Supporting Information

Three Component Coupling Based on the “Cation Pool” Method

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General Remarks. GC analysis was performed on a gas chromatograph (SHIMADZU GC-14B) equipped with a flame ionization detector using a fused-silica capillary. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on Varian Gemini 2000, Varian MERCURYplus-400, JEOL A-500 or JEOL ECA-600 with Me_4Si as an internal standard, unless otherwise noted. NMR spectra of the carbamates were usually very broad and sometimes separated into two signals due to their rotamers. Especially in cases where two diastereomers exist, the ^{13}C NMR spectra were complicated and a few signals were occasionally missing. Mass spectra were obtained on a JEOL JMS SX-102A mass spectrometer. Elemental analyses were carried out at the Kyoto University Elemental Analysis Center. IR spectra were measured with a SHIMADZU FTIR 8100 spectrometer. Thin-layer chromatography (TLC) was carried out by using Merck precoated silica gel F₂₅₄ plates (thickness 0.25 mm). Gel permeation chromatography (GPC) was carried out on a Japan Analytical Industry LC-908 equipped with JAIGEL-1H and 2H using CHCl_3 as an eluant. All reactions were carried out under an Ar atmosphere, unless otherwise noted.

Materials. Tetrabutylammonium tetrafluoroborate was purchased from TCI and dried at 50 °C/1 mmHg overnight before use. Dichloromethane was washed with water, distilled from P_2O_5 , redistilled from dried K_2CO_3 to remove a trace amount of acid, and stored over molecular sieves 4A. THF was purchased from Kanto as a dehydrated solvent. 2,3-Dihydropyrrole-1-carboxylic acid methyl ester (**3**) was prepared according to the literature.¹

Generation of *N*-Acyliminium Ion Pool. The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca. 320 mg, dried at 250 °C/1 mmHg for 1 h before use) and a platinum plate cathode (40 mm x 20 mm). In the anodic chamber was placed a solution of carbamate (0.400 mmol) in 0.3 M $\text{Bu}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2$ (8.0 mL). In the cathodic chamber were placed 0.3 M $\text{Bu}_4\text{NBF}_4/\text{CH}_2\text{Cl}_2$ (8.0 mL) and trifluoromethanesulfonic acid (150.1 mg, 1.00 mmol). The constant current electrolysis (8 mA) was carried out at -78 °C with magnetic stirring until 2.5 F/mol of electricity was consumed.

2-Allyl-3-(butyl(methoxycarbonyl)amino)methyl-1-(methoxycarbonyl)-pyrrolidine (5**). A Typical Procedure for Three Component Coupling Reaction Using *N*-Acyliminium Ion Pool.**

The electrolysis of carbamate (**1**) (85.8 mg, 0.395 mmol) was carried out as described above. Compound **3** (32.2 mg, 0.253 mmol) (dissolved in 0.3 mL of CH_2Cl_2) was added dropwise to the cation pool thus generated in the anodic chamber at -78 °C and stirred for ten minutes at the same temperature. Then, allyltrimethylsilane (90.7 mg, 0.794 mmol) was added to the cation pool at -78 °C. After ten minutes triethylamine (145.2 mg, 1.43 mmol) was added to the reaction mixture at -78 °C. The solvent was removed under reduced pressure and the residue was quickly filtered through a short column of silica gel (2 x 10 cm) to remove Bu_4NBF_4 . The silica gel was washed with ether (200 mL). The solvent was removed under reduced pressure and the crude product

was purified with flash chromatography (hexane/EtOAc 3:1) to give title compound as a mixture of two diastereomers (total 51.8 mg, 66% yield, diastereomer ratio was 93:7 (determined by GC)): TLC R_f 0.42 (hexane/EtOAc 1:1); ^1H NMR (300 MHz, CDCl_3) δ 0.92 (t, $J = 6.9$ Hz, 3H), 1.20-1.37 (m, 2H), 1.40-1.75 (m, 3H), 1.88-2.07 (m, 1H), 2.09-2.57 (m, 3H), 2.95-3.77 (m, 13H), 5.00-5.15 (m, 2H), 5.63-5.89 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.6, 19.8, 25.6 and 26.1 and 26.6, 29.8 and 30.3, 37.5 and 38.3, 40.5 and 41.2, 44.8, 47.4, 48.3 and 48.6 and 49.3 and 49.7, 52.1, 52.3, 59.1 and 59.6 and 60.0 and 60.3, 117.4, 134.4, 155.4 and 155.4, 156.6 and 156.8; IR (neat) 2957, 1705, 1456 cm^{-1} ; LRMS (CI) m/e 313 (MH^+), 281 ($\text{M}^+ - \text{CH}_3\text{O}$), 271 ($\text{M}^+ - \text{C}_3\text{H}_5$); HRMS (CI) calcd for $\text{C}_{16}\text{H}_{29}\text{N}_2\text{O}_4$ (MH^+): 313.2127, found: 313.2130.

3-(Butyl(methoxycarbonyl)amino)methyl-2-(cyclohex-2-enyl)-1-(methoxycarbonyl)pyrrolidine (6).

Prepared from **3** (32.6 mg, 0.256 mmol) and **1** (86.7 mg, 0.399 mmol) and 3-(trimethylsilyl)cyclohexene (204.3 mg, 1.32 mmol), and purified with flash chromatography (hexane/EtOAc 4:1). A mixture of two diastereomers (total 37.7 mg, 42% yield, diastereomer ratio 99:1 (determined by GC)): TLC R_f 0.57 (hexane/EtOAc 1:1); ^1H NMR (300 MHz, CDCl_3) δ 0.92 (t, $J = 7.5$ Hz, 3H), 1.19-1.40 (m, 3H), 1.40-1.88 (m, 6H), 1.89-2.10 (m, 3H), 2.29-2.80 (m, 2H), 2.93-3.80 (m, 7H), 3.68 (s, 3H), 3.70 (s, 3H), 5.33-5.67 (m, 1H), 5.72-5.85 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.8, 19.9, 21.7, 25.3, 26.3, 26.9 and 27.3, 29.8 and 30.5, 38.3 and 38.6, 39.2 and 39.5, 45.4, 47.6, 49.6 and 49.9 and 50.6 and 51.0, 52.2, 52.4, 63.7 and 64.2 and 64.6 and 64.9, 127.2, 128.5 and 129.4, 156.0, 156.7; IR (neat) 2955, 1705, 1446 cm^{-1} ; LRMS (CI) m/e 353 (MH^+), 321 ($\text{M}^+ - \text{CH}_3\text{O}$), 271 ($\text{M}^+ - \text{C}_6\text{H}_9$); HRMS (CI) calcd for $\text{C}_{19}\text{H}_{33}\text{N}_2\text{O}_4$ (MH^+): 353.2440, found: 353.2440.

3-(Butyl(methoxycarbonyl)amino)methyl-1-methoxycarbonyl-2-(2-oxo-2-phenylethyl)pyrrolidine (7).

Prepared from **3** (31.4 mg, 0.247 mmol) and **1** (87.0 mg, 0.400 mmol) and 1-phenyl-1-(trimethylsilyloxy)ethene (249.4 mg, 1.30 mmol), and purified with flash chromatography (hexane/EtOAc 4:1). A mixture of two diastereomers (total 56.4 mg, 58% yield, diastereomer ratio 99:1 (determined by GC)): TLC R_f 0.24 (hexane/EtOAc 1:1); ^1H NMR (300 MHz, CDCl_3) δ 0.90 (t, $J = 7.2$ Hz, 3H), 1.14-1.81 (m, 5H), 1.89-2.05 (m, 1H), 2.28-2.48 (m, 1H), 2.74-3.83 (m) and 3.61 (s) and 3.71 (s) (total 14H, two rotamers), 4.00-4.15 (m, 1H), 7.40-7.63 (m, 3H), 7.94 (d, $J = 7.5$ Hz) and 8.03 (d, $J = 7.5$ Hz) (total 2H, two rotamers); ^{13}C NMR (125 MHz, CDCl_3) δ 13.8, 19.9, 24.5 and 25.4 and 25.9, 29.8 and 30.3, 41.5, 42.6 and 43.1, 44.7 and 45.2, 46.4 and 47.2, 48.0 and 48.5 and 49.0, 52.3, 56.9 and 58.0 and 58.7, 128.0 and 128.2, 128.6, 133.3, 136.5, 155.3 and 156.7 and 157.5, 198.1 and 198.8; IR (neat) 2957, 1684, 1451 cm^{-1} ; LRMS (EI) m/e 390 (M^+), 359 ($\text{M}^+ - \text{CH}_3\text{O}$), 271 ($\text{M}^+ - \text{C}_8\text{H}_7\text{O}$); HRMS (EI) calcd for $\text{C}_{21}\text{H}_{30}\text{N}_2\text{O}_5$ (M^+): 390.2155, found: 390.2157.

3-(Butyl(methoxycarbonyl)amino)methyl-2-(1-methoxycarbonyl-1-methylethyl)-1-(methoxycarbonyl)pyrrolidine (8).

Prepared from **3** (33.8 mg, 0.266 mmol) and **1** (87.3 mg, 0.402 mmol) and methyl trimethylsilyl dimethylketene acetal (240.8 mg, 1.38 mmol), and purified with flash chromatography (hexane/EtOAc 3:1). A mixture of two diastereomers (total 67.3 mg, 68% yield, diastereomer ratio 99:1 (determined by GC)): TLC R_f 0.43 (hexane/EtOAc 1:1); ^1H NMR (300 MHz, CDCl_3) δ 0.92 (t, $J = 6.9$ Hz, 3H), 1.05-1.37 (m, 2H), 1.15 (s, 3H), 1.19 (s, 3H), 1.40-1.75 (m, 3H), 1.80-2.03 (m, 1H), 2.25-2.56 (m,

1H), 2.85-3.48 (m, 5H), 3.68 (s, 6H), 3.70 (s, 3H), 3.55-3.88 (m, 1H), 3.92-4.14 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 13.7 and 13.8, 19.9, 21.3, 23.7 and 23.9, 26.9, 29.7 and 30.4, 39.5 and 40.1, 46.4, 47.7, 50.0, 51.0, 51.9, 52.4, 52.4, 65.6 and 66.8, 156.6, 157.3, 157.8; IR (neat) 2957, 1788, 1447 cm⁻¹; LRMS (CI) m/e 373 (MH⁺), 341 (M⁺ - CH₃O), 271 (M⁺ - C₅H₉O₂); HRMS (CI) calcd for C₁₈H₃₃N₂O₆ (MH⁺): 373.2339, found: 373.2342.

3-(Butyl(methoxycarbonyl)amino)methyl-2-ethyl-1-(methoxycarbonyl)-pyrrolidine (9).

Prepared from **3** (34.2 mg, 0.269 mmol) and **1** (87.0 mg, 0.400 mmol) and ethyl magnesium bromide (3.0 M diethyl ether solution, 0.450 ml, 1.35 mmol), and purified with flash chromatography (hexane/EtOAc 3:1). A mixture of two diastereomers (total 35.2 mg, 44% yield, diastereomer ratio 67:33 (determined by GC): TLC *R_f* 0.50 (hexane/EtOAc 1:1); ¹H NMR (300 MHz, CDCl₃) δ 0.86 (t, *J* = 6.9 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H), 1.21-1.89 (m, 7H), 1.90-2.05 (m, 1H), 2.23-2.49 (m, 1H), 2.96-4.00 (m, 7H), 3.68 (s, 3H), 3.69 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 10.2, 13.7, 19.9, 25.7 and 26.2 and 26.7 and 26.9, 29.9 and 30.5, 40.5 and 40.8 and 41.4, 44.6 and 44.9, 47.6, 48.7 and 49.0, 49.9 and 50.3, 52.1, 52.4, 61.2 and 61.6 and 62.2, 155.3 and 155.8 and 155.9, 156.8 and 156.8; IR (neat) 2959, 1705, 1451 cm⁻¹; LRMS (EI) m/e 300 (M⁺), 271 (M⁺ - C₂H₅), 269 (M⁺ - CH₃O); HRMS (EI) calcd for C₁₅H₂₈N₂O₄ (M⁺): 300.2049, found: 300.2049.

3-(Butyl(methoxycarbonyl)amino)methyl-2-phenyl-1-(methoxycarbonyl)-pyrrolidine (10).

Prepared from **3** (32.3 mg, 0.254 mmol) and **1** (86.3 mg, 0.397 mmol) and phenyl magnesium bromide (2.18 M ether solution, 0.583 ml, 1.27 mmol), and purified with flash chromatography (hexane/EtOAc 3:1). A mixture of two diastereomers (total 45.0 mg, 51% yield, diastereomer ratio 88:12 (determined by GC): TLC *R_f* 0.38 (hexane/EtOAc 1:1); ¹H NMR (300 MHz, CDCl₃) δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.16-1.80 (m, 5H), 1.88-2.12 (m, 1H), 2.31-2.60 (m, 1H), 2.94-3.88 (m, 6H), 3.68 (s, 6H), 4.56-4.68 (m, 1H), 7.05-7.37 (m, 5H); ¹³C NMR (125 MHz, CDCl₃) δ 13.8, 19.9, 25.4 and 26.0, 26.8, 29.9 and 30.4, 45.8 and 46.2 and 46.6 and 46.9, 47.5, 48.5 and 49.1 and 49.5, 52.4, 52.5, 63.6 and 64.1 and 64.6, 125.5, 126.9, 128.4, 142.7 and 143.1, 155.5 and 155.9, 156.8 and 157.3; IR (neat) 2957, 1705, 1453 cm⁻¹; LRMS (CI) m/e 349 (MH⁺), 317 (M⁺ - CH₃O), 271 (M⁺ - C₆H₅); HRMS (CI) calcd for C₁₉H₂₉N₂O₄ (MH⁺): 349.2127, found: 349.2133.

The stereochemistry of **10** was determined by the following transformation.

3-(N'-Butyl-N'-methoxycarbonylamino)methyl-1-methyl-2-phenylpyrrolidine (20). In a 20 mL round-bottomed flask were placed LiAlH₄ (12.0 mg, 0.316 mmol) and Et₂O (5 mL). 3-(Butyl(methoxycarbonyl)amino)methyl-1-methoxy-

carbonyl-2-phenylpyrrolidine (**10**) (33.5 mg, 0.096 mmol) was added at 0 °C. The mixture was heated under reflux for 2.5 h, and then water (2 mL) and *aq* potassium sodium (+)-tartrate (20 %, 10 mL) were added. The organic phase was separated and the aqueous phase was extracted with Et₂O (20 mL x 3). The combined organic phase was dried over Na₂SO₄. The solvent was removed under reduced pressure and the crude product was purified with flash chromatography (EtOAc added 1% Et₃N) to give the title compound (21.7 mg, 87% yield): ¹H NMR (300 MHz, CDCl₃) δ 0.86 (t, *J* = 7.2 Hz, 3H), 1.12-2.64 (m, 19H), 3.16-3.24 (m) and 3.19 (d, *J* = 8.4 Hz) (total 1H, two diastereomers), 7.20-7.39 (m, 5H); LRMS (EI) *m/e* 260 (M⁺); HRMS (EI) calcd for C₁₇H₂₈N₂ (M⁺): 260.2252, found: 260.2246.

¹H NMR spectrum of **20** derived from **10**.

The major isomer was determined as the *trans* isomer by comparison of the ¹H NMR spectrum with that of the authentic sample of *trans*-**20**.

^1H NMR spectrum of **20** derived from **10**

^1H NMR spectrum of authentic *trans*-**20**

The authentic sample of *trans*-**20** was prepared by the following transformation starting from *trans*-1-methyl-4-carboxyl-5-phenyl-2-pyrrolidinon (**21**).²

2,3-*trans*-3-(Butylmethylamino)methyl-1-methyl-2-phenylpyrrolidine (20).

A mixture of *trans*-1-methyl-5-oxo-2-phenylpyrrolidine-3-carboxylic acid (**21**) (96.0 mg, 43.8 mmol) and thionyl chloride (220.9 mg, 1.86 mmol) was heated at 55 °C for 1 h. The excess thionyl chloride was removed under vacuum, and the resulting solid chloride was dissolved in dry THF (10 mL). Butylmethylamine (260.1 mg, 2.98 mmol) was added to the resulting solution under ice cooling and the solution was stirred at room temperature for 5 h. HCl (10 mL) was added at 0 °C. Aqueous phase was separated and extracted with Et₂O (10 mL x 3). The combined organic phase was dried over Na₂SO₄. The solvent was removed under reduced pressure to obtain *trans*-1-Methyl-5-oxo-2-phenylpyrrolidine-3-carboxylic acid butyl methyl amide (86.3 mg, 67% yield): ^1H NMR (300 MHz, CDCl₃) δ 0.67 (t, J = 7.2 Hz) and 0.84 (t, J = 7.2 Hz) (total 3H), 0.90-1.10 (m, 2H), 1.10-1.30 (m, 2H), 1.30-1.48 (m, 1H), 2.50-2.73 (m, 6H), 2.73-3.00 (m, 2H), 3.12-3.41 (m, 2H), 4.78 (dd, J = 2.9 Hz, J = 6.8 Hz, 1H),

7.13-7.40 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.4 and 13.6, 19.5 and 19.8, 28.1, 29.0 and 30.5, 33.9 and 34.7, 35.0 and 35.4, 44.3 and 44.4, 47.9 and 49.5, 67.2 and 67.5, 126.6, 128.4, 128.4, 129.0, 139.4, 139.6, 170.9 and 171.1, 173.0 and 173.0; IR (neat) 2950, 1939, 1456, 1418 cm^{-1} ; LRMS (EI) m/e 288 (M^+); HRMS (EI) calcd for $\text{C}_{17}\text{H}_{24}\text{N}_2\text{O}_2$ (M^+): 288.1838, found 288.1836.

This compound was used for the next transformation without purification. In a 20 mL round-bottomed flask were placed LiAlH_4 (44.0 mg, 1.16 mmol) and Et_2O (3 mL). *trans*-1-Methyl-5-oxo-2-phenylpyrrolidine-3-carboxylic acid butyl methyl amide (42.0 mg, 0.146 mmol) in THF (3 mL) was added at 0 $^\circ\text{C}$. The mixture was heated under reflux for 19.5 h, and then water (2 mL) and *aq* potassium sodium (+)-tartrate (20%, 10 mL) were added. The organic phase was separated and the aqueous phase was extracted with Et_2O (20 mL x 3). The combined organic phase was dried over Na_2SO_4 . The solvent was removed under reduced pressure and the crude product was purified with flash chromatography (EtOAc containing 1% Et_3N) to give the title compound (30.1 mg, 79% yield): ^1H NMR (300 MHz, CDCl_3) δ 0.86 (t, $J = 7.2$ Hz, 3H), 1.12-1.41 (m, 4H), 1.56-1.70 (m, 1H), 2.02 (s) and 2.03 (s) (total 3H), 2.05-2.40 (m, 10H), 2.62 (d, $J = 6.9$ Hz, 1H), 3.16-3.24 (m, 1H), 7.20-7.39 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3) δ 14.0, 20.6, 28.9, 29.3, 40.6, 42.5, 45.8, 55.9, 57.8, 61.5, 76.8, 127.1, 128.0, 128.2, 142.5; IR (neat) 2957, 2770, 1453, 700 cm^{-1} ; LRMS (EI) m/e 260 (M^+); HRMS (EI) calcd for $\text{C}_{17}\text{H}_{28}\text{N}_2$ (M^+): 260.2252, found: 260.2246.

^1H NMR spectrum of *trans* **20**.

2-Allyl-3-(butyl(methoxycarbonyl)amino)methyl-1-(methoxycarbonyl)-piperidine (12).

Prepared from **11** (38.9 mg, 0.276 mmol) and **1** (86.4 mg, 0.397 mmol) and allyltrimethylsilane (160.8 mg, 1.41 mmol), and purified with flash chromatography (hexane/EtOAc 3:1). A mixture of two diastereomers (total 56.2 mg, 62% yield, diastereomer ratio 91:9 (determined by GC): TLC R_f 0.58 (hexane/EtOAc 1:1); ^1H NMR (300 MHz, CDCl_3) δ 0.91 (t, $J = 7.2$ Hz, 3H), 1.20-1.83 (m, 8H), 1.84-2.08 (m, 1H), 2.20-2.58 (m, 2H), 2.76-2.92 (m, 1H), 2.93-3.54 (m, 4H), 3.67 (s, 6H), 3.85-4.28 (m, 2H), 4.97-5.12 (m, 2H), 5.60-5.84 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.8, 20.0, 20.5 and 20.8, 29.8 and 30.4, 34.2, 35.3, 38.7, 47.5, 48.0, 48.9, 52.1, 52.4, 52.4, 117.1, 134.6, 156.0, 157.0; IR (neat) 2956, 1700, 1449 cm^{-1} ; LRMS (CI) m/e 327 (MH^+), 295 ($\text{M}^+ - \text{CH}_3\text{O}$), 285 ($\text{M}^+ - \text{C}_3\text{H}_5$); HRMS (CI) calcd for $\text{C}_{17}\text{H}_{31}\text{N}_2\text{O}_4$ (MH^+): 327.2284, found: 327.2285; Anal calcd for $\text{C}_{17}\text{H}_{30}\text{N}_2\text{O}_4$: C, 62.55; H, 9.26; N, 8.58, found: C, 62.43; H, 9.40; N, 8.31.

3-(Butyl(methoxycarbonyl)amino)methyl-2-ethyl-1-(methoxycarbonyl)-piperidine (13).

Prepared from **11** (37.8 mg, 0.268 mmol) and **1** (86.4 mg, 0.397 mmol) and ethyl magnesium bromide (3.0 M ether solution, 0.45 ml, 1.34 mmol), and purified with flash chromatography (hexane/EtOAc 5:1). A mixture of two diastereomers (total 59.5 mg, 71% yield, diastereomer ratio 61:39 (determined by GC): TLC R_f 0.53 (hexane/EtOAc 1:1); ^1H NMR (500 MHz, CDCl_3) δ 0.84 (t, $J = 7.2$ Hz, 3H), 0.92 (t, $J = 7.2$ Hz, 3H), 1.17-2.04 (m, 11H), 2.64-2.89 (m, 1H), 2.90-3.75 (m, 10H), 3.79-4.28 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 9.7 and 10.4, 13.8, 17.0, 19.9 and 20.6 and 20.9, 23.2 and 23.6, 25.2 and 25.5, 29.7 and 30.4, 34.9, 38.0 and 38.5, 47.5 and 48.1, 49.0 and 49.3, 52.3, 52.4, 53.9 and 54.2, 156.3, 156.9; IR (neat) 2959, 1700, 1451 cm^{-1} ; LRMS (EI) m/e 314 (M^+), 285 ($\text{M}^+ - \text{C}_2\text{H}_5$), 170 ($\text{M}^+ - \text{CH}_2\text{N}(\text{C}_4\text{H}_9)\text{CO}_2\text{CH}_3$); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{30}\text{N}_2\text{O}_4$ (M^+): 314.2206, found: 314.2206.

3-(Butyl(methoxycarbonyl)amino)methyl-1-(methoxycarbonyl)-2-phenyl-piperidine (14).

Prepared from **11** (36.5 mg, 0.259 mmol) and **1** (86.8 mg, 0.399 mmol) and phenyl magnesium bromide (2.18 M ether solution, 0.59 ml, 1.29 mmol), and purified with flash chromatography (hexane/EtOAc 4:1). A mixture of two diastereomers (total 43.2 mg, 46% yield, diastereomer ratio 98:2 (determined by GC): TLC R_f 0.43

(hexane/EtOAc 1:1); ^1H NMR (500 MHz, CDCl_3) δ 0.93 (t, $J = 7.5$ Hz, 3H), 1.16-1.84 (m, 8H), 2.56-2.93 (m) and 2.07-3.82 (m, 6H), 3.71 (s, 3H), 3.74 (s, 3H), 4.07-4.18 (m, 1H), 5.18-5.31 (m, 1H), 7.15-7.39 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.8, 20.0, 21.3, 29.9 and 30.5, 34.3 and 35.0, 40.1, 48.1 and 48.4, 49.6, 52.4, 52.8, 55.4, 55.5, 126.4, 126.7, 128.6, 139.5, 157.2; IR (neat) 2955, 1700, 1447 cm^{-1} ; LRMS (EI) m/e 362 (M^+), 303 ($\text{M}^+ - \text{CO}_2\text{CH}_3$), 218 ($\text{M}^+ - \text{CH}_2\text{N}(\text{C}_4\text{H}_9)\text{CO}_2\text{CH}_3$); HRMS (EI) calcd for $\text{C}_{20}\text{H}_{30}\text{N}_2\text{O}_4$ (M^+): 362.2206, found: 362.2203.

The stereochemistry of **14** was determined by the following transformation.

3-(Butylmethylamino)methyl-1-methyl-2-phenyl-piperidine (22). In a 100 mL round-bottomed flask were placed LiAlH_4 (158.2 mg, 4.17 mmol) and Et_2O (50 mL). **14** (502.3 mg, 1.39 mmol) in Et_2O (10 mL) was added at 0 $^\circ\text{C}$. The mixture was heated under reflux for 1 h. Water (2 mL) and *aq* potassium sodium (+)-tartrate (20 %, 50 mL) were added. The organic phase was separated and the aqueous phase was extracted with Et_2O (50 mL x 3). The combined organic phase was dried over Na_2SO_4 . The solvent was removed under reduced pressure and the crude product was purified with flash chromatography (EtOAc containing 1% Et_3N) to give **23** (266.4 mg, 70% yield): ^1H NMR (300 MHz, CDCl_3) δ 0.85 (t, $J = 6.6$ Hz, 3H), 0.73-2.68 (m, 21H), 3.03 (d, $J = 10.8$ Hz, 1H), 7.13-7.40 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3) δ 14.0, 20.6, 25.4, 29.2, 30.1, 41.1, 42.9 and 43.0, 44.6 and 44.7, 57.6, 57.7, 60.8, 75.0 and 75.1, 127.1, 128.2, 142.8; IR (neat) 2934, 1453, 735 cm^{-1} ; LRMS (EI) m/e 274 (M^+), 259 ($\text{M}^+ - \text{CH}_3$), 188 ($\text{M}^+ - \text{N}(\text{C}_4\text{H}_9)\text{CH}_3$); HRMS (EI) calcd for $\text{C}_{18}\text{H}_{30}\text{N}_2$ (M^+): 274.2409, found: 274.2407.

Because the rotamers do not exist in compound **23**, the stereochemistry was easily determined as *trans* based on the coupling constant between two protons on the ring ($J = 10.8$ Hz) according to the literature.³

2-Allyl-3-(cyclohexyl(methoxycarbonyl)amino)methyl-1-(methoxycarbonyl)pyrrolidine (16).

Prepared from **3** (33.0 mg, 0.260 mmol) and

N-methoxycarbonyl-*N*-(trimethylsilylmethyl)-cyclohexylamine (98.3 mg, 0.404 mmol) and allyltrimethylsilane (148.1 mg, 1.30 mmol), and purified with flash chromatography (hexane/EtOAc 3:1). A mixture of two diastereomers (total 61.8 mg, 70% yield, diastereomer ratio 91:9 (determined by GC): TLC R_f 0.53 (hexane/EtOAc 1:1); ^1H NMR (300 MHz, CDCl_3) δ 0.99-1.16 (m, 1H), 1.20-1.55 (m) and 1.56-1.85 (m) (total 10H), 1.86-2.05 (m, 1H), 2.08-2.56 (m, 3H), 2.96-3.81 (m, 12H), 5.01-5.15 (m, 2H), 5.64-5.85 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 25.4, 25.9, 26.7, 31.0, 37.6, 38.5, 42.0, 42.5, 45.0, 45.7, 52.1, 52.2, 57.0, 59.2 and 60.3, 117.4, 134.6 and 134.7, 155.5, 156.7; IR (neat) 2934, 1698, 1451 cm^{-1} ; LRMS (CI) m/e 339 (MH^+), 307 ($\text{M}^+ - \text{CH}_3\text{O}$), 297 ($\text{M}^+ - \text{C}_3\text{H}_5$); HRMS (CI) calcd for $\text{C}_{18}\text{H}_{31}\text{N}_2\text{O}_4$ (MH^+): 339.2284, found: 339.2281.

6-(Butyl(methoxycarbonyl)amino)-4-phenylsulfanyl-1-hexene (18).

The electrolysis of carbamate (**1**) (54.3 mg, 0.25 mmol) was carried out as described above. Phenyl vinyl sulfide (23.0 mg, 0.169 mmol) (neat) was added dropwise to the cation pool (**2**) thus-generated at $-78\text{ }^\circ\text{C}$ and the mixture was stirred for one second at $-78\text{ }^\circ\text{C}$. Then Allyltrimethylsilane (181.2 mg, 1.59 mmol) was added at $-78\text{ }^\circ\text{C}$. Immediately the cooling bath was removed, and the resulting solution was stirred 20 min. The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (2 x 10 cm) of silica gel to remove Bu_4NBF_4 . The silica gel was washed with ether (200 mL). The crude product was purified with flash chromatography (hexane/EtOAc 10:1) to give (**9**) (total 30.4 mg, 56% yield): TLC R_f 0.53 (hexane/EtOAc 3:1); ^1H NMR (400 MHz, CDCl_3) δ 0.90 (t, $J = 7.4\text{ Hz}$, 3H), 1.20-1.35 (m, 2H), 1.40-1.52 (m, 2H), 1.65-1.80 (m, 1H), 1.78-1.95 (m, 1H), 2.27-2.44 (m, 2H), 3.06-3.28 (m, 3H), 3.28-3.52 (m, 3H), 3.65 (s, 3H), 5.05-5.14 (m, 2H), 5.80-5.93 (m, 1H), 7.20-7.31 (m, 3H), 7.40 (d, $J = 3.9\text{ Hz}$, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 20.0, 30.7, 31.1, 32.7, 39.4, 44.9, 45.6, 46.3, 47.6, 47.8, 52.7, 117.3, 126.8, 128.7, 132.1, 134.4, 134.8, 156.5; IR (neat) 2957, 1703 cm^{-1} ; LRMS (FAB) m/e 322 (MH^+), 290 ($\text{M}^+ - \text{OCH}_3$), 280 ($\text{M}^+ - \text{C}_3\text{H}_5$), 212 ($\text{M}^+ - \text{SC}_6\text{H}_5$); HRMS (FAB) calcd for $\text{C}_{18}\text{H}_{27}\text{N}_1\text{O}_2\text{S}_1$ (MH^+): 322.1841, found: 322.1838.

Methyl 5-(Butyl(methoxycarbonyl)amino)-2,2-dimethyl-3-phenylsulfanyl-pentanoate (19).

Prepared from **1** (53.8 mg, 0.245 mmol), phenyl vinyl sulfide (22.6 mg, 0.166 mmol) and, methyl trimethylsilyl dimethyl ketene acetal (292.7 mg, 1.68 mmol) and purified with flash chromatography (hexane/EtOAc 5:1) (47.4 mg, 75% yield): TLC R_f 0.39 (hexane/EtOAc 3:1); ^1H NMR (400 MHz, CDCl_3) δ 0.89 (t, $J = 7.2\text{ Hz}$, 3H), 1.24 (s, 3H), 1.26 (s, 3H), 1.38-1.52 (m, 2H), 1.58-1.72 (m, 2H), 1.79-2.05 (m, 2H),

2.92-3.23 (m, 2H), 3.23-3.44 (m, 3H), 3.53 (s, 3H), 3.64 (s, 3H), 7.15-7.45 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 20.0, 21.8, 23.5, 30.4 and 30.8, 31.4 and 32.0, 45.9 and 46.8, 47.3, 48.4, 51.8, 52.4, 55.5, 126.5, 128.7, 130.8, 136.9, 156.5, 176.5; IR(neat) 2957, 1732, 1705 cm^{-1} ; LRMS (EI) m/e 381 (M^+), 322 ($\text{M}^+ - \text{CO}_2\text{CH}_3$), 272 ($\text{M}^+ - \text{SC}_6\text{H}_5$); HRMS (EI) calcd for $\text{C}_{20}\text{H}_{31}\text{NO}_4\text{S}$ (M^+): 381.1974, found: 381.1973.

^1H and ^{13}C NMR spectra of **5-10**, **12-14**, **16** are as follows:

¹H NMR spectrum of **5**.

¹³C NMR spectrum of **5**.

^1H NMR spectrum of **6**.

^{13}C NMR spectrum of **6**.

¹H NMR spectrum of 7.

¹³C NMR spectrum of 7.

¹H NMR spectrum of **8**.

^{13}C NMR spectrum of **8**.

¹H NMR spectrum of **9**.

¹³C NMR spectrum of **9**.

¹H NMR spectrum of **12**.

^{13}C NMR spectrum of **12**.

¹H NMR spectrum of **13**.

¹³C NMR spectrum of **13**.

¹H NMR spectrum of **14**.

¹³C NMR spectrum of **14**.

¹H NMR spectrum of **16**.

¹³C NMR spectrum of **16**.

^1H NMR spectrum of **19**.

^{13}C NMR spectrum of **19**.

DFT calculations. The DFT calculations were carried out at B3LYP/6-31G(d) level using the Gaussian 2003W, Revision-B.05.⁴ Geometries were fully optimized. All the optimized structures were local minima according to the vibration analysis.

Geometry optimization of **4** gave six structures, **4a**, **4a'**, **4b**, **4b'**, **4c**, and **4c'**. Among these structures **4b** is the most stable among three. Relative energies and geometries of these structures are shown below:

4a (15.8 kcal/mol)

4b (0 kcal/mol)

4c (12.6 kcal/mol)

4a' (16.6 kcal/mol)

4b' (1.3 kcal/mol)

4c' (13.6 kcal/mol)

4a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.088877	1.307760	0.328974
2	6	0	-1.897040	0.323072	1.200023
3	6	0	0.401578	1.017350	0.663017
4	6	0	1.405358	1.093670	-0.533030
5	6	0	0.345420	-0.305205	1.312895
6	7	0	-0.863455	-0.692042	1.580761
7	6	0	-1.124821	-1.972298	2.253525
8	8	0	-0.226812	-2.718422	2.526879
9	7	0	1.376689	2.391499	-1.173740
10	8	0	-2.417498	-2.080444	2.455441
11	6	0	-2.857944	-3.305100	3.124724
12	6	0	1.006135	2.476321	-2.589066

13	6	0	1.983058	3.493400	-0.595904
14	8	0	2.377916	3.211106	0.677666
15	8	0	2.126598	4.569983	-1.131808
16	6	0	3.049280	4.301735	1.349524
17	1	0	-1.276210	1.114294	-0.731320
18	1	0	-1.363782	2.343797	0.529417
19	1	0	-2.715946	-0.178909	0.684410
20	1	0	-2.283772	0.761875	2.124126
21	1	0	0.799739	1.724788	1.409605
22	1	0	2.407240	0.852568	-0.160723
23	1	0	1.133337	0.346415	-1.284180
24	1	0	1.178259	-0.950291	1.584431
25	1	0	-2.390883	-3.365230	4.108632
26	1	0	-2.581006	-4.167080	2.516310
27	1	0	-3.937954	-3.203529	3.202492
28	1	0	0.985726	3.527571	-2.871870
29	1	0	0.014514	2.041238	-2.749364
30	1	0	1.732288	1.952129	-3.222481
31	1	0	3.304668	3.917494	2.336975
32	1	0	2.386225	5.165718	1.426615
33	1	0	3.949701	4.584648	0.801171

4b

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	1.801664	1.790673	0.006872
2	6	0	3.024332	2.545257	-0.314268
3	6	0	1.710163	0.479115	-0.168553
4	6	0	0.731645	2.523531	0.707098
5	6	0	-0.638565	1.878817	0.520663
6	8	0	0.681268	-0.231833	0.153354
7	8	0	2.728439	-0.132462	-0.719930
8	6	0	-0.638623	0.382278	0.785663
9	6	0	2.654049	-1.575065	-0.936392
10	7	0	-1.726098	-0.127243	0.098702
11	6	0	-2.258219	-1.374180	0.448017
12	6	0	-2.273832	0.800144	-0.917425
13	6	0	-1.270404	1.968801	-0.888490
14	8	0	-3.333615	-1.636796	-0.298898
15	8	0	-1.780203	-2.075692	1.312635
16	6	0	-3.988606	-2.897681	-0.018196
17	1	0	3.466296	2.932398	0.609210
18	1	0	2.763312	3.381489	-0.968441
19	1	0	3.740651	1.900036	-0.816512
20	1	0	0.722690	3.540776	0.305788
21	1	0	0.991040	2.591588	1.771201
22	1	0	-1.316773	2.330486	1.254939
23	1	0	-0.549421	0.018655	1.805867
24	1	0	3.618245	-1.827921	-1.371971

25	1	0	1.840181	-1.802691	-1.625610
26	1	0	2.505876	-2.084354	0.016253
27	1	0	-2.339000	0.313629	-1.892891
28	1	0	-3.281928	1.108899	-0.624007
29	1	0	-1.752622	2.933392	-1.062954
30	1	0	-0.504682	1.836053	-1.661054
31	1	0	-4.824422	-2.943669	-0.714508
32	1	0	-4.340659	-2.914632	1.015000
33	1	0	-3.295711	-3.724730	-0.184709

4c

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.478487	1.513231	-0.894714
2	6	0	-2.621339	-0.023986	-0.852154
3	6	0	-1.084807	1.819558	-0.271955
4	6	0	-0.007050	2.226605	-1.352350
5	6	0	-0.731941	0.549020	0.400410
6	7	0	-1.537982	-0.423882	0.096484
7	6	0	-1.325201	-1.774960	0.615962
8	8	0	-0.390667	-2.027396	1.325779
9	7	0	1.297445	2.521841	-0.818512
10	8	0	-2.286172	-2.553306	0.169957
11	6	0	-2.226872	-3.949228	0.600267
12	6	0	1.682897	3.919752	-0.611606
13	6	0	2.236958	1.536270	-0.609652
14	8	0	1.671566	0.297350	-0.787041
15	8	0	3.388377	1.710589	-0.282073
16	6	0	2.597204	-0.805795	-0.627274
17	1	0	-2.557969	1.890562	-1.917339
18	1	0	-3.269190	1.985815	-0.307265
19	1	0	-2.434047	-0.517567	-1.809199
20	1	0	-3.577481	-0.375619	-0.463420
21	1	0	-1.114843	2.628886	0.466594
22	1	0	0.050580	1.436153	-2.104191
23	1	0	-0.396407	3.126540	-1.836829
24	1	0	0.078647	0.368396	1.095343
25	1	0	-3.084009	-4.421460	0.125642
26	1	0	-2.298892	-3.994590	1.687790
27	1	0	-1.289625	-4.392685	0.261323
28	1	0	0.967133	4.419094	0.051292
29	1	0	1.722842	4.458198	-1.565039
30	1	0	2.669642	3.937984	-0.151486
31	1	0	3.362884	-0.762966	-1.404011
32	1	0	1.992884	-1.706743	-0.729368
33	1	0	3.071726	-0.764995	0.354380

4a'

1	6	0	-0.401139	-1.483732	1.685266
2	6	0	-1.174839	-2.121988	0.514567
3	6	0	0.453764	-0.356451	1.041011
4	6	0	0.608967	0.955422	1.876685
5	6	0	-0.192380	-0.159288	-0.271932
6	7	0	-1.070405	-1.073915	-0.548175
7	6	0	-1.862348	-1.189380	-1.775280
8	7	0	1.206767	0.698806	3.169643
9	8	0	-2.602695	-2.120316	-1.917623
10	6	0	0.442552	1.007275	4.381361
11	6	0	2.563386	0.459231	3.301550
12	8	0	3.144921	0.306227	2.078164
13	8	0	3.156291	0.374096	4.354188
14	6	0	4.573030	0.081919	2.121868
15	8	0	-1.605503	-0.173341	-2.572266
16	6	0	-2.333407	-0.164380	-3.842574
17	1	0	-1.099750	-1.051344	2.407614
18	1	0	0.210139	-2.215953	2.213584
19	1	0	-2.228841	-2.322944	0.708483
20	1	0	-0.717460	-3.034340	0.121094
21	1	0	1.487154	-0.687116	0.841976
22	1	0	1.204423	1.669182	1.296487
23	1	0	-0.377527	1.396250	2.048317
24	1	0	0.003717	0.635628	-0.986069
25	1	0	1.035982	0.702753	5.241925
26	1	0	-0.504695	0.458513	4.385594
27	1	0	0.233560	2.081433	4.456077
28	1	0	4.881217	-0.013402	1.080753
29	1	0	4.797497	-0.829156	2.679987
30	1	0	5.072621	0.928762	2.595968
31	1	0	-1.988347	0.732503	-4.351994
32	1	0	-3.404848	-0.121693	-3.643038
33	1	0	-2.084365	-1.063901	-4.406867

4b'

1	7	0	1.458836	2.121773	0.605457
2	6	0	2.693077	2.917619	0.709240
3	6	0	1.437719	0.905598	0.076271
4	6	0	0.257567	2.663297	1.265076
5	6	0	-1.034954	2.141812	0.644140
6	8	0	0.390276	0.153826	0.015324
7	8	0	2.556916	0.444900	-0.426408
8	6	0	-1.065006	0.628596	0.498829
9	6	0	2.564473	-0.879374	-1.039273
10	7	0	-1.969280	0.358698	-0.507747
11	6	0	-2.589953	-0.872933	-0.747734
12	6	0	-2.299350	1.535173	-1.343161

13	6	0	-1.364637	2.625032	-0.788447
14	8	0	-3.393452	-1.026603	-1.636374
15	8	0	-2.171684	-1.799222	0.128726
16	6	0	-2.792427	-3.099985	-0.018215
17	1	0	2.940432	3.067224	1.764848
18	1	0	2.531382	3.889438	0.234871
19	1	0	3.512705	2.402842	0.214441
20	1	0	0.301764	3.751622	1.169253
21	1	0	0.304163	2.425489	2.335512
22	1	0	-1.856233	2.410030	1.320112
23	1	0	-1.168821	0.013228	1.387170
24	1	0	3.595758	-1.020445	-1.355502
25	1	0	1.886991	-0.894834	-1.893776
26	1	0	2.273668	-1.628824	-0.302517
27	1	0	-2.132899	1.314155	-2.399450
28	1	0	-3.357823	1.780285	-1.214337
29	1	0	-1.833125	3.611713	-0.789503
30	1	0	-0.451557	2.691967	-1.390386
31	1	0	-2.343373	-3.718457	0.757623
32	1	0	-2.583261	-3.504535	-1.010299
33	1	0	-3.871639	-3.018953	0.124678

4c'

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.560367	0.818325	-2.814773
2	6	0	-1.639348	-0.705476	-2.584584
3	6	0	-0.834244	1.393646	-1.563075
4	6	0	0.644821	1.847561	-1.863238
5	6	0	-0.890488	0.270487	-0.596944
6	7	0	-1.325196	-0.830992	-1.130366
7	6	0	-1.481387	-2.120104	-0.463126
8	7	0	1.357634	2.359980	-0.719043
9	8	0	-1.154913	-2.014604	0.809713
10	6	0	1.468990	3.809626	-0.539154
11	6	0	2.061654	1.531558	0.124760
12	8	0	1.791855	0.215920	-0.168230
13	8	0	2.790431	1.882875	1.024560
14	6	0	2.556931	-0.731946	0.611884
15	6	0	-1.301019	-3.235793	1.601747
16	8	0	-1.863551	-3.070950	-1.085085
17	1	0	-1.022700	1.051732	-3.737110
18	1	0	-2.562801	1.243784	-2.902040
19	1	0	-0.897648	-1.284798	-3.140399
20	1	0	-2.621082	-1.143625	-2.768231
21	1	0	-1.349745	2.260510	-1.132260
22	1	0	1.184661	1.011488	-2.313225
23	1	0	0.569255	2.642324	-2.610745

24	1	0	-0.638888	0.301988	0.454982
25	1	0	0.473837	4.267434	-0.511934
26	1	0	2.047414	4.260412	-1.353346
27	1	0	1.976982	3.999817	0.405030
28	1	0	3.623709	-0.592686	0.427777
29	1	0	2.235755	-1.715409	0.268004
30	1	0	2.355279	-0.602099	1.676936
31	1	0	-0.982387	-2.955611	2.603318
32	1	0	-0.664449	-4.017022	1.184428
33	1	0	-2.345621	-3.549704	1.591110

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