## Supporting Information

# Enantioselective Intermolecular C-H Functionalization of Allylic and Benzylic sp ${ }^{3}$ $\mathbf{C}-\mathrm{H}$ Bonds using N -Sulfonyl-1,2,3-triazoles 

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## 1. Experimental Section

### 1.1 General Considerations

All reactions were conducted in oven-dried glassware under an inert atmosphere of dry argon. All reagents were used as received from commercial suppliers, unless otherwise stated. All solvents were purchased from Sigma Aldrich, dried over calcium hydride, and freshly distilled prior to use in synthesis. Proton $\left({ }^{1} \mathrm{H}\right)$ NMR spectra were recorded at 400 or 500 MHz on a Varian400 or an Inova-500 spectrometer, respectively. Carbon-13 $\left({ }^{13} \mathrm{C}\right)$ NMR spectra were recorded at 100 or 125 MHz on a Varian- 400 or an Inova- 500 spectrometer, respectively. NMR spectra were recorded in deuterated chloroform $\left(\mathrm{CDCl}_{3}\right)$ solutions, with residual chloroform $\left(\delta 7.26 \mathrm{ppm}\right.$ for ${ }^{1} \mathrm{H}$ NMR and $\delta 77.16 \mathrm{ppm}$ for ${ }^{13} \mathrm{C}$ NMR) as the internal standard, and were reported in parts per million (ppm). Abbreviations for signal couplings are as follows: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sex, sextet; sep, septet; and m, multiplet. Coupling constants were taken from the spectra directly and are uncorrected. Infrared (IR) Spectra were collected on a Nicolet Impact Series 10 FT-IR. Mass spectrometric determinations were carried out on a Thermo Finnigan LTQ-FTMS spectrometer with nano-spray ionization (NSI). Optical rotations were measured on a PerkinElmer 341 polarimeter. High performance liquid chromatography (HPLC) analysis was performed on a Varian Prostar 350 with hexanes/isopropanol as eluent. Analytical thin layer chromatography (TLC) was performed on silica gel plates using ultraviolet (UV) light or stained with either $\mathrm{KMnO}_{4}$ or phosphomolybdic acid (PMA). Flash column chromatography was performed with silica gel $60 \AA(230-400 \mathrm{mesh})$ according to the literature procedure. ${ }^{1}$ 4-Phenyl- $N$-mesyltriazole, ${ }^{2} \mathrm{Rh}_{2}(S \text {-NTV })_{4},{ }^{3} \mathrm{Rh}_{2}(S \text {-NTTL })_{4},{ }^{4} \mathrm{Rh}_{2}(S \text {-4-Cl-NTTL })_{4},{ }^{5} \mathrm{Rh}_{2}(S$-PTTL $) 4,{ }^{6}$ $\mathrm{Rh}_{2}(S \text {-TCPTTL })_{4},{ }^{7} \mathrm{Rh}_{2}(S \text {-PTAD })_{4},{ }^{8}$ and $\mathrm{Rh}_{2}\left(S\right.$-TCPTAD) ${ }_{4}{ }^{9}$ were all prepared according to literature procedures.

### 1.2 Catalyst Structures



S1. $\mathrm{Rh}_{2}(\mathrm{~S}-\mathrm{NTV})_{4}$ $M W=1391.02$


S2. $\mathrm{Rh}_{2}(\mathrm{~S}-\mathrm{NTTL})_{4}$ $M W=1447.13$


S3. $\mathrm{Rh}_{2}(\mathrm{~S}-4-\mathrm{CI}-\mathrm{NTTL})_{4}$ $M W=1584.90$


S4. $\mathrm{Rh}_{2}(\mathrm{~S}-\mathrm{PTTL})_{4}$
$M W=1250.92$


S5. $\mathrm{Rh}_{2}(S-T C P T T L)_{4}$
$M W=1801.99$


S6. $\mathrm{Rh}_{2}(\mathrm{~S}-\mathrm{PTAD})_{4}$
$M W=1563.38$


S7. $\mathrm{Rh}_{2}(\mathrm{~S} \text {-TCPTAD })_{4}$
$M W=2114.45$

### 1.3 General Procedures

### 1.3.1 Triazole Reactions

The same general procedure was used for both the allylic and benzylic systems, unless otherwise indicated. Two 10 mL round bottom flasks (RBF), one with magnetic stir bar, were flamed dried under vacuum then purged with dry argon and allowed to cool to room temperature (rt). This was repeated three times followed by an additional 15 min under vacuum. The RBF with the magnetic stir bar was then charged with 4-phenyl- $N$-mesyltriazole ( $224 \mathrm{mg}, 1.0 \mathrm{mmol}, 1$ equiv) and dirhodium catalyst ( $1 \mathrm{~mol} \%$ ) followed by three successive vacuum/argon cycles. Both flasks were transferred from Schlenk line to argon balloon. The other RBF was charged with the respective substrate ( $4.0 \mathrm{mmol}, 4$ equiv) and chlorinated solvent ( 2 mL ) via syringes equipped with oven dried needles. The respective substrate and solvent were then added to the RBF containing the 4-phenyl- $N$-mesyltriazole and dirhodium catalyst and allowed to react at rt for 18-24 h. Solvent was removed via rotary evaporation. The reaction mixture was diluted with 4 mL THF and reduced with $1 \mathrm{M} \mathrm{LiAlH}_{4}$ in THF ( $1.2 \mathrm{~mL}, 1.2 \mathrm{mmol}, 1.2$ equiv) at $0^{\circ} \mathrm{C}$ for 1 h . The reaction mixture was quenched by slowly adding $\mathrm{Na}_{2} \mathrm{SO}_{4} \cdot 10 \mathrm{H}_{2} \mathrm{O}$ until bubbling stopped and maintaining $0^{\circ} \mathrm{C}$ for an additional 15 min . The crude product was isolated by vacuum filtration using a 60 mL medium porosity fritted funnel with a smoothly packed layer of Celite ${ }^{\circledR}$ and $\mathrm{DCM}(50 \mathrm{~mL})$ as the eluent. DCM was removed via rotary evaporation. The desired product was purified via flash chromatography eluting with either hexane/ethyl acetate (EtOAc) or hexane/isopropanol (IPA) to afford the analytically pure allylic or benzylic product.

### 1.3.2 Diazo Reactions

The same procedural guidelines were followed for reactions using methyl phenyl diazoacetate in place of the 4-phenyl- $N$-mesyltriazole substrate. Two 10 mL round bottom flasks (RBF), one with magnetic stir bar, were flamed dried under vacuum then purged with dry argon and allowed to cool to room temperature (rt). This was repeated three times followed by an additional 15 min under vacuum. The RBF with the magnetic stir bar was then charged with the dirhodium catalyst ( $1 \mathrm{~mol} \%$ ) followed by three successive vacuum/argon cycles. Both flasks were transferred from Schlenk line to argon balloon. The RBF containing the catalyst was charged with chlorinated solvent ( 1 mL ) and the respective substrate ( $4.0 \mathrm{mmol}, 4$ equiv). The other RBF was charged with methyl phenyl diazoacetate ( $176.2 \mathrm{mg}, 1.0 \mathrm{mmol}, 1$ equiv) and chlorinated solvent ( 1 mL ) via syringes equipped with oven dried needles. The diazoacetate and chlorinated solvent mixture was added dropwise over 1 h to the solution of catalyst, substrate, and chlorinated solvent. After addition, the reaction was allowed to proceed an additional $17-23 \mathrm{~h}$ until reaction completion. The crude product was isolated by vacuum filtration using a 60 mL medium porosity fritted funnel with a smoothly packed layer of Celite ${ }^{\circledR}$ and $\mathrm{DCM}(50 \mathrm{~mL})$ as the eluent. DCM was removed via rotary evaporation. The desired product was purified via flash chromatography eluting with either hexane/EtOAc or hexane/IPA to afford the analytically pure allylic or benzylic product.

### 1.4 Optimization of the Allylic System



Optimization Procedure: Performed using General Procedure 1.3.1 with variations of catalyst, solvent, substrate, and conditions.

Table 1. Screening of $\mathrm{Rh}(\mathrm{II})$-catalysts for enantioselective $\mathrm{sp}^{3}$ functionalization of the alkenes ${ }^{a}$

| entry | catalyst | $3^{\circ} \mathbf{1 ~}^{\text {º}}$ | $3^{\circ} \%$ yield $^{\text {b }}$ | \% ee |
| :---: | :---: | :---: | :---: | :---: |
| 1 | $\mathrm{Rh}_{2}\left(S\right.$-NTTL) ${ }_{4}$ | $>30: 1$ | 83 | 84 |
| 2 | $\mathrm{Rh}_{2}(S \text {-PTTL })_{4}$ | $>30: 1$ | 57 | 78 |
| 3 | $\mathrm{Rh}_{2}(S \text {-PTAD })_{4}$ | $>30: 1$ | 54 | 79 |
| 4 | $\mathrm{Rh}_{2}\left(\mathrm{~S}\right.$-TCPTAD) ${ }_{4}$ | >30:1 | 29 | 73 |

${ }^{a} \mathrm{Rh}(\mathrm{II})$-catalyst ( $1 \mathrm{~mol} \%$ ), $\mathrm{CHCl}_{3}$ (2 mL), trans-4-methyl-2-pentene (4 equiv), rt, 18h. ${ }^{b}$ Isolated yields.

Table 2. Screening of the reaction conditions ${ }^{a, b}$

| entry | solvent | alkene equiv | T ${ }^{\circ} \mathrm{C}$ | c, M | $3^{\circ}: 1^{\text {0 }}$ | $3^{0} \%$ yield $^{c}$ | \% ee |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | $\mathrm{CHCl}_{3}$ | 2 | rt | 0.5 | >30:1 | 74 | 77 |
| 2 | $\mathrm{CHCl}_{3}$ | 4 | rt | 0.5 | $>30: 1$ | 83 | 84 |
| 3 | $\mathrm{CHCl}_{3}$ | 8 | rt | 0.5 | >30:1 | 77 | 84 |
| 4 | $\mathrm{CHCl}_{3}$ | 4 | rt | 1.0 | $>30: 1$ | 77 | 83 |
| 5 | $\mathrm{CHCl}_{3}$ | 4 | rt | 0.25 | $>30: 1$ | 76 | 83 |
| 6 | $\mathrm{CHCl}_{3}$ | 4 | 40 | 0.5 | >30:1 | 78 | 83 |
| 7 | $\mathrm{CHCl}_{3}$ | 4 | 0 | 0.5 | $\mathrm{n} / \mathrm{a}$ | 0 | n/a |
| $8^{d}$ | $\mathrm{CHCl}_{3}$ | 4 | rt | 0.5 | $>30: 1$ | 74 | 84 |
| $9{ }^{e}$ | $\mathrm{CHCl}_{3}$ | 4 | rt | 0.5 | >30:1 | 82 | 83 |
| $10^{f}$ | $\mathrm{CHCl}_{3}$ | 4 | rt | 0.5 | $>30: 1$ | 80 | 83 |
| 11 | DCM | 4 | rt | 0.5 | $>30: 1$ | 73 | 85 |
| 12 | DCM | 4 | reflux | 0.5 | >30:1 | 70 | 82 |
| 13 | 1,2-DCE | 4 | rt | 0.5 | $>30: 1$ | 63 | 86 |
| 14 | 1,2-DCE | 4 | 40 | 0.5 | >30:1 | 72 | 67 |
| 15 | TFT | 4 | rt | 0.5 | $\mathrm{n} / \mathrm{a}$ | 0 | n/a |
| 16 | TFT | 4 | 40 | 0.5 | >30:1 | 69 | 79 |
| 17 | EtOAc | 4 | rt | 0.5 | $\mathrm{n} / \mathrm{a}$ | 0 | n /a |
| 18 | EtOAc | 4 | 40 | 0.5 | $\mathrm{n} / \mathrm{a}$ | 0 | n/a |

${ }^{\bar{a}} \mathrm{Rh}_{2}(S \text {-NTTL })_{4}(1 \mathrm{~mol} \%)$ and trans-4-methyl-2-pentene were used for this optimization. ${ }^{b} 18 \mathrm{~h}$ reaction time unless otherwise indicated. ${ }^{c}$ Isolated yields. ${ }^{d} 4 \AA$ molecular sieves. ${ }^{e} 6 \mathrm{~h}$ reaction time. ${ }^{f} 12 \mathrm{~h}$ reaction time.

### 1.5 Optimization of the Benzylic System



Optimization Procedure: Performed using General Procedure 1.3.1 with variations of catalyst, solvent, substrate, and conditions.

Table 3. Screening of $\mathrm{Rh}(\mathrm{II})$-catalysts for enantioselective $\mathrm{sp}^{3}$ functionalization of arenes ${ }^{a}$

| entry | catalyst | $\mathbf{3}^{\mathbf{o}} \mathbf{1 0}^{\mathbf{0}}$ | $\mathbf{3}^{\mathbf{o}} \mathbf{\text { \% }}$ yield ${ }^{b}$ | \% ee |
| :---: | :--- | :---: | :---: | :---: |
| 1 | $\mathrm{Rh}_{2}(S-\mathrm{NTTL})_{4}$ | $80: 20$ | 52 | 74 |
| 2 | $\mathrm{Rh}_{2}(\mathrm{~S}-4-\mathrm{Cl}-\mathrm{NTTL})_{4}$ | $\mathrm{n} / \mathrm{a}$ | 0 | $\mathrm{n} / \mathrm{a}$ |
| 3 | $\mathrm{Rh}_{2}(\mathrm{~S}-\mathrm{PTTL})_{4}$ | $71: 29$ | 20 | 65 |
| $4^{c}$ | $\mathrm{Rh}_{2}(\mathrm{~S}-\mathrm{TCPTTL})_{4}$ | $80: 20$ | 28 | 43 |
| 5 | $\mathrm{Rh}_{2}(\mathrm{~S}-\mathrm{PTAD})_{4}$ | $64: 36$ | 10 | 70 |
| 6 | $\mathrm{Rh}_{2}(\mathrm{~S}-\mathrm{TCPTAD})_{4}$ | $67: 33$ | 9 | 50 |
| $7^{d}$ | $\mathrm{Rh}_{2}(\mathrm{~S}-\mathrm{NTV})_{4}$ | $83: 17$ | 53 | 62 |
| $8^{d}$ | $\mathrm{Rh}_{2}(\mathrm{~S}-\mathrm{NTAD})_{4}$ | $78: 22$ | 55 | 66 |

${ }^{\bar{a}} \mathrm{Rh}(\mathrm{II})$-catalyst ( $1 \mathrm{~mol} \%$ ), 1,2-DCE ( 2 mL ), $p$-cymene (4 equiv), rt, $24 \mathrm{~h} .{ }^{b}$ Isolated yields. ${ }^{c}$ Reaction ran at $45{ }^{\circ} \mathrm{C}$. ${ }^{d}$ Reaction ran for 18 h .

Table 4. Screening of the reaction conditions ${ }^{a, b}$

| entry | solvent | arene equiv | T ${ }^{\circ} \mathrm{C}$ | c, M | $3^{\circ}: 1^{\text { }}$ | $3^{\circ} \%$ yield $^{\text {c }}$ | \% ee |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | $\mathrm{CHCl}_{3}$ | 4 | rt | 0.5 | 79:21 | 59 | 68 |
| 2 | 1,2-DCE | 4 | rt | 0.5 | 80:20 | 52 | 74 |
| $3^{\text {d }}$ | 1,2-DCE | 4 | rt | 0.5 | 80:20 | 43 | 77 |
| $4^{e}$ | 1,2-DCE | 4 | rt | 0.5 | 83:17 | 54 | 65 |
| 5 | DMB | 4 | 50 | 0.5 | $\mathrm{n} / \mathrm{a}$ | 0 | n/a |

${ }^{a} \mathrm{Rh}_{2}(S \text {-NTTL })_{4}$ and $p$-cymene were used for this screening. ${ }^{b} 24 \mathrm{~h}$ reaction time unless otherwise stated. ${ }^{c}$ Isolated yields. ${ }^{d} 3 \mathrm{~h}$ reaction time. ${ }^{e} 4 \AA$ molecular sieves.

## 2. Procedures and Characterization Data



## (S,E)-N-(3,3-dimethyl-2-phenylhex-4-en-1-yl)methanesulfonamide (3a)

Prepared by General Procedure 1.3 .1 with $1(224 \mathrm{mg}, 1.0 \mathrm{mmol}, 1.0$ equiv), trans-4-methyl-2pentene ( $337 \mathrm{mg}, 4.0 \mathrm{mmol}, 4.0$ equiv), $\left\{\mathrm{Rh}_{2}(S-\mathrm{NTTL})_{4}\right\}(14.5 \mathrm{mg}, 0.01 \mathrm{mmol}, 1 \mathrm{~mol} \%$ ), and $\mathrm{CHCl}_{3}(2 \mathrm{~mL})$ at rt for 18 h . Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4 mL THF then reduced with $1 \mathrm{M} \mathrm{LiAlH}_{4}$ in THF ( $1.2 \mathrm{~mL}, 1.2 \mathrm{mmol}, 1.2$ equiv) at $0{ }^{\circ} \mathrm{C}$ for 1 h . The reaction mixture was quenched by slow addition of $\mathrm{Na}_{2} \mathrm{SO}_{4} \cdot 10 \mathrm{H}_{2} \mathrm{O}$ until bubbling stopped followed by 15 additional min at $0^{\circ} \mathrm{C}$. The crude brown product was obtained via vacuum filtration over a thin layer of Celite ${ }^{\circledR}$ packed atop a 60 mL medium porosity fritted funnel using DCM ( 50 mL ) as eluent. Purification by flash chromatography $\left(\mathrm{SiO}_{2}\right.$; hexanes/EtOAc, 7:3; $\mathrm{R}_{\mathrm{f}} 0.26$ ) afforded the title compound as a tan oil ( $235 \mathrm{mg}, 83 \%$ yield). Crystal structure to confirm stereochemistry was obtained by dissolving 30 mg of the tan oil in 2 mL hexanes and allowing the title compound to crash out of solution as pure white needles over a 24 h period. Crystallographic analysis confirmed the suspected $S$ stereochemistry at the chiral center (see attached crystallographic file for further information).
$\mathbf{M P}=74{ }^{\circ} \mathrm{C}$
$[\boldsymbol{\alpha}]^{\mathbf{2 0}}{ }_{\mathbf{D}}-17.1^{\circ}\left(c \quad 0.5, \mathrm{CHCl}_{3}\right)$
${ }^{1} \mathbf{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.33-7.24(\mathrm{~m}, 3 \mathrm{H}), 7.15(\mathrm{dd}, J=8.5,3.5,1.7 \mathrm{~Hz}, 2 \mathrm{H}), 5.47-5.42$ $(\mathrm{m}, 1 \mathrm{H}), 5.40-5.32(\mathrm{~m}, 1 \mathrm{H}), 3.85(\mathrm{dd}, J=8.6,3.4 \mathrm{~Hz}, 1 \mathrm{H}), 3.57(\mathrm{ddd}, J=12.9,8.8,4.2 \mathrm{~Hz}, 1 \mathrm{H})$, $3.36(\mathrm{td}, J=12.2,3.6 \mathrm{~Hz}, 1 \mathrm{H}), 2.75(\mathrm{~s}, 3 \mathrm{H}), 2.65(\mathrm{dd}, J=11.7,4.1 \mathrm{~Hz}, 1 \mathrm{H}), 1.70(\mathrm{dd}, J=6.4,1.6$ $\mathrm{Hz}, 3 \mathrm{H}$ ), 0.97 (s, 3H), 0.89 (s, 3H)
${ }^{13} \mathbf{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 138.7,138.4,129.8,128.6,128.5,127.4,123.3,56.5,44.2,40.3$, 38.7, 27.9, 24.3, 18.3

FTIR (neat): $v_{\max } / \mathrm{cm}^{-1} 3289,3027,2863,1542,1409,1364,1319,1150,1072,972,855,778,751$, 704
HRMS (NSI): $m / z 282.1518\left[(\mathrm{M}-\mathrm{H})^{+}\right.$requires 282.1522], Calcd for $\mathrm{C}_{15} \mathrm{H}_{24} \mathrm{NO}_{2} \mathrm{~S}$
HPLC: $84 \%$ ee, Chiralcel OD column, $2 \%$ isopropanol/hexanes, $1.0 \mathrm{~mL} / \mathrm{min}, \mathrm{UV}: 230 \mathrm{~nm}, \mathrm{t}_{\mathrm{r}}$ : 36.0 min (major), 25.6 min (minor)

(S)-N-(3,3,5-trimethyl-2-phenylhex-4-en-1-yl)methanesulfonamide (7a)

Prepared by General Procedure 1.3 .1 with $1(224 \mathrm{mg}, 1.0 \mathrm{mmol}, 1.0$ equiv), trans-2,4-dimethyl-2pentene ( $393 \mathrm{mg}, 4.0 \mathrm{mmol}, 4.0$ equiv), $\left\{\mathrm{Rh}_{2}(S-\mathrm{NTTL})_{4}\right\}(14.5 \mathrm{mg}, 0.01 \mathrm{mmol}, 1 \mathrm{~mol} \%$ ), and $\mathrm{CHCl}_{3}(2 \mathrm{~mL})$ at rt for 18 h . Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4 mL THF then reduced with $1 \mathrm{M} \mathrm{LiAlH}_{4}$ in $\mathrm{THF}(1.2 \mathrm{~mL}, 1.2 \mathrm{mmol}, 1.2$ equiv) at $0{ }^{\circ} \mathrm{C}$ for 1 h . The reaction mixture was quenched by slow addition of $\mathrm{Na}_{2} \mathrm{SO}_{4} \cdot 10 \mathrm{H}_{2} \mathrm{O}$ until bubbling stopped followed by 15 additional min at $0^{\circ} \mathrm{C}$. The crude brown product was obtained via vacuum filtration over a thin layer of Celite ${ }^{\circledR}$ packed atop a 60 mL medium porosity fritted funnel using $\mathrm{DCM}(50 \mathrm{~mL})$ as eluent. Purification by flash chromatography $\left(\mathrm{SiO}_{2}\right.$; hexanes/EtOAc, 7:3; $\mathrm{R}_{\mathrm{f}} 0.30$ ) afforded a tan oil containing a 1.5:1 mixture of the title compound and the $1^{\circ}$ insertion product (7b), respectively ( $154 \mathrm{mg}, 52 \%$ combined yield). Further purification for characterization purposes were performed by additional flash chromatography $\left(\mathrm{SiO}_{2}\right.$; hexanes/EtOAc, 7:3): The leading fractions contained the excess of 7a while the tail fractions contained an inseparable mix of the regioisomers (in all cases the $\mathrm{R}_{\mathrm{f}}$ values were identical).
$[\boldsymbol{\alpha}]^{\mathbf{2 0}}{ }_{\mathbf{D}}+8.7^{\circ}\left(c 0.5, \mathrm{CHCl}_{3}\right)$
${ }^{1}$ H NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.34-7.24(\mathrm{~m}, 3 \mathrm{H}), 7.19-7.16(\mathrm{~m}, 2 \mathrm{H}), 5.11$ (quin, $J=2.7 \mathrm{~Hz}, 1 \mathrm{H}$ ), 3.85 (dd, $J=8.2,2.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.66$ (ddd, $J=12.5,8.6,4.1 \mathrm{~Hz}, 1 \mathrm{H}), 3.47(\mathrm{td}, J=11.9,3.7 \mathrm{~Hz}$, $1 \mathrm{H}), 2.85(\mathrm{dd}, J=11.7,3.9 \mathrm{~Hz}, 1 \mathrm{H}), 2.78(\mathrm{~s}, 3 \mathrm{H}), 1.73(\mathrm{~d}, J=1.4,3 \mathrm{H}), 1.67(\mathrm{~d}, J=1.3,3 \mathrm{H}), 1.05-$ 1.01 (m, 6H)
${ }^{13} \mathbf{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 138.8,132.4,131.9,129.9,128.5,127.4,56.6,44.1,40.4,38.9$, 28.8, 28.6, 26.4, 19.2

FTIR (neat): $v_{\max } / \mathrm{cm}^{-1} 3287,2964,2928,1602,1494,1452,1409,1365,1316,1147,1094,1071$, 967, 909, 931, 781, 733, 702
HRMS (NSI): $m / z 296.1677$ [(M-H) ${ }^{+}$requires 296.1679], Calcd for $\mathrm{C}_{16} \mathrm{H}_{26} \mathrm{NO}_{2} \mathrm{~S}$
HPLC: $74 \%$ ee, Chiralcel OD column, $1 \%$ isopropanol/hexanes, $1.0 \mathrm{~mL} / \mathrm{min}, ~ U V: 230 \mathrm{~nm}, \mathrm{t}_{\mathrm{r}}$ : 49.6 min (major), 41.6 min (minor)


## ( $R, E$ )- $\boldsymbol{N}$-(4,6-dimethyl-2-phenylhept-4-en-1-yl)methanesulfonamide (7b)

Prepared by General Procedure 1.3 .1 with $1(224 \mathrm{mg}, 1.0 \mathrm{mmol}, 1.0$ equiv), trans-2,4-dimethyl-2pentene ( $393 \mathrm{mg}, 4.0 \mathrm{mmol}, 4.0$ equiv), $\left\{\mathrm{Rh}_{2}(S-\mathrm{NTTL})_{4}\right\}(14.5 \mathrm{mg}, 0.01 \mathrm{mmol}, 1 \mathrm{~mol} \%$ ), and $\mathrm{CHCl}_{3}(2 \mathrm{~mL})$ at rt for 18 h . Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4 mL THF then reduced with $1 \mathrm{M} \mathrm{LiAlH}_{4}$ in THF ( $1.2 \mathrm{~mL}, 1.2 \mathrm{mmol}, 1.2$ equiv) at $0{ }^{\circ} \mathrm{C}$ for 1 h . The reaction mixture was quenched by slow addition of $\mathrm{Na}_{2} \mathrm{SO}_{4} \cdot 10 \mathrm{H}_{2} \mathrm{O}$ until bubbling stopped followed by 15 additional min at $0^{\circ} \mathrm{C}$. The crude brown product was obtained via vacuum filtration over a thin layer of Celite ${ }^{\circledR}$ packed atop a 60 mL medium porosity fritted funnel using $\mathrm{DCM}(50 \mathrm{~mL})$ as eluent. Purification by flash chromatography $\left(\mathrm{SiO}_{2}\right.$; hexanes/EtOAc, 7:3; $\mathrm{R}_{\mathrm{f}} 0.30$ ) afforded a tan oil containing a 1.5:1 mixture of 7 a and the title compound, respectively ( $154 \mathrm{mg}, 52 \%$ combined yield). Further purification for characterization purposes were performed by additional flash chromatography $\left(\mathrm{SiO}_{2}\right.$; hexanes/EtOAc, 7:3): The leading fractions contained $7 \mathbf{a}$ while the tail fractions contained an inseparable mix of the regioisomers (in all cases the $\mathrm{R}_{\mathrm{f}}$ values were identical).
$[\boldsymbol{\alpha}]^{\mathbf{2 0}}{ }_{\mathbf{D}}-12.2^{\circ}\left(c \quad 0.5, \mathrm{CHCl}_{3}\right)$
${ }^{1} \mathbf{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 7.36-7.14(\mathrm{~m}, 10 \mathrm{H}), 5.11(\mathrm{~s}, 1 \mathrm{H}), 4.92-4.86(\mathrm{~d}, J=8.9 \mathrm{~Hz}, 1 \mathrm{H})$, $4.24(\mathrm{dd}, J=7.8,4.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.99(\mathrm{dd}, J=8.6,3.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.65$ (ddd, $J=12.4,8.3,3.9 \mathrm{~Hz}, 1 \mathrm{H})$, $3.52-3.47$ (dd, $J=12.0,3.8 \mathrm{~Hz}, 2 \mathrm{H}) 3.46-3.37(\mathrm{~m}, 1 \mathrm{H}), 3.20(\mathrm{ddd}, J=12.8,9.3,4.9 \mathrm{~Hz}, 1 \mathrm{H})$, $3.03-2.93(\mathrm{~m}, 1 \mathrm{H}), 2.85(\mathrm{dd}, J=11.7,3.9 \mathrm{~Hz}, 1 \mathrm{H}), 2.77-2.75(\mathrm{~m}, 4 \mathrm{H}), 2.72(\mathrm{~s}, 3 \mathrm{H}), 2.46-2.28$ (m, 2H), 2.23 (dd, $J=13.5,7.6 \mathrm{~Hz}, 1 \mathrm{H}), 1.73(\mathrm{~s}, 3 \mathrm{H}), 1.67(\mathrm{~s}, 3 \mathrm{H}), 1.58(\mathrm{~s}, 3 \mathrm{H}), 1.04$ (d, $J=7.9$ $\mathrm{Hz}, 6 \mathrm{H}), 0.89(\mathrm{~d}, J=6.7 \mathrm{~Hz}, 3 \mathrm{H}), 0.75(\mathrm{~d}, J=6.6 \mathrm{~Hz}, 3 \mathrm{H})$
${ }^{13} \mathbf{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 141.8,138.8,136.1,132.3,131.9,129.9,129.3,128.9,128.4$, $128.0,127.3,127.2,56.5,48.2,44.4,44.3,44.1,40.2,38.8,28.7,28.6,27.2,26.3,23.1,22.9,19.2$, 16.0

FTIR (neat): $v_{\max } / \mathrm{cm}^{-1} 3289,2957,1602,1495,1453,1410,1364,1316,1148,1094,1074,969$, 833, 758, 702
HRMS (NSI): $m / z 296.1677$ [(M-H) ${ }^{+}$requires 296.1679], Calcd for $\mathrm{C}_{16} \mathrm{H}_{26} \mathrm{NO}_{2} \mathrm{~S}$
HPLC: $1^{\circ}-94 \%$ ee, Chiralcel OD column, $1 \%$ isopropanol/hexanes, $1.0 \mathrm{~mL} / \mathrm{min}$, UV: 230 nm , $\mathrm{t}_{\mathrm{r}}: 100.3 \mathrm{~min}$ (major), 63.5 min (minor) $3^{\circ}-$ See S 7 .


N -((2R,3S,E)-3-methyl-2-phenylhept-4-en-1-yl)methanesulfonamide (8 - major)
Prepared by General Procedure 1.3 .1 with $1(224 \mathrm{mg}, 1.0 \mathrm{mmol}, 1.0$ equiv), trans-3-heptene ( 336 $\mathrm{mg}, 4.0 \mathrm{mmol}, 4.0$ equiv), $\left\{\mathrm{Rh}_{2}(S-\mathrm{NTTL})_{4}\right\}(14.5 \mathrm{mg}, 0.01 \mathrm{mmol}, 1 \mathrm{~mol} \%)$, and $\mathrm{CHCl}_{3}(2 \mathrm{~mL})$ at rt for 18 h . Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4 mL THF then reduced with $1 \mathrm{M} \mathrm{LiAlH}_{4}$ in THF ( $1.2 \mathrm{~mL}, 1.2 \mathrm{mmol}, 1.2$ equiv) at $0{ }^{\circ} \mathrm{C}$ for 1 h . The reaction mixture was quenched by slow addition of $\mathrm{Na}_{2} \mathrm{SO}_{4} \cdot 10 \mathrm{H}_{2} \mathrm{O}$ until bubbling stopped followed by 15 additional min at $0^{\circ} \mathrm{C}$. The crude brown product was obtained via vacuum filtration over a thin layer of Celite ${ }^{\circledR}$ packed atop a 60 mL medium porosity fritted funnel using DCM ( 50 $\mathrm{mL})$ as eluent. Purification by flash chromatography $\left(\mathrm{SiO}_{2}\right.$; hexanes/EtOAc, 6:4; $\left.\mathrm{R}_{\mathrm{f}} 0.32\right)$ afforded a tan oil containing a 7:3 diastereomeric ratio of the title compound and $\mathbf{8}$ - minor, respectively ( $225 \mathrm{mg}, 80 \%$ combined yield). Further purification for characterization purposes were performed by additional flash chromatography $\left(\mathrm{SiO}_{2}\right.$; hexanes/EtOAc, 6:4): The leading fractions contained the minor diastereomer, the tail fractions contained the major diastereomer, and the middle fractions contained a mix of the diastereomers (in all cases the Rf values were identical).
$[\boldsymbol{\alpha}]^{\mathbf{2 0}}{ }_{\mathbf{D}}-2.7^{\circ}\left(c 0.5, \mathrm{CHCl}_{3}\right)$
${ }^{1} \mathbf{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.34-7.29(\mathrm{~m}, 2 \mathrm{H}), 7.25-7.23(\mathrm{~m}, 1 \mathrm{H}), 7.14-7.09(\mathrm{~m}, 2 \mathrm{H})$, 5.36 (dtd, $J=15.4,6.4,0.9 \mathrm{~Hz}, 1 \mathrm{H}), 5.11$ (ddt, $J=15.3,8.4,1.5 \mathrm{~Hz}, 1 \mathrm{H}), 4.02-3.89$ (m, 1H), 3.52 (ddd, $J=12.6,8.4,5.1 \mathrm{~Hz}, 1 \mathrm{H}), 3.36$ (ddd, $J=12.6,10.3,3.9 \mathrm{~Hz}, 1 \mathrm{H}), 2.82$ (s, 3H), $2.78-$ $2.71(\mathrm{~m}, 1 \mathrm{H}), 2.44(\mathrm{~h}, J=6.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.98-1.88(\mathrm{~m}, 2 \mathrm{H}), 0.98(\mathrm{~d}, J=6.8 \mathrm{~Hz}, 3 \mathrm{H}), 0.87(\mathrm{t}, J=$ 7.4 Hz, 3H)
${ }^{13} \mathbf{C}$ NMR (125 MHz, $\left.\mathrm{CDCl}_{3}\right): \delta 139.4,133.0,131.1,129.1,128.7,127.3,51.8,46.2,40.4,40.0$, 29.9, 25.7, 18.9, 14.0

FTIR (neat): $v_{\max } / \mathrm{cm}^{-1} 3291,3028,2961,2927,2872,2853,1454,1411,1374,1320,1079,972$, 847, 758, 703
HRMS (NSI): $m / z 282.1522$ [(M-H) ${ }^{+}$requires 282.1522], Calcd for $\mathrm{C}_{15} \mathrm{H}_{24} \mathrm{NO}_{2} \mathrm{~S}$
HPLC: 97\% ee, Chiralcel OD column, $1 \%$ isopropanol/hexanes for 80 minutes then $10 \%$ isopropanol/hexanes to flush out major enantiomer, $1 \mathrm{~mL} / \mathrm{min}, \mathrm{UV}: 230 \mathrm{~nm}, \mathrm{t}_{\mathrm{r}}: 71.2 \mathrm{~min}$ (minor), 133.3 min (major)

$N$-((2S,3S,E)-3-methyl-2-phenylhept-4-en-1-yl)methanesulfonamide (8 - minor)
Prepared by General Procedure 1.3 .1 with $1(224 \mathrm{mg}, 1.0 \mathrm{mmol}, 1.0$ equiv), trans-3-heptene ( 336 $\mathrm{mg}, 4.0 \mathrm{mmol}, 4.0$ equiv), $\left\{\mathrm{Rh}_{2}(S-\mathrm{NTTL})_{4}\right\}(14.5 \mathrm{mg}, 0.01 \mathrm{mmol}, 1 \mathrm{~mol} \%)$, and $\mathrm{CHCl}_{3}(2 \mathrm{~mL})$ at rt for 18 h . Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4 mL THF then reduced with $1 \mathrm{M} \mathrm{LiAlH}_{4}$ in THF ( $1.2 \mathrm{~mL}, 1.2 \mathrm{mmol}, 1.2$ equiv) at $0{ }^{\circ} \mathrm{C}$ for 1 h . The reaction mixture was quenched by slow addition of $\mathrm{Na}_{2} \mathrm{SO}_{4} \cdot 10 \mathrm{H}_{2} \mathrm{O}$ until bubbling stopped followed by 15 additional min at $0^{\circ} \mathrm{C}$. The crude brown product was obtained via vacuum filtration over a thin layer of Celite ${ }^{\circledR}$ packed atop a 60 mL medium porosity fritted funnel using DCM ( 50 $\mathrm{mL})$ as eluent. Purification by flash chromatography $\left(\mathrm{SiO}_{2} ;\right.$ hexanes/EtOAc, 6:4; $\left.\mathrm{R}_{\mathrm{f}} 0.32\right)$ afforded a tan oil containing a 7:3 diastereomeric ratio of $\mathbf{8}$ - major and the title compound, respectively ( $225 \mathrm{mg}, 80 \%$ combined yield). Further purification for characterization purposes were performed by additional flash chromatography $\left(\mathrm{SiO}_{2}\right.$; hexanes/EtOAc, 6:4): The leading fractions contained the minor diastereomer, the tail fractions contained the major diastereomer, and the middle fractions contained a mix of the diastereomers (in all cases the Rf values were identical).
$[\boldsymbol{\alpha}]^{\mathbf{2 0}}{ }_{\mathbf{D}}-45.0^{\circ}\left(c \quad 0.5, \mathrm{CHCl}_{3}\right)$
${ }^{1} \mathbf{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 7.39-7.31(\mathrm{~m}, 2 \mathrm{H}), 7.26(\mathrm{tt}, J=6.6,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.19-7.14(\mathrm{~m}$, $2 \mathrm{H}), 5.56(\mathrm{dt}, J=15.2,6.5 \mathrm{~Hz}, 1 \mathrm{H}), 5.30(\mathrm{ddt}, J=15.3,9.0,1.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.92(\mathrm{dd}, J=8.9,4.0 \mathrm{~Hz}$, $1 \mathrm{H}), 3.56$ (ddd, $J=13.0,8.7,4.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.20-3.12(\mathrm{~m}, 1 \mathrm{H}), 2.72$ (s, 3 H$), 2.53$ (td, $J=10.2$, $4.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.37-2.27(\mathrm{~m}, 1 \mathrm{H}), 2.10-2.00(\mathrm{~m}, 2 \mathrm{H}), 1.00(\mathrm{t}, J=7.5 \mathrm{~Hz}, 3 \mathrm{H}), 0.77(\mathrm{~d}, J=6.7$ $\mathrm{Hz}, 3 \mathrm{H})$
${ }^{13}$ C NMR (125 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 140.8,133.3,132.7,129.1,128.5,127.4,52.2,47.6,41.4,40.2$, 29.8, 25.7, 20.0, 14.0

FTIR (neat): $v_{\max } / \mathrm{cm}^{-1} 3286,3027,2966,2923,1494,1453,1430,1330,1319,1087,968,849$, 782, 766, 701
HRMS (NSI): $m / z 282.1522$ [(M-H) ${ }^{+}$requires 282.1522], Calcd for $\mathrm{C}_{15} \mathrm{H}_{24} \mathrm{NO}_{2} \mathrm{~S}$
HPLC: $89 \%$ ee, Chiralcel OD column, $1 \%$ isopropanol/hexanes, $1 \mathrm{~mL} / \mathrm{min}$, UV: $230 \mathrm{~nm}, \mathrm{t}_{\mathrm{r}}: 59.8$ $\min$ (major), 51.5 min (minor)

$\boldsymbol{R}$ - $N$-(3-(4-isopropylcyclohexa-1,3-dien-1-yl)-2-phenylpropyl)methanesulfonamide (9)
Prepared by General Procedure 1.3.1 with $1(67 \mathrm{mg}, 0.3 \mathrm{mmol}, 1.0$ equiv), $\alpha$-terpinene ( 168 mg , $1.2 \mathrm{mmol}, 4.0$ equiv), $\left\{\mathrm{Rh}_{2}(S-\mathrm{NTTL})_{4}\right\}(4.3 \mathrm{mg}, 0.003 \mathrm{mmol}, 1 \mathrm{~mol} \%)$, and $\mathrm{CHCl}_{3}(0.6 \mathrm{~mL})$ at rt for 18 h . Solvent was removed via rotary evaporation and the reaction mixture was diluted with 1.2 mL THF then reduced with $1 \mathrm{M} \mathrm{LiAlH}_{4}$ in THF ( $0.36 \mathrm{~mL}, 0.36 \mathrm{mmol}, 1.2$ equiv) at $0{ }^{\circ} \mathrm{C}$ for 1 h. The reaction mixture was quenched by slow addition of $\mathrm{Na}_{2} \mathrm{SO}_{4} \cdot 10 \mathrm{H}_{2} \mathrm{O}$ until bubbling stopped followed by 15 additional min at $0^{\circ} \mathrm{C}$. The crude brown product was obtained via vacuum filtration over a thin layer of Celite ${ }^{\circledR}$ packed atop a 60 mL medium porosity fritted funnel using $\mathrm{DCM}(50$ mL ) as eluent. Purification by flash chromatography $\left(\mathrm{SiO}_{2}\right.$; hexanes/EtOAc, 6.75:3.25; $\mathrm{R}_{\mathrm{f}} 0.25$ ) afforded the title compound as a tan oil ( $52 \mathrm{mg}, 51 \%$ yield). Upon separation a mix of insertion products were acquired in such minor yields that further characterization was unable to be performed ( $3 \mathrm{mg},<3 \%$ combined yield of minor products).
$[\boldsymbol{\alpha}]^{\mathbf{2 0}}{ }_{\mathbf{D}}+3.3^{\circ}\left(c 0.5, \mathrm{CHCl}_{3}\right)$
${ }^{1} \mathbf{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 7.35-7.30(\mathrm{~m}, 2 \mathrm{H}), 7.27-7.18(\mathrm{~m}, 3 \mathrm{H}), 5.62(\mathrm{~d}, J=5.42 \mathrm{~Hz}, 1 \mathrm{H})$, $5.55(\mathrm{~d}, J=5.42 \mathrm{~Hz}, 1 \mathrm{H}), 4.12(\mathrm{t}, J=6.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.48-3.42(\mathrm{~m}, 1 \mathrm{H}), 3.24-3.17(\mathrm{~m}, 1 \mathrm{H}), 3.01(\mathrm{~m}$, $1 \mathrm{H}), 2.74(\mathrm{~s}, 3 \mathrm{H}), 2.48-2.36(\mathrm{~m}, 2 \mathrm{H}), 2.31-2.21(\mathrm{~m}, 1 \mathrm{H}), 2.10-1.95(\mathrm{~m}, 4 \mathrm{H}), 1.00(\mathrm{~d}, J=7 \mathrm{~Hz}, 6 \mathrm{H})$ ${ }^{13} \mathbf{C}$ MR (125 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 144.2,141.8,133.4,129.0,127.9,127.3,122.1,116.3,48.3,47.8$, 44.5, 41.6, 40.3, 34.6, 27.4, 25.5, 24.1, 21.2

FTIR (neat): $v_{\max } / \mathrm{cm}^{-1} 3288,3028,2959,2928,2870,1653,1603,1495,1454,1432,1316,1234$, 1147, 1077, 970, 909, 831, 759, 730, 700
HRMS (NSI): $m / z 334.1833$ [(M-H) ${ }^{+}$requires 334.1835], Calcd for $\mathrm{C}_{19} \mathrm{H}_{28} \mathrm{NO}_{2} \mathrm{~S}$
HPLC: $96 \%$ ee, Chiralcel OD column, $2 \%$ isopropanol/hexanes, $1 \mathrm{~mL} / \mathrm{min}, \mathrm{UV}: 254 \mathrm{~nm}, \mathrm{t}_{\mathrm{r}}: 66.9$
$\min$ (major), 48.0 min (minor)


## (S)-N-(3-methyl-2-phenyl-3-(p-tolyl)butyl)methanesulfonamide (11a)

Prepared by General Procedure 1.3 .1 using with $1(223 \mathrm{mg}, 1.00 \mathrm{mmol})$, $p$-cymene ( $626 \mu \mathrm{~L}, 4.00$ $\mathrm{mmol}),\left\{\mathrm{Rh}_{2}(S-\mathrm{NTTL})_{4}\right\}(14.5 \mathrm{mg}, 0.01 \mathrm{mmol}, 1.00 \mathrm{~mol} \%)$ and $1,2-\mathrm{DCE}(2.0 \mathrm{~mL})$ at room temperature for 24 h . Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4.0 mL THF then reduced with $1 \mathrm{M} \mathrm{LiAlH}_{4}$ in THF ( $1.2 \mathrm{~mL}, 1.2 \mathrm{mmol}, 1.2$ equiv) at $0{ }^{\circ} \mathrm{C}$ for 1 h . The reaction was quenched by slow addition of $\mathrm{Na}_{2} \mathrm{SO}_{4} \cdot 10 \mathrm{H}_{2} \mathrm{O}$ until bubbling stopped followed by 15 additional min at $0^{\circ} \mathrm{C}$. The crude brown product was obtained via vacuum filtration over a thin layer ( 1.27 cm ) of Celite ${ }^{\circledR}$ packed atop a 60 mL medium porosity fritted funnel using DCM ( 50 mL ) as eluent. Crude ${ }^{1} \mathrm{H}$ NMR revealed a $4: 1$ regioselective ratio for tertiary over primary insertion. Purification by flash chromatography ( $\mathrm{SiO}_{2}$; hexanes/EtOAc, 7:3, $\mathrm{R}_{\mathrm{f}} 0.31$ ) afforded the title compound as a clear oil ( $157 \mathrm{mg}, 47 \%$ ). Combined yield with the primary $\mathrm{C}-\mathrm{H}$ insertion product ( $249 \mathrm{mg}, 75 \%$ ).
$[\boldsymbol{\alpha}]^{\mathbf{2 0}}{ }_{\mathbf{D}}+1.8^{\circ}\left(c 1.0, \mathrm{CHCl}_{3}\right)$
${ }^{1} \mathbf{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 7.32-7.24(\mathrm{~m}, 3 \mathrm{H}), 7.28-7.25(\mathrm{~m}, 2 \mathrm{H}), 7.15-7.11(\mathrm{~m}, 2 \mathrm{H})$, $7.08-7.05(\mathrm{~m}, 2 \mathrm{H}), 3.71(\mathrm{br} \mathrm{d}, J=4.9 \mathrm{~Hz}, 1 \mathrm{H}), 3.35(\mathrm{td}, J=12.2,11.7,3.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.27$ (ddd, $J$ $=12.6,8.3,4.1 \mathrm{~Hz}, 1 \mathrm{H}), 3.05(\mathrm{dd}, J=11.5,4.1 \mathrm{~Hz}, 1 \mathrm{H}), 2.64(\mathrm{~s}, 3 \mathrm{H}), 2.34(\mathrm{~s}, 3 \mathrm{H}), 1.29(\mathrm{~s}, 3 \mathrm{H})$, $1.21(\mathrm{~s}, 3 \mathrm{H})$
${ }^{13} \mathbf{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 144.3,138.3,135.9,130.1,129.1,128.4,127.6,126.3,57.5,43.9$, 40.4, 40.2, 29.3, 23.8, 21.0

FTIR (neat): $v_{\max } / \mathrm{cm}^{-1} 3287,3027,2968,1513,1453,1407,1315,1146$
HRMS (NSI) $m / z 332.16774\left[(\mathrm{M}+\mathrm{H})^{+}\right.$requires 332.16788], Calcd for $\mathrm{C}_{19} \mathrm{H}_{26} \mathrm{O}_{2} \mathrm{NS}$
HPLC: $74 \%$ ee, Chiralcel OD-H column, $3 \%$ isopropanol/hexanes, $1 \mathrm{~mL} / \mathrm{min}, \mathrm{UV}: 210 \mathrm{~nm}, \mathrm{t}_{\mathrm{R}}$ : 25.9 min (minor), $\mathrm{t}_{\mathrm{R}}: 30.9 \mathrm{~min}$ (major)

(S)-N-(3-(4-isopropylphenyl)-2-phenylpropyl)methanesulfonamide (11b)

Prepared by General Procedure 1.3 .1 using with $1(223 \mathrm{mg}, 1.00 \mathrm{mmol})$, $p$-cymene ( $626 \mu \mathrm{~L}, 4.00$ $\mathrm{mmol}),\left\{\mathrm{Rh}_{2}(S-\mathrm{NTTL})_{4}\right\}(14.5 \mathrm{mg}, 0.01 \mathrm{mmol}, 1.00 \mathrm{~mol} \%)$ and $1,2-\mathrm{DCE}(2.0 \mathrm{~mL})$ at room temperature for 24 h . Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4.0 mL THF then reduced with $1 \mathrm{M} \mathrm{LiAlH}_{4}$ in THF ( $1.2 \mathrm{~mL}, 1.2 \mathrm{mmol}, 1.2$ equiv) at $0{ }^{\circ} \mathrm{C}$ for 1 h . The reaction was quenched by slow addition of $\mathrm{Na}_{2} \mathrm{SO}_{4} \cdot 10 \mathrm{H}_{2} \mathrm{O}$ until bubbling stopped followed by 15 additional min at $0^{\circ} \mathrm{C}$. The crude brown product was obtained via vacuum filtration over a thin layer ( 1.27 cm ) of Celite ${ }^{\circledR}$ packed atop a 60 mL medium porosity fritted funnel using DCM ( 50 mL ) as eluent. Crude ${ }^{1} \mathrm{H}$ NMR revealed a $4: 1$ regioselective ratio for tertiary over primary insertion. Purification by flash chromatography ( $\mathrm{SiO}_{2}$; hexanes/EtOAc, 7:3, $\mathrm{R}_{\mathrm{f}} 0.27$ ) afforded the title compound as a clear oil. Combined yield with the tertiary $\mathrm{C}-\mathrm{H}$ insertion product ( $249 \mathrm{mg}, 75 \%$ ).
$[\boldsymbol{\alpha}]^{\mathbf{2 0}}{ }_{\mathbf{D}}+9.1^{\circ}\left(c 0.4, \mathrm{CHCl}_{3}\right)$
${ }^{1} \mathbf{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 7.36-7.31(\mathrm{~m}, 2 \mathrm{H}), 7.28-7.24\left(\mathrm{~m}, 1 \mathrm{H}\right.$, coincidental with $\left.\mathrm{CDCl}_{3}\right)$, $7.22-7.18(\mathrm{~m}, 2 \mathrm{H}), 7.12-7.08(\mathrm{~m}, 2 \mathrm{H}), 7.03-6.99(\mathrm{~m}, 23.43(\mathrm{ddd}, J=12.7,7.7,4.9 \mathrm{~Hz}, 1 \mathrm{H})$, $3.35-3.25(\mathrm{~m}, 1 \mathrm{H}), 3.14-3.05(\mathrm{~m}, 2 \mathrm{H}), 3.00-2.81(\mathrm{~m}, 3 \mathrm{H}), 2.71(\mathrm{~s}, 3 \mathrm{H}), 1.22(\mathrm{~d}, J=6.9 \mathrm{~Hz}$, 6H)
${ }^{13} \mathbf{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 147.1,141.4,136.3,129.1,129.0,128.0,127.5,126.7,48.0,47.8$, 40.3, 39.9, 33.8, 24.1

FTIR (neat): $v_{\max } / \mathrm{cm}^{-1} 3288,2959,2929,1514,1453,1410,1316,1148$
HRMS (NSI) $m / z 332.16773\left[(\mathrm{M}+\mathrm{H})^{+}\right.$requires 332.16788], Calcd for $\mathrm{C}_{19} \mathrm{H}_{26} \mathrm{O}_{2} \mathrm{NS}$
HPLC: $95 \%$ ee, Chiralcel OD-H column, $5 \%$ isopropanol/hexanes, $1 \mathrm{~mL} / \mathrm{min}, \mathrm{UV}: 210 \mathrm{~nm}, \mathrm{t}_{\mathrm{R}}$ : 26.3 min (minor), $\mathrm{t}_{\mathrm{R}}: 46.4 \mathrm{~min}$ (major)

methyl ( $\boldsymbol{S}$ )-3-methyl-2-phenyl-3-(p-tolyl)butanoate (13)
Prepared by General Procedure 1.3 .2 with methyl phenyl diazoacetate ( $176.2 \mathrm{mg}, 1.0 \mathrm{mmol}, 1$ equiv), $p$-cymene ( $536 \mathrm{mg}, 4.0 \mathrm{mmol}, 4.0$ equiv), $\left.\mathrm{Rh}_{2}(S-\mathrm{NTTL})_{4}\right\}(14.5 \mathrm{mg}, 0.01 \mathrm{mmol}, 1.00 \mathrm{~mol}$ $\%)$ and $1,2-\mathrm{DCE}(2.0 \mathrm{~mL})$ at room temperature for 18 h . The crude brown product was obtained via vacuum filtration over a thin layer of Celite ${ }^{\circledR}$ packed atop a 60 mL medium porosity fritted funnel using DCM ( 50 mL ) as eluent. Purification by flash chromatography $\left(\mathrm{SiO}_{2}\right.$; hexanes/isopropanol, 9.5:0.5, $\mathrm{R}_{\mathrm{f}} 0.20$ ) afforded the title compound as a clear oil ( $144 \mathrm{mg}, 51 \%$ ).
$[\boldsymbol{\alpha}]^{\mathbf{2 0}}{ }_{\mathbf{D}}-20.3^{\circ}\left(c \quad 0.5, \mathrm{CHCl}_{3}\right)$
${ }^{1} \mathbf{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 7.27-7.17(\mathrm{~m}, 7 \mathrm{H}), 7.11-7.06(\mathrm{~m}, 2 \mathrm{H}), 3.91-3.86(\mathrm{~m}, 1 \mathrm{H})$, $3.46(\mathrm{~d}, J=1.1 \mathrm{~Hz}, 3 \mathrm{H}), 2.37-2.29(\mathrm{~s}, 3 \mathrm{H}), 1.47(\mathrm{~s}, 3 \mathrm{H}), 1.32(\mathrm{~s}, 3 \mathrm{H})$
${ }^{13} \mathbf{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 173.1,144.3,135.7,130.2,128.7,127.8,127.3,126.4,62.4,51.5$, 41.0, 26.7, 24.9, 21.1

FTIR (neat): $v_{\max } / \mathrm{cm}^{-1} 3089,3060,3027,2971,2949,2877,1733,1599,1582,1515,1495,1454$, $1480,1432,1409,1362,1326,1267,1198,1163,1138,1115,1095,1079,1019,815,749,701$
HRMS (method NSI): $m / z 283.16916\left[(\mathrm{M}-\mathrm{H})^{+}\right.$requires 283.16926], Calcd for $\mathrm{C}_{19} \mathrm{H}_{23} \mathrm{O}_{2}$
HPLC: $20 \%$ ee, Chiralcel ODR, $2.5 \%$ isopropanol/hexanes, $1 \mathrm{~mL} / \mathrm{min}, \mathrm{UV}: 254 \mathrm{~nm}, \mathrm{t}_{\mathrm{r}}: 4.09 \mathrm{~min}$ (major), 5.11 min (minor)

methyl ( $R, E$ )-3,3-dimethyl-2-phenylhex-4-enoate (14)
Prepared by General Procedure 1.3 .2 with methyl phenyl diazoacetate ( $176.2 \mathrm{mg}, 1.0 \mathrm{mmol}, 1$ equiv), trans-4-methyl-2-pentene ( $337 \mathrm{mg}, 4.0 \mathrm{mmol}, 4.0$ equiv), $\left.\mathrm{Rh}_{2}(S-\mathrm{NTTL})_{4}\right\}(14.5 \mathrm{mg}, 0.01$ $\mathrm{mmol}, 1.00 \mathrm{~mol} \%)$ and $\mathrm{CHCl}_{3}(2.0 \mathrm{~mL})$ at room temperature for 18 h . The crude brown product was obtained via vacuum filtration over a thin layer of Celite ${ }^{\circledR}$ packed atop a 60 mL medium porosity fritted funnel using $\mathrm{DCM}(50 \mathrm{~mL})$ as eluent. Purification by flash chromatography $\left(\mathrm{SiO}_{2}\right.$; hexanes/EtOAc, 7:3, $\mathrm{R}_{\mathrm{f}} 0.70$ ) afforded the title compound as a clear oil ( $96 \mathrm{mg}, 41 \%$ ).
$[\boldsymbol{\alpha}]^{\mathbf{2 0}}{ }_{\mathbf{D}}-3.0^{\circ}\left(c 0.5, \mathrm{CHCl}_{3}\right)$
${ }^{1} \mathbf{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.39-7.35(\mathrm{~m}, 2 \mathrm{H}), 7.32-7.24(\mathrm{~m}, 3 \mathrm{H}), 5.62(\mathrm{dd}, J=15.9,1.9$
$\mathrm{Hz}, 1 \mathrm{H}), 5.28(\mathrm{dq}, J=15.1,6.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.63(\mathrm{~d}, J=0.7 \mathrm{~Hz}, 3 \mathrm{H}), 3.50(\mathrm{~s}, 1 \mathrm{H}), 1.67(\mathrm{ddd}, J=6.4$, $1.6,0.6 \mathrm{~Hz}, 3 \mathrm{H}), 1.06(\mathrm{~d}, J=5.6 \mathrm{~Hz}, 6 \mathrm{H})$
${ }^{13} \mathbf{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 173.3,138.0,135.9,130.2,127.7,127.3,122.9,61.5,51.5,39.5$, 26.6, 24.5, 18.2

FTIR (neat): $v_{\max } / \mathrm{cm}^{-1} 3029,2963,1736,1497,1454,1433,1363,1199,1165,1140,1021,974$
HRMS (NSI): $m / z 233.15353$ [(M+H) ${ }^{+}$requires 233.15361], Calcd for $\mathrm{C}_{15} \mathrm{H}_{21} \mathrm{O}_{2}$
HPLC: $20 \%$ ee, Chiralcel OD column, $0.1 \%$ isopropanol/hexanes, $0.5 \mathrm{~mL} / \mathrm{min}, \mathrm{UV}: 210 \mathrm{~nm}, \mathrm{t}_{\mathrm{r}}$ : 13.3 min (major), 39.3 min (minor)

(S)-N-(3-(4-methoxyphenyl)-3-methyl-2-phenylbutyl)methanesulfonamide (15)

Prepared by General Procedure 1.3 .1 using with $\mathbf{1}$ ( $223 \mathrm{mg}, 1.00 \mathrm{mmol}$ ), 4-isopropylanisole ( 639 $\mu \mathrm{L}, 4.00 \mathrm{mmol}),\left\{\mathrm{Rh}_{2}(S-\mathrm{NTTL})_{4}\right\}(14.5 \mathrm{mg}, 0.01 \mathrm{mmol}, 1.00 \mathrm{~mol} \%)$ and $1,2-\mathrm{DCE}(2.0 \mathrm{~mL})$ at room temperature for 24 h . Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4.0 mL THF then reduced with $1 \mathrm{M} \mathrm{LiAlH}_{4}$ in THF ( $1.2 \mathrm{~mL}, 1.2 \mathrm{mmol}, 1.2$ equiv) at $0{ }^{\circ} \mathrm{C}$ for 1 h . The reaction was quenched by slow addition of $\mathrm{Na}_{2} \mathrm{SO}_{4} \cdot 10 \mathrm{H}_{2} \mathrm{O}$ until bubbling stopped followed by 15 additional min at $0^{\circ} \mathrm{C}$. The crude brown product was obtained via vacuum filtration over a thin layer ( 1.27 cm ) of Celite ${ }^{\circledR}$ packed atop a 60 mL medium porosity fritted funnel using $\mathrm{DCM}(50 \mathrm{~mL})$ as eluent. Purification by flash chromatography $\left(\mathrm{SiO}_{2} ;\right.$ hexanes/EtOAc, 7:3, $\mathrm{R}_{\mathrm{f}} 0.16$ ) afforded the title compound as a colorless solid ( $154 \mathrm{mg}, 44 \%$ ).
$\left[\boldsymbol{\alpha}^{\mathbf{2 0}}{ }_{\mathbf{D}}{ }^{+3.0^{\circ}\left(c 0.984, \mathrm{CHCl}_{3}\right)}\right.$
${ }^{1} \mathbf{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.32-7.24(\mathrm{~m}, 3 \mathrm{H}), 7.22-7.19(\mathrm{~m}, 2 \mathrm{H}), 7.06-7.02(\mathrm{~m}, 2 \mathrm{H})$, $6.87-6.83(\mathrm{~m}, 2 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H}), 3.77-3.68(\mathrm{br} \mathrm{m}, 1 \mathrm{H}), 3.38-3.26(\mathrm{~m}, 2 \mathrm{H}), 3.02(\mathrm{dd}, J=11.0$, $4.6 \mathrm{~Hz}, 1 \mathrm{H}), 2.65(\mathrm{~s}, 3 \mathrm{H}), 1.29(\mathrm{~s}, 3 \mathrm{H}), 1.22(\mathrm{~s}, 3 \mathrm{H})$
${ }^{13} \mathbf{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 158.0,139.2,138.3,130.0,128.4,127.5,113.6,57.6,55.4,43.9$, 40.2, 40.1, 29.2, 24.2

FTIR (neat): $v_{\max } / \mathrm{cm}^{-1} 3286,2965,2836,1609,1512,1453,1409,1316,1250,1146$
HRMS (NSI) $m / z 348.16279\left[(\mathrm{M}+\mathrm{H})^{+}\right.$requires 348.16279], Calcd for $\mathrm{C}_{19} \mathrm{H}_{26} \mathrm{O}_{3} \mathrm{NS}$
HPLC: 77\% ee, Chiralcel OD-H column, $3 \%$ isopropanol/hexanes, $1 \mathrm{~mL} / \mathrm{min}, \mathrm{UV}: 210 \mathrm{~nm}, \mathrm{t}_{\mathrm{R}}$ : 50.6 min (minor), $\mathrm{t}_{\mathrm{R}}: 55.5 \mathrm{~min}$ (major)


## (S)-N-(3-(4-isopropylphenyl)-3-methyl-2-phenylbutyl)methanesulfonamide (16)

Prepared by General Procedure 1.3 .1 using with $1(223 \mathrm{mg}, 1.00 \mathrm{mmol})$, $p$-cymene ( $626 \mu \mathrm{~L}, 4.00$ $\mathrm{mmol}),\left\{\mathrm{Rh}_{2}(S-\mathrm{NTTL})_{4}\right\}(14.5 \mathrm{mg}, 0.01 \mathrm{mmol}, 1.00 \mathrm{~mol} \%)$ and $1,2-\mathrm{DCE}(2.0 \mathrm{~mL})$ at room temperature for 24 h . Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4.0 mL THF then reduced with $1 \mathrm{M} \mathrm{LiAlH}_{4}$ in THF ( $1.2 \mathrm{~mL}, 1.2 \mathrm{mmol}, 1.2$ equiv) at $0{ }^{\circ} \mathrm{C}$ for 1 h . The reaction was quenched by slow addition of $\mathrm{Na}_{2} \mathrm{SO}_{4} \cdot 10 \mathrm{H}_{2} \mathrm{O}$ until bubbling stopped followed by 15 additional min at $0^{\circ} \mathrm{C}$. The crude brown product was obtained via vacuum filtration over a thin layer ( 1.27 cm ) of Celite ${ }^{\circledR}$ packed atop a 60 mL medium porosity fritted funnel using $\mathrm{DCM}(50 \mathrm{~mL})$ as eluent. Purification by flash chromatography $\left(\mathrm{SiO}_{2}\right.$; hexanes $i i-\mathrm{Pr}$, 2:1, $\mathrm{R}_{\mathrm{f}} 0.39$ ) afforded the title compound as waxy and amorphous yellow solid over time ( 215 mg , 64\%).
$[\boldsymbol{\alpha}]^{\mathbf{2 0}}{ }_{\mathbf{D}}+1.8^{\circ}\left(c 1.005, \mathrm{CHCl}_{3}\right)$
${ }^{1} \mathbf{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 7.32-7.26(\mathrm{~m}, 3 \mathrm{H}), 7.25-7.21(\mathrm{~m}, 2 \mathrm{H}), 7.20-7.16(\mathrm{~m}, 2 \mathrm{H})$, $7.08-7.04(\mathrm{~m}, 2 \mathrm{H}), 3.71-3.57$ (br m, 1H), 3.36 (ddd, $J=12.6,11.5,3.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.27$ (ddd, $J=$ $12.6,8.3,4.0 \mathrm{~Hz}, 1 \mathrm{H}), 3.04(\mathrm{dd}, J=11.4,4.0 \mathrm{~Hz}, 1 \mathrm{H}), 2.90(\mathrm{sep}, J=6.9 \mathrm{~Hz}, 1 \mathrm{H}), 2.63(\mathrm{~s}, 3 \mathrm{H})$, 1.30 (s, 3H), 1.26 (d, $J=6.9 \mathrm{~Hz}, 6 \mathrm{H}), 1.21$ (s, 3H)
${ }^{13} \mathbf{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 147.0,144.6,138.4,130.0,128.4,127.6,126.4,126.4,57.6,43.9$, 40.4, 40.1, 33.7, 29.3, 24.1, 23.7

FTIR (neat): $v_{\max } / \mathrm{cm}^{-1} 3261,2959,2869,1510,1441,1388,1145$
HRMS (NSI) $m / z 360.19921\left[(\mathrm{M}+\mathrm{H})^{+}\right.$requires 360.19918], Calcd for $\mathrm{C}_{21} \mathrm{H}_{30} \mathrm{O}_{2} \mathrm{NS}$
HPLC: 66\% ee, Chiralcel OD-R column, $5 \%$ isopropanol/hexanes, $1 \mathrm{~mL} / \mathrm{min}, \mathrm{UV}: 210 \mathrm{~nm}, \mathrm{t}_{\mathrm{R}}$ : 11.8 min (minor), $\mathrm{t}_{\mathrm{R}}: 14.6 \mathrm{~min}$ (major)

(S)-N-(3-(4-bromophenyl)-3-methyl-2-phenylbutyl)methanesulfonamide (17)

Prepared by General Procedure 1.3 .1 with $1(223 \mathrm{mg}, 1.0 \mathrm{mmol}, 1.0$ equiv), 1-bromo-4isopropylbenzene ( $796 \mathrm{mg}, 0.61 \mathrm{~mL}, 4.0 \mathrm{mmol}, 4.0$ equiv), $\mathrm{Rh}_{2}(S-\mathrm{NTTL})_{4}(14.5 \mathrm{mg}, 0.01 \mathrm{mmol}$, 0.01 equiv), and 1,2-DCE ( 2 mL ) at rt for 24 h . Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4 mL THF then reduced with $1 \mathrm{M} \mathrm{LiAlH}_{4}$ in THF ( 1.2 mL , $1.2 \mathrm{mmol}, 1.2$ equiv) at $0{ }^{\circ} \mathrm{C}$ for 1 h . The reaction mixture was quenched by slow addition of $\mathrm{Na}_{2} \mathrm{SO}_{4} \cdot 10 \mathrm{H}_{2} \mathrm{O}$ until bubbling stopped followed by 15 additional min at $0^{\circ} \mathrm{C}$. The crude brown product was obtained via vacuum filtration over a thin layer of Celite ${ }^{\circledR}$ packed atop a 60 mL medium porosity fritted funnel using $\mathrm{DCM}(50 \mathrm{~mL})$ as eluent. Purification by flash chromatography $\left(\mathrm{SiO}_{2} ;\right.$ hexanes/EtOAc, $\left.7: 3 ; \mathrm{R}_{\mathrm{f}} 0.25\right)$ afforded the title compound as an amorphous white solid ( $160 \mathrm{mg}, 40 \%$ yield).
$[\boldsymbol{\alpha}]^{\mathbf{2 0}}{ }_{\mathbf{D}}+8.1^{\circ}\left(c 0.4, \mathrm{CHCl}_{3}\right)$
${ }^{1} \mathbf{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 7.45-7.41(\mathrm{~m}, 2 \mathrm{H}), 7.30-7.24(\mathrm{~m}, 3 \mathrm{H}), 7.17-7.13(\mathrm{~m}, 2 \mathrm{H})$, $7.04-7.00(\mathrm{~m}, 2 \mathrm{H}), 3.87-3.68(\mathrm{br} \mathrm{m}, 1 \mathrm{H}), 3.39-3.25(\mathrm{~m}, 2 \mathrm{H}), 3.04(\mathrm{dd}, J=11.5,4.5 \mathrm{~Hz}, 1 \mathrm{H})$, $2.66(\mathrm{~s}, 3 \mathrm{H}), 1.30(\mathrm{~s}, 3 \mathrm{H}), 1.22(\mathrm{~s}, 3 \mathrm{H})$
${ }^{13} \mathbf{C}$ NMR (125 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 146.4,137.7,131.3,130.0,128.5,128.4,127.7,120.4,57.2,43.6$, 40.6, 40.4, 28.7, 24.3

FTIR (neat): $v_{\text {max }} / \mathrm{cm}^{-1} 3286,2969,1492,1453,1396,1317,1147$
HRMS (NSI) $m / z 396.06294\left[(\mathrm{M}+\mathrm{H})^{+}\right.$requires 396.06274], Calcd for $\mathrm{C}_{18} \mathrm{H}_{23} \mathrm{O}_{2} \mathrm{NBrS}$
HPLC: $82 \%$ ee, Chiralcel OD-H column, $5 \%$ isopropanol/hexanes, $1 \mathrm{~mL} / \mathrm{min}, \mathrm{UV}: 210 \mathrm{~nm}, \mathrm{t}_{\mathrm{R}}$ :
24.4 min (minor), $\mathrm{t}_{\mathrm{R}}: 38.8 \mathrm{~min}$ (major)


## (S)-N-(3-methyl-2,3-diphenylbutyl)methanesulfonamide (18a)

Prepared by General Procedure 1.3 .1 with $1(223 \mathrm{mg}, 1.0 \mathrm{mmol}, 1.0$ equiv), cumene ( $481 \mathrm{mg}, 0.56$ $\mathrm{mL}, 4.0 \mathrm{mmol}, 4.0$ equiv), $\mathrm{Rh}_{2}(S-\mathrm{NTTL})_{4}(14.5 \mathrm{mg}, 0.01 \mathrm{mmol}, 0.01$ equiv), and 1,2-DCE ( 2 mL ) at rt for 24 h . Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4 mL THF then reduced with $1 \mathrm{M} \mathrm{LiAlH}_{4}$ in THF ( $1.2 \mathrm{~mL}, 1.2 \mathrm{mmol}, 1.2$ equiv) at $0{ }^{\circ} \mathrm{C}$ for 1 h . The reaction mixture was quenched by slow addition of $\mathrm{Na}_{2} \mathrm{SO}_{4} \cdot 10 \mathrm{H}_{2} \mathrm{O}$ until bubbling stopped followed by 15 additional $\min$ at $0^{\circ} \mathrm{C}$. The crude brown product was obtained via vacuum filtration over a thin layer of Celite ${ }^{\circledR}$ packed atop a 60 mL medium porosity fritted funnel using DCM ( 50 mL ) as eluent. Purification by flash chromatography $\left(\mathrm{SiO}_{2}\right.$; hexanes/EtOAc, 7:3) afforded the title compound $\mathbf{1 8 a}\left(\mathrm{R}_{\mathrm{f}} 0.23\right)$ as a clear oil ( $77 \mathrm{mg}, 24 \%$ yield) and $\mathbf{1 8 b}\left(\mathrm{R}_{\mathrm{f}} 0.58\right)$ as a crystalline solid ( $31 \mathrm{mg}, 10 \%$ ).
$[\boldsymbol{\alpha}]^{\mathbf{2 0}}{ }_{\mathbf{D}}+6.3^{\circ}\left(c 0.65, \mathrm{CHCl}_{3}\right)$
${ }^{1} \mathbf{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 7.35-7.21(\mathrm{~m}, 8 \mathrm{H}), 7.08-7.04(\mathrm{~m}, 2 \mathrm{H}), 3.76(\mathrm{br} \mathrm{dd}, J=7.9,3.3$ $\mathrm{Hz}, 1 \mathrm{H}$ ), 3.37 (td, $J=12.2,3.8 \mathrm{~Hz}, 1 \mathrm{H}$ ), 3.26 (ddd, $J=12.4,8.3,3.9 \mathrm{~Hz}, 1 \mathrm{H}$ ), 3.07 (dd, $J=11.6$, $3.9 \mathrm{~Hz}, 1 \mathrm{H}) 2.62(\mathrm{~s}, 3 \mathrm{H}), 1.33(\mathrm{~s}, 3 \mathrm{H}), 1.23(\mathrm{~s}, 3 \mathrm{H})$
${ }^{13} \mathbf{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 147.4,138.2,130.0,128.38,128.36,127.6,126.43,126.41,57.5$, 43.8, 40.7, 40.1, 29.0, 23.8

FTIR (neat): $v_{\max } / \mathrm{cm}^{-1} 3286,2967,1601,1496,1408,1315,1145$
HRMS (NSI) $m / z 318.15194\left[(\mathrm{M}+\mathrm{H})^{+}\right.$requires 318.15223], Calcd for $\mathrm{C}_{18} \mathrm{H}_{24} \mathrm{O}_{2} \mathrm{NS}$
HPLC: $72 \%$ ee, Chiralcel OD-H column, $2 \%$ isopropanol/hexanes, $1 \mathrm{~mL} / \mathrm{min}, \mathrm{UV}: 210 \mathrm{~nm}, \mathrm{t}_{\mathrm{R}}$ :
50.4 min (minor), $\mathrm{t}_{\mathrm{R}}: 58.2 \mathrm{~min}$ (major)

(3aS,7aS)-6-isopropyl-1-(methylsulfonyl)-3-phenyl-3a,7a-dihydro-1H-indole (18b)
See procedure for 18a.
$[\boldsymbol{\alpha}]^{\mathbf{2 0}}{ }_{\mathbf{D}}-142^{\circ}\left(c 0.3, \mathrm{CHCl}_{3}\right)$
${ }^{1} \mathbf{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta{ }^{1} \mathrm{H}$ NMR ( 500 MHz , Chloroform- $d$ ) $\delta 7.36-7.33(\mathrm{~m}, 4 \mathrm{H}), 7.26-$ $7.23(\mathrm{~m}, 1 \mathrm{H}), 6.85(\mathrm{~d}, J=1.7 \mathrm{~Hz}, 1 \mathrm{H}), 5.97-5.84(\mathrm{~m}, 1 \mathrm{H}), 5.76(\mathrm{dd}, J=7.3,2.1 \mathrm{~Hz}, 2 \mathrm{H}), 4.88$ (dd, $J=12.8,5.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.46-4.16(\mathrm{~m}, 1 \mathrm{H}), 2.93(\mathrm{~s}, 3 \mathrm{H}), 2.37(\mathrm{sep}, J=6.8 \mathrm{~Hz}, 1 \mathrm{H}), 1.08$ (dd, $J=6.8,3.3 \mathrm{~Hz}, 6 \mathrm{H}$ )
${ }^{13} \mathbf{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 144.3,132.8,129.0,127.3,126.1,125.3,124.9,124.3,123.9$, 113.1, 59.6, 42.5, 39.0, 33.7, 21.3, 21.0

FTIR (neat): $v_{\max } / \mathrm{cm}^{-1} 2961,2929,1629,1447,1342,1152$
HRMS (NSI) $m / z 316.13646\left[(\mathrm{M}+\mathrm{H})^{+}\right.$requires 316.13658], Calcd for $\mathrm{C}_{18} \mathrm{H}_{22} \mathrm{O}_{2} \mathrm{NS}$
HPLC: 92\% ee, Chiralcel SS-Whelk column, 7.5\% isopropanol/hexanes, $1 \mathrm{~mL} / \mathrm{min}, \mathrm{UV}: 210 \mathrm{~nm}$, $\mathrm{t}_{\mathrm{R}}: 20.3 \mathrm{~min}$ (major), $\mathrm{t}_{\mathrm{R}}: 24.2 \mathrm{~min}$ (minor)


## (R)-N-(3-(4-methoxyphenyl)-2-phenylpropyl)methanesulfonamide (20)

Prepared by General Procedure 1.3 .1 with $1(223 \mathrm{mg}, 1.0 \mathrm{mmol}, 1.0$ equiv), 4-methylanisole ( 489 $\mathrm{mg}, 0.50 \mathrm{~mL}, 4.0 \mathrm{mmol}, 4.0$ equiv), $\mathrm{Rh}_{2}(S-\mathrm{NTTL})_{4}(14.5 \mathrm{mg}, 0.01 \mathrm{mmol}, 0.01$ equiv), and $1,2-$ DCE $(2 \mathrm{~mL})$ at rt for 24 h . Solvent was removed via rotary evaporation and the reaction mixture was diluted with 4 mL THF then reduced with $1 \mathrm{M} \mathrm{LiAlH}_{4}$ in THF ( $1.2 \mathrm{~mL}, 1.2 \mathrm{mmol}, 1.2$ equiv) at $0{ }^{\circ} \mathrm{C}$ for 1 h . The reaction mixture was quenched by slow addition of $\mathrm{Na}_{2} \mathrm{SO}_{4} \cdot 10 \mathrm{H}_{2} \mathrm{O}$ until bubbling stopped followed by 15 additional min at $0^{\circ} \mathrm{C}$. The crude brown product was obtained via vacuum filtration over a thin layer of Celite ${ }^{\circledR}$ packed atop a 60 mL medium porosity fritted funnel using DCM ( 50 mL ) as eluent. Purification by flash chromatography $\left(\mathrm{SiO}_{2}\right.$; hexanes/EtOAc, 7:3; $\mathrm{R}_{\mathrm{f}} 0.26$ ) afforded the title compound as a tan oil ( $118 \mathrm{mg}, 37 \%$ yield).
$[\boldsymbol{\alpha}]^{\mathbf{2 0}}{ }_{\mathbf{D}}+19.4^{\circ}\left(c 0.40, \mathrm{CHCl}_{3}\right)$
${ }^{1} \mathbf{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 7.37-7.33(\mathrm{~m}, 2 \mathrm{H}), 7.29-7.25\left(\mathrm{~m}, 1 \mathrm{H}\right.$, coincidental with $\left.\mathrm{CDCl}_{3}\right)$, $7.20-7.17(\mathrm{~m}, 2 \mathrm{H}) 7.01-6.97(\mathrm{~m}, 2 \mathrm{H}), 6.81-6.77(\mathrm{~m}, 2 \mathrm{H}), 4.06-3.90(\mathrm{br} \mathrm{m}, 1 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H})$, $3.49-3.41(\mathrm{~m}, 1 \mathrm{H}), 3.32$ (ddd, $J=12.8,9.3,4.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.12-3.04(\mathrm{~m}, 1 \mathrm{H}), 2.91$ (d, $J=7.5$ $\mathrm{Hz}, 2 \mathrm{H}$ ), 2.76 (s, 3H)
${ }^{13} \mathbf{C}$ NMR (125 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 158.3,141.2,131.0,130.1,129.1,128.0,127.5,114.0,55.4,48.3$, 47.8, 40.4, 39.5

FTIR (neat): $v_{\max } / \mathrm{cm}^{-1} 3286,2928,1611,1511,1316,1244,1146$
HRMS (NSI) $m / z 320.13159\left[(M+H)^{+}\right.$requires 320.13149], Calcd for $\mathrm{C}_{17} \mathrm{H}_{22} \mathrm{O}_{3} \mathrm{NS}$
HPLC: $93 \%$, Chiralcel AD-H column, $8 \%$ isopropanol/hexanes, $1 \mathrm{~mL} / \mathrm{min}, \mathrm{UV}: 210 \mathrm{~nm}, \mathrm{t}_{\mathrm{R}}: 18.1$ $\min$ (minor), $\mathrm{t}_{\mathrm{R}}: 19.7 \min$ (major)

## 3. References

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4. NMR Data for New Compounds


Supporting Information Figure 1. ${ }^{1} \mathrm{H}$ NMR Spectrum of 3a, $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 2. ${ }^{13} \mathrm{C}$ NMR Spectrum of 3a, $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 3. ${ }^{1} \mathrm{H}$ NMR Spectrum of 7a, $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 4. ${ }^{13} \mathrm{C}$ NMR Spectrum of $7 \mathrm{a}, 125 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 5. ${ }^{1} \mathrm{H}$ NMR Spectrum of $\mathbf{7 a}$ and $\mathbf{7 b}$ mix, $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 6. ${ }^{13} \mathrm{C}$ NMR Spectrum of 7a and 7b mix, $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 7. ${ }^{1} \mathrm{H}$ NMR Spectrum of Major Diastereomer of 8, $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 8. ${ }^{13} \mathrm{C}$ NMR Spectrum of Major Diastereomer of 8, $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 9. ${ }^{1} \mathrm{H}$ NMR Spectrum of Minor Diastereomer of 8, $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$



Supporting Information Figure 10. ${ }^{13} \mathrm{C}$ NMR Spectrum of Minor Diastereomer of 8, $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 11. ${ }^{1} \mathrm{H}$ NMR Spectrum of $\mathbf{9}, 500 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 12. ${ }^{13} \mathrm{C}$ NMR Spectrum of $\mathbf{9}, 125 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 13. ${ }^{1} \mathrm{H}$ NMR Spectrum of $\mathbf{1 1 a}, 500 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 14. ${ }^{13} \mathrm{C}$ NMR Spectrum of $\mathbf{1 1 a}, 125 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 15. ${ }^{1} \mathrm{H}$ NMR Spectrum of 11b, $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 16. ${ }^{13} \mathrm{C}$ NMR Spectrum of $\mathbf{1 1 b}, 125 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 17. ${ }^{1} \mathrm{H}$ NMR Spectrum of $\mathbf{1 3}, 400 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 18. ${ }^{13} \mathrm{C}$ NMR Spectrum of $\mathbf{1 3}, 100 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 19. ${ }^{1} \mathrm{H}$ NMR Spectrum of $\mathbf{1 4}, 500 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 20. ${ }^{13} \mathrm{C}$ NMR Spectrum of $\mathbf{1 4}, 100 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 21. ${ }^{1} \mathrm{H}$ NMR Spectrum of 15, $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 22. ${ }^{13} \mathrm{C}$ NMR Spectrum of $\mathbf{1 5}, 125 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 23. ${ }^{1} \mathrm{H}$ NMR Spectrum of 16, $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 24. ${ }^{13} \mathrm{C}$ NMR Spectrum of $\mathbf{1 6}, 125 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 25. ${ }^{1} \mathrm{H}$ NMR Spectrum of 17, $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 26. ${ }^{13} \mathrm{C}$ NMR Spectrum of $\mathbf{1 7}, 125 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 27. ${ }^{1} \mathrm{H}$ NMR Spectrum of 18a, $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 28. ${ }^{13} \mathrm{C}$ NMR Spectrum of $\mathbf{1 8 a}, 125 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 29. ${ }^{1} \mathrm{H}$ NMR Spectrum of $\mathbf{1 8 b}$, $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$



Supporting Information Figure 30. ${ }^{13} \mathrm{C}$ NMR Spectrum of $\mathbf{1 8 b}, 125 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 31. ${ }^{1} \mathrm{H}$ NMR Spectrum of 20, $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$


Supporting Information Figure 32. ${ }^{13} \mathrm{C}$ NMR Spectrum of $\mathbf{2 0}, 125 \mathrm{MHz}, \mathrm{CDCl}_{3}$
5. HPLC Traces


| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 25.38 | 49.35 | 521.4 | 471.8 | 49.347 |
| 2 | UNKNOWN | 36.07 | 50.65 | 382.0 | 484.3 | 50.653 |
|  |  |  |  |  |  |  |
| Total |  |  | 100.00 | 903.4 | 956.2 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :--- | :---: | :---: | :---: | :---: | :---: |
| 2 | UNKNOWN | 25.55 | 8.04 | 117.5 | 98.8 | 8.037 |
| 1 | UNKNOWN | 36.04 | 91.96 | 871.2 | 1131.0 | 91.963 |
|  |  |  |  |  |  |  |
| Total |  |  |  |  |  | 1229.9 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :--- | :---: | :---: | :---: | :---: | :---: |
| 3 | UNKNOWN | 41.38 | 19.80 | 404.5 | 600.9 | 19.799 |
| 2 | UNKNOWN | 49.83 | 20.17 | 362.6 | 612.1 | 20.166 |
| 4 | UNKNOWN | 61.55 | 29.81 | 348.7 | 904.7 | 29.809 |
| 1 | UNKNOWN | 99.65 | 30.23 | 273.4 | 917.4 | 30.226 |
|  |  |  | 100.00 | 1389.2 | 3035.1 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 40.73 | 49.79 | 658.9 | 1046.5 | 49.793 |
| 2 | UNKNOWN | 49.29 | 50.21 | 601.3 | 1055.2 | 50.207 |
|  |  |  |  |  |  |  |
| Total |  |  | 100.00 | 1260.3 | 2101.7 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 | UNKNOWN | 41.63 | 13.24 | 56.0 | 86.0 | 13.238 |
| 1 | UNKNOWN | 49.64 | 86.76 | 334.7 | 563.9 | 86.762 |
|  |  |  |  |  |  |  |
| Total |  |  |  | 390.7 | 650.0 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 | UNKNOWN | 63.47 | 2.80 | 9.7 | 17.0 | 2.802 |
| 1 | UNKNOWN | 100.34 | 97.20 | 180.4 | 590.0 | 97.198 |
|  |  |  | 100.00 | 190.1 | 607.0 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 50.25 | 11.01 | 203.7 | 552.5 | 11.005 |
| 2 | UNKNOWN | 62.13 | 11.80 | 268.5 | 592.6 | 11.805 |
| 3 | UNKNOWN | 68.16 | 38.01 | 576.3 | 1908.4 | 38.014 |
| 4 | UNKNOWN | 132.60 | 39.18 | 825.4 | 1966.8 | 39.176 |
|  |  |  |  |  |  |  |
| Total |  |  | 100.00 | 1874.0 | 5020.3 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 49.85 | 49.18 | 156.8 | 395.3 | 49.180 |
| 2 | UNKNOWN | 60.56 | 50.82 | 204.2 | 408.5 | 50.820 |
|  |  |  |  |  |  |  |
| Total |  |  |  |  |  | 861.0 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 51.50 | 5.54 | 29.3 | 63.3 | 5.535 |
| 2 | UNKNOWN | 59.81 | 94.46 | 507.4 | 1080.4 | 94.465 |
|  |  |  |  |  |  |  |
| Total |  |  | 100.00 | 536.6 | 1143.7 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 53.49 | 0.84 | 16.3 | 38.6 | 0.845 |
| 2 | UNKNOWN | 62.46 | 15.12 | 300.5 | 690.6 | 15.115 |
| 3 | UNKNOWN | 71.17 | 1.45 | 29.3 | 66.3 | 1.451 |
| 4 | UNKNOWN | 133.32 | 82.59 | 1368.9 | 3773.4 | 82.589 |
|  |  |  |  |  |  |  |
| Total |  |  | 100.00 | 1715.0 | 4568.9 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 48.71 | 49.59 | 15.5 | 29.9 | 49.586 |
| 2 | UNKNOWN | 67.19 | 50.41 | 12.9 | 30.4 | 50.414 |
|  |  |  | 100.00 |  |  |  |
| Total |  |  | 28.4 | 60.4 | 100.000 |  |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 | UNKNOWN | 48.01 | 1.68 | 0.9 | 1.6 | 1.678 |
| 1 | UNKNOWN | 66.85 | 98.32 | 39.6 | 93.8 | 98.322 |
|  |  |  |  |  |  |  |
| Total |  |  |  | 40.5 | 95.4 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 25.22 | 48.82 | 905.8 | 1030.2 | 48.822 |
| 2 | UNKNOWN | 30.92 | 51.18 | 1018.9 | 1079.9 | 51.178 |
|  |  |  |  |  |  |  |
| Total |  |  | 100.00 | 1924.7 | 2110.1 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 25.91 | 13.42 | 22.7 | 26.2 | 13.419 |
| 2 | UNKNOWN | 30.93 | 86.58 | 147.4 | 169.2 | 86.581 |
|  |  |  |  |  |  |  |
| Total |  |  | 100.00 | 170.1 | 195.4 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 25.92 | 50.68 | 944.1 | 902.2 | 50.678 |
| 2 | UNKNOWN | 46.57 | 49.32 | 498.1 | 878.1 | 49.322 |
|  |  |  |  |  |  |  |
| Total |  |  | 100.00 | 1442.3 | 1780.3 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 26.30 | 2.34 | 7.5 | 7.0 | 2.343 |
| 2 | UNKNOWN | 46.36 | 97.66 | 163.2 | 290.3 | 97.657 |
|  |  |  |  |  |  |  |
| Total |  |  | 100.00 | 170.7 | 297.2 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 4.24 | 50.57 | 95.7 | 12.3 | 50.565 |
| 2 | UNKNOWN | 5.32 | 49.43 | 77.1 | 12.1 | 49.435 |
|  |  |  |  |  |  |  |
| Total |  |  | 100.00 | 172.7 | 24.4 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 4.09 | 60.39 | 50.9 | 6.7 | 60.389 |
| 2 | UNKNOWN | 5.11 | 39.61 | 27.2 | 4.4 | 39.611 |
|  |  |  | 100.00 | 78.1 |  |  |
| Total |  |  |  |  |  |  |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 13.15 | 50.47 | 104.8 | 52.2 | 50.468 |
| 2 | UNKNOWN | 38.41 | 49.53 | 24.7 | 51.2 | 49.532 |
|  |  |  |  |  |  |  |
| Total |  |  | 100.00 | 129.5 | 103.4 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 13.31 | 59.84 | 81.5 | 39.5 | 59.836 |
| 2 | UNKNOWN | 39.30 | 40.16 | 15.1 | 26.5 | 40.164 |
|  |  |  |  |  |  |  |
| Total |  |  | 100.00 | 96.6 | 65.9 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 49.64 | 49.25 | 116.0 | 240.1 | 49.254 |
| 2 | UNKNOWN | 55.18 | 50.75 | 113.6 | 247.4 | 50.746 |
|  |  |  |  |  |  |  |
| Total |  |  |  |  | 229.7 | 487.4 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 50.63 | 11.30 | 29.5 | 59.5 | 11.296 |
| 2 | UNKNOWN | 55.52 | 88.70 | 213.8 | 467.1 | 88.704 |
|  |  |  |  |  |  |  |
| Total |  |  | 100.00 | 243.4 | 526.5 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 11.74 | 50.57 | 21.7 | 10.3 | 50.566 |
| 2 | UNKNOWN | 14.68 | 49.43 | 18.3 | 10.1 | 49.434 |
|  |  |  | 100.00 | 40.0 | 20.4 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 11.75 | 16.65 | 12.2 | 5.7 | 16.649 |
| 2 | UNKNOWN | 14.62 | 83.35 | 52.0 | 28.4 | 83.351 |
|  |  |  |  |  |  |  |
| Total |  |  | 100.00 | 64.2 | 34.1 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 24.24 | 49.77 | 500.3 | 505.9 | 49.766 |
| 2 | UNKNOWN | 38.88 | 50.23 | 334.1 | 510.6 | 50.234 |
|  |  |  |  |  |  |  |
| Total |  |  |  |  |  | 100.00 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 24.44 | 9.10 | 73.8 | 77.1 | 9.100 |
| 2 | UNKNOWN | 38.76 | 90.90 | 531.1 | 770.0 | 90.900 |
|  |  |  | 100.00 | 604.9 | 847.1 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 48.49 | 50.11 | 578.3 | 1232.3 | 50.106 |
| 2 | UNKNOWN | 57.28 | 49.89 | 557.4 | 1227.1 | 49.894 |
|  |  |  |  |  |  |  |
| Total |  |  | 100.00 | 1135.7 | 2459.4 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 50.37 | 13.90 | 155.9 | 368.0 | 13.895 |
| 2 | UNKNOWN | 58.21 | 86.10 | 1117.6 | 2280.5 | 86.105 |
|  |  |  |  |  |  |  |
| Total |  |  | 100.00 | 1273.4 | 2648.6 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 2 | UNKNOWN | 20.52 | 50.46 | 161.5 | 91.6 | 50.458 |
| 1 | UNKNOWN | 24.31 | 49.54 | 129.8 | 90.0 | 49.542 |
|  |  |  |  |  |  |  |
| Total |  |  | 100.00 | 291.2 | 181.6 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 20.30 | 95.90 | 215.3 | 124.0 | 95.898 |
| 2 | UNKNOWN | 24.23 | 4.10 | 8.2 | 5.3 | 4.102 |
|  |  |  | 100.00 | 223.5 | 129.3 | 100.000 |



| $\#$ | Name | Time [Min] | Quantity [\% Area] | Height [mAU] | Area [mAU.Min] | Area \% [\%] |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | UNKNOWN | 18.15 | 49.13 | 113.9 | 49.6 | 49.134 |
| 2 | UNKNOWN | 19.70 | 50.87 | 109.1 | 51.4 | 50.866 |
|  |  |  | 100.00 |  |  |  |
| Total |  |  | 223.1 | 101.0 | 100.000 |  |



