Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Formation of a robust, double-walled LiMOF from an L-shaped di-substituted *N*-heterocyclic adamantane-based ligand.

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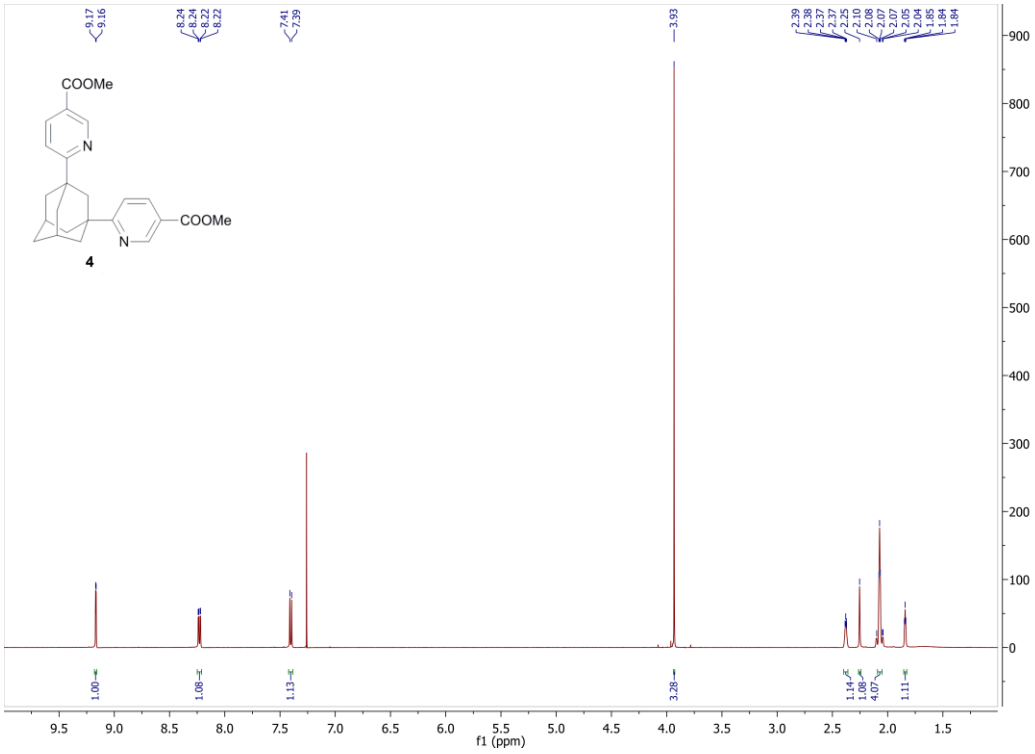
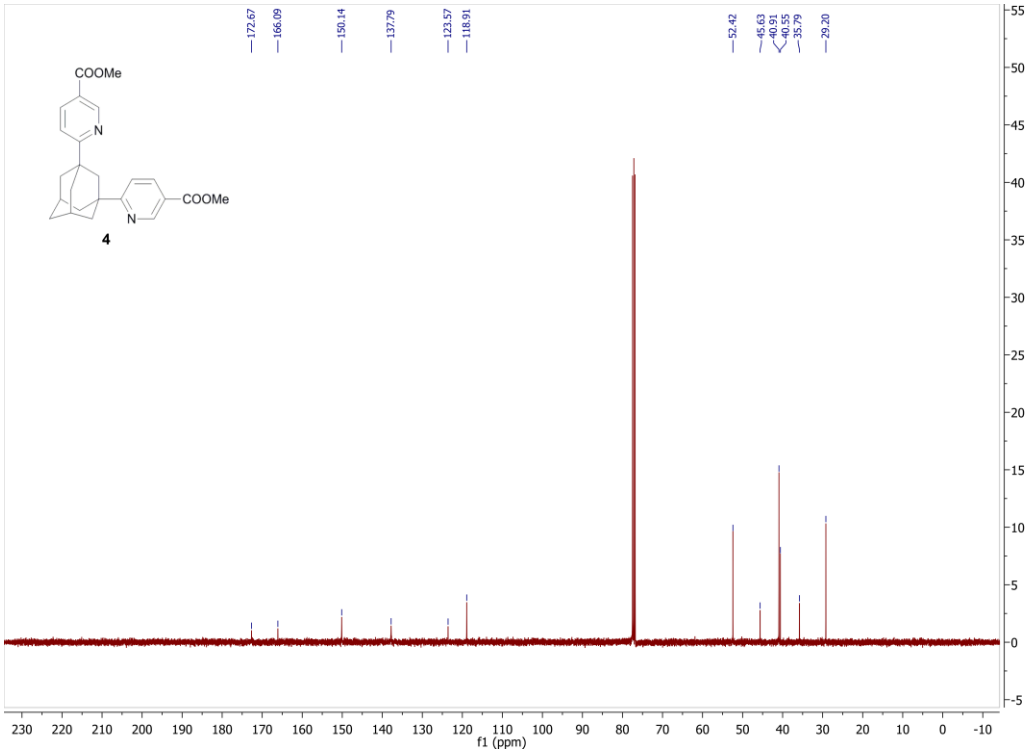
^{1}H NMR and ^{13}C NMR spectra of 1,3-bis(methylpyridine-3'-carboxylate)adamantane (4)

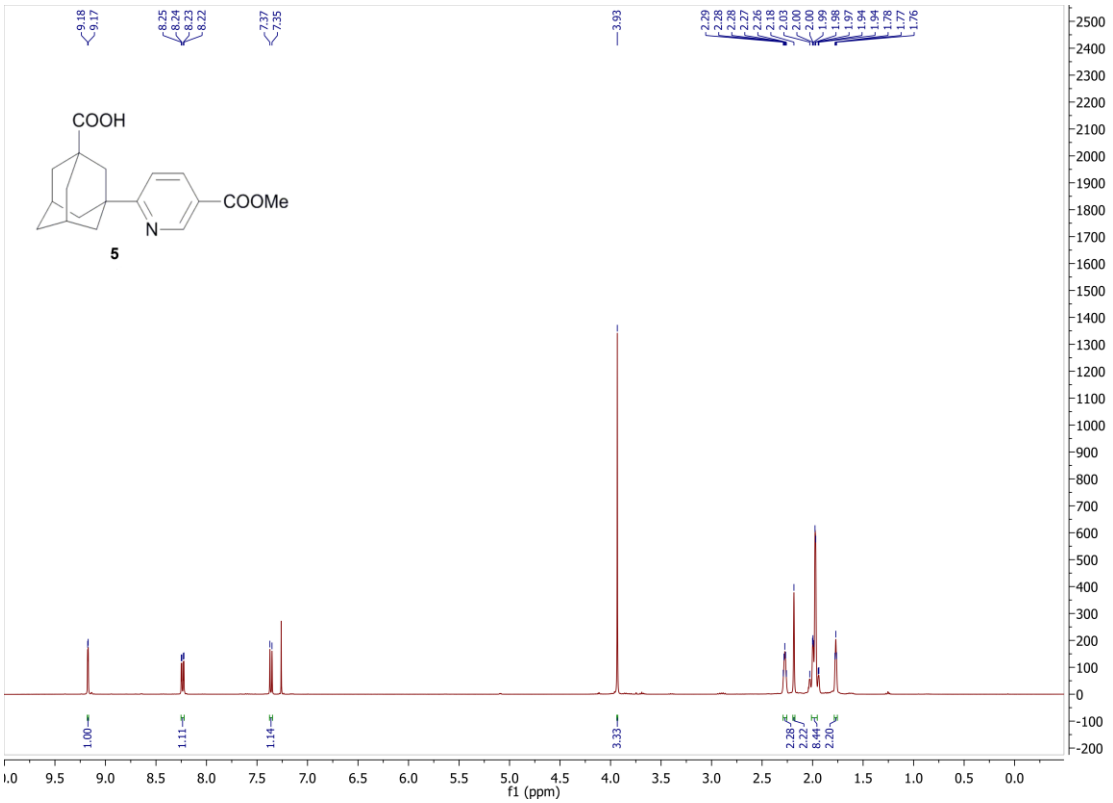


^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K).

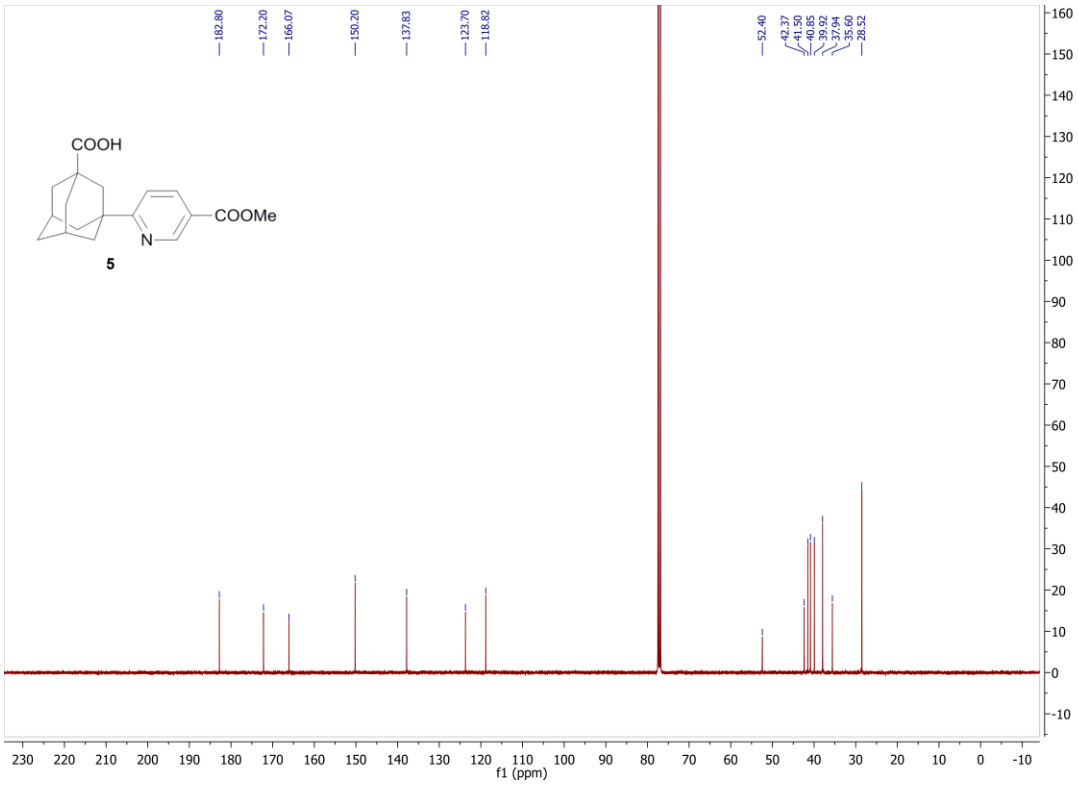


^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K).

^{1}H NMR and ^{13}C NMR spectra of 1-carboxy-3-(methylpyridine-3'-carboxylate)adamantane (5)

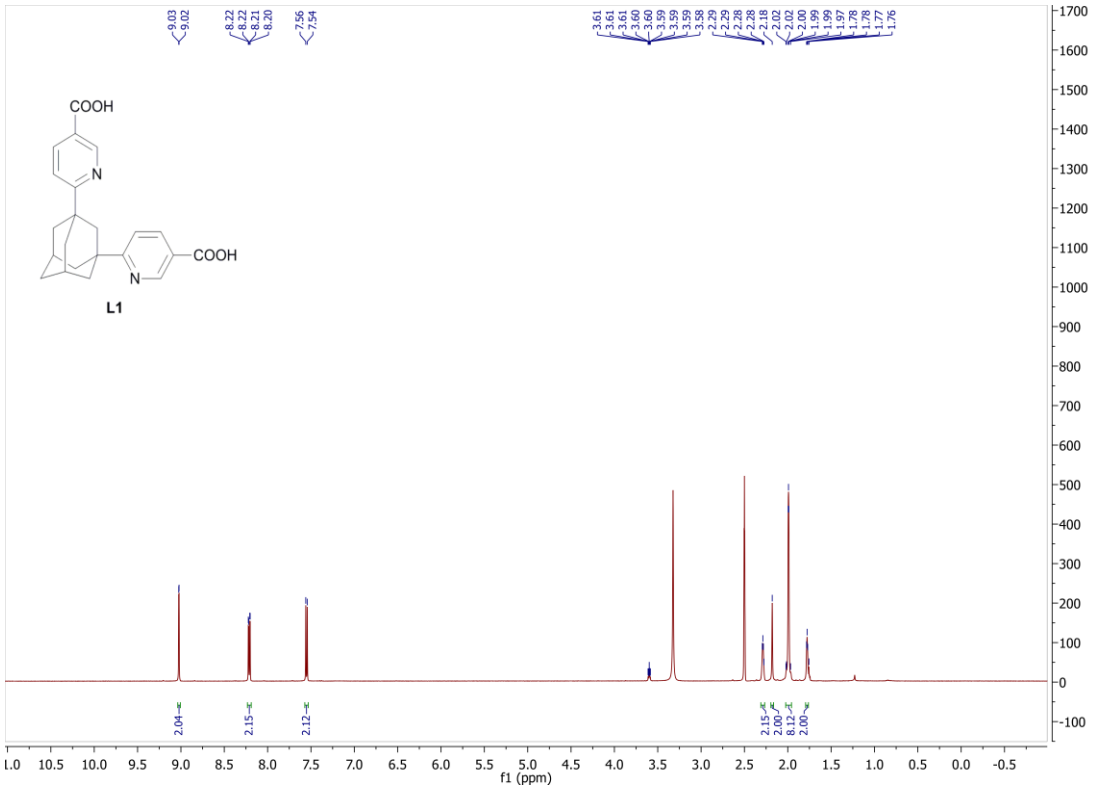


^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K).

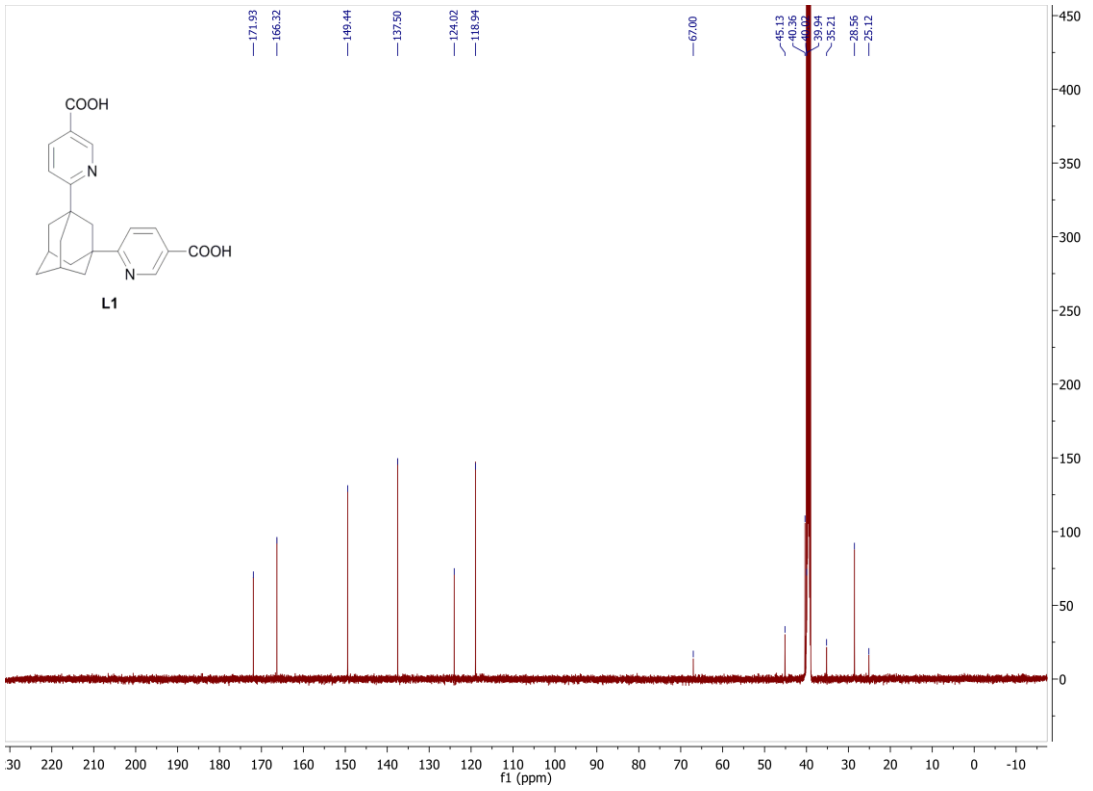


^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K).

^{1}H NMR and ^{13}C NMR spectra of 1,3-bis(3'-carboxypyridine)adamantane (L1)

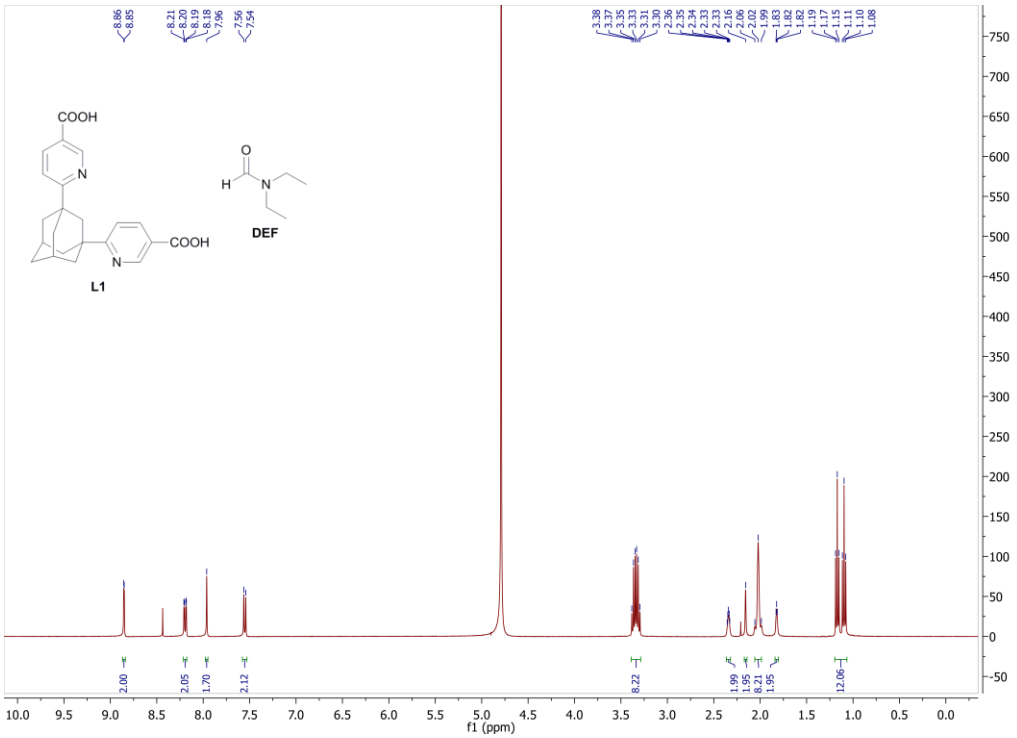


^{1}H NMR spectrum (500 MHz, DMSO-d_6, 298 K). The signals at 3.60 and 1.76 ppm are residual THF peaks.



^{13}C NMR spectrum (125 MHz, DMSO-d_6, 298 K). The signals at 67.0 and 25.1 ppm are residual THF peaks.

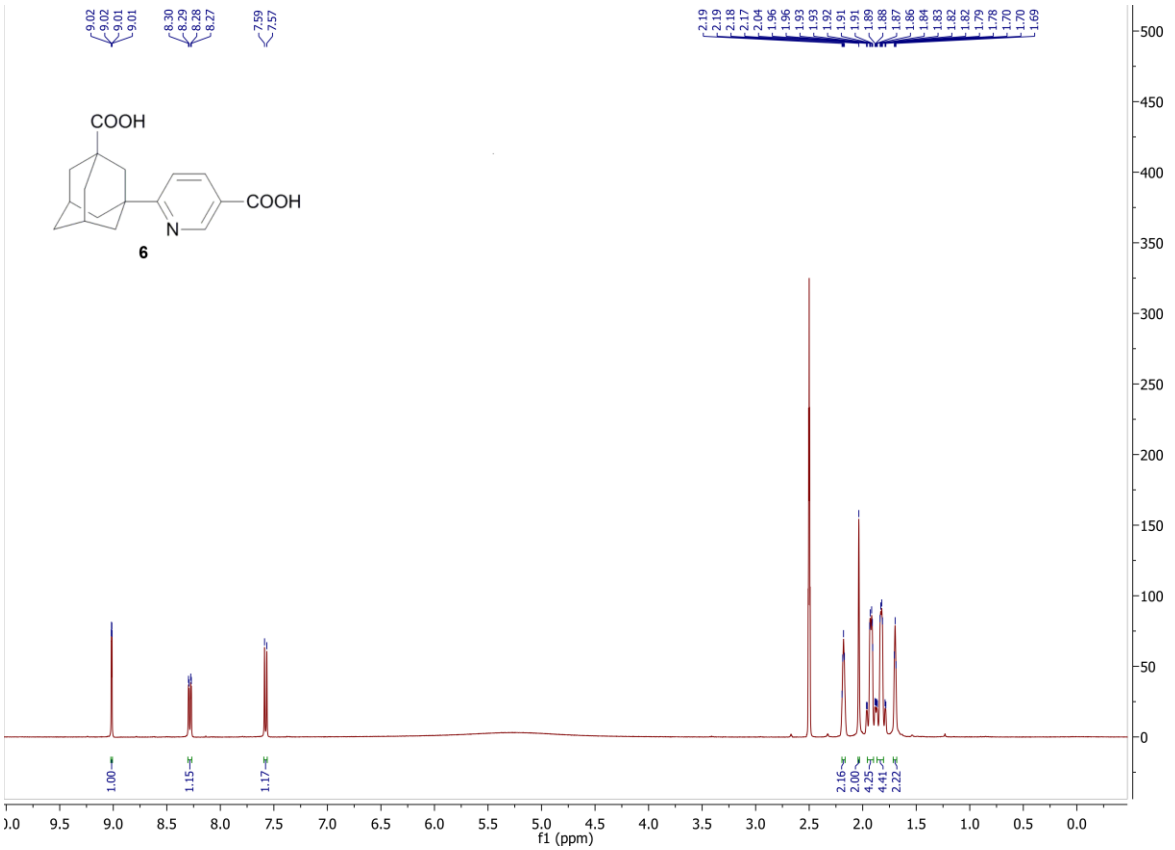
^{1}H NMR spectrum of the digested bulk LiMOF



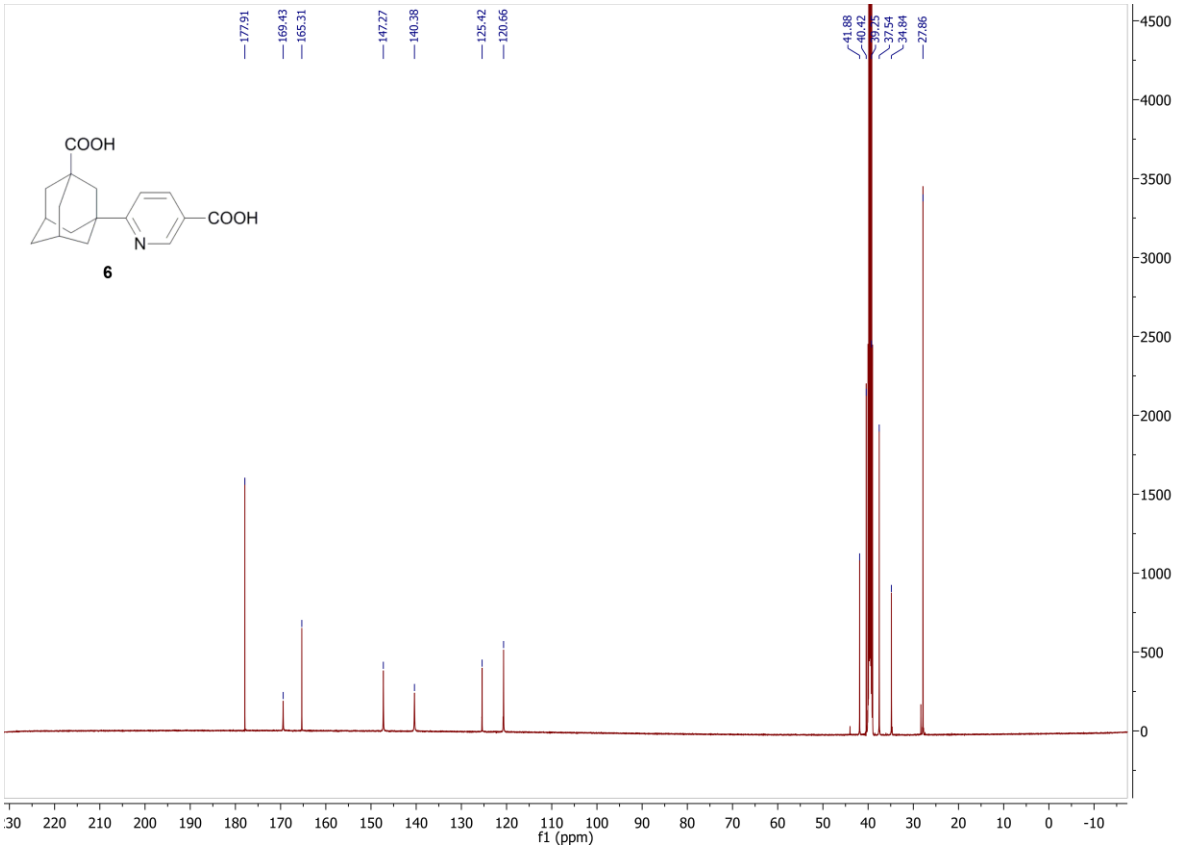
^{1}H NMR spectrum (400 MHz, D_2O/DCl, 298 K).

^{1}H and ^{13}C NMR spectra of 1-carboxy-3-(3'-carboxypyridine)adamantane (6)

1-Carboxy-3-(methylpyridine-3'-carboxylate)adamantane (350 mg, 1.11 mmol) was dissolved in THF (10 mL), to which a 5 M NaOH solution (2 mL) was added and the reaction mixture was left to stir at 50 °C for 16 h. The solution was then concentrated *in vacuo*, dissolved in water (10 mL) and acidified with conc. HCl until a pH of 3 was reached. The resultant precipitate was filtered and dried to afford **6** (313 mg, 94**%**). ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) δ 9.01 (dd, *J* = 2.2, 0.7 Hz, 1H), 8.28 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 2.18 (t, *J* = 3.1 Hz, 2H), 2.04 (s, 2H), 1.97-1.87 (m, 4H), 1.87-1.78 (m, 4H), 1.70 (d, *J* = 3.1 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6, 298 K) δ 177.9, 169.4, 165.3, 147.3, 140.4, 125.4, 120.7, 41.9, 40.4, 39.8, 39.3, 37.5, 34.8, 27.9. ESI-MS (+): *m/z* calcd. for $C_{17}H_{20}NO_4$ [**6** + H^+]: 302.13923; found: 302.13999. IR ν_{max}/cm^{-1}: 2924, 2854, 1727, 1685, 1431, 828, 763, 674.



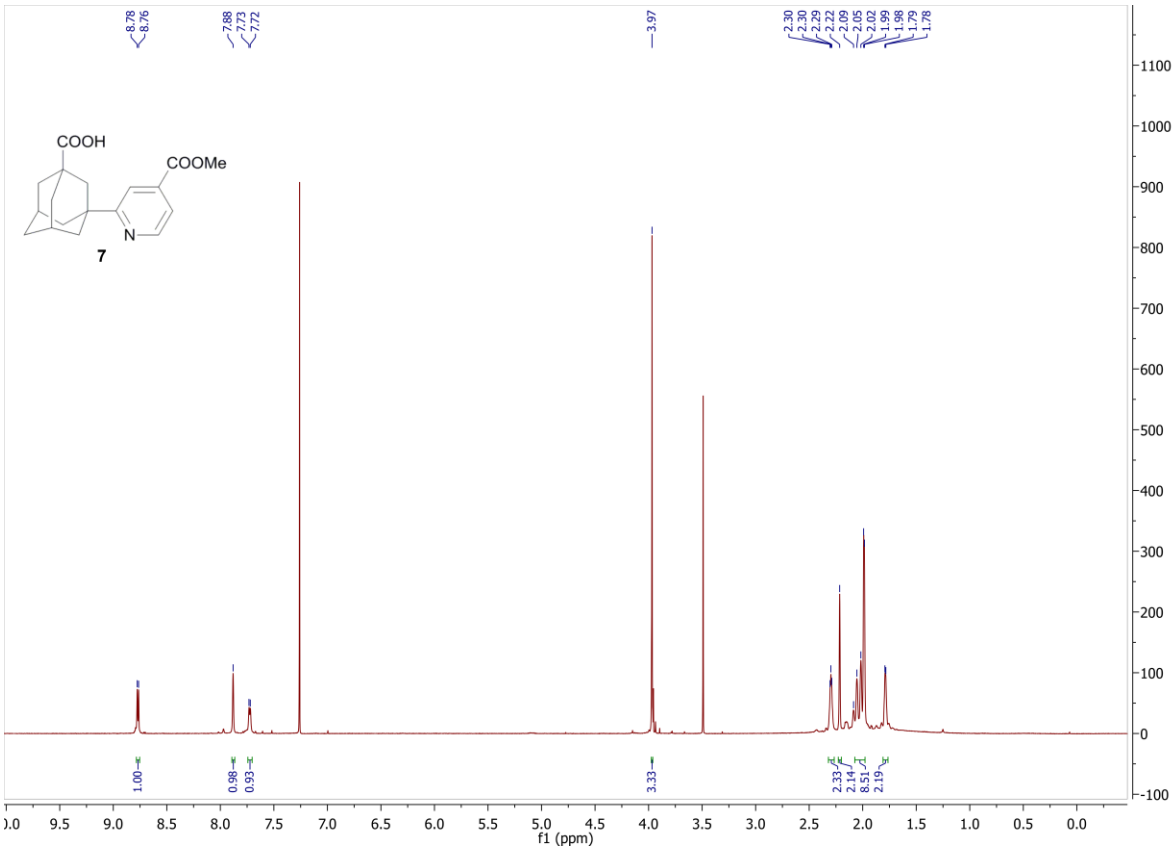
^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K).



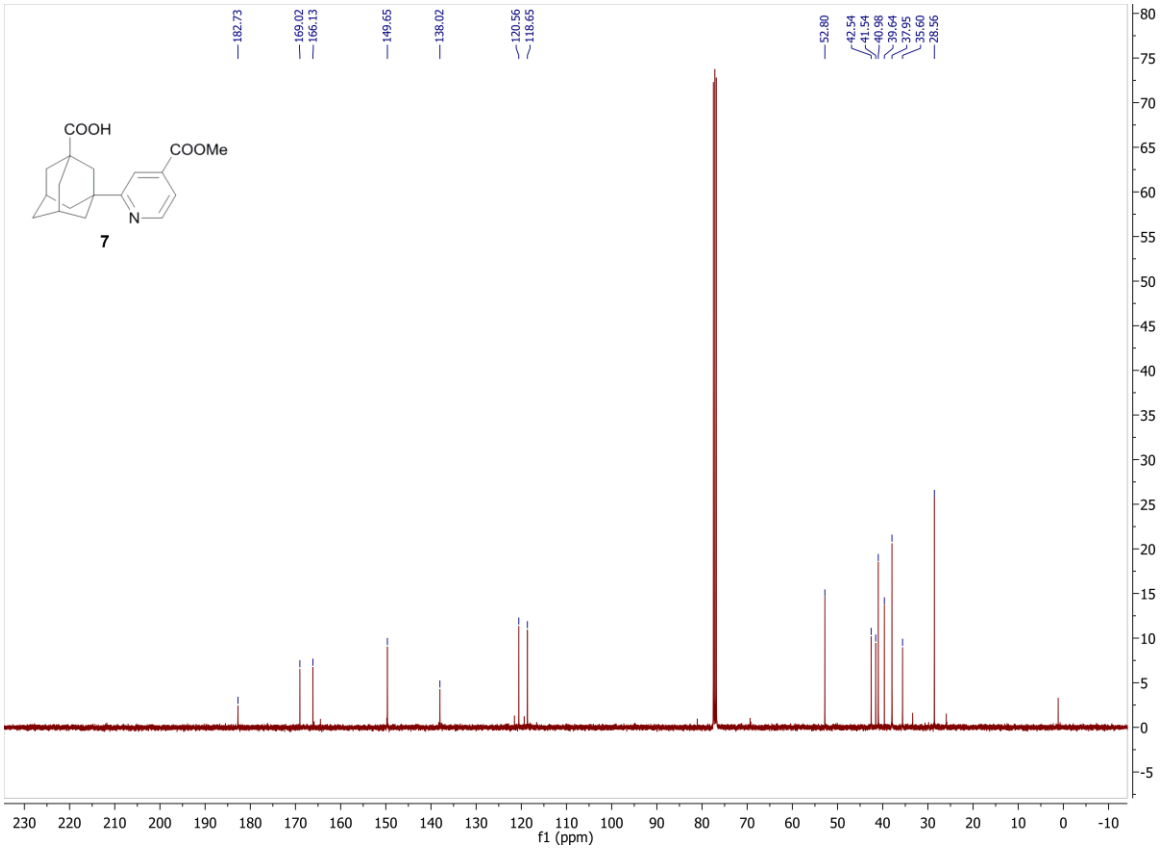
^{13}C NMR spectrum (125 MHz, DMSO-d_6, 298 K).

^{1}H and ^{13}C NMR spectra of 1-carboxy-3-(methylpyridine-4-carboxylate)adamantane (7)

PIFA (0.641 g, 1.49 mmol, 1 equiv.), 1,3-dicarboxyadamantane (1.08 g, 4.82 mmol, 3 equiv.) and methyl isonicotinate (0.617 g, 4.50 mmol, 3 equiv.) were combined in dry THF (40 mL) under an argon atmosphere. The mixture was irradiated using *hv* mercury lamps (254 nm) for 8 h. DCM was added to the reaction mixture and the organic layer was washed with saturated aq. $NaHCO_3$. The organic layer was then dried over Na_2SO_4 and concentrated *in vacuo*. The compound was purified by distillation to remove unreacted methyl isonicotinate and the remaining crude mixture was subjected to column chromatography on silica gel (70:30 PE:EtOAc) to yield **7** (0.61 g, 40%).^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.77 (dd, *J* = 5.0, 0.8 Hz, 1H), 7.88 (s, 1H), 7.72 (dd, *J* = 5.0, 1.5 Hz, 1H), 3.97 (s, 3H), 2.30-2.29 (m, 2H), 2.22 (s, 2H), 2.09-1.99 (m, 8H), 1.79-1.78 (bs, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ 182.7, 169.0, 166.1, 149.6, 138.0, 120.6, 118.6, 52.8, 42.5, 41.5, 41.0, 39.6, 38.0, 35.6, 28.6. ESI-MS (+): *m/z* calcd. for $C_{18}H_{22}NO_4$ [**7** + H^+]: 316.15488; found: 316.15422. IR ν_{max}/cm^{-1}: 2908, 2856, 1731, 1694, 1437, 1421, 1280, 1207, 759, 691.



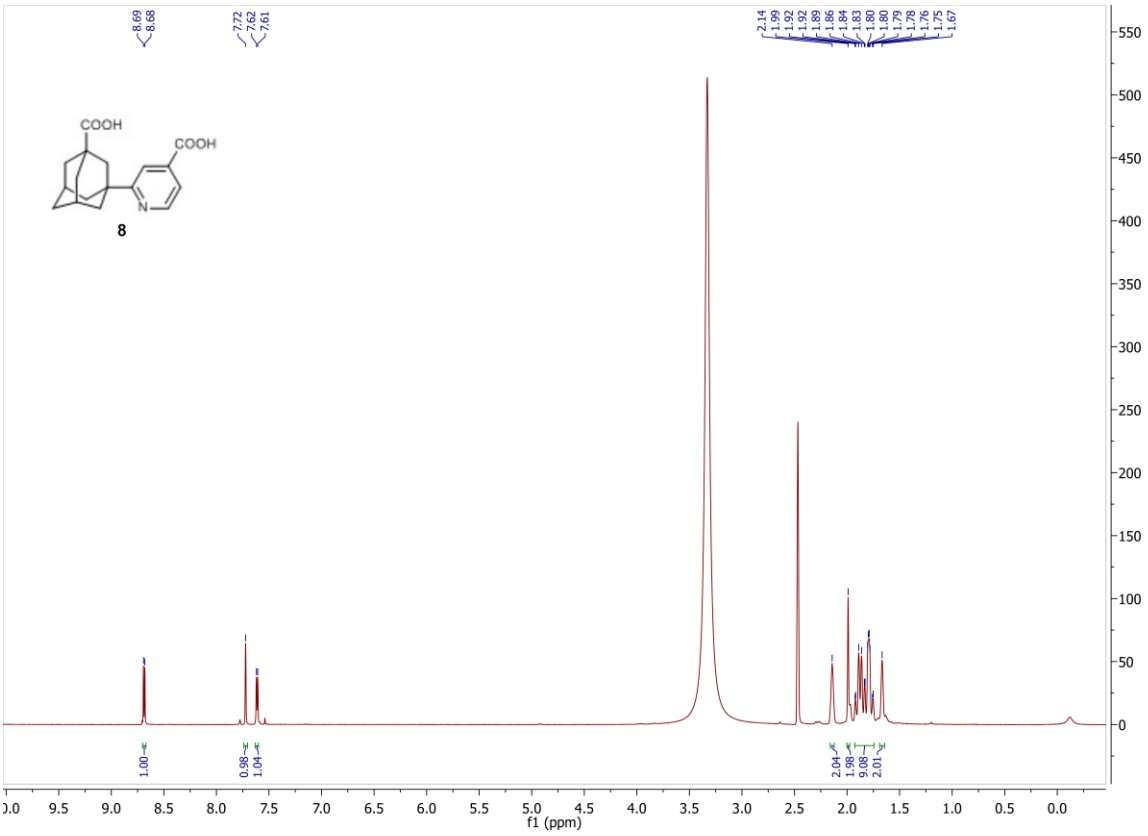
^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K).



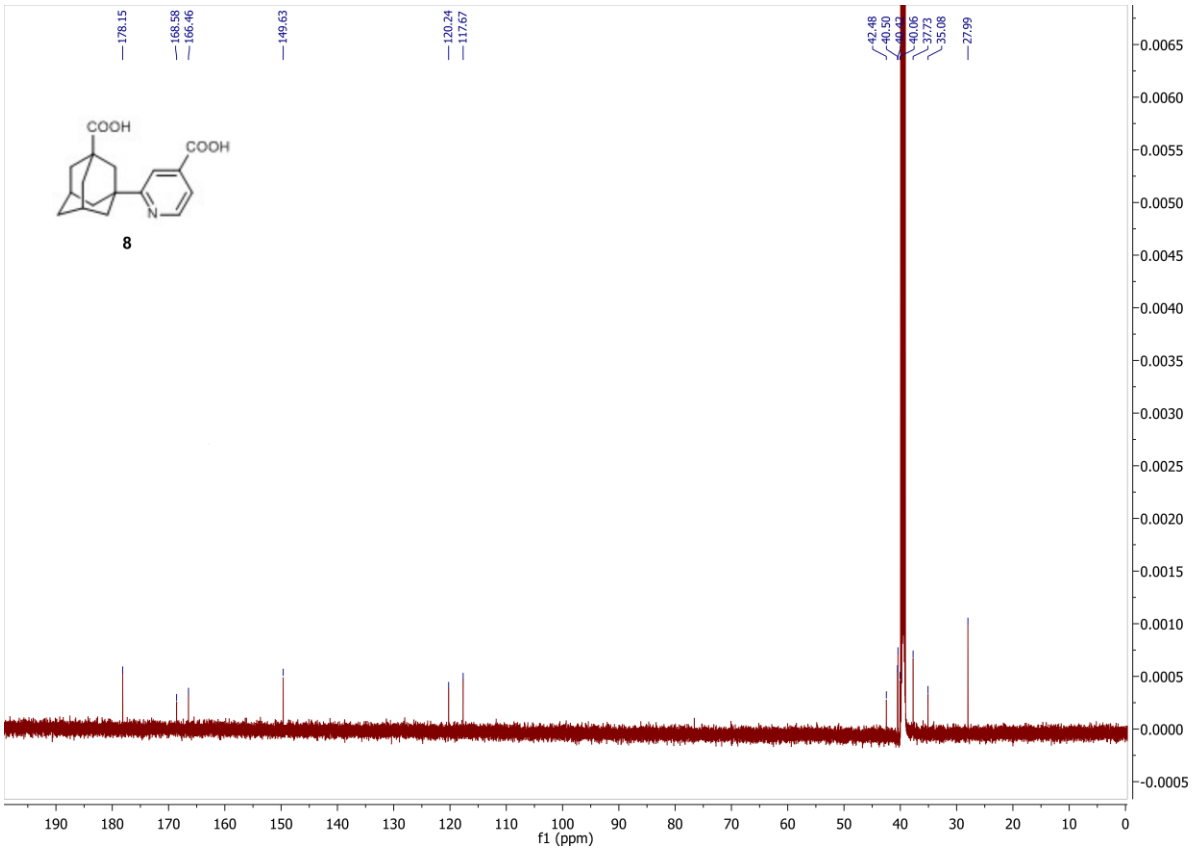
^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K).

^{1}H and ^{13}C NMR spectra of 1-carboxy-3-(4-carboxypyridine)adamantane (8)

1-Carboxy-3-(methylpyridine-4-carboxylate)adamantane (1.01 g, 3.20 mmol) was dissolved THF (10 mL), to which a 5 M NaOH solution (2 mL) was added and the reaction mixture was left to stir at 50 °C for 16 h. The solution was concentrated *in vacuo*, dissolved in water (10 mL) and acidified with conc. HCl until a pH of 3 was reached. The resultant white precipitate was filtered and dried to provide **8** (652 mg, 68%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.69 (d, *J* = 5.0 Hz, 1H), 7.72 (s, 1H), 7.61 (d, *J* = 5.0 Hz, 1H), 2.14 (s, 2H), 1.99 (s, 2H), 1.92-1.86 (m, 4H), 1.84-1.75 (m, 4H), 1.67 (bs, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 178.2, 168.6, 166.5, 149.6, 120.2, 117.7 (2 x C), 42.5, 40.5, 40.4, 40.1, 37.7, 35.1, 28.0. ESI-MS (+): *m/z* calcd. for $C_{17}H_{20}NO_4$ [**8** + H^+]: 302.13923; found: 302.13868. IR ν_{max}/cm^{-1}: 3011, 2852, 1691, 1613, 1450, 814, 769, 674.



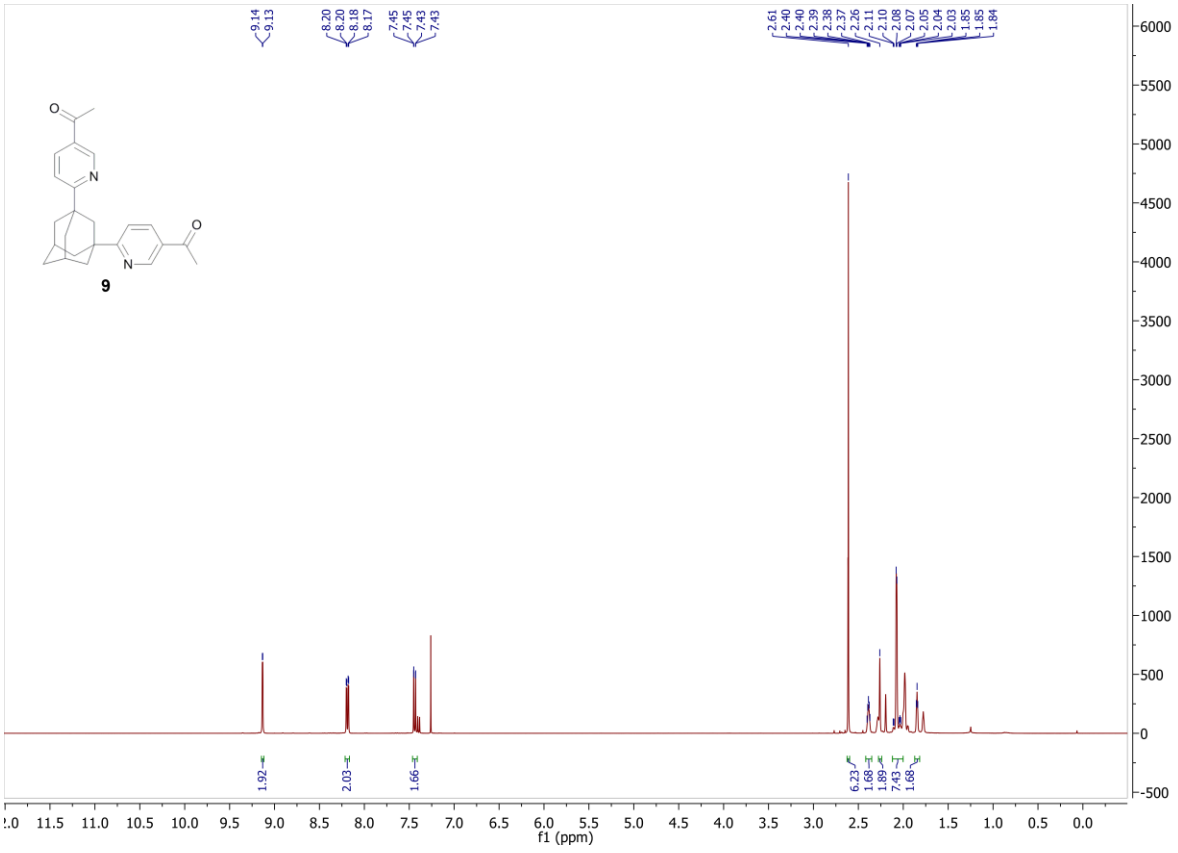
^{1}H NMR spectrum (400 MHz, DMSO-d_6, 298 K).



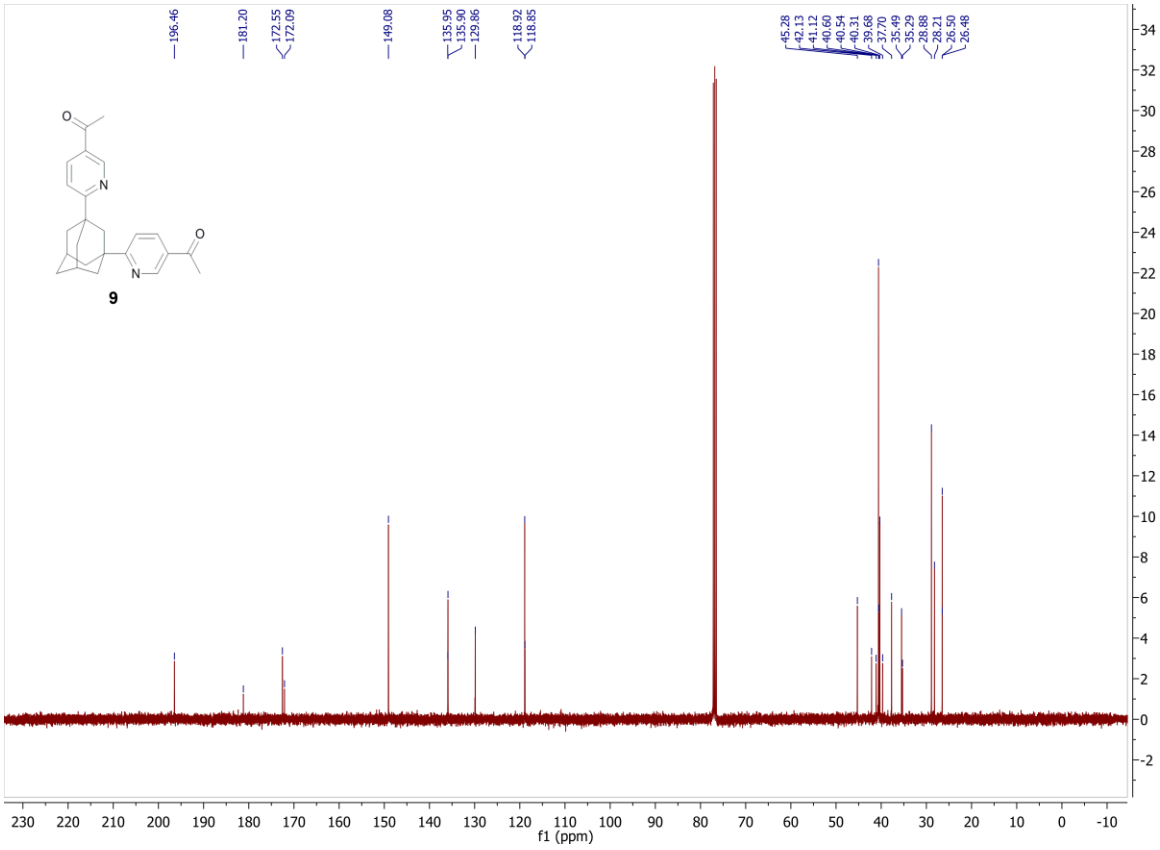
^{13}C NMR spectrum (600 MHz, DMSO-d_6, 298 K).

^{1}H and ^{13}C NMR spectra of 1,3-*bis*(3'-acetylpyridine)adamantane (9)

PIFA (1.32 g, 2.97 mmol, 2 equiv.), 1,3-dicarboxyadamantane (1.02 g, 4.55 mmol, 3 equiv.) and 3-acetylpyridine (1.10 g, 1 mL, 9.10 mmol, 6 equiv.) were combined in dry THF (40 mL) under an argon atmosphere. The mixture was irradiated using *hv* mercury lamps (254 nm) for 8 h. At 8 h, DCM was added to the reaction mixture and the organic layer was washed with saturated aq. $NaHCO_3$. The organic layer was then dried over Na_2SO_4 and concentrated *in vacuo*. The crude reaction mixture was purified by column chromatography on silica gel (80:20 PE:EtOAc) to afford **9** (0.61 g, 36%). Calcd for $C_{25}H_{30}N_2O_2$·1MeOH: C, 73.9 H, 7.4 N, 6.9. Found: C, 73.9, H, 7.1 N, 6.7.^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (d, *J* = 2.1 Hz, 2H), 8.19 (dd, *J* = 8.4, 2.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 2.61 (s, 6H), 2.40-2.37 (m, 2H), 2.26 (s, 2H), 2.08-2.05 (m, 8H), 1.85-1.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 172.5, 149.1, 136.0, 129.9, 118.9, 45.3, 40.6, 40.3, 35.5, 28.9, 26.5. ESI-MS (+): *m/z* calcd. for $C_{24}H_{27}N_2O_2$ [**9** + H^+]: 375.2073; found: 375.2062. IR ν_{max}/cm^{-1}: 2849, 1702, 1679, 1450, 1376, 825, 761.



^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K). 30% contamination of mono-substituted 1-carboxy-3-(3'-acetylpyridine)adamantane in spectra, as determined by NMR.



^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K). 30% contamination of mono-substituted 1-carboxy-3-(3'-acetylpyridine)adamantane in spectra, as determined by NMR.

1.2 X-ray crystal structures with an ellipsoid view

1.2.1 X-ray crystal structure of compound 4

The slow evaporation of **4** from 80:20 petroleum ether:EtOAc provided colourless X-ray quality crystals. Compound **4** crystallized in the triclinic space group *P*-1. The asymmetric unit comprised of one complete **4** molecule (Figure 1).

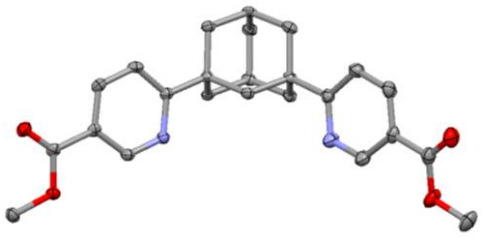


Figure 1: View of the contents of the asymmetric unit, comprising of one complete **4** molecule. Hydrogens were omitted. Colour coding: carbon (grey), nitrogen (purple) and oxygen (red).

1.2.2 X-ray crystal structure of compound 5

The slow evaporation of **5** from 70:30 petroleum ether:EtOAc provided colourless X-ray quality crystals. Compound **5** crystallized in the triclinic space group *P*-1. The asymmetric unit comprised of one complete **4** molecule (Figure 2).

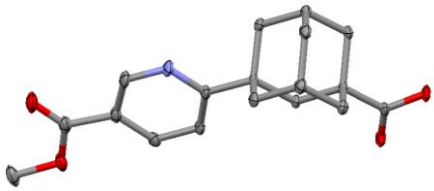


Figure 2: View of the contents of the asymmetric unit, comprising of one complete **5** molecule. Hydrogens were omitted. Colour coding: carbon (grey), nitrogen (purple) and oxygen (red).

1.2.3 X-ray crystal structure of compound 8

The diffusion of diethyl ether into a solution of **8** in ethanol provided colourless X-ray quality crystals. Compound **8** crystallized in the monoclinic space group $P2_1/c$. The asymmetric unit comprised of one complete **8** molecule (Figure 3).

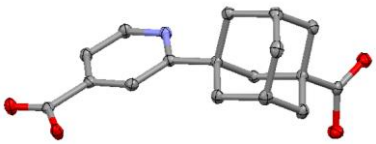


Figure 3: View of the contents of the asymmetric unit, comprising of one complete **8** molecule. Hydrogens were omitted. Colour coding: carbon (grey), nitrogen (purple) and oxygen (red).

1.2.4 X-ray crystal structure of compound 9

The diffusion of diethyl ether into a solution of **9** in ethanol provided colourless X-ray quality crystals. Compound **9** crystallized in the orthorhombic space group *Pnma*. The asymmetric unit comprised of one half of a **9** molecule, with the other half generated by a mirror plane (Figure 4).

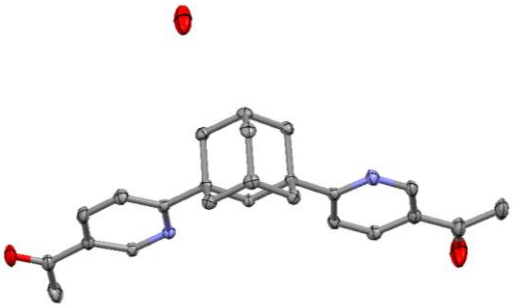


Figure 4: View of a water molecule and complete **9** molecule generated through a mirror plane. Hydrogens were omitted. Colour coding: carbon (grey), nitrogen (purple) and oxygen (red).

1.2.5 X-ray crystal structure of compound L1

The diffusion of diethyl ether into a solution of **L1** in methanol afforded colourless X-ray quality crystals. Compound **L1** crystallized in the monoclinic space group *C*2/*c*. The asymmetric unit comprised of one half of a **L1** molecule, with the other half generated through a 2-fold symmetry axis (Figure 5).

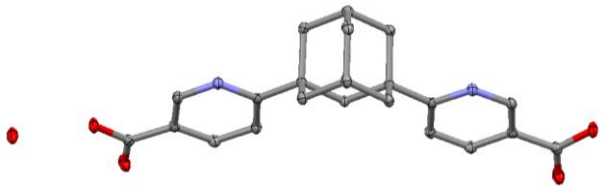


Figure 5: View of a water molecule and complete **L1** molecule generated through a 2-fold symmetry axis. Hydrogens were omitted. Colour coding: carbon (grey), nitrogen (purple) and oxygen (red).

1.2.6 X-ray crystal structure of Cu-L1

The **L1** ligand (50.1 mg, 0.133 mmol) and $Cu(BF4)_2 \cdot H_2O$ (63.2 mg, 0.264 mmol, 2 equiv.) were dissolved in hot MeOH (15 mL) and the solution was sonicated for 5 mins. To this, DEF (5 mL) was added and the solution was left at 80 °C for 7-10 d to afford **Cu-L1** blue block-like crystals (Figure 6).

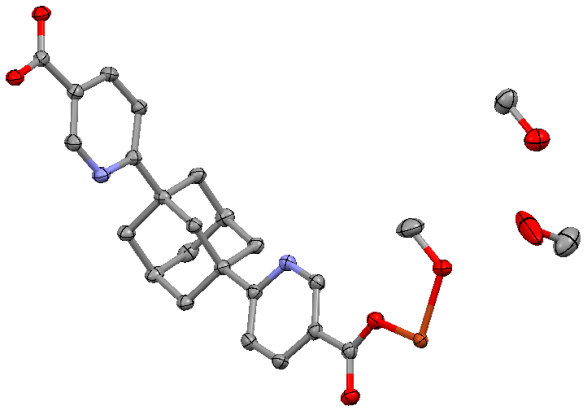


Figure 6: View of **Cu-L1** asymmetric unit. Colour coding: carbon (grey), nitrogen (purple), oxygen (red) and copper (orange).

1.2.7 X-ray crystal structure of Zn-L1

The **L1** ligand (49.9 mg, 0.133 mmol) and $Zn(CF_3SO_3)_2$ (48.2 mg, 0.132 mmol, 1 equiv.) were dissolved in hot MeOH (15 mL) and the solution was sonicated for 5 mins. To this, DEF (5 mL) was added and the solution was left at 80 °C for 10-15 d to afford **Zn-L1** as small colourless crystalline rhomboids. The asymmetric unit consisted of one-half of a deprotonated **L1** ligand, one half of a Zn(II) cation and one coordinated methanol molecule. The complete **L1** ligand was generated by a mirror plane (Figure 7).

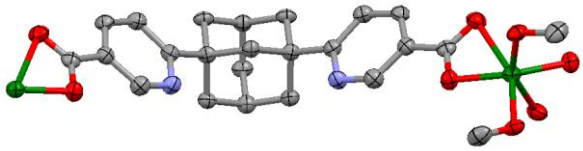


Figure 7: View of **Zn-L1** key components. The complete **L1** ligand generated by a mirror plane, and a 2-fold symmetry axis runs through the Zn cation. Colour coding: carbon (grey), nitrogen (purple), oxygen (red) and zinc (green).

1.2.8 X-ray crystal structure of LiMOFs

The **L1** ligand (50.6 mg, 0.133 mmol) and $LiOH{\cdot}H_2O$ (49.8 mg, 1.18 mmol, 9 equiv.) were dissolved in hot MeOH (15 mL) and the solution was sonicated for 15 mins. To this, DEF (5 mL) was added and the solution was left at 85 °C for 24-72 h to afford **LiMOF** as large colourless crystalline needles.

1.2.8.1 X-ray crystal structure LiMOF12

The asymmetric unit consisted of two deprotonated **L1** ligands, four Li(I) cations, two uncoordinated water molecules and n*solvent* molecules (Figure 8).

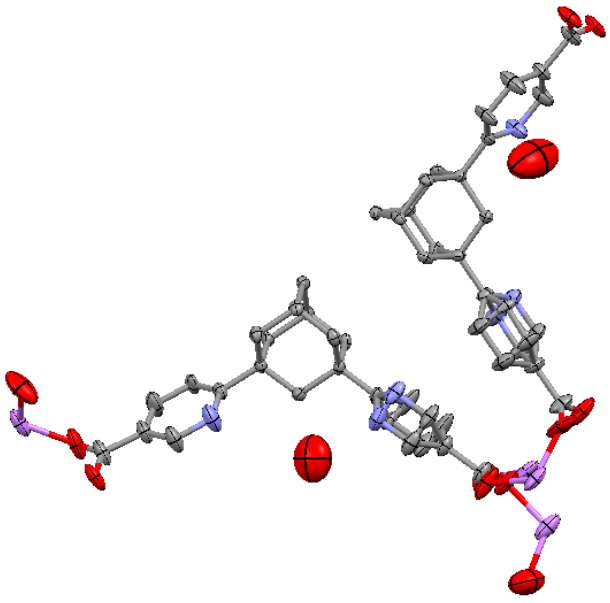


Figure 8 View of the contents of **LiMOF12** asymmetric unit. Colour coding: carbon (grey), nitrogen (purple), oxygen (red) and lithium (pink).

1.2.8.2 X-ray crystal structure LiMOF30

The asymmetric unit was large, containing nine deprotonated **L1** ligands, two one-halves of deprotonated **L1** ligands, 18 Li(I) cations, four uncoordinated water molecules, two coordinated DEF molecules and n*solvent* molecules (Figure 9).

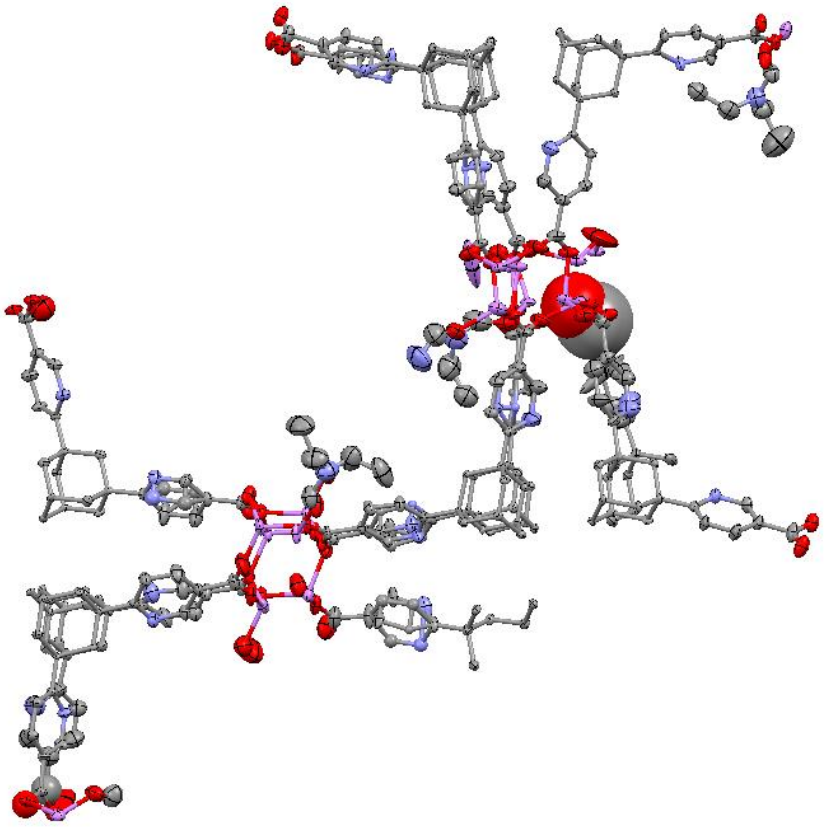


Figure 9 View of the contents of **LiMOF30** asymmetric unit. Colour coding: carbon (grey), nitrogen (purple), oxygen (red) and lithium (pink).

1.2.8.3 X-ray crystal structure LiMOF50

The asymmetric unit consisted of eight deprotonated **L1** ligands, 16 Li(I) cations, two coordinated DEF molecules and n*solvent* molecules (Figure 10).

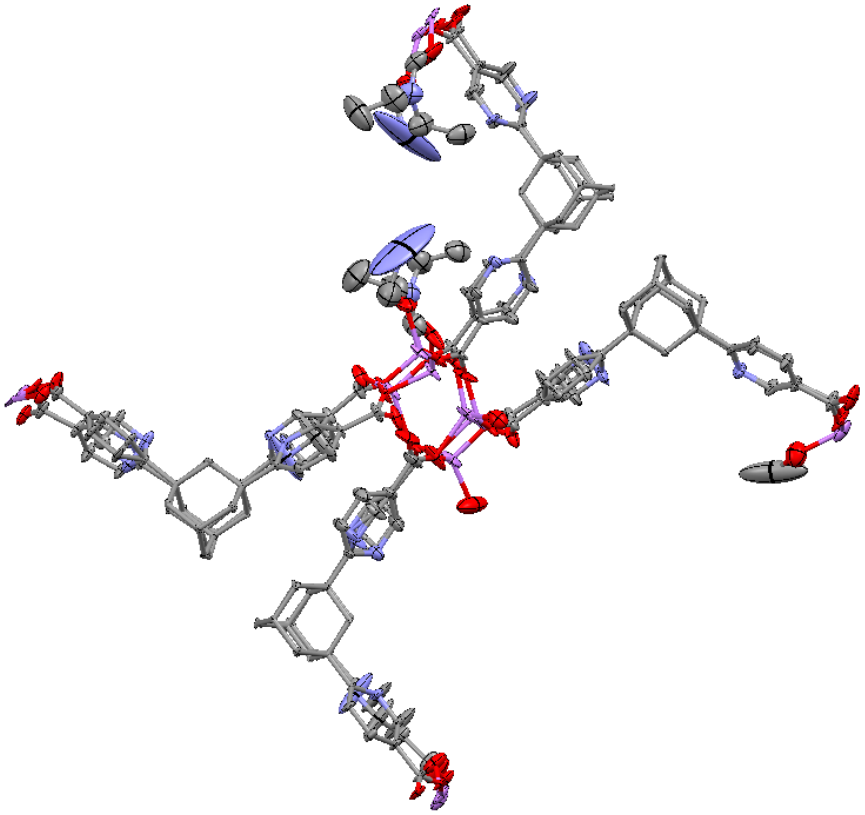


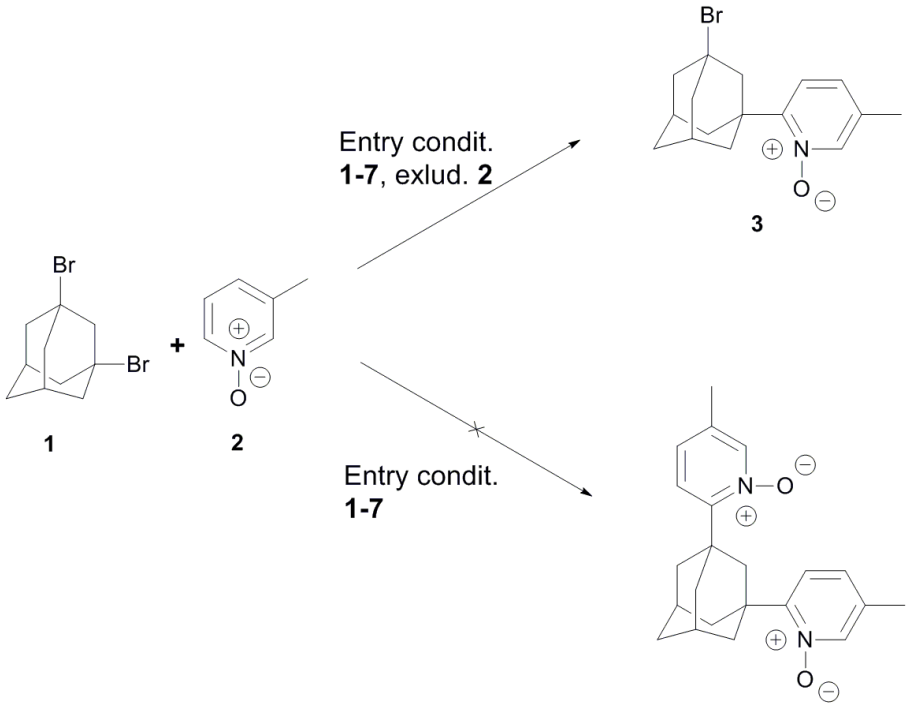
Figure 10 View of the contents of **LiMOF50** asymmetric unit. Colour coding: carbon (grey), nitrogen (purple), oxygen (red) and lithium (pink).

1.3 Crystallography Information for compounds 8 and 9 (not included in main text)

Structure	**8**	**9**
Formula	$C_{17}H_{19}NO_4$	$C_{24}H_{26.42}N_2O_{2.21}$
Formula weight	301.33	378.25
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	*Pnma*
***a*/Å**	14.9191(2)	11.2609(4)
***b*/Å**	7.49250(10)	6.7138(3)
***c*/Å**	13.0292(2)	25.8248(8)
α/°	90	90
β/°	94.0620(10)	90
γ/°	90	90
***V*/Å^3**	1452.76(4)	1952.44(13)
Z	4	4
***T*/K**	100.01(10)	100.02(10)
μ/mm^{-1}	0.807	0.654
Total reflections	13894	9991
Unique reflections (R_{int})	2851 (0.0198)	1954 (0.0391)
R_1 indices [$I>2\sigma(I)$]	0.0334	0.0416
ω*R*2 (all data)	0.0853	0.1172

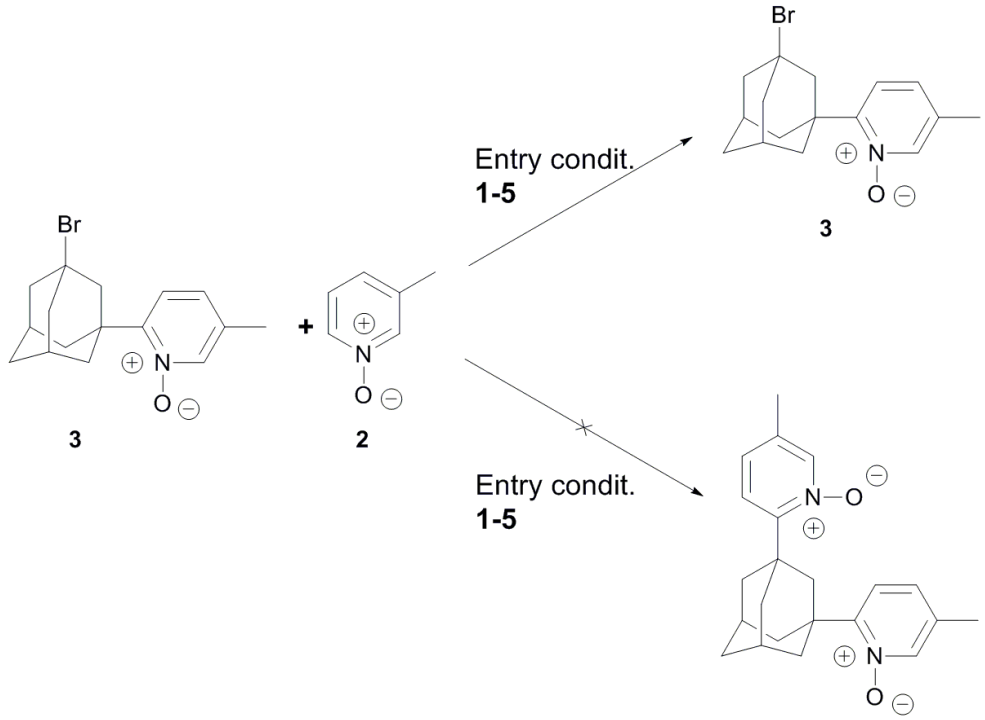
1.4 Reaction conditions trailed towards the synthesis of 1,3-bis(3'-methylpyridine-*N*-oxide)adamantane.

All entries were conducted using the same ratio of 1,3-dibromoadamantane **1** and 3-methylpyridine-*N*-oxide **2** (1:4, respectively). The table showcases the different Pd-catalysts, solvent, time and Pd-catalyst mol % attempted. There was no significant change in yield when conditions were altered, and there was no evidence of a second coupling reaction occurring.



Entry	Pd-Catalyst	Mol % of Pd-catalyst	Solvent	Time (hr)	Temp (°C)	Product/yield
1	$Pd(OAc)_2dppf$	5	Toluene	12	100	**3**, 59%
2	$Pd(PPh_3)_4$	5	Toluene	12	100	No reaction
3	$Pd(OAc)_2(TTBP)_2$	5	Toluene	12	100	**3**, 53%
4	$Pd(OAc)_2dppf$	10	Toluene	12	100	**3**, 49%
5	$Pd(OAc)_2(TTBP)_2$	10	Toluene	12	100	**3**, 45%
6	$Pd(OAc)_2dppf$	10	Xylene	24	130	**3**, 40%
7	$Pd(OAc)_2(TTBP)_2$	10	Xylene	24	130	**3**, 35%

The final attempt to synthesise 1,3-*bis*(3'-methylpyridine-*N*-oxide)adamantane, was to re-subject the accumulated **3** to selected reaction conditions described above. Treatment of **3** with various Pd-catalysts, of varying mol %, for 12-24 hours only returned unreacted starting material **3**. All entries were conducted using the same ratio of mono-substituted **3** and 3-methylpyridine-*N*-oxide **2** (1:4, respectively) in toluene at 100 °C.



Entry	Pd-Catalyst	Mol % of Pd-catalyst	Time (hr)	Product
1	$Pd(OAc)_2dppf$	5	12	**3**
2	$Pd(PPh_3)_4$	5	12	**3**
3	$Pd(OAc)_2(TTBP)_2$	5	12	**3**
4	$Pd(OAc)_2dppf$	10	24	**3**
5	$Pd(OAc)_2(TTBP)_2$	10	24	**3**

1.5 Synthesis and X-ray structure solution details of LiMOF analogues

The solvothermal reaction of $LiOH{\cdot}H_2O$ and **L1** in a solvent mixture of 1:3 v/v DEF and MeOH at 85 °C provided **LiMOF** as large crystalline needles. Numerous data sets were collected and confirmed three crystallographically different but topologically analogous frameworks: **LiMOF12**, **LiMOF30** and **LiMOF50**.

1.5.1 LiMOF12 structure solution details

In comparison to the LiMOF30 and LiMOF50 frameworks, the LiMOF12 framework behaved quite well during solving and refinement. The asymmetric unit consisted of two deprotonated **L1** ligands, four Li(I) cations, two uncoordinated water molecules and n*solvent* molecules. Two pyridine rings, N2 (N2A) and N3 (N3A), were each disordered over two positions with site occupancies of 0.61 (0.39) and 0.66 (0.34), respectively. All nitrogens pointed into the channels, and the disorder did not alter this. The SQUEEZE routine of PLATON was applied to remove any unbound DEF molecules within the channels of the framework. The SQUEEZE routine resulted in an approximate 53% decrease of the R_1 value, reducing from 16.99 to 8.93%. In a total void volume of 6434 $Å^3$, 1345 electrons were SQUEEZE'd from the structure, equating to 168 electrons per unit cell (total electron count/Z = 1345/8 = 168). The SQUEEZE'd electron density was attributed to three DEF molecules, each molecule accounting for 56 electrons, equivalent to 1.5 DEF molecules per **L1** ligand.

1.5.2 LiMOF30 structure solution details

Multiple **LiMOF30** data sets were collected, however, the quality of the data was very poor. Attempts were made to increase the quality of the crystals, by varying the solvent v/v ratio, excluding the use of MeOH, variation in temperature, and/or using a controlled environment (oven) rather than an oil bath, but the quality of the obtained **LiMOF** crystals remained the same. Analysis of the crystal data suggested the centrosymmetric space group *C*2/*m*. However, the structure could not be adequately solved in this space group. For this reason, the structure was solved in the non-centrosymmetric space group *C*2. The asymmetric unit was large, containing nine deprotonated **L1** ligands, two one-halves of deprotonated **L1** ligands, 18 Li(I) cations, four uncoordinated water molecules, two coordinated DEF molecules and n*solvent* molecules. Four pyridine rings, N13 (N13A), N3 (N3A), N2 (N2A) and N12 (N12A), were each disordered over two positions with site occupancies of 0.68 (0.32), 0.57 (0.43), 0.71 (0.29) and 0.85 (0.15), respectively. The disorder on these rings was extensive and for this reason the hydrogens were intentionally left off and the disordered component was kept isotropic, otherwise it would not hold up in refinement. The SQUEEZE routine of PLATON was applied to remove any unbound DEF molecules within the channels of the framework. The SQUEEZE routine resulted in a decrease of the R_1 value from 25.2 to 19.5%. In a total void volume of 14931 Å, 3144 electrons were SQUEEZE'd from the unit cell, equating to 786 electrons per asymmetric unit (total electron count/Z = 3144/4 = 786). The SQUEEZE'd electron density was attributed to 14 DEF molecules (786/56 = 14); equivalent to 1.4 DEF molecules per **L1** ligand (14/10 = 1.4), which was very similar to the results obtained for the previously discussed analogue. Post SQUEEZE, four coordinated DEF molecules were identified, however, only two of the four were able to be satisfactorily modelled. Numerous attempts were made to model the additional DEF

molecules, including DFIX, ISOR commands and remaining isotropic, however, each time the refinement became unstable. The decision was made to keep the oxygen and/or nitrogen atoms associated with the additional coordinated DEF molecules, but even then the thermal parameters were poor which showcases the extent of the disorder. The hydrogens have been deliberately left off the disorder components and the atoms have been left isotropic, otherwise the structure would not hold up in refinement.

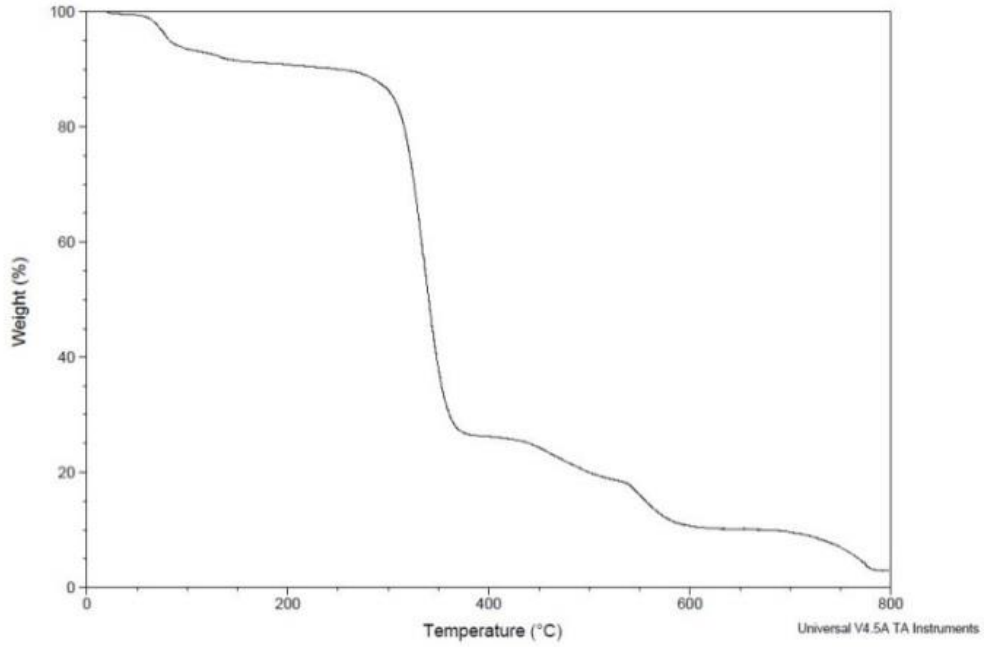
1.5.3 LiMOF50 structure solution details

Multiple **LiMOF50** data sets were collected, however, the quality of the data was again very poor. The structure was refined in the centrosymmetric space group *C*2/*c* and the asymmetric unit consisted of eight deprotonated **L1** ligands, 16 Li(I) cations, two coordinated DEF molecules and n*solvent* molecules. Four pyridine rings, N13 (N13A), N3 (N3A), N2 (N2A) and N12 (N12A), were each disordered over two positions with site occupancies of 0.68 (0.32), 0.57 (0.43), 0.71 (0.29) and 0.85 (0.15), respectively. The PLATON SQUEEZE routine provided a slight decrease of the R_1 value from 21.7 to 20.0%. In a total void volume of 19692 $Å^3$, 3108 electrons were SQUEEZE'd from the unit cell, equating to 388.5 electrons per asymmetric unit (total electron count/Z = 3108/8 = 388.5). The SQUEEZE'd electron density was attributed to approximately seven DEF molecules (388.5/56 = 6.94); equivalent to approximately 1 DEF molecule per ligand (6.94/8 = 0.87), still consistent with the values obtained for both **LiMOF12** and **LiMOF30**. Post SQUEEZE, four coordinated DEF molecules were identified, however, only two of the four were able to be satisfactorily modelled. Numerous attempts were made to model the additional DEF molecules, including DFIX, ISOR commands and remaining isotropic, however, each time the refinement became unstable. The decision was made to keep the oxygen and/or nitrogen atoms associated with the additional coordinated DEF molecules, but even then the thermal parameters were poor which showcases the extent of the disorder. Furthermore, the final structure was left with a few high residual electron density peaks associated with the remaining parts of the partially accounted for coordinated DEF molecules.

1.6 Thermal gravimetric analysis (TGA)

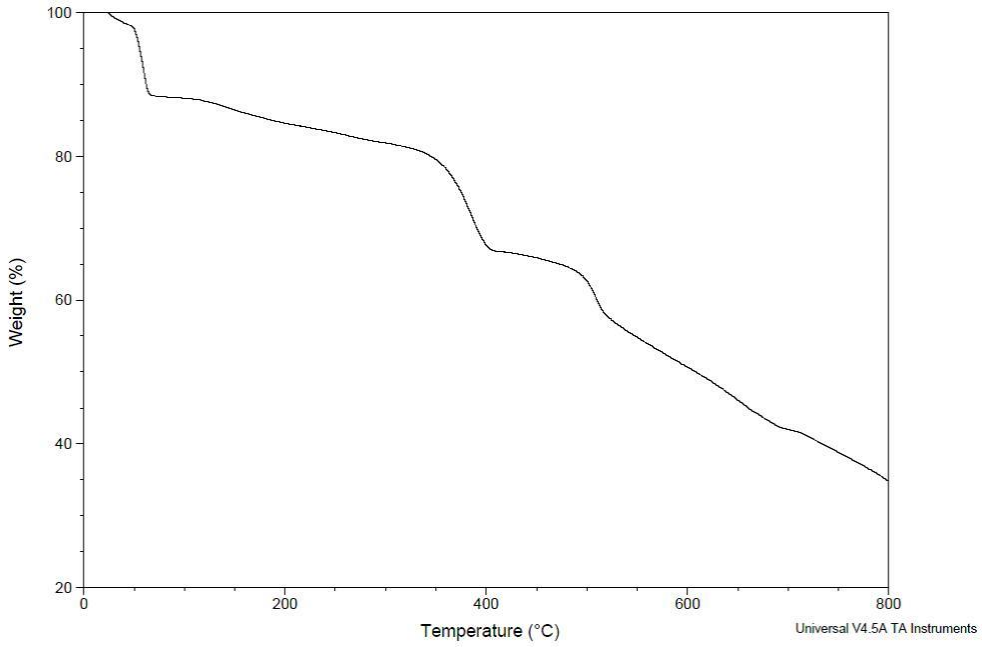
1.6.1 L1 ligand

Thermal gravimetric analysis (TGA) results of the native **L1** ligand indicated stability up to 250 °C.



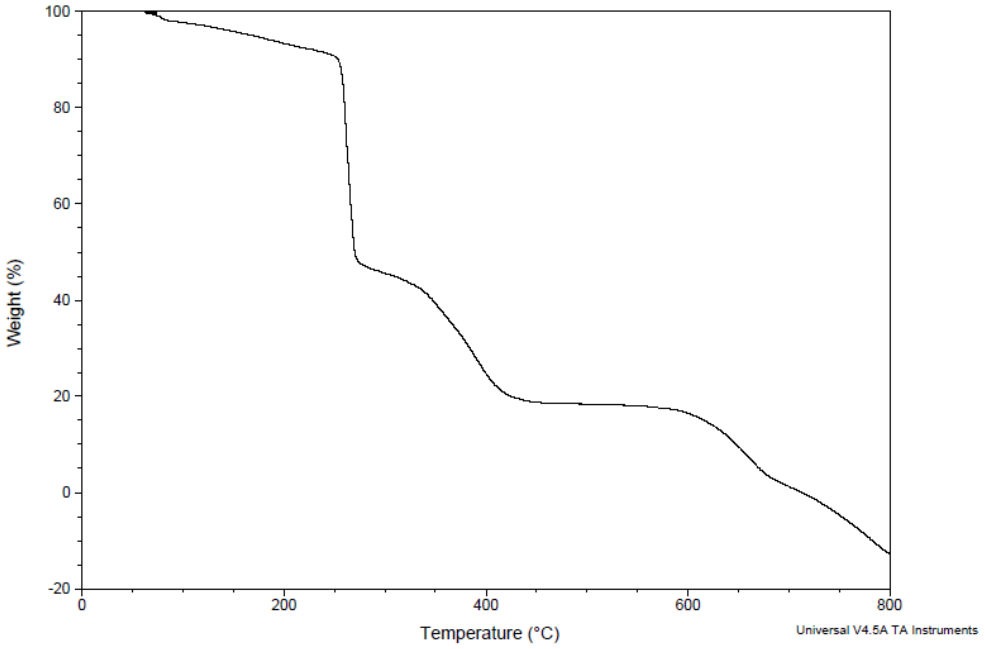
1.6.2 LiMOF bulk sample

The TGA of the single crystals of bulk **LiMOF** sample indicated that the framework was stable up to approximately 300-350 °C.



1.6.3 Cu-L1

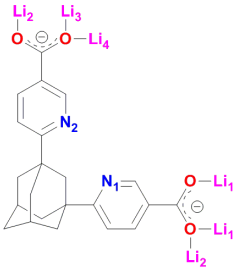
The TGA of the single crystals of **Cu-L1** indicated that the framework was stable up to approximately 230 °C.

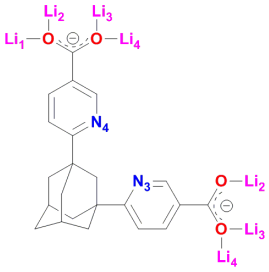


1.7 L1 ligand coordination to Li(I) cations

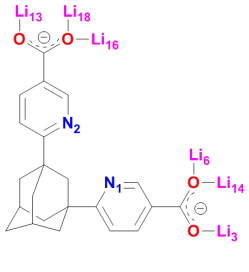
Across all three analogous **LiMOF** frameworks, the **L1** ligand was bound to a minimum of three Li(I) cation centres and a maximum of seven Li(I) cation centres.

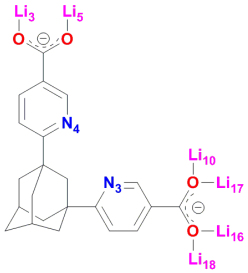
1.7.1 L1 ligand coordination to Li(I) cations within LiMOF12

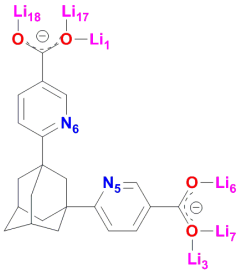


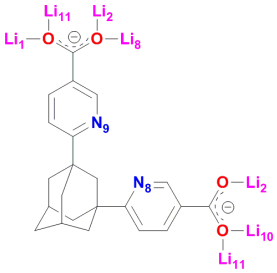


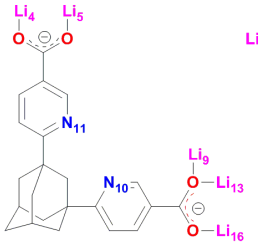
1.7.2 L1 ligand coordination to Li(I) cations within LiMOF30

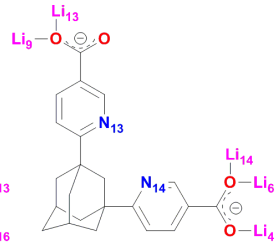


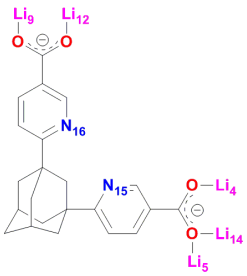


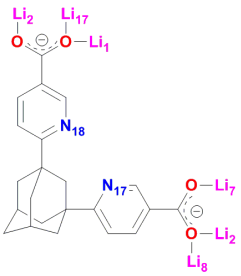


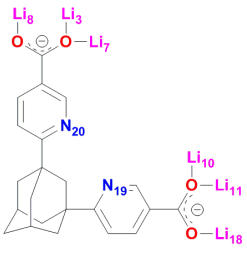


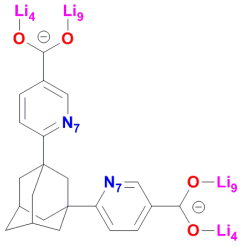












1.7.3 L1 ligand coordination to Li(I) cations within LiMOF50