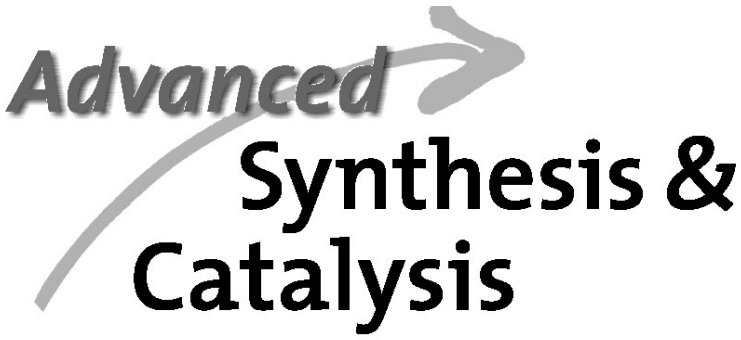

Supporting Information

A Tandem Nitroalkene Conjugate Addition/[3+2] Cycloaddition Approach to the Synthesis of the Pentacyclic Core of (±)-Scandine

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Supporting Information

General Experimental

Bulb-to-bulb distillations were done on a Büchi GKR-50 Kugelrohr apparatus and corresponding boiling points (bp) refer to air bath temperatures and are uncorrected. Melting points (mp) were determined on a Thomas-Hoover capillary melting point apparatus in sealed tubes and are uncorrected. Analytical TLC was performed on Merck Silica gel plates with QF-254 indicator. Visualization was accomplished with a UV light and/or a $KMnO_4$ or anisaldehyde solution. Column chromatography was performed by the method of Still with 230-400 mesh silica gel, or standard grade 150 mesh basic alumina.[1] Solvents for extraction and chromatography were technical grade and distilled from the indicated drying agents: dichloromethane ($CaCl_2$), ethyl acetate (K_2CO_3). Diethyl ether and hexanes were reagent grade.

^{1}H NMR spectra were recorded on Varian Unity-400, Unity-500, or Inova-500 spectrometers in the indicated deuterated solvent. Data are reported in the following order: chemical shift in ppm (δ) (multiplicity, which are indicated by br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet)); coupling constants (*J*, Hz); integration; assignment. Infrared spectra (IR) were obtained on a Mattson Galaxy 5020 spectrophotometer. Peaks are reported in cm^{-1} with the following relative intensities: s (strong, 67-100%), m (medium, 34-66%), w (weak, 1-33%). Mass spectra were performed by the University of Illinois Mass Spectroscopy Center. Low and high-resolution electron impact (EI, ionization voltages of 70 eV), and low-resolution field ionization (FI) mass spectra were obtained on a VG VSE spectrometer. Low-resolution

fast atom bombardment (FAB) mass spectra were obtained on a VG ZAB-SE spectrometer in magic bullet (3/1, dithiothreitol/dithioerythitol) or 3-nitrobenzyl alcohol. Electrospray ionization (ESI) mass spectrometry were performed on methanol solutions. Data are reported in the form of *m/e* (intensity relative to base = 100). Elemental analyses were performed by the University of Illinois Microanalytical Service Laboratory.

All reactions were performed in oven-dried (140 °C) or flame-dried glassware under an inert atmosphere of dry N_2. Low temperature experiments which proceeded for longer than 8 h were maintained using a Neslab CryoCool®-100 bath cooler. The reaction temperatures refer to internal temperatures measured by Teflon-coated thermocouples, unless otherwise noted. Reaction solvents tetrahydrofuran (Fisher, HPLC grade), diethyl ether (Fisher, BHT stabilized ACS grade) and methylene chloride (Fisher, unstabilized HPLC grade) were dried by percolation through two columns packed with neutral alumina under a positive pressure of argon. Reaction solvents hexane (Fisher, OPTIMA grade) and toluene (Fisher, ACS grade) were dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant, a supported copper catalyst for scavenging oxygen, under a positive pressure of argon.

Iodometric methods were used for the titration of *meta*-chloroperbenzoic acid solutions.[2] *n*-Butyl lithium solutions were titrated following the method of Gilman.[3] Ethylmagnesium chloride solutions were titrated with 1,10-phenanthroline.[4] Brine refers to a saturated aqueous solution of NaCl.

Literature Procedures

The following compounds were prepared by literature methods: dimethyl (2,4-pentadienyl)propanedioate,[5] *tert*-butyldimethylsilyl trifluoromethanesulfonate,[6] *para*-toluenesulfonic anhydride,[7] nitroethene,[8] disiamylborane,[9] methanesulfonic anhydride,[10] trimethylsilyl triflate.[6]

Commercial Chemicals

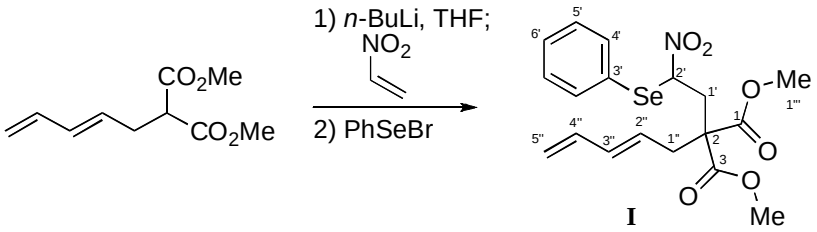
The following chemicals were obtained from commercial suppliers and purified according to the indicated procedure. If no purification is listed, the compound was used as received from the manufacturer.

Reagent	**Supplier**	**Purification**
Acetonitrile	Fisher Scientific	Distilled (CaH_2)
Ammonium chloride	Fisher Scientific	
Ammonium hydroxide	Fisher Scientific	
Benzyl bromide	Aldrich Chemical Co.	
BH_3•THF	Aldrich Chemical Co.	
Bromine	Aldrich Chemical Co.	
o-bromoaniline	Aldrich Chemical Co.	Distilled
t-Butyl acetate	Aldrich Chemical Co.	Distilled
n-Butyl lithium	FMC	
t-butyldimethylsilyl chloride	Gelest Inc.	
n-Butyl vinyl ether	Aldrich Chemical Co.	Distilled (Na)
Celite	Fisher Scientific	Washed (conc. HCl)
Chloroform	Fisher Scientific	P_2O_5
m-CPBA	Aldrich Chemical Co.	Washed[2]
Diisopropylamine	Fisher Scientific	Distilled (CaH_2)
Dimethylformamide	Fisher Scientific	Dried (4Å MS)
Diphenyl diselenide	Aldrich Chemical Co.	
Ethyl acetate	Fisher Scientific	
Ethylmagnesium chloride	Aldrich Chemical Co.	
H_2O		Deionized
Heptane	Fisher Scientific	
o-Iodoaniline	Aldrich Chemical Co.	Recrystallized (pet ether)
Magnesium sulfate	Fisher Scientific	

Methanol	Fisher Scientific	
2-Methyl-2-butene	Aldrich Chemical Co.	Distilled (Na)
Methyl iodide	Aldrich Chemical Co.	
$NaHCO_3$	Fisher Scientific	
Palladium acetate	Strem Chemical	
Palladium on carbon (5%)	Aldrich Chemical Co.	
Potassium carbonate	Fisher Scientific	
Pyridine	Fisher Scientific	Distilled (CaH_2)
Raney nickel	Activated Metals	
Sodium hydride	Acros	Washed (hexanes)
Sodium perborate	Mallinckrodt	
Sodium sulfate	Fisher Scientific	
Sodium thiosulfate	Fisher Scientific	
Tetrabutylammonium chloride	Aldrich Chemical Co.	
Triethylamine	Fisher Scientific	Distilled (CaH_2)
Triethylsilyl chloride	Gelest Inc.	
Trimethylsilyl chloride	Aldrich Chemical Co.	Distilled
Trimethylaluminum	Aldrich Chemical Co.	
Triphenylphosphine	Aldrich Chemical Co.	Recrystallized (Hex.)

Procedures

Dimethyl 2-(2-Nitro-2-phenylselenylethyl)-2-(2,4-pentadienyl)propanedioate (I).



The reaction was conducted in a 500 mL (three neck) round bottom flask, with a gas inlet, septum, stir bar, and thermocouple, To a solution of *n*-butyllithium (1.46 M, 6.85 mL, 10.00 mmol, 1.0 equiv) in THF (86 mL) at –78 °C (IPA/CO_2), was added a solution dimethyl (2,4-pentadienyl)propanedioate (1.982 g, 10.00 mmol) in THF (50 mL) dropwise via cannula over 20 min. The solution turns slightly green before returning to yellow upon full addition. The cannula was then washed with THF (7 mL). The reaction mixture was warmed to 0 °C over 15 min, before being cooled back to –75 °C. To the yellow solution was added nitroethene (0.7227 g, 9.99 mmol, 0.99 equiv) in THF (50 mL) dropwise via cannula over 25 min. The cannula was again washed with THF (7 mL). The solution was stirred at –76 °C for 35 min, before warming to 0 °C.

In a separate 100 mL round bottom flask, a solution of $(PhSe)_2$ (1.951 g, 6.25 mmol, 0.625 equiv) and Br_2 (0.32 mL, 6.21 mmol, 0.621 equiv) in THF (29 mL) was prepared at room temperature. This solution was added via cannula, over 5 min, to the reaction mixture. The color of the reaction mixture gradually turned from yellow to dark orange. The resulting solution was stirred at 0 °C for 1 h and then was warmed to room temperature and stirred for 2.5 h. Upon dilution with Et_2O (100 mL), the reaction mixture was washed with H_2O (100 mL) and brine (100 mL). The aqueous layers were back extracted with Et_2O (2x50 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated *in vacuo*, The resulting yellow oil was purified by column chromatography (SiO_2, hexanes/EtOAc, 15/1→8/1→6/1→5/1→2/1) to provide **I** (3.299 g, 77%) as a yellow oil. An analytical sample of **I** was obtained by further column chromatography (SiO_2, hexanes/EtOAc, 8/1).

Analytical Data for **I**:

^{1}H NMR: (500 MHz, $CDCl_3$)

7.60 (d, *J* = 7.1, 2 H, HC(4')), 7.45 (t, *J* = 7.3, 1 H, HC(6')), 7.37 (t, *J* = 7.1, 2 H, HC(5')), 6.27 (dt, *J* = 10.3, 17.1, 1 H, HC(4'')), 6.05 (dd, *J* = 10.5, 15.1, 1 H, HC(3'')), 5.81 (dd, *J* = 3.2, 5.6, 1 H, HC(2')), 5.39 (dt, *J* = 7.8, 15.4, 1 H, HC(2'')), 5.16 (d, *J* = 17.3, 1 H, HC(5'')), 5.08 (d, *J*, = 10.3, 1 H, HC(5'')), 3.72 (s, 3 H, HC(1''')), 3.62 (s, 3 H, HC(1''')), 2.73 (m, 2 H, HC(1') HC(1'')), 2.61 (m, 2 H, HC(1') HC(1''))

^{13}C NMR: (125 MHz, $CDCl_3$)

170.58 (C(1)), 170.02 (C(3)), 136.71 (C(5')), 136.49 (C(4'')), 136.38 (C(3')), 130.41 (C(2'')), 129.82 (C(4')), 126.37 (C(3'')), 126.30 (C(6')), 117.77 (C(5'')), 79.56 (C(2')), 56.61 (C(2)), 53.11 (C(1''')), 52.70 (C(1''')), 38.09 (C(1'')), 37.16 (C(1'))

IR: ($CDCl_3$)

3011 (w), 2936 (w), 2845 (w), 1734 (s), 1552 (s), 1438 (s), 1345 (m), 1269 (m), 1210 (s), 1168 (m)

MS: (ESI)

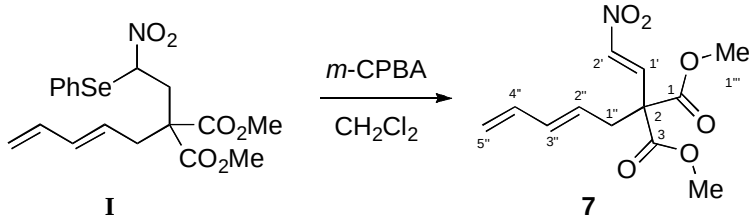
450 (70, M^++Na), 448 (35), 403 (34), 381 (100), 379 (52), 349 (65), 347 (32), 336 (48)

TLC: R_f = 0.29 (hexanes/EtOAc, 4/1, UV)

Analysis: $C_{18}H_{21}NO_6Se$ (426.33)

Calculated:	C: 50.71%	H: 4.97%	N: 3.29%
Found:	C: 50.43%	H: 4.95%	N: 3.25%

Dimethyl 2-(2-Nitroethenyl)-2-(2,4-pentadienyl)propanedioate (7).



I **7**

The reaction was conducted in a 250 mL (three neck) round bottom flask, with gas inlet, septum, stir bar, and thermocouple. To a solution of **I** (4.290 g, 10.06 mmol) in THF (100 mL) at –77 °C was added *m*-CPBA (98%, 2.171 g, 12.58 mmol, 1.25 equiv) in one portion. The resulting homogeneous solution was stirred at –77 °C (IPA/CO_2) for 1 h. The cooling bath was removed, and the solution was allowed to warm to room temperature for 2 h. The solution was diluted with Et_2O (100 mL) and washed twice with sat. aqueous sodium bicarbonate (100 mL) and once with brine (100 mL). The aqueous layers were back extracted with Et_2O (2x50 mL). The combined organic layers were combined, dried over $MgSO_4$, and concentrated *in vacuo*. The resulting yellow oil was purified by column chromatography (SiO_2, hexanes/EtOAc, 15/1→8/1→6/1→4/1), providing **7** (2.582 g, 95%) as a yellow solid. An analytical sample was obtained by recrystallization (hexanes).

Analytical Data for **7**:

M.P.: 82-83 °C (hexanes)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.49 (d, *J* = 13.9, 1 H, HC(1')), 7.12 (d, *J* = 13.9, 1 H, HC(2')), 6.25 (dt, *J* = 10.3, 16.8, 1 H, HC(4'')), 6.12 (dd, *J* = 10.5, 14.9, 1 H, HC(3'')), 5.47 (dt, *J* = 7.6, 15.1, 1 H, HC(2'')), 5.18 (d, *J* = 16.6, 1 H, HC(5'')), 5.08 (d, *J* = 10.3, 1 H, HC(5'')), 3.80 (s, 6 H, HC(1''')), 2.90 (d, *J* = 7.6, 2 H, HC(1''))

^{13}C NMR: (125 MHz, $CDCl_3$)

168.33 (C(1)), 141.89 (C(1')), 139.36 (C(4'')), 136.73 (C(2')), 136.13 (C(2'')), 125.55 (C(3'')), 118.29 (C(5'')), 58.32 (C(2)), 53.76 (C(1''')),

38.81 (C(1'')).

IR: ($CDCl_3$)

3091 (w), 3012 (w), 2957 (w), 2846 (w), 1739 (s), 1534 (s), 1436 (m), 1354 (m), 1265 (m), 1212 (m), 909 (s)

MS: (CI, 130 eV)

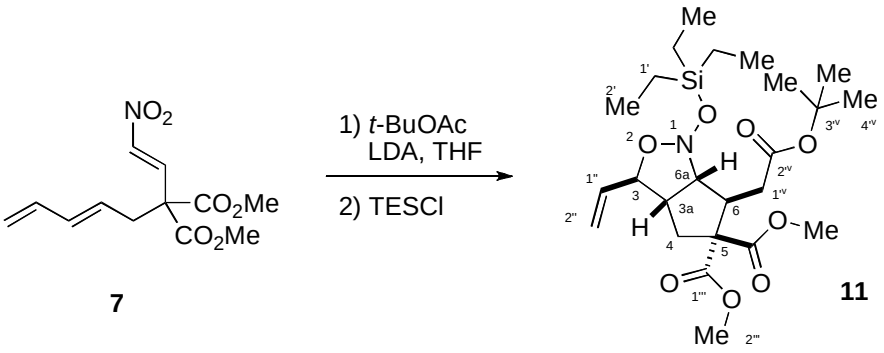
270 (3), 223 (25), 191 (24), 159 (20), 67 (100)

TLC: R_f = 0.24 (hexanes/EtOAc, 4/1, UV)

Analysis: $C_{12}H_{15}NO_6$ (269.25)

Calculated:	C: 53.53%	H: 5.62%	N: 5.20%
Found:	C: 53.33%	H: 5.50%	N: 5.00%

[*rel*-3*S*, 3a*R*, 6*S*, 6a*R*]-6-*tert*-Butoxycarbonylmethyl-1-(triethyl-silyloxy)-3-vinyl-tetrahydrocyclopenta[*c*]isoxazole-5,5-dicarboxylic Acid Dimethyl Ester (11).



7 **11**

A solution of LDA was prepared in a 100 mL (three neck) round bottom flask, with a gas inlet, septum, stir bar, and thermocouple. To a solution of diisopropylamine (1.75 mL, 12.48 mmol, 1.25 equiv) in THF (50 mL) at 1 °C (ice) was added a solution of *n*-butyllithium (1.46 M in hexanes, 8.55 mL, 12.48 mmol, 1.25 equiv). The solution was stirred at 1 °C for 20 min, then cooled to –75 °C. *t*-Butyl acetate (1.66 mL, 12.46 mmol, 1.25 equiv) was added to the solution, which was then stirred at –75 °C for 20 min.

In a separate 250 mL (three neck) round bottom flask, with a gas inlet, septum, stir bar, and thermocouple, a solution of **7** (2.693 g, 10.00 mmol) in THF (50 mL) was cooled to –75 °C (IPA/CO_2). The enolate solution was then added via cannula over 15

min, during which the reaction color became yellow/orange. The solution was maintained at –75 °C for 30 min, at which time triethylsilyl chloride (3.37 mL, 20 mmol, 2.0 equiv) was added. The light yellow solution was stirred at –75 °C for 1.5 h, and then allowed to warm to room temperature for 2.5 h. The solution was diluted with Et_2O (100 mL), and washed with H_2O (50 mL) and brine (50 mL). The aqueous layers were back extracted with Et_2O (2x50 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated *in vacuo*. The yellow oil was purified by column chromatography (SiO_2 (washed with 5% triethylamine in hexanes (500 mL), EtOAc (500 mL), hexanes/EtOAc, 10/1 (250 mL)), hexanes/EtOAc, 10/1) to give **11** (4.883 g, 98%) as a slightly yellow oil. An analytical sample was obtained purification by further column chromatography (SiO_2 (washed with 5% triethylamine in hexanes (100 mL), EtOAc (100 mL), hexanes/EtOAc, 10/1 (50 mL)), hexanes/EtOAc, 10/1).

Analytical Data for **11**:

^{1}H NMR: (500 MHz, C_6D_6)

6.33 (ddd, *J* = 9.0, 10.0, 19.0, 1 H, HC(1’’)), 4.90 (d, *J* = 10.0, 1 H, HC(2’’)), 4.87 (d, *J* = 17.1, 1 H, HC(2’’)), 4.55 (dd, *J* = 8.5, 10.7, 1 H, HC(6a)), 4.24 (dd, *J* = 3.2, 9.0, 1 H, HC(3)), 3.37 (s, 3 H, HC(2’’’)), 3.27 (m, 1 H, HC(1’^{v})), 3.23 (s, 3 H, HC(2’’’)), 3.07 (m, 2 H, HC(3a), HC(6)), 2.91 (dd, *J* = 4.4, 17.3, 1 H, HC(1’^{v})), 2.66 (dd, *J* = 9.0, 13.9, 1 H, HC(4)), 2.13 (dd, *J* = 6.6, 13.3, 1 H, HC(4)), 1.38 (s, 9 H, HC(4’^{v})), 1.07 (t, *J* = 7.8, 9 H HC(2’)), 0.79 (qd, *J* = 2.2, 7.6, 6 H, HC(1’))

^{13}C NMR: (125 MHz, C_6D_6)

171.09 (C(2’^{v})), 170.91 (C(1’’’)), 170.54 (C(1’’’)), 141.98 (C(1’’)), 115.71 (C(2’’)), 93.72 (C(3)), 85.77 (C(6a)), 79.87 (C(3’^{v})), 62.25 (C(5)), 52.16 (C(2’’’)), 51.91 (C(2’’’)), 47.47 (C(3a)), 45.63 (C(6)), 39.72 (C(4)), 34.95 (C(1’^{v})), 27.99 (C(4’^{v})), 6.97 (C(2’)), 4.59 (C(1’))

IR: (C_6D_6)

2954 (w), 2876 (w), 1737 (s), 1266 (m), 1154 (m)

MS: (ESI)

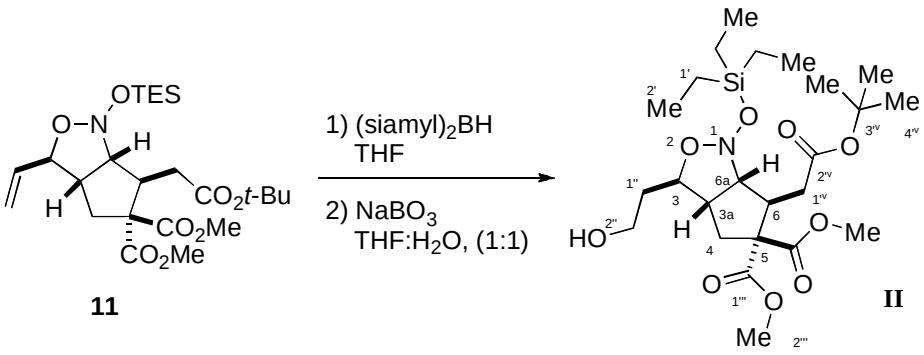
538 (M+Na, 100), 522 (73), 334 (60)

TLC: R_f = 0.26 (hexane/EtOAc, 4/1, UV)

Analysis: $C_{10}H_{20}Si$ (499.68)

Calculated:	C: 57.69%	H: 8.27%	N: 2.80%
Found:	C: 57.83%	H: 8.24%	N: 2.95%

[*rel*-3*S*, 3a*R*, 6*S*, 6a*R*]-6-*tert*-Butoxycarbonylmethyl-1-(triethyl-silyloxy)-3-(2-hydroxy)ethyl-tetrahydrocyclopenta[*c*]isoxazole-5,5-dicarboxylic Acid Dimethyl Ester (II).



A solution of $(siamyl)_2BH$ was prepared in a 10 mL (two neck) round bottom flask, with a gas inlet, septum, and stir bar. To a solution of BH_3•THF (1.0 M in THF, 2.14 mL, 2.14 mmol, 2.0 equiv) at –10 °C was added 2-methyl-2-butene (0.45 mL, 4.25 mmol, 4.0 equiv). The solution was stirred at –10 °C for 2 h.

In a separate 25 mL (two neck) round bottom flask, with a gas inlet, septum, stir bar, and thermocouple, **11** (0.525 g, 1.05 mmol) was dissolved in THF (5 mL) at room temperature (22 °C). The borane solution was then added via cannula. The temperature of the reaction increased 2 °C, and a small amount of gas evolution was observed. The solution was then stirred for 2 h at room temperature, at which time H_2O (5 mL) was added. After the gas evolution had ceased, $NaBO_3$ (1.150 g, 7.45 mmol, 7.0 equiv) was added in one portion. The heterogeneous slurry was vigorously stirred for 3 h. The slurry was then filtered through a sintered glass funnel, and the salts were washed with Et_2O (20 mL). The biphasic solution was separated, and the organic layer was washed with H_2O (15 mL) and brine (15 mL). The aqueous layers were back extracted with Et_2O

(2x10 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated *in vacuo*. The crude oil was purified by column chromatography at 0 °C, in a jacketed glass column (SiO_2 (washed with 5% triethylamine in hexanes (150 mL), EtOAc (150 mL), hexanes/EtOAc, 1/1 (100 mL)), hexanes/EtOAc, 1/1) to give **II** (0.406 g, 75%) as a colorless oil. An analytical sample was obtained by further column chromatography at 0 °C, in a jacketed glass column (SiO_2 (washed with 5% triethylamine in hexanes (100 mL), EtOAc (100 mL), hexanes/EtOAc, 1/1 (50 mL)), hexanes/EtOAc, 2/1→3/2→1/1).

Analytical Data for **II**:

^{1}H NMR: (500 MHz, C_6D_6)

4.52 (dd, *J* = 8.3, 10.7, 1 H, HC(6a)), 4.01 (ddd, *J* = 3.4, 5.8, 8.8, 1 H, HC(3)), 3.50 (m, 2 H, HC(2'')), 3.36 (s, 3 H, HC(2''')), 3.26 (s, 3 H, HC(2''')), 3.25 (dd, *J* = 7.3, 17.3, 1 H, HC(1'^{v})), 3.06 (ddd, *J* = 4.4, 6.3, 10.7, 1 H, HC(6)), 2.98 (m, 1 H, HC(3a)), 2.94 (dd, *J* = 4.4, 17.3, 1 H, HC(1'^{v})), 2.67 (dd, *J* = 8.8, 14.2, 1 H, HC(4)), 2.15 (m, 1 H, HC(1'')), 2.11 (dd, *J* = 6.4, 14.2, 1 H, HC(4)), 1.70 (sextet, *J* = 5.6, 1 H, HC(1'')), 1.38 (s, 9 H, HC(3'^{v})), 1.06 (t, *J* = 7.8, 9 H, HC(2')), 0.77 (m, 6 H, HC(1'))

^{13}C NMR: (125 MHz, C_6D_6)

171.24 (C(1''')), 171.01 (C(2'^{v})), 170.64 (C(1''')), 90.25 (C(3)), 85.23 (C(6a)), 79.90 (C(3'^{v})), 62.27 (C(5)), 60.34 (C(2'')), 52.20 (C(2''')), 51.96 (C(2''')), 47.48 (C(6)), 45.60 (C(3a)), 41.25 (C(1'')), 39.92 (C(4)), 34.88 (C(1'^{v})), 27.98 (C(4'^{v})), 6.95 (C(2')), 4.53 (C(1'))

IR: ($CDCl_3$)

3626 (w), 2956 (m), 2914 (m), 2877 (m), 1732 (s), 1457 (m), 1436 (m), 1369 (m), 1266 (s), 1155 (s)

MS: (ESI)

518 (M^+, 23), 462 (10), 386 (68), 330 (100)

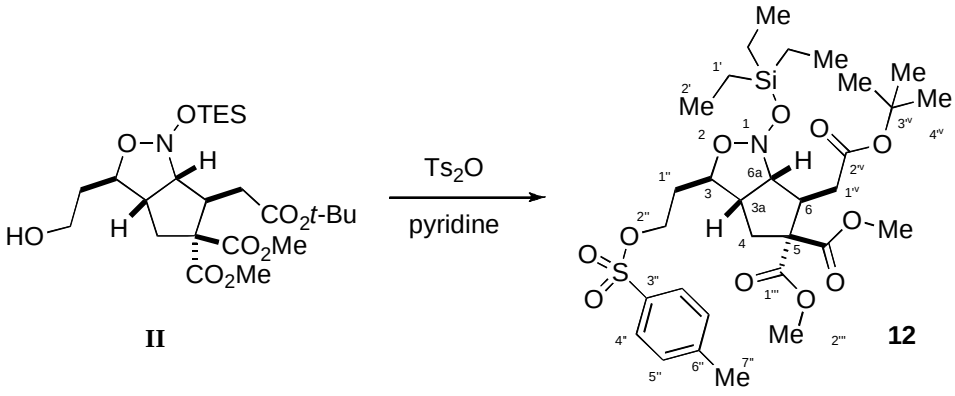
TLC: R_f = 0.36 (hexane/EtOAc, 1/1, $KMnO_4$)

Analysis: $C_{24}H_{49}NO_9Si$ (517.70)

Calculated: C: 55.68% H: 8.37% N: 2.71%

Found: C: 55.46% H: 8.13% N: 2.88%

[*rel*-3*S*, 3a*R*, 6*S*, 6a*R*]-6-*tert*-Butoxycarbonylmethyl-1-(triethyl-silyloxy)-3-((2-toluenesulfonyl)ethyl)tetrahydrocyclopenta[*c*]isoxazole-5,5-dicarboxylic Acid Dimethyl Ester (12).



II **12**

The reaction was conducted in a 50 mL (three neck) round bottom flask, with a gas inlet, septum, stir bar, and thermocouple. To a solution of **II** (1.235 g, 2.39 mmol) in pyridine (24 mL) at 0 °C (ice) was added toluenesulfonic anhydride (1.560 g, 4.78 mmol, 2.0 equiv) in one portion. The color of the reaction became orange, while the internal temperature rose to 9 °C before returning to 0 °C. The solution was stirred for 10 min, and then was poured into a biphasic mixture of sat. aqueous sodium bicarbonate (25 mL) and Et_2O (25 mL) at 0 °C. The biphasic slurry was stirred for 5 min, and then the phases were separated. The organic layer was washed with brine (25 mL), and the aqueous layers were then back extracted with Et_2O (2x25 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated *in vacuo*. To the resulting oil was added heptane (50 mL), and the solution was again concentrated *in vacuo*. The orange oil was the purified by column chromatography (SiO_2 (washed with 5% triethylamine in hexanes (150 mL), EtOAc (150 mL), hexanes/EtOAc, 4/1 (100 mL)), hexanes/EtOAc, 4/1→2/1) to provide **12** (1.532 g, 96%) as a slightly yellow oil.

Analytical Data for **12**:

^{1}H NMR: (500 MHz, C_6D_6)

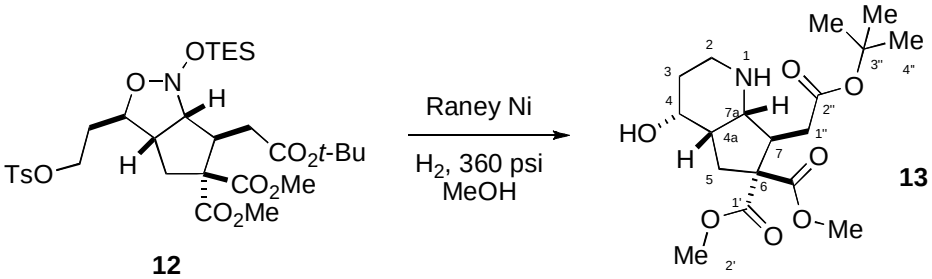
7.77 (d, *J* = 8.3, 1 H, HC(4'')), 6.73 (d, *J* = 7.8, 1 H, HC(5'')), 4.43 (dd, *J* = 8.5, 10.5, 1 H, HC(6a)), 4.06 (m, 2 H, HC(2'')), 3.79 (ddd, *J* = 2.7, 5.6, 8.8, 1 H, HC(3)), 3.36 (s, 3 H, HC(2'''), 3.26 (s, 3 H, HC(2''')), 3.16 (m, 1 H, HC(1'^{v})), 2.84-2.94 (m, 1 H, HC(6) HC(1'^{v})), 2.79 (qd, *J* = 2.7, 8.8, 1 H, HC(3a)), 2.67 (dd, *J* = 9.0, 13.9, 1 H, HC(4)), 2.14 (ddt, *J* = 4.1, 9.3, 14.4, 1 H, HC(1'')), 1.88 (dd, *J* = 7.3, 14.4, 1 H, HC(4)), 1.87 (s, 3 H, HC(7'')), 1.77 (sextet, *J* = 6.8, 1 H, HC(1'')), 1.35 (s, 9 H, HC(3'^{v})), 0.95 (t, *J* = 7.8, 9 H, HC(2')), 0.56-0.73 (m, 6 H, HC(1'))

^{13}C NMR: (125 MHz, C_6D_6)

171.06 (C(2'^{v})), 170.94 (C(1''')), 170.37 (C(1''')), 144.11 (C(6'')), 134.06 (C(3'')), 129.74 (C(4'') C(5'')), 87.81 (C(3)), 84.02 (C(6a)), 79.89 (C(3'^{v})), 67.91 (C(2'')), 62.14 (C(5)), 52.16 (C(2''')), 51.97 (C(2''')), 47.50 (C(3a)), 45.68 (C(6)), 39.86 (C(1'')), 37.75 (C(4)), 34.58 (C(1'^{v})), 27.96 (C(4'^{v})), 20.98 (C(7'')), 6.89 (C(2')), 4.40 (C(1'))

TLC: R_f = 0.58 (hexanes/EtOAc, 1/1, UV)

[*rel-4R, 4aR, 7S, 7aR*]-*7-tert*-Butoxycarbonylmethyl-4-hydroxyoctahydro-cyclopenta[*b*]pyridine-6,6-dicarboxylic Acid Dimethyl Ester (13).



12 **13**

To a steel autoclave with a glass insert was added Raney nickel (3.309 g, washed with H_2O (25 mL) and MeOH (3 x 25 mL)) and **12** (1.134 g, 1.64 mmol) in MeOH (15 mL). The vessel was sealed and pressurized to 360 psi of hydrogen. The slurry was then

stirred at room temperature for 36 h. The heterogeneous mixture was filtered through Celite, and the filter cake was washed with MeOH (300 mL) without allowing the level of the solvent to fall below the level of the filter pad. The filtrate was concentrated *in vacuo*, and the residue was dissolved in EtOAc (25 mL). The organic solution was then washed with sat. aqueous sodium bicarbonate (25 mL) and brine (25 mL). The aqueous layers were back extracted with EtOAc (2x20 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated *in vacuo*. The resulting oil was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH/NH_4OH, 90/9.5/0.5→80/19.5/0.5). The resulting oil was dissolved in CH_2Cl_2 (40 mL), dried over MgSO4, and concentrated to provide **13** (0.407 g, 67%) as a colorless oil. An analytical sample was obtained by further column chromatography (SiO_2, CH_2Cl_2/MeOH/NH_4OH, 10/1/0 →80/19.5/0.5), followed by azeotropic drying with benzene (20 mL).

Analytical Data for **13**:

^{1}H NMR: (500 MHz, $CDCl_3$)

3.83 (dt, *J* = 4.4, 8.5, 1 H, HC(4)), 3.69 (s, 3 H, HC(2')), 3.66 (s, 3 H, HC(2')), 3.05 (dt, *J* = 3.9, 11.2, 1 H, HC(7)), 2.98 (m, 2 H, HC(2), HC(7a)), 2.79 (s(br), 2H, HN(1), HO), 2.56 (ddd, *J* = 4.6, 9.3, 11.9, 1 H, HC(2)), 2.46 (m, 3 H, HC(5) HC(4a) HC(1'')), 2.35 (m, 1 H, HC(5)), 2.16 (dd, *J* = 11.2, 16.4, 1 H, HC(1'')), 1.70 (m, 1 H, HC(3)), 1.64 (m, 1 H, HC(3)), 1.40 (s, 9 H, HC(4''))

^{13}C NMR: (125 MHz, $CDCl_3$)

172.51 (C(1'')), 172.41 (C(2''')), 172.24 (C(1'')), 81.28 (C(3'')), 68.09 (C(4)), 63.79 (C(7a)), 62.07 (C(6)), 52.91 (C(2'')), 52.71 (C(2'')), 47.52 (C(7)), 42.91 (C(4a)), 41.80 (C(2)), 36.40 (C(1'')), 33.22 (C(5)), 29.58 (C(3)), 28.25 (C(4''))

IR: ($CDCl_3$)

3685 (w), 3610 (w), 2954 (m), 1729 (s), 1435 (m), 1369 (m), 1256 (s), 1155 (s)

MS: (ESI)

372 (M^+H, 100), 316 (38)

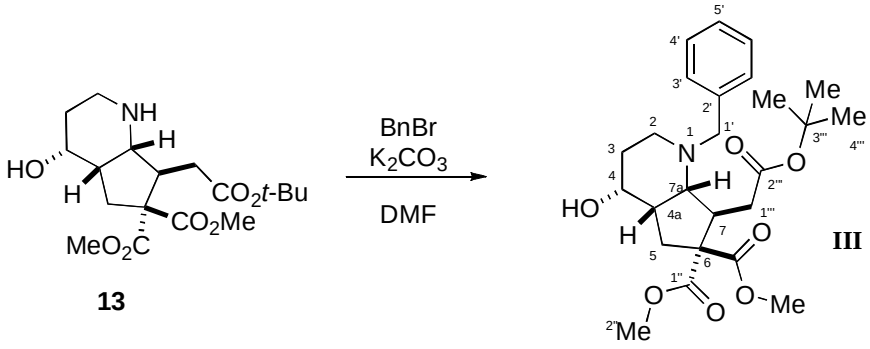
HRMS: $C_{18}H_{30}NO_7$

Calculated: 372.2022

Found: 372.2023

TLC: R_f = 0.23 (CH_2Cl_2/MeOH, 9/1, $KMnO_4$)

[*rel-4R, 4aR, 7S, 7aR*]-1-Benzyl-*7-tert*-butoxycarbonylmethyl-4-hydroxy-octahydro-cyclopenta[*b*]pyridine -6,6-dicarboxylic Acid Dimethyl Ester (III).



13 **III**

The reaction was conducted in a 50 mL one neck) round bottom flask, with a gas inlet, septum, To a solution of **13** (0.408 g, 1.10 mmol) in DMF (10 mL) was added K_2CO_3 (0.758 g, 5.48 mmol, 5.0 equiv) and benzyl bromide (0.26 mL, 2.19 mmol, 2.0 equiv). The heterogeneous mixture was stirred for 2.5 h. The slurry was then diluted with Et_2O (15 mL), and was washed with H_2O (10 mL) and brine (10 mL). The aqueous layers were combined and back extracted with Et_2O (5x10 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was then purified by column chromatography (SiO_2, hexanes/EtOAc, 3/2→1/1→2/3) to provide **III** (0.393 g, 78%) as a colorless oil. An analytical sample was obtained by further column chromatography (SiO_2, hexanes/EtOAc, 3/2→1/1).

Analytical Data for **III**:

^{1}H NMR: (500 MHz, $CDCl_3$)

7.20-7.32 (m, 5 H, HC(3'-5')), 4.32 (d, *J* = 13.7, 1 H, HC(1')), 3.90 (dt, *J* = 5.4, 10.5, 1 H, HC(4)), 3.88 (dd, *J* = 4.9, 10.5, 1 H, HC(7)), 3.72 (s, 3 H,

HC(2’’)), 3.71 (s, 3 H, HC(2’’)), 2.80 (d, *J* = 13.7, 1 H, HC(1’), 2.76 (dt, *J* = 3.4, 11.9, 1 H, HC(2)), 2.64 (m, 1 H, HC(4a)), 2.59 (t, *J* = 12.9, 1 H, HC(5)), 2.54 (dd, *J* = 8.0, 12.9, 1 H, HC(5)), 2.39 (d, *J* = 3.6, 1 H, HC(7a)), 2.24 (ABX, 2 H, HC(1’’)), 1.76 (td, *J* = 3.4, 11.7, 1 H, HC(2)), 1.60 (m, 2 H, HC(3), 1.46 (s, 9 H, HC(4’’’))

^{13}C NMR: (125 MHz, $CDCl_3$)

172.51 (C(1’’)), 172.24 (C(2’’’)), 171.27 (C(1’’)), 139.50 (C(2’), 129.14 (C(4’)), 128.30 (C(3’)), 126.91 (C(5’)), 81.13 (C(3’’’)), 70.61 (C(7a)), 68.99 (C(4)), 62.15 (C(6)), 58.45 (C(1’)), 53.13 (C(2’’’)), 52.82 (C(2’’’)), 49.97 (C(2)), 44.91 (C(7)), 43.70 (C(4a)), 37.04 (C(1’’’)), 32.22 (C(5)), 28.89 (C(3)), 28.30 (C(4’’’))

IR: ($CDCl_3$)

3610 (w) , 2954 (m), 2804 (m), 1731 (s), 1453 (m), 1435 (m), 1369 (m), 1254 (s), 1155 (m), 1063 (m)

MS: (ESI)

462 (M^+, 100)

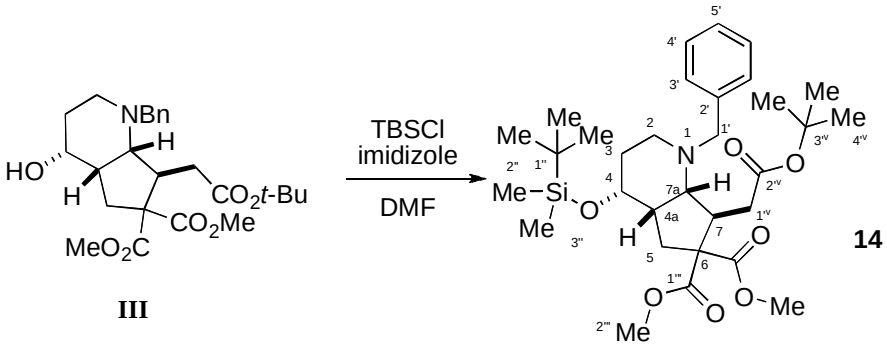
HRMS: $C_{25}H_{35}NO_7$

Calculated: 462.2492

Found: 462.2479

TLC: R_f = 0.21 (hexanes/EtOAc, 1/1, UV)

[*rel-4R, 4aR, 7S, 7aR*]-1-Benzyl-*7-tert*-butoxycarbonylmethyl-4-(1,1-dimethylethyl)dimethylsilyl)oxyoctahydrocyclopenta[*b*]pyridine-6,6-dicarboxylic Acid Dimethyl Ester (14).



III **14**

To a solution of **III** (1.125 g, 2.44 mmol) in DMF (25 mL) was added *t*-butyldimethylsilyl chloride (0.923 g, 6.12 mmol, 2.5 equiv) and imidazole (0.417 g, 6.12 mmol, 2.5 equiv). The solution was stirred for 12 h at room temperature, at which time it was diluted with Et_2O (15 mL). The solution was washed with H_2O (50 mL) and brine (25 mL). The aqueous layers were then combined and back extracted with Et_2O (4x25 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated *in vacuo*. The resulting oil was then purified by column chromatography (SiO_2, hexanes/EtOAc, 8/1→6/1) to give **14** (1.181 g, 84%) as a colorless oil. An analytical sample was obtained by further column chromatography (SiO_2, hexanes/EtOAc, 10/1→8/1).

Analytical Data for **14**:

^{1}H NMR: (500 MHz, $CDCl_3$)

7.19-7.29 (m, 5 H, HC(3'-5')), 4.32 (d, *J* = 13.7, 1 H, HC(1')), 3.87 (dd, *J* = 5.1, 10.7, 1 H, HC(7)), 3.84 (m, 1 H, HC(4)), 3.73 (s, 3 H, HC(2'''')), 3.71 (s, 3 H, HC(2''')), 2.79 (d, *J* = 13.7, 1 H, HC(1')), 2.71 (dt, *J* = 3.4, 11.7, 1 H, HC(2)), 2.48-2.62 (m, 3 H, HC(5), HC(4a)), 2.34 (d, *J* = 2.9, 1 H, HC(7a)), 2.29 (dd, *J* = 4.9, 15.4, 1 H, HC(1'^{v})), 2.15 (dd, *J* = 11.0, 15.4, 1 H, HC(1'^{v})), 1.67 (m, 2 H, HC(2) HC(3)), 1.47 (s, 9 H, HC(3'^{v})), 1.42 (m, 1 H, HC(3)), 0.88 (s, 9 H, HC(2'')), 0.08 (s, 3 H, HC(3'')), 0.04 (s, 3 H, HC(3''))

^{13}C NMR: (125 MHz, $CDCl_3$)

172.63 (C(1’’’)), 172.39 (C(2’^{v})), 171.33 (C(1’’’)), 139.65 (C(2’)), 129.15 (C(4’)), 128.25 (C(3’)), 126.82 (C(5’)), 81.07 (C(3’^{v})), 70.62 (C(7a)), 69.51 (C(4)), 61.95 (C(6)), 58.45 (C(1’)), 53.03 (C(2’’’)), 52.69 (C(2’’’)), 50.26 (C(7)), 44.96 (C(2)), 44.54 (C(4a)), 37.21 (C(1’^{v})), 32.85 (C(5)), 29.73 (C(3)), 28.32 (C(4’^{v})), 26.04 (C(2’’)), 18.24 (C(1’’)), -4.42 (C(3’’)), -4.52 (C(3’’))

IR: ($CDCl_3$)

2954 (m), 2857 (m), 1731 (s), 1452 (m), 1435 (m), 1369 (m), 1253 (s), 1153 (m), 1098 (m)

MS: (ESI)

576 (M^+, 100)

HRMS: $C_{31}H_{49}NO_7Si$

Calculated: 576.3357

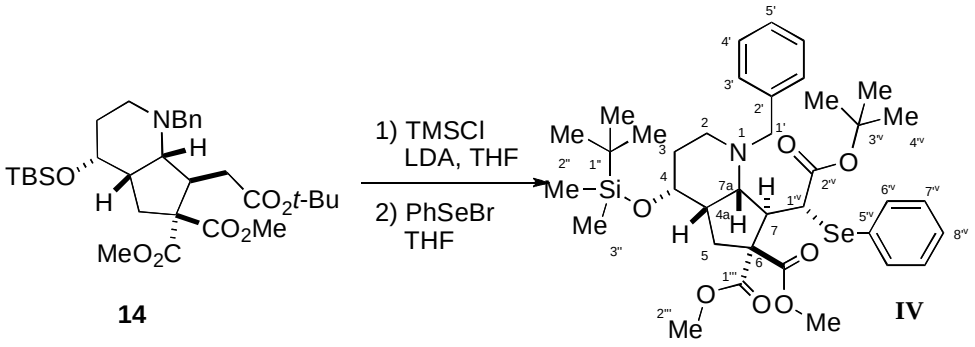
Found: 576.3352

TLC: R_f = 0.40 (hexanes/EtOAc, 4/1, UV)

Analysis: $C_{31}H_{49}NO_7Si$ (575.81)

Calculated:	C: 64.66%	H: 8.58%	N: 2.43%
Found:	C: 64.39%	H: 8.56%	N: 2.67%

[*rel-4R, 4aR, 7S, 7aR*]-1-Benzyl-*7-tert*-butoxycarbonyl-phenylselenylmethyl-4-(1,1-dimethylethyl)dimethylsilyl)oxyoctahydrocyclopenta[*b*]pyridine-6,6-dicarboxylic Acid Dimethyl Ester (IV).



An LDA solution was prepared in a 25 mL (two neck) round bottom flask, with a gas inlet, septum, and stir bar. To a solution of diisopropylamine (0.23 mL, 1.64 mmol, 2.0 equiv) in THF (4 mL) at 0 °C (external, ice) was added a solution *n*-butyllithium (1.46 M in hexanes, 1.11 mL, 1.64 mmol, 2.0 equiv). The solution was stirred at 0 °C for 20 min, and then cooled to –78 °C (external, IPA/CO_2).

In a separate 25 mL (two neck) round bottom flask, with a gas inlet, septum, stir bar, and thermocouple, trimethylsilyl chloride (0.52 mL, 4.09 mmol, 5.0 equiv) was added to a solution of **14** (0.471 g, 0.82 mmol) in THF (4 mL) at –107 °C (THF/N_2). The LDA solution was then added dropwise via a cannula cooled to –78 °C (IPA/CO_2) over 15 min. The resulting mixture was stirred at 107 °C for 15 min, before being allowed to warm to room temperature over 30 min. The solution was then concentrated *in vacuo*, and dissolved in Et_2O (10 mL). The resulting slurry was filtered through Celite (acid washed) and the filter cake was washed with Et_2O (5 mL). The filtrate was concentrated *in vacuo*, and dissolved again in Et_2O (10 mL). The slurry was again filtered through Celite (acid washed) and the filter cake was washed with Et_2O (5 mL). The filtrate was concentrated *in vacuo* to provide the crude silyl ketene acetal.

A PhSeBr solution was prepared in a 10 mL (two neck) round bottom flask, with a gas inlet, septum, and stir bar. Br_2 (0.027 mL, 0.52 mmol, 0.625 equiv) was added to a solution of $(PhSe)_2$ (0.160 g, 0.51 mmol, 0.625 equiv) in THF (4 mL). The solution was then cooled to –78 °C (external, IPA/CO_2).

In a separate 25 mL (two neck) round bottom flask, with a gas inlet, septum, stir

bar, and thermocouple, was added the PhSeBr solution dropwise over 15 min via a cannula cooled to –78 °C to a solution of the crude silyl ketene acetal in THF (4 mL) at –106 °C (THF/N_2). The dark brown solution was stirred at –106 °C for 15 min, and then allowed to warm to room temperature over 30 min. The solution was then poured into sat. aqueous bicarbonate (15 mL), and was diluted with Et_2O (15 mL). The biphasic solution was separated and the organic layer was washed with brine (10 mL). The aqueous layers were combined and back extracted with Et_2O (2x10 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated *in vacuo*. The resulting yellow oil was purified by column chromatography (SiO_2, hexane/EtOAc, 20/1→18/1→15/1→12/1→4/1) to give **IVa** (0.310 g, 52%) as a slightly yellow oil and **IVb** (0.091 g, 15%) as a yellow oil. An analytical sample of **IVa** was obtained by further column chromatography (SiO_2, hexanes/EtOAc, 15/1), followed by precipitation from Et_2O as a white solid.

Analytical Data for **IVa**:

M.P.: 49-52 °C (Et_2O)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.63 (m, 2 H, HC(6'^{v})), 7.27 (m, 5 H, HC(7''^{v}-8'^{v}) HC(3')), 7.19 (m, 3 H, HC(4'-5')), 4.34 (d, *J* = 14.2, 1 H, HC(1')), 3.96 (d, *J* = 11. 2, 1 H, HC(1'^{v})), 3.87 (dt, *J* = 5.4, 10.5, 1 H, HC(4)), 3.75 (s, 3 H, HC(2''')), 3.70 (d, *J* = 11.2, 1 H, HC(7)), 3.67 (s, 3 H, HC(2''')), 2.86 (t, *J* = 12.9, 1 H, HC(5)), 2.73 (m, 3 H, HC(2) HC(4a) HC(1')), 2.55 (d, *J* = 3.9, 1 H, HC(7a)), 2.37 (dd, *J* = 7.1, 13.1, 1 H, HC(5)), 1.71 (m, 2 H, HC(2) HC(3)), 1.47 (m, 1 H, HC(3)), 1.34 (s, 9 H, HC(4'^{v})), 0.88 (s, 9 H, HC(2'')), 0.07 (s, 3 H, HC(3'')), 0.04 (s, 3 H, HC(3''))

^{13}C NMR: (125 MHz, $CDCl_3$)

173.28 (C(1''')), 173.23 (C(2'^{v})), 171.43 (C(1''')), 140.22 (C(2')), 134.59 (C(6'^{v})), 129.36 (C(5'^{v})), 129.14 (C(7'^{v})), 128.59 (C(4')), 128.30 (C(3')), 128.20 (C(8'^{v})), 126.75 (C(5')), 81.59 (C(3'^{v})), 69.85 (C(7a)), 69.33 (C(4)), 61.19 (C(6)), 58.16 (C(1')), 53.05 (C(2''')), 53.00 (C(2''')), 50.60 (C(7)), 50.50 (C(2)), 46.69 (C(1'^{v})), 45.24 (C(4a)), 35.00 (C(5)), 29.63

(C(3)), 28.01 (C(4''')), 26.01 (C(2'')), 18.23 (C(1'')), -4.40 (C(3'')), -4.48 (C(3''))

IR: ($CDCl_3$)

2953 (m), 2926 (m), 2852 (w), 1719 (s), 1369 (m), 1255 (s), 1166 (m), 1100 (m)

MS: (ESI)

732 (M^+, 100), 730 (50), 676 (33)

TLC: R_f = 0.40 (hexanes/EtOAc, 4/1, UV)

Analysis: $C_{37}H_{53}NO_7SeSi$ (730.88)

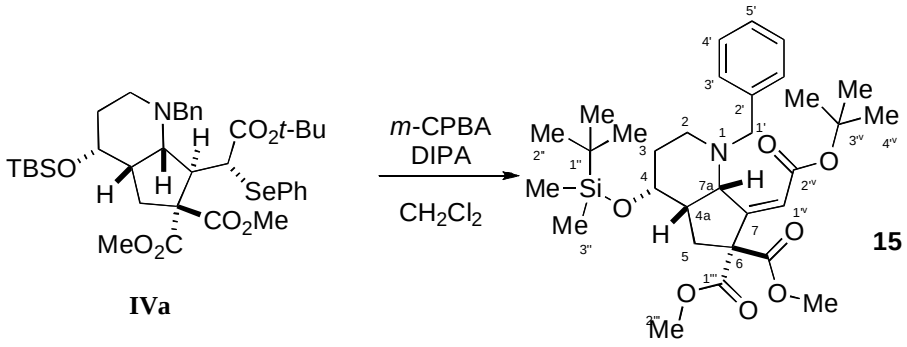
Calculated:	C: 60.80%	H: 7.31%	N: 1.92%
Found:	C: 60.64%	H: 7.62%	N: 2.04%

Analytical Data for **IVb**:

^{1}H NMR: (500 MHz, $CDCl_3$)

7.64 (m, 2 H, HC(6''')), 7.28 (m, 5 H, HC(7'''-8''') HC(3')), 7.22 (m, 3 H, HC(4'-5')), 4.08 (d, *J* = 13.9, 1 H, HC(1')), 4.02 (d, *J* = 10.5, 1 H, HC(1''')), 3.81 (d, *J* = 10.5, 1 H, HC(7)), 3.78 (dt, *J* = 5.1, 10.5, 1 H, HC(4)), 3.70 (s, 3 H, HC(2''')), 3.61 (s, 3 H, HC(2''')), 3.28 (d, *J* = 4.1, 1 H, HC(7a)), 2.88 (d, *J* = 13.7, 1 H, HC(1')), 2.81 (dd, *J* = 11.2, 13.4, 1H, HC(5)), 2.76 (dt, *J* = 3.4, 12.2, 1 H, HC(2)), 2.51 (m, 1 H, HC(4a)), 2.39 (dd, *J* = 8.3, 13.4, 1 H, HC(5)), 1.78 (td, *J* = 1.9, 12.0, 1 H, HC(3)), 1.65 (qd, *J* = 3.4, 12.4, 1 H, HC(2)), 1.45 (m, 1 H, HC(3)), 1.38 (s, 9 H, HC(4''')), 0.86 (s, 9 H, HC(2'')), 0.02 (s, 3 H, HC(3'')), 0.00 (s, 3 H, HC(3''))

[*rel-4R, 4aR, 7S, 7aR*]-1-Benzyl-*7-tert*-butoxycarbonylmethylene-4-(1,1-dimethylethyl)dimethylsilyl)oxyoctahydrocyclopenta[*b*]pyridine-6,6-dicarboxylic Acid Dimethyl Ester (15).



The reaction was conducted in a 25 mL (one neck) round bottom flask, with a gas inlet, septum, stir bar, and thermocouple. To a solution of **IVa** (0.438 g, 0.60 mmol) in CH_2Cl_2 (6 mL) at –77 °C (IPA/CO_2) was added *m*-CPBA (0.212 g, 1.2 mmol, 2.0 equiv) in one portion. The solution was stirred at –77 °C for 30 min, at which time diisopropylamine (0.17 mL, 1.20 mmol, 2.0 equiv) was added. The solution was then allowed to warm to room temperature over 1.5 h, during which time the color of the solution became yellow. The solution was diluted with Et_2O (15 mL), and was washed with sat. aqueous sodium bicarbonate (2x10 mL) and with brine (10 mL). The aqueous layers were back extracted with Et_2O (2x10 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated *in vacuo*. The yellow oil was then purified by column chromatography (SiO_2, hexanes/EtOAc, 15/1) to provide **15** (0.297 g, 86%) as a yellow solid. An analytical sample was obtained by further column chromatography (SiO_2, hexanes/EtOAc, 15/1), followed by precipitation from Et_2O as a white solid.

Analytical Data for **15**:

M.P.: 130-132 °C (Et_2O)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.25 (t, *J* = 6.8, 2 H, HC(4')), 7.18 (t, *J* = 7.0, 1 H, HC(5')), 7.13 (d, *J* = 7.3, 2 H, HC(3')), 6.02 (s, 1 H, HC(1'^{v})), 4.22 (d, *J* = 2.9, 1 H, HC(7a)), 3.97 (dt, *J* = 5.1, 10.7, 1 H, HC(4)), 3.95 (d, *J* = 13.4, 1 H, HC(1')), 3.77

(s, 3 H, HC(2’’’)), 3.66 (s, 3 H, HC(2’’’)), 3.00 (d, *J* = 13.9, 1 H, HC(1’)), 2.93 (t, *J* = 11.0, 1 H, HC(5)), 2.71 (dt, *J* = 3.2, 11.7, 1 H, HC(2)), 2.42 (m, 2 H, HC(4a) HC(5)), 1.93 (td, *J* = 1.7, 13.7, 1 H, HC(2)), 1.76 (qd, *J* = 3.9, 12.7, 1 H, HC(3)), 1.52 (m, 1 H, HC(3)), 1.50 (s, 9 H, HC(4’^{v})), 0.88 (s, 9 H, HC(2’’)), 0.06 (s, 3 H, HC(3’’)), 0.04 (s, 3 H, HC(3’’))

^{13}C NMR: (125 MHz, $CDCl_3$)

172.14 (C(1’’’)), 170.40 (C(1’’’)), 165.30 (C(2’^{v})), 156.90 (C(7)), 140.57 (C(2’)), 128.33 (C(3’-4’)), 126.71 (C(5’)), 123.92 (C(1’^{v})), 81.12 (C(3’^{v})), 69.05 (C(4)), 64.31 (C(7a)), 63.62 (C(6)), 57.16 (C(1’)), 53.38 (C(2’’’)), 53.24 (C(2’’’)), 49.88 (C(2)), 45.50 (C(4a)), 31.89 (C(5)), 30.24 (C(3)), 28.38 (C(4’^{v})), 25.97 (C(2’’)), 18.24 (C(1’’)), -4.50 (C(3’’)), -4.58 (C(3’’))

IR: ($CDCl_3$)

2949 (m), 2926 (m), 2889 (w), 1728 (s), 1706 (s), 1451 (m), 1432 (m), 1369 (m), 1255 (s), 1164 (s), 1097 (s)

MS: (ESI)

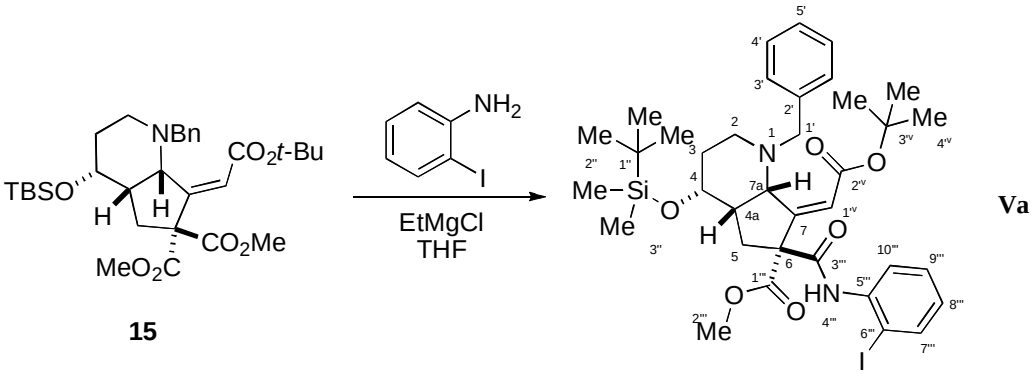
574 (M^+, 87), 518 (100)

TLC: R_f = 0.42 (hexanes/EtOAc, 4/1, UV)

Analysis: $C_{31}H_{47}NO_7Si$ (573.81)

Calculated:	C: 64.89%	H: 8.26%	N: 2.44%
Found:	C: 64.84%	H: 8.56%	N: 2.59%

[*rel-4R, 4aR,* 6*S, 7S, 7aR*]-1-Benzyl-*7-tert*-butoxycarbonylmethylene-4-(1,1-dimethylethyl)dimethylsilyl)oxy-6-(2-iodophenyaminocarbonyl)-octahydrocyclopenta[*b*]pyridine-6-carboxylic Acid Methyl Ester (Va).



15 **Va**

The reaction was conducted in a 25 mL (two neck) round bottom flask, with a gas inlet, septum, stir bar, and thermocouple. To a solution of *ortho*-iodoaniline (0.439 g, 2.00 mmol, 3.0 equiv) and **15** (0.382 g, 0.66 mmol) in THF (5 mL) at –15 °C (ethylene glycol/CO_2) was added a solution of ethylmagnesium chloride (2.0 M in Et_2O, 0.92 mL, 2.75 equiv) dropwise via cannula over 10 min. The resulting yellow solution was stirred at –15 °C for 50 min, at which time MeOH (0.5 mL) was added. The color of the reaction dissipated, and the solution is warmed to room temperature. The reaction solution was diluted with Et_2O (12 mL) and washed with H_2O (12 mL) and brine (12 mL). The combined aqueous layers were then back extracted with Et_2O (2x10 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated *in vacuo*. The yellow oil was then purified by column chromatography (SiO_2, benzene/EtOAc, 1/0→100/1→50/1) to give **Va** (0.430 g, 85%) as a colorless oil along with **Vb** (0.070 g, 14%) as a colorless oil. An analytical sample of **Va** was obtained by recrystallization (hexanes at –20 °C), providing **Va** as colorless prisms.

Analytical Data for **Va**:

M.P.: 140-142 °C (hexanes)

^{1}H NMR: (500 MHz, $CDCl_3$)

8.18 (dd, *J* = 1.5, 8.3, 1 H, HC(10’’’)), 8.09 (s, 1 H, HN(4’’’)), 7.80 (dd, *J*

= 1.5, 8.1, 1 H, HC(7’’’)), 7.37 (td, *J* = 1.5, 8.5, 1 H, HC(9’’’)), 7.26 (t, *J* = 7.3, 2 H, HC(3’)), 7.19 (t, *J* = 7.1, 1 H, HC(5’)), 7.15 (d, *J* = 7.3, 1 H, HC(4’)), 6.88 (td, *J* = 1.5, 7.8, 1 H, HC(8’’’)), 6.31 (s, 1 H, HC(1’^{v})), 4.35 (d, *J* = 2.9, 1 H, HC(7a)), 4.03 (dt, *J* = 5.1, 10.7, 1 H, HC(4)), 3.93 (d, *J* = 13.9, 1 H, HC(1’)), 3.73 (s, 3 H, HC(2’’’)), 3.30 (t, *J* = 11.5, 1 H, HC(5)), 3.06 (d, *J* = 14.1, 1 H, HC(1’)), 2.77 (dt, *J* = 2.9, 11.7, 1 H, HC(2)), 2.50 (m, 2 H, HC(4a) HC(5)), 1.97 (t, *J* = 1.7, 13.4, 1 H, HC(2)), 1.85 (qd, *J* = 3.9, 12.9, 1 H, HC(3)), 1.56 (m, 1 H, HC(3)), 1.50 (s, 9 H, HC(3’^{v})), 0.87 (s, 9 H, HC(2’’)), 0.05 (s, 3 H, HC(3’’)), 0.04 (s, 3 H, HC(3’’))

^{13}C NMR: (125 MHz, $CDCl_3$)

171.27 (C(1’’’)), 169.09 (C(3’’’)), 165.12 (C(2’^{v})), 157.46 (C(7)), 140.35 (C(2’)), 139.16 (C(7’’’)), 138.17 (C(5’’’)), 129.48 (C(9’’’)), 128.43 (C(3’)), 128.13 (C(4’)), 126.78 (C(5’)), 126.66 (C(8’’’)), 125.01 (C(1’^{v})), 122.60 (C(10’’’)), 90.25 (C(6’’’), 81.27 (3’^{v}), 69.12 (C(4)), 65.73 (C(6)), 64.34 (C(7a)), 57.14 (C(1’)), 53.82 (C(2’’’)), 49.96 (C(2)), 45.57 (C(4a)), 32.03 (C(5)), 30.23 (C(3)), 28.40 (C(4’^{v})), 26.05 (C(2’’)), 18.26 (C(1’’’)), -4.39 (C(3’’))

IR: ($CDCl_3$)

3359 (w), 2953 (m), 2926 (m), 2853 (m), 1742 (m), 1708 (s), 1585 (m), 1521 (s), 1432 (s), 1369 (s), 1250 (s), 1159 (s), 1093 (s)

MS: (ESI)

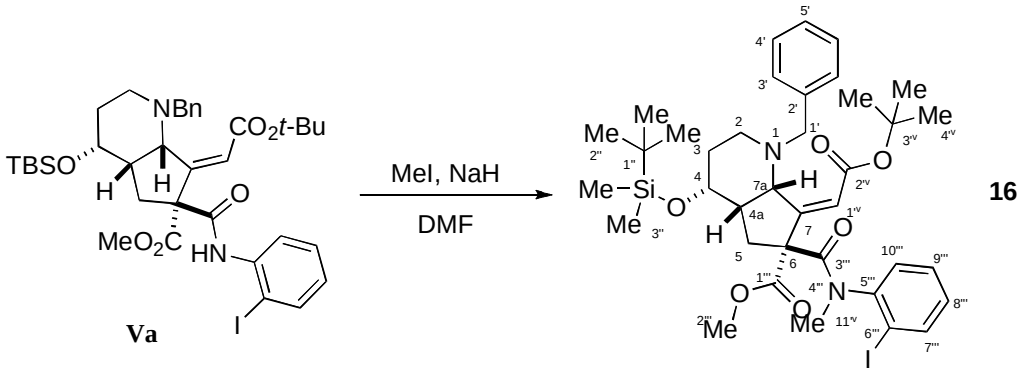
761 (M^+, 100)

TLC: R_f = 0.44 (hexanes/EtOAc, 4/1, UV)

Analysis: $C_{36}H_{49}IN_2O_6Si$ (760.79)

Calculated:	C: 56.84%	H: 6.49%	N: 3.68%
Found:	C: 56.56%	H: 6.54%	N: 3.70%

[*rel-4R, 4aR,* 6*S, 7S, 7aR*]-1-Benzyl-*7-tert*-butoxycarbonylmethylene-4-(1,1-dimethylethyl)dimethylsilyl)oxy-6-[(2-iodopheny)methylaminocarbonyl]octahydro-cyclopenta[*b*]pyridine-6-carboxylic Acid Methyl Ester (16).



The reaction was conducted in a 25 mL (three neck) round bottom flask, with a gas inlet, septum, stir bar, and thermocouple. To a solution of **Va** (0.763 g, 1.00 mmol) in DMF (10 mL) at 0 °C (ice) was added methyl iodide (0.25 mL, 4.02 mmol, 4.0 equiv), followed by sodium hydride (0.048 g, 2.00 mmol, 2.0 equiv). The color of the solution became slightly yellow and gas evolution was observed. The slurry was stirred at 0 °C for 20 min, and then allowed to warm to room temperature for 1 h. The slurry was then poured into H_2O (30 mL), and was diluted with Et_2O (30 mL). The layers were separated, and the organic layer was washed with brine (15 mL). The aqueous layers were combined and back extracted with Et_2O (2x15 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated *in vacuo*. The yellow oil was purified by column chromatography (SiO_2, hexanes/EtOAc, 10/1→8/1→6/1) to provide **16** (0.674 g, 87%) as a colorless oil. An analytical sample was obtained by recrystallization (hexanes at –20 °) to provide **16** as colorless prisms.

Analytical Data for **16**:

M.P.: 119-120 °C (hexanes)

^{1}H NMR: (500 MHz, $CDCl_3$)

The peaks observed by ^{1}H NMR were too broad to interpret at room temperature.

7.85-7.94 (m, 1 H), 7.00-7.45 (m, 9 H), 6.15-6.32 (m, 1 H), 1.65-4.15 (m, 17 H), 1.42-1.58 (m, 9 H), 0.85-0.90 (m, 9 H), 0.00-0.10 (m, 6 H)

^{1}H NMR: (500 MHz, d^{7}-DMF, 150 °C)

7.91 (d, *J* = 7.7, 1 H, HC(10’’’)), 7.44 (t, *J* = 7.5, 1 H, HC(9’’’)), 7.24 (m, 3 H, HC(7’’’) HC(3’)), 7.14 (m, 3 H, HC(5’) HC(4’)), 7.09 (t, *J* = 7.3, 1 H, C(8’’’)), 6.15 (s, 1 H, HC(1’^{v})), 4.00 (m, 2 H, HC(4) HC(7a)), 3.83 (d, *J* = 13.5, 1 H, HC(1’)), 3.57 (s, 3 H, HC(2’’’)), 3.22 (t, *J* = 12.0, 1 H, HC(5)), 3.11 (s, 3 H, HC(11’’’)), 2.93 (d, *J* = 13.7, 1 H, HC(1’)), 2.65 (d, *J* = 11.1, 1 H, HC(2)), 2.48 (s, 1 H, HC(5)), 2.34 (q, *J* = 6.8, 1 H, HC(4a)), 1.89 (t, *J* = 11.1, 1 H, HC(2)), 1.65 (m, 1 H, HC(3)), 1.55 (m, 1 H, HC(3)), 1.49 (s, 9 H, HC(4’^{v})), 0.90 (s, 9 H, HC(2’’)), 0.06 (s, 6 H, HC(3’’))

^{13}C NMR: (125 MHz, d^{7}-DMF, 150 °C)

170.48 (C(1’’’)), 170.03 (C(3’’’)), 165.27 (C(2’^{v})), 156.09 (C(7)), 140.45 (C(2’)), 137.78 (C(5’’’)), 130.24 (C(9’’’)), 128.64 (C(3’)), 128.58 (C(4’)), 127.06 (C(5’)), 126.02 (C(1’^{v})), 81.39 (3’^{v}), 69.47 (C(4)), 64.59 (C(6) C(7a)), 57.27 (C(1’)), 53.23 (C(2’’’)), 49.90 (C(2)), 44.88 (C(4a)), 39.13 (C(5)), 30.72 (C(3)), 28.72 (C(4’^{v})), 26.45 (C(2’’)), 18.32 (C(1’’)), -3.95 (C(3’’))

The following carbons were not observed: C(7’’’), C(8’’’), C(10’’’), C(6’’’)

IR: ($CDCl_3$)

2952 (s), 2926 (s), 2857 (m), 1740 (m), 1706 (s), 1662 (s), 1471 (m), 1364 (s), 1230 (s), 1159 (s), 1097 (s)

MS: (ESI)

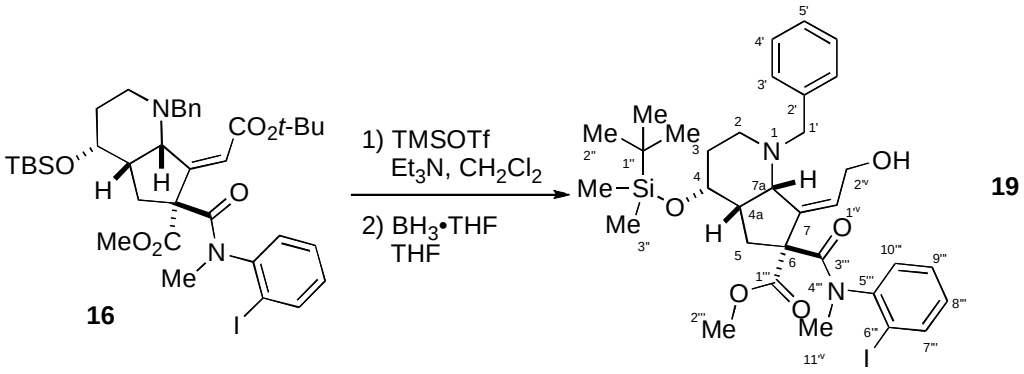
775 (M^{+}, 100)

TLC: R_f = 0.26 (hexanes/EtOAc, 4/1, UV)

Analysis: $C_{37}H_{51}IN_2O_6Si$ (774.80)

Calculated:	C: 57.36%	H: 6.63%	N: 3.62%
Found:	C: 57.45%	H: 6.89%	N: 3.54%

[*rel-4R, 4aR,* 6*S, 7aR*]-1-Benzyl-4-(1,1-dimethylethyl)dimethylsilyl)oxy-7-(2-hydroxy-ethylidine)-6-[(2-iodopheny)methylaminocarbonyl]-octahydro-cyclopenta[*b*]pyridine-6-carboxylic Acid Methyl Ester (19).



The reaction was conducted in a 25 mL (three neck) round bottom flask, with a gas inlet, septum, stir bar, and thermocouple. To a solution of **16** (0.711 g, 0.92 mmol) in CH_2Cl_2 (10 mL) at 0 °C (ice) was added triethylamine (1.30 mL, 9.31 mmol, 10.0 equiv) and trimethylsilyl triflate (0.83 mL, 4.58 mmol, 5.0 equiv). The solution was stirred at 0 °C for 15 min, and at room temperature for 45 min. The solution was then diluted with Et_2O (20 mL), and washed with phosphate buffer (pH 7, 15 mL) and Brine (15 mL). The aqueous layers were back extracted twice with Et_2O (15 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated *in vacuo* to provide the crude acid.

To a solution of the crude acid in THF (10 mL) was added BH_3•THF (1.0 M, 1.83 mL, 1.83 mmol, 2.0 equiv (based on **355**)), at which time gas evolution was observed. The solution was then stirred at room temperature for 6 h. A second portion of BH_3•THF (1.0 M, 0.92 mL, 0.92 mmol, 1.0 equiv) was added, and the solution was stirred for 4 h. A third portion of BH_3•THF (1.0 M, 0.46 mL, 0.46 mmol, 0.5 equiv) was then added, and the solution was stirred for an additional 3.5 h. The solution was then diluted with Et_2O (20 mL) and H_2O (15 mL) was added. After the gas evolution had ceased, the layers were separated, and the organic layer was washed with brine (15 mL). The aqueous layers were combined and back extracted with Et_2O (2x15 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexane/EtOAc, 2/1→1/1→1/2) to provide **19** (0.561 g,

87%) as a colorless oil. An analytical sample was obtained by recrystallization (hexanes at –20 °C), affording **19** a colorless prisms.

Analytical Data for **19**:

M.P.: 206-207 °C (hexanes)

^{1}H NMR: (500 MHz, $CDCl_3$)

The peaks observed by ^{1}H NMR were too broad to interpret at room temperature.

7.85-7.94 (m, 1 H), 7.00-7.45 (m, 9 H), 6.15-6.32 (m, 1 H), 1.65-4.45 (m, 20 H), 1.42-1.58 (m, 9 H), 0.85-0.90 (m, 9 H), 0.00-0.10 (m, 6 H)

^{1}H NMR: (500 MHz, d^7-DMF, 150 °C)

7.89 (d, *J* = 7.7, 1 H, HC(10’’’), 7.43 (t, *J* = 7.9, 1 H, HC(9’’’)), 7.21 (m, 6 H, HC(7’’’) HC(3’-5’)), 7.06 (t, *J* = 7.9, 1 H, HC(8’’’)), 5.97 (t, *J* = 6.2, 1 H, HC(1’^{v})), 4.23 (dd, *J* = 7.1, 13.3, 1 H, HC(2’^{v})), 4.14 (dd, *J* = 6.2, 13.5, 1 H, HC(2’^{v})), 3.96 (m, 3 H, HC(4) HC(7a) HC(1’)), 3.56 (s, 3 H, HC(2’’’)), 3.24 (m, 1 H, HC(5)), 3.12 (s, 3 H, HC(11’’’)), 2.79 (d, *J* = 11.6, 1 H, HC(1’)), 2.59 (d, *J* = 10.9, 1 H, HC(2)), 2.48 (s, 1 H, HC(5)), 2.36 (s, 1 H, HC(4a)), 1.81 (t, *J* = 10.3, 1 H, HC(2)), 1.62 (q, *J* = 10.9, 1 H, HC(3)), 1.52 (s, 1 H, HC(3)), 0.89 (s, 9 H, HC(2’’)), 0.04 (s, 6 H, HC(3’’))

^{13}C NMR: (125 MHz, d^7-DMF, 150 °C)

171.79 (C(1’’’)), 170.98 (C(3’’’)), 140.33 (C(2’)), 130.16 (C(7)), 129.86 (C(1’^{v})), 128.89 (C(3’)), 128.52 (C(4’)), 126.98 (C(5’)), 69.91 (C(4)), 65.39 (C(6)), 63.74 (C(7a)), 59.99 (C(2’^{v})), 57.38 (C(1’)), 52.76 (C(2’’’)), 49.43 (C(2)), 45.19 (C(4a)), 39.16 (C(5)), 30.80 (C(3)), 26.47 (C(2’’)), 18.33 (C(1’’)), -3.94 (C(3’’))

The following carbons were not observed: C(7’’’), C(8’’’), C(10’’’), C(6’’’), C(5’’’), C(9’’’)

IR: ($CDCl_3$)

3607 (w), 2950 (s), 2926 (s), 2888 (m), 2855 (m), 1735 (s), 1653 (s), 1471 (s), 1431 (m), 1367 (s), 1246 (s), 1095 (s)

MS: (ESI)

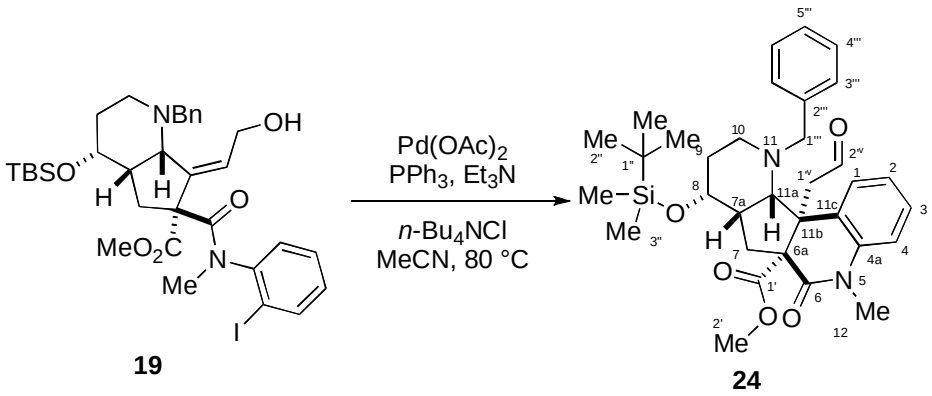
705 (M^+, 100)

TLC: R_f = 0.18 (hexanes/EtOAc, 1/1, UV)

Analysis: $C_{33}H_{45}IN_2O_5Si$ (704.71)

Calculated:	C: 56.24%	H: 6.44%	N: 3.98%
Found:	C: 56.17%	H: 6.46%	N: 3.97%

[*rel*-6a*S*, 7a*R*, 8*R*, 11a*R*, 11b*R*]11-Benzyl-8-((1,1-dimethylethyl)dimethylsilyl)oxy-5-methyl-6-oxo-11b-(2-oxoethyl)-5,6,7,7a,8,9,10,11,1,1a,11b-decahydro-pipridino[2',3':3,4)cyclopenta[1,2-*c*]quinolinone-6a-carboxylic Acid Methyl Ester (24).



19 **24**

The reaction was conducted in a 35 mL (one neck) round bottom flask, with a gas Intel, septum, stir bar, and reflux condenser, under an atmosphere of argon. To a mixture of $Bu_4NCl•H_2O$ (0.493 g, 1.77 mmol, 2.0 equiv), $Pd(OAc)_2$ (0.020 g, 0.089 mmol, 0.1 equiv), and triphenylphosphine (0.046 g, 0.177 mmol, 0.2 equiv) was added a solution of **19** (0.625 g, 0.89 mmol) in acetonitrile (18 mL). To the yellow solution was added triethylamine (0.23 mL, 1.78 mmol, 2.0 equiv), and the solution was heated to reflux (85 °C, bath temperature) for 12 h. During this time the reaction color became light brown, and a black precipitate began to form. The solution was cooled to room temperature, and was diluted with Et_2O (30 mL). The mixture was washed with H_2O (15 mL), and brine (15 mL). The aqueous layers were combined and back extracted with Et_2O (2x15 mL).

The organic layers were combined, dried over $MgSO_4$, and concentrated *in vacuo*. The resulting oil was purified by column chromatography (SiO_2, hexanes/acetone/triethylamine, 10/1/0.1→8/2/0.1) to give a slightly yellow oil. The oil was dissolved in Et_2O (15 mL) and was washed with a sat. aqueous solution of $Na_2S_2O_3$ (10 mL), H_2O (10 mL), and brine (10 mL). The aqueous layers were back extracted with Et_2O (2x10 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated *in vacuo* to provide **24** (0.451, 88%) as a colorless oil. An analytical sample was obtained by recrystallization (hexanes/EtOAc, -20 °C), providing **24** as colorless prisms.

Analytical Data for **24**:

M.P.: 145-147 °C (hexanes/EtOAc)

^{1}H NMR: (500 MHz, $CDCl_3$)

9.39 (s, 1 H, HC(2'^{v})), 7.00-7.30 (m, 9 H, HC(1-4) HC(3'''-5''')), 4.01 (s, 1 H, HC(8)), 3.49 (s, 3 H, HC(2')), 3.45 (m, 2 H, HC(1''') HC(1'^{v})), 3.44 (s, 3 H, HC(12)), 3.09 (m, 4 H, HC(11a) HC(10) HC(1''') HC(1'^{v})), 2.85 (ABX, 2 H, HC(7)), 2.46 (dt, *J* = 3.2, 13.9, 1 H, HC(10)), 2.27 (dt, *J* = 5.6, 9.3, 1 H, HC(7a)), 1.48 (tt, *J* = 2.9, 11.2, 1 H, HC(9)), 1.38 (m, 1 H, HC(9)), 0.97 (s, 9 H, HC(2'')), 0.16 (s, 3 H, HC(3'')), 0.08 (s, 3 H, HC(3''))

^{13}C NMR: (125 MHz, $CDCl_3$)

201.68 (C(2'^{v}), 171,17 (C(1'), 168.22 (C(6)), 139.41 (C(11c)), 138.19 (C(2''')), 128.84 (C(3''')), 128.34 (C(4''')), 128.23 (C(1)), 128.02 (C(5''')), 127.17 (C(3)), 126.58 (C(4a)), 123.10 (C(2)), 115.19 (C(4)), 68.89 (C(11a)), 65.21 (C(8)), 63.14 (C(1''')), 59.09 (C(6a)), 53.35 (C(2')), 52.92 (C(1'^{v})), 41.85 (C(12)), 41.40 (C(10)), 34.88 (C(7a)), 31.51 (C(7)), 30.74 (C(11b)), 27.07 (C(9)), 26.07 (C(2'')), 18.38 (C(1'')), -4.52 (C(3'')), -4.78 (C(3''))

IR: ($CDCl_3$)

2952 (m), 2926 (m), 2854 (w), 1731 (s), 1716 (s), 1659 (s), 1600 (m), 1471 (m), 1458 (s), 1373 (s), 1249 (s), 1051 (m)

MS: (ESI)

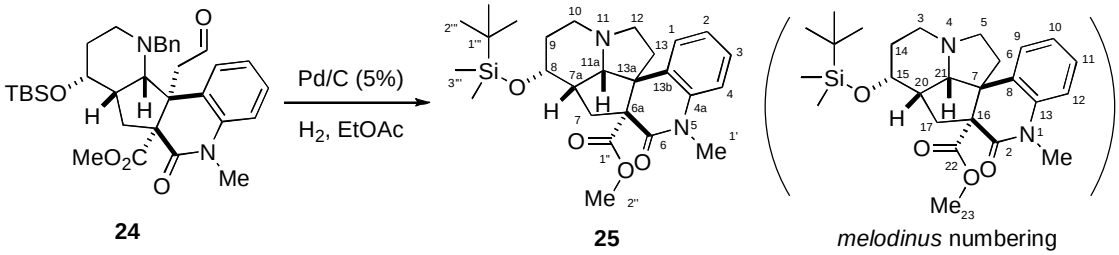
577 (M^+, 100)

TLC: R_f = 0.21 (CH_2Cl_2/MeOH, 18/1, UV)

Analysis: $C_{33}H_{44}N_2O_5Si$ (576.80)

Calculated:	C: 68.72%	H: 7.69%	N: 4.86%
Found:	C: 68.67%	H: 7.86%	N: 4.96%

[*rel*-6a*S*, 7a*R*, 8*R*, 11a*R*, 13a*R*]-8-((1,1-Dimethylethyl)dimethylsilyl)oxy-5-methyl-6,7,7a,8,9,11a,12,13-octahydro-10*H*-indolizino[1',8':2,3,4)cyclopenta[1,2-*c*]quinolinone-6a-carboxylic Acid Methyl Ester (25).



The reaction was conducted in a 25 mL (one neck) round bottom flask, with a stir bar, connected to a glass manifold with a hydrogen chamber. To a solution of **24** (0.342 g, 0.59 mmol) in EtOAc (12 mL) was added palladium on carbon (5%, 0.063 g, 0.030 mmol, 0.05 equiv.). The slurry was stirred under 1 atm of hydrogen for 12 h., at which time it was filtered through Celite, and the filter cake was washed with EtOAc (25 mL). The filtrate was concentrated *in vacuo*, and the residue was purified by column chromatography (SiO_2, EtOAc/hexanes, 2/1→3/1) to provide **25** (0.246 g, 88%) as a white solid. An analytical sample was obtained by recrystallization (hexanes, -20 °C) to provide **25** and colorless needles.

Analytical Data for **25**:

M.P.: 103-105 °C (hexanes)

^{1}H NMR: (500 MHz, $CDCl_3$)

7.48 (d, *J* = 7.6, 1 H, HC(1)), 7.27 (t, *J* = 9.0, 1 H, HC(3)), 7.10 (t, *J* = 7.6,

1H, HC(2)), 7.05 (d, *J* = 8.3, 1 H, HC(4)), 3.87 (dt, *J* = 5.4, 11.2, 1 H, HC(8)), 3.61 (s, 3 H, HC(2'')), 3.43 (s, 3 H, HC(1')), 3.21 (q, *J* = 7.8, 1 H, HC(12)), 3.05 (m, 3 H, HC(10), HC(12), HC(11a)), 2.73 (dd, *J* = 6.1, 13.2, 1 H, HC(7)), 2.61 (m, 3 H, HC(10), HC(13), HC(7)), 1.97 (m, 2 H, HC(13), HC(7a)), 1.85 (qd, *J* = 4.1, 12.4, 1 H, HC(9)), 1.4 (m, 1 H, HC(9)), 0.97 (s, 9 H, HC(2''')), 0.16 (s, 3 H, HC(3''')), 0.08 (s, 3 H, HC(3'''))

^{13}C NMR: (125 MHz, $CDCl_3$)

171.06 (C(1'')), 167.95 (C(6)), 138.27 (C(13b) C(4a)), 127.78 (C(3)), 127.06 (C(1)), 123.56 (C(2)), 114.64 (C(4)), 78.68 (C(11a)), 70.03 (C(8)), 64.43 (C(6a)), 58.10 (C(13a)), 53.29 (C(12)), 52.76 (C(2'')), 46.41 (C(10)), 43.90 (C(7a), 39.26 (C(13)), 35.85 (C(7)), 30.63 (C(1')), 26.52 (C(9)), 26.06 (C(2''')), 18.31 (C(1'''), -4.44 (C(3''')), -4.50 (C(3'''))

IR: ($CDCl_3$)

2949 (s), 2930 (s), 2847 (m), 1739 (s), 1656 (s), 1594 (m), 1470 (s), 1372 (s), 1240 (s), 1098 (s)

MS: (ESI)

471 (M^+, 100)

TLC: R_f = 0.44 (CH_2Cl_2/MeOH, 18/1, UV)

Analysis: $C_{26}H_{38}N_2O_4Si$ (470.68)

Calculated:	C: 66.35%	H: 8.14%	N: 5.95%
Found:	C: 66.33%	H: 8.28%	N: 6.00%

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