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Supporting Information

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Modulable C_2 Symmetric Analogues of NHPI as Enantioselective Catalysts for Aerobic Oxidation: Kinetic Resolution of Oxazolidines

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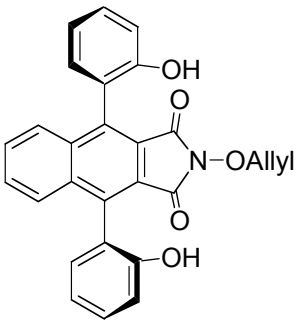
1- Synthesis of the precatalysts **4a** and **4b**

Synthesis of (*aS*,*aS*)-**4a**



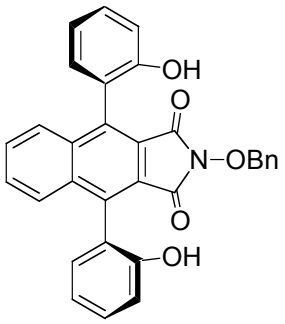
4a

To a suspension of (*aS*,*aS*)-**1**•1/2AcOEt[1] (1.33 g, 3.14 mmol) in anhydrous acetonitrile (30 mL) at room temperature, were added di-*tert*-butyl dicarbonate (Boc_2O, 2.3 g, 10.5 mmol), followed by DMAP (38 mg, 10 mol %). After 30 min (TLC indicated no remaining starting material), 0.23 mL of an aqueous solution of hydroxylamine (50 wt %, 3.6 mmol) was added, the mixture was stirred overnight at room temperature and concentrated under reduced pressure, giving crude **3**. Crude **3** was dissolved in 30 mL of acetone, K_2CO_3 (0.953 g, 2.2 equiv) was added, followed by allyl bromide (0.570 mL, 2.1 equiv). The reaction mixture was stirred for 6 h then filtered, the solvent was evaporated under reduced pressure and the residue was crystallized by stirring at room temperature in hexane/AcOEt, 9:1 overnight. After filtration and drying, a white solid (2.2 g) was obtained. The solid was dissolved in CH_2Cl_2 (10 mL), TFA (5 mL) was added dropwise at 0 °C (during the addition temperature raised to 25 °C), and the reaction was stirred for 2 h at RT. After completion of the reaction (TLC monitoring), the solvent was removed under reduced pressure. Flash chromatography (elution: hexane/Et_2O, 4:1) gave (*aS*,*aS*)-**4a** as a solid 1:1 ether solvate (1.44 g, 90 % yield from diphenol **1**). R_f 0.21 (hexane/AcOEt 2:1); m.p. 179-180 °C (from AcOEt); $[\alpha]_D^{25}$ = +111 (*c* = 1 in $CHCl_3$); ^{1}H NMR (300 MHz, [D_6] DMSO): δ = 4.59 (d, 2H, *J* = 6.5 Hz), 5.31-5.38 (m, 2H), 5.90-6.10 (m, 1H), 6.98-7.67 (m, 12H), 9.44 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 78.65, 116.45, 120.61, 121.25, 121.53, 122.18, 128.66, 129.43, 130.46, 131.13, 131.31, 135.75, 136.41, 153.69, 163.10 ppm; IR (ATR): $\tilde{\nu}$ = 3359, 3069, 2924, 2839, 1767, 1711, 1590, 1502, 1448, 1372, 1286, 1222, 1143, 1103, 1046, 1019, 943, 840, 744 cm^{-1}; MS (ESI$^+$): *m/z* (%): 476 (72) [*M*+39]$^+$, 460 (100) [*M*+23]$^+$, 438 (24) [*M*+H]$^+$; Anal. (determined on the ether solvate) calcd for $C_{31}H_{29}NO_6$: C, 72.78; H, 5.71; N, 2.74. Found: C, 72.39; H, 5.26, N, 2.9; HRMS (*M*H$^+$, ESI): *m/z* calcd for $C_{27}H_{20}NO_5$: 438.1336. Found: 438.1334.

Synthesis of (*aS*,*aS*)-**4b**

Crude **3**, prepared as described previously from (*aS*,*aS*)-**1**•1/2AcOEt[1] (1.57 g, 3.69 mmol), was dissolved in 30 mL of DMSO. K_2CO_3 (1.54 g, 3 equiv) was added, followed by benzyl

bromide (0.460 mL, 1.05 equiv), the reaction mixture was stirred for 2 h at RT, then poured into water (30 mL) and extracted with AcOEt (3 x 30 mL). The organic layer was washed with water (2 x 30 mL) and brine (30 mL) and dried over anhydrous sodium sulfate. After evaporation of the solvent at reduced pressure, the residue was dissolved in CH_2Cl_2 (10 mL), TFA (5 mL) was added drop wise at 0 °C (the temperature raised to 25 °C during addition) and the reaction was stirred overnight at RT. After completion of the reaction (TLC monitoring), the solvent was removed under reduced pressure. Flash chromatography (eluent: hexane/AcOEt, 2:1) afforded (*aS*,*aS*)-**4b**, which was stirred overnight in a hexane/AcOEt/DMSO 80:15:5 mixture, funishing a crystalline (*aS*,*aS*)-**4b**•DMSO 1:1 solvate (1.93 g, 88 % yield from diphenol **1**),.



4b

R_f 0.35 (CH_2Cl_2/AcOEt, 95:5); m.p. 194-195 °C (from DMSO); $[\alpha]_D^{25}$ = +107 (*c* = 0.85 in $CHCl_3$); ^{1}H NMR (300 MHz, [D_6] DMSO) δ = 5.05-5.13 (m, 2H), 6.96-7.68 (m, 17H), 9.48 ppm (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS) δ = 79.9, 115.57, 118.85, 121.20, 121.29, 128.04, 128.41, 128.93, 128.99, 129.41, 129.72, 131.07, 134.10, 134.83, 136.47, 154.97, 161.58 ppm; IR (ATR): $\tilde{\nu}$ = 3148, 2868, 2712, 1771, 1726, 1597, 1517, 1490, 1449, 1378, 1285, 1222, 1141, 1101, 1047, 1020, 988, 942, 837, 742, 700 cm^{-1}; MS (ESI$^+$): *m/z* (%): 505 (100) [*M*+18]$^+$, 488 (50) [*M*+H]$^+$; Anal. (determined on the DMSO solvate) calcd for $C_{33}H_{27}NO_6S$: C, 70.07; H, 4.81; N, 2.48. Found: C, 70.09; H, 4.86; N, 2.67; HRMS (*M*H$^+$, ESI): *m/z* calcd for $C_{31}H_{22}NO_5$: 488.1492. Found: 488.1480.

2- Synthesis of the catalysts

General procedure for allyl deprotection (Method A)

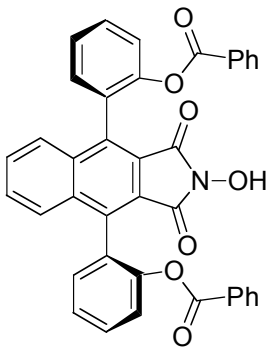
To a solution of *O*-allyl protected *N*-hydroxyimide (0.1 mmol) in CH_2Cl_2 (0.5 mL) was added sodium 2-ethylhexanoate (0.3 mL of a 0.5 M solution in AcOEt, 1.5 equiv), followed by PPh_3 (6 mg, 10 mol %) and tetrakis(triphenylphosphine)palladium(0) (2.5 mg, 2 mol %). The mixture was stirred for 1 h at RT, then 2 mL of acetone was added and the red precipitate formed was filtered. To this precipitate was added acetic acid (1 mL of a 0.1 M aqueous solution) and the aqueous phase was extracted with AcOEt. The organic phase was dried over anhydrous Na_2SO_4 and the solvent removed under vacuum. Pure product was obtained without further purification. Alternatively, if no precipitation occurs after the addition of acetone, acetic acid (2 mL of a 0.1 M aqueous solution) was added to the reaction medium, which was next extracted with AcOEt. The organic phase was dried over Na_2SO_4 and the solvent removed under vacuum. The crude product was purified by column chromatography over silica gel.

General procedure for benzyl deprotection (Method B)

To a solution of *O*-benzyl protected *N*-hydroxyimide (0.1 mmol) in AcOEt (5 mL) was added 10 wt % palladium on carbon (25 mg). The mixture was stirred at room temperature and normal pressure under an hydrogen atmosphere (balloon) until completion (TLC monitoring). The catalyst was removed by filtration over Celite and the solvent was removed under vacuum. Concentration of the filtrate afforded the crude product, which was used with no more purification or purified by flash column chromatography.

Diester (*aS*,*aS*)-**5a**

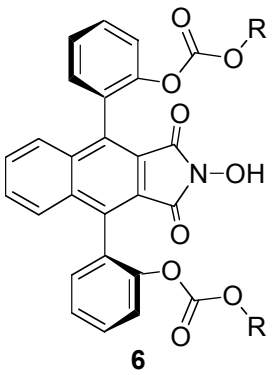
To a solution of (*aS*,*aS*)-**4b**•DMSO (30.3 mg, 0.05 mmol), triethylamine (0.25 mL, 0.11 mmol) and DMAP (1.2 mg, 20 mol %) in anhydrous dichloromethane (3 mL), was added dropwise benzoyl chloride (13 μL, 0.11 mmol, 2.2 equiv). The reaction mixture was stirred for a few minutes at room temperature until completion of the reaction (TLC monitoring). The solvent was removed under reduced pressure, the residue was purified by flash column chromatography (elution CH_2Cl_2/AcOEt, 99:1). From the resulting white solid (33 mg), 20 mg were subjected to debenzylation by general method B, affording (*aS*,*aS*)-**5a** as a white powder (15 mg, 80 %



5a

overall yield). R_f 0.3 (CH_2Cl_2/AcOEt, 4:1); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 7.17-7.22 (m, 6H), 7.37-7.48 (m, 6H), 7.52-7.63 (m, 8H), 7.75-7.80 ppm (m, 2H);[2] ^{13}C NMR (75 MHz, $CDCl_3$): δ = 121.53, 122.93, 124.63, 125.95, 127.36, 128.48, 128.93, 129.48, 129.81, 130.43, 131.51, 133.58, 135.07, 135.27, 149.18, 162.01, 164.60 ppm; MS (ESI^+): *m/z* (%): 644 (46) $[M+39]^+$, 628 (100) $[M+23]^+$. HRMS (MNa^+, ESI): *m/z* calcd for $C_{38}H_{23}NO_7Na$: 628.1366. Found: 628.1361.

Dicarbonate (*aS*,*aS*)-**6a**

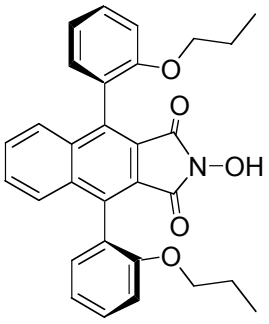

6

To a well-stirred solution of (*aS*,*aS*)-**4a**•Et_2O (46 mg, 0.09 mmol), triethylamine (0.5 mL, 0.22 mmol) and DMAP (0.55 mg, 5 mol %), in anhydrous dichloromethane (3 mL) at 0 °C, was added methyl chloroformate (17 μL, 0.22 mmol). The reaction mixture was stirred for a few minutes at room temperature until completion of the reaction (TLC monitoring). It was next washed with water and extracted with CH_2Cl_2. The organic phase was dried over anhydrous Na_2SO_4 then evaporated under reduced pressure. The crude was deallylated using general procedure A, affording (*aS*,*aS*)-**6a** (R = Me) as a yellow powder (36 mg, 78 % overall yield). R_f 0.22 (CH_2Cl_2/AcOEt 4:1); $[\alpha]_D^{25}$ = +23.4 (*c* = 0.7 in THF); ^{1}H NMR (300 MHz, [D_6] DMSO): δ = 3.47 (s, 6H), 7.48-7.71 (m, 12H). 10.8 ppm (bs, 1H); ^{13}C NMR (75 MHz, [D_6] DMSO): δ = 55.30, 121.72, 122.16, 126.02, 126.57, 127.56, 129.38, 130.19, 131.66, 133.21, 134.10, 148.59, 152.69, 162.00 ppm; MS (DCI^+, NH_3 + isobutane): *m/z* (%): 531 (100) $[M+18]^+$, 264 (30).

Dicarbonate (*aS*,*aS*)-**6b**

The same procedure used for the synthesis of (*aS*,*aS*)-**6a**, replacing methyl chloroformate by phenyl chloroformate (32.5 μL, 0.22 mmol, 2.4 equiv), gave (*aS*,*aS*)-**6b** (R = Ph) as a yellow powder **(**45 mg, 78 % overall yield). R_f 0.22 (CH_2Cl_2/AcOEt, 4:1); $[\alpha]_D^{25}$ = +24.2 (*c* = 0.45 in THF); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 6.67 (m, 4H), 7.41-7.81 ppm (m, 19H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 120.61, 121.96, 122.31, 126.37, 126.54, 128.46, 129.51, 129.72, 130.68, 131.67, 134.60, 135.11, 149.02, 150.77, 151.16, 158.86, 161.85 ppm; MS (ESI^+): *m/z* (%): 676 (57) $[M+39]^+$, 660 (100) $[M+23]^+$, 638 (20) $[M+H]^+$.

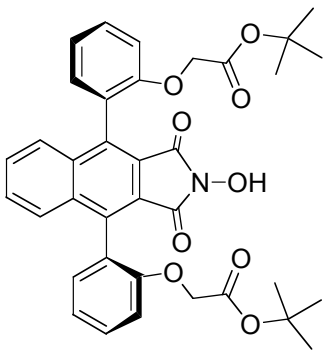
Diether (*aS*,*aS*)-**7a**



7a

Diphenol (*aS*,*aS*)-**4b**•DMSO (24.3 mg, 0.041 mmol) was dissolved in DMSO (2 mL). K_2CO_3 (170 mg, 30 equiv) was added, followed by allyl bromide (8 µL, 2.2 equiv), the reaction was stirred for 6 h at RT, then filtered. To the filtrate was added water (20 mL) and the mixture was extracted with AcOEt. After drying of the organic phase with Na_2SO_4, the solvent was evaporated and the residue was purified on a silica gel column to afford 13 mg of product. After debenzylation according to general method B, (*aS*,*aS*)-**7a** has been obtained as a yellow amourphous solid (9 mg, 46 % overall yield). R_f 0.25 (CH_2Cl_2/AcOEt, 4:1); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.56-0.64 (m, 6H), 1.42-1.48 (m, 4H), 3.82-3.90 (m, 4H), 7.05-7.79 ppm (m, 13H); MS (ESI$^+$): *m/z* (%): 520 (99) [*M*+39]$^+$, 504 (100) [*M*+23]$^+$, 482 (22) [*M*+H]$^+$. HRMS (*M*Na$^+$, ESI): *m/z* calcd for $C_{30}H_{27}NO_5Na$: 504.1781. Found: 504.1777.

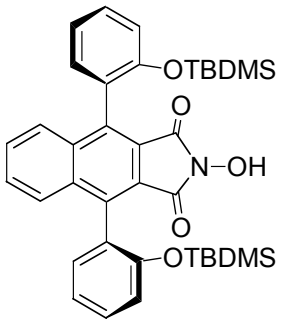
Diether (*aS*,*aS*)-**7b**



7b

Diphenol (*aS*,*aS*)-**4b**•DMSO (243 mg, 0.41 mmol,) was dissolved in acetone (15 mL). K_2CO_3 (1.7 g, 30 equiv) was added, followed by bromo-*tert*-butylacetate (0.466 mL, 3.2 mmol), the reaction mixture was stirred overnight at RT. After filtration of solids, the reaction mixture was poured into water (50 mL), extracted with AcOEt and dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum and the residue was purified on a silica gel column (eluent: hexane/AcOEt, 2:1), affording 240 mg of a white solid. Debenzylation of 40 mg of this compound has been performed according to general method B. Catalyst (*aS*,*aS*)-**7b** has been obtained as a yellowish solid (34 mg, 80 % overall yield). R_f 0.35 (CH_2Cl_2/AcOEt, 4:1); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.37 (s, 18H), 4.38-4.45 (m, 4H), 6.90-7.86 ppm (m, 13H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 28.17, 66.62, 82.18, 112.27, 121.35, 121.71, 124.03, 128.44, 128.79, 130.22, 131.68, 135.99, 156.18, 156.23, 162.66, 167.90 ppm; IR (ATR): $\tilde{\nu}$ = 3442, 2953, 1772, 1718, 1635, 1500, 1420, 1370, 1218, 1154, 1103, 1042, 1022, 996, 744 cm^{-1}; MS (ESI$^+$): *m/z* (%): 664 (61) [*M*+39]$^+$, 648 (100) [*M*+23]$^+$. HRMS (*M*Na$^+$, ESI): *m/z* calcd for $C_{36}H_{35}NO_9Na$: 648.2204. Found: 648.2201.

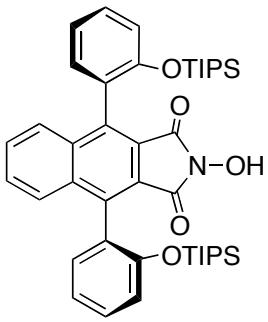
Disilylether (*aS*,*aS*)-**8a**



8a

To a solution of (*aS*,*aS*)-**4b**•DMSO (170 mg, 0.287 mmol) in anhydrous THF (3 mL), was added TBDMSCl (216 mg, 1.43 mmol) and imidazole (100 mg, 1.43 mmol). The mixture was stirred at room temperature overnight, then water (250 mL) was added and the mixture was extracted with 200 mL of AcOEt. The organic layer was separated, washed with brine (250 mL), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (elution hexane/AcOEt, 9:1) to give 200 mg of a white solid. Debenzylation of 110 mg of this compound has been performed according to general method B, affording catalyst (*aS*,*aS*)-**8a** as a white solid (95 mg, 97 % overall yield). R_f 0.27 (Hexane/AcOEt, 4:1); m.p. 223-224 °C; $[\alpha]^{25}_D$ = +18.5 (*c* = 1 in MeOH): ^{1}H NMR (300 MHz, DMSO [D_6], TMS): δ = -0.06 (s, 6H), -0.05 (s, 6H), 0.33 (s, 18H), 7.03-7.66 (m, 12H), 10.74 ppm (s, 1H); ^{13}C NMR (75 MHz, [D_6] DMSO, TMS): δ = -4.9, -4.65, 17.04, 24.55, 118.87, 121.17, 121.37, 126.07, 127.73, 128.87, 130.04, 130.82, 134.67, 135.93, 152.63, 162.36 ppm; IR (ATR): $\tilde{\nu}$ = 3129, 3064, 2925, 2852, 1776, 1707, 1598, 1577, 1489, 1452, 1365, 1277, 1249, 1145, 1103, 1051, 1024, 915, 835, 747 cm^{-1}; MS (ESI$^+$) *m/z* (%): 727 (100), 664 (78) [*M*+39]$^+$, 648 (95) [*M*+23]$^+$, 626 (48) [*M*+1]$^+$, 550 (35), 534 (32); HRMS (*M*H$^+$, ESI): *m/z* calcd for $C_{36}H_{44}NO_5Si_2$: 626.2752. Found: 626.2731.

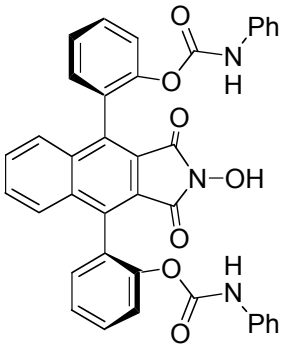
Disilylether (*aS*,*aS*)-**8b**



8b

The same procedure as above was used, starting from (*aS*,*aS*)-**4b**•DMSO (116 mg, 0.197 mmol) and replacing TBSCl by TIPSCl (193 mg, 1 mmol). Catalyst (*aS*,*aS*)-**8b** was obtained as a white solid (70 mg, 50 % overall yield). R_f 0.29 (Hexane/AcOEt, 4:1); m.p. 193-195 °C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.72-0.76 (m, 36H), 0.94-1.04 (m, 6H), 6.97- 7.75 ppm (m, 13H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 12.77, 17.74, 118.34, 120.70, 121.34, 125.69, 128.68, 128.73, 130.15, 131.22, 135.57, 138.01, 153.62, 162.18 ppm; IR (ATR): $\tilde{\nu}$ = 3432, 3067, 2941, 2864, 1773, 1730, 1597, 1575, 1491, 1453, 1366, 1281, 1256, 1140, 1104, 1047, 1019, 918, 881, 826, 740 cm^{-1}; MS (ESI$^+$): *m/z* (%): 749 (100) [*M*+39]$^+$, 733 (95) [*M*+23]$^+$; HRMS (*M*H$^+$, ESI): *m/z* calcd for $C_{42}H_{56}NO_5Si_2$: 710.3691. Found: 710.3696.

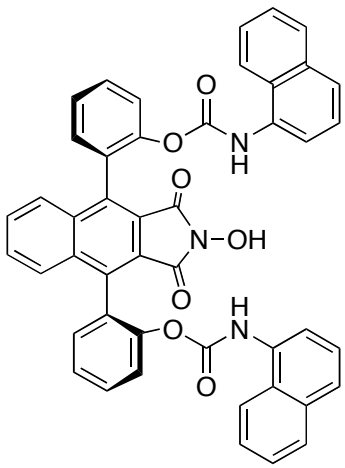
Dicarbamate (*aS*,*aS*)-**9a**



9a

To a solution of (*aS*,*aS*)-**4b**•DMSO (52.2 mg, 0.088 mmol) in anhydrous dichloromethane (2 mL) was added DMAP (4.3 mg, 40 mol %) and phenylisocyanate (23.4 μL, 0.22 mmol, 2.5 equiv). The reaction mixture was stirred at room temperature until completion of the reaction (1 day, TLC monitoring). The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (elution CH_2Cl_2/AcOEt, 98:2), giving 58 mg of a white solid. Debenzylation of 45 mg of this compound was performed using general procedure B, affording (*aS*,*aS*)-**9a** as a white solid (36.5 mg, 84 % overall yield). R_f 0.20 (CH_2Cl_2/AcOEt, 4:1); m.p. 165-166 °C; $[\alpha]_D^{25}$ = +200 (*c* = 0.85 in $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 6.95-7.57 (m, 23H) 7.80 ppm (bs, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 118.94, 121.54, 122.68, 123.77, 125.52, 127.35, 128.71, 128.89, 129.69, 130.12, 131.56, 133.84, 135.28, 137.39, 148.78, 152.37, 162.18 ppm; IR (ATR): $\tilde{\nu}$ = 3372, 2912, 1771, 1717, 1594, 1539, 1449, 1378, 1316, 1194, 1048, 1020, 825, 780 cm^{-1}; MS (ESI$^+$): *m/z* (%): 674 (100) [*M*+39]$^+$, 658 (75) [*M* +23]$^+$; HRMS (*M*Na$^+$, ESI): *m/z* calcd for $C_{38}H_{25}N_3O_7Na$: 658.1584. Found: 658.1582.

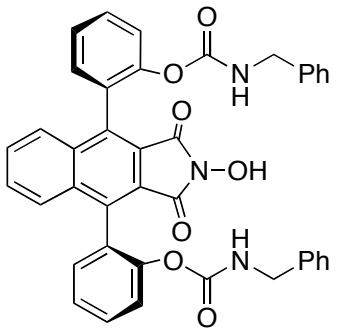
Dicarbamate (*aS*,*aS*)-**9b**



9b

The same procedure as for the synthesis of (*aS*,*aS*)-**9a** was followed, starting from (*aS*,*aS*)-**4b**•DMSO (85.4 mg, 0.144 mmol) and replacing phenylisocyanate by 1-naphthylisocyanate (43 μL, 0.3 mmol). Catalyst (*aS*,*aS*)-**9b** was obtained as a yellow solid (33 mg, 31 % overall yield). R_f 0.26 (CH_2Cl_2/AcOEt 4:1); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 7.05-7.83 ppm (m, 27H); IR (ATR): $\tilde{\nu}$ = 3446, 3059 2910, 1772, 1717, 1540, 1488, 1215, 1193, 1051, 1021 cm^{-1}; MS (ESI$^+$) *m/z* (%): 775 (60.7) [*M*+39]$^+$, 758 (100) [*M*+23]$^+$; HRMS (*M*Na$^+$, ESI): *m/z* calcd for $C_{46}H_{29}N_3O_7Na$: 758.1897. Found: 758.1894.

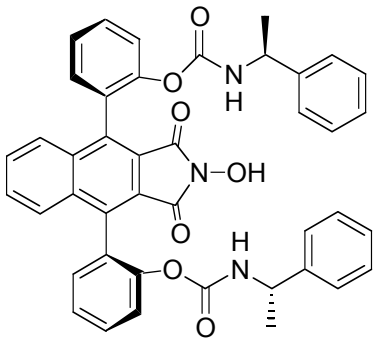
Dicarbamate (*aS*,*aS*)-**9c**



9c

The same procedure as for the synthesis of (*aS*,*aS*)-**9a** was followed, starting from (*aS*,*aS*)-**4a**•Et_2O (51 mg, 0.1 mmol) and replacing phenylisocyanate by benzylisocyanate (0.27 µL, 0.22 mmol). Deallylation by general procedure A gave catalyst (*aS*,*aS*)-**9c** as a yellow powder (45 mg, 68 % overall yield). R_f 0.22 (CH_2Cl_2/AcOEt, 4:1); m.p. 130-131°C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.60-4.10 (m, 4H), 5.85 (bs, 1H), 6.74-7.70 ppm (m, 24H); IR (ATR): $\tilde{\nu}$ = 3339, 2922, 1773, 1721, 1599, 1539, 1486, 1451 1384, 1217, 1198 cm^{-1}; MS (DCI$^+$, NH_3+ isobutane): *m/z* (%): 681 (42) [*M*+18]$^+$, 548 (100), 414 (55), 315 (64); HRMS (*M*Na$^+$, ESI): *m/z* calcd for $C_{40}H_{29}N_3O_7Na$: 686.1897. Found: 686.1892.

Dicarbamate (*aS*,*aS*,*S*,*S*)-**9d**



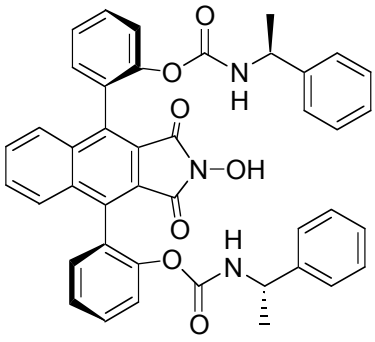
9d

The same procedure as for the synthesis of (*aS*,*aS*)-**9a** was followed, starting from (*aS*,*aS*)-**4b**•DMSO (118 mg, 0.199 mmol) and replacing phenylisocyanate by (*S*)-1-phenylethylisocyanate (61 µL, 0.44 mmol). Catalyst (*aS*,*aS*)-**9d** was obtained as a white powder (132 mg, 96 % overall yield). R_f 0.27 (CH_2Cl_2/AcOEt 4:1); m.p. 136-137°C; $[\alpha]_D^{25}$ = -30.8 (c = 1 in $CHCl_3$); ^{1}H NMR (300 MHz, [D_6] DMSO, TMS): δ = 1.19 (d, 6H, *J* = 7.02 Hz), 4.39-4.44 (m, 2H), 6.71-7.74 (m, 24H), 10.83 ppm (bs, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 21.87, 50.45, 121.22, 122.56, 123.04, 125.25, 125.66, 127.06, 127.46, 128.46, 129.5, 130.04, 131.56, 134.90, 135.62, 142.83, 149.02, 153.22, 163.12 ppm ; IR (ATR): $\tilde{\nu}$ = 3322, 3063, 2972, 2927, 1771, 1712, 1602, 1519, 1485, 1444, 1363, 1214, 1194, 1147, 1100, 1068, 1050, 1021, 955, 906 cm^{-1}; MS (ESI$^-$) *m/z* (%): 764 (13), 730 (57) [*M*+39]$^+$, 714 (100) [*M*+23]$^+$; Anal. calcd for $C_{42}H_{35}N_3O_8$ (H_2O solvate): C, 71.07; H, 4.97; N, 5.92. Found: C, 71.73; H, 5.07; N, 5.91; HRMS (*M*Na$^+$, ESI): *m/z* calcd for $C_{42}H_{33}N_3O_7Na$: 714.2210. Found: 714.2204.

Dicarbamate (*aR*,*aR*,*S*,*S*)-**9e**

To a solution of (*aS*,*aS*)-**4a**•Et_2O (prepared from (*aR*,*aR*)-**1)** (78.2 mg, 0.153 mmol) in anhydrous dichloromethane (4 mL) was added DMAP (14.3 mg, 80 mol %) and (*S*)-1-

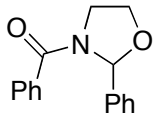
phenylethylisocyanate (46 µL, 0.33 mmol). The reaction mixture was stirred at room temperature until completion of the reaction (about 1 day, TLC monitoring). The solvent was removed under reduced pressure. The residue was purified by flash column chromatography (elution CH_2Cl_2/AcOEt, 98:2), giving 99 mg of a white solid. Deallylation of 40 mg of this compound was performed using general procedure A, affording catalyst (*aR*,*aR*,*S*,*S*)-**9e** as a yellow solid (36 mg, 84 % overall yield). R_f 0.27 (CH_2Cl_2/AcOEt 4:1); m.p. 131-132°C; $[\alpha]_D^{25}$ = -84 (c = 0.5 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.94 (d, 6H), 4.50 (m, 2H), 6.82 (bs, 2H), 7.09-7.81 (m, 24H), 8.45 ppm (bs, 1H); IR (ATR): $\tilde{\nu}$ = 3322, 3063, 2972, 2927, 1771, 1712, 1602, 1519, 1485, 1444, 1363, 1214, 1194, 1147, 1100, 1068, 1050, 1021, 955, 906 cm^{-1}; MS (ESI$^-$) *m/z* (%): 764 (13), 730 (57) $[M+39]^+$, 714 (100) $[M+23]^+$.



9e

3- Synthesis of the oxazolidines

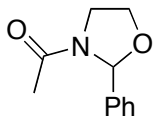
Oxazolidine (±)-**10a**[3]



10a

A solution of benzaldehyde (3.4 mL, 33 mmol) and ethanolamine (2.1 mL, 35 mmol) in toluene (200 mL) was refluxed in a Dean-Stark apparatus for 6 h. The solvent was evaporated giving the crude imine as a yellow oil (4.62 g, 94 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.94 (bs, 1H), 3.72 (t, 2H, J=5.1 Hz), 3.89 (t, 2H, J=5.1 Hz), 7.37-7.39 (m, 3H), 7.66-7.69 (m, 2H), 8.26 ppm (s, 1H). ^{13}C NMR (75Mhz, $CDCl_3$): δ = 62.31, 63.45, 128.28, 128.66, 130.90, 135.89, 163.29 ppm. To the stirred solution of imine (1.38 g, 9.2 mmol) in AcOEt (50 mL) was added pyridine (1.56 g, 20 mmol) and benzoyl chloride (1.4 g, 10 mmol). The solution was allowed to stir for 2.5 h at RT, then filtered and the solvent removed at reduced pressure. Flash chromatography of the crude afforded pure (±)-**10a (**2 g, 87 %) as a viscous oil. R_f 0.55 (hexane/AcOEt, 1:1); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.80-4.15 (bm, 4H), 6.47 (bs, 1H), 7.34-7.50 ppm (bm, 10H); ^{1}H NMR (300 MHz, [D_6] DMSO, TMS, 80 °C): δ = 3.76-4.16 (m, 4H), 6.50 (s, 1H), 7.32-7.40 ppm (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 48.48 (broad peak), 66.7 (broad peak), 89.54 (broad peak), 126.80, 127.59, 128.41, 128.91, 130.09, 130.80, 135.92, 138.69, 169.73 ppm; IR (KBr disk): $\tilde{\nu}$ = 3506, 3061, 3034, 2985, 2943, 2886, 1717, 1640, 1578, 1491, 1448, 1406, 1368, 1218, 1194, 1067, 1027, 938, 946, 784, 756, 718, 698 cm^{-1}; MS (DCI, NH_3 + isobutane) m/z = 254 (100) $[M+1]^+$, 149 (13); Anal. calcd for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.86; H, 6.04; N, 5.47.

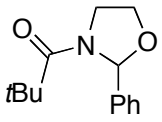
Oxazolidine (±)-**10b**



10b

The same procedure as for (±)-**10a** was used, replacing benzoyl chloride by acetyl chloride (776 µL, 10 mmol), furnishing (±)-**10b** as a yellow liquid (1.52 g, 80 % yield). R_f 0.36 (hexane/AcOEt, 1:1); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.85 (s, 1.7H, 1st rotamer) 2.16 (s, 1.3H, 2nd rotamer), 3.62-4.15 (m, 4H), 6.07 (s, 0.42H, 1st rotamer), 6.38 (s, 0.58H, 2nd rotamer), 7.30-7.41 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ (major rotamer) = 22.64, 45.83, 64.69, 89.55, 126.47, 128.70, 129.41, 132.93, 168.14 ppm; IR (KBr disk): $\tilde{\nu}$ = 3315, 3064, 3034, 2955, 2888, 1718, 1652, 1558, 1450, 1419, 1370, 1273, 1238, 1177, 1087, 1049, 1027, 989, 945, 759, 716, 619 cm^{-1}; MS (DCI$^+$, NH_3 + isobutane) *m/z* = 192 (100) $[M+1]^+$, 150 (12).

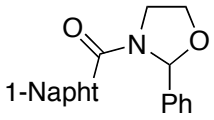
Oxazolidine (±)-**10c**



10c

The same procedure as for (±)-**10a** was used, replacing benzoyl chloride by pivaloyl chloride (123 µL, 1 mmol), furnishing (±)-**10c** as a colorless liquid (175 mg, 75 % yield). R_f 0.40 (hexane/AcOEt, 1:1); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.24 (s, 9H), 3.63-3.73 (m, 1H), 3.92-4.04 (m, 3H), 6.35 (s, 1H), 7.24-7.35 ppm (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 26.95, 38.76, 45.78, 65.70, 90.10, 126.05, 127.94, 128.05, 138.88, 175.35 ppm; IR (KBr disk): $\tilde{\nu}$ = 3373, 3055, 3033, 2967, 2877, 1720, 1632, 1529, 1480, 1407, 1363, 1208, 1159, 1071, 1028, 938, 950, 757, 699 cm^{-1}; MS (DCI$^+$, NH_3 + isobutane) *m/z* = 234 (100) $[M+1]^+$, 128 (7).

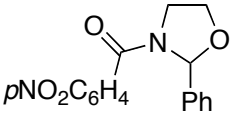
Oxazolidine (±)-**10d**



10d

The same procedure as for (±)-**10a** was used, replacing benzoyl chloride by 1-naphthoyl chloride (190 mg, 1 mmol), furnishing (±)-**10d** as an amorphous solid (209 mg, 69 % yield). R_f 0.49 (hexane/AcOEt, 1:1); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.87-4.16 (bm, 4H), 5.70 (bs, 1H), 7.41-7.60 ppm (bm, 12H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 47.09, 66.17, 88.98, 124.49, 125.40, 126.47, 126.60, 127.21, 128.04, 128.48, 128.77, 129.53, 129.89, 133.50, 134.00, 138.81, 168.82 ppm; IR (ATR): $\tilde{\nu}$ = 3290, 3055, 2944, 2884, 1714, 1633, 1585, 1508, 1461, 1418, 1365, 1215, 1176, 1064, 912, 782, 754, 698 cm^{-1}; MS (DCI$^+$, NH_3 + isobutane) *m/z* = 321 (20) $[M+18]^+$, 304 (100) $[M+1]^+$, 155 (5).

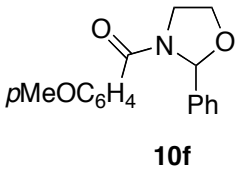
Oxazolidine (±)-**10e**



10e

The same procedure as for (±)-**10a** was used, replacing benzoyl chloride by *p*-nitrobenzoyl chloride (1.85 g, 10 mmol), furnishing (±)-**10e** as a white solid (2.29 g, 77 % yield). R_f 0.40 (hexane/AcOEt, 1:1); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.65-4.22 (bm, 4H), 5.97 (bs, 0.4H, 1st rotamer), 6.5 (bs, 0.6H, 2nd rotamer), 7.35-8.3 ppm (bm, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 123.76, 126.85, 128.75, 129.37, 167.38 ppm;[4] IR (ATR): $\tilde{\nu}$ = 3111, 3070, 2935, 2894, 1617, 1638, 1597, 1351 cm^{-1}; MS (DCI$^+$, NH_3 + isobutane) *m/z* = 298 (100) $[M]^+$, 193 (10), 150 (7).

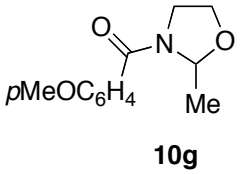
Oxazolidine (±)-**10f**



10f

The same procedure as for (±)-**10a** was used, replacing benzoyl chloride by *p*-methoxybenzoyl chloride (1.35 mL, 10 mmol), furnishing (±)-**10f** as a white solid (1.86 g, 66 % yield). R_f 0.40 (hexane/AcOEt, 1:1); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.78-4.14 (bm, 4H), 3.82 (s, 3H), 6.44 (bs, 1H), 6.86 (bd, 2H), 7.35-7.55 ppm (bm, 7H); IR (ATR): $\tilde{\nu}$ = 3072, 2951, 2880, 1621, 1605, 1571 cm^{-1}; MS (DCI$^+$, NH_3 + isobutane) *m/z* = 283 (100) $[M]^+$, 135 (7); Anal. calcd for $C_{17}H_{17}NO_3$: C, 72.02; H, 6.05; N, 4.95. Found: C, 70.22; H, 6.11; N, 5.05.

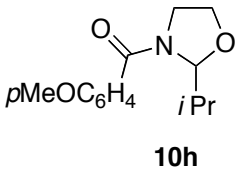
Oxazolidine (±)-**10g**



10g

The same procedure as for (±)-**10a** was used, replacing benzaldehyde and benzoyl chloride by acetaldehyde (170 µL, 3 mmol) and *p*-methoxybenzoyl chloride (400 µL, 3 mmol), furnishing (±)-**10g** as a colorless liquid (265 mg, 40 % yield). R_f 0.33 (hexane/AcOEt, 1:1); ^{1}H NMR (300 MHz, [D_6] DMSO, TMS): δ = 1.37 (d, 3H, *J* = 5.4 Hz), 3.38-4.09 (m, 4H), 3.81 (s, 3H), 5.39 (q, 1H, *J* = 5.4 Hz), 6.99 (d, 2H), 7.57 ppm (d, 2H); IR (ATR): $\tilde{\nu}$ = 3067, 2993, 2939, 2882, 2848, 1620, 1604, 1570, 1510, 1419, 1400, 1372, 1302, 1249, 1216, 1184, 1113, 1059, 1015, 967, 884, 844, 762 cm^{-1}; MS (DCI$^+$, NH_3 + isobutane) *m/z* = 222 (100) $[M+1]^+$, 135 (5).

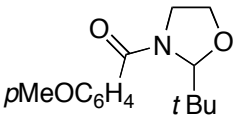
Oxazolidine (±)-**10h**



10h

The same procedure as for (±)-**10a** was used, replacing benzaldehyde and benzoyl chloride by isobutyraldehyde (456 µL, 5 mmol) and *p*-methoxybenzoyl chloride (670 µL, 5 mmol), furnishing (±)-**10h** as a colorless liquid (846 mg, 68 % yield). R_f 0.52 (hexane/AcOEt, 1:1); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.86 (d, 3H), 0.94 (d, 3H), 2.15 (b peak, 1H), 3.80 (s, 3H), 3.6-4.04 (m, 4H), 5.27 (d, 1H), 6.99 (d, 2H), 7.57 ppm (d, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 17.98, 30.87, 55.39, 66.28, 92.85, 113.61, 128.49, 129.66, 161.57, 169.38 ppm; IR (ATR): $\tilde{\nu}$ = 3465, 2962, 2874, 1788, 1727, 1620, 1604, 1573, 1511, 1419, 1402, 1383, 1304, 1252, 1171, 1110, 1065, 1027, 942, 905, 842, 767, 618 cm^{-1}; MS (DCI$^+$, NH_3 + isobutane) *m/z* = 250 (100) $[M+1]^+$, 135 (7); Anal. calcd for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68; N, 5.62. Found: C, 67.4; H, 7.66; N, 5.43.

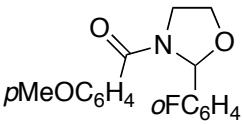
Oxazolidine (±)-**10i**



10i

The same procedure as for (±)-**10a** was used, replacing benzaldehyde and benzoyl chloride by pivaldehyde (833 µL, 7.5 mmol) and *p*-methoxybenzoyl chloride (1 mL, 7.5 mmol), furnishing (±)-**10i** as a white solid (1.42 g, 72 % yield). R_f 0.64 (hexane/AcOEt, 1:1); m.p. 84-85°C; ^{1}H NMR (300 MHz, [D_6] DMSO, TMS): δ = 0.92 (s, 9H), 3.61-4.00 (m, 4H), 3.82(s, 3H), 5.43(s, 1H), 7.01 (d, 2H), 7.60 ppm (d, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 25.40, 37.94, 50.18, 55.47, 66.59, 94.14, 113.66, 128.49, 130.21, 161.88, 171.53 ppm; IR (ATR): $\tilde{\nu}$ = 2966, 2860, 1617, 1640, 1605, 1571 cm^{-1}; MS (DCI$^+$, NH_3 + isobutane) *m/z* = 264 (100) [*M*+1]$^+$, 135 (7); Anal. calcd for $C_{15}H_{21}NO_3$: C, 68.42; H, 8.04; N, 5.32. Found: C, 68.56; H, 8.08; N, 5.43.

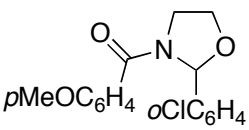
Oxazolidine (±)-**10j**



10j

The same procedure as for (±)-**10a** was used, replacing benzaldehyde and benzoyl chloride by *o*-fluorobenzaldehyde (1.06 mL, 10 mmol) and *p*-methoxybenzoyl chloride (1.35 mL, 10 mmol), furnishing (±)-**10j** as a white solid (2.98 g, 95 % yield). R_f 0.41 (hexane/AcOEt, 1:1); m.p. 95-96°C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.77 (s, 3H), 3.91-4.16 (m, 4H), 6.53 (bs, 1H), 6.83-7.51 ppm (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 47.73 (broad peak), 55.30, 66.64 (broad peak), 86.52, 113.51, 115.99 (d, *J* (^{13}C,^{19}F) = 21 Hz), 123.92 (d, *J* (^{13}C,^{19}F) = 3 Hz), 125.63 (d, *J* (^{13}C,^{19}F) = 12 Hz), 127.76, 128.81 (broad peak), 129.53 (broad peak), 130.66 (d, *J* (^{13}C,^{19}F) = 8 Hz), 160.95 (d, *J* (^{13}C,^{19}F) = 249 Hz), 161.58, 168.88 ppm; IR (ATR): $\tilde{\nu}$ = 3069, 2985, 2888, 1622, 1602, 1570, 1514, 1423, 1403, 1368, 1307, 1256, 1231, 1183, 1111, 1072, 1020, 983, 855, 757 cm^{-1}; MS (DCI$^+$, NH_3 + isobutane) m/z = 302 (100) [*M*+1]$^+$, 135 (15); Anal. calcd for $C_{17}H_{16}ClNO_3$: C, 67.76; H, 5.35; N, 4.65. Found: C, 67.91; H, 5.36; N, 4.66.

Oxazolidine (±)-**10k**

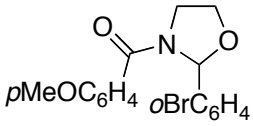


10k

The same procedure as for (±)-**10a** was used, replacing benzaldehyde and benzoyl chloride by *o*-chlorobenzaldehyde (1.12 mL, 10 mmol) and *p*-methoxybenzoyl chloride (1.35 mL, 10 mmol), furnishing (±)-**10k** as a white solid (3.05 g, 96 % yield). R_f 0.41 (hexane/AcOEt, 1:1); m.p. 105-106°C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.79 (s, 3H), 3.94-4.14 (m, 4H), 6.63 (bs, 1H),

6.83-7.44 ppm (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 48.0 (broad peak), 55.41, 66.3 (broad peak), 88.42, 113.66, 126.88, 127.79, 128.29 (broad peak), 129.63 (broad peak), 130.37, 132.10, 133.78, 135.47, 161.72, 169.18 ppm; IR (ATR): $\tilde{\nu}$ = 3068, 2961, 2893, 1620, 1604, 1569, 1511, 1422, 1402, 1364, 1302, 1252, 1213, 1178, 1068, 1017, 984, 843, 755 cm^{-1}; MS (DCI$^+$, NH_3 + isobutane) *m/z* = 318 (100) [*M*+1]$^+$, 282 (13), 135 (18); Anal. calcd for $C_{17}H_{16}ClNO_3$: C, 64.26; H, 5.08; N, 4.417. Found: C, 64.22; H, 5.06; N, 4.31.

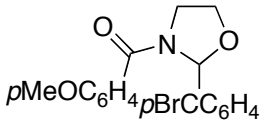
Oxazolidine (±)-**10l**



10l

The same procedure as for (±)-**10a** was used, replacing benzaldehyde and benzoyl chloride by *o*-bromobenzaldehyde (1.17 mL, 10 mmol) and *p*-methoxybenzoyl chloride (1.35 mL, 10 mmol), furnishing (±)-**10l** as a white solid (3.36 g, 93 % yield). R_f 0.41 (hexane/AcOEt, 1:1); m.p. 117-118°C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.54- 4.12 (bm, 7H), 6.58 (bs, 1H), 7.18-7.74 ppm (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 42.99 (broad peak), 55.46, 62.73 (broad peak), 90.29, 113.71, 123.408, 127.54, 127.90, 128.33 (broad peak), 129.68 (broad peak), 130.54, 133.73, 137.00, 161.77, 169.30 ppm; IR (ATR): $\tilde{\nu}$ = 3309, 2948, 2890, 2839, 1620, 1606, 1569, 1509, 1422, 1402, 1364, 1303, 1252, 1213, 1181, 1068, 1017, 847, 762 cm^{-1}; MS (DCI$^+$, NH_3 + isobutane) *m/z* = 362 (100) [*M*]$^+$, 282 (24); Anal. calcd for $C_{15}H_{21}NO_3$: C, 56.38; H, 4.46; N, 3.87. Found: C, 56.84; H, 4.51; N, 3.63.

Oxazolidine (±)-**10m**

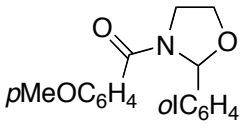


10m

The same procedure as for (±)-**10a** was used, replacing benzaldehyde and benzoyl chloride by *p*-bromobenzaldehyde (0.925 g, mmol) and *p*-methoxybenzoyl chloride (675 µL, 5 mmol), furnishing as (±)-**10m** a white solid (1.08 g, 60 % yield). Rf = 0.41 (hexane/AcOEt, 1/1); m.p. 81-82°C; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.75-4.15 (m, 4H), 3.81 (s, 3H), 6.40 (bs, 1H), 6.88 (bd, 2H), 7.361-7.503 ppm (m, 6H); ^{1}H NMR (300 MHz, [D_6] DMSO, TMS): δ = 3.80- 4.12 (m, 4H), 3.83 (s, 3H), 6.24 (bs, 1H), 6.97 (d, 2H), 7.43(d, 2H), 7.57 ppm (d, 4H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 47.77 (broad peak), 55.47, 66.38 (broad peak), 89.29, 113.71, 122.92, 127.75, 128.68 (broad peak), 129.78 (broad peak), 131.66, 138.03, 161.84, 169.52 ppm; IR (ATR): $\tilde{\nu}$ = 3071, 2985, 2959, 2931, 2897, 2838, 1623, 1602, 1570, 1512,

1422, 1393, 1357, 1307, 1255, 1220, 1178, 1075, 1027, 983, 852, 838, 804 cm^{-1}; MS (DCI^+, NH_3 + isobutane) *m/z* = 362 (100) $[M]^+$, 282 (27).

Oxazolidine (±)-**10n**



10n

The same procedure as for (±)-**10a** was used, replacing benzaldehyde and benzoyl chloride by *o*-iodobenzaldehyde (0.46 g, 2 mmol) and *p*-methoxybenzoyl chloride (270 µL, 2 mmol), furnishing (±)-**10n** as a white solid (720 mg, 88 % yield). R_f 0.41 (hexane/AcOEt, 1:1); m.p. 112-113°C; ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.82 (s, 3H), 4.04-4.13 (m, 4H), 6.43 (bs, 1H), 7.03-7.88 ppm (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ = 55.43, 93.9, 97.88, 113.73, 127.80, 128.38 (broad peak), 129.00, 129.70 (broad peak), 130.72, 139.72, 140.40, 161.76, 169.32 ppm;[4] IR (ATR): $\tilde{\nu}$ = 3317, 3060, 2955, 2884, 1617, 1605, 1568, 1509, 1420, 1399, 1360, 1302, 1252, 1213, 1178, 1065, 1014, 984, 842, 755 cm^{-1}; MS (DCI^+, NH_3 + isobutane) *m/z* = 310 (100) $[M\text{-}99]^+$ 282 (50); Anal. calcd for $C_{17}H_{16}INO_3$: C, 49.9; H, 3.95; N, 3.43. Found: C, 50.17; H, 4.06; N, 3.42.

4- General procedures for the oxidations

Reaction on a 1 mmol scale

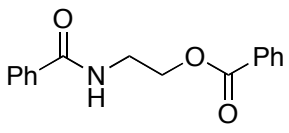
In 50 mL round bottom flask equipped with a stirring bar, acetonitrile (10 mL), oxazolidine (1 mmol), CuCl (5 mg, 0.05 mmol, 5 mol %) and catalyst (1 to 4 mol %) were combined. The flask was closed with a septum and flushed with oxygen. A balloon filled with oxygen was then connected to the flask and stirring was maintained at a controled temperature. Samples were analyzed using GC and/or TLC. After reaction, a standard was added and the conversion was measured relative to the standard by GC or NMR. The enantiomeric excess of the remaining oxazolidine was determined after purification by column chromatography.

Fast screening on a 10-20 μmol scale

Oxazolidine (10 μL or 20 μL of a 1 M solution in acetonitrile), CuCl (25 μL or 50 μL of a 0.02 M solution in acetonitrile, 5 mol %) and catalyst (10 μL to 40 μL of a 0.01 M solution in acetonitrile, 1 to 4 mol %) were combined in 2 mL flask . The appropriate volume of acétonitrile was added to adjust the concentration of oxazolidine to 10^{-1} or 10^{-2} M. The flask was closed with a septum, flushed with oxygen and 1 mL of gaseous oxygen was introduced using a syringe. The flask was kept at controlled temperature (no stirring required). Samples were analyzed by GC and/or TLC. At appropriate time, the reaction was quenched by hydroquinone (1 equiv relative to the initial amount of oxazolidine) and a standard was added. Conversions were measured relative to the standard by GC or NMR. The enantiomeric excess of the remaining oxazolidine was determined after purification by semi-preparative TLC.

Oxidation product **11a**[5]

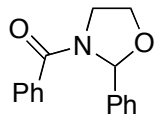
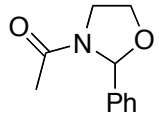
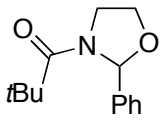
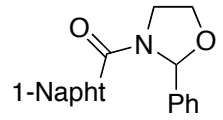
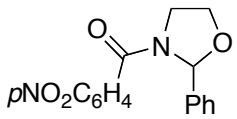
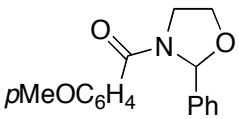
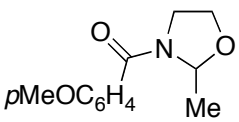
Oxidative ring opening product **11a** of oxazolidine (±)-**10a** has been isolated after column cromatography purification, as a white solid; R_f 0.52 (hexane/AcOEt, 1:1); m.p. 83-84 °C (lit[3]: m.p. 85-88 °C); 1H NMR (300 MHz, $CDCl_3$, TMS): δ = 3.88 (t, 2H), 4.56 (t, 2H), 6.64 (bs, 1H), 7.42-8.07 ppm (m, 10H); IR (ATR): $\tilde{\nu}$ = 3385, 3065, 2985, 2939, 2896 1696, 1642, 1602, 1581, 1519, 1484, 1453, 1337, 1281, 1261, 1131, 1071, 1027, 976, 923, 703, 681 cm^{-1}; MS (DCI^+, NH_3 + isobutane) m/z = 287 (39) $[M+18]^+$, 270 (100), 148 (99).

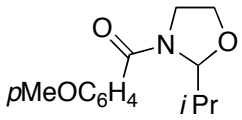
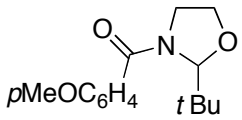
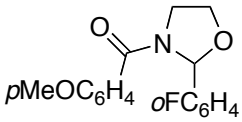
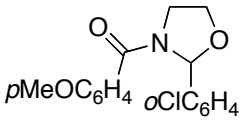
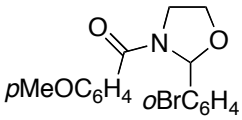
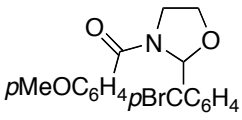
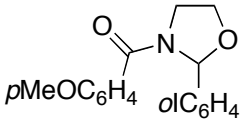


11a

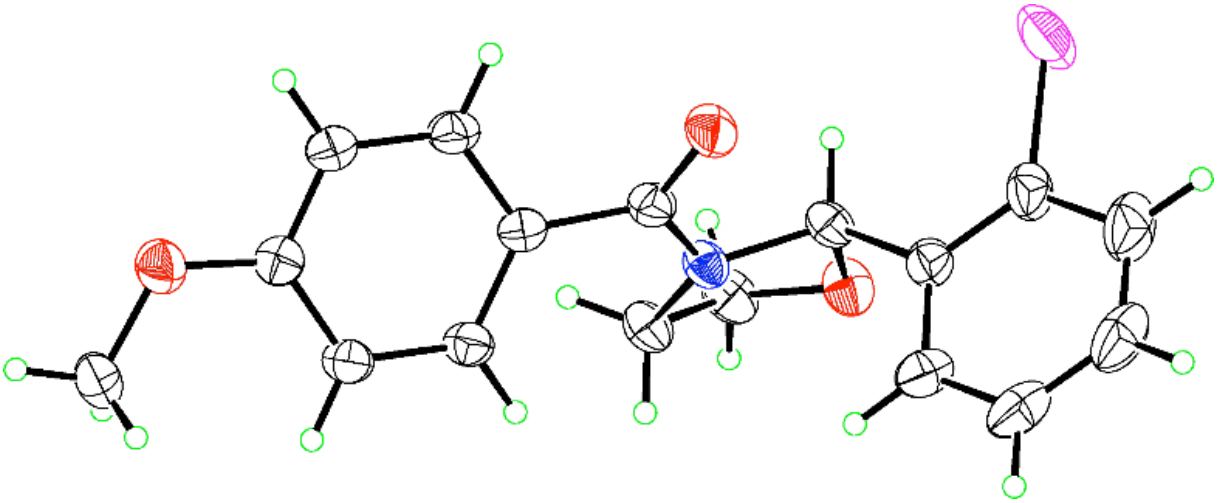
5- Determination of the oxidation conversion and of the *ee* of *N*-acyloxazolidines

Table SM 1. Methods used for the determination of conversions and *ee*

Oxazolidine	Assay	Method	Conditions	Retention times (min)
 **10a**	Conversion	GC BPX5 column	150 °C 2 min, 20 °C/min to 250 °C, 10 min	9.9
	ee	HPLC Chiralpak AS	*i*PrOH/Hexane 50:50 1.0 mL/min	9.0 13.9
 **10b**	Conversion	GC BPX5 column	150 °C 2 min, 20 °C/min to 250 °C, 10 min	7.1
	ee	HPLC Chiralpak AS	*i*PrOH/Hexane 33:67 1.0 mL/min	14.9 21.5
 **10c**	Conversion	GC BPX5 column	150 °C 2 min, 20 °C/min to 250 °C, 10 min	8
	ee	HPLC Chiralpak AS	*i*PrOH/Hexane 5:95 1.0 mL/min	9.1 13.3
 **10d**	Conversion	GC BPX5 column	150 °C 2 min, 20 °C/min to 280 °C, 15 min	15.3
	ee	HPLC Chiralpak AS	*i*PrOH/Hexane 50:50 1.0 mL/min	22.3 24.6
 **10e**	Conversion	NMR [D_6] DMSO	Triphenylmethane used as a standard	
	ee	HPLC Chiralpak AS	*i*PrOH/Hexane 50:50 1.0 mL/min	19.3 25.6
 **10f**	Conversion	NMR [D_6] DMSO	Triphenylmethane used as a standard	
	ee	HPLC Chiralpak AS	*i*PrOH/Hexane 50:50 1.0 mL/min	9.8 19.3
 **10g**	Conversion	^{1}H NMR [D_6] DMSO	Triphenylmethane used as a standard	
	ee	HPLC Chiralpak AS	*i*PrOH/Hexane 20:80 1.0 mL/min	10.3 15.6

Oxazolidine	Assay	Method	Conditions	Retention times (min)
 **10h**	Conversion	^{1}H NMR [D$_6$] DMSO	Triphenylmethane used as a standard	
	ee	HPLC Chiralpak AS	*i*PrOH/Hexane 10:90 1.0 mL/min	13.4 26.9
 **10i**	Conversion	^{1}H NMR [D$_6$] DMSO	Triphenylmethane used as a standard	
	ee	HPLC Chiralpak AS	*i*PrOH/Hexane 10:90 1.0 mL/min	7.0 10.5
 **10j**	Conversion	^{1}H NMR [D$_6$] DMSO	Triphenylmethane used as a standard	
	ee	HPLC Chiralpak AS	*i*PrOH/Hexane 50:50 1.0 mL/min	8.4 23.6
 **10k**	Conversion	^{1}H NMR [D$_6$] DMSO	Triphenylmethane used as a standard	
	ee	HPLC Chiralpak AS	*i*PrOH/Hexane 50:50 1.0 mL/min	10.6 31.5
 **10l**	Conversion	^{1}H NMR [D$_6$] DMSO	Triphenylmethane used as a standard	
	ee	HPLC Chiralpak AS	*i*PrOH/Hexane 50:50 1.0 mL/min	9.0 13.9
 **10m**	Conversion	^{1}H NMR [D$_6$] DMSO	Triphenylmethane used as a standard	
	ee	HPLC Chiralcel OD-H	*i*PrOH/Hexane 5:95 1.0 mL/min	40.7 49.5
 **10n**	Conversion	^{1}H NMR [D$_6$] DMSO	Triphenylmethane used as a standard	
	ee	HPLC Chiralpak AS	*i*PrOH/Hexane 50:50 1.0 mL/min	14.0 34.6

6- ORTEP drawing of (*R*)-**10l**



7- References and notes

[1] M. Nechab, B. M. Panchal, C. Philouze, C. Einhorn, J. Einhorn, *Tetrahedron: Asymmetry* **2005**, *16*, 1681-1684.

[2] The NOH signal was not detected.

[3] S. G. Kon'kova, A.E. Badasyan, O. S. Attaryan, A. K. Khachatryan, M. S. Sargsyan, V. V. Dovlatyan, *Khim. Zh. Armenii* **1997**, *50*, 161-166.

[4] Under standard NMR conditions, some signals were not detected because of too large peak broadening.

[5] H. Stamm, T. Mall, R. Falkenstein, J. Werry, D. Speth, *J. Org. Chem.* **1989**, *54*, 1603-1607.