Controllable Diastereoselective Cyclopropanation. Enantioselective Synthesis of Vinylcyclopropanes *via* Chiral Telluronium Ylides

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Supporting information

General Information

General methods. Infrared spectra were recorded on a Nicolet AVATAR-360 spectrometer. ¹H NMR and ¹³C NMR spectra were recorded on Varian Mercury 300 or Bruker AM-300 instruments. Chemical shifts are quoted in ppm, referenced to the non-deuterated residual solvent or TMS. Low-resolution mass spectra (m/z) were recorded on HP5989A. High-resolution mass spectra were recorded on Concept 1H. GC-MS was recorded on VARIAN CP-3800 (GC) and VARIAN Saturn 2000 (MS). Microanalyses were performed using an Elemantar Vario EL. Ee values were determined by chiral HPLC on a Chiralcel OD-H or AD column and chiral GC on a Chirasil-DexCB capillary column. All reaction flasks were dried by flame. And all reactions were carried out under argon unless otherwise noted. THF and toluene were dried by distilled over sodium-benzophenone ketyl prior to use. DMF was distilled over calcium hydride under nitrogen, and stored in MS 4Å. Triethylamine was distilled over calcium hydride under nitrogen. (2S, 5S)-Hexane-2, 5-diol was prepared by baker's yeast reduction of 2, 5-hexanedione.¹

1. Preparation of telluronium salts 1a, 1b, 1c.

(2S, 5S)-2, 5-hexanediol-dimethanesulfonate was prepared according to the literature² and isolated as a pale yellow oil in quantitative yield. ¹H NMR (300 MHz, CDCl₃) δ 4.81-4.92 (m, 2H), 3.03 (s, 6H), 1.70-1.90 (m, 4H), 1.44 (d, *J* = 6.0 Hz, 6H).

Te (2.87 g, 22.5 mmol) and NaBH₄ (2.21 g, 58.5 mmol) were mixed with 100 mL of DMF and the resulting mixture was heated to 80-90 °C for 3-4 hours under argon. After it became pale yellow, the resulting mixture was cooled to room temperature. To this solution was added (2S, 5S)-2,5-hexanediol-dimethanesulfonate (6.17 g, 22.5 mmol) in DMF. Then the mixture was warmed to 40 °C and stirred overnight. After the mixture was allowed to cool to room temperature, 100 mL of water was added. The extraction was carried out with ether (3 × 80 mL). The organic layers were combined, washed with brine and dried over MgSO₄. After concentration, the residue was purified by chromatography on silica gel (pure petroleum ether) to give the telluride. Yield: 3.22 g (68%). $[\alpha]_D^{20} = +198.1^\circ$ ($c = 1.61$, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 4.30-4.15 (m, 2H), 2.39-2.28 (m, 2H), 1.71-1.61 (m, 8H). ¹³C NMR (75 MHz, CDCl₃): 44.778, 25.919, 25.785. MS (EI) m/z (%) 55 (100), 210 (M^+ , Te¹²⁶, 0.37), 212 ($M^+ + 2$, Te¹²⁸, 1.87), 214 ($M^+ + 4$, Te¹³⁰, 1.01), 420 ($2M^+$, Te¹²⁶, 12.14), 422 ($2M^+ + 2$, Te¹²⁸, 18.72), 424 ($2M^+ + 4$, Te¹³⁰, 23.32).

The mixture of telluride (3.22 g, 15.3 mmol) and trimethylsilyl allylic bromide (2.96 g, 15.3 mmol) was stirred in ethyl ether at room temperature under argon for 4-5 hours. The solid was collected and washed with ethyl ether to afford salt **1a'** as a white solid. Yield: 5.31 g (86%). $[\alpha]_D^{20} = +146.3^\circ$ ($c = 1.02$, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 6.20-6.09 (m, 1H), 6.02 (d, $J = 18.6$ Hz, 1H), 4.40-4.30 (m, 1H), 3.90 (dd, $J = 10.2$ Hz, $J = 6.0$ Hz, 1H), 3.48-3.40 (m, 2H), 2.85-2.78 (m, 1H), 2.41-2.34 (m, 2H), 1.85-1.64 (m, 7H), 0.07 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): 138.539, 136.695, 50.482, 50.408, 41.197, 39.887, 30.917, 18.623, 18.440, -1.549. IR (KBr, cm⁻¹): 1595. Anal. Calcd. for C₁₂H₂₅BrSiTe: C, 35.56; H, 6.22. Found: C, 35.57; H, 6.35. mp 142-144 °C.

Salt **1a** (9.20 g, 90% yield) was readily obtained by mixing salt **1a'** (6.40 g, 15.8 mmol) with NaBPh₄ (5.25 g, 15.8 mmol) in methanol at room temperature. $[\alpha]_D^{20} = +108.1^\circ$ ($c = 1.00$, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.50 (m, 8H), 7.08 (t, $J = 6.9$ Hz, 8H), 6.93 (t, $J = 6.9$ Hz, 4H), 5.76 (d, $J = 18.3$ Hz, 1H), 5.61-5.50 (m, 1H), 3.01-2.98 (m, 1H), 2.78-2.64 (m, 3H), 2.36-2.32 (m, 1H), 2.14-2.08 (m, 1H), 1.33 (d, $J = 6.9$ Hz, 3H), 1.45-1.26 (m, 2H), 1.13 (d, $J = 7.2$ Hz, 3H), 0.08 (s,

9H). ^{13}C NMR (75 MHz, CDCl_3): 165.083, 164.429, 163.772, 163.128, 141.426, 136.092, 133.827, 125.782, 125.742, 122.002, 52.673, 50.740, 40.939, 40.816, 27.703, 19.086, 16.971, -1.618. IR (KBr, cm^{-1}): 3053, 1603, 744, 705. Anal. Calcd. for $\text{C}_{36}\text{H}_{45}\text{BSiTe}$: C, 67.12; H, 7.04. Found: C, 67.34; H, 7.16. mp 148-149 °C.

Salt **1b'** (44% yield) was prepared using the same procedure for the preparation of telluronium salts **1a'**. $[\alpha]_{\text{D}}^{20} = +114.1^\circ$ (c = 0.52, acetone). ^1H NMR (300 MHz, CDCl_3 +acetone- d_6) δ 5.16 (m, 1H), 4.97 (m, 1H), 4.49 (m, 1H), 3.75 (ABd, $J = 9.9$ Hz, 1H), 3.56 (ABd, $J = 9.9$ Hz, 1H), 3.58-3.49 (m, 1H), 2.89 (m, 1H), 2.44 (m, 2H), 2.09-2.02 (m, 1H), 2.00 (s, 3H), 1.79 (d, $J = 7.2$ Hz, 3H), 1.74 (d, $J = 7.5$ Hz, 3H). IR (KBr, cm^{-1}): 3085, 1635. Anal. Calcd. for $\text{C}_{10}\text{H}_{19}\text{BrTe}$: C, 34.64; H, 5.52. Found: C, 34.40; H, 5.40. mp 130-132 °C.

Salt **1b** (91% yield) was prepared using the same procedure for the preparation of telluronium salts **1a**. $[\alpha]_{\text{D}}^{20} = +80.8^\circ$ (c = 0.53, acetone). ^1H NMR (300 MHz, CDCl_3 +DMSO- d_6) δ 7.18 (m, 8H), 6.92 (t, $J = 6.9$ Hz, 8H), 6.79 (t, $J = 6.9$ Hz, 4H), 5.13 (s, 1H), 4.99 (s, 1H), 3.86-3.78 (m, 1H), 3.58 (ABd, $J = 10.8$ Hz, 1H), 3.53 (m, 1H), 3.44 (ABd, $J = 10.8$ Hz, 1H), 2.70-2.64 (m, 1H), 2.41-2.35 (m, 1H), 1.98-1.78 (m, 2H), 1.86 (s, 3H), 1.55 (d, $J = 7.2$ Hz, 3H), 1.47 (d, $J = 7.2$ Hz, 3H). IR (KBr, cm^{-1}): 3050, 1579, 744, 705. Anal. Calcd. for $\text{C}_{34}\text{H}_{39}\text{TeB}$: C, 69.68; H, 6.71. Found: C, 69.56; H, 6.58. mp 137-139 °C.

Salt **1c'** (90% yield) was prepared using the same procedure for the preparation of telluronium salts **1a'**. $[\alpha]_{\text{D}}^{20} = +109.7^\circ$ (c = 0.62, CHCl_3). ^1H NMR (300 MHz, CDCl_3 +acetone- d_6) δ 6.06-6.03 (m, 1H), 5.39 (d, $J = 17.1$ Hz, $J = 10.1$ Hz, 1H), 5.28 (d, $J = 10.2$ Hz, 1H), 4.30 (m, 1H), 3.80 (m, 1H), 3.51-3.41 (m, 2H), 2.80 (m, 1H), 2.41-2.37 (m, 2H), 1.89-1.74 (m, 7H); IR (KBr, cm^{-1}): 3085, 2795, 1635, 891; Anal. Calcd. for $\text{C}_9\text{H}_{17}\text{TeBr}$: C, 32.49; H, 5.15. Found: C, 32.50; H, 4.97. mp

114-115.5 °C.

Salt **1c** (89% yield) was prepared using the same procedure for the preparation of telluronium salts **1a**. $[\alpha]_D^{20} = +83.4^\circ$ ($c = 0.61$, acetone). ^1H NMR (300 MHz, $\text{CDCl}_3 + \text{acetone-}d_6$) δ 6.48 (m, 8H), 6.08 (t, $J = 6.9$ Hz, 8H), 5.93 (t, $J = 6.6$ Hz, 4H), 5.22-5.08 (m, 1H), 4.61 (d, $J = 17.1$ Hz, 1H), 4.49 (d, $J = 9.9$ Hz, 1H), 3.15 (m, 2H), 2.97-2.93 (m, 2H), 2.02-1.95 (m, 1H), 1.73-1.67 (m, 1H), 1.20-1.12 (m, 2H), 0.81 (d, $J = 7.2$ Hz, 3H), 0.78 (d, $J = 7.2$ Hz, 3H). IR (KBr, cm^{-1}): 3051, 1579, 746, 707. Anal. Calcd. for $\text{C}_{33}\text{H}_{37}\text{BrTe}$: C, 69.29; H, 6.52. Found: C, 68.79; H, 6.41. mp 145-146.5 °C.

2. General procedure for the cyclopropanation between chiral telluronium ylides and

α , β -unsaturated compounds. **Condition A.** To a solution of chiral telluronium salt **4a** (644 mg, 1.0 mmol) in the mixture of toluene and THF (10 mL, 1/10, v/v) was added a solution of LiTMP (1.03 mmol, made from 2,2,6,6-tetramethylpiperidine and n-butyl lithium *in situ*) and HMPA (3.0 mmol) at -95 °C. The resulting mixture was stirred for 4 minutes under argon, and then a solution of α , β -unsaturated compounds (0.4 mmol) in THF was added. After 4-5 hours, the reaction was quenched by water. The mixture was filtrated through short silica gel column and washed with ethyl acetate. The filtrate was concentrated and the residue was purified by flash chromatography to afford the desired product.

***Trans*-(1S,2S,3S)-2-phenyl-*cis*-3-((trimethylsilyl)vinyl)-1-(methoxycarbonyl)cyclopropane (Entry 1, Table 1)^{4a}**

Prepared according to **condition A**. Yield: 105 mg (95%); *cis/trans*: 96/4; HPLC analysis (Chiralcel AD, 10/100 $^i\text{PrOH}$ /hexanes, 0.9 mL/min, 210 nm; t_r (minor) = 4.68 min, t_r (major) = 6.41 min) gave the isomeric composition of the product: 96% ee. $[\alpha]_D^{20} = -90.5^\circ$ ($c = 1.00$, CHCl_3). ^1H NMR(300 MHz, CDCl_3) δ 7.38-7.17 (m, 3H), 7.20-7.17 (m, 2H), 6.25-6.16 (m, 1H), 6.01 (d, $J = 18.0$ Hz, 1H), 3.80 (s, 3H), 2.88 (t, $J = 5.7$ Hz, 1H), 2.40-2.36 (m, 2H), 0.06 (s, 9H). ^{13}C NMR(75 MHz, CDCl_3):171.160, 141.584, 139.185, 133.146, 128.473, 126.520, 126.109, 51.769, 37.064, 32.244,

30.768, -1.269. MS (EI) m/z (%) 73 (100), 274(M^+ , 2.30). mp 72-74 °C.

***Trans*-(1*S*,2*S*,3*S*)-2-phenyl-*cis*-3-((trimethylsilyl)vinyl)-1-(Ethoxycarbonyl)cyclopropane (Entry 2, Table 1)^{4b}**

Prepared according to **condition A**. Yield: 111 mg (97%); *cis/trans*: 98/2; HPLC analysis (Chiralcel AD, 6/100 ¹PrOH/hexanes, 0.5 mL/min, 210 nm; t_r (minor) = 4.21 min, t_r (major) = 5.78 min) gave the isomeric composition of the product: 97% ee. $[\alpha]_D^{20} = -85.6^\circ$ ($c = 1.13$, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.35-7.14 (m, 5H), 6.25-6.12 (m, 1H), 5.98 (d, $J = 18.3$ Hz, 1H), 4.22 (q, $J = 7.2$ Hz, 2H), 2.85 (t, $J = 5.7$ Hz, 1H), 2.36-2.32 (m, 2H), 1.32 (t, $J = 7.2$ Hz, 3H), 0.12 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): 170.599, 141.687, 139.178, 132.973, 128.345, 126.403, 126.016, 60.596, 37.058, 31.969, 30.930, 14.261, -1.337. MS (EI) m/z (%) 73(100), 288(M^+ , 4.43).

***Trans*-(1*S*,2*S*,3*S*)-2-(4-methoxyphenyl)-*cis*-3-((trimethylsilyl)vinyl)-1-(methyloxycarbonyl)cyclopropane (Entry 3, Table 1)^{4a}**

Prepared according to **condition A**. Yield: 77 mg (63%)³; *cis/trans*: 97/3; HPLC analysis (Chiralcel OD-H, 5/100 ¹PrOH/hexanes, 0.4 mL/min, 210 nm; t_r (minor) = 12.16 min, t_r (major) = 32.64 min) gave the isomeric composition of the product: 94% ee. $[\alpha]_D^{20} = -78.5^\circ$ ($c = 1.03$, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.04 (d, $J = 8.4$ Hz, 2H), 6.82 (d, $J = 8.4$ Hz, 2H), 6.15-6.06 (m, 1H), 5.91 (d, $J = 18.6$ Hz, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 2.75 (t, $J = 6.3$ Hz, 1H), 2.25-2.21 (m, 2H), 0.06 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): 171.531, 158.396, 141.815, 132.922, 131.194, 127.315, 113.910, 55.294, 51.754, 36.804, 31.687, 30.611, -1.240. MS (EI) m/z (%) 73(100), 304(M^+ , 6.60). mp 79-81 °C.

***Trans*-(1*S*,2*S*,3*S*)-2-(4-methylphenyl)-*cis*-3-((trimethylsilyl)vinyl)-1-(methyloxycarbonyl)cyclopropane (Entry 4, Table 1)^{4a}**

Prepared according to **condition A**. Yield: 102 mg (88%); *cis/trans*: 98/2; HPLC analysis (Chiralcel OD-H, 1/200 ¹PrOH/hexanes, 0.7 mL/min, 210 nm; t_r (minor) = 6.91 min, t_r

(major) = 12.05 min) gave the isomeric composition of the product: 97% ee. $[\alpha]_D^{20} = -84.5^\circ$ (c = 1.18, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.09 (d, *J* = 7.8 Hz, 2H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.15-6.06 (m, 1H), 5.91 (d, *J* = 18.3 Hz, 1H), 3.71 (s, 3H), 2.76 (t, *J* = 6.0 Hz, 1H), 2.31 (s, 3H), 2.25 (t, *J* = 4.8 Hz, 2H), 0.05 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): 171.643, 142.036, 136.437, 136.404, 133.238, 129.434, 126.341, 52.031, 37.288, 32.308, 30.958, 21.273, -0.957. MS (EI) *m/z* (%) 73(100), 288(M⁺, 3.88). mp 47-49 °C.

***Trans*-(1*S*,2*S*,3*S*)-2-(4-trifluoromethylphenyl)-*cis*-3-((trimethylsilyl)vinyl)-1-(methoxycarbonyl)cyclopropane (Entry 5, Table 1)^{4b}**

Prepared according to **condition A**. Yield: 136 mg, (99%); *cis/trans*: 88/12; HPLC analysis (Chiralcel AD, 1/100 ⁱPrOH/hexanes, 0.5 mL/min, 210 nm; *t_r*(major) = 11.22 min, *t_r*(minor) = 12.57 min) gave the isomeric composition of the product: 96% ee. $[\alpha]_D^{20} = -73.1^\circ$ (c = 1.01, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 6.30 (dd, *J* = 18.3 Hz, *J* = 7.5 Hz, 1H), 6.17 (d, *J* = 18.6 Hz, 1H), 3.95 (s, 3H), 3.05 (t, *J* = 5.7 Hz, 1H), 2.57-2.51 (m, 2H), 0.03 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): 170.714, 143.456, 142.294, 140.892, 134.030, 129.004, 126.407, 125.463 (q), 51.892, 37.245, 31.771, 30.922, -1.300. MS (EI) *m/z* (%) 73(100), 342(M⁺, 1.77). mp 58-60 °C.

***Trans*-(1*S*,2*S*,3*S*)-2-(furyl)-*cis*-3-((trimethylsilyl)vinyl)-1-(phenylcarbonyl)cyclopropane (Entry 6, Table 1)^{4c}**

Prepared according to **condition A**. Yield: 90 mg (81%); *cis/trans* = 94/6; HPLC analysis (Chiralcel OD-H, 1/100 ⁱPrOH/hexanes, 0.7 mL/min, 210 nm; *t_r*(minor) = 5.93 min, *t_r*(major) = 9.48 min) gave the isomeric composition of the product: 97% ee. $[\alpha]_D^{20} = -85.9^\circ$ (c = 1.22, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.26 (d, *J* = 1.8 Hz, 1H), 6.29 (dd, *J* = 3.6 Hz, *J* = 1.8 Hz, 1H), 6.11-6.02 (m, 2H), 5.96 (d, *J* = 18.6 Hz, 1H), 4.16 (q, *J* = 6.9 Hz, 2H), 2.81 (t, *J* = 5.7 Hz, 1H), 2.44-2.35 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H), 0.07 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): 170.473, 152.438, 141.026, 140.965, 133.767, 110.544, 105.458, 60.787, 34.456, 29.120, 25.405, 14.363, -1.215. MS (EI) *m/z* (%) 73(100),

278 (M^+ , 2.92).

***Trans*-(1*S*,2*S*,3*S*)-2-(methyl)-*cis*-3-((trimethylsilyl)vinyl)-1-(methyloxycarbonyl)cyclopropane**

(Entry 7, Table 1)^{4c}

Prepared according to **condition A**. Yield: 48 mg (57%); *cis/trans*: 92/8; GC analysis (Chirasil-DexCB, 120 °C (10min), 120 °C -170 °C , 1 °C /min, 8.0 psi/N₂; *t_r* (minor) = 12.76 min, *t_r* (major) = 13.20 min) gave the isomeric composition of the product: 94% ee. $[\alpha]_D^{20} = -113.4^\circ$ (*c* = 1.16, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 5.97 (dd, *J* = 18.3 Hz, *J* = 8.4 Hz, 1H), 5.82 (d, *J* = 18.0 Hz, 1H), 3.65 (s, 3H), 1.78-1.62 (m, 3H), 1.13 (d, *J* = 5.4 Hz, 3H), 0.03 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): 172.102, 143.038, 131.773, 51.463, 36.211, 29.437, 23.218, 17.348, -1.230. MS (EI) *m/z* (%) 89(100), 212 (M^+ , 3.84).

***Trans*-(1*S*,2*S*,3*S*)-2-(phenyl)-*cis*-3-((trimethylsilyl)vinyl)-1-(phenylcarbonyl)cyclopropane** (Entry

8, Table 1)^{4d}

Prepared according to **condition A**. Yield: 121 mg (95%); *cis/trans*: 98/2; HPLC analysis (Chiralcel Chiralcel AD, 1/100 ⁱPrOH/hexanes, 1.0 mL/min, 210 nm; *t_r* (major) = 7.12 min, *t_r* (minor) = 10.94 min) gave the isomeric composition of the product: 95% ee. $[\alpha]_D^{20} = +29.9^\circ$ (*c* = 1.03, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 8.05-8.02 (m, 2H), 7.62-7.49 (m, 3H), 7.38-7.23 (m, 5H), 6.12 (dd, *J* = 18.3 Hz, *J* = 8.4 Hz, 1H), 5.96 (d, *J* = 18.6 Hz, 1H), 3.30 (dd, *J* = 9.0 Hz, *J* = 5.7 Hz, 1H), 3.21 (t, *J* = 5.4 Hz, 1H), 2.70-2.62 (m, 1H), 0.05 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): 196.564, 141.477, 140.005, 138.643, 133.434, 133.034, 128.800, 128.777, 128.377, 126.799, 126.582, 40.475, 36.406, 33.192, -0.966. MS (EI) *m/z* (%) 105(100), 320 (M^+ , 28.63). mp 96-98 °C.

***Trans*-(1*S*,2*S*,3*S*)-2-(4-bromophenyl)-*cis*-3-((trimethylsilyl)vinyl)-1-(phenylcarbonyl)**

cyclopropane (Entry 9, Table 1)^{4e}

Prepared according to **condition A**. Yield: 150 mg (94%); *cis/trans*: 99/1; HPLC analysis (Chiralcel AD, 3/100 ⁱPrOH/hexanes, 0.7 mL/min, 210 nm; *t_r* (major) = 8.68 min, *t_r* (minor) =

16.16 min) gave the isomeric composition of the product: 99% ee. $[\alpha]_D^{20} = +16.5^\circ$ ($c = 1.05$, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.99-7.96 (m, 2H), 7.57-7.40 (m, 5H), 7.08-7.05 (m, 2H), 6.02 (dd, $J = 18.3$ Hz, $J = 8.1$ Hz, 1H), 5.91 (d, $J = 18.3$ Hz, 1H), 3.21 (dd, $J = 9.0$ Hz, $J = 5.7$ Hz, 1H), 3.12 (t, $J = 6.3$ Hz, 1H), 2.60-2.54 (m, 1H), 0.01 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3): 195.982, 140.785, 138.923, 138.217, 133.662, 132.932, 131.569, 128.582, 128.140, 128.127, 120.200, 39.978, 36.019, 32.113, -1.237. MS (EI) m/z (%) 105(100), 398 (M^+ , Br^{79} , 4.32), 400 ($\text{M}^+ + 2$, Br^{81} , 4.43). mp 136.5-138 °C.

***Trans*-(1S,2S,3S)-2-(4-chlorophenyl)-*cis*-3-((trimethylsilyl)vinyl)-1-(*t*-butylcarbonyl)cyclopropane (Entry 10, Table 1)^{4c}**

Prepared according to **condition A**. Yield: 132 mg (99%); *cis/trans*: 99/1; HPLC analysis (Chiralcel AD, 1/100 $^i\text{PrOH}$ /hexanes, 0.6 mL/min, 210 nm; t_r (major) = 7.63 min, t_r (minor) = 8.59 min) gave the isomeric composition of the product: 96% ee. $[\alpha]_D^{20} = -34.8^\circ$ ($c = 1.11$, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.33-7.28 (m, 2H), 7.13-7.10 (m, 2H), 5.93-5.92 (m, 2H), 2.98 (t, $J = 5.7$ Hz, 1H), 2.80 (dd, $J = 9.0$ Hz, $J = 5.1$ Hz, 1H), 2.42-2.34 (m, 1H), 1.22 (s, 9H), 0.09 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3): 210.339, 141.545, 138.389, 132.272, 132.123, 128.564, 127.766, 43.627, 38.905, 34.583, 30.653, 25.547, -1.588. MS (EI) m/z (%) 57(100), 334 (M^+ , 6.87). mp 70-72 °C.

***Trans*-(1S,2S,3S)-2-(*n*-butyl)-*cis*-3-((trimethylsilyl)vinyl)-1-(*t*-butylcarbonyl)cyclopropane (Entry 11, Table 1)**

Prepared according to **condition A**. Yield: 87 mg (78%); *cis/trans*: 98/2 (GC-MS); HPLC analysis (Chiralcel AD, hexanes, 1.0 mL/min, 210 nm; t_r (minor) = 4.44 min, t_r (minor) = 4.77 min) gave the isomeric composition of the product: 99% ee. $[\alpha]_D^{20} = -83.9^\circ$ ($c = 1.20$, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 5.71-5.69 (m, 2H), 2.16 (dd, $J = 8.7$ Hz, $J = 5.7$ Hz, 1H), 1.77-1.68 (m, 2H), 1.35-1.18 (m, 6H), 1.05 (s, 9H), 0.80 (t, $J = 7.2$ Hz, 3H), 0.07 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3): 211.570, 143.453, 131.057, 43.894, 37.929, 32.379, 30.996, 28.414, 26.161, 22.291, 13.983, -1.176. IR (film, cm^{-1}) 1690, 1611. MS (EI) m/z (%) 57(100), 280(M^+ , 7.06). HRMS Calcd for $\text{C}_{17}\text{H}_{32}\text{OSi}$: 280.222. Found: 280.222.

***Trans*-(1*S*,2*S*,3*S*)-2-(*n*-butyl)-*cis*-3-((trimethylsilyl)vinyl)-1-(heptylcarbonyl)cyclopropane (Entry 12, Table 1)**

Prepared according to **condition A**. Yield: 63 mg (49%); *cis/trans*: 96/4(GC-MS); HPLC analysis (Chiralcel AD, 1/200 ¹PrOH/hexanes, 0.5 mL/min, 210 nm; *t_r*(major) = 7.38 min, *t_r*(minor) = 8.05 min) gave the isomeric composition of the product: 98% ee. [α]_D²⁰ = -67.1° (*c* = 1.38, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 5.96 (dd, *J* = 19.5 Hz, *J* = 8.4 Hz, 1H), 5.76 (d, *J* = 18.9 Hz, 1H), 2.47 (t, *J* = 7.2 Hz, 2H), 2.02 (dd, *J* = 8.4 Hz, *J* = 5.1 Hz, 1H), 1.89-1.73 (m, 2H), 1.61-1.54 (m, 2H), 1.36-1.25 (m, 14H), 0.90-0.85 (m, 6H), 0.01 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): 208.068, 143.095, 131.002, 44.660, 38.224, 36.409, 32.441, 31.665, 30.996, 29.489, 29.150, 29.074, 24.091, 22.599, 22.299, 14.064, 13.990, -1.184. IR (film, cm⁻¹) 1697, 1610. MS (EI) *m/z* (%) 73 (100), 322 (M⁺, 9.42). HRMS Calcd for C₂₀H₃₈OSi: 322.269. Found: 322.269.

***Trans*-(1*S*,2*S*,3*S*)-2-(phenyl)-*cis*-3-((trimethylsilyl)vinyl)-1-(piperidinylcarbonyl)cyclopropane (Entry 13, Table 1)^{4e}**

Prepared according to **condition A**. Yield: 24 mg (83%), conversion: 23%; *cis/trans*: 99/1; HPLC analysis (Chiralcel AD, 5/100 ¹PrOH/hexanes, 0.6 mL/min, 210 nm; *t_r*(major) = 27.01 min, *t_r*(minor) = 30.84 min) gave the isomeric composition of the product: 93% ee. [α]_D²⁰ = -72.3° (*c* = 0.7, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.29-7.13 (m, 5H), 5.88 (d, *J* = 18.6 Hz, 1H), 5.73 (dd, *J* = 18.6 Hz, *J* = 8.4 Hz, 1H), 3.93 (m, 1H), 3.74 (m, 1H), 3.40 (m, 1H), 3.20 (m, 1H), 2.95 (t, *J* = 5.7 Hz, 1H), 2.33 (dd, *J* = 9.6 Hz, *J* = 5.7 Hz, 1H), 2.27-2.16 (m, 1H), 1.68-1.45 (m, 6H), 0.04 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): 166.945, 143.481, 140.277, 131.968, 128.331, 126.345, 126.107, 46.520, 43.221, 35.683, 31.465, 29.636, 26.923, 25.809, 24.595, -1.155. MS (EI) *m/z* (%) 112 (100), 327(M⁺, 6.57). mp 114-115.5 °C.

***Trans*-(1*S*,2*S*,3*S*)-2-(4-bromophenyl)-*cis*-3-(methylvinyl)-1-(phenylcarbonyl)cyclopropane (Entry 14, Table 1)**

Prepared according to **condition A**. Yield: 110 mg (81%); *cis/trans*: 97/3 (GC-MS); HPLC analysis (Chiralcel ODH, 1/100 ¹PrOH/hexanes, 0.7 mL/min, 210 nm; *t_r* (minor) = 12.95 min, *t_r* (major) = 17.41 min) gave the isomeric composition of the product: 96% ee. [α]_D²⁰ = +165.3° (*c* = 1.10, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 8.08-8.02 (m, 2H), 7.58-7.41 (m, 5H), 7.14-7.10 (m, 2H), 5.02-4.99 (m, 2H), 3.29 (dd, *J* = 6.9 Hz, *J* = 5.4 Hz, 1H), 3.14 (dd, *J* = 9.6 Hz, *J* = 5.1 Hz, 1H), 2.56 (t, *J* = 8.4 Hz, 1H), 1.65 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): 194.662, 139.127, 138.508, 137.967, 132.915, 131.503, 128.606, 128.489, 128.104, 120.188, 114.652, 39.807, 35.164, 28.957, 23.178. MS (EI) *m/z* (%) 105 (100), 340 (*M*⁺, Br⁷⁹, 1.96), 342 (*M*⁺+2, Br⁸¹, 1.90). HRMS Calcd for C₁₉H₁₇OBr: 340.046. Found: 340.046. mp 108-110 °C.

***Trans*-(1*S*,2*S*,3*S*)-2-phenyl-*cis*-3-(vinyl)-1-(methoxycarbonyl)cyclopropane (Entry 15, Table 1)^{4a}**

Prepared according to **condition A**. Yield: 34 mg (42%); *cis/trans*: 93/7; HPLC analysis (Chiralcel AD, 1/100 ¹PrOH/hexanes, 0.8 mL/min, 210 nm; *t_r* (minor) = 7.20 min, *t_r* (major) = 8.61 min) gave the isomeric composition of the product: 95% ee. [α]_D²⁰ = -12.5° (*c* = 1.03, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.33-7.22 (m, 3H), 7.14-7.11 (m, 2H), 6.02-5.90 (m, 1H), 5.28 (dd, *J* = 17.4 Hz, *J* = 2.1 Hz, 1H), 5.12 (dd, *J* = 10.2 Hz, *J* = 2.1 Hz, 1H), 3.73 (s, 3H), 2.76 (t, *J* = 6.0 Hz, 1H), 2.31-2.27 (m, 2H). ¹³C NMR (75 MHz, CDCl₃): 171.354, 139.103, 134.120, 128.511, 126.589, 126.153, 116.766, 51.889, 34.544, 32.041, 30.217. MS (EI) *m/z* (%) 142 (100), 202 (*M*⁺, 6.25).

***Trans*-(1*S*,2*S*,3*S*)-2-(4-bromophenyl)-*cis*-3-((trimethylsilyl)vinyl)-1-(methoxycarbonyl)cyclopropane**

Prepared according to condition A. Yield: 138 mg (97%); *cis/trans*: 97/3; HPLC analysis (Chiralcel AD, 1/100 ¹PrOH/hexanes, 0.3 mL/min, 210 nm; *t_r* (major) = 21.57 min, *t_r* (minor major) = 23.17 min) gave the isomeric composition of the product: 96% ee. [α]_D²⁰ = -78.0° (*c* = 1.07, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.42-7.37 (m, 2H), 7.00-6.86 (m, 2H), 6.06-6.03 (m, 1H), 5.92 (d, *J* = 18.3 Hz, 1H), 3.72 (s, 3H), 2.74 (t, *J* = 5.7 Hz, 1H), 2.26-2.22 (m, 2H), 0.04 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): 170.893, 141.154, 138.290, 133.630, 131.522, 127.934, 120.218, 51.877, 36.918,

31.604, 30.713, -1.266. MS (EI) m/z (%): 73 (100), 352 (M^+ , Br⁷⁹, 0.90), 354 (M^{+2} , Br⁸¹, 0.88). HRMS Calcd for C₁₆H₂₁O₂BrSi : 352.049 . Found: 352.049. mp 87.5-89 °C.

3. General procedure for *trans*-cyclopropanation between chiral telluronium ylides and α , β -unsaturated compounds. Condition B. To a solution of telluronium salt **4a** (515 mg, 0.8 mmol) in the mixture of toluene and THF (10 mL, 1/10, v/v) was added a solution of LDA (0.8 mmol made from diisopropylamine and n-butyllithium *in situ*) and LiBr (1.6 mmol) at -95 °C. The resulting mixture was stirred for 4 minutes under argon, and a solution of α , β -unsaturated compounds (0.4 mmol) in THF was added. After stirring at -78 °C for 4-5 hours, the reaction was quenched by water. The mixture was filtrated through short silica gel column and washed with ethyl acetate. The filtrate was concentrated and the residue was purified by flash chromatography to afford the desired product.

***Trans*-(1S,2S,3R)-2-phenyl--*trans*-3-((trimethylsilyl)vinyl)-1-(methoxycarbonyl) cyclopropane (Entry 1, Table 2)^{4f}**

Prepared according to **Condition B**. Yield: 107 mg (98%); *trans/cis*: 96/4; HPLC analysis (Chiralcel AD, 1/100 ⁱPrOH/hexanes, 0.3 mL/min, 210 nm; t_r (major) = 20.15 min, t_r (minor) = 22.84 min) gave the isomeric composition of the product: 81% ee. $[\alpha]_D^{20} = -54.2^\circ$ (c = 1.14, CHCl₃), lit^{4f}. $[\alpha]_D^{20} = -61.5^\circ$ (c = 1.08, CHCl₃, 97% ee). ¹H NMR (300 MHz, CDCl₃) δ 7.28-7.15(m, 5H), 5.85 (d, J = 18.6 Hz, 1H), 5.26(dd, J = 18.3 Hz, J = 8.7 Hz, 1H), 3.70 (s, 3H), 2.91 (dd, J = 9.6 Hz, J = 5.4 Hz, 1H), 2.42 (dt, J = 9.6 Hz, J = 6.0 Hz, 1H), 2.20 (t, J = 5.1 Hz, 1H), -0.11 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): 173.281, 142.031, 135.768, 133.211, 128.802, 128.052, 126.588, 51.563, 34.282, 32.072, 26.936, -1.767.

***Trans*-(1S,2S,3R)-2-(4-methoxyphenyl)-*cis*-3-((trimethylsilyl)vinyl)-1-(methoxyxycarbonyl)cyclopropane (Entry 2, Table 2)^{4f}**

Prepared according to **Condition B**. Yield: 106 mg (87%); *trans/cis*: 98/2; HPLC analysis (Chiralcel AD, 1/200 ⁱPrOH/hexanes, 0.7 mL/min, 210 nm; t_r (major) = 14.60 min, t_r (minor) = 21.25 min) gave the isomeric composition of the product: 80% ee. $[\alpha]_D^{20} = -49.7^\circ$ (c = 1.10, CHCl₃), lit^{4f}. $[\alpha]_D^{20} = -65.1^\circ$ (c = 1.40, CHCl₃, 96% ee). ¹H NMR (300 MHz, CDCl₃) δ 7.13-7.09 (m, 2H), 6.84-6.80 (m, 2H), 5.88 (d, J = 18.6 Hz, 1H), 5.29 (dd, J = 18.6 Hz, J = 9.3 Hz, 1H), 3.79 (s, 3H),

3.73 (s, 3H), 2.88 (dd, $J = 9.6$ Hz, $J = 5.4$ Hz, 1H), 2.42 (dt, $J = 9.0$ Hz, $J = 4.8$ Hz, 1H), 2.15 (t, $J = 5.1$ Hz, 1H), -0.07 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3): 173.469, 158.255, 142.175, 132.985, 130.172, 127.860, 113.481, 55.211, 51.985, 34.580, 31.612, 27.480, -1.378.

***Trans*-(1S,2S,3R)-2-(4-methylphenyl)-*trans*-3-((trimethylsilyl)vinyl)-1-methoxycarbonyl cyclopropane (Entry 3, Table 2)^{4f}**

Prepared according to **Condition B**. Yield: 113mg (98%); *trans/cis*: 97/3; HPLC analysis (Chiralcel OD-H, 1/200 $^i\text{PrOH}$ /hexanes, 0.7 mL/min, 210 nm; t_r (major) = 7.38 min, t_r (minor) = 19.22 min) gave the isomeric composition of the product: 83% ee. $[\alpha]_D^{20} = -55.6^\circ$ ($c = 1.05$, CHCl_3), lit^{4f}. $[\alpha]_D^{20} = -55.2^\circ$ ($c = 1.41$, CHCl_3 , 97% ee). ^1H NMR (300 MHz, CDCl_3) δ 7.09 (m, 4H), 5.88 (d, $J = 18.3$ Hz, 1H), 5.32 (dd, $J = 20.0$ Hz, $J = 9.3$ Hz, 1H), 3.75 (s, 3H), 2.90 (dd, $J = 9.6$ Hz, $J = 5.4$ Hz, 1H), 2.43 (dt, $J = 9.3$ Hz, $J = 4.8$ Hz, 1H), 2.30 (s, 3H), 2.19 (t, $J = 4.5$ Hz, 1H), -0.05 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3): 173.427, 142.058, 136.165, 132.984, 132.705, 128.924, 128.772, 51.925, 34.603, 31.998, 27.335, 21.006, -1.407.

***Trans*-(1S,2S,3R)-2-(4-trifluoromethylphenyl)-*trans*-3-((trimethylsilyl)vinyl)-1-(methoxycarbonyl) cyclopropane (Entry 4, Table 2)^{4b}**

Prepared according to **Condition B**. Yield: 134 mg (98%); *trans/cis*: 93/7; HPLC analysis (Chiralcel AD, 1/200 $^i\text{PrOH}$ /hexanes, 0.5 mL/min, 210 nm; t_r (major) = 10.69 min, t_r (minor) = 12.29 min) gave the isomeric composition of the product: 68% ee. $[\alpha]_D^{20} = -30.9^\circ$ ($c = 1.10$, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.54 (d, $J = 8.1$ Hz, 2H), 7.30 (d, $J = 8.4$ Hz, 2H), 5.9 (d, $J = 17.7$ Hz, 1H), 5.26 ($J = 18.4$ Hz, $J = 8.4$ Hz, 1H), 3.76 (s, 3H), 2.97 (dd, $J = 9.6$ Hz, $J = 5.4$ Hz, 1H), 2.51 (dt, $J = 9.0$ Hz, $J = 4.5$ Hz, 1H), 2.28 (t, $J = 4.8$ Hz, 1H), -0.08 (s, 9H); ^{13}C NMR (75 MHz, CDCl_3): 72.913, 140.657, 140.041, 134.322, 129.388, 128.728, 126.388, 124.999 (q), 52.137, 34.396, 31.754, 27.058, -1.506.

***Trans*-(1S,2S,3R)-2-(methyl)-*trans*-3-((trimethylsilyl)vinyl)-1-(methoxycarbonyl)cyclopropane (Entry 5, Table 2)^{4f}**

Prepared according to **Condition B**. Yield: 59 mg (70%); *trans/cis*: 82/18; Chiral GC analysis (Chirasil-DexCB, 90 °C (20 min), 90 °C -180 °C, 1 °C /min, 8.0 psi/N₂; *t_r*(major) = 49.89 min, *t_r*(minor) = 50.43 min) gave the isomeric composition of the product: 43% ee. $[\alpha]_D^{20} = +52.0^\circ$ (*c* = 1.36, CHCl₃). ¹H NMR(300 MHz, CDCl₃) δ 5.83 (d, *J* = 17.1 Hz, 1H), 5.67 (dd, *J* = 18.6 Hz, *J* = 8.7 Hz, 1H), 3.65 (s, 3H), 2.15 (dt, *J* = 8.7 Hz, *J* = 4.5 Hz, 1H), 1.7-1.6 (m, 1H), 1.49 (t, *J* = 4.5 Hz, 1H), 1.12 (d, *J* = 6.3 Hz, 3H), 0.05 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): 173.899, 141.617, 133.261, 51.699, 33.628, 28.873, 23.059, 12.449, -1.211.

***Trans*-(1*S*,2*S*,3*R*)-2-(phenyl)-*trans*-3-((trimethylsilyl)vinyl)-1-piperidiny)carbony)cyclopropane (Entry 6, Table 2)^{4b}**

Prepared according to **Condition B**. Yield: 108 mg (83%); *trans/cis*: 100/0; HPLC analysis (Chiralcel OD-H, 5/100 ⁱPrOH/hexanes, 0.7 mL/min, 210 nm; *t_r*(major) = 11.36 min, *t_r*(minor) = 14.34 min) gave the isomeric composition of the product: 92% ee. $[\alpha]_D^{20} = -23.5^\circ$ (*c* = 1.22, CHCl₃), lit^{4b}, $[\alpha]_D^{20} = -22.1^\circ$ (*c* = 1.29, CHCl₃, 97% ee). ¹H NMR (300 MHz, CDCl₃) δ 7.28-7.18 (m, 5H), 5.86 (d, *J* = 18.3 Hz, 1H), 5.37 (dd, *J* = 18.6 Hz, *J* = 9.3 Hz, 1H), 3.67-3.58 (m, 4H), 2.92 (dd, *J* = 9.3 Hz, *J* = 5.4 Hz, 1H), 2.45 (dt, *J* = 9.3 Hz, *J* = 5.4 Hz, 1H), 2.35 (t, *J* = 5.1 Hz, 1H), 1.68-1.57 (m, 6H), -0.07 (s, 9H); ¹³C NMR (75 MHz, CDCl₃): 169.878, 143.228, 137.284, 132.573, 129.349, 128.304, 126.639, 47.094, 43.693, 33.829, 31.892, 26.923, 26.403, 25.767, 24.925, -1.073. Recrystallization (58 mg) from *n*-hexane gave the product. Yield: 49 mg (85%), >99% ee. mp: 80-82 °C.

***Trans*-(1*S*,2*S*,3*R*)-2-phenyl--*trans*-3-((trimethylsilyl)vinyl)-1-(methoxycarbonyl)cyclopropane (Entry 7, Table 2)^{4a}**

Prepared according to **Condition B**. 47 mg, Yield: 58%; *trans/cis*: 93/7; HPLC analysis (Chiralcel AD, 1/100 ⁱPrOH/hexanes, 0.8 mL/min, 210 nm; *t_r*(major) = 9.03 min, *t_r*(minor) = 10.72 min) gave the isomeric composition of the product: 61% ee. $[\alpha]_D^{20} = -11.4^\circ$ (*c* = 0.95, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.33-7.20 (m, 5H), 5.26 (dd, *J* = 16.8 Hz, *J* = 2.4 Hz, 1H), 5.20-5.08 (m, 1H), 5.00 (dd, *J* = 9.6 Hz, *J* = 2.4 Hz, 1H), 3.75 (s, 3H), 2.95 (dd, *J* = 9.3 Hz, *J* = 5.1 Hz, 1H), 2.45 (dt,

$J = 9.0$ Hz, $J = 4.5$ Hz, 1H), 2.22 (t, $J = 4.5$ Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3): 173.385, 135.738, 134.215, 128.968, 128.264, 126.739, 116.979, 52.042, 32.385, 31.966, 26.691. MS (EI) m/z (%): 142 (100), 202 (M^+ , 4.34).

4. General procedure for catalytic asymmetric cyclopropanation

To a mixture of α , β -unsaturated compounds (0.25 mmol), Cs_2CO_3 (0.27 mmol), and telluronium salt **4a** (0.05 mmol) in THF (0.5 mL) was added trimethylsilyl allylic bromide (0.5 mmol) in portions over 8 hours at reflux. After the reaction was complete (monitored by GC), the resulting mixture was filtrated through short silica gel column and washed with ethyl acetate. The filtrate was concentrated, and the residue was purified by flash chromatography to afford the desired product.

(1 of Scheme 3)^{4d} Prepared according to general procedure. Yield: 73 mg (91%); *cis/trans*: 90/10; HPLC analysis (Chiralcel AD, 3/100 $^i\text{PrOH}$ /hexanes, 0.6 mL/min, 210 nm; t_r (major) = 10.95 min, t_r (minor) = 15.56 min) gave the isomeric composition of the product: 86% ee.

(2 of Scheme 3)^{4c} Prepared according to general procedure. Yield: 83 mg (94%); *cis/trans*: 91/9; HPLC analysis (Chiralcel AD, 3/100 $^i\text{PrOH}$ /hexanes, 0.7 mL/min, 210 nm; t_r (major) = 10.18 min, t_r (minor) = 16.98 min) gave the isomeric composition of the product: 89% ee. $[\alpha]_D^{20} = +23.0^\circ$ ($c = 1.00$, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.98 (d, $J = 7.5$ Hz, 2H), 7.57-7.45 (m, 3H), 7.26 (d, $J = 8.4$ Hz, 2H), 7.13 (d, $J = 8.4$ Hz, 2H), 6.03 (dd, $J = 18.6$ Hz, $J = 8.1$ Hz, 1H), 5.92 (d, $J = 18.3$ Hz, 1H), 3.21 (dd, $J = 9.0$ Hz, $J = 5.4$ Hz, 1H), 3.14 (t, $J = 6.0$ Hz, 1H), 2.60-2.53 (m, 1H), 0.01 (s, 9H). ^{13}C NMR (75 MHz, CDCl_3): 196.280, 141.047, 138.532, 138.487, 133.869, 133.159, 132.457, 128.873, 128.816, 128.373, 127.996, 40.226, 36.287, 32.292, -1.028.

Determination of Absolute Configuration. The absolute configuration of both *trans*-(1*S*,2*S*,3*S*)-2-(4-bromophenyl)-*cis*-3-((trimethylsilyl)vinyl)-1-(phenylcarbonyl)cyclopropane and *trans*-(1*S*,2*S*,3*S*)-2-(4-bromophenyl)-*cis*-3-((trimethylsilyl)vinyl)-1-(methoxycarbonyl)cyclopropane were assigned by X-ray diffraction analysis (The crystal data were collected by a Bruker SMART APEX CCD with monochromated Mo K α radiation.).

Figure 1. ORTEP plot of *Trans*-(1*S*,2*S*,3*S*)-2-(4-bromophenyl)-*cis*-3-((trimethylsilyl)vinyl)-1-(phenylcarbonyl) cyclopropane. (Table 1, Entry 9)

Figure2. ORTEP plot of *trans*-(1*R*,2*R*,3*R*)-2-(4-bromophenyl)-*cis*-3-((trimethylsilyl)vinyl)-1-(methoxycarbonyl) cyclopropane.

The absolute configuration of cyclopropane compounds **4** in Table 2 (entries 1, 2, 3, 6) was determined by comparing the optical rotation with those of the known compounds^{4f, 4b, 4g}.

Figure 3. ORTEP plot of salt **1a'**.

Proposed models for the diastereoselectivities in Condition A and B: In the presence of lithium ion without HMPA, a possible mechanism could be envisioned to proceed *via* a chelating six-membered ring transition state, which is formed by coordination of lithium ion with carbonyl oxygen and ylidic carbanion simultaneously. Transition state A might be anticipated to be more stable than transition state B because the telluryl group is much bulkier than the vinyl one. This leads to compound **4** as the major products. In the presence of HMPA, however, HMPA might block the formation of the six-membered ring transition state because its strong ability of coordination with lithium ion. The mechanistic pathway, in this case, is similar to the well-accepted mechanism for some arsonium and sulfonium ylide cyclopropanation.⁵ And thus, this reaction affords compound **3** as the major products.

Figure 4. Proposed models for the diastereoselectivities in Condition A and B:

Determination of diastereoselectivities. The ratios of compounds **3** and **4** were easily determined by GC and/or GC-MS and/or ¹H NMR. The ratios by GC were similar to those by ¹H NMR.

Table S-I GC conditions and retention times of compounds **3** and **4**

		Retention time (min)	
Entry		Cis	trans
		(major)	(minor)
1	Table 1, Entry 1 ^a	10.693	10.519
2	Table 1, Entry 2 ^a	11.003	10.797
3	Table 1, Entry 3 ^a	11.743	11.414
4	Table 1, Entry 4 ^a	11.060	10.711
5	Table 1, Entry 5 ^a	10.585	10.291
6	Table 1, Entry 6 ^a	10.047	9.952
11	Table 1, Entry 11 ^b	9.879	10.417
12	Table 1, Entry 12 ^b	12.021	12.167
13	Table 1, Entry 13 ^a	13.343	-
14	Table 1, Entry 14 ^b	13.710	13.166

^a The diastereomeric ratios were determined by GC (SPBTM-5 Capillary column, 50 °C (2.0 min), 50 °C-280 °C (20 °C/min), 280 (15.0min), 9.0 psi/N₂). ^b The diastereomeric ratios of products were determined by GC-MS (HP-5 Capillary column, 150 °C (2.0 min), 150–250 °C (10 °C/min), 250 (13.0 min).

Table S-II^a

		Retention time (min)	
Entry		Cis	trans
		(minor)	(major)
1	Table 2, Entry 1	10.803	10.652
2	Table 2, Entry 2	11.715	11.430
3	Table 2, Entry 3	11.037	10.825
4	Table 2, Entry 4	10.439	10.204
5 ^b	Table 2, Entry 6	-	13.163

^a The diastereomeric ratios were determined by GC (SPBTM-5 Capillary column, 50 °C (2.0 min), 50-280 °C (20 °C/min), 280 (15.0 min), 9.0 psi/N₂. ^b No *cis* product was determined.

major
(1S,2S,3S)

minor
(1R,2R,3R)

3

Table S-III . HPLC conditions for compounds 3 (Entries1-15, Table 1)

Entry		Column	Conditions Hexane : <i>i</i> -PrOH	Flow (mL/min)	Retention time (min)	
					major	minor
1	Table 1, Entry 1	AD	100 : 10	0.9	6.41	4.68
2	Table 1, Entry 2	AD	100 : 6	0.5	5.78	4.21
3	Table 1, Entry 3	OD-H	100 : 5	0.4	32.64	12.16
4	Table 1, Entry 4	OD-H	200 : 1	0.7	12.05	6.91
5	Table 1, Entry 5	AD	100 : 1	0.5	11.22	12.57
6	Table 1, Entry 6	OD-H	100 : 1	0.7	9.48	5.93
7	Table 1, Entry 7	DexCB ^a			13.20	12.76
8	Table 1, Entry 8	AD	100 : 1	1.0	7.12	10.94
	1 of Scheme 3	AD	100 : 3	0.6	10.95	15.56
9	Table 1, Entry 9	AD	100 : 3	0.7	8.68	16.16
10	Table 1, Entry 10	AD	100 : 1	0.6	7.63	8.59
11	Table 1, Entry 11	AD	100 : 0	1.0	4.77	4.44
12	Table 1, Entry 12	AD	200 : 1	0.5	7.38	8.05
13	Table 1, Entry 13	AD	100 : 5	0.6	27.01	30.84
14	Table 1, Entry 14	OD-H	100 : 1	0.7	17.41	12.95
15	Table 1, Entry 15	AD	100 : 1	0.8	8.61	7.20
16	2 of Scheme 3	AD	100 : 3	0.7	10.18	16.98

^a Determined by GC using chiral stationary phases: Chirasil-DexCB, 120 °C (10 min), 120-170 °C (1 °C /min), 8.0 psi/N₂.

4

Table S-III . HPLC conditions for compounds 4 (Entries 1-7, Table 2)

Entry		Column	Conditions Hexane : <i>i</i> -PrOH	Flow (mL/min)	Retention time (min)	
					major	minor
1	Table 2, Entry 1	AD	100 : 1	0.3	20.15	22.84
2	Table 2, Entry 2	AD	200 : 1	0.7	14.60	21.25
3	Table 2, Entry 3	OD-H	200 : 1	0.7	7.38	19.22
4	Table 2, Entry 4	AD	200 : 1	0.5	10.69	12.29
5	Table 2, Entry 5	DexCB ^a			49.89	50.43
6	Table 2, Entry 6	OD-H	100 : 5	0.7	11.36	14.34
7	Table 2, Entry 7	AD	100 : 1	0.8	9.03	10.72

^a Determined by GC using chiral stationary phases: Chirasil-DexCB, 90 °C (20 min), 90 -180 °C (1 °C /min), 8.0 psi/N₂ .

References and notes.

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^1H NMR of, Entries 1-15, Table 1

(Table 1, Entry 6)

(Table 1, Entry 14)

90/06

96

¹H NMR of Table 2, Entry 1-7

(Table 2, Entry 7)

Table 1, Entry 1:

Chiralcel AD, 10/100 $^i\text{PrOH}$ /hexanes, 0.9 mL/min, 210 nm; $t_r(\text{minor}) = 4.68$ min, $t_r(\text{major}) = 6.41$ min

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		4.670	5804156.42	704424.41	50.19
2		6.408	5759847.77	284964.18	49.81
			11564004.19	989388.59	100.00

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		4.684	365119.49	43976.07	2.07
2		6.408	17296752.93	840586.35	97.93
			17661872.41	884562.42	100.00

Table 1, Entry 2:

Chiralcel AD, 6/100 ⁱPrOH/hexanes, 0.5 mL/min, 210 nm; t_r (minor) = 4.21 min, t_r (major) = 5.78 min

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		4.207	13204329.12	1.76e+06	50.09
2		5.769	13155965.55	693281.36	49.91
			26360294.66	2.46e+06	100.00

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		4.214	658879.59	90974.96	1.49
2		5.782	43705272.74	2.25e+06	98.51
			44364152.33	2.34e+06	100.00

Table 1, Entry 3:

Chiralcel OD-H, 5/100 ⁱPrOH/hexanes, 0.4 mL/min, 210 nm; *t_r* (minor) = 12.16 min, *t_r* (major) = 32.44 min

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		12.124	2194277.05	96018.51	11.21
2		14.057	7661062.16	292995.32	39.15
3		16.550	7598298.48	244822.34	38.83
4		32.550	2116155.12	30751.03	10.81
			19569792.81	664587.20	100.00

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		12.158	1626998.51	74447.61	2.78
2		32.640	56947846.11	782196.83	97.22
			58574844.61	856644.43	100.00

Table 1, Entry 4:

Chiralcel OD-H, 1/200 ⁱPrOH/hexanes, 0.7 mL/min, 210 nm; t_r (minor) = 6.91 min, t_r (major) = 12.05 min

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		6.949	3936935.95	304231.89	9.36
2		7.435	17254642.78	1.20e+06	41.01
3		12.835	3883090.82	128188.14	9.23
4		19.802	17003365.98	347939.85	40.41
			42078035.53	1.98e+06	100.00

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		6.913	255269.21	22155.48	1.41
2		12.046	17865635.34	650516.71	98.59
			18120904.55	672672.18	100.00

Table 1, Entry 5:

Chiralcel AD, 1/100 ⁱPrOH/hexanes, 0.5 mL/min, 210 nm; *t_r* (major) = 11.22 min, *t_r* (minor) = 12.57 min

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		9.510	28397855.15	1.75e+06	38.87
2		10.395	28384973.57	1.72e+06	38.85
3		11.240	8246329.42	437837.97	11.29
4		12.597	8033664.37	412316.93	11.00
			73062822.51	4.32e+06	100.00

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		9.502	469045.27	30831.81	3.52
2		10.378	1307389.21	84828.05	9.81
3		11.221	11295879.69	617057.96	84.77
4		12.571	253169.23	14780.22	1.90
			13325483.40	747498.04	100.00

Table 1, Entry 6:

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		5.952	6198570.77	616091.86	17.83
2		6.565	11189429.09	999104.31	32.19
3		8.081	11160475.07	697052.31	32.10
4		10.108	6215755.40	326960.35	17.88
			34764230.33	2.64e+06	100.00

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		5.935	165737.45	16359.73	1.34
2		6.587	746997.79	65348.59	6.04
3		7.803	6472.89	518.78	0.05
4		9.476	11454713.92	636082.52	92.57
			12373922.05	718309.62	100.00

Table 1, Entry 7:

Chirasil-DexCB, 120 °C (10min), 120 °C -170 °C , 1 °C /min, 8.0 psi/N₂; t_r(minor) = 12.76 min, t_r(major) = 13.20 min

PERCENT (AREA) \ MANUALLY ALTERED						
Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	2.542	51044416	995.1816		94.3483	95.7791
2	12.805	1126041	17.5533	T	2.0813	1.6894
3	13.278	1220446	17.0320		2.2558	1.6392
4	18.003	473465	6.2595	T	0.8751	0.6024
5	18.270	127060	1.5475	T	0.2349	0.1489
6	18.463	110648	1.4643		0.2045	0.1409
6 Peaks > Area Reject			54102076 Total Area			
6 Peaks > Height Reject			1039.038 Total Height

PERCENT (AREA) \ MANUALLY ALTERED

pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	2.535	58975016	994.9551		94.9774	95.6793
2	12.757	90535	1.3776	V	0.1458	0.1325
3	13.202	2982200	43.1676	T	4.8027	4.1512
4	13.503	45952	0.3851		0.0740	0.0370
4 Peaks > Area Reject			62093704	Total Area		
4 Peaks > Height Reject			1039.885	Total Height		

Table 1, Entry 8:

Chiralcel Chiralcel AD, 1/100 iPrOH/hexanes, 1.0 mL/min, 210 nm; t_r (major) = 7.12 min, t_r (minor) = 10.94 min

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		7.099	16460201.70	1.04e+06	49.63
2		10.786	16704587.79	767778.55	50.37
			33164789.49	1.81e+06	100.00

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		7.120	29068309.36	1.79e+06	97.70
2		10.937	683000.34	33682.57	2.30
			29751309.70	1.82e+06	100.00

Table 1, Entry 9:

Chiralcel AD, 3/100 $i\text{-PrOH}$ /hexanes, 0.7 mL/min, 210 nm; t_r (major) = 8.68 min,
 t_r (minor) = 16.16 min

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		6.129	3564791.76	282769.54	9.18
2		9.109	15762777.87	876462.23	40.57
3		10.706	3362921.65	157379.09	8.66
4		16.572	16161088.87	509798.89	41.60
			38851580.15	1.83e+06	100.00

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		8.676	14498460.19	874777.41	99.47
2		16.163	77062.78	3529.05	0.53
			14575522.97	878306.45	100.00

Table 1, Entry 10:

Chiralcel AD, 1/100 $i\text{PrOH}$ /hexanes, 0.6 mL/min, 210 nm; t_r (major) = 7.63 min,
 t_r (minor) = 8.59 min

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		7.652	4227727.19	347591.40	49.60
2		8.598	4296060.14	315623.63	50.40
			8523787.34	663215.03	100.00

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		7.625	12549517.18	1.01e+06	97.95
2		8.589	262434.42	22475.55	2.05
			12811951.59	1.03e+06	100.00

Table 1, Entry 11:

Chiralcel AD, hexanes, 1.0 mL/min, 210 nm; t_r (minor) = 4.44 min, t_r (minor) = 4.77 min

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		4.428	11880993.14	1.25e+06	50.03
2		4.806	11867304.77	1.08e+06	49.97
			23748297.91	2.33e+06	100.00

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		4.439	100394.36	12857.53	0.43
2		4.773	23428438.58	1.96e+06	99.57
			23528832.94	1.97e+06	100.00

Table 1, Entry 12:

CCCCCCCC[C@H]1C=C[C@@H]1C Chiralcel AD, 1/200 ⁱPrOH/hexanes, 0.5 mL/min, 210 nm; t_r (major) = 7.38 min, t_r (minor) = 8.05 min

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		7.487	21134734.98	1.59e+06	50.70
2		8.216	20551301.83	1.43e+06	49.30
			41686036.81	3.02e+06	100.00

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		7.385	10144449.10	781394.24	99.02
2		8.052	100516.14	7003.28	0.98
			10244965.25	788397.52	100.00

Table 1, Entry 13:

Chiralcel AD, 5/100 ⁱPrOH/hexanes, 0.6 mL/min, 210 nm; t_r (major) = 27.01 min, t_r (minor) = 30.84 min

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		12.452	1497424.46	71668.47	11.78
2		15.122	1531622.12	53122.80	12.05
3		26.994	4808291.02	109649.16	37.82
4		30.783	4877474.00	95327.03	38.36
			12714811.59	329767.47	100.00

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		27.009	22711513.67	507882.18	96.38
2		30.840	853635.46	16715.53	3.62
			23565149.13	524597.72	100.00

Table 1, Entry 14:

Chiralcel ODH, 1/100 ⁱPrOH/hexanes, 0.7 mL/min, 210 nm; t_r (minor) = 12.95 min,
 t_r (major) = 17.41 min

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		13.022	20660996.67	726534.86	49.92
2		17.681	20725008.76	525756.73	50.08
			41386005.43	1.25e+06	100.00

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		12.950	542559.31	21275.22	1.79
2		17.408	29727619.49	748381.13	98.21
			30270178.80	769656.35	100.00

Table 1, Entry 15:

Chiralcel AD, 1/100 ⁱPrOH/hexanes, 0.8 mL/min, 210 nm; t_r (minor) = 7.20 min, t_r (major) = 8.61 min

Chiralcel AD, 1/100 $i\text{PrOH}$ /hexanes, 0.3 mL/min, 210 nm; t_r (major) = 21.57 min, t_r (minor major) = 23.17 min

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		21.337	11806505.87	326065.87	50.48
2		22.880	11583313.47	309903.91	49.52
			23389819.34	635969.78	100.00

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		21.573	46247711.90	1.28e+06	98.12
2		23.166	884475.24	28627.53	1.88
			47132187.14	1.31e+06	100.00

Table 2, Entry 1:

Chiralcel AD, 1/100 ⁱPrOH/hexanes, 0.3 mL/min, 210 nm; t_r (major) = 20.15 min, t_r (minor) = 22.84 min

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		21.337	11806505.87	326065.87	50.48
2		22.880	11583313.47	309903.91	49.52
			23389819.34	635969.78	100.00

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		20.147	48965824.59	1.06e+06	90.59
2		22.838	5085861.99	93956.06	9.41
			54051686.58	1.15e+06	100.00

Table 2, Entry 2:

Chiralcel AD, 1/200 $i\text{PrOH}$ /hexanes, 0.7 mL/min, 210 nm; t_r (major) = 14.60 min, t_r (minor) = 21.25 min

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		14.955	39790971.39	1.17e+06	50.07
2		21.660	39685856.50	807760.36	49.93
			79476827.90	1.98e+06	100.00

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		14.600	25131335.02	797575.67	89.92
2		21.250	2818487.19	62978.57	10.08
			27949822.21	860554.25	100.00

Table 2, Entry 3:

Chiralcel OD-H, 1/200 ⁱPrOH/hexanes, 0.7 mL/min, 210 nm; *t_r*(major) = 7.38 min, *t_r*(minor) = 19.22 min

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		6.949	3936935.95	304231.89	9.36
2		7.435	17254642.78	1.20e+06	41.01
3		12.835	3883090.82	128188.14	9.23
4		19.802	17003365.98	347939.85	40.41
			42078035.53	1.98e+06	100.00

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		7.381	18004342.40	1.27e+06	91.91
2		19.221	1583711.94	36231.39	8.09
			19588054.34	1.30e+06	100.00

Table 2, Entry 4:

Chiralcel AD, 1/200 ¹PrOH/hexanes, 0.5 mL/min, 210 nm; t_r (major) = 10.69 min, t_r (minor) = 12.29 min

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		10.702	13949725.13	728574.08	42.91
2		12.343	14130070.32	682522.71	43.47
3		13.388	2238389.87	82251.25	6.89
4		15.099	2189407.03	78917.20	6.74
			32507592.34	1.57e+06	100.00

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		10.689	7628360.81	392407.63	79.61
2		12.285	1470573.77	70894.47	15.35
3		13.288	479741.89	18968.49	5.01
4		14.797	2998.33	169.03	0.03
			9581674.80	482439.62	100.00

67.7%

Table 2, Entry 5:

Chirasil-DexCB, 90 °C (20min), 90 °C -180 °C , 1 °C /min, 8.0psi/N₂; t_r (major) = 49.89 min, t_r (minor) = 50.43 min

PERCENT (AREA) \ MANUALLY ALTERED

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	2.545	63844768	994.7662		92.5138	96.2166
2	38.177	877987	7.7761		1.2722	0.7521
3	39.760	923865	7.5943		1.3387	0.7345
4	49.872	1724504	12.7103	T	2.4989	1.2294
5	50.353	1639948	11.0350		2.3764	1.0673

5 Peaks > Area Reject 69011072 Total Area
5 Peaks > Height Reject 1033.882 Total Height

PERCENT (AREA) \ MANUALLY ALTERED

Pk #	RT	Area	Height	BC	Area Percent	Height Percent
1	2.515	64360472	994.6821		98.0066	98.8124
2	38.138	40735	0.3725		0.0620	0.0370
3	39.705	188078	1.7511		0.2864	0.1740
4	49.890	774265	6.9323	T	1.1790	0.6887
5	50.427	305953	2.8987		0.4659	0.2880

5 Peaks > Area Reject 65669504 Total Area
 5 Peaks > Height Reject 1006.637 Total Height

Table 2, Entry 6:

Chiralcel OD-H, 5/100 ⁱPrOH/hexanes, 0.7 mL/min, 210 nm; *t_r* (major) = 11.36 min, *t_r* (minor) = 14.34 min

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		11.442	7466912.91	347556.53	50.72
2		14.512	7254526.37	231063.34	49.28
			14721439.28	578619.88	100.00

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		11.358	17000389.48	795038.37	95.81
2		14.345	743983.08	26674.92	4.19
			17744372.56	821713.30	100.00

Table 2, Entry 7:

Chiralcel AD, 1/100 ⁱPrOH/hexanes, 0.8 mL/min, 210 nm; t_r (major) = 9.03 min, t_r (minor) = 10.72 min

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		8.978	13801848.01	835169.26	49.93
2		10.613	13837872.39	713712.41	50.07
			27639720.40	1.55e+06	100.00

report

Peak #	Component Name	Time [min]	Area [uV*sec]	Height [uV]	Area [%]
1		9.027	20009805.12	1.21e+06	80.47
2		10.720	4857370.61	253397.64	19.53
			24867175.72	1.47e+06	100.00

1 of Scheme 3

Chiralcel AD, 3/100 ⁱPrOH/hexanes, 0.6 mL/min, 210 nm; t_r (major) = 10.95 min, t_r (minor) = 15.56 min

2 of Scheme 3

 Chiralcel AD, 3/100 *i*PrOH/hexanes, 0.7 mL/min, 210 nm; t_r (major) = 10.18 min, t_r (minor) = 16.98 min

X-Ray Analysis of Trans-(1*S*,2*S*,3*S*)-2-(4-bromophenyl)-cis-3-((trimethylsilyl)vinyl)-1-(phenylcarbonyl) cyclopropane. (Table 1, Entry 9)

Table 1. Crystal data and structure refinement for cd23130.

Identification code	cd23130
Empirical formula	C21 H23 O Si Br
Formula weight	399.39
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 6.1465(5) Å alpha = 90 deg. b = 16.5995(14) Å beta = 90 deg. c = 19.9580(16) Å gamma = 90 deg.
Volume	2036.3(3) Å ³
Z, Calculated density	4, 1.303 Mg/m ³
Absorption coefficient	2.082 mm ⁻¹
F(000)	824
Crystal size	0.382 x 0.156 x 0.077 mm
Theta range for data collection	1.60 to 28.28 deg.
Limiting indices	-7<=h<=8, -21<=k<=21, -26<=l<=19
Reflections collected / unique	12465 / 4701 [R(int) = 0.0621]
Completeness to theta = 28.28	95.5 %
Absorption correction	Sadabs
Max. and min. transmission	1.00000 and 0.48390
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4701 / 5 / 276
Goodness-of-fit on F²	0.746
Final R indices [I>2sigma(I)]	R1 = 0.0380, wR2 = 0.0557
R indices (all data)	R1 = 0.0837, wR2 = 0.0612
Absolute structure parameter	0.006(7)
Largest diff. peak and hole	0.423 and -0.289 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd23130.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Br	8016(1)	5162(1)	8455(1)	91(1)
Si	2139(2)	7118(1)	3744(1)	57(1)
O	-1079(4)	4363(1)	5167(1)	69(1)
C(1)	2684(5)	4485(2)	5370(1)	45(1)
C(2)	2494(5)	5132(2)	5887(1)	45(1)
C(3)	3452(5)	5337(2)	5214(1)	49(1)
C(4)	2338(6)	5863(2)	4735(1)	52(1)
C(5)	3307(6)	6389(2)	4342(2)	53(1)
C(6)	-864(5)	7122(2)	3791(2)	102(1)
C(7)	3033(7)	6857(2)	2881(1)	100(1)
C(8)	3182(6)	8125(2)	3956(2)	90(1)
C(9)	758(5)	4140(2)	5039(1)	48(1)
C(10)	1140(5)	3496(2)	4536(1)	46(1)
C(11)	-546(6)	2993(2)	4338(2)	62(1)
C(12)	-240(8)	2423(2)	3843(2)	76(1)
C(13)	1714(9)	2369(2)	3534(2)	80(1)
C(14)	3416(8)	2853(2)	3715(2)	76(1)
C(15)	3135(6)	3415(2)	4219(2)	56(1)
C(16)	3845(4)	5136(2)	6501(1)	45(1)
C(17)	5876(5)	4797(2)	6520(1)	51(1)
C(18)	7132(6)	4809(2)	7098(1)	52(1)
C(19)	6320(5)	5166(2)	7659(1)	55(1)
C(20)	4322(6)	5512(2)	7661(2)	69(1)
C(21)	3091(6)	5494(2)	7085(2)	58(1)

Table 3. Bond lengths [Å] and angles [deg] for cd23130.

Br-C(19)	1.899(3)
Si-C(8)	1.839(3)
Si-C(5)	1.846(3)
Si-C(6)	1.848(3)
Si-C(7)	1.859(3)
O-C(9)	1.215(3)
C(1)-C(9)	1.472(4)
C(1)-C(2)	1.494(3)
C(1)-C(3)	1.524(4)
C(1)-H(1)	0.93(2)
C(2)-C(16)	1.481(3)
C(2)-C(3)	1.504(4)
C(2)-H(2)	0.97(2)
C(3)-C(4)	1.465(4)
C(3)-H(3)	0.94(2)
C(4)-C(5)	1.315(4)
C(4)-H(4)	0.90(2)
C(5)-H(5)	0.906(15)
C(6)-H(6)	0.9600
C(6)-H(7)	0.9600
C(6)-H(8)	0.9600
C(7)-H(10)	0.9600
C(7)-H(9)	0.9600
C(7)-H(11)	0.9600
C(8)-H(14)	0.9600
C(8)-H(12)	0.9600
C(8)-H(13)	0.9600
C(9)-C(10)	1.484(4)
C(10)-C(15)	1.386(4)
C(10)-C(11)	1.390(4)
C(11)-C(12)	1.379(5)
C(11)-H(15)	0.92(2)
C(12)-C(13)	1.353(6)
C(12)-H(16)	0.93(3)
C(13)-C(14)	1.368(5)
C(13)-H(17)	0.921(17)
C(14)-C(15)	1.383(4)
C(14)-H(18)	0.97(3)
C(15)-H(19)	0.948(17)
C(16)-C(17)	1.370(3)

C(16)-C(21)	1.387(4)
C(17)-C(18)	1.388(4)
C(17)-H(20)	0.949(19)
C(18)-C(19)	1.362(4)
C(18)-H(21)	0.914(16)
C(19)-C(20)	1.356(4)
C(20)-C(21)	1.377(4)
C(20)-H(22)	0.93(2)
C(21)-H(23)	0.912(16)

C(8)-Si-C(5)	108.16(15)
C(8)-Si-C(6)	109.47(17)
C(5)-Si-C(6)	110.96(17)
C(8)-Si-C(7)	108.79(18)
C(5)-Si-C(7)	109.35(15)
C(6)-Si-C(7)	110.1(2)
C(9)-C(1)-C(2)	121.8(3)
C(9)-C(1)-C(3)	121.3(3)
C(2)-C(1)-C(3)	59.79(18)
C(9)-C(1)-H(1)	113.1(12)
C(2)-C(1)-H(1)	116.8(12)
C(3)-C(1)-H(1)	114.2(12)
C(16)-C(2)-C(1)	122.0(2)
C(16)-C(2)-C(3)	121.2(3)
C(1)-C(2)-C(3)	61.09(18)
C(16)-C(2)-H(2)	115.5(12)
C(1)-C(2)-H(2)	115.6(13)
C(3)-C(2)-H(2)	110.0(13)
C(4)-C(3)-C(2)	122.3(3)
C(4)-C(3)-C(1)	122.8(3)
C(2)-C(3)-C(1)	59.12(17)
C(4)-C(3)-H(3)	114.7(14)
C(2)-C(3)-H(3)	113.7(14)
C(1)-C(3)-H(3)	113.0(14)
C(5)-C(4)-C(3)	124.9(3)
C(5)-C(4)-H(4)	120.0(16)
C(3)-C(4)-H(4)	115.1(16)
C(4)-C(5)-Si	130.1(3)
C(4)-C(5)-H(5)	111.6(15)
Si-C(5)-H(5)	118.0(15)
Si-C(6)-H(6)	109.5
Si-C(6)-H(7)	109.5
H(6)-C(6)-H(7)	109.5
Si-C(6)-H(8)	109.5

H(6)-C(6)-H(8)	109.5
H(7)-C(6)-H(8)	109.5
Si-C(7)-H(10)	109.5
Si-C(7)-H(9)	109.5
H(10)-C(7)-H(9)	109.5
Si-C(7)-H(11)	109.5
H(10)-C(7)-H(11)	109.5
H(9)-C(7)-H(11)	109.5
Si-C(8)-H(14)	109.5
Si-C(8)-H(12)	109.5
H(14)-C(8)-H(12)	109.5
Si-C(8)-H(13)	109.5
H(14)-C(8)-H(13)	109.5
H(12)-C(8)-H(13)	109.5
O-C(9)-C(1)	122.3(3)
O-C(9)-C(10)	120.6(3)
C(1)-C(9)-C(10)	117.1(3)
C(15)-C(10)-C(11)	118.1(3)
C(15)-C(10)-C(9)	121.2(3)
C(11)-C(10)-C(9)	120.5(3)
C(12)-C(11)-C(10)	121.0(4)
C(12)-C(11)-H(15)	124.1(16)
C(10)-C(11)-H(15)	114.9(16)
C(13)-C(12)-C(11)	119.6(4)
C(13)-C(12)-H(16)	121.5(19)
C(11)-C(12)-H(16)	118.9(19)
C(12)-C(13)-C(14)	121.3(4)
C(12)-C(13)-H(17)	122(2)
C(14)-C(13)-H(17)	117(3)
C(13)-C(14)-C(15)	119.5(4)
C(13)-C(14)-H(18)	126(2)
C(15)-C(14)-H(18)	115(2)
C(14)-C(15)-C(10)	120.5(4)
C(14)-C(15)-H(19)	120.1(17)
C(10)-C(15)-H(19)	118.8(17)
C(17)-C(16)-C(21)	117.2(3)
C(17)-C(16)-C(2)	122.1(3)
C(21)-C(16)-C(2)	120.6(3)
C(16)-C(17)-C(18)	121.6(3)
C(16)-C(17)-H(20)	120.4(12)
C(18)-C(17)-H(20)	118.0(12)
C(19)-C(18)-C(17)	119.1(3)
C(19)-C(18)-H(21)	119.8(16)
C(17)-C(18)-H(21)	121.0(16)

C(20)-C(19)-C(18)	121.2(3)
C(20)-C(19)-Br	119.8(2)
C(18)-C(19)-Br	119.0(3)
C(19)-C(20)-C(21)	119.1(3)
C(19)-C(20)-H(22)	116.2(17)
C(21)-C(20)-H(22)	124.6(17)
C(20)-C(21)-C(16)	121.8(3)
C(20)-C(21)-H(23)	120.2(16)
C(16)-C(21)-H(23)	118.0(16)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd23130.

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
Br	105(1)	109(1)	60(1)	-17(1)	-28(1)	-2(1)
Si	51(1)	61(1)	58(1)	14(1)	-1(1)	-1(1)
O	51(2)	99(2)	57(1)	-13(1)	9(1)	5(1)
C(1)	46(2)	48(2)	42(2)	1(1)	-1(2)	9(2)
C(2)	44(2)	49(2)	41(2)	3(1)	2(1)	9(2)
C(3)	43(2)	59(2)	44(2)	5(2)	0(2)	4(2)
C(4)	43(2)	60(2)	51(2)	4(2)	4(2)	2(2)
C(5)	41(2)	61(2)	56(2)	4(2)	-4(2)	-2(2)
C(6)	61(3)	110(3)	134(3)	39(3)	-5(2)	3(2)
C(7)	128(3)	118(3)	54(2)	14(2)	-3(2)	8(3)
C(8)	86(3)	65(2)	117(3)	17(2)	-5(2)	10(2)
C(9)	50(2)	58(2)	36(2)	9(2)	4(2)	4(2)
C(10)	60(2)	43(2)	37(2)	7(1)	-6(2)	-2(2)
C(11)	64(3)	66(2)	58(2)	14(2)	-4(2)	-3(2)
C(12)	98(4)	59(3)	69(3)	-1(2)	-25(3)	-16(3)
C(13)	115(4)	59(2)	64(3)	-15(2)	-15(3)	12(3)
C(14)	84(3)	75(3)	69(2)	-18(2)	2(2)	8(3)
C(15)	61(2)	55(2)	52(2)	-6(2)	5(2)	2(2)
C(16)	54(2)	40(2)	41(2)	-1(2)	8(2)	-1(2)
C(17)	56(2)	59(2)	38(2)	-8(2)	7(2)	9(2)
C(18)	54(2)	50(2)	53(2)	-4(2)	-3(2)	6(2)
C(19)	71(2)	55(2)	40(2)	-9(2)	-6(2)	-7(2)
C(20)	77(3)	81(3)	47(2)	-25(2)	4(2)	9(2)
C(21)	55(2)	68(2)	51(2)	-7(2)	2(2)	14(2)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd23130.

	x	y	z	U(eq)
H(6)	-1311	7266	4236	152
H(7)	-1408	6595	3684	152
H(8)	-1434	7506	3477	152
H(10)	2623	7280	2579	150
H(9)	2353	6363	2745	150
H(11)	4585	6792	2874	150
H(14)	2764	8260	4405	134
H(12)	2586	8514	3651	134
H(13)	4740	8126	3921	134
H(1)	3800(30)	4114(11)	5427(9)	18(6)
H(2)	1070(40)	5374(13)	5931(10)	34(7)
H(3)	4970(40)	5389(13)	5219(11)	40(8)
H(4)	880(40)	5809(14)	4722(12)	47(9)
H(5)	4750(30)	6414(13)	4425(11)	35(8)
H(15)	-1850(40)	3072(14)	4560(11)	49(9)
H(16)	-1390(50)	2089(17)	3727(14)	77(11)
H(17)	1990(60)	1979(15)	3217(13)	108(13)
H(18)	4870(60)	2840(20)	3524(16)	103(13)
H(19)	4240(40)	3798(14)	4310(13)	69(10)
H(20)	6490(30)	4568(11)	6128(10)	28(6)
H(21)	8440(30)	4550(13)	7115(12)	48(9)
H(22)	3910(40)	5771(14)	8056(13)	64(9)
H(23)	1760(30)	5738(14)	7074(12)	52(9)

Table 6. Torsion angles [deg] for cd23130.

C(9)-C(1)-C(2)-C(16)	139.1(3)
C(3)-C(1)-C(2)-C(16)	-110.6(3)
C(9)-C(1)-C(2)-C(3)	-110.2(3)
C(16)-C(2)-C(3)-C(4)	-136.4(3)
C(1)-C(2)-C(3)-C(4)	111.6(3)
C(16)-C(2)-C(3)-C(1)	112.0(3)
C(9)-C(1)-C(3)-C(4)	0.2(4)
C(2)-C(1)-C(3)-C(4)	-110.8(3)
C(9)-C(1)-C(3)-C(2)	111.1(3)
C(2)-C(3)-C(4)-C(5)	142.8(3)
C(1)-C(3)-C(4)-C(5)	-145.5(3)
C(3)-C(4)-C(5)-Si	-177.1(2)
C(8)-Si-C(5)-C(4)	125.6(3)
C(6)-Si-C(5)-C(4)	5.6(4)
C(7)-Si-C(5)-C(4)	-116.0(3)
C(2)-C(1)-C(9)-O	0.2(4)
C(3)-C(1)-C(9)-O	-71.4(4)
C(2)-C(1)-C(9)-C(10)	-179.7(2)
C(3)-C(1)-C(9)-C(10)	108.7(3)
O-C(9)-C(10)-C(15)	158.2(3)
C(1)-C(9)-C(10)-C(15)	-21.9(4)
O-C(9)-C(10)-C(11)	-17.5(4)
C(1)-C(9)-C(10)-C(11)	162.4(3)
C(15)-C(10)-C(11)-C(12)	0.5(4)
C(9)-C(10)-C(11)-C(12)	176.3(3)
C(10)-C(11)-C(12)-C(13)	-1.8(5)
C(11)-C(12)-C(13)-C(14)	1.9(6)
C(12)-C(13)-C(14)-C(15)	-0.6(6)
C(13)-C(14)-C(15)-C(10)	-0.7(5)
C(11)-C(10)-C(15)-C(14)	0.7(4)
C(9)-C(10)-C(15)-C(14)	-175.1(3)
C(1)-C(2)-C(16)-C(17)	28.6(4)
C(3)-C(2)-C(16)-C(17)	-44.7(4)
C(1)-C(2)-C(16)-C(21)	-151.9(3)
C(3)-C(2)-C(16)-C(21)	134.8(3)
C(21)-C(16)-C(17)-C(18)	0.0(4)
C(2)-C(16)-C(17)-C(18)	179.6(3)
C(16)-C(17)-C(18)-C(19)	0.1(4)
C(17)-C(18)-C(19)-C(20)	-0.4(5)
C(17)-C(18)-C(19)-Br	178.7(2)

C(18)-C(19)-C(20)-C(21)	0.6(5)
Br-C(19)-C(20)-C(21)	-178.6(2)
C(19)-C(20)-C(21)-C(16)	-0.4(5)
C(17)-C(16)-C(21)-C(20)	0.1(4)
C(2)-C(16)-C(21)-C(20)	-179.4(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd23130 [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
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X-Ray Analysis of *Trans* - (1*R*,2*R*,3*R*)-2-(4-bromophenyl) - *cis* - 3 - ((trimethylsilyl)vinyl)-1-(methyloxycarbonyl) cyclopropane.

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	C ₁₆ H ₂₁ O ₂ BrSi
Formula Weight	353.33
Crystal Color, Habit	colorless, prismatic
Crystal Dimensions	0.20 X 0.20 X 0.20 mm
Crystal System	orthorhombic
Lattice Type	Primitive
No. of Reflections Used for Unit	
Cell Determination (2 θ range)	4 (16.4 - 19.2°)
Omega Scan Peak Width	
at Half-height	0.33°
Lattice Parameters	a = 14.983(2) Å b = 20.812(6) Å c = 5.729(4) Å V = 1786.3(1) Å ³
Space Group	P2 ₁ 2 ₁ 2 ₁ (#19)
Z value	4
D _{calc}	1.314 g/cm ³
F ₀₀₀	728.00
μ (MoK α)	23.74 cm ⁻¹

B. Intensity Measurements

Diffractometer	Rigaku AFC7R
Radiation	MoK α ($\lambda = 0.71069 \text{ \AA}$) graphite monochromated
Attenuator	Zr foil (factor = 7.96)
Take-off Angle	6.0°
Detector Aperture	3.0 mm horizontal 3.0 mm vertical
Crystal to Detector Distance	235 mm
Voltage, Current	50kV, 100mA
Temperature	25.0°C
Scan Type	ω
Scan Rate	20.0°/min (in ω) (up to 4 scans)
Scan Width	(1.52 + 0.30 tan θ)°
$2\theta_{\max}$	55.0°
No. of Reflections Measured	Total: 5069
Unique: 2403 ($R_{\text{int}} = 0.000$)	
Corrections	Lorentz-polarization Absorption (trans. factors: 0.7672 - 0.9935) Decay (4.37% decline)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR92)
Refinement	Full-matrix least-squares on F
Function Minimized	$\Sigma w (Fo - Fc)^2$
Least Squares Weights	1
Anomalous Dispersion	All non-hydrogen atoms
No. Observations ($I > 3.00\sigma(I)$)	2071
No. Variables	203
Reflection/Parameter Ratio	10.20
Residuals: R ($I > 3.00\sigma(I)$)	0.042
Residuals: Rw ($I > 3.00\sigma(I)$)	0.043
Goodness of Fit Indicator	0.74
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	1.10 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.90 e ⁻ /Å ³

Table 1. Atomic coordinates and $B_{\text{iso}}/B_{\text{eq}}$

atom	x	y	z	B_{eq}	atom	x	y	z	B_{eq}
Br(1)	0.97185(5)	0.49011(4)	0.3827(2)	7.94(3)	C(16)	0.7706(5)	0.3626(4)	0.565(1)	4.9(2)
Si(1)	0.2877(1)	0.3697(1)	0.7384(5)	4.81(5)	H(1)	0.5960(4)	0.3397(3)	0.044(1)	4.6(2)
O(1)	0.5007(4)	0.2214(2)	0.302(1)	5.1(2)	H(2)	0.6193(4)	0.2999(3)	0.514(1)	4.9(2)
O(2)	0.5407(3)	0.2370(2)	-0.070(1)	5.1(1)	H(3)	0.5372(4)	0.4097(3)	0.328(1)	5.2(2)
C(1)	0.5710(4)	0.3207(3)	0.180(1)	3.8(2)	H(4)	0.4437(5)	0.1726(3)	-0.092(2)	8.1(3)
C(2)	0.6205(4)	0.3342(3)	0.405(1)	4.1(2)	H(5)	0.5124(5)	0.1673(3)	-0.293(2)	8.1(3)
C(3)	0.5316(4)	0.3653(3)	0.363(1)	4.4(2)	H(6)	0.5369(5)	0.1426(3)	-0.046(2)	8.1(3)
C(4)	0.5334(5)	0.2541(3)	0.151(2)	3.8(2)	H(7)	0.4520(5)	0.3087(3)	0.580(1)	5.7(2)
C(5)	0.5053(5)	0.1746(3)	-0.131(2)	6.8(3)	H(8)	0.3900(4)	0.4303(3)	0.495(1)	6.0(2)
C(6)	0.4538(5)	0.3503(3)	0.511(1)	4.8(2)	H(9)	0.1811(5)	0.4050(4)	0.462(2)	9.0(3)
C(7)	0.3871(4)	0.3886(3)	0.562(1)	5.0(2)	H(10)	0.1999(5)	0.3324(4)	0.425(2)	9.0(3)
C(8)	0.1890(5)	0.3649(4)	0.538(2)	7.5(3)	H(11)	0.1367(5)	0.3545(4)	0.624(2)	9.0(3)
C(9)	0.3022(5)	0.2922(3)	0.898(2)	6.8(3)	H(12)	0.3097(5)	0.2584(3)	0.788(2)	8.1(3)
C(10)	0.2706(6)	0.4362(4)	0.952(1)	7.9(3)	H(13)	0.2510(5)	0.2839(3)	0.991(2)	8.1(3)
C(11)	0.7058(4)	0.3727(3)	0.397(1)	3.9(2)	H(14)	0.3535(5)	0.2947(3)	0.995(2)	8.1(3)
C(12)	0.7208(5)	0.4181(3)	0.226(2)	5.1(2)	H(15)	0.2616(6)	0.4752(4)	0.869(1)	9.5(3)
C(13)	0.8011(5)	0.4535(3)	0.222(2)	5.3(2)	H(16)	0.3222(6)	0.4400(4)	1.047(1)	9.5(3)
C(14)	0.8630(5)	0.4420(4)	0.388(2)	5.2(2)	H(17)	0.2201(6)	0.4277(4)	1.047(1)	9.5(3)
C(15)	0.8511(5)	0.3976(4)	0.564(2)	5.3(2)	H(18)	0.6751(5)	0.4256(3)	0.115(2)	6.1(2)
H(19)	0.8136(5)	0.4828(3)	0.099(2)	6.4(3)					
H(20)	0.8964(5)	0.3913(4)	0.678(2)	6.4(3)					

$$B_{\text{eq}} = 8/3\pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa*bb*)\cos\gamma + 2U_{13}(aa*cc*)\cos\beta + 2U_{23}(bb*cc*)\cos\alpha)$$

Table 2. Anisotropic Displacement Parameters

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Br(1)	0.0545(4)	0.0799(6)	0.167(1)	-0.0131(5)	0.0137(7)	-0.0341(8)
Si(1)	0.055(1)	0.063(1)	0.065(2)	0.001(1)	0.005(1)	-0.000(2)
O(1)	0.084(4)	0.056(3)	0.054(4)	-0.013(3)	0.006(3)	0.010(3)
O(2)	0.072(4)	0.057(3)	0.063(4)	-0.015(3)	0.009(4)	-0.006(3)
C(1)	0.049(4)	0.044(4)	0.052(6)	-0.009(3)	0.003(4)	0.005(4)
C(2)	0.054(4)	0.046(4)	0.056(6)	-0.005(4)	-0.000(5)	0.002(5)
C(3)	0.053(4)	0.046(4)	0.067(6)	-0.005(4)	0.013(5)	0.005(5)
C(4)	0.044(4)	0.053(5)	0.045(6)	0.006(4)	0.003(5)	-0.011(5)
C(5)	0.103(7)	0.061(5)	0.092(8)	-0.011(5)	0.002(7)	-0.025(6)
C(6)	0.058(5)	0.050(5)	0.073(6)	-0.004(4)	0.008(5)	0.001(5)
C(7)	0.057(4)	0.049(5)	0.084(7)	-0.007(4)	0.006(5)	-0.002(5)
C(8)	0.072(5)	0.116(8)	0.097(9)	-0.017(6)	-0.006(6)	0.019(8)
C(9)	0.073(5)	0.065(5)	0.118(8)	0.005(4)	0.009(7)	0.021(7)
C(10)	0.141(9)	0.073(6)	0.087(8)	0.005(6)	0.032(8)	-0.009(6)
C(11)	0.047(4)	0.040(4)	0.060(5)	0.007(4)	-0.004(5)	-0.003(5)
C(12)	0.053(4)	0.062(5)	0.077(7)	-0.006(4)	-0.008(5)	0.011(5)
C(13)	0.058(5)	0.051(5)	0.093(8)	-0.011(4)	0.003(6)	0.009(5)
C(14)	0.047(4)	0.049(5)	0.103(8)	-0.002(4)	0.010(6)	-0.019(6)
C(15)	0.048(5)	0.067(6)	0.087(8)	0.001(4)	-0.016(5)	-0.008(6)
C(16)	0.074(5)	0.054(5)	0.060(7)	-0.003(4)	0.001(5)	0.017(5)

The general temperature factor expression:

$$\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$$

Table 3. Bond lengths (Å)

Distance 0.000 0.000 Angles 0.000 0.000

Br(1) C(14) 1.915(7) Si(1) C(7) 1.843(7)

Si(1) C(8) 1.874(8) Si(1) C(9) 1.869(7)

Si(1) C(10) 1.863(7) O(1) C(4) 1.205(7)

O(2) C(4) 1.321(8) O(2) C(5) 1.445(7)

C(1) C(2) 1.512(9) C(1) C(3) 1.518(9)

C(1) C(4) 1.505(9) C(2) C(3) 1.500(8)

C(2) C(11) 1.508(8) C(3) C(6) 1.476(8)

C(6) C(7) 1.311(8) C(11) C(12) 1.380(9)

C(11) C(16) 1.384(9) C(12) C(13) 1.410(9)

C(13) C(14) 1.35(1) C(14) C(15) 1.38(1)

C(15) C(16) 1.409(9)

Table 4. Bond lengths involving hydrogens (Å)

atom	atom	distance	atom	atom	distance
Distance	0.000	1.55	H(9)	H(11)	1.55(5)
Angles	0.000	1.55	H(10)	H(11)	1.55(4)
O(2)	H(4)	1.98(4)	H(12)	H(13)	1.55(4)
O(2)	H(5)	1.98(7)	H(12)	H(14)	1.55(4)
O(2)	H(6)	1.97(2)	H(13)	H(14)	1.55(2)
C(1)	H(1)	0.95(2)	H(15)	H(16)	1.55(4)
C(2)	H(2)	0.95(2)	H(9)	H(11)	1.55(5)
C(3)	H(3)	0.95(1)	H(10)	H(11)	1.55(4)
C(5)	H(4)	0.95(1)	H(12)	H(13)	1.55(4)
C(5)	H(5)	0.95(1)	H(12)	H(14)	1.55(4)
C(5)	H(6)	0.95(2)	H(15)	H(17)	1.55(5)
C(6)	H(7)	0.95(2)	H(16)	H(17)	1.55(2)
C(6)	H(8)	1.92(3)	H(15)	H(17)	1.55(5)
C(7)	H(7)	1.93(4)	H(9)	H(10)	1.55(2)
C(7)	H(8)	0.95(2)			
C(8)	H(9)	0.95(2)			
C(8)	H(10)	0.95(2)			
C(8)	H(11)	0.95(2)			
C(9)	H(12)	0.95(2)			
C(9)	H(13)	0.95(2)			
C(9)	H(14)	0.95(2)			
C(10)	H(15)	0.95(2)			
C(10)	H(16)	0.95(2)			
C(10)	H(17)	0.95(2)			
C(12)	H(18)	0.95(2)			
C(13)	H(19)	0.95(2)			
C(15)	H(20)	0.95(2)			
C(16)	H(21)	0.95(2)			
H(4)	H(5)	1.55(4)			
H(4)	H(6)	1.55(3)			
H(5)	H(6)	1.55(4)			

Table 5. Bond angles (°)

atom	atom	atom	angle	atom	atom	atom	angle
C(7)	Si(1)	C(8)	108.2(4)				
C(7)	Si(1)	C(9)	111.1(3)				
C(8)	Si(1)	C(9)	110.3(4)				
C(7)	Si(1)	C(10)	108.1(4)				
C(8)	Si(1)	C(10)	109.4(4)				
C(9)	Si(1)	C(10)	109.6(4)				
C(4)	O(2)	C(5)	116.0(6)				
C(2)	C(1)	C(3)	59.3(4)				
C(2)	C(1)	C(4)	116.5(6)				
C(3)	C(1)	C(4)	119.5(6)				
C(1)	C(2)	C(3)	60.5(4)				
C(1)	C(2)	C(11)	119.3(7)				
C(3)	C(2)	C(11)	121.2(6)				
C(1)	C(3)	C(2)	60.1(4)				
C(1)	C(3)	C(6)	125.0(6)				
C(2)	C(3)	C(6)	121.2(6)				
O(1)	C(4)	O(2)	124.8(7)				
O(1)	C(4)	C(1)	126.5(8)				
O(2)	C(4)	C(1)	108.7(7)				
C(3)	C(6)	C(7)	126.9(7)				
Si(1)	C(7)	C(6)	127.4(6)				
C(2)	C(11)	C(12)	121.6(7)				
C(2)	C(11)	C(16)	119.6(7)				
C(12)	C(11)	C(16)	118.9(7)				
C(11)	C(12)	C(13)	120.7(8)				
C(12)	C(13)	C(14)	118.7(8)				
Br(1)	C(14)	C(13)	118.8(7)				
Br(1)	C(14)	C(15)	118.1(7)				
C(13)	C(14)	C(15)	123.1(7)				
C(14)	C(15)	C(16)	117.4(8)				
C(11)	C(16)	C(15)	121.3(8)				

Table 6. Bond angles involving hydrogens (°)

atom	atom	atom	angle	atom	atom	atom	angle
C(4)	O(2)	H(4)	100.3(7)	C(6)	C(7)	H(7)	26.3(6)
C(5)	O(2)	H(4)	26.8(6)	Si(1)	C(7)	H(8)	117.1(7)
C(4)	O(2)	H(5)	142.9(7)	C(6)	C(7)	H(8)	115.5(9)
C(5)	O(2)	H(5)	26.9(6)	H(7)	C(7)	H(8)	141.7(9)
H(4)	O(2)	H(5)	46.1(6)	Si(1)	C(8)	H(9)	109.5(8)
C(4)	O(2)	H(6)	101.3(7)	Si(1)	C(8)	H(10)	108.7(8)
C(5)	O(2)	H(6)	27.1(6)	H(9)	C(8)	H(10)	109.5(1)
H(4)	O(2)	H(6)	46.2(6)	Si(1)	C(8)	H(11)	110.3(8)
H(5)	O(2)	H(6)	46.3(6)	H(9)	C(8)	H(11)	109.5(1)
C(2)	C(1)	H(1)	115.2(8)	H(10)	C(8)	H(11)	109.5(1)
C(3)	C(1)	H(1)	117.6(8)	Si(1)	C(9)	H(12)	109.1(7)
C(4)	C(1)	H(1)	116.3(8)	Si(1)	C(9)	H(13)	109.7(7)
C(1)	C(2)	H(2)	114.3(8)	H(12)	C(9)	H(13)	109.5(1)
C(3)	C(2)	H(2)	114.4(8)	Si(1)	C(9)	H(14)	109.6(7)
C(11)	C(2)	H(2)	115.8(8)	H(12)	C(9)	H(14)	109.5(1)
C(1)	C(3)	H(3)	114.4(8)	H(13)	C(9)	H(14)	109.5(1)
C(2)	C(3)	H(3)	112.1(8)	Si(1)	C(10)	H(15)	109.1(8)
C(6)	C(3)	H(3)	113.5(8)	Si(1)	C(10)	H(16)	109.0(8)
O(2)	C(5)	H(4)	109.9(8)	H(15)	C(10)	H(16)	109.5(1)
O(2)	C(5)	H(5)	109.6(8)	Si(1)	C(10)	H(17)	110.3(8)
H(4)	C(5)	H(5)	109.5(1)	H(15)	C(10)	H(17)	109.5(1)
O(2)	C(5)	H(6)	108.9(8)	H(16)	C(10)	H(17)	109.5(1)
H(4)	C(5)	H(6)	109.5(1)	C(11)	C(12)	H(18)	118.2(9)
H(5)	C(5)	H(6)	109.5(1)	C(13)	C(12)	H(18)	121.1(9)
C(3)	C(6)	H(7)	117.0(8)	C(12)	C(13)	H(19)	121.1(9)
C(7)	C(6)	H(7)	116.1(9)	C(14)	C(13)	H(19)	120.1(1)
C(3)	C(6)	H(8)	100.4(7)	C(14)	C(15)	H(20)	120.3(1)
C(7)	C(6)	H(8)	26.5(6)	C(16)	C(15)	H(20)	122.4(1)
H(7)	C(6)	H(8)	142.6(9)	C(11)	C(16)	H(21)	119.0(9)
Si(1)	C(7)	H(7)	101.2(6)	C(15)	C(16)	H(21)	119.7(9)
C(5)	H(4)	H(6)	35.3(7)	C(10)	H(15)	H(16)	35.3(7)
H(5)	H(4)	H(6)	60.0(7)	C(10)	H(15)	H(17)	35.3(7)
O(2)	H(5)	C(5)	43.5(6)	H(16)	H(15)	H(17)	60.0(7)
O(2)	H(5)	H(4)	67.0(6)	C(10)	H(16)	H(15)	35.3(7)
C(5)	H(5)	H(4)	35.3(7)	C(10)	H(16)	H(17)	35.3(7)
O(2)	H(5)	H(6)	66.6(6)	H(15)	H(16)	H(17)	60.0(7)

C(5)	H(5)	H(6)	35.3(7)	C(10)	H(17)	H(15)	35.3(7)
H(4)	H(5)	H(6)	60.0(7)	C(10)	H(17)	H(16)	35.3(7)
O(2)	H(6)	C(5)	43.9(6)	H(15)	H(17)	H(16)	60.0(7)
O(2)	H(6)	H(4)	67.2(6)	C(10)	H(15)	H(16)	35.3(7)
C(5)	H(6)	H(4)	35.3(7)	C(10)	H(15)	H(17)	35.3(7)
O(2)	H(6)	H(5)	67.1(6)	H(16)	H(15)	H(17)	60.0(7)
C(5)	H(6)	H(5)	35.3(7)				
H(4)	H(6)	H(5)	60.0(7)				
C(6)	H(7)	C(7)	37.6(7)				
C(6)	H(8)	C(7)	38.0(7)				
C(8)	H(9)	H(10)	35.3(7)				
C(8)	H(9)	H(11)	35.3(7)				
H(10)	H(9)	H(11)	60.0(7)				
C(8)	H(10)	H(9)	35.3(7)				
C(8)	H(10)	H(11)	35.3(7)				
H(9)	H(10)	H(11)	60.0(7)				
C(8)	H(11)	H(9)	35.3(7)				
C(8)	H(11)	H(10)	35.3(7)				
H(9)	H(11)	H(10)	60.0(7)				
C(9)	H(12)	H(13)	35.3(7)				
C(9)	H(12)	H(14)	35.3(7)				
H(13)	H(12)	H(14)	60.0(7)				
C(9)	H(13)	H(12)	35.3(7)				
C(9)	H(13)	H(14)	35.3(7)				
H(12)	H(13)	H(14)	60.0(7)				
C(9)	H(14)	H(12)	35.3(7)				
C(9)	H(14)	H(13)	35.3(7)				
H(12)	H(14)	H(13)	60.0(7)				

Table 7. Torsion angles(°)

atom	atom	atom	atom	angle	atom	atom	atom	atom	angle
C(8)	Si(1)	C(7)	C(6)	-108.8(1)	C(12)	C(11)	C(16)	C(15)	-0.0(2)
C(9)	Si(1)	C(7)	C(6)	12.4(2)	C(11)	C(12)	C(13)	C(14)	0.3(2)
C(10)	Si(1)	C(7)	C(6)	132.7(1)	C(12)	C(13)	C(14)	Br(1)	-179.9(8)
C(5)	O(2)	C(4)	O(1)	0.7(2)	C(12)	C(13)	C(14)	C(15)	-0.9(2)
C(5)	O(2)	C(4)	C(1)	-178.3(8)	Br(1)	C(14)	C(15)	C(16)	-180.0(7)
C(3)	C(1)	C(2)	C(3)	0.0(6)	C(13)	C(14)	C(15)	C(16)	1.0(2)
C(3)	C(1)	C(2)	C(11)	-111.5(1)	C(14)	C(15)	C(16)	C(11)	-0.5(2)
C(4)	C(1)	C(2)	C(3)	-110.1(1)	C(12)	C(11)	C(16)	C(15)	-0.0(2)
C(4)	C(1)	C(2)	C(11)	138.4(1)	C(11)	C(12)	C(13)	C(14)	0.3(2)
C(2)	C(1)	C(3)	C(2)	0.0(6)	C(12)	C(13)	C(14)	Br(1)	-179.9(8)
C(2)	C(1)	C(3)	C(6)	-109.1(1)	C(12)	C(13)	C(14)	C(15)	-0.9(2)
C(4)	C(1)	C(3)	C(2)	105.2(1)	Br(1)	C(14)	C(15)	C(16)	-180.0(7)
C(4)	C(1)	C(3)	C(6)	-4.0(2)	C(13)	C(14)	C(15)	C(16)	1.0(2)
C(2)	C(1)	C(4)	O(1)	37.4(2)					
C(2)	C(1)	C(4)	O(2)	-143.7(9)					
C(3)	C(1)	C(4)	O(1)	-30.8(2)					
C(3)	C(1)	C(4)	O(2)	148.2(9)					
C(1)	C(2)	C(3)	C(1)	0.0(5)					
C(1)	C(2)	C(3)	C(6)	115.2(1)					
C(11)	C(2)	C(3)	C(1)	108.3(1)					
C(11)	C(2)	C(3)	C(6)	-136.4(1)					
C(1)	C(2)	C(11)	C(12)	28.5(1)					
C(1)	C(2)	C(11)	C(16)	-151.6(9)					
C(3)	C(2)	C(11)	C(12)	-42.9(1)					
C(3)	C(2)	C(11)	C(16)	137.1(1)					
C(1)	C(3)	C(6)	C(7)	-136.5(1)					
C(2)	C(3)	C(6)	C(7)	150.1(1)					
C(3)	C(6)	C(7)	Si(1)	177.7(7)					
C(2)	C(11)	C(12)	C(13)	-179.9(9)					
C(16)	C(11)	C(12)	C(13)	0.2(2)					
C(2)	C(11)	C(16)	C(15)	-179.9(9)					

Table 8. Distances beyond the asymmetric unit out to 3.60 Å

atom	atom	distance	ADC	atom	atom	distance	ADC
BR(1)	C(13)	2.824(7)	(1)	C(2)	C(6)	2.593(9)	(1)
BR(1)	C(14)	1.915(7)	(1)	C(2)	C(11)	1.508(8)	(1)
BR(1)	C(15)	2.839(8)	(1)	C(2)	C(12)	2.52(1)	(1)
SI(1)	C(6)	2.838(7)	(1)	C(2)	C(16)	2.50(1)	(1)
SI(1)	C(7)	1.843(7)	(1)	C(3)	C(4)	2.61(1)	(1)
SI(1)	C(8)	1.874(8)	(1)	C(3)	C(6)	1.476(8)	(1)
SI(1)	C(9)	1.869(7)	(1)	C(3)	C(7)	2.494(9)	(1)
SI(1)	C(10)	1.863(7)	(1)	C(3)	C(11)	2.621(9)	(1)
O(1)	O(2)	2.239(7)	(1)	C(3)	C(12)	3.14(1)	(1)
O(1)	C(1)	2.424(8)	(1)	C(4)	C(5)	2.35(1)	(1)
O(1)	C(2)	3.014(8)	(1)	C(4)	C(6)	3.11(1)	(1)
O(1)	C(3)	3.050(8)	(1)	C(5)	C(14)	3.55(1)	(2,1,-1)
O(1)	C(4)	1.205(7)	(1)	C(6)	C(7)	1.311(8)	(1)
O(1)	C(5)	2.66(1)	(1)	C(6)	C(9)	3.40(1)	(1)
O(1)	C(5)	3.40(1)	(1,1,0,0,1)	C(7)	C(8)	3.012(9)	(1)
O(1)	C(6)	3.019(9)	(1)	C(7)	C(9)	3.06(1)	(1)
O(1)	C(8)	3.469(9)	(2,1,0,0,1)	C(7)	C(10)	3.00(1)	(1)
O(1)	C(15)	3.429(9)	(2,1,-1,0,1)	C(8)	C(9)	3.07(1)	(1)
O(2)	C(1)	2.299(9)	(1)	C(8)	C(10)	3.05(1)	(1)
O(2)	C(2)	3.592(9)	(1)	C(9)	C(10)	3.05(1)	(1)
O(2)	C(4)	1.321(8)	(1)	C(11)	C(12)	1.380(9)	(1)
O(2)	C(5)	1.445(7)	(1)	C(11)	C(13)	2.42(1)	(1)
C(1)	C(2)	1.512(9)	(1)	C(11)	C(14)	2.762(9)	(1)
C(1)	C(3)	1.518(9)	(1)	C(11)	C(15)	2.43(1)	(1)
C(1)	C(4)	1.505(9)	(1)	C(11)	C(16)	1.384(9)	(1)
C(1)	C(6)	2.66(1)	(1)	C(12)	C(13)	1.410(9)	(1)
C(1)	C(11)	2.606(9)	(1)	C(12)	C(14)	2.38(1)	(1)
C(1)	C(12)	3.036(9)	(1)	C(12)	C(15)	2.78(1)	(1)
C(2)	C(3)	1.500(8)	(1)	C(12)	C(16)	2.38(1)	(1)
C(2)	C(4)	2.57(1)	(1)	C(13)	C(14)	1.35(1)	(1)
C(15)	C(16)	1.409(9)	(1)				

*ADC (S, L, TX, TY, TZ) represents:

S: Symmetry operation number. -S is inversion of operation S.

- (1) X, Y, Z
- (2) $X+1/2, -Y+1/2, -Z$
- (3) $-X, Y+1/2, -Z+1/2$
- (4) $-X+1/2, -Y, Z+1/2$

L: Lattice translation.

- (1) $0, 0, 0$

TX, TY, TZ: Unit cell translation along the x, y, and z directions.

Table 9. Distances beyond the asymmetric unit out to 3.60 Å

atom	atom	distance	ADC	atom	atom	distance	ADC
BR(1)	H(3)	3.3(2)	(4,1,1,1)	O(2)	H(12)	3.6(4)	(1,1,0,0,-1)
BR(1)	H(5)	3.4(2)	(2)	O(2)	H(13)	3.2(7)	(2,1,0,0,1)
BR(1)	H(6)	3.5(1)	(2)	O(2)	H(14)	3.1(5)	(1,1,0,0,-1)
BR(1)	H(8)	3.5(2)	(4,1,1,1,-1)	C(1)	H(1)	0.95(2)	(1)
BR(1)	H(16)	3.5(1)	(4,1,1,1,-1)	C(1)	H(2)	2.09(5)	(1)
BR(1)	H(18)	3.1(2)	(4,1,1,1)	C(1)	H(3)	2.10(7)	(1)
BR(1)	H(19)	2.9(1)	(1)	C(1)	H(7)	2.9(1)	(1)
BR(1)	H(20)	2.9(1)	(1)	C(1)	H(14)	3.5(4)	(1,1,0,0,-1)
SI(1)	H(7)	2.91(9)	(1)				
SI(1)	H(8)	2.43(9)	(1)	C(1)	H(18)	2.71(7)	(1)
SI(1)	H(9)	2.37(8)	(1)	C(2)	H(1)	2.10(3)	(1)
SI(1)	H(10)	2.36(8)	(1)				
SI(1)	H(11)	2.38(4)	(1)	C(2)	H(2)	0.95(2)	(1)
SI(1)	H(12)	2.36(3)	(1)	C(2)	H(3)	2.06(5)	(1)
SI(1)	H(13)	2.4(1)	(1)				
SI(1)	H(14)	2.4(1)	(1)	C(2)	H(7)	2.77(8)	(1)
SI(1)	H(15)	2.35(7)	(1)	C(2)	H(12)	3.6(3)	(2,1,0,0,1)
SI(1)	H(16)	2.4(1)	(1)				
SI(1)	H(17)	2.4(1)	(1)	C(2)	H(18)	2.7(1)	(1)
O(1)	H(1)	3.2(2)	(1)	C(2)	H(21)	2.63(9)	(1)
O(1)	H(2)	2.7(1)	(1)				
O(1)	H(4)	2.6(1)	(1)	C(3)	H(1)	2.13(6)	(1)
O(1)	H(5)	3.6(2)	(1)	C(3)	H(2)	2.08(6)	(1)
O(1)	H(5)	2.6(2)	(1,1,0,0,1)				
O(1)	H(6)	2.6(1)	(1)	C(3)	H(3)	0.95(1)	(1)
O(1)	H(7)	2.5(1)	(1)	C(3)	H(7)	2.09(7)	(1)
O(1)	H(10)	3.6(2)	(2,1,0,0,1)				
O(1)	H(11)	2.6(4)	(2,1,0,0,1)	C(3)	H(8)	2.63(8)	(1)
O(1)	H(14)	3.2(3)	(1,1,0,0,-1)	C(3)	H(18)	2.9(1)	(1)
O(1)	H(20)	2.8(6)	(2,1,-1,0,1)				
O(2)	H(1)	2.38(7)	(1)	C(4)	H(1)	2.11(6)	(1)
O(2)	H(2)	3.0(2)	(1,1,0,0,-1)	C(4)	H(2)	2.6(1)	(1)
O(2)	H(4)	1.98(4)	(1)				
O(2)	H(5)	1.98(7)	(1)	C(4)	H(3)	3.4(1)	(1)
O(2)	H(6)	1.97(2)	(1)	C(4)	H(4)	2.6(1)	(1)

O(2)	H(7)	2.8(3)	(1,1,0,0,-1)				
O(2)	H(10)	3.4(5)	(2)	C(4)	H(5)	3.1(2)	(1)
O(2)	H(11)	3.5(8)	(2,1,0,0,1)	C(4)	H(6)	2.6(1)	(1)
C(5)	H(11)	3.6(9)	(2,1,0,0,1)	C(9)	H(11)	3.2(1)	(1)
C(5)	H(12)	3.4(5)	(1,1,0,0,-1)	C(9)	H(12)	0.95(2)	(1)
C(5)	H(14)	3.5(7)	(1,1,0,0,-1)	C(9)	H(13)	0.95(2)	(1)
C(5)	H(20)	3.4(1)	(2,1,-1,0,1)	C(9)	H(14)	0.95(2)	(1)
C(6)	H(1)	3.4(2)	(1)	C(9)	H(16)	3.2(1)	(1)
C(6)	H(2)	2.69(5)	(1)	C(9)	H(17)	3.2(1)	(1)
C(6)	H(3)	2.05(7)	(1)	C(9)	H(21)	3.6(3)	(2,1,-1,0,2)
C(6)	H(7)	0.95(2)	(1)	C(10)	H(8)	3.2(1)	(1)
C(6)	H(8)	1.92(3)	(1)	C(10)	H(8)	3.6(1)	(1,1,0,0,1)
C(6)	H(12)	3.3(2)	(1)	C(10)	H(9)	3.2(1)	(1)
C(6)	H(14)	3.5(2)	(1,1,0,0,-1)	C(10)	H(9)	3.3(1)	(1,1,0,0,1)
C(6)	H(14)	3.4(2)	(1)	C(10)	H(9)	3.4(1)	(4,1,0,1)
C(7)	H(3)	2.66(9)	(1)	C(10)	H(11)	3.2(2)	(1)
C(7)	H(7)	1.93(4)	(1)	C(10)	H(13)	3.19(5)	(1)
C(7)	H(8)	0.95(2)	(1)	C(10)	H(14)	3.21(8)	(1)
C(7)	H(9)	3.16(6)	(1)	C(10)	H(15)	0.95(2)	(1)
C(7)	H(10)	3.14(9)	(1)	C(10)	H(15)	3.05(2)	(4,1,0,1)
C(7)	H(12)	3.2(2)	(1)	C(10)	H(16)	0.95(2)	(1)
C(7)	H(14)	3.2(2)	(1)	C(10)	H(17)	0.95(2)	(1)
C(7)	H(15)	3.1(2)	(1)	C(11)	H(1)	2.7(1)	(1)
C(7)	H(16)	3.3(1)	(1,1,0,0,-1)	C(11)	H(2)	2.10(6)	(1)
C(7)	H(16)	3.1(1)	(1)	C(11)	H(3)	2.67(5)	(1)
C(8)	H(2)	3.6(2)	(2,1,-1,0,1)	C(11)	H(12)	3.3(5)	(2,1,0,0,1)
C(8)	H(5)	3.1(1)	(2,1,-1)	C(11)	H(18)	2.01(7)	(1)
C(8)	H(8)	3.31(8)	(1)	C(11)	H(19)	3.3(2)	(1)
C(8)	H(9)	0.95(2)	(1)	C(11)	H(19)	3.2(2)	(4,1,1,1)
C(8)	H(10)	0.95(2)	(1)	C(11)	H(20)	3.3(1)	(1)
C(8)	H(11)	0.95(2)	(1)	C(11)	H(21)	2.02(7)	(1)
C(8)	H(12)	3.2(2)	(1)	C(12)	H(1)	2.7(1)	(1)
C(8)	H(13)	3.2(2)	(1)	C(12)	H(2)	3.3(2)	(1)
C(8)	H(15)	3.2(2)	(1)	C(12)	H(3)	2.82(5)	(1)
C(8)	H(15)	3.5(2)	(4,1,0,1,-1)	C(12)	H(18)	0.95(2)	(1)
C(8)	H(17)	3.1(2)	(1,1,0,0,-1)	C(12)	H(19)	2.07(6)	(1)
C(8)	H(17)	3.2(2)	(1)	C(12)	H(19)	3.01(6)	(4,1,1,1)

C(9)	H(4)	3.3(6)	(1,1,0,0,1)	C(12)	H(21)	3.2(2)	(1)
C(9)	H(7)	2.9(1)	(1)	C(13)	H(4)	3.5(7)	(2)
C(9)	H(10)	3.2(1)	(1)	C(13)	H(18)	2.07(4)	(1)
C(9)	H(10)	3.5(1)	(1,1,0,0,1)	C(13)	H(18)	3.39(4)	(4,1,1,1)
C(13)	H(19)	0.95(2)	(1)	C(16)	H(2)	2.63(6)	(1)
C(13)	H(19)	3.06(2)	(4,1,1,1)	C(16)	H(12)	3.3(4)	(2,1,0,0,1)
C(13)	H(20)	3.2(2)	(1)	C(16)	H(18)	3.2(2)	(1)
C(14)	H(4)	3.2(1)	(2)	C(16)	H(19)	3.5(3)	(4,1,1,1)
C(14)	H(5)	3.2(1)	(2)	C(16)	H(20)	2.08(5)	(1)
C(14)	H(18)	3.2(1)	(1)	C(16)	H(21)	0.95(2)	(1)
C(14)	H(18)	3.1(1)	(4,1,1,1)	C(16)	H(2)	2.63(6)	(1)
C(14)	H(19)	2.00(7)	(1)	C(16)	H(12)	3.3(4)	(2,1,0,0,1)
C(14)	H(19)	3.30(7)	(4,1,1,1)	C(16)	H(18)	3.2(2)	(1)
C(14)	H(20)	2.03(8)	(1)	C(16)	H(19)	3.5(3)	(4,1,1,1)
C(14)	H(21)	3.2(2)	(1)	C(16)	H(20)	2.08(5)	(1)
C(15)	H(4)	3.4(1)	(2)	C(16)	H(21)	0.95(2)	(1)
C(15)	H(5)	3.2(1)	(2)	C(16)	H(2)	2.63(6)	(1)
C(15)	H(19)	3.3(2)	(1)	C(16)	H(12)	3.3(4)	(2,1,0,0,1)
C(15)	H(19)	3.6(2)	(1,1,0,0,1)	C(16)	H(18)	3.2(2)	(1)
C(15)	H(19)	3.5(2)	(4,1,1,1)	C(16)	H(19)	3.5(3)	(4,1,1,1)
C(15)	H(20)	0.95(2)	(1)				
C(15)	H(21)	2.05(6)	(1)				

*ADC (S, L, TX, TY, TZ) represents:

S: Symmetry operation number. -S is inversion of operation S.

(1) X, Y, Z

(2) X+1/2, -Y+1/2, -Z

(3) -X, Y+1/2, -Z+1/2

(4) -X+1/2, -Y, Z+1/2

L: Lattice translation.

(1) 0, 0, 0

TX, TY, TZ: Unit cell translation along the x, y, and z directions.

Table 10. Least Squares Planes

Plane number 1

Co-ordinates of the defining atoms projected onto the best plane

Type Serial XP YP ZP

C 1 0.865 -0.151 0.000

C 2 -0.300 0.813 0.000

C 3 -0.565 -0.663 0.000

Co-ordinates of other atoms projected onto the best plane

Type Serial XP YP ZP

C 4 1.678 -0.223 1.265

C 6 -1.229 -1.321 1.142

C 11 -0.561 1.655 -1.223

Plane number 2

Co-ordinates of the defining atoms projected onto the best plane

Type Serial XP YP ZP

C 11 -1.398 -0.046 -0.002

C 12 -0.738 1.166 0.001

C 13 0.672 1.217 0.002

C 14 1.362 0.057 -0.005

C 15 0.755 -1.182 0.004

C 16 -0.654 -1.213 0.000

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X-Ray Analysis of Salt 1a'

Table 1. Crystal data and structure refinement for cd23170.

Identification code	cd23170
Empirical formula	C ₁₂ H ₂₅ Si Te Br
Formula weight	404.92
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P2(1)2(1)2
Unit cell dimensions	a = 11.8162(10) Å alpha = 90 deg. b = 14.1277(11) Å beta = 90 deg. c = 10.3477(8) Å gamma = 90 deg.
Volume	1727.4(2) Å ³
Z, Calculated density	4, 1.557 Mg/m ³
Absorption coefficient	4.081 mm ⁻¹
F(000)	792
Crystal size	0.330 x 0.180 x 0.163 mm
Theta range for data collection	1.97 to 28.25 deg.
Limiting indices	-14 ≤ h ≤ 15, -18 ≤ k ≤ 15, -13 ≤ l ≤ 13
Reflections collected / unique	10625 / 4046 [R(int) = 0.0839]
Completeness to theta = 28.25	97.0 %
Absorption correction	Sadabs
Max. and min. transmission	1.00000 and 0.65876
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4046 / 2 / 150

Goodness-of-fit on F^2	0.812
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0392$, $wR_2 = 0.0667$
R indices (all data)	$R_1 = 0.0646$, $wR_2 = 0.0720$
Absolute structure parameter	-0.005(18)
Extinction coefficient	0.00208(11)
Largest diff. peak and hole	0.534 and -0.484 e. $\text{\AA}^{-3}$

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd23170.

$U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Br	1571(1)	-1215(1)	3988(1)	73(1)
Te	1315(1)	1163(1)	3912(1)	55(1)
Si	2500(2)	3707(2)	384(2)	95(1)
C(1)	1347(5)	946(4)	6002(6)	66(1)
C(2)	2561(5)	1095(5)	6379(6)	79(2)
C(3)	3377(5)	756(5)	5344(8)	88(2)
C(4)	3159(4)	1252(4)	4092(7)	68(2)
C(5)	513(6)	1566(5)	6729(6)	92(2)
C(6)	3766(6)	888(5)	2896(7)	101(3)
C(7)	1078(5)	2681(3)	3879(8)	71(2)
C(8)	1303(6)	3003(4)	2534(7)	79(2)
C(9)	2188(5)	3416(5)	2103(6)	72(2)
C(10)	1275(8)	3610(9)	-629(8)	258(8)
C(11)	3216(8)	4834(7)	243(9)	168(5)
C(12)	3553(12)	2839(9)	-240(13)	298(10)

Table 3. Bond lengths [Å] and angles [deg] for cd23170.

Te-C(7)	2.163(5)
Te-C(1)	2.185(6)
Te-C(4)	2.191(5)
Si-C(10)	1.793(8)
Si-C(11)	1.808(9)
Si-C(12)	1.863(11)
Si-C(9)	1.863(7)
C(1)-C(2)	1.501(7)
C(1)-C(5)	1.518(8)
C(1)-H(1)	0.974(19)
C(2)-C(3)	1.519(8)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(4)	1.496(9)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(6)	1.521(9)
C(4)-H(4)	0.989(19)
C(5)-H(5A)	0.9600
C(5)-H(5B)	0.9600
C(5)-H(5C)	0.9600
C(6)-H(6A)	0.9600
C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600
C(7)-C(8)	1.488(9)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(9)	1.278(8)
C(8)-H(8)	0.9300
C(9)-H(9)	0.9300
C(10)-H(10A)	0.9619
C(10)-H(10B)	0.9619
C(10)-H(10C)	0.9619
C(11)-H(11A)	0.9600
C(11)-H(11B)	0.9600
C(11)-H(11C)	0.9600
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600

C(7)-Te-C(1)	99.0(3)
C(7)-Te-C(4)	94.1(2)
C(1)-Te-C(4)	84.6(2)
C(10)-Si-C(11)	113.4(5)
C(10)-Si-C(12)	106.6(6)
C(11)-Si-C(12)	103.8(5)
C(10)-Si-C(9)	112.5(4)
C(11)-Si-C(9)	111.4(4)
C(12)-Si-C(9)	108.5(4)
C(2)-C(1)-C(5)	114.2(6)
C(2)-C(1)-Te	104.7(4)
C(5)-C(1)-Te	113.5(4)
C(2)-C(1)-H(1)	103(3)
C(5)-C(1)-H(1)	116(3)
Te-C(1)-H(1)	103(3)
C(1)-C(2)-C(3)	112.3(5)
C(1)-C(2)-H(2A)	109.1
C(3)-C(2)-H(2A)	109.1
C(1)-C(2)-H(2B)	109.2
C(3)-C(2)-H(2B)	109.2
H(2A)-C(2)-H(2B)	107.9
C(4)-C(3)-C(2)	110.7(5)
C(4)-C(3)-H(3A)	109.5
C(2)-C(3)-H(3A)	109.5
C(4)-C(3)-H(3B)	109.5
C(2)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	108.1
C(3)-C(4)-C(6)	117.7(6)
C(3)-C(4)-Te	102.6(4)
C(6)-C(4)-Te	112.4(5)
C(3)-C(4)-H(4)	108(3)
C(6)-C(4)-H(4)	114(3)
Te-C(4)-H(4)	100(3)
C(1)-C(5)-H(5A)	109.5
C(1)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(1)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(4)-C(6)-H(6A)	109.5
C(4)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(4)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5

H(6B)-C(6)-H(6C)	109.5
C(8)-C(7)-Te	107.1(4)
C(8)-C(7)-H(7A)	110.3
Te-C(7)-H(7A)	110.3
C(8)-C(7)-H(7B)	110.3
Te-C(7)-H(7B)	110.3
H(7A)-C(7)-H(7B)	108.5
C(9)-C(8)-C(7)	127.7(6)
C(9)-C(8)-H(8)	116.1
C(7)-C(8)-H(8)	116.2
C(8)-C(9)-Si	126.6(5)
C(8)-C(9)-H(9)	116.7
Si-C(9)-H(9)	116.7
Si-C(10)-H(10A)	109.6
Si-C(10)-H(10B)	109.6
H(10A)-C(10)-H(10B)	109.3
Si-C(10)-H(10C)	109.6
H(10A)-C(10)-H(10C)	109.3
H(10B)-C(10)-H(10C)	109.3
Si-C(11)-H(11A)	109.5
Si-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
Si-C(11)-H(11C)	109.4
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
Si-C(12)-H(12A)	109.5
Si-C(12)-H(12B)	109.4
H(12A)-C(12)-H(12B)	109.5
Si-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd23170.

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
Br	76(1)	52(1)	91(1)	-5(1)	-2(1)	5(1)
Te	57(1)	44(1)	65(1)	-4(1)	5(1)	3(1)
Si	124(2)	87(2)	74(1)	17(1)	-31(1)	-14(1)
C(1)	78(4)	60(4)	59(3)	-1(3)	4(4)	-5(3)
C(2)	101(5)	68(4)	69(4)	-8(4)	-20(4)	4(4)
C(3)	63(5)	61(4)	138(7)	11(5)	-18(4)	-9(3)
C(4)	51(3)	48(3)	103(5)	-3(5)	18(3)	3(3)
C(5)	103(5)	109(6)	64(4)	-24(4)	6(4)	5(4)
C(6)	77(4)	88(6)	139(7)	-13(5)	28(5)	17(4)
C(7)	60(4)	44(3)	107(5)	-13(4)	-6(4)	12(2)
C(8)	74(4)	63(4)	99(5)	6(4)	-31(5)	-1(4)
C(9)	70(4)	64(4)	80(5)	3(4)	-18(3)	-3(3)
C(10)	214(11)	420(20)	141(9)	127(12)	-96(8)	-182(14)
C(11)	270(13)	145(9)	87(6)	-5(6)	37(8)	-100(9)
C(12)	510(30)	262(17)	118(9)	-10(10)	51(15)	240(18)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for cd23170.

	x	y	z	U(eq)
H(2A)	2712	758	7177	95
H(2B)	2688	1764	6537	95
H(3A)	4148	877	5620	105
H(3B)	3290	79	5225	105
H(5A)	603	1470	7641	138
H(5B)	-245	1403	6479	138
H(5C)	653	2219	6525	138
H(6A)	4564	1002	2980	152
H(6B)	3485	1212	2146	152
H(6C)	3634	221	2807	152
H(7A)	311	2841	4131	85
H(7B)	1598	2985	4475	85
H(8)	731	2889	1936	95
H(9)	2731	3589	2710	86
H(10A)	726	4075	-376	387
H(10B)	955	2989	-542	387
H(10C)	1489	3714	-1513	387
H(11A)	3771	4890	915	252
H(11B)	2674	5337	322	252
H(11C)	3581	4873	-584	252
H(12A)	3779	3017	-1097	447
H(12B)	3219	2220	-260	447
H(12C)	4203	2832	317	447
H(1)	1250(40)	265(15)	6090(50)	75(17)
H(4)	3240(40)	1941(16)	4240(50)	59(16)

Table 6. Torsion angles [deg] for cd23170.

C(7)-Te-C(1)-C(2)	-86.9(4)
C(4)-Te-C(1)-C(2)	6.5(4)
C(7)-Te-C(1)-C(5)	38.3(5)
C(4)-Te-C(1)-C(5)	131.7(5)
C(5)-C(1)-C(2)-C(3)	-159.1(6)
Te-C(1)-C(2)-C(3)	-34.3(6)
C(1)-C(2)-C(3)-C(4)	58.0(7)
C(2)-C(3)-C(4)-C(6)	-170.3(6)
C(2)-C(3)-C(4)-Te	-46.3(6)
C(7)-Te-C(4)-C(3)	119.9(5)
C(1)-Te-C(4)-C(3)	21.2(4)
C(7)-Te-C(4)-C(6)	-112.7(5)
C(1)-Te-C(4)-C(6)	148.6(5)
C(1)-Te-C(7)-C(8)	167.0(4)
C(4)-Te-C(7)-C(8)	81.8(5)
Te-C(7)-C(8)-C(9)	-103.2(7)
C(7)-C(8)-C(9)-Si	173.8(5)
C(10)-Si-C(9)-C(8)	14.3(9)
C(11)-Si-C(9)-C(8)	142.8(7)
C(12)-Si-C(9)-C(8)	-103.5(8)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for cd23170 [Å and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
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