Electronic Supplementary Material (ESI) for CrystEngComm.

# Supplementary Information

# An XRD and NMR crystallographic investigation of the structure of 2,6-lutidinium hydrogen fumarate

Emily K. Corlett[a], Helen Blade[b], Leslie P. Hughes[b], Philip J. Sidebottom[c], David Walker[a], Richard I. Walton[d] and Steven P. Brown[a]

[a]Department of Physics, University of Warwick, Coventry, CV4 7AL; [b]AstraZeneca, Macclesfield, SK10 2NA; [c]Syngenta, Jealott's Hill, RG42 6EY; [d]Department of Chemistry, University of Warwick, Coventry, CV4 7AL

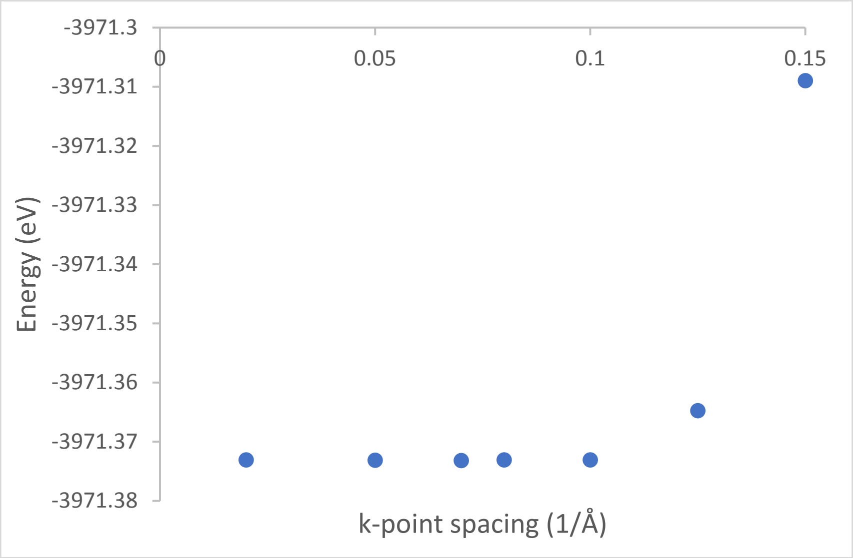

*Figure S1: Convergence of energy with decreasing k-point spacing in the DFT (CASTEP) calculations for the literature structure (181445).*

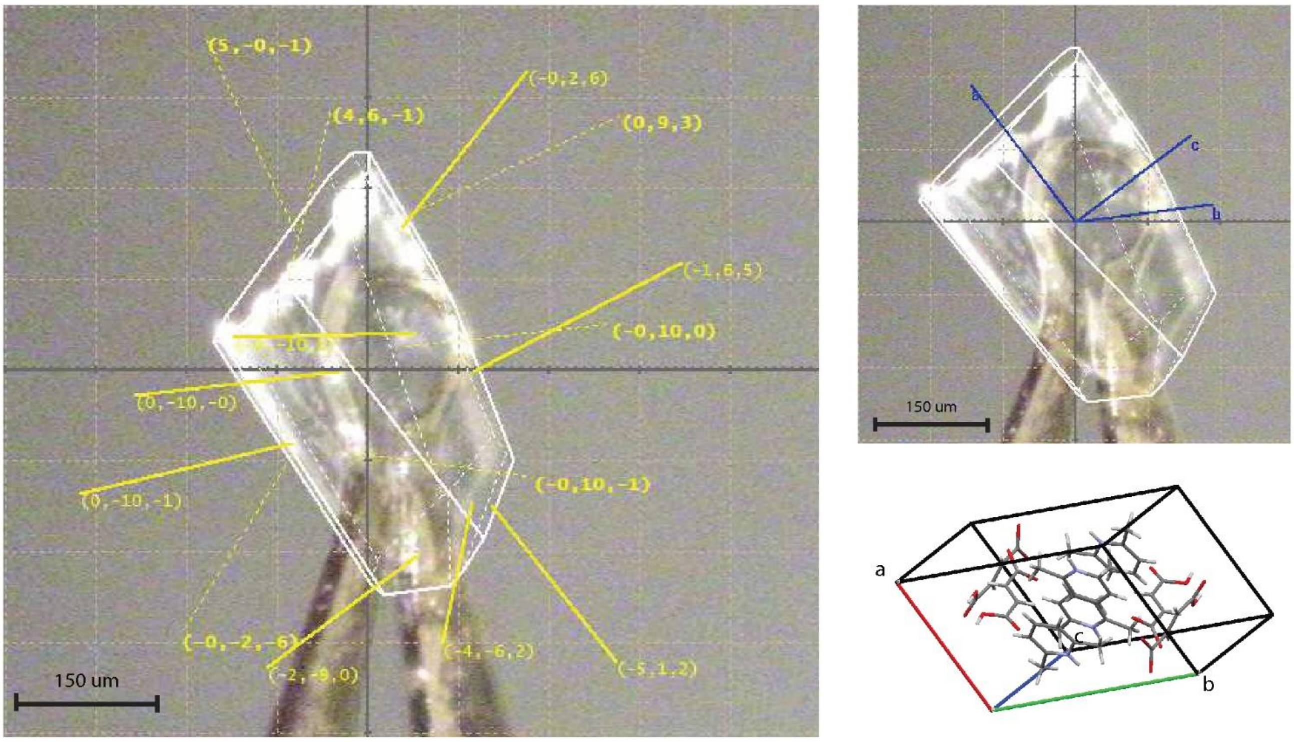

*Figure S2: A 2,6-lutidinium fumarate plate crystal of sufficient quality for SXRD with (left) labelling of the (hkl) planes for each face and (top right) the corresponding alignment of the unit cell axes. The literature structure (181445) unit cell, oriented the same way, is also shown (bottom right).*

*Table S1: Comparison of the fractional coordinates of the atoms in the asymmetric unit of 2,6-lutidinium hydrogen fumarate structure, for the literature structure (181445) and the Rietveld refined positions for the high-resolution synchrotron structure. All atoms have an occupancy of 1*

| | 181445[a] | | | MAC[b] RT | | | |
|---|---|---|---|---|---|---|---|
| **Atom** | **x** | **y** | **z** | **x** | **y** | **z** | **Uiso (Å$^2$)** |
| **O1** | 0.30136(14) | 0.86276(9) | 0.01990(17) | 0.2978(3) | 0.86374(19) | 0.0178(4) | 1.94(10) |
| **O2** | 0.08188(14) | 0.81554(9) | −0.02052(18) | 0.0775(3) | 0.81443(19) | −0.0284(4) | 2.16(10) |
| **O3** | 0.26795(17) | 0.85651(10) | 0.66876(19) | 0.2681(3) | 0.85867(19) | 0.6752(4) | 2.11(10) |
| **O4** | 0.4098(2) | 0.96976(12) | 0.6903(2) | 0.4088(4) | 0.9681(2) | 0.6951(4) | 4.72(14) |
| **C8** | 0.20194(19) | 0.84136(12) | 0.0809(3) | 0.1995(5) | 0.8439(3) | 0.0910(7) | 0.50(15) |
| **C9** | 0.22464(19) | 0.84836(12) | 0.2866(3) | 0.2125(5) | 0.8436(3) | 0.3025(7) | 0.79(14) |
| **C10** | 0.3156(2) | 0.90267(12) | 0.3964(3) | 0.3197(4) | 0.9004(3) | 0.3671(6) | 0.63(15) |
| **C11** | 0.3358(2) | 0.91336(13) | 0.6002(3) | 0.3371(5) | 0.9148(4) | 0.5902(8) | 3.4(2) |
| **N** | −0.15263(17) | 0.77978(10) | 0.0572(2) | −0.1491(4) | 0.7833(4) | 0.0584(5) | 1.21(12) |
| **C1** | −0.0946(2) | 0.62644(14) | 0.0555(3) | −0.0866(4) | 0.6209(3) | 0.0576(5) | 0.84(14) |
| **C2** | −0.1951(2) | 0.69710(13) | 0.0642(3) | −0.1890(6) | 0.6934(4) | 0.0580(5) | 1.03(14) |
| **C3** | −0.3288(2) | 0.68343(15) | 0.0810(3) | −0.3259(6) | 0.6775(3) | 0.0848(5) | 1.06(14) |
| **C4** | −0.4131(2) | 0.75330(16) | 0.0901(3) | −0.4180(4) | 0.7533(4) | 0.0897(5) | 0.23(15) |
| **C5** | −0.3655(2) | 0.83706(15) | 0.0812(3) | −0.3703(6) | 0.8387(4) | 0.0726(6) | 2.82(16) |
| **C6** | −0.2335(2) | 0.85013(13) | 0.0628(3) | −0.2317(7) | 0.8548(4) | 0.0597(6) | 2.97(18) |
| **C7** | −0.1739(3) | 0.93811(14) | 0.0482(4) | −0.1618(4) | 0.9432(3) | 0.0620(5) | 0.58(14) |

[a] Structure determined by Pan et al.[1]

[b] Multi-Analysing Crystals, high resolution synchrotron scan

*Table S2: Crystallographic data, instrumental parameters and final residuals for Rietveld refined model[a] of 2,6-lutidinium hydrogen fumarate against high-resolution synchrotron data recorded at 300 K*

| **Formula** ($Z$ = 4) | $C_{11}H_{13}O_4N$ | | | |
|---|---|---|---|---|
| ***a* (Å)** | ***b* (Å)** | ***c* (Å)** | ***β* (°)** | ***V* (Å$^3$)** |
| 9.906752(18) | 15.35923(3) | 7. 501959(12) | 107.78973(12) | 1086.917(4) |

| | | | |
|---|---|---|---|
| **Number of parameters refined** | 96 | **Space group** | $P2_1/c$ |
| **Scale factor** | 0.0000698(2) | **Zero point** | –0.00237(2) |
| **PseudoVoigt peak width parameters (°$^2$)** | U 0.00229(8) | V –0.00007(2) | W 0.00250(4) |
| $R_{wp}$ | 10.11 % | $R_p$ | 7.66 % |
| $R_{exp}$ | 3.07 % | $R_{bragg}$ | 5.59 % |

[a] R-factors are described by Toby[2]

*Table S3: Longer-range C···H proximities between 1.2 and 2.8 Å for 2,6-lutidinium hydrogen fumarate*

| **C** | **$\delta_{iso}^{exp}$ (ppm)** | **H** | **$\delta_{iso}^{exp}$ (ppm)** | **Separation[a] (Å)** |
|---|---|---|---|---|
| C1 | 152.6 | H10 | 17.7 | 2.11 |
| | | H4 | 2.1 | 2.12 |
| | | H6 | 2.1 | 2.13 |
| | | H1 | 6.3 | 2.15 |
| | | H5 | 2.1 | 2.15 |
| C2 | 123.8 | H2 | 7.0 | 2.16 |
| | | H6 | 2.1 | 2.69 |
| C3 | 146.4 | H3 | 7.9 | 2.17 |
| | | H1 | 6.3 | 2.17 |
| C4 | 128.2 | H2 | 7.0 | 2.14 |
| | | H9 | 2.1 | 2.64 |
| C5 | 152.6 | H10 | 17.7 | 2.09 |
| | | H9 | 2.1 | 2.13 |
| | | H7 | 2.1 | 2.14 |
| | | H3 | 7.9 | 2.15 |
| | | H8 | 2.1 | 2.15 |
| C6 | 19.6 | H10 | 17.7 | 2.60 |
| | | H1 | 6.3 | 2.77 |
| C7 | 19.6 | H10 | 17.7 | 2.57 |
| | | H3 | 7.9 | 2.77 |
| C8 | 173.4 | H11 | 7.9 | 2.21 |
| | | *H13* | *15.8* | *2.38* |
| | | *H10* | *17.7* | *2.53* |
| | | H12 | 7.0 | 2.75 |
| C9 | 142.7 | H12 | 7.0 | 2.13 |
| C10 | 132.4 | H11 | 7.9 | 2.12 |
| C11 | 169.9 | H13 | 15.8 | 2.00 |
| | | H12 | 7.0 | 2.19 |
| | | H11 | 7.9 | 2.73 |
| | | *H2* | *7.0* | *2.79* |

[a] H-H distances are taken from the DFT (CASTEP) optimised structure. Intermolecular proximities are denoted using italic font.

*Table S4: The fractional coordinates of the atoms in the asymmetric unit of the 2,6-lutidinium hydrogen fumarate structural model refined against high-resolution synchrotron data recorded at 100 K (see Fig. 6)*

| Atom | x | y | z | Uiso (Å$^2$) |
|---|---|---|---|---|
| **O1** | 0.2015(7) | 0.3633(4) | 0.9938(8) | 1.6(2) |
| **O2** | 0.4325(7) | 0.3129(4) | 1.0401(8) | 0.50(19) |
| **O3** | 0.2306(6) | 0.3553(4) | 0.3237(8) | 0.54(18) |
| **O4** | 0.0971(7) | 0.4692(4) | 0.3150(8) | 0.9(2) |
| **C8** | 0.3048(12) | 0.3378(6) | 0.9306(16) | –0.5(3) |
| **C9** | 0.2836(10) | 0.3391(6) | 0.7157(14) | 0.1(3) |
| **C10** | 0.1838(10) | 0.4028(7) | 0.6286(14) | 1.3(3) |
| **C11** | 0.1764(11) | 0.4102(9) | 0.4447(19) | 4.6(4) |
| **N** | 0.6530(8) | 0.2762(7) | 0.9528(10) | 1.1(2) |
| **C1** | 0.6990(13) | 0.1914(8) | 0.9569(13) | 2.5(3) |
| **C2** | 0.8357(13) | 0.1713(6) | 0.9261(11) | 1.7(3) |
| **C3** | 0.9130(9) | 0.2484(8) | 0.9087(12) | 0.3(3) |
| **C4** | 0.8719(11) | 0.3396(7) | 0.9228(12) | –0.1(3) |
| **C5** | 0.7304(13) | 0.3594(7) | 0.9383(13) | 2.0(3) |
| **C6** | 0.5933(7) | 0.1099(5) | 0.9585(9) | –2.3(2) |
| **C7** | 0.6668(9) | 0.4436(6) | 0.9566(10) | –0.5(3) |

*Table S5: Crystallographic data, instrumental parameters and final residuals for Rietveld refined model[a] of 2,6-lutidinium hydrogen fumarate against high-resolution synchrotron data recorded at 100 K*

| **Formula** ($Z$ = 4) | $C_{11}H_{13}O_4N$ | | | |
|---|---|---|---|---|
| ***a*** **(Å)** | ***b*** **(Å)** | ***c*** **(Å)** | ***β*** **(°)** | ***V*** **(Å$^3$)** |
| 9.83062(5) | 15.16849(9) | 7.48175(3) | 108.8958(4) | 1055.524(9) |

| | | | |
|---|---|---|---|
| **Number of parameters refined** | 96 | **Space group** | $P2_1/c$ |
| **Scale factor** | 0.00000729(5) | **Zero point** | –0.00232(6) |
| **PseudoVoigt peak width parameters (°$^2$)** | U 0.0037(3) | V –0.00018(6) | W 0.0025(2) |
| $R_{wp}$ | 19.37 % | $R_p$ | 14.95 % |
| $R_{exp}$ | 18.88 % | $R_{\mathrm{bragg}}$ | 4.92 % |

[a] R-factors are described by Toby[2]

*Table S6: GIPAW calculated chemical shifts for the CCDC structure 181445 of 2,6-lutidinium hydrogen fumarate and 1876100 and the difference between them*

| Atom | 181445 $\delta_{iso}^{calc}$ (ppm) | 1876100 $\delta_{iso}^{calc}$ (ppm) | $\Delta\delta_{iso}^{calc}$ (ppm) |
|---|---|---|---|
| **H4/H5/H6** | 2.1 | 2.1 | 0.0 |
| **H7/H8/H9** | 2.1 | 2.1 | 0.0 |
| **H1** | 6.3 | 6.4 | 0.0 |
| **H2** | 6.9 | 6.8 | 0.0 |
| **H12** | 7.5 | 7.5 | 0.0 |
| **H3** | 7.9 | 7.9 | 0.0 |
| **H11** | 8.0 | 8.0 | 0.1 |
| **H13** | 17.7 | 17.6 | −0.1 |
| **H10** | 17.7 | 17.9 | 0.2 |
| **C7** | 14.3 | 14.6 | 0.3 |
| **C6** | 15.5 | 16.1 | 0.6 |
| **C2** | 124.3 | 124.7 | 0.3 |
| **C4** | 129.1 | 129.3 | 0.1 |
| **C10** | 134.7 | 135.1 | 0.3 |
| **C9** | 145.3 | 144.9 | −0.4 |
| **C3** | 145.8 | 145.5 | −0.3 |
| **C5** | 152.4 | 152.1 | −0.3 |
| **C1** | 152.6 | 152.6 | 0.1 |
| **C11** | 172.3 | 172.5 | 0.2 |
| **C8** | 175.2 | 175.4 | 0.2 |

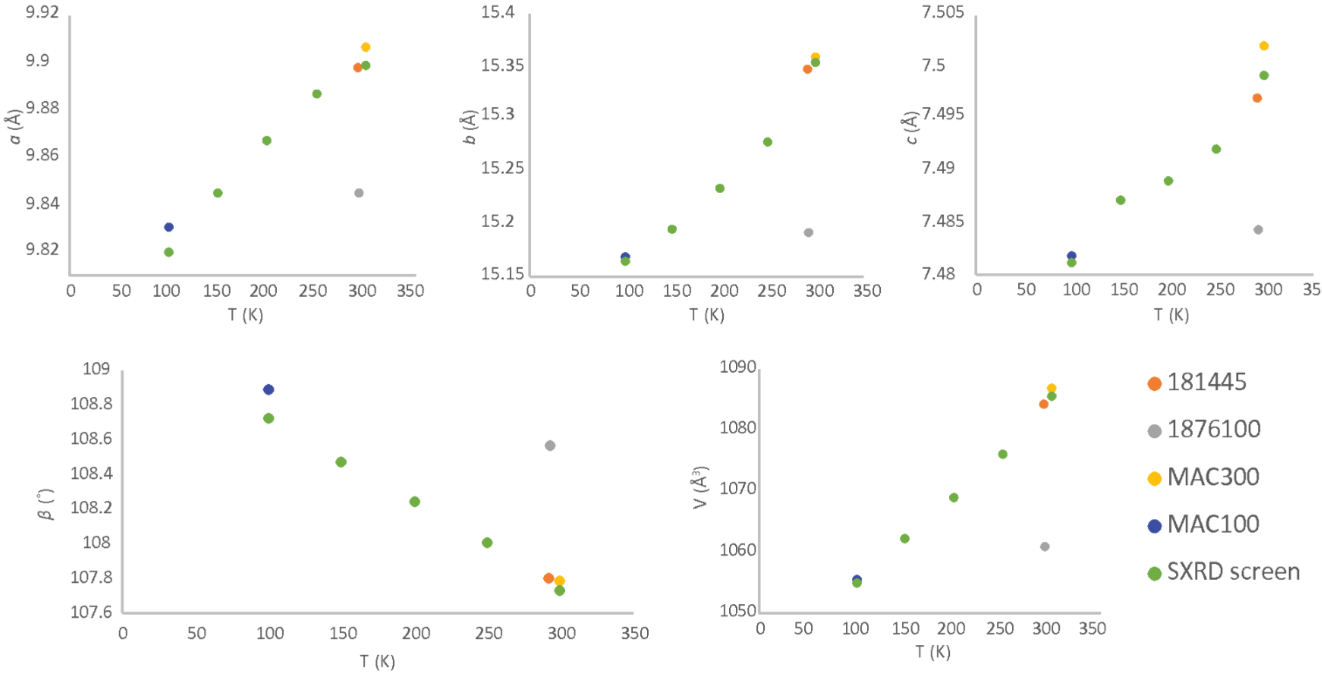

*Figure S3: Graphs showing the change in the value of the unit cell parameters of 2,6-lutidinium hydrogen fumarate with temperature. MAC refers to high resolution synchrotron PXRD data recorded with a Multi-Analysing Crystal detector.*

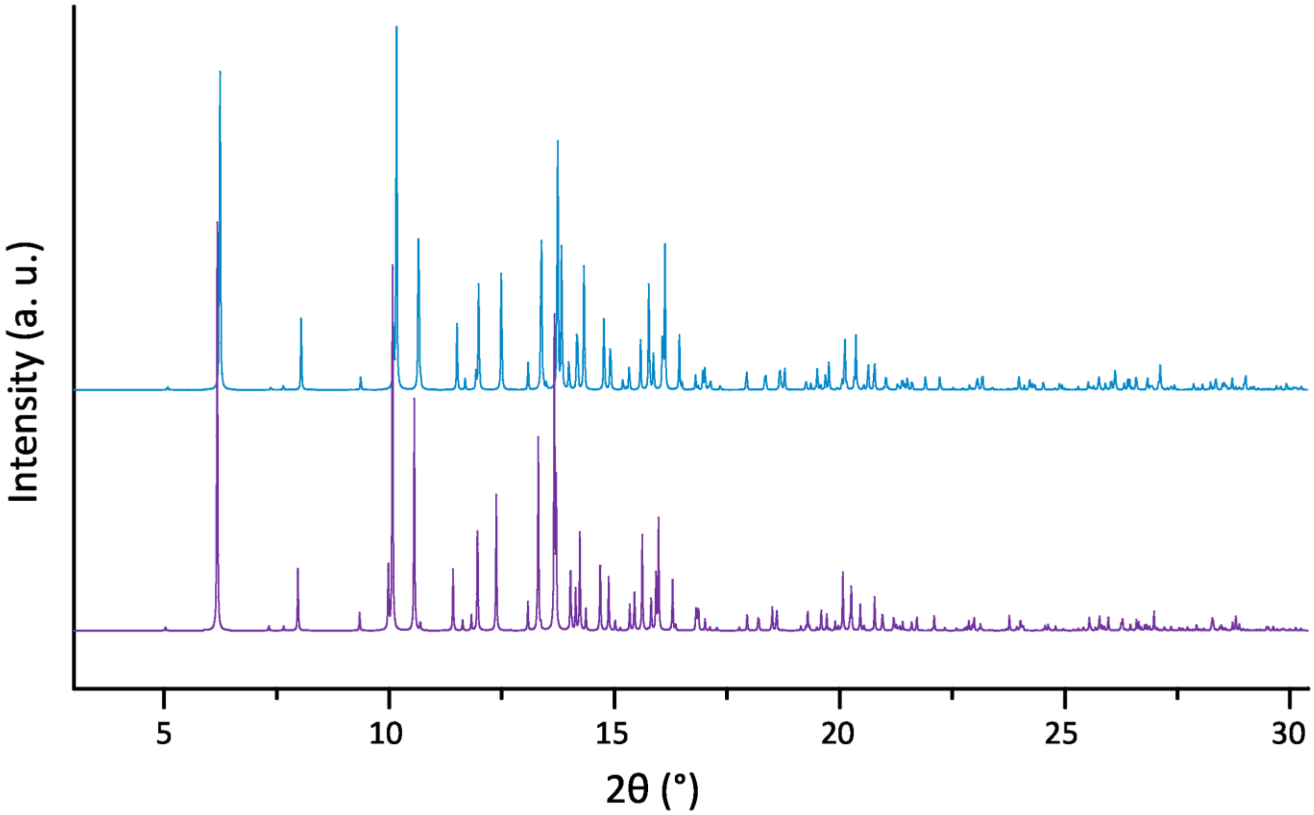

*Figure S4: Simulated PXRD patterns of 2,6-lutidinium hydrogen fumarate for the CCDC structures 181445 (purple, bottom) and 1876100 (blue, top).*

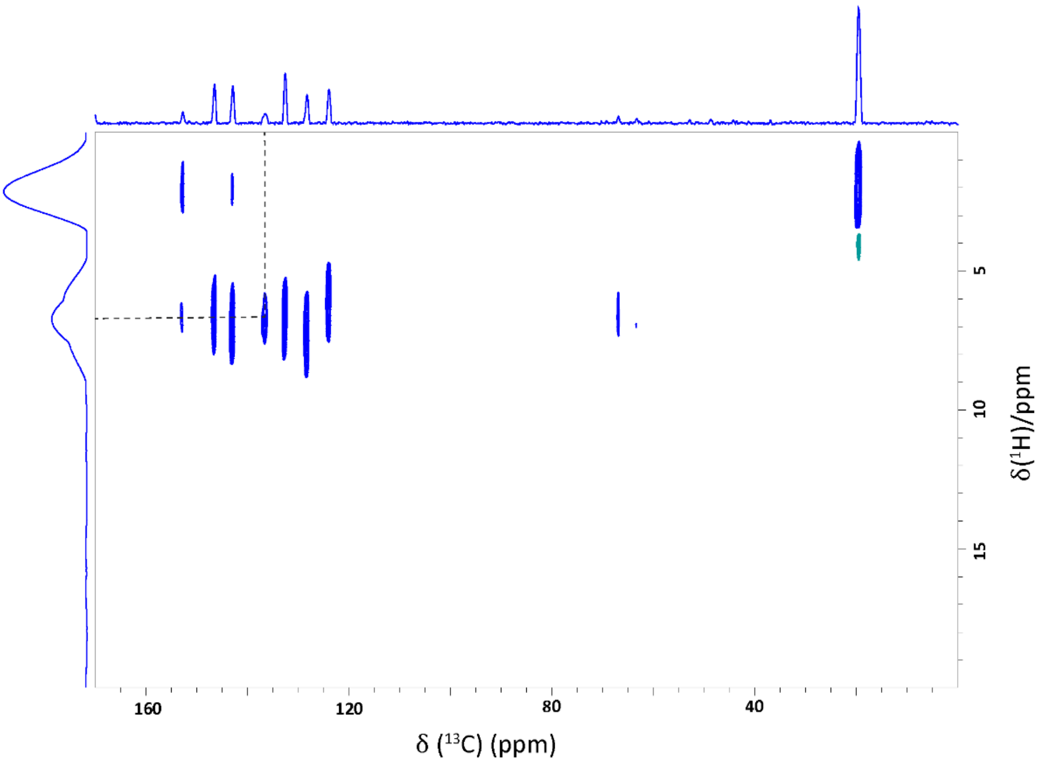

*Figure S5: A $^{1}$H (500 MHz)-$^{13}$C CP (200 µs) HETCOR MAS (12.5 kHz) NMR spectrum of 2,6-lutidinium hydrogen fumarate with fumaric acid present. The dashed grey lines show the CH correlation for the fumaric acid backbone. The base contour level is at 6.2% of the maximum peak height.*

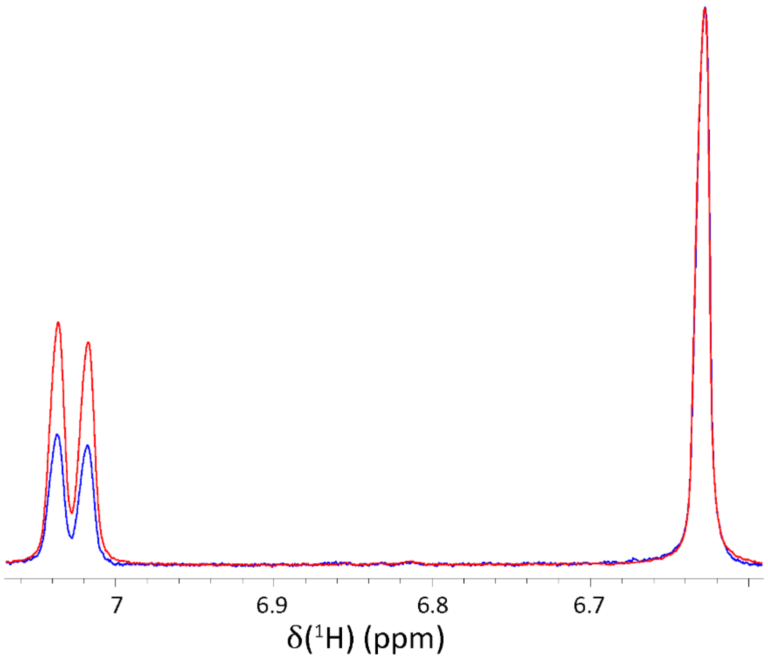

*Figure S6: Solution-state $^1$H (400 MHz, one pulse) NMR spectra of 2,6-lutidinium hydrogen fumarate dissolved in d6-DMSO. A sample made up freshly from a single crystal is shown in red and a sample made up from a powder that had been stored under ambient conditions for more than 2 weeks is shown in blue. The doublet at 7.01 ppm corresponds to H1 and H3 on 2,6-lutidine and the singlet at 6.61 ppm corresponds to H11 and H12 on fumaric acid.*

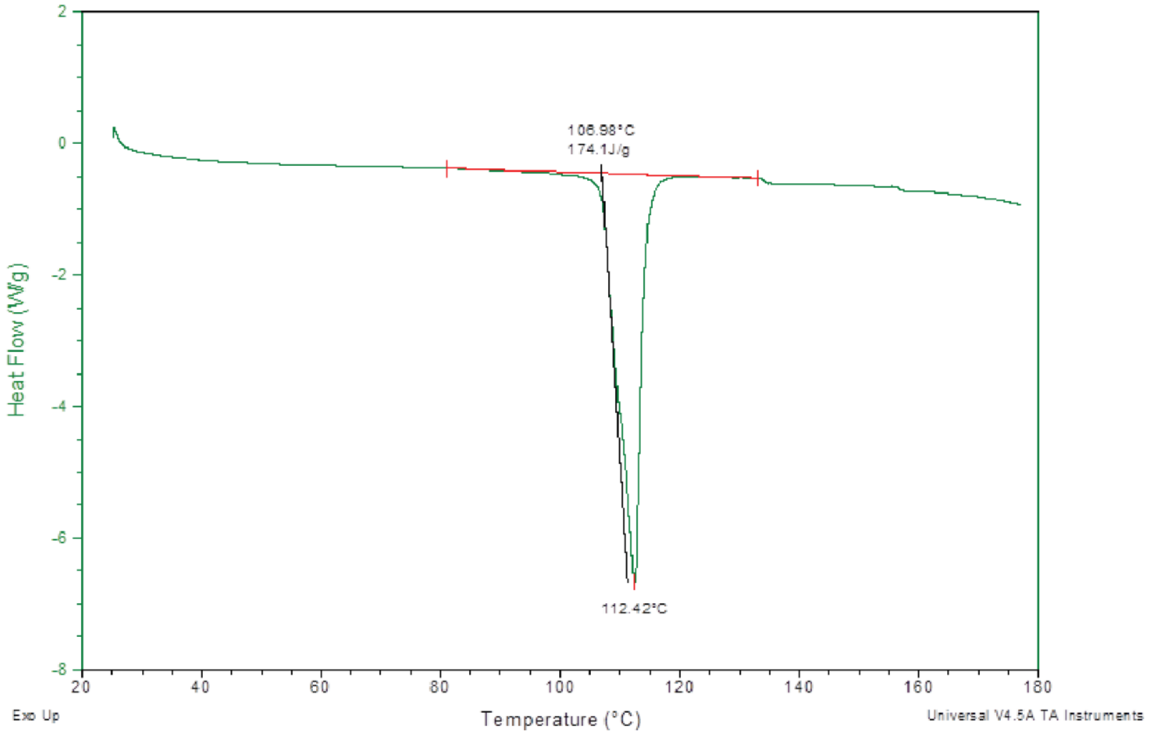

*Figure S7:DSC of small plate crystals of 2,6-lutidinium hydrogen fumarate recorded on a TA Instruments DSC 2000 with a ramp of 10°C/min from 20-180°C.*

1. Y. J. Pan, Z. M. Jin, C. R. Sun and C. W. Jiang, *Chem. Lett*, 2001, **30**, 1008-1009.
2. B. Toby, *Powder Diffr.*, 2006, **21**, 67-70.