

Supplementary Information Table 1 Crystallographic data for sulfides **1** to **4**.

Compound	1	2	R-3	4
Formula	C ₁₃ H ₁₁ BrS	C ₁₅ H ₁₆ O ₂ S	C ₁₆ H ₁₈ O ₂ S	C ₁₆ H ₁₈ O ₂ S
Formula Weight	279.19	260.34	274.36	274.36
T/K	240(2)	293(2)	123(2)	120(2)
Crystal System	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	5.6004(3)	30.458(3)	8.1016(3)	7.8617(2)
<i>b</i> /Å	13.8743(7)	5.4558(6)	5.30912(18)	22.6828(6)
<i>c</i> /Å	15.1686(9)	8.0849(5)	16.8806(5)	8.5775(2)
α /°	93.515(2)	90	90	90
β /°	90.117(2)	90.494(7)	97.057(3)	115.3340(10)
γ /°	93.332(3)	90	90	90
<i>V</i> /Å ³	1174.40(11)	1343.4(2)	720.57(4)	1382.48(6)
<i>Z</i>	4	4	2	4
$\rho_{\text{calc}}/\text{gcm}^{-3}$	1.579	1.287	1.265	1.318
μ/mm^{-1}	3.640	0.232	1.951 (Cu)	0.229
2 θ max/°	55.02	51.02	134.98	55.06
Total reflections	10468	3712	6182	11010
Unique reflections	5295	2500	2485	3068
Refls <i>I</i> > 2 σ (<i>I</i>)	3738	1702	2398	2682
<i>R</i> _{int}	0.0517	0.0805	0.0257	0.0268
Parameters	272	165	176	176
<i>R</i> ₁ [<i>F</i> , <i>I</i> > 2 σ (<i>I</i>)]	0.0786	0.0400	0.0348	0.0325
<i>wR</i> ₂ (<i>F</i> ² , all data)	0.2224	0.1069	0.0977	0.0871
Flack	-	-	0.42(2)	-
Hooft ^a			0.427(5) ^b	

^a as implemented in PLATON
^b racemic twin