A New Class of Chiral Organogermanes Derived from C₂-Symmetric Dithiols: Synthesis, Characterization and Stereoselective Free Radical Reactions

Giovanna Gualtieri, Steven J. Geib and Dennis P. Curran

Department of Chemistry, University of Pittsburgh, Pittsburgh, PA15260, USA

Supporting Information

Contains complete experimental and crystallographic details, and copies of the ¹H and ¹³C NMR spectra of all new compounds (89 pages).

Experimental Section

All reactions were performed under nitrogen or argon atmosphere in oven dried glassware. Tetrahydrofuran, benzene and toluene were distilled under Ar from sodium/benzophenone prior to use. Methylene chloride and triethylamine were distilled from calcium hydride under Ar. All other solvents and commercial reagents were purchased from Aldrich or other chemical suppliers and used without further purification.

HPLC analyses for the reduction of halides with **7a** and **7b** were carried out on a Rainin analytical HPLC instrument equipped with a Regis (*S,S*) Whelk-O 1 chiral column (25 cm × 4.6 mm I.D.) and a Hewlett Packard diode array detector both at 220 and 254 nm wavelengths, using hexane/isopropanol mixtures as eluent. Semi-preparative chiral HPLC purifications of **7a** and **7b** were conducted on a Waters 590 instrument equipped with a Regis (*S,S*) Whelk-O 1 chiral column (25 cm × 10.0 mm I.D.) and a Waters R401 differential refractometer, using hexane as eluent.

HPLC analyses of the hydrogermylation reactions with **7b** were performed on a Waters 600 instrument equipped with a Waters RCM 8x10 mm Novapak normal phase cartridge

column, and a Waters 440 UV detector at 254 nm wavelength, using ethyl acetate/hexane mixtures as eluent. Semi-preparative HPLC purifications were conducted on a Waters 590 instrument equipped with a Waters PrepLC 25 mm Novapak normal phase cartridge column and a Waters R401 differential refractometer, using ethyl acetate/hexane mixtures as eluent.

^1H NMR spectra were recorded on a Bruker AF-300 NMR spectrometer at 300 MHz or a Bruker AM-500 NMR, and are reported in parts per million (ppm) downfield from tetramethylsilane, using residual CHCl_3 (7.27 ppm), C_6H_6 (7.15 ppm) or CH_2Cl_2 (5.31 ppm) as internal standards. ^{13}C NMR spectra were recorded on a Bruker AF-300 NMR spectrometer at 75 MHz or a Bruker AM-500 NMR at 125 MHz, and are reported in ppm downfield from tetramethylsilane, using the middle resonance of CDCl_3 (77.23 ppm) or CD_2Cl_2 (54.00 ppm) as internal standard. ^{119}Sn NMR spectra were recorded on a Bruker AM-500 NMR at 186.5 MHz and are reported in ppm downfield from tetramethyltin.

$\text{BuSn}(\text{O}i\text{-Pr})_2\text{Cl}$,¹ 3-iodo-3-methoxymethyl chromanone (**13**)² and methyl 2-bromo-2-phenyl-3,3-butanoate (**15**)³ were prepared according to literature.

Single Crystal X-ray Diffraction Studies

X-ray crystal structures were determined for all compounds using a single crystal on a Siemens P3 diffractometer with graphite-monochromated $\text{MoK}\alpha$ ($\lambda = 0.71073$ Å) radiation. The parameters used during the collection of diffraction data are tabulated in Appendix B. Crystals were adhered to fine glass fibers with epoxy and placed in a cold N_2 stream (210 K) for data collection.

¹ Gaur, D. P.; Srivastava, G.; Mehrotra, R. C. *J. Organomet. Chem.* **1973**, 63, 221.

² Murakata, M.; Tsutsui, H.; Hoshino, O. *J. Chem. Soc., Chem. Commun.* **1995**, 481.

³ Schwarzkopf, K.; Blumenstein, M.; Hayen, A.; Metzger, J. O. *Eur. J. Org. Chem.* **1998**, 177.

For each structure, unit-cell dimensions were derived from the least-squares fit of the angular settings of 25 reflection with $21^\circ < 2\theta < 30^\circ$. Psi-scans were used to correct the data for absorption. No decay (<1%) occurred in three standard reflections during any data collection.

Each structure was solved via direct methods which located the positions of the non-hydrogen atoms. For **5b**, **6**, **7b** and **19a**, idealized atom positions were calculated for the remaining hydrogen atoms ($d(\text{C-H}) = 0.96\text{\AA}$, $U = 1.2U_{iso}$ of attached carbon). Hydrogen atom positions were located and refined for **2a**, **5a** and **20**. Each structure contains one molecule in the asymmetric unit with no crystallographically imposed symmetry, except for **20**, which has two crystallographically independent but chemically similar molecules per asymmetric unit.

Three structures (**5b**, **6** and **7b**) are isomorphous, crystallizing in Pbca; all three are characterized by weak diffraction.

Final difference Fourier syntheses showed only chemically insignificant electron density (largest difference peaks less than 1.0 $\text{\AA}$ from Ge). An inspection of F_o vs. F_c values and trends based upon $\sin \theta$, Miller index, or parity group failed to reveal any systematic error in the data. All computer programs used in the data collection and refinements are contained in the Siemens program packages P3 and SHELXTL (version 5.10).

General procedures for the preparation of stannanes 2a-d and germanes 5a,b. **Procedure A.** Triethylamine (2 equiv) was added to a 0.15 M stirred solution of the appropriate dithiol (**1a** or **1b**) (1 equiv) and the appropriate dialkyltin dichloride, monoalkyltin trichloride or germanium chloride (1.1 equiv) in THF at 0 °C. After addition was complete, the reaction mixture was stirred for 0.5-2 h at room temperature, then diluted with diethyl ether and filtered. The solvent was removed under reduce pressure to yield crude product. **Procedure B.** 1,1'-Dinaphthalene-2,2'-dithiol (**1a**) (1 mmol) and $\text{Bu}_2\text{Sn}(\text{OMe})_2$ or $\text{BuSn}(\text{O}i\text{-Pr})_2\text{Cl}$ (1.1 mmol) were dissolved in toluene (35 mL) at room temperature. The resulting mixture was heated at 130 °C and the

solvent distilled off over a period of ca. 1 h. A few mL of methanol were added and the solvent removed under reduced pressure to afford the crude product.

4-Butyl-4-chloro-3,5-dithia-4-stanna-cyclohepta[2,1-a;3,4-a']dinaphthalene (2a). Obtained in 91% by procedure B as an off white solid. Alternatively, obtained in quantitative yield by procedure A. A small portion was recrystallized from CHCl₃ to give colorless crystals; mp 145-147 °C. ¹H NMR (300 MHz, CDCl₃) (C₂-symmetric pattern) δ 0.91, (t, 3H, *J* = 7.3 Hz), 1.34 (m, 2H), 1.76 (m, 2H), 1.99 [t, 2H, *J* = 7.5 Hz, ²*J* (^{117/119}Sn, ¹H) = 60.2 Hz], 6.94 (d, 2H, *J* = 8.3 Hz), 7.25 (t, 2H, *J* = 7.5 Hz), 7.48 (t, 2H, *J* = 7.5 Hz), 7.83 (d, 2H, *J* = 8.4 Hz), 7.93 (m, 4H); (non-C₂-symmetric pattern) δ 0.91, (t, 3H, *J* = 7.3 Hz), 1.34 (m, 2H), 1.76 (m, 2H), 2.00 (t, 2H, *J* = 7.4 Hz), 6.91 (d, 2H, *J* = 8.4 Hz), 6.98 (d, 2H, *J* = 8.4 Hz), 7.24 (t, 1H, *J* = 7.2 Hz), 7.27 (t, 1H, *J* = 7.3 Hz), 7.46 (t, 1H, *J* = 7.2 Hz), 7.48 (t, 1H, *J* = 7.3 Hz), 7.78 (d, 1H, *J* = 8.6 Hz), 7.85 (d, 1H, *J* = 8.6 Hz), 7.90-7.96 (m, 4H). ¹³C NMR (75 MHz, CDCl₃) δ 13.63, 26.35 [¹*J* (^{117/119}Sn, ¹³C) = 84.0 Hz], 27.67 [²*J* (^{117/119}Sn, ¹³C) = 39.8 Hz], 29.71, 126.69, 127.02, 128.28, 128.82, 132.91, 133.07, 133.36, 142.41 (only 8 aromatic signals observed out of 20 expected). ¹¹⁹Sn NMR (186.5 MHz, CDCl₃) δ 158.6. IR (film, NaCl plates, cm⁻¹) 3053, 2957, 2924, 2870, 2853, 1581, 1502, 1313. LRMS *m/z* (rel inten) 528 (M⁺, 6), 435 (4), 316 (8), 284 (100), 84 (19). HRMS calcd for C₂₄H₂₁ClS₂¹²⁰Sn 527.9795, found 527.9787.

4-Phenyl-4-chloro-3,5-dithia-4-stanna-cyclohepta[2,1-a;3,4-a']dinaphthalene (2b). Obtained in quantitative yield by procedure A as white foamy solid. A small portion was recrystallized from CHCl₃; mp 218.5-220 °C. ¹H NMR (300 MHz, CDCl₃) (C₂-symmetric pattern) δ 6.97 (d, 2H, *J* = 8.5 Hz), 7.27 (m, 3H), 7.45-7.52 (m, 6H), 7.86 (d, 2H, *J* = 8.5 Hz), 7.93-7.97 (m, 4H); (non-C₂-symmetric pattern) δ 6.94 (d, 1H, *J* = 8.5 Hz), 7.00 (d, 1H, *J* = 8.5 Hz), 7.27 (m, 3H), 7.43-7.51 (m, 6H), 7.78 (d, 1H, *J* = 8.6 Hz), 7.89-8.01 (m, 5H). ¹³C NMR (75 MHz, CDCl₃) δ 126.74, 126.85, 126.98, 127.04, 127.28, 127.63, 128.02, 128.28, 128.41, 129.05, 129.11, 129.83, 131.81, 132.87, 132.96, 133.10, 133.29, 133.49, 134.92, 139.92, 142.12, 143.03 (22 aromatic signals observed out of 24 expected). ¹¹⁹Sn NMR (186.5 MHz, CDCl₃) δ 80.90. IR

(film, NaCl plates, cm^{-1}) 3052, 1503, 1431, 1314, 1261. LRMS m/z (rel inten) 548 (M^+ , 5), 316 (24), 284 (100). HRMS calcd for $\text{C}_{26}\text{H}_{17}\text{ClS}_2^{120}\text{Sn}$ 547.9482, found 547.9458.

4,4-Dibutyl-3,5-dithia-4-stanna-cyclohepta[2,1-a;3,4-a']dinaphthalene (2c). White amorphous solid (68% yield) obtained by procedure B, after purification by filtration through a short silica gel column ($\text{CH}_2\text{Cl}_2/\text{Hex}$ 1:1). ^1H NMR (300 MHz, CDCl_3) δ 0.91 (t, 6H, $J = 7.2$ Hz), 1.31 (m, 4H), 1.46 (m, 4H), 1.60 (m, 4H), 6.97 (d, 2H, $J = 8.4$ Hz), 7.23 (t, 2H, $J = 7.7$ Hz), 7.44 (t, 2H, $J = 7.5$ Hz), 7.84-7.94 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 13.70, 20.85 [$^1J(^{117}\text{Sn}, ^{13}\text{C}) = 317.6$ Hz, $^1J(^{119}\text{Sn}, ^{13}\text{C}) = 333.3$ Hz], 26.83 [$^2J(^{117/119}\text{Sn}, ^{13}\text{C}) = 67.6$ Hz], 28.26, 125.92, 126.43, 126.59, 128.06, 130.65, 132.94, 133.14, 133.31, 142.25 (9 aromatic signals observed out of 10 expected). IR (film, NaCl plates, cm^{-1}) 3051, 2955, 2921, 2869, 2851, 1582, 1502, 1462. LRMS m/z (rel inten) 550 (M^+ , 2) 493 (10), 316 (28), 297 (15), 282 (100), 141 (13). HRMS calcd for $\text{C}_{28}\text{H}_{30}\text{S}_2^{120}\text{Sn}$ 550.0811, found 550.0815.

4,4-Diphenyl-3,5-dithia-4-stanna-cyclohepta[2,1-a;3,4-a']dinaphthalene (2d). Obtained in 87% yield by procedure A, after recrystallization from CHCl_3 ; mp 268-270 $^\circ\text{C}$. ^1H NMR (300 MHz, CDCl_3) δ 6.98 (d, 2H, $J = 8.5$ Hz), 7.24 (m, 2H), 7.37-7.48 (m, 12H), 7.75 (d, 2H, $J = 8.5$ Hz), 7.84 (d, 2H, $J = 8.6$ Hz), 7.93 (d, 2H, $J = 8.2$ Hz). ^{13}C NMR (75 MHz, CDCl_3) δ 126.24, 126.63, 126.76, 128.21, 128.37, 129.28, 129.61, 130.67, 133.24, 133.58, 136.16, 138.63, 142.61 (13 aromatic signals observed out of 14 expected). ^{119}Sn NMR (186.5 MHz, CDCl_3) δ 70.96. IR (film, NaCl plates, cm^{-1}) 3063, 3051, 3020, 2987, 1582, 1501, 1429, 1314, 1071. LRMS m/z (rel inten) 590 (M^+ , 7), 513 (3), 316 (2), 284 (100), 229 (4), 197 (3), 141 (2). HRMS calcd for $\text{C}_{32}\text{H}_{22}\text{S}_2^{120}\text{Sn}$ 590.0185, found 590.0206.

4-Butyl-4-iodo-3,5-dithia-4-stanna-cyclohepta[2,1-a;3,4-a']dinaphthalene (4a). Toluene (2 mL) was added to a solution of sodium iodide (100 mg, 0.66 mmol) in acetone (1 mL) and the resulting mixture concentrated to dryness. Then, **2a** (106 mg, 0.2 mmol) was added followed by 1.3 mL acetone. The reaction mixture was refluxed for 1.5 h, then diluted with water and extracted with CH_2Cl_2 (3×20 mL). The organic phase was dried over MgSO_4 , filtered and

concentrated to afford 116 mg (94%) of **3** as a yellowish foamy solid, ^1H NMR (300 MHz, CDCl_3) δ 0.90 (t, 3H, $J = 7.3$ Hz), 1.35 (m, 2H), 1.69 (m, 2H), 2.03 (t, 2H, $J = 7.8$ Hz), 6.91 (d, 1H, $J = 8.5$ Hz), 6.97 (d, 1H, $J = 8.5$ Hz), 7.24 (m, 2H), 7.47 (t, 1H, $J = 6.9$ Hz), 7.48 (t, 1H, $J = 6.3$), 7.76-7.95 (m, 6H). ^{13}C NMR DEPT 135 (75 MHz, CDCl_3) δ 13.67(+), 25.91(-), 28.55(-), 29.84(-), 126.63(+), 126.70(+), 126.95(+), 128.27(+), 128.84(+), 131.58(+). ^{119}Sn NMR (186.5 MHz, CDCl_3) δ 35.0. IR (film, NaCl plates, cm^{-1}) 3052, 2957, 2923, 2870, 2852, 1581, 1502, 1314, 1263. LRMS m/z (rel inten) 620 (M^+ , 9), 563 (2), 493 (6), 435 (4), 316 (5), 284 (100). HRMS calcd for $\text{C}_{24}\text{H}_{21}\text{IS}_2^{120}\text{Sn}$ 619.9151, found 619.9131.

4-tert-Butyl-4-chloro-3,5-dithia-4-germa-cyclohepta[2,1-a;3,4-a']dinaphthalene (5a).

Obtained in quantitative yield by procedure A as a white foamy solid. The crude product is shown to be pure by ^1H NMR analysis, but it can also be recrystallized from CHCl_3 to give 95% yield of colorless crystals; mp (racemic) 188.5-190.5 °C. $[\alpha]_{\text{D}}^{23} (R) = +136.8$ ($c = 1$, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 1.25 (s, 9H), 6.92 (d, 1H, $J = 8.5$ Hz), 7.00 (d, 1H, $J = 8.5$ Hz), 7.22 (t, 1H, $J = 7.8$), 7.25 (t, 1H, $J = 8.0$ Hz), 7.47 (t, 1H, $J = 7.2$ Hz), 7.48 (t, 1H, $J = 7.7$), 7.80 (t, 1H, $J = 8.3$ Hz), 7.87 (d, 1H, $J = 4.6$), 7.94 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3) δ 26.83, 40.89, 126.59, 126.81, 127.01, 128.05, 128.21, 128.40, 128.66, 128.83, 129.67, 132.78, 132.97, 133.04, 133.19, 133.40, 133.48, 141.96 142.30 (17 aromatic signals observed out of 20 expected). IR (film, NaCl plates, cm^{-1}) 3053, 2947, 2930, 2889, 2859, 1503, 1456, 1367, 1315, 1173. LRMS m/z (rel inten) 482 (M^+ , 8), 284 (100), 130 (14), 115 (5), 100 (10), 84 (21), 74 (8), 57 (95). HRMS calcd for $\text{C}_{24}\text{H}_{21}\text{Cl}^{74}\text{GeS}_2$ 481.9985, found 481.9962.

4-tert-Butyl-4-chloro-2,6-bis-trimethylsilyl-3,5-dithia-4-germa-cyclohepta[2,1-a;3,4-

a']dinaphthalene (5b). Obtained in 97% yield after recrystallization from hexanes by procedure A; mp (racemic) 208-209.5 °C; mp [(*S*), hexanes] 252-253 °C. $[\alpha]_{\text{D}}^{23} (S) = +30.3$ ($c = 1$, THF). ^1H NMR (300 MHz, CDCl_3) δ 0.56 (s, 9H), 0.57 (s, 9H), 1.17 (s, 9H), 6.53 (d, 1H, $J = 8.4$ Hz), 6.67 (d, 1H, $J = 8.5$ Hz), 7.15 (dt, 1H, $J = 8.1$, 0.9 Hz), 7.19 (dt, 1H, $J = 8.1$, 0.9 Hz), 7.41 (dt, 1H, $J = 7.5$, 0.8 Hz), 7.43 (dt, 1H, $J = 7.6$, 0.8 Hz), 7.88 (d, 1H, $J = 7.0$ Hz), 7.91 (d, 1H, $J = 7.2$

Hz), 8.08 (s, 1H), 8.15 (s, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 1.25, 1.40, 26.45, 41.09, 125.78, 126.08, 126.41, 126.60, 127.22, 127.43, 128.24, 128.47, 132.49, 132.66, 133.55, 133.74, 134.47, 136.28, 136.32, 141.35, 142.25, 142.37, 142.47 (19 aromatic signals observed out of 20 expected). IR (film, NaCl plates, cm^{-1}) 3056, 2948, 2893, 2859, 1556, 1487, 1457, 1366, 1247, 1172, 1121. LRMS m/z (rel inten) 626 (M^+ , 21), 462 (37), 428 (100), 341 (33), 325 (18), 137 (21), 95 (24), 81 (60), 69 (96). HRMS calcd for $\text{C}_{30}\text{H}_{37}\text{Cl}^{70}\text{GeS}_2\text{Si}_2$ 622.0806, found 622.0832.

4-tert-Butyl-2,6-bis-trimethylsilyl-3,5-dithia-4-germa-cyclohepta[2,1-a;3,4-a']dinaphthalen-4-ol (6). A solution of **5b** (100 mg, 0.16 mmol) in diethyl ether (10 mL) was mixed with an aqueous solution of NH_4OH (10 mL) and stirred for 30 min at room temperature. The organic layer was separated and dried over MgSO_4 , filtered and concentrated. The residue was recrystallized from hexanes to afford quantitative yield of **6** as a white solid, mp 201-203 °C [(*S*), hexanes]. ^1H NMR (300 MHz, CDCl_3) δ 0.56 (s, 9H), 0.57 (s, 9H), 1.23 (s, 9H), 6.60 (d, 1H, J = 8.4 Hz), 6.66 (d, 1H, J = 8.4 Hz), 7.17 (d, 1H, J = 7.4 Hz), 7.19 (d, 1H, J = 7.8 Hz), 7.41 (d, 1H, J = 7.9 Hz), 7.43 (d, 1H, J = 7.1 Hz), 7.89 (d, 1H, J = 7.1 Hz), 7.91 (d, 1H, J = 7.3 Hz), 8.08 (s, 1H), 8.14 (s, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 1.01, 1.40, 26.68, 36.52, 125.91, 126.04, 126.26, 126.39, 127.25, 127.34, 128.23, 128.36, 132.28, 132.52, 133.04, 133.61, 133.75, 135.26, 136.01, 136.22, 141.57, 141.83, 142.67, 142.71. IR (film, NaCl plates, cm^{-1}) 3624, 3406, 3058, 2959, 2892, 2861, 1247. LRMS m/z (rel inten) 608 (M^+ , 15), 535 (7), 428 (100), 325 (8). HRMS calcd for $\text{C}_{30}\text{H}_{38}^{74}\text{GeOS}_2\text{Si}_2$ 608.1114, found 608.1112.

4-tert-Butyl-3,5-dithia-4-germa-cyclohepta[2,1-a;3,4-a']dinaphthalene (7a). A solution of **5a** (150 mg, 0.31 mmol) in 8 mL THF was added to a stirred suspension of NaBH_4 in 2 mL THF at 0 °C. After addition was complete the ice bath was removed and the mixture stirred at room temperature for 1 h 40 min. The reaction mixture was poured into a saturated NaCl solution (20 mL) and extracted with diethyl ether (3 $\times$ 30 mL). The combined organic extracts were washed with an aqueous solution of Na_2CO_3 (pH 11.5-12, 3 $\times$ 20 mL), dried over MgSO_4 and concentrated under reduced pressure to afford 142 mg (quant.) of **7a** as a white foamy solid. The

purity of the crude product was estimated to be $\geq 90\%$ by ^1H NMR analysis. When higher purity was needed, the product was purified by short column chromatography (diethyl ether/hexanes 1:99) followed by washings with an aqueous solution of Na_2CO_3 solution. An analytically pure sample was obtained by chiral preparative HPLC eluting with hexanes; $[\alpha]_{\text{D}}^{23} (R) = -116.6$ ($c = 1.75$, benzene); mp (R) ≈ 100 °C; ^1H NMR (300 MHz, C_6D_6) δ 0.94 (s, 9H), 6.00 (s, 1H), 6.84 (t, 1H, $J = 6.8$ Hz), 6.84 (t, 1H, $J = 6.2$ Hz), 7.10 (m, 4H), 7.58 (m, 4H), 7.79 (d, 1H, $J = 8.6$ Hz), 7.90 (d, 1H, $J = 8.6$ Hz). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 27.76, 32.85, 126.70, 126.87, 126.97, 127.04, 128.68, 129.17, 129.40, 130.48, 133.20, 133.31, 133.52, 133.60, 133.75, 133.91, 142.23, 142.55 (16 aromatic signals observed out of 20 expected). IR (film, NaCl plates, cm^{-1}) 3049, 3002, 2951, 2925, 2887, 2856, 2022 (vs, Ge–H), 1502, 1466, 1458, 1263. LRMS m/z (rel inten) 448 (M^+ , 11), 391 (19), 284 (100), 252 (10), 57 (12). HRMS calcd for $\text{C}_{24}\text{H}_{22}^{74}\text{GeS}_2$ 448.0375, found 448.0375.

4-tert-Butyl-2,6-bis-trimethylsilyl-3,5-dithia-4-germa-cyclohepta[2,1-a;3,4-a']dinaphthalene (7b). LiBH_4 (2.0 M soln in THF, 6.2 mL, 12.4 mmol) was added to a stirred solution of **5b** (388 mg, 0.62 mmol) in THF (20 mL) at 0 °C. The reaction mixture was then kept at -8 °C without stirring for 5 days, after which TLC analysis showed complete consumption of starting material. The reaction mixture was diluted with diethyl ether and poured into 100 mL of cold dilute NH_4Cl aqueous solution with stirring. The organic layer was separated and the aqueous layer extracted with diethyl ether (2×30 mL). The combined organic extracts were dried over MgSO_4 , filtered and concentrated. After purification, 285 mg (78%) of **7b** were obtained as white crystals. The crude product was generally purified either by recrystallization from hexanes (for racemic samples) or by semi-preparative chiral HPLC (for enantiomerically pure samples). $[\alpha]_{\text{D}}^{23} (S) = +134.7$ ($c = 1$, THF); $[\alpha]_{\text{D}}^{23} (R) = -137.5$ ($c = 1$, THF); mp (racemic) 193-203 °C (dec.). ^1H NMR (300 MHz, C_6D_6) δ 0.63 (s, 9H), 0.65 (s, 9H), 0.95 (s, 9H), 5.95 (s, 1H), 6.84 (m, 2H), 7.06 (d, 1H, $J = 9.0$ Hz), 7.12 (m, 1H), 7.65 (br d, 2H, $J = 8.1$ Hz), 8.16 (s, 1H), 8.20 (s, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 1.05, 1.68, 27.48, 33.37, 125.96, 126.33, 126.51, 126.58, 127.41,

127.44, 128.73, 128.81, 132.77, 133.05, 133.92, 134.06, 134.71, 135.01, 136.43, 136.88, 142.28, 142.43, 142.56, 142.90. IR (film, NaCl plates, cm^{-1}) 3047, 2951, 2927, 2891, 2856, 2027 (s, Ge-H), 1263, 1246. LRMS m/z (rel inten) 592 (M^+ , 18), 535 (30), 519 (17), 325 (13), 73 (100). HRMS calcd for $\text{C}_{30}\text{H}_{38}^{74}\text{GeS}_2\text{Si}_2$ 592.1165, found 592.1180.

7-Bromo-1,1-diphenyl-1-heptene (9). A solution of diethyl benzhydrylphosphonate⁴ (1.1 g, 3.6 mmol) in THF (5 mL) was added dropwise to *n*-BuLi (1.6 M soln in hexanes, 2.25 mL, 3.6 mmol) at 0 °C. After addition was complete, the ice bath was removed and the mixture stirred at room temperature for 1 h. A solution of 6-bromohexanal⁵ (646 mg, 3.6 mmol) in THF (3 mL) was added dropwise and the resulting mixture stirred for 20 h. The reaction was quenched with saturated aqueous NH_4Cl solution and extracted with diethyl ether. The organic phase was dried over MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (hexanes) to afford 479 mg (41%) of **9** as a colorless oil. ^1H NMR (300 MHz, CDCl_3) δ 1.48 (m, 4H), 1.84 (m, 2H), 2.16 (m, 2H), 3.40 (t, 2H, $J = 6.8$ Hz), 6.11 (t, 1H, $J = 7.5$ Hz), 7.15-7.45 (m, 10H). ^{13}C NMR (75 MHz, CDCl_3) δ 27.93, 29.22, 29.65, 32.74, 34.05, 127.03, 127.09, 127.38, 128.27, 128.35, 129.75, 130.07, 140.35, 142.03, 142.89. IR (film, NaCl plates, cm^{-1}) 3079, 3055, 3022, 2929, 2854, 1598, 1494, 1443, 1073, 1030. LRMS m/z (rel inten) 330 ($\text{M}^+ + 2$, 34), 328 (M^+ , 34), 249 (29), 193 (92), 178 (53), 165 (63), 115 (100), 91 (88). HRMS calcd for $\text{C}_{19}\text{H}_{21}\text{Br}$ 328.0827, found 328.0825.

General procedure for determination of the kinetic constant for hydrogen transfer from 7a and 7b.

In a sealed tube purged with Ar were placed **9** (1 equiv), AIBN (10-25 mol%) and the appropriate germanium hydride (1.8-3 equiv) dissolved in benzene- d_6 (0.5-2.0 mL). The mixture was immersed in an oil bath at the appropriate temperature and stirred for 4-11 h. After cooling to room temperature, the reaction was diluted with diethyl ether, filtered and

⁴ Newcomb, M. *Tetrahedron*, **1993**, 49, 1151.

⁵ Hon, Y.-S.; Chang, F.-J.; Lu, L.; Lin, W.-C. *Tetrahedron* **1998**, 54, 5233.

concentrated. Benzyl ether (for reactions with **7a**) or *p*-dimethoxybenzene (for reactions with **7b**) was added as an internal standard and the crude reaction mixture was analyzed by ^1H NMR spectroscopy (CDCl_3) to obtain the yield and ratio of 1,1-diphenyl-1-heptene (**12**) (reduced) to (diphenylmethyl)cyclohexane (**11**) (cyclized) (see Scheme 4 and Table 1). The combined yields of **12** and **11** calculated by NMR ranged between 84 and 105% for different runs. Compounds **12** and **11** were identified by comparison to their ^1H NMR and GC/MS spectra. No traces of residual starting material were found. (Diphenylmethylene)cyclohexane was not detected by GC/MS analysis.

The kinetic constants for **7a** and **7b** were derived from the following equations:

$$\begin{aligned}\log k_{\text{c(T)}} (\text{s}^{-1}) &= 9.7 - 5.4/2.3RT \\ k_{\text{H(T)}} &= k_{\text{c(T)}} \mathbf{11/12} [\text{Y-H}]_{\text{m}}^{-1} \\ \text{where } [\text{Y-H}]_{\text{m}} &= (2[\text{hydride}] - [\mathbf{9}])/2\end{aligned}$$

*General procedure for the reduction of **13** with (R)-**7a** and **7b**.*

A solution of (R)-**7a** or (R)-**7b** (1.5-2 equiv) and **13** (1 equiv) (0.05 M) in toluene (0.05 M) was cooled to $-78\text{ }^\circ\text{C}$. Then, either AIBN (20 mol%), or Et_3B (1.0 M soln in hexanes, 20 mol%) was added as initiator. For the reaction in entry 4, Table 2, 5 mL of oxygen were introduced in the reaction mixture via syringe after addition of Et_3B . The reaction progress was monitored by TLC analysis, and additional Et_3B was added periodically if needed until consumption of starting material was complete. The crude reaction mixture was concentrated and *p*-dimethoxybenzene was added as internal standard for yield determination by ^1H NMR. In some cases, isolated yields were calculated instead. The crude product was subjected to column chromatography (ethyl acetate/hexanes 2:98) to afford **14** in variable ees (see Table 2). Enantiomeric excesses were calculated by HPLC using isopropanol/hexanes 5:95 as eluent and a flow rate of 1 mL/min; (t_{R} of (R)-(-)-**14** = 15.7 min, t_{R} of (S)-(+)-**14** = 17.1 min).

*General procedure for the reduction of **15** with (R)-**7a**.*

A solution of (*R*)-**7a** (63 mg, 0.14 mmol) in toluene (1 mL) was added to **15** (20 mg, 0.07 mmol) at -78°C . Then, either AIBN (3 mg, 0.02 mmol), or Et_3B (1.0 M soln in hexanes, 35 μL , 0.035 mmol, 0.5 equiv) was added and the resulting mixture was stirred at the appropriate temperature. The reaction progress was monitored by TLC analysis (benzene/hexanes 3:7), and additional Et_3B was added periodically until the starting material had reacted completely. The crude reaction mixture was concentrated and *p*-dimethoxybenzene was added as an internal standard to determine the yield of **16** by ^1H NMR. After removal of the solvent, the residue was treated with LiAlH_4 (1.0 M soln in THF, 0.5 mL) in 1 mL THF at room temperature for 2 h. The reaction mixture was quenched with an aqueous solution of sodium potassium tartrate and extracted with diethyl ether (3×15 mL). The organic phase was back-extracted with an aqueous solution of Na_2CO_3 (3×15 mL). After drying over MgSO_4 and concentrating, the residue was passed through a silica gel plug eluting first with diethyl ether/hexanes 2:98 and then with pure diethyl ether, to afford alcohol **17** in variable ees (see Table 2). Enantiomeric excesses were calculated by HPLC using isopropanol/hexanes 1:99 as eluent and a flow rate of 3 mL/min; (t_{R} of (*S*)-(-)-**17** = 7.8 min, t_{R} of (*R*)-(+)-**17** = 12.8 min).

General procedure for the reduction of 15 with (R)- and (S)-7b.

Et_3B (1.0 M soln in hexanes, 12 μL , 0.012 mmol) was added to a solution of **7b** (75 mg, 0.18 mmol) and **15** (23 mg, 0.08 mmol) in toluene (1.6 mL) at the appropriate temperature. The reaction progress was monitored by TLC analysis, and additional Et_3B (12 μL) was added periodically until the starting material had reacted completely (with the exception of entry 9, Table 2). The crude reaction mixture was concentrated and *p*-dimethoxybenzene was added as an internal standard to determine the yield of **16** by ^1H NMR. and subjected to two successive chromatographic separations (using either hexanes, diethyl ether/hexanes 2:98 or benzene/hexanes 20:80 as eluent) to afford the reduced product **16** in variable ees (Table 2). Enantiomeric excesses were calculated by chiral HPLC using isopropanol 0.04% in hexane as eluent and a flow rate of 1 mL/min (t_{R} of (*R*)-(+)-**16** = 8.5 min, t_{R} of (*S*)-(-)-**16** = 10.7 min).

General procedure for hydrogermylation of methyl methacrylate with 7a and 7b. In a sealed tube purged with argon were placed methyl methacrylate (1.2 equiv, 23 μ L, 0.22 mmol), AIBN (3 mg, 0.02 mmol) and the germanium hydride (**7a**) (81 mg, 0.18 mmol) dissolved in toluene (benzene for reactions at room temperature, 1 mL). The mixture was irradiated with a 450 W medium pressure mercury lamp and stirred at the appropriate temperature until TLC analysis showed product formation and complete conversion of the germanium hydride.

In the reactions with Et₃B, 1.5-2 equiv of methyl methacrylate were used, and triethylborane (1.0 M soln in hexanes, 25 mol%) was added to a solution of the reactants at the appropriate reaction temperature and the resulting mixture was stirred until TLC analysis showed product formation and complete conversion of the germanium hydride. Additional triethylborane (25 mol%) was added periodically if needed.

After completion, the crude mixture was concentrated under reduced pressure and analyzed by HPLC. Then, it was subjected to column chromatography (ethyl acetate/hexanes 2:98) or preparative HPLC to afford the adducts **18a/19a** and **18b/19b** in variable yields and diastereoisomeric ratios (see Table 3).

Methyl 3-(4-tert-butyl-3,5-dithia-4-germa-cyclohepta[2,1-a;3,4-a']dinaphthalen-4-yl)-2-methyl-propionate (18a/19a). Isolation of the pure minor (faster eluting) isomer was achieved after three column chromatographic purifications of the crude mixture (first and second column eluting with hexanes, third column eluting with diethyl ether 2.5% in hexanes) of a sample of combined major/minor mixtures from all reactions run with racemic **7a**. [(*R,S*) minor, faster eluting]: colorless solid, mp 128-129.5 °C (racemic, hexanes). ¹H NMR (300 MHz, C₆D₆) δ 1.01 (d, 3H, *J* = 7.1 Hz), 1.11 (s, 9H), 1.32 (dd, 1H, *J* = 13.6, 4.7 Hz), 1.84 (dd, 1H, *J* = 13.6, 9.9 Hz), 2.30 (ddq, 1H, *J* = 9.9, 4.7, 7.1 Hz), 3.11 (s, 3H), 6.83 (m, 2H), 7.07 (m, 4H), 7.58 (m, 3H), 7.64 (d, 1H, *J* = 8.8 Hz), 7.85 (d, 1H, *J* = 8.2 Hz), 7.88 (d, 1H, *J* = 8.3 Hz). ¹³C NMR (75 MHz, CDCl₃) δ 21.08, 23.68, 27.85, 33.56, 35.89, 51.92, 126.07, 126.13, 126.56, 126.64, 126.76, 126.82, 127.97, 128.15, 128.26, 129.93, 130.78, 133.07, 133.10, 133.21, 133.24, 133.68, 141.87, 142.20, 177.01 (18 aromatic signals observed out of 20 expected). IR (film, NaCl plates, cm⁻¹)

3052, 2948, 2926, 2888, 2855, 1732 (vs, C=O), 1458, 1212. LRMS m/z (rel inten) 491 ($M^+ - C_4H_9$, 100), 421 (9), 389 (10), 316 (15), 282 (85), 141 (12). HRMS calcd for $C_{25}H_{21}^{74}GeO_2S_2$ ($M^+ - C_4H_9$) 491.0195, found 491.0196. [(*R,R*) major, slower eluting]: 1H NMR of a mixture of major/minor 3.5:1 (300 MHz, C_6D_6) δ 0.96 (d, 3H, $J = 7.0$ Hz), 1.04 (s, 9H), 1.22 (dd, 1H, $J = 13.7, 7.5$ Hz), 1.86 (dd, 1H, $J = 13.7, 6.7$ Hz), 2.75 (m, 1H), 3.34 (s, 3H), 6.81 (m, 2H), 7.07 (m, 4H), 7.61 (m, 4H), 7.86 (d, 2H, $J = 8.6$ Hz), 7.95 (d, 2H, $J = 8.4$ Hz). ^{13}C NMR of a mixture of major/minor 3.5:1 (75 MHz, $CDCl_3$): (major only) δ 20.45, 23.50, 27.79, 33.65, 36.14, 52.02, 177.05; (overlapping major/minor aromatic signals) δ 126.07, 126.13, 126.54, 126.61, 126.70, 127.62, 127.92, 128.09, 128.21, 128.30, 129.76, 129.88, 130.47, 133.73, 133.02, 133.10, 133.15, 133.19, 133.60, 141.85, 142.15.

Methyl 3-(4-*tert*-butyl-2,6-bis-trimethylsilyl-3,5-dithia-4-germa-cyclohepta[2,1-*a*;3,4-*a'*]dinaphthalen-4-yl)-2-methyl-propionate (18b/19b). [(*R,S*) minor, faster eluting]: white amorphous solid, 1H NMR (500 MHz, CD_2Cl_2) δ 0.55 (s, 9H), 0.57 (s, 9H), 0.85 (d, 3H, $J = 6.7$ Hz), 1.07 (s, 9H), 1.23 (dd, 1H, $J = 12.9, 3.6$ Hz), 1.72 (dd, 1H, $J = 12.9, 10.0$ Hz), 1.77 (ddq, 1H, $J = 10.0, 6.7, 3.6$ Hz), 3.27 (s, 3H), 6.48 (d, 1H, $J = 8.6$ Hz), 6.57 (d, 1H, $J = 8.6$ Hz), 7.13 (dt, 1H, $J = 4.9, 0.9$ Hz), 7.17 (dt, 1H, $J = 4.6, 0.9$ Hz), 7.39 (t, 1H, $J = 4.4$ Hz), 7.43 (t, 1H, $J = 4.4$ Hz), 7.89 (d, 1H, $J = 8.2$ Hz), 7.93 (d, 1H, $J = 8.1$ Hz), 8.10 (s, 1H), 8.15 (s, 1H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 1.09, 1.47, 21.29, 23.11, 27.45, 33.89, 35.89, 51.84 (OMe), 125.66, 125.75, 126.11, 126.30, 127.22, 127.34, 128.59, 132.54, 132.96, 133.97, 134.03, 135.08, 136.20, 136.54, 141.74, 142.22, 142.38, 142.57, 177.11 (18 aromatic signals observed out of 20 expected). IR (film, NaCl plates, cm^{-1}) 3059, 3030, 2952, 2892, 2857, 1734 (vs, C=O), 1246. LRMS m/z (rel inten) 677 ($M^+ - CH_3$, 1), 635 (42), 428 (12), 119 (9), 89 (10), 73 (100). HRMS calcd for $C_{31}H_{37}^{74}GeO_2S_2Si_2$ ($M^+ - C_4H_9$) 635.0985, found 635.0986. [(*R,R*) major, slower eluting]: white amorphous solid, mp (racemic, hexanes) 124-127 °C. $[\alpha]_D^{23}$ (*R,R*) = -77.3 ($c = 1$, THF). 1H NMR (300 MHz, $CDCl_3$) δ 0.54 (s, 9H), 0.58 (s, 9H), 0.85 (d, 3H, $J = 6.9$ Hz), 1.07 (s, 9H), 1.36 (dd, 1H, $J = 13.8, 9.5$ Hz), 1.70 (dd, 1H, $J = 13.8, 4.3$ Hz), 2.22 (m, 1H), 3.52 (s,

3H), 6.55 (d, 1H, $J = 8.4$ Hz), 6.59 (d, 1H, $J = 8.4$ Hz), 7.14 (t, 1H, $J = 7.7$ Hz), 7.17 (t, 1H, $J = 8.1$ Hz), 7.39 (t, 1H, $J = 7.0$ Hz), 7.42 (t, 1H, $J = 7.1$ Hz), 7.86 (d, 1H, $J = 8.5$ Hz), 7.89 (d, 1H, $J = 7.5$ Hz), 8.08 (s, 1H), 8.10 (s, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 1.07, 1.49, 19.97, 22.84, 27.42, 33.55, 35.43, 51.77 (OMe), 125.62, 125.85, 125.95, 127.01, 127.10, 128.19, 132.19, 132.54, 133.58, 133.73, 134.40, 135.66, 135.87, 141.59, 141.69, 141.94, 142.35, 177.16 (17 aromatic signals observed out of 20 expected). IR (film, NaCl plates, cm^{-1}) 3057, 3033, 2952, 2892, 2858, 1735 (vs, C=O), 1557, 1459, 1246. LRMS m/z (rel inten) 677 ($\text{M}^+ - \text{CH}_3$, 34), 635 (61), 519 (7), 461 (7), 428 (32), 325 (13), 263 (12), 105 (21), 89 (27), 73 (100). HRMS calcd for $\text{C}_{31}\text{H}_{37}^{74}\text{GeO}_2\text{S}_2\text{Si}_2$ ($\text{M}^+ - \text{C}_4\text{H}_9$) 635.0985, found 635.0993.

3-(4-*tert*-Butyl-2,6-bis-trimethylsilyl-3,5-dithia-4-germa-cyclohepta[2,1-a;3,4-

a']dinaphthalen-4-yl)-2-methyl-propan-1-ol (20). DIBAL (1.0 M soln in hexanes, 0.45 mL, 0.45 mmol) was added to a solution of (*R,R/S,S*)-**18b** (100 mg, 0.14 mmol) in CH_2Cl_2 (5 mL) at -60 °C. After stirring for 90 min, the reaction mixture was quenched with an aqueous solution of sodium potassium tartrate, extracted with diethyl ether (3×15 mL) dried over MgSO_4 , filtered and concentrated. The residue was purified by flash chromatography (ethyl acetate 1% to 5% in hexanes, gradient elution) to afford 80 mg (86%) of the title compound as a white solid, mp (racemic, hexanes) 199-201 °C. ^1H NMR (500 MHz, CDCl_3) δ 0.53 (s, 9H), 0.58 (s, 9H), 0.74 (d, 3H, $J = 6.6$ Hz), 1.03-1.12 (m, 1H), 1.07 (s, 9H), 1.27-1.40 (m, 2H), 3.03 (d, 2H, $J = 3.5$ Hz), 6.53 (d, 1H, $J = 8.5$ Hz), 6.61 (d, 1H, $J = 8.5$ Hz), 7.14 (quintet, 2H, $J = 7.3$ Hz), 7.37 (t, 1H, $J = 8.6$ Hz), 7.39 (t, 1H, $J = 7.5$ Hz), 7.86 (d, 1H, $J = 10.3$ Hz), 7.88 (d, 1H, $J = 8.6$ Hz), 8.08 (s, 1H), 8.10 (s, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 1.11, 1.49, 20.05, 22.85, 27.48, 32.55, 33.38, 69.56 (C-OH), 125.61, 125.65, 125.81, 126.07, 127.00, 127.24, 128.19, 132.20, 132.43, 133.60, 133.76, 134.87, 135.55, 135.79, 135.86, 135.90, 141.64, 141.67, 142.32, 142.58. IR (film, NaCl plates, cm^{-1}) 3585, 3420 (br), 2953, 2928, 2891, 2858, 1246. LRMS m/z (rel inten) 649 ($\text{M}^+ - \text{CH}_3$, 2.4), 607 (61), 551 (15), 428 (30), 341 (13), 119 (24), 73 (100). HRMS calcd for $\text{C}_{30}\text{H}_{37}^{74}\text{GeOS}_2\text{Si}_2$ ($\text{M}^+ - \text{C}_4\text{H}_9$) 607.1036, found 607.1065.

ORTEP of 2a

Table 1. Crystal data and structure refinement for 2a.

Identification code	gio1
Empirical formula	C ₂₄ H ₂₁ Cl S ₂ Sn
Formula weight	527.67
Temperature	208(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 10.153(4) Å alpha = 90 deg. b = 12.508(6) Å beta = 99.59(3) c = 17.877(7) Å gamma = 90 deg.
Volume, Z	2238(2) Å ³ , 4
Density (calculated)	1.566 Mg/m ³
Absorption coefficient	1.455 mm ⁻¹
F(000)	1056
Crystal size	0.40 x 0.35 x 0.35 mm
Theta range for data collection	2.00 to 24.00 deg.
Limiting indices	0 ≤ h ≤ 11, 0 ≤ k ≤ 14, -20 ≤ l ≤ 20
Reflections collected	3728
Independent reflections	3513 [R(int) = 0.0162]
Absorption correction	Semi-empirical from psi-scans
Max. and min. transmission	0.5796 and 0.5228
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3491 / 0 / 337
Goodness-of-fit on F ²	1.253
Final R indices [I > 2σ(I)]	R ₁ = 0.0331, wR ₂ = 0.0844
R indices (all data)	R ₁ = 0.0423, wR ₂ = 0.1051
Largest diff. peak and hole	0.597 and -0.313 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 2a. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U (eq)
Sn	8194 (1)	1558 (1)	1564 (1)	32 (1)
Cl	8969 (2)	196 (1)	843 (1)	57 (1)
S (1)	6051 (1)	1050 (1)	1844 (1)	38 (1)
C (1)	7226 (5)	231 (4)	3238 (3)	30 (1)
S (2)	9667 (1)	1363 (1)	2757 (1)	38 (1)
C (2)	6606 (5)	9 (4)	2511 (3)	34 (1)
C (3)	6361 (6)	-1054 (5)	2262 (3)	43 (1)
C (4)	6730 (7)	-1877 (5)	2744 (4)	49 (2)
C (5)	7395 (6)	-1707 (4)	3491 (3)	37 (1)
C (6)	7829 (6)	-2559 (5)	3994 (4)	45 (1)
C (7)	8468 (6)	-2375 (5)	4707 (4)	47 (2)
C (8)	8711 (6)	-1325 (5)	4963 (3)	39 (1)
C (9)	8331 (5)	-483 (4)	4498 (3)	34 (1)
C (10)	7651 (5)	-633 (4)	3746 (3)	31 (1)
C (11)	7486 (5)	1364 (4)	3505 (3)	29 (1)
C (12)	8553 (5)	1930 (4)	3322 (3)	30 (1)
C (13)	8795 (6)	2993 (4)	3576 (3)	37 (1)
C (14)	7991 (6)	3482 (5)	3997 (3)	38 (1)
C (15)	6873 (5)	2947 (4)	4191 (3)	34 (1)
C (16)	5982 (6)	3439 (5)	4617 (3)	45 (1)
C (17)	4945 (7)	2900 (6)	4824 (4)	55 (2)
C (18)	4704 (7)	1847 (6)	4598 (4)	56 (2)
C (19)	5530 (6)	1322 (5)	4179 (3)	40 (1)
C (20)	6625 (5)	1867 (4)	3949 (3)	32 (1)
C (21)	8295 (7)	3048 (5)	991 (3)	41 (1)
C (22)	8303 (7)	3988 (5)	1502 (3)	45 (1)
C (23)	7064 (7)	4130 (5)	1864 (4)	49 (2)
C (24)	7071 (7)	5139 (5)	2305 (4)	56 (2)

Table 3. Bond lengths [Å] and angles [deg] for 2a.

Sn-C (21)	2.137 (6)
Sn-Cl	2.350 (2)
Sn-S (1)	2.398 (2)
Sn-S (2)	2.404 (2)
S (1)-C (2)	1.792 (5)
C (1)-C (2)	1.374 (7)
C (1)-C (10)	1.432 (7)
C (1)-C (11)	1.505 (6)
S (2)-C (12)	1.785 (5)
C (2)-C (3)	1.412 (8)
C (3)-C (4)	1.354 (8)
C (4)-C (5)	1.408 (8)
C (5)-C (6)	1.417 (8)
C (5)-C (10)	1.429 (7)
C (6)-C (7)	1.350 (9)
C (7)-C (8)	1.399 (9)
C (8)-C (9)	1.358 (7)
C (9)-C (10)	1.416 (7)
C (11)-C (12)	1.378 (7)
C (11)-C (20)	1.421 (7)
C (12)-C (13)	1.413 (7)
C (13)-C (14)	1.346 (8)
C (14)-C (15)	1.410 (8)
C (15)-C (16)	1.416 (8)
C (15)-C (20)	1.429 (7)
C (16)-C (17)	1.353 (9)
C (17)-C (18)	1.388 (10)
C (18)-C (19)	1.380 (9)
C (19)-C (20)	1.422 (8)
C (21)-C (22)	1.487 (8)
C (22)-C (23)	1.518 (9)
C (23)-C (24)	1.488 (9)
C (21)-Sn-Cl	108.8 (2)
C (21)-Sn-S (1)	116.7 (2)
Cl-Sn-S (1)	108.72 (6)
C (21)-Sn-S (2)	116.2 (2)
Cl-Sn-S (2)	101.38 (6)
S (1)-Sn-S (2)	103.87 (5)
C (2)-S (1)-Sn	97.8 (2)
C (2)-C (1)-C (10)	119.4 (5)
C (2)-C (1)-C (11)	121.2 (4)
C (10)-C (1)-C (11)	119.4 (4)
C (12)-S (2)-Sn	95.9 (2)
C (1)-C (2)-C (3)	121.2 (5)
C (1)-C (2)-S (1)	121.7 (4)
C (3)-C (2)-S (1)	117.1 (4)
C (4)-C (3)-C (2)	120.0 (5)
C (3)-C (4)-C (5)	121.8 (6)
C (4)-C (5)-C (6)	122.5 (5)
C (4)-C (5)-C (10)	118.6 (5)
C (6)-C (5)-C (10)	118.9 (5)
C (7)-C (6)-C (5)	121.4 (6)

C (6) -C (7) -C (8)	120.1 (6)
C (9) -C (8) -C (7)	120.7 (5)
C (8) -C (9) -C (10)	121.5 (5)
C (9) -C (10) -C (5)	117.5 (5)
C (9) -C (10) -C (1)	123.4 (5)
C (5) -C (10) -C (1)	119.1 (4)
C (12) -C (11) -C (20)	119.1 (4)
C (12) -C (11) -C (1)	120.8 (4)
C (20) -C (11) -C (1)	120.1 (4)
C (11) -C (12) -C (13)	120.6 (5)
C (11) -C (12) -S (2)	121.8 (4)
C (13) -C (12) -S (2)	117.6 (4)
C (14) -C (13) -C (12)	121.1 (5)
C (13) -C (14) -C (15)	120.7 (5)
C (14) -C (15) -C (16)	122.6 (5)
C (14) -C (15) -C (20)	118.9 (5)
C (16) -C (15) -C (20)	118.5 (5)
C (17) -C (16) -C (15)	121.8 (6)
C (16) -C (17) -C (18)	120.0 (6)
C (19) -C (18) -C (17)	121.1 (6)
C (18) -C (19) -C (20)	120.3 (6)
C (11) -C (20) -C (19)	122.2 (5)
C (11) -C (20) -C (15)	119.6 (5)
C (19) -C (20) -C (15)	118.2 (5)
C (22) -C (21) -Sn	113.0 (4)
C (21) -C (22) -C (23)	115.7 (5)
C (24) -C (23) -C (22)	113.2 (6)

Symmetry transformations used to generate equivalent atoms:

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

	U11	U22	U33	U23	U13	U12
Sn	40 (1)	28 (1)	29 (1)	1 (1)	8 (1)	7 (1)
Cl	84 (1)	46 (1)	42 (1)	-6 (1)	10 (1)	30 (1)
S (1)	36 (1)	40 (1)	35 (1)	5 (1)	0 (1)	0 (1)
C (1)	31 (3)	29 (3)	29 (3)	-1 (2)	6 (2)	-5 (2)
S (2)	33 (1)	45 (1)	36 (1)	3 (1)	5 (1)	4 (1)
C (2)	37 (3)	29 (3)	34 (3)	0 (2)	4 (2)	-3 (2)
C (3)	55 (4)	39 (3)	32 (3)	-6 (3)	-3 (3)	-4 (3)
C (4)	68 (4)	29 (3)	49 (4)	-7 (3)	8 (3)	-10 (3)
C (5)	44 (3)	31 (3)	38 (3)	4 (2)	9 (2)	-5 (2)
C (6)	51 (4)	26 (3)	59 (4)	3 (3)	11 (3)	-1 (3)
C (7)	50 (4)	38 (3)	55 (4)	22 (3)	11 (3)	6 (3)
C (8)	41 (3)	45 (3)	30 (3)	5 (2)	3 (2)	0 (3)
C (9)	39 (3)	34 (3)	31 (3)	-1 (2)	6 (2)	-2 (2)
C (10)	35 (3)	26 (3)	31 (3)	1 (2)	8 (2)	-2 (2)
C (11)	37 (3)	22 (2)	25 (2)	2 (2)	0 (2)	0 (2)
C (12)	34 (3)	31 (3)	24 (2)	2 (2)	0 (2)	1 (2)
C (13)	46 (3)	36 (3)	28 (3)	1 (2)	2 (2)	-14 (3)
C (14)	56 (4)	26 (3)	30 (3)	-1 (2)	-3 (2)	-9 (3)
C (15)	41 (3)	28 (3)	31 (3)	-1 (2)	0 (2)	4 (2)
C (16)	55 (4)	38 (3)	40 (3)	-10 (3)	0 (3)	14 (3)
C (17)	52 (4)	69 (5)	46 (4)	-14 (3)	12 (3)	10 (3)
C (18)	44 (4)	67 (5)	59 (4)	-11 (3)	17 (3)	-7 (3)
C (19)	40 (3)	39 (3)	41 (3)	-7 (3)	9 (2)	-6 (3)
C (20)	40 (3)	32 (3)	22 (2)	3 (2)	-4 (2)	-1 (2)
C (21)	55 (4)	34 (3)	36 (3)	1 (2)	15 (3)	-2 (3)
C (22)	61 (4)	31 (3)	45 (3)	2 (3)	11 (3)	-6 (3)
C (23)	52 (4)	34 (3)	61 (4)	-6 (3)	11 (3)	3 (3)
C (24)	54 (4)	41 (4)	73 (5)	-13 (3)	17 (4)	9 (3)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 2a.

	x	y	z	U (eq)
H (3)	5871 (48)	-1216 (39)	1784 (29)	27 (13)
H (4)	6545 (60)	-2514 (55)	2606 (35)	53 (19)
H (6)	7611 (60)	-3219 (52)	3791 (34)	52 (18)
H (7)	8686 (54)	-2805 (46)	4991 (32)	33 (16)
H (8)	9110 (57)	-1204 (47)	5473 (34)	49 (17)
H (9)	8441 (47)	188 (42)	4682 (27)	25 (13)
H (13)	9554 (51)	3351 (41)	3412 (28)	32 (13)
H (14)	8254 (63)	4050 (54)	4186 (36)	55 (19)
H (16)	6035 (61)	4093 (55)	4746 (35)	54 (19)
H (17)	4346 (59)	3256 (47)	5073 (33)	46 (16)
H (18)	4015 (73)	1472 (57)	4688 (40)	70 (22)
H (19)	5392 (50)	634 (45)	4027 (29)	33 (14)
H (21B)	7514 (67)	3017 (51)	608 (37)	59 (19)
H (21A)	8931 (68)	2888 (55)	779 (38)	60 (21)
H (22A)	9046 (50)	3944 (40)	1986 (29)	31 (13)
H (22B)	8495 (57)	4668 (52)	1321 (33)	50 (17)
H (23A)	7011 (60)	3502 (52)	2152 (35)	52 (18)
H (23B)	6446 (65)	4108 (52)	1410 (38)	60 (19)
H (24A)	7890 (58)	5134 (45)	2779 (32)	43 (15)
H (24B)	6299 (71)	5235 (55)	2513 (38)	67 (21)
H (24C)	7216 (66)	5833 (59)	2031 (38)	68 (21)

ORTEP of 5a

Table 1. Crystal data and structure refinement for 5a.

Identification code	gio997
Empirical formula	C ₂₄ H ₂₁ Cl Ge S ₂
Formula weight	481.57
Temperature	213(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic
Space group	P2 ₁ /n
Unit cell dimensions	a = 6.6165(13) Å alpha = 90 deg. b = 10.511(2) Å beta = 93.83(3) c = 31.746(6) Å gamma = 90 deg.
Volume	2202.8(8) Å ³
Z, Calculated density	4, 1.452 Mg/m ³
Absorption coefficient	1.709 mm ⁻¹
F(000)	984
Crystal size	0.37 x 0.33 x 0.33 mm
Theta range for data collection	2.04 to 24.99 deg.
Limiting indices	0 ≤ h ≤ 7, 0 ≤ k ≤ 12, -37 ≤ l ≤ 37
Reflections collected / unique	4218 / 3867 [R(int) = 0.0302]
Completeness to theta = 24.99	99.7 %
Max. and min. transmission	0.6024 and 0.5705
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3867 / 0 / 337
Goodness-of-fit on F ²	1.159
Final R indices [I > 2σ(I)]	R ₁ = 0.0457, wR ₂ = 0.1086
R indices (all data)	R ₁ = 0.0812, wR ₂ = 0.1403
Largest diff. peak and hole	0.918 and -0.534 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 5a. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U (eq)
Ge	4716 (1)	5871 (1)	1748 (1)	28 (1)
Cl	3450 (3)	3988 (2)	1622 (1)	48 (1)
S (1)	7904 (2)	5991 (2)	1582 (1)	40 (1)
C (1)	7541 (8)	6085 (5)	1020 (2)	30 (1)
S (2)	2809 (2)	7064 (2)	1309 (1)	36 (1)
C (2)	8249 (9)	5059 (6)	785 (2)	41 (2)
C (3)	8020 (9)	5082 (6)	357 (2)	41 (2)
C (4)	7052 (8)	6099 (5)	134 (2)	32 (1)
C (5)	6713 (10)	6125 (7)	-308 (2)	45 (2)
C (6)	5706 (10)	7108 (7)	-506 (2)	45 (2)
C (7)	4960 (10)	8101 (7)	-273 (2)	45 (2)
C (8)	5275 (9)	8134 (6)	152 (2)	36 (1)
C (9)	6367 (8)	7138 (5)	375 (2)	28 (1)
C (10)	6696 (8)	7150 (5)	824 (2)	29 (1)
C (11)	6188 (8)	8308 (5)	1061 (2)	29 (1)
C (12)	7495 (8)	9387 (5)	1046 (2)	31 (1)
C (13)	9224 (9)	9402 (6)	805 (2)	35 (1)
C (14)	10407 (10)	10468 (7)	789 (2)	46 (2)
C (15)	9940 (11)	11557 (7)	1015 (2)	48 (2)
C (16)	8315 (10)	11586 (6)	1250 (2)	42 (2)
C (17)	7034 (9)	10509 (5)	1273 (2)	32 (1)
C (18)	5298 (10)	10526 (6)	1505 (2)	40 (2)
C (19)	4072 (10)	9507 (6)	1514 (2)	41 (2)
C (20)	4517 (8)	8383 (5)	1295 (2)	28 (1)
C (21)	4550 (9)	6181 (6)	2356 (2)	35 (1)
C (22)	2341 (12)	6239 (9)	2448 (3)	58 (2)
C (23)	5640 (16)	5092 (9)	2603 (2)	58 (2)
C (24)	5601 (16)	7442 (8)	2465 (3)	60 (2)

Table 3. Bond lengths [Å] and angles [deg] for 5a.

Ge-C (21)	1.966 (5)
Ge-Cl	2.1763 (17)
Ge-S (2)	2.2081 (16)
Ge-S (1)	2.2112 (16)
S (1)-C (1)	1.789 (6)
C (1)-C (10)	1.380 (8)
C (1)-C (2)	1.409 (8)
S (2)-C (20)	1.791 (5)
C (2)-C (3)	1.357 (9)
C (3)-C (4)	1.412 (9)
C (4)-C (5)	1.406 (9)
C (4)-C (9)	1.425 (8)
C (5)-C (6)	1.359 (10)
C (6)-C (7)	1.388 (10)
C (7)-C (8)	1.354 (9)
C (8)-C (9)	1.432 (8)
C (9)-C (10)	1.427 (8)
C (10)-C (11)	1.482 (8)
C (11)-C (20)	1.374 (8)
C (11)-C (12)	1.429 (8)
C (12)-C (13)	1.418 (8)
C (12)-C (17)	1.425 (8)
C (13)-C (14)	1.369 (8)
C (14)-C (15)	1.397 (10)
C (15)-C (16)	1.349 (10)
C (16)-C (17)	1.419 (8)
C (17)-C (18)	1.406 (9)
C (18)-C (19)	1.345 (9)
C (19)-C (20)	1.412 (8)
C (21)-C (22)	1.511 (10)
C (21)-C (24)	1.525 (9)
C (21)-C (23)	1.540 (9)
C (21)-Ge-Cl	106.62 (18)
C (21)-Ge-S (2)	117.29 (18)
Cl-Ge-S (2)	101.70 (7)
C (21)-Ge-S (1)	109.96 (19)
Cl-Ge-S (1)	111.66 (7)
S (2)-Ge-S (1)	109.33 (6)
C (1)-S (1)-Ge	100.07 (18)
C (10)-C (1)-C (2)	121.4 (5)
C (10)-C (1)-S (1)	121.2 (4)
C (2)-C (1)-S (1)	117.3 (4)
C (20)-S (2)-Ge	96.89 (18)
C (3)-C (2)-C (1)	119.9 (6)
C (2)-C (3)-C (4)	122.1 (6)
C (5)-C (4)-C (3)	123.5 (6)
C (5)-C (4)-C (9)	119.1 (6)
C (3)-C (4)-C (9)	117.4 (5)
C (6)-C (5)-C (4)	121.0 (6)

C (5) -C (6) -C (7)	120.5 (6)
C (8) -C (7) -C (6)	120.9 (7)
C (7) -C (8) -C (9)	120.9 (6)
C (4) -C (9) -C (10)	120.7 (5)
C (4) -C (9) -C (8)	117.6 (5)
C (10) -C (9) -C (8)	121.7 (5)
C (1) -C (10) -C (9)	118.2 (5)
C (1) -C (10) -C (11)	122.4 (5)
C (9) -C (10) -C (11)	119.3 (5)
C (20) -C (11) -C (12)	118.9 (5)
C (20) -C (11) -C (10)	122.6 (5)
C (12) -C (11) -C (10)	118.5 (5)
C (13) -C (12) -C (17)	118.1 (5)
C (13) -C (12) -C (11)	122.6 (5)
C (17) -C (12) -C (11)	119.3 (5)
C (14) -C (13) -C (12)	120.9 (6)
C (13) -C (14) -C (15)	120.3 (6)
C (16) -C (15) -C (14)	120.9 (6)
C (15) -C (16) -C (17)	120.8 (6)
C (18) -C (17) -C (16)	121.9 (6)
C (18) -C (17) -C (12)	119.0 (5)
C (16) -C (17) -C (12)	119.0 (5)
C (19) -C (18) -C (17)	121.0 (6)
C (18) -C (19) -C (20)	120.7 (6)
C (11) -C (20) -C (19)	121.0 (5)
C (11) -C (20) -S (2)	120.1 (4)
C (19) -C (20) -S (2)	118.9 (4)
C (22) -C (21) -C (24)	110.7 (7)
C (22) -C (21) -C (23)	111.0 (6)
C (24) -C (21) -C (23)	109.8 (6)
C (22) -C (21) -Ge	108.3 (5)
C (24) -C (21) -Ge	108.2 (4)
C (23) -C (21) -Ge	108.8 (5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 5a.
The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Ge	30 (1)	28 (1)	28 (1)	2 (1)	6 (1)	-2 (1)
Cl	64 (1)	32 (1)	48 (1)	-7 (1)	5 (1)	-7 (1)
S (1)	27 (1)	55 (1)	39 (1)	18 (1)	4 (1)	4 (1)
C (1)	23 (3)	34 (3)	34 (3)	5 (2)	6 (2)	-3 (2)
S (2)	25 (1)	42 (1)	41 (1)	10 (1)	3 (1)	-3 (1)
C (2)	29 (3)	33 (3)	62 (4)	6 (3)	14 (3)	1 (3)
C (3)	38 (3)	25 (3)	62 (4)	-6 (3)	20 (3)	-2 (3)
C (4)	26 (3)	33 (3)	38 (3)	-2 (2)	12 (2)	-9 (2)
C (5)	38 (3)	52 (4)	47 (4)	-22 (3)	18 (3)	-8 (3)
C (6)	40 (4)	65 (5)	31 (3)	-1 (3)	4 (3)	-12 (3)
C (7)	50 (4)	46 (4)	38 (4)	7 (3)	3 (3)	-9 (3)
C (8)	42 (3)	34 (3)	32 (3)	1 (3)	6 (3)	-4 (3)
C (9)	23 (3)	28 (3)	34 (3)	1 (2)	8 (2)	-8 (2)
C (10)	22 (3)	30 (3)	38 (3)	8 (2)	9 (2)	-4 (2)
C (11)	29 (3)	25 (3)	31 (3)	5 (2)	-2 (2)	0 (2)
C (12)	28 (3)	34 (3)	30 (3)	7 (2)	-2 (2)	2 (2)
C (13)	36 (3)	28 (3)	41 (3)	2 (3)	7 (3)	0 (2)
C (14)	37 (4)	46 (4)	57 (4)	10 (3)	10 (3)	-4 (3)
C (15)	45 (4)	34 (4)	63 (5)	2 (3)	-8 (3)	-11 (3)
C (16)	54 (4)	29 (3)	40 (4)	-4 (3)	-6 (3)	-1 (3)
C (17)	42 (3)	27 (3)	25 (3)	6 (2)	-5 (2)	-3 (2)
C (18)	57 (4)	31 (3)	33 (3)	-1 (3)	-1 (3)	6 (3)
C (19)	46 (4)	45 (4)	33 (3)	4 (3)	13 (3)	9 (3)
C (20)	26 (3)	29 (3)	28 (3)	5 (2)	1 (2)	0 (2)
C (21)	47 (3)	37 (3)	22 (3)	0 (2)	10 (2)	0 (3)
C (22)	58 (5)	76 (6)	42 (4)	-4 (4)	18 (4)	6 (4)
C (23)	80 (6)	59 (5)	33 (4)	9 (4)	-9 (4)	9 (5)
C (24)	96 (7)	48 (5)	36 (4)	-9 (4)	-1 (4)	-20 (5)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 5a.

	x	y	z	U (eq)
H (2)	8880 (100)	4350 (70)	950 (20)	60 (20)
H (3)	8320 (70)	4420 (50)	218 (16)	13 (13)
H (5)	7180 (90)	5560 (60)	-454 (19)	35 (18)
H (6)	5340 (80)	6920 (50)	-847 (18)	33 (15)
H (7)	4300 (90)	8800 (60)	-412 (19)	37 (17)
H (8)	4820 (90)	8720 (60)	330 (20)	42 (18)
H (13)	9640 (70)	8650 (50)	666 (15)	14 (12)
H (14)	11420 (90)	10450 (60)	584 (18)	34 (16)
H (15)	10670 (100)	12200 (60)	1020 (20)	41 (18)
H (16)	7940 (100)	12310 (70)	1480 (20)	60 (20)
H (18)	5030 (90)	11260 (60)	1629 (19)	37 (17)
H (19)	3010 (100)	9440 (60)	1650 (20)	43 (18)
H (22C)	1600 (90)	7020 (60)	2300 (20)	44 (18)
H (22B)	2150 (100)	6370 (70)	2720 (20)	50 (20)
H (22A)	1680 (120)	5480 (90)	2300 (30)	80 (30)
H (23C)	7000 (160)	5070 (100)	2580 (30)	110 (40)
H (23A)	5610 (100)	5250 (60)	2880 (20)	48 (19)
H (23B)	4940 (140)	4260 (90)	2600 (30)	90 (30)
H (24C)	5000 (100)	8030 (70)	2300 (20)	50 (20)
H (24A)	5670 (130)	7590 (90)	2780 (30)	100 (30)
H (24B)	7030 (150)	7460 (90)	2350 (30)	100 (30)

ORTEP of 5b

Table 1. Crystal data and structure refinement for 5b.

Identification code	gio1098b
Empirical formula	C ₃₀ H ₃₇ Cl Ge S ₂ Si ₂
Formula weight	625.94
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 15.740(3) Å alpha = 90 deg. b = 9.759(2) Å beta = 90 deg. c = 40.578(8) Å gamma = 90 deg.
Volume	6233(2) Å ³
Z, Calculated density	8, 1.334 Mg/m ³
Absorption coefficient	1.298 mm ⁻¹
F(000)	2608
Crystal size	0.20 x 0.20 x 0.35 mm
Theta range for data collection	2.39 to 23.99 deg.
Limiting indices	0 ≤ h ≤ 18, 0 ≤ k ≤ 11, -46 ≤ l ≤ 0
Reflections collected / unique	4880 / 4880 [R(int) = 0.0000]
Completeness to theta = 23.99	99.9 %
Absorption correction	Empirical
Max. and min. transmission	0.9025 and 0.6908
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4880 / 0 / 320
Goodness-of-fit on F ²	1.267
Final R indices [I > 2sigma(I)]	R ₁ = 0.1152, wR ₂ = 0.2356
R indices (all data)	R ₁ = 0.2382, wR ₂ = 0.2938
Largest diff. peak and hole	2.912 and -1.041 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 5b.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U (eq)
Ge	9499 (1)	1074 (2)	4205 (1)	47 (1)
Cl	10521 (3)	605 (6)	4551 (1)	80 (2)
S (1)	9566 (2)	3231 (4)	4038 (1)	35 (1)
Si (1)	11136 (3)	5029 (5)	4408 (1)	41 (1)
C (1)	10754 (8)	2353 (13)	3595 (3)	25 (3)
S (2)	9848 (2)	-322 (4)	3804 (1)	38 (1)
Si (2)	8500 (2)	-1674 (5)	3224 (1)	40 (1)
C (2)	10602 (8)	3112 (13)	3881 (3)	28 (3)
C (3)	11283 (7)	3851 (14)	4040 (3)	27 (3)
C (4)	12069 (8)	3678 (13)	3910 (3)	30 (3)
C (5)	12258 (7)	2865 (14)	3640 (3)	27 (3)
C (6)	13092 (9)	2676 (17)	3525 (4)	45 (4)
C (7)	13266 (9)	1842 (18)	3267 (4)	55 (5)
C (8)	12611 (10)	1133 (17)	3117 (3)	51 (4)
C (9)	11812 (9)	1301 (15)	3218 (4)	42 (4)
C (10)	11607 (8)	2152 (13)	3480 (3)	24 (3)
C (11)	10044 (8)	1839 (14)	3385 (3)	24 (3)
C (12)	9621 (8)	609 (13)	3439 (3)	27 (3)
C (13)	9041 (7)	89 (14)	3207 (3)	28 (3)
C (14)	8849 (8)	841 (16)	2930 (4)	39 (4)
C (15)	9223 (8)	2112 (16)	2876 (3)	37 (4)
C (16)	9026 (9)	2936 (19)	2592 (3)	45 (4)
C (17)	9412 (11)	4168 (19)	2547 (4)	55 (5)
C (18)	9999 (9)	4675 (15)	2768 (3)	42 (4)
C (19)	10208 (8)	3966 (15)	3045 (3)	36 (4)
C (20)	9870 (9)	2629 (15)	3099 (3)	35 (4)
C (21)	10296 (11)	6338 (17)	4330 (4)	67 (5)
C (22)	10899 (11)	4079 (17)	4791 (3)	60 (5)
C (23)	12168 (10)	5882 (19)	4488 (3)	66 (5)
C (24)	7435 (9)	-1482 (19)	3420 (4)	66 (5)
C (25)	9102 (11)	-3047 (16)	3450 (5)	77 (6)
C (26)	8358 (9)	-2286 (18)	2788 (4)	66 (5)
C (27)	8464 (11)	703 (18)	4451 (5)	73 (6)
C (28)	8440 (11)	1675 (19)	4745 (4)	71 (6)
C (29)	7717 (11)	1086 (19)	4157 (4)	71 (5)
C (30)	8491 (11)	-783 (17)	4549 (4)	66 (6)

Table 3. Bond lengths [Å] and angles [deg] for 5b.

Ge-C (27)	1.944 (15)
Ge-Cl	2.184 (5)
Ge-S (2)	2.192 (4)
Ge-S (1)	2.214 (4)
S (1)-C (2)	1.756 (13)
Si (1)-C (23)	1.853 (16)
Si (1)-C (22)	1.850 (13)
Si (1)-C (21)	1.866 (16)
Si (1)-C (3)	1.897 (14)
C (1)-C (2)	1.395 (16)
C (1)-C (10)	1.436 (16)
C (1)-C (11)	1.492 (17)
S (2)-C (12)	1.774 (13)
Si (2)-C (24)	1.863 (15)
Si (2)-C (25)	1.880 (18)
Si (2)-C (26)	1.879 (16)
Si (2)-C (13)	1.922 (14)
C (2)-C (3)	1.445 (16)
C (3)-C (4)	1.354 (17)
C (4)-C (5)	1.384 (17)
C (5)-C (10)	1.399 (16)
C (5)-C (6)	1.406 (17)
C (6)-C (7)	1.35 (2)
C (7)-C (8)	1.38 (2)
C (8)-C (9)	1.333 (18)
C (9)-C (10)	1.386 (17)
C (11)-C (12)	1.390 (17)
C (11)-C (20)	1.423 (17)
C (12)-C (13)	1.406 (17)
C (13)-C (14)	1.376 (18)
C (14)-C (15)	1.391 (19)
C (15)-C (16)	1.441 (19)
C (15)-C (20)	1.450 (19)
C (16)-C (17)	1.36 (2)
C (17)-C (18)	1.38 (2)
C (18)-C (19)	1.358 (18)
C (19)-C (20)	1.426 (19)
C (27)-C (30)	1.50 (2)
C (27)-C (28)	1.53 (2)
C (27)-C (29)	1.72 (2)
C (27)-Ge-Cl	104.4 (6)
C (27)-Ge-S (2)	118.4 (6)
Cl-Ge-S (2)	99.37 (18)
C (27)-Ge-S (1)	112.0 (5)
Cl-Ge-S (1)	111.15 (19)
S (2)-Ge-S (1)	110.55 (14)
C (2)-S (1)-Ge	95.4 (4)
C (23)-Si (1)-C (22)	104.7 (7)
C (23)-Si (1)-C (21)	110.1 (8)
C (22)-Si (1)-C (21)	109.9 (8)
C (23)-Si (1)-C (3)	107.7 (6)
C (22)-Si (1)-C (3)	112.5 (7)

C(21)-Si(1)-C(3)	111.6(6)
C(2)-C(1)-C(10)	120.3(11)
C(2)-C(1)-C(11)	121.6(11)
C(10)-C(1)-C(11)	117.9(10)
C(12)-S(2)-Ge	104.6(4)
C(24)-Si(2)-C(25)	108.5(8)
C(24)-Si(2)-C(26)	109.0(7)
C(25)-Si(2)-C(26)	107.0(8)
C(24)-Si(2)-C(13)	108.9(7)
C(25)-Si(2)-C(13)	115.6(6)
C(26)-Si(2)-C(13)	107.7(7)
C(1)-C(2)-C(3)	120.6(12)
C(1)-C(2)-S(1)	119.8(10)
C(3)-C(2)-S(1)	119.6(9)
C(4)-C(3)-C(2)	116.2(12)
C(4)-C(3)-Si(1)	119.5(9)
C(2)-C(3)-Si(1)	124.3(9)
C(3)-C(4)-C(5)	125.1(12)
C(4)-C(5)-C(10)	119.8(11)
C(4)-C(5)-C(6)	122.6(13)
C(10)-C(5)-C(6)	117.6(12)
C(7)-C(6)-C(5)	121.6(14)
C(6)-C(7)-C(8)	119.4(14)
C(9)-C(8)-C(7)	120.5(15)
C(8)-C(9)-C(10)	121.8(14)
C(9)-C(10)-C(5)	119.1(12)
C(9)-C(10)-C(1)	123.3(12)
C(5)-C(10)-C(1)	117.6(11)
C(12)-C(11)-C(20)	120.3(12)
C(12)-C(11)-C(1)	124.0(11)
C(20)-C(11)-C(1)	115.5(12)
C(11)-C(12)-C(13)	121.2(12)
C(11)-C(12)-S(2)	118.5(10)
C(13)-C(12)-S(2)	120.3(11)
C(14)-C(13)-C(12)	119.8(13)
C(14)-C(13)-Si(2)	114.1(10)
C(12)-C(13)-Si(2)	126.0(11)
C(13)-C(14)-C(15)	120.8(13)
C(14)-C(15)-C(16)	122.2(14)
C(14)-C(15)-C(20)	120.6(13)
C(16)-C(15)-C(20)	117.1(14)
C(17)-C(16)-C(15)	120.3(14)
C(16)-C(17)-C(18)	122.0(14)
C(19)-C(18)-C(17)	121.1(14)
C(18)-C(19)-C(20)	120.2(13)
C(11)-C(20)-C(19)	123.3(13)
C(11)-C(20)-C(15)	117.1(14)
C(19)-C(20)-C(15)	119.0(12)
C(30)-C(27)-C(28)	113.1(15)
C(30)-C(27)-C(29)	114.4(16)
C(28)-C(27)-C(29)	113.1(14)
C(30)-C(27)-Ge	106.9(11)
C(28)-C(27)-Ge	107.9(12)
C(29)-C(27)-Ge	100.2(10)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 5b.
The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Ge	63 (1)	40 (1)	38 (1)	-2 (1)	22 (1)	-10 (1)
Cl	83 (3)	90 (4)	67 (3)	0 (3)	-30 (3)	10 (3)
S (1)	34 (2)	39 (2)	33 (2)	-2 (2)	12 (2)	-4 (2)
Si (1)	51 (3)	42 (3)	29 (2)	-6 (2)	0 (2)	-6 (2)
C (1)	47 (8)	18 (7)	11 (6)	5 (6)	-4 (6)	4 (7)
S (2)	50 (2)	33 (2)	32 (2)	-1 (2)	3 (2)	0 (2)
Si (2)	32 (2)	45 (3)	43 (2)	-14 (2)	0 (2)	-6 (2)
C (2)	39 (8)	22 (8)	22 (7)	1 (6)	-9 (6)	1 (7)
C (3)	16 (7)	35 (8)	31 (7)	13 (7)	-6 (6)	-8 (7)
C (4)	31 (8)	27 (9)	32 (7)	-2 (7)	-9 (6)	-12 (7)
C (5)	30 (8)	32 (9)	20 (7)	4 (6)	5 (6)	2 (7)
C (6)	31 (8)	62 (12)	42 (9)	-3 (9)	-7 (8)	0 (8)
C (7)	23 (8)	63 (13)	79 (13)	4 (11)	0 (8)	-5 (9)
C (8)	52 (11)	58 (12)	44 (9)	1 (9)	21 (8)	10 (10)
C (9)	35 (9)	37 (10)	53 (10)	-8 (8)	0 (8)	-11 (8)
C (10)	27 (7)	24 (8)	21 (7)	-1 (6)	1 (6)	3 (6)
C (11)	21 (7)	35 (9)	18 (7)	-2 (6)	14 (6)	-2 (7)
C (12)	37 (8)	26 (8)	19 (6)	-8 (6)	7 (6)	17 (7)
C (13)	9 (6)	36 (9)	40 (8)	-14 (8)	-5 (6)	2 (6)
C (14)	17 (7)	54 (11)	46 (9)	-19 (8)	8 (7)	5 (8)
C (15)	29 (8)	44 (10)	39 (9)	-6 (8)	3 (7)	21 (8)
C (16)	31 (9)	75 (13)	28 (8)	-21 (8)	-16 (7)	20 (9)
C (17)	66 (12)	59 (13)	41 (9)	6 (9)	-17 (9)	24 (11)
C (18)	56 (10)	34 (9)	35 (8)	-4 (8)	10 (8)	-13 (8)
C (19)	42 (8)	42 (9)	25 (7)	12 (7)	-9 (6)	-18 (8)
C (20)	53 (9)	39 (9)	13 (7)	-6 (7)	5 (7)	19 (8)
C (21)	95 (14)	46 (11)	59 (11)	-9 (9)	-27 (10)	8 (10)
C (22)	102 (13)	63 (12)	16 (7)	18 (8)	-9 (8)	-4 (11)
C (23)	79 (13)	80 (14)	38 (9)	-19 (10)	-11 (8)	-20 (11)
C (24)	36 (9)	83 (14)	80 (11)	-22 (11)	10 (9)	-17 (10)
C (25)	74 (12)	23 (10)	135 (18)	-18 (11)	-4 (13)	-24 (10)
C (26)	36 (9)	68 (13)	96 (14)	-31 (11)	14 (10)	-24 (9)
C (27)	85 (13)	43 (12)	90 (14)	14 (10)	73 (12)	12 (10)
C (28)	84 (13)	82 (14)	46 (10)	-20 (10)	42 (10)	-6 (12)
C (30)	81 (13)	59 (13)	59 (11)	-6 (10)	49 (10)	-16 (11)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 5b.

	x	y	z	U (eq)
H (4A)	12526	4151	4012	36
H (6A)	13545	3145	3631	54
H (7A)	13833	1743	3190	66
H (8A)	12731	524	2941	62
H (9A)	11370	823	3107	50
H (14A)	8456	488	2774	47
H (16A)	8624	2616	2435	53
H (17A)	9274	4696	2357	67
H (18A)	10262	5535	2727	50
H (19A)	10581	4362	3202	44
H (21A)	10235	6924	4525	100
H (21B)	9755	5877	4285	100
H (21C)	10456	6900	4140	100
H (22A)	10827	4729	4973	90
H (22B)	11369	3454	4841	90
H (22C)	10374	3552	4762	90
H (23A)	12112	6495	4678	98
H (23B)	12336	6413	4293	98
H (23C)	12601	5187	4534	98
H (24A)	7110	-778	3302	100
H (24B)	7505	-1210	3651	100
H (24C)	7131	-2357	3409	100
H (25A)	9193	-2761	3679	116
H (25B)	9652	-3194	3343	116
H (25C)	8775	-3901	3447	116
H (26A)	8053	-1588	2661	100
H (26B)	8030	-3140	2788	100
H (26C)	8915	-2448	2689	100
H (28A)	7927	1500	4875	106
H (28B)	8435	2625	4667	106
H (28C)	8943	1525	4883	106
H (29A)	7148	928	4247	107
H (29B)	7805	500	3964	107
H (29C)	7774	2049	4092	107
H (30A)	7978	-1011	4675	100
H (30B)	8994	-950	4686	100
H (30C)	8518	-1356	4351	100

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Table 1. Crystal data and structure refinement for 6.

Identification code	gio1198a
Empirical formula	C ₃₀ H ₃₈ Ge O S ₂ Si ₂
Formula weight	607.49
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	orthorhombic, Pbca
Unit cell dimensions	a = 15.740(3) Å alpha = 90 deg. b = 9.759(2) Å beta = 90 deg. c = 40.578(8) Å gamma = 90 deg.
Volume	6233(2) Å ³
Z, Calculated density	8, 1.295 Mg/m ³
Absorption coefficient	1.215 mm ⁻¹
F(000)	2544
Crystal size	0.30 x 0.20 x 0.20 mm
Theta range for data collection	2.01 to 24.03 deg.
Limiting indices	0 ≤ h ≤ 18, 0 ≤ k ≤ 11, -46 ≤ l ≤ 0
Reflections collected / unique	4884 / 4884 [R(int) = 0.0000]
Completeness to theta = 24.03	99.5 %
Max. and min. transmission	0.7932 and 0.7120
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4884 / 0 / 325
Goodness-of-fit on F ²	1.024
Final R indices [I > 2σ(I)]	R ₁ = 0.1172, wR ₂ = 0.2313
R indices (all data)	R ₁ = 0.2524, wR ₂ = 0.3084
Largest diff. peak and hole	3.418 and -1.147 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 6. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U (eq)
Ge	9594 (1)	1116 (2)	4240 (1)	59 (1)
O	10459 (8)	816 (13)	4531 (3)	84 (4)
S (1)	9635 (3)	3254 (4)	4049 (1)	46 (1)
Si (1)	11249 (3)	4980 (5)	4410 (1)	48 (1)
C (1)	10807 (9)	2339 (14)	3606 (3)	31 (3)
S (2)	9906 (3)	-324 (4)	3836 (1)	50 (1)
Si (2)	8520 (3)	-1751 (5)	3269 (1)	55 (1)
C (2)	10679 (8)	3108 (15)	3882 (3)	35 (3)
C (3)	11361 (10)	3825 (15)	4038 (3)	40 (4)
C (4)	12158 (9)	3646 (16)	3901 (3)	45 (4)
C (5)	12325 (10)	2784 (16)	3628 (3)	44 (4)
C (6)	13141 (10)	2584 (18)	3500 (4)	53 (5)
C (7)	13268 (11)	1760 (20)	3239 (4)	62 (5)
C (8)	12603 (12)	1045 (18)	3090 (4)	60 (5)
C (9)	11805 (11)	1240 (18)	3212 (4)	58 (5)
C (10)	11620 (9)	2111 (15)	3478 (3)	35 (4)
C (11)	10076 (9)	1810 (15)	3397 (3)	37 (4)
C (12)	9667 (9)	591 (15)	3463 (3)	38 (4)
C (13)	9051 (9)	-7 (17)	3241 (3)	43 (4)
C (14)	8879 (9)	764 (18)	2970 (4)	50 (5)
C (15)	9219 (10)	2038 (17)	2897 (3)	44 (4)
C (16)	8997 (11)	2790 (20)	2608 (4)	60 (5)
C (17)	9369 (13)	3990 (20)	2548 (4)	71 (6)
C (18)	9969 (13)	4549 (18)	2760 (4)	64 (5)
C (19)	10221 (10)	3834 (15)	3037 (3)	47 (4)
C (20)	9843 (9)	2552 (14)	3111 (3)	37 (4)
C (21)	10511 (12)	6385 (17)	4331 (4)	74 (6)
C (22)	10983 (11)	4031 (17)	4793 (3)	56 (5)
C (23)	12331 (11)	5749 (19)	4484 (4)	67 (5)
C (24)	7493 (14)	-1570 (20)	3469 (5)	103 (8)
C (25)	9128 (15)	-3087 (19)	3490 (6)	124 (10)
C (26)	8366 (13)	-2390 (20)	2846 (5)	95 (7)
C (27)	8605 (17)	738 (19)	4488 (5)	92 (8)
C (28)	8563 (13)	1670 (20)	4791 (4)	90 (7)
C (29)	7810 (11)	1080 (30)	4235 (7)	140 (11)
C (30)	8575 (12)	-714 (19)	4595 (5)	80 (6)

Table 3. Bond lengths [Å] and angles [deg] for 6.

Ge-O	1.827 (11)
Ge-C (27)	1.89 (2)
Ge-S (2)	2.213 (4)
Ge-S (1)	2.226 (4)
S (1)-C (2)	1.783 (14)
Si (1)-C (21)	1.826 (17)
Si (1)-C (22)	1.857 (15)
Si (1)-C (23)	1.885 (17)
Si (1)-C (3)	1.892 (14)
C (1)-C (2)	1.362 (18)
C (1)-C (10)	1.400 (18)
C (1)-C (11)	1.520 (18)
S (2)-C (12)	1.796 (15)
Si (2)-C (24)	1.82 (2)
Si (2)-C (25)	1.85 (2)
Si (2)-C (26)	1.842 (18)
Si (2)-C (13)	1.900 (16)
C (2)-C (3)	1.430 (19)
C (3)-C (4)	1.382 (19)
C (4)-C (5)	1.42 (2)
C (5)-C (6)	1.40 (2)
C (5)-C (10)	1.426 (19)
C (6)-C (7)	1.35 (2)
C (7)-C (8)	1.39 (2)
C (8)-C (9)	1.36 (2)
C (9)-C (10)	1.40 (2)
C (11)-C (12)	1.380 (19)
C (11)-C (20)	1.416 (18)
C (12)-C (13)	1.448 (19)
C (13)-C (14)	1.36 (2)
C (14)-C (15)	1.39 (2)
C (15)-C (20)	1.404 (19)
C (15)-C (16)	1.43 (2)
C (16)-C (17)	1.33 (2)
C (17)-C (18)	1.39 (2)
C (18)-C (19)	1.38 (2)
C (19)-C (20)	1.418 (19)
C (27)-C (30)	1.48 (2)
C (27)-C (28)	1.53 (2)
C (27)-C (29)	1.65 (3)
O-Ge-C (27)	103.6 (9)
O-Ge-S (2)	102.2 (4)
C (27)-Ge-S (2)	116.9 (6)
O-Ge-S (1)	110.8 (4)
C (27)-Ge-S (1)	113.1 (6)
S (2)-Ge-S (1)	109.36 (16)
C (2)-S (1)-Ge	94.8 (5)
C (21)-Si (1)-C (22)	112.2 (8)
C (21)-Si (1)-C (23)	107.7 (9)
C (22)-Si (1)-C (23)	105.7 (7)
C (21)-Si (1)-C (3)	111.5 (7)
C (22)-Si (1)-C (3)	113.0 (7)
C (23)-Si (1)-C (3)	106.2 (7)

C(2)-C(1)-C(10)	121.9(13)
C(2)-C(1)-C(11)	122.3(12)
C(10)-C(1)-C(11)	115.5(12)
C(12)-S(2)-Ge	105.1(5)
C(24)-Si(2)-C(25)	108.3(11)
C(24)-Si(2)-C(26)	109.4(9)
C(25)-Si(2)-C(26)	106.3(11)
C(24)-Si(2)-C(13)	109.2(8)
C(25)-Si(2)-C(13)	115.7(8)
C(26)-Si(2)-C(13)	107.8(8)
C(1)-C(2)-C(3)	121.5(13)
C(1)-C(2)-S(1)	119.5(11)
C(3)-C(2)-S(1)	119.1(10)
C(4)-C(3)-C(2)	116.2(13)
C(4)-C(3)-Si(1)	118.7(11)
C(2)-C(3)-Si(1)	125.1(11)
C(3)-C(4)-C(5)	123.9(14)
C(6)-C(5)-C(4)	122.9(15)
C(6)-C(5)-C(10)	119.4(14)
C(4)-C(5)-C(10)	117.7(14)
C(7)-C(6)-C(5)	120.8(16)
C(6)-C(7)-C(8)	121.9(16)
C(9)-C(8)-C(7)	117.7(15)
C(8)-C(9)-C(10)	123.6(16)
C(1)-C(10)-C(9)	124.9(14)
C(1)-C(10)-C(5)	118.6(13)
C(9)-C(10)-C(5)	116.5(14)
C(12)-C(11)-C(20)	118.7(13)
C(12)-C(11)-C(1)	122.5(13)
C(20)-C(11)-C(1)	118.7(13)
C(11)-C(12)-C(13)	122.6(14)
C(11)-C(12)-S(2)	119.7(11)
C(13)-C(12)-S(2)	117.8(11)
C(14)-C(13)-C(12)	114.5(14)
C(14)-C(13)-Si(2)	117.2(11)
C(12)-C(13)-Si(2)	128.1(12)
C(13)-C(14)-C(15)	126.4(14)
C(14)-C(15)-C(20)	117.2(14)
C(14)-C(15)-C(16)	123.0(16)
C(20)-C(15)-C(16)	119.7(15)
C(17)-C(16)-C(15)	119.7(16)
C(16)-C(17)-C(18)	122.2(16)
C(19)-C(18)-C(17)	120.0(16)
C(18)-C(19)-C(20)	119.9(15)
C(15)-C(20)-C(19)	118.5(13)
C(15)-C(20)-C(11)	120.4(13)
C(19)-C(20)-C(11)	121.1(13)
C(30)-C(27)-C(28)	109.4(16)
C(30)-C(27)-C(29)	111(2)
C(28)-C(27)-C(29)	110.2(18)
C(30)-C(27)-Ge	111.7(15)
C(28)-C(27)-Ge	110.4(15)
C(29)-C(27)-Ge	104.6(13)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 6.
The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Ge	71 (1)	53 (1)	51 (1)	-2 (1)	21 (1)	-9 (1)
O	95 (10)	88 (10)	70 (8)	4 (7)	-31 (8)	8 (9)
S (1)	46 (2)	47 (2)	44 (2)	-5 (2)	13 (2)	-1 (2)
Si (1)	64 (3)	45 (3)	35 (2)	-4 (2)	-7 (2)	-2 (2)
C (1)	36 (8)	32 (8)	26 (7)	11 (7)	0 (7)	-14 (7)
S (2)	64 (3)	46 (2)	40 (2)	2 (2)	9 (2)	2 (2)
Si (2)	45 (3)	52 (3)	69 (3)	-5 (3)	-1 (3)	-13 (3)
C (2)	34 (8)	38 (9)	34 (8)	-2 (7)	-12 (7)	7 (7)
C (3)	56 (10)	34 (8)	30 (8)	0 (7)	4 (7)	5 (8)
C (4)	41 (9)	63 (12)	31 (8)	3 (8)	-11 (7)	-1 (9)
C (5)	55 (11)	48 (10)	30 (8)	10 (7)	-13 (8)	0 (9)
C (6)	34 (9)	66 (12)	59 (11)	2 (10)	3 (9)	-4 (9)
C (7)	41 (11)	86 (14)	60 (12)	11 (11)	4 (9)	29 (11)
C (8)	70 (13)	71 (12)	38 (8)	-10 (9)	15 (10)	-6 (12)
C (9)	62 (12)	67 (12)	44 (10)	1 (9)	0 (9)	6 (10)
C (10)	36 (9)	45 (10)	24 (7)	-4 (7)	-1 (7)	-2 (7)
C (11)	43 (9)	38 (9)	29 (8)	-13 (7)	2 (7)	-9 (8)
C (12)	30 (8)	44 (9)	41 (8)	-8 (7)	4 (7)	-2 (8)
C (13)	30 (8)	67 (11)	33 (8)	-18 (8)	1 (7)	-9 (8)
C (14)	20 (8)	83 (14)	46 (10)	-26 (10)	-7 (7)	-8 (9)
C (15)	37 (9)	60 (11)	36 (9)	-2 (8)	-2 (8)	4 (8)
C (16)	55 (11)	86 (14)	37 (10)	6 (9)	-21 (9)	-1 (11)
C (17)	106 (17)	65 (13)	43 (10)	9 (11)	4 (11)	33 (13)
C (18)	104 (15)	42 (10)	47 (10)	12 (9)	0 (11)	-12 (11)
C (19)	57 (10)	42 (9)	43 (8)	5 (8)	-1 (8)	-16 (9)
C (20)	51 (10)	36 (8)	22 (7)	1 (7)	1 (7)	1 (8)
C (21)	94 (15)	58 (12)	69 (12)	-20 (9)	-19 (11)	10 (11)
C (22)	75 (12)	57 (11)	36 (8)	-1 (8)	-15 (8)	-6 (10)
C (23)	77 (13)	84 (14)	41 (9)	-11 (10)	-13 (9)	-16 (11)
C (24)	83 (14)	110 (19)	115 (17)	-42 (16)	11 (15)	-29 (14)
C (25)	130 (20)	43 (13)	200 (30)	-11 (16)	-70 (20)	-3 (13)
C (26)	104 (17)	100 (17)	82 (14)	-28 (13)	-11 (13)	-41 (15)
C (27)	160 (20)	48 (12)	71 (14)	-6 (11)	53 (15)	-12 (14)
C (28)	99 (16)	93 (16)	78 (13)	-23 (12)	63 (12)	4 (13)
C (29)	37 (12)	150 (20)	230 (30)	-50 (20)	-14 (16)	17 (15)
C (30)	73 (13)	90 (16)	79 (13)	-11 (12)	56 (11)	-18 (12)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 6.

	x	y	z	U (eq)
H (0A)	10434	25	4599	126
H (4A)	12611	4119	3994	54
H (6A)	13601	3028	3597	64
H (7A)	13815	1656	3157	75
H (8A)	12701	458	2914	72
H (9A)	11358	770	3113	69
H (14A)	8495	402	2819	60
H (16A)	8594	2448	2462	72
H (17A)	9222	4466	2358	85
H (18A)	10200	5406	2715	77
H (19A)	10639	4193	3174	57
H (21A)	9951	6022	4296	111
H (21B)	10690	6879	4138	111
H (21C)	10503	6993	4517	111
H (22A)	10430	3626	4771	83
H (22B)	10984	4652	4976	83
H (22C)	11396	3324	4829	83
H (23A)	12308	6345	4672	101
H (23B)	12502	6263	4293	101
H (23C)	12735	5030	4524	101
H (24A)	7224	-2446	3484	154
H (24B)	7142	-959	3342	154
H (24C)	7571	-1195	3686	154
H (25A)	8808	-3924	3493	185
H (25B)	9231	-2793	3712	185
H (25C)	9660	-3236	3380	185
H (26A)	8096	-3273	2854	143
H (26B)	8907	-2471	2739	143
H (26C)	8013	-1763	2726	143
H (28A)	8059	1466	4915	135
H (28B)	8550	2610	4722	135
H (28C)	9054	1517	4927	135
H (29A)	7280	915	4345	210
H (29B)	7850	507	4044	210
H (29C)	7838	2027	4169	210
H (30A)	8067	-870	4720	121
H (30B)	9062	-914	4728	121
H (30C)	8575	-1298	4404	121

ORTEP of 7b

Table 1. Crystal data and structure refinement for 7b.

Identification code	gio599a
Empirical formula	C ₃₀ H ₃₈ Ge S ₂ Si ₂
Formula weight	591.49
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 15.7160(10) Å alpha = 90 deg. b = 9.761(3) Å beta = 90 deg. c = 40.615(6) Å gamma = 90 deg.
Volume	6230(2) Å ³
Z, Calculated density	8, 1.261 Mg/m ³
Absorption coefficient	1.211 mm ⁻¹
F(000)	2480
Crystal size	0.30 x 0.20 x 0.20 mm
Theta range for data collection	2.01 to 25.00 deg.
Limiting indices	0 ≤ h ≤ 18, 0 ≤ k ≤ 11, -48 ≤ l ≤ 0
Reflections collected / unique	5469 / 5469 [R(int) = 0.0000]
Completeness to theta = 25.00	99.6 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5469 / 0 / 320
Goodness-of-fit on F ²	1.708
Final R indices [I > 2sigma(I)]	R ₁ = 0.1411, wR ₂ = 0.3086
R indices (all data)	R ₁ = 0.2464, wR ₂ = 0.3538
Largest diff. peak and hole	5.885 and -1.315 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 7b.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U (eq)
Ge	9669 (1)	1159 (2)	4253 (1)	58 (1)
S (1)	9680 (2)	3293 (4)	4049 (1)	39 (1)
Si (1)	11326 (3)	4972 (4)	4409 (1)	41 (1)
C (1)	10823 (8)	2324 (11)	3596 (3)	27 (3)
S (2)	9942 (2)	-310 (4)	3849 (1)	44 (1)
Si (2)	8534 (3)	-1786 (4)	3293 (1)	49 (1)
C (2)	10727 (7)	3112 (13)	3885 (3)	30 (3)
C (3)	11411 (8)	3832 (12)	4033 (3)	32 (3)
C (4)	12204 (8)	3639 (12)	3885 (3)	33 (3)
C (5)	12353 (8)	2809 (13)	3620 (3)	33 (3)
C (6)	13181 (9)	2581 (15)	3482 (3)	50 (4)
C (7)	13292 (10)	1758 (18)	3224 (4)	60 (4)
C (8)	12622 (9)	1057 (15)	3085 (3)	45 (4)
C (9)	11816 (9)	1242 (15)	3202 (3)	47 (4)
C (10)	11658 (8)	2120 (12)	3472 (3)	31 (3)
C (11)	10098 (8)	1796 (13)	3402 (3)	34 (3)
C (12)	9674 (8)	567 (14)	3476 (3)	37 (3)
C (13)	9072 (8)	-15 (14)	3258 (3)	36 (3)
C (14)	8874 (8)	717 (15)	2984 (4)	46 (4)
C (15)	9211 (8)	1996 (16)	2910 (3)	43 (4)
C (16)	8981 (10)	2737 (16)	2622 (3)	52 (4)
C (17)	9366 (11)	3957 (18)	2547 (4)	64 (5)
C (18)	9962 (10)	4515 (15)	2766 (4)	53 (4)
C (19)	10217 (8)	3807 (14)	3032 (3)	38 (3)
C (20)	9831 (7)	2535 (13)	3115 (3)	28 (3)
C (21)	10558 (11)	6421 (15)	4341 (4)	78 (6)
C (22)	11007 (11)	3985 (17)	4771 (3)	66 (5)
C (23)	12408 (10)	5700 (18)	4496 (3)	71 (5)
C (24)	7462 (11)	-1547 (19)	3479 (4)	91 (6)
C (25)	9149 (14)	-3131 (18)	3515 (6)	116 (8)
C (26)	8381 (11)	-2437 (18)	2870 (4)	85 (6)
C (27)	8625 (13)	798 (18)	4489 (4)	77 (6)
C (28)	8593 (13)	1830 (20)	4783 (4)	107 (8)
C (29)	7872 (14)	1070 (30)	4247 (8)	170 (13)
C (30)	8577 (13)	-652 (19)	4594 (5)	102 (7)

Table 3. Bond lengths [Å] and angles [deg] for 7b.

Ge-C (27)	1.933 (16)
Ge-S (2)	2.221 (4)
Ge-S (1)	2.241 (4)
S (1)-C (2)	1.785 (12)
Si (1)-C (22)	1.829 (14)
Si (1)-C (23)	1.877 (15)
Si (1)-C (21)	1.880 (15)
Si (1)-C (3)	1.893 (12)
C (1)-C (2)	1.410 (15)
C (1)-C (10)	1.420 (16)
C (1)-C (11)	1.479 (16)
S (2)-C (12)	1.793 (13)
Si (2)-C (26)	1.849 (15)
Si (2)-C (24)	1.859 (17)
Si (2)-C (25)	1.863 (19)
Si (2)-C (13)	1.929 (14)
C (2)-C (3)	1.420 (16)
C (3)-C (4)	1.398 (16)
C (4)-C (5)	1.366 (16)
C (5)-C (10)	1.417 (16)
C (5)-C (6)	1.434 (18)
C (6)-C (7)	1.333 (19)
C (7)-C (8)	1.375 (19)
C (8)-C (9)	1.365 (17)
C (9)-C (10)	1.413 (17)
C (11)-C (12)	1.404 (18)
C (11)-C (20)	1.431 (16)
C (12)-C (13)	1.415 (17)
C (13)-C (14)	1.358 (18)
C (14)-C (15)	1.39 (2)
C (15)-C (20)	1.386 (16)
C (15)-C (16)	1.422 (18)
C (16)-C (17)	1.37 (2)
C (17)-C (18)	1.40 (2)
C (18)-C (19)	1.344 (18)
C (19)-C (20)	1.422 (17)
C (27)-C (30)	1.48 (2)
C (27)-C (28)	1.56 (2)
C (27)-C (29)	1.56 (3)
C (27)-Ge-S (2)	114.4 (6)
C (27)-Ge-S (1)	111.0 (6)
S (2)-Ge-S (1)	109.04 (13)
C (2)-S (1)-Ge	93.1 (4)
C (22)-Si (1)-C (23)	107.3 (7)
C (22)-Si (1)-C (21)	109.8 (8)
C (23)-Si (1)-C (21)	108.9 (8)
C (22)-Si (1)-C (3)	111.0 (6)
C (23)-Si (1)-C (3)	108.0 (6)
C (21)-Si (1)-C (3)	111.7 (6)
C (2)-C (1)-C (10)	118.1 (11)
C (2)-C (1)-C (11)	123.5 (11)
C (10)-C (1)-C (11)	118.3 (10)

C (12) -S (2) -Ge	105.7 (4)
C (26) -Si (2) -C (24)	107.5 (8)
C (26) -Si (2) -C (25)	106.0 (10)
C (24) -Si (2) -C (25)	111.2 (10)
C (26) -Si (2) -C (13)	107.2 (7)
C (24) -Si (2) -C (13)	108.4 (7)
C (25) -Si (2) -C (13)	116.1 (7)
C (1) -C (2) -C (3)	122.9 (11)
C (1) -C (2) -S (1)	117.7 (9)
C (3) -C (2) -S (1)	119.3 (9)
C (4) -C (3) -C (2)	115.1 (10)
C (4) -C (3) -Si (1)	119.4 (9)
C (2) -C (3) -Si (1)	125.5 (9)
C (5) -C (4) -C (3)	124.9 (11)
C (4) -C (5) -C (10)	118.9 (11)
C (4) -C (5) -C (6)	123.7 (12)
C (10) -C (5) -C (6)	117.4 (11)
C (7) -C (6) -C (5)	121.3 (13)
C (6) -C (7) -C (8)	121.4 (14)
C (9) -C (8) -C (7)	120.2 (13)
C (8) -C (9) -C (10)	120.8 (13)
C (9) -C (10) -C (5)	118.8 (12)
C (9) -C (10) -C (1)	121.5 (11)
C (5) -C (10) -C (1)	119.7 (11)
C (12) -C (11) -C (20)	117.7 (11)
C (12) -C (11) -C (1)	123.4 (11)
C (20) -C (11) -C (1)	118.9 (11)
C (11) -C (12) -C (13)	121.8 (12)
C (11) -C (12) -S (2)	118.4 (10)
C (13) -C (12) -S (2)	119.7 (10)
C (14) -C (13) -C (12)	117.0 (12)
C (14) -C (13) -Si (2)	115.6 (10)
C (12) -C (13) -Si (2)	127.3 (10)
C (13) -C (14) -C (15)	124.2 (12)
C (20) -C (15) -C (14)	118.7 (12)
C (20) -C (15) -C (16)	118.7 (14)
C (14) -C (15) -C (16)	122.5 (13)
C (17) -C (16) -C (15)	120.8 (14)
C (16) -C (17) -C (18)	119.5 (14)
C (19) -C (18) -C (17)	120.7 (14)
C (18) -C (19) -C (20)	120.8 (12)
C (15) -C (20) -C (19)	119.2 (11)
C (15) -C (20) -C (11)	120.2 (12)
C (19) -C (20) -C (11)	120.5 (11)
C (30) -C (27) -C (28)	113.2 (15)
C (30) -C (27) -C (29)	107.9 (19)
C (28) -C (27) -C (29)	110.3 (17)
C (30) -C (27) -Ge	111.1 (12)
C (28) -C (27) -Ge	106.8 (12)
C (29) -C (27) -Ge	107.5 (13)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 7b.
The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Ge	73 (1)	54 (1)	47 (1)	-3 (1)	18 (1)	2 (1)
S (1)	39 (2)	41 (2)	36 (2)	-4 (2)	6 (2)	2 (2)
Si (1)	55 (3)	38 (2)	30 (2)	-5 (2)	-6 (2)	2 (2)
C (1)	38 (7)	18 (6)	25 (6)	2 (5)	2 (6)	-7 (6)
S (2)	56 (2)	43 (2)	32 (2)	0 (2)	6 (2)	-1 (2)
Si (2)	37 (2)	47 (3)	63 (3)	-10 (2)	0 (2)	-7 (2)
C (2)	30 (7)	32 (7)	29 (6)	6 (6)	2 (6)	-1 (6)
C (3)	44 (8)	34 (7)	17 (6)	-2 (6)	-9 (6)	-4 (7)
C (4)	24 (7)	42 (8)	33 (7)	3 (6)	-5 (5)	-1 (6)
C (5)	36 (8)	37 (8)	25 (6)	1 (6)	1 (6)	-3 (6)
C (6)	44 (9)	61 (10)	46 (9)	-2 (8)	-12 (7)	-16 (8)
C (7)	56 (11)	83 (12)	40 (8)	-2 (9)	12 (8)	15 (10)
C (8)	43 (9)	67 (10)	26 (6)	-15 (7)	0 (6)	0 (8)
C (9)	46 (9)	59 (10)	34 (7)	-14 (7)	-4 (7)	-7 (8)
C (10)	38 (8)	32 (8)	23 (6)	1 (6)	3 (6)	-2 (6)
C (11)	41 (8)	32 (7)	29 (7)	-9 (6)	3 (6)	-1 (7)
C (12)	31 (8)	46 (8)	35 (7)	-8 (6)	14 (6)	2 (7)
C (13)	30 (7)	45 (9)	34 (7)	4 (7)	-4 (6)	-2 (6)
C (14)	22 (7)	57 (10)	61 (10)	-30 (8)	-11 (7)	1 (7)
C (15)	27 (7)	63 (11)	40 (8)	-23 (8)	-15 (6)	19 (7)
C (16)	65 (11)	54 (10)	36 (8)	-13 (7)	-23 (7)	14 (9)
C (17)	88 (13)	62 (12)	41 (9)	3 (9)	10 (9)	30 (11)
C (18)	59 (10)	43 (9)	56 (9)	-8 (8)	-5 (8)	-7 (8)
C (19)	44 (8)	52 (8)	20 (6)	4 (6)	-8 (6)	6 (7)
C (20)	27 (7)	36 (7)	20 (6)	-6 (6)	7 (5)	4 (6)
C (21)	106 (15)	38 (10)	89 (13)	-15 (9)	-48 (11)	26 (9)
C (22)	90 (13)	64 (11)	44 (8)	5 (8)	-8 (8)	-2 (10)
C (23)	86 (13)	80 (12)	47 (8)	-22 (9)	-11 (9)	-29 (10)
C (24)	63 (12)	113 (16)	98 (13)	-25 (13)	20 (11)	-36 (11)
C (25)	108 (17)	40 (11)	200 (20)	15 (14)	-58 (17)	-21 (11)
C (26)	111 (15)	78 (13)	65 (11)	-41 (10)	15 (10)	-53 (12)
C (27)	99 (15)	66 (12)	66 (11)	17 (10)	45 (11)	-2 (11)
C (28)	137 (18)	121 (17)	64 (11)	-28 (12)	87 (12)	1 (14)
C (29)	63 (15)	150 (30)	290 (40)	-30 (30)	-10 (20)	0 (16)
C (30)	128 (17)	81 (14)	97 (14)	28 (12)	80 (13)	-5 (13)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 7b.

	x	y	z	U (eq)
H	10480 (50)	960 (80)	4543 (19)	0 (20)
H (4A)	12666	4110	3973	39
H (6A)	13650	3015	3575	60
H (7A)	13833	1655	3135	72
H (8A)	12718	455	2912	54
H (9A)	11364	785	3103	56
H (14A)	8487	338	2836	56
H (16A)	8563	2390	2483	62
H (17A)	9233	4412	2353	76
H (18A)	10183	5383	2727	63
H (19A)	10651	4154	3164	46
H (21A)	10526	6971	4537	116
H (21B)	10005	6057	4291	116
H (21C)	10751	6975	4161	116
H (22A)	10962	4585	4958	99
H (22B)	11425	3291	4815	99
H (22C)	10466	3560	4731	99
H (23A)	12380	6282	4686	106
H (23B)	12597	6223	4309	106
H (23C)	12801	4966	4536	106
H (24A)	7185	-2420	3498	137
H (24B)	7129	-958	3340	137
H (24C)	7520	-1141	3693	137
H (25A)	8826	-3965	3520	174
H (25B)	9260	-2832	3736	174
H (25C)	9678	-3288	3404	174
H (26A)	8110	-3318	2878	127
H (26B)	8923	-2520	2763	127
H (26C)	8029	-1811	2749	127
H (28A)	8079	1684	4906	161
H (28B)	8603	2747	4700	161
H (28D)	9076	1681	4923	161
H (29A)	7342	904	4358	255
H (29D)	7920	474	4060	255
H (29B)	7890	2008	4174	255
H (30D)	8053	-805	4710	153
H (30A)	9048	-856	4736	153
H (30B)	8600	-1234	4404	153

ORTEP of 19a

Table 1. Crystal data and structure refinement for 19a.

Identification code	gio298
Empirical formula	C ₂₉ H ₃₀ Ge O ₂ S ₂
Formula weight	547.24
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 10.035(2) Å alpha = 90 deg. b = 9.3460(19) Å beta = 98.94(3) deg. c = 28.948(6) Å gamma = 90 deg.
Volume	2681.9(9) Å ³
Z, Calculated density	4, 1.355 Mg/m ³
Absorption coefficient	1.322 mm ⁻¹
F(000)	1136
Crystal size	0.21 x 0.24 x 0.36 mm
Theta range for data collection	2.29 to 26.00 deg.
Limiting indices	0 ≤ h ≤ 7, 0 ≤ k ≤ 11, -35 ≤ l ≤ 35
Reflections collected / unique	4143 / 3830 [R(int) = 0.0447]
Completeness to theta = 26.00	72.6 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3830 / 0 / 307
Goodness-of-fit on F ²	1.057
Final R indices [I > 2σ(I)]	R ₁ = 0.0619, wR ₂ = 0.1240
R indices (all data)	R ₁ = 0.1337, wR ₂ = 0.1604
Largest diff. peak and hole	0.556 and -0.315 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 19a. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U (eq)
Ge	3124 (1)	4654 (1)	5965 (1)	49 (1)
S (1)	4702 (2)	3519 (2)	5627 (1)	53 (1)
S (2)	3963 (2)	4724 (2)	6728 (1)	51 (1)
O (1)	1840 (7)	2861 (7)	4964 (2)	91 (2)
O (2)	2523 (7)	621 (6)	5135 (2)	76 (2)
C (1)	6213 (7)	3975 (8)	6019 (2)	39 (2)
C (2)	7088 (8)	4949 (8)	5840 (2)	49 (2)
C (3)	8268 (9)	5303 (9)	6108 (3)	59 (2)
C (4)	8651 (9)	4752 (8)	6555 (3)	49 (2)
C (5)	9881 (9)	5113 (9)	6852 (3)	65 (3)
C (6)	10196 (10)	4578 (10)	7285 (3)	74 (3)
C (7)	9336 (10)	3638 (9)	7470 (3)	69 (3)
C (8)	8143 (8)	3262 (8)	7205 (2)	50 (2)
C (9)	7748 (8)	3789 (7)	6740 (2)	40 (2)
C (10)	6536 (8)	3402 (8)	6459 (2)	41 (2)
C (11)	5573 (9)	2396 (8)	6640 (2)	41 (2)
C (12)	5924 (9)	899 (8)	6695 (2)	41 (2)
C (13)	7076 (9)	330 (9)	6547 (3)	53 (2)
C (14)	7402 (10)	-1073 (9)	6609 (3)	64 (3)
C (15)	6596 (12)	-1995 (10)	6820 (3)	72 (3)
C (16)	5473 (11)	-1486 (9)	6967 (3)	63 (3)
C (17)	5058 (10)	-34 (8)	6897 (2)	50 (2)
C (18)	3882 (10)	518 (9)	7033 (3)	59 (2)
C (19)	3533 (8)	1928 (9)	6977 (2)	52 (2)
C (20)	4413 (9)	2861 (8)	6781 (2)	45 (2)
C (21)	1506 (8)	3451 (9)	5883 (3)	61 (2)
C (22)	1643 (8)	1922 (8)	5715 (3)	53 (2)
C (23)	2013 (9)	1892 (10)	5234 (3)	56 (2)
C (24)	2934 (11)	518 (11)	4679 (3)	98 (4)
C (25)	343 (9)	1068 (9)	5727 (3)	79 (3)
C (26)	2823 (9)	6668 (8)	5752 (3)	56 (2)
C (27)	1876 (10)	6683 (10)	5290 (3)	90 (3)
C (28)	2211 (9)	7485 (8)	6120 (3)	74 (3)
C (29)	4181 (9)	7322 (9)	5691 (3)	79 (3)

Table 3. Bond lengths [Å] and angles [deg] for 19a.

Ge-C (21)	1.958 (8)
Ge-C (26)	1.989 (8)
Ge-S (2)	2.240 (2)
Ge-S (1)	2.252 (2)
S (1)-C (1)	1.799 (7)
S (2)-C (20)	1.799 (8)
O (1)-C (23)	1.192 (9)
O (2)-C (23)	1.343 (10)
O (2)-C (24)	1.446 (9)
C (1)-C (10)	1.374 (9)
C (1)-C (2)	1.418 (10)
C (2)-C (3)	1.352 (10)
C (3)-C (4)	1.392 (10)
C (4)-C (5)	1.430 (11)
C (4)-C (9)	1.437 (10)
C (5)-C (6)	1.342 (11)
C (6)-C (7)	1.395 (11)
C (7)-C (8)	1.362 (10)
C (8)-C (9)	1.433 (9)
C (9)-C (10)	1.400 (9)
C (10)-C (11)	1.500 (10)
C (11)-C (20)	1.363 (10)
C (11)-C (12)	1.445 (10)
C (12)-C (13)	1.400 (10)
C (12)-C (17)	1.420 (10)
C (13)-C (14)	1.357 (10)
C (14)-C (15)	1.388 (12)
C (15)-C (16)	1.352 (11)
C (16)-C (17)	1.425 (11)
C (17)-C (18)	1.398 (11)
C (18)-C (19)	1.367 (11)
C (19)-C (20)	1.420 (10)
C (21)-C (22)	1.521 (10)
C (22)-C (23)	1.495 (11)
C (22)-C (25)	1.534 (10)
C (26)-C (27)	1.516 (11)
C (26)-C (28)	1.516 (11)
C (26)-C (29)	1.529 (11)
C (21)-Ge-C (26)	115.0 (4)
C (21)-Ge-S (2)	108.3 (3)
C (26)-Ge-S (2)	107.0 (2)
C (21)-Ge-S (1)	107.6 (3)
C (26)-Ge-S (1)	113.2 (3)
S (2)-Ge-S (1)	105.09 (8)
C (1)-S (1)-Ge	101.2 (2)
C (20)-S (2)-Ge	96.1 (2)
C (23)-O (2)-C (24)	115.3 (7)
C (10)-C (1)-C (2)	121.3 (7)
C (10)-C (1)-S (1)	123.2 (6)
C (2)-C (1)-S (1)	115.4 (5)
C (3)-C (2)-C (1)	118.9 (7)
C (2)-C (3)-C (4)	122.3 (8)

C (3) -C (4) -C (5)	124.0 (8)
C (3) -C (4) -C (9)	118.6 (8)
C (5) -C (4) -C (9)	117.4 (7)
C (6) -C (5) -C (4)	121.9 (8)
C (5) -C (6) -C (7)	121.5 (8)
C (8) -C (7) -C (6)	119.3 (8)
C (7) -C (8) -C (9)	122.0 (8)
C (10) -C (9) -C (8)	123.0 (7)
C (10) -C (9) -C (4)	119.2 (7)
C (8) -C (9) -C (4)	117.8 (7)
C (1) -C (10) -C (9)	119.7 (7)
C (1) -C (10) -C (11)	119.7 (7)
C (9) -C (10) -C (11)	120.6 (6)
C (20) -C (11) -C (12)	118.7 (7)
C (20) -C (11) -C (10)	122.1 (7)
C (12) -C (11) -C (10)	119.1 (7)
C (13) -C (12) -C (17)	118.7 (8)
C (13) -C (12) -C (11)	122.2 (8)
C (17) -C (12) -C (11)	119.0 (8)
C (14) -C (13) -C (12)	121.4 (9)
C (13) -C (14) -C (15)	120.9 (9)
C (16) -C (15) -C (14)	119.5 (9)
C (15) -C (16) -C (17)	122.0 (9)
C (18) -C (17) -C (12)	119.1 (7)
C (18) -C (17) -C (16)	123.5 (8)
C (12) -C (17) -C (16)	117.4 (9)
C (19) -C (18) -C (17)	122.3 (8)
C (18) -C (19) -C (20)	118.3 (8)
C (11) -C (20) -C (19)	122.5 (7)
C (11) -C (20) -S (2)	119.8 (6)
C (19) -C (20) -S (2)	117.7 (7)
C (22) -C (21) -Ge	117.6 (6)
C (23) -C (22) -C (21)	111.2 (7)
C (23) -C (22) -C (25)	110.2 (7)
C (21) -C (22) -C (25)	111.2 (7)
O (1) -C (23) -O (2)	123.5 (8)
O (1) -C (23) -C (22)	124.5 (9)
O (2) -C (23) -C (22)	112.0 (7)
C (27) -C (26) -C (28)	110.4 (7)
C (27) -C (26) -C (29)	109.9 (7)
C (28) -C (26) -C (29)	110.3 (7)
C (27) -C (26) -Ge	109.0 (6)
C (28) -C (26) -Ge	108.6 (5)
C (29) -C (26) -Ge	108.6 (5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 19a.
The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Ge	46 (1)	48 (1)	51 (1)	5 (1)	4 (1)	0 (1)
S (1)	51 (2)	63 (1)	44 (1)	-2 (1)	6 (1)	-3 (1)
S (2)	59 (2)	48 (1)	47 (1)	1 (1)	8 (1)	5 (1)
O (1)	92 (6)	91 (5)	88 (5)	36 (4)	9 (4)	9 (4)
O (2)	98 (6)	60 (4)	76 (4)	-3 (3)	30 (4)	-12 (4)
C (1)	27 (6)	56 (5)	35 (4)	1 (3)	10 (3)	1 (4)
C (2)	40 (7)	65 (6)	39 (4)	12 (4)	-1 (4)	5 (4)
C (3)	71 (8)	50 (5)	60 (5)	17 (4)	23 (5)	1 (5)
C (4)	48 (7)	41 (4)	60 (5)	-3 (4)	12 (4)	-1 (5)
C (5)	57 (8)	60 (6)	77 (6)	2 (5)	6 (5)	-11 (5)
C (6)	53 (8)	70 (6)	90 (7)	-4 (6)	-22 (5)	-12 (6)
C (7)	75 (8)	57 (6)	67 (6)	5 (5)	-18 (5)	-6 (6)
C (8)	54 (7)	45 (5)	48 (4)	1 (4)	-1 (4)	5 (4)
C (9)	27 (6)	42 (4)	51 (4)	-5 (4)	-2 (4)	1 (4)
C (10)	31 (6)	43 (4)	50 (5)	1 (4)	7 (4)	-1 (4)
C (11)	41 (7)	48 (5)	32 (4)	-1 (3)	2 (4)	-4 (4)
C (12)	48 (7)	49 (5)	25 (4)	1 (3)	0 (4)	4 (5)
C (13)	58 (7)	47 (5)	52 (5)	-4 (4)	4 (4)	0 (5)
C (14)	75 (8)	54 (6)	64 (6)	-6 (5)	10 (5)	8 (6)
C (15)	97 (10)	42 (5)	75 (6)	-3 (5)	6 (6)	9 (6)
C (16)	92 (9)	41 (5)	53 (5)	11 (4)	-1 (5)	-18 (5)
C (17)	64 (8)	51 (6)	32 (4)	1 (3)	0 (4)	-17 (5)
C (18)	68 (8)	62 (6)	49 (5)	6 (4)	16 (5)	-25 (6)
C (19)	42 (6)	64 (6)	50 (5)	4 (4)	14 (4)	-5 (5)
C (20)	47 (7)	53 (5)	36 (4)	5 (4)	14 (4)	-1 (5)
C (21)	44 (6)	63 (6)	77 (6)	3 (5)	14 (5)	-1 (5)
C (22)	43 (6)	48 (5)	64 (5)	9 (4)	-2 (4)	-5 (4)
C (23)	42 (7)	66 (6)	56 (5)	9 (5)	-7 (4)	-17 (5)
C (24)	112 (10)	113 (9)	80 (7)	-26 (6)	43 (6)	-28 (8)
C (25)	70 (8)	69 (6)	101 (7)	13 (5)	23 (6)	-24 (6)
C (26)	51 (7)	47 (5)	69 (5)	5 (4)	7 (5)	6 (5)
C (27)	100 (9)	73 (7)	82 (7)	15 (5)	-30 (6)	3 (6)
C (28)	78 (8)	47 (5)	94 (7)	19 (5)	9 (6)	15 (5)
C (29)	71 (8)	61 (6)	105 (8)	33 (5)	10 (6)	-1 (6)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 19a.

	x	y	z	U (eq)
H (2A)	6853	5338	5543	59
H (3A)	8844	5935	5989	70
H (5A)	10480	5737	6741	79
H (6A)	11007	4839	7467	89
H (7A)	9573	3272	7770	83
H (8A)	7568	2645	7331	60
H (13A)	7630	926	6403	64
H (14A)	8176	-1422	6508	77
H (15A)	6827	-2955	6861	87
H (16A)	4954	-2103	7119	76
H (18A)	3318	-96	7165	70
H (19A)	2739	2268	7065	62
H (21A)	1173	3411	6180	73
H (21B)	821	3924	5662	73
H (22A)	2371	1460	5928	63
H (24A)	3294	-419	4640	148
H (24B)	3613	1224	4652	148
H (24C)	2169	679	4441	148
H (25A)	464	105	5626	119
H (25B)	-386	1507	5522	119
H (25C)	139	1058	6040	119
H (27A)	1718	7653	5187	134
H (27B)	1035	6246	5330	134
H (27C)	2274	6158	5061	134
H (28A)	2040	8455	6019	110
H (28B)	2827	7478	6409	110
H (28C)	1379	7040	6166	110
H (29A)	4048	8291	5583	119
H (29B)	4572	6775	5465	119
H (29C)	4775	7310	5984	119

ORTEP of 20

Table 1. Crystal data and structure refinement for 20.

Identification code	gio1099
Empirical formula	C ₃₄ H ₄₅ Ge O S ₂ Si ₂
Formula weight	662.59
Temperature	210(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P $\bar{1}$
Unit cell dimensions	a = 11.990(2) Å alpha = 69.11(3)
deg.	
	b = 17.614(4) Å beta = 87.96(3)
deg.	
	c = 19.631(4) Å gamma = 71.00(3)
deg.	
Volume	3647.5(13) Å ³
Z, Calculated density	4, 1.207 Mg/m ³
Absorption coefficient	1.044 mm ⁻¹
F(000)	1396
Crystal size	? x ? x ? mm
Theta range for data collection	1.80 to 22.50 deg.
Limiting indices	0 ≤ h ≤ 11, -17 ≤ k ≤ 18, -21 ≤ l ≤ 21
Reflections collected / unique	9843 / 9292 [R(int) = 0.0709]
Completeness to theta = 22.50	97.5 %
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	9292 / 0 / 721
Goodness-of-fit on F ²	0.909
Final R indices [I > 2sigma(I)]	R ₁ = 0.0721, wR ₂ = 0.1521
R indices (all data)	R ₁ = 0.1762, wR ₂ = 0.2075
Largest diff. peak and hole	0.444 and -0.371 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 20. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U (eq)
Ge	3825 (1)	5351 (1)	7305 (1)	47 (1)
S (2)	2314 (2)	5936 (2)	6426 (2)	48 (1)
S (1)	3189 (2)	4576 (2)	8339 (2)	49 (1)
Si (2)	2735 (3)	4739 (2)	5219 (2)	50 (1)
O	6159 (10)	2842 (7)	6851 (6)	116 (4)
Si (1)	2164 (3)	5309 (2)	9720 (2)	60 (1)
C (1)	1674 (9)	5246 (6)	8271 (5)	41 (3)
C (2)	1292 (9)	5618 (7)	8813 (5)	39 (3)
C (3)	149 (10)	6191 (7)	8682 (6)	49 (3)
C (4)	-631 (9)	6405 (7)	8083 (6)	44 (3)
C (5)	-1788 (10)	7020 (7)	7968 (7)	54 (3)
C (6)	-2545 (10)	7201 (8)	7389 (7)	64 (4)
C (7)	-2202 (10)	6784 (8)	6891 (7)	66 (4)
C (8)	-1086 (10)	6176 (7)	6987 (6)	52 (3)
C (9)	-272 (9)	5977 (7)	7586 (5)	40 (3)
C (10)	899 (9)	5367 (7)	7697 (5)	41 (3)
C (11)	1809 (9)	5038 (6)	6604 (5)	38 (3)
C (12)	1215 (8)	4811 (7)	7228 (5)	42 (3)
C (13)	818 (8)	4092 (7)	7423 (5)	39 (3)
C (14)	226 (9)	3820 (7)	8063 (6)	55 (3)
C (15)	-147 (10)	3140 (7)	8221 (7)	62 (3)
C (16)	2 (10)	2672 (8)	7744 (7)	63 (3)
C (17)	581 (10)	2909 (8)	7128 (6)	57 (3)
C (18)	977 (9)	3613 (7)	6961 (6)	45 (3)
C (19)	1581 (9)	3871 (7)	6317 (6)	52 (3)
C (20)	2015 (8)	4554 (7)	6127 (5)	36 (3)
C (21)	2729 (15)	4121 (9)	10175 (7)	116 (6)
C (22)	3411 (14)	5719 (13)	9645 (8)	139 (8)
C (23)	1137 (13)	5729 (10)	10336 (7)	102 (5)
C (24)	1569 (11)	5002 (9)	4490 (6)	81 (4)
C (25)	3890 (11)	3701 (7)	5303 (7)	74 (4)
C (26)	3400 (10)	5610 (7)	4925 (6)	63 (3)
C (27)	4140 (11)	6374 (8)	7339 (7)	65 (4)
C (28)	5190 (11)	6108 (9)	7897 (7)	87 (4)
C (29)	4419 (13)	6882 (9)	6558 (7)	92 (5)
C (30)	3041 (11)	6964 (7)	7532 (7)	73 (4)
C (31)	5163 (10)	4497 (8)	7090 (6)	64 (3)
C (32)	5782 (11)	3641 (8)	7690 (7)	70 (4)
C (33)	6403 (13)	3718 (10)	8302 (8)	106 (5)
C (34)	6653 (13)	3019 (11)	7397 (9)	107 (5)
Ge'	6372 (1)	401 (1)	1639 (1)	46 (1)
S (1')	8370 (2)	-180 (2)	1754 (2)	48 (1)
S (2')	5843 (2)	884 (2)	2563 (2)	49 (1)
Si (1')	10406 (3)	793 (2)	1053 (2)	59 (1)
Si (2')	4355 (3)	-305 (3)	3798 (2)	69 (1)
O'	5852 (10)	-2330 (7)	2675 (6)	125 (4)

C(1')	8854 (9)	361 (6)	2253 (6)	41 (3)
C(2')	9627 (9)	854 (6)	1902 (5)	39 (3)
C(3')	9983 (9)	1245 (6)	2301 (5)	44 (3)
C(4')	9636 (9)	1200 (7)	3014 (5)	45 (3)
C(5')	10055 (10)	1585 (8)	3414 (7)	64 (3)
C(6')	9745 (11)	1515 (8)	4104 (6)	65 (4)
C(7')	9001 (11)	1037 (8)	4431 (7)	67 (4)
C(8')	8596 (10)	643 (7)	4070 (6)	53 (3)
C(9')	8887 (9)	709 (6)	3341 (5)	42 (3)
C(10')	8529 (9)	267 (6)	2955 (5)	39 (3)
C(11')	6667 (9)	-114 (6)	3279 (5)	40 (3)
C(12')	7869 (9)	-347 (6)	3343 (5)	37 (3)
C(13')	8589 (10)	-1179 (7)	3853 (5)	43 (3)
C(14')	9836 (10)	-1482 (7)	3906 (6)	53 (3)
C(15')	10473 (11)	-2284 (8)	4395 (7)	65 (3)
C(16')	9880 (13)	-2824 (8)	4861 (7)	68 (4)
C(17')	8682 (12)	-2546 (7)	4811 (6)	58 (3)
C(18')	7982 (10)	-1717 (7)	4304 (6)	48 (3)
C(19')	6738 (11)	-1437 (7)	4263 (6)	53 (3)
C(20')	6045 (9)	-650 (7)	3752 (6)	46 (3)
C(21')	11337 (13)	-349 (9)	1260 (8)	105 (5)
C(22')	11382 (12)	1463 (10)	892 (7)	93 (5)
C(23')	9418 (13)	1233 (10)	183 (6)	98 (5)
C(24')	3458 (10)	-35 (11)	2929 (7)	103 (5)
C(25')	4003 (13)	-1205 (10)	4498 (9)	127 (6)
C(26')	3875 (12)	652 (8)	4092 (7)	91 (5)
C(27')	5711 (10)	1425 (7)	746 (6)	55 (3)
C(28')	4348 (11)	1725 (9)	723 (7)	91 (5)
C(29')	6074 (12)	1205 (9)	61 (7)	88 (4)
C(30')	6157 (12)	2146 (8)	743 (7)	87 (4)
C(31')	5809 (10)	-559 (8)	1732 (6)	61 (3)
C(32')	6690 (11)	-1397 (7)	1705 (7)	62 (3)
C(33')	7110 (12)	-1283 (9)	945 (7)	89 (4)
C(34')	6150 (13)	-2116 (9)	1953 (8)	92 (5)

Table 3. Bond lengths [Å] and angles [deg] for 20.

Ge-C (31)	1.961 (11)
Ge-C (27)	1.982 (11)
Ge-S (2)	2.250 (3)
Ge-S (1)	2.271 (3)
S (2)-C (11)	1.791 (10)
S (1)-C (1)	1.794 (11)
Si (2)-C (25)	1.855 (12)
Si (2)-C (26)	1.858 (11)
Si (2)-C (24)	1.861 (12)
Si (2)-C (20)	1.920 (9)
O-C (34)	1.413 (16)
Si (1)-C (22)	1.842 (14)
Si (1)-C (21)	1.851 (14)
Si (1)-C (23)	1.861 (12)
Si (1)-C (2)	1.906 (10)
C (1)-C (10)	1.398 (13)
C (1)-C (2)	1.427 (13)
C (2)-C (3)	1.379 (13)
C (3)-C (4)	1.391 (13)
C (4)-C (9)	1.409 (13)
C (4)-C (5)	1.422 (14)
C (5)-C (6)	1.358 (15)
C (6)-C (7)	1.396 (15)
C (7)-C (8)	1.384 (14)
C (8)-C (9)	1.422 (13)
C (9)-C (10)	1.430 (13)
C (10)-C (12)	1.525 (13)
C (11)-C (12)	1.393 (13)
C (11)-C (20)	1.443 (13)
C (12)-C (13)	1.419 (13)
C (13)-C (18)	1.414 (13)
C (13)-C (14)	1.428 (13)
C (14)-C (15)	1.343 (14)
C (15)-C (16)	1.426 (15)
C (16)-C (17)	1.374 (14)
C (17)-C (18)	1.397 (14)
C (18)-C (19)	1.438 (14)
C (19)-C (20)	1.388 (13)
C (27)-C (30)	1.522 (16)
C (27)-C (28)	1.535 (16)
C (27)-C (29)	1.563 (16)
C (31)-C (32)	1.510 (15)
C (32)-C (33)	1.504 (16)
C (32)-C (34)	1.511 (17)
Ge'-C (31')	1.966 (10)
Ge'-C (27')	1.967 (11)
Ge'-S (2')	2.255 (3)
Ge'-S (1')	2.262 (3)
S (1')-C (1')	1.808 (10)
S (2')-C (11')	1.803 (10)
Si (1')-C (21')	1.857 (14)
Si (1')-C (22')	1.861 (12)
Si (1')-C (23')	1.878 (13)
Si (1')-C (2')	1.900 (10)

Si (2')-C (25')	1.849 (14)
Si (2')-C (24')	1.873 (13)
Si (2')-C (26')	1.883 (13)
Si (2')-C (20')	1.927 (11)
O'-C (34')	1.396 (15)
C (1')-C (10')	1.386 (13)
C (1')-C (2')	1.464 (13)
C (2')-C (3')	1.367 (12)
C (3')-C (4')	1.427 (13)
C (4')-C (5')	1.401 (14)
C (4')-C (9')	1.427 (14)
C (5')-C (6')	1.365 (14)
C (6')-C (7')	1.406 (15)
C (7')-C (8')	1.346 (13)
C (8')-C (9')	1.434 (13)
C (9')-C (10')	1.424 (13)
C (10')-C (12')	1.517 (13)
C (11')-C (12')	1.362 (13)
C (11')-C (20')	1.447 (13)
C (12')-C (13')	1.444 (13)
C (13')-C (14')	1.408 (14)
C (13')-C (18')	1.420 (14)
C (14')-C (15')	1.372 (15)
C (15')-C (16')	1.422 (16)
C (16')-C (17')	1.352 (16)
C (17')-C (18')	1.432 (15)
C (18')-C (19')	1.406 (15)
C (19')-C (20')	1.391 (14)
C (27')-C (30')	1.528 (15)
C (27')-C (29')	1.538 (15)
C (27')-C (28')	1.542 (15)
C (31')-C (32')	1.527 (15)
C (32')-C (33')	1.522 (16)
C (32')-C (34')	1.528 (15)
C (31)-Ge-C (27)	115.7 (5)
C (31)-Ge-S (2)	111.3 (4)
C (27)-Ge-S (2)	102.8 (4)
C (31)-Ge-S (1)	104.6 (4)
C (27)-Ge-S (1)	115.4 (4)
S (2)-Ge-S (1)	106.81 (11)
C (11)-S (2)-Ge	100.1 (3)
C (1)-S (1)-Ge	101.4 (3)
C (25)-Si (2)-C (26)	109.2 (5)
C (25)-Si (2)-C (24)	108.6 (6)
C (26)-Si (2)-C (24)	107.6 (6)
C (25)-Si (2)-C (20)	106.9 (5)
C (26)-Si (2)-C (20)	117.1 (5)
C (24)-Si (2)-C (20)	107.3 (5)
C (22)-Si (1)-C (21)	108.9 (8)
C (22)-Si (1)-C (23)	108.2 (8)
C (21)-Si (1)-C (23)	106.5 (7)
C (22)-Si (1)-C (2)	114.6 (6)
C (21)-Si (1)-C (2)	109.5 (6)
C (23)-Si (1)-C (2)	108.7 (6)
C (10)-C (1)-C (2)	122.1 (9)
C (10)-C (1)-S (1)	118.6 (7)

C(2)-C(1)-S(1)	119.2(8)
C(3)-C(2)-C(1)	115.5(9)
C(3)-C(2)-Si(1)	118.6(8)
C(1)-C(2)-Si(1)	125.6(8)
C(2)-C(3)-C(4)	124.9(10)
C(3)-C(4)-C(9)	118.7(10)
C(3)-C(4)-C(5)	122.2(10)
C(9)-C(4)-C(5)	119.1(10)
C(6)-C(5)-C(4)	121.0(11)
C(5)-C(6)-C(7)	120.5(11)
C(8)-C(7)-C(6)	120.2(11)
C(7)-C(8)-C(9)	120.5(10)
C(4)-C(9)-C(8)	118.6(10)
C(4)-C(9)-C(10)	119.0(9)
C(8)-C(9)-C(10)	122.4(9)
C(1)-C(10)-C(9)	119.1(9)
C(1)-C(10)-C(12)	122.2(9)
C(9)-C(10)-C(12)	118.4(9)
C(12)-C(11)-C(20)	120.6(9)
C(12)-C(11)-S(2)	117.7(7)
C(20)-C(11)-S(2)	121.7(8)
C(11)-C(12)-C(13)	121.4(9)
C(11)-C(12)-C(10)	120.8(9)
C(13)-C(12)-C(10)	117.7(9)
C(18)-C(13)-C(12)	119.7(9)
C(18)-C(13)-C(14)	116.4(10)
C(12)-C(13)-C(14)	123.8(9)
C(15)-C(14)-C(13)	121.7(11)
C(14)-C(15)-C(16)	121.2(11)
C(17)-C(16)-C(15)	118.5(11)
C(16)-C(17)-C(18)	120.6(11)
C(17)-C(18)-C(13)	121.4(10)
C(17)-C(18)-C(19)	121.3(10)
C(13)-C(18)-C(19)	117.3(10)
C(20)-C(19)-C(18)	124.1(9)
C(19)-C(20)-C(11)	116.8(9)
C(19)-C(20)-Si(2)	113.2(7)
C(11)-C(20)-Si(2)	130.0(8)
C(30)-C(27)-C(28)	109.9(10)
C(30)-C(27)-C(29)	108.0(11)
C(28)-C(27)-C(29)	109.9(10)
C(30)-C(27)-Ge	109.9(8)
C(28)-C(27)-Ge	111.1(9)
C(29)-C(27)-Ge	108.0(8)
C(32)-C(31)-Ge	119.6(8)
C(33)-C(32)-C(31)	113.5(12)
C(33)-C(32)-C(34)	109.3(12)
C(31)-C(32)-C(34)	111.9(11)
O-C(34)-C(32)	114.9(13)
C(31')-Ge'-C(27')	114.2(5)
C(31')-Ge'-S(2')	111.2(3)
C(27')-Ge'-S(2')	104.5(3)
C(31')-Ge'-S(1')	104.8(4)
C(27')-Ge'-S(1')	114.5(3)
S(2')-Ge'-S(1')	107.71(11)
C(1')-S(1')-Ge'	104.0(3)
C(11')-S(2')-Ge'	95.4(3)

C(21')-Si(1')-C(22')	109.1(7)
C(21')-Si(1')-C(23')	111.2(7)
C(22')-Si(1')-C(23')	105.9(6)
C(21')-Si(1')-C(2')	107.5(5)
C(22')-Si(1')-C(2')	107.1(5)
C(23')-Si(1')-C(2')	115.8(5)
C(25')-Si(2')-C(24')	106.5(7)
C(25')-Si(2')-C(26')	108.6(7)
C(24')-Si(2')-C(26')	109.2(7)
C(25')-Si(2')-C(20')	108.4(6)
C(24')-Si(2')-C(20')	115.5(5)
C(26')-Si(2')-C(20')	108.5(6)
C(10')-C(1')-C(2')	122.6(9)
C(10')-C(1')-S(1')	119.7(8)
C(2')-C(1')-S(1')	117.7(7)
C(3')-C(2')-C(1')	115.8(9)
C(3')-C(2')-Si(1')	118.2(8)
C(1')-C(2')-Si(1')	124.7(7)
C(2')-C(3')-C(4')	124.0(10)
C(5')-C(4')-C(9')	119.1(10)
C(5')-C(4')-C(3')	122.1(10)
C(9')-C(4')-C(3')	118.7(9)
C(6')-C(5')-C(4')	121.5(11)
C(5')-C(6')-C(7')	119.9(10)
C(8')-C(7')-C(6')	120.6(11)
C(7')-C(8')-C(9')	121.5(11)
C(10')-C(9')-C(4')	119.1(9)
C(10')-C(9')-C(8')	123.3(10)
C(4')-C(9')-C(8')	117.5(9)
C(1')-C(10')-C(9')	119.6(9)
C(1')-C(10')-C(12')	121.3(9)
C(9')-C(10')-C(12')	118.9(9)
C(12')-C(11')-C(20')	122.1(10)
C(12')-C(11')-S(2')	118.2(8)
C(20')-C(11')-S(2')	119.7(8)
C(11')-C(12')-C(13')	121.0(10)
C(11')-C(12')-C(10')	123.0(9)
C(13')-C(12')-C(10')	115.7(9)
C(14')-C(13')-C(18')	119.5(10)
C(14')-C(13')-C(12')	123.6(10)
C(18')-C(13')-C(12')	116.9(10)
C(15')-C(14')-C(13')	121.0(12)
C(14')-C(15')-C(16')	120.3(12)
C(17')-C(16')-C(15')	119.5(11)
C(16')-C(17')-C(18')	122.2(12)
C(19')-C(18')-C(13')	121.0(10)
C(19')-C(18')-C(17')	121.4(11)
C(13')-C(18')-C(17')	117.6(11)
C(20')-C(19')-C(18')	122.0(10)
C(19')-C(20')-C(11')	116.8(10)
C(19')-C(20')-Si(2')	117.9(8)
C(11')-C(20')-Si(2')	125.0(8)
C(30')-C(27')-C(29')	109.2(10)
C(30')-C(27')-C(28')	110.1(11)
C(29')-C(27')-C(28')	108.2(10)
C(30')-C(27')-Ge'	110.1(8)
C(29')-C(27')-Ge'	110.4(8)

C (28') -C (27') -Ge'	108.8 (8)
C (32') -C (31') -Ge'	119.1 (7)
C (33') -C (32') -C (31')	111.8 (10)
C (33') -C (32') -C (34')	110.2 (11)
C (31') -C (32') -C (34')	110.7 (10)
O' -C (34') -C (32')	114.3 (12)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 20. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
Ge	40 (1)	58 (1)	52 (1)	-26 (1)	9 (1)	-23 (1)
S (2)	51 (2)	53 (2)	44 (2)	-18 (2)	7 (1)	-25 (2)
S (1)	43 (2)	56 (2)	47 (2)	-20 (2)	9 (1)	-16 (2)
Si (2)	49 (2)	63 (2)	41 (2)	-24 (2)	13 (2)	-20 (2)
O	125 (9)	101 (8)	124 (9)	-57 (7)	35 (8)	-25 (7)
Si (1)	62 (2)	81 (3)	46 (2)	-30 (2)	7 (2)	-26 (2)
C (1)	56 (7)	42 (7)	40 (6)	-20 (6)	13 (6)	-31 (6)
C (2)	40 (7)	47 (7)	42 (7)	-20 (6)	11 (5)	-25 (6)
C (3)	58 (8)	50 (7)	59 (8)	-36 (6)	29 (7)	-28 (7)
C (4)	34 (7)	57 (8)	40 (7)	-16 (6)	4 (5)	-16 (6)
C (5)	49 (8)	50 (8)	66 (8)	-24 (7)	17 (7)	-20 (7)
C (6)	37 (8)	57 (8)	91 (10)	-26 (8)	16 (7)	-8 (6)
C (7)	44 (8)	67 (9)	67 (9)	-9 (8)	-15 (7)	-11 (7)
C (8)	46 (7)	67 (8)	47 (7)	-27 (6)	3 (6)	-18 (7)
C (9)	41 (7)	53 (7)	36 (6)	-20 (6)	19 (5)	-27 (6)
C (10)	40 (7)	50 (7)	44 (7)	-25 (6)	20 (5)	-23 (6)
C (11)	37 (6)	41 (7)	36 (6)	-13 (5)	-2 (5)	-12 (5)
C (12)	34 (6)	56 (7)	48 (7)	-30 (6)	6 (5)	-19 (6)
C (13)	37 (6)	49 (7)	38 (6)	-20 (6)	10 (5)	-21 (6)
C (14)	59 (8)	47 (8)	64 (8)	-26 (6)	26 (6)	-20 (7)
C (15)	60 (8)	45 (8)	79 (9)	-17 (7)	31 (7)	-25 (7)
C (16)	46 (8)	62 (9)	95 (10)	-36 (8)	25 (7)	-31 (7)
C (17)	54 (8)	68 (9)	62 (8)	-29 (7)	16 (6)	-29 (7)
C (18)	44 (7)	47 (7)	47 (7)	-18 (6)	0 (6)	-18 (6)
C (19)	60 (8)	67 (8)	46 (7)	-34 (7)	1 (6)	-27 (7)
C (20)	31 (6)	53 (7)	28 (6)	-21 (5)	2 (5)	-10 (5)
C (21)	155 (16)	93 (12)	54 (9)	6 (8)	-12 (10)	-18 (11)
C (22)	142 (15)	260 (20)	69 (10)	-57 (13)	10 (10)	-142 (17)
C (23)	113 (12)	141 (14)	70 (10)	-73 (10)	22 (9)	-27 (11)
C (24)	68 (9)	113 (12)	62 (9)	-30 (8)	12 (7)	-32 (9)
C (25)	96 (10)	73 (9)	83 (9)	-49 (8)	32 (8)	-49 (8)
C (26)	70 (9)	72 (9)	60 (8)	-34 (7)	28 (7)	-31 (7)
C (27)	69 (9)	72 (9)	75 (9)	-35 (8)	13 (7)	-43 (8)
C (28)	73 (10)	114 (12)	98 (11)	-46 (10)	-4 (8)	-52 (9)
C (29)	127 (13)	96 (11)	74 (10)	-28 (9)	16 (9)	-69 (10)
C (30)	84 (10)	50 (8)	90 (10)	-29 (8)	-3 (8)	-23 (8)
C (31)	48 (7)	77 (9)	63 (8)	-26 (8)	24 (6)	-17 (7)
C (32)	54 (8)	68 (10)	79 (10)	-23 (8)	9 (7)	-12 (7)
C (33)	83 (11)	116 (13)	107 (12)	-55 (11)	-19 (10)	2 (10)
C (34)	84 (12)	135 (15)	100 (13)	-53 (12)	16 (10)	-25 (11)
Ge'	42 (1)	56 (1)	43 (1)	-20 (1)	2 (1)	-19 (1)
S (1')	40 (2)	65 (2)	55 (2)	-37 (2)	6 (1)	-22 (2)
S (2')	46 (2)	52 (2)	43 (2)	-18 (2)	4 (1)	-9 (2)
Si (1')	60 (2)	85 (3)	53 (2)	-40 (2)	17 (2)	-36 (2)
Si (2')	56 (2)	86 (3)	68 (2)	-30 (2)	23 (2)	-29 (2)
O'	162 (11)	147 (10)	83 (8)	-11 (7)	9 (7)	-109 (9)
C (1')	44 (7)	31 (6)	46 (7)	-13 (5)	-7 (5)	-9 (5)
C (2')	43 (7)	25 (6)	50 (7)	-17 (5)	6 (5)	-9 (5)

C (3')	53 (7)	48 (7)	51 (7)	-32 (6)	17 (6)	-28 (6)
C (4')	55 (7)	46 (7)	40 (7)	-20 (6)	0 (6)	-19 (6)
C (5')	61 (8)	82 (9)	77 (9)	-40 (8)	18 (7)	-48 (8)
C (6')	82 (9)	94 (10)	58 (8)	-55 (8)	15 (7)	-50 (8)
C (7')	88 (10)	79 (9)	63 (8)	-46 (8)	13 (7)	-43 (8)
C (8')	66 (8)	74 (9)	43 (7)	-34 (7)	20 (6)	-40 (7)
C (9')	45 (7)	42 (7)	38 (6)	-22 (6)	7 (5)	-6 (6)
C (10')	41 (7)	41 (7)	37 (6)	-13 (5)	4 (5)	-18 (5)
C (11')	39 (7)	45 (7)	43 (7)	-18 (6)	4 (5)	-18 (6)
C (12')	53 (8)	30 (6)	28 (6)	-13 (5)	3 (5)	-10 (6)
C (13')	58 (8)	44 (7)	38 (7)	-29 (6)	4 (6)	-15 (7)
C (14')	51 (8)	46 (8)	59 (8)	-24 (7)	-5 (6)	-6 (6)
C (15')	68 (9)	55 (9)	71 (9)	-32 (8)	-8 (8)	-9 (8)
C (16')	95 (12)	39 (8)	61 (9)	-15 (7)	-38 (8)	-7 (8)
C (17')	79 (10)	45 (8)	47 (7)	-3 (6)	-18 (7)	-29 (7)
C (18')	57 (8)	50 (8)	43 (7)	-24 (6)	3 (6)	-17 (7)
C (19')	79 (10)	42 (8)	48 (7)	-23 (6)	21 (7)	-28 (7)
C (20')	48 (7)	59 (8)	43 (7)	-29 (6)	14 (6)	-25 (7)
C (21')	102 (12)	117 (13)	121 (13)	-77 (11)	43 (10)	-33 (10)
C (22')	95 (11)	155 (14)	64 (9)	-41 (9)	33 (8)	-89 (11)
C (23')	113 (12)	158 (15)	49 (8)	-41 (9)	27 (8)	-76 (11)
C (24')	40 (8)	183 (16)	98 (11)	-62 (11)	14 (7)	-43 (9)
C (25')	89 (12)	117 (14)	171 (17)	-31 (12)	61 (11)	-59 (11)
C (26')	82 (10)	81 (10)	87 (10)	-31 (9)	10 (8)	2 (8)
C (27')	51 (8)	54 (8)	53 (8)	-14 (6)	10 (6)	-15 (6)
C (28')	66 (10)	94 (11)	85 (11)	-17 (9)	0 (8)	-9 (8)
C (29')	86 (10)	118 (12)	59 (9)	-22 (9)	6 (8)	-45 (9)
C (30')	109 (12)	60 (9)	81 (10)	-8 (8)	-4 (9)	-32 (9)
C (31')	61 (8)	81 (10)	62 (8)	-27 (7)	15 (6)	-51 (8)
C (32')	67 (9)	38 (7)	85 (10)	-18 (7)	-6 (7)	-26 (7)
C (33')	98 (11)	100 (12)	92 (11)	-58 (10)	29 (9)	-39 (9)
C (34')	101 (12)	66 (10)	108 (13)	-19 (9)	-6 (10)	-40 (9)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 20.

	x	y	z	U (eq)
H (3A)	-123	6456	9024	59
H (5A)	-2034	7307	8298	64
H (6A)	-3307	7610	7323	77
H (7A)	-2730	6917	6490	79
H (8A)	-864	5892	6654	62
H (14A)	95	4125	8382	66
H (15A)	-514	2970	8655	74
H (16A)	-288	2211	7849	75
H (17A)	711	2596	6816	69
H (19A)	1689	3558	6005	63
H (21A)	3172	3964	10637	173
H (21B)	3244	3870	9862	173
H (21C)	2069	3905	10264	173
H (22A)	3807	5534	10128	209
H (22B)	3116	6344	9432	209
H (22C)	3967	5496	9334	209
H (23A)	1571	5574	10801	153
H (23B)	509	5481	10417	153
H (23C)	797	6352	10112	153
H (24A)	1903	5102	4022	122
H (24B)	925	5517	4469	122
H (24C)	1273	4525	4599	122
H (25A)	4278	3768	4854	110
H (25B)	3526	3261	5392	110
H (25C)	4470	3531	5709	110
H (26A)	3733	5641	4462	95
H (26B)	4021	5485	5292	95
H (26C)	2794	6156	4867	95
H (28A)	5323	6619	7905	130
H (28B)	5895	5750	7760	130
H (28C)	5017	5785	8379	130
H (29A)	4571	7389	6560	138
H (29B)	3748	7057	6208	138
H (29C)	5112	6515	6420	138
H (30A)	3200	7464	7546	110
H (30B)	2831	6655	8007	110
H (30C)	2390	7150	7165	110
H (31A)	4881	4377	6690	77
H (31C)	5761	4771	6903	77
H (32A)	5169	3385	7902	84
H (33A)	5844	4112	8494	160
H (33B)	7044	3935	8118	160
H (33C)	6720	3155	8688	160
H (34A)	7280	3255	7194	128
H (34B)	7023	2474	7806	128
H (3'A)	10486	1563	2093	53
H (5'A)	10562	1898	3204	77
H (6'A)	10028	1786	4360	78

H (7 'A)	8785	993	4905	80
H (8 'A)	8112	318	4302	64
H (14B)	10238	-1130	3602	63
H (15B)	11305	-2477	4421	78
H (16B)	10317	-3370	5201	82
H (17B)	8297	-2909	5118	70
H (19B)	6363	-1793	4590	63
H (21D)	11742	-403	834	158
H (21E)	10838	-708	1383	158
H (21F)	11916	-534	1669	158
H (22D)	11792	1450	459	139
H (22E)	11956	1235	1312	139
H (22F)	10905	2053	820	139
H (23D)	9897	1171	-215	148
H (23E)	8976	1838	74	148
H (23F)	8871	916	241	148
H (24D)	2622	132	3005	154
H (24E)	3674	-536	2789	154
H (24F)	3613	437	2544	154
H (25D)	3154	-1042	4529	191
H (25E)	4398	-1336	4969	191
H (25F)	4274	-1710	4363	191
H (26D)	3023	835	4115	136
H (26E)	4088	1121	3741	136
H (26F)	4265	493	4571	136
H (28D)	4012	2230	284	137
H (28E)	4101	1866	1151	137
H (28F)	4074	1266	718	137
H (29D)	5741	1715	-374	132
H (29E)	5778	756	56	132
H (29F)	6930	1005	70	132
H (30D)	5826	2648	302	130
H (30E)	7015	1952	758	130
H (30F)	5915	2296	1168	130
H (31B)	5451	-702	2197	73
H (31D)	5174	-347	1341	73
H (32B)	7389	-1570	2050	74
H (33D)	7688	-1821	954	133
H (33E)	7470	-836	800	133
H (33F)	6440	-1120	598	133
H (34C)	5436	-1940	1629	110
H (34D)	6715	-2633	1899	110