Electronic Supplementary Material (ESI) for CrystEngComm.

SUPPORTING INFORMATION

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Table S1. Crystallography Parameters of Vanillin and Vanillic acid Co-crystals.

Compound	**VAN-INM** (1: 1)	**VAN-THB-2H_2O** (1: 1: 2)	**VA-CAF-NAM** (1: 1: 1)	**VA-INM** (1: 2)
Structural formula	$C_{14}H_{14}N_2O_4$	$C_{15}H_{20}N_4O_7$	$C_{22}H_{24}N_6O_7$	$C_{20}H_{20}N_4O_6$
Formula weight (g mol^{-1})	274.27	368.35	484.47	412.40
Temp. (K)	293 (2)	173 (2)	173 (2)	173 (2)
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a (Å)	7.8201 (16)	8.3765 (10)	9.8016 (14)	19.046 (2)
b (Å)	8.3180 (17)	8.4985 (10)	10.7859 (15)	7.1278 (8)
c (Å)	11.360 (2)	12.2641 (14)	11.3248 (16)	15.6486 (18)
α (°)	91.58 (3)	79.403 (2)	70.022 (3)	90
β (°)	92.89 (3)	76.928 (2)	78.358 (3)	113.193 (2)
γ (°)	116.34 (3)	80.829 (2)	86.692 (3)	90
V ($Å^3$)	660.3 (3)	829.6 (2)	1102.0 (3)	1952.7 (4)
Z	2	2	2	4
$D_{calc.}$(g cm^{-3})	1.379	1.475	1.460	1.403
F (000)	288	388	508	864
Absorption coefficient (mm^{-1})	0.103	0.118	0.111	0.106
θ range	1.80-28.20	1.72-28.33	1.95-27.28	2.33-28.35
Reflection collected	9448	15774	12503	23004
No data I> 2δ(I)	2594	3649	3560	3424
Final R indices [I> 2δ(I)]	R_1 = 0.0390 wR_2 = 0.1069	R_1 = 0.0385 wR_2 = 0.1065	R_1 = 0.0540 wR_2 = 0.1374	R_1 = 0.0446 wR_2 = 0.1035
R indices (all data)	R_1 = 0.0493 wR_2 = 0.1146	R_1 = 0.0431 wR_2 = 0.1108	R_1 = 0.0768 wR_2 = 0.1519	R_1 = 0.0705 wR_2 = 0.1168
Goodness-of-fit on F^2	1.057	1.062	1.046	1.039
Largest diff. peak and hole (e $Å^{-3}$)	0.325; -0.193	0.355; -0.261	0.582; -0.284	0.243; -0.224

Table S2. Crystallography Parameters of Vanillic acid Co-crystals and Salts

Compound	**VA-HEXA** (1: 1)	**VA-PHZ** (2: 3)	**VA-PZO** (1: 1)	**VA^--PPZ^+-H_2O** (2: 2: 1)	**VA^--$DABCO^+$-H_2O** (2: 2: 1)
Structural formula	$C_{14}H_{20}N_4O_4$	$C_{26}H_{20}N_3O_4$	$C_{12}H_{12}N_2O_5$	$C_{12}H_{19}N_2O_{4.5}$	$C_{28}H_{42}N_4O_9$
Formula weight (g mol^{-1})	308.34	438.45	264.24	263.29	578.65
Temp. (K)	173 (2)	173 (2)	173 (2)	173 (2)	173 (2)
Crystal system	Orthorhombic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	*Pbca*	$P\bar{1}$	$P\bar{1}$	*C*2/*c*	$P2_1/c$
a (Å)	17.887 (2)	7.1376 (4)	7.3089 (6)	30.274 (3)	25.812 (2)
b (Å)	7.0953 (9)	9.5383 (5)	7.3878 (6)	6.7982 (7)	10.0083 (9)
c (Å)	23.419 (3)	16.6511 (9)	10.8979 (9)	14.2368 (14)	11.1713 (10)
α (°)	90	98.3390 (10)	94.1980 (10)	90	90
β (°)	90	101.0090 (10)	90.084 (2)	115.727 (2)	99.700 (2)
γ (°)	90	108.2880 (10)	98.0510 (10)	90	90
V ($Å^3$)	2972.2 (6)	1030.7 (1)	581.1 (1)	2639.6 (5)	2844.6 (4)
Z	8	2	2	8	4
$D_{calc.}$(g cm^{-3})	1.378	1.413	1.510	1.325	1.351
F (000)	1312	458	276	1128	1240
Absorption coefficient (mm^{-1})	0.103	0.097	0.120	0.102	0.101
θ range	1.74-28.32	1.28-28.34	1.87-28.32	2.86-28.35	1.60-28.39
Reflection collected	38485	13988	14056	18650	33471
No data I> 2δ(I)	3036	4180	2626	2851	5794
Final R indices [I> 2δ(I)]	R_1 = 0.0382 wR_2 = 0.0945	R_1 = 0.0399 wR_2 = 0.1025	R_1 = 0.0346 wR_2 = 0.0975	R_1 = 0.0428 wR_2 = 0.1164	R_1 = 0.0518 wR_2 = 0.1290
R indices (all data)	R_1 = 0.0492 wR_2 = 0.1019	R_1 = 0.0501 wR_2 = 0.1084	R_1 = 0.0374 wR_2 = 0.1004	R_1 = 0.0491 wR_2 = 0.1223	R_1 = 0.0640 wR_2 = 0.1361
Goodness-of-fit on F^2	1.026	1.068	1.042	1.039	1.054
Largest diff. peak and hole (e $Å^{-3}$)	0.352; -0.234	0.308; -0.206	0.371; -0.216	0.533; -0.223	0.278; -0.296

Thermal Analysis

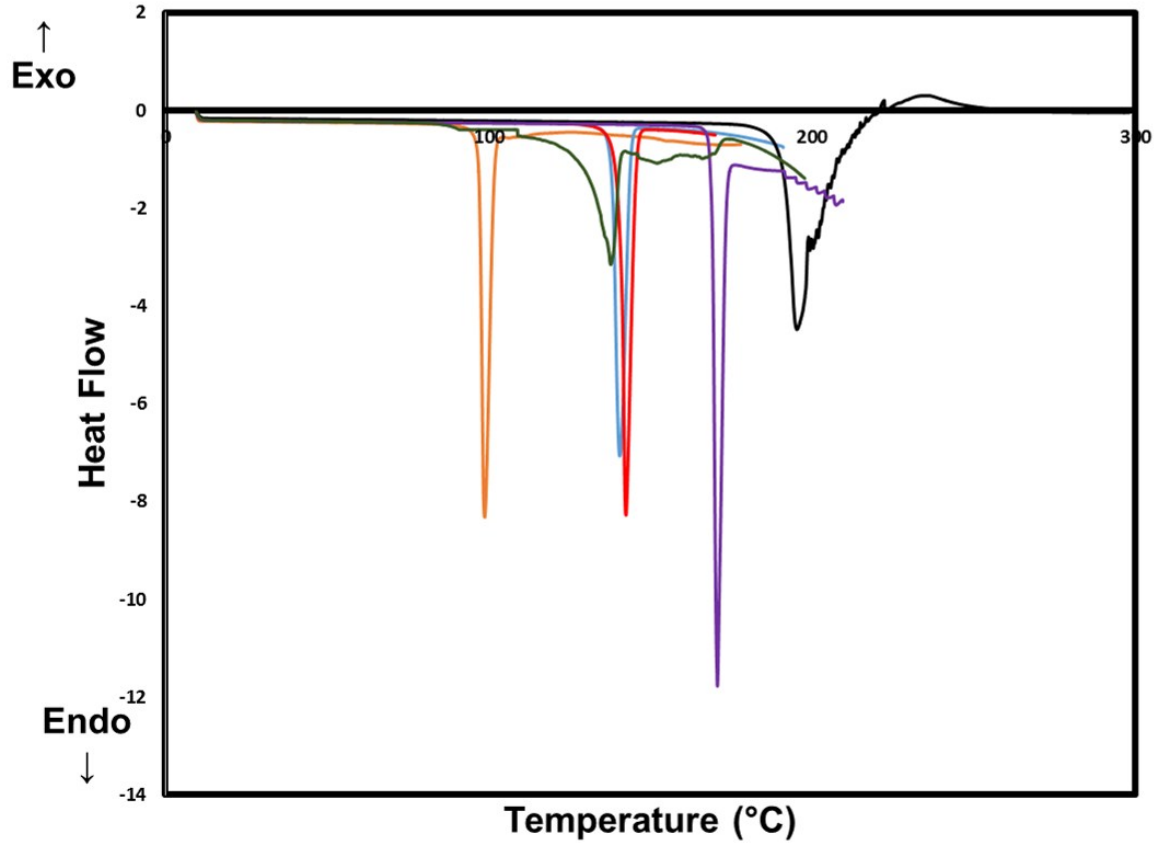

Figure S1. DSC traces of the co-crystals **VAN-INM** (orange), **VA-PZO** (green), **VA-CAF-NAM** (blue), **VA-INM** (red), **VA-PHZ** (purple) and **VA-HEXA** (black).

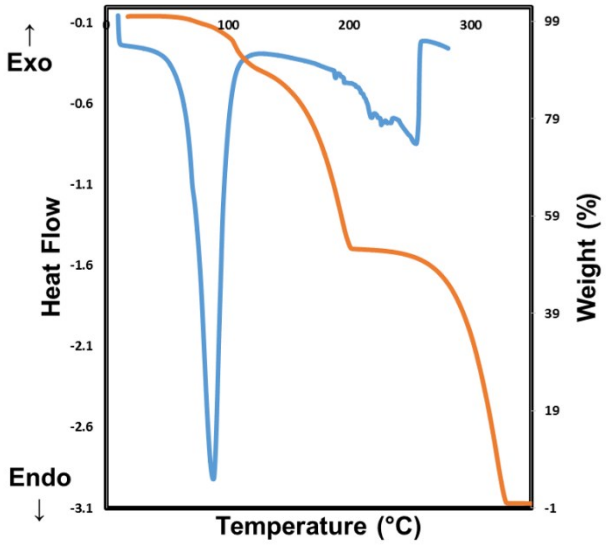

Figure S2. DSC and TG plots of **VAN-THB-H_2O** (1: 1: 2).

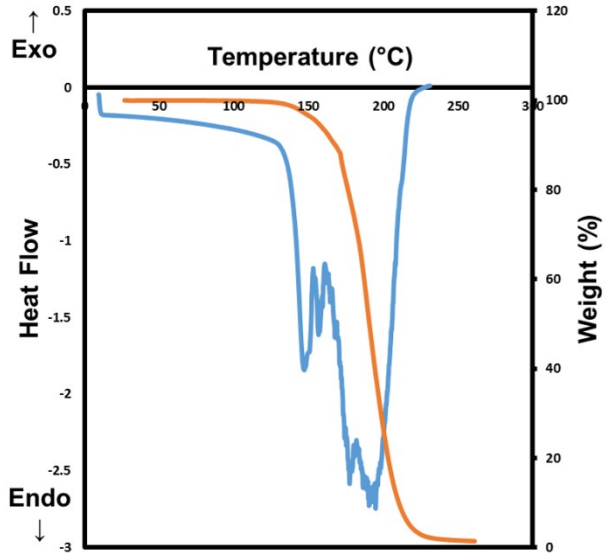

Figure S3. DSC and TG plots of **VA$^-$-PPZ$^+$-H$_2$O** (2: 2: 1).

Powder X-ray Diffraction

Table S3. Grinding Experiments

Compound	Neat grinding	Liquid-assisted grinding
VAN-INM (1: 1)	×	✓
VAN-THB-H$_2$O (1: 1: 2)	×	×
VA-CAF-NAM (1: 1: 1)	×	✓
VA-INM (1: 2)	×	×
VA-HEXA (1: 1)	✓	✓
VA-PHZ (2: 3)	Partially converted	✓
VA-PZO (1: 1)	✓	✓
VA$^-$-PPZ$^+$-H$_2$O (2: 2: 1)	×	✓
VA$^-$-DABCO$^+$-H$_2$O (2: 2: 1)	×	×
×: the physical mixture/unidentified phase formed, ✓: same as co-crystallization		

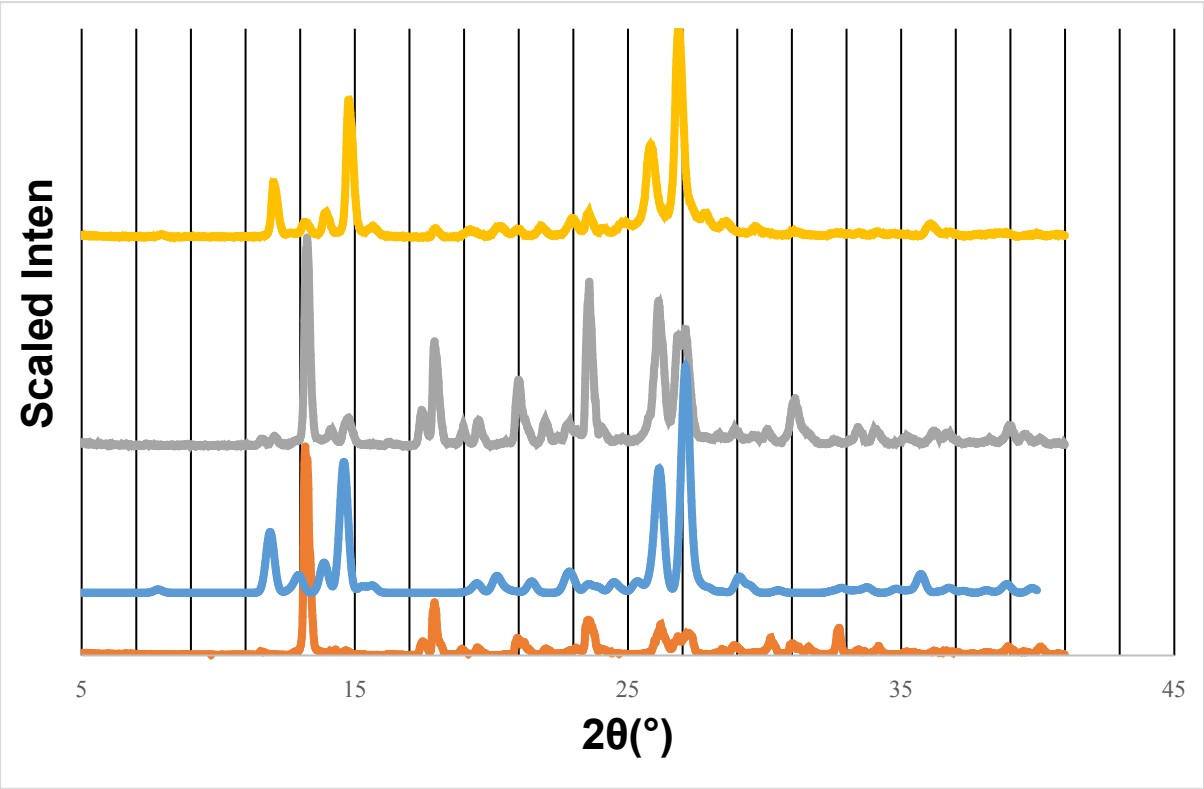

Figure S4. PXRD patterns of **VAN-INM** (1: 1) calculated (blue), physical mixture (orange), ground product (gray) and liquid-assisted ground product (yellow).

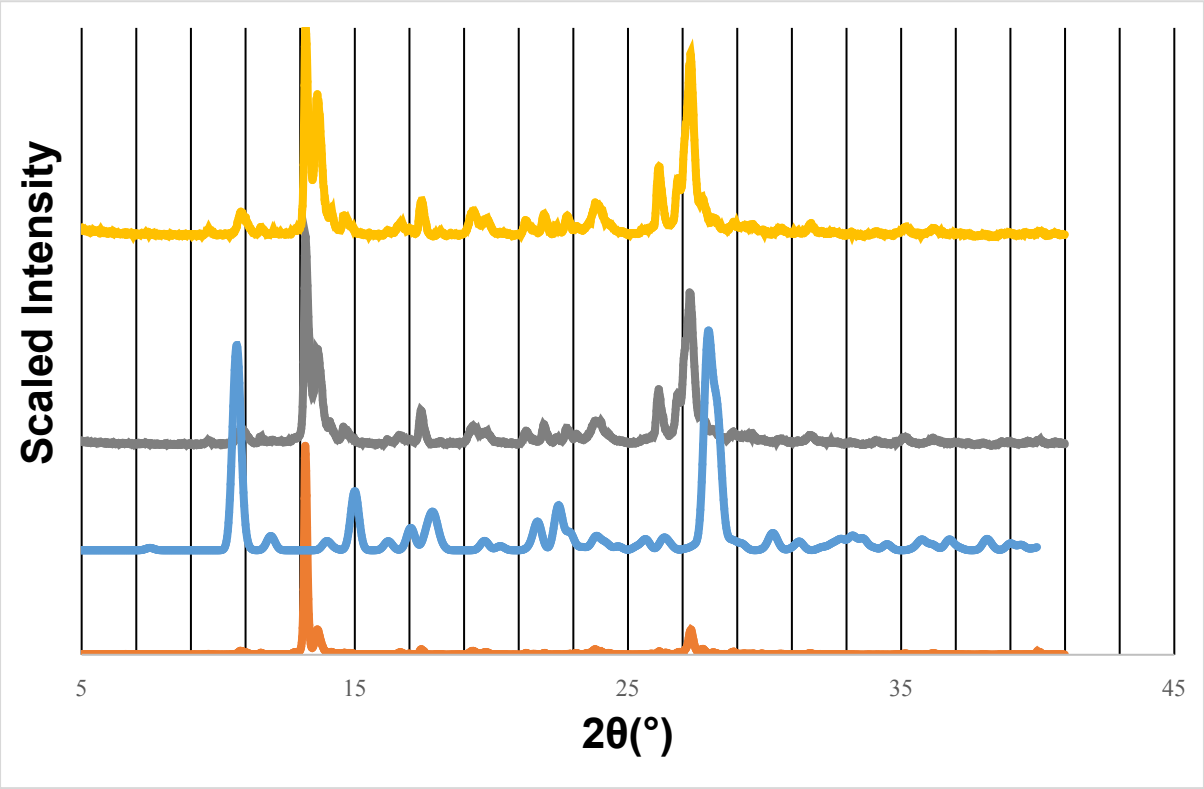

Figure S5. PXRD patterns of **VAN-THB-H_2O** (1: 1: 2) calculated (blue), physical mixture (orange), ground product (gray) and liquid-assisted ground product (yellow).

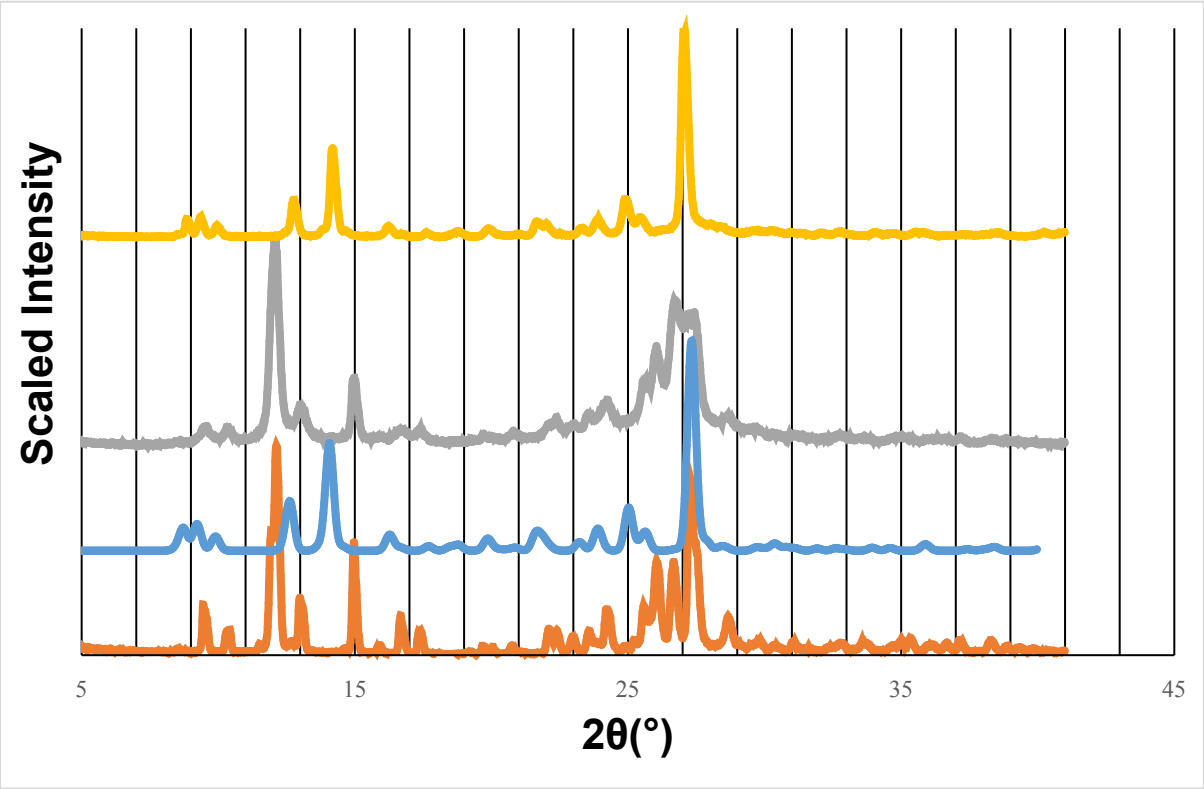

Figure S6. PXRD patterns of **VA-CAF-NAM** (1: 1: 1) calculated (blue), physical mixture (orange), ground product (gray) and liquid-assisted ground product (yellow).

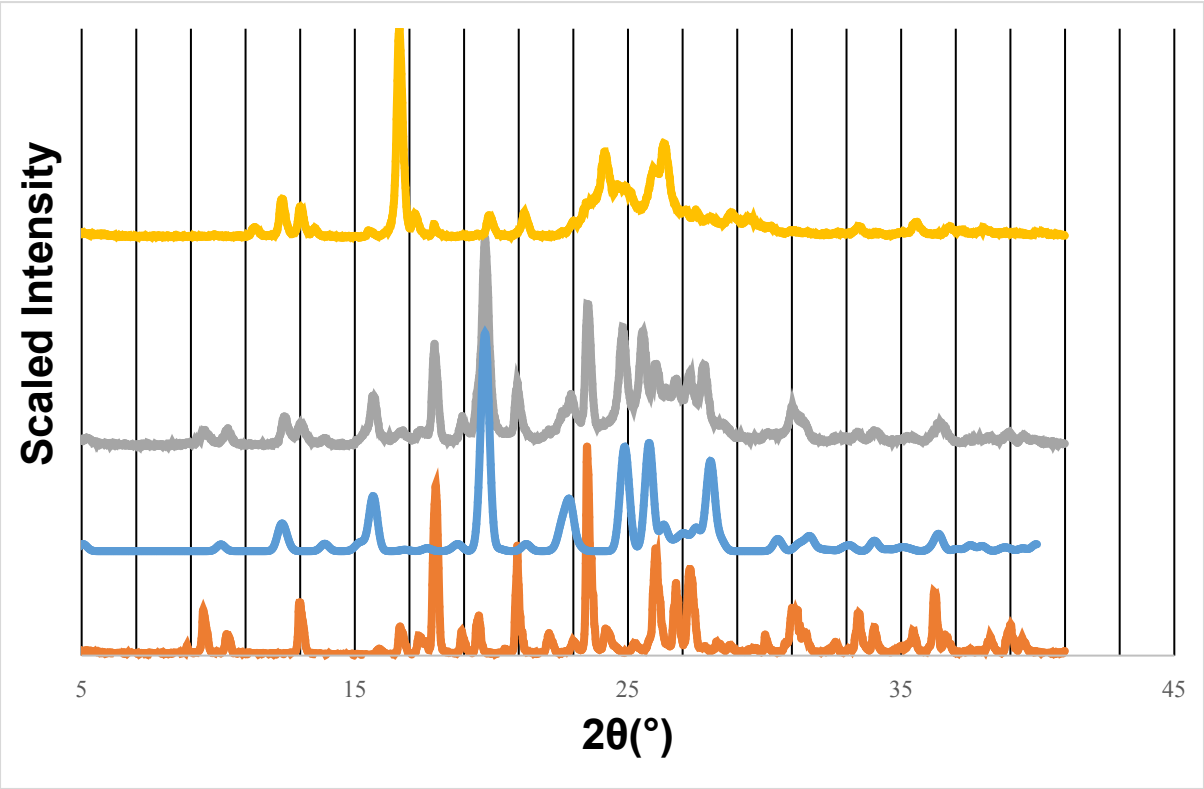

Figure S7. PXRD patterns of **VA-INM** (1: 2) calculated (blue), physical mixture (orange), ground product (gray) and liquid-assisted ground product (yellow).

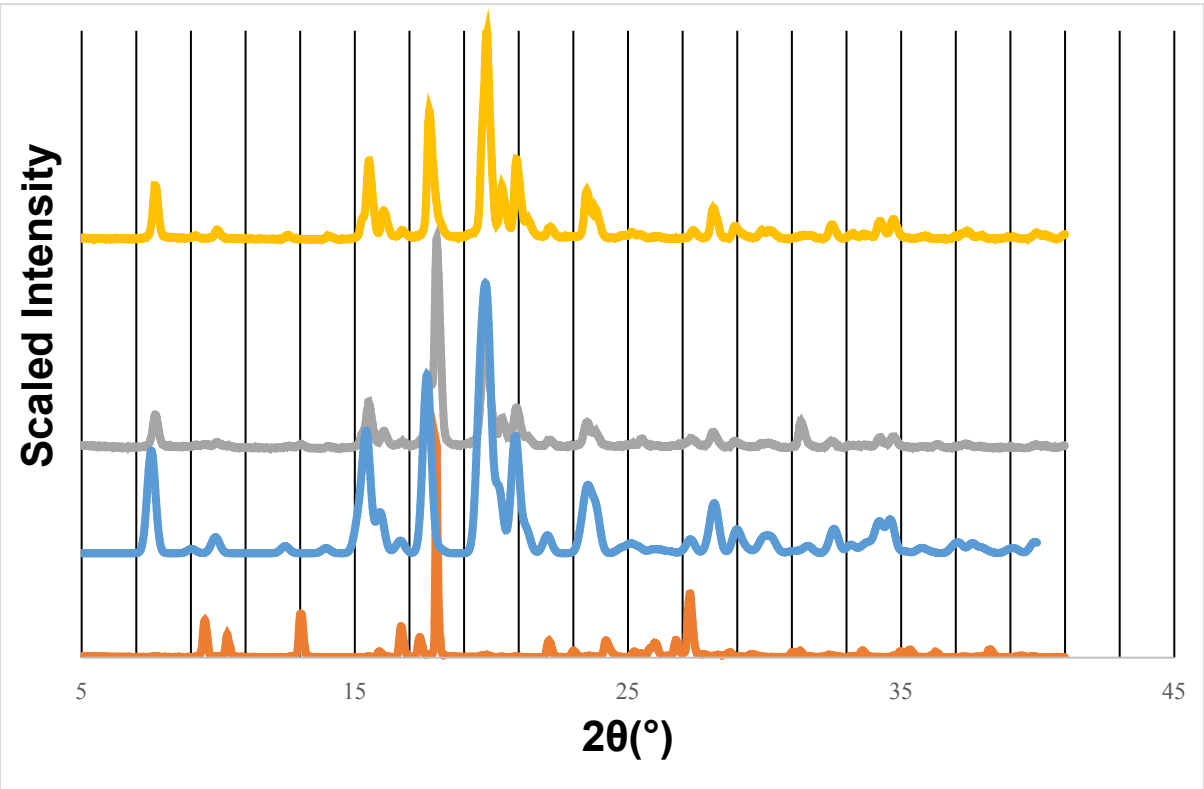

Figure S8. PXRD patterns of **VA-HEXA** (1: 1) calculated (blue), physical mixture (orange), ground product (gray) and liquid-assisted ground product (yellow).

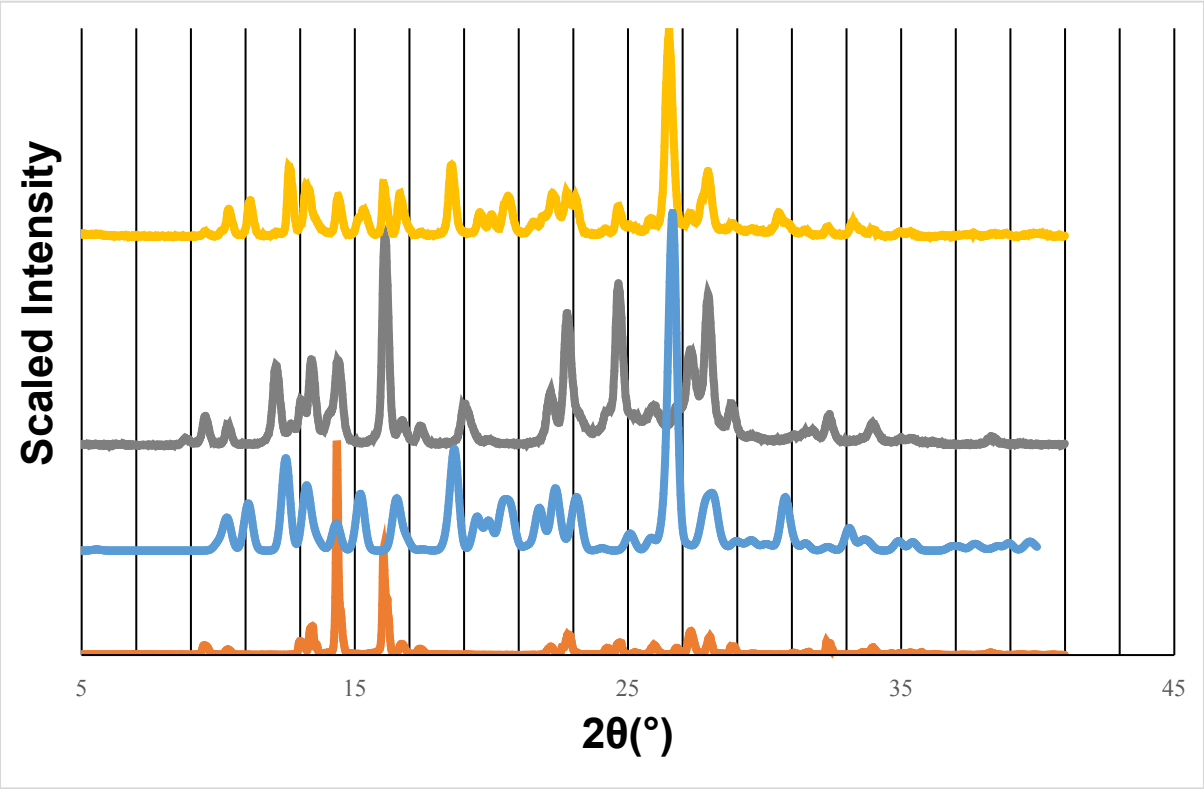

Figure S9. PXRD patterns of **VA-PHZ** (2: 3) calculated (blue), physical mixture (orange), ground product (gray) and liquid-assisted ground product (yellow).

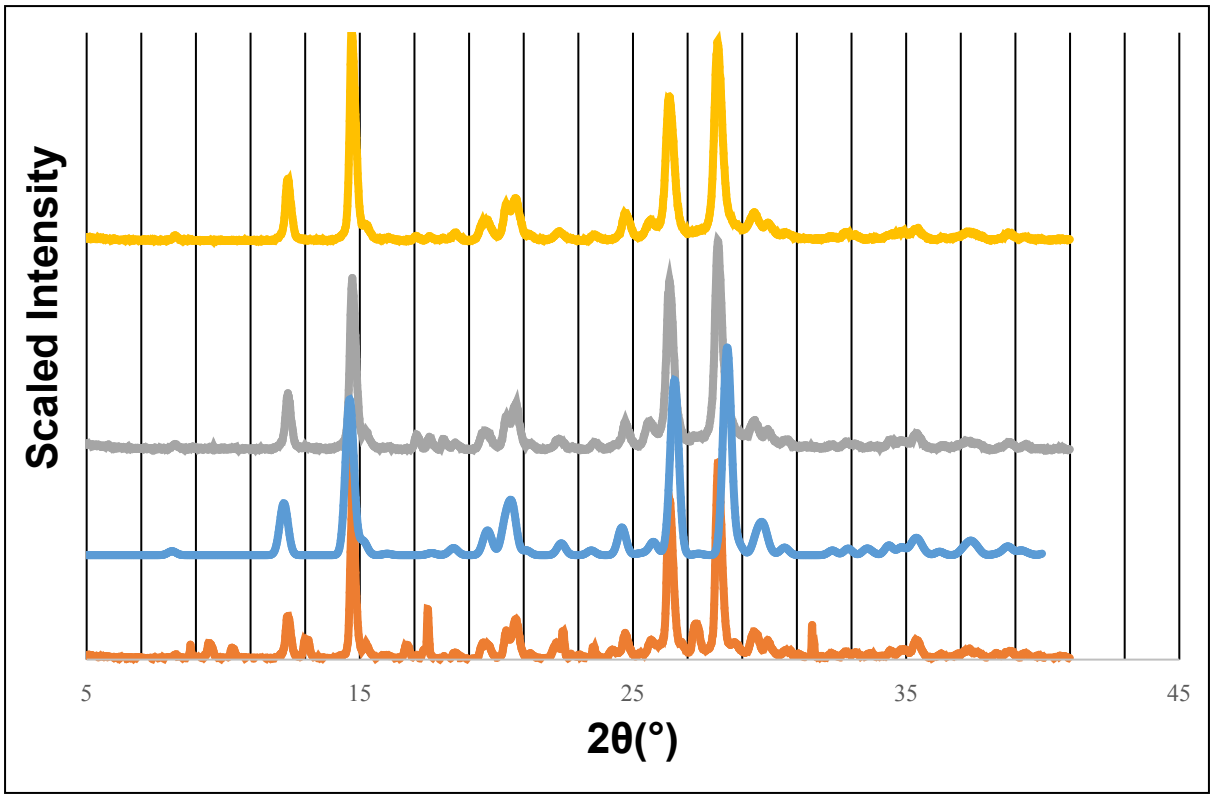

Figure S10. PXRD patterns of **VA-PZO** (1: 1) calculated (blue), physical mixture (orange), ground product (gray) and liquid-assisted ground product (yellow).

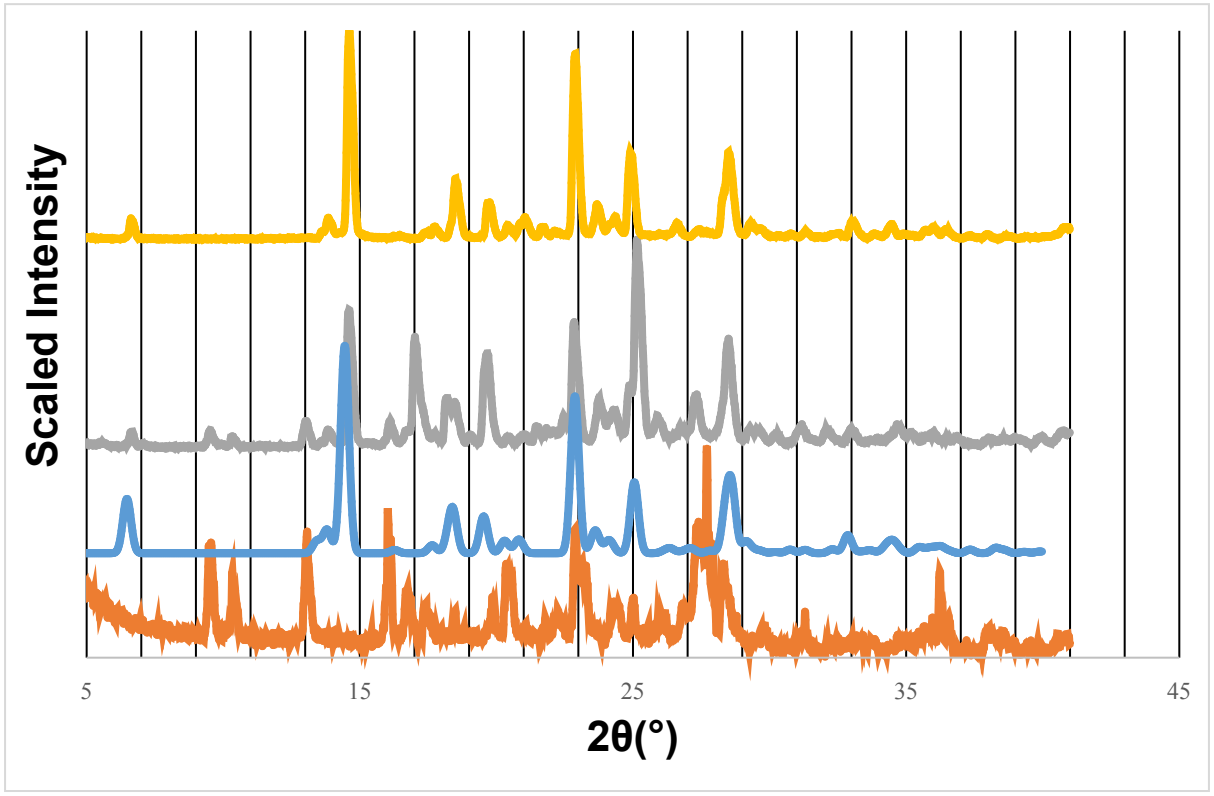

Figure S11. PXRD patterns of **VA$^-$-PPZ$^+$-H$_2$O** (2: 2: 1) calculated (blue), physical mixture (orange), ground product (gray) and liquid-assisted ground product (yellow).

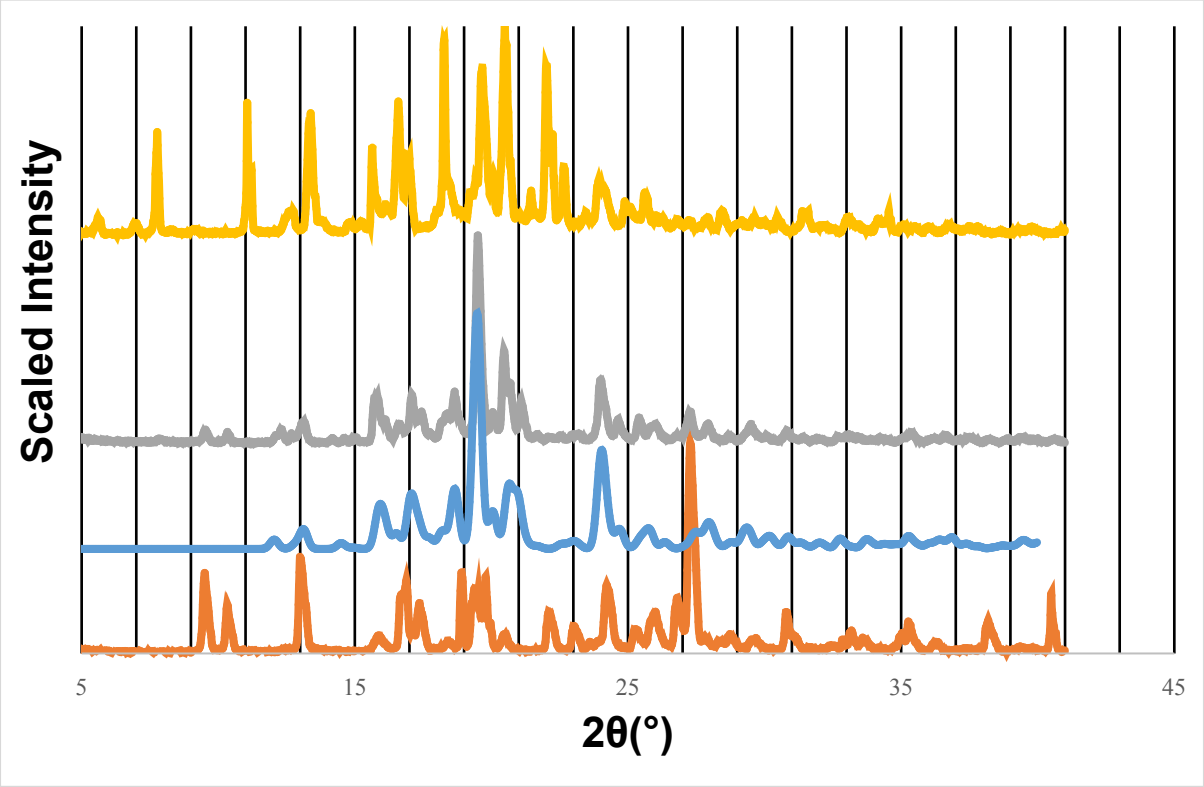

Figure S12. PXRD patterns of **VA$^-$-DABCO$^+$-H$_2$O** (2: 2: 1) calculated (blue), physical mixture (orange), ground product (gray) and liquid-assisted ground product (yellow).

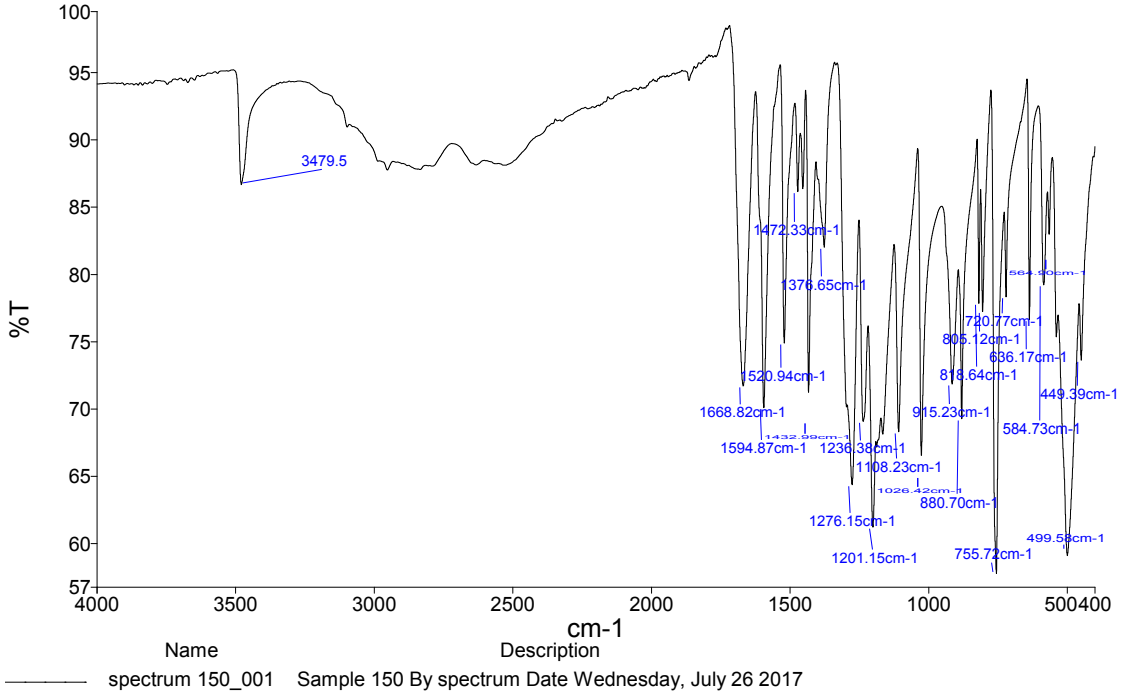

Figure S13. IR spectrum of vanillic acid (VA).

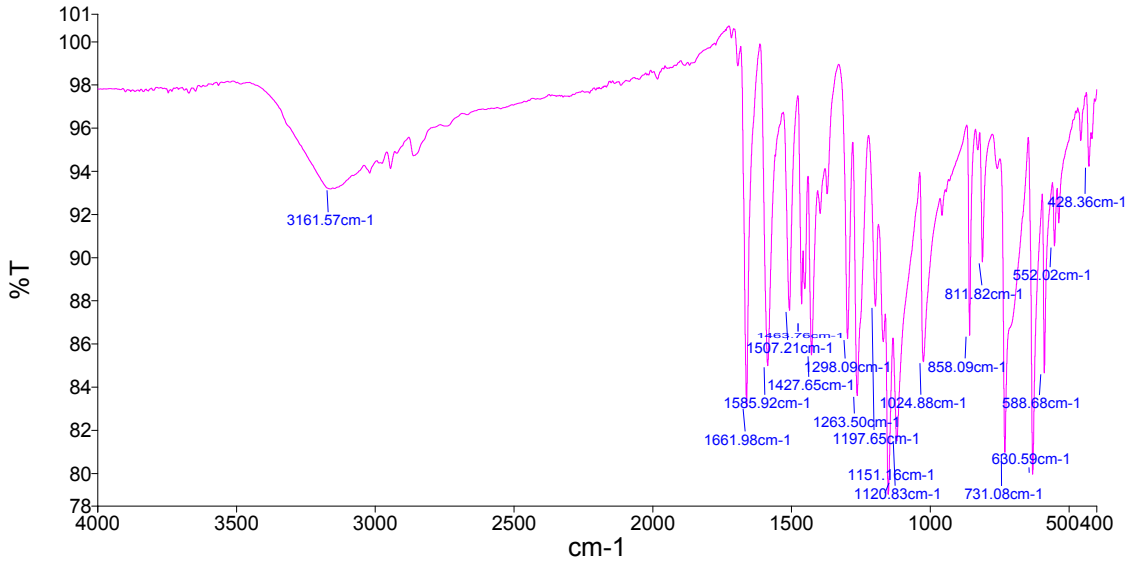

Figure S14. IR spectrum of vanillin (VAN).

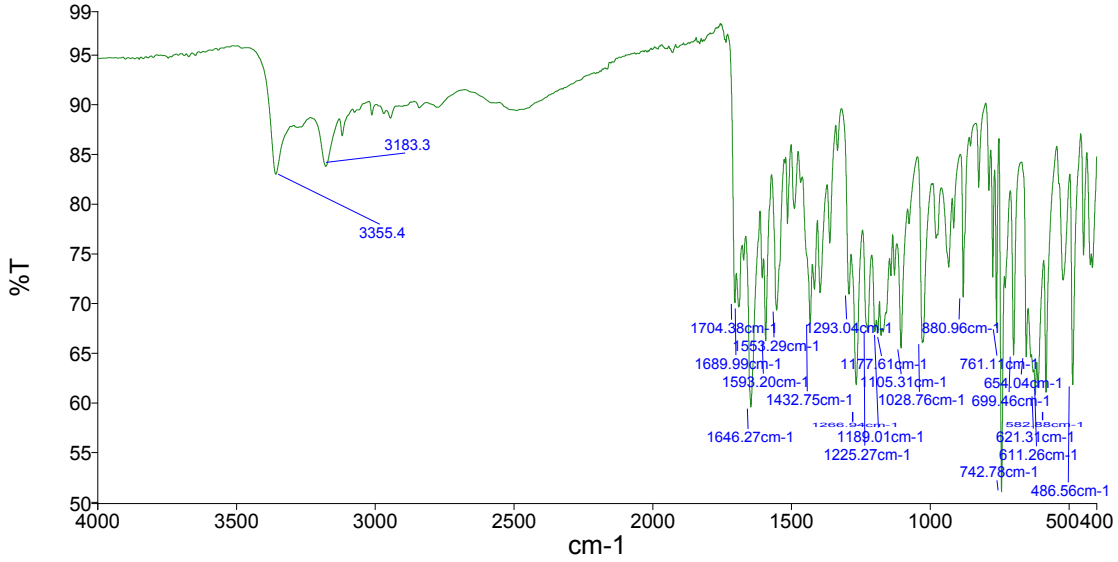

Figure S15. IR spectrum of **VA-CAF-NAM** (1: 1: 1).

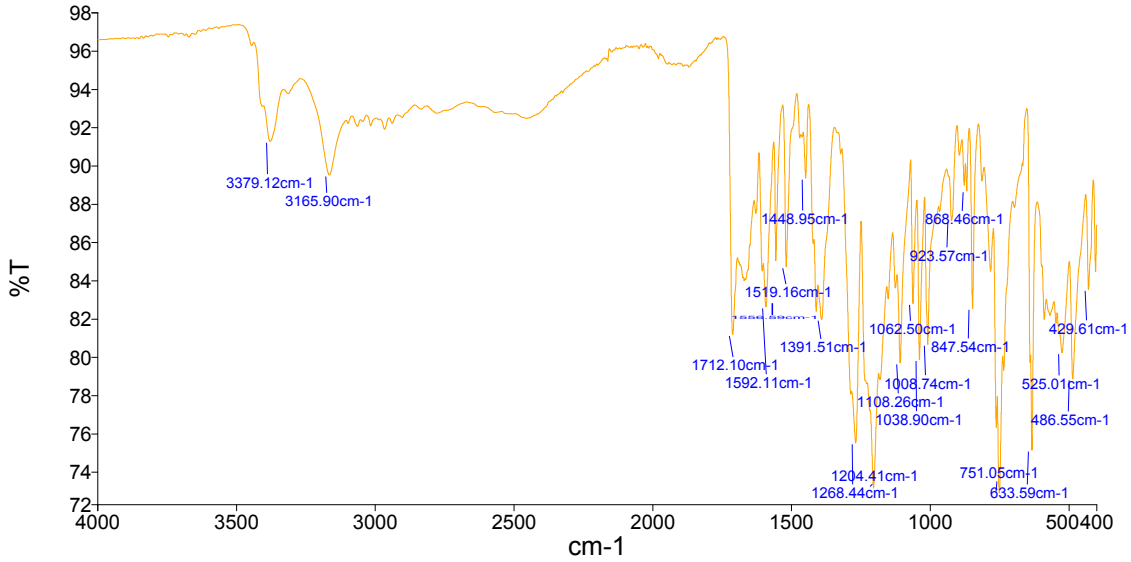

Figure S16. IR spectrum of **VA-INM** (1: 2).

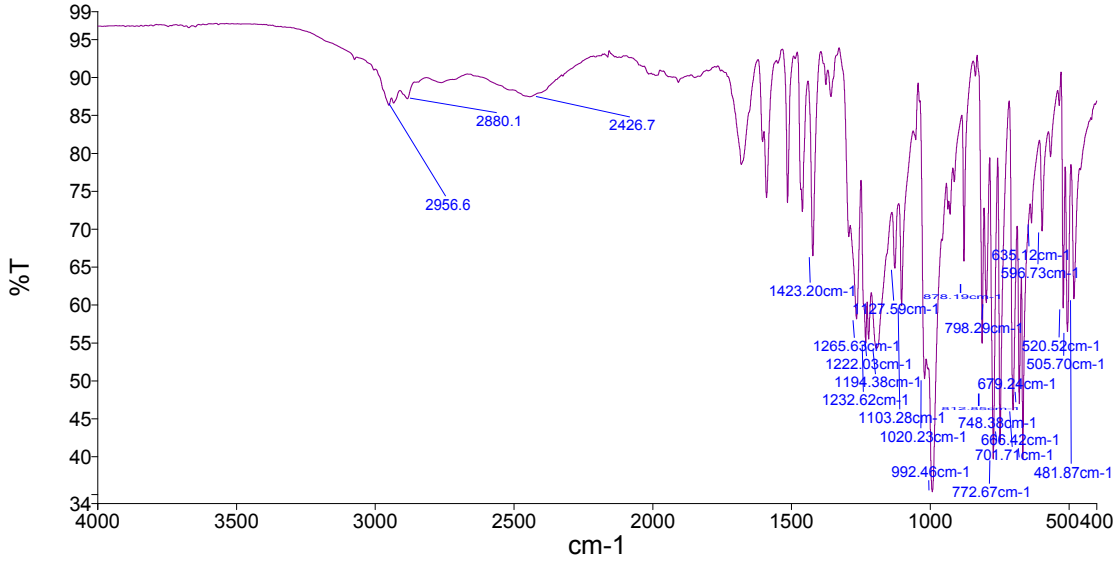

Figure S17. IR spectrum of **VA-HEXA** (1: 1).

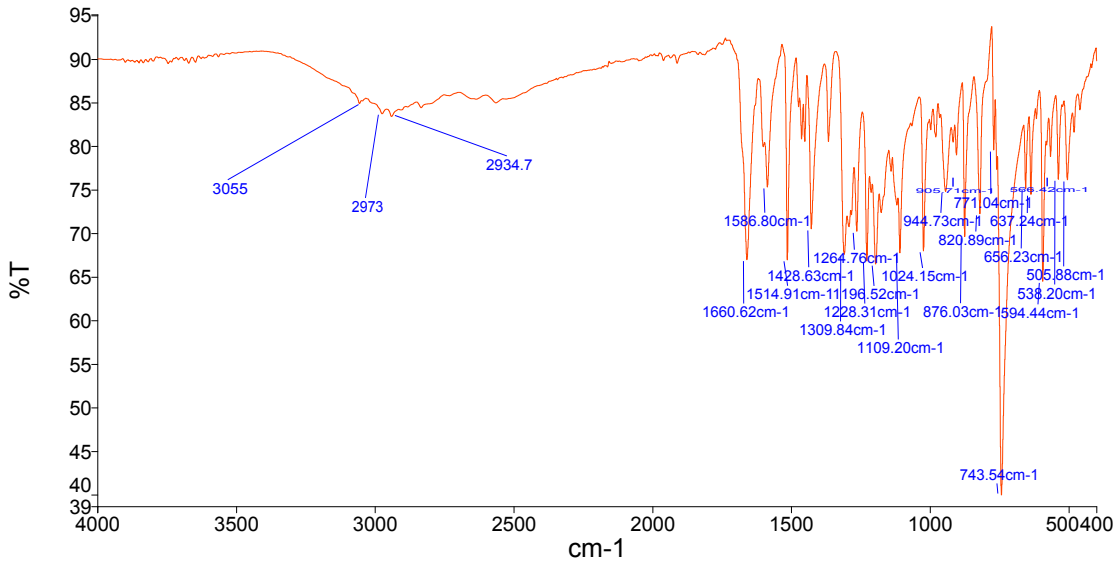

Figure S18. IR spectrum of **VA-PHZ** (2: 3).

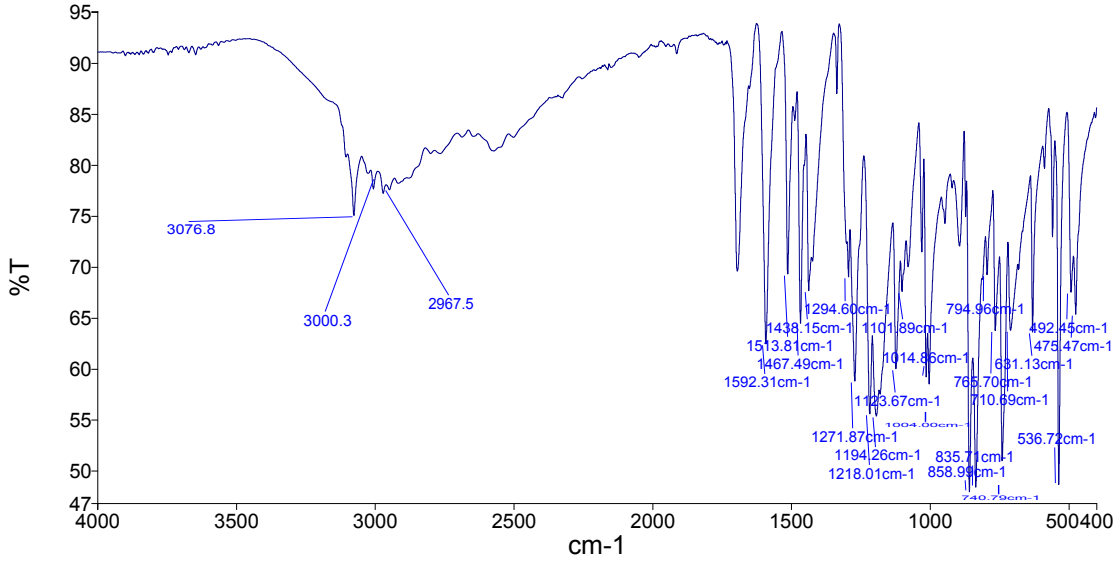

Figure S19. IR spectrum of **VA-PZO** (1: 1).

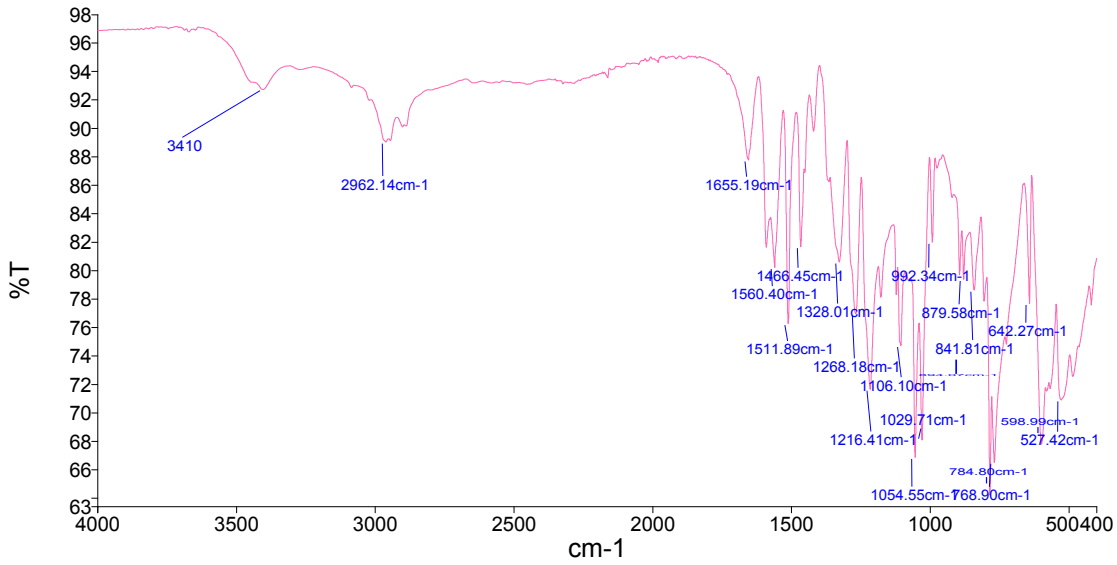

Figure S20. IR spectrum of **VA^{-}-DABCO^{+}-H_2O** (2: 2: 1).

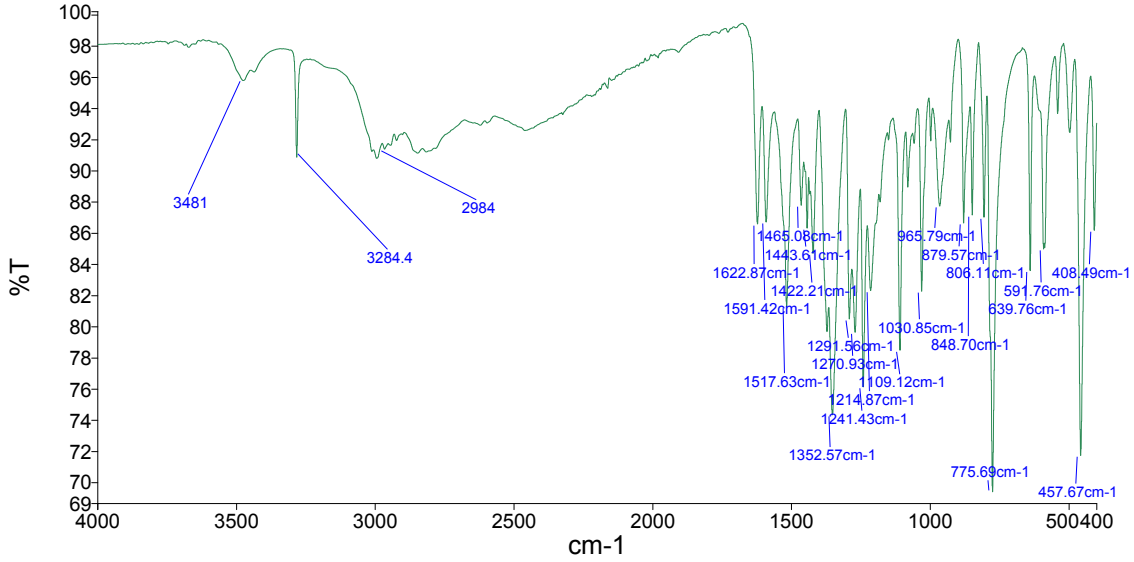

Figure S21. IR spectrum of **VA^{-}-PPZ^{+}-H$_2$O** (2: 2: 1).

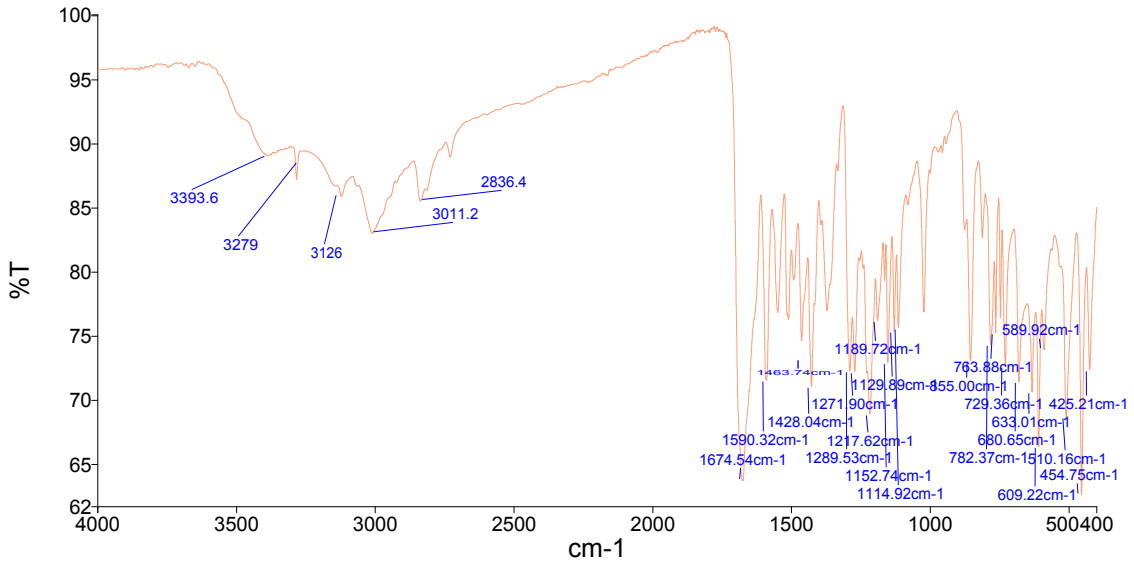

Figure S22. IR spectrum of **VAN-THB-H$_2$O** (1: 1: 2).

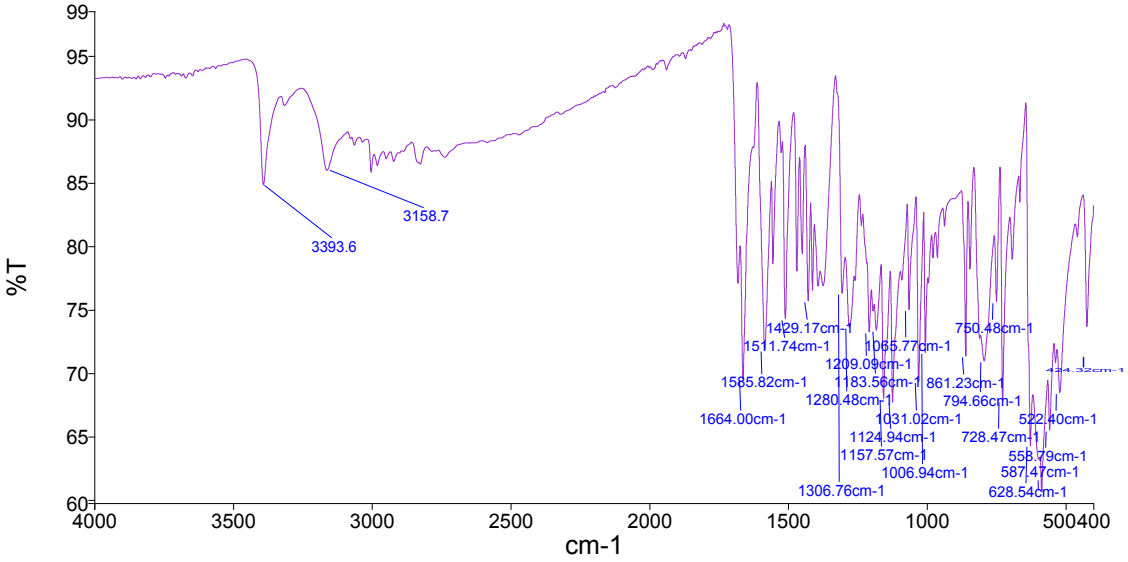

Figure S23. IR spectrum of **VAN-INM** (1: 1).