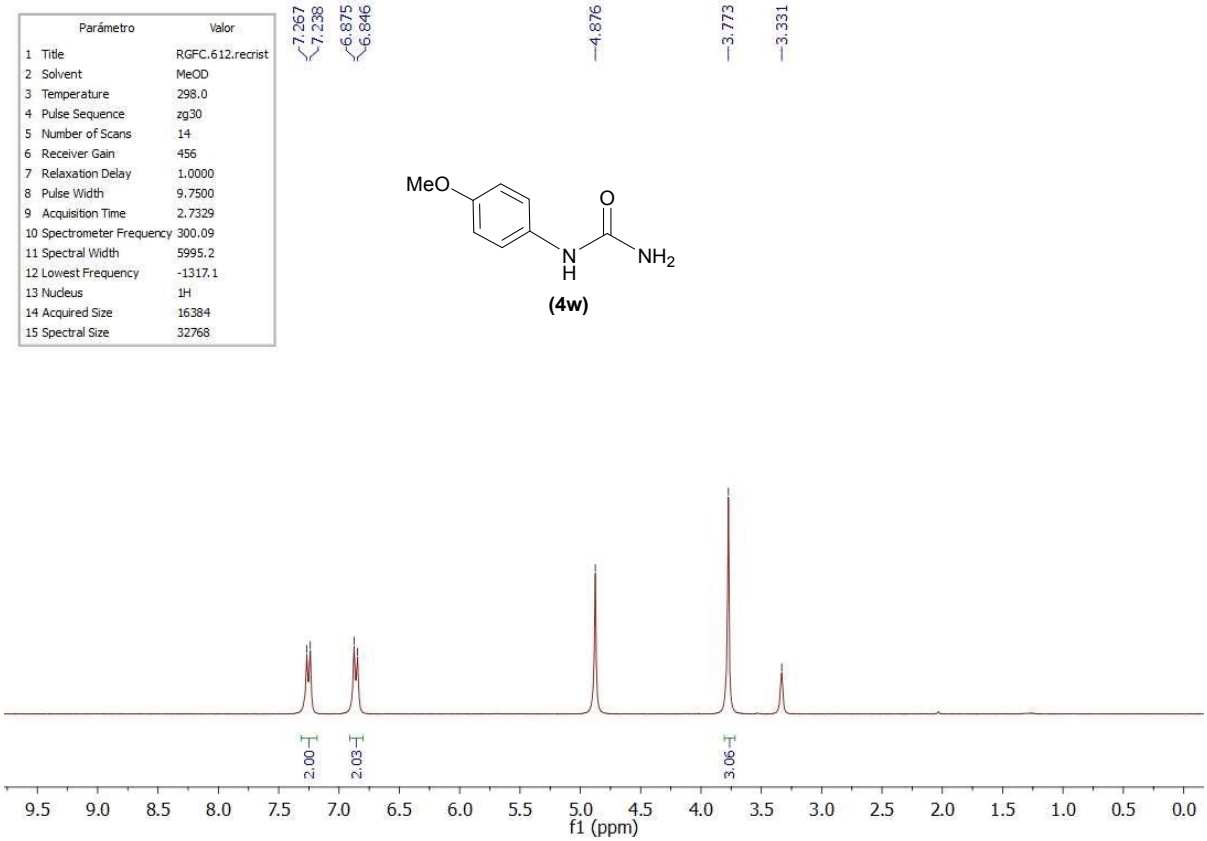

Figure S51. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of urea **4w**.

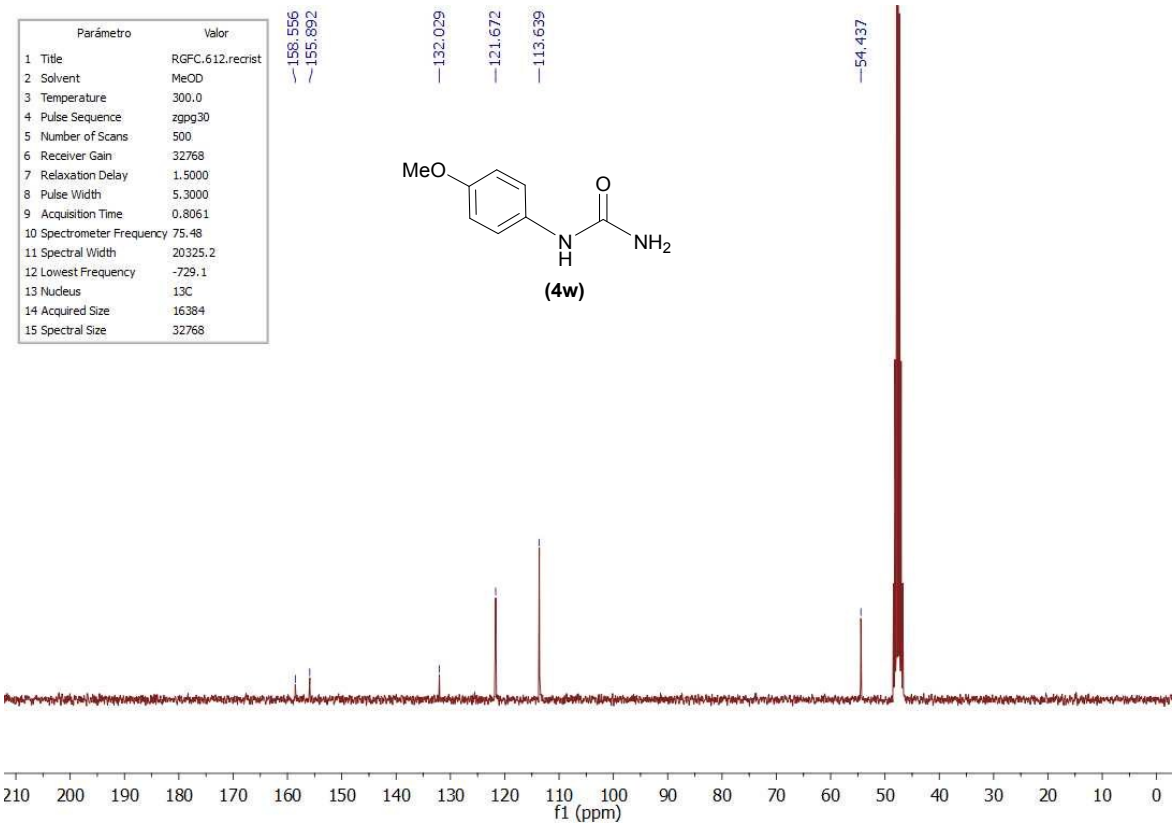

Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD, 75 MHz) of urea **4w**.

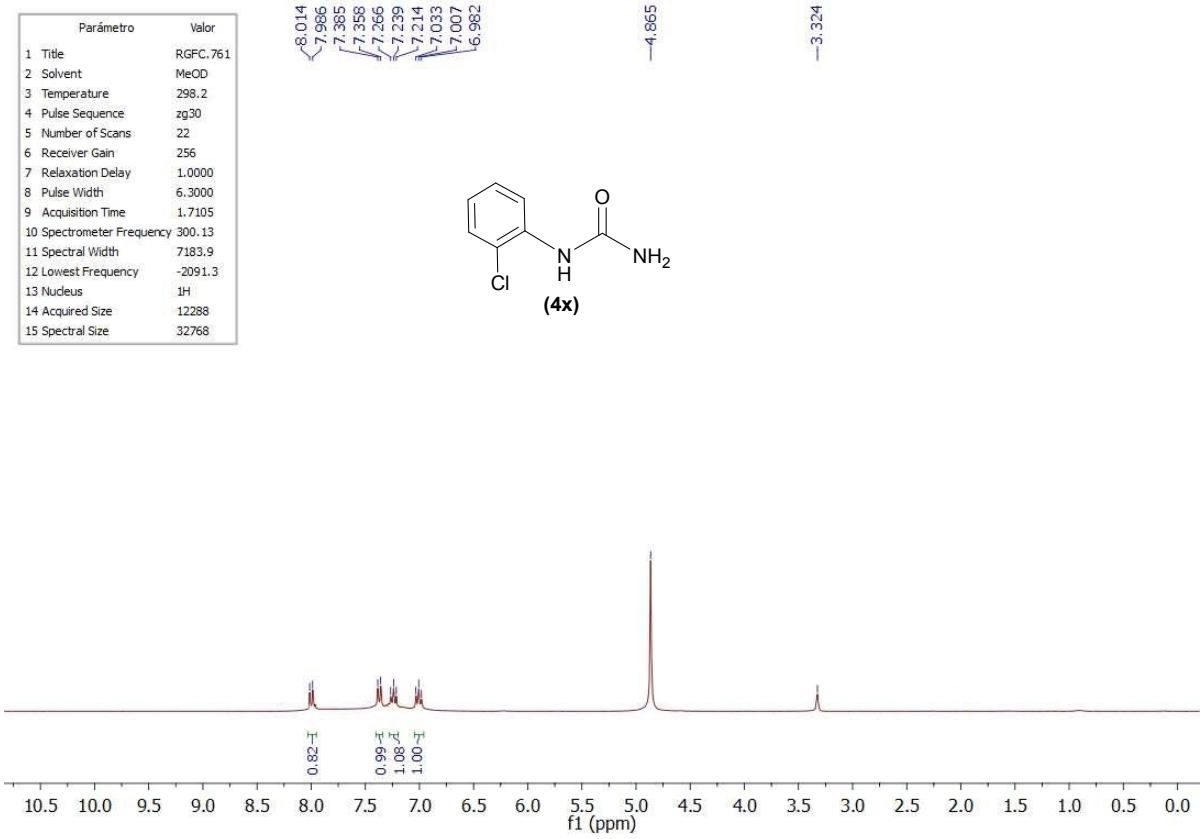

Figure S53. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of urea **4x**.

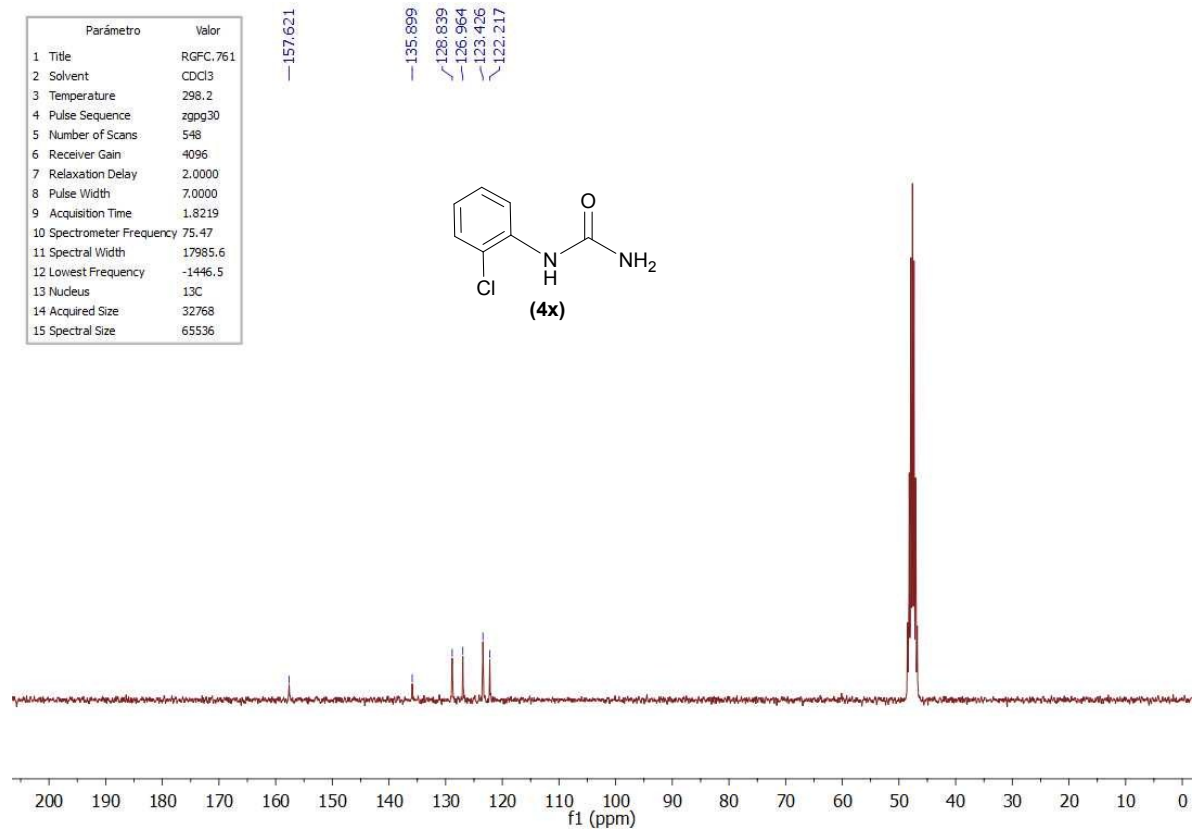

Figure S54. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD, 75 MHz) of urea **4x**.

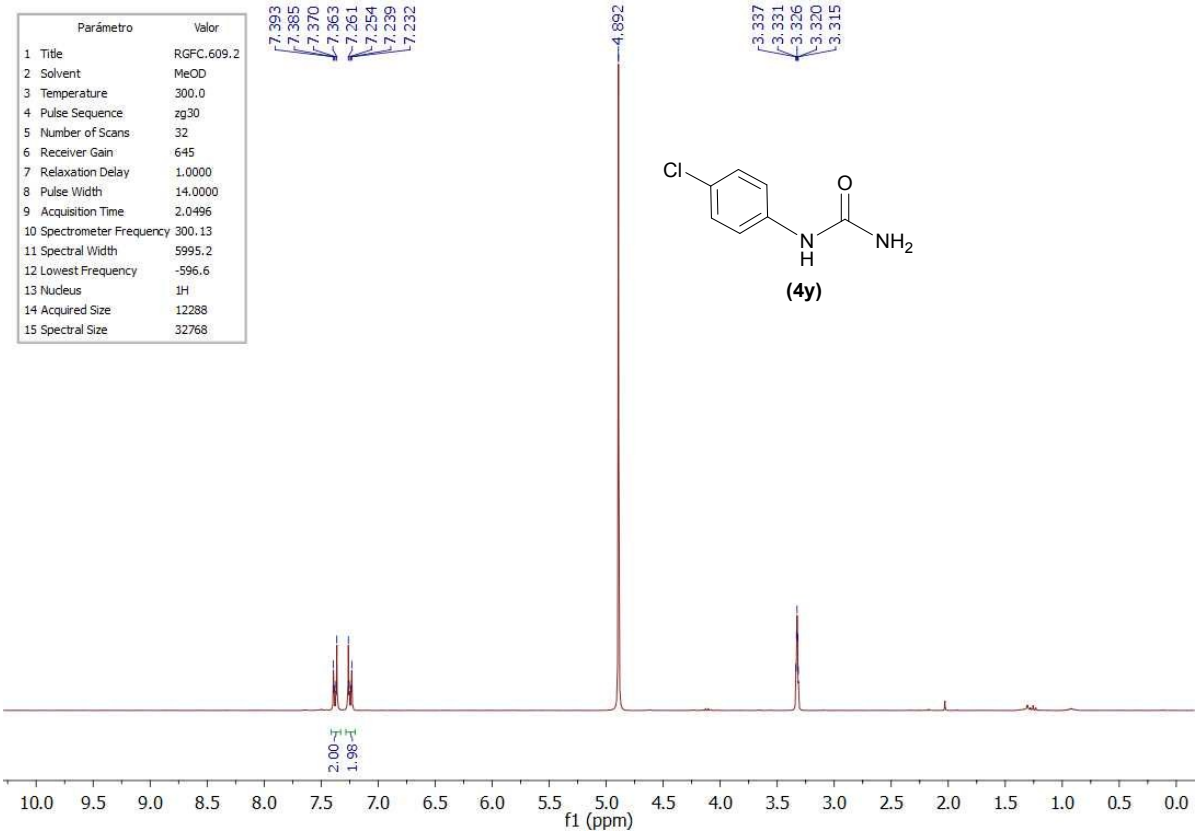

Figure S55. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of urea **4y**.

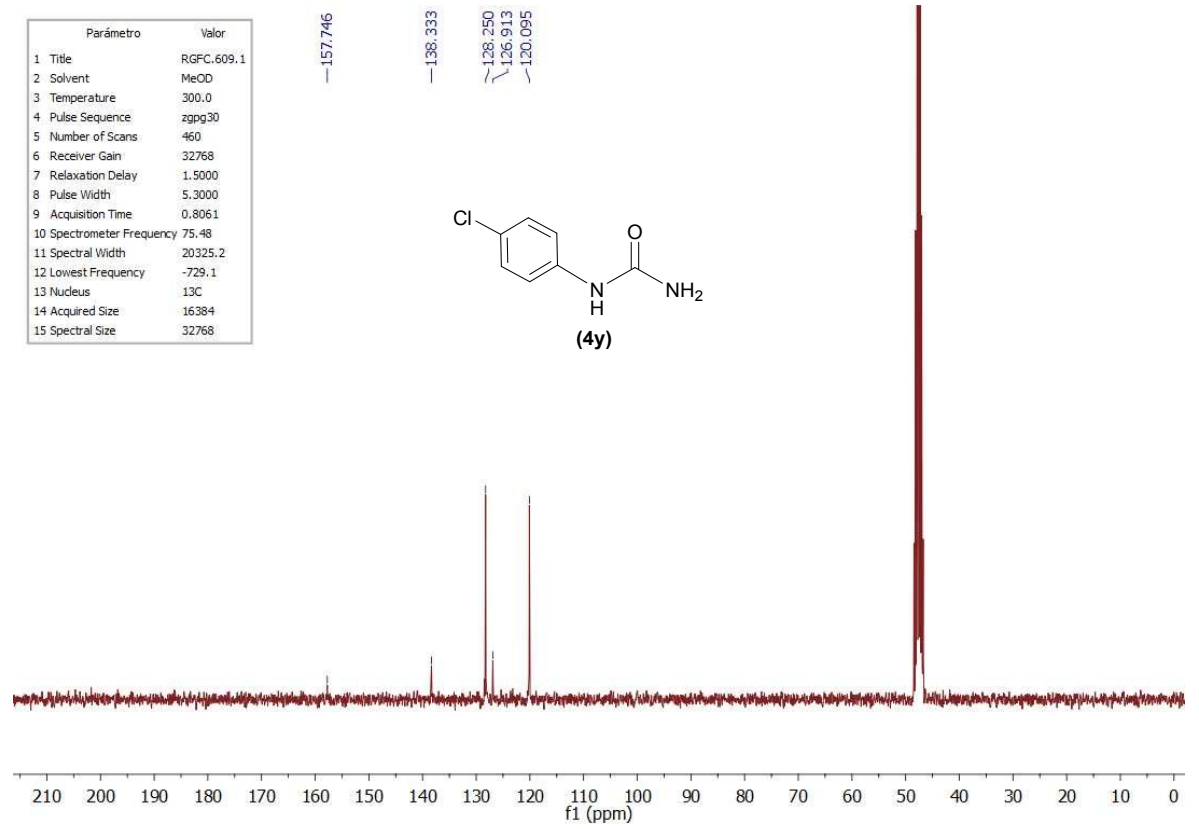

Figure S56. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD, 75 MHz) of urea **4y**.

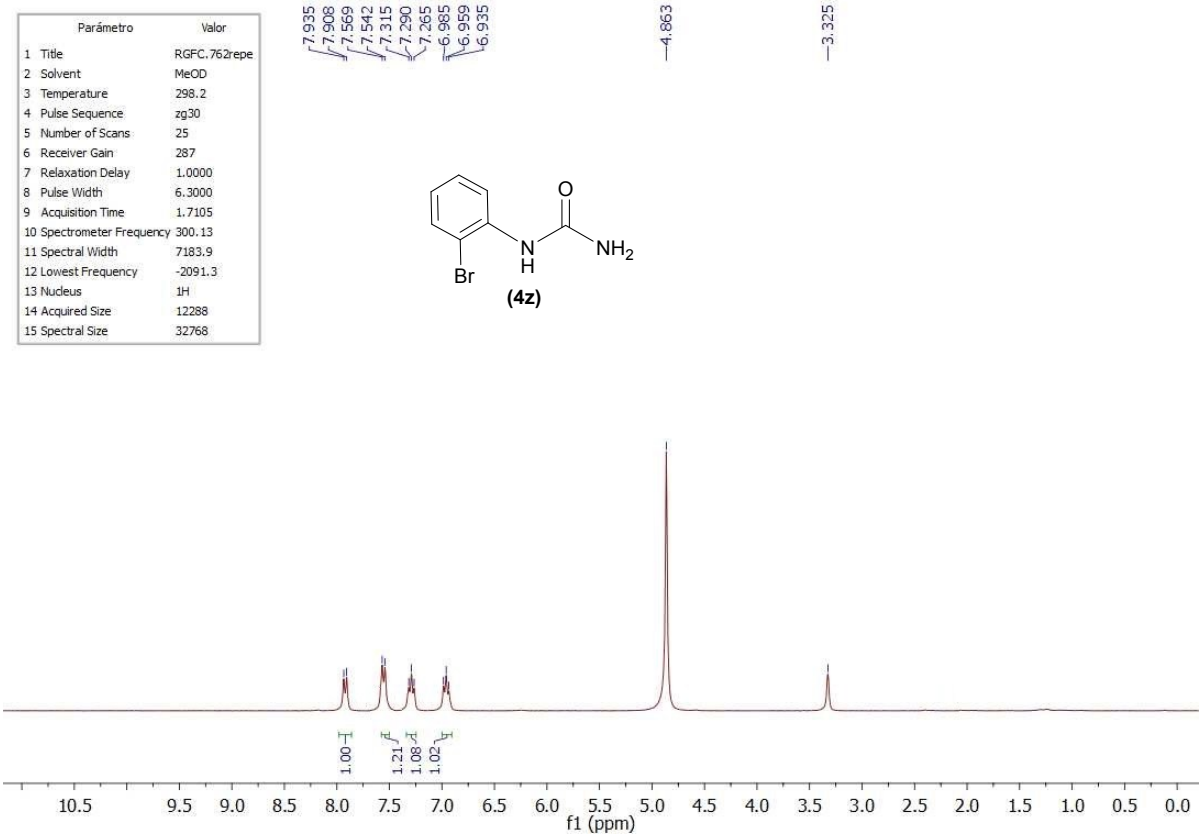

Figure S57. ^{1}H NMR spectrum (CD_3OD, 300 MHz) of urea **4z**.

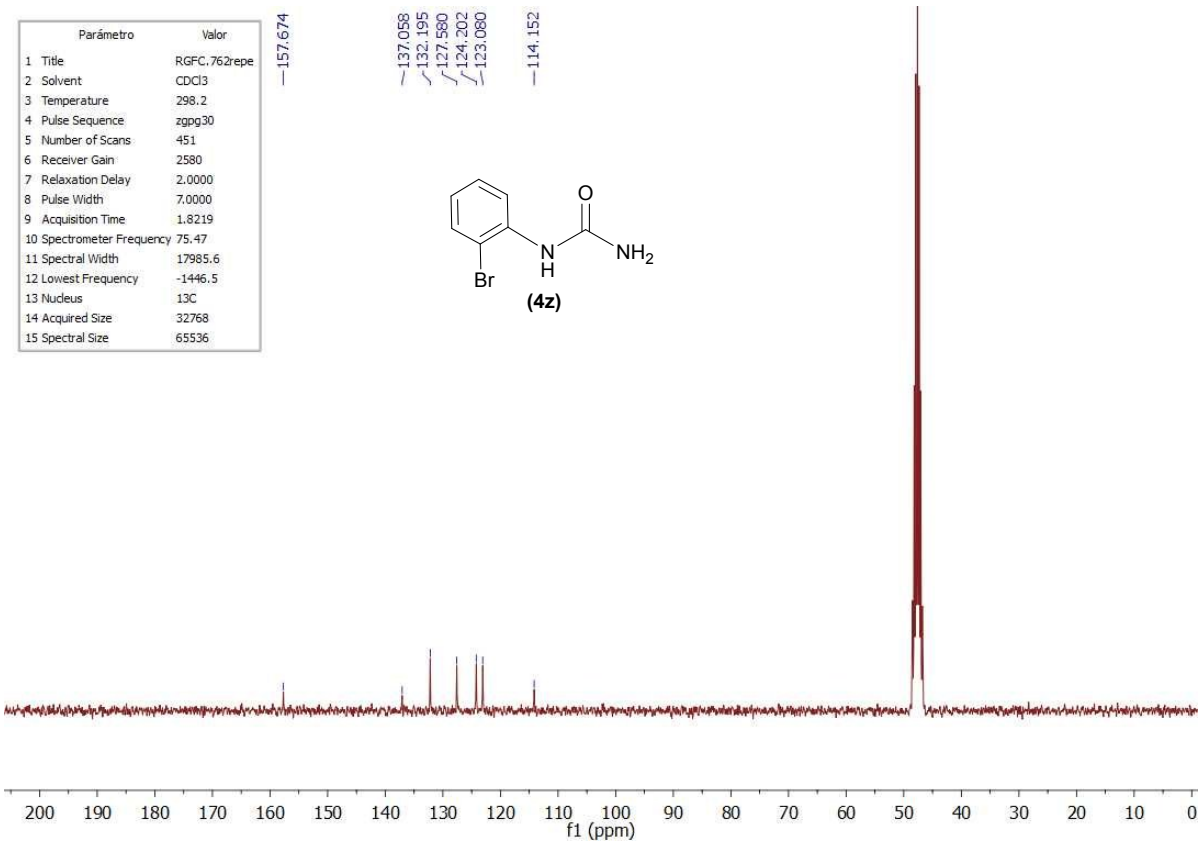

Figure S58. $^{13}C\{^{1}H\}$ NMR spectrum (CD_3OD, 75 MHz) of urea **4z**.

Details and justification about the computational protocol used

The geometry and energy of the stable species (starting complexes, **1-OH-cyan_M**, and intermediates, **2-OH-cyan_M**) and transition states (**TS1-OH-cyan_M** and **TS2-OH-cyan_M**) involved in the [MCl_2(η^6-*p*-cymene)(PMe_2OH)] (M = Ru, Os)-catalyzed hydration of cyanamide (**cyan**) were fully optimized in water solution with the Polarizable Continuum Model (PCM)[1] and the Universal Force Field (UFF) radii[2] in conjunction with the hybrid density functional B3LYP[3] and the 6-31+G(d,p) basis set for nonmetal atoms[4] together with the valence double-ζ basis set LANL2DZ plus the effective core potential of Hay and Wadt for the Ru and Os atoms,[5] and by using a modified Schlegel analytical gradient optimization method.[6] The default ("FineGrid") integration grid with 75 radial shells and 302 angular points was employed in these computations. The same computational protocol was also used to fully optimize the rate-determining transition state of the intermolecular mechanism in water solution (**TS1-H_2O-cyan_M**) as well as the key species of the intramolecular mechanism (**1-OH-dmcyan_Ru**, **TS1-OH-dmcyan_Ru**, **2-OH-dmcyan_Ru**, **TS2-OH-dmcyan_Ru**, and **3-OH-dmcyan_Ru**) and the direct OH/OMe exchange in the [RuCl(η^6-*p*-cymene)(PMe_2OH)(dmcyan)]$^+$ complex (**1-OH-exchange-dmcyan_Ru**, **TS-exchange-dmcyan_Ru**, and **1-OMe-exchange-dmcyan_Ru**) for the reactivity of [$RuCl_2$(η^6-*p*-cymene)(PMe_2OH)] towards dimethylcyanamide (**dmcyan**) in methanol solution. Relative dielectric permittivities of 78.36 and 32.6 were assumed to simulate water and methanol as the solvents experimentally employed, respectively. Based on previous investigations on the hydration of acetonitrile and benzonitrile catalyzed by [MCl_2(η^6-*p*-cymene)(PMe_2OH)] (M = Ru, Os),[7] the most significant contribution to the free energy of solvation (*i.e.* the electrostatic solute-solvent interaction), was only considered in the PCM calculations. In addition to this, we also remark that the PCM model used here has been designed only for predicting thermodynamic magnitudes at room temperature. Almost all continuum solvation models have the same limitation.[8] To the best of our knowledge, only a few have incorporated the effect of temperature through parametrization processes using compounds containing only H, C, N, O, N, F, S, and Cl, but not metals.[8] This fact just allows us to make an approximate comparison of our thermochemical results at 298.15 K with the experimental data obtained at 313.15 K, although it is reasonably reliable considering the temperature difference and the computational protocol here used (see below).

On the whole, it is well-known that B3LYP geometries fit well the experimental ones (see for instance ref. 7 and references therein). In this scenario and aiming at obtaining more accurate energies, we underwent more sophisticated single-point energy calculations on the PCM-B3LYP/6-31+G(d,p) (LANL2DZ for Ru and Os) geometries by using the highly accurate domain localized pair natural orbital-coupled cluster method with single, double, and perturbative triple excitations (DLPNO-CCSD(T)).[9] This methodology can recover more than 99.9% of the CCSD(T) electron correlation energy with a computational cost similar to a Density Functional Theory method. Since CCSD (T) is widely accepted as the state-of-art in quantum chemistry, the feasible computational approach DLPNO-CCSD (T) has started to be used in order to obtain highly accurate energies for medium and large size systems.[10] In the present work, DLPNO-CCSD(T) was used in conjunction with the def2-TZVPP[11] basis set and the conductor-like polarizable continuum model (CPCM).[12] The SCF convergence criterion TightSCF (energy change = 1.000×10^{-8} a.u.) as well as the default "NormalPNO" DLPNO settings (TCutPairs = 1.000×10^{-4}, TCutPNO = 3.330×10^{-7}, TCutMKN = 1.000×10^{-3}) were used as recommended for most computational applications in terms of cost/efficiency ratio.[13] The resolution of identity (RI)[14] approximation was used to speed up both the calculation of the

bielectronic integrals in the SCF procedure and the integral transformation of the DLPNO-CCSD(T)-like part using the auxiliary Coulomb+Exchange-fitting basis set def2/JK[15] and the correlation fitting auxiliary basis set def2-TZVPP/C[16], respectively. The all-electron def2-TZVPP basis set of the Karlsruhe group was used on all the non-metal elements (H: *5s2p1d* $\rightarrow$ *3s2p1d*; C, N, O: *11s6p2d1f* $\rightarrow$ *5s3p2d1f*; P, Cl: *14s9p3d1f* $\rightarrow$ *5s5p3d1f*).[11b] The valence electrons of the Ru and Os atoms were also described with the corresponding def2-TZVPP basis set (*7s7p5d2f1g* $\rightarrow$ 6s4p3d2f1g and 8s7p6d2f1g $\rightarrow$ *6s4p3d2f1g*, respectively)[11b] while the quasi-relativistic effective core potential (ECP) of the Stuttgart type was employed to represent 28 and 60 inner electrons of such transition metals, respectively.[11a] Concerning condensed-phase computations, CPCM represents the solvent as a dielectric polarizable continuum.[17] The solute is placed in a cavity of approximately molecular shape, which is created in the continuum medium by the GEPOL algorithm using a solvent-excluding surface.[18] The solvent reaction field is represented by polarization charges on the cavity surface, which are in turn determined by the solute.

Theoretical results concerning the species **1-OH-S_M** and **TS1-OH-S_M** (**S** = **actn** (acetonitrile), **bzn** (benzonitrile), and **cyan** (cyanamide); **M** = **Ru** and **Os**) were analyzed in terms of electron delocalization indexes (DI) within the framework of Bader's Quantum Theory of Atoms in Molecules. DI show the approximate number of electron pairs shared between two atoms and can be defined by the following equation:[19]

$$\mathrm{DI} = 4\sum_{i,j}^{N/2} S_{ij}(A)\, S_{ij}(B) \qquad (1)$$

The sums in equation (1) run over $N/2$ occupied molecular orbitals. $S_{ij}(A)$ ($S_{ij}(B)$) is the overlap between orbitals *i* and *j* within the basin of atom *A* (*B*).

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Table S1. PCM-B3LYP/6-31+G(d,p) (LANL2DZ for Ru and Os) absolute energies in water solution without and with including thermal corrections (E and G, respectively), and CPCM-DLPNO-CCSD(T)/def2-TZVPP//PCM-B3LYP/6-31+G(d,p) (LANL2DZ for Ru and Os) absolute energies in water solution without and with including thermal corrections (E' and G', respectively) of the critical structures involved in the most energy-demanding steps for the intramolecular mechanism found for the [MCl_2(η^6-*p*-cymene)(PMe_2OH)] (M = Ru (**1**), Os (**2**))-catalyzed hydration of acetonitrile (**actn**), benzonitrile (**bzn**), and cyanamide (**cyan**).[a,b,c] For comparison purposes with the intramolecular mechanism in the cyanamide case, the corresponding absolute energy values of the rate-determining TS located for the intermolecular mechanism, **TS1-H_2O-cyan_Ru** and **TS1-H_2O-cyan_Os**, have also been included.

Species	E	G	E'	G'
1-OH-actn_Ru	-1879.188466	-1878.807460	-1877.544367	-1877.163361
TS1-OH-actn_Ru	-1879.149323	-1878.759350	-1877.503540	-1877.113567
2-OH-actn_Ru	-1879.200147	-1878.810854	-1877.553147	-1877.163854
TS2-OH-actn_Ru	-1879.168717	-1878.775910	-1877.516004	-1877.123197
1-OH-actn_Os	-1876.349266	-1875.964542	-1873.232627	-1872.847903
TS1-OH-actn_Os	-1876.308852	-1875.919415	-1873.191871	-1872.802434
2-OH-actn_Os	-1876.361984	-1875.972061	-1873.242242	-1872.852319
TS2-OH-actn_Os	-1876.329269	-1875.937797	-1873.205651	-1872.814179
1-OH-bzn_Ru	-2070.931828	-2070.500118	-2068.917997	-2068.486287
TS1-OH-bzn_Ru	-2070.890809	-2070.452544	-2068.878111	-2068.439846
2-OH-bzn_Ru	-2070.945281	-2070.507725	-2068.928647	-2068.491091
TS2-OH-bzn_Ru	-2070.912653	-2070.474624	-2068.894339	-2068.456310
1-OH-bzn_Os	-2068.093189	-2067.661714	-2064.606288	-2064.174813
TS1-OH-bzn_Os	-2068.050643	-2067.612634	-2064.565820	-2064.127811
2-OH-bzn_Os	-2068.106958	-2067.669638	-2064.617242	-2064.179922
TS2-OH-bzn_Os	-2068.072843	-2067.633609	-2064.582261	-2064.143027
1-OH-cyan_Ru	-1895.229925	-1894.855097	-1893.580090	-1893.205262
TS1-OH-cyan_Ru	-1895.191961	-1894.813289	-1893.539897	-1893.161225
2-OH-cyan_Ru	-1895.255286	-1894.875604	-1893.601842	-1893.222160
TS2-OH-cyan_Ru	-1895.221192	-1894.839477	-1893.565136	-1893.183421
TS1-H_2O-cyan_Ru	-1895.174410	-1894.794723	-1893.522621	-1893.142934
1-OH-cyan_Os	-1892.390324	-1892.017971	-1889.266411	-1888.894058
TS1-OH-cyan_Os	-1892.351754	-1891.974607	-1889.228218	-1888.851071
2-OH-cyan_Os	-1892.417564	-1892.037671	-1889.290990	-1888.911097
TS2-OH-cyan_Os	-1892.381865	-1891.999865	-1889.253862	-1888.871862
TS1-H_2O-cyan_Os	-1892.334648	-1891.954640	-1889.211734	-1888.831726

[a]All the energies are in hartree. [b]Electrostatic solvation terms have only been considered in these computations. [c]G' = G – E + E'.

Table S2. PCM-B3LYP/6-31+G(d,p) (LANL2DZ for Ru and Os) relative energies in water solution without and with including thermal corrections (ΔE and ΔG, respectively), and CPCM-DLPNO-CCSD(T)/def2-TZVPP//PCM-B3LYP/6-31+G(d,p) (LANL2DZ for Ru and Os) relative energies in water solution without and with including thermal corrections (ΔE' and ΔG', respectively) of the critical structures involved in the most energy-demanding steps for the intramolecular mechanism found for the [MCl_2(η^6-*p*-cymene)(PMe_2OH)] (M = Ru (**1**), Os (**2**))-catalyzed hydration of acetonitrile (**actn**), benzonitrile (**bzn**), and cyanamide (**cyan**).[a,b,c] For comparison purposes with the intramolecular mechanism in the cyanamide case, the corresponding relative energy values of the rate-determining TS located for the intermolecular mechanism, **TS1-H_2O-cyan_Ru** and **TS1-H_2O-cyan_Os**, have also been included.

Species	ΔE	ΔG	ΔE'	ΔG'
1-OH-actn_Ru	0.0	0.0	0.0	0.0
TS1-OH-actn_Ru	24.6	30.2	25.6	31.2
2-OH-actn_Ru	-7.3	-2.1	-5.5	-0.3
TS2-OH-actn_Ru	12.4	19.8	17.8	25.2
1-OH-actn_Os	0.0	0.0	0.0	0.0
TS1-OH-actn_Os	25.4	28.3	25.6	28.5
2-OH-actn_Os	-8.0	-4.7	-6.0	-2.8
TS2-OH-actn_Os	12.5	16.8	16.9	21.2
1-OH-bzn_Ru	0.0	0.0	0.0	0.0
TS1-OH-bzn_Ru	25.7	29.9	25.0	29.1
2-OH-bzn_Ru	-8.4	-4.8	-6.7	-3.0
TS2-OH-bzn_Ru	12.0	16.0	14.8	18.8
1-OH-bzn_Os	0.0	0.0	0.0	0.0
TS1-OH-bzn_Os	26.7	30.8	25.4	29.5
2-OH-bzn_Os	-8.6	-5.0	-6.9	-3.2
TS2-OH-bzn_Os	12.8	17.6	15.1	19.9
1-OH-cyan_Ru	0.0	0.0	0.0	0.0
TS1-OH-cyan_Ru	23.8	26.2	25.2	27.6
2-OH-cyan_Ru	-15.9	-12.9	-13.6	-10.6
TS2-OH-cyan_Ru	5.5	9.8	9.4	13.7
TS1-H_2O-cyan_Ru	34.8	37.9	36.1	39.1
1-OH-cyan_Os	0.0	0.0	0.0	0.0
TS1-OH-cyan_Os	24.2	27.2	24.0	27.0
2-OH-cyan_Os	-17.1	-12.4	-15.4	-10.7
TS2-OH-cyan_Os	5.3	11.4	7.9	13.9
TS1-H_2O-cyan_Os	34.9	39.7	34.3	39.1

[a]All the energies are in kcal/mol. [b]Electrostatic solvation terms have only been considered in these computations. [c]$\Delta G' = \Delta G - \Delta E + \Delta E'$.

Table S3. PCM-B3LYP/6-31+G(d,p) (LANL2DZ for Ru and Os) optimized cartesian coordinates (in Å) in water solution of the critical structures involved in the most energy-demanding steps for the intra- and intermolecular mechanisms found for the cyanamide (**cyan**) hydration catalyzed by complexes [$MCl_2(\eta^6$-*p*-cymene)(PMe_2OH)] (M = Ru and Os). Analogous data previously reported for the intramolecular mechanism of the hydration of acetonitrile (**actn**) and benzonitrile (**bzn**) have also been included. Imaginary vibrational frequencies are also given for the transition states located. Only the electrostatic solvation terms have been considered in these computations.

1-OH-cyan_Ru

C	1.951657	1.931309	-1.313342
C	2.174805	0.656640	-1.830571
C	2.659442	-0.417818	-0.997691
C	2.929285	-0.132181	0.354538
C	2.671711	1.170489	0.891585
C	2.169328	2.215035	0.081034
Ru	0.713891	0.426610	0.025287
N	-0.961689	1.623424	-0.000360
C	-1.928476	2.270805	-0.041081
N	-2.998543	3.032841	-0.156780
C	2.942280	-1.763324	-1.642838
C	4.280003	-1.671659	-2.414072
C	1.935421	3.596955	0.626287
P	-0.105388	-0.386679	2.067562
C	0.219881	0.697943	3.503597
Cl	-0.656433	-1.346842	-1.039588
C	0.549305	-2.026669	2.550957
O	-1.722772	-0.515588	2.185382
C	2.948441	-2.951455	-0.673075
O	-3.063136	-2.688875	1.521044
O	-4.807161	-2.462891	-0.542125
O	-3.608440	-0.746026	-2.262866
O	-4.790753	1.869033	-2.112546
H	-0.229552	0.254150	4.396696
H	1.294716	0.814940	3.658435
H	-0.222320	1.681081	3.324085
H	0.099238	-2.336454	3.498968
H	0.309028	-2.755177	1.773341
H	1.635125	-1.973161	2.664066
H	2.871133	1.360207	1.939759
H	3.308397	-0.905406	1.010845
H	1.541517	2.706256	-1.952384
H	1.937980	0.452231	-2.869113
H	-4.812981	2.332994	-2.962593
H	-5.009652	-3.284839	-1.008013
H	-5.716252	1.780077	-1.840669
H	-4.420355	-1.846247	-1.215427
H	-3.958901	0.165329	-2.222906
H	-2.689228	-0.715868	-1.933951
H	-2.161495	-1.339634	1.818606
H	-3.578874	-2.945220	2.297430
H	-3.706073	-2.632164	0.767389
H	1.824737	3.583226	1.712688
H	2.792612	4.234668	0.378857
H	1.044588	4.051668	0.185844
H	2.143409	-1.929379	-2.375326
H	4.459988	-2.608511	-2.950867
H	4.274070	-0.858168	-3.146426
H	5.115927	-1.505999	-1.725298
H	2.010641	-3.019176	-0.115342
H	3.072101	-3.879489	-1.239695
H	3.777976	-2.894234	0.040406
H	-3.721371	2.718498	-0.816958
H	-3.315898	3.523942	0.671416

TS1-OH-cyan_Ru

(ν=319i cm^{-1})

C	2.807817	-0.034733	-0.556541
C	2.707656	-0.211890	0.840816
C	2.174540	0.824396	1.674646
C	1.732497	2.050464	1.122990
C	1.893112	2.252962	-0.294733
C	2.407134	1.239371	-1.102349
Ru	0.618602	0.326262	0.136729
Cl	-0.304612	-0.872102	-1.882400
C	1.168755	3.142488	1.988951
C	3.394148	-1.076432	-1.495030
C	3.337162	-2.514865	-0.965135
N	-1.252171	1.307599	0.326989
C	-2.197038	1.015542	1.001447
N	-3.382565	1.309295	1.546671
P	-0.530626	-1.260515	1.486755
O	-2.082052	-0.881278	1.578182
C	4.844446	-0.676865	-1.851280
C	0.051075	-1.353494	3.228831
C	-0.444759	-3.008569	0.939655
O	-4.039148	-2.095702	0.187445
O	-4.768777	-0.572496	-1.841536
O	-2.782377	0.530686	-2.846042
O	-2.303260	2.816573	-1.828040
H	-0.571737	-2.072623	3.770603
H	1.094658	-1.677086	3.279178
H	-0.045805	-0.372679	3.701087
H	-1.067160	-3.624467	1.596434
H	-0.795407	-3.091290	-0.090240
H	0.590521	-3.357700	0.994249
H	2.086319	0.659623	2.741810
H	3.004514	-1.150103	1.292972
H	1.546883	3.178026	-0.743130
H	2.445673	1.384609	-2.176890
H	-1.792718	2.517538	-1.039237
H	-5.280829	-1.103764	-2.467252
H	-1.730777	3.410612	-2.334040
H	-3.639349	0.064625	-2.423389
H	-2.653027	1.491855	-2.502632
H	-1.963477	0.021416	-2.562465
H	-3.297900	-1.690692	0.713727
H	-4.731855	-2.325681	0.820888
H	-4.530620	-1.164962	-1.065851
H	0.365436	3.677594	1.476271
H	0.782558	2.743648	2.929799
H	1.959503	3.866011	2.222727
H	2.798980	-1.033343	-2.415311
H	2.317541	-2.802597	-0.694937
H	3.687497	-3.202678	-1.740851
H	3.983046	-2.654555	-0.091088
H	5.251041	-1.376130	-2.589091
H	4.896868	0.330637	-2.276290
H	5.485863	-0.706486	-0.963214
H	-3.796541	0.589300	2.123616
H	-3.491605	2.258498	1.886648

2-OH-cyan_Ru

C	2.906572	0.048389	0.778243
C	2.400005	1.322423	1.193044
C	1.926030	2.270759	0.256546
C	1.992392	1.918664	-1.138044
C	2.456793	0.664520	-1.537361
C	2.913036	-0.317160	-0.581018
Ru	0.737742	0.315507	0.028599
N	-1.110298	1.278126	-0.174578
C	-2.130174	1.030473	0.593203
N	-3.343489	1.600559	0.501847
C	1.426192	3.621287	0.687415
C	3.444154	-1.645426	-1.091055
C	4.887132	-1.447898	-1.609564
P	-0.411915	-0.487291	1.848278
C	-0.775017	-2.256345	2.074433
Cl	-0.280851	-1.501066	-1.334110
C	-0.057766	0.127080	3.528992
O	-2.001439	0.140230	1.606984
C	3.376433	-2.788204	-0.069513
O	-3.032238	2.318518	-2.251088
O	-2.962917	-0.323751	-2.872244
O	-5.000709	-1.599514	-1.495895
O	-4.349717	-1.869735	1.199278
H	2.374306	1.562291	2.249860
H	3.238292	-0.652086	1.534750
H	1.615116	2.613397	-1.881138
H	2.424333	0.397098	-2.588193
H	-1.308953	1.923683	-0.936196
H	-5.221734	-2.480976	-1.824365
H	-3.380682	2.901369	-2.937332
H	-3.687648	-0.796329	-2.400490
H	-3.065105	1.391426	-2.601618
H	-2.137693	-0.644532	-2.460725
H	-3.637783	-1.287925	1.508143
H	-5.064742	-1.780720	1.844358
H	-4.795100	-1.708492	-0.540693
H	1.109818	3.611660	1.732718
H	2.231977	4.357455	0.581007
H	0.588803	3.952935	0.068592
H	2.814511	-1.919673	-1.946078
H	5.249881	-2.378485	-2.057726
H	4.942383	-0.662290	-2.369891
H	5.561758	-1.177743	-0.789418
H	4.054474	-2.622805	0.775148
H	2.362096	-2.919729	0.318121
H	3.679561	-3.723415	-0.550110
H	-1.520001	-2.394676	2.862750
H	-1.120328	-2.683610	1.132317
H	0.154006	-2.752950	2.370600
H	-0.844558	-0.199679	4.214669
H	0.899882	-0.284972	3.861557
H	-0.001037	1.217490	3.526088
H	-4.095007	1.251888	1.078338
H	-3.570312	2.067433	-0.376794

TS2-OH-cyan_Ru

(ν=92i cm^{-1})

C	-3.068775	0.829447	-0.292209
C	-2.247702	1.909097	-0.640065
C	-1.192351	2.359731	0.233024
C	-1.000720	1.674358	1.445962
C	-1.796348	0.527103	1.759043
C	-2.856872	0.092776	0.920325
Ru	-0.901960	0.034726	-0.234094
N	-1.454499	-1.573139	-1.420049
C	-1.328473	-2.832544	-1.033151
O	-0.689379	-3.142920	0.031692
C	-0.398592	3.590325	-0.169848
C	-1.234970	4.849230	0.160102
C	-3.758912	-1.048891	1.300882
P	0.655980	-1.504929	0.705853
O	1.809062	-0.287179	1.388274
Cl	0.820195	0.572277	-1.992310
C	1.952410	-2.371704	-0.278025
C	0.522584	-2.386575	2.314307
N	-1.830415	-3.864545	-1.802962
C	1.002024	3.686182	0.447612
O	4.213730	-0.416516	1.927748
O	5.470436	-0.180864	-0.178448
O	3.965360	1.261337	-1.807652
H	1.443953	-2.235222	2.880773
H	-0.315550	-1.998428	2.896053
H	0.361811	-3.448133	2.130454
H	1.523301	-3.185458	-0.859450
H	2.426564	-1.647868	-0.942209
H	2.700986	-2.776313	0.409913
H	-1.602378	-0.006775	2.682436
H	-0.221859	1.974556	2.135456
H	-3.832492	0.495382	-0.987142
H	-2.391579	2.403350	-1.594638
H	-1.944270	-1.415392	-2.293114
H	4.785309	-0.364028	1.016630
H	4.250896	1.354792	-2.726886
H	4.920423	0.327469	-0.843678
H	3.012223	1.033606	-1.839614
H	5.748779	-1.005862	-0.601115
H	3.160257	-0.421168	1.716156
H	1.690691	0.542324	0.899422
H	4.468657	-1.187396	2.458645
H	-4.015783	-1.656074	0.428887
H	-3.291712	-1.691452	2.050499
H	-4.692091	-0.657450	1.723594
H	-0.282751	3.541255	-1.259187
H	1.611250	2.813222	0.194818
H	1.513244	4.569696	0.053055
H	0.967375	3.790247	1.537459
H	-0.716639	5.742843	-0.202027
H	-2.222259	4.815758	-0.311216
H	-1.375565	4.950421	1.242123
H	-1.894016	-4.755594	-1.329985
H	-2.602648	-3.663300	-2.424101

TS1-H_2O-cyan_Ru

(ν=586i cm^{-1})

C	2.455691	0.576084	0.957312
C	1.613473	1.695730	1.255979
C	1.058978	2.489708	0.225867
C	1.417840	2.178496	-1.134857
C	2.220079	1.079741	-1.423041
C	2.742351	0.228938	-0.378742
Ru	0.428047	0.297396	-0.058406
Cl	0.198027	-1.783424	-1.474439
N	-1.499528	0.927231	-0.669270
C	-2.529063	1.455031	-0.337466
N	-3.657166	2.024649	-0.852583
P	-0.531095	-0.874259	1.755813
C	0.003098	-0.299800	3.421371
C	-0.156995	-2.667357	1.835378
O	-2.134251	-0.799516	1.825350
O	-2.899332	1.459532	1.412919
O	-3.760278	-2.086410	0.235212
O	-2.708750	-2.247363	-1.992764
O	-2.594545	0.034433	-3.168628
H	-0.503659	-0.915340	4.171180
H	1.083746	-0.400696	3.552034
H	-0.284769	0.743467	3.570834
H	-0.678208	-3.093414	2.698392
H	-0.483319	-3.162254	0.920024
H	0.919517	-2.816623	1.952069
C	0.197405	3.682762	0.532876
H	1.389005	1.935734	2.288052
H	0.994237	2.765197	-1.942906
H	2.850271	-0.019385	1.770976

H	2.416374	0.818474	-2.457633
C	3.662754	-0.914929	-0.769876
H	-3.205592	-2.192691	-1.039781
H	-1.723050	-2.272813	-1.801195
H	-2.811101	-1.379379	-2.522977
H	-3.849879	1.519318	1.603655
H	-3.115033	-1.647214	0.876651
H	-4.043519	-2.925874	0.623711
H	-2.564651	0.410222	1.663770
H	-1.997151	0.447397	-2.502023
H	-2.120209	0.027246	-4.012285
H	-4.108052	2.728137	-0.281779
H	-3.564014	2.305675	-1.822712
C	3.785008	-2.026041	0.280209
H	3.239248	-1.356804	-1.679831
C	5.052712	-0.338419	-1.126592
H	5.704178	-1.139908	-1.489594
H	4.989502	0.425146	-1.908520
H	5.524262	0.112956	-0.246426
H	4.395160	-2.840391	-0.122502
H	4.276237	-1.673644	1.194053
H	2.807141	-2.437331	0.544801
H	-0.604588	3.791874	-0.200965
H	-0.242888	3.610134	1.529598
H	0.810819	4.591209	0.495211

1-OH-cyan_Os

C	2.025521	0.755306	-1.782825
C	2.550442	-0.385250	-1.061667
C	2.858707	-0.217388	0.305852
C	2.581663	1.028288	0.969684
C	2.048067	2.143962	0.266412
C	1.806163	1.984046	-1.145792
Os	0.664561	0.361365	0.060028
P	-0.152360	-0.651891	2.035752
C	0.333142	-2.402580	2.263460
C	2.820373	-1.666703	-1.831625
C	2.889623	-2.930762	-0.966341
C	1.802269	3.462699	0.946515
Cl	-0.754172	-1.309848	-1.131327
N	-1.024557	1.502035	0.119572
C	-1.996877	2.142017	0.129497
N	-3.070123	2.906048	0.078549
C	4.117783	-1.487033	-2.652759
O	-1.771794	-0.632693	2.226263
C	0.353566	0.171889	3.586957
O	-3.316602	-2.625635	1.429841
O	-5.002749	-2.272676	-0.662347
O	-3.711607	-0.589417	-2.350809
O	-4.775457	2.066379	-2.109647
H	-0.121265	-0.329983	4.434712
H	1.439053	0.125667	3.702649
H	0.041799	1.218967	3.560362
H	-0.118791	-2.791911	3.180547
H	-0.007844	-2.987632	1.406538
H	1.421388	-2.476069	2.334576
H	2.786640	1.122296	2.029232
H	3.251612	-1.043357	0.884243
H	1.351312	2.798518	-1.699609
H	1.748367	0.638594	-2.824521
H	-4.698665	2.606001	-2.910376
H	-5.235230	-3.080077	-1.139568
H	-5.723753	2.018420	-1.917846
H	-4.578133	-1.668153	-1.323364
H	-4.029509	0.333131	-2.293685
H	-2.793387	-0.595595	-2.020650
H	-2.299988	-1.374977	1.810220
H	-3.861367	-2.879147	2.186992
H	-3.938756	-2.513015	0.665227
H	1.690358	3.337469	2.025955
H	2.653305	4.130182	0.766438
H	0.906011	3.949474	0.553939
H	1.988566	-1.785431	-2.536258
H	4.284898	-2.370659	-3.276888
H	4.067523	-0.613399	-3.310383
H	4.983417	-1.367685	-1.991562
H	1.980237	-3.062427	-0.374449
H	3.001398	-3.806470	-1.613043
H	3.750173	-2.915509	-0.288197
H	-3.753305	2.698380	-0.661687
H	-3.440580	3.251258	0.957148

TS1-OH-cyan_Os

(ν=302i cm^{-1})

C	-2.114069	0.673176	-1.694694
C	-1.648721	1.931993	-1.222353
C	-1.795119	2.225847	0.185147
C	-2.300025	1.259249	1.064159
C	-2.707194	-0.049891	0.604868
C	-2.635173	-0.313149	-0.787018
Os	-0.574404	0.284853	-0.147321
P	0.593565	-1.393578	-1.393339
C	0.529820	-3.096652	-0.714790
C	-1.086498	2.961181	-2.164156
C	-3.275147	-1.033071	1.615663
C	-3.185555	-2.504460	1.191393
Cl	0.386591	-0.764776	1.941114
N	1.297941	1.215271	-0.360210
C	2.256094	0.927951	-1.016577
N	3.436641	1.216650	-1.563947
C	-4.733796	-0.639381	1.938217
O	2.139816	-1.012950	-1.541185
C	-0.014321	-1.627429	-3.112365
O	4.104036	-2.123310	-0.095684
O	4.862710	-0.487931	1.823565
O	2.902628	0.668367	2.798484
O	2.402869	2.908925	1.679806
H	0.593735	-2.393474	-3.603888
H	-1.061267	-1.944352	-3.122650
H	0.082806	-0.688814	-3.664082
H	1.149639	-3.756598	-1.329604
H	0.891457	-3.100829	0.314779
H	-0.503348	-3.455925	-0.731479
H	-2.030622	0.439370	-2.749073
H	-2.926423	-1.282102	-1.172503
H	-1.424287	3.167413	0.575066
H	-2.300630	1.463209	2.129597
H	1.859751	2.579651	0.929927
H	5.385482	-0.982506	2.470292
H	1.859096	3.539559	2.173001
H	3.755798	0.175234	2.383370
H	2.770462	1.610980	2.414228
H	2.078664	0.151797	2.554879
H	3.356113	-1.756941	-0.643806
H	4.787577	-2.409190	-0.716207
H	4.611488	-1.123963	1.085603
H	-0.286465	3.534265	-1.689218
H	-0.693617	2.494984	-3.070749
H	-1.878128	3.662103	-2.454752
H	-2.683199	-0.911814	2.530936
H	-2.159696	-2.786280	0.940229
H	-3.520092	-3.142646	2.015199
H	-3.828006	-2.721686	0.330764
H	-5.129407	-1.287620	2.727022
H	-4.808363	0.396894	2.283607
H	-5.371521	-0.751072	1.053861
H	3.895163	0.461361	-2.056635
H	3.526734	2.134581	-1.985924

2-OH-cyan_Os

C	2.789620	-0.371061	-0.600950
C	2.820506	-0.003214	0.763545
C	2.312059	1.267925	1.194303
C	1.803237	2.219297	0.266205
C	1.869827	1.880144	-1.137199

C	2.331523	0.624567	-1.550339
Os	0.676249	0.282989	0.036808
Cl	-0.373792	-1.511933	-1.353546
C	1.297610	3.561829	0.715796
C	3.309228	-1.699303	-1.124746
C	3.250854	-2.846759	-0.107833
N	-1.184892	1.220466	-0.181247
C	-2.201784	0.983220	0.600440
O	-2.072655	0.101146	1.616638
P	-0.482252	-0.544967	1.845796
C	-0.127090	0.031183	3.538298
N	-3.407469	1.564852	0.508756
C	4.745293	-1.504990	-1.660579
C	-0.863845	-2.314602	2.037341
O	-3.086882	2.312131	-2.230798
O	-3.070445	-0.321114	-2.889947
O	-5.105299	-1.579313	-1.497528
O	-4.452511	-1.879543	1.194351
H	2.290340	1.498412	2.252878
H	3.150197	-0.713083	1.511682
H	1.467767	2.570371	-1.871255
H	2.269422	0.357973	-2.599738
H	-1.386917	1.873369	-0.935640
H	-5.342512	-2.455051	-1.829998
H	-3.407531	2.919010	-2.909741
H	-3.794856	-0.787508	-2.411057
H	-3.141594	1.393387	-2.599863
H	-2.244696	-0.651391	-2.488793
H	-3.728953	-1.316243	1.510211
H	-5.165881	-1.783107	1.840220
H	-4.896836	-1.697360	-0.544019
H	0.964167	3.527857	1.755488
H	2.103947	4.300754	0.638309
H	0.467891	3.904544	0.092678
H	2.666451	-1.967541	-1.971801
H	5.099728	-2.433673	-2.119395
H	4.793571	-0.714782	-2.416754
H	5.432072	-1.242161	-0.848028
H	3.940043	-2.686880	0.728927
H	2.241427	-2.978112	0.292130
H	3.545850	-3.780485	-0.596473
H	-1.618196	-2.459780	2.815264
H	-1.202936	-2.722766	1.084508
H	0.057190	-2.824932	2.335215
H	-0.910117	-0.313626	4.218978
H	0.832912	-0.385433	3.858424
H	-0.072874	1.121351	3.558611
H	-4.158680	1.239814	1.099079
H	-3.630445	2.044197	-0.364119

TS2-OH-cyan_Os

(ν=182i cm^{-1})

C	-2.702564	0.122319	1.042836
C	-2.942404	0.860263	-0.167056
C	-2.105228	1.922372	-0.559061
C	-1.003628	2.354227	0.271574
C	-0.793450	1.685955	1.497341
C	-1.599096	0.550136	1.843834
Os	-0.817506	0.059436	-0.160641
Cl	0.847832	0.530673	-1.996596
C	-0.184862	3.551707	-0.180563
C	1.227657	3.627035	0.411632
C	-3.606668	-1.001908	1.467227
N	-1.430030	-1.501407	-1.390324
C	-1.276407	-2.783094	-1.084753
N	-1.803390	-3.767554	-1.894270
P	0.737170	-1.540739	0.687333
C	0.572559	-2.427963	2.288727
O	-0.595622	-3.147084	-0.065630
C	-0.980478	4.841244	0.126890
O	1.954196	-0.397071	1.432611
C	2.013930	-2.381895	-0.345528
O	4.328436	-0.634771	1.917262
O	5.599719	-0.180642	-0.180845
O	4.007072	1.255653	-1.767778
H	1.559621	-2.783930	2.597661
H	0.207631	-1.730378	3.044594
H	-0.111100	-3.268815	2.193768
H	1.554029	-3.035663	-1.083315
H	2.610104	-1.620734	-0.849363
H	2.660694	-2.976339	0.306700
H	-1.378262	0.011979	2.758626
H	0.019668	1.972562	2.151954
H	-3.722370	0.525082	-0.843123
H	-2.262953	2.397838	-1.520470
H	-1.962260	-1.304077	-2.229424
H	4.892922	-0.498212	1.037267
H	4.281803	1.390660	-2.685073
H	5.023615	0.319974	-0.823197
H	3.058690	1.014344	-1.801635
H	5.950638	-0.950804	-0.649686
H	3.239747	-0.587289	1.702679
H	1.834104	0.474670	1.025529
H	4.573454	-1.464521	2.355365
H	-3.952537	-1.575702	0.603532
H	-3.094620	-1.679952	2.154011
H	-4.488173	-0.598450	1.979867
H	-0.088402	3.467215	-1.269511
H	1.805878	2.726511	0.185025
H	1.760046	4.478102	-0.024141
H	1.212825	3.773952	1.497077
H	-0.444636	5.710147	-0.268516
H	-1.976128	4.822292	-0.327344
H	-1.099981	4.977004	1.207712
H	-1.841368	-4.688087	-1.478818
H	-2.595548	-3.535218	-2.478284

TS1-H_2O-cyan_Os

(ν=566i cm^{-1})

C	2.429308	0.487427	0.960559
C	1.604414	1.620222	1.277184
C	1.038054	2.429368	0.252618
C	1.389018	2.128949	-1.117116
C	2.165014	1.008974	-1.422653
C	2.677232	0.133061	-0.388216
Os	0.417007	0.287338	-0.039725
Cl	0.084079	-1.767626	-1.488843
N	-1.484042	0.886559	-0.669814
C	-2.538409	1.388291	-0.381120
N	-3.708633	1.825889	-0.929053
P	-0.586739	-0.887704	1.763044
C	-0.004231	-0.386419	3.434537
C	-0.307223	-2.699951	1.800408
O	-2.186420	-0.732823	1.865710
O	-2.886112	1.535671	1.369438
O	-3.853294	-2.000853	0.355192
O	-2.868313	-2.236626	-1.869276
O	-2.690996	0.005682	-3.190789
H	-0.521408	-1.003556	4.175570
H	1.073835	-0.530546	3.544957
H	-0.251047	0.661880	3.618722
H	-0.838544	-3.118658	2.660533
H	-0.666820	-3.161662	0.880057
H	0.761922	-2.904382	1.900850
C	0.190918	3.627570	0.581434
H	1.386393	1.850530	2.312544
H	0.951996	2.715291	-1.918021
H	2.813398	-0.128043	1.763828
H	2.325338	0.740114	-2.461336
C	3.556057	-1.036896	-0.799938
H	-3.348305	-2.141528	-0.880627
H	-1.880555	-2.270260	-1.712516
H	-2.977794	-1.404904	-2.435265
H	-3.835931	1.621229	1.553696
H	-3.180198	-1.558855	0.979171
H	-4.146805	-2.829094	0.760523

H	-2.577878	0.497247	1.669798
H	-1.968591	0.365080	-2.634274
H	-2.347277	-0.064391	-4.092944
H	-4.141961	2.624737	-0.482395
H	-3.678542	1.898747	-1.940951
C	3.656661	-2.156768	0.243128
H	3.104050	-1.460610	-1.704738
C	4.957581	-0.505180	-1.175369
H	5.577683	-1.324704	-1.553056
H	4.906433	0.264302	-1.952558
H	5.457970	-0.073825	-0.301000
H	4.226929	-2.992616	-0.174016
H	4.178903	-1.826506	1.148078
H	2.669074	-2.530344	0.526570
H	-0.602356	3.766131	-0.157069
H	-0.263833	3.531112	1.569834
H	0.816585	4.528181	0.576960

1-OH-actn_Ru

C	2.683751	1.054184	1.008161
C	2.152541	2.187048	0.350119
C	1.914800	2.083915	-1.066590
C	2.147730	0.892028	-1.750168
C	2.659875	-0.274567	-1.072298
C	2.948093	-0.163141	0.301694
Ru	0.715112	0.400109	0.082425
P	-0.064923	-0.673400	2.021846
C	0.485111	-2.407537	2.227974
Cl	-0.663703	-1.236168	-1.168855
N	-0.964547	1.564185	0.234600
C	-1.895731	2.248479	0.297283
C	-3.071634	3.101306	0.362899
O	-1.682689	-0.709920	2.184513
C	0.398834	0.155518	3.584324
O	-3.121762	-2.745003	1.350500
O	-4.949658	-2.190826	-0.561675
O	-3.651112	-0.578287	-2.292158
O	-4.687912	2.037469	-2.427429
H	-3.650905	2.859276	1.258558
H	-2.764011	4.149705	0.407475
H	-3.688112	2.935067	-0.527173
H	-0.083910	-0.359815	4.419732
H	1.482470	0.127320	3.720766
H	0.069595	1.197053	3.558231
H	0.044104	-2.821149	3.139977
H	0.165260	-2.994920	1.364650
H	1.574847	-2.444762	2.302861
H	2.898900	1.109851	2.068775
H	3.349451	-1.007770	0.846988
C	1.907540	3.481803	1.074705
H	1.483894	2.929145	-1.593227
H	1.899899	0.823367	-2.803801
H	-4.504500	2.501454	-3.256614
H	-5.282546	-2.956789	-1.047675
H	-5.651488	2.044265	-2.337464
H	-4.523673	-1.595899	-1.232957
H	-3.961759	0.350465	-2.333044
H	-2.728996	-0.564412	-1.972843
H	-2.180164	-1.478473	1.769407
H	-3.599782	-3.099140	2.112490
H	-3.804857	-2.568080	0.651080
H	1.830992	3.326877	2.153038
H	2.742927	4.166776	0.886627
H	0.994433	3.967292	0.721515
C	2.944583	-1.520860	-1.891686
H	2.120426	-1.614086	-2.609098
C	4.248691	-1.300482	-2.693910
H	4.426093	-2.158524	-3.349987
H	4.198392	-0.402526	-3.317716
H	5.107545	-1.201501	-2.020760
C	3.013056	-2.819476	-1.079187
H	2.098357	-2.980009	-0.502413
H	3.135636	-3.666638	-1.760860
H	3.866825	-2.828419	-0.392504

TS1-OH-actn_Ru

(ν=320i cm^{-1})

C	-1.854607	-2.255350	0.355388
C	-2.377090	-1.521366	-0.708878
C	-2.811619	-0.155313	-0.546855
C	-2.727406	0.412896	0.741777
C	-2.177229	-0.331496	1.835558
C	-1.711507	-1.656458	1.657624
Ru	-0.610550	-0.259180	0.231514
N	1.247086	-1.113555	0.741130
C	2.232031	-0.618258	1.199379
C	3.578651	-0.767754	1.772954
P	0.502421	1.651072	1.085741
C	-0.071321	2.224314	2.735417
Cl	0.328541	0.334054	-2.027329
C	0.406122	3.176906	0.073004
O	2.059823	1.323040	1.264436
O	3.965429	2.069840	-0.487103
O	4.719521	-0.002295	-1.951108
O	2.738669	-1.371858	-2.562571
O	2.259381	-3.249814	-0.893906
H	3.588307	-0.386208	2.796802
H	3.842530	-1.828700	1.775697
H	4.310964	-0.208608	1.187342
H	0.563862	3.055789	3.057676
H	-1.109422	2.566088	2.693597
H	0.011600	1.411257	3.461012
H	1.032680	3.950883	0.527621
H	0.750693	2.967364	-0.940798
H	-0.628309	3.530269	0.034031
H	-2.101244	0.131858	2.811837
H	-3.047959	1.433672	0.908867
C	-1.137928	-2.446924	2.800742
H	-1.488991	-3.263024	0.188854
H	-2.404141	-1.965850	-1.698342
H	1.752864	-2.762668	-0.207334
H	5.240805	0.302282	-2.707174
H	1.698339	-3.974766	-1.204278
H	3.598876	-0.800930	-2.308037
H	2.604601	-2.176466	-1.938739
H	1.928348	-0.787918	-2.447240
H	3.247189	1.853462	0.166835
H	4.655302	2.536887	0.002687
H	4.473083	0.804873	-1.408142
H	-0.307818	-3.075366	2.469104
H	-0.785502	-1.790885	3.599702
H	-1.912943	-3.103726	3.213893
C	-3.412895	0.564917	-1.742086
H	-2.815616	0.272008	-2.614175
C	-3.383607	2.095356	-1.643338
H	-2.371942	2.466453	-1.457409
H	-3.734623	2.527945	-2.585259
H	-4.042161	2.466349	-0.850013
C	-4.854896	0.054066	-1.965245
H	-5.273888	0.508126	-2.869104
H	-4.887545	-1.033346	-2.087073
H	-5.497636	0.322210	-1.119093

2-OH-actn_Ru

C	2.318967	0.206104	1.797093
C	1.831753	1.530646	1.697665
C	1.912406	2.174848	0.412957
C	2.408774	1.491399	-0.697912
C	2.888699	0.132528	-0.603092
C	2.861697	-0.479840	0.662933
Ru	0.682452	0.175885	0.230865
P	-0.438716	-1.644299	1.068917
C	-0.058571	-2.300938	2.727812
C	1.308857	2.267233	2.899267
C	3.461008	-0.531519	-1.842959
C	3.446328	-2.065230	-1.803147

Cl	-0.284368	-0.325524	-2.003526
N	-1.178022	1.003219	0.684598
C	-2.166040	0.320294	1.139048
O	-2.024456	-1.011815	1.332305
C	-3.509783	0.858489	1.510126
C	-0.806394	-3.114662	0.061773
C	4.890684	0.004325	-2.086600
O	-2.288059	3.454979	-0.396220
O	-2.785911	1.741683	-2.467617
O	-5.001660	0.096943	-2.098639
O	-4.455021	-2.100336	-0.447805
H	-3.677644	0.696055	2.579710
H	-3.567309	1.923525	1.286425
H	-4.294734	0.327401	0.964994
H	2.280839	-0.302508	2.753532
H	3.204175	-1.499805	0.785385
H	1.524215	3.181157	0.295742
H	2.388550	1.973978	-1.669298
H	-1.394092	1.989499	0.487883
H	-5.381739	-0.238528	-2.921270
H	-1.800996	4.233490	-0.695399
H	-3.582745	1.176841	-2.345201
H	-2.514205	2.934513	-1.207418
H	-2.028017	1.131446	-2.385379
H	-3.761548	-1.988756	0.220295
H	-5.207933	-2.490701	0.017227
H	-4.825216	-0.690898	-1.539366
H	0.991111	1.573826	3.680821
H	2.104778	2.900823	3.308688
H	0.469475	2.916210	2.637931
H	2.834389	-0.209706	-2.683480
H	5.285662	-0.406506	-3.021266
H	4.909029	1.096219	-2.163098
H	5.561093	-0.292504	-1.272262
H	4.131965	-2.461332	-1.045762
H	2.443158	-2.452376	-1.601639
H	3.772014	-2.456568	-2.771729
H	-1.527263	-3.756961	0.575208
H	-1.184988	-2.804137	-0.912688
H	0.127645	-3.666680	-0.080404
H	-0.853326	-2.982771	3.043349
H	0.887110	-2.849341	2.684198
H	0.030365	-1.481697	3.444258

TS2-OH-actn_Ru

(ν=66i cm^{-1})

C	-2.177844	1.983976	-0.616592
C	-1.086526	2.412282	0.222384
C	-0.890173	1.742210	1.442727
C	-1.716196	0.628259	1.794027
C	-2.814313	0.220131	0.991417
C	-3.030892	0.944278	-0.227353
Ru	-0.891443	0.061093	-0.215310
P	0.627279	-1.515911	0.721983
C	1.878379	-2.452679	-0.255259
Cl	0.789960	0.492215	-2.035183
N	-1.558574	-1.516722	-1.370370
C	-1.463665	-2.785713	-1.028489
C	-2.136498	-3.859565	-1.858077
O	-0.801378	-3.146310	0.000214
C	0.445679	-2.394453	2.326778
O	1.816847	-0.359537	1.403954
O	4.252615	-0.548053	1.903364
O	5.432717	-0.354713	-0.229237
O	3.934624	1.140162	-1.790870
H	-2.829457	-4.421213	-1.223881
H	-2.685656	-3.450749	-2.709211
H	-1.380241	-4.561459	-2.223032
H	1.419352	-2.417899	2.822806
H	-0.260303	-1.866651	2.971030
H	0.085431	-3.407160	2.153804
H	1.417101	-3.285063	-0.782676
H	2.344864	-1.770541	-0.967710
H	2.639821	-2.836269	0.430528
H	-1.519404	0.104808	2.722770
H	-0.087801	2.029873	2.110494
H	-3.826049	0.629508	-0.895616
H	-2.328637	2.467029	-1.575808
H	-2.087552	-1.325668	-2.213547
H	4.802610	-0.511856	0.955163
H	4.229914	1.284449	-2.700425
H	4.876220	0.177675	-0.874516
H	2.979748	0.921288	-1.843525
H	5.662786	-1.190811	-0.659719
H	3.213200	-0.533381	1.725939
H	1.714730	0.488235	0.945002
H	4.501724	-1.320163	2.435301
C	-3.747483	-0.880197	1.416312
H	-4.052288	-1.490065	0.561895
H	-3.282174	-1.528689	2.161922
H	-4.652395	-0.447413	1.859590
C	-0.258899	3.605118	-0.223761
H	-0.159872	3.523187	-1.312871
C	1.152266	3.669428	0.373201
H	1.726221	2.767057	0.142188
H	1.690198	4.520555	-0.055457
H	1.135444	3.808984	1.459520
C	-1.047388	4.900357	0.082396
H	-0.503223	5.765389	-0.309952
H	-2.041199	4.889054	-0.375962
H	-1.170192	5.034920	1.162897

1-OH-actn_Os

C	2.862323	0.173103	-0.229184
C	2.496744	-0.539990	-1.423471
C	1.857392	-1.808009	-1.361394
C	1.610936	-2.369207	-0.054488
C	1.920710	-1.650952	1.106497
C	2.550083	-0.347258	1.046046
Os	0.627332	-0.267045	-0.241962
N	-1.133082	-1.042933	-0.883601
C	-2.126196	-1.523790	-1.234334
C	-3.377318	-2.131290	-1.656143
C	1.508697	-2.573525	-2.607661
C	2.920503	0.339168	2.349986
C	3.126792	1.854832	2.241068
P	-0.024699	1.731528	-1.341100
C	0.644479	1.941849	-3.028871
Cl	-0.701850	0.581982	1.690942
C	0.432947	3.279544	-0.476576
O	-1.617404	1.874723	-1.652735
C	4.177718	-0.348070	2.930281
O	-3.286440	3.025257	0.026768
O	-5.121902	1.434426	1.215016
O	-3.699938	-0.561550	2.347877
O	-4.482267	-3.101171	1.426699
H	-4.018714	-1.372542	-2.113428
H	-3.177386	-2.919686	-2.387161
H	-3.881737	-2.559603	-0.783086
H	0.223235	2.850982	-3.467183
H	1.733084	2.030773	-2.998527
H	0.371436	1.080599	-3.643306
H	0.043178	4.135032	-1.036149
H	0.011342	3.272685	0.530662
H	1.521093	3.358300	-0.408243
H	2.709935	-0.102630	-2.391146
H	3.331476	1.143920	-0.322117
H	1.085364	-3.314729	0.026369
H	1.636342	-2.052881	2.072575
H	-4.053019	-3.863230	1.840772
H	-5.651168	1.864473	1.899582
H	-5.431977	-3.247778	1.541017
H	-4.648403	0.682227	1.657282
H	-3.918801	-1.463471	2.031748
H	-2.771094	-0.389837	2.104570
H	-2.207210	2.251171	-0.933300
H	-3.760553	3.714290	-0.457897

H	-3.978783	2.464684	0.465761
H	1.414023	-1.906428	-3.467319
H	2.302829	-3.298419	-2.822216
H	0.574601	-3.127271	-2.486048
H	2.088375	0.160974	3.041544
H	4.414019	0.081209	3.909056
H	4.031354	-1.425079	3.060080
H	5.041664	-0.196953	2.273339
H	2.247970	2.352492	1.823433
H	3.304664	2.267776	3.238730
H	3.997916	2.106407	1.625838

TS1-OH-actn_Os

(ν=303i cm^{-1})

C	-1.627645	-1.656351	1.588673
C	-1.747564	-2.228116	0.268078
C	-2.260854	-1.468404	-0.792223
C	-2.711295	-0.107461	-0.605701
C	-2.656494	0.433435	0.702843
C	-2.114124	-0.334060	1.791969
Os	-0.568649	-0.237485	0.211210
Cl	0.402035	0.407326	-2.024337
C	-3.289329	0.640248	-1.796040
C	-4.747800	0.181102	-2.017737
C	-1.055842	-2.461609	2.722944
N	1.291787	-1.078527	0.666508
C	2.291402	-0.637519	1.143841
C	3.633742	-0.826483	1.708210
P	0.574410	1.667588	1.100044
O	2.125393	1.330569	1.305406
C	-0.025420	2.242394	2.739208
C	0.503460	3.199688	0.093712
C	-3.201687	2.167986	-1.690607
O	4.049625	2.084973	-0.407124
O	4.796941	0.060634	-1.931461
O	2.828523	-1.283358	-2.608771
O	2.315040	-3.222396	-1.015055
H	3.645168	-0.493659	2.749062
H	3.888659	-1.888726	1.661763
H	4.371279	-0.246705	1.149955
H	0.598988	3.077598	3.071984
H	-1.064794	2.578257	2.680989
H	0.049951	1.430068	3.466484
H	1.120358	3.971000	0.565077
H	0.869043	2.996416	-0.913953
H	-0.530057	3.553015	0.034079
H	-2.044258	0.111770	2.776600
H	-2.973884	1.452456	0.883711
H	-1.351186	-3.219486	0.077546
H	-2.246249	-1.881677	-1.795067
H	1.787834	-2.767335	-0.325527
H	5.327955	0.385688	-2.672141
H	1.770495	-3.943758	-1.361448
H	3.689148	-0.718210	-2.322624
H	2.685973	-2.109883	-2.019184
H	2.018086	-0.706543	-2.482382
H	3.322522	1.863061	0.237761
H	4.742493	2.531495	0.097298
H	4.549492	0.851692	-1.363598
H	-0.245831	-3.109403	2.379026
H	-0.673252	-1.812627	3.514092
H	-1.839756	-3.098006	3.150526
H	-2.704091	0.331232	-2.670493
H	-2.173446	2.496867	-1.516607
H	-3.548226	2.618456	-2.625970
H	-3.835491	2.559888	-0.887279
H	-5.153424	0.650681	-2.919846
H	-4.816703	-0.904597	-2.141190
H	-5.380197	0.468701	-1.170072

2-OH-actn_Os

C	-2.782868	-0.432737	-0.640985
C	-2.232768	0.292466	-1.751606
C	-1.687852	1.596396	-1.587568
C	-1.756763	2.189644	-0.271542
C	-2.260849	1.462389	0.813462
C	-2.766715	0.113260	0.662402
Os	-0.623539	0.165203	-0.204641
N	1.258900	0.952588	-0.653270
C	2.225057	0.255988	-1.142930
C	3.569026	0.781944	-1.526547
C	-1.133537	2.366889	-2.753722
C	-3.339419	-0.598144	1.876340
C	-4.764745	-0.065792	2.145336
P	0.457127	-1.673096	-1.071591
C	0.827411	-3.150481	-0.075242
Cl	0.396476	-0.368497	2.009164
C	0.034006	-2.324039	-2.720824
O	2.052186	-1.064218	-1.364029
C	-3.332511	-2.128961	1.773013
O	2.390644	3.397925	0.394094
O	2.895070	1.721961	2.491856
O	5.098433	0.075026	2.091432
O	4.538366	-2.150121	0.479697
H	3.714125	0.643940	-2.602934
H	3.648812	1.840069	-1.277879
H	4.355585	0.224694	-1.010613
H	-2.208533	-0.173485	-2.729684
H	-3.138142	-1.442561	-0.803910
H	-1.329965	3.172943	-0.106385
H	-2.201985	1.890527	1.808189
H	1.500616	1.932439	-0.451895
H	5.499732	-0.252549	2.907159
H	1.897831	4.179338	0.676004
H	3.688899	1.154312	2.360440
H	2.619942	2.896316	1.216324
H	2.135625	1.113795	2.418156
H	3.834648	-2.073160	-0.181824
H	5.289251	-2.549082	0.018618
H	4.913742	-0.717661	1.542043
H	-0.792638	1.694116	-3.543818
H	-1.916730	3.012956	-3.167565
H	-0.299491	3.004488	-2.450285
H	-2.708054	-0.315568	2.727271
H	-5.162504	-0.513412	3.061803
H	-4.775672	1.022084	2.268308
H	-5.437991	-0.322817	1.319701
H	-4.022884	-2.490010	1.002486
H	-2.332079	-2.511749	1.551455
H	-3.656778	-2.559017	2.725593
H	1.544845	-3.789376	-0.597151
H	1.211981	-2.848182	0.899504
H	-0.105816	-3.703613	0.067284
H	0.807542	-3.022345	-3.051780
H	-0.921269	-2.853456	-2.656609
H	-0.055402	-1.504167	-3.436252

TS2-OH-actn_Os

(ν=148i cm^{-1})

C	-2.955721	0.807138	-0.169705
C	-2.140585	1.880988	-0.574985
C	-1.047700	2.344701	0.249781
C	-0.823485	1.696148	1.483396
C	-1.605365	0.548150	1.844121
C	-2.699985	0.088845	1.049194
Os	-0.813128	0.048129	-0.156638
N	-1.401094	-1.537379	-1.359318
C	-1.215222	-2.808640	-1.061902
O	-0.515239	-3.151597	-0.050828
C	-0.254400	3.552988	-0.218764
C	-1.082313	4.828109	0.062864

C	-3.579003	-1.049488	1.488577
P	0.774684	-1.507737	0.719972
O	1.956382	-0.323796	1.449267
Cl	0.834090	0.526963	-2.001592
C	2.089539	-2.339661	-0.271827
C	0.613537	-2.382929	2.327765
C	-1.826224	-3.899745	-1.910547
C	1.152828	3.671834	0.378688
O	4.348554	-0.475004	1.914551
O	5.564032	-0.197720	-0.234778
O	3.982860	1.285756	-1.777887
H	-2.480434	-4.516561	-1.286497
H	-2.404181	-3.503635	-2.748334
H	-1.032112	-4.546635	-2.295806
H	1.604363	-2.719385	2.646442
H	0.230557	-1.686812	3.076023
H	-0.054142	-3.236915	2.234248
H	1.691918	-3.193746	-0.815629
H	2.505293	-1.613299	-0.971871
H	2.878130	-2.676867	0.406400
H	-1.374164	0.027016	2.766172
H	-0.017693	2.008991	2.135057
H	-3.731233	0.449769	-0.839483
H	-2.308996	2.342342	-1.541402
H	-1.960033	-1.362073	-2.186014
H	4.896266	-0.411603	1.008476
H	4.253114	1.446495	-2.692382
H	4.990998	0.320652	-0.867488
H	3.035825	1.039328	-1.813718
H	5.828757	-1.011271	-0.686849
H	3.266117	-0.466071	1.720342
H	1.806933	0.540234	1.035884
H	4.616742	-1.251300	2.430280
H	-3.922787	-1.635048	0.632018
H	-3.047118	-1.713418	2.174051
H	-4.462693	-0.659333	2.007619
H	-0.150579	3.452352	-1.305669
H	1.755360	2.783509	0.167276
H	1.665328	4.530156	-0.066547
H	1.129043	3.833338	1.461891
H	-0.565422	5.702738	-0.344841
H	-2.074904	4.777579	-0.395615
H	-1.210733	4.979231	1.140599

1-OH-bzn_Ru

C	3.274497	-1.048017	-0.487499
C	2.369000	-2.026333	-1.011286
C	1.413910	-2.658861	-0.184773
C	1.400758	-2.311039	1.212617
C	2.265450	-1.342164	1.716495
C	3.222410	-0.672244	0.869259
Ru	1.103776	-0.359635	-0.113151
N	-0.933518	-0.531757	-0.133504
C	-2.083735	-0.687300	-0.169258
C	-3.495321	-0.897766	-0.235331
C	0.488798	-3.715128	-0.721785
C	4.182615	0.318092	1.503735
C	4.755229	1.362704	0.538588
P	0.873421	0.837823	-2.126520
C	1.053616	-0.155864	-3.649866
Cl	0.851577	1.826296	1.018030
C	2.041909	2.231078	-2.358220
O	-0.600712	1.469853	-2.396376
C	5.312836	-0.470608	2.205716
O	-1.642319	3.560087	-1.173704
O	-3.213495	3.252789	1.027715
O	-1.752443	2.012884	2.921962
O	-2.760580	-0.437882	3.828057
H	0.825269	0.478737	-4.511199
H	2.076786	-0.527996	-3.741596
H	0.362257	-1.001292	-3.626445
H	1.798164	2.741117	-3.295169
H	1.952400	2.928447	-1.522928
H	3.068819	1.859390	-2.406011
H	2.416523	-2.289329	-2.061383
H	3.987082	-0.582293	-1.156633
H	0.662458	-2.764655	1.865429
H	2.192502	-1.051118	2.758949
H	-2.937921	-0.478817	4.778138
H	-3.588395	4.073528	1.373508
H	-3.578671	-0.727099	3.400102
H	-2.721925	2.825453	1.778393
H	-2.102826	1.150885	3.233394
H	-0.928291	1.820487	2.433893
H	-0.925913	2.215540	-1.809812
H	-2.186300	4.010476	-1.833827
H	-2.211266	3.460214	-0.368194
H	0.331072	-3.596420	-1.795943
H	0.930961	-4.703711	-0.548714
H	-0.478846	-3.692470	-0.215529
H	3.614456	0.849649	2.276252
H	5.970945	0.224301	2.737015
H	4.919316	-1.187447	2.933405
H	5.915153	-1.021047	1.474355
H	3.957794	1.917516	0.037876
H	5.364947	2.077822	1.099154
H	5.401844	0.910696	-0.221705
C	-4.376581	0.176931	-0.003797
C	-5.750714	-0.045227	-0.085691
C	-6.245383	-1.317891	-0.392807
C	-5.365191	-2.382447	-0.620676
C	-3.988615	-2.181393	-0.544169
H	-3.990386	1.162469	0.236449
H	-6.436189	0.777574	0.090929
H	-7.317034	-1.480798	-0.454735
H	-5.750520	-3.368575	-0.859150
H	-3.300465	-3.000376	-0.722547

TS1-OH-bzn_Ru

(ν=296i cm^{-1})

C	-1.684864	-2.449713	-0.781648
C	-2.067710	-1.603937	-1.883254
C	-2.921703	-0.520273	-1.682333
C	-3.469358	-0.218555	-0.382574
C	-3.144381	-1.081919	0.685343
C	-2.255230	-2.188146	0.487166
Ru	-1.153783	-0.328470	-0.120558
Cl	-0.920926	2.142133	-0.514289
C	-4.432679	0.949483	-0.252559
C	-5.818335	0.519653	-0.786994
C	-0.754788	-3.610506	-1.001633
N	0.866883	-0.598256	-0.634468
C	1.875348	-0.531762	0.006085
C	3.314749	-0.732368	0.055234
P	-0.120609	0.016880	1.985174
O	1.457970	0.187146	1.790812
C	-0.324057	-1.361827	3.183465
C	-0.687264	1.475452	2.939220
C	-4.546732	1.528720	1.163306
O	2.680481	2.585813	1.538301
O	3.279555	3.108550	-0.984097
O	1.354259	2.506807	-2.424831
O	1.453272	0.114723	-3.361133
H	0.248915	-1.129745	4.086951
H	-1.375382	-1.496297	3.453344
H	0.058952	-2.287793	2.747579
H	-0.084750	1.568859	3.848321
H	-0.584413	2.375312	2.330901
H	-1.737985	1.347204	3.215143
H	-1.999314	-2.823921	1.326606
H	-3.540728	-0.895864	1.675551
H	-1.633456	-1.775187	-2.862582
H	-3.135352	0.149416	-2.508737
H	1.121509	-0.388608	-2.586584
H	3.545852	4.036128	-1.055130
H	0.866564	-0.084202	-4.104899
H	2.201418	2.765820	-1.827909

H	1.451746	1.590941	-2.868664
H	0.558717	2.437098	-1.812344
H	2.214848	1.715765	1.661633
H	3.431145	2.579747	2.147171
H	3.084750	2.924653	-0.015366
H	0.028738	-3.357370	-1.719891
H	-0.287174	-3.928760	-0.067330
H	-1.321046	-4.457791	-1.406922
H	-4.051134	1.740365	-0.909631
H	-3.570278	1.828506	1.553341
H	-5.188691	2.414816	1.142765
H	-4.999272	0.816453	1.862321
H	-6.502604	1.374213	-0.772360
H	-5.761570	0.150199	-1.815944
H	-6.247539	-0.272339	-0.162922
C	4.010336	-0.781171	-1.170516
C	5.383831	-1.020733	-1.178632
C	6.073358	-1.217664	0.023064
C	5.382454	-1.172586	1.238324
C	4.008670	-0.928502	1.261172
H	3.480298	-0.627264	-2.103802
H	5.914922	-1.051264	-2.125092
H	7.143088	-1.403969	0.011350
H	5.913168	-1.326283	2.172924
H	3.465023	-0.884020	2.195533

2-OH-bzn_Ru

C	3.448122	-0.870948	0.416864
C	2.631832	-1.546059	1.380964
C	1.840560	-0.829994	2.310986
C	1.903722	0.607308	2.271417
C	2.668577	1.261579	1.305529
C	3.453956	0.533709	0.336773
Ru	1.234818	-0.234414	0.174075
N	-0.814775	-0.259667	0.572113
C	-1.647088	-1.044590	-0.026716
C	-3.111127	-1.118705	0.174403
C	1.014967	-1.537613	3.349504
C	4.296018	1.314091	-0.657474
C	5.558266	1.848441	0.057536
P	0.511184	-1.885272	-1.242005
C	0.537796	-1.700374	-3.053046
Cl	0.687875	1.456868	-1.564322
C	0.933775	-3.635768	-0.954259
O	-1.173604	-1.916342	-0.940977
C	4.669829	0.530186	-1.922266
O	-1.675704	2.027821	2.220830
O	-0.974794	3.676829	0.188348
O	-3.282648	4.405714	-1.134708
O	-5.127378	2.331691	-1.189918
H	2.620978	-2.629729	1.399142
H	4.018929	-1.461586	-0.288743
H	1.296872	1.185728	2.959061
H	2.637191	2.344364	1.248279
H	-1.193208	0.421869	1.240689
H	-3.177372	4.718760	-2.042759
H	-1.297333	2.305275	3.064719
H	-1.776024	3.936184	-0.323733
H	-1.417868	2.712124	1.550723
H	-0.467972	3.072500	-0.387190
H	-4.953745	1.610498	-0.565778
H	-6.047054	2.589636	-1.036424
H	-3.946050	3.680448	-1.169899
H	0.758704	-2.549773	3.028700
H	1.588417	-1.609566	4.281476
H	0.093661	-0.991784	3.566706
H	3.691614	2.177144	-0.961819
H	6.130286	2.482323	-0.627529
H	5.305451	2.446217	0.939089
H	6.203120	1.022481	0.378154
H	5.355800	-0.295733	-1.703435
H	3.784476	0.124550	-2.420578
H	5.178626	1.196657	-2.625352
H	-0.074092	-2.480991	-3.513508
H	0.168483	-0.710583	-3.323050
H	1.572617	-1.801281	-3.393461
H	0.307905	-4.269245	-1.589067
H	1.984531	-3.797621	-1.212250
H	0.773509	-3.893589	0.094374
C	-3.764851	-0.255754	1.075154
C	-5.146061	-0.350183	1.251240
C	-5.889449	-1.299307	0.537354
C	-5.243592	-2.155840	-0.357918
C	-3.862567	-2.067934	-0.541186
H	-3.209857	0.489450	1.635552
H	-5.641666	0.314570	1.952422
H	-6.963593	-1.367851	0.680300
H	-5.812265	-2.893307	-0.915641
H	-3.366353	-2.733091	-1.237476

TS2-OH-bzn_Ru

(ν=77i cm^{-1})

C	0.079958	-3.131971	-0.093900
C	-1.127154	-2.915421	-0.766134
C	-2.237312	-2.253968	-0.124784
C	-2.067710	-1.816202	1.199534
C	-0.804883	-1.972304	1.855026
C	0.283446	-2.644783	1.241234
Ru	-0.302099	-0.844601	-0.022000
N	1.634674	-0.487394	-0.648941
C	2.504898	0.217012	0.045209
O	2.135466	0.880050	1.076355
C	-3.545560	-2.138617	-0.888498
C	-4.266578	-3.506745	-0.848236
C	1.576508	-2.891891	1.968723
P	-0.051149	1.226508	1.122581
O	-1.813386	1.619387	1.287105
Cl	-1.069319	0.445896	-2.035785
C	0.344861	2.826645	0.295129
C	0.230439	1.453937	2.925185
C	3.947908	0.280659	-0.356628
C	-4.476247	-1.018079	-0.409266
O	-2.992730	3.771130	1.530028
O	-3.138464	4.831952	-0.691207
O	-3.152981	2.870036	-2.465439
H	-0.426282	2.247963	3.288096
H	-0.007477	0.533572	3.461983
H	1.272439	1.714087	3.105575
H	1.400131	2.889069	0.037457
H	-0.265429	2.910323	-0.605569
H	0.092062	3.643869	0.977491
H	-0.687893	-1.595180	2.864706
H	-2.872221	-1.317432	1.725133
H	0.903227	-3.609448	-0.615275
H	-1.226832	-3.233287	-1.798210
H	1.977457	-0.919502	-1.498850
H	-3.024884	4.276726	0.581466
H	-3.074764	3.098551	-3.401898
H	-3.107351	4.128134	-1.403065
H	-2.513259	2.144617	-2.306953
H	-2.453906	5.484360	-0.897040
H	-2.429726	2.855886	1.462297
H	-2.287112	1.141902	0.587912
H	-2.646097	4.349341	2.227364
H	2.430216	-2.822491	1.290008
H	1.716770	-2.176563	2.782377
H	1.571452	-3.900601	2.399041
H	-3.278339	-1.932402	-1.931947
H	-3.988257	-0.039985	-0.456650
H	-5.357944	-0.975845	-1.056055
H	-4.830358	-1.184537	0.613730
H	-5.170126	-3.466770	-1.464895
H	-3.631631	-4.312472	-1.229763
H	-4.562347	-3.760174	0.175918
C	4.711117	1.396203	0.024874
C	6.055601	1.492035	-0.339763
C	6.657741	0.467503	-1.078344

C	5.908231	-0.654181	-1.449030
C	4.561110	-0.747565	-1.092016
H	4.240067	2.183813	0.602869
H	6.632879	2.363967	-0.046247
H	7.704877	0.539074	-1.357676
H	6.372814	-1.459876	-2.009701
H	4.001653	-1.636369	-1.368029

1-OH-bzn_Os

C	3.215296	-0.926417	-0.366989
C	2.356428	-1.945675	-0.907931
C	1.389074	-2.602823	-0.100969
C	1.311212	-2.226989	1.289973
C	2.112533	-1.200294	1.802512
C	3.083955	-0.512875	0.977054
Os	1.026997	-0.356135	-0.081277
N	-0.979640	-0.561536	-0.135246
C	-2.130233	-0.722436	-0.170409
C	0.524989	-3.701577	-0.654446
C	3.971425	0.535712	1.625117
C	4.539384	1.583469	0.660246
P	0.805643	0.803519	-2.136475
C	1.113509	-0.194603	-3.635846
Cl	0.598106	1.846385	1.000234
C	1.899815	2.258766	-2.339454
O	-0.690380	1.348090	-2.482082
C	5.103593	-0.187122	2.390498
O	-1.782935	3.496856	-1.401995
O	-3.402652	3.354173	0.782620
O	-2.085979	2.143601	2.803509
O	-3.282223	-0.199637	3.755409
H	0.913865	0.421908	-4.516929
H	2.153297	-0.529928	-3.662476
H	0.454215	-1.065662	-3.643661
H	1.676250	2.740977	-3.295656
H	1.730655	2.962318	-1.521758
H	2.946682	1.944411	-2.328998
H	2.445843	-2.220574	-1.951551
H	3.927772	-0.440512	-1.021073
H	0.553052	-2.679056	1.920510
H	1.969662	-0.874933	2.827002
H	-3.466561	-0.205239	4.705059
H	-3.748881	4.207613	1.075156
H	-4.122903	-0.416054	3.328127
H	-2.961850	2.941431	1.571424
H	-2.493521	1.314307	3.134426
H	-1.248437	1.892371	2.370586
H	-1.050272	2.119620	-1.953417
H	-2.309474	3.916702	-2.095496
H	-2.365030	3.453230	-0.601142
H	0.409133	-3.607083	-1.736422
H	0.993206	-4.670381	-0.443554
H	-0.464311	-3.702171	-0.191312
H	3.347478	1.059059	2.359187
H	5.707951	0.545651	2.934523
H	4.711126	-0.907098	3.115813
H	5.760220	-0.724191	1.696738
H	3.742464	2.099986	0.119572
H	5.101111	2.330825	1.228947
H	5.230828	1.142650	-0.066387
C	-3.539699	-0.937154	-0.229029
C	-4.420713	0.157752	-0.120077
C	-4.035445	-2.245209	-0.404551
C	-5.794582	-0.068410	-0.188719
H	-4.034765	1.162153	0.019763
C	-5.411966	-2.449699	-0.471254
H	-3.348804	-3.080418	-0.488861
C	-6.290863	-1.365273	-0.364225
H	-6.478585	0.770159	-0.104998
H	-5.798579	-3.454545	-0.607526
H	-7.362470	-1.531329	-0.417368

TS1-OH-bzn_Os

(ν=285i cm^{-1})

C	1.502839	-2.522382	0.024732
C	1.909835	-2.046017	1.325234
C	2.789470	-0.960683	1.439697
C	3.344677	-0.301222	0.279755
C	2.997027	-0.810906	-0.995604
C	2.080212	-1.912096	-1.124089
Os	1.057876	-0.318991	0.028560
Cl	0.833814	1.884421	1.224372
C	4.325578	0.841145	0.489774
C	5.702606	0.257056	0.877314
C	0.537161	-3.668043	-0.102497
N	-0.952761	-0.669807	0.433788
C	-1.972435	-0.460382	-0.156113
P	0.022672	0.722421	-1.860539
O	-1.567577	0.735950	-1.685120
C	0.327872	-0.110061	-3.469762
C	0.522564	2.451826	-2.206201
C	4.453397	1.800593	-0.700454
O	-2.927628	2.904227	-0.847096
O	-3.503670	2.729622	1.719451
O	-1.600624	1.806613	2.992578
O	-1.654972	-0.751350	3.297037
H	-0.214387	0.427167	-4.254183
H	1.393518	-0.114601	-3.715852
H	-0.038039	-1.138906	-3.427140
H	-0.047636	2.830868	-3.059770
H	0.338693	3.074675	-1.329721
H	1.589599	2.479263	-2.444474
H	1.798487	-2.262446	-2.109304
H	3.385290	-0.341725	-1.890492
H	1.466198	-2.476577	2.216230
H	3.001311	-0.553741	2.422776
H	-1.250467	-1.043756	2.455815
H	-3.790993	3.598463	2.034140
H	-1.118117	-1.118485	4.014051
H	-2.441195	2.200636	2.449106
H	-1.687817	0.810547	3.194250
H	-0.779092	1.899350	2.424882
H	-2.413437	2.121563	-1.186349
H	-3.696622	2.994498	-1.425756
H	-3.310515	2.811801	0.734770
H	-0.223323	-3.631683	0.681174
H	0.040085	-3.658364	-1.075189
H	1.080733	-4.615146	-0.003622
H	3.951768	1.416214	1.345728
H	3.483696	2.214727	-0.989389
H	5.107958	2.634108	-0.427315
H	4.898072	1.311481	-1.574351
H	6.398682	1.068521	1.113392
H	5.634973	-0.395586	1.753714
H	6.125251	-0.325133	0.050465
C	-3.400992	-0.691582	-0.269012
C	-4.092719	-1.123365	0.881915
C	-4.088271	-0.556257	-1.487712
C	-5.454637	-1.410895	0.804529
H	-3.568732	-1.226381	1.825296
C	-5.450411	-0.851784	-1.551633
H	-3.547572	-0.223430	-2.363677
C	-6.137037	-1.277551	-0.409976
H	-5.982472	-1.738650	1.694896
H	-5.975164	-0.749384	-2.496579
H	-7.197570	-1.504280	-0.465013

2-OH-bzn_Os

C	3.278656	-0.860164	0.395187
C	2.455021	-1.556986	1.342849
C	1.628927	-0.855652	2.266356
C	1.683765	0.587668	2.247604
C	2.452198	1.261788	1.291566

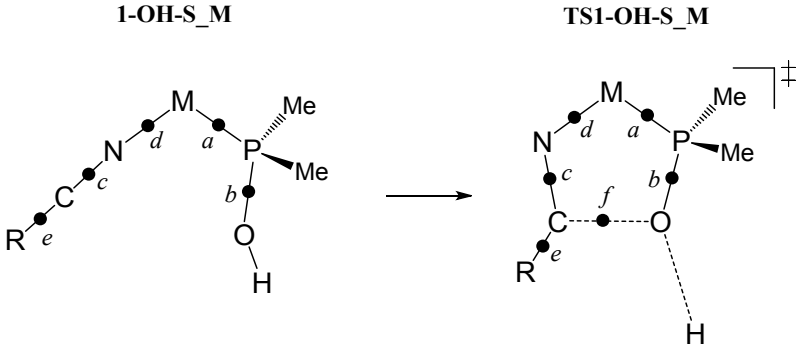
C	3.253322	0.549699	0.316131
Os	1.086890	-0.247159	0.164926
N	-0.969689	-0.268351	0.532186
C	-1.800129	-1.053988	-0.077364
C	0.797527	-1.585098	3.285483
C	4.089960	1.349680	-0.668167
C	5.346025	1.885187	0.054854
P	0.366971	-1.872379	-1.294899
C	0.390419	-1.648324	-3.101820
Cl	0.502774	1.473719	-1.549141
C	0.791928	-3.627212	-1.046908
O	-1.322613	-1.913388	-0.997624
C	4.471964	0.584560	-1.942012
O	-1.801695	1.978391	2.231099
O	-0.906165	3.740085	0.376288
O	-3.096319	4.815310	-0.909325
O	-4.889876	2.775367	-1.486862
H	2.450528	-2.640363	1.346486
H	3.854631	-1.435726	-0.318102
H	1.047989	1.153009	2.919498
H	2.392830	2.343046	1.232082
H	-1.355498	0.389134	1.219840
H	-2.948295	5.324120	-1.717183
H	-1.512627	2.208855	3.122966
H	-1.656196	4.138682	-0.123793
H	-1.484912	2.698773	1.627742
H	-0.458599	3.134164	-0.244041
H	-4.490786	1.895379	-1.433095
H	-5.664245	2.742262	-0.907899
H	-3.742830	4.111416	-1.140655
H	0.549500	-2.592574	2.943518
H	1.361802	-1.670344	4.221708
H	-0.129849	-1.048866	3.500718
H	3.478474	2.210771	-0.963518
H	5.913906	2.534132	-0.619589
H	5.086047	2.467854	0.944514
H	5.998172	1.060870	0.365061
H	5.163530	-0.239033	-1.731928
H	3.591094	0.178869	-2.447885
H	4.977824	1.263505	-2.635328
H	-0.243267	-2.402886	-3.575553
H	0.043926	-0.644493	-3.349261
H	1.420298	-1.768452	-3.450537
H	0.182923	-4.248796	-1.708913
H	1.848194	-3.777255	-1.288872
H	0.614046	-3.911883	-0.008215
C	-3.260035	-1.137554	0.133286
C	-3.992735	-2.156677	-0.503163
C	-3.929907	-0.220647	0.966028
C	-5.369749	-2.260831	-0.304726
H	-3.483092	-2.864044	-1.146264
C	-5.307080	-0.331799	1.156086
H	-3.391988	0.580878	1.461853
C	-6.030862	-1.350053	0.524877
H	-5.924169	-3.053091	-0.798171
H	-5.816027	0.380591	1.798172
H	-7.102814	-1.431187	0.678334
P	0.004242	1.410292	1.086407
O	-1.759106	1.776727	1.417808
Cl	-0.844198	0.423886	-2.055024
C	0.242135	2.981189	0.151529
C	0.450632	1.737692	2.840223
C	-4.315541	-0.969239	-0.909517
O	-2.997345	3.875921	1.501559
O	-3.336423	4.716650	-0.816592
O	-3.204038	2.613306	-2.448882
H	-0.225780	2.494339	3.243477
H	0.344784	0.823698	3.428325
H	1.482070	2.081910	2.899001
H	1.269753	3.078880	-0.191766
H	-0.436588	2.984167	-0.701945
H	-0.000380	3.819511	0.810951
H	-1.087227	-1.137134	2.932115
H	-3.076017	-1.041890	1.449895
H	1.043469	-3.469508	-0.022943
H	-0.872569	-3.256321	-1.569878
H	2.064836	-1.176417	-1.210519
H	-3.112524	4.280446	0.531333
H	-3.216611	2.779054	-3.401534
H	-3.252342	3.965142	-1.467902
H	-2.492612	1.957248	-2.297034
H	-2.739528	5.419415	-1.109819
H	-2.386125	2.956477	1.487340
H	-2.301196	1.167212	0.894705
H	-2.643107	4.539234	2.113761
H	2.235881	-2.566800	2.046438
H	1.306674	-1.748765	3.318517
H	1.168248	-3.500381	3.105884
H	-2.875834	-1.958805	-2.150359
H	-3.831234	0.011100	-0.924340
H	-5.070151	-0.978769	-1.702005
H	-4.843342	-1.088923	0.043075
H	-4.809991	-3.494398	-1.884653
H	-3.320737	-4.293514	-1.354483
H	-4.466955	-3.668476	-0.153339
C	3.976390	0.355535	-0.489154
C	4.954544	0.867659	0.378633
C	4.365860	-0.123946	-1.751107
C	6.298974	0.878281	0.001680
H	4.651690	1.249527	1.347612
C	5.709792	-0.102218	-2.130946
H	3.625706	-0.491136	-2.455935
C	6.680649	0.393071	-1.253931
H	7.047260	1.267007	0.686196
H	5.996104	-0.466117	-3.113231
H	7.725619	0.406308	-1.549636

TS2-OH-bzn_Os

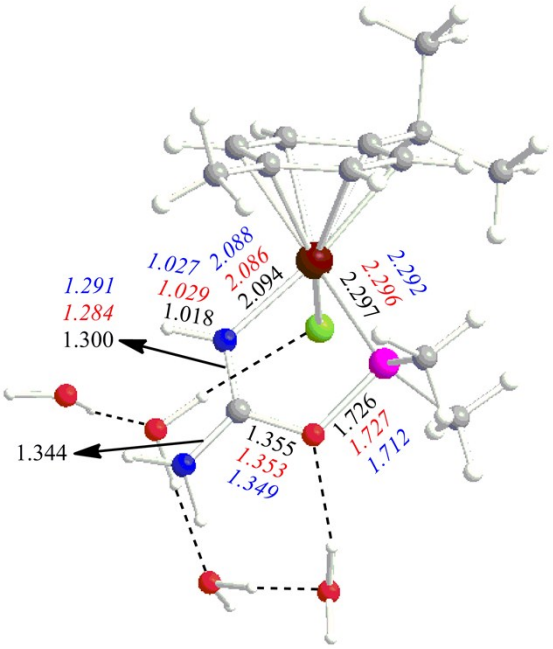
(ν=157i cm^{-1})

C	0.140208	-2.973949	0.318514
C	-0.948707	-2.846580	-0.569346
C	-2.143715	-2.138368	-0.180454
C	-2.194822	-1.573209	1.114005
C	-1.045624	-1.633535	1.969097
C	0.131846	-2.365944	1.617627
Os	-0.267576	-0.755064	0.095946
N	1.684025	-0.514345	-0.545807
C	2.546086	0.349483	-0.043492
O	2.185980	1.194224	0.843923
C	-3.309363	-2.100422	-1.153352
C	-4.014556	-3.476738	-1.132779
C	1.278810	-2.547612	2.574136

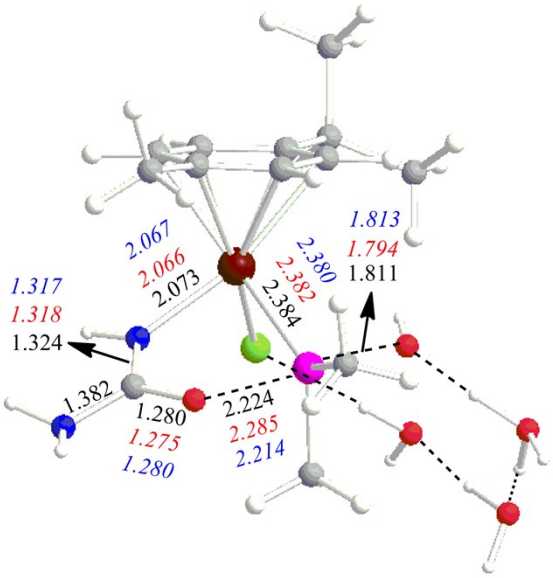
Table S4. Electron delocalization indexes (DI) for the most relevant chemical bonds and interaction distances involved in the metallacycle formation step of the intramolecular mechanism found for the [MCl_2(η^6-*p*-cymene)(PMe_2OH)] (M = Ru (**1**), Os (**2**))-catalyzed hydration of the substrates (**S**) acetonitrile (**actn**), benzonitrile (**bzn**), and cyanamide (**cyan**). Electron density (ρ(r), e/Å^3) at the most relevant bond critical points (BCP) located are also given in parenthesis.



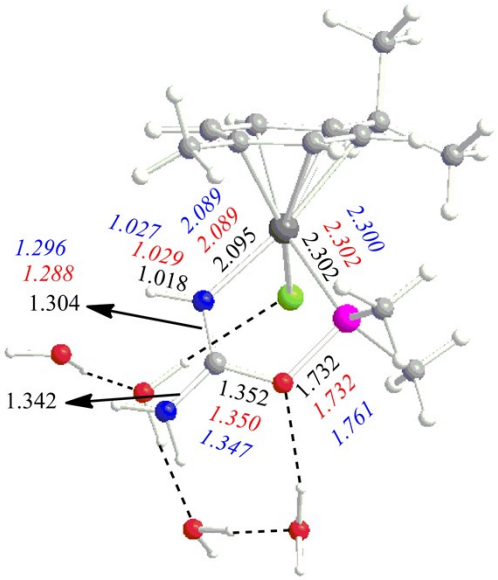
			DI					
M	R	Species	*a*	*b*	*c*	*d*	*e*	*f*
Ru	CH_3	**1-OH-actn_Ru**	0.8912	0.6970	2.0311	0.6921	1.0420	
			(0.0970)	(0.1644)	(0.4516)	(0.0914)	(0.2645)	
		TS1-OH-actn_Ru	0.8679	0.7529	1.7812	0.6518	0.9960	0.3775
			(0.0946)	(0.1752)	(0.4378)	(0.0841)	(0.2654)	(0.0766)
Ru	Ph	**1-OH-bzn_Ru**	0.8918	0.6993	2.0123	0.7022	1.0836	
			(0.0961)	(0.1640)	(0.4479)	(0.0924)	(0.2810)	
		TS1-OH-bzn_Ru	0.8663	0.7503	1.7663	0.6543	1.0346	0.3689
			(0.0948)	(0.1759)	(0.4347)	(0.0847)	(0.2757)	(0.0740)
Ru	NH_2	**1-OH-cyan_Ru**	0.8941	0.6946	1.9076	0.6748	1.1775	
			(0.0975)	(0.1641)	(0.4434)	(0.0888)	(0.3522)	
		TS1-OH-cyan_Ru	0.8595	0.7525	1.6840	0.6250	1.0891	0.3255
			(0.0931)	(0.1754)	(0.4340)	(0.0808)	(0.3477)	(0.0718)
Os	CH_3	**1-OH-actn_Os**	0.9230	0.6912	1.9993	0.7821	1.0430	
			(0.1027)	(0.1635)	(0.4483)	(0.1079)	(0.2645)	
		TS1-OH-actn_Os	0.8891	0.7515	1.7723	0.7151	1.0002	0.3590
			(0.1004)	(0.1756)	(0.4368))	(0.0972)	(0.2661)	(0.0719)
Os	Ph	**1-OH-bzn_Os**	0.9252	0.6929	1.9771	0.8033	1.0886	
			(0.1030)	(0.1634)	(0.4439)	(0.1105)	(0.2816)	
		TS1-OH-bzn_Os	0.8912	0.7503	1.7663	0.6543	1.0346	0.3689
			(0.0948)	(0.1759)	(0.4347)	(0.0847)	(0.2757)	(0.0740)
Os	NH_2	**1-OH-cyan_Os**	0.9258	0.6878	1.8787	0.7596	1.1819	
			(0.1037)	(0.1631)	(0.4409)	(0.1047)	(0.3522)	
		TS1-OH-cyan_Os	0.8894	0.7522	1.6714	0.6943	1.0949	0.3107
			(0.1000)	(0.1756)	(0.4326)	(0.0949)	(0.3471)	(0.0680)



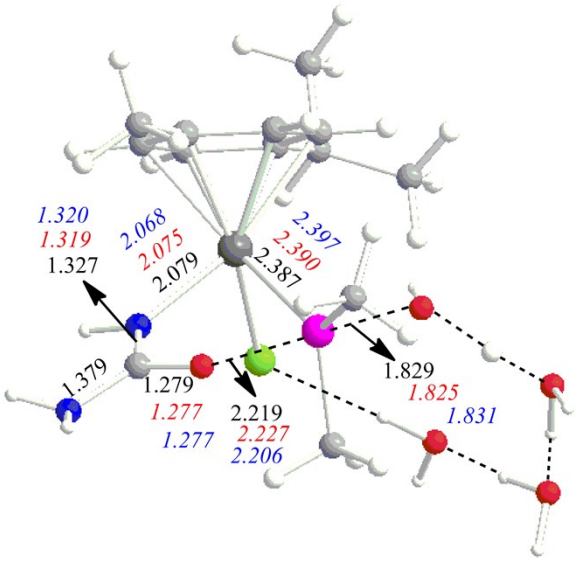
2-OH-cyan_Ru



TS2-OH-cyan_Ru



2-OH-cyan_Os



TS2-OH-cyan_Os

Figure S59. PCM-B3LYP/6-31+G(d,p) (LANL2DZ for Ru and Os) optimized geometries of the species involved in the step for the metallacycle cleavage of the intermediate immediately formed after the hydroxyl nucleophilic attack along the intramolecular mechanism found for the cyanamide hydration catalyzed by [MCl_2(η^6-*p*-cymene)(PMe_2OH)] (M = Ru (**1**), Os (**2**)) in water solution. Relevant distances are given in black colour in Å. For comparison purposes, analogous data obtained for the hydration of acetonitrile (red colour) and benzonitrile (blue colour) are displayed as well.

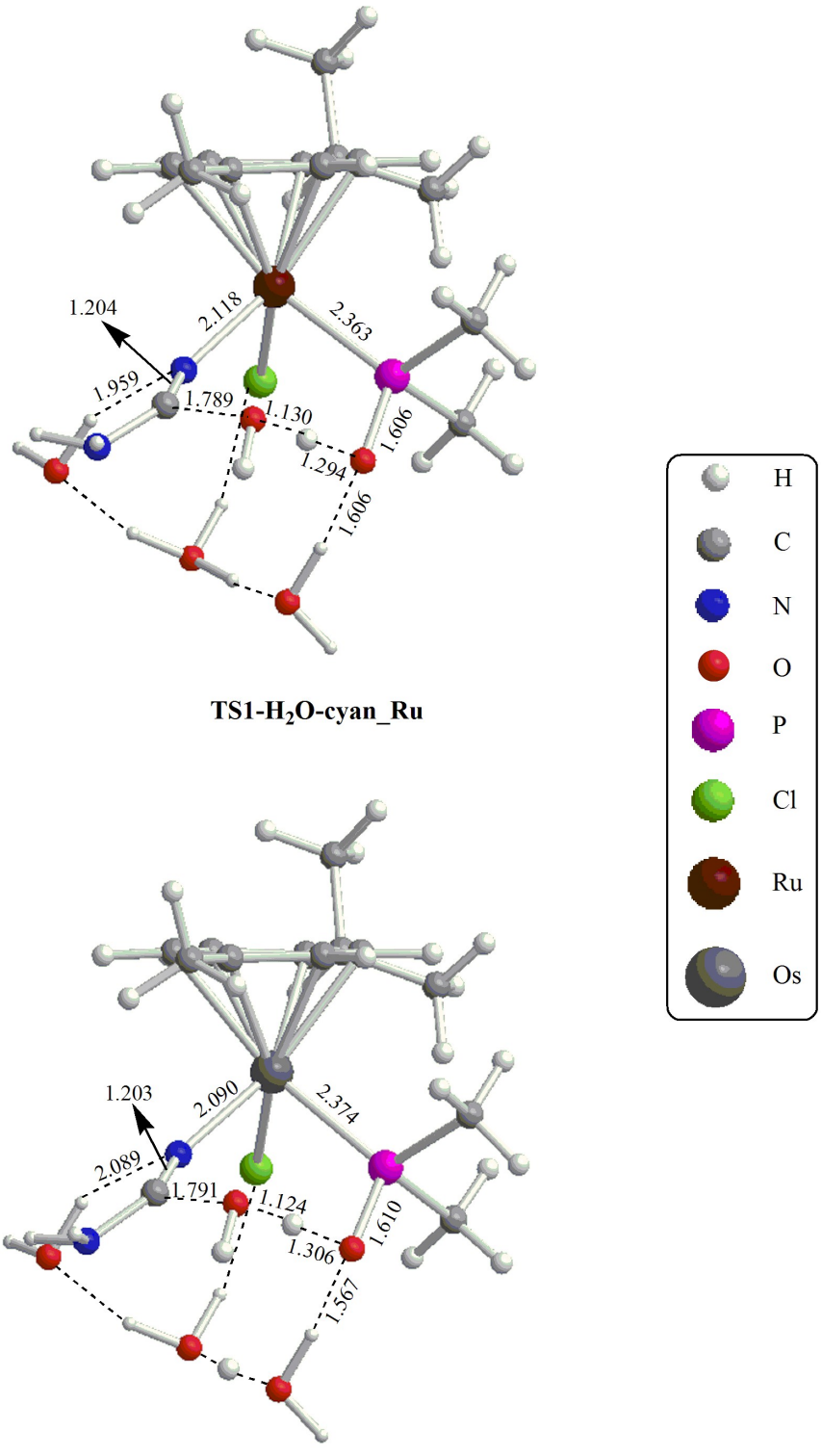
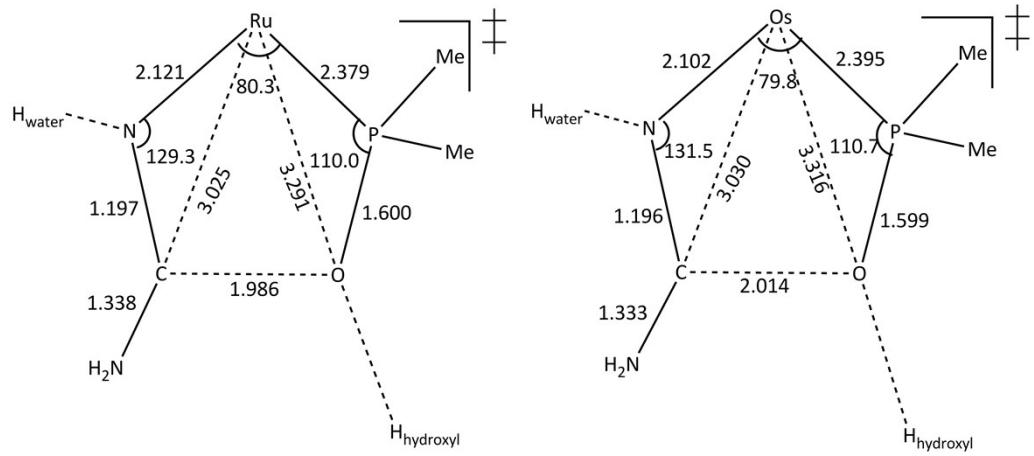
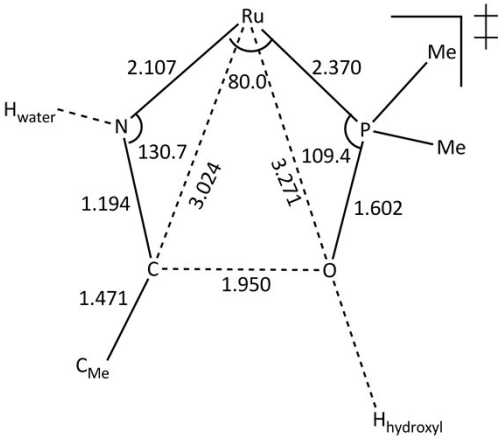


Figure S60. PCM-B3LYP/6-31+G(d,p) (LANL2DZ for Ru and Os) optimized geometry of the transition states of the nucleophilic attack on the nitrile carbon atom of a water molecule (intermolecular mechanism) found for the cyanamide hydration catalyzed by [$MCl_2(\eta^6$-*p*-cymene)(PMe_2OH)] (M = Ru (**1**), Os (**2**)) in water solution. Relevant distances are given in Å.

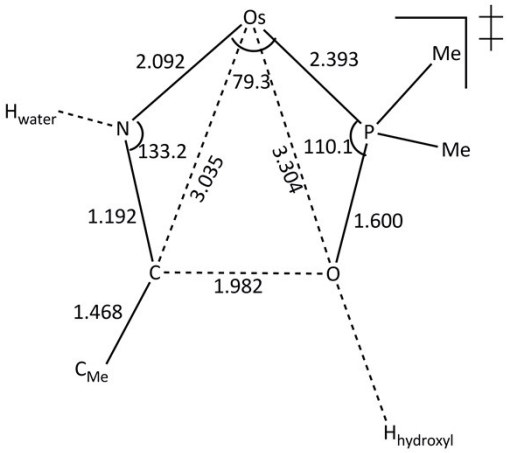


TS1-OH-cyan_Ru

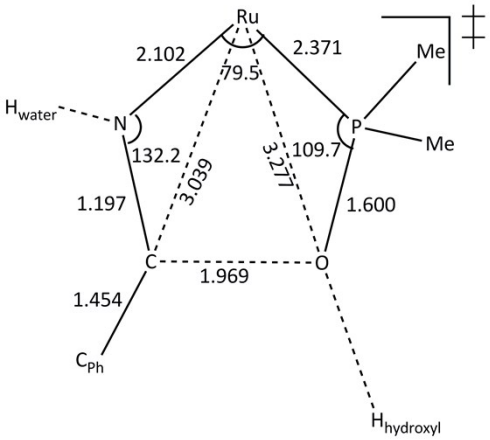
TS1-OH-cyan_Os



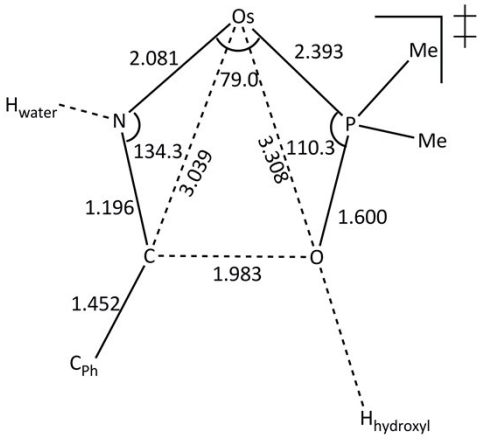
TS1-OH-actn_Ru



TS1-OH-actn_Os



TS1-OH-bzn_Ru



TS1-OH-bzn_Os

Figure S61. Schematic view of the three triangles defined in the metallacycle of **TS1-OH-S_M** (**S** (substrate) = cyanamide (**cyan**); **M** = **Ru**, **Os**)). Relevant PCM-B3LYP/6-31+G(d,p) (LANL2DZ) bond lengths (in angstroms) and bond angles (in degrees) are displayed. For comparison purposes, analogous data corresponding to **TS1-OH-S_M** (**S** = acetonitrile (**actn**), benzonitrile (**bzn**); **M** = **Ru**, **Os**) are also included.

Table S5. PCM-B3LYP/6-31+G(d,p) (LANL2DZ for Ru) absolute energies in methanol solution without and with including thermal corrections (E and G, respectively), and CPCM-DLPNO-CCSD(T)/def2-TZVPP//PCM-B3LYP/6-31+G(d,p) (LANL2DZ for Ru) absolute energies in methanol solution without and with including thermal corrections (E' and G', respectively) of the critical structures involved in the most energy-demanding steps for the intramolecular mechanism found for the reactivity of [$RuCl_2(\eta^6$-*p*-cymene)(PMe_2OH)] towards dimethylcyanamide (**dmcyan**).[a,b,c]

Species	E	G	E'	G'
1-OH-dmcyan_Ru	-2131.034155	-2130.507569	-2128.901829	-2128.375243
TS1-OH-dmcyan_Ru	-2130.992964	-2130.460911	-2128.860232	-2128.328179
2-OH-dmcyan_Ru	-2131.059241	-2130.526334	-2128.928268	-2128.395361
TS2-OH-dmcyan_Ru	-2131.019742	-2130.485497	-2128.889322	-2128.355077
3-OH-dmcyan_Ru	-2131.028982	-2130.492858	-2128.897030	-2128.360906

[a]All the energies are in hartree. [b]Electrostatic solvation terms have only been considered in these computations. [c]$G' = G - E + E'$.

Table S6. PCM-B3LYP/6-31+G(d,p) (LANL2DZ for Ru) relative energies in methanol solution without and with including thermal corrections (ΔE and ΔG, respectively), and CPCM-DLPNO-CCSD(T)/def2-TZVPP//PCM-B3LYP/6-31+G(d,p) (LANL2DZ for Ru) relative energies in water solution without and with including thermal corrections (ΔE' and ΔG', respectively) of the critical structures involved in the most energy-demanding steps for the intramolecular mechanism found for the reactivity of [$RuCl_2(\eta^6$-*p*-cymene)(PMe_2OH)] towards dimethylcyanamide (**dmcyan**).[a,b,c]

Species	ΔE	ΔG	ΔE'	ΔG'
1-OH-dmcyan_Ru	0.0	0.0	0.0	0.0
TS1-OH-dmcyan_Ru	25.8	29.3	26.1	29.5
2-OH-dmcyan_Ru	-15.7	-11.8	-16.6	-12.6
TS2-OH-dmcyan_Ru	9.0	13.9	7.8	12.7
3-OH-dmcyan_Ru	3.2	9.2	3.0	9.0

[a]All the energies are in kcal/mol. [b]Electrostatic solvation terms have only been considered in these computations. [c]$\Delta G' = \Delta G - \Delta E + \Delta E'$.

Table S7. PCM-B3LYP/6-31+G(d,p) (LANL2DZ for Ru) optimized cartesian coordinates (in Å) in methanol solution of the critical structures involved in the most energy-demanding steps for the intramolecular mechanism found for the reactivity of [$RuCl_2(\eta^6$-*p*-cymene)(PMe_2OH)] towards dimethylcyanamide (**dmcyan**). Imaginary vibrational frequencies are also given for the transition states located. Only the electrostatic solvation terms have been considered in these computations.

1-OH-dmcyan_Ru

C	-2.670943	1.165466	-1.529742
C	-3.179639	1.238604	-0.180622
C	-3.609018	0.041815	0.426835
C	-3.482381	-1.210781	-0.257023
C	-2.948011	-1.283439	-1.563441
C	-2.569756	-0.049213	-2.202611
Ru	-1.408986	-0.301697	-0.150930
P	-0.789170	-1.437744	1.812590
C	-1.105260	-0.515599	3.364214
C	-3.316688	2.607759	0.462957
C	-4.538848	3.327235	-0.154388
C	-2.842593	-2.589461	-2.301009
Cl	0.178296	1.456182	0.590993
N	0.179841	-1.263196	-1.047068
C	1.060532	-1.842192	-1.549473
N	2.048768	-2.523168	-2.084737
C	3.368303	-1.880586	-2.236485
C	-3.407000	2.594971	1.993758
C	1.733147	-3.651174	-2.980328
O	0.760158	-1.916242	1.903554
C	-1.615625	-3.048383	2.070867
O	2.818505	-0.411445	2.438693
O	4.545338	0.087700	0.411137
O	4.430416	2.534793	-0.742605
O	1.938012	2.540584	-1.843192
H	-1.172297	-3.537449	2.943120
H	-2.683867	-2.901470	2.247650
H	-1.478885	-3.680201	1.190189
H	-0.739429	-1.102297	4.212362
H	-0.587797	0.445289	3.327757
H	-2.177761	-0.340026	3.481287
H	-3.799303	-2.121559	0.237245
H	-4.016186	0.053084	1.429930
H	-2.134614	-0.079256	-3.195940
H	-2.316268	2.072206	-2.007771
H	1.336608	2.198855	-1.149713
C	5.907254	-0.344956	0.482917
C	1.347873	3.692381	-2.459163
H	4.511006	0.996950	0.019702
H	3.539228	2.603620	-1.162934
C	4.653675	3.682453	0.083943
H	1.488932	-1.229744	2.029154
C	3.541248	-0.965343	3.544706
H	3.448587	-0.217212	1.699429
H	-1.948206	-2.619847	-2.927876
H	-2.820624	-3.436091	-1.611302
H	-3.713448	-2.706650	-2.957245
H	-2.417993	3.170929	0.183758
H	-2.544494	2.096536	2.443503
H	-3.429551	3.625082	2.362319
H	-4.321073	2.104324	2.346719
H	-4.603813	4.346322	0.239887
H	-4.468751	3.390732	-1.244874
H	-5.467390	2.803385	0.098601
H	3.437627	-1.360581	-3.199002
H	3.535061	-1.177372	-1.418742
H	4.129654	-2.662827	-2.193195
H	1.682736	-3.318201	-4.023321
H	2.520212	-4.401458	-2.876189
H	0.779155	-4.093029	-2.691253
H	0.399282	3.433920	-2.943166
H	1.176300	4.493768	-1.730981
H	2.047691	4.046240	-3.219064
H	4.321469	-0.274208	3.882494
H	2.830715	-1.119068	4.359838
H	3.998537	-1.927957	3.285309
H	6.369249	-0.351929	-0.511466
H	6.498570	0.296294	1.148198
H	5.912147	-1.363250	0.878662
H	4.651806	4.602220	-0.512646
H	3.895974	3.764036	0.872923
H	5.635801	3.567712	0.548307

TS1-OH-dmcyan_Ru

(ν=290i cm^{-1})

C	2.972965	1.567897	0.588160
C	3.436187	0.646864	-0.421388
C	3.494803	-0.722068	-0.086748
C	3.046206	-1.180304	1.194534
C	2.541887	-0.278814	2.160703
C	2.546976	1.125628	1.839118
Ru	1.323230	-0.094712	0.232583
P	0.301350	-2.025800	-0.637948
C	0.339848	-2.238810	-2.458146
C	3.920676	1.207805	-1.747970
C	5.326947	1.820073	-1.557673
C	2.092394	-0.750430	3.516421
Cl	0.212890	1.193731	-1.594474
N	-0.531178	-0.003471	1.251688
C	-1.370405	-0.875991	1.320413
N	-2.310893	-1.441065	2.070984
C	-3.512086	-2.083071	1.525867
C	3.913593	0.201413	-2.905196
C	-2.396027	-0.985955	3.469300
O	-1.246964	-2.058314	-0.212711
C	0.991791	-3.622215	-0.038740
O	-3.132210	-1.080941	-1.917730
O	-4.515993	0.836181	-0.762292
O	-3.329711	2.910335	-0.217141
O	-1.736770	2.462090	1.640591
H	0.392066	-4.442260	-0.446665
H	2.029757	-3.744927	-0.361103
H	0.947258	-3.658046	1.052573
H	-0.231487	-3.130298	-2.736025
H	-0.083281	-1.355959	-2.939389
H	1.376467	-2.361337	-2.785356
H	3.079392	-2.238989	1.423189
H	3.851154	-1.445555	-0.809494
H	2.154319	1.836594	2.558005
H	2.898640	2.621709	0.341400
H	-1.218017	1.620416	1.517181
C	-5.841368	0.958029	-1.310763
C	-0.914539	3.506390	2.190243
H	-3.829635	1.992139	-0.491393
H	-2.621739	2.740011	0.546092
C	-2.768167	3.617809	-1.360260
H	-2.421481	-1.437449	-1.325498
C	-3.795409	-2.162255	-2.583346
H	-4.001935	0.101892	-1.216247
H	1.238000	-0.170017	3.873072
H	1.817462	-1.807643	3.498991
H	2.908050	-0.622932	4.238679

H	3.231416	2.020423	-2.007236
H	2.925544	-0.247764	-3.036371
H	4.178875	0.713924	-3.835476
H	4.645550	-0.600261	-2.755658
H	5.653251	2.300686	-2.485842
H	5.338451	2.574490	-0.764804
H	6.057471	1.044567	-1.300517
H	-4.297193	-1.344532	1.324931
H	-3.257072	-2.611060	0.611672
H	-3.877327	-2.799514	2.264755
H	-3.068398	-0.124675	3.562394
H	-2.780862	-1.807990	4.077502
H	-1.403955	-0.707904	3.823740
H	-0.521532	3.197073	3.162704
H	-0.087824	3.752303	1.516842
H	-1.549402	4.383835	2.323821
H	-4.537490	-1.729457	-3.257621
H	-3.083000	-2.748947	-3.173068
H	-4.303988	-2.822619	-1.870766
H	-6.348997	1.755057	-0.765922
H	-5.804253	1.208564	-2.375288
H	-6.387178	0.021797	-1.168716
H	-2.456501	4.603169	-1.014466
H	-1.921438	3.059698	-1.763474
H	-3.560582	3.717684	-2.101128

2-OH-dmcyan_Ru

C	-1.257640	-1.661506	1.760626
C	-1.709090	-2.220917	0.564332
C	-2.835884	-1.673530	-0.155906
C	-3.491489	-0.562598	0.406570
C	-3.011703	0.034358	1.617354
C	-1.893488	-0.490390	2.307926
Ru	-1.276181	0.053641	0.170671
N	0.550170	0.893830	0.765445
C	0.902635	2.113139	0.456434
N	2.094627	2.699802	0.689986
C	3.136718	1.961707	1.402929
C	-3.283520	-2.353073	-1.438609
C	-4.133248	-1.467019	-2.358685
C	-1.409015	0.111669	3.596825
P	-1.520310	2.230720	-0.510658
C	-2.602987	3.375064	0.411033
Cl	-0.169558	-0.426419	-2.015428
C	-1.745111	2.697722	-2.255835
O	0.014806	2.901693	-0.198424
C	-4.024769	-3.664352	-1.091596
C	2.281003	4.151590	0.584891
O	2.963549	-0.020747	-2.647628
C	3.198370	1.328505	-3.071946
O	4.742677	-1.249019	-0.989632
C	5.825260	-1.774090	-1.764252
O	3.507479	-2.802457	0.847629
C	2.885105	-3.939726	0.243833
O	1.992354	-1.150560	2.390842
C	2.652487	-1.018639	3.649455
H	-2.416236	4.403255	0.088406
H	-3.646480	3.118626	0.204474
H	-2.415400	3.285435	1.483085
H	-1.585282	3.772546	-2.378512
H	-1.048373	2.131846	-2.874973
H	-2.769081	2.446899	-2.548568
H	-3.513577	0.911460	2.010017
H	-4.336464	-0.113104	-0.099841
H	-0.361431	-2.045395	2.236964
H	-1.164676	-3.052291	0.129297
H	1.193793	0.324036	1.321540
H	3.964080	-2.268699	0.150254
H	2.519077	-1.764516	1.823003
H	2.026299	-0.117943	-2.384691
H	4.103275	-0.790733	-1.585813
H	-0.318527	0.089539	3.653078
H	-1.750683	1.143288	3.707896
H	-1.799741	-0.470109	4.440344

TS2-OH-dmcyan_Ru

(ν=172i cm^{-1})

C	-3.084214	0.740923	1.118685
C	-3.256305	1.353052	-0.161794
C	-2.398132	2.367567	-0.618358
C	-1.343363	2.873696	0.213679
C	-1.168678	2.295920	1.485418
C	-1.992662	1.204928	1.902422
Ru	-1.139678	0.481166	-0.050617
Cl	0.662208	0.777004	-1.771308
C	-0.517495	4.041133	-0.298127
C	0.868979	4.181104	0.342415
C	-4.043645	-0.304366	1.618188
N	-1.826589	-1.064862	-1.252760
C	-1.948150	-2.313357	-0.815004
N	-2.561956	-3.287862	-1.561739
C	-2.851056	-4.590522	-0.964352
P	0.137333	-1.296528	0.914666
C	-0.207508	-2.062660	2.560107
O	-1.443063	-2.632270	0.327416
O	1.702279	-0.535564	1.533796
C	1.718331	0.625639	2.373113
C	1.149101	-2.404079	-0.163433
C	-1.337548	5.342089	-0.129972
C	-3.300870	-2.936355	-2.771171
O	3.977156	-1.383410	1.549954
C	4.245273	-2.708212	2.073762
O	5.163922	-0.665901	-0.511850
C	5.467070	-1.584069	-1.578884
O	3.745188	1.426961	-1.286795
C	4.169919	2.311154	-2.334474
H	0.135878	-1.411783	3.364997
H	-1.273327	-2.257149	2.664812
H	0.334011	-3.010837	2.623580
H	0.609645	-2.605755	-1.086672
H	2.091929	-1.920484	-0.414794
H	1.334154	-3.349125	0.353781
H	-1.814203	0.752822	2.872501
H	-0.391489	2.651802	2.147364
H	-4.028917	0.975929	-0.824121
H	-2.530117	2.769662	-1.616661
H	-2.212382	-0.844654	-2.160548
H	4.494814	-1.142252	0.660315
H	4.658330	0.120489	-0.866072
H	2.789313	1.231594	-1.390019
H	2.919577	-1.082636	1.514593
H	-4.372622	-0.958957	0.807217

H	-3.592690	-0.917564	2.401377
H	-4.932758	0.180812	2.039022
H	-0.376387	3.871730	-1.372499
H	1.458544	3.268053	0.222354
H	1.412300	4.997800	-0.143086
H	0.805957	4.423313	1.409249
H	-0.788639	6.183338	-0.565285
H	-2.310042	5.277590	-0.627934
H	-1.509841	5.558918	0.930268
H	-2.759675	-5.366435	-1.729829
H	-2.138297	-4.790154	-0.166699
H	-3.867920	-4.628561	-0.548430
H	-3.638229	-3.856252	-3.250872
H	-4.182509	-2.316376	-2.556765
H	-2.661456	-2.410128	-3.487448
H	0.965782	0.560149	3.165202
H	2.704862	0.685139	2.839592
H	1.548719	1.522533	1.775970
H	5.315179	-2.778560	2.270093
H	3.689341	-2.810453	3.005311
H	3.936140	-3.473457	1.358468
H	6.093952	-1.089411	-2.325893
H	6.018070	-2.420234	-1.145455
H	4.552415	-1.955603	-2.052454
H	3.623184	3.258576	-2.285020
H	5.233179	2.505451	-2.180536
H	4.026222	1.857673	-3.321576

3-OH-dmcyan_Ru

C	-1.272931	2.343895	1.350917
C	-1.714695	1.261115	2.149367
C	-2.777636	0.402177	1.737509
C	-3.300815	0.623461	0.436571
C	-2.882608	1.717158	-0.367356
C	-1.874422	2.603022	0.085571
Ru	-1.059758	0.319170	0.163486
N	-1.501949	-1.239595	-1.154576
C	-2.149644	-2.396644	-0.932388
N	-2.259712	-3.304482	-2.002356
C	-3.281755	-4.342998	-1.900420
C	-3.358802	-0.654399	2.636307
C	-1.485236	3.791259	-0.779388
C	-0.130364	4.420522	-0.428114
P	0.458298	-1.174489	1.097384
O	1.894877	-0.530734	1.697396
C	1.887362	0.615300	2.574530
Cl	0.672100	0.862453	-1.559092
C	1.209917	-2.405052	-0.023714
C	-0.156561	-2.195624	2.488597
C	-2.611893	4.849479	-0.715934
O	-2.624982	-2.711166	0.190983
C	-1.930057	-2.902759	-3.366063
O	4.541298	-1.144238	1.333472
C	5.110943	-2.333236	1.914787
O	5.203147	-0.094461	-0.815051
C	5.320948	-0.979058	-1.967440
O	3.619361	1.785981	-1.071035
C	3.948833	2.889142	-1.942141
H	0.611733	-2.910009	2.797895
H	-0.436961	-1.573771	3.340922
H	-1.045223	-2.720057	2.124667
H	1.662930	-1.895447	-0.875488
H	1.961785	-2.986389	0.516795
H	0.428978	-3.075641	-0.386372
H	-1.256036	1.104121	3.119898
H	-0.482478	2.983727	1.720901
H	-4.041410	-0.066300	0.047642
H	-3.320431	1.853590	-1.349876
H	-1.098443	-1.111003	-2.072286
H	4.945890	-0.598747	0.073806
H	4.520989	0.707239	-0.971056
H	2.679124	1.514654	-1.195258
H	3.569454	-1.092950	1.477614
H	-3.470554	-1.591732	2.086255
H	-2.731845	-0.823160	3.514508
H	-4.345357	-0.329976	2.988438
H	-1.432428	3.421227	-1.810696
H	0.671281	3.677201	-0.433690
H	0.114549	5.189912	-1.166938
H	-0.152282	4.907054	0.553659
H	-2.369956	5.686059	-1.379473
H	-3.575955	4.436359	-1.027606
H	-2.720430	5.242692	0.301218
H	-2.979138	-5.209283	-2.496959
H	-3.388061	-4.643954	-0.859924
H	-4.262073	-3.997407	-2.267164
H	-1.999613	-3.779054	-4.014893
H	-2.609213	-2.130888	-3.761461
H	-0.902083	-2.534247	-3.436014
H	1.389160	0.380962	3.519891
H	2.932196	0.858557	2.771462
H	1.400879	1.463129	2.087774
H	6.188278	-2.282987	1.752938
H	4.906458	-2.353544	2.988269
H	4.710160	-3.233964	1.440271
H	5.647766	-0.370302	-2.809124
H	6.076469	-1.725822	-1.727630
H	4.360800	-1.452177	-2.180424
H	3.312089	3.744931	-1.706252
H	4.990671	3.146960	-1.748714
H	3.826013	2.607495	-2.991874

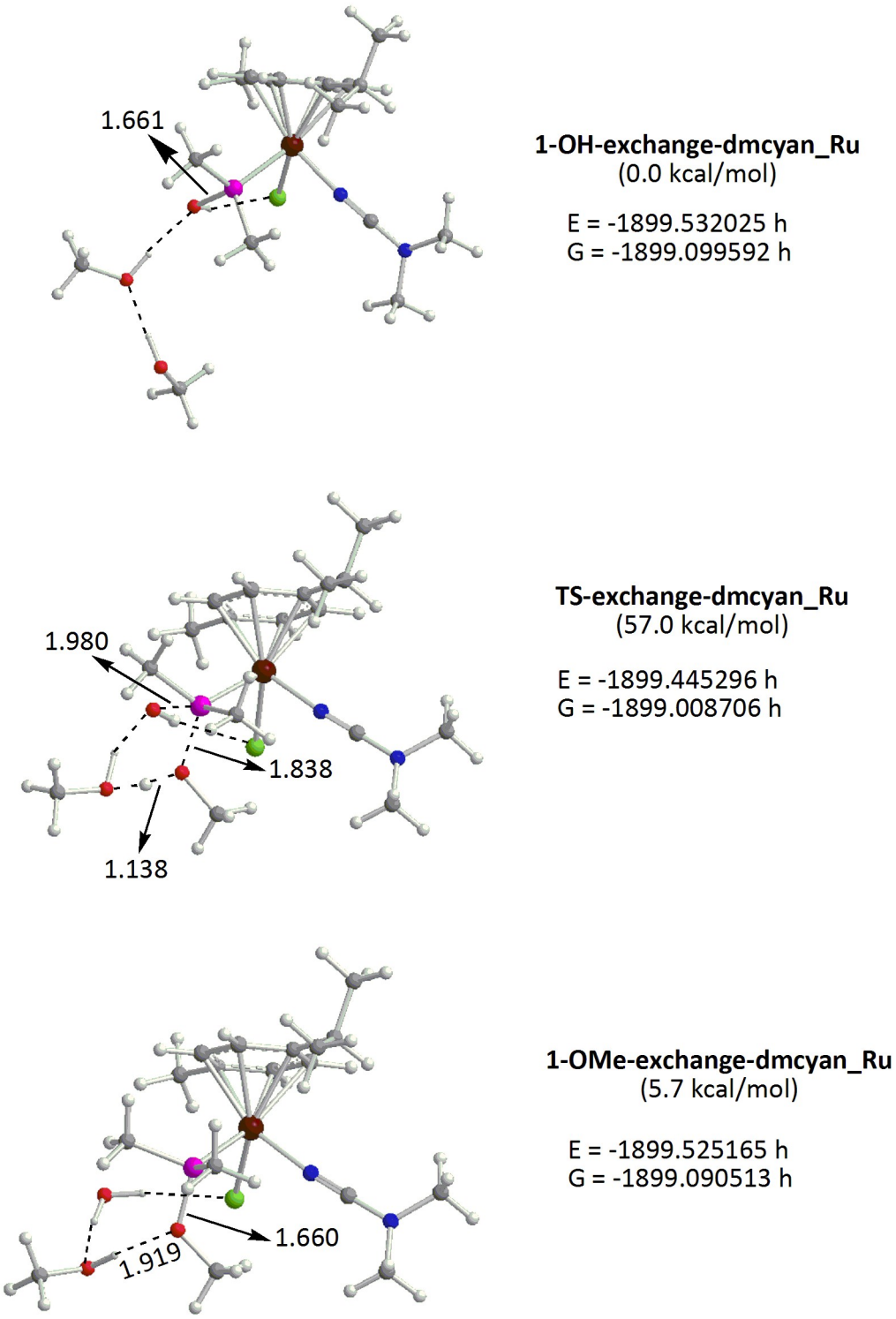


Figure S62. PCM-B3LYP/6-31+G(d,p) (LANL2DZ for Ru) optimized structures in methanol solution along with their absolute energies without and with including thermal corrections (E and G, respectively) of the main species for the direct OH/OMe exchange on the P-donor ligand in the [RuCl(η^6-*p*-cymene)(PMe_2OH)($N{\equiv}CNMe_2$)]$^+$ complex without the involvement of dimethylcyanamide. Relative energies with including thermal corrections in parenthesis and some relevant bond distances in angstroms are also given.

Table S8. PCM-B3LYP/6-31+G(d,p) (LANL2DZ for Ru) optimized cartesian coordinates (in Å) in methanol solution of the critical structures involved in the direct OH/OMe exchange on the P-donor ligand in the [RuCl(η^6-*p*-cymene)(PMe_2OH)($N{\equiv}CNMe_2$)]$^+$ without the involvement of dimethylcyanamide.

1-OH-exchange-dmcyan_Ru

[RuCl(η^6-*p*-cymene)(PMe_2OH)($N{\equiv}CNMe_2$)]$^+$

C	-3.000175	-0.651839	0.524184
C	-2.179385	-1.702806	0.994314
C	-1.554514	-2.616306	0.085799
C	-1.730260	-2.487294	-1.307021
C	-2.611326	-1.449412	-1.785281
C	-3.227656	-0.568926	-0.899000
C	-1.084802	-3.437220	-2.274898
C	-3.727864	0.312748	1.445541
C	-5.165740	-0.207702	1.675771
P	1.007781	-0.550296	0.901105
O	6.190977	1.337615	0.623880
C	-3.016535	0.580705	2.778757
H	-0.915205	-3.403889	0.468399
H	-1.996389	-1.811267	2.055719
H	-2.745678	-1.320323	-2.853693
H	-3.836681	0.240474	-1.288446
H	-0.273753	-3.996295	-1.803610
H	-1.836701	-4.153035	-2.628367
H	-0.690557	-2.904793	-3.143648
H	-3.802518	1.264412	0.905331
H	-5.727349	0.513194	2.278352
H	-5.701544	-0.350892	0.731996
H	-5.152545	-1.164203	2.210285
H	-1.990894	0.929693	2.625852
H	-3.559530	1.355640	3.328733
H	-2.990000	-0.310084	3.416312
Cl	0.680087	-0.285636	-2.354660
O	2.256906	-1.279918	0.084280
H	2.095083	-1.162247	-0.879213
H	4.118169	-1.246970	0.372950
O	5.092409	-1.213812	0.415169
H	5.800903	0.439644	0.564925
C	6.415558	1.824446	-0.697587
H	6.851528	2.823893	-0.612895
H	7.116272	1.187553	-1.256330
H	5.480503	1.902720	-1.270297
C	0.975957	-1.543799	2.433197
H	0.656054	-2.567731	2.225026
H	1.981502	-1.564127	2.864237
H	0.288408	-1.086667	3.151601
C	1.706581	1.053256	1.431515
H	0.987933	1.571965	2.071985
H	2.633009	0.879479	1.986949
H	1.915150	1.672172	0.556063
N	-0.861820	1.572002	-0.359917
C	-0.911505	2.736180	-0.442447
N	-0.972613	4.038885	-0.574888
Ru	-0.906370	-0.494058	-0.445352
C	5.570837	-2.275566	1.248683
H	5.293275	-3.254098	0.839289
H	6.660299	-2.200427	1.274267
H	5.185337	-2.188958	2.271953
C	-2.135318	4.776129	-0.048290
H	-2.359566	5.598792	-0.731695
H	-2.997786	4.110678	0.004402
H	-1.918853	5.177312	0.948184
C	0.256290	4.801149	-0.862559
H	0.010228	5.602798	-1.563435
H	0.665416	5.232044	0.057934
H	0.996432	4.142591	-1.318083

TS-exchange-dmcyan_Ru

(ν=457i cm^{-1})

C	-2.207056	-1.600117	0.462161
C	-1.055387	-2.100528	1.109897
C	0.011975	-2.686371	0.353226
C	-0.047389	-2.775527	-1.051877
C	-1.240478	-2.293291	-1.702028
C	-2.289096	-1.736581	-0.971438
C	1.054223	-3.405051	-1.858136
C	-3.402386	-1.023748	1.202621
C	-4.488858	-2.119228	1.312684
P	1.496499	0.208783	0.990853
O	2.737254	1.499330	0.575740
C	-3.083244	-0.430076	2.580072
H	0.898086	-3.036993	0.868336
H	-0.960705	-2.029698	2.186039
H	-1.294835	-2.317223	-2.785251
H	-3.154660	-1.340605	-1.491694
H	1.973435	-3.486264	-1.275067
H	0.750134	-4.412006	-2.168323
H	1.259390	-2.823128	-2.760811
H	-3.804345	-0.221080	0.572215
H	-5.387062	-1.702450	1.779392
H	-4.768914	-2.514789	0.331350
H	-4.137876	-2.953080	1.930674
H	-2.306597	0.336630	2.517525
H	-3.983987	0.035291	2.991737
H	-2.760379	-1.197637	3.291947
Cl	0.926275	0.289350	-2.409916
O	2.754644	-0.888229	-0.073825
H	2.448998	-0.787392	-0.992779
H	4.182744	-0.322390	-0.163782
O	4.798058	0.506759	-0.161506
H	3.766977	1.144652	0.244799
C	2.394261	2.818743	0.070271
H	2.101010	3.463793	0.897961
H	3.296420	3.209787	-0.402753
H	1.598351	2.734025	-0.670455
C	2.157773	-0.741390	2.428765
H	2.548359	-1.711453	2.129740
H	2.962599	-0.150544	2.878753
H	1.369623	-0.853430	3.177322
C	0.656502	1.499512	2.097024
H	-0.133975	0.977157	2.643204
H	1.367863	1.915412	2.818897
H	0.190501	2.309523	1.537140
N	-1.218511	1.296198	-0.385528
C	-1.819149	2.286788	-0.537719
N	-2.491547	3.396608	-0.749123
Ru	-0.308619	-0.567782	-0.410097
C	5.928624	0.385180	0.724783
H	6.602995	-0.383440	0.340018
H	6.442345	1.347518	0.738370
H	5.610012	0.123851	1.738875
C	-3.965423	3.346003	-0.774312
H	-4.323160	4.118316	-1.459589
H	-4.291084	2.370243	-1.136550
H	-4.379082	3.525110	0.225191
C	-1.860118	4.694299	-0.447992
H	-2.256667	5.436378	-1.145002
H	-2.078513	5.005760	0.580229
H	-0.780838	4.617655	-0.586366

1-OMe-exchange-dmcyan_Ru (5a)

C	-2.247079	-1.619114	0.420765
C	-1.151291	-2.092762	1.174496
C	-0.013229	-2.679069	0.531129
C	0.052134	-2.799656	-0.870664
C	-1.081332	-2.345886	-1.636678
C	-2.189888	-1.779782	-1.012208
C	1.222119	-3.442123	-1.558202
C	-3.517984	-1.063283	1.039699
C	-4.563263	-2.200602	1.121365
P	1.133566	0.448757	1.272034
O	2.254985	1.549467	0.736986
C	-3.330134	-0.389845	2.404471
H	0.819412	-3.024576	1.132295
H	-1.159937	-2.012882	2.254610
H	-1.040427	-2.395506	-2.719117
H	-3.006373	-1.399112	-1.616963
H	2.115656	-3.423444	-0.931491
H	0.975925	-4.487957	-1.778812
H	1.443743	-2.941753	-2.503516
H	-3.902609	-0.310973	0.340675
H	-5.513338	-1.801682	1.490565
H	-4.744218	-2.657227	0.143228
H	-4.230827	-2.985378	1.809699
H	-2.589359	0.412577	2.357856
H	-4.280292	0.046799	2.726362
H	-3.024150	-1.104275	3.176416
Cl	1.238973	0.122794	-2.129625
O	4.186712	-1.318842	-1.378123
H	3.306430	-1.001093	-1.643798
H	4.574727	-0.563975	-0.889229
O	4.989065	0.980095	0.046528
H	4.114925	1.202780	0.415507
C	1.859878	2.787145	0.099678
H	1.240476	3.383846	0.774650
H	2.785364	3.324609	-0.109333
H	1.333869	2.578639	-0.833013
C	2.284267	-0.675742	2.135243
H	2.890229	-1.216462	1.404766
H	2.931086	-0.092282	2.796228
H	1.717478	-1.391372	2.735835
C	0.280202	1.349713	2.622412
H	-0.271769	0.636491	3.240065
H	1.022347	1.861611	3.242124
H	-0.425785	2.077011	2.216230
N	-1.245451	1.263162	-0.531766
C	-1.882011	2.218006	-0.753227
N	-2.598647	3.277011	-1.049503
Ru	-0.291070	-0.561309	-0.305097
C	5.980304	1.032399	1.078944
H	6.936728	0.776226	0.618708
H	6.052594	2.038462	1.508219
H	5.768599	0.312905	1.879050
C	-4.059833	3.137787	-1.197500
H	-4.394715	3.842634	-1.961681
H	-4.300782	2.124155	-1.518046
H	-4.567425	3.355717	-0.251489
C	-2.068742	4.623634	-0.767682
H	-2.451992	5.306326	-1.529130
H	-2.386425	4.966220	0.223273
H	-0.980260	4.609775	-0.819874

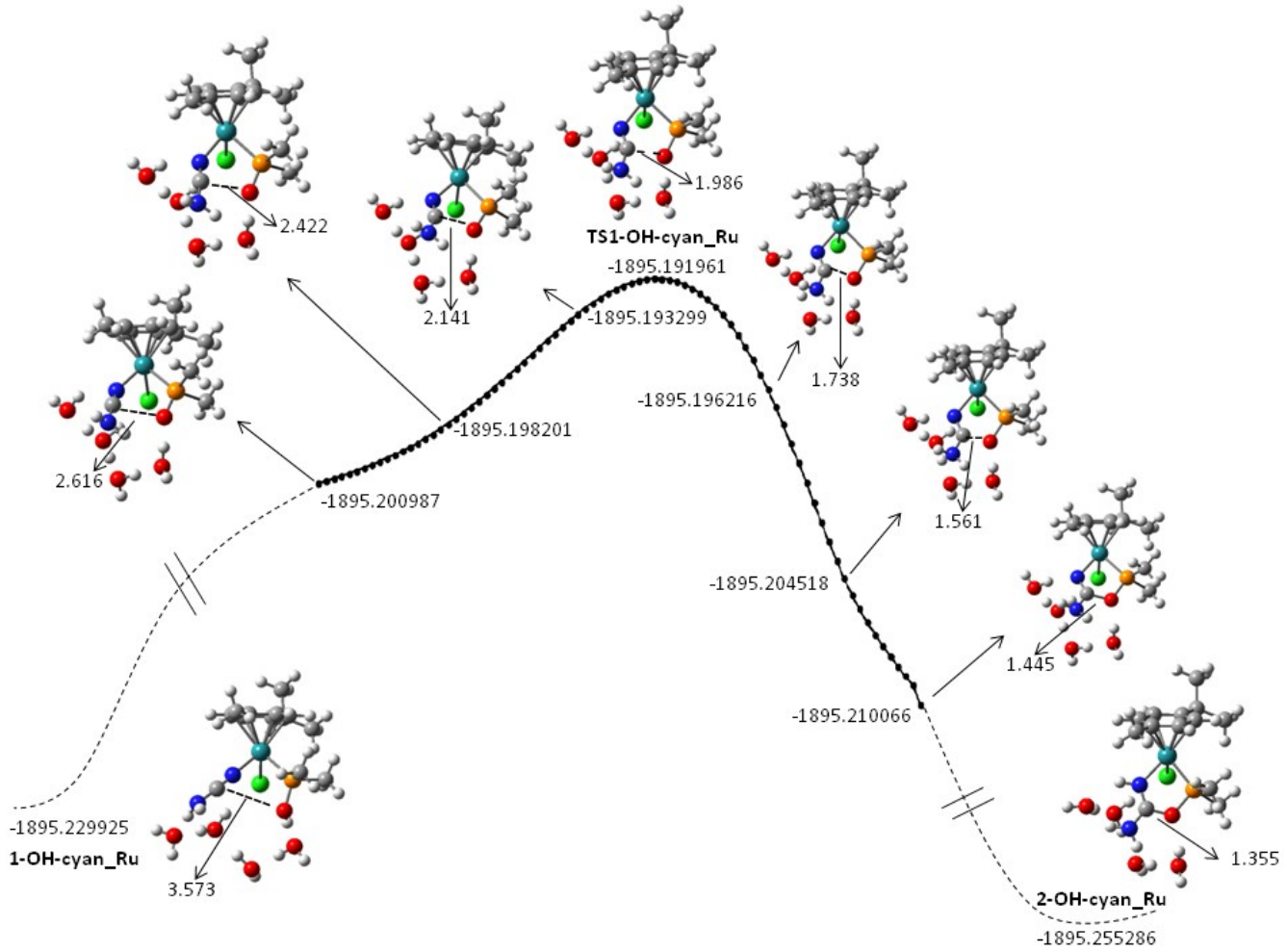


Figure S63. Schematic view of some of the most significant structures found along the IRC path obtained for the transition state **TS1-OH-cyan_Ru** connecting the energy minima **1-OH-cyan_Ru** and **2-OH-cyan_Ru** in water solution at the PCM-B3LYP/6-31+G(d,p) (LANL2DZ for Ru) level. Distances between the attacking hydroxyl oxygen atom and the attacked N≡C carbon atom and absolute energies without including thermal corrections are displayed in angstroms and hartree, respectively.

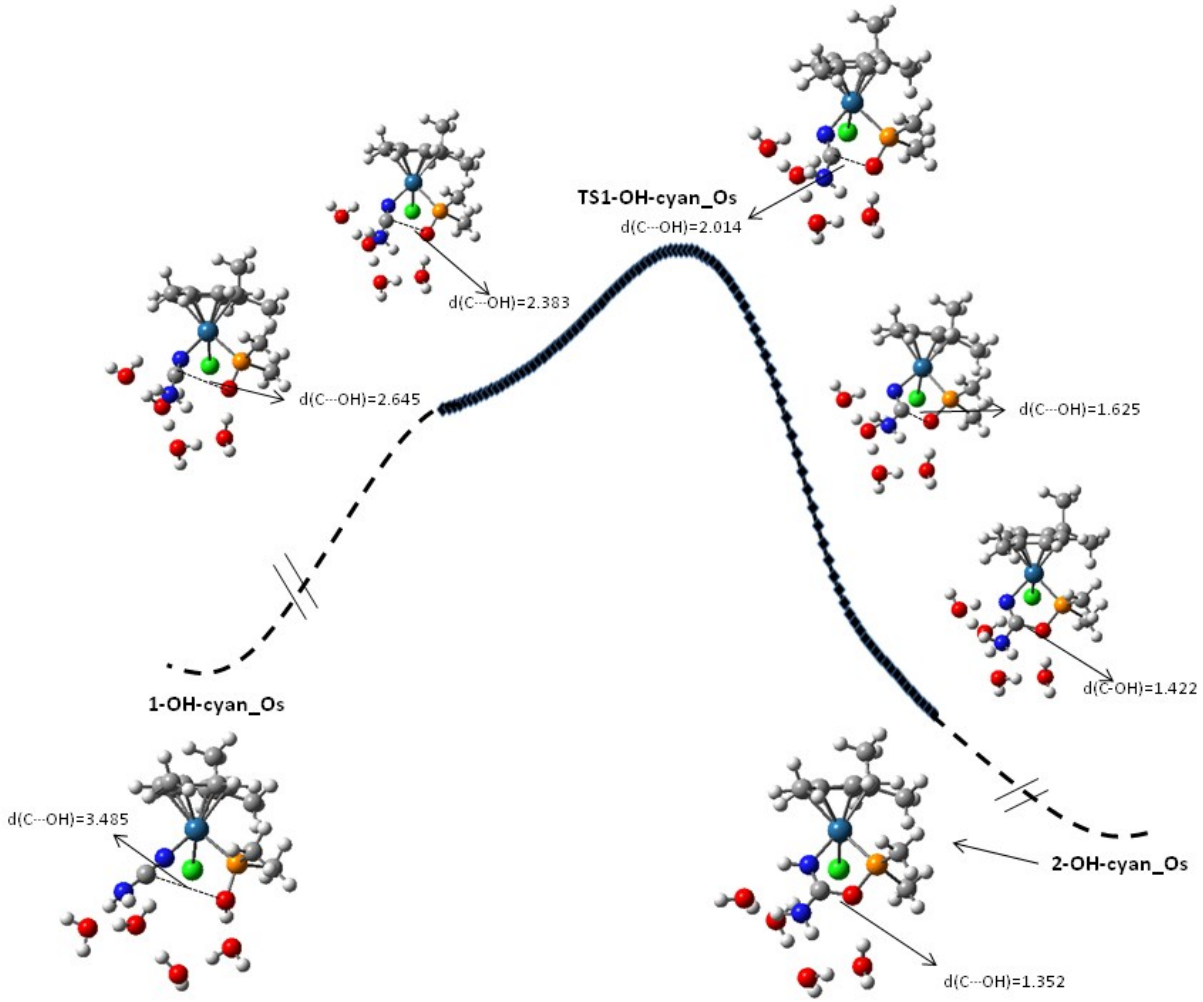


Figure S64. Schematic view of some of the most significant structures found along the IRC path obtained for the transition state **TS1-OH-cyan_Os** connecting the energy minima **1-OH-cyan_Os** and **2-OH-cyan_Os** in water solution at the PCM-B3LYP/6-31+G(d,p) (LANL2DZ for Os) level. Distances between the attacking hydroxyl oxygen atom and the attacked N≡C carbon atom are displayed in angstroms.

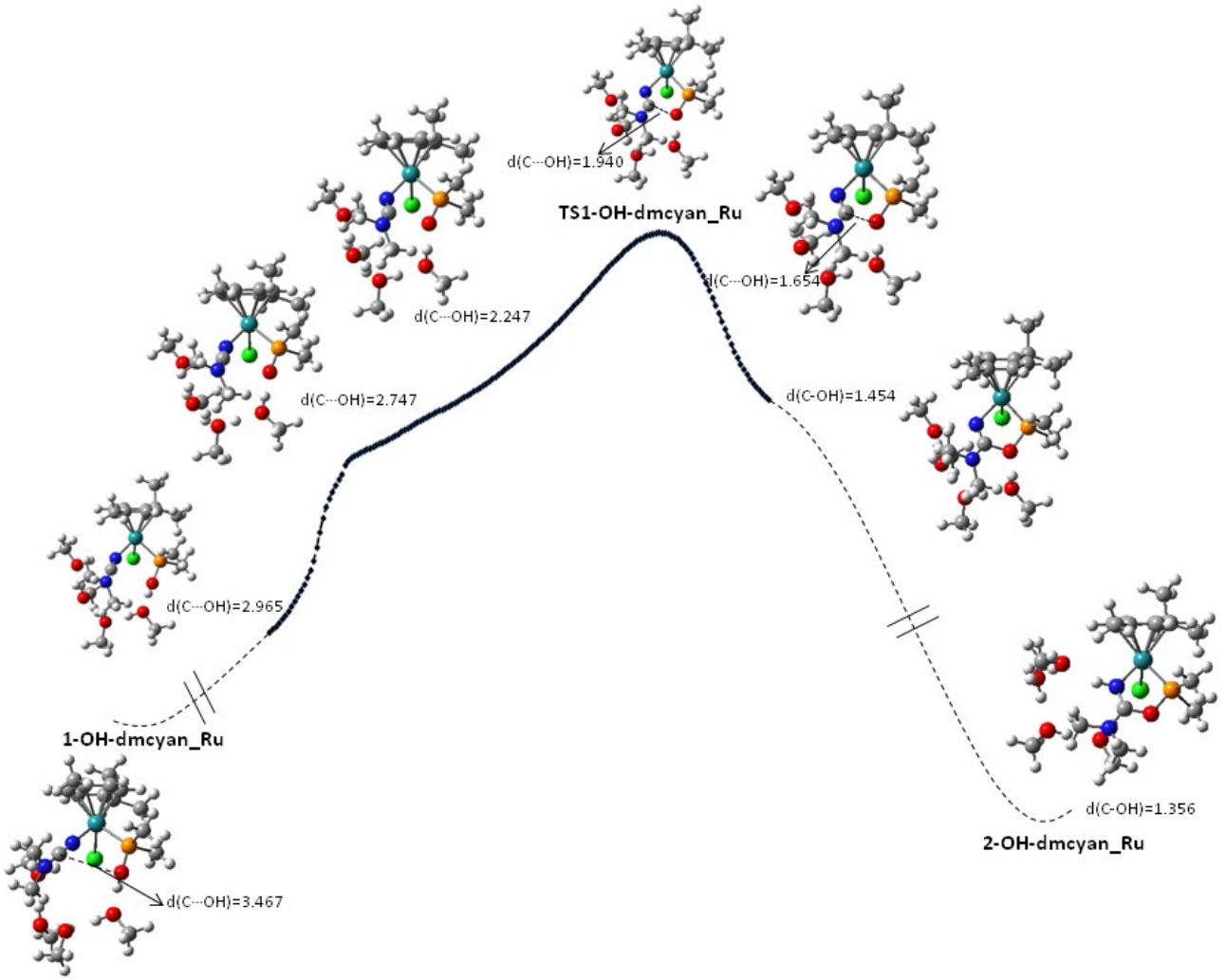


Figure S65. Schematic view of some of the most significant structures found along the IRC path obtained for the transition state **TS1-OH-dmcyan_Ru** connecting the energy minima **1-OH-dmcyan_Ru** and **2-OH-dmcyan_Ru** in methanol solution at the PCM-B3LYP/6-31+G(d,p) (LANL2DZ for Ru) level. Distances between the attacking hydroxyl oxygen atom and the attacked N≡C carbon atom are displayed in angstroms.