# Supporting Information 

# Facile Construction of Three Contiguous Stereogenic Centers via Dynamic Kinetic Resolution in Asymmetric Transfer Hydrogenation of Quinolines 

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## 1. General and Materials:

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

Materials: Commercially available reagents were used throughout without further purification other than those detailed below. The solvents for asymmetric transfer hydrogenation reaction were purchased without further purification.

## 2. Synthesis of 4-Substituted-1,2,3,4-tetrahydroacridines:

1,2,3,4-Tetrahydroacridine and 4-substituted-1,2,3,4-tetrahydroacridine derivatives 1a, 1i, $\mathbf{1 f}$ are known compounds and can be conveniently synthesized from the easily accessible starting materials according to the known literature procedures. ${ }^{[1]}$

### 2.1. Synthesis of 4-substituted-1,2,3,4-tetrahydroacridines (1b-1h): ${ }^{[2]}$



General procedure for synthesis of 4-substituted-1,2,3,4-tetrahydroacridine derivatives: To a stirred solution of 1,2,3,4-tetrahydroacridine ( $0.412 \mathrm{~g}, 2.3 \mathrm{mmol}$ ) in anhydrous $\mathrm{Et}_{2} \mathrm{O}(20 \mathrm{~mL})$ at $0{ }^{\circ} \mathrm{C}$ under nitrogen was added a solution of $2.5 \mathrm{M} n$-butyllithium in hexanes $(1.0 \mathrm{~mL}, 2.5 \mathrm{mmol}$, 1.08 equiv). The resultant yellow solution was stirred at $0{ }^{\circ} \mathrm{C}$ for 10 min and stirred at room temperature for 2 h . After cooling down below $0{ }^{\circ} \mathrm{C}$, R-X ( $2.8 \mathrm{mmol}, 1.2$ equiv) was added to the solution and stirred for overnight. A solution of saturated ammonium chloride ( 5 mL ) was added to quench the reaction. This reaction mixture was then warmed to room temperature and was extracted with $\mathrm{Et}_{2} \mathrm{O}(3 \times 10 \mathrm{~mL})$. The extracts were combined, dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc $=15: 1$ ) to yield the products $\mathbf{1 b} \mathbf{- 1 h}$.

4-Ethyl-1,2,3,4-tetrahydroacridine (1b): $62 \%$ yield, yellow oil, $\mathrm{R}_{f}=0.50$ (petroleum ether/EtOAc $=15: 1) ;{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.00(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.79(\mathrm{~s}, 1 \mathrm{H}), 7.69(\mathrm{~d}$,
 $J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.59(\mathrm{dd}, J=11.2,4.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.43(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.06-$ $2.92(\mathrm{~m}, 3 \mathrm{H}), 2.23-2.17(\mathrm{~m}, 1 \mathrm{H}), 2.10-2.05(\mathrm{~m}, 1 \mathrm{H}), 1.99-(\mathrm{m}, 1 \mathrm{H}), 1.87-$ $1.77(\mathrm{~m}, 2 \mathrm{H}), 1.71-1.65(\mathrm{~m}, 1 \mathrm{H}), 1.05(\mathrm{t}, J=7.5 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( 100 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 162.7,146.9,134.8,130.9,128.6,128.2,127.1,126.8,125.5,43.1,29.7,28.1,27.0,20.1$, 11.8; HRMS (ESI) $m / z$ Calculated for $\mathrm{C}_{15} \mathrm{H}_{18} \mathrm{~N}[\mathrm{M}+\mathrm{H}]^{+}$212.1439, found 212.1437.

[^0]4-Propyl-1,2,3,4-tetrahydroacridine (1c): $42 \%$ yield, yellow oil, $\mathrm{R}_{f}=0.48$ (petroleum ether/EtOAc $=15: 1) ;{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.01(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.79(\mathrm{~s}, 1 \mathrm{H}), 7.69(\mathrm{~d}$,
 $J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.60(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.43(\mathrm{t}, J=7.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.07(\mathrm{dd}, J=$ $10.0,4.5 \mathrm{~Hz}, 1 \mathrm{H}), 2.96(\mathrm{dd}, \mathrm{J}=10.1,6.0 \mathrm{~Hz}, 2 \mathrm{H}), 2.16-2.05(\mathrm{~m}, 2 \mathrm{H}), 2.00-$ $1.94(\mathrm{~m}, 1 \mathrm{H}), 1.88-1.76(\mathrm{~m}, 2 \mathrm{H}), 1.64-1.44(\mathrm{~m}, 3 \mathrm{H}), 0.98(\mathrm{t}, J=7.3 \mathrm{~Hz}, 3 \mathrm{H})$; ${ }^{13} \mathrm{C}$ NMR (100 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 162.8,146.8,134.7,130.8,128.6,128.2,127.1$, $126.8,125.5,41.6,37.7,29.6,27.6,20.6,20.0,14.3$; HRMS (ESI) $\mathrm{m} / \mathrm{z}$ Calculated for $\mathrm{C}_{16} \mathrm{H}_{20} \mathrm{~N}$ $[\mathrm{M}+\mathrm{H}]^{+} 226.1596$, found 226.1600 .

4-Butyl-1,2,3,4-tetrahydroacridine (1d): $41 \%$ yield, pale solid, $\mathrm{mp}=41-42{ }^{\circ} \mathrm{C}, \mathrm{R}_{f}=0.60$ (petroleum ether/EtOAc $=15: 1) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.01(\mathrm{~d}, \mathrm{~J}=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.78(\mathrm{~s}$,
 $1 \mathrm{H}), 7.69(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.59(\mathrm{ddd}, J=8.3,6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.46-7.38$ (m, 1H), 3.06 (dd, $J=10.0,4.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.96(\mathrm{dd}, J=10.3,6.1 \mathrm{~Hz}, 2 \mathrm{H}), 2.20$ $-2.03(\mathrm{~m}, 2 \mathrm{H}), 2.03-1.91(\mathrm{~m}, 1 \mathrm{H}), 1.89-1.72(\mathrm{~m}, 2 \mathrm{H}), 1.65(\mathrm{dd}, J=7.8,2.4$ $\mathrm{Hz}, 1 \mathrm{H}), 1.51-1.29(\mathrm{~m}, 4 \mathrm{H}), 0.93(\mathrm{t}, J=7.2 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( 100 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 163.0,146.9,135.0,131.0,128.7,128.4,127.2,126.9,125.7,41.9,35.4,29.9,29.8,27.6$, 23.2, 20.1, 14.4; HRMS (ESI) $\mathrm{m} / \mathrm{z}$ Calculated for $\mathrm{C}_{17} \mathrm{H}_{22} \mathrm{~N}[\mathrm{M}+\mathrm{H}]^{+} 240.1752$, found 240.1750 .

4-Allyl-1,2,3,4-tetrahydroacridine (1e): $81 \%$ yield, yellow oil, $\mathrm{R}_{f}=0.68$ (petroleum ether/EtOAc $=10: 1) ;{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.00(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.78(\mathrm{~s}, 1 \mathrm{H}), 7.68(\mathrm{~d}$,
 $J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.59(\mathrm{ddd}, J=8.4,6.9,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.42(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H})$, $6.02-5.78(\mathrm{~m}, 1 \mathrm{H}), 5.07$ (ddd, $J=13.6,10.9,0.6 \mathrm{~Hz}, 2 \mathrm{H}), 3.21-3.08(\mathrm{~m}, 1 \mathrm{H})$, $3.05-2.91(\mathrm{~m}, 3 \mathrm{H}), 2.51-2.36(\mathrm{~m}, 1 \mathrm{H}), 2.14-1.90(\mathrm{~m}, 2 \mathrm{H}), 1.86-1.72(\mathrm{~m}$, $2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 161.8,147.2$, 137.7, 135.0, 131.1, 128.8, 128.5, 127.3, 127.0, 125.8, 116.4, 41.4, 39.9, 29.9, 27.5, 20.3; HRMS (ESI) $\mathrm{m} / \mathrm{z}$ Calculated for $\mathrm{C}_{16} \mathrm{H}_{18} \mathrm{~N}[\mathrm{M}+\mathrm{H}]^{+}$224.1439, found 224.1438 .

4-Ethyl-7-methoxy-1,2,3,4-tetrahydroacridine (1g): $61 \%$ yield, pale solid, $\mathrm{mp}=92-93{ }^{\circ} \mathrm{C}$, $\mathrm{R}_{f}=0.67$ (petroleum ether/EtOAc $\left.=10: 1\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.90(\mathrm{~d}, J=9.2 \mathrm{~Hz}, 1 \mathrm{H})$,
 $7.68(\mathrm{~s}, 1 \mathrm{H}), 7.27-7.24(\mathrm{~m}, 1 \mathrm{H}), 6.96(\mathrm{~d}, J=2.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.90(\mathrm{~s}, 3 \mathrm{H})$, $2.93(\mathrm{t}, J=6.7 \mathrm{~Hz}, 3 \mathrm{H}), 2.20-2.14(\mathrm{~m}, 1 \mathrm{H}), 2.09-2.03(\mathrm{~m}, 1 \mathrm{H}), 1.97-$ $1.92(\mathrm{~m}, 1 \mathrm{H}), 1.87-1.73(\mathrm{~m}, 2 \mathrm{H}), 1.69-1.64(\mathrm{~m}, 1 \mathrm{H}), 1.03(\mathrm{t}, J=7.4 \mathrm{~Hz}$, $3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 160.0,157.1,143.0,133.7,131.1,130.0,127.8,120.9,104.3$, 55.4, 42.8, 29.7, 28.1, 27.1, 20.1, 11.8; HRMS (ESI) $\mathrm{m} / \mathrm{z}$ Calculated for $\mathrm{C}_{16} \mathrm{H}_{20} \mathrm{NO}[\mathrm{M}+\mathrm{H}]^{+}$ 242.1545 , found 242.1543 .

4-Ethyl-7-fluoro-1,2,3,4-tetrahydroacridine (1h): 53\% yield, a yellow oil, $\mathrm{R}_{f}=0.67$ (petroleum ether/EtOAc $=10: 1) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.08-7.91(\mathrm{~m}, 1 \mathrm{H}), 7.35(\mathrm{t}, J=$
 $8.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.30-7.19(\mathrm{~m}, 1 \mathrm{H}), 2.93(\mathrm{~s}, 3 \mathrm{H}), 2.30-2.12(\mathrm{~m}, 1 \mathrm{H}), 2.11-$ $2.02(\mathrm{~m}, 1 \mathrm{H}), 2.03-1.88(\mathrm{~m}, 1 \mathrm{H}), 1.89-1.74(\mathrm{~m}, 2 \mathrm{H}), 1.72-1.58(\mathrm{~m}, 1 \mathrm{H})$, $1.04(\mathrm{t}, J=7.4 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 162.1,160.1(\mathrm{~d}, J=$ $244.0 \mathrm{~Hz}), 144.1,134.2(\mathrm{~d}, J=5.3 \mathrm{~Hz}), 132.0,131.2(\mathrm{~d}, J=9.1 \mathrm{~Hz}), 127.6(\mathrm{~d}, J=9.0 \mathrm{~Hz}), 118.5$ $(\mathrm{d}, J=15.0 \mathrm{~Hz}), 109.7(\mathrm{~d}, J=21.0 \mathrm{~Hz}), 43.2,29.8,28.2,27.2,20.2,12.0 ;{ }^{19} \mathrm{~F}$ NMR ( 376 MHz , $\mathrm{CDCl}_{3}$ ) $\delta-115.3$; HRMS (ESI) $\mathrm{m} / \mathrm{z}$ Calculated for $\mathrm{C}_{15} \mathrm{H}_{17} \mathrm{NF}[\mathrm{M}+\mathrm{H}]^{+} 230.1345$, found 242.1340 .

### 2.2. Synthesis of 4-phenyl-1,2,3,4-tetrahydroacridine (1i):



Typical procedure: a mixture of 2-aminobenzyl alcohol ( $0.616 \mathrm{mg}, 5.0 \mathrm{mmol}$ ), 2-phenylcyclohexanone ( $1.307 \mathrm{mg}, 7.5 \mathrm{mmol}$ ), $\mathrm{RuCl}_{2}\left(\mathrm{PPh}_{3}\right)_{3}(0.024 \mathrm{mg}, 0.025 \mathrm{mmol})$ and $\mathrm{KO}^{t} \mathrm{Bu}$ $(0.561 \mathrm{mg}, 5.0 \mathrm{mmol})$ in 1,4-dioxane $(10 \mathrm{ml})$ was placed in a dry 50 mL Schlenk tube. The system was flushed with argon and allowed to react at $80^{\circ} \mathrm{C}$ for 16 h . The reaction mixture was filtered through a short silica gel column (ethyl acetate), washed with brine and dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$. Removal of the solvent left a crude mixture, which was separated by flash chromatography on silica gel (petroleum ether/EtOAc $=15: 1$ ) to yield the product $\mathbf{1 i}$.

4-Phenyl-1,2,3,4-tetrahydroacridine (1i): Pale solid, $72 \%$ yield, $\mathrm{mp}=133-134{ }^{\circ} \mathrm{C}, \mathrm{R}_{f}=$ 0.43 (petroleum ether/EtOAc $=15: 1) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.00-7.83(\mathrm{~m}, 2 \mathrm{H}), 7.70(\mathrm{~d}$,
 $J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.54(\mathrm{t}, J=7.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.41(\mathrm{t}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.17(\mathrm{dt}, J=$ $13.2,7.1 \mathrm{~Hz}, 3 \mathrm{H}), 6.96(\mathrm{~d}, J=7.1 \mathrm{~Hz}, 2 \mathrm{H}), 4.54(\mathrm{~d}, J=4.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.16-2.85$ (m, 2H), $2.38-2.07(\mathrm{~m}, 2 \mathrm{H}), 1.98-1.63(\mathrm{~m}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 160.3,147.1,146.3,135.2,131.5,129.1,128.8,128.4,128.1,127.4,126.8,125.9,125.8,48.3$, 32.6, 29.3, 19.2; HRMS (ESI) $m / z$ Calculated for $\mathrm{C}_{19} \mathrm{H}_{18} \mathrm{~N}[\mathrm{M}+\mathrm{H}]^{+} 260.1439$, found 260.1440 .

## 3. Synthesis of Dimethyl 2,6-dipropyl-1,4-dihydropyridine-3,5-dicarboxylate (4g)



In a dry Schlenk tube, $7.209 \mathrm{~g}(50.0 \mathrm{mmol}, 2.0$ eq. $)$ of methyl 3-oxohexanoate, $2.538 \mathrm{~g}(25.0$ $\mathrm{mmol}, 1.0 \mathrm{eq}$.) of formaldehyde solution ( $37-40 \%$ ) and $2.891 \mathrm{~g}(37.5 \mathrm{mmol}, 1.5 \mathrm{eq}$.$) of ammonium$ acetatein at $80{ }^{\circ} \mathrm{C}$ under a nitrogen atmosphere. The solution was stirred until complete consumption of methyl 3-oxohexanoate (monitored by TLC). Allowed to stand at room temperature and to facilitate crystallization of the compounds, the reaction mixture was scratched with a glass rod. Yellow crystals of dimethyl 2,6-dipropyl-1,4-dihydropyridine-3,5-dicarboxylate was formed. The product was recrystallized from ethanol. ${ }^{[3]}$

Dimethyl 2,6-dipropyl-1,4-dihydropyridine-3,5-dicarboxylate (4g): Yellow solid, 32\% yield, $\mathrm{mp}=107-108{ }^{\circ} \mathrm{C}, \mathrm{R}_{f}=0.46$ (petroleum ether/EtOAc $=10: 1$ ); ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )
 $\delta 5.31(\mathrm{~s}, 1 \mathrm{H}), 3.69(\mathrm{~s}, 6 \mathrm{H}), 3.27(\mathrm{~s}, 2 \mathrm{H}), 2.61-2.49(\mathrm{~m}, 4 \mathrm{H}), 1.56$ (dd, $\mathrm{J}=$ $15.3,7.5 \mathrm{~Hz}, 4 \mathrm{H}), 0.97(\mathrm{t}, J=7.3 \mathrm{~Hz}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $168.1,149.9,98.8,51.1,34.3,25.1,21.8,14.1$; HRMS (ESI) $\mathrm{m} / \mathrm{z}$ Calculated for $\mathrm{C}_{15} \mathrm{H}_{24} \mathrm{NO}_{4}[\mathrm{M}+\mathrm{H}]^{+}$283.1778, found 283.1741.

[^1]
## 4. Typical Procedure for Asymmetric Transfer Hydrogenation of 4-Substituted -1,2,3,4-tetrahydroacridines 2:



Typical procedure: In a dry Schlenk tube, 4-substituted-1,2,3,4-tetrahydroacridines $\mathbf{1}$ $(0.20 \mathrm{mmol})$, and phosphoric acid $(R)-3 \mathbf{f}(5.8 \mathrm{mg}, 0.01 \mathrm{mmol})$ and Hanztsch ester $\mathbf{4 g}(134.9 \mathrm{mg}$, 0.48 mmol ) were dissolved in 1,4 -dioxane ( 3 mL ) at $25^{\circ} \mathrm{C}$ under a nitrogen atmosphere. The solution was stirred until complete consumption of $\mathbf{1}$ (monitored by TLC). After removal of the solvent under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate, $30: 1$ ) to afford the desired products.

Typical procedure for preparation of racemates of 2: In a dry Schlenk tube, 4-substituted -1,2,3,4-tetrahydroacridines 1 ( 0.20 mmol ), and 1,1'-Binaphthyl-2,2'-diylhydrogenphosphate ( 3.5 $\mathrm{mg}, 0.01 \mathrm{mmol}$ ), and Hanztsch ester $4 \mathbf{a}(134.9 \mathrm{mg}, 0.48 \mathrm{mmol}$ ) were dissolved in 1,4 -dioxane ( 3 mL ) at $25^{\circ} \mathrm{C}$ under a nitrogen atmosphere. The solution was stirred until complete consumption of 1 (monitored by TLC). After removal of the solvent under reduced pressure, the residue was purified by flash chromatography (petroleum ether/ethyl acetate, 30:1) to afford the desired products.
(4S,4aS,9aR)-4-Methyl-1,2,3,4,4a,9,9a,10-octahydroacridine (2a): Pale solid, $\mathrm{mp}=51-53$ ${ }^{\circ} \mathrm{C}, 99 \%$ yield, $\mathrm{R}_{f}=0.82$ (petroleum ether/EtOAc $=30: 1$ ), $82 \%$ ee, $[\alpha]^{21}{ }_{\mathrm{D}}=-45.8\left(c 0.90, \mathrm{CHCl}_{3}\right)$; ${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 6.96(\mathrm{~m}, 2 \mathrm{H}), 6.56(\mathrm{t}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.46(\mathrm{~d}, J$ $=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 3.50(\mathrm{brs}, 1 \mathrm{H}), 3.03(\mathrm{dd}, J=10.4,4.5 \mathrm{~Hz}, 1 \mathrm{H}), 2.65(\mathrm{dd}, J=16.0$, $4.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.43$ (dd, $J=15.9,11.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.09-1.91(\mathrm{~m}, 1 \mathrm{H}), 1.90-1.80$ $(\mathrm{m}, 1 \mathrm{H}), 1.79-1.70(\mathrm{~m}, 1 \mathrm{H}), 1.67-1.58(\mathrm{~m}, 2 \mathrm{H}), 1.57-1.45(\mathrm{~m}, 2 \mathrm{H}), 0.98(\mathrm{~d}$, $J=7.1 \mathrm{~Hz}, 4 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $\left.100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 145.0,129.0,126.7,120.9,116.4,113.3,58.6$, 34.9, 32.6, 32.4, 31.4, 30.1, 19.9, 11.9; HPLC (OJ-H, elute: Hexanes/i-PrOH = 95/5, detector: 254 nm , flow rate: $0.8 \mathrm{~mL} / \mathrm{min}$ ), $30^{\circ} \mathrm{C}, \mathrm{t}_{1}=11.7 \mathrm{~min}$ (maj), $\mathrm{t}_{2}=18.0 \mathrm{~min}$; HRMS (ESI) $\mathrm{m} / \mathrm{z}$ Calculated for $\mathrm{C}_{14} \mathrm{H}_{20} \mathrm{~N}[\mathrm{M}+\mathrm{H}]^{+} 202.1596$, found 202.1591.
(4R,4aS,9aR)-4-methyl-1,2,3,4,4a,9,9a,10-octahydroacridine (2a'): $\mathrm{R}_{f}=0.83$ (petroleum ether/EtOAc $=30: 1$ ); ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 6.94(\mathrm{dd}, J=14.8,7.5 \mathrm{~Hz}, 2 \mathrm{H}), 6.56(\mathrm{dd}, J=$
 $10.6,4.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.46(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 3.58(\mathrm{~s}, 1 \mathrm{H}), 3.37(\mathrm{t}, J=2.6 \mathrm{~Hz}, 1 \mathrm{H})$, 3.04 (dd, $J=16.2,5.7 \mathrm{~Hz}, 1 \mathrm{H}), 2.41$ (d, $J=15.3 \mathrm{~Hz}, 1 \mathrm{H}), 1.86$ (s, 1H), $1.77-$ $1.62(\mathrm{~m}, 2 \mathrm{H}), 1.33(\mathrm{dt}, J=8.0,6.3 \mathrm{~Hz}, 5 \mathrm{H}), 1.01(\mathrm{~d}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 144.0,129.8,126.5,119.7,116.6,113.6,54.3,36.0,34.9,34.0,27.4,26.0$, 25.9, 18.5; HRMS (ESI) $\mathrm{m} / \mathrm{z}$ Calculated for $\mathrm{C}_{14} \mathrm{H}_{20} \mathrm{~N}[\mathrm{M}+\mathrm{H}]+$ 202.1596, found 202.1599.
(4S,4aS,9aR)-4-Ethyl-1,2,3,4,4a,9,9a,10-octahydroacridine (2b): Pale solid, $\mathrm{mp}=66-68$ ${ }^{\circ} \mathrm{C}, 91 \%$ yield, $\mathrm{R}_{f}=0.83$ (petroleum ether/EtOAc $=30: 1$ ), $88 \% \mathrm{ee},[\alpha]^{20}{ }_{\mathrm{D}}=-49.2\left(c 1.0, \mathrm{CHCl}_{3}\right)$; ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 6.99-6.86(\mathrm{~m}, 2 \mathrm{H}), 6.54(\mathrm{td}, J=7.4,0.9 \mathrm{~Hz}, 1 \mathrm{H}), 6.45(\mathrm{~d}, J=7.9$ $\mathrm{Hz}, 1 \mathrm{H}$ ), 3.48 (brs, 1H), 3.06 (dd, $J=10.5,4.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.62(\mathrm{dd}, J=16.0,4.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.40$ (dd, $J=16.0,11.7 \mathrm{~Hz}, 1 \mathrm{H}), 1.89-1.80(\mathrm{~m}, 2 \mathrm{H}), 1.75-1.59(\mathrm{~m}, 3 \mathrm{H}), 1.54-1.38(\mathrm{~m}, 3 \mathrm{H}), 1.36-1.22$

$(\mathrm{m}, 1 \mathrm{H}), 1.05-0.95(\mathrm{~m}, 1 \mathrm{H}), 0.92(\mathrm{t}, J=7.4 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( 100 MHz , $\mathrm{CDCl}_{3}$ ) $\delta 145.0,129.0,126.7,120.8,116.3,113.3,59.3,40.6,35.0,32.6,30.8$, 27.2, 19.9, 17.3, 12.9; HPLC (OJ-H, elute: Hexanes $/ i-\mathrm{PrOH}=95 / 5$, detector: 254 nm , flow rate: $0.8 \mathrm{~mL} / \mathrm{min}$ ), $30^{\circ} \mathrm{C}, \mathrm{t}_{1}=9.2 \mathrm{~min}$ (maj), $\mathrm{t}_{2}=16.1 \mathrm{~min}$; HRMS (ESI) $\mathrm{m} / \mathrm{z}$ Calculated for $\mathrm{C}_{15} \mathrm{H}_{22} \mathrm{~N}[\mathrm{M}+\mathrm{H}]^{+}$216.1752, found 216.1758 .
(4S,4aS,9aR)-4-Propyl-1,2,3,4,4a,9,9a,10-octahydroacridine (2c): Pale solid, $\mathrm{mp}=39-40$ ${ }^{\circ} \mathrm{C}, 84 \%$ yield, $\mathrm{R}_{f}=0.80$ (petroleum ether/EtOAc $=30: 1$ ), $84 \%$ ee, $[\alpha]_{\mathrm{D}}^{22}=-39.9\left(c 0.80, \mathrm{CHCl}_{3}\right)$;
 ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.00-6.85(\mathrm{~m}, 2 \mathrm{H}), 6.55(\mathrm{t}, J=7.1 \mathrm{~Hz}, 1 \mathrm{H})$, 6.46 (d, $J=7.9 \mathrm{~Hz}, 1 \mathrm{H}$ ), 3.48 (brs, 1H), 3.05 (dd, $J=10.5,4.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.63$ $(\mathrm{dd}, J=16.0,4.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.41(\mathrm{dd}, J=15.9,11.7 \mathrm{~Hz}, 1 \mathrm{H}), 1.91-1.63(\mathrm{~m}, 4 \mathrm{H})$, $1.62-1.39(\mathrm{~m}, 6 \mathrm{H}), 1.37-1.15(\mathrm{~m}, 2 \mathrm{H}), 1.05-0.95(\mathrm{~m}, 1 \mathrm{H}), 0.92(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 145.0,129.0,126.7,120.8,116.3,113.2,59.2,38.4,35.0,32.6,30.8,27.9$, 27.0, 21.6, 20.0, 14.5; HPLC (OJ-H, elute: Hexanes $/ i-\operatorname{PrOH}=95 / 5$, detector: 254 nm , flow rate: $0.8 \mathrm{~mL} / \mathrm{min}$ ), $30{ }^{\circ} \mathrm{C}, \mathrm{t}_{1}=7.2 \mathrm{~min}(\mathrm{maj}), \mathrm{t}_{2}=8.3 \mathrm{~min}$; HRMS (ESI) $\mathrm{m} / \mathrm{z}$ Calculated for $\mathrm{C}_{16} \mathrm{H}_{24} \mathrm{~N}$ $[\mathrm{M}+\mathrm{H}]^{+} 230.1909$, found 230.1918 .
(4S,4aS,9aR)-4-Butyl-1,2,3,4,4a,9,9a,10-octahydroacridine (2d): Pale solid, $\mathrm{mp}=44-45$ ${ }^{\circ} \mathrm{C}, 71 \%$ yield, $\mathrm{R}_{f}=0.81$ (petroleum ether/ $\mathrm{EtOAc}=30: 1$ ), $85 \%$ ee, $[\alpha]^{21}{ }_{\mathrm{D}}=-37.9\left(c 0.87, \mathrm{CHCl}_{3}\right)$;
 ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.00-6.84(\mathrm{~m}, 2 \mathrm{H}), 6.55(\mathrm{td}, J=7.4,0.9 \mathrm{~Hz}$, $1 \mathrm{H}), 6.46$ (d, $J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 3.48$ (brs, 1H), 3.06 (dd, $J=10.5,4.4 \mathrm{~Hz}, 1 \mathrm{H}$ ), 2.63 (dd, $J=16.0,4.8 \mathrm{~Hz}, 1 \mathrm{H}$ ), 2.41 (dd, $J=16.0,11.7 \mathrm{~Hz}, 1 \mathrm{H}), 1.89-1.77$ $(\mathrm{m}, 2 \mathrm{H}), 1.76-1.63(\mathrm{~m}, 2 \mathrm{H}), 1.63-1.46(\mathrm{~m}, 4 \mathrm{H}), 1.45-1.28(\mathrm{~m}, 4 \mathrm{H}), 1.23-1.12(\mathrm{~m}, 1 \mathrm{H}), 1.06$ $-0.94(\mathrm{~m}, 1 \mathrm{H}), 0.91(\mathrm{t}, J=7.1 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $\left.100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 145.0,129.0,126.7,120.8$, 116.3, 113.2, 59.2, 38.6, 35.0, 32.6, 30.8, 30.7, 27.8, 24.3, 23.1, 20.0, 14.2; HPLC (OJ-H, elute: Hexanes $/ i-\operatorname{PrOH}=98 / 2$, detector: 254 nm , flow rate: $0.7 \mathrm{~mL} / \mathrm{min}$ ), $30^{\circ} \mathrm{C}, \mathrm{t}_{1}=9.7 \mathrm{~min}(\mathrm{maj}), \mathrm{t}_{2}=$ 11.1 min ; HRMS (ESI) $\mathrm{m} / \mathrm{z}$ Calculated for $\mathrm{C}_{17} \mathrm{H}_{26} \mathrm{~N}[\mathrm{M}+\mathrm{H}]^{+} 244.2065$, found 244.2068.
(4R,4aS,9aR)-4-Allyl-1,2,3,4,4a,9,9a,10-octahydroacridine (2e): Pale oil, 82\% yield, $\mathrm{R}_{f}=$ 0.65 (petroleum ether/EtOAc $=30: 1$ ), $89 \%$ ee, $[\alpha]^{22}{ }_{\mathrm{D}}=-52.6\left(c 0.67, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $(400 \mathrm{MHz}$,
 $\left.\mathrm{CDCl}_{3}\right) \delta 6.96-6.74(\mathrm{~m}, 2 \mathrm{H}), 6.49(\mathrm{td}, J=7.4,0.9 \mathrm{~Hz}, 1 \mathrm{H}), 6.39(\mathrm{~d}, J=7.9 \mathrm{~Hz}$, $1 \mathrm{H}), 5.81-5.61(\mathrm{~m}, 1 \mathrm{H}), 5.06-4.81(\mathrm{~m}, 2 \mathrm{H}), 3.46(\mathrm{~s}, 1 \mathrm{H}), 3.04(\mathrm{dd}, J=10.5$, $4.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.57(\mathrm{dd}, J=16.0,4.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.35(\mathrm{dd}, J=15.9,11.8 \mathrm{~Hz}, 2 \mathrm{H})$, $2.08-1.88(\mathrm{~m}, 1 \mathrm{H}), 1.86-1.70(\mathrm{~m}, 3 \mathrm{H}), 1.70-1.54(\mathrm{~m}, 1 \mathrm{H}), 1.50-1.30(\mathrm{~m}$, $3 \mathrm{H}), 1.01-0.87(\mathrm{~m}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 144.8,138.5,129.0,126.7,120.8,116.5$, $115.5,113.4,58.8,38.2,34.9,32.5,30.8,29.7,27.5,19.8$; HPLC (OJ-H, elute: Hexanes/i-PrOH $=$ $95 / 5$, detector: 254 nm , flow rate: $0.8 \mathrm{~mL} / \mathrm{min}$ ), $30{ }^{\circ} \mathrm{C}$, $\mathrm{t}_{1}=11.2 \mathrm{~min}(\mathrm{maj}), \mathrm{t}_{2}=13.0 \mathrm{~min}$; HRMS (ESI) $\mathrm{m} / \mathrm{z}$ Calculated for $\mathrm{C}_{16} \mathrm{H}_{22} \mathrm{~N}[\mathrm{M}+\mathrm{H}]^{+}$228.1752, found 228.1741 .
(4R,4aS,9aR)-4-Benzyl-1,2,3,4,4a,9,9a,10-octahydroacridine (2f): Pale solid, $\mathrm{mp}=72-74$ ${ }^{\circ} \mathrm{C}, 82 \%$ yield, $\mathrm{R}_{f}=0.82$ (petroleum ether $/ \mathrm{EtOAc}=30: 1$ ), $67 \%$ ee, $[\alpha]^{22}{ }_{\mathrm{D}}=-103.9\left(c 1.03, \mathrm{CHCl}_{3}\right)$;
 ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.35-7.26(\mathrm{~m}, 2 \mathrm{H}), 7.23-7.15(\mathrm{~m}, 3 \mathrm{H}), 6.95$ (dd, $J=15.1,7.4 \mathrm{~Hz}, 2 \mathrm{H}), 6.59(\mathrm{dd}, J=10.5,4.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.45(\mathrm{~d}, J=7.9 \mathrm{~Hz}$, $1 \mathrm{H}), 3.57(\mathrm{~s}, 1 \mathrm{H}), 3.19(\mathrm{dd}, J=10.5,4.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.03(\mathrm{dd}, J=14.0,3.6 \mathrm{~Hz}$, $1 \mathrm{H}), 2.69(\mathrm{dd}, J=16.0,4.7 \mathrm{~Hz}, 1 \mathrm{H}), 2.51(\mathrm{ddd}, J=27.6,14.9,11.2 \mathrm{~Hz}, 2 \mathrm{H}), 2.18-2.04(\mathrm{~m}, 1 \mathrm{H})$, $2.00-1.78(\mathrm{~m}, 2 \mathrm{H}), 1.74-1.59(\mathrm{~m}, 2 \mathrm{H}), 1.61-1.47(\mathrm{~m}, 1 \mathrm{H}), 1.46-1.32(\mathrm{~m}, 1 \mathrm{H}), 1.99-0.99(\mathrm{~m}$, $1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 144.8,142.4,129.1,129.0,128.3,126.8,125.7,120.8,116.6$, 113.5, 59.0, 40.8, 34.9, 32.6, 31.7, 30.9, 27.5, 20.0; HPLC (AD-H, elute: Hexanes/i-PrOH = 98/2,
detector: 254 nm , flow rate: $0.8 \mathrm{~mL} / \mathrm{min}$ ), $30^{\circ} \mathrm{C}, \mathrm{t}_{1}=10.1 \mathrm{~min}(\mathrm{maj}), \mathrm{t}_{2}=13.0 \mathrm{~min}$; HRMS (ESI) $\mathrm{m} / \mathrm{z}$ Calculated for $\mathrm{C}_{20} \mathrm{H}_{24} \mathrm{~N}[\mathrm{M}+\mathrm{H}]^{+}$278.1909, found 278.1906.
(4S,4aS,9aR)-4-Ethyl-7-methoxy-1,2,3,4,4a,9,9a,10-octahydroacridine (2g): Pale solid, $\mathrm{mp}=71-72{ }^{\circ} \mathrm{C}, 60 \%$ yield, $\mathrm{R}_{f}=0.67$ (petroleum ether/EtOAc $=30: 1$ ), $87 \% \mathrm{ee},[\alpha]^{29}{ }_{\mathrm{D}}=-45.5(c$
 $\left.1.03, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 6.60(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.55$ ( $\mathrm{s}, 1 \mathrm{H}$ ), $6.44(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.73(\mathrm{~s}, 3 \mathrm{H}), 3.29(\mathrm{~s}, 1 \mathrm{H}), 3.03(\mathrm{~d}, J=10.6$ $\mathrm{Hz}, 1 \mathrm{H}), 2.69-2.59(\mathrm{~m}, 1 \mathrm{H}), 2.51-2.36(\mathrm{~m}, 1 \mathrm{H}), 1.86(\mathrm{~d}, J=12.7 \mathrm{~Hz}$, $2 \mathrm{H}), 1.68(\mathrm{dd}, J=13.0,7.4 \mathrm{~Hz}, 3 \mathrm{H}), 1.59-1.21(\mathrm{~m}, 4 \mathrm{H}), 0.97(\mathrm{dt}, J=14.2,8.8 \mathrm{~Hz}, 4 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (100 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 151.5,139.4,122.2,114.8,114.5,113.05,59.6,56.1,40.7,35.4,32.9$, 31.1, 27.4, 20.0, 17.5, 13.0; HPLC (OJ-H, elute: Hexanes $/ \mathrm{i}-\mathrm{PrOH}=95 / 5$, detector: 254 nm , flow rate: $0.8 \mathrm{~mL} / \mathrm{min}$ ), $30{ }^{\circ} \mathrm{C}, \mathrm{t}_{1}=11.7 \mathrm{~min}(\mathrm{maj}), \mathrm{t}_{2}=15.8 \mathrm{~min}$; HRMS (ESI) $\mathrm{m} / \mathrm{z}$ Calculated for $\mathrm{C}_{16} \mathrm{H}_{24} \mathrm{NO}[\mathrm{M}+\mathrm{H}]^{+} 246.1858$, found 246.1861.
(4S,4aS,9aR)-4-Ethyl-7-fluoro-1,2,3,4,4a,9,9a,10-octahydroacridine (2h): Pale oil, 97\% yield, $\mathrm{R}_{f}=0.69$ (petroleum ether/EtOAc $=30: 1$ ), $88 \%$ ee, $[\alpha]^{29}{ }_{\mathrm{D}}=-53.5\left(c 0.80, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR
 $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 6.64$ (ddd, $\left.J=9.1,7.5,4.3 \mathrm{~Hz}, 2 \mathrm{H}\right), 6.37$ (dd, $J=8.5,4.8$ $\mathrm{Hz}, 1 \mathrm{H}), 3.41$ (brs, 1H), $3.02(\mathrm{dd}, J=10.6,4.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.60(\mathrm{dd}, J=16.3,5.0$ $\mathrm{Hz}, 1 \mathrm{H}), 2.38$ (dd, $J=16.0,11.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.84(\mathrm{dd}, J=12.9,2.6 \mathrm{~Hz}, 2 \mathrm{H})$, $1.71-1.59(\mathrm{~m}, 3 \mathrm{H}), 1.54-1.38(\mathrm{~m}, 2 \mathrm{H}), 1.37-1.23(\mathrm{~m}, 2 \mathrm{H}), 1.03-0.87(\mathrm{~m}, 4 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 155.1(\mathrm{~d}, J=233 \mathrm{~Hz}), 141.2,122.0(\mathrm{~d}, J=6.6 \mathrm{~Hz}), 115.1(\mathrm{~d}, J=21 \mathrm{~Hz})$, $113.79(\mathrm{~d}, J=7.6 \mathrm{~Hz}), 113.1(\mathrm{~d}, J=22 \mathrm{~Hz}), 59.3,40.5,35.0,32.5,30.6,27.1,19.8,17.3,12.8 ;{ }^{19} \mathrm{~F}$ NMR ( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta-129.2$; HPLC (OJ-H, elute: Hexanes $/ i-\mathrm{PrOH}=95 / 5$, detector: 254 nm , flow rate: $0.8 \mathrm{~mL} / \mathrm{min}$ ), $30{ }^{\circ} \mathrm{C}, \mathrm{t}_{1}=6.9 \mathrm{~min}(\mathrm{maj}), \mathrm{t}_{2}=7.7 \mathrm{~min}$; HRMS (ESI) $\mathrm{m} / \mathrm{z}$ Calculated for $\mathrm{C}_{15} \mathrm{H}_{21} \mathrm{NF}[\mathrm{M}+\mathrm{H}]^{+} 234.1658$, found 234.1668 .
(4R,4aR,9aR)-4-Phenyl-1,2,3,4,4a,9,9a,10-octahydroacridine (2i): Pale oil, 40\% yield, $\mathrm{R}_{f}=$ 0.60 (petroleum ether/EtOAc $=30: 1$ ), $46 \%$ ee, $[\alpha]^{29}{ }_{\mathrm{D}}=+32.4\left(c 0.16, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $(400 \mathrm{MHz}$,
 $\left.\mathrm{CDCl}_{3}\right) \delta 7.44(\mathrm{~d}, J=7.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.31-7.23(\mathrm{~m}, 2 \mathrm{H}), 7.20(\mathrm{dt}, J=9.4,4.3 \mathrm{~Hz}$, $1 \mathrm{H}), 6.92(\mathrm{dd}, J=16.9,8.0 \mathrm{~Hz}, 2 \mathrm{H}), 6.57(\mathrm{td}, J=7.4,1.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.34(\mathrm{~d}, J=$ $8.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.48(\mathrm{brs}, 1 \mathrm{H}), 3.43-3.15(\mathrm{~m}, 2 \mathrm{H}), 2.75(\mathrm{dd}, J=15.9,4.6 \mathrm{~Hz}, 1 \mathrm{H})$, $2.48(\mathrm{dd}, J=15.9,11.5 \mathrm{~Hz}, 1 \mathrm{H}), 2.34-2.20(\mathrm{~m}, 1 \mathrm{H}), 2.08-1.98(\mathrm{~m}, 2 \mathrm{H}), 1.98-1.85(\mathrm{~m}, 1 \mathrm{H})$, $1.63-1.49(\mathrm{~m}, 3 \mathrm{H}), 1.17-1.04(\mathrm{~m}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 144.5,142.3,130.1$, 129.1, 128.2, 126.7, 126.1, 121.1, 116.6, 113.9, 58.6, 43.5, 35.8, 32.8, 32.2, 31.4, 20.7;HPLC (OJ-H, elute: Hexanes $/ \mathrm{i}-\mathrm{PrOH}=90 / 10$, detector: 254 nm , flow rate: $1.0 \mathrm{~mL} / \mathrm{min}$ ), $30{ }^{\circ} \mathrm{C}, \mathrm{t}_{1}=9.4$ $\min (m a j), \mathrm{t}_{2}=13.2 \mathrm{~min}$; HRMS (ESI) $\mathrm{m} / \mathrm{z}$ Calculated for $\mathrm{C}_{19} \mathrm{H}_{22} \mathrm{~N}[\mathrm{M}+\mathrm{H}]^{+}$264.1752, found 264.1745.
(4R,4aS,9aS)-4-phenyl-1,2,3,4,4a,9,9a,10-octahydroacridine (2i'): Pale oil, $9 \%$ yield, $\mathrm{R}_{f}=$ 0.59 (petroleum ether/EtOAc $=30: 1$ ); ${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.32(\mathrm{t}, J=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.23$
 $(\mathrm{d}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.16(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.98(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.92(\mathrm{t}, J=$ $7.5 \mathrm{~Hz}, 1 \mathrm{H}), 6.60(\mathrm{t}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 6.25(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 3.72(\mathrm{~s}, 1 \mathrm{H}), 3.32$ (dd, $J=10.7,4.1 \mathrm{~Hz}, 1 \mathrm{H}$ ), $3.09(\mathrm{dd}, J=15.1,12.1 \mathrm{~Hz}, 1 \mathrm{H}), 2.77$ (dd, $J=15.3$, $7.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.63-2.46(\mathrm{~m}, 2 \mathrm{H}), 1.90-1.84(\mathrm{~m}, 2 \mathrm{H}), 1.65(\mathrm{qd}, J=12.1,6.3 \mathrm{~Hz}, 3 \mathrm{H}), 1.27(\mathrm{~s}$, $1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 144.1,143.1,129.6,128.7,128.1,126.9,126.7,120.4,116.8$, 114.1, 57.5, 46.6, 33.3, 31.8, 30.6, 27.7, 20.8; HRMS (ESI) m/z Calculated for $\mathrm{C}_{19} \mathrm{H}_{22} \mathrm{~N}[\mathrm{M}+\mathrm{H}]^{+}$ 264.1752, found 264.1776 .
none (5b) Pale solid, $\mathrm{mp}=154-156{ }^{\circ} \mathrm{C}, 94 \%$ yield, $\mathrm{R}_{f}=0.21$ (petroleum ether/EtOAc $=30: 1$ ),
 $98 \%$ ee, $[\alpha]^{29}{ }_{\mathrm{D}}=+355.4\left(c 1.77, \mathrm{CHCl}_{3}\right) ;{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.28(\mathrm{~d}$, $J=7.9 \mathrm{~Hz}, 2 \mathrm{H}), 7.11(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.96(\mathrm{dd}, J=34.5,7.3 \mathrm{~Hz}, 3 \mathrm{H}), 6.83$ $(\mathrm{d}, J=7.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.47(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 4.05(\mathrm{~d}, J=11.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.82(\mathrm{~s}$, $1 \mathrm{H}), 2.57-2.33(\mathrm{~m}, 2 \mathrm{H}), 1.91(\mathrm{~s}, 1 \mathrm{H}), 1.80(\mathrm{~d}, J=13.4 \mathrm{~Hz}, 1 \mathrm{H}), 1.59(\mathrm{~s}, 2 \mathrm{H})$, $1.49-1.33(\mathrm{~m}, 2 \mathrm{H}), 1.17(\mathrm{~s}, 2 \mathrm{H}), 0.89(\mathrm{t}, \mathrm{J}=7.4 \mathrm{~Hz}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( 100 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 169.9,139.2,136.3,136.2,131.1,130.1,126.9,126.3,125.3,123.7,67.6,40.1,39.1$, 35.2, 33.5, 27.2, 21.2, 18.9, 12.9; HPLC (AD-H, elute: Hexanes $/ i-\operatorname{PrOH}=95 / 5$, detector: 254 nm , flow rate: $1.0 \mathrm{~mL} / \mathrm{min}$ ), $30{ }^{\circ} \mathrm{C}, \mathrm{t}_{1}=12.0 \mathrm{~min}(\mathrm{maj}), \mathrm{t}_{2}=20.1 \mathrm{~min} ;$ HRMS (ESI) $\mathrm{m} / \mathrm{z}$ Calculated for $\mathrm{C}_{22} \mathrm{H}_{24} \mathrm{NOBrNa}[\mathrm{M}+\mathrm{Na}]^{+} 420.0939$, found 420.0940 .

## 5. The Determination of the Absolute Configuration of $\mathbf{2 b}$



A mixture of 4-bromobenzoyl chloride ( $88 \mathrm{mg}, 0.40 \mathrm{mmol}$ ), $\mathrm{Et}_{3} \mathrm{~N}(56 \mu \mathrm{~L}, 0.40 \mathrm{mmol})$ and 4-Ethyl-1,2,3,4,4a,9,9a,10-octahydroacridine $2 \mathbf{b}$ ( $82 \mathrm{mg}, 0.38 \mathrm{mmol}$ ) dissolved in $5 \mathrm{~mL} \mathrm{CH} \mathrm{Cl}_{2}$ was stirred for 2 h . After concentrating in vacuo, the resulting precipitate was directly purified by column chromatography on silica gel using hexane/EtOAc (30:1) to give the corresponding $N$-4-bromobenzoyl derivative $\mathbf{5 b}$. The product was recrystallized from DCM/hexane, and ee up to $>98 \%$.

CCDC 994490 contains the structure and supplementary crystallographic data for the crystal structure of (4-bromophenyl) ((4S,4aS,9aR)-4-ethyl-2,3,4,4a,9,9a-hexahydroacridin-10(1H)-yl) methanone 5b. These data can be obtained free of charge via www.ccdc.com.ac.uk/data request/cif from the Cambridge Crystallographic Data Centre.
6.1 Copy of NMR for 4-Substituted-1,2,3,4-tetrahydroacridines


```
~N~N~NNNNNN
```

1H NMR MC-5-96 CDCL3
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )



```
M0
```




13C NMR MC-5-96 in CDCl3


1H NMR MC-5-97B CDCL3






## 13 C NMR MC-5-97B in CDCl3


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


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

##  

1H NMR MC-5-100B in CDCl3


|  | .$_{\infty}$ |  |
| :---: | :---: | :---: |
| $\stackrel{( }{\square}$ | \% |  |
|  | I | - |

13C NMR MC-5-100B in CDCl3




1 H N MR MC-6-20B in CDCl3


$\stackrel{\infty}{\infty}$
13C MR MC-6-21B1 in CDC13

> | 3 |
| :--- |
| $\stackrel{3}{\overleftarrow{ }}$ |






1H NMR MC-7-24A in CDCl3


## 13 C NMR MC-7-24A in CDCl3


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


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




1H NMR MC-7-26A1 in CDCl3



```
N-%
\ NNNM=AmN
%
```


$\stackrel{\text { ® }}{\stackrel{\circ}{\circ}}$

13C NMR MC-7-26A1 in CDCI3


19 F NMR MC-7-26A1 in CDCl3

${ }^{19}$ F NMR ( $376 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )




1H NMR MC-5-11 in CDCl3





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\ \
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13C NMR MC-5-11 in CDCl3

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


### 6.2 Copy of NMR for 4g



1H NMR MC-b-18 CDCL3



$\underset{\infty}{\underset{\omega}{1}}$


## 13C NMR MC-b-18 CDCL3


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



1H NMR MC-6-10A in CDCl3

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


## 13C NMR MC-6-10A in CDCl3




##  iososioniogiv

1H NMR MC-10-15A2 in CDCl3


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


## 



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

##  <br> oigiog in ionigus

1H NMR MC-6-11A in CDCl3

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产 㽃祭
8
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## 13C NMR MC－6－11A in CDCl3


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






1H NMR MC-6-12A in CDCl3


## 13C NMR MC-6-12A in CDCl3



2c $\bar{n}-\mathrm{Pr}$
${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ )


|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 180 | 170 | 160 | 150 | 140 | 130 | 120 | 110 | $\begin{array}{r} 100 \\ \mathrm{f} 1 \end{array}$ |  | 80 | 70 | 60 | 50 | 40 | 30 | 20 | 10 | c |

##  

1H NMR MC-6-12B in CDCl3


## 13C NMR MC-6-12B in CDCl3


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


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





1H NMR MC-6-86A in CDCl
G:/新 NMR 2013/238/fid


## 13 C NMR MC-6-86A in CDCl3



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

##  <br> 

1 H NMR MC-6-11B in CDCl3

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



## 13C NMR MC-6-11B in CDCl3




都


1 H NMR MC-7-26C in CDCl3



[^2]13 C NMR MC-7-26C in CDC13

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


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1H NMR MC-7-29A in CDCl3

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19F NMR MC-7-29A in CDCl3

${ }^{19} \mathrm{~F}$ NMR $\left(376 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$


##  

1H NMR MC-7-99 in CDCl3

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


## 13 C NMR MC-7-99 in CDCl3


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



##  <br> N-NN二,

1H NMR MC-11-8B CDCL3

$\rightarrow$ -

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

$8 \quad 8 \quad$ \&FBR

13 C NMR MC-11-8B CDCL3




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N-iNTigoyd
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## 1H NMR MC-6-20 in CDCl3




5b

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




| $\stackrel{\infty}{\infty}$ |  |
| :---: | :---: |
| $\stackrel{8}{6}$ |  |
| I | $\xrightarrow{\sim}$ |

13 C MR MC-6-20 in CDC13

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





Sorted Ev
Multiplier:
Pilution: $\quad \vdots \quad \begin{aligned} & 1.0000 \\ & 1.0000\end{aligned}$

si mal 1: virl h, wavelengche 254 nm


Instrument 1 11/13/2013 4:45:11 pme



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Iniection pare : 8/21/2013 4:10:53 m
*)
Last chmmed : 8/21/2013 4:07.54 PN b% FZ
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## sorted by : sicmal <br> 

Sigmal 1: vid 1 h , Wavelengrh=254 min
$4305.28476 \quad 287.44314$
)-2a
*** End of Report ***




Sorted Ev ,
Multiplier:
$\stackrel{\text { Sicmal }}{:} \quad 1.0000$

gigmal 1: vivi 1 h, Wavelengrhe 254 mm




Tatals: $\quad 482.00060 \quad 27.76760$
(

Data File :atyzoote74.D
Sample Name: MC-6-11A
acc. inerator : zhou
Iniection Date : 8/27/2013 11:02:30 an Location: vial






$==================$ Area Percent Report


Si gmal 1: vir 1 h, Wavelengch=254 nm

$$
\begin{aligned}
& \text { Totals : } \quad 307.31247 \quad 25.68549 \\
& \text { *** End of Report *** }
\end{aligned}
$$




Last changed : $12 / 27 / 20110: 10: 2106 \mathrm{Am}$




$\begin{aligned} & \text { Sorted fv } \\ & \text { Hultiplier: }\end{aligned} \quad: \quad \int_{\text {Sicmsl }} 1.0000$

Signal 1: wnil $\mathrm{A}_{\text {, }}$ Wavelength 254 mm




Tatals: $\quad 992.27283 \quad 83.74216$
$=-=-=-=-=-=-=-=-==-=$

Acc. Operatar $: \quad$ Instrument


Last chanced $: 12 / 27 / 20114: 17$ :03 pm




$\begin{aligned} & \text { Sorted Ev } \\ & \text { Hultiplier: }\end{aligned} \quad: \quad: \quad: \quad$ Sicmsil 1.0000








Signal 1: VmD 1 in, Wavelength=254



hec. Tnstrument $\vdots$ Instrument 1 Location: Fial









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\begin{aligned}
& \text { Totals: } \quad 994.41075 \quad 59.4295
\end{aligned}
$$

 $\qquad$ sample Mame: MC-6-86E(+_)


ast chanced : S/16/2012 af:12:47 Aif by $2:$









$\qquad$


[^3]
Si mal 1: NWO 1 A , Wavelengch $=254$ nil

$(-)-2 e$
Results ortained with enhanced inteqratov!
${ }^{t+t}$ End of Report tt





iomal 1: vid 1 h , Wavelength $=254 \mathrm{~nm}$
 (+l-)-2f Bn

Totals: 2399.66933179 .29160




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lum,
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Sorted By

Signal 1: Vuld 1 in, Wawelength $=254$


Totals: 1250.36693102 .1339




[modifified after loading $z X$




| Sorted Ev |  |
| :--- | :--- |
| Miltinlier | $\vdots$ |
| Dilution |  |\(\quad \begin{aligned} \& Simsel <br>

\& 1.0000 <br>
\& 1.0000\end{aligned}\)
Si mal 1: NWD 1 h, Tavelengthe 254 mm
 Tatals:
$4156.03223 \quad 822.08064$

hanced integrator!
${ }^{* * *}$ End of Report ***



last chanced : 7/19/2012 2:39:14 pM by ZX



Sorted FV
Hultinlie
$\xrightarrow[\substack{\text { Si.mal } \\ \text { i.0000 } \\ 1.00000}]{ }$
Sigmal 1: WWi A, Wavelengthe 254 nill

 (+I-)-2h
Totals :
$2837.17358 \quad 324.92316$
Results obtained with enhemced intecrator
*** End of Peport **


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M=========================================================== L
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Sorted FV
Hultiplier

| sicmal |
| :---: |
| 1.00000 |

Signal 1: VWT1 A, Wavelengche254 min
 $\begin{array}{ccccc}\frac{1}{2} & 7.669 \mathrm{~V} & 0.1460 & 67.27153 & 7.06579 \\ \text { Tatals : } & & 1152.73552 & 133.49640\end{array}$


Resulta obtained with erihanced intecrator:
$====================-================$

Act. Instrument: Tnstrument 1









simal




Data File D: 11 Mz200363.D
Smuple Name: MC-7-99








Sorted fr
Hultiplier: : Sicms1 1.0000


$$
\begin{aligned}
& \text { Sicmal 1: wnil } 1 \text { a Wavelengthe } 254 \text { nim }
\end{aligned}
$$

$$
\begin{aligned}
& \begin{array}{ccccccc}
\frac{1}{2} .374 \text { 区E } & 0.2803 & 539.14673 & 29.28313 & 74.2562 \\
13 & 13.156 & \text { EB } & 0.6150 & 186.91609 & 4.56129 & 25.7436
\end{array} \\
& \text { Tatals : } \quad 726.06282 \quad 33.84442 \\
& \text { *** End of Report *** }
\end{aligned}
$$


$(-)-2 i$


Act. Inservurent: Tistrument 1 :









Data File D: 11 Hz005s19.
Semple Name: MC-6-20A
${ }^{\text {Acc. }}$ Act. Inerator $:$ Zhistrument
Acq. Thistrament: Instrument 1
Crietion Date : 11/23/2013 7:29:52 AM







Sorted Fv ,
Multiplier:
$\begin{array}{lll}\text { Piltiptier: } & \vdots & \begin{array}{l}1.0000 \\ 1.0000\end{array}\end{array}$
iliution:
Si Emal 1: Whir 1 A , Wavelengrh $=254 \mathrm{~nm}$


*** End of Report ***


[^0]:    1. (a) C. S. Cho, B. T. Kim, T.-J. Kim, S. C. Shim, Chem. Commun. 2001, 2576; (b) H. Vander Mierde, P. Van Der Voort, D. De Vos, F. Verpoort, Eur. J. Org. Chem. 2008, 1625; (c) R. Martínez, D. J. Ramón, M. Yus, J. Org. Chem. 2008, 73, 9778; (d) V. A. Stonik, V. I. Vysotskii, M. N. Tilichenko, Khim. Geterotsikl. Soedin. 1972, 8, 611.
    2. D.-W. Wang, X.-B. Wang, D.-S. Wang, S.-M. Lu, C.-B. Yu, Y.-G. Zhou, Y.-X. Li, J. Org. Chem. 2009, 74, 2780.
[^1]:    [3] M. Anniyappan, D. Muralidharan, P. T. Perumal, Synth. Commun. 2002, 32, 659.

[^2]:    
    
    

[^3]:    

