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Supplementary Information

for

The 2,6-dimercaptoazulene motif: efficient synthesis and completely regioselective metallation of its 6-mercapto terminus

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A. SYNTHETIC PROCEDURES AND CHARACTERIZATION

A1. General procedures, starting materials and equipment. Unless specified otherwise, all operations were performed under an atmosphere of 99.5% argon further purified by passage through columns of activated BASF catalyst and molecular sieves. All connections involving the gas purification systems were made of glass, metal, or other materials impermeable to air. Solutions were transferred via stainless steel needles (cannulas) whenever possible. Standard Schlenk techniques were employed with a double manifold vacuum line. Both CH_2Cl_2 and CD_2Cl_2 were distilled over CaH_2. Deuterated chloroform was distilled over P_2O_5. Tetrahydrofuran (THF) was distilled from Na/benzophenone. Pentane was distilled from Na/benzophenone dissolved in a minimum amount of diglyme. Benzene was distilled over freshly cut potassium metal. Methanol was distilled over Mg turnings. Other solvents were used as received from commercial sources.

Infrared spectra were recorded on a PerkinElmer Spectrum 100 FTIR spectrometer with liquid samples sealed in 0.1 mm NaCl cells or solid samples as KBr pellets. NMR samples were analyzed on Bruker Avance 400 or 500 spectrometers. ^{1}H and ^{13}C NMR chemical shifts are given with reference to residual solvent resonances relative to $SiMe_4$. ^{31}P NMR chemical shifts are referenced externally to 85% aqueous H_3PO_4 (a sealed capillary tube containing 85% aqueous H_3PO_4 was inserted into each sample tube subject to ^{31}P NMR analysis). UV-Vis spectra were recorded at 24 °C using a CARY 100 spectrophotometer.

Melting points are uncorrected and were determined for samples in capillary tubes sealed under argon. Elemental analyses were carried out by ALS Environmental (formerly Columbia Analytical Services), Tucson, Arizona and by Micro-Analysis, Inc., Wilmington, Delaware. Mass-spectral data were obtained in the Mass-spectrometry facility at the University of Kansas.

2-Mercaptoazulene (**1a**),[1] 2-mercapto-1,3-diethoxycarbonylazulene (**1b**),[1] 6-bromo-1,3-diethoxycarbonylazulene,[2] 2-amino-6-bromo-1,3-diethoxycarbonylazulene (**3**),[3] 2-hydroxy-6-bromo-1,3-diethoxy-carbonylazulene (**7**),[4] and $Au(PPh_3)Cl$[5] were prepared according to literature procedures. Other reagents were obtained from commercial sources and used as received.

A2. Synthesis of 6-mercapto-1,3-diethoxycarbonylazulene (2b). This procedure constitutes a slightly modified version of the synthesis reported by Nozoe *et al.*[6] Magenta-colored 6-bromo-1,3-diethoxycarbonylazulene (0.500 g, 1.424 mmol) and 16.0 g of 68% aqueous sodium hydrosulfide (285 mmol) were added to 240 mL of 70% aqueous ethanol. The resulting suspension was refluxed for 20 minutes. After cooling to room temperature, the reaction mixture was diluted with 250 mL of deionized water. The resulting solution was acidified with aqueous sulfuric acid to afford a pink precipitate, which was extracted with CH_2Cl_2 (2×100 mL). The red methylene chloride extracts were combined, dried over sodium sulfate, and filtered. The solvent was removed under vacuum and the residue was recrystallized from benzene to provide blood red, crystalline **2b** (0.302 g, 0.992 mmol) in a 71% yield. Anal. calcd for $C_{16}H_{16}O_4S$: C, 63.14; H, 5.30. Found: C, 62.96; H, 5.03. IR (KBr): ν_{SH} 2528 w; ν_{CO} 1675 s cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 1.44 (t, $^{3}J_{HH}$ = 6 Hz, 6H, C*H*$_3$), 4.23 (s, 1H, S*H*), 4.41 (q, $^{3}J_{HH}$ = 6 Hz, 4H, C*H*$_2$), 7.60 (d, $^{3}J_{HH}$ = 12 Hz, 2H,

$H^{5,7}$), 8.66 (s, 1H, H^{2}), 9.46 (d, $^{3}J_{HH}$ = 12 Hz, 2H, $H^{4,8}$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ 14.6 (CH_3), 60.1 (CH_2), 117.2, 128.9, 137.3, 141.4, 141.7, 152.3 (azulenic *C*), 165.0 (CO_2Et) ppm. UV-Vis (CH_2Cl_2, λ_{max} ($\varepsilon\times10^{-3}$ M^{-1} cm^{-1}), 24 °C): 270 (11.5), 280 (12.1), 335 (55.9), 370 (15.4), 390 (2.3) sh, 470 (0.8) br nm.

A3. Synthesis of 2,6-dichloro-1,3-diethoxycarbonylazulene (4). Dry HCl(g) was bubbled through a solution of 2-amino-6-bromo-1,3-diethoxycarbonylazulene (1.248 g, 3.408 mmol) in 250 mL of benzene at room temperature. The HCl treatment was stopped after 2 hrs and isoamyl nitrite (0.798 g, 6.812 mmol) was added to the reaction mixture with stirring. The solution darkened from orange to black, then gradually acquired green color and, finally, turned red. After 24 hrs of stirring at room temperature, the reaction mixture was poured into 200 mL of distilled H_2O. The organic layer was separated, washed vigorously with deionized H_2O (3×50 mL), dried over anhydrous Na_2SO_4, and filtered. All solvent was removed from the filtrate under vacuum to give a red oil. Recrystallization of the product from EtOH provided a red crystalline solid, which was filtered off and dried at 10^{-2} torr to afford **4** (0.592 g, 1.735 mmol) in a 51% yield. Mp: 162 °C (lit.[7] 160 -161 °C). IR (CH_2Cl_2): ν_{CO} 1693 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 1.48 (t, $^{3}J_{HH}$ = 7.0 Hz, 6H, CH_3), 4.50 (q, $^{3}J_{HH}$ = 7.0 Hz, 4H, CH_2), 7.80 (d, $^{3}J_{HH}$ = 10.0 Hz, 2H $H^{5,7}$), 9.33 (d, $^{3}J_{HH}$ = 10.0 Hz, 2H, $H^{4,8}$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz, 26 °C): δ 14.35 (CH_3), 60.88 (CH_2), 116.70, 131.10, 135.91, 139.80, 143.42, 147.50 (azulenic *C*), 163.98 (CO_2Et) ppm.

Note: it is imperative to conduct this reaction under inert atmosphere (e.g., argon) to avoid substantial reduction in the yield of **4**. Performing the above reaction without protection from air resulted in a poor yield of **4** and the formation of multiple other products which have not been fully characterized.

A4. Synthesis of 2-chloro-6-mercapto-1,3-diethoxycarbonylazulene (5). Red crystals of **4** (0.109 g, 0.319 mmol) and 2.00 g of 68% aqueous sodium hydrosulfide (24.3 mmol) were added to 40 mL of 70% aqueous ethanol. The resulting solution/slurry was brought to reflux and stirred for 1 hr. After cooling to room temperature, the flask contents were poured into 200 mL of deionized water and acidified slowly with aqueous sulfuric acid until a pink precipitate formed. This pink solid was filtered off and extracted with CH_2Cl_2 (3×15 mL). The organic extracts were combined, washed vigorously with H_2O (2×25 mL), dried over anhydrous Na_2SO_4, and filtered. All solvent was removed from the filtrate under vacuum to leave an orange residue, which was recrystallized by layering its solution in CH_2Cl_2 with pentane to afford **5** (0.088 g, 0.260 mmol) in an 82% yield. Mp: 142-144 °C. HRMS (*m/z*, ES-): found for $[M-H]^-$ 337.0337; calcd for $C_{16}H_{14}ClO_4S^-$ 337.0307. IR (KBr): ν_{SH} 2521 w; ν_{CO} 1675 s cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C): δ 1.46 (t, $^{3}J_{HH}$ = 7.0 Hz, 6H, CH_3), 4.23 (s, 1H, S*H*), 4.47 (q, $^{3}J_{HH}$ = 7.0 Hz, 4H, CH_2), 7.54 (d, $^{3}J_{HH}$ = 11.2 Hz, 2H, $H^{5,7}$), 9.15 (d, $^{3}J_{HH}$ = 11.2 Hz, 2H, $H^{4,8}$,) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz, 25 °C): δ 14.37 (CH_3), 60.65 (CH_2), 116.18, 129.33, 136.03, 139.08, 141.41, 151.86 (azulenic *C*), 164.20 (CO_2Et) ppm.

A5. Synthesis of 2,6-di(2-methoxycarbonylethylthio)-1,3-diethoxycarbonylazulene (6) from **4**. Methyl-3-mercaptopropionate (0.130 g, 1.082 mmol) was added to a solution of **4** (0.136 g, 0.399 mmol) in 10 mL of pyridine. The mixture was refluxed for 4 hrs with

stirring, then cooled to room temperature and poured into 25 mL of CH_2Cl_2. The resulting solution was washed with 3M H_2SO_4 (2×25 mL), then once with 25 mL of deionized H_2O, dried over anhydrous Na_2SO_4, and concentrated under vacuum to give a red oil. The red oil was dissolved in a minimum amount of CH_2Cl_2 and layered with pentane to form orange crystals upon solvent diffusion at room temperature. The crystals were filtered off and dried at 10^{-2} torr to afford **6** (0.163 g, 0.320 mmol) in an 80% yield. Mp: 94 °C. HRMS (*m/z*, ES+): found for $[M+H]^+$ 509.1300; calcd for $C_{24}H_{29}O_8S_2^+$ 509.1298. IR (CH_2Cl_2): ν_{CO} 1737 s, 1690 s cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, 20 °C): δ 1.47 (t, $^3J_{HH}$ = 7.2 Hz, 6H, CH_2CH_3), 2.59 (t, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2), 2.79 (t, $^3J_{HH}$ = 7.4 Hz, 2H, CH_2), 3.30 (t, $^3J_{HH}$ = 7.6 Hz, 2H, CH_2), 3.40 (t, $^3J_{HH}$ = 7.4 Hz, 2H, CH_2), 3.64 (s, 3H, CO_2CH_3), 3.74 (s, 3H, CO_2CH_3), 4.49 (q, $^3J_{HH}$ = 7.2 Hz, 4H, CH_2CH_3), 7.45 (d, $^3J_{HH}$ = 11.3 Hz, 2H, $H^{5,7}$), 8.94 (d, $^3J_{HH}$ = 11.3 Hz, 2H, $H^{4,8}$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz, 25 °C): δ 14.43 (CH_2CH_3), 28.13 (CH_2), 30.70 (CH_2), 33.01 (CH_2), 34.41 (CH_2), 51.74 (CO_2CH_3), 52.15 (CO_2CH_3), 60.90 (CH_2CH_3), 119.85, 126.86, 134.09, 139.08, 147.80, 153.33 (azulenic *C*), 162.29 (CO_2Et), 171.49 (CO_2Me), 171.99 (CO_2Me) ppm.

A6. Synthesis of 6-bromo-2-(trifluoromethylsulfonyl)oxy-1,3-diethoxycarbonyl-azulene (8). Triethylamine (0.20 mL, 1.43 mmol) was added to a solution of 2-hydroxy-6-bromo-1,3-diethoxycarbonylazulene (0.344 g, 0.937 mmol) in 25 mL of CH_2Cl_2 at room temperature with stirring. The reaction mixture darkened. To the resulting solution, triflic anhydride (0.530 g, 1.879 mmol) dissolved in 10 mL of CH_2Cl_2 was added dropwise. Upon the addition of Tf_2O, the mixture turned red and was stirred at room temperature for a period of one hour. Then, the reaction flask contents were poured into 100 mL of deionized H_2O. The organic layer was separated, washed sequentially with 25 mL of H_2O and 25 mL of brine, and dried over anhydrous Na_2SO_4. Following filtration, all solvent was removed from the filtrate under vacuum to afford red microcrystals of **8**. While the product can be used in the next step without further purification, it can be recrystallized by layering its CH_2Cl_2 solution with pentane to provide spectroscopically pure **8** (0.450 g, 0.900 mmol) in a 96% yield. HRMS (*m/z*, ES+): found for $[M+Na]^+$ 520.9473 and 522.9448; calcd for $C_{17}H_{14}{}^{79}BrF_3NaO_7S^+$ 520.9488, calcd for $C_{17}H_{14}{}^{81}BrF_3NaO_7S^+$ 522.9467. ^1H NMR ($CDCl_3$, 400 MHz, 20 °C): δ 1.46 (t, $^3J_{HH}$ = 7.1 Hz, 6H, CH_3), 4.49 (q, $^3J_{HH}$ = 7.1 Hz, 4H, CH_2), 8.15 (d, $^3J_{HH}$ = 11.4 Hz, 2H, $H^{5,7}$), 9.54 (d, $^3J_{HH}$ = 11.4 Hz, 2H, $H^{4,8}$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz, 25 °C): δ 14.10 (CH_3), 61.23 (CH_2), 109.40 (azulenic C), 118.70 (q, $^1J_{CF}$ = 320.0 Hz, CF_3), 135.28, 138.66, 138.78, 140.34, 152.37 (azulenic *C*), 162.80 (CO_2Et) ppm.

A7. Synthesis of 6 from 8. Methyl-3-mercaptopropionate (0.03 mL, 0.27 mmol) was added, with stirring, to a solution of **8** (0.054 g, 0.108 mmol) in 3 mL of pyridine. The reaction mixture was heated to 90 °C and stirred at this temperature for 4 hrs. After cooling to room temperature, the contents of the reaction flask were poured into 25 mL of 3M H_2SO_4. The resulting mixture was extracted with CH_2Cl_2 (3×10mL). The organic extracts were combined, washed sequentially with 10 mL of 3M H_2SO_4, 10mL of H_2O, and 10 mL of brine, and dried over anhydrous Na_2SO_4. Filtration followed by solvent removal from the filtrate on a rotary evaporator provided a red oil. This red oil was crystallized by layering its solution in a minimum amount of CH_2Cl_2 with pentane to afford **6** (0.041 g, 0.081 mmol) in

a 75% yield. The product was spectroscopically identical to the sample of **6** obtained through the procedure A5 described above.

A8. Synthesis of 2,6-dimercapto-1,3-diethoxycarbonylazulene (9). Absolute ethanol, deionized H_2O, and 3M H_2SO_4 were all purged with argon for 30 minutes prior to their use in the following procedure. A solution of sodium ethoxide prepared by *carefully* dissolving sodium metal (0.030 g, 1.305 mmol) in 20 mL of EtOH was transferred into a flask containing a suspension of **6** (0.150 g, 0.295 mmol) in 10 mL of EtOH. Following the addition of the sodium ethoxide solution, the reaction mixture was stirred for 4 hrs at room temperature while acquiring red color. Then, the mixture was diluted with 300 mL of H_2O and slowly acidified with 3M H_2SO_4 until formation of a yellow precipitate. At this point, the reaction flask was opened to the air atmosphere. The precipitate was filtered off, washed extensively with water and dried at 10^{-2} torr. The yellow solid was dissolved in a minimum amount of CH_2Cl_2 and the resulting solution was layered with pentane. Upon solvent diffusion, small, yellow, needlelike crystals formed. These crystals were filtered off and dried at 10^{-2} torr to afford **9** (0.084 g, 0.250 mmol) in an 85% yield. Mp: 112-114 °C (dec). Anal. calcd for $C_{16}H_{16}O_4S_2$: C, 57.12; H, 4.79. Found C, 56.66; H, 4.31. HRMS (*m/z*, ES-): found for $[M-H]^-$ 335.0414; calcd for $C_{16}H_{15}O_4S_2^-$, 335.0417. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.50 (t, $^3J_{HH}$ = 7.2 Hz, 6H, C*H*$_3$), 4.12 (s, 1H, S*H*), 4.50 (q, $^3J_{HH}$ = 7.2 Hz, 4H, C*H*$_2$), 7.56 (d, $^3J_{HH}$ = 11.4 Hz, 2H, *H*^{5,7}), 7.58 (s, 1H, S*H*), 9.18 (d, $^3J_{HH}$ = 11.4 Hz, 2H, *H*^{4,8}) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 126 MHz, 25 °C): δ 14.50 (*C*H$_3$), 60.64 (*C*H$_2$), 114.50, 130.12, 133.88, 141.44, 148.07, 153.53 (azulenic *C*), 165.79 (*C*O$_2$) ppm. IR (KBr): ν_{SH} 2540 m, 2450 w br; ν_{CO} 1683 s sh, 1666 s cm^{-1}. UV-Vis (CH_2Cl_2, λ_{max} ($\varepsilon\times10^{-3}$ M^{-1} cm^{-1}), 24 °C): 230 (9.3), 250 (13.8), 270 (14.3), 275 (14.1) ~335 (47.3) sh, 340 (53.5), ~405 (10.9) sh, 420 (15.0) nm.

Note: if the acidification is performed without rigorous protection from air, only minute amounts of the desired compound **9** can be isolated. Indeed, upon acidification of the reaction mixture under normal atmospheric conditions, the solution turns red and little to no yellow precipitate forms. Following extraction and work up, the major product gives the following ^{1}H NMR (C_6D_6, 400 MHz, 21 °C) spectrum: δ 1.10 (t, $^3J_{HH}$ = 8 Hz, 6H, C*H*$_3$), 4.21 (q, $^3J_{HH}$ = 8 Hz, 4H, C*H*$_2$), 7.34 (d, 12 Hz, 2H, *H*^{5,7}), 8.26 (s, 1H, S*H*), 9.29 (d, $^3J_{HH}$ = 8 Hz, 2H, *H*^{4,8}) ppm, which does not feature a characteristic resonance for the 6-S*H* mercapto hydrogen nucleus and could correspond to the disulfide species.

A9. Synthesis of [Ph_3PAu](1,3-diethoxycarbonyl-2-mercapto-6-azulenethiolate) (10). A solution of Ph_3AuCl (0.177 g, 0.382 mmol) and **9** (0.120 g, 0.357 mmol) in 10 mL of THF was treated with triethylamine (0.054 mL, 0.389 mmol) with stirring at room temperature. The color of the reaction mixture changed from orange to red-orange upon the addition of the base. After stirring for 5 hrs, the mixture was concentrated under vacuum to about 5 mL and *ca.* ~5 mL of pentane was added to the reaction flask to precipitate the crude product as an orange powder. This solid was filtered off and re-dissolved in a minimum amount of CH_2Cl_2. The resulting solution was carefully layered with pentane. After slow diffusion of pentane into the CH_2Cl_2 layer at room temperature, orange crystals formed. These crystals were filtered off, washed with pentane, and dried at 10^{-2} torr to afford **10** (0.282 g, 0.355 mmol) in a 99.4% yield. Mp: 179-181 °C. Anal. calcd for $C_{34}H_{30}AuO_4PS_2$: C, 51.39; H, 3.81. Found: C, 51.53; H, 4.02. IR (KBr): ν_{SH} 2438 w br; ν_{CO} 1680 s, 1657 s cm^{-1}. ^{1}H

NMR ($CDCl_3$, 400 MHz, 25 °C): δ 1.48 (t, $^3J_{HH}$ = 8 Hz, 6H, C*H*$_3$), 4.47 (q, $^3J_{HH}$ = 8 Hz, 4H, C*H*$_2$), 7.49 (s, 1H, S*H*) 7.55 (m, 15 H, P*Ph*$_3$), 8.20 (d, $^3J_{HH}$ = 12 Hz, 2H, *H*^{5,7}), 8.97 (d, $^3J_{HH}$ = 12 Hz, 2H, *H*^{4,8}) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz, 25 °C): δ 14.5 (*C*H_3), 60.2 (*C*H_2), 113.2, 128.6, 129.0, 129.4 (d, $^2J_{CP}$ = 11.3 Hz), 132.0 (d, $^3J_{CP}$ = 2.5 Hz), 132.4, 134.1 (d, $^1J_{CP}$ = 13.8 Hz), 135.6, 141.1, 149.9, 165.3 (*C*O_2Et), 166.2 (*C*O_2Et) ppm. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, 25 °C): 37.54 ppm. $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 25 °C): 37.89 ppm. UV-Vis (CH_2Cl_2, λ_{max} ($\varepsilon\times10^{-3}$ M^{-1} cm^{-1}), 24 °C): 235 (35.4), 245 (32.8), 275 (26.2), ~295 (15.1) sh, 325 (21.0), 365 (41.6), ~425 (25.2) sh, 445 (39.1) nm.

A10. Synthesis of [Ph$_3$PAu]$_2$(η^1:η^1-1,3-diethoxycarbonyl-2,6-azulenedithiolate) (11). All manipulations in the following procedure were conducted with protection from ambient laboratory lighting. A solution prepared by dissolving NaOH (0.0115 g, 0.2875 mmol) in 7 mL of dry methanol was transferred via cannula to a flask containing a solid mixture of **10** (0.0459 g, 0.0578 mmol) and Ph_3PAuCl (0.0286 g, 0.0578 mmol). The resulting suspension was stirred for 30 minutes at room temperature and then diluted with 7 mL of CH_2Cl_2. After stirring for *ca.* 24 hrs in the dark, all solvent was removed under vacuum to leave an orange-red residue. This solid was extracted with CH_2Cl_2 (2×15 mL). The extracts were combined, concentrated under reduced pressure and passed through a 1.5 cm plug of basic alumina using a 1:10 MeOH/CH_2Cl_2 eluent to remove any trace of **10** from the product. Solvent removal from the red band and drying of the resulting product at 10^{-2} torr provided **11** (0.0660 g, 0.0527 mmol), which can be recrystallized at -30 °C by layering its solution in CH_2Cl_2 with pentane, in a 92% yield. Anal. calcd for $C_{52}H_{44}Au_2O_4P_2S_2$: C, 49.85; H, 3.54. Found: C, 49.72; H, 3.28. HRMS (*m/z*, ES+): found for $[M+H]^+$ 1253.1685; calcd for $C_{52}H_{45}Au_2O_4P_2S_2^+$ 1253.1566. IR (KBr): ν_{CO} 1681 s cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz, 20 °C): δ 1.32 (t, $^3J_{HH}$ = 7 Hz, 6H, C*H*$_3$), 4.23 (q, $^3J_{HH}$ = 7 Hz, 4H, C*H*$_2$), 7.53 (m, 30 H, P*Ph*$_3$) 8.01 (d, $^3J_{HH}$ = 11.0 Hz, 2H, *H*^{5,7}) 8.42 (d, $^3J_{HH}$ = 11.0 Hz, 2H, *H*^{4,8}) ppm. $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 22 °C): 37.19 (broad singlet) ppm. ^{31}P NMR (202 MHz, CD_2Cl_2, -40 °C): 37.95, 36.19 ppm. UV-Vis (CH_2Cl_2, λ_{max} ($\varepsilon\times10^{-3}$ M^{-1} cm^{-1}), 24 °C): 290 (17.0), ~320 (24.0) sh, ~340 (32.2), 365 (40.3), ~450 (28.9) sh, 475 (38.8) nm.

B. X-RAY CHRYSTALLOGRAPHIC WORK

B1. Experimental

X-ray quality red-orange crystals of **2b**, red rectangular crystals **3**, red needle-shaped crystals of **4**, and red block-shaped crystals of **10** were grown by carefully layering pentane over relatively dilute solutions of these compounds in CH_2Cl_2 at room temperature and then cooling the samples to +4 °C (**2b**) or -30 °C (**4** and **10**) for a period of 1-2 weeks.

Intensity data for all samples were collected using diffractometers with a Bruker SMART APEX CCD area detector and graphite-monochromated MoKα radiation (λ= 0.71073 Å).[8] Lattice constants were determined with the Bruker SAINT software package.[9] The data were corrected empirically for variable absorption effects using equivalent reflections.[10] The space groups for **2b**, **4**, and **10** were determined by statistical tests and verified by subsequent refinements. The Bruker software package SHELXTL was used to solve the structure using "direct methods" techniques.[11] All stages of weighted full-matrix least-squares refinement were conducted using F_o^2 data.[12]

The positions of hydrogen atoms bonded to carbons were initially determined by geometry and refined by a riding model. For **2b** and **10**, the hydrogen atoms bonded to sulfur atoms were located on a difference map, and their positions were refined independently. Hydrogen atom displacement parameters were set to 1.2 (1.5 for methyl) times the isotropic equivalent displacement parameters of the bonded atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters. All displacement ellipsoids are drawn at the 50% probability level.

The asymmetric unit of **2b** contains two crystallographically independent $C_{16}H_{16}O_4S$ molecules. The asymmetric unit of **4** contains one $C_{16}H_{14}Cl_2O_4$ molecule. For **4**, the final difference map shows two peaks > 2 $e^-/Å^3$. These peaks were located *ca.* 0.9 Å from the two chlorine atoms. The vector between the two chlorine atoms and the two large peaks in the difference map are approximately the same. Therefore, it is likely that these extra peaks represent an example of whole molecule disorder.

There are two molecules $C_{34}H_{30}AuO_4PS_2$ per asymmetric unit of **10**. The selected crystal of **10** exhibited racemic twinning as was shown by the refined value of the Flack parameter.[13] The polar axis restraints were taken from Flack and Schwarzenbach.[14] No aurophilic Au···Au interactions are present in the solid state structure of **10**.

Table S1. Crystal data and structure refinement for **2b**.

Empirical formula	$C_{16}H_{16}O_4S$	
Formula weight	304.35	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1} - C_i^1$ (No. 2)	
Unit cell dimensions	a = 10.845(1) Å	α = 109.364(2)°
	b = 12.173(2) Å	β = 106.530(3)°
	c = 12.236(2) Å	γ = 98.626(2)°
Volume	1406.8(3) Å^3	
Z	4	
Density (calculated)	1.437 Mg/m^3	
Absorption coefficient	0.243 mm^{-1}	
F(000)	640	
Crystal size	0.17 x 0.17 x 0.10 mm^3	
Theta range for data collection	2.76° to 26.00°	
Index ranges	$-13 \le h \le 13$, $-15 \le k \le 14$, $-15 \le l \le 15$	
Reflections collected	12191	
Independent reflections	5491 [R_{int} = 0.039]	
Completeness to theta = 26.00°	99.4 %	
Absorption correction	Multi-scan	
Max. and min. transmission	1.000 and 0.912	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5491 / 0 / 391	
Goodness-of-fit on F^2	0.960	
Final R indices [$I>2\sigma(I)$]	R_1 = 0.052, wR_2 = 0.124	
R indices (all data)	R_1 = 0.081, wR_2 = 0.135	
Largest diff. peak and hole	0.66 and -0.31 e$^-$/Å^3	

$R_1 = \Sigma \, ||F_O| - |F_C|| \, / \, \Sigma \, |F_O|$

$wR_2 = \{ \, \Sigma \, [w(F_O^2 - F_C^2)^2] \, / \, \Sigma \, [w(F_O^2)^2] \, \}^{1/2}$

Table S2. Atomic coordinates and equivalent isotropic displacement parameters for **2b**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
S(1)	2224(1)	3473(1)	8672(1)	25(1)
O(1)	5726(2)	1221(2)	3273(2)	23(1)
O(2)	2300(2)	-2497(1)	2726(2)	22(1)
O(3)	5948(2)	2946(2)	4835(2)	26(1)
O(4)	1126(2)	-2138(2)	3988(2)	25(1)
C(1)	4329(2)	1145(2)	4390(2)	19(1)
C(2)	3725(2)	-91(2)	3676(2)	19(1)
C(3)	2756(2)	-507(2)	4097(2)	19(1)
C(4)	1873(2)	445(2)	5765(2)	20(1)
C(5)	1776(2)	1338(2)	6752(2)	22(1)
C(6)	2547(2)	2549(2)	7389(2)	20(1)
C(7)	3566(2)	3146(2)	7123(2)	22(1)
C(8)	4072(2)	2699(2)	6206(2)	20(1)
C(9)	2716(2)	472(2)	5100(2)	17(1)
C(10)	3740(2)	1536(2)	5294(2)	18(1)
C(11)	5398(2)	1876(2)	4213(2)	20(1)
C(12)	6786(2)	1855(2)	3022(2)	25(1)
C(13)	6930(3)	963(2)	1902(2)	29(1)
C(14)	1968(2)	-1761(2)	3625(2)	19(1)
C(15)	1679(3)	-3776(2)	2330(2)	24(1)
C(16)	2213(3)	-4459(2)	1388(2)	28(1)
S(2)	1265(1)	4742(1)	6231(1)	26(1)
O(21)	4471(2)	2350(2)	629(2)	22(1)
O(22)	1065(2)	-1315(1)	204(2)	21(1)
O(23)	4710(2)	4106(2)	2156(2)	29(1)
O(24)	-18(2)	-926(2)	1543(2)	24(1)
C(21)	3164(2)	2306(2)	1833(2)	20(1)
C(22)	2538(2)	1069(2)	1134(2)	20(1)
C(23)	1614(2)	677(2)	1610(2)	17(1)
C(24)	831(2)	1653(2)	3344(2)	20(1)
C(25)	773(2)	2572(2)	4352(2)	21(1)
C(26)	1527(2)	3789(2)	4931(2)	21(1)
C(27)	2513(3)	4356(2)	4618(2)	24(1)
C(28)	2991(2)	3898(2)	3685(2)	21(1)
C(29)	1627(2)	1670(2)	2629(2)	18(1)
C(30)	2626(2)	2720(2)	2777(2)	18(1)
C(31)	4173(2)	3029(2)	1585(2)	22(1)
C(32)	5430(3)	2979(2)	276(3)	27(1)
C(33)	5630(3)	2048(2)	-785(2)	27(1)

C(34)	803(2)	-568(2)	1144(2)	18(1)
C(35)	285(2)	-2563(2)	-311(2)	21(1)
C(36)	680(3)	-3257(2)	-1359(2)	25(1)

Table S3. Bond lengths [Å] for **2b**.

S(1)-C(6)	1.765(3)	S(2)-C(26)	1.758(2)
S(1)-H(1S)	1.23(3)	S(2)-H(2S)	1.26(3)
O(1)-C(11)	1.340(3)	O(21)-C(31)	1.346(3)
O(1)-C(12)	1.451(3)	O(21)-C(32)	1.446(3)
O(2)-C(14)	1.346(3)	O(22)-C(34)	1.342(3)
O(2)-C(15)	1.453(3)	O(22)-C(35)	1.447(3)
O(3)-C(11)	1.217(3)	O(23)-C(31)	1.216(3)
O(4)-C(14)	1.217(3)	O(24)-C(34)	1.221(3)
C(1)-C(2)	1.401(3)	C(21)-C(22)	1.403(3)
C(1)-C(10)	1.415(3)	C(21)-C(30)	1.420(3)
C(1)-C(11)	1.464(3)	C(21)-C(31)	1.463(3)
C(2)-C(3)	1.396(3)	C(22)-C(23)	1.394(3)
C(3)-C(9)	1.416(3)	C(23)-C(29)	1.415(3)
C(3)-C(14)	1.462(3)	C(23)-C(34)	1.462(3)
C(4)-C(5)	1.375(3)	C(24)-C(25)	1.388(3)
C(4)-C(9)	1.390(3)	C(24)-C(29)	1.396(3)
C(5)-C(6)	1.405(3)	C(25)-C(26)	1.406(3)
C(6)-C(7)	1.406(3)	C(26)-C(27)	1.397(3)
C(7)-C(8)	1.376(3)	C(27)-C(28)	1.374(3)
C(8)-C(10)	1.397(3)	C(28)-C(30)	1.403(3)
C(9)-C(10)	1.477(3)	C(29)-C(30)	1.469(3)
C(12)-C(13)	1.506(3)	C(32)-C(33)	1.508(3)
C(15)-C(16)	1.498(3)	C(35)-C(36)	1.498(3)

Table S4. Bond angles [°] for **2b.**

C(6)-S(1)-H(1S)	100(1)	C(2)-C(3)-C(14)	125.5(2)
C(11)-O(1)-C(12)	116.4(2)	C(9)-C(3)-C(14)	125.7(2)
C(14)-O(2)-C(15)	114.4(2)	C(5)-C(4)-C(9)	130.8(2)
C(2)-C(1)-C(10)	108.3(2)	C(4)-C(5)-C(6)	128.7(2)
C(2)-C(1)-C(11)	124.5(2)	C(5)-C(6)-C(7)	127.8(2)
C(10)-C(1)-C(11)	127.1(2)	C(5)-C(6)-S(1)	118.2(2)
C(3)-C(2)-C(1)	109.7(2)	C(7)-C(6)-S(1)	114.1(2)
C(2)-C(3)-C(9)	108.8(2)	C(8)-C(7)-C(6)	129.2(2)

C(7)-C(8)-C(10)	130.3(2)	C(22)-C(23)-C(34)	125.0(2)
C(4)-C(9)-C(3)	126.9(2)	C(29)-C(23)-C(34)	126.2(2)
C(4)-C(9)-C(10)	126.7(2)	C(25)-C(24)-C(29)	130.5(2)
C(3)-C(9)-C(10)	106.4(2)	C(24)-C(25)-C(26)	128.5(2)
C(8)-C(10)-C(1)	126.7(2)	C(27)-C(26)-C(25)	127.8(2)
C(8)-C(10)-C(9)	126.4(2)	C(27)-C(26)-S(2)	114.0(2)
C(1)-C(10)-C(9)	106.9(2)	C(25)-C(26)-S(2)	118.2(2)
O(3)-C(11)-O(1)	122.9(2)	C(28)-C(27)-C(26)	130.1(2)
O(3)-C(11)-C(1)	125.4(2)	C(27)-C(28)-C(30)	129.6(2)
O(1)-C(11)-C(1)	111.7(2)	C(24)-C(29)-C(23)	126.4(2)
O(1)-C(12)-C(13)	106.9(2)	C(24)-C(29)-C(30)	126.8(2)
O(4)-C(14)-O(2)	122.1(2)	C(23)-C(29)-C(30)	106.8(2)
O(4)-C(14)-C(3)	126.2(2)	C(28)-C(30)-C(21)	126.7(2)
O(2)-C(14)-C(3)	111.7(2)	C(28)-C(30)-C(29)	126.8(2)
O(2)-C(15)-C(16)	107.2(2)	C(21)-C(30)-C(29)	106.6(2)
C(26)-S(2)-H(2S)	98(1)	O(23)-C(31)-O(21)	122.3(2)
C(31)-O(21)-C(32)	116.4(2)	O(23)-C(31)-C(21)	126.1(2)
C(34)-O(22)-C(35)	115.0(2)	O(21)-C(31)-C(21)	111.6(2)
C(22)-C(21)-C(30)	108.5(2)	O(21)-C(32)-C(33)	107.3(2)
C(22)-C(21)-C(31)	124.6(2)	O(24)-C(34)-O(22)	122.0(2)
C(30)-C(21)-C(31)	126.9(2)	O(24)-C(34)-C(23)	125.9(2)
C(23)-C(22)-C(21)	109.4(2)	O(22)-C(34)-C(23)	112.0(2)
C(22)-C(23)-C(29)	108.8(2)	O(22)-C(35)-C(36)	107.9(2)

Table S5. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **2b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	29(1)	16(1)	25(1)	2(1)	13(1)	1(1)
O(1)	23(1)	19(1)	28(1)	7(1)	15(1)	0(1)
O(2)	27(1)	9(1)	25(1)	1(1)	13(1)	-2(1)
O(3)	26(1)	16(1)	31(1)	5(1)	12(1)	-4(1)
O(4)	25(1)	18(1)	29(1)	6(1)	14(1)	-2(1)
C(1)	18(1)	15(1)	22(1)	6(1)	6(1)	1(1)
C(2)	20(1)	16(1)	19(1)	5(1)	7(1)	2(1)
C(3)	18(1)	14(1)	21(1)	5(1)	6(1)	2(1)
C(4)	21(1)	13(1)	22(1)	4(1)	6(1)	0(1)
C(5)	23(1)	17(1)	26(1)	7(1)	10(1)	0(1)
C(6)	20(1)	15(1)	23(1)	6(1)	9(1)	3(1)
C(7)	21(1)	14(1)	23(1)	3(1)	4(1)	0(1)
C(8)	20(1)	12(1)	22(1)	4(1)	6(1)	-2(1)

C(9)	15(1)	13(1)	20(1)	5(1)	6(1)	1(1)
C(10)	16(1)	13(1)	22(1)	6(1)	7(1)	1(1)
C(11)	18(1)	19(1)	21(1)	8(1)	6(1)	1(1)
C(12)	20(1)	22(1)	33(2)	12(1)	12(1)	-1(1)
C(13)	33(2)	27(2)	33(2)	13(1)	20(1)	6(1)
C(14)	20(1)	13(1)	18(1)	2(1)	7(1)	4(1)
C(15)	30(1)	8(1)	28(1)	1(1)	12(1)	-4(1)
C(16)	33(2)	15(1)	30(2)	2(1)	13(1)	0(1)
S(2)	32(1)	18(1)	24(1)	2(1)	14(1)	4(1)
O(21)	23(1)	16(1)	28(1)	5(1)	15(1)	0(1)
O(22)	22(1)	11(1)	24(1)	1(1)	11(1)	-3(1)
O(23)	31(1)	16(1)	36(1)	5(1)	16(1)	-3(1)
O(24)	27(1)	15(1)	26(1)	3(1)	14(1)	-5(1)
C(21)	18(1)	14(1)	22(1)	5(1)	5(1)	0(1)
C(22)	22(1)	16(1)	20(1)	5(1)	9(1)	4(1)
C(23)	14(1)	14(1)	19(1)	4(1)	4(1)	0(1)
C(24)	18(1)	14(1)	24(1)	6(1)	6(1)	-1(1)
C(25)	20(1)	17(1)	23(1)	6(1)	9(1)	2(1)
C(26)	26(1)	18(1)	18(1)	4(1)	9(1)	7(1)
C(27)	28(1)	11(1)	24(1)	3(1)	7(1)	-2(1)
C(28)	23(1)	13(1)	25(1)	4(1)	12(1)	-1(1)
C(29)	18(1)	14(1)	19(1)	5(1)	6(1)	2(1)
C(30)	17(1)	13(1)	21(1)	6(1)	6(1)	0(1)
C(31)	20(1)	18(1)	25(1)	8(1)	8(1)	3(1)
C(32)	23(1)	23(1)	33(2)	9(1)	15(1)	-1(1)
C(33)	26(1)	24(1)	31(2)	11(1)	14(1)	2(1)
C(34)	19(1)	16(1)	17(1)	4(1)	6(1)	2(1)
C(35)	20(1)	11(1)	25(1)	1(1)	9(1)	-3(1)
C(36)	27(1)	14(1)	29(1)	4(1)	10(1)	0(1)

Table S6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **2b**.

	x	y	z	U(eq)
H(1S)	1430(30)	2720(20)	8770(20)	35(8)
H(2)	3941	-573	3006	23
H(4)	1260	-321	5491	24
H(5)	1097	1107	7043	27
H(7)	3961	3976	7653	26
H(8)	4758	3273	6191	24
H(12A)	7633	2153	3743	30

H(12B)	6557	2554	2855	30
H(13A)	7628	1362	1691	44
H(13B)	6081	663	1201	44
H(13C)	7176	284	2086	44
H(15A)	696	-3952	1961	29
H(15B)	1899	-4013	3047	29
H(16A)	1826	-5329	1109	42
H(16B)	3187	-4267	1761	42
H(16C)	1975	-4227	677	42
H(2S)	310(30)	4000(30)	6220(20)	34(8)
H(22)	2717	575	444	24
H(24)	231	889	3102	24
H(25)	142	2350	4696	25
H(27)	2916	5189	5132	28
H(28)	3670	4462	3648	25
H(32A)	6286	3387	985	32
H(32B)	5090	3597	14	32
H(33A)	6253	2449	-1067	40
H(33B)	4770	1632	-1470	40
H(33C)	5996	1458	-506	40
H(35A)	-679	-2616	-617	25
H(35B)	461	-2901	332	25
H(36A)	184	-4111	-1708	38
H(36B)	1640	-3181	-1050	38
H(36C)	474	-2933	-2003	38

Table S7. Crystal data and structure refinement for **4**.

Empirical formula	$C_{16}H_{14}Cl_2O_4$	
Formula weight	341.17	
Crystal system	triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 3.9099(11) Å	α = 82.606(5)°
	b = 13.413(4) Å	β = 86.888(6)°
	c = 14.207(4) Å	γ = 82.453(6)°
Volume	731.9(4) Å^3	
Z, Z'	2, 1	
Density (calculated)	1.548 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	352	
Crystal size	0.46 x 0.18 x 0.07 mm^3	
Absorption coefficient	0.459 mm^{-1}	
Absorption correction	Semi-empirical	
Max. and min. transmission	0.9686 and 0.8167	
Theta range for data collection	1.54 to 25.25°	
Reflections collected	7409	
Independent reflections	2654 [R(int) = 0.0499]	
Data / restraints / parameters	2654 / 0 / 201	
wR(F^2 all data)	$wR2$ = 0.1876	
R(F obsd data)	$R1$ = 0.0700	
Goodness-of-fit on F^2	1.017	
Observed data [I > 2σ(I)]	1994	
Largest and mean shift / s.u.	0.000 and 0.000	
Largest diff. peak and hole	2.253 and -0.309 e/Å^3	

$R_1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$

$wR_2 = \{ \, \Sigma \, [w(F_o^{\,2} - F_c^{\,2})^2] \, / \, \Sigma \, [w(F_o^{\,2})^2] \, \}^{1/2}$

Table S8. Atomic coordinates and equivalent isotropic displacement parameters for **4**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cl(1)	0.9917(3)	0.15437(7)	0.34224(7)	0.0186(3)
Cl(2)	0.0842(3)	0.77431(8)	0.17220(7)	0.0218(3)
O(1)	0.2612(8)	0.3645(2)	0.5094(2)	0.0276(8)
O(2)	0.5872(7)	0.2155(2)	0.50316(19)	0.0182(7)
O(3)	1.0970(8)	0.3471(2)	0.0581(2)	0.0253(8)
O(4)	1.2189(7)	0.2006(2)	0.15037(19)	0.0177(7)
C(1)	0.5927(11)	0.3373(3)	0.3672(3)	0.0141(9)
C(2)	0.8106(11)	0.2761(3)	0.3073(3)	0.0169(9)
C(3)	0.8582(11)	0.3307(3)	0.2163(3)	0.0159(9)
C(4)	0.6400(10)	0.5042(3)	0.1409(3)	0.0152(9)
C(5)	0.4595(11)	0.6022(3)	0.1353(3)	0.0184(9)
C(6)	0.2636(11)	0.6481(3)	0.2051(3)	0.0176(9)
C(7)	0.1856(11)	0.6100(3)	0.2979(3)	0.0169(9)
C(8)	0.2900(10)	0.5136(3)	0.3455(3)	0.0148(9)
C(9)	0.5005(10)	0.4320(3)	0.3123(3)	0.0135(9)
C(10)	0.6667(10)	0.4280(3)	0.2173(3)	0.0139(9)
C(11)	0.4649(11)	0.3103(3)	0.4641(3)	0.0153(9)
C(12)	0.4416(11)	0.1829(3)	0.5944(3)	0.0163(9)
C(13)	0.5748(11)	0.0729(3)	0.6202(3)	0.0216(10)
C(14)	1.0635(11)	0.2969(3)	0.1342(3)	0.0166(9)
C(15)	1.4241(11)	0.1627(3)	0.0722(3)	0.0165(9)
C(16)	1.5966(11)	0.0584(3)	0.1078(3)	0.0182(9)

Table S9. Bond lengths [Å] for **4**.

Cl(1)-C(2)	1.714(4)	C(3)-C(14)	1.466(6)
Cl(2)-C(6)	1.759(4)	C(4)-C(10)	1.390(5)
O(1)-C(11)	1.220(5)	C(4)-C(5)	1.403(6)
O(2)-C(11)	1.356(5)	C(4)-H(4)	0.9500
O(2)-C(12)	1.426(5)	C(5)-C(6)	1.379(6)
O(3)-C(14)	1.208(5)	C(5)-H(5)	0.9500
O(4)-C(14)	1.351(5)	C(6)-C(7)	1.385(6)
O(4)-C(15)	1.441(5)	C(7)-C(8)	1.401(6)
C(1)-C(9)	1.417(5)	C(7)-H(7)	0.9500
C(1)-C(2)	1.429(6)	C(8)-C(9)	1.397(6)
C(1)-C(11)	1.457(6)	C(8)-H(8)	0.9500
C(2)-C(3)	1.417(6)	C(9)-C(10)	1.470(6)
C(3)-C(10)	1.419(6)	C(12)-C(13)	1.504(5)

C(12)-H(12A)	0.9900	C(15)-H(15A)	0.9900
C(12)-H(12B)	0.9900	C(15)-H(15B)	0.9900
C(13)-H(13A)	0.9800	C(16)-H(16A)	0.9800
C(13)-H(13B)	0.9800	C(16)-H(16B)	0.9800
C(13)-H(13C)	0.9800	C(16)-H(16C)	0.9800
C(15)-C(16)	1.508(5)		

Table S10. Bond angles [°] for **4.**

C(11)-O(2)-C(12)	115.9(3)	C(3)-C(10)-C(9)	107.6(3)
C(14)-O(4)-C(15)	116.1(3)	O(1)-C(11)-O(2)	120.1(4)
C(9)-C(1)-C(2)	106.7(4)	O(1)-C(11)-C(1)	125.5(4)
C(9)-C(1)-C(11)	124.4(4)	O(2)-C(11)-C(1)	114.4(4)
C(2)-C(1)-C(11)	128.8(4)	O(2)-C(12)-C(13)	108.0(3)
C(3)-C(2)-C(1)	110.4(4)	O(2)-C(12)-H(12A)	110.1
C(3)-C(2)-Cl(1)	125.3(3)	C(13)-C(12)-H(12A)	110.1
C(1)-C(2)-Cl(1)	124.3(3)	O(2)-C(12)-H(12B)	110.1
C(2)-C(3)-C(10)	107.2(4)	C(13)-C(12)-H(12B)	110.1
C(2)-C(3)-C(14)	128.4(4)	H(12A)-C(12)-H(12B)	108.4
C(10)-C(3)-C(14)	124.4(4)	C(12)-C(13)-H(13A)	109.5
C(10)-C(4)-C(5)	129.5(4)	C(12)-C(13)-H(13B)	109.5
C(10)-C(4)-H(4)	115.3	H(13A)-C(13)-H(13B)	109.5
C(5)-C(4)-H(4)	115.3	C(12)-C(13)-H(13C)	109.5
C(6)-C(5)-C(4)	128.7(4)	H(13A)-C(13)-H(13C)	109.5
C(6)-C(5)-H(5)	115.7	H(13B)-C(13)-H(13C)	109.5
C(4)-C(5)-H(5)	115.7	O(3)-C(14)-O(4)	121.0(4)
C(5)-C(6)-C(7)	129.7(4)	O(3)-C(14)-C(3)	125.6(4)
C(5)-C(6)-Cl(2)	115.7(3)	O(4)-C(14)-C(3)	113.4(3)
C(7)-C(6)-Cl(2)	114.6(3)	O(4)-C(15)-C(16)	107.3(3)
C(6)-C(7)-C(8)	128.5(4)	O(4)-C(15)-H(15A)	110.2
C(6)-C(7)-H(7)	115.7	C(16)-C(15)-H(15A)	110.2
C(8)-C(7)-H(7)	115.7	O(4)-C(15)-H(15B)	110.2
C(9)-C(8)-C(7)	129.2(4)	C(16)-C(15)-H(15B)	110.2
C(9)-C(8)-H(8)	115.4	H(15A)-C(15)-H(15B)	108.5
C(7)-C(8)-H(8)	115.4	C(15)-C(16)-H(16A)	109.5
C(8)-C(9)-C(1)	124.5(4)	C(15)-C(16)-H(16B)	109.5
C(8)-C(9)-C(10)	127.4(3)	H(16A)-C(16)-H(16B)	109.5
C(1)-C(9)-C(10)	108.0(3)	C(15)-C(16)-H(16C)	109.5
C(4)-C(10)-C(3)	125.4(4)	H(16A)-C(16)-H(16C)	109.5
C(4)-C(10)-C(9)	127.0(4)	H(16B)-C(16)-H(16C)	109.5

Table S11. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl(1)	24(1)	12(1)	18(1)	1(1)	3(1)	3(1)
Cl(2)	28(1)	14(1)	21(1)	2(1)	-1(1)	3(1)
O(1)	40(2)	14(2)	25(2)	3(1)	2(2)	7(1)
O(2)	22(2)	12(2)	17(2)	3(1)	4(1)	2(1)
O(3)	32(2)	21(2)	19(2)	2(1)	6(1)	4(1)
O(4)	19(2)	14(2)	18(2)	-3(1)	4(1)	5(1)
C(1)	16(2)	13(2)	14(2)	-3(2)	-1(2)	-3(2)
C(2)	16(2)	22(2)	14(2)	-5(2)	0(2)	-6(2)
C(3)	14(2)	16(2)	19(2)	-7(2)	-2(2)	-1(2)
C(4)	15(2)	20(2)	12(2)	-3(2)	1(2)	-6(2)
C(5)	18(2)	20(2)	16(2)	1(2)	0(2)	-1(2)
C(6)	17(2)	13(2)	22(2)	1(2)	-4(2)	0(2)
C(7)	17(2)	20(2)	14(2)	-3(2)	0(2)	-3(2)
C(8)	16(2)	16(2)	13(2)	-4(2)	1(2)	-6(2)
C(9)	15(2)	14(2)	13(2)	-3(2)	-1(2)	-3(2)
C(10)	12(2)	14(2)	16(2)	-2(2)	1(2)	-1(2)
C(11)	18(2)	11(2)	17(2)	-2(2)	-4(2)	1(2)
C(12)	18(2)	13(2)	17(2)	3(2)	-2(2)	-4(2)
C(13)	22(2)	13(2)	27(2)	4(2)	-1(2)	2(2)
C(14)	17(2)	15(2)	18(2)	-1(2)	-2(2)	-1(2)
C(15)	15(2)	18(2)	15(2)	-2(2)	3(2)	2(2)
C(16)	16(2)	19(2)	18(2)	-4(2)	-1(2)	3(2)

Table S12. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **4**.

	x	y	z	U(eq)
H(4)	0.7617	0.4875	0.0842	0.018
H(5)	0.4743	0.6423	0.0753	0.022
H(7)	0.0425	0.6551	0.3340	0.020
H(8)	0.2056	0.5021	0.4095	0.018
H(12A)	0.1866	0.1917	0.5927	0.020
H(12B)	0.5089	0.2236	0.6421	0.020
H(13A)	0.4940	0.0327	0.5750	0.032
H(13B)	0.4895	0.0499	0.6845	0.032

H(13C)	0.8278	0.0645	0.6181	0.032
H(15A)	1.5999	0.2080	0.0497	0.020
H(15B)	1.2757	0.1592	0.0188	0.020
H(16A)	1.7330	0.0623	0.1627	0.027
H(16B)	1.7486	0.0318	0.0572	0.027
H(16C)	1.4203	0.0133	0.1265	0.027

Table S13. Crystal data and structure refinement for **10**.

Empirical formula	$C_{34}H_{30}AuO_4PS_2$	
Formula weight	794.64	
Crystal system	Orthorhombic	
Space group	$Pca2_1$	
Unit cell dimensions	a = 23.574(2) Å	α = 90°
	b = 11.1504(10) Å	β = 90°
	c = 23.342(2) Å	γ = 90°
Volume	6135.7(9) $Å^3$	
Z, Z'	8, 2	
Density (calculated)	1.720 Mg/m^3	
Wavelength	0.71073 Å	
Temperature	100(2) K	
F(000)	3136	
Crystal size	0.32 x 0.30 x 0.12 mm^3	
Absorption coefficient	5.022 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.5840 and 0.2964	
Theta range for data collection	1.73 to 25.50°	
Reflections collected	37712	
Independent reflections	10050 [R(int) = 0.0404]	
Data / restraints / parameters	10050 / 1 / 768	
$wR(F^2$ all data)	$wR2$ = 0.0721	
$R(F$ obsd data)	$R1$ = 0.0294	
Goodness-of-fit on F^2	0.998	
Observed data [I > 2σ(I)]	9157	
Absolute structure parameter	0.240(6)	
Largest and mean shift / s.u.	0.030and 0.001	
Largest diff. peak and hole	1.203 and -0.548 e/$Å^3$	

$R_1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$

$wR_2 = \{ \, \Sigma \, [w(F_o^2 - F_c^2)^2] \, / \, \Sigma \, [w(F_o^2)^2] \, \}^{1/2}$

Table S14. Atomic coordinates and equivalent isotropic displacement parameters for **10**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Au(1A)	0.511393(8)	0.22633(2)	0.546817(10)	0.01557(7)
S(1A)	0.75786(7)	0.91000(17)	0.47579(10)	0.0251(4)
S(2A)	0.55849(7)	0.24323(15)	0.45997(8)	0.0179(4)
P(1A)	0.46345(7)	0.21203(15)	0.63066(9)	0.0149(4)
O(1A)	0.74025(19)	0.8309(4)	0.5987(2)	0.0236(11)
O(2A)	0.69756(19)	0.6607(4)	0.6216(2)	0.0232(11)
O(3A)	0.7198(2)	0.6713(5)	0.3262(2)	0.0332(13)
O(4A)	0.7378(2)	0.8551(4)	0.3603(2)	0.0265(12)
C(1A)	0.7030(3)	0.7079(6)	0.5239(3)	0.0156(16)
C(2A)	0.7206(3)	0.7738(6)	0.4760(3)	0.0190(16)
C(3A)	0.7044(3)	0.7116(7)	0.4256(3)	0.0209(17)
C(4A)	0.6498(3)	0.5259(6)	0.4043(3)	0.0191(16)
C(5A)	0.6172(3)	0.4266(6)	0.4150(3)	0.0194(16)
C(6A)	0.6004(3)	0.3744(6)	0.4672(3)	0.0168(15)
C(7A)	0.6166(3)	0.4156(6)	0.5209(3)	0.0195(16)
C(8A)	0.6473(2)	0.5144(5)	0.5360(3)	0.0178(14)
C(9A)	0.6731(3)	0.6044(6)	0.5035(3)	0.0179(15)
C(10A)	0.6737(3)	0.6077(6)	0.4417(3)	0.0184(16)
C(11A)	0.7158(3)	0.7405(7)	0.5823(4)	0.0223(19)
C(12A)	0.7105(3)	0.6860(7)	0.6821(3)	0.0246(18)
C(13A)	0.6874(3)	0.5826(6)	0.7165(3)	0.0248(17)
C(14A)	0.7205(3)	0.7417(6)	0.3660(3)	0.0235(17)
C(15A)	0.7605(3)	0.8880(8)	0.3049(3)	0.032(2)
C(16A)	0.7148(3)	0.9092(8)	0.2614(4)	0.037(2)
C(17A)	0.5108(2)	0.2192(6)	0.6929(4)	0.0181(18)
C(18A)	0.5569(3)	0.2974(6)	0.6900(3)	0.0191(15)
C(19A)	0.5915(3)	0.3127(7)	0.7369(3)	0.0224(16)
C(20A)	0.5812(3)	0.2497(7)	0.7857(4)	0.0271(17)
C(21A)	0.5366(3)	0.1711(7)	0.7885(4)	0.0293(18)
C(22A)	0.5005(3)	0.1564(8)	0.7427(4)	0.029(2)
C(23A)	0.4122(3)	0.3328(6)	0.6416(3)	0.0177(16)
C(24A)	0.3953(3)	0.4033(7)	0.5964(3)	0.0263(17)
C(25A)	0.3553(3)	0.4929(8)	0.6054(4)	0.035(2)
C(26A)	0.3331(3)	0.5116(7)	0.6590(3)	0.0233(17)
C(27A)	0.3496(3)	0.4428(7)	0.7045(4)	0.0263(18)
C(28A)	0.3896(3)	0.3530(6)	0.6966(3)	0.0208(15)
C(29A)	0.4230(3)	0.0748(6)	0.6387(3)	0.0152(16)
C(30A)	0.4504(3)	-0.0317(7)	0.6509(3)	0.0225(17)
C(31A)	0.4200(3)	-0.1379(7)	0.6550(3)	0.0227(17)
C(32A)	0.3619(3)	-0.1360(7)	0.6461(3)	0.0192(17)

C(33A)	0.3345(3)	-0.0315(6)	0.6334(3)	0.0186(15)
C(34A)	0.3644(2)	0.0747(6)	0.6298(3)	0.0161(15)
Au(1B)	0.257865(8)	0.72326(2)	0.539559(10)	0.01562(7)
S(1B)	0.01475(7)	1.40395(16)	0.62809(9)	0.0242(4)
S(2B)	0.21361(7)	0.73428(15)	0.62814(8)	0.0180(4)
P(1B)	0.30606(7)	0.71845(16)	0.45587(9)	0.0163(4)
O(1B)	0.02315(19)	1.3244(5)	0.5038(2)	0.0277(12)
O(2B)	0.07028(19)	1.1604(4)	0.4770(2)	0.0233(11)
O(3B)	0.0910(2)	1.1991(4)	0.7755(2)	0.0303(12)
O(4B)	0.0298(2)	1.3347(5)	0.7412(2)	0.0270(12)
C(1B)	0.0652(3)	1.1996(6)	0.5756(3)	0.0172(16)
C(2B)	0.0521(3)	1.2678(6)	0.6260(3)	0.0187(15)
C(3B)	0.0728(3)	1.2077(6)	0.6750(3)	0.0175(16)
C(4B)	0.1298(3)	1.0193(6)	0.6918(3)	0.0166(15)
C(5B)	0.1605(2)	0.9203(6)	0.6782(3)	0.0151(14)
C(6B)	0.1719(2)	0.8673(6)	0.6258(3)	0.0152(15)
C(7B)	0.1508(3)	0.9057(6)	0.5733(3)	0.0167(15)
C(8B)	0.1185(2)	1.0057(6)	0.5590(3)	0.0189(16)
C(9B)	0.0967(3)	1.0968(6)	0.5937(3)	0.0163(15)
C(10B)	0.1018(3)	1.1028(6)	0.6560(3)	0.0183(17)
C(11B)	0.0504(3)	1.2352(6)	0.5180(4)	0.0266(19)
C(12B)	0.0567(3)	1.1883(7)	0.4186(3)	0.0174(16)
C(13B)	0.0843(3)	1.0931(7)	0.3829(3)	0.0301(19)
C(14B)	0.0664(3)	1.2429(6)	0.7348(3)	0.0220(16)
C(15B)	0.0238(3)	1.3846(8)	0.7983(3)	0.029(2)
C(16B)	-0.0204(3)	1.4812(8)	0.7943(3)	0.033(2)
C(17B)	0.2607(2)	0.7276(6)	0.3932(4)	0.0165(17)
C(18B)	0.2127(3)	0.8015(6)	0.3957(3)	0.0206(16)
C(19B)	0.1786(3)	0.8156(7)	0.3488(3)	0.0237(17)
C(20B)	0.1904(3)	0.7560(7)	0.2985(3)	0.030(2)
C(21B)	0.2379(3)	0.6806(8)	0.2953(4)	0.034(2)
C(22B)	0.2722(3)	0.6668(7)	0.3431(3)	0.0224(16)
C(23B)	0.3553(3)	0.8438(6)	0.4489(3)	0.0146(16)
C(24B)	0.3921(3)	0.8679(6)	0.4941(3)	0.0220(16)
C(25B)	0.4326(3)	0.9586(6)	0.4891(3)	0.0222(16)
C(26B)	0.4335(3)	1.0265(7)	0.4419(3)	0.0240(18)
C(27B)	0.3959(3)	1.0072(7)	0.3959(4)	0.0248(17)
C(28B)	0.3579(3)	0.9141(6)	0.4004(3)	0.0221(16)
C(29B)	0.3485(3)	0.5842(6)	0.4458(3)	0.0165(15)
C(30B)	0.3214(3)	0.4730(7)	0.4441(4)	0.0241(18)
C(31B)	0.3518(3)	0.3694(7)	0.4368(4)	0.031(2)
C(32B)	0.4111(3)	0.3736(7)	0.4343(3)	0.0220(18)
C(33B)	0.4389(3)	0.4827(6)	0.4382(3)	0.0226(16)
C(34B)	0.4079(3)	0.5857(7)	0.4438(3)	0.0202(16)

Table S15. Bond lengths [Å] for **10**.

Au(1A)-P(1A)	2.2655(19)	C(17A)-C(22A)	1.380(11)
Au(1A)-S(2A)	2.3190(19)	C(17A)-C(18A)	1.397(9)
S(1A)-C(2A)	1.755(7)	C(18A)-C(19A)	1.376(10)
S(1A)-H(1A)	1.20(8)	C(18A)-H(18A)	0.9500
S(2A)-C(6A)	1.772(7)	C(19A)-C(20A)	1.360(11)
P(1A)-C(29A)	1.813(7)	C(19A)-H(19A)	0.9500
P(1A)-C(23A)	1.827(7)	C(20A)-C(21A)	1.370(10)
P(1A)-C(17A)	1.833(8)	C(20A)-H(20A)	0.9500
O(1A)-C(11A)	1.223(9)	C(21A)-C(22A)	1.376(11)
O(2A)-C(11A)	1.348(9)	C(21A)-H(21A)	0.9500
O(2A)-C(12A)	1.473(9)	C(22A)-H(22A)	0.9500
O(3A)-C(14A)	1.217(9)	C(23A)-C(24A)	1.375(10)
O(4A)-C(14A)	1.336(8)	C(23A)-C(28A)	1.407(10)
O(4A)-C(15A)	1.447(9)	C(24A)-C(25A)	1.390(10)
C(1A)-C(2A)	1.401(10)	C(24A)-H(24A)	0.9500
C(1A)-C(9A)	1.434(10)	C(25A)-C(26A)	1.373(11)
C(1A)-C(11A)	1.442(11)	C(25A)-H(25A)	0.9500
C(2A)-C(3A)	1.417(11)	C(26A)-C(27A)	1.368(11)
C(3A)-C(10A)	1.417(10)	C(26A)-H(26A)	0.9500
C(3A)-C(14A)	1.479(11)	C(27A)-C(28A)	1.388(9)
C(4A)-C(5A)	1.370(9)	C(27A)-H(27A)	0.9500
C(4A)-C(10A)	1.383(10)	C(28A)-H(28A)	0.9500
C(4A)-H(4A)	0.9500	C(29A)-C(30A)	1.381(9)
C(5A)-C(6A)	1.408(10)	C(29A)-C(34A)	1.397(9)
C(5A)-H(5A)	0.9500	C(30A)-C(31A)	1.386(10)
C(6A)-C(7A)	1.389(10)	C(30A)-H(30A)	0.9500
C(7A)-C(8A)	1.365(9)	C(31A)-C(32A)	1.386(9)
C(7A)-H(7A)	0.9500	C(31A)-H(31A)	0.9500
C(8A)-C(9A)	1.398(9)	C(32A)-C(33A)	1.365(10)
C(8A)-H(8A)	0.9500	C(32A)-H(32A)	0.9500
C(9A)-C(10A)	1.441(10)	C(33A)-C(34A)	1.380(9)
C(12A)-C(13A)	1.507(10)	C(33A)-H(33A)	0.9500
C(12A)-H(12A)	0.9900	C(34A)-H(34A)	0.9500
C(12A)-H(12B)	0.9900	Au(1B)-P(1B)	2.260(2)
C(13A)-H(13A)	0.9800	Au(1B)-S(2B)	2.3191(19)
C(13A)-H(13B)	0.9800	S(1B)-C(2B)	1.756(7)
C(13A)-H(13C)	0.9800	S(1B)-H(1B)	1.15(8)
C(15A)-C(16A)	1.500(11)	S(2B)-C(6B)	1.780(7)
C(15A)-H(15A)	0.9900	P(1B)-C(17B)	1.815(8)
C(15A)-H(15B)	0.9900	P(1B)-C(29B)	1.816(7)
C(16A)-H(16A)	0.9800	P(1B)-C(23B)	1.823(7)
C(16A)-H(16B)	0.9800	O(1B)-C(11B)	1.229(9)
C(16A)-H(16C)	0.9800	O(2B)-C(11B)	1.354(9)

O(2B)-C(12B)	1.434(8)	C(17B)-C(22B)	1.379(11)
O(3B)-C(14B)	1.216(9)	C(17B)-C(18B)	1.401(9)
O(4B)-C(14B)	1.347(8)	C(18B)-C(19B)	1.369(10)
O(4B)-C(15B)	1.451(8)	C(18B)-H(18B)	0.9500
C(1B)-C(9B)	1.429(10)	C(19B)-C(20B)	1.378(11)
C(1B)-C(2B)	1.434(10)	C(19B)-H(19B)	0.9500
C(1B)-C(11B)	1.444(11)	C(20B)-C(21B)	1.401(11)
C(2B)-C(3B)	1.412(10)	C(20B)-H(20B)	0.9500
C(3B)-C(10B)	1.426(10)	C(21B)-C(22B)	1.385(11)
C(3B)-C(14B)	1.458(10)	C(21B)-H(21B)	0.9500
C(4B)-C(5B)	1.357(9)	C(22B)-H(22B)	0.9500
C(4B)-C(10B)	1.413(9)	C(23B)-C(28B)	1.378(10)
C(4B)-H(4B)	0.9500	C(23B)-C(24B)	1.394(10)
C(5B)-C(6B)	1.386(10)	C(24B)-C(25B)	1.394(9)
C(5B)-H(5B)	0.9500	C(24B)-H(24B)	0.9500
C(6B)-C(7B)	1.391(10)	C(25B)-C(26B)	1.336(11)
C(7B)-C(8B)	1.392(9)	C(25B)-H(25B)	0.9500
C(7B)-H(7B)	0.9500	C(26B)-C(27B)	1.408(10)
C(8B)-C(9B)	1.396(9)	C(26B)-H(26B)	0.9500
C(8B)-H(8B)	0.9500	C(27B)-C(28B)	1.374(10)
C(9B)-C(10B)	1.462(10)	C(27B)-H(27B)	0.9500
C(12B)-C(13B)	1.498(10)	C(28B)-H(28B)	0.9500
C(12B)-H(12C)	0.9900	C(29B)-C(30B)	1.396(9)
C(12B)-H(12D)	0.9900	C(29B)-C(34B)	1.401(8)
C(13B)-H(13D)	0.9800	C(30B)-C(31B)	1.369(10)
C(13B)-H(13E)	0.9800	C(30B)-H(30B)	0.9500
C(13B)-H(13F)	0.9800	C(31B)-C(32B)	1.400(10)
C(15B)-C(16B)	1.501(11)	C(31B)-H(31B)	0.9500
C(15B)-H(15C)	0.9900	C(32B)-C(33B)	1.385(10)
C(15B)-H(15D)	0.9900	C(32B)-H(32B)	0.9500
C(16B)-H(16D)	0.9800	C(33B)-C(34B)	1.368(10)
C(16B)-H(16E)	0.9800	C(33B)-H(33B)	0.9500
C(16B)-H(16F)	0.9800	C(34B)-H(34B)	0.9500

Table S16. Bond angles [°] for **10**.

P(1A)-Au(1A)-S(2A)	178.56(6)	C(23A)-P(1A)-Au(1A)	113.5(3)
C(2A)-S(1A)-H(1A)	97(3)	C(17A)-P(1A)-Au(1A)	112.2(2)
C(6A)-S(2A)-Au(1A)	104.5(2)	C(11A)-O(2A)-C(12A)	117.4(6)
C(29A)-P(1A)-C(23A)	105.1(3)	C(14A)-O(4A)-C(15A)	116.3(6)
C(29A)-P(1A)-C(17A)	105.9(3)	C(2A)-C(1A)-C(9A)	107.5(6)
C(23A)-P(1A)-C(17A)	105.1(3)	C(2A)-C(1A)-C(11A)	124.1(6)
C(29A)-P(1A)-Au(1A)	114.3(2)	C(9A)-C(1A)-C(11A)	128.3(6)

C(1A)-C(2A)-C(3A)	109.1(6)	O(4A)-C(15A)-C(16A)	112.3(6)
C(1A)-C(2A)-S(1A)	127.1(6)	O(4A)-C(15A)-H(15A)	109.2
C(3A)-C(2A)-S(1A)	123.8(6)	C(16A)-C(15A)-H(15A)	109.2
C(2A)-C(3A)-C(10A)	108.5(7)	O(4A)-C(15A)-H(15B)	109.2
C(2A)-C(3A)-C(14A)	126.8(7)	C(16A)-C(15A)-H(15B)	109.2
C(10A)-C(3A)-C(14A)	124.5(7)	H(15A)-C(15A)-H(15B)	107.9
C(5A)-C(4A)-C(10A)	130.3(7)	C(15A)-C(16A)-H(16A)	109.5
C(5A)-C(4A)-H(4A)	114.9	C(15A)-C(16A)-H(16B)	109.5
C(10A)-C(4A)-H(4A)	114.9	H(16A)-C(16A)-H(16B)	109.5
C(4A)-C(5A)-C(6A)	130.5(7)	C(15A)-C(16A)-H(16C)	109.5
C(4A)-C(5A)-H(5A)	114.7	H(16A)-C(16A)-H(16C)	109.5
C(6A)-C(5A)-H(5A)	114.7	H(16B)-C(16A)-H(16C)	109.5
C(7A)-C(6A)-C(5A)	124.5(6)	C(22A)-C(17A)-C(18A)	119.7(7)
C(7A)-C(6A)-S(2A)	120.8(5)	C(22A)-C(17A)-P(1A)	122.6(5)
C(5A)-C(6A)-S(2A)	114.6(5)	C(18A)-C(17A)-P(1A)	117.6(6)
C(8A)-C(7A)-C(6A)	130.3(7)	C(19A)-C(18A)-C(17A)	120.0(7)
C(8A)-C(7A)-H(7A)	114.9	C(19A)-C(18A)-H(18A)	120.0
C(6A)-C(7A)-H(7A)	114.9	C(17A)-C(18A)-H(18A)	120.0
C(7A)-C(8A)-C(9A)	132.1(7)	C(20A)-C(19A)-C(18A)	119.8(7)
C(7A)-C(8A)-H(8A)	114.0	C(20A)-C(19A)-H(19A)	120.1
C(9A)-C(8A)-H(8A)	114.0	C(18A)-C(19A)-H(19A)	120.1
C(8A)-C(9A)-C(1A)	127.6(7)	C(19A)-C(20A)-C(21A)	120.6(8)
C(8A)-C(9A)-C(10A)	124.5(7)	C(19A)-C(20A)-H(20A)	119.7
C(1A)-C(9A)-C(10A)	107.9(6)	C(21A)-C(20A)-H(20A)	119.7
C(4A)-C(10A)-C(3A)	125.4(7)	C(20A)-C(21A)-C(22A)	120.9(8)
C(4A)-C(10A)-C(9A)	127.7(7)	C(20A)-C(21A)-H(21A)	119.5
C(3A)-C(10A)-C(9A)	106.9(7)	C(22A)-C(21A)-H(21A)	119.5
O(1A)-C(11A)-O(2A)	118.8(7)	C(21A)-C(22A)-C(17A)	119.0(7)
O(1A)-C(11A)-C(1A)	127.0(7)	C(21A)-C(22A)-H(22A)	120.5
O(2A)-C(11A)-C(1A)	114.1(6)	C(17A)-C(22A)-H(22A)	120.5
O(2A)-C(12A)-C(13A)	106.8(6)	C(24A)-C(23A)-C(28A)	119.9(6)
O(2A)-C(12A)-H(12A)	110.4	C(24A)-C(23A)-P(1A)	120.4(6)
C(13A)-C(12A)-H(12A)	110.4	C(28A)-C(23A)-P(1A)	119.7(6)
O(2A)-C(12A)-H(12B)	110.4	C(23A)-C(24A)-C(25A)	119.5(7)
C(13A)-C(12A)-H(12B)	110.4	C(23A)-C(24A)-H(24A)	120.3
H(12A)-C(12A)-H(12B)	108.6	C(25A)-C(24A)-H(24A)	120.3
C(12A)-C(13A)-H(13A)	109.5	C(26A)-C(25A)-C(24A)	120.4(7)
C(12A)-C(13A)-H(13B)	109.5	C(26A)-C(25A)-H(25A)	119.8
H(13A)-C(13A)-H(13B)	109.5	C(24A)-C(25A)-H(25A)	119.8
C(12A)-C(13A)-H(13C)	109.5	C(27A)-C(26A)-C(25A)	121.0(7)
H(13A)-C(13A)-H(13C)	109.5	C(27A)-C(26A)-H(26A)	119.5
H(13B)-C(13A)-H(13C)	109.5	C(25A)-C(26A)-H(26A)	119.5
O(3A)-C(14A)-O(4A)	122.5(7)	C(26A)-C(27A)-C(28A)	119.6(7)
O(3A)-C(14A)-C(3A)	124.7(7)	C(26A)-C(27A)-H(27A)	120.2
O(4A)-C(14A)-C(3A)	112.8(7)	C(28A)-C(27A)-H(27A)	120.2

C(27A)-C(28A)-C(23A)	119.6(7)	C(4B)-C(5B)-H(5B)	114.5
C(27A)-C(28A)-H(28A)	120.2	C(6B)-C(5B)-H(5B)	114.5
C(23A)-C(28A)-H(28A)	120.2	C(5B)-C(6B)-C(7B)	125.3(6)
C(30A)-C(29A)-C(34A)	119.4(6)	C(5B)-C(6B)-S(2B)	115.8(5)
C(30A)-C(29A)-P(1A)	120.1(5)	C(7B)-C(6B)-S(2B)	118.8(5)
C(34A)-C(29A)-P(1A)	120.4(5)	C(6B)-C(7B)-C(8B)	130.8(7)
C(29A)-C(30A)-C(31A)	120.5(6)	C(6B)-C(7B)-H(7B)	114.6
C(29A)-C(30A)-H(30A)	119.7	C(8B)-C(7B)-H(7B)	114.6
C(31A)-C(30A)-H(30A)	119.7	C(7B)-C(8B)-C(9B)	130.2(7)
C(30A)-C(31A)-C(32A)	119.2(7)	C(7B)-C(8B)-H(8B)	114.9
C(30A)-C(31A)-H(31A)	120.4	C(9B)-C(8B)-H(8B)	114.9
C(32A)-C(31A)-H(31A)	120.4	C(8B)-C(9B)-C(1B)	127.1(7)
C(33A)-C(32A)-C(31A)	120.8(7)	C(8B)-C(9B)-C(10B)	125.4(6)
C(33A)-C(32A)-H(32A)	119.6	C(1B)-C(9B)-C(10B)	107.5(6)
C(31A)-C(32A)-H(32A)	119.6	C(4B)-C(10B)-C(3B)	125.6(7)
C(32A)-C(33A)-C(34A)	120.3(6)	C(4B)-C(10B)-C(9B)	126.6(6)
C(32A)-C(33A)-H(33A)	119.9	C(3B)-C(10B)-C(9B)	107.8(6)
C(34A)-C(33A)-H(33A)	119.9	O(1B)-C(11B)-O(2B)	119.2(8)
C(33A)-C(34A)-C(29A)	119.8(6)	O(1B)-C(11B)-C(1B)	126.9(7)
C(33A)-C(34A)-H(34A)	120.1	O(2B)-C(11B)-C(1B)	113.9(6)
C(29A)-C(34A)-H(34A)	120.1	O(2B)-C(12B)-C(13B)	106.1(6)
P(1B)-Au(1B)-S(2B)	176.20(6)	O(2B)-C(12B)-H(12C)	110.5
C(2B)-S(1B)-H(1B)	97(4)	C(13B)-C(12B)-H(12C)	110.5
C(6B)-S(2B)-Au(1B)	105.4(2)	O(2B)-C(12B)-H(12D)	110.5
C(17B)-P(1B)-C(29B)	105.5(3)	C(13B)-C(12B)-H(12D)	110.5
C(17B)-P(1B)-C(23B)	105.0(3)	H(12C)-C(12B)-H(12D)	108.7
C(29B)-P(1B)-C(23B)	105.6(3)	C(12B)-C(13B)-H(13D)	109.5
C(17B)-P(1B)-Au(1B)	113.5(2)	C(12B)-C(13B)-H(13E)	109.5
C(29B)-P(1B)-Au(1B)	114.1(2)	H(13D)-C(13B)-H(13E)	109.5
C(23B)-P(1B)-Au(1B)	112.3(2)	C(12B)-C(13B)-H(13F)	109.5
C(11B)-O(2B)-C(12B)	117.5(6)	H(13D)-C(13B)-H(13F)	109.5
C(14B)-O(4B)-C(15B)	117.1(6)	H(13E)-C(13B)-H(13F)	109.5
C(9B)-C(1B)-C(2B)	107.2(7)	O(3B)-C(14B)-O(4B)	121.6(7)
C(9B)-C(1B)-C(11B)	128.3(6)	O(3B)-C(14B)-C(3B)	126.3(6)
C(2B)-C(1B)-C(11B)	124.4(6)	O(4B)-C(14B)-C(3B)	112.1(6)
C(3B)-C(2B)-C(1B)	109.7(6)	O(4B)-C(15B)-C(16B)	106.6(6)
C(3B)-C(2B)-S(1B)	124.1(6)	O(4B)-C(15B)-H(15C)	110.4
C(1B)-C(2B)-S(1B)	126.1(6)	C(16B)-C(15B)-H(15C)	110.4
C(2B)-C(3B)-C(10B)	107.7(7)	O(4B)-C(15B)-H(15D)	110.4
C(2B)-C(3B)-C(14B)	127.7(7)	C(16B)-C(15B)-H(15D)	110.4
C(10B)-C(3B)-C(14B)	124.5(7)	H(15C)-C(15B)-H(15D)	108.6
C(5B)-C(4B)-C(10B)	130.3(7)	C(15B)-C(16B)-H(16D)	109.5
C(5B)-C(4B)-H(4B)	114.8	C(15B)-C(16B)-H(16E)	109.5
C(10B)-C(4B)-H(4B)	114.8	H(16D)-C(16B)-H(16E)	109.5
C(4B)-C(5B)-C(6B)	131.0(7)	C(15B)-C(16B)-H(16F)	109.5

H(16D)-C(16B)-H(16F)	109.5	C(24B)-C(25B)-H(25B)	120.3
H(16E)-C(16B)-H(16F)	109.5	C(25B)-C(26B)-C(27B)	122.1(7)
C(22B)-C(17B)-C(18B)	118.9(7)	C(25B)-C(26B)-H(26B)	119.0
C(22B)-C(17B)-P(1B)	122.7(5)	C(27B)-C(26B)-H(26B)	119.0
C(18B)-C(17B)-P(1B)	118.3(6)	C(28B)-C(27B)-C(26B)	117.8(8)
C(19B)-C(18B)-C(17B)	120.6(7)	C(28B)-C(27B)-H(27B)	121.1
C(19B)-C(18B)-H(18B)	119.7	C(26B)-C(27B)-H(27B)	121.1
C(17B)-C(18B)-H(18B)	119.7	C(27B)-C(28B)-C(23B)	121.5(7)
C(18B)-C(19B)-C(20B)	120.5(7)	C(27B)-C(28B)-H(28B)	119.3
C(18B)-C(19B)-H(19B)	119.8	C(23B)-C(28B)-H(28B)	119.3
C(20B)-C(19B)-H(19B)	119.8	C(30B)-C(29B)-C(34B)	117.8(6)
C(19B)-C(20B)-C(21B)	119.7(7)	C(30B)-C(29B)-P(1B)	118.9(5)
C(19B)-C(20B)-H(20B)	120.1	C(34B)-C(29B)-P(1B)	123.0(5)
C(21B)-C(20B)-H(20B)	120.1	C(31B)-C(30B)-C(29B)	121.0(6)
C(22B)-C(21B)-C(20B)	119.4(8)	C(31B)-C(30B)-H(30B)	119.5
C(22B)-C(21B)-H(21B)	120.3	C(29B)-C(30B)-H(30B)	119.5
C(20B)-C(21B)-H(21B)	120.3	C(30B)-C(31B)-C(32B)	119.9(7)
C(17B)-C(22B)-C(21B)	120.9(7)	C(30B)-C(31B)-H(31B)	120.1
C(17B)-C(22B)-H(22B)	119.6	C(32B)-C(31B)-H(31B)	120.1
C(21B)-C(22B)-H(22B)	119.6	C(33B)-C(32B)-C(31B)	120.0(7)
C(28B)-C(23B)-C(24B)	118.9(7)	C(33B)-C(32B)-H(32B)	120.0
C(28B)-C(23B)-P(1B)	122.6(6)	C(31B)-C(32B)-H(32B)	120.0
C(24B)-C(23B)-P(1B)	118.5(5)	C(34B)-C(33B)-C(32B)	119.4(6)
C(25B)-C(24B)-C(23B)	120.2(7)	C(34B)-C(33B)-H(33B)	120.3
C(25B)-C(24B)-H(24B)	119.9	C(32B)-C(33B)-H(33B)	120.3
C(23B)-C(24B)-H(24B)	119.9	C(33B)-C(34B)-C(29B)	121.8(7)
C(26B)-C(25B)-C(24B)	119.4(7)	C(33B)-C(34B)-H(34B)	119.1
C(26B)-C(25B)-H(25B)	120.3	C(29B)-C(34B)-H(34B)	119.1

Table S17. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **10**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Au(1A)	14(1)	17(1)	15(1)	0(1)	1(1)	-2(1)
S(1A)	27(1)	18(1)	30(1)	-1(1)	7(1)	-6(1)
S(2A)	18(1)	21(1)	15(1)	-1(1)	1(1)	-5(1)
P(1A)	14(1)	16(1)	15(1)	1(1)	1(1)	1(1)
O(1A)	23(2)	21(3)	26(3)	-1(2)	-5(2)	-11(2)
O(2A)	25(2)	24(3)	21(3)	-2(2)	-4(2)	-7(2)
O(3A)	45(3)	25(3)	29(4)	-1(3)	15(3)	-8(3)
O(4A)	36(3)	24(3)	19(3)	5(2)	7(2)	-10(2)
C(1A)	10(3)	16(4)	21(4)	-2(3)	0(3)	-3(3)

C(2A)	14(3)	17(4)	26(4)	-3(3)	6(3)	5(3)
C(3A)	25(4)	19(4)	19(4)	4(3)	0(3)	7(3)
C(4A)	21(3)	21(4)	15(4)	-1(3)	5(3)	4(3)
C(5A)	15(3)	24(4)	18(4)	-5(3)	-3(3)	2(3)
C(6A)	14(3)	20(4)	16(4)	8(3)	-1(3)	0(3)
C(7A)	25(3)	17(4)	17(4)	3(3)	0(3)	-2(3)
C(8A)	13(3)	27(3)	14(4)	1(3)	-4(3)	-2(2)
C(9A)	16(3)	18(4)	19(4)	4(3)	2(3)	7(3)
C(10A)	12(3)	22(4)	21(4)	-1(3)	-1(3)	7(3)
C(11A)	7(3)	15(4)	45(6)	8(3)	-1(3)	-3(3)
C(12A)	26(4)	31(5)	17(4)	-9(3)	-9(3)	1(3)
C(13A)	28(3)	21(4)	25(5)	-1(3)	-5(3)	-3(3)
C(14A)	24(4)	19(4)	27(5)	4(3)	3(3)	-3(3)
C(15A)	34(5)	35(5)	28(6)	6(4)	3(3)	-16(4)
C(16A)	46(5)	31(5)	34(5)	-6(4)	14(4)	11(4)
C(17A)	14(3)	19(4)	22(5)	-1(3)	3(3)	3(3)
C(18A)	27(3)	8(3)	22(4)	3(3)	-5(3)	2(3)
C(19A)	20(3)	20(4)	27(5)	-4(3)	-1(3)	0(3)
C(20A)	24(3)	39(5)	18(4)	0(4)	-4(3)	4(3)
C(21A)	21(4)	42(5)	24(4)	10(4)	-2(3)	2(3)
C(22A)	17(3)	44(5)	27(5)	6(4)	6(3)	-5(3)
C(23A)	15(3)	12(4)	27(5)	-6(3)	-1(3)	-5(3)
C(24A)	25(4)	34(5)	20(4)	8(3)	8(3)	7(3)
C(25A)	37(4)	45(5)	24(5)	22(4)	-1(4)	13(4)
C(26A)	25(4)	15(4)	31(5)	-4(4)	3(3)	3(3)
C(27A)	20(3)	35(5)	24(5)	-9(4)	-1(3)	0(3)
C(28A)	22(3)	24(4)	16(4)	7(3)	-2(3)	2(3)
C(29A)	17(3)	17(4)	11(4)	-1(3)	3(3)	-2(3)
C(30A)	10(3)	31(5)	26(5)	4(3)	1(3)	7(3)
C(31A)	21(3)	22(4)	26(5)	4(3)	2(3)	4(3)
C(32A)	20(4)	21(4)	17(4)	-3(3)	8(3)	-7(3)
C(33A)	18(3)	27(4)	11(4)	-3(3)	1(3)	2(3)
C(34A)	19(3)	10(3)	19(4)	-1(3)	-5(3)	5(3)
Au(1B)	14(1)	17(1)	16(1)	0(1)	1(1)	2(1)
S(1B)	29(1)	18(1)	26(1)	0(1)	-1(1)	5(1)
S(2B)	18(1)	19(1)	17(1)	3(1)	2(1)	4(1)
P(1B)	14(1)	17(1)	18(1)	-2(1)	2(1)	1(1)
O(1B)	25(2)	31(3)	27(3)	1(2)	-5(2)	3(2)
O(2B)	29(3)	22(3)	19(3)	-3(2)	-2(2)	6(2)
O(3B)	42(3)	26(3)	23(3)	-6(2)	-1(3)	12(2)
O(4B)	29(3)	31(3)	22(3)	-2(2)	2(2)	12(2)
C(1B)	11(3)	17(4)	23(4)	-7(3)	-1(3)	-5(3)
C(2B)	17(3)	15(4)	24(4)	-3(3)	-2(3)	-6(3)
C(3B)	12(3)	20(4)	21(4)	1(3)	1(3)	-6(3)
C(4B)	19(3)	22(4)	8(4)	-1(3)	-6(3)	-6(3)

C(5B)	16(3)	19(4)	11(4)	2(3)	-5(3)	4(3)
C(6B)	10(3)	17(4)	19(4)	2(3)	0(3)	-7(2)
C(7B)	16(3)	21(4)	14(4)	-5(3)	0(3)	-2(3)
C(8B)	16(3)	22(4)	19(4)	1(3)	-5(3)	-2(3)
C(9B)	17(3)	14(4)	18(4)	0(3)	1(3)	-1(3)
C(10B)	15(3)	12(4)	29(5)	0(3)	-5(3)	0(3)
C(11B)	24(4)	10(4)	46(5)	-3(3)	-5(3)	3(3)
C(12B)	17(3)	23(4)	12(4)	8(3)	-5(3)	4(3)
C(13B)	32(4)	38(5)	21(5)	-3(4)	-13(3)	4(4)
C(14B)	18(3)	23(4)	26(5)	1(3)	3(3)	1(3)
C(15B)	34(4)	32(5)	21(6)	-6(3)	5(3)	3(4)
C(16B)	35(4)	32(5)	33(6)	4(3)	17(4)	11(3)
C(17B)	15(3)	14(4)	21(5)	-1(3)	1(3)	-9(3)
C(18B)	22(3)	20(4)	20(4)	-5(3)	5(3)	1(3)
C(19B)	25(4)	23(4)	23(5)	2(3)	1(3)	7(3)
C(20B)	33(4)	29(5)	28(6)	7(3)	-4(3)	0(4)
C(21B)	34(5)	36(4)	31(6)	-10(4)	5(4)	2(3)
C(22B)	21(3)	29(4)	17(4)	-4(3)	1(3)	-3(3)
C(23B)	15(3)	9(3)	20(4)	0(3)	7(3)	3(3)
C(24B)	29(4)	17(4)	20(4)	-4(3)	1(3)	-5(3)
C(25B)	17(3)	25(4)	24(5)	-3(3)	-2(3)	-5(3)
C(26B)	21(4)	17(4)	34(5)	-15(4)	0(3)	-5(3)
C(27B)	23(3)	23(4)	29(5)	2(3)	2(3)	3(3)
C(28B)	19(3)	21(4)	27(5)	-5(3)	-1(3)	3(3)
C(29B)	10(3)	23(4)	16(4)	-6(3)	2(3)	-1(3)
C(30B)	14(3)	22(4)	37(5)	-3(4)	3(3)	-8(3)
C(31B)	33(4)	15(4)	45(6)	-6(4)	-2(4)	-1(3)
C(32B)	27(4)	16(4)	23(5)	0(3)	4(3)	4(3)
C(33B)	17(3)	26(4)	25(4)	0(3)	0(3)	0(3)
C(34B)	18(3)	22(4)	20(4)	3(3)	3(3)	-3(3)

Table S18. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **10**.

	x	y	z	U(eq)
H(1A)	0.762(3)	0.920(6)	0.527(3)	0.030
H(4A)	0.6570	0.5410	0.3649	0.023
H(5A)	0.6039	0.3863	0.3818	0.023
H(7A)	0.6044	0.3673	0.5521	0.023
H(8A)	0.6520	0.5239	0.5762	0.021
H(12A)	0.6924	0.7620	0.6942	0.030
H(12B)	0.7520	0.6931	0.6878	0.030

H(13A)	0.6460	0.5796	0.7124	0.037
H(13B)	0.6972	0.5934	0.7570	0.037
H(13C)	0.7039	0.5074	0.7025	0.037
H(15A)	0.7859	0.8233	0.2912	0.039
H(15B)	0.7836	0.9618	0.3090	0.039
H(16A)	0.6865	0.9644	0.2772	0.056
H(16B)	0.6966	0.8328	0.2518	0.056
H(16C)	0.7315	0.9441	0.2268	0.056
H(18A)	0.5645	0.3401	0.6556	0.023
H(19A)	0.6225	0.3671	0.7353	0.027
H(20A)	0.6051	0.2601	0.8180	0.032
H(21A)	0.5305	0.1262	0.8225	0.035
H(22A)	0.4689	0.1038	0.7454	0.035
H(24A)	0.4108	0.3909	0.5593	0.032
H(25A)	0.3432	0.5415	0.5742	0.042
H(26A)	0.3059	0.5734	0.6646	0.028
H(27A)	0.3338	0.4563	0.7414	0.032
H(28A)	0.4017	0.3054	0.7280	0.025
H(30A)	0.4903	-0.0323	0.6566	0.027
H(31A)	0.4389	-0.2109	0.6637	0.027
H(32A)	0.3408	-0.2084	0.6490	0.023
H(33A)	0.2947	-0.0319	0.6269	0.022
H(34A)	0.3452	0.1474	0.6214	0.019
H(1B)	0.019(3)	1.428(6)	0.580(3)	0.029
H(4B)	0.1266	1.0349	0.7316	0.020
H(5B)	0.1770	0.8806	0.7101	0.018
H(7B)	0.1601	0.8552	0.5418	0.020
H(8B)	0.1098	1.0132	0.5194	0.023
H(12C)	0.0716	1.2685	0.4082	0.021
H(12D)	0.0151	1.1880	0.4128	0.021
H(13D)	0.1253	1.0932	0.3899	0.045
H(13E)	0.0770	1.1091	0.3423	0.045
H(13F)	0.0686	1.0146	0.3932	0.045
H(15C)	0.0603	1.4186	0.8116	0.035
H(15D)	0.0117	1.3218	0.8256	0.035
H(16D)	-0.0552	1.4478	0.7778	0.050
H(16E)	-0.0064	1.5461	0.7697	0.050
H(16F)	-0.0283	1.5128	0.8326	0.050
H(18B)	0.2038	0.8422	0.4303	0.025
H(19B)	0.1464	0.8668	0.3509	0.028
H(20B)	0.1665	0.7660	0.2660	0.036
H(21B)	0.2464	0.6393	0.2608	0.040
H(22B)	0.3040	0.6147	0.3412	0.027
H(24B)	0.3897	0.8225	0.5285	0.026
H(25B)	0.4592	0.9721	0.5189	0.027

H(26B)	0.4604	1.0897	0.4393	0.029
H(27B)	0.3967	1.0569	0.3629	0.030
H(28B)	0.3330	0.8979	0.3694	0.027
H(30B)	0.2814	0.4691	0.4480	0.029
H(31B)	0.3326	0.2948	0.4334	0.037
H(32B)	0.4322	0.3017	0.4299	0.026
H(33B)	0.4792	0.4859	0.4369	0.027
H(34B)	0.4272	0.6604	0.4464	0.024

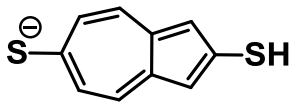
C. DFT CALCULATIONS

C1. Experimental

All Density Functional Theory (DFT) calculations were performed using the ORCA (v.2.9.1) program.[15] Geometric optimizations for the gold complexes were performed spin-restricted using the BP86 functional[16] with a TZVP basis set.[17] The resolution of identity approximation (RI) was used along with the SV/J auxiliary basis set,[18] and the Zero-Order Regular Approximation (ZORA).[19] Single point energy and time-dependent DFT (TD-DFT) calculations were then performed using the B3LYP functional[20] with ZORA, a TZVP basis set, and a TZV/J auxiliary basis set.[18]

Geometric optimizations and single point energy calculations for the strictly organic molecules were performed using the B3LYP functional with a TZVP basis set, the RIJCOSX approximation, and a TZV/J auxiliary basis set.[18,20,21] The solvation effects of tetrahydrofuran (THF) [$\varepsilon = 7.25$] were modeled using the conductor-like screening model (COSMO), as implemented in ORCA.[22] For the structures featuring ethyl ester substituents attached to the azulenic framework, multiple conformations of the ester groups were probed to ensure selection of the lowest energy scenarios. Molecular and orbital images were produced using the Molekel (v.5.4.0.8) program with isodensity values set at ±0.03.[23] The final Cartesian coordinates for all optimized structures are provided below.

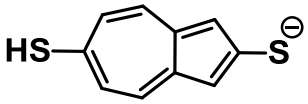
Table S19. Cartesian coordinates (Å) for the optimized structure of the 2-mercapto-6-azulenethiolate anion.



Atom	x	y	z
C	0.134537	0.132992	0.007379
H	-0.832694	0.439687	-0.365331
C	1.367558	0.356796	-0.627131
C	2.404983	-0.171989	0.160281
C	1.825685	-0.757804	1.301112
C	2.515286	-1.421958	2.336757
C	2.049074	-2.048984	3.466577
C	0.712909	-2.225465	3.956279
C	-0.452687	-1.709586	3.298886
C	-0.585002	-0.999144	2.130308
C	0.384438	-0.562333	1.205175
H	-1.608079	-0.733064	1.866738
H	-1.374058	-1.935578	3.823857
S	0.498485	-3.107384	5.419573
H	2.800299	-2.499090	4.105998
H	3.597346	-1.449983	2.213483
H	3.460177	-0.138764	-0.073382
S	1.575367	1.221452	-2.183007

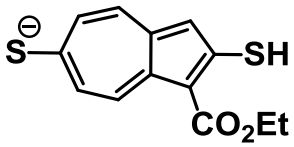
H	1.608544	0.147811	-3.013425

Table S20. Cartesian coordinates (Å) for the optimized structure of the 6-mercapto-2-azulenethiolate anion.



Atom	x	y	z
C	0.015712	0.049779	0.016326
H	-0.954444	0.378830	-0.329689
C	1.229748	0.235724	-0.724515
C	2.280263	-0.324694	0.076981
C	1.762526	-0.846945	1.247134
C	2.475414	-1.485763	2.272403
C	2.015952	-2.056940	3.452777
C	0.709236	-2.145199	3.951799
C	-0.470240	-1.638583	3.386163
C	-0.658354	-0.966070	2.185671
C	0.276705	-0.600554	1.206931
H	-1.684294	-0.677273	1.968617
H	-1.368787	-1.805720	3.970901
S	0.533534	-2.977669	5.560830
H	0.212431	-4.221587	5.120984
H	2.777961	-2.507665	4.079792
H	3.548941	-1.557236	2.112760
H	3.321251	-0.335749	-0.216360
S	1.384567	0.969300	-2.255639

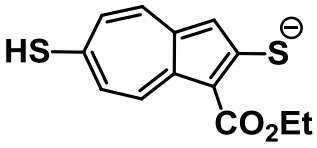
Table S21. Cartesian coordinates (Å) for the optimized structure of the 2-mercapto-1-ethoxycarbonyl-6-azulenethiolate anion.



Atom	x	y	z
C	0.405582	0.935826	-0.980775
C	-7.021987	1.126369	0.523276
C	-4.134797	-0.205324	0.845208
C	-4.808968	1.925790	-0.354914
C	-3.926088	0.961514	0.079678
C	-6.218176	2.076565	-0.188342

C	-3.861019	-2.159168	2.045085
C	-6.668438	-0.025014	1.173956
C	-3.154523	-1.167921	1.287130
C	-1.731964	-1.199756	1.069807
C	0.156257	-0.152916	0.043354
C	-5.409619	-0.644982	1.349155
C	-5.209715	-1.840260	2.075703
H	0.469719	-1.131857	-0.325510
H	-0.151001	0.734210	-1.897888
H	0.093040	1.909264	-0.597045
O	-0.944619	-2.048781	1.491480
S	-3.214162	-3.604795	2.849335
H	-4.364182	2.728021	-0.934007
H	-1.929564	-3.358476	2.483848
S	-6.987477	3.459154	-0.860636
H	-5.983140	-2.406573	2.575442
H	-8.075585	1.382012	0.545693
H	0.703180	0.038597	0.971279
H	-7.492762	-0.556704	1.646587
O	-1.252175	-0.164392	0.309398
H	-2.901156	1.134043	-0.215920
H	1.469337	0.986559	-1.228376

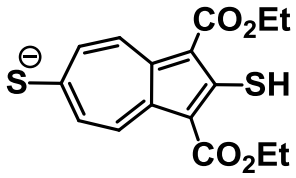
Table S22. Cartesian coordinates (Å) for the optimized structure of the 6-mercapto-1-ethoxycarbonyl-2-azulenethiolate anion.



Atom	x	y	z
C	-0.000405	-0.019360	-0.060946
O	-1.376588	-0.127026	0.308213
C	-1.695295	-1.074836	1.226246
C	-3.124763	-1.156428	1.495676
C	-4.222553	-0.654774	0.679859
C	-5.417063	-0.915058	1.427691
H	-6.400198	-0.634649	1.076857
C	-5.133564	-1.566758	2.604055
C	-3.655709	-1.759242	2.661089
C	-2.957621	-2.415305	3.672936
C	-3.440269	-3.051407	4.825715
C	-4.734255	-3.170364	5.314025
C	-5.919136	-2.646259	4.752473
C	-6.085624	-1.960631	3.570842
H	-7.106893	-1.666659	3.340555

H	-6.821170	-2.815554	5.331049
S	-4.912386	-4.048134	6.896260
H	-5.532766	-5.163787	6.436056
H	-2.677614	-3.536741	5.426272
H	-1.887367	-2.473601	3.525697
S	-4.246990	0.041566	-0.870793
O	-0.819521	-1.743016	1.762393
C	0.062687	0.974765	-1.203101
H	1.096453	1.115430	-1.532346
H	-0.341319	1.940002	-0.891788
H	-0.533489	0.619842	-2.044514
H	0.588421	0.313148	0.800062
H	0.383358	-1.000465	-0.354087

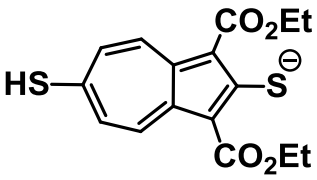
Table S23. Cartesian coordinates (Å) for the optimized structure of the 2-mercapto-1,3-diethoxycarbonyl-6-azulenethiolate anion.



Atom	x	y	z
C	0.181844	-0.028039	0.139241
C	-1.075743	-0.583194	0.775431
H	-1.117057	-1.670000	0.678282
H	-1.952672	-0.160429	0.278078
H	-1.127367	-0.323697	1.835006
O	1.314495	-0.557489	0.846626
C	2.544055	-0.170676	0.381240
C	3.663388	-0.584693	1.197811
C	5.020372	-0.241027	0.918907
C	5.852094	-0.827344	1.897744
C	5.014473	-1.555757	2.812465
C	5.480988	-2.276942	3.940265
C	4.809142	-3.010169	4.883214
C	3.413820	-3.271011	5.057560
C	2.424705	-2.714159	4.186380
C	2.529775	-1.923852	3.068415
C	3.660235	-1.394478	2.397674
H	1.582648	-1.660381	2.622931
H	1.412152	-2.978382	4.472197
S	2.912572	-4.268805	6.358900
H	5.430455	-3.480532	5.637628
H	6.556813	-2.257111	4.057820
C	7.299855	-0.743606	2.007799
O	7.830403	0.267779	1.253808

C	9.255837	0.418225	1.283295
C	9.579443	1.799351	0.745396
H	10.657950	1.974732	0.795954
H	9.078115	2.563332	1.340517
H	9.249682	1.907853	-0.289394
H	9.614254	0.290649	2.305595
H	9.713854	-0.369053	0.676787
O	8.021319	-1.451199	2.692646
S	5.607890	0.718670	-0.453158
H	4.368720	0.834721	-0.998632
O	2.599448	0.485454	-0.658723
H	0.205391	1.063712	0.199623
H	0.247989	-0.304785	-0.914825

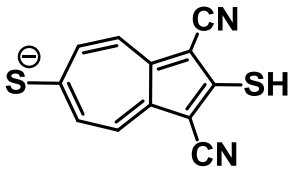
Table S24. Cartesian coordinates (Å) for the optimized structure of the 6-mercapto-1,3-diethoxycarbonyl-2-azulenethiolate anion.



Atom	x	y	z
C	0.449340	-0.032080	-0.184010
C	0.735282	0.271877	-1.644019
H	1.552286	0.989549	-1.724255
H	-0.155394	0.688055	-2.125330
H	1.035714	-0.630648	-2.179936
O	1.651593	-0.571166	0.382416
C	1.859631	-0.407049	1.706734
C	3.226915	-0.751381	2.117409
C	4.451567	-0.503336	1.374358
C	5.525411	-1.017981	2.209593
C	4.988850	-1.595408	3.371662
C	5.706205	-2.244227	4.387960
C	5.259231	-2.838728	5.562085
C	3.967504	-2.927663	6.082890
C	2.793250	-2.407910	5.524722
C	2.597957	-1.745793	4.323482
C	3.523923	-1.378038	3.332122
H	1.579474	-1.437132	4.124833
H	1.897138	-2.547770	6.120201
S	3.815073	-3.753190	7.696060
H	3.174086	-4.873156	7.280019
H	6.032393	-3.311268	6.158837
H	6.770199	-2.323420	4.207269
C	6.965901	-0.960797	1.946944
O	7.323916	0.123423	1.224992

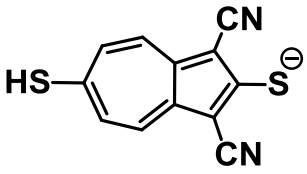
C	8.674670	0.204165	0.758257
C	8.683142	1.224609	-0.363228
H	9.697021	1.360640	-0.751227
H	8.310981	2.187338	-0.007192
H	8.031434	0.895115	-1.172865
H	9.329016	0.502484	1.584139
H	9.006164	-0.779312	0.417735
O	7.799301	-1.764554	2.342820
S	4.582736	0.237533	-0.145284
O	0.968532	-0.029411	2.452765
H	-0.356878	-0.765108	-0.072406
H	0.156229	0.861620	0.369601

Table S25. Cartesian coordinates (Å) for the optimized structure of the 2-mercapto-1,3-dicyano-6-azulenethiolate anion.



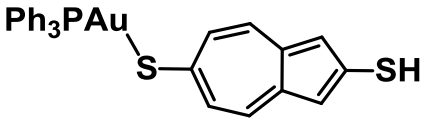
Atom	x	y	z
C	-0.088193	-0.024921	-0.078622
C	-1.378457	0.381353	-0.472260
N	-2.444207	0.709372	-0.789181
C	1.090091	0.107895	-0.837217
C	2.160684	-0.430005	-0.091738
C	1.644382	-0.922338	1.148456
C	2.403730	-1.552209	2.159093
C	2.012763	-2.076413	3.362314
C	0.721677	-2.145537	3.987098
C	-0.471786	-1.619001	3.383013
C	-0.674279	-0.988230	2.183494
C	0.242095	-0.665832	1.158693
H	-1.700068	-0.688063	1.984236
H	-1.355331	-1.756361	3.995955
S	0.602095	-2.886949	5.523617
H	2.799610	-2.521443	3.960552
H	3.464854	-1.643200	1.940550
C	3.503403	-0.472241	-0.508375
N	4.604619	-0.500258	-0.873227
S	1.157118	0.828520	-2.453803
H	2.466311	0.561601	-2.661559

Table S26. Cartesian coordinates (Å) for the optimized structure of the 6-mercapto-1,3-dicyano-2-azulenethiolate anion.



Atom	x	y	z
C	0.007975	0.011182	-0.046508
C	-1.293514	0.383883	-0.446230
N	-2.384679	0.662669	-0.716185
C	1.218026	0.227127	-0.810163
C	2.276971	-0.320845	0.010474
C	1.754724	-0.866400	1.190407
C	2.480616	-1.514229	2.196917
C	2.029985	-2.113966	3.366770
C	0.734171	-2.196119	3.885423
C	-0.442998	-1.671221	3.336292
C	-0.639070	-1.004053	2.137078
C	0.292813	-0.644794	1.155017
H	-1.662476	-0.708531	1.926990
H	-1.336606	-1.812144	3.934700
S	0.583457	-3.030024	5.494086
H	-0.121486	-4.110877	5.079303
H	2.797332	-2.595121	3.963332
H	3.550534	-1.580381	2.023882
C	3.649592	-0.329052	-0.319201
N	4.787256	-0.364613	-0.534776
S	1.351270	0.948559	-2.323341

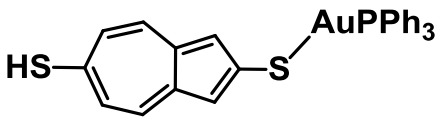
Table S27. Cartesian coordinates (Å) for the optimized structure of [Ph_3PAu](2-mercapto-6-azulenethiolate).



Atom	x	y	z
H	2.002766	-2.119427	-0.270296
C	2.965590	-2.486417	0.078883
C	4.144933	-1.722566	0.230365
C	5.190476	-2.545401	0.704940
C	4.681912	-3.848948	0.863078
C	5.396017	-4.966674	1.312485
C	4.974846	-6.279522	1.515955
C	3.701917	-6.861672	1.315683
C	-1.936978	-8.503574	2.266787
C	-3.161253	-8.754450	1.630403

C	-4.055840	-7.704911	1.396821
C	-3.735447	-6.405205	1.797744
C	-2.512525	-6.150957	2.428533
C	-1.611767	-7.192822	2.656341
C	-1.279503	-11.313149	1.656175
C	-2.219441	-12.217594	2.173991
C	-2.634799	-13.309550	1.406623
C	-2.113747	-13.506091	0.124194
C	-1.171438	-12.611034	-0.392000
C	-0.751012	-11.519683	0.371490
C	2.544225	-6.216698	0.823229
C	2.355680	-4.885409	0.459504
C	3.252819	-3.810164	0.462216
H	6.211749	-2.231814	0.911371
C	-0.963996	-10.282998	4.387001
C	-2.152493	-9.979270	5.068092
C	-2.306667	-10.354624	6.406300
C	-1.279352	-11.032315	7.069049
C	-0.090378	-11.329708	6.394584
C	0.071387	-10.951918	5.060378
H	-2.952696	-9.439608	4.559419
S	3.664582	-8.614642	1.701281
Au	1.450297	-9.190643	2.114984
P	-0.704357	-9.837813	2.610496
H	-0.649475	-6.988097	3.130058
H	-2.253115	-5.136768	2.734851
H	-4.434168	-5.588095	1.611922
H	-5.004238	-7.906244	0.896653
H	-3.414352	-9.765221	1.308728
H	0.001322	-10.830946	-0.020410
H	-0.752744	-12.767557	-1.386762
H	-2.435609	-14.362801	-0.469872
H	-3.362637	-14.012237	1.815716
H	-2.618333	-12.077618	3.179772
H	1.346278	-4.643325	0.108577
H	1.670031	-6.861909	0.707221
H	5.737080	-6.960197	1.902758
H	6.447706	-4.778147	1.553557
S	4.224355	0.009277	-0.148167
H	5.516408	0.185515	0.239642
H	1.009112	-11.162591	4.541496
H	0.719703	-11.845844	6.911833
H	-1.400861	-11.320675	8.114063
H	-3.230967	-10.110246	6.932263

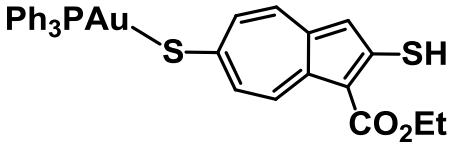
Table S28. Cartesian coordinates (Å) for the optimized structure of [Ph_3PAu](6-mercapto-2-azulenethiolate).



Atom	x	y	z
H	4.052840	-1.020154	-1.040053
C	4.587370	-0.648843	-0.168187
C	5.642903	0.299199	-0.197564
C	6.092195	0.521799	1.130789
C	5.331919	-0.271922	2.003194
C	5.467960	-0.334314	3.393738
C	4.760644	-1.087913	4.332808
C	3.707247	-1.996765	4.122870
C	3.108994	-2.374807	2.905372
C	3.400369	-1.946810	1.609880
C	4.357637	-1.029605	1.162510
H	6.892389	1.200000	1.420754
C	4.828607	0.400767	-6.901148
C	4.776696	-0.421277	-8.036838
C	5.467634	-0.055117	-9.196541
C	6.210311	1.128439	-9.228827
C	6.269417	1.946829	-8.095534
C	5.587161	1.582978	-6.932925
C	3.529199	-1.811121	-5.460398
C	2.318755	-2.280831	-5.992582
C	2.076808	-3.656054	-6.071137
C	3.037433	-4.565668	-5.619516
C	4.242956	-4.100388	-5.082980
C	4.487164	-2.728384	-4.996173
C	2.302579	0.863593	-5.476777
C	1.753676	1.234736	-6.714013
C	0.515588	1.882954	-6.764204
C	-0.178752	2.164538	-5.583964
C	0.368912	1.802150	-4.348908
C	1.607856	1.160096	-4.292659
H	2.296680	1.029823	-7.637924
S	2.980368	-2.833868	5.545405
H	3.733213	-2.220901	6.497153
H	2.783634	-2.396515	0.825026
H	2.298703	-3.105892	2.983386
H	5.077564	-0.947023	5.369091
H	6.251701	0.305445	3.812831
S	6.371633	1.119793	-1.578553
Au	5.114232	0.522544	-3.439218

P	3.927677	-0.008782	-5.339369
H	5.650217	2.210939	-6.041467
H	6.856602	2.866002	-8.111999
H	6.750375	1.409416	-10.134056
H	5.427634	-0.700707	-10.075416
H	4.207274	-1.351234	-8.014407
H	5.417368	-2.363106	-4.555618
H	4.990223	-4.806124	-4.717820
H	2.843532	-5.637983	-5.677769
H	1.131596	-4.015883	-6.480272
H	1.560579	-1.575176	-6.335092
H	2.047902	0.902137	-3.327225
H	-0.162275	2.031272	-3.424280
H	-1.142523	2.673638	-5.625534
H	0.097622	2.174078	-7.728860

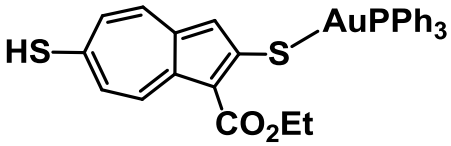
Table S29. Cartesian coordinates (Å) for the optimized structure of [Ph_3PAu](1-ethoxycarbonyl-2-mercapto-6-azulenethiolate).



Atom	x	y	z
C	-0.121847	0.245355	0.311400
C	0.686216	-0.835896	1.003912
H	1.685714	-0.447601	1.245462
H	0.808223	-1.716189	0.358844
H	0.207437	-1.151062	1.940332
O	-1.434692	-0.312166	0.015491
C	-2.311179	0.536350	-0.606630
C	-3.618674	-0.033913	-0.883260
C	-4.675358	0.703902	-1.525665
C	-5.808831	-0.115296	-1.642785
H	-6.756956	0.177686	-2.088634
C	-5.518567	-1.374499	-1.088756
C	-4.128162	-1.346983	-0.602688
C	-3.460215	-2.416456	0.005172
C	-3.908502	-3.703437	0.319393
C	-5.158652	-4.318207	0.114064
C	-6.281953	-3.728051	-0.517682
C	-6.425866	-2.449428	-1.031500
H	-7.406085	-2.238066	-1.472084
H	-7.154719	-4.378127	-0.617053
S	-5.229177	-6.017934	0.675616
Au	-7.470084	-6.537503	1.023651

P	-9.655180	-7.121364	1.461936
C	-10.846035	-5.792027	0.980603
C	-12.043336	-6.062986	0.302587
C	-12.907307	-5.016112	-0.035628
C	-12.583596	-3.699564	0.302498
C	-11.387346	-3.425854	0.975270
C	-10.516925	-4.465292	1.307864
H	-9.575163	-4.246530	1.815078
H	-11.125190	-2.399041	1.233586
H	-13.258288	-2.885008	0.035494
H	-13.834796	-5.233473	-0.567206
H	-12.298895	-7.087510	0.030253
C	-10.212163	-8.643436	0.573725
C	-11.166371	-9.518758	1.114483
C	-11.565060	-10.648526	0.394375
C	-11.014503	-10.910716	-0.863563
C	-10.058193	-10.044290	-1.402397
C	-9.653033	-8.916457	-0.685541
H	-8.889033	-8.250661	-1.094045
H	-9.616911	-10.251758	-2.377807
H	-11.324012	-11.796381	-1.420331
H	-12.303640	-11.328757	0.821536
H	-11.589576	-9.326407	2.101292
C	-9.996438	-7.446855	3.249677
C	-11.222496	-7.116149	3.846879
C	-11.440766	-7.400934	5.198371
C	-10.439919	-8.013766	5.957964
C	-9.213809	-8.337183	5.367202
C	-8.988731	-8.051155	4.019247
H	-8.023544	-8.282849	3.563976
H	-8.424794	-8.802006	5.959998
H	-10.611502	-8.230705	7.013251
H	-12.393862	-7.136185	5.658632
H	-12.001586	-6.625224	3.261831
H	-3.168409	-4.331932	0.821847
H	-2.429255	-2.212203	0.291663
S	-4.636426	2.364727	-2.101295
H	-3.328478	2.525374	-1.673890
O	-1.962907	1.694981	-0.885881
H	0.345300	0.570976	-0.628896
H	-0.248972	1.134378	0.945365

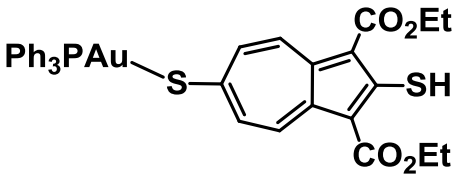
Table S30. Cartesian coordinates (Å) for the optimized structure of [Ph_3PAu](1-ethoxycarbonyl-6-mercapto-2-azulenethiolate).



Atom	x	y	z
C	5.221211	5.143500	-6.555233
C	4.961060	6.324797	-7.266418
C	3.720047	6.510364	-7.884095
C	2.736519	5.521191	-7.796415
C	2.991616	4.343947	-7.084738
C	4.226396	4.155868	-6.460762
C	7.646402	6.484122	-5.572206
C	8.604017	6.947755	-6.486108
C	9.180890	8.210359	-6.313913
C	8.803414	9.015333	-5.235711
C	7.850559	8.554563	-4.320620
C	7.279279	7.290997	-4.481275
C	7.850979	3.902593	-6.968228
C	7.579357	3.958580	-8.344001
C	8.381085	3.250988	-9.244625
C	9.456418	2.488136	-8.779202
C	9.726526	2.425791	-7.408112
C	8.923731	3.123824	-6.503372
C	7.703060	2.995304	-0.682498
C	8.761583	3.863332	-1.035666
C	9.699048	3.910879	0.002846
C	9.210129	3.022590	1.079337
C	7.971987	2.466381	0.632692
C	7.176283	1.522702	1.422453
C	5.203590	0.181065	1.498113
C	4.012206	-0.140628	0.616029
C	9.845493	2.777687	2.299189
C	11.051638	3.283166	2.801414
C	11.960203	4.177326	2.219705
C	11.872851	4.798707	0.953284
C	10.880377	4.673643	-0.008361
H	9.312806	2.085483	2.954886
P	6.841638	4.826222	-5.724224
H	4.417069	3.246293	-5.887554
H	2.222794	3.573885	-7.004207
H	1.767838	5.669909	-8.275443
H	3.521881	7.433758	-8.430276
H	5.721647	7.104921	-7.329218
H	6.554351	6.921608	-3.752301

H	7.560667	9.174333	-3.470965
H	9.257344	9.998159	-5.102868
H	9.930678	8.561866	-7.024562
H	8.907398	6.321602	-7.326153
H	9.118156	3.053688	-5.430671
H	10.556858	1.822151	-7.038797
H	10.078657	1.934408	-9.483740
H	8.160759	3.293480	-10.312599
H	6.735175	4.543552	-8.712352
Au	6.633271	3.758857	-3.689027
S	6.296870	2.631324	-1.678111
H	8.824666	4.409944	-1.974325
O	7.460233	1.102712	2.544186
O	6.036609	1.126212	0.776657
H	3.355663	-0.857667	1.130917
H	3.430728	0.763746	0.393185
H	4.334618	-0.586332	-0.334001
H	5.799211	-0.714364	1.729919
H	4.899559	0.630843	2.454939
H	11.039729	5.260002	-0.919297
H	12.699026	5.466349	0.692692
S	13.446629	4.643474	3.121811
H	13.193058	3.909379	4.238144
H	11.312460	2.915338	3.796854

Table S31. Cartesian coordinates (Å) for the optimized structure of [Ph_3PAu](1,3-diethoxycarbonyl-2-mercapto-6-azulenethiolate) (**10**).

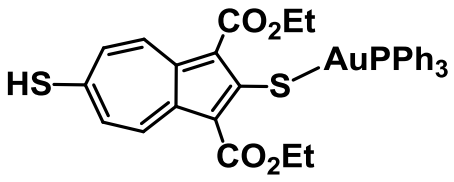


Atom	x	y	z
C	0.167696	-0.127384	-0.251053
C	1.531772	-2.036456	0.211604
C	2.897538	-2.521989	0.425184
C	4.104829	-1.762494	0.448138
C	5.209460	-2.645061	0.710579
C	4.679791	-3.974063	0.855066
C	5.403254	-5.150711	1.128562
C	4.977028	-6.462903	1.312539
C	3.681413	-7.023412	1.262101
C	-1.971238	-8.677273	1.849501
C	-3.159235	-9.051072	1.204170
C	-4.031478	-8.068401	0.724121
C	-3.723535	-6.714787	0.884218

C	-2.537988	-6.338535	1.525730
C	-1.662425	-7.314825	2.004175
C	-1.271568	-11.539349	1.767799
C	-2.149400	-12.415162	2.424026
C	-2.510564	-13.623634	1.820440
C	-2.000130	-13.962567	0.564238
C	-1.120262	-13.094124	-0.090142
C	-0.750397	-11.889298	0.510710
C	2.503186	-6.309641	0.949297
C	2.316949	-4.956378	0.705055
C	3.235028	-3.889748	0.672993
C	6.594291	-2.197067	0.806391
C	8.892454	-2.766671	1.147824
C	9.729600	-4.001459	1.415152
C	0.338631	1.360542	-0.489068
C	-1.121989	-10.051751	4.303821
C	-2.375698	-9.717601	4.839217
C	-2.607397	-9.852122	6.211514
C	-1.592349	-10.316968	7.053086
C	-0.339347	-10.643318	6.523233
C	-0.101241	-10.507132	5.154038
O	1.490321	-0.692381	-0.043355
S	3.636064	-8.778026	1.585489
Au	1.412089	-9.334670	2.011860
P	-0.764680	-9.918366	2.495697
H	-0.731324	-7.017452	2.490742
H	-2.283843	-5.283804	1.639172
H	-4.401384	-5.950933	0.501234
H	-4.951286	-8.365628	0.218403
H	-3.399752	-10.105958	1.065717
H	-0.046223	-11.220314	0.010419
H	-0.711362	-13.359315	-1.065611
H	-2.281431	-14.907937	0.098469
H	-3.189205	-14.303765	2.337651
H	-2.543406	-12.160137	3.408257
H	1.287221	-4.653420	0.504054
H	1.596150	-6.918035	0.896640
H	5.774527	-7.172637	1.548132
H	6.477991	-5.009500	1.228203
O	7.502952	-3.193529	1.045550
H	9.179754	-2.269138	0.210315
H	8.977166	-2.027393	1.957292
H	10.787639	-3.714209	1.498075
H	9.636185	-4.730770	0.598668
H	9.434320	-4.487447	2.355271

O	6.985770	-1.026183	0.690241
S	4.204588	-0.027027	0.198318
H	5.578748	-0.050908	0.381160
O	0.505405	-2.715549	0.248606
H	-0.302484	-0.631962	-1.108440
H	-0.449879	-0.334832	0.635394
H	-0.646338	1.822309	-0.648846
H	0.957551	1.550383	-1.375948
H	0.811735	1.846981	0.374296
H	0.883329	-10.739564	4.742892
H	0.459396	-10.992920	7.178710
H	-1.774737	-10.416122	8.124298
H	-3.581632	-9.585096	6.623443
H	-3.165610	-9.339931	4.188270

Table S32. Cartesian coordinates (Å) for the optimized structure of [Ph_3PAu](1,3-diethoxycarbonyl-6-mercapto-2-azulenethiolate).

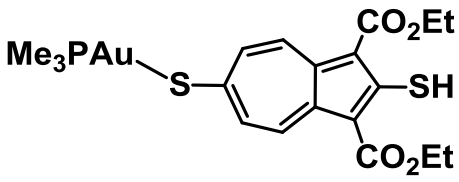


Atom	x	y	z
C	1.107587	2.009710	-0.717105
O	2.195533	1.257169	-0.112141
C	3.431318	1.452404	-0.645996
C	4.462107	0.648989	0.037576
C	4.599837	0.396302	1.436381
C	5.630025	-0.582563	1.615230
C	6.175572	-0.895852	0.336502
C	7.219247	-1.796312	0.085635
C	7.826440	-2.156256	-1.117510
C	7.543309	-1.722941	-2.423559
S	8.506902	-2.369079	-3.795235
H	9.330206	-3.159088	-3.054537
C	6.555987	-0.801436	-2.826086
C	5.638511	-0.099620	-2.051650
C	5.440864	-0.103086	-0.661337
H	4.984887	0.579892	-2.603376
H	6.503920	-0.600775	-3.900396
H	8.635156	-2.885116	-1.016517
H	7.629676	-2.270196	0.979250
C	6.107283	-1.184125	2.869349
O	5.169611	-1.135901	3.858086
C	5.588571	-1.659192	5.148781
H	5.874960	-2.714056	5.027581

H	6.481777	-1.109666	5.480165
C	4.425796	-1.488328	6.107354
H	4.705647	-1.874210	7.098371
H	3.542794	-2.040108	5.759334
H	4.153809	-0.430077	6.210233
O	7.207435	-1.708175	3.035053
S	3.772842	1.236779	2.753891
Au	3.778018	3.464688	2.064165
P	3.911066	5.719921	1.599338
C	3.207826	6.746908	2.967829
C	3.800251	7.947451	3.387423
C	3.223047	8.687468	4.424217
C	2.054670	8.236511	5.044538
C	1.463862	7.037448	4.632201
C	2.040588	6.290451	3.603113
H	1.593834	5.342365	3.297180
H	0.558363	6.675553	5.120618
H	1.608881	8.813987	5.855729
H	3.691613	9.617258	4.749352
H	4.717129	8.300163	2.913990
C	5.653670	6.302465	1.390037
C	5.977529	7.394625	0.570016
C	7.305863	7.816159	0.459213
C	8.315229	7.149022	1.159712
C	7.997170	6.054287	1.969700
C	6.671641	5.628204	2.083401
H	6.423619	4.759252	2.696997
H	8.783480	5.521133	2.505313
H	9.351928	7.476050	1.066040
H	7.552273	8.663889	-0.182079
H	5.195502	7.907509	0.008078
C	3.042438	6.283867	0.067657
C	2.281998	7.462729	0.030737
C	1.664449	7.858731	-1.160262
C	1.803146	7.082558	-2.314707
C	2.554635	5.903154	-2.276843
C	3.169101	5.496893	-1.090068
H	3.729109	4.559760	-1.072543
H	2.656317	5.283329	-3.168487
H	1.319756	7.392595	-3.242349
H	1.072705	8.775232	-1.182444
H	2.166538	8.068779	0.930219
O	3.624124	2.159651	-1.634839
H	1.292318	3.082854	-0.558618
H	1.107271	1.825860	-1.801585

C	-0.178495	1.552233	-0.056559
H	-1.028623	2.105720	-0.480051
H	-0.149414	1.732080	1.026135
H	-0.346734	0.480055	-0.225154

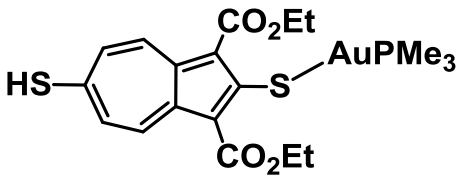
Table S33. Cartesian coordinates (Å) for the optimized structure of [Me_3PAu](1,3-diethoxycarbonyl-2-mercapto-6-azulenethiolate).



Atom	x	y	z
C	0.047406	0.055711	-0.123799
C	0.240323	1.511822	-0.501929
H	-0.739176	1.975951	-0.686743
H	0.845265	1.606404	-1.413255
H	0.738634	2.066478	0.304275
O	1.364243	-0.512268	0.113585
C	1.388332	-1.829619	0.483331
C	2.751492	-2.320640	0.706210
C	3.976119	-1.601156	0.572344
C	5.071714	-2.476388	0.892454
C	4.518773	-3.759512	1.229504
C	5.228450	-4.915967	1.605034
C	4.783976	-6.189838	1.944521
C	3.475309	-6.716745	2.020369
C	2.294211	-5.993612	1.743482
C	2.126415	-4.672889	1.351939
C	3.068650	-3.655056	1.111303
H	1.092471	-4.356097	1.199384
H	1.367800	-6.564039	1.854941
S	3.422556	-8.431419	2.507789
Au	1.194312	-9.100317	2.610805
P	-0.957317	-9.887106	2.775227
C	-2.252482	-8.591966	2.529849
H	-2.121499	-7.800206	3.278092
H	-2.140043	-8.146184	1.533631
H	-3.258160	-9.024181	2.625609
C	-1.402993	-11.204326	1.556122
H	-0.730779	-12.061543	1.685091
H	-2.443351	-11.529729	1.694389
H	-1.272774	-10.813926	0.539040
C	-1.378772	-10.636754	4.413187
H	-0.708003	-11.482372	4.607996
H	-1.229952	-9.888998	5.201925

H	-2.420950	-10.984375	4.426885
H	5.578524	-6.897751	2.195529
H	6.309873	-4.795235	1.634358
C	6.470742	-2.064233	0.859855
O	7.364560	-3.046467	1.193289
C	8.768498	-2.656895	1.168248
C	9.584293	-3.873364	1.559679
H	10.653131	-3.614814	1.551066
H	9.427526	-4.701753	0.855348
H	9.325746	-4.218257	2.569930
H	9.019161	-2.300268	0.159256
H	8.916075	-1.819073	1.864504
O	6.884503	-0.933288	0.564331
S	4.104400	0.082521	0.091303
H	5.486000	0.037287	0.195895
O	0.352276	-2.483210	0.603043
H	-0.446743	-0.517280	-0.922560
H	-0.556928	-0.057553	0.788071

Table S34. Cartesian coordinates (Å) for the optimized structure of [Me_3PAu](1,3-diethoxycarbonyl-6-mercapto-2-azulenethiolate).



Atom	x	y	z
C	-0.056394	0.203204	0.505974
O	1.044087	-0.633991	0.951630
C	2.264154	-0.363272	0.409890
C	3.309028	-1.255413	0.951044
C	3.555855	-1.590728	2.316662
C	4.549994	-2.623072	2.349138
C	4.960871	-2.889626	1.010473
C	5.929235	-3.820907	0.614443
C	6.404989	-4.137711	-0.658810
C	6.027680	-3.617332	-1.907539
S	6.829197	-4.225113	-3.396481
H	7.633082	-5.137026	-2.785585
C	5.058066	-2.627350	-2.166920
C	4.253051	-1.930213	-1.273522
C	4.181373	-2.007881	0.127062
H	3.588129	-1.190591	-1.726268
H	4.918085	-2.364209	-3.219427
H	7.183114	-4.905917	-0.672960
H	6.393387	-4.364674	1.439158
C	5.108150	-3.313240	3.521179

O	4.295396	-3.223536	4.612088
C	4.807333	-3.828838	5.831127
H	4.967331	-4.902513	5.653649
H	5.785260	-3.382540	6.064459
C	3.788418	-3.575161	6.925550
H	4.139905	-4.021505	7.866893
H	2.817740	-4.022284	6.673488
H	3.642193	-2.498963	7.083772
O	6.169011	-3.935508	3.545104
S	2.887660	-0.775975	3.736838
Au	2.817427	1.439896	3.008182
P	2.898156	3.596090	2.223146
C	1.266454	4.436227	1.977802
H	0.730477	4.482055	2.933896
H	1.406997	5.453428	1.586064
H	0.667243	3.853057	1.267889
C	3.854476	4.804251	3.249022
H	3.382618	4.898989	4.234746
H	4.875427	4.428814	3.389055
H	3.888526	5.788996	2.762492
C	3.693931	3.669498	0.558475
H	4.744452	3.367253	0.651069
H	3.192364	2.953462	-0.105945
H	3.637527	4.684912	0.141711
O	2.426206	0.468605	-0.481743
H	0.135082	1.234013	0.844264
H	-0.080690	0.209452	-0.593274
C	-1.328444	-0.360463	1.109384
H	-2.188251	0.251460	0.800451
H	-1.275878	-0.362738	2.205901
H	-1.499719	-1.390045	0.768640

Table S35. TDDFT-calculated optical transitions for the lower energy portion of the electronic excitation spectrum of **10**.

Calc. Transition (nm)	Calc. Transition w/ 35nm Offset (nm)	Oscillator Strength	Composition (%)	Experimental Transition (nm)
410	445	0.3756	70.6% HOMO→LUMO 9.7% HOMO→LUMO+3 5.2% HOMO-1→LUMO+1 4.9% HOMO-1→LUMO 4.1% HOMO-1→LUMO+2	445

			1.1% HOMO→LUMO+8	
		0.0031	56.8% HOMO→LUMO+1	
			37.1% HOMO→LUMO+2	
			2.8% HOMO-1→LUMO	
380	415	0.0224	41.6% HOMO→LUMO+3	425
			10.0% HOMO-1→LUMO	
			9.2% HOMO→LUMO+1	
			9.2% HOMO→LUMO+2	
			5.1% HOMO-1→LUMO+1	
			3.5% HOMO-1→LUMO+2	
			2.4% HOMO→LUMO	
			1.0% HOMO-2→LUMO	
		0.0435	43.5% HOMO→LUMO+3	
			24.7% HOMO-1→LUMO	
			18.7% HOMO→LUMO+2	
			4.5% HOMO→LUMO+1	
			1.5% HOMO→LUMO+4	
		0.0042	94.7% HOMO→LUMO+4	
			1.2% HOMO→LUMO+5	
			1.0% HOMO-1→LUMO	
		0.0015	96.7% HOMO→LUMO+5	
			1.5% HOMO→LUMO+4	
332	367	0.0312	56.5% HOMO-1→LUMO+1	365
			40.7% HOMO-1→LUMO+2	
		0.0034	64.8% HOMO→LUMO+6	
			22.9% HOMO→LUMO+7	
			3.6% HOMO→LUMO+9	
			2.3% HOMO-1→LUMO+3	
			1.3% HOMO-2→LUMO+1	
		0.0334	81.6% HOMO-1→LUMO+3	
			5.4% HOMO→LUMO+7	
			5.2% HOMO-1→LUMO+2	
			1.9% HOMO-1→LUMO	
			1.5% HOMO-1→LUMO+1	
			1.1% HOMO-1→LUMO+4	

D. FIGURES

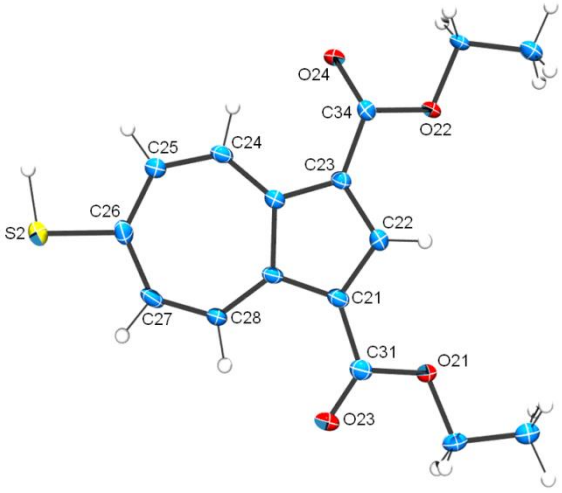


Figure S1. Thermal ellipsoid plot for one of two crystallographically independent molecules of **2b** in the asymmetric unit. See Figure 3 of the main manuscript for the thermal ellipsoid plot of the other molecule.

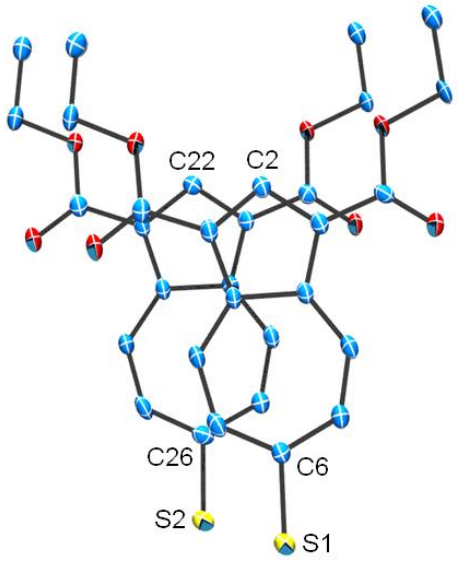


Figure S2. Thermal ellipsoid drawing of the asymmetric unit of **2b** that emphasizes π-stacking interaction (d = 3.67 Å) between the azulenic scaffolds of the two crystallographically independent molecules of **2b**. All hydrogen atoms are omitted for clarity.

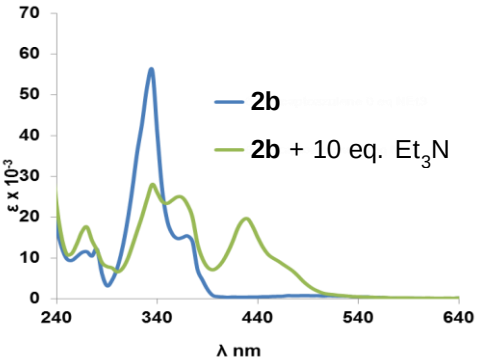


Figure S3. UV-vis spectra of **2b** before and after treatment with excess Et_3N in CH_2Cl_2.

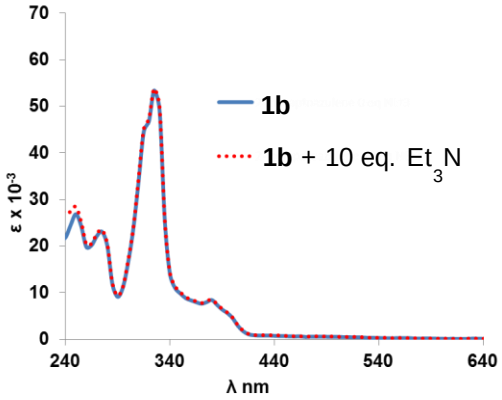


Figure S4. UV-vis spectra of **1b** before and after treatment with excess Et_3N in CH_2Cl_2.

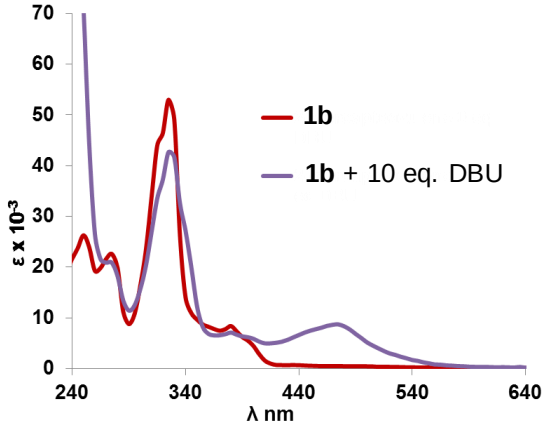


Figure S5. UV-vis spectra of **1b** before and after treatment with excess DBU (DBU = diazabicyclo[5.4.0]undec-7-ene) in CH_2Cl_2.

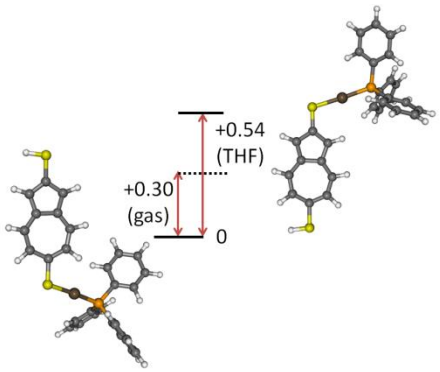


Figure S6. DFT-calculated energy differences (ΔE, in kcal/mol) between hypothetical isomeric complexes [Ph_3PAu](2-mercapto-6-azulenethiolate) and [Ph_3PAu](6-mercapto-2-azulenethiolate) in the gas phase and in THF.

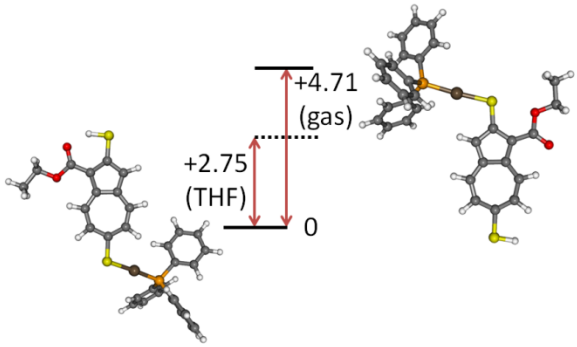


Figure S7. DFT-calculated energy differences (ΔE, in kcal/mol) between hypothetical isomeric complexes [Ph_3PAu](2-mercapto-1-ethoxycarbonyl-6-azulenethiolate) and [Ph_3PAu](6-mercapto-1-ethoxycarbonyl-2-azulenethiolate) in the gas phase and in THF.

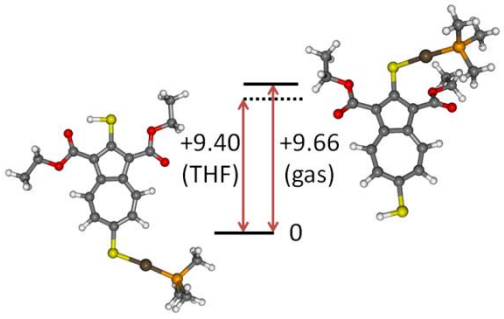


Figure S8. DFT-calculated energy differences (ΔE, in kcal/mol) between hypothetical isomeric complexes [Me_3PAu](2-mercapto-1,3-diethoxycarbonyl-6-azulenethiolate) and [Me_3PAu](6-mercapto-1,3-diethoxycarbonyl-2-azulenethiolate) in the gas phase and in THF.

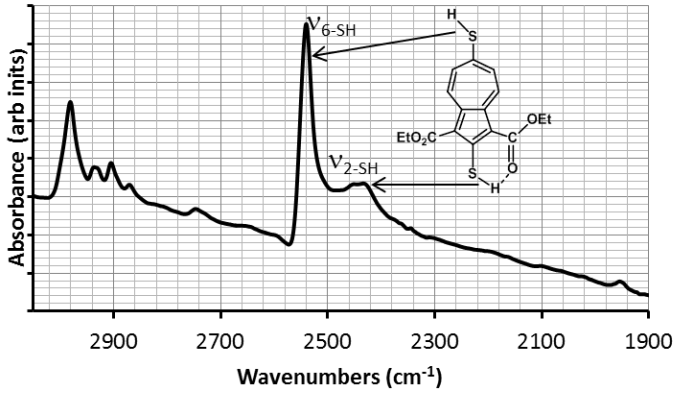


Figure S9. FTIR spectrum (KBr) of **9** in the ν(S-H) region.

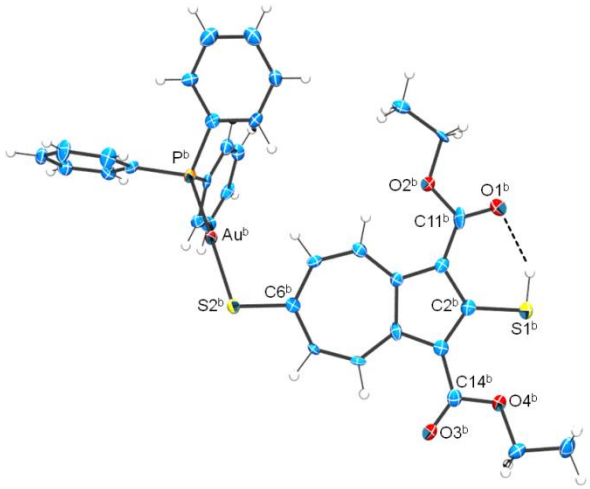


Figure S10. Thermal ellipsoid plot for one of two crystallographically independent molecules of **10** in the asymmetric unit. See Figure 7 of the main manuscript for the thermal ellipsoid plot of the other molecule.

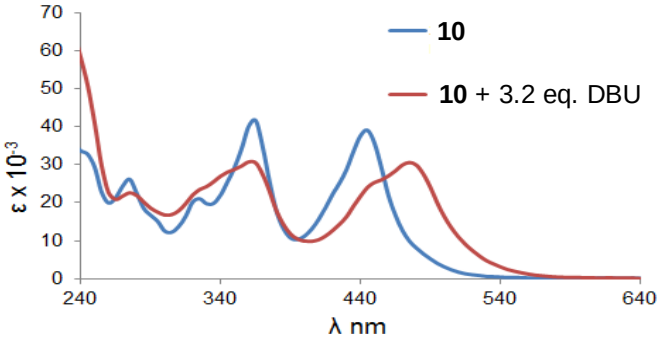


Figure S11. UV-vis spectra of **10** before and after treatment with excess DBU in CH_2Cl_2.

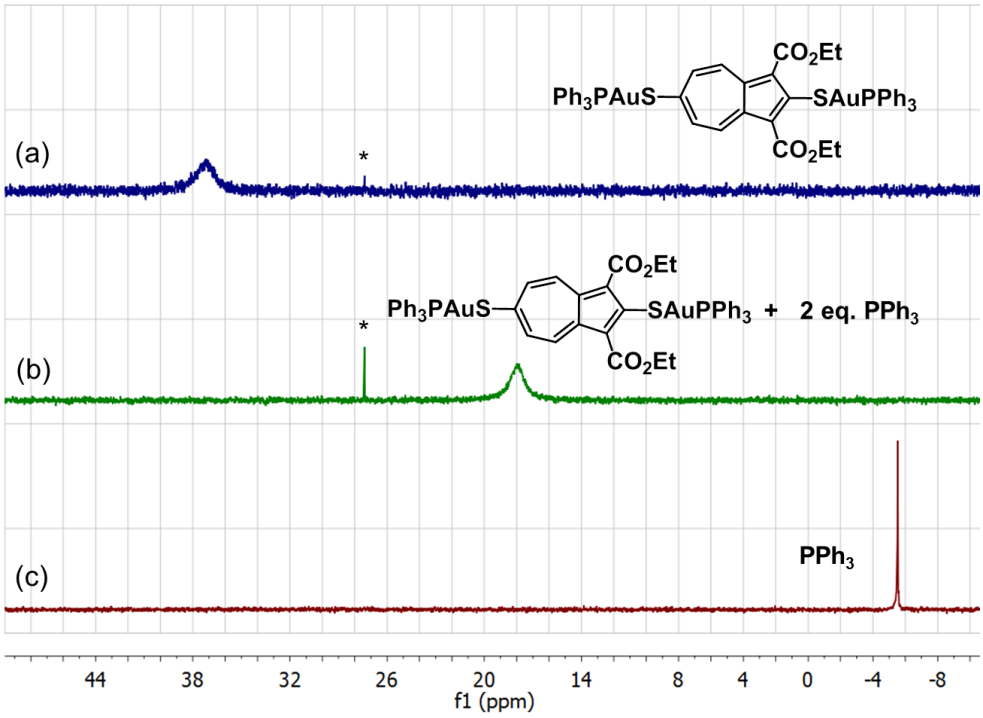


Figure S12. $^{31}P\{^{1}H\}$ NMR spectra (202 MHz, CD_2Cl_2, 22 °C, 85% aq. H_3PO_4 external reference) of (a) **11**, (b) **11** + 2 eq. PPh_3, and (c) PPh_3. Asterisks denote an $O{=}PPh_3$ impurity.

E. REFERENCES

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