Supplementary Material

Evaluation of protonation sites in two MacMillan catalysts in solution by gas phase predissociation spectroscopy and electronic structure calculations

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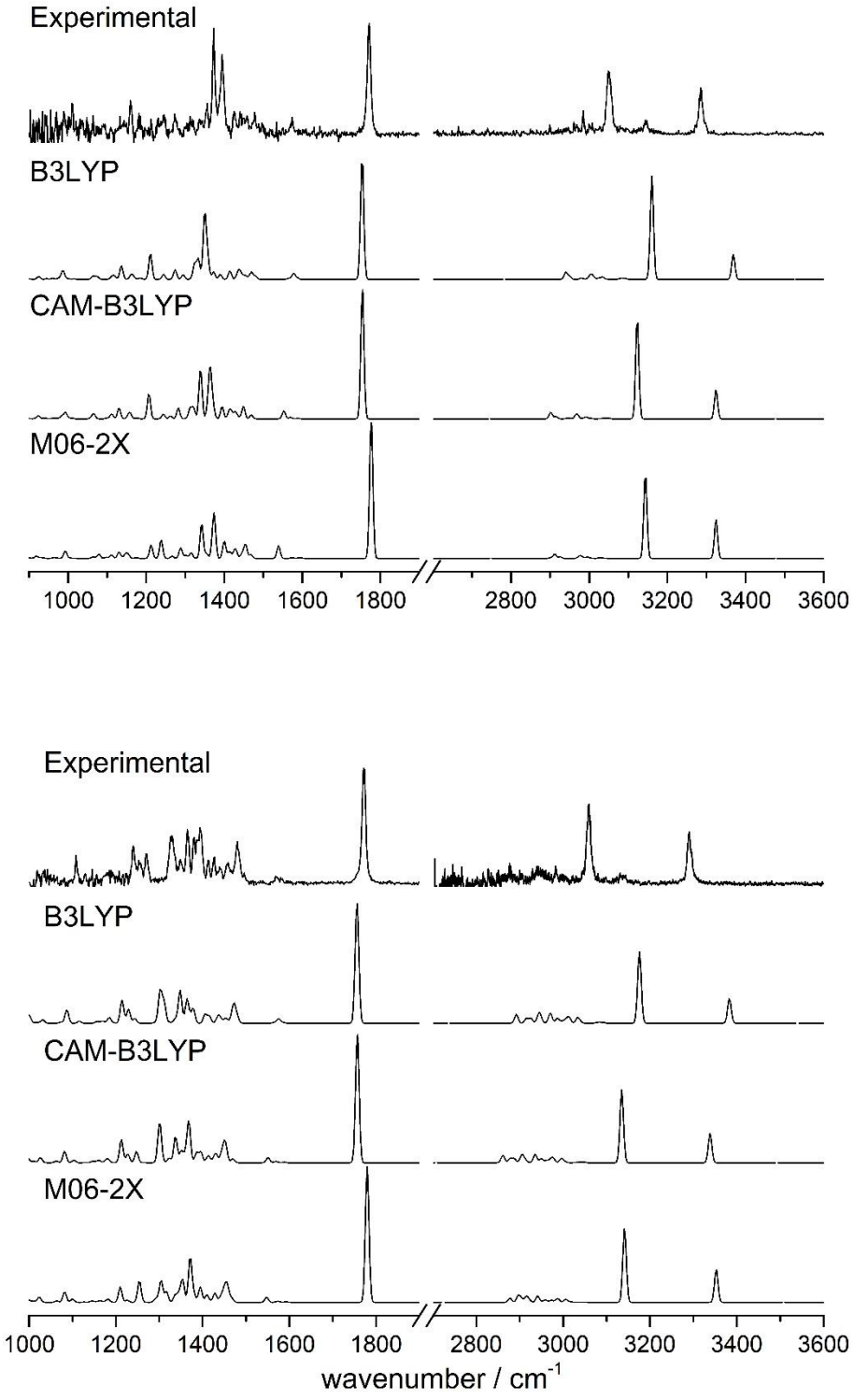

Figure S1. Comparison of the predissociation spectra of the tagged catalysts with calculated spectra with different functionals and same basis set, 6-311+G(3df,2p) for the protonated species at the amine group. Top: $[Cat1+H]^+$ Bottom: $[Cat2+H]^+$.

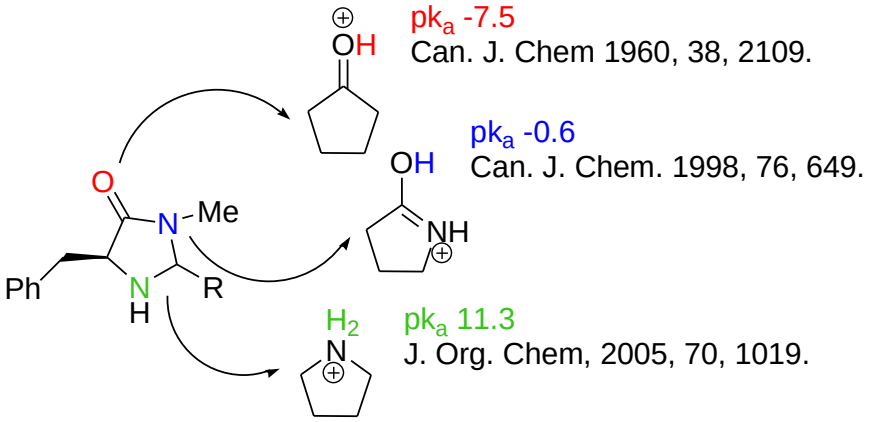

Figure S2. pK_a in H_2O for molecules representing the protonation sites of the imidazolidinones. The amide species protonates in the oxygen, given the stabilization by the resonance of the lone pair of the nitrogen atom. That makes the basicity of the amide much higher than the equivalent ketone (7 units of pka). Therefore the protonation on the nitrogen of the amide would be indeed the less favorable of all.

Table S1. Frequency values in cm^{-1} of some bands of the higher energy protomers calculated at B3LYP/6-311+g(3df,2p) level of theory

	$[Cat1+H]^+$		$[Cat2+H]^+$	
	Protonation site		Protonation site	
	N amide	O amide	N amide	O amide
OH stretch		3647		3646
Amine NH stretch	3385	3378	3398	3391
Amide NH strech	3342		3345	
Carbonyl stretch	1866	1648	1868	1675

Table S2. SMD parameters used for the 1:1 (v/v) mixture of Methanol Water as solvent, as defined in Gaussian09 Software

Symbol	Parameter	Value
ε	Eps	64,63261[a]
n*2/nd20^2*	EpsInf	1,79426[b]
α	HbondAcidity	0,703[a]
β	HbondBasicity	0,386[a]
γ	SurfaceTensionAtInterface	52,54957[c]
ϕ	CarbonAromaticity	0
ψ	ElectronegativeHalogenicity	0

[a]The values were considered as a weighted average of metanol and water values, considering the molar fraction of the mixture from Ref [1]

[b]Experimental values from Ref [2]

[c]Experimental value from Ref [3]

Equilibrium geometry for 1st Generation MacMillan catalyst, $[oCat1+H]^+$, with different protonation sites at B3LYP/6-311+(3df,2p) level of theory.

$[Cat1+H]^+$ protonated at the amine nitrogen

6	1.220383000	1.312218000	-0.158232000
7	1.840987000	0.371656000	0.612612000
6	1.898921000	-0.963171000	0.036002000
6	1.497993000	-2.059954000	1.013671000
1	1.418064000	-3.019178000	0.501558000
1	2.258612000	-2.168887000	1.784245000
1	0.549305000	-1.830161000	1.498552000
6	3.227769000	-1.257849000	-0.659903000
1	4.028891000	-1.260643000	0.076527000
1	3.217098000	-2.241560000	-1.130902000
1	3.467060000	-0.501465000	-1.407278000
6	2.566502000	0.728717000	1.825519000
1	3.635669000	0.545943000	1.715257000
1	2.408473000	1.790510000	1.992294000
1	2.190543000	0.173423000	2.683115000
8	1.125512000	2.492178000	0.061765000
6	-0.813904000	0.994659000	-1.717624000
1	-0.838859000	2.084670000	-1.733448000
1	-1.054575000	0.652966000	-2.725108000
6	-1.803917000	0.437037000	-0.721000000
6	-2.450544000	-0.777684000	-0.976169000
6	-2.069312000	1.100504000	0.480703000
6	-3.336599000	-1.322176000	-0.049356000
1	-2.305338000	-1.278137000	-1.927990000
6	-2.956446000	0.558073000	1.402082000
1	-1.595605000	2.051913000	0.684961000
6	-3.587187000	-0.655261000	1.142658000
1	-3.842736000	-2.252017000	-0.270492000
1	-3.165227000	1.090275000	2.320221000
1	-4.283462000	-1.068666000	1.859292000
7	0.799751000	-0.837817000	-1.040338000
6	0.642677000	0.620941000	-1.397113000
1	1.290396000	0.836465000	-2.246879000
1	-0.103585000	-1.153508000	-0.655441000
1	1.017995000	-1.422569000	-1.845943000

$[Cat1+H]^+$ protonated at amide nitrogen

6	1.120901000	1.404939000	0.177194000
7	1.760399000	0.258495000	1.028520000

6	2.176740000	-0.792737000	-0.086180000
6	2.178052000	-2.214007000	0.443469000
1	2.490868000	-2.873383000	-0.364441000
1	2.884834000	-2.335588000	1.262795000
1	1.192113000	-2.536011000	0.774458000
6	3.567499000	-0.360104000	-0.551040000
1	4.302446000	-0.473513000	0.246413000
1	3.866360000	-0.993613000	-1.383005000
1	3.593152000	0.672801000	-0.899476000
6	0.795282000	-0.176684000	2.088321000
1	1.268091000	-0.924321000	2.716744000
1	0.531844000	0.696824000	2.679091000
1	-0.097432000	-0.579133000	1.618683000
8	0.987940000	2.477090000	0.640755000
6	-0.629429000	1.078202000	-1.666602000
1	-0.772857000	2.158475000	-1.679143000
1	-0.680269000	0.737938000	-2.701071000
6	-1.695860000	0.406249000	-0.834829000
6	-2.131848000	-0.885678000	-1.143147000
6	-2.266424000	1.061663000	0.259944000
6	-3.096156000	-1.516696000	-0.363383000
1	-1.745425000	-1.390127000	-2.021612000
6	-3.233771000	0.433821000	1.036742000
1	-1.975182000	2.079257000	0.489877000
6	-3.645097000	-0.859438000	0.731499000
1	-3.431960000	-2.511216000	-0.624194000
1	-3.679828000	0.962066000	1.868699000
1	-4.405366000	-1.342707000	1.329657000
7	1.177699000	-0.593890000	-1.101064000
6	0.820046000	0.813974000	-1.190338000
1	1.487626000	1.337694000	-1.883700000
1	0.356489000	-1.167145000	-0.940966000
1	2.584685000	0.651717000	1.483066000

$[Cat1+H]^+$ protonated at amide oxygen

6	1.230938000	1.175923000	-0.216928000
7	1.885751000	0.403941000	0.579784000
6	1.914869000	-1.027501000	0.013629000
6	1.584966000	-2.041817000	1.096427000
1	1.496785000	-3.024854000	0.635772000
1	2.374154000	-2.101101000	1.843619000
1	0.643194000	-1.805436000	1.591724000
6	3.292688000	-1.262191000	-0.604015000

1	4.087000000	-1.198907000	0.138652000
1	3.312019000	-2.260699000	-1.035808000
1	3.498824000	-0.547739000	-1.400351000
6	2.624760000	0.831837000	1.764871000
1	3.682382000	0.611077000	1.635368000
1	2.494923000	1.899545000	1.909521000
1	2.250436000	0.298767000	2.635646000
8	1.167915000	2.467075000	-0.017018000
6	-0.802772000	0.753570000	-1.763791000
1	-0.876696000	1.828386000	-1.957659000
1	-0.996912000	0.271963000	-2.721953000
6	-1.831154000	0.320819000	-0.744986000
6	-2.490220000	-0.901643000	-0.894304000
6	-2.137603000	1.114181000	0.363028000
6	-3.420853000	-1.327632000	0.047721000
1	-2.293381000	-1.515769000	-1.764974000
6	-3.067890000	0.691110000	1.304805000
1	-1.673264000	2.085869000	0.485592000
6	-3.707748000	-0.534080000	1.151359000
1	-3.929296000	-2.272243000	-0.089334000
1	-3.304097000	1.324344000	2.149201000
1	-4.437723000	-0.859439000	1.879682000
7	0.873053000	-0.971840000	-1.004407000
6	0.660190000	0.417159000	-1.393888000
1	1.286906000	0.680935000	-2.256939000
1	0.006042000	-1.345764000	-0.631896000
1	0.622733000	2.911353000	-0.680916000

Equilibrium geometry for 2nd Generation MacMillan catalyst, $[Cat2+H]^+$, with different protonation sites at B3LYP/6-311+(3df,2p) level of theory.

$[Cat2+H]^+$ protonated at the amine nitrogen

6	-0.527932000	1.996531000	0.040547000
7	-1.528116000	1.156801000	-0.378008000
6	-1.823264000	0.077442000	0.545271000
6	-2.134177000	-1.336532000	-0.015088000
6	-2.443239000	1.593011000	-1.429867000
1	-3.460329000	1.674871000	-1.046536000
1	-2.104378000	2.571936000	-1.757573000
1	-2.428670000	0.914020000	-2.278606000
8	-0.169801000	3.018559000	-0.484124000

6	1.591482000	1.440531000	1.422258000
1	1.900691000	2.453258000	1.161191000
1	1.891279000	1.271840000	2.457444000
6	2.238786000	0.419358000	0.515016000
6	2.596829000	-0.837190000	1.015196000
6	2.469296000	0.696995000	-0.835482000
6	3.166787000	-1.798865000	0.184491000
1	2.477919000	-1.051462000	2.072083000
6	3.041116000	-0.262007000	-1.662154000
1	2.217856000	1.671197000	-1.234321000
6	3.386660000	-1.511740000	-1.156534000
1	3.456029000	-2.758534000	0.590836000
1	3.229354000	-0.028466000	-2.701281000
1	3.840559000	-2.251182000	-1.801903000
7	-0.539243000	0.063152000	1.375369000
6	0.058910000	1.444816000	1.339356000
1	-0.370271000	2.015061000	2.165098000
1	0.143317000	-0.578652000	0.946028000
1	-0.723826000	-0.269179000	2.319662000
1	-2.624453000	0.360269000	1.239111000
6	-1.125297000	-1.750879000	-1.096166000
1	-1.154066000	-1.087526000	-1.958600000
1	-0.093803000	-1.780225000	-0.735729000
1	-1.360618000	-2.756371000	-1.443230000
6	-2.087286000	-2.331676000	1.164539000
1	-2.739899000	-2.023651000	1.985119000
1	-2.436663000	-3.306289000	0.828798000
1	-1.079766000	-2.488021000	1.557101000
6	-3.566846000	-1.356042000	-0.581681000
1	-3.827336000	-2.377455000	-0.856259000
1	-4.296167000	-1.020942000	0.157789000
1	-3.677799000	-0.745171000	-1.472978000

$[Cat2+H]^+$ protonated at amide nitrogen

6	0.145881000	2.017172000	0.023619000
7	1.206554000	1.192206000	0.831480000
6	1.866079000	0.350328000	-0.344289000
6	2.778912000	-0.833041000	0.031430000
6	0.505591000	0.497149000	1.958489000
1	1.235431000	-0.003573000	2.583291000
1	-0.023743000	1.252264000	2.534468000
1	-0.205836000	-0.216116000	1.554582000

8	-0.311226000	2.998930000	0.480823000
6	-1.513487000	1.070160000	-1.691786000
1	-1.999822000	2.045479000	-1.703458000
1	-1.512397000	0.702175000	-2.717847000
6	-2.254370000	0.113372000	-0.787346000
6	-2.272646000	-1.256752000	-1.062842000
6	-2.934612000	0.578624000	0.341247000
6	-2.935764000	-2.143374000	-0.220189000
1	-1.797830000	-1.631225000	-1.962585000
6	-3.600199000	-0.306305000	1.182316000
1	-2.970202000	1.641024000	0.548929000
6	-3.596163000	-1.669745000	0.907430000
1	-2.952205000	-3.198848000	-0.455956000
1	-4.138040000	0.071484000	2.041478000
1	-4.123385000	-2.355901000	1.555952000
7	0.773183000	0.091213000	-1.214936000
6	-0.035234000	1.298570000	-1.305721000
1	0.402984000	1.974717000	-2.051713000
1	0.221753000	-0.715608000	-0.944514000
1	1.873550000	1.857034000	1.223325000
1	2.500096000	1.118894000	-0.796268000
6	2.025361000	-2.081253000	0.520614000
1	2.743150000	-2.886608000	0.673099000
1	1.508271000	-1.935886000	1.466654000
1	1.305085000	-2.443209000	-0.213981000
6	3.536377000	-1.195304000	-1.266199000
1	4.113734000	-0.350276000	-1.644049000
1	4.233806000	-2.006391000	-1.061047000
1	2.856468000	-1.521449000	-2.050898000
6	3.803762000	-0.369887000	1.081715000
1	4.538738000	-1.155943000	1.249195000
1	4.350380000	0.514213000	0.746453000
1	3.354737000	-0.149909000	2.051566000

$[Cat2+H]^+$ protonated at amide oxygen

6	-0.571730000	1.880529000	0.120990000
7	-1.562522000	1.191414000	-0.335684000
6	-1.832942000	0.006450000	0.613539000
6	-2.187604000	-1.348355000	-0.047534000
6	-2.443923000	1.648337000	-1.410973000
1	-3.472142000	1.629184000	-1.057727000

1	-2.174601000	2.661749000	-1.691296000
1	-2.348161000	0.996768000	-2.274822000
8	-0.215901000	3.010470000	-0.433386000
6	1.530019000	1.271292000	1.522138000
1	1.899908000	2.295234000	1.408107000
1	1.748466000	0.997756000	2.554149000
6	2.245323000	0.337904000	0.573435000
6	2.588192000	-0.951601000	0.985853000
6	2.574828000	0.733716000	-0.724573000
6	3.230767000	-1.828457000	0.117795000
1	2.374287000	-1.266505000	2.000312000
6	3.216903000	-0.140246000	-1.593449000
1	2.358672000	1.741071000	-1.061352000
6	3.542265000	-1.425831000	-1.174995000
1	3.499224000	-2.819392000	0.457903000
1	3.476954000	0.187664000	-2.590737000
1	4.050058000	-2.103106000	-1.847724000
7	-0.633386000	-0.025909000	1.420499000
6	-0.007320000	1.286748000	1.389466000
1	-0.403192000	1.915385000	2.201570000
1	0.017260000	-0.714966000	1.058747000
1	0.541068000	3.411745000	0.015478000
1	-2.685498000	0.341273000	1.213422000
6	-1.157549000	-1.755840000	-1.112891000
1	-1.121584000	-1.053069000	-1.946286000
1	-0.147420000	-1.850034000	-0.712741000
1	-1.427398000	-2.728557000	-1.522918000
6	-2.215209000	-2.397739000	1.085200000
1	-2.917193000	-2.117972000	1.871865000
1	-2.538489000	-3.354146000	0.675920000
1	-1.240434000	-2.545634000	1.546109000
6	-3.596512000	-1.303701000	-0.668341000
1	-3.892622000	-2.312223000	-0.954314000
1	-4.338663000	-0.938802000	0.043821000
1	-3.652980000	-0.694960000	-1.568065000

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