Supplemental material for:

Highly Regioselective Oxidative Csp2-H Amination for Indolosesquiterpene Alkaloids: Total Synthesis of (+)-Dioridamycin

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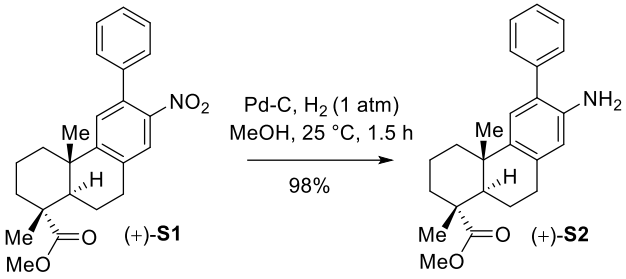
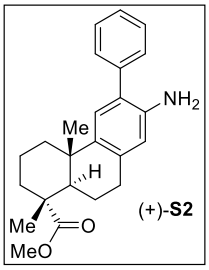
Materials and Methods

Unless otherwise stated, reactions were carried out using oven dried glass ware with Teflon coated magnetic stirring bars were used to stir the reactions. The Syringe was used to transfer the solvents and liquid reagents. Tetrahydrofuran (THF) Diethyl ether (Et_2O) were distilled over sodium/benzophenone ketyl. Dichloromethane CH_2Cl_2) was distilled over calcium hydride. All other solvents like MeOH, EtOAc, DMF, Dichloroethane (DCE) and reagents were used as received. Reaction temperatures above 25 °C were maintained by using oil bath on a magnetic stirrer. Thin layer chromatography (TLC) analysis was performed by using silica gel precoated plates (0.25 mm) 60 (F-254), Visualized by UV irradiation, yellow dip stain and other stains. Silica gel of particle size 230-400 and 100-200 mesh were used to perform flash chromatography. Digital melting point apparatus is used to record the melting points. ^{1}H-NMR spectra were recorded by using 400, 500 MHz spectrometers, ^{13}C-NMR operating frequencies are 100, 125 MHz respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvents ($CDCl_3$) signal (δ = 7.29 for 1H NMR and δ = 77.0 for ^{13}C NMR) and (CD_3OD) signal (δ = 3.33 for ^{1}H NMR and δ = 49.0 for ^{13}C NMR). Data for ^{1}H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, and number of hydrogen). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). IR spectra were recorded on a FT-IR system (Spectrum BX) and are reported in frequency of absorption (cm^{-1}). Only selected IR absorbencies are reported. High Resolution Mass Spectrometry (HRMS) data was recorded on MicrOTOF-Q-II mass spectrometer using methanol as solvent.

Synthesis of compound (+)-S2:



In an oven-dried round-bottom flask compound (**+**)-**S1** (1.1 g, 2.79 mmol, 1.0 equiv.) was taken in MeOH (20 mL) and degassed with N_2 balloon for 10 minutes. To this solution Pd/C (10% w/w) (110 mg) was added and a H_2 gas balloon (1 atm.) was placed with the reaction vessel and stirring continued until the full consumption of starting material (1.5 h), as confirmed by TLC analysis. The reaction mixture was filtered, evaporated to dryness under the reduced pressure. The crude product was purified by flash column chromatography with 20% EtOAc in *n*-hexane to afford (+)-**S2** as yellow foam (996 mg, 98%). For characterization of compound (+)-**S1** see ref. 1.



Methyl (1*R*,4a*S*,10a*R***)-7-amino-1,4a-dimethyl-6-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-**S2**]: (+)-**S2** was obtained as colourless liquid (2.79 mmol scale of reaction; 996 mg; 98%). R_f = 0.2 (10 % EtOAc in *n*-hexane).

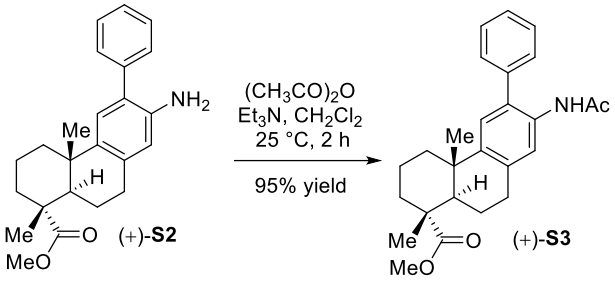
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (h, *J* = 8.8, 8.0 Hz, 4H), 7.37 (qt, *J* = 6.5, 2.3 Hz, 1H), 7.05 (s, 1H), 6.50 (s, 1H), 3.71 (s, 3H), 2.89 (td, *J* = 10.3, 9.5, 7.1 Hz, 2H), 2.30 (dd, *J* = 12.5, 2.4 Hz, 2H), 1.92 – 1.84 (m, 1H), 1.84 – 1.75 (m, 2H), 1.69 (ddd, *J* = 15.6, 10.2, 2.5 Hz, 2H), 1.54 (td, *J* = 12.6, 4.1 Hz, 1H), 1.47 – 1.41 (m, 1H), 1.31 (s, 3H), 1.26 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 179.2, 140.9, 140.5, 139.9, 135.5, 129.2, 128.7, 126.9, 126.4, 126.0, 115.5, 51.9, 47.7, 45.2, 38.2, 36.7, 36.6, 29.8, 25.3, 21.7, 18.6, 16.5.

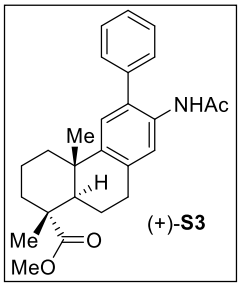
IR (neat) υ_{max} 3402, 3353, 2832, 1713, 1678, 1619, 1281, 1155, 764 cm^{-1}.

$[\alpha]^{25}_{589}$ = +31.50 (*c* = 0.92, CH_3OH).

Synthesis of 2-aryl acetanilide (+)-S3:



In an oven dried round-bottom flask, compound (+)-**S2** (121 mg, 0.33 mmol., 1.0 equiv.) was taken in CH_2Cl_2 (5 mL) and Et_3N (55 μL, 0.396 mmol., 1.2 equiv.) was added to the reaction mixture. Next, acetic anhydride (37 μL, 0.363 mmol., 1.1 equiv.) was added to the reaction mixture at 25 ºC and stirring continued until the full consumption of starting material. Upon completion (2 h), as monitored by TLC analysis, it was extracted with CH_2Cl_2 (5 mL X 2). The organic layers were dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. The crude product was purified by flash column chromatography with 40% EtOAc in *n*-hexane to afford (+)-**S3** as yellow foam (127 mg, 95%).



Methyl (1*R*,4a*S*,10a*R***)-7-acetamido-1,4a-dimethyl-6-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-**S3**]: (+)-**S3** was obtained as yellow foam (0.33 mmol scale of reaction; 127 mg; 95%). R_f = 0.2 (30 % EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.13 (s, 1H), 7.04 (s, 1H), 3.70 (s, 3H), 3.02 – 2.94 (m, 2H), 2.28 (dd,

J = 12.6, 2.3 Hz, 2H), 2.02 (s, 3H), 1.88 (ddd, *J* = 21.6, 12.7, 9.0 Hz, 1H), 1.79 (t, *J* = 11.0 Hz, 2H), 1.73 – 1.65 (m, 2H), 1.58 – 1.43 (m, 2H), 1.30 (s, 3H), 1.25 (s, 3H).

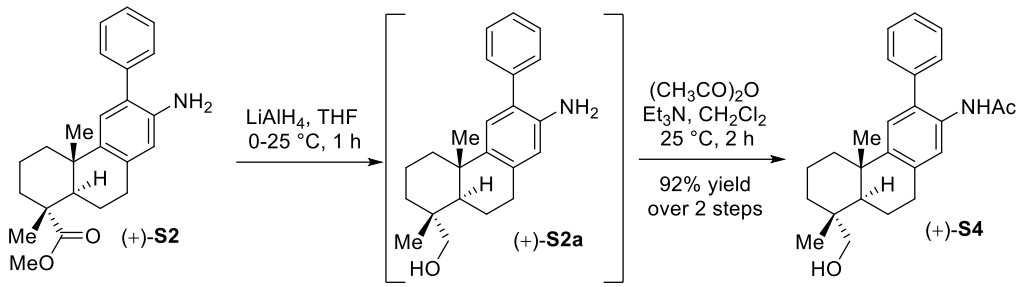
^{13}C NMR (125 MHz, $CDCl_3$): δ 179.0, 168.3, 146.1, 138.7, 135.6, 131.9, 130.4, 129.3, 129.0, 127.7, 126.0, 122.2, 52.0, 47.6, 44.8, 38.0, 37.0, 36.6, 29.9, 25.1, 24.5, 21.6, 18.5, 16.5.

IR (neat) υ_{max} 3021, 2763, 1807, 1719, 1676, 1520, 1199, 908, 721 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ H]^+$ calcd. for $[C_{26}H_{29}O_3N + H]^+$ 406.2226, found 406.2224.

$[\alpha]^{25}_{589}$ = +55.30 (*c* = 0.85, $CHCl_3$).

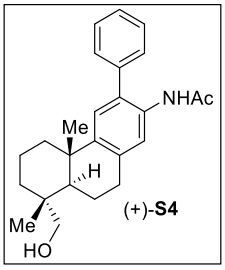
Synthesis of 2-aryl acetanilide (+)-S4:



In an oven dried round-bottom flask, compound (+)-**S2** (557 mg, 1.53 mmol., 1.0 equiv.) was taken in dry THF (8 mL) and $LiAlH_4$ (47 mg, 1.22 mmol., 0.8 equiv.) was added to the reaction mixture portion wise and the reaction mixture at 25 ºC was stirring continued until the full consumption of starting material. Upon completion (1 h), as monitored by TLC analysis, it was extracted with EtOAc (8 mL X 2). The organic layers were dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. The crude product (+)-**S2a** was charged for the next step.

Next, in a round-bottom flask, compound (+)-**S2a** (1.53 mmol., 1.0 equiv.) was taken in CH_2Cl_2 (8 mL) and Et_3N (255 μL, 1.84 mmol., 1.2 equiv.) was added to the reaction mixture. Next, acetic anhydride (184 μL, 1.84 mmol., 1.1 equiv.) was added to the reaction mixture at 25 ºC and stirring continued until the full consumption of starting material. Upon completion (2 h),

as monitored by TLC analysis, it was extracted with CH_2Cl_2 (6 mL X 2). The organic layers were dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. The crude product was purified by flash column chromatography with 55% EtOAc in *n*-hexane to afford (+)-**S4** as yellow solid (531 mg, 92% yield over 2 steps).



***N*-((**4b*S*,8*R*,8a*R*)**-8-(hydroxymethyl)-4b,8-dimethyl-3-phenyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-2-yl)acetamide** [(+)-**S4**]: (+)-**S4** was obtained as yellow solid. M.P. 178-182 ∘C (1.53 mmol scale of reaction; 531 mg; 92% yield over 2 steps). R_f = 0.25 (50 % EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.40 (dd, *J* = 23.7, 7.4 Hz, 3H), 7.14 (s, 1H), 7.07 (s, 1H), 3.51 (d, *J* = 10.9 Hz, 1H), 3.25 (d, *J* = 10.9 Hz, 1H), 3.05 – 2.91 (m, 2H), 2.27 (d, *J* = 12.9 Hz, 1H), 2.03 (s, 3H), 1.84 (td, *J* = 12.1, 10.9, 6.1 Hz, 2H), 1.79 – 1.74 (m, 2H), 1.48 (td, *J* = 13.0, 4.0 Hz, 2H), 1.41 (td, *J* = 8.8, 4.1 Hz, 2H), 1.26 (s, 3H), 0.91 (s, 3H).

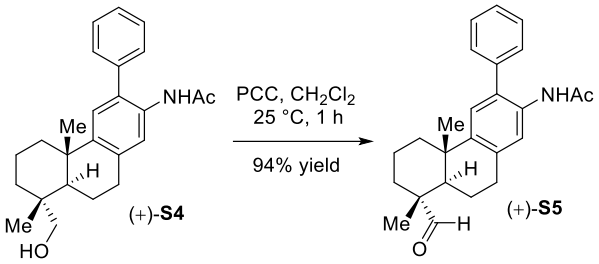
^{13}C NMR (125 MHz, $CDCl_3$): δ 168.5, 146.6, 138.8, 135.7, 131.6, 130.3, 129.4, 129.0, 127.6, 126.2, 122.2, 72.1, 43.8, 38.5, 37.9, 37.4, 35.0, 30.0, 29.7, 25.3, 24.5, 18.7, 18.6, 17.4.

IR (neat) υ_{max} 3307, 3187, 3053, 2869, 1679, 1602, 1587, 1256, 1178, 971 cm^{-1}.

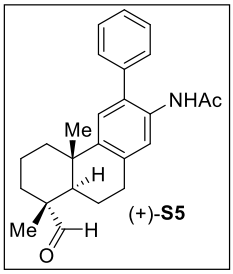
HRMS (ESI) *m/z*: $[M+ H]^+$ calcd. for $[C_{25}H_{31}O_2N + H]^+$ 378.2433, found 378.2427.

$[\alpha]^{25}_{589}$ = +67.10 (*c* = 0.63, $CHCl_3$).

Synthesis of compound (+)-S5:



In an oven dried round-bottom flask, compound (+)-**S4** (360 mg, 0.95 mmol., 1.0 equiv.) was taken in CH_2Cl_2 (8 mL) and to the reaction mixture PCC (247 mg, 1.14 mmol., 1.2 equiv.) was added. Next, the reaction mixture at 25 ºC was stirring continued until the full consumption of starting material. Upon completion (1 h), as monitored by TLC analysis, it was concentrated in a rotary evaporator under reduced pressure. The crude product was purified by flash column chromatography with 30-40% EtOAc in *n*-hexane to afford (+)-**S5** as yellow liquid (335 mg, 94%).



***N*-((**4b*S*,8*R*,8a*R*)**-8-formyl-4b,8-dimethyl-3-phenyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-2-yl)acetamide** [(+)-**S5**]: (+)-**S5** was obtained as yellow liquid. (0.95 mmol scale of reaction; 335 mg; 94%). R_f = 0.3 (30 % EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.31 (s, 1H), 7.92 (s, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 7.3 Hz, 2H), 7.14 (s, 1H), 7.04 (s, 1H), 2.99 (d, *J* = 8.0 Hz, 2H), 2.33 (d, *J* = 13.0 Hz, 1H), 2.03 (s, 3H), 1.95 (d, *J* = 12.8 Hz, 1H), 1.90 – 1.79 (m, 3H), 1.55 – 1.45 (m, 2H), 1.37 (d, *J* = 13.8 Hz, 2H), 1.27 (s, 3H), 1.19 (s, 3H).

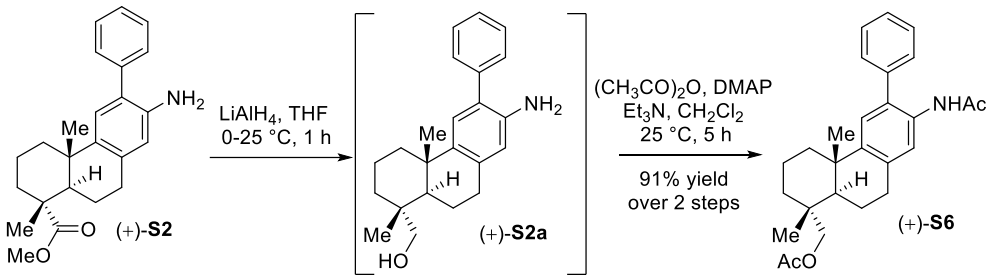
^{13}C NMR (125 MHz, $CDCl_3$): δ 206.0, 168.3, 145.3, 138.6, 135.3, 132.1, 130.5, 129.3, 129.0, 127.8, 126.0, 122.3, 49.8, 42.8, 37.9, 36.4, 32.1, 29.6, 25.2, 24.5, 21.2, 17.7, 14.1.

IR (neat) υ_{max} 3107, 2963, 2829, 1727, 1630, 1435, 1287, 1215, 1109, 820 cm^{-1}.

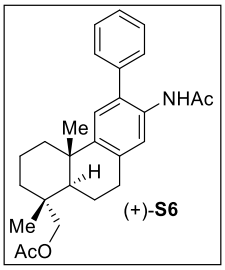
HRMS (ESI) *m/z*: $[M+ H]^+$ calcd. for $[C_{25}H_{29}O_2N + H]^+$ 376.2226, found 376.2271.

$[\alpha]^{25}_{589}$ = +49.67 (*c* = 0.51, $CHCl_3$).

Synthesis of compound (+)-S6:



In an oven dried round-bottom flask, compound (+)-**S2a** (180 mg, 0.49 mmol., 1.0 equiv.) was taken in CH_2Cl_2 (5 mL) and Et_3N (220 μL, 1.58 mmol., 3.2 equiv.) and DMAP (12 mg, 0.1 mmol., 0.2 equiv.) were added to the reaction mixture. Next, acetic anhydride (110 μL, 1.08 mmol., 2.2 equiv.) was added to the reaction mixture at 25 ºC and stirring continued until the full consumption of starting material. Upon completion (5 h), as monitored by TLC analysis, it was extracted with CH_2Cl_2 (5 mL X 2). The organic layers were dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. The crude product was purified by flash column chromatography with 40% EtOAc in *n*-hexane to afford (+)-**S6** as yellow solid (187 mg, 91% yield over 2 steps).



((1*R*,4a*S*,10a*R*)**-7-Acetamido-1,4a-dimethyl-6-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl acetate** [(+)-**S6**]: (+)-**S6** was obtained as colorless liquid. (0.49 mmol scale of reaction; 187 mg; 91% yield over 2 steps). R_f = 0.28 (40 % EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.15 (s, 1H), 7.03 (s, 1H), 4.01 (d, *J* = 11.0 Hz, 1H), 3.73 (d, *J* = 11.1

Hz, 1H), 3.01 (dd, *J* = 17.5, 6.0 Hz, 1H), 2.91 (dt, *J* = 17.9, 9.0 Hz, 1H), 2.27 (d, *J* = 12.9 Hz, 1H), 2.07 (s, 3H), 2.03 (s, 3H), 1.86 – 1.74 (m, 3H), 1.70 (d, *J* = 13.0 Hz, 2H), 1.46 (h, *J* = 12.9, 12.2 Hz, 3H), 1.26 (s, 3H), 0.97 (s, 3H).

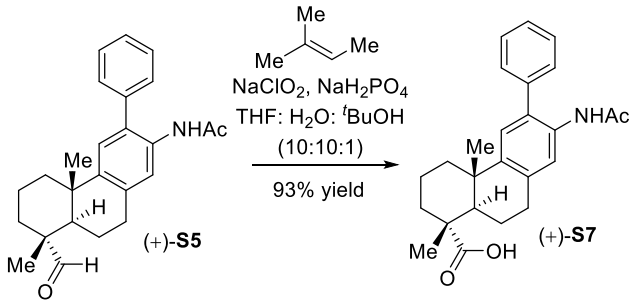
^{13}C NMR (125 MHz, $CDCl_3$): δ 171.3, 168.3, 146.4, 138.7, 135.7, 131.8, 130.5, 129.3, 129.0, 127.7, 126.2, 122.3, 72.3, 44.1, 38.4, 37.5, 36.8, 35.5, 30.1, 25.3, 24.5, 21.0, 18.9, 18.5, 17.5.

IR (neat) υ_{max} 3390, 2923, 2829, 2655, 1704, 1697, 1565, 1454, 1176, 923, 663 cm^{-1}.

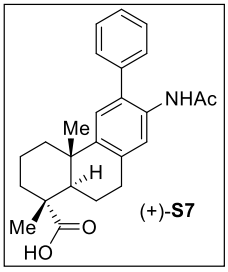
HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{27}H_{33}O_3N + Na]^+$ 442.2353, found 442.2357.

$[\alpha]^{25}_{589}$ = +71.20 (*c* = 0.67, $CHCl_3$).

Synthesis of compound (+)-S7:



In an oven dried round-bottom flask, compound (+)-**S5** (142 mg, 0.38 mmol., 1.0 equiv.) was taken in a mixture of tetrahydrofuran, *tert*-butanol and water [THF: H_2O: ^{t}BuOH (10:10:1)] at 25 °C and 2-methyl-2-butene (400 μL, 3.80 mmol, 10.0 equiv.) was added to the reaction vessel. After 5 minutes of stirring, NaH_2PO_4 (228 mg, 1.90 mmol, 5.0 equiv.) was added to the reaction mixture and it was cooled to 0 °C. Then $NaClO_2$ (103 mg, 1.14 mmol, 3.0 equiv.) was added portion wise over a period of 10 minutes. The reaction mixture was allowed to warm to 25 °C and stirring was continued for an additional 2 h. After complete consumption of the starting material (as judged by TLC), it was diluted with water and pH<3 was maintained by addition of 2(*N*) HCl. Next, mixture was extracted with EtOAc (15 mL X 3) and organic layer was dried over Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude product was purified by flash column chromatography with 50-60% EtOAc in *n*-hexane to afford (+)-**S7** as white foam (138 mg, 93%).



(1*R*,4a*S*,10a*R***)-7-Acetamido-1,4a-dimethyl-6-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylic acid** [(+)-**S7**]: (+)-**S7** was obtained as white foam (0.38 mmol scale of reaction; 138 mg; 93%). R_f = 0.2 (50 % EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.40 (dd, *J* = 23.1, 7.5 Hz, 3H), 7.13 (s, 1H), 7.05 (s, 1H), 3.01 (dd, *J* = 9.7, 5.5 Hz, 2H), 2.29 (d, *J* = 12.5 Hz, 2H), 2.03 (s, 3H), 1.92 (q, *J* = 11.2 Hz, 1H), 1.83 (t, *J* = 11.4 Hz, 2H), 1.74 (d, *J* = 10.1 Hz, 2H), 1.65 – 1.51 (m, 2H), 1.32 (s, 3H), 1.26 (s, 3H).

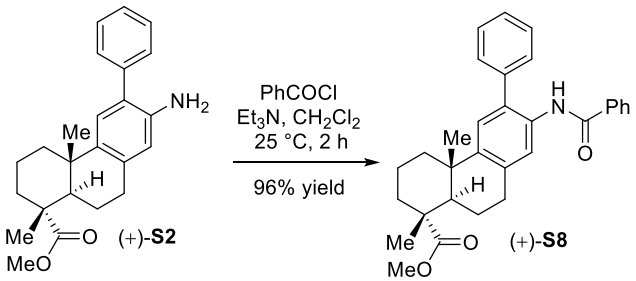
^{13}C NMR (125 MHz, $CDCl_3$): δ 184.1, 168.4, 146.0, 138.7, 135.6, 131.8, 130.4, 129.3, 129.0, 127.7, 126.0, 122.3, 47.4, 44.6, 38.0, 37.0, 36.7, 29.9, 25.1, 24.5, 21.6, 18.5, 16.3.

IR (neat) υ_{max} 3421, 2873, 2702, 1700, 1643, 1475, 1349, 923, 631 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ H]^+$ calcd. for $[C_{25}H_{29}O_3N + H]^+$ 392.2226, found 392.2238.

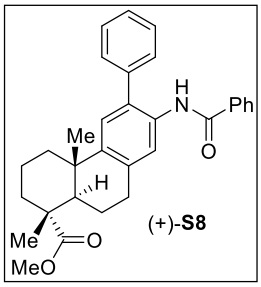
$[\alpha]^{25}_{589}$ = +37.90 (*c* = 0.37, CH_3OH).

Synthesis of compound (+)-S8:



In an oven dried round-bottom flask, compound (+)-**S2** (103 mg, 0.28 mmol., 1.0 equiv.) was taken in CH_2Cl_2 (5 mL) and Et_3N (47 μL, 0.34 mmol., 1.2 equiv.) was added to the reaction mixture. Next, PhCOCl (36 μL, 0.31 mmol., 1.1 equiv.) was added to the reaction mixture at

25 ºC and stirring continued until the full consumption of starting material. Upon completion (2 h), as monitored by TLC analysis, it was extracted with CH_2Cl_2 (5 mL X 2). The organic layers were dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. The crude product was purified by flash column chromatography with 15% EtOAc in *n*-hexane to afford (+)-**S8** as white solid (126 mg, 96% yield).



Methyl (1*R*,4a*S*,10a*R*)-7-benzamido-1,4a-dimethyl-6-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate [(+)-**S8**]: (+)-**S8** was obtained as white solid. MP = 130 - 134 °C (0.28 mmol scale of reaction; 126 mg; 96%). R_f = 0.2 (10 % EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.92 (s, 1H), 7.62 (d, *J* = 7.7 Hz, 2H), 7.46 (tt, *J* = 28.0, 7.8 Hz, 8H), 7.19 (s, 1H), 3.71 (d, *J* = 2.7 Hz, 3H), 3.04 (d, *J* = 8.3 Hz, 2H), 2.31 (d, *J* = 12.5 Hz, 2H), 1.92 (q, *J* = 11.3 Hz, 1H), 1.82 (d, *J* = 9.9 Hz, 2H), 1.71 (dd, *J* = 21.6, 7.8 Hz, 2H), 1.57 (t, *J* = 12.2 Hz, 1H), 1.49 (d, *J* = 13.2 Hz, 1H), 1.32 (s, 3H), 1.28 (s, 3H).

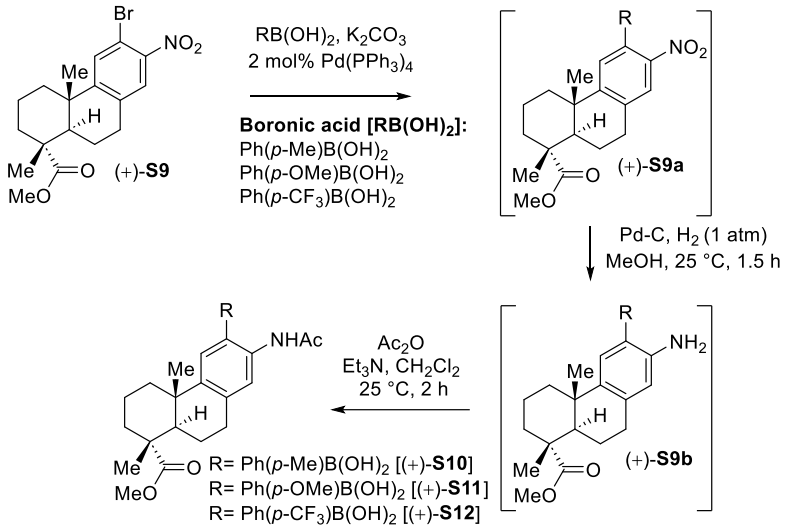
^{13}C NMR (125 MHz, $CDCl_3$): δ 179.0, 164.9, 146.0, 138.6, 135.8, 134.9, 132.1, 131.6, 130.4, 129.5, 129.1, 128.7, 128.5, 127.9, 126.8, 125.9, 121.5, 52.0, 47.7, 44.9, 38.0, 37.1, 36.7, 30.0, 25.1, 21.6, 18.5, 16.5.

IR (neat) υ_{max} 3066, 3015, 2867, 2834, 1785, 1707, 1623, 1447, 1209, 1087, 836 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ H]^+$ calcd. for $[C_{31}H_{33}O_3N + H]^+$ 468.2539, found 468.2529.

$[\alpha]^{25}_{589}$ = +44.70 (*c* = 0.52, $CHCl_3$).

Synthesis of compound (+)-S10, (+)-S11, and (+)-S12:



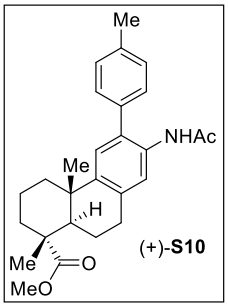
General Procedure:

A round-bottom flask was charged with (+)-**S9** (1.0 equiv.) and functionalized benzene boronic acid (1.2 equiv.) in a mixture of benzene (9 mL), EtOH (3 mL), and water (3 mL) at room temperature under argon atmosphere. Next, potassium carbonate (2.0 equiv.) was added to the reaction mixture followed by the addition of catalyst, tetrakis(triphenylphosphine)palladium(0) (0.02 equiv.) at the same temperature. Then the reaction mixture was placed on a pre-heated oil bath maintaining temperature of 80 °C. Upon completion of the reaction (~10 h), as monitored by TLC analysis, it was extracted with EtOAc. The combined organic layers were washed with brine and dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. The crude product was purified by flash chromatography.

Next, in round-bottom flask compound **(+)-S9a** (1.0 equiv.) was taken in MeOH and degassed with N_2 balloon for 10 minutes. To this solution Pd/C (10% w/w) was added and a H_2 gas balloon (1 atm.) was placed with the reaction vessel and stirring continued until the full consumption of starting material (1.5 h), as confirmed by TLC analysis. The reaction mixture was filtered, evaporated to dryness under the reduced pressure. The crude product was purified by flash column chromatography with 20% EtOAc in *n*-hexane to afford corresponding (+)-**S9b**.

After that, in a round-bottom flask, compound (+)-**S9b** (1.0 equiv.) was taken in CH_2Cl_2 and Et_3N (1.2 equiv.) was added to the reaction mixture. Next, acetic anhydride (1.1 equiv.) was added to the reaction mixture at 25 ºC and stirring continued until the full consumption of

starting material. Upon completion (2 h), as monitored by TLC analysis, it was extracted with CH_2Cl_2. The organic layers were dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. The crude product was purified by flash column chromatography with EtOAc in *n*-hexane to afford corresponding products. For characterization of compound (+)-**S9** see ref. 1.



Methyl (1*R*,4a*S*,10a*R***)-7-acetamido-1,4a-dimethyl-6-(*p*-tolyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-**S10**]: (+)-**S10** was obtained as white foam (0.373 mmol scale of reaction; 141 mg; 90% over 3 steps). R_f = 0.2 (40 % EtOAc in *n*-hexane).

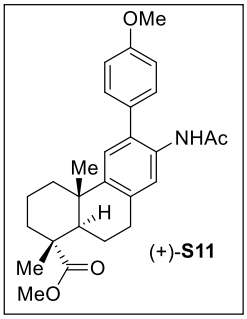
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.32 – 7.25 (m, 4H), 7.11 (s, 1H), 7.07 (s, 1H), 3.70 (s, 3H), 2.97 (dd, *J* = 9.8, 5.0 Hz, 2H), 2.44 (s, 3H), 2.27 (dd, *J* = 12.5, 2.2 Hz, 2H), 2.03 (s, 3H), 1.88 (td, *J* = 12.9, 6.4 Hz, 1H), 1.79 (d, *J* = 10.2 Hz, 1H), 1.70 (dt, *J* = 26.3, 10.7 Hz, 3H), 1.52 (dd, *J* = 13.9, 10.1 Hz, 1H), 1.48 – 1.42 (m, 1H), 1.30 (s, 3H), 1.24 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 179.0, 168.2, 145.9 137.5, 135.7, 135.4, 132.0, 130.2, 129.7, 129.2, 126.0, 122.0, 52.0, 47.6, 44.8, 38.0, 37.0, 36.6, 29.9, 25.1, 24.5, 21.6, 21.2, 18.5, 16.5.

IR (neat) υ_{max} 2988, 2821, 1798, 1702, 1627, 1573, 1465, 1086, 746 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ H]^+$ calcd. for $[C_{27}H_{33}O_3N + H]^+$ 420.2533, found 420.2535.

$[\alpha]^{25}_{589}$ = +59.32 (*c* = 0.7, $CHCl_3$).



Methyl (1*R*,4a*S*,10a*R*)-7-acetamido-6-(4-methoxyphenyl)-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate [(+)-**S11**]: (+)-**S11** was obtained as colourless liquid. (0.383 mmol scale of reaction; 135 mg; 81% over 3 steps). R_f = 0.23 (30 % EtOAc in *n*-hexane).

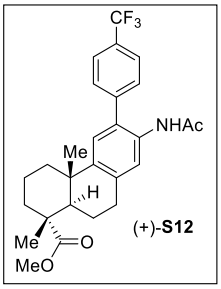
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (s, 1H), 7.26 (d, *J* = 2.1 Hz, 1H), 7.25 – 7.24 (m, 1H), 7.06 (s, 1H), 6.98 (d, *J* = 8.7 Hz, 3H), 3.85 (s, 3H), 3.66 (s, 3H), 2.93 (dd, *J* = 7.9, 3.4 Hz, 2H), 2.23 (dd, *J* = 12.5, 2.3 Hz, 2H), 2.00 (s, 3H), 1.87 – 1.80 (m, 1H), 1.76 (d, *J* = 9.7 Hz, 1H), 1.72 – 1.64 (m, 2H), 1.62 – 1.61 (m, 1H), 1.50 (dd, *J* = 12.7, 3.7 Hz, 1H), 1.42 (q, *J* = 5.4, 4.2 Hz, 1H), 1.26 (s, 3H), 1.20 (s, 3H)

^{13}C NMR (126 MHz, $CDCl_3$): δ 179.0, 168.2, 159.2, 145.9, 135.3, 132.1, 130.8, 130.5, 130.0, 126.0, 122.0, 114.4, 55.4, 52.0, 47.6, 44.8, 38.0, 37.0, 36.6, 29.8, 25.1, 24.5, 21.6, 18.5, 16.5.

IR (neat) υ_{max} 3007, 2865, 2743, 1821, 1699, 1580, 1289, 1067, 782 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{27}H_{33}O_4N + Na]^+$ 458.2302, found 458.2315.

$[\alpha]^{25}_{589}$ = +53.37 (*c* = 0.35, $CHCl_3$).



Methyl (1*R*,4a*S*,10a*R*)-7-acetamido-1,4a-dimethyl-6-(4-(trifluoromethyl)phenyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate [(+)-**S12**]: (+)-**S12** was obtained

as white foam. (0.356 mmol scale of reaction; 145 mg; 86% over 3 steps). R_f = 0.3 (30 % EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.73 (d, *J* = 7.9 Hz, 2H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.12 (s, 1H), 6.89 (s, 1H), 3.70 (s, 3H), 3.02 – 2.94 (m, 2H), 2.27 (dt, *J* = 12.6, 2.7 Hz, 2H), 2.04 (s, 3H), 1.93 – 1.82 (m, 1H), 1.81 – 1.75 (m, 2H), 1.68 (d, *J* = 7.3 Hz, 2H), 1.56 – 1.42 (m, 2H), 1.30 (s, 3H), 1.24 (s, 3H).

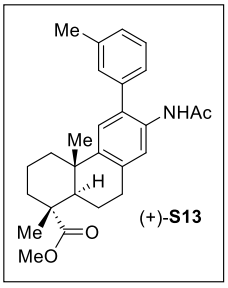
^{13}C NMR (125 MHz, $CDCl_3$): δ 178.9, 168.5, 146.8, 142.7, 136.5, 131.5, 129.8, 129.7, 126.0, 125.8, 123.6, 52.0, 47.6, 44.7, 38.0, 37.1, 36.6, 29.8, 25.1, 24.3, 21.5, 18.5, 16.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.43.

IR (neat) υ_{max} 3035, 2994, 2873, 2834, 1715, 1683, 1457, 1326, 1188, 857, 683 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{27}H_{3o}F_3O_3N + Na]^+$ 496.2076, found 496.2085.

$[\alpha]^{25}_{589}$ = +68.90 (*c* = 0.57, $CHCl_3$).



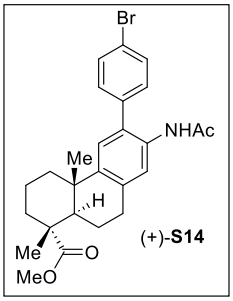
Methyl (1*R*,4a*S*,10a*R*)-7-acetamido-1,4a-dimethyl-6-(*m*-tolyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate [(+)-**S13**]: (+)-**S13** was obtained as colourless liquid. (0.400 mmol scale of reaction; 136 mg; 74% over 3 steps). R_f = 0.23 (30 % EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 1H), 7.32 (d, J = 7.9 Hz, 1H), 7.19 (d, J = 7.7 Hz, 1H), 7.14 – 7.12 (m, 2H), 7.08 (s, 1H), 7.04 – 7.02 (m, 1H), 3.66 (s, 3H), 2.93 (dd, J = 6.8, 3.3 Hz, 2H), 2.40 (s, 3H), 2.23 (s, 1H), 1.99 (s, 3H), 1.80 (s, 2H), 1.79 – 1.73 (m, 3H), 1.68 (s, 2H), 1.63 (s, 1H), 1.26 (s, 3H), 1.21 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.1, 168.3, 138.9, 138.7, 135.5, 132.0, 130.4, 130.2, 128.9, 128.5, 126.3, 126.0, 122.0, 60.5, 52.1, 47.7, 44.9, 38.1, 37.1, 36.7, 29.9, 25.2, 24.6, 21.7, 21.6, 21.1, 18.6, 16.6, 14.3.

IR (neat) υ_{max} 3007, 2865, 2743, 1821, 1699, 1580, 1289, 1067, 782 cm^{-1}.

$[\alpha]^{25}_{589}$ = +57.22 (*c* = 0.35, $CHCl_3$).



Methyl (1*R*,4a*S*,10a*R*)-7-acetamido-6-(4-bromophenyl)-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate [(+)-**S14**]: (+)-**S14** was obtained as colourless liquid. (0.450 mmol scale of reaction; 161 mg; 74% over 3 steps). R_f = 0.22 (30 % EtOAc in *n*-hexane).

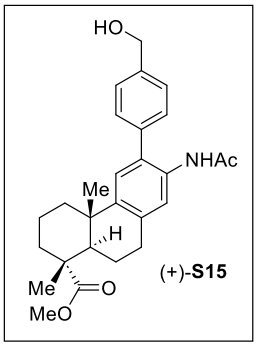
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.59 – 7.56 (m, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.05 (s, 1H), 6.85 (s, 1H), 3.66 (s, 3H), 2.95 – 2.92 (m, 2H), 2.22 (dd, *J* = 12.5, 2.3 Hz, 2H), 2.01 (s, 3H), 1.89 – 1.77 (m, 2H), 1.76 – 1.71 (m, 2H), 1.70 – 1.62 (m, 3H), 1.53 – 1.44 (m, 2H), 1.41 (s, 1H), 1.26 (s, 3H), 1.20 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 179.0, 168.3, 137.7, 136.1, 132.1, 131.7, 131.0, 129.6, 125.8, 123.0, 121.9, 52.0, 47.6, 44.7, 38.0, 37.1, 36.6, 29.8, 25.1, 24.4, 21.5, 18.5, 16.5.

IR (neat) υ_{max} 3007, 2865, 2743, 1821, 1699, 1580, 1289, 1067, 782 cm^{-1}.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $[C_{26}H_{31}BrNO_3 + H]^+$ 484.1487, found 484.1475.

$[\alpha]^{25}_{589}$ = +58.41 (*c* = 0.35, $CHCl_3$).



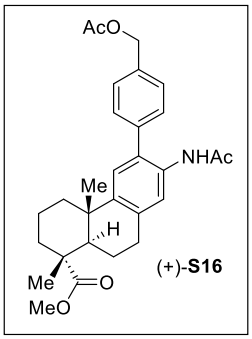
Methyl (1*R*,4a*S*,10a*R*)-7-acetamido-6-(4-(hydroxymethyl)phenyl)-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate [(+)-**S15**]: (+)-**S15** was obtained as yellow liquid. (0.450 mmol scale of reaction; 153 mg; 78% over 3 steps). R_f = 0.31 (70 % EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.08 (s, 1H), 7.05 (s, 1H), 4.73 (s, 2H), 3.65 (s, 3H), 2.95 – 2.91 (m, 2H), 2.23 (dd, *J* = 12.6, 2.2 Hz, 2H), 2.03 (d, *J* = 8.6 Hz, 1H), 1.98 (s, 3H), 1.87 – 1.80 (m, 2H), 1.75 (d, *J* = 10.0 Hz, 2H), 1.72 – 1.66 (m, 2H), 1.26 (s, 3H), 1.20 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.2, 168.6, 146.3, 140.5, 138.1, 135.7, 131.9, 130.4, 129.5, 127.7, 126.1, 122.6, 64.9, 52.1, 47.7, 44.9, 38.1, 37.1, 36.7, 29.9, 29.8, 25.2, 24.5, 18.6, 16.6.

IR (neat) υ_{max} 3007, 2865, 2743, 1821, 1870, 1699, 1580, 1289, 1067, 782 cm^{-1}.

$[\alpha]^{25}_{589}$ = +67.59 (*c* = 0.45, $CHCl_3$).



Methyl (1*R*,4a*S*,10a*R*)-7-acetamido-6-(4-(acetoxymethyl)phenyl)-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate [(+)-**S16**]: (+)-**S16** was obtained

as yellow liquid. (0.450 mmol scale of reaction; 153 mg; 64% over 3 steps). R_f = 0.31 (70 % EtOAc in *n*-hexane).

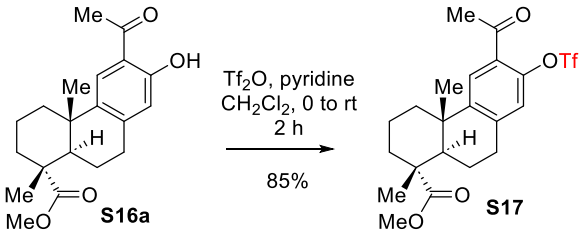
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.07 (s, 1H), 6.99 – 6.96 (m, 1H), 5.15 (s, 2H), 3.66 (s, 3H), 2.94 (dd, *J* = 8.5, 4.1 Hz, 2H), 2.23 (dd, *J* = 12.5, 2.3 Hz, 2H), 2.13 (s, 3H), 2.00 (s, 3H), 1.85 – 1.79 (m, 1H), 1.76 (d, *J* = 9.9 Hz, 1H), 1.70 (d, *J* = 14.7 Hz, 2H), 1.64 (s, 1H), 1.52 – 1.43 (m, 2H), 1.26 (s, 3H), 1.20 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 179.0, 170.9, 168.3, 146.2, 138.8, 135.8, 135.5, 131.8, 130.0, 129.5, 128.8, 126.0, 122.6, 65.9, 52.0, 47.6, 44.8, 38.0, 37.0, 36.6, 29.8, 25.1, 24.5, 21.6, 21.0, 18.5, 16.5.

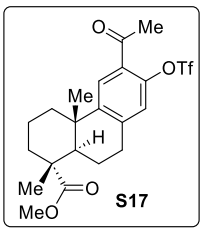
IR (neat) υ_{max} 3012, 2814, 2748, 1824, 1845, 1644, 1536, 1278, 1065, 789 cm^{-1}.

$[\alpha]^{25}_{589}$ = +58.50 (*c* = 0.3, $CHCl_3$).

Synthesis of triflate derivative S17:



To a stirred solution of *ortho*-hydroxy acetophenone **S16a** (300 mg, 0.908 mmol, 1.0 equiv.) in CH_2Cl_2 (10 mL) at 0 °C was added pyridine (0.01 mL, 2.02 mmol, 1.5 equiv.) and trifluoromethanesulfonic anhydride (0.08 mL, 1.8 mmol, 1.2 equiv.) consecutively dropwise over 5 min. Then the reaction was allowed to run at room temperature. After 6 h the reaction was quenched with water, extracted into CH_2Cl_2 (15 mL X 3) and the organic phase washed with 1 M hydrochloric acid (10 mL), water (5 mL) and brine (5 mL). The organic phase was dried over anhydrous sodium sulfate, filtered and the solvent removed *in vacuo* and the crude product was purified by silica gel chromatography with 20% EtOAc in n-hexane to afford the product **S17** as yellow liquid (250 mg, 85%).



(1R,4aS,10aR)- methyl 6-acetyl-1,4a-dimethyl-7-(((trifluoromethyl)sulfonyl)oxy)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate [**S17**]: **S17** was obtained as yellow liquid (0.90 mmol scale of reaction; 85% yield). R*f* = 0.25 (10% EtOAc in n-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (s, 1H), 6.95 (s, 1H), 3.67 (s, 3H), 2.96 – 2.91 (m, 2H), 2.59 (s, 3H), 2.33 (d, *J* = 12.5 Hz, 1H), 2.20 – 2.15 (m, 1H), 1.85 – 1.80 (m, 1H), 1.79 – 1.73 (m, 3H), 1.69 (d, *J* = 3.5 Hz, 1H), 1.50 (q, *J* = 2.8, 2.4 Hz, 2H), 1.27 (s, 3H), 1.21 (d, *J* = 0.8 Hz, 3H).

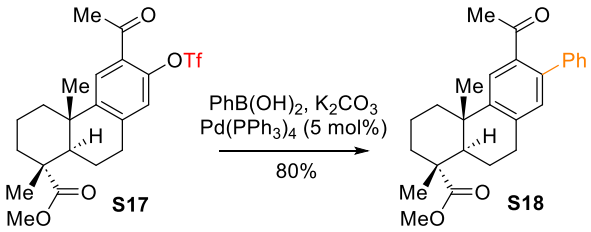
^{13}C NMR (125 MHz, $CDCl_3$): δ 196.5, 178.6, 150.1, 144.5, 142.7, 129.4, 127.4, 122.6, 117.3, 52.1, 47.4, 44.2, 37.8, 37.4, 36.5, 29.9, 25.0, 20.1, 18.3, 16.5.

IR (neat) υ_{max} 2958, 2848, 2369, 1710, 1489, 1234, 1112, 965, 786, 720 cm-1.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{21}H_{25}F_3O_6S + Na]^+$ 485.1222, found 485.1220.

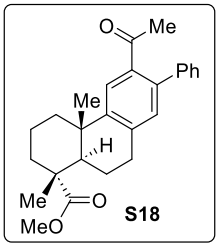
$[\alpha]^{25}$ 589 = +46.5 (c = 0.5, $CHCl_3$).

Synthesis of biaryl derivative S18:



A sealed tube or a round-bottom flask equipped with reflux condenser with N_2 atmosphere was charged with K_2CO_3 (50 mg, 0.17 mmol, 2.0 equiv.), Phenylboronic acid (70 mg, 0.35 mmol, 1.2 equiv.), compound **S17** (80 mg, 0.17 mmol, 1.0 equiv.) and $Pd(PPh_3)_4$ (10 mg, 0.01 mmol,

0.05 equiv.), using a mixture of Benzene (5 mL), EtOH (2 mL) in H_2O (2 mL). The reaction mixture was heated at 90 °C (oil bath) with stirring for 8 h. The resulting mixture was diluted with H_2O (2 mL) and extracted with EtOAc (3 × 7 mL). The organic layer was dried (Na_2SO_4) and then filtered. The solvent was removed in vacuo, and the crude product was purified by silica gel chromatography with 20% EtOAc in *n*-hexane to afford the product **S18** as yellow foam (60 mg, 78%).



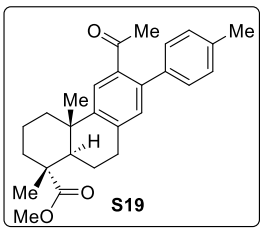
(1*R*,4a*S*,10a*R*)-**Methyl -6-acetyl-1,4a-dimethyl-7-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [**S16**]: **S16** was obtained as yellow foam (0.17 mmol scale of reaction; 78% yield). R_f = 0.35 (10% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, *J* = 1.9 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 11.4 Hz, 1H), 7.61 (dd, *J* = 7.5, 1.9 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 2H), 6.99 (s, 1H), 3.71 (s, 3H), 2.97 (dd, *J* = 8.8, 4.7 Hz, 2H), 2.63 (s, 3H), 2.36 (d, *J* = 13.1 Hz, 1H), 2.21 (dd, *J* = 12.5, 2.2 Hz, 1H), 1.87 (ddd, *J* = 13.1, 9.1, 3.9 Hz, 2H), 1.79 (d, *J* = 8.5 Hz, 2H), 1.74 – 1.71 (m, 1H), 1.57 – 1.50 (m, 2H), 1.31 (s, 3H), 1.25 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 204.7, 179.0, 167.7, 148.9, 140.9, 138.6, 138.5, 138.0, 131.0, 130.9, 128.8, 128.6, 127.6, 124.5, 61.6, 52.0, 47.6, 44.7, 37.9, 37.2, 36.7, 30.5, 29.8, 25.0, 21.4, 18.4, 16.5, 14.1.

IR (neat) υ_{max} 2958, 2848, 2369, 1710, 1489, 1234, 1112, 965, 786, 720 cm^{-1}.

$[\alpha]_{589}^{25}$ = +46.5 (c = 0.5, $CHCl_3$).



(1*R*,4a*S*,10a*R*)- **Methyl 6-acetyl-1,4a-dimethyl-7-(*p*-tolyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate**: **S19** was obtained as yellow foam (0.20 mmol scale of reaction; 78% yield). R*f* = 0.40 (10% EtOAc in n-hexane).

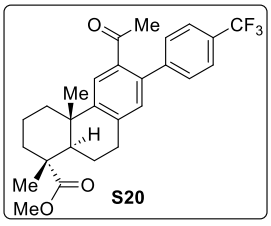
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (s, 1H), 7.19 (s, 4H), 7.02 (s, 1H), 3.66 (s, 3H), 2.96 – 2.91 (m, 2H), 2.38 (s, 4H), 2.26 – 2.21 (m, 1H), 1.96 (s, 3H), 1.91 – 1.82 (m, 1H), 1.79 – 1.75 (m, 2H), 1.72 (d, *J* = 3.1 Hz, 1H), 1.66 (d, *J* = 6.2 Hz, 1H), 1.55 (d, *J* = 12.8 Hz, 1H), 1.45 (dtd, *J* = 13.2, 4.8, 2.2 Hz, 1H), 1.28 (s, 3H), 1.25 (d, *J* = 0.7 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 196.5, 178.6, 150.1, 144.5, 142.7, 129.4 127.4, 122.6, 117.3, 52.1, 47.4, 44.2, 37.8, 37.4, 36.5, 29.9, 29.5, 25., 20.9, 18.3, 16.5.

IR (neat) υ_{max} 2958, 2848, 2369, 1710, 1489, 1234, 1112, 965, 786, 720 cm-1.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{27}H_{32}O_3 + H]^+$ 405.2430, found 405.2426.

$[\alpha]^{25}_{589}$ = +63.5 (c = 0.5, $CHCl_3$).



(1*R*,4a*S*,10a*R*)- **Methyl -6-acetyl-1,4a-dimethyl-7-(4-(trifluoromethyl)phenyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate**: **S20** was obtained as yellow foam (0.25 mmol scale of reaction; 80% yield). R*f* = 0.35 (10% EtOAc in n-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 – 7.62 (m, 2H), 7.52 (s, 1H), 7.42 – 7.39 (m, 2H), 7.00 (s, 1H), 3.67 (s, 3H), 2.97 – 2.93 (m, 2H), 2.38 (d, *J* = 12.5 Hz, 1H), 2.26 – 2.22 (m, 1H), 2.07 (s,

3H), 1.86 (s, 1H), 1.84 – 1.79 (m, 2H), 1.76 (s, 2H), 1.74 (s, 1H), 1.69 (d, *J* = 3.7 Hz, 1H), 1.29 (s, 3H), 1.26 – 1.25 (m, 3H)..

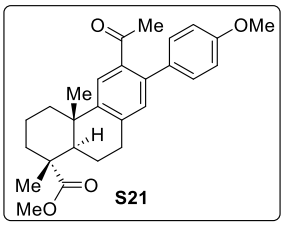
^{13}C NMR (125 MHz, $CDCl_3$): δ 178.9, 149.7, 144.8, 139, 131.2, 129.1, 125.4, 124.9, 77.2, 52, 47.6, 44.6, 37.9, 37.3, 36.6, 30.4, 29.8, 29.7, 25, 21.3, 18.4, 16.5.

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.44

IR (neat) υ_{max} 2958, 2848, 2369, 1710, 1489, 1234, 1112, 965, 786, 720 cm-1.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{27}H_{30}F_3O_3 + H]^+$ 459.2147, found 459.2140.

$[\alpha]_{589}^{25}$ = +60.5 (c = 0.5, $CHCl_3$).



(1*R*,4a*S*,10a*R*)- **Methyl 6-acetyl-7-(4-methoxyphenyl)-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate**: **S21**was obtained as yellow foam (0.20 mmol scale of reaction; 80% yield). R*f* = 0.25 (10% EtOAc in n-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44 (s, 1H), 7.24 – 7.22 (m, 1H), 7.21 (d, *J* = 2.1 Hz, 1H), 7.01 (d, *J* = 1.0 Hz, 1H), 6.94 (s, 1H), 6.91 (s, 1H), 3.83 (s, 3H), 3.66 (s, 3H), 2.94 (dd, *J* = 9.0, 4.6 Hz, 2H), 2.37 (d, *J* = 12.2 Hz, 1H), 2.23 (dd, *J* = 12.5, 2.3 Hz, 1H), 1.96 (s, 3H), 1.89 – 1.82 (m, 1H), 1.77 (d, *J* = 11.2 Hz, 2H), 1.66 (d, *J* = 6.3 Hz, 1H), 1.54 (d, *J* = 12.7 Hz, 1H), 1.45 (dd, *J* = 13.0, 2.3 Hz, 1H), 1.28 (s, 3H), 1.24 (d, *J* = 0.7 Hz, 3H).

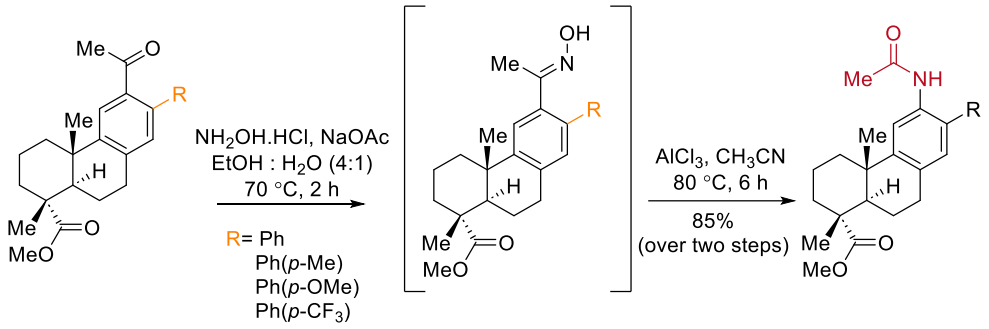
^{13}C NMR (125 MHz, $CDCl_3$): δ 196.5, 178.6, 150.1, 144.5, 142.7, 129.4, 127.4, 122.6, 117.3, 52.1, 47.4, 44.2, 37.8, 37.3, 36.5, 29.9, 29.5, 25, 20.9, 18.3, 16.5.

IR (neat) υ_{max} 2958, 2848, 2369, 1710, 1489, 1234, 1112, 965, 786, 720 cm-1.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{27}H_{32}O_4 + H]^+$ 421.2379, found 421.2381.

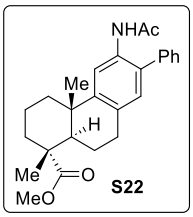
$[\alpha]^{25}_{589}$ = +61.5 (c = 0.5, $CHCl_3$).

Synthesis of biaryl acetanilide derivative:



The acetophenone (1.0 equiv.) was dissolved in EtOH (4 mL) in H_2O (1 mL). Sodium acetate (1.2 equiv.) and hydroxylamine hydrochloride (2.2 equiv.) were added before heating the mixture to reflux. After 1 h of stirring under reflux, the reaction was allowed to cool to ambient temperature and concentrated to dryness *in vacuo*. To the residue was added EtOAc (7 mL X 3) and washed with H_2O (5 mL X 2). The organic layer was dried (Na_2SO_4), filtered and concentrated *in vacuo* to afford the crude product oxime, which was used in the next reaction without further purification.

A mixture of oxime (1.0 equiv.) and anhydrous $AlCl_3$ (1.0 equiv.) in acetonitrile (5 mL) was stirred for 4 h at 80˚C under N_2. The mixture was evaporated under reduced pressure to dryness. The residue was washed with dichloromethane (10 mL X 2) and the mixture was evaporated under reduced pressure. Finally, the crude products were purified by flash chromatography with 60% EtOAc in *n*-hexane to afford acetanilide as brown foam (50 mg, 85% yield).



(1*R*,4a*S*,10a*R*) **Methyl -6-acetamido-1,4a-dimethyl-7-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [**S22**]: Following the general procedure **S22** was

obtained as brown foam (0.10 mmol scale of reaction; 85% yield). R_f = 0.2 (20% EtOAc in *n*-hexane).

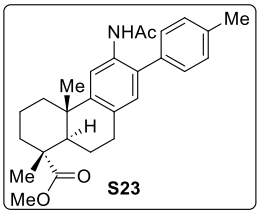
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.43 – 7.35 (m, 4H), 7.07 (s, 1H), 6.94 (s, 1H), 3.69 (s, 3H), 2.90 (s, 2H), 2.42 (d, *J* = 13.0 Hz, 1H), 2.28 (d, *J* = 12.5 Hz, 1H), 2.03 (s, 4H), 1.88 (t, *J* = 11.1 Hz, 2H), 1.80 (t, *J* = 9.9 Hz, 4H), 1.69 (s, 1H), 1.32 (s, 3H), 1.30 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 179.1, 168.3, 149.7, 138.3, 132.4, 131.4, 130.4, 130.1, 129.2, 128.9, 127.7, 118.2, 52, 47.8, 44.8, 38, 37.4, 36.7, 29.4, 24.9, 24.5, 21.6, 18.5, 16.5.

IR (neat) υ_{max} 2968, 1745, 1690, 1564, 1215 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{26}H_{31}NO_3 + H]^+$ 406.2382, found 406.2367.

$[\alpha]^{25}_{589}$ = +76.2 (c = 0.6, $CHCl_3$).



(1*R*,4a*S*,10a*R*) **Methyl -6-amino-1,4a-dimethyl-7-(p-tolyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [**S23**]: Following the general procedure **S23** was obtained as brown foam (0.12 mmol scale of reaction; 85% yield). R_f = 0.3 (20% EtOAc in *n*-hexane).

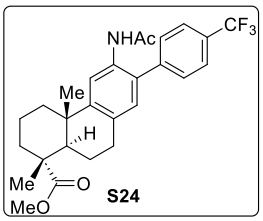
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.30 (d, *J* = 7.5 Hz, 2H), 7.09 – 7.05 (m, 1H), 7.01 (d, *J* = 8.5 Hz, 2H), 6.91 (s, 1H), 3.88 (s, 3H), 3.69 (s, 3H), 2.93 – 2.86 (m, 2H), 2.41 (d, *J* = 12.7 Hz, 1H), 2.27 (d, *J* = 2.2 Hz, 1H), 2.04 (s, 3H), 1.91 – 1.86 (m, 1H), 1.84 – 1.76 (m, 3H), 1.68 (d, *J* = 8.1 Hz, 1H), 1.31 (s, 3H), 1.30 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 179.1, 168.20, 149.5, 137.5, 135.2, 132.5, 131.2, 130.4, 129.85, 129.7, 129.1, 117.8, 51.9, 47.7, 44.8, 38, 37.4, 36.7, 29.7, 29.4, 24.9, 24.6, 21.6, 21.2, 18.5, 16.5.

IR (neat) υ_{max} 2968, 1745, 1690, 1564, 1215 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{26}H_{31}NO_3 + H]^+$ 406.2382, found 406.2387.

$[\alpha]^{25}_{589}$ = +76.2 (c = 0.6, $CHCl_3$).



(1*R*,4a*S*,10a*R*)- **Methyl -6-acetamido-1,4a-dimethyl-7-(4-(trifluoromethyl)phenyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [**S24**]: Following the general procedure **S24** was obtained as brown foam (0.12 mmol scale of reaction; 80% yield). R_f = 0.20 (20% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 2H), 6.91 (s, 1H), 6.86 (s, 1H), 3.66 (s, 3H), 2.90 – 2.82 (m, 2H), 2.38 – 2.31 (m, 1H), 2.24 (dd, *J* = 12.5, 2.2 Hz, 1H), 2.02 (s, 3H), 1.90 – 1.79 (m, 2H), 1.76 (s, 3H), 1.66 (d, *J* = 6.1 Hz, 1H), 1.56 (d, *J* = 11.6 Hz, 1H), 1.28 (s, 3H), 1.26 (s, 3H).

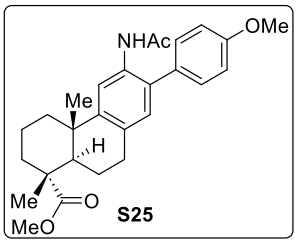
^{13}C NMR (125 MHz, $CDCl_3$): δ 179,174.7, 168.4,165.9,147.2, 142, 141, 132.4, 132.2, 132.1, 130.4, 129.6, 125.8, 119.4, 52, 47.7, 44.7, 37.9, 37.4, 36.7, 29.7, 24.9, 24.9, 24.4, 21.5, 18.5, 16.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.43

IR (neat) υ_{max} 2968, 1745, 1690, 1564, 1215 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{27}H_{30}F_3NO_3 + H]^+$ 474.2256, found 474.2247.

$[\alpha]^{25}_{589}$ = +76.2 (c = 0.6, $CHCl_3$).



(1*R*,4a*S*,10a*R*)- **Methyl -6-acetamido-7-(4-methoxyphenyl)-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate [S25]:** Following the general procedure **S25** was obtained as brown foam (0.12 mmol scale of reaction; 80% yield). R_f = 0.20 (30% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.30 (d, *J* = 7.5 Hz, 2H), 7.09 – 7.05 (m, 1H), 7.01 (d, *J* = 8.5 Hz, 2H), 6.91 (s, 1H), 3.88 (s, 3H), 3.69 (s, 3H), 2.93 – 2.86 (m, 2H), 2.41 (d, *J* = 12.7 Hz, 1H), 2.27 (d, *J* = 2.2 Hz, 1H), 2.04 (s, 3H), 1.91 – 1.86 (m, 1H), 1.84 – 1.76 (m, 3H), 1.68 (d, *J* = 8.1 Hz, 1H), 1.31 (s, 3H), 1.30 (s, 3H).

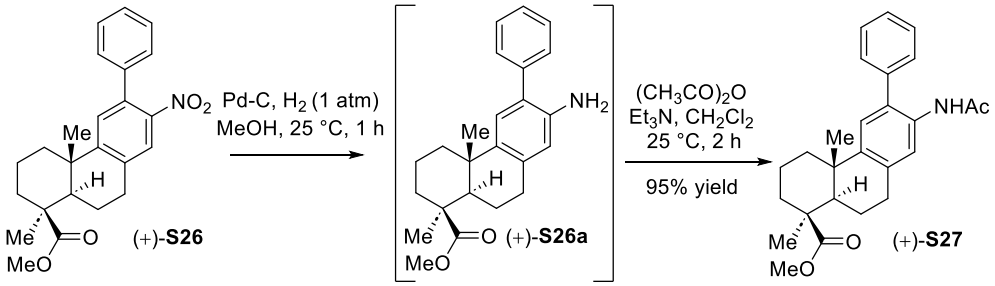
^{13}C NMR (125 MHz, $CDCl_3$): δ 179.1, 168.2, 159.2, 149.4, 132.6, 131.2, 131.4, 130.4, 130.4, 130.4,129.6, 117.8, 114.4, 114.4, 55.4, 51.9, 47.7, 44.8, 38, 38, 36.7, 29.7, 24.9, 24.6, 21.6, 18.5, 16.5.

IR (neat) υ_{max} 2968, 1745, 1690, 1564, 1215 cm^{-1}.

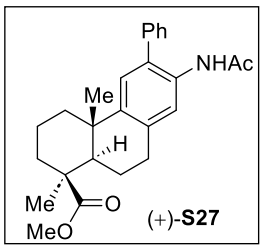
HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{27}H_{33}NO_4 + H]^+$ 430.2488, found 430.2488.

$[\alpha]^{25}_{589}$ = +76.2 (c = 0.6, $CHCl_3$).

Synthesis of compound (+)-S27:



Following the procedure described for (+)-**S3**, compound (+)-**S27** was prepared from (+)-**S26**. For the synthesis of compound (+)-**S26** see ref. 3.



Methyl (1*S*,4a*S*,10a*R***)-7-acetamido-1,4a-dimethyl-6-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-**S27**]: The compound **(**+**)-S27** was obtained as yellow gel (0.386 mmol scale of reaction, 149 mg, 95% over 2 steps). R_f = 0.35 (40% EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.45 (t, *J* = 7.3 Hz, 2H), 7.38 (d, *J* = 7.4 Hz, 1H), 7.33 (d, *J* = 6.8 Hz, 2H), 7.11 (s, 1H), 7.03 (s, 1H), 3.65 (s, 3H), 2.99 – 2.93 (m, 1H), 2.87 – 2.79 (m, 1H), 2.28 – 2.22 (m, 2H), 2.22 – 2.14 (m, 2H), 1.99 (s, 3H), 1.60 – 1.53 (m, 2H), 1.41 – 1.37 (m, 1H), 1.27 (s, 3H), 1.13 – 1.04 (m, 2H), 1.02 (s, 3H).

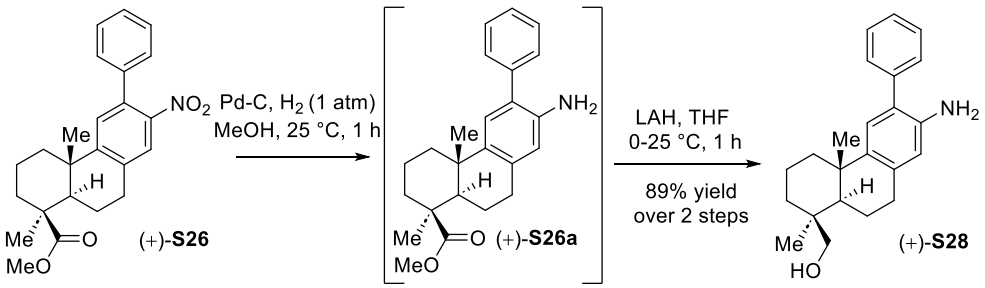
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.0, 168.4, 144.7, 138.7, 136.1, 131.9, 130.6, 129.4, 129.1, 127.8, 127.5, 122.1, 52.9, 51.4, 44.1, 39.5, 38.4, 37.7, 32.1, 28.6, 24.6, 23.1, 21.0, 20.0.

IR (film) υ_{max} 3300, 2906, 2510, 1720, 1640, 1500, 1213, 1154, 951, 718 cm^{-1}.

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd. for $[C_{26}H_{31}O_3N + H]^+$ 406.2377; found 406.2387.

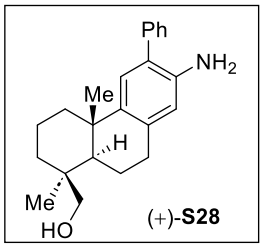
$[\alpha]_D^{25}$ = +65.25 (c = 0.4, $CHCl_3$).

Synthesis of compound (+)-S28:



In an oven-dried round-bottom flask compound **(+)-S26** (502 mg, 1.27 mmol, 1.0 equiv.) was taken in MeOH (20 mL) and degassed with N_2 balloon for 10 minutes. To this solution Pd/C (10% w/w) (50 mg) was added and a H_2 gas balloon (1 atm.) was placed with the reaction vessel and stirring continued until the full consumption of starting material (1 h), as confirmed by TLC analysis. The reaction mixture was filtered, evaporated to dryness under the reduced pressure. The crude product (+)-**S26a** was charged for the next step.

Next, in a round-bottom flask, compound (+)-**S26a** (1.27 mmol., 1.0 equiv.) was taken in dry THF (15 mL) and $LiAlH_4$ (39 mg, 1.02 mmol., 0.8 equiv.) was added to the reaction mixture portion wise and the reaction mixture at 25 ºC was stirring continued until the full consumption of starting material. Upon completion (1 h), as monitored by TLC analysis, it was extracted with EtOAc (6 mL X 2). The organic layers were dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. The crude product was purified by flash column chromatography with 20% EtOAc in *n*-hexane to afford (+)-**S28** as white foam (380 mg, 89% yield over 2 steps).



((1*S*,4a*S*,10a*R*)**-7-amino-1,4a-dimethyl-6-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methanol** [(+)-**S28**]: **(**+**)-S28** was obtained as white foam (1.27 mmol scale of reaction, 380 mg, 89% yield over 2 steps). R_f = 0.45 (20% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 – 7.42 (m, 4H), 7.36 (tt, *J* = 5.7, 2.7 Hz, 1H), 7.05 (s, 1H), 6.51 (s, 1H), 3.89 (d, *J* = 10.9 Hz, 1H), 3.60 – 3.55 (m, 1H), 2.95 – 2.78 (m, 3H), 2.30 (d, *J* =

12.9 Hz, 1H), 2.04 – 1.98 (m, 1H), 1.90 (d, *J* = 13.6 Hz, 1H), 1.77 – 1.66 (m, 2H), 1.62 (dt, *J* = 14.0, 3.6 Hz, 1H), 1.55 (dd, *J* = 12.7, 1.9 Hz, 1H), 1.51 – 1.44 (m, 1H), 1.22 (s, 3H), 1.09 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 141.1, 140.5, 139.8, 135.4, 129.2, 128.7, 127.0, 126.8, 126.3, 115.6, 65.3, 51.6, 39.2, 38.7, 37.2, 35.3, 30.8, 26.9, 25.9, 19.2, 19.0.

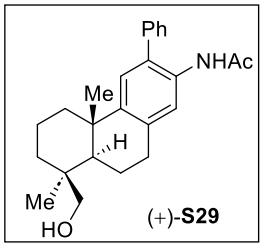
IR (film) υ_{max} 3240, 2930, 1740, 1589, 1590, 1217, 1154, 946, 796 cm^{-1}.

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd. for $[C_{23}H_{29}ON + H]^+$ 336.2322; found 336.2328.

$[\alpha]^{25}_{589}$ = +78.45 (c = 0.3, $CHCl_3$).

Synthesis of compound (+)-S29:

Following the procedure described for (+)-**S4**, compound (+)-**S29** was prepared from (+)-**S28**.



***N*-((**4b*S*,8*S*,8a*R*)**-8-(Hydroxymethyl)-4b,8-dimethyl-3-phenyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-2-yl)acetamide** [(+)-**S29**]: (+)-**S29** was obtained as yellow oil (0.378 mmol scale of reaction, 124 mg, 87%). R_f = 0.35 (40% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 7.5 Hz, 2H), 7.14 (s, 1H), 7.07 (s, 1H), 3.88 (d, *J* = 10.9 Hz, 1H), 3.58 (d, *J* = 10.9 Hz, 1H), 3.02 (dd, *J* = 17.6, 6.5 Hz, 1H), 2.91 (ddd, *J* = 17.8, 11.2, 7.3 Hz, 1H), 2.30 (d, *J* = 12.9 Hz, 1H), 2.03 (s, 3H), 1.91 (d, *J* = 13.9 Hz, 1H), 1.77 (dd, *J* = 12.4, 6.6 Hz, 1H), 1.73 (d, *J* = 5.5 Hz, 1H), 1.70 (s, 1H), 1.62 (d, *J* = 13.9 Hz, 1H), 1.54 (d, *J* = 12.7 Hz, 1H), 1.46 (t, *J* = 12.3 Hz, 1H), 1.21 (s, 3H), 1.09 (s, 3H), 1.06 – 1.01 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 168.4, 146.3, 138.7, 135.5, 131.7, 130.4, 129.3, 129.0, 127.7, 126.4, 122.2, 65.2, 51.2, 39.0, 38.7, 37.6, 35.2, 30.9, 26.8, 25.8, 24.5, 19.1, 18.9.

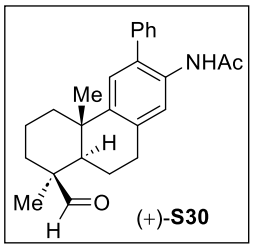
IR (film) υ_{max} 3460, 3210, 2850, 1690, 1580, 1500, 1213, 1154, 987, 736 cm^{-1}.

HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. for $[C_{25}H_{31}O_2N + H]^+$ 378.2428; found 378.2426.

$[\alpha]^{25}_{589}$ = +44.49 (c = 0.3, $CHCl_3$).

Synthesis of compound (+)-S30:

Following the procedure described for (+)-**S4**, compound (+)-**S30** was prepared from (+)-**S29**.



***N*-((**4b*S*,8*S*,8a*R*)**-8-Formyl-4b,8-dimethyl-3-phenyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-2-yl)acetamide** [(+)-**S30**]: [(+)-**S30** was obtained as yellow oil (0.288 mmol scale of reaction, 86 mg, 79%). R_f = 0.30 (20% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.86 (s, 1H), 7.95 (s, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.42 (d, *J* = 7.3 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.14 (s, 1H), 7.07 (s, 1H), 3.08 (dd, *J* = 17.2, 6.0 Hz, 1H), 2.96 (ddd, *J* = 17.7, 11.9, 6.8 Hz, 1H), 2.29 – 2.23 (m, 3H), 2.07 (dd, *J* = 12.9, 6.2 Hz, 1H), 2.03 (s, 3H), 1.77 (dd, *J* = 14.3, 3.5 Hz, 1H), 1.74 – 1.71 (m, 1H), 1.69 – 1.62 (m, 2H), 1.43 (dt, *J* = 11.6, 7.0 Hz, 1H), 1.14 (s, 3H), 1.09 (s, 3H).

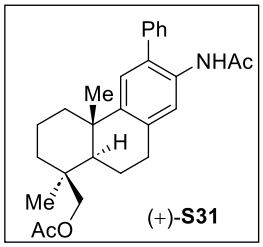
^{13}C NMR (125 MHz, $CDCl_3$): δ 205.6, 168.3, 144.0, 138.5, 135.2, 132.0, 130.5, 129.3, 129.0, 127.8, 126.8, 122.0, 51.9, 48.6, 38.4, 37.9, 33.8, 31.2, 24.5, 24.2, 24.1, 19.2, 18.8.

IR (film) υ_{max} 3328, 2906, 2510, 1769, 1620, 1431, 1320, 1213, 1154, 951, 718, 650 cm^{-1}.

$[\alpha]_D^{25}$ = +85.78 (*c* = 0.5, $CHCl_3$).

Synthesis of compound (+)-S31:

Following the procedure described for (+)-**S6**, compound (+)-**S31** was prepared from (+)-**S28**.



((1*S*,4a*S*,10a*R*)**-7-Acetamido-1,4a-dimethyl-6-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl acetate** [(+)-**S31**]: (+)-**S31** was obtained as yellow oil (0.336 mmol scale of reaction, 126 g, 89%). R_f = 0.35 (40% EtOAc in hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.47 (d, *J* = 7.4 Hz, 2H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.38 – 7.35 (m, 2H), 7.14 (s, 1H), 7.08 (s, 1H), 4.35 (d, *J* = 11.0 Hz, 1H), 4.02 (d, *J* = 11.1 Hz, 1H), 3.02 (dd, *J* = 17.4, 6.3 Hz, 1H), 2.91 (ddd, *J* = 17.9, 11.6, 7.3 Hz, 1H), 2.47 – 2.35 (m, 1H), 2.30 (d, *J* = 12.8 Hz, 1H), 2.09 (s, 3H), 2.02 (s, 3H), 1.78 – 1.67 (m, 3H), 1.63 – 1.59 (m, 1H), 1.56 – 1.53 (m, 1H), 1.46 (dd, *J* = 13.1, 4.2 Hz, 1H), 1.24 (s, 3H), 1.12 (dd, *J* = 13.8, 4.0 Hz, 1H), 1.08 (s, 3H).

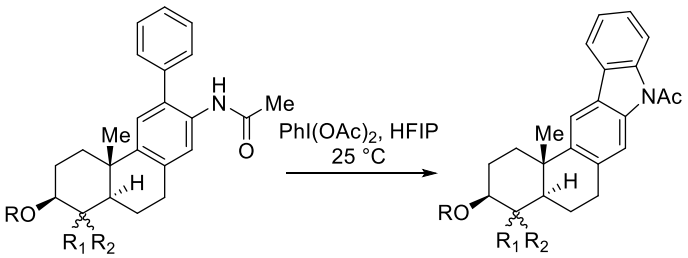
^{13}C NMR (125 MHz, $CDCl_3$): δ 171.4, 168.4, 146.1, 138.7, 135.4, 131.8, 130.5, 129.3, 129.0, 127.7, 126.4, 122.1, 66.9, 51.3, 38.8, 37.6, 37.1, 36.0, 30.9, 27.4, 25.7, 24.5, 21.0, 19.2, 18.9.

IR (film): υ_{max} 3410, 2915, 2550, 1700, 1690, 1530, 1253, 1145, 956, 738 cm^{-1}.

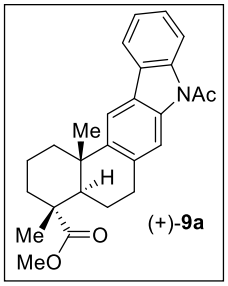
HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. for $[C_{27}H_{33}O_3N + H]^+$ 420.2533; found 420.2538.

$[\alpha]_D^{25}$ = +52.78 (*c* = 0.6, $CHCl_3$).

General procedure for PIDA Mediated Intramolecular C-N bond Formation:



In an oven-dried round-bottom flask acetanilide (1.0 equiv.) was taken in 1,1,1,3,3,3-hexafluoropropan-2-ol under an inert atmosphere. To the solution $PhI(OAc)_2$ (1.3 equiv.) was added and stirred the mixture at room temperature. After completion of reaction (monitored by TLC), it was quenched with saturated $Na_2S_2O_3$ solution then reaction mixture was extracted with CH_2Cl_2 (5 mL X 3). The organic layers were dried over Na_2SO_4 and concentrated on rotary evaporator under reduced pressure. Then the crude product was purified by flash column chromatography with 20- 60% EtOAc in *n*-Hexane to afford pentacyclic compounds.



Methyl (4*R*,4a*R*,13b*S*)**-8-acetyl-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazole-4-carboxylate** [(+)-**9a**]: (+)-**9a** was obtained as white foam (0.2 mmol scale of reaction; 77 mg; 97%). R_f = 0.3 (10 % EtOAc in *n*-hexane).

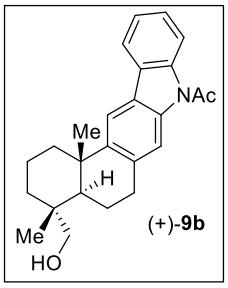
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.3 Hz, 1H), 7.97 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.87 (d, *J* = 6.1 Hz, 2H), 7.45 (ddd, *J* = 8.5, 7.3, 1.4 Hz, 1H), 7.38 (td, *J* = 7.5, 1.0 Hz, 1H), 3.72 (s, 3H), 3.13 (dd, *J* = 9.0, 4.7 Hz, 2H), 2.86 (s, 3H), 2.53 (dd, *J* = 12.0, 3.1 Hz, 1H), 2.33 (dd, *J* = 12.6, 2.4 Hz, 1H), 1.98 – 1.90 (m, 1H), 1.89 – 1.80 (m, 3H), 1.76 – 1.70 (m, 1H), 1.70 – 1.63 (m, 1H), 1.54 (dtd, *J* = 13.3, 5.0, 2.5 Hz, 1H), 1.35 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 179.0, 170.0, 145.8, 138.9, 137.0, 135.1, 126.9, 126.8, 124.7, 123.6, 119.4, 116.4, 116.2, 115.1, 52.0, 47.6, 44.9, 38.5, 37.4, 36.7, 30.9, 27.7, 25.5, 21.7, 18.6, 16.6.

IR (neat) υ_{max} 3391, 2887, 1717, 1673, 1399, 1206, 997, 765 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ H]^+$ calcd. for $[C_{26}H_{29}O_3N + H]^+$ 404.2226, found 404.2233.

$[\alpha]^{25}_{589}$ = +34.70 (*c* = 0.87, CH_3OH).



1-((4*R*,4a*R*,13b*S*)**-4-(Hydroxymethyl)-4,13b-dimethyl-1,2,3,4,4a,5,6,13b-octahydro-8H-naphtho[2,1-*b*]carbazol-8-yl)ethan-1-one** [(+)-**9b**]: (+)-**9b** was obtained as colourless foam (0.24 mmol scale of reaction; 80.5 mg; 90%). R_f = 0.3 (40 % EtOAc in *n*-hexane).

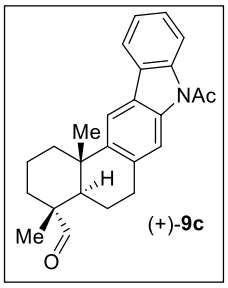
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.89 (s, 1H), 7.85 (s, 1H), 7.47 – 7.42 (m, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 3.54 (d, *J* = 10.9 Hz, 1H), 3.28 (d, *J* = 10.9 Hz, 1H), 3.13 (ddd, *J* = 14.9, 10.2, 7.5 Hz, 2H), 2.85 (s, 3H), 2.51 (dt, *J* = 12.9, 3.5 Hz, 1H), 1.94 – 1.80 (m, 4H), 1.77 (dd, *J* = 12.3, 2.3 Hz, 1H), 1.55 (qd, *J* = 13.2, 4.0 Hz, 2H), 1.45 (dt, *J* = 12.7, 3.6 Hz, 1H), 1.33 (s, 3H), 0.96 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 170.0, 146.3, 138.9, 136.8, 135.3, 126.9, 126.7, 124.6, 123.6, 119.4, 116.4, 116.1, 115.2, 72.1, 43.8, 38.9, 38.0, 37.8, 35.1, 31.0, 27.7, 25.6, 19.0, 18.7, 17.5.

IR (neat): υ_{max} 3341, 2888, 2497, 1762, 1683, 1564, 1197, 1161, 973 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ H]^+$ calcd. for $[C_{25}H_{29}O_2N + H]^+$ 376.2271, found 376.2282.

$[\alpha]^{25}_{589}$ = +29.90 (*c* = 0.68, CH_3OH).



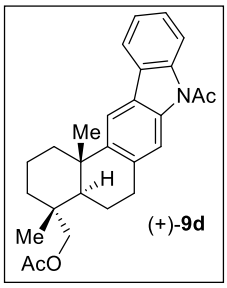
(4*R*,4a*R*,13b*S*)**-8-Acetyl-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazole-4-carbaldehyde** [(+)-**9c**]: (+)-**9c** was obtained as colourless liquid (0.19 mmol scale of reaction; 66 mg; 91%). R_f = 0.5 (20 % EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.34 (s, 1H), 8.21 (d, *J* = 8.4 Hz, 1H), 7.98 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.90 (d, *J* = 4.3 Hz, 2H), 7.46 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1H), 7.39 (td, *J* = 7.5, 1.0 Hz, 1H), 3.17 – 3.10 (m, 2H), 2.87 (s, 3H), 2.58 (dt, *J* = 13.1, 3.6 Hz, 1H), 2.02 (dd, *J* = 12.8, 2.0 Hz, 1H), 1.92 (ttd, *J* = 10.9, 5.2, 2.5 Hz, 3H), 1.64 (dd, *J* = 12.7, 4.8 Hz, 2H), 1.57 – 1.51 (m, 1H), 1.45 – 1.40 (m, 1H), 1.34 (s, 3H), 1.24 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 206.1, 170.0, 145.1, 138.9, 137.1, 134.8, 126.9, 126.8, 124.8, 123.6, 119.4, 116.4, 116.3, 115.1, 49.8, 42.9, 38.3, 36.8, 32.1, 30.7, 27.7, 25.5, 21.4, 17.8, 14.2.

IR (neat): υ_{max} 2937, 2487, 1741, 1638, 1493, 1289, 1199, 903, 698 cm^{-1}.

$[\alpha]^{25}_{589}$ = +32.10 (*c* = 0.57, CH_3OH).



((4*R*,4a*R*,13b*S***)-8-Acetyl-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazol-4-yl)methyl acetate** [(+)-**9d**]: (+)-**9d** was obtained as white foam (0.25 mmol scale of reaction; 100 mg; 96%). R_f = 0.35 (15 % EtOAc in *n*-hexane).

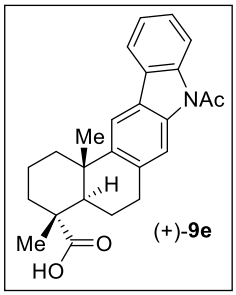
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 10.2 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 4.04 (d, *J* = 11.0 Hz, 1H), 3.77 (d, *J* = 11.0 Hz, 1H), 3.21 – 3.13 (m, 1H), 3.10 – 3.02 (m, 1H), 2.87 (s, 3H), 2.53 (dt, *J* = 12.9, 3.4 Hz, 1H), 2.07 (s, 3H), 1.93 – 1.83 (m, 3H), 1.82 – 1.76 (m, 1H), 1.74 (dd, *J* = 11.5, 3.4 Hz, 1H), 1.58 (dd, *J* = 13.1, 3.8 Hz, 1H), 1.52 (dt, *J* = 9.0, 4.4 Hz, 2H), 1.34 (s, 3H), 1.02 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 171.3, 170.0, 146.1, 138.9, 136.9, 135.2, 126.9, 126.8, 124.7, 123.6, 119.4, 116.4, 116.2, 115.3, 72.5, 44.3, 38.8, 37.9, 36.9, 35.6, 31.1, 27.7, 25.6, 21.0, 19.1, 18.6, 17.6.

IR (neat) υ_{max} 2961, 2593, 1732, 1681, 1606, 1252, 1189, 967, 761 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{27}H_{31}O_3N + Na]^+$ 440.2196, found 440.2235.

$[\alpha]^{25}_{589}$ = +31.30 (*c* = 0.41, CH_3OH).



(4*R*,4a*R*,13b*S***)-8-Acetyl-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazole-4-carboxylic acid** [(+)-**9e**]: (+)-**9e** was obtained as light yellow foam (0.27 mmol scale of reaction; 94 mg; 89% yield). R_f = 0.3 (40 % EtOAc in *n*-hexane).

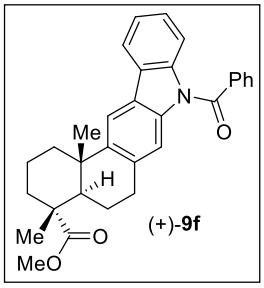
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.3 Hz, 1H), 7.97 (d, *J* = 7.5 Hz, 1H), 7.88 (d, *J* = 4.0 Hz, 2H), 7.49 – 7.42 (m, 1H), 7.38 (q, *J* = 6.5, 5.7 Hz, 1H), 3.16 (d, *J* = 7.6 Hz, 2H), 2.87 (s, 3H), 2.55 (d, *J* = 12.8 Hz, 1H), 2.35 (d, *J* = 12.5 Hz, 1H), 1.99 (t, *J* = 10.5 Hz, 1H), 1.94 – 1.79 (m, 4H), 1.73 – 1.62 (m, 2H), 1.37 (s, 3H), 1.34 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 184.5, 170.0, 145.7, 138.9, 137.0, 135.1, 126.9, 126.8, 124.7, 123.6, 119.4, 116.4, 116.3, 115.1, 47.4, 44.7, 38.4, 37.4, 36.8, 30.9, 27.6, 25.5, 21.8, 18.6, 16.3.

IR (neat) υ_{max} 3387, 3010, 2953, 2467, 1683, 1475, 1365, 1107, 691 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{25}H_{27}O_3N + Na]^+$ 412.1883, found 412.1877.

$[\alpha]^{25}_{589}$ = +25.80 (*c* = 0.46, CH_3OH).



Methyl (4*R*,4a*R*,13b*S***)-8-benzoyl-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazole-4-carboxylate** [(+)-**9f**]: (+)-**9f** was obtained as light yellow foam (0.237 mmol scale of reaction; 78 mg; 71% yield). R_f = 0.3 (10 % EtOAc in *n*-hexane).

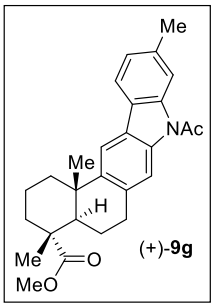
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.7 Hz, 1H), 7.89 (s, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.22 (s, 1H), 3.70 (s, 3H), 2.95 (dd, *J* = 10.1, 7.1 Hz, 2H), 2.54 (d, *J* = 12.7 Hz, 1H), 2.30 (dd, *J* = 12.5, 2.3 Hz, 1H), 1.87 (dt, *J* = 33.2, 13.5 Hz, 4H), 1.70 (dd, *J* = 17.9, 10.6 Hz, 2H), 1.50 – 1.45 (m, 1H), 1.34 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 179.1, 169.5, 145.8, 139.3, 137.5, 136.0, 134.7, 132.1, 128.9, 128.8, 126.6, 126.2, 124.3, 123.3, 119.4, 115.9, 115.8, 115.0, 52.0, 47.6, 44.9, 38.5, 37.5, 36.7, 30.7, 25.5, 21.7, 18.6, 16.6.

IR (neat): υ_{max} 3188, 2934, 2849, 1709, 1678, 1456, 1369, 1179, 918, 682 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{31}H_{31}O_3N + Na]^+$ 488.2196, found 488.2179.

$[\alpha]^{25}_{589}$ = +38.40 (*c* = 0.71, CH_3OH).



Methyl (4*R*,4a*R*,13b*S*)**-8-acetyl-4,10,13b-trimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazole-4-carboxylate** [(+)-**9g**]: (+)-**9g** was obtained as yellow gel (0.269 mmol scale of reaction; 103.5 mg; 92%). R_f = 0.2 (10 % EtOAc in *n*-hexane).

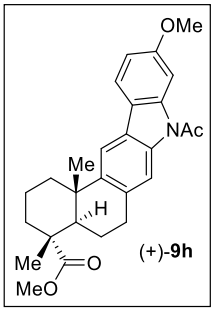
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.82 (q, *J* = 4.7 Hz, 3H), 7.20 (d, *J* = 7.9 Hz, 1H), 3.71 (s, 3H), 3.12 (dd, *J* = 9.3, 4.7 Hz, 2H), 2.86 (s, 3H), 2.55 (s, 4H), 2.37 – 2.28 (m, 1H), 1.95 (td, *J* = 13.2, 6.6 Hz, 1H), 1.87 – 1.81 (m, 2H), 1.72 (d, *J* = 8.9 Hz, 1H), 1.69 – 1.61 (m, 2H), 1.54 (dd, *J* = 12.3, 5.6 Hz, 1H), 1.35 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 179.1, 170.0, 145.7, 139.3, 137.0, 136.9, 134.5, 124.9, 124.8, 124.4, 119.0, 116.9, 116.1, 114.8, 52.0, 47.6, 44.9, 38.5, 37.4, 36.7, 30.9, 27.7, 25.4, 22.3, 21.8, 18.6, 16.6.

IR (neat) υ_{max} 3068, 2926, 1706, 1614, 1506, 1467, 1206, 1035, 738 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{27}H_{31}O_3N + Na]^+$ 418.2377, found 418.2399.

$[\alpha]^{25}_{589}$ = +44.4 (*c* = 0.81, CH_3OH).



Methyl (4*R*,4a*R*,13b*S*)**-8-acetyl-10-methoxy-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazole-4-carboxylate** [(+)-**9h**]: (+)-**9h** was obtained as yellow gel (0.245 mmol scale of reaction; 45 mg; 42% yield). R_f = 0.3 (10 % EtOAc in *n*-hexane).

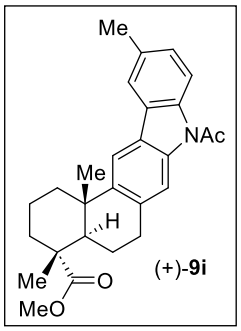
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (d, *J* = 2.4 Hz, 1H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.74 (s, 1H), 7.66 (s, 1H), 6.94 (dd, *J* = 8.5, 2.3 Hz, 1H), 3.90 (s, 3H), 3.68 (s, 3H), 3.10 – 3.03 (m, 3H), 2.48 (d, *J* = 13.1 Hz, 1H), 2.32 – 2.25 (m, 1H), 1.83 – 1.75 (m, 4H), 1.70 – 1.66 (m, 2H), 1.59 (d, *J* = 8.7 Hz, 1H), 1.49 (ddt, *J* = 12.5, 5.8, 2.5 Hz, 2H), 1.31 (s, 3H), 1.28 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 179.18, 170.22, 159.47, 145.81, 140.39, 136.88, 133.56, 125.02, 120.24, 119.80, 115.89, 114.57, 111.20, 102.33, 55.85, 52.11, 47.72, 45.02, 38.50, 37.47, 36.76, 30.97, 27.75, 25.49, 21.85, 18.69, 16.67.

IR (neat) υ_{max} 2976, 2904, 2837, 1831, 1713, 1589, 1176, 1023, 882, 680 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ H]^+$ calcd. for $[C_{27}H_{31}O_4N + H]^+$ 434.2331, found 434.2330.

$[\alpha]^{25}_{589}$ = +52.70 (*c* = 0.3, CH_3OH).



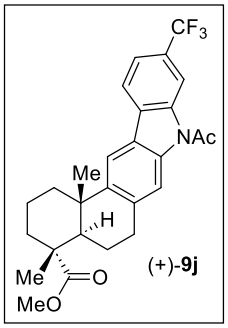
Methyl (4*R*,4a*R*,13b*S*)**-8-acetyl-4,11,13*b*-trimethyl-2,3,4,4a,5,6,8,13*b*-octahydro-1*H*-naphtho[2,1-*b*]carbazole-4-carboxylate** [(+)-**9i**]: (+)-**9i** was obtained as white foam (0.2 mmol scale of reaction; 58 mg; 69% yield). R_f = 0.22 (10 % EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.84 – 7.81 (m, 3H), 7.22 – 7.19 (m, 1H), 3.71 (s, 3H), 3.12 (dd, J = 9.0, 4.7 Hz, 2H), 2.86 (s, 3H), 2.55 (s, 3H), 2.52 (d, J = 13.6 Hz, 1H), 2.33 (dd, J = 12.7, 2.5 Hz, 1H), 1.99 – 1.92 (m, 1H), 1.91 – 1.84 (m, 2H), 1.83 – 1.73 (m, 2H), 1.72 – 1.63 (m, 2H), 1.35 (s, 3H), 1.32 (s, 3H).

13C NMR (126 MHz, $CDCl_3$): δ 179.0, 169.8, 145.7, 137.2, 137.0, 135.0, 133.2, 127.8, 127.2, 124.7, 119.6, 116.1, 115.0, 52.0, 47.6, 44.9, 385, 37.4, 36.7, 30.9, 27.6, 25.4, 21.8, 21.2, 18.6, 16.6.

IR (neat) υ_{max} 3391, 2887, 1717, 1673, 1399, 1206, 997, 765 cm^{-1}.

$[\alpha]^{25}_{589}$ = +37.47 (*c* = 0.85, CH_3OH).



Methyl (4*R*,4a*R*,13b*S*)**-8-acetyl-4,13b-dimethyl-10-(trifluoromethyl)-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazole-4-carboxylate** [(+)-**9j**]: (+)-**9j** was obtained as yellow foam (0.222 mmol scale of reaction; 87 mg; 83%). R_f = 0.25 (10 % EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.60 (s, 1H), 7.97 (dt, *J* = 8.2, 0.8 Hz, 1H), 7.87 (s, 1H), 7.68 (s, 1H), 7.60 – 7.55 (m, 1H), 3.69 (s, 3H), 3.13 – 3.06 (m, 2H), 2.82 (s, 3H), 2.53 – 2.45 (m, 1H), 2.29 (dd, *J* = 12.5, 2.4 Hz, 1H), 1.96 – 1.88 (m, 1H), 1.85 – 1.76 (m, 3H), 1.72 – 1.68 (m, 1H), 1.66 – 1.58 (m, 1H), 1.52 (ddt, *J* = 11.9, 4.7, 2.4 Hz, 1H), 1.32 (s, 3H), 1.29 (d, *J* = 0.7 Hz, 3H).

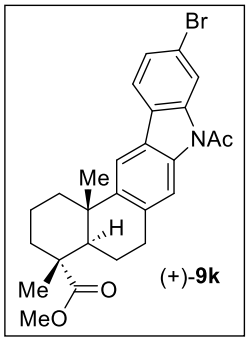
^{13}C NMR (125 MHz, $CDCl_3$): δ 179.1, 169.9, 146.3, 138.5, 137.5, 136.7, 123.7, 120.6, 120.6, 119.5, 116.1, 115.9, 52.1, 47.7, 44.9, 38.5, 37.5, 36.8, 31.1, 27.7, 25.5, 21.7, 18.6, 16.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.43

IR (neat) υ_{max} 3013, 2894, 1710, 1667, 1468, 1381, 1213, 1187, 993, 634 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ H]^+$ calcd. for $[C_{27}H_{28}F_3O_3N + H]^+$ 472.2100, found 472.2100.

$[\alpha]^{25}_{589}$ = +39.0 (*c* = 0.47, CH_3OH).



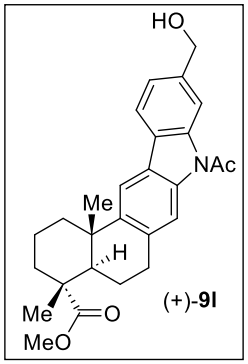
Methyl (4*R*,4a*R*,13b*S*)-8-acetyl-10-bromo-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1*H*-naphtho[2,1-*b*]carbazole-4-carboxylate [(+)-**9k**]: (+)-**9k** was obtained as white foam (0.2 mmol scale of reaction; 80 mg; 83%). R_f = 0.28 (10 % EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (s, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.74 (s, 1H), 7.59 – 7.57 (m, 1H), 7.51 (dd, J = 8.2, 1.7 Hz, 1H), 3.71 (s, 3H), 3.13 (dd, J = 9.1, 4.8 Hz, 2H), 2.86 (s, 3H), 2.34 – 2.30 (m, 2H), 1.94 – 1.87 (m, 2H), 1.84 (dd, J = 9.3, 2.8 Hz, 3H), 1.75 (d, J = 7.8 Hz, 2H), 1.65 (t, J = 4.4 Hz, 2H), 1.35 (s, 3H), 1.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.1, 169.9, 146.2, 139.8, 136.8, 135.7, 126.9, 125.7, 124.1, 120.4, 120.3, 119.9, 116.0, 115.4, 52.1, 47.7, 44.9, 38.5, 37.5, 36.8, 31.0, 27.7, 25.5, 21.7, 18.7, 16.7.

IR (neat) υ_{max} 3391, 2887, 1717, 1673, 1399, 1206, 997, 765 cm^{-1}.

$[\alpha]^{25}_{589}$ = +41.68 (*c* = 0.85, CH_3OH).



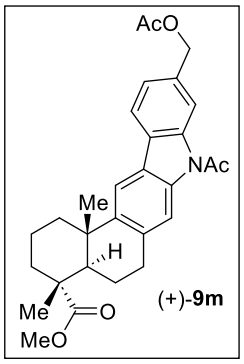
Methyl (4R,4aR,13bS)-8-acetyl-10-(hydroxymethyl)-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazole-4-carboxylate [(+)-**9l**]: (+)-**9l** was obtained as white foam (0.2 mmol scale of reaction; 80 mg; 83%). R_f = 0.28 (10 % EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (s, 1H), 7.86 (d, *J* = 0.8 Hz, 1H), 7.81 (s, 1H), 7.76 (s, 1H), 7.35 – 7.33 (m, 1H), 4.80 (s, 2H), 3.67 (s, 3H), 3.08 (dd, *J* = 9.1, 4.8 Hz, 2H), 2.79 (s, 3H), 2.48 (d, *J* = 12.5 Hz, 1H), 2.41 – 2.33 (m, 1H), 1.95 – 1.86 (m, 2H), 1.79 (q, *J* = 2.9 Hz, 3H), 1.71 – 1.66 (m, 2H), 1.31 (s, 3H), 1.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 179.2, 170.2, 145.9, 140, 137.2, 135.2, 124.6, 123.1, 122.8, 122.5, 119.4, 116.2, 115.2, 113.5, 65.9, 60.5, 52.1, 47.7, 45, 37.5, 36.8, 31, 27.8, 25.5, 18.9, 16.7, 14.3.

IR (neat) υ_{max} 3364, 2883, 1726, 1675, 1342, 1217, 974, 735 cm^{-1}.

$[\alpha]^{25}_{589}$ = +44.6 (*c* = 0.3, CH_3OH).



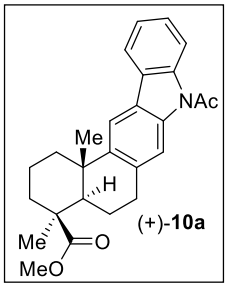
Methyl (4R,4aR,13bS)-10-(acetoxymethyl)-8-acetyl-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-b]carbazole-4-carboxylate [(+)-**9m**]: (+)-**9m** was obtained as white foam (0.2 mmol scale of reaction; 80 mg; 83%). R_f = 0.28 (10 % EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (s, 1H), 7.91 (dd, *J* = 7.9, 0.6 Hz, 1H), 7.84 (s, 1H), 7.76 (s, 1H), 7.36 (dd, *J* = 7.9, 1.5 Hz, 1H), 5.24 (s, 2H), 3.68 (s, 3H), 3.10 (dd, *J* = 9.0, 4.7 Hz, 2H), 2.85 (s, 3H), 2.48 (s, 1H), 2.36 – 2.25 (m, 1H), 2.12 (s, 3H), 1.96 – 1.86 (m, 2H), 1.83 (s, 1H), 1.77 (s, 2H), 1.69 (d, *J* = 8.3 Hz, 1H), 1.52 – 1.48 (m, 1H), 1.31 (s, 3H), 1.28 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 179.0, 171.0, 170.0, 145.9, 139.1, 137.2, 135.4, 134.6, 126.8, 124.4, 124.1, 119.4, 116.9, 116.0, 115.4, 67.0, 52.1, 47.6, 44.9, 38.4, 37.4, 36.7, 31.0, 27.7, 25.4, 21.7, 21.1, 18.6, 16.6.

IR (neat) υ_{max} 3365, 2877, 1765, 1623, 1344, 1225, 987, 745 cm^{-1}.

$[\alpha]^{25}_{589}$ = +53.4 (*c* = 0.85, CH_3OH).



(4*S*,4a*R*,13b*S***)-Methyl 8-acetyl-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazole-4-carboxylate** [(+)-**10a**]: (+)-**10a** was obtained as yellow foam (0.236 mmol scale of reaction, 88 mg, 92%). R_f = 0.65 (10% EtOAc in hexane).

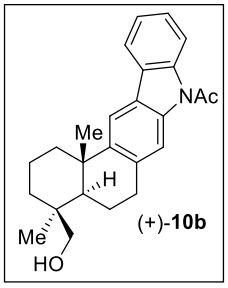
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.91 (s, 1H), 7.88 (s, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 3.71 (s, 3H), 3.14 (dd, *J* = 16.9, 5.3 Hz, 1H), 3.08 – 2.99 (m, 1H), 2.88 (s, 3H), 2.49 (d, *J* = 12.7 Hz, 1H), 2.32 (dd, *J* = 27.4, 13.8 Hz, 2H), 2.11 (dq, *J* = 21.3, 8.7, 6.8 Hz, 2H), 1.73 (d, *J* = 13.4 Hz, 1H), 1.66 (d, *J* = 12.3 Hz, 1H), 1.56 – 1.50 (m, 1H), 1.34 (s, 3H), 1.20 – 1.17 (m, 1H), 1.15 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 177.9, 170.0, 144.3, 138.9, 136.9, 135.5, 126.9, 126.8, 124.9, 123.6, 119.4, 116.6, 116.3, 116.1, 52.9, 51.3, 44.1, 40.0, 38.7, 37.6, 33.2, 28.6, 27.7, 23.6, 21.2, 20.1.

IR (film): υ_{max} 2950, 2510, 1710, 1680, 1530, 1213, 1100, 990 cm^{-1}.

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $[C_{26}H_{29}O_3N + H]^+$ 404.2220; found 404.2224.

$[\alpha]^{25}_{589}$ = +86.27 (c = 0.3, $CHCl_3$).



1-((4*S*,4a*R*,13b*S*)**-4-(Hydroxymethyl)-4,13b-dimethyl-2,3,4,4a,5,6-hexahydro-1H-naphtho[2,1-*b*]carbazol-8(13bH)-yl)ethanone** [(+)-**10b**]: (+)-**10b** was obtained as yellow foam (0.232 mmol scale of reaction, 76 mg, 88% yield). R_f = 0.60 (20% EtOAc in *n*-hexane).

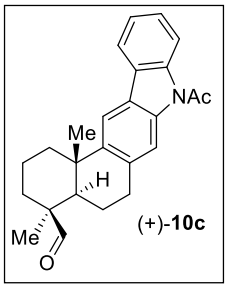
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 7.6 Hz, 1H), 7.89 (s, 1H), 7.87 (s, 1H), 7.45 (t, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 3.96 – 3.91 (m, 1H), 3.63 (d, *J* = 11.0 Hz, 1H), 3.17 (dd, *J* = 17.3, 6.6 Hz, 1H), 3.07 (td, *J* = 10.8, 10.2, 5.6 Hz, 1H), 2.87 (d, *J* = 1.9 Hz, 3H), 2.55 (d, *J* = 12.7 Hz, 1H), 2.09 (dd, *J* = 13.2, 7.4 Hz, 1H), 1.96 (d, *J* = 14.0 Hz, 1H), 1.82 (tt, *J* = 12.9, 7.1 Hz, 2H), 1.75 – 1.70 (m, 1H), 1.61 (d, *J* = 12.9 Hz, 2H), 1.29 – 1.28 (m, 3H), 1.12 (d, *J* = 1.8 Hz, 3H), 1.10 – 1.06 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 170.0, 146.1, 138.9, 136.9, 135.0, 126.9, 126.8, 124.7, 123.6, 119.4, 116.3, 116.1, 115.5, 65.3, 51.3, 39.4, 38.8, 38.0, 35.2, 32.0, 27.7, 26.8, 26.2, 19.3, 19.1.

IR (film): υ_{max} 3350, 2900, 2510, 1770, 1690, 1566, 1213, 1150, 936 cm^{-1}.

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $[C_{25}H_{29}O_2N + H]^+$ 376.2271; found 376.2272.

$[\alpha]^{25}_{589}$ = +76.56 (*c* = 0.1, $CHCl_3$).



(4*S*,4a*R*,13b*S*)**-8-Acetyl-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazole-4-carbaldehyde** [(+)-**10c**]: (+)-**10c** was obtained as colorless oil (0.15 mmol scale of reaction, 40.6 mg, 73% yield). R_f = 0.75 (20% EtOAc in *n*-hexane).

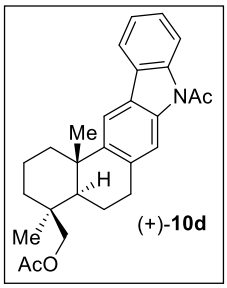
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.91 (s, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.98 – 7.93 (m, 2H), 7.90 (s, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 3.23 (dd, *J* = 16.9, 5.9 Hz, 1H), 3.13 (ddd, *J* = 17.5, 11.6, 6.7 Hz, 1H), 2.88 (s, 3H), 2.52 (d, *J* = 12.9 Hz, 1H), 2.31 (d, *J* = 14.4 Hz, 2H), 2.16 (dd, *J* = 12.6, 6.1 Hz, 1H), 1.86 (t, *J* = 14.0 Hz, 1H), 1.81 – 1.72 (m, 2H), 1.57 – 1.53 (m, 1H), 1.20 (s, 1H), 1.18 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 205.6, 170.0, 143.9, 137.1, 134.7, 126.9, 126.7, 124.9, 123.6, 119.5, 116.3, 116.2, 116.0, 52.0, 48.7, 38.9, 38.3, 33.9, 32.3, 27.7, 24.6, 24.2, 19.3, 19.0.

IR (film): υ_{max} 2956, 255, 1756, 1640, 1485, 1320, 1213, 1196, 910, 715, 667 cm^{-1}.

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd. for $[C_{25}H_{27}O_2N + H]^+$ 374.2115; found 374.2108.

$[\alpha]^{25}_{589}$ = +54.13 (*c* = 0.4, $CHCl_3$).



((4*S*,4a*R*,13b*S*)**-8-Acetyl-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazol-4-yl)methyl acetate** [(+)-**10d**]: (+)-**10d** was obtained as yellow oil (0.197 mmol scale of reaction, 67 mg, 81%). R_f = 0.6 (10% EtOAc in hexane).

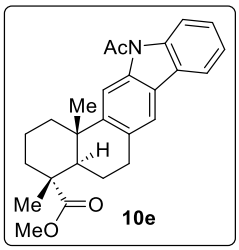
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.3 Hz, 1H), 7.94 – 7.91 (m, 1H), 7.85 (d, *J* = 6.4 Hz, 2H), 7.43 – 7.39 (m, 1H), 7.36 – 7.32 (m, 1H), 4.36 (d, *J* = 11.1 Hz, 1H), 4.04 (dd, *J* = 11.1, 1.1 Hz, 1H), 3.17 – 3.11 (m, 1H), 3.08 – 2.98 (m, 1H), 2.83 (s, 3H), 2.54 – 2.48 (m, 1H), 2.08 (s, 3H), 1.83 (dt, *J* = 11.8, 2.0 Hz, 2H), 1.79 – 1.67 (m, 2H), 1.61 – 1.57 (m, 2H), 1.56 – 1.51 (m, 1H), 1.28 (s, 3H), 1.15 – 1.10 (m, 1H), 1.07 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 170.0, 145.9, 138.9, 136.9, 134.9, 126.9, 126.8, 124.8, 123.6, 119.4, 116.3, 116.2, 115.5, 67.0, 51.4, 39.3, 38.0, 37.2, 36.0, 31.9, 27.6, 27.4, 26.1, 21.0, 19.4, 19.0.

IR (film): υ_{max} 2950, 2580, 1740, 1675, 1593, 1235, 1167, 956, 750 cm^{-1}.

HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd. for $[C_{27}H_{31}O_3N + H]^+$ 418.2377; found 418.2403.

$[\alpha]^{25}_{589}$ = +18.17 (*c* = 0.4, $CHCl_3$).



(4*R*,4a*R*,13b*S*)-**methyl 12-acetyl-4,13b-dimethyl-2,3,4,4a,5,6,12,13b-octahydro-1H-naphtho[1,2-b]carbazole-4-carboxylate** [**10e**]: **10e** was obtained as white foam (0.02 mmol scale of reaction; 68% yield). R_f = 0.5 (10% EtOAc in *n*-hexane).

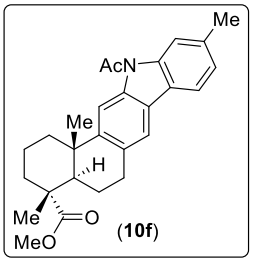
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (s, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.94 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.66 (s, 1H), 7.47 (d, *J* = 1.4 Hz, 1H), 7.37 (td, *J* = 7.5, 1.0 Hz, 1H), 3.71 (s, 3H), 3.12 – 3.08 (m, 2H), 2.89 (s, 3H), 2.49 (d, *J* = 12.7 Hz, 1H), 2.40 – 2.33 (m, 2H), 1.99 – 1.94 (m, 1H), 1.84 – 1.81 (m, 2H), 1.67 (d, *J* = 7.2 Hz, 2H), 1.53 (d, *J* = 9.5 Hz, 1H), 1.35 (s, 3H), 1.33 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 179.1, 170, 137.7, 131.1, 126.8, 126.5, 124.3, 123.6, 119.7, 119.6, 116.1, 112.1, 52, 47.7, 44.9, 38.5, 38.1, 36.7, 29.9, 27.7, 25.4, 21.7, 18.6, 16.6.

IR (neat) υ_{max} 3437, 2906, 1746, 1651, 1446, 1225, 1023, 834, 714, 546 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{26}H_{29}NO_3 + H]^+$ 404.2226, found 404.2212.

$[\alpha]^{25}_{589}$ = +51.6 (c = 0.3, $CHCl_3$).



(4*R*,4a*R*,13b*S*) **Methyl -12-acetyl-4,10,13b-trimethyl-2,3,4,4a,5,6,12,13b-octahydro-1H-naphtho[1,2-b]carbazole-4-carboxylate** [(**10f**)]: **10f** was obtained as yellow foam (0.06 mmol scale of reaction; 72% yield). R_f = 0.4 (10% EtOAc in *n*-hexane).

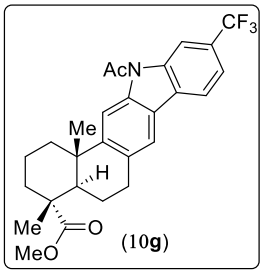
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (s, 1H), 7.95 (s, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.57 (s, 1H), 7.15 (ddd, *J* = 7.8, 1.3, 0.6 Hz, 1H), 3.68 (d, *J* = 0.9 Hz, 3H), 3.06 (dd, *J* = 9.2, 4.8 Hz, 2H), 2.84 (d, *J* = 0.8 Hz, 3H), 2.51 (s, 3H), 2.42 (d, *J* = 1.8 Hz, 2H), 2.32 – 2.28 (m, 1H), 1.91 (t, *J* = 9.1 Hz, 1H), 1.83 – 1.77 (m, 3H), 1.71 – 1.63 (m, 2H), 1.31 (s, 3H), 1.29 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 179.2, 170.1, 149.1, 139.5, 137.7, 137.1, 131, 124.8, 124.5, 124.2, 119.4, 119.4, 116.7, 112.1, 52.1, 47.8, 45.1, 38.6, 38.2, 36.8, 27.8, 25.5, 22.4, 21.8, 18.7, 16.7.

IR (neat): υ_{max} 3437, 2906, 1746, 1651, 1446, 1225, 1023, 834, 714, 546 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{27}H_{31}NO_3 + H]^+$ 418.2382, found 418.2375.

$[\alpha]^{25}_{589}$ = +55.6 (c = 0.3, $CHCl_3$).



(4*R*,4a*R*,13b*S*)- **Methyl 12-acetyl-4,13b-dimethyl-10-(trifluoromethyl)-2,3,4,4a,5,6,12,13b-octahydro-1H-naphtho[1,2-b]carbazole-4-carboxylate** [(**10g**)]: **10g** was obtained as yellow foam (8.63 mmol scale of reaction; 65% yield). R_f = 0.5 (10% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.55 (s, 1H), 8.04 (s, 1H), 7.98 (dt, *J* = 8.0, 0.7 Hz, 1H), 7.68 (d, *J* = 1.1 Hz, 1H), 7.60 (ddd, *J* = 8.1, 1.6, 0.7 Hz, 1H), 3.68 (s, 3H), 3.11 – 3.06 (m, 2H), 2.88 (s, 3H), 2.43 (d, *J* = 12.2 Hz, 1H), 2.31 (dd, *J* = 12.5, 2.4 Hz, 1H), 1.98 – 1.83 (m, 2H), 1.80 (q, *J* = 4.2, 3.3 Hz, 2H), 1.78 – 1.67 (m, 2H), 1.66 – 1.59 (m, 1H), 1.32 (s, 3H), 1.30 – 1.29 (m, 3H).

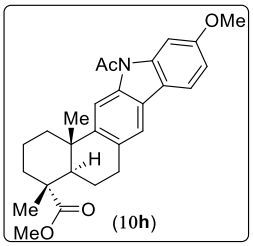
^{13}C NMR (125 MHz, $CDCl_3$): δ 179, 169.9, 151, 138.7, 138.3, 131.6, 129, 123.3, 120.7, 120.6, 120.6, 119.8, 111.8, 52.1, 47.8, 44.9, 38.6, 38.3, 36.7, 29.8, 27.8, 25.5, 21.7, 18.7, 16.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.10

IR (neat) υ_{max} 3437, 2906, 1746, 1651, 1446, 1225, 1023, 834, 714, 546 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{27}H_{28}F_3NO_3 + H]^+$ 472.2100, found 472.2108.

$[\alpha]^{25}_{589}$ = +54.6 (c = 0.3, $CHCl_3$).



(4*R*,4a*R*,13b*S*)- **Methyl -12-acetyl-10-methoxy-4,13b-dimethyl-2,3,4,4a,5,6,12,13b-octahydro-1H-naphtho[1,2-b]carbazole-4-carboxylate** [(**10h**)]: **10h** was obtained as yellow foam (8.63 mmol scale of reaction; 60% yield). R_f = 0.35 (10% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (s, 1H), 7.82 (s, 1H), 7.76 (dd, *J* = 8.5, 0.5 Hz, 1H), 7.52 (s, 1H), 6.94 – 6.91 (m, 1H), 3.90 (s, 3H), 3.68 (s, 3H), 3.07 – 3.03 (m, 2H), 2.83 (d, *J* = 0.5 Hz, 3H), 2.44 – 2.40 (m, 2H), 2.32 – 2.28 (m, 1H), 1.90 (s, 1H), 1.80 (d, *J* = 11.3 Hz, 2H), 1.76 (d, *J* = 3.0 Hz, 1H), 1.65 (s, 1H), 1.61 (s, 1H), 1.31 (s, 3H), 1.28 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 179.2, 170.1, 165.1, 159.5, 148.2, 140.5, 131, 120, 119, 111, 102.3, 55.9, 52.1, 47.8, 45.1, 38.6, 38.1, 36.7, 27.8, 25.5, 21.8, 18.7, 16.7.

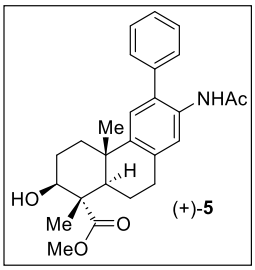
IR (neat): υ_{max} 3437, 2906, 1746, 1651, 1446, 1225, 1023, 834, 714, 546 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{27}H_{31}NO_4 + H]^+$ 434.2331, found 434.2339.

$[\alpha]_{589}^{25}$ = +55.6 (c = 0.3, $CHCl_3$).

Synthesis of compound (+)-5:

For the synthesis of compound (+)-**5** see ref. 1.



Methyl (1*S*,2*S*,4a*S*,10a*R*)-7-acetamido-2-hydroxy-1,4a-dimethyl-6-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate [(+)-**5**]: (+)-**5** was obtained as white foam. (0.473 mmol scale of reaction; 183 mg; 92% yield); R_f = 0.25 (50% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.11 (s, 1H), 7.06 (s, 1H), 4.04 (dd, *J* = 11.6, 4.7 Hz, 1H), 3.75 (s, 3H), 3.05 – 2.88 (m, 2H), 2.30 (dt, *J* = 13.2, 3.5 Hz, 1H), 2.16 (dd, *J* = 12.5, 2.2 Hz, 1H), 2.02 (s, 3H), 1.98 – 1.91 (m, 1H), 1.87 (dt, *J* = 10.9, 4.2 Hz, 1H), 1.79 (qd, *J* = 13.1, 3.3 Hz, 1H), 1.70 – 1.62 (m, 1H), 1.49 – 1.43 (m, 1H), 1.27 (s, 3H), 1.24 (s, 3H).

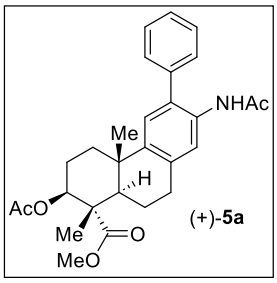
^{13}C NMR (125 MHz, $CDCl_3$): δ 177.7, 168.4, 145.2, 138.5, 135.3, 132.1, 130.6, 129.3, 129.0, 127.8, 126.2, 122.2, 75.1, 53.7, 52.3, 45.5, 36.8, 36.6, 30.0, 27.2, 25.2, 24.5, 21.3, 10.7.

IR (neat): υ_{max} 3286, 2971, 2698, 1837, 1749, 1596, 1191, 1083, 909 cm^{-1}.

$[\alpha]^{25}_{589}$ = +67.00 (*c* = 0.71, CH_3OH).

For the synthesis of compound (+)-**5** see ref. 1.

Synthesis of compound (+)-5a:



Methyl (1*S*,2*S*,4a*S*,10a*R*)**-7-acetamido-2-acetoxy-1,4a-dimethyl-6-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-**5a**]: (+)-**5a** was obtained as white foam. (0.513 mmol scale of reaction; 228 mg; 96% yield); R_f = 0.2 (30% EtOAc in *n*-hexane).

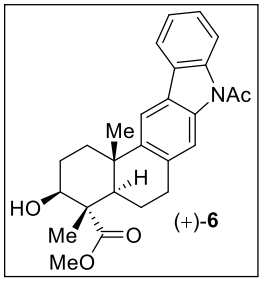
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 5.23 (dd, *J* = 11.6, 4.5 Hz, 1H), 3.69 (s, 3H), 3.03 – 2.88 (m, 2H), 2.32 (dt, *J* = 13.2, 3.3 Hz, 1H), 2.27 (dd, *J* = 12.6, 2.3 Hz, 1H), 2.02 (s, 6H), 1.99 – 1.91 (m, 2H), 1.84 – 1.71 (m, 2H), 1.41 (dqd, *J* = 11.5, 4.2, 2.8, 2.1 Hz, 1H), 1.32 (s, 3H), 1.26 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 176.3, 170.1, 168.4, 144.9, 138.5, 135.2, 132.1, 130.7, 129.3, 129.0, 127.8, 126.1, 122.2, 77.3, 52.4, 52.1, 45.6, 36.7, 36.3, 29.9, 25.1, 24.5, 24.0, 21.1, 21.0, 11.7.

IR (neat): υ_{max} 2971, 2755, 1816, 1739, 1627, 1201, 1069, 981 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ H]^+$ calcd. for $[C_{27}H_{33}O_5N + H]^+$ 464.2437, found 464.2426.

$[\alpha]^{25}_{589}$ = +95.10 (*c* = 0.91, CH_3OH).



Methyl (3*S*,4*S*,4a*R*,13b*S*)-8-acetyl-3-hydroxy-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazole-4-carboxylate [(+)-**6**]: (+)-**6** was obtained as yellow oil (0.39 mmol scale of reaction; 154 mg; 94%). R_f = 0.3 (40 % EtOAc in *n*-hexane).

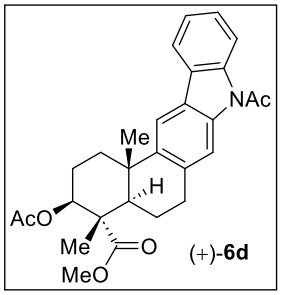
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.3 Hz, 1H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.89 (s, 1H), 7.86 (d, *J* = 2.2 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.41 – 7.35 (m, 1H), 4.17 – 4.09 (m, 1H), 3.77 (d, *J* = 2.3 Hz, 3H), 3.12 (qd, *J* = 17.1, 7.8 Hz, 2H), 2.86 (d, *J* = 2.3 Hz, 3H), 2.56 (dd, *J* = 12.8, 3.1 Hz, 1H), 2.22 – 2.17 (m, 1H), 2.05 – 1.95 (m, 2H), 1.90 (d, *J* = 12.6 Hz, 1H), 1.80 (t, *J* = 13.2 Hz, 1H), 1.58 – 1.50 (m, 1H), 1.32 (t, *J* = 2.8 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 177.7, 170.0, 145.0, 138.9, 137.1, 134.8, 126.9, 126.7, 124.8, 123.6, 119.4, 116.3, 116.3, 115.3, 75.2, 53.7, 52.3, 45.6, 37.2, 37.0, 31.1, 27.7, 27.3, 25.6, 21.4, 10.8.

IR (neat): υ_{max} 3341, 2837, 1642, 1517, 1483, 1357, 889 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{26}H_{29}O_4N + Na]^+$ 442.1989, found 442.2019.

$[\alpha]^{25}_{589}$ = +83.78 (*c* = 0.53, $CHCl_3$).



Methyl (3*S*,4*S*,4a*R*,13b*S*)**-3-acetoxy-8-acetyl-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazole-4-carboxylate** [(+)-**6d**]: (+)-**6d** was obtained as light yellow foam (0.43 mmol scale of reaction; 189 mg; 95% yield). R_f = 0.34 (30 % EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.90 (s, 1H), 7.85 (s, 1H), 7.49 – 7.44 (m, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 5.29 (dd, *J* = 11.3, 4.5 Hz, 1H), 3.71 (s, 3H), 3.18 – 3.06 (m, 2H), 2.87 (s, 3H), 2.61 – 2.55 (m, 1H), 2.33 (dd, *J* = 12.6, 2.4 Hz, 1H), 2.09 (d, *J* = 8.0 Hz, 1H), 2.05 (s, 3H), 2.04 – 1.97 (m, 1H), 1.90 (tt, *J* = 15.0, 7.5 Hz, 2H), 1.51 – 1.46 (m, 1H), 1.37 (s, 3H), 1.34 (s, 3H).

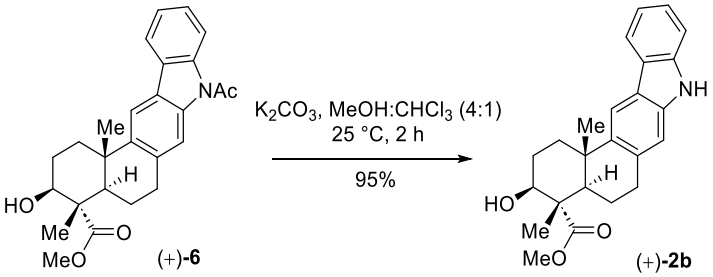
^{13}C NMR (125 MHz, $CDCl_3$): δ 176.4, 170.1, 170.0, 144.7, 138.9, 137.2, 134.7, 127.0, 126.7, 124.9, 123.6, 119.5, 116.3, 115.3, 76.8, 52.4, 52.1, 45.7, 37.1, 36.8, 30.9, 27.7, 25.5, 24.1, 21.2, 21.1, 11.8.

IR (neat) υ_{max} 3242, 2139, 1703, 1665, 1523, 1147, 985, 789 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{28}H_{31}O_5N + Na]^+$ 484.2100, found 484.2105.

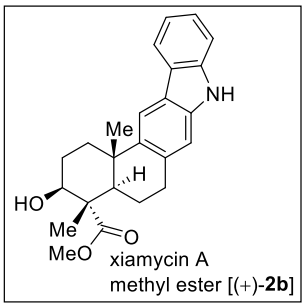
$[\alpha]^{25}_{589}$ = +55.30 (*c* = 0.80, $CHCl_3$).

Total synthesis of (+)**-xiamycin A methyl ester** [(+)-**2b**]**:**



In an oven dried round-bottom flask, (+)-**6** (107 mg, 0.255 mmol, 1.0 equiv.) was taken in a mixture of methanol and chloroform [MeOH: $CHCl_3$ (4:1)] solvent (5 mL). To this solution was added K_2CO_3 (141 mg, 1.02 mmol, 4.0 equiv.) at 25 ºC and stirring was continued for an additional 2 h. After completion of the reaction (judged by TLC analysis), the reaction mixture was diluted with water (3 mL). Next, it was extracted with dichloromethane (5 mL X 2). The

organic layers were dried over Na_2SO_4 and concentrated on a rotary evaporator under reduced pressure. Next, the crude methyl ester was purified by flash column chromatography with 30% EtOAc in *n*-hexane to afford the naturally occurring xiamycin A methylester (+)-**2b** as a white foam (91.4 mg, 95% yield).



Methyl (3*S*,4*S*,4a*R*,13b*S*)-**3-hydroxy-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1*H*-naphtho[2,1-*b*]carbazole-4-carboxylate** [(+)-**2b**]**:** Natural product xiamycin A methylester (+)-**2b** was obtained as white foam (0.255 mmol scale, 91.4 mg, 95% yield). R_f = 0.2 (30% EtOAc in *n*-hexane)

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (d, *J* = 7.8 Hz, 1H), 7.92 (s, 1H), 7.86 (s, 1H), 7.37 – 7.34 (m, 2H), 7.21 – 7.16 (m, 1H), 7.04 (s, 1H), 4.12 – 4.06 (m, 1H), 3.74 (s, 3H), 3.12 – 3.03 (m, 2H), 2.60 – 2.54 (m, 1H), 2.22 (dd, *J* = 12.5, 2.4 Hz, 1H), 2.04 – 1.92 (m, 2H), 1.89 – 1.79 (m, 2H), 1.48 (ddt, *J* = 13.3, 6.0, 2.9 Hz, 1H), 1.30 (s, 6H).

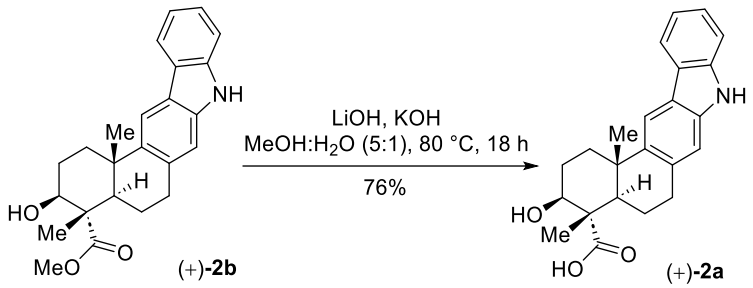
^{13}C NMR (125 MHz, $CDCl_3$): δ 178.0, 141.1, 140.1, 138.3, 133.5, 125.5, 123.6, 122.1, 120.0, 119.3, 115.7, 110.6, 109.9, 75.4, 53.9, 52.4, 46.0, 37.5, 37.3, 30.9, 27.5, 25.9, 21.6, 10.8.

IR (neat): υ_{max} 3375, 2917, 2863, 1705, 1586, 1442, 1211, 911, 797 cm^{-1}.

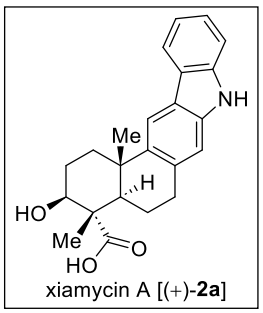
HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $[C_{24}H_{27}O_3N + H]^+$ 378.2069, found 378.2070.

$[\alpha]^{25}_{589}$ = +110.3 (*c* = 0.67, CH_3OH); lit.[3] $[\alpha]_D^{21}$ = +162.4 (*c* = 1.3, CH_3OH).

Total synthesis of xiamycin A [(+)-**2a**]**:**



In an oven dried round-bottom flask xiamycin A methyl ester [(+)-**2b**] (47 mg, 0.125 mmol, 1.0 equiv.) was taken in a mixture of methanol and water [MeOH: H_2O (5:1)] at 25 °C. Next, KOH (210 mg, 3.74 mmol, 30 equiv.) and LiOH (60 mg, 2.5 mmol, 20 equiv.) were added subsequently and the reaction mixture was heated under reflux at 80 ºC. After completion of the reaction as confirmed by TLC analysis (18 h), the reaction mixture was quenched with 6(*N*) HCl at 0 ºC and the pH of the reaction mixture was adjusted to ~1-2. Then whole reaction mixture was extracted with EtOAc (6 mL X 2). The combined organic layers were collected, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography with ~80-90% EtOAc to afford the naturally occurring xiamycin A [(+)-**2a**] as white foam (34.5 mg, 76% yield).



(3*S*,4*S*,4a*R*,13b*S*)-**3-Hydroxy-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazole-4-carboxylic acid** [(+)-**2a**]**:** Natural product xiamycin A [(+)-**2a**] was obtained as white foam (0.125 mmol scale, 34.5 mg, 76% yield). R_f = 0.2 (70% EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, CD_3OD): δ 7.96 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.92 (s, 1H), 7.35 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.28 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.08 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.04 (s, 1H), 4.14 – 4.04 (m, 1H), 3.12 – 2.94 (m, 2H), 2.60 (dt, *J* = 13.2, 3.4 Hz, 1H), 2.17 – 2.10 (m, 1H), 1.99 – 1.92 (m, 1H), 1.91 – 1.82 (m, 2H), 1.76 – 1.65 (m, 1H), 1.52 (ddt, *J* = 13.2, 7.2, 2.2 Hz, 1H), 1.27 (s, 3H), 1.23 (s, 3H).

^{13}C NMR (100 MHz, CD_3OD): δ 181.3, 142.0, 141.7, 140.1, 134.0, 126.1, 124.6, 123.1, 120.6, 119.3, 116.3, 111.5, 110.8, 76.3, 54.9, 47.9, 39.0, 38.3, 32.0, 28.6, 26.3, 22.6, 11.4.

IR (neat): υ_{max} 3352, 2946, 2258, 1673, 1408, 1009, 912, 848 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{23}H_{25}O_3N + Na]^+$ 386.1727, found 386.1739.

$[\alpha]^{25}_{589}$ = +105.8 (*c* = 0.48, CH_3OH); lit.[3] $[\alpha]_D^{21}$ = +137.6 (*c* = 5.3, CH_3OH).

Comparison of ^{1}H-NMR Data of (+)-Xiamycin A [(+)-**2a**] of this report with natural (+)-**2a** by Hertweck[4] and with literature by Baran[5] and Sarpong[6]:

Hertweck's report on isolation of (+)-Xiamycin A [(+)-**2a**] (^{1}H-NMR, 300 MHz, CD_3OD)[4]			
δ (ppm)	Int.	mult.	*J* (Hz)
7.96	1H	dd	*J* = 7.7, 1.1 Hz
7.92	1H	s	-
7.34	1H	dd	*J* = 8.0, 1.1 Hz
7.27	1H	ddd	*J* = 8.0, 7.4, 1.1Hz
7.08	1H	ddd	*J* = 8.1, 7.3, 1.1Hz
7.05	1H	s	-
4.09	1H	dd	*J* = 9.1, 7.1 Hz
3.09	1H	dd	*J* = 16.7, 6.1
3.02	1H	m	-
2.61	1H	td	*J* = 13.1, 3.0 Hz
2.15	1H	dd	*J* = 12.5, 2.0 Hz
2.00	1H	ddd	*J* = 13.4, 12.8, 7.0 Hz
1.89	2H	m	-
1.74	1H	m	-
1.53	1H	m	-
1.29	3H	s	-
1.23	3H	s	-

Baran's Total Synthesis of (+)-Xiamycin A [(+)-**2a**] (^{1}H-NMR, 600 MHz, CD_3OD)[5]			
δ (ppm)	Int.	mult.	*J* (Hz)
7.97	1H	dt	*J* = 7.8, 1.0 Hz
7.94	1H	s	-
7.35	1H	dt	*J* = 8.1, 0.9 Hz
7.29	1H	ddd	*J* = 8.1, 7.1, 1.2 Hz
7.09	1H	t	*J* = 7.9, 7.1, 1.0 Hz
7.06	1H	s	-
4.10	1H	dd	*J* = 9.3, 7.1 Hz
3.14 – 3.07	1H	m	-
3.06 – 2.98	1H	m	-
2.63	1H	dt	*J* = 13.1, 3.5 Hz
2.16	1H	dd	*J* = 12.6, 2.2 Hz
2.01	1H	tdd	*J* = 12.8, 11.3, 6.9
1.94 – 1.86	2H	m	-
1.78 – 1.70	1H	m	-
1.57 – 1.52	1H	m	-
1.29	3H	s	-
1.24	3H	s	-

Sarpong's Total Synthesis of (+)-Xiamycin A [(+)-**2a**] (^{1}H-NMR, 700 MHz, CD_3OD)[6]			
δ (ppm)	Int.	mult.	*J* (Hz)
7.97	1H	d	*J* = 8.0 Hz
7.94	1H	s	-
7.35	1H	d	*J* = 8.0 Hz
7.29	1H	t	*J* = 7.9 Hz
7.09	1H	t	*J* = 7.5 Hz
7.07	1H	s	-

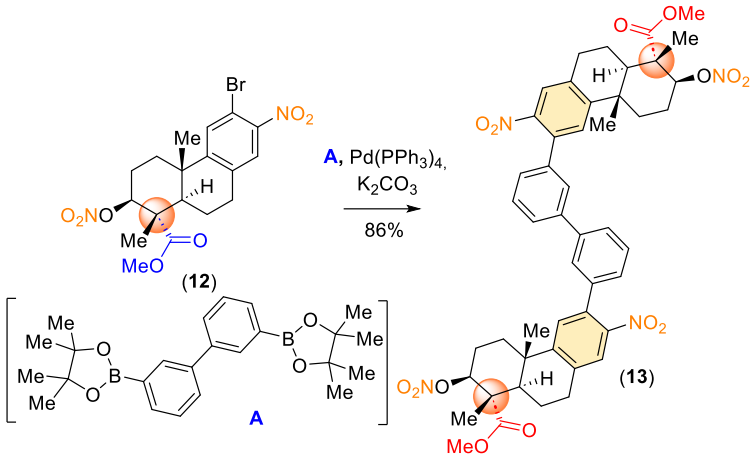
4.10	1H	dd	*J* = 10.5, 7.5 Hz
3.15-3.08	1H	m	-
3.08-2.99	1H	m	-
2.64	1H	d	*J* = 12.8 Hz
2.14	1H	d	*J* = 11.8 Hz
2.08-1.98	1H	m	-
1.93-1.88	2H	m	-
1.78-1.72	1H	m	-
1.58-1.53	1H	m	-
1.30	3H	s	-
1.25	3H	s	-

This Synthesis: (+)-Xiamycin A [(+)-2**a**] (^{1}H-NMR, 400 MHz, CD_3OD)			
δ (ppm)	Int.	mult.	*J* (Hz)
7.96	1H	dd	*J* = 7.8, 1.0 Hz
7.92	1H	s	-
7.35	1H	dt	*J* = 8.1, 1.0 Hz
7.28	1H	ddd	*J* = 8.2, 7.0, 1.2 Hz
7.08	1H	ddd	*J* = 8.0, 7.0, 1.1 Hz
7.04	1H	s	-
4.14 – 4.04	1H	m	-
3.12 – 2.94	2H	m	-
2.60	1H	dt	*J* = 13.2, 3.4 Hz
2.17 – 2.10	1H	m	-
1.99 – 1.92	1H	m	-
1.91 – 1.82	2H	m	-
1.76 – 1.65	1H	m	-
1.52	1H	ddt	*J* = 13.2, 7.2, 2.2 Hz
1.27	3H	s	-
1.23	3H	s	-

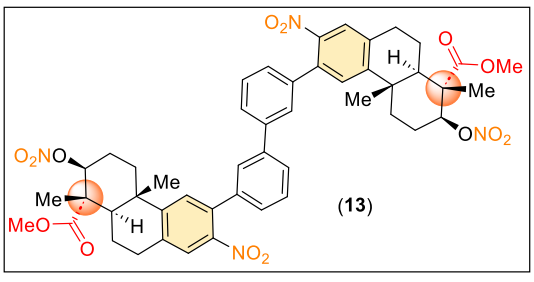
Comparison of ^{13}C-NMR Data:

Hertweck's isolation of (+)-Xiamycin A [(+)-**2a**] (^{13}C-NMR, 125.77 MHz, CD_3OD)[4]	Baran's Synthesis: (+)-Xiamycin A [(+)-**2a**] (^{13}C-NMR, 151 MHz, CD_3OD)[5]	Sarpong's Synthesis: (+)-Xiamycin A [(+)-**2a**] (^{13}C-NMR, 176 MHz, CD_3OD)[6]	This Synthesis: (+)-Xiamycin A [(+)-**2a**] (^{13}C-NMR, 100 MHz, CD_3OD)
181.3	181.4	181.3	181.3
142.0	142.0	142.0	142.0
141.8	141.8	141.8	141.7
140.1	140.1	140.1	140.1
134.0	134.0	134.0	134.0
126.0	126.1	126.0	126.1
124.7	124.7	124.6	124.6
123.1	123.1	123.1	123.1
120.5	120.6	120.6	120.6
119.3	119.3	119.3	119.3
116.3	116.4	116.4	116.3
111.5	111.4	111.4	111.5
110.8	110.8	110.8	110.8
76.3	76.3	76.3	76.3
54.9	54.9	54.9	54.9
47.9	47.9	47.9	47.9
39.0	39.0	39.0	39.0
38.3	38.3	38.3	38.3
32.0	32.0	32.1	32.0
28.6	28.6	28.7	28.6
26.3	26.3	26.3	26.3
22.6	22.6	22.6	22.6
11.4	11.4	11.4	11.4

Synthesis of *bis*-nitro Compound (13) *via* sequential Suzuki-Miyaura Coupling:



A round-bottom flask was charged with (+)-**12** (113 mg, 0.249 mmol, 1.0 equiv.) and 3,3'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1'-biphenyl (51 mg, 0.125 mmol, 0.5 equiv.) in a mixture of benzene (3 mL), EtOH (1 mL), and water (1 mL) at room temperature under argon atmosphere. Next, potassium carbonate (34 mg, 0.496 mmol, 2.0 equiv.) was added to the reaction mixture followed by the addition of catalyst, tetrakis(triphenylphosphine)palladium(0) (7 mg, 0.006 mmol, 0.02 equiv.) at the same temperature. Then the reaction mixture was placed on a pre-heated oil bath maintaining temperature of 80 °C. Upon completion of the reaction (3 h), as monitored by TLC analysis, it was extracted with EtOAc (10 mL X 2). The combined organic layers were washed with brine (5 mL X 1) and dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. The crude product was purified by flash chromatography with 15% EtOAc in *n*-hexane to furnish (+)-**13** as a white foam (97 mg, 86% yield).



Dimethyl 6,6'-([1,1'-biphenyl]-3,3'-diyl)(1*S*,1'*S*,2*S*,2'*S*,4a*S*,4a'*S*,10a*R*,10a'*R*)-bis(1,4a-dimethyl-7-nitro-2-(nitrooxy)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate) [(+)-**13**]: (+)-**13** was obtained as yellowish foam (0.249 mmol scale of reaction; 97 mg; 86%). R_f = 0.55 (20 % EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, *J* = 9.2 Hz, 2H), 7.50 – 7.46 (m, 2H), 7.30 (s, 1H), 7.28 – 7.25 (m, 1H), 5.45 (dd, *J* = 11.8, 4.3 Hz, 1H), 3.74 (d, *J* = 1.9 Hz, 3H), 3.04 (d, *J* = 6.7 Hz, 1H), 2.97 (td, *J* = 10.7, 5.4 Hz, 1H), 2.47 (dt, *J* = 13.3, 3.3 Hz, 1H), 2.22 (dd, *J* = 12.5, 2.2 Hz, 1H), 2.14 (tdd, *J* = 9.5, 6.0, 4.1 Hz, 1H), 2.05 – 1.92 (m, 2H), 1.83 (ddd, *J* = 13.7, 11.3, 3.7 Hz, 1H), 1.51 (ddd, *J* = 13.2, 6.5, 2.8 Hz, 1H), 1.33 (d, *J* = 2.6 Hz, 3H), 1.29 (s, 3H).

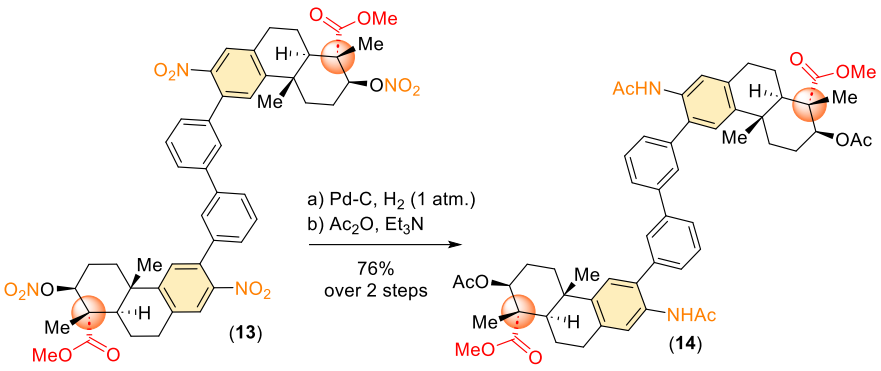
^{13}C NMR (125 MHz, $CDCl_3$): δ 152.8, 146.9, 141.1, 138.4, 135.6, 134.1, 129.1, 128.4, 127.2, 127.0, 124.8, 85.5, 52.9, 51.4, 46.2, 37.5,37.6, 36.0, 29.3, 24.9, 22.6, 20.3, 11.7.

IR (neat): υ_{max} 3337, 2851, 1743, 1632, 1383, 1211, 935, 756 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ NH_4]^+$ calcd. for $[C_{48}H_{50}N_4O_{14} + NH_4]^+$ 924.3667, found 924.3669.

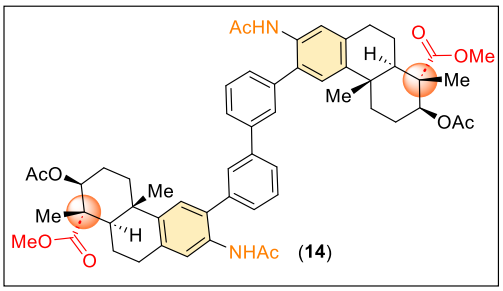
$[\alpha]^{25}_{589}$ = +94.5 (*c* = 0.2, $CHCl_3$).

Synthesis of *bis*-acetenalide compound (14) *via* reduction followed by acetyl protection from compound (13):



In an oven-dried round-bottom flask *bis*-nitro compound (**+**)-**13** (80 mg, 0.088 mmol, 1.0 equiv.) was taken in MeOH (5 mL) and degassed with N_2 balloon for 10 minutes. To this solution Pd/C (20% w/w) (22 mg) was added and a H_2 gas balloon (1 atm.) was placed with the reaction vessel and stirring continued until the full consumption of starting material (4 h), as confirmed by TLC analysis. The reaction mixture was filtered, evaporated to dryness under the reduced pressure. The crude *bis*-aniline was charged for the next step without further purification.

In an oven dried round-bottom flask *bis*-aniline was taken in CH_2Cl_2 (3 mL) and Et_3N (49 µL, 0.361 mmol., 4.1 equiv.) was added to the reaction mixture. Next, acetic anhydride (34 µL, 0.361 mmol., 4.1 equiv.) and DMAP (4 mg, 0.0361 mmol., 0.4 equiv.) was added to the reaction mixture at 25 ºC and stirring continued until the full consumption of starting material. Upon completion (6 h), as monitored by TLC analysis, it was extracted with CH_2Cl_2 (5 mL X 2). The organic layers were dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. The crude product was purified by flash column chromatography with 60-80% EtOAc in *n*-hexane to afford (+)-**14** as yellow foam (62 mg, 76% over 2 steps).



Dimethyl 6,6'-([1,1'-biphenyl]-3,3'-diyl)(1*S*,1'*S*,2*S*,2'*S*,4a*S*,4a'*S*,10a*R*,10a'*R*)-bis(7-acetamido-2-acetoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate) [(+)-**14**]: (+)-**14** was obtained as yellowish foam (0.088 mmol scale of reaction; 62 mg; 76%). R_f = 0.25 (70 % EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (s, 1H), 7.61 (s, 1H), 7.55 (d, *J* = 4.9 Hz, 2H), 7.34 (d, *J* = 7.0 Hz, 1H), 7.15 – 7.09 (m, 1H), 7.05 (s, 1H), 5.20 (dd, *J* = 11.2, 4.4 Hz, 1H), 3.66 (s, 3H), 3.03 – 2.94 (m, 1H), 2.94 (d, *J* = 3.4 Hz, 1H), 2.30 (d, *J* = 8.3 Hz, 1H), 2.28 – 2.19 (m, 1H), 2.00 (s, 3H), 1.99 (s, 3H), 1.93 (s, 2H), 1.79 (d, *J* = 12.9 Hz, 2H), 1.39 (d, *J* = 2.9 Hz, 1H), 1.29 (s, 3H), 1.25 (s, 3H).

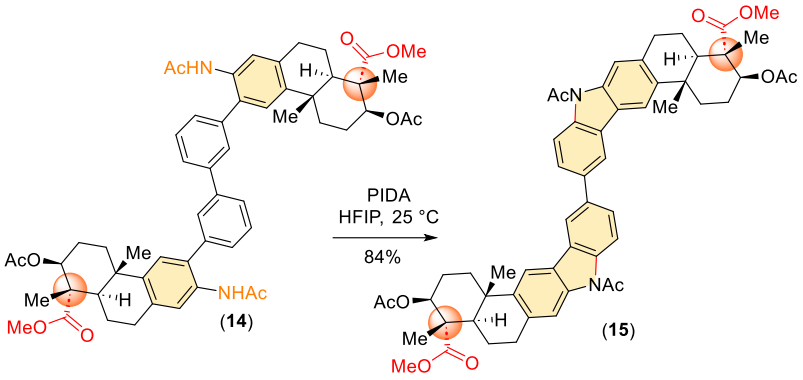
^{13}C NMR (125 MHz, $CDCl_3$): δ 176.4, 170.2, 168.4, 154.7, 151.7, 145.2, 141.6, 139.4, 135.6, 132.2, 129.6, 128.5, 128.2, 126.6, 122.6, 52.5, 52.1, 45.6, 39.3, 36.8, 36.4, 32.0, 25.2, 24.0, 22.8, 21.2, 14.2, 11.7.

IR (neat): υ_{max} 3331, 2847, 1727, 1653, 1338, 1291, 987, 737 cm^{-1}.

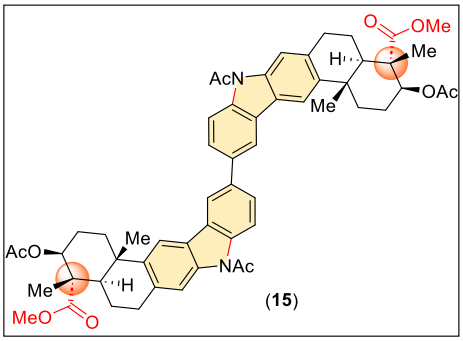
HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $[C_{56}H_{64}O_{10}N_2 + H]^+$ 925.4639, found 925.4634.

$[\alpha]^{25}_{589}$ = +82.7 (*c* = 0.1, $CHCl_3$).

Intramolecular Oxidative C-N coupling of *bis*-Acetenalide Compound (14):



In an oven-dried round-bottom flask *bis*-acetanilide (48 mg, 0.052 mmol, 1.0 equiv.) was taken in 1,1,1,3,3,3- hexafluoropropan-2-ol under an inert atmosphere. To the solution $PhI(OAc)_2$ (40 mg, 0.124 mmol, 2.4 equiv.) was added and stirred the mixture at room temperature. After completion of reaction (monitored by TLC), it was quenched with saturated $Na_2S_2O_3$ solution then reaction mixture was extracted with CH_2Cl_2 (5 mL X 3). The organic layers were dried over Na_2SO_4 and concentrated on rotary evaporator under reduced pressure. Then the crude product was purified by flash column chromatography with 20- 60% EtOAc in *n*-hexane to afford pentacyclic compounds **15**.



Dimethyl (3*S*,3'*S*,4*S*,4a*R*,4'*S*,4'a*R*,13b*S*,13'b*S*)-3,3'-diacetoxy-8,8'-diacetyl-4,4',13b,13'b-tetramethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13*b*,13'*b*-hexadecahydro-1*H*,1'*H*-[11,11'-binaphtho[2,1-*b*]carbazole]-4,4'-dicarboxylate [(+)-**15**]: (+)-**15** was obtained as white solid (0.052 mmol scale of reaction; 40 mg; 84%). Rf = 0.3 (40 % EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.5 Hz, 1H), 8.24 (d, *J* = 1.9 Hz, 1H), 7.95 (s, 1H), 7.89 (s, 1H), 7.77 (dd, *J* = 8.7, 1.9 Hz, 1H), 5.30 – 5.24 (m, 1H), 3.69 (s, 3H), 3.20 – 3.05 (m,

2H), 2.88 (s, 3H), 2.61 (d, *J* = 3.8 Hz, 1H), 2.33 (dd, *J* = 12.4, 2.4 Hz, 1H), 2.02 (s, 3H), 2.01 (s, 1H), 1.93 (s, 1H), 1.89 (d, *J* = 9.3 Hz, 2H), 1.48 (dd, *J* = 6.0, 3.2 Hz, 1H), 1.35 (s, 3H), 1.34 (s, 3H).

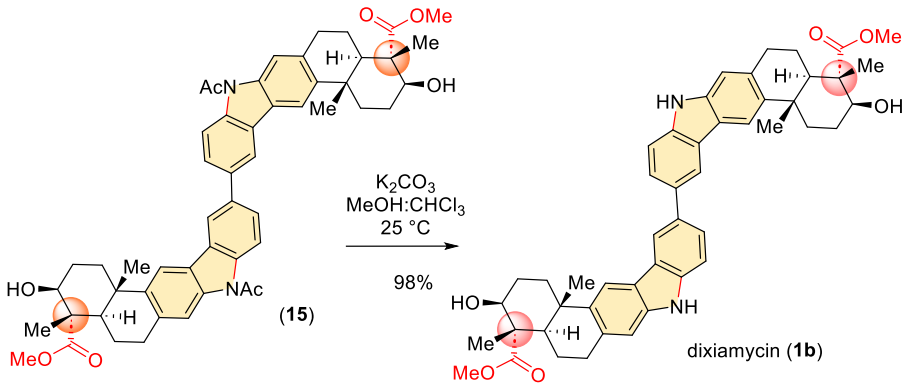
^{13}C NMR (125 MHz, $CDCl_3$) δ 176.4, 170.1, 169.9, 144.9, 138.2, 137.6, 136.7, 135.0, 127.4, 126.3, 124.9, 117.9, 116.6, 116.3, 115.5, 77.2, 52.4, 52.1, 45.7, 37.2, 31.9, 31.0, 27.7, 25.4, 24.1, 21.1, 14.1, 11.8.

IR (neat) υ_{max} 3378, 2832, 1795, 1631, 1347, 1253, 918, 713 cm^{-1}.

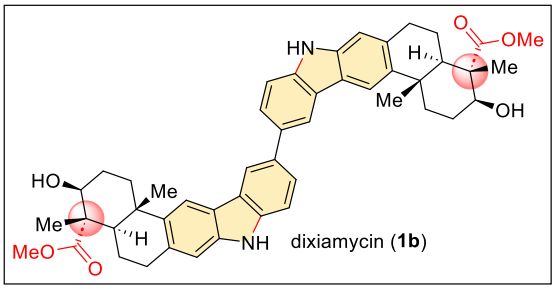
HRMS (ESI) *m/z*: $[M+ H]^+$ calcd. for $[C_{56}H_{60}O_{10}N_2 + H]^+$ 921.4326, found 921.4329.

MP 183 – 185 ºC; $[\alpha]^{25}_{589}$ = +93.4 (*c* = 0.02, $CHCl_3$).

Total synthesis of dixiamycin (1b):



In an oven dried round-bottom flask, (+)-**15** (32 mg, 0.0347 mmol, 1.0 equiv.) was taken in a mixture of methanol and chloroform [MeOH: $CHCl_3$ (4:1)] (2 mL). To this solution was added K_2CO_3 (19 mg, 0.139 mmol, 4.0 equiv.) at 25 ºC and stirring was continued for an additional 2 h. After completion of the reaction (judged by TLC analysis), the reaction mixture was diluted with water (3 mL). Next, it was extracted with dichloromethane (5 mL X 2). The organic layers were dried over Na_2SO_4 and concentrated on a rotary evaporator under reduced pressure. Next, the crude methyl ester was purified by flash column chromatography with pure EtOAc in *n*-hexane to afford dixiamycin (+)-**1b** as a brown solid (26 mg, 98% yield).



Dimethyl (3*S*,3'*S*,4*S*,4a*R*,4'*S*,4'a*R*,13b*S*,13'b*S*)**-3,3'-dihydroxy-4,4',13b,13'b-tetramethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13b,13'b-hexadecahydro-1*H*,1'*H*-[11,11'-binaphtho[2,1-b]carbazole]-4,4'-dicarboxylate** [(+)-**1b**]: (+)-**1b** was obtained as brown solid (0.0347 mmol scale of reaction; 26 mg; 98%). R_f = 0.5 (70 % EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.00 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.05 (s, 1H), 4.10 (d, *J* = 6.7 Hz, 1H), 3.73 (d, *J* = 5.2 Hz, 3H), 3.08 (t, *J* = 8.6 Hz, 2H), 2.59 (d, *J* = 11.2 Hz, 1H), 2.25 – 2.19 (m, 1H), 2.03 (d, *J* = 5.9 Hz, 1H), 1.91 (s, 1H), 1.80 (d, *J* = 10.3 Hz, 2H), 1.50 – 1.46 (m, 1H), 1.30 (s, 3H), 1.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 141.2, 139.2, 138.8, 133.8, 133.5, 125.4, 124.3, 122.3, 118.5, 115.8, 110.7, 110.1, 75.4, 53.9, 52.4, 46.0, 37.4, 32.0, 29.5, 25.9, 22.8, 14.2, 10.8.

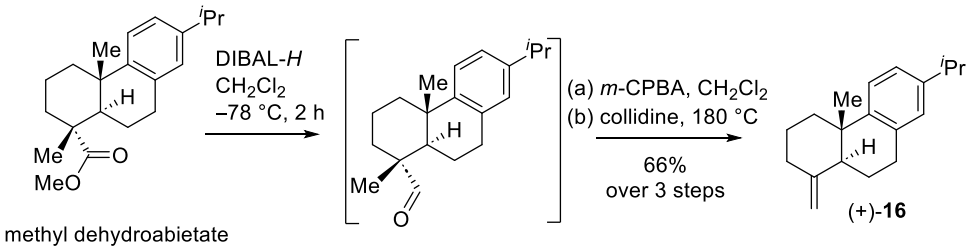
IR (neat) υ_{max} 3430, 2925, 1765, 1653, 1466, 1385, 1290, 1052, 953, 845, 762, 669 cm^{-1}.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $[C_{48}H_{52}O_6N_2 + H]^+$ 753.3904, found 753.3910.

m.p. 223 – 225 ºC; $[\alpha]^{25}_{589}$ = +89.4 (*c* = 0.02, CH_3OH).

Synthesis of *epi*-11 from Methyl Dehydroabietate:

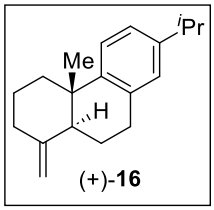
Synthesis of compound (+)**-16:**



An oven-dried round-bottom flask was charged with the methyl dehydroabietate (12 g, 38.15 mmol, 1.0 equiv.) in anhydrous CH_2Cl_2 (120 mL), maintaining inertness with N_2 gas balloon and was cooled to −78 °C, over an acetone bath followed by the addition of a solution of DIBAL-*H* (1 M in hexanes, 40 mL, 40.0 mmol, 1.05 equiv.) in dropwise manner over 30 min. The reaction mixture was stirred at the same temperature for an additional 2 h until the full consumption of the starting material. After complete consumption of the starting material, a saturated aqueous solution of potassium sodium tartrate (50 mL) was added slowly to the reaction mixture, and the resultant mixture was stirred vigorously for another 1 h at 25 °C. The resulting biphasic mixture was then transferred to a separating funnel and the organic layer was separated. The aqueous layer was further extracted with CH_2Cl_2 (70 mL X 2). The combined organic layers were concentrated under reduced pressure and the crude product was taken for the next step. R_f = 0.4 (2.5% EtOAc in hexane).

Solid *m*-CPBA (7.9 g, 45.78 mmol, 1.2 equiv.) and $NaHCO_3$ (8.01 g, 95.37 mmol, 2.5 equiv.) were directly added to a solution of crude aldehyde in CH_2Cl_2 and the mixture was stirred at 25 °C for 4 h until the full consumption of starting material. After completion of the reaction, the solution was extracted with CH_2Cl_2 and water. The aqueous phase was extracted thrice with CH_2Cl_2. The organic layer was washed with $NaHCO_3$ solution and filtered. The organic filtrate was dried over anhydrous Na_2SO_4 and concentrated in rotary evaporator under vacuum and the crude product was taken for the next step. R_f = 0.42 (2.5% EtOAc in hexane).

A solution of the crude product in 2,6-lutidine (22 mL) was stirred under reflux condition at 180 °C for 8 h (TLC monitoring). The mixture was cooled to 25 °C and the solution was diluted with EtOAc and the brown solution was washed with 2 (*N*) HCl and brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated in rotary evaporator under vacuum. The crude product was purified by flash chromatography with *n*-Hexane to afford (+)-**16** as colorless liquid (6.4 g, 66% yield over 3 steps).



(+)-**16**

(4a*S*,10a*S*)-**7-Isopropyl-4a-methyl-1-methylene-1,2,3,4,4a,9,10,10a-octahydrophenanthrene** [(+)-**16**]: The compound (+)-**16** was obtained as colorless oil (24.61 mmol scale of reaction; 6.4 g; 66% over 3steps). R_f = 0.7 (in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.1 Hz, 1H), 7.02 (dd, *J* = 8.0, 2.1 Hz, 1H), 6.94 (s, 1H), 4.86 (d, *J* = 1.9 Hz, 1H), 4.61 (d, *J* = 1.9 Hz, 1H), 2.91 (dd, *J* = 10.0, 5.6 Hz, 2H), 2.90 – 2.77 (m, 1H), 2.41 – 2.35 (m, 1H), 2.31 – 2.26 (m, 1H), 2.23 (dd, *J* = 11.7, 2.5 Hz, 1H), 2.06 (dt, *J* = 13.0, 6.2 Hz, 1H), 1.88 – 1.79 (m, 2H), 1.78 – 1.68 (m, 2H), 1.62 – 1.53 (m, 1H), 1.26 (s, 3H), 1.24 (s, 3H), 1.01 (s, 3H).

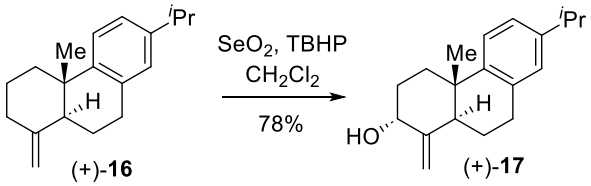
^{13}C NMR (100 MHz, $CDCl_3$): δ 150.8, 145.8, 144.7, 135.0, 127.2, 125.5, 124.0, 106.4, 48.0, 39.3, 38.5, 36.5, 33.6, 30.1, 24.1, 23.9, 22.9, 21.5.

IR (neat): ν_{max} 2932, 1745, 1628, 1562, 1132, 1065 cm^{-1}.

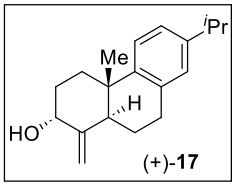
HRMS (ESI) *m*/*z*: $[M+H]^+$ calcd. for $[C_{19}H_{26} + H]^+$ 255.2113; Found 255. 2107.

$[\alpha]^{25}_{589}$ = +159.20 (c = 1.0, $CHCl_3$).

Procedure for the allylic oxidation of compound (+)-**16:**



To a solution of compound (+)-**16** (11.12 g, 43.7 mmol, 1.0 equiv.) in CH_2Cl_2, ^{t}BuOOH (70% in water) (16.8 mL, 131.12 mmol, 3.0 equiv.) and SeO_2 (2.42 g, 21.86 mmol, 0.5 equiv.) were added. The mixture was stirred at 25 ºC for 8 h. After completion of the reaction saturated solution of $Na_2S_2O_3$ was added to the reaction mixture and the mixture was washed with brine. The organic phase was separated, dried over Na_2SO_4 and concentrated to give the crude product. The crude product was purified by column chromatography with *n*-Hexane: EtOAc (9:1) to afford (+)-**17** as colorless oil (9.20 g, 78% yield).



(2*R*,4a*S*,10a*R*)-**7-Isopropyl-4a-methyl-1-methylene-1,2,3,4,4a,9,10,10a-octahydrophenanthren-2-ol** [(+)-**17**]: The compound (+)-**17** was obtained as colorless oil (43.7 mmol scale of reaction; 9.20 g; 78%). (R_f = 0.32 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, *J* = 8.1 Hz, 1H), 7.06 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.98 (d, *J* = 2.1 Hz, 1H), 5.09 (s, 1H), 4.77 (t, *J* = 1.8 Hz, 1H), 4.39 – 4.36 (m, 1H), 2.99 – 2.93 (m, 2H), 2.91 – 2.87 (m, 1H), 2.81 (ddd, *J* = 10.9, 3.5, 1.8 Hz, 1H), 2.11 – 2.06 (m, 1H), 2.01 (d, *J* = 6.3 Hz, 1H), 1.95 (dd, *J* = 5.9, 3.3 Hz, 2H), 1.84 – 1.79 (m, 2H), 1.29 (s, 3H), 1.28 (s, 3H), 1.02 (s, 3H).

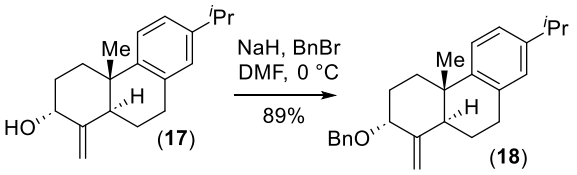
^{13}C NMR (125 MHz, $CDCl_3$): δ 151.8, 145.9, 144.2, 134.7, 127.1, 125.3, 124.0, 109.9, 72.9, 41.6, 39.0, 33.5, 30.2, 29.9, 24.0, 23.9, 22.0, 20.9.

IR (neat): ν_{max} 3641, 2958, 1749, 1622, 1456, 1254, 986 cm^{-1}.

HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $[C_{19}H_{26}O + H]^+$ 271.2062; Found 271.2056.

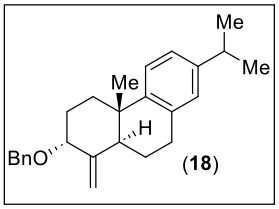
$[\alpha]^{25}_{589}$ = +157.40 (c = 0. 2, $CHCl_3$).

Synthesis of compound (+)-18:



Allylic alcohol **17** (7 g, 23.2 mmol, 1.0 equiv.) was taken in an oven dried round bottom flask dissolved in 50 mL of DMF maintaining N_2 inertness and set on an ice bath. Sodium hydride (1.86 g, 46.5 mmol, 2.0 equiv.) was added in portion-wise manner to the reaction vessel and stirred for 15 min at 0 °C. Then benzyl bromide (4.22 mL, 34.8 mmol, 1.5 equiv.) was directly added to the solution and the reaction mixture was allowed to stir at 25 °C for 1 h until the full

consumption of starting material (monitored by TLC). The reaction was quenched with excess of saturated aqueous NH_4Cl solution. Then the solution was extracted with EtOAc and water. The aqueous phase was extracted with EtOAc (60 mL X 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude product was purified by flash chromatography with 5% EtOAc in *n*-hexane to afford (+)**-18** as yellow liquid (7.88 g, 89% yield).



(2*R*,4a*S*,10a*R***)-2-(Benzyloxy)-7-isopropyl-4a-methyl-1-methylene-1,2,3,4,4a,9,10,10a-octahydrophenanthrene** [(+)-**18**]: (+)-**18** was obtained as colourless liquid (23.2 mmol scale; 7.88 g; 89%). R_f = 0.5 (5% EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.26 (m, 4H), 7.24 – 7.19 (m, 2H), 7.00 (ddd, *J* = 8.1, 1.7, 0.7 Hz, 1H), 6.93 (dd, *J* = 1.9, 0.8 Hz, 1H), 5.05 (t, *J* = 1.5 Hz, 1H), 4.88 (t, *J* = 1.7 Hz, 1H), 4.45 (dd, *J* = 12.0, 0.6 Hz, 1H), 4.27 (d, *J* = 12.0 Hz, 1H), 3.94 (d, *J* = 3.3 Hz, 1H), 2.91 (dd, *J* = 10.1, 5.3 Hz, 2H), 2.87 – 2.80 (m, 1H), 2.66 (ddt, *J* = 9.1, 5.9, 1.6 Hz, 1H), 2.05 (dd, *J* = 10.7, 1.4 Hz, 2H), 1.99 (dd, *J* = 12.7, 3.5 Hz, 1H), 1.93 – 1.86 (m, 1H), 1.81 – 1.76 (m, 2H), 1.24 (s, 3H), 1.22 (s, 3H), 1.00 (s, 3H).

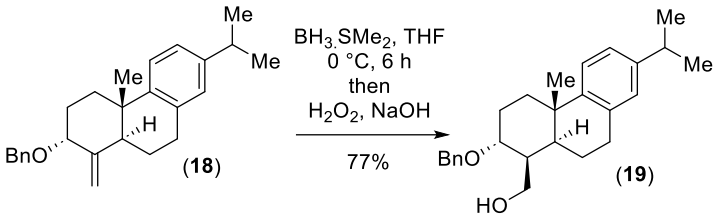
^{13}C NMR (126 MHz, $CDCl_3$): δ 149.3, 145.8, 144.4, 139.1, 134.7, 128.2, 127.5, 127.2, 127.1, 125.3, 123.9, 111.3, 79.3, 69.0, 42.0, 39.0, 33.5, 33.0, 29.9, 29.3, 24.0, 22.4, 21.0.

IR (neat): ν_{max} 2865, 1813, 1641, 1473, 1118, 957, 856 cm^{-1}.

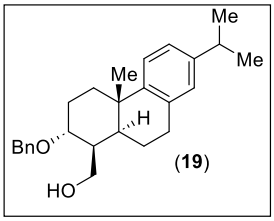
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd. for $[C_{26}H_{32}O + Na]^+$ 383.2351, found 383.2345.

$[\alpha]^{25}_{589}$ = +47.03 (*c* = 1.0, $CHCl_3$).

Synthesis of compound (+)-19:



In an oven dried round-bottom flask a solution of benzyl ether (**18**) (5.23 g, 14.5 mmol, 1.0 equiv.) in anhydrous THF (60 mL) at 0 °C under an N_2 atmosphere $Me_2S.BH_3$ (1.37 mL, 14.5 mmol, 1.0 equiv.). The mixture was then stirred at 25 °C for 8 h. Then 4(M) NaOH (50 mL), and 30% H_2O_2 (20 mL) were added and stir the mixture was stirred at 25 °C for 4 h. After completion of the reaction (confirmed by TLC analysis), the reaction mixture was then extracted with 50% EtOAc in *n*-hexane (40 mL X 2). The organic layers were collected, dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. It was purified by flash chromatography using 25% EtOAc in *n*-hexane to afford (+)-**19** as white gel (4.22 g, 77% yield).



((1*S*,2*R*,4a*S*,10a*S***)-2-(Benzyloxy)-7-isopropyl-4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methanol** [(+)-**19**]: (+)-**19** was obtained as white gel (14.5 mmol scale; 4.22 g; 77%). R_f = 0.42 (20% EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 – 7.36 (m, 4H), 7.33 (td, *J* = 6.0, 2.5 Hz, 1H), 7.19 (d, *J* = 8.3 Hz, 1H), 7.02 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.92 (d, *J* = 2.1 Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.23 (t, *J* = 2.6 Hz, 1H), 3.63 (dd, *J* = 9.6, 2.7 Hz, 1H), 3.50 (t, *J* = 9.8 Hz, 1H), 3.01 – 2.89 (m, 2H), 2.88 – 2.83 (m, 1H), 2.31 (ddd, *J* = 13.0, 5.4, 2.1 Hz, 1H), 2.10 (dtd, *J* = 12.4, 4.4, 2.1 Hz, 1H), 2.03 (dt, *J* = 12.4, 3.1 Hz, 1H), 1.96 – 1.85 (m, 3H), 1.81 – 1.73 (m, 1H), 1.60 (ddt, *J* = 12.9, 7.0, 1.8 Hz, 1H), 1.27 (s, 3H), 1.25 (s, 3H), 1.04 (s, 3H).

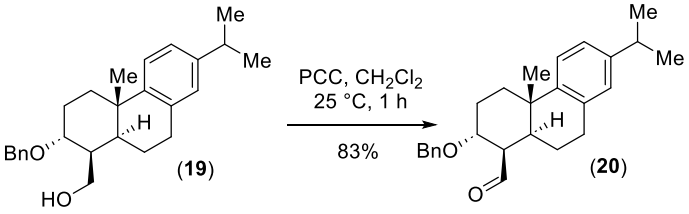
^{13}C NMR (125 MHz, $CDCl_3$): δ 145.8, 145.7, 138.4, 134.8, 128.4, 127.6, 127.6, 127.0, 124.7, 123.96, 73.0, 69.3, 67.8, 48.6, 37.5, 36.7, 33.5, 31.9, 30.5, 25.6, 24.6, 24.0, 23.6.

IR (neat) ν_{max} 3438, 2865, 1873, 1651, 1414, 1137, 998 cm^{-1}.

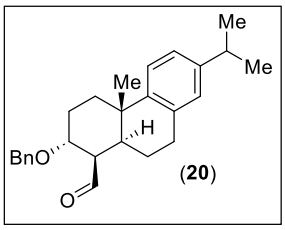
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd. for $[C_{26}H_{34}O_2 + Na]^+$ 401.2456, found 401.2451.

$[\alpha]^{25}_{589}$ = +68.4 (*c* = 0.1, $CHCl_3$).

Synthesis of compound (+)-20:



In an oven dried round-bottom flask the alcohol **19** (438 mg, 1.157 mmol, 1.0eq.) was charged in CH_2Cl_2 under N_2 atmosphere. Pyridinium chlorochromate (300 mg, 6.98 mmol, 1.2 eq.) was added to the reaction mixture and then it was stirred at 25 ºC for 2 h. After completion of the reaction (monitored by TLC) the crude product was purified by flash chromatography with *n*-Hexane-EtOAc (9:1) to afford **20** as white foam (361 mg, 83% yield).



(1*R*,2*R*,4a*S*,10a*S***)-2-(Benzyloxy)-7-isopropyl-4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carbaldehyde** [(+)-**20**]: (+)-**20** was obtained as white gel (1.15 mmol scale; 361 mg; 83%). R_f = 0.36 (10% EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.23 (d, *J* = 3.7 Hz, 1H), 7.40 – 7.34 (m, 4H), 7.33 – 7.30 (m, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 7.04 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.94 (d, *J* = 2.1 Hz, 1H), 4.62 (d, *J* = 3.4 Hz, 2H), 3.67 (dt, *J* = 12.0, 5.2 Hz, 1H), 2.97 – 2.80 (m, 4H), 2.47 (dt, *J* = 13.5, 3.7 Hz, 1H), 2.26 (d, *J* = 4.3 Hz, 1H), 2.23 – 2.14 (m, 1H), 2.04 – 1.96 (m, 1H), 1.93 – 1.86 (m, 2H), 1.62 – 1.55 (m, 1H), 1.27 (s, 3H), 1.25 (s, 3H), 1.14 (s, 3H).

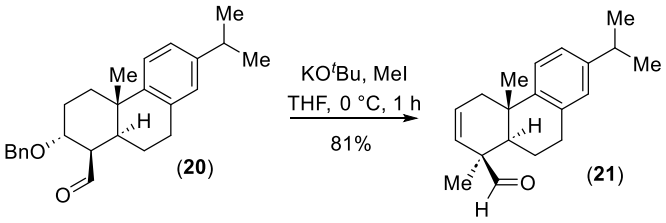
^{13}C NMR (125 MHz, $CDCl_3$): δ 204.5, 146.3, 143.8, 138.2, 134.7, 128.5, 127.7, 127.6, 127.2, 124.8, 124.2, 77.9, 70.3, 54.8, 45.7, 36.8, 36.4, 33.5, 30.3, 26.3, 26.0, 24.1, 24.0, 24.0.

IR (neat) ν_{max} 2878, 1853, 1681, 1455, 1164, 987, 874 cm^{-1}.

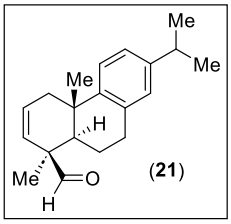
HRMS (ESI) *m/z*: $[M + Na]^+$ calcd. for $[C_{26}H_{32}O_2 + Na]^+$ 399.2300, found 399.2295.

$[\alpha]^{25}_{589}$ = +45.23 (*c* = 0.1, $CHCl_3$).

Synthesis of compound (+)-21:



In an oven dried round-bottom flask compound **20** (421 mg, 1.16 mmol, 1.0 equiv.) was taken in THF (12 mL) at 25 °C under an argon atmosphere. To this solution KO^{t}Bu (313.29 mg, 2.79 mmol, 2.5 equiv.) at 0 °C and methyl iodide (0.086 mL, 1.39 mmol, 1.2 equiv.) was added and stirred for an additional 1 h. After completion of the reaction (confirmed by TLC analysis), it was quenched with saturated aqueous $Na_2S_2O_3$ solution (10 mL). The reaction mixture was then extracted with EtOAc (10 mL X 2). The organic layers were collected, dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. It was purified by flash chromatography using 5% EtOAc in *n*-hexane to afford (+)-**21** as yellow liquid (266 mg, 81% yield).



(1*S*,4a*S*,10a*R***)-7-Isopropyl-1,4a-dimethyl-1,4,4a,9,10,10a-hexahydrophenanthrene-1-carbaldehyde** [(+)-**21**]: (+)-**21** was obtained as white foam (1.16 mmol scale; 266 mg; 81%). R_f = 0..52 (5% EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.86 (d, *J* = 1.8 Hz, 1H), 7.19 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.06 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.93 (d, *J* = 2.4 Hz, 1H), 5.95 (ddt, *J* = 9.7, 5.7, 1.9 Hz, 1H), 5.69 (ddq, *J* = 10.0, 2.8, 1.4 Hz, 1H), 2.95 (ddd, *J* = 16.3, 5.4, 2.6 Hz, 1H), 2.91 – 2.78 (m, 2H), 2.69 – 2.58 (m, 1H), 2.27 – 2.13 (m, 2H), 1.95 – 1.83 (m, 2H), 1.27 (s, 3H), 1.26 (s, 3H), 1.24 (s, 3H), 1.19 (s, 3H).

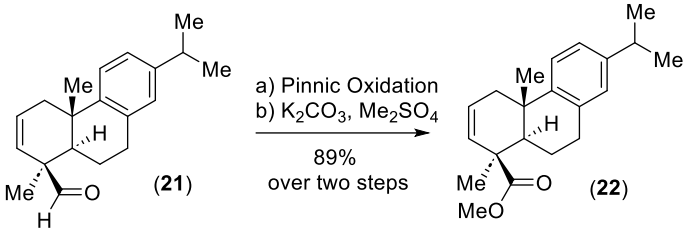
^{13}C NMR (125 MHz, $CDCl_3$): δ 205.4, 146.2, 143.7, 134.63, 129.8, 127.8, 126.8, 126.1, 124.6, 50.7, 50.0, 50.1, 40.1, 36.6, 33.6, 31.5, 25.5, 24.1, 23.3, 20.1.

IR (neat) ν_{max} 2868, 1813, 1639, 1443, 1135, 918, 875 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{20}H_{26}O + H]^+$ 283.2062, found 283.2056.

$[\alpha]^{25}_{589}$ = +65.3 (*c* = 0.3, $CHCl_3$).

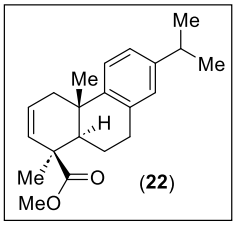
Synthesis of compound (+)-22:



In an oven dried round-bottom flask to a solution of the aldehyde compound **21** (358 mg, 1.267 mmol, 1.00 eq.) in a mixed solvent system of THF: H_2O: ^{t}BuOH (10:10:1), 2-Methyl-2-butene (1.346 mL, 12.67 mmol, 10.0 eq.) was added. Then a mixture of $NaClO_2$ (343 mg, 3.801 mmol, 3.00 eq.) and KH_2PO_4 (861 mg, 6.33 mmol, 5.0 eq.) at 0 °C. The mixture was warmed to room temperature and stirred for 2 h and 10 ml of water was added. Then it was extracted three times with EtOAc and dried over Na_2SO_4 and concentrated in a rotary evaporator under vacuum to afford 364 mg of the corresponding acid compound as white

foam. The crude product was charged for the next step without further purification. R_f = 0.25 (10% EtOAc in *n*-hexane).

In an oven-dried round-bottom flask crude acid was taken and dissolved in acetone solvent then K_2CO_3(349 mg, 2.53 mmol, 2.0 equiv.) and Me_2SO_4 (0.239 mL, 2.53 mmol, 2.0 equiv.) added simultaneously and stirred for 1h in 60 °C. Finally work up was done by CH_2Cl_2/H_2O. The organic filtrate was dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude products were purified by flash chromatography with n-Hexane-EtOAc (20:1) to afford compound **22** as yellow gel (352.32 mg, 68% yield over 2 steps), R_f= 0.42 (5% EtOAc in hexane).



(**22**)

Methyl (1*S*,4a*S*,10a*R*)**-7-isopropyl-1,4a-dimethyl-1,4,4a,9,10,10a-hexahydrophenanthrene-1-carboxylate** [(+)-**22**]: (+)-**22** was obtained as colourless liquid (1.26 mmol scale; 352 g; 89%over 2 steps). R_f = 0.42 (5% EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 – 7.19 (m, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.94 (s, 1H), 5.85 – 5.75 (m, 2H), 3.70 (d, *J* = 3.0 Hz, 3H), 2.94 (dd, *J* = 17.1, 4.7 Hz, 1H), 2.89 – 2.76 (m, 2H), 2.60 (dd, *J* = 17.6, 4.4 Hz, 1H), 2.31 (dd, *J* = 14.7, 4.4 Hz, 1H), 2.18 (d, *J* = 17.6 Hz, 1H), 1.94 (dd, *J* = 13.2, 4.8 Hz, 1H), 1.79 (d, *J* = 12.3 Hz, 1H), 1.43 (d, *J* = 2.9 Hz, 3H), 1.29 (s, 3H), 1.27 (d, *J* = 4.4 Hz, 3H), 1.19 (s, 3H).

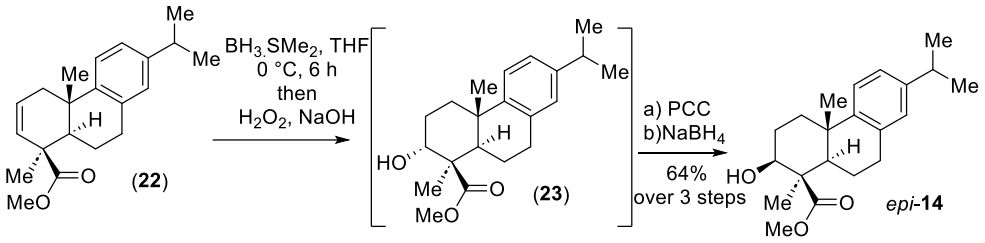
^{13}C NMR (125 MHz, $CDCl_3$): δ 176.3, 145.8, 144.2, 135.1, 131.6, 128.4, 127.8, 127.7, 126.7, 126.3, 124.9, 124.4, 51.7, 50.5, 45.3, 40.7, 36.6, 33.5, 31.8, 27.8, 24.0, 23.7, 21.3.

IR (neat) ν_{max} 3333, 2844, 1887, 1693, 1488, 1111, 957 cm^{-1}.

HRMS (ESI) *m/z*: $[M + H]^+$ calcd. for $[C_{21}H_{28}O_2 + H]^+$ 313.2168, found 313.2156.

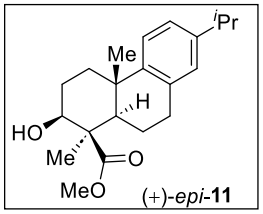
$[\alpha]^{25}_{589}$ = +47.2 (*c* = 1.0, $CHCl_3$).

Synthesis of compound (+)-4-*epi*-14:



In an oven dried round-bottom flask to a solution of compound **22** (235 mg, 0.682 mmol, 1.0 equiv.) in anhydrous THF (10 mL) at 0 °C under an N_2 atmosphere $Me_2S.BH_3$ (64.7 µL, 0.682 mmol, 1.0 equiv.) was added. The mixture was then stirred at 25 °C for 8 h. After completion of the reaction (confirmed by TLC analysis), 4 M NaOH (2 mL), and 30% H_2O_2 (1 mL) were added and stir the mixture was stirred at 25 °C for 4 h. Then the solution was extracted with ethyl acetate and water. The aqueous phase was extracted thrice with ethyl acetate. The organic filtrate was dried over anhydrous Na_2SO_4 and concentrated in a rotary evaporator under vacuum to afford the secondary hydroxy compound **23** and its epimer as a 3:1 mixture as yellow gel (441 mg). The crude product was charged for the next step without purification. The crude product was charged in CH_2Cl_2 under N_2 atmosphere. Pyridinium chlorochromate (175.9 mg, 0.818 mmol, 1.2 eq.) was added to the reaction mixture and then it was stirred at 25 ºC for 2 h. After completion of the reaction (monitored by TLC) the crude product was purified by flash chromatography with *n*-hexane-EtOAc (14:1) to afford the aldehyde as white foam which was charged for the next step.

To a stirred solution of the aldehyde (196 mg, 0.583 mmol, 1.0 equiv.) in MeOH (2 mL) at 0 °C was added $NaBH_4$ (22 mg, 0.583 mmol, 1.0 equiv.) and allowed to warm up to rt. After 30 min, the reaction was quenched with saturated aqueous NH_4Cl (3 mL) and the aqueous mixture was extracted with EtOAc and water. The aqueous layer was then extracted three times with EtOAc and dried over Na_2SO_4 and concentrated in a rotary evaporator under vacuum. The crude product was purified by column chromatography with *n*-hexane-EtOAc (3:1) to afford *epi*-**11** as colorless oil (144 mg, 64% yield over 3 steps).



Methyl (1*S*,2*S*,4a*S*,10a*R*)-**2-hydroxy-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-*epi*-**11**]: (+)-*epi*-**11** was obtained as white foam (0.682 mmol scale; 144 mg; 64% over 3 steps). R_f = 0.22 (10% EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (d, *J* = 8.1 Hz, 1H), 6.99 (dd, *J* = 8.5, 2.1 Hz, 1H), 6.88 (d, *J* = 2.1 Hz, 1H), 3.67 (s, 3H), 3.14 (dd, *J* = 12.3, 4.7 Hz, 1H), 2.86 (dd, *J* = 5.6, 1.9 Hz, 1H), 2.84 – 2.74 (m, 2H), 2.33 – 2.27 (m, 1H), 2.23 – 2.16 (m, 1H), 2.15 – 2.11 (m, 1H), 1.99 – 1.88 (m, 2H), 1.52 (dd, *J* = 13.7, 4.3 Hz, 1H), 1.48 (s, 3H), 1.43 (dd, *J* = 12.2, 1.8 Hz, 1H), 1.21 (d, *J* = 7.3 Hz, 6H), 1.04 (s, 3H).

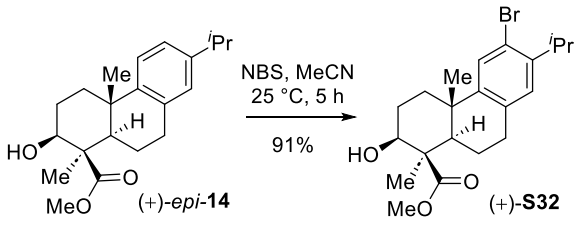
^{13}C NMR (125 MHz, $CDCl_3$): δ 178.5, 146.0, 144.7, 134.8, 126.8, 125.6, 124.2, 78.2, 52.5, 51.2, 49.0, 38.1, 37.8, 33.5, 32.2, 29.1, 24.0, 23.6, 22.8, 21.1.

IR (neat) ν_{max} 3352, 2862, 1827, 1621, 1435, 1164, 952 cm^{-1}.

HRMS (ESI) *m/z*: $[M + Na]^+$ calcd. for $[C_{21}H_{30}O_3 + Na]^+$ 353.2087, found 353.2082.

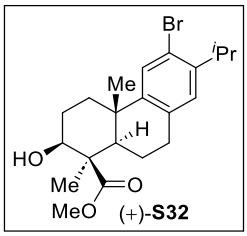
$[\alpha]^{25}_{589}$ = +75.40 (*c* = 0.3, $CHCl_3$).

Synthesis of compound (+)-S39:



In an oven dried round-bottom flask β-hydroxy compound (+)-*epi*-**14** (880 g, 2.66 mmol, 1.0 equiv.) was taken in CH_3CN (12 mL) at 25 °C under an argon atmosphere. To this solution was added a recrystallized *N*-bromo succinimide [NBS (568 mg, 3.19 mmol, 1.2 equiv.)] at 25 °C and stirred for an additional 4 h. After completion of the reaction (confirmed by TLC analysis),

it was quenched with saturated aqueous $Na_2S_2O_3$ solution (2 mL). The reaction mixture was then extracted with 50% EtOAc in *n*-hexane (10 mL X 2). The organic layers were collected, dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. It was purified by flash chromatography using 25% EtOAc in *n*-hexane to afford (+)-**S32** as white foam (990 mg, 91% yield).



Methyl (1*R*,2*S*,4a*S*,10a*R*)-**6-bromo-2-hydroxy-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-**S32**]**:** (+)-**S32** was obtained as white foam (2.66 mmol scale, 990 mg, 91% yield). R_f = 0.5 (20% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (s, 1H), 6.94 (s, 1H), 3.71 (s, 3H), 3.52 (d, *J* = 11.9 Hz, 1H), 3.31 – 3.24 (m, 1H), 3.17 (s, 1H), 2.89 (dd, *J* = 16.9, 5.3 Hz, 1H), 2.76 (dd, *J* = 12.7, 5.8 Hz, 1H), 2.29 – 2.26 (m, 1H), 2.21 – 2.16 (m, 2H), 1.98 (ddd, *J* = 19.7, 10.3, 5.6 Hz, 2H), 1.94 – 1.88 (m, 1H), 1.51 (s, 3H), 1.23 (d, *J* = 2.9 Hz, 6H), 1.07 (s, 3H).

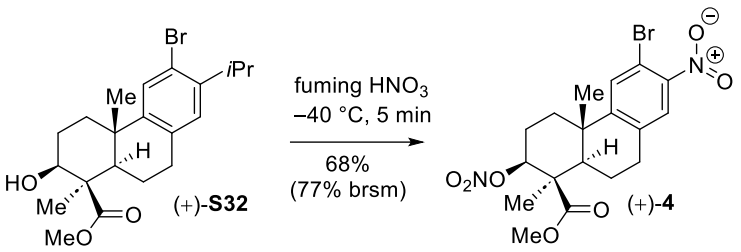
^{13}C NMR (125 MHz, $CDCl_3$): δ 178.3, 146.8, 144.4, 134.5, 129.9, 127.0, 121.7, 78.0, 52.1, 51.3, 48.9, 38.0, 37.9, 32.3, 31.7, 29.0, 23.5, 22.9, 22.8, 22.8, 20.9.

IR (neat) υ_{max} 3312, 2815, 2786, 1654, 1639, 1524, 1416, 1319, 846, 763 cm^{-1}.

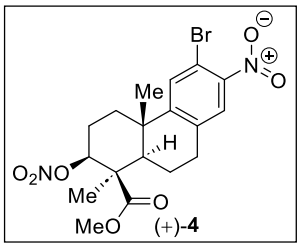
HRMS (ESI) *m*/*z*: [M+ Na]$^+$ calcd. for [$C_{21}H_{29}BrO_3$ + Na]$^+$ 431.1192, found 431.1147.

$[\alpha]^{25}_{589}$ = +48.3 (*c* = 0.65, $CHCl_3$).

Synthesis of compound (+)-4:



An oven-dried round-bottom flask was charged with 2 mL of fuming nitric acid and it was cooled to – 40 °C. Then compound (+)**-S32** (873 mg, 2.13 mmol, 1.0 equiv.) was directly charged into the reaction vessel and scratched well with a spatula (5 minutes) maintaining the – 40 °C temperature. After 5 minutes (TLC analysis showed product formation), the reaction mixture was quenched with water (5 mL) and saturated $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (10 mL X 3). The organic layers were dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure and purified by column chromatography 10% EtOAc in *n*-hexane to afford compound (+)**-4** as light green foam [663 mg, 68% yield (77% BRSM)].



Methyl (1*R*,2*S*,4a*S*,10a*R*)**-6-bromo-1,4a-dimethyl-7-nitro-2-(nitrooxy)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)**-4**]**:** (+)**-4** was obtained as a light green foam following the procedure described above. (2.13 mmol scale, 663 mg, 68% yield); R_f = 0.5 (20% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): 7.62 (s, 1H), 7.59 (s, 1H), 4.79 (dd, *J* = 12.4, 4.5 Hz, 1H), 3.75 (s, 3H), 3.05 – 2.99 (m, 1H), 2.86 (dt, *J* = 12.6, 6.6 Hz, 1H), 2.70 (dd, *J* = 13.2, 4.1 Hz, 1H), 2.47 – 2.43 (m, 1H), 2.30 (dd, *J* = 14.3, 6.7 Hz, 1H), 2.12 (dd, *J* = 13.3, 4.2 Hz, 1H), 1.88 (dd, *J* = 13.1, 6.0 Hz, 1H), 1.71 (d, *J* = 4.2 Hz, 1H), 1.66 – 1.61 (m, 2H), 1.48 (s, 3H), 1.14 (s, 3H).

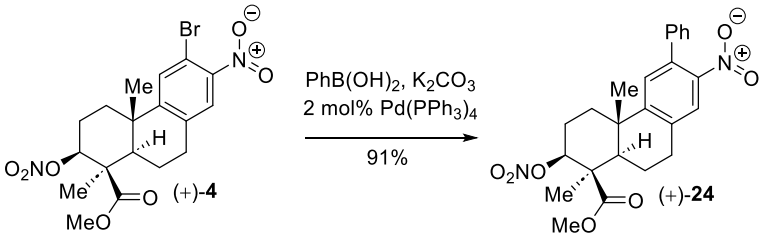
^{13}C NMR (125 MHz, $CDCl_3$): δ 173.0, 153.4, 147.3, 135.8, 132.2, 126.3, 111.6, 87.3, 51.9, 51.6, 48.4, 38.4, 36.8, 30.6, 23.8, 23.6, 22.7, 19.8.

IR (neat): υ_{max} 1842, 1734, 1590, 1372, 1274, 1132, 1012, 937, 728 cm^{-1}.

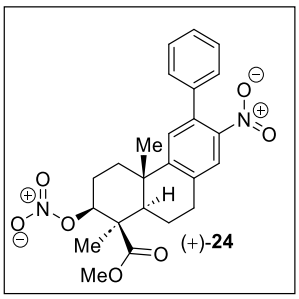
HRMS (ESI) *m*/*z*: [M+ Na]$^+$ calcd. for [$C_{18}H_{21}BrN_2O_7$ + Na]$^+$ 479.0424, found 479.0475.

$[\alpha]^{25}_{589}$ = +74.2 (*c* = 0.8, $CHCl_3$).

Synthesis of compound (+)-24:



A round-bottom flask was charged with (+)-**4** (623 g, 1.36 mmol, 1.0 equiv.) and benzene boronic acid (199 mg, 1.63 mmol, 1.2 equiv.) in a mixture of benzene (9 mL), EtOH (3 mL), and water (3 mL) at room temperature under argon atmosphere. Next, potassium carbonate (376 mg, 2.72 mmol, 2.0 equiv.) was added to the reaction mixture followed by the addition of catalyst, tetrakis(triphenylphosphine)palladium(0) (32 mg, 0.027 mmol, 0.02 equiv.) at the same temperature. Then the reaction mixture was placed on a pre-heated oil bath maintaining temperature of 80 °C. Upon completion of the reaction (10 h), as monitored by TLC analysis, it was extracted with 20% EtOAc in *n*-hexane (10 mL X 2). The combined organic layers were washed with brine (5 mL X 1) and dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. The crude product was purified by flash chromatography with 15% EtOAc in *n*-hexane to furnish (+)-**24** as a white solid (558 mg, 91% yield).



Methyl (1*R*,2*S*,4a*S*,10a*R*)-**1,4a-dimethyl-7-nitro-2-(nitrooxy)-6-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-**24**]**:** (+)-**24** was obtained as a white solid; (MP: 148-152 °C); (1.35 mmol scale, 558 mg, 91% yield); R_f = 0.5 (20% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.43 (d, *J* = 6.9 Hz, 3H), 7.29 (d, *J* = 7.2 Hz, 3H), 4.81 (dd, *J* = 12.4, 4.4 Hz, 1H), 3.76 (d, *J* = 1.8 Hz, 3H), 3.11 (dd, *J* = 17.6, 5.8 Hz, 1H), 2.97 (dd, *J* = 12.1, 6.6 Hz, 1H), 2.73 – 2.67 (m, 1H), 2.51 – 2.47 (m, 1H), 2.35 – 2.31 (m, 1H), 2.12 – 2.08 (m, 1H), 1.93 (dt, *J* = 13.2, 6.5 Hz, 1H), 1.70 (d, *J* = 12.2 Hz, 2H), 1.50 (s, 3H), 1.18 (s, 3H).

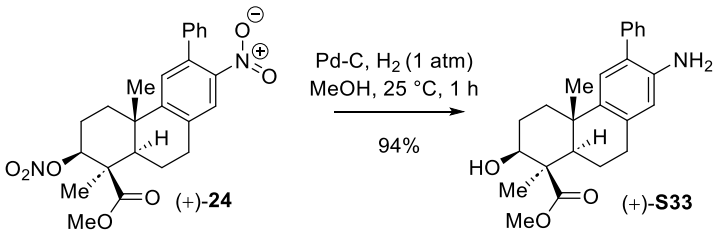
^{13}C NMR (125 MHz, $CDCl_3$): δ 173.1, 151.9, 146.9, 137.8, 135.5, 134.2, 129.1, 128.6, 128.1, 127.9, 124.7, 87.6, 52.0, 51.9, 48.5, 38.4, 36.9, 30.8, 23.9, 23.6, 22.7, 20.1.

IR (neat) υ_{max} 1863, 1758, 1631, 1314, 1161, 1037, 987, 725 cm^{-1}.

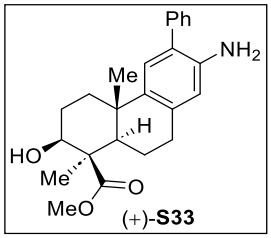
HRMS (ESI) *m*/*z*: $[M+ H]^+$ calcd. for $[C_{24}H_{26}N_2O_7 + H]^+$ 455.1813, found 455.1822.

$[\alpha]^{25}_{589}$ = +32.2 (*c* = 0.83, $CHCl_3$).

Synthesis of compound (+)-S41:



In an oven-dried round-bottom flask compound **(+)-24** (510 mg, 1.12 mmol, 1.0 equiv.) was taken in MeOH (10 mL) and degassed with N_2 balloon for 10 minutes. To this solution was added Pd/C (10% w/w) (51 mg) and a H_2 gas balloon (1 atm.) was placed with the reaction vessel and stirring continued until the full consumption of starting material (1 h), as confirmed by TLC analysis. The reaction mixture was filtered, evaporated to dryness under the reduced pressure, and it was purified by column chromatography with 30% EtOAc in *n*-hexane to afford **(+)-S33** as a yellow foam (409 mg, 96% yield).



Methyl (1*R*,2*S*,4a*S*,10a*R*)-**7-amino-2-hydroxy-1,4a-dimethyl-6-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate** [(+)-**S33**]**:** (+)-**S33** was obtained as a yellow foam (1.12 mmol scale, 409 mg, 94% yield); R_f = 0.2 (20% EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 4.2 Hz, 4H), 7.34 – 7.31 (m, 1H), 7.01 (s, 1H), 6.48 (s, 1H), 3.68 (s, 3H), 3.16 (d, *J* = 7.5 Hz, 1H), 2.88 – 2.83 (m, 1H), 2.80 – 2.70 (m, 2H), 2.28 – 2.24 (m, 1H), 2.18 – 2.15 (m, 1H), 2.14 – 2.11 (m, 1H), 1.93 (dd, *J* = 13.3, 4.8 Hz, 2H), 1.55 – 1.51 (m, 1H), 1.49 (s, 3H), 1.05 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 178.6, 140.6, 139.6, 138.6, 135.6, 129.2, 128.9, 128.0, 127.2, 126.7, 115.5, 78.3, 52.8, 51.4, 49.1, 38.4, 37.6, 32.0, 29.2, 23.6, 23.0, 21.2.

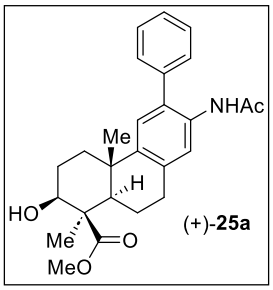
IR (neat): υ_{max} 3642, 2871, 2738, 1817, 1681, 1216, 1163, 1067, cm^{-1}.

HRMS (ESI) *m*/*z*: $[M+ Na]^+$ calcd. for $[C_{24}H_{29}NO_3 + Na]^+$ 402.2040, found 402.2027.

$[\alpha]^{25}_{589}$ = +54.3 (*c* = 0.85, $CHCl_3$).

Synthesis of compound (+)-25a:

Following the procedure described for (+)-**S4**, compound (+)-**25a** was prepared from compound (+)-**S33**. (ref.2)



Methyl (1*R*,2*S*,4a*S*,10a*R*)-7-acetamido-2-hydroxy-1,4a-dimethyl-6-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate [(+)-**25a**]: (+)-**25a** was obtained as reddish foam. (0.61 mmol scale, 224 mg, 95% yield). R_f = 0.2 (30 % EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.49 (t, *J* = 7.3 Hz, 2H), 7.42 (d, *J* = 7.3 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.14 (s, 1H), 7.06 (s, 1H), 3.72 (s, 3H), 3.53 (d, *J* = 12.0 Hz, 1H), 3.23 – 3.16 (m, 1H), 3.01 (dd, *J* = 17.7, 4.6 Hz, 1H), 2.87 (td, *J* = 17.5, 15.1, 6.0 Hz, 1H), 2.30 (d, *J* = 13.2 Hz, 1H), 2.26 – 2.16 (m, 2H), 2.02 (s, 3H), 2.00 – 1.93 (m, 2H), 1.53 (s, 3H), 1.46 (d, *J* = 7.1 Hz, 1H), 1.09 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 178.5, 168.3, 143.7, 138.5, 135.6, 132.1, 130.6, 129.3, 129.0, 127.8, 127.4, 121.9, 78.1, 52.4, 51.3, 49.0, 38.1, 37.9, 32.1, 29.0, 24.5, 23.5, 22.9, 21.0.

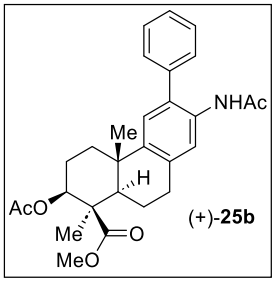
IR (neat): υ_{max} 3337, 2913, 2798, 1863, 1745, 1187, 1142, 881 cm^{-1}.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $[C_{26}H_{31}O_4N + H]^+$ 422.2326, found 422.2351.

$[\alpha]^{25}_{589}$ = +60.50 (*c* = 0.67, $CHCl_3$).

Synthesis of compound (+)-25b:

Following the procedure described for (+)-**S4**, compound (+)-**25b** was prepared rom compound (+)-**S33**. (ref.3)



Methyl (1*R*,2*S*,4a*S*,10a*R*)-7-acetamido-2-acetoxy-1,4a-dimethyl-6-phenyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate [(+)-**25b**]: (+)-**25b** was obtained as white foam. (0.37 mmol scale, 161 mg, 94% yield). R_f = 0.18 (30 % EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.12 (s, 1H), 7.06 (s, 1H), 4.63 (dd, *J* = 12.2, 4.6 Hz, 1H), 3.73 (s, 3H),

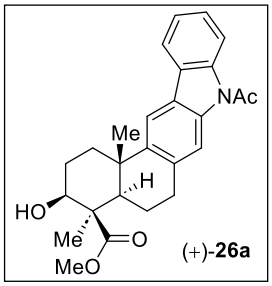
3.07 – 3.00 (m, 1H), 2.90 (ddd, *J* = 17.9, 12.1, 6.8 Hz, 1H), 2.59 – 2.49 (m, 1H), 2.35 (dt, *J* = 13.3, 3.6 Hz, 1H), 2.26 – 2.19 (m, 1H), 2.11 (s, 3H), 2.02 (s, 3H), 1.94 – 1.89 (m, 1H), 1.86 – 1.81 (m, 1H), 1.63 (ddd, *J* = 12.3, 7.7, 2.9 Hz, 2H), 1.35 (s, 3H), 1.14 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 174.3, 171.0, 168.3, 144.2, 138.5, 135.3, 132.2, 130.5, 129.3, 129.0, 127.8, 126.8, 121.9, 79.1, 51.8, 51.2, 48.2, 37.7, 37.2, 31.2, 24.7, 24.5, 23.7, 23.0, 21.4, 20.5.

IR (neat): υ_{max} 2995, 2751, 1832, 1736, 1699, 1617, 1267, 1188, 730 cm^{-1}.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd. for $[C_{28}H_{33}O_5N + H]^+$ 464.2437, found 464.2425.

$[\alpha]^{25}_{589}$ = +52.00 (*c* = 0.64, $CHCl_3$).



Methyl (3*S*,4*R*,4a*R*,13b*S*)-8-acetyl-3-hydroxy-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazole-4-carboxylate ([(+)-**26a**]: (+)-**26a** was obtained as white foam (0.18 mmol scale of reaction; 60 mg; 79%). R_f = 0.32 (20% EtOAc in *n*-hexane).

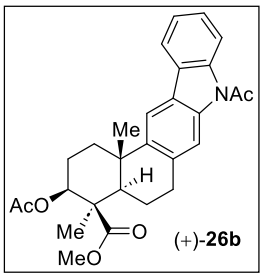
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.3 Hz, 1H), 7.92 (ddd, *J* = 7.6, 1.4, 0.7 Hz, 1H), 7.86 (s, 1H), 7.85 (s, 1H), 7.44 – 7.39 (m, 1H), 7.34 (td, *J* = 7.4, 1.0 Hz, 1H), 3.70 (s, 3H), 3.55 (d, *J* = 12.0 Hz, 1H), 3.21 (tt, *J* = 7.5, 3.3 Hz, 1H), 3.15 – 3.07 (m, 1H), 2.98 (ddd, *J* = 17.2, 12.6, 5.9 Hz, 1H), 2.83 (d, *J* = 1.7 Hz, 3H), 2.50 (dd, *J* = 13.2, 3.6 Hz, 1H), 2.27 – 2.20 (m, 2H), 2.05 – 1.99 (m, 2H), 1.73 – 1.66 (m, 1H), 1.63 (dd, *J* = 13.4, 3.9 Hz, 1H), 1.52 (s, 3H), 1.14 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 178.5, 170.0, 143.6, 138.9, 137.1, 135.1, 127.0, 126.7, 125.0, 123.6, 119.5, 116.6, 116.3, 116.2, 78.1, 52.5, 51.4, 49.1, 38.6, 38.3, 33.2, 29.2, 27.7, 23.6, 23.5, 21.2.

IR (neat) υ_{max} 3343, 2831, 1648, 1517, 1488, 1372, 914 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{26}H_{29}O_4N + Na]^+$ 442.1989, found 442.1992.

$[\alpha]^{25}_{589}$ = +112.7 (*c* = 0.78, $CHCl_3$).



Methyl (3*S*,4*R*,4a*R*,13b*S*)**-3-acetoxy-8-acetyl-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazole-4-carboxylate** ([(+)-**26b**]: (+)-**26b** was obtained as as a yellow gel (0.27 mmol scale of reaction; 101 mg; 81%). R_f = 0.35 (30% EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.3 Hz, 1H), 7.91 (ddd, *J* = 7.6, 1.4, 0.7 Hz, 1H), 7.86 (s, 1H), 7.83 (s, 1H), 4.67 – 4.63 (m, 1H), 3.71 (s, 3H), 3.17 – 3.09 (m, 1H), 3.01 (ddd, *J* = 17.3, 11.8, 6.5 Hz, 1H), 2.82 (d, *J* = 1.1 Hz, 3H), 2.63 – 2.53 (m, 2H), 2.24 (ddt, *J* = 13.7, 6.7, 1.9 Hz, 1H), 2.11 (s, 3H), 1.98 – 1.93 (m, 1H), 1.87 (ddd, *J* = 12.3, 6.2, 1.6 Hz, 1H), 1.70 (d, *J* = 10.8 Hz, 1H), 1.67 – 1.63 (m, 1H), 1.34 (s, 3H), 1.20 – 1.18 (m, 3H).

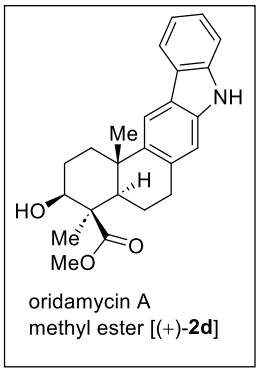
^{13}C NMR (125 MHz, $CDCl_3$): δ 174.3, 171.0, 170.0, 144.1, 138.9, 137.1, 134.7, 126.9, 126.7, 124.9, 123.6, 119.5, 116.2, 116.2, 116.0, 79.0, 51.9, 51.3, 48.3, 38.2, 37.6, 32.3, 27.6, 24.9, 23.8, 23.4, 21.4, 20.7.

IR (neat) υ_{max} 2942, 2741, 1837, 1701, 1123, 1498, 1063, 918 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{28}H_{31}O_5N + Na]^+$ 484.2100, found 484.2101.

$[\alpha]^{25}_{589}$ = +60.7 (*c* = 0.68, $CHCl_3$).

Preparation of (+)**-Oridamycin A methyl ester [**(+)**-2b] from** (+)**-26b:** Following the procedure mentioned for compound (+)**-6** deacetylation to addressed xiamycin A methylester [(+)-**2b**], (+)-oridamycin A methyl ester [(+)-**2d**] was prepared from (+)-**26b**.



oridamycin A
methyl ester [(+)-**2d**]

Methyl (3*S*,4*R*,4a*R*,13b*S*)-**3-hydroxy-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazole-4-carboxylate** [(+)-**2d**]**:** Oridamycin A methylester (+)-**2d** was obtained as white solid [MP: 106–108 ºC] (0.173 mmol scale, 63.8 mg, 98% yield). R_f = 0.25 (40% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CHCl_3$): δ 8.02 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 2.3 Hz, 1H), 7.87 (s, 1H), 7.38 (d, *J* = 4.6 Hz, 2H), 7.21 (dd, *J* = 8.3, 5.7 Hz, 1H), 7.09 (s, 1H), 3.78 (dd, *J* = 26.0, 2.6 Hz, 1H), 3.74 (s, 3H), 3.28 – 3.21 (m, 1H), 3.17 – 3.09 (m, 1H), 3.03 (td, *J* = 16.8, 14.9, 5.8 Hz, 1H), 2.59 (dd, *J* = 13.1, 3.2 Hz, 1H), 2.27 (q, *J* = 9.2, 5.3 Hz, 2H), 2.11 – 2.02 (m, 2H), 1.68 (dd, *J* = 15.8, 12.1 Hz, 1H), 1.57 (s, 3H), 1.20 (d, *J* = 2.4 Hz, 3H).

^{13}C NMR (125 MHz, CD_3OD): δ 178.6, 140.1, 139.5, 138.2, 133.7, 125.5, 123.5, 122.3, 120.0, 119.2, 117.1, 110.5, 109.7, 78.2, 52.9, 51.3, 49.1, 39.0, 38.4, 33.1, 29.3, 23.8, 23.7, 21.3.

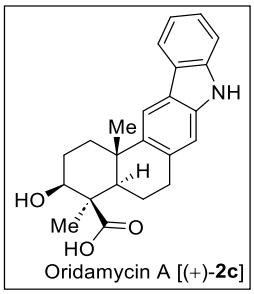
IR (neat) υ_{max} 3361, 2974, 2838, 1712, 1667,1523, 1412, 1233, 743, 591 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ H]^+$ calcd. for $[C_{24}H_{27}O_3N + H]^+$ 378.2069, found 378.2070.

$[\alpha]^{25}_{589}$ = +76.7 (*c* = 0.65, $CHCl_3$).

Total Synthesis of (+)**-Oridamycin A [**(+)**-2c] from** [(+)-**2d**]**:** Following the above-mentioned procedure for compound (+)-**2b** to synthesize the xiamycin A [(+)-**2a**] via

saponification, the total synthesis of (+)-oridamycin A [(+)-**2c**] was accomplished from oridamycin A methylester [(+)-**2d**] via saponification.



Oridamycin A [(+)-**2c**]

(3*S*,4*S*,4a*R*,13b*S*)-**3-Hydroxy-4,13b-dimethyl-2,3,4,4a,5,6,8,13b-octahydro-1H-naphtho[2,1-*b*]carbazole-4-carboxylic acid** [(+)-**2c**]**:** Oridamycin A [(+)-**2c**] was obtained as white foam (0.117 mmol scale, 32 mg, 75% yield). R_f = 0.2 (50% EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, CD_3OD): δ 7.98 (d, *J* = 6.7 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.07 (s, 1H), 3.27 (dd, *J* = 12.2, 4.5 Hz, 1H), 3.10 (dd, *J* = 16.2, 5.1 Hz, 1H), 3.02 – 2.93 (m, 1H), 2.61 (dt, *J* = 13.1, 3.6 Hz, 1H), 2.39 – 2.29 (m, 1H), 2.25 (dd, *J* = 14.1, 6.2 Hz, 1H), 2.15 (qd, *J* = 12.8, 5.2 Hz, 1H), 1.95 (dq, *J* = 12.4, 3.9 Hz, 1H), 1.65 – 1.59 (m, 1H), 1.55 (d, *J* = 4.1 Hz, 1H), 1.52 (s, 3H), 1.29 (s, 3H).

^{13}C NMR (125 MHz, CD_3OD): δ 181.0, 142.0, 140.3, 140.0, 134.4, 126.0, 124.5, 123.1, 120.5, 119.3, 117.4, 111.3, 110.6, 79.0, 54.0, 49.7, 39.9, 39.5, 33.9, 30.2, 24.7, 24.5, 22.4.

IR (neat) υ_{max} 3364, 2937, 2218, 1653, 1437, 1031, 929, 869 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{23}H_{25}O_3N + Na]^+$ 386.1727, found 386.1736.

$[\alpha]^{25}_{589}$ = +92.1 (*c* = 0.73, CH_3OH); lit.[7] $[\alpha]_D^{22}$ = +100.3 (*c* = 0.4, CH_3OH).

Comparison of ^{1}H-NMR Data of (+)-Oridamycin A [(+)-**2c**] of this report with natural (+)-**2a** by Takada[7] and with literature by Sarpong[6] and Krische[8]:

Takada's report on the isolation of (+)-Oridamycin A [(+)-**2c**] (^{1}H-NMR, 600 MHz, CD_3OD)[7]

δ (ppm)	Int.	mult.	*J* (Hz)
7.93	1H	d	*J* = 8.0 Hz
7.93	1H	s	-
7.32	1H	d	*J* = 8.0 Hz
7.25	1H	dt	*J* = 8.1, 1.4 Hz
7.05	1H	dt	*J* = 8.1, 1.4 Hz
7.03	1H	s	-
3.22	1H	dd	*J* = 12.2, 4.6 Hz
3.06	1H	ddd	*J* = 16.3, 5.4, 2.3
2.94	1H	ddd	*J* = 16.3, 5.4, 2.3
2.57	1H	dt	*J* = 13.6, 3.6 Hz
2.30	1H	dq	*J* = 12.6, 2.3 Hz
2.23	1H	m	-
2.09	1H	dt	*J* = 12.7, 5.4
1.90	1H	qd	*J* = 13.6, 3.6 Hz
1.58	1H	dt	*J* = 13.6, 4.1 Hz
1.56	1H	m	-
1.48	3H	s	-
1.26	3H	s	-

Sarpong's Synthesis of (+)-Oridamycin A [(+)-**2c**] (^{1}H-NMR, 700 MHz, CD_3OD)[6]			
δ (ppm)	Int.	mult.	*J* (Hz)
7.96	1H	d	*J* = 8.0 Hz
7.96	1H	s	-
7.34	1H	d	*J* = 8.0 Hz
7.28	1H	t	*J* = 7.6 Hz
7.08	1H	d	*J* = 7.6 Hz
7.07	1H	s	-
3.26	1H	d	*J* = 11.5 Hz
3.10	1H	dd	*J* = 16.2, 4.6 Hz

2.98	1H	dd	*J* = 16.5, 4.6 Hz
2.60	1H	dd	*J* = 13.2, 2.0 Hz
2.38-2.31	1H	m	-
2.25	1H	dd	*J* = 13.9, 6.0 Hz
2.20-2.15	1H	m	-
1.98-1.92	1H	m	-
1.65-1.60	1H	m	-
1.57-1.45	4H	m	-
1.29	3H	s	-

Krische's report (+)-Oridamycin A [(+)-**2c**] (^{1}H-NMR, 500 MHz, CD_3OD)[8]			
δ (ppm)	Int.	mult.	*J* (Hz)
7.96	1H	dt	*J* = 8.1, 1.0 Hz
7.96	1H	s	-
7.34	1H	dt	*J* = 8.1, 0.9 Hz
7.28	1H	ddd	*J* = 8.1, 7.1, 1.2 Hz
7.08	1H	ddd	*J* = 8.1, 7.1, 1.2 Hz
7.06	1H	s	-
3.25	1H	dd	*J* = 12.2, 4.4 Hz
3.08	1H	ddd	*J* = 17.2, 5.6, 1.9 Hz
2.97	1H	dddd	*J* = 16.5, 12.7, 6.2, 1.3 Hz
2.60	1H	dt	*J* = 13.2, 3.7 Hz
2.32	1H	qd	*J* = 13.3, 3.8 Hz
2.28-2.19	1H	m	-
2.20-2.07	1H	m	-
1.93	1H	dq	*J* = 13.1, 3.9 Hz
1.61	1H	td	*J* = 13.5, 3.9 Hz
1.52	1H	dd	*J* = 12.2, 2.1 Hz
1.50	3H	s	-
1.28	3H	s	-

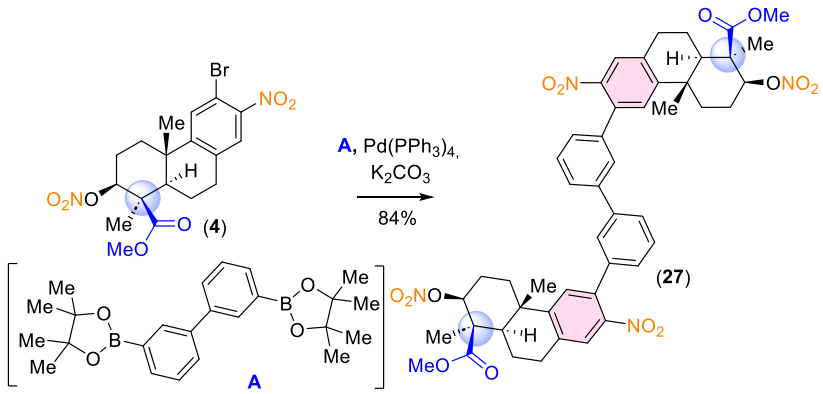
This Synthesis of (+)-Oridamycin A [(+)-**2c**] (^{1}H-NMR, 500 MHz, CD_3OD)			
δ (ppm)	Int.	mult.	*J* (Hz)
7.98	2H	d	*J* = 6.7 Hz
7.36	1H	d	*J* = 8.1 Hz
7.30	1H	t	*J* = 7.6 Hz
7.10	1H	t	*J* = 7.5 Hz
7.07	1H	s	-
3.27	1H	dd	*J* = 12.2, 4.5 Hz
3.10	1H	dd	*J* = 16.2, 5.1 Hz
3.02 – 2.93	1H	m	-
2.61	1H	dt	*J* = 13.1, 3.6 Hz
2.39 – 2.29	1H	m	-
2.25	1H	dd	*J* = 14.1, 6.2 Hz
2.15	1H	qd	*J* = 12.8, 5.2 Hz
1.95	1H	dq	*J* = 12.4, 3.9 Hz
1.65 – 1.59	1H	m	-
1.55	1H	d	*J* = 4.1 Hz
1.52	3H	s	-
1.29	3H	s	-

Comparison of ^{13}C-NMR Data:

Takada's report (+)-Oridamycin A [(+)-**2c**] (^{13}C-NMR, 151 MHz, CD_3OD)[7]	Sarpong's report (+)-Oridamycin A [(+)-**2c**] (^{13}C-NMR, 176 MHz, CD_3OD)[6]	Krische's report (+)-Oridamycin A [(+)-**2c**] (^{13}C-NMR, 125 MHz, CD_3OD)[8]	This report (+)-Oridamycin A [(+)-**2c**] (^{13}C-NMR, 125 MHz, CD_3OD)
181.0	181.0	181.0	181.0
142.0	142.0	142.1	142.0
140.3	140.3	140.4	140.3
140.1	140.1	140.1	140.0

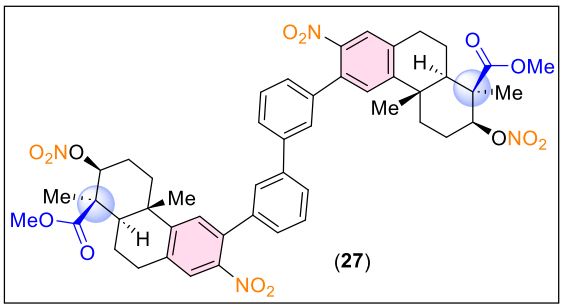
134.5	134.5	134.5	134.4
126.1	126.0	126.1	126.0
124.6	124.6	124.6	124.5
123.2	123.2	123.3	123.1
120.5	120.6	120.6	120.5
119.3	119.3	119.3	119.3
117.5	117.5	117.5	117.4
111.4	111.4	111.4	111.3
110.7	110.7	110.7	110.6
79.1	79.0	79.1	79.0
54.1	54.0	54.1	54.0
48.7	49.8	49.8	49.7
40.0	39.9	40.0	39.9
39.6	39.6	39.6	39.5
34.0	34.0	34.0	33.9
30.3	30.2	30.3	30.2
24.8	24.8	24.8	24.7
24.6	24.5	24.6	24.5
22.5	22.5	22.5	22.4

Synthesis of *bis*-nitro compound (27) *via* double Suzuki-Miyaura coupling:



A round-bottom flask was charged with (+)-**4** (435 mg, 0.951 mmol, 1.0 equiv.) and 3,3'-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1'-biphenyl (193 mg, 0.475 mmol, 0.5 equiv.) in a mixture of benzene (3 mL), EtOH (1 mL), and water (1 mL) at room temperature

under argon atmosphere. Next, potassium carbonate (263 mg, 1.9 mmol, 2.0 equiv.) was added to the reaction mixture followed by the addition of catalyst, tetrakis(triphenylphosphine)palladium(0) (27 mg, 0.024 mmol, 0.025 equiv.) at the same temperature. Then the reaction mixture was placed on a pre-heated oil bath maintaining temperature of 80 °C. Upon completion of the reaction (3 h), as monitored by TLC analysis, it was extracted with EtOAc (10 mL X 2). The combined organic layers were washed with brine (5 mL X 1) and dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. The crude product was purified by flash chromatography with 20-30% EtOAc in *n*-hexane to furnish (+)-**27** as a white solid (361.0 mg, 84% yield).



Dimethyl 6,6'-([1,1'-biphenyl]-3,3'-diyl)(1*R*,1'*R*,2*S*,2'*S*,4a*S*,4a'*S*,10a*R*,10a'*R*)-bis(1,4a-dimethyl-7-nitro-2-(nitrooxy)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate) [(+)-**27**]: (+)-**27** was obtained as colorless foam (0.475 mmol scale of reaction; 361.0 mg; 84%). R_f = 0.22 (20 % EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.59 (ddd, *J* = 7.8, 1.8, 1.1 Hz, 1H), 7.48 (dd, *J* = 7.7, 0.5 Hz, 1H), 7.45 (dt, *J* = 1.8, 0.9 Hz, 1H), 7.32 (s, 1H), 7.29 – 7.21 (m, 1H), 4.78 (dd, *J* = 12.2, 4.4 Hz, 1H), 3.73 (s, 3H), 3.08 (dd, *J* = 17.5, 5.7 Hz, 1H), 2.93 (ddd, *J* = 17.9, 12.1, 6.7 Hz, 1H), 2.73 – 2.61 (m, 1H), 2.51 – 2.44 (m, 1H), 2.33 – 2.26 (m, 1H), 2.11 – 2.04 (m, 1H), 1.90 (ddd, *J* = 12.3, 6.0, 1.7 Hz, 1H), 1.76 – 1.65 (m, 2H), 1.47 (s, 3H), 1.15 (s, 3H).

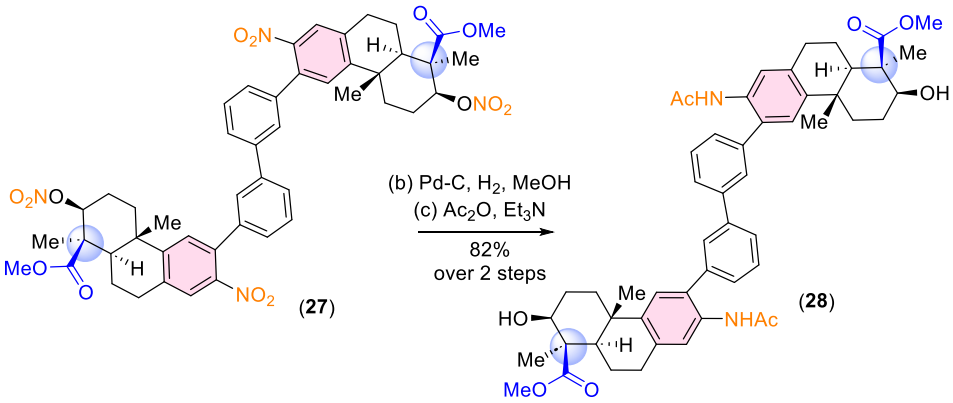
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 173.1, 152.1, 146.8, 141.1, 138.4, 135.7, 134.0, 129.2, 129.1, 127.2, 127.0, 124.8, 87.6, 52.0, 51.9, 48.5, 38.5, 37.0, 30.8, 23.8, 23.6, 22.7, 20.1.

IR (neat): υ_{max} 3334, 2857, 1733, 1635, 1378, 1223, 931, 751 cm^{-1}.

HRMS (ESI) *m/z*: $[M+ NH_4]^+$ calcd. for $[C_{48}H_{50}N_4O_{14} + NH_4]^+$ 924.3667, found 924.3683.

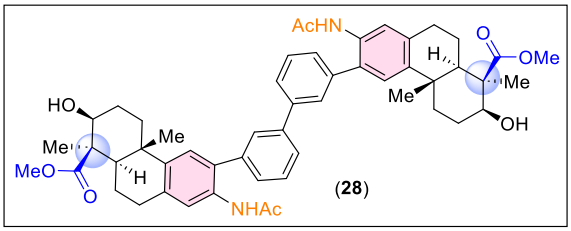
$[\alpha]^{25}_{589}$ = +105.0 (*c* = 0.2, $CHCl_3$).

Synthesis of *bis*-acetenalide compound (28) from compound (27):



In an oven-dried round-bottom flask *bis*-nitro compound (+)-**27** (155 mg, 0.171 mmol, 1.0 equiv.) was taken in MeOH (5 mL) and degassed with N_2 balloon for 10 minutes. To this solution Pd/C (20% w/w) (32 mg) was added and a H_2 gas balloon (1 atm.) was placed with the reaction vessel and stirring continued until the full consumption of starting material (4 h), as confirmed by TLC analysis. The reaction mixture was filtered, evaporated to dryness under the reduced pressure. The crude *bis*-aniline was charged for the next step without further purification.

In an oven dried round-bottom flask *bis*-aniline was taken in CH_2Cl_2 (3 mL) and Et_3N (48 µL, 0.342 mmol., 2.1 equiv.) was added to the reaction mixture. Next, acetic anhydride (32 µL, 0.342 mmol., 2.1 equiv.) was added to the reaction mixture at 25 ºC and stirring continued until the full consumption of starting material. Upon completion (6 h), as monitored by TLC analysis, it was extracted with CH_2Cl_2 (5 mL X 2). The organic layers were dried over Na_2SO_4 and concentrated in a rotary evaporator under reduced pressure. The crude product was purified by flash column chromatography with 60-80% EtOAc in *n*-hexane to afford (+)-**28** as yellow foam (117 mg, 82% over 2 steps).



Dimethyl 6,6'-([1,1'-biphenyl]-3,3'-diyl)(1*R*,1'*R*,2*S*,2'*S*,4a*S*,4a'*S*,10a*R*,10a'*R*)-bis(7-acetamido-2-hydroxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate) [(+)-**28**]: (+)-**28** was obtained as yellowish foam (0.171 mmol scale of reaction; 117 mg; 82%). R_f = 0.35 (70 % EtOAc in *n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.15 (s, 1H), 7.07 (s, 1H), 3.69 (s, 3H), 3.52 (d, *J* = 11.9 Hz, 1H), 3.15 (td, *J* = 12.1, 4.6 Hz, 1H), 2.99 (dd, *J* = 17.2, 5.2 Hz, 1H), 2.84 (ddd, *J* = 17.5, 12.7, 6.0 Hz, 1H), 2.28 – 2.15 (m, 2H), 2.09 (d, *J* = 9.7 Hz, 1H), 2.00 (s, 3H), 1.97 – 1.92 (m, 2H), 1.87 (d, *J* = 6.7 Hz, 1H), 1.49 (s, 3H), 1.06 (s, 3H).

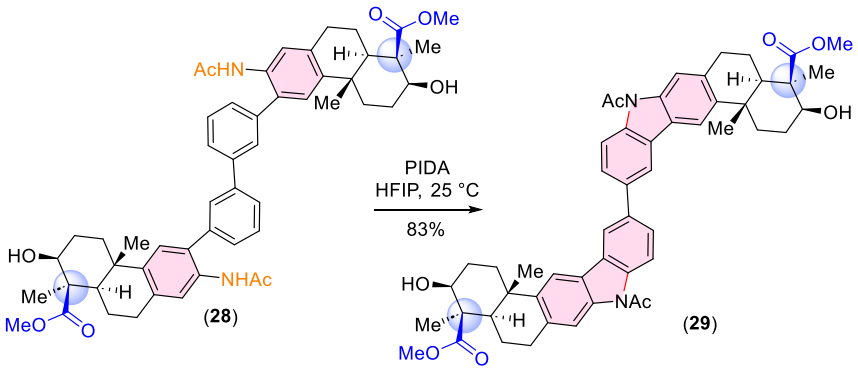
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 178.6, 168.5, 144.1, 141.6, 139.3, 136.0, 132.1, 130.7, 129.6, 128.5, 128.2, 127.5, 126.7, 122.5, 78.1, 52.4, 51.5, 49.0, 38.2, 38.0, 32.1, 29.1, 24.6, 23.6, 23.0, 21.0.

IR (neat) υ_{max} 3328, 2853, 1733, 1648, 1345, 1287, 991, 725 cm^{-1}.

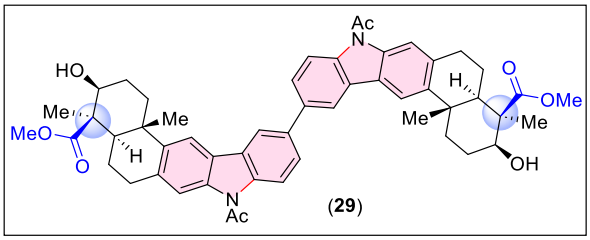
HRMS (ESI) *m/z*: [M+ H]$^+$ calcd. for [$C_{52}H_{60}O_8N_2$ + H]$^+$ 841.4428, found 841.4435.

[α] $^{25}_{589}$ = +97.35 (*c* = 0.7, $CHCl_3$).

Intramolecular oxidative C-N coupling of *bis*-acetenalide compound (28):



In an oven-dried round-bottom flask *bis*-acetanilide (64 mg, 0.076 mmol, 1.0 equiv.) was taken in 1,1,1,3,3,3- hexafluoropropan-2-ol (2 mL) under an inert atmosphere. To the solution $PhI(OAc)_2$ (59 mg, 0.076 mmol, 2.4 equiv.) was added and stirred the mixture at room temperature. After completion of reaction (monitored by TLC), it was quenched with saturated $Na_2S_2O_3$ solution then reaction mixture was extracted with CH_2Cl_2 (5 mL X 3). The organic layers were dried over Na_2SO_4 and concentrated on rotary evaporator under reduced pressure. Then the crude product was purified by flash column chromatography with 70- 80% EtOAc in *n*-Hexane to afford carbazole compounds **29**.



(**29**)

Dimethyl (3*S*,3'*S*,4*R*,4a*R*,4'*R*,4'a*R*,13b*S*,13'b*S***)-8,8'-diacetyl-3,3'-dihydroxy-4,4',13b,13'b-tetramethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13*b*,13'*b*-hexadecahydro-1*H*,1'*H*-[11,11'-binaphtho[2,1-*b*]carbazole]-4,4'-dicarboxylate** [(+)-**29**]: (+)-**29** was obtained as white foam (0.045 mmol scale of reaction; 35 mg; 86%). R_f = 0.3 (40 % EtOAc in n-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.8 Hz, 1H), 8.21 (d, *J* = 1.8 Hz, 1H), 7.97 (d, *J* = 4.9 Hz, 1H), 7.88 (s, 1H), 7.75 (dt, *J* = 8.7, 1.6 Hz, 1H), 3.72 (d, *J* = 2.3 Hz, 1H), 3.71 (s, 3H), 3.22 (dd, *J* = 12.0, 4.6 Hz, 1H), 3.14 (dd, *J* = 16.9, 5.2 Hz, 1H), 3.08 – 2.92 (m, 1H), 2.87 (d, *J* = 1.4 Hz, 3H), 2.61 – 2.53 (m, 1H), 2.26 (dd, *J* = 12.9, 4.6 Hz, 2H), 2.09 – 2.03 (m, 2H), 1.65 (d, *J* = 4.1 Hz, 1H), 1.53 (s, 3H), 1.18 (s, 3H).

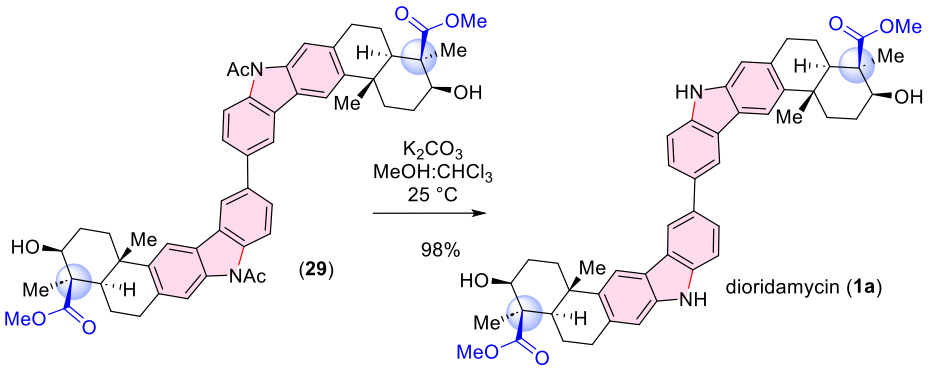
^{13}C{^{1}H) NMR (101 MHz, $CDCl_3$): δ 178.5, 170.0, 143.8, 138.3, 137.6, 136.8, 135.5, 127.4, 126.4, 125.1, 118.0, 117.0, 116.3, 78.1, 52.6, 51.5, 49.1, 38.7, 38.5, 33.4, 29.2, 27.8, 23.7, 23.6, 21.3.

IR (neat) υ_{max} 3366, 2838, 1783, 1627, 1353, 1248, 922, 719 cm^{-1}.

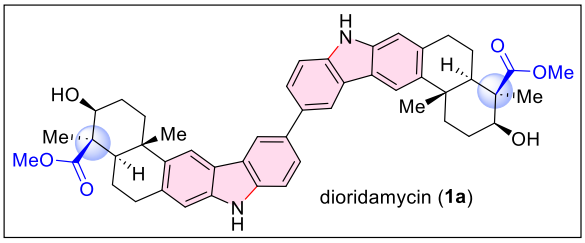
HRMS (ESI) *m/z*: $[M+ H]^+$ calcd. for $[C_{52}H_{56}O_8N_2 + H]^+$ 837.4115, found 837.4117.

$[\alpha]^{25}_{589}$ = +103.4 (*c* = 0.1, $CHCl_3$).

Total synthesis of dioridamycin (1a):



In an oven dried round-bottom flask, (+)-**29** (47 mg, 0.056 mmol, 1.0 equiv.) was taken in a mixture of methanol and chloroform [MeOH: $CHCl_3$ (4:1)] solvent (2 mL). To this solution was added K_2CO_3 (16 mg, 0.112 mmol, 4.0 equiv.) at 25 ºC and stirring was continued for an additional 2 h. After completion of the reaction (judged by TLC analysis), the reaction mixture was diluted with water (3 mL). Next, it was extracted with dichloromethane (5 mL X 2). The organic layers were dried over Na_2SO_4 and concentrated on a rotary evaporator under reduced pressure. Next, the crude methyl ester was purified by flash column chromatography with pure EtOAc in *n*-hexane to afford unnatural dioridamycin (+)-**1a** as a white foam (42 mg, 98% yield).



Dimethyl (3*S*,3'*S*,4*R*,4a*R*,4'*R*,4'a*R*,13b*S*,13'b*S*)**-3,3'-dihydroxy-4,4',13b,13'b-tetramethyl-2,2',3,3',4,4a,4',4'a,5,5',6,6',8,8',13*b*,13'*b*-hexadecahydro-1*H*,1'*H*-[11,11'-binaphtho[2,1-b]carbazole]-4,4'-dicarboxylate** [(+)-**1a**]: (+)-**1a** was obtained as brown foam (0.056 mmol scale of reaction; 42 mg; 98%). R_f = 0.4 (70 % EtOAc in *n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 – 8.26 (m, 1H), 8.04 (s, 1H), 7.86 (s, 1H), 7.71 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.47 – 7.38 (m, 1H), 7.08 (s, 1H), 3.71 (s, 3H), 3.58 (d, *J* = 11.7 Hz, 1H), 3.22

(s, 1H), 3.11 (dd, *J* = 16.9, 5.0 Hz, 1H), 3.08 – 2.95 (m, 1H), 2.60 (d, *J* = 13.2 Hz, 1H), 2.24 (dd, *J* = 14.8, 7.0 Hz, 2H), 2.09 – 1.99 (m, 2H), 1.67 (d, *J* = 4.0 Hz, 1H), 1.53 (s, 3H), 1.18 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 178.6, 139.6, 139.1, 138.7, 133.8, 133.8, 125.4, 124.1, 122.5, 118.5, 117.2, 110.6, 109.8, 78.2, 52.9, 51.3, 49.1, 39.1, 38.4, 33.10, 29.3, 23.8, 23.7, 21.4.

IR (neat) υ_{max} 3436, 2921, 1761, 1658, 1460, 1374, 1287, 967, 884, 752, cm^{-1}.

HRMS (ESI) *m/z*: $[M+ Na]^+$ calcd. for $[C_{48}H_{52}O_6N_2 + Na]^+$ 775.3723, found 775.3730.

$[\alpha]^{25}_{589}$ = +107.74 (*c* = 0.1, CH_3OH).

Crystal Data and Structure Refinement of (+)-**24**

A colorless block 0.25 × 0.21 × 0.15 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 293.15 K using omega scans. Crystal-to-detector distance was 43.92 mm and exposure time was 0.50 seconds per frame at low angles and 2.00 seconds at high angles, using a scan width of 0.5°. The 2Θ range for data collection /° 6.866 to 139.414. A total of 16632 reflections were collected covering the indices $-9 \leq h \leq 10$, $-11 \leq k \leq 11$, $-16 \leq l \leq 16$. 5867 reflections were founded to be symmetry independent, with an R_{int} of 0.0630. Indexing and unit cell refinement indicated a primitive, triclinic lattice. The space group was found to be P1/c (No. 14). CrysAlis^{Pro} 1.171.41.115a (Rigaku Oxford Diffraction, 2021) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2018/2) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by least-squares (SHELXL-2018/3). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2018/3.

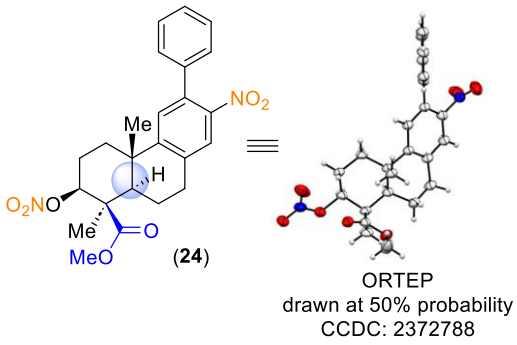


Figure S1. Single crystal XRD structure of compound (+)-**24**. ORTEP drawn at 50% probability level.

Table 1 Crystal data and structure refinement for sk-no2 .Identification code	sk-no2
Empirical formula	C24H26N2O7
Formula weight	454.47
Temperature/K	293
Crystal system	triclinic
Space group	P1
a/Å	8.9599(5)

b/Å	9.7829(5)
c/Å	13.9325(5)
α/°	104.835(4)
β/°	103.742(4)
γ/°	99.489(4)
Volume/Å3	1113.12(10)
Z	2
ρcalcg/cm3	1.356
μ/mm-1	0.835
F(000)	480.0
Crystal size/mm3	0.25 × 0.21 × 0.15
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.866 to 139.414
Index ranges	-9 ≤ h ≤ 10, -11 ≤ k ≤ 11, -16 ≤ l ≤ 16
Reflections collected	16632
Independent reflections	5867 [Rint = 0.0630, Rsigma = 0.0541]
Data/restraints/parameters	5867/3/601
Goodness-of-fit on F2	1.110
Final R indexes [I>=2σ (I)]	R1 = 0.0795, wR2 = 0.2111
Final R indexes [all data]	R1 = 0.0818, wR2 = 0.2212
Largest diff. peak/hole / e Å-3	0.69/-0.42

Table S2: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for skNO2. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O24	0(5)	2583(4)	6053(3)	39.6(9)
O64	2761(5)	9736(4)	3032(3)	42.1(9)
O57	3598(5)	7742(4)	4006(3)	40.2(9)
O31	-877(5)	410(4)	6908(3)	42.6(9)
O56	11243(5)	6584(6)	-150(4)	55.6(12)
O62	4849(5)	11539(4)	3307(4)	47.0(10)
O29	249(5)	-1384(4)	6352(3)	43.4(9)
O27	1131(6)	4897(5)	6221(4)	56.0(11)
O60	2669(6)	6654(5)	4976(3)	50.0(10)
N54	10327(6)	7247(5)	-545(4)	42.7(11)
N25	-19(6)	3873(5)	5812(4)	43.2(11)
O26	-1263(6)	3809(5)	5195(3)	50.7(10)
N58	3541(7)	6599(5)	4438(4)	46.3(12)

Table S2: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for skNO2. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O23	11019(6)	3294(7)	10228(4)	70.5(15)
O55	10391(6)	7601(6)	-1305(4)	61.5(12)
C34	8474(7)	8978(6)	1425(4)	39.0(12)
O22	10537(6)	2857(7)	11572(4)	69.6(15)
C47	9574(7)	8634(6)	909(4)	40.7(12)
C13	7422(7)	3298(6)	10634(4)	37.4(11)
C43	6890(6)	8208(6)	989(4)	35.7(11)
N21	10113(6)	2916(6)	10676(4)	47.0(12)
C65	4500(7)	9133(6)	1030(4)	39.6(11)
C61	4173(6)	10160(6)	3228(4)	36.8(11)
O59	4318(8)	5744(6)	4256(4)	68.9(16)
C5	1491(6)	2589(6)	6786(4)	35.8(11)
C42	5624(6)	8366(6)	1556(4)	35.0(11)
C46	9084(7)	7584(7)	-57(4)	39.5(12)
C28	213(7)	28(6)	6646(4)	36.2(11)
C35	9040(7)	10168(6)	2465(4)	41.5(12)
C45	7513(7)	6863(6)	-565(4)	36.6(11)
C12	8399(7)	2576(6)	10151(4)	39.0(11)
C3	3153(6)	3322(6)	8613(4)	37.3(11)
C14	5839(6)	2949(6)	10069(4)	35.3(11)
C39	4616(7)	7705(6)	3310(4)	38.1(11)
C44	6448(7)	7179(6)	-14(4)	36.1(11)
C41	4736(6)	6825(6)	1491(4)	36.1(11)
C6	1637(7)	1010(6)	6534(4)	36.6(11)
C51	5942(8)	3855(7)	-3650(4)	48.0(14)
C40	3658(7)	6850(6)	2196(4)	38.2(11)
C52	5225(7)	4993(7)	-3396(5)	45.2(13)
C37	6495(7)	9201(6)	2731(4)	36.1(11)
C7	3275(6)	1071(6)	7295(4)	35.3(11)
C50	7153(7)	3660(7)	-2889(5)	45.8(13)
C48	6979(7)	5792(6)	-1621(4)	37.2(12)
C36	7670(7)	10586(6)	2843(5)	42.4(12)
C19	9736(7)	6673(6)	12880(4)	41.3(12)
C53	5734(7)	5954(7)	-2387(4)	40.3(12)
C38	5400(7)	9303(6)	3456(4)	36.3(11)
C4	1565(7)	3309(6)	7898(4)	35.7(11)
C16	7264(7)	4279(6)	12445(4)	39.4(12)
C15	7997(6)	4406(6)	11676(4)	36.4(11)
C2	3484(6)	1792(6)	8467(4)	35.4(11)

Table S2: Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for skNO2. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	5225(6)	1973(6)	9064(4)	36.3(11)
C8	3845(8)	-343(7)	7134(5)	45.8(13)
C32	1680(7)	473(7)	5409(4)	42.8(13)
C49	7656(7)	4624(6)	-1894(4)	39.9(12)
C30	-1100(8)	-2389(6)	6374(5)	48.6(14)
C17	7769(7)	5318(6)	13419(4)	41.0(12)
C10	6225(7)	1200(6)	8630(4)	40.3(12)
C20	9234(7)	5632(6)	11912(4)	40.4(12)
C33	2436(7)	900(6)	8925(4)	40.2(12)
C11	7826(7)	1562(7)	9184(5)	43.3(13)
C18	9001(7)	6507(7)	13641(4)	44.5(13)
C66	6404(7)	10011(7)	4600(4)	45.7(13)
C9	5643(7)	62(6)	7573(5)	43.5(13)
C63	3739(9)	12411(7)	3074(8)	62.0(19)

Table 3: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for skNO2. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O24	41(2)	40.1(19)	23.2(17)	1.2(14)	-3.1(15)	0.8(16)
O64	39(2)	44(2)	34.2(19)	3.9(16)	7.7(16)	1.3(17)
O57	47(2)	41(2)	28.5(18)	7.0(15)	10.1(16)	6.0(17)
O31	37(2)	42(2)	34.9(19)	-0.9(16)	3.6(16)	1.6(16)
O56	41(2)	73(3)	38(2)	-2(2)	6.8(19)	13(2)
O62	40(2)	35(2)	53(2)	0.6(18)	9.2(19)	2.2(16)
O29	51(2)	31.7(19)	34.9(19)	-1.5(15)	6.2(17)	4.0(16)
O27	52(3)	48(2)	60(3)	18(2)	8(2)	1(2)
O60	59(3)	53(2)	31.4(19)	6.6(17)	15.7(19)	2(2)
N54	36(2)	47(3)	31(2)	-0.9(19)	7.2(19)	-4(2)
N25	46(3)	46(3)	34(2)	10(2)	8(2)	9(2)
O26	55(3)	55(2)	32(2)	9.8(18)	-1.1(19)	12(2)
N58	62(3)	39(2)	30(2)	1.7(19)	13(2)	6(2)
O23	41(3)	103(4)	43(3)	-5(3)	12(2)	-5(3)
O55	62(3)	79(3)	41(2)	17(2)	20(2)	2(2)
C34	38(3)	41(3)	25(2)	2(2)	2(2)	-1(2)

Table 3: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for skNO2. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
O22	52(3)	93(4)	55(3)	31(3)	-3(2)	9(3)
C47	34(3)	48(3)	26(2)	1(2)	2(2)	-4(2)
C13	37(3)	40(3)	27(2)	5(2)	5(2)	4(2)
C43	35(3)	37(3)	26(2)	2(2)	5(2)	1(2)
N21	38(3)	50(3)	40(3)	2(2)	4(2)	4(2)
C65	38(3)	39(3)	29(3)	0(2)	3(2)	1(2)
C61	35(3)	41(3)	25(2)	1(2)	7(2)	2(2)
O59	115(5)	62(3)	59(3)	29(2)	50(3)	48(3)
C5	33(3)	42(3)	22(2)	3(2)	1(2)	3(2)
C42	34(3)	38(3)	23(2)	0.7(19)	4(2)	-1(2)
C46	38(3)	46(3)	26(2)	4(2)	7(2)	1(2)
C28	40(3)	37(3)	17(2)	-2.7(18)	-1.6(19)	2(2)
C35	37(3)	42(3)	28(3)	-1(2)	1(2)	-6(2)
C45	37(3)	37(3)	25(3)	2(2)	6(2)	0(2)
C12	33(3)	42(3)	33(3)	7(2)	1(2)	3(2)
C3	35(3)	39(3)	24(2)	-2.3(19)	3(2)	1(2)
C14	34(3)	36(3)	28(3)	3(2)	6(2)	4(2)
C39	37(3)	46(3)	24(2)	3(2)	7(2)	4(2)
C44	35(3)	36(3)	27(2)	3(2)	4(2)	0(2)
C41	35(3)	38(3)	23(2)	-1.8(19)	3(2)	4(2)
C6	38(3)	41(3)	18(2)	-2.0(19)	2(2)	1(2)
C51	47(3)	53(3)	27(3)	-4(2)	8(2)	-2(3)
C40	39(3)	36(3)	26(3)	-2(2)	6(2)	-3(2)
C52	43(3)	55(3)	27(3)	8(2)	5(2)	0(3)
C37	33(3)	40(3)	22(2)	0(2)	2(2)	0(2)
C7	35(3)	38(3)	21(2)	-0.4(19)	2(2)	2(2)
C50	42(3)	47(3)	36(3)	-1(2)	10(2)	1(2)
C48	36(3)	43(3)	24(3)	3(2)	7(2)	0(2)
C36	37(3)	40(3)	35(3)	-3(2)	6(2)	-2(2)
C19	34(3)	43(3)	35(3)	6(2)	2(2)	-1(2)
C53	37(3)	46(3)	29(3)	5(2)	5(2)	2(2)
C38	36(3)	37(3)	23(2)	-2.2(19)	2(2)	1(2)
C4	39(3)	33(2)	22(2)	-1.5(19)	0(2)	3(2)
C16	38(3)	40(3)	30(3)	5(2)	3(2)	0(2)
C15	32(3)	42(3)	26(2)	6(2)	0(2)	2(2)
C2	34(3)	37(3)	20(2)	-4.1(19)	0.6(19)	1(2)
C1	34(3)	36(3)	29(3)	2(2)	4(2)	2(2)
C8	46(3)	41(3)	33(3)	-6(2)	6(2)	1(2)
C32	43(3)	50(3)	21(2)	-2(2)	4(2)	4(2)
C49	41(3)	41(3)	29(3)	6(2)	7(2)	3(2)

Table 3: Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for skNO2. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C30	57(4)	36(3)	40(3)	5(2)	4(3)	1(3)
C17	40(3)	47(3)	31(3)	8(2)	8(2)	9(2)
C10	39(3)	40(3)	30(3)	1(2)	4(2)	3(2)
C20	37(3)	43(3)	31(3)	8(2)	3(2)	0(2)
C33	39(3)	43(3)	25(2)	1(2)	0(2)	0(2)
C11	40(3)	46(3)	34(3)	2(2)	8(2)	6(2)
C18	45(3)	44(3)	28(3)	0(2)	-1(2)	1(2)
C66	45(3)	52(3)	21(2)	-5(2)	0(2)	1(3)
C9	42(3)	39(3)	36(3)	-3(2)	4(2)	10(2)
C63	57(4)	41(3)	95(6)	24(4)	31(4)	14(3)

Table 4: Bond Lengths for skNO2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O24	N25	1.388(6)	C28	C6	1.531(8)
O24	C5	1.474(6)	C35	C36	1.521(9)
O64	C61	1.204(7)	C45	C44	1.385(8)
O57	N58	1.398(6)	C45	C48	1.485(7)
O57	C39	1.479(7)	C12	C11	1.371(8)
O31	C28	1.203(7)	C3	C4	1.527(7)
O56	N54	1.240(7)	C3	C2	1.545(7)
O62	C61	1.350(7)	C14	C1	1.397(7)
O62	C63	1.446(8)	C39	C40	1.520(7)
O29	C28	1.345(7)	C39	C38	1.544(8)
O29	C30	1.439(8)	C41	C40	1.531(8)
O27	N25	1.216(7)	C6	C7	1.575(7)
O60	N58	1.203(7)	C6	C32	1.532(7)
N54	O55	1.207(7)	C51	C52	1.385(10)
N54	C46	1.476(8)	C51	C50	1.401(9)
N25	O26	1.216(7)	C52	C53	1.396(8)
N58	O59	1.190(7)	C37	C36	1.521(8)
O23	N21	1.203(7)	C37	C38	1.564(8)
C34	C47	1.386(8)	C7	C2	1.556(6)
C34	C43	1.398(8)	C7	C8	1.534(8)
C34	C35	1.518(7)	C50	C49	1.382(8)
O22	N21	1.234(8)	C48	C53	1.409(8)
C47	C46	1.387(8)	C48	C49	1.390(8)
C13	C12	1.400(8)	C19	C20	1.384(8)

Table 4: Bond Lengths for skNO2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C13	C14	1.386(8)	C19	C18	1.402(9)
C13	C15	1.484(7)	C38	C66	1.542(7)
C43	C42	1.535(8)	C16	C15	1.404(8)
C43	C44	1.417(7)	C16	C17	1.388(8)
N21	C12	1.475(7)	C15	C20	1.401(8)
C65	C42	1.515(8)	C2	C1	1.541(7)
C61	C38	1.512(8)	C2	C33	1.533(8)
C5	C6	1.529(7)	C1	C10	1.409(8)
C5	C4	1.510(7)	C8	C9	1.524(9)
C42	C41	1.554(8)	C17	C18	1.378(9)
C42	C37	1.566(6)	C10	C11	1.395(8)
C46	C45	1.387(8)	C10	C9	1.511(7)

Table 5: Bond Angles for skNO2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N25	O24	C5	114.7(4)	C40	C39	C38	113.7(4)
N58	O57	C39	113.8(4)	C45	C44	C43	123.4(5)
C61	O62	C63	114.5(5)	C40	C41	C42	113.6(4)
C28	O29	C30	115.3(5)	C5	C6	C28	110.6(4)
O56	N54	C46	117.3(5)	C5	C6	C7	104.8(4)
O55	N54	O56	123.5(5)	C5	C6	C32	109.2(4)
O55	N54	C46	119.2(5)	C28	C6	C7	114.4(4)
O27	N25	O24	119.5(5)	C28	C6	C32	108.3(4)
O26	N25	O24	112.3(5)	C32	C6	C7	109.5(4)
O26	N25	O27	128.2(5)	C52	C51	C50	119.9(5)
O60	N58	O57	111.4(5)	C39	C40	C41	109.6(5)
O59	N58	O57	119.6(5)	C51	C52	C53	119.7(5)
O59	N58	O60	129.0(6)	C36	C37	C42	110.4(4)
C47	C34	C43	119.6(5)	C36	C37	C38	117.8(4)
C47	C34	C35	118.6(5)	C38	C37	C42	114.9(4)
C43	C34	C35	121.8(5)	C2	C7	C6	115.2(4)
C34	C47	C46	119.9(5)	C8	C7	C6	116.8(5)
C12	C13	C15	123.9(5)	C8	C7	C2	110.4(4)
C14	C13	C12	116.0(5)	C49	C50	C51	119.9(6)
C14	C13	C15	120.1(5)	C53	C48	C45	119.2(5)
C34	C43	C42	123.6(5)	C49	C48	C45	122.8(5)
C34	C43	C44	118.0(5)	C49	C48	C53	118.1(5)
C44	C43	C42	118.3(5)	C37	C36	C35	108.6(5)

Table 5: Bond Angles for skNO2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O23	N21	O22	123.5(6)	C20	C19	C18	119.9(5)
O23	N21	C12	118.4(5)	C52	C53	C48	120.9(5)
O22	N21	C12	118.0(5)	C61	C38	C39	111.3(4)
O64	C61	O62	121.7(5)	C61	C38	C37	114.4(4)
O64	C61	C38	126.7(5)	C61	C38	C66	107.9(4)
O62	C61	C38	111.6(5)	C39	C38	C37	104.8(4)
O24	C5	C6	106.3(4)	C66	C38	C39	108.2(5)
O24	C5	C4	111.8(4)	C66	C38	C37	110.1(5)
C4	C5	C6	115.4(4)	C5	C4	C3	109.2(4)
C43	C42	C41	108.8(4)	C17	C16	C15	121.2(5)
C43	C42	C37	107.7(4)	C16	C15	C13	120.4(5)
C65	C42	C43	107.9(4)	C20	C15	C13	121.6(5)
C65	C42	C41	110.9(4)	C20	C15	C16	117.9(5)
C65	C42	C37	114.1(4)	C3	C2	C7	108.6(4)
C41	C42	C37	107.3(4)	C1	C2	C3	108.3(4)
C47	C46	N54	116.8(5)	C1	C2	C7	107.5(4)
C47	C46	C45	123.2(5)	C33	C2	C3	110.2(5)
C45	C46	N54	120.0(5)	C33	C2	C7	114.1(4)
O31	C28	O29	121.8(5)	C33	C2	C1	108.0(4)
O31	C28	C6	126.3(5)	C14	C1	C2	118.7(5)
O29	C28	C6	111.8(5)	C14	C1	C10	118.8(5)
C34	C35	C36	112.1(5)	C10	C1	C2	122.4(5)
C46	C45	C48	123.2(5)	C9	C8	C7	108.0(5)
C44	C45	C46	115.7(5)	C50	C49	C48	121.5(5)
C44	C45	C48	121.1(5)	C18	C17	C16	120.0(5)
C13	C12	N21	119.9(5)	C1	C10	C9	122.5(5)
C11	C12	C13	122.3(5)	C11	C10	C1	118.0(5)
C11	C12	N21	117.8(5)	C11	C10	C9	119.4(5)
C4	C3	C2	113.2(4)	C19	C20	C15	121.0(5)
C13	C14	C1	123.4(5)	C12	C11	C10	121.2(5)
O57	C39	C40	110.6(4)	C17	C18	C19	120.0(5)
O57	C39	C38	106.9(4)	C10	C9	C8	112.7(5)

Table 6: Torsion Angles for skNO2.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O24	C5	C6	C28	-58.9(5)	C12	C13	C14	C1	-1.9(8)
O24	C5	C6	C7	177.5(4)	C12	C13	C15	C16	-128.1(6)
O24	C5	C6	C32	60.2(6)	C12	C13	C15	C20	54.5(8)

Table 6: Torsion Angles for skNO2.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O24	C5	C4	C3	-178.2(4)	C3	C2	C1	C14	44.8(7)
O64	C61	C38	C39	5.3(7)	C3	C2	C1	C10	-134.7(5)
O64	C61	C38	C37	123.9(6)	C14	C13	C12	N21	177.8(5)
O64	C61	C38	C66	-113.2(6)	C14	C13	C12	C11	-1.2(8)
O57	C39	C40	C41	-180.0(4)	C14	C13	C15	C16	53.4(7)
O57	C39	C38	C61	-57.4(5)	C14	C13	C15	C20	-124.0(6)
O57	C39	C38	C37	178.4(4)	C14	C1	C10	C11	-6.7(8)
O57	C39	C38	C66	60.9(5)	C14	C1	C10	C9	176.5(5)
O31	C28	C6	C5	-1.0(7)	C39	O57	N58	O60	-178.2(4)
O31	C28	C6	C7	117.0(6)	C39	O57	N58	O59	2.5(8)
O31	C28	C6	C32	-120.6(6)	C44	C43	C42	C65	-72.6(6)
O56	N54	C46	C47	70.5(7)	C44	C43	C42	C41	47.8(6)
O56	N54	C46	C45	-109.6(6)	C44	C43	C42	C37	163.9(5)
O62	C61	C38	C39	-177.1(4)	C44	C45	C48	C53	52.8(7)
O62	C61	C38	C37	-58.6(6)	C44	C45	C48	C49	-127.2(6)
O62	C61	C38	C66	64.3(6)	C41	C42	C37	C36	167.8(4)
O29	C28	C6	C5	175.2(4)	C41	C42	C37	C38	-56.1(6)
O29	C28	C6	C7	-66.9(5)	C6	C5	C4	C3	60.2(6)
O29	C28	C6	C32	55.5(6)	C6	C7	C2	C3	-54.1(6)
N54	C46	C45	C44	175.6(5)	C6	C7	C2	C1	-171.1(4)
N54	C46	C45	C48	-3.1(8)	C6	C7	C2	C33	69.1(6)
N25	O24	C5	C6	-151.5(4)	C6	C7	C8	C9	155.5(5)
N25	O24	C5	C4	81.8(5)	C51	C52	C53	C48	0.5(9)
N58	O57	C39	C40	90.9(5)	C51	C50	C49	C48	0.4(9)
N58	O57	C39	C38	-144.8(4)	C40	C39	C38	C61	64.9(6)
O23	N21	C12	C13	-124.3(6)	C40	C39	C38	C37	-59.3(6)
O23	N21	C12	C11	54.8(8)	C40	C39	C38	C66	-176.8(5)
O55	N54	C46	C47	-110.7(6)	C52	C51	C50	C49	-1.6(10)
O55	N54	C46	C45	69.3(7)	C37	C42	C41	C40	53.0(6)
C34	C47	C46	N54	-178.3(5)	C7	C2	C1	C14	162.0(5)
C34	C47	C46	C45	1.7(9)	C7	C2	C1	C10	-17.5(7)
C34	C43	C42	C65	110.3(6)	C7	C8	C9	C10	45.7(7)
C34	C43	C42	C41	-129.3(5)	C50	C51	C52	C53	1.1(9)
C34	C43	C42	C37	-13.3(7)	C48	C45	C44	C43	-178.9(5)
C34	C43	C44	C45	2.4(8)	C36	C37	C38	C61	68.8(6)
C34	C35	C36	C37	47.5(6)	C36	C37	C38	C39	-169.0(5)
O22	N21	C12	C13	52.7(8)	C36	C37	C38	C66	-52.8(7)
O22	N21	C12	C11	-128.3(7)	C53	C48	C49	C50	1.2(9)
C47	C34	C43	C42	171.9(5)	C38	C39	C40	C41	59.8(6)
C47	C34	C43	C44	-5.2(8)	C38	C37	C36	C35	155.1(5)
C47	C34	C35	C36	170.6(5)	C4	C5	C6	C28	65.6(6)

Table 6: Torsion Angles for skNO2.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C47	C46	C45	C44	-4.4(8)	C4	C5	C6	C7	-58.0(6)
C47	C46	C45	C48	176.9(5)	C4	C5	C6	C32	-175.3(5)
C13	C12	C11	C10	0.1(9)	C4	C3	C2	C7	52.8(6)
C13	C14	C1	C2	-173.6(5)	C4	C3	C2	C1	169.2(4)
C13	C14	C1	C10	5.9(8)	C4	C3	C2	C33	-72.8(6)
C13	C15	C20	C19	178.6(5)	C16	C15	C20	C19	1.1(8)
C43	C34	C47	C46	3.3(9)	C16	C17	C18	C19	0.5(9)
C43	C34	C35	C36	-10.7(8)	C15	C13	C12	N21	-0.7(8)
C43	C42	C41	C40	169.3(4)	C15	C13	C12	C11	-179.7(6)
C43	C42	C37	C36	50.8(6)	C15	C13	C14	C1	176.7(5)
C43	C42	C37	C38	-173.1(4)	C15	C16	C17	C18	0.7(8)
N21	C12	C11	C10	-178.9(6)	C2	C3	C4	C5	-55.5(6)
C65	C42	C41	C40	-72.2(6)	C2	C7	C8	C9	-70.5(6)
C65	C42	C37	C36	-68.9(6)	C2	C1	C10	C11	172.8(5)
C65	C42	C37	C38	67.1(6)	C2	C1	C10	C9	-4.0(9)
C5	O24	N25	O27	-1.7(7)	C1	C10	C11	C12	3.9(9)
C5	O24	N25	O26	179.0(4)	C1	C10	C9	C8	-10.6(8)
C5	C6	C7	C2	55.1(6)	C8	C7	C2	C3	171.0(5)
C5	C6	C7	C8	-173.0(5)	C8	C7	C2	C1	54.0(6)
C42	C43	C44	C45	-174.9(5)	C8	C7	C2	C33	-65.7(6)
C42	C41	C40	C39	-55.7(6)	C32	C6	C7	C2	172.2(5)
C42	C37	C36	C35	-70.3(6)	C32	C6	C7	C8	-55.9(7)
C42	C37	C38	C61	-63.8(6)	C49	C48	C53	C52	-1.7(8)
C42	C37	C38	C39	58.3(6)	C30	O29	C28	O31	0.0(7)
C42	C37	C38	C66	174.5(5)	C30	O29	C28	C6	-176.4(4)
C46	C45	C44	C43	2.3(8)	C17	C16	C15	C13	-179.0(5)
C46	C45	C48	C53	-128.6(6)	C17	C16	C15	C20	-1.4(8)
C46	C45	C48	C49	51.4(8)	C20	C19	C18	C17	-0.8(9)
C28	C6	C7	C2	-66.1(6)	C33	C2	C1	C14	-74.5(6)
C28	C6	C7	C8	65.8(6)	C33	C2	C1	C10	106.0(6)
C35	C34	C47	C46	-178.0(5)	C11	C10	C9	C8	172.7(6)
C35	C34	C43	C42	-6.8(8)	C18	C19	C20	C15	0.0(8)
C35	C34	C43	C44	176.1(5)	C9	C10	C11	C12	-179.2(6)
C45	C48	C53	C52	178.3(5)	C63	O62	C61	O64	-3.8(8)
C45	C48	C49	C50	-178.8(5)	C63	O62	C61	C38	178.6(6)

Table 7: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for skNO2.

Atom	***x***	***y***	***z***	**U(eq)**
H47	10638.32	9106.66	1210.86	49
H65A	5057.78	10105.69	1122.4	59
H65B	3644.59	9170.3	1332.51	59
H65C	4086.55	8609.14	302.05	59
H5	2362.51	3155.99	6632.87	43
H35A	9683.3	11021.69	2400.63	50
H35B	9698.31	9836.27	2974.75	50
H3A	3173.12	3736.32	9328.53	45
H3B	3992.19	3945.43	8482.35	45
H14	5149.21	3386.26	10374.39	42
H39	5447.45	7219.47	3533.14	46
H44	5388.31	6690.88	-317.83	43
H41A	4101.63	6320.05	778.13	43
H41B	5507.54	6277.94	1678.19	43
H51	5620.22	3221.24	-4324.84	58
H40A	2808.17	7298.3	1967.34	46
H40B	3192.17	5861.29	2156.31	46
H52	4408.14	5115.17	-3896.58	54
H37	7164.61	8573.92	2951.28	43
H7	4048.68	1736.38	7129.69	42
H50	7618.17	2882.24	-3053.87	55
H36A	8057.49	11187.27	3564.35	51
H36B	7156.91	11138.5	2435.16	51
H19	10558.86	7481.48	13026.47	50
H53	5244.48	6712.46	-2216.44	48
H4A	707.82	2778.93	8073.36	43
H4B	1450.5	4298.7	7986.66	43
H16	6423.8	3485.42	12300.2	47
H8A	3377.9	-951.29	7489.05	55
H8B	3533.37	-881.35	6400	55
H32A	722.29	528.6	4949.04	64
H32B	1773.14	-517.67	5248.12	64
H32C	2571.65	1073.36	5324.59	64
H49	8465.32	4489.53	-1395.56	48
H30A	-2041.91	-2307.69	5913.62	73
H30B	-1187.22	-2165.57	7067.96	73
H30C	-970.48	-3364.91	6156.04	73
H17	7275.64	5210.56	13921.26	49
H20	9726.15	5748.75	11411.01	48
H33A	2679.47	1374.65	9656.88	60

Table 7: Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for skNO2.

Atom	*x*	*y*	*z*	U(eq)
H33B	2629.46	-56.54	8812.3	60
H33C	1342.96	823.26	8592.57	60
H11	8518.03	1106.55	8893.19	52
H18	9344.54	7199.65	14294.24	53
H66A	6885.74	11011.91	4709.96	69
H66B	7213.97	9502.07	4758.38	69
H66C	5738.59	9958.27	5043.44	69
H9A	6002.47	-805.95	7624.75	52
H9B	6101.75	427.74	7096.29	52
H63A	3118.73	12010.18	2358.5	93
H63B	4308.64	13391.84	3199.93	93
H63C	3053.77	12410.57	3509.25	93

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