Supporting information

A Zwitterionic Salt-Cocrystal: *In*-Vitro Insights from Niraparib Tosylate an Anti-Cancer Drug

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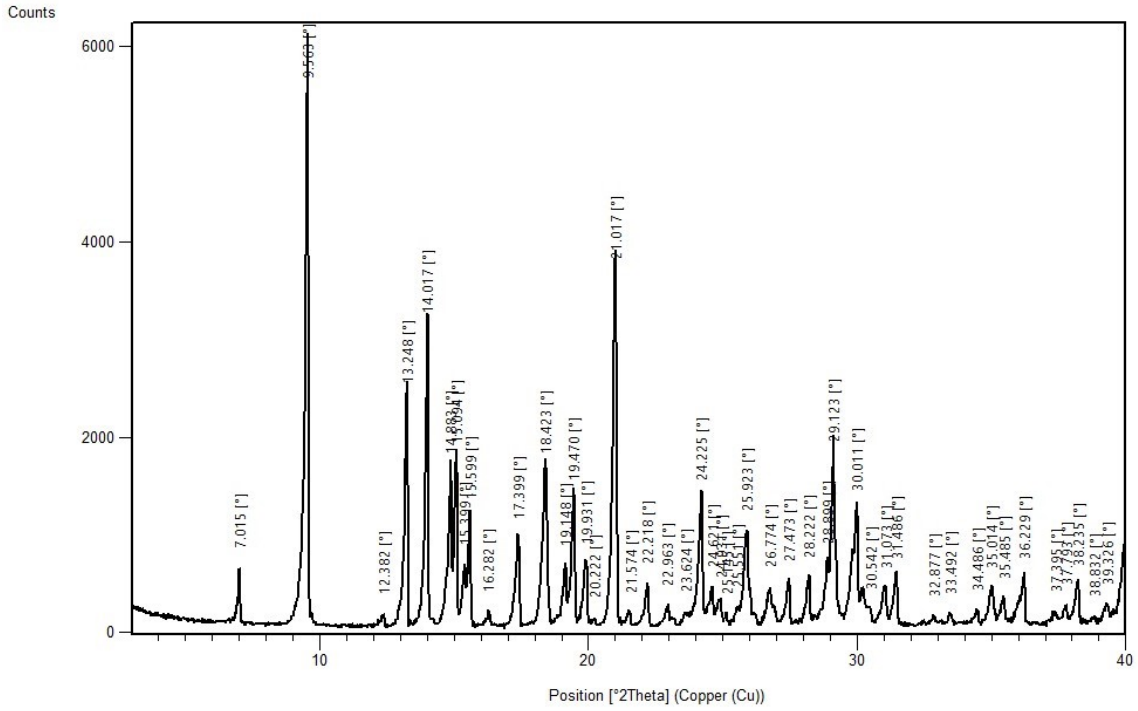

Figure S1: Powder X-ray Diffraction pattern of NIR.TOS.H_2O (Form I).

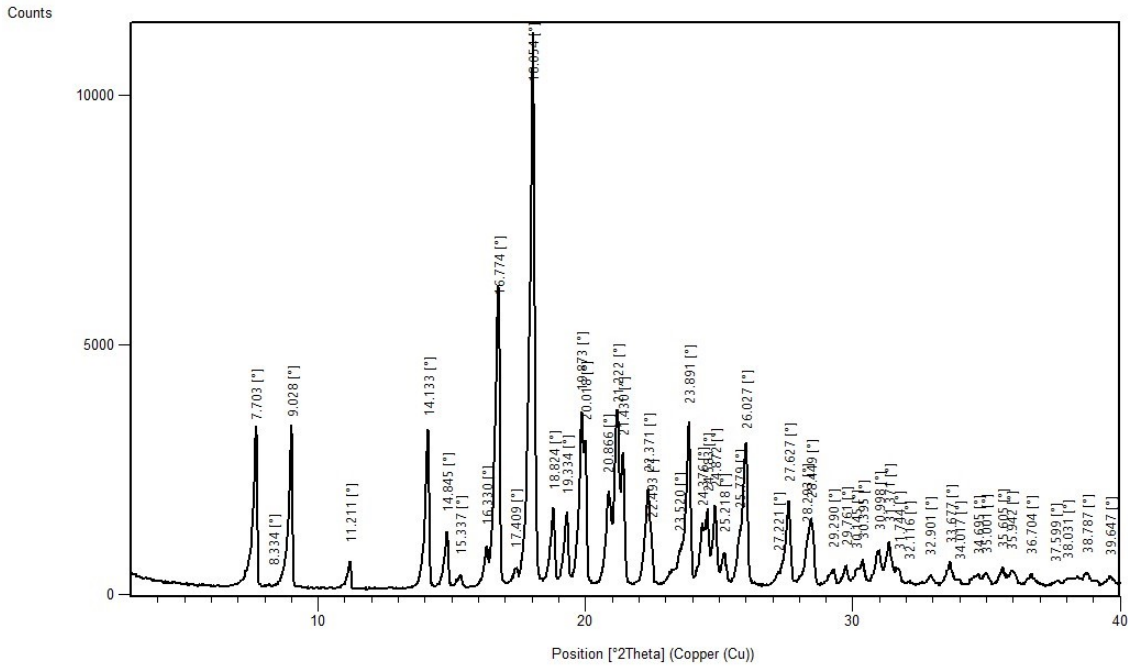

Figure S2: Powder X-ray Diffraction pattern of NIR.TOS.PRO (Zwitterionic salt-cocrystal).

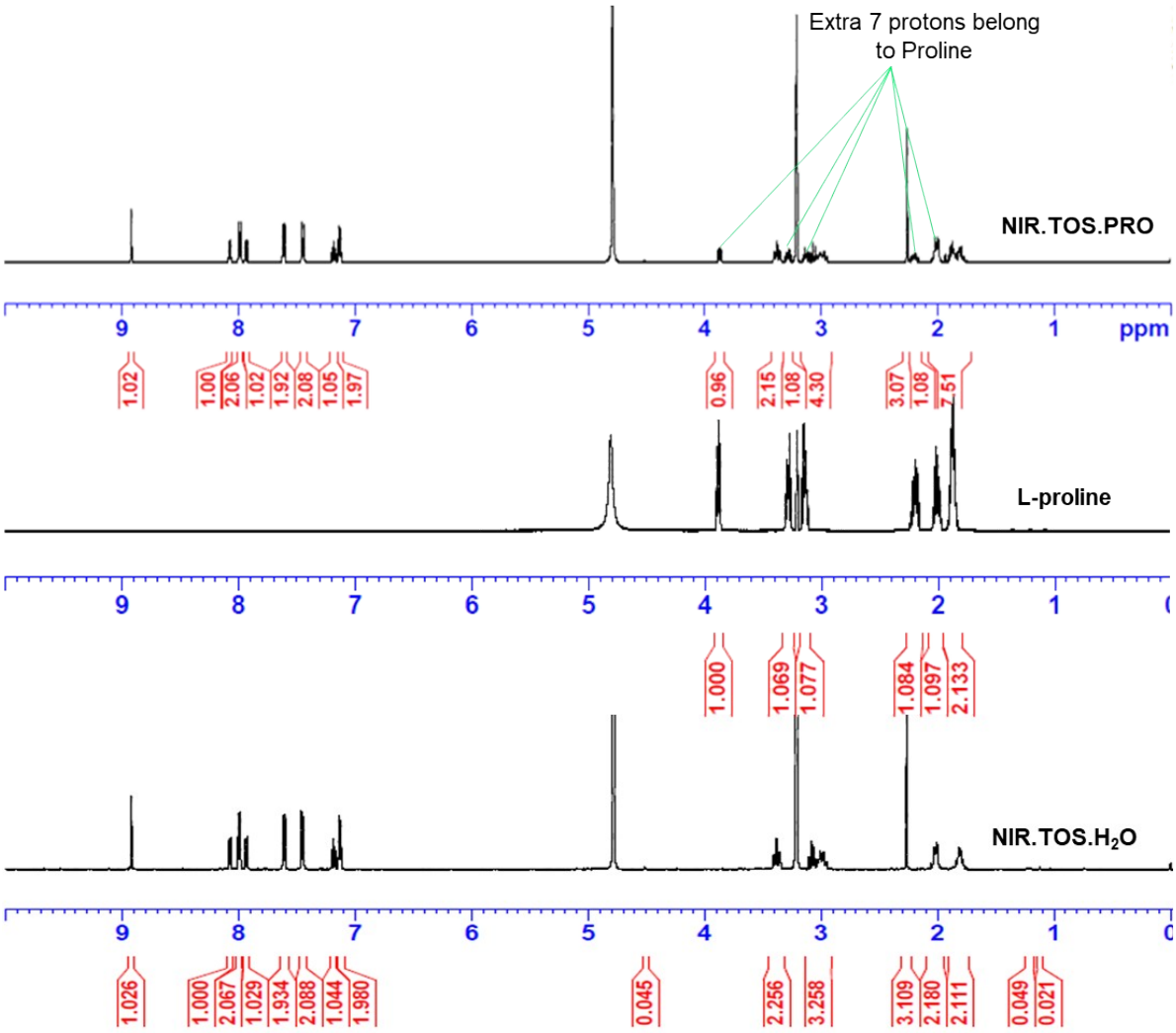

Figure S3. ^{1}H-NMR spectra comparison of NIR.TOS.PRO with its starting materials NIR.TOS.H_2O and L-proline.

Table S1: Experimental polymorph screening details.

Slurry crystallization				
S. No.	**Input Form**	**Solvent**	**Temp. (°C)**	**Result**
1	Amorphous	1,2-Dimethoxy ethane	45-50	Form I
2	Form I	1,2-Dimethoxyethane	45-50	Form I
3	Amorphous	1,2-Propanediol	0-5	Form I
4	Amorphous	1,4-Dioxane	0-5	Form I
5	Form I	1,4-Dioxane	25-30	Form I
6	Form I	1,4-Dioxane	45-50	Form I
7	Form I	2,2,2-Trifluoroethanol	35-40	Solid material not isolated
8	Amorphous	2-Butanol	35-40	Form I
9	Form I	2-Butanol	60-65	Form I

10	Amorphous	2-Methoxy ethanol	0-5	Form I
11	Form I	2-Methoxyethanol	45-50	Form I
12	Amorphous	2-Methyl Tetrahydrofuran	0-5	Form I
13	Form I	2-Methyl Tetrahydrofuran	45-50	Form I
14	Form I	2-Pentanol	35-40	Form I
15	Form I	Acetic Acid	25-30	Form I
16	Form I	Acetone + water	25-30	Form I
17	Form I	Acetone + water	70-75	Form I
18	Amorphous	Acetonitrile	25-30	Form I
19	Amorphous	Acetonitrile	65-70	Form I
20	Form I	Acetonitrile	35-40	Form I
21	Form I	Acetonitrile	70-75	Form I
22	Form I	Acetonitrile + 2-butanol	70-75	Form I
23	Form I	Acetonitrile + 2-butanol + Dimethyl sulfoxide	70-75	Form I
24	Amorphous	Anisole	0-5	Form I
25	Form I	Benzyl alcohol	35-40	Solid material not isolated
26	Form I	Benzyl alcohol	-5 to -10	Form I
27	Amorphous	Chloroform	0-5	Form I
28	Amorphous	Dichloromethane	0-5	Form I
29	Amorphous	Dichloromethane	25-30	Form I
30	Amorphous	Diethyl ether	10-15	Form I
31	Amorphous	Diethyl ether	-5 to -20	Form I
32	Form I	Diethylene glycol	35-40	Solid material not isolated
33	Amorphous	Di isopropyl ether	0-5	Form I
34	Amorphous	Di isopropyl ether	25-30	Form I
35	Amorphous	Dimethoxymethane	0-5	Form I
36	Form I	Dimethoxymethane	25-30	Form I
37	Form I	Ethanol	0-5	Form I
38	Form I	Ethanol	35-40	Form I
39	Amorphous	Ethanol + 1,4-Dioxane	25-30	Form I
40	Form I	Ethanol + water	50-55	Form I
41	Amorphous	Ethylene glycol mono propyl ether	0-5	Form I
42	Form I	Formic Acid	25-30	Form I
43	Form I	Glycerol	35-40	Form I
44	Amorphous	Heptane	0-5	Form I
45	Amorphous	Heptane	25-30	Form I
46	Amorphous	Heptane	65-70	Form I
47	Amorphous	Heptane + Acetonitrile	25-30	Form I
48	Form I	Heptane + Acetonitrile	25-30	Form I
49	Amorphous	Heptane + Acetonitrile	55-60	Form I

50	Form I	Hexanoic acid	35-40	Form I
51	Amorphous	Isobutyl acetate	25-30	Form I
52	Form I	Isobutyl acetate	55-60	Form I
53	Form I	Isopropanol	25-30	Form I
54	Form I	Isopropanol	55-60	Form I
55	Form I	Methanol	45-50	Form I
56	Amorphous	Methanol	-5-0	Form I
57	Amorphous	Petroleum ether	25-30	Form I
58	Amorphous	Petroleum ether	-5 to -10	Form I
59	Amorphous	Petroleum ether + Acetonitrile	25-30	Form I
60	Amorphous	Petroleum ether + Acetonitrile	-5 to -10	Form I
61	Amorphous	Petroleum ether + Ethyl acetate	25	Form I
62	Amorphous	Petroleum ether + Heptane	25-30	Form I
63	Form I	pH 4.5 buffer	25-30	Form I
64	Amorphous	pH 4.5 buffer	25-30	Form I
65	Form I	pH 6.8 buffer	25-30	Form I
66	Form I	Sulfolane	35-40	Form I
67	Form I	Xylene	95-100	Form I

Recrystallization

S. No.	Input Form	Solvent	Temp. (°C)	Result
1	Form I	Dimethyl formamide	0-5	Form I
2	Form I	Dimethyl acetamide	0-5	Form I
3	Form I	Dimethyl sulfoxide	0-5	Form I
4	Form I	Methanol	-20 to -25	Form I
5	Form I	Ethanol	-20 to -25	Form I
6	Form I	Methanol + Ethanol	-20 to -25	Form I
7	Form I	Methanol + DMSO	0-5	Form I
8	Form I	2-Methoxy ethanol	-20 to -25	Form I
9	Form I	2-Ethoxy ethanol	-20 to -25	Form I
10	Form I	N-Methyl pyrrolidine	0-5	Form I
10	Form I	Acetic acid	-20 to -25	Form I
11	Form I	Formic acid	-20 to -25	Solid material not isolated

Normal anti-solvent addition

S. No.	Input Form	Solvent	Anti-solvent	Temp. (°C)	Result
1	Form I	Acetic acid	n-Heptane	40-45	Form I
2	Form I	Acetic Acid	n-Heptane	-10 to -15	Form I
3	Form I	Acetic acid + Ethanol	Methyl tertiary butyl ether	25-30	Form I
4	Amorphous	Benzyl alcohol	Dichloromethane + Ethyl acetate	0-5	Form I
5	Form I	Dimethyl sulfoxide	Acetone	0-5	Form I

6	Form I	Dimethyl sulfoxide + Ethanol	Methyl tertiary butyl ether	-5 to -10	Form I
7	Form I	Dimethyl sulfoxide + Methanol	Methyl tertiary butyl ether	25-30	Form I
8	Amorphous	Formic acid	Acetone + Methyl tertiary butyl ether	25-30	Form I
9	Form I	Formic acid	Hexane + Methyl tertiary butyl ether	70-75	Form I
10	Form I	N-Methyl pyrrolidine	Acetone	0-5	Form I
11	Form I	Ethanol	Acetone	0-5	Form I
12	Form I	N-Methyl pyrrolidine + Methanol	Methyl tertiary butyl ether	25-30	Form I
13	Form I	Trichloroacetic acid	Heptane + Methyl tertiary butyl ether	70-75	Form I
14	Form I	Trichloroacetic acid	Methyl tertiary butyl ether	70-75	Form I
15	Form I	Trifluoroethanol	Methyl tertiary butyl ether	-5 to -10	Form I
16	Form I	Methanol	Methyl tertiary butyl ether	25-30	Form I
17	Form I	Methanol	Diethyl ether	25-30	Form I
18	Form I	Trifluoroethanol + Methanol	Methyl tertiary butyl ether	25-30	Form I
Reverse antisolvent addition					
S. No.	**Input Form**	**Anti-solvent**	**Solvent**	**Temp. (°C)**	**Result**
1	Form I	1,4-Dioxane	Acetic acid	-10 to -15	Form I
2	Form I	1,4-Dioxane	Dimethyl acetamide	-10 to -20	Form I
3	Form I	1,4-dioxane + Chloroform	Formamide	65-70	Form I
4	Form I	Chloroform	Dimethyl acetamide	65-70	Form I
5	Form I	Chloroform + Methyl tertiary butyl ether	Dimethyl acetamide	65-70	Form I
6	Form I	Dichloromethane	Dimethyl sulfoxide	-15 to -20	Form I
7	Form I	Dichloromethane + acetonitrile	N-Methyl pyrrolidine	50-55	Form I
8	Form I	Dichloromethane + Acetonitrile	Formamide	50-55	Form I
9	Form I	Diethyl ether	Dimethyl sulfoxide	-15 to -20	Form I
10	Form I	Dimethyl carbonate	2-Methoxyethanol	65-70	Form I

11	Form I	Heptane	Ethanol + Methanol	0-5	Form I
12	Form I	Methyl tertiary butyl ether	Acetic acid + 1,4-Dioxane	-10 to -15	Form I
13	Form I	Methyl tertiary butyl ether	Dimethyl acetamide	-10 to -15	Form I
14	Form I	n-Heptane	Methanol + 1,4-Dioxane	-15 to -20	Form I
15	Form I	Toluene	Dimethyl sulfoxide	65-70	Form I
16	Form I	Vinyl acetate	2-Methoxyethanol	65-70	Form I
17	Form I	Water	Benzyl alcohol	0-5	Form I
18	Form I	Xylene	Formamide	65-70	Form I

Reactive crystallization

S. No.	Input Form	PTSA (mole eqv.)	Solvent	Antisolvent	Temp. (°C)	Result
1	Niraparib free base	1	1,2 Dichloroethane + Methanol	Heptane	-15 to -20	Form I
2	Niraparib free base	1	1,2 Propanediol	Methyl tertiary butyl ether	50-55	Form I
3	Niraparib free base	1	1,2 Propanediol	Water	0-5	Form I
4	Niraparib free base	1	1,2 Propanediol	Heptane	-15 to -20	Form I
5	Niraparib free base	1	1,4 Dioxane	NA	50-55	Form I
6	Niraparib free base	1	1,4 Dioxane	NA	0-5	Form I
7	Niraparib free base	1	1,4-Dioxane + Ethanol	Heptane	-5 to -10	Form I
8	Niraparib free base	1	2-Hexanone	Heptane	-5 to -10	Form I
9	Niraparib free base	1	Acetone + Acetic acid	NA	25-30	Form I
10	Niraparib free base	1	Acetonitrile + 1,4 Dioxane	Ethanol + Water	25-80	Form I
11	Niraparib free base	1	Anisole + Ethanol	Heptane	-5 to -10	Form I
12	Niraparib free base	1	Ethanol	NA	50-55	Form I
13	Niraparib free base	1	Ethanol	NA	0-5	Form I
14	Niraparib free base	2	Ethanol	Heptane	0-5	Form I
15	Niraparib free base	1.5	Ethanol	NA	0-5	Form I

16	Niraparib free base	1.5	Ethanol	Heptane	0-5	Form I
17	Niraparib free base	1	Ethanol	Heptane	-15 to -20	Form I
18	Niraparib free base	1	Ethanol	n-Hexane	-15 to -20	Form I
19	Niraparib free base	1	Ethanol+1,4-Dioxane	Heptane	-15 to -20	Unstable novel form
20	Niraparib free base	1	Ethanol + Dichloromethane	Heptane	-15 to -20	Form I
21	Niraparib free base	1	Ethyl formate + Ethanol	Heptane	-15 to -20	Form I
22	Niraparib free base	1	Formic acid	Methyl tertiary butyl ether	-5 to -10	Form I
23	Niraparib free base	1	Formic acid + Acetone	Methyl tertiary butyl ether	0-5	Form I
24	Niraparib free base	1	Isopropyl acetate	NA	-15 to -20	Form I
25	Niraparib free base	1	MEK	Heptane	-15 to -20	Form I
26	Niraparib free base	1	Methanol	NA	25-30	Form I
27	Niraparib free base	1	Methanol	NA	60-65	Form I
28	Niraparib free base	2	Methanol	DIPE	0-5	Form I
29	Niraparib free base	1	Methanol	Methyl tertiary butyl ether + Heptane	0-5	Form I
30	Niraparib free base	1	Methanol	n-Hexane	-15 to -20	Form I
31	Niraparib free base	1	Methyl isobutyl ketone	NA	-15 to -20	Form I
32	Niraparib free base	1	Methyl isobutyl ketone	Heptane	-15 to -20	Form I
33	Niraparib free base	0.5	Methyl isobutyl ketone	Heptane	-15 to -20	Form I
34	Niraparib free base	1	Methyl isobutyl ketone	Heptane	25-30	Form I
35	Niraparib free base	1	Methyl isobutyl ketone + Ethanol	Heptane	-15 to -20	Form I
36	Niraparib free base	1	Nitromethane	Heptane	-15 to -20	Form I
37	Niraparib free base	1	Tetrahydrofuran + Acetone	Heptane	-15 to -20	Form I

38	Niraparib free base	1	Trifluoroethanol	Heptane	-15 to -20	Form I

Table S2: Experimental cocrystal screening details.

Cocrystallization							
S. No.	**Input Form**	**Coformer**	**Mole eqv.**	**Solvent**	**Antisolvent**	**Temp. (°C)**	**Result**
1	Form I	2,5-Dihydroxy benzoic acid	1	Methanol	NA	25-30	Form I
2	Form I	2,5-Dihydroxy benzoic acid	2	Isopropanol	NA	25-30	PM
3	Form I	2,5-Dihydroxy benzoic acid	1.2	Ethyl acetate	NA	25-30	PM
4	Form I	2,5-Dihydroxy benzoic acid	2	Methanol	NA	50-55	PM
5	Form I	2,5-Dihydroxy benzoic acid	2	Tetrahydrofuran	NA	35-40	PM
6	Form I	2,5-Dihydroxy benzoic acid	1	Acetone	NA	35-40	PM
7	Form I	Benzoic acid	2	2,2,2-Trifluoroethanol	Methyl tertiary butyl ether	25-30	PM
8	Form I	Benzoic acid	2	Ethanol	NA	25-30	Form I
9	Form I	Benzoic acid	2	Ethanol	Ethyl acetate	25-30	PM
10	Form I	Benzoic acid	3	Ethanol	Acetone	25-30	PM
11	Form I	Aspartame	1.2	Isopropanol	NA	35-40	PM
12	Form I	Aspartame	1	Isopropanol	NA	70-75	PM
13	Form I	Aspartame	1	Ethyl acetate	NA	70-75	PM
14	Form I	Aspartame	1	Acetonitrile	NA	70-75	PM
15	Form I	Caffeine	1	Methanol	NA	55-60	Form I
16	Form I	Caffeine	2	Tetrahydrofuran	NA	45-50	Form I
17	Form I	Caffeine	3	Methanol	Methyl tertiary butyl ether	55-60	PM
18	Form I	Citric acid	1	Acetone	NA	25-30	Form I
19	Form I	Citric acid	1.2	Isopropyl acetate	NA	50-55	Form I
20	Form I	Citric acid	1	Tetrahydrofuran	NA	25-30	PM
21	Form I	Citric acid	1	Acetonitrile	NA	-5-0	PM
22	Form I	D-Proline	1	Acetonitrile	NA	70-75	Form I

23	Form I	D-Proline	2	Methanol	Acetonitrile	70-75	Form I
24	Form I	D-Tartaric acid	1	Acetone	NA	25-30	Form I
25	Form I	D-Tartaric acid	2	Methanol	NA	25-30	Form I
26	Form I	D-Tartaric acid	1	Methanol	Methyl tertiary butyl ether	35-40	PM
27	Form I	Fumaric acid	1	Methanol	NA	35-40	Form I
28	Form I	Fumaric acid	2	Methanol	Methyl tertiary butyl ether	35-40	PM
29	Form I	Fumaric acid	2	Isobutanol	NA	35-40	PM
30	Form I	Fumaric acid	2	Ethyl acetate	NA	35-40	PM
31	Form I	Fumaric acid	2	Isopropyl acetate	NA	35-40	PM
32	Form I	L-Histidine	1.2	Methanol + Acetonitrile	NA	60-65	PM
33	Form I	L-Histidine	1.2	Ethanol + Acetonitrile	NA	`-15 to -20	Form I
34	Form I	L-Aspartic acid	1.2	Acetonitrile	NA	25-30	PM
35	Form I	L-Aspartic acid	1.2	Methanol + Acetonitrile + water	NA	70-75	Form I
36	Form I	L-Malic acid	3	Methanol	NA	25-30	Form I
37	Form I	L-Malic acid	3	Methanol + Acetone	NA	35-40	Form I
38	Form I	L-Malic acid	3	Isopropanol	NA	50-55	Form I
39	Form I	L-Malic acid	3	Dichloromethane	NA	25-30	Form I
40	Form I	L-Malic acid	3	Methanol	Methyl tertiary butyl ether	35-40	Form I
41	Form I	Methyl paraben	2	2,2,2-Trifluoroethanol	Methyl tertiary butyl ether	25-30	PM
42	Form I	Methyl paraben	2	Ethanol	Ethyl acetate	25-30	PM
43	Form I	Methyl paraben	1	Methanol	Acetonitrile	65-70	PM
44	Form I	Methyl paraben	2	Acetonitrile	NA	70-75	PM
45	Form I	Nicotinamide	2	Ethanol	Ethyl acetate	25-30	PM
46	Form I	Nicotinamide	2	Ethanol	NA	25-30	PM

47	Form I	Nicotinamide	2	Acetonitrile	NA	25-30	Form I
48	Form I	Nicotinamide	1	Methanol	Acetonitrile	70-75	Form I
49	Form I	Nicotinamide	1	Methanol	n-Heptane	65-70	Form I
50	Form I	Nicotinamide	3	Acetonitrile	NA	70-75	Form I
51	Form I	Oxalic acid dihydrate	1	Methanol	NA	25-30	Form I
52	Form I	Oxalic acid dihydrate	1.2	Ethanol	NA	30-35	Form I
53	Form I	Oxalic acid dihydrate	3	Ethanol	NA	-15 to -10	PM
54	Form I	Oxalic acid dihydrate	3	Methanol	n-Butyl acetate	0-5	PM
55	Form I	Succinic acid	1	Methanol	NA	35-40	Form I
56	Form I	Succinic acid	2	Ethanol	NA	35-40	PM
57	Form I	Succinic acid	2	Isopropanol	NA	35-40	PM
58	Form I	Succinic acid	2	2,2,2-Trifluoroethanol + Methyl tertiary butyl ether	NA	25-30	Form I
59	Form I	Succinic acid	1	Methanol + Ethanol	Ethyl acetate	25-30	Form I
60	Form I	Succinic acid	2	Acetonitrile	Acetone	35-40	PM
61	Form I	Maleic acid	1	Methanol	NA	45-50	PM
62	Form I	Maleic acid	3	Methanol	Methyl tertiary butyl ether	35-40	PM
63	Form I	Maleic acid	3	Methanol	1,4-dioxane	20-25	Form I
64	Form I	Maleic acid	1	Methanol	Acetone	45-50	Form I
65	Form I	Maleic acid	1.2	Methanol + Tetrahydrofuran	n-Heptane	25-30	Form I
66	Form I	Maleic acid	1	Dimethyl carbonate	NA	25-30	Form I
67	Form I	Maleic acid	1	Ethyl acetate	NA	25-30	PM
68	Form I	Maleic acid	1	Acetonitrile	NA	25-30	Form I
69	Form I	Maleic acid	2	Acetonitrile	NA	25-30	PM
70	Form I	Maleic acid	2	Dimethyl formamide	Dimethyl carbonate	50-55	Form I
71	Form I	Maleic acid	2	Dimethyl formamide	Methyl tertiary	50-55	Form I

					butyl ether		
72	Form I	Maleic acid	3	Dimethyl sulfoxide	Methyl isobutyl ketone	50-55	PM
73	Form I	Maleic acid	3	Dimethyl sulfoxide	Ethyl acetate	50-55	PM
74	Form I	Maleic acid	3	Dimethyl sulfoxide	Anisole	50-55	PM
75	Form I	Maleic acid	2	Ethanol	NA	25-30	PM
76	Form I	Maleic acid	1.2	Ethanol	Heptane + Methyl tertiary butyl ether	15-20	Form I
77	Form I	Maleic acid	2	Ethanol	Water	0 - 5	Form I
78	Form I	Maleic acid	3	Ethanol	Ethyl acetate	-5 to 0	PM
79	Amorphous	Maleic acid	1.2	Ethanol	NA	25-30	Form I
80	Amorphous	Maleic acid	2	2-ethoxy ethanol	NA	0-5	Form I
81	Amorphous	Maleic acid	2	Acetonitrile	NA	70-75	PM
82	Amorphous	Maleic acid	2	Ethyl acetate + acetone	NA	70-75	PM
83	Amorphous	Maleic acid	1.2	Ethanol + Methanol	Pentane	25-30	PM
84	Amorphous	Maleic acid	2	Ethanol + Tetrahydrofuran + Methanol	Pentane	25-30	PM
85	Niraparib free base	PTSA & Oxalic acid	1 & 2	Ethanol + Acetonitrile	NA	25-30	Form I
86	Niraparib free base	PTSA & Maleic acid	1 & 1	Ethanol	Ethyl acetate	35-40	Form I
87	Niraparib free base	PTSA & D-Tartaric acid	1 & 1	Ethyl acetate + Methanol	NA	25-30	PM
88	Niraparib free base	PTSA & Succinic acid	1 & 1	Ethanol	Ethyl acetate	25-30	Form I
89	Niraparib free base	PTSA & Succinic acid	1 & 2	Acetonitrile + Ethanol	NA	25-30	PM
90	Niraparib free base	PTSA & Fumaric acid	1 & 1	Acetonitrile + Ethanol	NA	35-40	Form I
91	Niraparib free base	PTSA & L-Malic acid	1 & 1	Ethanol	Ethyl acetate	35-40	Form I

92	Form I	L-Proline	1	Methanol	NA	25-30	Form I
93	Form I	L-Proline	1	Acetonitrile	NA	40-45	PM
94	Form I	L-Proline	1	Methanol	Acetonitrile	25-30	PM
95	Form I	L-Proline	1	Methanol	Petroleum ether	0-10	Form III
96	Form I	L-Proline	2	Acetone + Water	NA	45-50	Form I
97	Form I	L-Proline	2	Acetonitrile + Water	NA	70-75	Form I
98	Form I	L-Proline	2	Tetrahydrofuran + Water	NA	45-50	Form I
99	Form I	L-Proline	1.2	Methanol	NA	50-55	PM of Form I & NIR.TOS.PRO
100	Form I	L-Proline	1.2	Methanol	Acetonitrile	50-55	PM of Form I & NIR.TOS.PRO
101	Form I	L-Proline	1.2	2,2,2-Trifluoroethanol	Acetonitrile	70-75	NIR.TOS.PRO
102	Form I	L-Proline	1.2	Methanol	Acetonitrile	70-75	NIR.TOS.PRO
103	Form I	L-Proline	1.2	Acetonitrile	NA	70-75	NIR.TOS.PRO

Note: In the above table, niraparib tosylate monohydrate is mentioned as Form I. PM stands for physical mixture of Form I and respective coformer. NIR.TOS.PRO stands for niraparib tosylate L-proline zwitterionic salt-cocrystal. In few experiments, Form III or physical mixture of Form I and Form III were observed during in-process PXRD analysis, however they eventually converted to the stable Form I after final filtration or drying. The experimental NIR.TOS.PRO hits are highlighted in violet colour.

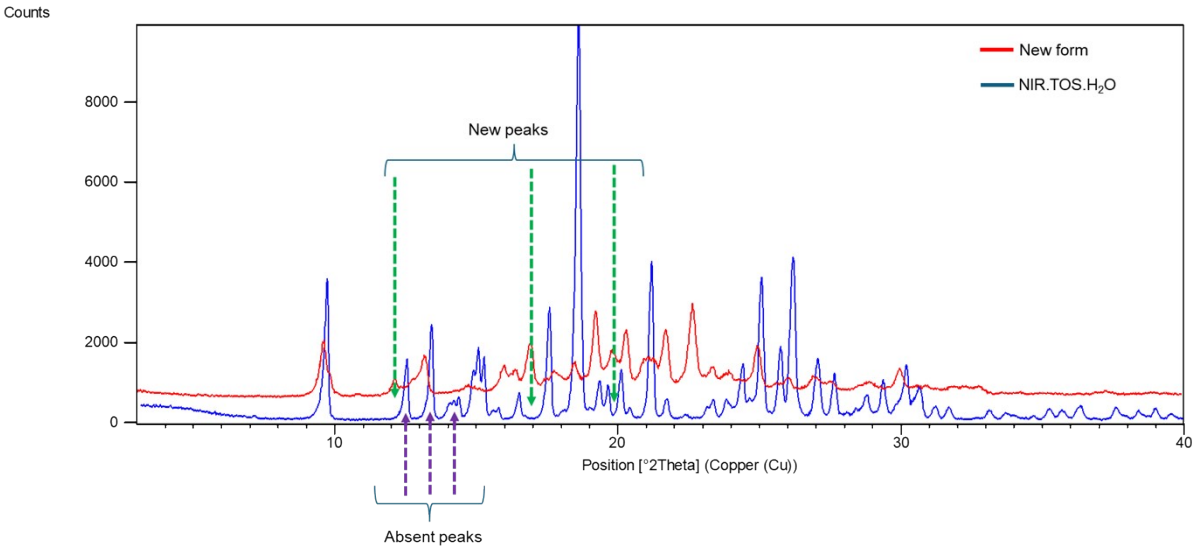

Figure S4: PXRD pattern of new polymorph in comparison with NIR.TOS.H_2O.

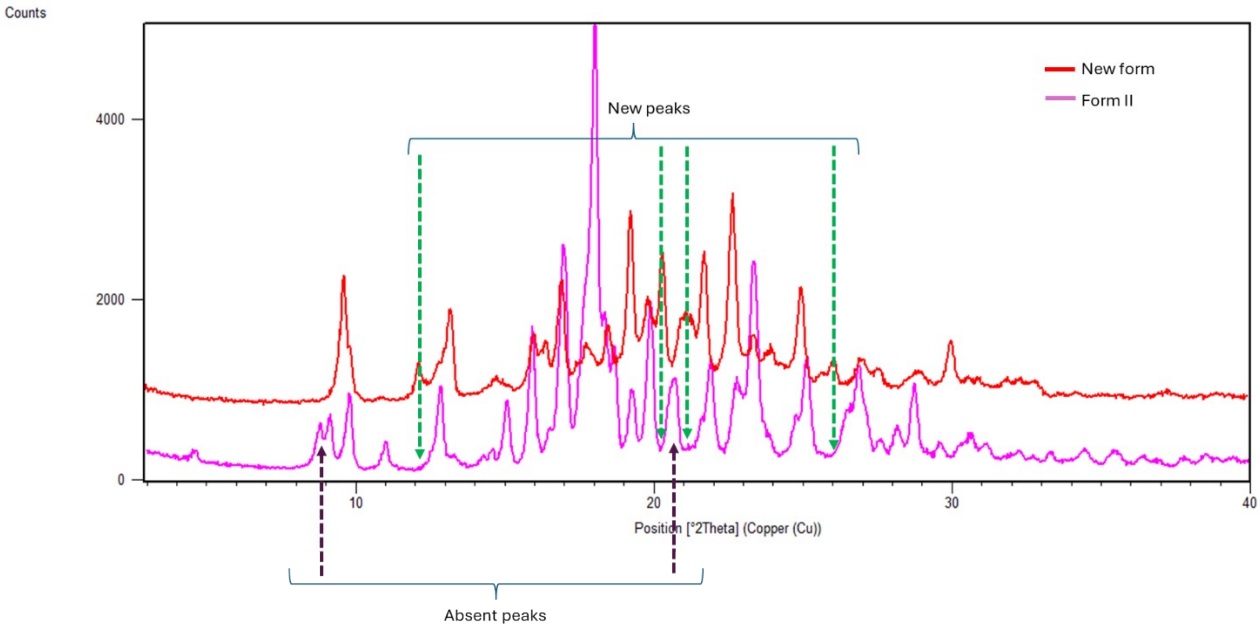

Figure S5: PXRD pattern of new polymorph in comparison with Form II of Niraparib tosylate.

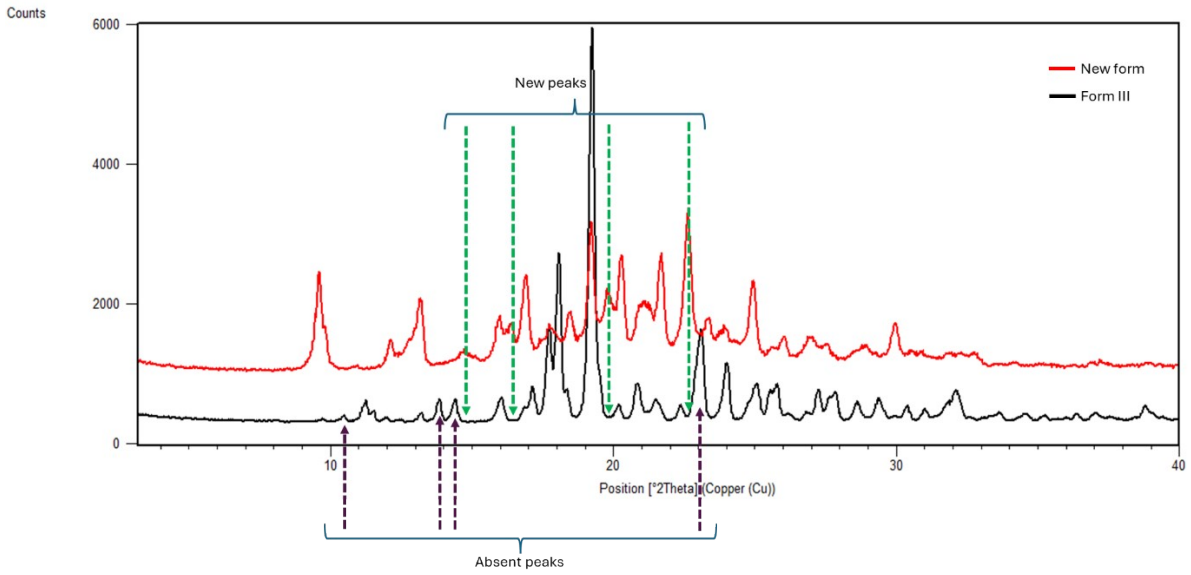

Figure S6: PXRD pattern of new polymorph in comparison with Form III of Niraparib tosylate.

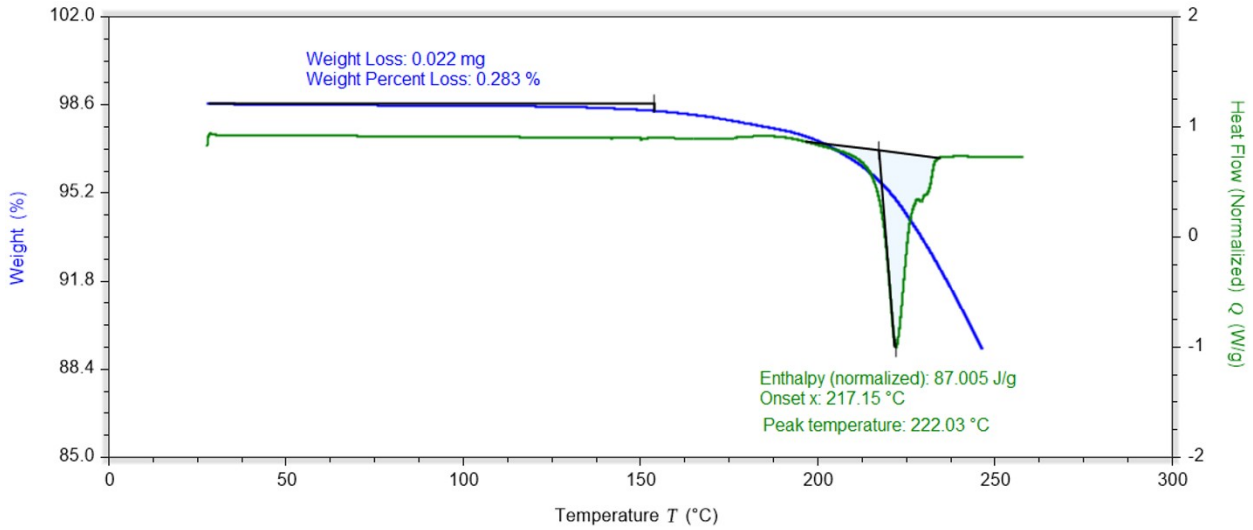

Figure S7: DSC & TGA overlay of new polymorph of Niraparib tosylate.

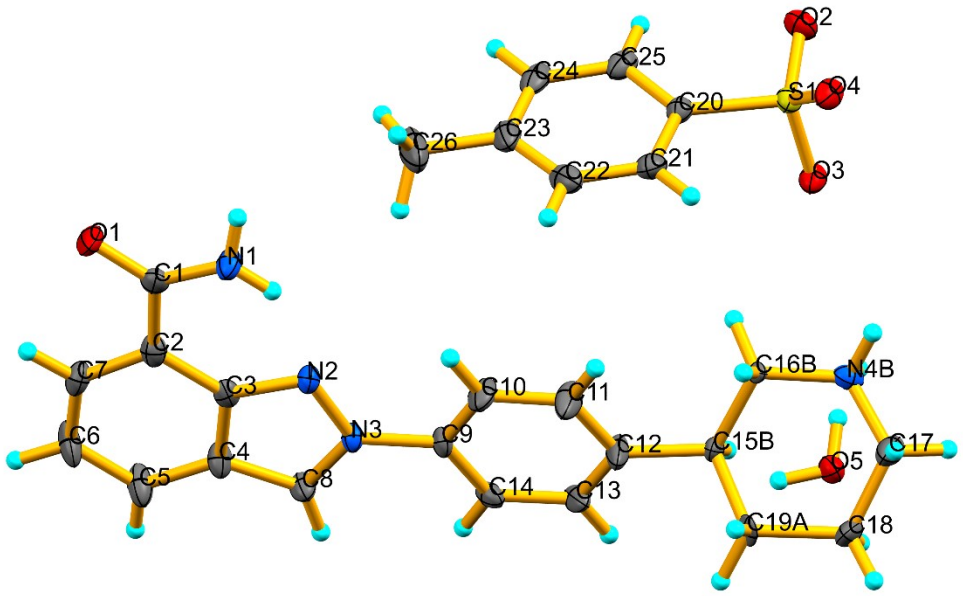

Figure S8. ORTEP representation of NIR.TOS.H_2O drawn at 50% probability of non-hydrogen atoms. The piperidyl ring in Niraparib has disorder, which is omitted for clarity.

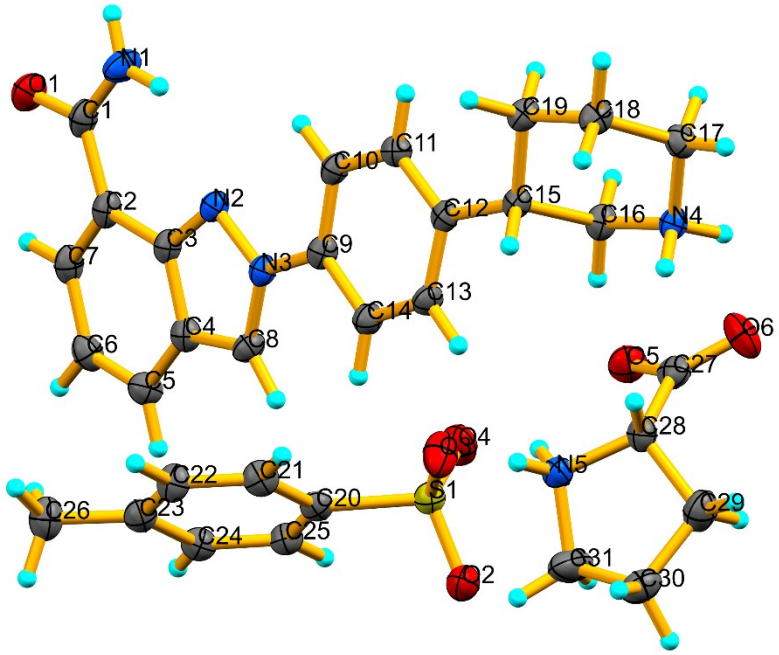

Figure S9. ORTEP representation of NIR.TOS.PRO drawn at 50% probability of non-hydrogen atoms.

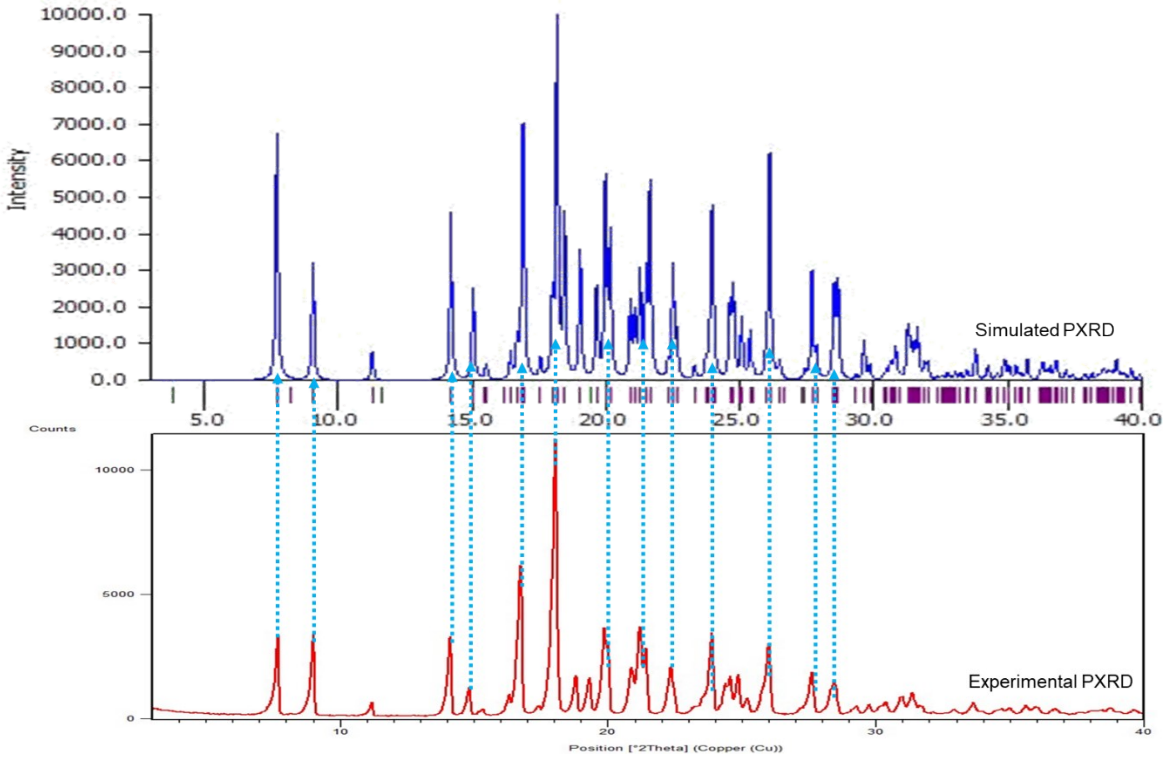

Figure S10. Experimental and simulated PXRD patterns of NIR.TOS.PRO with one-to one correspondence.

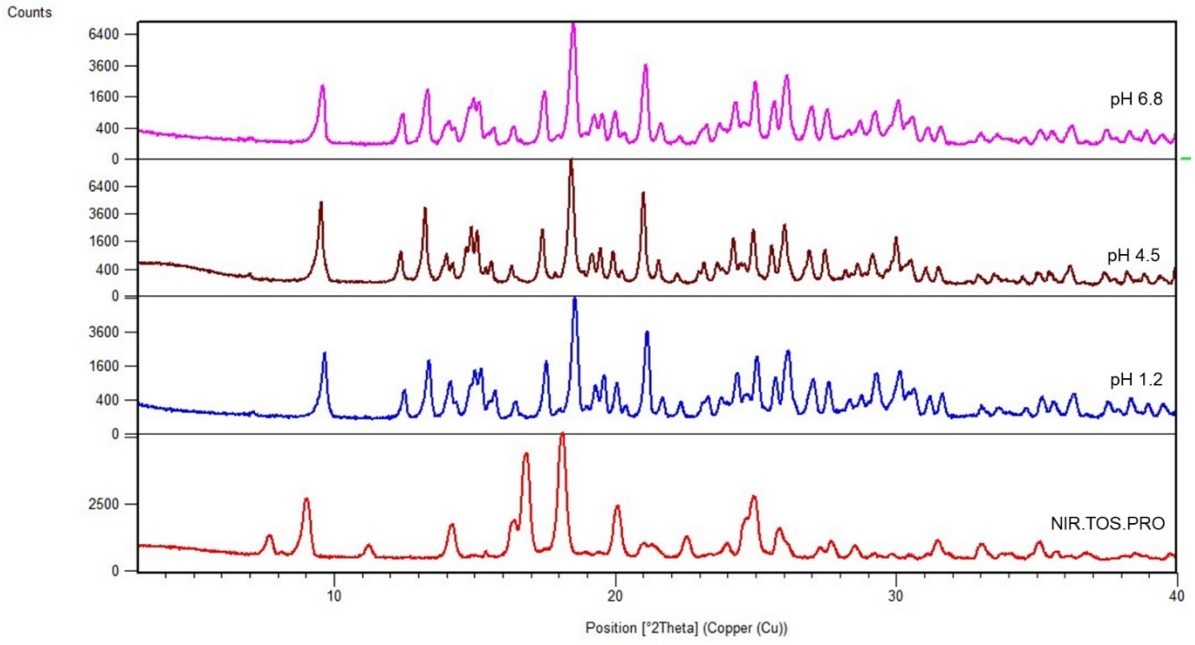

Figure S11: Powder X-ray diffraction patterns of NIR.TOS.PRO (red pattern) in pH 1.2 (blue), 4.5 (brown) and 6.8 (pink) buffers (characterized with the residue after dissolution experiment). The salt-cocrystal is dissociated in all the media and converted to NIR.TOS.H_2O.

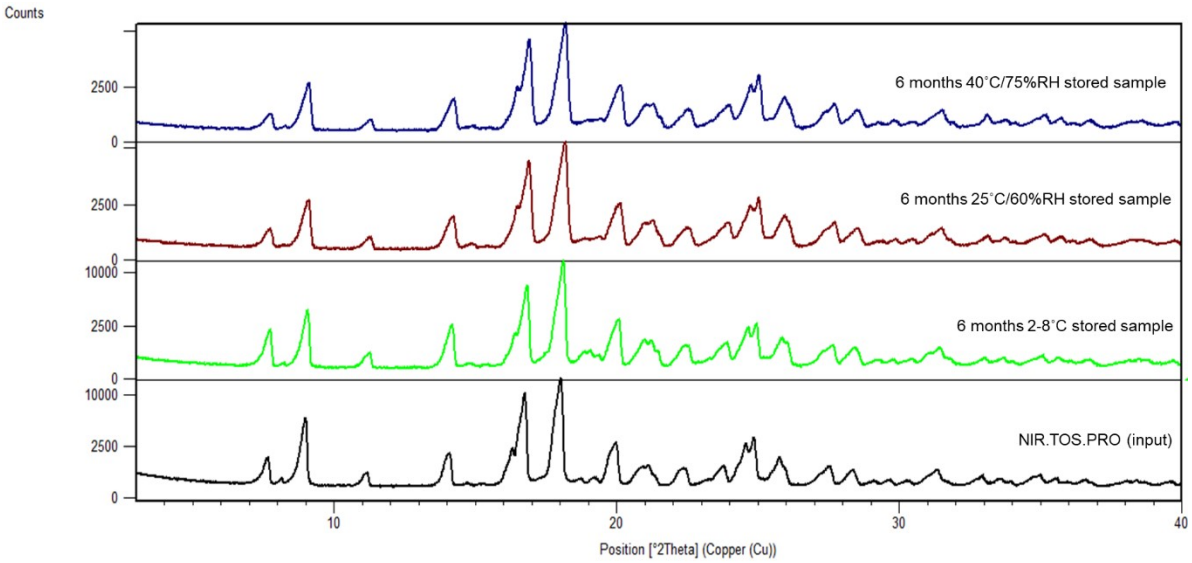

Figure S12: Overlay of powder X-ray diffraction patterns of 6-mopnths stored stability samples of NIR.TOS.PRO in comparison with the input.

Table S3: Torsion angles that are majorly deviated in NIR.TOS.H_2O and NIR.TOS.PRO.

Considered consecutive atoms	**NIR.TOS.H_2O**	**NIR.TOS.PRO**
C12-C15-C16-N4 (τ1)	177.16°	-171.03°
C12-C15-C19-C18 (τ2)	52.45°	175.96°

Table S4: Hydrogen bond parameters of NIR.TOS.H_2O and NIR.TOS.PRO.

Interaction	**D–H/Å**	**H···A/Å**	**D···A/Å**	**∠D–H···A/°**	**Symmetry code**
NIR.TOS.H_2O					
N4B –H4BA···O1	0.92	2.13	2.98(9)	152	1-x, 2-y, 1-z
N1–H1A···O4	0.84(11)	2.22(11)	2.93(7)	143(10)	1-x, 2-y, 1-z
N4B –H4BB···O5	0.92	2.06	2.95(9)	162	1-x, 2-y, 1-z
N4A –H4AA···O5	0.92	1.88	2.75(9)	158	1-x, 2-y, 1-z
N4A –H4AB···O5	0.92	1.91	2.83(9)	175	x, y, z
O5–H5A···N4A	0.85	2.12	2.75(9)	131	1+x, y, z
O5–H5B···O3	0.85	1.93	2.76(5)	163	x, y, z
C16A–H16D···O2	0.99	2.60	3.57(18)	168	x, y, z
C17 –H17D···O1	0.99	2.40	3.27(9)	146	1-x, 2-y, 1-z
NIR.TOS.PRO					
N1–H1A···O6	0.83(3)	2.05(3)	2.87(3)	174(3)	1-x, -1/2+y, 2-z
N4–H4A···O1	0.92	1.88	2.69(3)	145	1-x, -1/2+y, 1-z
N4–H4B···O5	0.92	1.87	2.78(3)	166	x, y, z
N5–H5A···O4	0.92	1.80	2.70(3)	167	x, y, z
C8–H8 ···O3	0.95	2.55	3.50(3)	177	1-x, -1/2+y, 1-z
C26 –H26C···O6	0.98	2.57	3.53(4)	165	2-x, -1/2+y, 1-z