Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Table S1. Lattice parameters and superconductivity for samples prepared at different conditions. All samples were prepared with 5 mmol of Fe powder, 6 mmol of selenourea (Sigma Aldrich, 98%) and 50 mmol of LiOD in 5 mL D_2O except for (*:).

Conditions (°C, d)	***a* (Å)**	***c* (Å)**	***Tc* (K)**	**SC Vol%**
120, 4.5*	3.7793(1)	9.3030(5)	34.7	25%
120, 5	3.7806(1)	9.3025(4)	31.9	29%
140, 4	3.7863(1)	9.2904(3)	21.7	32%
160, 4	3.7808(1)	9.2652(2)	20.9	22%
180, 4	3.8011(1)	9.2090(3)	12.8	0.52%
200, 4	3.8145(1)	9.1822(2)	14.5	0.81%
200, 8	3.8257(2)	9.1717(3)	0	0%

Table S2. Lattice constants are superconductivity for single crystal samples prepared at different conditions. Samples are prepared at almost identical conditions except for temperature and reaction time. Samples that are indicated by (*) were prepared using Sn powder instead of Fe powder.

	Conditions (°C, d)	***a* (Å)**	***c* (Å)**	**T_c (K)**
OH	120, 5*	3.7883	9.2731	42
	120, 2	3.7898	9.2736	37
	120, 4	3.7901	9.2602	32
	130, 4	3.7931	9.2524	25
	140, 4	3.7938	9.2451	10
	160, 4	3.7965	9.2322	0
	180, 4	3.8008	9.2222	0
	200, 4	3.8108	9.1954	N/A
OD	120, 5*	3.7893	9.2611	42
	120, 5	3.7845	9.2716	37
	130, 4	3.7901	9.2755	39
	140, 4	3.7889	9.2706	38
	160, 4	3.7908	9.2563	21
	180, 4	3.7908	9.2524	24
	200, 4	3.7986	9.2293	N/A

Table S3. Rietveld refinement of synchrotron PXRD data collected at 7 K for a superconducting sample of ($^7Li_{1-x}Fe_xOD$)FeSe. The sample is fitted to a *P4/nmm* space group with origin choice 1. The tetrahedral angles α_1 and α_2 represent the Se–Fe–Se angles in and out of the basal plane, respectively.

a = 3.7761(1) Å, *c* = 9.1105(2) Å, Rwp = 12.24%, T_c = 25 K						
Atom	**Wyckoff site**	***x***	***y***	***z***	**Occ.**	U_{iso} **(Å²)**
Li/Fe1	2b	0	0	0.5	0.824/0.176(2)	0.0110
Fe2	2a	0.5	0.5	0	0.972(2)	0.0051
O	2c	0.5	0	0.4252(3)	1	.0029(2)
Se	2c	0	0.5	0.1603(1)	1	0.0033(7)
α_1 **(°)**	α_2 **(°)**	**Fe-Fe (Å)**		**Fe-Se (Å)**		
104.55(2)	111.99(1)	2.6701(1)		2.3871(3)		

Table S4. Rietveld refinements of synchrotron PXRD data collected at 7 K for single crystal samples of ($Li_{1-x}Fe_xOH$)FeSe. The samples are fitted to a *P4/nmm* space group with origin choice 1. The tetrahedral angles α_1 and α_2 represent the Se–Fe–Se angles in and out of the basal plane, respectively.

a = 3.7746(1) Å, *c* = 9.1310(2) Å, Rwp = 12.84%, T_c = 37 K						
Atom	**Wyckoff site**	***x***	***y***	***z***	**Occ.**	U_{iso} **(Å²)**
Li/Fe1	2b	0	0	0.5	0.828/0.172(1)	0.0125
Fe2	2a	0.5	0.5	0	0.978(2)	0.0063
O	2c	0.5	0	0.4282(3)	1	0.0030(6)
Se	2c	0	0.5	0.1604(1)	1	0.0033(2)
α_1 **(°)**	α_2 **(°)**	**Fe-Fe (Å)**		**Fe-Se (Å)**		
104.37(1)	112.08(1)	2.6691(1)		2.3890(3)		
a = 3.7778(1) Å, *c* = 9.1069(1) Å, Rwp = 11.06%, T_c = 10 K						
Atom	**Wyckoff site**	***x***	***y***	***z***	**Occ.**	U_{iso} **(Å²)**
Li/Fe1	2b	0	0	0.5	0.815/0.185(1)	0.0115
Fe2	2a	0.5	0.5	0	0.927(2)	0.0021
O	2c	0.5	0	0.4253(3)	1	0.0018(1)
Se	2c	0	0.5	0.1609(1)	1	0.0019(6)
α_1 **(°)**	α_2 **(°)**	**Fe-Fe (Å)**		**Fe-Se (Å)**		
104.38(2)	112.07(1)	2.6713(1)		2.3908(3)		
a = 3.7807(1) Å, *c* = 9.1102(24) Å, Rwp = 12.26%, non-superconducting						
Atom	**Wyckoff site**	***x***	***y***	***z***	**Occ.**	U_{iso} **(Å²)**
Li/Fe1	2b	0	0	0.5	0.826/0.174(2)	0.0139
Fe2	2a	0.5	0.5	0	0.917(2)	0.0053
O	2c	0.5	0	0.4259(4)	1	.0032(9)
Se	2c	0	0.5	0.1607(1)	1	0.0061(2)
α_1 **(°)**	α_2 **(°)**	**Fe-Fe (Å)**		**Fe-Se (Å)**		
104.54(3)	111.99(2)	2.6734(1)		2.3901(5)		

Table S5. Rietveld refinement of neutron powder diffraction data of the sample shown in Figure 2. The sample is fitted to a *P4/nmm* space group with origin choice 1. The tetrahedral angles α_1 and α_2 represent the Se–Fe–Se angles in and out of the basal plane, respectively.

a = 3.7770(1) Å, *c* = 9.1725(3) Å, Rwp = 6.16%, non-superconducting						
Atom	**Wyckoff site**	***x***	***y***	***z***	**Occ.**	**U_{iso} (Å²)**
Li/Fe1	2b	0	0	0.5	0.834/0.166(6)	0.0083
Fe2	2a	0.5	0.5	0	1	0.0025(6)
O	2c	0.5	0	0.4252(5)	1	0.0048(10)
D	2c	0.5	0	0.3208(6)	1	0.0286(15)
Se	2c	0	0.5	0.1618(3)	1	0.0004(8)
α_1 (°)	**α_2 (°)**	**Fe-Fe (Å)**		**Fe-Se (Å)**		
103.69(10)	112.44(6)	2.6708(1)		2.4016(17)		

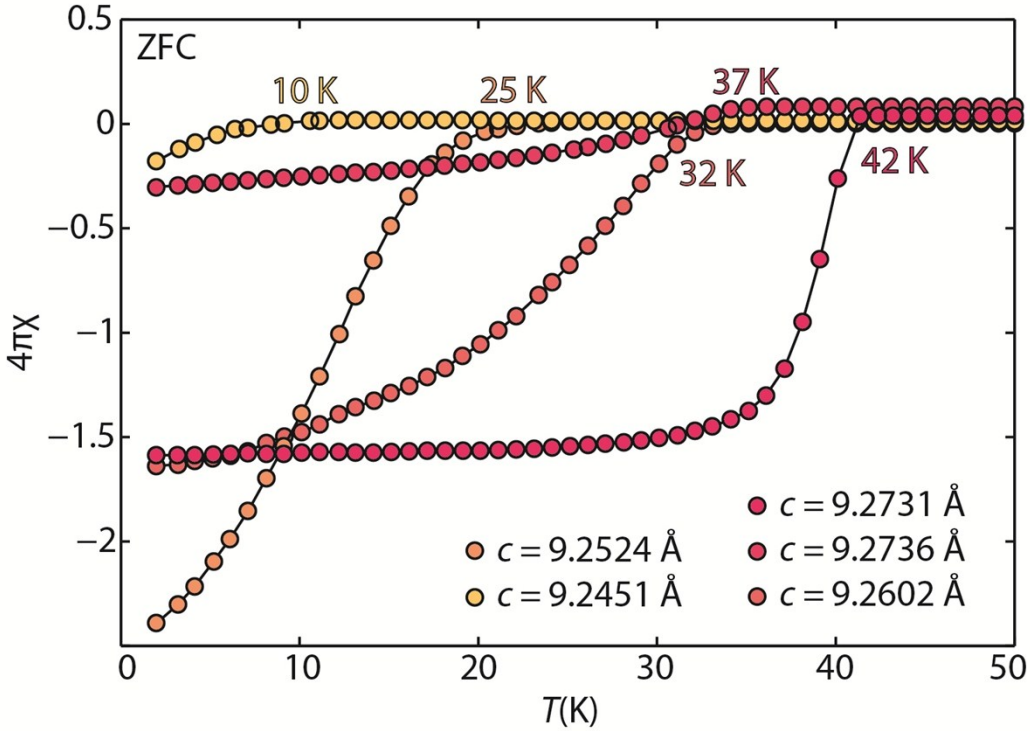

Figure S1. Magnetic susceptibility of single crystal ($Li_{1-x}Fe_xOH$)FeSe samples described in Table S2. Zero-field cooled lines illustrate drop in Tc associated with an increase in lattice parameter *c*

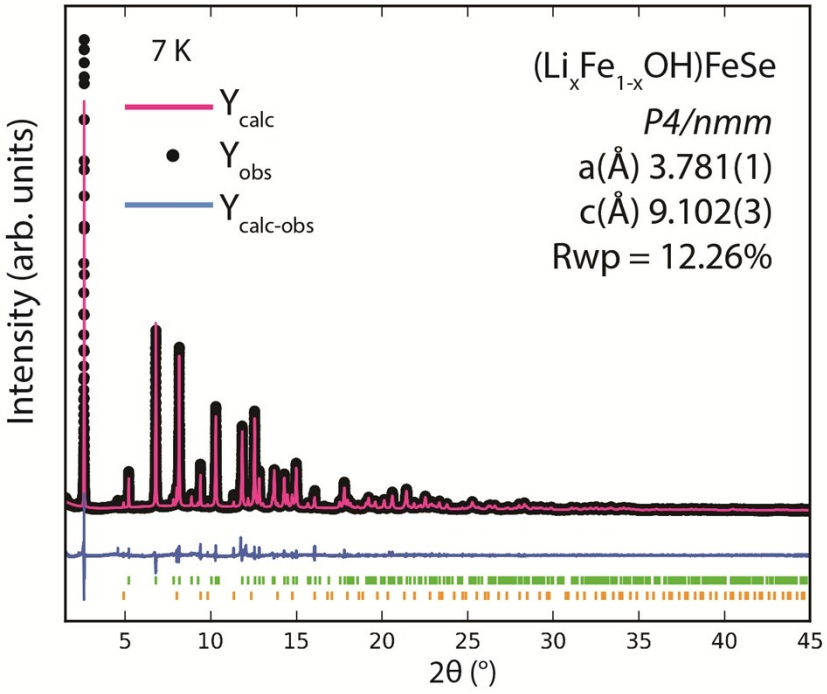

Figure S2. Synchrotron X-ray diffraction pattern of a non-superconducting single crystal ($Li_{1-x}Fe_xOH$)FeSe sample prepared at 160 °C for 4 d. Green and yellow ticks indicate the ($Li_{1-x}Fe_xOH$)FeSe and Fe_3O_4 phases, respectively.

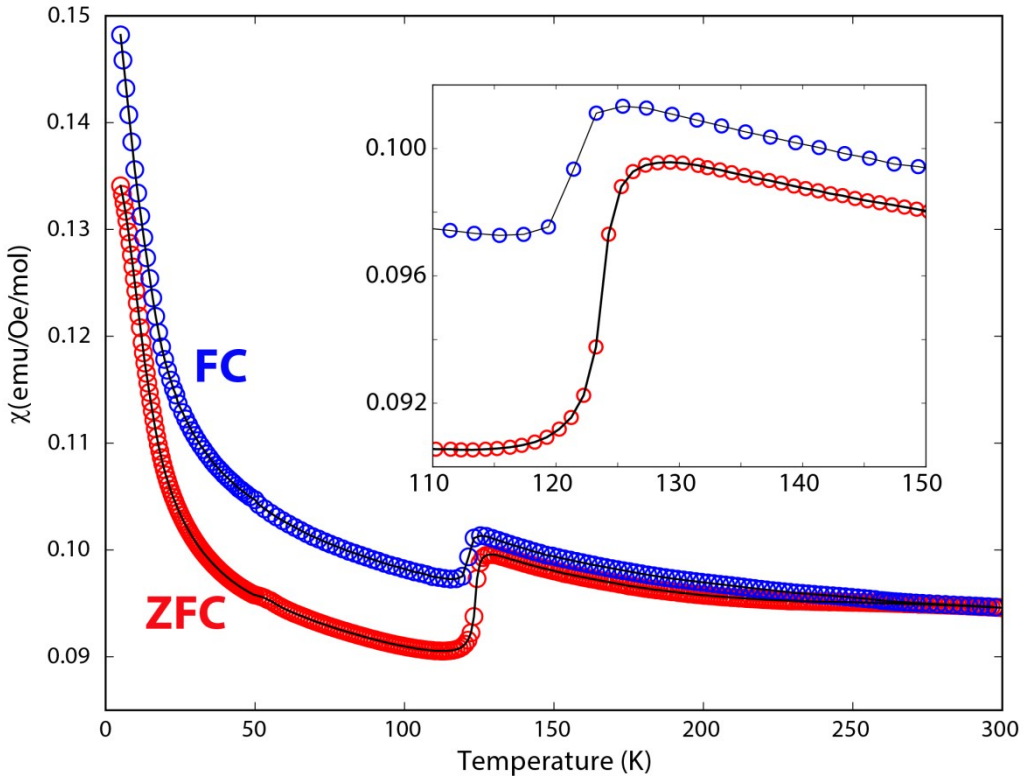

Fig. S3 Magnetic susceptibility at 1000 Oe for a non-superconducting single crystal ($Li_{1-x}Fe_xOH$)FeSe sample.The sample consisted of minor Fe_3O_4 impurity revealed by synchrotron XRD (Fig. S2).