## Supporting Information

Iron (III)-catalyzed intramolecular stereospecific substitution of the OH group in stereogenic secondary and tertiary alcohols<br>Rahul A. Watile ${ }^{1}$, Anon Bunrit ${ }^{1}$, Emi Lagerspets ${ }^{2}$, Ingela Lanekoff, ${ }^{3}$ Srijit Biswas ${ }^{4}$, Timo Repo ${ }^{2, *}$ and Joseph S. M. Samec ${ }^{1, *}$<br>${ }^{1}$ Department of Organic Chemistry, Stockholm University, 106 91, Stockholm, Sweden.<br>${ }^{2}$ Department of Chemistry, University of Helsinki, A. I. Virtasen aukio 1, P.O. Box 55, 00014, Finland.<br>${ }^{3}$ Department of Chemistry, BMC, Uppsala University, Box 599, 75124, Uppsala, Sweden.<br>${ }^{4}$ Division of Molecular Synthesis and Drug Discovery, Centre of Bio-Medical Research, SGPGIMS Campus, Raebareli Road, Lucknow, 226014, India.

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## 1. Checklist of characterization data of all compounds

a. Checklist of characterization data of synthesized intermediates
Code

|  | Known | 1 |  |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |

b. Checklist of characterization data of starting alcohols
Code

| 1i |  | Known | 1 | / | - | - |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1j |  | New | 1 | 1 | / | / |
| 1k |  | Known | 1 | 1 | - | - |
| 11 |  | New | 1 | / | / | 1 |
| 1m |  | New | 1 | / | / | / |
| 1n |  | Known | 1 | 1 | 1 | 1 |
| 10 |  | Known | 1 | 1 | - | - |
| 1p |  | New | 1 | 1 | 1 | 1 |
| 1 ${ }^{\prime}$ |  | Known | 1 | 1 | 1 | / |
| 1h" |  | New | 1 | 1 | 1 | 1 |


| 3a |  | New | / | / | / | / |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 3b |  | New | / | / | / | / |
| 3c |  | New | / | / | / | / |

c. Checklist of characterization data of products

| Code | Compound | New/ <br> Known | $\begin{gathered} { }^{\mathbf{1}} \mathrm{H}- \\ \text { NMR } \end{gathered}$ | $\begin{gathered} { }^{13} \mathrm{C}- \\ \text { NMR } \end{gathered}$ | IR | HRMS |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 a |  | Known | / | / | / | / |
| 2b |  | Known | / | / | / | / |
| 2c |  | New | / | / | / | / |
| 2d |  | New | / | / | / | / |


| 2e |  | New | 1 | 1 | / | 1 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 f |  | New | 1 | 1 | / | 1 |
| 2g |  | New | 1 | 1 | / | / |
| 2h |  | Known | / | / | / | / |
| 2 i |  | Known | / | 1 | / | / |
| 2j |  | New | 1 | / | / | / |
| 2k |  | Known | 1 | 1 | - | - |
| 21 |  | New | 1 | / | 1 | / |

(1)

## 2. General information:

Unless otherwise noted, all reactions were carried out in oven-dried 5 ml vial. All the reagents and solvents were bought from commercial sources and were used without further purification. All reactions were executed with oven-dried glassware under inert condition using argon. 1,2-Dichloroethane (DCE) was distilled using $\mathrm{CaH}_{2}$. Dry THF, diethyl ether and toluene were obtained from a VAC solvent purifier. NMR spectra were recorded with a 400 $\mathrm{MHz}\left({ }^{1} \mathrm{H}\right)$ and $100 \mathrm{MHz}\left({ }^{13} \mathrm{C}\right)$ spectrometer as solutions in $\mathrm{CDCl}_{3}$. Chemical shifts ( $\delta$ ) are reported in parts per million ( ppm ) and are referenced to $\mathrm{CDCl}_{3}(\delta=7.26 \mathrm{ppm})$ as an internal standard. All coupling constants $(J)$ are expressed in Hz. The description of the signals include: $\mathrm{s}=$ singlet, $\mathrm{d}=$ doublet, $\mathrm{t}=$ triplet, $\mathrm{m}=$ multiplet and $\mathrm{dd}=$ doublet of doublets, at $=$ apparent triplet. IR spectra were recorded by a Perkin Elmer FT-IR Spectrometer. HighResolution Mass Spectra (HRMS) were performed with a micrOTOF (Bruker) spectrometer by Na-formate. The molecular fragments are quoted as the relation between mass and charge $(\mathrm{m} / \mathrm{z})$. The enantiospecificity (e.s.) of products were determined by chiral HPLC using the corresponding racemic compounds as references. The routine monitoring of reactions was performed by crude ${ }^{1} \mathrm{H}$ NMR.

## 3. List of abbreviations

$\mathrm{Cb} \quad N, N^{\prime}$-diisopripylcarbamoyl
Me Methyl
$n$-Hex $\quad n$-hexyl
PE Petroleum ether 40/60 fraction
Ph Phenyl
$s \mathrm{Bu} \quad$ sec-butyl
THF Tetrahydrofuran
DMF N,N-Dimethylformamide
TLC Thin Layer Chromatography
DCE Dichloroethane
DPPF 1,1'-Ferrocenediyl-bis(diphenylphosphine)
4. General Scheme $A$ for the synthesis of 1a, 1b, 1c, 1d, 1e, 1f, and 1g:


## 5. General Method A to synthesize 1a, 1b, 1c, 1d, 1e, 1f, and 1g:

To a solution of 2-pyrrolidinone ( 30 mmol ) in 30 mL dry DMF was added CuI ( $10 \mathrm{~mol} \%$ ), anhydrous $\mathrm{K}_{2} \mathrm{CO}_{3}$ (1.1 equiv.) and aryl bromide (2 equiv.). The reaction mixture was refluxed for 48 h . After completion of the reaction, the reaction mixture was allowed to attain room temperature. Aqueous saturated $\mathrm{NH}_{4} \mathrm{Cl}(50 \mathrm{ml})$ was then added and the aqueous layer was separated and extracted with EtOAc $(4 \times 50 \mathrm{ml})$. The combined organic phase were washed with brine ( $1 \times 50 \mathrm{~mL}$ ), dried over anhydrous $\mathrm{MgSO}_{4}$ and concentrated under reduced pressure to give the crude product. Purification was carried out by silica gel column chromatography to afford $N$-aryl-2-pyrrolidinones $\mathbf{A}$.

An oven-dried round-bottomed flask equipped with a magnetic stir bar was charged with dry THF ( 20 mL ) and $N$-aryl-2-pyrrolidinones $\mathbf{A}(10 \mathrm{mmol})$ under argon atmosphere. The solution was cooled to $0{ }^{\circ} \mathrm{C}$ and aryl magnesium bromide (1.1 equiv, in 4 mL THF) was added dropwise. The reaction was allowed to attain room temperature and was run at the same temperature for 3 h . The reaction was quenched with saturated $\mathrm{NH}_{4} \mathrm{Cl}$ solution ( 30 mL )
extracted into diethyl ether $(3 \times 50 \mathrm{~mL})$. The combined organics were dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude residues (ketones, B1B7) were directly used for the next step (i.e. CBS-reduction) without further purification.

Ketones (B1-B7) were reduced to the alcohols enantioselectively by Corey-Bakshi-Shibata (CBS) reduction method. An oven-dried round-bottomed flask equipped with a magnetic stir bar was charged with $\mathrm{BH}_{3} /$ THF complex (1.2 equiv.) and chiral oxazaborolidine catalyst (R-CBS-Ox, $10 \mathrm{~mol} \%$ ) under argon. The solution was cooled to $0^{\circ} \mathrm{C}$ and stirred for 15 min . Ketones B1-B7 ( 5 mmol ) dissolved in dry THF ( 10 mL ) were added dropwise and the reaction was continued for 2 h at same temperature. After completion of reaction (TLC), the reaction was quenched with saturated $\mathrm{NH}_{4} \mathrm{Cl}$ solution ( 30 mL ), extracted into ethyl acetate $(3 \times 50 \mathrm{~mL})$. The combined organics were dried over sodium sulfate, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography to afford the alcohols

## 1a-1g.

## 6. General Scheme B to synthesize 1h and 1i:




## 7. General Method B to synthesize 1h and 1i:

4-Oxo-4-arylbutyric acid $\mathbf{C}$ ( 10 mmol ) was dissolved in methanol ( 10 mL ). Acetyl chloride (1.2 equiv.) was added dropwise and the reaction mixture was stirred at room temperature for overnight. After completion of the reaction (TLC), the reaction mixture was extracted into DCM ( $3 \times 50 \mathrm{~mL}$ ). The combined organics were washed with water $(2 \times 50 \mathrm{~mL})$ and brine ( $1 \times 50 \mathrm{~mL}$ ); dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated under reduced pressure to obtain the corresponding methyl esters D. Esters D were used in the next step without further purification.

Ester D ( 5 mmol ) dissolved in dry THF ( 10 mL ) were added dropwise to a solution of $\operatorname{RuCl}(p-c y m e n e)[(S, S)$-Ts-DPEN $(5 \mathrm{~mol} \%)$ in $5: 2$ formic acid / triethylamine ( 10 mL ) under argon and stirred for 48 h at $30^{\circ} \mathrm{C}$ oil bath. After completion of the reaction, the reaction was quenched with saturated $\mathrm{NaHCO}_{3}$ solution ( 30 mL ) and extracted into $\mathrm{DCM}(3 \times 50 \mathrm{~mL})$. The combined organic layers were washed with water $(2 \times 50 \mathrm{~mL})$ and brine $(1 \times 50 \mathrm{~mL})$; dried on anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated under reduced pressure. The residue was purified by column chromatography to obtain a non-separable mixture of alcohol $(\mathbf{E})$ and lactone $(\mathbf{F})$.

A mixture of $\mathbf{E}$ and $\mathbf{F}$ (approx. 5 mmol ) were reduced by using $\mathrm{LiAlH}_{4}$ ( 0.5 equiv.) in dry THF ( 20 mL ) at room temperature to obtain the products $\mathbf{1 h}$ and $\mathbf{1 i}$ in quantitative yields.
8. General Scheme C for the synthesis of $\mathbf{1 j}, \mathbf{1 k}$, and 11 :



## 9. General Method $\mathbf{C}$ to synthesize $\mathbf{1 j}, \mathbf{1 k}$, and 11 :

Alcohols $\mathbf{1} \mathbf{j}, \mathbf{1 k}$ and $\mathbf{1 l}$ were prepared by ring opening of lactam $\mathbf{A} \mathbf{2}$ with Grignard reagent. After completion by TLC, the following ketones were in situ reduced by $\mathrm{NaBH}_{4}$ for 1 hour to obtain racemate alcohols. Crude reaction mixtures were purified by silica gel column chromatography to obtain G1, G2, and G3 in $56 \%, 45 \%$ and $55 \%$ yields.

Alcohols G1, G2, and G3 were used to perform kinetic resolution with Candida Antarctica lipase- $B(C A L-B)$ in the excess amount of vinyl acetate for 12 hours. After completion of the reaction, crude mixtures were purified by silica gel column chromatography to alcohols $\mathbf{H 1}$, H2, H3 in $45 \%, 48 \%$ and $45 \%$ yields and acetylated products $\mathbf{I} 1, \mathbf{I} \mathbf{I}, \mathbf{I} \mathbf{3}$ in $40 \%, 43 \%, 45 \%$ yields, respectively.

Acetylated compounds $\mathbf{I 1}, \mathbf{I} \mathbf{2}, \mathbf{I} \mathbf{3}$ were used to perform deprotection in the present of $\mathrm{K}_{2} \mathrm{CO}_{3}$ in MeOH for 2 hours. After completion by TLC, crude mixtures were purified by silica gel column chromatography to alcohols $\mathbf{1 j}, \mathbf{1 k}$, and $\mathbf{1 1}$ in $90 \%, 95 \%$ and $93 \%$ yields, respectively.

## 10. General Scheme $D$ for the synthesis of $1 m$ and 1 n :



## 11. General Method $D$ for the synthesis of $\mathbf{1 m}$ and $1 \mathbf{n}$ :

N -aryl lactam K1 and K2 were prepared following a similar procedure as described in general method 5. To a solution of $\gamma$-lactam $\mathbf{J}$ ( 30 mmol ) in 30 mL dry DMF was added CuI ( 10 $\mathrm{mol} \%$ ), anhydrous $\mathrm{K}_{2} \mathrm{CO}_{3}$ (1.1 equiv.), and aryl bromide (2 equiv.). The reaction mixture was refluxed for 48 h . After completion of the reaction, the reaction mixture was allowed to attain room temperature. Aqueous saturated $\mathrm{NH}_{4} \mathrm{Cl}(50 \mathrm{ml})$ was then added and the aqueous layer was separated and extracted with ethyl acetate $(4 \times 50 \mathrm{ml})$. The combined organic phase were washed with brine ( $1 \times 50 \mathrm{~mL}$ ), dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated under reduced pressure to give the crude product. Purification is carried out by usual silica gel column chromatography to afford pure K1 and K2.

A warm solution of N -aryl lactam $\mathbf{K}(10 \mathrm{mmol})$ in dry benzene $(30 \mathrm{ml})$ was added slowly to a well stir solution of phenyl lithium ( 10 mmol ) under argon atmosphere. The reaction mixture
was stirred at reflux for 2 h under argon atmosphere. Benzene and ice-water were added at ice temperature. The combined organic phase was separated, washed with water, dried over sodium sulfate and concentrated under reduced pressure. The crude residues (ketones, L1-L2) were directly used without further purification for the CBS-reduction, after which the crude reaction mixtures were purified by silica gel column chromatography to obtain pure alcohols $\mathbf{1 m}$ and $\mathbf{1 n}$.

## 12. General Scheme $\mathbf{E}$ for the synthesis of 10 and 1 p:



## 13. General Method $\mathbf{E}$ for the synthesis of 10 and 1 p :

An oven-dried round-bottomed flask equipped with a magnetic stir bar was charged with dry THF ( 20 mL ) and chroman-2-one ( 10 mmol ) under argon atmosphere. The solution was cooled to $0{ }^{\circ} \mathrm{C}$ and aryl magnesium bromide (1.1 equiv, in 4 mL THF) was added dropwise. The reaction was allowed to attain room temperature and was run at the same temperature for 3 h . The reaction was quenched with saturated $\mathrm{NH}_{4} \mathrm{Cl}$ solution ( 30 mL ) extracted into diethyl ether $(3 \times 50 \mathrm{~mL})$. The combined organics were dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude (ketones, M1 and M2) was directly used without further purification for the CBS-reduction after which the crude reaction mixtures were purified by silica gel column chromatography to obtain pure $\mathbf{1 0}$ and $\mathbf{1 p}$ in $34 \%$ and $39 \%$ overall yields respectively.

## 14. General Scheme $\mathbf{F}$ for the synthesis of enantiomerically enriched tertiary alcohols

 3a, 3b, and 3c:


Q

$$
\mathrm{Y}=\mathrm{OH}, \mathbf{3 c}=98 \%, \text { er }(\mathrm{R} / \mathrm{S})=96: 4
$$

## 15. General Method $\mathbf{F}$ for the synthesis of enantiomerically enriched tertiary alcohols 3a

## 3b and 3c:

Step 1: Preparation of enantiomerically enriched secondary benzylic alcohols $\mathbf{N}$ via Noyori's asymmetric reduction: Acetophenone $(1.0 \mathrm{~g}, 8.33 \mathrm{mmol})$ was added to a solution of $\mathrm{RuCl}(p-$ cymene) $[(S, S)$-Ts-DPEN ( $52.9 \mathrm{mg}, 0.083 \mathrm{mmol}, 1.0 \mathrm{~mol} \%$ ) in 5:2 formic acid / triethylamine ( 15 mL ) under argon and stirred at $28^{\circ} \mathrm{C}$ for 24 h . After completion of the reaction, saturated $\mathrm{NaHCO}_{3}$ solution ( 50 mL ) was added and stirred for another 15 min . The reaction mixture was extracted into DCM ( $3 \times 50 \mathrm{~mL}$ ). The combined organic layers were washed with water $(2 \times 50 \mathrm{~mL})$ and brine $(1 \times 50 \mathrm{~mL})$; dried over anhydrous $\mathrm{MgSO}_{4}$ and concentrated under reduced pressure. Purification of the crude residue by column chromatography afforded pure alcohol $\mathbf{N}$ in $90 \%$ yield.

Step 2: The following procedure is representative of the preparation of secondary carbamates $\mathbf{O}$ from chiral secondary benzylic alcohol: A solution of alcohol $\mathbf{N}(5 \mathrm{mmol})$, diisopropylcarbamoyl chloride ( 1.1 equiv.), and triethyl amine ( 1.1 equiv.) in anhydrous DCM ( 30 mL ) was refluxed for 24 h . After completion of the reaction (TLC), the reaction mixture was poured in water ( 50 mL ). The mixture was extracted with diethyl ether ( $3 \times 50$ $\mathrm{mL})$. The combined organic parts were washed with water $(2 \times 50 \mathrm{~mL})$ and brine $(1 \times 50 \mathrm{~mL})$; dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated under reduced pressure. The crude product was purified by usual silica gel column chromatography to afford pure carbamate $\mathbf{O}$.

Step 3: Lithiation/borylation of chiral secondary carbamates to tertiary allylic alcohol $\mathbf{P}$ : To a stirred solution of (S)-1-Phenylethyl diisopropylcarbamate $\mathbf{O}(1 \mathrm{~g}, 4.01 \mathrm{mmol})$ in 20 mL anhydrous diethyl ether at $-78^{\circ} \mathrm{C}$ was added $s-\operatorname{BuLi}(3.4 \mathrm{~mL}$ of 1.4 M solution, $4.8 \mathrm{mmol}, 1.2$ equiv.) drop wise under an atmosphere of argon. The resulting light yellow homogeneous solution was stirred at $-78{ }^{\circ} \mathrm{C}$ for 30 min and neat vinylboronic acid pinacol ester ( $1 \mathrm{~mL}, 6$ mmol, 1.5 equiv.) was added drop wise with vigorous stirring. The reaction mixture was then stirred for 45 minutes at $-78{ }^{\circ} \mathrm{C}$. A methanol solution of magnesium bromide ( $6.0 \mathrm{~mL}, 6.0$ $\mathrm{mmol} ; 1 \mathrm{M})$ was added dropwise under argon. The reaction mixture was stirred at $-78{ }^{\circ} \mathrm{C}$ for an additional 15 min . and then allowed to attain room temperature and was run at the same temperature for 16 h . The reaction was quenched with the addition of an ice cold solution of 3 M aqueous sodium hydroxide ( 14.8 mL ) and $30 \%$ aqueous $\mathrm{H}_{2} \mathrm{O}_{2}(8.5 \mathrm{~mL})$ and stirred at room temperature for an additional 2 hours. The reaction mixture was extracted by $\mathrm{Et}_{2} \mathrm{O}(3 \times 50 \mathrm{~mL})$. The combined organic layers were washed with water ( $1 \times 50 \mathrm{~mL}$ ) and brine ( $1 \times 50 \mathrm{~mL}$ ) and concentrated under reduced pressure. The crude product was purified by column chromatography to obtain tertiary allylic alcohol $\mathbf{P}(474.7 \mathrm{mg}, 80 \%)$ as a colorless oil.

Step 4: Palladium-catalyzed vinylations of iodoanilines $\mathbf{Q}$ :

A mixture of $\mathbf{Q}(1.0 \mathrm{mmol})$, 2-phenylbut-3-en-2-ol $\mathbf{P}(5.0 \mathrm{mmol}), \mathrm{Pd}(\mathrm{OAc})_{2}(0.10 \mathrm{mmol})$, and DPPF as ligand ( 0.20 mmol ) in the presence of $\mathrm{K}_{2} \mathrm{CO}_{3}$ (1.5 equiv.) in toluene : $\mathrm{H}_{2} \mathrm{O}(1: 1,2.0$ mL ) were heated with stirring in a sealed tube at the temperatures $100^{\circ} \mathrm{C}$ for 3 h . After completion of the reaction (TLC), saturated $\mathrm{K}_{2} \mathrm{CO}_{3}$ solution ( 30 mL ) was added and the reaction mixture was extracted into ethyl acetate three times. The combined organic layers were washed with saturated $\mathrm{NaCl}(1 \times 50 \mathrm{~mL})$; dried over anhydrous $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated under reduced pressure. The residue was purified by column chromatography to obtain a pure alcohol $\mathbf{R}$.

## Step 3: Hydrogenation of a tertiary alcohol R:

Tertiary alcohol $\mathbf{R}(1 \mathrm{mmol})$ was dissolved in $\mathrm{ACN}(10 \mathrm{~mL})$ at room temperature. $\mathrm{Pd} / \mathrm{C}(10 \%$ wt) was added under argon atmosphere, and the reaction vessel was cooled to $0^{\circ} \mathrm{C}$. Then, the atmosphere was substituted with $\mathrm{H}_{2}(1 \mathrm{~atm})$ and the reaction mixture was stirred at the same temperature for 1 h . After the completion of reaction (TLC), the mixture was filtered through a tight packed pad of Celite®. The filtrate was concentrated and purified via silica gel (100200 mess) column chromatography to obtain pure $\mathbf{3 a}, \mathbf{3 b}$, and $\mathbf{3 c}$.

## 16. General Scheme G for the synthesis of 2-iodo-N-phenylaniline (Q):



## 17. General Method G for the synthesis of 2-iodo-N-phenylaniline (Q):

To a solution of 2-iodoaniline ( $2.0 \mathrm{mmol}, 438.04 \mathrm{mg}$ ) and 2-(Trimethylsilyl)phenyl trifluoromethanesulfonate ( $2.2 \mathrm{mmol}, 656.37 \mathrm{mg}$ ) in acetonitrile ( 20 mL ) was added CsF (4.0 $\mathrm{mmol}, 607.6 \mathrm{mg}$ ). The reaction was allowed to stir at room temperature for 12 h . After completion of the reaction (TLC), $\mathrm{H}_{2} \mathrm{O}(10 \mathrm{~mL})$ was added carefully and stirred for 15 min . The mixture was extracted with $\mathrm{DCM}(3 \times 50 \mathrm{~mL})$ and the combined organic layers were
washed with water $(1 \times 50 \mathrm{~mL})$ and brine $(1 \times 50 \mathrm{~mL})$ ) ; dried over anhydrous $\mathrm{MgSO}_{4}$ and concentrated under reduced pressure. The residue was purified by column chromatography to obtain 2-iodo-N-phenylaniline (Q, 92.0\%).

## 18. General Scheme $\mathbf{H}$ for the synthesis of dioxygen-centered nucleophiles $\mathbf{1 h}^{\prime}$



## 19. General Method H for the synthesis of dioxygen-centered nucleophiles $\mathbf{1 h}^{\prime}$

A mixture of 2-bromoacetophenone ( $10 \mathrm{mmol}, 199 \mathrm{mg}$ ), anhydrous $\mathrm{K}_{2} \mathrm{CO}_{3}$ (1 equiv. 138mg, 10 mmol ), and methyl ethyl ketone ( 2 equiv. 144 mg ) in acetone ( 20 mL ) was stirred at room temperature for 12 h . After completion of the reaction it was diluted with water, extracted in DCM, washed with water, brine and dried over the anhydrous sodium sulphate. The solvent was removed under vacuum. The crude product was recrystallized from 2-propanol gave pure compound dimethyl 2-(2-oxo-2-phenylethyl)malonate $\mathbf{S}(90 \%, 225 \mathrm{mg})$. The compound $\mathbf{S}$ (approx. 8 mmol ) was reduced by using $\mathrm{LiAlH}_{4}$ ( 0.5 equiv.) in dry THF ( 20 mL ) at room temperature to obtain the products (3-(hydroxymethyl)-1-phenylbutane-1,4-diol) $\mathbf{1 h}^{\prime}$ in quantitative yields.

## 20. General Scheme I for the synthesis of dinucleofuges $1 h^{\prime \prime}$



## 21. General Method I for the synthesis of dinucleofuges $1 h^{\prime \prime}$

Similar to the synthesis of di-O-centered nucleophiles $\mathbf{1} \mathbf{h}^{\prime \prime}$, a substitution reaction of ethyl bromoacetate with dibenzoylmethane generated ethyl 3-benzoyl-4-oxo-4-phenylbutanoate $\mathbf{T}$, followed by then $\mathrm{LiAlH}_{4}$ reduction to give 2-(hydroxy(phenyl)methyl)-1-phenylbutane-1,4diol $\mathbf{1 h}^{\prime \prime}$.

## 22. Table S1: Optimization of reaction conditions for secondary benzylic alcohols*

|  |  | cat.$(10 \mathrm{~mol}$ <br> MS ( $3 \AA$ ) <br> Solvent |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Entry | Catalysts | Solvent | Temp ( ${ }^{\circ} \mathbf{C}$ ) | Yield $(\%)^{\dagger}$ | $\begin{gathered} \text { e.s. } \\ (\%)^{\ddagger} \end{gathered}$ |
| 1 | $\mathrm{FeF}_{3}$ (III) | DCE | 90 | 15 | 0 |
| 2 | $\mathrm{FeCl}_{2}$ (II) | DCE | 90 | 20 | 92 |
| 3 | $\mathrm{Fe}\left(\mathrm{NO}_{3}\right)_{3} \cdot\left(\mathrm{H}_{2} \mathrm{O}\right)$ | DCE | 90 | NR | 0 |
| 4 | $\mathrm{Fe}(\mathrm{acac})_{3}$ | DCE | 90 | NR | 0 |
| 5 | $\mathrm{Fe}_{4}\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]_{3}$ | DCE | 90 | NR | 0 |
| 6 | $\mathrm{Fe}\left(\mathrm{ClO}_{4}\right)_{2} \cdot 4 \mathrm{H}_{2} \mathrm{O}$ | DCE | 90 | 10 | 91.1 |
| 7 | $\mathrm{Fe}(\mathrm{EDTA})$ sodium salt | DCE | 90 | NR | 0 |
| 8 | $\mathrm{Fe}_{2} \mathrm{O}_{3}$ | DCE | 90 | 10 | 93 |
| 9 | $\mathrm{FeCl}_{3}$ | DCE | 90 | 35 | 92 |
| 10 | Ferric citrate | DCE | 90 | NR | 0 |
| 11 | Iron(III) tartrate | DCE | 90 | NR | 0 |
| 12 | $\mathrm{Fe}(\mathrm{OTf})_{3}$ | DCE | 90 | 62 | 96 |
| 13 | $\mathrm{Fe}(\mathrm{OTf})_{3}$ | DCE | 110 | 85 | 80 |
| 14 | $\mathrm{Fe}(\mathrm{OTf})_{3}$ | ACN | 90 | 13 | 0 |
| 15 | $\mathrm{Fe}(\mathrm{OTf})_{3}$ | $\mathrm{MeNO}_{2}$ | 90 | 10 | 92 |
| 16 | $\mathrm{Fe}(\mathrm{OTf})_{3}$ | 1, 2 dibromomethane | 90 | 05 | 0 |
| 17 | $\mathrm{Fe}(\mathrm{OTf})_{3}$ | $\mathrm{CDCl}_{3}$ | 90 | 14 | 95 |
| 18 | $\mathrm{Fe}(\mathrm{OTf})_{3}$ | Toluene | 90 | 32 | 0 |
| 19 | $\mathrm{Fe}(\mathrm{OTf})_{3}$ | 1,4 dioxane | 90 | 23 | 90 |
| 20 | $\mathrm{Fe}(\mathrm{OTf})_{3}$ | Hexane | 90 | 21 | 99 |
| 21 | $\mathrm{Fe}(\mathrm{OTf})_{3}+\mathrm{AgBF}_{4}(10 \mathrm{~mol} \%)$ | DCE | 90 | NR | 0 |
| 22 | $\mathrm{Fe}(\mathrm{OTf})_{3}+\mathrm{AgSbF}_{6}(10 \mathrm{~mol} \%)$ | DCE | 90 | NR | 0 |
| 23 | $\mathrm{Fe}(\mathrm{OTf})_{3}+\mathrm{AgPF}_{6}(10 \mathrm{~mol} \%)$ | DCE | 90 | NR | 0 |
| 24 | $\mathrm{Fe}(\mathrm{OTf})_{3}{ }^{\S}+\mathrm{MS}(3 \AA)$ | DCE | 90 | 98 | 99 |
| 25 | MS ( $3 \AA$ ) | DCE | 90 | NR | 0 |
| 26 | $\mathrm{Fe}(\mathrm{OTf})_{3}+\mathrm{CF}_{3} \mathrm{SO}_{3} \mathrm{H}$ ( $\left.5 \mathrm{~mol} \%\right)$ | DCE | 90 | 31 | 88 |
| 27 | $\mathrm{CF}_{3} \mathrm{SO}_{3} \mathrm{H}(10 \mathrm{~mol} \%)$ | DCE | 90 | NR | 0 |
| 28 | Without catalyst | DCE | 90 | NR | 0 |
| 29 | $\mathrm{Cu}(\mathrm{OTf})_{2}$ | DCE | 90 | $<10$ | 0 |
| 30 | $\mathrm{Ni}(\mathrm{OTf})_{2}$ | DCE | 90 | <10 | 0 |
| 31 | $\mathrm{Mn}(\mathrm{OTf})_{2}$ | DCE | 90 | $<10$ | 0 |
| 32 | $\mathrm{Co}(\mathrm{OTf})_{2}$ | DCE | 90 | $<10$ | 0 |

Reaction condition: *All reactions were performed using 0.5 mmol of $\mathbf{1 a}, 0.050 \mathrm{mmol}$ of catalyst ( $10 \mathrm{~mol} \%$ ) in DCE as solvent $(2.0 \mathrm{~mL})$, MS $(3 \AA)=300 \mathrm{mg}$, at $90^{\circ} \mathrm{C}$ temperature for time 24 h under argon atmosphere. ${ }^{\dagger}$ NMR yield. ${ }^{\dagger}$ Enantiospecificity was determined by chiral stationary phase HPLC analysis.
${ }^{8}$ The purity of catalyst has been determined by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) analysis. NR, no reaction.

## 23. Table S2: Optimization of reaction conditions for tertiary alcohols*



| Entry | Solvent (mL) | Temp ( ${ }^{\circ} \mathbf{C}$ ) | Time (h) | Yield (\%) $^{\dagger}$ | e.s. (\%) |
| :---: | :--- | :---: | :---: | :---: | :---: |
| ${ }^{\ddagger}$ |  |  |  |  |  |
| 1 | DCE | 90 | 24 | 100 | 09 |
| 2 | $n$-Hexane | 90 | 24 | 100 | 26.8 |
| 3 | DCE $+n$-Hexane $(0.5+0.5)$ | 90 | 24 | 100 | 40 |
| 4 | DCE $+n$-Hexane $(0.4+0.6)$ | 90 | 24 | 100 | 32.2 |
| 5 | DCE $+n$-Hexane $(0.3+0.7)$ | 90 | 24 | 100 | 32.2 |
| 6 | DCE $+n$-Hexane $(0.2+0.8)$ | 90 | 24 | 100 | 29 |
| 7 | DCE $+n$-Hexane $(0.25+0.25)$ | 90 | 24 | 100 | 36 |
| 8 | DCE $+n$-Hexane $(01+01)$ | 90 | 24 | 100 | 35 |
| 9 | DCE $+n$-Hexane $(0.5+0.5)$ | 80 | 24 | 100 | 50.53 |
| 10 | DCE $+n$-Hexane $(0.5+0.5)$ | 60 | 24 | 100 | 64 |
| 11 | DCE $+n$-Hexane $(0.5+0.5)$ | rt | 48 | 98 | 96 |

Reaction condition : *All reactions were performed using 0.2 mmol of $\mathbf{3 a}, \mathrm{MS}(3 \AA)=100 \mathrm{mg}$, and 0.020 mmol of catalyst $(10 \mathrm{~mol} \%)$ in the indicated solvent $(01 \mathrm{~mL})$ under argon atmosphere. ${ }^{\dagger}$ NMR yield. ${ }^{\dagger}$ Enantiomeric excess was determined by chiral stationary phase HPLC analysis. NR, no reaction.

## 24. Inductively Coupled Plasma Mass Spectrometry analysis of $\mathrm{Fe}(\mathrm{OTf})_{3}$ catalyst

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used for detecting trace elemental impurities in the $\mathrm{Fe}(\mathrm{OTf})_{3}$ catalyst (purity $90.00 \%$, Table S1). The major metal impurities were individually screened as catalysts for the transformation (entry 29-32, Table S1). However, none of the trace metals outperformed $\mathrm{Fe}(\mathrm{OTf})_{3}$ as catalyst in the intramolecular substitution reaction.

## 25. Rate order determination

The reaction of $\mathbf{1 a}$ to $\mathbf{2 a}$ was performed using five different concentrations of catalyst $(0,5$, 10,15 , and $20 \mathrm{~mol} \%$ ). The reactions were monitored by using ${ }^{1} \mathrm{H}$ NMR spectroscopy and the initial rates were determined below $20 \%$ conversion. Duplicates of the reactions were made and the data is the mean value of these duplicates.



Fig S1: Rate order determination
Reaction condition: 1a ( 0.2 mmol ), DCE ( 1 mL ), MS ( $3 \AA$ ) ( 200 mg ), and catalyst ( $0,5,10,15$, and $20 \mathrm{~mol} \%$ ) were heated in an oil bath at $90^{\circ} \mathrm{C}$. Initial rates of the reaction were determined below $20 \%$ conversion (up to 2h) by ${ }^{1} \mathrm{H}$ NMR spectroscopy. The values are the mean value of two reactions.

## 26. In-situ UV-visible spectroscopy analysis

$N$-methyl anisole (1r), represent an $N$-centered nucleophile exhibits the absorption bands at $320 \mathrm{~cm}^{-1}$ (Fig. 2) in UV-vis spectrum in DCE. When Fe is added a blue shift to $275 \mathrm{~cm}^{-1}$ is observed. A similar trend is found in the UV-vis spectrum for the substrate 1a (Fig. 3).


Fig. S2: Interaction of $\mathrm{Fe}(\mathrm{OTf})_{3}$ with nucleophile (1r)


Fig.S3: Interaction of $\mathrm{Fe}(\mathrm{OTf})_{3}$ with 1a

## 27. ESI-MS/MS of intermediate of the standard reaction



Fig.S4: ESI-MS/MS of intermediate of the reaction

## 28. Characterization data of all starting alcohols:

All characterization data for alcohols 1a, 1c, 1d, 1e, 1f, 1g, 1j, 1k, 11, 1m, 1n, 10, 1p, 3a, 3b, and $\mathbf{3 c}$ which are not reported previously, are supplemented below. Alcohols $\mathbf{1 b}, \mathbf{1 h}$, and $\mathbf{1 i}$ were previously reported and the obtained NMR data (see copies of NMR attached below) matched with the reported values.

## (S)-4-((4-methoxyphenyl)amino)-1-phenylbutan-1-ol (1a) ${ }^{1}$



IR (neat) 3360.64, 3028, 2932.25, 2831, 1617, 1512.40, 1455, 1296, 1235.54, 1178, 1119, 1119.18, 1034.64, 913, 819, 749, $701 \mathrm{~cm}^{-1} .{ }^{\mathbf{1}} \mathbf{H} \mathbf{N M R}(400 \mathrm{MHz}$, Chloroform-d) $\delta=7.37-$ 7.33 (m, 4H), $7.30-7.27(\mathrm{~m}, 1 \mathrm{H}), 6.78(\mathrm{~d}, J=9.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.61(\mathrm{~d}, J=8.9 \mathrm{~Hz}, 2 \mathrm{H}), 4.72$ (dd, $J=7.5,5.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.75(\mathrm{~s}, 3 \mathrm{H}), 3.11(\mathrm{t}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 1.89(\mathrm{dddd}, J=10.2,8.4,6.7,5.7$ $\mathrm{Hz}, 1 \mathrm{H}), 1.81-1.71(\mathrm{~m}, 1 \mathrm{H}), 1.70-1.60(\mathrm{~m}, 2 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C} \mathbf{N M R}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=$ $152.5,144.6,142.0,128.5,127.6,125.8,114.9,114.7,74.3,55.8,45.4,36.8,26.0 \mathrm{ppm}$. HRMS (ESI) calcd. for $\mathrm{C}_{17} \mathrm{H}_{22} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}] \mathrm{m} / \mathrm{z} 272.1572$ found $\mathrm{m} / \mathrm{z}$ 272.1645. The enantiomeric ratio of 1a was determined by HPLC analysis using Daicel Chiralcel OD-H column: $n$-Hexane: isopropanol $=90: 10$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1 ), 232 $\mathrm{nm}($ channel 2$): \mathrm{t}_{1}($ major $)=25.45 \mathrm{~min}, \mathrm{t}_{2}($ minor $)=30.12 \mathrm{~min}$.

## (S)-1-phenyl-4-(phenylamino)butan-1-ol (1b) ${ }^{1}$



IR (neat) $3354.64,3029,2930.25,2835,1615,1510.40,1465,1316,1145.54,1178,1119.18$, 1034.64, 911, 819, 750, $711 \mathrm{~cm}^{-1} .{ }^{\mathbf{1}} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta 7.36(\mathrm{~d}, J=4.3 \mathrm{~Hz}$, 4H), $7.32-7.25(\mathrm{~m}, 1 \mathrm{H}), 7.21-7.12(\mathrm{~m}, 2 \mathrm{H}), 6.70(\mathrm{tt}, J=7.3,1.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.63-6.54(\mathrm{~m}$, $2 \mathrm{H}), 4.73(\mathrm{dd}, J=7.5,5.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.14(\mathrm{t}, J=6.9 \mathrm{~Hz}, 2 \mathrm{H}), 1.97-1.82(\mathrm{~m}, 2 \mathrm{H}), 1.81-1.72$ $(\mathrm{m}, 1 \mathrm{H}), 1.69-1.60(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta=148.3,144.5,129.2,128.5$, 127.6, 125.8, 117.4, 112.9, 74.3, 43.9, 36.6, 25.9 ppm . HRMS (ESI) calcd. for $\mathrm{C}_{16} \mathrm{H}_{20} \mathrm{NO}$ $[\mathrm{M}+\mathrm{H}] \mathrm{m} / \mathrm{z} 242.1548$ found $m / z 242.1545$. The enantiomeric ratio of $\mathbf{1 b}$ was determined by HPLC analysis using Daicel Chiralcel OD-H column: $n$-Hexane $:$ isopropanol $=90: 10$, flow
rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}($ channel 1$), 232 \mathrm{~nm}($ channel 2$): \mathrm{t}_{1}($ major $)=22.1 \mathrm{~min}, \mathrm{t}_{2}$ $($ minor $)=32.8 \mathrm{~min}$.
(S)-1-(4-fluorophenyl)-4-((4-methoxyphenyl)amino)butan-1-ol (1c)


IR (neat) 3367.48, 2994, 2935.19, 2834.38, 1603, 1511.78, 1464, 1386, 1235.4, 1179, 1092.8, 1035.34, 821.49, 755, 718, $574 \mathrm{~cm}^{-1} .{ }^{\mathbf{1}} \mathbf{H}$ NMR ( 400 MHz , Chloroform-d) $\delta 7.36-7.31$ (m, $4 \mathrm{H}), 7.26(\mathrm{~d}, 1 \mathrm{H}), 4.89(\mathrm{t}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.14-4.06(\mathrm{~m}, 1 \mathrm{H}), 3.98-3.89(\mathrm{~m}, 1 \mathrm{H}), 2.38-$ $2.27(\mathrm{~m}, 1 \mathrm{H}), 2.05-1.96(\mathrm{~m}, 1 \mathrm{H}), 1.86-1.76(\mathrm{~m}, 1 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C} \mathbf{N M R}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $=162.3\left(J_{\mathrm{C}-\mathrm{F}}=320 \mathrm{~Hz}\right), 152.8,141.6,127.5\left(J_{\mathrm{C}-\mathrm{F}}=10 \mathrm{~Hz}\right), 115.3\left(J_{\mathrm{C}-\mathrm{F}}=20 \mathrm{~Hz}\right), 115.1$, 114.9, 73.6, 55.8, 45.6, 37.0, 25.9 ppm . HRMS (ESI) calcd. for $\mathrm{C}_{17} \mathrm{H}_{21} \mathrm{FNO}_{2}[\mathrm{M}+\mathrm{H}] \mathrm{m} / \mathrm{z}$ 290.1569 found $m / z$ 290.1551. The enantiomeric ratio of $\mathbf{1 c}$ was determined by HPLC analysis using Daicel Chiralcel OD-H column: $n$-Hexane: isopropanol $=90: 10$, flow rate 1.0 $\mathrm{mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1 ), 232 $\mathrm{nm}($ channel 2$): \mathrm{t}_{1}($ major $)=22.81 \mathrm{~min}, \mathrm{t}_{2}($ minor $)=28.03 \mathrm{~min}$.
(S)-1-(4-chlorophenyl)-4-((4-methoxyphenyl)amino)butan-1-ol (1d)


IR (neat) $3370.58,2935,2830.34,1616,1512.28,1463,1365,1295,1237.31,1179,1088.9$, 1036.44, 818.9, 770, 702, $475 \mathrm{~cm}^{-1} .{ }^{1} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta=7.29(\mathrm{~d}, J=5.5$ $\mathrm{Hz}, 4 \mathrm{H}), 6.81-6.75(\mathrm{~m}, 2 \mathrm{H}), 6.66-6.56(\mathrm{~m}, 2 \mathrm{H}), 4.70(\mathrm{dd}, J=7.4,5.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.75(\mathrm{~s}$, $3 \mathrm{H}), 3.10(\mathrm{~s}, 2 \mathrm{H}), 1.89-1.79(\mathrm{~m}, 2 \mathrm{H}), 1.77-1.62(\mathrm{~m}, 2 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C} \mathbf{N M R}(100 \mathrm{MHz}$,
$\left.\mathrm{CDCl}_{3}\right) \delta=152.8,141.6,127.5,127.4,115.4,115.2,115.1,114.9,73.6,55.8,45.6,37.0,25.9$ ppm. HRMS (ESI) calcd. for $\mathrm{C}_{17} \mathrm{H}_{21} \mathrm{ClNO}_{2}[\mathrm{M}+\mathrm{H}] \mathrm{m} / \mathrm{z} 306.1267$ found $\mathrm{m} / \mathrm{z}$ 306.1255. The enantiomeric ratio of 1d was determined by HPLC analysis using Daicel Chiralcel OD-H column: $n$-Hexane: isopropanol $=90: 10$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1$), 232$ $\mathrm{nm}($ channel 2$): \mathrm{t}_{1}($ major $)=45.3 \mathrm{~min}, \mathrm{t}_{2}($ minor $)=53.7 \mathrm{~min}$.

## (S)-4-((4-methoxyphenyl)amino)-1-(3-(trifluoromethoxy)phenyl)butan-1-ol (1e)



IR (neat) $3371.68,2934,2831.44,1606,1513.81,1465,1360,1190,1240.71,1201,1080.1$, $811.9,765,701,470 \mathrm{~cm}^{-1} .{ }^{1} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta=7.36(\mathrm{t}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H})$, $7.26(\mathrm{~s}, 1 \mathrm{H}), 7.23(\mathrm{~s}, 1 \mathrm{H}), 7.15-7.10(\mathrm{~m}, 1 \mathrm{H}), 6.81-6.74(\mathrm{~m}, 2 \mathrm{H}), 6.65-6.56(\mathrm{~m}, 2 \mathrm{H}), 4.76$ (t, $J=6.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.75(\mathrm{~s}, 3 \mathrm{H}), 3.12(\mathrm{td}, J=6.7,1.7 \mathrm{~Hz}, 2 \mathrm{H}), 1.87(\mathrm{dd}, J=7.3,6.2 \mathrm{~Hz}, 2 \mathrm{H})$, $1.78-1.67(\mathrm{~m}, 1 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C} \mathbf{N M R}\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta==152.5,149.4,147.2,142.2$, 129.7, 124.1, 121.7, 119.7, 119.2, 118.3, 114.9, 114.8, 73.5, 55.8, 45.2, 37.1, 26.0 ppm . HRMS (ESI) calcd. for $\mathrm{C}_{18} \mathrm{H}_{21} \mathrm{~F}_{3} \mathrm{NO}_{3}[\mathrm{M}+\mathrm{H}] \mathrm{m} / \mathrm{z} 356.1395$ found $\mathrm{m} / \mathrm{z}$ 356.1385. The enantiomeric ratio of $\mathbf{1 e}$ was determined by HPLC analysis using Daicel Chiralcel OD-H column: $n$-Hexane: isopropanol $=90: 10$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1 ), 232 $\mathrm{nm}($ channel 2$): \mathrm{t}_{1}($ major $)=16.01 \mathrm{~min}, \mathrm{t}_{2}($ minor $)=21.1 \mathrm{~min}$.
(S)-4-((4-methoxyphenyl)amino)-1-(p-tolyl)butan-1-ol (1f)


IR (neat) 3361.8, 2937, 2830.86, 1614, 1511.98, 1462, 1293, 1235, 1179, 1119.8, 1035.67, 818.6, $518.77 \mathrm{~cm}^{-1} .{ }^{1} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta=7.24(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 2 \mathrm{H}), 7.17-$ $7.13(\mathrm{~m}, 2 \mathrm{H}), 6.80-6.75(\mathrm{~m}, 2 \mathrm{H}), 6.67-6.60(\mathrm{~m}, 2 \mathrm{H}), 4.68(\mathrm{dd}, J=7.5,5.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.75(\mathrm{~s}$, $3 \mathrm{H}), 3.14-3.07(\mathrm{~m}, 3 \mathrm{H}), 2.34(\mathrm{~s}, 3 \mathrm{H}), 1.94-1.81(\mathrm{~m}, 2 \mathrm{H}), 1.78-1.71(\mathrm{~m}, 1 \mathrm{H}), 1.65(\mathrm{dt}, J=$ $9.1,6.2 \mathrm{~Hz}, 1 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR $\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=152.7,141.6,137.2,129.1,125.8$, 115.1, 114.9, 99.9, 74.1, 55.8, 45.7, 36.7, 25.9, 21.1 ppm. HRMS (ESI)calcd. for $\mathrm{C}_{18} \mathrm{H}_{23} \mathrm{NO}_{2} \mathrm{Na}[\mathrm{M}+\mathrm{Na}] \mathrm{m} / \mathrm{z} 308.1618$ found $\mathrm{m} / \mathrm{z} 308.1621$. The enantiomeric ratio of $\mathbf{1 f}$ was determined by HPLC analysis using Daicel Chiralcel AD column: $n$-Hexane : isopropanol $=$ 90:10, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1), 232 nm (channel 2): $\mathrm{t}_{1}$ (major) $=28.8$ $\min , \mathrm{t}_{2}($ minor $)=29.6 \mathrm{~min}$.

## (S)-1-(3-methoxyphenyl)-4-((4-methoxyphenyl)amino)butan-1-ol (1g)



IR (neat) 3370, 3030, 2831, 1616, 1505, 1468, 1440, 1417, 1311, 1267, 1170, 1118, 1094, 1030. 817, $755 \mathrm{~cm}^{-1} .{ }^{\mathbf{1}} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta 7.30-7.22(\mathrm{~m}, 1 \mathrm{H}), 6.92(\mathrm{dd}, J=$ $4.2,1.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.81(\mathrm{ddd}, J=8.3,2.6,1.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.79-6.75(\mathrm{~m}, 2 \mathrm{H}), 6.59(\mathrm{~d}, J=8.9 \mathrm{~Hz}$, $2 \mathrm{H}), 4.68(\mathrm{dd}, J=7.2,5.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H}), 3.74(\mathrm{~s}, 3 \mathrm{H}), 3.09(\mathrm{t}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 1.94-$ $1.81(\mathrm{~m}, 2 \mathrm{H}), 1.78-1.70(\mathrm{~m}, 1 \mathrm{H}), 1.69-1.61(\mathrm{~m}, 1 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 159.7, 152.4, 146.4, 129.4, 118.1, 114.9, 114.8, 114.6, 112.9, 111.3, 74.1, 55.8, 55.2, 45.2, 36.8, 25.9 ppm . HRMS (ESI) calcd. for $\mathrm{C}_{18} \mathrm{H}_{24} \mathrm{NO}_{3}[\mathrm{M}+\mathrm{H}] \mathrm{m} / \mathrm{z} 302.1752$ found $m / z 302.1751$. The enantiomeric ratio of $\mathbf{1 g}$ was determined by HPLC analysis using Daicel Chiralcel AD column: $n$-Hexane: isopropanol $=90: 10$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1 ), 232 $\mathrm{nm}($ channel 2$): \mathrm{t}_{1}($ major $)=42.5 \mathrm{~min}, \mathrm{t}_{2}($ minor $)=48.9 \mathrm{~min}$.

## (S)-1-phenylbutane-1,4-diol (1h) ${ }^{2}$


${ }^{1} \mathbf{H}$ NMR $(400 \mathrm{MHz}$, Chloroform- $d$ ) $\delta=7.39-7.32(\mathrm{~m}, 4 \mathrm{H}), 7.28(\mathrm{~d}, J=5.7 \mathrm{~Hz}, 1 \mathrm{H}), 4.74$ $(\mathrm{t}, J=6.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.72-3.66(\mathrm{~m}, 2 \mathrm{H}), 1.87(\mathrm{td}, J=7.0,5.9 \mathrm{~Hz}, 2 \mathrm{H}), 1.74-1.63(\mathrm{~m}$, 2H)ppm. ${ }^{13} \mathbf{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=144.7$, 128.4, 127.5, 125.8, $74.3,62.8,36.2$, 29.2. HRMS (ESI) calcd. for $\mathrm{C}_{10} \mathrm{H}_{15} \mathrm{O}_{2}[\mathrm{M}+\mathrm{H}] \mathrm{m} / \mathrm{z} 167.1070$ found $\mathrm{m} / \mathrm{z}$ 167.1076. The enantiomeric ratio of $\mathbf{1 h}$ was determined by HPLC analysis using Daicel Chiralcel OD-H column: $n$-Hexane : isopropanol $=95: 5$, flow rate $0.5 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}: \mathrm{tl}$ (minor) $=44.3$ $\min , \mathrm{t} 2($ major $)=48.4 \mathrm{~min}$.

## (S)-1-(4-fluorophenyl)butane-1,4-diol (1i) ${ }^{3}$


${ }^{1} \mathbf{H}$ NMR $(400 \mathrm{MHz}$, Chloroform- $d$ ) $\delta=7.28(\mathrm{ddd}, J=8.0,5.1,2.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.07-6.94(\mathrm{~m}$, $2 \mathrm{H}), 4.66(\mathrm{t}, J=6.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.70-3.55(\mathrm{~m}, 2 \mathrm{H}), 3.08(\mathrm{~s}, 2 \mathrm{H}), 1.80(\mathrm{q}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 1.69$ $-1.56(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathbf{C}$ NMR $\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=162.0\left(\mathrm{~J}_{\mathrm{C}-\mathrm{F}}=244 \mathrm{~Hz}\right), 140.4,140.4,127.3$ $\left(J_{\mathrm{C}-\mathrm{F}}=8 \mathrm{~Hz}\right), 115.2\left(J_{\mathrm{C}-\mathrm{F}}=20 \mathrm{~Hz}\right), 73.6,62.7,36.5,29.0 . \mathrm{ppm}$ HRMS (ESI) calcd. for $\mathrm{C}_{10} \mathrm{H}_{13} \mathrm{FNaO} 2[\mathrm{M}+\mathrm{Na}] \mathrm{m} / \mathrm{z} 207.0797$ found $\mathrm{m} / \mathrm{z}$ 207.0797. The enantiomeric ratio of $\mathbf{1 i}$ was determined by HPLC analysis using Daicel Chiralcel AD column: $n$-Hexane: isopropanol $=$ 95:5, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1 ), 232 nm (channel 2): $\mathrm{t}_{1}$ (major) $=111.0$ $\min , \mathrm{t}_{2}($ minor $)=118.4 \mathrm{~min}$.
(S)-6-((4-methoxyphenyl)amino)hexan-3-ol (1j) ${ }^{3}$


IR (neat) $\mathrm{cm}^{-1} 3382,3030,2931,2870,1661,1614,1510,1451,1354,1311,1217,1170$, 1118, 1040, 1036. 917, $754 \mathrm{~cm}^{-1} .{ }^{1} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta=6.85-6.74(\mathrm{~m}$, $2 \mathrm{H}), 6.69-6.56(\mathrm{~m}, 2 \mathrm{H}), 5.88(\mathrm{ddd}, J=17.2,10.4,6.1 \mathrm{~Hz}, 1 \mathrm{H}), 5.24(\mathrm{dt}, J=17.2,1.5 \mathrm{~Hz}$, $1 \mathrm{H}), 5.12(\mathrm{dt}, J=10.4,1.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.13(\mathrm{dtd}, J=5.9,4.7,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.76(\mathrm{~s}, 3 \mathrm{H}), 3.16-$ $3.02(\mathrm{~m}, 4 \mathrm{H}), 1.81-1.57(\mathrm{~m}, 4 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=152.1,142.4$, 141.0, 114.8, 114.4, 114.4, 72.5, 55.7, 45.0, 34.6, 25.4 ppm. HRMS (ESI) calcd. for $\mathrm{C}_{13} \mathrm{H}_{20} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}] 222.1489 \mathrm{~m} / \mathrm{z}$ found $222.1498 \mathrm{~m} / \mathrm{z}$. The enantiomeric ratio of $\mathbf{1} \mathbf{j}$ was determined by HPLC analysis using Daicel Chiralcel OJ-H column: $n$-Hexane: isopropanol $=$ 90:10, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1), 232 nm (channel 2 ): $\mathrm{t}_{1}$ (major) $=46.3$ $\min , \mathrm{t}_{2}($ minor $)=49.7 \mathrm{~min}$.

## (R)-5-((4-methoxyphenyl)amino)pentan-2-ol (1k) ${ }^{3}$


${ }^{1} \mathbf{H}$ NMR $(400 \mathrm{MHz}$, Chloroform- $d$ ) $\delta=6.83-6.76(\mathrm{~m}, 2 \mathrm{H}), 6.65-6.59(\mathrm{~m}, 2 \mathrm{H}), 3.90-3.81$ $(\mathrm{m}, 1 \mathrm{H}), 3.77(\mathrm{~s}, 3 \mathrm{H}), 3.11(\mathrm{td}, J=6.8,2.0 \mathrm{~Hz}, 2 \mathrm{H}), 1.82-1.64(\mathrm{~m}, 2 \mathrm{H}), 1.57(\mathrm{tdd}, J=8.3$, $5.9,3.8 \mathrm{~Hz}, 2 \mathrm{H}), 1.22(\mathrm{~d}, J=6.2 \mathrm{~Hz}, 3 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C} \mathbf{N M R}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=152.2$, $142.5,114.8,114.4,67.7,55.7,45.2,36.9,26.0,23.6 \mathrm{ppm}$.

The enantiomeric ratio of $\mathbf{1 k}$ was determined by HPLC analysis using Daicel Chiralcel OJ-H column: $n$-Hexane : isopropanol $=85: 15$, flow rate $0.5 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1 ), 232 $\mathrm{nm}($ channel 2$): \mathrm{t}_{1}($ major $)=58.9 \mathrm{~min}, \mathrm{t}_{2}($ minor $)=63.2 \mathrm{~min}$.

## (R)-6-((4-methoxyphenyl)amino)hex-1-en-3-ol (11) ${ }^{3}$



IR (neat) $\mathrm{cm}^{-1} 3382,3029,2935,2874,2833,1660,1615,1513.49,1456.9,1385,1238.21$, $1179,1111,1036.69,969,819.74,753 \mathrm{~cm}^{-1} .{ }^{1} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta=6.84-$ $6.74(\mathrm{~m}, 2 \mathrm{H}), 6.69-6.57(\mathrm{~m}, 2 \mathrm{H}), 3.77(\mathrm{~s}, 3 \mathrm{H}), 3.56(\mathrm{dddd}, J=8.5,7.5,4.9,3.7 \mathrm{~Hz}, 1 \mathrm{H})$, $3.19-3.02(\mathrm{~m}, 2 \mathrm{H}), 2.86(\mathrm{~s}, 2 \mathrm{H}), 1.81-1.39(\mathrm{~m}, 6 \mathrm{H}), 0.96(\mathrm{t}, J=7.5 \mathrm{~Hz}, 3 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=152.0,142.3,114.6,114.4,72.9,55.6,45.2,34.6,30.2,25.9$, 10.0 ppm . HRMS (ESI) calcd. For $\mathrm{C}_{13} \mathrm{H}_{22} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}] 224.1645 \mathrm{~m} / \mathrm{z}$ found $224.2652 \mathrm{~m} / \mathrm{z}$. The enantiomeric ratio of $\mathbf{1 1}$ was determined by HPLC analysis using Daicel Chiralcel OJ-H column: $n$-Hexane: isopropanol $=80: 20$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1 ), 232 $\mathrm{nm}($ channel 2$): \mathrm{t}_{1}($ major $)=14.8 \mathrm{~min}, \mathrm{t}_{2}($ minor $)=15.4 \mathrm{~min}$.

## (S)-5-((4-methoxyphenyl)amino)-1-phenylpentan-1-ol (1m) ${ }^{4}$



IR (neat) 3362.14, 3029, 2935.27, 2833, 1611, 1522.80, 1450, 1206, 1230.44, 1186, 1121, 1044.51, 911, 820, $789 \mathrm{~cm}^{-1} .{ }^{1} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta=7.39-7.31(\mathrm{~m}, 4 \mathrm{H})$, $7.29(\mathrm{dd}, J=6.3,2.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.81-6.73(\mathrm{~m}, 2 \mathrm{H}), 6.59-6.52(\mathrm{~m}, 2 \mathrm{H}), 4.72-4.61(\mathrm{~m}, 1 \mathrm{H})$, $3.74(\mathrm{~s}, 3 \mathrm{H}), 3.05(\mathrm{t}, J=7.0 \mathrm{~Hz}, 2 \mathrm{H}), 1.91-1.80(\mathrm{~m}, 1 \mathrm{H}), 1.80-1.70(\mathrm{~m}, 1 \mathrm{H}), 1.68-1.58$ $(\mathrm{m}, 2 \mathrm{H}), 1.57-1.48(\mathrm{~m}, 1 \mathrm{H}), 1.40(\mathrm{ddd}, J=10.3,7.9,5.5 \mathrm{~Hz}, 1 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR (100 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=152.0,144.7,142.6,128.5,127.6,125.8,114.9,114.1,74.5,55.8,44.8$, 38.8, 29.5, 23.4 ppm. HRMS (ESI) calcd. for $\mathrm{C}_{18} \mathrm{H}_{24} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}] \mathrm{m} / \mathrm{z} 286.1811$ found $\mathrm{m} / \mathrm{z}$ 286.1807. The enantiomeric ratio of $\mathbf{1 m}$ was determined by HPLC analysis using Daicel

Chiralcel OD-H column: $n$-Hexane: isopropanol $=90: 10$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1), $232 \mathrm{~nm}($ channel 2$): \mathrm{t}_{1}($ minor $)=29.23 \mathrm{~min}, \mathrm{t}_{2}($ major $)=31.38 \mathrm{~min}$.

## (S)-3-(2-((4-methoxyphenyl)amino)phenyl)-1-phenylpropan-1-ol (1n) ${ }^{4}$



IR (neat) 3366.44, 3031, 2945.55, 2823, 1615, 1520.79, 1441, 1216, 1202.40, 1184, 1116, 1040.50, 916, 821, 780, 711, $498 \mathrm{~cm}^{-1} .{ }^{1} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta=7.34(\mathrm{~m}, 4 \mathrm{H})$, $7.31-7.26(\mathrm{~m}, 1 \mathrm{H}), 7.18-7.14(\mathrm{~m}, 1 \mathrm{H}), 7.13-7.05(\mathrm{~m}, 2 \mathrm{H}), 7.01-6.94(\mathrm{~m}, 2 \mathrm{H}), 6.89-$ $6.82(\mathrm{~m}, 3 \mathrm{H}), 4.68(\mathrm{dd}, J=8.7,4.4 \mathrm{~Hz}, 0 \mathrm{H}), 3.80(\mathrm{~s}, 1 \mathrm{H}), 2.82-2.68(\mathrm{~m}, 1 \mathrm{H}), 2.16-1.99(\mathrm{~m}$, $0 \mathrm{H}) \mathrm{pmp} .{ }^{13} \mathbf{C}$ NMR (101 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta=154.8,144.4,142.9,137.0,130.0,129.7,128.5$, 127.7, 126.9, 125.8, 121.3, 120.5, 116.8, 114.7, 73.4, 55.6, 39.0, 27.1 ppm . HRMS (ESI) calcd. for $\mathrm{C}_{22} \mathrm{H}_{23} \mathrm{NO}_{2} \mathrm{Na}[\mathrm{M}+\mathrm{Na}] \mathrm{m} / \mathrm{z} 356.1621$ found $\mathrm{m} / \mathrm{z} 235.1631$.

The enantiomeric ratio of $\mathbf{1 n}$ was determined by HPLC analysis using Daicel Chiralcel OD-H column: $n$-Hexane: isopropanol $=90: 10$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}($ channel 1$), 232$ $\mathrm{nm}($ channel 2$): \mathrm{t}_{1}($ major $)=26.2 \mathrm{~min}, \mathrm{t}_{2}($ minor $)=46.6 \mathrm{~min}$.
(S)-2-(3-hydroxy-3-phenylpropyl)phenol (10)

${ }^{1} \mathbf{H}$ NMR $(400 \mathrm{MHz}$, Chloroform- $d) \delta=7.41-7.27(\mathrm{~m}, 6 \mathrm{H}), 7.21-7.12(\mathrm{~m}, 2 \mathrm{H}), 6.91(\mathrm{td}, J$ $=7.5,1.4 \mathrm{~Hz}, 2 \mathrm{H}), 4.66(\mathrm{dd}, J=10.3,3.6 \mathrm{~Hz}, 1 \mathrm{H}), 2.99(\mathrm{ddd}, J=14.2,10.6,6.1 \mathrm{~Hz}, 1 \mathrm{H})$,
$2.77(\mathrm{ddd}, J=14.3,6.5,4.1 \mathrm{~Hz}, 1 \mathrm{H}), 2.51(\mathrm{~d}, J=35.1 \mathrm{~Hz}, 1 \mathrm{H}), 2.14(\mathrm{dddd}, J=14.3,10.3$, 6.1, $4.1 \mathrm{~Hz}, 1 \mathrm{H}), 2.05-1.90(\mathrm{~m}, 1 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=154.6,143.9$, $130.5,128.6,127.9,127.7,127.1,125.8,120.8,116.2,73.1,39.3,25.9 \mathrm{ppm}$.

The enantiomeric ratio of $\mathbf{1 0}$ was determined by HPLC analysis using Daicel Chiralcel OJ-H column: $n$-Hexane: isopropanol $=90: 10$, flow rate $0.5 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1 ), 232 $\mathrm{nm}($ channel 2$): \mathrm{t}_{1}($ major $)=43.8 \mathrm{~min}, \mathrm{t}_{2}($ minor $)=46.4 \mathrm{~min}$.
(S)-2-(3-(4-fluorophenyl)-3-hydroxypropyl)phenol (1p)


IR (neat) 3357, 2934.80, 2836.60, 1622, 1555, 1513, 1473, 1464, 1237, 1179, 1116, 1035, 992, 922, $821 \mathrm{~cm}^{-1} .{ }^{1} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta=7.34-7.27(\mathrm{~m}, 2 \mathrm{H}), 7.15$ (ddd, $J$ $=8.5,7.0,1.6 \mathrm{~Hz}, 2 \mathrm{H}), 7.08-6.98(\mathrm{~m}, 2 \mathrm{H}), 6.95-6.83(\mathrm{~m}, 2 \mathrm{H}), 4.63(\mathrm{dd}, J=10.2,3.6 \mathrm{~Hz}$, $1 \mathrm{H}), 2.95$ (ddd, $J=14.1,10.3,6.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.75$ (ddd, $J=14.3,6.7,4.2 \mathrm{~Hz}, 2 \mathrm{H}), 2.10$ (dddd, $J=14.3,10.4,6.2,4.2 \mathrm{~Hz}, 1 \mathrm{H}), 1.95(\mathrm{dddd}, J=14.0,10.3,6.7,3.6 \mathrm{~Hz}, 1 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C} \mathbf{N M R}$ $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=162.3\left(J_{\mathrm{C}-\mathrm{F}}=240 \mathrm{~Hz}\right), 154.4,139.7,139.7,130.6,127.7,127.5\left(J_{\mathrm{C}-\mathrm{F}}=\right.$ $10 \mathrm{~Hz}), 127.1,120.8,116.1,115.4\left(J_{\mathrm{C}-\mathrm{F}}=20 \mathrm{~Hz}\right), 72.4,39.4,25.9 \mathrm{ppm}$. HRMS (ESI) calcd. for $\mathrm{C}_{15} \mathrm{H}_{15} \mathrm{FO}_{2} \mathrm{Na}[\mathrm{M}+\mathrm{Na}] 269.0948 \mathrm{~m} / \mathrm{z}$ found $269.0973 \mathrm{~m} / \mathrm{z}$. The enantiomeric ratio of $\mathbf{1 p}$ was determined by HPLC analysis using Daicel Chiralcel AD column: n-Hexane : isopropanol $=90: 10$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}($ channel 1$), 232 \mathrm{~nm}($ channel 2$): \mathrm{t}_{1}$ $($ minor $)=12.3 \mathrm{~min}, \mathrm{t}_{2}($ major $)=16.2 \mathrm{~min}$.

## (S)-2-phenyl-4-(2-(phenylamino)phenyl)butan-2-ol (3a) ${ }^{5}$



IR (neat) 3355, 3141, 2901.89, 2853.68, 1609.54, 1515.43, 1389.12, 1360, 1256, 1223.34, 1189.64, 1155, 1015, 816, 711, $459 \mathrm{~cm}^{-1} .{ }^{\mathbf{1}} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta=7.47-7.42$ $(\mathrm{m}, 2 \mathrm{H}), 7.39-7.33(\mathrm{~m}, 2 \mathrm{H}), 7.29-7.26(\mathrm{~m}, 1 \mathrm{H}), 7.25-7.21(\mathrm{~m}, 2 \mathrm{H}), 7.15-7.08(\mathrm{~m}, 2 \mathrm{H})$, $6.96-6.86(\mathrm{~m}, 5 \mathrm{H}), 2.66-2.57(\mathrm{~m}, 1 \mathrm{H}), 2.40(\mathrm{ddd}, J=14.0,11.0,5.1 \mathrm{~Hz}, 1 \mathrm{H}), 2.18-2.00$ $(\mathrm{m}, 1 \mathrm{H}), 1.59(\mathrm{~s}, 3 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=147.2,144.2,140.5,132.3$, 129.9, 129.2, 128.3, 126.8, 126.7, 124.7, 121.8, 120.2, 119.2, 117.2, 74.8, 44.0, 30.6, 26.2 ppm. HRMS (ESI) calcd. for $\mathrm{C}_{22} \mathrm{H}_{23} \mathrm{NONa}[\mathrm{M}+\mathrm{Na}] \mathrm{m} / \mathrm{z} 340.1671$ found $\mathrm{m} / \mathrm{z} 340.1672$. The enantiomeric ratio of 3a was determined by HPLC analysis using Daicel Chiralcel OD-H column: $n$-Hexane: isopropanol $=90: 10$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1 ), 232 $\mathrm{nm}\left(\right.$ channel 2) $: \mathrm{t}_{1}($ minor $)=8.7 \mathrm{~min}, \mathrm{t}_{2}($ major $)=10.1 \mathrm{~min}$.

## (S)-2-(3-hydroxy-3-phenylbutyl)phenol (3b) ${ }^{5}$



IR (neat) $3361.83,3058,3028,2975,2929,1582.51,1489,1455.94,1374,1243,1218,1119$, $1065,1029,944,890,753.71,699,548 \mathrm{~cm}^{-1} .{ }^{1} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta=7.54-$ $7.44(\mathrm{~m}, 2 \mathrm{H}), 7.37(\mathrm{dd}, J=8.5,6.9 \mathrm{~Hz}, 2 \mathrm{H}), 7.30-7.23(\mathrm{~m}, 1 \mathrm{H}), 7.11-7.05(\mathrm{~m}, 1 \mathrm{H}), 7.00$ $(\mathrm{dd}, J=7.4,1.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.87-6.75(\mathrm{~m}, 2 \mathrm{H}), 6.57(\mathrm{~s}, 1 \mathrm{H}), 2.65(\mathrm{td}, J=9.4,4.8 \mathrm{~Hz}, 1 \mathrm{H})$, 2.46 (ddt, $J=15.8,9.4,4.7 \mathrm{~Hz}, 1 \mathrm{H}), 2.21(\mathrm{ddd}, J=14.3,9.4,6.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.07(\mathrm{ddd}, J=14.5$, $9.4,5.5 \mathrm{~Hz}, 1 \mathrm{H}), 1.63(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathbf{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=153.83,147.10,130.01$,
$128.32,127.46,126.79,125.44,124.67,120.38,115.95,75.47,43.86,30.49,24.76 \mathrm{ppm}$. HRMS (ESI) calcd. for $\mathrm{C}_{16} \mathrm{H}_{18} \mathrm{O}_{2} \mathrm{Na}[\mathrm{M}+\mathrm{Na}] \mathrm{m} / z 265.1211$ found $m / z$ 265.1199.

The enantiomeric ratio of $\mathbf{3 b}$ was determined by HPLC analysis using Daicel Chiralcel OD-H column: $n$-Hexane: isopropanol $=90: 10$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1), 232 $\mathrm{nm}($ channel 2$): \mathrm{t}_{1}($ minor $)=11.1 \mathrm{~min}, \mathrm{t}_{2}($ major $)=12.8 \mathrm{~min}$.

## (R)-2-(3-hydroxy-3,7-dimethyloctyl)phenol (3c) ${ }^{5}$



IR (neat) $3338.03,3071,3036,2953,2868,1593.65,1490,1457.54,1366,1243,1175,1089$, 1041, 912, 847, $751.42 \mathrm{~cm}^{-1} .{ }^{1} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta=7.09-6.97(\mathrm{~m}, 2 \mathrm{H})$, $6.82-6.72(\mathrm{~m}, 2 \mathrm{H}), 2.71-2.56(\mathrm{~m}, 2 \mathrm{H}), 1.74-1.66(\mathrm{~m}, 2 \mathrm{H}), 1.53-1.38(\mathrm{~m}, 3 \mathrm{H}), 1.31-$ $1.22(\mathrm{~m}, 2 \mathrm{H}), 1.18(\mathrm{~s}, 3 \mathrm{H}), 1.10(\mathrm{dd}, J=7.7,1.1 \mathrm{~Hz}, 2 \mathrm{H}), 0.80(\mathrm{~d}, J=6.6 \mathrm{~Hz}, 6 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=154.0,129.9,128.8,127.4,120.1,116.2,73.9,42.4,40.9,39.3$, 27.8, 26.7, 24.3, 22.6, 21.9 ppm . HRMS (ESI) calcd. for $\mathrm{C}_{16} \mathrm{H}_{26} \mathrm{O}_{2} \mathrm{Na}[\mathrm{M}+\mathrm{Na}] \mathrm{m} / \mathrm{z} 273.1837$ found $m / z$ 273.1825. The enantiomeric ratio of $\mathbf{3 c}$ was determined by HPLC analysis using Daicel Chiralcel OJ-H column: $n$-Hexane: isopropanol $=90: 10$, flow rate $0.5 \mathrm{~mL} / \mathrm{min}, \lambda=254$ $\mathrm{nm}\left(\right.$ channel 1), $232 \mathrm{~nm}\left(\right.$ channel 2) $: \mathrm{t}_{1}($ major $)=15.8 \mathrm{~min}, \mathrm{t}_{2}($ minor $)=21.2 \mathrm{~min}$.

## 29. Experimental procedures and characterization data of all final products:

## (R)-1-(4-methoxyphenyl)-2-phenylpyrrolidine (2a) ${ }^{7}$



To an oven-dried 5 ml vial equipped with a magnetic stir bar was added substrate aminoalcohol 1a ( $135.5 \mathrm{mg}, 0.5 \mathrm{mmol}$ ), MS ( $3 \AA$ ) ( 300 mg ), and $\mathrm{Fe}(\mathrm{OTf})_{3}(25.05 \mathrm{mg}, 0.05 \mathrm{mmol})$. The tube was sealed with a teflon-lined cap, connected to a vacuum and backfilled with argon three times by piercing with a needle attached to a Schlenk line. Then 2.0 ml of anhydrous DCE was added by syringe and the mixture was stirred at $90^{\circ} \mathrm{C}$ for 24 hours. After this, the reaction was cooled to room temperature and the crude was concentrated under vacuum. The crude residue was purified by column chromatography with ethyl acetate and hexanes (1:20) as solvent to obtain the pure product 2a $(98 \%, 133 \mathrm{mg}$ ) as colorless oil. IR (neat) 3059, 3044, 2966, 2901, 2829, 1618, 1513, 1490, 1450, 1363, 1262, 1240, 1179, 1174, 1042, 966, 811.93, $770.69,747.12,589 / 98,519.20 \mathrm{~cm}^{-1} .{ }^{1} \mathbf{H}$ NMR $(400 \mathrm{MHz}$, Chloroform- $d) \delta=7.37-7.32(\mathrm{~m}$, $4 \mathrm{H}), 7.28(\mathrm{~d}, J=4.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.82-6.74(\mathrm{~m}, 2 \mathrm{H}), 6.66(\mathrm{~d}, J=8.9 \mathrm{~Hz}, 2 \mathrm{H}), 4.73(\mathrm{dd}, J=7.5$, $5.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.75(\mathrm{~s}, 3 \mathrm{H}), 3.12(\mathrm{td}, J=6.8,1.9 \mathrm{~Hz}, 2 \mathrm{H}), 1.94-1.84(\mathrm{~m}, 2 \mathrm{H}), 1.81-1.73(\mathrm{~m}$, $1 \mathrm{H}), 1.72-1.64(\mathrm{~m}, 1 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR (101 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta=131.7,128.5,127.6,125.8$, 115.3, 115.2, 114.9, 99.9, 74.3, 55.8, 45.8, 36.8, 25.9 ppm. HRMS (ESI) calcd. for $\mathrm{C}_{17} \mathrm{H}_{20} \mathrm{NONa}[\mathrm{M}+\mathrm{Na}] m / z 254.1546$ found $m / z 254.1539$.

The enantiomeric ratio of 2a was determined by HPLC analysis using Daicel Chiralcel OJ-H column: $n$-Hexane : isopropanol $=95: 05$, flow rate $0.5 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1 ): $\mathrm{t}_{1}$ $($ minor $)=13.1 \mathrm{~min}, \mathrm{t}_{2}($ major $)=14.4 \mathrm{~min}$.
(R)-1,2-diphenylpyrrolidine (2b)

$S / R=92: 8$

$R / S=90: 10$

Alcohol 1b ( $120.5 \mathrm{mg}, 0.5 \mathrm{mmol}$ ), MS ( $3 \AA$ ) ( 300 mg ), and the catalyst $\mathrm{Fe}(\mathrm{OTf})_{3}(25.05 \mathrm{mg}$, 0.05 mmol ) were treated as described for $\mathbf{1 a}$ for 48 h . After completion of reaction (TLC), the crude was concentrated under vacuum and purified by a fast column chromatographic using silica gel (mess 100-200) and dichloromethane eluent obtain pure 2b ( $115.6 \mathrm{mg}, 0.96 \mathrm{mmol}$, $96 \%$ yield) as colorless oil. IR (neat) 3060, 3034, 2965, 2911, 2834, 1601, 1512, 1455, 1362, 1264, 1239, 1180, 1101, 1034, 965, 812.73, 771.90, $740.13,584 \mathrm{~cm}^{-1} .{ }^{1} \mathbf{H} \mathbf{N M R}(400 \mathrm{MHz}$, Chloroform- $d$ ) $\delta=7.36-7.19(\mathrm{~m}, 5 \mathrm{H}), 7.15(\mathrm{t}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 6.64(\mathrm{t}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.50$ (d, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 4.73(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.70(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.42(\mathrm{q}, J=8.4 \mathrm{~Hz}$, $1 \mathrm{H}), 2.38(\mathrm{tt}, J=11.0,7.9,5.9 \mathrm{~Hz}, 1 \mathrm{H}), 2.00(\mathrm{~m}, \mathrm{~Hz}, 3 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C} \mathbf{N M R}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ $\delta=147.1,144.6,128.9,128.4,126.6,125.9,115.7,112.3,62.9,49.1,36.0,23.0$ ppm. HRMS (ESI) calcd. for $\mathrm{C}_{16} \mathrm{H}_{17} \mathrm{NNa}[\mathrm{M}+\mathrm{Na}] \mathrm{m} / \mathrm{z} 246.1261$ found $m / z 246.1251$.

The enantiomeric ratio of $\mathbf{2 b}$ was determined by HPLC analysis using Daicel Chiralcel OJ-H column: $n$-Hexane: isopropanol $=95: 5$, flow rate $0.5 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1$), 232$ $\mathrm{nm}($ channel 2$): \mathrm{t}_{1}($ major $)=8.3 \mathrm{~min}, \mathrm{t}_{2}($ minor $)=9.9 \mathrm{~min}$.
(R)-2-(4-fluorophenyl)-1-(4-methoxyphenyl)pyrrolidine (2c)


1c
S/R=98:2

$R / S=95: 5$

Alcohol 1c ( $144.5 \mathrm{mg}, 0.5 \mathrm{mmol}$ ), MS ( $3 \AA \AA^{\text {) }}$ ( 300 mg ), and the catalyst $\mathrm{Fe}(\mathrm{OTf})_{3}(25.05 \mathrm{mg}$, 0.05 mmol ) were treated as described for $\mathbf{1 a}$ for 24 h and purified as described for $\mathbf{1 a}$ to obtain

2c ( $128.7 \mathrm{mg}, 0.474 \mathrm{mmol}, 95 \%$ yield) as a yellowish oil. IR (neat) 3061, 3045, 2963, 2911, $2815,1611,1525,1493,1451,1362,1281,1229,1178,1177,1044,965,812.23,771.19$, 737.12, 701.38, $523.21 \mathrm{~cm}^{-1} .{ }^{1} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta=7.20(\mathrm{~s}, 2 \mathrm{H}), 7.03-$ $6.89(\mathrm{~m}, 2 \mathrm{H}), 6.81-6.70(\mathrm{~m}, 2 \mathrm{H}), 6.42(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 4.60(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.71(\mathrm{~s}$, $3 \mathrm{H}), 3.64-3.70(\mathrm{~m} 1 \mathrm{H}), 3.34(\mathrm{q}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.38(\mathrm{t}, J=10.3 \mathrm{~Hz}, 1 \mathrm{H}), 1.98(\mathrm{~s}, 2 \mathrm{H}), 1.88$ (s, 1H) ppm. ${ }^{13} \mathbf{C}$ NMR $\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=161.2\left(J_{\mathrm{C}-\mathrm{F}}=240 \mathrm{~Hz}\right), 150.9,141.9,140.7$, $127.3\left(J_{\mathrm{C}-\mathrm{F}}=10 \mathrm{~Hz}\right), 115.2\left(J_{\mathrm{C}-\mathrm{F}}=20 \mathrm{~Hz}\right), 114.8,113.0,62.8,55.9,49.7,36.3,23.2 \mathrm{ppm}$. HRMS (ESI) calcd. for $\mathrm{C}_{17} \mathrm{H}_{19} \mathrm{NFO}[\mathrm{M}+\mathrm{H}] \mathrm{m} / \mathrm{z} 272.1447$ found $\mathrm{m} / \mathrm{z}$ 272.1445. The enantiomeric ratio of 2c was determined by HPLC analysis using Daicel Chiralcel OJ-H column: $n$-Hexane : isopropanol $=95: 5$, flow rate $0.5 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1 ), 232 $\mathrm{nm}($ channel 2$): \mathrm{t}_{1}($ minor $)=10.4 \mathrm{~min}, \mathrm{t}_{2}($ major $)=19.9 \mathrm{~min}$.
(R)-2-(4-chlorophenyl)-1-(4-methoxyphenyl)pyrrolidine (2d)


1d
S/R= 97:3


R/S= 97:3

Alcohol 1d (152.5 mg, 0.5 mmol ), MS ( $3 \AA$ ) ( 300 mg ), and the catalyst $\mathrm{Fe}(\mathrm{OTf})_{3}(25.05 \mathrm{mg}$, 0.05 mmol ) were treated as described for $\mathbf{1 a}$ for 24 h and purified as described for $\mathbf{1 a}$ to obtain 2d ( $140.6 \mathrm{mg}, 0.489 \mathrm{mmol}, 98 \%$ yield) as a yellowish oil. IR (neat) 3060, 3055, 2910, 2825, $1615,1531,1490,1450,1356,1280,1232.45,1188,1167.35,1063.54,960,811.33,770.29$, $717.11,701.41,520.83 \mathrm{~cm}^{-1} .{ }^{1} \mathbf{H}$ NMR (400 MHz, Chloroform- $d$ ) $\delta=7.33-7.23(\mathrm{~m}, 2 \mathrm{H})$, $7.19(\mathrm{~s}, 2 \mathrm{H}), 6.82-6.70(\mathrm{~m}, 2 \mathrm{H}), 6.41(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 4.59(\mathrm{dd}, J=8.6,2.7 \mathrm{~Hz}, 1 \mathrm{H})$, $3.71(\mathrm{~s}, 3 \mathrm{H}), 3.70(\mathrm{~s}, 1 \mathrm{H}), 3.34(\mathrm{q}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.44-2.28(\mathrm{~m}, 1 \mathrm{H}), 1.98(\mathrm{~s}, 2 \mathrm{H}), 1.87(\mathrm{~s}$, 1H). ${ }^{13} \mathbf{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=151.0,143.7,141.9,132.2,128.6,127.3,114.9,113.1$, 62.9, 55.9, 49.7, 36.2, 23.3 ppm . HRMS (ESI) calcd. for $\mathrm{C}_{17} \mathrm{H}_{19} \mathrm{ClNO}[\mathrm{M}+\mathrm{H}] \mathrm{m} / \mathrm{z} 288.1158$
found $m / z$ 288.11150. The enantiomeric ratio of 2d was determined by HPLC analysis using Daicel Chiralcel OJ-H column: $n$-Hexane : isopropanol $=95: 5$, flow rate $0.5 \mathrm{~mL} / \mathrm{min}, \lambda=254$ $\mathrm{nm}\left(\right.$ channel 1), $232 \mathrm{~nm}($ channel 2$): \mathrm{t}_{1}($ minor $)=24.0 \mathrm{~min}, \mathrm{t}_{2}($ major $)=33.4 \mathrm{~min}$.

## (R)-1-(4-methoxyphenyl)-2-(3-(trifluoromethoxy)phenyl)pyrrolidine (2e)


$S / R=97: 3$


1,2-Dichloroethane $90^{\circ} \mathrm{C}, 24 \mathrm{~h}$

$R / S=97: 3$

Alcohol $\mathbf{1 e}(177.5 \mathrm{mg}, 0.5 \mathrm{mmol})$, MS ( $3 \AA \AA^{\text {) }}$ ( 300 mg ), and the catalyst $\mathrm{Fe}(\mathrm{OTf})_{3}(25.05 \mathrm{mg}$, 0.05 mmol ) were treated as described for 1 a for 24 h and purified as described for $\mathbf{1 a}$ to obtain 2d ( $165.5 \mathrm{mg}, 0.485 \mathrm{mmol}, 91 \%$ yield) as a yellowish oil. IR (neat) 3061, 3053, 2921, 2822, $1611,1521,1493,1451,1352,1271,1222.35,1178,1060.57,963,801.34,771,701.41 \mathrm{~cm}^{-1}$. ${ }^{1} \mathbf{H}$ NMR $(400 \mathrm{MHz}$, Chloroform- $d$ ) $\delta=7.31(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.18(\mathrm{dd}, J=7.7,1.3 \mathrm{~Hz}$, $1 \mathrm{H}), 7.13-7.04(\mathrm{~m}, 2 \mathrm{H}), 6.81-6.71(\mathrm{~m}, 2 \mathrm{H}), 6.47-6.38(\mathrm{~m}, 2 \mathrm{H}), 4.62(\mathrm{dd}, J=8.5,2.5 \mathrm{~Hz}$, $1 \mathrm{H}), 3.72(\mathrm{~s}, 3 \mathrm{H}), 3.71-3.63(\mathrm{~m}, 1 \mathrm{H}), 3.35(\mathrm{td}, J=8.7,7.1 \mathrm{~Hz}, 1 \mathrm{H}), 2.40(\mathrm{~m}, 1 \mathrm{H}), 2.00(\mathrm{~m}$, $2 \mathrm{H}), 1.91(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathbf{C} \mathbf{N M R}\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=151.1,149.6,147.9,141.8,129.8,124.2$, 119.2, 118.8, 118.5, 114.8, 113.1, 63.1, 55.9, 49.7, 36.1, 23.3 ppm HRMS (ESI) calcd. for $\mathrm{C}_{18} \mathrm{H}_{18} \mathrm{~F}_{3} \mathrm{NO}_{2}[\mathrm{M}+\mathrm{H}] \mathrm{m} / \mathrm{z} 338.1323$ found $\mathrm{m} / \mathrm{z} 338.1320$. The enantiomeric ratio of 2e was determined by HPLC analysis using Daicel Chiralcel OJ-H column: $n$-Hexane : isopropanol $=$ 90:10, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1 ), 232 nm (channel 2 ): $\mathrm{t}_{1}$ (major) $=7.18$ $\min , \mathrm{t}_{2}($ minor $)=9.5 \mathrm{~min}$.

## (R)-1-(4-methoxyphenyl)-2-(p-tolyl)pyrrolidine (2f)


$S / R=98: 2$


R/S=91:9

Alcohol $\mathbf{1 f}(143.5 \mathrm{mg}, 0.5 \mathrm{mmol})$, MS ( $3 \AA$ ) ( 300 mg ), and the catalyst $\mathrm{Fe}(\mathrm{OTf})_{3}(25.05 \mathrm{mg}$, 0.05 mmol ) were treated as described for $\mathbf{1 a}$ for 24 h and purified as described for $\mathbf{1 a}$ to obtain 2f ( $124.1 \mathrm{mg}, 0.464 \mathrm{mmol}, 93 \%$ yield) as a colorless oil. IR (neat) $3068,3050,2911,2821$, $1609,1530,1491,1453,1372,1273,1231.42,1137,1166.32,1064.43,961,816.43,771.49$, $707.13,521.93 \mathrm{~cm}^{-1} .{ }^{1} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta=7.27-7.17(\mathrm{~m}, 4 \mathrm{H}), 6.91-6.81$ $(\mathrm{m}, 2 \mathrm{H}), 6.60-6.51(\mathrm{~m}, 2 \mathrm{H}), 4.72(\mathrm{dd}, J=8.3,2.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H}), 3.80-3.75(\mathrm{~m}$, $1 \mathrm{H}), 3.45(\mathrm{td}, J=8.9,6.6 \mathrm{~Hz}, 1 \mathrm{H}), 2.53-2.45(\mathrm{~m}, 1 \mathrm{H}), 2.44(\mathrm{~s}, 3 \mathrm{H}), 2.21-2.09(\mathrm{~m}, 1 \mathrm{H})$, $2.08-1.96(\mathrm{~m}, 2 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR ( $\left.100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=150.7,142.2,142.1,136.0,129.1$, 125.8, 114.8, 112.9, 63.1, 55.9, 49.6, 43.4, 36.3, 23.3, 21.0 ppm . HRMS (ESI) calcd. for $\mathrm{C}_{18} \mathrm{H}_{22} \mathrm{NO}[\mathrm{M}+\mathrm{H}] \mathrm{m} / \mathrm{z} 268.1705$ found $\mathrm{m} / \mathrm{z} 268.1696$.

The enantiomeric ratio of $\mathbf{2 f}$ was determined by HPLC analysis using Daicel Chiralcel OJ-H column: $n$-Hexane : isopropanol $=95: 5$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1), 232 $\mathrm{nm}($ channel 2$): \mathrm{t}_{1}($ major $)=11.4 \mathrm{~min}, \mathrm{t}_{2}($ major $)=12.5 \mathrm{~min}$.

## (R)-2-(3-methoxyphenyl)-1-(4-methoxyphenyl)pyrrolidine (2g)


$\mathrm{S} / \mathrm{R}=98: 2$
1g


1,2-Dichloroethane $90^{\circ} \mathrm{C}, 24 \mathrm{~h}$


$R / S=98: 2$

Alcohol $\mathbf{1 g}(150.5 \mathrm{mg}, 0.5 \mathrm{mmol})$, MS ( $3 \AA$ ) $\left(300 \mathrm{mg}\right.$ ), and the catalyst $\mathrm{Fe}(\mathrm{OTf})_{3}(25.05 \mathrm{mg}$, 0.05 mmol ) were treated as described for $\mathbf{1 a}$ for 24 h and purified as described for $\mathbf{1 a}$ to obtain $\mathbf{2 g}(119.4 \mathrm{mg}, 0.421 \mathrm{mmol}, 88 \%$ yield) as a colorless oil. IR (neat) 3068, 3050, 2911, 2821,
$1609,1530,1491,1453,1372,1273,1231.42,1137,1166.32,1064.43,961,816.43,771.49$, $707.13,521.93 \mathrm{~cm}^{-1} .{ }^{1} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta=7.22(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.94-$ $6.64(\mathrm{~m}, 5 \mathrm{H}), 6.44(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 4.65-4.50(\mathrm{~m}, 1 \mathrm{H}), 3.77(\mathrm{~s}, 3 \mathrm{H}), 3.71(\mathrm{~s}, 3 \mathrm{H}), 3.67(\mathrm{~d}$, $J=10.1 \mathrm{~Hz}, 1 \mathrm{H}), 3.34(\mathrm{q}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.37(\mathrm{tt}, J=11.5,7.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.12-1.80(\mathrm{~m}$, $3 \mathrm{H}) .{ }^{13} \mathbf{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=159.8,150.9,147.2,142.2,129.4,118.3,114.8,113.0$, $111.9,111.6,63.5,55.9,55.1,49.7,36.2,23.4 \mathrm{ppm}$. HRMS (ESI) calcd. for $\mathrm{C}_{18} \mathrm{H}_{22} \mathrm{NO}_{2}$ $[\mathrm{M}+\mathrm{H}] \mathrm{m} / \mathrm{z} 284.1649$ found $\mathrm{m} / \mathrm{z} 284.1645$.

The enantiomeric ratio of $\mathbf{2 g}$ was determined by HPLC analysis using Daicel Chiralcel OJ-H column: $n$-Hexane : isopropanol $=95: 05$, flow rate $0.5 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1 ), 232 $\mathrm{nm}($ channel 2$): \mathrm{t}_{1}($ minor $)=27.8 \mathrm{~min}, \mathrm{t}_{2}($ major $)=35.4 \mathrm{~min}$.

## (R)-2-phenyltetrahydrofuran (2h) ${ }^{7}$



Alcohol $\mathbf{1 h}(83 \mathrm{mg}, 0.5 \mathrm{mmol})$, MS ( $3 \AA$ ) $\left(300 \mathrm{mg}\right.$ ), and the catalyst $\mathrm{Fe}(\mathrm{OTf})_{3}(25.05 \mathrm{mg}, 0.05$ mmol) were treated as described for 1 a for 12 h . After completion of reaction (TLC), the crude was concentrated under vacuum and purified by a fast column chromatographic using silica gel (mess 100-200) and dichloromethane eluent obtain pure $\mathbf{2 h}(82 \mathrm{mg}, 0.98 .8 \mathrm{mmol}$, $99 \%$ yield) as colorless oil. ${ }^{1}$ H NMR $(400 \mathrm{MHz}$, Chloroform- $d) \delta=7.37-7.30(\mathrm{~m}, 4 \mathrm{H}), 7.28$ - $7.22(\mathrm{~m}, 1 \mathrm{H}), 4.90(\mathrm{t}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.10(\mathrm{dt}, J=8.3,6.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.94(\mathrm{td}, J=7.8,6.4$ $\mathrm{Hz}, 1 \mathrm{H}), 2.38-2.26(\mathrm{~m}, 1 \mathrm{H}), 2.07-1.95(\mathrm{~m}, 2 \mathrm{H}), 1.87-1.76(\mathrm{~m}, 1 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR (101 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=143.4,128.2,127.1,125.6,80.7,68.6,34.6,26.0 \mathrm{ppm}$. The enantiomeric ratio of 2h was determined by HPLC analysis using Daicel Chiralcel OJ-H column: $n$-Hexane : isopropanol $=95: 05$, flow rate $0.5 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}($ channel 1$): \mathrm{t}_{1}($ minor $)=9.2 \mathrm{~min}, \mathrm{t}_{2}$ $($ major $)=10.1 \mathrm{~min}$.

## (R)-2-(4-fluorophenyl)tetrahydrofuran (2i) ${ }^{8}$



Alcohol $1 \mathbf{1 i}(83 \mathrm{mg}, 0.5 \mathrm{mmol})$, MS ( $3 \AA$ ) $(300 \mathrm{mg})$, and the catalyst $\mathrm{Fe}(\mathrm{OTf})_{3}(25.05 \mathrm{mg}, 0.05$ mmol ) were treated as described for $\mathbf{1 a}$ for 12 h . After completion of reaction (TLC), the crude was concentrated under vacuum and purified by a fast column chromatographic using silica gel (mess 100-200) and dichloromethane eluent obtain pure $\mathbf{2 i}(82 \mathrm{mg}, 0.98 .8 \mathrm{mmol}$, $99 \%$ yield) as colorless oil. ${ }^{1} \mathbf{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=7.31-7.26(\mathrm{~m}, 2 \mathrm{H}), 7.03-6.98(\mathrm{~m}$, $2 \mathrm{H}), 4.85(\mathrm{t}, J=6.8 \mathrm{~Hz}), 4.08(\mathrm{q}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.94(\mathrm{q}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 2.34-2.26(\mathrm{~m}, 1 \mathrm{H})$, 2.04-1.96(m, 1H), 1.80-1.71 (m, 1H) ppm. ${ }^{13} \mathbf{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=162.0\left(J_{\mathrm{C}-\mathrm{F}}=\right.$ $250 \mathrm{~Hz}), 139.1,139.0,127.2\left(J_{\mathrm{C}-\mathrm{F}}=10 \mathrm{~Hz}\right), 115.0\left(J_{\mathrm{C}-\mathrm{F}}=20 \mathrm{~Hz}\right), 80.1,68.6,34.6,25.9 \mathrm{ppm}$. The enantiomeric ratio of $\mathbf{2 i}$ was determined by HPLC analysis using Daicel Chiralcel OJ-H column: $n$-Hexane : isopropanol $=80: 20$, flow rate $0.5 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1 ): $\mathrm{t}_{1}$ $($ major $)=12.3 \mathrm{~min}, \mathrm{t}_{2}($ minor $)=13.8 \mathrm{~min}$.

## (R)-1-(4-methoxyphenyl)-2-vinylpyrrolidine (2j) ${ }^{9}$



1j
$\mathrm{S} / \mathrm{R}=99: 1$


R/S=94:6

Alcohol $\mathbf{1 j}$ ( $110.5 \mathrm{mg}, 0.5 \mathrm{mmol}$ ), MS ( $3 \AA$ ) ( 300 mg ), and the catalyst $\mathrm{Fe}(\mathrm{OTf})_{3}(25.05 \mathrm{mg}$, $0.05 \mathrm{mmol})$ were treated as described for $\mathbf{1 a}$ at $100^{\circ} \mathrm{C}$ for 48 h . After completion of reaction (TLC), the crude was concentrated under vacuum and purified by the column chromatographic using silica gel (mess 100-200) to obtain pure $\mathbf{2 j}$ ( $89 \mathrm{mg}, 0.438 \mathrm{mmol}, 88 \%$ yield) as colorless oil. IR (neat) $\mathrm{cm}^{-1} 3040,2955.9,2890,2875,2821,1616.5,1575.6,1513$,
$1460,1365,1274,1241.5,1181,1166,1045,970,820,591 \mathrm{~cm}^{-1} .{ }^{1} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta=6.87-6.81(\mathrm{~m}, 2 \mathrm{H}), 6.61-6.55(\mathrm{~m}, 2 \mathrm{H}), 5.84(\mathrm{ddd}, J=17.1,10.2,5.4 \mathrm{~Hz}$, $1 \mathrm{H}), 5.19-5.08(\mathrm{~m}, 2 \mathrm{H}), 4.10$ (dddd, $J=6.7,5.4,2.6,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.77(\mathrm{~s}, 3 \mathrm{H}), 3.49$ (ddd, $J$ $=8.4,7.0,2.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.22(\mathrm{td}, J=8.7,6.9 \mathrm{~Hz}, 1 \mathrm{H}), 2.21-1.91(\mathrm{~m}, 4 \mathrm{H}), 1.83(\mathrm{ddt}, J=8.7$, $6.1,3.0 \mathrm{~Hz}, 1 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=150.8,142.5,139.9,114.8,114.3$, 112.9, 61.4, 55.9, 49.2, 32.7, 23.3 ppm . HRMS (ESI) calcd. for $\mathrm{C}_{13} \mathrm{H}_{18} \mathrm{NO}[\mathrm{M}+\mathrm{H}] 204.1383$ $\mathrm{m} / \mathrm{z}$ found $204.1386 \mathrm{~m} / \mathrm{z}$. The enantiomeric ratio of $\mathbf{2} \mathbf{j}$ was determined by HPLC analysis using Daicel Chiralcel OJ-H column: $n$-Hexane: isopropanol $=99.5: 0.5$, flow rate 0.5 $\mathrm{mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}($ channel 1$): \mathrm{t}_{1}($ major $)=60.5 \mathrm{~min}, \mathrm{t}_{2}($ minor $)=63.1 \mathrm{~min}$.

## (S)-1-(4-methoxyphenyl)-2-methylpyrrolidine (2k)



1k


$\mathrm{S} / \mathrm{R}=2: 98$

Alcohol $\mathbf{1 k}$ ( $104.5 \mathrm{mg}, 0.5 \mathrm{mmol}$ ), MS ( $3 \AA$ ) ( 300 mg ), and the catalyst $\mathrm{Fe}(\mathrm{OTf})_{3}(25.05 \mathrm{mg}$, 0.05 mmol ) were treated as described for $\mathbf{1 a}$ at $100^{\circ} \mathrm{C}$ for 48 h . After completion of reaction (TLC), the crude was concentrated under vacuum and purified by the column chromatographic using silica gel (mess $100-200$ ) to obtain pure $2 \mathrm{k}(76.4 \mathrm{mg}, 0.4 \mathrm{mmol}, 80 \%$ yield) as colorless oil. IR (neat) $\mathrm{cm}^{-1} 3045,2961,2930,2874,2824,1616,1575,1464,1329$, $1275,1245,1181,1164,1041,970,811.6,591 \mathrm{~cm}^{-1} .{ }^{1} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta=$ $6.97-6.87(\mathrm{~m}, 2 \mathrm{H}), 6.68-6.56(\mathrm{~m}, 2 \mathrm{H}), 3.85(\mathrm{td}, J=6.5,2.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.82(\mathrm{~s}, 3 \mathrm{H}), 3.52-$ $3.43(\mathrm{~m}, 1 \mathrm{H}), 3.17(\mathrm{td}, J=8.8,7.0 \mathrm{~Hz}, 1 \mathrm{H}), 2.21-1.91(\mathrm{~m}, 3 \mathrm{H}), 1.75(\mathrm{dp}, J=5.3,2.6,2.2$ $\mathrm{Hz}, 1 \mathrm{H}), 1.23(\mathrm{~d}, J=6.2 \mathrm{~Hz}, 3 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=150.6,142.2,114.9$, $112.7,55.9,54.0,48.9,33.1,23.3,19.5 \mathrm{ppm}$. The enantiomeric ratio of $\mathbf{2 k}$ was determined by

HPLC analysis using Daicel Chiralcel OJ-H column: $n$-Hexane : isopropanol = 99.5:0.5, flow rate $0.5 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}($ channel 1$): \mathrm{t}_{1}($ minor $)=30.0 \mathrm{~min}, \mathrm{t}_{2}($ major $)=60.6 \mathrm{~min}$.

## (S)-2-ethyl-1-(4-methoxyphenyl)pyrrolidine (21)



$R / S=99: 1$
$S / R=96.5: 3.5$
Alcohol 11 ( $111.5 \mathrm{mg}, 0.5 \mathrm{mmol}$ ), MS ( $3 \AA$ ) ( 300 mg ), and the catalyst $\mathrm{Fe}(\mathrm{OTf})_{3}(25.05 \mathrm{mg}$, 0.05 mmol ) were treated as described for $\mathbf{1 a}$ at $100^{\circ} \mathrm{C}$ for 48 h . After completion of reaction (TLC), the crude was concentrated under vacuum and purified by the column chromatographic using silica gel (mess 100-200) to obtain pure $21(85.07 \mathrm{mg}, 0.419 \mathrm{mmol}$, $83 \%$ yield) as colorless oil. IR (neat) $\mathrm{cm}^{-1} 3044,2960.59,2931,2873,2829,1619.75$, $1574.68,1512.9,1464,1363,1327,1274,1240.55,1180,1163,1044,969,810.9,590,525$ $\mathrm{cm}^{-1} .{ }^{1} \mathbf{H}$ NMR $(400 \mathrm{MHz}$, Chloroform- $d$ ) $\delta=7.01-6.93(\mathrm{~m}, 2 \mathrm{H}), 6.69-6.60(\mathrm{~m}, 2 \mathrm{H}), 3.87$ $(\mathrm{s}, 3 \mathrm{H}), 3.62(\mathrm{tt}, J=7.2,2.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.57-3.48(\mathrm{~m}, 1 \mathrm{H}), 3.25-3.14(\mathrm{~m}, 1 \mathrm{H}), 2.20-1.99$ $(\mathrm{m}, 3 \mathrm{H}), 1.99-1.81(\mathrm{~m}, 2 \mathrm{H}), 1.50-1.33(\mathrm{~m}, 1 \mathrm{H}), 1.06(\mathrm{t}, J=7.5 \mathrm{~Hz}, 3 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR (100 MHz, $\mathrm{CDCl}_{3}$ ) $\delta=150.5,142.4,114.9,112.5,60.4,55.7,49.0,29.8,26.0,23.5,10.5$ ppm. HRMS (ESI) calcd. For $\mathrm{C}_{13} \mathrm{H}_{20} \mathrm{NO}[\mathrm{M}+\mathrm{H}] 206.1539 \mathrm{~m} / \mathrm{z}$ found $206.1546 \mathrm{~m} / \mathrm{z}$. The enantiomeric ratio of $\mathbf{2 l}$ was determined by HPLC analysis using Daicel Chiralcel OJ-H column: $n$-Hexane $:$ isopropanol $=99.5: 0.5$, flow rate $0.5 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1 ): $\mathrm{t}_{1}$ $($ minor $)=25.8 \mathrm{~min}, \mathrm{t}_{2}($ minor $)=63.8 \mathrm{~min}$.

## (R)-1-(4-methoxyphenyl)-2-phenylpiperidine (2m)



Alcohol 1m (142.58 mg, 0.5 mmol$)$, MS ( $3 \AA$ ) ( 300 mg ), and the catalyst $\mathrm{Fe}(\mathrm{OTf})_{3}(25.05 \mathrm{mg}$, 0.05 mmol ) were treated as described for $\mathbf{1 a}$ for 24 h and purified as described for $\mathbf{1 a}$ to obtain $\mathbf{2 m}$ ( $116.1 \mathrm{mg}, 0.434 \mathrm{mmol}, 87 \%$ yield) as a colorless oil. IR (neat) 3060, 3044, 2956, 2915, 2830, 1611, 1512, 1491, 1451, 1360, 1261, 1245, 1180, 1171, 961.56, 811.75, 771.69, 748.15, $590.1,521.25 \mathrm{~cm}^{-1} .{ }^{1} \mathbf{H}$ NMR ( 400 MHz , Chloroform-d) $\delta=7.19-7.14(\mathrm{~m}, 2 \mathrm{H}), 7.13-7.06$ $(\mathrm{m}, 2 \mathrm{H}), 7.03-6.96(\mathrm{~m}, 1 \mathrm{H}), 6.87-6.76(\mathrm{~m}, 2 \mathrm{H}), 6.63-6.52(\mathrm{~m}, 2 \mathrm{H}), 3.96(\mathrm{dd}, J=9.5,3.3$ $\mathrm{Hz}, 1 \mathrm{H}), 3.61(\mathrm{~s}, 3 \mathrm{H}), 3.35-3.25(\mathrm{~m}, 1 \mathrm{H}), 2.81(\mathrm{ddd}, J=12.0,10.1,3.5 \mathrm{~Hz}, 1 \mathrm{H}), 1.90-1.81$ $(\mathrm{m}, 1 \mathrm{H}), 1.72$ (dddd, $J=15.0,13.4,10.5,6.4 \mathrm{~Hz}, 4 \mathrm{H}), 1.47-1.38(\mathrm{~m}, 1 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR $\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=144.7,128.0,127.4,126.1,123.7,113.7,99.9,92.9,64.4,56.4,55.3$, 36.1, 26.5, 24.1 ppm . HRMS (ESI) calcd. for $\mathrm{C}_{18} \mathrm{H}_{22} \mathrm{NO}[\mathrm{M}+\mathrm{H}] \mathrm{m} / \mathrm{z} 268.1702$ found $\mathrm{m} / \mathrm{z}$ 268.1696. The enantiomeric ratio of $\mathbf{2 m}$ was determined by HPLC analysis using Daicel Chiralcel OJ-H column: $n$-Hexane : isopropanol $=95: 05$, flow rate $0.5 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ $($ channel 1$), 232 \mathrm{~nm}($ channel 2$): \mathrm{t}_{1}($ minor $)=13.6 \mathrm{~min}, \mathrm{t}_{2}($ major $)=20.5 \mathrm{~min}$.

## (R)-1-(4-methoxyphenyl)-2-phenyl-1,2,3,4-tetrahydroquinoline (2n)




Alcohol 1n ( $166.58 \mathrm{mg}, 0.5 \mathrm{mmol})$, MS ( $3 \AA$ ) ( 300 mg ), and the catalyst $\mathrm{Fe}(\mathrm{OTf})_{3}(25.05 \mathrm{mg}$, 0.05 mmol ) were treated as described for $\mathbf{1 a}$ for 24 h and purified as described for $\mathbf{1 a}$ to obtain 2n ( $157.5 \mathrm{mg}, 0.5 \mathrm{mmol}, 100 \%$ yield) as a colorless oil. IR (neat) $3013,2931,2852,1602$, $1508,1451,1361,1289.97,1238.08,1211,1179,1101,933.6,827.75,756.69,700.08,552.2$ $\mathrm{cm}^{-1} .{ }^{1} \mathbf{H}$ NMR $(400 \mathrm{MHz}$, Chloroform- $d$ ) $\delta=7.21(\mathrm{~d}, J=4.4 \mathrm{~Hz}, 4 \mathrm{H}), 7.15(\mathrm{dd}, J=4.8,3.7$ $\mathrm{Hz}, 1 \mathrm{H}), 7.07-7.01(\mathrm{~m}, 2 \mathrm{H}), 6.99-6.94(\mathrm{~m}, 1 \mathrm{H}), 6.93-6.85(\mathrm{~m}, 1 \mathrm{H}), 6.78-6.70(\mathrm{~m}, 2 \mathrm{H})$, $6.60(\mathrm{td}, J=7.3,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.52(\mathrm{dd}, J=8.3,1.1 \mathrm{~Hz}, 1 \mathrm{H}), 4.78(\mathrm{~d}, J=4.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.71(\mathrm{~s}$, $3 \mathrm{H}), 2.71-2.52(\mathrm{~m}, 2 \mathrm{H}), 2.25(\mathrm{ddt}, J=12.9,11.4,4.9 \mathrm{~Hz}, 1 \mathrm{H}), 2.14-2.02(\mathrm{~m}, 1 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=156.8,145.2,144.2,140.5,129.2,128.3,128.2,126.7,126.7$, 126.7, 122.4, 116.8, 114.7, 114.1, 63.7, 55.4, 28.9, 23.7 ppm. HRMS (ESI) calcd. for $\mathrm{C}_{22} \mathrm{H}_{21} \mathrm{NNaO}[\mathrm{M}+\mathrm{Na}] m / z 338.1508$ found $m / z 338.1515$.

The enantiomeric ratio of $\mathbf{2 n}$ was determined by HPLC analysis using Daicel Chiralcel OJ-H column: $n$-Hexane : isopropanol $=96: 4$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1), 232 $\mathrm{nm}($ channel 2$): \mathrm{t}_{1}($ minor $)=10.5 \mathrm{~min}, \mathrm{t}_{2}($ major $)=11.9 \mathrm{~min}$.

## (R)-2-phenylchromane (2o)



Alcohol $\mathbf{1 0}$ ( $114 \mathrm{mg}, 0.5 \mathrm{mmol}$ ), MS ( $3 \AA$ ) ( 300 mg ), and the catalyst $\mathrm{Fe}(\mathrm{OTf})_{3}(25.05 \mathrm{mg}$, $0.05 \mathrm{mmol})$ were treated as described for $\mathbf{1 a}$ at $-20^{\circ} \mathrm{C}$ for 48 h . After completion of reaction (TLC), the crude was concentrated under vacuum and purified by the column chromatographic using silica gel (mess 100-200) to obtain pure $\mathbf{2 0}$ ( $95 \mathrm{mg}, 0.454 \mathrm{mmol}, 91 \%$ yield) as colorless oil. ${ }^{1} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta=7.50-7.38(\mathrm{~m}, 4 \mathrm{H}), 7.38-$ $7.31(\mathrm{~m}, 1 \mathrm{H}), 7.21-7.08(\mathrm{~m}, 2 \mathrm{H}), 6.99-6.85(\mathrm{~m}, 2 \mathrm{H}), 5.10(\mathrm{dd}, J=10.1,2.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.03$
(dddd, $J=17.3,11.2,6.0,1.1 \mathrm{~Hz}, 1 \mathrm{H}), 2.83(\mathrm{ddd}, J=16.5,5.3,3.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.25(\mathrm{dddd}, J=$ 13.7, $5.9,3.3,2.5 \mathrm{~Hz}, 1 \mathrm{H}$ ), 2.13 (dddd, $J=13.7,11.3,10.1,5.3 \mathrm{~Hz}, 1 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR ( 100 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=155.1,141.7,129.5,128.5,127.8,127.3,125.9,121.8,120.3,116.9,76.7$, 29.9, 25.1 ppm . The enantiomeric ratio of $\mathbf{2 0}$ was determined by HPLC analysis using Daicel Chiralcel JM column: $n$-Hexane: isopropanol $=98: 2$, flow rate $0.5 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ $($ channel 1$): \mathrm{t}_{1}($ major $)=8.9 \mathrm{~min}, \mathrm{t}_{2}($ minor $)=14.2 \mathrm{~min}$.

## ( $R$ )-2-(4-fluorophenyl)chromane (2p)



Alcohol $\mathbf{1 p}(123 \mathrm{mg}, 0.5 \mathrm{mmol})$, MS ( $3 \AA$ ) $\left(300 \mathrm{mg}\right.$ ), and the catalyst $\mathrm{Fe}(\mathrm{OTf})_{3}(25.05 \mathrm{mg}$, 0.05 mmol ) were treated as described for $\mathbf{1 a}$ at $-20^{\circ} \mathrm{C}$ for 48 h . After completion of reaction (TLC), the crude was concentrated under vacuum and purified by the column chromatographic using silica gel (mess 100-200) to obtain pure $\mathbf{2 p}$ ( $92 \mathrm{mg}, 0.419 \mathrm{mmol}, 81 \%$ yield) as colorless oil. ${ }^{1} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta=7.47-7.39(\mathrm{~m}, 2 \mathrm{H}), 7.21-$ $7.06(\mathrm{~m}, 4 \mathrm{H}), 6.97-6.87(\mathrm{~m}, 2 \mathrm{H}), 5.08(\mathrm{dd}, J=10.2,2.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.15-2.94(\mathrm{~m}, 1 \mathrm{H}), 2.84$ (ddd, $J=16.5,5.3,3.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.23(\mathrm{dddd}, J=13.7,5.8,3.2,2.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.10(\mathrm{dddd}, J=$ $13.7,11.3,10.2,5.3 \mathrm{~Hz}, 1 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=162.4\left(J_{\mathrm{C}-\mathrm{F}}=250 \mathrm{~Hz}\right)$, $154.9,137.5,137.5,129.5,127.73\left(J_{\mathrm{C}-\mathrm{F}}=10 \mathrm{~Hz}\right), 127.4,121.7,120.4,116.9,115.3\left(J_{\mathrm{C}-\mathrm{F}}=20\right.$ Hz ), $30.00,25.04 \mathrm{ppm}$. ppm. The enantiomeric ratio of $\mathbf{2 p}$ was determined by HPLC analysis using Daicel Chiralcel JM-column: $n$-Hexane : isopropanol $=95: 5$, flow rate $1 \mathrm{~mL} / \mathrm{min}, \lambda=$ $254 \mathrm{~nm}\left(\right.$ channel 1): $\mathrm{t}_{1}($ major $)=6.5 \mathrm{~min}, \mathrm{t}_{2}($ minor $)=9.7 \mathrm{~min}$.

## (R)-2-methyl-1,2-diphenyl-1,2,3,4-tetrahydroquinoline (4a)


$S / R=99: 1$
$R / S=98: 2$
Alcohol 3a ( $158.5 \mathrm{mg}, 0.5 \mathrm{mmol})$ and the catalyst $\mathrm{Fe}(\mathrm{OTf})_{3}(25.05 \mathrm{mg}, 0.05 \mathrm{mmol})$ in $\mathrm{DCE}+$ $n$-Hexane (1:1) were treated as described for 1a at room temperature for 48 h and purified as described for 1a to obtain $\mathbf{4 a}(146.51 \mathrm{mg}, 0.5 \mathrm{mmol}, 98 \%$ yield) as a white color solid. IR (neat) 3028, 3057.11, 29.79.30, 2935.16, 2845, 1602, 1591, 1575.59, 1492, 1455.32, 1378, $1319,1236.83,1156,1132,1072,1026,1003,933.49,841,763,746,699.48 \mathrm{~cm}^{-1} .{ }^{\mathbf{1}} \mathbf{H}$ NMR (400 MHz, Chloroform- $d$ ) $\delta=7.47-7.36(\mathrm{~m}, 2 \mathrm{H}), 7.29(\mathrm{tt}, J=4.0,3.3 \mathrm{~Hz}, 4 \mathrm{H}), 7.24-7.18$ (m, 2H), $7.18-7.13(\mathrm{~m}, 2 \mathrm{H}), 6.98-6.84(\mathrm{~m}, 2 \mathrm{H}), 6.61(\mathrm{td}, J=7.3,1.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.33(\mathrm{dd}, J=$ 8.3, 1.2 Hz, 1H), 2.71 (dt, $J=16.3,4.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.40(\mathrm{ddd}, J=16.7,12.3,5.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.25$ (ddd, $J=12.8,5.3,3.6 \mathrm{~Hz}, 1 \mathrm{H}), 2.15(\mathrm{td}, J=12.6,4.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.44(\mathrm{~s}, 3 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR $\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=147.6,146.3,144.3,131.0,129.2,129.1,128.2,126.5,126.5,126.3$, 125.9, 121.7, 116.4, 114.7, 61.3, 37.8, 29.4, 24.8 ppm . HRMS (ESI) calcd. for $\mathrm{C}_{22} \mathrm{H}_{21} \mathrm{NNa}$ [M+Na] $m / z 322.1570$ found $m / z 322.1574$.

The enantiomeric ratio of $\mathbf{4 a}$ was determined by HPLC analysis using Daicel Chiralcel OD-H column: $n$-Hexane : isopropanol $=99: 1$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1 ), 232 $\mathrm{nm}($ channel 2$): \mathrm{t}_{1}($ major $)=4.7 \mathrm{~min}, \mathrm{t}_{2}($ minor $)=5.6 \mathrm{~min}$.

## (R)-2-methyl-2-phenylchromane (4b)



Alcohol 3b (121.5 mg, 0.5 mmol$)$ and the catalyst $\mathrm{Fe}(\mathrm{OTf})_{3}(25.05 \mathrm{mg}, 0.05 \mathrm{mmol})$ in $\mathrm{DCE}+$ $n$-Hexane (1:1) were treated as described for $\mathbf{1 a}$ at $-15^{\circ} \mathrm{C}$ temperature for 48 h and purified as described for 1a to obtain $\mathbf{4 b}(122 \mathrm{mg}, 0.5 \mathrm{mmol}, 100 \%$ yield) as a white color solid. IR (neat) 3060, 3024.55, 2977.79, 2929, 2849, 16010.53, 1582, 1522.56, 1488, 1456, 1446, $1373,1340.54,1305.83,1243.57,1167,1119,1069,1029,971,945.49,826,753,699.68,548$ $\mathrm{cm}^{-1} .{ }^{1} \mathbf{H}$ NMR $(400 \mathrm{MHz}$, Chloroform- $d$ ) $\delta=7.38(\mathrm{dd}, J=8.4,1.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.30(\mathrm{ddd}, J=$ $7.8,6.8,1.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.24-7.18(\mathrm{~m}, 1 \mathrm{H}), 7.17-7.10(\mathrm{~m}, 1 \mathrm{H}), 7.04-6.91(\mathrm{~m}, 2 \mathrm{H}), 6.81(\mathrm{td}$, $J=7.4,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.67(\mathrm{dt}, J=16.1,4.9 \mathrm{~Hz}, 1 \mathrm{H}), 2.51-2.34(\mathrm{~m}, 2 \mathrm{H}), 2.09(\mathrm{ddd}, J=13.7$, $10.5,5.4 \mathrm{~Hz}, 1 \mathrm{H}), 1.66(\mathrm{~s}, 3 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=154.1,145.6,129.3$, 128.3, 127.3, 126.7, 124.9, 121.6, 119.9, 116.9, 78.3, 32.9, 30.1, 22.6 ppm. HRMS (ESI) calcd. for $\mathrm{C}_{16} \mathrm{H}_{16} \mathrm{NNa}[\mathrm{M}+\mathrm{Na}] \mathrm{m} / \mathrm{z} 247.1231$ found $m / z 322.1225$.

The enantiomeric ratio of $\mathbf{4 b}$ was determined by HPLC analysis using Daicel Chiralcel OD-H column: $n$-Hexane : isopropanol $=99: 1$, flow rate $0.5 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1 ), 232 $\mathrm{nm}($ channel 2$): \mathrm{t}_{1}($ major $)=20.1 \mathrm{~min}, \mathrm{t}_{2}($ minor $)=22.2 \mathrm{~min}$.

## (S)-2-methyl-2-(4-methylpentyl)chromane (4c)



Alcohol 3c ( $125.15 \mathrm{mg}, 0.5 \mathrm{mmol}$ ) and the catalyst $\mathrm{Fe}(\mathrm{OTf})_{3}(25.05 \mathrm{mg}, 0.05 \mathrm{mmol})$ in DCE $+n$-Hexane (1:1) were treated as described for 1a at $-15^{\circ} \mathrm{C}$ temperature for 48 h and purified as described for $\mathbf{1 a}$ to obtain $\mathbf{4 c}(106 \mathrm{mg}, 0.456 \mathrm{mmol}, 92 \%$ yield) as a colorless oil. IR (neat) 3374, 3041, 2928, 2865, 1603, 1515, 1430, 1319, 1254, 1214, 1170, 1155, 1063, 1023, 824, $693 \mathrm{~cm}^{-1} .{ }^{\mathbf{1}} \mathbf{H}$ NMR (400 MHz, Chloroform-d) $\delta 7.12-7.02(\mathrm{~m}, 2 \mathrm{H}), 6.84-6.75(\mathrm{~m}, 2 \mathrm{H})$, $2.75(\mathrm{t}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 1.86-1.72(\mathrm{~m}, 2 \mathrm{H}), 1.60-1.50(\mathrm{~m}, 2 \mathrm{H}), 1.37(\mathrm{ddd}, J=14.4,9.5,7.6$
$\mathrm{Hz}, 2 \mathrm{H}), 1.28(\mathrm{~s}, 3 \mathrm{H}), 1.24-1.08(\mathrm{~m}, 3 \mathrm{H}), 0.86(\mathrm{~d}, J=6.6 \mathrm{~Hz}, 6 \mathrm{H}) .{ }^{\mathbf{1 3}} \mathbf{C} \mathbf{~ N M R}(101 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right) \delta=153.8,129.4,127.2,121.1,119.4,117.2,76.2,39.8,39.3,30.6,27.9,24.2,22.6$, 22.6, 22.1, 21.4 ppm . HRMS (ESI) calcd. for $\mathrm{C}_{16} \mathrm{H}_{24} \mathrm{ONa}[\mathrm{M}+\mathrm{Na}] \mathrm{m} / \mathrm{z} 255.1719$ found $\mathrm{m} / \mathrm{z}$ 255.1713. The enantiomeric ratio of $\mathbf{4 c}$ was determined by HPLC analysis using Daicel Chiralcel OD-H column: $n$-Hexane : isopropanol $=99: 1$, flow rate $1.0 \mathrm{~mL} / \mathrm{min}, \lambda=254 \mathrm{~nm}$ (channel 1), $232 \mathrm{~nm}($ channel 2$): \mathrm{t}_{1}($ major $)=6.3 \mathrm{~min}, \mathrm{t}_{2}($ minor $)=3.9 \mathrm{~min}$.

## 30. Characterization data of synthesized intermediates

## 3-(hydroxymethyl)-1-phenylbutane-1,4-diol (1 ${ }^{\prime}$ )



IR (neat) $3337.11,3063,3031,2931.01,1603,1493,1453,1348,1205,1218,1156,1028$, $913.78,849,757.33,700.74,553.70 \mathrm{~cm}^{-1} .{ }^{1} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta=7.38-$ $7.30(\mathrm{~m}, 4 \mathrm{H}), 7.29-7.22(\mathrm{~m}, 1 \mathrm{H}), 4.80(\mathrm{dd}, J=8.7,4.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.80-3.58(\mathrm{~m}, 4 \mathrm{H}), 2.75(\mathrm{~s}$, $3 \mathrm{H}), 1.93(\mathrm{q}, J=5.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.86-1.69(\mathrm{~m}, 2 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C} \mathbf{N M R}\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=$ 144.8, 128.5, 127.6, 125.6, 72.8, 65.4, 65.3, 40.5, 38.6 ppm . HRMS (ESI) calcd. for $\mathrm{C}_{11} \mathrm{H}_{16} \mathrm{NaO}_{3}[\mathrm{M}+\mathrm{Na}] m / z 219.0994$ found $m / z 219.0992$.

## 2-(hydroxy(phenyl)methyl)-1-phenylbutane-1,4-diol (1 ${ }^{\prime \prime}$ )



IR (neat) 3314.70, 3027, 2924.74, 1603, 1493, 1450, 1342, 1202, 1217, 1089, 1047.97, 1028.09, 913.28, 744.08, 701.12, $655 \mathrm{~cm}^{-1} .{ }^{\mathbf{1}} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta=7.45-$ $7.35(\mathrm{~m}, 4 \mathrm{H}), 7.34-7.24(\mathrm{~m}, 3 \mathrm{H}), 7.23-7.11(\mathrm{~m}, 3 \mathrm{H}), 5.05(\mathrm{~d}, J=4.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.96(\mathrm{~d}, J=$ $2.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.55(\mathrm{t}, J=6.1 \mathrm{~Hz}, 2 \mathrm{H}), 2.15(\mathrm{dtd}, J=7.2,4.6,2.2 \mathrm{~Hz}, 1 \mathrm{H}), 1.80(\mathrm{ddt}, J=14.2$, 8.0, $6.1 \mathrm{~Hz}, 1 \mathrm{H}), 1.60-1.46(\mathrm{~m}, 1 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR $\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=143.1,142.7$,
128.5, 128.1, 127.4, 126.8, 125.8, 125.5, 75.4, 72.4, 60.8, 48.4, 27.3 ppm . HRMS (ESI) calcd. for $\mathrm{C}_{17} \mathrm{H}_{20} \mathrm{NaO}_{3}[\mathrm{M}+\mathrm{Na}] \mathrm{m} / z 295.1305$ found $\mathrm{m} / \mathrm{z}$ 295.1298.

## 1-(4-methoxyphenyl)piperidin-2-one (K2)



IR (neat) 2953, 2905, 2839, 1683, 1652, 1601, 1510, 1492, 1459, 1360.65, 1331, 1295, 1268, 1247.94, 1223, 1178, 1105, 1031, 830, 755, 730.61, $601,575,556.49 \mathrm{~cm}^{-1} .{ }^{\mathbf{1}} \mathbf{H} \mathbf{N M R}(400$ MHz , Chloroform- $d$ ) $\delta=7.19-7.10(\mathrm{~m}, 2 \mathrm{H}), 6.93-6.87(\mathrm{~m}, 2 \mathrm{H}), 3.80(\mathrm{~s}, 3 \mathrm{H}), 3.62-3.56$ $(\mathrm{m}, 2 \mathrm{H}), 2.58-2.50(\mathrm{~m}, 2 \mathrm{H}), 1.97-1.87(\mathrm{~m}, 4 \mathrm{H}) .{ }^{13} \mathbf{C}$ NMR $\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=153.8$, $129.4,127.2,121.1,119.4,117.2,76.2,39.8,39.3,30.6,27.9,24.2,22.6,22.6,22.0,21.4$ ppm.
(S)-1-phenylethan-1-ol (N)

${ }^{1}$ H NMR $(400 \mathrm{MHz}$, Chloroform- $d$ ) $\delta=7.40-7.32(\mathrm{~m}, 4 \mathrm{H}), 7.31-7.24(\mathrm{~m}, 1 \mathrm{H}), 4.89(\mathrm{q}, J=$ $6.4 \mathrm{~Hz}, 1 \mathrm{H}), 1.50(\mathrm{~d}, J=6.5 \mathrm{~Hz}, 3 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR $\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=145.8,128.4$, 127.4, 125.3, 70.4, 25.1 ppm .
(S)-1-phenylethyl diisopropylcarbamate (O)

${ }^{1} \mathbf{H}$ NMR $(400 \mathrm{MHz}$, Chloroform- $d$ ) $\delta=7.40-7.29(\mathrm{~m}, 4 \mathrm{H}), 7.31-7.22(\mathrm{~m}, 1 \mathrm{H}), 5.85(\mathrm{q}, J=$ $6.6 \mathrm{~Hz}, 1 \mathrm{H}), 1.55(\mathrm{~d}, J=6.6 \mathrm{~Hz}, 3 \mathrm{H}), 1.20(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 12 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR ( 101 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta=155.0,142.8,128.4,127.4,126.0,72.7,46.1$ (br), 22.8, 21.3 (br) ppm.

## 2-iodo-N-phenylaniline ( $\mathbf{Q}$ )


${ }^{1} \mathbf{H}$ NMR $(400 \mathrm{MHz}$, Chloroform- $d$ ) $\delta=7.83-7.76(\mathrm{~m}, 1 \mathrm{H}), 7.34(\mathrm{dd}, J=8.5,7.4 \mathrm{~Hz}, 2 \mathrm{H})$, $7.24-7.20(\mathrm{~m}, 2 \mathrm{H}), 7.15(\mathrm{dt}, J=7.8,1.1 \mathrm{~Hz}, 2 \mathrm{H}), 7.09-7.02(\mathrm{~m}, 1 \mathrm{H}), 6.64(\mathrm{ddd}, J=7.9$, $5.4,3.3 \mathrm{~Hz}, 1 \mathrm{H}), 5.93(\mathrm{~s}, 1 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta=143.9,141.9,139.5$, 129.4, 129.0, 122.5, 121.9, 119.9, 115.9, 88.8 ppm .

## 1-(4-methoxyphenyl)pyrrolidin-2-one (A2)


${ }^{1}$ H NMR ( 400 MHz , Chloroform- $d$ ) $\delta=7.52-7.44(\mathrm{~m}, 2 \mathrm{H}), 6.93-6.82(\mathrm{~m}, 2 \mathrm{H}), 3.80(\mathrm{~d}, J=$ $6.9 \mathrm{~Hz}, 2 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H}), 2.56(\mathrm{t}, J=8.1 \mathrm{~Hz}, 2 \mathrm{H}), 2.18-2.05(\mathrm{~m}, 2 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR (101 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=173.8,156.5,132.6,121.7,113.9,55.4,49.1,32.4,17.9 \mathrm{ppm}$.

## (5-phenyltetrahydrofuran-3-yl)methanol (2h')


${ }^{1}$ H NMR ( 400 MHz , Chloroform- $d$ ) $\delta=7.41-7.32(\mathrm{~m}, 10 \mathrm{H}), 7.29(\mathrm{dq}, J=6.0,2.9 \mathrm{~Hz}, 3 \mathrm{H})$, $5.00(\mathrm{t}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.88(\mathrm{dd}, J=9.4,6.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.24(\mathrm{dd}, J=8.8,7.1 \mathrm{~Hz}, 1 \mathrm{H}), 4.04$ (dd, $J=8.8,7.5 \mathrm{~Hz}, 1 \mathrm{H}$ ), 3.95 (dd, $J=8.8,5.6 \mathrm{~Hz}, 1 \mathrm{H}$ ), 3.77 (dd, $J=8.8,5.9 \mathrm{~Hz}, 2 \mathrm{H}$ ), 3.69 (dd, $J=10.9,7.0 \mathrm{~Hz}, 2 \mathrm{H}), 3.65(\mathrm{dd}, J=6.9,1.9 \mathrm{~Hz}, 2 \mathrm{H}), 2.72-2.54(\mathrm{~m}, 2 \mathrm{H}), 2.48(\mathrm{ddd}, J=$
$12.5,8.1,6.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.19(\mathrm{ddd}, J=12.3,7.2,5.0 \mathrm{~Hz}, 1 \mathrm{H}), 2.00(\mathrm{ddd}, J=12.7,8.5,7.3 \mathrm{~Hz}$, $1 \mathrm{H}), 1.90-1.80(\mathrm{~m}, 2 \mathrm{H}), 1.77(\mathrm{~s}, 1 \mathrm{H}), 1.55(\mathrm{ddd}, J=12.4,9.4,7.8 \mathrm{~Hz}, 1 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=143.1,142.3,128.3,128.3,127.3,127.2,125.7,125.5,81.2,80.1$, $71.1,70.9,65.1,64.5,42.4,41.7,37.8,37.3 \mathrm{ppm}$. HRMS (ESI) calcd. for $\mathrm{C}_{11} \mathrm{H}_{14} \mathrm{NaO}_{2}$ [M+Na] $\mathrm{m} / \mathrm{z} 201.0886$ found $m / z 201.0881$.

## Phenyl(2-phenyltetrahydrofuran-3-yl)methyl acetate (2h")



IR (neat) 3063, 3032, 2947, 2875.58, 1738, 1494, 1455, 1371, 1233.84, 1063, 1024, 962, 913, $756.71,700 \mathrm{~cm}^{-1} .{ }^{1} \mathbf{H}$ NMR ( 400 MHz , Chloroform- $d$ ) $\delta=7.38-7.33(\mathrm{~m}, 8 \mathrm{H}), 7.32-7.27$ $(\mathrm{m}, 2 \mathrm{H}), 7.25-7.18(\mathrm{~m}, 4 \mathrm{H}), 7.08(\mathrm{ddd}, J=7.9,1.6,0.6 \mathrm{~Hz}, 3 \mathrm{H}), 5.79(\mathrm{~d}, J=9.7 \mathrm{~Hz}, 1 \mathrm{H})$, $4.78(\mathrm{~d}, J=6.3 \mathrm{~Hz}, 1 \mathrm{H}), 4.02-3.98(\mathrm{~m}, 1 \mathrm{H}), 3.98-3.92(\mathrm{~m}, 1 \mathrm{H}), 2.88-2.77(\mathrm{~m}, 1 \mathrm{H}), 2.11$ $(\mathrm{s}, 3 \mathrm{H}), 2.09-2.03(\mathrm{~m}, 1 \mathrm{H}), 1.91-1.83(\mathrm{~m}, 1 \mathrm{H}) \mathrm{ppm} .{ }^{13} \mathbf{C}$ NMR $\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta=$ 173.8, 156.5, 132.6, 121.7, 113.9, 55.4, 49.1, 32.4, 17.9 ppm. HRMS (ESI) calcd. for $\mathrm{C}_{19} \mathrm{H}_{20} \mathrm{NaO}_{3}[\mathrm{M}+\mathrm{Na}] \mathrm{m} / \mathrm{z} 319.1305$ found $m / z 319.1310$.

## 31. Reference

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12. Copies of HPLC chromatograms for all starting alcohols and products:

1a:


1a: racemates


1b:


1b: racemates


1c:


## 1c: racemates



1d:


## 1d: racemates



1e:


## 1e: racemates



1f:


## 1f: racemates



1g:


## 1g: racemates



1h:


1h: racemates


1i:


## 1i: racemates



1 j :


## 1 j : racemates



1k:


## 1k : racemates



11:


## 11 : racemates



## 1m:



## 1m: racemates



1n:


1n: racemates


10:


10: racemates

$1 p:$


## 1p: racemates



3a:


3a: racemates


3b:


3b: racemates


3c:


3c: racemates


2a:


## 2a: racemates



2b:


2b: racemates


2c:


## 2c: racemates



2d:


2d: racemates


2e


2e: racemates


2f:


## 2f: racemates



2g:


## 2g: racemates



2h:


2h: racemates

$2 i$


## 2i: racemates



2j

$2 \mathbf{j}$ : racemates


2k


2k: racemates


## 21



## 21 : racemates



2m


## 2m:racemates



2n:


2n: racemates


20


## 20 : racemates



2p

$2 p$ : racemates


4a:


4a: racemates


4b:


4b: racemates


4c:


## 4c: racemates



## 33. Copies of NMR for all starting alcohols and products:

1a $\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$

$170 \quad 160 \quad 1$
100
$\mathrm{f} 1(\mathrm{ppm})$

## 1b $\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$

JS-RW-SS-phenyl-151128. ஜ0.fid


RW-JS-272-SM-Ph-13CNMR-170712.10.fid



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| 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |

## 1c $\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$



JS-RW-46-B-pure-20151203.11.fid


1d ( ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\mathrm{CDCl}_{3}$ )
JS-RW-50-B-pure-20151203.10.fid



JS-RW-50-B-pure-20151203.11.fid


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| 200 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | $\begin{gathered} 110 \\ \text { f1 }(\mathrm{ppm}) \end{gathered}$ | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 |

## 1e $\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$

JS-RW-39-pure-es 1103.10. fid
RW-JS-40-B-pure-13CNMR-170628.10.fid

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| 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |

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


JS-RW-47-B-pure-151203.11.fid


|  |  | 1 | 1 |  |  |  | 1 |  |  |  |  | 1 | 70 |  |  | 1 | 1 | 1 |  |
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| :00 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | $\begin{gathered} 100 \\ \mathrm{f} 1(\mathrm{ppm}) \end{gathered}$ | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |

## 1g ( ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$






JS-RW-48-A-pure-13C-NMR-151203.10.fid




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


RW-JS-266-SM-pure-13CNMR-170519.10.fid




| , | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | , | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
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| 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | $\begin{gathered} 100 \\ \mathrm{f} 1(\mathrm{ppm}) \end{gathered}$ | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |

$1 \mathbf{i}\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$

RW-JS-SB-401-F-SM-alcohol-20170616.10.fi̊


RW-JS-SB-401-F-SM-alcohol-20170616.11.fid


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

AB5-141-AC-170622.10.fid


AB5-141-AC-170622.11.fid


1k $\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$
AB4-60-AP1-160227-2.10.fid


AB4-60-AP1-160227-2.11.fid


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## $11\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$

AB5-142-AC-160815.10.fid



AB5-142-AC-160815.11.fid


## 1m ( ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\mathrm{CDCl}_{3}$ )

JS-RW-69-b-1H-NMR-160211.10.fid $\frac{\mathrm{U}}{0}$



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| :00 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | $\begin{aligned} & 100 \\ & \mathrm{f} 1(\mathrm{ppm}) \end{aligned}$ | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |

## 1n $\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$

RW-JS-85-B-pure-1HNMR-170519.10.fid
0


RW-JS-85-B-pure-13CNMR-170519.10.fid





| 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |

## $10\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$

AB6-176A-AC1-170622.10.fid


AB6-176A-AC1-170622.12.fid


1p ( ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\mathrm{CDCl}_{3}$ )

AB7-19-AC1-170622.10.fid

## 



AB7-19-AC1-170622.12.fid


1h ' $\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$



RW-JS-265-SM-pure-anon-13CNMR170521.10.fid




| 1 |  |  | 1 |  |  |  |  |  |  |  |  | 1 | 1 | 1 | 1 |  |  |  |  |  |
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| 200 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |

1h" ${ }^{\prime \prime}\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$



RW-JS-268-SM-pure-re-20170616.12.fid




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| 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |

## 3a $\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$

RW-JS-259-B-pure-1HNMR-170413.10.fid




RW-JS-259-B-pure-13CNMR-170413.10.fid





## 3b $\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$

RW-JS-219-B-pure-1HNMR -re-20170520.10.fid M
0
0



## 3c $\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$

RW-JS-13
8




RW-JS-130-A-pure-13CNMR160701.10.fid

| $\begin{aligned} & \stackrel{\rightharpoonup}{0} \\ & \stackrel{1}{\oplus} \end{aligned}$ |
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2a ( ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\mathrm{CDCl}_{3}$ )

JS-RW-29-pure-151203.10.fid
응


JS-RW-29-pure-13C-NMR-151203.10.fid


## 2b $\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$

JS-RW-59-M-151212.10用


RW-JS-272-productpur-13CNMR-170712.10.fid

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| :---: | :---: |
| 守 |  |
|  | $\sim$ |

$\mathcal{L}^{77.317} 77.000 \mathrm{CDCl} 3$

76.682 ${ }_{-62.890}$| -49.082 |
| :--- |
| -36.057 |
| -23.068 |



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| 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | $\begin{gathered} 100 \\ \mathrm{f} 1(\mathrm{ppm}) \end{gathered}$ | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |

2c ( ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$


[^0]2d ( ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\mathrm{CDCl}_{3}$ )


RW-JS-55-B-pure-13CNMR-re2170521.10.fid

| $\int_{-77.000 \mathrm{CDCl}}{ }^{77.318}$ |
| :---: |
| ${ }_{76.684}$ |
| $-62.877$ |
| -55.886 |
| -49.732 |
| -36.218 |
| - 23.278 |



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| 200 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | $\begin{array}{r} 110 \\ f 1 \end{array}$ | $\begin{aligned} & 100 \\ & \mathrm{~m}) \end{aligned}$ | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |

## 2e（ ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR， $\left.\mathrm{CDCl}_{3}\right)$

RW－JS．56．B9్రure－1HNMR－re20170627．10．fid


RW－JS．56．B－pure－13CNMR－re20170627．10．fid

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## $2 f\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$





RW-JS-202B-pure-13CNMR-re20170521.10.fid

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| 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |

2g ( ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\mathrm{CDCl}_{3}$ )


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RW-JS-54-B-pure-13CNMRre2-170521.10.fid




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| 200 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |

2h ( ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\mathrm{CDCl}_{3}$ )

RW-JS-266-@f.pure-1HNMRre170523.10.fid


RW-JS-266-A-pure-13CNMRre170523.10.fid
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| 200 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | $\begin{aligned} & 100 \\ & \mathrm{f} 1(\mathrm{ppm}) \end{aligned}$ | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | 0 |

## $2 \mathbf{2}\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$

RW-JS-269-B-pure-1HNMR-1응709.10.fid



RW-JS-269-B-pure-13CNMR-170709.10.fid

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2j( ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$

AB5-120-P-AC1-170624.10.fid



AB5-120-P-AC1-170624.11.fid


2k $\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$

AB5-123-AC1-160803.20.fid

##  




AB5-123-AC1-160803.21.fid

$21\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$

AB5-22-AC3-170622.10.fid


AB5-22-AC3-170622.11.fid

$\mathbf{2 m}\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$


JS-RW-70-H-13-CNMR-160304.10.fid

$\substack{77.317 \\ 77.308 \\ 76.683}$
-64.446
-56.389
-55.258

-36.138

-26.472
-24.150

[^1]2n ( ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$

JS-RW-86-pure-20160314.10.fid
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JS-RW-86-pure-13CNMR-20160314.10.fid

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-28.914
-23.731

$20\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$

AB6-179-5-AP2-170214-2.10.fid



AB6-179-5-AP2-170214-2.11.fid


2p ( ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\mathrm{CDCl}_{3}$ )

AB7-25-AF-170622.10.fid


AB7-25-AF-170622.11.fid


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$\begin{array}{lllllllllllllllllll}30 & 170 & 160 & 150 & 140 & 130 & 120 & 110 & 100 & \begin{array}{cc}90 & 80 \\ f 1(\mathrm{ppm})\end{array} & 70 & 60 & 50 & 40 & 30 & 20 & 10 & 0\end{array}$

2h' $\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$

AB7-61-AC-170530.10.fid



AB7-61-AC-170530.11.fid

$\begin{array}{llllllllllllllllll}30 & 170 & 160 & 150 & 140 & 130 & 120 & 110 & 100 & \begin{array}{cc}90 & 80 \\ f 1 & (\mathrm{ppm})\end{array} & 70 & 60 & 50 & 40 & 30 & 20 & 10 & 0\end{array}$

## 2h" $\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$

RW-JS-86-OAc-II-re-1HNMR-170611.10.fid 응


RW-JS-86-OAc-II-re-13NMR-170611.10.fid


| 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | T | 1 | 1 | 1 | 1 | 1 | 1 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |

4a ( ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\mathrm{CDCl}_{3}$ )


RW-JS-254-A-pure-13CNMR-170413.10.fid


4b ( ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\mathrm{CDCl}_{3}$ )
RW-JS-221-B-pure-1HNMR170202. 胃.fid


RW-JS-221-B-pure-13CNMR170202.10.fid

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| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | $\begin{gathered} 100 \\ \mathrm{f} 1(\mathrm{nDm}) \end{gathered}$ | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |

$4 c\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$

RW응S-136-B-160701.10.fid


RW-JS_136-C-13CNMR-pure-160702.10.fid



A1 $\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$

RW-JS-01-1HNMR-170603.10.fid


RW-JS-01-13CNMR-170603.10.fid



-32.373
-17.929


| T | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 200 | 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | $\begin{gathered} 100 \\ \mathrm{f} 1(\mathrm{ppm}) \end{gathered}$ | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |

$\mathbf{K}\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$


RW-JS-199-pure-13CNMR-161129.10.fid

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| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 90 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |

## $\mathbf{M}\left({ }^{1} \mathrm{H}\right.$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\left.\mathrm{CDCl}_{3}\right)$

RW-JS-109-1HNMR-170603.10.fid

## 名





RW-JS-109-13CNMR-170603.10.fid



|  |  | 1 |  |  |  |  |  |  |  | 1 | 1 | 10 |  | 1 |  |  |  | 1 |
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| 190 | 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | 100 | 90 | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 |

J ( ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR, $\mathrm{CDCl}_{3}$ )


RW-JS-2Phethanol-13CNMR-170603.10.fid

$\stackrel{m}{\underset{\sim}{j}}$


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


[^0]:    $\begin{array}{lllllllllllll}210 & 200 & 190 & 180 & 170 & 160 & 150 & 140 & 130 & 120 & 110 & 100 \\ & & & & & & & & & & \mathrm{f1}(\mathrm{ppm})\end{array}$

[^1]:    $\begin{array}{lllllllllllllllllllllllllllllllllllllllllllll}150 & 145 & 140 & 135 & 130 & 125 & 120 & 115 & 110 & 105 & 100 & 95 & 90 & 85 & 80 & 75 & 70 & 65 & 60 & 55 & 50 & 45 & 40 & 35 & 30 & 25 & 20 & 15 & 10 & 5 & 0\end{array}$

