Supporting Information

Highly Enantioselective Pd-Catalyzed Asymmetric Hydrogenation of Activated Imines

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General: All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques or in an nitrogen-filled glovebox, unless otherwise noted. ¹H NMR, ¹³C NMR and ³¹P NMR spectra were recorded on Bruker DRX-400 spectrometers. The chemical shifts for ¹H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard. The chemical shifts for ¹³C NMR were recorded in ppm downfield using the central peak of deuterochloroform (77.23 ppm) as the internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. Optical rotations were measured with JASCO P-1010 polarimeter. Flash column chromatography was performed on silica gel (200-300 mesh). TLC analysis was performed using glass-backed plates coated with 0.2 mm silica.

Materials: Commercially available reagents were used throughout without further purification other than those detailed below. THF and Et_2O were distilled over sodium benzopheneone ketyl under nitrogen. Methylene chloride was distilled over calcium hydride. CF₃CH₂OH and acetone were stilled from anhydrous CaSO₄. The other solvent, which was on the asymmetric hydrogenation reactions, were purchased from Aldrich without further purification. SynPhos was prepared according to the literature.¹

The preparation of imines



N-Diphenylphosphinyl imines (3): It was prepared according to the literatures.² Imines 3 all are known compounds.³ Representative spectroscopic dates are following: *N*-(1-Phenylethylidene)-diphenylphosphinamide (3a): White solid, ¹H NMR (400 MHz, CDCl₃): $\delta = 2.97$ (d, J = 2.0 Hz, 3H), 7.43-7.50 (m, 9H), 7.98-8.00 (m, 4H), 8.08-9.10 (m, 2H).

$$R^{1} R^{2} \xrightarrow{1) \text{ p-toluenesulfinamide, Ti(OEt)_4, CH_2Cl_2}}{2) \text{ m-CPBA, CH_2Cl_2}} R^{1} R^{2}$$

General procedure for the synthesis of *N*-tosyl imines (5): It was prepared according to the modified procedures reported in the literature.⁴ To a Schlenck flask equipped with a condenser were charged with the corresponding ketone (5 mmol), racemic p-toluenesulfinamide (1.552 g, 10 mmol) and Ti(OEt)₄ (3.2 mL, 15 mmol) in 50 mL CH₂Cl₂. The solution was heated under reflux for 2-4 days and monitored by TLC. 20 mL CH₃OH and a few drops of NaHCO₃ were added. Then the solution was filtered through anhydrous Na₂SO₄ and washed with EtOAc. The solvent was removed in vacuo and the crude product was purified by column chromatography using petroleum ether and EtOAc to obtain the corresponding p-tolylsulfinimine.

In a dried flask, to a stirred solution of the corresponding p-tolylsulfinimine in CH₂Cl₂ was added dry m-CPBA (monitored by TLC) at room temperature (the reaction can be carried out in the air without special handling). When the reaction was completed, the solution was concentrated in vacuo. The residue was dissolved in Et₂O, washed with saturated solution of NaHCO₃ twice, dried over anhydrous Na_2SO_4 , and concentrated to give a residue which was quickly purified by column chromatography using petroleum ether and EtOAc to give the corresponding N-tosyl imines ($\mathbf{5}$)^{4,5} (>90%)purity). Representative spectroscopic dates are following: (E)-1-Phenyl-N-tosylethanimine (5a): White solid, ¹H NMR (400 MHz, CDCl₃): $\delta = 2.45$ (s, 3H), 2.99 (s, 3H), 7.35 (d, J = 8.2 Hz, 2H), 7.39-7.43 (m, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.89-7.94 (m, 4H).



N-Sulfonylimines (7): It was prepared from the saccharin according to the literatures.⁶

3-Methyl-1,2-benzisothiazole 1,1-Dioxide (7a):^{6a} White solid, ¹H NMR (400 MHz, CDCl₃): δ = 2.68 (s, 3H), 7.69-7.79 (m, 3H), 7.91-7.93 (m, 1H).

3-Butyl-1,2-benzisothiazole 1,1-Dioxide (7b):^{6c} White solid, ¹H NMR (400 MHz, CDCl₃): $\delta = 0.99$ (t, J = 7.3 Hz, 3H), 1.49-1.54 (m, 2H), 1.84-1.91 (m, 2H), 2.96-2.99 (m, 2H), 7.70-7.75 (m, 3H), 7.90-7.92 (m, 1H).

3-Benzyl-1,2-benzisothiazole 1,1-Dioxide (7c):^{6b} White solid, ¹H NMR (400 MHz, CDCl₃): δ = 4.30 (s, 2H), 7.30-7.32 (m, 1H), 7.35-7.36 (m, 4H), 7.58-7.70 (m, 3H), 7.89 (d, *J* = 7.4 Hz, 1H).

$$R \xrightarrow{O} \frac{\text{MeSO}_2\text{NHBoc/LDA}}{\text{THF, -78°C to rt}} R \xrightarrow{OH} R \xrightarrow{OH} 2 \text{DPCC, CH}_2\text{Cl}_2 \xrightarrow{N-S} 10 \text{DPCC, CH}_2\text{Cl}_2 \xrightarrow{N-S} 11 \text{DPCC, CH}_2 \xrightarrow{N-S} 11 \text{DPCC$$

General procedure for the synthesis of N-sulfonylimines (11): N-Sulfonylimines 11 were prepared from corresponding substituted oxiranes 9 according to the procedures reported in the literature.⁷ The known compounds oxiranes 9d, 9f, 9g were synthesized according to the literature.⁸ MeSO₂NHBoc was synthesized from MeSO₂NH₂ and (Boc)O₂ according to the literature.⁹ PCC was synthesized from pyridine and CrO₃ according to the literature.¹⁰

[(4-Trifluoromethyl-phenoxy)methyl]oxirane (9e): To a solution of 4-trifluoromethylphenol (4.053 g, 25 mmol) in dry DMF (50 ml) was added NaH (1.000g, 25 mmol, 60% dispersion in mineral oil) and the reaction mixture was stirred for 30 min at rt. After the epichlorohydrin was added, the reaction was stirred for 5h at 30 °C. The water (100 ml) was added, and the mixture was extracted with ether (40 ml × 3). The combined organic layer was washed with 1 N NaOH (80 ml × 1) and dried with anhydrous Na₂SO₄. Evaporation of solvent and purification of the residue by column chromatography (petroleum ether/EtOAc = 20:1) gave **9e** as a colorless oil (2.294 g, 42%). ¹H NMR (400 MHz, CDCl₃): δ = 2.76-2.78 (m, 1H), 2.91-2.93 (m, 1H), 3.35-3.39 (m, 1H), 3.96 (dd, *J* = 5.8, 11.0 Hz, 1H), 4.30 (dd, *J* = 2.8, 10.8 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 44.7, 50.1, 69.1, 114.8, 123.6 (q, *J* = 32 Hz), 124.6 (q, *J* = 269 Hz), 127.1 (d, *J* = 3 Hz), 161.1; HRMS Calculated for C₁₀H₉O₂F₃ (M⁺) 218.0555, found: 218.0553.

tert-Butyl-N-[(3-hydroxynonyl)-sulfonyl]-carbamate (10c): Yellow oil, ¹H NMR (400 MHz, CDCl₃): $\delta = 0.87$ -0.90 (m, 3H), 1.28-1.35 (m, 7H), 1.47-1.49 (m, 3H), 1.51 (s, 9H), 1.86-1.90 (m, 1H), 2.03-2.06 (m, 1H), 3.52-3.60 (m, 2H), 3.75-3.77 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 14.1$, 22.6, 25.5, 28.0, 29.2, 30.5, 31.8, 37.4, 49.9, 69.9, 84.3, 150.0; HRMS Calculated for C₁₀H₂₀NO₄S [M - C₄H₉O]⁺ 250.1113, found: 250.1122.

tert-Butyl-N-[(3-hydroxy-4-phenoxy-butyl)-sulfonyl]-carbamate (10d): Yellow oil, Yield: 86%, ¹H NMR (400 MHz, CDCl₃): δ = 1.51 (s, 9H), 2.09-2.17 (m, 2H), 3.61-3.71 (m, 2H), 3.89 (dd, J = 6.6, 9.3 Hz, 1H), 4.01 (dd, J = 3.6, 9.4 Hz, 1H), 4.16-4.18 (m, 1H), 6.90 (d, J = 8.4 Hz, 2H), 6.98 (t, J = 7.3 Hz, 1H), 7.27-7.32 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 27.2, 28.0, 49.7, 68.2, 71.4, 84.5, 114.7, 121.5, 129.7, 150.1, 158.4; HRMS Calculated for C₁₅H₂₃NO₆S (M⁺) 345.1246, found: 345.1250.

tert-Butyl-N-[(3-hydroxy-4-(4-trifluoromethyl-phenoxy)-butyl)-sulfonyl]-carbamate (10e): White solid, Yield: 79%, ¹H NMR (400 MHz, CDCl₃): $\delta = 1.50$ (s, 9H), 2.09-2.19 (m, 2H), 3.63-3.70 (m, 2H), 3.95 (dd, J = 6.5, 9.3 Hz, 1H), 4.03 (dd, J = 3.7, 9.4 Hz, 1H), 4.19-4.21 (m, 1H), 6.96 (d, J = 8.7 Hz, 2H), 7.55 (d, J = 8.7 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 27.2$, 28.1, 49.9, 68.1,71.8, 84.8, 114.7, 123.8 (q, J = 33 Hz), 124.5 (q, J = 270 Hz), 127.2 (d, J = 3 Hz), 150.0,160.9; HRMS Calculated for C₁₆H₂₂NO₆F₃NaS [M + Na]⁺ 436.1018, found: 436.1031.

tert-Butyl-N-[(3-hydroxy-4-(4-methyl-phenoxy)-butyl)-sulfonyl]-carbamate (10f): Yellow oil, Yield: 54%, ¹H NMR (400 MHz, CDCl₃): δ = 1.50 (s, 9H), 2.05-2.14 (m, 2H), 2.28 (s, 3H), 2.71 (br, 1H), 3.59-3.69 (m, 1H), 3.86 (dd, *J* = 6.6, 9.4 Hz, 1H), 3.96 (dd, *J* = 3.7, 9.4 Hz, 1H), 4.11-4.13 (m,

1H), 6.78-6.81 (m, 2H), 7.08 (d, J = 8.4 Hz, 2H), 7.55 (br, 1H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 20.7, 27.2, 28.1, 49.9, 68.3, 71.8, 84.7, 114.7, 130.2, 130.9, 150.0, 156.3;$ HRMS Calculated for C₁₆H₂₅NO₆S (M⁺) 359.1403, found: 359.1405.

tert-Butyl-N-[(3-hydroxy-4-(2-methyl-phenoxy)-butyl)-sulfonyl]-carbamate (10g): Yellow oil, ¹H NMR (400 MHz, CDCl₃): $\delta = 1.49$ (s, 9H), 2.07-2.19 (m, 2H), 2.22 (s, 3H), 3.60-3.69 (m, 2H), 3.88-3.92 (m, 1H), 3.96-4.16 (m, 1H), 4.16-4.18 (m, 2H), 6.79 (d, J = 7.9 Hz, 1H), 6.87-6.90 (m, 1H), 7.12-7.16 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 16.4$, 27.3, 28.1, 49.9, 68.4, 71.5, 84.6, 111.4, 121.3, 126.9, 127.1, 131.0, 150.0, 156.4; HRMS Calculated for C₁₆H₂₅NO₆S (M⁺) 359.1403, found: 359.1412.

tert-Butyl-N-[(3-hydroxy-4-(naphthalen-2-yloxy)-butyl)-sulfonyl]-carbamate (10h): White solid, Yield: 75%, ¹H NMR (400 MHz, CDCl₃): $\delta = 1.51$ (s, 9H), 2.14-2.21 (m, 2H), 2.54 (d, J = 4.6 Hz, 1H), 3.65-3.74 (m, 2H), 4.02 (dd, J = 6.7, 9.3 Hz, 1H), 4.13 (dd, J = 3.5, 9.4 Hz, 1H), 4.23-4.24 (m, 1H), 7.09-7.16 (m, 3H), 7.34-7.38 (m, 1H), 7.44-7.47 (m, 1H), 7.72-7.78 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 27.3$, 28.2, 50.1, 68.3, 71.7, 84.8, 107.3, 118.7, 124.2, 126.8, 127.0, 127.9, 129.5, 129.9, 134.6, 149.8, 156.4; HRMS Calculated for C₁₉H₂₅NO₆S (M⁺) 395.1403, found: 395.1410.

tert-Butyl-N-[(3-hydroxy-4-(benzyloxy)-butyl)-sulfonyl]-carbamate (10i): Yellow oil, ¹H NMR (400 MHz, CDCl₃): $\delta = 1.48$ (s, 9H), 1.92-2.00 (m, 2H), 2.85 (br, 1H), 3.37 (dd, J = 6.8, 9.5 Hz, 1H), 3.48-3.53 (m, 2H), 3.55-3.58 (m, 1H), 3.93-3.94 (m, 1H), 4.54 (s, 2H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 27.2, 28.1, 49.8, 68.5, 73.6, 84.4, 128.0, 128.1, 128.7, 137.7, 150.1.$

3-Phenyl-4,5-dihydro-isothiazole 1,1-Dioxide (11a):⁷ White solid, ¹H NMR (400 MHz, CDCl₃): $\delta = 3.43-3.47$ (m, 2H), 3.66-3.70 (m, 2H), 7.51-7.55 (m, 2H), 7.64-7.68 (m, 1H), 8.02-8.04 (m, 2H).

3-Methyl-4,5-dihydro-isothiazole 1,1-Dioxide (11b):⁷ White solid, ¹H NMR (400 MHz, CDCl₃): $\delta = 2.34$ (s, 3H), 3.19-3.23 (m, 2H), 3.25-3.29 (m, 2H).

3-*n***-Hexyl-4,5-dihydro-isothiazole 1,1-Dioxide (11c):** White solid, ¹H NMR (400 MHz, CDCl₃): $\delta = 0.88-0.91$ (m, 3H), 1.31-1.38 (m, 6H), 1.70-1.74 (m, 2H), 2.53-2.57 (m, 2H), 3.17-3.20 (m, 2H), 3.23-3.26 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 14.2$, 22.6, 25.5, 28.9, 31.5, 35.8, 36.9, 44.2, 185.5; HRMS Calculated for C₇H₁₂NO₂S [M - C₂H₅]⁺ 174.0589, found: 174.0585.

3-(Phenoxy-methyl)-4,5-dihydro-isothiazole 1,1-Dioxide (11d): White solid, Yield: 60%, ¹H NMR (400 MHz, CDCl₃): δ = 3.27-3.31 (m, 2H), 3.39-3.43 (m, 2H), 4.99 (s, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 7.05 (t, *J* = 7.4 Hz, 1H), 7.32-7.36 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 34.3, 43.6, 67.7, 114.6, 122.7, 130.2, 157.4, 182.1; HRMS Calculated for C₁₀H₁₁NO₃S (M⁺) 225.0460, found: 225.0460.

3-[(4-Trifluoromethyl-phenoxy)methyl]-4,5-dihydro-isothiazole 1,1-Dioxide (11e): White solid, Yield: 65%, ¹H NMR (400 MHz, CDCl₃): δ = 3.30-3.34 (m, 2H), 3.40-3.43 (m, 2H), 5.04 (s, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H); ¹³C NMR (100 MHz, d-DMSO): δ = 33.9, 43.6, 67.2, 115.2, 115.8, 121.8, 122.1, 123.1, 125.8, 127.0, 160.3, 182.8; HRMS Calculated for C₁₁H₁₀NO₃SF₃ (M⁺) 293.0333, found: 293.0335.

3-[(4-Methyl-phenoxy)methyl]-4,5-dihydro-isothiazole 1,1-Dioxide (11f): White solid, Yield: 54%, ¹H NMR (400 MHz, CDCl₃): δ = 2.30 (s, 3H), 3.26-3.29 (m, 2H), 3.37-3.41 (m, 2H), 4.96 (s, 2H), 6.80-6.82 (m, 2H), 7.12 (d, *J* = 8.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 20.7, 34.3, 43.6, 67.8, 114.5, 130.6, 132.1, 155.4, 182.5; HRMS (EI) Calculated for C₁₁H₁₃NO₃S: 239.0616, found: 239.0620.

3-[(2-Methyl-phenoxy)methyl]-4,5-dihydro-isothiazole 1,1-Dioxide (11g): White solid, ¹H

NMR (400 MHz, CDCl₃): δ = 2.27 (s, 3H), 3.27-3.31 (m, 2H), 3.42-3.45 (m, 2H), 4.99 (s, 2H), 6.77 (d, *J* = 8.5 Hz, 1H), 6.94-6.97 (m, 1H), 7.16-7.20 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 16.4, 34.4, 43.6, 67.7, 111.0, 122.3, 126.9, 127.4, 131.5, 155.5, 182.4; HRMS Calculated for C₁₁H₁₃NO₃S (M⁺) 239.0616, found: 239.0619.

3-[(Naphthalen-2-yloxy)methyl]-4,5-dihydro-isothiazole 1,1-Dioxide (11h): Gray solid, Yield: 54%, ¹H NMR (400 MHz, CDCl₃): δ = 3.28-3.31 (m, 2H), 3.43-3.46 (m, 2H), 5.11 (s, 2H), 7.13 (d, J = 2.5 Hz, 1H), 7.18 (dd, J = 2.6, 8.9 Hz, 1H), 7.40-7.42 (m, 1H), 7.47-7.51 (m, 1H), 7.75-7.82 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 34.4, 43.7, 67.7, 107.3, 118.2, 124.9, 127.2, 127.3, 127.9, 129.8, 130.5, 134.4, 155.3, 182.0; HRMS Calculated for C₁₄H₁₃NO₃S (M⁺) 275.0616, found: 275.0618.

3-(Benzyloxy-methyl)-4,5-dihydro-isothiazole 1,1-Dioxide (11i): Yellowish solid, ¹H NMR (400 MHz, CDCl₃): δ = 3.19-3.23 (m, 2H), 3.26-3.30 (m, 2H), 4.42 (s, 2H), 4.62 (s, 2H), 7.32-7.40 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ = 34.3, 43.6, 69.6, 74.0, 128.2, 128.6, 128.9, 136.6, 183.3; HRMS Calculated for C₁₁H₁₃NO [M - SO₂]⁺ 175.0997, found: 175.1008.

Typical procedure for asymmetric hydrogenation of imines: (*S*)-SegPhos (2.9 mg, 0.0048 mmol) and Pd(CF₃CO₂)₂ (1.3 mg, 0.004 mmol) were placed in a dried Schlenk tube under nitrogen atmosphere, and degassed anhydrous acetone was added. The mixture was stirred at r.t. for 1 h. The solvent was removed under vacuum to give the catalyst. This catalyst was taken into a glove box filled with nitrogen and dissolved in dry TFE. To the mixture of imine (0.2 mmol) and 4A MS (50 mg if it was added) was added this catalyst solution, and then the mixture was transferred to an autoclave. The autoclave was stirred under directed condition (oil bath temperature was showed if it was heated). After release of the hydrogen, the autoclave was opened and the reaction mixture was evaporated. Conversion was directly determined by ¹H NMR spectroscopy. The enantiomeric excess was determined by HPLC after purification on silica gel using petroleum ether and EtOAc. Observingly, containing 1% Et₃N should be utilized, otherwise the remains on silica gel resulted in lower isolated yield for purification of *N*-(diphenylphosphinyl)amines. The absolute configuration was determined by comparison of rotation sign with literature data or by analogue.

A large scale experiments on the asymmetric hydrogenation of 11d (SCHEME 2 in text): (*S*)-SegPhos (60.4 mg, 0.099 mmol) and Pd(CF₃CO₂)₂ (29.9 mg, 0.09 mmol) were placed in a dried Schlenk tube under nitrogen atmosphere, and degassed anhydrous acetone (8 ml) was added. The mixture was stirred at r.t. for 2 h. The solvent was removed under vacuum to give the catalyst. This catalyst was taken into a glove box filled with nitrogen and dissolved in dry TFE (16 ml). To the mixture of **11d** (1.014 g, 4.5 mmol) was added this catalyst solution, and then the mixture was transferred to an autoclave. The autoclave was stirred at rt for 20 h. After release of the hydrogen, the autoclave was opened and the reaction mixture was evaporated. The residue was purified by flash column chromatography (petroleum ether / EtOAc: 1/1) to give **12d** (1.013 g, yield 99%, 93% ee). The obtained **12d** was recrystallized from 10 ml EtOH/H₂O (3/2, V/V) to give the white solid (738 mg, yield 72%, >99% ee).

Racemates of aryl glycine **2f** were prepared by the reduction of the corresponding imines under 1 atm H_2 with 5% Pd/C at rt for 20 min. Racemates of *N*-(diphenylphosphinyl)amines **4** were prepared by the reduction of the corresponding imines using NaBH₄ in THF. Racemates of **2a**, *N*-tosylamines **6** and sultams **8**, **12**, **14** were prepared by the reduction of the corresponding imines using NaBH₄ in MeOH.

Preparation of complex PdCl₂-(S)-SYNPHOS:¹¹ $PdCl_2(CH_3CN)_2$ (77.8 mg, 0.3 mmol) was suspended in 5 mL of benzene. (S)-SYNPHOS (287 mg, 0.45mmol) was added and the mixture was stirred at room temperature. The yellow precipitate was collected by filtration and washed with Et_2O , and dried in vacuo: yield of $[Pd((S)-SYNPHOS)][Cl]_2$ 242 mg (99%).

Preparation of complex Pd(OTf)₂-(**S**)-**SYNPHOS**:¹² The orange powder [Pd((S)-SYNPHOS)][Cl]₂ (0.210 g, 0.257 mmol) was placed into a Schlenk flask equipped with a stirbar and dissolved in CH₂Cl₂ (16 mL). Then, 0.159 g (0.620 mmol) of AgOTf was added, and the resulting solution was stirred under nitrogen for 20 h at room temperature. The precipitate was filtered, and the filtrate was reduced in volume to about 3 mL in vacuo. Then 5 ul (0.334 mmol) of distilled water was added, followed by the addition 12 mL of Et₂O. The yellow precipitate was collected by filtration and washed with Et₂O and was dried in vacuo: yield of [Pd((S)-SYNPHOS)(H₂O)][OTf]₂ 254 mg (93%).

4-Methoxy-N-(1-phenylethyl)benzenamine (2a):¹³ Yellow oil, ¹H NMR (400 MHz, CDCl₃): $\delta = 1.50$ (d, J = 6.8 Hz, 3H), 3.69 (s, 3H), 4.40-4.42 (m, 1H), 6.46-6.48 (m, 2H), 6.68-6.70 (m, 2H), 7.22-7.25 (m, 1H), 7.29-7.37 (m, 4H); HPLC (Chiralcel OD-H column, hexane/*i*PrOH 97/3, 1.0 mL min⁻¹, 254 nm): t₁ = 10.3 min (R), t₂ = 11.4 min (S).

Ethyl 2-(4-methoxyphenylamino)-2-phenylacetate (2f):¹⁴ Yellow oil, ¹H NMR (400 MHz, CDCl₃): $\delta = 1.20$ (t, J = 7.2 Hz, 3H), 3.70 (s, 3H), 4.10-4.26 (m, 2H), 5.00 (s, 1H), 6.55 (d, J = 8.8 Hz, 2H), 6.72 (d, J = 8.8 Hz, 2H), 7.28-7.36 (m, 3H), 7.48-7.50 (m, 2H); HPLC (Chiralcel OJ-H column, hexane/*i*PrOH 70/30, 1.0 mL min⁻¹, 254 nm): t₁ = 21.2 min, t₂ = 24.1 min.

N-(1-Phenyl-ethyl)-diphenylphosphinamide (4a):^{2,3} White solid, 95% *ee* (R), $[\alpha]^{26}_{D}$ = +38.3 (*c* 0.54, EtOH); ¹H NMR (400 MHz, CDCl₃): δ = 1.58 (d, *J* = 6.7 Hz, 3H), 3.17 (dd, *J* = 5.9, 9.1 Hz, 1H), 4.36-4.43 (m, 1H), 7.26-7.45 (m, 11H), 7.80-7.85 (m, 2H), 7.89-7.93 (m, 2H); HPLC (Chiralpak AS-H column, hexane/*i*PrOH 80/20, 1.0 mL min⁻¹, 254 nm): t₁ = 12.9 min (R), t₂ = 24.4 min (S).

N-[1-(4-Methylphenyl)ethyl]-diphenylphosphinamide (4b):³ White solid, 97% *ee* (S), $[\alpha]_{D}^{8} = -66.5$ (*c* 1.08, MeOH); R_f = 0.22 (PE/EtOAc, 2:1); ¹H NMR (400 MHz, CDCl₃): $\delta = 1.56$ (d, J = 6.8 Hz, 3H), 2.34 (s, 3H), 3.14-3.17 (m, 1H), 4.32-4.39 (m, 1H), 7.15 (dd, J = 8.0, 20.4 Hz, 4H), 7.37-7.48 (m, 6H), 7.81-7.91 (m, 4H); HPLC (Chiralpak AS-H column, hexane/*i*PrOH 80/20, 1.0 mL min⁻¹, 254 nm): t₁ = 11.4 min (R), t₂ = 15.8 min (S).

N-[1-(4-Methoxylphenyl)ethyl]-diphenylphosphinamide (4c):³ White solid, 96% *ee* (S), $[\alpha]_{D}^{8}$ = -66.4 (*c* 1.30, MeOH); ¹H NMR (400 MHz, CDCl₃): δ = 1.55 (d, *J* = 6.7 Hz, 3H), 3.12 (dd, *J* = 5.9, 9.4 Hz, 1H), 3.80 (s, 3H), 4.31-4.41 (m, 1H), 6.85 (d, *J* = 8.7Hz, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 7.37-7.48 (m, 6H), 7.81-7.91 (m, 4H); HPLC (Chiralpak AS-H column, hexane/*i*PrOH 80/20, 1.0 mL min⁻¹, 254 nm): t₁ = 15.9 min (R), t₂ = 26.8 min (S).

N-[1-(4-Fluorophenyl)ethyl]-diphenylphosphinamide (4d):³ White solid, 94% *ee* (S), $[\alpha]_D^8 = -41.9 (c \ 1.04, MeOH)$; ¹H NMR (400 MHz, CDCl₃): $\delta = 1.55 (d, J = 6.8 \text{ Hz}, 3\text{H})$, 3.11 (dd, J = 5.9, 9.2 Hz, 1H), 4.35-4.42 (m, 1H), 6.98 (t, J = 8.7 Hz, 2H), 7.23-7.25 (m, 2H), 7.36-7.37 (m, 2H), 7.44-7.46 (m, 4H), 7.78-7.81 (m, 2H), 7.88-7.92 (m, 2H); HPLC (Chiralpak AS-H column, hexane/*i*PrOH 80/20, 1.0 mL min⁻¹, 254 nm): t₁ = 10.0 min (R), t₂ = 27.0 min (S).

N-[1-(4-Chlorophenyl)ethyl]-diphenylphosphinamide (4e):³ White solid, 94% *ee* (S), $[\alpha]_{D}^{8} = -73.4 (c \ 1.14, MeOH); {}^{1}H NMR (400 MHz, CDCl_{3}): \delta = 1.55 (d, J = 6.8 Hz, 3H), 3.17 (dd, J = 6.8 Hz), 3.17 (dd, J = 6.8 Hz),$

= 5.7, 9.5 Hz, 1H), 4.33-4.40 (m, 1H), 7.24 (dd, J = 8.5, 23.0 Hz, 4H), 7.37-7.47 (m, 6H), 7.79 (dd, J = 7.0, 12.0, 2H), 7.90 (dd, J = 6.9, 11.9 Hz, 2H); HPLC (Chiralpak AS-H column, hexane/*i*PrOH 80/20, 1.0 mL min⁻¹, 254 nm): t₁ = 11.4 min (R), t₂ = 26.3 min (S).

N-[1-(3-Methoxylphenyl)ethyl]-diphenylphosphinamide (**4f**):³ White solid, 96% *ee* (S), $[\alpha]_D^8 = -52.1 (c \ 1.32, MeOH)$; ¹H NMR (400 MHz, CDCl₃): $\delta = 1.57 (d, J = 6.8 \text{ Hz}, 3\text{H})$, 3.22 (dd, J = 5.9, 9.5 Hz, 1H), 3.78 (s, 3H), 4.31-4.39 (m, 1H), 6.82-6.88 (m, 3H), 7.21-7.23 (m, 1H), 7.36-7.47 (m, 6H), 7.80-7.93 (m, 4H); HPLC (Chiralpak AS-H column, hexane/*i*PrOH 80/20, 1.0 mL min⁻¹, 254 nm): $t_1 = 14.5 \text{ min (R)}, t_2 = 29.4 \text{ min (S)}.$

N-[1-(3-Methoxylphenyl)ethyl]-diphenylphosphinamide (**4g**):³ White solid, 99% *ee* (S), $[\alpha]_{D}^{8} = -22.1$ (*c* 1.13, MeOH); ¹H NMR (400 MHz, CDCl₃): $\delta = 1.50$ (d, J = 6.8 Hz, 3H), 3.69 (s, 3H), 3.87 (dd, J = 8.0, 10.5 Hz, 1H), 4.36-4.43 (m, 1H), 6.78-6.82 (m, 2H), 6.97 (s, 1H), 7.19 (t, J = 7.7 Hz, 1H), 7.33-7.38 (m, 6H), 7.72 (dd, J = 7.3, 11.9 Hz, 2H), 7.79 (dd, J = 7.1, 11.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 25.1$, 49.6, 55.4, 111.2, 121.0, 128.3 (d, J = 7.0 Hz), 128.5, 131.7, 131.8, 128.1 (d, J = 108.6 Hz), 131.7, 131.8, 132.0 (d, J = 9.3 Hz), 132.8 (d, J = 9.4 Hz), 133.0, 133.1, 133.8 (d, J = 119.7 Hz), 157.0; ³¹P NMR (162 MHz, CDCl₃): $\delta = 22.9$; HRMS Calculated for C₂₁H₂₂NO₂P (M+1) 352.1461, found 352.1451; HPLC (Chiralpak AS-H column, hexane/*i*PrOH 80/20, 1.0 mL min⁻¹, 254 nm): t₁ = 11.9 min (*R*), t₂ = 21.3 min (S).

N-(1-Naphthalen-1-yl-ethyl)-diphenylphosphinamide (**4h**):² White solid; ¹H NMR (400 MHz, CDCl₃): $\delta = 1.70$ (d, J = 6.7 Hz, 3H), 3.35-3.38 (m, 1H), 5.23-5.25 (m, 1H), 7.26-7.27 (m, 2H), 7.41-7.51 (m, 7H), 7.62 (m, 1H), 7.74-7.78 (m, 3H), 7.86-7.93 (m, 4H).

N-(1-Naphthalen-2-yl-ethyl)-diphenylphosphinamide (4i):^{2,3} White solid, 93% *ee* (S), $[\alpha]_{D}^{8} = -77.8$ (*c* 1.02, MeOH); ¹H NMR (400 MHz, CDCl₃): $\delta = 1.66$ (d, J = 6.7 Hz, 3H), 3.27-3.31 (m, 1H), 4.51-4.61 (m, 1H), 7.32-7.33 (m, 2H), 7.43-7.48 (m, 7H), 7.65 (s, 1H), 7.80-7.83 (m, 5H), 7.93 (m, 2H); HPLC (Chiralpak AS-H column, hexane/*i*PrOH 80/20, 1.0 mL min⁻¹, 254 nm): t₁ = 21.6 min (R), t₂ = 27.7 min (S).

N-(1-Furylethyl)-diphenylphosphinamide (4j):³ White solid, 87% *ee* (S), $[\alpha]_{D}^{8} = -42.1$ (*c* 0.60, CH₂Cl₂); ¹H NMR (400 MHz, CDCl₃): $\delta = 1.60$ (d, J = 6.8 Hz, 3H), 3.19 (dd, J = 6.6, 10.3 Hz, 1H), 4.38-4.44 (m, 1H), 6.13 (d, J = 3.2 Hz, 1H), 6.28 (dd, J = 1.9, 3.2 Hz, 1H), 7.35 (m, 1H), 7.42-7.49 (m, 6H), 7.87-7.95 (m, 4H); HPLC (Chiralpak AS-H column, hexane/*i*PrOH 80/20, 1.0 mL min⁻¹, 254 nm): t₁ = 12.1 min (R), t₂ = 17.0 min (S).

N-(1-Phenyl-propyl)-diphenylphosphinamide (4k):³ White solid, 87% *ee* (S), $[\alpha]_{D}^{8} = -38.5$ (*c* 1.26, MeOH); ¹H NMR (400 MHz, CDCl₃): $\delta = 0.79$ (t, J = 7.4 Hz, 3H), 1.80-1.89 (m, 1H), 1.97-2.04 (m, 1H), 3.25 (dd, J = 6.4, 9.4 Hz, 1H), 4.08-4.11 (m, 1H), 7.14-7.16 (m, 2H), 7.23-7.33 (m, 5H), 7.42-7.44 (m, 4H), 7.73-7.87 (m, 4H); HPLC (Chiralpak AS-H column, hexane/*i*PrOH 80/20, 1.0 mL min⁻¹, 254 nm): t₁ = 9.6 min (R), t₂ = 17.7 min (S).

1-Phenyl-N-tosylethanamine (6a):⁵ White solid, 96% *ee* (*S*), $[\alpha]_{D}^{15} = -63.7$ (*c* 0.95, EtOH); ¹H NMR (400 MHz, CDCl₃): $\delta = 1.43$ (d, J = 6.8 Hz, 3H), 2.39 (s, 3H), 4.44-4.48 (m, 1H), 4.77 (d, J = 6.7 Hz, 1H) 7.09-7.11 (m, 2H), 7.17-7.21 (m, 5H), 7.62 (d, J = 8.2 Hz, 2H); HPLC (Chiralcel OD-H column, iPrOH/hexane 20/80, 1.0 mL min⁻¹, 254nm): t₁ = 6.4 min (*R*), t₂ = 7.4 min (*S*).

1-(4-Fluorophenyl)-N-tosylethanamine (6b):⁵ White solid, 96% *ee* (*S*), $[\alpha]^{15}{}_{D} = -58.2$ (*c* 1.02, EtOH); ¹H NMR (400 MHz, CDCl₃): $\delta = 1.39$ (d, J = 6.9 Hz, 3H), 2.39 (s, 3H), 4.42-4.49 (m, 1H), 4.90 (d, J = 6.6 Hz, 1H), 6.87 (t, J = 8.7 Hz, 2H), 7.05-7.09 (m, 2H), 7.19 (d, J = 8.1 Hz, 2H), 7.60 (d, J = 8.2 Hz, 2H); HPLC (Chiralcel OD-H column, iPrOH/hexane 20/80, 1.0 mL min⁻¹, 254nm): t₁ = 6.3 min (*R*), t₂ = 6.9 min (*S*).

1-(4-Methoxyphenyl)-N-tosylethanamine (6c):⁵ White solid, 97% *ee* (*S*), $[\alpha]_{D}^{15} = -65.3$ (*c* 0.75, EtOH); ¹H NMR (400 MHz, CDCl₃): $\delta = 1.40$ (d, J = 6.8 Hz, 3H), 2.39 (s, 3H), 3.76 (s, 3H), 4.38-4.44 (m, 1H), 4.77 (br, 1H), 6.71-6.74 (m, 2H), 7.00-7.03 (m, 2H), 7.20 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 8.0 Hz, 2H); HPLC (Chiralcel OJ-H column, iPrOH/hexane 20/80, 0.8 mL min⁻¹, 254nm): t₁ = 22.5 min (*S*), t₂ = 26.6 min (*R*).

1-(3-Methoxyphenyl)-N-tosylethanamine (6d):⁵ Colorless oil, 93% *ee* (*S*), $[\alpha]_{D}^{15} = -46.5$ (*c* 1.02, EtOH); ¹H NMR (400 MHz, CDCl₃): $\delta = 1.41$ (d, J = 6.8 Hz, 3H), 2.38 (s, 3H), 3.69 (s, 3H), 4.39-4.46 (m, 1H), 4.98 (d, J = 6.9 Hz, 1H), 6.58 (t, J = 1.9 Hz, 1H), 6.69-6.72 (m, 2H), 7.11 (t, J = 7.9 Hz, 1H), 7.18 (d, J = 8.1 Hz, 2H), 7.62 (d, J = 8.2 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 21.7$, 23.7, 53.8, 55.3, 111.9, 113.2, 118.6, 127.3, 129.6, 129.8, 137.8, 143.3, 143.8, 159.8; HPLC (Chiralcel OD-H column, iPrOH/hexane 20/80, 0.8 mL min⁻¹, 254nm): t₁ = 9.2 min (*R*), t₂ = 10.2 min (*S*).

1-(2-Methoxyphenyl)-N-tosylethanamine (6e):¹⁵ White solid, 94% *ee* (*S*), $[\alpha]^{15}_{D} = -33.8$ (*c* 0.90, EtOH); ¹H NMR (400 MHz, CDCl₃): $\delta = 1.45$ (d, J = 7.0 Hz, 3H), 2.31 (s, 3H), 3.70 (s, 3H), 4.50-4.58 (m, 1H), 5.50 (d, J = 9.5 Hz, 1H), 6.61 (t, J = 8.2 Hz, 1H), 6.73 (t, J = 7.4 Hz, 1H), 6.91 (dd, J = 1.5, 7.5 Hz, 1H), 7.03 (d, J = 8.1 Hz, 2H), 7.06-7.11 (m, 1H), 7.49 (d, J = 8.2 Hz, 2H); HPLC (Chiralcel OJ-H column, iPrOH/hexane 20/80, 0.8 mL min⁻¹, 254nm): t₁ = 13.6 min (*S*), t₂ = 15.5 min (*R*).

1-(Naphthalen-2-yl)-N-tosylethanamine (6f):⁵ White solid, 95% *ee* (*S*), $[\alpha]^{15}_{D} = -53.8$ (*c* 1.10, EtOH); ¹H NMR (400 MHz, CDCl₃): $\delta = 1.51$ (d, J = 6.8 Hz, 3H), 2.24 (s, 3H), 4.60-4.67 (m, 1H), 4.90-4.95 (m, 1H), 7.03 (d, J = 8.1 Hz, 2H), 7.20 (dd, J = 1.6, 7.7 Hz, 1H), 7.43-7.46 (m, 3H), 7.57 (d, J = 8.2 Hz, 2H), 7.65-7.67 (m, 2H), 7.73-7.75 (m, 1H); HPLC (Chiralcel OD-H column, iPrOH/hexane 20/80, 0.8 mL min⁻¹, 254nm): t₁ = 10.2 min (*R*), t₂ = 11.9 min (*S*).

1-Phenyl-N-tosylpropan-1-amine (6g):⁵ White solid, 88% *ee* (*S*), $[\alpha]^{15}_{D} = -43.3$ (*c* 0.70, EtOH); ¹H NMR (400 MHz, CDCl₃): $\delta = 0.78$ (t, J = 7.4 Hz, 3H), 1.68-1.85 (m, 2H), 2.36 (s, 3H), 4.19 (q, J = 7.2 Hz, 1H), 4.76 (d, J = 6.5 Hz, 1H), 6.99-7.01 (m, 2H), 7.11 (d, J = 8.1 Hz, 2H), 7.14-7.16 (m, 3H), 7.53 (d, J = 8.2 Hz, 2H); HPLC (Chiralcel OD-H column, iPrOH/hexane 20/80, 0.8 mL min⁻¹, 254nm): t₁ = 6.8 min (*R*), t₂ = 7.9 min (*S*).

3,3-Dimethyl-N-tosylbutan-2-amine (6h):⁵ White solid, 91% *ee* (*S*), $[\alpha]_{D}^{15} = -28.5$ (*c* 0.92, EtOH); ¹H NMR (400 MHz, CDCl₃): $\delta = 0.82$ (s, 9H), 0.89 (d, J = 6.8 Hz, 3H), 2.43 (s, 3H), 3.02-3.09 (m, 1H), 4.12 (d, J = 9.6 Hz, 1H), 7.30 (d, J = 8.2 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H); HPLC (Chiralpak AS-H column, iPrOH/hexane 20/80, 0.8 mL min⁻¹, 254nm): t₁ = 8.6 min (*S*), t₂ = 11.5 min (*R*).

3-Methyl-1,2-benzisothiazoline 1,1-Dioxide (8a):^{6a, 6c} White solid, 91% *ee* (*R*), $[\alpha]_{D}^{15} = 23.7$ (*c* 0.90, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 1.62$ (d, J = 6.6 Hz, 3H), 4.77 (br, 1H), 4.78-4.81 (m, 1H), 7.40 (d, J = 7.8 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 7.62-7.66 (m, 1H), 7.78 (d, J = 7.8 Hz, 1H); HPLC (Chiralcel OD-H column, iPrOH/hexane 20/80, 0.8 mL min⁻¹, 254nm): t₁ = 12.4 min (*S*), t₂ = 15.2 min (*R*).

3-Butyl-1,2-benzisothiazoline 1,1-Dioxide (8b):^{6c} White solid, 90% *ee* (*R*), $[\alpha]_{D}^{15} = 46.6$ (*c* 1.12, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 0.92$ (t, J = 7.2 Hz, 3H), 1.36-1.48 (m, 4H), 1.75-1.78 (m, 1H), 1.97-1.99 (m, 1H), 4.67-4.72 (m, 1H), 4.95 (br, 1H), 7.39 (d, J = 7.6 Hz, 1H), 7.52 (t, J = 7.4 Hz, 1H), 7.62(t, J = 7.6 Hz, 1H), 7.77 (d, J = 7.6 Hz, 1H); HPLC (Chiralcel OD-H column, iPrOH/hexane 20/80, 0.8 mL min⁻¹, 254nm): t₁ = 9.2 min (*S*), t₂ = 16.1 min (*R*).

3-Benzyl-1,2-benzisothiazoline 1,1-Dioxide (8c):^{6b, 6c} White solid, 88% *ee* (*R*), $[\alpha]^{15}_{D} = 42.3$ (*c*

1.00, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 3.01$ (dd, J = 9.6, 13.8 Hz, 1H), 3.28 (dd, J = 4.8, 13.8 Hz, 1H), 4.64 (d, J = 3.4 Hz, 1H), 4.86-4.91 (m, 1H), 7.27-7.37 (m, 6H), 7.55-7.62 (m, 2H), 7.80 (d, J = 7.6 Hz, 1H); HPLC (Chiralcel OD-H column, iPrOH/hexane 20/80, 0.8 mL min⁻¹, 254nm): $t_1 = 15.0 \min(S)$, $t_2 = 19.2 \min(R)$.

3-Phenyl-1,2-thiazolidine 1,1-Dioxide (12a):¹⁶ White solid, 79% *ee* (S), $[\alpha]_{D}^{15} = -30.8$ (c 0.46, EtOH); ¹H NMR (400 MHz, CDCl₃): δ = 2.39-2.41 (m, 1H), 2.75-2.78 (m, 1H), 3.17-3.25 (m, 1H), 3.33-3.38 (m, 1H), 4.60 (br, 1H), 4.71-4.76 (m, 1H), 7.32-7.42 (m, 5H); HPLC (Chiralcel OD-H column, iPrOH/hexane 20/80, 0.8 mL min⁻¹, 254nm): $t_1 = 20.9 min(S)$, $t_2 = 25.0 min(R)$.

3-Methyl-1,2-thiazolidine 1,1-Dioxide (12b): Colorless oil, 88% *ee* (*R*), $[\alpha]_{D}^{30} = 0.4$ (*c* 0.60, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 1.34$ (d, J = 6.3 Hz, 3H), 2.03-2.08 (m, 1H), 2.52-2.54 (m, 2H), 2.52-2.54 (m, 2 1H), 3.10-3.18 (m, 1H), 3.21-3.27 (m, 1H), 3.72-3.76 (m, 1H), 4.13 (br, 1H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 21.5$, 32.0, 48.6, 51.1; HRMS Calculated for C₄H₉NO₂S (M⁺) 135.0354, found 135.0350. Ee of this product was determined by the analysis of products derived by the cinnamyl bromine.

 $\sim \overset{O_2}{\underset{l}{\sim}}$ Ph[^] N-Cinnamyl-3-Methyl-1,2-thiazolidine 1,1-Dioxide: To a solution of

12b in THF was added sodium hydride (60% dispersion in mineral oil) at 0°C. After the reaction mixture was stirred for 30 min at rt, the cinnamyl bromine (2 equiv.) was introduced. To accelerate the reaction, tetrabutylammonium bromide (TBAB) as PTC was added, and then the reaction was stirred overnight. The water was added, and the mixture was extracted with ether. The organic extracts were dried over Na₂SO₄ and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc) to give a colorless oil: 88% ee (*R*), ¹H NMR (400 MHz, CDCl₃): $\delta = 1.26-1.29$ (m, 3H), 1.97-2.03 (m, 1H), 2.42-2.44 (m, 1H), 3.04-3.08 (m, 1H), 3.24-3.27 (m, 1H), 3.49-3.52 (m, 1H), 3.79-3.85 (m, 1H), 3.95-3.99 (m, 1H), 6.21-6.28 (m, 1H), 6.59 (d, J = 15.9 Hz, 1H), 7.23-7.27 (m, 1H), 7.30-7.34 (m, 2H), 7.37-7.39 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 20.1, 27.5, 45.1, 46.8, 53.2, 124.5, 126.7, 128.2, 128.8, 2000, 12000, 1200, 1200, 1200, 1200, 1200, 1200, 1200, 1200, 1200, 1200, 1200, 1200, 1200, 1200, 12$ 134.2, 136.4; HRMS Calculated for C13H17NO2S (M⁺) 251.0980, found 251.0973; HPLC (Chiralcel OJ-H column, iPrOH/hexane 30/70, 0.8 mL min⁻¹, 254nm): t₁ = 19.1 min (S), t₂ = 25.9 $\min(R)$.

3-Hexyl-1,2-thiazolidine 1,1-Dioxide (12c):^{16b} White solid, 90% *ee* (*R*), $[\alpha]_{D}^{27} = 8.7$ (*c* 1.02, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 0.85 \cdot 0.89$ (m, 3H), 1.27-1.39 (m, 8H), 1.51-1.63 (m, 2H), 2.02-2.10 (m, 1H), 2.46-2.52 (m, 1H), 3.05-3.13 (m, 1H), 3.17-3.23 (m, 1H), 3.53-3.59 (m, 1H), 4.36 (br, 1H); 13 C NMR (100 MHz, CDCl₃): $\delta = 14.2, 22.7, 26.2, 29.1, 30.1, 31.8, 36.1, 48.2, 55.5;$ HRMS Calculated for C₉H₁₉NO₂S (M⁺) 205.1137, found: 205.1139. Ee of this product was determined by the analysis of products derived by the cinnamyl bromine.

N-Cinnamyl-3-Hexyl-1,2-thiazolidine 1,1-Dioxide: It was prepared in Ph N^{-S} $n^{-C_{6}H_{13}}$ (m 8H) 1.46-1.49 (m 1H) 1.73-1.79 (m 1H) 2.01-2.08 (m 1H) (m, 8H), 1.46-1.49 (m, 1H), 1.73-1.79 (m, 1H), 2.01-2.08 (m, 1H),

2.37-2.43 (m, 1H), 2.96-3.04 (m, 1H), 3.20-3.27 (m, 1H), 3.37-3.41 (m, 1H), 3.82 (dd, J = 8.1, 15.8 Hz, 1H), 3.98 (dd, J = 5.4, 15.8 Hz, 1H), 6.20-6.27 (m, 1H), 6.58 (d, J = 15.8 Hz, 1H), 7.23-7.27 (m, 1H)1H), 7.30-7.39 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 14.2, 22.7, 24.4, 25.0, 29.3, 31.8, 33.6,$ 45.8, 46.8, 57.2, 124.5, 126.7, 128.1, 128.8, 134.3, 136.4; HRMS Calculated for C₁₈H₂₇NO₂S (M⁺) 321.1763, found: 321.1762; HPLC (Chiralcel OJ-H column, iPrOH/hexane 20/80, 0.8 mL min⁻¹,

254nm): $t_1 = 11.8 \min(S)$, $t_2 = 15.4 \min(R)$.

3-Phenoxy-methyl-1,2-thiazolidine 1,1-Dioxide (12d): White solid, 92% *ee* (*S*), $[\alpha]_{D}^{30} = 14.1$ (*c* 1.12, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 2.35-2.38$ (m, 1H), 2.59-2.61 (m, 1H), 3.15-3.26 (m, 2H), 3.99-4.07 (m, 3H), 4.74 (br, 1H), 6.79 (d, *J* = 7.9 Hz, 2H), 7.00 (t, *J* = 7.4 Hz, 1H), 7.28-7.33 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 25.9$, 47.5, 53.3, 69.6, 114.7, 121.9, 129.8, 158.1; HRMS Calculated for C₁₀H₁₃NO₃S (M⁺) 227.0616, found: 227.0619; HPLC (Chiralcel OD-H column, iPrOH/hexane 20/80, 0.8 mL min⁻¹, 254nm): t₁ = 25.2 min (*R*), t₂ = 37.4 min (*S*).

3-[(4-Trifluoromethyl-phenoxy)methyl]-1,2-thiazolidine 1,1-Dioxide (12e): White solid, 93% *ee* (*S*), $[\alpha]^{27}{}_{\rm D}$ = 11.1 (*c* 1.04, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ = 2.35-2.38 (m, 1H), 2.64-2.66 (m, 1H), 3.14-3.21 (m, 1H), 3.26-3.30 (m, 1H), 4.05-4.11 (m, 3H), 4.75 (d, *J* = 4.9 Hz, 1H), 6.97 (d, *J* = 8.7 Hz, 2H), 7.57 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ = 25.7, 47.4, 53.1, 70.1, 114.7, 124.1 (q, *J* = 32 Hz), 124.4 (q, *J* = 270 Hz), 127.3 (d, *J* = 3 Hz), 160.6; HRMS Calculated for C₁₁H₁₂NO₃SF₃ (M⁺) 295.0490, found: 295.0497; HPLC (Chiralcel OJ-H column, iPrOH/hexane 30/70, 0.8 mL min⁻¹, 254nm): t₁ = 17.6 min (*R*), t₂ = 19.6 min (*S*).

3-[(4-Methyl-phenoxy)methyl]-1,2-thiazolidine 1,1-Dioxide (12f): White solid, 91% *ee* (*S*), $[\alpha]^{27}_{D} = 11.1$ (*c* 0.93, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 2.29$ (s, 3H), 2.34-2.37 (m, 1H), 2.57-2.60 (m, 1H), 3.15-3.25 (m, 2H), 3.97-4.04 (m, 3H), 4.70 (d, J = 4.7 Hz, 1H), 6.77-6.80 (m, 2H), 7.09 (d, J = 8.5 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 20.7$, 34.3, 43.6, 67.8, 114.5, 130.6, 132.1, 155.4, 182.5; HRMS Calculated for C₁₁H₁₅NO₃S (M⁺) 241.0773, found: 241.0772; HPLC (Chiralcel OJ-H column, iPrOH/hexane 30/70, 0.8 mL min⁻¹, 254nm): t₁ = 24.8 min (*R*), t₂ = 26.4 min (*S*).

3-[(2-Methyl-phenoxy)methyl]-1,2-thiazolidine 1,1-Dioxide (12g): White solid, 92% *ee* (*S*), $[\alpha]^{27}_{D} = 13.8$ (*c* 1.14, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 2.22$ (s, 3H), 2.34-2.41 (m, 1H), 2.60-2.64 (m, 1H), 3.14-3.28 (m, 2H), 4.01-4.03 (m, 3H), 4.82 (br, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.88-6.92 (m, 1H), 7.13-7.17 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 16.4$, 25.9, 47.4, 53.4, 69.8, 111.2, 121.5, 126.9, 127.1, 131.1, 156.2; HRMS Calculated for C₁₁H₁₅NO₃S (M⁺) 241.0773, found: 241.0781; HPLC (Chiralcel OD-H column, iPrOH/hexane 30/70, 0.8 mL min⁻¹, 254nm): t₁ = 14.1 min (*R*), t₂ = 17.1 min (*S*).

3-[(Naphthalen-2-yloxy)methyl]-1,2-thiazolidine 1,1-Dioxide (12h): White solid, 90% *ee* (*S*), $[\alpha]^{27}_{D} = 1.9$ (*c* 0.99, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 2.35-2.40$ (m, 1H), 2.59-2.63 (m, 1H), 3.15-3.21 (m, 1H), 3.24-3.28 (m, 1H), 4.04-4.07 (m, 1H), 4.10-4.15 (m, 2H), 4.83 (d, *J* = 5.9 Hz, 1H), 7.12-7.14 (m, 2H), 7.35-7.38 (m, 1H), 7.44-7.47 (m, 1H), 7.71-7.78 (m, 3H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 25.9$, 47.5, 53.3, 69.8, 107.2, 118.5, 124.3, 126.8, 127.0, 127.9, 129.5, 129.9, 134.5, 156.0; HRMS Calculated for C₁₄H₁₅NO₃S (M⁺) 277.0773, found: 277.0778; HPLC (Chiralcel OD-H column, iPrOH/hexane 30/70, 0.8 mL min⁻¹, 254nm): t₁ = 35.1 min (*S*), t₂ = 40.7 min (*R*).

3-(Benzyloxy-methyl)-1,2-thiazolidine 1,1-Dioxide (12i): Colorless oil, 86% *ee* (*S*), $[\alpha]^{30}_{D} = 10.5$ (*c* 1.12, CHCl₃); ¹H NMR (400 MHz, CDCl₃): $\delta = 2.19-2.25$ (m, 1H), 2.43-2.47 (m, 1H), 3.10-3.16 (m, 2H), 3.49-3.52 (m, 1H), 3.57-3.60 (m, 1H), 3.77-3.78 (m, 1H), 4.55 (s, 2H), 4.64 (d, *J* = 5.2 Hz, 1H), 7.30-7.38 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 26.1$, 47.6, 53.9, 71.6, 73.6, 128.0, 128.2, 128.8, 137.5; HRMS Calculated for C₁₁H₁₅NO₃S (M⁺) 241.0773, found: 241.0782; HPLC (Chiralcel OD-H column, iPrOH/hexane 20/80, 0.8 mL min⁻¹, 254nm): t₁ = 19.2 min (*R*), t₂ = 24.6 min (*S*).



3-Hydroxymethyl-1,2-thiazolidine 1,1-Dioxide (13): To a solution of (S)-**12i** (52mg, 0.22mmol, 86% *ee*) in MeOH (2 ml) was added 5% Pd/C (104 mg, 50% H₂O) (the reaction can be carried out in the air without special handling). The mixture was transferred to an autoclave, was stirred under 10 atm of hydrogen at rt for 4h. After release of the hydrogen, the autoclave was opened and the reaction mixture was passed on a short silica gel column. The solvent was removed and gave **13** as a colorless oil (31 mg, 95%). 86% *ee* (*S*), $[\alpha]^{29}_{D} = 12.8 (c \ 0.75, CHCl_3)$; ¹H NMR (400 MHz, CDCl_3): $\delta = 2.25-2.35$ (m, 1H), 2.37 (br, 1H), 2.45-2.53(m, 1H), 3.09-3.16 (m, 1H), 3.22-3.28 (m, 1H), 3.61-3.66 (m, 1H) \perp 3.76-3.81 (m, 2H), 4.77 (br, 1H); ¹³C NMR (100 MHz, CDCl_3): $\delta = 25.0, 47.9, 55.7, 64.6$; HRMS Calculated for C₄H₉NO₃SNa [M + Na]⁺ 174.0201, found: 174.0209.

The experimental details of non linear effects:



(S)-SynPhos solution(3.8 mg/2.0 ml): 19.0 mg (S)-SynPhos in 10.0 ml acetone

(R)-SynPhos solution (3.8 mg/2.0 ml): 9.5 mg (R)-SynPhos in 5.0 ml acetone

Preparation of catalyst: X ml (S)-SynPhos solution and Y ml (R)-SynPhos solution were placed in a dried Schlenk tube under nitrogen atmosphere, and stirred for a few minutes. Then $Pd(CF_3CO_2)_2$ (1.7 mg, 0.005 mmol) was added and the mixture was stirred at rt for 1h. The solvent was removed under vacuum to give the corresponding catalyst.

					100%					
Entry	(S)-SynPhos ee	X / Y	12d ee		80% -					/
1	100%	-	88%		0070					
2	80%	1.80 / 0.20	64%	12d	60%				/	
3	60%	1.60 / 0.40	47%	oť				•		
4	40%	1.40 / 0.60	30%	8	40%		/			
5	20%	1.20 / 0.80	12%	•						
Conversion all are >95%					20% -					
				-						
					0% •					
			• 、		0%	20%	40%	60%	80%	100%

ee of (S)-SynPhos

12d ee (Y axis) versus ligand ee (X axis)



Reference

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Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

76 formula(e) evaluated with 6 results within limits (up to 50 closest results for each mass)



9e HRMS







Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%



10c HRMS







Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron lons

168 formula(e) evaluated with 9 results within limits (up to 50 closest results for each mass)











Single Mass Analysis Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0

Selected filters: None

Monoisotopic Mass, Even Electron lons 6 formula(e) evaluated with 2 results within limits (up to 10 closest results for each mass) Elements Used: C: 0-50 H: 0-60 N: 1-1 O: 6-6 F: 3-3 Na: 0-1 S: 1-1 C: 0-50 YW-6-26D 06102300 48 (0.896) 436.1031 TOF MS ES+ 7.43e3 %-380.0446 849.2188 0 m/z 525 575 725 825 850 400 425 450 475 500 550 600 625 650 675 700 750 775 800 Minimum: Maximum: -1.55.0 100.0 5.0 Mass Calc. Mass mDa PPM DBE i-FIT Formula -1.1 1.3 -2.5 3.0 5549726.0 C18 H21 N O6 F3 S 5549723.0 C16 H22 N O6 F3 Na S 🗸 436.1042 436.1018 7.5 436.1031 4.5



Page 1







Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions 288 formula(e) evaluated with 9 results within limits (up to 50 closest results for each mass)



Page 1







S61

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron lons 82 formula(e) evaluated with 3 results within limits (up to 50 closest results for each mass)



10g HRMS







Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions 116 formula(e) evaluated with 4 results within limits (up to 50 closest results for each mass)















Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

170 formula(e) evaluated with 4 results within limits (up to 50 closest results for each mass)



11c HRMS






Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions 169 formula(e) evaluated with 7 results within limits (up to 50 closest results for each mass)





11d HRMS







Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions 277 formula(e) evaluated with 7 results within limits (up to 50 closest results for each mass)





Page 1







Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

177 formula(e) evaluated with 7 results within limits (up to 50 closest results for each mass)



11f HRMS







Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

177 formula(e) evaluated with 7 results within limits (up to 50 closest results for each mass)









Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron lons 197 formula(e) evaluated with 7 results within limits (up to 50 closest results for each mass)









S95

Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

178 formula(e) evaluated with 3 results within limits (up to 50 closest results for each mass)



11i HRMS









Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions 157 formula(e) evaluated with 6 results within limits (up to 50 closest results for each mass)









Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

184 formula(e) evaluated with 5 results within limits (up to 50 closest results for each mass)



HRMS







S108
Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions 202 formula(e) evaluated with 3 results within limits (up to 50 closest results for each mass)









S112

Single Mass Analysis Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron lons 256 formula(e) evaluated with 4 results within limits (up to 50 closest results for each mass)

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Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions 171 formula(e) evaluated with 7 results within limits (up to 50 closest results for each mass)



12d HRMS







Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions 169 formula(e) evaluated with 3 results within limits (up to 50 closest results for each mass)



Page 1







Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron lons 133 formula(e) evaluated with 6 results within limits (up to 50 closest results for each mass)



12f HRMS







Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions 160 formula(e) evaluated with 6 results within limits (up to 50 closest results for each mass)



12g HRMS







Single Mass Analysis Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions 160 formula(e) evaluated with 6 results within limits (up to 50 closest results for each mass)



12h HRMS







Single Mass Analysis

Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0 Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions 133 formula(e) evaluated with 7 results within limits (up to 50 closest results for each mass)









Single Mass Analysis

Page 1

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0 Selected filters: None Monoisotopic Mass, Even Electron lons 3 formula(e) evaluated with 2 results within limits (up to 6 closest results for each mass) Elements Used: C: 0-50 H: 0-100 N: 1-1 O: 3-3 Na: 0-1 S: 1-1 Ru: 0-1 . HWS 06090709 16 (0.297) 1: TOF MS ES+ 3.59e3 174.0209 100-%-_____ m/z 173.900 173.950 174.000 174.050 174.100 174.150 Minimum: -1.5 Maximum: 5.0 50.0 50.0 Mass Calc. Mass mDa PPM DBE i-FIT Formula 174.0201 174.0225 0.8 -1.6 0.5 3.5 5547724.5 C4 H9 N O3 Na S 5547755.0 C6 H8 N O3 S 174.0209 4.6 -9.2 O_2 HN-S HO 13 HRMS



Data File C:\HPCHEM\1\DATA\ZHOU-05\YZ002723.D

Sample Name: YW-4-82

AS-H, H/i-PrOH=80/20, 1.0 mL/min



Instrument 1 3/17/2007 2:27:24 PM WANG

Page 1 of 1

Data File C:\HPCHEM\1\DATA\ZHOU-05\YZ002749.D

Sample Name: YW-4-86G

AS-H, H/i-PrOH=80/20, 1.0 mL/min



Instrument 1 3/17/2007 2:32:36 PM WANG

Page 1 of 1
Data File C:\HPCHEM\1\DATA\ZHOU-05\YZ002902.D

Sample Name: YW-4-97D

AS-H, H/i-PrOH=80/20, 1.0 mL/min



Instrument 1 3/17/2007 2:36:27 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-05\YZ002908.D

Sample Name: YW-5-24D1

AS-H, H/i-PrOH=80/20, 1.0 mL/min



Instrument 1 3/17/2007 2:38:55 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-05\YZ002914.D

AS-H, H/i-PrOH=80/20, 1.0 mL/min



Instrument 1 3/17/2007 2:42:24 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-05\YZ002915.D

Sample Name: YW-5-24C

AS-H, H/i-PrOH=80/20, 1.0 mL/min



Instrument 1 3/17/2007 2:45:49 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-05\YZ002910.D

Sample Name: YW-5-97B(R)

AS-H, H/i-PrOH=80/20, 1.0 mL/min

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Signal 1: VWD1 Peak RetTime Ty # [min] 	A, Waveleng pe Width [min] [] 0.4440	gth=254 nm Area H mAU *s [mA 	eight Ar U 1 1 1.87478 49.	ea *	HN (+/-)-4d
Signal 1: VWD1 Peak RetTime Ty # [min] 	A, Waveleng pe Width [min] 0.4440 1.5190	yth=254 nm Area H MAU *s [mA 3481.85571 12 3504.50293 3	eight Ar U 1 1 1.87478 49. 5.04414 50.	ea * 8379 1621 F	HN ⁻¹ (0)1 H ₂ (+/-)-4d
Signal 1: VWD1 Peak RetTime Ty # [min] 	A, Waveleng pe Width [min] 0.4440 1.5190	th=254 nm Area H mAU *s ImA 	eight Ar U 1 1.87478 49. 5.04414 50.	ea 8379 1621 F	HN ⁻¹ (0) ¹ H ₂ (+/-)-4d
Signal 1: VWD1 Peak RetTime Ty # [min] 	A, Waveleng pe Width [min] 0.4440 1.5190	rth=254 nm Area H mAU *s [mA 3481.85571 12 3504.50293 3 6986.35864 15	eight Ar U 1 1.87478 49. 5.04414 50. 6.91892	ea ⁸³⁷⁹ 1621 F	HN ⁻¹ (0) ¹ H ₂ (+/-)-4d
Signal 1: VWD1 Peak RetTime Ty # [min] 1	A, Waveleng pe Width [min] 	th=254 nm Area H mAU *s [mA 	eight Ar U 1 1.87478 49. 5.04414 50. 6.91892 or!	ea *	HN ⁻¹ (0) ¹ H ₂ (+/-)-4d
Signal 1: VWD1 Peak RetTime Ty # [min] 1 10.010 VB 2 27.007 BB Totals : Results obtain	A, Waveleng pe Width [min] 0.4440 1.5190 ed with enh	th=254 nm Area H mAU *s [mA 	eight Ar U 1 1.87478 49. 5.04414 50. 6.91892 or!	ea 8379 1621 F	HN (0) H2 (+/-)-4d
Signal 1: VWD1 Peak RetTime Ty # [min] 	A, Waveleng pe Width [min] 0.4440 1.5190 ed with enh	th=254 nm Area H mAU *s [mA 	eight Ar U 1 1.87478 49. 5.04414 50. 6.91892 or! 	ea 8379 1621 F	HN ⁻¹ (0) ¹ H ₂ (+/-)-4d

Instrument 1 3/17/2007 2:48:40 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-05\YZ002911.D

Sample Name: YW-5-24A

AS-H, H/i-PrOH=80/20, 1.0 mL/min



Instrument 1 3/17/2007 2:50:14 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-05\YZ002912.D

Sample Name: YW-4-97E

AS-H, H/i-PrOH=80/20, 1.0 mL/min



Instrument 1 3/17/2007 2:52:45 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-05\YZ002913.D

Sample Name: YW-4-24B

AS-H, H/i-PrOH=80/20, 1.0 mL/min



Instrument 1 3/17/2007 2:53:53 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-05\YZ002933.D

Sample Name: YW-5-34B (rac)

AS-H, H/i-PrOH=80/20, 1.0 mL/min



Instrument 1 3/17/2007 3:07:02 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-05\YZ002934.D

Sample Name: YW-5-33B

AS-H, H/i-PrOH=80/20, 1.0 mL/min



Instrument 1 3/17/2007 3:09:00 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-05\YZ002931.D

Sample Name: YW-5-34A (rac)

AS-H, H/i-PrOH=80/20, 1.0 mL/min



Instrument 1 3/17/2007 3:11:19 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-05\YZ002964.D

Sample Name: YW-5-35C

AS-H, H/i-PrOH=80/20, 1.0 mL/min



Instrument 1 3/17/2007 3:20:18 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-05\YZ002807.D

Sample Name: YW-4-97C(R)

AS-H, H/i-PrOH=80/20, 1.0 mL/min



Instrument 1 3/17/2007 3:27:22 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-05\YZ002962.D

Sample Name: YW-5-35A

AS-H, H/i-PrOH=80/20, 1.0 mL/min



Instrument 1 3/17/2007 3:30:41 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-05\YZ002929.D

Sample Name: YW-5-13C (Rac)

AS-H, H/i-PrOH=80/20, 1.0 mL/min



Instrument 1 3/17/2007 3:33:38 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-05\YZ002994.D

Sample Name: YW-5-35C'

AS-H, H/i-PrOH=80/20, 1.0 mL/min



Instrument 1 3/17/2007 3:35:14 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-05\YZ002927.D

Sample Name: YW-5-13B (rac)

AS-H, H/i-PrOH=80/20, 1.0 mL/min



Instrument 1 3/17/2007 3:37:58 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-05\YZ002963.D

Sample Name: YW-5-35B

AS-H, H/i-PrOH=80/20, 1.0 mL/min



Instrument 1 3/17/2007 3:39:54 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003349.D

Sample Name: YW-5-81(R)

OD-H, H/i-PrOH=80/20, 1.0 mL/min, 30 C



Instrument 1 3/16/2007 3:08:52 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003430.D

Sample Name: YW-5-88D

OD-H, H/i-PrOH=80/20, 1.0 mL/min, 30 C



Instrument 1 3/16/2007 3:10:50 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003501.D

Sample Name: YW-5-96B

OD-H, H/i-PrOH=80/20, 1.0 mL/min



Instrument 1 3/16/2007 3:14:45 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003502.D

Sample Name: YW-5-100A

OD-H, H/i-PrOH=80/20, 1.0 mL/min



Instrument 1 3/16/2007 3:16:41 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003521.D

Sample Name: YW-5-96C

0J-H, H/i-PrOH=80/20, 0.8 mL/min



Instrument 1 3/16/2007 3:19:18 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003522.D

Sample Name: YW-5-100E

0J-H, H/i-PrOH=80/20, 0.8 mL/min



Instrument 1 3/16/2007 3:20:48 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003510.D

Sample Name: YW-5-95F

OD-H, H/i-PrOH=80/20, 0.8 mL/min



Instrument 1 3/16/2007 3:22:48 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003511.D

Sample Name: YW-5-101F

OD-H, H/i-PrOH=80/20, 0.8 mL/min



Instrument 1 3/16/2007 3:27:44 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003519.D

Sample Name: YW-5-95G

0J-H, H/i-PrOH=80/20, 0.8 mL/min



Instrument 1 3/16/2007 3:31:56 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003520.D

Sample Name: YW-5-100D

0J-H, H/i-PrOH=80/20, 0.8 mL/min



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Instrument 1 3/16/2007 3:33:39 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003508.D

Sample Name: YW-5-95E

OD-H, H/i-PrOH=80/20, 0.8 mL/min



Instrument 1 3/16/2007 3:35:44 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003509.D

Sample Name: YW-5-101G

OD-H, H/i-PrOH=80/20, 0.8 mL/min



Instrument 1 3/16/2007 3:37:08 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003503.D

Sample Name: YW-5-96D (RAC)

OD-H, H/i-PrOH=80/20, 0.8 mL/min



Instrument 1 3/16/2007 3:41:50 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003504.D

Sample Name: YW-5-100B

OD-H, H/i-PrOH=80/20, 0.8 mL/min



Instrument 1 3/16/2007 3:43:09 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003514.D

Sample Name: YW-5-96A

AS-H, H/i-PrOH=80/20, 0.8 mL/min



Instrument 1 3/17/2007 2:18:11 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003515.D

Sample Name: YW-5-100C

AS-H, H/i-PrOH=80/20, 0.8 mL/min

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2 11.440 BP	0.3284	92.71068	4.18370	4.2627	⊂ ∣ (-)-6h	
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Instrument 1 3/17/2007 2:23:08 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003562.D

Sample Name: YW-6-6B

OD-H, H/i-PrOH=80/20, 0.8 mL/min



Instrument 1 3/16/2007 1:45:33 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003572.D

Sample Name: YW-6-10B

OD-H, H/i-PrOH=80/20, 0.8 mL/min



Instrument 1 3/16/2007 1:50:51 PM WANG
Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003524.D

Sample Name: YW-6-6A

OD-H, H/i-PrOH=80/20, 0.8 mL/min



Instrument 1 3/16/2007 1:54:07 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003592.D

Sample Name: YW-6-12A

OD-H, H/i-PrOH=80/20, 0.8 mL/min



Instrument 1 3/16/2007 2:13:33 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003564.D

Sample Name: YW-6-6C

OD-H, H/i-PrOH=80/20, 0.8 mL/min



Instrument 1 3/16/2007 1:56:37 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003591.D

Sample Name: YW-6-12B

OD-H, H/i-PrOH=80/20, 0.8 mL/min



Instrument 1 3/16/2007 2:03:38 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003566.D

Sample Name: YW-6-8B

OD-H, H/i-PrOH=80/20, 0.8 mL/min



Instrument 1 3/16/2007 2:07:43 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003575.D

Sample Name: YW-6-9B

OD-H, H/i-PrOH=80/20, 0.8 mL/min



Instrument 1 3/16/2007 2:09:37 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003741.D

OJ-H, H/i-PrOH=70/30, 0.8 mL/min



Instrument 1 3/16/2007 2:16:01 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003742.D

Sample Name: YW-6-43B

OJ-H, H/i-PrOH=70/30, 0.8 mL/min



Instrument 1 3/16/2007 2:17:37 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003758.D

Sample Name: YW-6-51A

0J-H, H/i-PrOH=80/20, 0.8 mL/min



Instrument 1 3/16/2007 2:21:10 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003759.D

Sample Name: YW-6-51B

0J-H, H/i-PrOH=80/20, 0.8 mL/min



Instrument 1 3/16/2007 2:22:58 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003616.D

Sample Name: YW-6-18C

OD-H, H/i-PrOH=80/20, 0.8 mL/min



Instrument 1 3/16/2007 2:28:08 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003617.D

Sample Name: YW-6-18B

OD-H, H/i-PrOH=80/20, 0.8 mL/min



Instrument 1 3/16/2007 2:30:41 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003746.D

```
Sample Name: YW-6-50B (Rac)
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OJ-H, H/i-PrOH=70/30, 0.8 mL/min



Instrument 1 3/16/2007 2:37:02 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003747.D

Sample Name: YW-6-47B

OJ-H, H/i-PrOH=70/30, 0.8 mL/min



Instrument 1 3/16/2007 2:40:05 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003748.D

Sample Name: YW-6-50C (Rac)

OJ-H, H/i-PrOH=70/30, 0.8 mL/min



Instrument 1 3/16/2007 2:43:34 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003749.D

Sample Name: YW-6-47C

OJ-H, H/i-PrOH=70/30, 0.8 mL/min



Instrument 1 3/16/2007 2:45:43 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003754.D

```
Sample Name: YW-6-50F (Rac)
```

OD-H, H/i-PrOH=70/30, 0.8 mL/min



Instrument 1 3/16/2007 2:50:22 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003755.D

Sample Name: YW-6-48F

OD-H, H/i-PrOH=70/30, 0.8 mL/min



Instrument 1 3/16/2007 2:51:45 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003752.D

```
Sample Name: YW-6-50D (Rac)
```

OD-H, H/i-PrOH=70/30, 0.8 mL/min



Instrument 1 3/16/2007 2:57:05 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003753.D

```
Sample Name: YW-6-47D (Rac)
```

OD-H, H/i-PrOH=70/30, 0.8 mL/min



Instrument 1 3/16/2007 2:59:28 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003762.D

Sample Name: YW-6-50E (rac)

OD-H, H/i-PrOH=80/20, 0.8 mL/min, 215 NM



Instrument 1 3/16/2007 3:03:09 PM WANG

Data File C:\HPCHEM\1\DATA\ZHOU-06\YZ003763.D

Sample Name: YW-6-53B

OD-H, H/i-PrOH=80/20, 0.8 mL/min, 215 NM



Instrument 1 3/16/2007 3:05:26 PM WANG