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Supporting Information

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Asymmetric Simmons-Smith Reaction of Allylic Alcohols with Al Lewis Acid/N Lewis Base Bifunctional Al(Salalen) Catalyst

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1. General

^{1}H and ^{13}C NMR spectra were measured on a JEOL JNM-AL-400 spectrometer at 400 and 100 MHz, respectively. All chemical shifts were recorded in δ (ppm) relative to tetramethylsilane (TMS). Infrared spectra were measured as a KBr disc on a SHIMADZU FTIR-8400 spectrophotometer, and only diagnostic absorptions are listed below. Optical rotation was measured with a JASCO P-1020 polarimeter. TOFMS spectra were obtained from BRUKER DALTONICS micrOTOF-KS1focus spectrometer. Enantiomeric excesses were determined by HPLC analysis using a SHIMADZU LC-10AT-VP equipped with an appropriate optically active column, as described below. TLC analysis was performed on Silica gel 60 F_{254}-coated glass plate (Merck). Solvents were used as supplied commercially, except for THF that was distilled from Na/Ph_2CO and CH_2Cl_2 that was distilled from CaH_2, before use. Allylic alcohols were synthesized according to the known procedures, except for commercially available cinnamyl alcohol and geraniol.

2. Asymmetric Simmons-Smith reaction

2.1. Synthesis of salalen ligands 2, 3, 4, 5 and 6

The ligands **2**, **3**, **4**, **5** and **6** were synthesized according to the reported procedures.[1a.b]

2.2. Data on optical rotation and HPLC analysis of cyclopropyl alcohols

(1*S*, 2*S*)-2-Phenylcyclopropylmethanol (Table 1, entry 9)

95% ee; $[\alpha]_D^{24}$= +80.1 (c= 0.27 in EtOH) ($[\alpha]_D$= +74.7 (c= 2.3 in EtOH) for the (1*S*, 2*S*)-isomer of 92% ee[2]); HPLC (Daicel Chiralcel OD-H, *n*-hexane: *i*PrOH= 9: 1, flow= 0.5 mL min^{-1}): *t*= 14.8 min (major), *t*= 19.9 min (minor).

(1*S*, 2*S*)-2-(4-Methoxyphenyl)cyclopropylmethanol (Table 2, entry 1)

94% ee; $[\alpha]_D^{24}$= +68.9 (c= 0.10 in EtOH) ($[\alpha]_D^{23}$= -63.5 (c= 1.05 in EtOH) for the (1*R*, 2*R*)-isomer of 94% ee[3]); HPLC (Daicel Chiralcel OD-H, *n*-hexane: *i*PrOH= 9: 1, flow= 0.5 mL min^{-1}): *t*= 17.8 min (major), *t*= 19.7 min (minor).

(1*S*, 2*S*)-2-(4-Chlorophenyl)cyclopropylmethanol (Table 2, entry 2)

94% ee; $[\alpha]_D^{24}$= +85.2 (c= 0.20 in $CHCl_3$) ($[\alpha]_D$= +72.4 (c= 3.0 in $CHCl_3$) for the (1*S*, 2*S*)-isomer of 82% ee[2]); HPLC (Daicel Chiralcel OD-H, *n*-hexane: *i*PrOH= 99: 1, flow= 0.5 mL min^{-1}): *t*= 15.6 min (major), *t*= 17.9 min (minor) after acetylation.

(1*R*, 2*S*)-2-Phenylcyclopropylmethanol (Table 2, entry 3)

58% ee; $[\alpha]_D^{24}$= -33.2 (c= 0.36 in EtOH) ($[\alpha]_D^{23}$= -49.7 (c= 1.02 in EtOH); for the (1*R*, 2*S*)-isomer of 92% ee[3]); HPLC (Daicel Chiralcel OJ-H, *n*-hexane: *i*PrOH= 95: 5, flow= 0.5 mL min^{-1}): *t*= 18.2 min (minor), *t*= 21.2 min (major).

(1*S*, 2*S*)-2-(2-Phenylethyl)cyclopropylmethanol (Table 2, entry 4)

86% ee; $[\alpha]_D^{24}$= +25.2 (c= 0.50 in $CHCl_3$) ($[\alpha]_D$= +14.8 (c= 2.2 in $CHCl_3$) for the (1*S*, 2*S*)-isomer of 60% ee[2]); HPLC (Daicel Chiralpak IA, *n*-hexane: *i*PrOH= 99: 1, flow= 0.5 mL min^{-1}): *t*= 41.7 min (minor), *t*= 44.6 min (major).

2-[(*t*-Butyldiphenylsilyloxy)methyl]cyclopropylmethanol (Table 2, entry 5)

90% ee; $[\alpha]_D^{24}$= +11.3 (c= 0.66 in $CHCl_3$) ($[\alpha]_D^{22}$= -12 (c= 0.32 in $CHCl_3$) for the material of 87% ee, the absolute configuration of which has not been determined[3]); HPLC (Daicel Chiralcel OD-H, *n*-hexane: *i*PrOH= 99: 1, flow= 0.5 mL min^{-1}): *t*= 12.1 min (major), *t*= 29.8 min (minor) after benzoylation.

(1*S*, 2*S*)-2-(Trityloxymethyl)cyclopropylmethanol (Table 2, entry 6)

87% ee; $[\alpha]_D^{24}$= +12.8 (c= 0.26 in $CHCl_3$) ($[\alpha]_D^{20}$= -7.3 (c= 2.52 in $CHCl_3$) for the (1*R*, 2*R*)-isomer of 69% ee[4]); HPLC (Daicel Chiralcel OD-H, *n*-hexane: *i*PrOH= 95: 5, flow= 0.5 mL min^{-1}): *t*= 17.9 min (major), *t*= 23.4 min (minor).

(1*S*, 2*S*)-2-Methyl-2-(4-methyl-3-pentenyl)cyclopropylmethanol (Table 2, entry 8)

70% ee; $[\alpha]_D^{25}$= +1.51 (c= 0.43 in $CHCl_3$) ($[\alpha]_D$= +2.16 (c= 5.83 in $CHCl_3$) for the (1*S*, 2*S*)-isomer of 93% ee[5]); HPLC (Daicel Chiralcel OD-H, *n*-hexane: *i*PrOH= 99: 1, flow= 0.5 mL min^{-1}): *t*= 8.7 min (major), *t*= 10.7 min (minor) after benzoylation.

3. References

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