SYNTHESIS OF OPTICALLY ACTIVE 2-ACETOXY-3-ALKYLIDENE-α-LYCORANES FOR A SYNTHETIC APPROACH TOWARD (+)-LYCORINE BY RADICAL REACTION

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Abstract – A radical-mediated synthesis of optically active 2α- and 2β-trimethylsilylmethyene-α-lycoranes (3,4), which are key intermediates for synthesis of (+)-lycorine (2), is described. Thus, both B and C rings in lycorine (2) were constructed by 6-exo mode radical cyclization. The former ring formation was performed in diastereoselective manner by radical cyclization via α-acylamino radical of (4S,5R)-4-acetoxy-N-(2-methoxy-, benzylxy-, and tert-butoxycarbonylethenyl-4,5-methylenedioxybenzyl)- or (4S,5R)-N-(2-tert-butoxycarbonylethenyl-4,5-methylenedioxybenzyl)-4-triethylsilyloxy-5-phenyl-selenyl-2-pyrrolidinones (10-12 or 19). The latter ring formation was accomplished by the reaction of (1S,10R,10aR,2’S)- and (1S,10R,10aR,2’R)-10-(2’-acetoxy-4’-trimethylsilyl-3’-butynyl)-1-imidazoylticarbonyloxy-7,8-methylenedioxy-1,2,3,5,10,10a-hexahydrobenz[f]indolizidines (28).

The Amaryllidaceae alkaloids have been focused as central role in the development of alkaloid chemistry. Among them, (-)-lycorine (1), which is one of representative alkaloids in this family, has pentacyclic structure contains in all trans oriented four contiguous chiral carbon centers. Moreover, it shows interesting and potential biological activities such as antineoplastic, antiviral, anti-inflammatory activities, inhibitory effect on tumour cell apoptosis, and DNA binding activity is also reported. Therefore, in past three decades, considerable synthetic studies have been reported. However, most of them were performed as racemic form except for only two papers on a synthesis of (-)-lycorine (1) and (+)-lycorine (2).
In continuation of our studies on the synthesis of *Amaryllidaceae* alkaloids, we have recently reported synthesis of optically active 2-methyllycoranes using combination of 6-exo and -endo mode radical reactions (Scheme 1). The methodology suggested a promise to make a potential intermediate for synthesis of optically active lycorine. In this paper, we describe the radical-mediated synthesis of optically active functionallized α-lycoranes (3,4) as candidates for synthesis of (+)-lycorine (2).

Synthesis of radical precursors (11-13) was as follows (Scheme 2). Reaction of 6-iodopiperonyl alcohol (5) and (3S)-acetoxy-2,5-pyrrolidinedione (6) under Mitsunobu conditions gave an imide (7) in 88% yield. Reduction of 8 with NaBH₄ followed by phenylselenenylation afforded seleno-alcohol (8) and -acetate (9) in 67 and 10% yields, respectively. The alcohol (8) was converted to the acetate (9) in 93% yield by conventional way. In order to examine the steric effect of ester moiety on diastereoselectivity in radical reaction, three kinds of radical precursors (10-12) were synthesized in 46-72% yields by Heck reaction of 9 with methyl, benzyl or tert-butyl acrylate.

All radical reactions were performed with AIBN and Bu₃SnH in boiling benzene using syringe pump technique to give unseparable mixture of diastereomers (Table 1). As a result, the selenide (12) bearing tert-butyl ester gave the best result to form products (15a,b) in both diastereoselectivity and chemical yield, although the diastereoselectivity was not affected by the bulkiness of ester group. Stereochemistry of cyclized products (13-15) was determined by NOE experiments. In all cases, only two of possible four diastereomers were obtained as similarly observed in our previous report. From above results,
Scheme 2. Reagents and conditions: a) DEAD, PPh₃, THF, rt; b) NaBH₄, THF-EtOH, 0 °C; PhSeH, p-TsOH, rt; c) Ac₂O, Py, rt; d) acrylates, Pd(OAc)₂, PPh₃, EtCN, 100 °C; e) AIBN, Bu₃SnH, benzene, Δ (Table 1); f) BH₃•THF, THF, rt; TMEDA, rt; NaOMe, MeOH, rt; g) TESCl, imidazole, DMF, rt

Table 1. Radical reaction of selenides (11-13).

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<th>Time (h)</th>
<th>Yield (%)a</th>
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a) Combined isolated yield of cyclized products (a,b).
b) Determined by ¹H-NMR spectral analysis.

diastereomeric mixture of lactams (15) was reduced with BH₃ followed by treatment with TMEDA and methanolysis to give separable amino alcohols (16a) and (16b) in 57 and 29% yields, respectively. The former (16a), which could be led to (+)-lycorine (2), was converted to TES ether (17a) in 89% yield.

Although TES ether (17a) was produced, unexpected low diastereoselectivity in radical reaction and number of steps promoted us to plan an alternative approach to TES ether (17a) as depicted in Scheme 3.

Scheme 3. Reagents and conditions: a) tert-butyl acrylate, Pd(OAc)₂, PPh₃, EtCN, 100 °C; b) TESCl, imidazole DMF, rt; c) AIBN, Bu₃SnH, benzene, Δ; d) BH₃•THF, THF, rt; TMEDA, rt
In this route, we anticipated that introduction of bulky silyl ether group would raise diastereoselectivity by its interaction with tert-butyl ester moiety in radical reaction. Thus, the iodide (8) was converted to tert-butyl ester (18) in 62% yield. As expected, radical reaction of 19, which was obtained by triethylsilylation of 18, gave 3.4 : 1 mixture of diastereomers (20a,b) in 87% yield. The lactams (20a,b) were led to 17a and 17b in 51 and 16% yields, respectively, by transformation similar to that described for 13, in which improved synthesis of 17a was achieved.

Furthermore, 17a was transformed to radical precursor for construction of C ring. Reduction of tert-butyl ester (17a) with DIBAH gave aldehyde (21) and alcohol (22) in 51 and 38% yields, respectively, along with unchanged 17a (4%). The alcohol (22) could be recycled to 21 in 66% yield by Dess-Martin oxidation. Treatment of aldehyde (21) with ethynylmagnesium bromide followed by acetylation furnished separable propargyl acetates (23a) and (23b) in 39 and 49% yields, respectively. Stereochemistry of 23a,b was determined by further conversion as described below. Desilylation of 23a,b with 1 N HCl gave alcohols (24a,b), treatment of which with N,N'-thiocarbonyldiimidazole in refluxing benzene furnished radical precursors (25a,b) (Scheme 4).

With radical precursors (25) in hand, we examined their radical cyclization. Initially, radical reaction of 25a was performed under various conditions using syringe pump technique (Table 2). Unfortunately, the reaction produced not only desired 6-exo cyclized product (29a) but also 7-endo cyclization product (30) (runs 1-6). The reaction in boiling benzene afforded 18% yield of reduced product (31), while that in boiling toluene diminished formation of 31. The reaction with tricyclohexyltin hydride [Cy3SnH]14 instead...
Scheme 5. Reagents and conditions: a) AIBN, Bu$_3$SnH or Cy$_3$SnH, benzene or toluene, $\Delta$ (Table 2)

Table 2. Radical reaction of imidazolides (28a, b and 29a, b).$^a$

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$^a$. Reaction was carried out in 0.01 M toluene solution for 0.5 h, unless otherwise noted.
$^b$. In 0.02 M benzene solution for 1 h.
$^c$. In 0.02 M benzene solution for 0.5 h.
$^d$. Not isolated.
$^e$. Determined as a trace amount.
$^f$. In 0.02 M toluene solution for 0.5 h.
of Bu3SnH in boiling toluene (0.01 M) gave the best result, in which desired product (29) was formed in 37% yield (run 6). Stereochemistry in each product was determined by NOE experiment. Interestingly, in similar reaction of 25b only 6-exo mode cyclization occurred to afford α-lycorane (32) and β-lycorane (33) along with reduced product (34). These results indicated that acetoxy group attached to propargyl carbon affected the course of the radical reaction.

We next turned our attention to use radical precursors with TMS group11c at terminal alkynyl moiety, because TMS group seemed to be bulky enough to suppress 7-endo cyclization. Synthesis of radical precursors (28a,b) was performed via 26 and 27 from 21 by the procedure similar to that described for conversion of 21 to 25a,b (Scheme 4).

As expected, radical reaction of 28a with Cy3SnH in boiling toluene (0.01 M) proceeded in only 6-exo mode cyclization to give α-lycoranes (3a,b) in each 42% yield as separable geometric isomers (Table 2, run 12). On the other hand, radical reaction of 28b with Bu3SnH or Cy3SnH afforded α-lycoranes (4a,b) in moderate yield along with about 10% yield of β-lycorane (35).

Unfortunately, further conversion of exo-alkene products (3,4,29) to keto compounds (36) by ozonolysis15a or osmium oxidation15b gave intractable mixture, in which the corresponding ketones (36) could not be determined at all. Also, desilylation of 3 or 4 under various conditions16 did not proceed without decomposition.

In conclusion, synthesis of optically active 2-acetoxy-3-alkylidene-α-lycoranes (3,4,29) by radical-mediated reaction was accomplished. For the construction of B ring, TES ether (19) was the best radical precursor to give the products (17a,b). TMS substituted acetylenes (28a,b), which were obtained from 17a, smoothly formed C ring by radical reaction to give functionallized α-lycoranes (3,4) in moderate to high yield. Further transformation of 3, 4, or 29 to (+)-lycorine (2) is now in progress.

EXPERIMENTAL

General. All melting points were measured on a Büchi or a Yanagimoto (hot plate) melting point apparatus and are uncorrected. IR spectra were performed with a Hitachi 260-10 spectrophotometer in CHCl3 solution. 1H and 13C NMR spectra were taken with a JEOL EX-270 (270 MHz) spectrometer in CDCl3 solution with tetramethylsilane as an internal standard. MS and HRMS spectra were measured on a Hitachi M-80 or a JEOL JMS D-300 spectrometer. Elementary analysis was performed with a Heraeus CHN-O-RAPID. Column chromatography was performed over silica gel (Merck Kiegelsel 60). Preparative TLCs were run on Merck 5744 or Merck 5715 plates. Organic extracts were dried over K2CO3, unless otherwise noted.

(3S)-3-Acetoxy-N-(2-ido-4,5-methyleneoxybenzyl)-2,5-pyrrolidinedione (7). To a stirred solution of 6-iodopiperonyl alcohol (5) (26.41 g, 95 mmol), (3S)-acetoxy-2,5-pyrrolidinedione (6)12 (15.70 g, 100
mmol), and PPh₃ (26.3 g, 100 mmol) in THF (150 mL) at 0°C was added DEAD (16 mL, 101.6 mmol) over a period of 20 min. After being stirred at rt for 1 h, the solvent was evaporated in vacuo to give a residue, to which was added benzene to form a precipitate. The precipitate was removed by suction filtration. The filtrate was evaporated in vacuo to give a residue, which was purified by column chromatography (benzene : AcOEt = 5 : 1) to afford 7 (34.96 g, 88%); mp 127-128°C (AcOEt-hexane); [α]D²⁴ -30.4° (c 1.01, CHCl₃); ¹H NMR δ 7.25, 6.69 (each 1H, s), 5.96 (2H, s), 5.44 (1H, dd, J = 5, 8.9 Hz), 4.70 (2H, s), 3.21 (1H, dd, J = 8.9, 18.5 Hz), 2.78 (1H, dd, J = 5, 18.5 Hz), 2.17 (3H, s); IR 1751, 1724 cm⁻¹; EI MS m/z 417 (M⁺); Anal. Calcd for C₁₄H₁₂NO₆I: C, 40.31; H, 2.90; N, 3.36. Found: C, 40.02; H, 2.88; N, 3.63.

(4S,5R)-4-Hydroxy- and (4S,5R)-4-Acetoxy-N-(2-iodo-4,5-methylenedioxybenzyl)-5-phenylselenyl-2-pyrrolidinone (8 and 9). To a stirred solution of 7 (30.0 g, 71.9 mmol) in THF (250 mL) and EtOH (120 mL) at 0°C was added NaBH₄ (2.78 g, 73 mmol) in small portions. After being stirred for 1.5 h, the reaction was quenched with water. The product was taken up in CHCl₃, and the extracts were washed with 3N HCl and brine, successively, dried (MgSO₄), and evaporated under reduced pressure to give crude alcohol. To the alcohol in CH₂Cl₂ (250 mL) were added PhSeH (9.9 mL, 93.3 mmol) and p-TsOH•H₂O (1.37 g, 7.2 mmol). After being stirred for 2 h, the reaction was quenched with water. The mixture was extracted with CHCl₃. The organic extracts were washed with brine, dried (MgSO₄), and evaporated in vacuo to give a residue, which was purified by column chromatography (hexane : AcOEt = 1 : 1 then AcOEt) to afford 8 (24.93 g, 67%) and 9 (3.86 g, 10%) as amorphous solid. A mixture of 8 (15.78 g, 30.4 mmol) and Ac₂O (5.5 mL) in pyridine (18 mL) was stirred for 12 h. Usual work-up gave a residue, which was purified by column chromatography (hexane : AcOEt = 10 : 1) to give 9 (15.80 g, 93%). 8; [α]D²³ -43.2° (c 1.06, CHCl₃); ¹H NMR δ 7.52-7.55 (2H, m), 7.23-7.55 (4H, m), 6.85 (1H, s), 5.95 (2H, s), 4.97, 4.31 (each 1H, d, J = 15.2 Hz), 4.58-4.70 (2H, m), 1.95-2.20 (2H, m); EI MS m/z 517 (M⁺); HRMS m/z calcd for C₁₈H₁₇NO₄Se (M⁺) 517.9368, found: 517.9358. 9; [α]D²⁹ -39.8° (c 1.0, CHCl₃); ¹H NMR δ 7.25-7.61 (5H, m), 7.26, 6.77 (each 1H, s), 5.97, 5.96 (each 1H, d, J = 2 Hz), 5.47 (1H, d, J = 5.4 Hz), 4.99, 4.30 (each 1H, d, J = 18.4 Hz), 4.64 (1H, s), 2.21 (1H, d, J = 18.4 Hz), 2.01 (1H, dd, J = 5.4, 18.4 Hz), 2.01 (3H, s); IR 1741, 1701 cm⁻¹; FAB MS m/z 560 [(M+H)⁺]; HR FAB MS m/z calcd for C₂₀H₁₉NO₅Se [(M+H)⁺] 559.9473, found: 559.9483.

General procedure for Heck reaction of aryl iodides (8,9). A solution of 8 or 9 (1 eq.), Pd(OAc)₂ (3 mol%), PPh₃ (12 mol%), Et₃N (2.5 eq.), and methyl, benzyl or tert-butyl acrylate (5 eq.) in propionitrile was heated at 100°C under an argon atmosphere. The solvent was evaporated in vacuo to give a residue, which was purified by column chromatography (CHCl₃ : AcOEt = 50 : 1 for 11 and 12; hexane : AcOEt = 1 : 1 for 10 and 18) to afford esters (10-12,18).
(4S,5R)-(E)-4-Acetoxy-N-(2-methoxycarbonylethenyl-4,5-methylenedioxybenzyl)-5-phenylselenyl-2-pyrrolidinone (10); from 9 (0.993 g, 1.78 mmol) in propionitrile (30 mL) for 17 h, 10 (0.420 g, 46%) as an oil and 9 (0.250 g, 25%) were obtained; [α]D27 -23.6° (c 1.02, CHCl3); 1H NMR δ 7.91, 6.20 (each 1H, d, J = 15.7 Hz), 7.56 (2H, d, J = 8.3 Hz), 7.30-7.41 (3H, m), 7.04, 6.75 (each 1H, s), 6.00 (2H, s), 5.42 (1H, d, J = 5.9 Hz), 5.21, 4.26 (each 1H, d, J = 15.1 Hz), 4.54 (1H, s), 3.80 (3H, s), 2.01-2.21 (2H, m), 1.94 (3H, s); IR 1743, 1693 cm\(^{-1}\); FAB MS m/z 538 [(M+Na)\(^+\)]; HR FAB MS m/z calcd for C24H23NO7NaSe [(M+Na)+] 538.0546, found: 538.0543.

(4S,5R)-(E)-4-Acetoxy-N-(2-benzyloxycarbonylethenyl-4,5-methylenedioxybenzyl)-5-phenylselenyl-2-pyrrolidinone (11); from 9 (1.937 g, 3.47 mmol) in propionitrile (40 mL) for 14 h, 11 (1.48 g, 72%) was obtained as an oil; 1H NMR δ 7.94, 6.24 (each 1H, d, J = 15.7 Hz), 7.25-7.61 (2H, m), 7.20-7.43 (8H, m), 7.04, 6.74 (each 1H, s), 6.00, 5.99 (each 1H, d, J = 1.3 Hz), 5.40 (1H, d, J = 5.6 Hz), 5.27, 4.22 (each 1H, d, J = 12.5 Hz), 5.21, 4.24 (each 1H, d, J = 15.2 Hz), 4.57 (1H, s), 1.96-2.09 (2H, m), 1.87 (3H, s, Ac); IR 1743 cm\(^{-1}\); FAB MS m/z 594 [(M+H)\(^+\)]; HR FAB MS m/z calcd for C30H28NO7Se [(M+H)+] 594.0986, found: 594.0987.

(4S,5R)-(E)-4-Acetoxy-N-(2-tert-butoxycarbonylethenyl-4,5-methylenedioxybenzyl)-5-phenylselenyl-2-pyrrolidinone (12); from 9 (6.235 g, 11.2 mmol) in propionitrile (230 mL) for 24 h, 12 (4.13 g, 66%) was obtained as an oil; 1H NMR δ 7.76, 6.11 (each 1H, d, J = 15.5 Hz), 7.56 (2H, d, J = 8.3 Hz), 7.26-7.40 (3H, m), 7.03, 6.75 (each 1H, s), 6.00, 5.99 (each 1H, d, J = 1.4 Hz), 5.41 (1H, d, J = 5.9 Hz), 5.23, 4.22 (each 1H, d, J = 15.1 Hz), 4.48 (1H, s), 2.01-2.18 (2H, m), 1.94 (3H, s), 1.53 (9H, s); IR 1743 cm\(^{-1}\); FAB MS m/z 558 [(M+H)\(^+\)]; HR FAB MS m/z calcd for C27H30NO7Se [(M+H)+] 558.1195, found: 558.1180.

(4S,5R)-(E)-N-(2-tert-Butoxycarbonylethenyl-4,5-methylenedioxybenzyl)-4-hydroxy-5-phenylselenyl-2-pyrrolidinone (18); from 8 (8.78 g, 17.0 mmol) in propionitrile (300 mL) for 9 h, 18 (5.41 g, 62%) was obtained as crystals; mp 171-172.5°C (AcOEt-hexane); [α]D24 -12.4° (c 1.01, CHCl3); 1H NMR δ 7.83, 6.15 (each 1H, d, J = 15.8 Hz), 7.50 (2H, d, J = 7.9 Hz), 7.26-7.34 (3H, m), 7.02, 6.80 (each 1H, s), 5.97 (2H, s), 5.17, 4.27 (each 1H, d, J = 15.3 Hz), 4.58 (1H, t, J = 5.3 Hz), 4.54 (1H, s), 2.57 (1H, d, J = 5.3 Hz), 2.14 (1H, d, J = 17.7 Hz), 1.99 (1H, dd, J = 5.3, 17.7 Hz), 1.52 (9H, s); IR 3400, 1697, 1632 cm\(^{-1}\); MS m/z 517 (M\(^+\)); HRMS m/z calcd for C25H27NO6Se (M\(^+\)) 517.1004, found: 517.1022.

**General procedure for radical reaction of selenides (10-12,19).** To a refluxed solution of selenides (10-12,19) (1 eq.) in benzene (32 mL per 1 mmol of selenide) was added a solution of AIBN (0.5 eq.) and Bu3SnH (3 eq.) in benzene (18 mL per 1 mmol of selenide) using syringe pump. After the mixture was refluxed for additional 1 h, the solvent was removed \textit{in vacuo} to give a residue, which was purified by column chromatography (hexane : AcOEt = 30 : 1 then 1 : 1) to afford cyclized products (13-15,20). Attempts to separate the diastereomeric mixtures were unsuccessful.
(1S,10R,10aR)- and (1S,10R,10aS)-1-Acetoxy-10-methoxycarbonylmethyl-7,8-methylenedioxy-1,2,3,5,10,10a-hexahydrobenz[f]indolizidin-3-ones (13a,b); from 10 (1.298 g, 2.50 mmol), 13a,b (0.757 g, 84%) was obtained as amorphous solid (addition time; 2.5 h); 1H NMR δ 6.66, 6.34 (1H, each s), 6.59, 6.56 (1H, each s), 5.93-5.95 (2H, m), 4.94, 4.15 (each 0.36H, d, J = 16.5 Hz, H-5), 4.80, 4.27 (each 0.64H, d, J = 17.3 Hz, H-5), 3.71, 3.65 (3H, each s), 3.55-3.91 (1H, m), 2.80-3.21 (3H, m), 2.20-2.60 (2H, m), 2.10, 2.09 (3H, each s); IR 1738, 1687 cm⁻¹; MS m/z 361 (M⁺); HRMS m/z calcd for C₁₈H₁₉NO₇ (M⁺) 361.1159, found: 361.1158.

(1S,10R,10aR)- and (1S,10R,10aS)-1-Acetoxy-10-benzyloxycarbonylmethyl-7,8-methylenedioxy-1,2,3,5,10,10a-hexahydrobenz[f]indolizidin-3-ones (14a,b); from 11 (0.711 g, 1.2 mmol), 14a,b (0.360 g, 69%) was obtained as an oil (addition time; 2 h); 1H NMR δ 7.18-7.36 (5H, m), 6.63, 6.62 (1H, each s), 6.56, 6.54 (1H, each s), 5.89-5.92 (2H, m), 4.93, 4.10 (each 0.67H, d, J = 16.5 Hz, H-5), 4.79, 4.25 (each 0.33H, d, J = 17.5 Hz, H-5), 3.47-3.88 (2H, m), 2.81-3.17 (3H, m), 2.25-2.54 (1H, m), 2.08, 2.06 (3H, each s); IR 1736, 1689 cm⁻¹; MS m/z 437 (M⁺); HRMS m/z calcd for C₂₄H₂₃NO₇ (M⁺) 437.1475, found: 437.1487.

(1S,10R,10aR)- and (1S,10R,10aS)-1-Acetoxy-10-(tert-butoxycarbonylmethyl)-7,8-methylenedioxy-1,2,3,5,10,10a-hexahydrobenz[f]indolizidin-3-ones (15a,b); from 12 (4.02 g, 7.20 mmol), 15a,b (2.443 g, 84%) was obtained as amorphous solid (addition time; 2 h); 1H NMR δ 6.69, 6.67 (1H, each s), 6.58, 6.56 (1H, each s), 5.92, 5.91 (2H, each s), 5.20-5.25 (1H, m), 4.94, 4.14 (each 0.67H, d, J = 16.5 Hz, H-5), 4.84, 4.24 (each 0.37H, d, J = 17.4 Hz, H-5), 3.76-3.89 (1H, m), 3.41-3.47, 2.90-3.08 (1H, each m), 2.69-3.15 (3H, m), 2.32-2.55 (1H, m), 2.10, 2.08 (3H, each s), 1.42, 1.41 (9H, each s); IR 1731, 1686 cm⁻¹; MS m/z 403 (M⁺); HRMS m/z calcd for C₂₁H₂₅NO₇ (M⁺) 403.1631, found: 403.1633.

(1S,10R,10aR)- and (1S,10R,10aS)-10-(tert-Butoxycarbonylmethyl)-1-triethylsilyloxy-7,8-methylenedioxy-1,2,3,5,10,10a-hexahydrobenz[f]indolizidine (16a and 16b). To a stirred solution of 15a,b (2.00 g, 4.96 mmol) in THF (140 mL) at rt was added BH₃•THF (20 mL, 20 mmol, 1 M in THF) over a period of 5 min. After being stirred for 2h, TMEDA (4.5 mL) was added to the mixture, and the mixture was stirred for overnight. Water was added to the mixture and the product was extracted with CHCl₃. The extracts
were washed with saturated NaHCO₃ and brine, successively, dried, and evaporated under reduced pressure to give a residue, which was taken up in Et₂O and the solid was filtered off. The filtrate was evaporated in vacuo to afford a residue, which was treated with NaOMe (0.603 g, 11.2 mmol) in MeOH (40 mL) at rt for 1 h. Then, the reaction was quenched with water and extracted with CHCl₃. The extracts were washed with brine, dried, and evaporated under reduced pressure to give a residue, which was subjected to column chromatography (AcOEt : MeOH = 50 : 1 the 10 : 1) to afford 16a (0.985 g, 57%) and 16b (0.505 g, 29%). 16a; oil; [α]D₃⁰ +85.9° (c 1.0, CHCl₃); ¹H NMR δ 6.77, 6.49 (each 1H, s), 5.90 (2H, s), 4.20 (1H, ddd, J = 3.3, 5.6, 8.7 Hz), 3.87, 3.45 (each 1H, d, J = 14.2 Hz), 3.19 (1H, dt, J = 5.5, 9.9 Hz), 3.11 (1H, t, J = 8.7 Hz), 2.83 (1H, dd, J = 5.8, 15.3 Hz), 2.72 (1H, dd, J = 4.8, 15.3 Hz), 2.53 (1H, q, J = 8.9 Hz), 2.18-2.356 (2H, m), 1.66-1.77 (1H, m), 1.41 (9H, s); IR 3400, 1703 cm⁻¹; MS m/z 347 (M⁺); HRMS m/z calcd for C₁₉H₂₅NO₅ (M⁺) 347.1734, found: 347.1748.

16b; oil; [α]D₃⁰ +42.2° (c 1.15, CHCl₃); ¹H NMR δ 6.56, 6.39 (each 1H, s), 5.82 (2H, s), 3.85, 3.27 (each 1H, d, J = 14.2 Hz), 3.79 (1H, dd, J = 7.9, 15.8 Hz), 3.36 (1H, dt, J = 4.6, 12.6 Hz), 3.16 (1H, dt, J = 4.6, 12.6 Hz), 2.73 (1H, dd, J = 9.9, 18.2 Hz), 2.44 (1H, dd, J = 6.9, 9.9 Hz), 2.38 (1H, dd, J = 3.6, 7.5 Hz), 2.26 (1H, dd, J = 2.4, 18.0 Hz), 2.04-2.18 (1H, m), 1.63-1.77 (1H, m), 1.40 (9H, s); IR 3500, 1705 cm⁻¹; MS m/z 347 (M⁺); HRMS m/z calcd for C₁₉H₂₅NO₅ (M⁺) 347.1734, found: 347.1737.

(1S,10R,10aR)-10-(tert-Butoxycarbonylmethyl)-1-triethylsilyloxy-7,8-methylenedioxy-1,2,3,5,10,10a-hexahydrobenz[f]indolizidine (17a). To a stirred solution of 16a (0.635 g, 1.83 mmol) and imidazole (0.436 g, 6.41 mmol) in DMF (16 mL) at rt was added a solution of chlorotriethylsilane (0.689 g, 16.6 mmol) in DMF (1 mL) over a period of 5 min. After being stirred for 0.5 h, the reaction was quenched with saturated aqueous NaHCO₃. The mixture was extracted with ether. The extracts were washed with brine, dried, and evaporated under reduced pressure to give a residue, which was purified by column chromatography (benzene : AcOEt = 3 : 1 then 1 : 1) to afford 17a (0.753 g, 89%) as an oil; [α]D₂⁵ +63.1° (c 1.27, CHCl₃); ¹H NMR δ 6.67, 6.47 (each 1H, s), 5.87, 5.86 (each 1H, d, J = 1.3 Hz), 4.16 (1H, ddd, J = 4.5, 6.4, 8.6 Hz), 3.81, 3.43 (each 1H, d, J = 14.2 Hz), 3.27 (1H, t, J = 8.3 Hz), 3.10 (1H, dt, J = 2.6, 8.8 Hz), 3.03 (1H, dd, J = 2.6, 16.9 Hz), 2.52 (1H, dd, J = 7.3, 16.9 Hz), 2.47-2.56 (1H, m), 2.18-2.29 (2H, m), 1.60-1.70 (1H, m), 1.41 (9H, s), 0.97 (9H, t, J = 7.9 Hz), 0.62 (6H, t, J = 7.9 Hz); IR 1720 cm⁻¹; MS m/z 461 (M⁺); HRMS m/z calcd for C₂₅H₃₉NO₅Si (M⁺) 461.2598, found: 461.2605.

(4S,5R)-(E)-N-[2-(tert-Butoxycarbonylthienyl)-4,5-methylenedioxybenzyl]-4-triethylsilyloxy-5-phenylselenylpyrrolidin-2-one (19). To a stirred solution of 18 (5.72 g, 11.1 mmol) and imidazole (0.436 g, 6.41 mmol) in DMF (16 mL) at rt was added a solution of chlorotriethylsilane (0.689 g, 16.6 mmol) in DMF (1 mL) over a period of 5 min. After being stirred for 2 h, similar work-up as described above gave a residue, which was purified by column chromatography (benzene : AcOEt = 40 : 1 then 10 : 1) to afford 19 (3.76 g, 54%); [α]D₃⁰ +5.1° (c 0.35, CHCl₃); ¹H NMR δ 7.88, 6.16 (each 1H, d, J = 15.5 Hz), 7.54 (2H,
d, $J = 7.9$ Hz), 7.30-7.37 (3H, m), 7.04, 6.83 (each 1H, s), 5.95, 5.96 (each 1H, $d, J = 1.5$ Hz), 5.16, 4.31 (each 1H, $d, J = 15.5$ Hz), 4.49 (1H, $t, J = 2.6$ Hz), 4.47 (1H, s), 2.10 (2H, $d, J = 2.6$ Hz), 1.53 (9H, s), 0.78 (9H, $t, J = 7.9$ Hz), 0.39 (6H, $t, J = 7.9$ Hz); IR 1709, 1630 cm$^{-1}$; FAB MS $m/z$ 632 [(M+H)$^+$]; HR FAB MS $m/z$ calcd for C$_{31}$H$_{42}$NO$_6$SeSi [(M+H)$^+$] 632.1947, found: 632.1950.

**Reduction of 20a,b.** To a stirred solution of 20a,b (2.30 g, 4.84 mmol) in THF (140 mL) at rt was added BH$_3$•THF (20 mL, 19.3 mmol, 0.92 M in THF) over a period of 10 min. After being stirred for 3.5 h, TMEDA (4.5 mL) was added to the mixture, and the mixture was stirred for overnight. Similar work-up as described above gave a residue, which was subjected to column chromatography (hexane : AcOEt = 10 : 1 then 4 : 1) to afford 17a (1.250 g, 56%) and 17b (0.0358 g, 16%). 1H-NMR spectrum of 17a was identical with that of 17a obtained from 16a.

(1S,10R,10aS)-10-(tert-Butoxycarbonylmethyl)-1-triethylsilyloxy-7,8-methylenedioxy-1,2,3,5,10,10a-hexahydrobenz[f]indolizidine (17b); oil; $[\alpha]_D^{32}$ +107.1 (c 1.05, CHCl$_3$); 1H NMR $\delta$ 6.71, 6.48 (each 1H, s), 5.88 (2H, s), 4.19 (1H, $dd, J = 2.8, 5.1, 7.9$ Hz), 3.96, 3.42 (each 1H, $d, J = 14.5$ Hz), 3.28 (1H, $t, J = 7.9$ Hz), 3.07 (1H, $dt, J = 1.8, 8.2$ Hz), 2.58 (1H, $dd, J = 4.3, 8.2$ Hz), 2.44-2.53 (2H, m), 2.36 (1H, $dd, J = 7.9, 15.5$ Hz), 1.96-2.11 (1H, m), 1.62-1.74 (1H, m), 1.43 (9H, s), 0.97 (9H, $t, J = 7.9$ Hz), 0.61 (6H, q, $J = 7.9$ Hz); IR 1728 cm$^{-1}$; MS $m/z$ 461 (M$^+$); HRMS $m/z$ calcd for C$_{25}$H$_{39}$NO$_5$Si (M$^+$) 461.2597, found: 461.2599.

(1S,10R,10aR)-1-Triethylsilyloxy-10-formylmethyl- and (1S,10R,10aS)-1-Triethylsilyloxy-10-hydroxyethyl-7,8-methylenedioxy-1,2,3,5,10,10a-hexahydrobenz[f]indolizidine (21 and 22). To a solution of 17a (1.313 g, 2.85 mmol) in CH$_2$Cl$_2$ (110 mL) at -78$^\circ$C was added DIBAH (8.5 mL, 8.5 mmol, 1 M in hexane) over a period of 15 min. After being stirred for 1 h, further DIBAH (6 mL, 6 mmol) was added over a period of 8 min and the mixture was stirred for additional 1 h. Then, the reaction was quenched with water. The mixture was extracted with CHCl$_3$. Usual work-up gave a residue, which was purified by column chromatography (hexane: AcOEt = 1:1 then 3:1 then AcOEt : MeOH = 10:1) to afford 21 (0.567 g, 51%), 22 (0.420 g, 38%), and 17a (0.058 g, 4.4%). 21; $[\alpha]_D^{24}$ +94.4 (c 1.01, CHCl$_3$); 1H NMR $\delta$ 9.79 (1H, $t, J = 1.5$ Hz), 6.56, 6.48 (each 1H, s), 5.88, 5.87 (each 1H, $d, J = 1.3$ Hz), 4.15 (1H, $dd, J = 4.6, 6.5, 8.8$ Hz), 3.84, 3.42 (each 1H, $d, J = 13.7$ Hz), 3.35-3.41 (1H, m), 3.09-3.20 (2H, m), 2.89 (1H, $dd, J = 1.5, 5.6, 19.7$ Hz), 2.52 (1H, $q, J = 8.8$ Hz), 2.16-2.30 (2H, m), 1.60-1.74 (1H, m), 0.95 (9H, $t, J = 7.7$ Hz), 0.60 (6H, q, $J = 7.7$ Hz); IR 1722 cm$^{-1}$; MS $m/z$ 389 (M$^+$); HRMS $m/z$ calcd for C$_{21}$H$_{31}$NO$_4$Si (M$^+$) 389.2022, found: 389.2032. 22; oil; $[\alpha]_D^{26}$ +94.2 (c 1.02, CHCl$_3$); 1H NMR $\delta$ 6.70, 6.46 (each 1H, s), 5.87 (2H, s), 4.08 (1H, $dd, J = 4.4, 7.3, 8.6$ Hz), 3.52 (2H, $t, J = 6.1$ Hz), 3.72, 3.49 (each 1H, $d, J = 14.5$ Hz), 2.92-3.05 (3H, m), 2.62 (1H, $q, J = 8.6$ Hz), 2.48 (1H, $t, J = 7.3$ Hz), 2.08-2.27 (3H, m), 1.60-1.71 (1H, m), 0.96 (9H, $t, J = 7.8$ Hz), 0.62 (6H, q, $J = 7.8$ Hz); IR 3500, 1738 cm$^{-1}$; MS $m/z$ 391 (M$^+$); HRMS $m/z$ calcd for C$_{21}$H$_{33}$NO$_4$Si (M$^+$) 391.2179, found: 391.2188.
Dess-Martin Oxidation of Alcohol (22). To a stirred suspension of 22 (0.696 g, 1.78 mmol) and NaHCO₃ (0.748 g, 8.89 mmol) in CH₂Cl₂ (40 mL) at rt was added Dess-Martin periodinane (1.608 g, 3.56 mmol) and brine, successively. After being stirred for 1 h, the mixture was washed with 10% aqueous Na₂S₂O₃ and brine, successively. Usual work-up gave a residue, which was purified by column chromatography (AcOEt : hexane = 1 : 1) to afford 21 (0.457 g, 66%). Its ¹H NMR spectral data were identical with those for the product obtained from 17a.

(1S,10R,10aR,2'S)- and (1S,10R,10aR,2'R)-10-(2'-Acetoxy-3'-butynyl)-1-triethylsilyloxy-7,8-methylenedioxy-1,2,3,5,10,10a-hexahydrobenz[f]indolizidine (23a and 23b). To a solution of 21 (0.495 g, 1.27 mmol) in THF (20 mL) was added 0.5 M ethynylmagnesium bromide in THF (5 mL, 2.5 mmol) at 0°C over a period of 4 min. After being stirred for 30 min, the reaction was quenched with water. The mixture was extracted with CHCl₃. Usual work-up gave an alcohol (0.567 g, 100%), which was treated with Ac₂O (0.404 g, 3.96 mmol) in pyridine (2.5 mL) for 20 h. Work-up as usual gave a residue, which was purified by preparative TLC (AcOEt : hexane = 1 : 1, two times) to afford 23a (0.226 g, 39%) and 23b (0.284 g, 49%).

23a; mp 78-79°C (hexane); [α] D₃¹ +53.9° (c 1.05, CHCl₃); ¹H NMR δ 6.78, 6.49 (each 1H, s), 5.89 (2H, s), 5.60 (1H, ddd, J = 2, 4.8, 9.2 Hz), 4.07 (1H, dd, J = 6.6, 12.9 Hz), 3.55, 3.48 (each 1H, d, J = 14.2 Hz), 2.95-3.02 (2H, m), 2.48-2.68 (3H, m), 2.46 (1H, d, J = 2 Hz), 2.31 (1H, dt, J = 5.3, 14.9 Hz), 2.14 (1H, dt, J = 8.1, 12.9 Hz), 1.82 (3H, s), 1.64-1.75 (1H, m), 0.99 (9H, t, J = 7.8 Hz), 0.50 (6H, q, J = 7.8 Hz); IR 1736 cm⁻¹; MS m/z 457 (M+); HRMS m/z calcd for C₂₅H₃₅NO₅Si (M+) 457.2282, found: 457.2295.

23b; mp 78-79°C (hexane); [α] D₃¹ +76.9° (c 1.0, CHCl₃); ¹H NMR δ 6.83, 6.51 (each 1H, s), 5.92, 5.91 (each 1H, d, J = 1.5 Hz), 5.42 (1H, dt, J = 2.0, 7.7 Hz), 4.07 (1H, dd, J = 6.3, 13.2 Hz), 3.70, 3.54 (each 1H, d, J = 14.4 Hz), 2.90-3.03 (2H, m), 2.66 (1H, q, J = 8.2 Hz), 2.22-2.50 (3H, m), 2.47 (1H, d, J = 2.0 Hz), 2.06 (3H, s), 2.06-2.18 (1H, m), 1.65-1.82 (1H, m), 0.99 (9H, t, J = 7.9 Hz), 0.65 (6H, q, J = 7.9 Hz); IR 1738 cm⁻¹; MS m/z 457 (M+); HRMS m/z calcd for C₂₅H₃₅NO₅Si (M+) 457.2282, found: 457.2285.

A solution of 23a (0.226 g, 0.49 mmol) and 1 N HCl (3 mL, 3 mmol) in THF (10 mL) was stirred at rt for 15 min. The mixture was diluted with CHCl₃ and saturated aqueous NaHCO₃ was added. Usual work-up gave a residue, which was purified by column chromatography (AcOEt then AcOEt : MeOH = 10 : 1) to afford 24a (0.153 g, 90%); mp 61-62°C (AcOEt-hexane); [α] D₂⁸ +71.6° (c 0.43, CHCl₃); ¹H NMR δ 6.86, 6.49 (each 1H, s), 5.90 (2H, s), 5.71 (1H, dt, J = 2.0, 6.6 Hz), 4.20 (1H, ddd, J = 2.6, 5.6, 11.2 Hz), 3.82, 3.46 (each 1H, d, J = 14.5 Hz), 2.97-3.08 (2H, m), 2.85 (1H, br s), 2.58 (1H, d, J = 2.0 Hz), 2.54 (1H, dd, J = 8.9, 14.9 Hz), 2.23-2.35 (4H, m), 2.01 (3H, s), 1.66-1.77 (1H, m); IR 3305, 1736 cm⁻¹; MS m/z 343 (M+); HRMS m/z calcd for C₁₉H₂₃NO₅Si (M+) 343.1417, found: 343.1407.
A solution of 23b (0.284 g, 0.62 mmol) and 1 N HCl (4 mL, 4 mmol) in THF (12 mL) was stirred at rt for 15 min. Similar work-up as described above gave a residue, which was purified by column chromatography (AcOEt then AcOEt : MeOH = 10 : 1) to afford 24b (0.201 g, 93%); mp 94-95˚C (AcOEt-hexane); [α]D 28 +83.8˚ (c 0.25, CHCl3); 1H NMR δ 6.84, 6.50 (each 1H, s), 5.92, 5.91 (each 1H, d, J = 1.3 Hz), 5.63 (1H, dt, J = 3.1, 5.4, 8.6 Hz), 3.82, 3.49 (each 1H, d, J = 14.2 Hz), 3.05 (1H, dt, J = 2.5, 8.7 Hz), 2.97 (1H, dd, J = 4.5, 9.2 Hz), 2.58 (1H, q, J = 8.7 Hz), 2.49 (1H, d, J = 2 Hz), 2.35-2.40 (2H, m), 2.25-2.29 (3H, m), 2.11 (3H, s), 1.67-1.77 (1H, m); IR 3305, 1738 cm -1; MS m/z 343 (M+); HRMS m/z calcd for C19H21NO5 (M+): 343.1417, found: 343.1427.

General procedure for synthesis of imidazolides (25,28)  A solution of alcohol (24 or 27) (1 eq.) and N, N'-thiocarbonyldiimidazole (2 eq.) in benzene (25 mL per 1 mmol of alcohol) was refluxed for 1 h. Removal of the solvent under reduced pressure gave a residue, which was purified by preparative TLC (AcOEt for 25; hexane : AcOEt = 1 : 5 for 28) to afford corresponding imidazolides (25,28).

(1S,10R,10aR,2'R)-10-(2'-Acetoxy-3'-butynyl)-1-imidazolylthiocarbonyloxy-7,8-methylenedioxy-1,2,3,5,10,10a-hexahydrobenz[f]indolizidine (25a); from 24a (0.065 g, 0.19 mmol), 25a (0.077 g, 90%) was obtained as an oil; [α]D 28 +97.1˚ (c 0.90, CHCl3); 1H NMR δ 8.39, 7.68, 7.05, 6.82, 6.53 (each 1H, s), 5.94 (2H, s), 5.68 (1H, ddd, J = 2.6, 5.4, 8.1 Hz), 5.52 (1H, dt, J = 2.0, 7.1 Hz), 3.89, 3.58 (each 1H, J = 14.3 Hz), 3.13-3.20 (2H, m), 2.92 (1H, dd, J = 5.9, 9.6 Hz), 2.53-2.65 (2H, m), 2.45 (1H, d, J = 2.0 Hz), 2.39 (1H, ddd, J = 5.3, 7.1, 14.9 Hz), 2.22 (1H, ddd, J = 4.3, 7.1, 14.9 Hz), 1.89-1.96 (1H, m), 1.88 (3H, s); IR 1740 cm-1; MS m/z 453 (M+); HRMS m/z calcd for C25H23N3O5Si (M+) 453.1359, found: 453.1352.

(1S,10R,10aR,2'R)-10-(2'-Acetoxy-4'-trimethylsilyl-3'-butynyl)-1-imidazolylthiocarbonyloxy-7,8-methylenedioxy-1,2,3,5,10,10a-hexahydrobenz[f]indolizidine (28a); from 27a (0.202 g, 0.49 mmol), 28a (0.250 g, 98%) was obtained as amorphous solid; [α]D 27 +110.9˚ (c 1.38, CHCl3); 1H NMR δ 8.39, 7.67, 7.06, 6.86, 6.53 (each 1H, s), 5.94 (2H, s), 5.71 (1H, ddd, J = 2.6, 5.2, 7.9 Hz), 5.45 (1H, dt, J = 2, 7.3 Hz), 3.90, 3.57 (each 1H, J = 14.2 Hz), 3.08-3.20 (2H, m), 2.84 (1H, dd, J = 5.6, 9.2 Hz), 2.52-2.66 (2H, m), 2.45 (1H, d, J = 2 Hz), 2.23-2.30 (2H, m), 2.06 (3H, s), 1.91-1.97 (1H, m); IR 1741 cm-1; MS m/z 453 (M+); HRMS m/z calcd for C25H23N3O5Si (M+) 453.1359, found: 453.1352.
0.12 (9H, s); IR 2179, 1740 cm\(^{-1}\); MS \(m/z\) 525 (M\(^+\)); HRMS \(m/z\) calcd for C\(_{26}\)H\(_{31}\)N\(_3\)O\(_5\)SSi (M\(^+\)) 525.1754, found: 525.1750.

\((1S,10aR,2'R)-10-(2''-Acetoxy-4''-trimethylsilyl-3''-butynyl)-1-imidazolylthiocarbonyloxy-7,8-methylenedioxy-1,2,3,5,10,10a-hexahydrobenz[f]indolizidine\) (28b): from 27b (0.140 g, 0.34 mmol), 28b (0.169 g, 95%) was obtained as amorphous solid; [\(\alpha\)]\(_D\) +111.7° (c 1.16, CHCl\(_3\)); 1H NMR \(\delta\) 8.35, 7.64, 7.04, 6.90, 6.51 (5H, each s), 5.92, 5.91 (each 1H, d, \(J = 1.3\) Hz), 5.71 (1H, ddd, \(J = 3\), 5.5, 7.4 Hz), 5.51 (1H, t, \(J = 7.1\) Hz), 3.89, 3.59 (each 1H, d, \(J = 14.3\) Hz), 3.06-3.16 (2H, m), 2.82 (1H, dd, \(J = 5.5\), 9.2 Hz), 2.43-2.65 (2H, m), 2.09-2.27 (2H, m), 2.03 (3H, s), 1.92-2.01 (1H, m), 0.12 (9H, s); IR 2179, 1740 cm\(^{-1}\); MS \(m/z\) 525 (M\(^+\)); HRMS \(m/z\) calcd for C\(_{26}\)H\(_{31}\)N\(_3\)O\(_5\)SSi (M\(^+\)) 525.1754, found: 525.1756.

Radical reaction of 25a,b. To a solution of 25a or 25b (0.041 g, 0.09 mmol) in benzene or toluene under reflux was added a solution of AIBN (0.007 g, 0.54 mmol) and Bu\(_3\)SnH (0.055 g, 0.18 mmol) or Cy\(_3\)SnH (0.067 g, 0.18 mmol) in benzene or toluene using syringe pump over a period of 30 min. Then, the solvent was removed in vacuo to give a residue, which was purified by column chromatography (hexane then CHCl\(_3\) : MeOH = 30 : 1) and preparative TLC (AcOEt : Et\(_3\)N = 25 : 2) to afford 29-31 or 32-34.

\(\alpha\)-Acetoxy-3-methylene-\(\alpha\)-lycorane (29): oil; [\(\alpha\)]\(_D\)\(_{28}\) +42.0° (c 1.03, CHCl\(_3\)); 1H NMR \(\delta\) 6.66, 6.62 (each 1H, s), 5.91 (2H, s), 5.60 (1H, t, \(J = 4.0\) Hz), 5.23, 5.11 (each 1H, s), 4.13, 3.84 (each 1H, d, \(J = 14.9\) Hz), 3.15 (1H, q, \(J = 8.9\) Hz), 3.02 (1H, dt, \(J = 7.6\), 9.2 Hz), 2.93 (1H, dt, \(J = 3.6\), 8.9 Hz), 2.80 (1H, dt, \(J = 4\), 11 Hz), 2.67 (1H, dd, \(J = 7.6\), 11 Hz), 2.44, 1.74 (each 1H, dt, \(J = 4\), 13.5 Hz), 2.10 (3H, s), 1.99-2.20 (2H, m); 13C NMR \(\delta\) 170.0, 146.6, 145.8, 143.9, 132.6, 128.1, 115.4, 107.1, 104.5, 100.8, 72.7, 64.9, 54.0, 53.8, 43.3, 31.8, 30.1, 29.3, 21.5; IR 1738 cm\(^{-1}\); MS \(m/z\) 327 (M\(^+\)); HRMS \(m/z\) calcd for C\(_{19}\)H\(_{21}\)NO\(_4\) (M\(^+\)) 327.1471, found: 327.1476.

18-Acetoxy-12-aza-5,7-dioxapentacyclo[10.7.1.0<2,10> .0<4,8>.0<15,20>]licos a-[2(10),3,8(9),16-tetraene (30): amorphous solid; 1H NMR \(\delta\) 6.74, 6.49 (each 1H, s), 5.89, 5.88 (each 1H, d, \(J = 1.3\) Hz), 5.51-5.66 (3H, m), 3.97, 3.44 (each 1H, d, \(J = 14.9\) Hz), 3.15-3.25 (2H, m), 2.87-2.98 (1H, m), 2.15-2.34 (3H, m), 2.09 (3H, s), 1.72-1.95 (3H, m); IR 1726 cm\(^{-1}\); MS \(m/z\) 327 (M\(^+\)); HRMS \(m/z\) calcd for C\(_{19}\)H\(_{21}\)NO\(_4\) (M\(^+\)) 327.1471, found: 327.1472.

\(2\beta\)-Acetoxy-3-methylene-\(\alpha\)-lycorane (32): oil; [\(\alpha\)]\(_D\)\(_{29}\) +22.9° (c 1.13, CHCl\(_3\)); 1H NMR \(\delta\) 6.65, 6.60 (each 1H, s, arom. Hx2), 5.91 (2H, s, OCH\(_3\)), 5.59 (1H, dd, \(J = 6.4\), 8.0 Hz, H-2), 5.12, 5.04 (each 1H, s, olefinic Hx2), 4.09, 3.83 (each 1H, d, \(J = 15.0\) Hz, H-7x2), 2.93 (1H, dt, \(J = 3.6\), 8.9 Hz, H-5), 3.20 (1H, q,
$J = 8.3$ Hz, H-3a), 3.10 (1H, q, $J = 8.9$ Hz, H-5), 2.70 (1H, ddd, $J = 3.4, 6.4, 12$ Hz, H-1), 2.68 (1H, dd, $J = 8.3, 12$ Hz, H-11c), 2.56 (1H, dt, $J = 3.4, 12$ Hz, H-11b), 2.13 (3H, s, Ac), 1.95-2.10 (2H, m, H-4x2), 1.42 (1H, d, $J = 8, 12$ Hz, H-1); $^{13}$C NMR $\delta$ 170.3 (s), 146.3 (s), 145.8 (s), 145.1 (s), 132.3 (s), 128.5 (s), 111.6 (t), 107.0 (d), 104.5 (d), 100.8 (t), 72.7 (d), 65.0 (d), 54.3 (t), 53.5 (t), 43.4 (d), 33.4 (d), 32.7 (t), 28.6 (t), 21.3 (q); IR 1740 cm$^{-1}$; MS $m/z$ 327 (M$^+$); HRMS $m/z$ calcd for C$_{19}$H$_{21}$NO$_4$ (M$^+$) 327.1471, found: 327.1476.

2$\beta$-Acetoxy-3-methylene-$\beta$-lycorane (33); oil; $^1$H NMR $\delta$ 6.80, 6.67 (each 1H, s, arom. Hx2), 5.91, 5.90 (each 1H, d, $J = 1.3$ Hz, OCH$_2$O), 5.48 (1H, dd, $J = 5.3, 11.2$ Hz, H-2), 4.92, 4.80 (each 1H, s, olefinic Hx2), 4.09, 3.39 (each 1H, d, $J = 14.5$ Hz, H-7x2), 3.50 (1H, ddd, $J = 5.7, 8.2, 9.8$ Hz, H-5), 2.81 (1H, t, $J = 10.9$ Hz, H-11b), 2.67 (1H, ddd, $J = 4.3, 5, 11.9$ Hz, H-1), 2.33-2.50 (2H, m, H-3a, H-5), 2.18 (3H, s, Ac), 1.90-2.09 (2H, m, H-4x2), 1.69 (1H, t, $J = 10.7$ Hz, H-11c), 1.42 (1H, q, $J = 11.8$ Hz, H-1); $^{13}$C NMR $\delta$ 170.1 (s), 146.5 (s), 146.1 (s), 146.0 (s), 129.4 (s), 128.4 (s), 107.0 (d), 105.3 (d), 102.7 (t), 100.9 (t), 73.8 (d), 71.8 (d), 57.0 (t), 54.2 (t), 46.1 (d), 38.8 (d), 35.6 (t), 23.4 (t), 21.1 (q); IR 1743 cm$^{-1}$; MS $m/z$ 327 (M$^+$); HRMS $m/z$ calcd for C$_{19}$H$_{21}$NO$_4$ (M$^+$) 327.1471, found: 327.1473.

(10$R$,10a$R$,2'$R$)-10-(2'-Acetoxy-3'-butynyl)-7,8-methylenedioxy-1,2,3,5,10,10a-hexahydrobenz[f]indolizidine (34); oil; $^1$H NMR $\delta$ 6.83, 6.50 (each 1H, s, arom. Hx2), 5.91, 5.90 (each 1H, d, $J = 1.3$ Hz, OCH$_2$O), 5.44 (1H, ddd, $J = 2, 5.3, 8.7$ Hz, CH$_2$OAc), 3.91, 3.30 (each 1H, d, $J = 14$ Hz, H-5x2), 3.20 (1H, dt, $J = 2.6, 8.5$ Hz), 2.78-2.88 (1H, m), 2.48 (1H, d, $J = 2$ Hz, C≡CH), 1.57-2.48 (7H, m), 2.09 (3H, s, Ac), 1.25-1.36 (1H, m); IR 2121, 1740 cm$^{-1}$; MS $m/z$ 327 (M$^+$); HRMS $m/z$ calcd for C$_{19}$H$_{21}$NO$_4$ (M$^+$) 327.1471, found: 327.1470.

(10$R$,10a$R$,2'$R$)-10-(2'-Acetoxy-3'-butynyl)-7,8-methylenedioxy-1,2,3,5,10,10a-hexahydrobenz[f]indolizidine (35); oil; $^1$H NMR $\delta$ 6.80, 6.45 (each 1H, s), 5.85 (2H, s), 5.65 (1H, dd, $J = 4.4, 9$ Hz), 4.08 (1H, ddd $J = 5, 5.9, 7.9$ Hz), 3.69, 3.43 (each 1H, d, $J = 14.5$ Hz), 2.93-3.04 (2H, m), 2.43-2.61 (3H, m), 2.28 (1H, dt, $J = 5$, 14.9 Hz), 2.14 (1H, ddd, $J = 9, 12.9, 16.4$ Hz), 1.75 (3H, s), 1.66 (1H, ddd, $J = 4.4, 8.2, 16.4$ Hz), 0.97 (9H, t, $J = 7.8$ Hz), 0.48 (6H, q, $J = 7.8$ Hz), 0.13 (9H, s); IR 2181, 1745 cm$^{-1}$; MS $m/z$ 529 (M$^+$); HRMS $m/z$ calcd for C$_{28}$H$_{43}$NO$_5$Si$_2$ (M$^+$) 529.2680, found: 529.2674.

(10$R$,10a$R$,2'$R$)-10-(2'-Acetoxy-3'-butynyl)-7,8-methylenedioxy-1,2,3,5,10,10a-hexahydrobenz[f]indolizidine (36); oil; $^1$H NMR $\delta$ 6.80, 6.45 (each 1H, s), 5.85 (2H, s), 5.65 (1H, dd, $J = 4.4, 9$ Hz), 4.08 (1H, ddd $J = 5, 5.9, 7.9$ Hz), 3.69, 3.43 (each 1H, d, $J = 14.5$ Hz), 2.93-3.04 (2H, m), 2.43-2.61 (3H, m), 2.28 (1H, dt, $J = 5$, 14.9 Hz), 2.14 (1H, ddd, $J = 9, 12.9, 16.4$ Hz), 1.75 (3H, s), 1.66 (1H, ddd, $J = 4.4, 8.2, 16.4$ Hz), 0.97 (9H, t, $J = 7.8$ Hz), 0.48 (6H, q, $J = 7.8$ Hz), 0.13 (9H, s); IR 2181, 1745 cm$^{-1}$; MS $m/z$ 529 (M$^+$); HRMS $m/z$ calcd for C$_{28}$H$_{43}$NO$_5$Si$_2$ (M$^+$) 529.2680, found: 529.2674.

(10$R$,10a$R$,2'$R$)-10-(2'-Acetoxy-3'-butynyl)-7,8-methylenedioxy-1,2,3,5,10,10a-hexahydrobenz[f]indolizidine (37); oil; $^1$H NMR $\delta$ 6.80, 6.45 (each 1H, s), 5.85 (2H, s), 5.65 (1H, dd, $J = 4.4, 9$ Hz), 4.08 (1H, ddd $J = 5, 5.9, 7.9$ Hz), 3.69, 3.43 (each 1H, d, $J = 14.5$ Hz), 2.93-3.04 (2H, m), 2.43-2.61 (3H, m), 2.28 (1H, dt, $J = 5$, 14.9 Hz), 2.14 (1H, ddd, $J = 9, 12.9, 16.4$ Hz), 1.75 (3H, s), 1.66 (1H, ddd, $J = 4.4, 8.2, 16.4$ Hz), 0.97 (9H, t, $J = 7.8$ Hz), 0.48 (6H, q, $J = 7.8$ Hz), 0.13 (9H, s); IR 2181, 1745 cm$^{-1}$; MS $m/z$ 529 (M$^+$); HRMS $m/z$ calcd for C$_{28}$H$_{43}$NO$_5$Si$_2$ (M$^+$) 529.2680, found: 529.2674.
(1S,10R,10aR,2’S)-10-(2’-Acetoxy-4’-trimethylsilyl-3’-butynyl)-1-hydroxy-7,8-methylenedioxy-1,2,3,5,10,10a-hexahydrobenz[f]indolizidine (27a). A solution of 26a (0.292 g, 0.55 mmol) and 1N HCl (3 mL, 3 mmol) in THF (10 mL) was stirred at rt for 15 min. Similar work-up as described above gave a residue, which was purified by preparative TLC (AcOEt : MeOH = 25 : 1) to afford 27a (0.216 g, 95%) as amorphous solid; [α]D27 -16.4° (c 1.17, CHCl3); 1H NMR δ 6.89, 6.44 (each 1H, s), 5.85 (2H, s), 5.63 (1H, t, J = 7.6 Hz), 4.19 (1H, ddd, J = 2.3, 5.6, 10.9 Hz), 3.79, 3.41 (each 1H, d, J = 13.9 Hz), 3.15 (1H, br s), 2.87-23.15 (2H, m), 2.48 (1H, q, J = 8.8 Hz), 2.15-2.31 (4H, m), 1.99 (3H, s), 1.60-1.73 (1H, m), 0.14 (9H, s); IR 2179, 1734 cm−1; MS m/z 415 (M+); HRMS m/z calcd for C22H29NO5Si (M+) 415.1815, found: 415.1819.

(1S,10R,10aR,2’R)-10-(2’-Acetoxy-4’-trimethylsilyl-3’-butynyl)-1-hydroxy-7,8-methylenedioxy-1,2,3,5,10,10a-hexahydrobenz[f]indolizidine (27b). A solution of 26b (0.244 g, 0.46 mmol) and 1N HCl (3 mL, 3 mmol) in THF (10 mL) was stirred at rt for 15 min. Similar work-up as described above gave a residue, which was purified by preparative TLC (AcOEt : MeOH = 25 : 1) to afford 27b (0.174 g, 91%) as amorphous solid; [α]D27 +97.2° (c 1.13, CHCl3); 1H NMR δ 6.85, 6.45 (each 1H, s), 5.86 (2H, s), 5.63 (1H, t, J = 6.9 Hz), 4.14 (1H, ddd, J = 2.6, 5.6, 12.9 Hz), 3.79, 3.43 (each 1H, d, J = 14.2 Hz), 3.01 (1H, t, J = 8.3 Hz), 2.81-3.04 (4H, m), 2.51 (1H, q, J = 8.8 Hz), 2.12-2.39 (3H, m), 2.07 (3H, s), 1.58-1.71 (1H, m), 0.11 (9H, s); IR 2177, 1740 cm−1; MS m/z 415 (M+); HRMS m/z calcd for C22H29NO5Si (M+) 415.1815, found: 415.1819.

Radical reaction of 28a (Table 2, run 12). To a solution of 28a (0.1053 g, 0.2 mmol) in toluene (13 mL) under reflux was added a solution of AIBN (0.016 g, 0.1 mmol) and tricyclohexyltin hydride (0.134 g, 0.36 mmol) in toluene (7 mL) over a period of 1 h. Then, the solvent was removed in vacuo to give a residue, which was purified by column chromatography (hexane then CHCl3 : MeOH = 10 : 1), followed by preparative TLC (CHCl3 : MeOH = 15 : 1) to afford 3a (0.0334 g, 42%) and 3b (0.0336 g, 42%).

(3Z)-2α-Acetoxy-3-trimethylsilylmethylene-α-lycorane (3a); [α]D25 -0.77° (c 1.51, CHCl3); 1H NMR δ 6.64, 6.62 (each 1H, s, arom. Hx2), 5.89, 5.88 (each 1H, d, J = 1.6 Hz, OCH3O), 5.73 (1H, t, J = 3 Hz, H-2), 5.72 (1H, s, olefinic H), 4.24, 3.73 (each 1H, d, J = 15.3 Hz, H-7x2), 3.34 (1H, q, J = 8.6 Hz, H-5), 3.03 (1H, ddd, J = 5.7, 8.6, 11.2 Hz, H-3a), 2.84 (1H, dt, J = 3.6, 8.6 Hz, H-5), 2.73 (1H, dd, J = 8.6, 10 Hz, H-11c), 2.71 (1H, dd, J = 10, 12.6 Hz, H-11b), 2.66 (1H, dt, J = 3, 13.7 Hz, H-1), 2.18-2.34 (1H, m, H-4), 2.04 (3H, s, Ac), 1.90-2.02 (1H, m, H-4), 1.49 (1H, ddd, J = 3, 12.6, 13.7 Hz, H-1), 0.13 (9H, s,
3C NMR δ 169.7, 151.3, 146.2, 145.4, 134.6, 133.0, 128.5, 106.8, 103.9, 100.5, 72.3, 64.9, 53.9, 53.6, 49.2, 30.7, 29.8, 27.2, 21.4, -0.1; IR 1736 cm⁻¹; MS m/z 339 (M⁺); HRMS m/z calcd for C₂₂H₂₉NO₄Si (M⁺) 339.1866, found: 339.1866.

(3E)-2α-Acetoxy-3-trimethylsilylmethylene-α-lycorane (3b); [α]D²⁵ -29.6° (c 1.03, CHCl₃); ¹H NMR δ 6.65, 6.62 (each 1H, s, arom. Hx2), 5.89 (2H, s, OCH₂O), 5.80 (1H, s, olefinic H), 5.54 (1H, t, J = 2.8 Hz, H-2), 4.29, 3.76 (each 1H, d, J = 15.5 Hz, H-7x2), 3.39 (1H, q, J = 8.6 Hz, H-5), 3.21 (1H, ddd, J = 6, 8.6, 10.6 Hz, H-3a), 2.80-2.91 (2H, m, H-5, H-11b), 2.69 (1H, dd, J = 6, 10.6 Hz, H-11c), 2.52 (1H, dt, J = 2.8, 13.9 Hz, H-1), 2.14-2.28 (1H, m, H-4), 1.91-2.01 (1H, m, H-4), 2.04 (3H, s, Ac), 1.55 (1H, ddd, J = 2.8, 12.9, 13.9 Hz, H-1), 0.12 (9H, s, SiMe₃); ¹³C NMR δ 169.8, 151.3, 146.3, 145.5, 134.9, 133.1, 128.6, 106.9, 103.9, 100.6, 77.6, 64.9, 53.9, 53.5, 43.9, 31.2, 29.5, 26.9, 21.6, -0.1; IR 1738 cm⁻¹; MS m/z 339 (M⁺); HRMS m/z calcd for C₂₂H₂₉NO₄Si (M⁺) 339.1866, found: 339.1849.

Radical reaction of 28b (Table 2, Run 13). To a solution of 28b (0.042 g, 0.08 mmol) in toluene (5 mL) under reflux was added a solution of AIBN (0.007 g, 0.04 mmol) and Bu₃SnH (0.047 g, 0.15 mmol) in toluene (3 mL) using syringe pump over a period of 30 min. Then, the solvent was removed in vacuo to give a residue, which was purified by column chromatography (hexane then CHCl₃ : MeOH = 10 : 1), followed by preparative TLC (AcOEt : MeOH = 30 : 1) to afford 4a (0.009 g, 27%), 4b (0.005 g, 16%) and 35 (0.003 g, 10%).

(3Z)-2β-Acetoxy-3-trimethylsilylmethylene-α-lycorane (4a); [α]D²⁵ +37.5° (c 1.09, CHCl₃); ¹H NMR δ 6.65, 6.54 (each 1H, s, arom. Hx2), 5.89, 5.88 (each 1H, d, J = 1.3 Hz, OCH₂O), 5.54-5.56 (2H, m, H-2, olefinic H), 3.98, 3.76 (each 1H, d, J = 14.9 Hz, H-7x2), 3.19 (1H, q, J = 8.6 Hz, H-5), 3.06 (1H, ddd, J = 2.3, 6.4, 8.7 Hz, H-3a), 2.86 (1H, dt, J = 5.0, 8.5, 13.8 Hz, H-1), 2.56-2.67 (2H, m, H-5, H-11c), 2.35 (1H, dt, J = 5, 12 Hz, H-11b), 2.02 (3H, s, Ac), 1.93-2.12 (2H, m, H-4x2), 1.45 (1H, dt, J = 3.2, 13.8 Hz, H-1), 0.14 (9H, s, SiMe₃); ¹³C NMR δ 170.2, 153.1, 146.4, 145.9, 131.9, 128.9, 128.6, 105.9, 100.9, 73.4, 65.2, 55.1, 53.0, 41.6, 35.8, 31.2, 28.2, 21.4, 0.3; IR 2924, 1716, 1621 cm⁻¹; MS m/z 339 (M⁺); HRMS m/z calcd for C₂₂H₂₉NO₄Si (M⁺) 339.1866, found: 339.1870.

(3E)-2β-Acetoxy-3-trimethylsilylmethylene-α-lycorane (4b); [α]D²⁵ -41.5° (c 0.56, CHCl₃); ¹H NMR δ 6.65, 6.61 (each 1H, s, arom. Hx2), 5.89 (2H, s, OCH₂O), 5.50-5.56 (2H, m, H-2, olefinic H), 4.27, 3.73 (each 1H, d, J = 15.8 Hz, H-7x2), 3.34-3.47 (2H, m, H-3a, H-5), 2.79-2.88 (1H, m, H-5), 2.66-2.76 (2H, m, H-11b, H-11c), 2.56 (1H, ddd, J = 2.6, 4.3, 12.5 Hz, H-1), 2.19 (3H, s, Ac), 1.94-2.08 (2H, m, H-4x2), 1.35-1.51 (1H, m, H-1), 0.13 (9H, s, SiMe₃); ¹³C NMR δ 170.4, 152.5, 146.6, 145.8, 133.0, 128.0, 122.2, 107.2, 104.2, 101.0, 73.0, 65.5, 54.0, 53.8, 45.8, 33.2, 31.8, 29.0, 21.4, 0.4; IR 1737 cm⁻¹; MS m/z 339 (M⁺); HRMS m/z calcd for C₂₂H₂₉NO₄Si (M⁺) 339.1866, found: 339.1874.

(3Z)-2β-Acetoxy-3-trimethylsilylmethylene-β-lycorane (35); [α]D²⁵ +19.0° (c 0.41, CHCl₃); ¹H NMR δ 6.65, 6.50 (each 1H, s, arom. Hx2), 5.89, 5.88 (each 1H, d, J = 1.3 Hz, OCH₂O), 5.56 (1H, dd, J = 4.5, 11
Hz, H-2), 5.29 (1H, s, olefinic H), 4.07, 3.38 (each 1H, d, J = 14.9 Hz, H-7x2), 3.48 (1H, dt, J = 5.6, 8.9 Hz, H-5), 2.36-2.53 (2H, m, H-3a, H-5), 2.87 (1H, t, J = 11 Hz, H-11b), 2.72 (1H, dt, J = 4.5, 11 Hz, H-1), 2.18 (3H, s, Ac), 1.84-2.12 (2H, m, H-4x2), 2.87 (1H, t, J = 11 Hz, H-11c), 1.36 (1H, q, J = 11 Hz, H-1), 0.13 (9H, s, SiMe₃); ¹³C NMR δ 170.2, 153.7, 146.2, 146.0, 129.5, 128.3, 117.5, 106.9, 105.3, 100.9, 77.2, 72.2, 57.2, 54.2, 49.2, 39.0, 36.1, 23.5, 22.1, 1.5; IR 1732 cm⁻¹; MS m/z 339 (M⁺); HRMS m/z calcd for C₂₂H₂₉NO₄Si (M⁺) 339.1866, found: 339.1875.

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REFERENCES AND NOTES


13. Similar reaction of TBS ether afforded 2.9 : 1 mixture of cyclized products in 92% yield.

