# Supporting Information for

## Oxidation of secondary amines catalyzed by dirhodium caprolactamate

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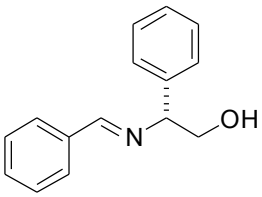
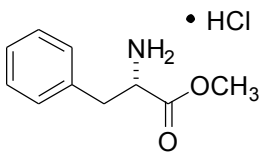
**General.** All reagents were commercially obtained unless otherwise noted and were purified according to the guidelines of Armarego and Chai.[1] Yields reported are for isolated yields after chromatography unless otherwise noted. *tert*-Butyl hydrogen peroxide (TBHP) was purchased from Aldrich as a 5.0-6.0 M solution in decane and stored over activated 3Å molecular sieves. The preparation of dirhodium(II) caprolactamate [$Rh_2(cap)_4.2CH_3CN$] has been previously described.[2] $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were obtained on a Bruker DRX-400 NMR as solutions in $CDCl_3$. Chemical shifts are reported in parts per million (ppm, δ) downfield from $Me_4Si$ (TMS); coupling constants are reported in Hertz (Hz). Thin layer chromatography (TLC) was performed on Merck 0.25 mm silica gel 60 $F_{254}$ plates with visualization by fluorescence quenching or aqueous $KMnO_4$ stain. Preparative chromatographic purification and Filtration were performed using Florisil$^{TM}$ (60-100 mesh) or SiliCycle (60Å, 40-63 mesh) silica gel. Anhydrous $CH_2Cl_2$ was purified prior to use by nitrogen forced-flow over activated alumina as described.[3]

**Representative Procedure (Table 2)**: A 10-mL vial equipped with a stirbar was charged with substrate (1.36 mmol, 100 mol%), acetonitrile (5 mL), and $Rh_2(cap)_4$ (0.013 mmol, 1.0 mol%). The vial was loosely sealed with a cap allowing inclusion of air. To the mixture was added TBHP (2.72 mmol, 2.0 equiv) in one portion via syringe to which the color of the solution immediately turned to deep red. After stirring for 16 hours, the solution was diluted with hexane and ether, then filtered through a short plug of Florisil™ wet with hexane, and washed down with ether. The solvent was evaporated to yield the analytically pure compounds whose spectral characteristics were identical to those previously reported.[4-12]

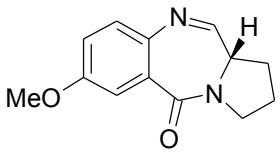



**b-[(Phenylmethylene)amino]-[*R*-(*E*)]-benzeneethanol** (Table 2, entry 9): A 10-mL vial equipped with a stirbar was charged with substrate (1.36 mmol, 100 mol%), acetonitrile (5 mL), and $Rh_2(cap)_4$ (0.013 mmol, 1.0 mol%). The vial was loosely sealed with a cap allowing inclusion of air. To the mixture was added TBHP (2.72 mmol, 2.0 equiv) in one portion via syringe to which the color of the solution immediately turned to deep red. After 16h, the solvent was removed under reduced pressure followed by flash chromatography (Florisil™) gave the product (90 %). $[\alpha]_D^{25}$ = +49.3 (*c* = 1.02, $CHCl_3$). Spectral and specific rotation data were identical to those previously reported.[10]




**Procedure for the Deprotection of a Benzylic Group**: A 10 mL vial equipped with a stirbar was charged with **4** (146 mg, 0.54 mmol, 100 mol%), $CH_3CN$ (2.0 mL), , and $Rh_2(cap)_4$ (4.0 mg, 0.0054 mmol, 1.0 mol%). The vial was loosely sealed with a cap allowing inclusion of air. To the mixture was added TBHP (0.33 mL, 2.2 mmol, 4 equiv) in one portion via syringe. After stirring for 16 hours, the solution was diluted with hexane and ether, then filtered through a short plug of silicagel wet with hexane, and washed down with ether. The solvent was removed under reduced pressure. The residue was dissolved with ether, then, anhydrous HCl (1.0 M in ether) was added at 0 $^oC$ and stirred for 6h at room temperature. The white precipitation was filtered and dried to give

**5**, l-phenylalanine methyl ester hydrochloride**,** as white powder (92 mg, 78 %). $[\alpha]_D^{22}$ = +38.1 (*c* = 2.0, EtOH). Spectral and specific rotation data were identical to those previously reported.[13]




**Procedure for the Oxidation of 6**: A 10 mL vial equipped with a stirbar was charged with **6** (90 mg, 0.39 mmol, 100 mol%), $CH_2Cl_2$ (1.4 mL), $K_2CO_3$ (54 mg, 0.39 mmol, 100 mol%), and $Rh_2(cap)_4$ (3.0 mg, 0.004 mmol, 1.0 mol%). The vial was loosely sealed with a cap allowing inclusion of air. To the mixture was added TBHP (0.13 mL, 0.77 mmol, 2 equiv) in one portion via syringe to which the color of the solution immediately turned to deep red. After 2h, the solvent was removed via under reduced pressure followed by flash chromatography (Florisil$^{TM}$) gave the product **7** as a colorless oil (72 mg, 80 %) whose spectral properties matched those in the literature:[14] $^1$H NMR (400 MHz, $CDCl_3$) 7.68 (d, *J* = 4.4 Hz, 1H), 7.52 (d, *J* = 3.0 Hz, 1H), 7.26 (d, *J* = 9.0 Hz, 1H), 7.08 (dd, *J* = 9.0, 3.0 Hz, 1H), 3.69-3.91 (m, 5H), 3.53-3.60 (m, 1H), 2.29-2.33 (m, 2H), 1.95-2.08 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) 164.6, 162.4, 157.7, 139.6, 128.9, 128.7, 119.3, 112.5, 55.6, 53.5, 46.7, 29.6, 24.0. $[\alpha]_D^{26}$ = +115 (c = 1.00, $CHCl_3$).[15]

**Reference**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