## Supporting Information

## Redox Deracemization of Phosphonate-Substituted Dihydropyrimidines

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## 1. General

General: All reactions were carried out under an atmosphere of nitrogen using the standard Schlenk techniques, unless otherwise noted. ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR spectra were recorded at room temperature in $\mathrm{CDCl}_{3}$ on 400 MHz instrument with tetramethylsilane (TMS) as internal standard. Enantiomeric excess was determined by HPLC analysis, using chiral column described below in detail. Optical rotations were measured by polarimeter. Flash column chromatography was performed on silica gel (200-300 mesh). All reactions were monitored by TLC analysis.

Materials: Commercially available reagents were used throughout without further purification. The anhydrous solvents for asymmetric transfer hydrogenation were also purchased without the further purification.

## 2. General Procedure for Synthesis of 3,4-Dihydropyrimidin-2-one

3,4-Dihydropyrimidin-2-one derivatives 1 can be conveniently prepared according to the known literature procedure with some minor modifications. ${ }^{1,2}$ The compound $\mathbf{1 m}, \mathbf{1 1}$ are known. ${ }^{2}$


General procedure: A mixture of 2,4-dichloropyrimidine $\mathbf{S - 1 a}(2.959 \mathrm{~g}, 20 \mathrm{mmol}$ ), the corresponding arylboronic acid ( 20 mmol ), $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}(0.231 \mathrm{~g}, 0.2 \mathrm{mmol})$ and sodium carbonate $(2.119 \mathrm{~g}, 20 \mathrm{mmol})$ in acetonitrile $(25 \mathrm{~mL})$ and water $(25 \mathrm{~mL})$ was stirred at reflux for 8 h , then cooled to ambient temperature, then extracted with ethyl acetate $(50 \mathrm{~mL} \times 3)$. The combined organic layer was dried over anhydrous sodium sulfate. After filtration, the solvent was removed under the reduced pressure, and the residue was purified by flash chromatography on silica gel to give the corresponding products $\mathbf{S}-\mathbf{1 b}$.

Subsequently, the above $\mathbf{S}-\mathbf{1 b}$ ( 10 mmol ) in $38 \%$ hydrogen chloride aqueous solution ( 5.0 mL ) was stirred at $100^{\circ} \mathrm{C}$ for 5 h before the mixture was cooled and the pH adjusted to 7 with aqueous sodium hydroxide $(1.0 \mathrm{M})$. The most water was removed under reduced pressure and the residue was extracted with chloroform ( $30 \mathrm{~mL} \times 3$ ). The combined organic layer was dried over anhydrous sodium sulfate. After filtration, the solvent was removed under reduced pressure and the crude product purified by flash chromatography on silica gel to give the corresponding products $\mathbf{S}-\mathbf{1 c}$.

A mixture of 2-hydroxypyrimidine $\mathbf{S - 1 c}$ ( 4 mmol ), diisopropyl phosphonate ( $8 \mathrm{mmol}, 2$ equiv), and zirconium chloride ( $0.2 \mathrm{mmol}, 5 \mathrm{~mol} \%$ ) in tetrahydrofuran $(20 \mathrm{~mL})$ was stirred at room temperature for 24 h . After the reaction was completed (determined by TLC), the solvent was removed under the reduced pressure. The residue was purified by flash chromatography on silica gel using the ethyl acetate/ triethylamine as eluent to give the racemic of 3,4-dihydropyrimidin- 2one derivatives 1 .

## 3. General Procedure for Redox Deracemization



A racemic of 3,4-Dihydropyrimidin-2-one derivatives 1 ( 0.10 mmol ), DDQ ( $25 \mathrm{mg}, 0.11 \mathrm{mmol}$, 1.1 equiv) in ethyl acetate ( 4 mL ) was stirred at room temperature for 5 min . After the reaction was completed (determined by TLC), chiral phosphoric acid ( $R$ )-2g(7.5 mg, $0.01 \mathrm{mmol}, 10 \mathrm{~mol} \%$ ) and Hantzsch ester 3a ( $31.5 \mathrm{mg}, 0.14 \mathrm{mmol}, 1.4$ equiv) was added. The mixture was stirred at room temperature for 24 h . The resulting mixture was concentrated in vacuo and further purification was performed by a silica gel column eluted with dichloromethane/methanol to give the optically active products 1 . The enantiomeric excesses were determined by chiral HPLC.

Diisopropyl (R)-(2-oxo-6-phenyl-1,2,3,4-tetrahydropyrimidin-4-yl)phosphonate (1a): 31 $\mathrm{mg}, 92 \%$ yield, new compound, white solid, $\mathrm{mp}: 157-158^{\circ} \mathrm{C}, \mathrm{R}_{f}=0.40$ (dichloromethane/ methanol
 $=10 / 1), 96 \% \mathrm{ee},[\alpha]^{20}{ }_{\mathrm{D}}=-26.45(c 0.31, \mathrm{MeOH}),{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.47-7.41(\mathrm{~m}, 5 \mathrm{H}), 6.79(\mathrm{~s}, 1 \mathrm{H}), 5.29(\mathrm{~s}, 1 \mathrm{H}), 5.10(\mathrm{~s}, 1 \mathrm{H}), 4.83-4.75(\mathrm{~m}, 2 \mathrm{H})$, 4.52-4.49 (m, 1H), 1.38-1.31 (m, 12H). ${ }^{13} \mathrm{C}$ NMR ( $\left.100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 153.8$, 138.3, 134.1 (d, $J=3.2 \mathrm{~Hz}), 129.3,128.8,125.1,90.7(\mathrm{~d}, J=9.1 \mathrm{~Hz}), 72.2$ (d, $J=7.7 \mathrm{~Hz}), 71.8(\mathrm{~d}, J=7.7 \mathrm{~Hz}), 51.8(\mathrm{~d}, J=160.5 \mathrm{~Hz}), 24.3(\mathrm{~d}, J=3.3 \mathrm{~Hz})$, $24.1(\mathrm{~d}, J=3.2 \mathrm{~Hz}), 24.1(\mathrm{~d}, J=4.0 \mathrm{~Hz}), 23.9(\mathrm{~d}, J=5.1 \mathrm{~Hz}) .{ }^{31} \mathrm{P}$ NMR (162 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 16.0. HPLC: Chiracel AD column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}$, $n$-hexane $/ i$-propanol $=80 / 20$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time $6.3 \mathrm{~min}(\mathrm{maj})$ and 7.2 min . HRMS (ESI) $\mathrm{m} / \mathrm{z}$ calculated for $\mathrm{C}_{16} \mathrm{H}_{24} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{P}[\mathrm{M}+\mathrm{H}]^{+}$339.1464, found 339.1466.

Diisopropyl (R)-(2-ox0-6-(p-tolyl)-1,2,3,4-tetrahydropyrimidin-4-yl)phosphonate (1b): 33 $\mathrm{mg}, 94 \%$ yield, new compound, white solid, $\mathrm{mp}: 168-169^{\circ} \mathrm{C}, \mathrm{R}_{f}=0.40$ (dichloromethane/ methanol
 $=10 / 1), 94 \% \mathrm{ee},[\alpha]^{20} \mathrm{D}=-42.12(c \quad 0.33, \mathrm{MeOH}) .{ }^{1} \mathrm{H}$ NMR $(400 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right) \delta 7.64(\mathrm{~s}, 1 \mathrm{H}), 7.35(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 2 \mathrm{H}), 7.18(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 2 \mathrm{H})$, $5.74(\mathrm{~s}, 1 \mathrm{H}), 5.03-5.02(\mathrm{~m}, 1 \mathrm{H}), 4.78-4.73(\mathrm{~m}, 2 \mathrm{H}), 4.45-4.42(\mathrm{~m}, 1 \mathrm{H}), 2.35$ $(\mathrm{s}, 3 \mathrm{H}), 1.35-1.27(\mathrm{~m}, 12 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 154.1,139.3$, $138.3(\mathrm{~d}, J=10.8 \mathrm{~Hz}), 131.2(\mathrm{~d}, J=3.1 \mathrm{~Hz}), 129.5,125.0(\mathrm{~d}, J=1.6 \mathrm{~Hz})$, 89.8 (d, $J=9.2 \mathrm{~Hz}$ ), 72.2 (d, $J=7.6 \mathrm{~Hz}$ ), 71.7 (d, $J=7.9 \mathrm{~Hz}$ ), 51.7 (d, $J=160.5 \mathrm{~Hz}$ ), 24.3 (d, $J=$ $3.0 \mathrm{~Hz}), 24.1(\mathrm{~d}, J=3.3 \mathrm{~Hz}), 24.1(\mathrm{~d}, J=1.5 \mathrm{~Hz}), 23.9(\mathrm{~d}, J=5.2 \mathrm{~Hz}), 21.3 .{ }^{31} \mathrm{P}$ NMR ( 162 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 16.2$. HPLC: Chiracel AD column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}, n$-hexane $/ i$-propanol $=80 / 20$, flow $=$ $1.0 \mathrm{~mL} / \mathrm{min}$, retention time 6.9 min (maj) and 7.8 min . HRMS (ESI) $\mathrm{m} / \mathrm{z}$ calculated for $\mathrm{C}_{17} \mathrm{H}_{26} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{P}$ $[\mathrm{M}+\mathrm{H}]^{+} 353.1626$, found 353.1625.

Diisopropyl (R)-(2-oxo-6-(m-tolyl)-1,2,3,4-tetrahydropyrimidin-4-yl)phosphonate (1c): 34

$\mathrm{mg}, 96 \%$ yield, new compound, white solid, $\mathrm{mp}: 129-130^{\circ} \mathrm{C}, \mathrm{R}_{f}=0.40$ (dichloromethane/ methanol $=10 / 1), 92 \% \mathrm{ee},[\alpha]^{20}{ }_{\mathrm{D}}=-52.43(c 0.34, \mathrm{MeOH}) .{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.53(\mathrm{~s}, 1 \mathrm{H}), 7.29-$ $7.24(\mathrm{~m}, 3 \mathrm{H}), 7.18(\mathrm{~d}, J=5.9 \mathrm{~Hz}, 1 \mathrm{H}), 5.75(\mathrm{~s}, 1 \mathrm{H}), 5.05(\mathrm{~s}, 1 \mathrm{H}), 4.81-4.71(\mathrm{~m}, 2 \mathrm{H}), 4.44(\mathrm{~d}, J=$ $\left.3.9 \mathrm{~Hz}, 1 \mathrm{H}), 2.37(\mathrm{~s}, 3 \mathrm{H}), 1.35-1.28(\mathrm{~m}, 12 \mathrm{H}) .{ }^{13} \mathrm{C} \mathrm{NMR} \mathrm{(100MHz,CDCl}_{3}\right) \delta 154.0,138.5,134.0$ $(\mathrm{d}, J=3.2 \mathrm{~Hz}), 130.0(\mathrm{~d}, J=4.2 \mathrm{~Hz}), 128.7(\mathrm{~d}, J=5.2 \mathrm{~Hz}), 125.8,122.2,90.4(\mathrm{~d}, J=7.8 \mathrm{~Hz}), 72.2$ (d, $J=6.8 \mathrm{~Hz}$ ), $71.8(\mathrm{~d}, J=7.2 \mathrm{~Hz}), 51.7(\mathrm{~d}, J=159.7 \mathrm{~Hz}), 24.3(\mathrm{~d}, J=3.1 \mathrm{~Hz}), 24.1(\mathrm{~d}, J=3.0 \mathrm{~Hz})$, $24.1(\mathrm{~d}, J=8.5 \mathrm{~Hz}), 23.9(\mathrm{~d}, J=5.1 \mathrm{~Hz}), 21.4 .{ }^{31} \mathrm{P}$ NMR $\left(162 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 16.1$. HPLC: Chiracel AD column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}$, $n$-hexane $/ i$-propanol $=80 / 20$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 5.3 $\min$ (maj) and 6.3 min . HRMS (ESI) $\mathrm{m} / \mathrm{z}$ calculated for $\mathrm{C}_{17} \mathrm{H}_{26} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{P}[\mathrm{M}+\mathrm{H}]^{+} 353.1626$, found 353.1624 .

Diisopropyl ( $R$ )-(6-(3,4-dimethylphenyl)-2-oxo-1,2,3,4-tetrahydropyrimidin-4-yl)phosphon ate (1d): $36 \mathrm{mg}, 98 \%$ yield, new compound, white solid, mp : $132-133{ }^{\circ} \mathrm{C}, \mathrm{R}_{f}=0.40$
 (dichloromethane/methanol $=10 / 1$ ), $90 \%$ ee, $[\alpha]^{20}{ }_{\mathrm{D}}=-39.72$ (c 0.36, $\mathrm{MeOH}) .{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.22(\mathrm{~s}, 1 \mathrm{H}), 7.17(\mathrm{~d}, J=0.8 \mathrm{~Hz}$, $2 \mathrm{H}), 6.69(\mathrm{~s}, 1 \mathrm{H}), 5.28(\mathrm{~s}, 1 \mathrm{H}), 5.07-5.05(\mathrm{~m}, 1 \mathrm{H}), 4.82-4.73(\mathrm{~m}, 2 \mathrm{H}), 4.51-$ $4.48(\mathrm{~m}, 1 \mathrm{H}), 2.29(\mathrm{~d}, J=2.5 \mathrm{~Hz}, 6 \mathrm{H}), 1.38-1.30(\mathrm{~m}, 12 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 100 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 154.1,138.3(\mathrm{~d}, J=10.7 \mathrm{~Hz}), 138.0,137.1,131.5(\mathrm{~d}, J=$ $3.0 \mathrm{~Hz}), 130.0,126.2,122.4,89.6(\mathrm{~d}, J=9.0 \mathrm{~Hz}), 72.2(\mathrm{~d}, J=7.6 \mathrm{~Hz}), 71.7$ (d, $J=7.9 \mathrm{~Hz}$ ), $51.7(\mathrm{~d}, J=160.2 \mathrm{~Hz}), 24.3(\mathrm{~d}, J=2.9 \mathrm{~Hz}), 24.1(\mathrm{~d}, J=4.1 \mathrm{~Hz}), 23.9(\mathrm{~d}, J=5.2$ Hz ), 19.8, 19.6. ${ }^{31} \mathrm{P}$ NMR ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 16.2. HPLC: Chiracel AD column, $254 \mathrm{~nm}, 3{ }^{\circ} \mathrm{C}$, $n$-hexane $/ i$-propanol $=80 / 20$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time $5.9 \mathrm{~min}(\mathrm{maj})$ and $6.9 \mathrm{~min} . \mathrm{HRMS}$ (ESI) $m / z$ calculated for $\mathrm{C}_{18} \mathrm{H}_{28} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{P}[\mathrm{M}+\mathrm{H}]^{+} 367.1778$, found 367.1777.

## Diisopropyl (R)-(6-(4-isopropylphenyl)-2-0xo-1,2,3,4-tetrahydropyrimidin-4-yl)phosphon

 ate (1e): $35 \mathrm{mg}, 92 \%$ yield, new compound, white solid, mp : $158-159{ }^{\circ} \mathrm{C}, \mathrm{R}_{f}=0.40$ (dichloromethane/methanol $=10 / 1$ ), $94 \%$ ee, $[\alpha]^{20}{ }_{\mathrm{D}}=-39.43$ (c 0.35, $\mathrm{MeOH}) .{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.52(\mathrm{~s}, 1 \mathrm{H}), 7.38(\mathrm{~d}, J=8.2 \mathrm{~Hz}$, $2 \mathrm{H}), 7.24(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 5.69(\mathrm{~s}, 1 \mathrm{H}), 5.03(\mathrm{dd}, J=5.2,3.4 \mathrm{~Hz}, 1 \mathrm{H})$, 4.77-4.74 (m, 2H), 4.48-4.46 (m, 1H), 2.94-2.88 (m, 1H), 1.35-1.28 (m, $12 \mathrm{H}), 1.24(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 154.0,150.2$, $138.2(\mathrm{~d}, J=10.9 \mathrm{~Hz}), 131.5(\mathrm{~d}, J=3.3 \mathrm{~Hz}), 126.9,125.1(\mathrm{~d}, J=1.8 \mathrm{~Hz}), 89.9(\mathrm{~d}, J=9.1 \mathrm{~Hz}), 72.1$ $(\mathrm{d}, J=7.6 \mathrm{~Hz}), 71.8(\mathrm{~d}, J=7.6 \mathrm{~Hz}), 51.7(\mathrm{~d}, J=160.4 \mathrm{~Hz}), 33.9,24.3(\mathrm{~d}, J=3.0 \mathrm{~Hz}), 24.2(\mathrm{~d}, J=$ $3.1 \mathrm{~Hz}), 24.1(\mathrm{~d}, J=4.0 \mathrm{~Hz}), 23.9(\mathrm{~d}, J=5.2 \mathrm{~Hz}), 23.8 .{ }^{31} \mathrm{P}$ NMR $\left(162 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 16.2$. HPLC: Chiracel OD column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}, n$-hexane $/ i$-propanol $=80 / 20$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 7.1 min (maj) and 7.7 min . $\mathrm{HRMS}(\mathrm{ESI}) \mathrm{m} / \mathrm{z}$ calculated for $\mathrm{C}_{19} \mathrm{H}_{30} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{P}[\mathrm{M}+\mathrm{H}]^{+} 381.1934$, found 381.1932.

Diisopropyl (R)-(6-(4-(tert-butyl)phenyl)-2-oxo-1,2,3,4-tetrahydropyrimidin-4-yl)phosph onate (1f): 37 mg , $94 \%$ yield, new compound, white solid, mp : 191-192 ${ }^{\circ} \mathrm{C}, \mathrm{R}_{f}=0.40$

$($ dichloromethane/methanol $=10 / 1), 95 \% \mathrm{ee},[\alpha]^{20}{ }_{\mathrm{D}}=-35.41(c 0.37, \mathrm{MeOH}) .{ }^{1} \mathrm{H}$ NMR $(400 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right) \delta 7.53(\mathrm{~s}, 1 \mathrm{H}), 7.40(\mathrm{~s}, 4 \mathrm{H}), 5.70(\mathrm{~s}, 1 \mathrm{H}), 5.06-5.04(\mathrm{~m}, 1 \mathrm{H}), 4.81-4.71(\mathrm{~m}, 2 \mathrm{H}), 4.48-4.46$ $(\mathrm{m}, 1 \mathrm{H}), 1.36-1.28(\mathrm{~m}, 21 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 154.0,152.4,138.1(\mathrm{~d}, J=10.8 \mathrm{~Hz})$, $131.1,125.7,124.8,90.0(\mathrm{~d}, J=9.3 \mathrm{~Hz}), 72.1(\mathrm{~d}, J=7.6 \mathrm{~Hz}), 71.8(\mathrm{~d}, J=7.7 \mathrm{~Hz}), 51.8(\mathrm{~d}, J=160.5$ $\mathrm{Hz}), 34.7,31.2,24.3(\mathrm{~d}, J=3.2 \mathrm{~Hz}), 24.2(\mathrm{~d}, J=3.3 \mathrm{~Hz}), 24.1(\mathrm{~d}, J=4.3 \mathrm{~Hz}), 23.9(\mathrm{~d}, J=5.1 \mathrm{~Hz})$. ${ }^{31} \mathrm{P}$ NMR ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 16.1. HPLC: Chiracel AD column, $254 \mathrm{~nm}, 30{ }^{\circ} \mathrm{C}$, $n$-hexane $/ i$ propanol $=80 / 20$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 6.3 min and $7.1 \mathrm{~min}(\mathrm{maj}) . \mathrm{HRMS}(E S I) \mathrm{m} / \mathrm{z}$ calculated for $\mathrm{C}_{20} \mathrm{H}_{32} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{P}[\mathrm{M}+\mathrm{H}]^{+}$395.2093, found 395.2092.

Diisopropyl (R)-(6-(4-chlorophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidin-4-yl)phosphonate (1g): $35 \mathrm{mg}, 94 \%$ yield, new compound, white solid, $\mathrm{mp}: 184-185^{\circ} \mathrm{C}, \mathrm{R}_{f}=0.40$ (dichloromethane/
 methanol $=10 / 1$ ), $95 \%$ ee, $[\alpha]^{20}{ }_{\mathrm{D}}=-39.72(c 0.35, \mathrm{MeOH}) .{ }^{1} \mathrm{H}$ NMR (400 $\left.\mathrm{MHz}, \mathrm{DMSO}_{6}\right) \delta 8.64(\mathrm{~s}, 1 \mathrm{H}), 7.51(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.46-7.44(\mathrm{~m}$, $2 \mathrm{H}), 6.95(\mathrm{~s}, 1 \mathrm{H}), 5.00-4.98(\mathrm{~m}, 1 \mathrm{H}), 4.65-4.56(\mathrm{~m}, 2 \mathrm{H}), 4.34-4.30(\mathrm{~m}, 1 \mathrm{H})$, 1.30-1.18 (m, 12H). ${ }^{13} \mathrm{C}$ NMR ( $\left.100 \mathrm{MHz}, \mathrm{DMSO}_{6}\right) \delta 153.7,138.0(\mathrm{~d}, J=$ $9.9 \mathrm{~Hz}), 133.8,133.2(\mathrm{~d}, J=3.8 \mathrm{~Hz}), 129.0,127.6(\mathrm{~d}, J=1.4 \mathrm{~Hz}), 91.9(\mathrm{~d}$, $J=7.7 \mathrm{~Hz}), 71.4(\mathrm{~d}, J=7.6 \mathrm{~Hz}), 71.2(\mathrm{~d}, J=7.6 \mathrm{~Hz}), 50.9(\mathrm{~d}, J=158.5 \mathrm{~Hz}), 24.5(\mathrm{~d}, J=3.0 \mathrm{~Hz})$, $24.4(\mathrm{~d}, J=3.5 \mathrm{~Hz}), 24.2(\mathrm{~d}, J=4.7 \mathrm{~Hz}), 24.1(\mathrm{~d}, J=5.0 \mathrm{~Hz}) .{ }^{31} \mathrm{P}$ NMR ( $\left.162 \mathrm{MHz}, \mathrm{DMSO}-\mathrm{d}_{6}\right) \delta$ 17.4. HPLC: Chiracel OD column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}, n$-hexane $/ i$-propanol $=80 / 20$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 6.3 min and 7.4 min (maj). $\mathrm{HRMS}(\mathrm{ESI}) \mathrm{m} / \mathrm{z}$ calculated for $\mathrm{C}_{16} \mathrm{H}_{23} \mathrm{ClN}_{2} \mathrm{O}_{4} \mathrm{P}[\mathrm{M}+\mathrm{H}]^{+}$ 373.0894, found 373.0893.

Diisopropyl (R)-(6-(3-chlorophenyl)-2-oxo-1,2,3,4-tetrahydropyrimidin-4-yl)phosphonate (1h): $36 \mathrm{mg}, 97 \%$ yield, new compound, white solid, mp : $165-166{ }^{\circ} \mathrm{C}, \mathrm{R}_{f}=0.40$
 (dichloromethane/methanol $=10 / 1$ ), $93 \%$ ee, $[\alpha]^{20}{ }_{\mathrm{D}}=-56.39$ (c 0.36, $\mathrm{MeOH}) .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.20(\mathrm{~s}, 1 \mathrm{H}), 7.44(\mathrm{~s}, 1 \mathrm{H}), 7.32(\mathrm{~d}$, $J=7.2 \mathrm{~Hz}, 3 \mathrm{H}), 5.88(\mathrm{~s}, 1 \mathrm{H}), 5.05(\mathrm{~s}, 1 \mathrm{H}), 4.79-4.71(\mathrm{~m}, 2 \mathrm{H}), 4.45-4.43$ $(\mathrm{m}, 1 \mathrm{H}), 1.34-1.27(\mathrm{~m}, 12 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 154.2,137.3$ (d, $J=10.8 \mathrm{~Hz}), 135.7(\mathrm{~d}, J=2.9 \mathrm{~Hz}), 134.7,130.0,129.2,125.5,123.4$, $91.7(\mathrm{~d}, J=9.3 \mathrm{~Hz}), 72.2(\mathrm{~d}, J=7.5 \mathrm{~Hz}), 72.0(\mathrm{~d}, J=7.7 \mathrm{~Hz}), 51.7(\mathrm{~d}, J=160.8 \mathrm{~Hz}), 24.2(\mathrm{~d}, J=$ $3.0 \mathrm{~Hz}), 24.1(\mathrm{~d}, J=3.8 \mathrm{~Hz}), 24.1(\mathrm{~d}, J=6.4 \mathrm{~Hz}), 23.9(\mathrm{~d}, J=5.1 \mathrm{~Hz}) .{ }^{31} \mathrm{P}$ NMR ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 15.9. HPLC: Chiracel AD column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}$, $n$-hexane $/ i$-propanol $=80 / 20$, flow $=1.0$ $\mathrm{mL} / \mathrm{min}$, retention time 5.7 min (maj) and 7.0 min . HRMS (ESI) $m / z$ calculated for $\mathrm{C}_{16} \mathrm{H}_{23} \mathrm{ClN}_{2} \mathrm{O}_{4} \mathrm{P}$ $[\mathrm{M}+\mathrm{H}]^{+} 373.0894$, found 373.0891 .

Diisopropyl (R)-(6-(4-ethylphenyl)-2-oxo-1,2,3,4-tetrahydropyrimidin-4-yl)phosphonate (1i): $34 \mathrm{mg}, 93 \%$ yield, new compound, white solid, $\mathrm{mp}: 156-157^{\circ} \mathrm{C}, \mathrm{R}_{f}=0.40$ (dichloromethane/
 methanol $=10 / 1), 81 \%$ ee, $[\alpha]^{20}{ }_{\mathrm{D}}=-34,72(c 0.36, \mathrm{MeOH}) .{ }^{1} \mathrm{H}$ NMR $(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.51(\mathrm{~s}, 1 \mathrm{H}), 7.37(\mathrm{~d}, J=6.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.21(\mathrm{~d}, J=6.4 \mathrm{~Hz}$, $2 \mathrm{H}), 5.69(\mathrm{~s}, 1 \mathrm{H}), 5.03(\mathrm{~s}, 1 \mathrm{H}), 4.75(\mathrm{~s}, 2 \mathrm{H}), 4.45(\mathrm{~s}, 1 \mathrm{H}), 2.64(\mathrm{~d}, J=6.7$ $\mathrm{Hz}, 2 \mathrm{H}), 1.33-1.23(\mathrm{~m}, 15 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 154.0,145.6$, $138.2(\mathrm{~d}, J=11.0 \mathrm{~Hz}), 131.4,128.3,125.0,89.9(\mathrm{~d}, J=9.2 \mathrm{~Hz}), 72.2(\mathrm{~d}, J$
$=7.7 \mathrm{~Hz}), 71.8(\mathrm{~d}, J=7.9 \mathrm{~Hz}), 51.7(\mathrm{~d}, J=160.5 \mathrm{~Hz}), 28.6,24.3(\mathrm{~d}, J=2.8 \mathrm{~Hz}), 24.1(\mathrm{~d}, J=3.8$ $\mathrm{Hz}), 23.9(\mathrm{~d}, J=5.2 \mathrm{~Hz}), 15.33(\mathrm{~s}) .{ }^{31} \mathrm{P}$ NMR ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 16.2. HPLC: Chiracel AD column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}$, $n$-hexane $/ i$-propanol $=80 / 20$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 7.1 min (maj) and 7.7 min . HRMS (ESI) $\mathrm{m} / \mathrm{z}$ calculated for $\mathrm{C}_{18} \mathrm{H}_{28} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{P}[\mathrm{M}+\mathrm{H}]^{+} 367.1784$, found 367.1781 .

Diisopropyl (R)-(6-(naphthalen-2-yl)-2-oxo-1,2,3,4-tetrahydropyrimidin-4-yl)phosphonate (1j): $30 \mathrm{mg}, 77 \%$ yield, new compound, white solid, $\mathrm{mp}: 156-157^{\circ} \mathrm{C}, \mathrm{R}_{f}=0.40$ (dichloromethane/
 methanol $=10 / 1), 49 \%$ ee, $[\alpha]^{20}{ }_{\mathrm{D}}=-74.58(c 0.30, \mathrm{MeOH}) .{ }^{1} \mathrm{H}$ NMR $(400$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.26-8.23(\mathrm{~m}, 1 \mathrm{H}), 7.85-7.84(\mathrm{~m}, 2 \mathrm{H}), 7.51-7.48(\mathrm{~m}, 4 \mathrm{H})$, $6.85(\mathrm{~s}, 1 \mathrm{H}), 5.77(\mathrm{~s}, 1 \mathrm{H}), 4.93-4.91(\mathrm{~m}, 1 \mathrm{H}), 4.83-4.72(\mathrm{~m}, 2 \mathrm{H}), 4.53-4.50$ $(\mathrm{m}, 1 \mathrm{H}), 1.40-1.33(\mathrm{~m}, 12 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 153.2,137.2$ (d, $J=10.4 \mathrm{~Hz}), 133.7,132.7(\mathrm{~d}, J=2.7 \mathrm{~Hz}), 130.8(\mathrm{~d}, J=1.9 \mathrm{~Hz}), 129.6$, 128.4, 126.6, 126.3, 126.1 (d, $J=2.9 \mathrm{~Hz}), 125.2,125.1,94.2(\mathrm{~d}, J=9.1 \mathrm{~Hz}), 72.1(\mathrm{~d}, J=7.4 \mathrm{~Hz})$, $71.7(\mathrm{~d}, J=7.7 \mathrm{~Hz}), 51.9(\mathrm{~d}, J=161.1 \mathrm{~Hz}), 24.3(\mathrm{~d}, J=3.6 \mathrm{~Hz}), 24.2,24.1,24.0 .{ }^{31} \mathrm{P}$ NMR (162 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 16.3. HPLC: Chiracel AD column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}, n$-hexane $/ i$-propanol $=80 / 20$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time $5.9 \mathrm{~min}(\mathrm{maj})$ and 7.7 min . HRMS (ESI) $\mathrm{m} / \mathrm{z}$ calculated for $\mathrm{C}_{20} \mathrm{H}_{26} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{P}[\mathrm{M}+\mathrm{H}]^{+}$389.1624, found 389.1627.

Diethyl (R)-(2-oxo-6-phenyl-1,2,3,4-tetrahydropyrimidin-4-yl)phosphonate (1k): 30 mg , $97 \%$ yield, new compound, white solid, $\mathrm{mp}: 157-158^{\circ} \mathrm{C}, \mathrm{R}_{f}=0.40$ (dichloromethane/methanol $=10 / 1$ ),
 $90 \% \mathrm{ee},[\alpha]^{20}{ }_{\mathrm{D}}=-35.68(c 0.30, \mathrm{MeOH}) .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.91$ $(\mathrm{s}, 1 \mathrm{H}), 7.52-7.41(\mathrm{~m}, 2 \mathrm{H}), 7.39-7.36(\mathrm{~m}, 3 \mathrm{H}), 6.27(\mathrm{~s}, 1 \mathrm{H}), 5.06(\mathrm{~s}, 1 \mathrm{H}), 4.45-$ $4.42(\mathrm{~m}, 1 \mathrm{H}), 4.20-4.13(\mathrm{~m}, 4 \mathrm{H}), 1.36-1.28(\mathrm{~m}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 100 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 154.5,138.7(\mathrm{~d}, J=10.5 \mathrm{~Hz}), 133.8(\mathrm{~d}, J=3.4 \mathrm{~Hz}), 129.3,128.8$, $125.2(\mathrm{~d}, J=1.9 \mathrm{~Hz}), 90.4(\mathrm{~d}, J=8.8 \mathrm{~Hz}), 63.6(\mathrm{~d}, J=7.3 \mathrm{~Hz}), 63.0(\mathrm{~d}, J=7.5$ $\mathrm{Hz}), 51.0(\mathrm{~d}, J=158.8 \mathrm{~Hz}), 16.6(\mathrm{~d}, J=5.0 \mathrm{~Hz}), 16.5(\mathrm{~d}, J=5.3 \mathrm{~Hz}) .{ }^{31} \mathrm{P}$ NMR ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 18.0. HPLC: Chiracel AD column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}, n$-hexane $/ i$-propanol $=80 / 20$, flow $=1.0$ $\mathrm{mL} / \mathrm{min}$, retention time 8.2 min (maj) and 8.9 min . HRMS (ESI) $\mathrm{m} / \mathrm{z}$ calculated for $\mathrm{C}_{14} \mathrm{H}_{20} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{P}$ $[\mathrm{M}+\mathrm{H}]^{+} 311.1117$, found 311.1116 .

Diisopropyl (R)-(6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidin-4-yl)phosphonate (11): 26 mg , $94 \%$ yield, white solid, $\mathrm{mp}: 122-123{ }^{\circ} \mathrm{C}, \mathrm{R}_{f}=0.40$ (dichloromethane/methanol $=10 / 1$ ), $5 \%$ ee, $[\alpha]^{20}{ }_{\mathrm{D}}$
 $\mathrm{Hz}), 18.5(\mathrm{~d}, J=2.5 \mathrm{~Hz}) .{ }^{31} \mathrm{P}$ NMR ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 16.6. HPLC: Chiracel AD column, 254 $\mathrm{nm}, 30^{\circ} \mathrm{C}, n$-hexane $/ i$-propanol $=80 / 20$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 5.2 min and 6.6 min (maj). HRMS (ESI) $m / z$ calculated for $\mathrm{C}_{11} \mathrm{H}_{22} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{P}[\mathrm{M}+\mathrm{H}]^{+}$277.1313, found 277.1312.
(1m): $33 \mathrm{mg}, 94 \%$ yield, white solid, $\mathrm{mp}: 158-159^{\circ} \mathrm{C}, \mathrm{R}_{f}=0.40$ (dichloromethane $/$ methanol $=10 / 1$ ), $84 \% \mathrm{ee},[\alpha]^{20}{ }_{\mathrm{D}}=-18.21(c 0.33, \mathrm{MeOH}) .{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.40-7.31(\mathrm{~m}, 5 \mathrm{H}), 6.50(\mathrm{~s}$, $1 \mathrm{H}), 5.53(\mathrm{~s}, 1 \mathrm{H}), 4.81-4.75(\mathrm{~m}, 2 \mathrm{H}), 4.13(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 1.82(\mathrm{~s}, 3 \mathrm{H})$,
 1.37-1.34 (m, 12H). ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 153.8,134.8(\mathrm{~d}, J=3.6$ $\mathrm{Hz}), 133.2(\mathrm{~d}, J=9.8 \mathrm{~Hz}), 128.8,128.7,128.4(\mathrm{~d}, J=2.8 \mathrm{~Hz}), 99.2(\mathrm{~d}, J=$ $6.4 \mathrm{~Hz}), 72.1(\mathrm{~d}, J=7.9 \mathrm{~Hz}), 71.5(\mathrm{~d}, J=7.8 \mathrm{~Hz}), 56.3(\mathrm{~d}, J=155.6 \mathrm{~Hz}), 24.4$ $(\mathrm{d}, J=3.1 \mathrm{~Hz}), 24.2,24.1,24.0(\mathrm{~d}, J=5.0 \mathrm{~Hz}), 16.7(\mathrm{~d}, J=1.5 \mathrm{~Hz}) .{ }^{31} \mathrm{P}$ NMR ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 16.9$. HPLC: Chiracel AD column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}, n-$ hexane $/ i$-propanol $=80 / 20$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time $5.2 \mathrm{~min}(\mathrm{maj})$ and 6.4 min . HRMS (ESI) $m / z$ calculated for $\mathrm{C}_{17} \mathrm{H}_{26} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{P}[\mathrm{M}+\mathrm{H}]^{+} 353.1654$, found 353.1652.

Diisopropyl (R)-(6-(3-methoxyphenyl)-5-methyl-2-oxo-1,2,3,4-tetrahydropyrimidin-4-yl) phosphonate (1n): $37 \mathrm{mg}, 97 \%$ yield, new compound, white solid, $\mathrm{mp}: 153-154{ }^{\circ} \mathrm{C}, \mathrm{R}_{f}=0.40$ (dichloromethane/methanol $=10 / 1$ ), $80 \%$ ee, $[\alpha]^{20}{ }_{\mathrm{D}}=-11.62(c$ 0.37,
 $\mathrm{MeOH}) .{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.33-7.28(\mathrm{~m}, 1 \mathrm{H}), 6.91-6.85(\mathrm{~m}$, $3 \mathrm{H}), 6.43(\mathrm{~s}, 1 \mathrm{H}), 5.47(\mathrm{~s}, 1 \mathrm{H}), 4.80-4.75(\mathrm{~m}, 2 \mathrm{H}), 4.12(\mathrm{~d}, J=8.2 \mathrm{~Hz}$, $1 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H}), 1.83(\mathrm{~s}, 3 \mathrm{H}), 1.36(\mathrm{t}, J=6.2 \mathrm{~Hz}, 12 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (100 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 159.7,153.6,136.1(\mathrm{~d}, J=3.4 \mathrm{~Hz}), 133.0(\mathrm{~d}, J=10.0$ $\mathrm{Hz}), 129.8,120.8(\mathrm{~d}, J=2.8 \mathrm{~Hz}), 114.5,113.9(\mathrm{~d}, J=2.8 \mathrm{~Hz}), 99.3(\mathrm{~d}, J$ $=6.4 \mathrm{~Hz}), 72.1(\mathrm{~d}, J=7.9 \mathrm{~Hz}), 71.5(\mathrm{~d}, J=7.7 \mathrm{~Hz}), 56.3(\mathrm{~d}, J=155.6 \mathrm{~Hz}), 55.3,24.4(\mathrm{~d}, J=3.1$ $\mathrm{Hz}), 24.2,24.1,24.0(\mathrm{~d}, J=5.0 \mathrm{~Hz}), 16.8(\mathrm{~d}, J=1.4 \mathrm{~Hz}) .{ }^{31} \mathrm{P} \mathrm{NMR}\left(162 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 16.9$. HPLC: Chiracel AD column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}$, $n$-hexane $/ i$-propanol $=80 / 20$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 5.9 min (maj) and 7.8 min . HRMS (ESI) m/z calculated for $\mathrm{C}_{18} \mathrm{H}_{28} \mathrm{~N}_{2} \mathrm{O}_{5} \mathrm{P}[\mathrm{M}+\mathrm{H}]^{+}$ 383.1727 , found 383.1729 .

Diisopropyl (R)-(2-oxo-5,6-diphenyl-1,2,3,4-tetrahydropyrimidin-4-yl) phosphonate (10): $39 \mathrm{mg}, 94 \%$ yield, new compound, white solid, $\mathrm{mp}: 188-189^{\circ} \mathrm{C}, \mathrm{R}_{f}=0.40$ (dichloromethane/
 methanol $=10 / 1), 88 \%$ ee, $[\alpha]^{20}{ }_{\mathrm{D}}=-19.23(c 0.39, \mathrm{MeOH}) .{ }^{1} \mathrm{H}$ NMR $(400 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right) \delta 7.26-7.11(\mathrm{~m}, 10 \mathrm{H}), 6.44(\mathrm{~s}, 1 \mathrm{H}), 5.57(\mathrm{~s}, 1 \mathrm{H}), 4.77-4.71(\mathrm{~m}, 1 \mathrm{H})$, 4.70-4.60 (m, 2H), 1.36-1.30 (m, 6H), 1.16-1.10 (m, 6H). ${ }^{13} \mathrm{C}$ NMR ( 100 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 154.2,137.0(\mathrm{~d}, J=4.7 \mathrm{~Hz}), 135.4,135.0(\mathrm{~d}, J=3.4 \mathrm{~Hz}), 130.3$, 128.6, 128.4, 128.0, 126.7, 118.8, $105.3(\mathrm{~d}, J=4.0 \mathrm{~Hz}), 71.7(\mathrm{~d}, J=8.0 \mathrm{~Hz})$, $56.0(\mathrm{~d}, J=157.5 \mathrm{~Hz}), 24.3(\mathrm{~d}, J=3.1 \mathrm{~Hz}), 24.1(\mathrm{~d}, J=4.4 \mathrm{~Hz}), 24.0(\mathrm{~d}, J=2.8 \mathrm{~Hz}), 23.6(\mathrm{~d}, J=$ $4.9 \mathrm{~Hz}) .{ }^{31} \mathrm{P}$ NMR ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 17.4. HPLC: Chiracel AD column, $254 \mathrm{~nm}, 30{ }^{\circ} \mathrm{C}, n-$ hexane $/ i$-propanol $=80 / 20$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time $5.8 \mathrm{~min}(\mathrm{maj})$ and $7.6 \mathrm{~min} . \mathrm{HRMS}$ (ESI) $m / z$ calculated for $\mathrm{C}_{22} \mathrm{H}_{28} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{P}[\mathrm{M}+\mathrm{H}]^{+} 415.1783$, found 415.1781 .

Failed example:
Under standard conditions, the redox deracemization of 4-(diphenylphosphoryl)-5-methyl- 6-phenyl-3,4-dihydropyrimi-din- $2(1 H)$-one, in which the isopropoxy group is replaced with a phenyl group, the reaction only underwent oxidation, without observation reduction products, the starting
material was recovered.



## 4. Determination of Absolute Configuration of Products

### 4.1 Determination of Absolute Configuration of Products 4 m

To determine the absolute configuration of $\mathbf{4 m}(93 \%$ ee $)$, firstly, $\mathbf{4 m}$ was upgraded to $>99 \%$ ee by recrystallization with $n$-hexane/ethyl acetate. Then, $n$-hexane was slowly added into the solution of $\mathbf{4 m}$ in ethyl acetate at $50^{\circ} \mathrm{C}$, then the solution was slowly cooled down to room temperature. The crystal was grown from the solution, which is suitable for X-ray diffraction analysis. The structure in Figure $\mathbf{S 2}$ showed that the absolute configuration of $4 \mathbf{m}$ is $(R)$. [CCDC 2080219] contains the structure and supplementary crystallographic data for $(R)-4 \mathbf{m}$. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc. cam.ac.uk.


Figure S2. X-ray crystallographic analysis of ( $R$ )-4m [CCDC 2080219]
ORTEP diagram of compound $\mathbf{4 m}$, thermal ellipsoids are drawn on $30 \%$ probability level Crystal data and structure refinement for $\mathbf{4 m}$.

| Identification code | $\mathbf{4 m}$ |
| :--- | :--- |
| Empirical formula | $\mathrm{C}_{21} \mathrm{H}_{29} \mathrm{~N}_{2} \mathrm{O}_{6} \mathrm{P}$ |
| Formula weight | 436.43 |
| Temperature | $293(2) \mathrm{K}$ |
| Wavelength | $0.71073 \AA$ |
| Crystal system | monoclinic |
| Space group | P 21 |
| Volume | $1162.84(4) \AA^{3}$ |
| Z | 2 |
| Density (calculated) | $1.246 \mathrm{Mg} / \mathrm{m}^{3}$ |


| Absorption coefficient | $0.155 \mathrm{~mm}^{-1}$ |
| :--- | :--- |
| $\mathrm{~F}(000)$ | 464 |
| Crystal size | $0.200 \times 0.160 \times 0.130 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 2.832 to $26.000^{\circ}$. |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.054 |
| Flack | $0.02(3)$ |
| Extinction coefficient | $0.031(11)$ |

### 4.2 Determination of Absolute Configuration of Products 4a

A racemic of 3,4-Dihydropyrimidin-2-one derivatives $\mathbf{1 a}(1.352 \mathrm{~g}, 4.0 \mathrm{mmol})$, DDQ ( $0.999 \mathrm{~g}, 4.4$ mmol, 1.1 equiv) in ethyl acetate ( 50 mL ) was stirred at room temperature for 10 min . After the reaction was completed (determined by TLC), chiral phosphoric acid (S)-2g(0.301 g, $0.4 \mathrm{mmol}, 10$ mol\%) and Hantzsch ester 3 a ( 1.261 g , $5.6 \mathrm{mmol}, 1.4$ equiv) was added. The mixture was stirred at room temperature for 24 h . The resulting mixture was concentrated in vacuo and further purification was performed by a silica gel column eluted with dichloromethane /methanol to give the optically active products $(S)-\mathbf{1 a} 1.243 \mathrm{~g}$ in $92 \%$ yield and $96 \%$ ee. $[\alpha]^{20}{ }_{\mathrm{D}}=+24.40(c 1.0, \mathrm{MeOH})$.

A solution of compound $(S) \mathbf{- 1 a}(1.056 \mathrm{~g}, 3 \mathrm{mmol})$ in dichloroethane $(60 \mathrm{~mL})$ was added DMAP ( $36.6 \mathrm{mg}, 0.3 \mathrm{mmol}$ ), $\mathrm{Et}_{3} \mathrm{~N}(3.036 \mathrm{~g}, 30 \mathrm{mmol}), \mathrm{Ac}_{2} \mathrm{O}(3.063 \mathrm{~g}, 30 \mathrm{mmol})$. The mixture was stirred at room temperature for 10 h . After the reaction was completed (determined by TLC). The resulting mixture was concentrated in vacuo and further purification was performed by a silica gel column eluted with hexane/ethyl acetate to give the optically active products $(S)-4 a 1.203 \mathrm{~g}$ in $92 \%$ yield and $\mathbf{9 2 \%}$ ee. To determine the absolute configuration of ( $S$ ) - $\mathbf{4 a}$ ( $96 \%$ ee), firstly, ( $S$ ) - $\mathbf{4 a}$ was upgraded to $>99 \%$ ee by recrystallization with $n$-hexane/ethyl acetate. Then, $n$-hexane was slowly added into the solution of $(S)-\mathbf{4 a}$ in ethyl acetate at $50^{\circ} \mathrm{C}$, then the solution was slowly cooled down to room temperature. The crystal was grown from the solution, which is suitable for X-ray diffraction analysis. The structure in Figure $\mathbf{S 1}$ showed that the absolute configuration of $\mathbf{4 a}$ is $(S)$. [CCDC 2100898] contains the structure and supplementary crystallographic data for $(S)-\mathbf{4 a}$. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc. cam.ac.uk.


Figure S1. X-ray Crystallographic Analysis of (S)-4a [CCDC 2100898]

ORTEP diagram of compound 4a, thermal ellipsoids are drawn on 30\% probability level Crystal data and structure refinement for $\mathbf{4 a}$.

| Identification code | $\mathbf{4 a}$ |
| :--- | :--- |
| Empirical formula | $\mathrm{C}_{20} \mathrm{H}_{27} \mathrm{~N}_{2} \mathrm{O}_{6} \mathrm{P}$ |
| Formula weight | 422.40 |
| Temperature | $190(0) \mathrm{K}$ |
| Wavelength | $1.34139 \AA$ |
| Crystal system | triclinic |
| Space group | P 1 |
| Volume | $2756.2(4) \AA^{3}$ |
| Z | 5 |
| Density (calculated) | $1.272 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.925 \mathrm{~mm}-1$ |
| F(000) | 1120 |
| Crystal size | $0.120 \times 0.100 \times 0.100 \mathrm{~mm}^{3}$ |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.040 |
| Flack | $0.049(11)$ |

## 5. Control Experiments



A compound of 2-hydroxypyrimindine $7 \mathrm{a}(33.6 \mathrm{mg}, 0.10 \mathrm{mmol}, 1.0$ equiv), chiral phosphoric acid $(R)-\mathbf{2 g}(7.5 \mathrm{mg}, 0.01 \mathrm{mmol}, 10 \mathrm{~mol} \%)$ and Hantzsch ester $\mathbf{3 a}(31.5 \mathrm{mg}, 0.14 \mathrm{mmol}, 1.4$ equiv) was added. The mixture was stirred at room temperature for 24 h . The resulting mixture was concentrated in vacuo and further purification was performed by a silica gel column chromatography eluted with dichloromethane/methanol to give the optically active product $(R)$-1a 31.1 mg in $92 \%$ yield and $96 \%$ ee. The enantiomeric excess was determined by chiral HPLC.


A compound of $(R) \mathbf{- 1 a}(33.8 \mathrm{mg}, 0.10 \mathrm{mmol}, 1.0$ equiv), $\mathrm{DDQ}(25 \mathrm{mg}, 0.11 \mathrm{mmol}, 1.1$ equiv) in ethyl acetate ( 4 mL ) was stirred at room temperature for 5 min . After the reaction was completed (determined by TLC), chiral phosphoric acid (S)-2g ( $7.5 \mathrm{mg}, 0.01 \mathrm{mmol}, 10 \mathrm{~mol} \%$ ) and Hantzsch ester $\mathbf{3 a}$ ( $31.5 \mathrm{mg}, 0.14 \mathrm{mmol}, 1.4$ equiv) was added. The mixture was stirred at room temperature for 24 h . The resulting mixture was concentrated in vacuo and further purification was performed by a silica gel column chromatography eluted with dichloromethane/methanol to give the optically active product ( $S$ )-1a 31.1 mg in $92 \%$ yield and $96 \%$ ee. The enantiomeric excess was determined by chiral HPLC.


The 4-(diisopropoxyphosphoryl)-6-phenylpyrimidin-2-yl 4-methylbenzenesulfonate 7a' (0.10 $\mathrm{mmol})$, chiral phosphoric acid $(R)-\mathbf{2 g}(7.5 \mathrm{mg}, 0.01 \mathrm{mmol}, 10 \mathrm{~mol} \%)$ and Hantzsch ester 3a (31.5 $\mathrm{mg}, 0.14 \mathrm{mmol}, 1.4$ equiv) in ethyl acetate ( 4 mL ) was stirred at room temperature for 24 hrs. The reaction was monitored by TLC. The reaction mixture was concentrated in vacuo and then tested the crude residue by ${ }^{1} \mathrm{HNMR}$ to find that starting material $7 \mathbf{a}^{\text {' }}$ remained $>95 \%$ NMR yield.

## 6. Redox Deracemization of 3,4-Dihydropyrimidin-2-ones at Gram Scale



A racemic of 3,4-Dihydropyrimidin-2-one derivatives $1 \mathbf{1 a}(1.352 \mathrm{~g}, 4.0 \mathrm{mmol}, 1.0$ equiv), DDQ $(0.999 \mathrm{~g}, 4.4 \mathrm{mmol}, 1.1$ equiv) in ethyl acetate $(50 \mathrm{~mL})$ was stirred at room temperature for 10 min . After the reaction was completed (determined by TLC), chiral phosphoric acid $(R) \mathbf{- 2 g}(0.301 \mathrm{~g}, 0.4$ mmol, $10 \mathrm{~mol} \%$ ) and Hantzsch ester $\mathbf{3 a}(1.261 \mathrm{~g}, 5.6 \mathrm{mmol}, 1.4$ equiv) was added. The mixture was stirred at room temperature for 24 h . The resulting mixture was concentrated in vacuo and further purification was performed by a silica gel column eluted with dichloromethane/methanol to give the optically active products $(R)-(-)-1 \mathrm{a} 1.243 \mathrm{~g}$ in $92 \%$ yield and $96 \%$ ee. The enantiomeric excesses were
determined
by
chiral
HPLC.

## 7. Synthesis of the Optically Active Products 5m and 6m

### 7.1 Synthesis DHPMs Derivative 4m



A solution of compound $(R) \mathbf{- 1 m}(0.352 \mathrm{~g}, 1 \mathrm{mmol})$ in dichloroethane $(20 \mathrm{~mL})$ was added DMAP ( $12.2 \mathrm{mg}, 0.1 \mathrm{mmol}), \mathrm{Et}_{3} \mathrm{~N}(1.012 \mathrm{~g}, 10 \mathrm{mmol}), \mathrm{Ac}_{2} \mathrm{O}(1.021 \mathrm{~g}, 10 \mathrm{mmol})$. The mixture was stirred at room temperature for 10 h . After the reaction was completed (determined by TLC). The resulting mixture was concentrated in vacuo and further purification was performed by a silica gel column eluted with hexane/ethyl acetate to give the optically active products $(R)-4 \mathrm{~m} 0.401 \mathrm{~g}$ in $92 \%$ yield and $92 \%$ ee. The enantiomeric excesses were determined by chiral HPLC.

Diisopropyl (R)-(1,3-diacetyl-5-methyl-2-oxo-6-phenyl-1,2,3,4-tetrahydropyrimidin-4-yl) phosphonate (4m): $401 \mathrm{mg}, 92 \%$ yield, new compound, white solid, mp: 103-104 ${ }^{\circ} \mathrm{C}, \mathrm{R}_{f}=0.30$
 $($ dichloromethane $/$ methanol $=50 / 1), 92 \% \mathrm{ee},[\alpha]^{20}{ }_{\mathrm{D}}=+36.30(c 0.98, \mathrm{MeOH})$. ${ }^{1} \mathrm{H}$ NMR ( 400 MHz, DMSO-d ${ }_{6}$ ) $\delta 7.37(\mathrm{t}, J=7.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.28(\mathrm{t}, J=8.1 \mathrm{~Hz}$, $3 \mathrm{H}), 5.26(\mathrm{~d}, J=20.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.68-4.58(\mathrm{~m}, 2 \mathrm{H}), 2.55(\mathrm{~s}, 3 \mathrm{H}), 2.29(\mathrm{~s}, 3 \mathrm{H})$, $1.89(\mathrm{~d}, J=2.2 \mathrm{~Hz}, 3 \mathrm{H}), 1.30-1.20(\mathrm{~m}, 12 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 100 MHz, DMSO- $\mathrm{d}_{6}$ ) $\delta 170.9(\mathrm{~d}, J=1.6 \mathrm{~Hz}), 169.6(\mathrm{~d}, J=2.0 \mathrm{~Hz}), 153.3,136.0(\mathrm{~d}, J=3.3 \mathrm{~Hz}), 135.5$ $(\mathrm{d}, J=9.0 \mathrm{~Hz}), 128.4,128.2,127.9,120.7(\mathrm{~d}, J=1.4 \mathrm{~Hz}), 72.4(\mathrm{~d}, J=7.3 \mathrm{~Hz}), 71.9(\mathrm{~d}, J=7.3 \mathrm{~Hz})$, $52.9(\mathrm{~d}, J=155.9 \mathrm{~Hz}), 26.4,26.1,24.3(\mathrm{~d}, J=3.5 \mathrm{~Hz}), 24.1(\mathrm{~d}, J=4.0 \mathrm{~Hz}), 23.9(\mathrm{~d}, J=3.0 \mathrm{~Hz})$, $23.8(\mathrm{~d}, J=2.0 \mathrm{~Hz}), 18.0(\mathrm{~d}, J=4.9 \mathrm{~Hz}) .{ }^{31} \mathrm{P}$ NMR ( 162 MHz, DMSO-d ${ }_{6}$ ) $\delta 16.7$. HPLC: Chiracel AD column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}$, $n$-hexane $/ i$-propanol $=80 / 20$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 4.1 $\min (\mathrm{maj})$ and 4.8 min . HRMS (ESI) m/z Calculated for $\mathrm{C}_{21} \mathrm{H}_{30} \mathrm{~N}_{2} \mathrm{O}_{6} \mathrm{P}[\mathrm{M}+\mathrm{H}]^{+}$437.1836, found 437.1837.

### 7.2 Synthesis DHPMs Derivative 5m



A solution of compound $(R)-4 \mathrm{~m}(43.6 \mathrm{mg}, 0.10 \mathrm{mmol})$ in methanol $(2.0 \mathrm{~mL})$ was added sodium borohydride ( $15.1 \mathrm{mg}, 0.40 \mathrm{mmol}$ ). The resulting solution was stirred at room temperature for 0.5 h. After the reaction was completed (determined by TLC). Methanol was removed in vacuo and the residue was diluted with water. The aqueous mixture was extracted with dichloromethane (10
$\mathrm{mL} \times 3$ ). The combined organic layer was washed twice with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give viscous oil. The crude product was purified by flash column chromatography using dichloromethane/methanol as eluent to give the desired products ( + )-5m 38.9 mg in $98 \%$ yield and $92 \%$ ee.

Diisopropyl (R)-(1-acetyl-5-methyl-2-oxo-6-phenyl-1,2,3,4-tetrahydropyrimidin-4-yl) phosphonate (5m): 38.9 mg , $98 \%$ yield, new compound, white solid, $\mathrm{mp}: 181-182{ }^{\circ} \mathrm{C}, \mathrm{R}_{f}=0.30$
 (hexanes/ethyl acetate $=20 / 1$ ), $92 \%$ ee, $[\alpha]^{20}{ }_{\mathrm{D}}=+86.73(c \quad 1.74, \mathrm{MeOH}) .{ }^{1} \mathrm{H}$ NMR ( 400 MHz, DMSO-d $)_{6} \delta 8.64(\mathrm{~d}, J=5.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.34(\mathrm{t}, J=7.4 \mathrm{~Hz}, 2 \mathrm{H})$, $7.24(\mathrm{t}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.16(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H}), 4.67-4.62(\mathrm{~m}, 2 \mathrm{H}), 4.01-3.96$ $(\mathrm{m}, 1 \mathrm{H}), 2.21(\mathrm{~s}, 3 \mathrm{H}), 1.85(\mathrm{~d}, J=2.1 \mathrm{~Hz}, 3 \mathrm{H}), 1.32-1.25(\mathrm{~m}, 12 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (100 MHz, DMSO-d ${ }_{6}$ ) $\delta 168.4(\mathrm{~d}, J=2.4 \mathrm{~Hz}), 154.7,137.1(\mathrm{~d}, J=3.5 \mathrm{~Hz})$, $135.7(\mathrm{~d}, J=9.4 \mathrm{~Hz}), 128.3,128.0(\mathrm{~d}, J=1.2 \mathrm{~Hz}), 127.5,120.0(\mathrm{~d}, J=1.2 \mathrm{~Hz}), 71.5(\mathrm{~d}, J=7.4 \mathrm{~Hz})$, $71.3(\mathrm{~d}, J=7.5 \mathrm{~Hz}), 54.0(\mathrm{~d}, J=153.6 \mathrm{~Hz}), 25.7,24.2(\mathrm{~d}, J=3.7 \mathrm{~Hz}), 24.1,24.1(\mathrm{~d}, J=1.5 \mathrm{~Hz})$, $24.0(\mathrm{~d}, J=4.3 \mathrm{~Hz}), 17.7(\mathrm{~d}, J=4.2 \mathrm{~Hz}) .{ }^{31} \mathrm{P}$ NMR ( $\left.162 \mathrm{MHz}, \mathrm{DMSO}_{6}\right) \delta$ 18.2. HPLC: Chiracel AD column, $254 \mathrm{~nm}, 30^{\circ} \mathrm{C}$, $n$-hexane $/ i$-propanol $=90 / 10$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 16.0 $\min$ (maj) and 18.0 min . HRMS (ESI) m/z Calculated for $\mathrm{C}_{19} \mathrm{H}_{28} \mathrm{~N}_{2} \mathrm{O}_{5} \mathrm{P}[\mathrm{M}+\mathrm{H}]^{+} 395.1729$, found 395.1728.

### 7.3 Synthesis DHPMs Derivative 6m



A mixture of compound $(R) \mathbf{- 1 m}(70.4 \mathrm{mg}, 0.20 \mathrm{mmol})$ in ethyl acetate $(5.0 \mathrm{~mL})$ was added $\mathrm{Pd} / \mathrm{C}(47.3 \mathrm{mg}, 0.01 \mathrm{mmol}, 5 \mathrm{~mol} \%)$ in a Schlenk tube. The Schlenk tube was carefully and quickly vacuum purged before being filled with hydrogen using an hydrogen balloon. The reaction mixture was then stirred at $50^{\circ} \mathrm{C}$ until the the reaction was completed (determined by TLC). Ethyl acetate was removed in vacuo and further purification was performed by a silica gel column eluted with dichloromethane /methanol to give the optically active products $(+)-6 \mathrm{~m} 67.3 \mathrm{mg}$ in $95 \%$ yield and $92 \%$ ee. The enantiomeric excesses were determined by chiral HPLC.

Diisopropyl ((R)-5-methyl-2-oxo-6-phenylhexahydropyrimidin-4-yl)phosphonate (6m): $67.3 \mathrm{mg}, 95 \%$ yield, new compound, colorless liquid, $\mathrm{R}_{f}=0.30$ (methanol/dichloromethane $=20 / 1$ ),
 $92 \% \mathrm{ee},[\alpha]^{20}{ }_{\mathrm{D}}=+73.11(c 0.70, \mathrm{MeOH}) .{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.38$ (t, $J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.33-7.26(\mathrm{~m}, 3 \mathrm{H}), 5.27(\mathrm{~s}, 1 \mathrm{H}), 5.00(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H})$, 4.82-4.72 (m, 3H), $4.04(\mathrm{dd}, J=14.2,2.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.42(\mathrm{~d}, J=3.3 \mathrm{~Hz}, 1 \mathrm{H})$, 1.38-1.34 (m, 12H), $0.89(\mathrm{~d}, J=6.9 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ $156.3(\mathrm{~d}, J=11.9 \mathrm{~Hz}), 138.9(\mathrm{~d}, J=3.7 \mathrm{~Hz}), 128.7(\mathrm{~s}), 128.0(\mathrm{~s}), 126.3(\mathrm{~s}), 71.9$ $(\mathrm{d}, J=6.8 \mathrm{~Hz}), 71.6(\mathrm{~d}, J=7.5 \mathrm{~Hz}), 60.2(\mathrm{~d}, J=18.8 \mathrm{~Hz}), 53.6(\mathrm{~d}, J=159.1 \mathrm{~Hz}), 32.9(\mathrm{~d}, J=4.4$
$\mathrm{Hz}), 24.2(\mathrm{~d}, J=3.6 \mathrm{~Hz}), 24.1(\mathrm{~d}, J=5.0 \mathrm{~Hz}), 24.0(\mathrm{~d}, J=3.6 \mathrm{~Hz}), 23.9(\mathrm{~d}, J=5.7 \mathrm{~Hz}), 7.6(\mathrm{~d}, J=$ 1.9 Hz ). ${ }^{31} \mathrm{P}$ NMR ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 18.5. HPLC: Chiracel AD column, $254 \mathrm{~nm}, 3{ }^{\circ} \mathrm{C}, n-$ hexane $/ i$-propanol $=80 / 20$, flow $=1.0 \mathrm{~mL} / \mathrm{min}$, retention time 7.9 min and $10.7 \mathrm{~min}(\mathrm{maj}) . \mathrm{HRMS}$ (ESI) $\mathrm{m} / \mathrm{z}$ Calculated for $\mathrm{C}_{17} \mathrm{H}_{28} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{P}[\mathrm{M}+\mathrm{H}]^{+} 355.1787$, found 355.1788 .

## 8. References

1. G.-S. Feng, M.-W. Chen, L. Shi and Y.-G. Zhou, Angew. Chem. Int. Ed., 2018, 57, 5853.
2. K.-R. Li, F.-J. Meng, W.-F. Jiang and L. Shi, Tetrahedron Lett. 2021, 73, 153149.
3. Copy of NMR, HPLC for Compounds


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1 H NMR FM-5-34A in CDCl3


1a ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$
13C NMR FM-5-34A in CDCl3


1a ${ }^{13} \mathrm{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$


| 30 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  |  | f1 (ppm) |  |  |  |  |  |  | 20 | 10 |

31P NMR FM-5-34A in CDCl3


1a ${ }^{31} \mathrm{P} \operatorname{NMR}\left(162 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$



1b ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



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13C NMR FM-5-34B in CDCl3


1b ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



31P NMR FM-5-34B in CDCl 3


1b ${ }^{31}$ P NMR ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


1H NMR FM-5-34C in CDCl3



1c ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$

13C NMR FM-5-34C in CDCl 3


1c ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



31P NMR FM-5-34C in CDCl3


1c ${ }^{31}$ P NMR ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



## 1H NMR FM-5-34D in CDCl3



1d ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )

13C NMR FM-5-34D in CDCI3


1d ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


| 30 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  |  | f1 (ppm) |  |  |  |  |  |  |  |  | ( |

31P NMR FM-5-34D in CDCI3


1d ${ }^{31}$ P NMR ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )




1e ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$

13C NMR FM-5-34E in CDCl3


1e ${ }^{13} \mathrm{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$


| 30 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | ( |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  |  | $\mathrm{f1}$ (ppm) |  |  |  |  |  |  |  |  |  |

31P NMR FM-5-34E in CDCl3


1e ${ }^{31} \mathrm{P}$ NMR ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


1H NMR FM-5-34F in CDCI3
〇

13C NMR FM-5-34F in CDCl3


1f ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


| 30 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | $($ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |

31P NMR FM-5-34F in CDCl3




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NNNNNNNNN
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1g ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{DMSO}^{\left.-\mathrm{d}_{6}\right)}$



13C NMR FM-5-34G in DMSO

1g ${ }^{13} \mathrm{C}$ NMR ( 100 MHz, DMSO- $\mathrm{d}_{6}$ )

| 30 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | ( |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  |  | $\mathrm{f1}$ (ppm) |  |  |  |  |  |  |  |  | ( |

31P NMR FM-5-34G in DMSO

$1 \mathbf{g}^{31}$ P NMR ( 162 MHz, DMSO- $\mathrm{d}_{6}$ )




1h ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )




1h ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



31P NMR FM-5-34 H in CDCl 3


1h ${ }^{31}$ P NMR ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



13C NMR FM-5-34I in CDCI3

$1 ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )

$\left.\begin{array}{lllllllllllllllllllllll}\hline 30 & 170 & 160 & 150 & 140 & 130 & 120 & 110 & 100 & 90 & 1 \\ \mathrm{f} 1(\mathrm{ppm})\end{array}\right)$

31P NMR FM-5-341 in CDCl3

$1 \mathbf{i}^{31}$ P NMR ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


1H NMR FM-5-34J in CDCl3


1j ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$


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13C NMR FM－5－34J in CDCI3

$\mathbf{1 j}^{13} \mathrm{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$

$\left.\begin{array}{lllllllllllllllllllllll}\hline 30 & 170 & 160 & 150 & 140 & 130 & 120 & 110 & 100 & 90 & 1 \\ \mathrm{f} 1(\mathrm{ppm})\end{array}\right)$

31P NMR FM-5-34J in CDCl3

$\mathbf{1 j}^{31} \mathrm{P}$ NMR ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )




1k ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



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13C NMR FM-5-34K in CDCl3

1k ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



31P NMR FM-5-34K in CDCl3

$\mathbf{1 k}{ }^{31}$ P NMR ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


## 1H NMR FM-5-34L in CDCl3

##  <br> 



1I ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )

13C NMR FM-5-34L in CDC13

$11{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


31P NMR FM-5-34L in CDCl3





1m ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )

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13C NMR FM－5－34M in CDCl3



1m ${ }^{13} \mathrm{C}$ NMR（ $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ）

$\left.\begin{array}{lllllllllllllllllllllll}\hline 30 & 170 & 160 & 150 & 140 & 130 & 120 & 110 & 100 & 90 & 1 \\ \mathrm{f} 1(\mathrm{ppm})\end{array}\right)$

31P NMR FM-5-34M in CDCl3


1m ${ }^{31}$ P NMR ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



1n ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )

13C NMR FM-5-34N in CDC13


1n ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


| 30 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |  |  |  |  | f1 (ppm) |  |  |  |  |  |  | 20 | 10 |

31P NMR FM-5-34N in CDCI3


1n ${ }^{31}$ P NMR ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


1H NMR FM-5-340 in CDCl3


10 ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$





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13C NMR FM－5－340 in CDCl3

$10{ }^{13} \mathrm{C}$ NMR（ $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ）


| 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |

31P NMR FM-5-340 in CDCl3

$10{ }^{31} \mathrm{P}$ NMR ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


1H NMR FM-5-57 in DMSO
(


4m ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , DMSO- $\mathrm{d}_{6}$ )





13C NMR FM-5-57 in DMSO


31P NMR FM-5-57 in DMSO

$4 \mathrm{~m}{ }^{31} \mathrm{P}$ NMR $\left(162 \mathrm{MHz}, \mathrm{DMSO}-\mathrm{d}_{6}\right)$




1H NMR FM-5-66 in DMSO

$5 \mathrm{~m}^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{DMSO}^{\left.-\mathrm{d}_{6}\right)}$



13C NMR FM-5-66 in DMSO

$5 m{ }^{13} \mathrm{C}$ NMR ( 100 MHz , DMSO- $\mathrm{d}_{6}$ )



31P NMR FM-5-66 in DMSO


5m ${ }^{31}$ P NMR ( 162 MHz , DMSO- $\mathrm{d}_{6}$ )




1 NMR FM-6-10 in CDCl3

$6 \mathrm{~m}^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )

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13C NMR FM－6－10 in CDCI3

$6 \mathrm{~m}{ }^{13} \mathrm{C}$ NMR（ $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ）



31P NMR FM-6-10 in CDCl3


6m ${ }^{31}$ P NMR ( $162 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )








| Data file: | FM-5-34-3-V-2020-10-28 16-31-24+08-00.dx |  |  |
| :---: | :---: | :---: | :---: |
| Sequence Name: | Singlesample | Project Name: | 1260 |
| Sample name: | FM-5-343 | Operator: | system |
| Instrument: | 161260 | Injection date: | 2020-10-28 16:45:37+08:00 |
| Acq. method: | FM-4-41.amx | Type: | Sample |
| Processing method: | GC_LC Area Percent_DefautMethod.pmx |  |  |
| Sample Info: | AD. Hexanefi-Proh $=80 / 20,1.0 \mathrm{~mL}$ min $, 300 \mathrm{CC}, 254$ |  |  |












$$
\begin{aligned}
& \text { FM-5-34-7-V-2020-10-30 11-20-48+08-00.dx }
\end{aligned}
$$










Signal:
RT [min]
VWDIA, Wavelength $=254$
Peak Width Base

$$
\begin{array}{rrrrr}
\text { RT [min] } & \text { Peak Width Base } & \text { Area } & \text { Height } & \text { Area\% } \\
5.569 & 1.062 & 741.51 & 62.72 & 50.02 \\
7.605 & 1.315 & 744.03 & 47.62 & 49.98 \\
7.5 \text { Sum } & 1428.54
\end{array}
$$


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| :---: | :---: | :---: | :---: |
| Sequence Name: | Singlesample | Project Name: | 1260 |
| Sample name: | FM-5-34-13 | Operator: | system |
| Instrument: | 161260 | Injection date: | 2020-11-02 16:16:27+08:00 |
| Acq. method: | FM-4-41.amx | Type: | Sample |
| Processing method: | GC_LC Area Percent_DefautiMemtod.pmx |  |  |
| Sample Info: | AD, Hexanefi-Proh $=80120,1.0 \mathrm{mLmin}, 30 \mathrm{oc}, 254 \mathrm{~nm}$ |  |  |



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& (-)-10
\end{aligned}
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| Data file: <br> Sequence Name: | -01-22 10-22-31+08-00.dx |  |  |
| :---: | :---: | :---: | :---: |
|  | SingleSample | Project Name: | 1260 |
| Sample name: | FM-5-57 | Operator: | SYSTEM |
| Instrument: | 161260 | Injection date: | 2021-01-22 10:37:17+08:00 |
| Acq. method: | FM-4-41.amx | Type: | Sample |
| Processing method: | GC_LC Area Percent_DefautMenthod.pmx |  |  |
| Sampi |  |  |  |



$(+)-4 m$




$(+)-5 m$

$(+\mid-)-6 m$



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