Supporting Information
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Supporting Information

Total Synthesis of Amphilectane-type Diterpenoid
(±)-7-Isocyanoamphilecta-11(20),15-diene

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Experimental Section

General

Melting points (mp) were measured using a Yazawa melting point apparatus BY-2 and are uncorrected. IR spectra were recorded using a Jasco FT/IR-620 spectrometer. UV spectra were recorded using a Jasco V-550 spectrophotometer. Single crystal X-ray diffraction was recorded using a MacScience Co., Ltd DIP2020 Image Plate. $^1$H- and $^{13}$C-NMR spectrum was recorded on a Varian Mercury-300 or Bruker DRX-400 or a Bruker Biospin AV-600 spectrometer. Chemical shifts are given on the δ (ppm) scale using tetramethylsilane (TMS) as the internal standard (s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet; br, broad). High resolution ESIMS (HRESIMS) spectra were obtained using a Micromass LCT spectrometer. Elemental analysis data were obtained using an Elementar Vario EL. Flash column chromatography was performed using Kanto Chemical Silica Gel 60N (spherical, neutral) 40-50 μm.

(3R*,4S*)-3-Allyl-2-(benzxyloxy)-4-methyltetrahydro-2H-pyran (3).

To a solution of lactone 2 (25.0 g, 162 mmol) in CH$_2$Cl$_2$ (800 mL) was added DIBAL-H (180 mL, 178 mmol, 1.02 M in hexane solution) at -78 °C. After stirring for 1 hr at -78 °C, the mixture was diluted with Et$_2$O, added MeOH and Na$_2$SO$_4$·10H$_2$O. After stirring for 10 hr, the mixture was dried. Removal of the solvent gave a crude lactol.

To a solution of the crude lactol in benzene (320 mL) were added BnOH (34.0 mL, 324 mmol) and TsOH·H$_2$O (640 mg, 3.36 mmol) at r.t. After refluxing for 30 min., a small amount of pyridine was added at r.t. and then stirred. Removal of the solvent gave residue which was then purified by silica gel column chromatography (hexane/EtOAc $=$ 3 : 1) to afford a diastereomeric mixture of benzyl acetal 3 (32.2 g, 81% yield for 2 steps) as a colorless oil. IR (neat) cm$^{-1}$: 2927; $^1$H-NMR (400 MHz, CDCl$_3$) δ: 7.19 (5H, m), 4.87 (2H, m), 4.64 (2H, m), 4.37-4.16 (1H, m), 3.89-3.72 (1H, m), 3.51-3.31 (1H, m), 2.29-2.12 (1H, m), 2.00 (1H, m), 1.69 (1H, m), 1.46-1.24 (4H, m), 0.91-0.80 (3H, m); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 138.5, 136.9, 135.5, 128.3, 128.3, 127.7, 127.6, 127.4, 116.4, 116.1, 102.6, 97.7, 70.2, 68.8, 64.3, 59.6, 46.8, 46.7, 34.6, 33.9, 33.3, 31.8, 31.6, 29.0, 19.9, 19.3; ESIMS $m/z$: 269 (M+Na, 100); HRESIMS $m/z$: 269.1504 (Calcd for C$_{16}$H$_{22}$O$_2$Na: M+Na, 269.1517).

(3-((3R*,4S*)-2-(Benzxyloxy)-4-methyltetrahydro-2H-pyran-3-yl)propoxy)(tert-butyl)dimethylsilane (4).
To a solution of the diastereomeric mixture of benzyl acetal 3 (52.0 g, 211 mmol) in THF (1.00 L) was added a solution of BH₃·THF complex (117 mL, 127 mmol, 1.09 M in THF solution) at 0 °C. After stirring for 2 hr at r.t., 1M NaOH solution (127 mL) and 35% aqueous H₂O₂ solution (64.0 mL) were added to the mixture at r.t. After stirring for 30 min, the resultant mixture was diluted with Et₂O, washed with H₂O and brine, and then dried. Removal of the solvent gave a crude alcohol.

To the crude alcohol in DMF (211 mL) were added imidazole (22.0 g, 317 mmol) and TBSCl (41.3 g, 274 mmol) and the mixture was stirred at 10 °C for 30 min. The mixture was diluted with Et₂O, washed with H₂O and brine, and then dried. Removal of the solvent gave a residue which was then purified by silica gel column chromatography (hexane/EtOAc = 50 : 1) to generate a diastereomeric mixture of silyl ether 4 (74.6 g, 93% yield for 2 steps) as a colorless oil. IR (neat) cm⁻¹: 2928; ¹H-NMR (400 MHz, CDCl₃) δ: 7.31 (5H, m), 4.88-4.22 (3H, m), 3.99-3.82 (1H, m), 3.60-3.42 (3H, m), 1.56-1.21 (9H, m), 0.98-0.89 (12H, m), 0.035 (6H, s); ¹³C-NMR (100 MHz, CDCl₃) δ: 138.2, 128.3, 127.9, 127.7, 127.4, 103.5, 97.6, 70.1, 68.6, 64.4, 63.6, 63.5, 59.6, 46.8, 46.3, 34.7, 33.9, 32.5, 29.9, 29.5, 29.3, 25.9, 24.7, 24.0, 20.0, 19.4, 18.3, -5.30; ESIMS m/z: 401 (M+Na, 23), 287 (100); HRESIMS m/z: 401.2477 (Calcd for C₂₂H₃₈O₃SiNa: M+Na, 401.2488).

(3R*,4S*)-3-(3-(tert-Butyldimethylsilyloxy)propyl)-4-methyltetrahydro-2H-pyran-2-ol (5).

![Diagram of 5](image)

To a solution of the diastereomeric mixture of silyl ether 4 (6.39 g, 16.9 mmol) in EtOAc (85.0 mL) was added a catalytic amount of Pd(OH)₂/C (400 mg) at r.t. After stirring the mixture for 1 h under hydrogen (balloon), the mixture was filtered through a short-path silica gel pad (EtOAc). The filtrate was then concentrated and the residue was then purified by silica gel column chromatography (hexane/EtOAc = 3 : 1) to generate a diastereomeric mixture of hemiacetal 5 (4.18 g, 86% yield) as a colorless oil. IR (neat) cm⁻¹: 3398, 2929, 2858; ¹H-NMR (400 MHz, CDCl₃) δ: 5.15 (0.5H, s), 4.44 (0.5H, m), 4.00 (1H, m), 3.62-3.46 (3H, m), 3.24 (0.5H, m), 2.38 (0.5H, m), 1.61-1.28 (8H, m), 1.07-0.89 (12H, m), 0.045 (6H, s); ¹³C-NMR (100 MHz, CDCl₃) δ: 99.3, 92.8, 65.2, 53.7, 63.4, 59.4, 48.7, 46.2, 34.6, 34.3, 33.3, 29.9, 29.6, 28.7, 25.9, 24.8, 24.4, 19.9, 19.3, 18.3, -5.27, -5.32; ESIMS m/z: 311 (M+Na, 100); HRESIMS m/z: 311.2034 (Calcd for C₁₅H₂₃O₃Si: M+H, 311.2018).

(5S*)-5-((S*)-4-(Trityloxy)butan-2-yl)non-1-en-4-ol (6).

![Diagram of 6](image)

To a solution of the diastereomeric mixture of hemiacetal 5 (10.0 g, 34.7 mmol) in Et₂O (170 mL) was added allyl magnesium bromide (87.0 mL, 87.0 mmol, 1.0 M in Et₂O solution) at 0 °C. After
stirring for 1.5 hr at 0 °C, the mixture was diluted with Et₂O, washed with saturated aqueous NH₄Cl solution, H₂O and brine, and then dried. Removal of the solvent gave a residue which was then purified by silica gel column chromatography (hexane/EtOAc = 2 : 1) to generate a diastereomeric mixture of diol (5:3, 10.3 g, 90% yield) as a colorless oil. IR (neat) cm⁻¹: 3358, 3076, 2930, 2858; ¹H-NMR (400 MHz, CDCl₃) δ: 5.81 (1H, m), 5.14 (2H, m), 3.75-3.58 (5H, m), 2.38-2.07 (3H, m), 1.88-1.25 (9H, m), 1.05-0.74 (12H, m), 0.049 (6H, s); ¹³C-NMR (100 MHz, CDCl₃) δ: 135.5, 135.5, 118.3, 118.1, 72.1, 71.9, 63.4, 63.3, 61.3, 61.2, 46.9, 39.9, 39.7, 38.6, 37.8, 32.6, 32.5, 29.5, 28.8, 26.0, 22.5, 22.2, 18.3, 16.9, 15.6, -5.27; ESIMS m/z: 331 (M+H, 100); HRESIMS m/z: 331.2644 (Calcd for C₁₈H₃₉O₃Si: M+H, 331.2668).

To a solution of the diastereomeric mixture of the above diol (1.97 g, 5.96 mmol) in pyridine (6.00 mL) was added TrCl (1.80 g, 6.56 mmol) at r.t. After stirring for 24 hr at r.t., the solution was concentrated and the residue was then purified by silica gel column chromatography (hexane/EtOAc = 20 : 1) to generate a diastereomeric mixture of alcohol 6 (6:5, 2.97 g, 87% yield) as a colorless oil. IR (neat) cm⁻¹: 3466, 2928, 2857; ¹H-NMR (400 MHz, CDCl₃) δ: 7.44 (5H, m), 7.25 (10H, m), 5.82 (1H, m), 5.11 (2H, m), 3.68-3.56 (3H, m), 3.14-3.04 (2H, m), 2.30-2.04 (2H, m), 1.85-1.77 (1H, m), 1.58-1.23 (8H, m), 0.90 (9H, s), 0.81-0.76 (3H, m), 0.054 (6H, s); ¹³C-NMR (100 MHz, CDCl₃) δ: 144.4, 135.7, 135.5, 128.7, 127.9, 127.7, 126.8, 118.0, 117.8, 86.4, 72.3, 72.0, 63.4, 63.4, 62.1, 47.2, 47.0, 40.4, 39.8, 35.8, 34.9, 32.7, 32.5, 30.7, 29.3, 25.9, 22.2, 22.1, 18.3, 16.3, 15.7, -5.26; ESIMS m/z: 595 (M+Na, 28), 481 (100); HRESIMS m/z: 595.3600 (Calcd for C₃₇H₆₂O₃SiNa: M+Na, 595.3583).

(4R*,5S*,E)-4-(3-(tert-Butyldimethylsilyloxy)propyl)-5-methyl-7-(trityloxy)hept-2-enal (7).

To a solution of the diastereomeric mixture of alcohol 6 (13.2 g, 23.0 mmol) in pyridine (46.0 mL) was added acetic anhydride (46.0 mL, 46.0 mmol) at r.t. After stirring for 14 hr, the mixture was concentrated. The residue was filtered through short-path silica gel column to afford the crude acetate. To the crude acetate were added CH₂Cl₂ (115 mL), MeOH (115 mL), and pyridine (9.30 mL, 115 mmol) at r.t.

The mixture was cooled to -78 °C, and stirred with O₃ bubbling until the solution turned blue. Then to the mixture was added Me₂S (8.50 mL, 115 mmol) and stirred for 3 hr, allowing its completion of consumption of the ozonide, DBU (10.0 mL, 69.0 mmol) was added to the mixture. After stirring for 30 min., the mixture was diluted with Et₂O, washed with sat.NH₄Cl aq., H₂O and brine and then dried. Removal of the solvent gave a residue which was then purified by silica gel column chromatography (hexane/EtOAc = 10 : 1) to generate aldehyde 7 (11.2 g, E/Z = >20 : 1, 87% yield for 2 steps) as a yellow oil. IR (neat) cm⁻¹: 3059, 2929, 2857, 1693; ¹H-NMR (400 MHz, CDCl₃) δ: 9.50 (1H, d, J = 7.8 Hz), 7.43 (5H, m), 7.28 (10H, m), 6.54 (1H, dd, J = 15.6, 9.4 Hz), 6.06 (1H, dd, J = 15.6, 7.9 Hz), 3.58 (2H, t, J = 5.8 Hz), 3.15 (1H, m), 3.05 (1H, m), 2.17 (1H, m), 1.80 (2H, m), 1.55-1.20 (5H, m), 0.89 (9H, s), 0.79 (3H, d, J = 6.8 Hz), 0.05 (6H, s); ¹³C-NMR (100 MHz, CDCl₃)
δ: 193.9, 161.5, 144.3, 128.6, 127.7, 126.9, 86.5, 62.8, 61.6, 48.2, 33.7, 33.6, 30.7, 26.7, 25.9, 18.3, 17.1; ESIMS m/z: 579 (M+Na, 10), 243 (100); HRESIMS m/z: 579.3272 (Calcd for C_{36}H_{48}O_{2}SiNa: M+Na, 579.3270)

*Anal.*: Calcd for C_{36}H_{48}O_{2}Si: C, 77.65; H, 8.69. Found: C, 78.01; H, 8.75.

**(SR*,6S*,E)-5-(3-(tert-Butyldimethylsilyloxy)propyl)-6-methyl-8-(trityloxy)oct-3-en-2-yl acetate (8).**

![Chemical structure](image)

(E/Z = >20:1)

To a solution of aldehyde 7 (7.60 g, 13.6 mmol) in THF (140 mL) was added methyl magnesium bromide (19.0 mL, 20.4 mmol, 1.06 M in THF solution) at 0 °C. After stirring for 30 min at 0 °C, the mixture was diluted with Et_{2}O, washed with saturated aqueous NH_{4}Cl solution, H_{2}O and brine, and then dried. Removal of the solvent gave residue which was then dissolved in pyridine (27.0 mL) and acetic anhydride (27 mL). After stirring for 5 hr at r.t., the solution was evaporated to afford the crude which was purified by silica gel column chromatography (hexane/EtOAc = 20:1) to generate a diastereomeric mixture of acetate 8 (8.12 g, 97% yield for 2 steps) as a colorless oil. IR (neat) cm⁻¹: 2930, 2857, 1738; ¹H-NMR (400 MHz, CDCl₃) δ: 7.40 (5H, m), 7.20 (10H, m), 5.41-5.26 (3H, m), 3.52 (2H, m), 3.08 (1H, m), 2.96 (1H, m), 1.98 (3H, s), 1.76 (2H, m), 1.70-1.20 (9H, m), 0.86 (9H, s), 0.68 (3H, d, J = 6.8 Hz), 0.012 (6H, s); ¹³C-NMR (100 MHz, CDCl₃) δ: 170.3, 144.4, 135.3, 135.2, 130.7, 130.6, 128.6, 127.7, 126.8, 86.3, 71.1, 71.1, 63.3, 62.0, 47.6, 47.6, 33.9, 33.3, 33.2, 30.9, 30.9, 27.2, 25.0, 21.4, 20.6, 20.5, 18.3, 17.2, 17.1; ESIMS m/z: 621 (M+Li, 100); HRESIMS m/z: 621.3959 (Calcd for C_{39}H_{54}O_{4}SiLi: M+Li, 621.3959); Anal.: Calcd for C_{39}H_{54}O_{4}Si: C, 76.17; H, 8.85. Found: C, 76.01; H, 8.88.

**(SR*,6S*,E)-6-Methyl-5-(3-oxopropyl)-8-(trityloxy)oct-3-en-2-yl acetate (9).**

![Chemical structure](image)

To a solution of acetate 8 (8.12 g, 13.2 mmol) was added TBAF (51.0 mL, 1.0 M in THF solution) at r.t. After stirring for 3 hr, the mixture was diluted with EtOAc, washed with sat.NH₄Cl aq., H₂O and brine and then dried. Removal of the solvent gave a residue which was then filtered through silica gel column to generate crude alcohol. To the solution of IBX (5.50 g, 19.8 mmol) in DMSO (130 mL) was added crude alcohol in THF (130 mL), and then stirred at r.t. After stirring for 10 hr, to the mixture was added sat.NaHCO₃ aq. and H₂O and stirred. The mixture was filtered through celite, washed with H₂O and brine, and then dried. Removal of the solvent gave a residue which was then purified by silica
gel column chromatography (hexane/EtOAc = 8 : 1) to generate a diastereomeric mixture of aldehyde 9 (6.04 g, 90% yield for 2 steps) as a colorless oil. IR (neat) cm⁻¹: 3059, 2931, 2873, 1732; ¹H-NMR (400 MHz, CDCl₃) δ: 9.69 (1H, d, J = 4.2 Hz), 7.39 (5H, m), 7.20 (10H, m), 5.37-5.23 (3H, m), 3.09 (1H, m), 2.96 (1H, m), 2.30 (2H, m), 1.99 (3H, s), 1.75-1.48 (5H, m), 1.25 (4H, m), 0.71 (3H, d, J = 6.8 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ: 202.7, 202.6, 170.3, 170.3, 144.3, 134.1, 133.8, 131.9, 131.8, 128.6, 127.7, 126.8, 86.4, 71.0, 70.7, 61.8, 47.4, 47.4, 42.2, 42.2, 34.0, 33.9, 33.3, 33.2, 23.3, 23.3, 21.4, 20.5, 20.5, 17.1; ESIMS m/z: 553 (M+Na, 100); HRESIMS m/z: 521.2662 (Calcd for C₃₇H₃₇O₃Na: M+Na, 521.2668); Anal.: Calcd for C₃₇H₃₇O₃: C, 79.48; H, 7.68. Found: C, 79.23; H, 7.71.

(R*,E)-5-((S*)-4-(Trityloxy)butan-2-yl)deca-3,9-diene-2,8-dione (10).

To a solution of aldehyde 9 (5.50 g, 11.0 mmol) in THF (110 mL) was added vinyl magnesium bromide (47.5 mL, 47.5 mmol, 1.00 M in THF solution) at 0 °C. After stirring for 60 min at r.t., the mixture was added saturated aqueous NH₄Cl solution, diluted with EtOAc, washed with H₂O and brine, and then dried. Removal of the solvent gave residue was purified by silica gel column chromatography (hexane/EtOAc = 1 : 1) to generate a diastereomeric mixture of allyl alcohol (4.64 g, 87% yield) as a colorless oil. IR (neat) cm⁻¹: 3372, 2928, 2871; ¹H-NMR (400 MHz, CDCl₃) δ: 7.44 (5H, m), 7.25 (10H, m), 5.82 (1H, m), 5.41 (2H, m), 5.19 (1H, m), 5.10 (1H, m), 4.27 (1H, m), 4.05 (1H, m), 3.12 (1H, m), 3.03 (1H, m), 1.81-1.65 (5H, m), 1.51-1.23 (8H, m), 0.75 (3H, m); ¹³C-NMR (100 MHz, CDCl₃) δ: 144.4, 141.3, 141.0, 135.8, 135.6, 132.5,132.4, 128.6, 127.7, 126.9, 114.7, 114.5, 86.3, 73.3, 73.2, 73.1, 68.9, 68.8, 62.0, 47.7, 47.6, 47.4, 35.1, 33.9, 33.2, 26.8, 26.6, 23.6, 17.2; ESIMS m/z: 507 (M+Na, 100); HRESIMS m/z: 507.2845 (Calcd for C₃₃H₃₆O₃Na: M+Na, 507.2875); Anal.: Calcd for C₃₃H₃₆O₃: C, 81.78; H, 8.32. Found: C, 81.19; H, 8.37.

To a solution of IBX (8.40 g, 29.9 mmol) in DMSO (140 mL) was added the above allyl alcohol (6.60 g, 13.6 mmol) in THF (140 mL), and then stirred at r.t. After stirring for 3.5 hr, to the mixture was added sat. NaHCO₃ aq. and H₂O and stirred. The mixture was filtered through celite, washed with H₂O and brine, and then dried. Removal of the solvent gave a residue which was then purified by silica gel column chromatography (hexane/EtOAc = 4 : 1) to generate bis(eneones) 10 (5.70 g, 88% yield) as a colorless oil. IR (neat) cm⁻¹: 3057, 2930, 2874; ¹H-NMR (400 MHz, CDCl₃) δ: 7.41 (5H, m), 7.25 (10H, m), 6.55 (1H, dd, J = 16.0, 9.6 Hz), 6.31 (1H, dd, J = 17.6, 10.4 Hz), 6.17 (1H, d, J = 17.7 Hz), 5.99 (1H, d, J = 15.9 Hz), 5.79 (1H, d, J = 10.6 Hz), 3.15 (1H, m), 3.03 (1H, m), 2.47 (2H, m), 2.23 (3H, s), 2.02 (1H, m), 1.78 (3H, m), 1.65 (1H, m), 1.56 (1H, m), 0.79 (3H, d, J = 6.6 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ:200.1, 198.3, 149.9, 144.3, 136.4, 132.5, 128.6, 128.1, 127.7, 126.9, 61.6, 47.8, 37.6, 34.0, 33.6, 27.0, 24.3, 17.0; ESIMS m/z: 503 (M+Na, 13), 165 (100); HRESIMS m/z: 503.2557 (Calcd for C₃₃H₃₆O₃Na: M+Na, 503.2562); Anal.: Calcd for C₃₃H₃₆O₃: C, 82.46; H, 7.55. Found: C, 82.22; H, 7.65.
(4R*,4aS*,8aR*)-6-(tert-Butyldimethylsilyloxy)-4-((S*)-4-(trityloxy)butan-2-yl)-2,3,4,4a,8,8a-hexa-hydronaphthalene-1(7H)-one (11).

To a solution of bis(enones) 10 (6.06 g, 12.6 mmol) and DIPEA (18.0 mL, 106 mmol) in CH₂Cl₂ (160 mL) was added TBSOTf (2.40 mL, 10.6 mmol) in CH₂Cl₂ (50 mL) dropwise at 0 °C and the mixture was stirred at r.t. for 2 hr. The mixture was diluted with Et₂O, washed with saturated aqueous NH₄Cl solution, H₂O and brine, and then dried. Removal of the solvent gave a residue which was then purified by silica gel column chromatography (hexane/EtOAc = 10 : 1) to generate silyl enol ether 11 (6.42 g, 86% yield) as a colorless oil. IR (neat) cm⁻¹: 2930, 1709, 1663; ¹H-NMR (400 MHz, CDCl₃) δ: 7.40 (5H, m), 7.20 (10H, m), 4.79 (1H, d, J = 4.2 Hz), 3.14 (1H, m), 3.08 (1H, m), 2.52 (1H, m), 2.40 (1H, m), 2.26-2.00 (6H, m), 1.69 (2H, m), 1.52 (4H, m), 0.85 (9H, s), 0.72 (3H, d, J = 6.9 Hz), 0.039 (6H, m); ¹³C-NMR (100 MHz, CDCl₃) δ: 214.6, 151.2, 144.3, 128.6, 127.7, 126.9, 106.9, 86.5, 62.1, 47.5, 43.2, 38.3, 38.2, 35.6, 29.2, 28.6, 25.6, 23.7, 23.0, 17.9, 14.7, -4.3, -4.5; ESIMS m/z: 595 (M+H, 13), 243 (100); HRESIMS m/z: 595.3614 (Calcd for C₃₀H₃₁O₃Si: M+H, 595.3607).

(4R*,4aR*,8aS*)-4-((S*)-4-(Trityloxy)butan-2-yl)hexahydronaphthalene-1,6(2H,7H)-dione (12).

To silyl enol ether 11 (6.42 g, 10.8 mmol) was added a mixture of TBAF (106 mmol) and AcOH (106 mmol) in THF (106 mL) and the mixture was stirred at r.t. for 10 min. The mixture was diluted with Et₂O, washed with saturated aqueous NaHCO₃ solution, H₂O and brine, and then dried. Removal of the solvent gave a residue which was then filtered through silica gel to generate a crude diketone.

To the crude diketone in CH₂Cl₂ (212 mL) was added DIPEA (37.0 mL, 212 mmol) and stirred. After stirring for 4 days, the mixture was diluted with Et₂O, washed with saturated aqueous NH₄Cl solution, H₂O and brine, and then dried. Removal of the solvent gave a residue which was then purified by silica gel column chromatography (hexane/EtOAc = 2 : 1) to generate diketone 12 (4.95g, 95% yield for 2 steps) as a colorless oil. IR (neat) cm⁻¹: 3058, 3022, 2958, 2874, 1712; ¹H-NMR (400 MHz, CDCl₃) δ: 7.44 (5H, m), 7.26 (10H, m), 3.13 (2H, t, J = 6.0 Hz), 2.61 (1H, m), 2.43 (2H, m), 2.33-2.17 (4H, m), 2.00 (2H, m), 1.85 (1H, m), 1.75-1.53 (5H, m), 1.38 (1H, m), 0.65 (3H, d, J = 6.9 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ: 210.2, 210.0, 144.1, 128.6, 127.8, 127.0, 86.4, 61.1, 52.1, 45.5, 45.1, 44.9, 41.1, 40.1, 35.1, 28.1, 25.1, 25.0, 13.1; ESIMS m/z: 503 (M+Na, 30), 391 (100); HRESIMS m/z: 503.2821 (Calcd for C₃₃H₃₉O₃: M+Na, 503.2562).

(S*)-3-((1R*,4aS*,8aR*)-4,7-Dioxodecahydronaphthalen-1-yl)butanal (13).
To a solution of diketone 12 (4.95 g, 10.3 mmol) in EtOAc (200 mL) was added a catalytic amount of Pd(OH)$_2$/C (2.00 g) at r.t. After stirring the mixture for 10 hr under hydrogen (balloon), the mixture was filtered through a short-path silica gel pad (EtOAc). The filtrate was then concentrated and dissolved in THF (255 mL). This solution was added to a solution of IBX (3.70 g, 13.4 mmol) in DMSO (255 mL) at r.t. After stirring for 6 hr, the mixture was added sat. NaHCO$_3$ aq. and H$_2$O and stirred. Then filtered through a short-path Celite pad (EtOAc). Filtrate was washed with H$_2$O and brine, and then dried. Removal of the solvent gave a residue which was then purified by silica gel column chromatography (hexane/EtOAc = 1 : 1) to afford aldehyde 13 (1.56 g, 64% yield for 2 steps) as a colorless oil. IR (neat) cm$^{-1}$: 3515, 2960, 2877, 2726, 1712; $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 9.75 (1H, s), 2.67 (1H, m), 2.49-2.16 (10H, m), 1.92 (1H, m), 1.82 (2H, m), 1.71 (2H, m), 0.77 (3H, d, $J = 6.8$ Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 209.5, 209.4, 201.4, 51.8, 49.3, 45.5, 45.2, 45.0, 40.8, 39.9, 25.9, 25.2, 24.9, 12.9; ESIMS m/z: 237 (M+H, 100); HRESIMS m/z: 237.1487 (Calcd for C$_{14}$H$_{20}$O$_2$: M+H, 237.1491); Anal.: Calcd for C$_{14}$H$_{20}$O$_2$: C, 71.16; H, 8.53. Found: C, 70.71; H, 8.53.

($S*,E$)-Methyl 5-((1R*,4aS*,8aR*)-4,7-dioxododecahydronaphthalen-1-yl)hex-2-enoate (14).

To aldehyde 13 (100 mg, 0.423 mmol) in THF (8.50 mL) was added Ph$_3$P=CHCO$_2$Me (221 mg, 0.635 mmol) and the mixture was stirred at r.t. for 7 hr. The mixture was diluted with Et$_2$O, washed with saturated aqueous NH$_4$Cl solution, H$_2$O and brine, and then dried. Removal of the solvent gave a residue which was then purified by silica gel column chromatography (hexane/EtOAc = 2 : 1) to afford unsaturated ester 14 (112 mg, 91%) as a colorless oil. IR (neat) cm$^{-1}$: 2967, 2867, 1702, 1651; $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 6.90 (1H, dd, $J = 15.6, 7.4$ Hz), 5.86 (1H, d, $J = 15.6$ Hz), 3.74 (3H, s), 2.63 (1H, m), 2.49-2.04 (8H, m), 1.94 (2H, m), 1.79-1.51 (5H, m), 0.77 (3H, d, $J = 6.9$ Hz); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 209.6, 209.4, 166.7, 147.5, 122.4, 51.9, 51.5, 45.3, 45.0, 40.8, 39.9, 37.9, 31.2, 25.0, 24.8, 12.9; ESIMS m/z: 293 (M+H, 70), 243 (100); HRESIMS m/z: 293.1751 (Calcd for C$_{17}$H$_{22}$O$_4$: M+H, 293.1753); Anal.: Calcd for C$_{17}$H$_{22}$O$_4$: C, 69.84; H, 8.27. Found: C, 69.63; H, 8.18; UV (sh, MeOH) $\lambda_{max}$ (e) nm: 209.5 (25497).

Methyl 2-((1S*,3S*,3aR*,3a1R*,6aS*,9aS*)-3-methyl-6,9-dioxododecahydro-1H-phenalen-1-yl)-acetate (15).
To a solution of unsaturated ester 14 (50.0 mg, 0.171 mL) in CH₂Cl₂ (8.60 mL) was added pyrrolidine (50.0 µg, 0.855 mmol) at r.t. After stirring for 2 hr, the mixture was diluted with Et₂O, added 10% aqueous HCl solution, H₂O and brine, and then the mixture was dried. Removal of the solvent gave a residue which was then purified by silica gel column chromatography (hexane/EtOAc = 3 : 1) to generate ester 15 (33.2 mg, 66% yield) as a white solid. m.p. 135-137 °C; IR (KBr) cm⁻¹: 2962, 2930, 2859, 1730, 1702; ¹H-NMR (400 MHz, CDCl₃) δ: 3.65 (3H, s), 2.61-2.17 (11H, m), 1.75 (2H, m), 1.39-1.24 (5H, m), 0.95 (3H, d, J = 6.4 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ: 210.8, 209.8, 173.1, 57.1, 54.0, 51.9, 51.4, 41.0, 40.8, 39.8, 38.5, 35.5, 32.2, 30.5, 27.3, 19.6; ESIMS m/z: 293 (M+H, 100); HRESIMS m/z: 293.1778 (Calcd for C₁₇H₂₅O₄: M+H, 293.1753); Anal.: Calcd for C₁₇H₂₄O₄: C, 69.84; H, 8.27. Found: C, 70.04; H, 8.47.

Crystal data and structure refinement for 15

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<th>Identification code</th>
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                       | c = 18.769(2) Å  
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                       | γ = 90°. |
| Volume              | 1535.1(3) Å³ |
| Z                   | 4 |
| Density (calculated) | 1.265 Mg/m³ |
| Absorption coefficient | 0.089 mm⁻¹ |
| F(000)              | 632 |
| Crystal size        | 0.34 x 0.27 x 0.21 mm³ |
| Theta range for data collection | 2.17 to 27.52°. |
| Index ranges        | -10<=h<=11, -11<=k<=11, -24<=l<=18 |
| Reflections collected | 8514 |
| Independent reflections | 3491 [R(int) = 0.0231] |
| Completeness to theta = 27.52° | 98.7 % |
| Absorption correction | Analytical |
| Max. and min. transmission | 0.9816 and 0.9705 |
| Refinement method   | Full-matrix least-squares on F² |
Data / restraints / parameters 3491 / 0 / 192
Goodness-of-fit on F² 0.990
Final R indices [I>2sigma(I)]
R1 = 0.0383, wR2 = 0.1056
R indices (all data)
R1 = 0.0451, wR2 = 0.1113
Largest diff. peak and hole 0.392 and -0.228 e.A⁻³


To a solution of unsaturated ester 14 (50.0 mg, 0.171 mL) in THF (17.0 mL) was added LHMDS (2.10 mL, 3.42 mmol, 1.60 M in THF solution) at -78 °C. After stirring for 1 hr at 0 °C, the mixture was diluted with Et₂O, added saturated aqueous NH₄Cl solution, H₂O and brine, and then the mixture was dried. Removal of the solvent gave a residue which was then purified by silica gel column chromatography (hexane/EtOAc = 2:1) to generate ester 16 (27.7 mg, 55% yield) as a colorless solid. m.p. 122-125 °C; IR (KBr) cm⁻¹: 2936, 1732; ¹H-NMR (400 MHz, CDCl₃) δ: 3.68 (3H, s), 2.66 (2H, m), 2.54-2.22 (8H, m), 1.82 (2H, m), 1.66-1.54 (4H, m), 1.23 (1H, m), 1.08 (1H, m), 0.80 (3H, d, J = 6.8 Hz); ¹³C-NMR (100 MHz, CDCl₃) δ: 214.7, 209.7, 172.8, 51.7, 50.1, 49.4, 46.7, 40.3, 40.0, 34.9, 34.5, 30.9, 30.8, 24.8, 24.3, 18.5; ESIMS m/z: 293 (M+H, 100); HRESIMS m/z: 293.1776 (Calcd for C₁₇H₂₅O₄: M+H, 293.1753)

Crystal data and structure refinement for 16
Identification code p21n
Empirical formula C₁₇H₂₄O₄
Formula weight 292.36
Temperature 90 K
Wavelength 0.71073 Å
Crystal system Monoclinic
Space group P 21/c
Unit cell dimensions a = 11.4263(14) Å α = 90°,
b = 7.2405(9) Å β = 120.160(5)°,
c = 20.7034(18) Å γ = 90°.
Volume 1481.0(3) Å³
Z 4
Density (calculated) 1.311 Mg/m³
Absorption coefficient 0.092 mm⁻¹
F(000) 632
Crystal size 0.37 x 0.35 x 0.16 mm³
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Index ranges  
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Reflections collected  
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Independent reflections  
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Completeness to theta = 27.51°  
98.7%  
Absorption correction  
Analytical  
Max. and min. transmission  
0.9854 and 0.9668  
Refinement method  
Full-matrix least-squares on F^2  
Data / restraints / parameters  
3365 / 0 / 192  
Goodness-of-fit on F^2  
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Final R indices [I>2sigma(I)]  
R1 = 0.0367, wR2 = 0.0981  
R indices (all data)  
R1 = 0.0408, wR2 = 0.1015  
Largest diff. peak and hole  
0.409 and -0.191 e.Å^3  

Methyl 2-((1S*,3S*,3aR*,3a1R*,6aS*,9aS*)-3-methyl-6-methylene-9-oxododecahydro-1H-phenalen-1-yl)acetate (17).

\[ \text{MeO}_2\text{C} \quad \xrightarrow{\text{Ph}_3\text{P}=\text{CH}_2} \quad \text{MeO}_2\text{C} \]

To a solution of Ph₃PCH₂I (158 mg, 0.390 mmol) in THF (10.0 mL) was added BuLi (195 μL, 0.325 mmol, 1.67 M in hexane) dropwise at 0 °C. After stirring for 1 hr, to this solution was added ester 15 (38 mg, 0.130 mmol) in THF (3.00 mL) dropwise, and then stirred for 30 min at the same temperature. The mixture was diluted with Et₂O, washed with saturated aqueous NH₄Cl solution, H₂O and brine and then dried. Removal of the solvent gave a residue which was then purified by silica gel column chromatography (hexane/EtOAc = 10 : 1) to afford ester 17 (33.1 mg, 88% yield) as a white solid. m.p. 94-96 °C; IR (KBr) cm⁻¹: 2985, 2909, 2859, 1728, 1695; ^1H-NMR (400 MHz, CDCl₃) δ: 4.73 (1H, s), 4.57 (1H, s), 3.65 (3H, s), 2.60 (1H, m), 2.37 (3H, m), 2.28 (2H, m), 2.12 (5H, m), 1.74 (2H, m), 1.04 (3H, m), 0.88 (5H, m); ^13C-NMR (100 MHz, CDCl₃) δ: 212.4, 173.4, 150.4, 105.6, 57.0, 55.0, 51.3, 49.1, 44.7, 42.0, 40.2, 39.0, 36.0, 35.9, 32.2, 31.5, 31.3, 19.7; ESIMS m/z: 291 (M+H, 100); HRESIMS m/z: 291.1977 (Calcd for C₁₈H₂₇O₃: M+H, 291.1960); Anal.: Calcd for C₁₈H₂₆O₃: C, 74.45%; H, 9.02. Found: C, 74.60%; H, 9.07.

2-((1S*,3S*,3aR*,3a1R*,6aS*,9aS*)-3-methyl-6,9-dimethylenedodecahydro-1H-phenalen-1-yl)acetic acid (18) and 1-((1S*,3S*,3aR*,3a1R*,6aS*,9aS*)-3-methyl-6,9-dimethylenedodecahydro-1H-phenalen-1-yl)propan-2-one (19).
To a solution of Bu$_3$SnCH$_2$TMS (750 mg, 1.98 mmol) in THF (10.0 mL) was added BuLi (195 µL, 0.325 mmol, 1.67 M in hexane) dropwise at 0 °C. After stirring for 1 hr, the mixture was cooled to -78 °C, then ester 17 (115 mg, 0.396 mmol) in THF (6.00 mL) was added to the mixture at the same temperature. After stirring for 20 min., the mixture was diluted with Et$_2$O, washed with saturated aqueous NH$_4$Cl solution, H$_2$O and brine, and then dried. Removal of the solvent gave a residue which was then dissolved in THF (20.0 mL) at r.t. To this solution was added 10% aqueous HCl solution (4.00 mL) and stirred for 40 min. The mixture was diluted with Et$_2$O, washed with H$_2$O and brine, and then dried. Removal of the solvent gave a residue which was then purified by silica gel column chromatography (hexane/EtOAc = 10 : 1) to afford both carboxylic acid 18 (36.6 mg, 34% yield for 2 steps) and ketone 19 (33.6 mg, 31% yield for 2 steps) as a white solid. For 18: m.p. 175-178 °C; IR (KBr) cm$^{-1}$: 2936, 2844, 1695, 1643; $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 4.83 (1H, s), 4.65 (1H, s), 4.60 (1H, s), 4.54 (1H, s), 2.95 (1H, dd, $J = 20.9, 2.6$ Hz), 2.37 (2H, m), 2.14-1.82 (8H, m), 1.61-1.42 (3H, m), 1.13 (1H, m), 0.90 (7H, m); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 179.2, 152.2, 151.0, 105.2, 104.5, 55.4, 50.9, 48.7, 46.0, 41.6, 39.5, 37.3, 36.3, 35.7, 33.7, 32.6, 31.9, 19.8; ESIMS $m/z$: 275 (M+H, 100); HRESIMS $m/z$: 275.2007 (Calcd for C$_{18}$H$_2$_O$_2$: M+H, 275.2011); Anal.: Calcd for C$_{18}$H$_2$_O$_2$: C, 78.79; H, 9.55. Found: C, 78.66; H, 9.26. For 19: m.p. 110-112 °C; IR (KBr) cm$^{-1}$: 2934, 2900, 2843, 1704, 1641; $^1$H-NMR (400 MHz, CDCl$_3$) $\delta$: 4.78 (1H, s), 4.65 (1H, s), 4.53 (1H, s), 4.47 (1H, s), 2.93 (1H, d, $J = 16.9$ Hz), 2.37 (2H, m), 2.19 (1H, m), 2.11 (3H, s), 2.08-1.95 (4H, m), 1.80 (2H, m), 1.43 (2H, m), 1.13 (1H, m), 0.89-0.72 (8H, m); $^{13}$C-NMR (100 MHz, CDCl$_3$) $\delta$: 209.1, 152.3, 105.0, 104.4, 55.4, 51.1, 49.5, 48.8, 46.0, 42.0, 37.4, 36.3, 35.7, 32.6, 32.3, 31.9, 30.6, 19.8; ESIMS $m/z$: 295 (M+Na, 100); HRESIMS $m/z$: 295.2032 (Calcd for C$_{19}$H$_{28}$ONa: M+Na, 295.2038); Anal.: Calcd for C$_{19}$H$_{28}$O: C, 83.77; H, 10.36. Found: C, 83.50; H, 10.09.

**Conversion of 18 to 19.**

To a solution of carboxylic acid 18 (34.0 mg, 0.124 mmol) in dry CH$_2$Cl$_2$ (6.00 mL) were added HN(OMe)Me·HCl (24.0 mg, 0.248 mmol), Et$_3$N (34.0 µL, 0.248 mmol) and EDC·HCl (71.0 mg, 0.372 mmol) and the mixture was stirred at 0 °C for 3 days. The mixture was diluted with Et$_2$O, washed with 10% aqueous HCl solution, H$_2$O and brine, and then dried. Removal of the solvent gave a residue which was then dissolved in THF (6.20 mL). To this solution was added methyl magnesium
bromide (380 μL, 0.426 mmol, 1.12 M in THF solution) at 0 °C. After stirring for 1 hr, the mixture was diluted with Et₂O, washed with 1M aqueous HCl solution, H₂O and brine, and then dried. Removal of the solvent gave a residue which was then purified by silica gel column chromatography (hexane/EtOAc = 40 : 1) to afford ketone 19 (33.9 mg, quantitative yield for 2 steps) as a white solid.

1-((1'S*,3a'R*,3a1'S*,4'S*,6'S*,6a'S*,9a'S*)-4'-Methyl-7'-methylene-1-tosylidodecahydrospiro-[aziridine-2,1'-phenalene]-6'-yl)propan-2-one (20).

To a solution of ketone 19 (20.0 mg, 0.0734 mmol), MS4A and PhI=NTs (82.0 mg, 0.220 mmol) in MeCN/CH₂Cl₂ (7.30 mL, 1:1) was added Cu(OTf)₂ (12.0 mg, 0.0332 mmol) at 0 °C. After stirring for 2 hr, the mixture was filtered through a short-path silica gel pad (Et₂O). Filtrate was concentrated to give a residue which was then purified by silica gel column chromatography (hexane/EtOAc = 10 : 1) to afford aziridine 20 (β/α = >20 : 1, 8.00 mg, 25% yield) as a yellow solid and starting material 19 (10.7 mg, 54% recovered). m.p. 161-163 °C; IR (KBr) cm⁻¹: 2855, 1713; ¹H-NMR (400 MHz, CDCl₃) δ: 7.80 (2H, d, J = 8.2 Hz), 7.29 (2H, d, J = 8.1 Hz), 4.72 (1H, s), 4.44 (1H, s), 2.88 (1H, d, J = 17.1 Hz), 2.49 (1H, m), 2.42 (4H, m), 2.34-2.04 (8H, m), 1.91-1.61 (4H, m), 1.51 (1H, m), 1.25 (1H, m), 0.99 (1H, m), 0.88-0.68 (8H, m); ¹³C-NMR (100 MHz, CDCl₃) δ: 208.8, 150.6, 143.6, 138.3, 129.4, 127.2, 105.4, 55.4, 53.0, 50.6, 49.4, 48.1, 45.0, 42.0, 37.0, 36.5, 35.5, 32.1, 31.4, 30.7, 29.7, 28.9, 21.5, 19.7; ESIMS m/z: 442 (M+H⁺, 100); HRESIMS m/z: 442.2397 (Calcd for C₂₆H₃₆NO₃S: M⁺H⁺, 442.2416). Anal.: Calcd for C₂₆H₃₅NO₃S: C, 70.71; H, 7.99; N, 3.17. Found: C, 70.73; H, 8.29; N, 2.93.

N-((1'S*,3aR*,3a1S*,4'S*,6'S*,6a'S*,9a'S*)-1,4-Dimethyl-6-(2-methylallyl)-7-methylenedodecahydro-1'H-phenalen-1-yl)-4-methylbenzenesulfonamide (21).

To a solution of Ph₃P=CH₂ (82.0 mg, 0.204 mmol) in THF (2.50 mL) was added BuLi (98.0 μL, 0.163 mmol, 1.67 M in hexane) dropwise at 0 °C. After stirring for 1 hr, to this solution was added aziridine 20 (18.0 mg, 0.0408 mmol) in THF (1.60 mL) dropwise, and then stirred for 45 min at the same temperature. The mixture was diluted with Et₂O, washed with saturated aqueous NH₄Cl solution,
H$_2$O and brine and then dried. Removal of the solvent gave a residue which was then dissolved in THF (3.80 mL) at 0 °C. To this solution was added LiEt$_3$H (450 μL, 0.491 mmol, 1.09 M in THF) at the same temperature and stirred for 2.5 hr. The mixture was diluted with Et$_2$O, washed with saturated aqueous NH$_4$Cl solution, H$_2$O and brine and then dried. Removal of the solvent gave a residue which was then purified by silica gel column chromatography (hexane/EtOAc = 30 : 1 to 10 : 1) to afford tosyl amide 21 (12.2 mg, 72% yield for 2 steps) as a pale yellow solid. m.p. 208-210 °C; IR (KBr) cm$^{-1}$: 3251, 2943, 2864; $^1$H-NMR (400 MHz, CDCl$_3$) δ: 7.75 (2H, d, J = 8.0 Hz), 7.27 (2H, d, J = 8.7 Hz), 4.77 (1H, s), 4.73 (1H, s), 4.63 (1H, s), 4.55 (1H, s), 2.60 (1H, d, J = 14.1 Hz), 2.42 (3H, s), 2.29 (1H, m), 2.02 (1H, m), 1.86-1.77 (2H, m), 1.74-1.65 (4H, m), 1.55-1.38 (6H, m), 1.23 (1H, m), 1.09-0.95 (5H, m), 0.88-0.78 (5H, m), 0.67 (2H, m); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 151.2, 144.6, 142.9, 140.9, 129.5, 126.9, 111.0, 105.0, 60.8, 51.6, 50.4, 50.2, 48.3, 43.2, 40.8, 39.4, 37.4, 35.6, 34.0, 29.8, 26.2, 22.6, 21.5, 19.8, 19.5; EIMS m/z: 464 (M+Na, 40), 579 (100); HRESIMS m/z: 464.2578 (Calcd for C$_{27}$H$_{30}$NO$_2$SNa: M+Na, 464.2599).

**7-Isocynoamphilecta-11(20),15-diene (1).**

To a solution of tosyl amide 21 (12.2 mg, 0.0276 mmol) in THF (2.80 mL) at -78 °C was added already prepared sodium naphthalenide in THF solution dropwise until the solution turned blue. The solution was warmed to 0 °C and added H$_2$O, and then filtered through a short-path celite pad (Et$_2$O). The solvent was evaporated to furnish a crude amine, which was dissolved in CH$_2$Cl$_2$ (2.80 mL). To this solution was added a small amount of acetic formic anhydride at r.t. and stirred for 30 min. The solution was then filtered through a short-path silica gel pad (CHCl$_3$) and the filtrate was concentrated to afford a crude formamide. To this residue were added CH$_2$Cl$_2$ (1.00 mL), pyridine (4.00 μL, 0.0476 mmol) and tosyl chloride (9.00 mg, 0.0476 mmol) at r.t. After stirring for 14 hr, the mixture was concentrated to afford a residue which was then purified by silica gel column chromatography (hexane : EtOAc = 40 : 1) to furnish 1 (6.50 mg, 79% yield for 3 steps) as a white solid. m.p. 100-102 °C; IR (KBr) cm$^{-1}$: 2928, 2869, 2131; $^1$H-NMR (400 MHz, CDCl$_3$) δ: 4.84 (1H, s), 4.74 (1H, s), 4.65 (1H, s), 4.60 (1H, s), 2.63 (1H, d, J = 14.1 Hz), 2.40 (1H, ddd, J = 12.2, 4.0, 2.9 Hz), 2.20 (1H, m), 2.01 (2H, m), 1.86 (3H, m), 1.72 (3H, m), 1.62 (1H, m), 151-142 (3H, m), 1.28 (5H, m), 1.64 (1H, m), 0.92-0.86 (4H, m), 0.81-0.62 (2H, m); $^{13}$C-NMR (100 MHz, CDCl$_3$) δ: 152.4, 150.7, 144.4, 111.1, 105.6, 60.7 (t), 51.3, 49.8, 48.3, 43.1, 40.9, 40.8, 37.2, 35.6, 34.0, 30.2, 25.5, 22.6, 20.7, 19.7; EIMS m/z: 297 (M, 1), 91 (90); HRESIMS m/z: 271.2434 (Calcd for C$_{20}$H$_{31}$: M-CN, 271.2426); Anal.: Calcd for C$_{21}$H$_{31}$N: C, 84.79; H, 10.50; N, 4.71. Found: C, 84.53; H, 10.36; N, 4.69.
References