Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Molecular electrostatic potential dependant selectivity of hydrogen bonding

Christer B Aakeröy*[a], Tharanga K Wijethunga[a] and John Desper[a]

Department of Chemistry, Kansas State University, Manhattan, KS 66506

aakeroy@ksu.edu

Supplementary Information

Table of content

Experimental – synthesis of acceptors

Synthesis of 1,1'-bis(pyridin-4-ylmethyl)-2,2'-biimidazole, A1

2,2'-Biimidazole (0.27g, 2 mmol) and NaOH (0.32 g, 8 mmol) were placed in a 100mL round bottomed flask with 20 mL of acetonitrile. The mixture was stirred at room temperature for two hours. 4-Picolyl chloride hydrochloride (0.65 g, 4 mmol) in acetonitrile (20 mL) was added to the mixture and refluxed for 24 hours at 50^0C – 60^0C. The reaction was monitored with TLC and after completion the solvent was removed by rotary evaporation. The residue was dissolved in water (50 mL) and extracted with methylene chloride (30 mL x 3). Organic layers were combined, dried over anhydrous $MgSO_4$ and rotary evaporated to obtain the dark brown color powder as the product. Yield: 0.35 g (56%); mp 157-160^0C (lit. 157-160^0C)[1]; ^{1}H NMR (δ_H; $CDCl_3$, 400MHz):8.49 (d, 4H), 7.11 (d, 2H), 6.94 (d, 2H), 6.91 (d, 4H), 5.84 (s, 4H).

Synthesis of 1,1'-bis(pyridin-3-ylmethyl)-2,2'-biimidazole, A2

2,2'-Biimidazole (0.27g, 2 mmol) and NaOH (0.32 g, 8 mmol) were placed in a 100mL round bottomed flask with 20 mL of acetonitrile. The mixture was stirred at room temperature for two hours. 3-Picolyl chloride hydrochloride (0.65 g, 4 mmol) in acetonitrile (20 mL) was added to the mixture and refluxed for 24 hours at 50^0C – 60^0C. The reaction was monitored with TLC and upon completion the solvent was removed by rotary evaporation. The residue was dissolved in water (50 mL) and extracted with methylene chloride (30 mL x 3). Organic layers were combined, dried over anhydrous $MgSO_4$ and rotary evaporated to obtain the brown color powder as the product. Yield: 0.45 g (71%); mp 112-115^0C (lit. 112-115^0C)1; ^{1}H NMR (δ_H; $CDCl_3$, 400MHz):8.46 (d, 2H), 8.45 (s, 2H), 7.39 (d, 2H), 7.17 (m, 2H), 7.11 (d, 2H), 6.95 (d, 2H), 5.78 (s, 4H).

Synthesis of 1,1'-bis(pyridin-2-ylmethyl)-2,2'-biimidazole, A3

2,2'-Biimidazole (0.27g, 2 mmol) and NaOH (0.32 g, 8 mmol) were placed in a 100mL round bottomed flask with 20 mL of acetonitrile. The mixture was stirred at room temperature for two hours. 2-Picolyl chloride hydrochloride (0.65 g, 4 mmol) in acetonitrile (20 mL) was added to the mixture and refluxed for 24 hours at 50^0C – 60^0C. The reaction was monitored with TLC and upon completion the solvent was removed by rotary evaporation. The residue was dissolved in water (50 mL) and extracted with methylene chloride (30 mL x 3). Organic layers were combined, dried over anhydrous $MgSO_4$ and rotary evaporated to obtain the pale brown color powder as the product. Yield: 0.25 g (40%); mp 180-183^0C (lit. 180-183^0C)1; ^{1}H NMR (δ_H;$CDCl_3$, 400MHz): 8.53 (d, 2H), 7.53 (t, 2H), 7.15 (t, 2H), 7.12 (s, 2H), 7.07 (s, 2H), 7.05 (d, 2H), 5.87 (s, 4H).

Synthesis of 1,1'-dibenzyl-2,2'-biimidazole, A4

2,2'-Biimidazole (0.33g, 2.48 mmol) and NaOH (0.39 g, 9.92 mmol) were placed in a 100mL round bottomed flask with 20 mL of acetonitrile. The mixture was stirred at room temperature

for two hours. Benzyl bromide (0.63 g, 5 mmol) in acetonitrile (20 mL) was added to the mixture and refluxed for 24 hours at 50^0C – 60^0C. The reaction was monitored with TLC and after completion the solvent was removed by rotary evaporation. The residue was dissolved in water (50 mL) and extracted with methylene chloride (30 mL x 3). Organic layers were combined, dried over anhydrous $MgSO_4$ and rotary evaporated to obtain the yellow color powder as the product. Yield: 0.69 g (89%); mp 144-146^{0}C (lit. 144-146^{0}C)1; ^{1}H NMR (δ_H; $CDCl_3$, 400MHz):5.70 (s, 4H), 6.93 (d, 2H), 7.03 (m, 4H), 7.12 (d, 2H), 7.24 (m, 6H).

NMR spectra

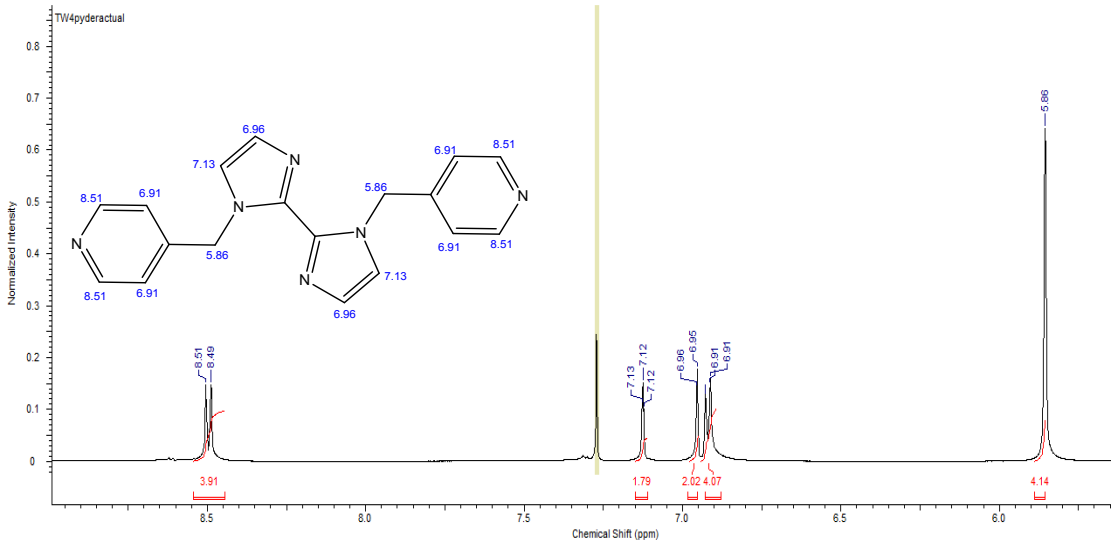


Figure S1: NMR spectrum of 1,1'-bis(pyridin-4-ylmethyl)-2,2'-biimidazole, **A1**

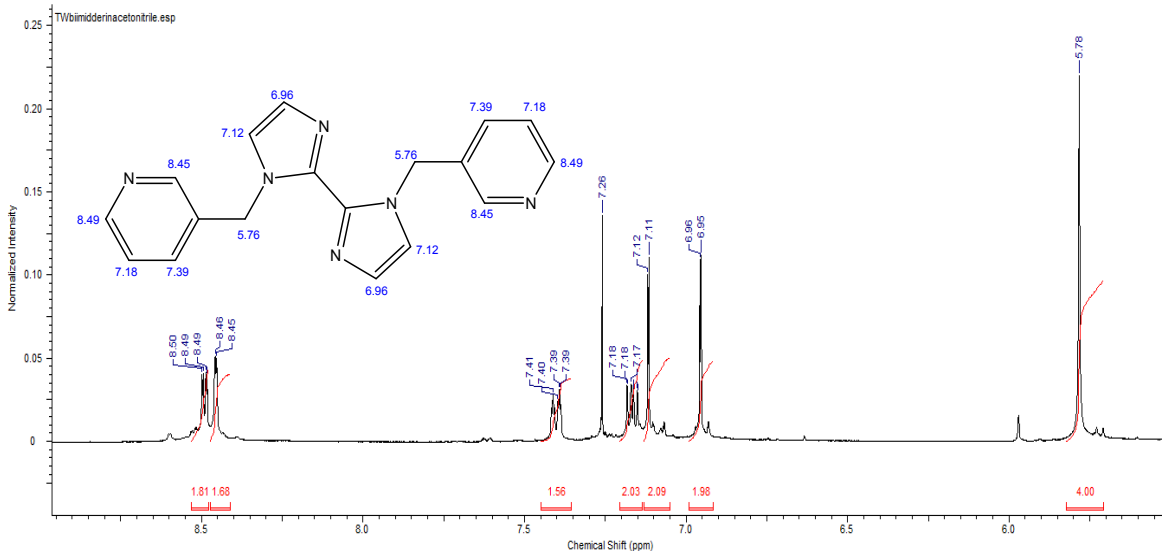


Figure S2: NMR spectrum of 1,1'-bis(pyridin-3-ylmethyl)-2,2'-biimidazole, **A2**

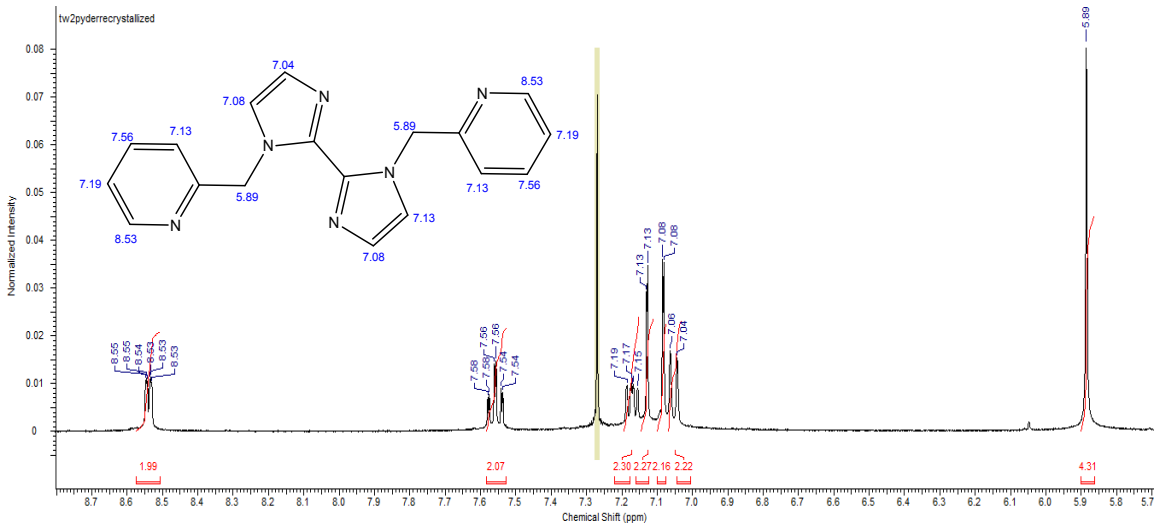


Figure S3: NMR spectrum of 1,1'-bis(pyridin-2-ylmethyl)-2,2'-biimidazole, **A3**

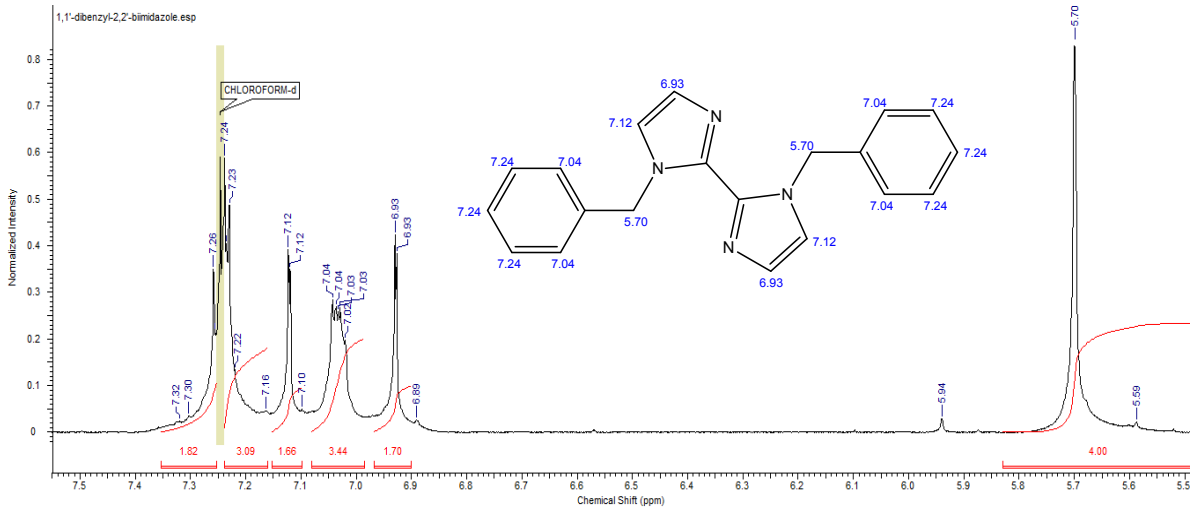


Figure S4: NMR spectrum of 1,1'-dibenzyl-2,2'-biimidazole, **A4**

IR data

Table S1: IR data

Mixture	Carbonyl stretch (cm^{-1})		O-H---N starches (cm^{-1})	Co-crystal?
	Di-acid	Ground mixture		
A1:Suc	1685	1692	2532,1870	Y
A1:Adi	1685	1687	2600,1900	Y
A1:Sub	1685	1688	2500,1906	Y
A1:Seb	1686	1689	2497,1896	Y
A1:Dod	1686	1689	2541,1914	Y
A1:Mal	1696	1692	2586,1900	Y
A1:Glu	1683	1694	2590,1900	Y
A1:Pim	1685	1688	2450,1900	Y
A1:Aze	1689	1688	2500,1940	Y
A2:Suc	1685	1686	2532,1900	Y
A2:Adi	1685	1688	2488,1915	Y
A2:Sub	1685	1689	2495,1900	Y
A2:Seb	1686	1686	2499,1924	Y
A2:Dod	1686	1686	2495,1922	Y
A2:Mal	1696	1716	2561,1964	Y
A2:Glu	1683	1701	2588,1941	Y
A2:Pim	1685	1690	2530,1941	Y
A2:Aze	1689	1690	2528,1924	Y
A3:Suc	1685	1695	2503,1943	Y
A3:Adi	1685	1691	2528,1895	Y
A3:Sub	1685	1690	2495,1850	Y
A3:Seb	1686	1701	2520,1888	Y
A3:Dod	1686	1698	2495,1865	Y
A3:Mal	1696	1708	2582,1980	Y
A3:Glu	1683	1689	2550,1957	Y
A3:Pim	1685	1689	2511,1942	Y
A3:Aze	1689	n/a	n/a	N
A4:Suc	1685	1681	n/a	N
A4:Adi	1685	1686	n/a	N
A4:Sub	1685	1686	n/a	N
A4:Seb	1686	1689	n/a	N
A4:Dod	1686	1686	n/a	N
A4:Mal	1696	1701	2586,1970	Y
A4:Glu	1683	1685	2600,1900	Y
A4:Pim	1685	1687	n/a	N
A4:Aze	1689	1686	n/a	N

Crystallographic data

Datasets were collected on a Bruker Kappa APEX II system using CuKα radiation (01_A1:Dod, 02_A1:Suc, 06_A3:Seb, 07_A3:Sub, 08_A3:Dod, 09_A1:Seb, 10_A4:Mal) or a on a Bruker APEX II system using MoKα radiation (03_A3:Adi, 04_A1:Sub, 05_A1:Adi, 11_A1:Glu, 12_A1:Mal, 13_A3:Pim). Data were collected using APEX2 software.[(a)] Initial cell constants were found by small widely separated "matrix" runs. Data collection strategies were determined using COSMO.[(b)] Scan speed and scan widths were chosen based on scattering power and peak rocking curves. All datasets were collected at -153 °C using an Oxford Croystream low-temperature device.

Unit cell constants and orientation matrix were improved by least-squares refinement of reflections thresholded from the entire dataset. Integration was performed with SAINT,[(c)] using this improved unit cell as a starting point. Precise unit cell constants were calculated in SAINT from the final merged dataset. Lorenz and polarization corrections were applied. Multi-scan absorption corrections were performed with SADABS[(d)].

Data were reduced with SHELXTL.[(e)] The structures were solved in all cases by direct methods without incident. Except as noted, hydrogen atoms were located in idealized positions and were treated with a riding model. All non-hydrogen atoms were assigned anisotropic thermal parameters. Refinements continued to convergence, using the recommended weighting schemes.

01 A1:Dod Both the amine and the diacid sit on crystallographic inversion centers. Coordinates of the unique carboxylic acid proton H31 were allowed to refine.

02 A1:Suc Both the amine and the diacid sit on crystallographic inversion centers. Coordinates of the unique carboxylic acid proton H31 were allowed to refine.

03 A3:Adi Both the amine and the diacid sit on crystallographic inversion centers. Coordinates of the unique carboxylic acid proton H31 were allowed to refine.

04 A1:Sub Both the amine and the diacid sit on crystallographic inversion centers. Coordinates of the unique carboxylic acid proton H31 were allowed to refine.

05 A1:Adi Both the amine and the diacid sit on crystallographic inversion centers. Coordinates of the unique carboxylic acid proton H31 were allowed to refine.

06 A3:Seb Both the amine and the diacid sit on crystallographic inversion centers. Coordinates of the unique carboxylic acid proton H31 were allowed to refine.

07 A3:Sub Both the amine and the diacid sit on crystallographic inversion centers. Coordinates of the unique carboxylic acid proton H31 were allowed to refine.

08 A3:Dod Both the amine and the diacid sit on crystallographic inversion centers. Coordinates of the unique carboxylic acid proton H31 were allowed to refine.

09 A1:Seb The crystal was a nonmerohedral twin and the data were processed with TWINABS[(f)]. Both the amine and the diacid sit on crystallographic inversion centers. Coordinates of the unique carboxylic acid proton H31 were allowed to refine.

10 A4:Mal Both the amine and the diacid sit on general positions. Coordinates of the carboxylic acid protons H51 and H53 were allowed to refine.

11 A1:Glu The amine sits on crystallographic inversion centers; the diacid sits on a general position, giving 1 : 2 amine : diacid stoichiometry. Coordinates of the carboxylic acid protons H31 and H35 were allowed to refine.

12 A1:Mal Both the amine and the diacid sit on general positions. Two orientations for one pyridine moiety (N41-C46) and one acid moiety (C53 / O53 / O54), representing different orientations of the –COOH group, were located in the difference map. Relative populations were allowed to refine. Thermal parameters were pairwise constrained using EADP commands. Geometry of the pyridine rings were restrained using the SAME command. All hydrogen atoms were included in calculated positions and were allowed to ride.

13 A3:Pim The amine sits on crystallographic inversion centers; the diacid sits on a general position, giving 1 : 2 amine : diacid stoichiometry. Coordinates of the carboxylic acid protons H31 and H37 were allowed to refine.

(a) APEXII v2009. 5-1, © 2009, Bruker Analytical X-ray Systems, Madison, WI.

(b) COSMO v1. 60, © 1999 - 2009, Bruker Analytical X-ray Systems, Madison, WI.

(c) SAINT v7. 60a, © 1997 - 2008, Bruker Analytical X-ray Systems, Madison, WI.

(d) SADABS v2008/1, © 2008, Bruker Analytical X-ray Systems, Madison, WI.

(e) SHELXTL v2008/4, © 2008, Bruker Analytical X-ray Systems, Madison, WI.

(f) TWINABS v2012/1, © 2012, Bruker Analytical X-ray Systems, Madison, WI.

Table S2: Crystallographic data

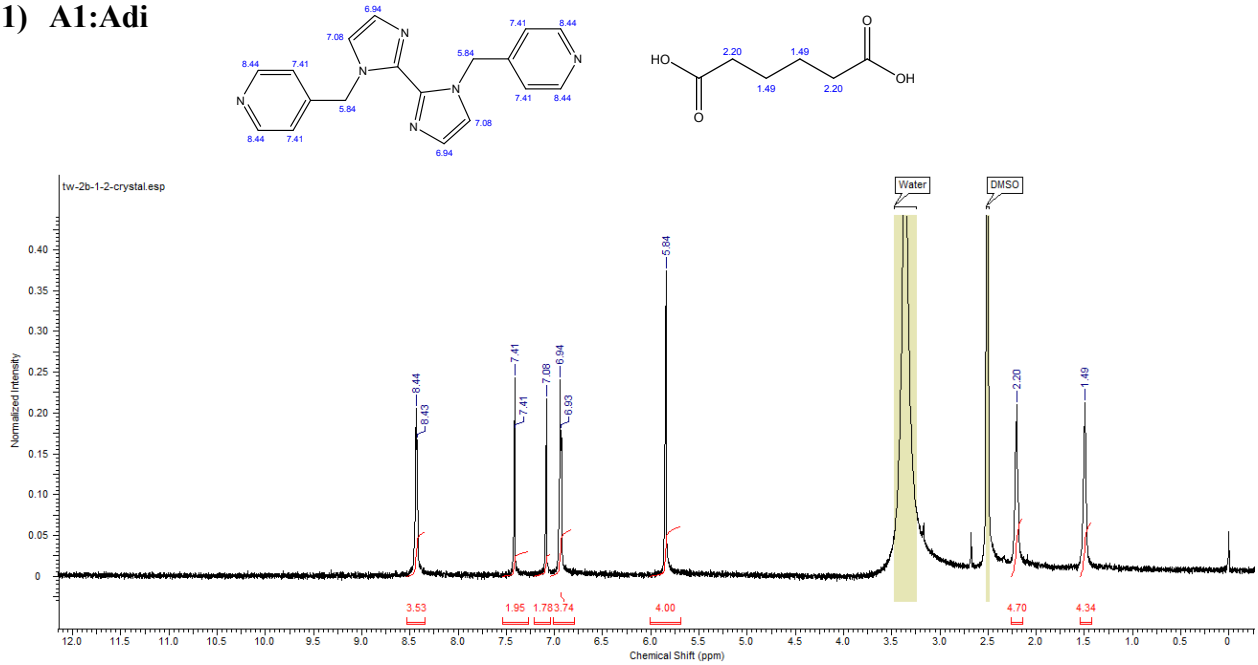
Code	A1:Dod	A1:Suc	A3:Adi	A1:Sub	A1:Adi	A3:Seb	A3:Sub
Systematic name	1,1'-di[(4-pyridyl)-methyl]-2,2'-biimidazole , HOOC-$(CH_2)_{10}$-COOH	1,1'-di[(4-pyridyl)-methyl]-2,2'-biimidazole , HOOC-$(CH_2)_2$-COOH	1,1'-di[(2-pyridyl)-methyl]-2,2'-biimidazole , HOOC-$(CH_2)_4$-COOH	1,1'-di[(4-pyridyl)-methyl]-2,2'-biimidazole , HOOC-$(CH_2)_6$-COOH	1,1'-di[(4-pyridyl)-methyl]-2,2'-biimidazole , HOOC-$(CH_2)_4$-COOH	1,1'-di[(2-pyridyl)-methyl]-2,2'-biimidazole , HOOC-$(CH_2)_8$-COOH	1,1'-di[(2-pyridyl)-methyl]-2,2'-biimidazole , HOOC-$(CH_2)_6$-COOH
Formula moiety	$(C_{18}H_{16}N_6)$ $(C_{12}H_{22}O_4)$	$(C_{18}H_{16}N_6)$ $(C_4H_6O_4)$	$(C_{18}H_{16}N_6)$ $(C_6H_{10}O_4)$	$(C_{18}H_{16}N_6)$ $(C_8H_{14}O_4)$	$(C_{18}H_{16}N_6)$ $(C_6H_{10}O_4)$	$(C_{18}H_{16}N_6)$ $(C_{10}H_{18}O_4)$	$(C_{18}H_{16}N_6)$ $(C_8H_{14}O_4)$
Empirical formula	$C_{30}H_{38}N_6O_4$	$C_{22}H_{22}N_6O_4$	$C_{24}H_{26}N_6O_4$	$C_{26}H_{30}N_6O_4$	$C_{24}H_{26}N_6O_4$	$C_{28}H_{34}N_6O_4$	$C_{26}H_{30}N_6O_4$
Molecular weight	546.66	434.46	462.51	490.56	462.51	518.61	490.56
Color, Habit	bronze prism	colorless prism	colourless plate	orange plate	bronze plate	colourless prism	colourless prism
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group, Z	P-1, 1	P-1, 1	P-1, 1	P-1, 1	P-1, 1	P-1, 1	P-1, 1
a, Å^3	5.6047(8)	4.8468(8)	5.0121(5)	5.6196(11)	5.5146(11)	5.2731(8)	5.1024(10)
b, Å^3	6.8589(10)	9.2594(16)	7.8964(8)	6.7825(13)	6.8100(14)	7.8464(11)	8.0128(15)
c, Å^3	18.879(3)	12.245(2)	15.1589(16)	16.078(3)	15.254(3)	17.163(3)	16.497(3)
α, °	97.644(5)	69.536(7)	78.403(4)	87.236(4)	79.288(6)	81.964(6)	99.940(9)
β, °	91.164(5)	89.567(7)	88.333(4)	82.669(4)	85.259(6)	88.938(6)	93.967(10)
γ, °	104.659(5)	85.993(7)	72.636(3)	75.451(4)	75.952(5)	72.499(6)	108.231(8)
Volume, Å^3	694.80(18)	513.50(15)	560.62(10)	588.22(19)	545.60(19)	670.38(17)	625.5(2)
Density, g/cm^3	1.307	1.405	1.370	1.385	1.408	1.285	1.302
Temperatur, °K	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
Crystal size, min x mid x max	0.22 x 0.28 x 0.32	0.236 x 0.239 x 0.543	0.10 x 0.26 x 0.36	0.12 x 0.30 x 0.36	0.10 x 0.32 x 0.38	0.14 x 0.26 x 0.32	0.20 x 0.28 x 0.32
X-ray wavelength, Å	1.54178	1.54178	0.71073	0.71073	0.71073	1.54178	1.54178
μ, mm^{-1}	0.716	0.827	0.096	0.096	0.099	0.715	0.737
Absorption corr	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Trans min / max	0.8032 / 0.8584	0.645 / 0.753	0.9662 / 0.9904	0.9662 / 0.9886	0.9634 / 0.9902	0.8035 / 0.9065	0.7983 / 0.8666
θ_{min}, °	2.36	3.85	1.37	3.10	3.13	5.21	2.74
θ_{max}, °	68.24	67.98	32.01	32.75	32.02	67.90	66.73
Reflections							
collected	9252	6345	12569	10698	7187	11734	9109
independent	2438	1799	3713	3929	3167	2326	2111
observed	2269	1660	3150	3433	2613	2145	1891
Threshold expression	>2σ (I)	>2σ (I)	>2σ (I)	>2σ (I)	>2σ (I)	>2σ (I)	>2σ (I)
R1 (observed)	0.0523	0.0507	0.0434	0.0458	0.0467	0.0327	0.0496
***w*R$_2$ (all)**	0.1716	0.1400	0.1317	0.1329	0.1358	0.0850	0.1580
Goodness of fit (all)	1.472	1.084	1.116	1.014	1.099	1.060	1.176
Δρ max / min	0.311 / -0.242	0.355 / -0.431	0.325 / -0.289	0.459 / -0.308	0.414 / -0.223	0.167 / -0.185	0.225 / -0.274
2θ limit	67.50	67.50	30.00	30.00	27.50	67.50	66.73
Completeness to 2θ limit	0.968	0.969	0.994	0.971	0.973	0.957	0.952

Code	A3:Dod	A1:Seb	A4:Mal	A1:Glu	A1:Mal	A3:Pim
Systematic name	1,1'-di[(2-pyridyl)-methyl]-2,2'-biimidazole, HOOC-$(CH_2)_{10}$-COOH	1,1'-di[(3-pyridyl)methyl]-2,2'-biimidazole, HOOCH-$(CH_2)_8$-COOH	1,1'-di[(phenyl)-methyl]-2,2'-biimidazole, HOOC-CH_2-COOH	1,1'-di[(4-pyridyl)-methyl]-2,2'-biimidazole, (HOOC-$(CH_2)_3$-$COOH)_2$	1,1'-di[(4-pyridyl)-methyl]-2,2'-biimidazole, HOOC-(CH_2)-COOH	1,1'-di[(2-pyridyl)methyl]-2,2'-biimidazole, [HOOC-$(CH_2)_5$-$COOH]_2$
Formula moiety	$(C_{18}H_{16}N_6)$ $(C_{12}H_{22}O_4)$	$(C_{18}H_{16}N_6)$ $(C_{10}H_{18}O_4)$	$(C_{20}H_{18}N_4)$ $(C_3H_4O_4)$	$(C_{18}H_{16}N_6)$ $(C_5H_8O_4)_2$	$(C_{18}H_{16}N_6)$ $(C_3H_4O_4)$	$(C_{18}H_{16}N_6)$ $(C_7H_{12}O_4)_2$
Empirical formula	$C_{30}H_{38}N_6O_4$	$C_{28}H_{34}N_6O_4$	$C_{23}H_{22}N_4O_4$	$C_{28}H_{32}N_6O_8$	$C_{21}H_{20}N_6O_4$	$C_{32}H_{40}N_6O_8$
Molecular weight	546.66	518.61	418.45	580.60	420.43	636.70
Color, Habit	colourless prism	orange plate	yellow prism	bronze prism	colourless needle	colourless plate
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group, Z	P-1, 1	P-1, 1	P2(1)/n, 4	P-1, 1	P2(1)/c, 4	P-1, 1
a, Å^3	5.2955(8)	5.6320(7)	11.4449(17)	7.6142(11)	14.797(3)	4.9161(10)
b, Å^3	7.8185(13)	6.8450(8)	8.9002(15)	8.6608(13)	4.5097(7)	8.0077(16)
c, Å^3	18.424(3)	17.748(2)	21.338(3)	11.0348(16)	29.886(5)	20.828(4)
α, °	85.042(10)	93.630(7)	90.00	102.357(5)	90.00	87.266(11)
β, °	83.543(10)	98.988(7)	94.855(10)	105.996(5)	104.056(8)	88.665(10)
γ, °	71.912(10)	104.670(7)	90.00	93.866(5)	90.00	72.608(9)
Volume, Å^3	719.4(2)	649.97(13)	2165.7(6)	677.09(17)	1934.6(6)	781.5(3)
Density, g/cm^3	1.262	1.325	1.283	1.424	1.444	1.353
Temperature, °K	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
Crystal size, min x mid x max	0.16 x 0.24 x 0.28	0.10 x 0.26 x 0.34	0.14 x 0.18 x 0.24	0.18 x 0.36 x 0.44	0.08 x 0.10 x 0.36	0.08 x 0.18 x 0.38
X-ray wavelength, Å	1.54178	1.54178	1.54178	0.71073	0.71073	0.71073
μ, mm^{-1}	0.692	0.737	0.737	0.106	0.104	0.099
Absorption corr	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
Trans min / max	0.8299 / 0.8974	0.7876 / 0.9299	0.8430 / 0.9039	0.9547 / 0.9811	0.9636 / 0.9918	0.9635 / 0.9922
θ_{min}, °	2.42	2.54	4.16	1.98	1.42	0.98
θ_{max}, °	68.34	68.93	67.60	32.68	30.08	31.05
Reflections						
collected	11812	4606	10824	17551	20190	21382
independent	2493	4606	3641	4555	5562	4657
observed	2079	3942	2941	4015	2992	2306
Threshold expression	>2σ (I)	>2σ (I)	>2σ (I)	>2σ (I)	>2σ (I)	>2σ (I)
R1 (observed)	0.0446	0.0550	0.0417	0.0422	0.0652	0.0996
***w*R$_2$ (all)**	0.1335	0.1976	0.1494	0.1231	0.1937	0.2647
Goodness of fit (all)	1.100	1.544	1.102	0.973	0.997	1.286
Δρ max / min	0.226 / -0.329	0.322 / -0.451	0.352 / -0.367	0.430 / -0.279	0.271 / -0.418	0.455 / -0.418
2θ limit	67.50	68.93	66.00	30.00	30.00	30.00
Completeness to 2θ limit	0.954	0.974	0.952	0.994	0.981	0.979

Stoichiometric studies – NMR data

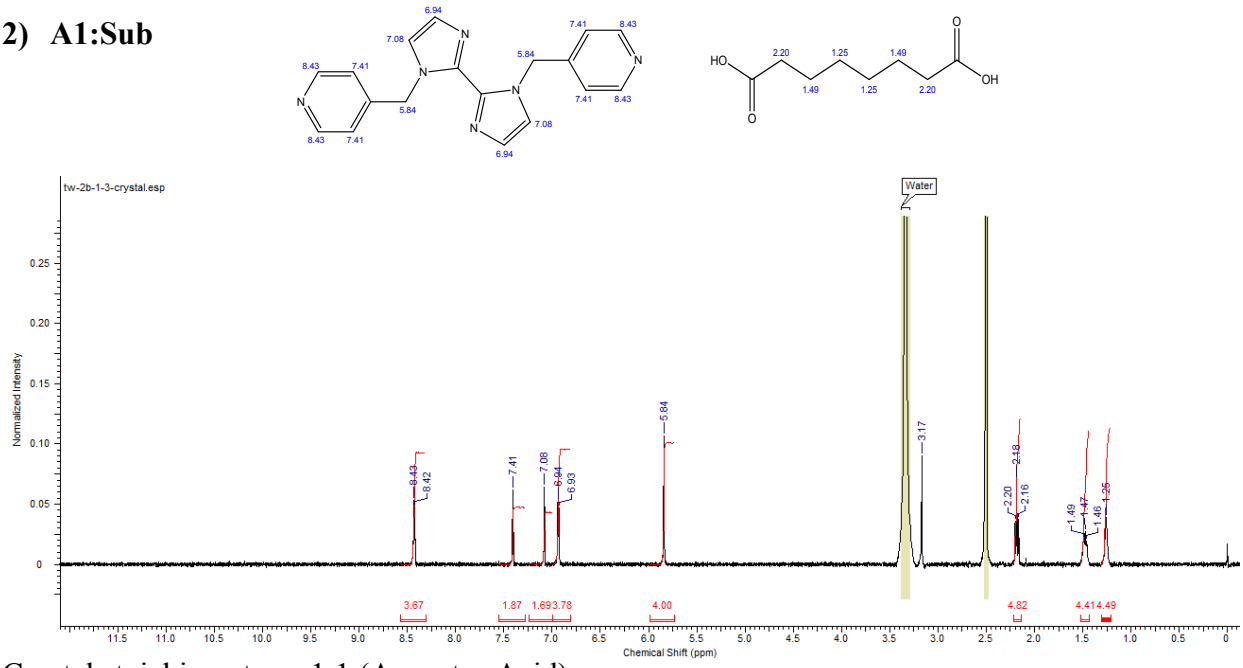
Mixed Stoichiometry 1:1 (Acceptor:Acid)

1) A1:Adi



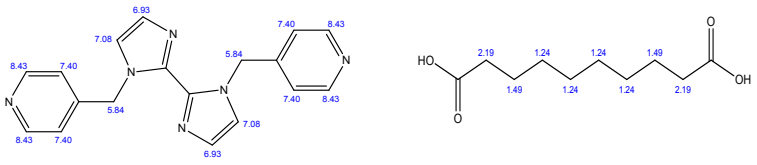
Crystal stoichiometry – 1:1 (Acceptor:Acid)

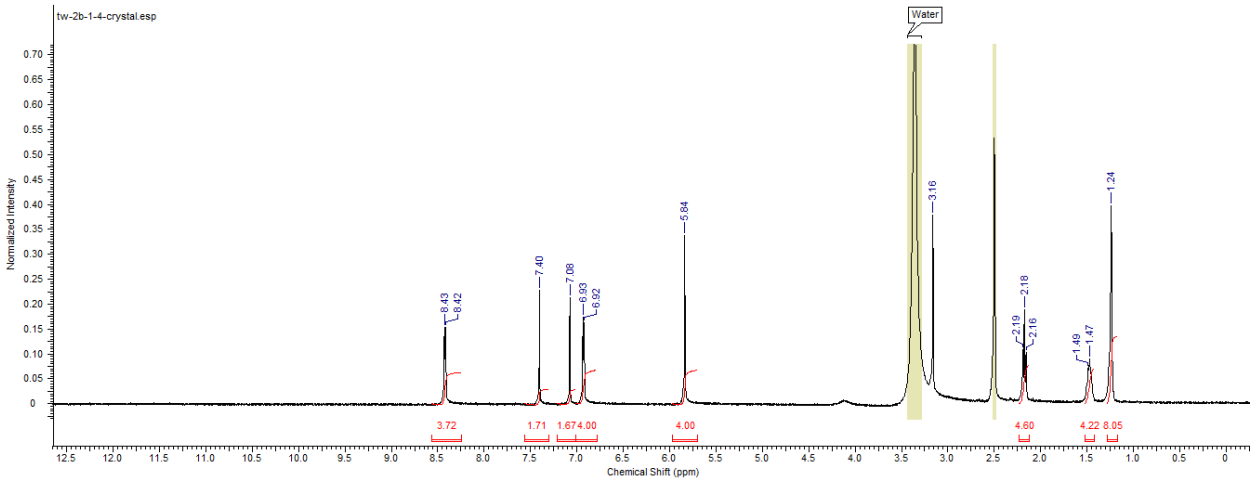
2) A1:Sub



Crystal stoichiometry – 1:1 (Acceptor:Acid)

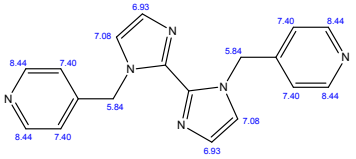
3) A1:Seb

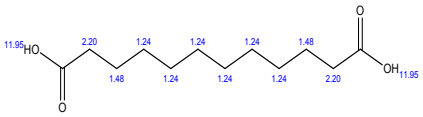


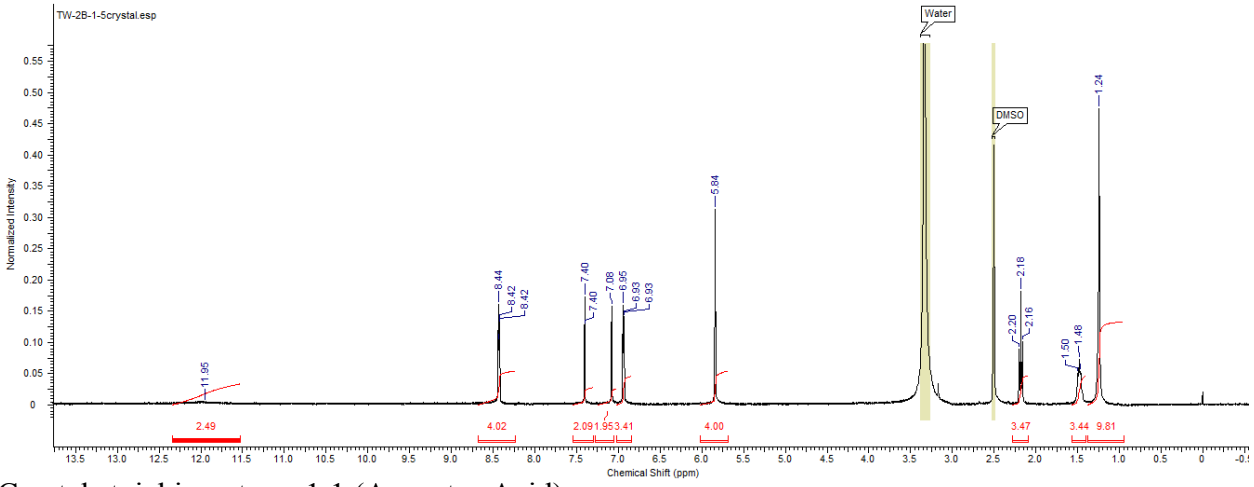


Crystal stoichiometry – 1:1 (Acceptor:Acid)

4) A1:Dod

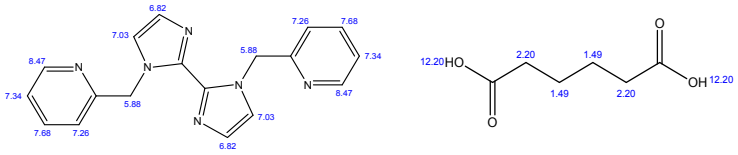


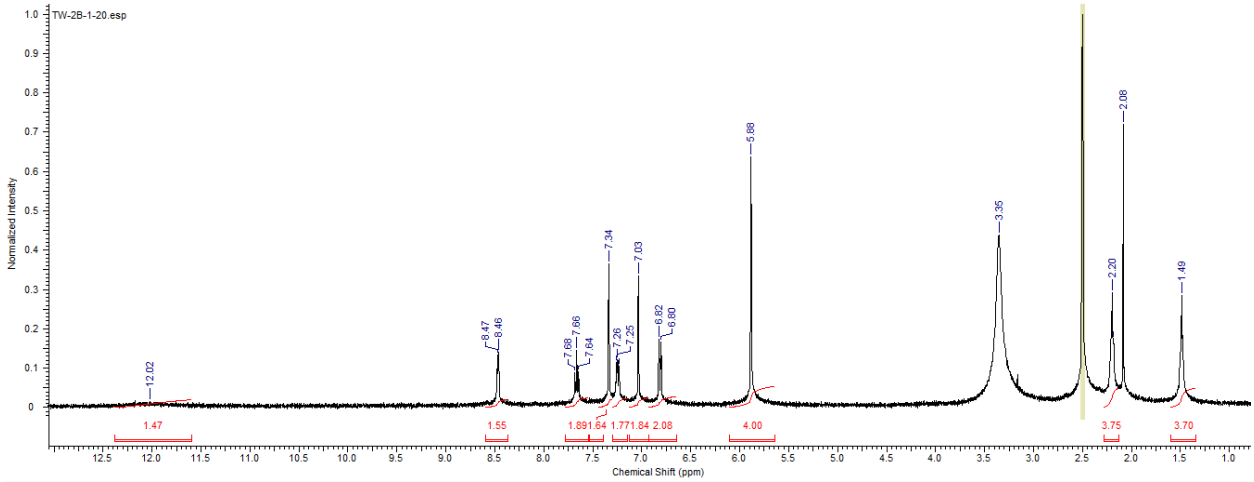




Crystal stoichiometry – 1:1 (Acceptor:Acid)

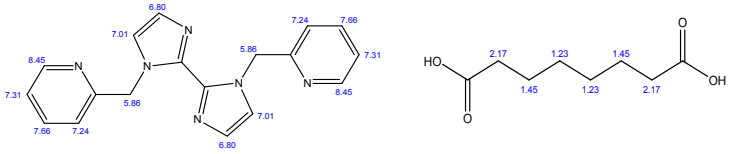
5) A3:Adi

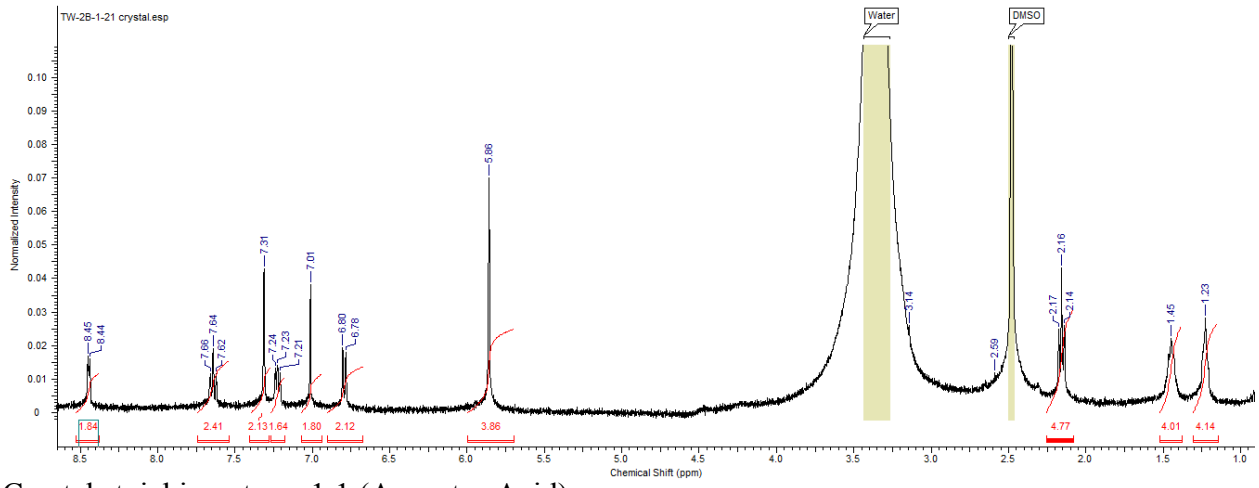




Crystal stoichiometry – 1:1 (Acceptor:Acid)

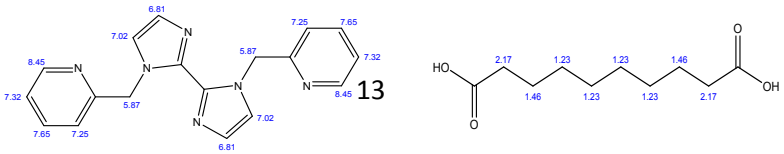
6) A3:Sub

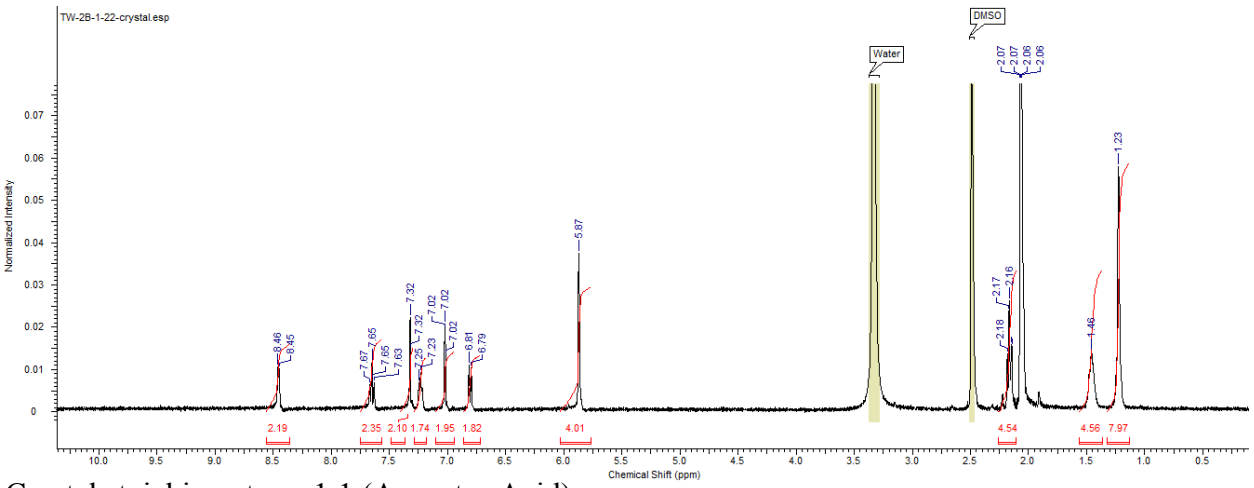




Crystal stoichiometry – 1:1 (Acceptor:Acid)

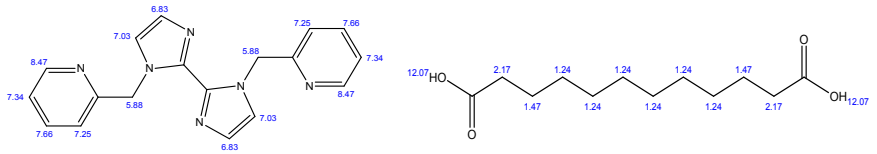
7) A3:Seb

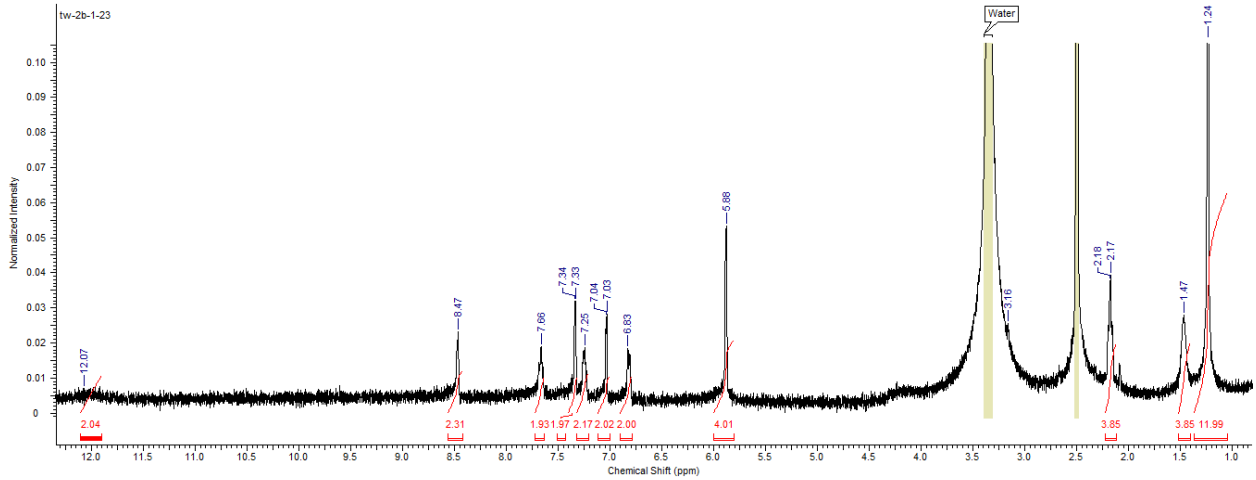




Crystal stoichiometry – 1:1 (Acceptor:Acid)

8) A3:Dod

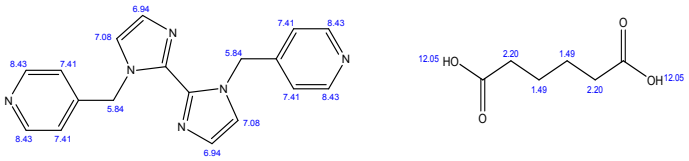


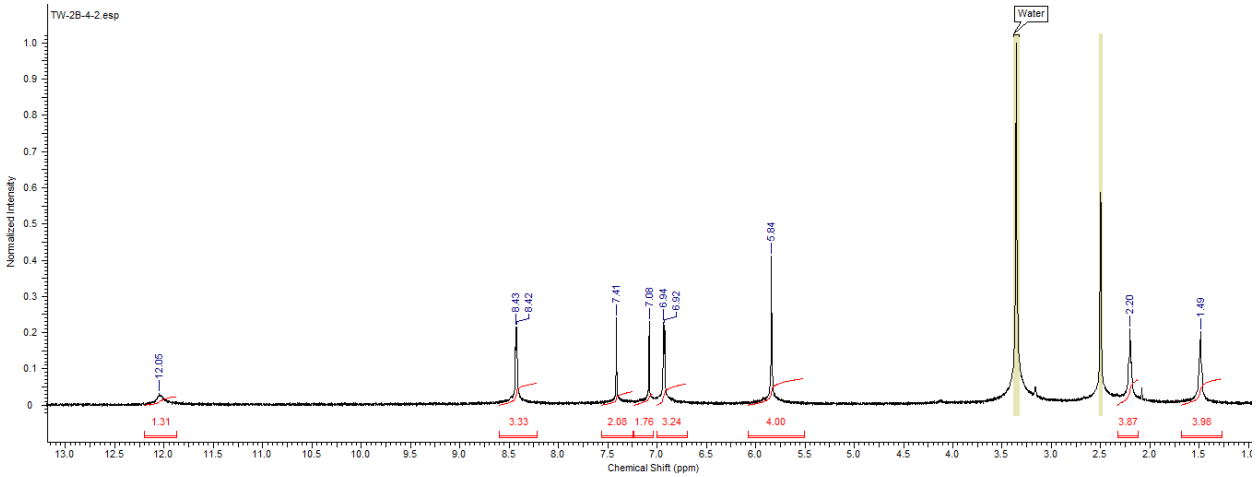


Crystal stoichiometry – 1:1 (Acceptor:Acid)

Mixed Stoichiometry 1:4 (Acceptor:Acid)

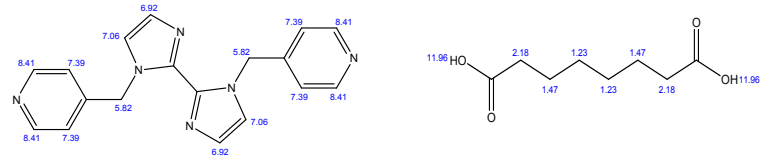
1) A1: Adi

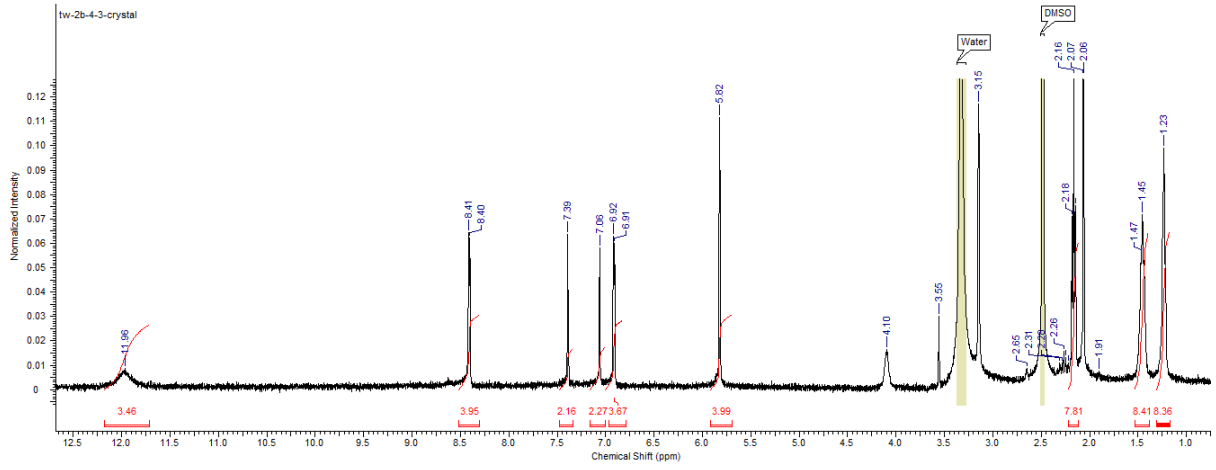




Crystal stoichiometry – 1:1 (Acceptor:Acid)

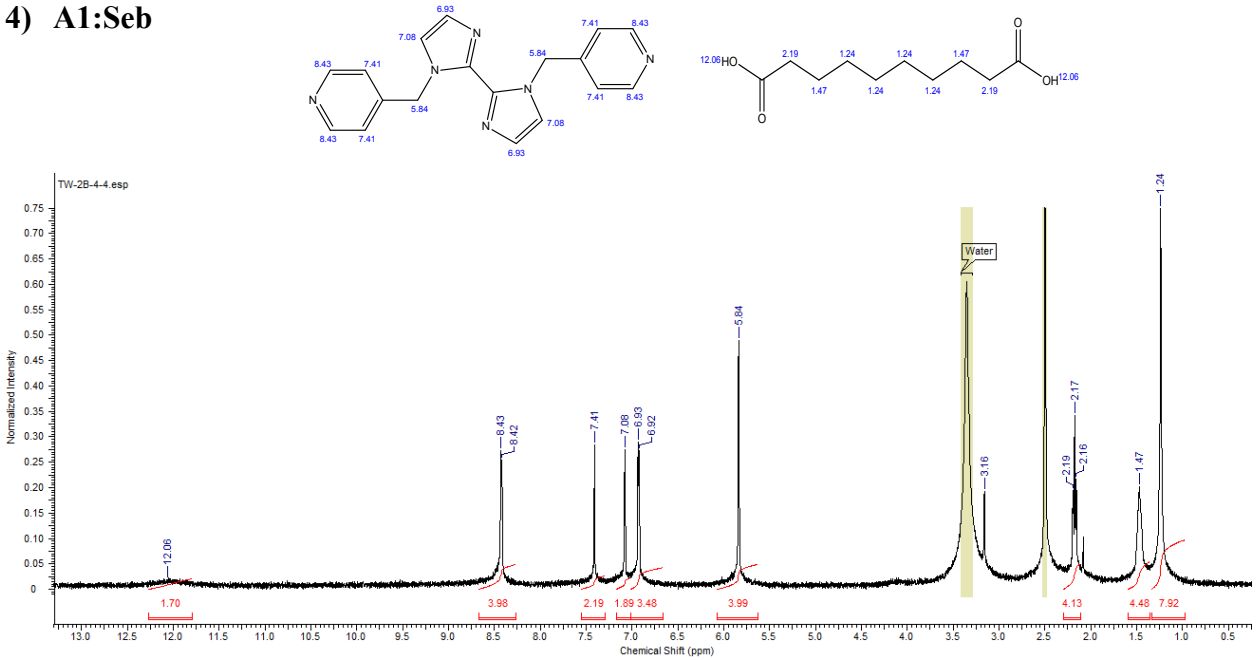
2) A1:Sub





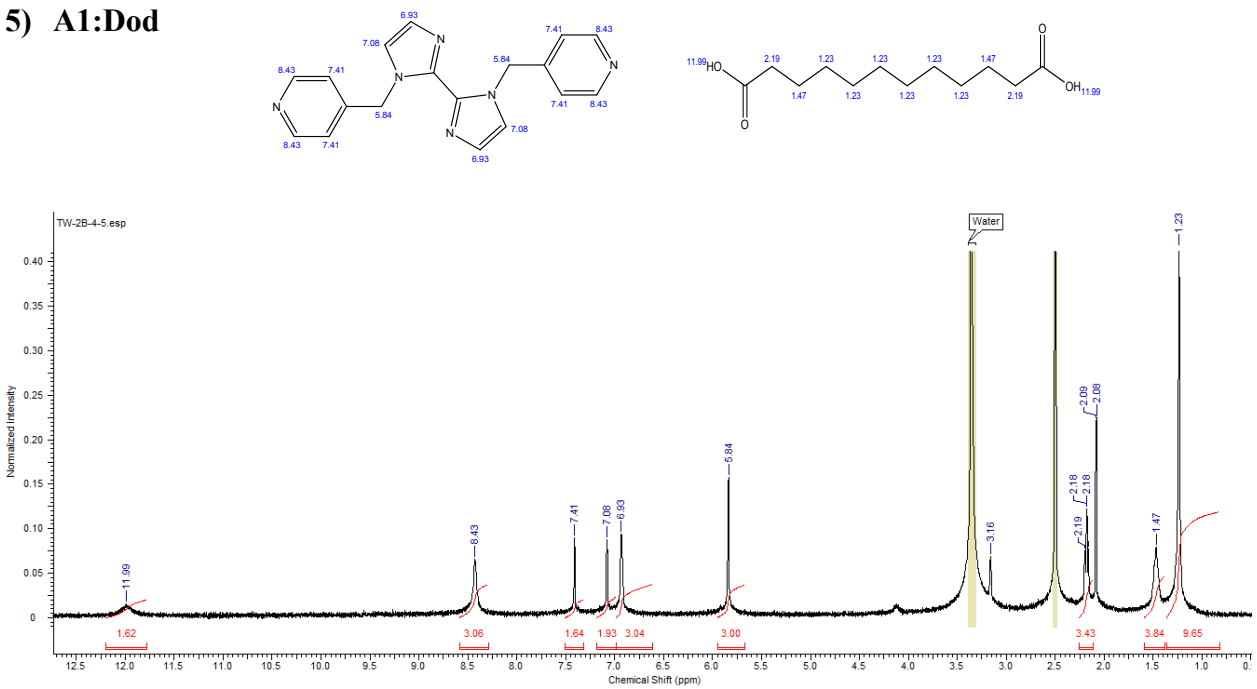
3) Crystal stoichiometry – 1:2 (Acceptor:Acid) - **A1:Sub$_2$**

4) A1:Seb



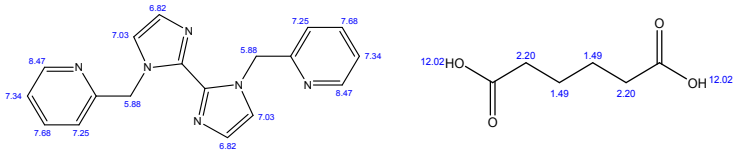
Crystal stoichiometry – 1:1 (Acceptor:Acid)

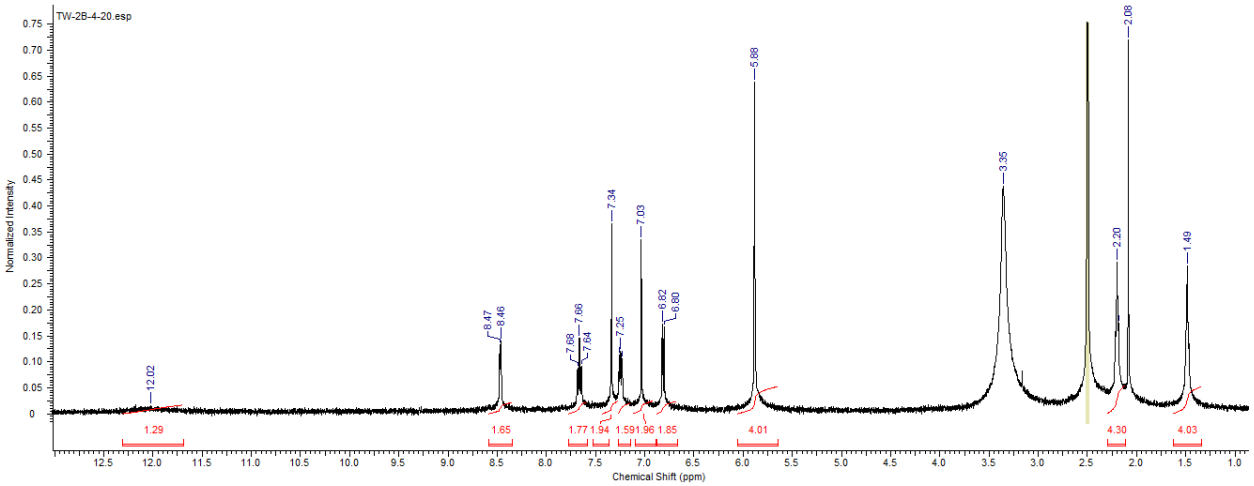
5) A1:Dod



Crystal stoichiometry – 1:1 (Acceptor:Acid)

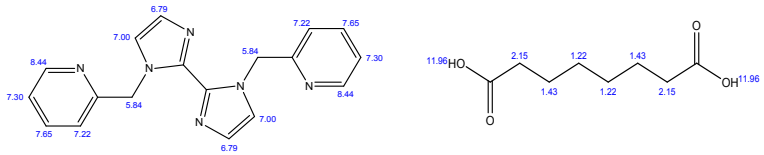
6) A3:Adi

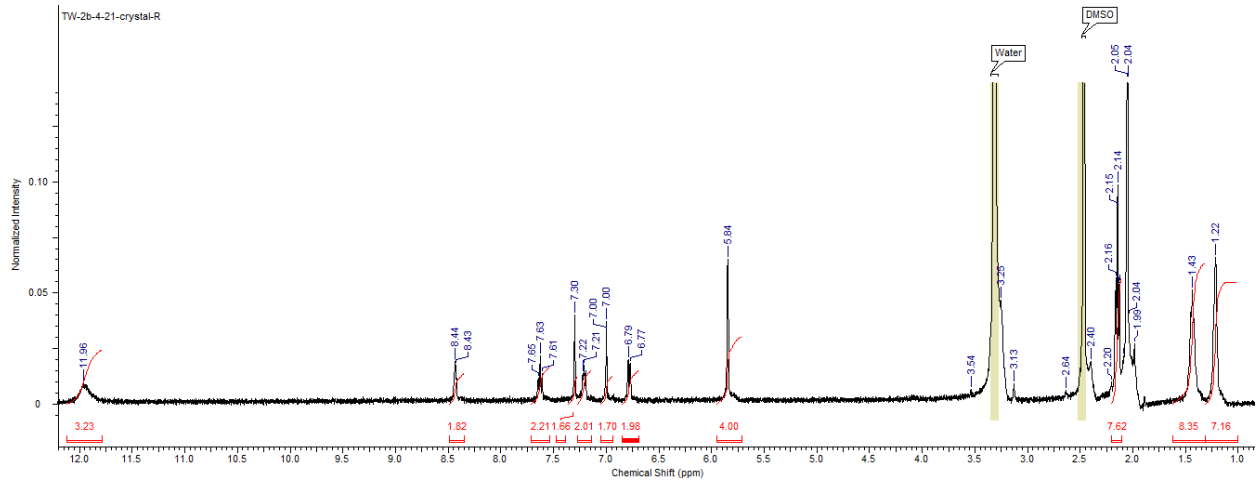




Crystal stoichiometry – 1:1 (Acceptor:Acid)

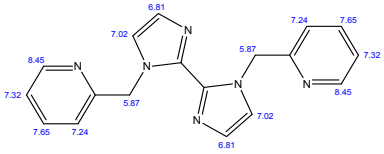
7) A3:Sub

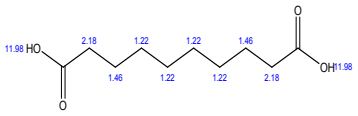


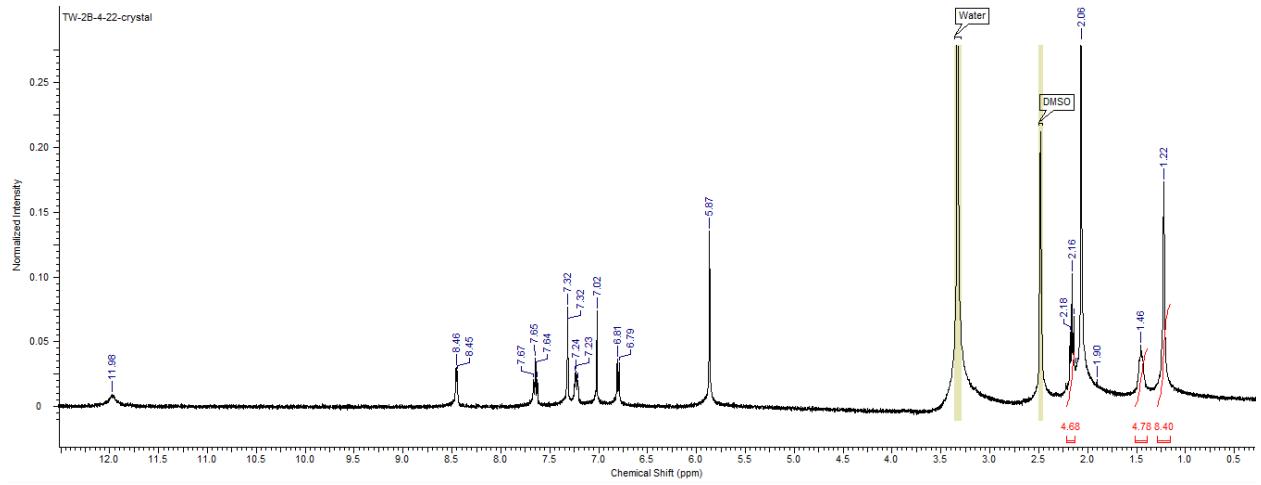


Crystal stoichiometry – 1:2 (Acceptor:Acid) – **A3:Sub$_2$**

8) A3:Seb

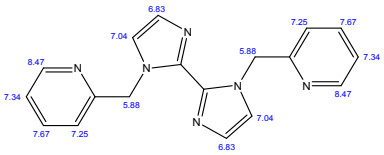


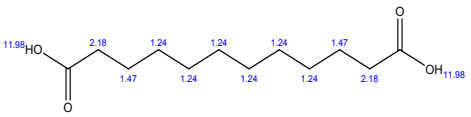


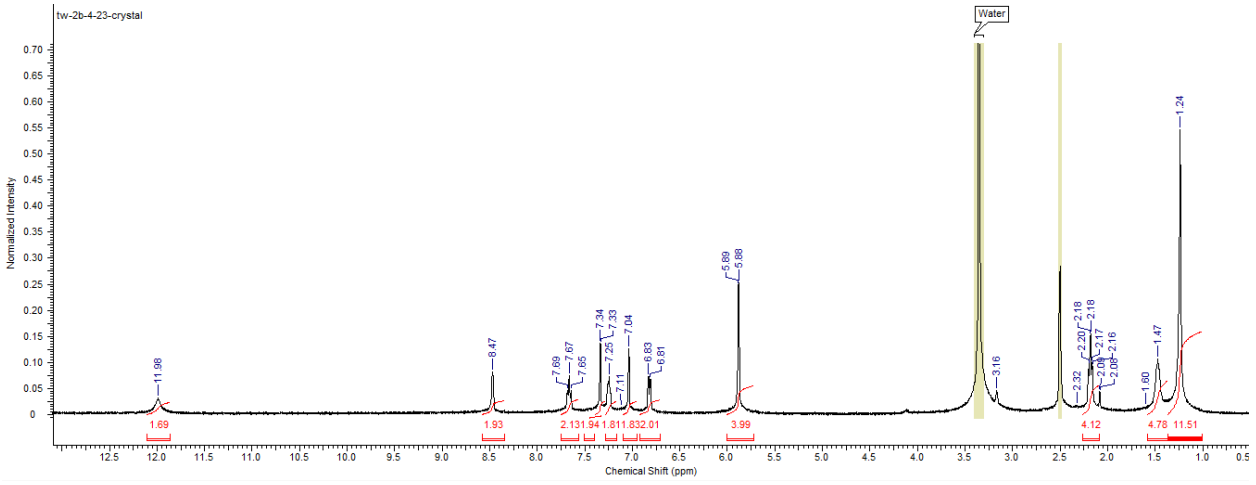


Crystal stoichiometry – 1:1 (Acceptor:Acid)

9) A3:Dod



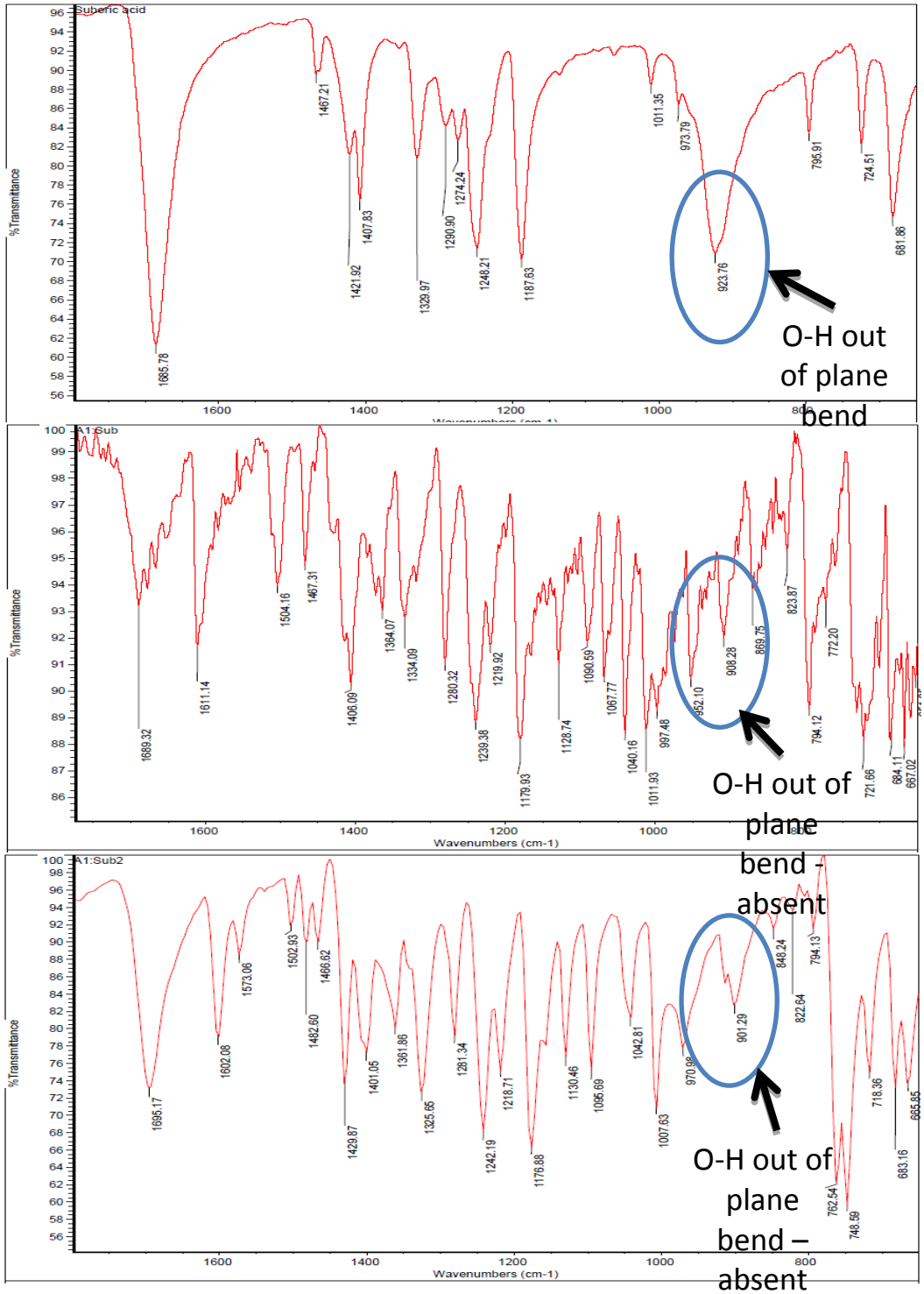




Crystal stoichiometry – 1:1 (Acceptor:Acid)

IR analysis for stoichiometric studies

O-H out of plane bend stretch analysis in the finger print region of Suberic acid, **A1:Sub** and **A1:Sub$_2$** Co-crystals are shown below. Similar results were observed for **A3:Sub** and **A3:Sub$_2$** co-crystals providing evidence for the absence of acid---acid dimer, thus the presence of four O-H---N hydrogen bond interactions leading to 1:2 co-crystal formation in **A1:Sub$_2$** and **A3:Sub$_2$**.



1 C.B. Aakeröy, T.K. Wijethunga, J. Desper, *J. Mol. Struct*., 2014, **1072**, 20.