

Electronic Supporting Information for

Gold(III) Assisted C-H activation of 1,4,7-trithiacyclonone: Synthesis and Spontaneous Resolution of a Bicyclic Chiral Sulfonium Salt

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Experimental Section	S2
X-ray Crystallographic Information (Table S1)	S8
¹³ C DEPT 135 NMR Spectrum of 2 (Figure S1)	S9
¹ H NMR Spectrum of 2 (Figure S2)	S10
NMR-Monitored Reaction Progress of 1 to form [[9]aneS ₃] ⁺ (Figure S3)	S11
Color Images of Chiral Crystals 3a and 3b (Figure S4)	S12

Experimental Section

General Considerations. All manipulations were carried out in air. Solvents were purchased from Aldrich and used as received. The reagents KAuCl_4 (Strem), $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Aldrich), 1,4,7-trithiacyclononane (Aldrich), and acetylacetonone (Aldrich) were used as received. The compounds $\text{Na}(\text{acac})$,¹ $(\text{TBA})[\text{AuCl}_4]$ (TBA = tetra-*n*-butyl ammonium),² $(\text{TBA})[\text{AuCl}_2]$,³ and $[[9]\text{aneS}_3](\text{BF}_4)$ ⁴ were prepared by published methods. NMR solvents were purchased from Cambridge Isotope Labs and used as received. NMR spectra were recorded at ambient temperature on a JEOL ECS 400 MHz spectrometer. ^1H and ^{13}C NMR chemical shifts were referenced to residual solvent. Elemental analyses were obtained from Atlantic Microlab, Inc.

X-ray Crystallography. The single-crystal X-ray diffraction data for compounds **1**, **2**, **3a**, and **3b** were collected on a Rigaku XtaLAB mini diffractometer⁵ using Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The diffractometer was equipped with an Oxford Cryosystems desktop cooler⁶ apparatus used to collect data at -100°C . The crystals were mounted on a MiTeGen micromount⁷ using STP oil. Preliminary cell constants were calculated from reflections harvested from one set of 12 images. A randomly oriented region of reciprocal space was surveyed to the extent of one sphere and to a resolution of 0.77 \AA . Three major sections of frames were collected with 1.0° steps in ω at three different ϕ settings. The frames were integrated using CrystalClear-SM Expert 3.1⁵ to give the *hkl* files corrected for L_p and decay. Data were corrected for absorption effects using a multiscan method (REQAB).⁵ The structures were solved by direct methods and refined on F^2 using the SHELXTL software package.⁸ All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Refinement details for selected

structures are provided below, and crystallographic parameters of all complexes are summarized in Table S1. ORTEP drawings were prepared using ORTEP-3⁹ and POV-Ray.¹⁰ Crystallographic data for the complexes have been deposited at the Cambridge Crystallographic Data Centre (977469-977472) and can be obtained free of charge via www.ccdc.cam.ac.uk.

The structure of **1** consists of an asymmetric unit composed of one entire unique $[\text{Au}[[9]\text{aneS}_3]\text{Cl}_2]^+$ cation and one entire unique $[\text{AuCl}_4]^-$ anion. No solvent or disorder is present in the structure. No close Au...Au intermolecular contacts less than the VDW radii sum are present. The closest intermolecular Au...Au contacts are between neighboring $[\text{AuCl}_4]^-$ anions whose molecular planes are parallel (4.253 Å, symmetry codes x, y, z and $-x, 2-y, -z$). The next closest intermolecular Au...Au contacts are between neighboring $[\text{AuCl}_4]^-$ anions whose molecular planes are also parallel (4.723 Å, symmetry codes x, y, z and $-x, 1-y, -z$). The $[\text{AuCl}_4]^-$ anions form a zigzag linear chain with alternating distances of 4.253 Å and 4.723 Å between neighboring Au atoms within the chain.

The structure of **2** consists of an asymmetric unit composed of one entire unique $[[9]\text{aneS}_3]^+$ cation and one entire unique $[\text{AuCl}_4]^-$ anion. No solvent or disorder is present in the structure. The $[[9]\text{aneS}_3]^+$ cation adopts a chair conformation of the six-membered ring and an envelope conformation of the five-membered ring. The chirality at atoms C6 and S2 have opposite handedness. As **2** crystallized in a centrosymmetric space group, the structure represents a racemic mixture; an equal amount of the $C6(R),S2(S)$ and the $C6(S),S2(R)$ are present in the structure. No close Au...Au intermolecular contacts less than the VDW radii sum are present. The closest intermolecular Au...Au contacts are between neighboring $[\text{AuCl}_4]^-$ anions whose molecular planes are nearly perpendicular (5.657 Å, symmetry codes x, y, z and $x-$

0.5, y, 0.5-z). The $[\text{AuCl}_4]^-$ anions form a zigzag type chain with this single-distance closest intermolecular approach.

The structure of **3a** consists of an asymmetric unit composed of one entire unique $[\text{9[ans]S}_3]^+$ cation and one entire unique $[\text{AuCl}_2]^-$ anion. No solvent or disorder is present in the structure. The $[\text{9[aneS}_3]^+]$ cation adopts the same ring conformations in **3a** as in **2**. This structure of **3a** exhibits a chiral space group. The absolute configuration at C6 is *R* and S2 is *S*. This is the same as one of the enantiomers of the $[\text{9[ans]S}_3]^+$ cation found in the structure of **2**. The Flack parameter¹¹ of 0.002(6) indicates a clear assignment of this enantiomer by anomalous dispersion, based on 1094 Friedel pairs.

The structure of **3b** consists of an asymmetric unit composed of one entire unique $[\text{9[ans]S}_3]^+$ cation and one entire unique $[\text{AuCl}_2]^-$ anion. No solvent or disorder is present in the structure. The $[\text{9[aneS}_3]^+]$ cation adopts the same ring conformations in **3b** as in **2** and **3a**. This structure of **3b** is isomorphous with **3a**. The absolute configuration at C6 is *S* and S2 is *R*. This is the same as one of the enantiomers of the $[\text{9[ans]S}_3]^+$ cation found in the structure of **2** and the opposite absolute configuration of that determined in **3a**. The Flack parameter¹¹ of -0.004(7) indicates a clear assignment of this enantiomer by anomalous dispersion, based on 1097 Friedel pairs.

[Au([9]aneS₃)Cl₂][AuCl₄] (1) Solid [9]aneS₃ (0.0458 g, 0.254 mmol) was added to a yellow solution of KAuCl₄ (0.192 g, 0.508 mmol) in CH₃NO₂ (2.5 mL) resulting in the immediate formation of a red-brown precipitate. The reaction mixture was stirred at rt for 1 hr. The precipitate was collected by vacuum filtration and dried in vacuo (0.155 g, 0.197 mmol, 78%). A portion of the precipitate (0.050 g, 0.0635 mmol) was stirred with distilled water (5 mL) for 30 min. The red brown precipitate was collected by vacuum filtration and dried in vacuo (0.038 g,

0.048 mmol, 76%). δ_{H} (400 MHz; CD_3NO_2) 4.05 - 3.70 (12 H, m, $-\text{CH}_2$) δ_{C} (100 MHz; CD_3NO_2) 41.33 ($-\text{CH}_2$). Found: C, 9.4; H, 1.4; Cl, 26.7. Calc. for $\text{C}_6\text{H}_{12}\text{Au}_2\text{Cl}_6\text{S}_3$: C, 9.2; H, 1.5; Cl, 27.0%.

[[9]aneS₃][AuCl₄] (2) This compound was first obtained as a minor product from an experiment involving heating a CH_3NO_2 solution of **1** to 90°C for 2h, followed by vapor diffusion of this mixture with diethyl ether at rt over 2 weeks. Subsequently, attempts to isolate a pure sample of **2** from **1** by the controlled heating of a dilute CH_3NO_2 solution of **1** (not isolated from the reaction to form **1**) at 60°C in a water bath over 2d followed by diffusion of diethyl ether into a CH_3NO_2 solution of the reaction mixture yielded a red crystalline solid. Elemental analysis of this solid was consistent with a solid solution with the formula $[[9]\text{aneS}_3][\text{AuCl}_4] (\text{K}[\text{AuCl}_2])_{0.75} \text{KCl}$. Found: C, 8.9; H, 1.5; Cl, 28.35. Calc. for $\text{C}_6\text{H}_{11}\text{S}_3\text{Au}_{1.75}\text{Cl}_{6.5}\text{K}_{1.75}$: C, 8.8; H, 1.4; Cl, 28.0%. Potassium was likely present as the heated solution sample of **1** was a crude product mixture from the formation of **1** (not an isolated sample that was then redissolved and heated). Upon stirring this solid solution with water, recollection by filtration, and drying, an elemental analysis consistent with the formula $[[9]\text{aneS}_3] [\text{AuCl}_2] (\text{K}[\text{AuCl}_4])_{0.85}$ was obtained. Found: C, 9.3; H, 1.3; Cl, 24.9. Calc. for $\text{C}_6\text{H}_{11}\text{S}_3\text{Au}_{1.85}\text{Cl}_{5.4}$: C, 9.4; H, 1.4; Cl, 24.9 %. This analysis is consistent with removal of some potassium by the water rinse. The filtrate obtained from the water rinse of the solid solution tested positive for the presence of potassium using the tetraphenylborate method.¹² Though rinsing the solid solution collected from the thermal decomposition reaction of **1** yielded the cation $[[9]\text{aneS}_3]^+$, this method does not provide pure samples of **2**, likely due in part to the reactivity of the $[\text{AuCl}_4]^-$ anion in aqueous solution to form $[\text{AuCl}_2]^-$.¹³

A different method was used to prepare an analytically pure sample of **2** using a strategy that involved separate synthesis of $[[9]aneS_3](BF_4)$ and $(TBA)[AuCl_4]$ followed by a metathesis to form **2**. Solid $[[9]aneS_3](BF_4)$ (0.075g, 0.282 mmol) was added to a solution of $(TBA)[AuCl_4]$ (0.164g, 0.282 mmol) in CH_3NO_2 (5 mL) immediately forming an orange precipitate. After stirring the reaction mixture for 5 min, the solid was collected by vacuum filtration, rinsed with diethyl ether (10 mL) and dried in vacuo (0.114g, 0.220 mmol, 78%). δ_H (400 MHz; CD_3NO_2) 5.30 (1H, t, J 4.1, CH), 4.23 (1H, ddd, J 13.2, 7.7, 3.0), 4.01-3.72 (5H, overlapping multiplets), 3.62 (1H, dt, J 12.5, 8.0), 3.43 (1H, dd, J 16.0, 5.0), 3.36-3.22 (1H, overlapping multiplets), 3.22-3.10 (1H, m) δ_C (100 MHz; CD_3NO_2) 61.32 (-CH), 49.57 (-CH₂), 37.23 (-CH₂), 36.02 (-CH₂), 28.16 (-CH₂), 25.35 (-CH₂). Found: C, 14.4; H, 2.1; Cl, 28.0. Calc. for $C_6H_{11}Au_1Cl_4S_3$: C, 13.9; H, 2.1; Cl, 27.4%.

$[[9]aneS_3][AuCl_2]$ (**3**) This compound was first obtained as a minor product from an attempted crystallization of **2** by diffusion of a CH_3NO_2 solution of **2** with diethyl ether at rt over 1 month. As attempts at controlled reduction of the $[AuCl_4]^-$ anion of **2** to form $[AuCl_2]^-$ were unsuccessful (Au^{III} to Au^I reduction accompanied by formation of a gold mirror), a different method was used to prepare an analytically pure sample. This strategy involved separate synthesis of $[[9]aneS_3](BF_4)$ and $(TBA)[AuCl_2]$ followed by a metathesis to form **3**. Solid $[[9]aneS_3](BF_4)$ (0.095g, 0.357 mmol) was added to a solution of $(TBA)[AuCl_2]$ (0.182g, 0.357mmol) in CH_3NO_2 (5 mL). Colorless crystals were obtained by vapor diffusion of this reaction mixture with diethyl ether (0.110g, 0.246 mmol, 69%). δ_H (400 MHz; CD_3NO_2) 5.32 (1H, t, J 4.0, CH), 4.24 (1H, ddd, J 13.1, 7.8, 3.0), 4.00-3.73 (5H, overlapping multiplets), 3.62 (1H, dt, J 12.4, 7.8), 3.44 (1H, dd, J 16.0, 5.5), 3.37-3.23 (1H, overlapping multiplets), 3.22-3.09 (1H, m) δ_C (100

MHz; CD₃NO₂) 61.29 (-CH), 49.61 (-CH₂), 37.22 (-CH₂), 36.01 (-CH₂), 28.14 (-CH₂), 25.35 (-CH₂). Found: C, 16.3; H, 2.4; Cl, 16.05. Calc. for C₆H₁₁Au₁Cl₂S₃: C, 16.1; H, 2.5; Cl, 15.85%.

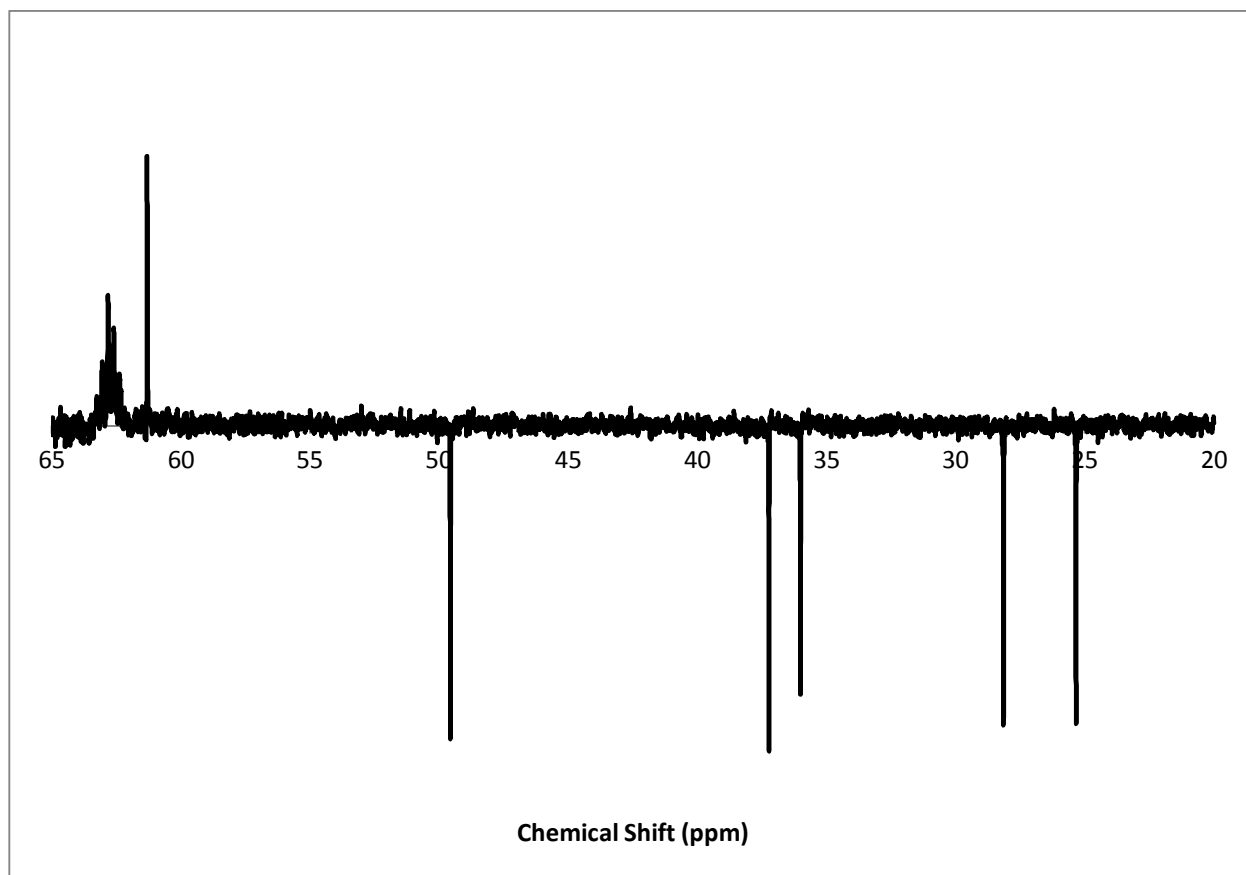
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Table S1. X-ray crystallographic data

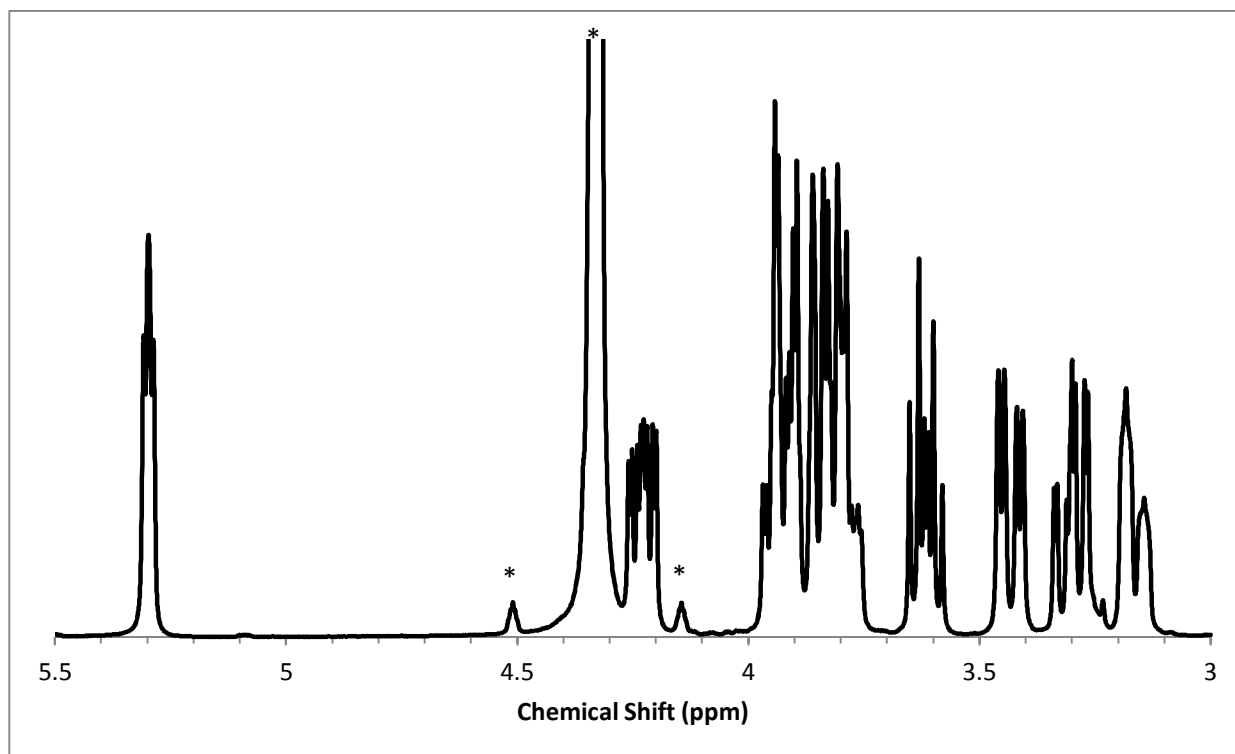
complex	1	2	3a	3b
Empirical Formula	C ₆ H ₁₂ Au ₂ Cl ₆ S ₃	C ₆ H ₁₁ AuCl ₄ S ₃	C ₆ H ₁₁ AuCl ₂ S ₃	C ₆ H ₁₁ AuCl ₂ S ₃
Formula Weight	786.99	518.11	447.21	447.21
T (K)	173(2)	173(2)	173(2)	173(2)
Crystal System	monoclinic	orthorhombic	monoclinic	monoclinic
Space Group	P2 ₁ /c	Pbca	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	15.358(2)	8.8163(11)	8.4391(10)	8.4404(17)
<i>b</i> (Å)	7.7560(11)	15.928(2)	9.0867(11)	9.0920(18)
<i>c</i> (Å)	15.739(3)	19.372(3)	14.9595(18)	14.985(3)
<i>α</i> (deg)	90	90	90	90
<i>β</i> (deg)	116.071(9)	90	90	90
<i>γ</i> (deg)	90	90	90	90
<i>V</i> (Å ³)	1684.1(5)	2720.3(7)	1147.1(3)	1149.9(4)
<i>Z</i>	4	4	4	4
<i>d</i> _{calc} (g/cm ³)	3.104	2.530	2.589	2.583
<i>μ</i> (mm ⁻¹)	18.762	12.060	13.827	13.794
Reflections Collected	12056	12616	10573	12006
Independent Reflections	3844 [R(int) = 0.0510]	3121 [R(int) = 0.0500]	2615 [R(int) = 0.0567]	2621 [R(int) = 0.0547]
Data / Restraints / Parameters	3844 / 0 / 154	3121 / 0 / 127	2615 / 0 / 109	2621 / 0 / 109
GOF on F ²	1.040	1.062	0.967	1.060
R1 (wR2 all data)	0.0441 (0.1144)	0.0366 (0.0844)	0.0251 (0.0512)	0.0228 (0.0528)
Flack Parameter			0.002(6)	-0.004(7)

Figure S1



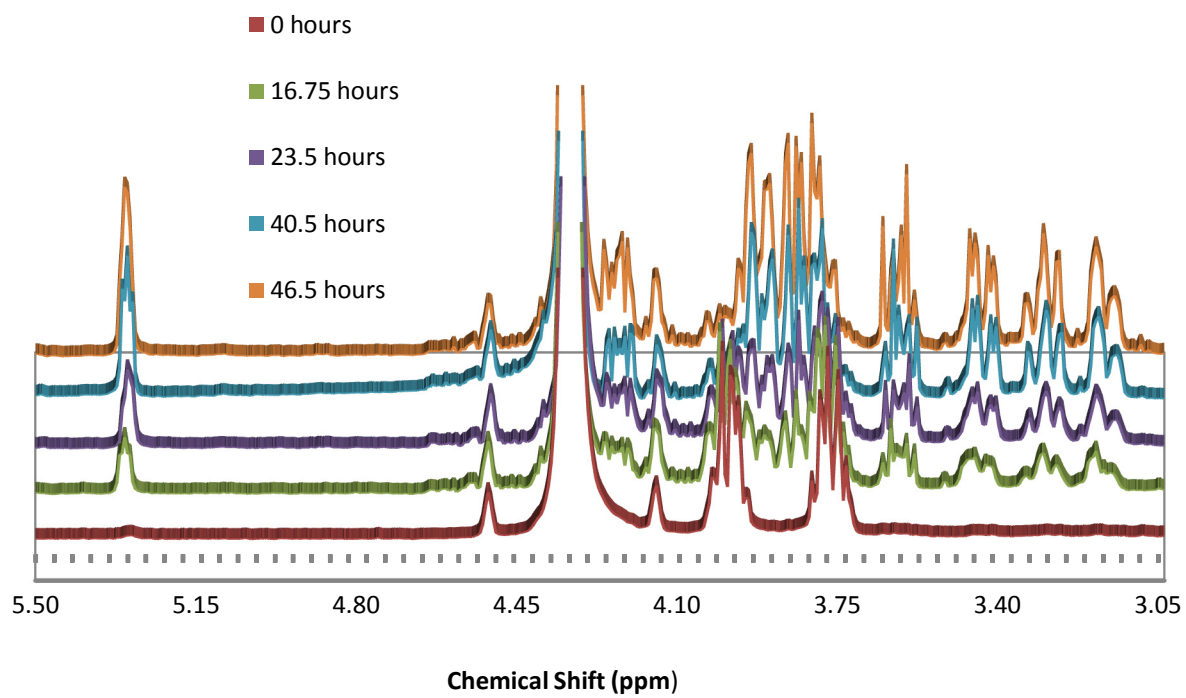
DEPT 135 ^{13}C NMR of **2** in CD_3NO_2 . Note phase of methine carbon (chiral C6) is positive, while the five remaining methylene carbons show a negative phase. The multiplet at 62.8ppm arises from the CD_3NO_2 .

Figure S2



^1H NMR of **2** in CD_3NO_2 . Asterisks indicate peaks due to CD_3NO_2 .

Figure S3



¹H NMR monitored NMR tube heated reaction of **1** in CD₃NO₂. Asterisks indicate peaks due to CD₃NO₂.

Figure S4

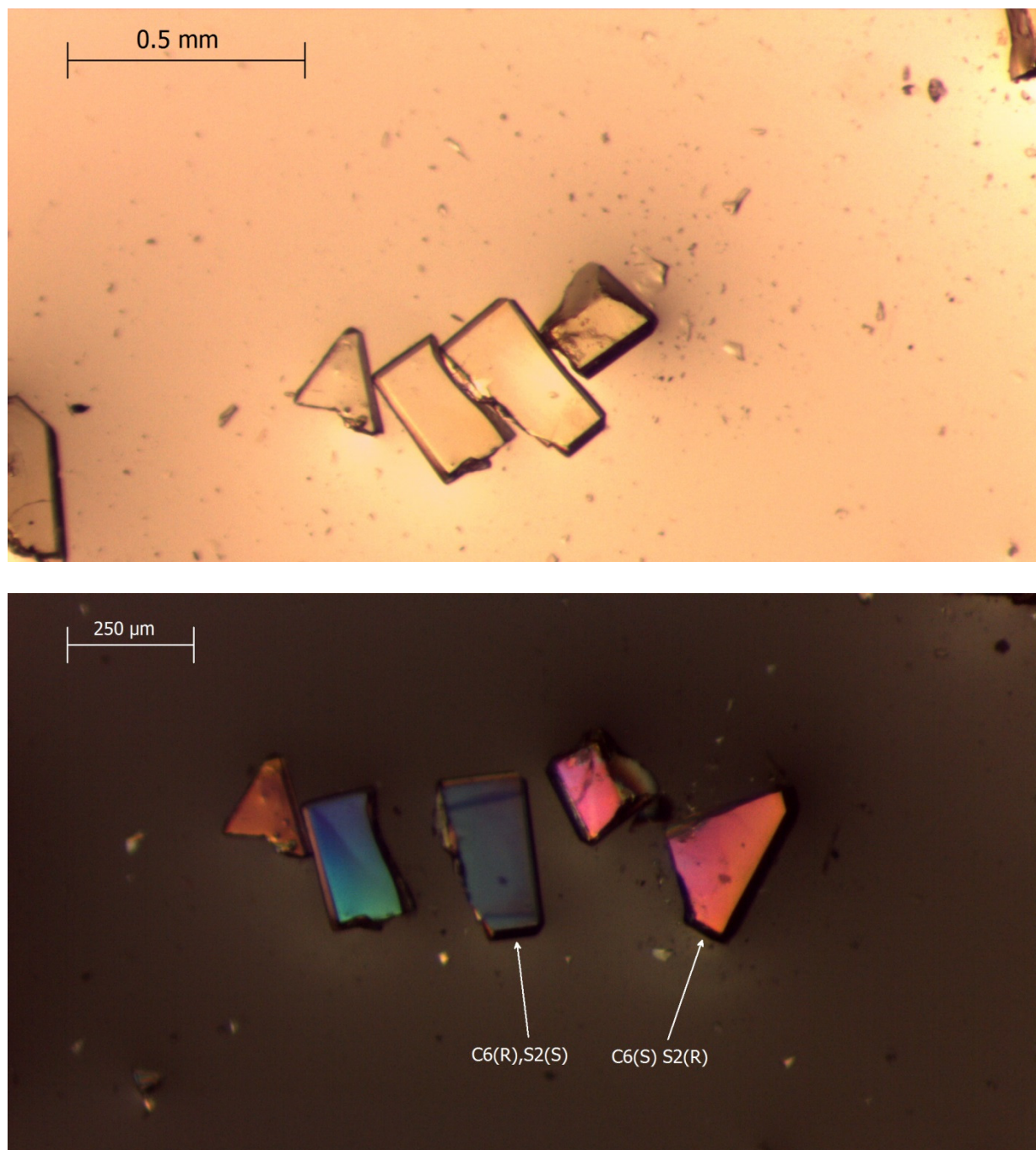


Image of crystals of **3a** and **3b** using transmitted unpolarized light (above). Image of crystals of **3a** and **3b** using transmitted polarized light, chiral center labels indicate the crystals used for data collection of **3a** and **3b** (below).