Electronic Supplementary Material (ESI) for Dalton Transactions.

" Experimental and Theoretical Studies of Structural Phase Transition in Novel Polar Perovskite-like $[C_2H_5NH_3][Na_{0.5}Fe_{0.5}(HCOO)_3]$ Formate "

by Maciej Ptak *et al.*

Table S1. Selected geometric parameters from the structure refinement (Å, º).

EtANaFe _297K			
Fe1—O7	1.999 (4)	Na—O4^{xv}	2.444 (6)
Fe1—O11	2.003 (5)	Na—O6^{xvi}	2.504 (4)
Fe1—O1	2.004 (5)	Na—O10	2.515 (4)
Fe1—O3	2.009 (4)	O5—C2	1.281 (6)
Fe1—O9	2.016 (4)	O8—C4	1.206 (7)
Fe1—O5	2.021 (3)	N2—C7	1.460 (8)
Na—O12^{xii}	2.384 (5)	C7—C8	1.491 (9)
Na—O8^{xiii}	2.405 (5)	N1—C9	1.475 (8)
Na—O2^{xiv}	2.429 (6)	C10—C9	1.446 (10)
O7—Fe1—O1	92.35 (15)	O12^{xii}—Na—O10	94.5 (2)
O11—Fe1—O1	178.12 (19)	O4^{xv}—Na—O10	84.32 (16)
O3—Fe1—O9	179.50 (17)	O6^{xvi}—Na—O10	179.2 (2)
O1—Fe1—O5	88.16 (15)	O12—C2—O5	123.7 (5)

O2^{xiv}—Na—O4^{xv}	172.37 (19)	O6—C3—O3	127.4 (5)
(EtANaFe _377K)			
Fe1—O1^{vi}	2.006 (2)	Na1—O4^{ix}	2.441 (2)
Fe1—O1	2.006 (2)	Na1—O4	2.441 (2)
Fe1—O3	2.010 (2)	Na1—O5^{xi}	2.532 (2)
Fe1—O3^{vi}	2.010 (2)	Na1—O5^{x}	2.532 (2)
Fe1—O2	2.015 (2)	O3—C2	1.275 (4)
Fe1—O2^{vi}	2.015 (2)	O6—C2	1.213 (4)
Na1—O6^{vii}	2.412 (3)	C6—N1	1.4601 (10)
Na1—O6^{viii}	2.412 (3)	C6—C7	1.4994 (10)
O1^{vi}—Fe1—O1	180.0	O6^{vii}—Na1—O5^{xi}	92.79 (9)
O1^{vi}—Fe1—O3	89.08 (8)	O6^{viii}—Na1—O5^{xi}	87.21 (9)
O1—Fe1—O3	90.92 (8)	O6—C2—O3	124.7 (3)
O6^{vii}—Na1—O6^{viii}	180.00 (15)	O5—C3—O2	127.6 (3)

Symmetry code(s): (i) *x*, *y*+1, *z*; (ii) *x*+1, *y*, *z*; (iii) *x*+1/2, -*y*+1, *z*-1/2; (iv) *x*+1/2, -*y*+1, *z*+1/2; (v) *x*+1, *y*+1, *z*; (vi) -*x*, -*y*, -*z*+1; (vii) *x*-1/2, -*y*+1/2, *z*-1/2; (viii) -*x*+1/2, *y*-1/2, -*z*+1/2; (ix) -*x*, -*y*, -*z*; (x) -*x*+1/2, *y*+1/2, -*z*+1/2; (xi) *x*-1/2, -*y*-1/2, *z*-1/2; (xii) *x*, *y*-1, *z*; (xiii) *x*-1, *y*, *z*; (xiv) *x*-1/2, -*y*+1, *z*+1/2; (xv) *x*-1/2, -*y*+1, *z*-1/2; (xvi) *x*-1, *y*-1, *z*.

Table S2. Selected hydrogen-bond parameters.

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
(EtANaFe at 297K)				
N2—H2A···O4^{v}	0.89	2.00	2.862 (6)	162.7
N2—H2B···O6^{iv}	0.89	1.97	2.852 (6)	169.2
N2—H2C···O5^{viii}	0.89	2.10	2.987 (6)	175.7
N2—H2C···O12^{viii}	0.89	2.52	3.145 (7)	127.7
N1—H1A···O1^{iii}	0.89	2.60	3.298 (7)	136.3
N1—H1A···O2^{iii}	0.89	2.13	2.960 (7)	155.1
N1—H1B···O7	0.89	2.14	2.974 (6)	156.4
N1—H1B···O8	0.89	2.46	3.219 (7)	143.7
N1—H1C···O10^{i}	0.89	1.98	2.860 (6)	168.9
(EtANaFe at 377K)				
N2—H2A···O4	0.89	2.14	2.94 (3)	149.6
N2—H2B···O3^{vi}	0.89	2.38	3.14 (2)	142.8
N2—H2B···O6^{vi}	0.89	2.49	3.26 (3)	146.2
N2—H2C···O5^{vii}	0.89	1.93	2.79 (2)	161.5
N1—H1A···O4	0.89	2.10	2.93 (2)	155.2
N1—H1B···O3^{vi}	0.89	2.03	2.919 (13)	175.7
N1—H1B···O6^{vi}	0.89	2.52	3.084 (18)	121.5
N1—H1C···O5^{vii}	0.89	2.05	2.924 (17)	168.9

Symmetry code(s): (i) *x*+1/2, -*y*+1, *z*+1/2; (ii) *x*, *y*+1, *z*; (iii) *x*-1/2, -*y*+1, *z*+1/2; (iv) *x*-1/2, -*y*+1, *z*-1/2; (v) *x*+1/2, -*y*+1, *z*-1/2; (vi) *x*+1/2, -*y*+1/2, *z*-1/2; (vii) -*x*+1, -*y*, -*z*+1; (viii) *x*, *y*-1, *z*.

Table S3 Atomic displacements after the symmetry change from $P2_1/n$ to Pn for EtANaFe. The analysis was done only for these atoms that are ordered in both phases, *i.e.,* metal centers, oxygen and carbon atoms from the formate linkers. The hydrogen atoms as well as the disordered over two positions in the $P2_1$/n phase EtA^+ cations were not included.

WP		Atom	Atomic Displacements			
			u_x	u_y	u_z	|u|
2a	(x,y,z)	Fe1	-0.0032	-0.0220	-0.0005	0.2076
2a	(x,y,z)	Na1	0.0006	0.0216	-0.0010	0.2027
2a	(x,y,z)	O1	-0.0010	-0.0206	0.0005	0.1935
2a	(x,y,z)	O1_2	-0.0027	0.0171	0.0003	0.1619
2a	(x,y,z)	O2	-0.0038	-0.0230	0.0013	0.2185
2a	(x,y,z)	O2_2	-0.0030	0.0230	-0.0021	0.2185
2a	(x,y,z)	O3	-0.0011	-0.0196	-0.0002	0.1841
2a	(x,y,z)	O3_2	-0.0002	0.0239	-0.0006	0.2243
2a	(x,y,z)	O4	0.0033	0.0037	0.0014	0.0467
2a	(x,y,z)	O4_2	-0.0011	-0.0050	0.0020	0.0535
2a	(x,y,z)	O5	0.0011	-0.0210	-0.0014	0.1979
2a	(x,y,z)	O5_2	-0.0047	0.0221	-0.0008	0.2110
2a	(x,y,z)	O6	0.0131	-0.0299	0.0027	0.3014
2a	(x,y,z)	O6_2	0.0043	0.0291	-0.0024	0.2768
2a	(x,y,z)	C1	-0.0012	-0.0045	-0.0010	0.0450
2a	(x,y,z)	C1_2	-0.0037	0.0050	-0.0002	0.0557
2a	(x,y,z)	C2	0.0076	-0.0292	0.0029	0.2827
2a	(x,y,z)	C2_2	0.0054	0.0304	0.0005	0.2885
2a	(x,y,z)	C3	-0.0042	-0.0238	-0.0020	0.2271
2a	(x,y,z)	C3_2	-0.0056	0.0253	0.0009	0.2419

NOTE: u_x, u_y and u_z are given in relative units. |u| is the absolute distance given in Å
Maximum atomic displacement in the distortion, Δ: 0.3014 Å
Total distortion amplitude: 1.3131 Å

Data form AMPLIMODES http://www.cryst.ehu.es

D. Orobengoa, C. Capillas, M. I. Aroyo, J. M. Perez-Mato, *J. Appl. Cryst. A* 2009, **42**, 820-833.

Table S4. IR and Raman frequencies (in cm^{-1}) of EtANaFe and suggested assignments.[a]

Raman	Raman	IR	IR	assignment

400 K	80 K	380 K	5 K	
		3141w,b	3158vw	$\nu(NH_3)$
	3067w,b	3090m,b	3078m	$\nu(NH_3)$
3030w, 3013w	3037w, 3031w 3012w			$\nu_{as}(CH_3)$ and $\nu_{as}(CH_2)$
2993w	2991m, 2988sh	2996vw	2992w	$\nu_{as}(CH_3)$ and $\nu_{as}(CH_2)$
2976m	2970m	2977vw	2972vw	$\nu_s(CH_3)$ and $\nu_s(CH_2)$
2953s	2950s, 2945s	2953vw	2948w	$\nu_s(CH_3)$ and $\nu_s(CH_2)$
2924w	2929w, 2922w 2910w		2920w, 2907vw	$\nu_s(CH_3)$ and $\nu_s(CH_2)$
2883sh	2884sh		2884sh, 2876m	$\nu_1(HCOO^-)$
2864s	2877s, 2872sh 2852m	2867m	2851w	$\nu_1(HCOO^-)$
	2819vw	2825w	2822m	$\nu(NH_3)$
2740w	2751w, 2734vw	2744w	2742w	$2\nu_2(HCOO^-)$
		2706w	2715w	$2\nu_2(HCOO^-)$
1666s	1671s			$\nu_4(HCOO^-)$
	1650w, 1631vw	1637s	1648s, 1629s	$\nu_4(HCOO^-)$ and $\delta_{as}(NH_3)$
1579w	1595sh, 1579w	1590s	1590s, 1575s	$\nu_4(HCOO^-)$
	1516vw	1490w,b	1507m	$\delta_s(NH_3)$
1454w	1459w, 1446w	1468vw, 1452vw	1470w, 1467w, 1460w, 1449w	$\delta(CH_3)$ and $\delta(CH_2)$
	1394vw	1399m	1399sh, 1396m	$\nu_5(HCOO^-)$
1380s	1383s, 1375sh 1365w	1383m	1386m, 1384m, 1375w	$\nu_5(HCOO^-)$
1334w 1302w	1335m, 1323w 1314vw, 1302w	1316s	1338w, 1319s, 1302m	$\nu_2(HCOO^-)$

1272vw	1273m	1270m	1277sh, 1271s	$\nu_2(HCOO^-)$ and $\rho(CH_2)$
		1225vw, 1205vw	1232w, 1211vw	$\rho(CH_3)$
1055m	1056sh, 1052s	1047w	1051w	$\nu_6(HCOO^-)$ and $\nu_{as}(CCN)$
	1048sh			
	1017w	1007w	1017w	$\rho(NH_3)$
999vw	999w, 989w	996w	999w	$\rho(NH_3)$
872s	875s	875vw	878vw	$\nu_s(CCN)$
		801sh	806s	$\nu_3(HCOO^-)$
793s	802sh, 798s 794m	793s	797s, 795s	$\nu_3(HCOO^-)$
781sh	784s		788s, 784s	$\nu_3(HCOO^-)$
		424w	429w	$\delta(CCN)$
			408w	$\delta(CCN)$
329w	336m			$T'(Na^+)$
	295w			$T'(HCOO^-)$, $T'(Na^+)$ and $T'(Fe^{3+})$
254w,b	273w, 270w			$T'(HCOO^-)$, $T'(Na^+)$ and $T'(Fe^{3+})$
	257w			
230w	238w			$T'(HCOO^-)$ and $T'(Fe^{3+})$
	227m, 215w			$T'(HCOO^-)$ and $T'(Fe^{3+})$
171m,b	201w, 191w			$L(HCOO^-)$
	174s, 169w			
147s	159s, 147s			$L(HCOO^-)$
117s,b	135w, 120s 107m, 104sh 99w			$L(HCOO^-)$
80m,b	90m, 84m			L(EtA) and T'(EtA)
	80w			

54w,b	73w, 68w	L(EtA) and T'(EtA)
	61w, 57vw	
38w,b	49vw, 46w	L(EtA) and T'(EtA)
	43w	

[a]Key: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; b, broad

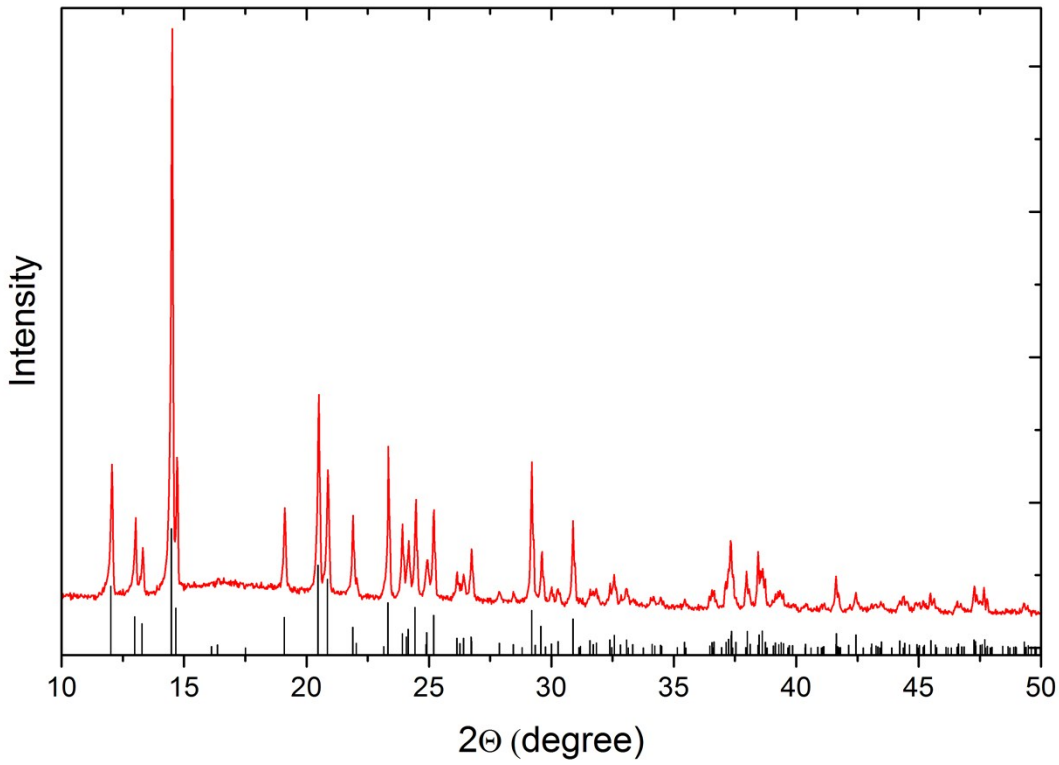

Figure S1. Powder XRD patterns for the as-prepared bulk sample of EtANaFe with the calculated one based on the single crystal structure at room temperature.

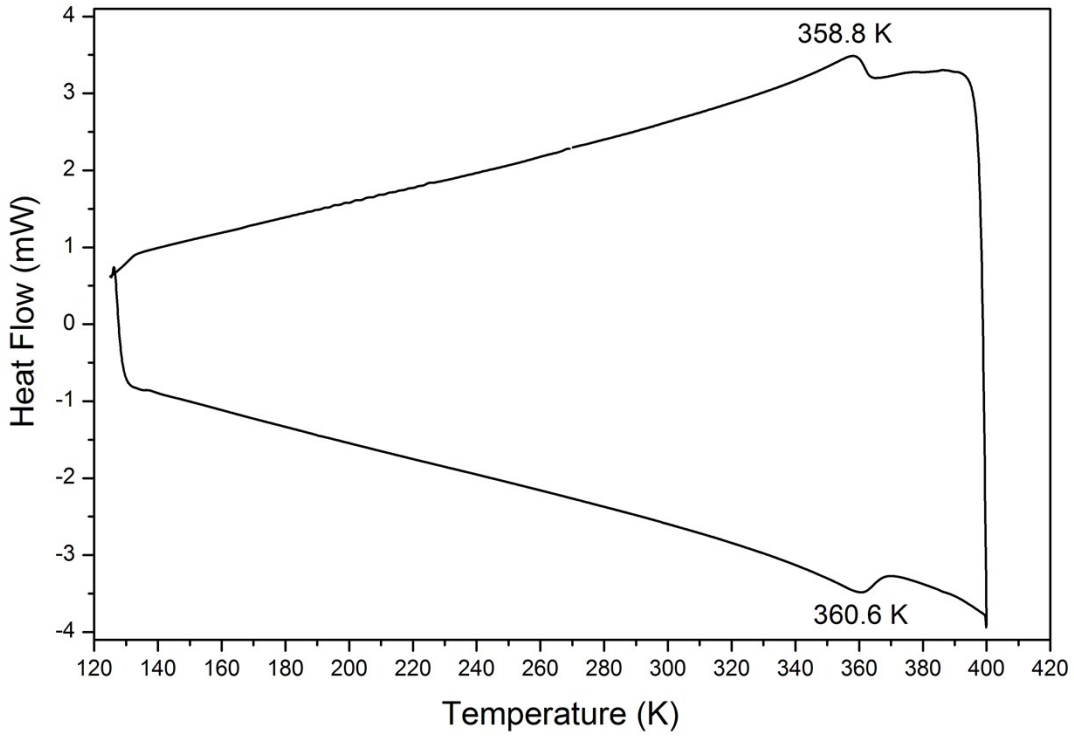

Figure S2. DSC traces for EtANaFe in heating and cooling mode.

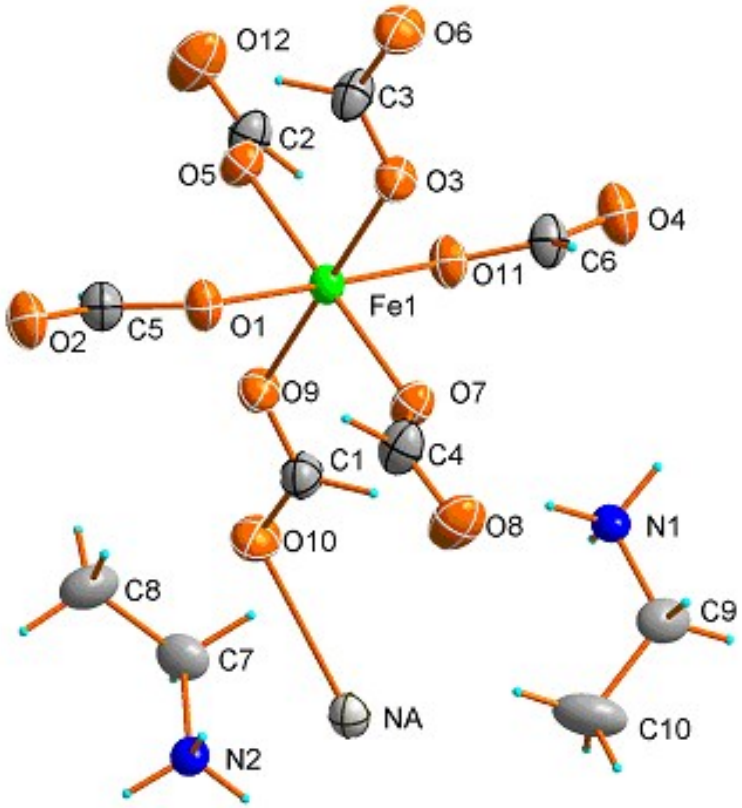

Figure S3. The content of the asymmetric unit in the polar phase *Pn* of EtANaFe formate, T=297 K.

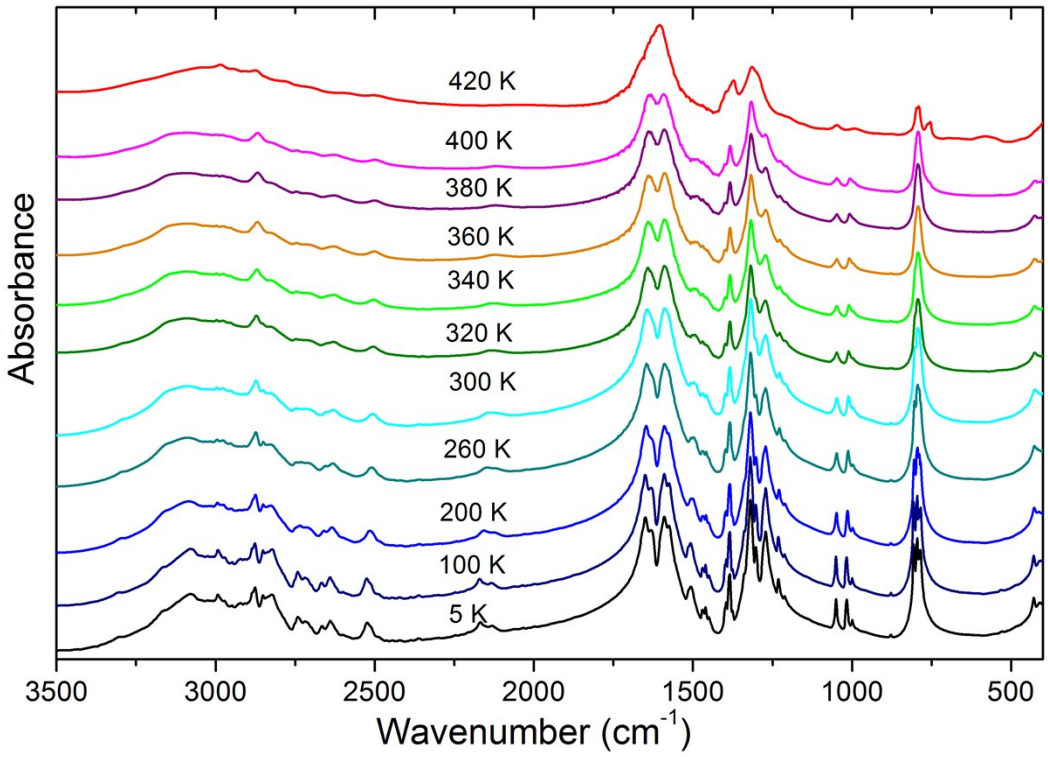

Figure S4. IR spectra of EtANaFe recorded at various temperatures corresponding to the spectral range 400-3500 cm^{-1}.

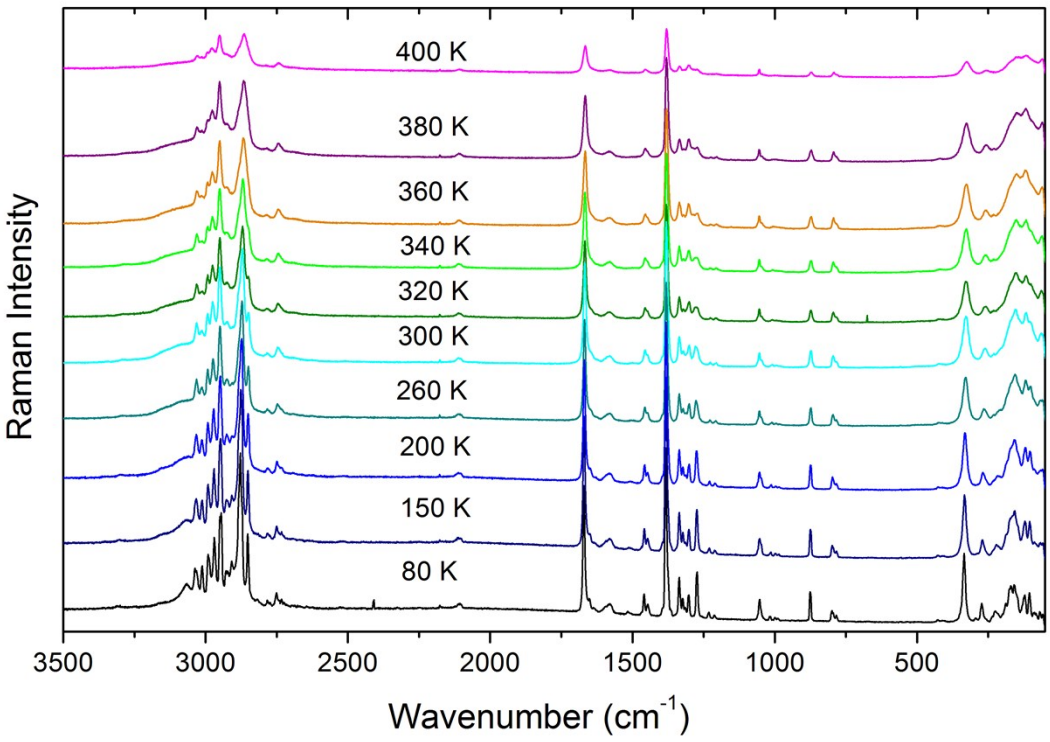

Figure S5. Raman spectra of EtANaFe recorded at various temperatures.