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An asymmetric synthesis of (+)-monomorine I

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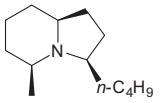
ABSTRACT

The synthesis of (+)-monomorine I, an indolizidine alkaloid isolated from *Monomorium pharaonis*, has been achieved. The 2,6-*cis*-piperidine ring moiety of (+)-monomorine I was constructed using diastereoselective aminopalladation. Chain elongation via cross-metathesis using Hoveyda-Grubbs 2nd catalyst followed by deprotection of the Cbz group and cyclic reductive hydroamination afforded (+)-monomorine I.

1. Introduction

Indolizidine alkaloids have attracted much attention due to their unique structures and biological activities.[1] Most of them possess alkyl side chains at the 3- and 5-positions. Due to their potential biological activities, much effort has been made towards their total synthesis.[2] (+)-Monomorine I **1**, which has a 3,5-disubstituted indolizidine skeleton, was isolated from the pharaoh's ant *Monomorium pharaonis*.[3] To date, several enantioselective syntheses of both enantiomers of monomorine I have been reported.[4,5] Quite recently, we reported the synthesis of (−)-isosolenopsin using diastereoselective aminopalladation.[6] Herein, we report a detailed study of diastereoselective aminopalladation[7] and its application to the synthesis of (+)-monomorine I **1** (Fig. 1).



(+)-monomorine I **1**

Figure 1. Structure of (+)-monomorine **1**.

2. Results and discussion

Our synthetic strategy is shown in Scheme 1. The complete carbon skeleton of **1** would be constructed from 2,6-*cis*-substituted piperidine ring **2** via deprotection followed by the formation of the imine and successive reduction of the double bond. Compound **3** would be synthesized from piperidine ring **4** and 2-octen-4-one using cross-metathesis[8] followed by reduction of the double bond. Piperidine ring **4** would be prepared from allyl alcohol **5** via diastereoselective aminopalladation (Scheme 1).

The diastereoselective aminopalladation to afford a 2,6-*cis*-piperidine ring has been reported by us before.[6] We examined further the diastereoselective aminopalladation of **5**. At first, we used the Boc group as a protecting group of the amino group. When the reaction time was 20 min, the ratio of *cis*: *trans* was 67:33. Extending the reaction time to 5 h gave the 2,6-*cis*-piperidine ring exclusively. Extraction of the reaction mixture in a thorough manner improved the isolated yield of piperidine ring **4b** up to 63% yield.[6] From these observations, this reaction should be reversible and the Pd π-complex should be present in equilibrium between complex A and B.[9] Complex B suffers from steric hindrance between the Boc group and the allylic alcohol. On the other hand, complex A is favorable because it has less steric hindrance and the chelation effect between Pd and two oxygens of the Boc group and allylic alcohol. When we used the Cbz group as a cyclization precursor, the yield of the cyclized products was 77%, however, the selectivity of *cis*/*trans* was 53:47 (Table 1, Fig. 2).

For the synthesis of (+)-monomorine I **1**, we examined the cross-metathesis of **4a** with a side chain.[8] At first, we used 4-benzyloxy-2-octene as the side chain. However, the cross-metathesis reaction did not proceed at all. Thus, we used commercially available 2-octen-4-one. Using 20 mol % of Grubbs 2nd catalyst afforded **3a** in 39% yield. Changing the catalyst to Hoveyda-Grubbs 2nd catalyst gave **3a** in high yield (Table 1).

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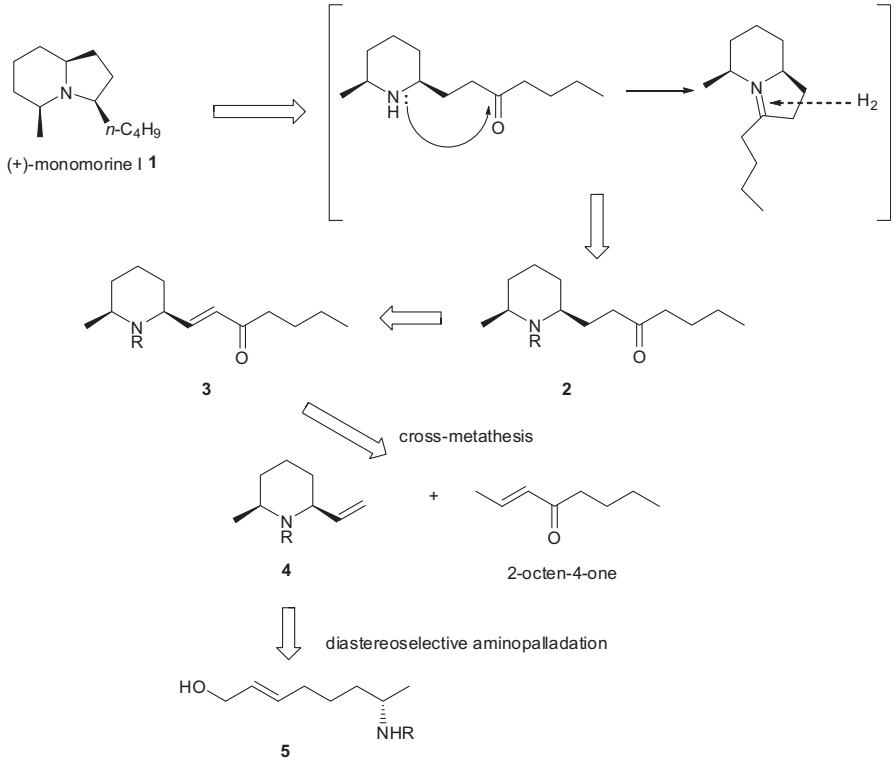
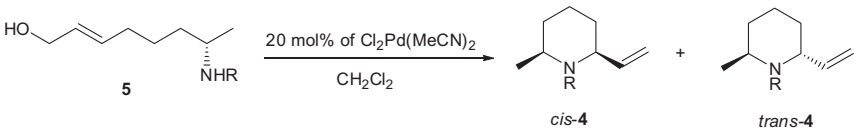


Scheme 1. Synthetic strategy of (+)-monomorine I **1**.

Table 1
Diastereoselective aminopalladation



Entry	R	Time (h)	Yield of *cis*-**4** and *trans*-**4** (%)	*cis*/*trans*
1	Boc	0.33	49	67:33
2	Boc	5	63	>98:2
3	Cbz	5	77	53:47

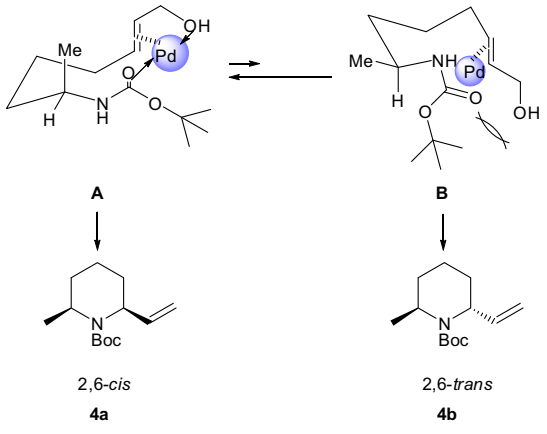
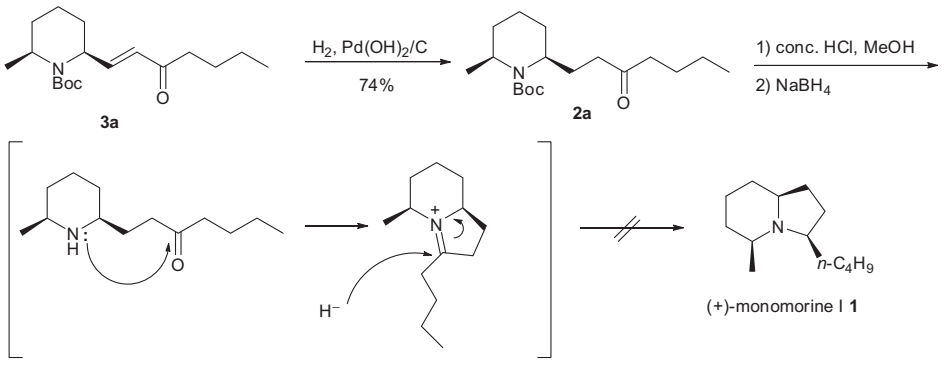


Figure 2. Proposed transition state forming 2,6-*cis*-piperidine **4a**.

Since the side chain had been successfully introduced, we focused on the synthesis of (+)-monomorine I **1**. The double bond of **3a** was hydrogenated using Pearlman's catalyst to give **2a**. Next, we tried to synthesize (+)-monomorine I **1** via a cyclic imine followed by reduction with $NaBH_4$. However, deprotection of the Boc group of **2a** using methanolic HCl followed by reduction with $NaBH_4$ gave a complex mixture (Scheme 2, Table 2).

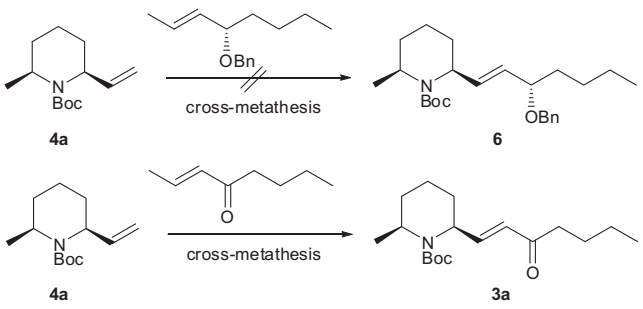
Next, we chose hydrogenolysis followed by reductive amination as reported by Iska et al.[4g] Reduction of the ketone **2a** with $NaBH_4$ gave alcohol **7**. Changing the protecting group of the amino group from a Boc group to a Cbz group followed by oxidation of the hydroxy group with Dess–Martin periodinane afforded **2b**. Finally, hydrogenolysis of the Cbz group and reductive amination *in situ* using Pearlman's catalyst under a hydrogen atmosphere furnished (+)-monomorine I **1** in 41% yield. The specific rotation value and spectroscopic data of synthetic **1** were in good agreement with the reported values (Scheme 3).[5h]

Although (+)-monomorine I **1** was synthesized from enone **3a**, it took six steps to synthesize and the yield of transformation from **7** to **2b** was 37% in three steps. We thus pursued a more efficient synthesis of **1**. As shown in Table 1, a bulky protecting group, such as a Boc group, was necessary to obtain high selectivity in the Pd(II)-catalyzed stereoselective aminopalladation. Thus, we used piperidine



Scheme 2. Attempt to synthesize (+)-monomorine I **1** via cyclic imine followed by reduction with $NaBH_4$.

Table 2
Cross-metathesis of piperidine ring **4a** with side chain



Entry	Catalyst (mol %)	Time (h)	Yield of **3a** (%)
1	Grubbs 2nd (10)	6	25
2	Grubbs 2nd (20)	6	39
3	Hoveyda-Grubbs 2nd (10)	7	94

4a as a chiral synthon. As shown in Scheme 3, compound **2b** could be transformed into monomorine I **1** using a one pot-operation. Thus, we tried to change the Boc group of **4a** to a Cbz group. Using the procedure reported by Lee et al. afforded the Cbz protected amine **8a** from **4a** in 78% yield.[10] The cross-metathesis of **8a** with 2-octen-4-one gave chain elongated product **9**. As shown in Table 3, Hoveyda-Grubbs 2nd catalyst gave **9** in 62% yield. Finally, reduction of the double bond, hydrogenolysis of the Cbz group, and the reductive amination *in situ* using Pearlman's catalyst under hydrogen atmosphere furnished (+)-monomorine I **1** in 67% yield as a single diastereomer through a one-pot procedure.[11] The specific rotation value and spectroscopic data of synthetic **1** were in good agreement with Scheme 3 (Scheme 4, Table 3).[5h]

3. Conclusion

In conclusion, synthesis of (+)-monomorine I **1** was achieved using stereoselective aminopalladation and cross-metathesis.

Table 3
Cross-metathesis of piperidine ring **8a** with 2-octen-4-one.

Entry	Catalyst	Time (h)	Yield of **9** (%)
1	Grubbs 1st	24	0
2	Grubbs 2nd	20	32
3	Hoveyda-Grubbs 2nd	20	62

Synthetic studies on other indolizidine alkaloids are currently underway.

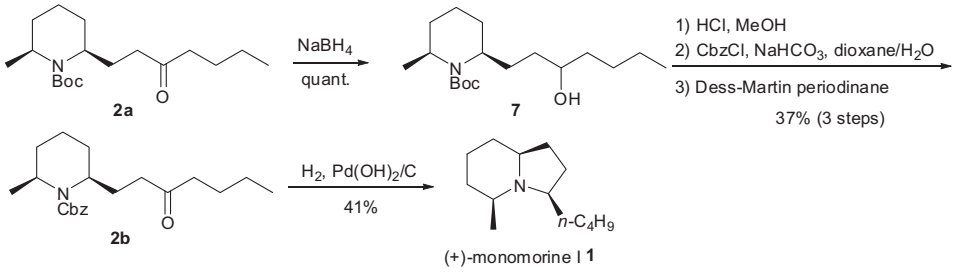
4. Experimental

4.1. General

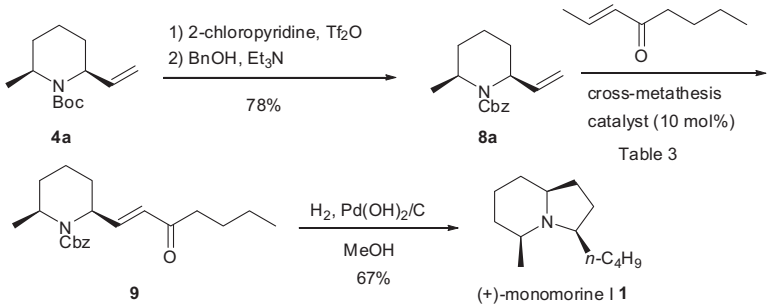
All reactions were carried out in dry solvents under an argon atmosphere, unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed using E. Merck Silica gel 60 F254 pre-coated plates (0.25 mm). Preparative thin-layer chromatography (PTLC) was performed using E. Merck Silica gel 60 F254 pre-coated plates (1.5 mm). Optical rotations were measured on JASCO DIP-1000 polarimeter at room temperature using the sodium D line. Infrared (IR) spectra were recorded as a thin film on a NaCl disk using JASCO FT-IR 480 Plus infrared spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 500 MHz spectrometer. Chemical shifts were reported in ppm on the δ scale relative to tetramethylsilane (TMS) ($\delta = 0.00$ for ^1H NMR), $CDCl_3$ ($\delta = 77.0$ for ^{13}C NMR) as internal reference. Signal patterns are indicated as s, singlet; d, doublet; t, triplet; m, multiplet; br, broaden peak. High resolution mass spectra were measured on JEOL GC mate II mass spectrometers.

4.1.1. (2*S*,6*S*,1′*E*)-*N*-*tert*-Butoxycarbonyl-2-methyl-6-(3′-oxohept-1′-enyl)piperidine 3a

A solution of piperidine ring **4a** (40 mg, 0.18 mmol), 2-octen-4-one (137 μL, 0.92 mmol), and Hoveyda-Grubbs 2nd catalyst (12.5 mg, 0.015 mmol) in CH_2Cl_2 (6 mL) was stirred for 7 h at



Scheme 3. Synthesis of (+)-monomorine I **1**.



Scheme 4. Synthesis of (+)-monomorine I (**1**) from **8a**.

reflux. After the reaction had been completed, the solvent was evaporated and the residue was purified with PTLC (hexane/AcOEt = 5:1) to afford **3a** (51 mg, 94%) as a colorless oil. $[\alpha]_D^{20} = -50$ (*c* 0.59, $CHCl_3$); IR (film) ν_{max} cm^{-1}: 2934, 1687, 1392, 1364, 1174, 1078 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 6.81 (1H, dd, *J* = 16.0, 5.0 Hz), 6.15 (1H, dd, *J* = 16.0, 1.5 Hz), 4.85–4.84 (1H, m), 4.38–4.34 (1H, m), 2.54 (2H, t, *J* = 7.5 Hz), 1.91–1.89 (1H, m), 1.74–1.50 (7H, m), 1.45 (9H, s), 1.39–1.30 (2H, m), 1.13 (3H, d, *J* = 7.0 Hz), 0.91 (3H, t, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 200.7, 155.0, 147.8, 129.3, 79.8, 50.4, 46.1, 40.4, 29.9, 28.4 (C × 3), 28.0, 26.3, 22.4, 20.4, 14.5, 13.9 ppm. HREIMS $[M]^+$: found, 309.2306, calcd for $C_{18}H_{31}NO_3$: 309.2304.

4.1.2. (2*S*,6*S*)-*N*-*tert*-Butoxycarbonyl-2-methyl-6-(3′-oxoheptyl) piperidine 2a

To a solution of **3a** (51 mg, 0.17 mmol) was added $Pd(OH)_2/C$ (4.8 mg) under a hydrogen atmosphere. After stirring for 16 h, the mixture was filtered. The filtrate was concentrated to afford **2a** (47 mg, 88%) as a colorless oil; $[\alpha]_D^{20} = -6.8$ (*c* 0.39, $CHCl_3$); IR (film) ν_{max} cm^{-1}: 2936, 2360, 1725, 1684, 1559, 1362, 1175, 1080 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 4.32–4.29 (1H, m), 4.10–4.09 (1H, m), 2.50–2.30 (4H, m), 1.84–1.49 (9H, m), 1.46 (9H, s), 1.34–1.25 (3H, m), 1.18 (3H, d, *J* = 7.0 Hz), 0.90 (3H, t, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 210.9, 155.4, 79.1, 42.6, 40.5, 30.2, 28.7, 28.5 (C × 2), 28.4 (C × 3), 28.1, 26.0, 22.3, 20.5, 14.1, 13.8 ppm. HREIMS: *m/z* $[M]^+$: found, 311.2464, calcd for $C_{18}H_{33}NO_3$: 311.2460.

4.1.3. (2*S*,6*S*,3′*RS*)-*N*-*tert*-Butoxycarbonyl-2-methyl-6-(3′-hydroxyheptyl)piperidine 7

To a solution of **2a** (47 mg, 0.15 mmol) in MeOH (5 mL) was added $NaBH_4$ (28 mg, 0.75 mmol) at 0 °C. After being stirred for 1.5 h, the solvent was evaporated and the solid material was removed by filtration. The filtrate was concentrated to give **7** (49 mg, quant.) as a colorless oil. $[\alpha]_D^{20} = -2.1$ (*c* 0.40, $CHCl_3$); IR (film) ν_{max} cm^{-1}: 3441, 2933, 2861, 1684, 1662, 1456, 1405, 1364, 1254, 1178, 1083 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 4.28–4.25 (1H, m), 4.10–4.04 (1H, m), 3.71 (0.4H, m), 3.63 (0.6H, m), 1.75–1.25 (26H, m), 1.15 (3H, d, *J* = 6.3 Hz), 0.91 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 155.6, 79.4, 79.1, 72.3, 37.2, 31.3, 30.2, 28.5 (C × 3), 28.0, 27.9, 27.6, 22.8, 20.4, 14.1, 13.9, 13.8 ppm. HREIMS $[M]^+$: found, 313.2622, calcd for $C_{18}H_{35}NO_3$: 313.2617.

4.1.4. (2*S*,6*S*)-*N*-Benzyloxycarbonyl-2-methyl-6-(3′-oxoheptyl) piperidine 2b

To a solution of **7** (40 mg, 0.13 mmol) in MeOH (5 mL) was added ten drops of conc. HCl. After being stirred for 10 min, the solvent was evaporated and saturated aqueous $NaHCO_3$ (5 mL) was added to the mixture. The mixture was extracted with EtOAc (10 mL × 3) and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was dissolved into dioxane–H_2O (5:1, 6.0 mL). To this solution, $NaHCO_3$ (109 mg, 1.3 mmol) and benzylchloroformate (91 μL, 0.64 mmol) were added. After being stirred for 26 h, benzylchloroformate (90 μL, 0.64 mmol) was added again and the mixture was further stirred for 24 h. The mixture was extracted with EtOAc (10 mL × 3) and the organic layer was washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated. This crude product was used for the next step without further purification. To a solution of the crude material was added $NaHCO_3$ (294 mg, 3.5 mmol) and Dess–Martin periodinane (445 mg, 1.1 mmol) in CH_2Cl_2 (10 mL) at 0 °C. After being stirred for 20 min, the mixture was diluted with diethyl ether (12 mL) and saturated aqueous $NaHCO_3$, after which $Na_2S_2O_3$ and water (2:2:1, 15 mL) were added to the mixture. The mixture was extracted with Et_2O (10 mL × 3) and the organic layer was washed with saturated aqueous $NaHCO_3$, water, brine, dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified with preparative TLC (hexane/EtOAc = 38:5) afforded **2b** as a colorless oil (16.5 mg, 37% in 3 steps); $[\alpha]_D^{20} = -6.6$ (*c* 0.83, $CHCl_3$); IR (film) ν_{max} cm^{-1}: 2936, 1720, 1684, 1653, 1559, 1409, 1308, 1072, 755 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.37–7.30 (5H, m), 5.13 (2H, s), 4.43–4.41 (1H, m), 4.19–4.18 (1H, m), 2.40–2.39 (1H, m), 2.31–2.28 (3H, m), 1.88–1.43 (9H, m), 1.31–1.23 (3H, m), 1.20 (3H, d, *J* = 7.0 Hz), 0.89 (3H, t, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 210.8, 155.9, 142.3, 137.0, 128.5 (C × 2), 127.9, 127.8, 66.9, 49.9, 46.1, 42.5, 40.3, 30.1, 28.7, 28.3, 25.9, 22.3, 20.6, 14.0, 13.9 ppm. HREIMS $[M]^+$: found, 345.2301, calcd for $C_{21}H_{31}NO_3$: 345.2304.

4.1.5. (+)-Monomorine I 1

To a solution of **2b** (15 mg, 0.05 mmol) was added $Pd(OH)_2/C$ (1.4 mg) under hydrogen atmosphere. After being stirred for 4 h, the mixture was filtered. The filtrate was concentrated to afford **1** (4.0 mg, 41%) as a colorless oil; $[\alpha]_D^{20} = +32$ (*c* 0.14, *n*-hexane), {lit. +33.8 (*c* 1.00, *n*-hexane)};[4h] IR (film) ν_{max} cm^{-1}: 2956, 2927, 2858, 1457, 1378, 1319, 1206, 1169, 1132, 1107, 1056; ^1H NMR (500 MHz, $CDCl_3$) δ: 2.48 (1H, brt, *J* = 8.3 Hz), 2.29–2.17 (1H, m), 2.11–2.05 (1H, m), 1.90–1.50 (6H, m), 1.49–1.15 (10H, m), 1.14 (3H, d, *J* = 6.0 Hz), 0.89 (3H, t, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 67.1, 62.9, 60.2, 39.7, 35.8, 30.9, 30.3, 29.8, 29.4, 24.9, 22.9 (C × 2), 14.0 ppm. HREIMS $[M]^+$: found, 195.1985, calcd for $C_{13}H_{25}N$: 195.1987.

4.1.6. (2*S*,6*S*)-*N*-Benzyloxycarbonyl-2-methyl-6-vinylpiperidine 8a

To a solution of **4a** (20 mg, 0.089 mmol) in CH_2Cl_2 (5.0 mL) were added 2-chloropyridine (25 μL, 0.27 mmol) and Tf_2O (22 μL, 0.13 mmol). After being stirred for 15 min, BnOH (28 μL, 0.27 mmol) and Et_3N (37 μL, 0.27 mmol) were added to the mixture. After the resulting mixture had been stirred for 1 h, the reaction was quenched with water. The mixture was extracted with

EtOAc (10 mL × 3) and the organic layer was washed with saturated aqueous $NaHCO_3$, water, brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified with preparative TLC (hexane/EtOAc = 3:1) afforded **8 a** (18 mg, 78%) as a colorless oil. $[\alpha]_D^{19} = -13.7$ (*c* 1.00, $CHCl_3$); IR (film) ν_{max} cm^{-1}: 3065, 3033, 2940, 2870, 1695, 1497, 1456, 1405, 1381, 1328, 1310, 1271, 1213, 1146, 1096, 1075, 1029, 981, 917, 771 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.40–7.28 (5H, m), 5.97–5.90 (1H, m), 5.15 (2H, s), 5.10 (2H, dd, *J* = 19.0, 10.5 Hz), 4.79–4.77 (1H, m), 4.45–4.40 (1H, m), 1.90–1.88 (1H, m), 1.77–1.60 (3H, m), 1.55–1.53 (1H, m), 1.49–1.44 (1H, m), 1.18 (3H, d, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 155.8, 140.0, 137.0, 128.4 (C × 2), 127.8, 127.7 (C × 2), 114.8, 66.9, 51.8, 46.6, 30.1, 27.9, 20.4, 14.2 ppm. HREIMS $[M]^+$: found, 259.1578, calcd for $C_{16}H_{21}NO_2$: 259.1572.

4.1.7. (2*S*,6*S*, 1′*E*)-*N*-Benzyloxycarbonyl-2-methyl-6-(3′-oxohept-1′-enyl)piperidine 9

To a solution of **8 a** (45 mg, 0.17 mmol) and 2-octen-4-one (129 μL, 0.87 mmol) was added Hoveyda-Grubbs 2nd catalyst (11 mg, 0.017 mmol) in CH_2Cl_2 (3.0 mL). After being stirred for 20 h at reflux, the solvent was evaporated and the residue was purified with preparative TLC (hexane/EtOAc = 5:1) to afford **9** (36 mg, 62%) as a colorless oil. $[\alpha]^{19}_D = -67.9$ (*c* 0.500, $CHCl_3$); IR (film) ν_{max} cm^{-1}: 2935, 2871, 1695, 1456, 1405, 1341, 1310, 1272, 1074, 975, 771 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.40–7.30 (5H, m), 6.81 (1H, dd, *J* = 16.0, 5.0 Hz), 6.12 (1H, d, *J* = 16.0 Hz), 5.18 (1H, d, *J* = 7.0 Hz), 5.14 (1H, d, *J* = 7.0 Hz), 4.95–4.92 (1H, m), 4.47–4.44 (1H, m), 2.50 (2H, t, *J* = 7.5 Hz), 1.93–1.91 (1H, m), 1.76–1.49 (7H, m), 1.36–1.25 (2H, m), 1.16 (3H, d, *J* = 7.0 Hz), 0.91 (3H, t, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 200.6, 155.6, 147.1, 136.7, 129.5, 128.5 (C × 2), 128.0, 127.9 (C × 2), 67.2, 50.6, 46.6, 40.4, 29.9, 27.8, 26.2, 22.4, 20.5, 14.4, 13.9 ppm. HREIMS $[M]^+$: found, 343.2145, calcd for $C_{21}H_{29}NO_3$: 343.2147.

4.1.8. (+)-Monomorine I 1 from 9

To a solution of **9** (36 mg, 0.10 mmol) in MeOH (2.0 mL) was added $Pd(OH)_2/C$ (3.0 mg) under a hydrogen atmosphere. After being stirred for 18 h, the mixture was filtered through a pad of Celite. The filtrate was concentrated. The residue was purified with alumina column chromatography (pH 9.0–11.0, hexane/Et_2O = 10:1) to afford **1** (13 mg, 67%) as a pale yellow oil. The physiochemical and spectroscopic data were in good accordance with those described above.

Acknowledgement

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