SUPPORTING INFORMATION

Simple design for metal-based halogen-bonded cocrystals utilizing the M-Cl···I motif

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EXPERIMENTAL DETAILS

Table S1. General and crystallographic data for the prepared cocrystals.

	(**1,4-tfib**)(**1**)	(**1,3-tfib**)$_2$(**1**)	(**1,2-tfib**)(**1**)
Molecular formula	$(CoCl_2C_{20}H_{16}N_4)(C_6F_4I_2)$	$(CoCl_2C_{20}H_{16}N_4)(C_6F_4I_2)_2$	$(CoCl_2C_{20}H_{16}N_4)(C_6F_4I_2)$
M_r	844.06	1245.92	844.06
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*P* 2$_1$/*c*	*C* 2/*c*	*P* 2$_1$/*n*
Crystal data:			
a / Å	12.6870(8)	16.5798(17)	7.8226(6)
b / Å	14.1661(10)	15.3912(9)	25.788(2)
c / Å	16.0110(12)	16.652(2)	14.3532(9)
α / °	90	90	90
β / °	104.732(7)	119.758(16)	99.146(7)
γ / °	90	90	90
V / Å^3	2783.0(3)	3689.0(9)	2858.6(4)
Z	4	4	4
D_{calc} / g cm^{-3}	2783.0(3)	2.243	1.961
λ(MoK_α) / Å	0.71073	0.71073	0.71073
T / K	295	295	295
Crystal size / mm^3	0.55 x 0.22 x 0.14	0.39 x 0.27 x 0.27	0.19 x 0.12 x 0.024
μ / mm^{-1}	3.079	4.029	2.997
F(*000*)	1612	2324	1612
Refl. collected/unique	5447/3309	3237/2086	5601/3265
Data/restraints/parameters	352	231	352
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	0.766; –0.444	0.408; –0.865	0.490; –0.451
$R[F^2>4\sigma(F^2)]$	0.0476	0.0302	0.0474
$wR(F^2)$	0.0938	0.0619	0.1060
Goodness-of-fit, *S*	0.995	0.836	0.911

	(1,2-tfib)$_2$(1)	**(ipfb)$_2$(1)**	**(1,3,5-tfib)(1)**(EtOH)
Molecular formula	$(CoCl_2C_{20}H_{16}N_4)(C_6F_4I_2)_2$	$(CoCl_2C_{20}H_{16}N_4)(C_6F_5I)_2$	$(CoCl_2C_{20}H_{16}N_4)(C_6F_3I_3)(C_2H_6O)$
M_r	1245.92	1030.12	1245.92
Crystal system	orthorhombic	monoclinic	triclinic
Space group	*P bcn*	*C* 2/*c*	*P –1*
Crystal data:			
a / Å	14.5049(5)	8. 2507(6)	8.5903(5)
b / Å	8.5031(4)	12. 9627(13)	12.7010(7)
c / Å	30.2853(13)	32. 399(2)	16.2950(11)
α / °	90	90	69.852(6)
β / °	90	92. 121(6)	88.600(5)
γ / °	90	90	84.665(5)
V / Å^3	3735.3(3)	3462.7(5)	1661.79(18)
Z	4	4	2
D_{calc} / g cm^{-3}	2.216	1.976	1.995
λ(MoK_α) / Å	0.71073	0.71073	0.71073
T / K	295	295	295
Crystal size / mm^3	0.37 x 0.35 x 0.20	0.57 x 0.30 x 0.11	0.31 x 0.12 x 0.032
μ / mm^{-1}	3.979	2.518	3.509
F(*000*)	2324.0	1972	946
Refl. collected/unique	3271/2230	3382/2897	5787/ 2467
Data/restraints/parameters	231	231	377
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	0.562; –0.848	0.731; –0.553	0.508; –0.379
$R[F^2>4\sigma(F^2)]$	0.0288	0.0450	0.0350
$wR(F^2)$	0.0577	0.0736	0.0478
Goodness-of-fit, *S*	0.858	1.172	0.646

	(**ofib**)$_2$(**1**)	(**1,3-tfib**)(**2**)	(**1,2-tfib**)(**2**)
Molecular formula	$(CoCl_2C_{20}H_{16}N_4)(C_4F_8I_2)_2$	$(CoCl_2C_{24}H_{16}N_4)(C_6F_4I_2)$	$(CoCl_2C_{24}H_{16}N_4)(C_6F_4I_2)$
M_r	1349.88	892.10	892.10
Crystal system	orthorhombic	triclinic	monoclinic
Space group	*P bca*	*P –1*	*P* $2_1/c$
Crystal data:			
a / Å	28.625(5)	8.1204(7)	13. 4604(9)
b / Å	16.4514(14)	13.9649(8)	23. 4681(15)
c / Å	16.8783(10)	14.1470(7)	9. 7735(9)
α / °	90	99.902(4)	90
β / °	90	100.089(5)	102.252(7)
γ / °	90	105.734(6)	90
V / Å^3	7948.4(15)	1478.96(18)	3017.0(4)
Z	8	2	4
D_{calc} / g cm^{-3}	2.256	2.003	1.964
λ(MoK_α) / Å	0.71073	0.71073	0.71073
T / K	295	295	295
Crystal size / mm^3	0.30 x 0.23 x 0.15	0.49 x 0.20 x 0.08	0.31 x 0.077 x 0.044
μ / mm^{-1}	3.776	2.903	2.846
F(*000*)	5032	854.0	1708
Refl. collected/unique	6968/4158	3659/2167	6922/3893
Data/restraints/parameters	496	388	388
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	0.915; –0.514	0.548; –0.453	0.700; –0.654
$R[F^2>4\sigma(F^2)]$	0.0328	0.0382	0.0474
$wR(F^2)$	0.0665	0.0744	0.0795
Goodness-of-fit, *S*	0.800	0.806	0.996

	(**ipfb**)$_2$(**2**)	(**1,3,5-tfib**)$_3$(**2**)	(**ofib**)(**2**)
Molecular formula	$(CoCl_2C_{24}H_{16}N_4)(C_6F_5I)_2$	$(CoCl_2C_{24}H_{16}N_4)(C_6F_3I_3)_3$	$(CoCl_2C_{24}H_{16}N_4)(C_4F_8I_2)$
M_r	1078.16	2019.52	944.08
Crystal system	monoclinic	triclinic	monoclinic
Space group	*C 2/c*	*P* –1	*I 2/a*
Crystal data:			
a / Å	7.9892(4)	9. 5760(4)	13.7036(12)
b / Å	13.5176(7)	13. 1124(6)	15.5273(10)
c / Å	33.897(2)	21. 2891(10)	15.8979(11)
α / °	90	100.877(4)	90
β / °	92.075(5)	99.440(4)	111.746(9)
γ / °	90	96.238(4)	90
V / Å^3	3658.3(4)	2562.6(2)	3142.0(4)
Z	4	2	4
D_{calc} / g cm^{-3}	1.958	2.617	1.996
λ(MoK_α) / Å	0.71073	0.71073	0.71073
T / K	295	295	295
Crystal size / mm^3	0.32 x 0.25 x 0.058	0.50 x 0.24 x 0.071	0.42 x 0.28 x 0.15
μ / mm^{-1}	2.388	5.929	2.756
F(*000*)	2068	1830	1804
Refl. collected/unique	3563 / 2695	10011 / 6539	2765 2305
Data/restraints/parameters	249	604	205
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e Å^{-3}	0.350; –0.439	1.276; – 1.584	1.379; –1.434
$R[F^2>4\sigma(F^2)]$	0.0338	0.0485	0.0599
$wR(F^2)$	0.0598	0.1161	0.1582
Goodness-of-fit, *S*	1.053	1.028	1.074

Table S2. Geometric parameters for the halogen bonds in prepared cocrystals. Distances between select atoms in a contact are denoted as *d*, while the corresponding angle is marked with α.

compound	*D*–I···*A*	*d*(*D*–I) / Å	*d*(I···*A*) / Å	α / °	symmetry operator
(1,4-tfib)(1)	C24–I2···Cl1	2.096(7)	3.061(2)	175	*2-x,1/2+y,1.5-z*
	C21–I1···I1	2.072(8)	3.8506(8)	147	*1-x,1-y,1-z*
(1,3-tfib)$_2$(1)	C11–I1···Cl1	2.092(5)	3.242(1)	165	*1/2-x,1/2+y,1.5-z*
	C13–I2···Cl1	2.099(5)	3.225(1)	177	*-x,y,1.5-z*
(1,2-tfib)(1)	C21–I1···Cl1	2.093(8)	3.198(2)	177	*-1/2+x,1/2-y,1/2+z*
	C22–I2···Cl2	2.111(7)	3.199(2)	170	*x,y,1+z*
(1,2-tfib)$_2$(1)	C11–I1···Cl1	2.095(4)	3.085(1)	177	*x, y, z*
	C12–I···F4	2.074(4)	3.259(3)	154	*x,-1+y,z*
(ipfb)$_2$(1)	C11–I1···Cl1	2.100(5)	3.094(1)	176	*x, y, z*
(1,3,5-tfib)(1)(EtOH)	C21–I1···Cl2	2.096(5)	3.235(1)	175	*x, y, z*
	C23–I2···Cl1	2.080(8)	3.343(2)	161	*-1+x,1+y,z*
(ofib)$_2$(1)	C21–I1···Cl1	2.156(7)	3.153(1)	176	*x, y, z*
	C24–I2---Cl1	2.157(6)	3.194(1)	174	*1-x, -1/2+y,1.5-z*
	C25–I3---Cl2	2.171(9)	3.170(1)	175	*1.5-x, -1/2+y, z*
	C27–I4···Cl2	2.125(9)	3.159(1)	175	*-1/2+x,1/2-y,1-z*
(1,3-tfib)(2)	C25–I1···Cl1	2.105(7)	3.188(2)	168	*2-x,1-y,1-z*
	C27–I2···Cl2	2.105(8)	3.174(2)	176	*2-x,1-y,-z*
(1,2-tfib)(2)	C25–I1···Cl1	2.106(7)	3.396(1)	176	*1-x,1-y,1-z*
	C26–I2···Cl2	2.110(6)	3.153(1)	171	*x, y, z*
(ipfb)$_2$(2)	C13–I1···Cl1	2.093(4)	3.136(1)	178	*x, y, z*
(1,3,5-tfib)$_3$(2)	C26–I1···Cl2	2.079(8)	3.471(2)	155	*1-x,-y,-z*
	C28–I2···Cl1	2.092(9)	3.367(2)	163	*1-x,1-y,-z*
	C36–I6···Cl1	2.095(8)	3.240(2)	168	*x,1+y,1+z*
	C32–I4···I5	2.078(9)	3.906(1)	165	*-1+x, y, z*
	C40–I8···I8	2.081(9)	3.768(1)	144	*1-x,1-y,1-z*
(ofib)(2)	C13–I1···Cl1	2.07(1)	3.167(2)	178	*1/2-x,1/2-y,1/2-z*

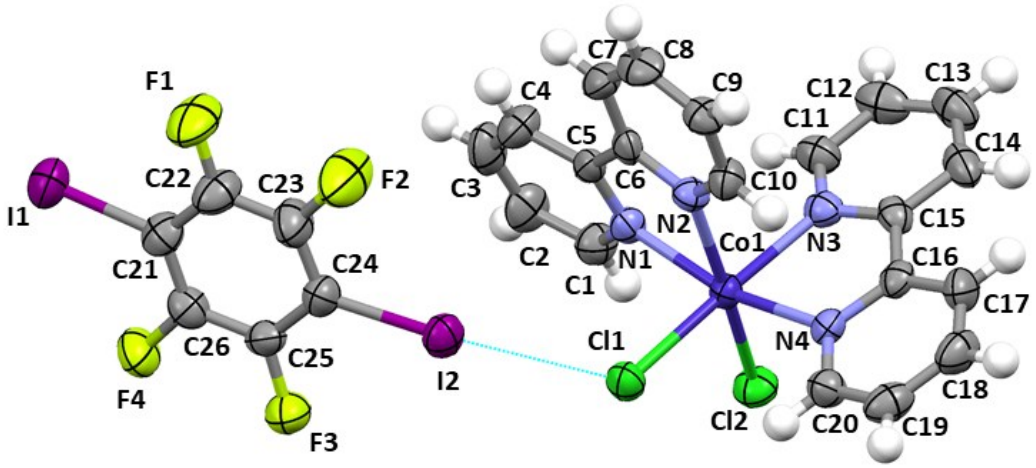

Figure S1. Molecular structure of (**1,4-tfib**)(**1**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, halogen bonds are marked with blue dashed lines, and H atoms are shown as small spheres of arbitrary radius.

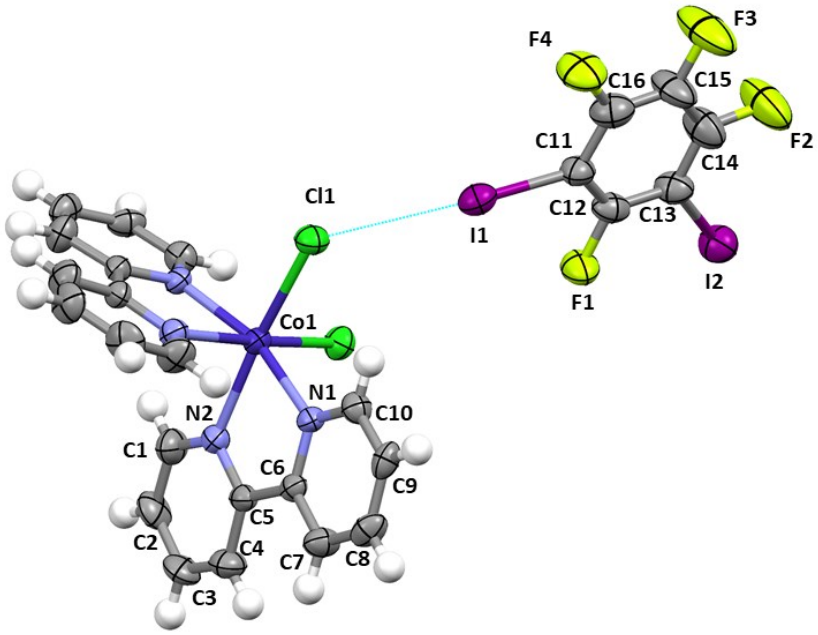

Figure S2. Molecular structure of (**1,3-tfib**)$_2$(**1**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, halogen bonds are marked with blue dashed lines, and H atoms are shown as small spheres of arbitrary radius.

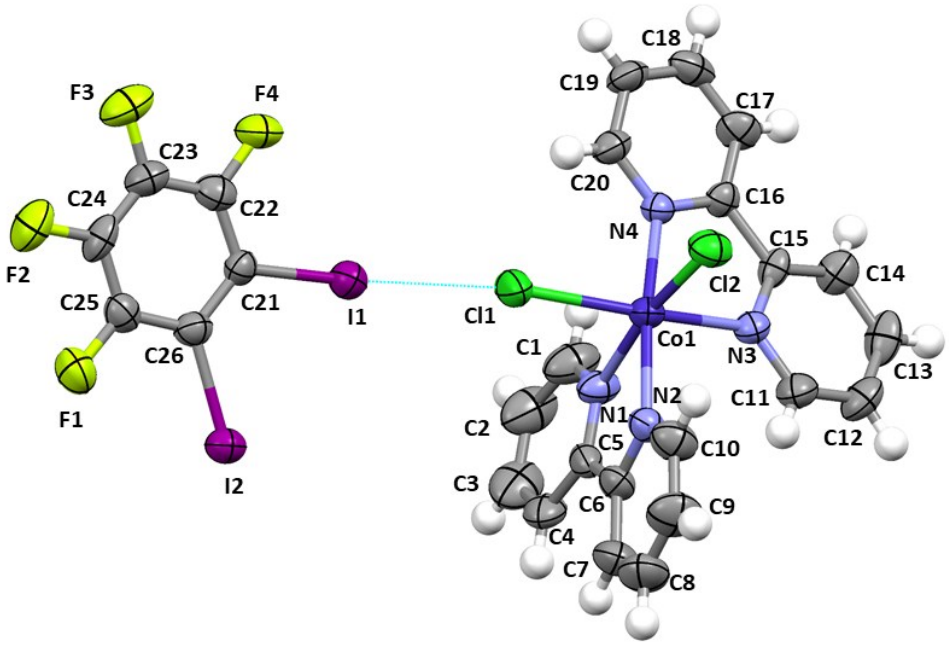

Figure S3. Molecular structure of (**1,2-tfib**)(**1**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, halogen bonds are marked with blue dashed lines, and H atoms are shown as small spheres of arbitrary radius.

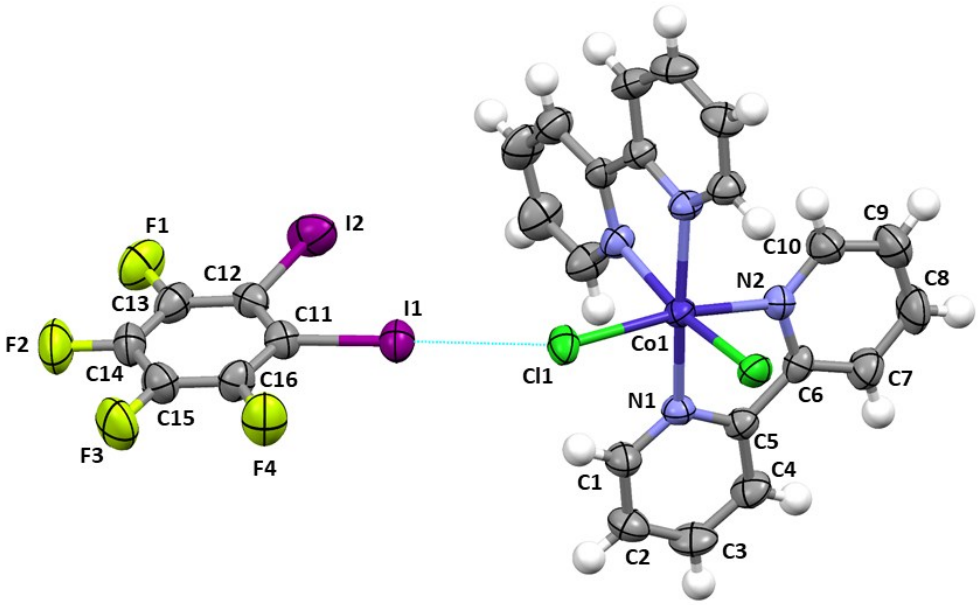

Figure S4. Molecular structure of (**1,2-tfib**)$_2$(**1**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, halogen bonds are marked with blue dashed lines, and H atoms are shown as small spheres of arbitrary radius.

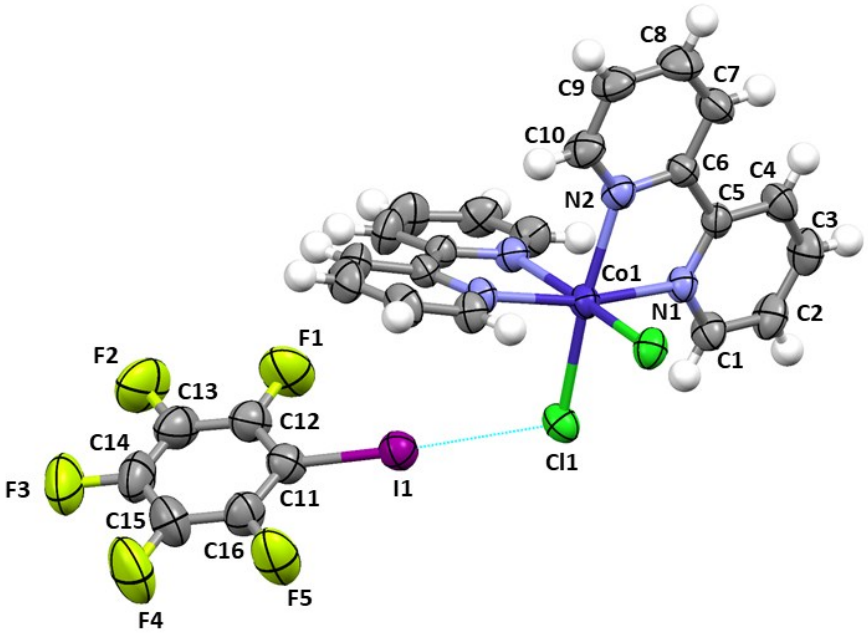

Figure S5. Molecular structure of (**ipfb**)$_2$(**1**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, halogen bonds are marked with blue dashed lines, and H atoms are shown as small spheres of arbitrary radius.

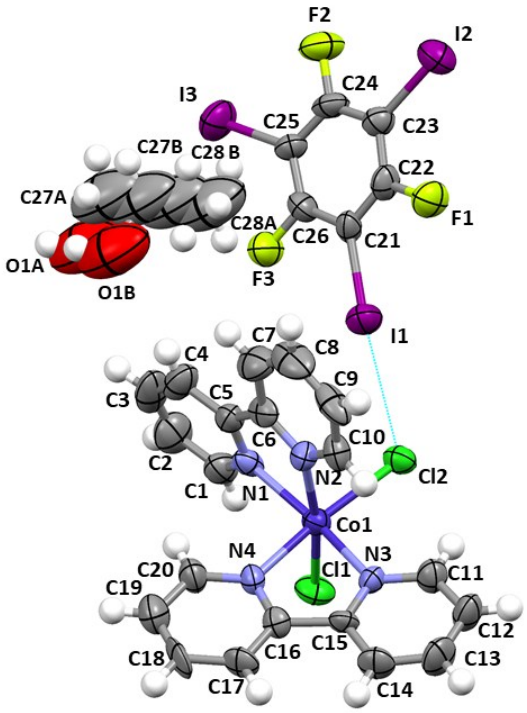

Figure S6. Molecular structure of (**135tfib)**(**1**)(EtOH) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, halogen bonds are marked with blue dashed lines, and H atoms are shown as small spheres of arbitrary radius.

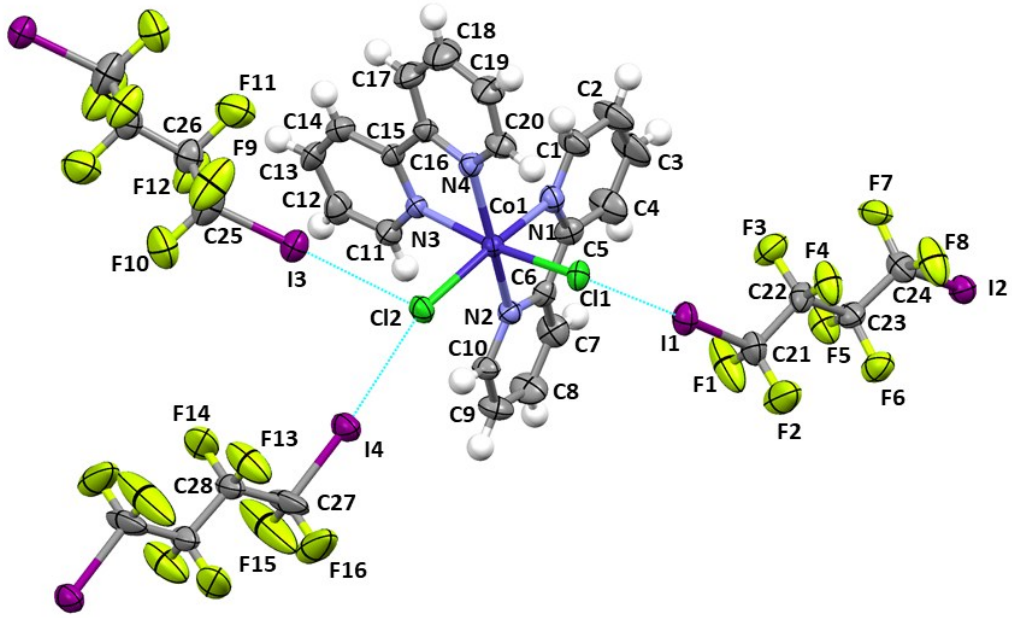

Figure S7. Molecular structure of **(ofib)**$_2$(**1**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, halogen bonds are marked with blue dashed lines, and H atoms are shown as small spheres of arbitrary radius.

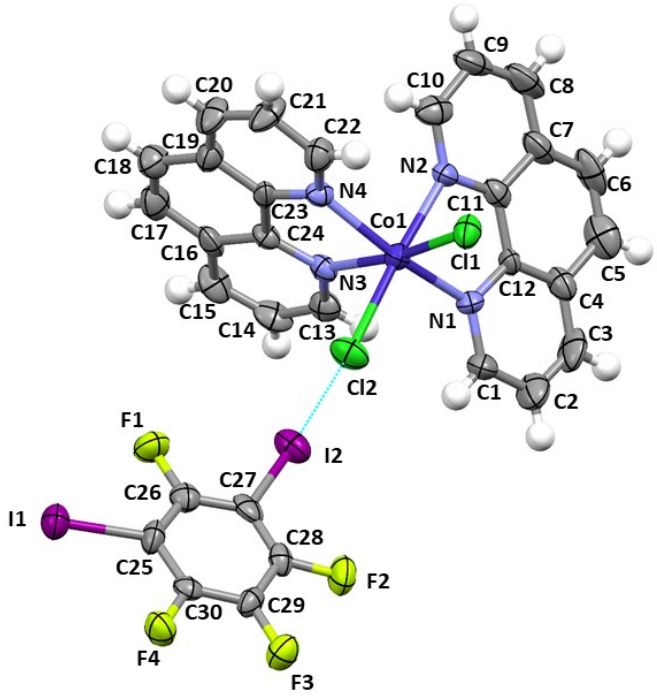

Figure S8. Molecular structure of (**1,3-tfib**)(**2**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, halogen bonds are marked with blue dashed lines, and H atoms are shown as small spheres of arbitrary radius.

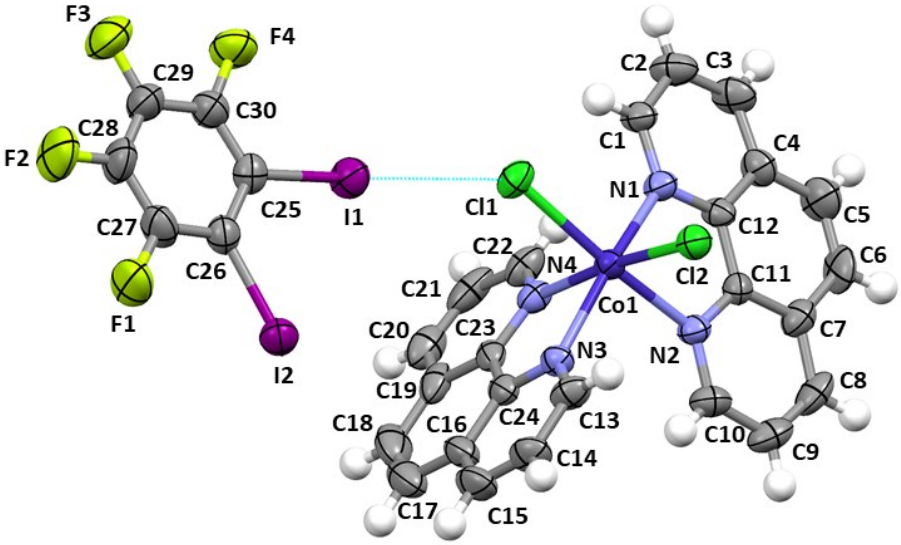

Figure S9. Molecular structure of (**1,2-tfib**)(**2**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, halogen bonds are marked with blue dashed lines, and H atoms are shown as small spheres of arbitrary radius.

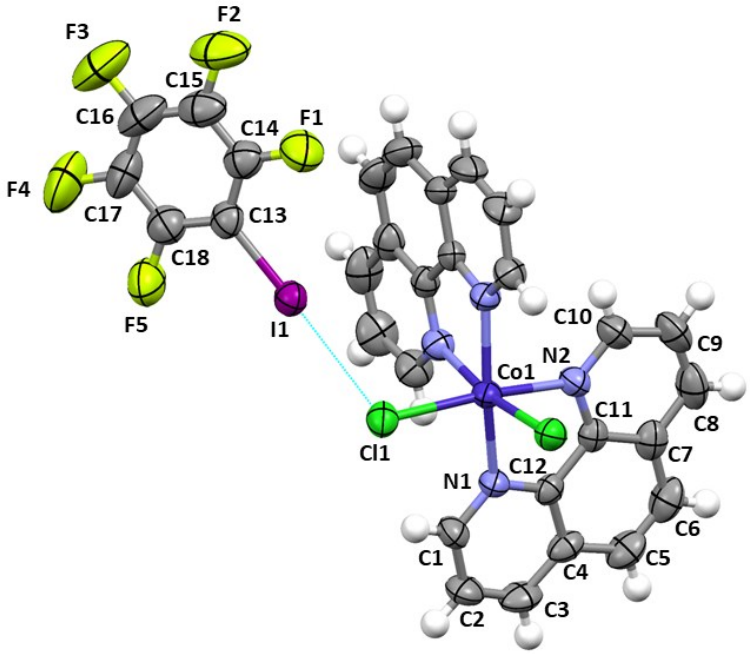

Figure S10. Molecular structure of (**ipfb**)$_2$(**2**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, halogen bonds are marked with blue dashed lines, and H atoms are shown as small spheres of arbitrary radius.

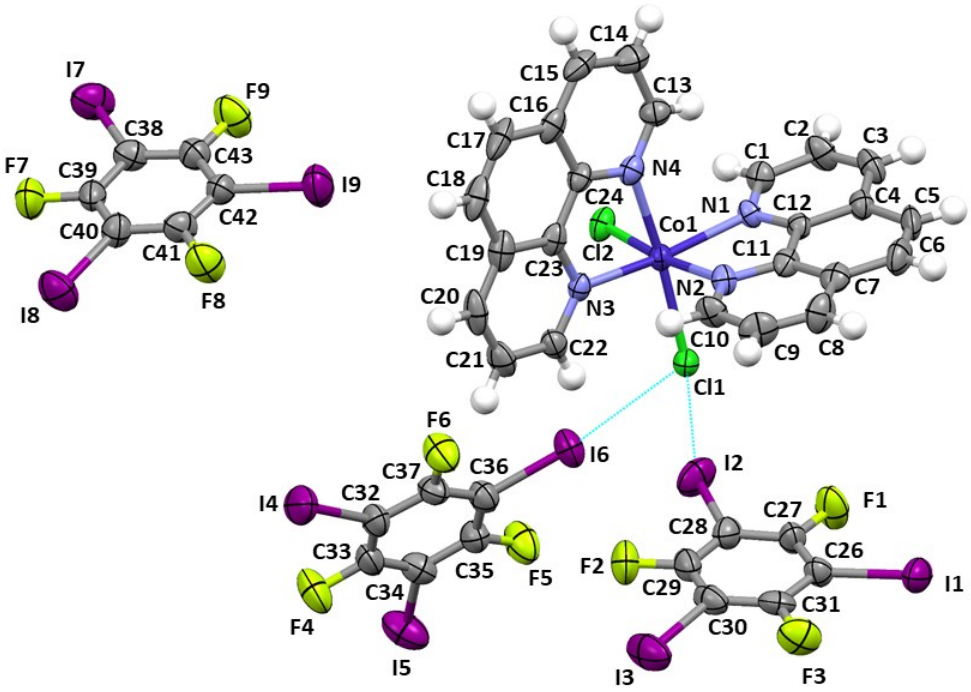

Figure S11. Molecular structure of (**1,3,5-tfib**)$_3$(**2**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, halogen bonds are marked with blue dashed lines, and H atoms are shown as small spheres of arbitrary radius.

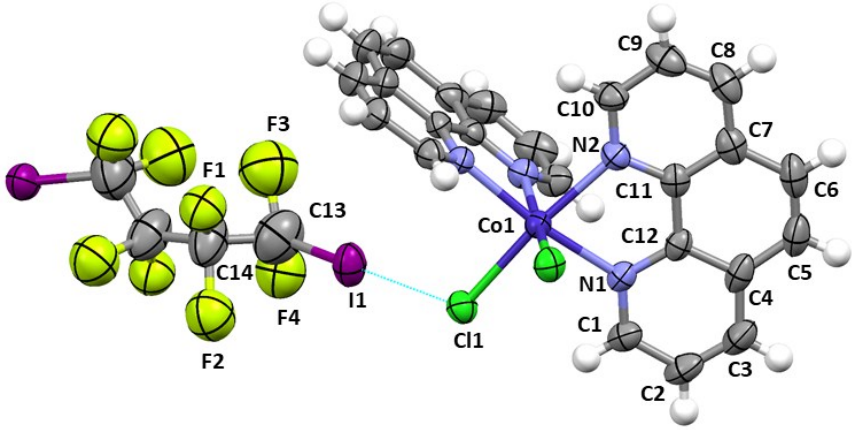

Figure S12. Molecular structure of (**ofib**)(**2**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50 % probability level, halogen bonds are marked with blue dashed lines, and H atoms are shown as small spheres of arbitrary radius.

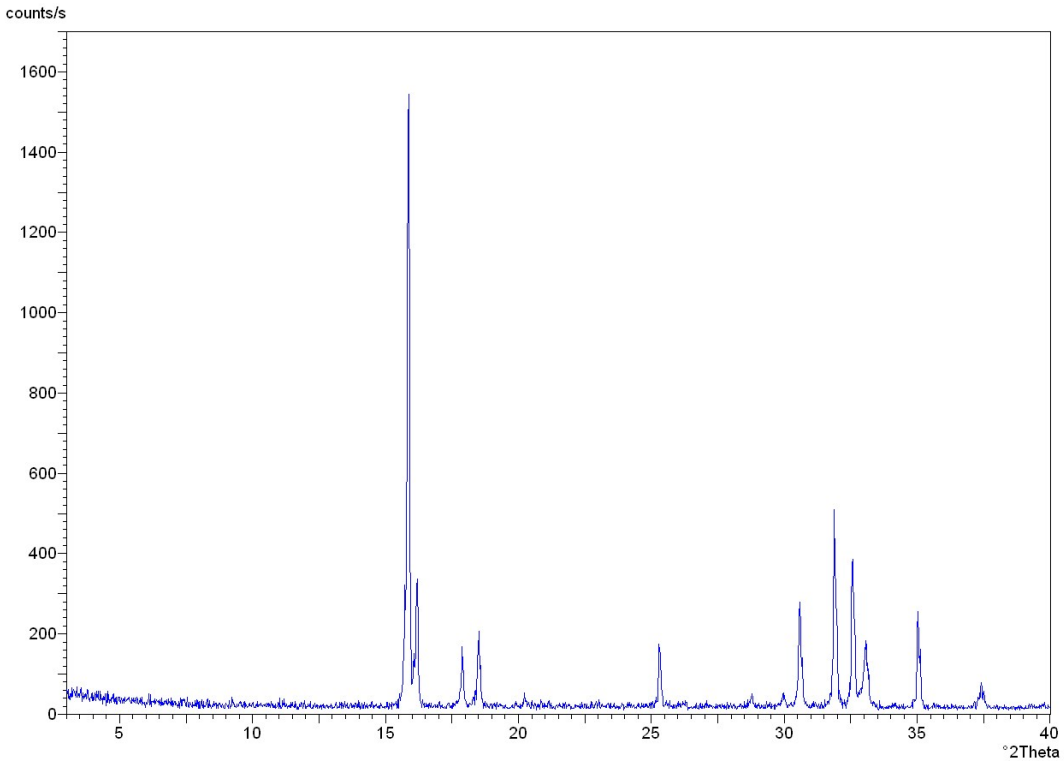

Figure S13. PXRD pattern of pure $CoCl_2 * 6H_2O$ reactant.

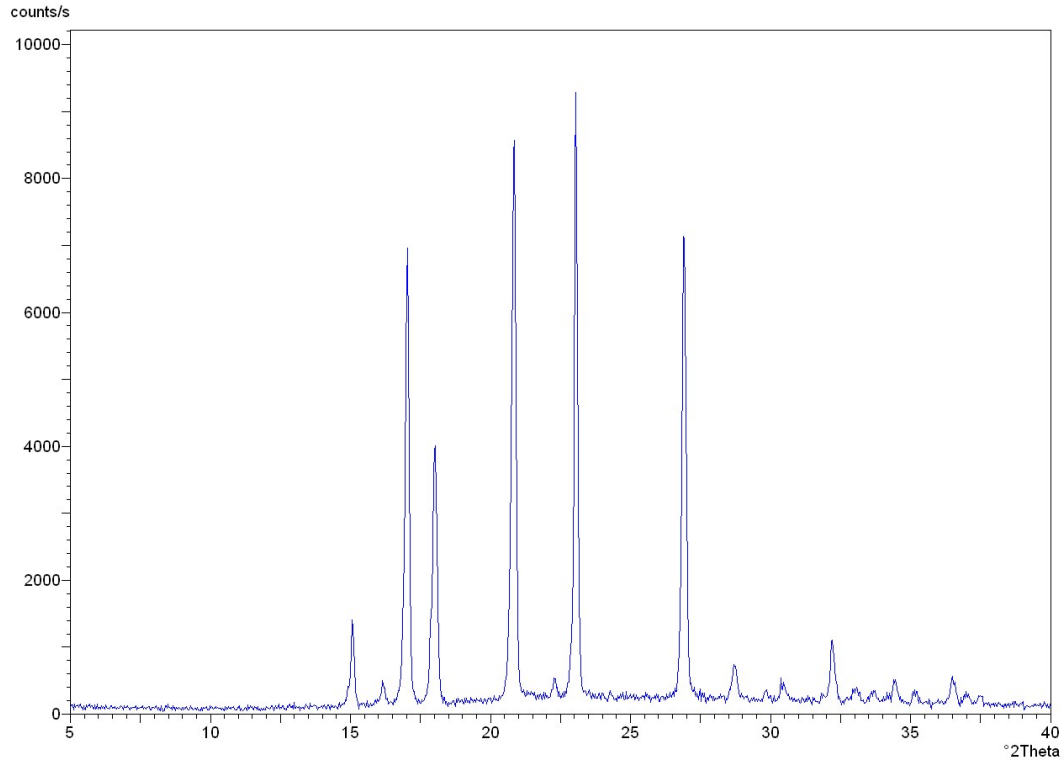

Figure S14. PXRD pattern of pure **bpy** reactant.

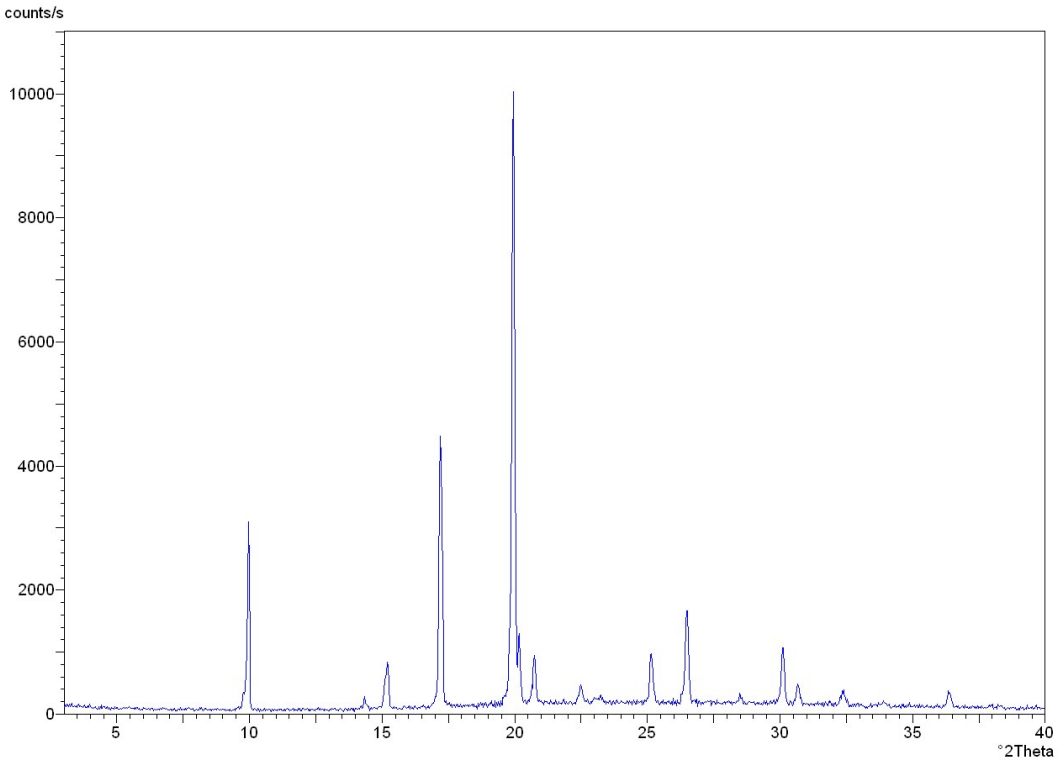

Figure S15. PXRD pattern of pure **phen** reactant.

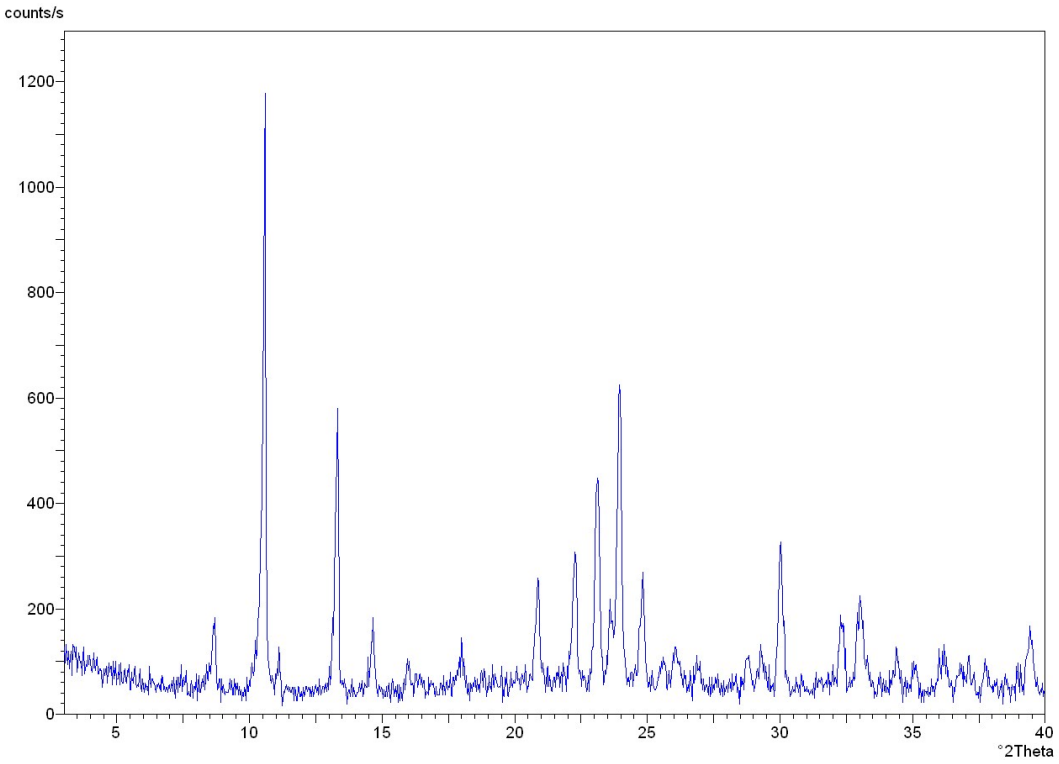

Figure S16. PXRD pattern of pure **1***$3H_20$ reactant.

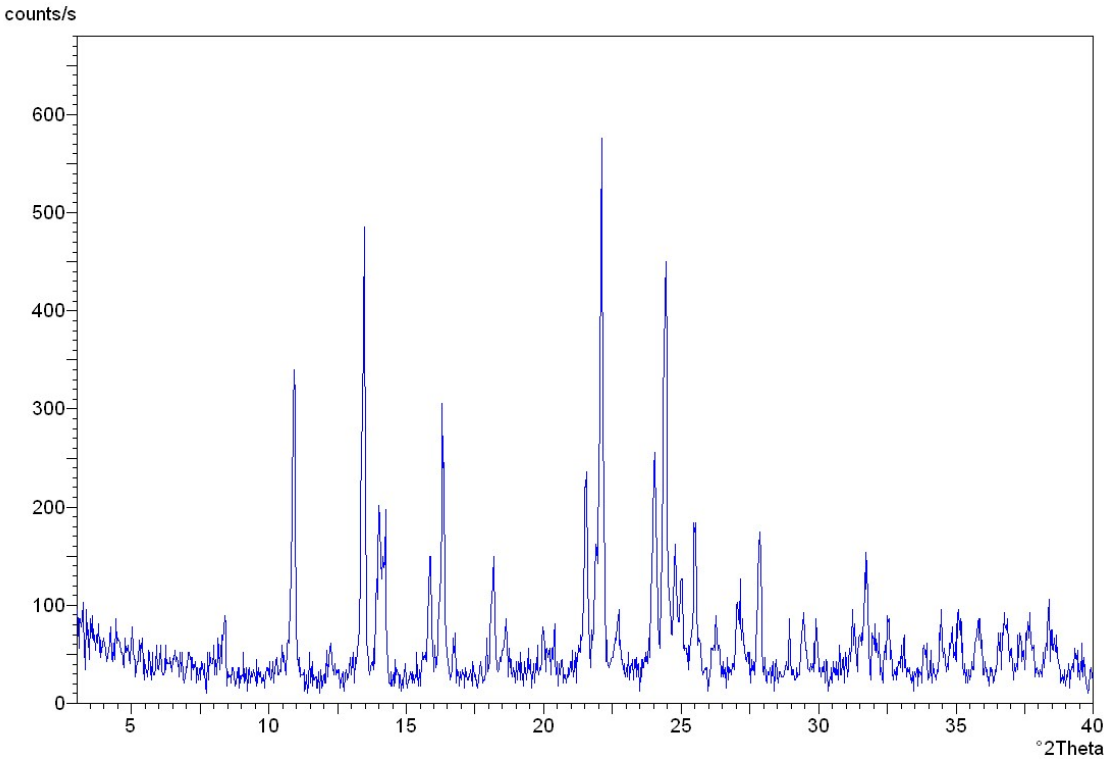

Figure S17. PXRD pattern of pure **2** reactant.

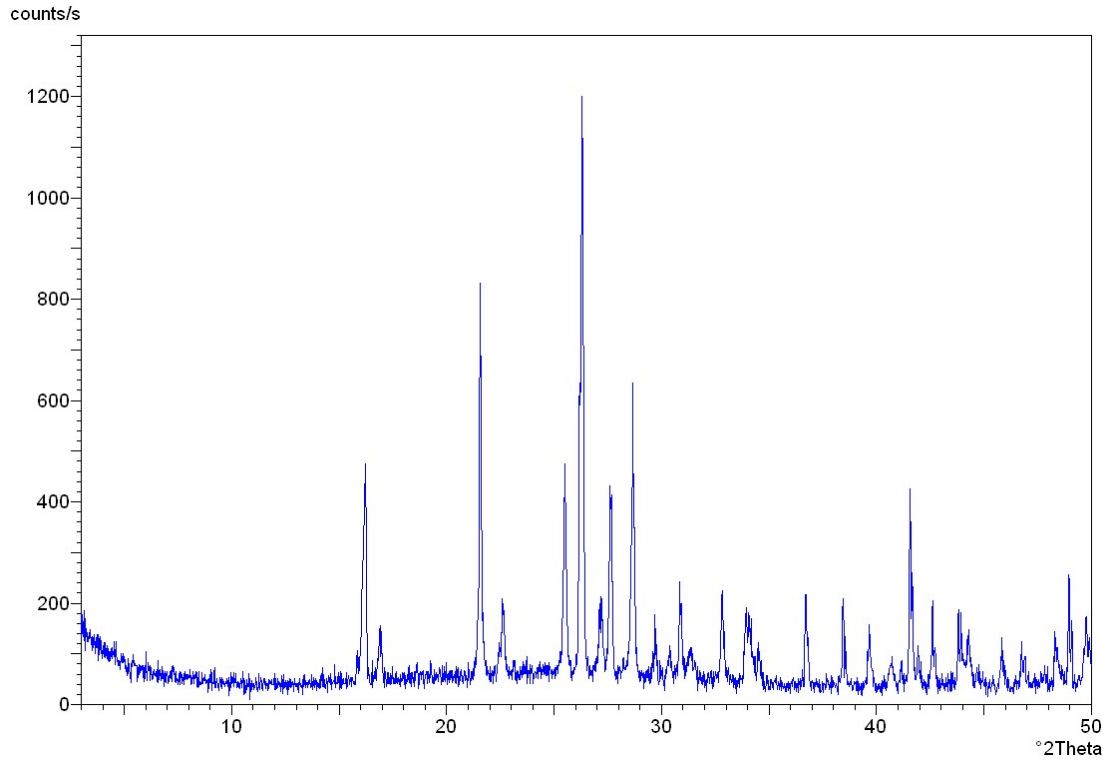

Figure S18. PXRD pattern of pure **1,4-tfib**.

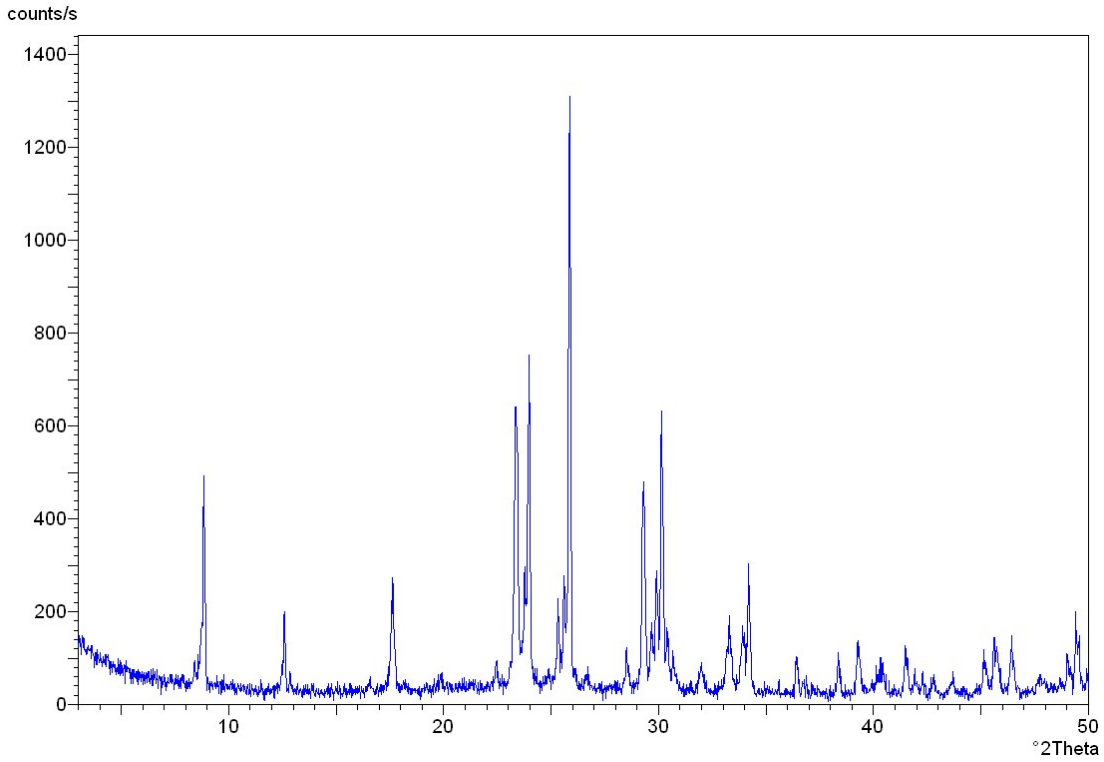

Figure S19. PXRD pattern of pure **1,2-tfib**.

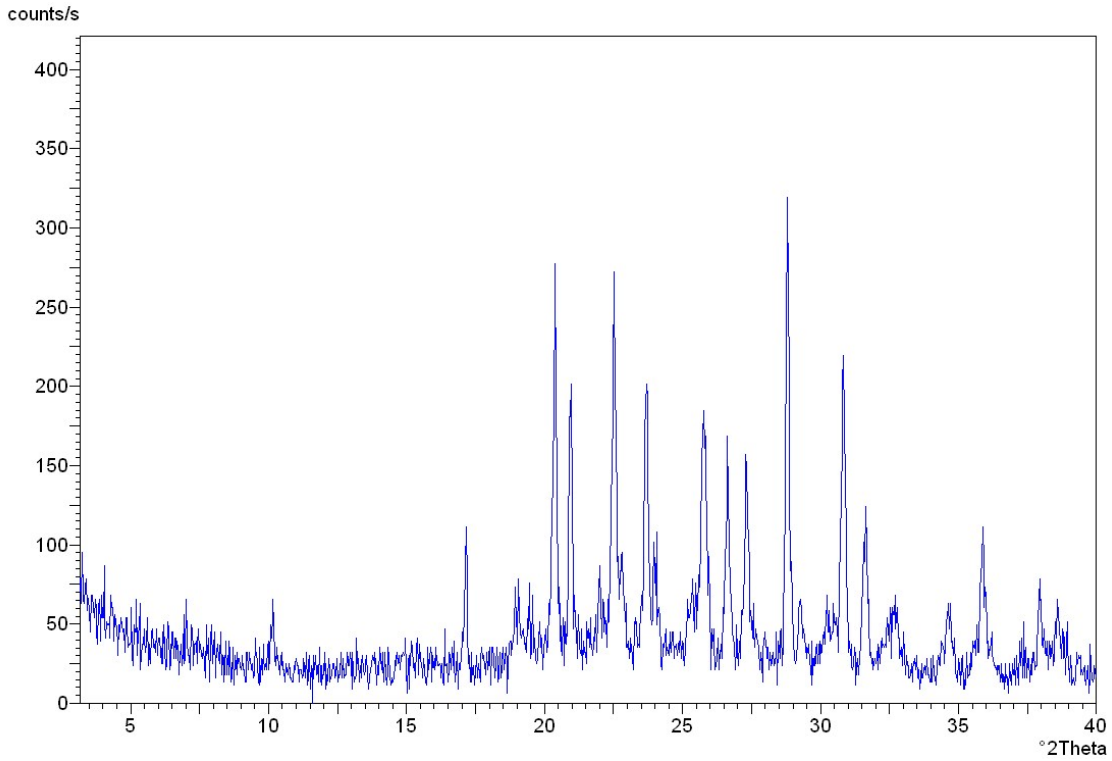

Figure S20. PXRD pattern of pure **1,3,5-tfib**.

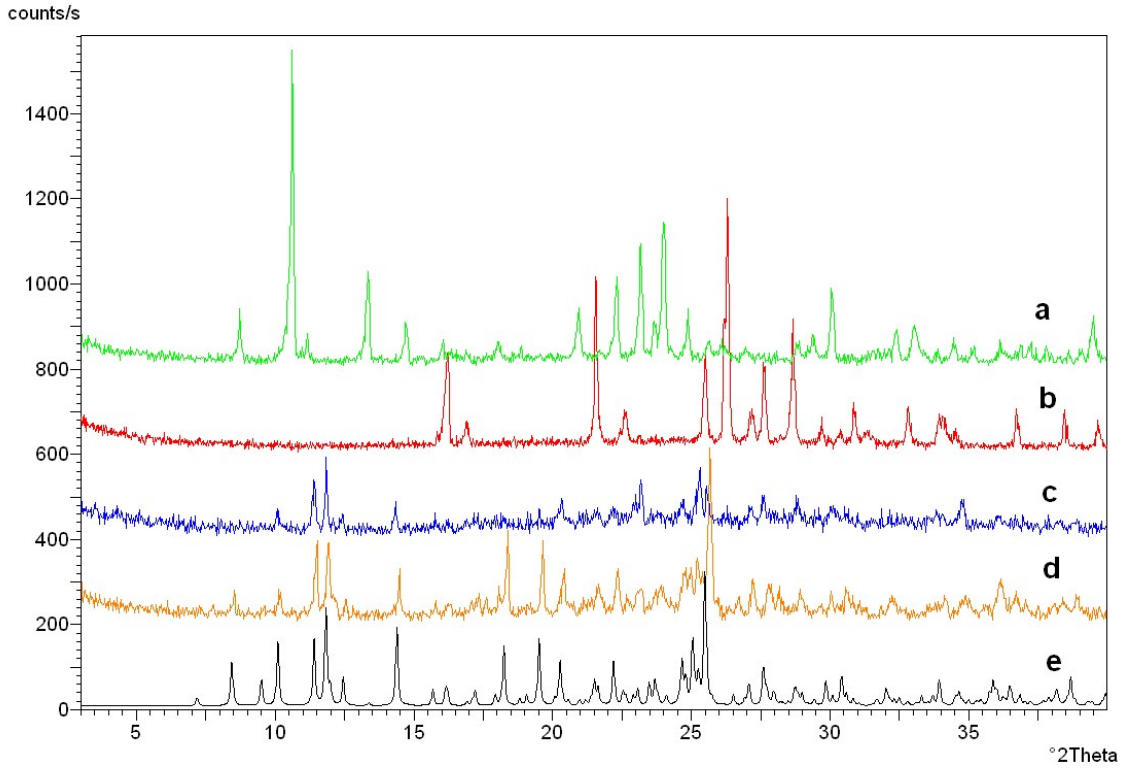

Figure S21. PXRD patterns of: a) pure **1***$3H_2O$, b) **1,4-tfib**, c) product obtained from the solution synthesis experiment, d) product obtained by grinding a mixture with a 1:1 molar ratio **1***$3H_2O$ to **1,4-tfib** in a ball mill for 10 min in the presence of 10 μL of ethanol, e) calculated diffractogram from structure (**1,4-tfib**)(**1**).

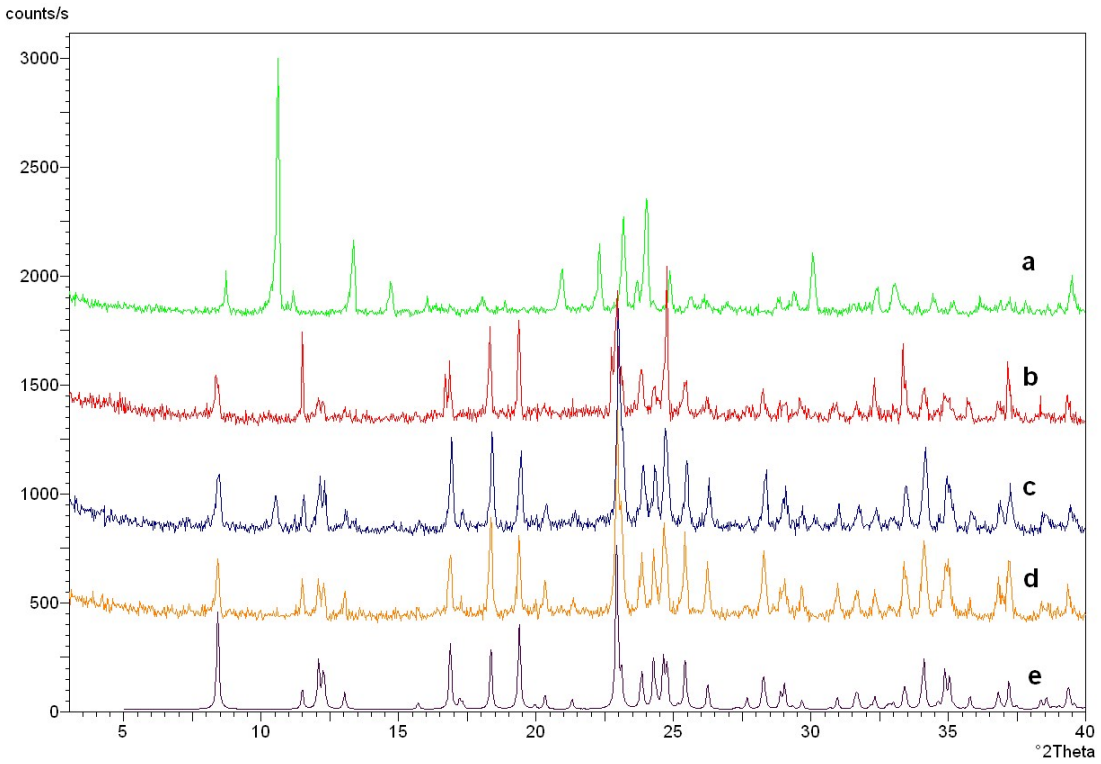

Figure S22. PXRD patterns of: a) pure **1***$3H_2O$, b) product obtained from the solution synthesis experiment, c) product obtained by grinding a mixture with a 1:1 molar ratio **1***$3H_2O$ to **1,3-tfib** in a ball mill for 30 min in the presence of 30 μL of ethanol, d) product obtained by grinding a mixture with a 1:2 molar ratio **1***$3H_2O$ to **1,3-tfib** in a ball mill for 30 min in the presence of 20 μL of ethanol, e) calculated diffractogram from structure (**1,3-tfib**)$_2$(**1**).

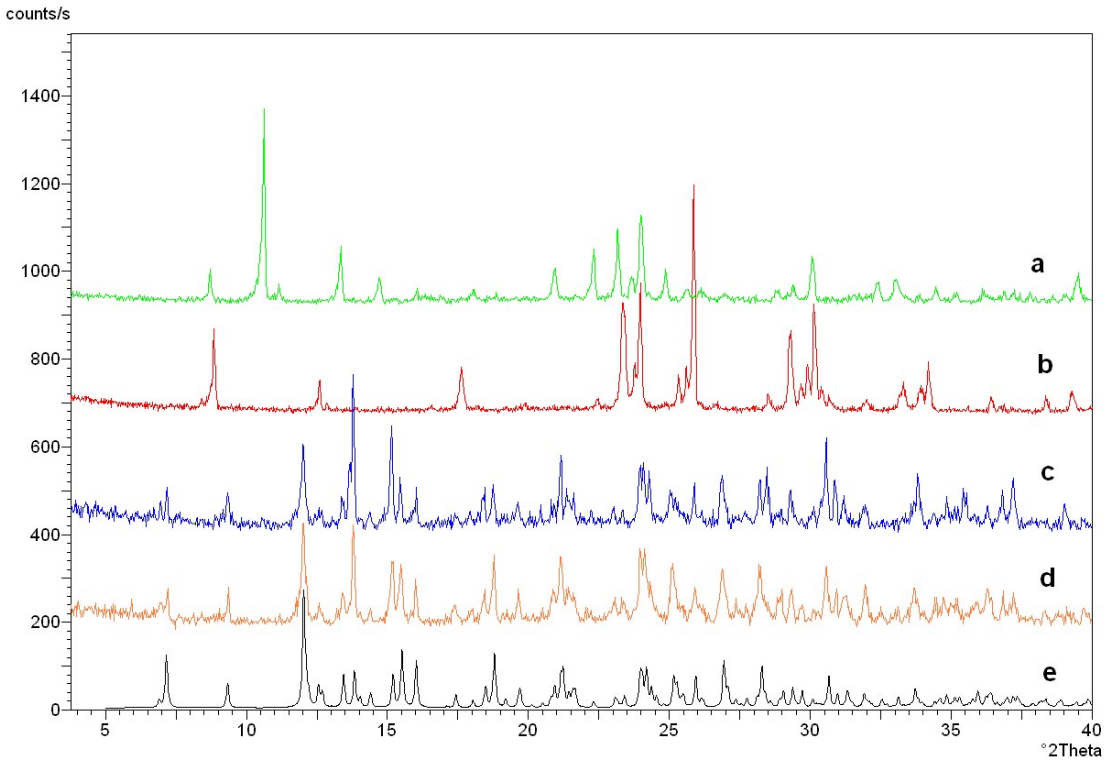

Figure S23. PXRD patterns of: a) pure **1***$3H_2O$, b) **1,2-tfib**, c) product obtained from the solution synthesis experiment, d) product obtained by grinding a mixture with a 1:1 molar ratio **1***$3H_2O$ to **1,2-tfib** in a ball mill for 30 min in the presence of 20 μL of ethanol, e) calculated diffractogram from structure (**1,2-tfib**)(**1**).

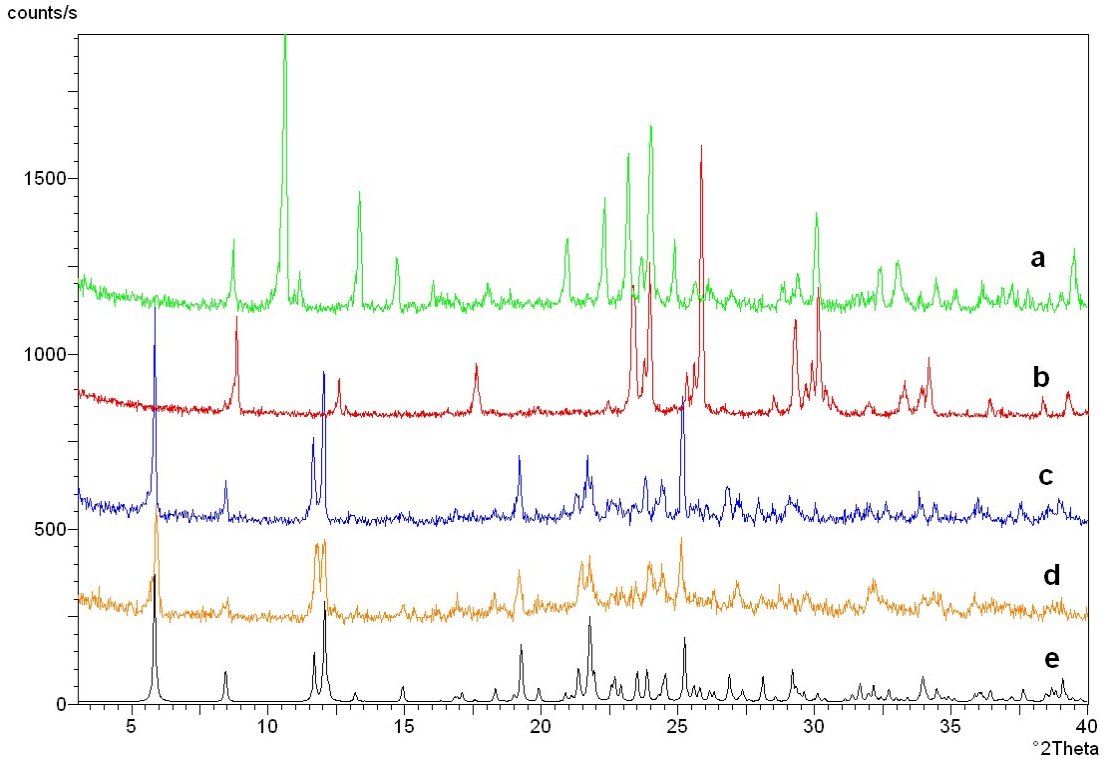

Figure S24. PXRD patterns of: a) pure **1***$3H_2O$, b) **1,2-tfib**, c) product obtained from the solution synthesis experiment, d) product obtained by grinding a mixture with a 1:2 molar ratio **1***$3H_2O$ to **1,2-tfib** in a ball mill for 30 min in the presence of 30 μL of ethanol, e) calculated diffractogram from structure (**12tfib**)$_2$(**1**).

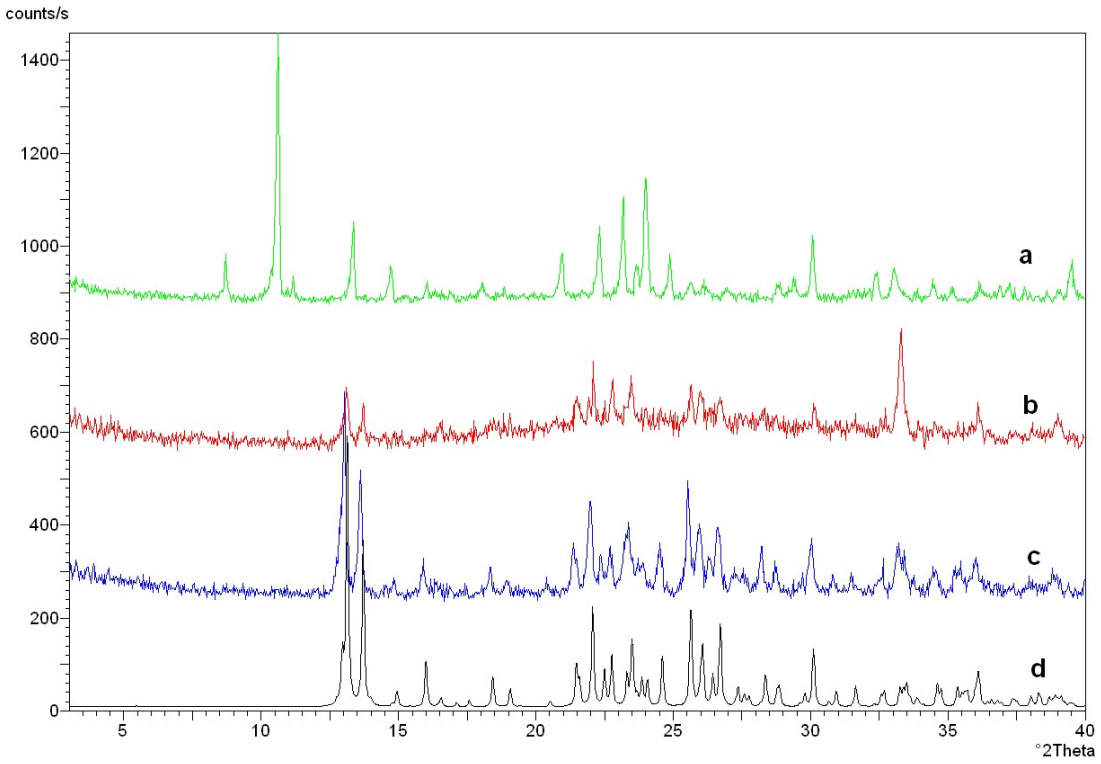

Figure S25. PXRD patterns of: a) pure **1***$3H_2O$, b) product obtained from the solution synthesis experiment, c) product obtained by grinding a mixture with a 1:2 molar ratio **1***$3H_2O$ to **ipfb** in a ball mill for 30 min in the presence of 30 μL of ethanol, d) calculated diffractogram from structure (**ipfb**)$_2$(**1**).

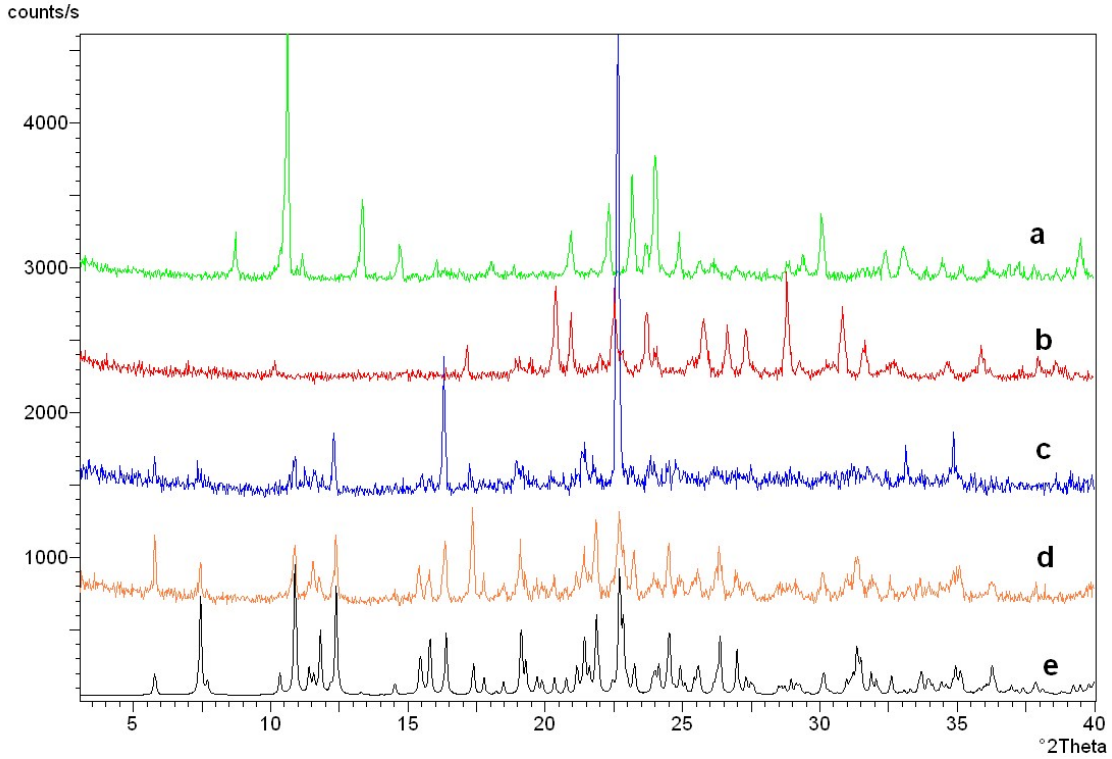

Figure S26. PXRD patterns of: a) pure **1***$3H_2O$, b) **1,3,5-tfib**, c) product obtained from the solution synthesis experiment, d) product obtained by grinding a mixture with a 1:1 molar ratio **1***$3H_2O$ to **1,3,5-tfib** in a ball mill for 10 min in the presence of 45 μL of ethanol, e) calculated diffractogram from structure (**1,3,5-tfib**)(**1**)(EtOH).

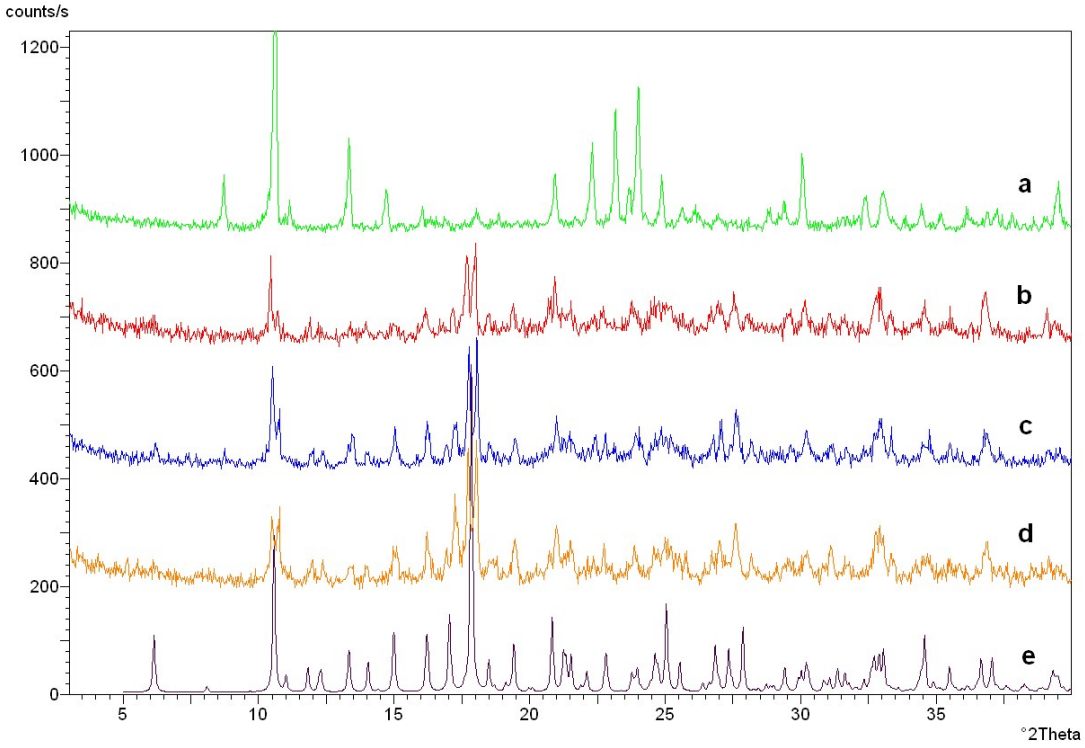

Figure S27. PXRD patterns of: a) pure **1***$3H_2O$, b) product obtained from the solution synthesis experiment, c) product obtained by grinding a mixture with a 1:1 molar ratio **1***$3H_20$ to **ofib** in a ball mill for 30 min in the presence of 30 μL of ethanol, d) product obtained by grinding a mixture with a 1:2 molar ratio **1***$3H_2O$ to **ofib** in a ball mill for 30 min in the presence of 20 μL of ethanol, e) calculated diffractogram from structure (**ofib**)$_2$(**1**).

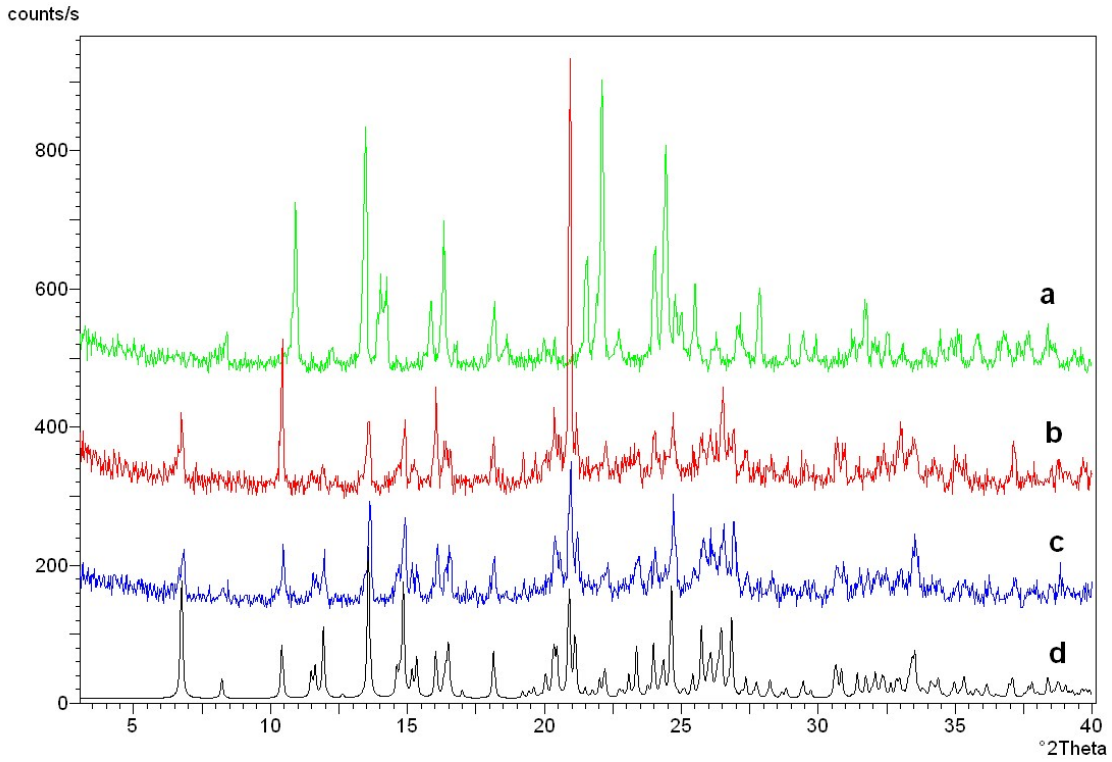

Figure S28. PXRD patterns of: a) pure **2**, b) product obtained from the solution synthesis experiment, c) product obtained by grinding a mixture with a 1:1 molar ratio **2** to **1,3-tfib** in a ball mill for 30 min in the presence of 30 μL of ethanol, d) calculated diffractogram from structure (**1,3-tfib**)(**2**).

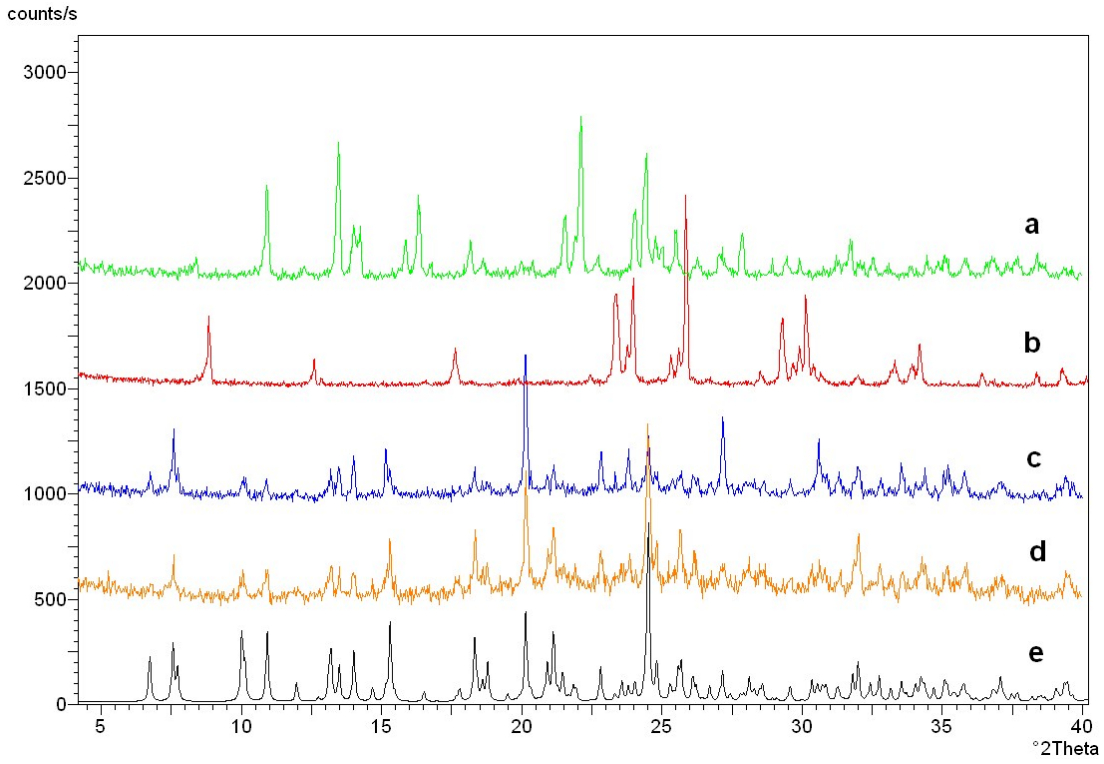

Figure S29. PXRD patterns of: a) pure **2**, b) **1,2-tfib**, c) product obtained from the solution synthesis experiment, d) product obtained by grinding a mixture with a 1:1 molar ratio **2** to **1,2-tfib** in a ball mill for 30 min in the presence of 40 μL of ethanol, e) calculated diffractogram from structure (**1,2-tfib**)(**2**).

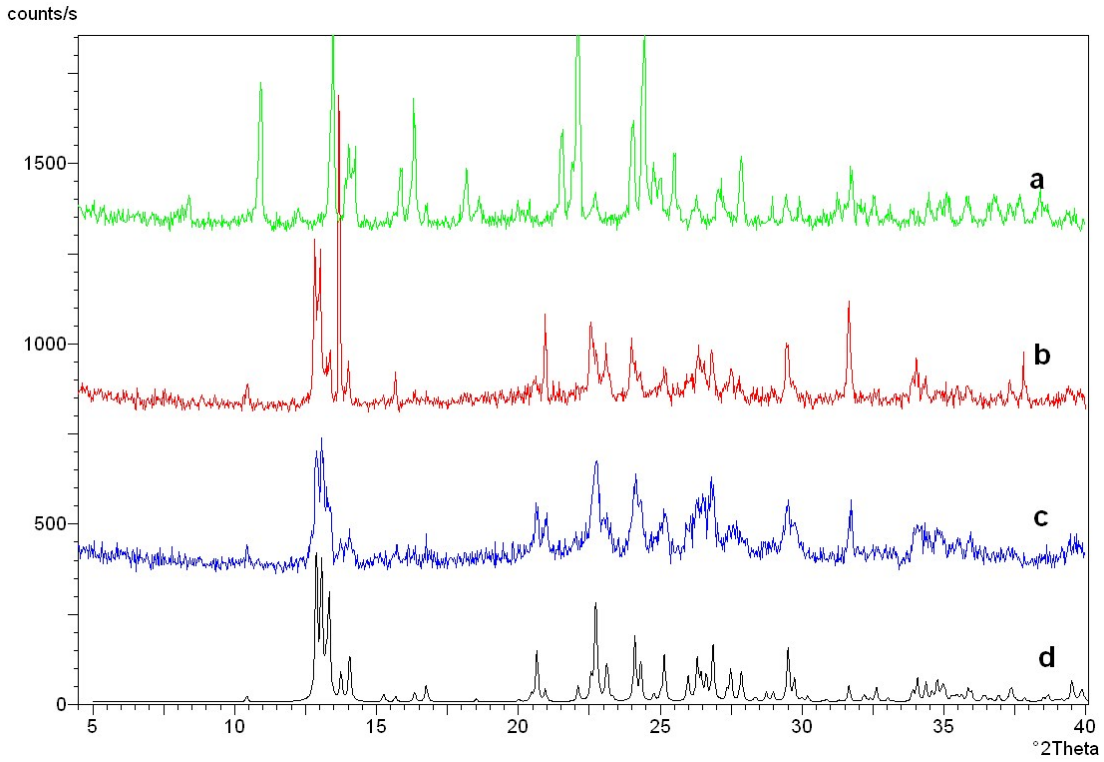

Figure S30. PXRD patterns of: a) pure **2**, b) **1,2-tfib**, c) product obtained from the solution synthesis experiment, d) product obtained by grinding a mixture with a 1:1 molar ratio **2** to **1,2-tfib** in a ball mill for 30 min in the presence of 40 μL of ethanol, e) calculated diffractogram from structure (**1,2-tfib**)(**2**).

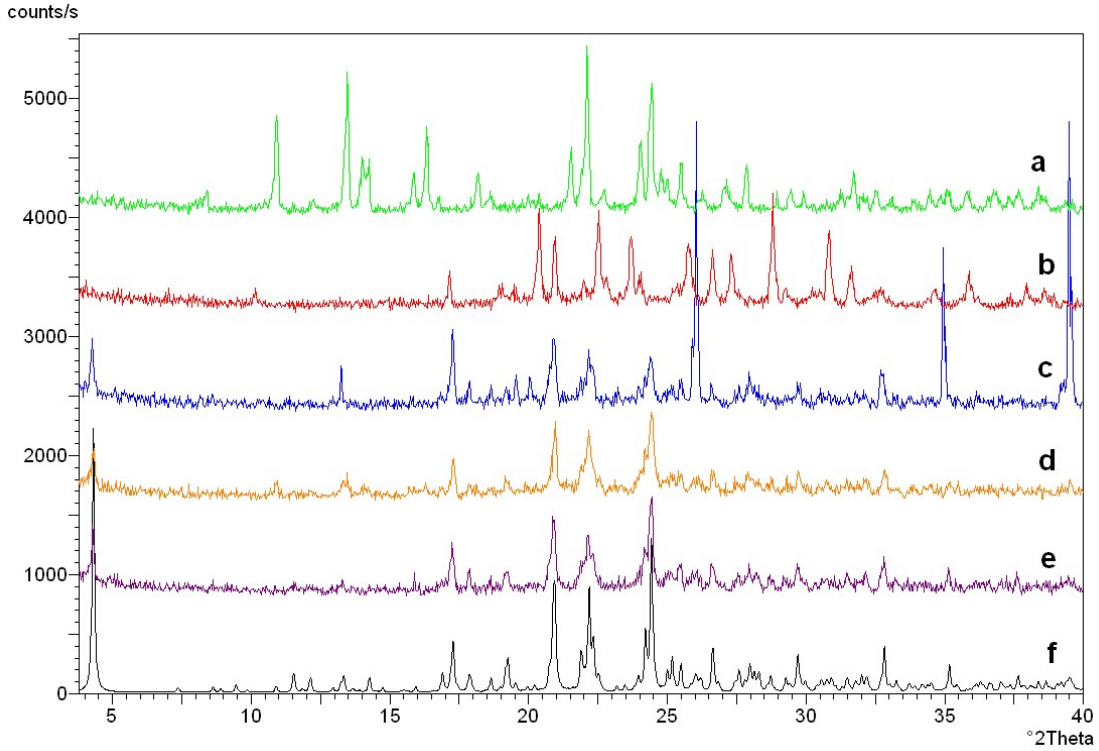

Figure S31. PXRD patterns of: a) pure **2** b) **1,3,5-tfib**, c) product obtained from the solution synthesis experiment, d) product obtained by grinding a mixture with a 1:1 molar ratio **2** to **1,3,5-tfib** in a ball mill for 20 min in the presence of 40 μL of ethanol, e) product obtained by grinding a mixture with a 1:3 molar ratio **2** to **1,3,5-tfib** in a ball mill for 30 min in the presence of 40 μL of ethanol f) calculated diffractogram from structure (**1,3,5-tfib**)$_3$(**2**).

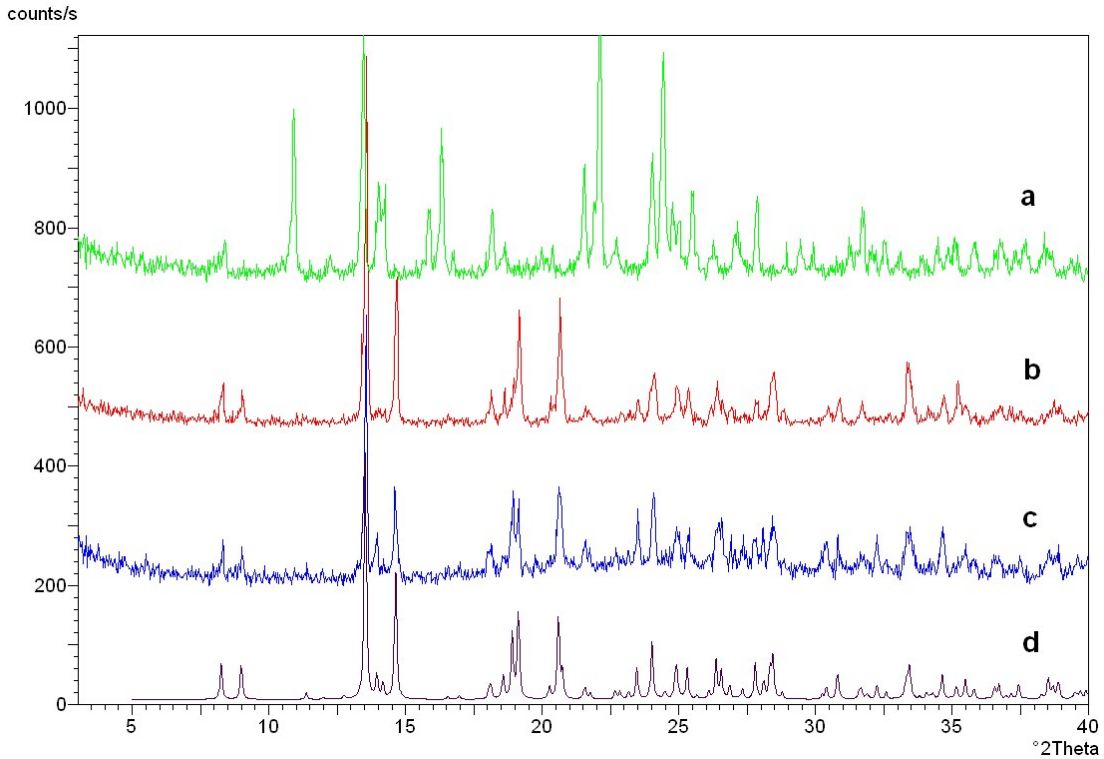

Figure S32. PXRD patterns of: a) pure **2**, b) product obtained from the solution synthesis experiment, c) product obtained by grinding a mixture with a 1:1 molar ratio **2** to **ofib** in a ball mill for 30 min in the presence of 40 μL of ethanol, d) calculated diffractogram from structure (**ofib**)(**2**).

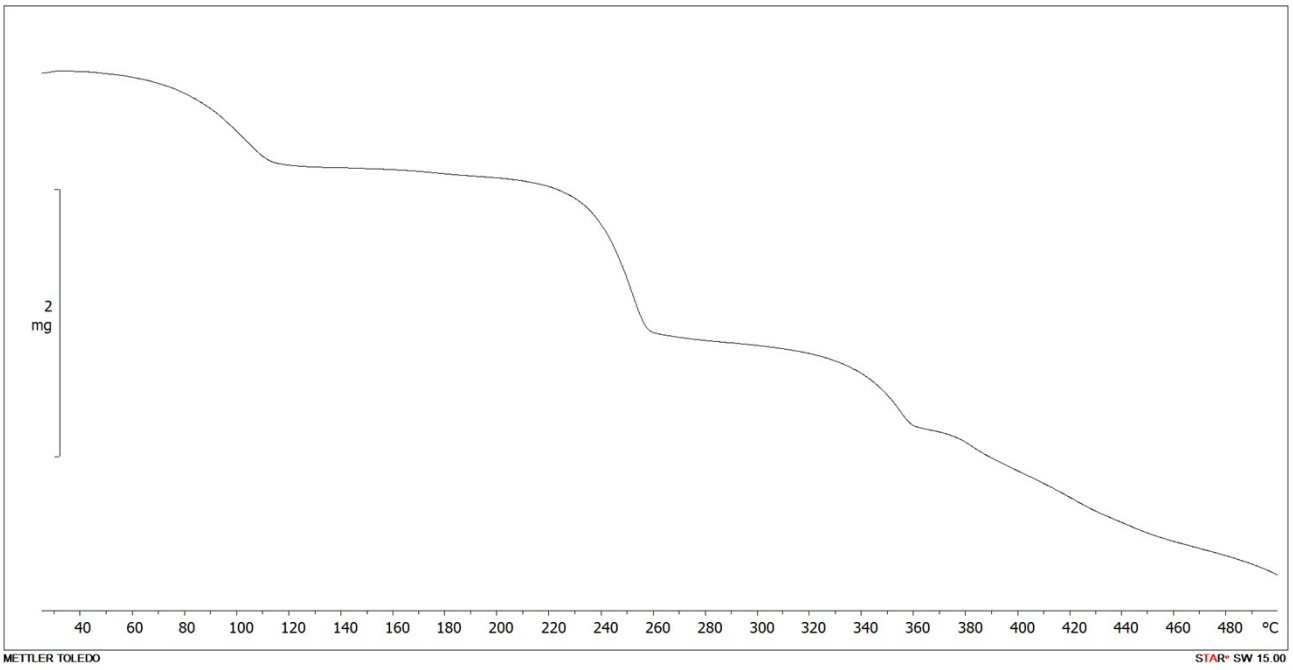

Figure S33. TG curve of pure **1***3H_2O.

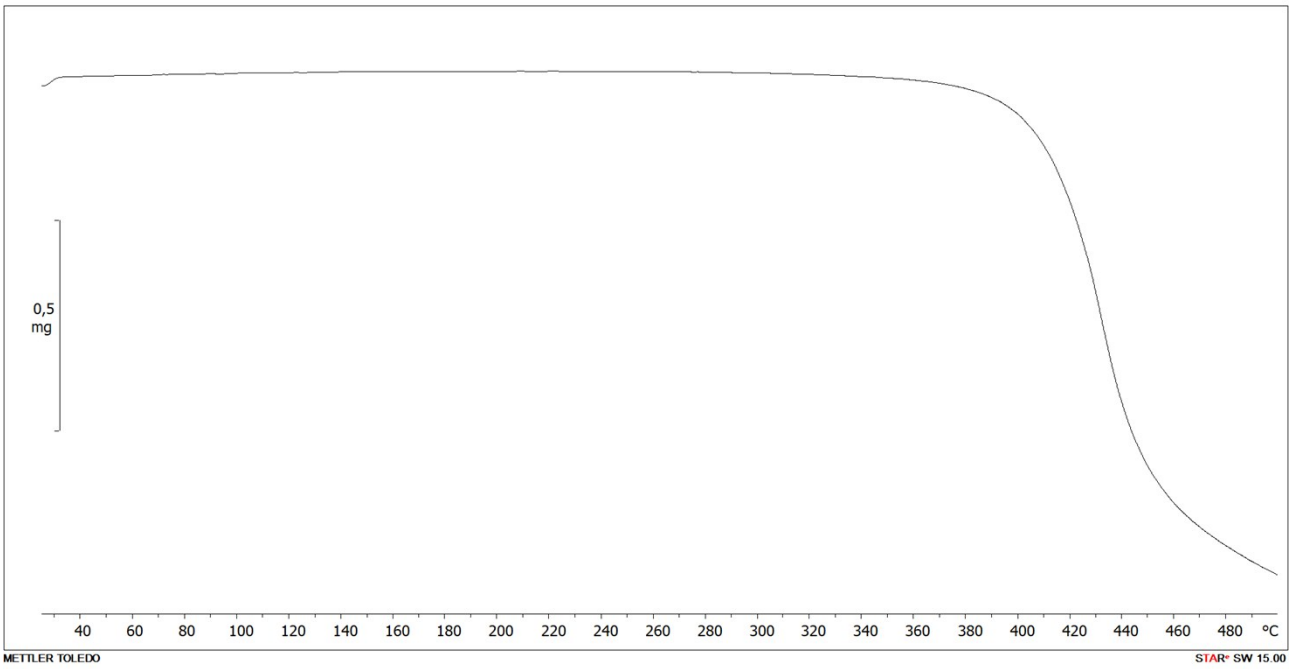

Figure S34. TG curve of pure **2**.

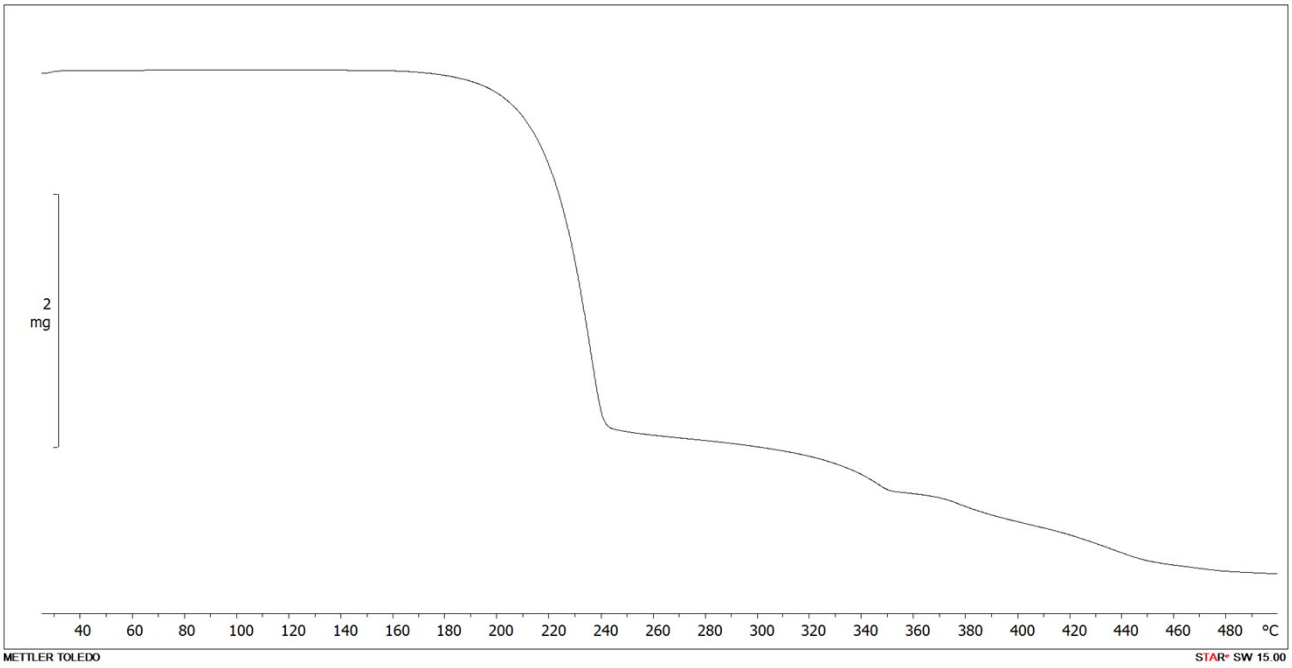

Figure S35. TG curve of the cocrystal (**1,4-tfib**)(**1**).

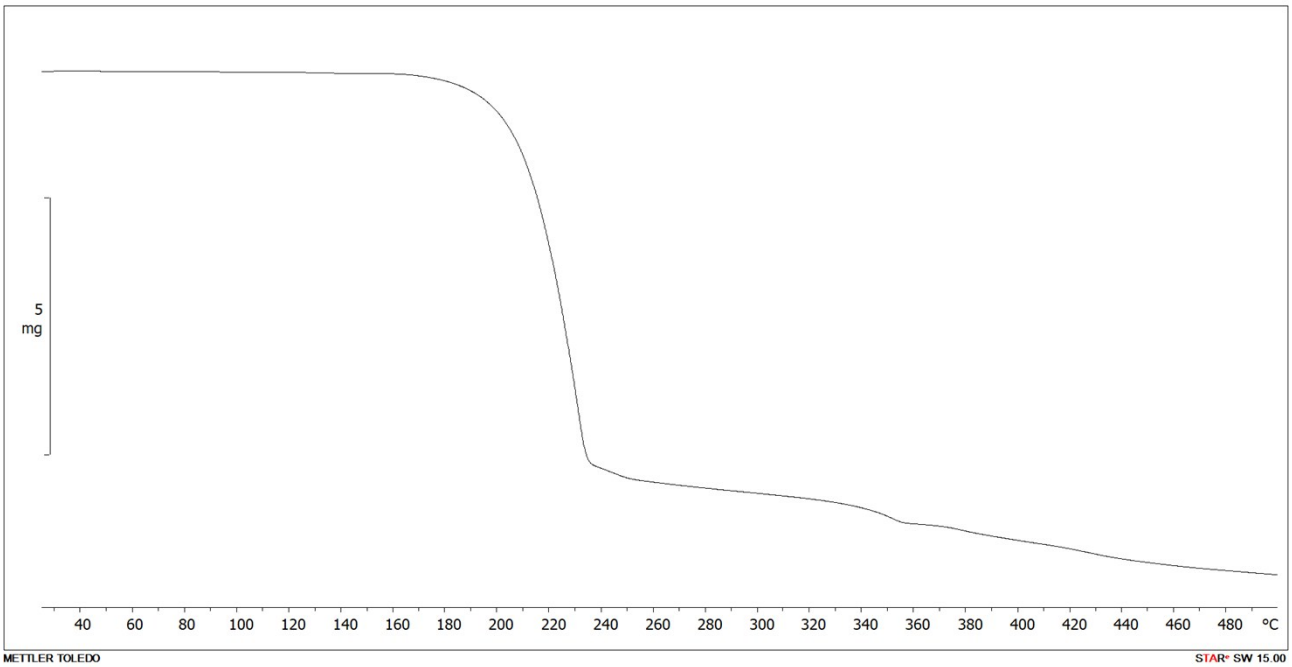

Figure S36. TG curve of the cocrystal (**1,3-tfib**)$_2$(**1**).

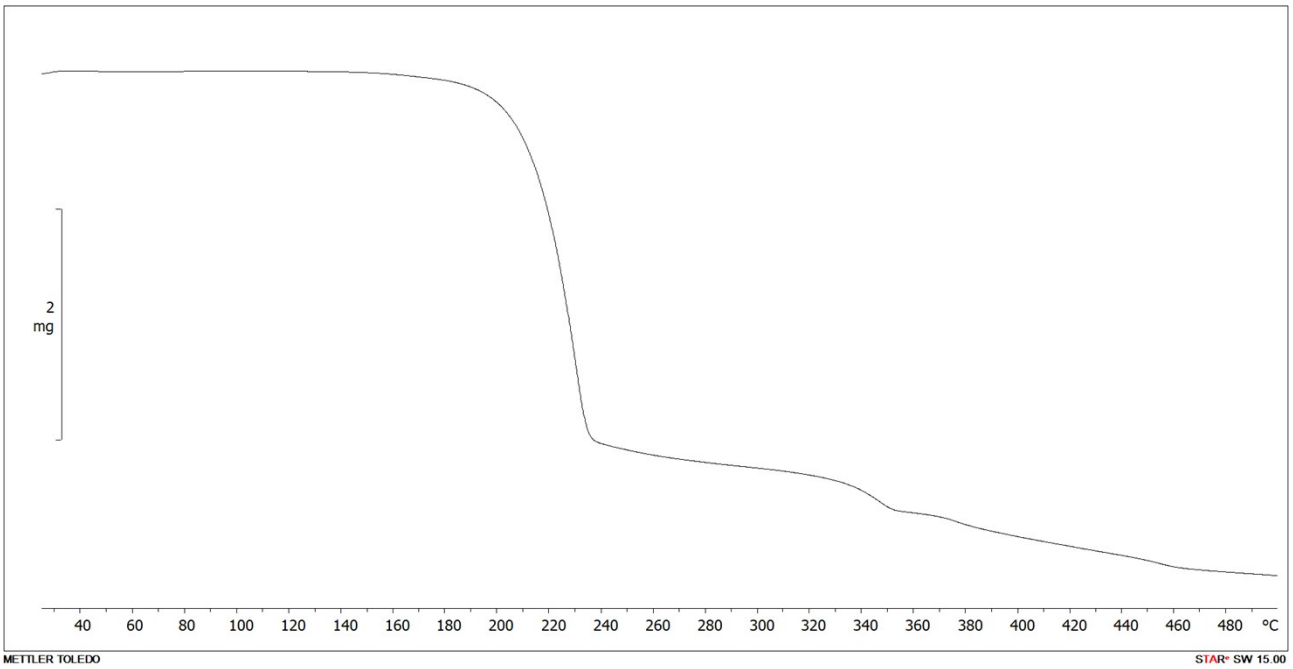

Figure S37. TG curve of the cocrystal (**1,2-tfib**)(**1**).

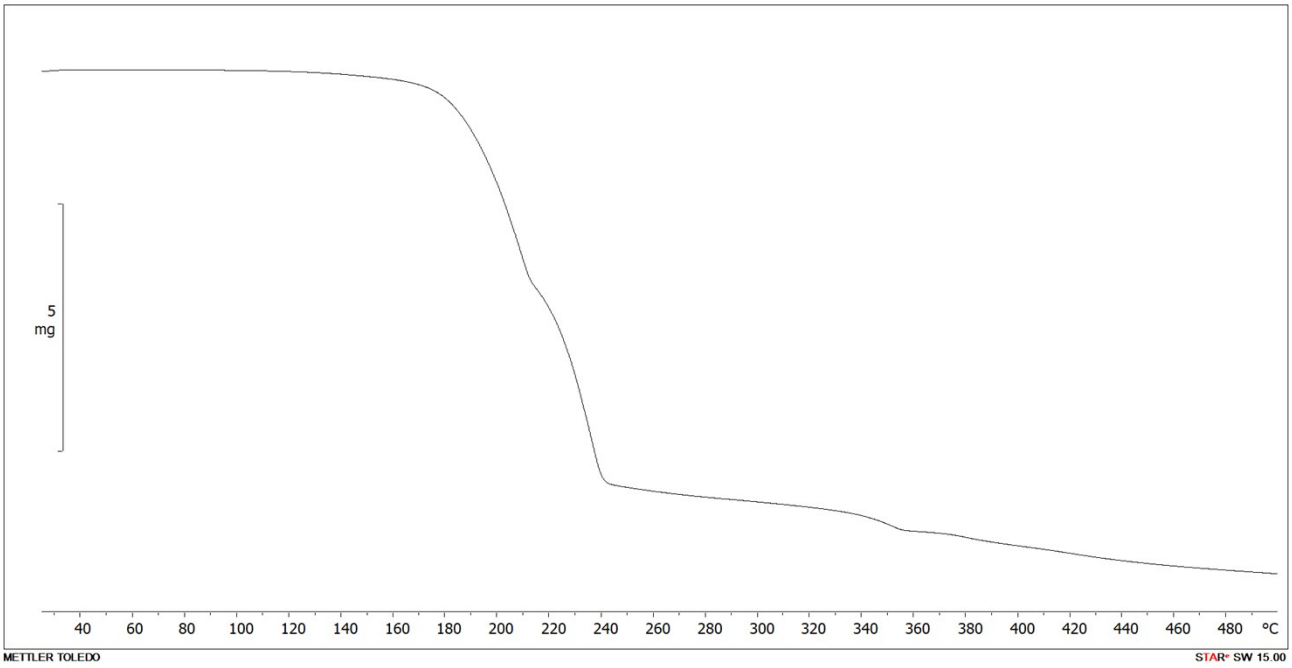

Figure S38. TG curve of the cocrystal (**1,2-tfib**)$_2$(**1**).

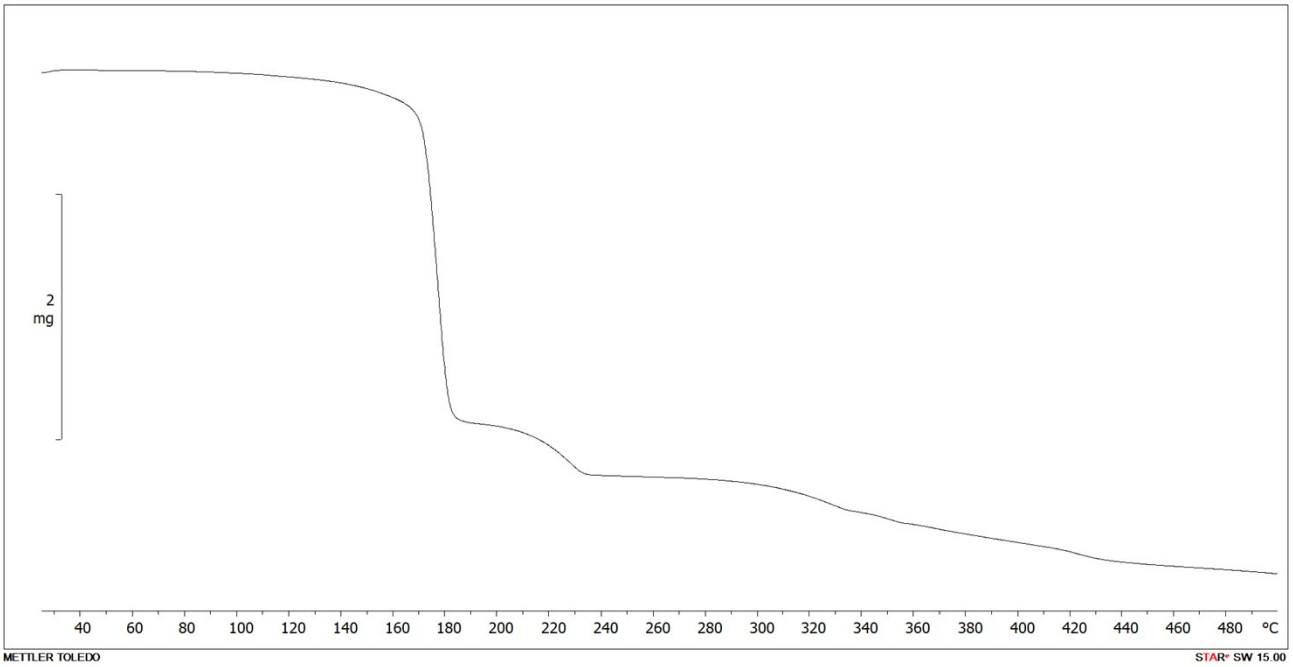

Figure S39. TG curve of the cocrystal (**ipfb**)$_2$(**1**).

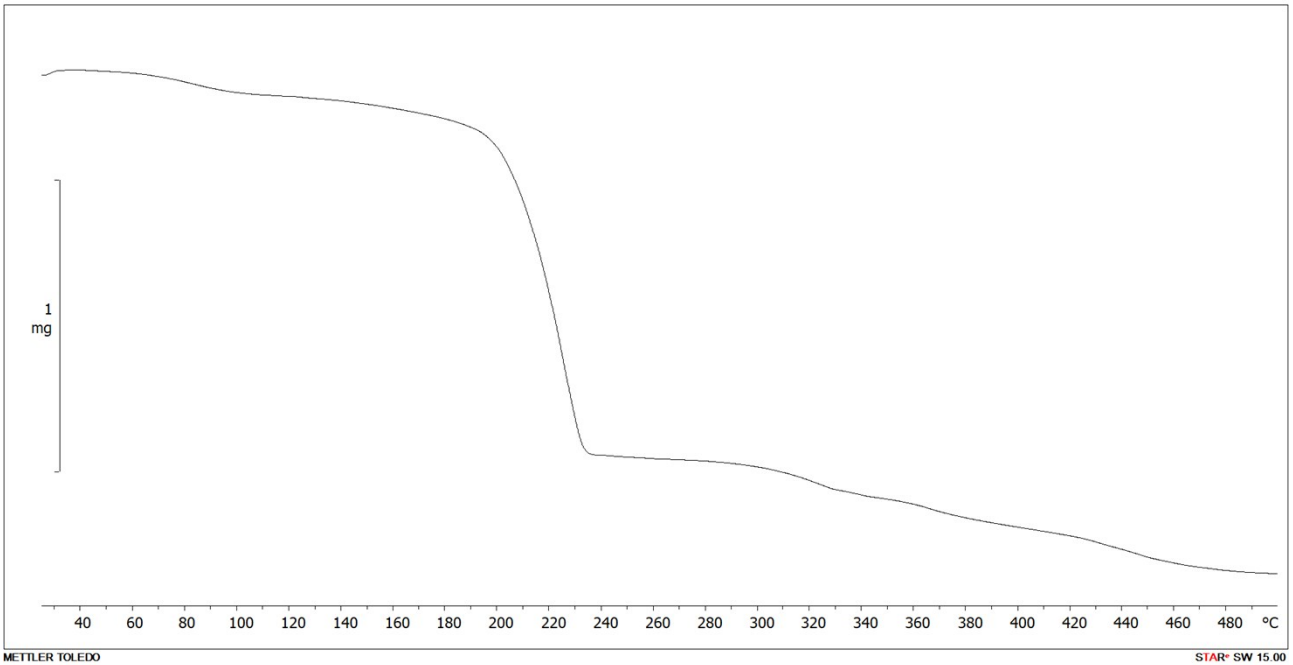

Figure S40. TG curve of the cocrystal (**1,3,5-tfib**)(**1**)(EtOH).

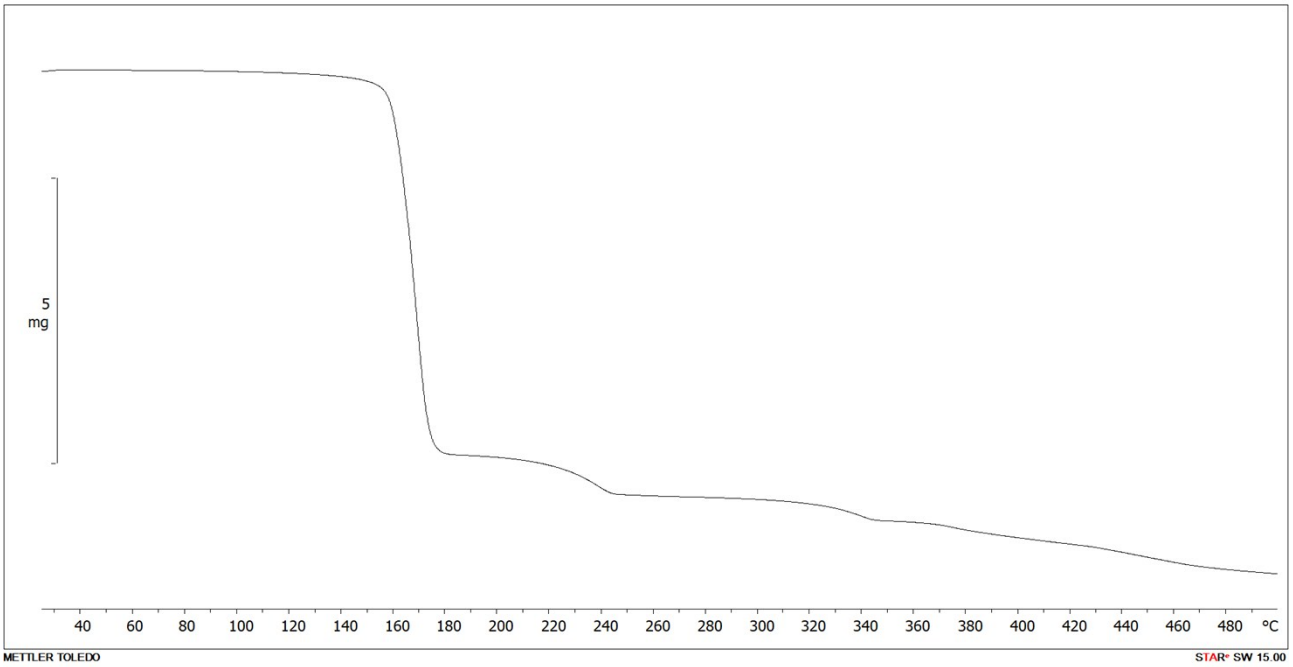

Figure S41. TG curve of the cocrystal (**ofib**)$_2$(**1**).

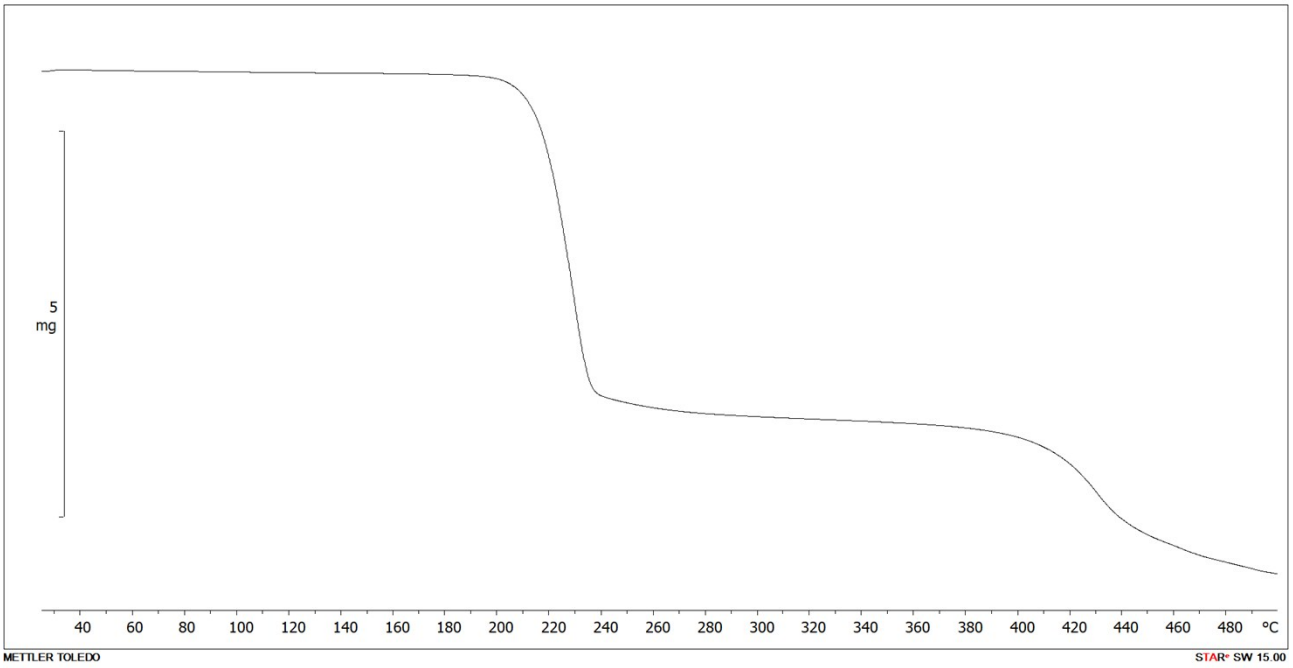

Figure S42. TG curve of the cocrystal (**1,3-tfib**)(**2**).

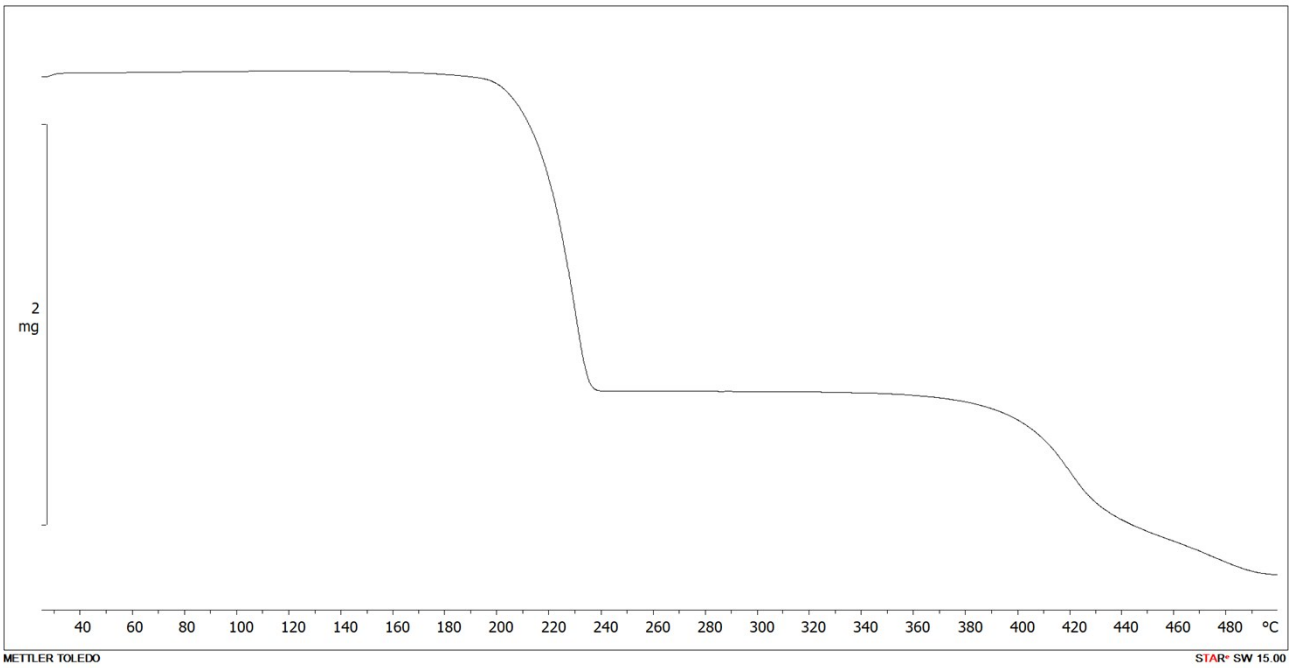

Figure S43. TG curve of the cocrystal (**1,2-tfib**)(**2**).

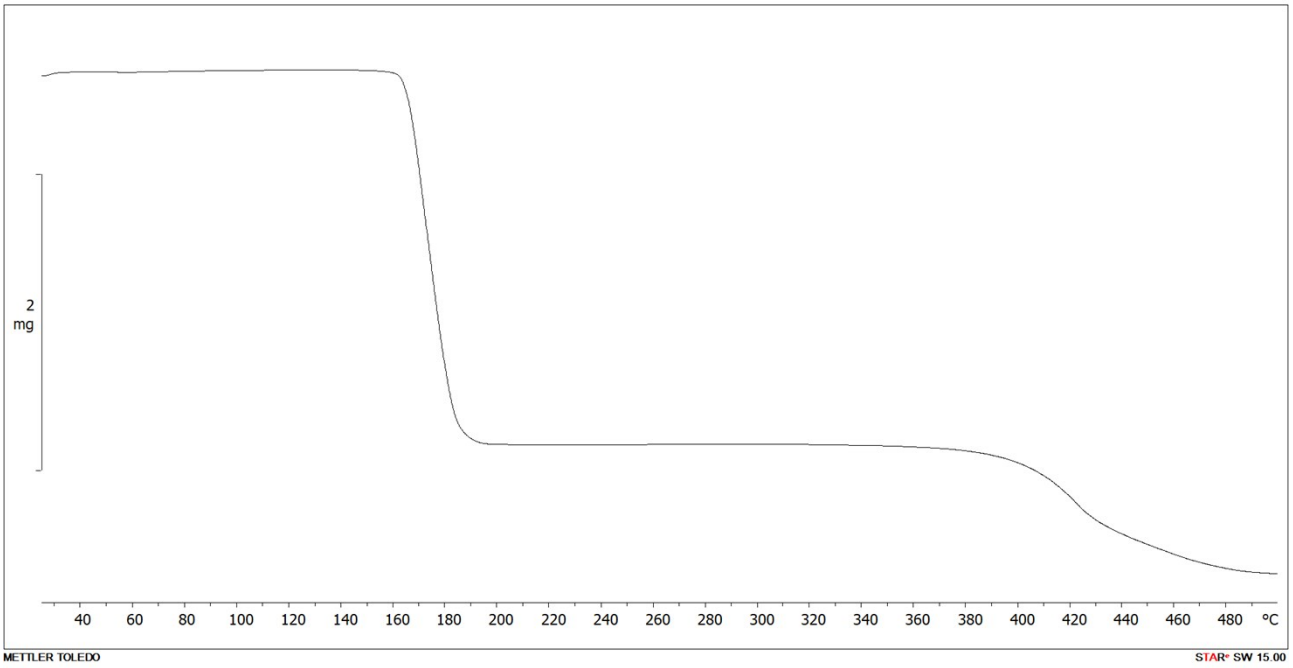

Figure S44. TG curve of the cocrystal (**ipfb**)$_2$(**2**).

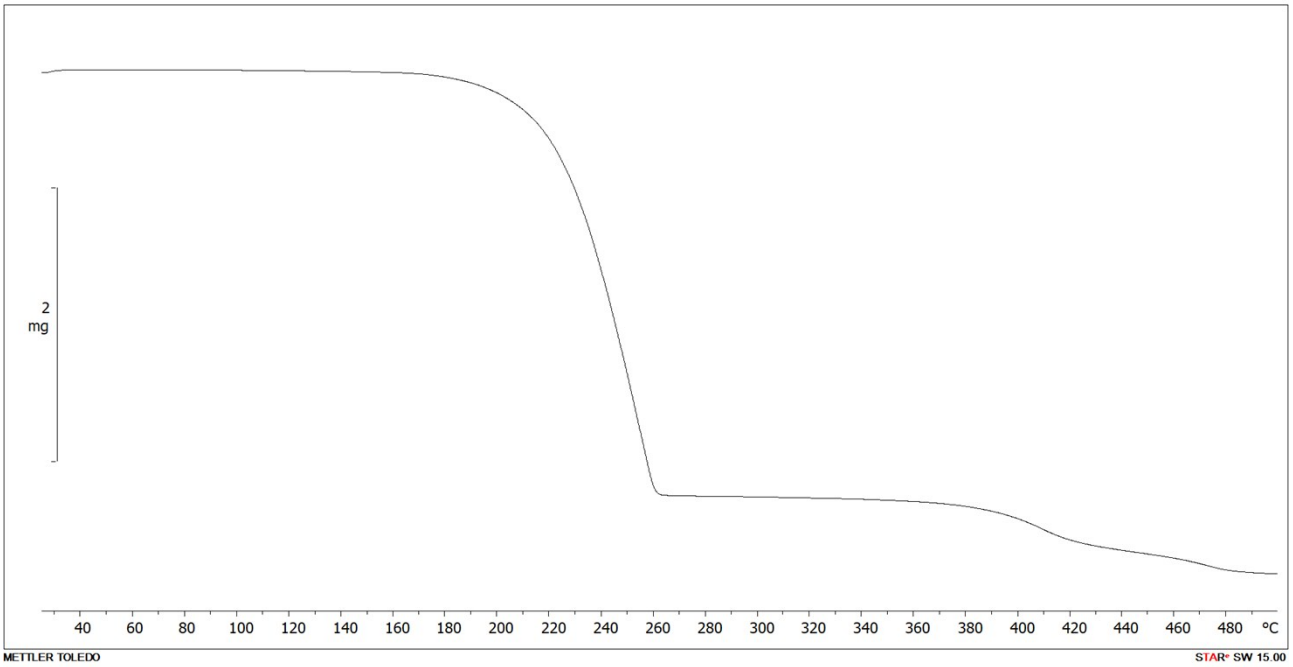

Figure S45. TG curve of the cocrystal (**1,3,5-tfib**)$_3$(**2**).

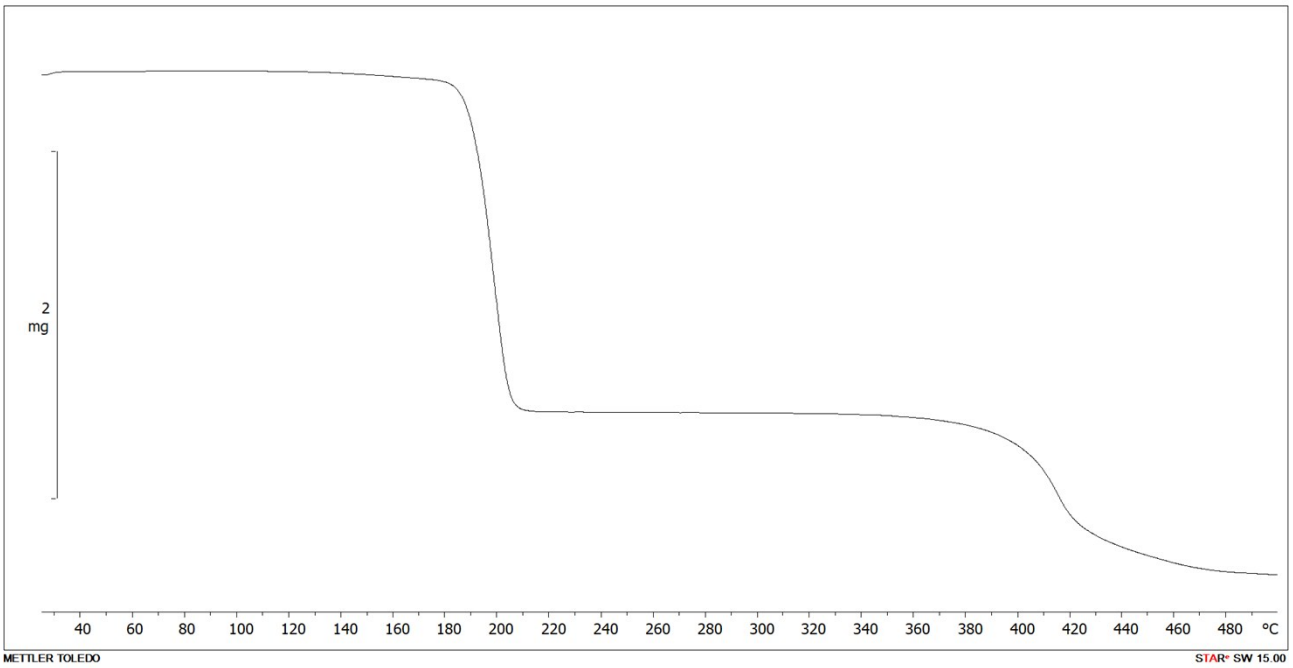

Figure S46. TG curve of the cocrystal (**ofib**)(**2**).