## Supporting Information

# Remarkably Efficient Enantioselective Titanium(IV)-(R)-H $\mathbf{8}$-BINOLate <br> Catalyst for Arylations to Aldehydes by Triaryl(tetrahydrofuran)aluminum Reagents 

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## Experimental Section

## 1. Reagent and General Techniques

$(R)-\mathrm{H}_{8}$ - $\mathrm{BINOL}(\mathrm{TCI})$ was used directly. $\mathrm{Ti}(\mathrm{O}-i-\mathrm{Pr})_{4}$ and $\mathrm{TiCl}_{4}$ were freshly distilled prior to use. Aldehydes were dried over $\mathrm{MgSO}_{4}$ or molecular sieves and distilled before use. Solvents were dried by refluxing for at least 24 h over sodium/benzophenone (THF or toluene) and were freshly distilled prior to use. All syntheses and manipulations were carried out under a dry nitrogen atmosphere.

## 2. Synthesis of Triaryl(tetrahydrofuran)aluminum, $\operatorname{AlAr}_{3}(\mathbf{T H F}):{ }^{\mathbf{1}}$.

Aluminum trichloride ( 1 eq ) in dried THF was added to a THF solution of arylmagnesium bromide (3 eq) at $0{ }^{\circ} \mathrm{C}$. This mixture was stirred at room temperature for 12 h and the solvent was removed under reduced pressure to afford a residue which was extracted with toluene or hexane ( $2 \times 50 \mathrm{~mL}$ ). The aluminum reagent was obtained from removing solvent completely or from crystallization.

Triphenyl(tetrahydrofuran)aluminum, $\mathbf{A I P h}_{\mathbf{3}}(\mathbf{T H F})$. Extraction and crystallization from toluene, $7.84 \mathrm{~g}(72.0 \%) .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.81-7.77(\mathrm{~m}, 6 \mathrm{H}, \mathrm{Ph})$, 7.34-7.31 (m, 9H, Ph), $4.18\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{OCH}_{2}\right), 2.03\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right) \mathrm{ppm}$.
$\mathbf{T r i}\left(\boldsymbol{p}\right.$-tolyl)(tetrahydrofuran)aluminum, $\mathbf{A l}(\boldsymbol{p} \text { - } \mathbf{T o l y l})_{\mathbf{3}}(\mathbf{T H F})$. Extraction with hot hexane and cool to room temperature, $2.27 \mathrm{~g}(61.0 \%)$. ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 7.68$ (d, $J=8 \mathrm{~Hz}, 4 \mathrm{H}, \mathrm{C}_{6} \mathrm{H}_{4} \mathrm{Me}$ ), $7.16\left(\mathrm{~d}, \mathrm{~J}=8 \mathrm{~Hz}, 6 \mathrm{H}, \mathrm{C}_{6} H_{4} \mathrm{Me}\right), 4.15\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{OCH}_{2}\right), 2.36(\mathrm{~s}, 9 \mathrm{H}$, Me ), 2.00 (m, $4 \mathrm{H}, \mathrm{CH}_{2}$ ) ppm.

Tri(4-methoxyphenyl)(tetrahydrofuran)aluminum, $\quad \mathbf{A l}\left(\mathbf{4}-\mathbf{M e O C}_{6} \mathbf{H}_{4}\right)_{\mathbf{3}}(\mathbf{T H F}) . \quad$ Pale yellow oil after removing toluene. ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 7.70\left(\mathrm{~m}, 6 \mathrm{H}, \mathrm{C}_{6} \mathrm{H}_{4} \mathrm{OMe}\right)$, $6.90\left(\mathrm{~m}, 6 \mathrm{H}, \mathrm{C}_{6} \mathrm{H}_{4} \mathrm{OMe}\right), 4.13\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{OCH}_{2}\right), 2.82(\mathrm{~s}, 9 \mathrm{H}, \mathrm{MeO}), 2.00\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right) \mathrm{ppm}$.
$\mathbf{T r i}(4-t r i m e t h y l s i l a n y l p h e n y l)(t e t r a h y d r o f u r a n) a l u m i n u m, ~ \quad \mathbf{A l}\left(4-\mathbf{M e}_{3} \mathbf{S i C}_{6} \mathbf{H}_{4}\right)_{\mathbf{3}}(\mathbf{T H F})$. White solid after removing hexane. ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 7.77(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 6 \mathrm{H}$, $\mathrm{C}_{6} H_{4} \mathrm{TMS}$ ), $7.47\left(\mathrm{~d}, \mathrm{~J}=7.6 \mathrm{~Hz}, 6 \mathrm{H}, \mathrm{C}_{6} H_{4} \mathrm{TMS}\right), 4.18\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{OCH}_{2}\right), 2.02\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{CH}_{2}\right)$, 0.26 (s, 9H, SiMe ${ }_{3}$ ) ppm.

Tri(2-naphthyl)(tetrahydrofuran)aluminum, $\mathbf{A l}(2-n a p h t h y l))_{3}(\mathbf{T H F})$. White solid after removing toluene. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 8.36-7.43(\mathrm{~m}, 21 \mathrm{H}), 4.17\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{OCH}_{2}\right)$, 1.99 (m, $4 \mathrm{H}, \mathrm{CH}_{2}$ ) ppm.

Tri(1-naphthyl)(tetrahydrofuran)aluminum, $\left.\mathbf{A l ( 1 - n a p h t h y l )})_{\mathbf{3}} \mathbf{( T H F}\right)$. White solid after removing toluene. ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 8.08-7.16(\mathrm{~m}, 21 \mathrm{H}), 4.30\left(\mathrm{~m}, 4 \mathrm{H}, \mathrm{OCH}_{2}\right)$, 1.99 (m, $4 \mathrm{H}, \mathrm{CH}_{2}$ ) ppm.

## 3. Synthesis of $\left[\left\{(R)-\mathrm{H}_{8}-\mathrm{BINOLate}\right\} \mathrm{Ti}(\mathrm{O}-i-\mathrm{Pr})_{2}\right]_{\mathrm{x}}(\mathbf{1})^{\mathbf{2}}$

To a solution of $(R)-\mathrm{H}_{8}-\mathrm{BINOL}(4.0 \mathrm{mmol})$ in 60 mL dried toluene, $\mathrm{Ti}(\mathrm{O}-i-\mathrm{Pr})_{4}(4.0$
$\mathrm{mmol}, 1.2 \mathrm{ml}$ ) was added slowly and the resulting solution was stirred at room temperature for 1 h . The reaction mixture was distilled azeotropically until the volume of the solution reached $\sim 3 \mathrm{~mL}$. The solution was then dried completely under reduced pressure to furnish an orange-red solid which was used as a catalyst precursor directly without further purification.

## 4. Reaction of $\mathrm{AlPh}_{3}(\mathrm{THF})$ and $\mathrm{Ti}(\mathrm{O}-i-\mathrm{Pr})_{4}{ }^{3}$

To a solution of $\mathrm{AlPh}_{3}(\mathrm{THF})(0.66 \mathrm{~g}, 2.0 \mathrm{mmol})$ in 20 mL dried toluene, $\mathrm{Ti}(\mathrm{O}-i-\mathrm{Pr})_{4}(0.60$ $\mathrm{ml}, 2.0 \mathrm{mmol}$ ) was added slowly. The resulting solution was stirred at room temperature for $10 \sim 20 \mathrm{~min}$, and then the solvent was removed completely under reduced pressure to afford a yellow oil. ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.90-7.87(\mathrm{~m}, 4 \mathrm{H}, \operatorname{PhAl}), 7.56-7.53(\mathrm{~m}, 2 \mathrm{H}$, $P h \mathrm{Ti}), 7.36-7.31(\mathrm{~m}, 6 \mathrm{H}, ~ P h A l), 7.16-7.10(\mathrm{~m}, 3 \mathrm{H}, ~ P h \mathrm{Ti}), 4.91$ (sept, $J=6 \mathrm{~Hz}, 2 \mathrm{H}$, $\mu_{2}-\mathrm{OCHMe} 2$ ), 4.38 (sept, $\left.J=6.4 \mathrm{~Hz}, 2 \mathrm{H}, \mathrm{TiOCHMe} 2\right), 1.35\left(\mathrm{~d}, J=6 \mathrm{~Hz}, 6 \mathrm{H}, \mu_{2}-\mathrm{OCHMe} e_{2}\right)$, $1.33\left(\mathrm{~d}, J=6 \mathrm{~Hz}, 6 \mathrm{H}, \mu_{2}-\mathrm{OCHMe} e_{2}\right), 1.10\left(\mathrm{~d}, J=6.4 \mathrm{~Hz}, \mathrm{TiOCH} M e_{2}\right) \mathrm{ppm}$.

## 5. General Procedure for the Addition of $\mathrm{AlAr}_{3}$ (THF) to Aldehydes

$\left[\left\{(R)-\mathrm{H}_{8}-\mathrm{BINOLate}\right\} \mathrm{Ti}(\mathrm{O}-i-\mathrm{Pr})_{2}\right]_{\mathrm{x}}(0.023 \mathrm{~g}, 0.05 \mathrm{mmol})$ and $\mathrm{Ti}(\mathrm{O}-i-\mathrm{Pr})_{4}$ were mixed in 2 mL of dry THF at room temperature. After stirring for $5 \mathrm{~min}, \mathrm{AlAr}_{3}(\mathrm{THF})$ was added, and the mixture was stirred another 10 min . The resulted solution was cooled to $0{ }^{\circ} \mathrm{C}$, treated with an aldehyde, allowed to react at this temperature for 10 min , and then quenched with 2 M NaOH . The aqueous phase was extracted with diethyl ether ( $3 \times 10 \mathrm{~mL}$ ), dried over $\mathrm{MgSO}_{4}$, filtered and concentrated. Chromatography of the residue on silica gel (elution with 10:1 hexane-EA) gave the alcohols. Enantiomeric purities of products were determined by HPLC using suitable chiral columns from Daicel.

## 6. Optimization of Asymmetric Catalytic $\mathrm{AlPh}_{3}$ (THF) Additions to 2-Chlorobenzaldehyde ${ }^{\mathrm{a}}$



$$
1.0 \text { eq. } \quad 1.2 \mathrm{eq} .
$$

| entry | $\mathrm{Ti}(\mathrm{O}-i-\mathrm{Pr})_{4}$ (eq.) | ${\text { Conversion }(\%)^{\mathrm{b}}}$ | ${\text { Yield }(\%)^{\mathrm{b}}}$ | $\mathrm{Ee}(\%)^{\mathrm{c}}$ |
| :---: | :---: | :---: | :---: | :---: |
| 1 | - | 80 | 70 | 0 |
| 2 | 0.25 | 100 | 74 | 25 |
| 3 | 0.50 | 100 | 79 | 58 |


| 4 | 0.75 | 100 | 88 | 80 |
| :---: | :---: | :---: | :---: | :---: |
| 5 | 1.00 | 100 | 97 | 89 |
| 6 | 1.25 | 100 | 100 | 93 |
| 7 | 1.50 | 100 | 100 | 93 |

${ }^{\text {a }} 2$-Chlorobenzaldehyde $/ \mathrm{AlPh}_{3}(\mathrm{THF}) / \mathbf{1}=0.5 / 0.6 / 0.05 \mathrm{mmol}$. ${ }^{\mathrm{b}}$ Conversions and yields were based on ${ }^{1} \mathrm{H}$ NMR spectra. ${ }^{\text {c }}$ Enantioselectivities were determined by HPLC.
7. Asymmetric $\mathrm{Al}(\text { p-tolyl })_{3}(\mathbf{T H F})$ Additions to Aldehydes Catalyzed by the in situ Formed 1/Ti(O-i-Pr)4 Catalyst ${ }^{\text {a }}$

| entry | RCHO | Product | Yield (\%) | Ee (\%) $)^{\mathrm{c}}$ |
| :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |
| 1 | 2-furyl aldehyde |  | $p$-Tol | 86 |
|  |  |  |  |  |
|  |  |  |  |  |

2 (E)- $\mathrm{PhCH}=\mathrm{CHCHO}$


91
$91(S)^{\mathrm{d}}$

3
$\mathrm{PhC} \equiv \mathrm{CCHO}$


96
94 (R)
${ }^{\text {a }}$ Substrate $/ \mathrm{Al}(p \text {-tolyl })_{3}(\mathrm{THF}) / \mathbf{1}=0.5 / 0.6 / 0.05 \mathrm{mmol} ; \mathrm{Ti}(\mathrm{O}-i-\mathrm{Pr})_{4}, 0.625 \mathrm{mmol}$, reaction time $=10 \mathrm{~min} .{ }^{\mathrm{b}}$ Isolated yields. ${ }^{\mathrm{c}}$ Enantioselectivities were determined by HPLC using suitable chiral column from Daicel. ${ }^{\mathrm{d}} \mathrm{Ti}(\mathrm{O}-i-\mathrm{Pr})_{4}, 0.75 \mathrm{mmol}$.

## 8. HPLC Analytic Conditions of Alcohol Products

| Entry | Product | column | Hexane/IPA | $(R)$ | $(S)$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $1^{4}$ | 2 | Chiralcel OJ | $80 / 20$ | 10.2 | 13.4 |
| $2^{5}$ |  | Chiralcel OD-H | $98 / 2$ | 19.7 | 18.3 |


| Entry | Product | column | Hexane/IPA | (R) | (S) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $3^{6}$ |  | Chiralcel OB-H | 90/10 | 9.5 | 15.6 |
| $4^{4}$ |  | Chiralcel OB-H | 94/6 | 9.1 | 11.6 |
| $5^{4}$ |  | Chiralcel OB-H | 90/10 | 9.7 | 21.2 |
| $6^{6}$ |  | Chiralcel OB-H | 95/5 | 9.6 | 12.1 |
| $7^{4}$ |  | Chiralcel OJ | 90/10 | 13.7 | 15.8 |
| $8^{7}$ |  | Chiralcel OD | 90/10 | 18.7 | 13.1 |
| $9^{6}$ |  | Chiralcel OJ | 90/10 | 24.9 | 27.7 |
| $10^{8}$ |  | Chiralcel OB-H | 94/6 | 7.1 | 11.4 |
| $11^{8}$ |  | Chiralcel OJ | 80/20 | 16.9 | 11.9 |


| Entry | Product | column | Hexane/IPA | (R) | (S) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $12^{6}$ |  | Chiralcel OD | 95/5 | 30.1 | 24.9 |
| $13^{6}$ |  | Chiralcel OD | 99.5/0.5 | 24.5 | 29.5 |
| $14^{9}$ |  | Chiralcel OD-H | 98/2 | 6.7 | 6.1 |
| $15^{6}$ |  | Chiralcel OD | 98/2 | 13.2 | 8.9 |
| $16^{10}$ |  | Chiralcel OD | 95/5 | 17.2 | 14.5 |
| $17^{11}$ |  | Chiralcel OD | 88/12 | 13.4 | 10.6 |
| $18^{12}$ |  | Chiralcel OD | 99/1 | 22.3 | 26.2 |
| $19^{13}$ |  | Chiralcel OD | 80/20 | 6.9 | 9.7 |
| $20^{14}$ |  | Chiralcel OD | 99/1 | 29.6 | 10.3 |
| $21^{15}$ |  | Chiralcel OD | 98/2 | 26.5 | 24.1 |


| Entry | Product | column | Hexane/IPA | (R) | (S) |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $22^{16}$ |  | Chiralcel OD | 90/10 | 10.8 | 15.4 |
| $23^{13}$ |  | Chiralcel OD | 90/10 | 9.0 | 17.5 |
| $24^{6}$ |  | Chiralcel OB-H | 90/10 | 8.7 | 12.6 |

Other conditions: flow rate $1 \mathrm{~mL} / \mathrm{min}$, detector UV, 254 nm

## 9. ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR Spectra of Phenyl-(4-trimethylsilanylphenyl)-methanol

${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.50-7.24(\mathrm{~m}, 9 \mathrm{H}), 5.81(\mathrm{~s}, 1 \mathrm{H}), 0.24(\mathrm{~s}, 9 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$
NMR ( $150 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 144.28,143.67,139.74,133.54,128.48,127.56 .126 .48,125.82$, 76.26, -1.16 ppm.

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