Supporting Information

Stanozolol-aromatic carboxylic acid crystalline complexes: flexible tautomeric/ionization states and supramolecular synthons

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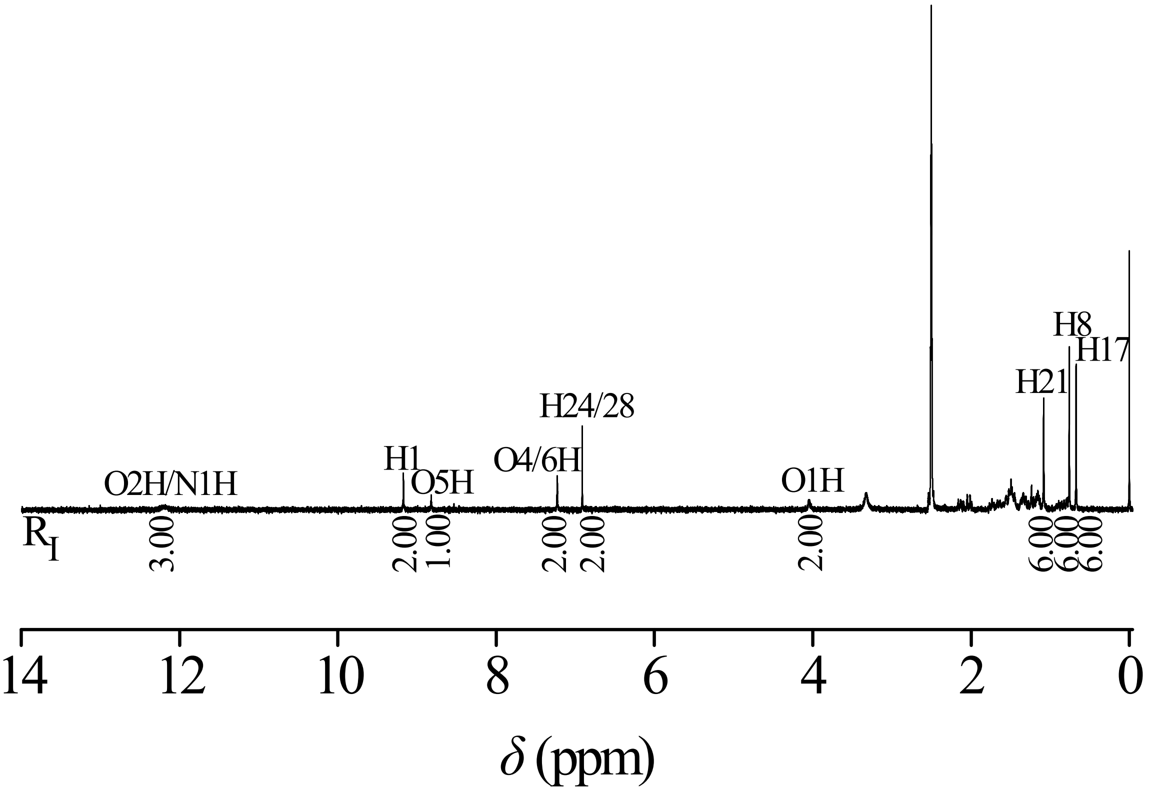
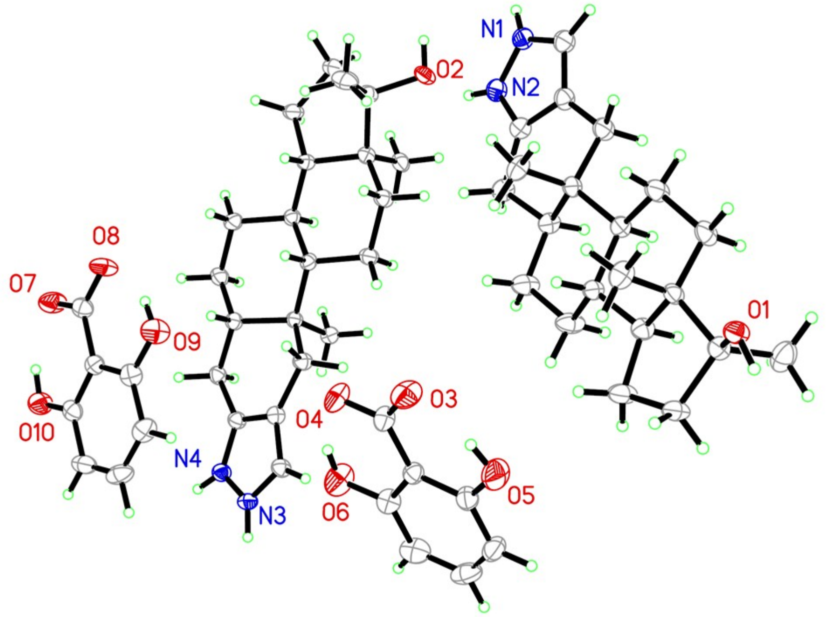
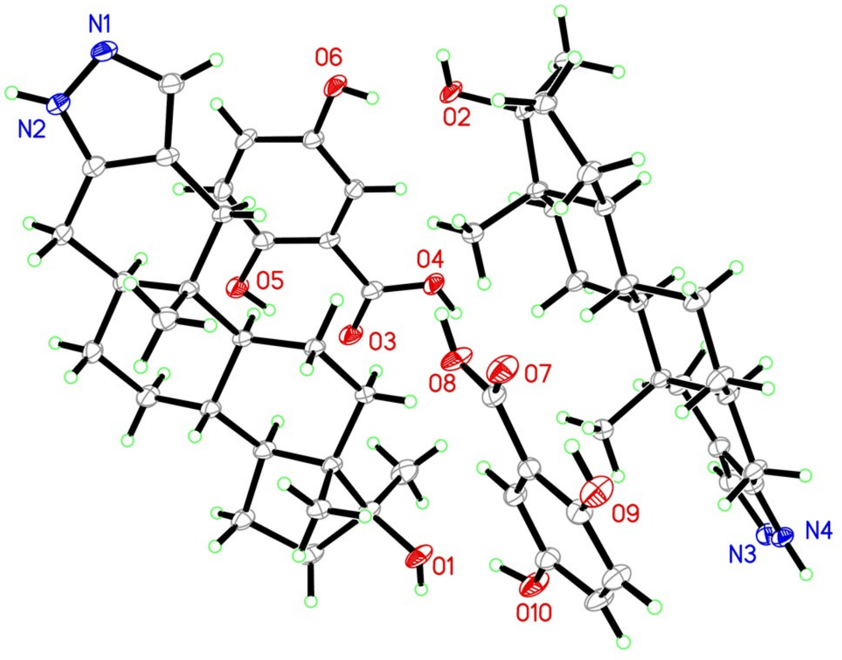


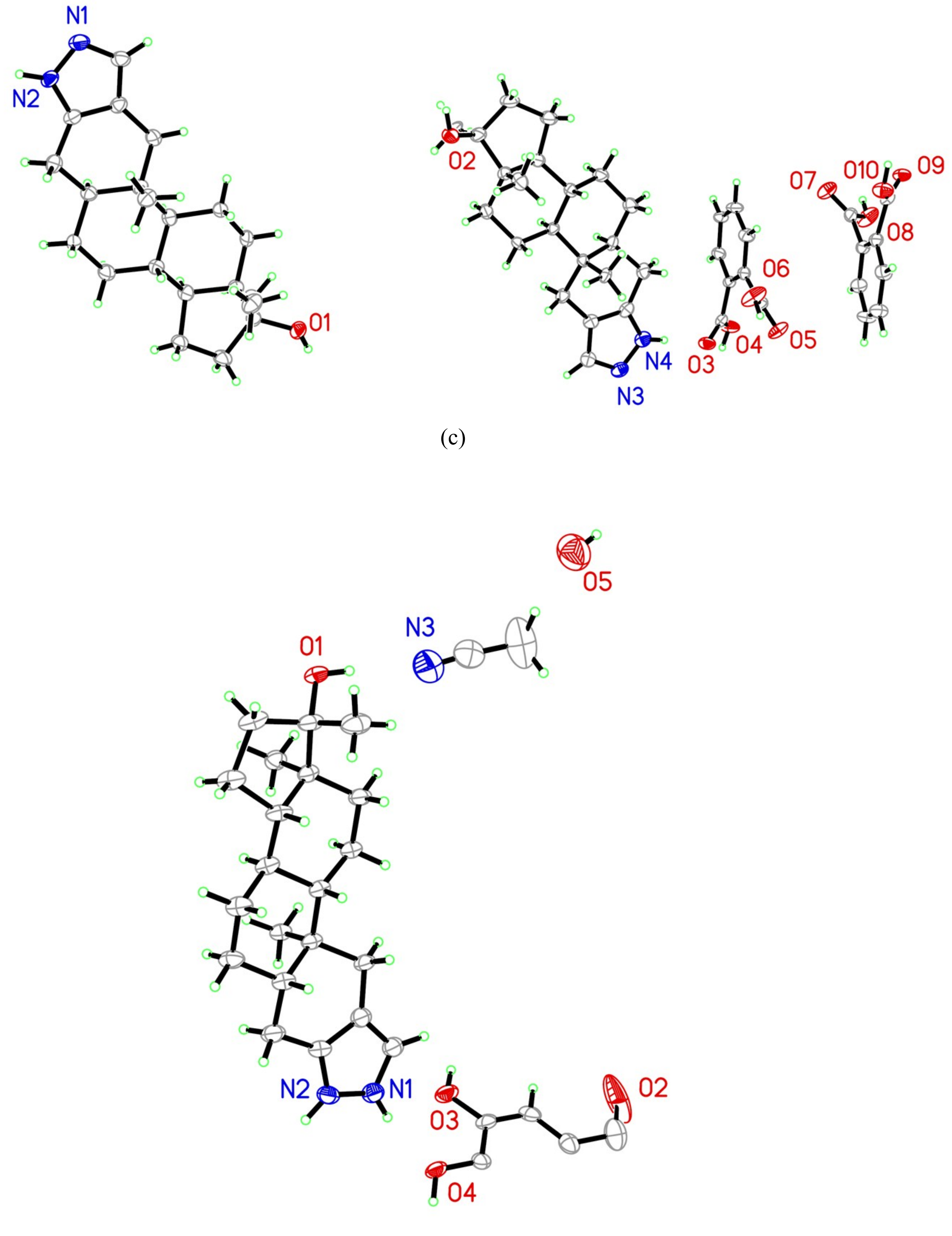
Fig. S1 ^{1}H NMR spectra of STAN-GA. R$_I$: relative integrals of the ^{1}H signals.


N1
O2
N2
O8
O7
O9
O1
O10
O4
O3
N4
O6
O5
N3

(a)


N1
O6
N2
O2
O4
O5
O3
O7
O8
O9
N3
N4
O1
O10

(b)



(c)

(d)

Fig. S2 Thermal ellipsoid drawings of asymmetric units of STAN-DBA (a), STAN-DHA (b), STAN-PHA (c), and STAN-GA-CH_3CN-H_2O (d) at 50% probability level.

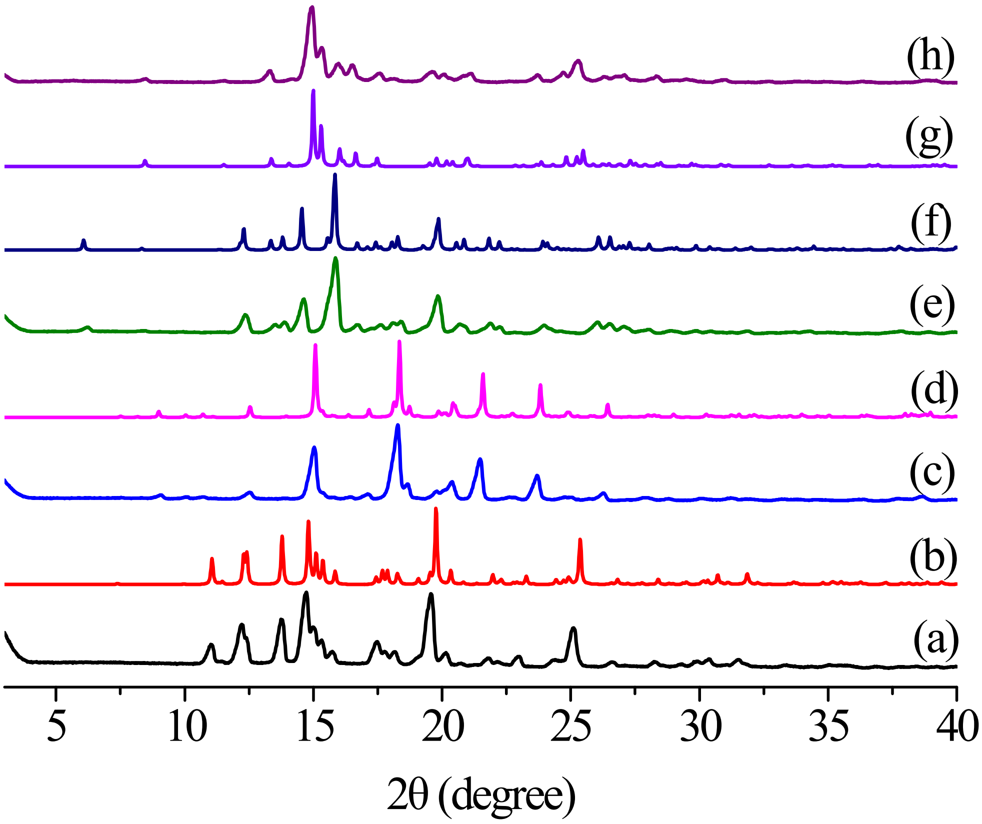


Fig. S3 Experimental and simulated powder XRD patterns of STAN-DBA (a-b), STAN-DHA (c-d), STAN-PHA (e-f), and STAN-GA-CH_3CN-H_2O (g-h).

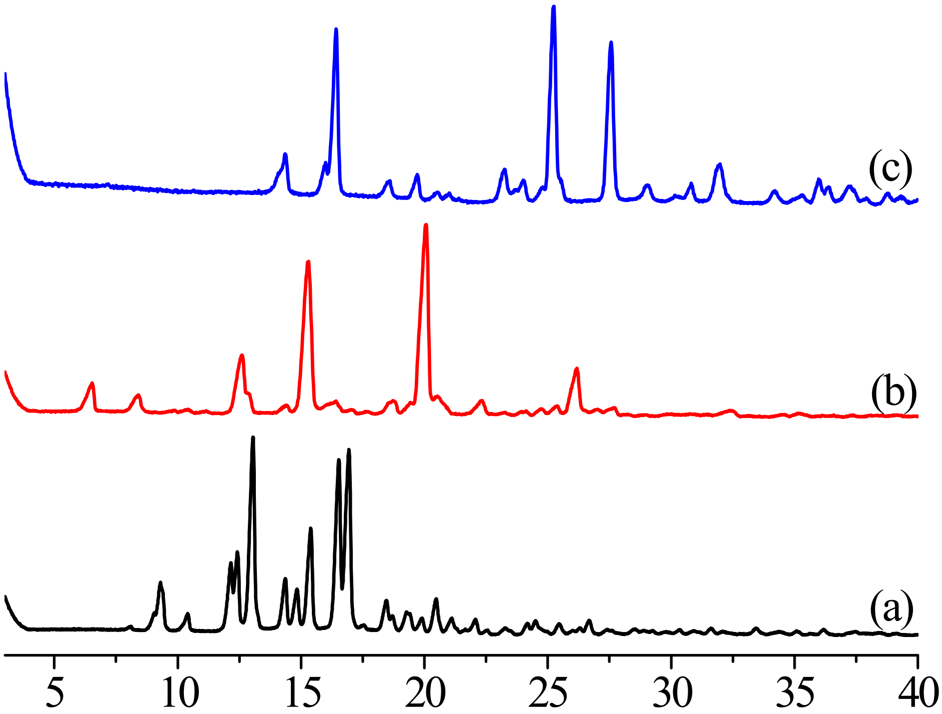


Fig. S4 powder XRD patterns of STAN form II (a), STAN-GA (b), and GA (c),

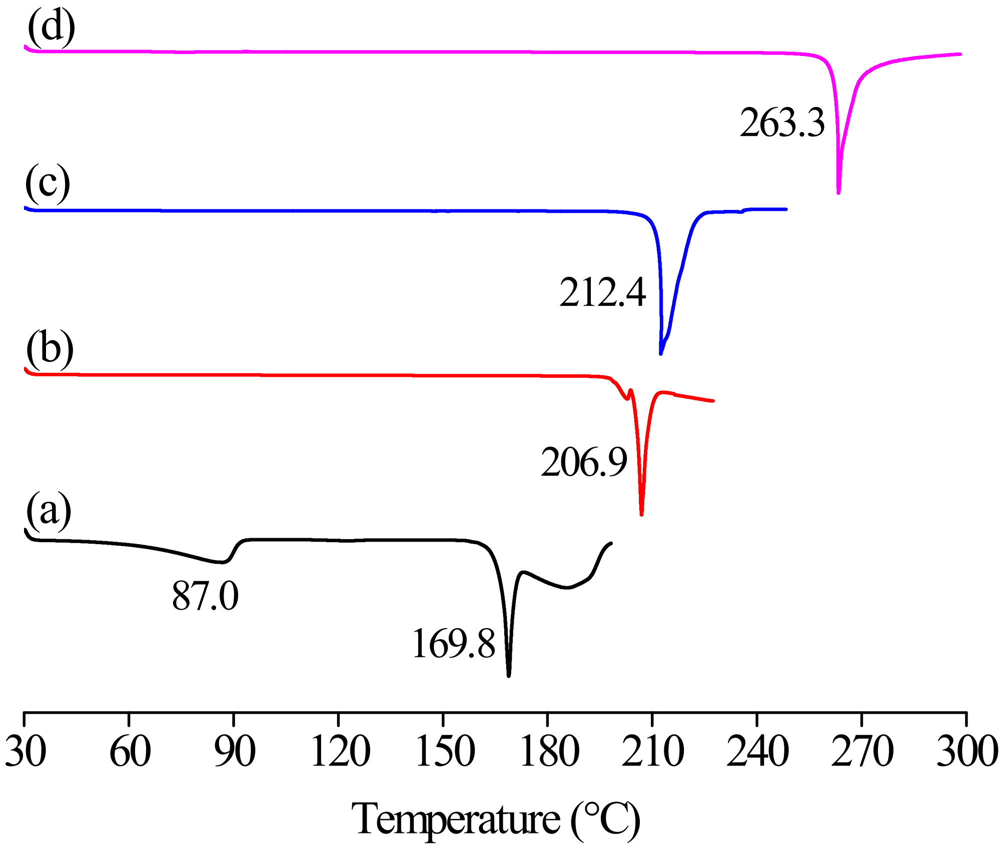


Fig. S5 DSC curves of DBA monohydrate (a), DHA (b), PHA (c), and GA (d).

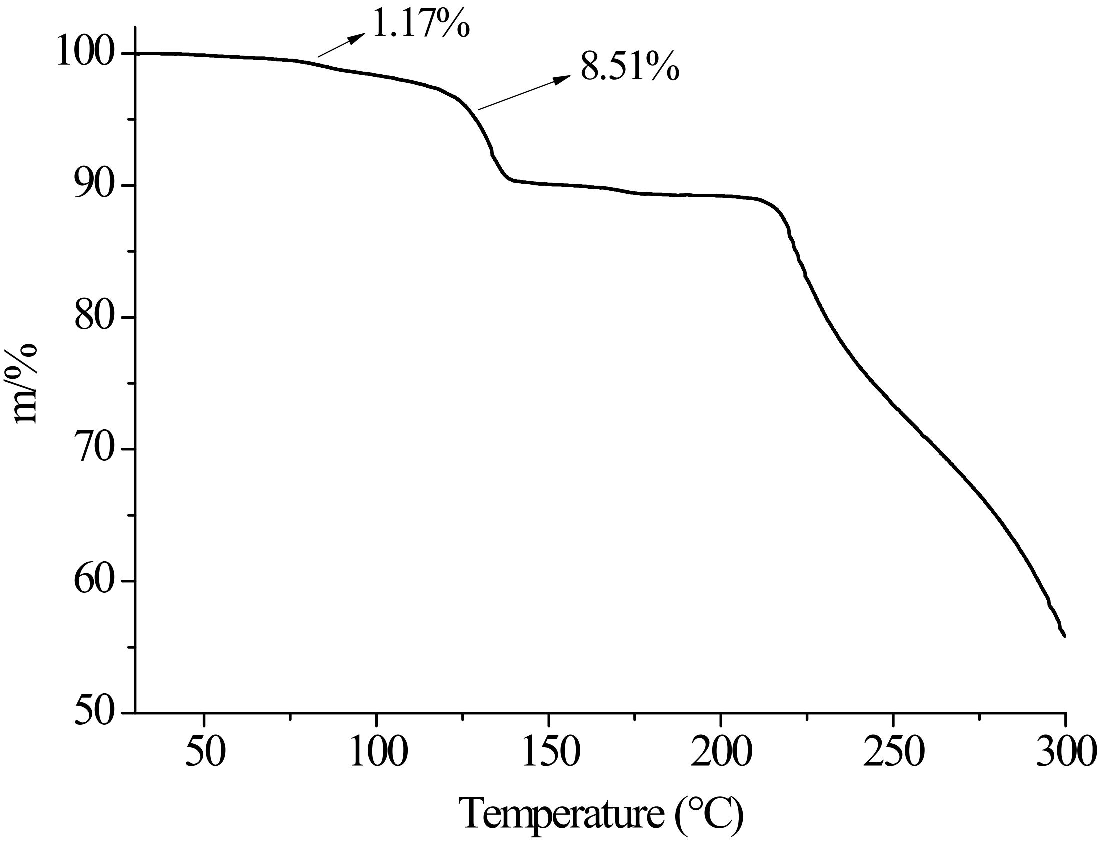


Fig. S6 TG curves of STAN-GA-CH_3CN-H_2O.

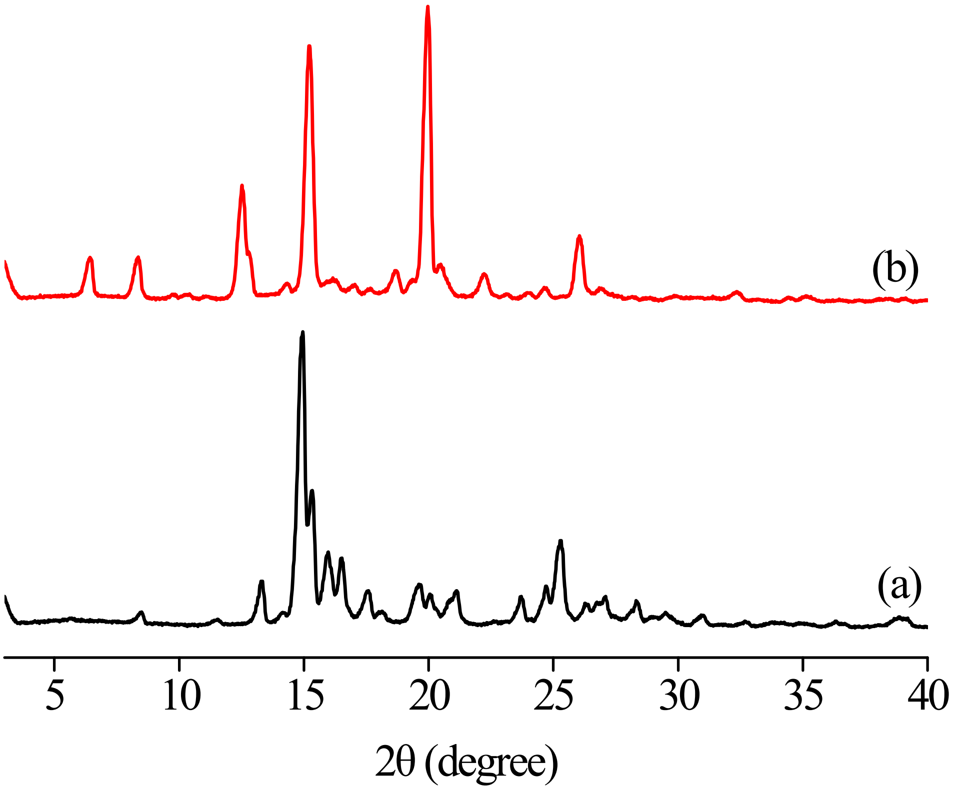


Fig. S7 Powder XRD patterns of STAN-GA-CH_3CN-H_2O before (a) and after desolvent (b).

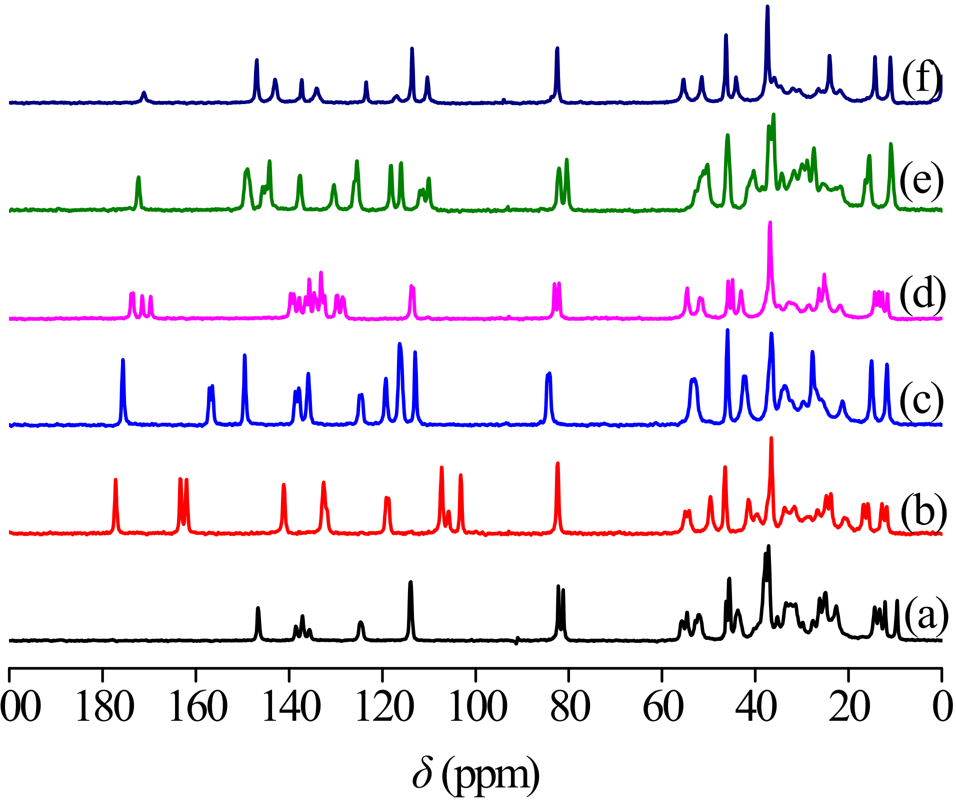


Fig. S8 ^{13}C CP/MAS TOSS NMR spectra of STAN (a), STAN-DBA (b), STAN-DHA (c), STAN-PHA (d), STAN-GA (e), and STAN-GA-CH_3CN-H_2O (f).

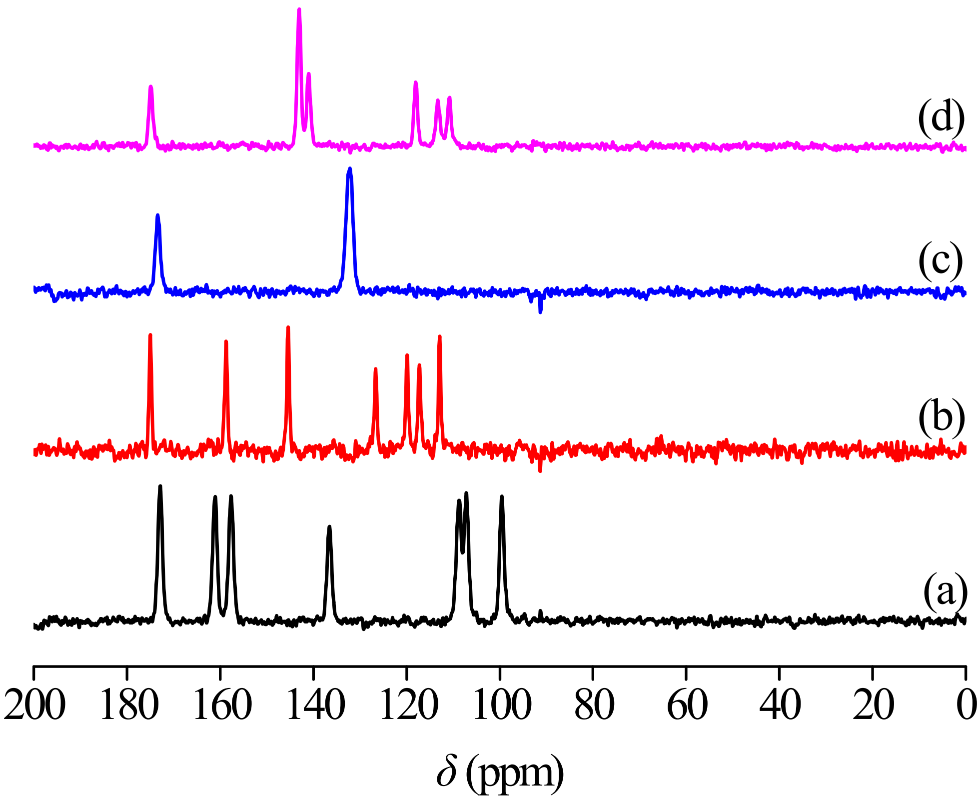


Fig. S9 ^{13}C CP/MAS TOSS NMR spectra of DBA monohydrate (a), DHA (b), PHA (c), and GA (d).

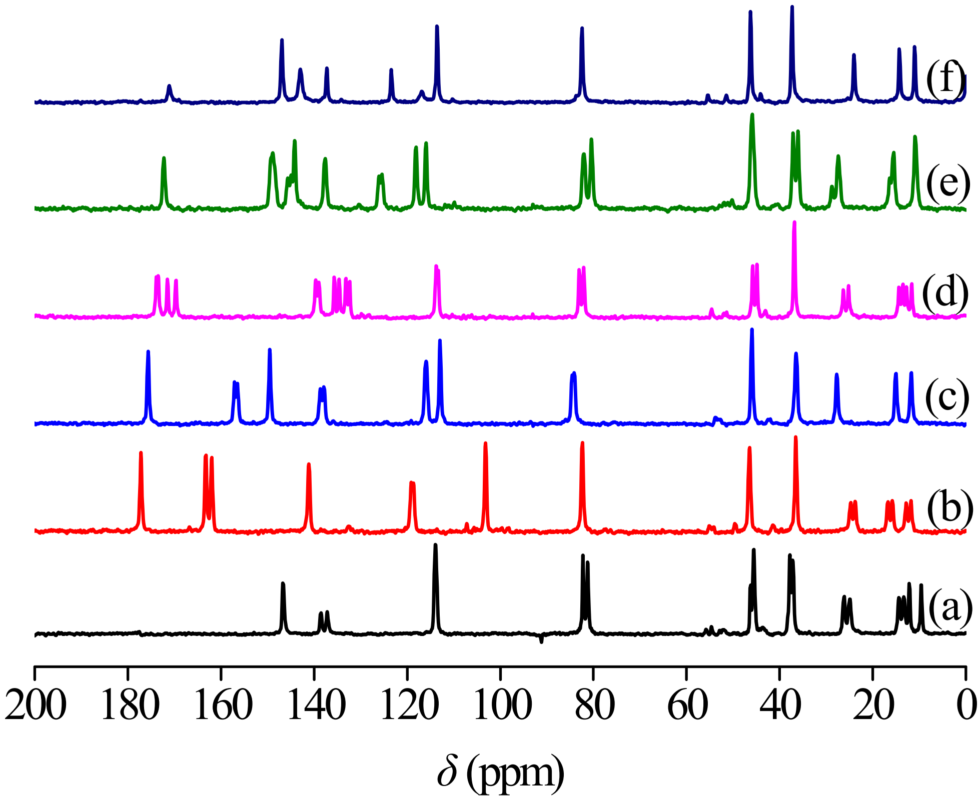


Fig. S10 ^{13}C CP/MAS NQS TOSS NMR spectra of STAN (a), STAN-DBA (b), STAN-DHA (c), STAN-PHA (d), STAN-GA (e), and STAN-GA-CH_3CN-H_2O (f).

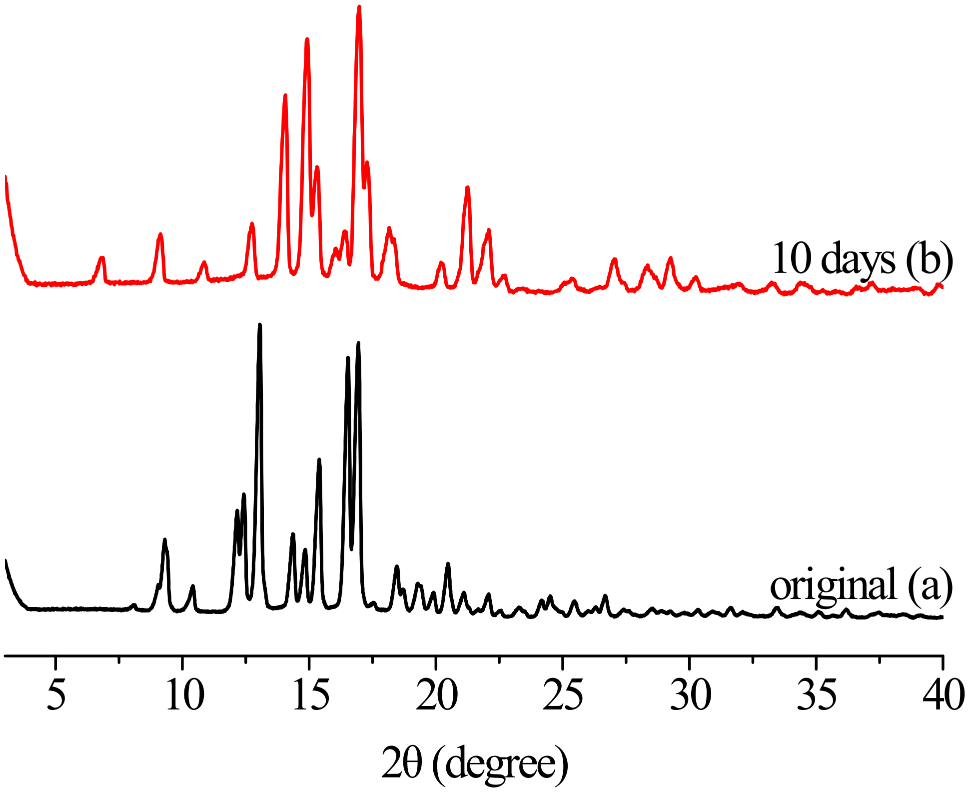


Fig. S11 Powder XRD patterns of STAN before (a) and after (b) 10 days equilibration under 25°C/95% RH.

Table S1 Signal assignment processes (for C1-C3) for STAN and its complexes

Sample	Tautomer A			Tautomer B			STAN cation		
	C1	C2	C3	C1	C2	C3	C1	C2	C3
STAN II	Y	Y	Y	NQS	Y	NQS			
STAN-SAC							DFT	DFT	DFT
STAN-AH							Y	Y	Y
STAN-DBA							NQS,DFT	Y	Y
STAN-DHA				Y	NQS	Y			
STAN-PHA				NQS,DFT	Y	NQS			
STAN-GA	NQS	Y	*	-, NQS			Y	NQS	*
STAN-GA-CH3CN-				NQS	Y	Y	NQS	Y	Y

* can not be accurately assigned

Y: can be assigned without assist;

NQS: can be assigned using NQS spectrum;

DFT: can be assigned using DFT calculation (Table S2);

-: can be excluded.

Table S2 Experimental and theoretical ^{13}C chemical shifts (C1-C3) for some STAN complexes*

Sample	C1	C2	C3
STAN-SAC	131.9[130.4]	120.1[120.2]	141.5[139.7]
STAN-DBA	131.9/132.6[129.9/130.5]	118.7/119.2[118.0/119.8]	141.1[139.1/139.2]
STAN-PHA	136.4/137.8[135.3/137.6]	113.4/113.8[112.5/112.9]	139.6/139.0[139.1/138.9]

* Theoretical values are given in []. The calculation method can be found in CrystEngComm, 2014, 16, 3141.