Supporting Information
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Supporting information

Total Synthesis of (+)-Eburnamonine

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General Procedures: Column chromatography was performed on silica gel, Acme grade 100-200 mesh. TLC plates were visualized either with UV, in an iodine chamber, or with phosphomolybdic acid spray, unless noted otherwise. Unless stated otherwise, all reagents were purchased from commercial sources and used without additional purification. THF was freshly distilled over Na-benzophenone ketyl. Melting points were uncorrected. Unless stated otherwise, ^1H NMR and ^{13}C NMR spectra were recorded either on a 400 MHz machine in CDCl_3 as solvent with TMS as reference unless otherwise indicated. Unless stated otherwise, all the reactions were performed under inert atmosphere. All the specific rotations were determined at 24 °C.

(*S,E*)-ethyl 4-((*tert* butyldimethylsilyl)oxy)-2-ethylpent-2-enoate (12**):** To a stirred solution of the ester **10** (0.42 g, 1.80 mmol) in dry CH_2Cl_2 (5 mL) was added DIBAL-H (1.0 M in toluene), (2.0 mL, 2.00 mmol) dropwise at -78°C for a period of 5 minutes under argon atmosphere. The reaction mixture was stirred at the same temperature for 30 minutes. After completion of the reaction (TLC), it was quenched by the addition of a saturated aqueous solution of potassium sodium tartrate (15 mL), diluted with Et_2O (10 mL) and stirred for one hour at room temperature. The aqueous layer was extracted with Et_2O (2×10 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated to yield the crude aldehyde which was used in the next step without further purification.

To a stirred solution of the crude aldehyde (obtained above) in dry toluene (10 mL) was added phosphorane **11** (1.35 g, 3.60 mmol) under nitrogen atmosphere and the reaction mixture was refluxed for 8 h. After completion of the reaction (TLC), it was cooled to room temperature and most of the solvent was evaporated off. The crude residue thus obtained was purified by silica gel column chromatography using petroleum ether: CH_2Cl_2 (7:3) as eluent to afford **12** (0.37 g, 73% for two steps) as a colourless oil. $[\alpha]_{\text{D}} -2.6$ (c 1.1, CHCl_3); IR (neat): ν_{max} 2960, 2935, 1717, 1239, 1087 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 6.63 (d, $J = 8.3$ Hz, 1H), 4.70-4.54 (m, 1H), 4.19 (q, $J = 7.1$ Hz, 2H), 2.39-2.15 (m, 2H), 1.30 (t, $J = 7.1$ Hz, 3H), 1.24 (d, $J = 6.3$ Hz, 3H), 1.03 (t, $J = 7.5$ Hz, 3H), 0.88 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.7, 145.1, 131.6, 65.6, 60.5, 25.8 (3C), 24.2, 20.4, 18.1, 14.2, 14.0, -4.5 , -4.7 ; HRMS: m/z calcd for $[\text{C}_{15}\text{H}_{30}\text{O}_3\text{Si}+\text{Na}]$ 309.1862; found: 309.1862.

(*S,E*)-6-ethyl-8,10,10,11,11-pentamethyl-2,4,9-trioxa-10-siladodec-6-ene (13**):** To a stirred solution of the ester **12** (0.75 g, 2.63 mmol) in dry CH_2Cl_2 (10 mL) was added DIBAL-H (1.0 M in toluene), (5.8 mL, 5.80 mmol) dropwise at -78°C for a period of 10 minutes under argon atmosphere. The reaction mixture was stirred at the same temperature

for one hour. After completion of the reaction (TLC), it was quenched by the addition of a saturated aqueous solution of potassium sodium tartrate (40 mL), diluted with EtOAc (25 mL) and stirred for one hour at room temperature. The aqueous layer was extracted with EtOAc (2 × 15 mL). The combined organic layers were washed with brine (15 mL) and dried over anhydrous Na₂SO₄. The crude residue obtained after evaporation of the solvent was purified by silica gel column chromatography using petroleum ether:ethyl acetate (9:1) as eluent to afford allylic alcohol (0.56 g, 93%) as a colourless oil. $[\alpha]_D +4.8$ (*c* 1.0, CHCl₃); IR (neat): $\nu_{\max}$ 3351, 2960, 2932, 1255, 1084 cm⁻¹; ¹HNMR (400 MHz, CDCl₃): δ 5.40 (d, *J* = 8.3 Hz, 1H), 4.58 (qd, *J*₁ = 6.5 Hz, *J*₂ = 6.3 Hz, 1 H), 4.02 (s, 2 H), 2.23-1.94 (m, 2H), 1.72 (bs, 1H), 1.19 (d, *J* = 6.2 Hz, 3H), 1.00 (t, *J* = 7.6 Hz, 3H), 0.86 (s, 9H), 0.04 (s, 3H), 0.02 (s, 3H); ¹³CNMR (100 MHz, CDCl₃): δ 138.9, 130.9, 66.0, 65.2, 25.8 (3C), 25.0, 21.2, 18.1, 13.3, -4.5, -4.7; HRMS: *m/z* calcd for [C₁₃H₂₈O₂Si+Na] 267.1756; found: 267.1753.

To a stirred solution of the allylic alcohol (0.13 g, 0.52 mmol) in dry CH₂Cl₂ (2 mL) were added diisopropylethylamine (0.54 mL, 3.12 mmol) and MOMCl (0.16 mL, 2.08 mmol) at 0 °C under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 6 hours. After completion of the reaction (TLC), it was poured into cold water (5 mL). It was then extracted with EtOAc (2 × 10 mL). The combined organic layers were washed with brine (5 mL) and dried over anhydrous Na₂SO₄. The crude residue obtained after evaporation of the solvent was purified by column chromatography using petroleum ether: EtOAc (9:1) as eluent to afford **13** (0.15 g, 97%) as a colourless oil. $[\alpha]_D -0.8$ (*c* 1.1, CHCl₃); IR (neat): $\nu_{\max}$ 2960, 2934, 115, 1087, 1047 cm⁻¹; ¹HNMR (400 MHz, CDCl₃): δ 5.43 (d, *J* = 8.3 Hz, 1H), 4.59 (s, 2H), 4.67-4.50 (m, 1H), 3.96 (s, 2H), 3.36 (s, 3H), 2.21-1.97 (m, 2H), 1.19 (d, *J* = 6.1 Hz, 3H), 1.00 (t, *J* = 7.5 Hz, 3H), 0.86 (s, 9H), 0.04 (s, 3H), 0.02 (s, 3H); ¹³CNMR (100 MHz, CDCl₃): δ 135.5, 133.2, 95.3, 70.2, 65.2, 55.2, 25.8 (3C), 25.0, 21.4, 18.1, 13.0, -4.4, -4.6; HRMS: *m/z* calcd for [C₁₅H₃₂O₃Si+Na] 311.2018; found: 311.2016

(*S,E*)-4-((methoxymethoxy)methyl)hex-3-en-2-ol (8): To a stirred solution of the TBS ether **13** (0.15 g, 0.51 mmol) in dry THF (3 mL) was added TBAF (1.0 M solution in THF), (0.78 mL, 0.77 mmol) at room temperature under nitrogen atmosphere. The reaction mixture was stirred at the same temperature for 6 h. After completion of the reaction (TLC), it poured into water (5 mL) and extracted with EtOAc (2 × 10 mL). The combined organic layers were washed with brine (5 mL) and dried over anhydrous Na₂SO₄. The residue obtained after evaporation of the solvent was purified by column chromatography using petroleum

ether:EtOAc (6:4) as eluent to afford alcohol **8** (0.08 g, 88 %) as a colourless oil. $[\alpha]_D -6.7$ (c 1.3, CHCl_3); IR (neat): ν_{max} 3423, 2969, 2936, 1150, 1046 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 5.42 (d, $J = 8.7$ Hz, 1H), 4.58 (s, 2H), 4.66-4.49 (m, 1H), 3.93 (s, 2H), 3.33 (s, 3H), 2.19 (bs, 1H), 2.24-1.19 (m, 2H), 1.21 (d, $J = 6.3$ Hz, 3H), 0.98 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 138.8, 131.4, 95.4, 70.2, 63.8, 55.2, 23.6, 21.4, 13.4; HRMS: m/z calcd for $[\text{C}_9\text{H}_{18}\text{O}_3+\text{Na}]$ 197.1154; found: 197.1155.

(*S,E*)-ethyl 3-ethyl-3-((methoxymethoxy)methyl)hex-4-enoate (14): To a stirred solution of the alcohol (0.26 g, 1.50 mmol) **8** in dry toluene (9 mL) were added triethylorthoacetate (1.5 mL, 7.5 mmol) and propionic acid (3 mol%) under nitrogen atmosphere. The resulting solution was heated at 120 °C for 8 hours. Later propionic acid (2 mol%) was added and the heating continued for further 7 hours. After completion of the reaction (TLC), the reaction mixture was cooled to room temperature and most of the solvent was evaporated off and the crude residue thus obtained was purified by silica gel column chromatography using petroleum ether:Et₂O (9:1) as eluent to afford **14** (0.29 g, 79%) as a colourless oil. $[\alpha]_D -4.7$ (c 1.0, CHCl_3); IR (neat): ν_{max} 2968, 2936, 1735, 1113, 1051 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 5.40-5.32 (m, 2H), 4.62 (s, 2H), 4.09 (q, $J = 7.1$ Hz, 2H), 3.52 (s, 2H), 3.35 (s, 3H), 2.41 (ABq, $J_1 = J_2 = 13.9$ Hz, 2H), 1.68 (d, $J = 5.0$ Hz, 3H), 1.52 (q, $J = 7.3$ Hz, 2H), 1.23 (t, $J = 7.2$ Hz, 3H), 0.83 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.9, 134.6, 124.1, 96.8, 71.5, 59.9, 55.2, 42.3, 39.7, 28.4, 18.4, 14.2, 7.9; HRMS: m/z calcd for $[\text{C}_{13}\text{H}_{24}\text{O}_4+\text{Na}]$ 267.1572; found: 267.1571.

(*S,E*)-(((3-ethyl-3-((methoxymethoxy)methyl)hex-4-en-1-yl)oxy)methyl)benzene (7): To a suspension of LiAlH_4 (90 mg, 2.30 mmol) in dry THF (2 mL) was added a solution of the ester (0.28 g, 1.15 mmol) **14** in dry THF (4 mL) dropwise over 10 minutes at 0 °C and stirred at the same temperature for 30 minutes. After completion of the reaction (TLC), the reaction mixture was cautiously quenched by addition of EtOAc (5 mL). The slurry thus obtained was filtered using EtOAc (30 mL) and dried over anhydrous Na_2SO_4 . The residue obtained after evaporation of the solvent was purified by column chromatography using petroleum ether:EtOAc (7:3) as eluent to afford the alcohol (0.21 g, 90%) as a colourless oil. $[\alpha]_D -8.2$ (c 1.0, CHCl_3); IR (neat): ν_{max} 3421, 2934, 2883, 1111, 1048 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 5.35 (dq, $J_1 = 16.0$ Hz, $J_2 = 6.1$ Hz, 1H), 5.25 (d, $J = 16.0$ Hz, 1H), 4.58 (s, 2H), 3.61 (t, $J = 6.8$ Hz, 2H), 3.38 (s, 2H), 3.33 (s, 3H), 2.48 (bs, 1H), 1.66 (d, $J = 6.2$ Hz, 3H), 1.75-1.56 (m, 2H), 1.39 (qd, $J_1 = 7.5$ Hz, $J_2 = 2.5$ Hz, 2H), 0.76 (t, $J = 7.5$ Hz, 3H);

^{13}C NMR (100 MHz, CDCl_3): δ 135.8, 123.9, 96.7, 72.2, 59.1, 55.3, 41.7, 38.6, 28.4, 18.4, 7.8; HRMS: m/z calcd for $[\text{C}_{11}\text{H}_{22}\text{O}_3+\text{Na}]$ 225.1467; found: 225.1467.

To a stirred solution of the alcohol (0.20 g, 1.00 mmol) in dry DMF (2 mL) was added NaH (60 % suspension in mineral oil), (80 mg, 2.00 mmol) at 0 °C under nitrogen atmosphere. The reaction mixture was stirred at the same temperature for 30 min. Later benzyl bromide (0.18 mL, 1.50 mmol) was added slowly and stirred for 2 hours at room temperature. After completion of the reaction (TLC), it was cautiously quenched with ice cold water. The resulting solution was poured into water (20 mL) and extracted with EtOAc (2×15 mL). The combined organic layers were washed with brine (15 mL) and dried over anhydrous Na_2SO_4 . The crude residue obtained after evaporation of the solvent was purified by column chromatography using petroleum ether:EtOAc (9:1) as eluent to afford **7** (0.27 g, 93%) as a colourless oil. $[\alpha]_{\text{D}} -3.0$ (c 1.0, CHCl_3); IR (neat): ν_{max} 2930, 2880, 1148, 1108, 1048 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.38-7.20 (m, 5H), 5.35 (dq, $J_1 = 16.0$ Hz, $J_2 = 5.9$ Hz, 1H), 5.27 (d, $J = 16.0$ Hz, 1 H), 4.57 (s, 2H), 4.47 (s, 2H), 3.49 (t, $J = 7.6$ Hz, 2H), 3.35 (dd, $J_1 = 12.5$ Hz, $J_2 = 9.5$ Hz, 2H), 3.30 (s, 3H), 1.83-1.61 (m, 2H), 1.67 (d, $J = 5.7$ Hz, 3H), 1.40 (qd, $J_1 = 7.5$ Hz, $J_2 = 3.8$ Hz, 2H), 0.79 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 138.6, 135.8, 128.3, 127.6, 127.4, 123.6, 96.7, 72.9, 72.0, 67.0, 55.2, 41.5, 34.6, 28.2, 18.5, 7.8; HRMS: m/z calcd for $[\text{C}_{18}\text{H}_{28}\text{O}_3+\text{Na}]$ 315.1936; found: 315.1933.

(S,E)-2-(2-(benzyloxy)ethyl)-2-ethylpent-3-en-1-ol (15): To a stirred solution of the MOM ether (0.43 g, 1.48 mmol) **7** in EtOH (10 mL) was added pyridinium *p*-toluenesulphonate (1.86 g, 7.40 mmol) and the resulting solution was refluxed for 12 hours. After completion of the reaction (TLC), it was cooled to room temperature and most of the solvent was evaporated off. The crude residue thus obtained was dissolved in CH_2Cl_2 (15 mL) and neutralized with solid NaHCO_3 (1.68 g, 20 mmol). The reaction mixture was filtered through a short pad of celite using CH_2Cl_2 (30 mL). The solvent was evaporated off and the residue thus obtained was purified by silica gel column chromatography using petroleum ether:EtOAc (8:2) as eluent to afford **15** (0.33 g, 91%) as a colourless oil. $[\alpha]_{\text{D}} -14.5$ (c 1.0, CHCl_3); IR (neat): ν_{max} 3442, 2930, 2877, 1098, 1042 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.42-7.23 (m, 5H), 5.37 (dq, $J_1 = 16.0$ Hz, $J_2 = 6.3$ Hz, 1H), 5.21 (dd, $J_1 = 16.0$ Hz, $J_2 = 1.0$ Hz, 1H), 4.50 (s, 2H), 3.54 (t, $J = 5.8$ Hz, 2H), 3.48 (dd, $J_1 = 11.4$ Hz, $J_2 = 6.2$ Hz, 1H), 3.36-3.31 (m, 1H), 2.82 (t, $J = 7.0$ Hz, 1H), 1.69 (d, $J = 6.2$ Hz, 3H), 1.70-1.66 (m, 2H), 1.39 (q, $J = 7.4$ Hz, 2H), 0.79 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 137.8, 135.9, 128.4

(2C), 127.7 (3C), 124.5, 73.2, 67.0, 66.9, 43.4, 34.5, 28.2, 18.5, 7.9; HRMS: m/z calcd for $[C_{16}H_{24}O_2+Na]$ 271.1674; found: 271.1684.

Synthesis of 16: To a stirred solution of the alcohol (45 mg, 0.18 mmol) **15** in dry CH_2Cl_2 (2 mL) were added $NaHCO_3$ (76 mg, 0.90 mmol) and Dess-Martin periodinane (115 mg, 0.27 mmol) at 0 °C under nitrogen atmosphere. The reaction mixture was warmed to room temperature and stirred for 1.5 h. After completion of the reaction (TLC), it was quenched with saturated aqueous solutions of $NaHCO_3$ (3 mL) and $Na_2S_2O_3$ (3 mL) and diluted with Et_2O (5 mL). The aqueous phase was extracted with Et_2O (2×5 mL). The combined organic layers were washed with brine (5 mL), dried over anhydrous Na_2SO_4 and concentrated. The crude aldehyde **6** thus obtained as a colourless oil was used as such in the next step without further purification.

To a stirred solution of the aldehyde **6** in dry CH_2Cl_2 (1 mL) was added tryptamine (25 mg, 0.16 mmol) at room temperature under nitrogen atmosphere. The reaction mixture was cooled to – 78 °C and CF_3CO_2H (0.02 mL, 0.24 mmol) was added slowly. It was then slowly warmed to – 20 °C and stirred at the same temperature for 8 hours. After completion of the reaction (TLC), it was cautiously quenched with a saturated aqueous solution of $NaHCO_3$ (3 mL). The resulting solution was poured into water (5 mL) and extracted with $EtOAc$ (2×10 mL). The combined organic layers were washed with brine (5 mL) and dried over anhydrous Na_2SO_4 . The crude residue obtained after evaporation of solvent was purified by a rapid silica gel column chromatography using petroleum ether: $EtOAc$ (3:7) as eluent to afford **16** (39 mg, 64% over two steps) as a pale yellow oil.

Preparation of 5: To a stirred solution of the amine **16** (39 mg, 0.10 mmol) in dry DMF (1 mL) were added K_2CO_3 (28 mg, 0.20 mmol) and allyl bromide (0.02 mL, 0.20 mmol) at 0 °C under nitrogen atmosphere. The reaction mixture was stirred at 10 °C for one hour. After completion of the reaction (TLC), it was poured into water (5 mL) and extracted with $EtOAc$ (2×10 mL). The combined organic layers were washed with brine (5 mL) and dried over anhydrous Na_2SO_4 . The crude diastereomeric mixture obtained after evaporation of the solvent was separated and purified by silica gel column chromatography using petroleum ether: $EtOAc$ (9:1) as eluent to afford **5** (24 mg, 56%) as a pale yellow foam. $[\alpha]_D -27.1$ (c 0.8, $CHCl_3$); IR (neat): ν_{max} 3366, 2929, 2879, 1458, 1094 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 9.07 (bs, 1H), 7.50 (d, $J = 7.5$ Hz, 1H), 7.41-7.27 (m, 5H), 7.17 (d, $J = 7.8$ Hz, 1H), 7.07-7.00 (m, 2H), 5.94 (dq, $J_1 = 16.0$ Hz, $J_2 = 6.8$ Hz, 1H), 5.27 (d, $J = 15.9$ Hz, 1H), 5.13 (ddt, $J_1 = 17.0$ Hz, $J_2 = 12.4$ Hz, $J_3 = 6.2$ Hz, 1H), 5.07 (d, $J = 12.7$ Hz, 1H), 5.01 (d, $J = 17.0$ Hz,

1H), 4.56 (s, 2H), 3.75 (s, 1H), 3.69 (dd, $J_1 = 6.0$ Hz, $J_2 = 5.2$ Hz, 2H), 3.53 (td, $J_1 = 7.5$ Hz, $J_2 = 5.0$ Hz, 1H), 3.18 (dd, $J_1 = 7.5$ Hz, $J_2 = 5.7$ Hz, 1H), 3.02 (dd, $J_1 = 7.5$ Hz, $J_2 = 5.8$ Hz, 1H), 2.92 (dd, $J_1 = 13.8$ Hz, $J_2 = 6.2$ Hz, 1H), 2.85-2.75 (m, 1H), 2.42 (dd, $J_1 = 15.7$ Hz, $J_2 = 5.3$ Hz, 1H), 2.19-2.09 (m, 1H), 2.09-1.99 (m, 1H), 1.80-1.70 (m, 1H), 1.68-1.58 (m, 1H), 1.55 (d, $J = 6.1$ Hz, 3H), 0.84 (t, $J = 7.4$ Hz, 3H) ; ^{13}C NMR (100 MHz, CDCl_3): δ 137.8, 137.7, 137.3, 135.5, 132.6, 128.6 (2C), 127.9 (3C), 127.1, 123.5, 120.9, 118.4, 117.7, 116.7, 110.6, 109.0, 73.7, 67.2, 62.6, 58.5, 46.3, 45.0, 34.0, 26.4, 18.4, 16.6, 8.9; HRMS: m/z calcd for $[\text{C}_{29}\text{H}_{36}\text{N}_2\text{O}+\text{H}]$ 429.2906; found: 429.2903.

Minor diastereomer: **(S)-2-allyl-1-((S,E)-1-(benzyloxy)-3-ethylhex-4-en-3-yl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole** $[\alpha]_{\text{D}} +4.4$ (c 0.7, CHCl_3); IR (neat): ν_{max} 3350, 2935, 2880, 1456, 1097 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 8.22 (bs, 1H), 7.51 (d, $J = 7.5$ Hz, 1H), 7.39-7.19 (m, 6H), 7.20-7.05 (m, 2H), 5.99-5.79 (m, 1H), 5.40 (d, $J = 16.1$ Hz, 1H), 5.32 (ddt, $J_1 = 15.9$ Hz, $J_2 = 11.8$ Hz, $J_3 = 5.9$ Hz, 1H), 5.05 (d, $J = 15.9$ Hz, 1H), 5.04 (d, $J = 11.3$ Hz, 1H), 4.50 (s, 2H), 3.67-3.49 (m, 3H), 3.46-3.36 (m, 1H), 3.20 (dd, $J_1 = 13.3$ Hz, $J_2 = 6.2$ Hz, 1H), 3.10-2.90 (m, 2H), 2.86-2.76 (m, 1H), 2.43 (dd, $J_1 = 15.7$ Hz, $J_2 = 4.8$ Hz, 1H), 2.22-2.12 (m, 1H), 2.00-1.90 (m, 1H), 1.67 (d, $J = 5.7$ Hz, 3H), 1.57 (q, $J = 7.3$ Hz, 2H), 0.79 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 138.3, 136.9, 135.6, 132.5, 128.4 (2C), 127.8 (2C), 127.6, 127.1, 123.6, 121.3, 118.9, 117.9, 116.7, 110.5, 109.8, 73.2, 67.1, 62.8, 58.7, 47.1, 44.7, 31.6, 29.4, 18.4, 16.6, 8.1; HRMS: m/z calcd for $[\text{C}_{29}\text{H}_{36}\text{N}_2\text{O}+\text{H}]$ 429.2906; found: 429.2906.

(1S,12bR)-1-(2-(benzyloxy)ethyl)-1-ethyl-1,4,6,7,12,12b-hexahydroindolo[2,3-

a]quinolizine (17): To a stirred solution of the diene **5** (24 mg, 0.06 mmol) in dry CH_2Cl_2 (6 mL) was added Grubbs 2nd generation catalyst (2 mg, 5 mol%) under argon atmosphere and the reaction mixture was stirred at room temperature for 5 hours. After completion of the reaction (TLC), most of the solvent was evaporated off and the crude residue thus obtained was purified by silica gel column chromatography using petroleum ether:EtOAc (7:3) as eluent to afford **17** (18 mg, 83%) as a yellow foam. $[\alpha]_{\text{D}} +179.2$ (c 0.6, CHCl_3); IR (neat): ν_{max} 3371, 2960, 2930, 1458, 1048 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.78 (bs, 1H), 7.49 (d, $J = 7.5$ Hz, 1H), 7.33 (d, $J = 8.0$ Hz, 1H), 7.34-7.06 (m, 7H), 5.87 (dd, $J_1 = 10.1$ Hz, $J_2 = 4.6$ Hz, 1H), 5.44 (d, $J = 10.1$ Hz, 1H), 4.36 (s, 2H), 3.64 (s, 1H), 3.58 (qd, $J_1 = 6.0$ Hz, $J_2 = 2.9$ Hz, 1H), 3.52 (qd, $J_1 = 6.0$ Hz, $J_2 = 3.0$ Hz, 1H), 3.33 (dd, $J_1 = 16.4$ Hz, $J_2 = 4.7$ Hz, 1H), 3.09 (dd, $J_1 = 10.9$ Hz, $J_2 = 4.8$ Hz, 1H), 3.01 (d, $J = 16.4$ Hz, 1H), 2.98-2.80 (m, 1H), 2.78 (d, $J = 16.4$ Hz, 1H), 2.58 (td, $J_1 = 8.4$ Hz, $J_2 = 3.0$ Hz, 1H), 2.02-1.92 (m, 1H), 1.87 (q, $J = 7.7$ Hz, 2H), 1.46-1.36 (m, 1H), 1.10 (t, $J = 7.6$ Hz, 3H) ; ^{13}C NMR (100 MHz, CDCl_3): δ

138.7, 136.2, 133.6, 132.9, 128.2 (2C), 127.5 (2C), 127.2, 126.8, 126.1, 121.5, 119.3, 117.9, 111.9, 110.7, 72.7, 68.0, 61.2, 55.1, 52.4, 43.0, 37.4, 32.5, 21.6, 8.9; HRMS: m/z calcd for $[C_{26}H_{30}N_2O+H]$ 387.2436; found: 387.2436.

2-((1*R*,12*bR*)-1-ethyl-1,2,3,4,6,7,12,12*b*-octahydroindolo[2,3-*a*]quinolizin-1-yl)ethanol (18): To a stirred solution of the alkene **17** (18 mg, 0.05 mmol) in dry ethanol (2 mL) was added pre- activated palladium on charcoal (10% w/w), (20 mg) under nitrogen atmosphere. The reaction mixture was then subjected to hydrogenation under hydrogen balloon and stirred at room temperature for 24 hours. After completion of the reaction (TLC), it was filtered through a short pad of celite using $CHCl_3$ (20 mL). The solvent was evaporated off and the crude residue thus obtained was purified by silica gel column chromatography using EtOAc:MeOH (19:1) as eluent to afford **18** (10 mg, 78%) as a white solid. $[\alpha]_D +85.8$ (c 0.4, $CHCl_3$); m.p. (165 °C-168 °C); IR (KBr): ν_{max} 3649, 3252, 2922, 1462, 1096 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 7.84 (bs, 1H), 7.47 (d, $J = 7.7$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.15 (t, $J = 7.3$ Hz, 1H), 7.09 (t, $J = 7.5$ Hz, 1H), 3.75 (td, $J_1 = 11.6$ Hz, $J_2 = 2.4$ Hz, 1H), 3.44 (dt, $J_1 = 11.8$ Hz, $J_2 = 4.4$ Hz, 1H), 3.36 (s, 1H), 3.09 (d, $J = 4.7$ Hz, 1H), 3.08 (s, 1H), 3.07-2.97 (m, 1H), 2.72-2.62 (m, 1H), 2.67 (s, 1H), 2.45 (td, $J_1 = 11.7$ Hz, $J_2 = 3.0$ Hz, 1H), 2.23-2.00 (m, 1H), 1.89-1.54 (m, 6H), 1.37 (d, $J = 15.0$ Hz, 1H), 1.26 (s, 1H), 1.12 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.0, 132.2, 126.7, 121.7, 119.4, 118.2, 111.9, 110.6, 67.1, 58.7, 56.3, 54.0, 40.9, 38.8, 35.7, 323., 23.0, 21.3, 8.5; HRMS: m/z calcd for $[C_{19}H_{26}N_2O+H]$ 299.2123; found: 299.2120.

Eburnamonine-(+)1**:** To a stirred solution of the alcohol **18** (10 mg, 0.03 mmol) in CH_2Cl_2 (1 mL) were added a small amount of 4 Å molecular sieves and *N*-methylmorpholine *N*-oxide (7 mg, 0.06 mmol) under nitrogen atmosphere at room temperature, followed by tetrapropylammoniumperruthenate (1 mg, 10 mol%) after 10 min. The reaction mixture was stirred for 1 h at room temperature. After completion of the reaction, it was filtered through a small pad of celite which was washed with CH_2Cl_2 (20 mL). The organic layer was washed with saturated Na_2SO_3 (8 mL), brine (5 mL), saturated $CuSO_4$ (5 mL) and dried over anhydrous Na_2SO_4 . The crude residue obtained after evaporation of the solvent was purified by rapid column chromatography using EtOAc as eluent to afford (+)**1** (4 mg, 40%) as a white solid. $[\alpha]_D + 87.5$ (c 0.2, $CHCl_3$), $[Lit^{3b} [\alpha]_D -88$ (c 0.09, $CHCl_3$) for the enantiomer]; m.p. (171 °C-172 °C) $[Lit^{3c}$ m.p. (173 °C-176 °C)]; IR (KBr): ν_{max} 2926, 2854, 1696, 1452, 1370 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, $J = 7.8$ Hz, 1H), 7.43 (d, $J = 7.2$ Hz, 1H),

7.39-7.23 (m, 2H), 3.99 (s, 1H), 3.34 (dd, $J_1 = 14.0$ Hz, $J_2 = 6.7$ Hz, 1H), 3.31-3.21 (m, 1H), 2.98-2.84 (m, 1H), 2.63 (Abq, $J_1 = J_2 = 16.7$ Hz, 2H), 2.57-2.45 (m, 1H), 2.53-2.40 (m, 1H), 2.40 (dd, $J_1 = 11.2$ Hz, $J_2 = 3.0$ Hz, 1H), 2.13-1.97 (m, 1H), 1.83-1.58 (m, 4H), 1.44 (q, $J = 13.7$ Hz, 2H), 1.03 (td, $J_1 = 13.7$ Hz, $J_2 = 3.8$ Hz, 1H), 0.93 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 167.6, 134.2, 132.0, 130.1, 124.3, 123.8, 118.1, 116.3, 112.6, 57.7, 50.7, 44.4, 44.3, 38.5, 28.4, 27.0, 20.7, 16.6, 7.6; HRMS: m/z calcd for $[\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}+\text{H}]$ 295.1810; found: 295.1811.