Electronic Supplementary Material (ESI) for Faraday Discussions.

Competition and selectivity in supramolecular synthesis: structural landscape around 1-(pyridylmethyl)-2,2'-biimidazoles

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Supplementary Information

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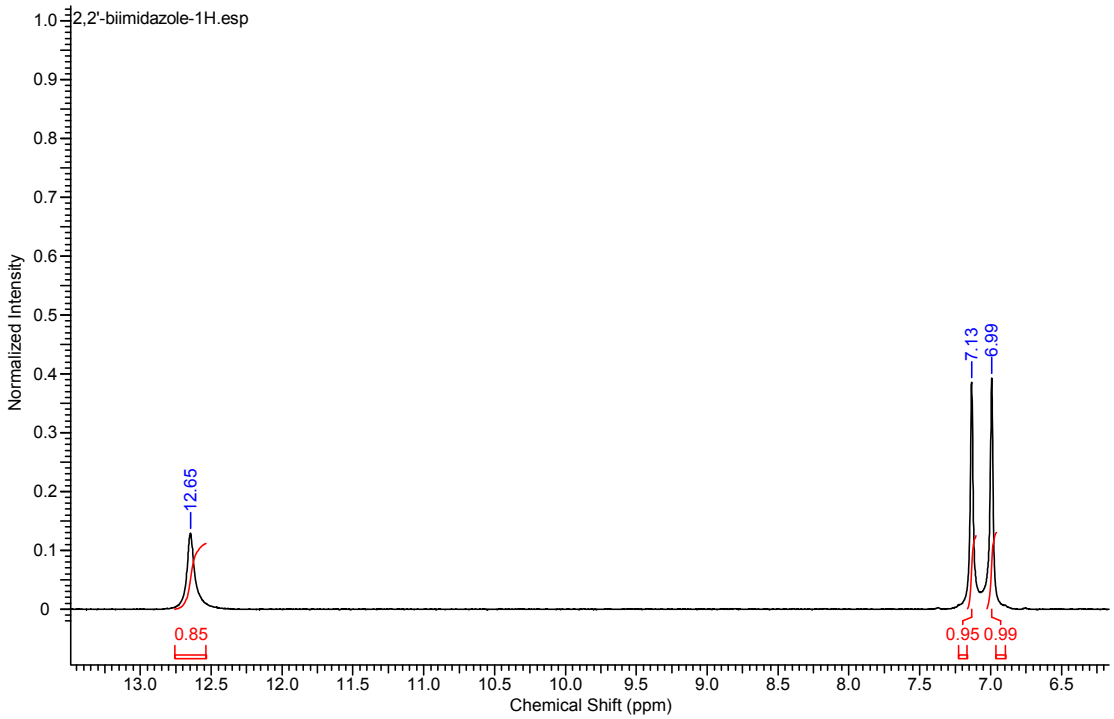

Figure S1: ^{1}H-NMR (400 MHz, DMSO-d6) spectrum of 2,2'-biimidazole

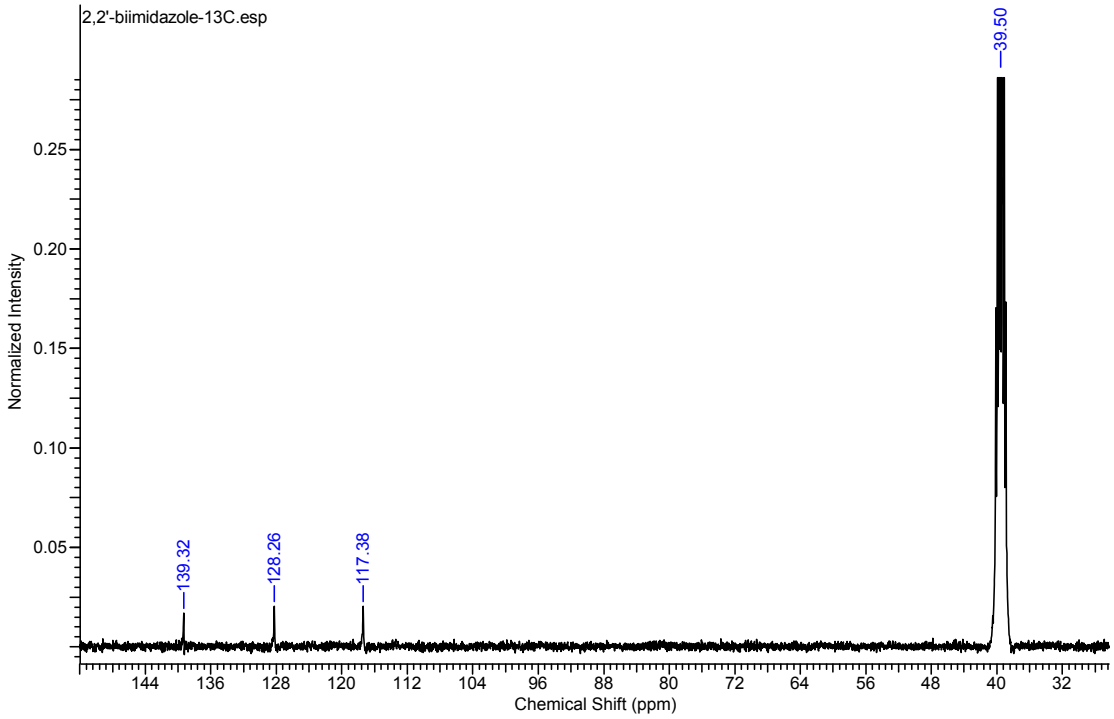

Figure S2: ^{13}C-NMR (100 MHz, DMSO-d6) spectrum of 2,2'-biimidazole

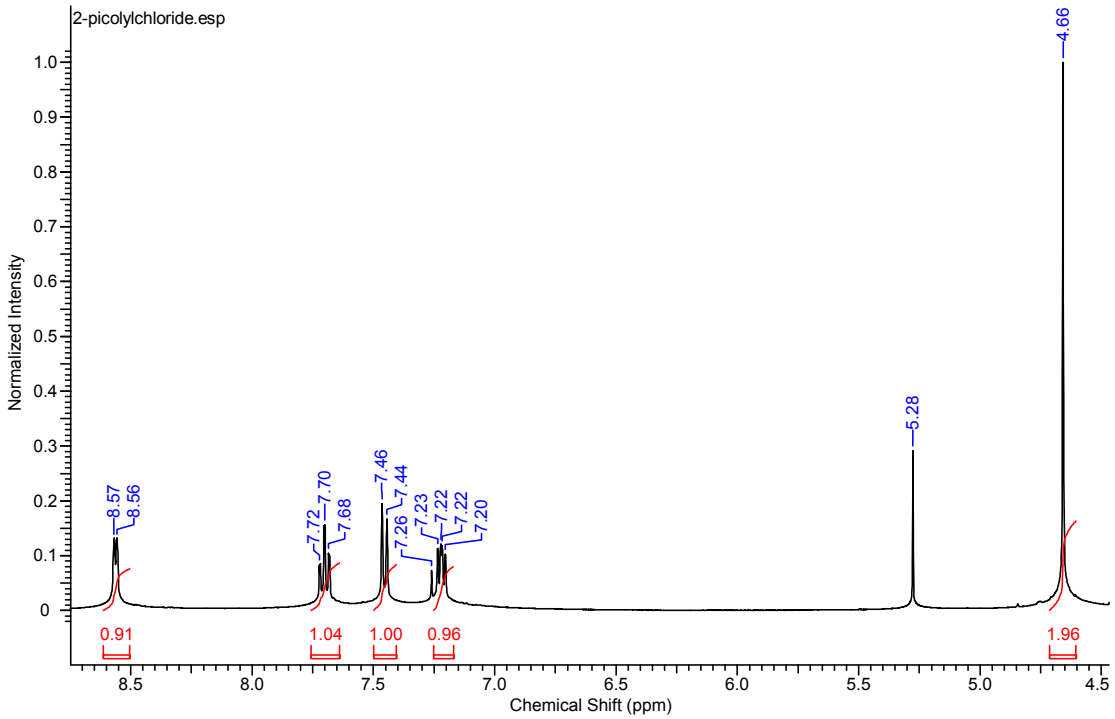

Figure S3: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 2-(chloromethyl)pyridine

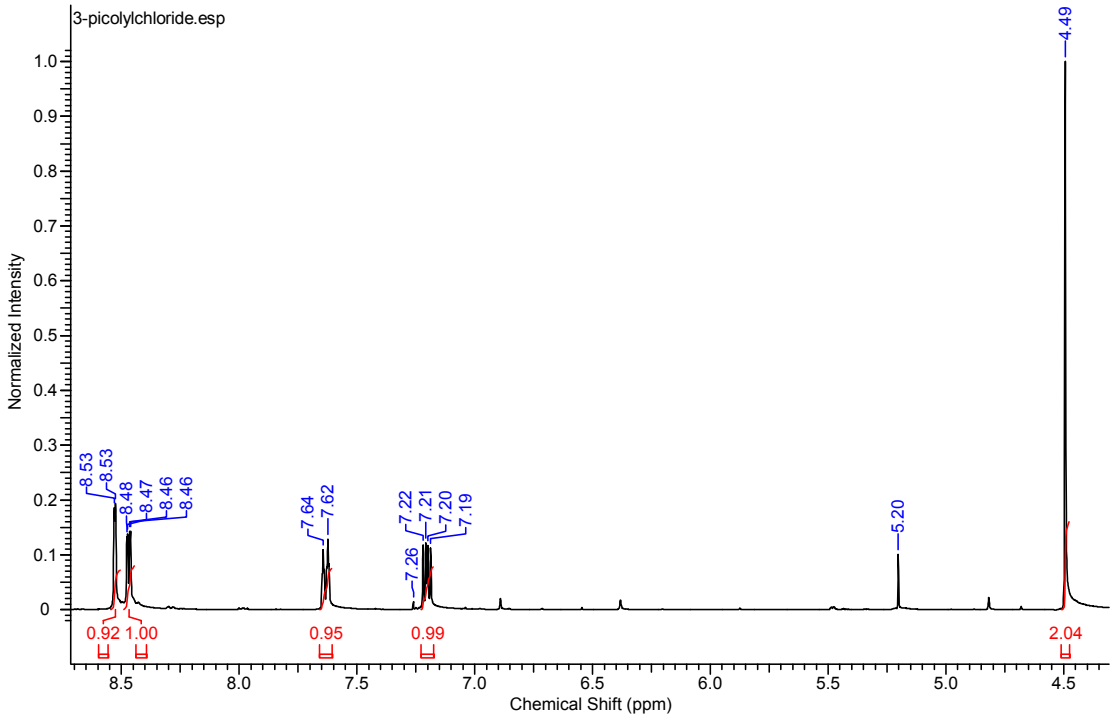

Figure S4: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3-(chloromethyl)pyridine

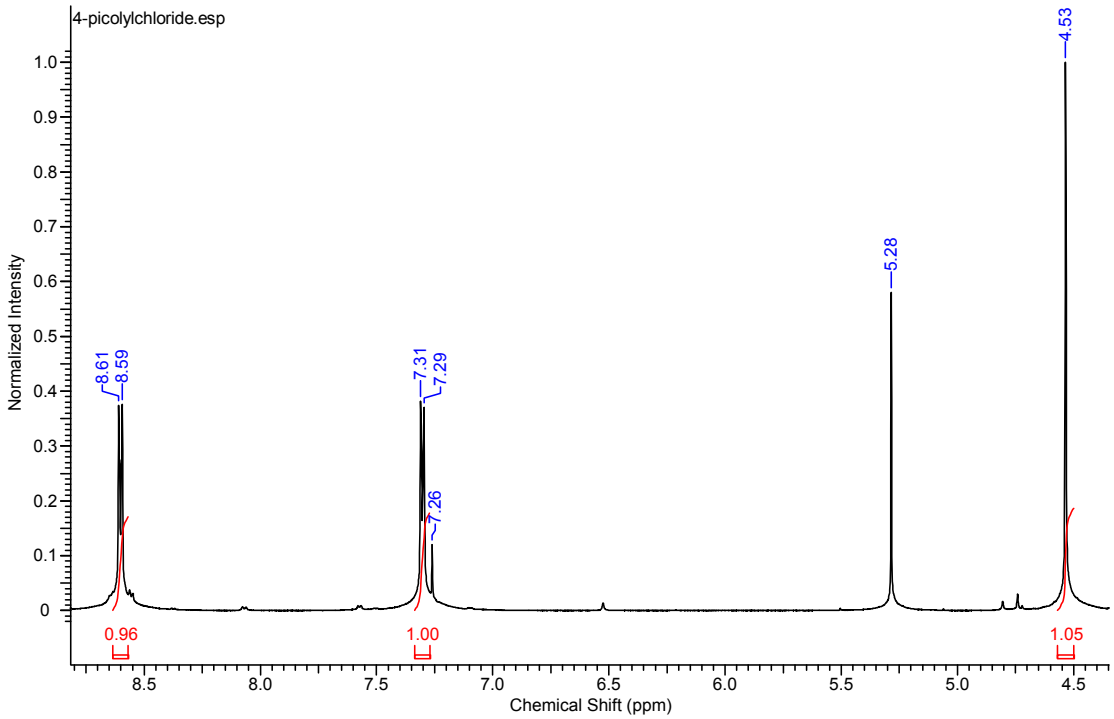

Figure S5: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 4-(chloromethyl)pyridine

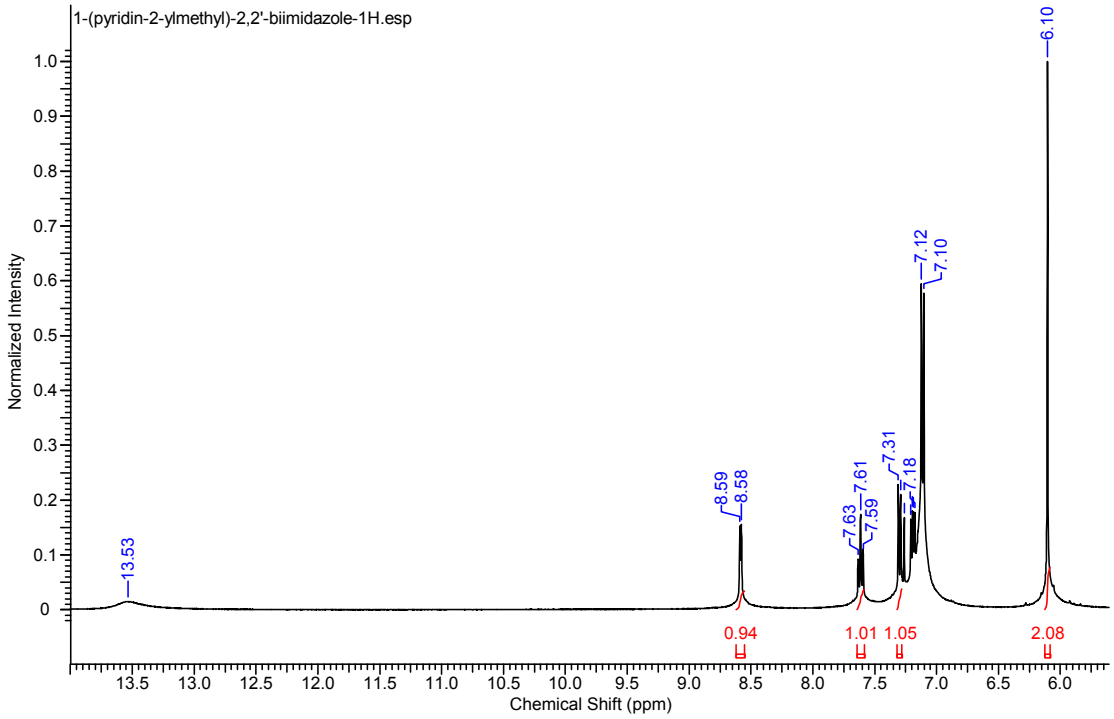

Figure S6: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 1-(pyridin-2-ylmethyl)-2,2'-biimidazole

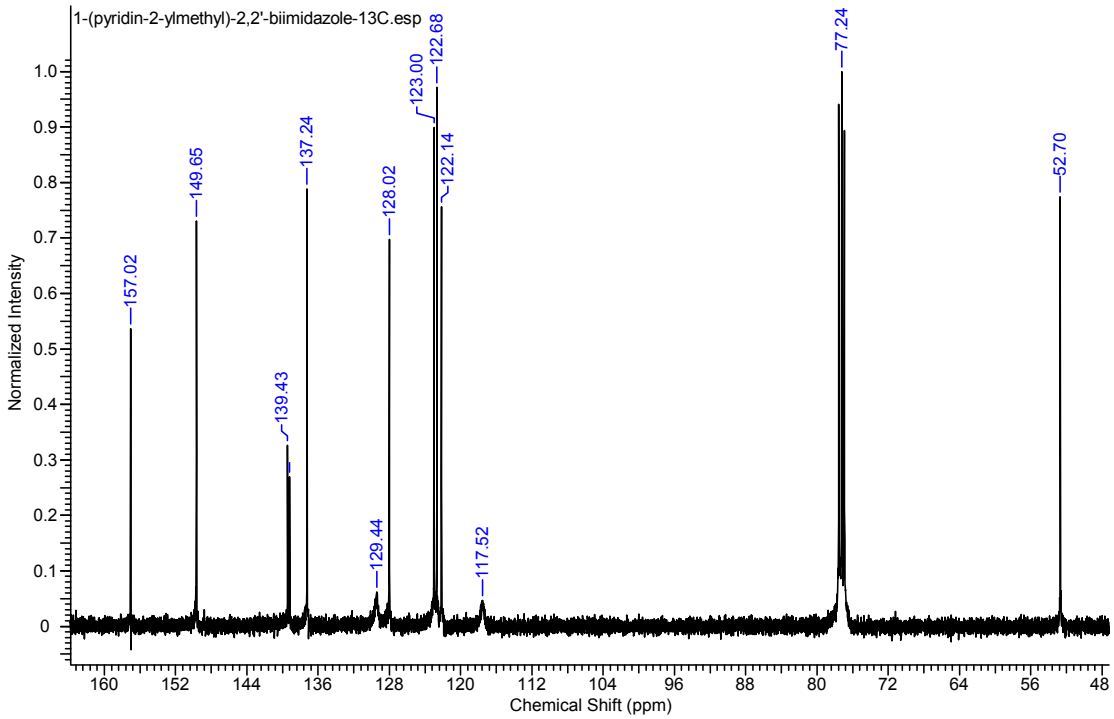

Figure S7: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 1-(pyridin-2-ylmethyl)-2,2'-biimidazole

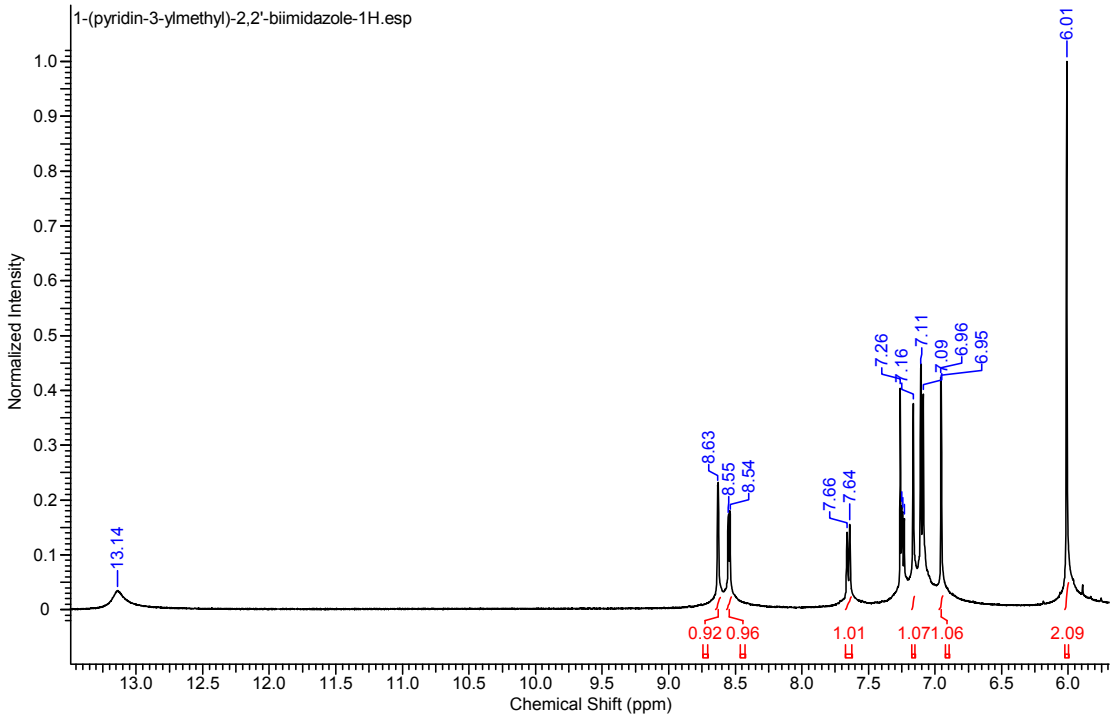

Figure S8: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 1-(pyridin-3-ylmethyl)-2,2'-biimidazole

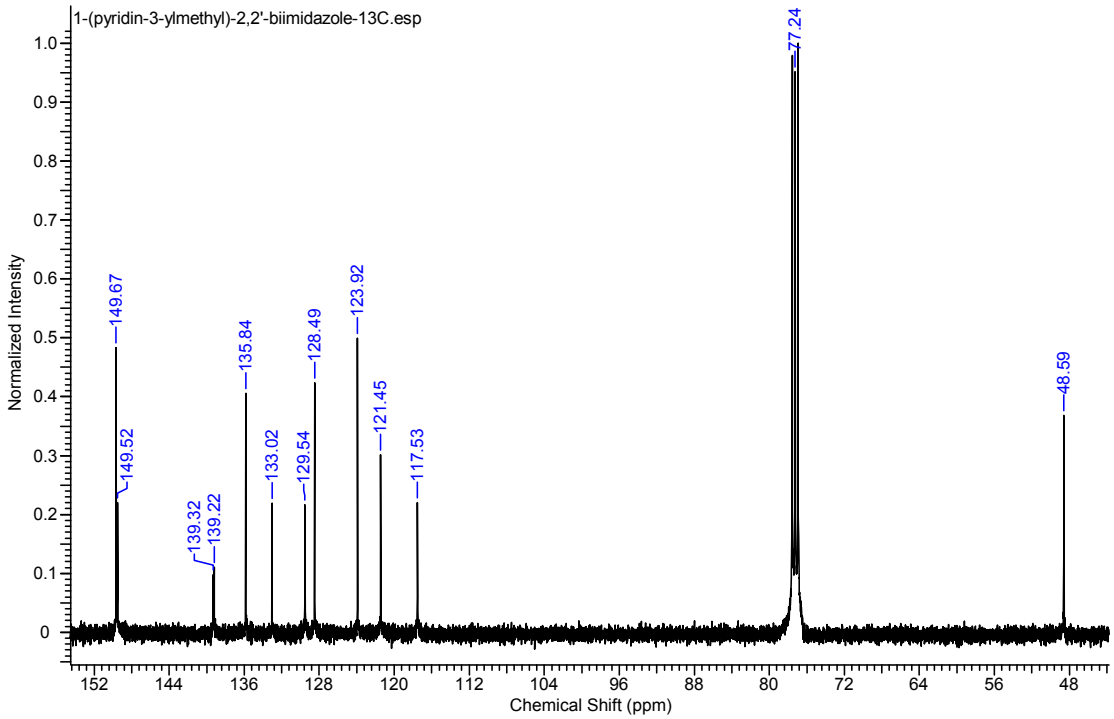

Figure S9: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 1-(pyridin-3-ylmethyl)-2,2'-biimidazole

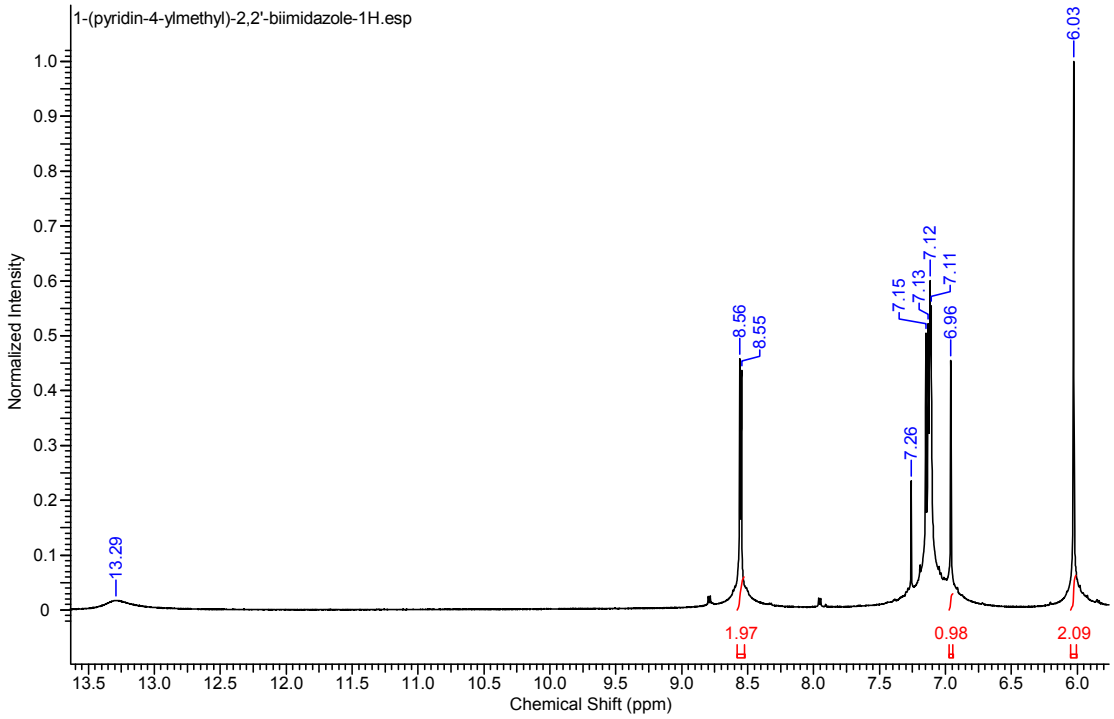

Figure S10: ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 1-(pyridin-4-ylmethyl)-2,2'-biimidazole

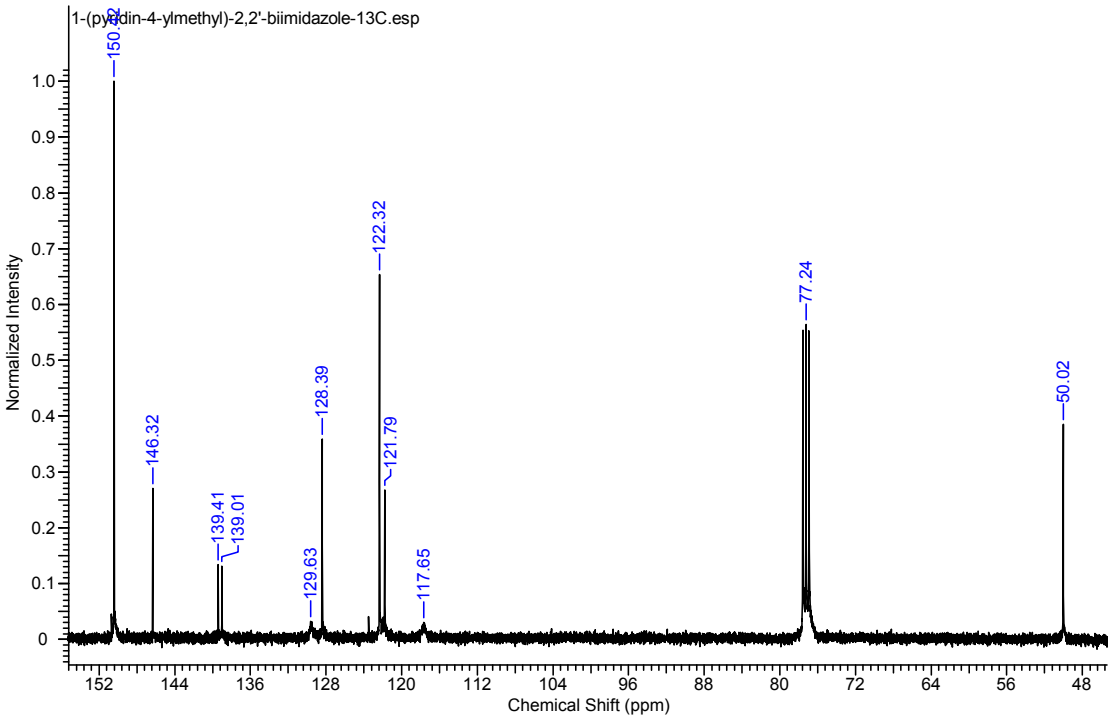

Figure S11: ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 1-(pyridin-4-ylmethyl)-2,2'-biimidazole

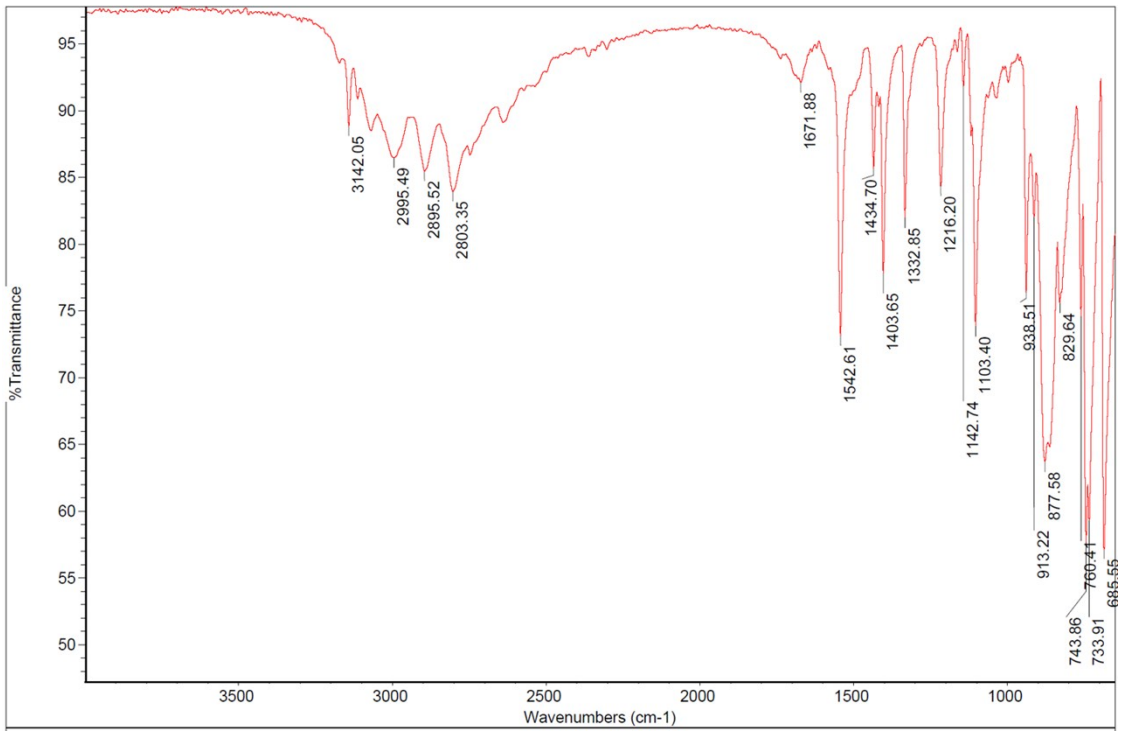

Figure S12: FT-IR spectrum of 2,2'-biimidazole

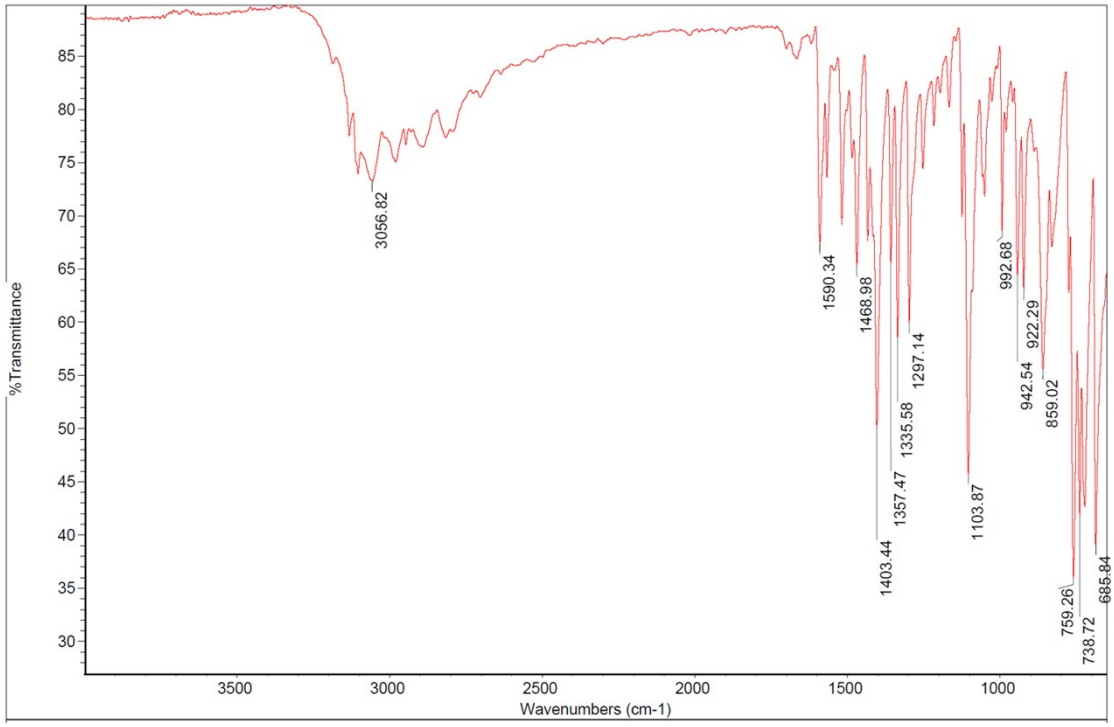

Figure S13: FT-IR spectrum of 1-(pyridin-2-ylmethyl)-2,2'-biimidazole

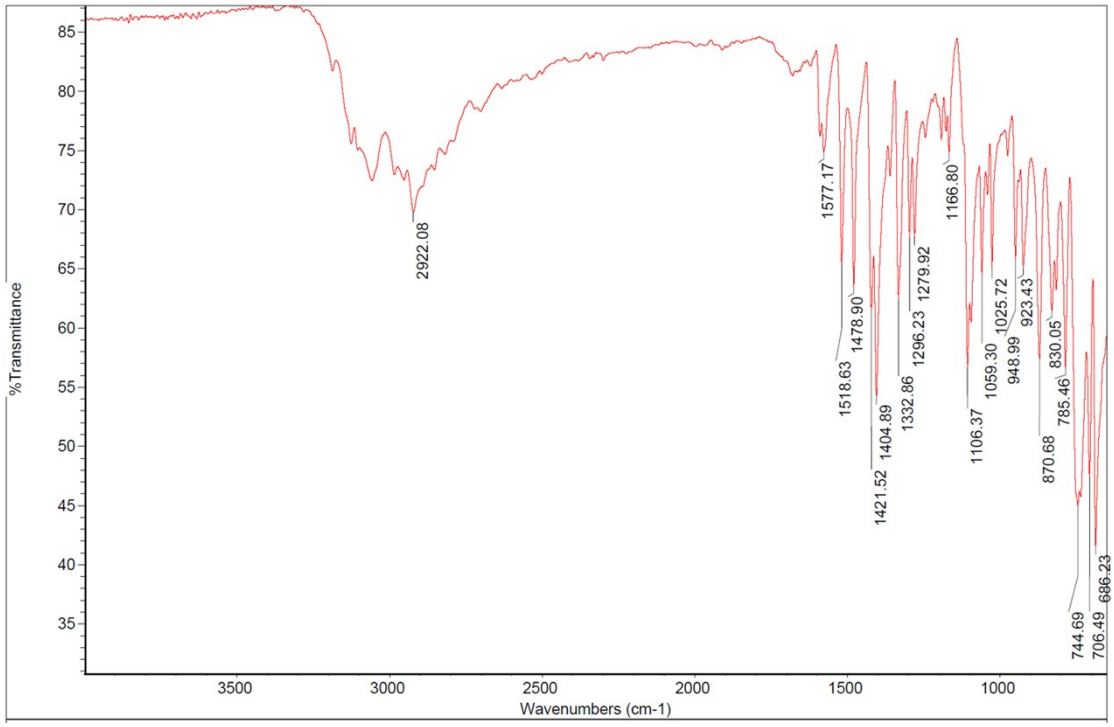

Figure S14: FT-IR spectrum of 1-(pyridin-3-ylmethyl)-2,2'-biimidazole

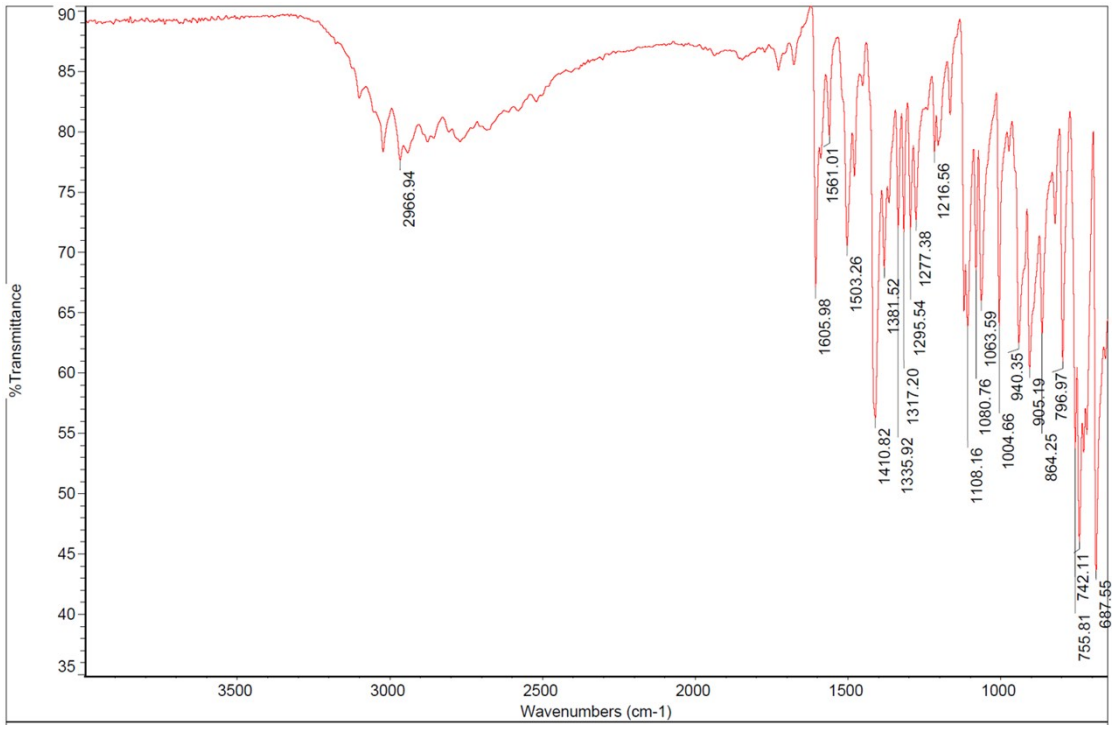

Figure S15: FT-IR spectrum of 1-(pyridin-4-ylmethyl)-2,2'-biimidazole

Crystallography Experimental Details

Datasets were collected on a Bruker Kappa APEX II system using MoKα radiation (**A1**; **A2**; **A3**; **A1:XBD2**; **A2:XBD2**; **A2:XBD3**; **A3:XBD1**; **A3:XBD2**; **A1:HBD2**; **A2:HBD1**; **A2:HBD3**; **A2:HBD5**; **A3:HBD2**), or on a Bruker MicroStar APEX II system using CuKα radiation (**A1:HBD4**; **A3:HBD1**). Data were collected using APEX2 software.[1] Initial cell constants were found by small widely separated "matrix" runs. Data collection strategies were determined using COSMO.[2] Scan speed and scan widths were chosen based on scattering power and peak rocking curves. Datasets were collected at 23 °C (**A1:HBD4**; **A3:HBD1**), -143 °C (**A2**; **A3**; **A1:XBD2**; **A2:XBD2**; **A2:HBD1**), and -153 °C (**A1**; **A2:XBD3**; **A3:XBD1**; **A3:XBD2**; **A1:HBD2**; **A2:HBD3**; **A2:HBD5**; **A3:HBD2**) using an Oxford Cryostream low-temperature device.

For the above datasets, unit cell constants and orientation matrix were improved by least-squares refinement of reflections thresholded from the entire dataset. Integration was performed with SAINT,[3] 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.[4]

For the above datasets, data were reduced with SHELXTL.[5] 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.

Also, datasets for **A1:HBD6** and **A3:HBD3** were collected on an Oxford Diffraction Xcalibur four-circle kappa geometry single-crystal diffractometer with Sapphire 3 CCD detector, using a graphite monochromated MoKα radiation, and applying the CrysAlisPro Software system[6] at 23 °C.

Data reduction, including Lorentz and polarization corrections as well as absorption correction, was done by CrysAlis RED program.[6] The structures were solved by direct methods implemented in the SHELXS-2013 program.[7] The coordinates and the anisotropic displacement parameters for all non-hydrogen atoms were refined by full-matrix least-squares methods based

on F^2 using the SHELXL-2013 program.[7] Except as noted, hydrogen atoms were located in idealized positions and were treated with a riding model.

A1 – Coordinates of the imidazole proton H21 was allowed to refine.

A2 – Coordinates of the imidazole proton H3 was allowed to refine.

A3 – Coordinates of the imidazole proton H10 was allowed to refine.

A1:XBD2 – Coordinates of the imidazole proton H10 was allowed to refine.

A2:XBD2 – Coordinates of the imidazole proton H10 was allowed to refine.

A2:XBD3 – Coordinates of the imidazole proton H21 was allowed to refine.

A3:XBD1 – The asymmetric unit contains eight molecules of the imidazole-based ligand and four molecules of 1,2-diiodo-3,4,5,6-tetrafluorobenzene. The structure is partially disordered. Consequently, neighboring atoms closer than d_{max} were restrained with an effective standard deviation to have the same U_{ij} components using SIMU commands. Relative populations were allowed to refine. Also, thermal parameters for closely located atoms were pairwise constrained using EADP commands.

A3:XBD2 – Coordinates of the imidazole protons H21_1, H21_2, H51_1 and H51_2, and methanol protons H1_1 and H2_2 were allowed to refine.

A1:HBD2 – Coordinates of the imidazole protons H13 and H21, and carboxylic acid proton H51 were allowed to refine.

A1:HBD4 – Coordinates of the imidazole protons H2 and H14, and carboxylic acid proton H29 were allowed to refine.

A1:HBD6 – Coordinates of the imidazole proton H1N and carboxylic acid proton H1O were allowed to refine.

A2:HBD1 – Coordinates of the imidazole proton H6 and carboxylic acid proton H25 were allowed to refine.

A2:HBD3 – Coordinates of the imidazole protons H21 and H51, and carboxylic acid protons H71 and H76 were allowed to refine.

A2:HBD5 – Coordinates of the imidazole proton H21 and carboxylic acid proton H41 were allowed to refine.

A3:HBD1 – The crystal was a non-merohedral twin and the data was processed with TWINABS.[8] The structure was solved using the processed data for Domain 1. Coordinates of the imidazole proton H14 and carboxylic acid proton H25 were allowed to refine.

A3:HBD2 – Coordinates of the imidazole proton H21, and carboxylic acid protons H41 and H44 were allowed to refine.

A3:HBD3 – Coordinates of the imidazole proton H1N, and carboxylic acid protons H1O and H2P were allowed to refine.

Table 1. Crystallographic data for the ligands and their cocrystals.

Code	**A1**	**A2**	**A3**	**A1:XBD2**	**A2:XBD2**
Formula moiety	$C_{12}H_{11}N_5$	$C_{12}H_{11}N_5$	$C_{12}H_{11}N_5$	$C_{12}H_{11}N_5$, $0.5(C_6F_4I_2)$	$C_{12}H_{11}N_5$, $0.5(C_6F_4I_2)$
Empirical formula	$C_{12}H_{11}N_5$	$C_{12}H_{11}N_5$	$C_{12}H_{11}N_5$	$C_{15}H_{11}F_2IN_5$	$C_{15}H_{11}F_2IN_5$
Molecular weight	225.26	225.26	225.26	426.19	426.19
Color, Habit	Pink, Prism	Colorless, Blocks	Orange, Blocks	Red, Plates	Red, Blocks
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group, *Z*	*C*2/*c*, 8	$P\bar{1}$, 2	*P*2(1)/*n*, 4	$P\bar{1}$, 2	$P\bar{1}$, 2
a, Å	21.5686(12)	5.493(2)	7.490(3)	5.0691(14)	5.4649(17)
b, Å	5.8077(3)	10.339(4)	9.841(4)	8.055(2)	11.660(4)
c, Å	18.0356(10)	10.611(4)	15.253(5)	19.750(5)	12.493(4)
α, º	90	112.83(2)	90	93.952(13)	84.163(17)
β, º	110.1298(16)	99.24(3)	99.072(17)	93.442(12)	80.913(13)
γ, º	90	94.16(3)	90	105.938(16)	76.728(13)
Volume, Å^3	2121.2(2)	542.1(4)	1110.2(7)	771.0(4)	763.3(4)
Density, g/cm^3	1.411	1.380	1.348	1.836	1.854
T, ºK	120(2)	130(2)	130(2)	130(2)	130(2)
Crystal size, min x mid x max	0.280 x 0.340 x 0.440	0.080 x 0.160 x 0.240	0.132 x 0.238 x 0.316	0.110 x 0.185 x 0.220	0.232 x 0.328 x 0.578
X-ray wavelength, Å	0.71073	0.71073	0.71073	0.71073	0.71073
μ, mm^{-1}	0.092	0.090	0.088	2.104	2.125
Trans min / max	0.96 / 0.97	0.88 / 0.99	0.97 / 0.99	0.66 / 0.80	0.37 / 0.64
θ_{min}, º	2.01	2.13	2.47	1.04	1.80
θ_{max}, º	31.85	25.95	25.61	26.37	26.66
Reflections					
collected	19578	14694	19586	16067	18709
independent	3354	2078	2077	3140	2999

observed	2892	1341	1700	2891	2877
R_{int}	0.0292	0.0770	0.0489	0.0453	0.0413
Threshold expression	$> 2\sigma(I)$	$> 2\sigma(I)$	$> 2\sigma(I)$	$> 2\sigma(I)$	$> 2\sigma(I)$
No. parameters	157	159	158	212	212
No. restraints	0	0	0	0	0
R_1 (observed)	0.0421	0.0892	0.0393	0.0236	0.0189
wR_2 (all)	0.1188	0.2587	0.0919	0.0768	0.0508
Goodness of fit (all)	1.083	1.101	1.082	1.218	1.138
ρ_{max}, ρ_{min}, e Å^{-3}	0.358, -0.315	0.736, -0.575	0.157, -0.266	0.661, -0.512	0.395, -0.555
Completeness to 2θ limit	0.987	0.980	0.998	0.993	0.932

Code	**A2:XBD3**	**A3:XBD1**	**A3:XBD2**	**A1:HBD2**	**A1:HBD4**
Formula moiety	$(C_{12}H_{11}N_5)$, $(C_6F_3I_3)$	$(C_{12}H_{11}N_5)_2$, $(C_6F_4I_2)$	$(C_{12}H_{11}N_5)_2$, $(C_6F_4I_2)$, (C_1H_4O)	$(C_{12}H_{11}N_5)$, $(C_4H_6O_4)$	$C_{12}H_{12}N_5$, $C_8H_{13}O_4$
Empirical formula	$C_{18}H_{11}F_3I_3N_5$	$C_{30}H_{22}F_4I_2N_{10}$	$C_{31}H_{26}F_4I_2N_{10}O$	$C_{16}H_{17}N_5O_4$	$C_{20}H_{25}N_5O_4$
Molecular weight	735.02	852.38	225.26	343.34	399.45
Color, Habit	Colorless, Plates	Pink, Prism	Colorless, Plates	Colorless, Plates	Violet, Irregular
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group, Z	$P2(1)/c$, 4	$P\bar{1}$, 8	$P\bar{1}$, 4	$P\bar{1}$, 2	$P\bar{1}$, 2
a, Å	16.0707(15)	17.386(2)	13.4945(9)	5.0716(9)	5.1948(2)
b, Å	9.0666(8)	19.378(3)	14.8017(10)	11.314(2)	10.8967(3)
c, Å	14.8610(14)	19.435(3)	19.3714(13)	14.051(3)	18.2317(6)
α, º	90	92.996(5)	111.285(2)	90.818(7)	105.5790(10)
β, º	107.218(3)	106.710(5)	92.518(2)	99.190(6)	95.6070(10)
γ, º	90	106.560(4)	112.668(2)	99.925(6)	100.1040(10)
Volume, Å^3	2068.3(3)	5946.5(14)	3249.9(4)	783.2(3)	967.21(6)

Density, g/cm^3	2.360	1.904	1.808	1.456	1.372
T, ºK	120(2)	120(2)	120(2)	120(2)	296(2)
Crystal size, min x mid x max	0.120 x 0.360 x 0.440	0.180 x 0.260 x 0.360	0.120 x 0.280 x 0.340	0.120 x 0.380 x 0.420	0.055 x 0.090 x 0.250
X-ray wavelength, Å	0.71073	0.71073	0.71073	0.71073	1.54178
μ, mm^{-1}	4.575	2.182	2.002	0.108	0.805
Trans min / max	0.24 / 0.61	0.51 / 0.69	0.54 / 0.79	0.96 / 0.99	0.82 / 0.96
θ_{min}, º	1.33	1.41	1.566	1.469	2.55
θ_{max}, º	32.05	31.26	31.980	31.033	70.29
Reflections					
collected	36298	115429	73862	11896	17758
independent	7154	37450	20434	4628	3369
observed	6416	22954	17311	3897	3347
R_{int}	0.0296	0.0550	0.0242	0.0192	0.0475
Threshold expression	> 2σ(I)	> 2σ(I)	> 2σ(I)	> 2σ(I)	> 2σ(I)
No. parameters	265	1178	885	235	275
No. restraints	0	528	0	0	2
R_1 (observed)	0.0220	0.0621	0.0275	0.0418	0.0471
wR$_2$ (all)	0.0496	0.1994	0.0654	0.1226	0.1150
Goodness of fit (all)	1.030	1.174	1.039	1.034	1.097
ρ_{max}, ρ_{min}, e Å^{-3}	0.850, -1.301	2.706, -3.336	1.239, -0.526	0.371, -0.357	0.580, -0.371
Completeness to 2θ limit	0.994	0.984	0.991	0.970	0.908

Code	**A1:HBD6**	**A2:HBD1**	**A2:HBD3**	**A2:HBD5**	**A3:HBD1**
Formula moiety	$C_{12}H_{11}N_5$, 0.5($C_{12}H_{22}O_4$)	$C_{12}H_{11}N_5$, $C_7H_6O_2$	$(C_{12}H_{11}N_5)_2$, ($C_6H_{10}O_4$)	$(C_{12}H_{11}N_5)_2$, ($C_{10}H_{18}O_4$)	$C_{12}H_{11}N_5$, $C_7H_6O_2$
Empirical formula	$C_{18}H_{22}N_5O_2$	$C_{19}H_{17}N_5O_2$	$C_{30}H_{32}N_{10}O_4$	$C_{34}H_{40}N_{10}O_4$	$C_{19}H_{17}N_5O_2$

Molecular weight	340.40	347.38	596.65	652.76	347.38
Color, Habit	Red, Blocks	Red, Blocks	Pink, Prism	Red, Plates	Violet, Parallelepiped
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group, Z	$P\bar{1}$, 2	$P\bar{1}$, 2	$P\bar{1}$, 2	$P\bar{1}$, 1	$P\bar{1}$, 2
a, Å	5.2936(3)	7.028(2)	8.0078(17)	5.7402(10)	6.42690(10)
b, Å	7.9437(5)	9.024(3)	10.167(2)	9.3514(16)	9.9656(2)
c, Å	22.8847(13)	13.602(4)	18.969(4)	14.973(3)	13.5194(3)
α, º	81.583(5)	90.229(19)	79.276(6)	97.467(5)	96.6910(10)
β, º	85.500(6)	91.564(17)	82.529(5)	91.771(6)	95.6860(10)
γ, º	70.615(5)	93.223(16)	70.640(5)	97.861(5)	100.6030(10)
Volume, Å^3	897.53(10)	860.9(4)	1427.8(5)	788.5(2)	838.84(3)
Density, g/cm^3	1.260	1.340	1.388	1.375	1.375
T, ºK	296(2)	130(2)	120(2)	120(2)	296(2)
Crystal size, min x mid x max	0.300 x 0.360 x 0.510	0.268 x 0.374 x 0.492	0.300 x 0.320 x 0.340	0.080 x 0.380 x 0.420	0.065 x 0.130 x 0.160
X-ray wavelength, Å	0.71073	0.71073	0.71073	0.71073	1.54178
μ, mm^{-1}	0.086	0.091	0.097	0.094	0.761
Trans min / max	0.95 / 1.00	0.96 / 0.98	0.86 / 0.97	0.76 / 0.99	0.89 / 0.95
θ_{min}, º	4.293	2.26	1.095	1.373	3.32
θ_{max}, º	24.999	25.73	31.509	31.023	69.93
Reflections					
collected	7915	18617	52300	14438	2977
independent	3140	3240	8898	4721	2977
observed	2254	2746	7471	3525	2905
R_{int}	0.0265	0.0398	0.0400	0.0338	0.6116
Threshold expression	$> 2\sigma(I)$	$> 2\sigma(I)$	$> 2\sigma(I)$	$> 2\sigma(I)$	$> 2\sigma(I)$
No. parameters	234	243	409	223	244

No. restraints	0	1	0	0	1
R_1 (observed)	0.0654	0.0360	0.0444	0.0484	0.0415
wR_2 (all)	0.1569	0.0980	0.1399	0.1436	0.1038
Goodness of fit (all)	1.095	1.049	1.083	1.115	1.136
ρ_{max}, ρ_{min}, e Å^{-3}	0.159, -0.172	0.176, -0.242	0.547, -0.322	0.335, -0.273	0.358, -0.289
Completeness to 2θ limit	0.994	0.984	0.995	0.970	0.937

Code	**A3:HBD2**	**A3:HBD3**
Formula moiety	$(C_{12}H_{11}N_5)$, $(C_4H_6O_4)$	$(C_{12}H_{11}N_5)$, $(C_6H_{10}O_4)$
Empirical formula	$C_{16}H_{17}N_5O_4$	$C_{18}H_{21}N_5O_4$
Molecular weight	343.34	371.40
Color, Habit	Red, Plates	Red, Blocks
Crystal system	Triclinic	Monoclinic
Space group, Z	$P\bar{1}$, 2	$P2(1)/n$, 4
a, Å	4.8081(7)	17.295(2)
b, Å	11.0210(17)	4.8014(7)
c, Å	14.819(2)	21.977(3)
α, º	97.881(6)	90
β, º	91.543(6)	90.912(11)
γ, º	90.181(6)	90
Volume, Å^3	777.5(2)	1824.7(4)
Density, g/cm^3	1.467	1.352
T, ºK	120(2)	296(2)
Crystal size, min x mid x max	0.080 x 0.340 x 0.400	0.280 x 0.310 x 0.530
X-ray wavelength, Å	0.71073	0.71073

μ, mm^{-1}	0.109	0.098
Trans min / max	0.77 / 0.99	0.95 / 1.00
θ_{min}, °	1.865	4.364
θ_{max}, °	30.567	26.999
Reflections		
collected	17051	9474
independent	4630	3958
observed	3399	2388
R_{int}	0.0441	0.0473
Threshold expression	$> 2\sigma(I)$	$> 2\sigma(I)$
No. parameters	235	257
No. restraints	0	0
R_1 (observed)	0.0519	0.0595
wR_2 (all)	0.1585	0.1791
Goodness of fit (all)	1.066	1.018
ρ_{max}, ρ_{min}, e $Å^{-3}$	0.402, -0.378	0.193, -0.179
Completeness to 2θ limit	0.985	0.997

1 APEX2 v2013.10-0, © 2013, Bruker Analytical X-ray Systems, Madison, WI.

2 COSMO v1.61, © 1999 - 2009, Bruker Analytical X-ray Systems, Madison, WI.

3 SAINT v8.34a, © 1997 - 2013, Bruker Analytical X-ray Systems, Madison, WI.

4 SADABS v2012/1, © 2012, Bruker Analytical X-ray Systems, Madison, WI.

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

6 Oxford Diffraction, Xcalibur CCD System, CrysAlis Software System, Version 171.31, Oxford Diffraction Ltd., 2004.

7 Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *A64*, 112–122.

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