# Supporting Information 

## FormalSyntheses of (-)-Platensimycin

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## Context

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## Experimental Details

## General Information:

All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on silica gel F254 plates. Column chromatography was performed on silica gel (200-300 meshes). Solvents for reaction were distilled prior to use, and all air- or moisture-sensitive reactions were conducted under an argon atmosphere. The melting points were measured using micro melting point apparatus. The optical rotations were measured using a $0.1-\mathrm{mL}$ cell with a $1-\mathrm{cm}$ path length. ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR spectra were recorded in $\mathrm{CDCl}_{3}$ solution on instruments $\left(400 \mathrm{MHz}\right.$ for ${ }^{1} \mathrm{H}$ NMR and 100 MHz for ${ }^{13} \mathrm{C}$ NMR) and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard. IR spectra were recorded on a fourier transform infrared spectrometer. EI-MS spectra (MS) were measured on spectrometer by direct inlet at 70 eV and signals were given in $\mathrm{m} / \mathrm{z}$ with relative intensity (\%) in brackets. High-resolution mass spectral analysis (HRMS) data were measured by means of the ESI technique on Fourier transform ion cyclotron resonance mass analyzer.

## Studies on the synthesis of (-)-platensimycin




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To a solution of $\mathbf{6}(4.6 \mathrm{~g}, 18 \mathrm{mmol})$ in $\mathrm{Et}_{2} \mathrm{O}(100 \mathrm{~mL})$ was added $t-\operatorname{BuLi}(1.6 \mathrm{M}, 13$ $\mathrm{mL}, 20.8 \mathrm{mmol}$ ) at $-78^{\circ} \mathrm{C}$ under an argon atmosphere. After stirring at $-78^{\circ} \mathrm{C}$ for two hours, the resulting mixture was warmed to $-30^{\circ} \mathrm{C}$ spontaneously, a solution of 7 (5.8 $\mathrm{g}, 23.4 \mathrm{mmol})$ in $\mathrm{Et}_{2} \mathrm{O}(5 \mathrm{~mL})$ was added dropwise. Then the resulting mixture was warmed to room temperature and stirred overnight before it was quenched with saturated aqueous $\mathrm{NH}_{4} \mathrm{Cl}(10 \mathrm{~mL})$. The organic layer was separated and aqueous layer
was extracted with $\mathrm{EtOAc} / \mathrm{Et}_{2} \mathrm{O}(1: 1)(3 \times 100 \mathrm{~mL})$. The combined organic layer was washed with brine ( $3 \times 30 \mathrm{~mL}$ ), dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated under vacuum. The residue was dissolved in acetone $/ \mathrm{H}_{2} \mathrm{O}(1: 1)(50 \mathrm{~mL})$ and PTS $\cdot \mathrm{H}_{2} \mathrm{O}(687 \mathrm{mg}, 3.6$ mmol ) was added at room temperature, 1 hour later, saturated aqueous $\mathrm{NaHCO}_{3}(10$ mL ) was added, most of the acetone was removed under vacuum. Aqueous layer was extracted with $\mathrm{EtOAc} / \mathrm{Et}_{2} \mathrm{O}(1: 1)(3 \times 100 \mathrm{~mL})$. The combined organic layer was washed with brine $(3 \times 30 \mathrm{~mL})$, dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated under vacuum. Then the residue was dissolved in $\mathrm{MeOH}(30 \mathrm{~mL})$ and $\mathrm{NaBH}_{4}(684 \mathrm{mg}, 18 \mathrm{mmol})$ was added at $0^{\circ} \mathrm{C}, 30$ minutes later, saturated aqueous $\mathrm{NH}_{4} \mathrm{Cl}(20 \mathrm{~mL})$ was added, most of the MeOH was removed under vacuum. Aqueous layer was extracted with EtOAc ( $3 \times 80 \mathrm{~mL}$ ). The combined organic layer was washed with brine $(3 \times 20 \mathrm{~mL})$, dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated under vacuum. The residue was dissolved in $\mathrm{MeOH}(30 \mathrm{~mL})$ and PTS $\cdot \mathrm{H}_{2} \mathrm{O}(687 \mathrm{mg}, 3.6 \mathrm{mmol})$ was added at room temperature, two hour later, saturated aqueous $\mathrm{NaHCO}_{3}(20 \mathrm{~mL})$ was added, most of the MeOH was removed under vacuum. The mixture was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 50 \mathrm{~mL})$ and EtOAc $(2 \times 50 \mathrm{~mL})$ respectively. The organic layer was washed with brine $(3 \times 20$ mL ). The combined organic layer was dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated under vacuum and the residue was purified via column chromatography on silica gel (petroleum ether: ethyl acetate $=1: 1$ ) to give product $\mathbf{8}$ as a colorless oil $(1.28 \mathrm{~g}, 5.77$ mmol, 32 \% yield). ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 7.01(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.98(\mathrm{~d}, J$ $=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.73(\mathrm{dd}, J=8.4 \mathrm{~Hz}, 2.4 \mathrm{~Hz}, 1 \mathrm{H}), 5.17(\mathrm{t}, J=6.6 \mathrm{~Hz}, 1 \mathrm{H}), 4.54(\mathrm{~s}, 2 \mathrm{H})$, $4.04(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 2 \mathrm{H}), 3.75(\mathrm{~s}, 3 \mathrm{H}), 3.24(\mathrm{brsm}, 4 \mathrm{H}), 1.60(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $\mathrm{CDCl}_{3}$, $100 \mathrm{MHz}) \delta 16.4,41.4,55.1,58.8,62.1,112.6,113.3,124.4,128.4,131.4,138.5$, 140.7, 158.3. $\mathrm{HRMS}(\mathrm{ESI})$ calcd for $\mathrm{C}_{13} \mathrm{H}_{22} \mathrm{O}_{3} \mathrm{~N}\left[\mathrm{M}+\mathrm{NH}_{4}\right]^{+}: 240.1594$, found 240.1597.


To a 50 mL round bottom flask containing $4 \AA \mathrm{MS}(200 \mathrm{mg})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(8.0 \mathrm{~mL})$ was added (+) DET ( $396 \mu \mathrm{~L}, 2.32 \mathrm{mmol}$ ), $\mathrm{Ti}(i-\mathrm{PrO})_{4}(588 \mu \mathrm{~L}, 1.94 \mathrm{mmol})$ successively at $-25^{\circ} \mathrm{C}$ under an argon atmosphere, 20 minutes later, $t-\mathrm{BuO}_{2} \mathrm{H}(5.5 \mathrm{M}, 700 \mu \mathrm{~L}, 3.87$ mmol ) was added. 40 minutes later, the mixture was cooled to $-50^{\circ} \mathrm{C}$ and a solution of $8(285 \mathrm{mg}, 1.29 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2.0 \mathrm{~mL})$ was added dropwise. 12 hours later, the
mixture was warmed to room temperature and saturated aqueous Roche salt ( 10 mL ) was added. After stirring at room temperature for 6 hours, the mixture was filtered via a short column on silica gel with EtOAc as eluent, the filtrate was concentrated under vacuum. The residue was purified via column chromatography on silica gel (petroleum ether: ethyl acetate $=1: 1$ ) to give product $\mathbf{9}$ as a white solid ( $274 \mathrm{mg}, 1.15$ mmol, $90 \%$ yield, $91 \%$ ee $) . \mathrm{Mp}: 79-81^{\circ} \mathrm{C} \cdot[\alpha]^{19}{ }_{\mathrm{D}}=-40.0\left(c=1.0, \mathrm{CHCl}_{3}\right) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 7.02(\mathrm{~d}, J=8.40 \mathrm{~Hz}, 1 \mathrm{H}), 6.76(\mathrm{dd}, J=8.4 \mathrm{~Hz}, 2.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.54$ (d, $J=2.0 \mathrm{~Hz}, 1 \mathrm{H}), 4.76(\mathrm{~d}, J=15.6 \mathrm{~Hz}, 1 \mathrm{H}), 4.72(\mathrm{~d}, J=15.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.67-3.85(\mathrm{~m}$, $3 \mathrm{H}), 3.77$ (s, 3H), 3.15 (brs, 2H), 3.01 (d, $J=15.6 \mathrm{~Hz}, 1 \mathrm{H}$ ), 2.41 (d, $J=16.0 \mathrm{~Hz}, 1 \mathrm{H})$, $1.19(\mathrm{~s}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right) \delta 18.3,33.1,55.2,62.6,62.7,75.2,77.1$, 108.6, 113.0, 124.0, 130.3, 134.4, 157.7. HRMS(ESI) calcd for $\mathrm{C}_{13} \mathrm{H}_{19} \mathrm{O}_{4}[\mathrm{M}+\mathrm{H}]^{+}$: 239.1278, found 239.1275. Enantiomeric excess is $91 \%$ determined by HPLC (Chiralcel AD, Hexane/Isopropanol 90/10, flow rate $=1.0 \mathrm{~mL} / \mathrm{min}, 230 \mathrm{~nm}$ ): major isomer: $t_{R}=16.83 \mathrm{~min}$; minor isomer: $\mathrm{t}_{\mathrm{R}}=20.37 \mathrm{~min}$.




To a solution of $9(168.5 \mathrm{mg}, 0.708 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(8.0 \mathrm{~mL})$ was added aqueous $\mathrm{NaHCO}_{3}(90 \mu \mathrm{~L})$ and $\mathrm{NaIO}_{4}(302 \mathrm{mg}, 1.42 \mathrm{mmol})$ successively at $0^{\circ} \mathrm{C}$. One hour later, the mixture was filtered via a short silica gel column with petroleum ether: ethyl acetate $=4: 1$ as elute, and the filtrate was concentrated under vacuum. The residue was dissolved in dry THF ( 5 mL ) and vinylmagnesium bromide solution ( $0.7 \mathrm{M}, 1.1$ $\mathrm{mL}, 0.77 \mathrm{mmol}$ ) was added at $0^{\circ} \mathrm{C}$ dropwise, 10 minutes later, saturated aqueous $\mathrm{NH}_{4} \mathrm{Cl}(5 \mathrm{~mL})$ was added. The organic layer was separated and aqueous layer was
extracted with EtOAc ( $3 \times 50 \mathrm{~mL}$ ). The combined organic layer was washed with brine ( $3 \times 10 \mathrm{~mL}$ ), dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated under vacuum. The residue was purified via column chromatography on silica gel (petroleum ether: ethyl acetate $=15: 1)$ to give product $\mathbf{1 0}^{\prime}(47.8 \mathrm{mg}, 29 \%$ yield $)$ and $\mathbf{1 0}\left(97.5 \mathrm{mg}, 59 \%\right.$ yield). $[\alpha]^{19}{ }_{\mathrm{D}}$ $=-41.0\left(c=1.0, \mathrm{CHCl}_{3}\right) .{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 7.04(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.77$ (dd, $J=8.4 \mathrm{~Hz}, 2.8 \mathrm{~Hz}, 1 \mathrm{H}$ ), 6.56 (d, $J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 5.92-6.01$ (m, 1H), 5.45 (dt, $J=$ $17.2 \mathrm{~Hz}, 1.4 \mathrm{~Hz}, 1 \mathrm{H}$ ), 5.31 (dt, $J=10.8 \mathrm{~Hz}, 1.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.80(\mathrm{~s}, 2 \mathrm{H}), 4.12(\mathrm{~d}, J=6.4$ $\mathrm{Hz}, 1 \mathrm{H}), 3.79(\mathrm{~s}, 3 \mathrm{H}), 3.11$ (d, $J=16.0 \mathrm{~Hz}, 1 \mathrm{H}), 2.78$ (brs, 1 H ), 2.31 (d, $J=16.0 \mathrm{~Hz}$, $1 \mathrm{H}), 1.17(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right) \delta 18.7,31.0,55.2,63.1,75.2,78.7$, 108.5, 113.0, 118.0, 124.4, 130.4, 134.5, 135.4, 157.7. HRMS(ESI) calcd for $\mathrm{C}_{14} \mathrm{H}_{22} \mathrm{O}_{4} \mathrm{~N}\left[\mathrm{M}+\mathrm{NH}_{4}\right]^{+}: 252.1594$, found 252.1591.

$[\alpha]^{19}{ }_{\mathrm{D}}=-40.0\left(c=1.0, \mathrm{CHCl}_{3}\right) .{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 7.02(\mathrm{~d}, J=8.4 \mathrm{~Hz}$, $1 \mathrm{H}), 6.77$ (dd, $J=8.4 \mathrm{~Hz}, 2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.57(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 5.88-5.97(\mathrm{~m}, 1 \mathrm{H})$, 5.39 (dt, $J=17.2 \mathrm{~Hz}, 1.4 \mathrm{~Hz}, 1 \mathrm{H}), 5.27-5.30(\mathrm{~m}, 1 \mathrm{H}), 4.77$ (s, 2H), 4.09 (d, $J=6.4 \mathrm{~Hz}$, 1 H ), 3.78 (s, 3 H ), 2.86 (d, $J=15.6 \mathrm{~Hz}, 1 \mathrm{H}$ ), 2.72 (brs, 1 H ), 2.46 (d, $J=15.6 \mathrm{~Hz}, 1 \mathrm{H}$ ), $1.16(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right) \delta 16.8,34.3,55.2,62.9,75.5,78.2,108.7$, 113.0, 117.7, 123.9, 130.2, 134.7, 135.5, 157.8. HRMS(ESI) calcd for $\mathrm{C}_{14} \mathrm{H}_{22} \mathrm{O}_{4} \mathrm{~N}\left[\mathrm{M}+\mathrm{NH}_{4}\right]^{+}: 252.1594$, found 252.1591.


To a solution of $\mathbf{1 0}^{\prime}(115 \mathrm{mg}, 0.49 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(6 \mathrm{~mL})$ was added pyridine ( 120 $\mu \mathrm{L}, 1.5 \mathrm{mmol})$ and TIPSOTf ( $180 \mu \mathrm{~L}, 97 \%, 0.64 \mathrm{mmol}$ ) successively at $0^{\circ} \mathrm{C}$. Three hours later, saturated aqueous $\mathrm{NaHCO}_{3}(5 \mathrm{~mL})$ was added. The organic layer was separated and aqueous layer was extracted with $\mathrm{Et}_{2} \mathrm{O}(3 \times 30 \mathrm{~mL})$. The combined organic layer was washed with saturated aqueous $\mathrm{CuSO}_{4}(2 \times 10 \mathrm{~mL})$, brine ( $3 \times 10$ mL ), dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate $=100: 1$ ) to give product $11^{\prime}$ as a colorless oil ( $173 \mathrm{mg}, 0.43 \mathrm{mmol}, 88 \%$ yield $) .[\alpha]^{21} \mathrm{D}=-11.0(c=1.0$, $\left.\mathrm{CHCl}_{3}\right) .{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 7.03(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.75(\mathrm{dd}, J=8.4 \mathrm{~Hz}$,
$2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.56(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 5.94-6.03(\mathrm{~m}, 1 \mathrm{H}), 5.24-5.32(\mathrm{~m}, 1 \mathrm{H}), 4.74(\mathrm{t}, J$ $=16.2 \mathrm{~Hz}, 2 \mathrm{H}), 4.20(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.79(\mathrm{~s}, 3 \mathrm{H}), 3.03(\mathrm{~d}, J=16.0 \mathrm{~Hz}, 1 \mathrm{H}), 2.56$ $(\mathrm{d}, J=15.6 \mathrm{~Hz}, 1 \mathrm{H}), 1.16(\mathrm{~s}, 3 \mathrm{H}), 1.06-1.09(\mathrm{~m}, 21 \mathrm{H}){ }^{13}{ }^{1} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right) \delta$ 12.7, 18.2, 18.5, 34.4, 55.3, 63.2, 76.0, 79.4, 108.6, 112.8, 117.3, 125.0, 130.3, 135.3, 138.1, 157.7. HRMS(ESI) calcd for $\mathrm{C}_{22} \mathrm{H}_{39} \mathrm{O}_{3} \mathrm{Si}[\mathrm{M}+\mathrm{H}]^{+}: 391.2663$, found 391.2670 .


To a solution of $\mathbf{1 0}(84 \mathrm{mg}, 0.36 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5 \mathrm{~mL})$ was added pyridine $(87 \mu \mathrm{~L}$, $1.10 \mathrm{mmol})$ and TIPSOTf $(130 \mu \mathrm{~L}, 97 \%, 0.47 \mathrm{mmol})$ successively at $0^{\circ} \mathrm{C}$. Three hours later, saturated aqueous $\mathrm{NaHCO}_{3}(5 \mathrm{~mL})$ was added. The organic layer was separated and aqueous layer was extracted with $\mathrm{Et}_{2} \mathrm{O}(3 \times 30 \mathrm{~mL})$. The combined organic layer was washed with saturated aqueous $\mathrm{CuSO}_{4}(2 \times 10 \mathrm{~mL})$, brine $(3 \times 10 \mathrm{~mL})$, dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate $=100: 1$ ) to give product 11 as a colorless oil ( $126 \mathrm{mg}, 0.31 \mathrm{mmol}, 86 \%$ yield $) .[\alpha]^{21}{ }_{\mathrm{D}}=-43.0\left(c=1.0, \mathrm{CHCl}_{3}\right)$. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 7.01(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.75(\mathrm{dd}, J=8.4 \mathrm{~Hz}, 2.4 \mathrm{~Hz}$, $1 \mathrm{H}), 6.56(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 5.88-5.97(\mathrm{~m}, 1 \mathrm{H}), 5.20-5.30(\mathrm{~m}, 1 \mathrm{H}), 4.72(\mathrm{~s}, 2 \mathrm{H}), 4.23$ (d, $J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.79(\mathrm{~s}, 3 \mathrm{H}), 2.80(\mathrm{~d}, J=16.0 \mathrm{~Hz}, 1 \mathrm{H}), 2.40(\mathrm{~d}, J=15.6 \mathrm{~Hz}, 1 \mathrm{H})$, $1.19(\mathrm{~s}, 3 \mathrm{H}), 1.09-1.10(\mathrm{~m}, 21 \mathrm{H}){ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right) \delta$ 12.7, 18.15, 18.19, 34.1, 55.3, 62.9, 76.1, 80.5, 108.7, 112.7, 117.0, 125.1, 130.2, 135.7, 137.9, 157.7. HRMS(ESI) calcd for $\mathrm{C}_{22} \mathrm{H}_{39} \mathrm{O}_{3} \mathrm{Si}[\mathrm{M}+\mathrm{H}]^{+}: 391.2663$, found 391.2661.


To a solution of a mixture of $\mathbf{1 1}$ and $\mathbf{1 1}^{\prime}(100 \mathrm{mg}, 0.256 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(5.0 \mathrm{~mL})$ was added $4 \AA(150 \mathrm{mg}), 2,6$-dibromopyridine $(243 \mathrm{mg}, 1.03 \mathrm{mmol})$ and $\mathrm{InCl}_{3}(6.0$ $\mathrm{mg}, 0.026 \mathrm{mmol}$. .) successively at room temperature under an argon atmosphere, 15 minutes later, DDQ ( $50 \mathrm{mg}, 0.51 \mathrm{mmol}$ ) was added in one potion. 6 hours later, the brown mixture was filtered via a short silica gel column with petroleum ether: ethyl acetate $=4: 1$ as elute to separate the $4 \AA$ molecular sieve and 2, 6-dibromopyridine, the filtrate was concentrated under vacuum. The residue was purified via by column chromatography on silica gel (petroleum ether: ethyl acetate $=10$ : 1 ) to give a
colorless oil ( 31 mg ) which was dissolved in absolute $\mathrm{MeOH}(3.0 \mathrm{~mL})$ and $\mathrm{Na}_{2} \mathrm{CO}_{3}$ ( $220 \mathrm{mg}, 2.1 \mathrm{mmol}$ ) was added, the resulting solution was stirred at $25^{\circ} \mathrm{C}$ for 12 hours. The yellow mixture was filtered via a short silica gel column with EtOAc as elute, the filtrate was concentrated under vacuum and the residue was dissolved in absolute $\mathrm{MeOH}(3.0 \mathrm{~mL})$ and $\mathrm{NaBH}_{4}(5.0 \mathrm{mg}, 0.13 \mathrm{mmol})$ was added at $0^{\circ} \mathrm{C}, 10$ minutes later, saturated aqueous $\mathrm{NH}_{4} \mathrm{Cl}(5 \mathrm{~mL})$ was added. The mixture was extracted with EtOAc $(3 \times 30 \mathrm{~mL})$. The combined organic layer was washed with brine $(3 \times 10 \mathrm{~mL})$, dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate $=20: 1$ ) to give product $\mathbf{1 3}$ as a colorless oil and $\mathbf{1 3}^{\prime}$ as a white solid ( $25.7 \mathrm{mg}, \mathbf{1 3}: 19.6 \mathrm{mg}, \mathbf{1 3}^{\prime}: 6.1 \mathrm{mg}, 43 \%$ yield $) .[\alpha]^{24}{ }_{\mathrm{D}}=+31.0\left(c=1.0, \mathrm{CHCl}_{3}\right) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 6.96(\mathrm{~d}, J=8.4$ $\mathrm{Hz}, 1 \mathrm{H}), 6.70(\mathrm{dd}, J=8.4 \mathrm{~Hz}, 2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.51(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.94(\mathrm{~d}, J=7.2$ $\mathrm{Hz}, 1 \mathrm{H}), 3.77$ (s, 3 H ), 3.57 (dd, $J=10.6 \mathrm{~Hz}, 7.0 \mathrm{~Hz}, 1 \mathrm{H}$ ), 3.44-3.49 (m, 1H), 2.92 (d, $J$ $=17.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.83(\mathrm{~d}, J=16.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.48-2.56(\mathrm{~m}, 1 \mathrm{H}), 2.26-2.31(\mathrm{~m}, 1 \mathrm{H}), 1.69$ (brs, 1H), $1.53(\mathrm{~s}, 3 \mathrm{H}), 1.49(\mathrm{dd}, J=12.2 \mathrm{~Hz}, 4.2 \mathrm{~Hz}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 100\right.$ $\mathrm{MHz}) \delta 28.2,35.9,39.7,49.5,55.2,64.6,77.1,81.8,108.9,112.7,124.2,129.2$, 142.3, 157.7. $\mathrm{HRMS}(\mathrm{ESI})$ calcd for $\mathrm{C}_{14} \mathrm{H}_{18} \mathrm{O}_{3} \mathrm{NH}_{4}\left[\mathrm{M}+\mathrm{NH}_{4}\right]^{+}: 252.1594$, found 252.1597.


Mp: 90-91 ${ }^{\circ} \mathrm{C} .[\alpha]^{24}{ }_{\mathrm{D}}=-12.0\left(c=1.0, \mathrm{CHCl}_{3}\right) .{ }^{1} \mathrm{H} \operatorname{NMR}\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 6.97(\mathrm{~d}$, $J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.73$ (dd, $J=8.2 \mathrm{~Hz}, 2.6 \mathrm{~Hz}, 1 \mathrm{H}), 6.57(\mathrm{~d}, J=2.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.97(\mathrm{~d}, J$ $=6.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.75-3.79(\mathrm{~m}, 4 \mathrm{H}), 3.58(\mathrm{dd}, J=10.4 \mathrm{~Hz}, 6.6 \mathrm{~Hz}, 1 \mathrm{H}), 2.97(\mathrm{~d}, J=16.0$ $\mathrm{Hz}, 1 \mathrm{H}), 2.63(\mathrm{~d}, J=16.0 \mathrm{~Hz}, 1 \mathrm{H}), 2.22-2.29(\mathrm{~m}, 1 \mathrm{H}), 2.13-2.18(\mathrm{~m}, 1 \mathrm{H}), 1.91-1.97$ $(\mathrm{m}, 1 \mathrm{H}), 1.49(\mathrm{~s}, 4 \mathrm{H}){ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right) \delta 21.9,41.7,43.5,46.3,55.3$, 64.3, 76.7, 80.6, 109.2, 112.8, 123.9, 129.9, 141.3, 157.7. HRMS(ESI) calcd for $\mathrm{C}_{14} \mathrm{H}_{19} \mathrm{O}_{3}[\mathrm{M}+\mathrm{H}]^{+}: 235.1329$, found 235.1330.


To a solution of $\mathbf{1 3}(80 \mathrm{mg}, 0.342 \mathrm{mmol})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}: \mathrm{Et}_{3} \mathrm{~N}(5: 1)(6.0 \mathrm{~mL})$ was added $\mathrm{TsCl}(98 \mathrm{mg}, 0.51 \mathrm{mmol})$ and DMAP ( 2.0 mg, Cat.) at room temperature. Three hours later, saturated aqueous $\mathrm{NaHCO}_{3}(5 \mathrm{~mL})$ was added. The organic layer was separated
and aqueous layer was extracted with $\mathrm{EtOAc} / \mathrm{Et}_{2} \mathrm{O}(1: 1)(3 \times 50 \mathrm{~mL})$. The combined organic layer was washed with brine ( $3 \times 10 \mathrm{~mL}$ ), dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate $=20: 1$ ) to give product $\mathbf{1 3 - 1}$ as a colorless oil ( $130 \mathrm{mg}, 0.335 \mathrm{mmol}, 98 \%$ yield). Mp: $84-86^{\circ} \mathrm{C} .[\alpha]^{25}{ }_{\mathrm{D}}=+4.0\left(c=1.0, \mathrm{CHCl}_{3}\right)$. ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 7.73(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.33(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.77$ (d, $J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.66$ (dd, $J=8.4 \mathrm{~Hz}, 2.8 \mathrm{~Hz}, 1 \mathrm{H}), 6.44$ (d, $J=2.8 \mathrm{~Hz}, 1 \mathrm{H}), 4.90$ (d, $J=6.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.97(\mathrm{dd}, J=9.8 \mathrm{~Hz}, 6.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.79(\mathrm{~d}, J=10.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.75(\mathrm{~s}$, $3 \mathrm{H}), 2.87(\mathrm{~d}, J=17.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.56(\mathrm{~d}, J=16.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.38-2.51(\mathrm{~m}, 5 \mathrm{H}), 1.48(\mathrm{~s}$, $3 \mathrm{H}), 1.34(\mathrm{dd}, J=12.0 \mathrm{~Hz}, 3.6 \mathrm{~Hz}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right) \delta 21.6,27.8$, $35.8,39.6,45.8,55.2,71.3,76.8,81.6,108.9,112.8,123.3,127.9,129.2,129.9,132.7$, 141.5, 144.9, 157.8. HRMS(ESI) calcd for $\mathrm{C}_{21} \mathrm{H}_{28} \mathrm{O}_{5} \mathrm{SN}\left[\mathrm{M}+\mathrm{NH}_{4}\right]^{+}: 406.1683$, found 406.1678.


To a solution of $\mathrm{AlCl}_{3}(121 \mathrm{mg}, 0.91 \mathrm{mmol})$ in $\mathrm{EtSH}(1.0 \mathrm{~mL})$ was added a solution of 13-1 (118 mg, 0.3 mmol$)$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3.0 \mathrm{~mL})$ at room temperature. One hour later, absolute methanol $(1.0 \mathrm{~mL})$ was added. The solution was extracted with EtoAc: $\mathrm{CH}_{2} \mathrm{Cl}_{2}(10: 1)(3 \times 30 \mathrm{~mL})$. The combined organic layer was washed with brine ( $3 \times$ 10 mL ), dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate $=5: 1$ ) to give product 14 as a white solid ( $90 \mathrm{mg}, 0.24 \mathrm{mmol}, 80 \%$ yield). $\mathrm{Mp}: 158^{\circ} \mathrm{C}$ (decomposed). $[\alpha]^{25}{ }_{\mathrm{D}}=+12.0\left(c=1.0, \mathrm{CHCl}_{3}\right) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 7.73(\mathrm{~d}, J=8.4 \mathrm{~Hz}$, $1 \mathrm{H}), 7.33(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.70(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.57(\mathrm{dd}, J=8.2 \mathrm{~Hz}, J=2.6$ $\mathrm{Hz}, 1 \mathrm{H}), 6.33(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 5.65(\mathrm{~s}, 1 \mathrm{H}), 4.83(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.97$ (dd, $J=$ $10.0 \mathrm{~Hz}, J=6.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.78(\mathrm{t}, J=9.8 \mathrm{~Hz}, 1 \mathrm{H}), 2.86(\mathrm{~d}, J=17.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.55(\mathrm{~d}, J$ $=17.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.35-2.49(\mathrm{~m}, 5 \mathrm{H}), 1.48(\mathrm{~s}, 3 \mathrm{H}), 1.32(\mathrm{dd}, J=11.8 \mathrm{~Hz}, J=3.4 \mathrm{~Hz}$, $1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right) \delta 21.6,27.8,35.8,39.5,45.8,71.3,76.7,81.9$, $110.4,114.3,123.0,127.8,129.4,129.9,132.5,141.5,145.0,154.0$. HRMS(ESI) calcd for $\mathrm{C}_{20} \mathrm{H}_{26} \mathrm{O}_{5} \mathrm{SN}\left[\mathrm{M}+\mathrm{NH}_{4}\right]^{+}: 392.1526$, found 392.1531.


To a solution of $\mathbf{1 4}(76 \mathrm{mg}, 0.20 \mathrm{mmol})$ in xylene $(5.0 \mathrm{~mL})$ was added TBAF $(1.0 \mathrm{M}$ in THF, $1.0 \mathrm{~mL}, 1.0 \mathrm{mmol}$ ) at room temperature under an argon atmosphere. The resulting mixture was heated to $135^{\circ} \mathrm{C}$ and stirred for 12 hours, then the mixture was cooled to room temperature and $10 \%$ citric acid aqueous solution ( 5.0 mL ) was added. The organic layer was separated and aqueous layer was extracted with EtOAc ( $3 \times 30$ $\mathrm{mL})$. The combined organic layer was washed with brine ( $3 \times 10 \mathrm{~mL}$ ), dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated under vacuum. The residue was purified via by column chromatography on silica gel (petroleum ether: ethyl acetate $=5: 1$ ) to give product 3 as white solid ( $34 \mathrm{mg}, 0.17 \mathrm{mmol}, 85 \%$ yield $) . \mathrm{Mp}: 87-89^{\circ} \mathrm{C} .[\alpha]^{21}{ }_{\mathrm{D}}=+30.0(c=0.5$, $\left.\mathrm{CHCl}_{3}\right) .{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{CDCl}_{3}, 400 \mathrm{MHz}\right) \delta 6.65(\mathrm{~d}, J=10.0 \mathrm{~Hz}, 1 \mathrm{H}), 6.29(\mathrm{dd}, J=9.8 \mathrm{~Hz}$, $1.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.09(\mathrm{~s}, 1 \mathrm{H}), 4.69(\mathrm{~d}, J=4.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.57(\mathrm{t}, J=6.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.13-2.24$ (m, 2H), 1.89-1.98 (m, 2H), 1.76 (d, $J=11.2 \mathrm{~Hz}, 1 \mathrm{H}), 1.52(\mathrm{~d}, J=3.2 \mathrm{~Hz}, 1 \mathrm{H}), 1.49$ $(\mathrm{s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{CDCl}_{3}, 100 \mathrm{MHz}\right) \delta 22.1,42.5,44.3,48.6,49.9,54.8,79.9,87.0$, 121.7, 129.9, 150.9, 160.5, 187.0. HRMS(ESI) calcd for $\mathrm{C}_{13} \mathrm{H}_{15} \mathrm{O}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 203.1067$, found 203.1069.

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Injection Date : 2/26/2014 10:59:31 AM
Sample Name : A188 Location : Vial 1
Acq. Operator : jzw
Method : C: \HPCHEM $\backslash 1$ \METHODS $\backslash$ ZHANGQW.M
Last changed : 2/26/2014 9:51:02 AM by tjm (modified after loading)

DAD1 B, Sig=230,10 Ref=360,100 (JZW\JZW14021.D)


## Area Percent Report

| Sorted By | $:$ | Signal |
| :--- | :--- | :--- | :--- |
| Multiplier | $:$ | 1.0000 |
| Dilution | $:$ | 1.0000 |
| Sample Amount | $:$ | 6.00000 [ng/ul] (not used in calc.) |

Signal 1: DAD1 B, Sig=230,10 Ref $=360,100$

| $\begin{gathered} \text { Peak } \\ \# \end{gathered}$ | $\begin{gathered} \text { RetTime } \\ {[\text { min] }} \end{gathered}$ | Type | $\begin{gathered} \text { Width } \\ {[\mathrm{min}]} \end{gathered}$ | $\begin{gathered} \text { Area } \\ {\left[\mathrm{mAU}{ }^{*} \mathrm{~s}\right]} \end{gathered}$ | Height <br> [mAU] | $\begin{gathered} \text { Area } \\ \% \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 17.661 | BB | 0.5272 | 708.37555 | 20.49508 | 49.4734 |
| 2 | 20.808 | PB | 0.6166 | 723.45624 | 17.85745 | 50.5266 |
| Total | s : |  |  | 1431.83179 | 38.35253 |  |

Results obtained with enhanced integrator!

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                                    Summed Peaks Report
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Signal 1: DAD1 B, Sig=230,10 Ref=360,100
$=======================================================================$
Final Summed Peaks Report


Signal 1: DAD1 B, Sig=230,10 Ref=360,100

Injection Date : 3/8/2014 5:06:53 PM
Sample Name : A195 Location : Vial 1
Acq. Operator : jzw
Acq. Method : C: \HPCHEM $\backslash 1 \backslash M E T H O D S \backslash Z H A N G Q W . M$
Last changed : 3/8/2014 2:37:32 PM by zsh (modified after loading)
Analysis Method : C: \HPCHEM $\backslash 1 \backslash$ METHODS $\backslash$ ZHANGQW.M
Last changed : 12/22/2013 8:06:40 PM by tjm



Signal 1: DAD1 B, Sig=230,10 Ref=360,100

| Peak \# | $\begin{gathered} \text { RetTime } \\ {[\text { min] }} \end{gathered}$ | Type | Width <br> [min] | $\begin{gathered} \text { Area } \\ {[m A U * s]} \end{gathered}$ | Height <br> [mAU] | Area \% |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | 16.835 | PB | 0.6196 | 3.73689 e 4 | 940.45966 | 95.4195 |
| 2 | 20.374 | PB | 0.6157 | 1793.84412 | 44.74361 | 4.5805 |
| Total | s : |  |  | 3.91628 e 4 | 985.20327 |  |

Results obtained with enhanced integrator!
$====================================================================$ Summed Peaks Report

Signal 1: DAD1 B, Sig=230,10 Ref $=360,100$

Final Summed Peaks Report

Signal 1: DAD1 B, Sig=230,10 Ref=360,100



















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