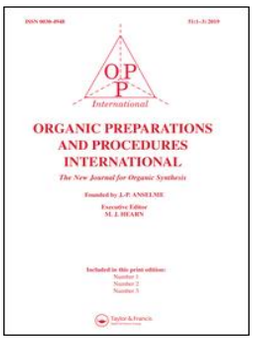

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EXPERIMENTAL PAPER

An Efficient and Highly Asymmetric Synthesis of (*S*)-2′,6′-Dimethyltyrosine

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The unnatural amino acid (*S*)-2,6-dimethyltyrosine [(*S*)-DMT, Figure 1] is a very important small molecule for the preparation of opioid receptor modulators. It has been used to effectively improve the affinity and selectivity of δ-opioids or to induce altogether new biological activity.[1,2] With the landmark discovery of H-Dmt-Tic-OH (Figure 2), many analogs have been designed and synthesized to develop new opioid receptor modulators.[3] This drug discovery campaign has resulted in SUPER-DALDA,[4] Bendavia,[5] and Eluxadoline,[6] potent μ-opioid receptor agonists or δ-opioid receptor antagonists.

Interestingly, the 2,6-dimethyl substituents of (*S*)-DMT make challenging the assembly of this unnatural amino acid. To date, several synthetic routes to (*S*)-DMT have been reported. An enantioselective hydrogenation of (*Z*)-2-acetamido-3-(4-acetoxy-2,6-dimethylphenyl)-2-propenoate in the presence of a chiral catalyst, [Rh(1,5-COD)(R,R-DIPAMP)]BF_4, was furnished to prepare (*S*)-*N*-Boc-2,6-dimethyltyrosine on kilogram scale under relatively forcing conditions (60 °C, 60 psi) and high catalyst loading (1 mol %).[7,8] Asymmetric alkylation of a Ni(II) complex of the chiral Schiff base derived from glycine with 4'-benzyloxy-2',6'-dimethylbenzyl bromide and a highly stereocontrolled monoalkylation of 2,5-diketopiperazine as a chiral synthon with 4-iodomethyl-3,5-dimethylphenyl ethylcarbonate were accomplished, respectively.[9–10] In addition, microwave-assisted Negishi coupling reaction for the synthesis of (*S*)-DMT has been developed starting from commercially available Boc-protected *L*-serine methyl ester (Boc-Ser-OMe) as a chiral synthon.[11] Recently, Pd-catalyzed *ortho*-dimethylation of an L-tyrosine derivative via metal catalyzed C-H bond activation produced (*S*)-DMT employing picolinamide as a directing group.[12] However, many of these routes have such disadvantages as comparatively expensive catalysts, scarce reagents or chiral auxiliaries. Therefore, the development of a shorter, convenient and highly enantioselective methodology for the practical synthesis of (*S*)-DMT is desirable.

The use of chiral auxiliaries to establish chiral centers in a highly stereoselective manner is one of the most important strategies in organic synthesis.[13,14] The well-known commercial Oppolzer chiral sultam, and its derivatives, have been widely used in asymmetric synthesis, including such applications as carbonyl α-alkylation, aldol

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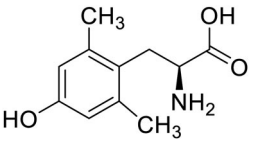
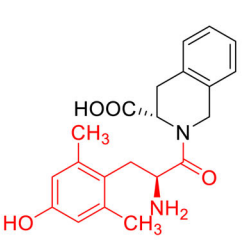
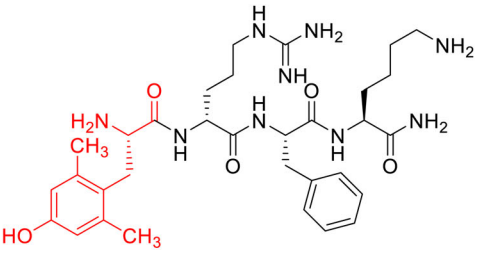
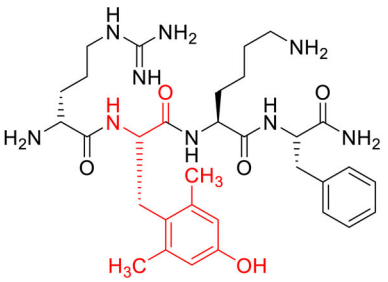


Figure 1. Structure of (*S*)-DMT.







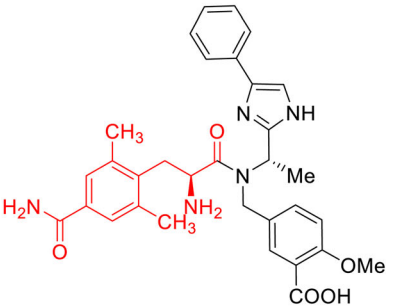
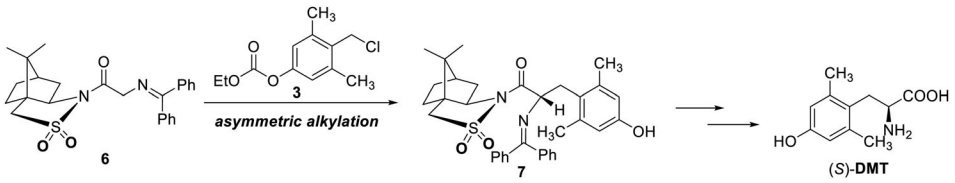


Figure 2. Structures of some potent δ-opioid receptor antagonists.

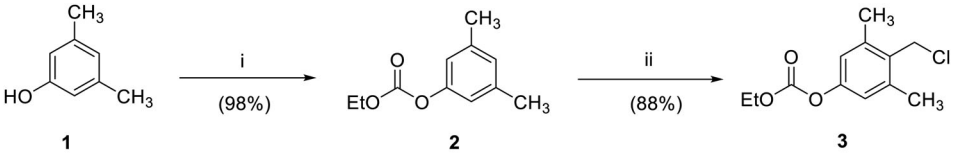
condensation, Diels-Alder cycloaddition, 1,3-dipolar cycloaddition, bis-hydroxylation, and asymmetric epoxidation.[15–18] We now report a convenient and economical asymmetric synthesis of (*S*)-DMT via an alkylation of Oppolzer's chiral sultam of glycine (**6**) with the corresponding *O*-carbethoxy-3,5-dimethyl-4-chloromethylphenol **3** as a key step (Scheme 1).

The starting point for the synthesis is provided in Scheme 2. This approach involves the preparation of *O*-carbethoxy-3,5-dimethyl-4-chloromethylphenol **3** in a two-step sequence from 3,5-dimethyl phenol **1.** Treatment of compound **1** with ethyl chloroformate in the presence of triethylamine afforded *O*-carbethoxy-3,5-dimethyl phenol **2** in a near quantitative yield (98%). This is directly used in the next step without further purification. Blanc-type chloromethylation of compound **2** with a mixture of chlorosulfonic acid and dimethoxymethane is conducted in the presence of anhydrous zinc chloride as a promoter under solvent-free conditions at 5-10 °C. This procedure which exclusively provides the desired product *O*-carbethoxy-3,5-dimethyl-4- chloromethylphenol **3** in 88% yield.[19]

The Oppolzer sultam has been successfully utilized for the asymmetric synthesis of α-amino acids.[15,16] Bearing this in mind, a novel synthetic route to prepare enantiomerically pure (*S*)-DMT was investigated. This was done via alkylation of the



Scheme 1. Synthetic strategy for (*S*)-DMT.



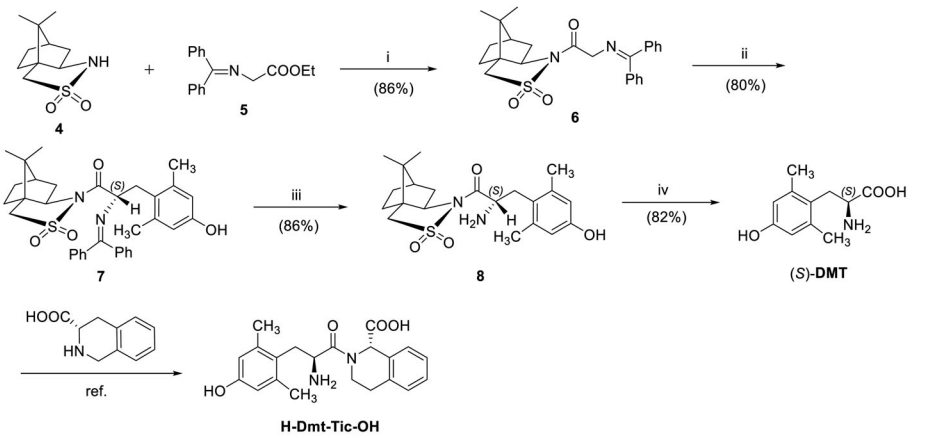
Scheme 2. Synthesis of *O*-carbethoxy-3,5-dimethyl-4-chloromethylphenol **3**.

appropriate chiral Oppolzer's sultam of glycine **6** with the corresponding *O*-carbethoxy-3,5-dimethyl-4-chloromethylphenol **3.** The ability of the chiral glycine intermediate **6**, prepared by Chassaing's method,[20] to direct highly diastereoselective alkylations has been demonstrated.[17] Therefore, with compound **3** in hand, we endeavored to perform the stereocontrolled synthesis of (*S*)-DMT (Scheme 3). The sultam derivative of ethyl *N*-(diphenylmethylene)glycinate **6** was prepared via Me_3Al-mediated acylation of sultam **4** with ethyl *N*-(diphenylmethylene)glycinate **5** at 50 °C for 12 h in 93% yield as a light yellow oil. The chiral glycine intermediate **6** was smoothly alkylated with benzyl chloride derivative **3** with n-BuLi and HMPA at -78 °C to provide **7** as a white solid in a good yield (80%). It is worthy to be noted that the ethoxy carbonyl protecting group on the phenol ring was simultaneously removed upon workup. Gratifyingly, only one single diastereoisomer was obtained, as determined by its NMR analysis. This was also confirmed as the desired *S*-configuration by the validation of the targeted product (*S*)-DMT. Subsequently, compound **7** was hydrolyzed with aqueous 1.0 M HCl at room temperature to remove the benzophenone group to give an 86% yield of amine **8**. Then, removal of the chiral auxiliary sultam was readily accomplished by treatment with 2.5 M LiOH in THF at 0 °C to give the desired (*S*)-DMT in 82% yield. We would like to point out that, according to the literature,[21] (*S*)-DMT can be easily converted to the potent δ-opioid receptor antagonist dipeptide, H-DmtTic-OH. This is done by condensation with (*S*)-1,2,3,4-tetrahydro-isoquinoline-3-carboxylic acid.[21]

In conclusion, we have developed an efficient and convenient route for the synthesis of (*S*)-DMT with excellent enantiomeric purity. Inexpensive reagents, use of a recyclable[18] chiral auxiliary, simplicity, and high yields, make this method attractive for preparing the target amino acid on a multi-gram scale. The use of this protocol for the preparation of other novel unnatural tyrosine derivatives is currently underway in our laboratory.

Experimental section

All reagents were commercially available and directly used without further treatment. ^{1}H NMR spectra were recorded at 500 MHz in $CDCl_3$ using TMS as internal standard.



i) Me_3Al, toluene, 50 °C, 24 h ii) **3**, n-BuLi/HMPA,THF, -78 °C-r.t.,3 h, iii) 1N HCl, THF, 0 °C, 4 h, then $NaHCO_3$ iv) LiOH, THF-H_2O, 0 °C, 1 h

Scheme 3. Asymmetric synthesis of (*S*)-DMT.

^{13}C NMR spectral measurements were performed at 125 MHz using TMS as an internal standard. EI-MS were determined on a PerkinElmer spectrometer. HRMS (ESI) were determined on a Therm LCQ TM Deca XP plus spectrometer. For product purification by flash column chromatography, silica gel (200 ~ 300 mesh) and light petroleum ether (PE, b.p. 60 ~ 90 °C) were used. All compounds were identified by comparison with ^1H NMR data reported in the references cited below. Melting points were measured on Buchi B-540 apparatus and are uncorrected. Elemental analyses were obtained on a VarioEL-3 instrument.

O-Carbethoxy-3,5-dimethylphenol (2)[22]

3,5-Dimethylphenol 1 (10.0 g, 81.84 mmol) was dissolved in CH_2Cl_2 (30 mL) at room temperature. The reaction was cooled to 0 °C and Et_3N (10.94 g, 108.04 mmol) was added. After addition, ethyl chloroformate (10.66 g, 98.22 mmol) was then added keeping the temperature below 10 °C. The reaction mixture continued to be stirred for 1.0 h and 3,5-dimethylphenol was completely consumed by TLC analysis (silica gel, petroleum ether/EtOAc 5/1). Water (20 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (2 x 30 mL), the organic extracts were combined, washed with dilute aqueous HCl, water, brine and dried over Na_2SO_4. Evaporation of the filtrate under reduced pressure produced 15.6 g (98.0%) **2** as a pale yellowish oil, which was used directly in the next step without further purification. $R_f = 0.69$ (silica gel, petroleum ether/EtOAc 5/1); ^1H NMR (500 MHz, $CDCl_3$) δ 6.90 (s, 1H), 6.83 (s, 2H), 4.33 (q, $J = 7.1$ Hz, 2H), 2.35 (s, 6H), 1.41 (t, $J = 7.1$ Hz, 3H).

O-Carbethoxy-3,5-dimethyl-4-chloromethylphenol (3)[23]

A three-necked flask was charged with anhydrous $ZnCl_2$ (0.35 g, 2.57 mmol), chlorosulfonic acid (3.60 g, 30.89 mmol), followed by dropwise addition of dimethoxymethane (2.35 g, 30.89 mmol) at -10 °C. After stirring for 30 minutes, *O*-carbethoxy-3,5-

dimethylphenol **2** (5.00 g, 25.74 mmol) was slowly added into the reaction mixture. The resulting mixture continued to be stirred at 5-10 °C for 2 hours. The reaction was monitored by TLC analysis (silica gel, petroleum ether/EtOAc 10/1). After completion, the reaction was placed in an ice bath and quenched by addition of water. After extraction with CH_2Cl_2, the organic phase was washed with 5% sodium carbonate solution, water and brine, then evaporated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc to give 5.50 g (88%) **3** as a colorless liquid. R_f = 0.39 (silica gel, petroleum ether/EtOAc 10/1); ^{1}H NMR ($CDCl_3$) δ 6.90 (s, 2H), 4.65 (s, 2H), 4.32 (q, J = 7.1 Hz, 2H), 2.44 (s, 6H), 1.40 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ = 153.4, 150.6, 139.1, 131.7, 129.0, 120.5, 120.3, 64.6, 40.2, 19.1, 18.5, 14.0.

1-((6R,7aR)-8,8-Dimethyl-2,2-dioxidotetrahydro-3H-3a,6-methanobenzo[c] isothiazol-1(4H)-yl)-2-((diphenylmethylene)amino)ethan-1-one (6)[20]

S-Camphorsultam **4** (1.5 g, 6.96 mmol) was dissolved in anhydrous toluene (30 mL). A solution of Me_3Al in hexane (8.4 mL, 8.4 mmol) was added dropwise at room temperature under argon. The reaction mixture was stirred for 30 minutes, followed by addition of a solution of the benzophenone imine of glycine ethyl ester **5** (2.04 g, 7.65 mmol) in toluene (25 mL). The reaction mixture was heated to 50 °C and stirred for an additional 24 hours. The reaction was cooled in an ice bath and quenched by addition of saturated sodium bicarbonate (40 mL). The mixture was transferred to a separatory funnel. The aqueous phase was extracted with ethyl acetate (3 x 50 mL). The combined organic phase was washed with 5% sodium carbonate solution, water and brine, then evaporated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc to give 2.61 g (86%) **6** as a light yellow oil. R_f = 0.30 (silica gel, petroleum ether/EtOAc 4/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, J = 5.2, 3.3 Hz, 2H), 7.47-7.43 (m, 3H), 7.40-7.38 (m, 1H), 7.34-7.31 (m, 2H),7.20-7.18 (m, 2H), 4.63 (d, J = 4.5 Hz, 2H), 3.90 (dd, J = 7.8, 4.9Hz, 1H), 3.42 (d, J = 12.3 Hz, 2H),2.11-2.05 (m, 1H), 1.41-1.38(m, 1H), 1.35 (d, J = 6.7 Hz, 1H), 1.13 (s, 4H), 0.95 (s, 6H).

(2S)-1-((6R,7aR)-8,8-Dimethyl-2,2-dioxidotetrahydro-3H-3a,6-methanobenzo[c] isothiazol-1(4H)-yl)-2-((diphenylmethylene)amino)-3-(4-hydroxy-2,6-dimethylphenyl)propan-1-one (7)

To a solution of *N*-(diphenylmethylene)glycine sultam **6** (2.1 g, 4.82 mmol) in anhydrous THF (20 mL) was added HMPA (3.4 g, 18.4 mmol) under argon, followed by dropwise addition of n-BuLi in hexane (2.2 mL, 5.5 mmol, 2.5 mol/L) at -78 °C. The reaction mixture was stirred for 10 minutes at this temperature and *O*-carbethoxy-3,5-dimethyl-4-chloromethylphenol **3** (1.28 g, 5.3 mmol) in anhydrous THF (20 mL) was added dropwise. After addition, the reaction was allowed to warm to room temperature for 3 hours. The reaction mixture was quenched by water and was extracted with ethyl acetate (3 × 30 mL). The combined organic phase was washed with saturated NH_4C1 solution, water and brine, then evaporated to dryness under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc to

give 2.20 g (80%) **7** as a white solid. mp. 102-103 °C; R_f = 0.33 (silica gel, petroleum ether/EtOAc 2/1); $[\alpha]_D^{20}$ = -88.5 (c = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, J = 5.2, 3.3 Hz, 2H), 7.40-7.34 (m, 4H), 7.31-7.28 (m, 4H), 6.35 (s, 2H), 5.17 (t, J = 7.8 Hz, 1H), 3.92 (dd, J = 7.7, 4.7 Hz, 1H), 3.34 (s, 2H), 3.28 (dd, J = 13.6, 7.5 Hz, 1H), 2.90-2.84 (m, 1H), 2.65 (d, J = 9.4 Hz, 1H), 2.34 (d, J = 24.7 Hz, 1H), 1.99 (s, 6H), 1.83 (dd, J = 12.7, 5.3 Hz, 2H), 1.76 (t, J = 3.8 Hz, 1H), 0.91-0.85 (m, 6H), 0.70 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 169.8, 154.1, 140.1, 139.5, 135.7, 130.1, 128.8, 128.1, 127.9, 114.8, 65.2, 64.4, 53.3, 48.2, 47.6, 44.6, 38.1, 34.2, 32.8, 26.4, 20.2, 20.1, 20.0, 19.8. HRMS (ESI): calcd. for $C_{34}H_{39}N_2O_4S$ $[M+H]^+$ 571.2625; found 571.2630.

Anal. Calcd for $C_{34}H_{38}N_2O_4S$: C, 71.55; H, 6.71; N, 4.91; S, 5.62. Found: C, 71.45; H, 6.63; N, 4.97; S, 5.50.

(2S)-2-Amino-1-((6R,7aR)-8,8-dimethyl-2,2-dioxidotetrahydro-3H-3a,6-methanobenzo[c]isothiazol-1(4H)-yl)-3-(4-hydroxy-2,6-dimethylphenyl)propan-1-one (8)

To a solution of **7** (1.68 g, 2.96 mmol) in THF (20 mL) was added aqueous 1.0 mol/L HCl (4.5 mL) at 0 °C. The reaction was stirred at 0 °C for 4 h. After adding 20 mL of H_2O, the two phases were separated, the aqueous layer was washed with ethyl acetate (20 mL), then was basified with saturated sodium bicarbonate and extracted with ethyl acetate (3 x 50 mL). The combined organic phase was dried with Na_2SO_4, filtered and evaporated to dryness. The residue was purified by flash column chromatography on silica gel eluting with petroleum ether/EtOAc to give 1.04 g **8** (86%) as a white solid. m.p. 208-209 °C; R_f = 0.23 (silica gel, petroleum ether/EtOAc 1/1); $[\alpha]_D^{20}$ = +23.5 (c = 1.0, MeOH); ^{1}H NMR (500 MHz, DMSO) δ 6.34 (s, 2H), 3.72 (d, J = 14.1 Hz, 2H), 3.06 (q, J = 14.0 Hz, 1H), 2.89 (dd, J = 13.8, 8.7 Hz, 1H), 2.70 (dd, J = 13.8, 6.6 Hz, 1H), 2.26 (s, 2H), 2.19 (s, 6H), 1.84-1.70 (m, 6H), 1.64 (s, 1H), 1.23-1.13 (m, 1H), 1.04 (s, 1H), 0.85 (s, 6H). ^{13}C NMR (125 MHz, DMSO) δ 167.4, 155.4, 138.0, 124.3, 114.8, 62.0, 54.2, 49.9, 47.0, 44.2, 35.3, 31.5, 26.4, 20.4, 20.3, 20.1, 20.0. HRMS (ESI): calcd. for $C_{21}H_{31}N_2O_4S$ $[M+H]^+$ 407.1999; found 407.2012.

Anal. Calcd for $C_{21}H_{30}N_2O_4S$: C, 62.04; H, 7.44; N, 6.89; S, 7.89. Found: C, 61.98; H, 7.35; N, 6.94; S, 7.74.

(S)-2,6-Dimethyltyrosine (S-DMT)[10]

Lithium hydroxide solution (2.7 mL, 6.64 mmol, 2.5 mol/L) was added to a stirred solution of **8** (0.90 g, 2.22 mmol) in THF (15 mL) at 0 °C. The resulting mixture was stirred at this temperature for an additional 1.0 h. THF was evaporated, the aqueous solution was acidified with 1.0 mol/L hydrochloric acid to pH 2 and the mixture was extracted with ethyl acetate (3 × 20 mL). The aqueous phase was neutralized with saturated sodium bicarbonate solution to pH 6-7. At this point, precipitation of a white solid occurred. The precipitate was filtered and dried under vacuum to afford white solid product (*S*)-DMT (300 mg, 82%). mp. 247-248 °C (lit.[10] 247-249 °C); R_f = 0.28 (silica gel, EtOAc/MeOH 2/1); $[\alpha]_D^{20}$ = +43.3 (c = 1.0, MeOH), lit.[10] $[\alpha]_D^{25}$ = +39.41(c = 1.017, MeOH); ^{1}H NMR (500 MHz, D_2O) δ 6.38 (s, 2H), 3.88 (t, J = 8.2 Hz, 1H), 3.01 (dd, J = 14.7, 8.5 Hz, 1H), 2.86 (dd, J = 14.7, 7.9 Hz, 1H), 2.01 (s, 6H). ^{13}C NMR (125 MHz, D_2O) δ =171.8, 154.2, 139.3, 123.3, 115.0, 52.5, 29.6, 19.2.

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