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Total synthesis of (+)-(*S*)-angustureine and the determination of the absolute configuration of the natural product angustureine

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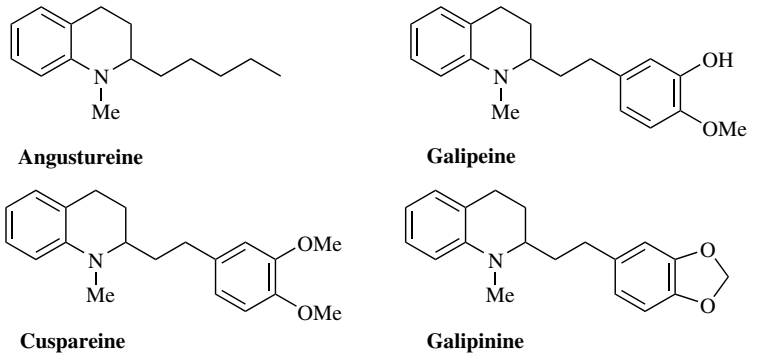
Abstract—Angustureine, isolated from the bark of *Galipea officinalis* Hancock, is a novel quinoline alkaloid with a *n*-pentyl side chain at the 2-position. The total synthesis of (+)-(*S*)-angustureine and a determination of the absolute configuration of the natural product angustureine were achieved using ring-closing metathesis (RCM) and the Mitsunobu reaction as key steps.

1. Introduction

A novel 2-substituted quinoline alkaloid, angustureine, was isolated from *Galipea officinalis* Hancock by Jacquemond-Collet et al. in 1999.[1] The same plant had been investigated previously, with five quinoline alkaloids reported by Rakotoson et al. in 1998.[2] Genus *Galipea* Aublet is composed of approximately 20 different species, including *Galipea officinalis* Hancock, a shrub indigenous to the mountains of Venezuela, which is known to contain 2-substituted quinoline alkaloids that were once used in folk medicine as a bitter tonic in dyspepsia, dysentery and chronic diarrhoea and for the treatment of fever.[3] The ethanolic extract of the bark of *G. officinalis*, called angostura, has been shown to have activity against *Mycobacterium tuberculosis*.[4] Recently, angustureine, galipeine, cuspareine and galipinine have also been reported to exhibit anti-malarial and cytotoxic activities (Fig. 1).[5]

We have been studying the development of anti-malarial agents[6] and the synthesis of nitrogen-containing heterocyclic compounds using ruthenium carbene catalysts **A**[7] and **B**[8] (Fig. 2).[9]

We recently developed a novel method for the synthesis of substituted 1,2-dihydroquinolines using ene–ene and silyl enol ether–ene metathesis, which gives the products



Angustureine **Galipeine** **Cuspareine** **Galipinine**

Figure 1. Structures of 2-substituted quinoline alkaloids with anti-malarial activity isolated from *Galipea officinalis*.

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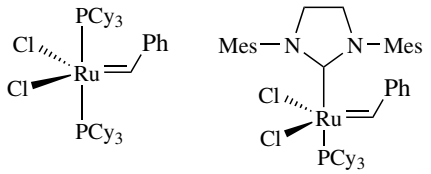


A B

Figure 2. Ruthenium catalysts.

in excellent yields under mild conditions[10] and applied this methodology to the synthesis of key intermediates for the anti-malarial agents quinine, chloroquine and PPMP-quinine hybrid.[11]

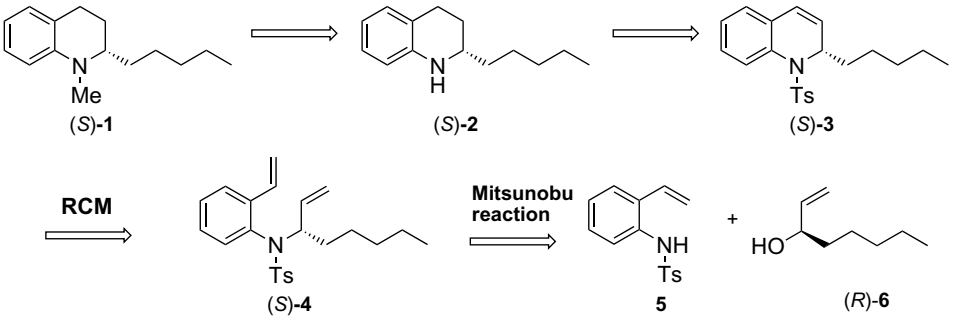
Although natural angustureine is one of the main isolated fractions (980 mg from 1 kg of dried bark), its absolute configuration had not yet been reported when we started this research project.[1] During our synthetic study, Zhou et al. reported the synthesis of angustureine using iridium-catalyzed hydrogenation.[12] Herein, we report our independent and original synthesis of enantiomerically pure (+)-(*S*)-angustureine and a determination of the absolute configuration of the natural product angustureine.

2. Results and discussion

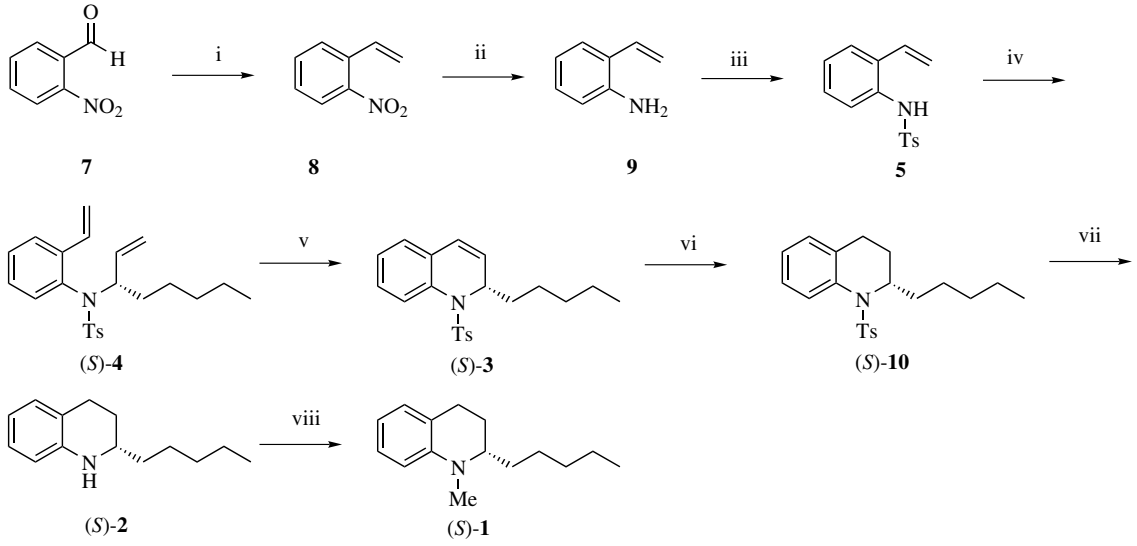
Our retrosynthesis of angustureine is outlined in Scheme 1, which relies on two key reactions. We envisioned that a 1,2-dihydroquinoline ring system could be effectively prepared using the RCM methodology developed in our laboratory.[10,11] The Mitsunobu reaction should then establish the (*S*)-configuration of the *n*-pentyl side chain.

As shown in Scheme 2, the synthesis of angustureine began with a Wittig olefination to convert the readily available 2-nitrobenzaldehyde **7** to olefin **8**. Compound **8** was then treated with Zn powder in AcOH to give aniline **9**. Tosylation of the resulting amino group gave tosylated aniline **5** in 86% yield.

A C-2 side chain was installed using the Mitsunobu reaction as the first key step, with the readily available (*R*)-alcohol **6** (99% ee) in the presence of DEAD and PPh_3 to give the desired α,ω-diene **4** in 78% yield.[13] With



Scheme 1. Retrosynthesis of (*S*)-angustureine.



Scheme 2. Synthesis of (*S*)-angustureine. Reagents and conditions: (i) Ph_3PMeBr, $KN(TMS)_2$, THF, rt, 1 h, 90%; (ii) Zn powder, AcOH, rt, overnight, 72%; (iii) TsCl, pyridine, CH_2Cl_2, rt, 1 h, 86%; (iv) **6**, DEAD, PPh_3, THF, rt, 2 h, 78%; (v) Ru catalyst **B**, CH_2Cl_2 0.01 M, 50 °C, 1 h, 92%; (vi) PtO_2, H_2, MeOH, rt, 12 h, 94%; (vii) anthracene sodium, DME, −65 °C, 10 min, 99%; (viii) MeI, K_2CO_3, THF, reflux, 10 h, 80%.

substrate **4** in hand, RCM as the second key step gave a quinoline skeleton using the second-generation Grubbs catalyst **B** in CH_2Cl_2 (0.01 M) at 50 °C for 1 h without degassing.[10,11] The corresponding 1,2-dihydroquinoline was obtained in 92% yield. Next, hydrogenation of dihydroquinoline **3** with Adam's catalyst in MeOH under an atmosphere of H_2 gave tetrahydroquinoline **10** in 94% yield with 99.7% ee after recrystallization, while subsequent detosylation resulted in tetrahydroquinoline **2** quantitatively. Finally, methylation of the free nitrogen gave (+)-(*S*)-angustureine in 80% yield. HPLC analysis showed that the synthesized (+)-(*S*)-angustureine had 94% ee, $[\alpha]_D^{23} = +7.9$ (*c* 1.00 $CHCl_3$); $[\alpha]_D^{26} = +4.4$ (*c* 1.00, CH_2Cl_2); $[\alpha]_D^{26} = +5.2$ (*c* 1.00, MeOH); $[\alpha]_D^{26} = +5.1$ (*c* 1.00, EtOH), {lit.[1] $[\alpha]_D = -7.2$. Although absolute configuration of synthetic angustureine was reported to be *R*, no data to support the result was presented.[12] In our synthesis, the absolute stereochemistry at 2-position was constructed by completely stereodefined manner and is *S* configuration. By comparison with the sign of absolute configurations of both natural and synthetic angustureine, the absolute stereochemistry of natural product was determined to be *R*.

3. Conclusion

In summary, the total synthesis of (+)-(*S*)-angustureine, unnatural angustureine, was achieved in eight steps from commercially available **7**, in an overall yield of 30%. Since previous reports on natural angustureine have shown that it possesses anti-mycobacterial and anti-malarial activity, unnatural angustureine may show similar and/or some other pharmacological activities, which would warrant additional investigation. Further synthetic study of other related 2-substituted quinoline alkaloids is currently underway.

4. Experimental

Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ at 25 °C unless otherwise noted, at 400 and 600 MHz, with TMS as an internal standard. Silica gel 60 N (Spherical, neutral, Kanto Chemical Co., Inc.) was used for column chromatography. The organic layers were dried over anhydrous Na_2SO_4. The enantiomeric excesses were determined by HPLC with chiral column (DAICEL CHIRALCEL OD-H). Substrates **6**, **7** and ruthenium carbene catalyst **B** were obtained commercially.

4.1. 2-Nitrostyrene 8

To a solution of Ph_3PMeBr (14.2 g, 39.6 mmol) in 30 mL of THF, was added a solution of $KN(TMS)_2$ in THF (79.4 mL, 39.6 mmol) at −78 °C under an Ar atmosphere. After the reaction mixture was stirred at −78 °C for 15 min, 2-nitrobenzaldehyde **7** (5.00 g, 33.0 mmol) in THF (50 mL) was added and the mixture warmed to rt for 1 h. The reaction was quenched by the addition of aq Rochelle's salt. The mixture was extracted with AcOEt and the combined organic layers washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (*n*-hexane/AcOEt = 5:1) to give 4.41 g (90%) of **8** as a yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.93 (1H, dd, J = 1.1, 8.4 Hz), 7.63 (1H, dd, J = 1.6, 7.6 Hz), 7.58 (1H, ddd, J = 1.1, 7.3, 7.3 Hz), 7.42 (1H, ddd, J = 1.7, 7.3, 8.4 Hz), 7.17 (1H, dd, J = 11.0, 17.3 Hz), 5.75 (1H, dd, J = 1.0, 17.3 Hz), 5.49 (1H, dd, J = 1.0, 11.0 Hz).

4.2. 2-Vinylaniline 9

To a solution of **8** (4.41 g, 29.5 mmol) in AcOH (50.0 mL), was added Zn powder (9.66 g, 148 mmol) in portions. The mixture was stirred at rt overnight and the reaction quenched by addition of satd aq $NaHCO_3$. The mixture was extracted with Et_2O and the combined organic layers washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (*n*-hexane/AcOEt = 10:1) to give 2.54 g (72%) of **9**[14] as a red-brown oil. ^{1}H NMR ($CDCl_3$) δ 7.28 (1H, dd, J = 1.5, 7.6 Hz), 7.08 (1H, ddd, J = 1.7, 7.8, 7.8 Hz), 6.76 (1H, ddd, J = 1.2, 7.8, 7.8 Hz), 6.75 (1H, dd, J = 11.2, 17.1 Hz), 6.67 (1H, dd, J = 0.7, 7.8 Hz), 5.62 (1H, dd, J = 1.5, 17.3 Hz), 5.31 (1H, dd, J = 1.5, 11.0 Hz), 3.74 (2H, br).

4.3. *N*-*p*-Toluenesulfonyl-2-vinylaniline 5

To a solution of **9** (2.50 g, 20.8 mmol) in 30.0 mL of CH_2Cl_2 under an Ar atmosphere, were added pyridine (51.0 mL, 62.4 mmol) and TsCl (4.80 g, 25.0 mmol). The mixture was stirred at rt for 1 h and the reaction quenched by water. The mixture was extracted with AcOEt and the combined organic layers washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by recrystallization from acetone to give 4.91 g (86%) of **5** as colourless needles. Mp 85 °C {lit.[15] 128–129 °C from AcOEt}; ^{1}H NMR ($CDCl_3$) δ 7.60 (2H, d, J = 8.5 Hz), 7.34 (2H, ddd, J = 1.7, 8.1, 8.1 Hz), 7.20–7.24 (3H, m), 7.16 (1H, ddd, J = 1.0, 7.3, 7.3 Hz), 6.51 (1H, dd, J = 11.0, 17.3 Hz), 6.39 (1H, br), 5.50 (1H, dd, J = 1.2, 17.3 Hz), 5.27 (1H, dd, J = 1.2, 11.0 Hz), 2.39 (3H, s); ^{13}C NMR ($CDCl_3$) δ 143.9, 136.4, 133.1, 132.6, 131.5, 129.6, 128.6, 127.2, 127.0, 126.4, 124.7, 118.4, 21.6; IR (KBr) 3296, 1631, 1600, 1488, 1342, 1154.

4.4. (*S*)-*N*-(3-Oct-1-enyl)-*N*-*p*-toluenesulfonyl-2-ethenylaniline 4

To a solution of **5** (1.00 g, 3.66 mmol), commercially available alcohol **6** (518 mg, 4.02 mmol, 99% ee) and triphenylphosphine (1.05 g, 4.02 mmol) in THF (50.0 mL) was added a solution of DEAD (2.2 M in toluene, 1.83 mL, 4.02 mmol) at 0 °C under an Ar atmosphere. After the reaction mixture was stirred at rt for 2 h, the solvent was removed by evaporator. The residue was purified by column chromatography on silica gel (*n*-hexane/AcOEt = 3:1) to give 1.20 g (78%) of **4** as a colourless oil. $[\alpha]_D^{23} = -36.6$ (*c* 1.00, $CHCl_3$); ^{1}H NMR (DMSO-d_6, 80 °C) δ 7.87 (1H, dd, J = 7.3, 7.7 Hz), 7.71 (2H, dd, J = 8.6, 9.3 Hz), 7.49–7.55 (3H, m), 7.34

(2H, d, $J = 7.3$ Hz), 6.85 (1H, d, $J = 7.7$ Hz), 5.98 (1H, dd, $J = 15.7$, 17.4 Hz), 5.40–5.56 (2H, m), 5.18–5.31 (2H, m), 4.58–4.67 (1H, m), 3.22 (3H, s), 1.30–1.59 (8H, m), 0.94–1.17 (3H, m): ^{13}C NMR (DMSO-d_6, 80 °C) δ 136.7, 134.2, 132.4, 129.4, 129.3, 129.1, 128.8, 128.3, 128.0, 127.8, 127.3, 126.1, 118.4, 115.4, 64.2, 33.3, 31.4, 26.0, 22.5, 21.4, 13.9; IR (neat) 3067, 3029, 2955, 2928, 2858, 1598; HRMS (FAB) $C_{23}H_{30}NO_2S$ calcd 384.1997, found 384.1965.

4.5. (*S*)-*N*-*p*-Toluenesulfonyl-2-*n*-pentyl-1,2-dihydroquinoline 3

To a solution of **4** (1.00 g, 3.07 mmol) in CH_2Cl_2 (307 mL), was added Grubbs catalyst **B** (130 mg, 0.15 mmol) under an Ar atmosphere. The mixture was stirred at 50 °C for 1 h. After removal of the solvent, the residue was purified by column chromatography on silica gel (*n*-hexane/AcOEt = 5:1) to give 848 mg (92%) of **3** as a colourless oil. $[\alpha]_D^{23} = -4.6$ (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.72 (1H, d, $J = 7.6$ Hz), 7.25 (3H, dd, $J = 8.8$, 8.8 Hz), 7.16 (1H, dd, $J = 0.7$, 7.3 Hz), 7.04 (2H, d, $J = 8.5$ Hz), 6.92 (1H, dd, $J = 1.2$, 7.6), 5.96 (1H, d, $J = 9.5$ Hz), 5.64 (1H, dd, $J = 5.6$, 9.7 Hz), 4.73–4.78 (1H, m), 2.31 (3H, s), 1.25–1.49 (8H, m), 0.86 (3H, dd, $J = 7.1$, 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 143.1, 136.3, 132.7, 129.1, 128.9, 128.7, 127.84, 127.81, 127.1, 129.4, 126.1, 123.7, 55.1, 33.1, 32.2, 24.8, 22.5, 21.5, 14.0; IR (neat) 3065, 3039, 2916, 2929, 2858, 1600; HRMS (FAB) $C_{21}H_{26}NO_2S$ calcd 356.1684, found 356.1661.

4.6. (*S*)-*N*-*p*-Toluenesulfonyl-2-*n*-pentyl-1,2,3,4-tetrahydroquinoline 10

To a solution of **3** (355 mg, 1.00 mmol) in MeOH (30 mL), was added PtO_2 (34 mg) under H_2 atmosphere. After the reaction mixture was stirred at rt for 12 h, the reaction mixture was filtrated through a celite pad. After removal of the solvent, the residue was purified by recrystallization from *n*-hexane to give 336 mg (94%, 99.7% ee) of **10** as white needles. Mp 85 °C; $[\alpha]_D^{23} = -121.4$ (*c* 1.00 $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.75 (1H, d, $J = 8.1$ Hz), 7.37 (2H, d, $J = 8.3$ Hz), 7.20 (1H, dd, $J = 7.8$, 7.8 Hz), 7.14 (2H, d, $J = 8.1$ Hz), 7.09 (1H, dd, $J = 7.3$, 7.6), 6.96 (1H, d, $J = 7.1$ Hz), 4.23–4.29 (1H, m), 2.38–2.45 (1H, m), 2.36 (3H, s), 1.85–1.92 (1H, m), 1.64–1.73 (1H, m), 1.54–1.58 (1H, m), 1.37–1.42 (4H, m), 1.25–1.33 (4H, m), 0.85 (3H, dd, $J = 6.8$, 7.1 Hz); ^{13}C NMR ($CDCl_3$) δ 143.2, 136.6, 135.2, 132.7, 129.3, 128.2, 127.4, 127.0, 126.5, 125.5, 55.6, 34.3, 31.5, 26.7, 25.4, 23.9, 22.5, 21.4, 14.0; HPLC (DAICEL CHIRALCEL OD-H: *n*-hexane/*i*-PrOH = 90:10, detector: 254 nm, flow rate:1.0 mL/min), (*S*) = 10.90 min, (*R*) = 12.61 min; IR (KBr) 3420, 2932, 2858, 1654; LRMS (EI) 358 [M^+, 100]. Anal. Calcd for $C_{21}H_{27}NO_2S$: C, 70.55; H, 7.61; N, 3.92. Found: C,70.36; H, 7.61; N, 3.86.

4.7. (*S*)-2-*n*-Pentyl-1,2,3,4-tetrahydroquinoline 2

To a solution of **10** (357 mg, 1.00 mmol) in 15.0 mL of DME, was added a solution of anthracene sodium (0.4 M in DME, 7.35 mL, 3.00 mmol) at −65 °C under an Ar atmosphere. After the reaction mixture was stirred at −65 °C for 10 min, the reaction was quenched by water. The mixture was extracted with AcOEt and the combined organic layers washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (*n*-hexane/AcOEt 10:1) to give 201 mg (99%) of **2** as a colourless oil. $[\alpha]_D^{23} = -11.5$ (*c* 1.00, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 6.94 (2H, d, $J = 7.3$ Hz), 6.59 (1H, dd, $J = 1.1$, 7.5 Hz), 6.46 (1H, dd, $J = 1.1$, 8.3 Hz), 3.76 (1H, br), 3.19–3.26 (1H, m), 2.68–2.84 (2H, m), 1.92–1.98 (2H, m), 1.31–1.64 (8H, m), 0.90 (3H, t, $J = 6.9$ Hz); ^{13}C NMR ($CDCl_3$) δ 144.7, 129.2, 126.7, 121.4, 116.8, 114.0, 51.6, 36.7, 31.9, 28.1, 26.4, 25.4, 22.6, 14.0; IR (neat) 3385, 2924, 2858, 1607; HRMS (FAB) $C_{14}H_{21}N$ calcd 203.1674, found 203.1682.

4.8. (*S*)-*N*-Methyl-2-*n*-pentyl-1,2,3,4-tetrahydroquinoline 1

To a solution of **2** (201 mg, 0.99 mmol) and K_2CO_3 (137 mg, 0.99 mmol) in 5.00 mL of THF, was added MeI (0.33 mL, 6.00 mmol) under an Ar atmosphere. After the reaction mixture was refluxed for 10 h, the reaction was quenched by water. Organic compounds were extracted with CH_2Cl_2 and combined organic layers washed with brine and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel (*n*-hexane/CH_2Cl_2 = 3:1) to give 171 mg (80%, 94% ee) of **1** as a pale yellow oil. $[\alpha]_D^{23} = +7.9$ (*c* 1.00, $CHCl_3$); $[\alpha]_D^{26} = +4.4$ (*c* 1.00, CH_2Cl_2); $[\alpha]_D^{26} = +5.2$ (*c* 1.00, MeOH); $[\alpha]_D^{26} = +5.1$ (*c* 1.00 EtOH), {lit.[1] $[\alpha]_D = -7.2$}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (1H, dd, $J = 7.5$, 7.9 Hz), 6.96 (1H, d, $J = 7.3$ Hz), 6.57 (1H, dd, $J = 7.1$, 8.3 Hz), 6.51 (1H, d, $J = 8.0$ Hz), 3.20–3.25 (1H, m), 2.92 (3H, s), 2.75–2.80 (1H, m), 2.61–2.67 (1H, m), 1.86–1.90 (2H, m), 1.26–1.41 (8H, m), 0.89 (3H, t, $J = 7.0$ Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 145.3, 128.6, 127.0, 121.8, 115.1, 110.3, 58.9, 37.9, 32.0, 31.1, 25.7, 24.4, 23.5, 22.7, 14.0; HPLC (DAICEL CHIRALCEL OD-H: *n*-hexane/*i*-PrOH = 95:5, detector: 254 nm, flow rate: 1.0 mL/min), (*S*) = 36.47 min, (*R*) = 39.78 min; IR (neat) 2928, 2856, 1603; HRMS (FAB) $C_{15}H_{23}N$ calcd 217.1830, found 217.1821.

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