Supplementary File

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Thermal decomposition of tris(O-ethyldithiocarbonato)-antimony(III) — a single source precursor for antimony sulfide thin films

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Table S1 Assignment of the IR absorption bands of KEX and SbEX [1-6]

IR frequency / cm^{-1}			Assignment[a]
KEX	SbEX	$(CH_3)_2CHOC(S)SC(O)OC_2H_5$ [6]	
3440	3435	-	ν(H-O-H)
2981	2987	2983	$\nu_{as}(CH_3)$
2955	2957	-	-
2933	2939	2938	$\nu_s(CH_3)$
-	2919	-	-
2890	2895	2905	$\nu(CH_3)$
2867	2868	-	-
1464	1468	1466	$\delta(CH_3)$
1439	1448	1445	$\delta(CH_3)$, $\delta(CH_2)$
1380	1386	1386	$\delta(CH_2)$, $\delta_s(CH_3)$
	1361	1351	
1173	**1230**	1244	ν_{as}(C-O-C)
1158	-	-	ν_{as}(C-O-C)
1141	1146	-	ν_{as}(C-O-C)
1118	(1135)	1134	ν_s(C-O-C)
1103	1112	-	ν_s(C-O-C)
1067	1075	1087	$\tau(CH_3)$, $\tau(CH_2)$
1050	1024	1018	ν_{as}(C=S)
1006	1001	-	ν_s(C=S)
863	874	874	ν(O-C-S)
-	847	840	ν(C-S)
815	813	800	$\rho(CH_2)$
446	436	464	δ(O-C-C)

[a] ν_s = symmetric stretching vibration; ν_{as} = asymmetric stretching vibration; δ = scissoring; ω = wagging; ρ = rocking, τ = twisting

[1] T. Chakrabarty, A. K. De, *Fresenius' Z. Anal. Chem.* 1968, 242, 152-159.
[2] C. Buchmaier, et al. *J. Mater. Sci.* 2017, 52, 10898-10914.
[3] P. Talonen, et al., *Phys. Chem. Chem. Phys.*, 1999, 1, 3661-3666.
[4] D. Barreca, *et al.*, *Appl. Organomet. Chem.* 2005, 19, 1002–1009.
[5] A. P. Chandra, *et al.*, *Int. J. Miner. Process.* 2012, 114-117, 16-26.
[6] L. C. Juncal, *et al.*, *Spectrochim. Acta, Part A*, 2015, 139, 346-355.

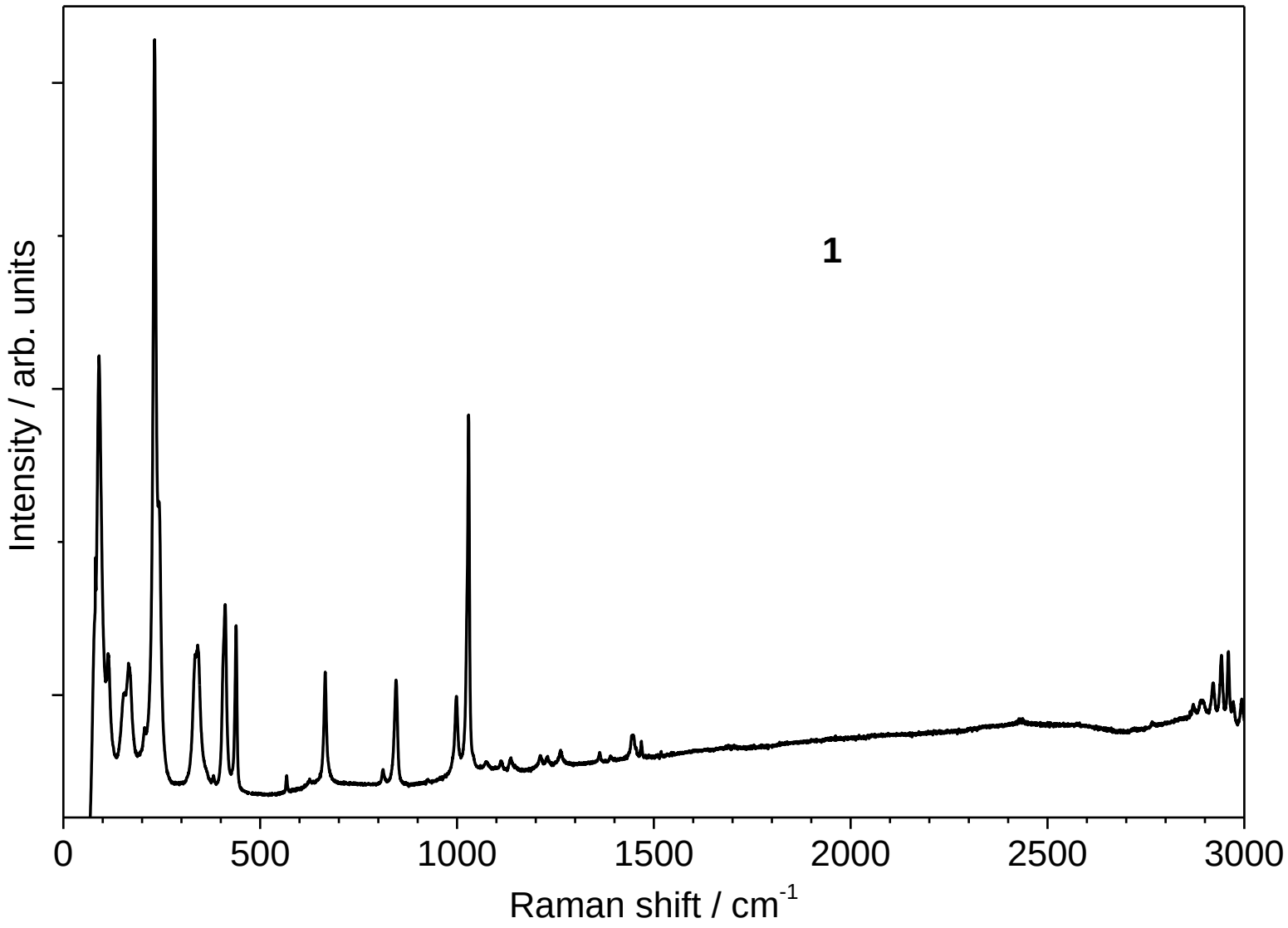

Fig. S1 Raman spectrum of as-synthesized compound **1** (SbEX – $Sb(S_2COCH_2CH_3)_3$) measured at 25°C in air

Table S2 Raman vibrational band centers of as-synthesized compound **1** (SbEX)

Raman shift / cm^{-1}				Assignment[a,b]		
SbEX	$Zn(2\text{-}PrX)_2$ [7]	$(CH_3)_2CHOC(S)\text{-}SC(O)OC_2H_5$ [6]	KEX [8]	Ref. [7]	Ref. [6]	Ref. [8]
91	87	-	-	Lattice mode	-	-
114	-	-	-	-	-	-
154	-	-	-	-	-	-
167	188	-	-	$\rho(CS_2)$	-	-
206	-	210	≈200	-	τ(C-O-C=S)	-
232	-	241	-	-	τ(C-C-O-C)	-
242	-		-	-		-
336	319	322	≈300	ν(Sb-S); ρ/δ_{IP}(S-C-S)	δ(O-C-S)	-
342		354	-		δ(O-C-C)	-
382	-	378	-	-	*δ(C-C-C)*	-
406	405	403	402	ν(Sb-S)	δ(O-C-C)	(O-C-C) bending
439	469	458	449	ρ/δ_{IP}(C-O-C)	δ(O-C-C)	$(C\text{-}O\text{-}C)_{trans}$ bending
567	572	562	582	$\omega(OCS_2)$	δ_{OOP}(C=S)	$\omega(OCS_2)_{OOP}$
665	652	667	666	$\nu(CS_2)_{IP}$	δ_{OOP}(C=O)	$\nu_s(CS_2)_{trans}$
812	809	799	-	*ν_{IP}(O-C-C₂)*	$\rho(CH_3)$	
845	-	850	867	-	$\nu(C\text{-}S)_{[(C(O)\text{-}S)]}$	ν(C-C-O-C)
998	-	1017	-	-	ν(C=S)	-
1029	1030		1051	$\nu_{OOP}(CS_2)$		$\nu_{as}(CS_2)$
1075	1090	1086	1096	*ν_{OOP}(C-C-C)*	$\nu(C\text{-}O)_{[O\text{-}C(H)]}$	$\rho(CH_3)$; $\rho(CH_2)$
1112	-	-	-	-	-	-
1136	1150	1144	1146	ν(C–C), ν[(S)C–O]	*ν(C-O)[O-C(O)]*	ν_{as}(C-O-C-S_2)
1212	1191	1182	-	ν_{OOP}(C-O-C)	*ν(C-O)[O-C(O)]*	-
1230	1235	-	-		$\nu(C\text{-}O)_{[O\text{-}C(S)]}$	-
1263	1250	1271	-		$\nu(C\text{-}O)_{[O\text{-}C(S)]}$	-
1363	1350	1350	-	ω(C-H) ∥ [O-C(H)]	δ(H-C-O)	-
1391	1390	1387	-	$\rho/\delta_{IP}(CH_3)_{IP}$	$\delta(CH_2)$	-
1446	1450	1451	1445	$\omega/\tau_{OOP}(CH_3)$	$\delta(CH_3)$	$bending_{as}(CH_3)$
1469			1461			$bending_{as}(CH_3)$
2871	2870	2873	2868	$\nu_{IP}(CH_3)$	$\nu_s(CH_3)$	$\nu_s(CH_3)$
2892	-	2900	-	-	$\nu_s(CH_2)$	-
2921	-	2926	-	-	$\nu_{as}(CH_3)$	-
2942	2940	2939	2935	$\nu_{OOP}(CH_3)$	$\nu_{as}(CH_2)$	$\nu_s(CH_2)$
2959	-	-	-	-	-	-
2972	-	2969	2961	-	$\nu_{as}(CH_3)$	$\nu_{as}(CH_3)$
2993	2988	2984	-	$\nu_{OOP}(CH_3)$	$\nu_{as}(CH_2)$	-

[a]Vibrations incompatible with SbEX in italic.

[b]ν_s = symmetric stretching vibration; ν_{as} = asymmetric stretching vibration; δ = scissoring; ω = wagging; ρ = rocking, τ = twisting, IP = in-plane, OOP = out-of-plane, ∥ = parallel to.

[6] L. C. Juncal, *et al.*, *Spectrochim. Acta, Part A*, 2015, 139, 346-355.
[7] D. Barreca et al., Appl. Organomet. Chem. 2005, 19, 1002-1009.
[8] R. Woods, G. A. Hope, Colloids Surf. A, 1998, 137, 319-328.

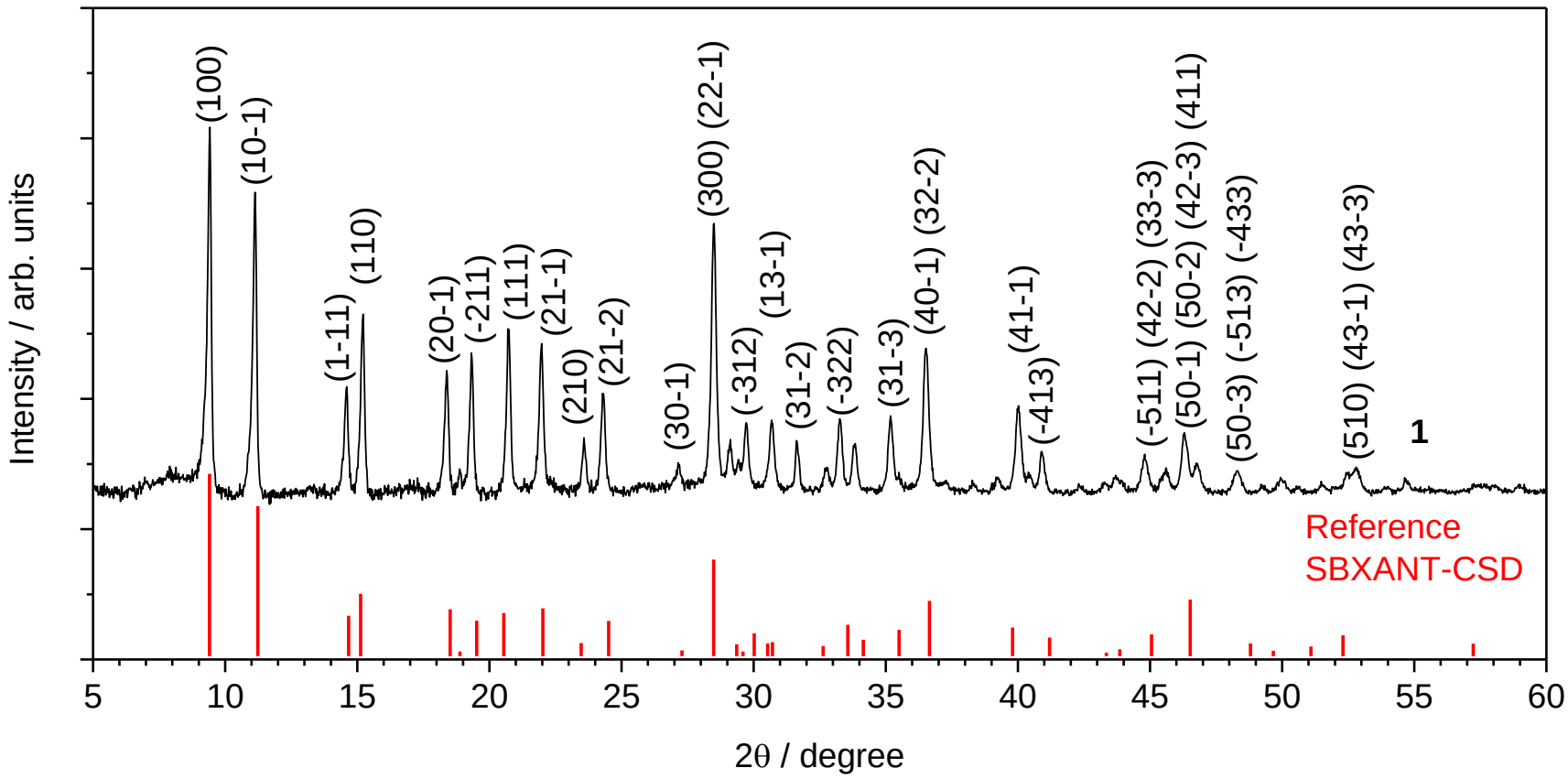

Fig. S2 Powder XRD pattern of **1** (SbEX – $Sb(S_2COCH_2CH_3)_3$) measured at 25°C in air, and SbEX reference intensities generated from CIF in CSD database originating from G. Gottardi, 1961, *Z. Kristallogr. – Cryst. Mater.*, 115, 451

Table 3 Numeric powder XRD data of **1** (SbEX – $Sb(S_2COCH_2CH_3)_3$) measured at 25°C in air

2θ (λ Cu $K_{α1}$ = 1.540593 Å)	d(Å)	Intensity
9.4159	9.38511	100
11.1274	7.94508	77
14.5878	6.06728	17.8
15.2044	5.8226	37.7
18.3751	4.82441	26.7
18.8681	4.69945	1.6
19.3175	4.59112	24.6
20.7203	4.28335	29
21.9634	4.04365	37.7
23.5852	3.76914	15.3
24.2959	3.66046	28
27.162	3.28038	3.6
28.4852	3.13093	69.3
29.0535	3.07097	7.6
29.4318	3.03235	3.3
29.7094	3.00464	14.6
30.6394	2.91553	17.5
31.628	2.82662	9.3
32.7186	2.73484	6
33.2462	2.69264	18.5
33.7979	2.64994	12.2
35.1764	2.54918	18.9
35.5051	2.52634	1.3
36.4942	2.4601	44.8
39.1734	2.29779	3.1
39.9971	2.25235	26
40.4122	2.23017	4.1
40.8947	2.20496	10.5
43.7609	2.06696	9.5
44.7644	2.02293	10.8
45.5828	1.98849	7.4
46.2752	1.96034	17.2
46.7587	1.94119	9.9
48.2419	1.88491	6.1
49.9375	1.82481	3.9
52.4215	1.74404	2
52.7714	1.73329	14.2
54.6403	1.67834	3.7
57.492	1.60169	4.5
60.2459	1.53489	2.5
65.2289	1.42917	5.5

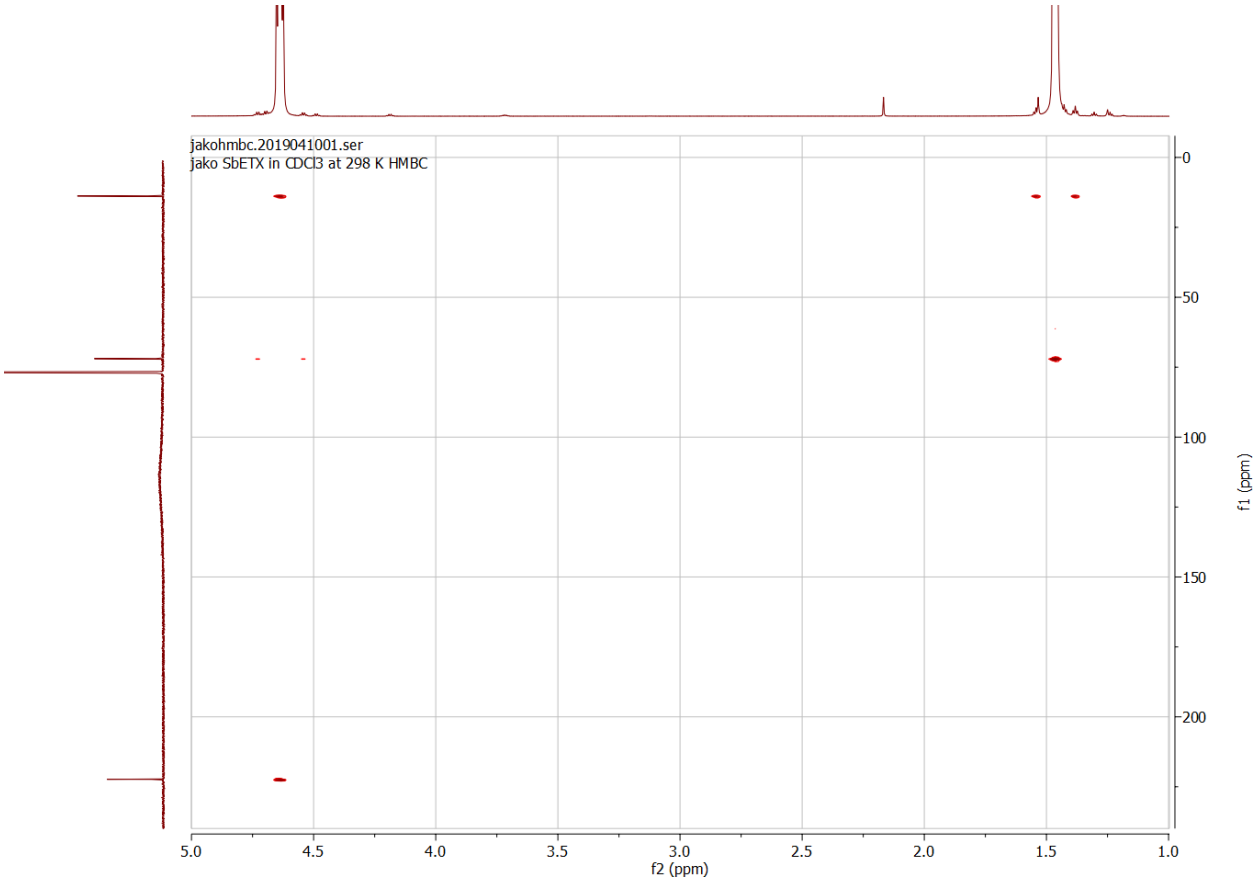

Fig. S3 HMBC NMR of compound **1** dissolved in $CDCl_3$, measured at 25°C

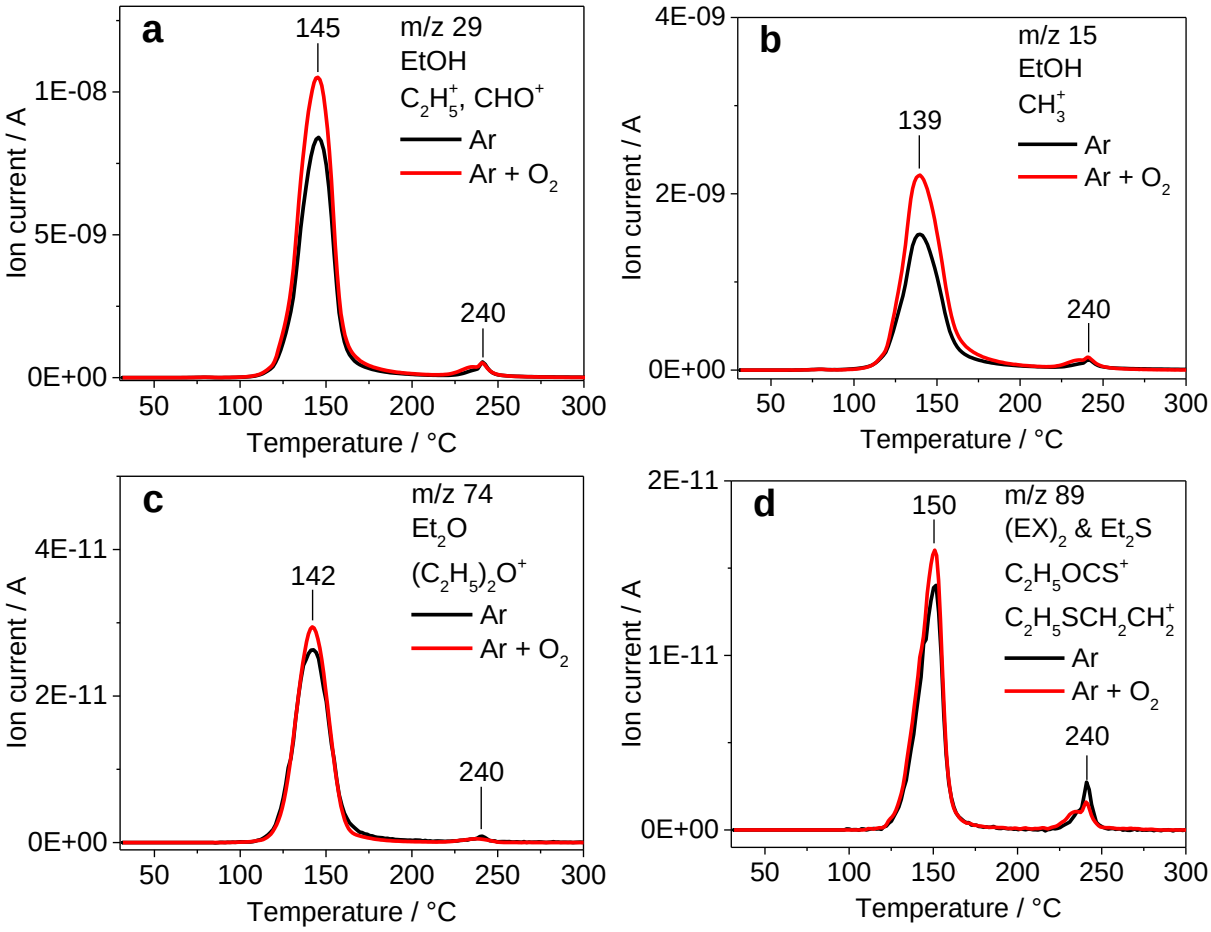

Fig. S4 Additional gas evolution profiles of gaseous species, represented by their characteristic mass spectroscopic ion fragments, from **1** in argon, and in air, as measured by in situ online coupled TG/DTA-EGA-MS system. Ar flow 60 mL min^{-1}, heating rate 10°min^{-1}, initial mass 11.6 mg; air flow 60 mL min^{-1}, heating rate 10°min^{-1}, initial mass 13.9 mg

Table S4 Peak centers, as measured in argon by in situ online EGA-MS, and assignment of peaks. Ar flow 60 mL min^{-1}, heating rate 10°min^{-1}, initial mass 11.6 mg. Air flow 60 mL min^{-1}, heating rate 10°min^{-1}, initial mass 13.9 mg

m/z	Peak center / °C		Assignment
	Ar	Air	
15	141	141	CH_3^+
18	138	143	H_2O^+
27	144	144	$C_2H_3^+$
28	138	144	$C_2H_4^+$ / CO^+
29	144	144	$C_2H_5^+$ / CHO^+
31	142	143	CH_3O^+
32	137	132	CH_3OH^+ / S^+
34	144	142	H_2S^+
43	143	142	CH_3CO^+
44	138	138	CO_2^+ / CS^+
45	144	143	$C_2H_5O^+$ / $OCOH^+$ / CSH^+
47	146	146	CH_3S^+
48	144	146	SO^+ / CH_3SH^+
60	141	141	OCS^+
62	146	146	$C_2H_5SH^+$ / $HOCSH^+$/ $OC^{34}S^+$
64	138	140	SO_2^+ / CH_3OSH^+
66	134	135	$^{34}SO_2^+$ / $S(OH)_2^+$
66	141	151	$^{34}SO_2^+$ / $S(OH)_2^+$
74	142	142	$(C_2H_5)_2O^+$
75	141	140	$C_2H_5SCH_2^+$ / CH_3OCS^+
76	136	136	CS_2^+ / CH_3OCSH^+ / SCO_2^+
89	148	148	$C_2H_5SC_2H_4^+$ / $C_2H_5OCS^+$