

Supplementary Information

Total synthesis of monoterpenoid indole alkaloid

(-)-arbophyllidine

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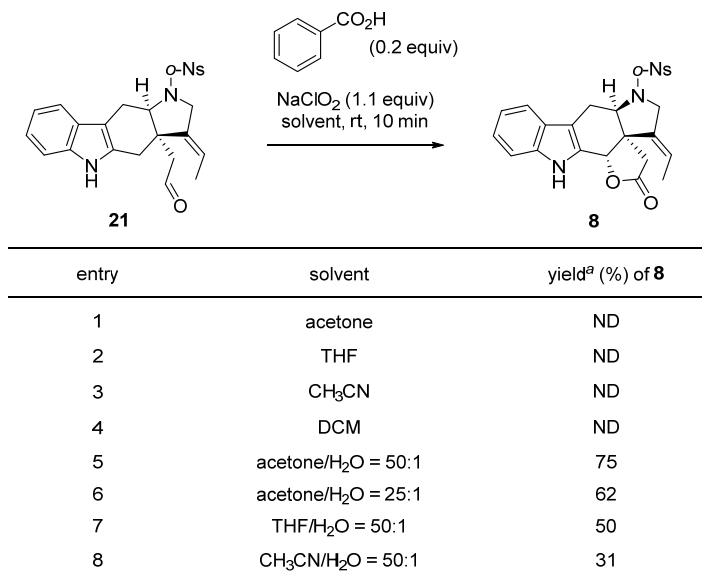
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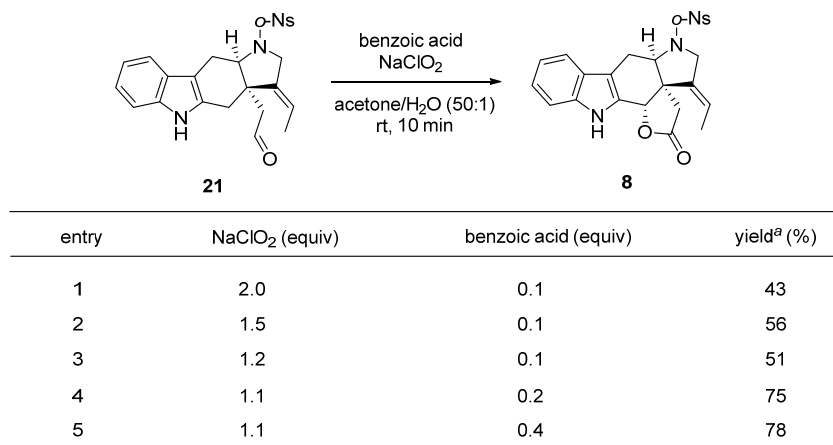
I. Optimization for NaClO₂-mediated Oxidative Lactonization

Table S1 Optimization of reaction solvents

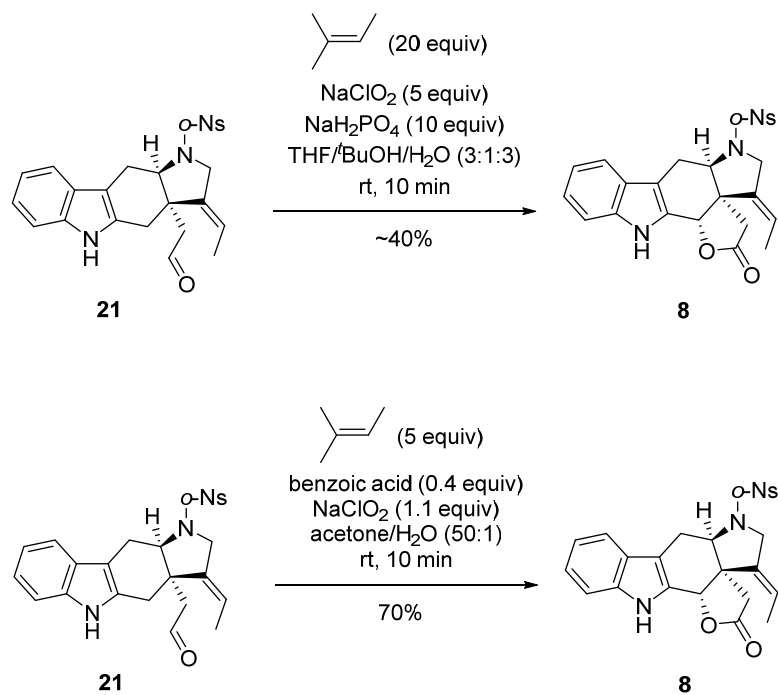


^aIsolated yields.

Table S2 Optimization of reaction conditions



^aIsolated yields.

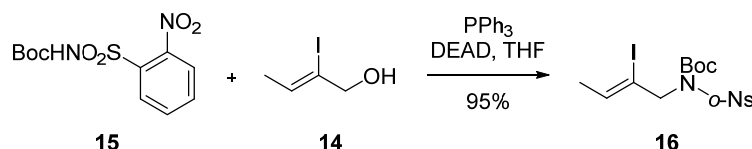


Scheme S1 Standard Pinnick oxidation result and relative experiment.

II. Experimental Procedures and Spectroscopic Data of Compounds

General Procedures. All reactions involving air or moisture sensitive reagents or intermediates were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Solvents purification was conducted according to Purification of Laboratory Chemicals (Peerrin, D. D. Armarego, W. L. and Perrins, D. R., Pergamon Press: Oxford, 1980). Yields refer to isolated compounds, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Tsingdao silica gel plates (60F-254) using Tsingdao silica gel (60, particle size 0.040-0.063 mm). And the silica gel from the same company was also used for flash column chromatography. NMR spectra were recorded on a Bruker AVANCE 400 (^1H : 400 MHz, ^{13}C : 100 MHz) or a Bruker AVANCE 500 (^1H : 500 MHz, ^{13}C : 125 MHz) instrument. Chemical shifts were reported in parts per million (ppm) with respect to the residual solvent signal CDCl_3 (^1H NMR: $\delta = 7.26$; ^{13}C NMR: $\delta = 77.00$). Peak multiplicities were reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, m = multiplet, br = broad signal. High resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer using ESI-TOF (electrospray ionization-time of flight). X-ray diffraction data were collected by using a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer.

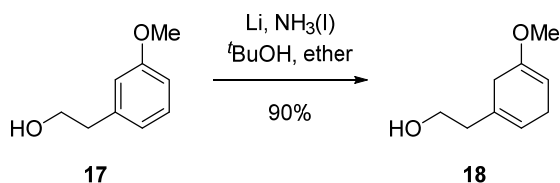
Note: There exist rotational isomers for most *N*-Boc compounds.



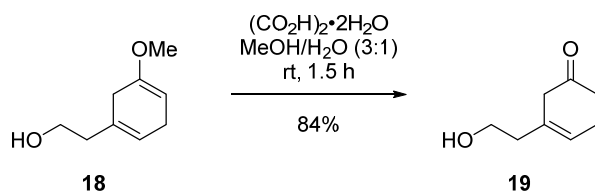
Synthesis of 16. DEAD (3.4 mL, 23.2 mmol) was added dropwise to a solution of **15**¹ (5.4 g, 17.9 mmol), PPh_3 (7.0 g, 26.8 mmol) and alcohol **14**² (3.5 g, 17.9 mmol) in dry THF (90 mL) at 0 °C under nitrogen balloon. The reaction mixture was warmed up to room temperature and further stirred overnight. After completion, the reaction mixture was concentrated and loaded on a silica gel column (hexane/ethyl acetate = 5:1) to get pure product **16** (8.2 g, 95%) as a white solid. TLC: $R_f = 0.6$ (ethyl acetate/hexane = 1:3). mp 105.2 – 106.9 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.36 – 8.31 (m, 1H), 7.79 – 7.73 (m, 3H), 6.00 (qt, $J = 6.3, 1.4$ Hz, 1H), 4.63 (t, $J = 1.5$ Hz, 2H), 1.80 (dt, $J = 6.4, 1.5$ Hz, 3H), 1.35 (s, 9H). ^{13}C NMR (125 MHz, CDCl_3) δ 149.9, 147.6, 134.6, 133.9, 133.0, 132.0, 131.5, 124.6, 102.7, 85.5, 57.9, 27.9, 21.9. HRMS (ESI-TOF) calculated for $\text{C}_{15}\text{H}_{19}\text{O}_6\text{N}_2\text{SiNa}$ ($[\text{M} + \text{Na}]^+$) 504.9901, found 504.9902.



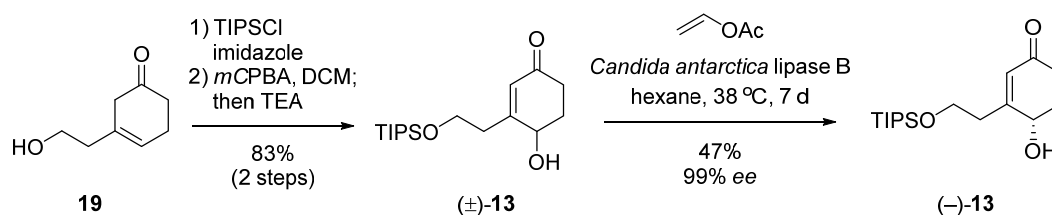
Synthesis of 12. To a solution of compound **16** (1.2 g, 2.5 mmol) in CH₂Cl₂ (10 mL) was added TFA (1 mL) at room temperature. The resulting solution was stirred for 12 h and was quenched with saturated NaHCO₃ (aq.). The aqueous phase was extracted with CH₂Cl₂ (3 × 15 mL). The combined organic layers were washed with brine and then were dried over Na₂SO₄. The solvent was removed *in vacuo* and the residue was then purified by flash column chromatography (silica, hexane/ethyl acetate = 4:1) to give product **12** (0.9 g, 95%) as a white solid. TLC: R_f = 0.5 (ethyl acetate/hexane = 1:3). mp 106.3 – 107.2 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.01 (d, *J* = 7.1 Hz, 1H), 7.90 (d, *J* = 7.6 Hz, 1H), 7.77 – 7.67 (m, 2H), 5.95 (t, *J* = 6.3 Hz, 1H), 5.93 (s, 1H), 4.12 (d, *J* = 6.2 Hz, 2H), 1.60 (d, *J* = 6.3 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 148.0, 134.9, 134.9, 133.6, 132.7, 131.0, 125.5, 103.6, 56.1, 21.5. HRMS (ESI-TOF) calculated for C₁₀H₁₁O₄N₂SiNa ([M + Na]⁺) 404.9376, found 404.9374.



Synthesis of 18. A solution of alcohol **17** (20 g, 131 mmol) in Et₂O (60 mL) was added to liquid NH₃ (250 mL) at -78 °C. Next, ^tBuOH (120 mL) was added to that solution, followed by the careful and slow addition of solid Li (4.5 g, 642 mmol). The resultant blue-colored slurry was then warmed to -50 °C and stirred for 6 h. Then, the ammonia was allowed to evaporate at room temperature overnight. Ethyl acetate (250 mL) and aqueous NH₄Cl solution (200 mL) were added and the mixture was stirred for 30 min. The mixture was partitioned after standing and the layers were separated. The aqueous phase was extracted with ethyl acetate (3 × 200 mL) and then the combined organic extracts were washed with brine for three times. The solvent was dried over Na₂SO₄ before it was removed *in vacuo* and the residue was then purified by flash column chromatography (silica, hexane/ethyl acetate = 4:1) to give **18** (18.2 g, 90%) as a colorless liquid. TLC: R_f = 0.4 (ethyl acetate/hexane = 1:3). ¹H NMR (500 MHz, CDCl₃) δ 5.41 (s, 1H), 4.54 (s, 1H), 3.58 (t, *J* = 6.6 Hz, 2H), 3.45 (s, 3H), 2.80 (br s, 1H), 2.74 – 2.68 (m, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 2.16 (t, *J* = 6.5 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 152.5, 130.7, 120.8, 90.2, 59.9, 53.6, 39.7, 31.2, 26.6. HRMS (ESI-TOF) calculated for C₉H₁₅O₂ ([M + H]⁺) 155.1067, found 155.1066.



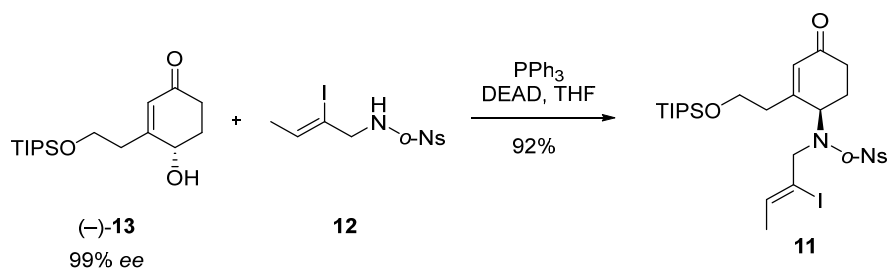
Synthesis of 19. To a solution of alcohol **18** (3.1 g, 20 mmol) in MeOH/H₂O (60 mL/20 mL) was added oxalic acid (252 mg, 2 mmol). The reaction mixture was allowed to stir at room temperature for 1.5 h. Then the mixture was diluted with brine (100 mL) and extracted with ethyl acetate (3 × 100 mL). The combined organic extracts were washed with brine for three times, dried over Na₂SO₄, filtered and concentrated *in vacuo*. The crude product was purified by silica gel column chromatography (hexane/ethyl acetate = 2:1) to afford **19** (2.4 g, 84%) as a colorless liquid. TLC: R_f = 0.5 (ethyl acetate/hexane = 1:1). ¹H NMR (400 MHz, CDCl₃) δ 5.74 (s, 1H), 3.73 (t, J = 6.3 Hz, 2H), 2.85 (br s, 2H), 2.47 (br s, 4H), 2.30 (t, J = 6.3 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 210.3, 132.8, 123.4, 60.2, 42.9, 39.7, 38.3, 25.1. HRMS (ESI-TOF) calculated for C₈H₁₂O₂Na ([M + Na]⁺) 163.0730, found 163.0730.



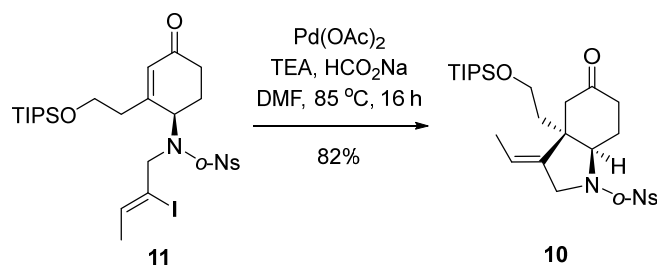
Synthesis of (–)-13. To a solution of alcohol **19** (7 g, 50 mmol) in dry CH₂Cl₂ (250 mL) was added imidazole (4.5 g, 65 mmol) and TIPSCl (11.3 mL, 53 mmol) at 0 °C. The resulting mixture was stirred at 0 °C for 10 min before it was warmed to room temperature to continue to stir for 10 min. Then it was quenched with aqueous NH₄Cl solution (200 mL) and extracted with CH₂Cl₂ (3 × 150 mL). Then the combined organic extracts were washed with brine, dried over Na₂SO₄ and concentrated under reduced pressure to obtain crude product which was used directly without further purification.

The crude product obtained from above was dissolved in CH₂Cl₂ (500 mL) and *m*CPBA (11.2 g, 55 mmol, 85% purity) was added over 30 min at 0 °C. The reaction was stirred for 1 h and saturated sodium bicarbonate solution (100 mL) and saturated sodium thiosulfate solution (100 mL) were added and the reaction stirred for 30 min. The layers were separated and the resulting aqueous layer was extracted with CH₂Cl₂ (3 × 100 mL). The combined organic layers were dried over MgSO₄ and filtered. To this solution triethylamine (14 mL, 100 mmol) was added and the resultant slurry was stirred at room temperature for 2 h. The mixture was then directly concentrated under reduced pressure to dryness and the residue purified by column chromatography (silica gel, hexane/ethyl acetate = 5:1) to give the racemic alcohol **13** (13 g, 83% over 2 steps).

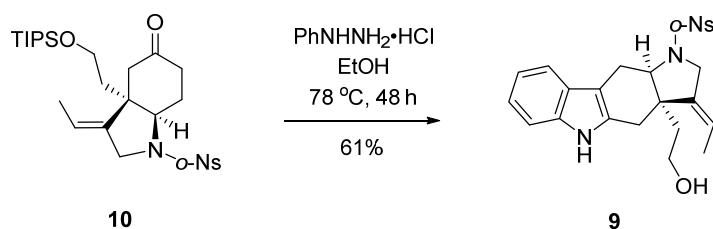
A mixture of racemic alcohol **13** (13 g, 41.6 mmol), vinyl acetate (19 ml, 210 mmol) and *Candida antarctica* lipase B (1.3 g, 10 wt%, 10000U/g) in 410 ml of hexane was magnetically stirred at 38 °C for 7 days. After this period, the reaction was stopped by filtration. Removal of the solvent followed by separation on a silica gel column (hexane/ethyl acetate = 5:1) yielded 6.1 g (47%) of (–)-**13** (99% *ee*) as a colorless crystal. The enantiomeric excess was determined by DAICEL CHIRALPAK IC (0.46 cm × 25 cm), hexane/ⁱPrOH = 70:30, flow rate: 1.0 mL/min, λ = 210 nm. TLC: R_f = 0.5 (ethyl acetate/hexane = 1:3). mp 63.8 – 64.6 °C. [α]²⁵_D -1.8 (*c* 1.0, CHCl₃). ¹H NMR (500 MHz, CDCl₃) δ 5.83 (s, 1H), 4.39 (dt, *J* = 8.1, 4.2 Hz, 1H), 4.26 (d, *J* = 4.2 Hz, 1H), 3.94 (ddd, *J* = 10.4, 6.7, 3.9 Hz, 1H), 3.92 – 3.85 (m, 1H), 2.70 (ddd, *J* = 13.8, 6.5, 3.7 Hz, 1H), 2.61 (ddd, *J* = 16.9, 6.5, 4.7 Hz, 1H), 2.50 (ddd, *J* = 13.9, 7.7, 3.9 Hz, 1H), 2.33 (ddd, *J* = 16.9, 10.4, 4.8 Hz, 1H), 2.24 (ddt, *J* = 15.8, 6.5, 4.6 Hz, 1H), 2.08 – 1.97 (m, 1H), 1.19 – 1.05 (m, 21H). ¹³C NMR (125 MHz, CDCl₃) δ 199.1, 165.0, 127.4, 67.6, 63.6, 37.8, 34.8, 31.4, 17.9, 11.8. HRMS (ESI-TOF) calculated for C₁₇H₃₂O₃SiNa ([M + Na]⁺) 335.2013, found 335.2012.



Synthesis of 11. A 100 mL two-neck flask equipped with magnetic stirring bar, stopper, thermometer, and nitrogen inlet was flame-dried and purged with nitrogen. DEAD (1.6 mL, 10.5 mmol) was added dropwise to a solution of PPh₃ (3.2 g, 12.1 mmol), compound (–)-**13** (3.1 g, 8.0 mmol, 99% *ee*) and **12** (2.5 g, 8.0 mmol) in dry THF (40 mL) at 0 °C under nitrogen balloon. The reaction mixture was warmed up to room temperature and further stirred overnight. After completion, the reaction mixture was concentrated *in vacuo* and loaded on a silica gel column (hexane/ethyl acetate = 5:1) to get pure product **11** (4.6 g, 92%) as a pale yellow liquid. TLC: R_f = 0.5 (ethyl acetate/hexane = 1:3). [α]²⁵_D 89.1 (*c* 1.0, CHCl₃). ¹H NMR (500 MHz, CDCl₃) δ 8.00 (dd, *J* = 7.7, 4.2 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.70 – 7.63 (m, 1H), 6.15 (s, 1H), 5.91 – 5.82 (m, 1H), 4.97 (d, *J* = 3.9 Hz, 1H), 4.53 (d, *J* = 16.9 Hz, 1H), 3.87 – 3.74 (m, 3H), 2.63 – 2.34 (m, 5H), 2.24 (dt, *J* = 16.0, 6.0 Hz, 1H), 1.60 – 1.55 (m, 3H), 1.10 – 0.97 (m, 21H). ¹³C NMR (125 MHz, CDCl₃) δ 197.3, 158.5, 147.8, 134.6, 134.4, 134.0, 132.2, 131.8, 131.4, 124.6, 103.9, 60.5, 58.2, 57.2, 36.6, 36.1, 29.2, 21.9, 18.0, 11.9. HRMS (ESI-TOF) calculated for C₂₇H₄₁O₆N₂ISSiNa ([M + Na]⁺) 699.1391, found 669.1390.

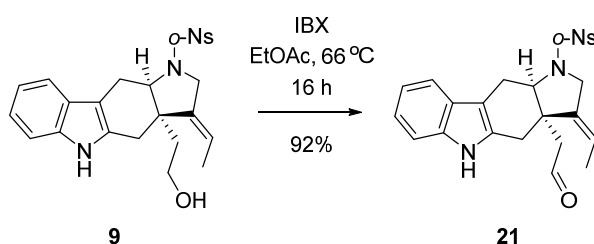


Synthesis of 10. Pd(OAc)_2 (10 mg, 0.044 mmol), HCO_2Na (61 mg, 0.9 mmol), triethylamine (0.3 mL, 2.2 mmol) and anhydrous DMF (3 mL) was added in a two-neck round-bottomed flask under argon. Argon was bubbled through the solution for 5 min which turned orange-brown. Compound **11** (300 mg, 0.44 mmol, predissolved in 1.5 mL of DMF) was added to the mixture. Argon was bubbled through the solution for an additional 5 min. The mixture was heated to 85 °C and stirred for 16 h. After this period the reaction mixture was cooled down to room temperature and filtered through a pad of celite. The organic fraction was extracted with ether, and the ethereal solution washed with brine, dried over MgSO_4 and concentrated under reduced pressure. Purification by chromatography on silica gel (hexane/ethyl acetate = 8:1 to 5:1) afforded 198 mg (82%) of product **10** as a brown solid. TLC: R_f = 0.5 (ethyl acetate/hexane = 1:3), mp 146.6 – 147.9 °C. $[\alpha]_D^{26}$ -72.8 (*c* 1.0, CHCl_3). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.06 – 8.03 (m, 1H), 7.71 (dq, J = 14.9, 7.5, 1.6 Hz, 2H), 7.63 – 7.60 (m, 1H), 5.51 (qd, J = 7.4, 5.5 Hz, 1H), 4.27 (t, J = 5.2 Hz, 1H), 4.19 – 4.13 (m, 1H), 4.09 – 4.03 (m, 1H), 3.74 – 3.63 (m, 2H), 2.98 (d, J = 15.5 Hz, 1H), 2.63 (d, J = 15.5 Hz, 1H), 2.35 (ddd, J = 18.0, 9.5, 5.2 Hz, 1H), 2.26 (dt, J = 11.5, 5.4 Hz, 1H), 2.21 – 2.08 (m, 2H), 1.77 (dt, J = 14.0, 7.0 Hz, 1H), 1.70 (dt, J = 7.4, 1.9 Hz, 3H), 1.60 (dt, J = 14.2, 6.1 Hz, 2H), 1.02 (dt, J = 6.8, 4.0 Hz, 21H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 210.1, 148.4, 138.8, 133.8, 131.9, 131.5, 130.8, 124.1, 120.2, 65.3, 59.8, 53.6, 49.2, 46.2, 41.2, 35.1, 27.6, 18.0, 13.5, 11.9. HRMS (ESI-TOF) calculated for $\text{C}_{27}\text{H}_{42}\text{O}_6\text{N}_2\text{SSiNa}$ ($[\text{M} + \text{Na}]^+$) 573.2425, found 573.2423.

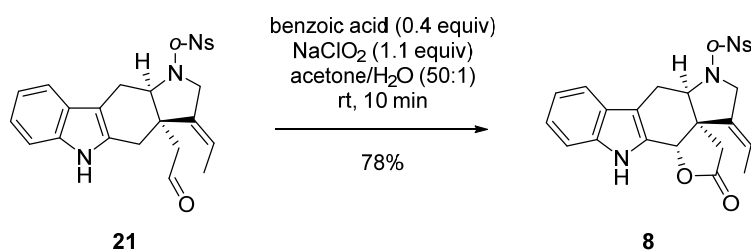


Synthesis of 9. In a flame-dried flask, the phenylhydrazine hydrochloride (29 mg, 0.2 mmol) and bicycle **10** (100 mg, 0.18 mmol) were dissolved in absolute EtOH (1.2 mL). The mixture was stirred under reflux (78 °C) for 48 h. Then the reaction mixture was cooled to room temperature and poured into water (15 mL). The crude product was extracted with ethyl acetate (3 × 20 mL). The organic phase was washed with brine, dried over Na_2SO_4 , and concentrated under reduced pressure. The resulting liquid was purified by silica gel column chromatography (hexane/ethyl acetate = 1:1) to give **9** (51 mg, 61%) as a yellow

liquid. TLC: $R_f = 0.3$ (ethyl acetate/hexane = 2:3). $[\alpha]^{25}_D 4.6$ (c 1.0, CHCl_3). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.06 (dd, $J = 7.9, 1.3$ Hz, 1H), 7.85 (s, 1H), 7.52 (td, $J = 7.8, 1.3$ Hz, 1H), 7.42 (td, $J = 7.7, 1.3$ Hz, 1H), 7.35 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.25 (d, $J = 8.1$ Hz, 1H), 7.11 (d, $J = 7.8$ Hz, 1H), 7.10 – 7.06 (m, 1H), 7.00 – 6.95 (m, 1H), 5.43 (qd, $J = 7.3, 5.4$ Hz, 1H), 4.31 – 4.23 (m, 1H), 4.18 – 4.13 (m, 1H), 4.10 (t, $J = 5.9$ Hz, 1H), 3.77 – 3.65 (m, 2H), 3.24 (d, $J = 17.0$ Hz, 1H), 3.07 (dd, $J = 16.5, 5.9$ Hz, 1H), 2.90 (d, $J = 17.0$ Hz, 1H), 2.82 (dd, $J = 16.5, 5.9$ Hz, 1H), 1.99 – 1.85 (m, 2H), 1.73 (dt, $J = 7.4, 1.8$ Hz, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 147.4, 138.4, 136.3, 134.0, 133.4, 131.9, 131.6, 130.4, 126.8, 124.2, 121.3, 119.2, 118.0, 117.7, 110.6, 105.7, 64.3, 59.5, 53.0, 48.9, 39.8, 31.0, 23.2, 13.3. HRMS (ESI-TOF) calculated for $\text{C}_{24}\text{H}_{25}\text{O}_5\text{N}_3\text{SNa}$ ($[\text{M} + \text{Na}]^+$) 490.1407, found 490.1406.

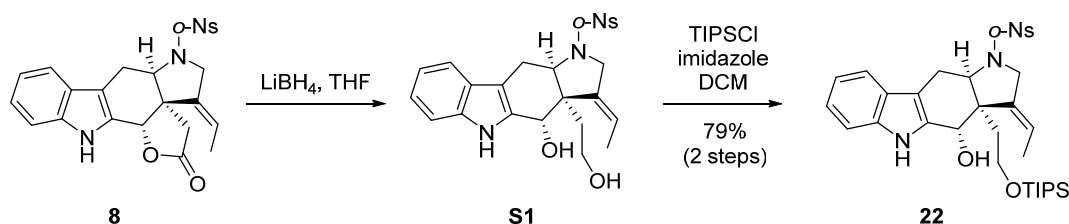


Synthesis of 21. To a solution of **9** (98 mg, 0.2 mmol) in fresh distilled ethyl acetate (4 mL) was added IBX (65 mg, 0.23 mmol). The reaction mixture was stirred at 66 °C for 16 h. After this period the reaction mixture was cooled down to room temperature and filtered through a pad of celite. The organic fraction was quickly purified by flash column chromatography (silica gel, hexane/ethyl acetate = 2:1) to give **21** (85 mg, 92%) as a light yellow oil. TLC: $R_f = 0.6$ (ethyl acetate/hexane = 1:1). $[\alpha]^{26}_D 8.8$ (c 1.0, CHCl_3). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.69 (t, $J = 2.3$ Hz, 1H), 8.10 (dd, $J = 8.0, 1.3$ Hz, 1H), 7.81 (s, 1H), 7.56 (td, $J = 7.8, 1.3$ Hz, 1H), 7.44 (td, $J = 7.7, 1.3$ Hz, 1H), 7.36 (dd, $J = 8.0, 1.2$ Hz, 1H), 7.26 (d, $J = 8.2$ Hz, 2H), 7.13 (d, $J = 7.9$ Hz, 1H), 7.12 – 7.08 (m, 1H), 7.01 – 6.97 (m, 1H), 5.53 – 5.46 (m, 1H), 4.38 – 4.33 (m, 1H), 4.26 – 4.21 (m, 1H), 4.19 (t, $J = 5.8$ Hz, 1H), 3.30 (d, $J = 17.2$ Hz, 1H), 3.07 (dd, $J = 16.9, 6.2$ Hz, 1H), 2.93 (d, $J = 17.2$ Hz, 1H), 2.92 (dd, $J = 16.9, 6.2$ Hz, 1H), 2.77 (dd, $J = 16.6, 2.4$ Hz, 1H), 2.67 (dd, $J = 16.6, 2.3$ Hz, 1H), 1.75 (dt, $J = 7.4, 1.9$ Hz, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 200.5, 147.4, 137.3, 136.3, 133.8, 133.5, 132.0, 130.6, 130.4, 126.6, 124.3, 121.6, 119.3, 118.6, 117.8, 110.7, 105.8, 64.0, 52.7, 49.9, 47.3, 30.7, 22.8, 13.5. HRMS (ESI-TOF) calculated for $\text{C}_{24}\text{H}_{23}\text{O}_5\text{N}_3\text{SNa}$ ($[\text{M} + \text{Na}]^+$) 488.1251, found 488.1251.



Synthesis of 8. To a solution of **21** (107 mg, 0.23 mmol) in acetone/ H_2O (2.5 mL/50 μL)

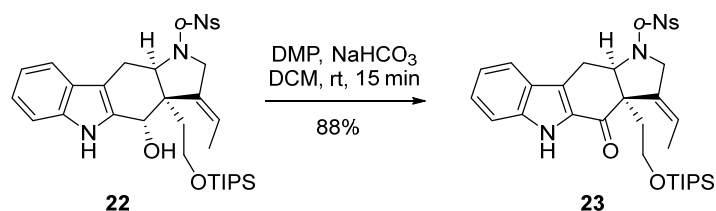
was added benzoic acid (10 mg, 0.09 mmol) and powdery NaClO₂ (23 mg, 0.25 mmol). The mixture was stirred for 10 min before brine (10 mL) was directly added to this solution. Then the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with saturated NaHCO₃ solution (3 × 50 mL) and brine (3 × 50 mL) before they were dried over Na₂SO₄. The solvents were removed *in vacuo* and the residue was then purified by flash column chromatography (silica gel, hexane/ethyl acetate = 2:1) to give **8** (86 mg, 78%) as a yellow oil. TLC: *R_f* = 0.5 (ethyl acetate/hexane = 1:1). [α]_D²⁵ 87.8 (*c* 1.0, CHCl₃). ¹H NMR (500 MHz, CDCl₃) δ 8.68 (s, 1H), 8.05 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.56 (td, *J* = 7.8, 1.2 Hz, 1H), 7.46 (td, *J* = 7.8, 1.3 Hz, 1H), 7.36 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 7.21 – 7.16 (m, 1H), 7.05 – 7.00 (m, 1H), 5.94 (s, 1H), 5.55 (q, *J* = 7.5 Hz, 1H), 4.31 – 4.24 (m, 1H), 4.21 – 4.14 (m, 2H), 3.18 (dd, *J* = 16.7, 5.6 Hz, 1H), 2.92 (dd, *J* = 16.6, 7.0 Hz, 1H), 2.82 (d, *J* = 18.4 Hz, 1H), 2.75 (d, *J* = 18.4 Hz, 1H), 1.71 (d, *J* = 7.5 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 174.5, 147.4, 137.5, 136.2, 134.0, 133.2, 132.2, 130.5, 127.3, 125.4, 124.4, 123.6, 112.0, 119.8, 119.2, 111.7, 109.2, 75.9, 63.9, 52.5, 52.4, 39.7, 22.7, 13.3. HRMS (ESI-TOF) calculated for C₂₄H₂₁O₆N₃SNa ([M + Na]⁺) 502.1043, found 502.1045.



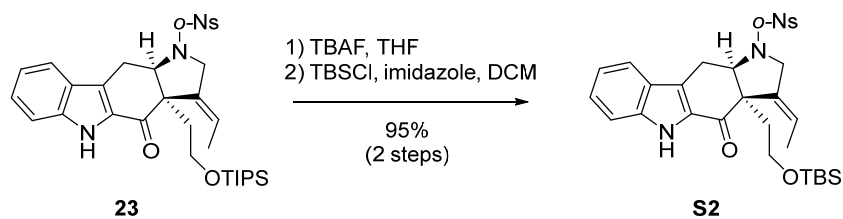
Synthesis of 22. To a solution of **8** (82 mg, 0.17 mmol) in dry THF (2 mL) was added LiBH₄ (1.0 M solution in THF, 0.5 mL, 0.5 mmol) at 0 °C. Then the reaction mixture was allowed to warm up to room temperature and stirred for 3 h. After this period the mixture was cooled to 0 °C and quenched with saturated NaHCO₃ solution (10 mL). The aqueous phase was extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated under vacuum to afford a yellow oil which was used directly without further purification.

To a stirred solution of crude diol obtained from above in CH₂Cl₂ (2 mL) was added imidazole (28 mg, 0.42 mmol) and TIPSCl (0.71 mL, 0.33 mmol) at 0 °C. The resultant mixture was stirred for 30 min at 0 °C. After this period, the reaction mixture was quenched with the saturated aqueous NH₄Cl solution (10 mL) and extracted with CH₂Cl₂ (3 × 15 mL). The combined organic layers were washed with brine, then dried over Na₂SO₄. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 5:1) to afford **22** (86 mg, 79% over two steps) as a yellow liquid. TLC: *R_f* = 0.4 (ethyl acetate/hexane = 1:3). [α]_D²⁵ -17.6 (*c* 1.0, CHCl₃). ¹H NMR (500 MHz, CDCl₃) δ 8.13 – 8.08 (m, 2H), 7.64 (td, *J* = 7.6, 1.5 Hz, 1H), 7.60 (td, *J* = 7.7, 1.5 Hz, 1H), 7.53 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.17 – 7.12 (m, 1H), 7.03 (td, *J* = 7.5, 0.8 Hz, 1H), 5.49 (qd, *J* = 7.4, 5.5 Hz, 1H), 5.45 (d, *J* = 6.4 Hz, 1H), 4.53

(d, $J = 6.4$ Hz, 1H), 4.36 (t, $J = 6.9$ Hz, 1H), 4.34 – 4.29 (m, 1H), 4.16 – 4.10 (m, 1H), 3.84 (t, $J = 5.2$ Hz, 2H), 3.24 (dd, $J = 16.4, 6.6$ Hz, 1H), 2.74 (dd, $J = 15.9, 7.1$ Hz, 1H), 2.18 (dt, $J = 11.0, 5.1$ Hz, 1H), 1.90 (dt, $J = 9.6, 4.4$ Hz, 1H), 1.78 (dt, $J = 7.3, 1.7$ Hz, 3H), 1.16 – 1.03 (m, 21H). ^{13}C NMR (125 MHz, CDCl_3) δ 147.7, 137.4, 136.8, 134.1, 133.5, 133.4, 131.9, 130.7, 126.6, 124.2, 122.2, 119.5, 119.3, 118.6, 111.1, 107.3, 65.5, 63.5, 60.7, 56.2, 52.4, 34.8, 24.3, 18.0, 13.7, 11.9. HRMS (ESI-TOF) calculated for $\text{C}_{33}\text{H}_{45}\text{O}_6\text{N}_3\text{SSiNa}$ ($[\text{M} + \text{Na}]^+$) 662.2691, found 662.2693.

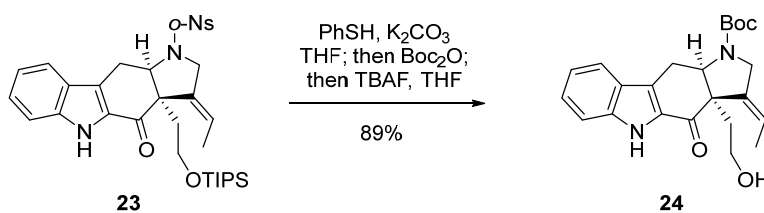


Synthesis of 23. To a stirred solution of alcohol **22** (132 mg, 0.21 mmol) in CH_2Cl_2 (4.5 mL) was added NaHCO_3 (56 mg, 0.66 mmol) and DMP (98 mg, 0.23 mmol) at 0 °C. The resultant mixture was stirred for 15 min at room temperature. Then the saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (10 mL) were added to the mixture. The mixture was stirred for 5 min at room temperature and extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were washed with brine, then dried over Na_2SO_4 . The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 5:1) to afford **23** (115 mg, 88%) as a colorless oil. TLC: $R_f = 0.6$ (ethyl acetate/hexane = 1:3). $[\alpha]_D^{26} -58.2$ (c 1.0, CHCl_3). ^1H NMR (500 MHz, CDCl_3) δ 9.33 (s, 1H), 8.03 (dd, $J = 7.9, 1.3$ Hz, 1H), 7.53 (td, $J = 7.7, 1.3$ Hz, 1H), 7.47 (td, $J = 7.7, 1.4$ Hz, 1H), 7.41 (ddd, $J = 9.3, 8.2, 2.2$ Hz, 3H), 7.37 – 7.33 (m, 1H), 7.08 (dd, $J = 11.1, 4.1$ Hz, 1H), 5.67 (qd, $J = 7.3, 5.5$ Hz, 1H), 4.80 (t, $J = 6.2$ Hz, 1H), 4.38 – 4.32 (m, 1H), 4.21 – 4.15 (m, 1H), 3.94 (ddd, $J = 10.0, 6.9, 5.4$ Hz, 1H), 3.78 (dt, $J = 10.0, 6.9$ Hz, 1H), 3.47 (dd, $J = 17.4, 5.6$ Hz, 1H), 3.26 (dd, $J = 17.4, 6.8$ Hz, 1H), 2.19 (dt, $J = 14.1, 7.0$ Hz, 1H), 2.10 (ddd, $J = 14.4, 6.5, 5.4$ Hz, 1H), 1.74 – 1.69 (m, 3H), 1.05 – 0.93 (m, 21H). ^{13}C NMR (125 MHz, CDCl_3) δ 189.2, 147.8, 134.0, 133.5, 133.4, 133.1, 131.7, 130.3, 130.1, 127.5, 125.4, 124.1, 123.8, 122.0, 121.5, 120.5, 112.5, 66.2, 60.0, 59.5, 53.4, 35.8, 23.8, 18.0, 13.2, 11.9. HRMS (ESI-TOF) calculated for $\text{C}_{33}\text{H}_{43}\text{O}_6\text{N}_3\text{SSiNa}$ ($[\text{M} + \text{Na}]^+$) 660.2534, found 660.2534.



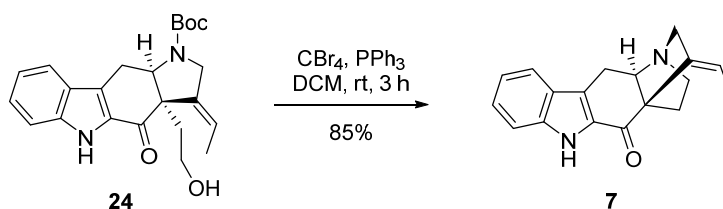
Synthesis of S2. To a stirred solution of compound **23** (65 mg, 0.11 mmol) in THF (1 mL) was added TBAF (1.0 in THF, 0.22 mL, 0.22 mmol) at room temperature. The resultant mixture was stirred for 5 h. Then the saturated aqueous NH₄Cl (5 mL) were added to the mixture. The mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with brine, then dried over Na₂SO₄, and concentrated under vacuum to afford a colorless oil which was used directly without further purification.

To a stirred solution of crude alcohol obtained from above in CH₂Cl₂ (1 mL) was added imidazole (19 mg, 0.28 mmol) and TBSCl (33 mg, 0.22 mmol) at 0 °C. The resultant mixture was stirred for 2 h at 0 °C. After this period, the reaction mixture was quenched with the saturated aqueous NH₄Cl solution (5 mL) and extracted with CH₂Cl₂ (3 × 10 mL). The combined organic layers were washed with brine, then dried over Na₂SO₄. The solvent was removed under vacuum, and the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 5:1) to afford **S2** (62 mg, 95% over two steps) as a white foam. TLC result: R_f = 0.6 (ethyl acetate/hexane = 1 : 3). ¹H NMR (500 MHz, CDCl₃) δ 8.78 (s, 1H), 8.05 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.56 (td, *J* = 7.6, 1.4 Hz, 1H), 7.52 (td, *J* = 7.7, 1.5 Hz, 1H), 7.45 – 7.34 (m, 4H), 7.09 (ddd, *J* = 7.9, 6.9, 0.9 Hz, 1H), 5.64 (qd, *J* = 7.3, 5.5 Hz, 1H), 4.80 (dd, *J* = 7.0, 5.9 Hz, 1H), 4.38 – 4.32 (m, 1H), 4.19 – 4.14 (m, 1H), 3.83 (ddd, *J* = 10.3, 6.9, 5.5 Hz, 1H), 3.66 (dt, *J* = 10.3, 6.8 Hz, 1H), 3.47 (dd, *J* = 17.3, 5.7 Hz, 1H), 3.22 (dd, *J* = 17.3, 7.2 Hz, 1H), 2.19 (dt, *J* = 14.9, 7.3 Hz, 1H), 2.01 (dt, *J* = 14.9, 7.3 Hz, 1H), 1.70 (dt, *J* = 7.4, 1.8 Hz, 3H), 0.77 (s, 9H), -0.05 (s, 3H), -0.07 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 189.0, 147.8, 138.9, 133.5, 133.4, 133.3, 131.7, 130.4, 130.1, 127.5, 125.4, 124.1, 123.8, 121.9, 121.5, 120.6, 112.5, 66.2, 59.7, 59.3, 53.3, 35.5, 25.8, 24.1, 18.1, 13.0, -5.5. HRMS (ESI-TOF) calculated for C₃₀H₃₇O₆N₃SSiNa ([M + Na]⁺) 618.2065, found 618.2066.

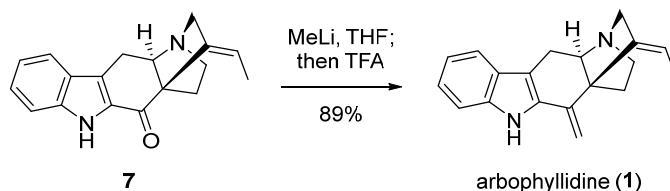


Synthesis of 24. To a solution of compound **23** (115 mg, 0.19 mmol) in THF (2 mL) was added K₂CO₃ (53 mg, 0.38 mmol) and thiophenol (30 μL, 0.30 mmol). The mixture was stirred at room temperature for 3 h before Boc₂O (88 μL, 0.38 mmol) was directly added to this solution. After stirring for another 10 min, TBAF (1.0 M solution in THF, 0.6 mL, 0.6 mmol) was added to this mixture. The resulting mixture was stirred at room temperature for 6 h. After this period the mixture was diluted with brine (20 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine and then were dried over Na₂SO₄. The solvents were removed *in vacuo* and the residue was then purified by flash column chromatography (silica gel,

hexane/ethyl acetate = 3:1) to give **24** (70 mg, 89% in one pot) as a colorless oil. TLC: $R_f = 0.4$ (ethyl acetate/hexane = 1:2). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.49 – 9.27 (m, 1H), 7.64 (d, $J = 5.8$ Hz, 1H), 7.54 – 7.31 (m, 2H), 7.16 (br s, 1H), 5.62 (br s, 1H), 4.73 – 4.47 (m, 1H), 4.31 – 4.01 (m, 2H), 3.95 (d, $J = 14.5$ Hz, 1H), 3.91 – 3.74 (m, 2H), 3.67 – 3.33 (m, 1H), 2.96 – 2.64 (m, 1H), 2.22 – 1.98 (m, 2H), 1.60 – 1.44 (m, 12H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 191.9, 154.2, 139.2, 134.2, 133.6, 130.7, 128.0, 125.6, 122.0, 121.7, 120.9, 112.6, 80.2, 65.9, 59.8, 59.4, 51.0, 36.8, 28.6, 25.0, 12.5. HRMS (ESI-TOF) calculated for $\text{C}_{23}\text{H}_{28}\text{O}_4\text{N}_2\text{Na}$ ($[\text{M} + \text{H}]^+$) 397.2122, found 397.2120.



Synthesis of 7. To a solution of **24** (20 mg, 0.05 mmol) in CH_2Cl_2 (2 mL) was added PPh_3 (40 mg, 0.15 mmol) and CBr_4 (50 mg, 0.15 mmol). The mixture was stirred at room temperature for 3 h and then was quenched with saturated aqueous NaHCO_3 solution. The aqueous phase was extracted with CH_2Cl_2 (5×10 mL). The combined organic layers were washed with brine and then were dried over Na_2SO_4 . The solvent was removed *in vacuo* and the residue was then purified by flash column chromatography (silica gel, $\text{CH}_2\text{Cl}_2/\text{MeOH} = 20:1$ to 15:1) to give compound **7** (12 mg, 85%) as a white foam. TLC: $R_f = 0.6$ ($\text{CH}_2\text{Cl}_2/\text{MeOH} = 8:1$). $[\alpha]_D^{25} -64.0$ (c 0.4, CHCl_3). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.08 (br s, 1H), 7.65 (d, $J = 8.0$ Hz, 1H), 7.42 (d, $J = 8.3$ Hz, 1H), 7.37 (dd, $J = 8.1, 7.1$ Hz, 1H), 7.17 (t, $J = 7.5$ Hz, 1H), 5.26 (q, $J = 7.0$ Hz, 1H), 3.86 (br d, $J = 15.2$ Hz, 1H), 3.45 (dd, $J = 10.6, 5.7$ Hz, 1H), 3.28 (dd, $J = 16.2, 5.8$ Hz, 1H), 3.25 – 3.15 (m, 2H), 2.93 (dd, $J = 16.2, 10.7$ Hz, 1H), 2.87 – 2.80 (m, 1H), 2.16 (td, $J = 11.1, 4.6$ Hz, 1H), 1.97 (ddd, $J = 11.8, 8.5, 5.2$ Hz, 1H), 1.50 (dt, $J = 7.1, 1.7$ Hz, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 192.8, 142.2, 138.6, 132.1, 127.0, 126.2, 125.7, 121.4, 120.6, 116.1, 112.5, 76.4, 62.2, 61.0, 55.6, 30.5, 21.9, 13.2. HRMS (ESI-TOF) calculated for $\text{C}_{18}\text{H}_{19}\text{ON}_2$ ($[\text{M} + \text{H}]^+$) 279.1492, found 279.1491.

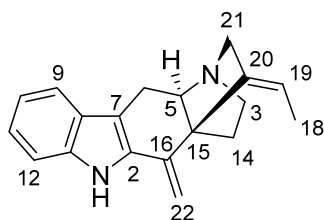


Synthesis of arbophyllidine (1). A magnetically stirred solution of ketone **7** (12 mg, 0.043 mmol) in THF (1 mL) was cooled to 0 °C and then treated with methyllithium (1.6 M solution in diethoxymethane, 22 μL , 0.22 mmol). The resulting mixture was

stirred at 0 °C for 1 h and then quenched with water (5 mL). After the resulting mixture was warmed to room temperature, the aqueous phase was extracted with CH₂Cl₂ (5 × 5 mL), and the combined organic phases were washed with brine before being dried (Na₂SO₄), filtered. To this obtained solution (ca. 25 mL) was added TFA (1 mL). The resulting mixture was stirred at room temperature for 6 h and then concentrated under reduced pressure to afford a yellow oil that was subjected to flash chromatography (silica gel, CH₂Cl₂/MeOH = 15:1) to give **1** (10.6 mg, 89%) as a white foam. TLC: R_f = 0.6 (CH₂Cl₂/MeOH = 8:1). [α]_D²⁵ -241.0 (*c* 0.1, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 8.10 (br s, 1H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.20 (td, *J* = 7.5, 1.0 Hz, 1H), 7.09 (td, *J* = 7.5, 1.0 Hz, 1H), 5.40 (s, 1H), 5.21 (s, 1H), 5.15 (q, *J* = 7.1 Hz, 1H), 3.80 (br d, *J* = 15.8 Hz, 1H), 3.26 – 3.17 (m, 1H), 3.13 (br d, *J* = 15.8 Hz, 1H), 3.10 – 3.05 (m, 2H), 2.89 (ddd, *J* = 12.4, 8.5, 5.0 Hz, 1H), 2.72 (dd, *J* = 17.8, 12.0 Hz, 1H), 2.08 (td, *J* = 10.9, 4.5 Hz, 1H), 1.95 (ddd, *J* = 11.2, 8.6, 5.2 Hz, 1H), 1.56 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 142.0, 140.1, 137.3, 133.1, 127.7, 123.2, 119.7, 119.0, 115.4, 112.7, 110.9, 107.1, 73.5, 60.0, 56.6, 56.3, 33.6, 21.1, 12.4. HRMS (ESI-TOF) calculated for C₁₉H₂₁N₂ ([M + H]⁺) 277.1699, found 277.1698.

III. Comparison of the Spectra of Natural and Synthetic products

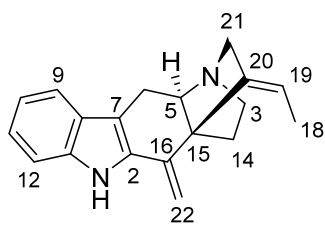
Comparison of ¹H NMR spectroscopic data of natural and synthetic arbophyllidine (1)



arbophyllidine (1)

position	natural δ ¹ H [ppm; mult; <i>J</i> (Hz)] 400 MHz ³	this work δ ¹ H [ppm; mult; <i>J</i> (Hz)] 400 MHz	deviation (natural – synthetic) $\Delta\delta$ (ppm)
3	3.22, m (α) 2.89, ddd (12.5, 8.5, 4.6) (β)	3.22, m (α) 2.89, ddd (12.4, 8.5, 5.0) (β)	0
5	3.07, m	3.07, m	0
6	3.07, m (α) 2.72, dd (17.3, 11.9) (β)	3.07, m (α) 2.72, dd (17.8, 12.0) (β)	0
9	7.48, d (8.0)	7.49, d (7.9)	0.01
10	7.08, td (7.5, 1.0)	7.09, td (7.5, 1.0)	0.01
11	7.19, td (7.5, 1.0)	7.20, td (7.5, 1.0)	0.01
12	7.32, d (8.0)	7.32, d (7.9)	0
14	2.09, td (11.0, 4.6) (α) 1.96, m (β)	2.08, td (10.9, 4.5) (α) 1.95, ddd (11.2, 8.6, 5.2) (β)	-0.01 -0.01
18	1.56, d (7.1)	1.56, d (7.1)	0
19	5.16, q (7.1)	5.15, q (7.1)	-0.01
21	3.81, br d (15.0) (α) 3.13, br d (15.0) (β)	3.80, br d (15.8) (α) 3.13, br d (15.8) (β)	-0.01
22	5.41, s (<i>b</i>) 5.21, s (<i>a</i>)	5.40, s (<i>b</i>) 5.21, s (<i>a</i>)	-0.01
NH	8.19, br s	8.10, br s	-0.09

Comparison of ^{13}C NMR spectroscopic data of natural and synthetic arbophyllidine (**1**)



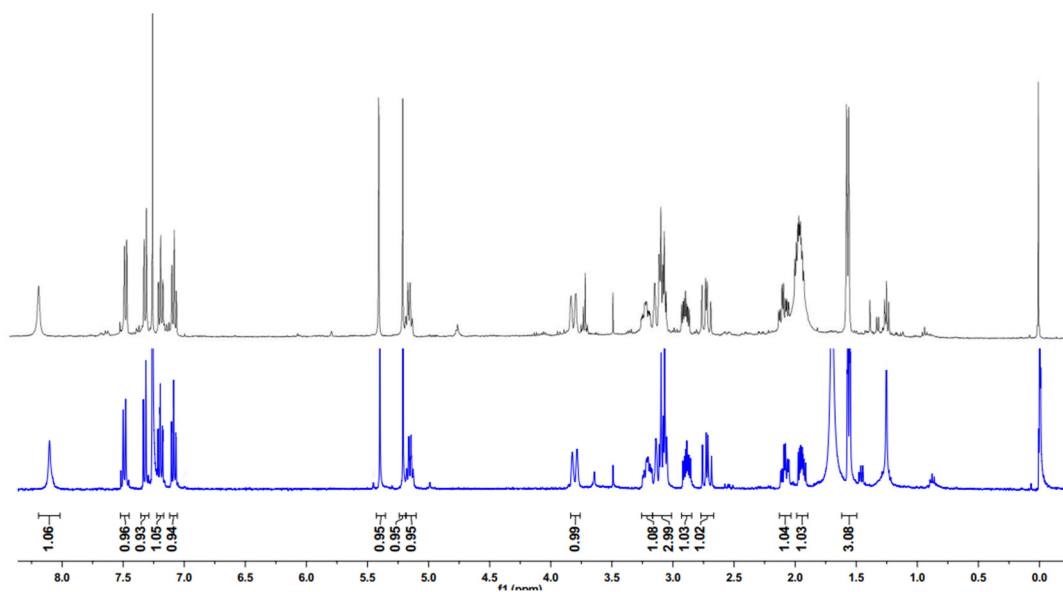
arbophyllidine (**1**)

position	natural $\delta^{13}\text{C}$ [ppm] 100 MHz ³	this work $\delta^{13}\text{C}$ [ppm] 100 MHz	deviation (natural – synthetic) $\Delta\delta$ (ppm)
2	133.1	133.1	0
3	56.2	56.3	0.1
5	73.4	73.5	0.1
6	21.1	21.1	0
7	112.6	112.7	0.1
8	127.7	127.7	0
9	119.0	119.0	0
10	119.6	119.7	0.1
11	123.2	123.2	0
12	110.9	110.9	0
13	137.3	137.3	0
14	33.5	33.6	0.1
15	56.5	56.6	0.1
16	140.0	140.1	0.1
18	12.4	12.4	0
19	115.5	115.4	-0.1
20	142.0	142.0	0
21	59.8	60.0	0.2
22	107.1	107.1	0

Arbophyllidine Comparison Spectra (^1H NMR, CDCl_3)

Top (black): natural, 400 MHz 3

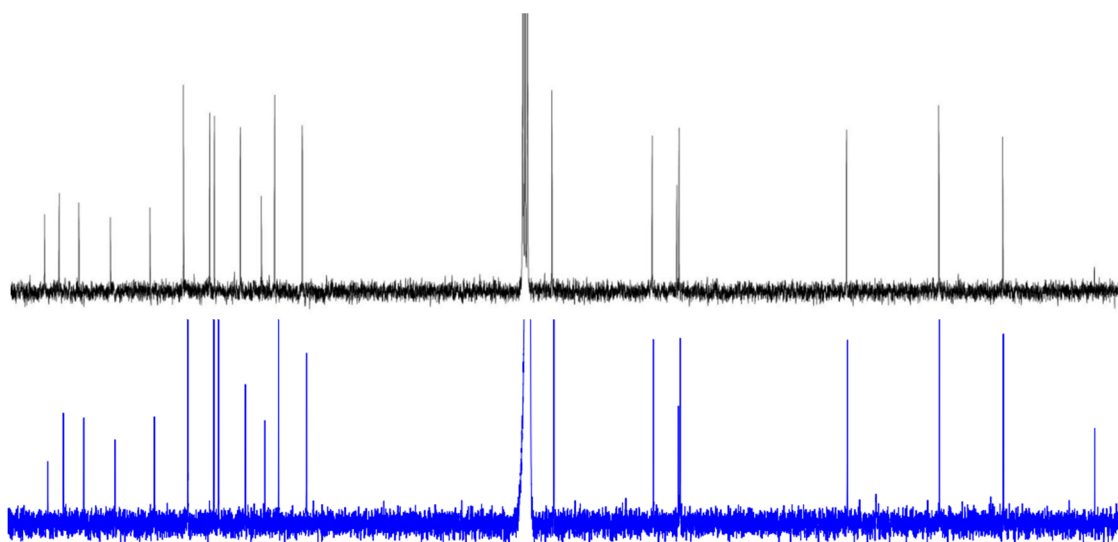
Bottom (blue): synthetic, 400 MHz



Arbophyllidine Comparison Spectra (^{13}C NMR, CDCl_3)

Top (black): natural, 100 MHz 3

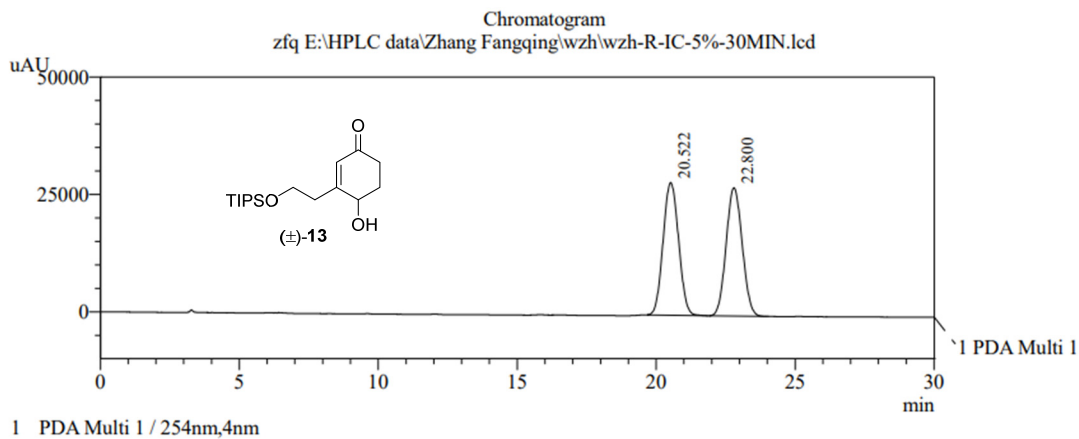
Bottom (blue): synthetic, 100 MHz



IV. HPLC Data of (±)-13 and (-)-13

Racemic compound **13**:

HPLC (DAICEL Chiralpak-IC column (0.46 cm × 25 cm); hexane/ⁱPrOH = 70:30; flow rate: 1.0 mL/min; λ = 210 nm)



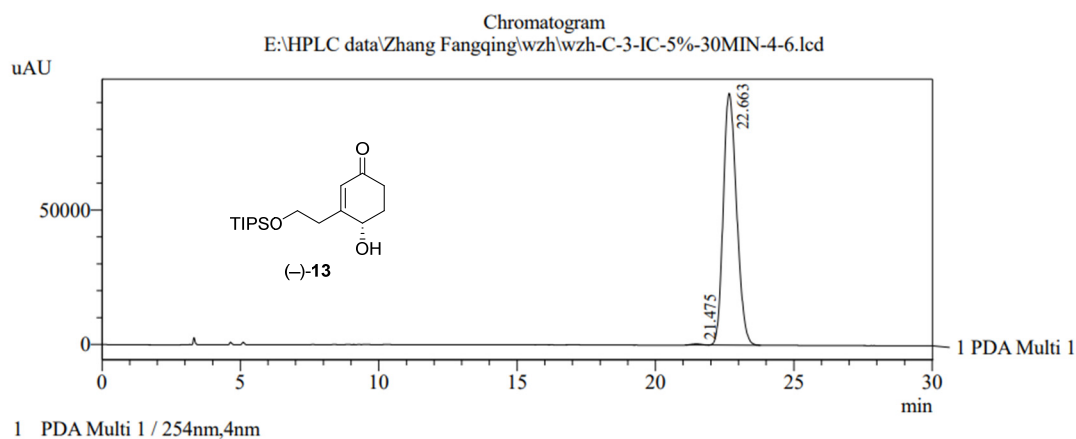
PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.522	1096837	28272	49.907	50.869
2	22.800	1100910	27306	50.093	49.131
Total		2197747	55578	100.000	100.000

Optically active compound (-)-**13**:

HPLC (DAICEL Chiralpak-IC column (0.46 cm × 25 cm); hexane/ⁱPrOH = 70:30; flow rate: 1.0 mL/min; λ = 210 nm)



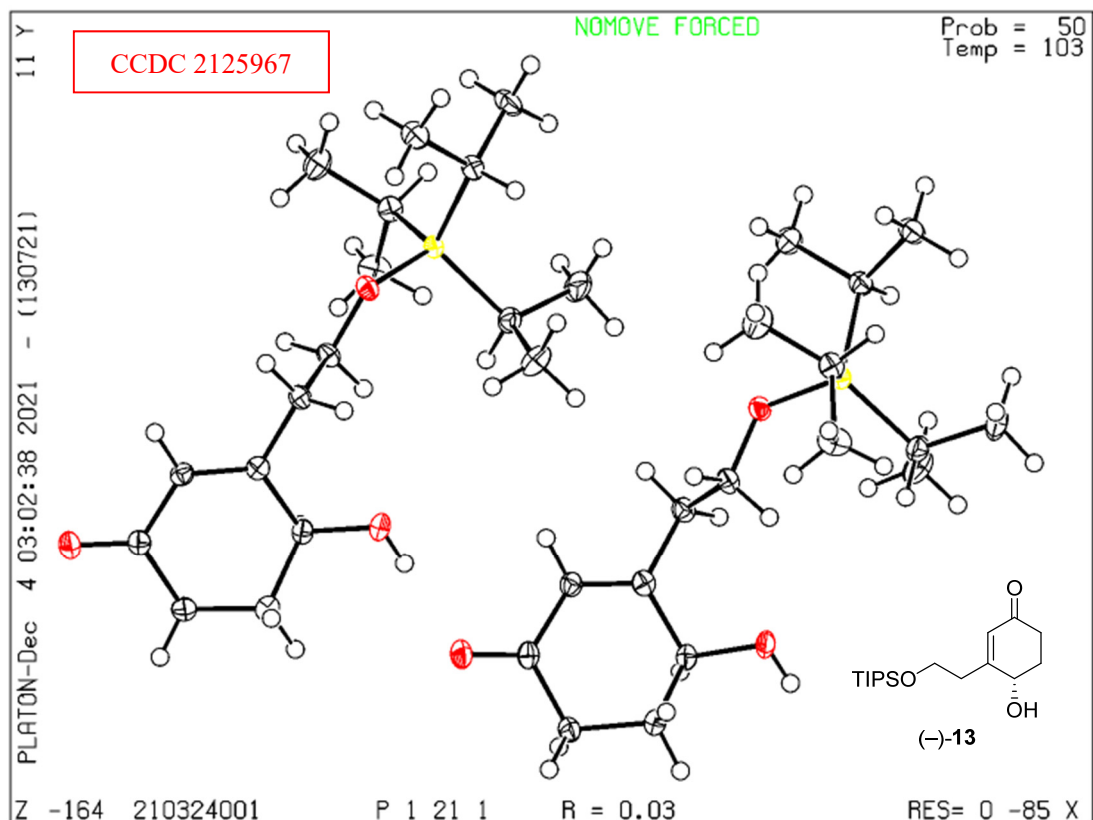
PeakTable

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.475	11565	448	0.367	0.476
2	22.663	3138353	93644	99.633	99.524
Total		3149919	94091	100.000	100.000

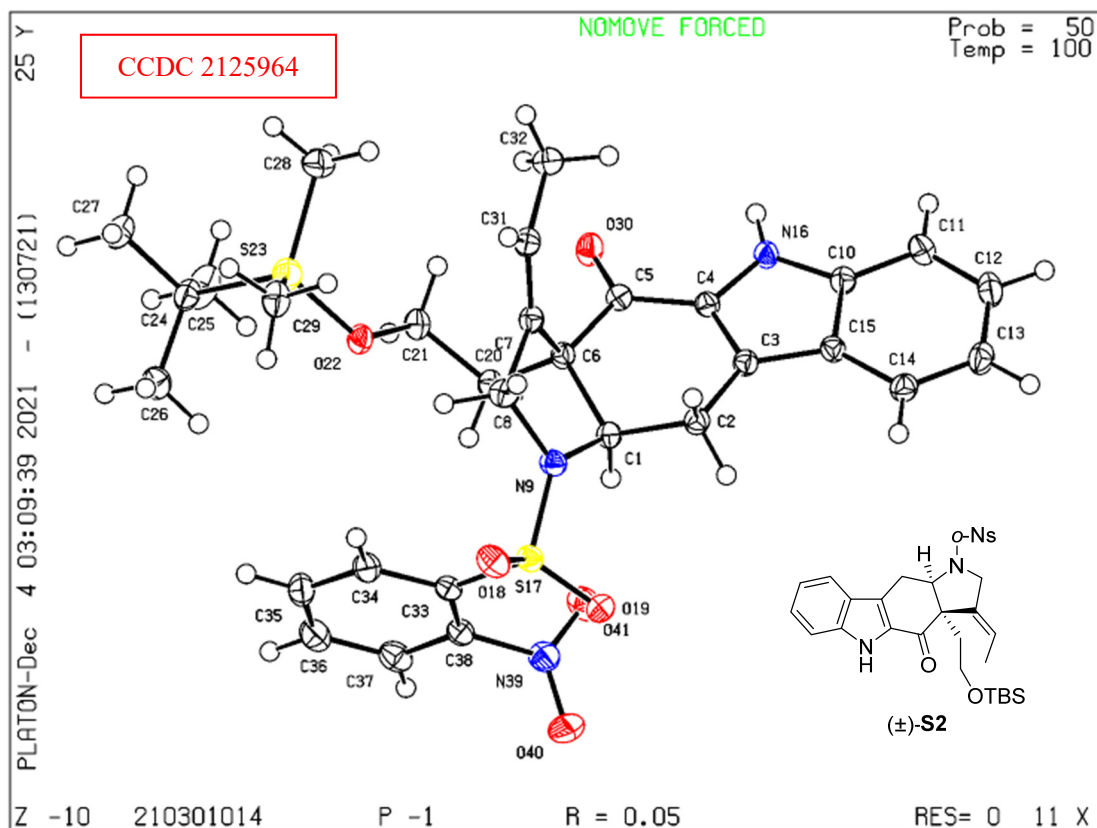
Compound (-)-**13**: $ee = 99.5\% - 0.5\% = 99.0\%$

V. X-Ray Structures of (-)-13 and (±)-S2



Crystal structure determination of (-)-13

Crystal Data for $C_{17}H_{32}O_3Si$ ($M=312.51$ g/mol): monoclinic, space group $P2_1$ (no. 4), $a = 14.5252(2)$ Å, $b = 7.35050(10)$ Å, $c = 17.1483(3)$ Å, $\beta = 97.157(2)^\circ$, $V = 1816.62(5)$ Å³, $Z = 5$, $T = 102(2)$ K, $\mu(\text{CuK}\alpha) = 1.495$ mm⁻¹, $D_{\text{calc}} = 1.428$ g/cm³, 20025 reflections measured ($6.132^\circ \leq 2\theta \leq 155.46^\circ$), 7181 unique ($R_{\text{int}} = 0.0284$, $R_{\text{sigma}} = 0.0202$) which were used in all calculations. The final R_1 was 0.0336 ($I > 2\sigma(I)$) and wR_2 was 0.1000 (all data).



Crystal structure determination of (±)-S2

Crystal Data for $C_{30}H_{37}N_3O_6S_2$ ($M = 599.74$ g/mol): triclinic, space group P-1 (no. 2), $a = 10.3131(7)$ Å, $b = 10.8522(7)$ Å, $c = 14.4337(17)$ Å, $\alpha = 78.839(8)^\circ$, $\beta = 82.179(8)^\circ$, $\gamma = 68.563(7)^\circ$, $V = 1471.4(2)$ Å³, $Z = 2$, $T = 100(2)$ K, $\mu(\text{CuK}\alpha) = 2.039$ mm⁻¹, $D_{\text{calc}} = 1.354$ g/cm³, 18019 reflections measured ($6.258^\circ \leq 2\theta \leq 153.408^\circ$), 5884 unique ($R_{\text{int}} = 0.0359$, $R_{\text{sigma}} = 0.0381$) which were used in all calculations. The final R_1 was 0.0460 ($I > 2\sigma(I)$) and wR_2 was 0.1329 (all data).

VI. DFT Calculations

All calculations are performed under Gaussian16 software.⁴ A popular hybrid functional, B3LYP⁵, is used for all atoms. The def2SVP basis set⁶ is used for the optimization of all structures in the gas phase, and the def2TZVP basis set is used for single-point calculations with Grimme's dispersion correction methods of D3 version⁷ and SMD solvent model⁸ after the optimized structure. The solvent acetone is consistent with the experimental conditions.

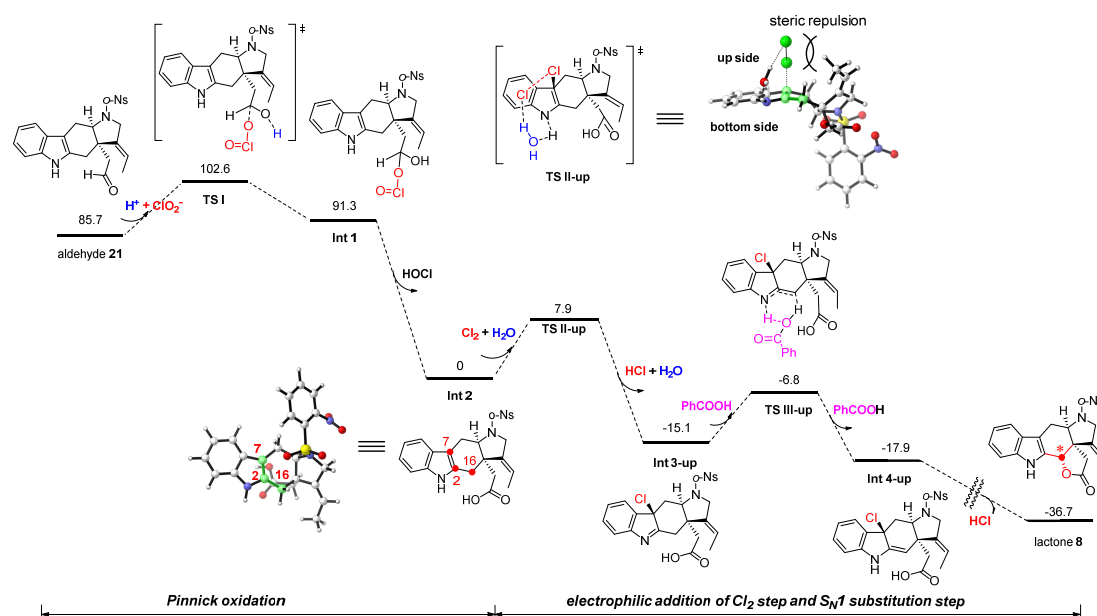


Fig. S1 Schematic diagram of the potential energy surface of the reaction of Cl₂ attacking the indole plane from above to generate lactone **8**.

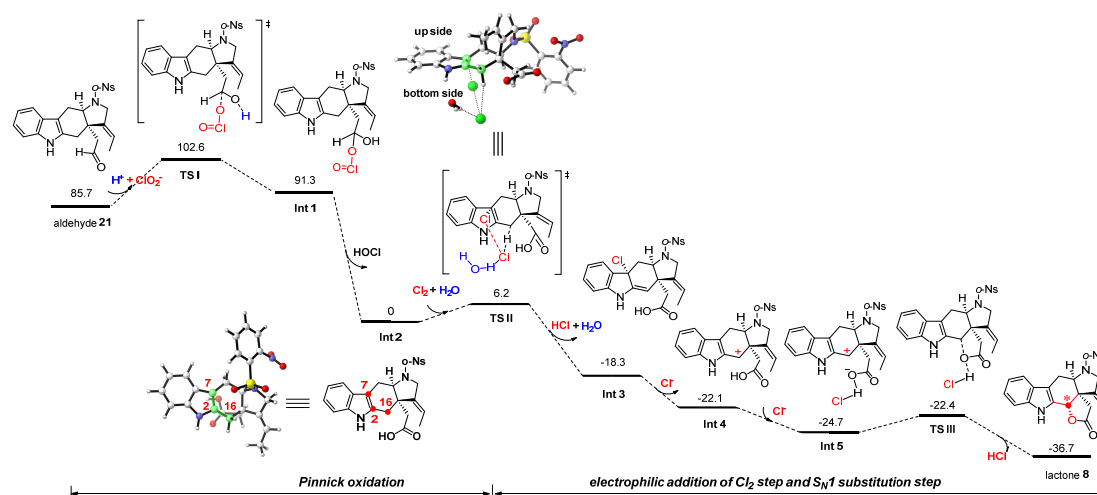


Fig. S2 A detailed schematic diagram of the potential energy surface for the formation of lactone **8** mediated by the byproducts of the Pinnick reaction.

In the process of Cl_2 attacking the indole $\text{C}2=\text{C}7$ double bond, **Int 3-C7** can be formed when the N-H proton was deprotonated. However, **Int 3-C7** is ~ 7 kcal/mol higher in energy than **Int 3**, therefore, this pathway is not favored.

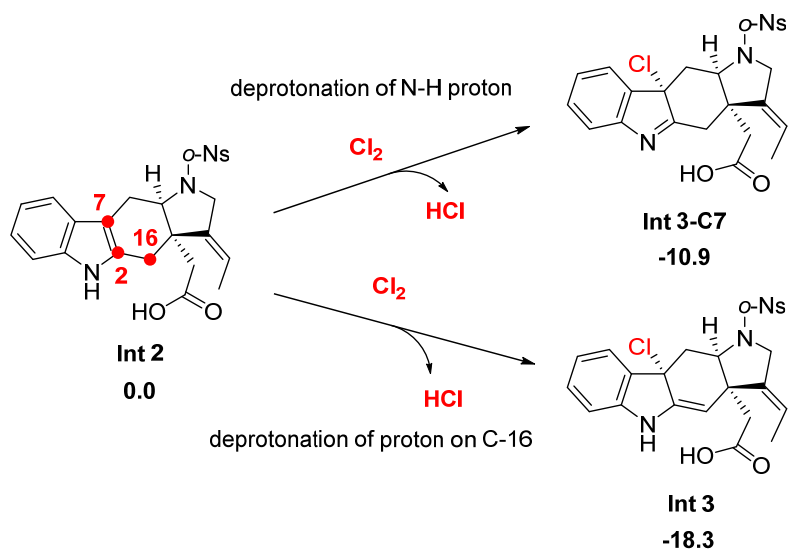


Fig. S3 Comparison of hydrogen deprotonation of N-H proton or the proton on C-16 during Cl_2 attacking the indole $\text{C}2=\text{C}7$ double bond.

References:

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Cartesian Coordinates (fig. S1):

Aldehyde:

C	3.37727500	1.53534100	0.33473800
C	4.46637600	0.81456400	-0.24082100
C	5.74377700	1.37775700	-0.36762300
C	5.92170100	2.68241600	0.08510100
C	4.85532300	3.41503800	0.65149900
C	3.58858700	2.85434100	0.77964900
C	2.23969300	0.65037800	0.31782000
C	2.66346300	-0.52634700	-0.24978600
H	6.57089900	0.81515000	-0.80763400
H	6.90598000	3.14944200	-0.00203800
H	5.03197300	4.43829300	0.99185000
H	2.76897500	3.42989000	1.21737700
N	3.99691500	-0.43037500	-0.60193300
C	-0.15289600	-0.18633400	0.31857700
C	0.39513700	-1.63698000	0.12657400
C	1.83005500	-1.72916400	-0.51344700
C	0.85485400	0.85538000	0.84275300
H	0.85628700	0.79416300	1.94722600
H	0.48938900	1.86247600	0.59854600
C	-0.61258900	-2.22357500	-0.85987900
C	-0.90694400	-1.10490100	-1.83533100
N	-0.75277800	0.10908200	-1.00444400
C	-1.22476300	-3.41399300	-0.94239600
C	0.62207200	-2.35953800	1.45668300
C	1.78108300	-3.30811100	1.19658900
S	-1.60027600	1.48993200	-1.36378300
O	-2.28748000	1.25453300	-2.62843100
O	-0.72110400	2.65246900	-1.21028500
C	-2.84088400	1.72156600	-0.02194100
C	-2.93024800	3.02475100	0.48346800
C	-3.67918400	0.74282200	0.53337000
C	-3.83741500	3.34237800	1.49730300
H	-2.26155700	3.78218000	0.07317900
C	-4.55486900	1.03991200	1.57909400
C	-4.64880800	2.34948500	2.04981400
H	-3.89608000	4.36960200	1.86396200
H	-5.15873100	0.23809000	2.00617500
H	-5.34930100	2.58730600	2.85326700
N	-3.68988100	-0.66177400	0.07365100
O	-3.85975800	-0.86230000	-1.11431700
O	-3.57174900	-1.52013500	0.93380600

H	-0.25222600	-2.88934400	1.85199300
H	0.95655600	-1.65055500	2.23335500
H	-1.96467100	-3.49385100	-1.74909600
C	-1.09710900	-4.66573300	-0.12358600
H	-2.01123200	-4.81597000	0.47818100
H	-1.02328000	-5.53946300	-0.79229100
H	-0.23598600	-4.70062700	0.55290600
O	2.12508400	-4.25985500	1.83563300
H	-0.96325800	-0.26934700	1.06734800
H	-1.90765200	-1.17304500	-2.27572400
H	-0.17659200	-1.07574100	-2.66533000
O	2.42624400	-2.91373800	0.06647500
H	4.55751400	-1.19607400	-0.95210600
H	1.77559800	-1.93653700	-1.59391400

TS I:

C	1.33298600	2.67903300	-0.18032400
C	2.21056900	2.81970300	-1.29737700
C	2.88533400	4.01677300	-1.56499500
C	2.67277900	5.08834500	-0.69903900
C	1.80742300	4.97167800	0.40915800
C	1.13780200	3.77963900	0.67490700
C	0.83188700	1.32865100	-0.22059500
C	1.40081100	0.71846400	-1.31167300
H	3.55629900	4.11043700	-2.42276800
H	3.18644200	6.03546400	-0.88236700
H	1.66380100	5.83189500	1.06789500
H	0.47002800	3.70183000	1.53725400
N	2.22297500	1.61213500	-1.96657100
C	-0.35852900	-0.85025700	0.34311400
C	0.71912000	-1.57732500	-0.54650200
C	1.14002200	-0.68257700	-1.74988500
C	-0.10842300	0.63038600	0.70904900
H	2.02698300	-1.11459300	-2.24008400
H	0.29547000	0.65521000	1.73709200
H	-1.06890600	1.16585600	0.77686800
H	0.32923000	-0.68724900	-2.49821000
H	2.79462800	1.39354400	-2.77106100
C	-0.07213600	-2.79569600	-1.05749900
C	-1.53153400	-2.62430800	-0.66093700
N	-1.65155800	-1.20508100	-0.29128400
C	0.34482400	-3.84071100	-1.78728700
C	1.93256800	-2.02971000	0.32105500
C	2.93624200	-0.97419500	0.68749800

S	-2.60685100	-0.19776200	-1.22594700	H	1.82350200	5.78004200	0.80684200
O	-3.45737600	-1.04523600	-2.05781900	H	0.59545000	3.69442500	1.37712600
O	-1.82445500	0.87916000	-1.84073700	N	2.29087800	1.41888200	-2.03776300
C	-3.64791600	0.62562300	0.01621500	C	-0.36431800	-0.87862600	0.35311700
C	-3.93619500	1.97610400	-0.20690800	C	0.68616200	-1.68555400	-0.50252400
C	-4.15672100	0.00921600	1.16661600	C	1.16137600	-0.84037900	-1.72436300
C	-4.73089000	2.68739900	0.69553400	C	-0.04191400	0.59512500	0.68679200
H	-3.50659900	2.46239600	-1.08422300	H	2.04091800	-1.31421400	-2.18405800
C	-4.91317400	0.72317300	2.09520300	H	0.38425400	0.61614700	1.70663300
C	-5.21702800	2.06304600	1.84709900	H	-0.97738100	1.17150500	0.76954900
H	-4.95413000	3.73924800	0.50399000	H	0.35993100	-0.84293900	-2.48321800
H	-5.25858200	0.22067800	3.00008600	H	2.84267900	1.15682800	-2.84312400
H	-5.82450800	2.62044000	2.56346600	C	-0.16911300	-2.86315500	-1.01073600
N	-3.90244800	-1.41427400	1.47375300	C	-1.62084000	-2.60665500	-0.63657500
O	-4.28909400	-2.23674100	0.66606700	N	-1.66558200	-1.17662200	-0.29400100
O	-3.35812900	-1.65498900	2.53812000	C	0.19967200	-3.93500000	-1.72754100
H	2.49555500	-2.81193500	-0.20173400	C	1.83784700	-2.21438700	0.40021700
H	1.55171400	-2.47058200	1.25457500	C	2.97768800	-1.26626400	0.76235200
H	-0.42656300	-4.57606800	-2.05372600	S	-2.58310600	-0.13770700	-1.22678500
C	1.71162400	-4.16903500	-2.31800600	O	-3.48615300	-0.95635300	-2.03219100
H	2.12088800	-5.07060100	-1.82747200	O	-1.76329400	0.89405600	-1.86825800
H	1.65169900	-4.40647400	-3.39381200	C	-3.56833500	0.74952200	0.01728200
H	2.44366200	-3.36019300	-2.19909300	C	-3.80888000	2.10612000	-0.22460400
O	3.91391500	-0.75960700	-0.10890400	C	-4.08181700	0.17209200	1.18515400
H	-0.39465100	-1.40722400	1.29436400	C	-4.56198800	2.86167200	0.67742800
H	-1.78999800	-3.23115100	0.22649400	H	-3.37488900	2.56084200	-1.11661600
H	-2.23940300	-2.88095000	-1.45661800	C	-4.79711900	0.92863200	2.11267100
H	2.63141400	-0.17366200	1.37232900	C	-5.05397100	2.27484700	1.84627400
Cl	5.33304200	-1.44219400	2.13441100	H	-4.74840700	3.91800900	0.47168600
O	3.74974400	-1.79479400	2.27404700	H	-5.14817900	0.45482600	3.03084600
O	5.45966600	0.07547400	1.50925800	H	-5.62930600	2.86644200	2.56177700
H	4.70780200	-0.16095800	0.48887300	N	-3.87306700	-1.25447000	1.51316800
Int 1:				O	-4.33442900	-2.07658800	0.74576000
C	1.42992700	2.57993700	-0.29683900	O	-3.28823800	-1.49536300	2.55628200
C	2.30285400	2.65583900	-1.42467100	H	2.32187200	-3.07684000	-0.07425400
C	2.99609000	3.82792900	-1.74913500	H	1.39745500	-2.58215200	1.33946700
C	2.80853200	4.94100300	-0.93051100	H	-0.60675700	-4.62896300	-2.00140000
C	1.94893200	4.88861900	0.18687000	C	1.55465700	-4.33851600	-2.23655600
C	1.26025800	3.72123000	0.50923900	H	1.89610800	-5.27216100	-1.75426800
C	0.90505700	1.23835300	-0.27520500	H	1.50229900	-4.55456100	-3.31748700
C	1.45767200	0.56931900	-1.33887600	H	2.33290500	-3.57944000	-2.08762100
H	3.66179700	3.87201500	-2.61504900	O	3.82597100	-1.13095600	-0.32684700
H	3.33653100	5.87007700	-1.15975200	H	-0.44603800	-1.40764100	1.31760000

H	-1.92273300	-3.18239600	0.25817200
H	-2.33254700	-2.83860700	-1.43642100
H	2.62444000	-0.28521800	1.12719300
Cl	4.77565700	-0.80967800	2.64669400
O	3.64883000	-1.92490400	1.86278100
O	5.85260800	-0.27271700	1.66253300
H	4.55109000	-0.53034200	-0.08474100

Int 2:

C	2.50388600	1.96432700	0.09747500
C	3.58109000	1.67108200	-0.79342100
C	4.60946000	2.58833000	-1.04079400
C	4.55423600	3.81823400	-0.38624800
C	3.49720400	4.12977600	0.49491700
C	2.47455100	3.21608900	0.74074200
C	1.65554300	0.80013500	0.11249900
C	2.22370500	-0.12318000	-0.72900700
H	5.42911300	2.35038400	-1.72372000
H	5.34362400	4.55392600	-0.56025900
H	3.48340900	5.10433900	0.98973200
H	1.65945800	3.46996500	1.42416400
N	3.37242100	0.40004400	-1.28758000
C	-0.14992300	-0.89111200	0.71290300
C	0.82501200	-2.00788200	0.17537900
C	1.67421400	-1.47876500	-1.01906400
C	0.41131900	0.53746700	0.89837400
H	2.48475000	-2.19041000	-1.24177300
H	0.62775000	0.66680600	1.97139200
H	-0.37041000	1.27831900	0.66699400
H	1.03416100	-1.43170900	-1.91636900
H	4.01834000	-0.11372700	-1.87124300
C	-0.16729000	-3.07755400	-0.31904800
C	-1.57426000	-2.50605100	-0.23273900
N	-1.37695500	-1.05370900	-0.10739700
C	0.07142500	-4.29991400	-0.81673700
C	1.70993600	-2.57640500	1.32643900
C	2.90560500	-1.73667300	1.72992200
S	-1.85381400	-0.06437500	-1.37227500
O	-2.75386900	-0.83863700	-2.22355700
O	-0.71892600	0.64703900	-1.96905200
C	-2.82355200	1.21905900	-0.52472700
C	-2.68705900	2.52405600	-1.00944200
C	-3.67020900	0.99162000	0.56805000

C	-3.39670300	3.57436400	-0.42201200
H	-1.99729400	2.70265500	-1.83590300
C	-4.34725900	2.04094300	1.18857600
C	-4.22431300	3.33434500	0.67779600
H	-3.28589300	4.58668400	-0.81682200
H	-4.96578800	1.83187800	2.06278000
H	-4.76781500	4.15545800	1.15034400
N	-3.87509000	-0.35641600	1.13921700
O	-4.31099500	-1.21637500	0.39845300
O	-3.62828900	-0.49013900	2.32591200
H	2.12503100	-3.54020000	1.01161000
H	1.07503300	-2.75233800	2.20713600
H	-0.81374700	-4.86990100	-1.13034400
C	1.37083300	-5.02356600	-1.03034700
H	1.44491600	-5.90717700	-0.37104700
H	1.42379300	-5.40775100	-2.06333600
H	2.26134800	-4.40407500	-0.86433500
O	3.99854300	-1.81427400	1.22253800
H	-0.47912900	-1.22947700	1.70932000
H	-2.10512700	-2.85542900	0.67213800
H	-2.20212500	-2.74201600	-1.09871000
O	2.63725000	-0.90201500	2.75483100
H	3.44055500	-0.37278000	2.90503100

TS II-up:

C	-2.86375500	-2.32623000	-0.13787200
C	-3.59043200	-2.01589800	1.03220800
C	-4.48879000	-2.90112300	1.61240800
C	-4.63846000	-4.15217800	0.99634500
C	-3.90835400	-4.48645800	-0.15279200
C	-3.01828100	-3.57415200	-0.73685100
C	-2.10806200	-1.10640700	-0.51054300
C	-2.31063900	-0.21367300	0.65004500
H	-5.05099700	-2.63715800	2.51011900
H	-5.33393900	-4.87831000	1.42329200
H	-4.04210600	-5.47153500	-0.60554500
H	-2.47063600	-3.83316200	-1.64575200
N	-3.20515600	-0.72423700	1.47020900
C	0.28086800	-0.31591500	-0.28315200
C	-0.16671600	1.08866200	0.27384500
C	-1.64958900	1.10311700	0.77818800
C	-0.75724200	-1.02772000	-1.18775400
H	-1.72169100	1.45360600	1.81391400

H	-0.37513800	-2.02639300	-1.43683700
H	-0.84527900	-0.47065500	-2.12972200
H	-2.26554700	1.80060400	0.19105600
H	-3.80339800	-0.05324700	2.01595300
C	0.14958500	1.98195500	-0.93391400
C	1.33035700	1.36630900	-1.67979300
N	1.47997200	0.04787200	-1.03428000
C	-0.42969300	3.11604600	-1.35571900
C	0.80582500	1.42680000	1.45463000
C	0.74939700	2.86026900	1.94125000
S	2.64950700	-1.04211700	-1.44817500
O	3.48175900	-0.42751200	-2.47669900
O	2.00364500	-2.34487900	-1.65333100
C	3.71042000	-1.31775100	0.01709300
C	3.53581600	-2.53047400	0.69346700
C	4.78860000	-0.49821000	0.39146700
C	4.38930500	-2.89744200	1.73813800
H	2.73905600	-3.19719400	0.36244100
C	5.67010700	-0.87807000	1.40330300
C	5.46054300	-2.07480000	2.09043200
H	4.22695700	-3.84392400	2.25868200
H	6.50959500	-0.22328100	1.64021000
H	6.14274700	-2.36500100	2.89241600
N	5.03797200	0.82145700	-0.22030800
O	4.07502000	1.55889200	-0.34910200
O	6.18822400	1.09905900	-0.49480300
H	1.83897200	1.26094900	1.12457900
H	0.58629200	0.75568000	2.30163700
H	-0.02460100	3.52261200	-2.29187600
C	-1.54182000	3.93084100	-0.75516800
H	-2.53390000	3.63249400	-1.14711300
H	-1.58949400	3.85880100	0.34034700
H	-1.40029000	4.99292300	-1.00886300
O	1.57081200	3.70704800	1.70990000
H	0.54513100	-0.98424300	0.55436800
H	2.25356400	1.94843600	-1.55783000
H	1.12647100	1.27142200	-2.75961000
O	-0.35007000	3.11046800	2.69801300
H	-0.31099600	4.05141700	2.94465300
Cl	-5.02093700	2.37889100	-1.06302900
Cl	-3.45887200	0.05330300	-1.50121400
O	-4.74719300	1.36875000	1.83932600
H	-4.91010600	1.65227600	0.88781000

H	-4.88706000	2.17421300	2.35326200
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Int 3-up:

C	3.82676500	1.44059000	0.18978500
C	4.70420100	0.34028100	0.10775400
C	6.02589300	0.44234500	0.53453200
C	6.45801300	1.67592000	1.04348600
C	5.58823500	2.77097700	1.12057500
C	4.25521200	2.66266300	0.68994600
C	2.50185300	0.95928800	-0.34364200
C	2.86163200	-0.47656000	-0.71571400
H	6.69479400	-0.41793000	0.46775600
H	7.49124100	1.78585300	1.38278400
H	5.95171500	3.72240100	1.51646900
H	3.58232900	3.52261800	0.73667900
N	4.07073100	-0.81096400	-0.43210200
C	0.16767600	-0.00941800	0.29511800
C	0.56056800	-1.44389200	-0.25619100
C	1.78327600	-1.35459600	-1.24209800
C	1.34170500	0.92604800	0.65746600
H	2.17184600	-2.35491700	-1.45233800
H	1.76556200	0.57231500	1.61285300
H	0.95542700	1.93808000	0.83515600
H	1.43341800	-0.91299700	-2.18800900
C	-0.68356600	-1.79795500	-1.07660100
C	-1.14953900	-0.50050200	-1.70088500
N	-0.77668300	0.52527800	-0.70962600
C	-1.34595900	-2.94520700	-1.29258100
C	0.87367300	-2.29567200	1.00234500
C	1.34847200	-3.73733300	0.97252000
S	-1.85512700	1.73045100	-0.32703000
O	-2.55726900	2.09681800	-1.55112900
O	-1.12541700	2.70977000	0.48091500
C	-3.11526700	1.06375000	0.82055900
C	-2.81302200	1.11440300	2.18910400
C	-4.39335700	0.62987100	0.43886100
C	-3.74098800	0.69779700	3.14518100
H	-1.85235800	1.52923900	2.49604500
C	-5.34243900	0.25528600	1.39225000
C	-5.00855600	0.26755800	2.74635200
H	-3.48005400	0.73712900	4.20503400
H	-6.33886000	-0.04155200	1.06057600
H	-5.74827600	-0.04100100	3.48826900

N	-4.85536800	0.54193500	-0.96725100
O	-4.32832300	-0.29413500	-1.68032800
O	-5.79178500	1.25064700	-1.27279100
H	-0.00144800	-2.30413400	1.66616200
H	1.67423600	-1.77571300	1.56019400
H	-2.24277700	-2.84265900	-1.91529600
C	-1.04705700	-4.35171500	-0.84320000
H	-1.72086400	-5.06043500	-1.34561800
H	-0.01725500	-4.65378700	-1.08411500
H	-1.18530100	-4.49063600	0.24087800
O	1.02400800	-4.54862400	1.80341400
H	-0.38396700	-0.18324900	1.23707300
H	-2.22495700	-0.49380300	-1.90697200
H	-0.62892200	-0.28535700	-2.65157400
O	2.23055400	-4.02948900	-0.00331900
H	2.50525500	-4.95314700	0.13563000
Cl	2.03834100	1.88466300	-1.85682000

TS III-up:

C	2.62068400	2.48162800	1.39266000
C	3.68268700	2.16763800	0.53424200
C	5.01408600	2.30435300	0.90601100
C	5.26534400	2.78020800	2.20118900
C	4.21629700	3.10655300	3.06924300
C	2.87846900	2.96218100	2.67006800
C	1.32899500	2.20094600	0.65803400
C	1.81828300	1.69166600	-0.68061600
H	5.82898500	2.04826800	0.22619100
H	6.29883400	2.89829400	2.53473800
H	4.44216700	3.47802100	4.07117300
H	2.06138600	3.22437200	3.34560100
N	3.14465300	1.70576400	-0.69403200
C	-0.65432800	0.53085100	0.28308600
C	-0.46282200	0.76111100	-1.26943600
C	1.02173200	0.95368400	-1.60931700
C	0.43691600	1.10031900	1.23434200
H	1.67010900	-0.06866500	-1.57232000
H	1.11232100	0.26242100	1.47015900
H	-0.03105000	1.43715700	2.16886200
H	1.23419400	1.17976100	-2.66066000
C	-1.40225700	1.94289200	-1.57476000
C	-2.44665900	2.04454900	-0.47337300
N	-2.00159500	1.05529400	0.51214400

C	-1.42439300	2.79966400	-2.60601000
C	-1.01630800	-0.53421000	-1.95325600
C	-1.12263400	-0.53383100	-3.46181900
S	-2.93514700	0.55729800	1.77675100
O	-4.18885500	1.30350800	1.71960700
O	-2.09876300	0.56110200	2.98337200
C	-3.32836300	-1.21361600	1.53706700
C	-2.59535900	-2.12672500	2.30320200
C	-4.40572300	-1.69788700	0.77640200
C	-2.90831400	-3.48897000	2.28562500
H	-1.79263700	-1.74662200	2.93536500
C	-4.75368600	-3.04841000	0.79131800
C	-3.99205600	-3.94995900	1.53656100
H	-2.31126100	-4.18532200	2.87841200
H	-5.61558300	-3.37491200	0.20810200
H	-4.25294000	-5.01050000	1.53327100
N	-5.20404800	-0.83670300	-0.11633200
O	-4.58695100	-0.09436100	-0.86247900
O	-6.41123000	-0.97287300	-0.08989100
H	-2.03452900	-0.71310100	-1.58393700
H	-0.36962800	-1.37469300	-1.65179300
H	-2.21444100	3.56144000	-2.55924800
C	-0.54357800	2.92318300	-3.81636000
H	0.13855300	3.78772900	-3.71748900
H	0.06014500	2.03241300	-4.02362200
H	-1.15966600	3.11612300	-4.71008800
O	-2.14519000	-0.62713000	-4.09040300
H	-0.64129300	-0.55234200	0.46573600
H	-3.45594400	1.80155800	-0.83197000
H	-2.46860700	3.05841800	-0.03989100
O	0.08633500	-0.45592900	-4.07563900
H	-0.08823400	-0.49969900	-5.03189800
Cl	0.43650100	3.78630000	0.42220100
C	4.35713300	-4.82201000	0.97677700
C	3.45079800	-3.78422400	0.75002900
C	3.61996600	-2.92030800	-0.34190700
C	4.70660500	-3.11220300	-1.20804500
C	5.61260600	-4.15181700	-0.98380600
C	5.44025100	-5.00752600	0.10986800
H	4.22040600	-5.49118800	1.83080400
H	2.59454100	-3.61877500	1.40676300
H	4.81991900	-2.43575500	-2.05711200
H	6.45580000	-4.29859900	-1.66451200

H	6.14944500	-5.82112900	0.28566000
C	2.62593200	-1.79786300	-0.56851600
O	1.63973400	-1.69934600	0.18314400
O	2.88271200	-1.00608200	-1.54697700
H	3.65361500	1.10867700	-1.35108100

Int 4-up:

C	3.95204600	1.21900500	0.12679400
C	4.79715200	0.30800200	0.79287600
C	6.08688700	0.67349000	1.18291000
C	6.51331400	1.97673500	0.89305400
C	5.68180400	2.88732800	0.22954600
C	4.39091900	2.50474500	-0.16504000
C	2.65727200	0.51282900	-0.19282100
C	2.80625600	-0.79548300	0.55768300
H	6.74400500	-0.02995500	1.69961200
H	7.51847500	2.28465300	1.19283600
H	6.04102900	3.89594200	0.01426600
H	3.74324700	3.20373700	-0.70002700
N	4.13482800	-0.90557900	0.95972900
C	0.10339400	0.26733300	0.28328900
C	0.37136000	-1.29162500	0.34361400
C	1.76523400	-1.59112400	0.85588300
C	1.35157400	1.19390400	0.20391900
H	1.52386500	1.61225100	1.20821700
H	1.12631700	2.03968000	-0.45750300
C	0.08832100	-1.75350400	-1.10374300
C	-0.73599500	-0.69982100	-1.82205100
N	-0.83326000	0.38364900	-0.83676200
C	0.45352700	-2.88360700	-1.72183400
C	-0.72568100	-1.88337500	1.29583100
C	-0.78958000	-3.39262400	1.38122900
S	-1.86260500	1.65713800	-1.00407100
O	-2.59237100	1.47433800	-2.25541400
O	-1.11995500	2.89099800	-0.72024000
C	-3.09396700	1.59024700	0.35326000
C	-2.92852000	2.51247800	1.39300900
C	-4.26945800	0.82140500	0.33113700
C	-3.89086100	2.63967400	2.39902400
H	-2.04656000	3.15353100	1.37739200
C	-5.25564800	0.97462000	1.30572600
C	-5.05851900	1.87600800	2.35295500
H	-3.73434600	3.35880600	3.20624300

H	-6.16544300	0.37770900	1.23034600
H	-5.82393300	1.98524200	3.12438500
N	-4.52401300	-0.21824700	-0.68431900
O	-3.61847500	-1.00535100	-0.90550000
O	-5.63348200	-0.25454500	-1.17834500
H	-1.70918900	-1.55504700	0.93378300
H	-0.55602900	-1.48830500	2.31026900
H	0.12314200	-2.98164500	-2.76471100
C	1.25450000	-4.04842200	-1.22296400
H	0.68889300	-4.98554800	-1.36198600
H	2.18757800	-4.15161800	-1.80524400
H	1.52863500	-3.97238400	-0.16442900
O	-1.58050100	-4.09817600	0.81127700
H	-0.42803900	0.55280400	1.20437600
H	-1.73719100	-1.06123100	-2.09195400
H	-0.22666900	-0.35590600	-2.73706000
O	0.15892000	-3.90501200	2.20907400
H	0.04129500	-4.87102300	2.19418200
Cl	2.65176000	0.19097800	-2.03941600
H	4.46607400	-1.64485000	1.56467200
H	1.90865300	-2.47374300	1.48048000

Lactone:

C	3.37727500	1.53534100	0.33473800
C	4.46637600	0.81456400	-0.24082100
C	5.74377700	1.37775700	-0.36762300
C	5.92170100	2.68241600	0.08510100
C	4.85532300	3.41503800	0.65149900
C	3.58858700	2.85434100	0.77964900
C	2.23969300	0.65037800	0.31782000
C	2.66346300	-0.52634700	-0.24978600
H	6.57089900	0.81515000	-0.80763400
H	6.90598000	3.14944200	-0.00203800
H	5.03197300	4.43829300	0.99185000
H	2.76897500	3.42989000	1.21737700
N	3.99691500	-0.43037500	-0.60193300
C	-0.15289600	-0.18633400	0.31857700
C	0.39513700	-1.63698000	0.12657400
C	1.83005500	-1.72916400	-0.51344700
C	0.85485400	0.85538000	0.84275300
H	0.85628700	0.79416300	1.94722600
H	0.48938900	1.86247600	0.59854600
C	-0.61258900	-2.22357500	-0.85987900

C	-0.90694400	-1.10490100	-1.83533100
N	-0.75277800	0.10908200	-1.00444400
C	-1.22476300	-3.41399300	-0.94239600
C	0.62207200	-2.35953800	1.45668300
C	1.78108300	-3.30811100	1.19658900
S	-1.60027600	1.48993200	-1.36378300
O	-2.28748000	1.25453300	-2.62843100
O	-0.72110400	2.65246900	-1.21028500
C	-2.84088400	1.72156600	-0.02194100
C	-2.93024800	3.02475100	0.48346800
C	-3.67918400	0.74282200	0.53337000
C	-3.83741500	3.34237800	1.49730300
H	-2.26155700	3.78218000	0.07317900
C	-4.55486900	1.03991200	1.57909400
C	-4.64880800	2.34948500	2.04981400
H	-3.89608000	4.36960200	1.86396200
H	-5.15873100	0.23809000	2.00617500
H	-5.34930100	2.58730600	2.85326700
N	-3.68988100	-0.66177400	0.07365100
O	-3.85975800	-0.86230000	-1.11431700
O	-3.57174900	-1.52013500	0.93380600
H	-0.25222600	-2.88934400	1.85199300
H	0.95655600	-1.65055500	2.23335500
H	-1.96467100	-3.49385100	-1.74909600
C	-1.09710900	-4.66573300	-0.12358600
H	-2.01123200	-4.81597000	0.47818100
H	-1.02328000	-5.53946300	-0.79229100
H	-0.23598600	-4.70062700	0.55290600
O	2.12508400	-4.25985500	1.83563300
H	-0.96325800	-0.26934700	1.06734800
H	-1.90765200	-1.17304500	-2.27572400
H	-0.17659200	-1.07574100	-2.66533000
O	2.42624400	-2.91373800	0.06647500
H	4.55751400	-1.19607400	-0.95210600
H	1.77559800	-1.93653700	-1.59391400

Cartesian Coordinates (fig. S2):

Aldehyde:

C	2.56087400	2.02790500	0.33384300
C	3.67158200	1.74604700	-0.51903100
C	4.70407200	2.67005800	-0.72231200
C	4.61654500	3.89558200	-0.06430500
C	3.52550900	4.19638200	0.77888200
C	2.50061400	3.27592600	0.98265000
C	1.71855700	0.85988700	0.30907700
C	2.32093100	-0.05473500	-0.52242800
H	5.54970800	2.44054200	-1.37568100
H	5.40695600	4.63714300	-0.20529700
H	3.48793800	5.16809900	1.27783400
H	1.66005900	3.52132000	1.63758300
N	3.49053600	0.47619500	-1.02827700
C	-0.11930300	-0.83858200	0.78869600
C	0.92761600	-1.92425600	0.35527700
C	1.75851900	-1.39544300	-0.84980800
C	0.42350300	0.59299800	1.01179400
H	2.54694100	-2.11748100	-1.10752400
H	0.55544100	0.73155600	2.09934300
H	-0.33946400	1.33463700	0.72652100
H	1.09642200	-1.31612000	-1.72834500
H	4.14536500	-0.02039900	-1.61743500
C	0.01643600	-3.05660900	-0.13607100
C	-1.39404100	-2.50281800	-0.30200400
N	-1.24350500	-1.04361400	-0.15323900
C	0.33565400	-4.31902400	-0.45498600
C	1.81286100	-2.29426200	1.60280000
C	3.29165600	-1.97044000	1.50051500
S	-1.72097900	-0.02540000	-1.38405100
O	-2.52948600	-0.81063300	-2.31304900
O	-0.60350700	0.78062200	-1.88594300
C	-2.80518600	1.16093200	-0.53344600
C	-2.74189700	2.49048500	-0.96381900
C	-3.67266500	0.83369000	0.51586700
C	-3.54282400	3.46572200	-0.36452800
H	-2.03812000	2.74821900	-1.75693400
C	-4.44323100	1.80779800	1.14952700
C	-4.39068400	3.12614800	0.69303600
H	-3.48871600	4.49834300	-0.71623800
H	-5.07858100	1.52297500	1.98977400
H	-5.00592500	3.88915700	1.17492900

N	-3.80221100	-0.54877800	1.02334900
O	-4.21213300	-1.39027000	0.24743500
O	-3.52753000	-0.72916800	2.19813200
H	1.73982300	-3.37591900	1.78556600
H	1.40887300	-1.79572800	2.49770000
H	-0.48697300	-4.94934100	-0.81997100
C	1.67250300	-5.00272900	-0.40277300
H	1.64662500	-5.86386100	0.28937100
H	1.91974900	-5.42064200	-1.39444900
H	2.50055500	-4.34754600	-0.10216900
O	4.06112000	-2.58698100	0.79871600
H	-0.53507100	-1.17479300	1.75400400
H	-2.07191600	-2.86752500	0.49141400
H	-1.85401200	-2.74605500	-1.26670600
H	3.66290900	-1.12934400	2.13765500

TS I:

C	1.33298600	2.67903300	-0.18032400
C	2.21056900	2.81970300	-1.29737700
C	2.88533400	4.01677300	-1.56499500
C	2.67277900	5.08834500	-0.69903900
C	1.80742300	4.97167800	0.40915800
C	1.13780200	3.77963900	0.67490700
C	0.83188700	1.32865100	-0.22059500
C	1.40081100	0.71846400	-1.31167300
H	3.55629900	4.11043700	-2.42276800
H	3.18644200	6.03546400	-0.88236700
H	1.66380100	5.83189500	1.06789500
H	0.47002800	3.70183000	1.53725400
N	2.22297500	1.61213500	-1.96657100
C	-0.35852900	-0.85025700	0.34311400
C	0.71912000	-1.57732500	-0.54650200
C	1.14002200	-0.68257700	-1.74988500
C	-0.10842300	0.63038600	0.70904900
H	2.02698300	-1.11459300	-2.24008400
H	0.29547000	0.65521000	1.73709200
H	-1.06890600	1.16585600	0.77686800
H	0.32923000	-0.68724900	-2.49821000
H	2.79462800	1.39354400	-2.77106100
C	-0.07213600	-2.79569600	-1.05749900
C	-1.53153400	-2.62430800	-0.66093700
N	-1.65155800	-1.20508100	-0.29128400
C	0.34482400	-3.84071100	-1.78728700

C	1.93256800	-2.02971000	0.32105500
C	2.93624200	-0.97419500	0.68749800
S	-2.60685100	-0.19776200	-1.22594700
O	-3.45737600	-1.04523600	-2.05781900
O	-1.82445500	0.87916000	-1.84073700
C	-3.64791600	0.62562300	0.01621500
C	-3.93619500	1.97610400	-0.20690800
C	-4.15672100	0.00921600	1.16661600
C	-4.73089000	2.68739900	0.69553400
H	-3.50659900	2.46239600	-1.08422300
C	-4.91317400	0.72317300	2.09520300
C	-5.21702800	2.06304600	1.84709900
H	-4.95413000	3.73924800	0.50399000
H	-5.25858200	0.22067800	3.00008600
H	-5.82450800	2.62044000	2.56346600
N	-3.90244800	-1.41427400	1.47375300
O	-4.28909400	-2.23674100	0.66606700
O	-3.35812900	-1.65498900	2.53812000
H	2.49555500	-2.81193500	-0.20173400
H	1.55171400	-2.47058200	1.25457500
H	-0.42656300	-4.57606800	-2.05372600
C	1.71162400	-4.16903500	-2.31800600
H	2.12088800	-5.07060100	-1.82747200
H	1.65169900	-4.40647400	-3.39381200
H	2.44366200	-3.36019300	-2.19909300
O	3.91391500	-0.75960700	-0.10890400
H	-0.39465100	-1.40722400	1.29436400
H	-1.78999800	-3.23115100	0.22649400
H	-2.23940300	-2.88095000	-1.45661800
H	2.63141400	-0.17366200	1.37232900
Cl	5.33304200	-1.44219400	2.13441100
O	3.74974400	-1.79479400	2.27404700
O	5.45966600	0.07547400	1.50925800
H	4.70780200	-0.16095800	0.48887300

Int 1:

C	1.42992700	2.57993700	-0.29683900
C	2.30285400	2.65583900	-1.42467100
C	2.99609000	3.82792900	-1.74913500
C	2.80853200	4.94100300	-0.93051100
C	1.94893200	4.88861900	0.18687000
C	1.26025800	3.72123000	0.50923900
C	0.90505700	1.23835300	-0.27520500

C	1.45767200	0.56931900	-1.33887600
H	3.66179700	3.87201500	-2.61504900
H	3.33653100	5.87007700	-1.15975200
H	1.82350200	5.78004200	0.80684200
H	0.59545000	3.69442500	1.37712600
N	2.29087800	1.41888200	-2.03776300
C	-0.36431800	-0.87862600	0.35311700
C	0.68616200	-1.68555400	-0.50252400
C	1.16137600	-0.84037900	-1.72436300
C	-0.04191400	0.59512500	0.68679200
H	2.04091800	-1.31421400	-2.18405800
H	0.38425400	0.61614700	1.70663300
H	-0.97738100	1.17150500	0.76954900
H	0.35993100	-0.84293900	-2.48321800
H	2.84267900	1.15682800	-2.84312400
C	-0.16911300	-2.86315500	-1.01073600
C	-1.62084000	-2.60665500	-0.63657500
N	-1.66558200	-1.17662200	-0.29400100
C	0.19967200	-3.93500000	-1.72754100
C	1.83784700	-2.21438700	0.40021700
C	2.97768800	-1.26626400	0.76235200
S	-2.58310600	-0.13770700	-1.22678500
O	-3.48615300	-0.95635300	-2.03219100
O	-1.76329400	0.89405600	-1.86825800
C	-3.56833500	0.74952200	0.01728200
C	-3.80888000	2.10612000	-0.22460400
C	-4.08181700	0.17209200	1.18515400
C	-4.56198800	2.86167200	0.67742800
H	-3.37488900	2.56084200	-1.11661600
C	-4.79711900	0.92863200	2.11267100
C	-5.05397100	2.27484700	1.84627400
H	-4.74840700	3.91800900	0.47168600
H	-5.14817900	0.45482600	3.03084600
H	-5.62930600	2.86644200	2.56177700
N	-3.87306700	-1.25447000	1.51316800
O	-4.33442900	-2.07658800	0.74576000
O	-3.28823800	-1.49536300	2.55628200
H	2.32187200	-3.07684000	-0.07425400
H	1.39745500	-2.58215200	1.33946700
H	-0.60675700	-4.62896300	-2.00140000
C	1.55465700	-4.33851600	-2.23655600
H	1.89610800	-5.27216100	-1.75426800
H	1.50229900	-4.55456100	-3.31748700

H	2.33290500	-3.57944000	-2.08762100
O	3.82597100	-1.13095600	-0.32684700
H	-0.44603800	-1.40764100	1.31760000
H	-1.92273300	-3.18239600	0.25817200
H	-2.33254700	-2.83860700	-1.43642100
H	2.62444000	-0.28521800	1.12719300
Cl	4.77565700	-0.80967800	2.64669400
O	3.64883000	-1.92490400	1.86278100
O	5.85260800	-0.27271700	1.66253300
H	4.55109000	-0.53034200	-0.08474100

Int 2:

C	2.50388600	1.96432700	0.09747500
C	3.58109000	1.67108200	-0.79342100
C	4.60946000	2.58833000	-1.04079400
C	4.55423600	3.81823400	-0.38624800
C	3.49720400	4.12977600	0.49491700
C	2.47455100	3.21608900	0.74074200
C	1.65554300	0.80013500	0.11249900
C	2.22370500	-0.12318000	-0.72900700
H	5.42911300	2.35038400	-1.72372000
H	5.34362400	4.55392600	-0.56025900
H	3.48340900	5.10433900	0.98973200
H	1.65945800	3.46996500	1.42416400
N	3.37242100	0.40004400	-1.28758000
C	-0.14992300	-0.89111200	0.71290300
C	0.82501200	-2.00788200	0.17537900
C	1.67421400	-1.47876500	-1.01906400
C	0.41131900	0.53746700	0.89837400
H	2.48475000	-2.19041000	-1.24177300
H	0.62775000	0.66680600	1.97139200
H	-0.37041000	1.27831900	0.66699400
H	1.03416100	-1.43170900	-1.91636900
H	4.01834000	-0.11372700	-1.87124300
C	-0.16729000	-3.07755400	-0.31904800
C	-1.57426000	-2.50605100	-0.23273900
N	-1.37695500	-1.05370900	-0.10739700
C	0.07142500	-4.29991400	-0.81673700
C	1.70993600	-2.57640500	1.32643900
C	2.90560500	-1.73667300	1.72992200
S	-1.85381400	-0.06437500	-1.37227500
O	-2.75386900	-0.83863700	-2.22355700
O	-0.71892600	0.64703900	-1.96905200

C	-2.82355200	1.21905900	-0.52472700
C	-2.68705900	2.52405600	-1.00944200
C	-3.67020900	0.99162000	0.56805000
C	-3.39670300	3.57436400	-0.42201200
H	-1.99729400	2.70265500	-1.83590300
C	-4.34725900	2.04094300	1.18857600
C	-4.22431300	3.33434500	0.67779600
H	-3.28589300	4.58668400	-0.81682200
H	-4.96578800	1.83187800	2.06278000
H	-4.76781500	4.15545800	1.15034400
N	-3.87509000	-0.35641600	1.13921700
O	-4.31099500	-1.21637500	0.39845300
O	-3.62828900	-0.49013900	2.32591200
H	2.12503100	-3.54020000	1.01161000
H	1.07503300	-2.75233800	2.20713600
H	-0.81374700	-4.86990100	-1.13034400
C	1.37083300	-5.02356600	-1.03034700
H	1.44491600	-5.90717700	-0.37104700
H	1.42379300	-5.40775100	-2.06333600
H	2.26134800	-4.40407500	-0.86433500
O	3.99854300	-1.81427400	1.22253800
H	-0.47912900	-1.22947700	1.70932000
H	-2.10512700	-2.85542900	0.67213800
H	-2.20212500	-2.74201600	-1.09871000
O	2.63725000	-0.90201500	2.75483100
H	3.44055500	-0.37278000	2.90503100

TS II:

C	-3.62547200	-1.59698800	-0.66885100
C	-4.60282900	-0.59085100	-0.49783900
C	-5.96428500	-0.84795100	-0.58584700
C	-6.34684700	-2.16499000	-0.87888700
C	-5.39071900	-3.17192000	-1.07467300
C	-4.02021400	-2.90069300	-0.96590600
C	-2.31887200	-0.96647700	-0.40287300
C	-2.63341100	0.46351700	-0.27043400
H	-6.70488500	-0.05961400	-0.43838100
H	-7.40890900	-2.40741600	-0.95950600
H	-5.72087900	-4.18655300	-1.30866800
H	-3.28222600	-3.69491600	-1.09816800
N	-3.94185800	0.64094100	-0.26734300
C	0.13107900	-0.38935900	-0.41168900
C	-0.17768000	1.15798900	-0.46196100

C	-1.62406500	1.51824900	-0.01906300
C	-0.98012000	-1.30209500	-0.98537600
H	-1.64611500	1.69335500	1.07250300
H	-0.70317800	-2.34979100	-0.80893200
H	-1.03515200	-1.16584600	-2.08056800
H	-1.96135300	2.45930100	-0.46033800
C	0.19990600	1.45928200	-1.92304800
C	1.33783200	0.51780400	-2.31355100
N	1.34546700	-0.46389500	-1.22123300
C	-0.28402300	2.33717100	-2.81697000
C	0.84061000	1.83585600	0.50998400
C	0.97666200	3.34226800	0.43751200
S	2.42436300	-1.70944400	-1.10790500
O	3.33447500	-1.60572400	-2.24414000
O	1.66624900	-2.93805600	-0.84323500
C	3.39650900	-1.45980400	0.41844000
C	3.05223200	-2.25944800	1.51397800
C	4.54110300	-0.65049200	0.51799500
C	3.80800600	-2.22545000	2.68952500
H	2.19701200	-2.92918100	1.42027400
C	5.32544200	-0.64653700	1.67115800
C	4.94837200	-1.42452600	2.76701000
H	3.50988600	-2.84480400	3.53820400
H	6.21987100	-0.02293600	1.69451200
H	5.55205600	-1.40608500	3.67690200
N	4.96342000	0.27170900	-0.55354800
O	4.09530600	0.96014600	-1.06394700
O	6.14994900	0.32134700	-0.81044000
H	1.84814900	1.44358000	0.32707700
H	0.54596600	1.57951600	1.54376000
H	0.17034300	2.27236700	-3.81465300
C	-1.32955300	3.41528500	-2.69148900
H	-2.34059400	3.03680800	-2.92835100
H	-1.35876500	3.87520500	-1.69544200
H	-1.12335000	4.21723400	-3.41691600
O	2.01850800	3.93570700	0.33583000
H	0.33640200	-0.69712200	0.62268100
H	2.30540500	1.03593000	-2.36535000
H	1.15518300	0.04595800	-3.29387000
O	-0.20722100	3.99784000	0.54928800
H	0.00694100	4.94717800	0.53654200
Cl	-2.11718000	0.81135800	3.80335700
Cl	-2.14849400	-0.95031900	1.68448200

O	-4.17833600	2.18164800	1.90165000
H	-3.61708400	1.67099400	2.55354500
H	-4.05319800	3.10043800	2.17360100
H	-4.32348500	1.43624300	0.29470400

Int 3:

C	-3.88729400	-1.19625800	-0.00305300
C	-4.80445600	-0.16944700	0.30941100
C	-6.17892700	-0.36598500	0.16648700
C	-6.61648600	-1.61171600	-0.30406200
C	-5.71317000	-2.63520200	-0.61730300
C	-4.33465300	-2.43112000	-0.45758000
C	-2.51035000	-0.69203100	0.32477400
C	-2.74471700	0.78562400	0.52226800
H	-6.89328600	0.42493200	0.40670900
H	-7.68878600	-1.78369500	-0.42936600
H	-6.08367300	-3.59520200	-0.98305900
H	-3.62416100	-3.23017500	-0.68339300
N	-4.11332000	0.96307000	0.73922000
C	-0.10066900	-0.15454700	-0.11510700
C	-0.34747200	1.39326600	0.02467400
C	-1.79076700	1.71599700	0.36625400
C	-1.33905700	-0.93233300	-0.60733300
H	-1.09397900	-1.99841400	-0.67710600
H	-1.63254600	-0.58427700	-1.61181600
H	-2.05427400	2.76496600	0.49430900
C	0.09181500	1.92026600	-1.36304800
C	0.93081000	0.85607200	-2.06032600
N	1.04297900	-0.20130000	-1.04220000
C	-0.14548000	3.09125000	-1.97185100
C	0.61686500	1.91162200	1.15142700
C	0.67990100	3.41365600	1.31296500
S	1.86100700	-1.61591700	-1.37862200
O	2.52232600	-1.45922500	-2.66732300
O	0.98052200	-2.76788900	-1.14309700
C	3.10848900	-1.75748000	-0.04073700
C	3.15332000	-3.00377000	0.59463500
C	3.99297800	-0.75892700	0.40007800
C	4.06227700	-3.25210800	1.62686900
H	2.44748700	-3.77030900	0.27394000
C	4.87650600	-0.98779400	1.45561900
C	4.92429600	-2.24398200	2.06053800
H	4.08195700	-4.23653300	2.09978600

H	5.51926700	-0.17102500	1.78522500
H	5.62919100	-2.42709800	2.87440800
N	4.04888400	0.58842700	-0.20289700
O	3.98839100	0.66360800	-1.41550600
O	4.18815700	1.52818600	0.56291500
H	1.64126400	1.58783800	0.93039300
H	0.28833400	1.46573100	2.10229300
H	0.29423300	3.19434400	-2.97358300
C	-0.89065300	4.31351400	-1.52212500
H	-1.22629000	4.27954800	-0.47993300
H	-0.24444100	5.20063500	-1.62917800
H	-1.77527400	4.48875200	-2.16043000
O	1.52202900	4.13625600	0.84518900
H	0.19548800	-0.57739900	0.85471200
H	1.92881800	1.22105900	-2.33662400
H	0.43752000	0.49226200	-2.97987400
O	-0.34313900	3.89808200	2.06231600
H	-0.20918300	4.86060200	2.11473100
Cl	-2.06416600	-1.43103800	2.02117500
H	-4.53767500	1.88083200	0.77019000

Int 4:

C	4.02742700	-1.37053500	0.07036700
C	4.96111000	-0.54853800	-0.67206900
C	6.27222700	-0.98619400	-0.92553200
C	6.62690300	-2.23197200	-0.43178600
C	5.72398700	-3.06023800	0.30438000
C	4.43787800	-2.64684700	0.55902500
C	2.82786700	-0.66020100	0.14778500
C	3.02653600	0.58473100	-0.55309200
H	6.98230900	-0.37478200	-1.48502000
H	7.64044100	-2.59953100	-0.61188000
H	6.07186300	-4.03063300	0.66305900
H	3.74053000	-3.27208500	1.12024900
N	4.34149900	0.60996500	-1.02577200
C	0.35683000	-0.21328300	0.07368900
C	0.65238100	1.30538900	-0.20171400
C	2.04775400	1.51716300	-0.71320100
C	1.52750300	-0.93451700	0.80066900
H	1.30835900	-2.00762600	0.88340600
H	1.58260700	-0.54829500	1.83637800
H	2.24041200	2.42738500	-1.28654700

C	0.33248200	1.89220000	1.19665200
C	-0.79254300	1.04445400	1.78528900
N	-0.83849200	-0.12291700	0.88789600
C	0.87963800	2.92229800	1.85505700
C	-0.38604000	1.83736800	-1.24793800
C	-0.46027500	3.34786400	-1.37662700
S	-1.83995400	-1.43212200	1.16132400
O	-2.62466600	-1.11513800	2.34684400
O	-0.98918100	-2.62647300	1.07871000
C	-2.98980800	-1.59604700	-0.24211100
C	-2.78801500	-2.69833200	-1.07967200
C	-4.16411800	-0.83815700	-0.40493900
C	-3.71579900	-3.01513900	-2.07764100
H	-1.91261500	-3.32671100	-0.91405600
C	-5.11122100	-1.17404100	-1.37010500
C	-4.87976200	-2.25903100	-2.21905500
H	-3.53557100	-3.87535400	-2.72593500
H	-6.01964400	-0.57480200	-1.44511100
H	-5.61779600	-2.51505600	-2.98213800
N	-4.44536400	0.37122200	0.39053400
O	-3.51238900	1.14529300	0.55543500
O	-5.58140300	0.53909500	0.77506400
H	-1.38640500	1.50245000	-0.94702100
H	-0.15428200	1.41047000	-2.23840300
H	0.46228700	3.11415100	2.85253900
C	1.95816700	3.87914300	1.45013300
H	2.31479500	3.73946300	0.42133500
H	1.59204400	4.91631500	1.53415300
H	2.82320700	3.80387600	2.13155000
O	-1.40640700	4.02217600	-1.08339300
H	0.14497500	-0.73921500	-0.87176500
H	-1.76061100	1.56424700	1.77681900
H	-0.56917800	0.75994300	2.82711200
O	0.68385800	3.87850900	-1.88839300
H	0.54609400	4.84075100	-1.95906700
H	4.75677900	1.35816200	-1.56897200

Int 5:

C	3.58254000	-1.76078100	0.23085400
C	4.56026900	-0.79668700	-0.23882500
C	5.81991100	-1.21961800	-0.71936200
C	6.08831600	-2.57458600	-0.69714400
C	5.14565000	-3.53599700	-0.21569000

C	3.90754000	-3.14684500	0.24291300
C	2.42646300	-1.03126000	0.54780800
C	2.74273600	0.33668900	0.31423400
H	6.54706500	-0.49585300	-1.09114400
H	7.05657200	-2.92958700	-1.05956600
H	5.42094600	-4.59280100	-0.22053900
H	3.18347600	-3.88011800	0.60525800
N	4.04848900	0.45162300	-0.14718400
C	0.01124400	-0.38912300	0.47419700
C	0.39276900	1.10727700	0.74464900
C	1.83794400	1.36272500	0.42223900
C	1.06098400	-1.40307300	1.00937900
H	0.77632000	-2.41838100	0.70027100
H	1.02925400	-1.39364900	2.11435600
H	2.20244300	2.37840400	0.24243500
C	-0.03906800	1.23242000	2.22275600
C	-1.25490000	0.32775900	2.41138800
N	-1.25879800	-0.48166600	1.18324000
C	0.47436400	1.96047200	3.22290900
C	-0.47712900	2.08363100	-0.10789100
C	0.08012900	2.40780300	-1.49796800
S	-2.39210100	-1.64043200	0.85565200
O	-3.36706500	-1.61151200	1.94139700
O	-1.68184000	-2.87096600	0.48825300
C	-3.25247800	-1.15069400	-0.67796300
C	-2.92177400	-1.86595200	-1.83391000
C	-4.32223400	-0.24103700	-0.74028500
C	-3.61486600	-1.65265100	-3.02925000
H	-2.13027800	-2.61334000	-1.77269100
C	-5.04601500	-0.05607400	-1.91767000
C	-4.68054600	-0.75267300	-3.07092600
H	-3.32915100	-2.21042900	-3.92367700
H	-5.88409400	0.64188400	-1.91503900
H	-5.23562400	-0.59296500	-3.99769700
N	-4.72081900	0.60389600	0.40164000
O	-3.82624000	1.17687400	1.00401300
O	-5.90892300	0.71752500	0.62376400
H	-0.55812600	3.05186900	0.41020000
H	-1.50909800	1.70877600	-0.18396900
H	-0.03059900	1.85653500	4.19299900
C	1.62363900	2.92248500	3.22396600
H	2.09329200	3.05463200	2.24127500
H	1.28920900	3.91644100	3.56761500

H	2.40585500	2.59779900	3.93193900
O	-0.35211200	3.29708000	-2.18075600
H	-0.12769500	-0.54562800	-0.60644900
H	-2.19361700	0.89355300	2.49401600
H	-1.15276900	-0.29360600	3.31714200
O	1.11781700	1.61822100	-1.81702800
H	4.29313600	1.30471400	-0.72535400
H	1.95231800	2.12362700	-2.16589900
Cl	3.70392000	2.88617800	-1.90055100

TS III:

C	-3.59529600	-1.77090600	-0.15262700
C	-4.57806900	-0.79758300	0.27254200
C	-5.85120700	-1.20281400	0.72703300
C	-6.12766600	-2.55796700	0.72653800
C	-5.17816400	-3.52993700	0.29059100
C	-3.92556800	-3.15315200	-0.14492700
C	-2.42569600	-1.04892000	-0.46356800
C	-2.74042400	0.31674700	-0.26955600
H	-6.58524800	-0.46846400	1.06325800
H	-7.10714700	-2.90016400	1.07048500
H	-5.45606000	-4.58596800	0.30956400
H	-3.19602500	-3.89699400	-0.47340500
N	-4.05289500	0.44809800	0.16241100
C	-0.00330700	-0.41000400	-0.42831300
C	-0.39044500	1.07462400	-0.74860300
C	-1.82769600	1.34658000	-0.39559600
C	-1.05891800	-1.44486900	-0.90598700
H	-0.77624600	-2.44296800	-0.54297300
H	-1.02760800	-1.49848800	-2.00956000
H	-2.20192100	2.37066600	-0.32892100
C	0.00913700	1.14423700	-2.23785500
C	1.22627900	0.23800700	-2.41296000
N	1.25540800	-0.52468100	-1.15565900
C	-0.52432900	1.82702600	-3.25944100
C	0.48548200	2.07952300	0.05577500
C	-0.06201300	2.39297800	1.45030100
S	2.39913000	-1.66604300	-0.80617500
O	3.35713000	-1.66923900	-1.90742600
O	1.70232900	-2.88670700	-0.38480800
C	3.28039100	-1.11790400	0.69555800
C	2.97372300	-1.79549400	1.88049500
C	4.34400800	-0.19909500	0.70959800

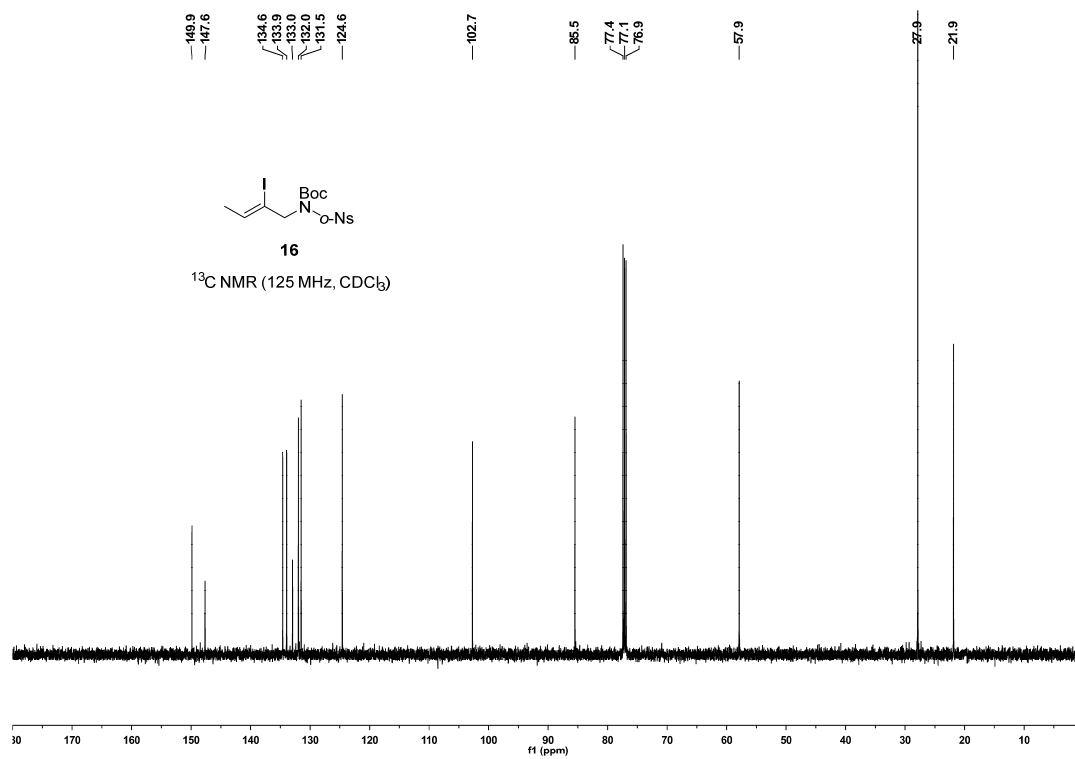
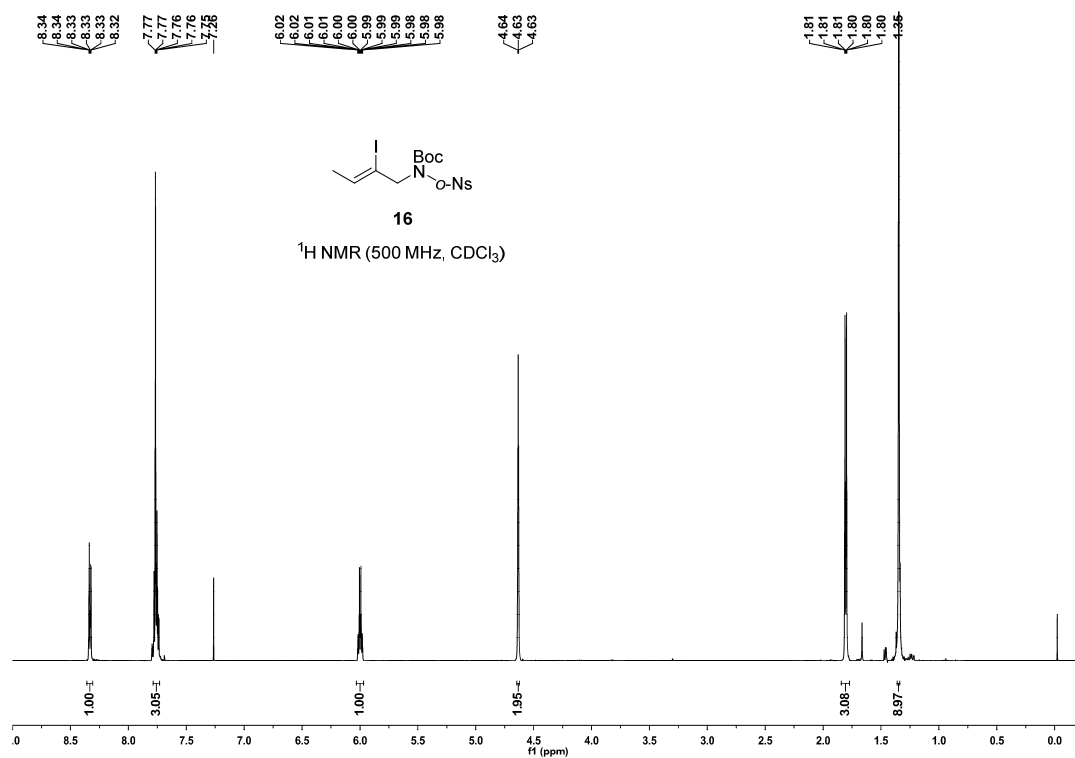
C	3.68393500	-1.53634000	3.05656900
H	2.18731900	-2.55041300	1.85743900
C	5.08485700	0.03137900	1.86820700
C	4.74304400	-0.62772600	3.05035600
H	3.41680300	-2.06522100	3.97400000
H	5.91736600	0.73484500	1.82836000
H	5.31135700	-0.43218300	3.96210800
N	4.71873100	0.60872100	-0.46674100
O	3.81139300	1.15759300	-1.07272300
O	5.90225500	0.71995800	-0.71305800
H	0.51684300	3.04446900	-0.47641900
H	1.53033000	1.74141300	0.11269700
H	-0.03485700	1.68085600	-4.23202700
C	-1.67715800	2.78466000	-3.28871000
H	-2.12799200	2.97072200	-2.30637200
H	-1.35305300	3.75846100	-3.69421600
H	-2.47210300	2.41934000	-3.96187700
O	0.45361300	3.16466900	2.21251700
H	0.15715000	-0.52809300	0.65446500
H	2.16026500	0.80519400	-2.53244800
H	1.11252300	-0.41713500	-3.29307000
O	-1.20786300	1.72743900	1.67760800
H	-4.32783800	1.31615000	0.67896100
H	-2.06894300	2.28992900	1.98996200
Cl	-3.69117500	3.03633900	1.79525400

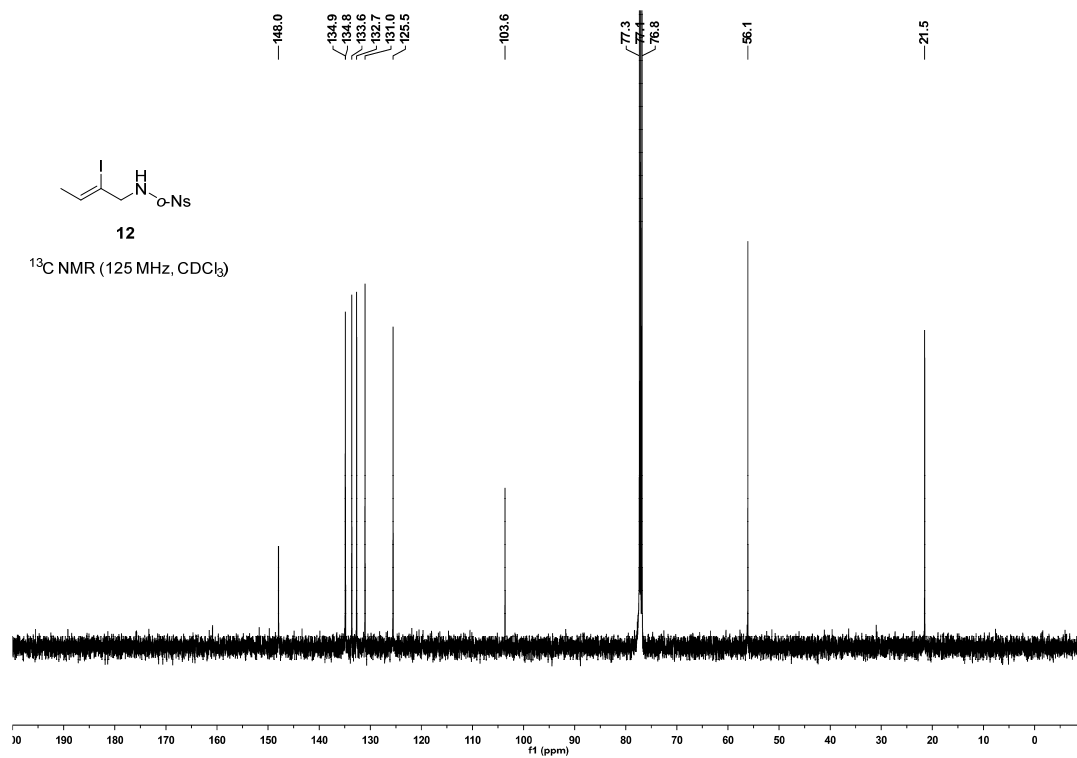
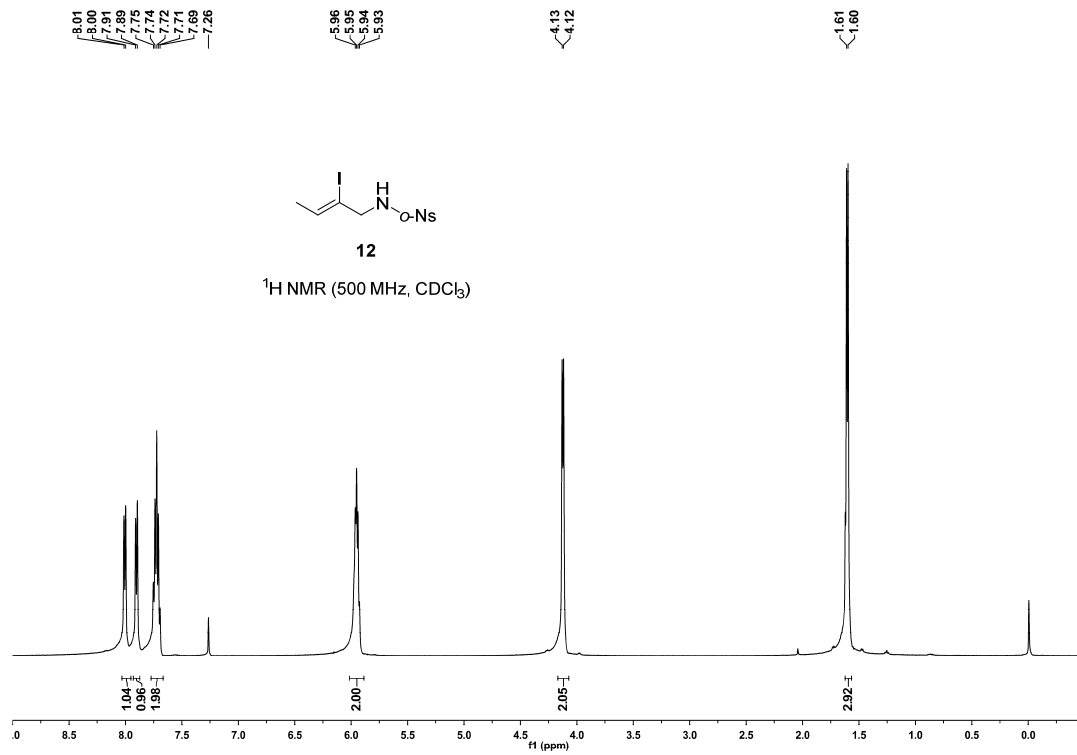
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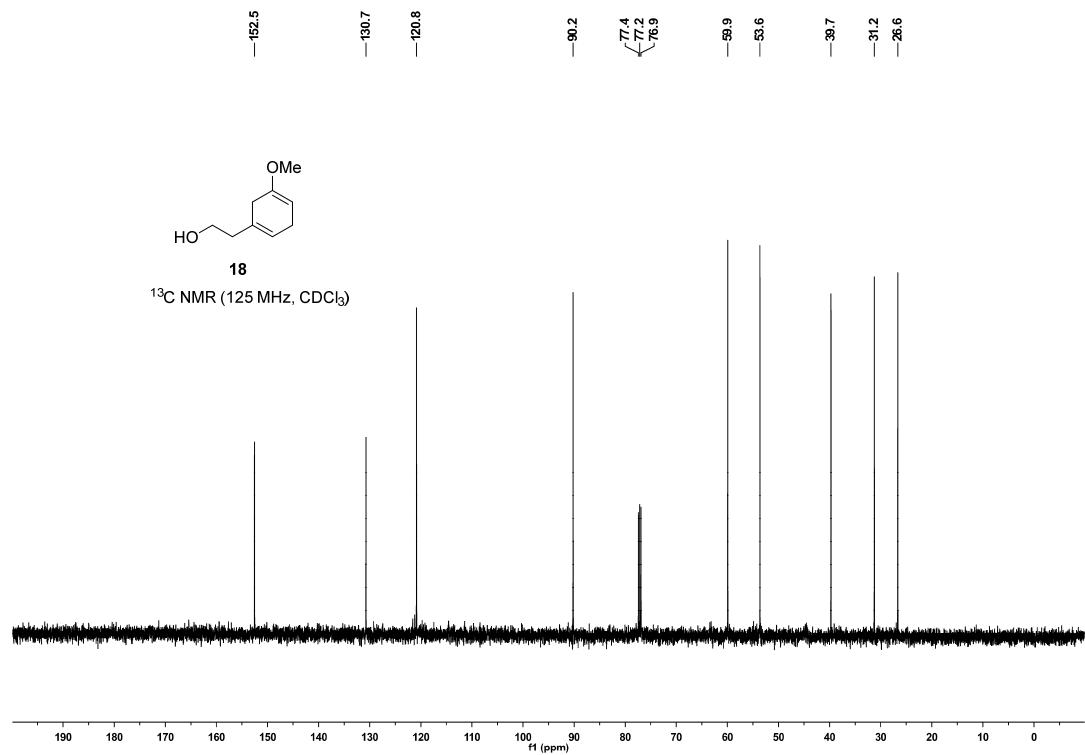
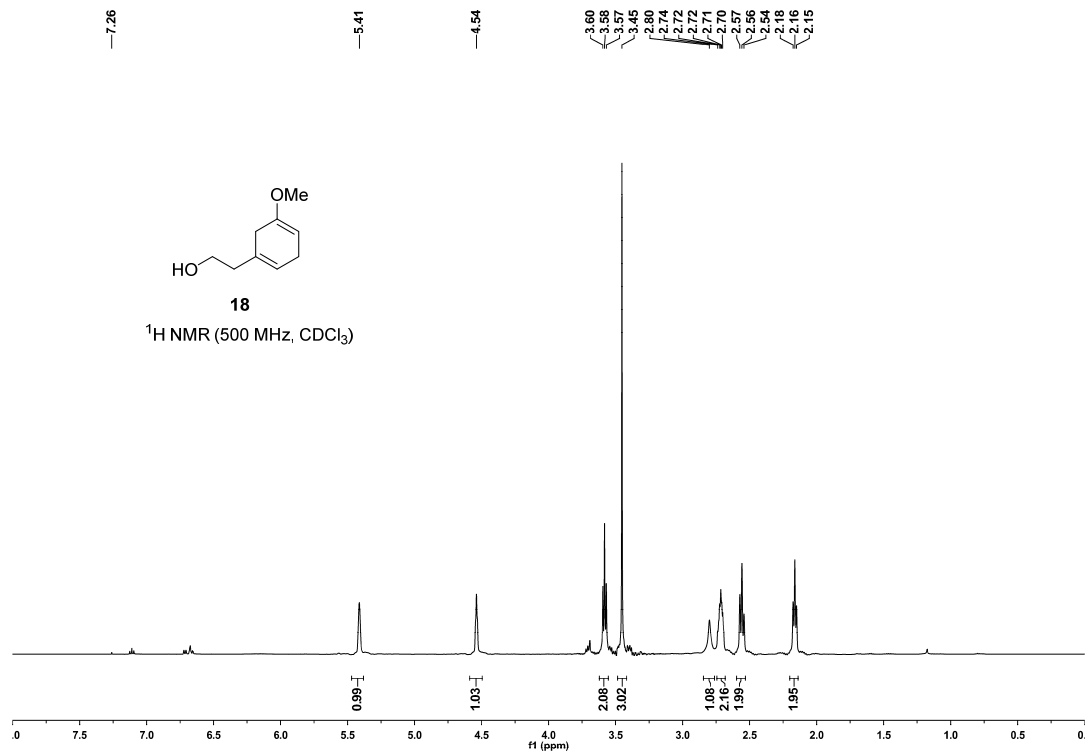
C	3.37727500	1.53534100	0.33473800
C	4.46637600	0.81456400	-0.24082100
C	5.74377700	1.37775700	-0.36762300
C	5.92170100	2.68241600	0.08510100
C	4.85532300	3.41503800	0.65149900
C	3.58858700	2.85434100	0.77964900
C	2.23969300	0.65037800	0.31782000
C	2.66346300	-0.52634700	-0.24978600
H	6.57089900	0.81515000	-0.80763400
H	6.90598000	3.14944200	-0.00203800
H	5.03197300	4.43829300	0.99185000
H	2.76897500	3.42989000	1.21737700
N	3.99691500	-0.43037500	-0.60193300
C	-0.15289600	-0.18633400	0.31857700
C	0.39513700	-1.63698000	0.12657400
C	1.83005500	-1.72916400	-0.51344700

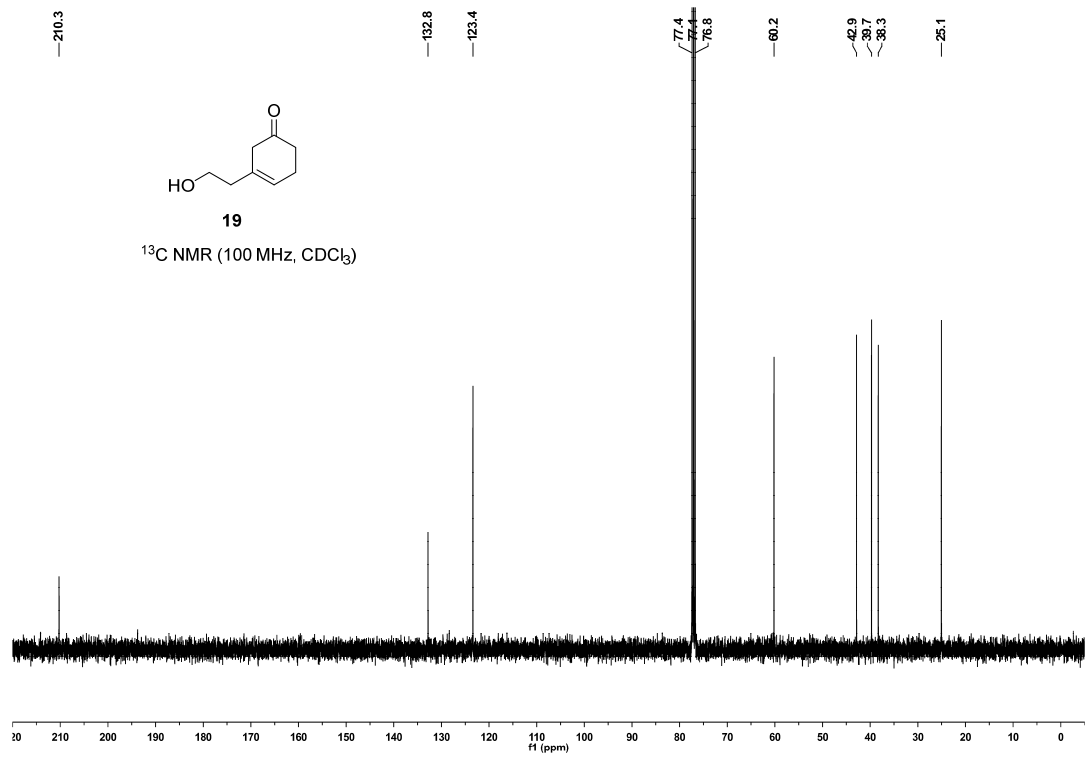
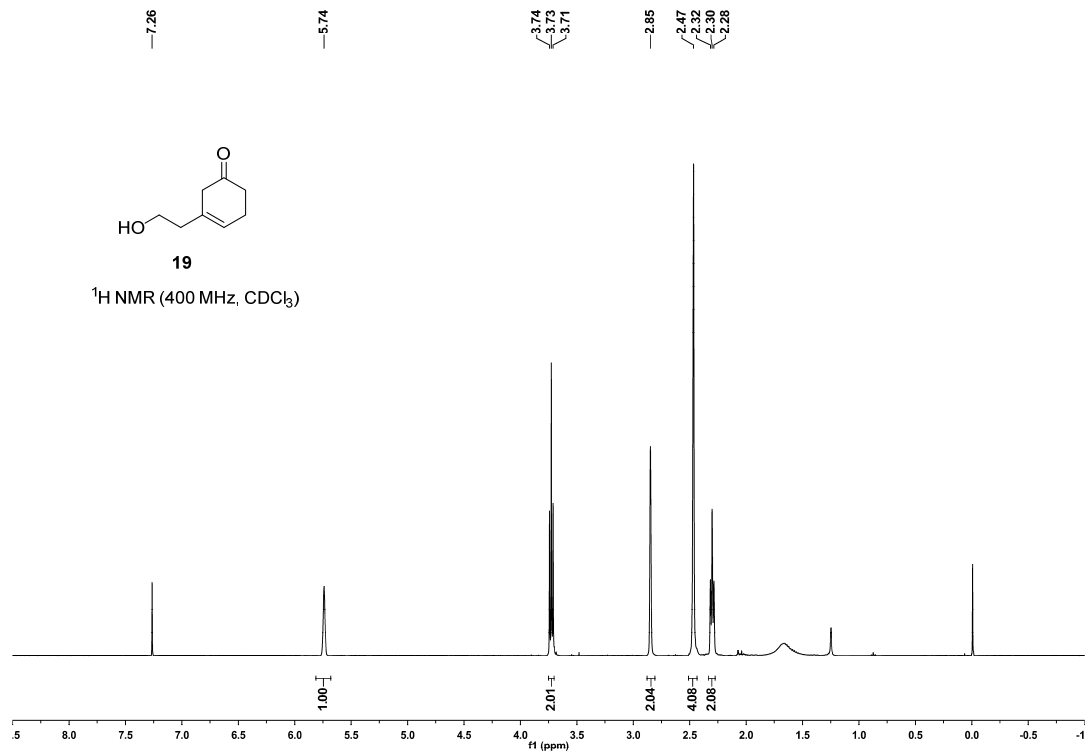
C	0.85485400	0.85538000	0.84275300
H	0.85628700	0.79416300	1.94722600
H	0.48938900	1.86247600	0.59854600
C	-0.61258900	-2.22357500	-0.85987900
C	-0.90694400	-1.10490100	-1.83533100
N	-0.75277800	0.10908200	-1.00444400
C	-1.22476300	-3.41399300	-0.94239600
C	0.62207200	-2.35953800	1.45668300
C	1.78108300	-3.30811100	1.19658900
S	-1.60027600	1.48993200	-1.36378300
O	-2.28748000	1.25453300	-2.62843100
O	-0.72110400	2.65246900	-1.21028500
C	-2.84088400	1.72156600	-0.02194100
C	-2.93024800	3.02475100	0.48346800
C	-3.67918400	0.74282200	0.53337000
C	-3.83741500	3.34237800	1.49730300
H	-2.26155700	3.78218000	0.07317900
C	-4.55486900	1.03991200	1.57909400
C	-4.64880800	2.34948500	2.04981400
H	-3.89608000	4.36960200	1.86396200
H	-5.15873100	0.23809000	2.00617500
H	-5.34930100	2.58730600	2.85326700
N	-3.68988100	-0.66177400	0.07365100
O	-3.85975800	-0.86230000	-1.11431700
O	-3.57174900	-1.52013500	0.93380600
H	-0.25222600	-2.88934400	1.85199300
H	0.95655600	-1.65055500	2.23335500
H	-1.96467100	-3.49385100	-1.74909600
C	-1.09710900	-4.66573300	-0.12358600
H	-2.01123200	-4.81597000	0.47818100
H	-1.02328000	-5.53946300	-0.79229100
H	-0.23598600	-4.70062700	0.55290600
O	2.12508400	-4.25985500	1.83563300
H	-0.96325800	-0.26934700	1.06734800
H	-1.90765200	-1.17304500	-2.27572400
H	-0.17659200	-1.07574100	-2.66533000
O	2.42624400	-2.91373800	0.06647500
H	4.55751400	-1.19607400	-0.95210600
H	1.77559800	-1.93653700	-1.59391400

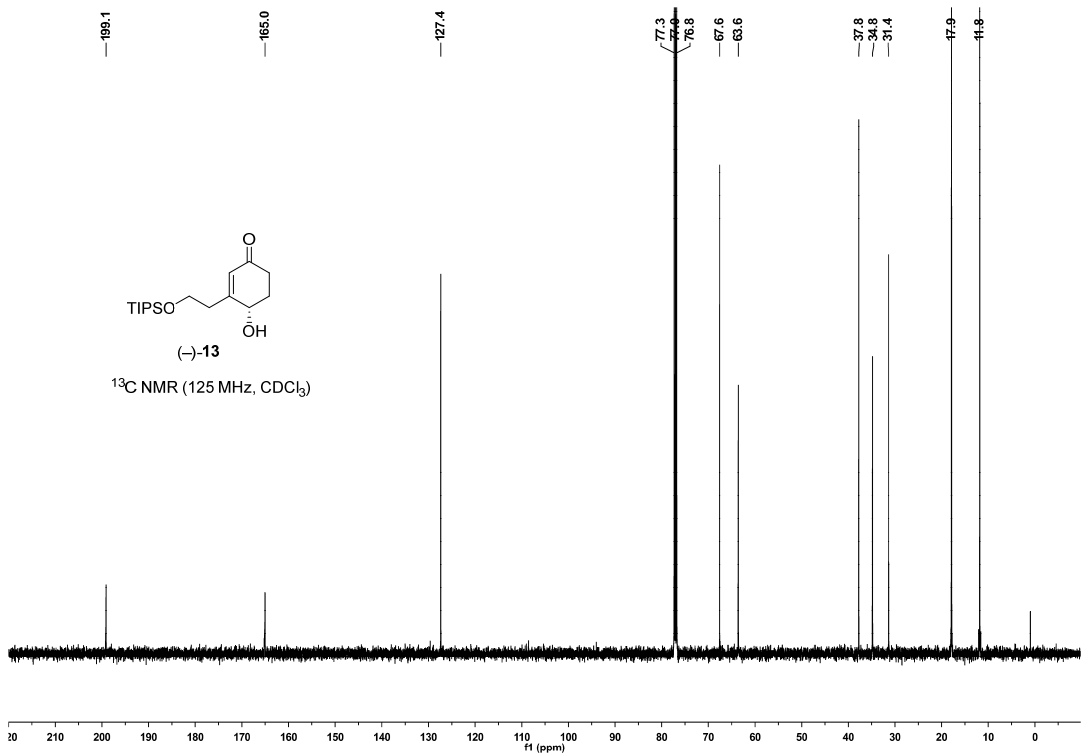
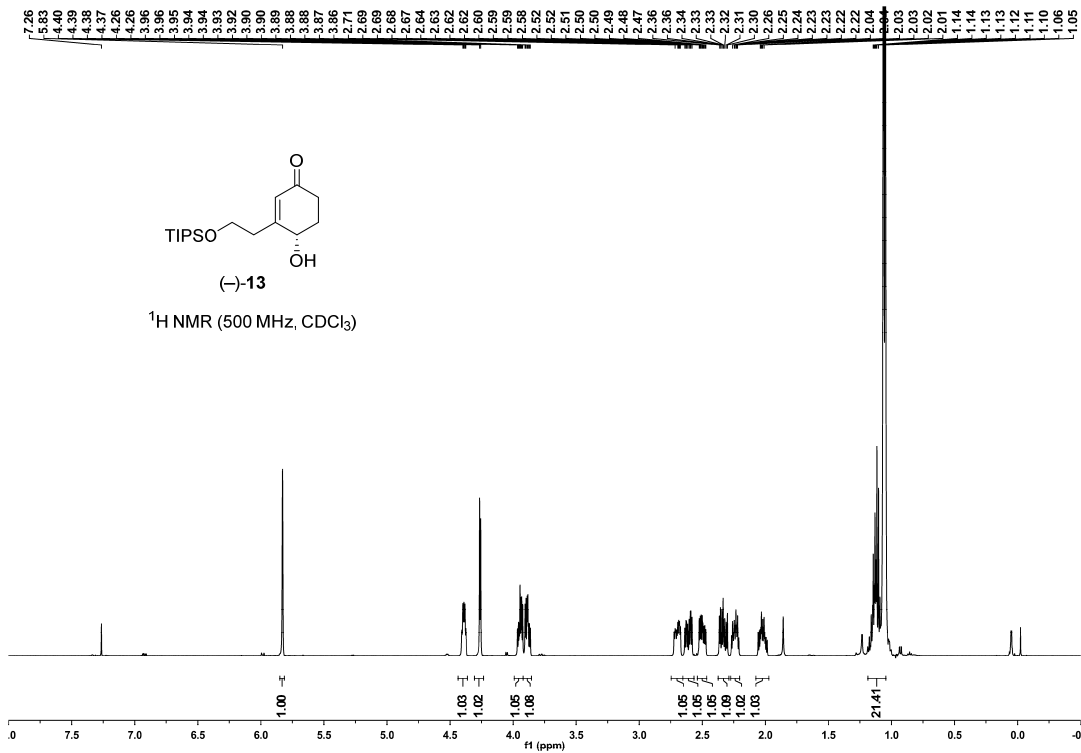
VII. ^1H and ^{13}C NMR Spectra of Compounds

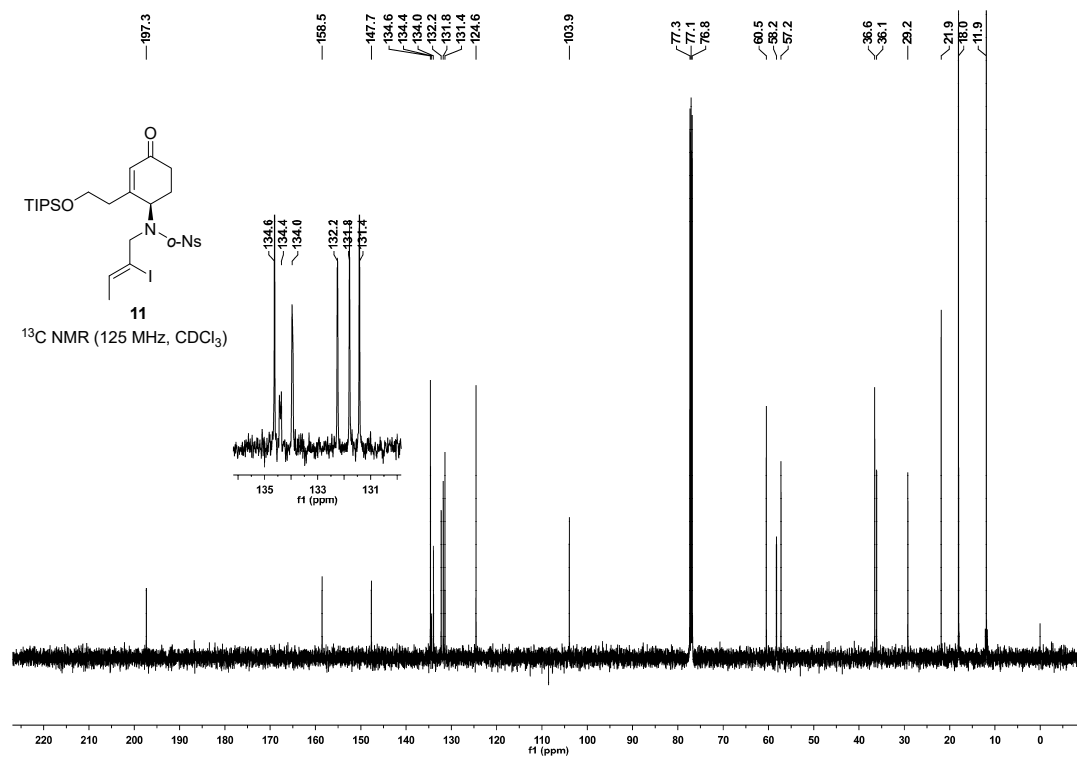
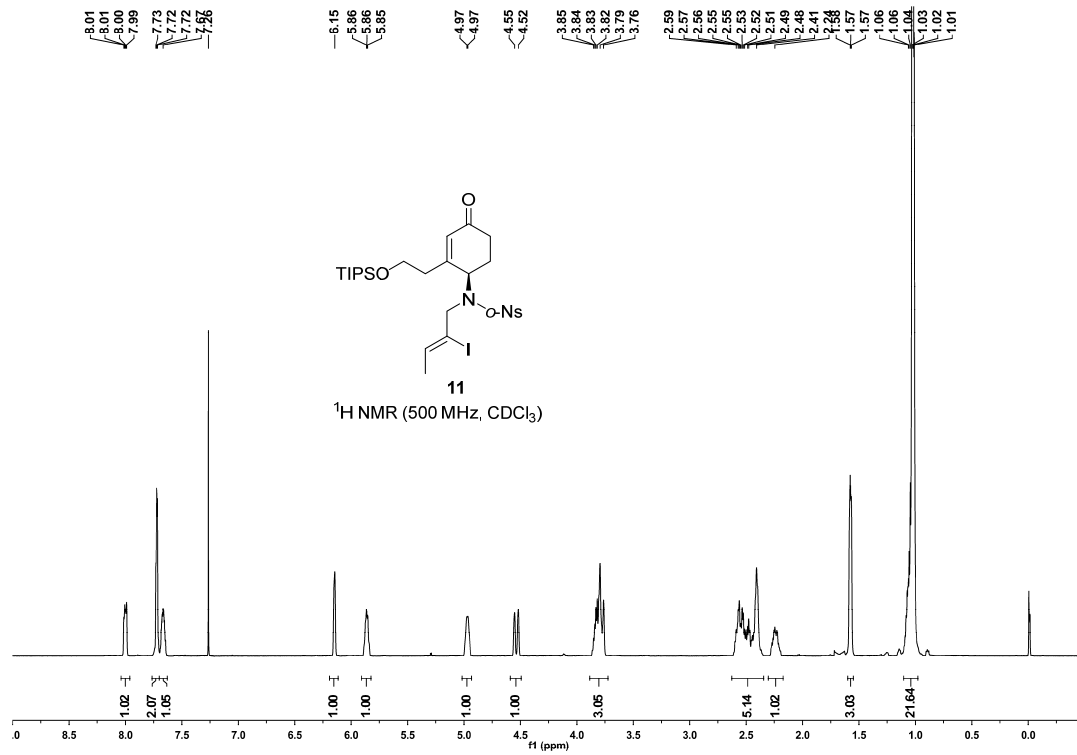


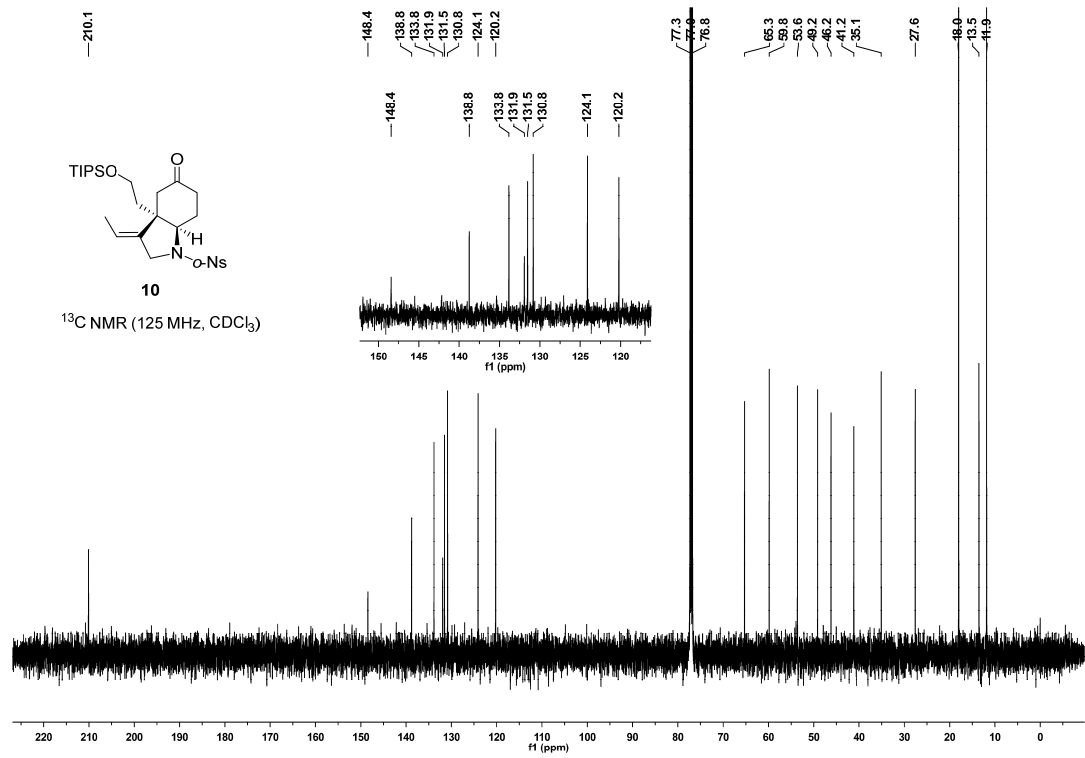
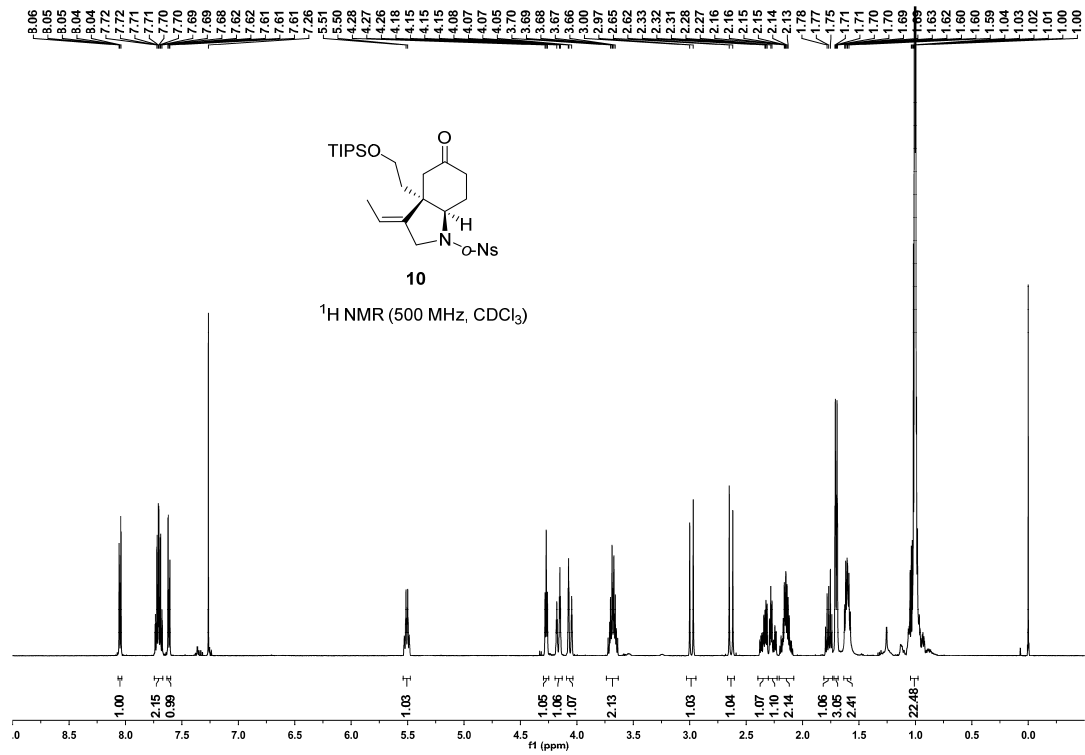


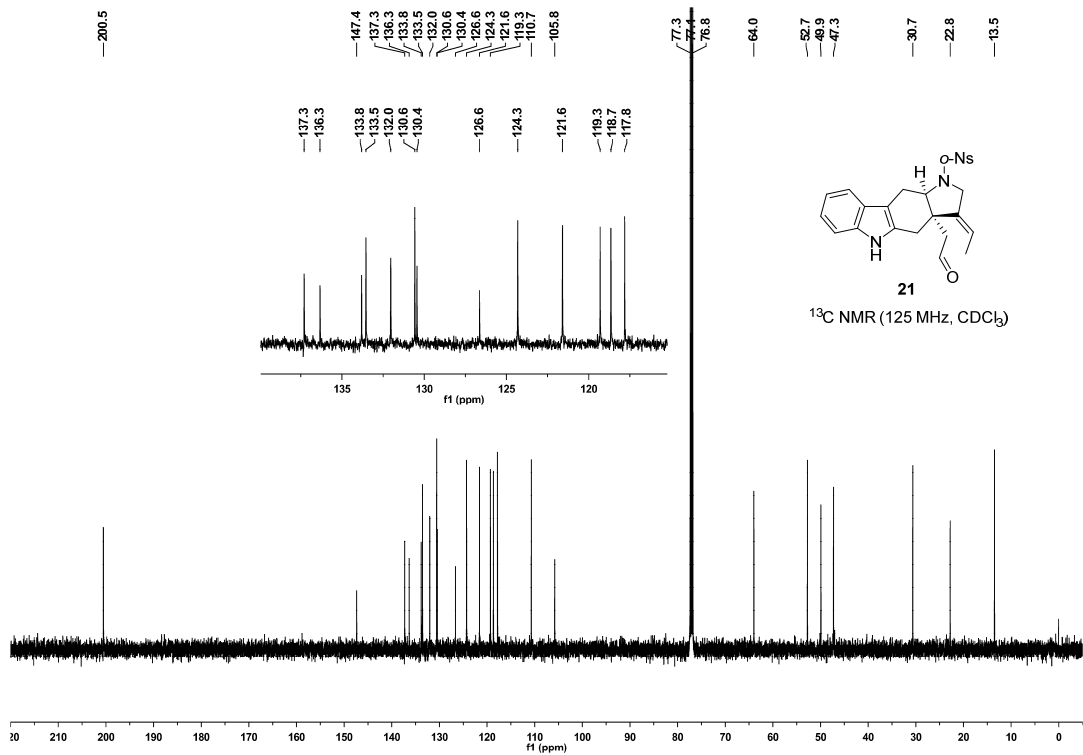
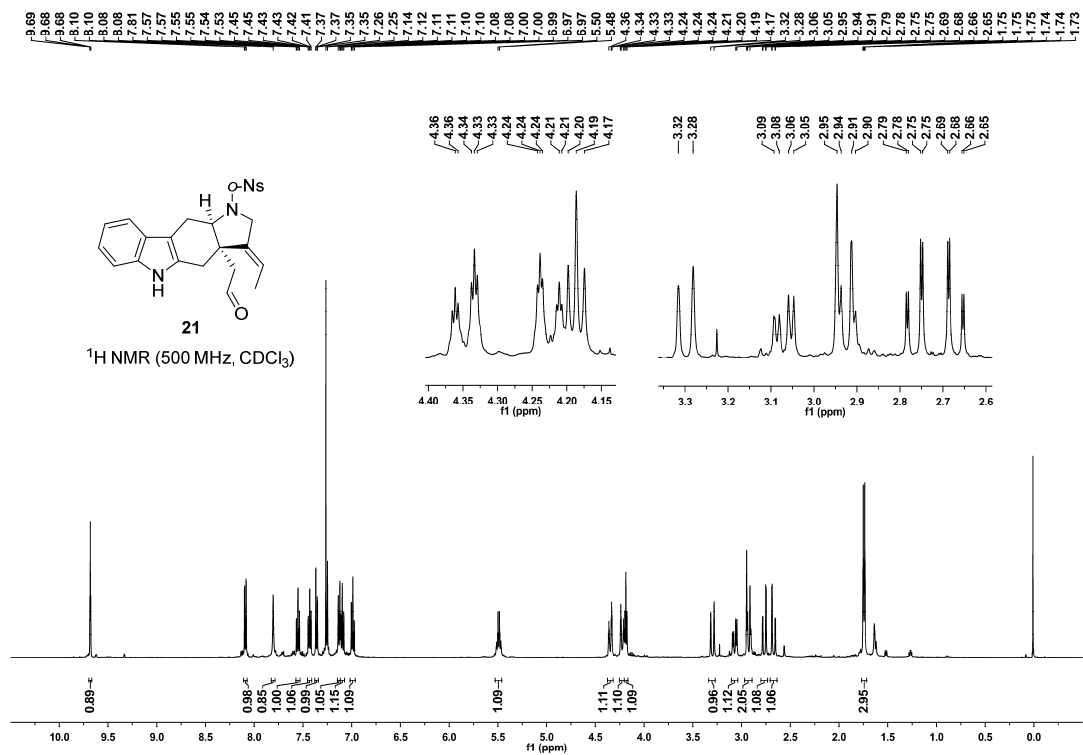


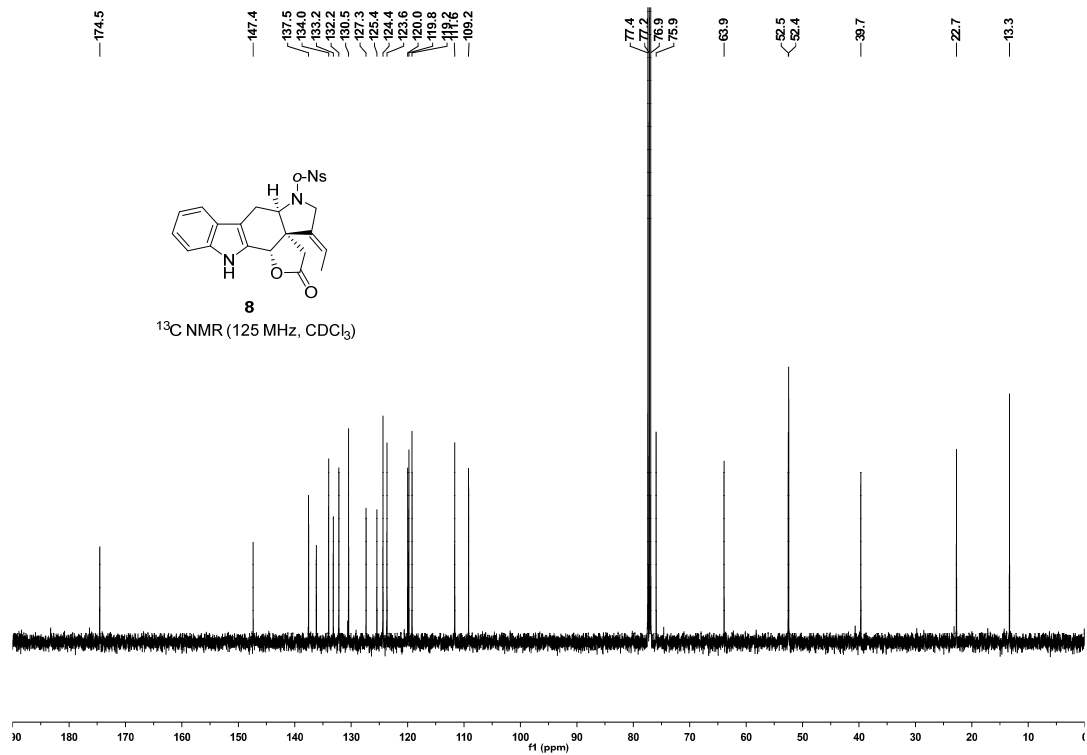
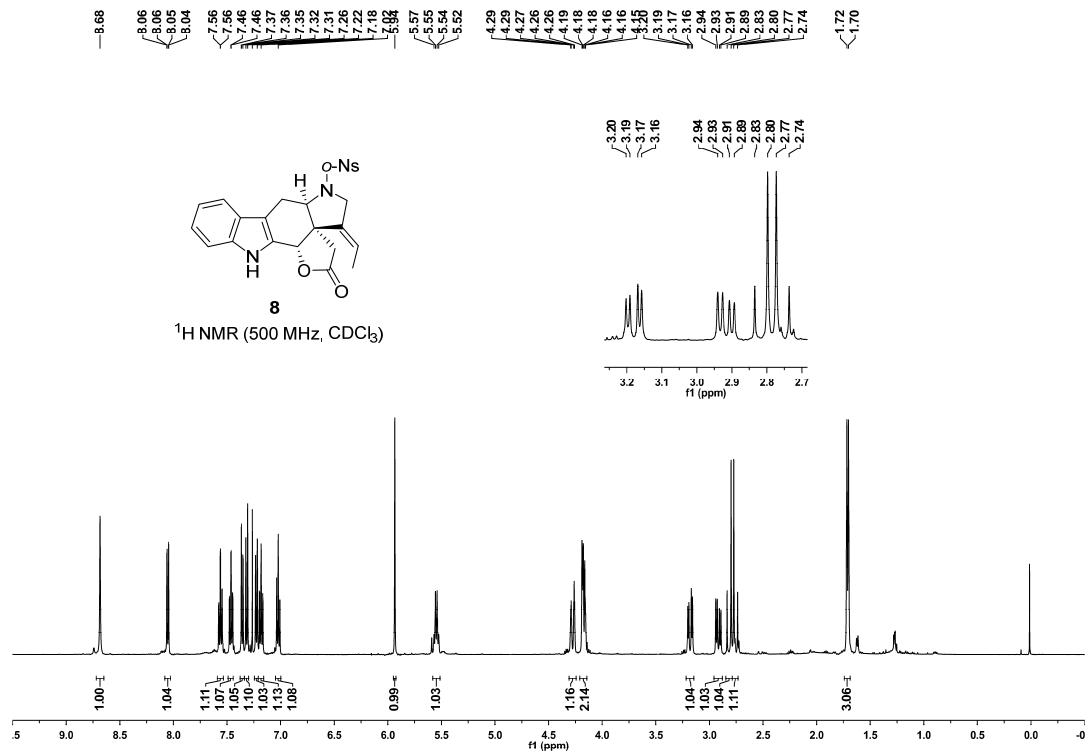




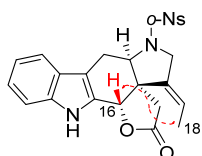








NOESY data of lactone **8**



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

