Supporting Information
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## Supporting Information

for

## Rh(I)-Catalyzed Intramolecular [3+2] Cycloaddition of

 trans-2-Allene-VinylcyclopropanesCheng-Hang Liu and Zhi-Xiang Yu*Beijing National Laboratory for Molecular Sciences (BNLMS),Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education,College of Chemistry, Peking University, Beijing 100871, China.Email: yuzx@pku.edu.cn
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## 1. General

Air and moisture sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of dry argon. Similarly sensitive liquids and solutions were transferred via syringe. Reactions were stirred using Teflon-coated magnetic stir bars. Elevated temperatures were maintained using Thermostat-controlled silicone oil baths. Organic solutions were concentrated using a Büchi rotary evaporator with a desktop vacuum pump. Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with phosphomolybdic acid stain followed by gentle heating. Purification of products was accomplished by flash chromatography on silica gel and the purified compounds showed a single spot by analytical TLC.

Tetrahydrofuran, 1,2-dimethoxyethane and toluene were distilled from sodium and benzophenone prior to use. Dioxane, 1,2-dichloroethane and chlorobenzene (SuperDry, with molecular sieves) were purchased from J\&K and used directly. Synthetic reagents were purchased from Acros, Aldrich, and Alfa Aesar and used without further purification, unless otherwise indicated.

NMR spectra were measured on Bruker ARX $400\left({ }^{1} \mathrm{H}\right.$ at $400 \mathrm{MHz},{ }^{13} \mathrm{C}$ at 101 MHz$)$ nuclear magnetic resonance spectrometers. ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra are reported relative to $\mathrm{Me}_{4} \mathrm{Si}(0.00 \mathrm{ppm})$ or residual solvent signals $\left(\mathrm{C}_{6} \mathrm{D}_{6}: 7.16 \mathrm{ppm}\right)$. Data for ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra are reported as follows: chemical shift (ppm, $\mathrm{s}=$ singlet, brs = broad singlet, $\mathrm{d}=$ doublet, $\mathrm{t}=$ triplet, $\mathrm{q}=$ quartet, $\mathrm{dd}=$ doublet of doublets, $\mathrm{dt}=$ doublet of triplets, $\mathrm{dm}=$ doublet of multiplet, $\mathrm{ddd}=$ doublet of doublet of doublets, tdd $=$ triplet of doublet of doublets, $m=$ multiplet $)$, coupling constant $(\mathrm{Hz})$, and integration. Data for ${ }^{13} \mathrm{C}-\mathrm{NMR}$ are reported in terms of chemical shift ( ppm ) relative to residual solvent peak $\left(\mathrm{CDCl}_{3}: 77.0 \mathrm{ppm}, \mathrm{C}_{6} \mathrm{D}_{6}: 128.0 \mathrm{ppm}\right) .{ }^{13} \mathrm{C}$ signals are analyzed as follows: $(+)=$ $\mathrm{CH} 3 / \mathrm{CH},(-)=\mathrm{CH} 2$, quaternary carbons and other carbons with no attached protons are not marked. The assignment resulted from DEPT- $135^{\circ}$. 2 C or 3 C in ${ }^{13} \mathrm{C}$-NMR represents the number of carbon atoms. Infrared spectra were recorded on Bruker Tensor 27 fourier transform infrared spectrometer (FT-IR) and were reported in wavenumbers $\left(\mathrm{cm}^{-1}\right)$. High-resolution mass spectra (HRMS) were recorded on Bruker Apex IV FTMS mass spectrometer (ESI) and ThermoFisher Q Exactive GC GC-MS mass spectrometer (EI).

## Abbreviations:

$\mathrm{Bs}=p$-bromobenzenesulfonyl
COD = 1,5-cyclooctadiene
COE = cyclooctene
DCE $=1,2$-dichloroethane
DCM = dichloromethane
DIAD = diisopropyl azodicarboxylate
DMF $=$ N,N-dimethylformamide
DMSO = dimethyl sulphoxide
EA = ethyl acetate

MS = molecular sieve
Ms = methylsulfonyl
Ns = p-nitrobenzenesulfonyl
$\mathrm{PDC}=$ pyridinium dichromate
$\mathrm{PE}=$ petroleum ether
TBS $=t$-butyldimethylsilyl
THF = tetrahydrofuran
TLC $=$ thin layer chromatography
Ts = p-toluenesulfonyl

## 2. Synthesis of Substrates

## Substrate (1a)



To a stirred solution of V1a ${ }^{1}$ ( $196 \mathrm{mg}, 2 \mathrm{mmol}$ ), tosylamide A1a ${ }^{2}$ ( $553 \mathrm{mg}, 2.2 \mathrm{mmol}$ ), and $\mathrm{PPh}_{3}(1.05 \mathrm{~g}, 4 \mathrm{mmol})$ in anhydrous THF ( 10 mL ) was added DIAD ( $810 \mathrm{mg}, 4 \mathrm{mmol}$ ) at $0{ }^{\circ} \mathrm{C}$ under $\mathrm{N}_{2}$. The mixture was then stirred for 5 h at room temperature. The reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1) to afford product $\mathbf{1 a}(417 \mathrm{mg}, 63 \%)$.

1a: white solid, m.p. $=45-48{ }^{\circ} \mathrm{C}$, $\mathrm{TLC} R_{\mathrm{f}}=0.68$ (PE/EA, $5: 1$ ). ${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta$ 7.70 (d, $J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.28(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 5.31$ (ddd, $J=17.1,10.2,8.6 \mathrm{~Hz}, 1 \mathrm{H}), 4.99$ (dd, $J=17.1,1.6 \mathrm{~Hz}, 1 \mathrm{H}), 4.85(\mathrm{dd}, J=10.2,1.6 \mathrm{~Hz}, 1 \mathrm{H}), 4.76-4.65(\mathrm{~m}, 1 \mathrm{H}), 3.96(\mathrm{dd}, J=15.1,6.7$ $\mathrm{Hz}, 1 \mathrm{H}$ ), $3.85(\mathrm{dd}, J=15.1,7.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.25(\mathrm{dd}, J=14.5,6.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.08(\mathrm{dd}, J=14.5,7.3$ $\mathrm{Hz}, 1 \mathrm{H}), 2.41(\mathrm{~s}, 3 \mathrm{H}), 1.65(\mathrm{~s}, 3 \mathrm{H}), 1.65(\mathrm{~s}, 3 \mathrm{H}), 1.32-1.24(\mathrm{~m}, 1 \mathrm{H}), 1.01-0.92(\mathrm{~m}, 1 \mathrm{H}), 0.65-0.60$ $(\mathrm{m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 203.3,143.0,140.3(+), 137.8,129.6(+, 2 \mathrm{C}), 127.0(+$, 2C), $112.5(-)$, 96.7, $84.4(+), 49.5(-), 46.7(-)$, $21.7(+), 21.5(+), 20.4(+), 20.3(+), 18.8(+)$, 12.4 (-). HRMS (ESI) calcd for $\mathrm{C}_{19} \mathrm{H}_{26} \mathrm{NO}_{2} \mathrm{~S}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 332.1679$. Found: 332.1685.

## Substrate (1b)



To a stirred solution of V1a ( $196 \mathrm{mg}, 2 \mathrm{mmol}$ ), tosylamide $\mathbf{A 1 b}^{3}$ ( $552 \mathrm{mg}, 2 \mathrm{mmol}$ ), and $\mathrm{PPh}_{3}(1.05 \mathrm{~g}, 4 \mathrm{mmol})$ in anhydrous THF ( 10 mL ) was added DIAD ( $808 \mathrm{mg}, 4 \mathrm{mmol}$ ) at $0{ }^{\circ} \mathrm{C}$ under $\mathrm{N}_{2}$. The mixture was then stirred for 6 h at room temperature. The reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1) to afford product $\mathbf{1 b}(451 \mathrm{mg}, 63 \%)$.

1b: light yellow oil, TLC $R_{\mathrm{f}}=0.81$ (PE/EA, $5: 1$ ). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.71(\mathrm{~d}, J=8.3$ $\mathrm{Hz}, 2 \mathrm{H}), 7.28(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 5.31(\mathrm{ddd}, J=17.1,10.5,8.5 \mathrm{~Hz}, 1 \mathrm{H}), 4.99(\mathrm{dd}, J=17.1,1.5$ $\mathrm{Hz}, 1 \mathrm{H}), 4.96-4.90(\mathrm{~m}, 1 \mathrm{H}), 4.85(\mathrm{dd}, J=10.5,1.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.95(\mathrm{dd}, J=15.0,6.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.88$ (dd, $J=15.0,7.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.24(\mathrm{dd}, J=14.5,6.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.12(\mathrm{dd}, J=14.5,7.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.41(\mathrm{~s}$, $3 \mathrm{H}), 1.98-1.88(\mathrm{~m}, 4 \mathrm{H}), 1.34-1.24(\mathrm{~m}, 1 \mathrm{H}), 1.04-0.99(\mathrm{~m}, 1 \mathrm{H}), 0.99-0.92(\mathrm{~m}, 6 \mathrm{H}), 0.68-0.58(\mathrm{~m}$, 2H). ${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 201.7$, 143.0, $140.2(+), 137.9,129.6(+, 2 \mathrm{C}), 127.1(+, 2 \mathrm{C})$, $112.5(-), 109.7,88.5(+), 49.6(-), 47.2(-), 25.5(-), 25.4(-), 21.8(+), 21.5(+), 19.0(+), 12.6$ $(-), 12.3(+, 2 \mathrm{C})$. HRMS (ESI) calcd for $\mathrm{C}_{21} \mathrm{H}_{30} \mathrm{NO}_{2} \mathrm{~S}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 360.1992$. Found: 360.1999.

## Substrate (1c)



To a stirred solution of V1a (196 mg, 2 mmol ), tosylamide A1c ${ }^{4}$ ( $641 \mathrm{mg}, 2.2 \mathrm{mmol}$ ), and $\mathrm{PPh}_{3}(1.05 \mathrm{~g}, 4 \mathrm{mmol})$ in anhydrous THF ( 10 mL ) was added DIAD ( $808 \mathrm{mg}, 4 \mathrm{mmol}$ ) at $0{ }^{\circ} \mathrm{C}$ under $\mathrm{N}_{2}$. The mixture was then stirred for 6 h at room temperature. The reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1) to afford product 1c (493 mg, 66\%)

1c: colorless oil, TLC $R_{\mathrm{f}}=0.63(\mathrm{PE} / \mathrm{EA}, 5: 1) .{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 7.70(\mathrm{~d}, J=8.2 \mathrm{~Hz}$, $2 \mathrm{H}), 7.27(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 5.31(\mathrm{ddd}, J=17.0,10.2,8.6 \mathrm{~Hz}, 1 \mathrm{H}), 5.00(\mathrm{dd}, J=17.0,1.5 \mathrm{~Hz}$, $1 \mathrm{H}), 4.85(\mathrm{dd}, J=10.2,1.5 \mathrm{~Hz}, 1 \mathrm{H}), 4.75-4.66(\mathrm{~m}, 1 \mathrm{H}), 3.97(\mathrm{dd}, J=15.0,6.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.87(\mathrm{dd}$, $J=15.0,7.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.26(\mathrm{dd}, J=14.4,6.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.08(\mathrm{dd}, J=14.4,7.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.41(\mathrm{~s}$, $3 \mathrm{H}), 2.09-2.01(\mathrm{~m}, 4 \mathrm{H}), 1.59-1.47(\mathrm{~m}, 6 \mathrm{H}), 1.32-1.23(\mathrm{~m}, 1 \mathrm{H}), 1.01-0.91(\mathrm{~m}, 1 \mathrm{H}), 0.66-0.58$ $(\mathrm{m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 200.1,143.0,140.3(+), 138.0,129.6(+, 2 \mathrm{C}), 127.1(+$, 2C), $112.5(-), 103.8,84.2(+), 49.4(-), 46.9(-), 31.3(-), 31.2(-), 27.2(-), 27.1(-), 25.9(-)$, $21.7(+), 21.5(+), 18.8(+), 12.4(-)$. HRMS (ESI) calcd for $\mathrm{C}_{22} \mathrm{H}_{30} \mathrm{NO}_{2} \mathrm{~S}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 372.1992$. Found: 372.1984

## Substrate (1d)



To a stirred solution of SA1d ${ }^{5}$ ( $492 \mathrm{mg}, 4 \mathrm{mmol}$ ), TsNHBoc ( $1.29 \mathrm{~g}, 4.76 \mathrm{mmol}$ ), and $\mathrm{PPh}_{3}$ $(2.08 \mathrm{~g}, 8 \mathrm{mmol})$ in anhydrous THF $(20 \mathrm{~mL})$ was added DIAD $(1.60 \mathrm{~g}, 8 \mathrm{mmol})$ at $0{ }^{\circ} \mathrm{C}$ under $\mathrm{N}_{2}$. The mixture was then stirred for 5 h at room temperature. The reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1) to afford intermediate, which was used directly in the following step.

A stirred solution of the above intermediate in DMSO $(50 \mathrm{~mL})$ was immersed in a preheated oil bath at $180^{\circ} \mathrm{C}$ for 20 min . The mixture was cooled to rt and diluted with ether. The solution was washed 5 times with water, and dried over $\mathrm{MgSO}_{4}$. After removing the solvent, the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 5:1) to afford tosylamide A1d ( $894 \mathrm{mg}, 81 \%, 2$ steps).

A1d: white solid, m.p. $=107-110{ }^{\circ} \mathrm{C}$, TLC $R_{\mathrm{f}}=0.34(\mathrm{PE} / \mathrm{EA}, 5: 1) .{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ : $\delta 7.75(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.31(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 5.06-4.93(\mathrm{~m}, 1 \mathrm{H}), 4.42(\mathrm{t}, J=5.4 \mathrm{~Hz}, 1 \mathrm{H})$, 3.56-3.51 (m, 2H), $2.43(\mathrm{~s}, 3 \mathrm{H}), 2.34-2.25(\mathrm{~m}, 4 \mathrm{H}), 1.70-1.61(\mathrm{~m}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 101 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 196.4,143.4,137.1,129.7$ (+, 2C), $127.2(+, 2 \mathrm{C}), 108.0,88.1(+), 42.2(-), 31.3(-)$, $26.9(-), 21.5(+)$. HRMS (ESI) calcd for $\mathrm{C}_{15} \mathrm{H}_{20} \mathrm{NO}_{2} \mathrm{~S}\left([\mathrm{M}+\mathrm{H}]^{+}\right)$: 278.1209. Found: 278.1208.

To a stirred solution of V1a (149 mg, 1.5 mmol ), tosylamide A1d ( $458 \mathrm{mg}, 1.65 \mathrm{mmol}$ ), and $\mathrm{PPh}_{3}(787 \mathrm{mg}, 3 \mathrm{mmol})$ in anhydrous THF ( 7 mL ) was added DIAD ( $607 \mathrm{mg}, 3 \mathrm{mmol}$ ) at $0{ }^{\circ} \mathrm{C}$ under $\mathrm{N}_{2}$. The mixture was then stirred for 16 h at room temperature. The reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1) to afford product $1 \mathbf{d}$ ( $347 \mathrm{mg}, 64 \%$ ).

1d: light yellow oil, TLC $R_{\mathrm{f}}=0.59(\mathrm{PE} / \mathrm{EA}, 5: 1) .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.70(\mathrm{~d}, J=8.2$ $\mathrm{Hz}, 2 \mathrm{H}), 7.27(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 5.31$ (ddd, $J=17.0,10.3,8.6 \mathrm{~Hz}, 1 \mathrm{H}), 4.99(\mathrm{dd}, J=17.0,1.2$ $\mathrm{Hz}, 1 \mathrm{H}), 4.85(\mathrm{dd}, J=10.3,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.83-4.75(\mathrm{~m}, 1 \mathrm{H}), 3.98(\mathrm{dd}, J=15.1,6.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.87$ (dd, $J=15.1,7.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.24(\mathrm{dd}, J=14.3,6.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.07(\mathrm{dd}, J=14.3,7.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.41(\mathrm{~s}$, $3 H), 2.36-2.25(\mathrm{~m}, 4 \mathrm{H}), 1.71-1.60(\mathrm{~m}, 4 \mathrm{H}), 1.31-1.24(\mathrm{~m}, 1 \mathrm{H}), 1.01-0.92(\mathrm{~m}, 1 \mathrm{H}), 0.65-0.58(\mathrm{~m}$, $2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 198.7,143.0,140.3(+), 137.9,129.6(+, 2 \mathrm{C}), 127.1(+, 2 \mathrm{C})$, $112.5(-), 105.2,86.8(+), 49.5(-), 46.8(-), 31.2(-), 31.1(-), 27.0(-, 2 C), 21.7(+), 21.5(+)$, $18.9(+), 12.4(-)$. HRMS (ESI) calcd for $\mathrm{C}_{21} \mathrm{H}_{28} \mathrm{NO}_{2} \mathrm{~S}\left([\mathrm{M}+\mathrm{H}]^{+}\right)$: 358.1835. Found: 358.1833.

## Substrate (1e)



To a stirred solution of V1a ( $150 \mathrm{mg}, 1.5 \mathrm{mmol}$ ), $\mathrm{PPh}_{3}(472 \mathrm{mg}, 1.8 \mathrm{mmol})$ and imidazole $(123 \mathrm{mg}, 1.8 \mathrm{mmol})$ in anhydrous DCM ( 6 mL ) was added $\mathrm{I}_{2}(571 \mathrm{mg}, 2.25 \mathrm{mmol})$ slowly and the resulting mixture was stirred for 1 hour in dark. Saturated aqueous $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ was added to quench the reaction. The layers were separated, and the aqueous layers were extracted with ether. The combined organic layer was dried over $\mathrm{MgSO}_{4}$ and concentrated. The crude product was purified by flash column chromatography on silica gel (eluted with PE) and concentrated, which was used directly in the next step.

To a solution of A1e ( $311 \mathrm{mg}, 1 \mathrm{mmol}$ ) in DMF $(5 \mathrm{~mL})$ was added NaH ( $60 \%$ purity, 72 mg , 1.80 mmol ) and stirred at $0^{\circ} \mathrm{C}$ for 10 min . Then a solution of the above iodide in DMF ( 5 mL ) was added and the reaction mixture was allowed to slowly warm to rt and stirred for 2 h . Saturated aqueous $\mathrm{NH}_{4} \mathrm{Cl}$ was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over $\mathrm{MgSO}_{4}$, and concentrated. After removing the solvent, the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1 then 10:1) to afford $\mathbf{1 e}(352 \mathrm{mg}, 90 \%)$.

1e: light yellow oil, TLC $R_{\mathrm{f}}=0.59(\mathrm{PE} / \mathrm{EA}, 5: 1) .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.74-7.69(\mathrm{~m}$, 2H), 7.34-7.26 (m, 6H), 7.24-7.19 (m, 1H), 5.29-5.18 (m, 2 H), 4.99-4.89 (m, 1H), 4.86-4.78 (m, $1 \mathrm{H}), 4.17-3.91(\mathrm{~m}, 2 \mathrm{H}), 3.27(\mathrm{dd}, J=14.4,6.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.12(\mathrm{dd}, J=14.4,7.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.41(\mathrm{~s}$, $3 \mathrm{H}), 2.08-2.04(\mathrm{~m}, 3 \mathrm{H}), 1.28-1.16(\mathrm{~m}, 1 \mathrm{H}), 0.99-0.90(\mathrm{~m}, 1 \mathrm{H}), 0.62-0.52(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 205.4,143.1,140.12 \& 140.11(+), 137.63 \& 137.61,136.3,129.7(+, 2 \mathrm{C})$, $128.4(+, 2 \mathrm{C}), 127.1(+, 2 \mathrm{C}), 127.0(+), 125.8(+, 2 \mathrm{C}), 112.62 \& 112.59(-), 102.2,88.8 \& 88.7$ $(+), 50.0 \& 49.9(-), 46.3 \& 46.2(-), 21.8 \& 21.7(+), 21.5(+), 18.85 \& 18.79(+), 17.0 \& 16.9$ $(+), 12.43 \& 12.41(-) . H R M S(E S I)$ calcd for $\mathrm{C}_{24} \mathrm{H}_{28} \mathrm{NO}_{2} \mathrm{~S}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 394.1835$. Found: 394.1840.

## Substrate (1f)



To a stirred solution of V1a (100 mg, 1 mmol ), tosylamide A1f ${ }^{3}$ ( $227 \mathrm{mg}, 0.80 \mathrm{mmol}$ ), and $\mathrm{PPh}_{3}(420 \mathrm{mg}, 1.6 \mathrm{mmol})$ in anhydrous THF ( 5 mL ) was added DIAD ( $325 \mathrm{mg}, 1.6 \mathrm{mmol}$ ) at $0{ }^{\circ} \mathrm{C}$ under $\mathrm{N}_{2}$. The mixture was then stirred overnight ( 16 h ) at room temperature. The reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1) to afford product $\mathbf{1 f}(260 \mathrm{mg}, 89 \%$ ).

1f: light yellow oil, TLC $R_{\mathrm{f}}=0.58$ (PE/EA, 5:1). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 8.34$ (d, $J=9.0$ $\mathrm{Hz}, 2 \mathrm{H}), 8.01(\mathrm{~d}, J=9.0 \mathrm{~Hz}, 2 \mathrm{H}), 5.30(\mathrm{ddd}, J=17.1,10.2,8.6 \mathrm{~Hz}, 1 \mathrm{H}), 5.01(\mathrm{dd}, J=17.1,1.1$ $\mathrm{Hz}, 1 \mathrm{H}), 4.88(\mathrm{dd}, J=10.2,1.1 \mathrm{~Hz}, 1 \mathrm{H}), 4.75-4.69(\mathrm{~m}, 1 \mathrm{H}), 4.01(\mathrm{dd}, J=15.2,6.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.91$ (dd, $J=15.2,7.1 \mathrm{~Hz}, 1 \mathrm{H}), 3.33(\mathrm{dd}, J=14.4,6.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.13(\mathrm{dd}, J=14.4,7.4 \mathrm{~Hz}, 1 \mathrm{H}), 1.66(\mathrm{~s}$, $3 \mathrm{H}), 1.65(\mathrm{~s}, 3 \mathrm{H}), 1.35-1.25(\mathrm{~m}, 1 \mathrm{H}), 1.00-0.90(\mathrm{~m}, 1 \mathrm{H}), 0.69-0.62(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 101 MHz , $\left.\mathrm{CDCl}_{3}\right): \delta 203.5,149.8,146.9,139.8(+), 128.2(+, 2 \mathrm{C}), 124.3(+, 2 \mathrm{C}), 113.0(-), 97.4,83.9(+)$, $49.8(-), 46.9(-), 21.9(+), 20.3(+), 20.2(+), 18.7(+), 12.4(-)$. HRMS (ESI) calcd for $\mathrm{C}_{18} \mathrm{H}_{23} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{~S}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 363.1373$. Found: 363.1379.

## Substrate (1g)



To a stirred solution of V1a ( $98 \mathrm{mg}, 1 \mathrm{mmol}$ ), tosylamide $\mathbf{A 1 g}{ }^{3}(346 \mathrm{mg}, 1.1 \mathrm{mmol})$, and $\mathrm{PPh}_{3}(524 \mathrm{~g}, 2 \mathrm{mmol})$ in anhydrous THF $(5 \mathrm{~mL})$ was added DIAD $(406 \mathrm{mg}, 2 \mathrm{mmol})$ at $0{ }^{\circ} \mathrm{C}$ under $\mathrm{N}_{2}$. The mixture was then stirred overnight ( 16 h ) at room temperature. The reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1) to afford product $\mathbf{1 g}$ ( $272 \mathrm{mg}, 68 \%$ ).

1g: white solid, m.p. $=37-40{ }^{\circ} \mathrm{C}$, TLC $R_{\mathrm{f}}=0.66(\mathrm{PE} / \mathrm{EA}, 5: 1) .{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta$ $7.68(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 2 \mathrm{H}), 7.62(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 2 \mathrm{H}), 5.31(\mathrm{ddd}, J=17.0,10.2,8.6 \mathrm{~Hz}, 1 \mathrm{H}), 5.00(\mathrm{dd}$, $J=17.0,1.5 \mathrm{~Hz}, 1 \mathrm{H}), 4.87(\mathrm{dd}, J=10.2,1.5 \mathrm{~Hz}, 1 \mathrm{H}), 4.76-4.68(\mathrm{~m}, 1 \mathrm{H}), 3.96(\mathrm{dd}, J=15.1,6.6$ $\mathrm{Hz}, 1 \mathrm{H}), 3.86(\mathrm{dd}, J=15.1,7.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.26(\mathrm{dd}, J=14.4,6.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.09(\mathrm{dd}, J=14.4,7.4$ $\mathrm{Hz}, 1 \mathrm{H}), 1.66(\mathrm{~s}, 3 \mathrm{H}), 1.65(\mathrm{~s}, 3 \mathrm{H}), 1.33-1.24(\mathrm{~m}, 1 \mathrm{H}), 1.00-0.92(\mathrm{~m}, 1 \mathrm{H}), 0.67-0.61(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 203.4,140.1,140.0(+), 132.3$ (+, 2C), 128.6 (+, 2C), 127.2, 112.7 (-), 97.0, $84.2(+), 49.6(-), 46.7(-), 21.8(+), 20.3(+), 20.2(+), 18.8(+), 12.4(-)$. HRMS (ESI) calcd for $\mathrm{C}_{18} \mathrm{H}_{23} \mathrm{BrNO}_{2} \mathrm{~S}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 396.0627$. Found: 396.0626.

## Substrate (1h)



A1h


1h

To a stirred solution of V1a (196 mg, 2 mmol ), tosylamide A1h ${ }^{3}$ ( $522 \mathrm{mg}, 2.2 \mathrm{mmol}$ ), and $\mathrm{PPh}_{3}(1.05 \mathrm{~g}, 4 \mathrm{mmol})$ in anhydrous THF $(10 \mathrm{~mL})$ was added DIAD $(808 \mathrm{mg}, 4 \mathrm{mmol})$ at $0{ }^{\circ} \mathrm{C}$ under $\mathrm{N}_{2}$. The mixture was then stirred for 6 h at room temperature. The reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1) to afford product $1 \mathrm{lh}(441 \mathrm{mg}, 69 \%)$.

1h: light yellow oil, TLC $R_{\mathrm{f}}=0.66(\mathrm{PE} / \mathrm{EA}, 5: 1) .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.85-7.79(\mathrm{~m}$, $2 \mathrm{H}), 7.58-7.46(\mathrm{~m}, 3 \mathrm{H}), 5.31$ (ddd, $J=17.1,10.2,8.5 \mathrm{~Hz}, 1 \mathrm{H}), 4.99(\mathrm{dd}, J=17.1,1.2 \mathrm{~Hz}, 1 \mathrm{H})$, $4.85(\mathrm{dd}, J=10.2,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.76-4.66(\mathrm{~m}, 1 \mathrm{H}), 3.98(\mathrm{dd}, J=15.1,6.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.87(\mathrm{dd}, J=$ $15.1,7.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.27(\mathrm{dd}, J=14.4,6.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.10(\mathrm{dd}, J=14.4,7.3 \mathrm{~Hz}, 1 \mathrm{H}), 1.65(\mathrm{~s}, 3 \mathrm{H})$, $1.64(\mathrm{~s}, 3 \mathrm{H}), 1.33-1.24(\mathrm{~m}, 1 \mathrm{H}), 1.00-0.91(\mathrm{~m}, 1 \mathrm{H}), 0.66-0.60(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 101 MHz , $\left.\mathrm{CDCl}_{3}\right): \delta 203.3,140.9,140.2(+), 132.3(+), 129.0(+, 2 \mathrm{C}), 127.0(+, 2 \mathrm{C}), 112.6(-), 96.8,84.4$ $(+), 49.6(-), 46.7(-), 21.7(+), 20.4(+), 20.3(+), 18.8(+), 12.4(-)$. HRMS (ESI) calcd for $\mathrm{C}_{18} \mathrm{H}_{24} \mathrm{NO}_{2} \mathrm{~S}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 318.1522$. Found: 318.1522.

## Substrate (1i)



To a stirred solution of V1a ( $150 \mathrm{mg}, 1.5 \mathrm{mmol}$ ) in anhydrous THF ( 7 mL ) was added $n-\mathrm{BuLi}$ $(1.6 \mathrm{M}, 1.2 \mathrm{~mL}, 1.92 \mathrm{mmol})$ at $-78^{\circ} \mathrm{C}$ under $\mathrm{N}_{2}$. The mixture was then stirred for 15 min at $-78^{\circ} \mathrm{C}$ and $\mathrm{MsCl}(206 \mathrm{mg}, 1.8 \mathrm{mmol})$ was added. After $5 \mathrm{~min}, \mathrm{LiBr}(651 \mathrm{mg}, 7.5 \mathrm{mmol})$ was added and the mixture was stirred for another 20 min at $-78^{\circ} \mathrm{C}$. The solution of bromide product was used in the next step directly.

To a stirred solution of $\mathbf{A 1 i} \mathbf{i}^{3}(212 \mathrm{mg}, 1 \mathrm{mmol})$ in DMF ( 5 mL ) was added $\mathrm{NaH}(80 \mathrm{mg}, 60 \%$ purity, 2 mmol ) at $0{ }^{\circ} \mathrm{C}$ under $\mathrm{N}_{2}$. After 30 min , the above THF solution of bromide was added at $-78{ }^{\circ} \mathrm{C}$ and the reaction mixture was stirred for 20 h at $60^{\circ} \mathrm{C}$. After the completion of this transformation, saturated aqueous $\mathrm{NH}_{4} \mathrm{Cl}$ was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over $\mathrm{MgSO}_{4}$, and concentrated. After removing the solvent, the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1) to afford $\mathbf{1 i}$ ( $102 \mathrm{mg}, 35 \%$ ).

1i: yellow oil, TLC $R_{\mathrm{f}}=0.63$ (PE/EA, 5:1). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 5.33$ (ddd, $J=17.0$, $10.2,8.7 \mathrm{~Hz}, 1 \mathrm{H}), 5.00(\mathrm{dd}, J=17.0,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.84(\mathrm{dd}, J=10.2,1.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.78-4.70(\mathrm{~m}$, $1 \mathrm{H}), 3.72(\mathrm{~s}, 3 \mathrm{H}), 3.71(\mathrm{~s}, 3 \mathrm{H}), 2.75-2.60(\mathrm{~m}, 2 \mathrm{H}), 2.00(\mathrm{dd}, J=14.4,6.5 \mathrm{~Hz}, 1 \mathrm{H}), 1.91(\mathrm{dd}, J=$ $14.4,7.3 \mathrm{~Hz}, 1 \mathrm{H}), 1.67-1.64(\mathrm{~m}, 6 \mathrm{H}), 1.21-1.12(\mathrm{~m}, 1 \mathrm{H}), 0.72-0.63(\mathrm{~m}, 1 \mathrm{H}), 0.61-0.48(\mathrm{~m}, 2 \mathrm{H})$. ${ }^{13} \mathrm{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 203.8,171.6,171.5,141.1$ (+), 111.9 (-), 95.2, 82.8 (+), 57.8,
$52.4(+, 2 C), 36.0(-), 32.8(-), 22.2(+), 20.5(+), 20.4(+), 15.8(+), 13.2(-)$. HRMS (ESI) calcd for $\mathrm{C}_{17} \mathrm{H}_{25} \mathrm{O}_{4}\left([\mathrm{M}+\mathrm{H}]^{+}\right):$293.1747. Found: 293.1742.

## Substrate (1j)



To a stirred solution of $\mathbf{V 1 j}{ }^{6}(174 \mathrm{mg}, 1 \mathrm{mmol})$, tosylamide A1a (278 mg, 1.1 mmol ), and $\mathrm{PPh}_{3}(524 \mathrm{~g}, 2 \mathrm{mmol})$ in anhydrous THF ( 5 mL ) was added DIAD ( $405 \mathrm{mg}, 2 \mathrm{mmol}$ ) at $0^{\circ} \mathrm{C}$ under $\mathrm{N}_{2}$. The mixture was then stirred overnight $(16 \mathrm{~h})$ at room temperature. The reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1) to afford product $\mathbf{1 j}$ ( $163 \mathrm{mg}, 40 \%$ ).

1j: colorless oil, TLC $R_{\mathrm{f}}=0.60(\mathrm{PE} / \mathrm{EA}, 5: 1) .{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 7.73-7.68(\mathrm{~m}, 2 \mathrm{H})$, $7.29-7.25(\mathrm{~m}, 6 \mathrm{H}), 7.21-7.15(\mathrm{~m}, 1 \mathrm{H}), 6.36(\mathrm{~d}, J=15.8 \mathrm{~Hz}, 1 \mathrm{H}), 5.67(\mathrm{dd}, J=15.8,8.7 \mathrm{~Hz}, 1 \mathrm{H})$, $4.78-4.70(\mathrm{~m}, 1 \mathrm{H}), 3.97(\mathrm{dd}, J=15.0,6.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.88(\mathrm{dd}, J=15.0,7.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.33(\mathrm{dd}, J=$ $14.4,6.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.10(\mathrm{dd}, J=14.4,7.5 \mathrm{~Hz}, 1 \mathrm{H}), 2.39(\mathrm{~s}, 3 \mathrm{H}), 1.69-1.64(\mathrm{~m}, 6 \mathrm{H}), 1.46-1.39(\mathrm{~m}$, $1 \mathrm{H}), 1.11-1.03(\mathrm{~m}, 1 \mathrm{H}), 0.77-0.69(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 203.4,143.0,137.9$, $137.4,132.4(+), 129.6(+, 2 C), 128.5(+, 2 C), 128.2(+), 127.1(+, 2 \mathrm{C}), 126.8(+), 125.6(+, 2 \mathrm{C})$, 96.7, $84.5(+), 49.6(-), 46.8(-), 21.6(+), 21.5(+), 20.4(+), 20.3(+), 19.3(+), 12.9(-)$. HRMS (ESI) calcd for $\mathrm{C}_{25} \mathrm{H}_{30} \mathrm{NO}_{2} \mathrm{~S}\left([\mathrm{M}+\mathrm{H}]^{+}\right)$: 408.1992. Found: 408.1992.

## Substrate (1k)



To a stirred solution of $\mathbf{V 1} \mathbf{k}^{7}(126 \mathrm{mg}, 1 \mathrm{mmol})$, tosylamide A1a ( $280 \mathrm{mg}, 1.1 \mathrm{mmol}$ ), and $\mathrm{PPh}_{3}(527 \mathrm{mg}, 2 \mathrm{mmol})$ in anhydrous THF ( 5 mL ) was added DIAD ( $404 \mathrm{mg}, 2 \mathrm{mmol}$ ) at $0^{\circ} \mathrm{C}$ under $\mathrm{N}_{2}$. The mixture was then stirred for 11 h at room temperature. The reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 50:1 then 20:1) to afford product $\mathbf{1 k}$ ( $199 \mathrm{mg}, 55 \%$ ).
$\mathbf{1 k}$ : colorless oil, TLC $R_{\mathrm{f}}=0.60(\mathrm{PE} / \mathrm{EA}, 5: 1) .{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 7.70(\mathrm{~d}, J=8.3 \mathrm{~Hz}$, $2 \mathrm{H}), 7.27(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 5.45(\mathrm{dt}, J=15.2,6.4 \mathrm{~Hz}, 1 \mathrm{H}), 4.92(\mathrm{dd}, J=15.2,8.3 \mathrm{~Hz}, 1 \mathrm{H})$, $4.75-4.67(\mathrm{~m}, 1 \mathrm{H}), 3.96(\mathrm{dd}, J=15.0,6.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.86(\mathrm{dd}, J=15.0,7.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.22(\mathrm{dd}, J=$ $14.3,6.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.07(\mathrm{dd}, J=14.3,7.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.41(\mathrm{~s}, 3 \mathrm{H}), 2.02-1.91(\mathrm{~m}, 2 \mathrm{H}), 1.66-1.63(\mathrm{~m}$, $6 \mathrm{H}), 1.23-1.15(\mathrm{~m}, 1 \mathrm{H}), 0.94(\mathrm{t}, J=7.4 \mathrm{~Hz}, 3 \mathrm{H}), 0.91-0.85(\mathrm{~m}, 1 \mathrm{H}), 0.58-0.51(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 203.3,142.9,137.9,130.8(+), 130.6(+), 129.6(+, 2 \mathrm{C}), 127.1(+$, 2C), 96.6, 84.5 (+), $49.7(-), 46.7(-), 25.4(-), 21.5(+), 20.6(+), 20.4(+), 20.3(+), 18.5(+)$, $13.8(+), 12.1(-)$. HRMS (ESI) calcd for $\mathrm{C}_{21} \mathrm{H}_{30} \mathrm{NO}_{2} \mathrm{~S}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 360.1992$. Found: 360.1990.

## Substrate (11)



To a solution of DME ( $1.17 \mathrm{~g}, 13 \mathrm{mmol}$ ) in $\mathrm{DCM}(50 \mathrm{~mL})$ was added $\mathrm{ZnEt}_{2}(1 \mathrm{M}, 20 \mathrm{~mL})$ and $\mathrm{CH}_{3} \mathrm{CHI}_{2}{ }^{8}(11.11 \mathrm{~g}, 39 \mathrm{mmol})$ successively at $0^{\circ} \mathrm{C}$ under $\mathrm{N}_{2}$. The mixture was then stirred for 30 min at $0^{\circ} \mathrm{C}$ and a solution of $\mathbf{S V 1 1}^{9}(2.63 \mathrm{~g}, 13 \mathrm{mmol})$ in $\mathrm{DCM}(50 \mathrm{~mL})$ was added. After 16 h , saturated aqueous $\mathrm{NH}_{4} \mathrm{Cl}$ was added to quench the reaction, and the mixture was extracted with ether. The combined extract was dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, and concentrated. The crude product was purified by flash column chromatography (eluted with PE/EA 5:1) to afford cyclopropane product ( $1.46 \mathrm{~g}, 49 \%$ ).

The cyclopropane product ( $1.46 \mathrm{~g}, 6.34 \mathrm{mmol}$ ) was dissolved in DCM ( 30 mL ), then PDC $(2.38 \mathrm{~g}, 6.34 \mathrm{mmol})$ and $4 \AA$ Á $\mathrm{MS}(1.5 \mathrm{~g})$ were added successively. The resulting mixture was stirred for 2 h at rt . After the accomplishment of the oxidation reaction, the mixture was filtered and the filtrate was concentrated. The crude aldehyde product was purified by flash column chromatography (eluted with PE/EA 20:1) and used in the next step directly.

To a mixture of methyltriphenylphosphonium bromide ( $4.98 \mathrm{~g}, 13.9 \mathrm{mmol}$ ) and $t$-BuOK $(1.42 \mathrm{~g}, 12.68 \mathrm{mmol})$ in round bottle was added THF ( 20 mL ) under an argon atmosphere at $0^{\circ} \mathrm{C}$, and the resulting solution was stirred for 30 min at $0^{\circ} \mathrm{C}$. Then a solution of the crude aldehyde product in THF ( 20 mL ) was added dropwise at $0^{\circ} \mathrm{C}$, and the resulting mixture was stirred for 1 h at room temperature. After that, saturated aqueous $\mathrm{NH}_{4} \mathrm{Cl}$ was added to quench the reaction, and the mixture was extracted with ether. The combined extract was washed with water and brine, dried over $\mathrm{MgSO}_{4}$, and concentrated. The crude product was purified by flash column chromatography (eluted with PE) to afford V11 ( $868 \mathrm{mg}, 60 \%$ for two steps, d.r. $=1.4: 1$ ).

V11: colorless oil, TLC $R_{\mathrm{f}}=0.76$ (PE/EA, 10:1). ${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 5.56$ (ddd, $J=$ $17.1,10.1,9.1 \mathrm{~Hz}, 1 \mathrm{H}), 5.44$ (ddd, $J=17.0,10.3,9.1 \mathrm{~Hz}, 1.4 \mathrm{H}), 5.09(\mathrm{dd}, J=17.1,1.8 \mathrm{~Hz}, 1 \mathrm{H})$, $5.02-4.95(\mathrm{~m}, 1 \mathrm{H}+1.4 \mathrm{H}), 4.82(\mathrm{dd}, J=10.3,1.6 \mathrm{~Hz}, 1.4 \mathrm{H}), 3.83(\mathrm{dd}, J=11.0,5.9 \mathrm{~Hz}, 1.4 \mathrm{H}), 3.63$ (dd, $J=10.9,5.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.55-3.47(\mathrm{~m}, 1 \mathrm{H}+1.4 \mathrm{H}), 1.41-1.33(\mathrm{~m}, 1 \mathrm{H}), 1.17-1.09(\mathrm{~m}, 1.4 \mathrm{H})$, $1.12(\mathrm{~d}, J=5.8 \mathrm{~Hz}, 3 \times 1.4 \mathrm{H}), 1.07(\mathrm{~d}, J=6.2 \mathrm{~Hz}, 3 \mathrm{H}), 1.02-0.93(\mathrm{~m}, 1 \mathrm{H}+2 \times 1.4 \mathrm{H}), 0.90(\mathrm{~s}$, $9 \times 1.4 \mathrm{H}), 0.89(\mathrm{~s}, 9 \mathrm{H}), 0.86-0.81(\mathrm{~m}, 1 \mathrm{H}), 0.06(\mathrm{~s}, 3 \times 1.4 \mathrm{H}), 0.06(\mathrm{~s}, 3 \times 1.4 \mathrm{H}), 0.04(\mathrm{~s}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 141.4 \& 137.4(+), 114.1 \& 111.3(-)$, $65.7 \& 62.2(-), 29.9 \& 28.4(+)$, $27.5 \& 25.1(+), 25.97 \& 25.95(+, 3 C), 19.4 \& 17.8(+), 18.35 \& 18.34,13.2 \& 12.4(+),-5.10 \&$ $-5.19 \&-5.12(+, 2 \mathrm{C},-5.10 \&-5.19$ belong to one isomer and -5.12 belongs to another). HRMS (EI) calcd for $\mathrm{C}_{9} \mathrm{H}_{17} \mathrm{OSi}\left(\left[\mathrm{M}-\mathrm{C}\left(\mathrm{CH}_{3}\right)_{3}\right]^{+}\right)$: 169.1043. Found: 169.1042.

V11 ( $860 \mathrm{mg}, 3.8 \mathrm{mmol}$ ) was dissolved in THF ( 8 mL ) and $\mathrm{Et}_{3} \mathrm{~N} \cdot 3 \mathrm{HF}$ ( $702 \mathrm{mg}, 4.35 \mathrm{mmol}$ ) was added. The resulting solution was stirred for 15 h at rt . After removing the solvent, the crude
product was purified by flash column chromatography on silica gel (eluted with $\mathrm{PE} / \mathrm{Et}_{2} \mathrm{O} 3: 1$ then $1: 1$ ) to afford alcohol ( $373 \mathrm{mg}, 88 \%$ ).

To a stirred solution of the above alcohol ( $112 \mathrm{mg}, 1 \mathrm{mmol}$ ), tosylamide A1a ( $276 \mathrm{mg}, 1.1$ mmol ), and $\mathrm{PPh}_{3}(523 \mathrm{mg}, 2 \mathrm{mmol})$ in anhydrous THF ( 5 mL ) was added DIAD ( $406 \mathrm{mg}, 2 \mathrm{mmol}$ ) at $0^{\circ} \mathrm{C}$ under $\mathrm{N}_{2}$. The mixture was then stirred for 5 h at room temperature. The reaction mixture was concentrated and the crude product was purified by flash column chromatography on silica gel (eluted with PE/EA 20:1) to afford product $11(219 \mathrm{mg}, 63 \%$, d.r. $=1.4: 1)$.

11: light yellow oil, TLC $R_{\mathrm{f}}=0.78(\mathrm{PE} / \mathrm{EA}, 5: 1) .{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 7.74-7.66(\mathrm{~m}$, $2 \mathrm{H}+2 \times 1.4 \mathrm{H}), 7.31-7.26(\mathrm{~m}, 2 \mathrm{H}+2 \times 1.4 \mathrm{H}), 5.47(\mathrm{ddd}, J=17.1,10.2,8.9 \mathrm{~Hz}, 1 \mathrm{H}), 5.33(\mathrm{ddd}, J=$ $17.1,10.3,8.0 \mathrm{~Hz}, 1.4 \mathrm{H}), 5.04(\mathrm{dd}, J=17.1,1.5 \mathrm{~Hz}, 1 \mathrm{H}), 4.98(\mathrm{dd}, J=10.2,1.5 \mathrm{~Hz}, 1 \mathrm{H}), 4.93(\mathrm{dd}$, $J=17.1,1.5 \mathrm{~Hz}, 1.4 \mathrm{H}), 4.82(\mathrm{dd}, J=10.3,1.5 \mathrm{~Hz}, 1.4 \mathrm{H}), 4.75-4.61(\mathrm{~m}, 1 \mathrm{H}+1.4 \mathrm{H}), 4.02-3.78(\mathrm{~m}$, $2 \mathrm{H}+2 \times 1.4 \mathrm{H}), 3.52(\mathrm{dd}, J=14.3,4.7 \mathrm{~Hz}, 1.4 \mathrm{H}), 3.22(\mathrm{dd}, J=14.3,6.9 \mathrm{~Hz}, 1 \mathrm{H}), 3.17-3.05(\mathrm{~m}$, $1 \mathrm{H}+1.4 \mathrm{H}), 2.41(\mathrm{~s}, 3 \mathrm{H}+3 \times 1.4 \mathrm{H}), 1.69-1.60(\mathrm{~m}, 6 \mathrm{H}+6 \times 1.4 \mathrm{H}), 1.35-1.28(\mathrm{~m}, 1 \mathrm{H}), 1.14-1.04(\mathrm{~m}$, $3 \times 1.4 \mathrm{H}), 1.01(\mathrm{~d}, J=6.3 \mathrm{~Hz}, 3 \mathrm{H}), 0.99-0.85(\mathrm{~m}, 1 \mathrm{H}+3 \times 1.4 \mathrm{H}), 0.77-0.69(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR $(101$ $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 203.22 \& 203.18,142.9,140.7 \& 136.4(+), 137.90 \& 137.89,129.61 \& 129.60$ $(+, 2 C), 127.09 \& 127.06(+, 2 C), 114.8 \& 111.9(-), 96.63 \& 96.59,84.5(+), 49.5 \& 46.3(-)$, $46.6 \& 44.9(-), 29.8(+), 26.6 \& 25.7(+), 23.2 \& 21.5(+), 20.44 \& 20.36(+), 20.29 \& 20.26(+)$, $19.0 \& 18.9(+), 12.9 \& 12.6(+)$. HRMS (ESI) calcd for $\mathrm{C}_{20} \mathrm{H}_{28} \mathrm{NO}_{2} \mathrm{~S}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 346.1835$. Found: 346.1834 .

## 3 [3+2] Cycloaddition



General procedure: To a mixture of $\mathrm{Rh}(\mathrm{CO})\left(\mathrm{PMe}_{3}\right)_{2} \mathrm{Cl}^{10}(3.2 \mathrm{mg}, 0.01 \mathrm{mmol}, 5 \mathrm{~mol} \%)$ and AgOTf ( $2.6 \mathrm{mg}, 0.01 \mathrm{mmol}, 5 \mathrm{~mol} \%$ ) was added DCE $(2 \mathrm{~mL})$ and stirred at room temperature under argon for 5 min . A solution of substrate $\mathbf{1}(0.2 \mathrm{mmol})$ in DCE ( 2 mL ) was added at room temperature, and the resulting solution was immersed into an oil bath and was stirred at $80^{\circ} \mathrm{C}$. After 20 h or 18 h , the reaction mixture was cooled to room temperature and concentrated. The crude product was purified by flash column chromatography on silica gel to afford the corresponding [3+2] cycloadduct 2 .

## Product (2a)



Reaction time: 20 h . Eluted with PE/EA 20:1
Run 1: $67.5 \mathrm{mg} 1 \mathbf{1 a}$ was converted to $49.8 \mathrm{mg} \mathbf{2 a}$, yield $74 \%$. Run 2: $66.7 \mathrm{mg} \mathbf{1 a}$ was converted to $48.1 \mathrm{mg} \mathbf{2 a}$, yield $72 \%$. So the average yield of two runs was $73 \%$.

2a: white solid, m.p. $=99-102{ }^{\circ} \mathrm{C}, \mathrm{TLC} R_{\mathrm{f}}=0.59(\mathrm{PE} / \mathrm{EA}, 5: 1) .{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta$ $7.70(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.33(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 5.65(\mathrm{ddd}, J=17.0,10.2,6.3 \mathrm{~Hz}, 1 \mathrm{H}), 4.90(\mathrm{~m}$, $1 \mathrm{H}), 4.83(\mathrm{~m}, 1 \mathrm{H}), 3.53-3.43(\mathrm{~m}, 1 \mathrm{H}), 3.34-3.25(\mathrm{~m}, 1 \mathrm{H}), 3.24-3.14(\mathrm{~m}, 2 \mathrm{H}), 3.14-3.05(\mathrm{~m}, 1 \mathrm{H})$, $2.95(\mathrm{dd}, J=9.5,7.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.71-2.58(\mathrm{~m}, 1 \mathrm{H}), 2.44(\mathrm{~s}, 3 \mathrm{H}), 1.69(\mathrm{dd}, J=12.5,6.9 \mathrm{~Hz}, 1 \mathrm{H})$, $1.62(\mathrm{~s}, 3 \mathrm{H}), 1.58(\mathrm{~s}, 3 \mathrm{H}), 1.56-1.48(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 143.3,139.7$ (+), $138.1,133.2,129.5(+, 2 \mathrm{C}), 127.6(+, 2 \mathrm{C}), 127.4,112.9(-), 52.8(-), 52.2(-), 47.1(+), 45.8(+)$, $41.7(+), 36.8(-), 22.0(+), 21.5(+), 21.0(+) . \mathrm{HRMS}(\mathrm{ESI})$ calcd for $\mathrm{C}_{19} \mathrm{H}_{26} \mathrm{NO}_{2} \mathrm{~S}\left([\mathrm{M}+\mathrm{H}]^{+}\right)$: 332.1679. Found: 332.1670.

## Product (2b)



Reaction time: 20 h. Eluted with PE/EA 20:1
Run 1: $72.5 \mathrm{mg} \mathbf{1 b}$ was converted to $54.3 \mathrm{mg} \mathbf{2 b}$, yield $75 \%$. Run 2: $72.6 \mathrm{mg} \mathbf{1 b}$ was converted to $51.5 \mathrm{mg} \mathbf{2 b}$, yield $71 \%$. So the average yield of two runs was $73 \%$.

2b: white solid, m.p. $=89-92{ }^{\circ} \mathrm{C}$, $\mathrm{TLC} R_{\mathrm{f}}=0.69(\mathrm{PE} / \mathrm{EA}, 5: 1) .{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta$ 7.71 (d, $J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.33(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 5.68$ (ddd, $J=16.6,10.2,6.1 \mathrm{~Hz}, 1 \mathrm{H}), 4.93-$ $4.80(\mathrm{~m}, 2 \mathrm{H}), 3.59-3.49(\mathrm{~m}, 1 \mathrm{H}), 3.35-3.27(\mathrm{~m}, 1 \mathrm{H}), 3.23-3.17(\mathrm{~m}, 2 \mathrm{H}), 3.15-3.04(\mathrm{~m}, 1 \mathrm{H})$,
$2.90(\mathrm{dd}, J=9.5,7.7 \mathrm{~Hz}, 1 \mathrm{H}), 2.68-2.56(\mathrm{~m}, 1 \mathrm{H}), 2.44(\mathrm{~s}, 3 \mathrm{H}), 2.04-1.88(\mathrm{~m}, 4 \mathrm{H}), 1.66(\mathrm{dd}, J=$ $12.5,6.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.55-1.44(\mathrm{~m}, 1 \mathrm{H}), 0.95(\mathrm{t}, J=7.5 \mathrm{~Hz}, 3 \mathrm{H}), 0.90(\mathrm{t}, J=7.5 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 143.3,140.4$ (+), 139.2, 137.1, 133.4, 129.6 ( + , 2C), 127.6 ( + , 2C), 113.0 $(-), 53.1(-), 52.0(-), 46.5(+), 45.4(+), 41.5(+), 36.6(-), 25.3(-), 24.1(-), 21.5(+), 12.9(+)$, $12.5(+)$. HRMS (ESI) calcd for $\mathrm{C}_{21} \mathrm{H}_{30} \mathrm{NO}_{2} \mathrm{~S}\left([\mathrm{M}+\mathrm{H}]^{+}\right)$: 360.1992. Found: 360.2002.

Product (2c)


Reaction time: 20 h . Eluted with PE/EA 20:1
Run 1: $75.0 \mathrm{mg} \mathbf{1 c}$ was converted to $55.0 \mathrm{mg} \mathbf{2 c}$, yield $73 \%$. Run 2: $75.4 \mathrm{mg} \mathbf{1 c}$ was converted to $55.4 \mathrm{mg} \mathbf{2 c}$, yield $73 \%$. So the average yield of two runs was $73 \%$.

2c: white solid, m.p. $=128-131^{\circ} \mathrm{C}, \mathrm{TLC} R_{\mathrm{f}}=0.59(\mathrm{PE} / \mathrm{EA}, 5: 1) .{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta$ $7.70(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 2 \mathrm{H}), 7.33(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 2 \mathrm{H}), 5.68(\mathrm{ddd}, J=16.4,10.2,5.9 \mathrm{~Hz}, 1 \mathrm{H}), 4.95-$ $4.80(\mathrm{~m}, 2 \mathrm{H}), 3.52-3.42(\mathrm{~m}, 1 \mathrm{H}), 3.39-3.30(\mathrm{~m}, 1 \mathrm{H}), 3.25-3.18(\mathrm{~m}, 1 \mathrm{H}), 3.18-3.06(\mathrm{~m}, 2 \mathrm{H})$, $2.93(\mathrm{dd}, J=9.5,7.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.66-2.56(\mathrm{~m}, 1 \mathrm{H}), 2.44(\mathrm{~s}, 3 \mathrm{H}), 2.08-1.93(\mathrm{~m}, 4 \mathrm{H}), 1.69(\mathrm{dd}, J=$ $12.5,6.9 \mathrm{~Hz}, 1 \mathrm{H}), 1.56-1.38(\mathrm{~m}, 7 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 143.3,140.5(+), 135.5$, $134.8,133.3,129.6(+, 2 C), 127.7(+, 2 C), 112.8(-), 53.1(-), 52.1(-), 46.2(+), 45.1(+), 41.5$ $(+), 36.5(-), 32.8(-), 31.7(-), 28.0(-), 27.6(-), 26.5(-), 21.5(+)$. HRMS (ESI) calcd for $\mathrm{C}_{22} \mathrm{H}_{30} \mathrm{NO}_{2} \mathrm{~S}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 372.1992$. Found: 372.1982.

## Product (2d)



Reaction time: 20 h . Eluted with PE/EA 20:1
Run 1: 71.1 mg 1d was converted to 42.2 mg 2d, yield $59 \%$. Run 2: 72.3 mg 1d was converted to $46.1 \mathrm{mg} \mathbf{2 d}$, yield $64 \%$. So the average yield of two runs was $62 \%$.

2d: white solid, m.p. $=129-132{ }^{\circ} \mathrm{C}, \mathrm{TLC} R_{\mathrm{f}}=0.40(\mathrm{PE} / \mathrm{EA}, 5: 1) .{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta$ $7.70(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.32(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 5.62(\mathrm{ddd}, J=17.1,10.2,7.1 \mathrm{~Hz}, 1 \mathrm{H}), 4.91-$ $4.81(\mathrm{~m}, 2 \mathrm{H}), 3.47-3.39(\mathrm{~m}, 1 \mathrm{H}), 3.22-3.11(\mathrm{~m}, 3 \mathrm{H}), 3.08-2.96(\mathrm{~m}, 2 \mathrm{H}), 2.74-2.64(\mathrm{~m}, 1 \mathrm{H})$, $2.44(\mathrm{~s}, 3 \mathrm{H}), 2.20-2.02(\mathrm{~m}, 4 \mathrm{H}), 1.76-1.53(\mathrm{~m}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 MHz, $\left.\mathrm{CDCl}_{3}\right): \delta 143.3$, $138.9(+), 138.7,134.6,133.1,129.5(+, 2 C), 127.7(+, 2 C), 112.8(+), 52.4(-), 52.3(-), 48.5$ $(+), 46.6(+), 41.9(+), 37.3(-), 31.8(-), 30.7(-), 26.7(-), 26.6(-), 21.5(+)$. HRMS (ESI) calcd for $\mathrm{C}_{21} \mathrm{H}_{28} \mathrm{NO}_{2} \mathrm{~S}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 358.1835$. Found: 358.1835.

## Product (2e)



2e-Z


2e-E

Reaction time: 20 h. Eluted with PE/EA 20:1
Run 1: $79.2 \mathrm{mg} \mathbf{1 e}$ was converted to $55.8 \mathrm{mg} \mathbf{2 e - Z}$ and $\mathbf{2 e - E}$, yield $70 \%$. Run 2: $78.9 \mathrm{mg} \mathbf{1 e}$ was converted to $51.7 \mathrm{mg} \mathbf{2 e - Z}$ and $\mathbf{2 e - E}$, yield $66 \%$. So the average yield of two runs was $68 \%$. $\mathbf{2 e}-\mathbf{Z}: \mathbf{2 e}-\mathbf{E}=1.2: 1$.
Compound $\mathbf{2 e}-\mathbf{Z}$ and $\mathbf{2 e}-\mathbf{E}$ were inseparable.
$\mathbf{2 e - Z}$ and 2e-E: colorless oil, TLC $R_{\mathrm{f}}=0.39(\mathrm{PE} / \mathrm{EA}, 5: 1) .{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 7.74$ $(\mathrm{d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.54(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \times 1.2 \mathrm{H}), 7.38-7.21(\mathrm{~m}, 5 \mathrm{H}+4 \times 1.2 \mathrm{H}), 7.21-7.16(\mathrm{~m}$, $1.2 \mathrm{H}), 7.14-7.05(2 \mathrm{H}+2 \times 1.2 \mathrm{H}), 5.76(\mathrm{ddd}, J=17.1,10.2,6.1 \mathrm{~Hz}, 1.2 \mathrm{H}), 5.48(\mathrm{ddd}, J=16.8$, $10.2,6.2 \mathrm{~Hz}, 1 \mathrm{H}), 5.07-4.98(\mathrm{~m}, 2 \times 1.2 \mathrm{H}), 4.73(\mathrm{~m}, 1 \mathrm{H}), 4.58(\mathrm{~m}, 1 \mathrm{H}), 3.60-3.51(\mathrm{~m}, 1 \mathrm{H}), 3.50-$ $3.42(\mathrm{~m}, 1.2 \mathrm{H}), 3.31-3.25(\mathrm{~m}, 2 \mathrm{H}), 3.25-3.21(\mathrm{~m}, 1 \mathrm{H}), 3.21-3.14(\mathrm{~m}, 2 \mathrm{H}), 3.14-3.09(\mathrm{~m}$, $2 \times 1.2 \mathrm{H}), 3.09-3.01(\mathrm{~m}, 1.2 \mathrm{H}), 2.86-2.78(\mathrm{~m}, 1.2 \mathrm{H}), 2.77-2.67(\mathrm{~m}, 1 \mathrm{H}+1.2 \mathrm{H}), 2.67-2.58(\mathrm{~m}$, $1.2 \mathrm{H}), 2.46(\mathrm{~s}, 3 \mathrm{H}), 2.42(\mathrm{~s}, 3 \times 1.2 \mathrm{H}), 1.95(\mathrm{~s}, 3 \mathrm{H}), 1.90(\mathrm{~s}, 3 \times 1.2 \mathrm{H}), 1.77-1.64(\mathrm{~m}, 1 \mathrm{H}+1.2 \mathrm{H})$, 1.63-1.55 (m, 1H+1.2H). ${ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 144.2(\mathbf{2 e}-\mathrm{Z}), 143.6,143.4,143.1$ (2e-Z), 142.0, 140.8 (2e-Z), 140.0 (+), 139.2 (+, 2e-Z), 133.6 ( $\mathbf{2 e - Z}$ ), 133.3 (2e-Z), 132.9, 132.6, 129.6 (+, 2C), 129.4 (+, 2C, 2e-Z), 128.4 (+, 2C, 2e-Z), 127.9 (+, 2C), $127.7(+, 2 C), 127.6(+$, 2C), 127.5 (+, 4C, 2e-Z), $126.5(+, 2 e-Z), 126.3(+), 113.4(-, \mathbf{2 e - Z ) , ~} 113.1(-), 53.0(-), 52.6(-$, $\mathbf{2 e - Z}), 52.2(-), 52.1(-, \mathbf{2 e - Z}), 47.4(+, \mathbf{2 e - Z}), 47.2(+), 46.0(+), 45.8(+, \mathbf{2 e - Z}), 41.8(+, \mathbf{2 e - Z})$, $41.4(+), 36.6(-), 36.4(-, \mathbf{2 e - Z}), 22.9(+), 22.0(+, \mathbf{2 e - Z ) ,} 21.5(+), 21.5(+, \mathbf{2 e - Z})$. HRMS (ESI) calcd for $\mathrm{C}_{24} \mathrm{H}_{28} \mathrm{NO}_{2} \mathrm{~S}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 394.1835$. Found: 394.1824.

Product (2f)


Reaction time: 20 h . Eluted with PE/EA 20:1
Run 1: 72.2 mg 1f was converted to $57.5 \mathrm{mg} \mathbf{2 f}$, yield $80 \%$. Run 2: 72.4 mg 1f was converted to $58.4 \mathrm{mg} \mathbf{2 f}$, yield $81 \%$. So the average yield of two runs was $80 \%$.

2f: white solid, m.p. $=154-156{ }^{\circ} \mathrm{C}$, TLC $R_{\mathrm{f}}=0.47(\mathrm{PE} / \mathrm{EA}, 5: 1) .{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta$ $8.39(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 2 \mathrm{H}), 8.01(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 2 \mathrm{H}), 5.65(\mathrm{ddd}, J=17.1,10.1,6.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.92(\mathrm{~m}$, $1 \mathrm{H}), 4.84(\mathrm{~m}, 1 \mathrm{H}), 3.60-3.51(\mathrm{~m}, 1 \mathrm{H}), 3.35-3.28(\mathrm{~m}, 1 \mathrm{H}), 3.28-3.19(\mathrm{~m}, 2 \mathrm{H}), 3.19-3.12(\mathrm{~m}, 1 \mathrm{H})$, $2.99(\mathrm{dd}, J=9.5,7.5 \mathrm{~Hz}, 1 \mathrm{H}), 2.75-2.65(\mathrm{~m}, 1 \mathrm{H}), 1.72(\mathrm{dd}, J=12.5,6.9 \mathrm{~Hz}, 1 \mathrm{H}), 1.64(\mathrm{~s}, 3 \mathrm{H})$, $1.58(\mathrm{~s}, 3 \mathrm{H}), 1.53-1.45(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 MHz, $\left.\mathrm{CDCl}_{3}\right): \delta 150.1,142.5,139.3(+), 137.5$, $128.6(+, 2 C), 128.0,124.3(+, 2 C), 113.3(-), 52.8(-), 52.2(-), 47.0(-), 45.8(-), 41.8(-), 36.8$ $(-), 22.0(-), 21.0(-)$. HRMS (ESI) calcd for $\mathrm{C}_{18} \mathrm{H}_{23} \mathrm{~N}_{2} \mathrm{O}_{4} \mathrm{~S}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 363.1373$. Found: 363.1375 .

## Product (2g)



Reaction time: 18 h . Eluted with PE/EA 20:1
Run 1: $78.7 \mathrm{mg} \mathbf{1 g}$ was converted to $61.2 \mathrm{mg} \mathbf{2 g}$, yield $78 \%$. Run 2: $79.2 \mathrm{mg} \mathbf{1 g}$ was converted to $59.7 \mathrm{mg} \mathrm{2g}$, yield $75 \%$. So the average yield of two runs was $76 \%$.

2g: white solid, m.p. $=120-122{ }^{\circ} \mathrm{C}, \mathrm{TLC} R_{\mathrm{f}}=0.58(\mathrm{PE} / \mathrm{EA}, 5: 1) .{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta$ $7.72-7.62(\mathrm{~m}, 4 \mathrm{H}), 5.65(\mathrm{ddd}, J=17.1,10.1,6.3 \mathrm{~Hz}, 1 \mathrm{H}), 4.91(\mathrm{~m}, 1 \mathrm{H}), 4.85(\mathrm{~m}, 1 \mathrm{H}), 3.52-3.44$ $(\mathrm{m}, 1 \mathrm{H}), 3.35-3.26(\mathrm{~m}, 1 \mathrm{H}), 3.26-3.08(\mathrm{~m}, 3 \mathrm{H}), 2.95(\mathrm{dd}, J=9.5,7.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.73-2.61(\mathrm{~m}$, $1 \mathrm{H}), 1.71(\mathrm{dd}, J=12.5,7.0 \mathrm{~Hz}, 1 \mathrm{H}), 1.63(\mathrm{~s}, 3 \mathrm{H}), 1.58(\mathrm{~s}, 3 \mathrm{H}), 1.55-1.48(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (101 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 139.5(+), 137.9,135.4,132.3(+, 2 \mathrm{C}), 129.1(+, 2 \mathrm{C}), 127.7,127.6,113.1$ $(-), 52.8(-), 52.2(-), 47.1(+), 45.8(+), 41.8(+), 36.8(-), 22.0(+), 21.0(+)$. HRMS (ESI) calcd for $\mathrm{C}_{18} \mathrm{H}_{23} \mathrm{BrNO}_{2} \mathrm{~S}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 396.0627$. Found: 396.0625.

## Product (2h)



Reaction time: 20 h. Eluted with PE/EA 20:1
Run 1: $64.7 \mathrm{mg} \mathbf{1 h}$ was converted to $48.5 \mathrm{mg} \mathbf{2 h}$, yield $75 \%$. Run 2: $63.2 \mathrm{mg} \mathbf{1 h}$ was converted to $48.7 \mathrm{mg} \mathbf{2 h}$, yield $77 \%$. So the average yield of two runs was $76 \%$.

2h: white solid, m.p. $=84-87{ }^{\circ} \mathrm{C}$, TLC $R_{\mathrm{f}}=0.53(\mathrm{PE} / \mathrm{EA}, 5: 1) .{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta$ $7.86-7.79(\mathrm{~m}, 2 \mathrm{H}), 7.64-7.50(\mathrm{~m}, 3 \mathrm{H}), 5.65(\mathrm{ddd}, J=17.0,10.1,6.3 \mathrm{~Hz}, 1 \mathrm{H}), 4.90(\mathrm{~m}, 1 \mathrm{H}), 4.83$ $(\mathrm{m}, 1 \mathrm{H}), 3.55-3.45(\mathrm{~m}, 1 \mathrm{H}), 3.34-3.25(\mathrm{~m}, 1 \mathrm{H}), 3.25-3.16(\mathrm{~m}, 2 \mathrm{H}), 3.16-3.06(\mathrm{~m}, 1 \mathrm{H}), 2.96(\mathrm{dd}$, $J=9.5,7.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.70-2.59(\mathrm{~m}, 1 \mathrm{H}), 1.69(\mathrm{dd}, J=12.5,6.9 \mathrm{~Hz}, 1 \mathrm{H}), 1.63(\mathrm{~s}, 3 \mathrm{H}), 1.58(\mathrm{~s}$, $3 \mathrm{H}), 1.54-1.45(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(101 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 139.6(+), 138.0,136.3,132.6(+)$, $128.9(+, 2 \mathrm{C}), 127.6(+, 2 \mathrm{C}), 127.5,113.0(-), 52.8(-), 52.2(-), 47.1(+), 45.8(+), 41.8(+), 36.8$ $(-), 22.0(+), 21.0(+)$ HRMS (ESI) calcd for $\mathrm{C}_{18} \mathrm{H}_{24} \mathrm{NO}_{2} \mathrm{~S}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 318.1522$. Found: 318.1516 .

## Product (2I)



Reaction time: 20 h. Eluted with PE/EA 20:1
Run 1: 69.9 mg 11 was converted to 49.6 mg 2l, yield $71 \%$. Run 2: $69.8 \mathrm{mg} \mathbf{1 1}$ was converted to 51.6 mg 2 l , yield $74 \%$. So the average yield of two runs was $72 \%$. d.r. $=1.4: 1$.

The two isomers were inseparable and the configuration of them was not determined.
21: colorless oil, TLC $R_{\mathrm{f}}=0.66$ (PE/EA, 5:1). ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.75-7.66(\mathrm{~m}$, $2 \mathrm{H}+2 \times 1.4 \mathrm{H}), 7.36-7.28(\mathrm{~m}, 2 \mathrm{H}+2 \times 1.4 \mathrm{H}), 5.62-5.44(\mathrm{~m}, 1 \mathrm{H}+1.4 \mathrm{H}), 5.00-4.83(\mathrm{~m}, 2 \mathrm{H}+2 \times 1.4 \mathrm{H})$, $3.61-3.52(\mathrm{~m}, 1.4 \mathrm{H}), 3.52-3.44(\mathrm{~m}, 1 \mathrm{H}), 3.29-3.21(\mathrm{~m}, 1 \mathrm{H}+1.4 \mathrm{H}), 3.21-3.08(\mathrm{~m}, 3 \mathrm{H}+1.4 \mathrm{H})$, $1 \mathrm{H}), 1.79-1.69(\mathrm{~m}, 1 \mathrm{H}+1.4 \mathrm{H}), 1.62-1.49(\mathrm{~m}, 6 \mathrm{H}+6 \times 1.4 \mathrm{H}), 0.90-0.76(\mathrm{~m}, 3 \mathrm{H}+3 \times 1.4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $101 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 143.3,143.2$ (major isomer), 141.1 (+, major isomer), 138.5 (major isomer), 138.1, $135.8(+$ ), 133.4 (major isomer), 133.1, $129.5(+, 2 \mathrm{C}), 129.4(+, 2 \mathrm{C}$, major isomer), 128.0 (major isomer), $127.60(+, 2 \mathrm{C}), 127.59(+, 2 \mathrm{C}$, major isomer), 127.4, $114.8(-), 113.8$ (-, major isomer), 54.6 ( - , major isomer), 54.4 (+, major isomer), $53.0(-)$, $52.7(+), 50.7(-), 48.8(+), 48.4(-$, major isomer), 46.1 (+, major isomer), 45.9 (+, major isomer), $45.7(+), 41.3(+$, major isomer), $40.8(+)$, $22.5(+$, major isomer), $21.9(+), 21.48(+)$, 21.47 ( + , major isomer), 21.1 ( + , major isomer), 20.7 ( + ), 14.6 ( + , major isomer), 14.3 (+). HRMS (ESI) calcd for $\mathrm{C}_{20} \mathrm{H}_{28} \mathrm{NO}_{2} \mathrm{~S}\left([\mathrm{M}+\mathrm{H}]^{+}\right): 346.1835$. Found: 346.1846.

## 4. Crystallographic Data



Table 1 Crystal data and structure refinement.

Identification code
Empirical formula
Formula weight
Temperature/K
Crystal system
Space group
a/Å
b/Å
c/Å
$\alpha{ }^{\circ}$
$\beta /{ }^{\circ}$
$\gamma^{\circ}$
Volume/A ${ }^{3}$
Z
$\rho_{\text {calc }} g / \mathrm{cm}^{3}$
$\mu / \mathrm{mm}^{-1}$
F(000)
Crystal size $/ \mathrm{mm}^{3}$
Radiation
$2 \Theta$ range for data collection $/{ }^{\circ}$
Index ranges
Reflections collected
Independent reflections
Data/restraints/parameters
Goodness-of-fit on $\mathrm{F}^{2}$
Final $R$ indexes $[\mathrm{I}>=2 \sigma(\mathrm{I})]$
Final R indexes [all data]
Largest diff. peak/hole / e $\AA^{-3}$
Flack parameter
exp_658
$\mathrm{C}_{19} \mathrm{H}_{25} \mathrm{NO}_{2} \mathrm{~S}$
331.46
180.0(2)
orthorhombic
P2 $2_{1} 2_{1} 2_{1}$
7.6052(4)
13.0656(5)
17.5426(9)

90
90 90
1743.14(14)

4
1.263
0.195
712.0
$0.15 \times 0.1 \times 0.1$
$\operatorname{MoK} \alpha(\lambda=0.71073)$
7.636 to 52.032
$-9 \leq \mathrm{h} \leq 9,-16 \leq \mathrm{k} \leq 16,-21 \leq 1 \leq 21$
8514
$3190\left[\mathrm{R}_{\text {int }}=0.0315, \mathrm{R}_{\text {sigma }}=0.0398\right]$
3190/0/211
1.031
$\mathrm{R}_{1}=0.0309, \mathrm{wR}_{2}=0.0796$
$\mathrm{R}_{1}=0.0323, \mathrm{wR}_{2}=0.0806$
0.15/-0.21
$0.19(4)$

Table 2 Fractional Atomic Coordinates ( $\times 10^{4}$ ) and Equivalent Isotropic Displacement Parameters $\left(\AA^{2} \times 10^{3}\right) . U_{e q}$ is defined as $1 / 3$ of of the trace of the orthogonalised $\mathrm{U}_{\mathrm{IJ}}$ tensor.

| Atom | $\boldsymbol{x}$ | $\boldsymbol{y}$ | $\boldsymbol{z}$ | $\boldsymbol{U}(\mathbf{e q})$ |
| :--- | :--- | :--- | :--- | :--- |
| S1 | $-1018.3(7)$ | $4427.5(4)$ | $6353.5(3)$ | $27.94(15)$ |
| O2 | $-1726(2)$ | $4526.5(13)$ | $7107.1(10)$ | $35.1(4)$ |
| O1 | $-2052(2)$ | $4728.1(13)$ | $5709.4(11)$ | $40.6(5)$ |
| N1 | $770(2)$ | $5118.3(14)$ | $6333.4(11)$ | $27.2(4)$ |
| C14 | $15(3)$ | $2550.9(17)$ | $6863.5(12)$ | $27.4(5)$ |
| C16 | $440(3)$ | $1071.5(17)$ | $6053.2(13)$ | $26.7(5)$ |
| C13 | $-407(3)$ | $3132.7(16)$ | $6230.0(12)$ | $25.5(5)$ |
| C15 | $458(3)$ | $1528.0(17)$ | $6770.3(13)$ | $28.2(5)$ |
| C18 | $-367(3)$ | $2704.0(17)$ | $5503.7(13)$ | $29.5(5)$ |
| C10 | $4500(3)$ | $6552.0(17)$ | $7863.7(13)$ | $26.6(5)$ |
| C5 | $4083(3)$ | $6551.0(15)$ | $7127.7(12)$ | $24.1(4)$ |
| C6 | $3715(3)$ | $5593.1(16)$ | $6651.2(12)$ | $26.2(4)$ |
| C17 | $65(3)$ | $1679.0(18)$ | $5420.2(13)$ | $30.1(5)$ |
| C7 | $2132(3)$ | $4938.2(16)$ | $6920.0(13)$ | $26.0(5)$ |
| C4 | $3876(3)$ | $7489.3(16)$ | $6620.5(13)$ | $29.9(5)$ |
| C8 | $5598(4)$ | $7844.8(19)$ | $6269.9(15)$ | $39.0(6)$ |
| C11 | $4847(3)$ | $7512.8(19)$ | $8311.4(14)$ | $34.2(5)$ |
| C3 | $2610(4)$ | $7109.8(18)$ | $6000.3(14)$ | $36.4(6)$ |
| C19 | $786(4)$ | $-61.7(17)$ | $5967.1(15)$ | $35.2(6)$ |
| C12 | $4646(3)$ | $5582(2)$ | $8324.2(15)$ | $36.0(5)$ |
| C2 | $3173(4)$ | $5997.2(19)$ | $5853.9(14)$ | $34.1(5)$ |
| C1 | $1667(4)$ | $5303.0(19)$ | $5604.3(14)$ | $37.8(6)$ |
| C9 | $7143(4)$ | $7433(2)$ | $6352.3(18)$ | $49.6(7)$ |

Table 3 Anisotropic Displacement Parameters $\left(\AA^{2} \times 10^{3}\right)$. The Anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U_{11}+2 h k a * b * U_{12}+\ldots\right]$.

| Atom | $\mathbf{U}_{\mathbf{1 1}}$ | $\mathbf{U}_{\mathbf{2 2}}$ | $\mathbf{U}_{\mathbf{3 3}}$ | $\mathbf{U}_{\mathbf{2 3}}$ | $\mathbf{U}_{\mathbf{1 3}}$ | $\mathbf{U}_{\mathbf{1 2}}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| S1 | $27.1(3)$ | $24.9(2)$ | $31.9(3)$ | $-6.3(2)$ | $-5.2(2)$ | $2.3(2)$ |
| O2 | $29.9(8)$ | $34.4(9)$ | $41.1(9)$ | $-12.4(8)$ | $5.6(7)$ | $-0.6(7)$ |
| O1 | $41.3(10)$ | $31.8(9)$ | $48.6(11)$ | $-5.4(8)$ | $-19.1(9)$ | $5.7(8)$ |
| N1 | $29.5(9)$ | $24.8(8)$ | $27.3(9)$ | $-0.8(8)$ | $-3.2(9)$ | $-1.9(7)$ |
| C14 | $30.1(12)$ | $30.9(11)$ | $21.1(10)$ | $-2.6(9)$ | $0.1(9)$ | $-4.3(9)$ |
| C16 | $26.1(11)$ | $23.7(11)$ | $30.3(11)$ | $-1.5(9)$ | $3.3(9)$ | $-6.1(9)$ |
| C13 | $25(1)$ | $23.3(10)$ | $28.4(11)$ | $-2.9(9)$ | $0.2(9)$ | $-1.5(8)$ |


| C15 | $31.7(12)$ | $27.9(10)$ | $25.0(11)$ | $3.6(9)$ | $-1.9(9)$ | $-6.3(9)$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| C18 | $38.6(12)$ | $27.2(11)$ | $22.6(10)$ | $0.6(9)$ | $-3.4(10)$ | $-0.4(10)$ |
| C10 | $22.2(11)$ | $25.4(10)$ | $32.1(11)$ | $1.3(9)$ | $0.9(9)$ | $0.7(9)$ |
| C5 | $23.6(10)$ | $19.1(9)$ | $29.7(10)$ | $0.8(9)$ | $3.3(9)$ | $1.7(9)$ |
| C6 | $25.6(11)$ | $21.7(9)$ | $31.2(11)$ | $-2.8(9)$ | $2.4(9)$ | $2.6(9)$ |
| C17 | $37.9(13)$ | $28.0(11)$ | $24.5(10)$ | $-5.0(9)$ | $1.4(10)$ | $-1.9(10)$ |
| C7 | $27.8(11)$ | $20.9(10)$ | $29.4(11)$ | $0.7(9)$ | $-2.2(10)$ | $0.5(9)$ |
| C4 | $37.9(12)$ | $20.7(10)$ | $31.1(10)$ | $1.8(9)$ | $1.1(11)$ | $2.1(10)$ |
| C8 | $53.1(16)$ | $27.8(11)$ | $36.0(13)$ | $3.5(11)$ | $5.2(12)$ | $-11.2(11)$ |
| C11 | $32.0(12)$ | $34.7(12)$ | $36.0(12)$ | $-4.4(11)$ | $-4.4(11)$ | $0.7(10)$ |
| C3 | $47.4(15)$ | $30.9(12)$ | $30.8(12)$ | $7(1)$ | $-5.3(11)$ | $-2.6(11)$ |
| C19 | $42.4(14)$ | $24.7(11)$ | $38.6(13)$ | $-1.7(10)$ | $-1.4(12)$ | $-3.4(10)$ |
| C12 | $34.7(12)$ | $35.1(12)$ | $38.2(13)$ | $9.3(11)$ | $-7.0(11)$ | $-1.4(11)$ |
| C2 | $43.5(14)$ | $33.1(12)$ | $25.7(11)$ | $-2.7(10)$ | $7.1(11)$ | $-5.3(11)$ |
| C1 | $51.7(15)$ | $36.2(13)$ | $25.6(11)$ | $-4.8(10)$ | $2.5(12)$ | $-8.6(12)$ |
| C9 | $42.6(15)$ | $51.8(16)$ | $54.4(17)$ | $3.8(15)$ | $11.8(15)$ | $-12.5(13)$ |

Table 4 Bond Lengths.

| Atom Atom |  | Length/A | Atom | Atom | Length/Å |
| :--- | :--- | :--- | :--- | :--- | :--- |
| S1 | O2 | $1.4332(18)$ | C10 | C5 | $1.330(3)$ |
| S1 | O1 | $1.4314(18)$ | C 10 | C 11 | $1.504(3)$ |
| S 1 | N 1 | $1.6328(19)$ | C 10 | C 12 | $1.507(3)$ |
| S 1 | C 13 | $1.768(2)$ | C 5 | C 6 | $1.531(3)$ |
| N 1 | C 7 | $1.479(3)$ | C 5 | C 4 | $1.523(3)$ |
| N 1 | C 1 | $1.469(3)$ | C 6 | C 7 | $1.551(3)$ |
| C 14 | C 13 | $1.384(3)$ | C 6 | C 2 | $1.551(3)$ |
| C 14 | C 15 | $1.388(3)$ | C 4 | C 8 | $1.519(4)$ |
| C 16 | C 15 | $1.392(3)$ | C 4 | C 3 | $1.535(3)$ |
| C 16 | C 17 | $1.395(3)$ | C 8 | C 9 | $1.301(4)$ |
| C 16 | C 19 | $1.511(3)$ | C 3 | C 2 | $1.537(3)$ |
| C 13 | C 18 | $1.392(3)$ | C 2 | C 1 | $1.525(4)$ |
| C 18 | C 17 | $1.387(3)$ |  |  |  |

Table 5 Bond Angles.
AtomAtom Atom Angle ${ }^{\circ}$
O2 S1 N1 106.42(10)
Atom Atom Atom Angle ${ }^{\circ}$

O2 S1 C13 107.34(10)
C5 $\quad$ C10 $\quad$ C12 $\quad 122.5(2)$
C11 C10 C12 114.1(2)

| O1 | S1 | O2 | 119.82(11) | C10 | C5 | C6 | 125.08(19) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| O1 | S1 | N1 | 106.79(10) | C10 | C5 | C4 | 126.24(19) |
| O1 | S1 | C13 | 108.08(10) | C4 | C5 | C6 | 108.68(18) |
| N1 | S1 | C13 | 107.89(10) | C5 | C6 | C7 | 115.27(18) |
| C7 | N1 | S1 | 118.71(14) | C5 | C6 | C2 | 105.23(17) |
| C1 | N1 | S1 | 119.74(15) | C7 | C6 | C2 | 104.79(18) |
| C1 | N1 | C7 | 107.88(18) | C18 | C17 | C16 | 120.9(2) |
| C13 | C14 | C15 | 119.4(2) | N1 | C7 | C6 | 104.14(17) |
| C15 | C16 | C17 | 118.5(2) | C5 | C4 | C3 | 102.63(18) |
| C15 | C16 | C19 | 120.5(2) | C8 | C4 | C5 | 113.2(2) |
| C17 | C16 | C19 | 120.9(2) | C8 | C4 | C3 | 110.64(19) |
| C14 | C13 | S1 | 119.23(17) | C9 | C8 | C4 | 127.4(2) |
| C14 | C13 | C18 | 120.6(2) | C4 | C3 | C2 | 104.4(2) |
| C18 | C13 | S1 | 120.19(17) | C3 | C2 | C6 | 104.21(18) |
| C14 | C15 | C16 | 121.1(2) | C1 | C2 | C6 | 104.85(19) |
| C17 | C18 | C13 | 119.4(2) | C1 | C2 | C3 | 113.7(2) |
| C5 | C10 | C11 | 123.4(2) | N1 | C1 | C2 | 101.31(18) |

Table 6 Torsion Angles.
$\begin{array}{lllll}A & \mathbf{B} & \mathbf{C} & \mathbf{D} & \text { Angle }\end{array}{ }^{\circ}$
S1 N1 C7 C6 171.48(14)
S1 N1 C1 C2 177.83(16)
S1 C13C18C17-178.08(19)
O2 S1 N1 C7 53.48(18)
O2 S1 N1 C1 -170.79(18)
O2 S1 C13C14 -25.9(2)
O2 S1 C13C18 153.56(19)
O1 S1 N1 C7 -177.44(16)
O1 S1 N1 C1 -41.7(2)
O1 S1 C13C14 -156.40(19)
O1 S1 C13C18 23.0(2)
N1 S1 C13C14 88.5(2)
N1 S1 C13C18 -92.1(2)
C14C13C18C17 1.3(4)
C13S1 N1 C7 -61.46(18)
C13S1 N1 C1 74.27(19)
C13C14C15C16 -1.7(4)
C13C18C17C16 0.7(4)
C15C14C13S1 178.57(18)

A B C D Angle ${ }^{\circ}$
C5 C6 C2 C3 -20.1(2)
C5 C6 C2 $\quad$ C1 $\quad$-139.9(2)
C5 $\quad$ C4 4 C8 $\quad$ C9 $\quad 0.9(4)$
C5 $\quad \mathrm{C} 4 \quad \mathrm{C} 3 \quad \mathrm{C} 2 \quad-37.8(2)$
C6 C5 C4 C8 $\quad$-94.0(2)
C6 $\quad \mathrm{C} 5 \quad \mathrm{C} 4 \quad \mathrm{C} 3 \quad 25.3(2)$
C6 C2 C1 N1 35.9(2)
C17 C16C15 C14 3.7(4)
C7 7 N1 C1 $\quad$ C2 $-42.2(2)$
C7 C6 C2 C3 101.8(2)
C7 C6 C2 C1 $\quad-17.9(2)$
C4 C5 C6 C7 $\quad$-118.2(2)
C4 C5 C6 C2 $\quad$-3.3(2)
C4 C3 C2 $\quad$ C6 $36.2(2)$
C4 C3 C2 C1 149.8(2)
C8 C4 C3 C2 83.3(2)
C11 C10C5 C6 -179.9(2)
C11 C10C5 C4 $-0.4(4)$
C3 $\quad \mathrm{C} 4 \quad \mathrm{C} 8 \quad \mathrm{C} 9 \quad-113.6(3)$

| C15C14 | C13C18 | -0.9(4) | C3 | C 2 C 1 | N1 | -77.3(2) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| C15C1 | C17C18 | -3.2(4) | C19 | C16C15 | C14 | -175.2(2) |
| C10C5 | C6 C7 | 61.3(3) | C19 | C16C17 | C18 | 175.7(2) |
| C10C5 | C6 C2 | 176.2(2) | C12 | C10C5 | C6 | -0.5(4) |
| C10C5 | C4 C8 | 86.5(3) | C12 | C10C5 | C4 | 178.9(2) |
| C10C5 | C 4 C 3 | -154.2(2) | C2 | C6 C7 | N1 | -7.0(2) |
| C5 C6 | C7 N1 | 108.2(2) | C1 | N1 C7 | C6 | 31.0(2) |

Table 7 Hydrogen Atom Coordinates $\left(\AA \times 10^{4}\right)$ and Isotropic Displacement Parameters ( $\AA^{2} \times 10^{3}$ ).

| Atom | $x$ | $\boldsymbol{y}$ | $z$ | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| H14 | 2 | 2843 | 7347 | 33 |
| H15 | 772 | 1141 | 7194 | 34 |
| H18 | -628 | 3101 | 5079 | 35 |
| H6 | 4776 | 5170 | 6613 | 31 |
| H17 | 105 | 1393 | 4935 | 36 |
| H7A | 2445 | 4219 | 6945 | 31 |
| H7B | 1726 | 5158 | 7418 | 31 |
| H4 | 3335 | 8049 | 6909 | 36 |
| H8 | 5540 | 8423 | 5961 | 47 |
| H11A | 4644 | 8099 | 7993 | 51 |
| H11B | 6046 | 7515 | 8484 | 51 |
| H11C | 4074 | 7538 | 8743 | 51 |
| H3A | 2722 | 7518 | 5541 | 44 |
| H3B | 1401 | 7141 | 6176 | 44 |
| H19A | -311 | -418 | 5913 | 53 |
| H19B | 1391 | -310 | 6410 | 53 |
| H19C | 1498 | -177 | 5523 | 53 |
| H12A | 3599 | 5492 | 8622 | 54 |
| H12B | 5645 | 5626 | 8657 | 54 |
| H12C | 4787 | 5009 | 7987 | 54 |
| H2 | 4157 | 5964 | 5494 | 41 |
| H1A | 900 | 5643 | 5242 | 45 |
| H1B | 2099 | 4671 | 5383 | 45 |
| H9A | 7279 | 6854 | 6655 | 60 |
| H9B | 8113 | 7718 | 6109 | 60 |

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