Supporting Information

“Asymmetric Hydrogenations for the Synthesis of Boc-Protected 4-Alkylprolinols and Prolines”

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***N*-tert-butyloxycarbonyl-(3-indolylmethyl)triphenylphosphonium bromide.**

A solution *N*-Boc-(3-bromomethyl)indole (1.40g, 4.35 mmol) in 15 mL of dry benzene was placed under Ar and treated with 1.20g (4.56 mmol) of triphenylphosphine. The mixture was warmed to 50°C and stirred for 18h. The white precipitate that formed was collected by vacuum filtration and rinsed with 3 portions of benzene. The white solid was dried under reduced pressure overnight in a desiccator to afford 2.10 g of the phosphonium salt (84%) which was used directly for Wittig olefination.

(*S*)-2-tert-butyldimethylsilyloxymethyl-*N*-tert-butyloxycarbonyl-4-(phenylthio)methylene-pyrrolidine (13**).**

A solution of diethyl(phenylthiomethyl)phosphonoacetate (.51 mL, 2.28 mmol) in 2 mL dry THF was placed under Ar and cooled to -78°C. Dropwise addition of 0.91 mL (2.28 mmol) of a 2.5M *n*-BuLi solution in hexanes was followed by addition of a solution of ketone **6** (250 mg, 760 μ mol) in 2 mL dry THF via cannula. The reaction was allowed to warm to rt and after 5 hr was quenched with sat. aq. NH₄Cl, extracted with Et₂O, dried over Na₂SO₄, and concentrated in vacuo. Purification by silica gel chromatography (5% EtOAc/Hex eluent) gave 241 mg of colorless oil **13** as a mixture of *E* and *Z*-isomers (73%). Molecular formula C₂₃H₃₇NO₃SSi. Molecular weight 435.71 g/mol; *R*_f = 0.49 (10% EtOAc/Hex). ¹H NMR (300 MHz, CDCl₃) δ 7.53-7.10 (m, 5H), 6.11 (m, 1H), 4.29-3.95 (m, 3H), 3.82-3.42 (m, 2H), 2.75 (m, 2H), 1.49 (s, 9H), 0.90 (s, 6H), 0.06 and 0.09 (2s, 6H); ES-MS: 436 [MH]⁺.

(*S*)-2-*tert*-butyldimethylsilyloxymethyl-*N*-*tert*-butyloxycarbonyl-4-(chloro)methylene-pyrrolidine (14**).**

Following a similar procedure to that described for the preparation of **13**, a cooled suspension of chloromethyltriphenylphosphoniumbromide (1.03 g, 2.96 mmol) in 8 mL of dry THF was treated with 1.18 mL (2.96mmol) of 2.5M *n*-BuLi in hexanes followed by a solution of ketone **6** in 3 mL of THF. After stirring 18h, the reaction was quenched and worked-up in the normal manner. Purification by silica gel chromatography (3% EtOAc/Hex eluent) afforded 184 mg of the vinyl chloride **14** as a colorless oil and as a mixture of *E* and *Z*-isomers (43%). Molecular formula C₁₇ClH₃₂NO₃SSi. Molecular weight 361.99 g/mol; *R*_f = 0.44 (10% EtOAc/Hex). ¹H NMR (300 MHz, CDCl₃) δ 5.93 (m, 1H), 4.15-3.88 (m, 3H), 3.60 (m, 1H), 2.76-2.64 (m, 3H), 1.46 (s, 9H), 0.85 (s, 6H), 0.01 (s, 6H); ES-MS: 385 [MNa]⁺.

S3

Compound 6

S4

Compound 7a

S5

Compound 9a

Compound 9b

S7

Compound 9c

S8

Compound 9d

S9

Compound 9e

S10

Compound 9f

S11

Compound 11b

S12

Compound 11c

S13

Compound 11d

S14

Compound 11e

S15

Compound 11f

Compound 1a

S17

Compound 1b

S18

Compound 1c

S19

Compound 1d

S20

Compound 1e

S21

Compound 2b

S22

Compound 2c

S23

Compound 2d

S24

Compound 2e