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Enantioselective synthesis of (*S*)-4-methyleneglutamic acid via tandem conjugate addition–elimination under phase-transfer catalytic conditions

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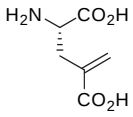
ABSTRACT

An efficient enantioselective synthetic method for (*S*)-4-methyleneglutamic acid is reported. Phase-transfer catalytic conjugate addition–elimination of the benzophenone imine of glycine *tert*-butyl ester in the presence of chiral *Cinchona*-derived catalysts give the corresponding conjugated addition products (>99% ee), which could be hydrolyzed to chiral (*S*)-4-methyleneglutamic acid.

1. Introduction

(*S*)-4-Methyleneglutamic acid (**1**), first isolated from germinated peanuts in 1951 and also found in a variety of other plants,[1] has been known to possess inhibitory activity against the central nervous system.[2] The peptide composed of Boc-4-methyleneGlu-Glu-Val has been shown to be a strong inhibitor of vitamin K-dependent carboxylation, an important process in blood clotting.[3]



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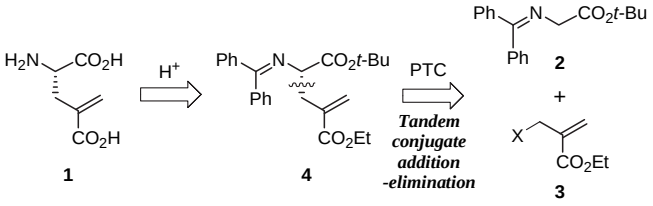
(*S*)-4-Methylene glutamic acid

As a part of our research program to study the structure–activity relationship of **1** and its derivatives, an efficient and practical synthetic method of **1** is need to be developed. Although there have been several synthetic methods for optically enriched **1**, all of the reported processes employed chiral substrates or enzymes for resolution, which might not be suitable for large scale preparation.[4] In the last decade, we have made efforts toward the development of novel cinchona alkaloid-derived chiral phase-transfer catalysts and their application in the enantioselective preparation of natural and nonnatural optically active amino acid derivatives, including the asymmetric alkylation of the *N*-(diphenylmethylene) glycine *tert*-butyl ester (**2**), a powerful route toward chiral amino acids.[5] In this article, an efficient catalytic enantioselective synthesis of **1** via asymmetric tandem conjugate addition–elimination under phase-transfer conditions is reported.

2. Results and discussion

In 2005, Ramachandran et al. reported quite excellent enantioselective synthetic method for 4-alkylidenyl glutamic acid methyl esters by tandem conjugate addition–elimination of activated allylic acetates under chiral PTC conditions.[6] Similarity of structures led us to adapt their method for the synthesis of (*S*)-4-methyleneglutamic acid. We envisioned that an asymmetric phase-transfer catalytic alkylation can be employed as a key step, as shown in the retrosynthetic analysis (Scheme 1), for introduction of the *S* chirality, followed by acidic hydrolysis to afford **1**.



Scheme 1. Strategy for the synthesis of (*S*)-4-methyleneglutamic acid (**1**).

Michael acceptors (**3a**–**d**) were prepared in two steps from ethyl acrylate (**5**) by the Baylis–Hillman reaction,[7] followed by

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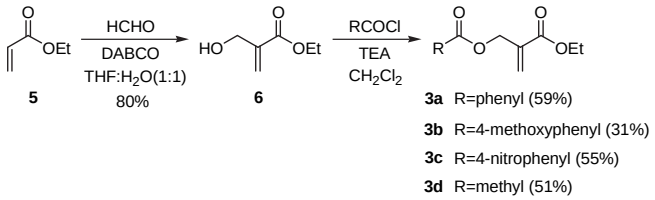
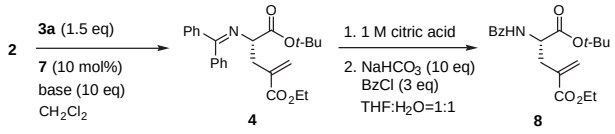
O-acylation (Scheme 2). Treatment of ethyl acrylate (**5**) with formaldehyde in the presence of DABCO in THF/H_2O (1:1) afforded ethyl 2-(hydroxymethyl) acrylate (**6**) in 80% yield. Acylation of **6** with the selected acid chlorides gave the corresponding Michael acceptors (**3a**–**d**).



Scheme 2. Preparation of Michael acceptors.

Catalytic asymmetric conjugate addition–elimination was carried out with ethyl 2-(acyloxymethyl)acrylate **3** and benzophenone imine of glycine ester **2** under phase-transfer conditions (Table 1). Four kinds of hydrocinchonidinium salts (**7a**–**d**, Fig. 1),[8] which have previously shown excellent capabilities as chiral phase-transfer catalysts in the asymmetric alkylation of **2**, were employed for chirality generation.

Table 1
Enantioselective tandem conjugate addition-elimination under PTC conditions[a]



Entry	7	Base	Temp (°C)	Time[b] (h)	Yield[c] (%)	ee (%)[d] (config.)[e]
1	**7a**	50% KOH	−40	16	93	64 (*S*)
2	**7b**	50% KOH	−40	20	87	78 (*S*)
3	**7c**	50% KOH	−40	16	86	76 (*S*)
4	**7d**	50% KOH	−40	26	84	90 (*S*)
5	**7d**	50% KOH	−55	30	85	92 (*S*)
6	**7d**	CsOH·H_2O	−78	12	91	92 (*S*)

[a] Reaction conducted with the benzophenone imine of glycine *tert*-butyl ester (**2**, 1.0 equiv), Michael acceptor (**3a**, 1.5 equiv), base (10.0 equiv), and PTC (**7**, 0.1 equiv).
[b] Reaction time of the first step.
[c] Isolated yield for the two steps.
[d] Enantiopurity determined by chiral HPLC analysis of *N*-benzoyl derivative **8** using a chiral column (DAICEL Chiralpak AD-H) with hexane/2-propanol as the solvent system.
[e] Absolute configuration determined by comparing with the optical rotation value of the 4-methyleneglutamic acid HCl salt, obtained by hydrolysis of **8** in 6.0 M HCl, with literature value.[4c]

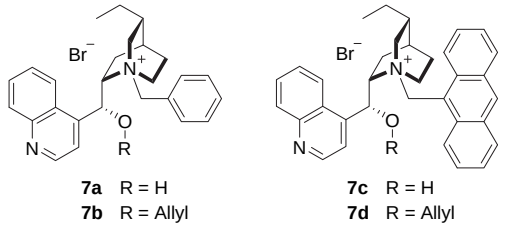
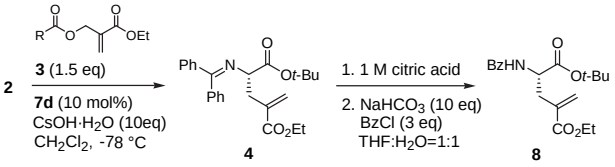


Figure 1. Phase-transfer catalysts.

Screening of PTC was first performed under the same conditions (**3a** Michael acceptor, 50% KOH base, CH_2Cl_2 solvent, and −40 °C reaction temperature), and the results are shown in Table 1. The *O*-allyl-*N*-(9-anthracenylmethyl) hydrocinchonidinium bromide (**7d**) gave the product with the highest enantioselectivity (entry 4, 84% yield, 90% ee). Generally, *C*(9)-*O*-allyl catalysts (entry 2, **7b**, 78% ee; entry 4, **7d**, 90% ee) showed higher enantioselectivities compared to those of *C*(9)–*OH* catalysts (entry 1, **7a**, 64% ee; entry 3, **7c**, 76% ee), respectively. Further tuning of the reaction conditions revealed that use of the CsOH·H_2O base at lower reaction temperature (−78 °C) was highly advantageous to improve both chemical and optical yields (entry 6, 91% yield, 92% ee).

Next, the Michael acceptor was optimized under the best reaction conditions (entry 6 in Table 1) to improve the enantioselectivity, which was not studied in the works of Ramachandran et al.[6] Asymmetric tandem conjugate addition–elimination of **2** with the prepared Michael acceptors (**3b**–**d**) were performed under reaction conditions of CsOH·H_2O in the presence of **7d** in dichloromethane at −78 °C (Table 2). Chemical yield and enantioselectivity were variable depending upon the leaving groups in the Michael acceptors. All afforded the conjugate addition–elimination product (**4**) in high enantioselectivities. It was expected that **3c**, with a better leaving group, would provide a higher chemical yield, but the lowest yield with moderate enantioselectivity was observed among the Michael acceptors (**3a**–**d**). The 4-methoxy-incorporated **3b** showed chemical and optical yields substantially higher than 4-nitro analogue **3c**. The smaller acetoxy group (**3d**) gave the highest chemical yield. The highest enantioselectivity was obtained with **3b** (entry 2, 99% ee). There is no clear evidence yet but we speculate that the 4-methoxybenzoyl group might play an important role for the high enantioselectivity in electronically or spatially in PTC reaction process. Hydrolysis of **8** (99% ee) in 6.0 M HCl gave the (*S*)-4-methyleneglutamic acid hydrochloride salt (**1**·HCl) in 97% yield. Absolute configuration was confirmed as *S* by comparing optical rotation with the reported value {$[\alpha]_D^{20}$ +13.5 (*c* 0.5, HCl); lit.[4c] $[\alpha]_D^{20}$ +13.2 (*c* 1.0, HCl)}.

Table 2
Enantioselective phase-transfer catalytic Michael reaction and elimination reaction[a]



Entry	3	R	Time[b] (h)	Yield[c] (%)	ee (%)[d] (config.)
1	**3a**	Phenyl	12	91	92 (*S*)
2	**3b**	4-Methoxyphenyl	14	90	99 (*S*)
3	**3c**	4-Nitrophenyl	13	77	93 (*S*)
4	**3d**	Methyl	12	95	96 (*S*)

[a] Reactions carried out with benzophenone imine of glycine *tert*-butyl ester **2** (1.0 equiv), Michael acceptor **3** (1.5 equiv), CsOH·H_2O (10.0 equiv), **7d** (0.1 equiv).
[b] Reaction time of the first step.
[c] Isolated yield for the two steps.
[d] Enantiopurity and absolute configuration were determined as Table 1.

3. Conclusions

A new enantioselective synthetic method of (*S*)-4-methyleneglutamic acid (**1**) under asymmetric phase-transfer catalytic tandem conjugate addition–elimination of the benzophenone imine of glycine *tert*-butyl ester (**2**) with chiral cinchona catalysts has been developed. Highly optically active **1**·HCl was prepared from **2** in three steps at 88% chemical yield and 99% ee.

4. Experimental

4.1. General

Infrared (IR) spectra were recorded on a JASCO FT/IR-300E and Perkin–Elmer 1710 FT spectrometer. ^{1}H NMR was measured at 300

or 400 MHz and ^{13}C NMR at 75, 100, or 125 MHz. Chemical shifts were recorded in parts per million relative to $CHCl_3$ (δ 7.24) and H_2O (δ 4.70) for ^1H NMR and relative to the central $CDCl_3$ (δ 77.21) resonance for ^{13}C NMR. Melting points were not corrected. Enantiomeric excess (ee) was determined by HPLC using 4.6 mm×250 mm Daicel Chiralpak AD-H column. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. High-resolution mass spectra (HRMS) were measured on a JEOL JMS-AX 505wA, JEOL JMS-HX/HX 110A spectrometer. Flash column chromatography was carried out using silica gel (230–400 mesh). For thin-layer chromatography (TLC) analysis, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. All solvents and commercially available chemicals were used without additional purification. Ethyl 2-(hydroxymethyl)acrylate (**6**) was prepared according to reported procedures.[7]

4.2. Ethyl 2-(benzoyloxymethyl)acrylate (3a)

To a cooled solution of ethyl 2-(hydroxymethyl)acrylate (**6**) (1.0 g, 7.68 mmol) in dichloromethane (30 mL) were added triethylamine (1.61 mL, 11.52 mmol) and benzoyl chloride (1.34 mL, 11.52 mmol). After stirring for 1 h, the reaction mixture was washed with brine (2×30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by column chromatography (hexanes/EtOAc=10:1) to afford **3a** (1.06 g, 59%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 8.06–8.03 (m, 2H), 7.58–7.53 (m, 1H), 7.46–7.40 (m, 2H), 6.40 (s, 1H), 5.91 (s, 1H), 5.05 (s, 2H), 4.24 (q, J=7.14 Hz, 2H), 1.29 (t, J=7.14 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.1, 135.5, 133.0, 130.4, 129.5, 128.3, 127.0, 62.7, 14.0 ppm; IR (KBr) ν 2983, 1789, 1725, 1602, 1452, 1416, 1315, 1274, 1213, 1175, 1111, 1070, 1027, 712 cm^{-1}; HRMS (FAB): calcd for $[C_{13}H_{15}O_4]^+$: 235.0970, found: 235.0964.

4.3. Ethyl 2-(4-methoxybenzoyloxymethyl)acrylate (3b)

To a cooled solution of ethyl 2-(hydroxymethyl)acrylate (**6**) (1.0 g, 7.68 mmol) in dichloromethane (30 mL) were added triethylamine (1.61 mL, 11.52 mmol) and 4-methoxybenzoyl chloride (2.62 g, 15.36 mmol). After stirring for 3 h, the reaction mixture was washed with brine (2×30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by column chromatography (hexanes/EtOAc=20:1) to afford **3b** (634 mg, 31%) as a white solid. Mp 40 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.13–7.98 (m, 2H), 6.93–6.88 (m, 2H), 6.38 (s, 1H), 5.89 (s, 1H), 5.02 (s, 2H), 4.24 (q, J=7.14 Hz, 2H), 3.85 (s, 3H), 1.28 (t, J=7.14 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 165.2, 135.7, 131.6, 126.8, 122.2, 113.6, 62.5, 60.9, 55.4, 14.1 ppm; IR (KBr) ν 2980, 1721, 1606, 1511, 1458, 1366, 1309, 1258, 1167, 1101, 1028, 848, 769, 696 cm^{-1}; HRMS (FAB): calcd for $[C_{14}H_{17}O_5]^+$: 265.1076, found: 265.1083.

4.4. Ethyl 2-(4-nitrobenzoyloxymethyl)acrylate (3c)

To a cooled solution of ethyl 2-(hydroxymethyl)acrylate (**6**) (1.0 g, 7.68 mmol) in dichloromethane (30 mL) were added triethylamine (1.64 mL, 11.78 mmol) and 4-nitrobenzoyl chloride (2.18 g, 11.78 mmol). After stirring for 10 min, the reaction mixture was washed with brine (2×30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by column chromatography (hexanes/EtOAc=20:1) to afford **3c** (1.21 g, 55%) as a pale yellow solid. Mp 78 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.29–8.18 (m, 4H), 6.44 (s, 1H), 5.93 (s, 1H), 5.08 (s, 2H), 4.25 (q, J=7.14 Hz, 2H), 1.29 (t, J=7.14 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 164.1, 150.6, 135.2, 135.1, 130.7, 128.2, 123.5, 63.8, 61.1, 14.1 ppm; IR (KBr) ν 3114, 1725, 1648, 1517, 1460, 1406, 1348, 1272, 1117, 1009, 963, 878, 854, 819, 784, 719 cm^{-1}; HRMS (FAB): calcd for $[C_{13}H_{14}O_6N]^+$: 280.0821, found: 280.0813.

4.5. Ethyl 2-(acetoxymethyl)acrylate (3d)

To a cooled solution of ethyl 2-(hydroxymethyl)acrylate (**6**) (1.0 g, 7.68 mmol) in dichloromethane (30 mL) were added triethylamine (2.75 mL, 19.74 mmol) and acetyl chloride (1.4 mL, 19.74 mmol). After stirring for 20 min, the reaction mixture was washed with brine (2×30 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by column chromatography (hexanes/EtOAc=20:1) to afford **3d** (1.21 g, 51%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 6.32 (s, 1H), 5.79 (s, 1H), 4.76 (s, 2H), 4.20 (q, J=7.14 Hz, 2H), 2.06 (s, 3H), 1.26 (t, J=7.14 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.2, 165.0, 135.3, 127.0, 62.3, 60.8, 20.7, 14.0 ppm; IR (KBr) ν 2984, 1748, 1725, 1643, 1370, 1305, 1231, 1178, 1050, 953, 816 cm^{-1}.

4.6. (*S*)-1-*tert*-Butyl 5-ethyl 2-(diphenylmethylene-amino)-4-methylenepentanedioate (4)

A suspension of *N*-(diphenylmethylene)glycine *tert*-butyl ester (**2**) (30 mg, 0.102 mmol), ethyl 2-(4-methoxybenzoyloxymethyl) acrylate (**3b**) (40.4 mg, 0.153 mmol), and chiral phase-transfer catalyst **7d** (6.2 mg, 0.010 mmol) in dichloromethane (0.5 mL) was cooled at −78 °C. Solid $CsOH\cdot H_2O$ (171 mg, 1.02 mmol) was then added to the reaction mixture. After stirring at −78 °C for 14 h, the reaction mixture was washed with brine (2×2 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by column chromatography (hexanes/EtOAc=20:1) to afford **4** (38 mg, 90%) as a pale yellow oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.59–7.57 (m, 2H), 7.39–7.26 (m, 6H), 7.11–7.08 (m, 2H), 6.17 (s, 1H), 5.60 (s, 1H), 4.18 (q, J=4.38 Hz, 1H), 4.03–3.91 (m, 2H), 3.00 (dd, J=13.53, 4.2 Hz, 1H), 2.79 (dd, J=13.35, 8.97 Hz, 1H), 1.43 (s, 9H), 1.11 (t, J=7.14 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 170.5, 166.4, 139.5, 136.8, 136.4, 130.1, 128.7, 128.4, 128.2, 128.0, 127.9, 81.1, 64.5, 60.4, 36.0, 28.0, 27.9, 13.9 ppm; IR (KBr) ν 2978, 1721, 1626, 1446, 1392, 1368, 1280, 1151, 1028, 950, 846, 781, 698 cm^{-1}; HRMS (FAB): calcd for $[C_{14}H_{17}O_5]^+$: 408.2175, found: 408.2165.

4.7. (*S*)-1-*tert*-Butyl 5-ethyl 2-benzamido-4-methylenepentanedioate (8)

A mixture of **4** (37.4 mg, 0.092 mmol), 1.0 M citric acid (1.5 mL), and tetrahydrofuran (1.5 mL) was stirred at room temperature for 2 h. Sodium bicarbonate was added to the mixture until the pH reached 7–8, and then benzoyl chloride (0.036 mL, 0.306 mmol) was added. The mixture was stirred for 5 h. The tetrahydrofuran was then evaporated and the residue diluted with ethyl acetate (3 mL). The mixture was washed with brine (2×3 mL), dried over anhydrous Na_2SO_4, and concentrated. The residue was purified by column chromatography (hexanes/EtOAc=10:1) to afford **8** (32 mg, 90%) as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.80–7.77 (m, 2H), 7.50–7.38 (m, 3H), 7.14 (d, J=6.96, 1H), 6.26 (s, 1H), 5.70 (s, 1H), 4.81–4.74 (m, 1H), 4.25–4.15 (m, 2H), 2.93–2.78 (m, 2H), 1.45 (s, 9H), 1.27 (t, J=7.14 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 167.2, 166.7, 136.1, 133.8, 131.4, 128.4, 126.9, 82.2, 61.1, 53.0, 34.4, 27.8, 25.2, 13.9 ppm; IR (KBr) ν 3347, 2979, 1719, 1645, 1580, 1533, 1488, 1368, 1309, 1228, 1154, 1026, 953, 846, 714 cm^{-1}; HRMS (FAB): calcd for $[C_{19}H_{26}O_5N]^+$: 348.1811, found: 348.1803. Enantiopurity was determined by chiral HPLC analysis (DIACEL Chiralcel AD-H, hexanes/2-propanol=9:1), flow rate=1.0 mL/min, 23 °C, λ=254 nm, retention time, minor 10.4 min, minor 20.7 min, 99% ee.

4.8. (*S*)-4-Methyleneglutamic acid hydrochloride (1·HCl)

A mixture of **8** (109 mg, 0.314 mmol) and 6.0 M HCl (2 mL) was refluxed for 24 h. Concentration of the reaction mixture in vacuo

afforded **1**·HCl (59.3 mg, 97%) as a pale yellow solid. Mp 196 °C; ^{1}H NMR (500 MHz, D_2O) δ 6.39 (s, 1H), 5.89 (s, 1H), 4.31–4.16 (m, 1H), 3.75 (d, J=10.5, 3H), 3.01–2.79 (m, 2H) ppm; ^{13}C NMR (100 MHz, D_2O) δ 171.3, 169.6, 133.6, 132.2, 52.3, 32.5 ppm; $[\alpha]_D^{20}$ +13.2 (*c* 0.5, HCl); lit.[4c] $[\alpha]_D$ +13.2 (*c* 1.0, HCl).

Acknowledgements

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.04.034.

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