Modulating *p*-hydroxycinnamate behavior as a ditopic linker or photoacid in copper(II) complexes by auxiliary pyridine ligand

Electronic Supplementary Information

Joan Soldevila-Sanmartín,[a] Teresa Calvet,[b] Merce Font-Bardia[c], Concepció Domingo[d], José A. Ayllón,*[,a] and Josefina Pons,*[,a]

[a]*Departament de Química, Universitat Autònoma de Barcelona, 08193-Bellaterra, Barcelona, Spain*

[b]*Mineralogia, Petrologia i Geologia Aplicada, Universitat de Barcelona, Martí i Franquès s/n, 08028-Barcelona, Spain.*

[c]*Unitat de Difracció de Raig-X, Centres Científics i Tecnològics de la Universitat de Barcelona (CCiTUB), Universitat de Barcelona, Solé i Sabarís, 1-3, 08028-Barcelona, Spain.*

[d]*Instituto de Ciencia de los Materiales de Barcelona (CSIC), Campus UAB, 08193 Bellaterra, Spain*

Table S1. Crystallographic Data for compounds **1-3**

Formula	$C_{72}H_{86}N_4O_{15}Cu_2$ (**1**)	$C_{32}H_{28}N_2O_8Cu$ (**2**)	$C_{42}H_{40}N_2O_8Cu$ (**3**)
Formula Weight	1374.52	632.10	764.30
Temperature (K)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073
System, space group	Monoclinic, C2/c	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
a (Å) b (Å) c (Å)	52.0046(17) 5.9991(2) 21.5105(8)	8.4342(3) 8.6978(3) 18.9953(7)	11.7498(5) 10.8664(5) 15.2007(8)
α (º)	90	90	90
β (º)	90.359(2)	96.953(2)	105.000(2)
γ (º)	90	90	90
U ($Å^3$) / Z	6710.7(4) / 4	1383.23(9) / 2	1874.66(15) / 2
D_{calc} (g cm^{-3}) / μ (mm^{-1})	1.360 / 0.704	1.518 / 0.848	1.354 / 0.639
F(000)	2896	654	798
Crystal size (mm^3)	0.104x0.081x0.057	0.308x0.268x0.144	0.397x0.373x0.284
hkl ranges	-63≤h≤64, -7≤k≤7, -24≤l≤26	-12≤h≤12, -12≤k≤12, -27≤l≤27	-14≤h≤14, -13≤k≤13, -19≤l≤19
2θ Range (º)	2.350 to 25.994	2.539 to 30.601	2.536 to 26.424
Reflections collected/unique/ [R_{int}]	14428/4433 [R(int)=0.0717]	44501/4253 [R(int)=0.0494]	22324/3801 [R(int)=0.0296]
Completeness to θ (%)	65.0	99.9	99.2
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. trans.	0.7453 and 0.6123	0.7461 and 0.7069	0.7454 and 0.6782
Data/restrains/parameters	4429/4/439	4253/0/199	3801/0/246
Goodness-of-fit on F^2	0.995	1.044	1.092
Final R indices [I>2σ (I)]	R_1 = 0.0451 wR_2 = 0.0906	R_1 = 0.0316 wR_2 = 0.0715	R_1 = 0.0330 wR_2 = 0.0856
R indices (all data)	R_1 = 0.0868 wR_2 =0.1171	R_1 = 0.0435 wR_2 =0.0760	R_1 = 0.0387 wR_2 =0.0925
Largest diff. peak and hole (e $Å^{-3}$)	+0.699, −0.477	+0.524, −0.285	+0.360, −0.417

Table S2. Crystallographic Data for compound **4** and **5**

Formula	$C_{121.50}H_{106}N_6O_{21.50}Cu_3$ (**4**)	$C_{71}H_{56}N_4O_9Cu_2$ (**5**)
Formula Weight	2184.74	1236.27
Temperature (K)	293(2)	100(2)
Wavelength (Å)	0.71073	0.71073
System, space group	Triclinic, P-1	Monoclinic, C2/c
a (Å) b (Å) c (Å)	12.9562(6) 15.7183(7) 16.1429(7)	13.6289(6) 25.4524(13) 34.1595(17)
α (º)	78.243(2)	90
β (º)	71.856(2)	92.4530(10)
γ (º)	66.888(2)	90
U ($Å^3$) / Z	2860.8(2) / 1	11838.7(10) / 8
D_{calc} (g cm^{-3}) / μ (mm^{-1})	1.268 / 0.623	1.387 / 0.783
F(000)	1136	5120
Crystal size (mm^3)	0.772x0.088x0.039	0.145x0.071x0.060
hkl ranges	-16≤h≤16, -19≤k≤19, -20≤l≤20	-17≤h≤14, -31≤k≤31, -42≤l≤42
2θ Range (º)	1.890 to 26.405	2.111 to 26.448
Reflections collected/unique/ [R_{int}]	66611/11680 [R(int)=0.0912]	156209/12168 [R(int)=0.0817]
Completeness to θ (%)	99.8	99.9
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. trans.	0.7454 and 0.6937	0.7454 and 0.7068
Data/restrains/parameters	11678/24/698	12168/0/777
Goodness-of-fit on F^2	1.017	1.024
Final R indices [I>2σ (I)]	R_1 = 0.0832 wR_2 = 0.22013	R_1 = 0.0404 wR_2 = 0.0769
R indices (all data)	R_1 = 0.1277 wR_2 =0.2534	R_1 = 0.0709 wR_2 =0.08065
Largest diff. peak and hole (e $Å^{-3}$)	+1.755, −1.985	+0.727, −0.397

PXRD patterns and Phase Purity Calculations

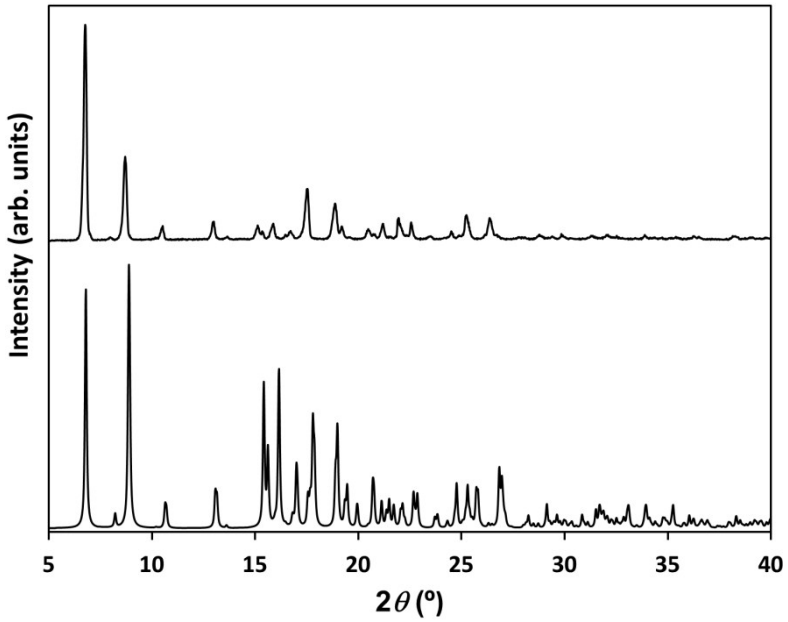

Figure S1. X-ray diffractogram of $[Cu(\mu\text{-pOHcinn})_2(4\text{-}^t\text{Bupy})_2(H_2O)][Cu(\mu\text{-pOHcinn})_2(4\text{-}^t\text{Bupy})_2(H_2O)_2]$ (**1,** up) measured at room temperature. Calculated pattern from resolved crystal structure is also included (down) as a reference, from monocrystal XRD measured at 100 K.

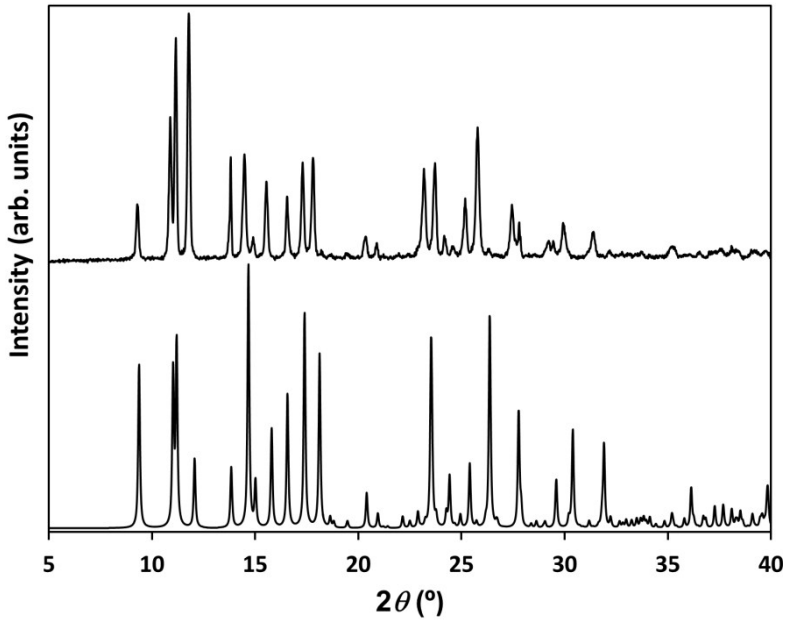

Figure S2. X-ray diffractogram of $[Cu(\mu\text{-pOHcinn})_2(4\text{-Acpy})_2]_n$ (**2,** up) measured at room temperature. Calculated pattern from resolved crystal structure is also included (down) as a reference, from monocrystal XRD measured at 100 K.

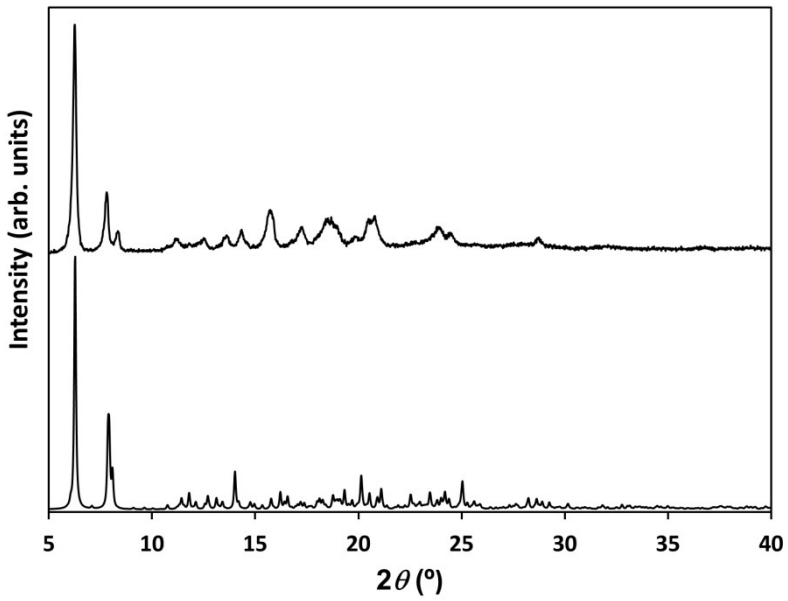

Figure S3. X-ray diffractogram of {[Cu(pOHcinn)$_2$(4-Phpy)$_2$]$_2$·[Cu(pOHcinn)$_2$(4-Phpy)$_2$]·1.5MeOH·H_2O (**4,** up) measured at room temperature. Calculated pattern from resolved crystal structure is also included (down) as a reference, from monocrystal XRD measured at 100 K.

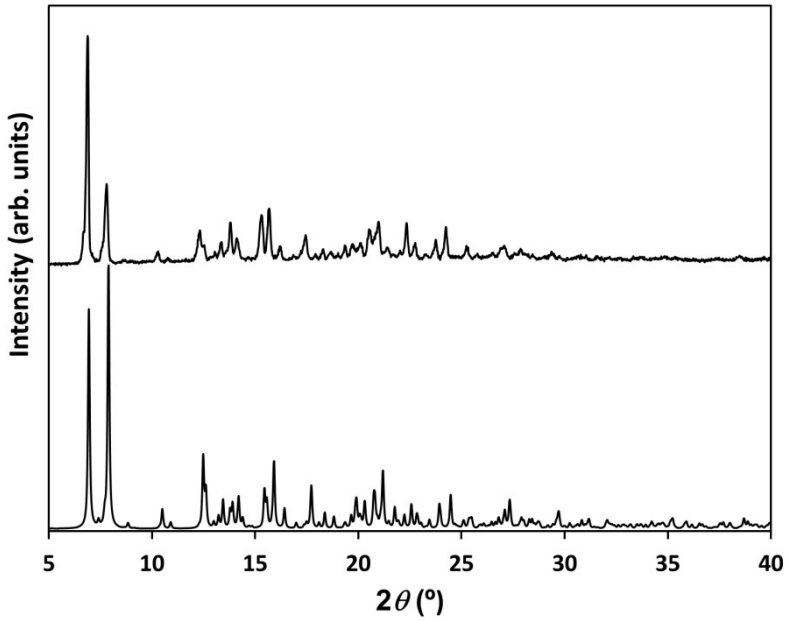

Figure S4. X-ray diffractogram of $[Cu_2(pOHcinn)_2(trans\text{-}4\text{-}Phpy)_4(\mu\text{-}pOcinn)_2Cu_2(pOHcinn)_2(cis\text{-}4\text{-}Phpy)_4]_n$ (**5,** up) measured at room temperature. Calculated pattern from resolved crystal structure is also included (down) as a reference, from monocrystal XRD measured at 100 K.

FTIR-ATR spectra

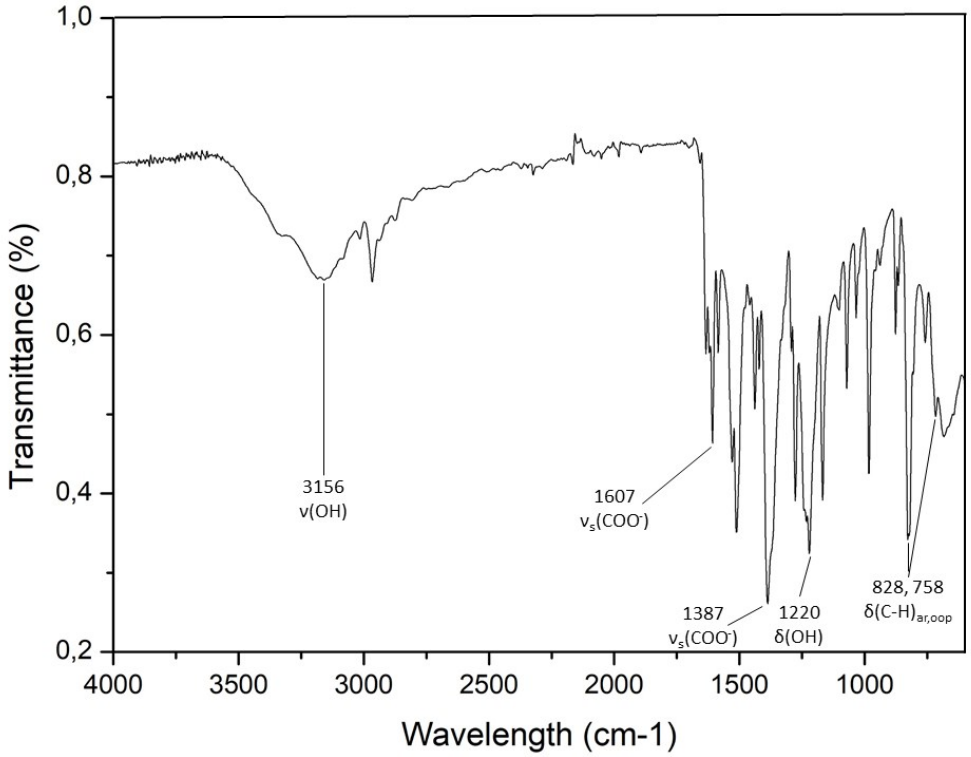

Figure S5. ATR-FTIR spectra of compound **1**.

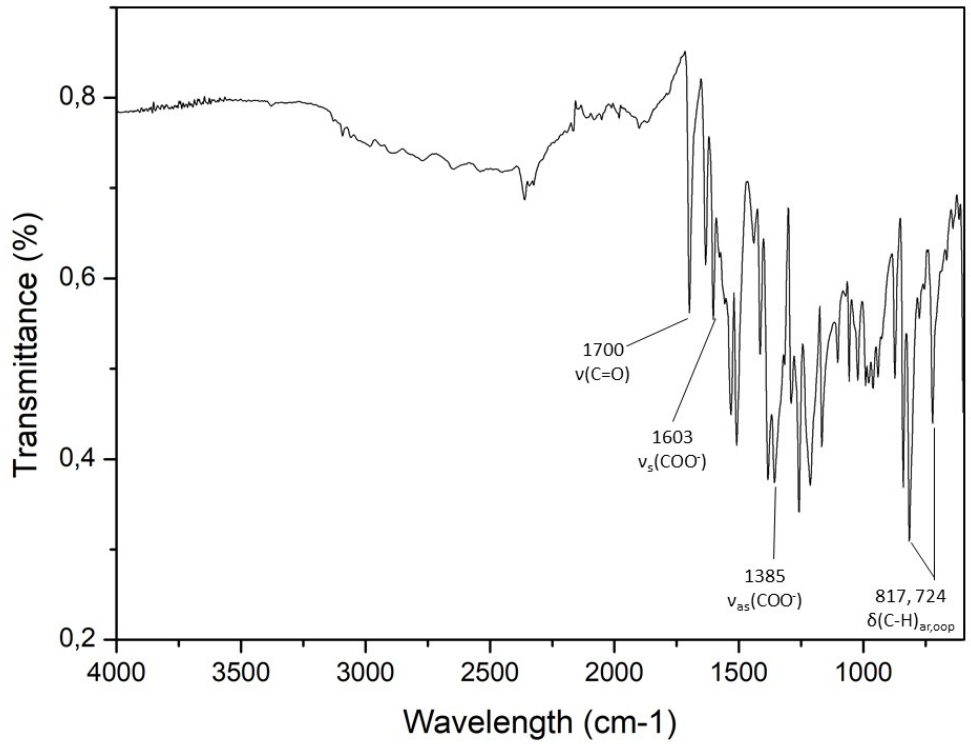

Figure S6. ATR-FTIR spectra of compound **2**.

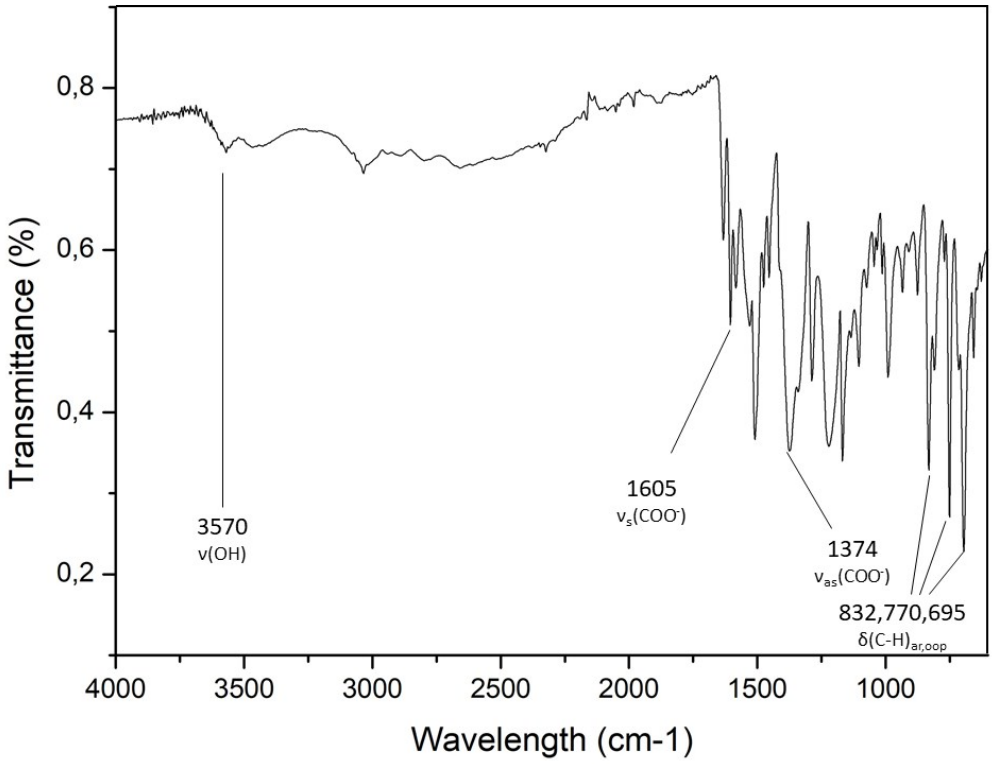

Figure S7. ATR-FTIR spectra of compound **3**.

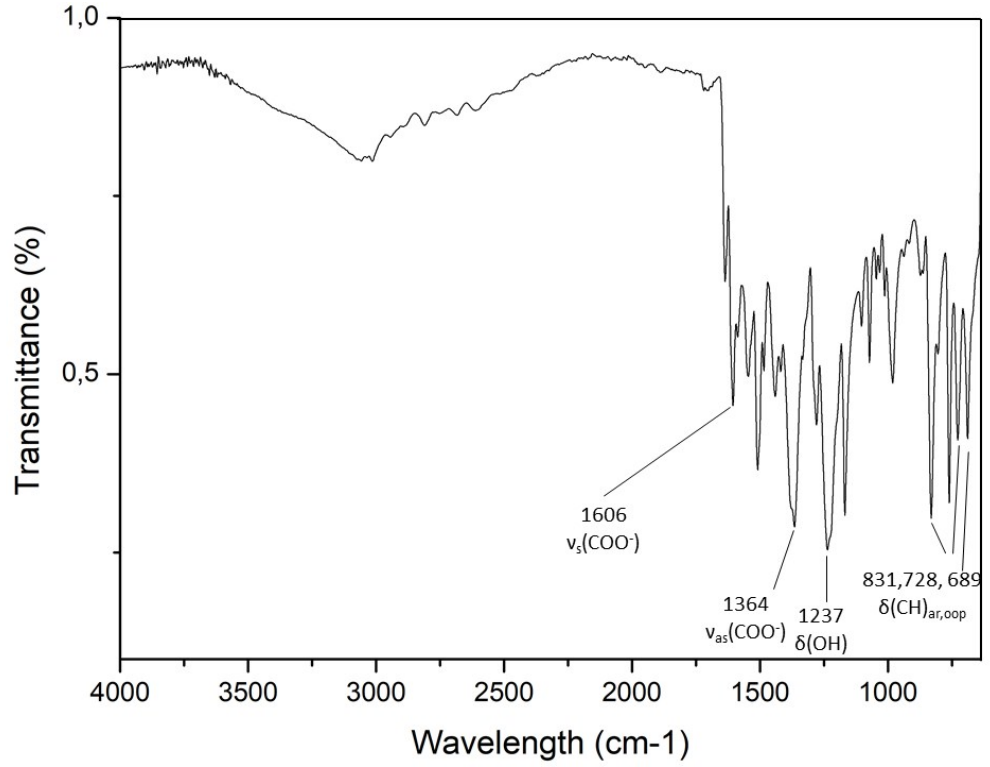

Figure S8. ATR-FTIR spectra of compound **4**.

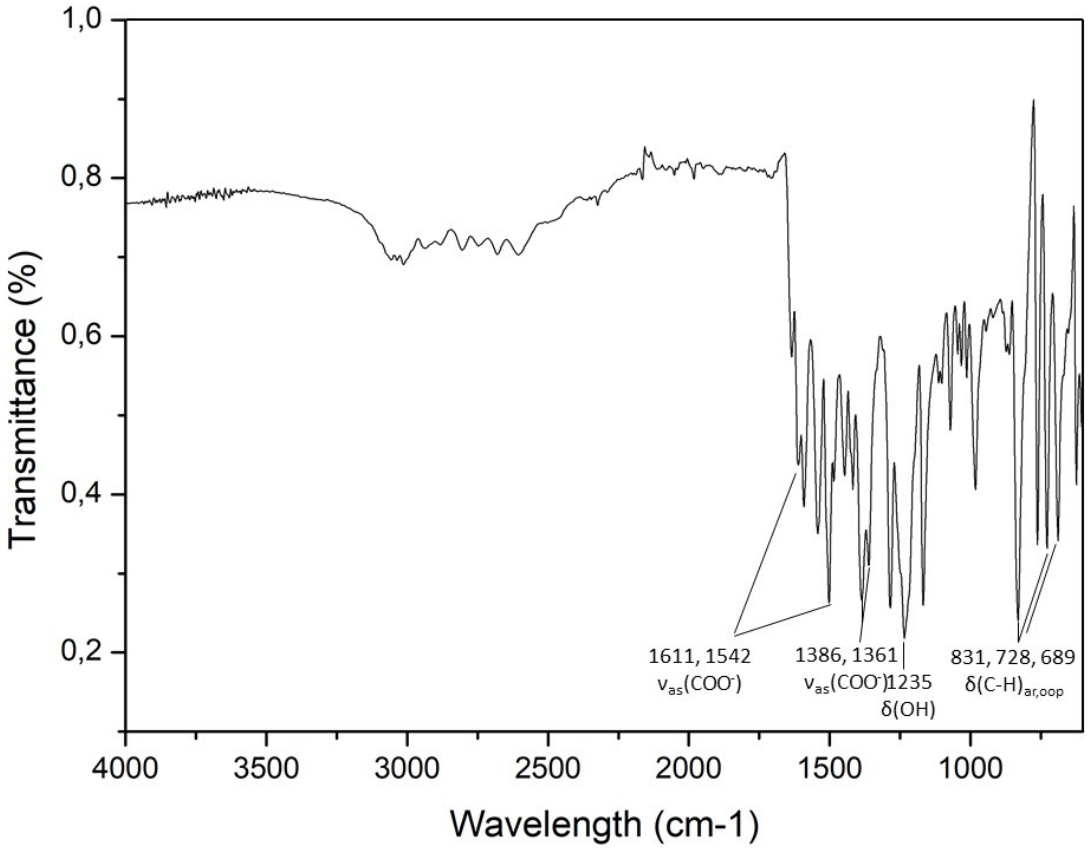

Figure S9. ATR-FTIR spectra of compound **5**.

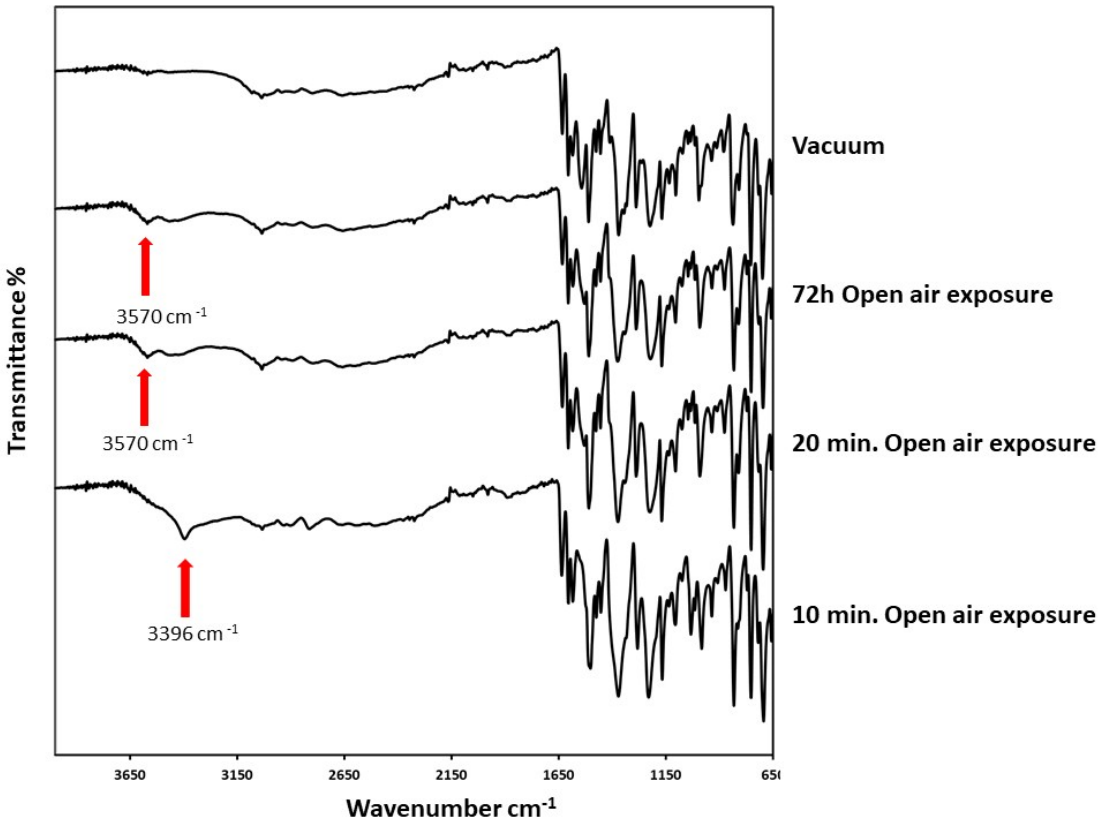

Figure S10. Temporal FTIR-ATR spectra of compound **3**. Note that the band at 3396 cm^{-1} corresponding to ν_{st}(OH) of MeOH decreases over time. Conversely, a band at 3570 cm^{-1} corresponding to ν_{st}(OH) of H_2O appears. Lastly, note that after exposure to vacuum, the 3500 cm^{-1}-3200 cm^{-1} region shows no bands related to ν_{st}(OH).