Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary material

On molecular complexes derived from amino acids and nicotinamides in combination with boronic acids

Javier Hernández-Paredes,[a] Ana L. Olvera-Tapia,[a] Jenniffer I. Arenas-García,[b] Herbert Höpfl,[a,*] Hugo Morales-Rojas,[a] Dea Herrera-Ruiz,[b] Ana Isabel Gonzaga-Morales,[b] and Lourdes Rodríguez-Fragoso[b]

a) Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos. Av. Universidad 1001, C.P. 62209. Cuernavaca, México. Tel., Fax: +52 777 3297997. E-mail: hhopfl@uaem.mx

b) Facultad de Farmacia, Universidad Autónoma del Estado de Morelos. Av. Universidad 1001, C.P. 62209. Cuernavaca, México.

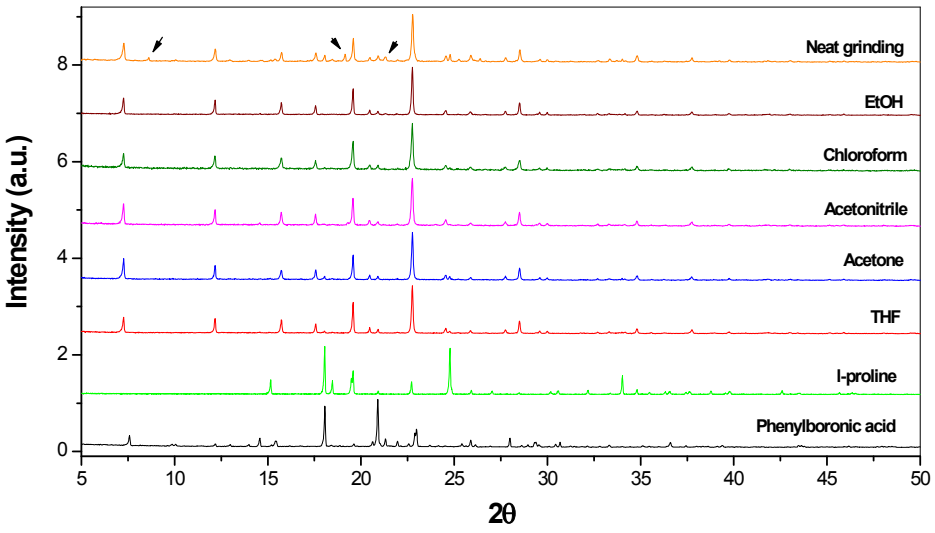

Figure S1. X-ray powder diffraction patterns of PBA–PRO obtained from neat and liquid-assisted grinding experiments. XRPD patterns of the starting materials are included for comparison.

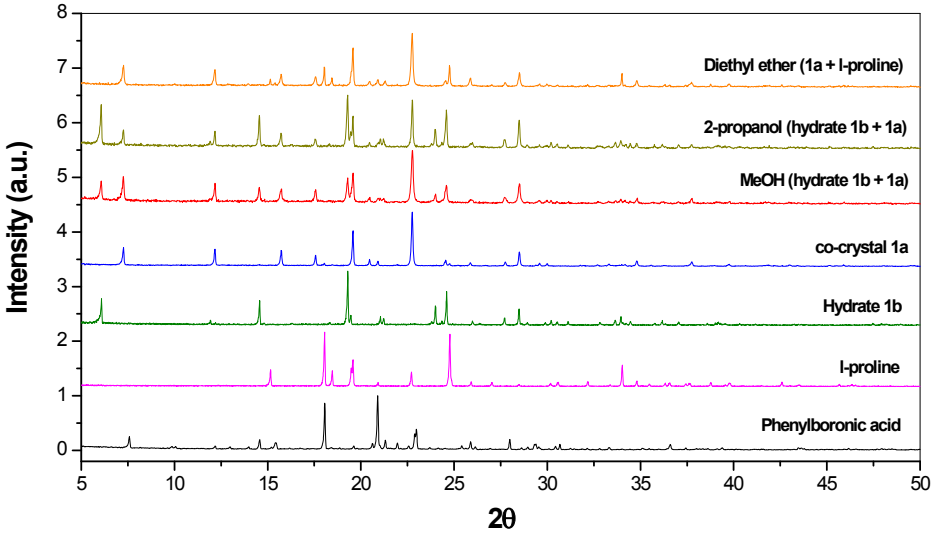

Figure S2. Liquid-assisted grinding of PBA and PRO using diethyl ether, 2-propanol and MeOH gives phase mixtures of PBA–PRO (**1a**) and PBA–PRO–H_2O (**1b**), as seen from the X-ray powder diffraction patterns.

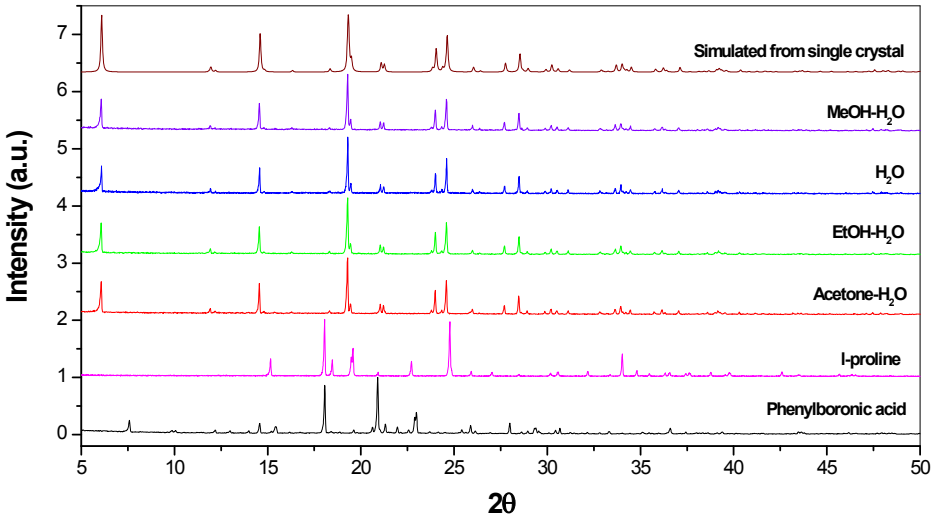

Figure S3. X-ray powder diffraction patterns of PBA–PRO–H_2O obtained from liquid-assisted grinding experiments. XRPD patterns of the starting materials and simulated XRPD data are included for comparison.

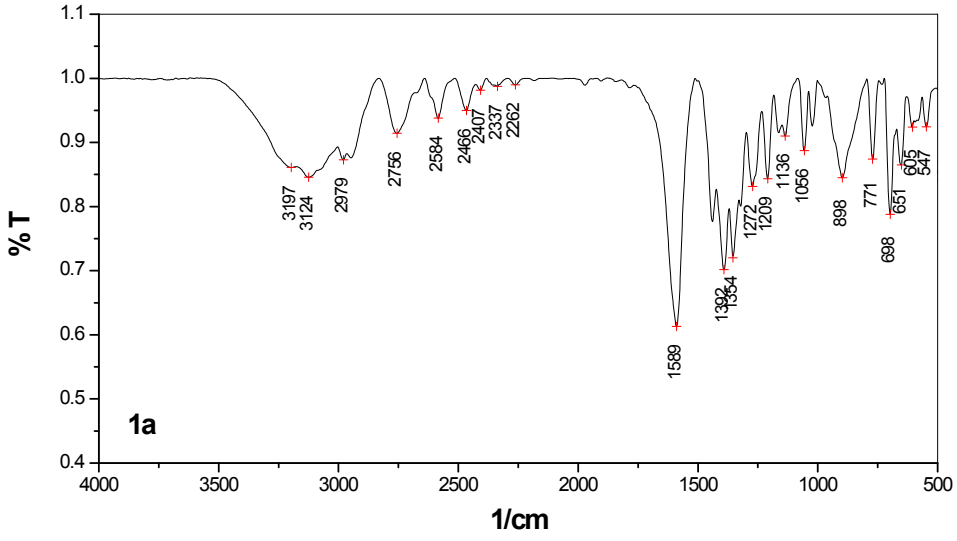

Figure S4. IR spectrum of PBA–PRO.

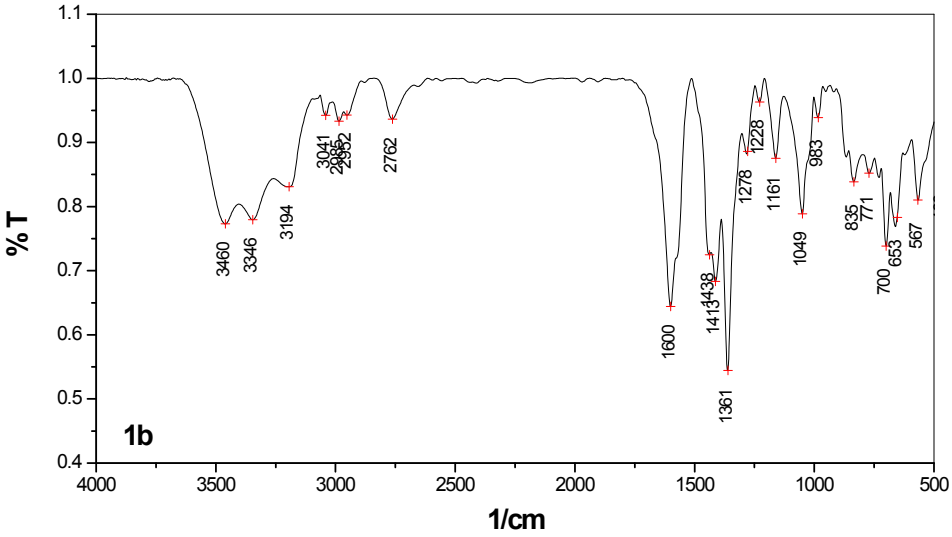

Figure S5. IR spectrum of PBA–PRO–H_2O.

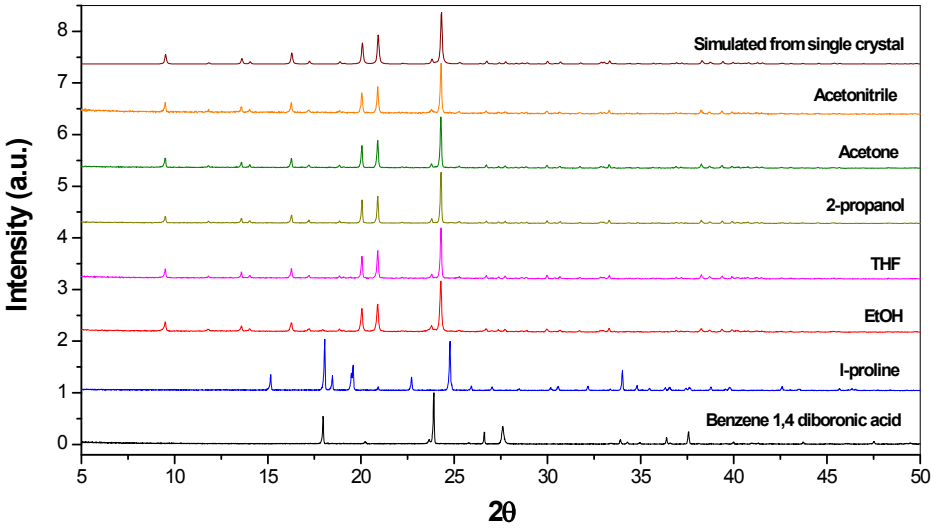

Figure S6. X-ray powder diffraction patterns of α-BDBA–PRO obtained from neat and liquid-assisted grinding experiments. XRPD patterns of the starting materials and simulated XRPD data are included for comparison.

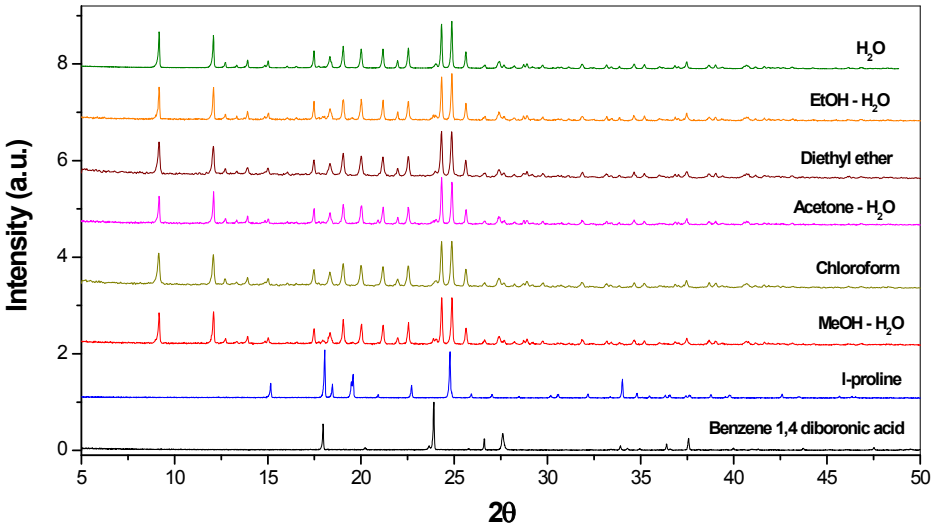

Figure S7. X-ray powder diffraction patterns of *β*-BDBA–PRO obtained from neat and liquid-assisted grinding experiments. XRPD patterns of the starting materials are included for comparison.

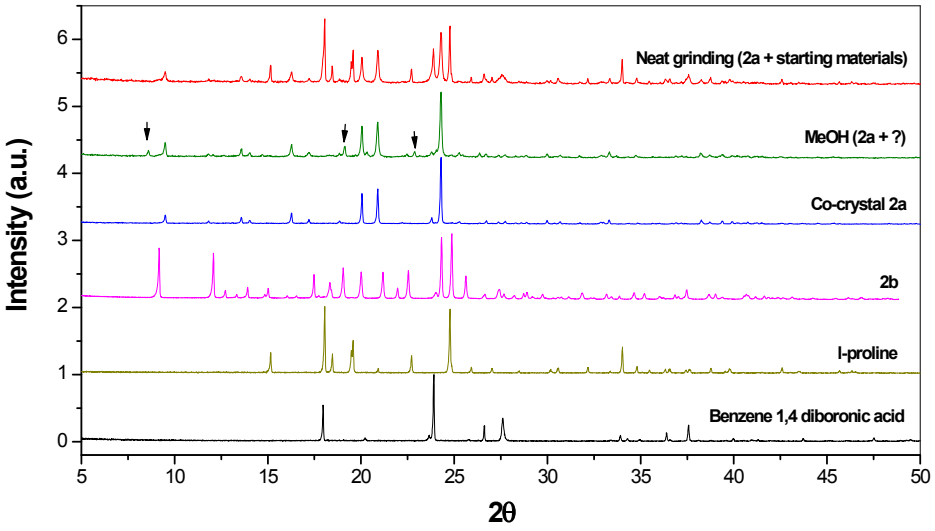

Figure S8. As seen from the X-ray powder diffraction patterns, liquid-assisted grinding using MeOH gives a phase mixture of *α*-BDBA–PRO (**2a**) and an unknown compound, while neat grinding gives a phase mixture of *α*-BDBA–PRO and starting materials. XRPD patterns of the starting materials and cocrystals *α*-BDBA–PRO (**2a**) and *β*-BDBA–PRO (**2b**) are included for comparison.

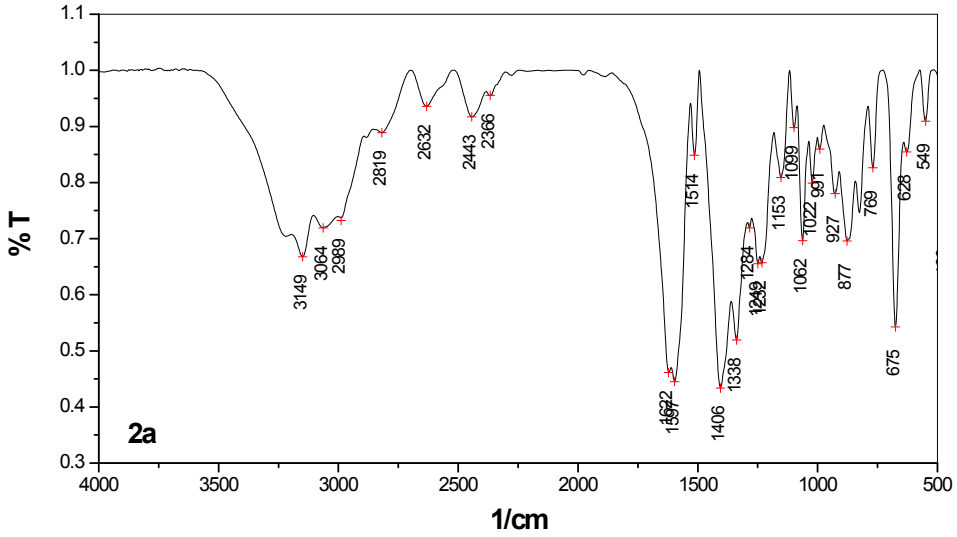

Figure S9. IR spectrum of α-BDBA–PRO.

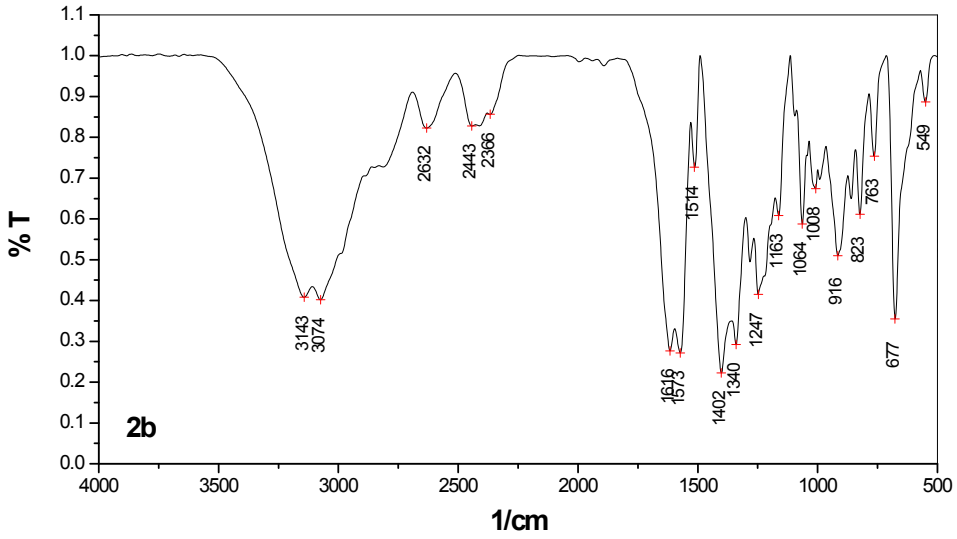

Figure S10. IR spectrum of β-BDBA–PRO.

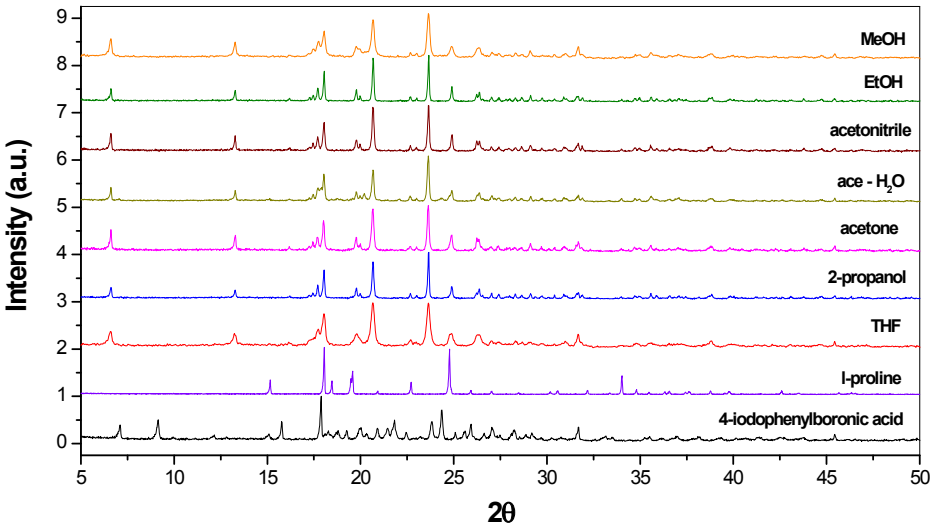

Figure S11. X-ray powder diffraction patterns of α-IPBA–PRO obtained from liquid-assisted grinding experiments. XRPD patterns of the starting materials are included for comparison.

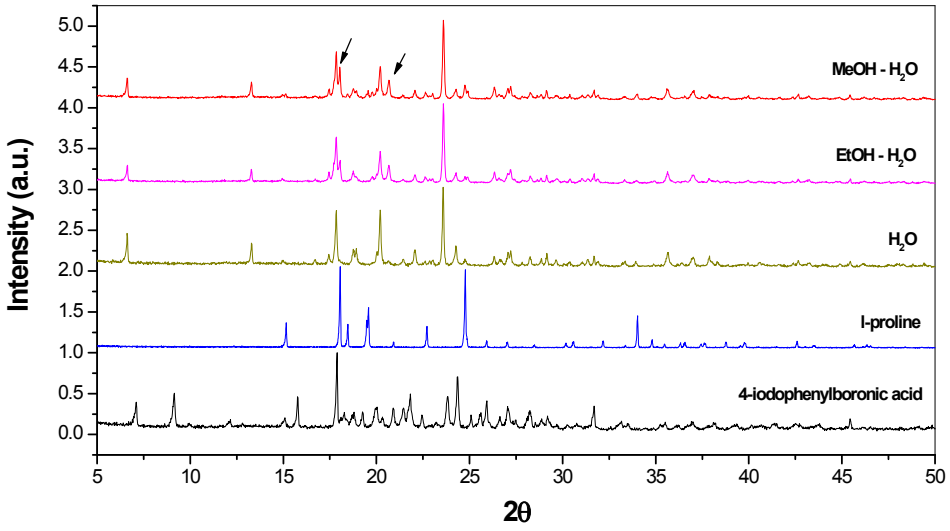

Figure S12. X-ray powder diffraction patterns of β-IPBA–PRO obtained from liquid-assisted grinding experiments. XRPD patterns of the starting materials are included for comparison.

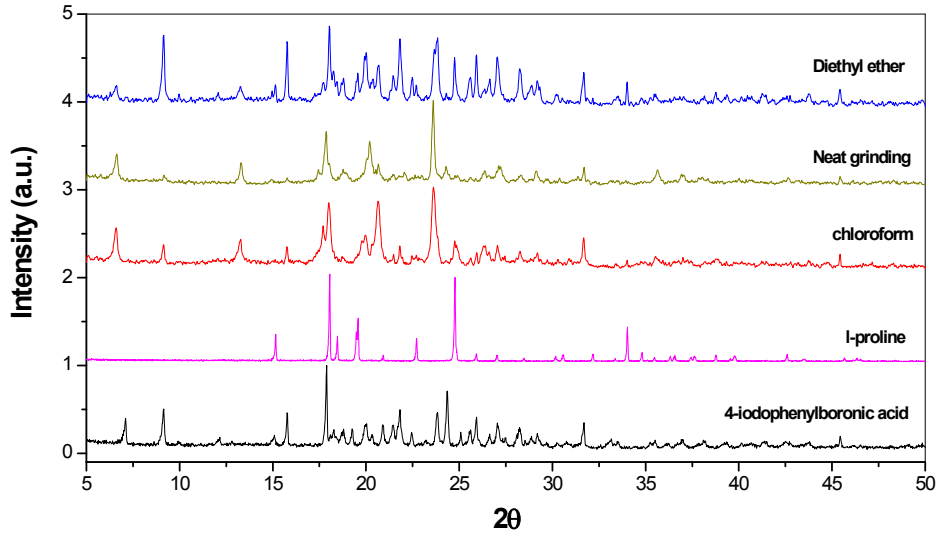

Figure S13. Neat grinding and liquid-assisted grinding of IPBA and PRO using diethyl ether and chloroform give phase mixtures, as seen from the X-ray powder diffraction patterns.

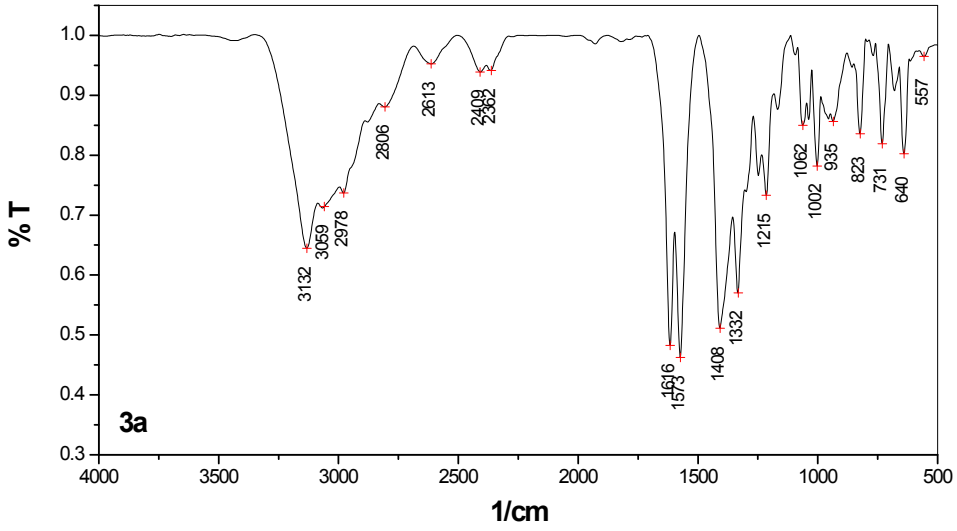

Figure S14. IR spectrum of α-IPBA–PRO.

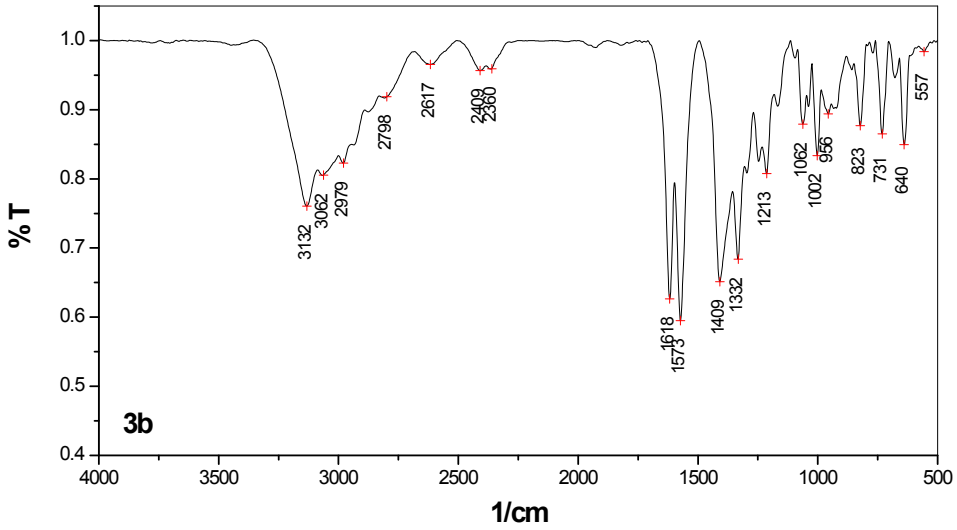

Figure S15. IR spectrum of *β*-IPBA–PRO.

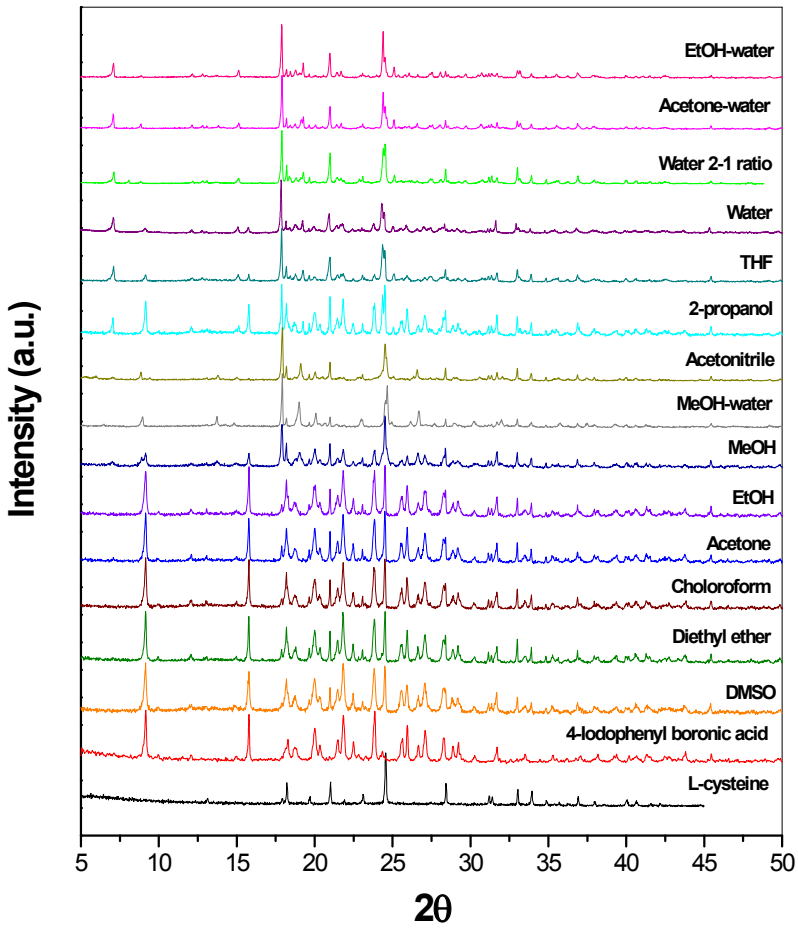

Figure S16. XRPD data of the co-crystal screening experiments with *L*-cysteine and 4-iodophenylboronic acid.

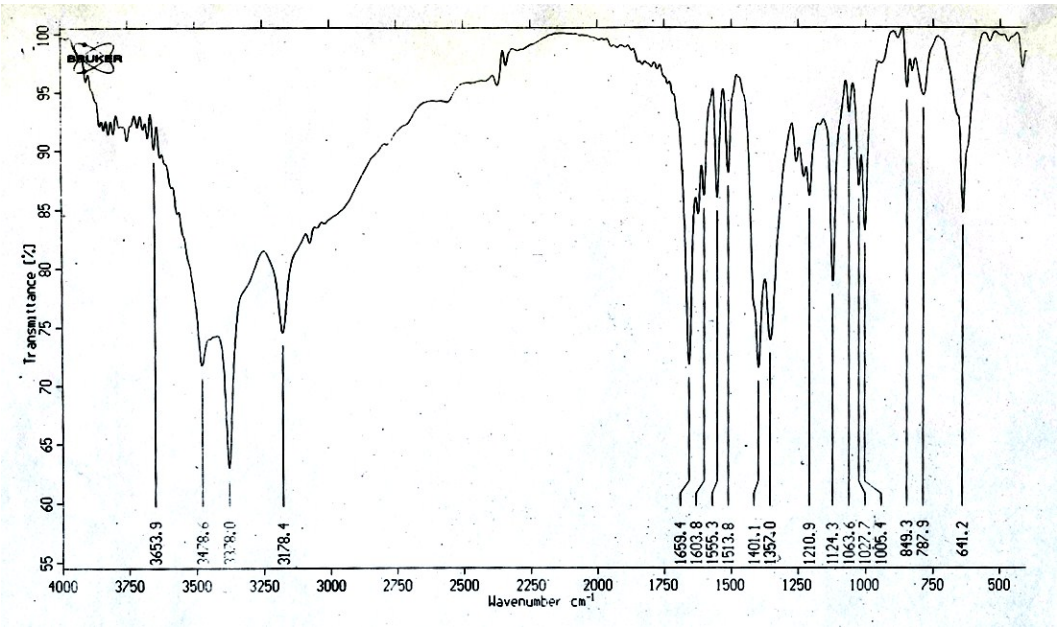

Figure S17. IR spectrum of BDBA–INA.

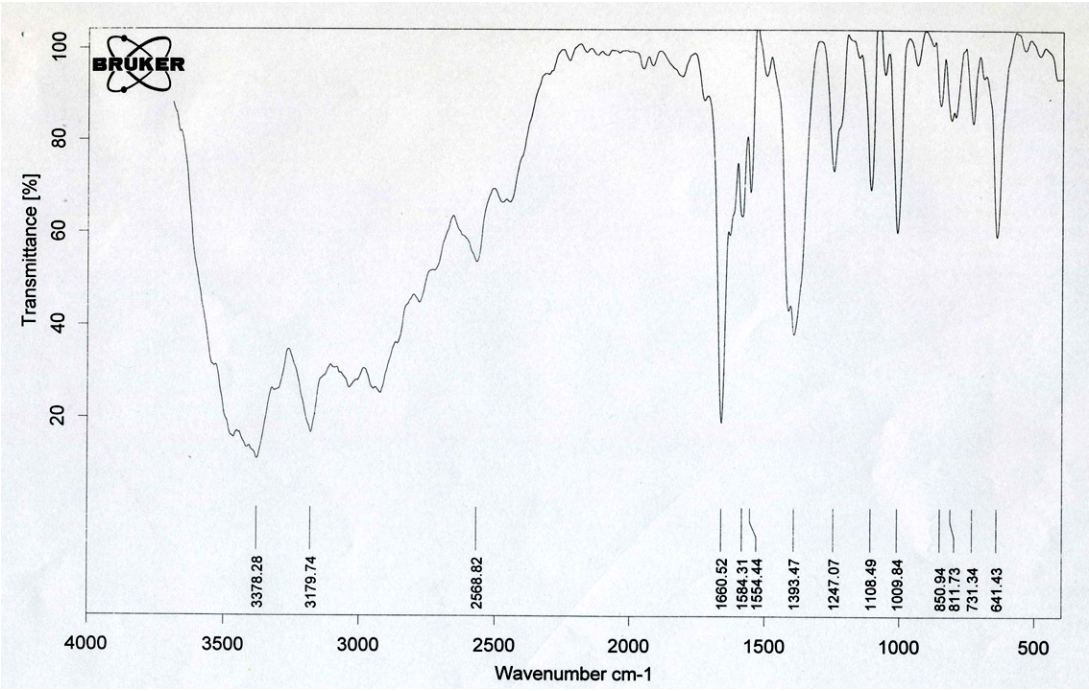

Figure S18. IR spectrum of IPBA–INA.

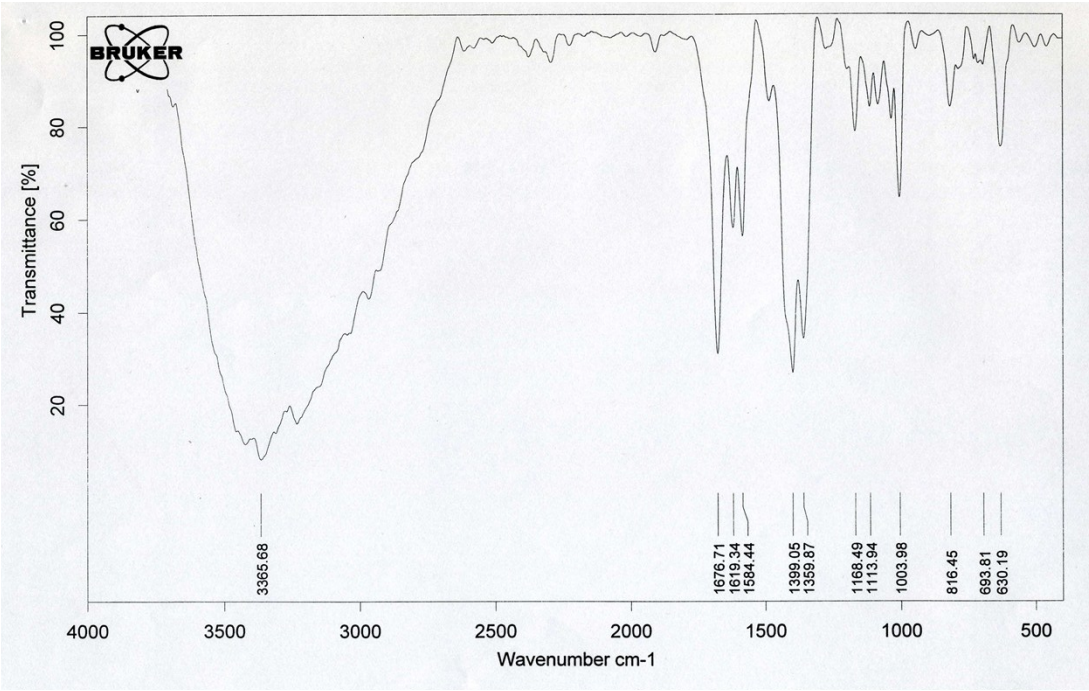

Figure S19. IR spectrum of IPBA–NA.

TG-DSC analysis

The molecular complexes PBA–PRO and PBA–PRO–H_2O are pseudopolymorphs, which is reflected in the TGA and DSC traces (Fig. S20-S23, Table 4). The TGA graph of PBA–PRO indicates an initial mass loss of ~10 %, starting at approximately 80 °C (T_{peak} = 91 °C), which is accompanied by an endothermic peak in the DSC plot. In accordance with previous studies, the degradation reaction can be attributed to the dehydration reaction of PBA to the corresponding anhydride, 1,3,5-triphenylboroxine (calcd.: 7.6 %).[47] There was no mass loss related to the following exothermal peak observed in the DSC trace at 160 °C, which may indicate a solid-solid transformation. After this transformation, the TGA graph showed that the retained mass started to decompose in the temperature range of 190-260 °C, which is related to a broad endothermic peak with minima at 251, 256 and 277 °C. Since the sublimation of pure PRO occurs at T_{peak} = 250 ºC,[48] it can be suggested that during this process first elimination of PRO takes place (calcd.: 48.6 %) followed by decomposition of 1,3,5-triphenylboroxine.

In general, the TGA and DSC traces of PBA–PRO–H_2O (Fig. S22-S23, Table 4) resemble the thermal behavior of PBA–PRO. However, the initial endothermic event started at a lower temperature (T_{onset} = 54 °C, T_{peak} = 63 °C) and the weight loss of ~14 % was larger, which indicates that first the loss of the crystal lattice water molecules occurred followed by dehydration of PBA (calcd.: 14.1 %).

Cocrystals α-BDBA–PRO and β-BDBA–PRO are polymorphs, thus giving very similar TGA and DSC curves (Fig. S24-27, Table 4). The TGA graph of α-BDBA–PRO showed an initial mass loss of ~9 % starting at about ~129 °C (T_{peak} = 149 ºC), which is in accordance with the loss of two stoichiometric equivalents of water (calcd.: 9.1 %) and can be attributed to the dehydration of BDBA.[49] The mass loss of ~58 % starting at ~267 °C (T_{peak} = 282 °C) is consistent with the elimination of two molecules of PRO (calcd.: 58.1 %).[48] In comparison, for the molecular complex β-BDBA–PRO the most remarkable difference is found in the DSC trace for the dehydration process The shift to higher temperature values (T_{onset} = 133 °C, T_{peak} = 155 °C) indicates that α-BDBA–PRO is thermodynamically more stable than β-BDBA–PRO .

For the polymorph pair α-BDBA–PRO/β-BDBA–PRO, the TGA and DSC curves of α-IPBA–PRO and β-IPBA–PRO are also strongly related (Fig. S28-S31, Table 4). The TGA trace

of α-IPBA–PRO indicates an initial mass loss of ~7% starting at about ~116 °C (T_{peak} = 127 ºC), which could be attributed to the dehydration of IPBA (calcd.: 5.0 %). There was an additional mass loss of ~5% related to an exothermal event observed in the DSC trace at T_{peak} = 182 °C, which may indicate that an additional decomposition reaction took place. After the reaction, the TGA graph showed a mass loss of ~25 % accompanied by a broad endothermic peak with minima at 274, 279 and 312 ºC similar to that observed for the remaining, above-described cocrystals with PRO. However, the relatively large difference with the calculated weight loss of 31.7 % indicates that the elimination of PRO took now place in two steps. For β-IPBA–PRO, in the DSC trace the first endothermic thermal event started at ~120 °C with peak minimum at 130 °C, which suggests that now polymorph II is thermodynamically more stable than α-IPBA–PRO.

The TGA graph of BDBA–INA (Fig. S32) indicates an initial mass loss of ~12 % starting at ~140 °C (T_{peak} = 157 ºC) that can be attributed to the dehydration of BDBA (calcd.: 8.8 %). The subsequent mass loss of ~62 % in the temperature range of 157-360 ºC is in good agreement with the complete sublimation of two stoichiometric equivalents of isonicotinamide (calcd.: 62.5 %).

The TGA and DSC curves of IPBA–INA (Fig. S33-34) indicate an initial mass loss of ~5 % starting at ~ 85°C (T_{peak} = 95 ºC) to give the corresponding boroxine upon dehydration of IPBA (calcd.: 4.9 %). After this event, there were two exothermic signals at 106 and 129 °C. Subsequent mass loss starts at ~145°C (T_{peak} = 152 ºC) and occurs in several steps. According to the sublimation point of INA (T_{peak} = 159 °C), the initial mass loss of ~25.5 % in the temperature range of 145-230 ºC should correspond to the elimination of this component.[49] However, the observed weight loss is significantly lower than the expected value (calcd.: 34.6 %), indicating that INA is lost in more than one step. The subsequent weight loss of 21.7 % in the temperature range of 230-290 °C exceeds the remanent mass of INA, indicating that also the decomposition of 1,3,5-tris-(4-iodophenyl)boroxine has initiated. The TGA and DSC graphs of IPBA–NA (Fig. S35-36) are similar to those of IPBA–INA. After an initial mass loss of ~5.8 % starting at ~70 °C (T_{peak} = 81 ºC) for the dehydration of IPBA (calcd.: 4.9 %), from 140 to 200 ºC there was a mass

loss of 11.4 % followed by a further loss of 12.3 % in the range of 200-230 ºC, which in sum are significantly lower than the expected weight loss for the sublimation of NA (calcd.: 34.6 %).

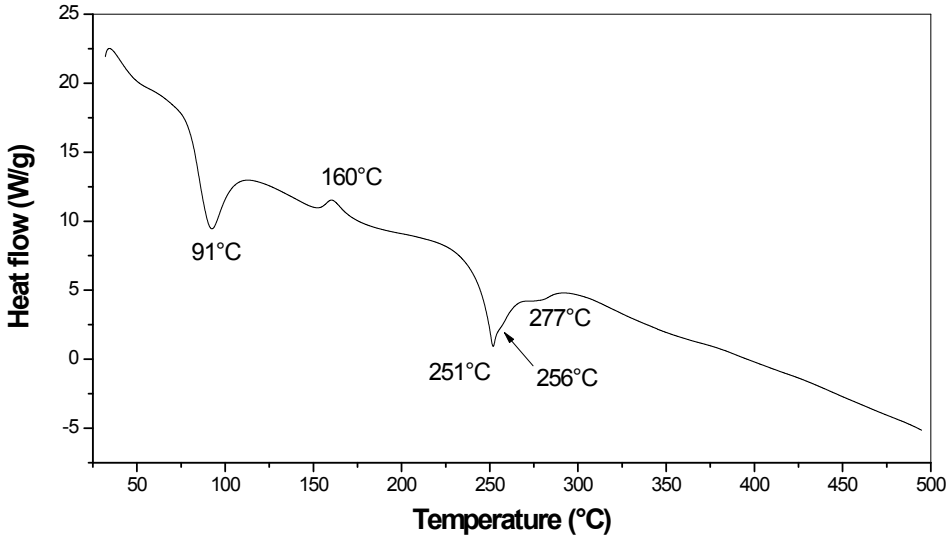

Figure S20. DSC trace of PBA–PRO.

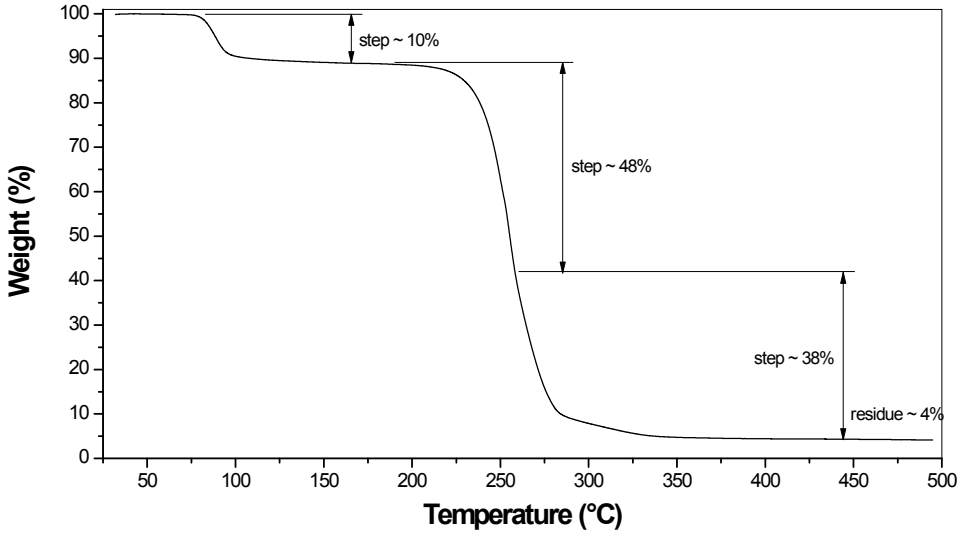

Figure S21. TGA trace of PBA–PRO.

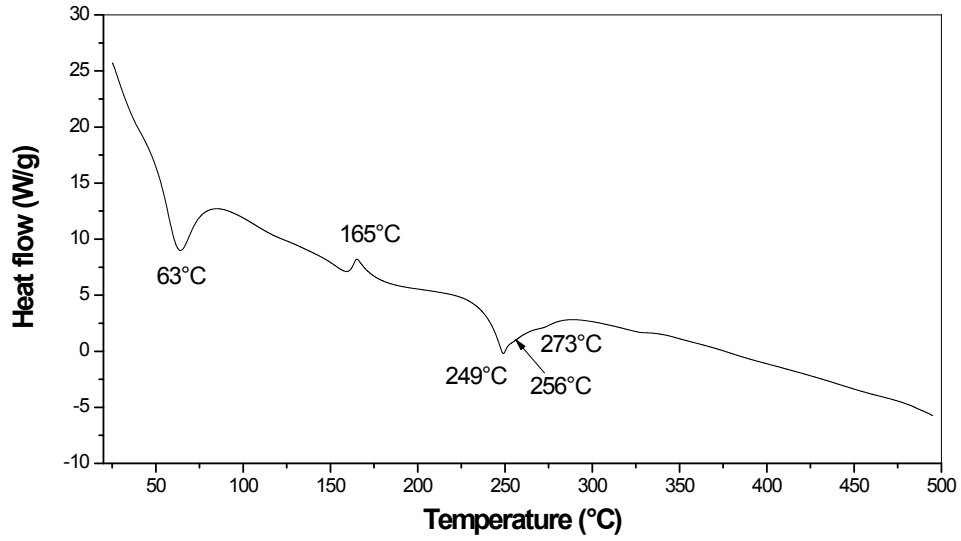

Figure S22. DSC trace of PBA–PRO–H_2O.

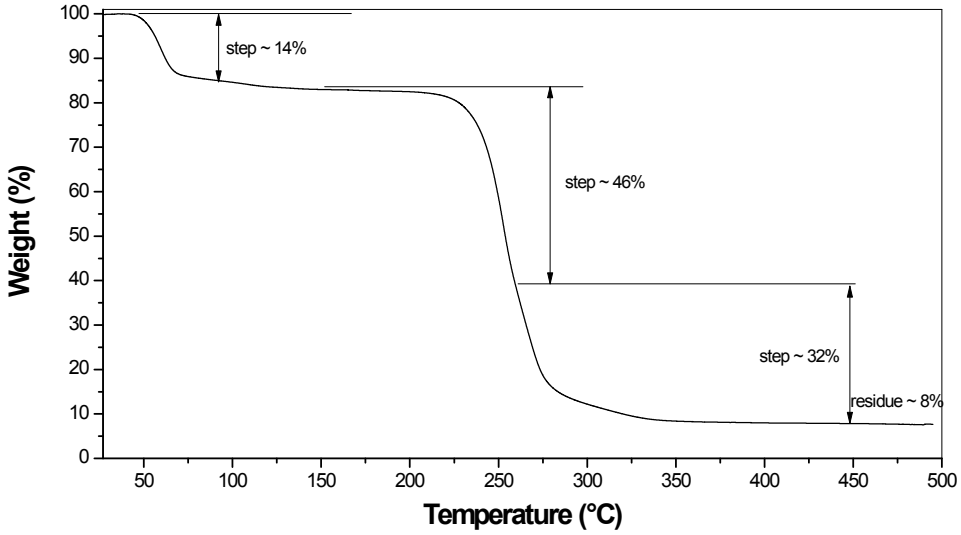

Figure S23. TGA trace of PBA–PRO–H_2O.

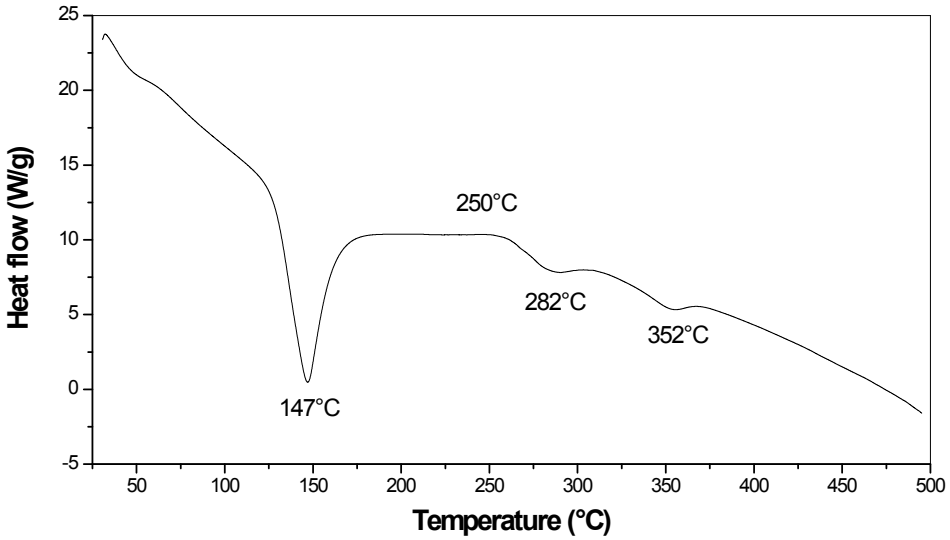

Figure S24. DSC trace of α-BDBA–PRO.

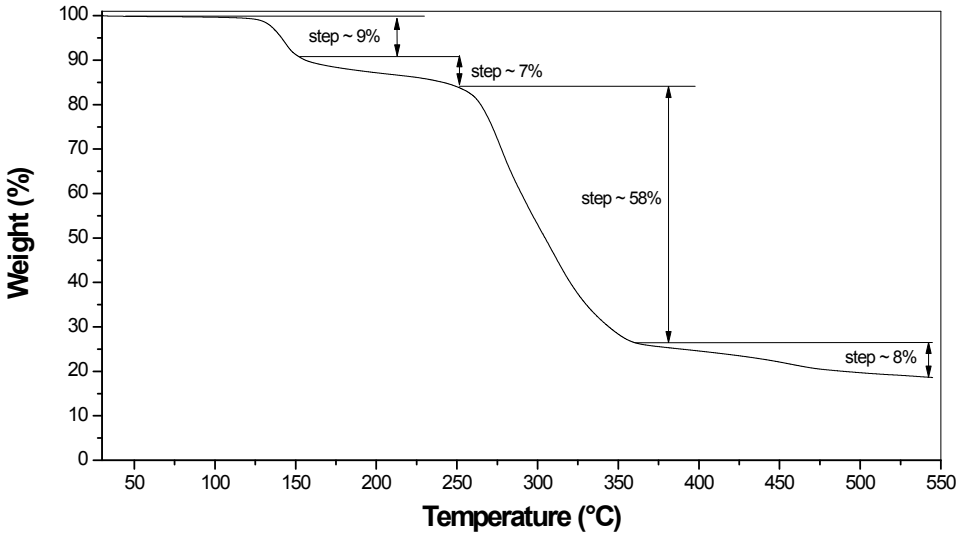

Figure S25. TGA trace of α-BDBA–PRO.

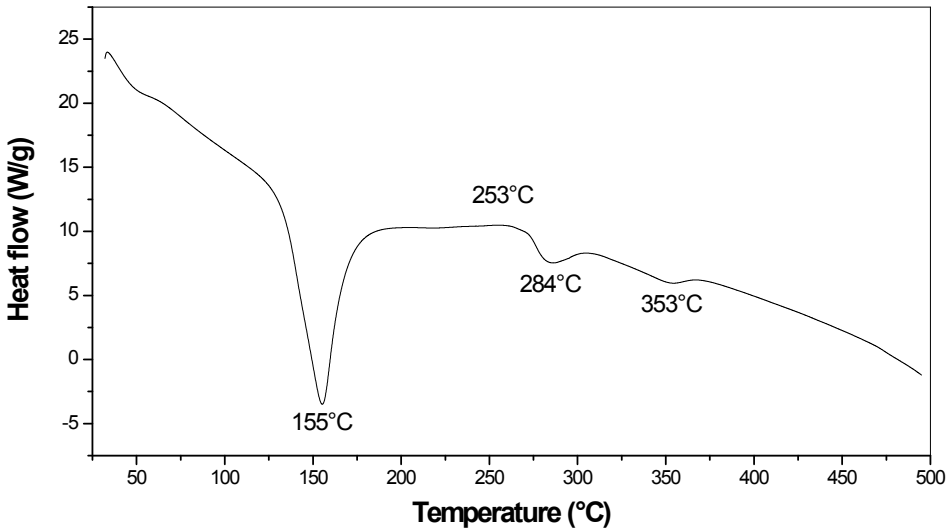

Figure S26. DSC trace of β-BDBA–PRO.

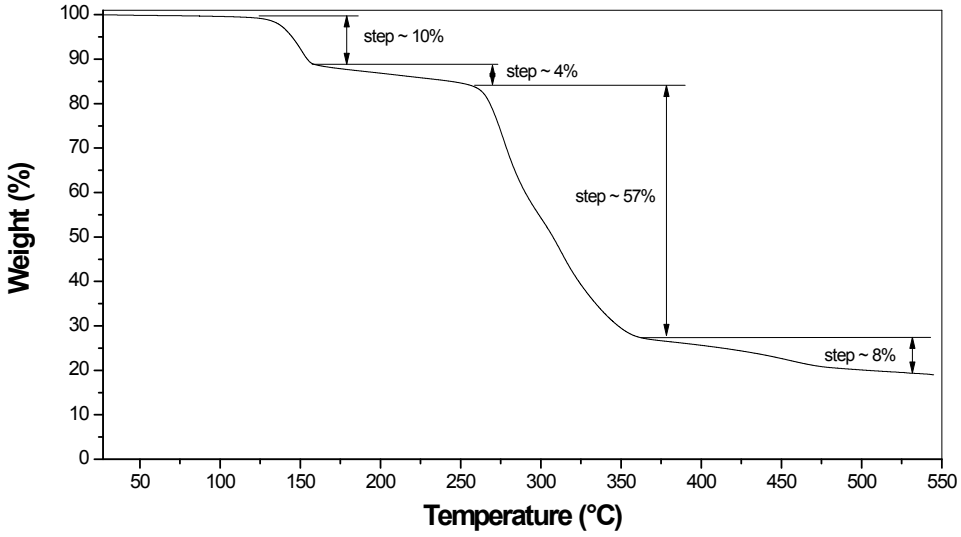

Figure S27. DSC trace of β-BDBA–PRO.

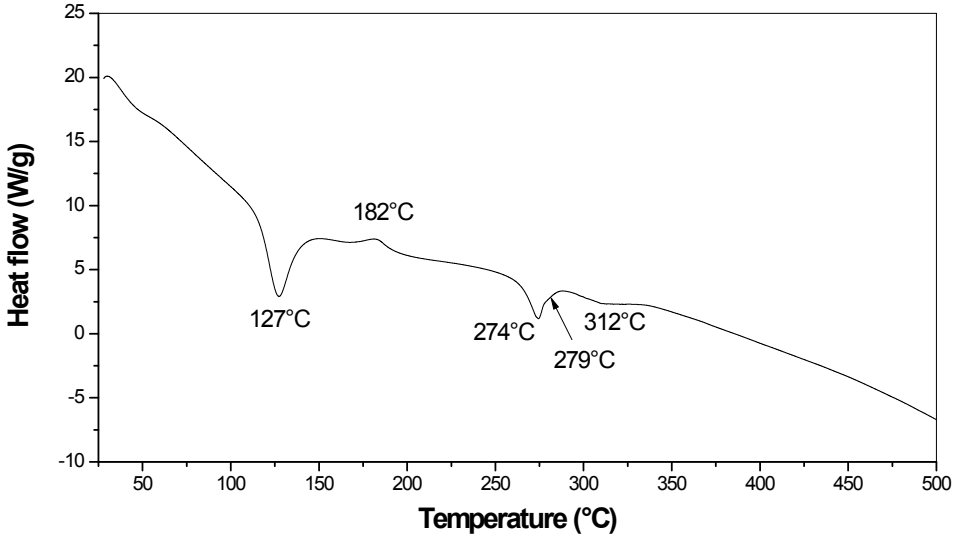

Figure S28. DSC trace of α-IPBA–PRO.

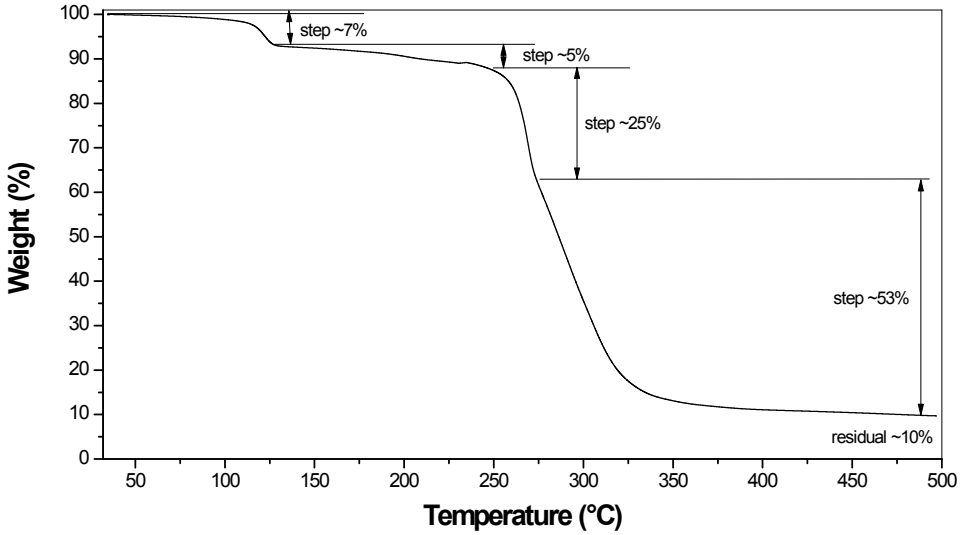

Figure S29. TGA trace of α-IPBA–PRO.

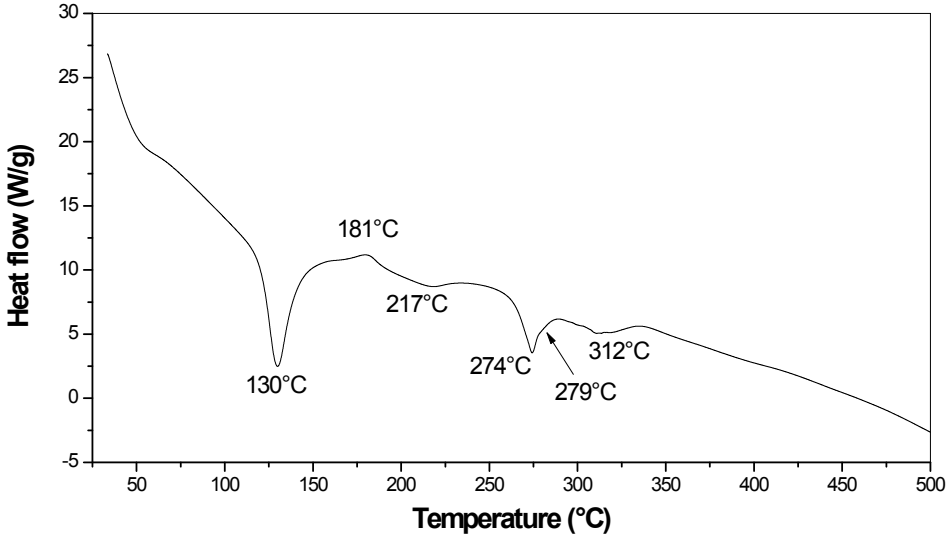

Figure S30. DSC trace of β-IPBA–PRO.

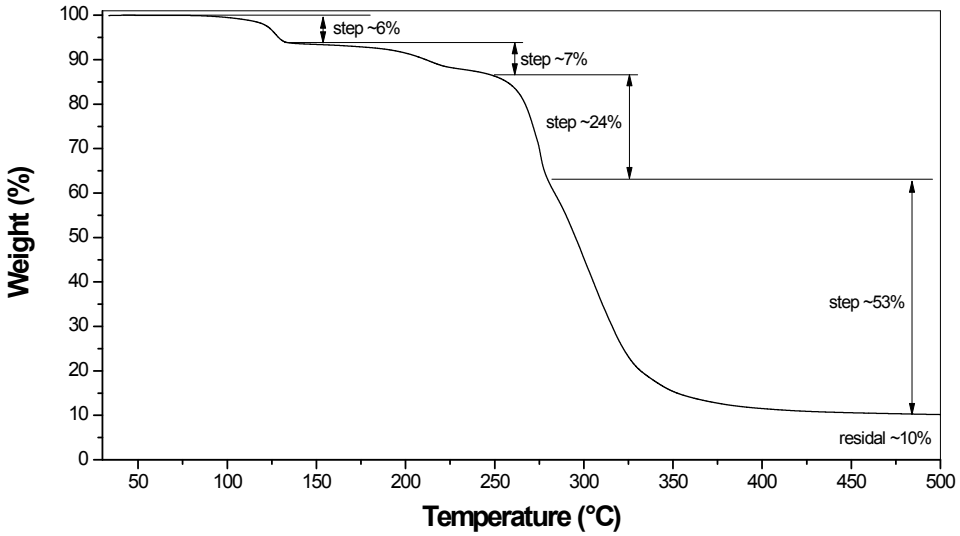

Figure S31. TGA trace of β-IPBA–PRO.

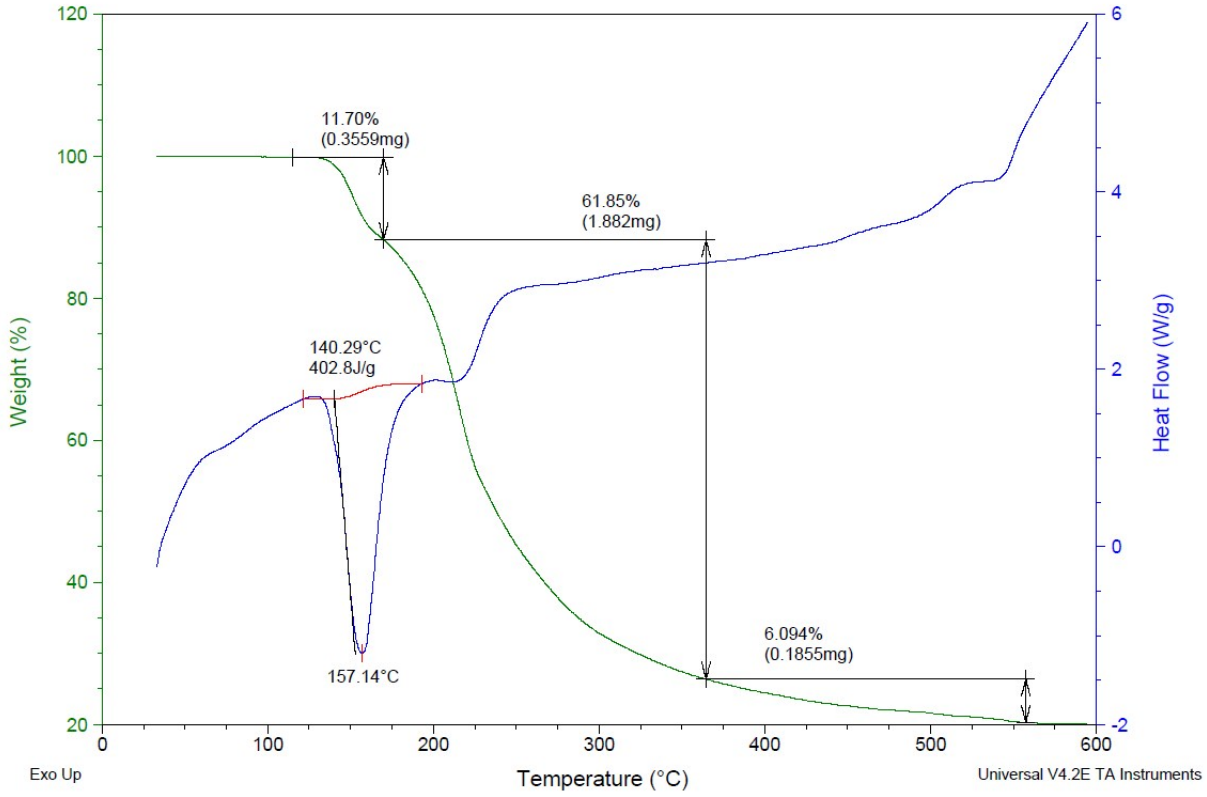

Figure S32. TGA and DSC traces of BDBA–INA.

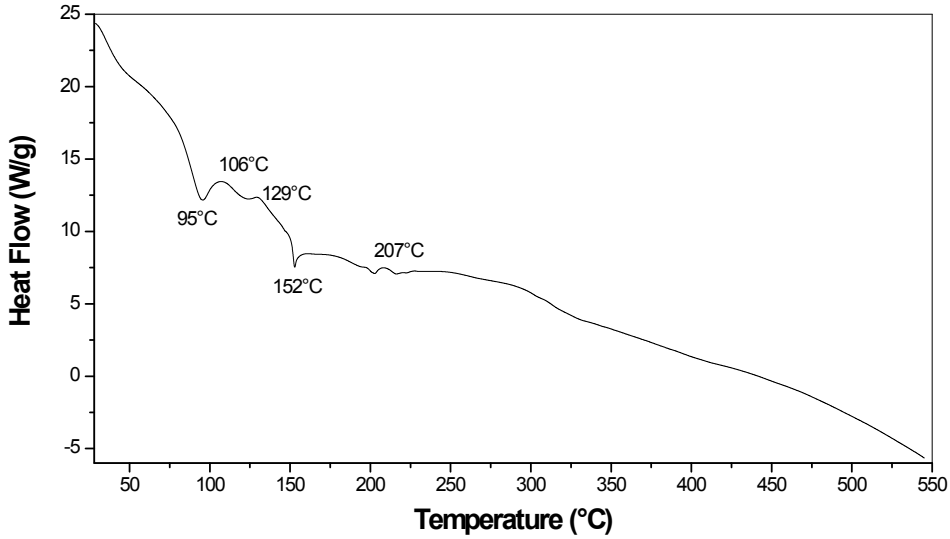

Figure S33. DSC trace of IPBA–INA.

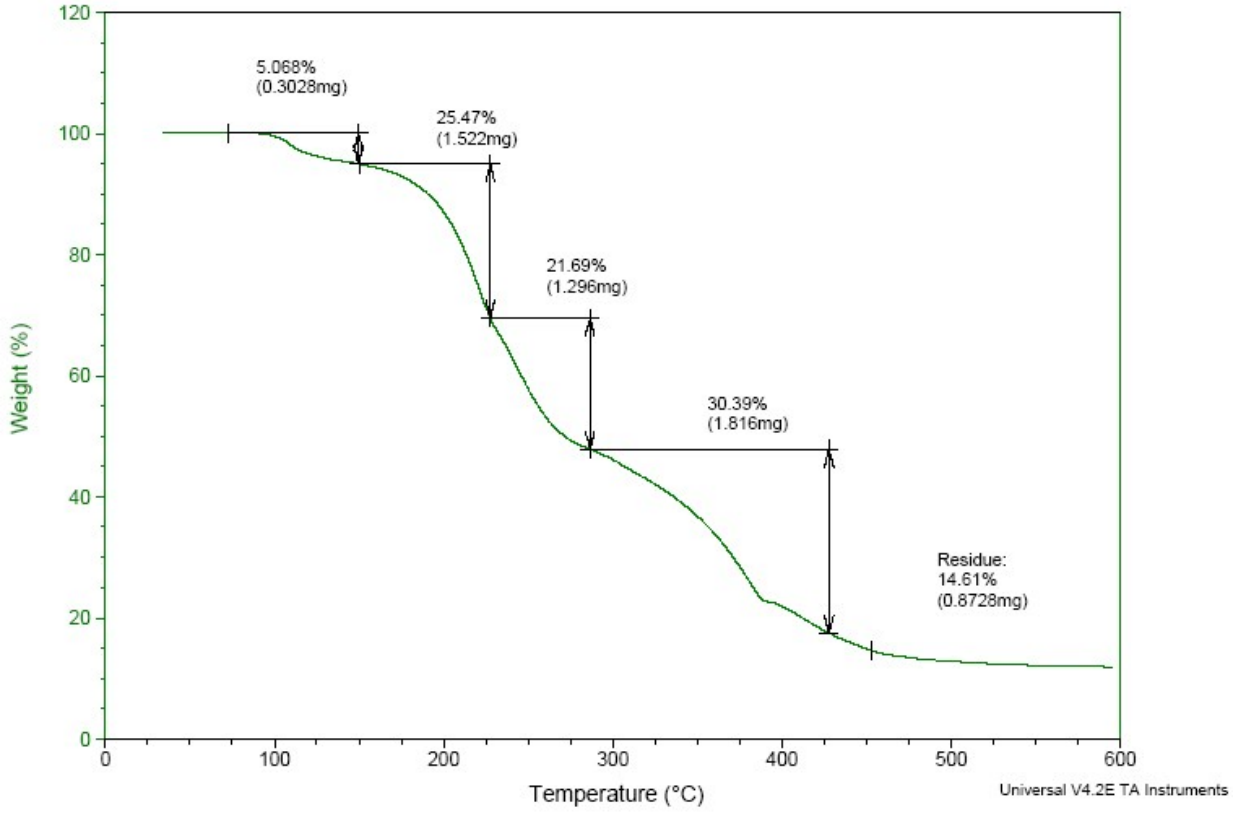

Figure S34. TGA trace of IPBA–INA.

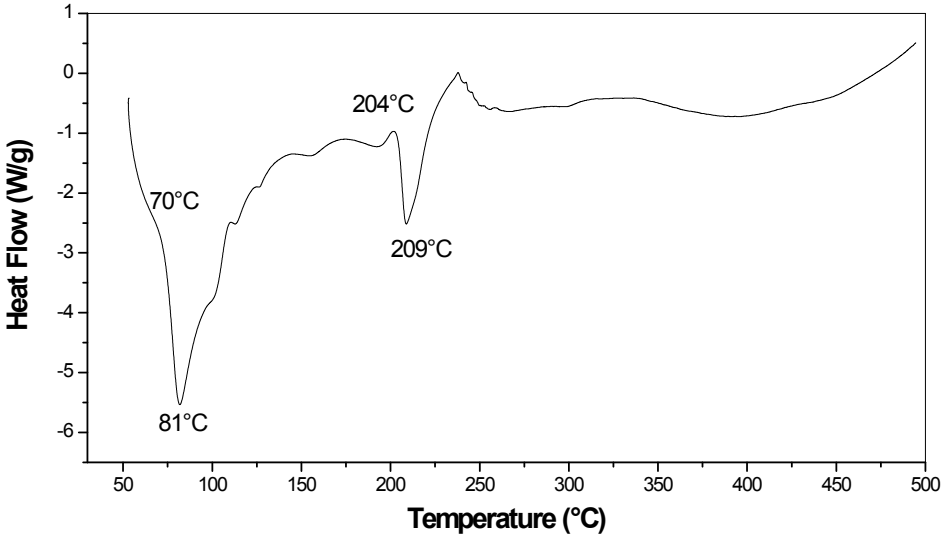

Figure S35. DSC trace of IPBA–NA.

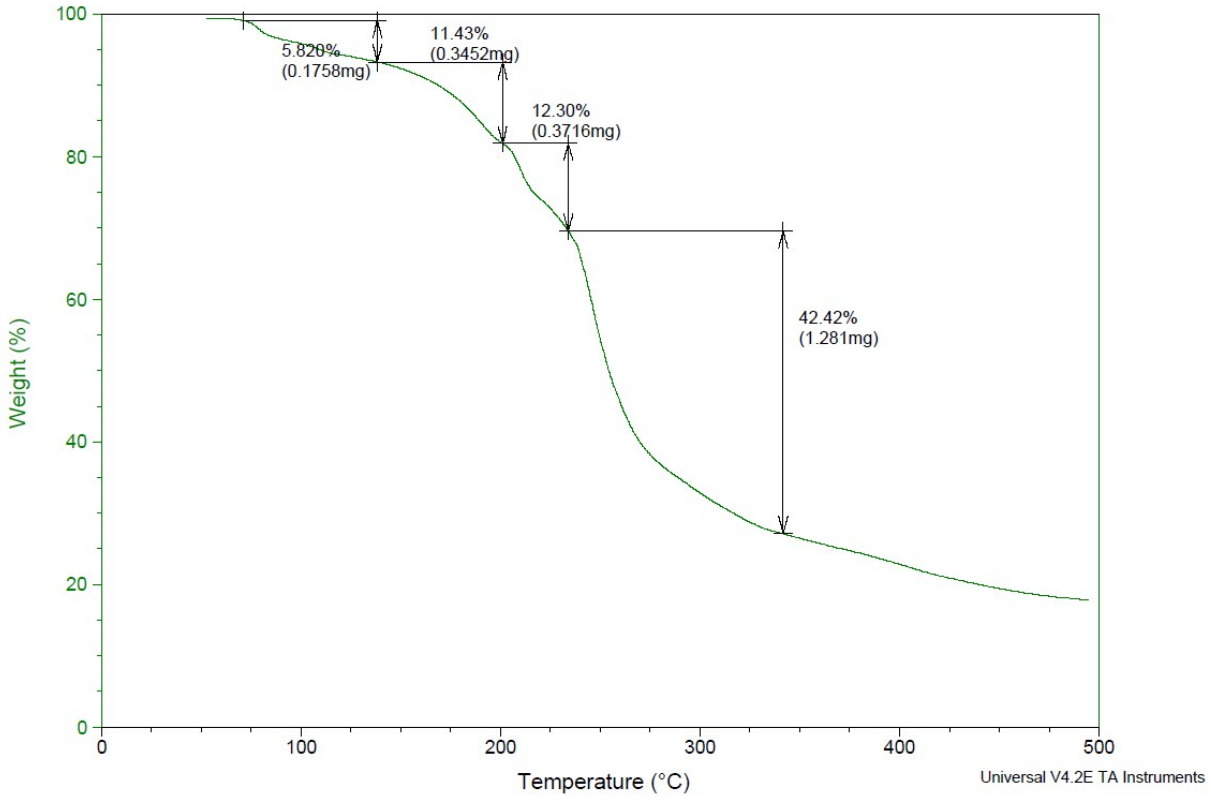

Figure S36. TGA trace of IPBA–NA.

Pawley Fit of the molecular complex *β*-BDBA-PRO (**2b**)

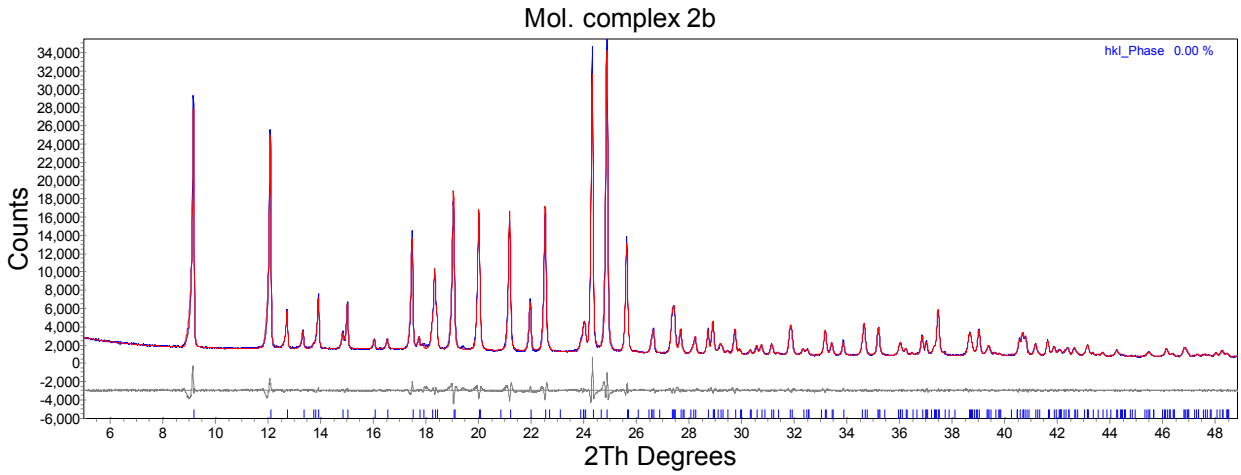

Figure S37. Pawley fit of *β*-BDBA-PRO (**2b**): calculated (red), experimental (blue) and the difference between experimental and calculated patterns (gray).

h	k	l	m	d	Th2	I
0	0	2	2	19.23750	4.58964	0.155
0	0	4	2	9.61875	9.18667	10.5
0	1	1	4	7.30545	12.10521	16.1
0	1	2	4	6.93979	12.74562	3.16
1	0	1	4	6.62535	13.35321	1.64
0	1	3	4	6.43603	13.74787	0.256
0	0	6	2	6.41250	13.79857	3.81e-006
1	0	2	4	6.34898	13.93731	5.16
1	0	3	4	5.95642	14.86085	1.59
0	1	4	4	5.88539	15.04124	5.25
1	0	4	4	5.51197	16.06675	1.3
0	1	5	4	5.34906	16.55949	1.41
1	0	5	4	5.06408	17.49847	17.8
1	1	0	4	4.98955	17.76193	1.82
1	1	1	8	4.94812	17.91188	0.889
0	1	6	4	4.85754	18.24873	1.99
1	1	2	8	4.82975	18.35463	12.8
0	0	8	2	4.80938	18.43305	6
1	1	3	8	4.65004	19.07048	28.4
1	0	6	4	4.64114	19.10739	4.45
1	1	4	8	4.42911	20.03128	24.3
0	1	7	4	4.42104	20.06826	9.57
1	0	7	4	4.25602	20.85488	3.81e-006
1	1	5	8	4.18649	21.20522	35
0	1	8	4	4.03911	21.98841	12.9
1	1	6	8	3.93790	22.56086	41.6
1	0	8	4	3.91211	22.71156	0.626
0	0	10	2	3.84750	23.09818	0.0124
0	2	0	2	3.72041	23.89867	2.19
0	1	9	4	3.70677	23.98789	2.12
0	2	1	4	3.70314	24.01180	3.4
1	1	7	8	3.69438	24.06956	7.26
0	2	2	4	3.65273	24.34821	95.5

1	0	9	4	3.60788	24.65556	0.000458
0	2	3	4	3.57310	24.89940	110
0	2	4	4	3.46990	25.65242	40.8
1	1	8	8	3.46269	25.70673	3.54
0	1	10	4	3.41764	26.05148	0.602
2	0	0	2	3.36291	26.48310	0.192
2	0	1	4	3.35014	26.58592	0.00233
0	2	5	4	3.34947	26.59134	3.33
1	0	10	4	3.33967	26.67077	9.38
2	0	2	4	3.31268	26.89218	0.0908
1	2	0	4	3.25554	27.37329	9.21
2	0	3	4	3.25294	27.39557	5.8
1	1	9	8	3.24639	27.45194	6.86
1	2	1	8	3.24394	27.47302	12.8
0	2	6	4	3.21802	27.69877	10.6
1	2	2	8	3.20990	27.77023	0.896
0	0	12	2	3.20625	27.80246	0.534
2	0	4	4	3.17449	28.08632	0.432
0	1	11	4	3.16544	28.16827	2.16
1	2	3	8	3.15546	28.25918	8.09
1	0	11	4	3.10319	28.74537	12.1
1	2	4	8	3.08370	28.93096	14.3
2	0	5	4	3.08149	28.95214	0.000562
0	2	7	4	3.08097	28.95715	2.92
2	1	0	4	3.06447	29.11655	0.911
2	1	1	8	3.05479	29.21080	4.37
1	1	10	8	3.04685	29.28864	3.25
2	1	2	8	3.02631	29.49192	1.95
1	2	5	8	2.99825	29.77429	14.4
2	1	3	8	2.98056	29.95512	2.65
2	0	6	4	2.97821	29.97928	0.14
0	1	12	4	2.94452	30.33051	0.457
0	2	8	4	2.94270	30.34975	2.29
2	1	4	8	2.91986	30.59289	5.37
1	2	6	8	2.90286	30.77647	5.92
1	0	12	4	2.89422	30.87070	0.547
2	0	7	4	2.86859	31.15348	4.6
1	1	11	8	2.86409	31.20363	2.87
2	1	5	8	2.84701	31.39566	1.59
0	2	9	4	2.80646	31.86125	12.6
1	2	7	8	2.80107	31.92419	14
2	1	6	8	2.76496	32.35249	3.91
2	0	8	4	2.75599	32.46071	1.6
0	1	13	4	2.75006	32.53263	3.27
0	0	14	2	2.74821	32.55507	1.66e-005
1	0	13	4	2.70894	33.04044	0.16
1	1	12	8	2.69735	33.18650	4.5
1	2	8	8	2.69595	33.20426	14.7
2	1	7	8	2.67657	33.45174	8.02
0	2	10	4	2.67453	33.47803	1.18
2	0	9	4	2.64312	33.88776	9.83
1	2	9	8	2.59003	34.60414	4.54
2	1	8	8	2.58441	34.68173	25.3
0	1	14	4	2.57800	34.77075	1.26
0	2	11	4	2.54836	35.18831	3.57
1	1	13	8	2.54550	35.22913	19
1	0	14	4	2.54403	35.25005	2.71
2	0	10	4	2.53204	35.42253	0.343
2	2	0	4	2.49478	35.96955	0.872
2	1	9	8	2.49065	36.03115	8.06
2	2	1	8	2.48955	36.04768	1.6
1	2	10	8	2.48524	36.11226	4.74
0	3	1	4	2.47513	36.26489	6.21
2	2	2	8	2.47406	36.28119	0.0564
0	3	2	4	2.45991	36.49720	2.12
2	2	3	8	2.44887	36.66752	1.35
0	3	3	4	2.43515	36.88158	18
0	2	12	4	2.42877	36.98202	0.000191
0	1	15	4	2.42496	37.04217	1.82

2	0	11	4	2.42420	37.05428	9.98
2	2	4	8	2.41487	37.20258	0.000121
1	1	14	8	2.40722	37.32519	4.61
0	0	16	2	2.40469	37.36599	2.1
0	3	4	4	2.40171	37.41402	3.81e-006
2	1	10	8	2.39705	37.48942	25
1	0	15	4	2.39663	37.49627	21.9
1	2	11	8	2.38304	37.71822	2.35
2	2	5	8	2.37317	37.88100	0.258
0	3	5	4	2.36067	38.08922	0.339
1	3	0	4	2.32708	38.66070	15
2	2	6	8	2.32502	38.69642	4.04
1	3	1	8	2.32284	38.73417	12.6
2	0	12	4	2.32057	38.77358	2.72
0	2	13	4	2.31614	38.85073	1.99
0	3	6	4	2.31326	38.90094	0.0981
1	3	2	8	2.31024	38.95387	1.13
2	1	11	8	2.30495	39.04687	28.5
1	3	3	8	2.28970	39.31774	2.13
0	1	16	4	2.28816	39.34515	1.18
1	2	12	8	2.28439	39.41289	9.06
1	1	15	8	2.28122	39.46988	2.72
2	2	7	8	2.27172	39.64181	3.21
1	0	16	4	2.26432	39.77690	0.808
1	3	4	8	2.26183	39.82246	0.00159
0	3	7	4	2.26075	39.84225	1.92
3	0	1	4	2.23814	40.26205	1.04
1	3	5	8	2.22746	40.46368	0.172
3	0	2	4	2.22687	40.47479	0.0001
2	0	13	4	2.22174	40.57234	16.7
2	1	12	8	2.21533	40.69487	18
2	2	8	8	2.21456	40.70978	6.81
0	2	14	4	2.21052	40.78746	5.42
3	0	3	4	2.20845	40.82733	16.8
0	3	8	4	2.20439	40.90588	4.58e-005
1	2	13	8	2.18993	41.18831	13.2
1	3	6	8	2.18750	41.23614	2.45
3	0	4	4	2.18342	41.31670	1.36
1	1	16	8	2.16624	41.65958	20.6
0	1	17	4	2.16529	41.67864	0.000315
2	2	9	8	2.15471	41.89286	11.8
3	0	5	4	2.15245	41.93900	1.23
3	1	0	4	2.14662	42.05825	3.53
0	3	9	4	2.14534	42.08442	0.0611
1	0	17	4	2.14505	42.09052	0.265
3	1	1	8	2.14329	42.12678	2.65
1	3	7	8	2.14293	42.13401	3.5
0	0	18	2	2.13750	42.24625	1.56
3	1	2	8	2.13338	42.33180	5.79
2	1	13	8	2.12887	42.42584	10
2	0	14	4	2.12801	42.44373	4.03e-005
3	1	3	8	2.11717	42.67173	11.2
3	0	6	4	2.11633	42.68953	0.00632
0	2	15	4	2.11175	42.78651	3.52
1	2	14	8	2.10001	43.03773	1.55
3	1	4	8	2.09508	43.14398	7.4
1	3	8	8	2.09475	43.15108	0.0144
2	2	10	8	2.09324	43.18371	10.8
0	3	10	4	2.08465	43.37065	4.25
3	0	7	4	2.07589	43.56301	2.34
3	1	5	8	2.06767	43.74514	5.63
1	1	17	8	2.06111	43.89162	8.75e-006
0	1	18	4	2.05441	44.04220	0.339
2	1	14	8	2.04598	44.23321	1.47
1	3	9	8	2.04389	44.28098	8.72
2	0	15	4	2.03947	44.38200	2.29
1	0	18	4	2.03710	44.43635	1.35e-005
3	1	6	8	2.03559	44.47106	1.27
3	0	8	4	2.03200	44.55380	0.765

2	2	11	8	2.03107	44.57532	0.404
0	3	11	4	2.02322	44.75762	0.0842
0	2	16	4	2.01956	44.84327	1.28
1	2	15	8	2.01478	44.95545	0.102
3	1	7	8	1.99954	45.31708	6.72e-005
2	3	0	4	1.99609	45.39956	1.46
2	3	1	8	1.99341	45.46404	2.53
1	3	10	8	1.99120	45.51736	6.32
3	0	9	4	1.98547	45.65607	1.13
2	3	2	8	1.98544	45.65703	0.00633
2	3	3	8	1.97235	45.97728	0.55
2	2	12	8	1.96895	46.06115	0.284
2	1	15	8	1.96692	46.11142	0.845
1	1	18	8	1.96480	46.16417	13
0	3	12	4	1.96180	46.23886	2.69
3	1	8	8	1.96022	46.27816	0.726
2	0	16	4	1.95606	46.38248	3.13
2	3	4	8	1.95445	46.42275	2.74
0	1	19	4	1.95393	46.43583	0.403
1	0	19	4	1.93902	46.81414	6.01
1	3	11	8	1.93746	46.85413	0.00328
3	0	10	4	1.93707	46.86401	12.2
1	2	16	8	1.93424	46.93678	5.43
0	2	17	4	1.93357	46.95413	2.36e-005
2	3	5	8	1.93215	46.99071	3.53
0	0	20	2	1.92375	47.20822	1.83
3	2	0	4	1.92024	47.29985	0.591
3	1	9	8	1.91835	47.34910	9.17e-005
3	2	1	8	1.91785	47.36232	5.15
3	2	2	8	1.91074	47.54934	3.76
2	2	13	8	1.90750	47.63519	1.81
2	3	6	8	1.90589	47.67783	3.39
0	3	13	4	1.90099	47.80840	3.14
3	2	3	8	1.89907	47.85983	1.14
2	1	16	8	1.89178	48.05578	8.98
3	0	11	4	1.88749	48.17195	1.58
1	3	12	8	1.88332	48.28545	6.29
3	2	4	8	1.88308	48.29196	7.9
2	0	17	4	1.87762	48.44136	3.6
1	1	19	8	1.87636	48.47605	0.688
2	3	7	8	1.87620	48.48033	3.93
3	1	10	8	1.87459	48.52462	0.665
3	2	5	8	1.86310	48.84334	3.81e-006
0	1	20	4	1.86251	48.85995	3.81e-006
0	4	0	2	1.86020	48.92446	3.81e-006
1	2	17	8	1.85830	48.97790	3.81e-006
0	4	1	4	1.85803	48.98536	3.81e-006
0	2	18	4	1.85339	49.11632	3.81e-006
0	4	2	4	1.85157	49.16773	3.81e-006
1	0	20	4	1.84958	49.22408	336
2	2	14	8	1.84719	49.29203	73.9

Rietveld refinements

Co-crystal PBA-PRO

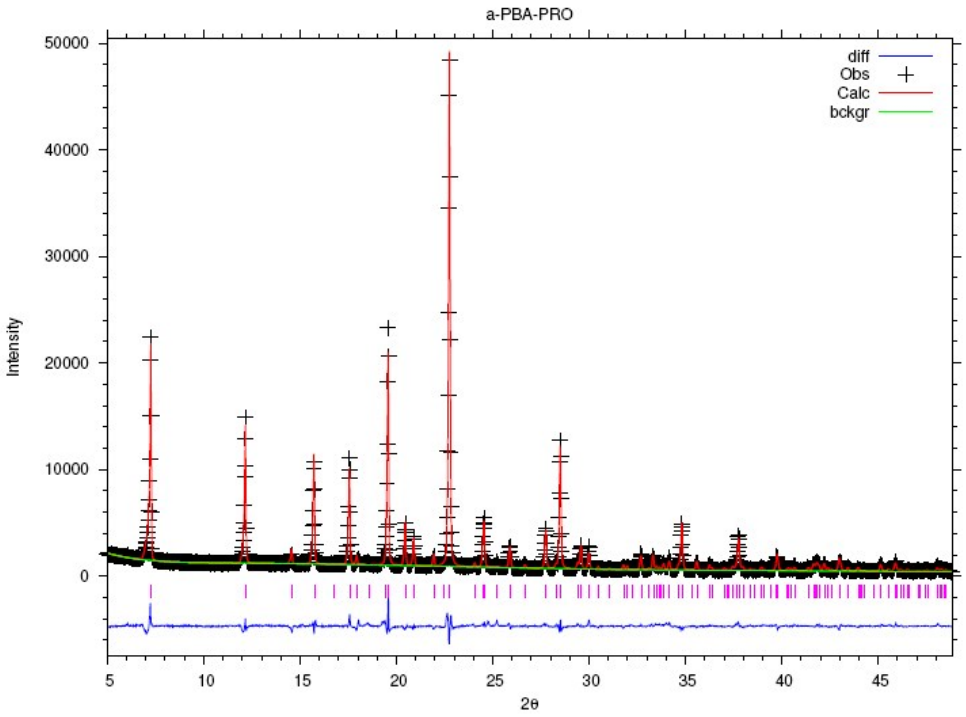

Figure S38. Rietveld refinement of PBA-PRO: calculated (red), experimental (black) and the difference between experimental and calculated patterns (blue).

Co-crystal α-IPBA-PRO

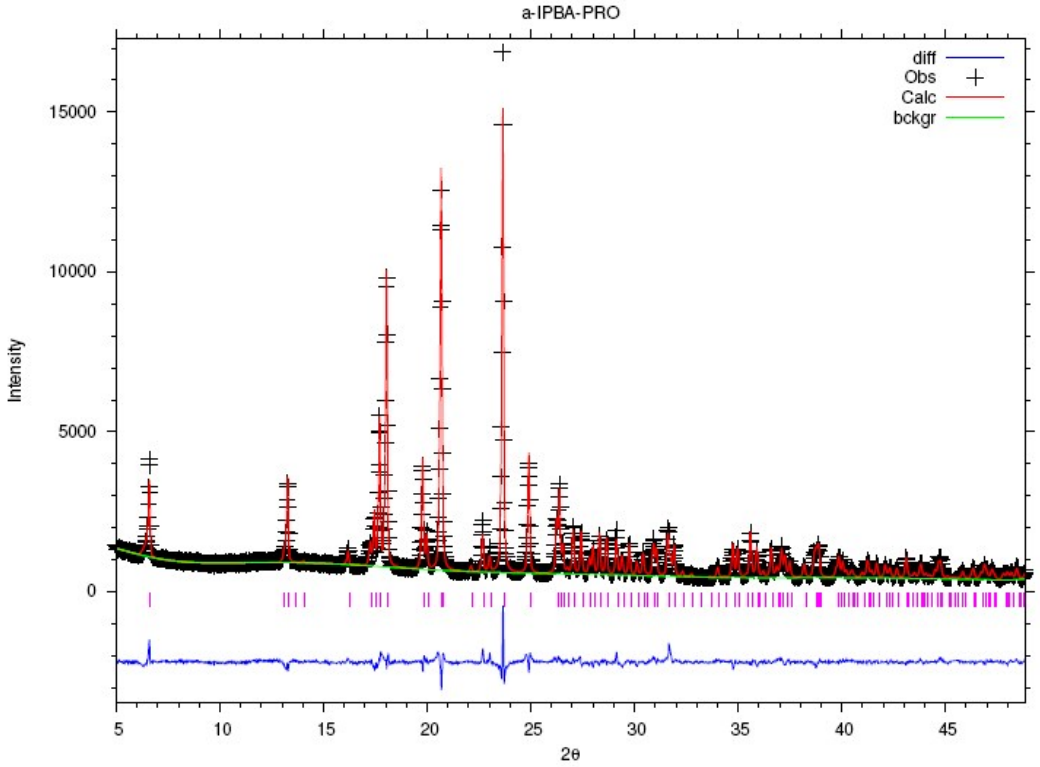

Figure S39. Rietveld refinement of α-IPBA-PRO: calculated (red), experimental (black) and the difference between experimental and calculated patterns (blue).

Cocrystal *β*-IPBA-PRO

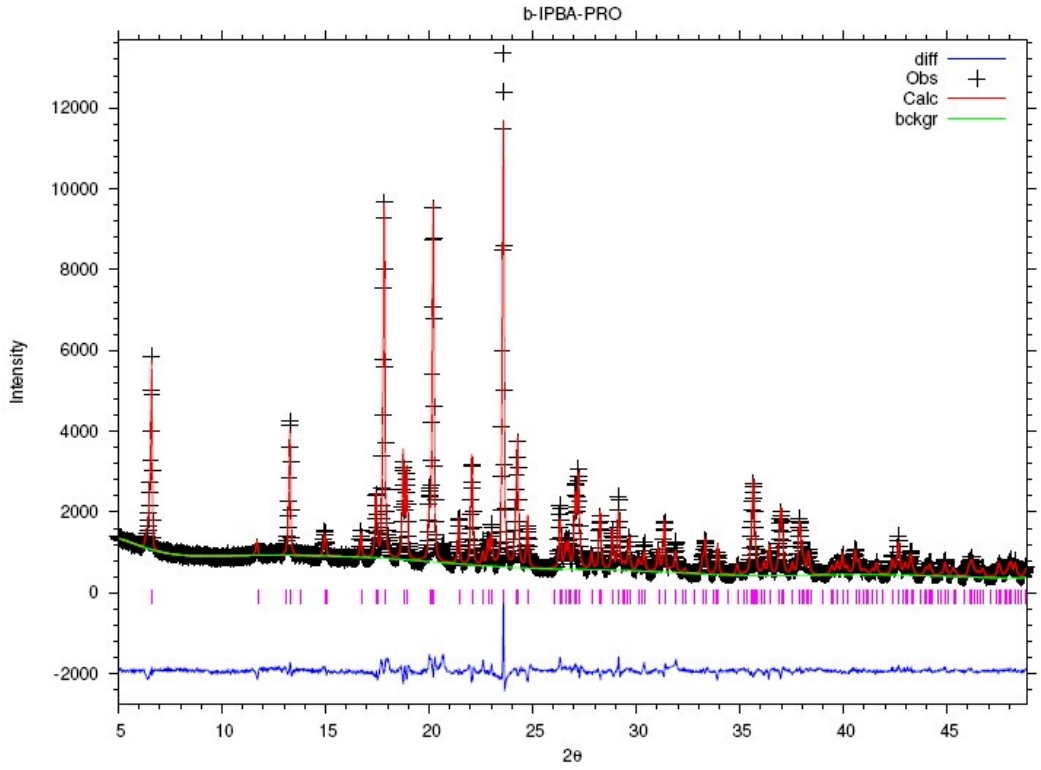

Figure S40. Rietveld refinement of *β*-IPBA-PRO: calculated (red), experimental (black) and the difference between experimental and calculated patterns (blue).

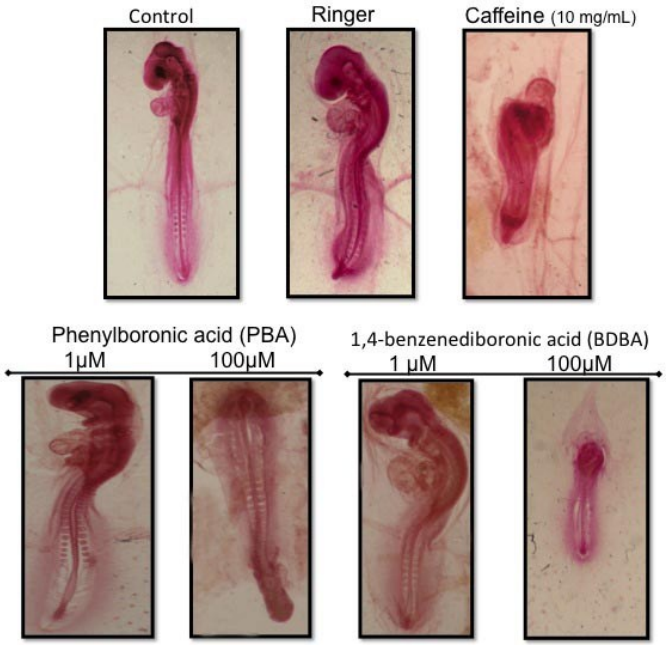

Figure S41. Morphological changes in chicken embryos treated with phenylboronic acid (PBA) and 1,4-benzenediboronic acid (BDBA).

Table S1. Results of the cytotoxicity assays for 4-carboxyphenylboronic, 2-naphthylboronic, 3-formylboronic, 4-cyanophenylboronic, 3-aminophenylboronic, 4-formylboronic, 3-carboxyphenylboronic, and 3-cyanophenylboronic acid using the human HEK-293Q and WRL-68 cell lines.

Compound	TD50 HEK-293Q [mM][a]	TD50 WRL-68 [mM][a]
4-Carboxyphenylboronic cid	> 5000	> 5000
2-Naphthylboronic acid	> 5000	> 5000
3-Formylphenylboronic acid	> 5000	> 5000
4-Cyanophenylboronic acid	> 5000	> 5000
3-Aminophenylboronic acid	> 5000	> 5000
4-Formylphenylboronic acid	> 5000	> 5000
3-Carboxyphenylboronic acid	> 5000	> 5000
3-Cyanophenylboronic acid	> 5000	> 5000

a) The TD_{50} values reported are the mean values from two experiments, which were carried out each eight-fold.