A NEW CHIRAL PYRROLIDINE- AND PYRROLIDINONE-ETHANOLS FOR ENANTIOSELECTIVE ADDITION OF DIETHYLZINC TO ARYLALDEHYDES

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Abstract – New chiral pyrrolidineethanols and unusual type of pyrrolidinoneethanol fused bicyclo[2.2.2]octane ring systems as backbones were synthesized and were used to the addition of diethylzinc to aromatic aldehydes to afford the secondary aryl alcohols leading to enantioselectivities up to 94% ee.

β-Amino alcohols have well established to be common chiral ligands in some catalytic asymmetric reactions1,2 because they are readily accessible in enantiomerically pure form in a few steps from commercially available α-amino acid precursors. In these ligands, pyrrolidinealcohol is one of the most efficient ligands and many derivatives have been synthesized until now.1b However, to the best of our knowledge, the pyrrolidinealcohols fused bicyclo[2.2.2]octane ring systems as backbones have never been involved as a ligand in this area. Herein, we wish to report the syntheses of three kinds of new typed chiral pyrrolidineethanols, fused a bicyclo-, dibenzobicyclo[2.2.2]octane ring systems (7a-c), and chiral pyrrolidinoneethanol fused a dinaphthobicyclo[2.2.2]octane ring systems (7d) and their application as chiral ligands to the enantioselective addition of diethylzinc to arylaldehydes.

Preparations of chiral ligands (7a-d) are described in Scheme 1. The precursors (5a-d) of ligands (7a-d) were obtained in quantitative yields by the Diels-Alder (DA) reactions of cyclohexadiene (4a), anthracene (4b), and pentacene (4c) with chiral maleimides (3a and 3b). Dienophiles (3a and 3b) were prepared easily by the reactions of maleic anhydride (1) with (1R,2S)-(−)-norephedrine (2a) or (R)-(−)-

∗ Dedicated to Professor Yuichi Kanaoka on the occasion of his 75th birthday.
2-phenylglycinol (2b).³

Scheme 1

Figure 1. X-Ray structure of 7d
Chiral ligand (7a) was obtained from catalytic hydrogenation followed by the reduction of 6 with LAH in 94% yield. Similarly, chiral ligands (7b and 7c) were also synthesized by the reductions of DA adducts (5b and 5c) with LAH in quantitative yields. However, the reductive conversion of succimide ring on DA adduct (5d) to pyrrolidine ring did not proceed in the similar reaction conditions (LAH, reflux, 12 h) to 5a-c and the reaction only gave chiral pyrrolidinoneethanol (7d). Finally the structure of pyrrolidinoneethanol (7d) was unambiguously determined by the X-Ray analysis (Figure 1).

We applied pyrrolidineethanols (7a-c) and pyrrolidinoneethanol (7d) as chiral ligands to the enantioselective additions of diethylzinc to benz-, α-naphthyl-, β-naphthyl-, and 2-ethoxybenzaldehydes (8a-d), respectively. The reaction was carried out in the presence of 5 mol% of chiral ligands at 0 °C for 18 h. First, the catalytic abilities of chiral ligands (7a-d) were tested using substrate (8a). Chiral ligand (7a) afforded the addition product [(R)-9a] in 95% yield with 84% ee (Entry 1). Further, the bulkier chiral ligand (7b) gave much better result regarding enantioselectivity (92% ee) (Entry 2). However, the ligand (7c) resulted in an extremely poor enantioselectivity (24% ee) (Entry 3). Interestingly, a different class of the bulkiest chiral ligand (7d) showed a good reactivity and enantioselectivity (92%, 88% ee) (Entry 4). Next, chiral ligand (7b), giving the highest enatioselectivity, was tested for three kinds of

Table 1: Enantioselective alkylation\(^b\) of aldehydes with Et\(_2\)Zn using 7a-d.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Ligand</th>
<th>Yield(%)</th>
<th>Ee(%) (^b)</th>
</tr>
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<tr>
<td>1</td>
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<td>7a</td>
<td>95</td>
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<td>4</td>
<td>8a</td>
<td>7d</td>
<td>92</td>
<td>88</td>
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<tr>
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<td>8b</td>
<td>7b</td>
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<td>86</td>
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<tr>
<td>6</td>
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<tr>
<td>7</td>
<td>8d</td>
<td>7b</td>
<td>87</td>
<td>94</td>
</tr>
</tbody>
</table>

\(^a\) All reactions were carried out in toluene-hexane(1:1) with 5 mol% of ligand at 0 °C.
\(^b\) Ee was determined by HPLC analysis using DAICEL chiral cel OB or OD.\(^c\)
substrates (8b-d). The reaction using substrate (8b) gave the product [(R)-9b] in 94% yield with 86% ee (Entry 5) and also the substrate (8c) gave (R)-9c in 95% and 90% ee (Entry 6). The best enantioselectivity (94% ee) was obtained when sterically most hindered substrate (8d) was used (Entry 7). Considering both the absolute configuration (R) and highly enantioselectivity (92% ee) of the obtained product (9a), this reaction may proceed passing through transition state A that is advocated by Noyori’s group in the addition reaction (Scheme 2).1c

![Scheme 2](image)

In conclusion, three kinds of new chiral pyrrolidineethanol ligands (7a-c) and unusual type of chiral pyrrolidinoneethanol ligand (7d) were developed, and especially, chiral ligand (7b) is efficient for the addition of diethylzinc to aromatic aldehydes.

**EXPERIMENTAL**

**General.** IR spectra were measured with a Perkin Elmer 1725X spectrophotometer. 1H-NMR spectra were recorded on a JEOL JNM-GSX 270 and a JEOL JNM-LA 600 spectrometers with TMS as an internal standard. MS spectra was taken on a JEOL-JNM-DX 303 spectrometer and elemental analysis was performed by a Perkin-Elmer 2400 CHN Elemental Analyzer. Optical rotations were measured with a JASCO-DPI-370 digital polarimeter.

**General procedure for the syntheses of dienophiles (3a,b).**

A mixture of maleic anhydride (1.96 g, 20 mmol) and (1R,2S)-(−)-norephedrine (3.02 g, 20 mmol) or (R)-(−)-2-phenylglycinol (2.78 g, 20 mmol) was refluxed in anhydrous toluene (300 mL). After 3 h, triethylamine (3.54 g, 60 mmol) was added and the solution was refluxed for 18 h. The solvent was
evaporated under a reduced pressure. The residue was diluted with CHCl₃ and the organic layer was washed with 1N-HCl, sat. NaHCO₃, and sat. NaCl. The organic layer was dried over MgSO₄, filtered, and concentrated in vacuo. The crude product was purified by column chromatography on SiO₂ with isopropyl ether as an eluent to give a white solids (3a and 3b).

**N-[(1S,2R)-1-Methyl-2-phenyl-2-hydroxyethyl]maleimide (3a):** Yield 23% (1.1 g), white solid, mp 108-110 °C (ether). [α] D²⁰ = -3.46° (c 1.7, CHCl₃). IR (KBr) cm⁻¹ : 3550, 1697, 768, 694. ¹H-NMR (CDCl₃) δ : 7.25-7.37 (m, 5H), 6.57 (s, 2H), 5.07 (dd, J = 2.6, 5.9 Hz, 1H), 4.39 (m, 1H), 3.12 (d, J = 2.6 Hz, 1H), 1.43 (d, J = 6.9 Hz, 3H). ¹³C-NMR (CDCl₃) δ : 170.71, 140.98, 133.80, 128.26, 127.89, 126.17, 75.26, 53.21, 13.52. Anal. Calcd for C₁₃H₁₃NO₃ : C, 67.52; H, 5.67; N, 6.06. Found : C, 67.44; H, 5.59; N, 5.91. MS m/z : 231 (M⁺).

**N-[(1R)-1-Phenyl-2-hydroxyethyl]maleimide (3b):** Yield 36% (1.56 g), white solid, mp 31-33 °C (ether). [α] D²⁰ = +50.72° (c 1.4, CHCl₃). IR (KBr) cm⁻¹ : 3308, 1702, 759, 696. ¹H-NMR (CDCl₃) δ : 7.25-7.37 (m, 5H), 6.66 (d, J = 1.3 Hz, 2H), 5.24 (dd, J = 5.2, 10.3 Hz, 1H), 4.50 (t, J = 10.3 Hz, 1H), 4.08 (dd, J = 5.2, 10.3 Hz, 1H), 2.79 (s, 1H). ¹³C-NMR (CDCl₃) δ : 171.02, 136.49, 133.98, 128.56, 128.01, 127.56, 61.84, 57.29. MS m/z : 217 (M⁺). HRMS calcd for C₁₂H₁₁NO₃ : 217.0739, found : 217.0734.

**General Procedure for the Preparations of the Diels-Alder Adducts (5a-d).**

A mixture of dienes (4a-c) (2.2 mmol) and dienophiles (3a,b) (2.2 mmol) was heated at 100 °C (toluene, 5 mL) or 130 °C (m-xylene, 5 mL) in a sealed tube for 48 h. The crude product was purified by column chromatography on SiO₂ with CHCl₃ as an eluent to give a white solids (5a-d).

**N-[(1S,2R)-1-Methyl-2-phenyl-2-hydroxyethyl]-4,7-etheno-3a,4,7,7a-tetrahydro-1H-isooindole-1,3(2H)-dione (5a):** Yield 98% (670 mg), white solid, mp 115-118 °C (ether). [α] D²⁰ = -6.31° (c 1.6, CHCl₃). IR (KBr) cm⁻¹ : 3394, 1766, 1681, 751, 703. ¹H-NMR (CDCl₃) δ : 7.27-7.38 (m, 5H), 5.98-6.02 (m, 2H), 4.98 (m, 1H), 4.37 (m, 1H), 3.82 (d, J = 2.0 Hz, 1H), 3.10 (m, 2H), 2.74-2.75 (m, 2H), 1.56 (m, 2H), 1.33-1.37 (m, 2H), 1.24 (d, J = 7.1 Hz, 3H). ¹³C-NMR (CDCl₃) δ : 179.45, 179.17, 140.96, 131.83, 131.63, 128.07, 127.54, 126.23, 74.95, 53.78, 43.77, 43.74, 31.65, 23.62, 23.46, 11.78. MS m/z : 311 (M⁺). HRMS calcd for C₁₉H₂₁NO₃ : 311.1522, found : 311.1519.
**N-[(1S,2R)-1-Methyl-2-phenyl-2-hydroxyethyl]-4,9[1',2']benzono-3a,4,9,9a-tetrahydro-1H-benz[f]isoindole-1,3(2H)-dione (5b):** Yield 99% (891 mg), white solid, mp 167-168 °C (ether). [α]$_D^{24}$ = +17.53° (c 1.5, CHCl$_3$). IR (KBr) cm$^{-1}$: 3528, 1770, 1689, 765, 702. $^1$H-NMR (CDCl$_3$) δ: 7.13-7.40 (m, 13H), 4.79 (s, 2H), 4.28 (s, 1H), 3.91-4.00 (m, 2H), 3.16 (t, J = 1.7 Hz, 2H), 0.68 (d, J = 7.1 Hz, 3H). $^{13}$C-NMR (CDCl$_3$) δ: 177.73, 177.55, 141.03, 140.98, 140.94, 138.46, 138.39, 128.02, 127.39, 127.00, 126.91, 126.66, 125.76, 124.91, 124.87, 124.15, 124.12, 74.66, 54.45, 46.61, 46.37, 45.70, 45.64, 22.90, 10.05. Anal. Calcd for C$_{27}$H$_{23}$NO$_3$: C, 79.20; H, 5.66; N, 3.42. Found: C, 78.92; H, 5.73; N, 3.50. MS m/z: 409 (M$^+$).

**N-[(1R)-1-Phenyl-2-hydroxyethyl]-4,9[1',2']benzono-3a,4,9,9a-tetrahydro-1H-benz[f]isoindole-1,3(2H)-dione (5c):** Yield 99% (861 mg), white solid, mp 174-176 °C (ether). [α]$_D^{24}$ = -11.42° (c 1.4, CHCl$_3$). IR (KBr) cm$^{-1}$: 3422, 1703, 1677, 760, 699. $^1$H-NMR (CDCl$_3$) δ: 7.34-7.38 (m, 2H), 7.08-7.28 (m, 9H), 6.88-6.91 (m, 2H), 4.90 (dd, J = 4.6, 8.7 Hz, 1H), 4.77 (t, J = 3.4 Hz, 2H), 4.10 (m, 1H), 3.68 (m, 1H), 3.19-3.20 (m, 2H), 1.75 (br s, 1H). $^{13}$C-NMR (CDCl$_3$) δ: 177.32, 177.07, 141.34, 141.31, 138.75, 138.73, 135.32, 128.37, 127.72, 127.40, 127.17, 126.95, 126.65, 125.08, 124.71, 124.14, 61.43, 57.92, 46.74, 46.62, 45.49. MS m/z: 395 (M$^+$). HRMS calcd for C$_{26}$H$_{21}$NO$_3$: 395.1522, found: 395.1492.

**N-[(1S,2R)-1-Methyl-2-phenyl-2-hydroxyethyl]-4,11[2',3']naphtho-3a,4,11,11a-tetrahydro-1H-naphtho[2,3-f]isoindole-1,3(2H)-dione (5d):** Yield 98% (1.1 g), white solid, mp 278 °C (ether). [α]$_D^{20}$ = +28.35° (c 0.7, CHCl$_3$). IR (KBr) cm$^{-1}$: 3424, 1690, 1657, 756, 703. $^1$H-NMR (CDCl$_3$) δ: 7.71-7.85 (m, 8H), 7.36-7.49 (m, 4H), 7.12-7.16 (m, 3H), 6.93-6.96 (m, 2H), 5.02 (s, 2H), 4.18 (s, 1H), 3.95 (d, J = 1.7 Hz, 1H), 3.82 (m, 1H), 3.31 (m, 2H), 0.38 (d, J = 6.9 Hz, 3H). $^{13}$C-NMR (CDCl$_3$) δ: 177.94, 177.36, 140.73, 137.79, 137.77, 135.16, 132.33, 132.28, 127.82, 127.49, 127.34, 127.22, 126.09, 126.05, 126.00, 125.54, 123.53, 123.51, 122.73, 74.40, 54.57, 46.54, 46.26, 45.56, 45.42, 9.72. MS m/z: 509 (M$^+$). HRMS calcd for C$_{35}$H$_{27}$NO$_3$: 509.1991, found: 509.2010.

**N-[(1S,2R)-1-Methyl-2-phenyl-2-hydroxyethyl]-4,7-ethano-3a,4,5,6,7,7a-hexahydro-1H-isoindole-1,3(2H)-dione (6):** A suspension of DA adduct (5a) (500 mg, 1.6 mmol) and 10% Pd-C (50 mg) in AcOEt (10 mL) was
stirred at rt in H$_2$ stream for 12 h. The suspension was diluted with AcOEt and was filtrated. Filtrate was evaporated under a reduced pressure and the residue was purified by SiO$_2$ column chromatography (CHCl$_3$) to give a white solid (6). Yield 81% (407 mg), white solid, mp 115-117°C (ether). $[\alpha]_D^{20} = -3.55^\circ$ (c 1.7, CHCl$_3$). IR (KBr) cm$^{-1}$: 3392, 1765, 1680, 747, 705. $^1$H-NMR (CDCl$_3$) $\delta$ : 7.24-7.43 (m, 5H), 5.11 (m, 1H), 4.54 (m, 1H), 3.63 (d, $J = 2.1$ Hz, 1H), 2.66-2.76 (m, 2H), 2.12 (m, 2H), 1.54-1.68 (m, 4H), 1.37 (d, $J = 7.1$ Hz, 3H), 1.11-1.35 (m, 4H). $^{13}$C-NMR (CDCl$_3$) $\delta$ : 180.67, 180.22, 141.04, 128.43, 128.21, 127.77, 127.59, 126.36, 74.96, 53.69, 43.39, 43.35, 26.12, 26.06, 24.85, 24.80, 21.27, 21.19, 12.27. MS m/z : 313 (M$^+$$^\ast$). HRMS calcd for C$_{19}$H$_{23}$NO$_3$ : 313.1678, found : 313.1690.

General procedure for the syntheses of chiral ligands (7a-d).

To a stirred suspension of LiAlH$_4$ (90 mg, 2.4 mmol) in dry THF (10 mL), DA adducts (5b-d, 6) (0.9 mmol) was added at 0 °C. The suspension was refluxed for 12 h. The reaction was quinched by addition to water, and filterated through celite 545. The filtrate was concentrated in vacuo to give the residue. The residue was chromatographed on SiO$_2$ column chromatography (ether : methanol = 10 : 1) to give a white solids (7a-d).

$N$-[(1$S$,2$R$)-1-Methyl-2-phenyl-2-hydroxyethyl]-4,7-ethano-1,3,3a,4,5,6,7,7a-octahydro-1$H$-isoindole (7a): Yield 26% (70 mg), white solid, mp 137-140 °C (ether). $[\alpha]_D^{20} = +18.67^\circ$ (c 1.7, CHCl$_3$). IR (KBr) cm$^{-1}$: 3530, 746, 703. $^1$H-NMR (CDCl$_3$) $\delta$ : 7.19-7.34 (m, 5H), 5.04 (d, $J = 3.1$ Hz, 1H), 2.94 (m, 1H), 2.62-2.83 (m, 3H), 2.43 (m, 1H), 2.24 (m, 2H), 1.73-1.86 (m, 2H), 1.49-1.62 (m, 7H), 1.30-1.41 (m, 2H), 0.80 (d, $J = 6.6$ Hz, 3H). $^{13}$C-NMR (CDCl$_3$) $\delta$ : 141.48, 127.88, 126.57, 125.63, 72.53, 65.69, 56.55, 56.38, 39.34, 39.20, 28.06, 27.91, 26.59, 26.49, 21.11, 21.09, 12.10. MS m/z : 285 (M$^+$$^\ast$). HRMS calcd for C$_{19}$H$_{27}$NO : 285.2093, found : 285.2081.

$N$-[(1$S$,2$R$)-1-Methyl-2-phenyl-2-hydroxyethyl]-4,9[b'1',2']benzeno-1,3,3a,4,9,9a-hexahydro-1$H$-benz[f]isoindole (7b): Yield 69% (288 mg), white solid, mp 150-152 °C (ether). $[\alpha]_D^{24} = +13.37^\circ$ (c 1.6, CHCl$_3$). IR (KBr) cm$^{-1}$: 3412, 751, 705. $^1$H-NMR (CDCl$_3$) $\delta$ : 7.08-7.32 (m, 13H), 4.67 (d, $J = 2.6$ Hz, 1H), 4.19 (dd, $J = 1.8$, 6.8 Hz, 2H), 2.46-2.73 (m, 6H), 2.00-2.09 (m, 2H), 0.44 (d, $J = 6.6$ Hz, 3H). $^{13}$C-NMR (CDCl$_3$) $\delta$ : 143.52, 143.45, 141.53, 141.63, 141.05, 127.72, 126.48, 125.77, 125.68, 125.56, 124.70, 124.40, 123.49, 123.46, 71.90, 64.96, 55.62, 55.26, 48.91, 48.86, 43.49, 43.37, 11.22. Anal.
Calcd for C_{27}H_{27}NO : C, 85.00; H, 7.13; N, 3.67. Found : C, 84.70; H, 7.19; N, 3.45. MS m/z : 381 (M⁺).

N-[(1R)-1-Phenyl-2-hydroxyethyl]-4,9[1',2']benzo-1,3,3a,4,9,9a-hexahydro-1H-benz[f]isoindole (7c): Yield 60% (200 mg), white solid, mp 70-72 °C (ether). [α]D^{24} = -34.31° (c 1.0, CHCl₃). IR (KBr) cm⁻¹ : 3427, 752, 704. ¹H-NMR (CDCl₃) δ : 7.03-7.30 (m, 11H), 6.92-6.94 (m, 2H), 4.15 (dd, J = 2.1, 12.4 Hz, 2H), 3.41-3.57 (m, 2H), 3.03 (t, J = 5.0 Hz, 1H), 2.45-2.55 (m, 4H), 2.29-2.39 (m, 2H), 1.98 (m, 1H). ¹³C-NMR (CDCl₃) δ : 143.61, 143.56, 141.94, 141.91, 138.13, 128.34, 127.85, 127.31, 125.72, 125.70, 125.62, 124.58, 124.33, 123.42, 68.56, 63.27, 55.32, 53.32, 49.02, 48.95, 43.51, 43.34. MS m/z : 367 (M⁺). HRMS calcd for C_{26}H_{25}NO : 367.1936, found : 367.1921.

N-[(1S,2R)-1-Methyl-2-phenyl-2-hydroxyethyl]-(R)-3-hydroxy-1,3,3a,4,11,11a-hexahydro-4,11-[2',3']naphtho-1H-naphtho[2,3-f]isoindole (7d): Yield 58% (270 mg), mp 151-153 °C (CH₂Cl₂). [α]D^{20} = -52.06° (c 1.2, CHCl₃). IR (KBr) cm⁻¹ : 3381, 1661, 749, 704. ¹H-NMR (CDCl₃) δ : 7.65-7.78 (m, 10H), 7.30-7.44 (m, 5H), 7.10-7.14 (m, 6H), 4.86-4.90 (m, 2H), 4.65-4.67 (m, 2H), 3.65 (dd, J = 1.3, 7.3 Hz, 1H), 3.27 (dd, J = 3.6, 9.4 Hz, 1H), 2.77 (dd, J = 2.9, 9.5 Hz, 1H), 0.01 (d, J = 7.1 Hz, 3H). ¹³C-NMR (CDCl₃) δ : 174.02, 140.35, 139.44, 138.83, 137.14, 136.57, 132.45, 132.40, 132.30, 128.17, 127.74, 127.57, 127.53, 127.49, 127.02, 125.68, 125.64, 125.54, 125.44, 123.40, 122.79, 122.48, 122.18, 82.99, 75.03, 53.20, 48.45, 46.85, 45.71, 7.36. MS m/z : 493 (M⁺-18).

General procedure for the enantioselective alkylation of aldehydes with Et₂Zn.

To a solution of chiral ligands [7a-d (0.0175 mmol)] in toluene (0.7 mL), diethylzinc (0.7 mmol, 0.7 mL of 1 M solution in hexane) was added at rt. After the mixture had been stirred at rt for 30 min, aldehydes (0.35 mmol) were introduced. The homogeneous solution was stirred for 18 h at 0°C and quenched with 10% HCl. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layers were dried (MgSO₄) and then evaporated under reduced pressure. The residue was purified by preparative TLC over silica gel using ether/n-hexane (1:1) to afford the corresponding chiral alcohols (9a-d), respectively.²c

X-Ray crystal structure determination

A plate crystal with sizes of 0.35 x 0.15 x 0.05 mm was mounted on a Rigaku/MSC Mercury CCD
diffractometer using MoK$_{\alpha}$ radiation ($\lambda = 0.71069$ Å) at the temperature of -100°C. Crystal data are as follows; MF = 2(C$_{35}$H$_{29}$NO$_3$)$\cdot$2(CH$_2$Cl)$_2$, MW = 1193.10, triclinic, $P_{\text{1}}$(#1), $a = 10.776$(3), $b = 12.122$(4), $c = 12.380$(3) Å, $\alpha = 86.69$(2) $\degree$, $\beta = 68.20$(1) $\degree$, $\gamma = 89.09$(2) $\degree$, $V = 1499.0$(7) Å$^3$, $Z = 1$, $D$(calcd)=1.322 g/cm$^3$. A total of 16814 reflection data were measured up to $2\theta = 55^\circ$, of which 10650 reflections including Freidel pairs were assigned as unique reflections($R_{\text{int}} = 0.029$). The structure was solved by the direct method and refined by the full-matrix least-squares method. Final refinement for all non-hydrogen atoms anisotropically and all hydrogen atoms fixed isotropically were converged to give $R$ of 0.053 and $R_w$ of 0.060 for 6778 observed data [$I_o > 3\sigma(I_o)$], 762 parameters, and GOF of 1.64. Two independent molecules in the unit cell take almost the same structure. Final Flack parameter was 0.05(7), thus indicating that the absolute structure was determined using anomalous dispersion effect of Cl atoms in solvents. The crystallographic data have been deposited (number CCDC XXXXXX) at the Cambridge Crystallographic Data Centre (CCDC) in CIF format.

REFERENCES