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# Synthesis and applications of (*R*)- and (*S*)-7,7'-dimethoxy-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene

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## Abstract

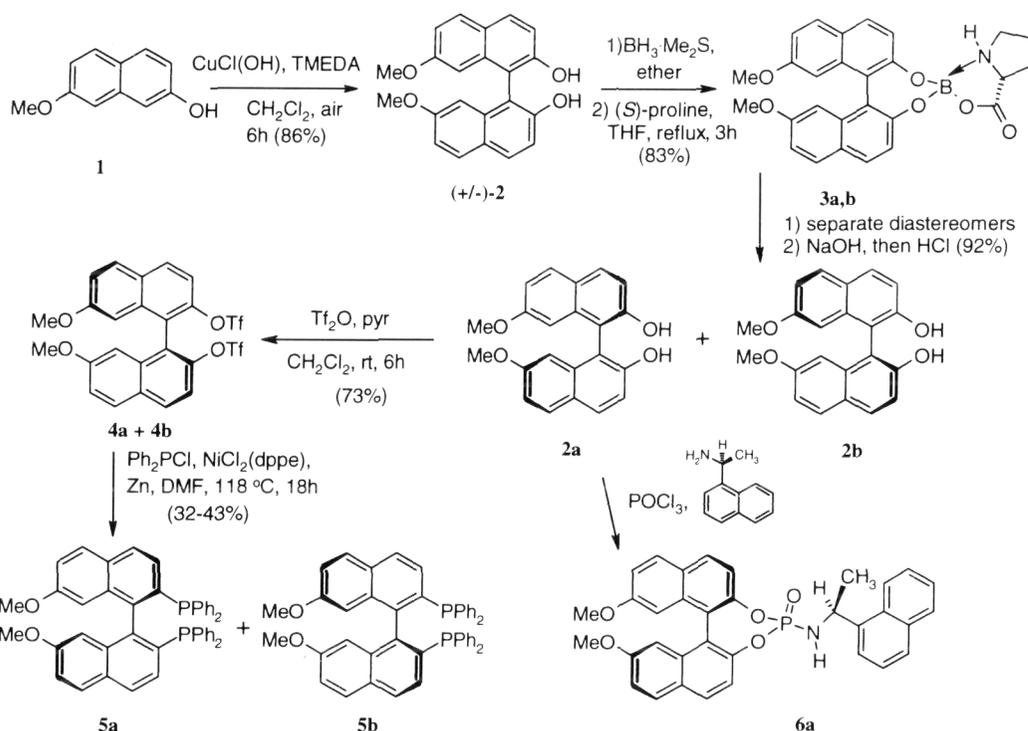
The synthesis of (*R*)- and (*S*)-7,7'-dimethoxy-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene **5a** and **5b** is described. The phosphorus atoms in (*S*)-(-)-**5b** are shown to be slightly more basic than the phosphorus atoms in (*S*)-BINAP by comparing the magnitude of the  $^1J(^{31}\text{P}-^{77}\text{Se})$  coupling constant in their respective diselenide derivatives. (*S*)-(-)-**5b** behaved similarly to (*S*)-BINAP in asymmetric Heck reactions. © 2000 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

In projects related to solid support bound catalysts<sup>1</sup> and fluorous biphasic catalysis<sup>2,3</sup> we required enantiomerically pure 7,7'-dimethoxy-2,2'-bis(diphenylphosphino)-1,1'-binaphthalenes **5a** and **5b** (Scheme 1) as suitable starting materials. Although compounds **5a** and **5b** have been synthesized once before,<sup>4</sup> the authors have not reported its use as an asymmetric catalyst although they claim in their patent that compounds **5a** and **5b** (and others) are useful as chiral ligands for catalytic asymmetric induction. A methoxy group was chosen to be a latent functional group that would be cleaved to the hydroxyl group so that the binaphthyl system could be connected to a solid support or fluorous tag. Since very few analogues of BINAP have been reported in which the remote ring from the binaphthyl bond is functionalized,<sup>1,5,6</sup> we were interested to determine how the methoxy group in the remote ring from the diphenylphosphino moiety would affect the basicity of the phosphorus atom and ultimately how the ees obtained with **5** would compare to BINAP. The decision to place the methoxy groups at the 7 and 7' positions was primarily due to the ready availability of 7-methoxy-2-naphthol **1** from commercial sources.<sup>7</sup>

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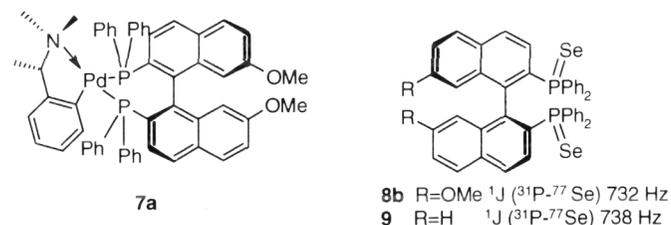


Scheme 1.

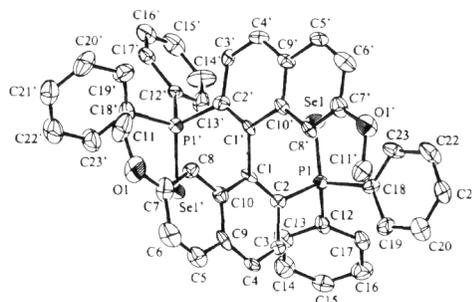
We herein report: (1) our synthesis and resolution of (±)-7,7'-dimethoxy-1,1'-bi-2-naphthol **2**; (2) conversion of **2a** and **2b** into **5a** and **5b**; (3) the relative basicity of the phosphorus atoms in **5** when compared to BINAP; and (4) the use of enantiopure **5b** in three palladium-catalyzed Heck reactions.

(±)-Binaphthol **2** was prepared according to the procedure reported by Koga and co-workers.<sup>8a</sup> Thus, 7-methoxy-2-naphthol **1** (3.05 g) was treated with a mixture of CuCl(OH)·TMEDA in dichloromethane for 20 h while bubbling oxygen into the mixture. Workup provided (±)-**2** in 86% yield. While binaphthols have been resolved using quinine<sup>6a,9</sup> and *N*-benzylcinchonidium chloride,<sup>10,11</sup> we found that the diastereomers formed by the interaction of (±)-**2** with these alkaloids could not be separated by column chromatography or by crystallization. The resolution procedure developed by Shan and co-workers<sup>12</sup> served our purpose well. Treatment of (±)-**2** with borane dimethyl sulfide complex followed by the addition of (*S*)-proline afforded two diastereomers **3a** and **3b** that were easily separable by column chromatography. Treatment of either **3a** or **3b** with a mixture of 2N NaOH and THF (0.5 h) followed by 2N HCl and ether gave **2a** or **2b** in 92% yield. Compound **2a** was shown to be enantiomerically pure by examining the <sup>31</sup>P NMR spectrum of **6a**;<sup>13</sup> only one signal at 12.18 ppm was observed in the <sup>31</sup>P NMR spectrum. The enantiomeric purity of **2b** was determined by comparing the specific rotation of **2b** ( $[\alpha]_D^{21} -117.6$  ( $c=0.30$ , THF)) with that obtained for **2a** ( $[\alpha]_D^{21} +117.2$  ( $c=0.27$ , THF); lit.<sup>14</sup>  $[\alpha]_D^{21} -126.4$  ( $c=1.0$ , CH<sub>3</sub>OH)). The diphenylphosphino groups were introduced using the procedure developed by Laneman and co-workers<sup>15a</sup> in which the bistriflate **4a** (or **4b**) was treated with Ph<sub>2</sub>PCl in the presence of NiCl<sub>2</sub>(dppe) and zinc (DMF, 110 °C, 32–43%) to provide **5a** (or **5b**). To be sure that

partial racemization had not occurred during the coupling reaction, compounds ( $\pm$ )-**5** and (+)-**5a** were converted<sup>16</sup> into complexes **7** (two diastereomers) and **7a**, respectively (Scheme 2). The <sup>31</sup>P NMR spectrum of **7a** showed only two doublets (37.4 and 10.31 ppm) indicating that the enantiomeric excess of **5a** (and **5b**) was > 97%. The absolute stereochemistry of **5b** was determined by obtaining a single crystal X-ray structure on the diselenide **8b** (Fig. 1).<sup>17</sup>

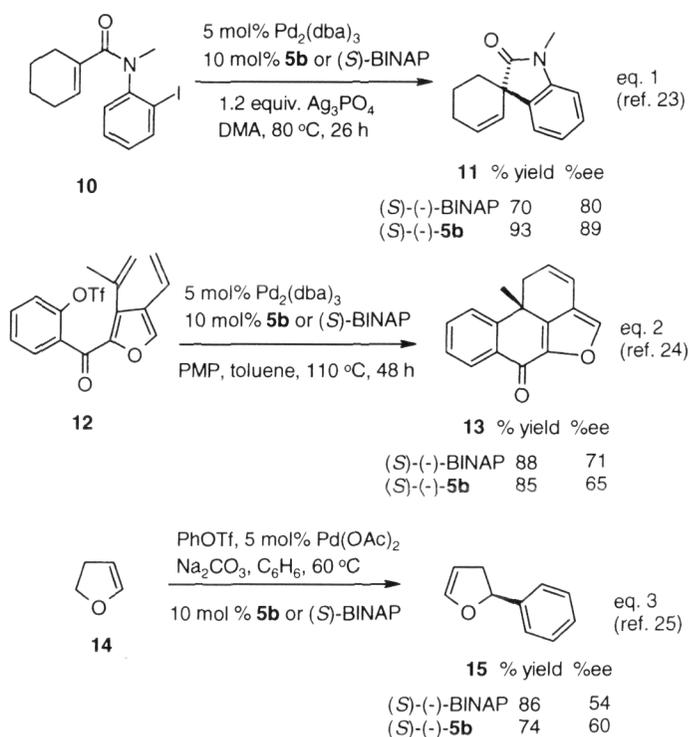


Scheme 2.

Figure 1. ORTEP of diselenide **8b**

Allen and Taylor have reported<sup>18</sup> that an increase in the  $^1J(^{31}\text{P}-^{77}\text{Se})$  coupling constant indicated that the *s*-character of the phosphorus lone pair orbital was increasing (i.e. becomes less basic). A comparison of the  $^1J(^{31}\text{P}-^{77}\text{Se})$  coupling values for **8b** and **9** indicated that the phosphorus atom in **5b** was more basic than that in BINAP, even though the methoxy group is in the remote ring to the phosphorus atom. The increased basicity in **5b** may allow it to complex more tightly to the palladium atom and thereby increase the ee in an asymmetric transformation. On the other hand, the placement of the methoxy groups at the 7 and 7' positions may alter the bite angle (P–Pd–P) and result in poorer ees.

Three different asymmetric Heck reactions were performed to compare the efficacy of **5b** to (*S*)-BINAP (Scheme 3).<sup>19–21</sup> Heck reaction on **10** with **5b** gave **11** in a higher yield and ee than with (*S*)-BINAP; however, treatment of **12** resulted in a slightly lower yield and ee. Finally, intermolecular Heck reaction on **14** with **5b** gave a slightly higher ee but at the expense of a lower yield. These results indicate that **5b** is a comparable catalyst to (*S*)-BINAP and that the position of the two methoxy groups at the 7 and 7' positions do not significantly lower the ee in simple palladium-catalyzed transformations. Work is continuing towards the application of derivatives of **5a** and **5b** in fluoros synthesis and in solid state applications.



Scheme 3.

## 2. Experimental

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ACE-200 ( $^1\text{H}$  200 MHz,  $^{13}\text{C}$  50 MHz) or a Varian XL-200 ( $^{31}\text{P}$  81 MHz) spectrometer. All spectra were obtained in  $\text{CDCl}_3$  unless otherwise mentioned and the chemical shifts (ppm) are relative to the  $\text{CHCl}_3$  peak as an internal reference (7.27 ppm for  $^1\text{H}$  and 77.00 for  $^{13}\text{C}$ ). The external standard for  $^{31}\text{P}$  NMR spectra was a solution of 85%  $\text{H}_3\text{PO}_4$  in  $\text{D}_2\text{O}$ . Mass spectra (MS) were run on either a Varian CH5 or a VG 7070 instrument. Ms. D. Fox, Department of Chemistry, University of Calgary, performed the microanalysis. All melting and boiling points are uncorrected. Anhydrous THF was distilled from sodium benzophenone ketyl. Anhydrous  $\text{CH}_2\text{Cl}_2$  and DMF were obtained from distillation from  $\text{CaH}_2$ .

### 2.1. Preparation of ( $\pm$ )-7,7'-dimethoxy-1,1'-binaphth-2-ol **2**<sup>10a</sup>

7-Methoxy-2-naphthol (**1**, 3.05 g, 17.5 mmol) and  $\text{CuCl}(\text{OH})\cdot\text{TMEDA}$  (40 mg, 0.18 mmol) were stirred in  $\text{CH}_2\text{Cl}_2$  (100 mL) for 20 h at rt while slowly bubbling oxygen through the mixture. The solution was filtered through Celite and the  $\text{CH}_2\text{Cl}_2$  removed to give a solid that was purified on a column of silica gel (hexanes:EtOAc, 3:1) to give **2** (2.6 g, 86%). Mp 149–151°C (lit.<sup>8b</sup> mp 151–152°C).

## 2.2. Resolution of ( $\pm$ )-**2**<sup>12</sup>

To a cooled (5°C) mixture of ( $\pm$ )-**2** (4.16 g, 6.0 mmol) in dry diethyl ether (120 mL) under Ar was added BH<sub>3</sub>·Me<sub>2</sub>S (8.0 mL of 2 M in THF, 16.0 mmol). The rate of addition was slow enough so that the temperature of the mixture remained below 20°C. The mixture was stirred at rt for an additional 3 h and the solvent was removed in vacuo. To the remaining solid was added dry THF (60 mL) followed by (*S*)-proline (1.5 g, 13 mmol). The mixture was refluxed for 3 h, cooled to rt whereupon a solid precipitated from the solution. The solid was filtered, washed with THF and dried in vacuo to provide a mixture of diastereomers **3a** and **3b**. The two diastereomers were separated on a column of silica gel (EtOAc:hexanes; 6:1) providing **3a** (*R<sub>f</sub>* 0.57) and **3b** (*R<sub>f</sub>* 0.45).

Compound **3a**: mp 261–263°C; [ $\alpha$ ]<sub>D</sub><sup>21</sup> +485.1 (*c* = 0.154, THF); <sup>1</sup>H NMR  $\delta$  0.3–0.6 (m, 1H), 0.8–1.0 (m, 1H), 1.0–1.15 (m, 2H), 2.45–2.7 (m, 2H), 3.85 (q, 1H), 6.3 (broad q, 1H, *N-H*), 6.54 (d, 2.3 Hz, 1H), 6.6 (d, 2.3 Hz, 1H), 6.95 (dd, 2.3 and 8.4 Hz, 1H), 6.96 (dd, 2.3 and 8.4 Hz, 1H), 7.1 (d, 8.2 Hz, 1H), 7.17 (d, 8.2 Hz, 1H), 7.47 (d, 8.2 Hz, 1H), 7.56 (d, 8.2 Hz, 1H), 7.72 (d, 8.4 Hz, 1H), 7.78 (d, 8.4 Hz, 1H); MS (EI) *m/z* 470 (7.77, M<sup>+</sup>+1), 469 (26, M<sup>+</sup> using <sup>11</sup>B), 468 (6.7, M<sup>+</sup> using <sup>10</sup>B), 374 (17), 70 (100).

Compound **3b**: mp 215–220°C (dec); [ $\alpha$ ]<sub>D</sub><sup>21</sup> –537.5 (*c* = 0.176, THF); <sup>1</sup>H NMR  $\delta$  1.2–1.45 (m, 1H), 1.6–1.95 (m, 3H), 1.96–2.1 (m, 1H), 2.2–2.41 (m, 1H), 4.37–4.51 (m, 1H), 6.1 (broad t, 1H, *N-H*), 6.43 (d, 2.1 Hz, 1H), 6.47 (d, 2.1 Hz, 1H), 6.75 (d, 8.7 Hz, 1H), 6.94 (d, 8.7 Hz, 1H), 7.02 (dd, 2.1 and 8.5 Hz, 2H), 7.56 (d, 8.5 Hz, 1H), 7.63 (d, 8.5 Hz, 1H), 7.67 (d, 8.7 Hz, 1H), 7.74 (d, 8.7 Hz, 1H); MS (EI) *m/z* 470 (7.77, M<sup>+</sup>+1), 469 (26, M<sup>+</sup> using <sup>11</sup>B), 468 (6.7, M<sup>+</sup> using <sup>10</sup>B), 374 (17), 70 (100).

## 2.3. (*R*)-7,7'-Dimethoxy-1,1'-bi-2-naphthol **2a** and (*S*)-7,7'-dimethoxy-1,1'-bi-2-naphthol **2b**<sup>12</sup>

Compound **3a** (or **3b**) (2.09 g, 4.5 mmol) was stirred with 2 M NaOH (50 mL) for 2 h and then treated with 10% HCl until the solution was pH 2. The aqueous layer was extracted with diethyl ether (3×50 mL), and the ether was dried (MgSO<sub>4</sub>) and removed to provide a solid which was recrystallized from hexanes to give **2a** (or **2b**) (1.41 g, 92%).

Compound **2a**: mp 150–151°C (lit.<sup>8b</sup> mp 151–152°C). [ $\alpha$ ]<sub>D</sub><sup>21</sup> +117.2 (*c* = 0.27, THF).

Compound **2b**: mp 149.5–151°C (lit.<sup>8b</sup> mp 151–152°C). [ $\alpha$ ]<sub>D</sub><sup>21</sup> –117.6 (*c* = 0.30, THF); lit.<sup>14</sup> [ $\alpha$ ]<sub>D</sub><sup>21</sup> –126.4 (*c* 1.0, CH<sub>3</sub>OH).

## 2.4. Preparation of (*R*)-**6a**<sup>13</sup>

To a mixture of **2a** (173 mg, 0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was slowly added POCl<sub>3</sub> (92 mg, 0.8 mmol). The mixture was brought to reflux and Et<sub>3</sub>N (120 mg, 0.19 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added slowly. The mixture was refluxed for 2 h, cooled to rt and the CH<sub>2</sub>Cl<sub>2</sub> layer washed with H<sub>2</sub>O and saturated brine. Removal of the solvent after drying (MgSO<sub>4</sub>) left a yellow solid that was used immediately. To a stirred suspension of the yellow solid in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added at 0°C over 30 min a mixture of (*S*)-1-(1-naphthyl)ethylamine (94 mg, 0.55 mmol) and Et<sub>3</sub>N (60 mg, 0.085 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The mixture was stirred at rt for 48 h. Workup with 4% HCl and brine gave, after drying (MgSO<sub>4</sub>) and evaporation of the solvent, a solid that was purified on a silica gel column (hexanes:EtOAc, 1:1). Recrystallization from hexanes/EtOAc gave **6a** (0.9 g, 80%). <sup>1</sup>H NMR  $\delta$  1.6 (broad s, 1H, *N-H*), 1.68 (d, 3H), 3.39 (s, 3H), 3.41 (s, 3H), 5.35 (broad q, 1H), 6.56 (d, 2.0 Hz, 1H), 6.65 (d, 2 Hz, 1H), 6.71 (d, 8.2 Hz, 1H), 6.72 (d, 8.2 Hz, 1H), 7.1 (dd,

2.0 and 8.0 Hz, 1H), 7.15 (dd, 2.0 and 8.0 Hz, 1H), 7.3–7.55 (m, 5H), 7.7–7.95 (m, 6H);  $^{31}\text{P}$  NMR (81 MHz,  $\text{D}_2\text{O}$ )  $\delta$  12.2; MS (EI)  $m/z$  561 (1.6,  $\text{M}^+$ ), 546 (32), 392 (100).

### 2.5. Preparation of the bistriflate (R)-4a

To a mixture of diol **2a** (692 mg, 2.0 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (30 mL) at  $0^\circ\text{C}$  under  $\text{N}_2$  was added pyridine (1.0 mL) and triflic anhydride (1.58 g, 5.6 mmol). After the mixture was stirred at  $0^\circ\text{C}$  for 5 h, the solvent was removed in vacuo to afford a solid which was dissolved in EtOAc (100 mL) and washed with 5% HCl and saturated brine. The organic layer was dried ( $\text{MgSO}_4$ ) and removed to leave a solid. The solid was recrystallized from hexanes to give **4a** (391 mg, 73%).

Compound (R)-**4a**:  $[\alpha]_{\text{D}}^{21} +260.3$  ( $c = 0.31$ , THF);  $^1\text{H}$  NMR  $\delta$  3.55 (s, 6H), 6.53 (d, 2.0 Hz, 2H), 7.26 (dd, 2.0 and 8.1 Hz, 2H), 7.48 (d, 8.4 Hz, 2H), 7.90 (d, 8.1 Hz, 2H), 8.06 (d, 8.4 Hz, 2H); MS (EI)  $m/z$  610 (30,  $\text{M}^+$ ), 328 (100); anal. calcd for  $\text{C}_{24}\text{H}_{16}\text{F}_6\text{O}_8\text{S}_2$ : C, 47.22; H, 2.64. Found: C, 47.57; H, 2.91.

Compound (S)-**4b**:  $[\alpha]_{\text{D}}^{21} -257.5$  ( $c = 0.29$ , THF).

### 2.6. (R)-7,7'-Dimethoxy-2,2'-bis(diphenylphosphino)-1,1'-binaphthalene **5a**<sup>15</sup>

To a solution of **4a** (610 mg, 1.0 mmol),  $\text{NiCl}_2(\text{dppe})$  (16 mg, 1.5 mol%) and  $\text{Ph}_2\text{PCl}$  (441 mg, 2.0 mmol) in anhydrous DMF (25 mL) was added Zn (207 mg, 3.2 mmol) slowly at  $5^\circ\text{C}$ . The mixture was heated at  $118^\circ\text{C}$  for 18 h. The reaction was cooled to rt and filtered through Celite. The DMF was removed under a high vacuum (0.01 torr) and the remaining oil placed in the refrigerator overnight. The resulting solid was purified further on a silica gel column ( $\text{CH}_2\text{Cl}_2:\text{MeOH}$ , 95:5) to give **5a** (218 mg, 32%).

Compound **5a**: mp  $> 360^\circ\text{C}$ ,  $[\alpha]_{\text{D}}^{21} +302.9$  ( $c = 0.104$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (lit.<sup>4</sup>)  $\delta$  3.12 (6H), 6.05 (2H), 7.02 (2H), 7.09–7.28 (20H), 7.39 (2H), 7.74 (2H), 7.83 (2H);  $^{13}\text{C}$  NMR (lit.<sup>4</sup>)  $\delta$  54.5, 105.7, 119.9, 127.4, 127.8, 127.98, 128.04, 128.3, 128.6, 128.8, 129.2 ( $\times 2$ ), 129.3, 132.0, 134.5, 157.4;  $^{31}\text{P}$  NMR (lit.<sup>4</sup>)  $\delta$  -14.9.

Compound **5b**: mp  $> 360^\circ\text{C}$ ,  $[\alpha]_{\text{D}}^{21} 299.6$  ( $c = 0.246$ ,  $\text{CHCl}_3$ ).

## Acknowledgements

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17. Compound **8a**: orthorhombic *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (#19); *a* = 14.146(5) Å, *b* = 20.905(4) Å, *c* = 13.125(4) Å, *V* = 3881.3(18) Å<sup>3</sup>; *Z* = 4; *R* = 0.0597; *R*<sub>w</sub> = 0.1464; Flack parameter = 0.018(2). Bijvoet analysis was performed. A refinement of the inverted structure was carried out which converged with *R* = 0.0762, *R*<sub>w</sub> = 0.1926; *S* = 1.16 and the Flack parameter = 1.02(2) and was therefore rejected as the absolute configuration present in the crystal.
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