D-Glucosamine as a novel chiral auxiliary for the stereoselective synthesis of P-
stereogenic phosphine oxides.


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I. Synthesis of compounds.


I-5. Sulfonylation of methyl 2-amino-4,6-O-benzylidene-2-deoxy-D-glucopyranoside.

I-6. References.

II. NMR data.

III. HPLC data.

IV. X-ray data.
I. Synthesis of compounds.

All reactions were performed under an argon atmosphere using Schlenk techniques. THF was freshly distilled over sodium/benzophenone. Dry dichloromethane stabilized on amylene was purchased from Aldrich and used as received. Phenylphosphonic dichloride and N-methylimidazole were freshly distilled under reduced pressure before use. Organometallics reagents were ordered from Aldrich or Acros® as solutions in THF unless otherwise specified, and used as received.

Analytical TLC was performed on ready-made plates coated with silica gel on aluminium (Merck 60 F254). Products were visualized by ultraviolet light and treatment with permanganate stain followed by gentle heating. Flash chromatography was performed using silica gel (60 Å, particle size 40-63μm).

NMR spectra were recorded on a Bruker ALS-300 MHz spectrometer with a QNP probe in CDCl3. 1H and 13C chemical shifts are reported in parts per million (ppm) downfield to tetramethylsilane using the residual solvent signal as internal standard. 31P spectra are decoupled 1H and referenced to H3PO4. Proton (1H) NMR information is given in the following format: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad signal), coupling constant (J) in Hertz (Hz), number of protons. UV spectra were recorded on a Shimadzu UVmini-1240. High resolution mass spectrometry spectra are recorded on BruckerMicrOQTOF-Q II XL. The enantiomeric excess was determined by chiral HPLC using a Chiralpak AD column (4.6mm x 25cm) or a Cellulose OD-H column (4.6mm x 20cm).


\[
\begin{align*}
\text{O} & \quad \text{O} & \quad \text{N} & \quad \text{H} && \text{CH}_3\text{COCl} & \quad \text{MeOH} \\
\text{O} & \quad \text{O} & \quad \text{N} & \quad \text{H} && r.t., 23 \text{ h} & \quad \text{O} & \quad \text{O} & \quad \text{N} & \quad \text{Ac} \\
\end{align*}
\]

In a Schlenk tube, N-acetyl-D-glucosamine (3.60 g, 16.27 mmol) was added on a cooled solution of acetyl chloride (5.75 g, 73.00 mmol) in freshly dried methanol (70 mL). The resulting mixture was stirred at room temperature for 23 hours. After concentration methyl N-acetyl-D-glucosamine was obtained in quantitative yield as a white solid in α/β anomic ratio of 3/2. 1H NMR (300 MHz, MeOH-d4), δ(ppm) = 4.70 (d, J = 3.6 Hz, 0.6H), 4.35 (d, J = 8.4 Hz, 0.4H), 3.95 (dd, J = 10.6, 3.4 Hz, 0.6H), 3.90 (dd, J = 11.9, 1.9 Hz, 0.4H), 3.85 (dd, J = 11.9, 2.4 Hz, 0.6H), 3.76 – 3.65 (m, 2H), 3.60 – 3.45 (m, 2H), 3.40 (s, 1.8H), 3.36 (s, 1.2H), 3.25 – 3.20 (m, 0.4H), 2.14 (s, 1.2H), 2.12 (s, 1.8H); 13C NMR (75 MHz, MeOH-d4), δ (ppm)
= 173.9 (C), 173.5 (C), 101.7 (CH), 76.6 (CH), 74.5 (CH), 72.3 (CH), 71.3 (CH),
70.8 (CH), 70.6 (CH), 61.2 (CH₂), 61.1 (CH₂), 56.7 (CH), 55.7 (CH), 54.7 (CH₃), 54.1 (CH₃),
20.6 (CH₃), 20.3 (CH₃). The NMR data are in agreement with the literature.¹


In a Schlenk tube, to a solution of methyl N-acetyl-D-glucosamine (3.62 g, 16.27 mmol) in
anhydrous DMF (40 mL), benzaldehyde dimethylacetal (4.95 g, 32.54 mmol) and p-toluene
sulfonic acid (0.06 g, 0.32 mmol) were added. The mixture was stirred at 70°C for 4 hours.
Then, the solvent was evaporated under reduced pressure, and the residue was partitioned
between chloroform (100 mL) and aqueous solution of saturated NaHCO₃ (50 mL). The
organic layer was extracted, washed with brine (30 mL), and dried over Na₂SO₄. After
filtration, and concentration, the two anomers were isolated by flash chromatography on silica
gel using a mixture of CHCl₃ / MeOH (98/2) as eluent.

Methyl 2-N-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside: white solid in 60%
yield, m.p.= 290°C. Rf = 0.40 (CHCl₃ / MeOH 9/1). ¹H NMR (300 MHz, CDCl₃), δ(ppm) =
7.53 – 7.46 (m, 2H), 7.40 – 7.32 (m, 3H), 5.89 (br d, J = 8.8 Hz, 1H), 5.56 (s, 1H), 4.72 (d, J
= 4.0 Hz, 1H), 4.28 (dd, J = 8.1, 2.9 Hz, 1H), 4.23 (ddd, J = 9.2, 8.8, 4.0 Hz, 1H), 3.90 (br dd,
J = 9.2, 9.1 Hz, 1H), 3.83 – 3.74 (m, 2H), 3.59 (dd, J = 9.1, 9.0 Hz, 1H), 3.41 (s, 3H), 3.12 (br
s, 1H), 2.14 (s, 3H); ¹³C NMR (75 MHz, CDCl₃), δ(ppm) = 171.5 (C), 137.1 (C), 129.2 (CH),
127.2 (2 x CH), 126.4 (2 x CH), 102.0 (CH), 98.8 (CH), 82.1 (CH), 71.0 (CH), 68.6 (CH₂),
62.3 (CH), 55.1 (CH₃), 54.0 (CH), 23.4 (CH₃). [α]²⁵READING = +46.3 (c = 1.00, MeOH), lit.¹ [α]²⁵READING
= +90 (c = 0.21, MeOH). The NMR data are in agreement with the literature.¹

Methyl 2-N-acetamido-4,6-O-benzylidene-2-deoxy-β-D-glucopyranoside: white solid in 26%
yield, m.p.= 285°C. Rf = 0.40 (CHCl₃ / MeOH 9/1). ¹H NMR (300 MHz, MeOH-d4), δ(ppm) =
7.56 – 7.45 (m, 2H), 7.41 - 7.28 (m, 3H), 5.61 (s, 1H), 4.45 (d, J = 8.4 Hz, 1H), 4.31 (dd, J
= 10.2, 4.8 Hz, 1H), 3.88 – 3.70 (m, 3H), 3.59 – 3.34 (m, 2H), 3.46 (s, 3H), 1.99 (s, 3H); ¹³C
NMR (75 MHz, MeOH-d4), δ(ppm) = 172.9 (C), 138.3 (C), 129.1 (CH), 128.2 (2 x CH),
126.7 (2 x CH), 103.3 (CH), 102.1 (CH), 82.0 (CH), 71.8 (CH), 68.8 (CH₂), 66.8 (CH), 57.0
(CH₃), 56.4 (CH), 22.1 (CH₃). [α]²⁵READING = -59.7 (c = 0.21, MeOH), lit.¹ [α]²⁵READING
= -57 (c = 0.21,
MeOH). The NMR data are in agreement with the literature.¹

The corresponding benzylidene acetal (1.14 g, 3.52 mmol) was added to a solution of KOH (4M, 30 mL) in ethanol. The mixture was heated under reflux for 4 hours. After TLC (CHCl₃ / MeOH 9/1) showed completion of the reaction, most of ethanol was evaporated. After dilution with dichloromethane (30 mL), the organic phase was washed twice with water (2 x 20 mL), dried over Na₂SO₄, and concentrated to give crude product as an orange solid in 97% yield. No further purification was necessary. m.p.= 155°C. ¹H NMR (300 MHz, CDCl₃), δ(ppm) = 7.54 – 7.45 (m, 2H), 7.42 – 7.32 (m, 3H), 5.53 (s, 1H), 4.67 (d, J = 3.7 Hz, 1H), 4.27 (dd, J = 8.6, 3.5 Hz, 1H), 3.84 – 3.57 (m, 3H), 3.46 (dd, J = 8.6, 8.6 Hz, 1H), 3.41 (s, 3H), 2.76 (dd, J = 9.4, 3.7 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃), δ(ppm): 137.4 (C), 129.4 (CH), 128.5 (2 x CH), 126.5 (2 x CH), 102.1 (CH), 101.4 (CH), 82.2 (CH), 71.9 (CH), 69.2 (CH₂), 62.7 (CH), 56.8 (CH), 55.6 (CH₃). [α]²⁵ D = +47.4 (c = 0.27, CHCl₃), lit.¹ [α]²⁵ D = +103.1 (c = 0.905, CHCl₃). The NMR data are in agreement with the literature.¹


The corresponding benzylidene acetal (0.20 g, 0.22 mmol) was added to a solution of KOH (4M, 6 mL) in ethanol. The mixture was heated under reflux for 4 hours. After TLC (CHCl₃ / MeOH 9/1) showed completion of the reaction, most of ethanol was evaporated. After dilution with dichloromethane (10 mL), the organic phase was washed twice with water (2 x 5 mL), dried over Na₂SO₄, and concentrated to give crude product as an orange solid in 73% yield. No further purification was necessary. m.p.= 155°C. ¹H NMR (300 MHz, CDCl₃), δ(ppm) = 7.55 – 7.45 (m, 2H), 7.42 – 7.32 (m, 3H), 5.54 (s, 1H), 4.33 (dd, J = 10.4, 4.8 Hz, 1H), 4.23 (d, J = 8.4 Hz, 1H), 3.78 (dd, J = 10.2, 10.2 Hz, 1H), 3.66 (dd, J = 9.2, 9.2 Hz, 1H), 3.57 – 3.40 (m, 2H), 3.54 (s, 3H), 2.79 (dd, J = 8.4, 8.4 Hz, 1H), 2.49 (br s, 2H); ¹³C NMR (75 MHz, CDCl₃), δ(ppm) = 137.0 (C), 129.2 (CH), 128.2 (2 x CH), 126.2 (2 x CH), 105.0 (CH), 101.8 (CH), 81.2 (CH), 72.8 (CH), 68.6 (CH₂), 66.3 (CH), 57.7 (CH), 57.3 (CH₃).
I-5. Sulfenylation of methyl 2-amino-4,6-O-benzylidene-2-deoxy-D-glucopyranoside.

\[
\begin{align*}
\text{OMe, NH}_2 & \quad \text{pTsCl, K}_2\text{CO}_3 \\
\text{Dioxane / H}_2\text{O (1/1)} & \quad \text{r.t., 4 h} \\
\text{r.t., 4 h} & \quad \text{OMe, NHTs}
\end{align*}
\]

α- or β-anomer of methyl 2-amino-4,6-benzylidine-2-deoxy-2-glucopyranoside (200 mg, 0.71 mmol) and K₂CO₃ (118 mg, 0.85 mmol) were dissolved in a 1/1 water / dioxane mixture (5 mL). p-Toluenesulfonyl chloride (149 mg, 0.78 mmol) was then added, and the mixture was stirred at room temperature for 4 hours. After concentration, the residue was dissolved in chloroform (10 mL), and washed successively with a saturated aqueous Na₂CO₃ solution (10 mL) and brine (10 mL). The organic phase was dried over MgSO₄, and concentrated. Purification was performed by column chromatography on silica gel using a mixture of Cyclohexane / EtOAc (7/3) as eluent.

**Methyl 4,6-O-benzylidene-2-deoxy-2-N-p-toluenesulfonamido-α-D-glucopyranoside 1**: white solid in 64% yield, m.p.= 182°C. Rf = 0.17 (Cyclohexane / EtOAc 7/3). ^1^H NMR (300 MHz, CDCl₃), δ (ppm) = 7.81 (d, J = 8.3 Hz, 2H), 7.48 – 7.40 (m, 2H), 7.38 – 7.29 (m, 5H), 5.50 (s, 1H), 5.04 (br d, J = 9.5 Hz, 1H), 4.38 (d, J = 3.8 Hz, 1H), 4.23 (dd, J = 9.0, 3.6 Hz, 1H), 3.84 (dd, J = 9.5, 9.5 Hz, 1H), 3.75 – 3.66 (m, 2H), 3.53 – 3.45 (m, 1H), 3.39 (ddd, J = 9.5, 9.5, 3.8 Hz, 1H), 3.29 (s, 3H), 2.43 (s, 3H); ^13^C NMR (75 MHz, CDCl₃), δ (ppm) = 143.6 (C), 137.3 (C), 136.6 (C), 129.5 (2 x CH), 128.9 (CH), 128.0 (2 x CH), 126.8 (2 x CH), 126.0 (2 x CH), 101.6 (CH), 98.4 (CH), 80.9 (CH), 69.1 (CH), 68.4 (CH₂), 61.9 (CH), 57.9 (CH), 55.2 (CH₃), 21.3 (CH₃). [α]̅²⁵_D = +36.0 (c = 0.97, CHCl₃), lit.[2] [α]̅²⁵_D = +34.4 (c = 0.77, CHCl₃). The NMR data are in agreement with the literature.[2,3]

**Methyl 4,6-O-benzylidene-2-deoxy-2-N-p-toluenesulfonamido-α-D-glucopyranoside 2**: white solid in 56% yield, m.p.= 180°C. Rf = 0.19 (Cyclohexane / EtOAc 7/3). ^1^H NMR (300 MHz, CDCl₃), δ (ppm) = 7.79 (d, J = 8.3 Hz, 2H), 7.52 – 7.42 (m, 2H), 7.40 – 7.28 (m, 5H), 5.51 (s, 1H), 5.26 (br s, 1H, NH), 4.29 (dd, J = 10.5, 4.9 Hz, 1H), 4.16 (d, J = 8.2 Hz, 1H), 3.90 (br dd, J = 9.3, 9.3 Hz, 1H), 3.72 (dd, J = 10.5, 10.5 Hz, 1H), 3.52 (dd, J = 9.3, 9.3 Hz, 1H), 3.43 – 3.32 (m, 2H), 3.22 – 3.12 (m, 4H), 2.44 (s, 3H); ^13^C NMR (75 MHz, CDCl₃), δ (ppm) = 143.6 (C), 137.4 (C), 136.9 (C), 125.5 (C), 123.3 (C), 122.7 (C), 121.3 (C), 101.6 (CH), 98.4 (CH), 80.9 (CH), 69.1 (CH), 68.4 (CH₂), 61.9 (CH), 57.9 (CH), 55.2 (CH₃), 21.3 (CH₃). [α]̅²⁵_D = +36.0 (c = 0.97, CHCl₃), lit.[2] [α]̅²⁵_D = +34.4 (c = 0.77, CHCl₃). The NMR data are in agreement with the literature.[2,3]
129.5 (2 x CH), 129.2 (CH), 128.3 (2 x CH), 127.5 (2 x CH), 126.3 (2 x CH), 102.5 (CH), 101.9 (CH), 80.9 (CH), 71.6 (CH), 68.5 (CH<sub>2</sub>), 66.2 (CH), 61.0 (CH), 57.0 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>).

\[ \left[ \alpha \right]_{D}^{25} = -58.0 \ (c = 0.965, \text{CHCl}_3), \text{lit.}\cite{4} \ [\alpha]_{D}^{25} = -56.9 \ (c = 0.56, \text{CHCl}_3). \] The NMR data are in agreement with the literature.\cite{4}

I-6. References.

\[ \begin{align*}
\end{align*} \]
II. NMR data.

$^1$H & $^{13}$C NMR of methyl 2-N-acetamido-2-deoxy-D-glucopyranoside.
$^1$H & $^{13}$C NMR of methyl 2-N-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside.
$^1$H & $^{13}$C NMR of methyl 2-N-acetamido-4,6-O-benzylidene-2-deoxy-β-D-glucopyranoside.

$^1$H NMR (300 MHz, MeOH-d$_4$)

$^{13}$C NMR (75 MHz, MeOH-d$_4$)
$^1$H & $^{13}$C NMR of methyl 2-amino-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside.
$^1$H & $^{13}$C NMR of methyl 2-amino-4,6-O-benzylidene-2-deoxy-$\beta$-D-glucopyranoside.

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^1$H & $^{13}$C NMR of methyl 4,6-O-benzylidene-2-deoxy-2-N-p-toluenesulfonamido-$\alpha$-D-glucopyranoside 1.

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^1$H & $^{13}$C NMR of methyl 4,6-O-benzylidene-2-deoxy-2-N-p-toluenesulfonamido-β-D-glucopyranoside 2.

$^1$H NMR (300 MHz, CDCl₃)

$^{13}$C NMR (75 MHz, CDCl₃)
\(^{31}P\) NMR of oxazaphospholidine derivative \(R_P-3\).

\(^{31}P\) NMR (121 MHz, CDCl\(_3\))

\(^{31}P\) NMR (121 MHz, CDCl\(_3\))

\(R_P\)-epimer (from obtained crystal)
$^1$H, $^{31}$P & $^{13}$C NMR of methyl 3-O-[(S)-(2-methoxyphenyl)phenylphosphinate]-4,6-O-benzylidene-2-deoxy-2-N-p-toluenesulfonamido-α-D-glucopyranoside $S_P$-5.

$^{31}$P NMR (121 MHz, CDCl$_3$)

$^1$H NMR (300 MHz, CDCl$_3$)
$^{31}$P NMR (121 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^1$H, $^{31}$P & $^{13}$C NMR of methyl 3-O-[(R)-methylphenylphosphinate]-4,6-O-benzylidene-2-deoxy-2-N-p-toluenesulfonamido-α-D-glucopyranoside $R_7$-6.

$^{31}$P NMR (121 MHz, CDCl$_3$)

$^1$H NMR (300 MHz, CDCl$_3$)
$^{31}P$ NMR (121 MHz, CDCl$_3$)

$^{13}C$ NMR (75 MHz, CDCl$_3$)
$^{31}$P NMR of not purified methyl 3-O-[(2-methoxyphenyl)phenylphosphinate]-4,6-O-benzylidene-2-deoxy-2-N-p-toluenesulfonamido-β-D-glucopyranoside 7.

$^{1}$H, $^{31}$P & $^{13}$C NMR of methyl 3-O-[(R)-(2-methoxyphenyl)phenylphosphinate]-4,6-O-benzylidene-2-deoxy-2-N-p-toluenesulfonamido-α-D-glucopyranoside R₁-5.
$^{31}P$ NMR (121 MHz, CDCl₃)

$^{13}C$ NMR (75 MHz, CDCl₃)
$^{1}$H, $^{31}$P & $^{13}$C NMR of o-anisylmethylphenylphosphine oxide $R_P$ or $S_P$-8.
$^1$H, $^{31}$P & $^{13}$C NMR of o-anisylethylphenylphosphine oxide S$_7$-9.

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{31}P$ NMR (121 MHz, CDCl$_3$)

$^{13}C$ NMR (75 MHz, CDCl$_3$)
$^1$H, $^{31}$P & $^{13}$C NMR of ethylmethylphenylphosphine oxide S$_{p}$-10.

$^1$H NMR (300 MHz, CDCl$_3$)

$^{31}$P NMR (121 MHz, CDCl$_3$)
$^1$H, $^{31}$P & $^{13}$C NMR of i-propylmethylphenylphosphine oxide $S_{P-11}$.

$^1$H NMR (300 MHz, CDCl$_3$)

$^1$C NMR (75 MHz, CDCl$_3$)
$^{31}$P NMR (121 MHz, CDCl₃)

$^{13}$C NMR (75 MHz, CDCl₃)
III. HPLC data.

HPLC of racemic and enriched o-anisylmethylphenylphosphine oxide 8.

ChiralpackAD
Heptane/IPA 85/15, 1 mL/min
Racemate

ChiralpackAD
Heptane/IPA 85/15, 0.5 mL/min
obtained from \( S_P-5 \)

ChiralpackAD
Heptane/IPA 85/15, 1 mL/min
obtained from \( R_P-6 \)
**HPLC of racemic and enriched o-anisylethylphenylphosphine oxide 9.**

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**ChiralpackAD**
Heptane/IPA 85/15, 1 mL/min obtained from $R_P$-5

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**ChiralpackAD**
Heptane/IPA 85/15, 1 mL/min Racemate

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**ChiralpackAD**
Heptane/IPA 85/15, 1 mL/min obtained from $S_P$-5
**HPLC of racemic and enriched ethylmethylphenylphosphine oxide 10.**

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**SOMME** 481,43 100,00

Cellulose OD-H
Heptane/IPA 95/5, 1 mL/min
Racemate

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**HPLC of racemic and enriched i-propylmethylphenylphosphine oxide 11.**

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**SOMME** 201,40 100,00

Cellulose OD-H
Heptane/IPA 95/5, 1 mL/min
obtained from $R_P$-6

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**HPLC of racemic and enriched i-propylmethylphenylphosphine oxide 11.**

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**SOMME** 213,30 100,00

Cellulose OD-H
Heptane/IPA 98/2, 1 mL/min
Racemate
Cellulose OD-H
Heptane/IPA 98/2, 1 mL/min
obtained from $R_P$-6
IV. X-ray data.

Crystal data of $R_P^{-3}$, $S_P^{-5}$ and $R_P^{-6}$ were collected at room temperature using a Geminini Oxford Diffractometer (MoKα radiation, $\lambda = 0.71069$ Å) equipped with a CCD camera and by using the related software. An absorption correction (analytical) has been applied to all the data sets. All the structures were solved by direct methods using the SIR97 program combined with Fourier Difference and the refined against F using the CRYSTALS program. In each structure, all atomic displacements for non-hydrogen atoms were refined using an anisotropic model. Hydrogen atoms have been placed by Fourier Difference account the hybridization of the supporting atoms and for the possible presence of hydrogen bonds in the case of donor atoms. Hydrogen atoms have been finally refined using a riding mode.

CCDC 1400048, 1400046 and 1400047 references contain the supplementary crystallographic data for $R_P^{-3}$, $S_P^{-5}$ and $R_P^{-6}$, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

[i] CrysAlisPro, version 1.171.34.40 (rel. 27-08-2010, CrysAlis171.NET), Oxford Diffraction Ltd.


**X-ray of oxazaphospholidine derivative $R_P^{-3}$.**

*X-ray diffraction analysis: CCDC 1400048; Empirical formula: C$_{27}$H$_{38}$NO$_8$PS; molecular weight = 557.6 g.mol$^{-1}$; crystal system: orthorhombic; space group: P2$_1$2$_1$2$_1$;*
\[ a = 11.8008(5) \, \text{Å}; \quad b = 14.3566(8) \, \text{Å}; \quad c = 16.680(1) \, \text{Å}; \quad V = 2825.9(3) \, \text{Å}^3; \]

Crystal description: needle; crystal color: colorless; crystal size: 0.133×0.135×0.232 mm\(^3\); Z = 4; T = 293 K;

d = 1.310; \mu = 0.219 mm\(^{-1}\); Number of independent reflections: 6417; \( R_{int} = 0.054; \)

\( R(F) = 0.0562; \quad R_w(F) = 0.0536; \quad S = 1.12; \quad \Delta \rho_{\text{min}} = -0.48 \, \text{e.Å}^{-3}; \quad \Delta \rho_{\text{max}} = +0.48 \, \text{e.Å}^{-3}; \)

Flack parameter = -0.2(2); Number of reflections used: 2690; Number of refined parameters: 343; absorption correction: analytical.

\textit{X-ray of phosphinate derivative S\textsubscript{P}-5.}

\[ X\text{-ray diffraction analysis: CCDC 1400046; Empirical formula: C\textsubscript{34}H\textsubscript{36}NO\textsubscript{9}PS; molecular weight = 665.7 g.mol}^{-1}; \] crystal system: orthorhombic; space group: \textit{P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1}};

\[ a = 16.3644(6) \, \text{Å}; \quad b = 15.9689(6) \, \text{Å}; \quad c = 12.8284(5) \, \text{Å}; \quad V = 3352.4(2) \, \text{Å}^3; \]

Crystal description: needle; crystal color: colorless; crystal size: 0.229×0.273×0.729 mm\(^3\); Z = 4; T = 293 K;

d = 1.331; \mu = 0.119 mm\(^{-1}\); Number of independent reflections: 7801; \( R_{int} = 0.021; \)

\( R(F) = 0.0422; \quad R_w(F) = 0.0511; \quad S = 1.07; \quad \Delta \rho_{\text{min}} = -0.17 \, \text{e.Å}^{-3}; \quad \Delta \rho_{\text{max}} = +0.21 \, \text{e.Å}^{-3}; \)

Flack parameter = -0.04(8); Number of reflections used: 4899; Number of refined parameters: 416; absorption correction: analytical.

\textit{X-ray of phosphinate derivative R\textsubscript{P}-6.}

\[ X\text{-ray diffraction analysis: CCDC 1400047; Empirical formula: C\textsubscript{31}H\textsubscript{40}NO\textsubscript{9}PS; molecular weight = 633.7 g.mol}^{-1}; \] crystal system: monoclinic; space group: \textit{P2\textsubscript{1}};
a = 10.2628(5) Å; b = 8.9164(4) Å; c = 18.5939(9) Å; β = 105.023(5); V = 1643.3(1) Å³;
crystal description: needle; crystal color: colorless; crystal size: 0.142×0.175×0.515 mm³;
Z = 2 ; T = 293 K; d = 1.289; µ = 0.200 mm⁻¹; Number of independent reflections: 6292;
R_{int} = 0.026; R(F) = 0.0409; R_w(F) = 0.0406; S = 1.15; Δρ_{min} = -0.23 e Å⁻³; Δρ_{max} = +0.19 e Å⁻³;
Flack parameter = 0.08(8); Number of reflections used: 3953; Number of refined parameters: 389; absorption correction: analytical.