Supporting Information

A Practical Synthesis of 5-Substituted 1H-Tetrazoles from Aldoximes employing Azide Anion from Diphenyl Phosphorazidate
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**General Experimental Information**

All the laboratory chemicals were purchased and used without purification unless otherwise stated. All reactions were magnetically stirred and monitored by thin layer chromatography using silica gel plates. Purification by column chromatography was performed on silica gel 60N (spherical, neutral, 63–210 μm, Kanto Chemical Co., Inc.). Melting points were determined in open-ended capillaries using a Bibby Scientific Ltd. Stuart® SMP30 instrument and are uncorrected. All nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-EX270 spectrometer. Chemical shifts (δ) are given in ppm, and coupling constants (J) are given in Hz. High-resolution mass spectra (HRMS) were measured by EI using JEOL MS-700. High-resolution EI mass spectra were calibrated with PFK. All high-performance liquid chromatography (HPLC) analyses were performed on Hitachi UV L-2140 and L-2400 detectors with a Hitachi L-2130 pump. The chiral HPLC conditions (column, mobile phase, flow rate, and detection wavelength) are indicated in the text.

**Color Identification Test of Azide Anion**

I. Oxime and Fe(NO$_3$)$_3$ in THF
II. DPPA and Fe(NO$_3$)$_3$ in THF
III. Oxime, DPPA, DBU and Fe(NO$_3$)$_3$ in THF
IV. NaN$_3$ and Fe(NO$_3$)$_3$ in water
V. Fe(NO$_3$)$_3$ in THF
Verification of the formation of phosphate intermediate

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\begin{align*}
\text{DPPA (1.5 eq.)} & \quad \text{DBU (3.0 eq.)} \quad \text{THF, rt, 2 h} \quad \text{Not Detected} \\
\text{PhN} & \quad \text{O} \quad \text{O} \quad \text{P} \quad \text{O} \quad \text{O} \quad \text{Ph} \\
\text{PhN} & \quad \text{O} \quad \text{O} \quad \text{P} \quad \text{O} \quad \text{O} \quad \text{Ph}
\end{align*}
\]

DPPA (0.15 mmol) and DBU (0.30 mmol) were added to a solution of oxime (0.10 mmol) in THF (1.0 mL). After stirring for 2 h at room temperature, the mixture was diluted with AcOEt (30 mL). Then, the mixture was washed with 1 N HCl, water, saturated aqueous NaHCO₃ and brine (25 mL), and dried over Na₂SO₄. Concentration of the solvent in vacuo followed by purification of the residue on silica gel column (AcOEt : n-hexane 1 : 3) gave the desired phosphate.

The phosphate derived from benzaldoxime did not be detected owing to instability and no other products were identified.

Diphenyl (((1-phenylethylidene)amino)oxy)phosphonate

Yield: 54%; colorless oil; ¹H NMR (270MHz, CDCl₃): δ 2.33 (d, J=3.5Hz, 3H), 7.19-7.44 (m, 13H), 7.66 (d, J=5.9Hz, 2H); HRMS-EI (m/z):[M]⁺ calcd for C₂₀H₁₈NO₄P 367.0973, found 367.0982.
HPLC Chart of rac-tert-Butyl 2-(1-methyl-1H-tetrazol-5-yl)pyrrolidine-1-carboxylate

Chiral HPLC: column, Daicel CHIRAL OD-3, 4.6 × 150 mm; solvent, 10:90 v/v iPrOH/n-hexane; flow rate, 1.0 ml/min; detector wavelength, 210 nm; retention time (R) 6.60 min and (S) 7.43 min.
HPLC Chart of (S)-tert-Butyl 2-(1-methyl-1H-tetrazol-5-yl)pyrrolidine-1-carboxylate

Chiral HPLC: column, Daicel CHIRAL OD-3, 4.6 × 150 mm; solvent, 10:90 v/v iPrOH/n-hexane; flow rate, 1.0 ml/min; detector wavelength, 210 nm; retention time (S) 7.58 min. >99% ee
HPLC Chart of rac-Benzyl (3-methyl-1-(2-methyl-2H-tetrazol-5-yl)butyl)carbamate and rac-Benzyl (3-methyl-1-(1-methyl-1H-tetrazol-5-yl)butyl)carbamate as mixture

Chiral HPLC: column, Daicel CHIRAL OD-3 4.6 × 150 mm; solvent, 10:90 v/v 'PrOH/n-hexane; flow rate, 1.0 ml/min; detector wavelength, 210 nm; retention times (R) 10.05 min, (S) 11.85 min, (S) 12.41 min, and (R) 25.49 min.
HPLC Chart of (S)-Benzy1 (3-methyl-1-(2-methyl-2H-tetrazol-5-yl)butyl)carbamate and (S)-Benzy1 (3-methyl-1-(1-methyl-1H-tetrazol-5-yl)butyl)carbamate as mixture.

Chiral HPLC: column, Daicel CHIRAL OD-3 4.6 × 150 mm; solvent, 10:90 v/v iPrOH/n-hexane; flow rate, 1.0 ml/min; detector wavelength, 210 nm; retention times (R) 9.97 min, (S) 11.63 min, (S) 12.17 min, and (R) 25.19 min. 97% ee
Copies of NMR spectra
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