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Square-planar and octahedral nickel complexes of an acylhydrazone ligand and the serendipitous isolation of a potential octahedral nickel acylhydrazone precursor

Supplementary Information

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Content:

Figure S1. ^{1}H NMR (400 MHz, dmso-d_6) of HL

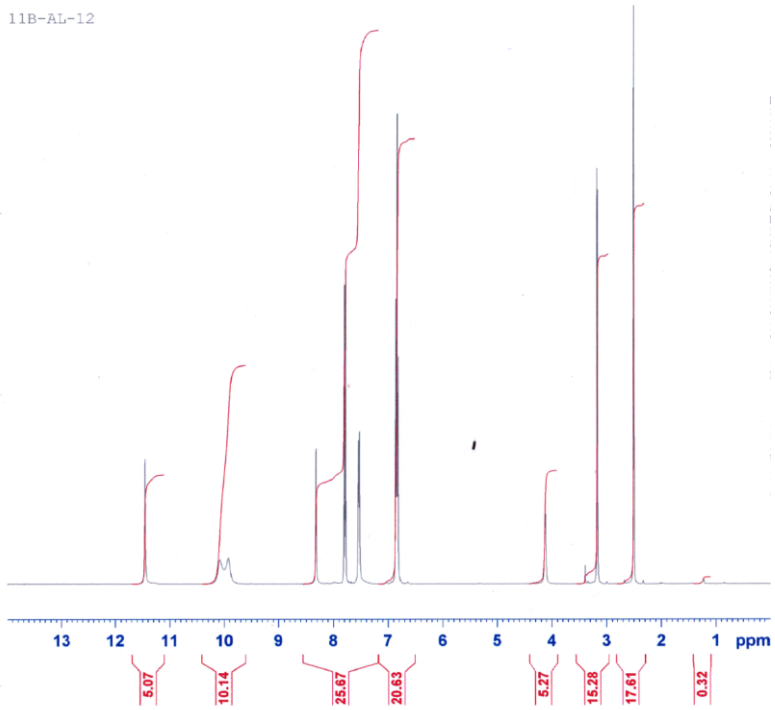


Figure S2. Ultraviolet-visible spectrum of HL in ethanol

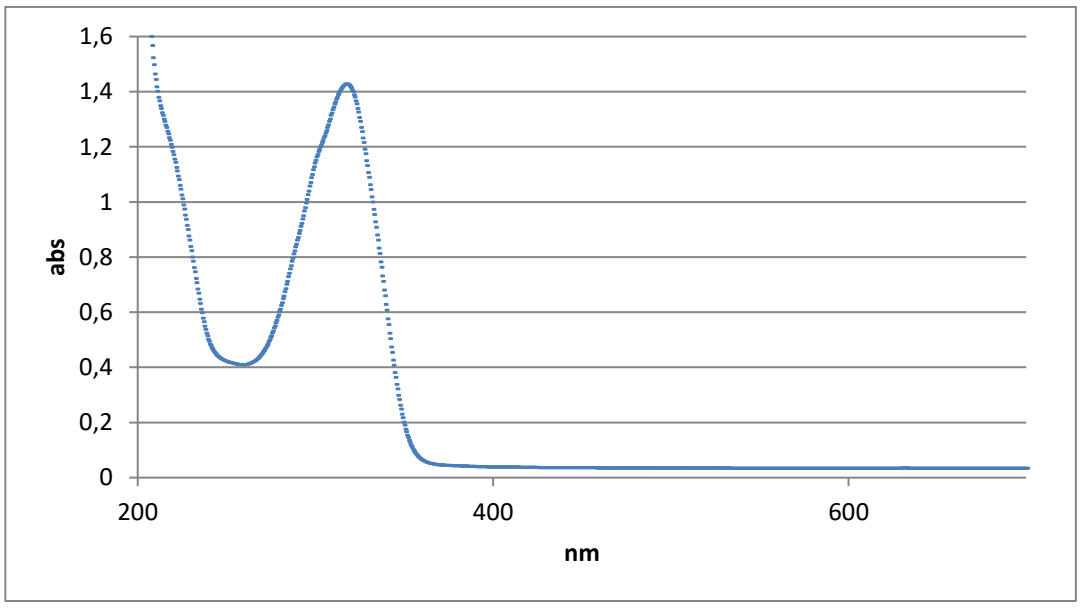


Figure S3. Ultraviolet-visible spectrum of HL + NaOH (1:0.5) in ethanol

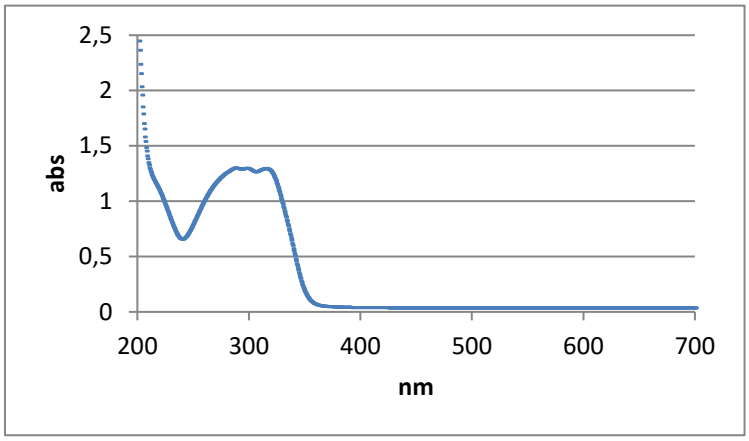


Figure S4. Ultraviolet-visible spectrum of HL + NaOH (1:1) in ethanol

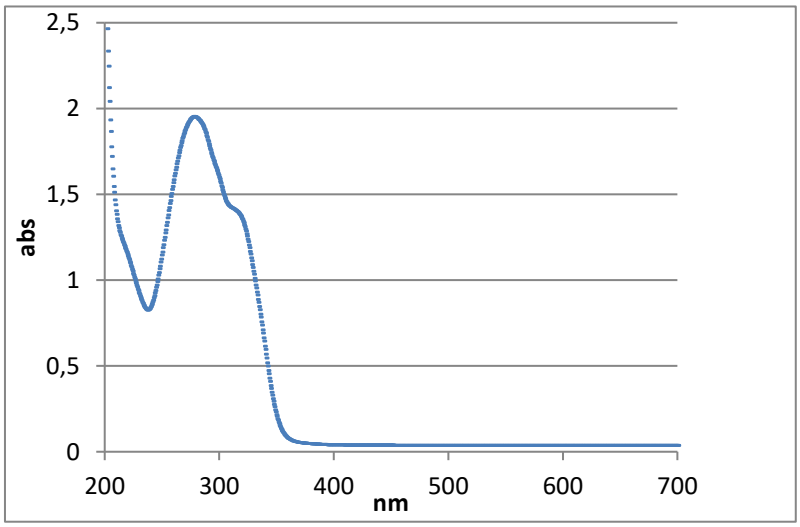


Figure S5. Ultraviolet-visible spectrum of HL + NaOH (1:2) in ethanol

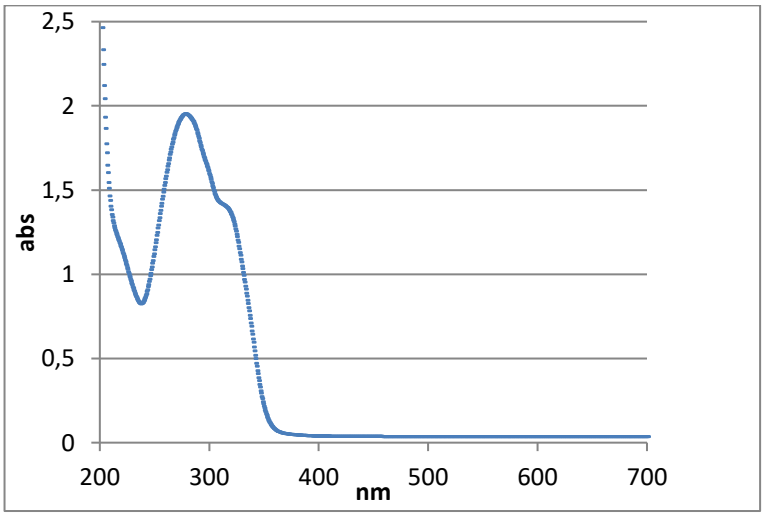


Figure S6. UV–vis diffuse reflectance spectrum of HL with KBr

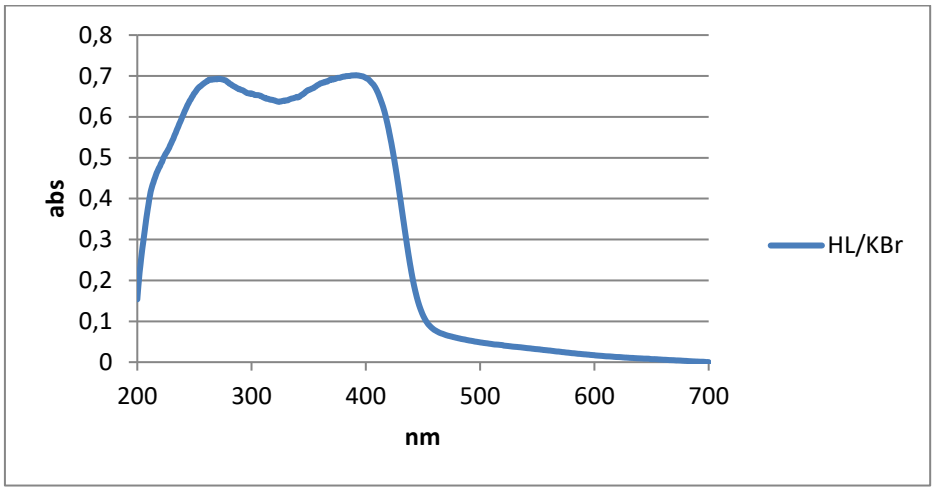


Figure S7. Ultraviolet-visible spectrum of **2** in ethanol.

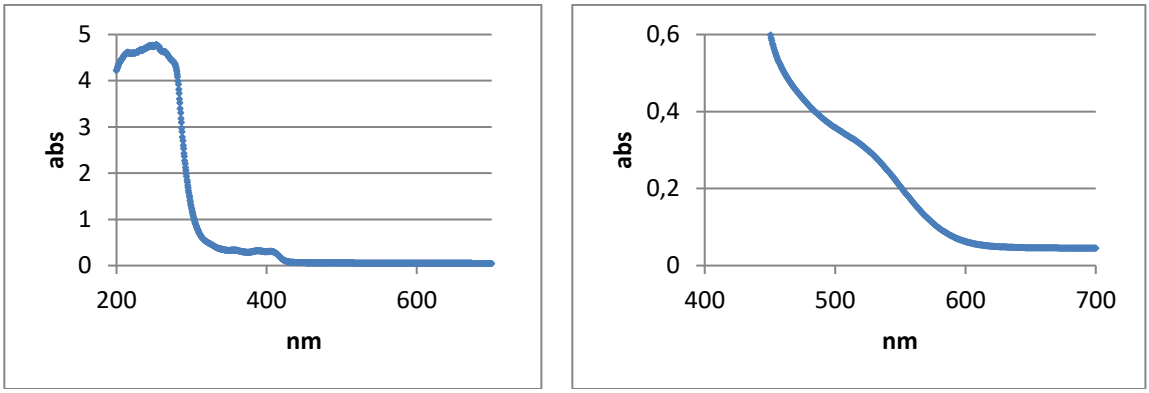


Figure S8. UV–vis diffuse reflectance spectrum of **2** with KBr.

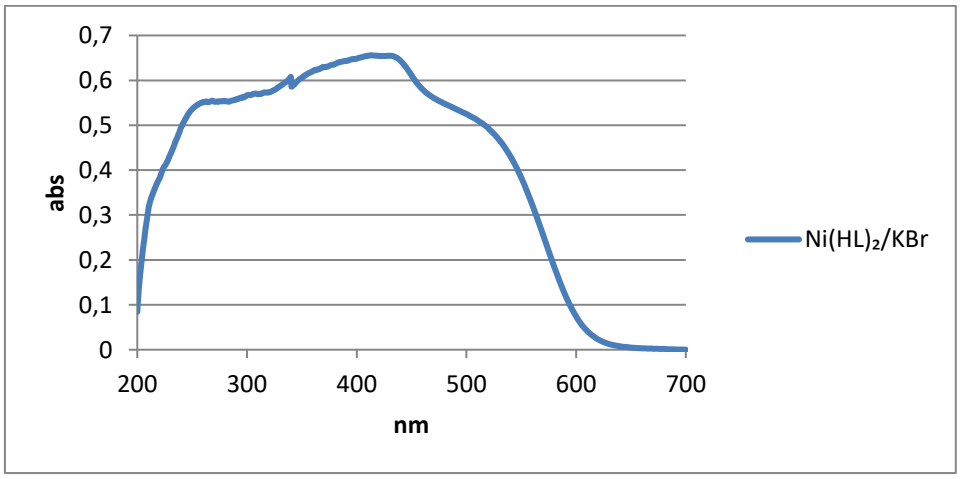
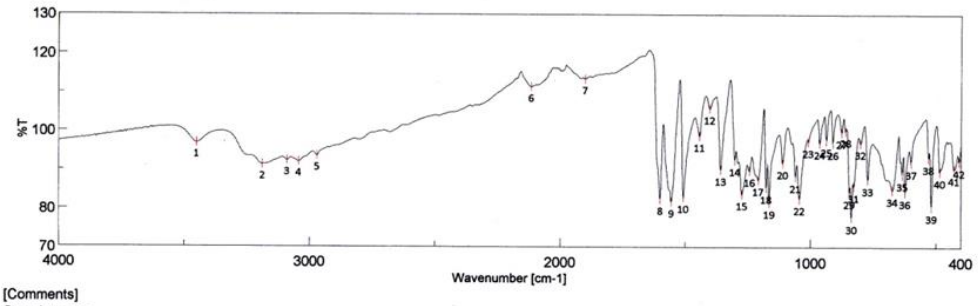


Figure S9. Infrared spectra (IR) of **HL (A), 2 (B), 2b (C)** and **3 (D)** in the range 4000-400 cm^{-1}

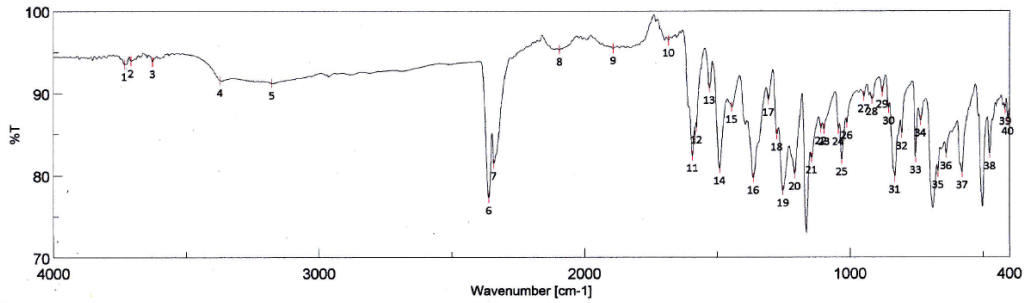


[Comments]
Sample name
Comment
User
Division
Company U.Vigo

[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3450.99	96.802	2	3188.72	91.2409	3	3090.37	92.2673
4	3044.09	92.0052	5	2970.8	93.5182	6	2116.49	111.334
7	1900.5	113.359	8	1601.59	82.3904	9	1556.27	81.6856
10	1508.06	82.8401	11	1443.46	98.6178	12	1402.96	105.733
13	1358.6	89.8998	14	1301.72	92.39	15	1273.75	83.6751
16	1243.86	89.6629	17	1209.15	87.3485	18	1177.33	85.3164
19	1165.76	81.4631	20	1111.76	91.6395	21	1060.66	88.142
22	1045.23	82.4179	23	1009.55	97.2085	24	964.233	96.8052
25	937.235	97.514	26	911.201	96.7924	27	876.488	99.5854

(A) IR Spectra of **HL**

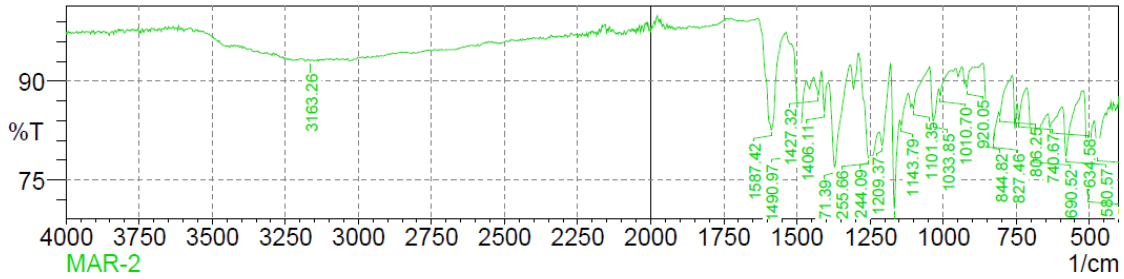


[Comments]
Sample name
Comment
User
Division
Company U.Vigo

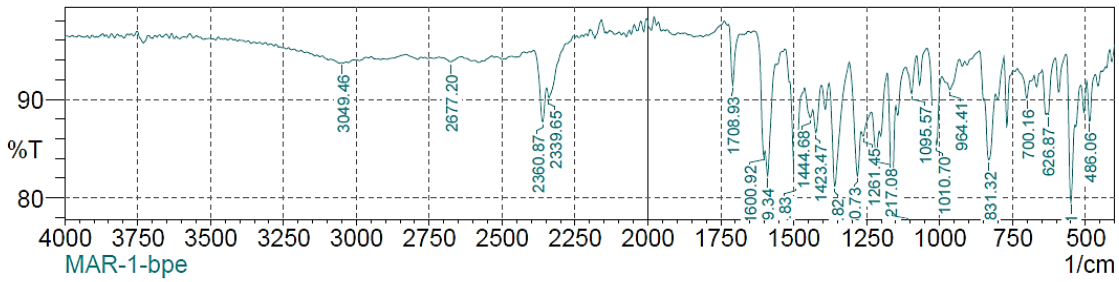
[Result of Peak Picking]

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1	3733.51	93.529	2	3709.41	93.9122	3	3627.45	93.8345
4	3372.89	91.5484	5	3179.08	91.1906	6	2360.44	77.2229
7	2341.16	81.3993	8	2094.32	95.3045	9	1892.79	95.4503
10	1683.55	96.4156	11	1592.91	82.3874	12	1578.45	85.7792
13	1529.27	90.6319	14	1490.7	80.8078	15	1445.39	88.3029
16	1364.39	79.6777	17	1307.5	89.1335	18	1275.68	84.9567
19	1252.54	78.1101	20	1209.15	80.1542	21	1145.51	82.1267
22	1109.83	85.6848	23	1098.26	85.5883	24	1044.26	85.5701
25	1031.73	81.8869	26	1012.45	86.3591	27	948.806	89.5898

(B) IR Spectra of **2**



(C) IR Spectra of **2b**



(D) IR Spectra of **3**

Table S1. Crystal and structure refinement data.

compound	**1a**	**2a**	**2b**	**3**
Empirical formula	C18 H23 N2 Ni0.5 O7	C28 H26 N4 Ni O8	C34 H40 N4 Ni O9	C26H21.06N4Ni0.50O3
Formula weight	865.43	605.24	707.41	466.88
Crystal system	Triclinic	Monoclinic	Monoclinic	Trigonal
Space group	P-1	C 2/c	P 2_1/n	R -3
CCDC ref.	2227433	2227434	2227435	2227436
a (Å)	7.8959(7)	20.6680(18)	10.8040(10)	34.338(2)
b (Å)	9.1120(7)	5.9629(5)	18.8611(14)	34.338(2)
c (Å)	13.1382(11)	23.892(2)	16.7162(14)	12.6009(11)
α (º)	93.469(5)	90	90	90
β (º)	94.076(4)	103.289(3)	99.623(3)	90
γ (º)	101.046(4)	90	90	120
V (Å^3)	922.74(13)	2865.7(4)	3358.4(5)	12867(2)
Z	2	4	4	18
λ(Å)	0.71073	0.71073	0.71073	1.54184
T (K)	173(2)	100(2)	100(2)	173(2)
ρ_{calcd} (g cm^{-3})	1.471	1.403	1.399	1.085
μ (mm^{-1})	0.601	0.732	0.638	0.886
F(000)	430	1256	1488	4375
Indep. ref.(R_{int})	3819 (0.0750)	3583 (0.0612)	8361 (0.0424)	5673(0.0502)
final *R* indices [*I*> *2σ(I)*]	R_1= 0.0571 wR_2= 0.1387	R_1= 0.0556 wR_2= 0.1314	R_1= 0.0524 wR_2= 0.1117	R_1= 0.00670 wR_2= 0.1924

Table S2. Main bond distances and angles (Å,°) in **2a** and **2b**

Compound	**2a**	**2b**
Ni(1)-O(1)	1.847(2)	1.8384(16)/1.8400(16)
Ni(1)-N(2)	1.875(2)	1.8628(19)/1.8734(18)
O(1)-C(1)	1.294(3)	1.296(3)/1.297(3)
N(2)-C(8)	1.281(4)	1.297(3)/1.298(3)
N(2)-N(1)	1.409(3)	1.407(3)/1.409(2)
N(1)-C(1)	1.321(4)	1.324(3)/1.322(3)
Angles		
O(1)-Ni(1)-N(2)	83.93(10)	83.97(7)/83.80(7)
O(1)-C(1)-N(1)	124.1(3)	123.2(2)/123.3(2)
O(1)-C(1)-C(2)	116.4(3)	118.16(19)/117.98(19)
C(1)-N(1)-N(2)	107.6(2)	107.66(17)/107.89(17)

Table S3. Main hydrogen bonds (Å) and angles (°) in **2a** and **2b**

D–H···A	D–H	H···A	D···A	D–H···A
Compound 2a				
O2-H2A…O1W	0.84	2.02	2.841(7)	167
O3-H3A...O3 #1	0.84	1.87	2.692(4)	164
O3-H3B...O1W #2	0.77(8)	1.94(8)	2.702(4)	172(5)
intramolecular				
C3-H3…O1	0.95	2.45	2.772(5)	100
C8-H8…O1#3	0.95	2.32	2.916(4)	120
C14-H14…N1	0.95	2.40	2.986(4)	120
#1= 1-x,4-y,1-z; #2=1/2+x,7/2-y,1/2+z #3=1/2-x,3/2-y,1-z				
Compound 2b				
O1E-H1E…N1B #1	0.81	2.04	2.841(3)	167(3)
O2A-H2A…O1E #2	0.85	1.87	2.706(3)	172(3)
O2B-H2B…O3B #3	0.80	1.97	2.751(3)	166(3)
O3A-H3A2…O2A #4	0.74	2.10	2.848(3)	177(3)
O3B-H3B2…O3E	0.79	1.84	2.624(2)	171(4)
O2E-H2E4…N1A #5	0.80	2.11	2.896(3)	169(4)
O3E-H3E4…O2E #6	0.81	1.94	2.742(3)	170(4)
intramolecular				
C8A-H8A… O1B	0.95	2.43	2.982(3)	117
C8B-H8B… O1A	0.95	2.39	2.938(3)	117
C14A-H14A… N1A	0.95	2.28	2.901(3)	122
C14B-H14B… N1B	0.95	2.34	2.906(3)	118
#1 = -1/2+x,1/2-y,-1/2+z ; #2 = 1+x,y,z; #3 = 1/2-x,-1/2+y,3/2-z; #4 = 5/2-x,-1/2+y,1/2-z #5 = 3/2-x,1/2+y,1/2-z #6 = 1-x,1-y,1-z				

Table S4. Main bond distances and angles (Å,°) in **1a**

Compound	**1**[a]		
Ni(1)-O(1)	2.012(2)	O(1)-Ni(1)-O(1W)	90.67(10)
Ni(1)-O(1W)	2.049(3)	O(1)-Ni(1)-N(2)	77.42(10)
Ni(1)-N(2)	2.171(3)	O(1W)-Ni(1)-N(2)	92.00(11)
O(1)-C(1)	1.256(4)	O(1)-C(1)-N(1)	120.4(3)
N(2)-C(8)	1.286(5)	O(1)-C(1)-C(2)	119.6(3)
N(2)-N(1)	1.402(4)	C(1)-N(1)-N(2)	117.4(3)
N(1)-C(1)	1.333(5)	O(1)-Ni(1)-O(1W)	90.67(10)
		O(1)-Ni(1)-N(2)	77.42(10)

Table S5. Main hydrogen bonds (Å) and angles (°) **1a**.

D–H···A	D–H	H···A	D···A	D–H···A
Compound 1a				
N1-H1...O1A	0.87	1.98	2.839(4)	170
O1E-H1E...O2A1	0.80(6)	1.81(6)	2.550(6)	152
O1E-H1E...O2A2	0.80(6)	2.028(6)	2.772(6)	156
O1W-H1W…O2 #1	0.89(6)	1.83(5)	2.716(4)	174
O2-H2...O1E #1	0.86(5)	1.71(5)	2.565(4)	175
O1W-H2W…O1A #2	0.86(6)	1.85(6)	2.712(3)	179
O3-H30A...O3 #3	0.84	1.88	2.708(7)	168
C7-H7… O1A1	0.95	2.39	3.293(5)	158
C8-H8… O1A	0.95	2.54	3.359(3)	144
C8-H8… O2A1	0.95	2.35	3.259(6)	159
intra				
C10-H10… O1 #4	0.95	2.42	2.933(5)	114
#1 = 1-x,1-y,-z; #2 =-1+x,y,z ; #3 = -x,-1-y,1-z; #4 = -x,-y,-z				

Table S6. Main bond distances and angles (Å,°) in **3**

Compound	**3**		
Ni(1)-O(1)#1	2.025(2)	O(1)#1-Ni(1)-O(1)	180.00(13)
Ni(1)-O(1)	2.025(2)	O(1)#1-Ni(1)-N(2)	100.96(9)
Ni(1)-N(2)	2.040(3)	O(1)-Ni(1)-N(2)	79.04(9)
Ni(1)-N(2)#1	2.040(3)	O(1)#1-Ni(1)-N(2)#1	79.04(9)
Ni(1)-N(10)	2.156(3)	O(1)-Ni(1)-N(2)#1	100.96(9)
Ni(1)-N(10)#1	2.156(3)	N(2)-Ni(1)-N(2)#1	180.0
N(1)-C(1)	1.332(4)	O(1)#1-Ni(1)-N(10)	89.95(11)
O(1)-C(1)	1.264(4)	O(1)-Ni(1)-N(10)	90.05(11)
N(1)-N(2)	1.396(3)	N(2)-Ni(1)-N(10)	90.54(10)
N(2)-C(8)	1.273(4)	N(2)#1-Ni(1)-N(10)	89.46(10)
		O(1)-Ni(1)-N(10)#1	89.95(11)
		N(2)-Ni(1)-N(10)#1	89.46(10)
		N(2)#1-Ni(1)-N(10)#1	90.53(10)
		N(10)-Ni(1)-N(10)#1	180.0
		O(1)-C(1)-N(1)	126.1(3)
		O(1)-C(1)-C(2)	117.5(3)
		C(1)-N(1)-N(2)	110.7(2)
#1 -x+2,-y+1,-z+1			

Table S7. Main hydrogen bonds (Å) and angles (°) **3**.

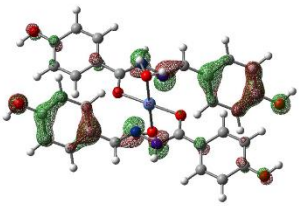
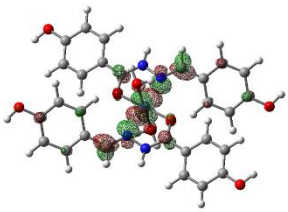
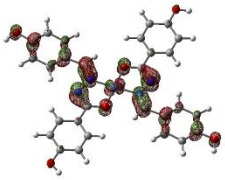
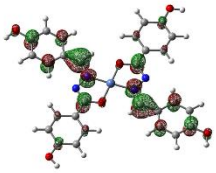
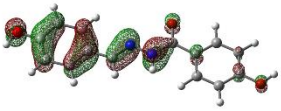
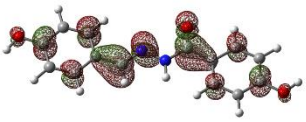
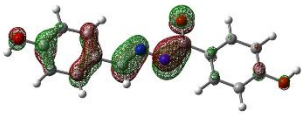
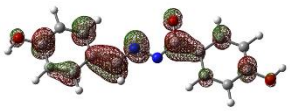
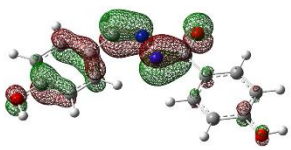
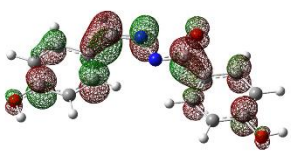
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(20)...N(1)#2	0.84	2.02	2.834(4)	163.0
O(2)-H(20)...N(2)#2	0.84	2.54	3.174(4)	133.4
O(3)-H(10)...N(32)#3	0.84	1.91	2.671(5)	150.9
C(22)-H(22)...O(1)#1	0.95	2.55	3.085(5)	115.7
C(26)-H(26)...O(1)	0.95	2.48	3.017(5)	116.0
C(34)-H(34)...O(3)#4	0.95	2.39	3.261(9)	151.9

Symmetry transformations used to generate equivalent atoms:

#1= -x+2,-y+1,-z+1; #2= -x+y+4/3,-x+5/3,z-1/3; #3= -y+1,x-y,z+1; #4 x,y,z-1

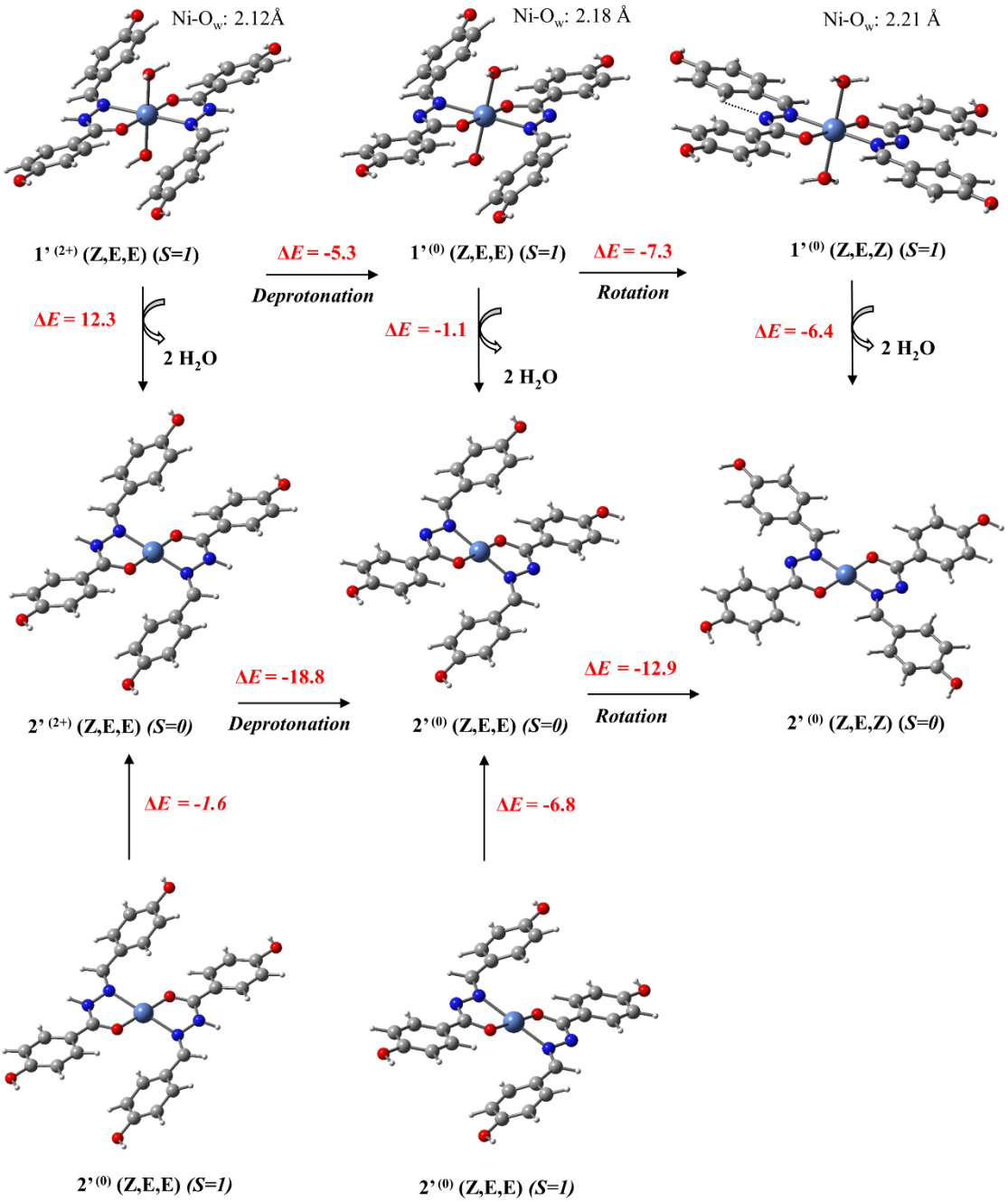
Theoretical calculations

Table S8. HOMO and LUMO plots (isovalue ±0.04 au) together with the HOMO-LUMO energy gap (H-L gap) computed at B3LYP/6-31++g(d,p)/SMD(ethanol).

	HOMO (H)	LUMO (L)	H-L gap
$[Ni(HL)_2(H_2O)_2]^{2+}$			E_{H-L} = 3.84 eV
NiL_2			E_{H-L} = 3.56 eV
LH			E_{H-L} = 4.11 eV
L^-			E_{H-L} = 3.75 eV
$*L^-$			E_{H-L} = 3.83 eV

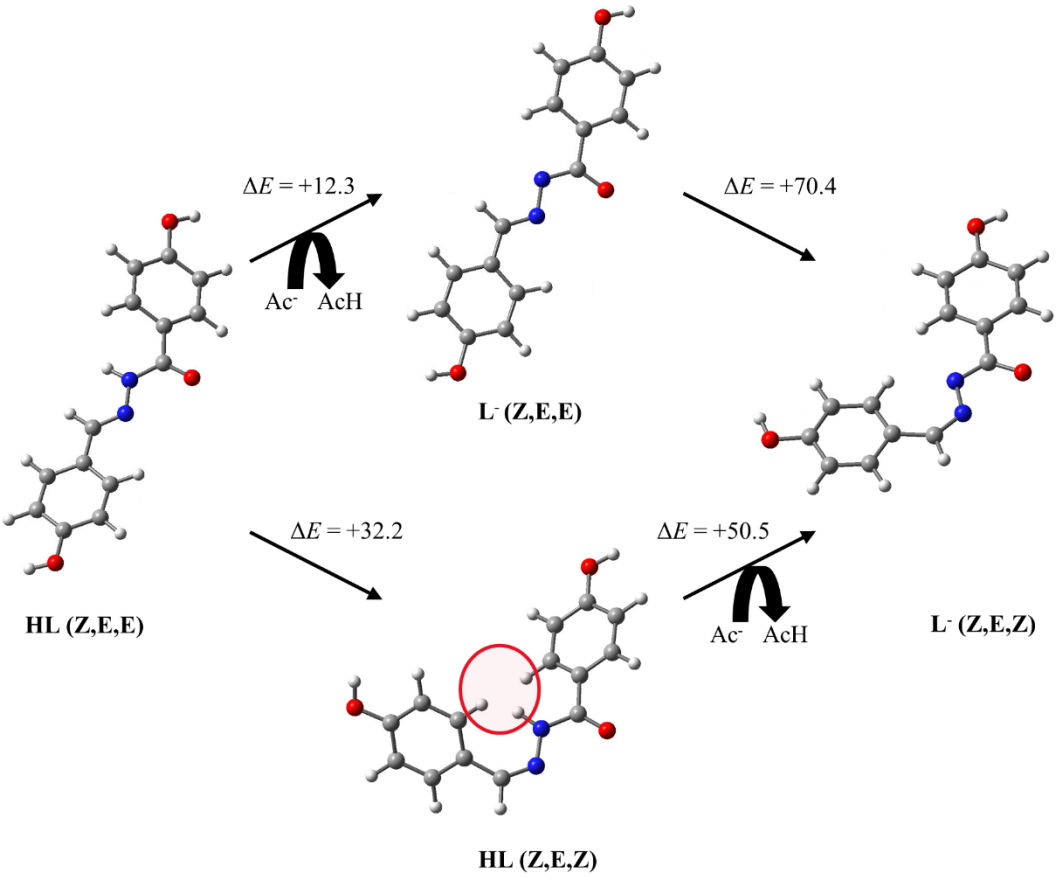
*HOMO and LUMO plots and H-L energy gap of the ligand in the geometry of the SP complex.

Scheme S1. Possible reaction sequences to get the square planar complex $[Ni(L)_2]$ (**2'**) from $[Ni(HL)_2(H_2O)_2]^{2+}$ (**1'**).
Optimized molecular geometries together with corresponding energy differences, ΔE, (in kcal·mol^{-1}) computed for each step at the B3LYP/6-31++g(d,p)/SMD(ethanol) level of theory. Low and high spin states have been evaluated in the SP arrangement when possible.



Scheme S2. HL and L^- geometries computed at the B3LYP/6-31++g(d,p)/SMD(ethanol) level of theory.

It is also shown the steric hindrance between hydrogen atoms preventing rotation before deprotonation. Energy differences, ΔE, in kcal·mol^{-1}.



Scheme S3. Evaluation of the spin state transition by addition of one and two pyridine ligands to **2'**.

Molecular geometries and energy differences, Δ*E*, computed at the B3LYP/6-31++g(d,p)/SMD(acetone) level of theory.

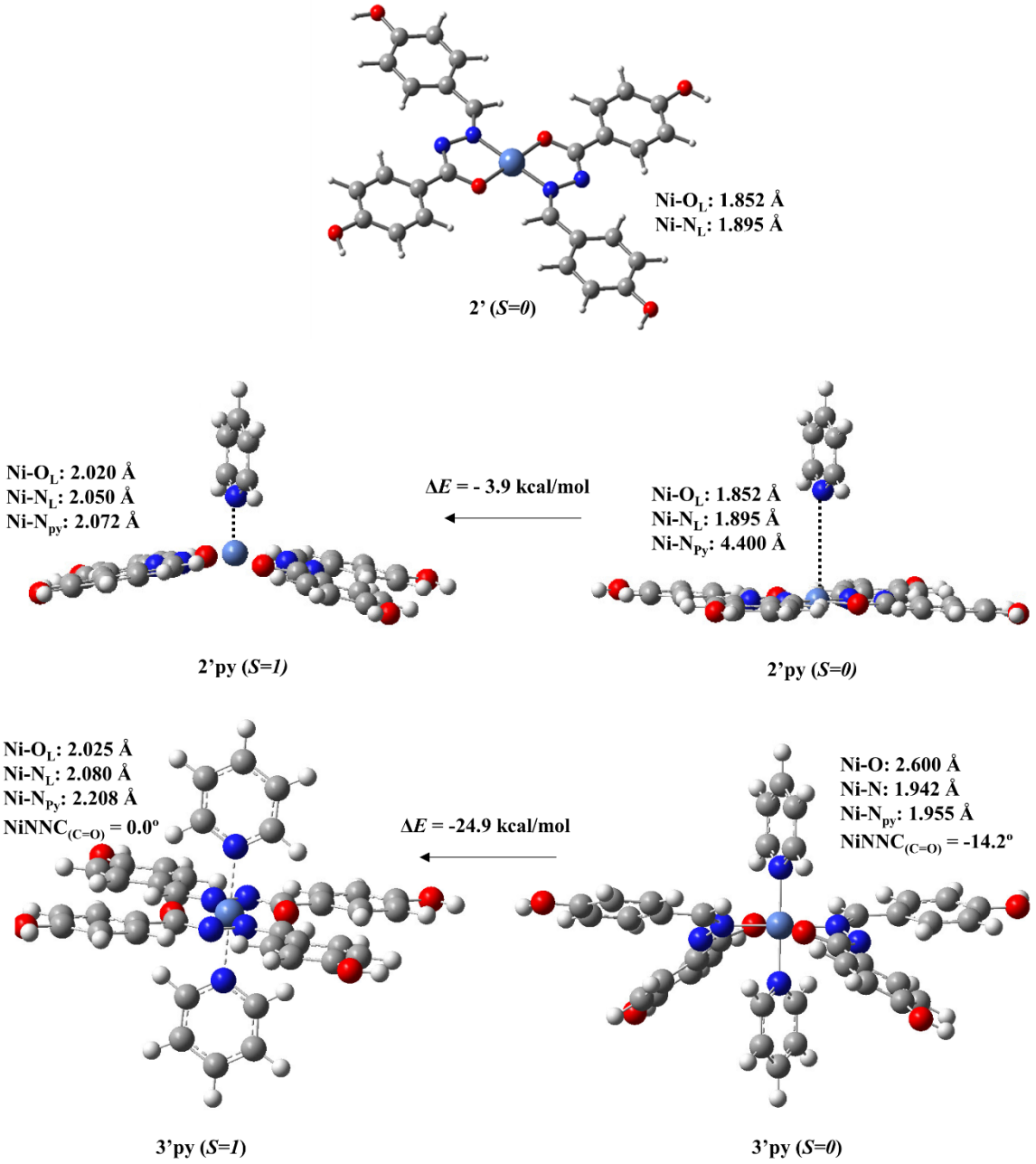
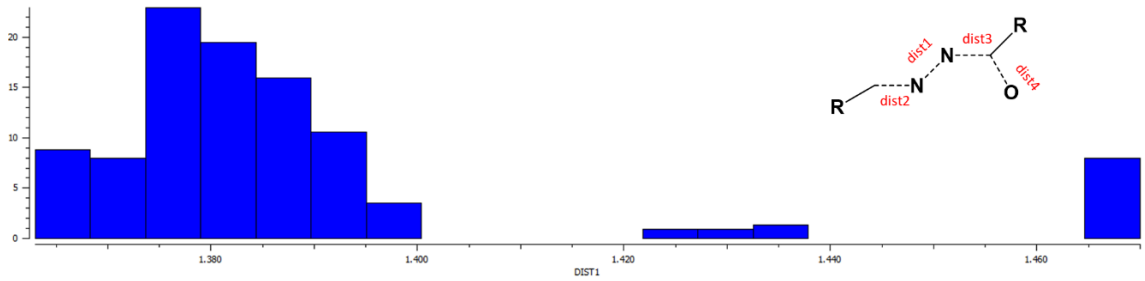
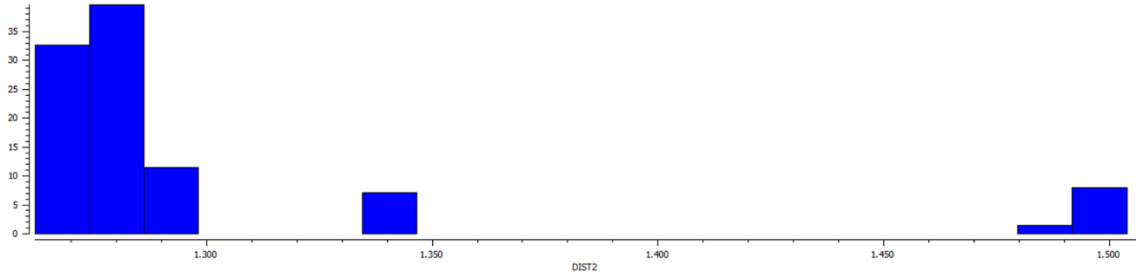


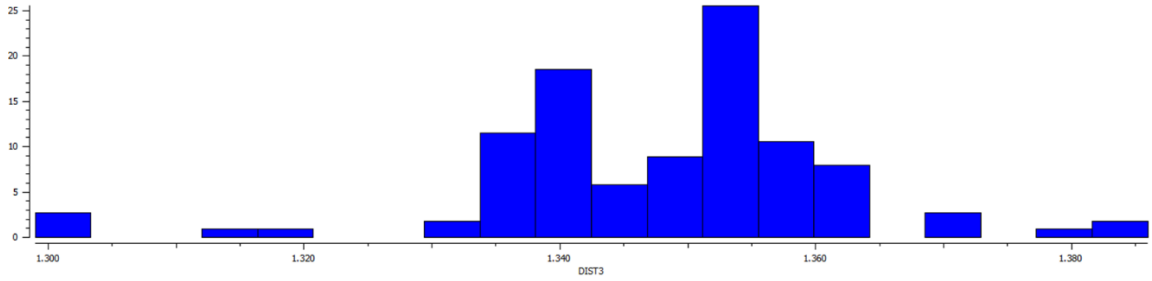
Figure S10. Cambridge Structural Database (CSD) distances analysis.



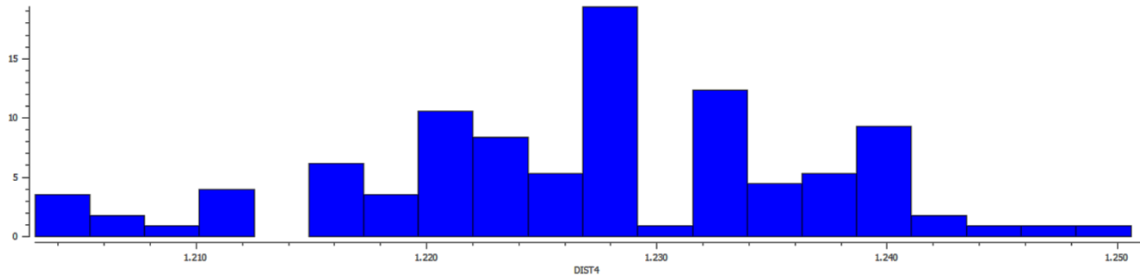
(a) Distance 1. N=N bonds



(b) Distance 2. C-N bonds

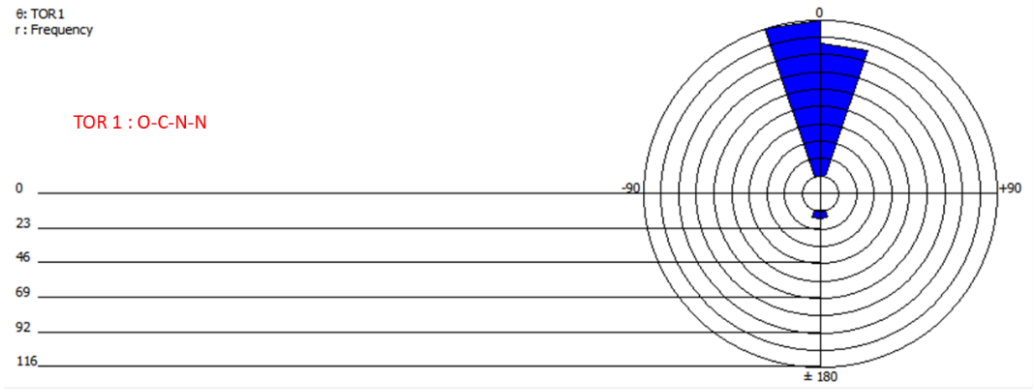


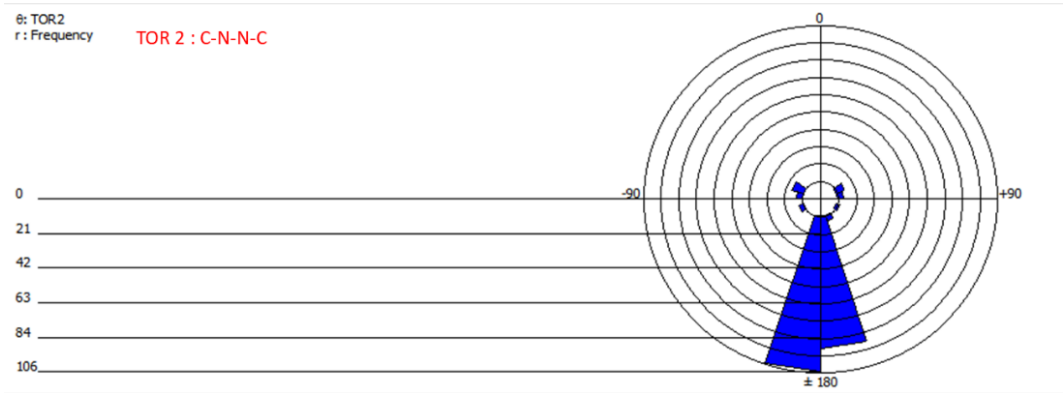
(c) Distance 3. N-C bonds

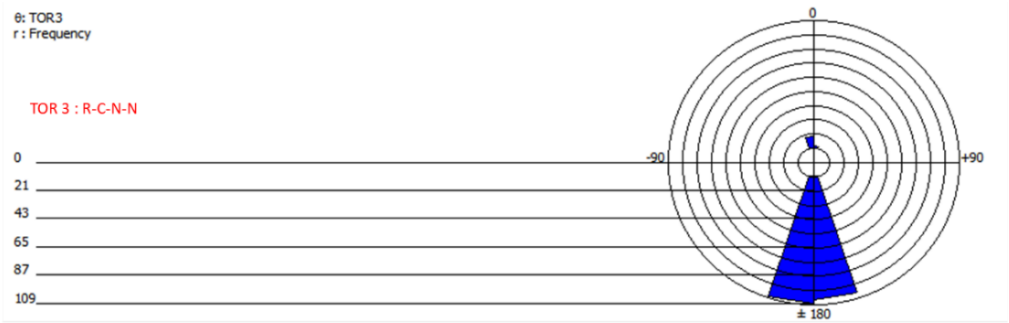


(d) Distance 4. C=O bonds

Figure S11. Cambridge Structural Database (CSD) torsion angles analysis.







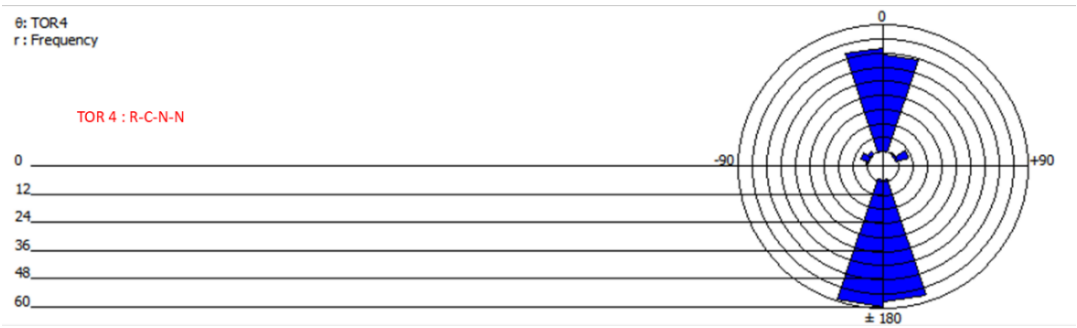


Figure S12. DRX of compound **2** (blue) compared with the calculated of single crystals of **2a** (red) and **2b** (green).