Supporting Information for:

Asymmetric Synthesis of Novel Vicinal Amino Alcohols via Intramolecular Ketone-*N*-Sulfinylimine Pinacol-Type Reductive Coupling Promoted by SmI₂

Yun-Hui Zhao*, Han-Wen Liu

Key Laboratory of Theoretical Chemistry and Molecular Simulation of Ministry of Education, Hunan Province

College Key Laboratory of QSAR/QSPR, Hunan University of Science and Technology, Xiangtan 411201, China

Tel: +86 731-58291859; Fax: +86 731-58291770

E-mail: zyh00041130@163.com

Table of Contents

General Information	2
General procedure for keto-imines and selected data for 1	2
General procedure characterization data for 2	5
Determination of <i>ees</i> for 2a , 2b	9
¹ H and ¹³ C NMR spectra	11
HPLC Spectra for 12a and 12b	25

General Information

Analytical TLC was carried out on precoated silica gel plates. Column chromatography was conducted with 300–400 mesh silica gel. NMR spectra were recorded at 400 MHz for ^1H NMR using SiMe_4 as an internal standard in CDCl_3 and 100 MHz for ^{13}C NMR. Enantiomeric excesses were determined by chiral HPLC analysis. Optical rotations were measured on a JASCO 1030 polarimeter. Tetrahydrofuran was used freshly distilled from sodium.

General procedure for keto-imines and selected data for 1

Synthesis of Component 7. To a solution of o-phthalaldehyde (6.7 g) in DCM (30 mL) was added carbethoxymethylenetriphenylphosphorane (17.42 g) in DCM (60 mL) in dropwise and the mixture stirred for 30 min at rt. The reaction mixture was evaporated, and the residue was dissolved in diethyl ether. After the precipitate was filtered, the filtrate was evaporated. The residue was purified by flash column chromatography (PE:EA=10:1) to give 3-(2-formylphenyl)-2(*E*)-propenoic acid ethyl ester as a pale yellow oil (7.34 g), yield 72%: ^1H NMR (400 MHz, CDCl_3) δ 10.18 (s, 1H), 8.43 (d, 1H, $J = 15.2$ Hz), 7.77 (m, 1H), 7.5 (m, 3H), 6.28 (d, 1H, $J = 15.2$ Hz), 4.19 (q, 2H, $J = 6.4$ Hz), 1.24 (t, 3H, $J = 6.4$ Hz).^[1]

Synthesis of Component 8.

Trimethyl Orthoformate (2.54 g, 24 mmol) was added to a solution of **7** (4.08 g, 20 mmol), *p*-toluenesulfonic acid (190 mg, 5% mol) and 4Å molecular sieve (5 g) in dry methanol (20 mL), the mixture was refluxed overnight. The resulting solution was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (PE:EA=10:1). Then the acetal was dissolved in methanol (20 mL) and 10% Pd/C (250 mg, 5%) was added, the mixture was stirred under hydrogen for 1.5h at 35 °C. Then the solution was filtered and the solvent was evaporated, the crude product was purified by flash column chromatography (PE:EA=10:1) to afford product **8** as colorless liquid in 82% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.61-7.13 (m, 4H), 5.50 (s, 1H), 4.12 (q, 2H, *J* = 7.2 Hz), 3.31 (s, 4H), 3.03 (t, 2H, *J* = 7.6 Hz), 2.59 (t, 2H, *J* = 7.6 Hz), 1.22 (t, 3H, *J* = 7.2 Hz). ¹³C NMR (100 MHz, CDCl₃) δ 173.1, 138.9, 135.6, 129.6, 128.7, 127.0, 126.1, 101.7, 60.5, 53.2, 35.7, 27.6, 14.3.

Synthesis of Component 10.

NaOH (3M, 10 mL) was added into a solution of compound **8** (2.52 g, 10 mmol) in mixture of THF and MeOH (v/v=1:1), the mixture was stirred at ambient temperature for 30 min. When the material was disappeared, the solution was neutralized by 3M HCl to PH =5. The organic acid was extracted with ethyl acetate (3 x 30 mL), dried over Na₂SO₄. The solvent was evaporated and the residue solid was used in the next step without further purification.

To a stirred solution of this solid carboxylic acid in CH₂Cl₂ (45 mL), 4-dimethyl- aminopyridine (DMAP) (1.22 g, 10 mmol), dimethylhydroxyamine hydrochloride (1.16 g, 12 mmol), *N*-methyl morpholine (1.21 g, 12 mmol.) and *N*-(3-dimethyl- aminopropyl)-*N*'-ethyl carbodiimide hydrochloride (WSCl.HCl) (2.29 g, 12 mmol) were added consecutively at room temperature. The reaction mixture was left stirring for 18 h. It was then washed with an aqueous solution of HCl 1N (3 x 10 mL), brine (1 x 10 mL), an aqueous solution of NaHCO₃ 5% (3 x 10 mL) and brine (1 x 10 mL). The organic layer was dried (Na₂SO₄) and concentrated under reduced pressure. The residue was purified by column chromatography (PE:EA=3:1) to get light yellow oil.

Trimethyl Orthoformate (1.27 g, 24 mmol) was added to a solution of amide, *p*-toluenesulfonic acid (95 mg, 5% mol) and 4Å molecular sieve (2 g) in dry methanol (10 mL), the mixture was refluxed overnight. The resulting solution was filtered and the filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography (PE:EA=10:1) to afford product **10** as

colorless oil in 78% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, 1H, $J = 6.8$ Hz), 7.25-7.20 (m, 3H), 5.51 (s, 1H), 3.59 (s, 3H), 3.32 (s, 6H), 3.17 (s, 3H), 3.04-2.96 (m, 2H), 2.71 (t, 2H, $J = 7.2$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 173.8, 139.7, 135.7, 129.8, 128.8, 126.9, 126.1, 101.8, 61.2, 53.4, 33.7, 27.2. HRMS (ESI) exact mass calculated for $(\text{C}_{14}\text{H}_{21}\text{NNaO}_4)$ requires m/z 290.1368, found m/z 290.1372.

General procedure for the synthesis of keto **11**

BuLi 2 ml (3.2 mmol, 1.6 M) was added into a solution of bromobenzene 0.32 ml (3.2 mmol) in 8 mL THF under nitrogen atmosphere at -78°C , the mixture was stirred at this temperature for 30 mins. And then a solution of **10** (267 mg, 1mmol) in 2 mL THF was added, the reaction solution was stirred for another 30 mins at -78°C . 3M HCl (1.5 mL) was added after the reaction was quenched with water and the mixture stirred at room temperature for 15min, then extracted with EA, washed with water. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography eluting with the appropriate mixture of EtOAc/ pet. ether (1:5) to afford the desired product as colorless liquid, yield 84%.

^1H NMR (400 MHz, CDCl_3) δ 10.22 (d, 1H, $J = 1.6$ Hz), 7.96-7.93 (m, 2H), 7.81 (d, 1H, $J = 7.6$ Hz), 7.53-7.48 (m, 2H), 7.45-7.37 (m, 4H), 3.45 (t, 2H, $J = 8.0$ Hz), 3.30 (t, 2H, $J = 8.0$ Hz). ^{13}C NMR (100 MHz, CDCl_3) δ 199.1, 193.1, 143.8, 136.8, 134.0, 133.9, 133.8, 133.2, 131.7, 128.7, 128.2, 127.0, 40.2, 27.6.

General procedure for the synthesis of keto-imine **1a**

(*R*)-*tert*-Butanesulfinamide (181 gm, 1.5 mmol) was stirred with aldehyde **11a** (1 mmol) in toluene (10 mL) in the presence of KHSO_4 (2 equiv) for 18 h at ambient temperature. KHSO_4 was then removed by filtration. The filtrate was concentrated to dryness. The residue was purified by flash chromatography to afford (*R*)-*tert*-butanesulfinylaldimine (**1a**) as a colorless liquid, yield 82%.

^1H NMR (400 MHz, CDCl_3) δ 8.82 (s, 1H), 7.92-7.85 (m, 3H), 7.55-7.51 (m, 1H), 7.44-7.40 (m, 3H),

7.36-7.32 (m, 2H), 3.49-3.19 (m, 4H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.8, 162.2, 142.8, 136.8, 133.2, 132.3, 131.9, 131.4, 131.2, 128.7, 128.1, 127.0, 57.7, 40.3, 27.8, 22.6. HRMS (ESI) exact mass calculated for $(\text{C}_{20}\text{H}_{23}\text{NNaO}_2\text{S})$ requires m/z 364.1347, found m/z 364.1344.

General procedure characterization data for 2

To a solution of SmI_2 (0.6 mmol) in THF (3 mL) under Ar was added dropwise a solution of **7** (0.2 mmol) in THF (2 mL), and the mixture was stirred at room temperature until all starting material has been consumed. The reaction was quenched by saturated $\text{Na}_2\text{S}_2\text{O}_3$ (3 mL), diluted with ethyl acetate, and the aqueous phase was extracted with ethyl acetate. The combined organic layer was dried (Na_2SO_4), filtered and concentrated. The residue was purified by silica gel flash column chromatography to afford **2**.

2a (*R*)-*N*-((1*S*,2*R*)-2-hydroxy-2-phenyl-1,2,3,4-tetrahydronaphthalen-1-yl)-tert-butylsulfonamide

$[\alpha]_{\text{D}}^{24} +60.8$ (c 0.99, CHCl_3).

Colorless oil, ^1H NMR (400 MHz, CDCl_3) δ 7.60-7.58 (m, 1H), 7.42 (d, 2H, $J = 8.0$ Hz), 7.32 (t, 2H, $J = 8.0$ Hz), 7.28-7.25 (m, 3H), 7.21-7.18 (m, 1H), 4.66 (d, 1H, **NH**, $J = 6.8$ Hz), 3.32 (d, 1H, $J = 6.8$ Hz), 3.10-3.03 (m, 2H), 2.88 (dt, 1H, $J = 16.8$ Hz, 4.8 Hz), 2.46-2.39 (m, 1H), 2.28-2.22 (m, 1H), 0.96 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.8, 136.8, 136.1, 129.6, 128.5, 128.4, 127.7, 127.6, 127.0, 126.6, 75.4, 63.5, 56.3, 31.7, 26.1, 22.8; **IR**(KBr, ν/cm^{-1}): 3371, 3241, 3059, 2928, 2864, 1612, 1495, 1448, 1042 cm^{-1} ; HRMS (ESI) 366.1509 $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{20}\text{H}_{25}\text{NO}_2\text{SNa}^+$ 366.1504.

2b (*R*)-*N*-((1*S*,2*R*)-2-hydroxy-2-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)-tert-butylsulfonamide

$[\alpha]_{\text{D}}^{24} +4.4$ (c 1.07, CHCl_3).

White solid. M.p.: 127-128 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.62-7.61 (m, 1H), 7.18-7.16 (m, 2H),

7.09-7.08 (m, 1H), 4.35 (d, 1H, **NH**, $J = 6.8$ Hz), 3.47 (d, 1H, $J = 6.8$ Hz), 2.98-2.92 (m, 2H), 2.84-2.78 (m, 1H), 1.92-1.86 (m, 2H), 1.27 (s, 9H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.4, 135.9, 129.9, 128.7, 127.5, 126.8, 71.5, 64.4, 56.7, 32.9, 26.6, 23.8, 23.2; **IR(KBr, ν/cm^{-1}): 3482, 3320, 3054, 2950, 2856, 1636, 1579, 1492, 1455, 1375, 1054 cm^{-1}** ; HRMS (ESI) 304.1344 $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{15}\text{H}_{23}\text{NO}_2\text{SNa}^+$ 304.1347.

$[\alpha]_{\text{D}}^{24} +47.8$ (c 0.38, CHCl_3).

2c (*R*)-*N*-((1*S*,2*R*)-2-hydroxy-2-*p*-tolyl-1,2,3,4-tetrahydronaphthalen-1-yl)-tert-butylsulfonamide

White solid. M.p.: 97-98 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.60-7.57 (m, 1H), 7.26-7.23 (m, 4H), 7.19-7.17 (m, 1H), 7.12 (d, **2H**, $J = 8.0$ Hz), 4.65 (d, 1H, **NH**, $J = 6.8$ Hz), 3.35 (d, 1H, $J = 6.8$ Hz), 3.09-3.00 (m, 2H), 2.87-2.82 (m, 1H), 2.42-2.34 (m, 1H), 2.32 (s, 3H), 2.26-2.20 (m, 1H), 0.98 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.7, 137.2, 136.9, 136.3, 129.4, 129.1, 128.4, 127.7, 126.9, 126.4, 75.4, 63.6, 56.4, 32.3, 26.2, 22.9, 21.1; **IR(KBr, ν/cm^{-1}): 3414, 3325, 3062, 2923, 2867, 1652, 1560, 1437, 1365, 1043, 738**

cm^{-1} ; HRMS (ESI) 380.1657 $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{21}\text{H}_{27}\text{NO}_2\text{SNa}^+$ 380.1660.

$[\alpha]_{\text{D}}^{24} +52.5$ (c 0.95, CHCl_3).

2d (*R*)-*N*-((1*S*,2*R*)-2-hydroxy-2-*m*-tolyl-1,2,3,4-tetrahydronaphthalen-1-yl)-tert-butylsulfonamide

Light yellow oil, ^1H NMR (400 MHz, CDCl_3) δ 7.57-7.55 (m, 1H), 7.26-7.24 (m, 3H), 7.21-7.12 (m, 3H), 7.07 (d, 1H, $J = 7.2$ Hz), 4.64 (d, 1H, **NH**, $J = 6.4$ Hz), 3.33 (d, 1H, $J = 6.4$ Hz), 3.11-3.03 (m, 1H), 2.92-2.83 (m, 2H), 2.45-2.38 (m, 1H), 2.33 (s, 3H), 2.26-2.20 (m, 1H), 0.96 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.8, 137.9, 136.8, 136.1, 129.7, 128.4, 128.3, 128.2, 127.7, 127.4, 126.9, 123.5, 75.4, 63.3, 56.3, 31.6, 26.0, 21.7; **IR(KBr, ν/cm^{-1}): 3415, 3313, 2923, 2854, 1653, 1617, 1560, 1493, 1457, 1184, 1040, 706 cm^{-1}** ; HRMS (ESI) 380.1651 $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{21}\text{H}_{27}\text{NO}_2\text{SNa}^+$ 380.1660.

2e (*R*)-*N*-((1*S*,2*R*)-2-hydroxy-2-cyclohexanyl-1,2,3,4-tetrahydronaphthalen-1-yl)-tert-butylsulfonamide

$[\alpha]_D^{24}$ -4.8 (*c* 1.02, CHCl₃).

White solid. M.p.: 201-202 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.50-7.47 (m, 1H), 7.19-7.16 (m, 2H), 7.09-7.07 (m, 1H), 4.40 (d, 1H, NH, *J* = 7.2 Hz), 3.09 (d, 1H, *J* = 7.2 Hz), 2.97-2.77 (m, 2H), 2.10-1.98 (m, 2H), 1.81-1.74 (m, 3H), 1.68-1.59 (m, 3H), 1.48-1.45 (m, 1H), 1.18 (s, br, 14H); ¹³C NMR (100 MHz, CDCl₃) δ 135.9, 135.6, 131.9, 128.7, 127.9, 126.8, 74.8, 59.8, 56.4, 41.7, 26.9, 26.4, 26.3, 26.0, 25.8, 25.7, 24.9, 22.9; IR(KBr, ν/cm⁻¹): 3370, 3316, 2904, 2841, 1645, 1493, 1450, 1365, 1043, 999 cm⁻¹; HRMS (ESI) 372.1978 [M+Na]⁺ calculated for C₂₀H₃₁NO₂SN⁺ 372.1973.

2f (*R*)-*N*-((1*S*,2*R*)-2-hydroxy-2-cyclopentyl-1,2,3,4-tetrahydronaphthalen-1-yl)-tert-butylsulfonamide

$[\alpha]_D^{24}$ +7.0 (*c* 1.02, CHCl₃).

Light yellow oil, ¹H NMR (400 MHz, CDCl₃) δ 7.54-7.51 (m, 1H), 7.20-7.16 (m, 2H), 7.12-7.10 (m, 1H), 4.26 (d, 1H, NH, *J* = 7.2 Hz), 3.18 (d, 1H, *J* = 7.2 Hz), 2.97-2.92 (m, 1H), 2.84-2.78 (m, 1H), 2.23-2.19 (m, 1H), 1.95-1.53 (m, 11H), 1.20 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 135.9, 135.7, 131.7, 128.8, 127.8, 126.8, 74.0, 62.2, 56.5, 44.7, 28.2, 26.1, 25.9, 25.8, 25.3, 25.1, 22.9; IR(KBr, ν/cm⁻¹): 3424, 3319, 3020, 2953, 2855, 1493, 1454, 1380, 1058, 758 cm⁻¹; HRMS (ESI) 358.1813 [M+Na]⁺ calculated for C₁₉H₂₉NO₂SN⁺ 358.1817.

2g (*R*)-*N*-((1*S*,2*R*)-2-hydroxy-2-benzyl-1,2,3,4-tetrahydronaphthalen-1-yl)-tert-butylsulfonamide

$[\alpha]_D^{24}$ +53.4 (*c* 0.99, CHCl₃).

White solid, M.p.: 170-171 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, 1H, *J* = 7.2 Hz), 7.34-7.20 (m, 7H), 7.14 (d, 1H, *J* = 6.4 Hz), 4.48 (d, 1H, NH, *J* = 8.0 Hz), 3.41 (d, 1H, *J* = 8.0 Hz), 2.95-2.88 (m, 3H),

2.79 (d, 1H, $J = 10.4$ Hz), 2.25 (s, 1H), 1.93-1.79 (m, 2H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.9, 136.2, 135.7, 130.8, 129.5, 128.8, 128.6, 127.7, 126.9, 126.8, 73.3, 65.1, 56.8, 41.5, 30.4, 26.2, 23.2; IR(KBr, ν/cm^{-1}): 3458, 3345, 3045, 2950, 2867, 1603, 1493, 1454, 1386, 1054, 756 cm^{-1} ; HRMS (ESI) 380.1655 $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{21}\text{H}_{27}\text{NO}_2\text{SNa}^+$ 380.1660.

2h (*R*)-*N*-((1*S*,2*R*)-2-hydroxy-2-isobutyl-1,2,3,4-tetrahydronaphthalen-1-yl)-tert-butylsulfonamide

$[\alpha]_{\text{D}}^{24} +7.1$ (c 1.03, CHCl_3).

Light yellow oil, ^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, 1H, $J = 6.8$ Hz), 7.22-7.20 (m, 2H), 7.11 (d, 1H, $J = 6.8$ Hz), 4.38 (d, 1H, NH, $J = 8.0$ Hz), 3.41 (d, 1H, $J = 8.0$ Hz), 2.97-2.75 (m, 2H), 2.09-1.83 (m, 4H), 1.39-1.36 (m, 2H), 1.30 (s, 9H), 1.05 (d, 3H, $J = 6.0$ Hz), 0.96 (d, 3H, $J = 6.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 136.3, 135.9, 129.5, 128.7, 127.6, 126.9, 73.9, 65.9, 56.9, 42.7, 30.4, 26.5, 25.2, 24.7, 23.6, 23.3; IR(KBr, ν/cm^{-1}): 3423, 3258, 3063, 2924, 2867, 1633, 1484, 1463, 1365, 1032, 759 cm^{-1} ; HRMS (ESI) 346.1816 $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{18}\text{H}_{29}\text{NO}_2\text{SNa}^+$ 346.1817.

2i (*R*)-*N*-((1*S*,2*R*)-2-hydroxy-2-isopropyl-1,2,3,4-tetrahydronaphthalen-1-yl)-tert-butylsulfonamide

$[\alpha]_{\text{D}}^{24} -9.5$ (c 1.10, CHCl_3).

Light yellow oil, ^1H NMR (400 MHz, CDCl_3) δ 7.52-7.49 (m, 1H), 7.20-7.18 (m, 2H), 7.12-7.10 (m, 1H), 4.36 (d, 1H, NH, $J = 7.2$ Hz), 3.13 (d, 1H, $J = 7.2$ Hz), 2.99-2.90 (m, 1H), 2.85-2.78 (m, 1H), 2.07-1.98 (m, 2H), 1.73-1.65 (m, 1H), 1.52 (s, 1H), 1.18 (s, 9H), 1.05 (d, 3H, $J = 6.4$ Hz), 0.98 (d, 3H, $J = 6.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 135.9, 135.5, 131.9, 128.7, 127.8, 126.8, 74.8, 60.5, 56.5, 31.8, 26.4, 25.1, 22.9, 16.5, 16.3; IR(KBr, ν/cm^{-1}): 3444, 3381, 3173, 3020, 2956, 2903, 1635, 1493, 1455, 1189, 1052, 738 cm^{-1} ; HRMS (ESI) 310.1819 $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{18}\text{H}_{29}\text{NO}_2\text{SH}^+$ 310.1835.

6 (*R*)-*N*-((3*R*,4*S*)-3-hydroxy-3-phenyl-3,4-dihydro-2*H*-chromen-4-yl)-*tert*-butylsulfonamide

$[\alpha]_{\text{D}}^{24} +74.3$ (*c* 0.96, CHCl_3).

Light yellow oil, ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, 1H, $J = 7.2$ Hz), 7.43 (d, 1H, $J = 6.4$ Hz), 7.37-7.23 (m, 5H), 7.03-6.94 (m, 2H), 4.65 (d, 1H, NH, $J = 6.4$ Hz), 4.59 (d, 1H, $J = 10.8$ Hz), 4.33 (d, 1H, $J = 10.8$ Hz), 3.73 (s, 1H), 3.41 (d, 1H, $J = 6.4$ Hz), 0.99 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.6, 140.6, 130.9, 129.7, 128.6, 128.2, 126.4, 122.1, 121.8, 117.0, 71.2, 69.5, 59.8, 56.4, 22.8; IR(KBr, ν/cm^{-1}): 3372, 3251, 3058, 2959, 2923, 2867, 1609, 1586, 1491, 1450, 1236, 1050, 754 cm^{-1} ; HRMS (ESI) 346.1472 $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{19}\text{H}_{23}\text{NO}_3\text{SH}^+$ 346.1477.

Determination of *ees* for 2a, 2b

The product **2a** (0.2 mmol) was treated with HCl–MeOH (4M, 1 mL), and the mixture was stirred at r.t. until all the starting material has been consumed. The solvent was removed under reduced pressure, the residue was taken up in DCM (5 mL) and cooled to 0 °C. Et_3N (0.10 mL, 0.71 mmol), cat. DMAP and Ac_2O (0.045 mL, 0.47 mmol) were added successively. The mixture was allowed to warm to r.t. and stirred overnight, quenched by water (10 mL), and extracted with ether (40 mL). The organic phase was washed with sat. aq. NaHCO_3 , brine, dried (Na_2SO_4), filtered and concentrated. The residue was purified by silica gel flash column chromatography to afford pure product **12a**.^[2]

12a *N*-((1*S*,2*R*)-2-hydroxy-2-phenyl-1,2,3,4-tetrahydronaphthalen-1-yl)acetamide

HPLC: Chiralcel OD-H column, detected at 214 nm, eluent: *n*-hexane/2-propanol = 70/30 (v/v), flow rate: 1.0 ml/min, $t_1 = 5.4$ min (minor), $t_2 = 7.3$ min (major), 97.5% *ee*. $[\alpha]_{\text{D}}^{27} -48.8$ (*c* 0.49, CHCl_3).

Colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.16 (m, 9H), 5.72 (d, 1H, $J = 8.0$ Hz), 5.48 (d, 1H, $J = 8.0$ Hz), 4.09 (s, 1H), 2.96-2.91 (m, 1H), 2.75-2.67 (m, 1H), 2.35-2.27 (m, 1H), 2.18-2.14 (m, 1H),

1.86 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.6, 144.1, 137.2, 136.1, 128.9, 128.2, 127.6, 127.4, 126.9, 126.6, 125.9, 58.5, 36.1, 26.9, 23.2; IR(KBr, ν/cm^{-1}): 3361, 3312, 3023, 2921, 2849, 1653, 1536, 1492, 1448, 1307, 1069, 952 cm^{-1} ; HRMS (ESI) 304.1310 $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{18}\text{H}_{19}\text{NO}_2\text{Na}^+$ 304.1313.

12b *N*-((1*S*,2*R*)-2-hydroxy-2-methyl-1,2,3,4-tetrahydronaphthalen-1-yl)acetamide

HPLC: Chiralcel AD-H column, detected at 214 nm, eluent: *n*-hexane/2-propanol = 90/10 (v/v), flow rate: 0.7 ml/min, t_1 = 11.3 min (major), t_2 = 12.5 min (minor), 97.0% *ee*. $[\alpha]_{\text{D}}^{27}$ +1.7 (*c* 1.04, CHCl_3). White solid. M.p.: 167-168 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.20-7.10 (m, 4H), 6.06 (d, 1H, J = 8.4 Hz), 5.10 (d, 1H, J = 8.4 Hz), 3.72 (s, br, 1H), 2.93-2.78 (m, 2H), 2.08 (s, 3H), 1.93-1.88 (m, 2H), 1.16 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.9, 136.1, 135.4, 129.1, 127.8, 127.5, 126.6, 72.2, 58.1, 34.8, 27.0, 23.3, 22.3; IR(KBr, ν/cm^{-1}): 3470, 3268, 3025, 2927, 2843, 1567, 1498, 1453, 1048 cm^{-1} ; HRMS (ESI) 242.1158 $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{13}\text{H}_{17}\text{NO}_2\text{Na}^+$ 242.1157.

Reference:

- [1] Shigematsu, N.; Hayashi, K.; Kayakiii, N.; Takase, S.; Hashimoto, M.; Tanaka, H. *J. Org. Chem.* **1993**, 58, 170.
- [2] Wang, B.; Wang, Y.-J. *Org. Lett.*, **2009**, 11, 3410.

¹H and ¹³C NMR spectra

HPLC Spectra for 12a and 12b

Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.463	5099.934	84273.703	1.2237
2		7.322	279576.750	6802325.000	98.7763
Total			284676.684	6886598.703	100.0000

Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.438	400741.469	7564919.500	50.1293
2		7.327	308718.219	7525899.500	49.8707
Total			709459.688	15090819.000	100.0000

Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.325	1101248.750	20955138.000	98.4942
2		12.553	17551.031	320360.313	1.5058
Total			1118799.781	21275498.313	100.0000

Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.233	589330.313	9751559.000	50.1613
2		12.370	461654.656	9688861.000	49.8387
Total			1050984.969	19440420.000	100.0000