Gaudichanolides A and B, Clerodane Diterpenes from *Baccharis gaudichaudiana*

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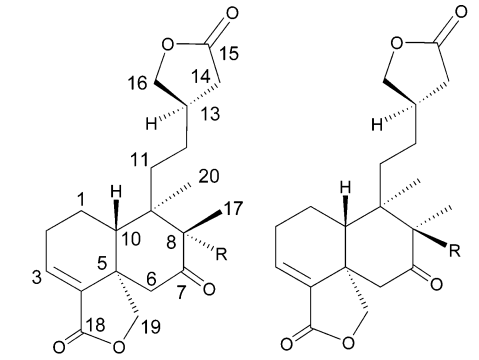
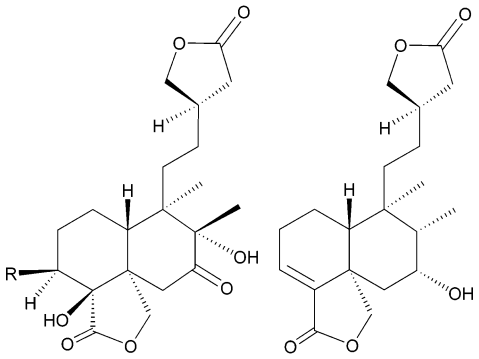
Two new clerodane diterpenoids, gaudichanolides A (**1**) and B (**2**), were isolated from the dried twigs of *Baccharis gaudichaudiana*, together with 7-oxo-16,19-dihydroxy-3,4-dehydroclerodan-15,20-diacid dilactone, spathulenol, 4,10-aromadendranediol, kobusone, *trans*-cosanyl ferulate, and defuscin. The structures and relative stereochemistry of **1** and **2** were elucidated by detailed 2D NMR spectroscopic experiments, and the absolute stereochemistry of **1** was determined by X-ray crystallographic analysis.

Baccharis is the largest genus in the family Asteraceae, with over 400 species distributed throughout the North and South American continents. *Baccharis gaudichaudiana* DC. is considered a folk medicine in South America and is used for the treatment of diabetes and gastrointestinal diseases. A previous study of constituents of this species revealed as characteristic metabolites clerodane-type diterpenes,[1] in addition to labdane-type diterpenes,[2] sweet, bitter, and neutral-tasting labdane-type diterpene glycosides,[3,4] apigenin, hispidulin, and various other flavonoids, spathulenol, and ursolic acid.[2−5] Interestingly, gaudichaudioside A, a labdane diterpene arabinoside, was isolated as a potential noncaloric sweetener in the early 1990s from this plant.[3] In the present study, two new clerodane-type diterpenes, designated as gaudichanolides A (**1**) and B (**2**), were isolated from the CH_2Cl_2 extract of the twigs of *B. gaudichaudiana*, together with six known compounds, 7-oxo-16,19-dihydroxy-3,4-dehydroclerodan-15,20-diacid dilactone (**3**),[6,7] spathulenol,[8] 4,10-aromadendranediol,[9] kobusone,[10] *trans*-cosanyl ferulate,[11] and defuscin.[12] The known compounds were identified by comparing their spectroscopic data to literature values. The structures of **1** and **2** were determined by detailed 2D NMR experiments. The absolute stereochemistry of **1** and the relative configuration of **3** were confirmed by X-ray crystallographic analysis of the *p*-bromobenzoate of **1** and a reduction product of **3**, respectively.





Gaudichanolide A (**1**) was obtained as a colorless oil with the molecular formula $C_{20}H_{26}O_6$, which was determined by HREIMS. The IR absorptions at 3483 and 1774 cm^{-1} indicated the presence of hydroxyl and carbonyl groups, respectively. The ^1H NMR spectrum displayed two tertiary methyl signals (δ 0.79 and 1.53), an olefinic signal (δ 6.87), and two oxymethylene signals. The ^{13}C NMR and DEPT spectra revealed a total of 20 signals including two methyls, six methylenes, two methines, two oxymethylenes, two olefinic carbons, two ester carbonyls, a ketone carbonyl, and three quaternary carbons. These NMR data together with the molecular formula suggested that **1** has four rings, including two lactone rings in the molecule. A $^1H-^1H$ COSY NMR experiment established the connectivity from H-10 to H-3 and from H-11 to H-14 and H-16. The presence of a γ-lactone ring (C-13 to C-16) was determined by the long-range couplings in the HMBC NMR spectrum (H-16/C-15 and H-16/C-14). The linkages of the other γ-lactone and ring junctions (C-5 and C-10) were established by additional HMBC correlations (H-19/C-4, C-6, C-18, H-10/C-5, C-19, and H-3/C-5, C-18), suggesting that the remaining three rings constitute a substituted decalin ring fused with a γ-lactone unit. The carbonyl and two methyl groups were attached to the C-7, C-8, and C-9 positions, respectively, on the basis of HMBC analysis, as shown in Figure 1. Finally, C-11 was positioned at C-9 by analysis of the HMBC spectrum (H-11/C-20, C-10, and C-8), indicating that **1** has the same planar structure as the known clerodane, 8β-hydroxy-7-oxo-*ent*-cleroda-3-en-15,18-diacid-16,19-dilactone.[7] However, the specific rotation and NMR data of **1** did not agree with those of the latter compound,[7] confirming that these two compounds are diastereomeric. A NOESY experiment revealed the relative stereochemistry of **1**, except for that of C-13, as in Figure 1.

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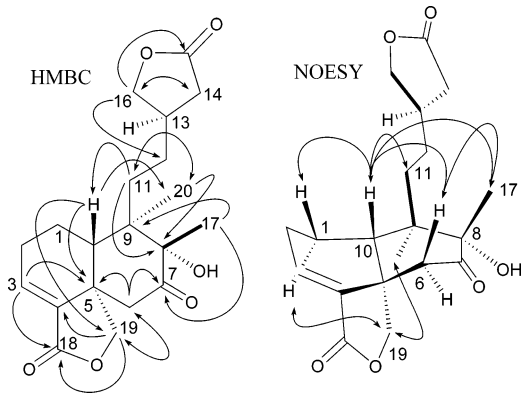

Figure 1. HMBC and NOESY correlations of **1**.

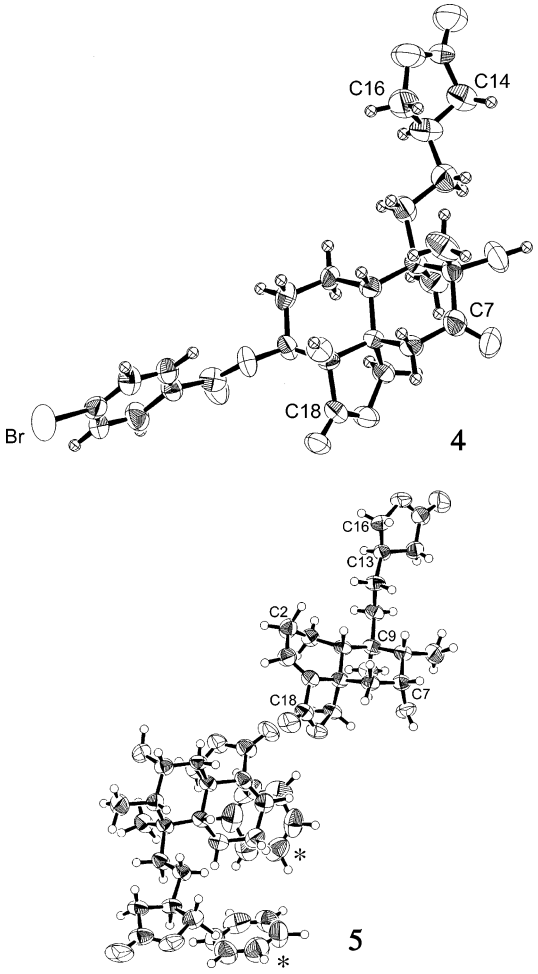

Figure 2. ORTEP diagrams of **4** and **5**. The crystal structure of **5** contains two benzene molecules.

To determine the absolute stereochemistry of **1**, a *p*-bromobenzoyl derivative was prepared. Compound **1** was oxidized with OsO_4 to afford a diol and then treated with *p*-bromobenzoyl chloride. The resultant *p*-bromobenzonate **4** was crystallized, and its structure was determined by X-ray crystallographic analysis, with the anomalous scattering factor correction for the brominated atom introduced to establish the absolute configuration of **4**.[13] An ORTEP diagram of **4** is shown in Figure 2. Accordingly, the absolute structure of **1** was determined as shown.

Gaudichanolide B (**2**) was isolated as a white powder and gave a molecular ion at *m/z* 346.1789 $[M]^+$ in the HREIMS, attributable to a molecular formula of $C_{20}H_{26}O_5$. The IR spectrum showed an absorption for a carbonyl group at 1775 cm^{-1}. The NMR spectra of **2** were very similar to those of **1**, suggesting **2** is also a clerodane-type diterpene. A comparison of the NMR data between **1** and **2** revealed the appearance of an additional methine signal and a secondary methyl signal, with no hydroxylated quaternary carbon signals, indicating that **2** is a dehydroxylated derivative of **1** at C-8. This was also supported by the lack of IR absorption attributable to a hydroxyl group and the molecular formula. Analysis of the $^1H-^1H$ COSY and HMBC spectra of this compound afforded the same correlations as in **1**. The NOESY spectrum of **2** displayed almost the same correlations as in **1**, except for the correlation between H-8 and H-20. These results suggested **2** is the epimer of **3** at C-8. However, the stereochemistry of C-13 (γ-lactone) could not be determined by the spectroscopic methods used.

The agreement of chemical shifts of the γ-lactone (C-13 to C-16) moieties among **1**−**3** strongly implied that the stereochemistry of the γ-lactone in both **2** and **3** is the same as in **1**. The stereochemistry of C-13 in **3** has not been reported previously. Therefore, **3** was reduced with $NaBH_4$ to give a 7α-hydroxy product (**5**), which yielded a single crystal for X-ray crystallographic analysis. The X-ray analysis of **5** indicated that the stereochemistry of C-13 in **3** was the same as that in **1** (Figure 2). However, the stereochemistry of C-13 in **2** could not be determined since it was not possible to obtain an appropriate crystal for X-ray analysis. From the NMR signals of the γ-lactone unit (C-12 to C-16, for **2**: δ_C 26.9, 36.6, 34.5, 177.0, 72.9; for **3**: δ_C 26.8, 35.9, 34.5, 176.3, 72.9) and on biogenetic grounds, H-13 in **2** should be in the same orientation as found in **1** and **3**.

Several clerodane diterpenes from *Baccharis* species have been reported as antifeedants, and some have a bitter taste apparently related to this activity. It is interesting to note that compounds **1** and **2** also have a bitter taste.

Experimental Section

General Experimental Procedures. Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. Optical rotations were measured with a Horiba SEPT-200 polarimeter. IR spectra were measured on a Perkin-Elmer 1720 FT-IR spectrometer ($CHCl_3$ solution). NMR spectra were recorded on Bruker ARX400 and JEOL Lambda 500 NMR spectrometers with TMS as internal standard. Mass spectra were obtained on a JEOL JMS-700 spectrometer. Column chromatography was carried out on silica gel 60 (230−400 mesh, Merck) or on Sephadex LH-20 (Amersham Biosciences), and TLC was performed using silica gel 60 F_{254} plates (Merck). X-ray crystallographic analysis was carried out on a Rigaku AFC-7R four-circle diffractometer.

Plant Material. *Baccharis gaudichaudiana* DC. was collected in the state of Sao Paulo, Brazil, in September 1997 and identified by Goro Hashimoto at the Centro de Pesquisas de Historia Natural (Sao Paulo, Brazil). A voucher specimen (No. OUS-1103) is deposited in the herbarium of Okayama University of Science.

Extraction and Isolation. Air-dried twigs of *B. gaudichaudiana* (1030 g) were extracted with CH_2Cl_2 (4 times with 2 L of solvent, each 7 days) at room temperature, and the organic layer was concentrated in vacuo to give a CH_2Cl_2-soluble extract (49.2 g). The extract was subjected to silica gel column chromatography with a $CHCl_3$−MeOH gradient solvent system (98:2 → 1:1). Eleven fractions (fractions A−K) were obtained. Fraction D (0.94 g) was subjected to silica gel column chromatography and eluted with *n*-hexane−acetone (7:1 → 5:1), to give 12 fractions (D1−D12). Fraction D4 (519 mg) was purified by silica gel column chromatography ($CHCl_3$−EtOAc, 9:1 → 1:1) to afford spathulenol (56 mg), defuscin (15 mg), and *trans*-cosanyl ferulate (13 mg). Fraction E (1.28 g) was applied to silica gel column chromatography and eluted

with *n*-hexane−acetone (7:1 → 5:1) to give 10 fractions (E1−E10). Fraction E3 (236 mg) was then subjected to silica gel column chromatography, via elution with $CHCl_3$−MeOH (95:5 → 6:4), to afford kobusone (26 mg) and 4,10-aromadendranediol (9 mg). Fraction H (8.0 g) was separated by silica gel column chromatography, eluting with $CHCl_3$−EtOAc solvent system (98:2 → 8:2), to afford four fractions (H1−H4). Fraction H1 (eluted with 5% EtOAc, 4.8 g) was applied on a silica gel column and eluted with *n*-hexane−acetone (8:1) to give **3** (3.32 g). Fraction H2 (eluted with 8% EtOAc, 326 mg) was subjected to Sephadex LH-20 column chromatography, developed with $CHCl_3$−MeOH (9:1), to afford **1** (129 mg). Compound **2** (60 mg) was isolated from fraction H3 (115.4 mg) by silica gel column chromatography, eluting with $CHCl_3$−acetone (8:2 → 6:4).

Gaudichanolide A (1): colorless oil; $[\alpha]_D^{20}$ −124.0° (*c* 0.2, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3483, 3026, 1774 cm^{-1}; ^1H NMR (500 MHz, C_5D_5N) δ 6.87 (1H, dd, J = 7.0, 2.4 Hz, H-3), 4.41 (1H, t, J = 8.6 Hz, H-16a), 4.20 (1H, d, J = 8.3 Hz, H-19a), 4.05 (1H, d, J = 8.3 Hz, H-19b), 3.96 (1H, t, J = 8.6 Hz, H-16b), 2.85 (2H, s, H-6), 2.71 (1H, dd, J = 16.7, 7.9 Hz, H-14a), 2.49 (1H, m, H-10), 2.42 (1H, m, H-13), 2.31 (1H, dd, J = 16.7, 8.6 Hz, H-14b), 2.17 (2H, m, H-2), 1.97 (1H, m, H-12a), 1.83 (1H, m, H-1a), 1.68 (1H, m, H-12b), 1.61 (2H, m, H-11), 1.53 (3H, s, CH_3-17), 1.01 (1H, m, H-1b), 0.79 (3H, s, CH_3-20); ^{13}C NMR (125 MHz, C_5D_5N) δ 211.4 (C, C-7), 177.3 (C, C-15), 168.0 (C, C-18), 137.8 (CH, C-3), 136.1 (C, C-4), 82.7 (C, C-8), 73.3 (CH_2, C-16), 71.3 (CH_2, C-19), 48.6 (CH, C-10), 48.2 (C, C-5), 47.1 (C, C-9), 46.6 (CH_2, C-6), 37.1 (CH, C-13), 35.3 (CH_2, C-11), 34.6 (CH_2, C-14), 28.8 (CH_2, C-12), 27.6 (CH_2, C-2), 22.9 (CH_3, C-17), 20.7 (CH_2, C-1), 16.0 (CH_3, C-20); HREIMS *m/z* 362.1737 (calcd for $C_{20}H_{26}O_6$, 362.1745) $[M]^+$.

Gaudichanolide B (2): amorphous powder; $[\alpha]_D^{20}$ −125.0° (*c* 0.2, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3025, 1775 cm^{-1}; ^1H NMR (500 MHz, C_5D_5N) δ 6.87 (1H, dd, J = 7.4, 2.0 Hz, H-3), 4.74 (1H, d, J = 8.0 Hz, H-19a), 4.33 (2H, m, H-16a, H-19b), 3.81 (1H, t, J = 8.0 Hz, H-16b), 2.87 (1H, d, J = 17.5 Hz, H-6a), 2.66 (2H, m, H-8, H-14a), 2.33 (2H, m, H-6b, H-13), 2.23 (2H, m, H-2a, H-14b), 2.07 (2H, m, H-2b, H-10), 1.60 (1H, m, H-1a), 1.29 (4H, m, H-11, H-12), 1.13 (3H, d, J = 6.7 Hz, CH_3-17), 1.09 (1H, m, H-1b), 0.88 (3H, s, CH_3-20); ^{13}C NMR (125 MHz, C_5D_5N) δ 211.0 (C, C-7), 177.0 (C, C-15), 168.0 (C, C-18), 136.6 (CH, C-3), 136.5 (C, C-4), 72.9 (CH_2, C-16, C-19), 52.4 (CH, C-8), 49.0 (CH_2, C-6), 45.8 (CH, C-10), 45.2 (C, C-5), 40.5 (C, C-9), 36.6 (CH, C-13), 35.0 (CH_2, C-11), 34.5 (CH_2, C-14), 27.7 (CH_2, C-2), 26.9 (CH_2, C-12), 24.3 (CH_3, C-20), 20.9 (CH_3, C-1), 9.3 (CH_3, C-17); HREIMS *m/z* 346.1789 (calcd for $C_{20}H_{26}O_5$, 362.1781) $[M]^+$.

7-Oxo-16,19-dihydroxy-3,4-dehydroclerodan-15,20-diacid dilactone (3): colorless oil; $[\alpha]_D^{20}$ −134.4° (*c* 1.1, $CHCl_3$) [lit. −128.8° (*c* 1.2, $CHCl_3$); −147° (*c* 0.1, $CHCl_3$)];[6,7] IR ($CHCl_3$) ν_{max} 3022, 1775 cm^{-1}; ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.0 (C, C-7), 176.3 (C, C-15), 167.8 (C, C-18), 137.0 (CH, C-3), 136.2 (C, C-4), 72.9 (CH_2, C-16), 71.0 (CH_2, C-19), 51.3 (CH, C-8), 50.5 (CH_2, C-6), 48.0 (C, C-5), 47.8 (CH, C-10), 43.6 (C, C-9), 35.9 (CH, C-13), 35.7 (CH_2, C-11), 34.5 (CH_2, C-14), 27.3 (CH_2, C-2), 26.8 (CH_2, C-12), 20.4 (CH_2, C-1), 19.0 (CH_3, C-20), 7.8 (CH_3, C-17); EIMS *m/z* 346 $[M]^+$.

Preparation of *p*-Bromobenzoyl Derivative of 1. Compound **1** (59 mg) was dissolved in 2 mL of THF−H_2O (2:1), and OsO_4 (0.1 equiv; 4.2 mg) and *N*-methylmorpholine *N*-oxide (5 equiv; 97 mg) were added into this solution. The solution was stirred for 2 h at room temperature. The resulting diol was extracted with $CHCl_3$ and further purified by silica gel column chromatography to give a diol form of **1** as a colorless oil (yield 53%); $[\alpha]_D^{20}$ −48.0° (*c* 0.1, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3519, 1777, 1712 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 4.45 (1H, dd, J = 8.9, 7.4 Hz, H-16a), 4.26 (1H, d, J = 9.8 Hz, H-19a), 3.97 (2H, m, H-16b, H-19b), 3.86 (1H, dd, J = 12.0, 4.9 Hz, H-3), 3.15 (1H, dd, J = 13.5, 1.4 Hz, H-6a), 2.64 (1H, dd, J = 17.2, 8.3 Hz, H-14a), 2.45 (1H, m, H-13), 2.27 (1H, d, J = 13.5 Hz, H-6b), 2.20 (1H, dd, J = 17.2, 8.2 Hz, H-14b), 2.11 (1H, m, H-10), 2.03 (1H, m, H-12a), 1.83 (2H, m, H-1a, H-2a), 1.71 (1H, m, H-2b), 1.56 (1H, m, H-12b), 1.46 (3H, m, H-1b, H-11), 1.40 (3H, s, CH_3-17), 0.60 (3H, s, CH_3-20); HREIMS *m/z* 396.1783 (calcd for $C_{20}H_{28}O_8$, 396.1784) $[M]^+$. The diol form of **1** (30 mg) was treated with *p*-bromobenzoyl chloride (3 equiv; 50 mg) and 4-(dimethylamino)pyridine (3 equiv; 28 mg) in 1 mL of pyridine for 12 h at room temperature. *N*,*N*-Dimethyl-1,3-propanediamine (3 equiv; 29 μL) was added to the reaction mixture and left for 30 min. The product was extracted with $CHCl_3$ and purified by silica gel column chromatography to give the *p*-bromobenzoate **4** as colorless prisms (yield 18%): mp >280 °C (dec); $[\alpha]_D^{20}$ −8.0° (*c* 0.05, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3734, 1772, 1717 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.87 (2H, d, J = 8.5 Hz, aromatic protons), 7.60 (2H, d, J = 8.5 Hz, aromatic protons), 5.24 (1H, dd, J = 12.3, 4.6 Hz, H-3), 4.45 (2H, m, H-16b, H-19b), 4.00 (2H, m, H-16a, H-19a), 3.18 (1H, m, H-6), 2.66 (1H, dd, J = 17.2, 8.2 Hz, H-14a), 2.47 (1H, d, J = 13.0 Hz), 1.43 (3H, s, CH_3-17), 0.65 (3H, s, CH_3-20); HRFABMS *m/z* 579.1209 (calcd for $C_{27}H_{32}O_9Br$, 579.1230) $[M + H]^+$.

Reduction of 3. Compound **3** (220 mg) was reduced with $NaBH_4$ (25 mg) in MeOH and purified by silica gel column chromatography to afford **5** (yield 30%) as colorless prisms (benzene); mp 84−85 °C; $[\alpha]_D^{20}$ −103.0° (*c* 0.2, $CHCl_3$); IR ($CHCl_3$) ν_{max} 3530, 1773, 1716, 1663 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.71 (1H, dd, J = 7.3, 1.8 Hz, H-3), 5.28 (1H, d, J = 7.6 Hz, H-19a), 4.45 (1H, dd, J = 8.9, 7.5 Hz, H-16a), 4.13 (1H, m, H-7), 3.92 (2H, m, H-16b, H-19b), 2.68 (1H, dd, J = 17.2, 2.3 Hz, H-14a), 2.49 (1H, m, H-13), 2.33 (2H, m, H-2a, H-6a), 2.17 (2H, m, H-2b, H-14b), 1.63 (3H, m, H-6b, H-8, H-10), 1.32 (6H, m, H-1, H-11, H-12), 1.03 (3H, d, J = 7.1 Hz, CH_3-17), 0.85 (3H, s, CH_3-20); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.7 (C, C-15), 169.8 (C, C-18), 139.1 (C, C-4), 134.9 (CH, C-3), 73.2 (CH_2, C-16), 72.6 (CH_2, C-19), 72.4 (CH, C-7), 48.2 (CH, C-10), 44.8 (C, C-5), 40.3 (CH and CH_2, C-6 and C-8), 38.3 (C, C-9), 36.2 (CH_2, C-11), 36.1 (CH, C-13), 34.6 (CH_2, C-14), 27.6 (CH_2, C-2), 26.5 (CH_2, C-12), 19.3 (CH_2, C-1), 19.2 (CH_3, C-20), 11.9 (CH_3, C-17); HREIMS *m/z* 348.1923 (calcd for $C_{20}H_{28}O_5$, 348.1937) $[M]^+$.

X-ray Crystal Structure Determination of 4 and 5. Crystal data of **4**: $C_{27}H_{31}O_9Br$, MW 579.45, orthorhombic, space group $P2_12_12_1$, a = 18.652(2) Å, b = 20.817(2) Å, c = 6.573(1) Å, V = 2552.1(6) $Å^3$, D_x = 1.508 g/cm^3, Z = 4. Crystal data of **5**: $C_{21}H_{30}O_5$, MW 362.46, monoclinic, space group $P2_1$, a = 12.003(1) Å, b = 10.310(1) Å, c = 18.742(1) Å, β = 90.15-(1), V = 2319.3(3) $Å^3$, D_x = 1.038 g/cm^3, Z = 4. A total of 2246 reflections were obtained for **4** (3884 for **5**), of which 22 245 (3689 for **5**) were unique (R_{int} = 136.920 for **4**, R_{int} = 0.089 for **5**), and were measured by a Rigaku AFC-7R diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.54178 Å). The crystal structures were solved by direct methods using the program teXsan, a crystallographic software package of Molecular Structure Corporation.[13] All atoms except hydrogen atoms were refined anisotropically by full-matrix least-squares methods on F^2 using the above software package to give a final *R*-factor of 0.050 (R_w 0.048 for all data) for **4** and 0.053 (R_w 0.046 for all data) for **5**, respectively, with a data-to-parameter ratio of 4.46 for **4** and 5.86 for **5**.[14] At the last stage, the anomalous scattering factor correction for the bromine atom of **4** was introduced into the structure-factor calculations to establish the absolute configuration of **4** (R = 0.050 for the drawing model, R = 0.054 for the inverted configuration).[15]

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(14) Crystallographic data of compounds **4** and **5** have been deposited at the Cambridge Crystallographic Data Centre under the reference numbers CCDC 273298 for **4** and CCDC 273299 for **5**. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).
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