

† Electronic Supplementary Information

**Study of molecular interactions and chemical reactivity of the nitrofuranoin
–3-aminobenzoic acid cocrystal using quantum chemical and spectroscopic
(IR, Raman, ^{13}C SS-NMR) approaches**

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Part I. FIGURES

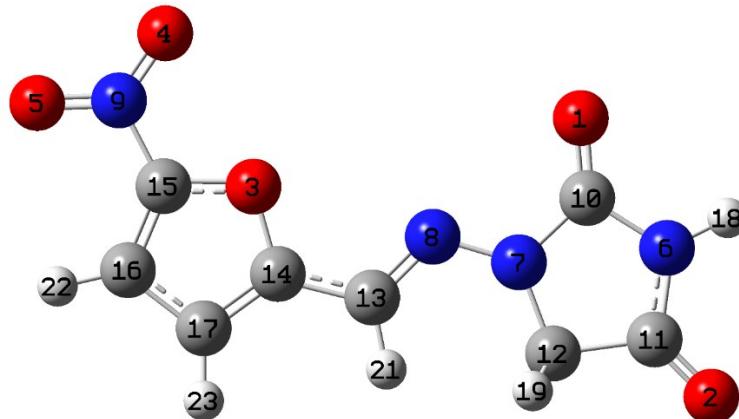


Fig. S1 Optimized structure for NF using wB97X-D/cc-pvTZ method and the atom numbering scheme adopted in this study.

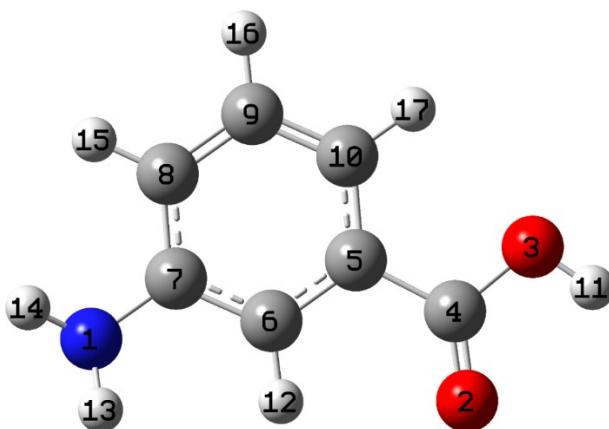


Fig. S2 Optimized structure for 3ABA using wB97X-D/cc-pvTZ method and the atom numbering scheme adopted in this study.

Vibrational assignments

NF-3ABA has hydrogen bonding that is reflected in both calculated IR and Raman spectra. To understand the effect of hydrogen bonding on IR and Raman spectra, we selected NH, OH and C=O stretching modes, as these bonds are involved in hydrogen bonding in the NF-3ABA. Calculated infrared spectra of NF-3ABA, NF and 3ABA which comprise of N-H, C=O and O-H stretching frequencies are shown in Fig. S7 (ESI†). The wavenumbers calculated using B3LYP/cc-pvTZ is given in the parenthesis.

Carbonyl group (C=O) vibrations are characteristic bands in vibrational spectra and for this reason; these types of bands have been subject of extensive studies.^{1,2} The carbonyl compounds give rise to strong bands in the region 1870-1650 cm⁻¹.³ The C16=O stretching mode is observed as medium band at 1827 cm⁻¹ in the IR spectrum and calculated as medium intensity band at 1837 (1808) cm⁻¹. The C12=O stretching mode is observed as medium band at 1788 cm⁻¹ in the IR spectrum and strong band at 1776 cm⁻¹ in the Raman spectrum, however, it is calculated as medium intensity band at 1751 (1722) cm⁻¹, which matches well with the value calculated using wB97X-D/cc-pvTZ. The same mode is calculated at 1798 (1771) cm⁻¹ for NF (API) and observed at 1782 cm⁻¹ in the IR spectrum of NF. The unusual lowering of the carbonyl stretching wavenumber is also contributed to the electron releasing effect of the C=O bond due to intra-molecular charge transfer, as reported earlier⁴ in addition to the intermolecular effect. This shift is clearly shown in the Fig. S7.

The position of N-H stretching band is dependent on the strength of hydrogen bond formed. In the observed FT-IR spectrum of NF-3ABA, the N5-H stretch is observed as a medium peak at 3150 cm⁻¹ in the IR spectrum and at 3151 cm⁻¹ in the Raman spectrum of NF-3ABA, whereas it is calculated as 3153 (3124) cm⁻¹, which matches well with the value calculated using wB97X-D/cc-pvTZ level of theory. The same mode is calculated at 3516 (3503) cm⁻¹ and observed at 3287 cm⁻¹ in the IR spectrum of NF. The N-H of Ring 2 is hydrogen bonded with C=O bond of carboxylic acid attached to the Ring 3 and the lowering of NH stretching wavenumber can be endorsed to the intermolecular N-H···O interaction.⁵ This lowering in the wavenumber from NF to NF-3ABA is clearly shown in the Fig. S7.

The stretching vibration C34=O27 is calculated to be 1693 (1660) cm⁻¹ and corresponds to the peak at 1688 cm⁻¹/ 1686 cm⁻¹ in IR/Raman spectrum, which matches well with the value calculated using wB97X-D/cc-pvTZ level of theory. The same mode is calculated at 1757 (1725) cm⁻¹ and observed at 1751 cm⁻¹/ 1696 cm⁻¹ in the IR/Raman spectrum of 3-ABA. The lowering of wavenumber (as shown in Fig. S7) is due to presence of hydrogen bond in the NF-3ABA. The non-hydrogen bonded (free) hydroxyl group absorbs strongly in the region 3700-3584 cm⁻¹. Whereas the existence of hydrogen bond can lower the O-H stretching frequency to the 3550-3200 cm⁻¹ region with increase in intensity and breadth.^{6,7} The IR spectrum in the high wavenumber region shows a broad band at 3200 cm⁻¹ and at 3216 cm⁻¹ in the Raman spectrum attributed to hydrogen bonded OH stretching vibrations, whereas it is calculated at 3252 (3218) cm⁻¹ in the case of NF-3ABA. The same mode is calculated at 3670 (3626) cm⁻¹ in the case of 3ABA and observed at 3559 cm⁻¹ in the IR spectra. This confirms that the OH group participate in intermolecular hydrogen bonding with a neighbouring molecule. The OH deformation mode appears as medium peak at 1400 cm⁻¹/1399 cm⁻¹ in the IR/Raman spectrum whereas it is calculated at 1405 (1396) cm⁻¹.

References-

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- 2 G. Socrates, *Wiley*, New York, 1980, 3rd Eds.
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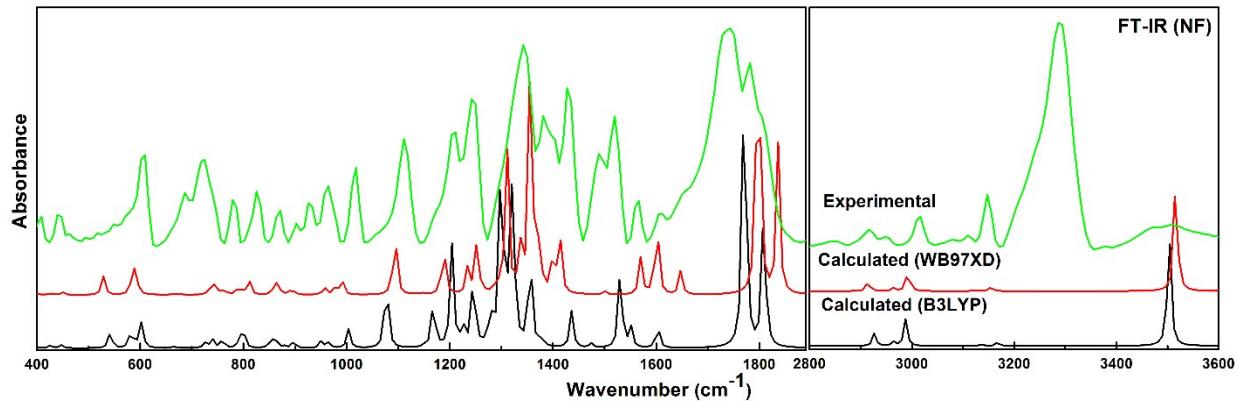


Fig. S3 Experimental and calculated FT-IR absorbance spectra of NF in the region, 400-3600 cm⁻¹.

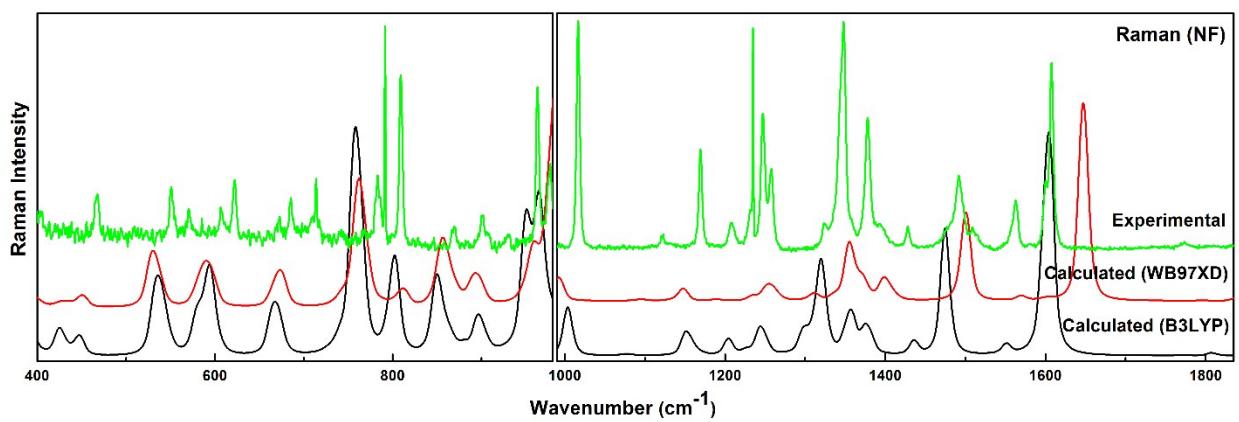


Fig. S4 Experimental and calculated Raman spectra of NF in the region, 400-1800 cm⁻¹.

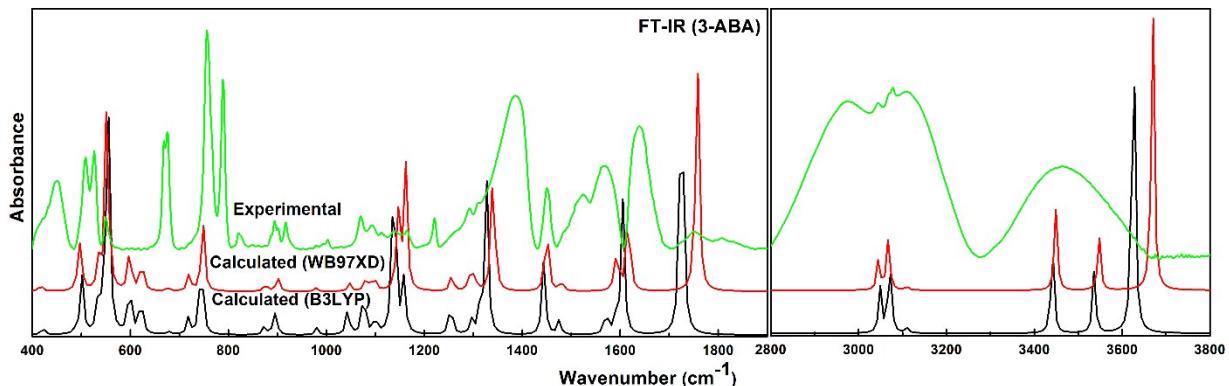


Fig. S5 Experimental and calculated FT-IR absorbance spectra of 3ABA in the region, 400-3800 cm⁻¹.

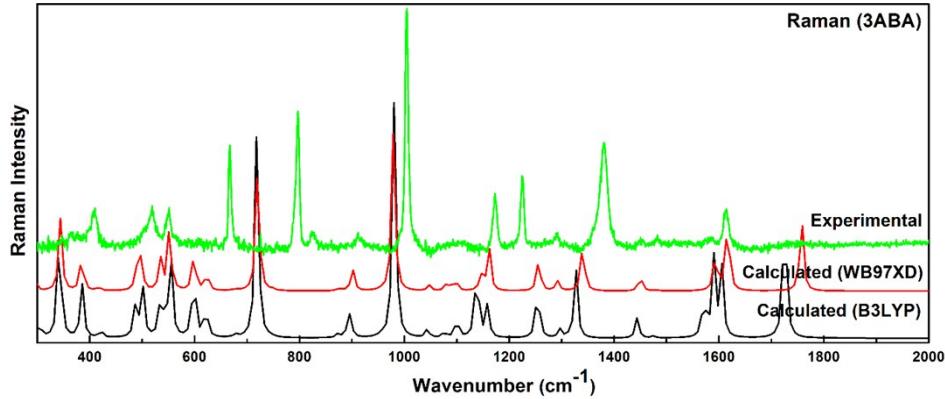


Fig. S6 Experimental and calculated Raman spectra of 3ABA in the region, 300-2000 cm^{-1} .

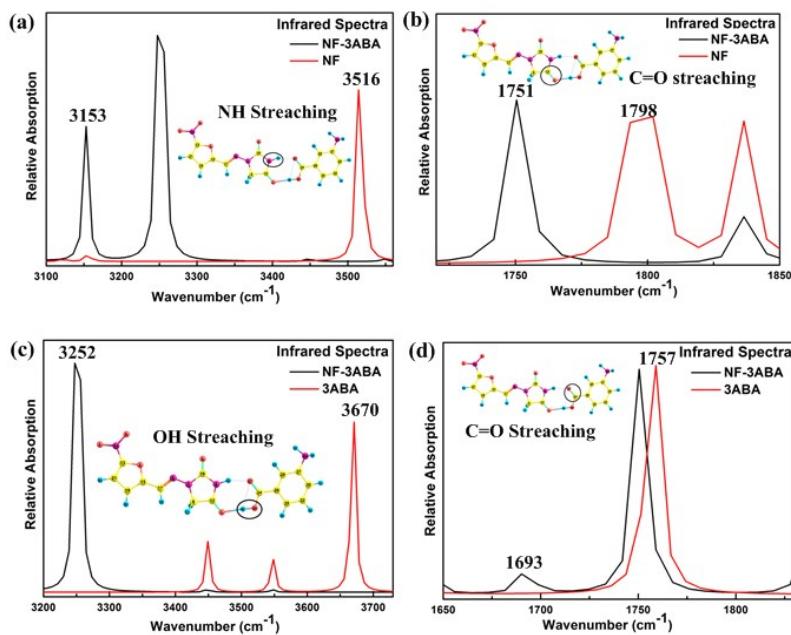


Fig. S7 Calculated infrared spectra of NF-3ABA, NF and 3ABA in the region of N-H, C=O and OH stretching using wb97X-D/cc-pvTZ level of theory.

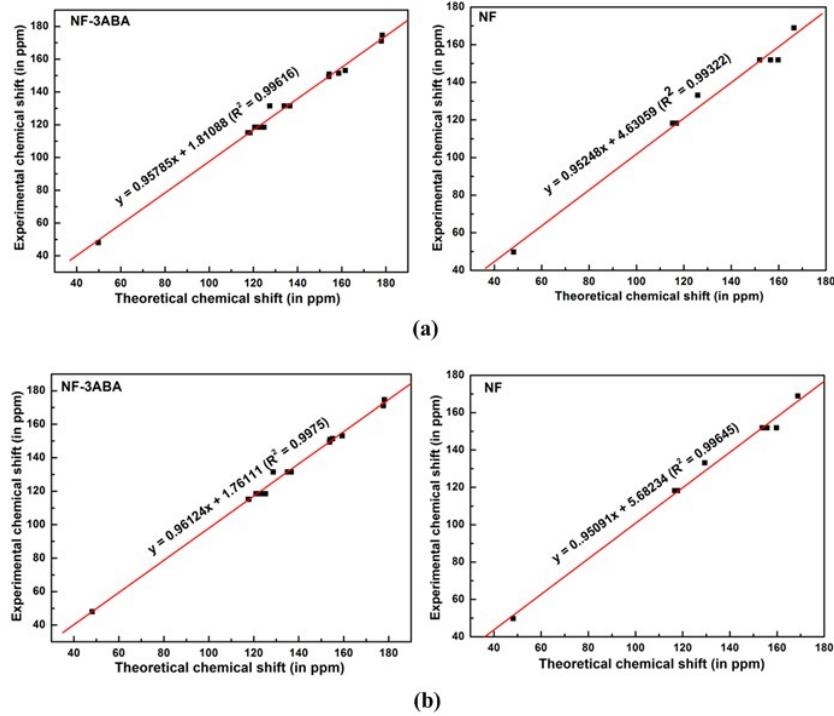


Fig. S8 ^{13}C NMR correlation graph of NF-3ABA and NF (a) using GIAO/B3LYP/cc-pVTZ. (b) GIAO/wB97X-D/cc-pVTZ

Reduced density gradient (RDG) and isosurface analysis

The multi-wavefunction analysis has been performed by reduced density gradient (RDG) plot and isosurface analysis of interactions to confirm the results obtain from the QTAIM analysis and the type of interactions present in the NF-3ABA. For this, initially the cube files were generated for the real spatial functions λ_{2p} (the product of second largest eigen value of Hessian matrix and electron density) and RDG by Multiwfn software. Furthermore, we have plotted a scatter graph with isosurface value of about 0.5 a.u by taking λ_{2p} in x-axis and RDG in y-axis as shown in Fig. S9 (ESI[†]). Each point in the graph corresponds to the critical points in AIM theory. If a horizontal line is drawn to the specified isosurface value (0.5 a.u), then the points crossing the line correspond to the RDG isosurfaces. It is seen from the graph that there are spike shaped collection of points in the region from -0.045 to 0.030 a.u and based on the value of λ_{2p} , the strength of the interactions were distinguished. In the figure shown, the points enclosed in the blue box correspond to hydrogen bonding interactions, the points enclosed in green box represent van der Waals interactions and the points enclosed in red box represent steric effect. Steric effect also has been observed where the ring is formed via hydrogen bonds. The isosurface density map for the non-bonded interactions is shown in Fig. S10 (ESI[†]), which indicates steric effect by red in colour and van der Waals interactions in dark green and hydrogen bond by blue in colour. From isosurface plot, the bond between imide NH, C=O of NF and acid C=O and -OH group in 3ABA is hydrogen bonded and represent by dark blue in colour showing its moderate nature.

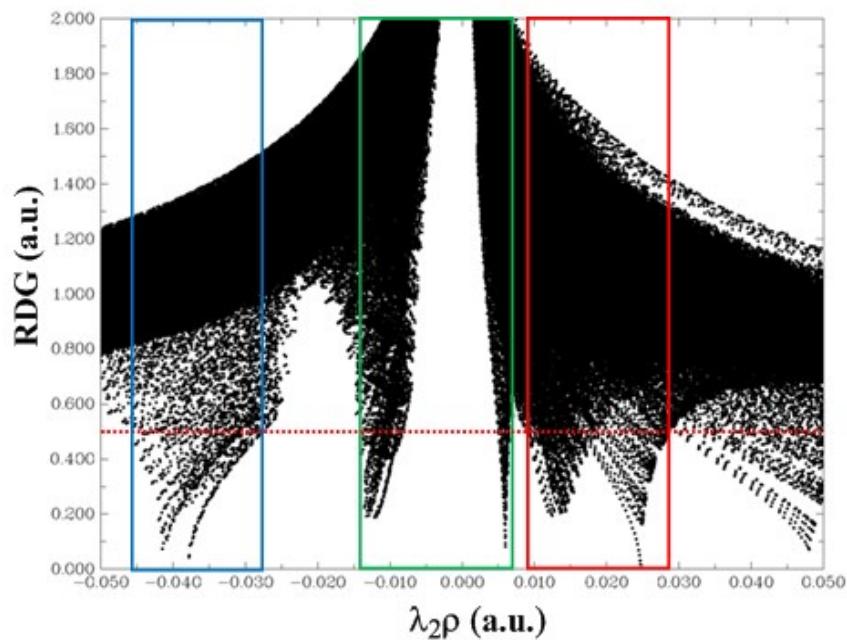


Fig. S9 Reduced density gradient plot of NF-3ABA.

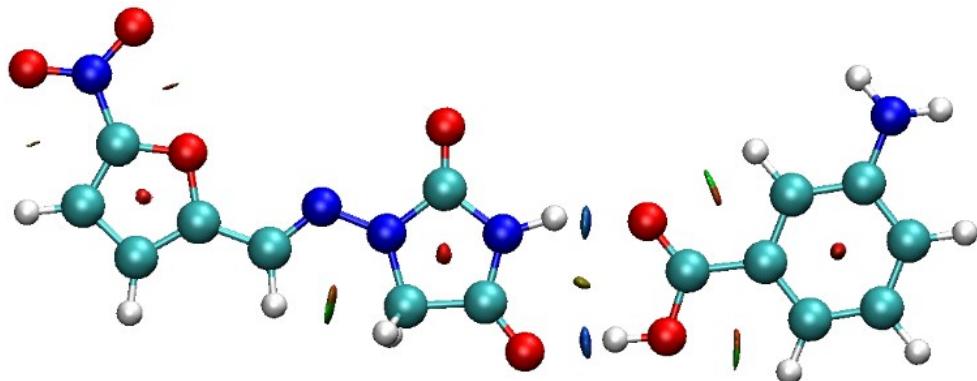


Fig. S10 Isosurface plot validating the presence of hydrogen bond, sterik effect and van der Waals interactions between the non-bonded atoms of NF-3ABA.

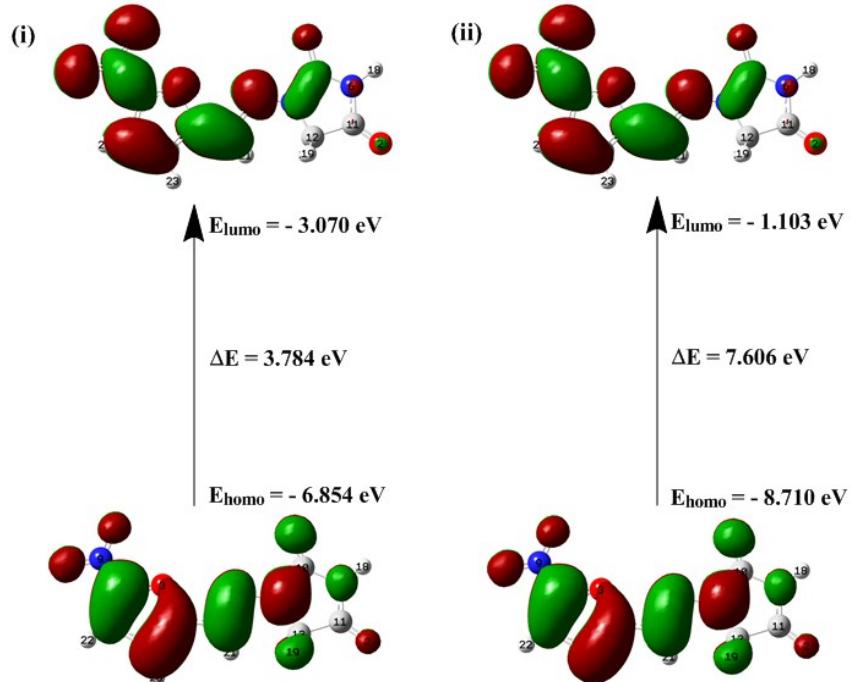


Fig. S11 HOMO-LUMO plot of NF with orbitals involved in electronic transitions in isolated (gaseous) phase (i) using B3LYP/cc-pvTZ method (ii) using wB97X-D/cc-pvTZ method.

Molecular electrostatic potential map of NF-3ABA

The molecular electrostatic potential (MEP) gives a pictorial method to recognize the relative polarity of the molecule. It can be used to analyse the electrophilic and the nucleophilic sites within the molecule where chemical reactions are likely to take place. The electrostatic potential is computed by creating an electrostatic potential grid. The different values of the electrostatic potential at the MEP surface are represented by different colours; red, electron rich; blue, electron deficient; light blue, slightly electron deficient region; yellow, slightly electron rich region; green, neutral; respectively.

The total electron density and electrostatic potential surface (ESP) of the molecules under investigation are constructed by using wB97X-D/cc-pvTZ method. The total electron density mapped with electrostatic potential surface of NF-3ABA is shown in Fig. S12. This orientation visibly show electrophilic region visible as red blob is localized over the NO_2 and carbonyl group attached to the ring R1 and R2 of the molecule respectively. In addition, a less negative area reflected as a yellowish blob is visible mainly over the oxygen atoms of carboxylic group attached to the ring R3 and a more nucleophilic region localised on the NH_2 and CH_2 group and is reflected as a bluish blob.

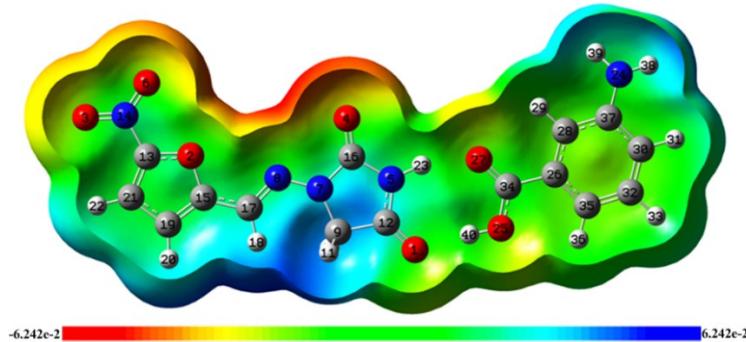


Fig. S12 Molecular electrostatic potential (MEP) formed using wB97X-D/cc-pvTZ method by mapping total density over electrostatic potential in gas phase for NF-3ABA cocrystal.

Part II. TABLES

Table S1 Comparison of geometrical parameters of NF and NF – 3-ABA.

Geometrical Parameters	Experimental		Calculated Optimized Parameters		
	NF-3ABA	NF	NF-3ABA		NF
			B3LYP/ cc-pvTZ	wB97X-D/ cc-pvTZ	B3LYP/ cc-pvTZ
Bond-Lengths (Å)					
O1-C12	1.2265	1.2063	1.2185	1.2138	1.2023
O1-H40	1.8004	-	1.7567	1.7393	-
O2-C13	1.3524	1.3477	1.3478	1.3366	1.3476
O2-C15	1.3722	1.3687	1.3581	1.3471	1.3582
O3-N14	1.2297	1.2285	1.2278	1.2168	1.2276
O4-C16	1.2042	1.1949	1.1938	1.1895	1.1954
N5-C12	1.3573	1.3531	1.3534	1.3491	1.3744
N5-C16	1.4038	1.3966	1.4058	1.4014	1.4041
N5-H23	0.9443	0.9205	1.0297	1.0277	1.0076
O6-N14	1.2369	1.2143	1.2202	1.2097	1.2200
N7-N8	1.3589	1.3626	1.3359	1.3348	1.3376
N7-C9	1.4484	1.4473	1.454	1.4438	1.4560
N7-C16	1.3779	1.373	1.4062	1.3974	1.4012
N8-C17	1.2877	1.2803	1.2826	1.2741	1.2824
C9-H10	0.99	0.9301	1.0927	1.0924	1.0924
C9-H11	0.9897	0.9856	1.0927	1.0924	1.0925
C9-C12	1.5046	1.5041	1.5205	1.5157	1.5270
C13-N14	1.4205	1.4113	1.4313	1.4341	1.4317
C13-C21	1.3488	1.3391	1.3617	1.3537	1.3617
C15-C17	1.4426	1.4369	1.4387	1.4449	1.4388
C15-C19	1.3654	1.3526	1.3753	1.3659	1.3751
C17-H18	0.9499	0.9887	1.0888	1.0888	1.0887
C19-H20	0.9499	0.9264	1.0763	1.0761	1.0763
C19-C21	1.4152	1.3985	1.414	1.4161	1.4141
C21-H22	0.9503	0.9226	1.0744	1.0743	1.0743
H23-O27	1.9059	-	1.7917	1.7766	-
N24-C37	1.3763	-	1.3907	1.388	-
N24-H38	0.8913	-	1.0067	1.0051	-
N24-H39	0.8831	-	1.0069	1.0053	-
O25-C34	1.3334	-	1.3284	1.3183	-
O25-H40	0.9024	-	0.989	0.985	-
C26-C28	1.3922	-	1.3927	1.3876	-
C26-C34	1.4832	-	1.4856	1.4867	-
C26-C35	1.3963	-	1.3958	1.3901	-
O27-C34	1.2228	-	1.2238	1.2184	-
C28-H29	0.9495	-	1.0815	1.0817	-
C28-C37	1.4039	-	1.3959	1.392	-
C30-H31	0.95	-	1.0832	1.0831	-
C30-C32	1.3901	-	1.3869	1.3832	-
C30-C37	1.4035	-	1.4015	1.3965	-
C32-H33	0.9496	-	1.0818	1.0814	-
C32-C35	1.3959	-	1.3881	1.3848	-
C35-H36	0.9501	-	1.0784	1.0787	-
Bond-Angles (°)					
C12-O1-H40	123.459	-	120.9708	120.6674	-
C13-O2-C15	104.6488	104.8201	106.1545	105.9937	106.1501
C12-N5-C16	112.7266	113.0228	113.7052	113.456	114.5001
C12-N5-H23	121.2363	118.9309	121.4627	121.4826	124.0161
C16-N5-H23	125.9011	127.9628	124.8322	125.0612	121.4838
N8-N7-C9	126.9954	127.5844	127.7022	127.3279	127.7318
N8-N7-C16	119.961	119.2865	120.1369	120.1792	119.8737
C9-N7-C16	113.0432	112.7821	112.1608	112.4905	112.3945

N7-N8-C17	116.2641	116.9209	119.2374	118.8607	119.1684	118.4241
N7-C9-H10	111.4725	110.1039	112.6891	112.722	112.4628	112.2900
N7-C9-H11	111.4709	108.3285	112.693	112.7753	112.4603	112.2684
N7-C9-C12	101.5498	101.6822	102.095	101.9351	102.8274	102.6677
H10-C9-H11	109.2916	114.8676	108.7025	108.9873	108.7933	109.0524
H10-C9-C12	111.4333	110.0802	110.2656	110.118	110.0875	110.2119
H11-C9-C12	111.477	110.9542	110.2628	110.1251	110.0899	110.2178
O1-C12-N5	126.5515	125.7485	127.3776	127.3319	127.5339	127.4732
O1-C12-C9	125.8732	127.0593	125.4381	125.4006	126.8962	126.9288
N5-C12-C9	107.55	107.1909	107.1843	107.2675	105.5698	105.5980
O2-C13-N14	114.6736	116.1495	117.7268	117.4979	117.6940	117.6787
O2-C13-C21	113.2776	113.0483	112.0792	112.5713	112.0877	112.6090
N14-C13-C21	132.0367	130.8022	130.194	129.9307	130.2183	129.7123
O3-N14-O6	124.1922	124.2619	126.1782	126.3585	126.2021	126.3634
O3-N14-C13	117.3027	117.4108	115.688	115.6197	115.6901	115.5733
O6-N14-C13	118.5007	118.3036	118.1337	118.0217	118.1078	118.0633
O2-C15-C17	117.7588	117.7624	119.8985	119.495	119.8172	119.642
O2-C15-C19	110.3699	109.6004	109.9942	110.4273	110.0025	110.5235
C17-C15-C19	131.8676	132.6225	130.1074	130.0777	130.1803	129.8344
O4-C16-N5	126.7129	126.6982	127.0092	126.9831	126.6614	126.5916
N8-C16-N7	128.2102	119.2865	128.1361	128.1664	119.8737	120.2185
N5-C16-N7	105.0768	105.2273	104.8547	104.8505	104.7082	104.6983
N8-C17-C15	119.474	119.0128	121.3508	120.811	121.2521	120.9265
N8-C17-H18	120.2754	126.0008	123.7601	124.1218	123.7857	123.9358
C15-C17-H18	120.2505	114.8383	114.8891	115.0672	114.9622	115.1376
C15-C19-H20	126.5221	121.4467	126.0529	126.1371	126.0786	126.0977
C15-C19-C21	106.9286	107.8642	106.7012	106.3962	106.6959	106.3187
H20-C19-C21	126.5493	130.6543	127.2458	127.4666	127.2255	127.5836
C13-C21-C19	104.768	104.6656	105.0709	104.6116	105.0638	104.6194
C13-C21-H22	127.6111	122.5127	125.9686	126.1239	126.0010	125.8516
C19-C21-H22	127.6209	132.7174	128.9605	129.2645	128.9352	129.5290
N5-H23-O27	157.9922	-	160.4478	160.6013	-	-
C37-N24-H38	118.1809	-	115.7955	115.5284	-	-
C37-N24-H39	120.7994	-	115.6535	115.3968	-	-
H38-N24-H39	118.6861	-	112.4012	112.3728	-	-
C34-O25-H40	107.7043	-	110.8117	110.8734	-	-
C28-C26-C34	116.8926	-	117.9153	117.8286	-	-
C28-C26-C35	121.058	-	120.5841	120.7937	-	-
C34-C26-C35	122.0484	-	121.5004	121.3771	-	-
H23-O27-C34	133.5836	-	131.7077	131.2132	-	-
C26-C28-H29	119.7716	-	118.7502	118.9412	-	-
C26-C28-C37	120.5158	-	120.677	120.5197	-	-
H29-C28-C37	119.7126	-	120.5727	120.5391	-	-
H31-C30-C32	119.4935	-	119.9019	119.8586	-	-
H31-C30-C37	119.5035	-	119.3914	119.4238	-	-
C32-C30-C37	121.003	-	120.706	120.717	-	-
C30-C32-H33	119.6468	-	119.3045	119.392	-	-
C30-C32-C35	120.6824	-	120.8806	120.8281	-	-
H33-C32-C35	119.6708	-	119.8149	119.7799	-	-
O25-C34-C26	114.4729	-	114.0079	113.9856	-	-
O25-C34-O27	122.4903	-	123.2221	123.455	-	-
C26-C34-O27	123.0369	-	122.77	122.5594	-	-
C26-C35-C32	118.5739	-	118.7904	118.7149	-	-
C26-C35-H36	120.6938	-	120.1354	120.2943	-	-
C32-C35-H36	120.7323	-	121.0741	120.9907	-	-
N24-C37-C28	120.3602	-	120.7975	120.7236	-	-
N24-C37-C30	121.4112	-	120.7773	120.7944	-	-
C28-C37-C30	118.1533	-	118.3619	118.4266	-	-
Dihedral-Angles (°)						
H40-O1-C12-N5	-2.2199	-	-0.1869	-0.9852	-	-
H40-O1-C12-C9	179.8419	-	179.784	178.9543	-	-
C12-O1-O25-C34	-2.7729	-	0.3716	1.7338	-	-

C15-O2-C13-N14	-179.749	-179.877	-179.9766	-179.9213	179.9624	179.987
C15-O2-C13-C21	-0.8596	0.1232	-0.0059	-0.0011	0.0047	0.0004
C13-O2-C15-C17	-178.616	-178.6492	179.9997	179.9598	179.9922	-179.9993
C13-O2-C15-C19	0.7777	0.1285	-0.0025	0.0157	0.0013	-0.0055
C16-N5-C12-O1	-179.739	-178.5668	179.8948	179.7283	-179.982	-179.9636
C16-N5-C12-C9	-1.4909	1.8169	-0.0805	-0.22	0.0027	0.0230
H23-N5-C12-O1	4.2609	4.4936	-0.0704	-0.1439	0.0256	-0.0794
H23-N5-C12-C9	-177.491	-175.1227	179.9543	179.9078	-179.9897	179.9071
C12-N5-C16-O4	-179.826	176.926	-179.9235	-179.7865	179.9988	179.9319
C12-N5-C16-N7	0.0781	-3.0362	0.0749	0.1942	-0.0095	-0.0392
H23-N5-C16-O4	-4.0486	-6.4717	0.0403	0.0804	-0.0086	0.0446
H23-N5-C16-N7	175.8558	173.5661	-179.9612	-179.939	179.9831	-179.9266
C12-N5-H23-O27	-2.7022	-	0.2127	0.5513	-	-
C16-N5-H23-O27	-178.147	-	-179.7485	-179.3054	-	-
C9-N7-N8-C17	-3.0811	-7.0713	0.1068	0.5546	-0.032	-0.122
C16-N7-N8-C17	177.1832	-179.7879	180.0046	179.9376	180.008	-179.9171
N8-N7-C9-H10	59.2325	68.1898	61.6334	61.3752	61.6470	61.8155
N8-N7-C9-H11	-63.1934	-58.1799	-61.8394	-62.5687	-61.5926	-61.4889
N8-N7-C9-C12	177.9945	-175.1289	179.8977	179.3867	-179.9737	-179.835
C16-N7-C9-H10	-121.016	-118.6982	-118.2712	-118.0475	-118.3905	-118.3765
C16-N7-C9-H11	116.5578	114.9321	118.256	118.0086	118.3699	118.3192
C16-N7-C9-C12	-2.2543	-2.017	-0.0069	-0.0359	-0.0112	-0.0269
N8-N7-C16-O4	1.1475	-3.1289	0.0482	0.426	-0.0299	-0.1075
N8-N7-C16-N5	-178.755	176.8326	-179.9502	-179.5543	179.9786	179.8629
C9-N7-C16-O4	-178.623	-176.8731	179.9609	179.895	-179.9957	-179.9302
C9-N7-C16-N5	1.4744	3.0883	-0.0375	-0.0854	0.0128	0.0402
N7-N8-C17-C15	-179.664	-179.7651	-179.9989	-179.8827	-180.0045	179.9881
N7-N8-C17-H18	0.3191	4.9006	0.0234	0.1322	0.0039	-0.0217
N7-C9-C12-O1	-179.562	-179.5106	-179.925	-179.8001	-180.0102	-180.011
N7-C9-C12-N5	2.1747	0.0992	0.0508	0.1495	0.0049	0.0023
H10-C9-C12-O1	-60.7723	-62.8121	-59.9488	-59.9406	-59.9762	-60.208
H10-C9-C12-N5	120.9647	116.7978	120.027	120.009	120.039	119.8054
H11-C9-C12-O1	61.6298	65.4629	60.0956	60.2755	59.9576	60.2085
H11-C9-C12-N5	-116.633	-114.9273	-119.9286	-119.7749	-120.0272	-119.7782
O2-C13-N14-O3	-176.641	-175.8332	-179.9757	179.9895	179.9138	179.9834
O2-C13-N14-O6	4.0944	5.8609	0.0292	0.0037	-0.0869	-0.0308
C21-C13-N14-O3	4.7331	4.1666	0.0598	0.0857	-0.1376	-0.0328
C21-C13-N14-O6	-174.532	-174.1392	-179.9352	-179.9002	179.8617	179.9531
O2-C13-C21-C19	0.5988	-0.311	0.0115	-0.0129	-0.0086	0.0045
O2-C13-C21-H22	-179.354	-177.0324	179.9995	-179.979	-179.9951	179.9904
N14-C13-C21-C19	179.24	179.6891	179.9775	179.8947	-179.9595	-179.98
N14-C13-C21-H22	-0.713	2.9678	-0.0344	-0.0714	0.054	0.0059
O2-C15-C17-N8	-4.5418	-0.5219	0.0424	0.4342	0.024	-0.0591
O2-C15-C17-H18	175.4746	175.3196	-179.978	-179.5795	180.0163	179.9499
C19-C15-C17-N8	176.2215	-178.957	-179.9549	-179.6343	180.0129	179.9485
C19-C15-C17-H18	-3.7622	-3.1154	0.0247	0.3521	0.0051	-0.0425
O2-C15-C19-H20	179.6014	-178.3909	-179.994	-179.9695	-179.9989	179.9925
O2-C15-C19-C21	-0.4412	-0.3191	0.0094	-0.0235	-0.0065	0.0082
C17-C15-C19-H20	-1.1191	0.1391	0.0036	0.0941	0.0114	-0.0145
C17-C15-C19-C21	178.8383	178.211	180.007	-179.96	-179.9962	180.0012
C15-C19-C21-C13	-0.0825	0.376	-0.0124	0.0216	0.0089	-0.0075
C15-C19-C21-H22	179.8705	176.6122	-180.0	179.9862	179.9949	-179.9927
H20-C19-C21-C13	179.8749	178.2077	-180.0089	179.9666	180.0012	-179.9915
H20-C19-C21-H22	-0.1721	-5.5561	0.0035	-0.0688	-0.0128	0.0233
N5-H23-O27-C34	-0.7293	-	0.3074	1.4738	-	-
H38-N24-C37-C28	-175.370	-	-157.4365	-156.996	-	-
H38-N24-C37-C30	7.8432	-	25.5058	25.753	-	-
H39-N24-C37-C28	-12.9401	-	-22.8749	-23.074	-	-
H39-N24-C37-C30	170.2733	-	160.0674	159.6749	-	-
H40-O25-C34-C26	-176.647	-	-179.9803	179.9242	-	-
H40-O25-C34-O27	3.3397	-	-0.0161	-0.122	-	-
C34-C26-C28-H29	-1.223	-	0.3243	0.349	-	-

C34-C26-C28-C37	178.7821	-	-179.823	-179.743	-	-
C35-C26-C28-H29	179.1177	-	-179.8449	-179.9248	-	-
C35-C26-C28-C37	-0.8771	-	0.0077	-0.0168	-	-
C28-C26-C34-O25	-177.968	-	-179.4364	-178.8927	-	-
C28-C26-C34-O27	2.0446	-	0.5993	1.153	-	-
C35-C26-C34-O25	1.6874	-	0.7345	1.3828	-	-
C35-C26-C34-O27	-178.299	-	-179.2298	-178.5715	-	-
C28-C26-C35-C32	0.6009	-	-0.072	-0.0482	-	-
C28-C26-C35-H36	-179.382	-	-179.9607	-179.8988	-	-
C34-C26-C35-C32	-179.040	-	179.7525	179.6681	-	-
C34-C26-C35-H36	0.9759	-	-0.1362	-0.1825	-	-
H23-O27-C34-O25	-1.1824	-	-0.4064	-1.4865	-	-
H23-O27-C34-C26	178.803	-	179.5547	178.4635	-	-
C26-C28-C37-N24	-176.786	-	-177.0966	-177.2727	-	-
C26-C28-C37-C30	0.1033	-	0.0307	0.0422	-	-
H29-C28-C37-N24	3.2188	-	2.7533	2.6339	-	-
H29-C28-C37-C30	-179.891	-	179.8806	179.9488	-	-
H31-C30-C32-H33	-1.2772	-	-0.3751	-0.3141	-	-
H31-C30-C32-C35	178.7432	-	179.6389	179.6393	-	-
C37-C30-C32-H33	178.7532	-	179.9246	179.9834	-	-
C37-C30-C32-C35	-1.2264	-	-0.0614	-0.0632	-	-
H31-C30-C37-N24	-2.1762	-	-2.5782	-2.3936	-	-
H31-C30-C37-C28	-179.031	-	-179.7061	-179.7066	-	-
C32-C30-C37-N24	177.7934	-	177.1236	177.3101	-	-
C32-C30-C37-C28	0.9381	-	-0.0043	-0.0028	-	-
C30-C32-C35-C26	0.4432	-	0.0988	0.0879	-	-
C30-C32-C35-H36	-179.573	-	179.9864	179.9374	-	-
H33-C32-C35-C26	-179.536	-	-179.8871	-179.9588	-	-
H33-C32-C35-H36	0.4471	-	0.0005	-0.1093	-	-

Table S2 Theoretical and experimental vibrational wavenumbers (in cm^{-1}) of NF-3ABA and their assignments using wB97X-D/cc-pvTZ level of theory.

Calculated		Experimental		Potential Energy Distribution (≥5%)		
Unscaled	Scaled	IR	Raman			
3710	3547	3470	3471	R3[v _a (NH ₂)](98)		
3608	3449	3362	3363	R3[v _s (NH ₂)](98)		
3401	3252	3200	3216	v(O25H)(89)+R2[v(N5H)](7)		
3304	3159			R1[v(CH)](99)		
3298	3153	3150	3151	R2[v(N5H)](88)+v(O25H)(8)		
3280	3136	3134	3135	R1[v(CH)](99)		
3247	3104	3119	3119	R3[v(CH)](99)		
3216	3074	3093	3100	R3[v(CH)](97)		
3214	3072	3063		R3[v(CH)](99)		
3185	3045	3049		R3[v(CH)](99)		
3125	2988	3010		v(C17H)(99)		
3101	2965	2961	2959	R2[v _a (CH ₂)](100)		
3055	2921	2918	2924	R2[v _s (CH ₂)](99)		
1922	1837	1827		R2[v(C16=O)(75)+v(NC)(11)]		
1832	1751	1788	1776	R2[v(C12=O)(64)+v(NC)(10)+v(C34=O)(5)]		
1771	1693	1688	1686	v(C34=O)(61)+v(O25C)(6)+δ(O25HC34)(6)+R3[v(C26C34)(5)+ρ(C34C) 5)]		
1721	1646	1653		v(N8C)(59)+R1[v(C15C17)(14)+ρ(C17H)(13)-v(CC)(6)]		
1692	1617	1620		R3[v(CC)(54)+δ(NH ₂)](10)+v(N24C)(7)+δ _{in} (CH)(14)+δ _a (5)]		
1675	1601			R1[v _a (NO ₂)(77)+ρ(NO ₂)(8)+v(CC)(7)]		
1666	1593	1603	1612	R3[δ(NH ₂)(41)+v(CC)(37)+δ _{in} (C35H)(5)]		
1661	1588	1583		R3[δ(NH ₂)](38)+v(CC)(39)+δ _{in} (C30H)(5)+δ _a (5)]		
1643	1571	1562	1566	R1[v(CC)(56)+v _a (NO ₂)(15)+δ _{in} (CH)(10)]+v(N8C)(8)		
1570	1500	1512	1512	R1[v(CC)(46)+δ _{ring} (13)+v(C15C17)(12)+v(C13N)(5)]+v(N8C)(6)		
1551	1482	1491	1485	R3[δ _{in} (CH)(47)+(CC)(36)]		
1519	1452	1464		R3[v(CC)(33)+δ _{in} (CH)][(19)+v(N24C)(7)+v(C26C34)(6)+δ _{in} (C26C34)(6)]		
1491	1426	1427	1437	R2[δ _{sc} (CH ₂)](83)		
1470	1405	1400	1399	δ(O25HC34)(31)+v(O25C)(16)+R3[(δ(C34OO)(7)+v(C26C34)(5)]		
1468	1403	1385	1382	R1[v(CO)(24)+v(C13N)(7)+v(CC)(11)]+δ(O25HC34)(7)		

1444	1381		R2[δ _{in} (NH)(38)+v(NC)(23)+v(C12=O)(7)]
1434	1371	1367	R1[v _s (NO ₂)(35)+v(CC)(11)+δ(NO ₂)(9)+v(C13N)(7)]+R2[δ _{in} (NH)](12)
1421	1359		R2[v(NC)(34)+δ _{in} (NH)(17)+δ _{in} (C12=O)(12)+v(CC)(10)+δ' _{ring} (5)]
1410	1348	1352	R1[p(C17H)(20)+v _s (NO ₂)(12)+v(CC)(7)]+R2[v(NC)(10)+δ _{ring} (6)+ω(CH ₂)(5)+v(N7N8)(5)]
1374	1313	1319	R2[w(CH ₂)(31)+v(CC)(7)+δ _{ring} (6)+v(NC)(8)+R1[p(C17H)](26)
1361	1302		R3[v(CC)(78)+δ _{in} (CH)(25)]
1357	1298	1288	R3[v(N24C)(17)+δ _{in} (CH)(43)+p(NH ₂)(7)+v(CC)(6)+δ _{ring} (5)]+δ(O25HC34)(5)
1324	1266	1263	R3[δ _{in} (CH)(36)+v(N24C)(12)+δ _{ring} (7)+v(CC)(7)+v(C26C34)(7)+δ(O25HC34)(13)]
1320	1262		R1[v(CO)(31)+δ' _{ring} (7)+δ _{in} (CH)(6)]+R2[v(NC)(12)+v(N7N8)(10)+δ(N8C17N7)(5)]
1312	1255	1250	R1[v(CC)(29)+v(C15C17)(9)+v(C15O)(9)+δ _{in} (CH)(9)]+R2[v(N7N8)(10)+v(NC)(6)]
1302	1245	1238	v(O25C)(32)+δ(O25HC34)(24)+R3[v(N24C)(10)+v(C26C34)(5)+δ _{in} (CH)(5)]
1296	1239		R1[v(C13O)(29)+v(CC)(8)+δ' _{ring} (6)+v(C13N)(6)+v(C15O)(6)]+R2[v(NC)(14)+v(N7N8)(13)]
1252	1197	1219	R2[w(CH ₂)(30)+v(NC)(40)+v(N7N8)(7)+δ _{ring} (5)]
1212	1158	1167	R2[v(CH ₂)](96)
1206	1153		R3[δ _{in} (CH)(75)+v(CC)(18)]
1202	1149		R1[δ _{in} (CH)(57)+v(C13N)(9)+v(C15C17)(5)+δ' _{ring} (5)]
1162	1111	1117	R2[v(NC)(55)+δ _{in} (C16=O)(9)+δ _{in} (NH)(8)+v(N7N8)(6)]
1153	1103	1109	R3[δ _{in} (CH)(40)+v(CC)(11)+v(CC)(10)+v(C26C34)(7)+p(NH ₂)(6)]+v(O25C)(9)
1139	1089	1067	R3[δ _{in} (CH)(30)+p(NH ₂)(18)+v(CC)(33)+v(C26C34)(5)]
1096	1048	1026	R3[p(NH ₂)(45)+v(CC)(37)+δ _{in} (CH)(8)]
1041	995	991	R1[δ _{in} (CH)(58)+v(CC)(25)+v(CO)(10)]
1027	982		R2[p(CH ₂)(68)+oop(C12=O)(17)+τ(7)]
1025	980	982	R1[v(CO)(42)+δ' _{ring} (14)+v(C15C17)(10)+δ _{in} (CH)(6)]
1025	980	984	R3[δ _{tring} (63)+v(CC)(34)]
1012	967		R3[oop(CH)(86)+puck(9)]
1002	958	966	R1[δ _{ring} (37)+v(C13N)(10)+δ _{in} (CH)(14)+v(CO)(11)+v(CC)(12)]
954	912	920	R3[v(CC)(25)+v(N24C)(14)+v(C26C34)(12)+δa(9)+δ _{in} (CH)(5)]+v(O25C)(8)
941	899	912	R3[oop(CH)(67)+puck(13)+oop(C26C34)(7)]
938	897	885	R2[v(CC)(56)+v(NC)(13)+δ _{in} (C12=O)(6)+ω(CH ₂)(5)]
932	891		R1[ω(C17H)(48)+oop(CH)(5)]+τ(N8C17)(21)+τ(O1H40)(6)
925	884	876	τ(O1H40)(48)+τ(O25H40)(32)+τ(O25C)(11)
916	876		R3[oop(CH)](72)+oop(C37N)(8)+puck(6)]
909	869		R1[oop(CH)(74)+τ(15)]
898	858	854	R2[δ(N8C17N7)(17)+v(NC)(21)+δ' _{ring} (9)+v(N7N8)(8)+R1[δ' _{ring} (15)+δ(C15C17N)(12)]
883	844	835	R2[oop(NH)(27)+τ(O1H40)(26)+τ(O27H)(21)+τ(O25H40)(18)+τ(O25C)(5)]
849	812	810	R1[δ _{sc} (NO ₂)(60)+δ' _{ring} (18)+δ _{ring} (9)]
836	799		R3[ω(C34C)(20)+oop(CH)(43)+puck(17)+oop(C26C34)(12)]
822	786	787	R1[oop(CH)(70)+τ'(9)+ω(N14C)(9)]
804	769	762	R2[v(NC)(20)+δ' _{ring} (7)+δ _{in} (C16=O)(5)+δ _{ring} (5)]+R1[δ' _{ring} (16)+δ _{ring} (11)+v(C15C17)(6)+(δ(C15C17N)(5))
782	747	752	R3[ω(C34C)(21)+oop(CH)(29)+(δ(C34OO)(9)+oop(C37N)(9))]
781	747		R1[ω(N14C)(62)+oop(C13N)(12)+oop(CH)(18)+τ'(5)]
777	743	737	R3[(δ(C34OO)(20)+ω(C34C)(11)+oop(CH)(17)+δ _{tring} (6)+δ' _a (6)]+δ(O1O25C34)(6)
767	733		R2[oop(C16=O)(71)τ'(14)+τ(9)]
708	677	687	R1[τ'(39)+oop(C15C17)(33)+τ(21)]
705	674	664	R3[puck(66)+oop(C32H)(13)+oop(C37N)(13)+oop(C26C34)(5)]
679	650	656	R2[δ _{ring} (25)+δ' _{ring} (12)+δ _{in} (C16=O)(11)+v(NC)(11)+δ _{in} (N7N)(9)+δ _{in} (C12=O)(6)]
641	613	625	R3[(δ(C34OO)(34)+δ _a (32)+δ' _a (12)]+δ(O1O25C34)(6)
621	593	609	R2[δ _{in} (C12=O)(22)+δ _{in} (C16=O)(15)+δ _{ring} (15)+δ _{in} (N7N)(10)+δ' _{ring} (9)+δ(N8C17N7)(6)]
612	585		R2[δ' _{ring} (33)+δ _{ring} (15)+v(NC)(17)+v(C12=O)(5)]
604	578	579	R1[τ(52)+τ'(24)+oop(C13N)(18)]
588	563	573	R2[oop(C12=O)(58)+p(CH ₂)(16)+τ(13)+γ(CH ₂)(7)]
570	545	550	R3[ω(N24C)(39)+oop(C37N)(17)+v(N24C)(6)+τ' _a (6)+puck(5)+τ _a (5)+oop(C26C34)(5)]
562	537		R3[δ' _a (32)+p(C34C)(31)+δ _{in} (C26C34)(7)+δ _a (5)]
535	511	514	R1[p(NO ₂)(43)+δ _{in} (C13N)(21)+δ _{in} (C15C17)(10)]+R2[δ(N8C17N7)](5)
523	500	471	R3[ω(N24C)(26)+oop(C37N)(19)+τ _a (13)+τ' _a (11)+oop(C26C34)(8)]
475	454	447	R3[δ' _a (18)+ω(N24C)(14)+p(C34C)(14)+v(N24C)(13)+δ _{in} (C26C34)(10)+δ _{in} (C37N)(6)]
458	438	431	R2[δ _{in} (C16=O)(16)+δ _{in} (C12=O)(12)]+R1[δ _{in} (C15C17)(11)+δ(C15C17N)(8)+p(NOO)(6)+v(NC)(5)]
445	425		R3[τ _a (36)+τ' _a (32)+oop(C26C34)(14)+oop(C30H)(9)]
426	407	422	R1[v(C13N)(21)+δ(NOO)(8)+δ _{ring} (7)]+R2[δ _{in} (C12=O)(14)+δ _{in} (C16=O)(6)]
418	400	407	R3[δ _a (31)+δ _{in} (C37N)(21)+v(C26C34)(13)+δ(C34OO)(6)]

393	376	-	38	$\tau(N8C17)(29)+R1[\tau'(16)+\tau(14)+oop(C15C17)(9)+\omega(C17H)(8)+oop(C13N)(7)]+R2[oop(N7N)](7)$
380	363	-		$R3[\delta_{in}(C37N)(38)+\rho(C34C)(16)+v(C26C34)(9)+v(CC)(6)]+v(O1H40)(10)$
310	296	-	302	$R3[\tau(N24C)](92)$
297	284	-		$R2[\delta_{in}(N7N)(18)+v(NC)(6)+\delta_{in}(C16=O)(15)+\delta(N8C17N7)(5)]+R1[\delta_{in}(C13N)(12)+\delta_{in}(C15C17)(10)+\rho(NOO)(6)+v(C15C17)(6)]$
294	281	-	260	$R2[\tau(N7N)(38)+oop(N7N)(21)+\tau'(11)]+R1[\tau(C15C17)(8)+oop(C15C17)(6)]+\tau(N8C17)(5)$
235	225	-	235	$R3[\delta_{in}(C26C34)(29)+\delta_{in}(C37N)(8)]+\delta(O1O25C34)(23)+v(O27H23)(8)+R1[\delta_{in}(C13N)](6)$
232	221	-	231	$R1[\delta_{in}(C13N)(18)+\rho(NOO)(11)+\delta(C15C17N)(7)+v(C15C17)(5)]+v(O1H40)(12)+R3[\delta_{in}(C26C34)](11)$
227	217	-	202	$R3[\tau'_a(44)+\tau_a(24)+puck(11)+oop(CH)(13)]$
204	195	-	187	$R1[oop(C13N)(50)+oop(C15C17)(6)]+R2[\tau(N7N)(13)+\tau'(7)]+\tau(N8C17)(5)$
181	173	-	179	$R2[\tau'(69)+oop(N7N)(13)]$
172	164	-		$R2[\tau'(15)+\tau(15)+oop(NH)(8)]+R3[oop(C26C34)(15)+\tau_a(11)+oop(C28H)(6)]+\tau(O1H40)(10)+\tau(O25C)(5)$
168	161	-		$v(O1H40)(27)+\delta(O1O25C34)(16)+R1[\delta_{in}(C13N)](15)+R2[\delta_{in}(N7N)(13)+\delta(N8C17N7)(9)]$
164	157	-	142	$R2[\tau(49)+oop(NH)(29)]+\tau(O25H40)(6)$
131	125	-	108	$R2[oop(N7N)](24)+R1[oop(C13N)(18)+oop(C15C17)(14)+\tau(C13N)(10)]$
91	87	-		$\delta(O1O25C34)(35)+v(O1H40)(22)+R1[\delta_{in}(C15C17)](7)+v(O27H23)(5)$
88	84	-		$v(O27H23)(35)+\delta(O1O25C34)(18)+\delta(O25HC34)(13)+v(O1H40)(12)$
87	83	-		$R1[\tau(C13N)](27)+R2[oop(N7N)(23)+\tau'(13)+oop(NH)(10)]+\tau(O27H)(8)$
68	65	-		$\tau(O25H40)(31)+R3[\tau(C26C34)](28)+\tau(O25C)(19)+\tau(O27H)(12)$
61	59	-		$R1[\tau(C13N)(32)+oop(C15C17)(6)]+R2[oop(NH)](13)+\tau(O27H)(9)+\tau(O1H40)(6)$
60	57	-		$v(O27H23)(12)+R1[\delta_{in}(C15C17)(11)+\delta(C15C17N)(11)+\tau(C13N)(5)]+\delta(O1O25C34)(10)+v(O1H40)(10)+R3[\rho(C34C)(9)+\delta_{in}(C26C34)(7)]$
38	36	-		$\tau(O1H40)(22)+R2[oop(N7N)(16)+\tau'(5)+R1[\tau(C15C17)(14)+\tau(C13N)(6)]+\tau(O25H40)(13)+\tau(O25C)(6)]$
26	25	-		$\tau(O25H40)(25)+R2[oop(N7N)](10)+R1[\tau(C15C17)(7)+\delta(C15C17N)(6)]+\tau(O1H40)(6)+v(O27H23)(6)$
25	24	-		$\tau(O25H40)(22)+R2[oop(N7N)](9)+R1[\tau(C15C17)(8)+\delta(C15C17N)(7)+\delta_{in}(C15C17)(5)]+v(O27H23)(7)+\tau(O1H40)(5)$
13	13	-		$\tau(O27H)(23)+R3[\tau(C26C34)](15)+\tau(O25H40)(12)+\tau(O25C)(12)+\tau(O1H40)(7)+R2[\tau(N7N)(6)+oop(NH)(5)]+R1[\tau(C15C17)](6)$
8	7	-	-	$R1[\tau(C15C17)](17)+\tau(O1H40)(13)+R2[\tau'(11)+oop(N7N)(10)+oop(NH)(7)]+\tau(O25H40)(8)+\tau(O27H)(5)+R3[\tau(C26C34)](5)$

Table S3 Theoretical and experimental vibrational wavenumbers (in cm^{-1}) of NF-3ABA and their assignments using B3LYP/cc-pvTZ level of theory.

Calculated		Experimental		Potential Energy Distribution ($\geq 5\%$)
Unscaled	Scaled	IR	Raman	
3665	3537	3470	3471	$R3[v_a(\text{NH}_2)](100)$
3566	3441	3362	3363	$R3[v_s(\text{NH}_2)](100)$
3335	3218	3200	3216	$v(O25H)(88)+R2[v(N5H)](7)$
3281	3167			$R1[v(CH)](98)$
3251	3138	3150	3151	$R1[v(CH)](99)$
3237	3124	3134	3135	$R2[v(N5H)](87)+v(O25H)(8)$
3223	3110	3119	3119	$R3[v(CH)](96)$
3188	3077	3093	3100	$R3[v(CH)](98)$
3182	3070	3063		$R3[v(CH)](95)$
3159	3048	3049		$R3[v(CH)](99)$
3094	2986	3010		$v(C17H)(99)$
3067	2959	2961	2959	$R2[v_a(\text{CH}_2)](100)$
3030	2924	2918	2924	$R2[v_s(\text{CH}_2)](99)$
1874	1808	1827		$R2[v(C16=O)(75)+v(NC)(10)]$
1785	1722	1788	1776	$R2[v(C12=O)(65)+v(NC)(10)+\delta_{in}(NH)(5)]$
1720	1660	1688	1686	$v(C34=O)(61)+\delta(O25HC34)(7)+R3[v(C26C34)(5)+\rho(C34C)(5)]+v(O25C)(5)$
1663	1605	1653		$R3[\delta(\text{NH}_2)(64)+v(N24C)(8)+v(CC)(15)]$
1660	1602	1620		$v(N8C)(53)+R1[v(C15C17)(15)+\rho(C17H)(15)+v(CC)(7)]$
1647	1590			$R3[\delta(\text{NH}_2)(23)+v(CC)(48)+\delta_{in}(CH)(7)+\delta_a(5)]$
1627	1570	1603	1612	$R3[v(CC)](64)+\delta_{in}(CH)(15)+\delta'_a(6)$
1606	1550	1583		$R1[v(CC)(40)+v_a(\text{NO}_2)(27)+\rho(\text{NO}_2)(6)+\delta_{in}(CH)(5)]+v(N8C)(7)$
1585	1530	1562	1566	$R1[v_a(\text{NO}_2)(68)+v(CC)(14)]$
1530	1476	1512	1512	$R3[\delta_{in}(CH)(48)+v(CC)(34)]$
1528	1475	1491	1485	$R1[v(CC)(42)+\delta_{ring}(13)+v(C15C17)(12)+v(C13N)(5)]+v(N8C)(5)R2[v(N7N8)](3)$
1497	1445	1464		$R3[v(CC)(37)+\delta_{in}(CH)(23)+\delta_{in}(C26C34)(6)+v(N24C)(6)+\rho(\text{NH}_2)(5)]$
1486	1434	1427	1437	$R2[\delta_{sc}(\text{CH}_2)](92)$

1446	1396	1400	1399	$\delta(O25HC34)(46)+v(O25C)(17)+v(C34=O)(8)+R3[(\delta(C34OO)(8)+v(C26C34)(6)]$
1427	1377	1385	1382	$R1[v(CC)(24)+v(CO)(26)+\delta_{in}(CH)(15)+\delta_{in}(C15C17)(5)+\rho(C17H)(5)]$
1421	1371			$R2[\delta_{in}(NH)(58)+v(C12=O)(9)+v(NC)(8)]$
1398	1349	1367	1372	$R2[\delta_{in}(NH)(11)+v(NC)(13)+v(N7N8)(5)]+R1[\rho(C17H)(9)+v(CC)(12)+v(O3N)(7)+v(N14=O6)(5)]$
1388	1339			$R2[v(NC)(32)+v(CC)(13)+\delta_{in}(C12=O)(12)+\delta_{ring}(5)]+R1[\rho(C17H)(6)]$
1364	1317	1352	1344	$R1[v_s(NO_2)(35)+v(C13N)(16)+\rho(C17H)(14)+\delta(NO_2)(11)+v(CC)(5)]$
1362	1314	1319	1321	$R3[v(CC)(79)+\delta_{in}(CH)(15)]$
1347	1300			$R3[\delta_{in}(CH)(46)+v(N24C)(12)+\rho(NH_2)(6)+v(CC)(10)]$
1343	1296	1288	1289	$R2[\omega(CH_2)(37)+v(CC)(8)+\delta_{ring}(6)+v(NC)(9)]+R1[\rho(C17H)(15)]$
1312	1266	1263	1264	$R3[v(N24C)(22)+\delta_{in}(CH)(28)+\delta_{ring}(11)+v(C26C34)(7)+v(CC)(9)]+\delta(O25HC34)(9)$
1292	1247			$R1[v(CC)(29)+v(C15C17)(12)+v(CO)(12)+v_s(NO_2)(13)+\delta_{in}(CH)(7)+\rho(C17H)(7)]$
1272	1228	1250	1252	$R2[v(N7N8)(20)+v(NC)(11)+\delta(N8C17N7)(5)]+R1[v(CO)](15)+v(O25C)(7)$
1271	1226	1238	1239	$v(O25C)(29)+\delta(O25HC34)(18)+R3[v(C26C34)(8)+v(N24C)(6)+\delta(C34OO)(5)]$
1249	1205			$R1[v(CO)(31)+\delta'_{ring}(9)+v(C13N)(7)+v(CC)(5)+R2[v(N7N8)(18)+v(NC)(7)]$
1211	1168	1219	1220	$R2[v(NC)(52)+\omega(CH_2)(22)+\delta'_{ring}(5)]$
1196	1154	1167	1176	$R3[\delta_{in}(CH)(72)+v(CC)(15)]$
1195	1154			$R1[\delta_{in}(CH)(45)+v(C13N)(9)+\delta'_{ring}(7)+v(CO)(6)+v(C15C17)(5)]$
1189	1148			$R2[\gamma(CH_2)](95)$
1145	1104	1117	1117	$R3[\delta_{in}(CH)(41)+\rho(NH_2)(16)+v(CC)(22)]+v(O25C)(6)$
1131	1091	1109		$R2[v(NC)(49)+\delta_{in}(C16=O)(8)+\delta_{in}(NH)(6)]$
1127	1087	1067		$R3[v(CC)(26)+\delta_{in}(CH)(17)+\rho(NH_2)(6)+v(C26C34)(5)]+R2[v(NC)](13)+v(O25C)(9)$
1086	1048	1026	1030	$R3[\rho(NH_2)(43)+v(CC)(38)+\delta_{in}(CH)(8)]$
1041	1004	991	993	$R1[\delta_{in}(CH)(63)+v(CC)(25)]$
1021	985			$R2[\rho(CH_2)(69)+oop(C12=O)(16)+\tau(7)]$
1016	981			$R3[\delta_{ring}(63)+v(CC)(36)]$
1001	966	982	984	$R1[v(CO)(53)+\delta'_{ring}(14)+v(C15C17)(8)]$
992	957			$R3[oop(CH)](87)+puck(9)]$
986	951	966	968	$R1[\delta_{ring}(42)+v(CO)(18)+v(CC)(13)+v(C13N)(8)]$
938	906	920	921	$R3[v(CC)(25)+v(N24C)(14)+v(C26C34)(12)+\delta_a(9)+\delta_{in}(C32H)(5)+v(O25C)(9)]$
931	898	912	912	$R1[\omega(C17H)(54)+oop(CH)(10)]+\tau(N8C17)(23)$
927	895	885	887	$R3[oop(CH)(71)+puck(9)+oop(C26C34)(8)+\tau_a(6)]$
919	887			$R2[v(CC)(58)+v(NC)(13)+\delta_{in}(C12=O)(6)+\delta_{in}(C16=O)(5)]$
911	879	876		$R1[oop(CH)(76)+\tau(13)]$
907	876			$R3[oop(CH)(43)+puck(7)+oop(C37N)(6)]+\tau(O25H40)(14)+\tau(O25C)(14)+R2[oop(NH)](6)$
905	874			$R3[oop(CH)(46)+oop(C37N)(6)+puck(6)]+\tau(O25H40)(13)+\tau(O25C)(12)+R2[oop(NH)](6)$
880	849	854		$R1[\delta'_{ring}(18)+\delta(C15C17N)(14)]+R2[\delta(N8C17N7)(16)+v(NC)(19)+\delta'_{ring}(8)+v(N7N8)(7)]$
873	843	835		$R2[oop(NH)](36)+\tau(O27H)(26)+\tau(O25H40)(18)+\tau(O25C)(16)$
830	801	810	812	$R1[\delta_{sc}(NO_2)(59)+\delta'_{ring}(17)+\delta_{ring}(7)+v(O3N)(5)]$
824	795			$R3[oop(CH)(49)+\omega(C34C)(19)+puck(16)+oop(C26C34)(12)]$
823	795	787		$R1[oop(CH)(82)+\tau'(6)]$
788	760	762	790	$R2[v(NC)(23)+\delta'_{ring}(7)+\delta_{in}(C16=O)(6)+R1[\delta'_{ring}(13)+\delta_{ring}(11)+v(C15C17)(6)+\delta(NOO-)(5)]$
772	745	752	754	$R3[\omega(C34C)(27)+oop(CH)(32)+oop(C37N)(9)+\delta(C34OO)(6)]$
767	740			$R3[(\delta(C34OO)(22)+\omega(C34C)(8)+\delta'a(7)+\delta_{ring}(7)+v(C26C34)(6)+oop(CH)(6)+v(CC)(7)]+\delta(O1O25C3)(4)(7)+v(O25C)(5)]$
767	740	737	736	$R1[\omega(N14C)(69)+oop(C13N)(15)+\tau'(8)+oop(CH)(5)]$
754	727			$R2[oop(C16=O)(69)+\tau'(14)+\tau(9)]$
699	674	687	696	$R3[puck(67)+oop(C37N)(14)+oop(CH)(12)+oop(C26C34)(5)]$
698	673		664	$R1[\tau'(36)+oop(C15C17)(34)+\tau(24)]$
691	667			$R2[\delta_{ring}(28)+v(NC)(14)+\delta'_{ring}(12)+\delta_{in}(C16=O)(10)+\delta_{in}(N7N)(8)+\delta_{in}(C12=O)(5)+v(CC)(5)]$
673	650	656	655	$R3[(\delta(C34OO)(36)+\delta_s(31)-\delta'_a(13)]+\delta(O1O25C34)(7)$
631	609	625	629	$R2[\delta_{in}(C12=O)(23)+\delta_{in}(C16=O)(16)+\delta_{ring}(13)+\delta_{in}(N7N)(10)+\delta'_{ring}(9)+\delta(N8C17N7)(6)]$
610	589	609	608	$R2[\delta'_{ring}(31)+\delta_{ring}(14)+v(NC)(17)+v(C12=O)(5)]$
602	581			$R1[\tau(51)+\tau'(25)+oop(C13N)(17)]$
596	575		579	$R2[oop(C12=O)(57)+\rho(CH_2)(15)+\tau(15)+\gamma(CH_2)(7)]$
583	562	573	570	$R3[\omega(N24C)(41)+oop(C37N)(16)+v(N24C)(6)+\tau'_a(6)+\tau_a(5)+oop(C26C34)(5)+puck(5)]$
564	544	550	550	$R3[\delta'_a(30)+\rho(C34C)(29)+\delta_{in}(C26C34)(6)+\delta_a(6)]$
554	534			$R1[\rho(NO_2)(43)+\delta_{in}(C13N)(21)+\delta_{in}(C15C17)(10)+v(CC)(5)]+R2[\delta(N8C17N7)(5)]$
534	515	511	514	$R3[\omega(N24C)(27)+oop(C37N)(19)+\tau'_a(14)+\tau_a(11)+oop(C26C34)(9)]$
516	498	471	471	$R3[\delta'_a(17)+\rho(C34C)(16)+v(N24C)(12)+\omega(N24C)(12)+\delta_{in}(C26C34)(11)+\delta_{in}(C37N)(7)]$
465	449	447		$R2[\delta(N8C17N7)(17)+\delta_{in}(C12=O)(8)+\delta_{in}(N7N)(5)]+R1[v(C13N)(13)+\delta_{in}(C15C17)(11)+\rho(NoO)(11)+\delta_{ring}(5)+\delta(NOO-)(5)]$
451	435		431	$R2[\delta_{in}(C16=O)(14)+\delta_{in}(C12=O)(14)+v(NC)(6)+R1[\delta_{in}(C15C17)(10)+\delta(C15C17N)(7)+v(C13N)(6)+\rho($

				NOO)(5)]
442	426	425	R3[τ_a (36)+ τ'_a (32)+oop(C26C34)(14)+oop(CH)(9)]	
417	403	422	R1[v(C13N)(20)+ δ (NOO)-(7)+ δ_{ring} (6)]+R2[δ_{in} (C12=O)(12)+ δ_{in} (C16=O)(5)]+R3[δ_{in} (C37N)(8)+ δ_a (5)]	
413	399	407	R3[δ_a (28)+ δ_{in} (C37N)(17)+v(C26C34)(13)+ δ (C34OO)(6)]+v(O1H40)(5)	
386	372	38	τ (N8C17)(27)+R1[τ' (16)+ τ (14)+oop(C15C17)(9)+w(C17H)(8)+oop(C13N)(7)+R2[oop(N7N)](8)	
374	361	-	R3[δ_{in} (C37N)(40)+p(C34C)(16)+v(C26C34)(9)+v(CC)(6)]+v(O1H40)(9)	
312	301	302	R3[τ (N24C)](92)	
309	298	-	R2[τ (N7N)(39)+oop(N7N)(23)+ τ' (10)]+R1[τ (C15C17)](12)+ τ (N8C17)(6)	
293	283	260	R2[δ_{in} (N7N)(18)+ δ_{in} (C16=O)(16)+v(NC)(7)+ δ (N8C17N7)(5)]+R1[δ_{in} (C13N)(13)+ δ_{in} (C15C17)(11)+ ρ (NOO)(7)+v(C15C17)(6)]	
232	224	235	R3[δ_{in} (C26C34)(32)+ δ_{in} (C37N)(9)]+ δ (O1O25C34)(23)+v(O27H23)(7)	
228	220	231	R1[δ_{in} (C13N)(21)+p(NoO)(12)+ δ (C15C17N)(8)+v(C15C17)(5)]+v(O1H40)(10)+R3[δ_{in} (C26C34)](6)	
228	220	202	R3[τ'_a (41)+ τ_a (23)+puck(11)+oop(CH)(12)]	
200	193	187	R1[oop(C13N)(49)+oop(C15C17)(7)+R2[τ (N7N)(13)+oop(NH)(5)]+ τ (N8C17)(6)]	
190	183	179	R2[τ' (71)+oop(N7N)(16)]	
172	166	-	R2[τ (20)+oop(NH)(9)+ τ' (5)]+R3[oop(C26C34)(17)+ τ_a (12)+oop(C28H)(7)]+ τ (O1O25)(8)+ τ (O25C)(8)	
166	160	-	R2[τ (48)+oop(NH)(33)]	
163	157	142	v(O1H40)(27)+ δ (O1O25C34)(18)+R2[δ_{in} (N7N)(13)+ δ (N8C17N7)(10)]+R1[δ_{in} (C13N)](13)	
133	128	108	R1[oop(C13N)(20)+oop(C15C17)(13)+ τ (C13N)(12)]+R2[τ (8)+ τ (C15C17)(5)+oop(N7N)(18)]	
91	88	-	R1[τ (C13N)(29)+ τ (C15C17)(6)]+R2[oop(N7N)(22)+oop(NH)(10)+ τ' (8)]+ τ (O27H)(9)]	
90	87	-	δ (O1O25C34)(46)+v(O1H40)(12)+R1[δ_{in} (C15C17)(9)+ δ (C15C17N)(5)]+ δ (O25HC34)(5)]	
84	81	-	v(O27H23)(39)+v(O1H40)(23)+ δ (O25HC34)(10)+ δ (O1O25C34)(6)]	
73	70	-	τ (O1O25)(38)+R3[τ (C26C34)](27)+ τ (O25C)(12)+ τ (O27H)(9)+ τ (O25H40)(8)]	
62	60	-	R1[τ (C13N)(35)+oop(C15C17)(8)]+R2[oop(NH)](15)+ τ (O25C)(10)+ τ (O27H)(9)]	
59	57	-	v(O27H23)(17)+R1[δ (C15C17N)(14)+ δ_{in} (C15C17)(14)]+v(O1H40)(11)+R3[p(C34C)(10)+ δ_{in} (C26C34)(7)]+ δ (O1O25C34)(9)+R2[δ (N8C17N7)](5)]	
43	41	-	R1[τ (C15C17)(25)+ τ (C13N)(14)]+ τ (O25C)(12)+R2[oop(N7N)(10)+ τ (N7N)(7)]+R3[τ (C26C34)](6)]	
29	28	-	τ (O1O25)(25)+R2[oop(N7N)](17)+ τ (O25H40)(17)+ τ (O27H)(10)+R3[τ (C26C34)](9)+ τ (N8C17)(5)]	
25	24	-	v(O27H23)(23)+R1[δ (C15C17N)(17)+ δ_{in} (C15C17)(10)]+R2[δ (N8C17N7)](14)+v(O1H40)(10)+R2[δ_{in} (N7N)](8)]	
22	21	-	R1[τ (C15C17)](17)+ τ (O1O25)(15)+ τ (O27H)(15)+R2[τ (N7N)(12)+oop(NH)(5)]+ τ (O25C)(10)+R3[τ (C26C34)](9)]	
12	12	-	τ (O25H40)(37)+ τ (O1O25)(25)+R2[oop(N7N)(16)+oop(NH)(10)]	

Table S4 Theoretical and experimental vibrational wavenumbers (in cm^{-1}) of NF and their assignments.

Scaled DFT		Potential Energy Distribution ($\geq 5\%$)		
B3LYP/cc-pvTZ	wB97X-D/cc-pvTZ	Raman	IR	
3503	3516	-	3287	R2[v(NH)](100)
3168	3156	-	3148	R1[v(CH)](96)
3137	3122	-	3109	R1[v(CH)](99)
2987	2993	-	3017	v(C13H)(99)
2964	2965	-	2948	R2[v _a (CH ₂)](100)
2927	2915	-	2916	R2[v _a (CH ₂)](99)
1809	1836	1980	1782	R2[v(C10=O)(63)+v(C11=O)(16)+ δ'_{ring} (6)+v(NC)(5)]
1771	1798	-	1744	R2[v(C11=O)(63)+v(C10=O)(16)+v(NC)(6)]
1603	1648	1608	1651	v(C13=N)(54)+R1[p(C13H)(15)+v(C13C14)(15)+v(CC)(6)]
1551	1601	1563	1605	R1[v(CC)(39)+v(N9=O4)(15)+v(NO)(12)+ ρ (NOO)(6)+ δ_{in} (CH)(8)]+v(C13=N)(7)]
1531	1570	-	1566	R1[v(N9=O4)(38)+v(NO)(30)+v(CC)(14)]+v(C13=N)(5)]
1475	1500	1509	1520	R1[v(CC)(42)+ δ_{ring} (13)+v(C13C14)(12)+v(NC)(5)]+v(C13=N)(5)]
1436	1413	1492	1489	R2[δ (CH ₂)](91)
1377	1401	1428	1427	R1[v(CC)(17)+v(OC)(28)+ δ_{in} (CH)(15)+v(CC)(7)+ δ_{in} (C13C14)(5)+ ρ (C13H)(5)]
1356	1374	1378	1381	R2[v(NC)(12)+ ω (CH ₂)(9)+v(NN)(6)]+R1[ρ (C13H)(11)+v(CC)(14)+ δ_{in} (CH)(5)]
1326	1357	-	1357	R2[δ_{in} (NH)(28)+v(NC)(16)+ ω (CH ₂)(5)+R1[v(NO)(8)+v(N9=O4)(6)+ ρ (C13H)(5)+v(NC)(5)]]
1318	1336	1348	1350	R1[ρ (C13H)(23)+v(NO)(17)+v(NC)(13)+v(N9=O4)(11)+ δ (NOO)(9)+v(CC)(9)]
1300	1310	1323	1342	R2[δ_{in} (NH)(28)+ ω (CH ₂)(17)+v(NC)(24)]
1279	1291	-	1279	R2[v(CC)(19)+ ω (CH ₂)(19)+v(NC)(25)+ δ_{in} (C11=O)(10)+ δ_{ring} (6)]+R1[ρ (C13H)](6)]
1246	1262	1258	1258	R1[v(CC)(28)+v(C13C14)(12)+v(OC)(11)+v(NO)(7)+ δ_{in} (CH)(7)+ ρ (C13H)(6)+v(N9=O4)(6)]

1225	1252	1247	1250	R2[v(NN)(20)+v(NC)(11)+δ(N8C13N7)(5)]+R1[v(OC)(25)+δ'ring(6)+δin(CH)(10)]
1204	1235	1235	1242	R2[v(NN)(23)+v(NC)(8)]+R1[v(OC)(28)+δ'ring(8)+v(NC)(6)]
1168	1188	1207	1211	R2[ω(CH ₂)(23)+v(NC)(49)]
1153	1147			R1[δ _{in} (CH)][49]+v(NC)(10)+δ'ring(8)+v(OC)(7)+v(C13C14)(5)]
1151	1132	1169		R2[γ(CH ₂)][96]
1077	1094	1121	1111	R2[v(NC)(60)+δ _{in} (C10=O)(10)+δ _{in} (NH)(10)+v(CC)(5)]
1004	991	1017	1018	R1[δ _{in} (CH)(63)+v(CC)(25)]
983	979			R2[ρ(CH ₂)(70)+oop(C11=O)(15)+τ(7)]
966	968	977		R1[v(OC)(52)+δ'ring(14)+v(C13C14)(8)]
951	957	962	964	R1[δ _{ring} (42)+v(OC)(18)+v(CC)(13)+v(NC)(8)]
898	894	902	926	R1[ω(C13H)(56)+oop(CH)(9)+τ(N8C13)(24)]
878	873		903	R1[oop(CH)(77)+τ(13)]
860	863		872	R2[v(CC)(54)+v(NC)(18)+δ _{in} (NH)(7)]
849	854	869		R1[δ'ring(17)+δ(C13C14N)(15)+R2[δ(N8C13N7)(17)+v(NC)(13)+δ'ring(8)+v(NN)(8)+v(NC)(6)]
801	810	809	833	R1[δ(NOO)(59)+δ'ring(17)+δring(7)+v(NO)(5)]
793	791		826	R1[oop(CH)(83)+τ'(6)]
760	764	783	779	R2[v(NC)(21)+δ'ring(8)+δ _{in} (C10=O)(5)+R1[δ'ring(15)+δ _{ring} (12)+v(C13C14)(7)+δ(NOO)(5)]
739	746		725	R1[ω(N9C)(68)+oop(C15N)(14)+τ'(8)+oop(CH)(5)]
725	734		725	R2[oop(C10=O)(70)+τ'(14)+τ(9)]
673	676	685		R1[τ'(36)+oop(C13C14)(34)+τ(24)]
667	670		687	R2[δ _{ring} (26)+v(NC)(16)+δ'ring(11)+δ _{in} (C10=O)(10)+δ _{in} (N7N)(10)+δ _{in} (C11=O)(5)+v(CC)(5)]
603	594		606	R2[oop(NH)(45)+oop(C11=O)(35)+τ(11)+ρ(CH ₂)(6)]
595	591	622		R2[δ _{in} (C11=O)(18)+δ'ring(16)+δ _{in} (C10=O)(14)+δ _{ring} (10)+δ _{in} (N7N)(10)+δ(N8C13N7)(6)+v(NC)(7)]
582	584			R2[δ'ring(23)+δ _{ring} (20)+v(NC)(14)]+R1[v(C13C14)][5]
581	583	606	571	R1[τ(52)+τ'(25)+oop(C15N)(17)]
542	534		548	R2[oop(NH)(43)+oop(C11=O)(33)+ρ(CH ₂)(12)+γ(CH ₂)(6)+τ(5)]
533	529	551		R1[ρ(NOO)(43)+δ _{in} (C15N)(21)+δ _{in} (C13C14)(10)+v(CC)(5)]
447	450	468	463	R2[δ(N8C13N7)(17)+δ _{in} (C10=O)(5)+δ _{in} (N7N)(5)]+R1[δ _{in} (C13C14)(14)+ρ(NOO)(12)+v(NC)(11)+δ _{ring} (6)+δ(C13C14N)(5)]
426	430	438	440	R1[v(NC)(19)+δ(NOO)(8)+δ _{in} (C13C14)(6)+δ(C13C14N)(6)+δ'ring(5)]+R2[δ _{in} (C11=O)(12)+δ _{in} (C10=O)(7)+v(NC)(5)+δ _{ring} (5)]
386	388	386	409	R2[δ _{in} (C11=O)(33)+δ _{in} (C10=O)(10)+v(NC)(6)+v(CC)(6)+v(NC)(9)]+R1[v(NC)(11)+δ _{ring} (6)]
373	373	381		τ(N8C13)(28)+R1[τ'(16)+τ(14)+oop(C13C14)(9)+ω(C13H)(8)+oop(C15N)(8)]+R2[oop(N7N)][8)
297	284			R2[τ(NN)(39)+τ(C13C14)(11)+oop(N7N)(23)+τ'(10)]+τ(N8C13)(6)
283	279	295	-	R2[δ _{in} (N7N)(18)+δ _{in} (C10=O)(17)+v(NC)(6)]+R1[δ _{in} (C15N)(13)+δ _{in} (C13C14)(12)+ρ(NOO)(7)+v(C13C14)(6)]
214	217	216	-	R1[δ _{in} (C15N)(33)+ρ(NOO)(18)+δ(C13C14N)(12)+v(C13C14)(6)+δ _{ring} (5)]
193	189	204	-	R1[oop(C15N)(50)+oop(C13C14)(7)]+τ(N8C13)(6)+R2[τ(NN)(14)+oop(N7N)(5)]
181	165	-	-	R2[τ'(76)+oop(N7N)(17)]
144	138	-	-	R2[τ(54)+oop(NH)(36)]
131	135	-	-	R2[δ _{in} (N7N)(30)+δ(N8C13N7)(20)]+R1[δ _{in} (C15N)(17)+δ _{in} (C13C14)(13)]
122	116	-	-	R2[τ(32)+oop(NH)(18)+oop(N7N)(5)]+R1[oop(C15N)(12)+oop(C13C14)(10)+τ(C15N)(10)]
77	70	-	-	R1[τ(C15N)(46)+τ(C13C14)(5)+R2[oop(N7N)(31)+τ'(5)+τ(NN)(5)]
49	50	-	-	R1[(δ(C13C14N)(35)+δ _{in} (C13C14)(29)+δ _{in} (C15N)(5)]+R2[δ(N8C13N7)(18)+δ _{in} (N7N)(6)]
44	36	-	-	R1[τ(C15N)(27)+τ(C13C14)(15)+oop(C13C14)(11)]+R2[oop(N7N)(24)+τ'(5)]
25	22	-	-	R1[τ(C13C14)][29]+R2[oop(N7N)(25)+τ(NN)(20)+τ(N8C13)(11)]

Table S5 Theoretical and experimental vibrational wavenumbers (in cm⁻¹) of 3-ABA and their assignments.

Scaled DFT		Potential Energy Distribution (≥5%)		
B3LYP/cc-pvTZ	WB97XD/cc-pvTZ	Raman	IR	
3626	3670	3559	R[v(OH)][100]	
3537	3548	3432	R[v _a (NH ₂)(99)]	
3441	3449	3300	R[v _s (NH ₂)(99)]	

3109	3110	3146	R[v(CH)](96)
3074	3068	3076	R[v(CH)](97)
3069	3065	3067	R[v(CH)](98)
3049	3045	3044	R[v(CH)](99)
1725	1757	1696	R[v(C4=O)(77)+v(C4C5)(10)]
1605	1617	1614	R[v(CC)(55)+δ(NH ₂)(9)+δ _a (8)+v(NC)(7)+δ _{in} (CH)(14)]
1590	1594	1611	R[δ(NH ₂)(27)+v(CC)(47)+δ' _a (7)+δ _{in} (CH)(7)]
1571	1588	1609	R[δ(NH ₂)(52)+v(CC)(31)]
1476	1480	1514	R[δ _{in} (CH)(45)+v(CC)(39)]
1444	1450	1482	R[v(CC)(38)+δ _{in} (CH)(23)+v(NC)(8)+δ _{in} (C4C5)(6)]
1327	1341	1381	R[v(O3C)(22)+v(C4C5)(20)+δ(O3HC)(19)+δ(C4OO)(13)]
1313	1302	1351	R[v(CC)(73)+δ _{in} (CH)(24)]
1297	1291	1327	R[δ _{in} (CH)(41)+v(NC)(12)+v(CC)(23)+ρ(NH ₂)(9)]
1254	1256	1286	R[v(NC)(26)+δ _{in} (CH)(31)+δ _{ring} (9)+v(CC)(10)+δ(O3HC)(5)]
1159	1161	1224	R[δ(O3HC)(33)+δ _{in} (CH)(26)+v(O3C)(15)+v(C4C5)(8)+v(CC)(9)]
1138	1146	1173	R[δ(O3HC)(20)+δ _{in} (CH)(46)+v(O3C)(12)+v(CC)(9)]
1100	1098	1144	R[δ _{in} (CH)(43)+ρ(NH ₂)(17)+v(CC)(19)+v(O3C)(7)]
1077	1082	1093	R[v(CC)(31)+δ _{in} (CH)(30)+v(O3C)(14)+v(C4C5)(6)]
1044	1047	1040	R[p(NH ₂)(47)+v(CC)(35)+δ _{in} (CH)(5)]
981	979	1005	R[δ _{ring} (64)+v(CC)(34)]
956	959	993	R[oop(CH)(85)+puck(10)]
897	902		R[v(CC)(25)+v(NC)(15)+v(C4C5)(11)+v(O3C)(10)+δ _a (9)+oop(CH)(5)+δ _{in} (CH)(5)]
893	895	912	R[oop(CH)(72)+oop(C4C5)(8)+t' _a (6)+puck(6)]
874	876	861	R[oop(CH)(67)+puck(15)+oop(CN)(10)]
795	794	824	R[ω(C4C)(24)+oop(CH)(47)+puck(13)+oop(C4C5)(12)]
745	748	797	R[ω(C4C)(27)+oop(CH)(42)+oop(CN)(13)+puck(7)]
719	720	726	R[δ' _a (21)+δ(C4OO)(16)+v(C4C5)(12)+δ _{ring} (11)+v(CC)(12)+v(O3C)(5)+v(NC)(5)]
678	677	667	R[puck(67)+oop(CH)(13)+oop(CN)(10)+oop(C4C5)(6)]
622	623	640	R[δ(C4OO)(49)+δ' _a (34)+δ(O3HC)(7)]
599	599	623	R[τ(O3C)(45)+oop(CN)(21)+τ _a (10)+oop(C4C5)(8)+ω(NC)(8)]
554	552	551	R[ω(NC)(53)+τ(O3C)(12)+δ _a (10)+v(NC)(6)+puck(5)]
536	535	549	R[δ _a (39)+ρ(C4C)(19)+v(NC)(17)]
501	498	519	R[τ _a (26)+oop(CN)(23)+ω(NC)(15)+τ(O3C)(9)+oop(C4C5)(6)+ω(C4C)(5)]
488	489	504	R[p(C4C)(23)+δ _{in} (C4C5)(18)+CN(13)+δ _a (12)+v(NC)(13)]
422	417	443	R[t' _a (68)+oop(C4C5)(14)+oop(CH)(5)]
385	385	410	R[δ _{in} (CN)(31)+δ' _a (26)+v(C4C5)(13)+p(C4C)(7)+δ(C4OO)(6)+δ _a (5)]
342	344	347	R[δ _{in} (CN)(35)+p(C4C)(19)+v(C4C5)(12)+δ(C4OO)(11)+v(CC)(8)]
304	297	321	R[τ(NC)](92)
219	219	-	R[τ _a (65)+puck(12)+oop(CH)(12)]
183	183	-	R[δ _{in} (C4C5)(62)+p(C4C)(17)+δ _{in} (CN)(10)]
150	146	-	R[oop(C4C5)(42)+t' _a (19)+oop(CH)(11)+ω(C4C)(9)+oop(CH)(6)]
58	54	-	R[τ(C4C5)(87)+τ _a (7)]

Table S6 (a) Calculated and observed ¹³C NMR chemical shifts (δ/ppm) of NF-3ABA, NF and 3ABA using wB97X-D/cc-pvTZ.

Atom	δ _{cal}	δ _{exp}	Atom	δ _{cal}	δ _{exp}
NF-3ABA					NF
C12	178.121	174.602	C11	168.796	168.9
C34	177.645	171.077	C15	159.744	151.9
C13	159.313	150.811	C14	155.744	151.9
C15	155.024	150.811	C10	153.666	151.9
C16	153.961	150.811	C13	129.32	133.1
C37	153.779	149.40	C17	117.869	118.2
C26	136.634	131.523	C16	116.652	118.2
C32	135.009	131.523	C12	48.1919	49.8
C17	128.662	131.523	3ABA		
C35	125.2	118.453	C4	171.356	172.399
C30	122.942	118.453	C7	154.204	136.859
C28	120.989	118.453	C 5	135.832	130.006
C21	117.762	115.075	C 9	135.066	126.873
C19	117.568	115.075	C10	124.881	126.873
C9	48.1229	47.950	C8	122.8	126.873
	-	-	C6	121.122	123.250

Table S6 (b) Calculated and observed ^{13}C NMR chemical shifts (δ /ppm) of NF-3ABA, NF and 3ABA using B3LYP/cc-pvTZ.

Atom	δ_{cal}	δ_{exp}	Atom	δ_{cal}	δ_{exp}
NF-3ABA			NF		
C34	178.37	174.602	C11	168.49	168.9
C12	177.921	171.077	C15	161.802	151.9
C13	161.601	150.811	C14	158.587	151.9
C15	158.621	150.811	C10	153.998	151.9
C37	154.304	150.811	C13	127.858	133.1
C16	154.179	149.40	C17	118.91	118.2
C26	136.49	131.523	C16	117.3	118.2
C32	133.945	131.523	C12	50.1449	49.8
C17	127.453	131.523	3ABA		
C35	124.825	118.453	C4	172.199	172.399
C30	123.009	118.453	C7	154.369	136.859
C28	120.64	118.453	C5	135.603	130.006
C19	118.501	115.075	C9	134.27	126.873
C21	117.492	115.075	C10	124.74	126.873
C9	49.7997	47.950	C8	122.536	126.873
			C6	120.709	123.250

Table S7 Results of correlation analysis for ^{13}C shifts (in ppm) with GIAO scheme.

Molecule	Functional	b	a	S_0	R^2	mae
NF-3ABA	B3LYP	0.95785±0.02	1.81088±3.25	2.76962	0.99616	4.46
	wB97X-D	0.96124±0.02	1.76111±2.62	2.23697	0.9975	3.87
NF	B3LYP	0.95248±0.04	4.63059±6.24	4.66822	0.99322	3.29
	wB97X-D	0.95091±0.03	5.68234±4.47	3.38138	0.99645	2.60

'a' is the intercept and b is the slope of the correlation line, ' R^2 ' is the square of correlation coefficient, ' S_0 ' is the standard deviation of the points from the correlation line, and 'mae' is the mean absolute error.

Table S8 Selected second order perturbation theory analysis of Fock matrix in NBO Basis of NF-3ABA using wB97X-D/cc-pvTZ level of theory.

Donor NBO (i)	ED(i)/e	Acceptor NBO (j)	ED(j)/e	E(2) ^a kcal/mol	E(j)-E(i) ^b	F(i,j) ^c a.u.
within unit 1						
$\pi\text{O6-N14}$	1.98470	$\pi(3)\text{O3}$	1.46697	10.34	0.23	0.083
		$\pi^*\text{O6-N14}$	0.61685	6.13	0.45	0.056
$\pi\text{N8-C17}$	1.93121	$\pi^*\text{C15-C19}$	0.30698	14.27	0.49	0.079
$\sigma\text{C9-C12}$	1.97456	$\sigma^*\text{N7-N8}$	0.02646	6.66	1.22	0.081
$\pi\text{C13-C21}$	1.80341	$\pi^*\text{O6-N14}$	0.61685	27.00	0.28	0.087
		$\pi^*\text{C15-C19}$	0.30698	23.15	0.43	0.091
$\sigma\text{C15-C17}$	1.97694	$\sigma^*\text{N7-N8}$	0.02646	6.14	1.27	0.079
$\pi\text{C15-C19}$	1.78384	$\pi^*\text{N8-C17}$	0.21481	21.73	0.41	0.084
		$\pi^*\text{C13-C21}$	0.29892	29.72	0.41	0.101
$\sigma\text{C17-H18}$	1.98049	$\sigma^*\text{O2-C15}$	0.02623	6.37	1.09	0.074
$\sigma\text{C19-C21}$	1.96940	$\sigma^*\text{C13-N14}$	0.11984	9.46	1.14	0.095
		$\sigma^*\text{C15-C17}$	0.03086	7.07	1.30	0.085
$n(1)\text{O1}$	1.96518	$\sigma^*\text{N5-C12}$	0.06726	6.63	1.33	0.085
$n(2)\text{O1}$	1.85055	$\sigma^*\text{N5-C12}$	0.06726	24.55	0.90	0.136
		$\sigma^*\text{C9-C12}$	0.07044	30.43	0.78	0.141
$n(2)\text{O2}$	1.69598	$\pi^*\text{C13-C21}$	0.29892	45.29	0.47	0.131
		$\pi^*\text{C15-C19}$	0.30698	46.48	0.48	0.133
$n(2)\text{O3}$	1.89149	$\sigma^*\text{O6-N14}$	0.05653	24.54	0.89	0.134
		$\sigma^*\text{C13-N14}$	0.11984	19.12	0.72	0.105
$n(3)\text{O3}$	1.46697	$\pi^*\text{O6-N14}$	0.61685	239.34	0.22	0.209
$n(2)\text{O4}$	1.82258	$\sigma^*\text{N5-C16}$	0.09367	38.50	0.78	0.158
		$\sigma^*\text{N7-C16}$	0.11084	40.99	0.77	0.162
$n(1)\text{N5}$	1.62062	$\pi^*\text{O1-C12}$	0.28629	101.02	0.37	0.177
		$\pi^*\text{O4-C16}$	0.28510	61.26	0.40	0.142

n(2)O6	1.88777	$\sigma^*O3-N14$	0.05834	25.25	0.88	0.135
		$\sigma^*C13-N14$	0.11984	22.25	0.72	0.113
n(1)N7	1.66646	$\pi^*O4-C16$	0.28510	66.38	0.41	0.149
		$\pi^*N8-C17$	0.21481	50.44	0.40	0.131
		$\sigma^*C9-H10$	0.02096	7.36	0.76	0.073
		$\sigma^*C9-H11$	0.02101	7.42	0.76	0.073
n(1)N8	1.90986	σ^*N7-C9	0.04285	16.91	0.85	0.108
		$\sigma^*C17-H18$	0.03332	13.13	0.91	0.099
$\pi^*O6-N14$	0.61685	$\pi^*C13-C21$	0.29892	22.41	0.14	0.075
from unit 1 to unit 2						
n(1)O1	1.96518	$\sigma^*O25-H40$	0.05126	6.53	1.31	0.083
n(2)O1	1.85055	$\sigma^*O25-H40$	0.05126	17.88	0.88	0.115
from unit 2 to unit 1						
n(1)O27	1.96208	$\sigma^*N5-H23$	0.04640	8.88	1.29	0.096
n(2)O27	1.86532	$\sigma^*N5-H23$	0.04640	12.04	0.86	0.093
within unit 2						
$\sigma O25-H40$	1.98560	$\sigma^*C26-C34$	0.06809	6.03	1.34	0.081
$\pi C26-C35$	1.65981	$\pi^*O27-C34$	0.27488	28.52	0.36	0.092
		$\pi^*C28-C37$	0.36933	29.45	0.39	0.096
		$\pi^*C30-C32$	0.33730	36.52	0.39	0.106
$\sigma C28-H29$	1.97408	$\sigma^*C26-C35$	0.02106	6.03	1.23	0.077
$\pi C28-C37$	1.61186	$\pi^*C26-C35$	0.39790	41.58	0.38	0.113
		$\pi^*C30-C32$	0.33730	32.04	0.39	0.101
$\pi C30-C32$	1.69067	$\pi^*C26-C35$	0.39790	31.34	0.39	0.101
		$\pi^*C28-C37$	0.36933	33.12	0.39	0.103
n(1)N24	1.85557	$\pi^*C28-C37$	0.36933	36.52	0.45	0.122
n(1)O25	1.97230	$\sigma^*O27-C34$	0.02314	11.02	1.36	0.109
n(2)O25	1.79319	$\pi^*O27-C34$	0.27488	79.36	0.46	0.173
n(2)O27	1.86532	$\sigma^*O25-C34$	0.07387	30.28	0.86	0.146
		$\sigma^*C26-C34$	0.06809	24.55	0.86	0.132
$\pi^*O27-C34$	0.27488	$\pi^*C26-C35$	0.39790	114.65	0.03	0.084

Table S9 Second order perturbation theory analysis of Fock matrix in NBO Basis of NF – 3-ABA acid using B3LYP/cc-pvTZ level of theory.

Donor NBO (i)	ED(i)/e	Acceptor NBO (j)	ED(j)/e	E (2) ^a K cal/mol	E(j)-E(i) ^b a.u.	F(i,j) ^c a.u.
within unit 1						
$\pi O6-N14$	1.98241	$n(3)O3$	1.47097	11.31	0.18	0.077
		$\pi^*O6-N14$	0.64423	7.58	0.32	0.053
		$\pi^*C13-C21$	0.31275	5.49	0.44	0.048
$\pi N8-C17$	1.91415	$\pi^*C15-C19$	0.32755	11.77	0.35	0.061
$\sigma C9-C12$	1.97380	σ^*N7-N8	0.02699	5.71	1.04	0.069
$\pi C13-C21$	1.77682	$\pi^*O6-N14$	0.64423	23.01	0.18	0.064
		$\pi^*C15-C19$	0.32755	14.72	0.30	0.061
$\sigma C15-C17$	1.97658	σ^*N7-N8	0.02699	5.22	1.10	0.068
$\pi C15-C19$	1.75257	$\pi^*N8-C17$	0.24757	18.25	0.28	0.063
		$\pi^*C13-C21$	0.31275	18.74	0.29	0.066
$\sigma C17-H18$	1.97906	$\sigma^*O2-C15$	0.02809	5.91	0.90	0.065
$\sigma C19-C21$	1.96995	$\sigma^*C13-N14$	0.11845	8.12	0.98	0.081
		$\sigma^*C15-C17$	0.02945	6.22	1.13	0.075
n(1)O1	1.96466	$\sigma^*N5-C12$	0.06843	5.56	1.15	0.072
n(2)O1	1.84785	$\sigma^*N5-C12$	0.06843	19.51	0.74	0.110
		$\sigma^*C9-C12$	0.07200	24.45	0.62	0.112
n(2)O2	1.69723	$\pi^*C13-C21$	0.31275	29.53	0.35	0.091
		$\pi^*C15-C19$	0.32755	30.35	0.35	0.093
n(2)O3	1.88959	$\sigma^*O6-N14$	0.05794	18.98	0.71	0.105
		$\sigma^*C13-N14$	0.11845	14.76	0.57	0.082
n(3)O3	1.47097	$\pi^*O6-N14$	0.64423	157.41	0.14	0.138
n(2)O4	1.81859	$\sigma^*N5-C16$	0.09490	29.82	0.62	0.124
		$\sigma^*N7-C16$	0.11407	32.40	0.61	0.128
n(1)N5	1.60670	$\pi^*O1-C12$	0.29579	73.47	0.26	0.125
		$\pi^*O4-C16$	0.29807	48.98	0.28	0.107
n(2)O6	1.88646	$\sigma^*O3-N14$	0.05999	19.55	0.70	0.106
		$\sigma^*C13-N14$	0.11845	17.04	0.56	0.088

n(1)N7	1.64349	π^* O4-C16 π^* N8-C17 σ^* C9-H10 σ^* C9-H11	0.29807 0.24757 0.02143 0.02143	49.59 38.66 5.82 5.83	0.29 0.27 0.62 0.62	0.109 0.095 0.059 0.059
n(1)N8	1.90422	σ^* N7-C9 σ^* C17-H18	0.04745 0.03522	14.42 10.49	0.68 0.75	0.089 0.080
π^* O6-N14	0.64423	π^* C13-C21	0.31275	21.52	0.12	0.065
π^* N8-C17	0.24757	π^* C15-C19	0.32755	142.31	0.01	0.071
from unit 1 to unit 2						
n(1)O1	1.96466	σ^* O25-H40	0.05142	5.18	1.13	0.069
n(2)O1	1.84785	σ^* O25-H40	0.05142	14.19	0.72	0.092
from unit 2 to unit 1						
n(1)O27	1.96133	σ^* N5-H23	0.04712	7.17	1.12	0.080
n(2)O27	1.86241	σ^* N5-H23	0.04712	9.58	0.70	0.075
within unit 2						
σ O25-H40	1.98555	σ^* C26-C34	0.06766	5.10	1.16	0.070
π C26-C35	1.65131	π^* O27-C34 π^* C28-C37 π^* C30-C32	0.28987 0.37247 0.33688	24.79 18.70 21.28	0.24 0.28 0.28	0.070 0.065 0.069
σ C28-H29	1.97591	σ^* C26-C35	0.02124	5.05	1.06	0.065
π C28-C37	1.61358	π^* C26-C35 π^* C30-C32	0.40188 0.33688	22.86 18.00	0.28 0.28	0.072 0.064
π C30-C32	1.69000	π^* C26-C35 π^* C28-C37	0.40188 0.37247	18.35 20.81	0.28 0.28	0.066 0.069
σ C35-H36	1.97472	σ^* C26-C28	0.01796	5.26	1.05	0.067
n(1)N24	1.84469	π^* C28-C37	0.37247	27.12	0.33	0.089
n(1)O25	1.97212	σ^* O27-C34	0.02330	9.08	1.17	0.092
n(2)O25	1.79134	π^* O27-C34	0.28987	56.27	0.32	0.122
n(2)O27	1.86241	σ^* O25-C34 σ^* C26-C34	0.07677 0.06766	24.20 19.76	0.68 0.70	0.116 0.107
π^* O27-C34	0.28987	π^* C26-C35	0.40188	62.81	0.04	0.075

^aE(2) means energy of hyper conjugative interaction (stabilization energy), ^bEnergy difference between donor (i) and acceptor (j) NBO orbitals, ^cF(i,j) is the Fock matrix element between i and j NBO orbitals.

Table S10 Selected reactivity descriptors as Fukui functions (f_k^+ , f_k^-), local softnesses (s_k^+ , s_k^-), local electrophilicity indices (ω_k^+ , ω_k^-) for NF – 3-ABA acid using wb97X-D/cc-pvTZ.

Sites	$f_k^+(e)$	$\omega_k^+(ev)$.	$s_k^+(ev^{-1})$	$f_k^-(e)$	$\omega_k^-(ev)$.	$s_k^-(ev^{-1})$	f_k^+/f_k^-	f_k^-/f_k^+
From Hirshfeld atomic charges								
O1	0.04371	0.12828	0.0063	0.03027	0.08884	0.00437	1.443894	0.692572
O2	0.02331	0.06839	0.00336	0.0397	0.11651	0.00572	0.587028	1.703497
O3	0.06084	0.17855	0.00877	0.1322	0.38797	0.01906	0.460222	2.172863
O4	0.06766	0.19855	0.00976	0.03654	0.10722	0.00527	1.851763	0.540026
N5	0.02175	0.06382	0.00314	0.01207	0.03543	0.00174	1.801441	0.555111
O6	0.05153	0.15123	0.00743	0.1272	0.3733	0.01834	0.405132	2.46833
N7	0.09185	0.26956	0.01324	0.01662	0.04878	0.0024	5.525597	0.180976
N8	0.06127	0.17981	0.00883	0.0805	0.23625	0.01161	0.761084	1.313916
C9	0.01669	0.04897	0.00241	0.00821	0.0241	0.00118	2.031905	0.492149
C12	0.01058	0.03104	0.00153	0.01044	0.03065	0.00151	1.012735	0.987426
C13	0.08536	0.25051	0.01231	0.04099	0.12028	0.00591	2.082689	0.480149
N14	0.01272	0.03732	0.00183	0.07236	0.21235	0.01043	0.175751	5.689864
C15	0.04693	0.13774	0.00677	0.05987	0.1757	0.00863	0.783941	1.275606
C16	0.02353	0.06905	0.00339	0.02403	0.07051	0.00346	0.97919	1.021252
C17	0.06122	0.17968	0.00883	0.05015	0.14717	0.00723	1.220915	0.819058
C19	0.08839	0.2594	0.01274	0.04709	0.13819	0.00679	1.877161	0.532719
C21	0.04638	0.13612	0.00669	0.06503	0.19085	0.00938	0.713218	1.402096
N24	0.00414	0.01214	0.0006	0.00305	0.00896	0.00044	1.354406	0.738331
O25	0.0049	0.01437	0.00071	0.00368	0.01079	0.00053	1.331702	0.750919

C26	-0.0046	-0.0134	-0.0007	-0.0039	-0.0113	-0.0006	1.183965	0.84462
O27	-0.0097	-0.0285	-0.0014	-0.0085	-0.0249	-0.0012	1.148135	0.870978
C28	-0.0007	-0.002	-1E-04	-0.001	-0.0028	-0.0001	0.708247	1.411936
C30	0.00924	0.0271	0.00133	0.00715	0.02097	0.00103	1.292512	0.773687
C32	0.00612	0.01797	0.00088	0.00495	0.01454	0.00071	1.236422	0.808785
C34	0.00214	0.00627	0.00031	0.00183	0.00536	0.00026	1.170318	0.854469
C35	0.00193	0.00568	0.00028	0.00133	0.00391	0.00019	1.451952	0.688728
C37	0.00363	0.01064	0.00052	0.00271	0.00794	0.00039	1.340481	0.746001