Supporting Information-1

Asymmetric One-Pot Synthesis of 1,3-Oxazolidines and 1,3-Oxazinanes via Hemiaminal Intermediates

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Contents:

General Considerations:

All reactions were carried out in flame-dried screw-cap test tubes with magnetic stirring. Ethyl acetate was dried over 4Å MS. THF was purified by passing through a column of activated alumina under dry argon atmosphere. Anhydrous dimethyl formamide was purchased from commercial sources and transferred under Argon atmosphere. Alcohols were obtained commercially and purified under standard methods or dried over 4Å MS before use. Chiral (*R*)-BINOL was purchased from commercial sources and used without further purification. Substituted BINOL phosphoric acids H(**P1**),[1] H(**P2**)[2] were synthesized according to the literature procedures. Ca(**P1**)$_2$,[3]Mg(**P1**)$_2$[4] were prepared as the reported procedures. Thin layer chromatography was performed on Merck TLC plates (silica gel 60 F_{254}). Flash column chromatography was performed with Merck silica gel (230-400 mesh). Enantiomeric excess (ee) was determined using a Varian Prostar HPLC with a 210 binary pump and a 335 diode array detector. Optical rotations were performed on a Rudolph Research Analytical Autopol IV polarimeter (λ 589) using a 700-µL cell with a path length of 1-dm. ^{1}HNMR and ^{13}C NMR were recorded on Bruker Avance DPX-250 (250 MHz) and Varian Inova-400 spectrometer with chemical shifts reported relative to tetramethylsilane (TMS). ^{31}PNMR was recorded on a Varian Inova-400 instrument with H_3PO_4 as an external standard. The HRMS data were measured on an Agilent 1100 LC/MS ESI/TOF mass spectrometer with electro-spray ionization. Compounds described in the literature were characterized by comparing their spectral data to the reported values.

Preparation of Catalyst, M[P2]$_n$:[4]

M[**P2**]$_n$ (M = Ca, Mg, Li, Al, Zn, Sr) were prepared by adding 'H[**P2**] washed with HCl' (10 mol%) and Ca(OMe)$_2$ (5 mol%) or Mg(O*t*Bu)$_2$ (5 mol%) or Li(O*i*Pr) (10 mol%) or Al(O*i*Pr)$_3$ (0.33 mol%) or Zn(OMe)$_2$ (5 mol%) or Sr(O*i*Pr)$_2$ (5 mol%) into a flame dried reaction tube. Evacuate the tube and filled with Argon three times. Added 1 ml of dry dichloromethane and 1 ml of anhydrous methanol to the reaction tube. Stirred the reaction mixture at room temperature for 1 h. Solvent was concentrated, added 1 ml dichloromethane and concentrated again under reduced pressure to obtain the catalyst as pale yellow solid.

Mg[P2]$_2$ Spectral data:

^{1}H NMR (400MHz, DMSO): δ 7.96 (d, *J* = 7.9 Hz, 2H), 7.75 (s, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.03 (m, 6H), 3.15 (d, *J* = 5.0 Hz, 1H), 3.00 – 2.85 (m, 3H), 2.63 – 2.51 (m, 2H), 1.26 (d, *J* = 6.7 Hz, 12H), 1.15 (d, *J* = 3.6 Hz, 12H), 1.06 (d, *J* = 6.7 Hz, 6H), 0.85 (d, *J* = 6.7 Hz, 6H). ^{31}P (400MHz, DMSO): δ 3.39. MS (MALDI) Calcd for $C_{100}H_{112}MgO_8P_2$ ($[M+H]^+$) m/z 1527.77 Found 1527.96.

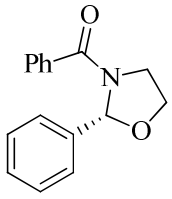
Experimental Section:

N-Acyl imines (**1a-k**) were synthesized according to the literature procedure and purified by sublimation.[5]

General procedure for the preparation of chiral 1,3-Oxazolidines:

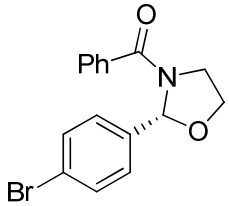
To a flame-dried reaction tube charged with 4Å molecular sieves 50mg (pre-activated in oven) was added N-benzoyl imine **1** (0.2 mmol), catalyst Mg[**P2**]$_2$ (0.005 mmol), the tube was evacuated and filled with argon. Added anhydrous toluene (1.0 ml) followed by 2-chloro ethanol

2 (0.4 mmol) *via* oven-dried syringe to the reaction mixture. The reaction was stirred at room temperature for 24h. The completion of reaction was monitored by TLC and toluene (1.0 ml) was removed by rotovap. Added anhydrous dimethyl formamide to the reaction tube and cooled to 0 °C. Added Cs_2CO_3 (0.4 mmol) and the solution was allowed to stir at room temperature for 4h. The crude product was purified by flash column chromatography (ethyl acetate : hexane) to get the pure 1,3-oxazolidine product **4** and the enantiomeric excess was determined by chiral HPLC analysis.



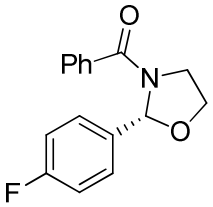
4a (*R*)-phenyl(2-phenyloxazolidin-3-yl)methanone[6]

The product was obtained by flash column chromatography as viscous oil(hexane : ethyl acetate, 1:1) 92% yield, 93% ee. HPLC Analysis: Chiralcel AD-H (hexane:iPrOH = 80:20, 1.0 mL/min), $t_{r\text{-major}}$ 9.36 min, $t_{r\text{-minor}}$ 15.53 min. $[\alpha]^{20}_D$= +140.7° (c =1.85, $CHCl_3$). ^{1}H NMR (400MHz, $CDCl_3$): δ 3.50-4.50 (bm, 4H), 6.0 (bs, 1st rotamer), 6.5 (bs, 2nd rotamer), 7.2-8.0 (bm, 10H). ^{13}C NMR (400MHz, $CDCl_3$): δ 48.31(broad peak), 66.66(broad peak), 89.35(broad peak), 126.70, 127.55, 128.30, 128.44, 128.80, 130.71, 135.80, 138.59, 169.58ppm. HRMS (ESI) calcd for $C_{16}H_{15}NO_2$ ($[M+H]^+$) m/z 254.1103, found 254.1186.



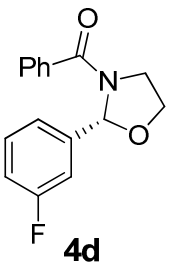
4b (*R*)-(2-bromophenyl)oxazolidin-3-yl)(phenyl)methanone

The product was obtained by flash column chromatography as viscous oil(hexane : ethyl acetate, 1:1) 99% yield, 93% ee. HPLC Analysis: Chiralcel AD-H (hexane:iPrOH = 80:20, 1.0 mL/min), $t_{r\text{-major}}$ 11.72 min, $t_{r\text{-minor}}$ 14.71 min. $[\alpha]^{20}_{D}$= +162.5° (c =2.25, $CHCl_3$). ^{1}H NMR (400MHz, $CDCl_3$): δ 3.50-4.50 (bm, 4H), 6.1 (bs, 1st rotamer), 6.5 (bs, 2nd rotamer), 7.2-8.0 (bm, 9H). ^{13}C NMR (400MHz, $CDCl_3$): δ 48.20(broad peak), 66.82(broad peak), 88.91(broad peak), 122.88, 127.54, 130.90, 135.53, 137.71, 169.59ppm. HRMS (ESI) calcd for $C_{16}H_{14}BrNO_2$ ($[M+H]^+$) m/z 332.0208, found 332.0285.



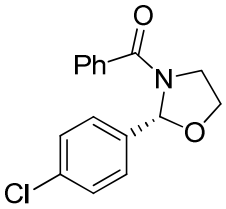
4c (*R*)-(2-(4-fluorophenyl)oxazolidin-3-yl)(phenyl)methanone

The product was obtained by flash column chromatography as viscous oil(hexane : ethyl acetate, 1:1) 93% yield, 90% ee. HPLC Analysis: Chiralcel AD-H (hexane:iPrOH = 80:20, 1.0 mL/min), $t_{r\text{-major}}$ 9.80 min, $t_{r\text{-minor}}$ 14.04 min. $[\alpha]^{20}_{D}$= +162.2° (c =2.15, $CHCl_3$). ^{1}H NMR (400MHz, $CDCl_3$): δ 3.50-4.50 (bm, 4H), 6.1 (bs, 1st rotamer), 6.5 (bs, 2nd rotamer), 6.9-7.9 (bm, 9H). ^{13}C NMR (400MHz, $CDCl_3$): δ 48.42(broad peak), 66.87(broad peak), 89.12(broad peak), 115.43, 115.65, 127.77, 128.56, 128.82, 128.91, 134.72, 135.85, 161.91, 164.37, 169.78ppm. HRMS (ESI) calcd for $C_{16}H_{14}FNO_2$ ($[M+H]^+$) m/z 272.1009, found 272.1090.



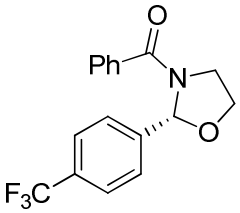
4d (*R*)-(2-(3-fluorophenyl)oxazolidin-3-yl)(phenyl)methanone

The product was obtained by flash column chromatography as viscous oil(hexane : ethyl acetate, 1:1) 94% yield, 97% ee. HPLC Analysis: Chiralcel AD-H (hexane:iPrOH = 90:10, 1.0 mL/min), $t_{\text{r-major}}$ 18.43 min, $t_{\text{r-minor}}$ 24.52 min. $[\alpha]^{20}_{D}$= +154.6° (c =1.25, $CHCl_3$). ^{1}H NMR (400MHz, $CDCl_3$): δ 3.50-4.50 (bm, 4H), 6.5(bs, 1H), 7.3-7.8 (bm, 9H). ^{13}C NMR (400MHz, $CDCl_3$): δ 47.35(broad peak), 65.75(broad peak), 88.17(broad peak), 126.70, 127.41, 127.56, 127.81, 130.07, 133.84, 134.75, 136.38, 168.80. HRMS (ESI) calcd for $C_{16}H_{14}FNO_2$ ($[M+H]^+$) m/z 272.1009, found 272.1087.



4e (*R*)-(2-(4-Chlorophenyl)oxazolidin-3-yl)(phenyl)methanone

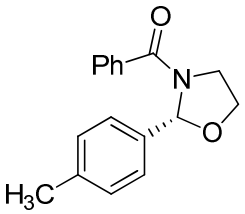
The product was obtained by flash column chromatography as viscous oil(hexane : ethyl acetate, 1:1) 94% yield, 95% ee. HPLC Analysis: Chiralcel AD-H (hexane:iPrOH = 90:10, 1.0 mL/min), $t_{\text{r-major}}$ 13.65 min, $t_{\text{r-minor}}$ 21.19 min. $[\alpha]^{20}_{D}$= +173.9° (c =1.3, $CHCl_3$). ^{1}H NMR (400MHz, $CDCl_3$): δ 3.50-4.40 (bm, 4H), 6.20-6.75 (bs, 1H), 6.8-8.0 (bm, 9H). ^{13}C NMR (400MHz, $CDCl_3$): δ 48.20(broad peak), 66.76(broad peak), 88.62(broad peak), 113.57, 113.79, 115.62, 115.83, 122.49, 122.51, 127.55, 128.36, 129.99, 130.07, 130.88, 161.57, 164.02, 169.64. HRMS (ESI) calcd for $C_{16}H_{14}ClNO_2$ ($[M+H]^+$) m/z 288.0713, found 288.0794.



4f

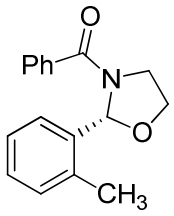
(*R*)-phenyl(2-(4-(trifluoromethyl)phenyl)oxazolidin-3-yl)methanone

The product was obtained by flash column chromatography as viscous oil(hexane : ethyl acetate, 1:1) 94% yield, 97% ee. HPLC Analysis: Chiralcel AD-H (hexane:iPrOH = 95:05, 1.0 mL/min), $t_{\text{r-major}}$ 25.23 min, $t_{\text{r-minor}}$ 26.96 min. $[\alpha]^{20}_{D}$= +152.4° (c =1.2, $CHCl_3$). ^{1}H NMR (400MHz, $CDCl_3$): δ 3.50-4.50 (bm, 4H), 6.20-6.75 (bs, 1H), 7.2-8.0 (bm, 9H). ^{13}C NMR (400MHz, $CDCl_3$): δ 48.21(broad peak), 66.89(broad peak), 88.73(broad peak), 125.39, 127.22, 127.55, 128.41, 131, 135.34, 142.52, 169.71ppm. HRMS (ESI) calcd for $C_{17}H_{14}F_3NO_2$ ($[M+H]^+$) m/z 322.0977, found 322.1058.



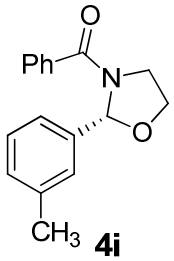
4g (*R*)-phenyl(2-(*p*-tolyl)oxazolidin-3-yl)methanone

The product was obtained by flash column chromatography as viscous oil(hexane : ethyl acetate, 1:1) 97% yield, 90% ee. HPLC Analysis: Chiralcel AD-H (hexane:iPrOH = 85:15, 1.0 mL/min), $t_{\text{r-major}}$ 13.32 min, $t_{\text{r-minor}}$ 17.56 min. $[\alpha]^{20}_{D}$= +104.3° (c =1.0, $CHCl_3$). ^{1}H NMR (400MHz, $CDCl_3$): δ 2.33(s, 3H), 3.50-4.50 (bm, 4H), 6.1 (bs, 1st rotamer), 6.5 (bs, 2nd rotamer), 7.0-7.9 (bm, 9H). ^{13}C NMR (400MHz, $CDCl_3$): δ 21.19, 48.35(broad peak), 66.57(broad peak), 89.35(broad peak), 126.59, 127.51, 128.25, 129.12, 130.63, 135.62, 135.86, 138.61, 169.45ppm. HRMS (ESI) calcd for $C_{17}H_{17}NO_2$ ($[M+H]^+$) m/z 268.1259, found 268.1336.



4h (R)-phenyl(2-(*o*-tolyl)oxazolidi-3-yl)methanone

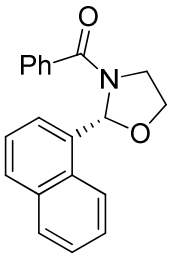
The product was obtained by flash column chromatography as viscous oil(hexane : ethyl acetate, 1:1) 98% yield, 96% ee. HPLC Analysis: Chiralcel AD-H (hexane:iPrOH = 80:20, 1.0 mL/min), $t_{r\text{-major}}$ 8.27 min, $t_{r\text{-minor}}$ 10.72 min. $[\alpha]^{20}_{D}$= +78.151° (c =1.8, $CHCl_3$). ^{1}H NMR (400MHz, $CDCl_3$): δ 2.0-2.7(bm, 3H), 3.50-4.50 (bm, 4H), 6.0-6.4 (bs, 1st rotamer), 6.4-6.8 (bs, 2nd rotamer), 7.0-7.9 (bm, 9H). ^{13}C NMR (400MHz, $CDCl_3$): δ 18.95, 45.17(broad peak, 1st rotomer), 48.95(broad peak, 2nd rotomer), 63.9(broad peak, 1st rotomer), 66.5(broad peak, 2nd rotomer), 88.02(broad peak), 125.85, 127.62, 128.28, 128.84, 130.95, 135.84, 136.88, 169.44 HRMS (ESI) calcd for $C_{17}H_{17}NO_2$ ($[M+H]^+$) m/z 268.1259, found 268.1336.



4i (R)-phenyl(2-(*m*-tolyl)oxazolidi-3-yl)methanone

The product was obtained by flash column chromatography as viscous oil(hexane : ethyl acetate, 1:1) 96% yield, 83% ee. HPLC Analysis: Chiralcel AD-H (hexane:iPrOH = 80:20, 1.0 mL/min), $t_{r\text{-major}}$ 7.60 min, $t_{r\text{-minor}}$ 10.03 min. $[\alpha]^{20}_{D}$= +103.7° (c =1.05, $CHCl_3$). ^{1}H NMR (400MHz, $CDCl_3$): δ 2.33(s, 3H), 3.50-4.50 (bm, 4H), 5.8-6.3 (bs, 1st rotamer), 6.3-6.75 (bs, 2nd rotamer), 7.0-7.9 (bm, 9H) ^{13}C NMR (400MHz, $CDCl_3$): δ 21.42, 48.38(broad peak), 66.62(broad peak), 89.39(broad peak),

123.67, 127.35, 128.26, 129.58, 135.82, 138.12, 138.46, 169.51. HRMS (ESI) calcd for $C_{17}H_{17}NO_2$ ([M+H]$^+$) m/z 268.1259, found 268.1329.



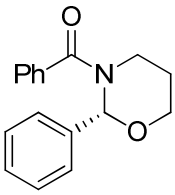
4j (R)-(2-(naphthalen-1-yl)oxazolidin-3-yl)(phenyl)methanone

The product was obtained by flash column chromatography as viscous oil(hexane : ethyl acetate, 1:1) 94% yield, 96% ee. HPLC Analysis: Chiralcel OD-H (hexane:iPrOH = 90:10, 1.0 mL/min), $t_{\text{r-minor}}$ 22.39 min, $t_{\text{r-major}}$ 32.33 min. $[\alpha]^{20}_D$= -3.75° (c =1.9, $CHCl_3$). ^{1}H NMR (400MHz, $CDCl_3$): δ 3.50-4.50 (bm, 4H), 6.4-6.8(bm, 1H), 7.25-8.0 (bm, 12H). ^{13}C NMR (400MHz, $CDCl_3$): δ(major rotamer) 48.63(broad peak), 66.44(broad peak), 89.12(broad peak), 124.07, 124.78, 125.95, 126.45, 128.37, 128.46, 128.62, 129.77, 130.79, 132.84, 134.13, 135.73, 170.01. HRMS (ESI) calcd for $C_{20}H_{17}NO_2$ ([M+H]$^+$) m/z 304.1259, found 304.1342.

General procedure for the synthesis of chiral 1,3-Oxazinanes:

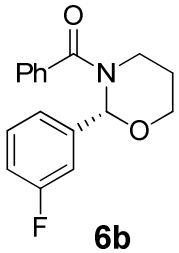
1,3-Oxazinanes were prepared according to the same procedure as described for the synthesis of chiral 1,3-Oxazolidines.

Analytical data:



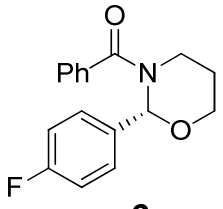
6a (R)-phenyl(2-phenyl-1,3-oxazinan-3-yl)methanone

The product was obtained by flash column chromatography as viscous oil(hexane : ethyl acetate, 1:1) 92% yield, 95% ee. HPLC Analysis: Chiralcel AD-H (hexane:iPrOH = 85:15, 1.0 mL/min), $t_{r\text{-major}}$ 8.68 min, $t_{r\text{-minor}}$ 14.71 min. $[\alpha]^{20}_{D}$= +133.75° (c =0.45, $CHCl_3$). ^{1}H NMR (400MHz, $CDCl_3$): δ 1.39-1.46(m, 1H), 1.9-2.2(m, 1H), 3.0-3.25(m, 1H), 3.7-3.9(m, 2H), 4.45(br, 1H), 6.5(br, 1H), 7.3-7.7(m, 10H). ^{13}C NMR (400MHz, $CDCl_3$): δ 25.95, 37.54(broad peak), 60.86, 84.10(broad peak), 126.98, 127.02, 128.26, 128.65, 129.14, 130.21, 135.29, 136.21, 171.59. HRMS (ESI) calcd for $C_{17}H_{17}NO_2$ ($[M+H]^+$) m/z 268.1332, found 268.1336.



6b (*R*)-(2-(3-fluorophenyl)-1,3-oxazinan-3-yl)(phenyl)methanone

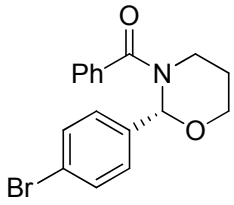
The product was obtained by flash column chromatography as viscous oil(hexane : ethyl acetate, 1:1) 93% yield, 95% ee. HPLC Analysis: Chiralcel AD-H (hexane:iPrOH = 85:15, 1.0 mL/min), $t_{r\text{-major}}$ 9.44 min, $t_{r\text{-minor}}$ 19.63 min. $[\alpha]^{20}_{D}$= +103.7° (c =1.8, $CHCl_3$). ^{1}H NMR (400MHz, $CDCl_3$): δ 1.36-1.48(m, 1H), 1.9-2.2(m, 1H), 3.0-3.25(m, 1H), 3.7-3.9(m, 2H), 4.45(br, 1H), 6.5(br, 1H), 7.3-7.7(m, 9H). ^{13}C NMR (400MHz, $CDCl_3$): δ 24.99, 37.33(broad peak), 60.02, 82.48(broad peak), 126.07, 127.65, 127.82, 128.47, 129.47, 133.42, 133.99, 134.20, 170.66. HRMS (ESI) calcd for $C_{17}H_{16}FNO_2$ ($[M+H]^+$) m/z 286.1165, found.



6c

(*R*)-(2-(4-fluorophenyl)-1,3-oxazinan-3-yl)(phenyl)methanone

The product was obtained by flash column chromatography as viscous oil(hexane : ethyl acetate, 1:1) 96% yield, 91% ee. HPLC Analysis: Chiralcel AD-H (hexane:iPrOH = 90:10, 1.0 mL/min), $t_{\text{r-major}}$ 12.40 min, $t_{\text{r-minor}}$ 21.65 min. $[\alpha]^{20}_{D}$= +91.09° (c =2.1, $CHCl_3$). ^{1}H NMR (400MHz, $CDCl_3$): δ 1.36-1.48(m, 1H), 1.9-2.2(m, 1H), 3.0-3.25(m, 1H), 3.7-3.9(m, 2H), 4.45(br, 1H), 6.5(br, 1H), 7.05-7.20(m, 2H), 7.3-7.6(m, 7H). ^{13}C NMR (400MHz, $CDCl_3$): δ 25.89, 38.17(broad peak), 60.75, 83.34(broad peak), 115.90, 116.25, 126.85, 127.01, 128.78, 130.30, 135.15, 160.70, 164.63, 171.53. HRMS (ESI) calcd for $C_{17}H_{16}FNO_2$ ($[M+H]^+$) m/z 286.1238, found 286.1246.

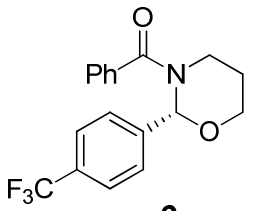


6d

(*R*)-(2-(4-bromophenyl)-1,3-oxazinan-3-yl)(phenyl)methanone

The product was obtained by flash column chromatography as viscous oil(hexane : ethyl acetate, 1:1) 91% yield, 89% ee. HPLC Analysis: Chiralcel AD-H (hexane:iPrOH = 85:15, 1.0 mL/min), $t_{\text{r-major}}$ 9.63 min, $t_{\text{r-minor}}$ 21.44 min. $[\alpha]^{20}_{D}$= +76.7° (c =0.9, $CHCl_3$). ^{1}H NMR (400MHz, $CDCl_3$): δ 1.35-1.5(m, 1H), 1.9-2.2(m, 1H), 3.0-3.25(m, 1H), 3.7-3.9(m, 2H), 4.45(br, 1H), 6.5(br, 1H), 7.3-7.6(m, 9H). ^{13}C NMR (400MHz,

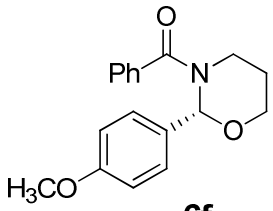
$CDCl_3$): δ 24.97, 37.17(broad peak), 60.03, 82.60(broad peak), 121.59, 126.05, 127.82, 127.97, 129.47, 131.43, 134.14, 134.52, 170.66. HRMS (ESI) calcd for $C_{17}H_{16}BrNO_2$ ($[M+H]^+$) m/z 346.0437, found 346.0442.



6e

(*R*)-phenyl(2-(4-(trifluoromethyl)phenyl)1,3-oxazinan-3-yl)methanone

The product was obtained by flash column chromatography as viscous oil(hexane : ethyl acetate, 1:1) 85% yield, 80% ee. HPLC Analysis: Chiralcel AD-H (hexane:iPrOH = 85:15, 1.0 mL/min), $t_{r\text{-major}}$ 7.33 min, $t_{r\text{-minor}}$ 16.07 min. $[\alpha]^{20}_D$= +86.46° (c =1.95, $CHCl_3$). ^{1}H NMR (400MHz, $CDCl_3$): δ 1.36-1.48(m, 1H), 1.9-2.2(m, 1H), 3.0-3.25(m, 1H), 3.7-3.9(m, 2H), 4.45(br, 1H), 6.5(br, 1H), 7.3-7.8(m, 9H). ^{13}C NMR (400MHz, $CDCl_3$): δ 25.75, 37.69(broad peak), 61.07, 83.54(broad peak), 122.58, 125.26, 126.11, 127.46, 134.86, 140.53, 171.59. HRMS (ESI) calcd for $C_{18}H_{16}F_3NO_2$ ($[M+H]^+$) m/z 336.1206, found 336.1217.



6f

(*R*)-(2-(4-methoxyphenyl)-1,3-oxazinan-3-yl)(phenyl)methanone

The product was obtained by flash column chromatography as viscous oil(hexane : ethyl acetate, 1:1) 85% yield, 80% ee. HPLC Analysis: Chiralcel AD-H (hexane:iPrOH = 85:15, 1.0 mL/min), $t_{r\text{-major}}$ 10.71 min, $t_{r\text{-minor}}$ 23.20 min. $[\alpha]^{20}_D$= +100.48° (c =0.45, $CHCl_3$). ^{1}H NMR (400MHz,

$CDCl_3$): δ 1.36-1.48(m, 1H), 1.9-2.2(m, 1H), 3.0-3.25(m, 1H), 3.4-3.9(m, 5H), 4.45(br, 1H), 6.5(br, 1H), 6.7-7.0(m, 2H), 7.3-7.9(m, 7H). ^{13}C NMR (400MHz, $CDCl_3$): δ 25.98, 37.84(broad peak), 55.37, 60.60, 84.13(broad peak), 114.49, 126.96, 127.97, 128.30, 128.62, 135.34, 159.58, 171.50. HRMS (ESI) calcd for $C_{18}H_{19}NO_3$ ($[M+H]^+$) m/z 298.1438, found 298.1454.

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