SUPPORTING MATERIAL

Total Synthesis of (+)-Batzelladine A and (-)-Batzelladine D via [4+2] Annulation of Vinyl Carbodiimides with *N*-Alkyl Imines.

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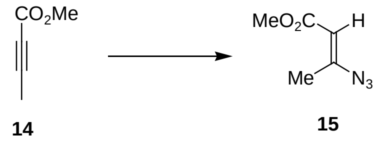
Complete reference 1(a): Patil, A. D.; Kumar, N. V.; Kokke, W. C.; Bean, M. F.; Freyer, A. J.; Debrosse, C.; Mai, S.; Truneh, A.; Faulkner, D. J.; Carte, B.; Breen, A. L.; Hertzberg, R. P.; Johnson, R. K.; Westley, J. W.; Potts, B. C. M. *J. Org. Chem.* **1995**, *60*, 1182-1188.

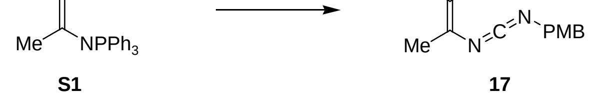
General Procedures. All reactions were performed in flame-dried modified Schlenk (Kjeldahl shape) flasks fitted with a glass stopper under a positive pressure of argon, unless otherwise noted. Air- and moisture-sensitive liquids and solutions were transferred via syringe. Organic solutions were concentrated by rotary evaporation below 30 °C at ca. 25 Torr. Flash column chromatography was performed employing 230-400 mesh silica gel. Thin-layer chromatography (analytical and preparative) was performed using glass plates pre-coated to a depth of 0.25 mm with 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Reaction temperatures maintained through the use of the following baths unless stated otherwise: above ambient temperature (oil bath), 0 ^{o}C (ice/water), -10 ^{o}C (acetone/ice), -20 °C (acetone, ice, CO_2), -78 ^{o}C (acetone/CO_2).

Materials. Dichloromethane (DCM), tetrahydrofuran (THF), DME, acetonitrile, diethyl ether, hexane, toluene, and benzene were purified by passage through two packed columns of neutral alumina under an argon atmosphere. Methanol was distilled from magnesium at 760 Torr. Chloroform, triethylamine, and pyridine were distilled from calcium hydride at 760 Torr. Dichloroethane (DCE), *N*,*N*-dimethylformamide (DMF), and Dimethylsulfoxide (DMSO) were dried over 4Å molecular sieves.

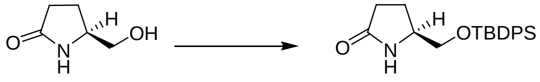
Instrumentation. Infrared (IR) spectra were obtained using a Perkin Elmer Spectrum BX spectrophotometer referenced to a polystyrene standard. Data are presented as the frequency of absorption (cm^{-1}). Proton and carbon-13 nuclear magnetic resonance (^{1}H NMR or ^{13}C NMR) spectra were recorded on a Varian 400, a Varian 500, or a Varian Inova 500 NMR spectrometer; chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to the residual protium in the NMR solvent ($CHCl_3$: δ 7.26 for ^{1}H NMR, δ 77.23 for ^{13}C NMR; CD_3OD: δ 3.31 for ^{1}H NMR, δ 49.00 for ^{13}C NMR). Data are presented as follows: chemical shift, multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, m = multiplet and/or multiple resonances), coupling constant in Hertz (Hz), integration. Optical rotations were recorded on a Jasco P-1020 polarimeter using a 200 μL 1.0 cm cell.



3-Azido-but-2-enoic acid methyl ester (15). A solution of tetramethylguanidinium azide (5.2 g, 33 mmol, 1.1 equiv) in $CHCl_3$ (10 mL) was added drop wise to a stirring solution of 1,4-But-2-ynoic acid methyl ester **14** (2.9g, 30 mmol, 1.0 equiv) in $CHCl_3$ (100 mL) at -10 °C (ice/acetone). The resulting solution was stirred for 3.5 h at –10 °C and then 14 h at RT . The reaction mixture was then diluted with water (100 mL). The product was then extracted with dichloromethane (3 x 100 mL). The combined organic layers were dried (sodium sulfate), filtered and concentrated. The clear light yellow oil was purified by flash column chromatography (7 % EtOAc in Hex) to provide *E*-**15** (1.8 g, 44 %) as a clear light yellow liquid. R_f = 0.48 (13 % EtOAc in Hex). All spectral data was consistent with reported values.

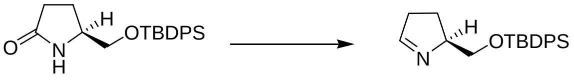


3-(4-Methoxy-benzyliminomethyleneamino)-but-2-enoic acid methyl ester (17). 4-Methoxybenzylisocyanate (0.100 mL, 0.74 mmol, 1.2 equiv) was added to a solution of iminophosphorane **S1** (0.218, 0.58 mmol, 1.0 equiv) in toluene (5 mL). The reaction was stirred at 80 °C for 4 h and then concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (88 % Hex in EtOAc) to provide carbodiimide **17** (0.102 g, 71 %) as a clear oil that turns light yellow upon standing. $R_f = 0.30$ (86 % Hex in EtOAc); ^{1}H (500 MHz, $CDCl_3$) δ 7.26-7.22 (m, 2H), 6.91-6.88 (m, 2H), 5.48 (q, *J* = 0.9 Hz, 1H), 4.46 (s, 2H), 3.81 (s, 3H), 3.66 (s, 3H), 2.25 (d, *J* = 0.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8, 159.6, 155.0, 134.9, 129.6, 129.0, 114.5, 109.3, 55.5, 51.1, 50.2, 19.7; FTIR (neat film; NaCl) 3056, 2943, 2132, 1706, 1624, 1513, 1437 cm^{-1}; HRMS (ESI)$^+$ *m/z* calcd for $C_{14}H_{17}N_2O_3$ [MH]$^+$ 261.1239, found 261.1260.



(*S*)-18 **(*S*)-S2**

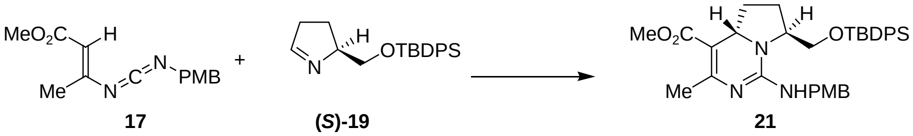
(*S*)- 5-(tert-Butyl-diphenyl-silanyloxymethyl)-pyrrolidin-2-one (S2). To a solution of **(*S*)-18** (3.11g, 27.0 mmol, 1.0 equiv) in DMF (25 mL) was added imidazole (3.8g, 40.5 mmol, 1.5 equiv) and TBDPSCl (9.0 ml, 54.0 mmol, 2.0 equiv). The solution was stirred at RT for 8 h. The solution was the diluted with diethyl ether (400 mL) and washed with water (3 X 400 mL), brine (200 mL), dried with magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (EA) to provide **(*S*)-S2** (8.2g, 83%). All spectral data was consistent with reported values.



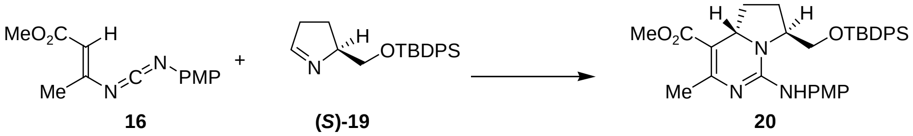
(*S*)-S2 **(*S*)-19**

(S)-2-(*tert*-Butyl-diphenyl-silanyloxymethyl)-3,4-dihydro-2*H*-pyrrole (19). To a solution of Cp_2ZrHCl (0.203 g, 0.787 mmol, 2.0 equiv) in tetrahydrofuran (6.0 mL) at –20 °C (ice, acetone, CO_2) was added lactam **S2** (0.138 g, 0.390 mmol, 1.0 equiv) in tetrahydrofuran (2.0 mL). After stirring 2.5 h at this temperature, the reaction mixture was loaded directly onto a short plug of silica gel (EtOAc) and concentrated *in vacuo* to afford imine **19** (0.087 g, 66%) as a clear oil. Used immediately without further purification. R*f* 0.6 (EtOAc); ^{1}H NMR (500 MHz, C_6D_6) δ 7.84 (m, 2H), 7.80 (m, 2H), 7.32 (br s, 1H,), 7.23 (m, 6H), 4.11 (m, 1H), 3.92 (dd, J =

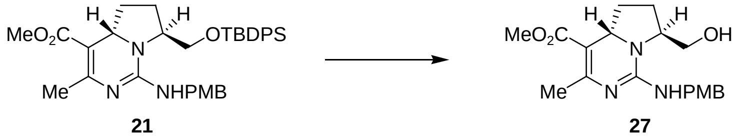
10.2, 4.6 Hz, 1H), 3.84 (dd, J = 10.2, 4.0 Hz, 1H), 2.16 (m, 1H), 1.93 (m, 1H), 1.55 (m, 2H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, C_6D_6) δ 166.4, 136.5, 136.4, 134.6, 134.3, 130.3, 128.4, 128.4, 75.4, 67.2, 37.6, 27.4, 23.6, 19.9; FTIR (neat film) 3071, 2931, 2858, 1625, 1427, 1112; HRMS (FAB)$^+$ *m/z* calcd for $C_{21}H_{28}NOSi$ [MH]$^+$ 338.1940, found 338.1941.



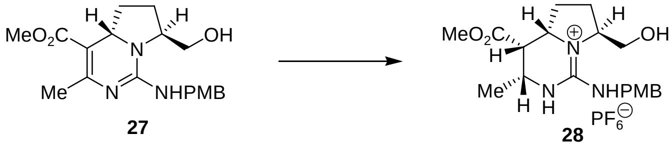
7-(tert-Butyl-diphenyl-silanyloxymethyl)-1-(4-methoxy-benzylamino)-3-methyl-4a,5,6,7-tetrahydro-pyrrolo[1,2-c]pyrimidine-4-carboxylic acid methyl ester (21). To a solution of carbodiimide **17** in dichloroethane (270 µL, 0.968 M, 1.0 equiv) at 23 ˚C was added imine **(*S*)-19** (0.087g, 0.258 mmol, 1.0 equiv) in dichloroethane (3 mL). After stirring for 4.5 h, the reaction mixture was diluted with dichloromethane (5 mL) and then concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (20:1 CH_2Cl_2/CH_3OH) to yield vinylogous carbamate **21** (0.152g, 98%) as a clear oil. R*f* 0.6 (2:1 EtOAc/Hex); ^{1}H NMR (500 MHz, C_6D_6) δ 7.61 (m, 4H) 7.23 (m, 2H,), 7.18 (m, 6H), 6.76 (m, 2H), 6.38 (br t, J = 5.8 Hz, 1H), 5.09 (dd, J = 14.7, 7.0 Hz, 1H), 4.41 (dd, J = 10.3, 4.3 Hz, 1H), 4.35 (dd, J = 14.7, 4.1 Hz, 1H) 3.93 (m, 1H), 3.56 (s, 3H), 3.29 (s, 3H), 3.23 (app t, J = 10.3 Hz, 1H), 3.15 (dd, J = 10.7, 2.8 Hz, 1H), 2.89 (s, 3H), 2.34 (ddd, J = 11.9, 7.3, 4.3 Hz, 1H), 1.36 (m, 1H), 1.17 (m, 1H), 0.97 (s, 9H), 0.31 (m, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 159.8, 136.2, 136.2, 133.1, 133.0, 130.8, 130.7, 130.1, 128.7, 128.7, 128.7, 114.7, 68.1, 66.1, 62.5, 58.6, 55.1, 50.4, 45.2, 35.7, 27.3, 24.2, 19.5; IR (neat film) 3359, 2922, 1731, 1685, 1438; HRMS (FAB)$^+$ *m/z* calcd for $C_{35}H_{44}N_3O_4Si$ [MH]$^+$ 598.3101, found 598.3103.



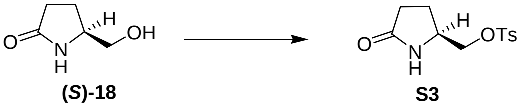
7-(tert-Butyl-diphenyl-silanyloxymethyl)-1-(4-methoxy-phenylamino)-3-methyl-4a,5,6,7-tetrahydro-pyrrolo[1,2-c]pyrimidine-4-carboxylic acid methyl ester (20). To a solution of carbodiimide **16** (0.685g, 2.6 mmol, 1.0 equiv) in dichloroethane (10mL) at 23 ˚C was added imine **(*S*)-19** (0.804g, 2.4 mmol, 1.0 equiv) . After stirring for 4.5 h, the reaction mixture was diluted with dichloromethane (5 mL) and then concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (20:1 CH_2Cl_2/CH_3OH) to yield vinylogous carbamate **20** (0.930g, 62%) as a clear oil. R*f* 0.6 (2:1 EtOAc/Hex); ^{1}H NMR (500 MHz, CD_3OD) δ 7.73-7.35 (m, 12H), 6.83 (m, 2H), 4.56 (m, 1H), 4.32 (m, 1H), 4.03 (m, 1H), 3.76 (s, 3H), 3.69 (dd, J = 10.8, 6.5 Hz, 1H), 3.67 (s, 3H), 2.47 (m, 1H), 2.15 (m, 1H), 2.00 (s, 3H), 1.53 (m, 1H), 1.09 (s, 9H), 1.05 (m, 1H).



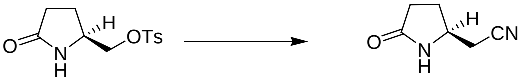
7-Hydroxymethyl-1-(4-methoxy-benzylamino)-3-methyl-4a,5,6,7-tetrahydro-pyrrolo[1,2-c]pyrimidine-4-carboxylic acid methyl ester (27). To a solution of vinylogous carbamate **21** (0.200 g, 0.33 mmol, 1.0 equiv) in THF (4 mL) at 23 ˚C was added TBAF (0.45 mL of a 1M solution in THF, 0.43 mmol, 1.3 equiv). After stirring 30 min, the solution was diluted with dichloromethane (10 mL) and then concentrated *in vacuo*. The resulting residue was purified by silica gel flash chromatography (25% CH_3OH in EtOAc) to afford **27** (0.116 g, 97%) as a clear oil. R_f = 0.2 (25% CH_3OH in EtOAc); ^{1}H NMR (500 MHz, CD_3OD) δ 7.25 (m, 2H), 6.88 (m, 2H), 4.45 (d, J = 14.6 Hz, 1H), 4.40 (dd, J = 14.5, 4.6 Hz, 1H), 4.39 (d, J = 14.6 Hz, 1H), 4.09 (m, 1H), 3.77 (s, 3H), 3.65 (s, 3H), 3.55 (dd, J = 11.2, 2.4 Hz, 1H), 3.43 (dd, J = 11.2, 9.6 Hz, 1H), 2.46 (m, 1H), 2.79 (d, J = 0.9 Hz, 3H), 1.99 (m, 1H), 1.49 (m, 1H), 1.27 (m, 1H); ^{13}C NMR (125 MHz) δ 168.4, 159.3, 154.8, 130.7, 128.9, 113.8, 98.5, 65.2, 62.9, 57.6, 54.5, 49.7, 44.4, 35.1, 24.4, 21.9, 20.6; FTIR (neat film) 3224 (m), 3175 (m), 3079 (m), 2923 (m), 1718 (s), 1655 (s), 1560 (m), 1513 (m), 1250 (s); HRMS $(ESI)^+$ *m/z* calcd for $C_{19}H_{26}N_3O_4$ $[MH]^+$ 360.1923, found 360.1913.



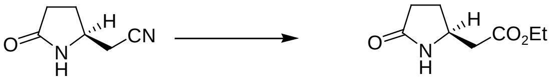
7-Hydroxymethyl-1-(4-methoxy-benzylamino)-4-methoxycarbonyl-3-methyl-3,4,4a,5,6,7-hexahydro-2H-pyrrolo[1,2-c]pyrimidin-8-ylium; hexafluorophosphate (28). To a test tube was added vinylogous carbamate **27** (0.102 g, 0.28 mmol, 1 equiv) in dichloromethane (2 mL) followed by Crabtree's Catalyst (0.228 g, 0.28 mmol, 1.0 equiv). The test tube was sealed in a stainless steel hydrogenation chamber. The chamber was flushed with hydrogen (3 x 300 psi) and then charged to 400 psi. After stirring at 23 ˚C and 400 psi for 24 h, the reaction mixture was diluted with dichloromethane (4 mL) and then concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (9:1 CH_2Cl_2/MeOH) to afford guanidinium salt **28** (0.117 g, 81%) as a yellow oil. R*f* 0.6 (9:1 CH_2Cl_2/CH_3OH); 1H NMR (500 MHz, CD_3OD) δ 7.31 (m, 2H), 6.93 (m, 2H), 4.41 (d, J = 14.4 Hz, 1H), 4.37 (d, J = 14.4 Hz, 1H), 4.11 (ddd, J = 7.7, 6.8, 3.9 Hz, 1H), 4.01 (m, 1H), 3.89 (m, 1H), 3.79 (s, 3H), 3.71 (s, 3H), 3.70 (dd, J = 11.3, 2.4 Hz, 1H), 3.52 (dd, J = 11.3, 8.8 Hz, 1H), 3.12 (app t, J = 4.2 Hz, 1H), 2.26 (m, 1H), 2.00 (m, 1H), 1.76 (m, 1H), 1.67 (m, 1H), 1.28 (d, J = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 170.3, 159.8, 153.2, 128.9, 128.2, 114.0, 64.6, 63.3, 61.8, 59.0, 54.5, 53.8, 51.2, 44.6, 27.2, 25.8, 16.6; FTIR (neat film) 3262 (m), 3149 (m), 2924 (s), 2841 (m), 1734 (s), 1611 (s), 1511 (m), 1401 (m), 1245 (m); HRMS $(ESI)^+$ *m/z* calcd for $C_{19}H_{28}N_3O_4$ $[MH]^+$ 362.2074, found 362.2069. An analytical sample of x-ray quality crystals was obtained from slow evaporation of a small portion of **28** from CH_2Cl_2/MeOH solvent, leading to its structure determination from x-ray diffraction.



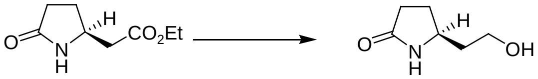
(S)-toluene-4-sulfonic acid 5-oxo-pyrrolidin-2-ylmethyl ester (S3). To a solution of **18** (7.5 g, 65 mmol, 1.0 equiv) in CH_2Cl_2 (100 mL) was added tosyl chloride (13.7 g, 72 mmol, 1.1 equiv), DMAP (1.2 g, 13 mmol, 0.2 equiv), and triethyl amine (10 mL, 72 mmol, 1.1 equiv). After stirring at RT for 14 h, the solution was diluted with CH_2Cl_2 (400 mL) and washed with 1N HCl (200 mL), water (3 X 400 mL), brine (400 mL), dried with sodium sulfate, filtered and concentrated *in vacuo* to provide **S3** (14.8g, 85%) as a fluffy white solid. Spectal data for **S3** was consistent with reported values.


S3 29

(*S*)- (5-Oxo-pyrrolidin-2-yl)-acetonitrile (29). To a solution of **S3** (9.8g, 36.4 mmol, 1.0 equiv) in acetonitrile (150 mL) was added potassium cyanide (6.0g, 92.1 mmol, 2.5 equiv). The solution was refluxed at 85 ˚C for 18 h. The solution was then diluted with acetonitrile (200 mL), filtered through celite, and concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (9:1 EA/MeOH) to afford **29** (4.1g, 91%) as a white solid. Spectal data for **29** was consistent with reported values.

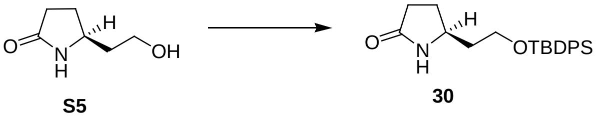

29 S4

(*S*)-(5-Oxo-pyrrolidin-2-yl)-acetic acid ethyl ester (S4). To a 500 mL round bottom flask equipped with a reflux condenser and KOH trap, was bubbled HCl gas through a solution of **29** (1.9g, 15.3 mmol, 1.0 equiv) in refluxing ethanol (150 mL) for 40 min. The solution was then heated for another 2 h. After the solution had cooled to RT, nitrogen gas was bubbled through the solution for 40 min. The solution was diluted with CH_2Cl_2 (300 mL) and washed with saturated sodium bicarbonate solution (3 X 200 mL), dried with sodium sulfate, filtered, and concentrated in vacuo to afford **S4** (2.3 g, 89%) as a clear liquid that was used without further purification. Spectral data for **S4** was consistent with reported values

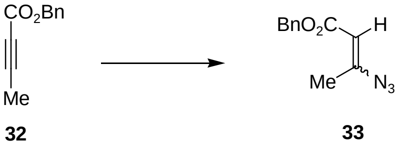

S4 S5

(*S*)-5-(2-Hydroxy-ethyl)-pyrrolidin-2-one (S5). To a solution of **S4** (3.5 g, 20.4 mmol, 1.0 equiv) in THF (20 mL) cooled to 0 ˚C, was added $LiBH_4$ (1.2 g, 60 mmol, 3.0 equiv) and methanol (2.5 mL, 60 mmol, 3.0 equiv). The solution was stirred for an additional 2 h at RT.

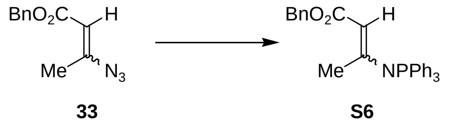
The reaction was then quenched with AcOH (2.0 mL) and concentrated in vacuo. The residue was purified by silica gel flash chromatography (9:1 CH_2Cl_2/MeOH) to provide **S5** (2.4g, 91%) as a white solid. Spectral data for **S5** was consistent with reported values



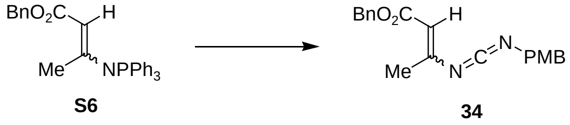
(*S*)-5-[2-(tert-Butyl-diphenyl-silanyloxy)-ethyl]-pyrrolidin-2-one (30). To a solution of **S5** (0.38g, 2.94 mmol, 1.0 equiv) in DMF (5 mL) was added imidazole (0.6g, 8.8 mmol, 3.0 equiv) and TBDPSCl (1.5 ml, 5.9 mmol, 2.0 equiv). The solution was stirred at RT for 8 h. The solution was the diluted with diethyl ether (200 mL) and washed with water (3 X 200 mL), brine (200 mL), dried with magnesium sulfate, filtered and concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (EA) to provide **30** (0.95g, 88%). Spectral data for **30** was consistent with reported values.



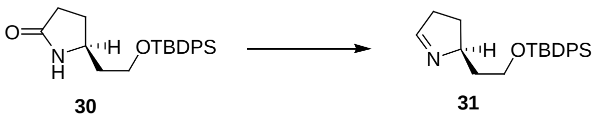
3-Azido-but-2-enoic acid benzyl ester (33). A solution of tetramethylguanidinium azide (1.1 g, 6.9 mmol, 2.0 equiv) in $CHCl_3$ (10 mL) was added drop wise to a stirring solution of 1,4-But-2-ynoic acid benzyl ester **32** (0.6 g, 2.9 mmol, 1.0 equiv) in $CHCl_3$ (20 mL) at -10 °C (ice/acetone). The resulting solution was stirred for 3.5 h at –10 °C and then diluted with water (50 mL). The product was then extracted with dichloromethane (3 x 100 mL). The combined organic layers were dried (sodium sulfate), filtered and concentrated. The clear light yellow oil was purified by flash column chromatography (7 % EtOAc in Hex) to provide *E*-**33** (0.421 g, 56 %) as a clear light yellow liquid and *Z*-**33** (0.210 g, 28%) as a white solid. *E*-**33** $R_f = 0.48$ (13 % EtOAc in Hex); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.32 (m, 5 H), 5.60 (q, *J* = 0.9 Hz, 1 H), 5.16 (s, 2H), 2.36 (d, *J* = 0.9 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 155.7, 136.3, 128.8, 128.4, 128.4, 105.0, 66.0, 16.7; FTIR (neat film) 3039, 2984, 2242, 2099, 1714, 1628 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{11}N_3O_2Na$ (M+Na) 240.0749, found 240.0755; *Z*-**33** $R_f = 0.30$ (10% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.29 (m, 5H), 5.26 (q, J = 1.0 Hz, 1H), 5.14 (s, 2H), 2.14 (d, J = 1.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.1, 149.3, 136.3, 128.7, 128.5, 128.3, 105.3, 65.9, 20.7; FTIR (neat film) 3034, 2932, 2102, 1714, 1626; HRMS (ESI)$^+$ *m/z* calcd for $C_{11}H_{11}N_3O_2Na$ $[M+Na]^+$ 240.0749, found 240.0758.



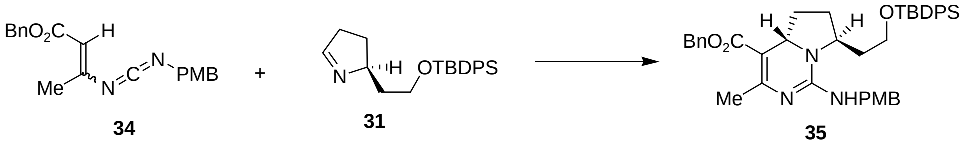
3-Azido-but-2-enoic acid benzyl ester (S6). A solution of azide *E*-**33** (0.421 g, 1.9 mmol, 1 equiv) in dichloromethane (10 mL) was added drop wise to a solution of triphenylphosphine (0.50 g, 1.9 mmol, 1.0 equiv) in dichloromethane (10 mL) over 15 minutes. The resulting bright yellow solution was stirred for 4 h at 23 °C. The mixture was then concentrated and recrystallized (CH_2Cl_2/Hex) to afford iminophosphorane *E*-**S6** (0.656 g, 75%) as a light brown solid. The same procedure was used to prepare iminophosphorane *Z*-**S6** in 58% yield. *E*-**S6**; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86-7.22 (m, 20H), 5.00 (s, 2H), 4.81 (s, 1H), 2.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.0, 133.0 (m), 132.9 (m), 132.4 (m), 132.4 (m), 129.1 (m), 129.0, 128.4, 127.8, 127.5, 65.7, 8.7; IR (neat film) 3055, 1677, 1537, 1114; HRMS (ESI)$^+$ calcd for $C_{29}H_{27}NO_2P$ [M+H] 452.1779, found 452.1779. *Z*-**S6**; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87-7.40 (m, 15H), 7.31-7.23 (m, 5H), 5.00 (s, 2H), 4.82 (s, 1H), 2.49 (bs, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 133.0 (m), 132.4, 132.3, 129.2-129.0 (m), 128.8, 128.7, 128.4, 127.8, 110.0, 65.7, 8.8; IR (neat film) 3028, 1677, 1537; HRMS (ESI)$^+$ *m/z* calcd for $C_{29}H_{27}NO_2P$ $[MH]^+$ 452.1779, found 452.1797.



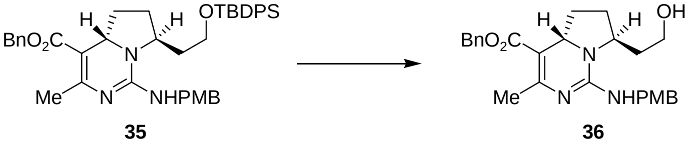
3-(4-Methoxy-benzyliminomethyleneamino)-but-2-enoic acid benzyl ester (34). 4-Methoxybenzylisocyanate (0.150 mL, 1.05 mmol, 1.1 equiv) was added to a solution of iminophosphorane **S6** (0.434 g, 0.96 mmol, 1.0 equiv) in toluene (4 mL). The reaction was stirred at 80 °C for 4h. The resulting mixture was cooled to ambient temperature and concentrated *in vacuo.* The residue was purified by silica gel flash chromatography (88 % Hex in EtOAc) to provide carbodiimide **34** (0.236 g, 73%) as a clear oil that turns light yellow upon standing. *E*-**34**: R_f = 0.30 (86 % Hex in EtOAc); ^{1}H NMR (500 MHz, C_6D_6) δ 7.19-7.02 (m, 5H), 6.87 (m, 2H), 6.66 (m, 2H), 5.90 (q, J = 0.9 Hz, 1H), 5.04 (s, 2H), 3.87, (s, 2H), 3.22 (s, 3H), 2.32 (d, J = 1.0 Hz, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 167.0, 160.2, 156.0, 137.5, 130.1, 129.31, 129.0, 128.8, 128.7, 128.3, 114.7, 110.2, 65.9, 55.1, 50.1, 19.9; IR (neat film) 3033, 2936, 2133, 1707, 1625, 1513, 1334; HRMS (ESI) calcd for $C_{20}H_{21}N_2O_3$ (M+1) 337.1552, found 337.1561; *Z*-**34**: R_f = 0.30 (4:1 Hex/EtOAc); ^{1}H NMR (500 MHz, C_6D_6) δ 7.19-7.00 (m, 5H), 6.87 (m, 2H), 6.66 (m, 2H), 5.90 (bs, 1H), 5.04 (s, 2H), 3.87 (s, 2H), 3.22 (s, 3H), 2.32 (bs, 3H); ^{13}C NMR (125 MHz, C_6D_6) δ 166.5, 159.7, 155.4, 137.0, 130.1, 129.3, 129.0, 128.8, 128.7, 128.3, 114.7, 110.2, 65.9, 55.1, 50.1, 19.9; IR (neat film) 2953, 2133, 1705, 1624, 1513, ; HRMS (ESI)$^+$ *m/z* calcd for $C_{20}H_{21}N_2O_3$ $[MH]^+$ 337.1552, found 337.1561.



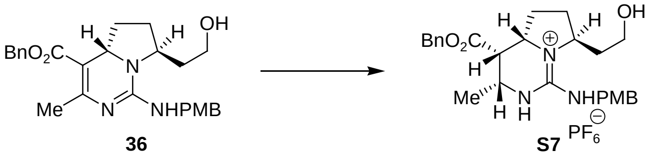
(S)-2-[2-(tert-Butyl-diphenyl-silanyloxy)-ethyl]-3,4-dihydro-2H-pyrrole (31). To a solution of Cp_2ZrHCl (0.254 g, 0.90 mmol, 1.7 equiv) in tetrahydrofuran (5.0 mL) at –20 °C (ice, acetone, CO_2) was added lactam **30** (0.185 g, 0.53 mmol, 1.0 equiv) in THF (2.0 mL). After stirring 2.5 h, the reaction mixture was loaded directly onto a short plug of silica (EtOAc) and concentrated *in vacuo* to afford imine **31** (0.108 g, 66%) as a clear oil. Used immediately without further purification. R*f* 0.7 (EtOAc); ^{1}H NMR (500 MHz, C_6D_6) δ ^{1}H NMR (500 MHz, C_6D_6) δ 7.82 (m, 4H), 7.23 (m, 6H), 7.12 (br t, J = 1.1 Hz, 1H), 4.15 (m, 1H), 4.04 (dt, J = 10.2, 6.5 Hz, 1H), 3.92 (dt, J = 10.2, 6.5 Hz, 1H), 2.02 (dt, J = 13.5, 7.4, 6.3 Hz, 1H), 1.94 (m, 1H), 1.83 (dddt, J = 9.9, 7.8, 2.0, 1.0 Hz, 1H), 1.71 (ddt, J = 13.5, 6.8, 6.7 Hz, 1H) 1.57 (dddd, J = 12.5, 9.8, 7.9, 4.4 Hz, 1H), 1.20 (s, 9H), 0.99 (dddd, J = 12.7, 10.1, 7.8, 7.2 Hz, 1H); ^{13}C NMR (125 MHz, C_6D_6) δ 164.7, 136.5, 136.4, 134.8, 130.3, 70.6, 62.7, 40.5, 36.9, 27.6, 27.5, 19.8; FTIR (neat film) 3071 (s), 2931 (s), 1960 (w), 1888 (w), 1827 (w), 1704 (m), 1621 (s); HRMS (ESI)$^+$ *m/z* calcd for $C_{22}H_{29}NOSi$ $[MH]^+$ 352.2097, observed 352.2090.



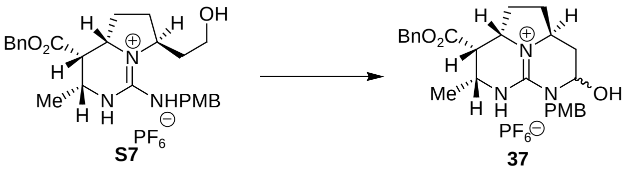
7-[2-(tert-Butyl-diphenyl-silanyloxy)-ethyl]-1-(4-methoxy-benzylamino)-3-methyl-4a,5,6,7-tetrahydro-pyrrolo[1,2-c]pyrimidine-4-carboxylic acid benzyl ester (35). To a solution of carbodiimide **34** (0.063g, 0.19 mmol, 1.0 equiv) in dichloroethane (1 mL) was added imine **31** (0.093g, 0.26 mmol, 1.3 equiv) in dichloroethane (1 mL). After stirring for 4.5 h, the reaction mixture was diluted with dichloromethane (5 mL) and then concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (20:1 CH_2Cl_2/CH_3OH) to yield vinylogous carbamate **35** (0.114g, 86%) as a clear oil. R_f = 0.5 (EtOAc); ^{1}H NMR (500 MHz, CD_3OD) δ 7.65-7.27 (m, 15H), 7.05 (m, 2H), 6.77 (m, 2H), 5.15 (AB, J = 12.4 Hz, 1H), 5.07 (AB, J = 12.4 Hz, 1H), 4.51 (AB, J = 15.1 Hz, 1H), 4.39 (AB, J = 15.1 Hz, 1H), 4.34 (dd, J = 10.2, 5.4 Hz, 1H), 4.31 (m, 1H), 3.80-3.70 (m, 2H), 3.74 (s, 3H), 2.38 (m, 1H), 2.25 (s, 3H), 1.95 (m, 1H), 1.63-1.46 (m, 3H), 1.35 (m, 1H), 0.98 (s, 9H); ^{13}C NMR (100 MHz, CD_3OD) δ 160.4, 138.6, 136.9, 136.8, 136.6, 134.6, 134.1, 131.4, 131.2, 131.0, 129.7, 129.7, 129.2, 129.1, 129.1, 129.1, 129.0, 115.0, 66.4, 62.2, 57.8, 56.9, 55.8, 45.1, 37.1, 28.8, 27.7, 27.5, 20.1; FTIR (neat film) 3350, 2931, 1687, 1661, 1594, 1492, 1220 cm^{-1}; HRMS (ESI)$^+$ *m/z*: Calcd for $C_{42}H_{50}N_3O_4Si$ [MH]$^+$ 688.3571, found 688.3570.



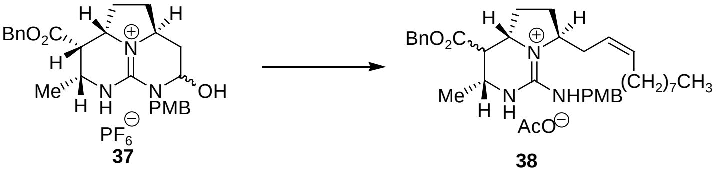
7-(2-Hydroxy-ethyl)-1-(4-methoxy-benzylamino)-3-methyl-4a,5,6,7-tetrahydro-pyrrolo[1,2-c]pyrimidine-4-carboxylic acid benzyl ester (36). To a solution of vinylogous carbamate **35** (0.161 g, 0.23 mmol, 1.0 equiv) in THF (3 mL) was added TBAF (0.26 mL of a 1M solution in THF, 0.26 mmol, 1.1 equiv). After stirring 30 min, the solution was diluted with dichloromethane (10 mL) and then concentrated *in vacuo*. The resulting residue was purified by silica gel flash chromatography (25% CH_3OH in EtOAc) to afford **36** (0.104 g, 99%) as a clear oil. R_f = 0.3 (25% CH_3OH in EtOAc); ^1H NMR (500 MHz, CD_3OD) δ 7.37-7.28 (m, 5H), 7.24 (m, 2H), 6.87 (m, 2H), 5.18 (AB, J = 12.5 Hz, 1H), 5.09 (AB, J = 12.5 Hz, 1H), 4.53 (AB, J = 14.4 Hz, 1H) 4.39 (dd, J = 9.1, 5.8 Hz, 1H), 4.37 (AB, J = 14.4 Hz, 1H), 4.23 (m, 1H), 3.77 (s, 3H), 3.65 (app dt, J = 11.1, 4.3 Hz, 1H), 3.49 (ddd, J = 11.1, 6.3, 5.1 Hz, 1H), 2.42 (m, 1H), 2.27 (s, 3H), 1.99 (m, 1H), 1.70-1.62 (m, 2H), 1.54 (app dq, J = 12.3, 9.5 Hz, 1H), 1.42 (m, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 168.9, 160.5, 138.5, 136.1, 132.1, 130.6, 130.2, 129.7, 129.2, 129.1, 128.7, 66.4, 58.8, 57.5, 57.2, 55.8, 45.8, 37.3, 36.6, 28.9, 27.3; FTIR (neat film) 3290, 2934, 1680, 1660, 1600, 1494, 1246; HRMS $(ESI)^+$ *m/z*: Calcd for $C_{26}H_{32}N_3O_4$ $[MH]^+$ 450.2393, found 450.2403.



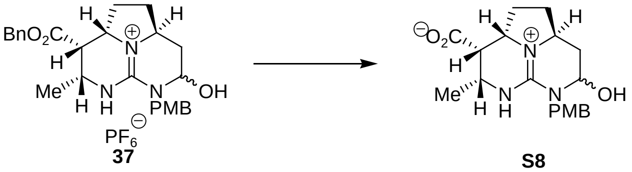
4-Benzyloxycarbonyl-7-(2-hydroxy-ethyl)-1-(4-methoxy-benzylamino)-3-methyl-3,4,4a,5,6,7-hexahydro-2H-pyrrolo[1,2-c]pyrimidin-8-ylium; hexafluorophosphate (S7). To a test tube was added vinylogous carbamate **36** (0.095 g, 0.21 mmol, 1.0 equiv) in dichloromethane (4 mL) followed by Crabtree's Catalyst (0.170 g, 0.21 mmol, 1.0 equiv). The test tube was sealed in a stainless steel hydrogenation chamber. The chamber was flushed with hydrogen (3 x 300 psi) and then charged to 400 psi. After stirring at 400 psi for 24 h, the reaction mixture was diluted with dichloromethane (4 mL) and then concentrated *in vacuo*, and the residue was purified by silica gel flash chromatography (9:1 CH_2Cl_2/CH_3OH) to afford guanidinium salt **S7** (0.101 g, 80%) as a yellow oil. R_f = 0.5 (9:1 CH_2Cl_2/CH_3OH); ^1H NMR (500 MHz, CD_3OD) δ 7.40-7.33 (m, 5H), 7.28 (m, 2H), 6.94 (m, 2H), 5.20 (AB, J = 11.8 Hz, 1H), 5.14 (AB, J = 11.8 Hz, 1H), 4.36 (AB, J = 14.9 Hz, 1H) 4.32 (AB, J = 14.9 Hz, 1H), 4.11-4.05 (m, 2H), 3.86 (dq, J = 6.6, 4.6 Hz, 1H), 3.79 (s, 3H), 3.67 (app dt, J = 11.2, 4.8 Hz, 1H), 3.50 (ddd, J = 11.9, 9.6, 4.0 Hz, 1H), 3.10 (app t, J = 4.3 Hz, 1H), 2.30 (m, 1H), 1.84-1.75 (m, 3H), 1.67 (m, 1H), 1.58 (m, 1H), 1.24 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 170.8, 161.0, 153.5, 137.1, 130.2, 130.2, 129.9, 129.8, 129.4, 115.3, 68.0, 58.6, 58.3, 55.9, 49.5, 46.0, 46.0, 37.1, 30.1, 27.9, 27.8, 17.8; FTIR (neat film) 3412, 2937, 1731, 1612, 1515, 1252; HRMS $(ESI)^+$ *m/z*: Calcd for $C_{26}H_{34}N_3O_4$ $[MH]^+$ 452.2549, found 452.2558.



3-Benzyloxycarbonyl-7-hydroxy-6-(4-methoxy-benzyl)-4-methyl 1,2,2a,3,4,5,6,7,8,8a-decahydro-5,6-diaza-8b-azonia-acenaphthylene; hexafluorophosphate (37). To a solution of guanidium salt **S7** (0.101 g, 0.17 mmol, 1.0 equiv) in acetonitrile (4 mL) at 45 ˚C was added DMSO (0.025 mL, 0.34 mmol, 2.0 equiv) followed by IBX (0.071 g, 0.25 mmol, 1.5 equiv). The reaction was stirred at this temperature for 18 h, filtered through celite (CH_3CN), and then concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (9:1 CH_2Cl_2/CH_3OH) to afford hemiaminal **37** (0.100 g, 99%) as a yellow oil (3:1 mixture of epimers). $R_f = 0.4$ (9:1 CH_2Cl_2/CH_3OH); (Major) ^{1}H NMR (500 MHz, CD_3OD) δ 7.41-7.30 (m, 5H), 7.29 (m, 2H), 6.92 (m, 2H), 5.23 (AB, J = 11.9 Hz, 1H), 5.12 (AB, J = 11.9 Hz, 1H), 4.97 (dd, J = 3.5, 1.6 Hz, 1H), 4.68 (AB, J = 13.3 Hz, 1H), 4.64 (AB, J = 13.3 Hz, 1H), 4.07 (ddd, J = 11.0, 6.5, 3.2 Hz, 1H), 3.87 (dq, J = 6.6, 5.3 Hz, 1H), 3.79 (s, 3H), 3.76 (m, 1H), 3.19 (dd, J = 5.1, 3.3 Hz, 1H), 2.25-2.13 (m, 3H), 1.76 (m, 1H), 1.67 (m, 1H), 1.57 (m, 1H), 1.08 (d, J = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 169.0, 159.5, 149.1, 135.9, 129.3, 129.0, 128.4, 128.3, 127.3, 113.9, 78.3, 66.5, 57.4, 54.5, 51.2, 49.6, 44.2, 35.1, 29.9, 28.0, 26.0, 16.8; IR (neat film) 3250, 2936, 1731, 1613, 1514, 1455, 1322, 1249; HRMS (ESI)$^+$ *m/z* calcd for $C_{26}H_{32}N_3O_4$ [MH]$^+$ 450.2393, found 450.2392.



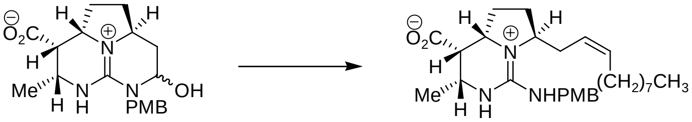
(4-Benzyloxycarbonyl-3-methyl-7-undec-2-enyl-hexahydro-pyrrolo[1,2-c]pyrimidin-1-ylidene)-(4-methoxy-benzyl)-ammonium; acetate (38).To a solution of benzyl ester **37** (0.012 g, 0.02 mmol, 1.0 equiv) in THF (0.60 mL) was added the ylide derived from triphenyl phosphonium bromide (0.2 mL of a 0.24M solution in THF, 0.05 mmol, 2.5 equiv) at RT. The reaction mixture was then stirred at this temperature for 18 h. The reaction mixture was then quenched with AcOH (0.020 mL), diluted with dichloromethane (3 mL) and concentrated *in vacuo* to afford crude alkene **38** as an inseparable mixture (4:1) of epimers as a colorless oil. R_f = 0.3 (4:1 CH_2Cl_2/CH_3OH); ^{1}H NMR (500 MHz, CD_3OD) (Diagnostic Peaks) δ 3.13 (app t, J = 4.4 Hz, 1H), (C7 epimer) 2.33 (app t, J = 10.5 Hz, 1H); FTIR (neat film) 3252, 2925, 2854, 1633, 1614, 1586, 1514, 1328, 1249; HRMS $(FAB)^+$ *m/z* calcd for $C_{35}H_{50}N_3O_3$ $[MH]^+$ 560.3852, found 560.3853.



37

S8

3-Hydroperoxycarbonyl-7-hydroxy-6-(4-methoxy-benzyl)-4-methyl-1,2,2a,3,4,5,6,7,8,8a-decahydro-5,6-diaza-8b-azonia-acenaphthylene (S8). To a solution of hemiaminal **37** (0.022 g, 0.04 mmol, 1.0 equiv) in methanol (2 mL) at 23 ˚C was added AcOH (0.015 mL, 0.20 mmol, 5.0 equiv), followed by 20% $Pd(OH)_2/C$ (0.016 g). The solution was stirred under an atmosphere of H_2 (1 atm) for 3 h. The reaction mixture was then filtered through celite and concentrated *in vacuo* to afford carboxylic acid **S8** (0.018 g, 99%) as a colorless oil. R_f = 0.2 (4:1 CH_2Cl_2/CH_3OH); (major) ^{1}H NMR (500 MHz, CD_3OD) δ 7.27 (m, 2H), 6.91 (m, 2H), 4.95 (dd, J = 3.3, 1.0 Hz, 1H), 4.69 (bs, 2H), 4.06 (ddd, J = 10.1, 5.6, 3.0 Hz, 1H), 3.86 (m, 2H), 3.78 (s, 3H), 3.04 (app t, J = 3.9 Hz, 1H), 2.27 (m, 2H), 1.86-1.68 (m, 4H), 1.21 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, CD_3OD) δ 197.5, 172.3, 160.8, 150.5, 130.5, 129.5, 115.2, 79.8, 58.6, 55.8, 52.6, 50.7, 45.7, 42.6, 36.5, 31.4, 29.7, 18.3; IR (neat film) 3417, 2928, 1714, 1614, 1514, 842; HRMS $(ESI)^+$ *m/z* calcd for $C_{19}H_{26}N_3O_4$ $[MH]^+$ 360.1923, found 360.1941.

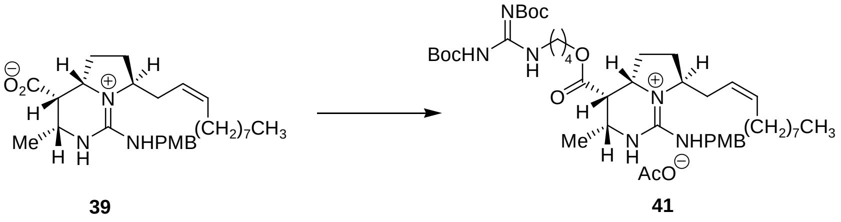


S8

39

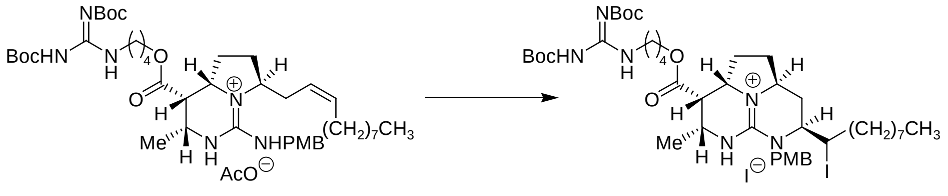
4-Carboxy-1-(4-methoxy-benzylamino)-3-methyl-7-undec-2-enyl-3,4,4a,5,6,7-hexahydro-2H-pyrrolo[1,2-c]pyrimidin-8-ylium (39). To a solution of carboxylic acid **S8**

(0.017 g, 0.034 mmol, 1.0 equiv) in THF (0.20 mL) was added the ylide derived from triphenyl phosphonium bromide (0.34 mL of a 0.45M solution in THF, 0.15 mmol, 4.5 equiv) at 50 ˚C. The reaction mixture was then stirred at this temperature for 18 h. The reaction mixture was then quenched with AcOH (0.0.20 mL), diluted with dichloromethane (3 mL) and concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (9:1 CH_2Cl_2/CH_3OH then 4:1 CH_2Cl_2/CH_3OH) to afford alkene **39** (0.015 g, 72%) as a colorless oil. R_f = 0.3 (4:1 CH_2Cl_2/CH_3OH); ^{1}H NMR (500 MHz, CD_3OD) δ 7.31 (m, 2H), 6.92 (m, 2H), 5.54 (m, 1H), 5.36 (m, 1H), 4.48 (AB, J = 15.4 Hz, 1H), 4.36 (AB, J = 15.4 Hz, 1H), 4.09 (m, 1H), 3.85 (m, 1H), 3.79 (s, 3H), 3.66 (dq, J = 6.8, 4.2 Hz, 1H), 2.70 (app t, J = 4.3 Hz, 1H), 2.45-2.33 (m, 2H), 2.22-2.11 (m, 2H), 2.00 (m, 2H), 1.88 (m, 1H), 1.76 (m, 1H), 1.36 (d, J = 6.8 Hz, 3H), 1.38-1.25 (m, 12H), 0.90 (t, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 161.0, 153.5, 135.2, 130.3, 130.0, 124.8, 115.3, 111.4, 61.3, 59.4, 55.9, 50.0, 49.1, 48.4, 45.7, 33.2, 32.0, 30.8, 30.6, 30.6, 29.9, 29.0, 28.7, 23.9, 18.5, 14.6; FTIR (neat film) 3252, 2925, 2854, 1614, 1586, 1514, 1328, 1249; HRMS (ESI)$^+$ *m/z* calcd for $C_{28}H_{44}N_3O_5$ $[MH]^+$ 470.3383, found 470.3404.

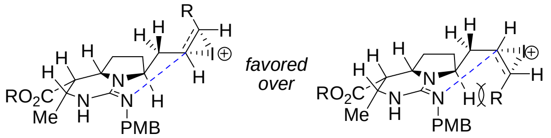


Ester 41. Cs_2CO_3 (5.0 mg, 0.015 mmol, 1.5 equiv) was added to a solution of carboxylic acid **39** (5.0 mg, 0.008 mmol, 1.0 equiv) and *N*^{2},*N*^{3}-Bis(*tert*-butoxycarbonyl)-*N*^{1}-(4-[methanesulfonyl)oxy]butyl)guanidine (22.0 mg, 0.05 mmol, 6.3 equiv) in DMF (0.150 mL) at 45 ˚C. The resulting suspension was stirred at this temperature for 18 h, and then quenched with AcOH (0.015 mL). The reaction mixture was diluted with acetonitrile (5 mL) and then concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (9:1 CH_2Cl_2/CH_3OH) to afford ester **41** (7.0 mg, 93%) as a colorless oil. R*f* = 0.2 (9:1 CH_2Cl_2/CH_3OH); ^{1}H NMR (500 MHz, CD_3OD) δ 7.30 (m, 2H), 6.92 (m, 2H), 5.57 (m, 1H), 5.35 (m, 1H), 4.51 (AB, J = 15.7 Hz, 1H), 4.42 (AB, J = 15.7 Hz, 1H), 4.16 (dt, J = 6.1, 1.9 Hz, 2H), 4.14 (m, 1H), 4.00 (ddd, J = 8.3, 6.9, 4.4 Hz, 1H), 3.83 (dq, J = 6.0, 3.2 Hz, 1H), 3.79 (s, 3H), 3.39 (dt, J = 7.1, 1.7 Hz, 2H), 3.12 (app t, J = 4.3 Hz, 1H), 2.45 (m, 1H), 2.37 (m, 1H), 2.23 (m,

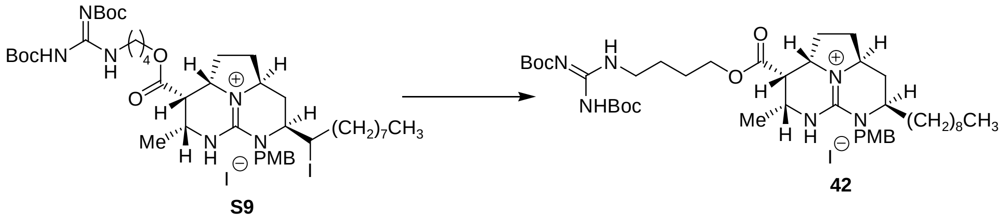
1H), 2.10 (m, 1H), 2.02 (m, 2H), 1.95 (s, 3H); 1.80 (m, 1H), 1.71-1.60 (m, 5H), 1.53 (s, 9H), 1.47 (s, 9H), 1.38-1.26 (m, 15H), 0.90 (t, J = 6.7 Hz, 3H); FTIR (neat film) 3333, 3152, 2928, 1723, 1633, 1415, 1135; HRMS (ESI)$^+$ *m/z* calcd for $C_{43}H_{71}N_6O_7$ $[MH]^+$ 783.5384, found 783.5367.



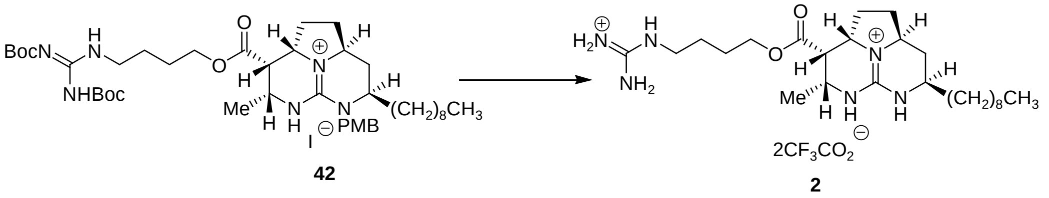
41 **S9**



Alkyl Iodide (S9). To a solution of ester **41** (5.0 mg, 0.005 mmol, 1.0 equiv) in dimethoxyethane (0.50 mL) at 23 ˚C was added potassium carbonate (3.0 mg, 0.02 mmol, 4.0 equiv) followed by iodide (6.0 mg, 0.02 mmol, 4.0 equiv). After stirring at this temperature for 24 h, the reaction was quenched with AcOH (0.015 mL), diluted with dichloromethane (5 mL), and concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (3:2 EtOAc/Hex) to afford alkyl iodide **S9** (4.0 mg, 70%) as a yellow oil. R_f = 0.3 (4:1 EtOAc/Hex); ^{1}H NMR (500 MHz, CD_3OD) δ 7.37 (m, 2H), 6.96 (m, 2H), 4.76 (AB, J = 15.3 Hz, 1H), 4.47 (dt, J = 11.7, 2.7 Hz, 1H), 4.29 (AB, J = 15.3 Hz, 1H), 4.23 (dt, J = 12.4, 5.9 Hz, 1H), 4.17 (dt, J = 12.4, 5.9 Hz, 1H), 4.16 (m, 1H), 4.00 (dq, J = 6.6, 5.0 Hz, 1H), 3.81 (s, 3H), 3.73 (ddd, J = 10.9, 7.9, 3.3 Hz, 1H), 3.55 (m, 1H), 3.41 (t, J = 6.7 Hz, 2H), 3.24 (dd, J = 4.8, 3.5 Hz, 1H), 2.79 (ddd, J = 13.2, 8.0, 2.8 Hz, 1H), 2.31 (m, 1H), 2.24 (m, 1H), 1.94-1.81 (m, 2H), 1.75-1.61 (m, 8H), 1.52 (s, 9H), 1.47 (s, 9H), 1.40-1.27 (m, 12H), 1.30 (d, J = 6.7 Hz, 3H) 0.92 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 170.9, 164.8, 161.6, 157.8, 154.4, 153.8, 131.1, 127.7, 115.1, 84.7, 80.6, 65.9, 61.2, 58.8, 56.8, 56.0, 51.0, 50.9, 45.5, 41.4, 34.9, 34.5, 34.3, 31.6, 31.2, 30.8, 30.6, 30.2, 29.8, 28.7, 28.4, 27.2, 27.0, 23.9, 18.6, 14.6; FTIR (neat film) 3314, 2924, 2848, 1727, 1613, 1514, 1328, 1251, 1174, 1135; HRMS (ESI)$^+$ *m/z* calcd for $C_{43}H_{70}N_6O_7I$ $[MH]^+$ 909.4351, found 909.4423.

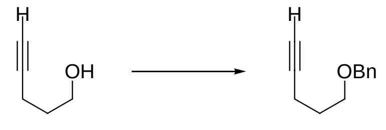


Ester 42. To a solution of alkyl iodide **S9** (3.0 mg, 0.003 mmol, 1.0 equiv) in ethyl acetate (1 mL) at 23 ˚C was added triethylamine (0.002 mL, 0.014 mmol, 5.0 equiv) and 10% Pd/C (5.0 mg). After the solution was rigorous degassed, a balloon of H_2 was inserted. The reaction was mixture was the allowed to stir for 4 h. The reaction mixture was then filtered through celite and concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (9:1 CH_2Cl_2/CH_3OH) to afford guanidine **42** (2.4 mg, 89%) as a yellow oil. R_f = 0.3 (9:1 CH_2Cl_2/CH_3OH); ^{1}H NMR (500 MHz, CD_3OD) δ 7.35 (m, 2H), 6.94 (m, 2H), 4.80 (AB, J = 15.4 Hz, 1H), 4.27 (dt, J = 12.8, 7.3 Hz, 1H), 4.24 (AB, J = 15.4 Hz, 1H), 4.17 (dt, J = 12.8, 6.4 Hz, 1H), 4.10 (m, 1H), 3.97 (dq, J = 6.6, 4.3 Hz, 1H), 3.80 (s, 3H), 3.49 (m, 1H), 3.41 (t, J = 6.8 Hz, 2H), 3.39 (m, 1H), 3.22 (dd, J = 4.8, 3.5 Hz, 1H), 2.41 (ddd, J = 13.0, 6.9, 2.5 Hz, 1H), 2.28 (m, 1H), 2.22 (m, 1H), 1.75-1.60 (m, 6H), 1.51 (s, 9H), 1.47 (s, 9H), 1.35-1.26 (m, 18H), 0.91 (t, J = 7.0 Hz, 3H); IR (neat film) 3326, 2968, 1727, 1614, 1514, 1464, 1166, 1034; HRMS $(FAB)^+$ *m/z* calcd for $C_{43}H_{71}N_6O_7$ $[MH]^+$ 783.5384, found 783.5381.



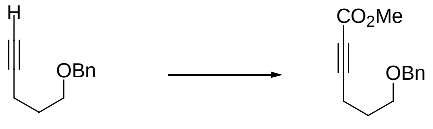
Batzelladine D ditrifluoroacetate (2). Trifluoroacetic acid (0.2 mL) was added to guanidine **42** (2.0 mg, 0.002 mmol, 1.0 equiv) at 23 ˚C. After stirring at this temperature for 12 h, the solution was diluted with methanol (2 mL) and concentrated *in vacuo* to afford batzelladine D bis(trifluoroacetate) salt **2** (1.4 mg, 82%) as a colorless oil. R_f = 0.3 (4:1 CH_2Cl_2/CH_3OH); 1H NMR (500 MHz, CD_3OD) δ 4.19 (t, J = 6.3 Hz, 2H), 3.97 (ddd, J = 10.5, 6.1, 3.3 Hz, 1H), 3.87 (dq, J = 6.7, 5.1 Hz, 1H), 3.55 (m, 2H), 3.22 (t, J = 7.0 Hz, 2H), 3.16 (dd, J

= 4.5, 3.1 Hz, 1H), 2.36 (ddd, J = 12.8, 5.1, 2.4 Hz, 1H), 2.23 (m, 2H), 1.76-1.54 (m, 6H), 1.42-1.27 (m, 17H), 1.27 (d, J = 7.0 Hz), 0.90 (t, J = 6.8 Hz, 3H); IR (neat film) 3354, 2928, 2856, 1726, 1681, 1651, 1644, 1455, 1205; HRMS (FAB)$^+$ *m/z* calcd for $C_{25}H_{47}N_6O_2$ $[MH]^+$ 463.3761; found 463.3763; $[\alpha]_D^{24}$ = -4.2 (*c* 0.56, MeOH).



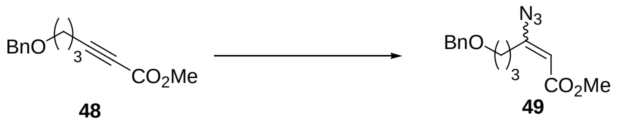
47 **S10**

Pent-4-ynyloxymethyl-benzene (S10). To a solution of **47** (6 mL, 64.2 mmol, 1.0 equiv) in THF (100 mL) cooled to 0 ˚C was added prewashed NaH (1.8 g, 70 mmol, 1.1 equiv) and stirred for 1 h. To this solution was added benzyl chloride (7.4 mL, 64.2 mmol, 1.0 equiv) and TBAI (0.1 g, 0.3 mmol, 0.04 equiv). This solution was heated at 70 ˚C for 8 h. After the solution had cooled to RT, it was diluted with ethyl acetate (300 mL), washed with water (2 X 300 mL), brine (200 mL), dried with sodium sulfate, filtered, and concentrated *in vacuo* to afford **S10** (9.0 g, 80%). Spectral data for **S10** was consistent with reported values.

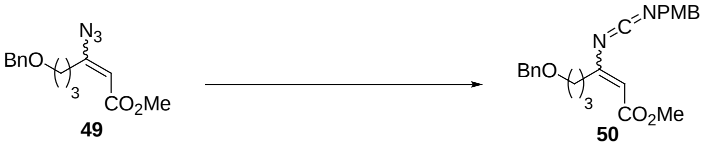


S10 **48**

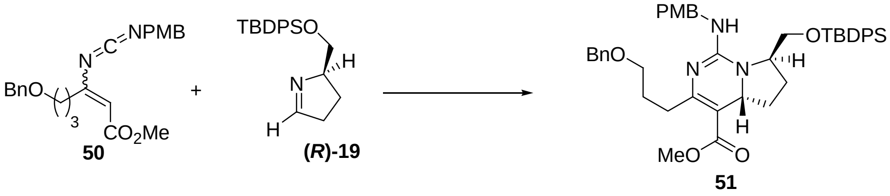
6-Benzyloxy-hex-2-ynoic acid methyl ester (48). To a solution of **S10** (9.0 g, 52 mmol, 1.0 equiv) in THF (150 mL) cooled to –78 ˚C, was added nBuLi (55 mL of a 1.6 M solution in hexanes, 75 mmol, 1.5 equiv). After stirring for 30 min, methyl chloroformate (8.2 mL, 104 mmol, 2.0 equiv) was added. The reaction was allowed to warm to RT and stirred for an additional 1 h. The reaction was then quenched with a saturated solution of NH_4Cl (50 mL), diluted with diethyl ether (300 mL), washed with water (2 X 300 mL), brine (300 mL), dried with magnesium sulfate, filtered, and concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (9:1 Hex/EA) to afford **48** (10.3g, 85%). Spectral data for **48** was consistent with reported values.


48 **49**

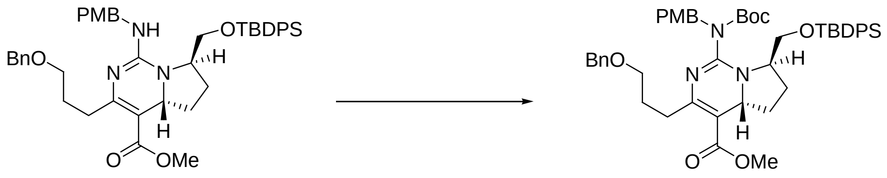
3-Azido-6-benzyloxy-hex-2-enoic acid methyl ester (49). Tetramethylguanidinium azide (7.0 g, 45 mmol, 1.5 equiv) was added to a stirring solution of **48** (7.0 g, 30.1 mmol, 1.0 equiv) in $CHCl_3$ (60 mL) at -10 °C (ice/acetone). The resulting solution was stirred for 1 h at -10 °C and then allowed to warm to RT over 16 h at which point the solution was diluted with CH_2Cl_2 (300 mL) and washed with water (3x200 mL). The combined organic layers were dried (sodium sulfate), filtered and concentrated. The clear light yellow oil was purified by flash column chromatography (4:1 Hex/EA) to provide *E*-**49** (4.0 g, 48%) as a clear light yellow liquid and *Z*-**49** (2.5 g, 30%) as a clear liquid. **49** (E). R*f* = 0.5 (4:1 Hex/EA); 1H NMR (500 MHz, $CDCl_3$) δ 7.38-7.26 (m, 5H), 5.53 (s, 1H), 4.51 (s, 2H), 3.69 (s, 3H), 3.53 (t, J = 6.4 Hz, 2H), 2.82 (m, 2H), 1.87 (m, 2H); ^{13}C NMR (125 MHz, CD_3OD) δ 166.4, 159.9, 145.3, 128.6, 127.9, 127.8, 104.5, 73.1, 69.6, 51.4, 28.1, 27.5; FTIR (neat film) 3064, 3030, 2949, 2856, 2111, 1719, 1619, 1496, 1435, 1264; HRMS $(ESI)^+$ *m/z* calcd for $C_{14}H_{18}N_3O_3$ $[M+H]^+$ 276.1348, found 276.1355. **49** (Z). R*f* = 0.3 (4:1 Hex/EA); 1H NMR (500 MHz, $CDCl_3$) δ 7.37-7.27 (m, 5H), 5.24 (s, 1H), 4.50 (s, 2H), 3.70 (s, 3H), 3.52 (t, J = 6.0 Hz, 2H), 2.47 (app t, J = 8.0 Hz, 2H), 1.88 (m, 2H); ^{13}C NMR (125 MHz, CD_3OD) δ 165.0, 152.7, 138.3, 128.7, 128.0, 127.9, 105.0, 73.3, 68.5, 51.4, 31.7, 27.7; FTIR (neat film) 3030, 2949, 2860, 2121, 1723, 1630, 1496, 1454, 1435, 1365, 1260; HRMS $(ESI)^+$ *m/z* calcd for $C_{14}H_{18}N_3O_3$ $[M+H]^+$ 276.1348, found 276.1353.


49 **50**

6-Benzyloxy-3-(4-methoxy-benzyliminomethyleneamino)-hex-2-enoic acid methyl ester (50). A solution of azides **49** (1.67 g, 6.1 mmol, 1 equiv) in dichloromethane (6 mL) was added drop wise to a solution of triphenylphosphine (1.57 g, 6.0 mmol, 0.98 equiv) in dichloromethane (10 mL) over 15 minutes. The resulting bright yellow solution was stirred for 4 h at 23 °C. The mixture was then concentrated under a stream of N_2 and then dissolved in toluene (10 mL). Methoxybenzylisocyanate (1.0 mL, 7.3 mmol, 1.2 equiv) was added. The reaction was stirred at 80 °C for 4h. The resulting mixture was cooled to ambient temperature and concentrated *in vacuo.* The residue was purified by silica gel flash chromatography (88 % Hex in EtOAc) to provide carbodiimide **50** (1.48 g, 63%) as a clear oil that turns light yellow upon standing. R*f* = 0.24 (5:1 Hex/EA); 1H NMR (500 MHz, $CDCl_3$) δ 7.35-7.20 (m, 7H), 6.86 (m, 2H), 5.46 (s, 1H), 4.49 (s, 2H), 4.42 (s, 2H), 3.78 (s, 3H), 3.65 (s, 3H), 3.47 (t, J = 6.5 Hz, 2H), 2.80 (m, 2H), 1.79 (m, 2H); **50** (Z). 1H NMR (500 MHz, $CDCl_3$) δ 7.38-7.25 (m, 5H), 7.21 (m, 2H), 6.87 (m, 2H), 5.49 (s, 1H), 4.50 (s, 2H), 4.42 (s, 2H), 3.77 (s, 3H), 3.66 (s, 3H), 3.49 (t, J = 6.5 Hz, 2H), 2.83 (m, 2H), 1.81 (m, 2H); ^{13}C NMR (125 MHz, CD_3OD) δ 167.2, 159.5, 159.2, 138.7, 133.5, 129.5, 128.9, 128.4, 127.7, 127.6, 114.3, 109.0, 72.9, 69.8, 55.3, 51.0, 49.9, 30.3, 28.0; FTIR (neat film) 3056, 2943, 2132, 1706, 1624, 1513, 1437 cm^{-1}; HRMS (ESI)$^+$ *m/z* calcd for $C_{23}H_{27}N_2O_4$ [M+H]$^+$ 395.1917, found 395.1971.

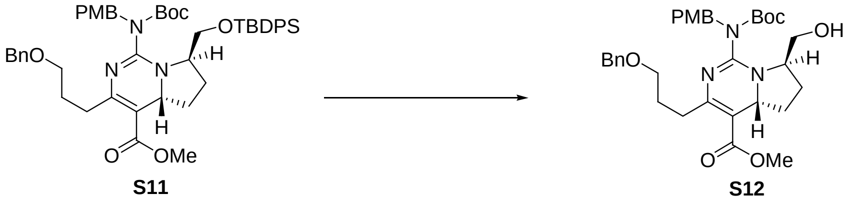


3-(3-Benzyloxy-propyl)-7-(tert-butyl-diphenyl-silanyloxymethyl)-1-(4-methoxy-benzylamino)-4a,5,6,7-tetrahydro-pyrrolo[1,2-c]pyrimidine-4-carboxylic acid methyl ester (51). To a solution of carbodiimide **50** (0.972, 2.5 mmol, 1.0 equiv) in dichloroethane (4 mL) was added imine **(*R*)-19** (1.1g, 3.3 mmol, 1.3 equiv) in dichloroethane (4 mL) at RT. After stirring for 14 h, the reaction mixture was concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (20:1 CH_2Cl_2/CH_3OH) to yield vinylogous carbamate **51** (1.61g, 89%) as a yellow oil. R*f* = 0.35 (20:1 DCM/MeOH); 1H NMR (500 MHz, $CDCl_3$) δ 7.68-7.21 (m, 15H), 7.14 (m, 2H), 6.78 (m, 2H), 6.40 (bt, J = 4.3 Hz, 1H), 4.78 (dd, J = 14.9, 6.6 Hz, 1H), 4.50 (s, 2H), 4.27 (dd, J = 10.2, 4.4 Hz, 1H), 4.19 (m, 1H), 4.08, (dd, J = 14.8, 3.4 Hz, 1H), 3.77 (s, 3H), 3.63 (s, 3H), 3.58 (t, J = 6.9 Hz, 2H), 3.48 (m, 2H), 2.92 (m, 1H), 2.66 (m, 1H), 2.35 (m, 1H), 1.98 (m, 2H), 1.82 (m, 1H), 1.47 (m, 1H), 1.03 (m, 1H), 0.95 (s, 9H); ^{13}C NMR (125 MHz, C_6D_6) δ 168.0, 163.2, 158.9, 155.1, 139.2, 136.8, 136.7, 132.4, 132.3, 132.1, 130.4, 130.3, 129.3, 128.5, 128.24, 128.2, 127.9, 127.5, 114.0, 98.0, 72.9, 71.2, 68.0, 62.4, 57.9, 55.5, 51.0, 44.5, 36.5, 33.0, 28.7, 27.0, 24.5, 19.2; FTIR (neat film) 3346, 2932, 2858, 1690, 1595, 1501, 1246, 1112, 1081; HRMS (ESI)$^+$ *m/z* calcd for $C_{44}H_{54}N_3O_5Si$ [M+H]$^+$ 732.3833, found 732.3815.



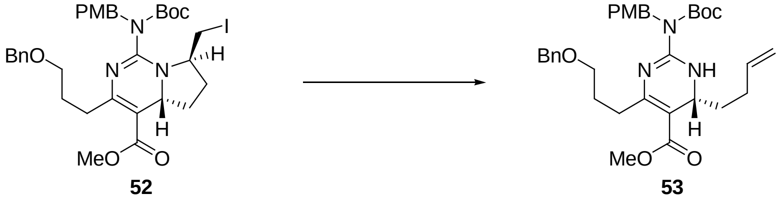
51 **S11**

3-(3-Benzyloxy-propyl)-1-[tert-butoxycarbonyl-(4-methoxy-benzyl)-amino]-7-(tert-butyl-diphenyl-silanyloxymethyl)-4a,5,6,7-tetrahydro-pyrrolo[1,2-c]pyrimidine-4-carboxylic acid methyl ester (S11). To a solution of **51** (0.370 g, 0.51 mmol, 1.0 equiv) in THF (5 mL) at 0 ˚C was added NaH (0.022g, 0.92 mmol, 1.8 equiv). After stirring for 30 min, DMAP (0.010 g, 0.08 mmol, .16 equiv) and Boc_2O (0.30 mL, 1.3 mmol, 2.5 equiv) were added and the solution was allowed to warm to RT. After stirring for 8 h, the solution was quenched with saturated NH_4Cl (1 mL) and then diluted with EtOAc (100 mL). The solution was washed with H_2O (2x100 mL) and brine (100 mL), dried (sodium sulfate), filtered, and then concentrated *in vacuo*. The yellow oil was purified by flash column chromatography (3:1 Hex/EtOAc) to provide **S11** (0.343 g, 81%) as a yellow oil. R*f* = 0.26 (3:2 Hex/EA); (all signals were severely broadened due to rotamers) 1H NMR (500 MHz, C_6D_6) δ 7.70-7.10 (br m, 17 H), 7.06 (br m, 2H), 6.45 (br s, 2H), 4.89 (br s, 1H), 4.66-4.40 (br m, 4H), 4.35- 4.00 (br m, 3H), 3.84-3.44 (br m, 8H), 3.13-2.22 (br m, 6H), 1.97 (br s, 2H), 1.73-1.16 (br m, 11H), 1.03 (br s, 9H); FTIR (neat film) 2932, 2858, 1714, 1613, 1514, 1429, 1368, 1249, 1113; HRMS (ESI)$^+$ *m/z* calcd for $C_{49}H_{62}N_3O_7Si$ [M+H]$^+$ 832.4357, found 832.4318.

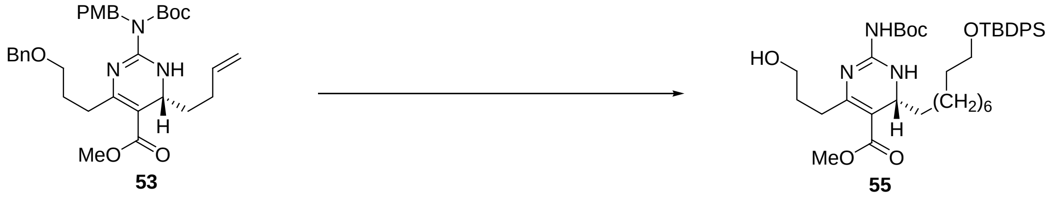


3-(3-Benzyloxy-propyl)-1-[tert-butoxycarbonyl-(4-methoxy-benzyl)-amino]-7-hydroxymethyl-4a,5,6,7-tetrahydro-pyrrolo[1,2-c]pyrimidine-4-carboxylic acid methyl ester (S12). To a solution of vinylogous carbamate **S11** (0.325 g, 0.4 mmol, 1.0 equiv) in THF (4 mL) was added AcOH (0.05 mL) followed by TBAF (1.6 mL of a 1M solution in THF, 1.6 mmol, 4.0 equiv). After stirring 2 h, the solution was diluted with EtOAc (100 mL). The solution was washed with H_2O (2x100 mL) and brine (100 mL), dried (sodium sulfate), filtered, and then concentrated *in vacuo*. The yellow oil was purified by flash column chromatography (1:1 Hex/EtOAc) to provide **S12** (0.210 g, 91%) as a yellow oil. R*f* = 0.2 (3:2 Hex/EA); 1H NMR (500 MHz, $CDCl_3$) δ 7.37-7.19 (m, 7H), 6.82 (m, 2H), 4.88 (brd, J = 14.0 Hz, 1H), 4.56-4.42 (m, 4H), 3.76 (s, 3H), 3.65 (s, 3H), 3.57 (t, J = 7.0 Hz, 2H), 3.36 (br m, 1H), 3.24 (br m, 1H), 2.97 (br m, 1H), 2.49 (br m, 1H), 2.20 (m, 2H), 1.51 (s, 9H), 1.17 (br m, 1H), 1.02 (br m, 1H), 0.78 (br m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 159.6, 158.2, 153.6, 139.0, 131.0, 128.5, 128.4, 127.8, 127.7, 127.6, 114.2, 105.2, 83.4, 73.0, 70.7, 63.0, 57.7, 55.5, 51.5, 51.2, 36.3, 31.9, 28.6, 28.5, 28.4, 22.1; FTIR (neat film) 3368, 2952, 1715, 1614, 1514, 1455, 1368, 1250, 1157, 1114; HRMS $(ESI)^+$ *m/z* calcd for $C_{33}H_{43}N_3O_7$ $[M+H]^+$ 594.3179, found 594.3162.

3-(3-Benzyloxy-propyl)-1-[tert-butoxycarbonyl-(4-methoxy-benzyl)-amino]-7-iodomethyl-4a,5,6,7-tetrahydro-pyrrolo[1,2-c]pyrimidine-4-carboxylic acid methyl ester (52). To a solution of **S12** (0.600 g, 1.0 mmol, 1.0 equiv) in toluene (10 mL) at RT was added triphenyl phosphine (0.400 g, 1.5 mmol, 1.5 equiv), imidazole (0.082 g, 1.2 mmol, 1.2 equiv), and iodine (0.382 g, 1.5 mmol, 1.5 equiv). After stirring for 1 h, the solution was diluted with EtOAc (250 mL), washed with H_2O (2x250 mL) and brine (100 mL), dried (sodium sulfate), filtered, and then concentrated *in vacuo*. The yellow residue was purified by flash column silica gel chromatography (3:2 Hex/EA) to afford **52** (0.690 g, 97%) as a bright yellow oil which was used immediately. (R*f* = 0.4 (3:2 Hex/EA); FTIR (neat film) 2935, 2848, 1707, 1611, 1513, 1432, 1368, 1249, 1154; HRMS (ESI)$^+$ *m/z* calcd for $C_{33}H_{42}IN_3O_6$ [M+H]$^+$ 704.2197, found 704.2173.



4-(3-Benzyloxy-propyl)-6-but-3-enyl-2-[tert-butoxycarbonyl-(4-methoxy-benzyl)-amino]-1,6-dihydro-pyrimidine-5-carboxylic acid methyl ester (53). To a solution of **52** (0.520 g, 0.74 mmol, 1.0 equiv) in THF (20 mL) at -78 ˚C was added *t*-BuLi (0.80 mL of a 1.7M solution in pentane, 1.55 mmol, 2.1 equiv) dropwise. After stirring at -78 ˚C for 20 min, the reaction was warmed to 23 ˚C and stirred for an additional 20 min at which point the reaction was quenched with a saturated solution of NH_4Cl (1 mL). The solution was then diluted with EtOAc (150 mL), washed with H_2O (200 mL), dried (sodium sulfate), filtered, and then concentrated *in vacuo*. The residue was purified by flash column silica gel chromatography (5:1 Hex/EA) to afford **53** (0.397 g, 93%) as a clear oil. R*f* = 0.4 (4:1 Hex/EA); 1H NMR (500 MHz, CD_3OD) δ 7.37-7.23 (m, 5H), 7.19 (m, 2H), 6.84 (m, 2H), 5.77 (m, 1H), 5.00-4.89 (m, 4H), 4.46-4.43 (m, 3H), 3.75 (s, 3H), 3.67 (s, 3H), 3.49 (t, J = 6.6 Hz, 2H), 2.81 (dt, J = 12.6, 7.8 Hz, 1H), 2.69 (dt, J = 12.6, 7.4 Hz, 1H), 2.10 (m, 1H), 1.99 (m, 1H), 1.82 (m, 2H), 1.57 –1.47 (m, 2H), 1.43 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 167.2, 161.9, 158.8, 155.2, 153.1, 138.2, 131.2, 128.9, 128.5, 127.8, 127.5, 115.0, 113.7, 102.5, 83.9, 72.8, 70.8, 55.4, 51.0, 50.1, 47.1, 35.3, 32.3, 29.0, 28.4, 28.2; FTIR (neat film)3315, 2947, 2853, 1698, 1612, 1532, 1514, 1485, 1149; HRMS (ESI)$^+$ *m/z* calcd for $C_{33}H_{44}N_3O_6$ [M+H]$^+$ 578.3230, found 578.3213



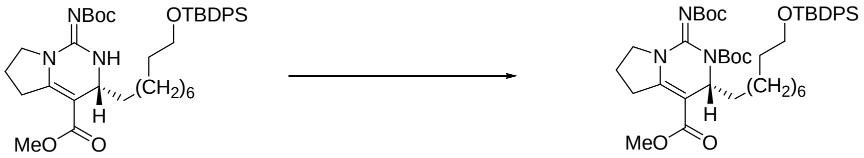
53 **55**

2-tert-Butoxycarbonylamino-6-[9-(tert-butyl-diphenyl-silanyloxy)-nonyl]-4-(3-hydroxy-propyl)-1,6-dihydro-pyrimidine-5-carboxylic acid methyl ester (55). To a solution of **53** (0.300 g, 0.68 mmol, 1.0 equiv) in CH_2Cl_2 (2.0 mL), was added **54** (1.0 g, 2.8 mmol, 4.0 equiv) and G2 (0.014 g, 0.02 mmol, .03 equiv). After stirring at 45 ˚C for 15 h, the solution was purified by flash column silica gel chromatography (7:2:1 Hex/Benzene/EA) to afford **S13** (0.340 g, 73%). To a solution of **S13** (0.180 g, 0.20 mmol, 1.0 equiv) in CH_2Cl_2/MeOH (1:6) (7.0 mL) was added AcOH (0.030 mL) followed by 10% $Pd(OH)_2$/C (100 mg). After the solution was rigorous degassed, a balloon of H_2 was inserted. The reaction mixture was then allowed to stir for 48 h. The reaction mixture was then filtered through celite and concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (1:1 Hex/EA) to afford **55** (0.132 g, 90%) as a clear oil. R*f* = 0.15 (1:1 Hex/EA); 1H NMR (500 MHz, CD_3OD) δ 7.65 (m, 4H), 7.45-7.33 (m, 6H), 4.38 (dd, J = 6.9, 4.7 Hz, 1H), 3.71 (s, 3H), 3.66 (t, J = 6.5 Hz, 2H), 3.60 (t, J = 6.5 Hz, 2H), 2.84 (m, 1H), 2.73 (m, 1H), 1.80 (m, 2H), 1.66-1.49 (m, 3H), 1.46 (s, 9H), 1.43-1.21 (m, 10H), 1.03 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.9, 155.2, 152.5, 151.2, 135.8, 134.3, 129.7, 127.8, 113.9, 86.9, 64.2, 60.7, 52.4, 51.0, 36.5, 32.8, 30.9, 29.7, 29.3, 28.1, 27.5, 27.0, 26.9, 26.0, 25.9, 24.4, 19.4; FTIR (neat film) 3314, 2947, 2853, 1698, 1640, 1612, 1532, 1514, 1392, 1149; HRMS $(ESI)^+$ *m/z* calcd for $C_{39}H_{60}N_3O_6Si$ $[M+H]^+$ 694.4251, found 694.4253.

55 **S14**

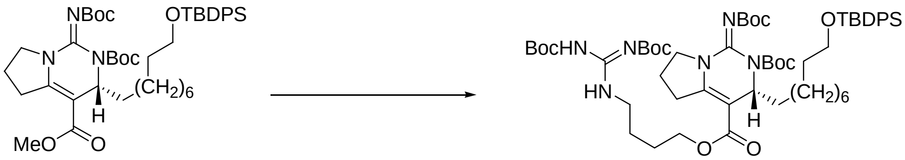
1-tert-Butoxycarbonylimino-3-[9-(tert-butyl-diphenyl-silanyloxy)-nonyl]-1,2,3,5,6,7-hexahydro-pyrrolo[1,2-c]pyrimidine-4-carboxylic acid methyl ester (S14). To a solution of **55** (0.080 g, 0.12 mmol, 1.0 equiv) in toluene (3 mL) was added triphenylphosphine

(0.050 g, 0.024 mmol, 2.0 equiv) and DIAD (0.060 mL, 0.024 mmol, 2.0 equiv). After stirring at 23 ˚C for 1 h, the solution was quenched with H_2O (0.02 mL) and concentrated *in vacuo.* The residue was purified by flash column silica gel chromatography (5:3:2 Hex/Benzene/EA) to provide **S14** (0.070 g, 90%) as a clear oil. R*f* = 0.4 (1:1 Hex/EA); 1H NMR (500 MHz, $CDCl_3$) δ 9.57 (bd, J = 3.7 Hz, 1H), 7.66 (m, 4H), 7.43-7.35 (m, 6H), 4.34 (app dt, J = 7.6, 3.7 Hz, 1H), 3.81 (m, 2H), 3.72 (s, 3H), 3.64, (t, J = 6.6 Hz, 2H), 3.24 (ddd, J = 18.2, 8.3, 4.2 Hz, 1H), 2.97 (app dt, J = 18.2, 9.4 Hz, 1H), 2.05-1.88 (m, 2H), 1.57-1.20 (m, 16H), 1.51 (s, 9H), 1.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 164.0, 155.8, 153.1, 135.8, 134.4, 129.7, 127.8, 99.4, 79.4, 64.2, 51.4, 50.6, 48.2, 37.2, 32.8, 32.0, 29.7, 29.6, 29.5, 28.5, 27.1, 26.0, 24.8, 21.6, 19.4, 8.7; FTIR (neat film) 3263, 2930, 2857, 1707, 1694, 1658, 1632, 1604, 1471, 1429; HRMS (ESI)$^+$ *m/z* calcd for $C_{39}H_{58}N_3O_5Si$ [M+H]$^+$ 676.4146, found 676.4139.



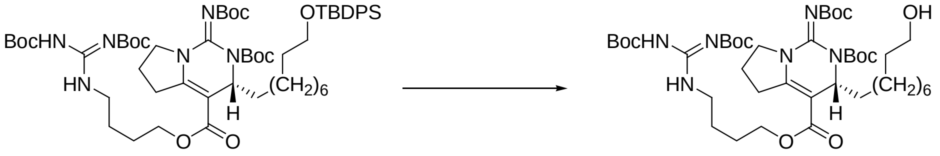
S14 **56**

1-tert-Butoxycarbonylimino-3-[9-(tert-butyl-diphenyl-silanyloxy)-nonyl]-3,5,6,7-tetrahydro-pyrrolo[1,2-c]pyrimidine-2,4-dicarboxylic acid 2-tert-butyl ester 4-methyl ester (56). To a solution of **S14** (0.100 g, 0.15 mmol, 1.0 equiv) in THF (2 mL) at 0 ˚C was added NaH (80%) (0.026g, 0.8 mmol, 6.0 equiv). After stirring for 15 min, DMAP (0.010 g, 0.08 mmol, .5 equiv) and Boc_2O (0.30 mL, 1.3 mmol, 2.5 equiv) were added and the solution was allowed to warm to RT. After stirring for 8 h, the solution was quenched with saturated NH_4Cl (1 mL) and then diluted with EtOAc (100 mL). The solution was washed with H_2O (2x100 mL) and brine (100 mL), dried (sodium sulfate), filtered, and then concentrated *in vacuo*. The yellow oil was purified by flash column chromatography (3:1 Hex/EtOAc) to provide **56** (0.098 g, 81%) as a yellow oil.R*f* = 0.46 (1:1 Hex/EA); 1H NMR (500 MHz, $CDCl_3$) δ 7.66 (m, 4H), 7.43-7.35 (m, 6H), 5.21 (dd, J = 8.2, 4.7 Hz, 1H), 3.95 (dt, J = 11.7, 7.7 Hz, 1H), 3.74 (s, 3H), 3.76-3.71 (m, 1H), 3.64 (t, J = 6.8 Hz, 2H), 3.23 (ddd, J = 18.0, 8.6, 4.5 Hz, 1H), 2.91 (app dt, J = 18.0, 9.0 Hz, 1H), 2.11- 1.93 (m, 2H), 1.60-1.23 (m, 16H), 1.51 (s, 9H), 1.49 (s, 9H), 1.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.2, 165.0, 159.1, 152.3, 151.1, 135.8, 134.4, 129.7, 127.8, 103.2, 83.4, 79.9, 64.2, 53.2, 51.5, 49.1, 33.8, 32.8, 31.4, 29.9, 29.8, 29.7, 29.6, 29.4, 28.5, 27.1, 26.0, 25.0, 21.6, 19.4; FTIR (neat film) 2930, 2856, 1741, 1697, 1614, 1457, 1428; HRMS (ESI)$^+$ *m/z* calcd for $C_{44}H_{66}N_3O_7Si$ [M+H]$^+$ 776.4670, found 776.4664.

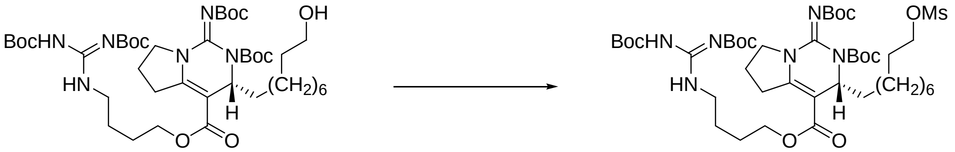


56 **58**

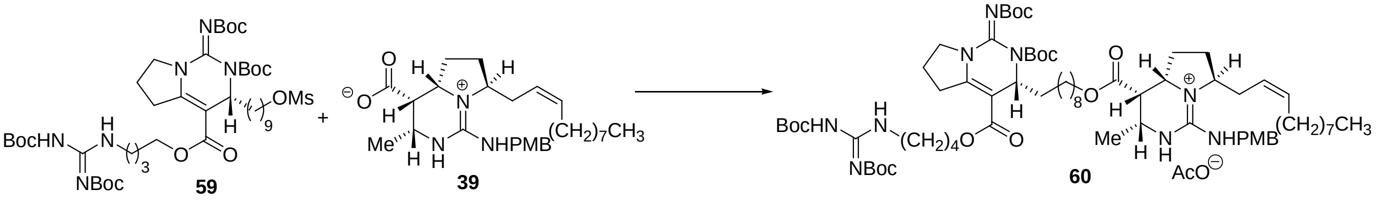
Vinylogous Carbamate 58. To **56** (0.044 g, 0.06 mmol, 1.0 equiv) was added a solution of EtSLi in HMPA (0.60 mL of a 1.6M solution). After stirring at 23 ˚C for 2 h, the reaction was quenched with a saturated solution of NH_4Cl (0.3 mL) and diluted with Et_2O (50 mL). After washing H_2O (5x30 mL), the combined aqueous layer was acidified to pH 3 with 0.1 N HCl and extracted with Et_2O (2x50 mL). The combined organic layers were then washed with 0.1N HCl (3x30 mL), dried (magnesium sulfate), filtered, and concentrated *in vacuo*. To a solution of the crude carboxylic acid in CH_2Cl_2 (0.20 mL), was added guanidine alcohol **57** (0.035 g, 0.1 mmol, 1.6 equiv), BOPCl (0.030 g, 0.1 mmol, 1.6 equiv), and Et_3N (0.025 mL, 0.17 mmol, 5 equiv). After stirring at 23 ˚C for 15 h, the solution was diluted with CH_2Cl_2 (2 mL) and concentrated *in vacuo*. The residue was purified by flash column silica gel chromatography (3:2 Hex/EA) to afford **58** (0.032 g, 55%). R*f* = 0.25 (7:3 Hex/EA); 1H NMR (500 MHz, $CDCl_3$) δ 11.50 (bs, 1H), 8.34 (bs, 1H), 7.66 (m, 4H), 7.43-7.35 (m, 6H), 5.21, (dd, J = 8.5, 4.2 Hz, 1H), 4.17, (m, 2H), 3.95 (app dt, J = 11.7, 8.0 Hz, 1H), 3.74 (ddd, J = 11.4, 8.6, 4.4, 1H), 3.63 (t, J = 6.6 Hz, 2H), 3.46 (m, 2H), 3.22 (ddd, J = 17.6, 8.5, 4.4 Hz, 1H), 2.91 (app dt, J = 18.0, 9.0 Hz, 1H), 2.11- 1.94 (m, 2H), 1.76-1.41 (m, 8H), 1.51 (s, 9H), 1.50 (s, 9H), 1.48 (s, 9H), 1.47 (s, 9H), 1.41-1.18 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ165.4, 159.1, 153.5, 152.2, 151.0, 145.0, 135.8, 134.4, 129.7, 127.8, 103.3, 83.3, 79.9, 77.4, 64.3, 64.25, 63.8, 53.2, 49.0, 33.9, 32.84, 32.8, 31.5, 29.9, 29.7, 29.6, 29.4, 28.5, 28.4, 28.34, 28.3, 28.2, 26.4, 26.05, 26.0, 25.99, 25.0, 21.6, 19.4; FTIR (neat film) 3333, 2930, 2856, 1741, 1720, 1695, 1640, 1614, 1456, 1244; HRMS (ESI)$^+$ *m/z* calcd for $C_{58}H_{91}N_6O_{11}Si$ [M+H]$^+$ 1075.6515, found 1075.6541.


58 **S15**

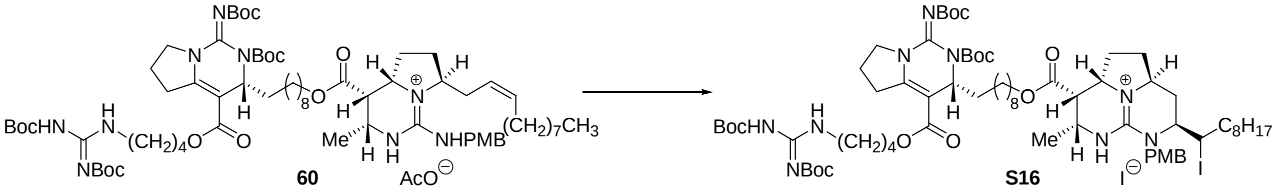
Vinylogous Carbamate S15. To a solution of **58** (0.020 g, 0.02 mmol, 1.0 equiv) in THF (0.40 mL) was added TBAF (0.03 mL of a 1M solution in THF, 0.03 mmol, 1.5 equiv). After stirring 30 min, the solution was diluted with dichloromethane (10 mL) and then concentrated *in vacuo*. The resulting residue was purified by silica gel flash chromatography (7:3 EA/Hex) to afford **S15** (0.015 g, 92%) as a clear oil. R*f* = 0.2 (1:1 Hex/EA); 1H NMR (500 MHz, $CDCl_3$) δ 11.5 (bs, 1H), 8.42 (bs, 1H), 5.21 (dd, J = 8.7, 4.5 Hz, 1H), 4.17 (m, 2H), 3.96 (dt, J = 11.7, 7.9 Hz, 1H), 4.37 (d, J = 14.4 Hz, 1H), 4.11 (ddd, J = 7.7, 6.8, 3.9 Hz, 1H), 3.74 (ddd, J = 12.3, 8.6, 4.5, 1H), 3.63 (t, J = 8.6 Hz, 2H), 3.50 (m, 2H), 3.23 (ddd, J = 17.8, 8.5, 4.4 Hz, 1H), 2.92 (app dt, J = 18.0, 9.0 Hz, 1H), 2.12-1.96 (m, 2H), 1.78-1.41 (m, 8H), 1.51 (s, 9H), 1.50 (s, 9H), 1.49 (s, 9H), 1.48 (s, 9H), 1.41-1.18 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.2, 163.6, 158.9, 156.2, 153.3, 152.1, 150.8, 144.8, 103.0, 83.2, 83.1, 79.7, 79.4, 63.6, 63.0, 53.0, 48.8, 40.5, 33.6, 32.8, 31.2, 29.7, 29.4, 29.3, 29.25, 29.0, 28.3, 28.1, 28.0, 26.3, 25.9, 25.7, 24.7, 21.4; FTIR (neat film) 3333, 2927, 2855, 1741, 1721, 1696, 1640, 1615, 1457; HRMS $(ESI)^+$ *m/z* calcd for $C_{42}H_{73}N_6O_{11}$ $[M+H]^+$ 837.5337, found 837.5362.


S15 **59**

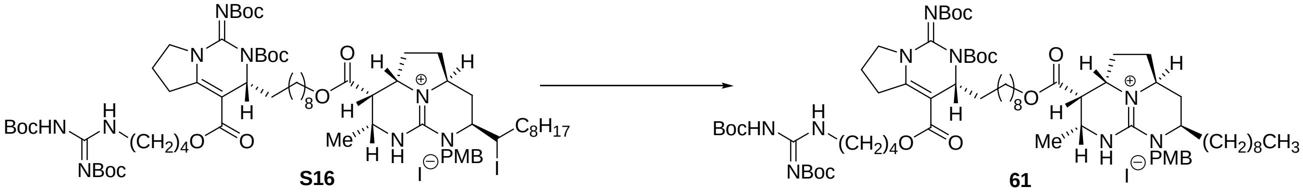
Mesylate 59. To a solution of **S15** (9.0 mg, 0.011 mmol, 1.0 equiv) in CH_2Cl_2 (0.40 mL) at 0 ˚C was added Et_3N (5.0 µL, 0.03 mmol, 2.5 equiv) followed by methanesulfonyl chloride (4.0 µL, 0.03 mmol, 2.5 equiv). After stirring for 1 h, the solution was diluted with H_2O (30 mL) and extracted with EtOAc (3x30 mL). The combined organic layer was dried (sodium sulfate), filtered, and then concentrated *in vacuo*. The residue was purified by flash column silica gel chromatography (1:1 Hex/EA) to afford **59** (9.5 mg, 97%) R*f* = 0.6 (3:2 EA/Hex); 1H NMR (500 MHz, $CDCl_3$) δ 11.50 (bs, 1H), 8.36 (bs, 1H), 5.21 (dd, J = 8.3, 4.4 Hz, 1H), 4.21 (t, J = 6.6 Hz, 2H), 4.16 (m, 1H), 3.95 (app dt, J = 11.7, 8.1 Hz, 1H), 3.74 (m, 1H), 3.47 (m, 1H), 3.22 (ddd, J = 18.0, 8.5, 4.4 Hz, 1H), 3.00 (s, 3H), 2.92 (app dt, J = 17.8, 9.0 Hz, 1H), 2.11-1.95 (m, 2H), 1.78-1.41 (m, 8H), 1.51 (s, 9H), 1.50 (s, 9H), 1.49 (s, 9H), 1.48 (s, 9H), 1.41-1.18 (m, 10H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.4, 163.2, 159.2, 156.4, 153.6, 152.3, 151.0, 145.0, 103.3, 83.33, 83.30, 79.9, 77.42, 70.41, 70.4, 63.8, 53.2, 49.1, 37.6, 33.8, 31.7, 31.5, 29.9, 29.6, 29.5, 29.4, 29.3, 29.2, 28.5, 28.4, 28.35, 28.3, 26.5, 26.0, 25.6, 21.6; FTIR (neat film) 3328, 2983, 1740, 1716, 1696, 1633, 1616, 1457, 1418; HRMS (ESI)$^+$ *m/z* calcd for $C_{43}H_{75}N_6O_{13}S$ $[M+H]^+$ 915.5113, found 915.5117.



Ester 60. Cs_2CO_3 (7.0 mg, 0.015 mmol, 1.4 equiv) was added to a solution of carboxylic acid **39** (5.0 mg, 0.008 mmol, 1.0 equiv) and mesylate **59** (7.0 mg, 0.008 mmol, 1.0 equiv) in DMF (0.20 mL) at 45 ˚C. The resulting suspension was stirred at this temperature for 18 h, and then quenched with AcOH (0.005 mL). The reaction mixture was diluted with acetonitrile (5 mL) and then concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (9:1 CH_2Cl_2/CH_3OH) to afford ester **60** (7.0 mg, 68%) as a colorless oil. R*f* = 0.20 (9:1 DCM/MeOH); 1H NMR (500 MHz, CD_3OD) δ 7.30 (m, 2H), 6.92 (m, 2H), 5.58 (m, 1H), 5.36 (m, 1H), 5.25 (dd, J = 8.4, 4.2 Hz, 1H), 4.50 (AB, J = 15.4 Hz, 1H), 4.42 (AB, J = 15.4 Hz, 1H), 4.25-4.07 (m, 3H), 4.00 (m, 1H), 3.88 (m, 1H), 3.82 (m, 1H), 3.79 (s, 3H), 3.72 (m, 1H), 3.40 (t, J = 6.7 Hz, 2H), 3.26 (ddd, J = 18.0, 8.2, 4.1 Hz, 1H), 3.09 (app t, J = 3.1 Hz, 1H), 3.02 (app dt, J = 18.0, 9.0 Hz, 1H), 2.46 (m, 1H), 2.37 (m, 1H), 2.26-1.98 (m, 7H), 1.95 (s, 3H); 1.84-1.54 (m, 10H), 1.53 (s, 9H), 1.49 (s, 9H), 1.48 (s, 9H), 1.47 (s, 9H), 1.45-1.25 (m, 30H), 0.90 (t, J = 6.8 Hz, 3H); FTIR (neat film) 3332, 2970, 2929, 2855, 1739, 1732, 1694, 1629, 1615, 1514, 1455, 1416, 1244, 1162, 1088; HRMS (ESI)$^+$ *m/z* calcd for $C_{70}H_{114}N_9O_{13}$ $[M+H]^+$ 1288.8536, found 1288.8484.

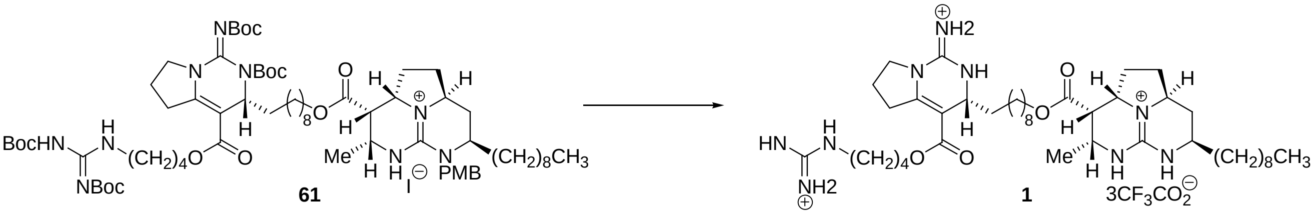


Alkyl Iodide S16. To a solution of ester **60** (4.0 mg, 0.003 mmol, 1.0 equiv) in dimethoxyethane (0.10 mL) at 23 ˚C was added cesium carbonate (3.0 mg, 0.009 mmol, 3.0 equiv) followed by iodide (2.0 mg, 0.018 mmol, 6.0 equiv). After stirring at this temperature for 18 h, the reaction was quenched with AcOH (0.015 mL), diluted with dichloromethane (5 mL), and concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (19:1 DCM/MeOH) to afford alkyl iodide **S16** (3.1 mg, 72%) as a yellow oil. R*f* = 0.40 (9:1 DCM/MeOH); 1H NMR (500 MHz, CD_3OD) δ 7.37 (m, 2H), 6.96 (m, 2H), 5.25 (dd, J = 8.5, 4.3 Hz, 1H), 4.76 (AB, J = 14.8 Hz, 1H), 4.47 (dt, J = 11.6, 2.8 Hz, 1H), 4.30 (AB, J = 14.8 Hz, 1H), 4.23-4.09 (m, 4H), 4.00 (m, 1H), 3.88 (m, 1H), 3.81 (s, 3H), 3.73 (m, 1H), 3.56 (m, 1H), 3.42 (t, J = 6.6 Hz, 2H), 3.26 (ddd, J = 18.1, 8.4, 4.4 Hz, 1H), 3.21 (app t, J = 2.8 Hz, 1H), 3.02 (app dt, J = 18.2, 9.1 Hz, 1H), 2.80 (m, 1H), 2.30 (m, 1H), 2.24 (m, 1H), 2.26-1.98 (m, 7H), 1.84-1.54 (m, 10H), 1.52 (s, 9H), 1.49 (s, 9H), 1.48 (s, 9H), 1.47 (s, 9H), 1.45-1.25 (m, 30H), 0.92 (t, J = 6.9 Hz, 3H); FTIR (neat film) 3313, 2971, 2925, 2852, 1734, 1721, 1700, 1685, 1654, 1638; HRMS (ESI)$^+$ *m/z* calcd for $C_{70}H_{113}IN_9O_{13}$ [M+2H/2]$^+$ 707.8785, found 707.8763.

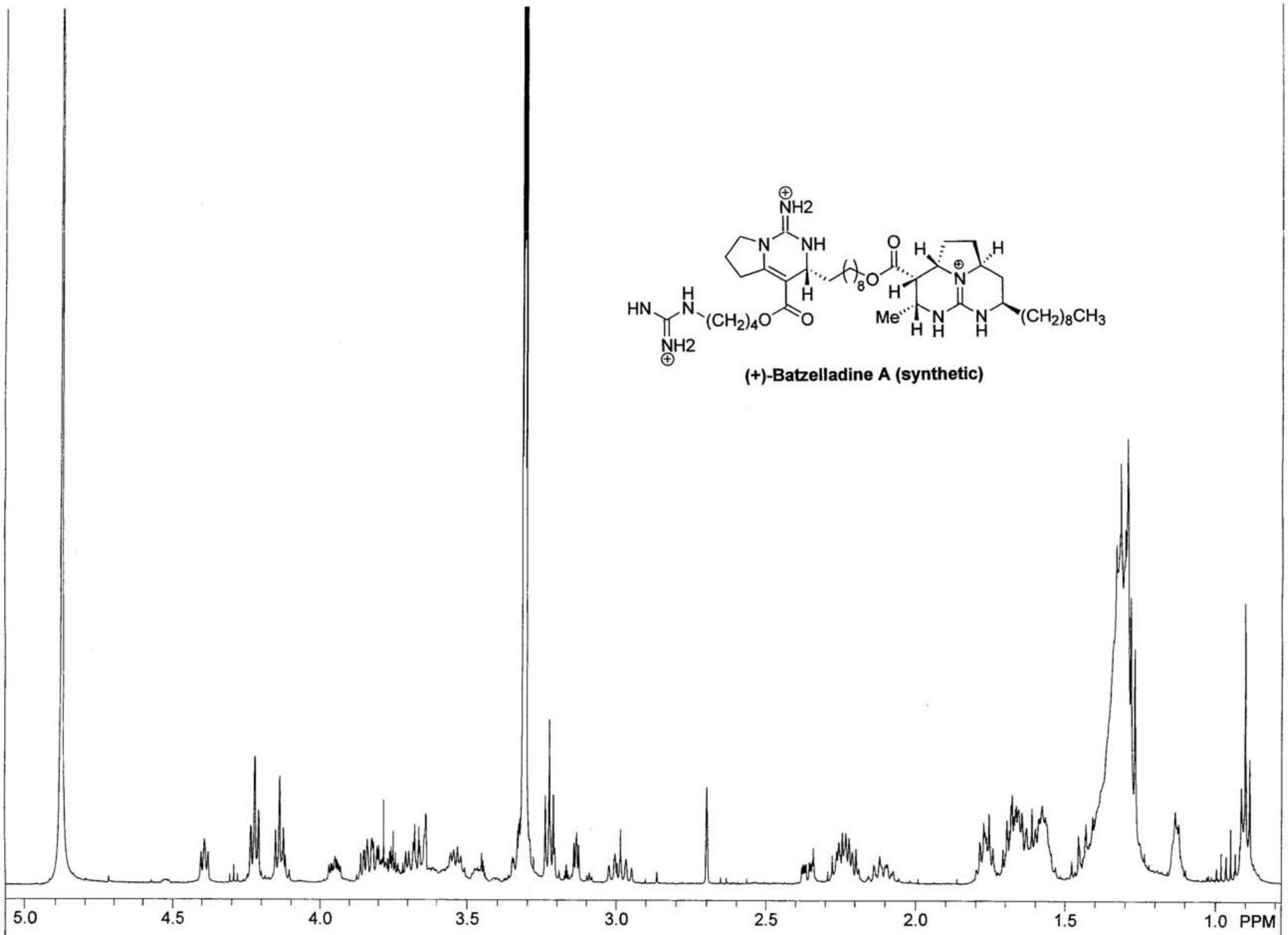


Guanidine 61. To a solution of alkyl iodide **S16** (3.1 mg, 0.002 mmol, 1.0 equiv) in ethyl acetate (0.30 mL) at 23 ˚C was added triethylamine (1 µL, 0.004 mmol, 2.0 equiv) and 10% Pd/C (2.0 mg). After the solution was rigorous degassed, a balloon of H_2 was inserted. The reaction was mixture was the allowed to stir for 5 h. The reaction mixture was then filtered through celite and concentrated *in vacuo*. The residue was purified by silica gel flash chromatography (9:1 CH_2Cl_2/CH_3OH) to afford guanidine **61** (2.0 mg, 71%) as a clear film. R*f* = 0.32 (9:1 DCM/MeOH); 1H NMR (500 MHz, CD_3OD) δ 7.35 (m, 2H), 6.94 (m, 2H), 5.25 (dd,

J = 7.5, 3.5 Hz, 1H), 4.81 (AB, J = 15.4 Hz, 1H), 4.24 (AB, J = 15.4 Hz, 1H), 4.24-4.05 (m, 3H), 3.95 (m, 1H), 3.89 (m, 1H), 3.80 (s, 3H), 3.71 (m, 1H), 3.62 (m, 1H), 3.49 (m, 1H), 3.41 (t, J = 6.7 Hz, 2H), 3.26 (ddd, J = 17.8, 8.2, 4.3 Hz, 1H), 3.19 (app t, J = 3.9 Hz, 1H), 3.02 (app dt, J = 18.3, 9.2 Hz, 1H), 2.41 (ddd, J = 12.8, 7.1, 1.3 Hz, 1H), 2.3-2.09 (m, 4H), 2.02 (m, 1H), 1.84-1.54 (m, 10H), 1.52 (s, 9H), 1.49 (s, 9H), 1.48 (s, 9H), 1.47 (s, 9H), 1.44-1.22 (m, 34H), 0.90 (t, J = 6.7 Hz, 3H); FTIR (neat film) 3313, 2971, 2925, 2852, 1734, 1721, 1700, 1685, 1654, 1638; HRMS (ESI)$^+$ *m/z* calcd for $C_{70}H_{115}N_9O_{13}$ [M+2H/2]$^+$ 644.9302, found 644.9291.



(+)-Batzelladine A tristrifluoroacetate (1). Trifluoroacetic acid (0.1 mL) was added to guanidine **61** (2.0 mg, 0.0015 mmol, 1.0 equiv) at 0 ˚C. After stirring at this temperature for 12 h, the solution was diluted with methanol (2 mL) and concentrated *in vacuo* to afford batzelladine A tris(trifluoroacetate) salt **1** (1.5 mg, 87%) as a colorless film. 1H NMR (500 MHz, CD_3OD) δ 4.39 (t, J = 6.1 Hz, 1H), 4.22 (t, J = 6.5 Hz, 2H), 4.14 (t, J = 6.5 Hz, 2H), 3.95 (ddd, J = 9.9, 6.1, 3.4 Hz, 1H), 3.83 (m, 2H), 3.67 (m, 1H), 3.54 (m, 1H), 3.32 (m, 1H), 3.23 (t, J = 7.1 Hz, 2H), 3.13 (dd, J = 4.6, 3.4 Hz, 1H), 2.99 (app dt, J = 18.2, 9.1 Hz, 1H), 2.36 (ddd, J = 12.9, 5.0, 2.4 Hz, 1H), 2.28-2.17 (m, 3H), 2.10 (m, 1H), 1.76 (m, 2H), 1.71-1.53 (m, 9H), 1.48-1.23 (m, 29H), 0.90 (t, J = 6.8 Hz, 3H); FTIR (neat film) 3350, 3189, 2928, 2853, 1733, 1697, 1682, 1651, 1641, 1548, 1347 cm^{-1}; HRMS (ESI)$^+$ *m/z* calcd for $C_{42}H_{74}N_9O_4$ [M+H]$^+$ 768.5864, found 768.5829; $[\alpha]_D^{24}$ = 4.34 (*c* 0.25, MeOH)..



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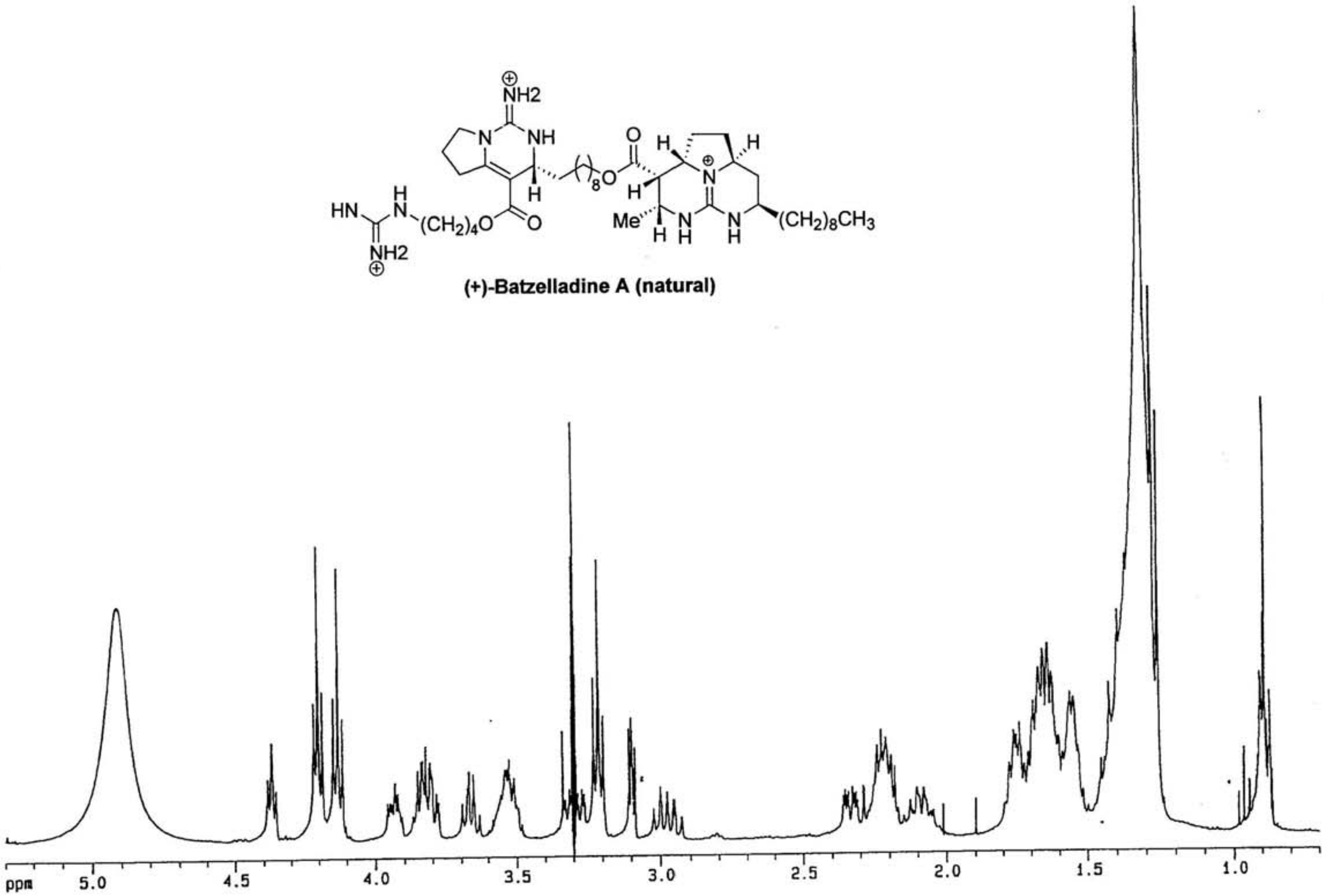
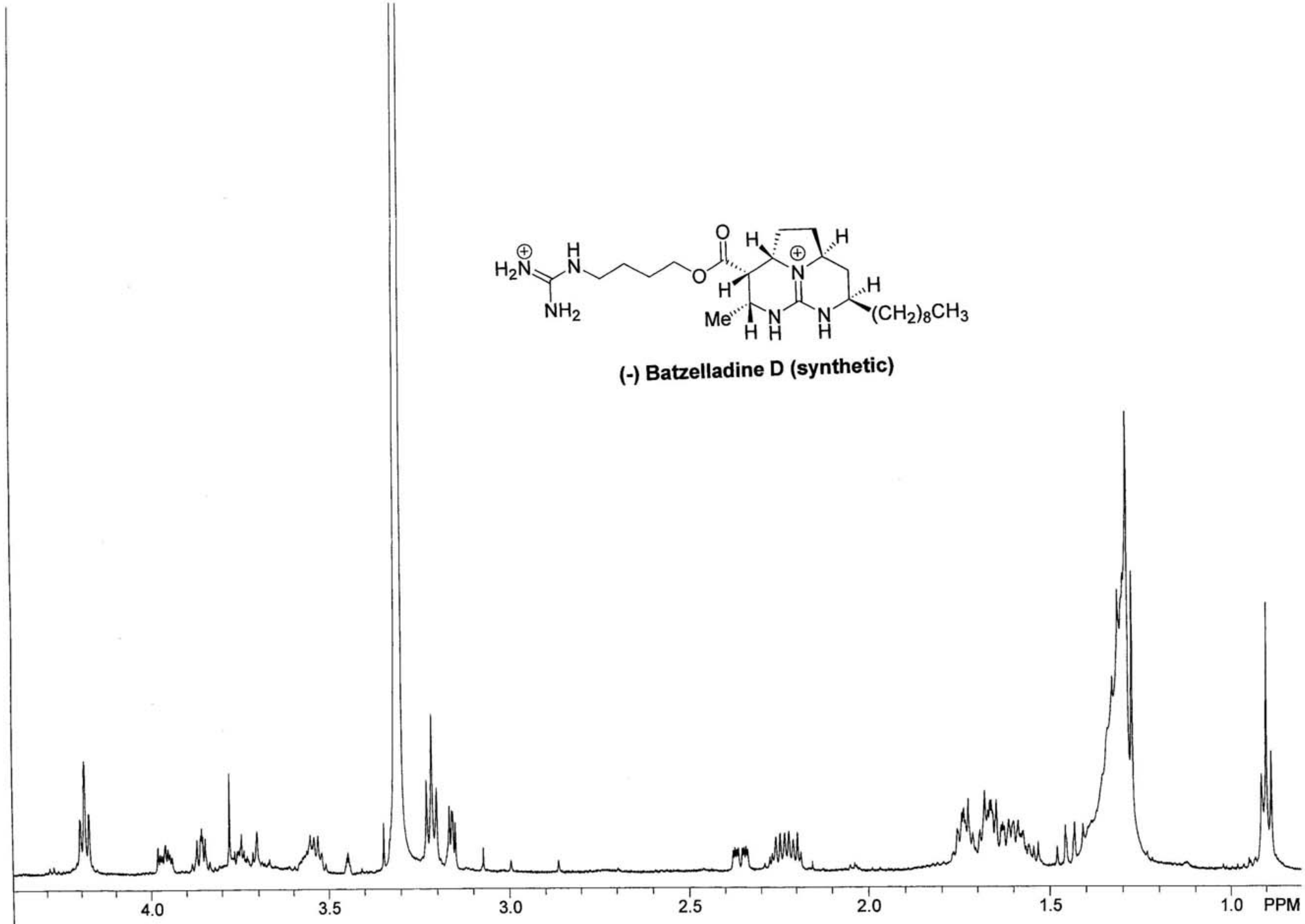
Proton NMR Spectrum of Batzelladine A in CD3OD



(+)-Batzelladine A (natural)



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STANDARD PROTON PARAMETERS

USER: -- DATE: Mar 22 2005

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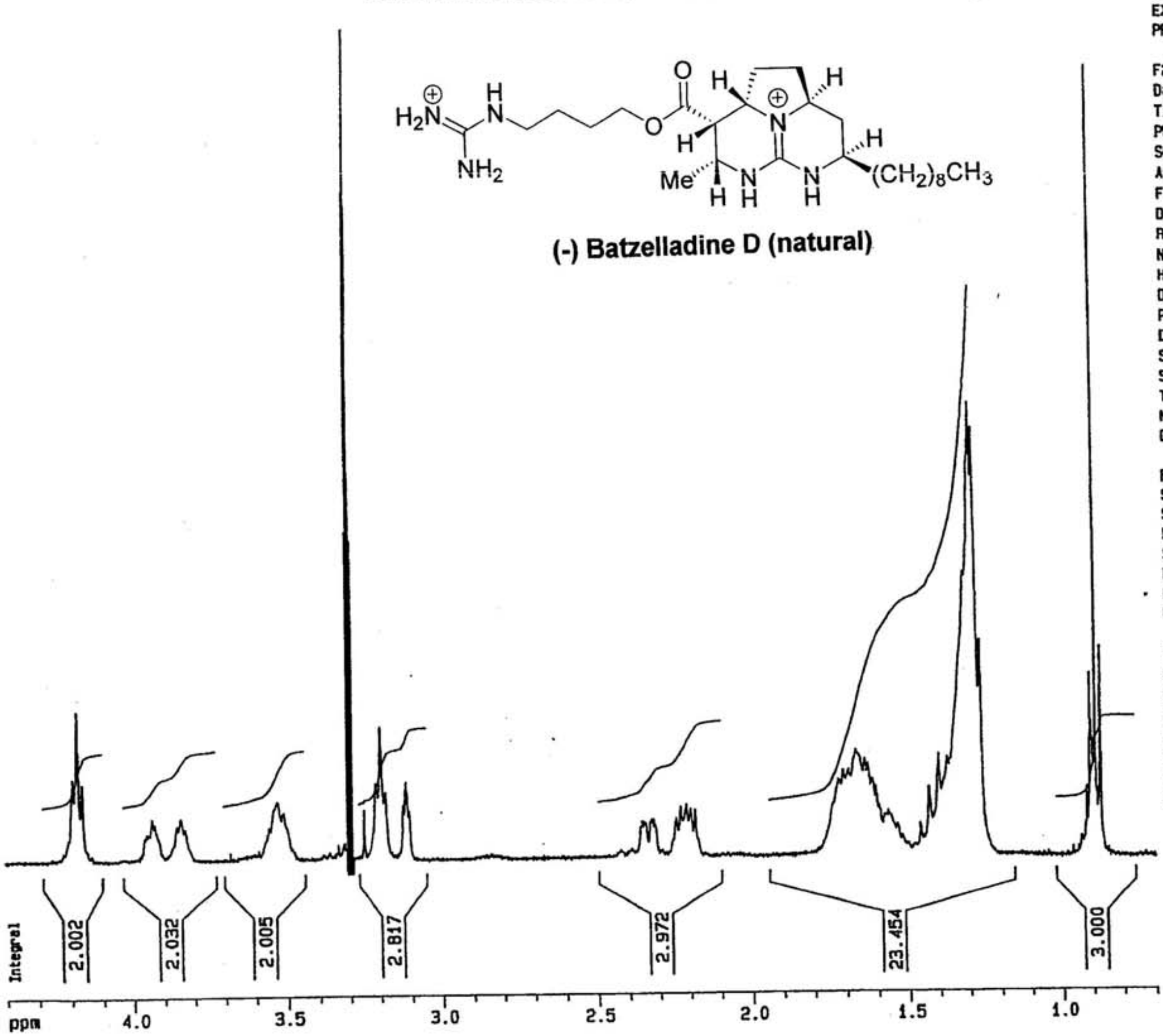
Batzelladine D Proton NMR Spectrum in CD3OD



(-) Batzelladine D (natural)

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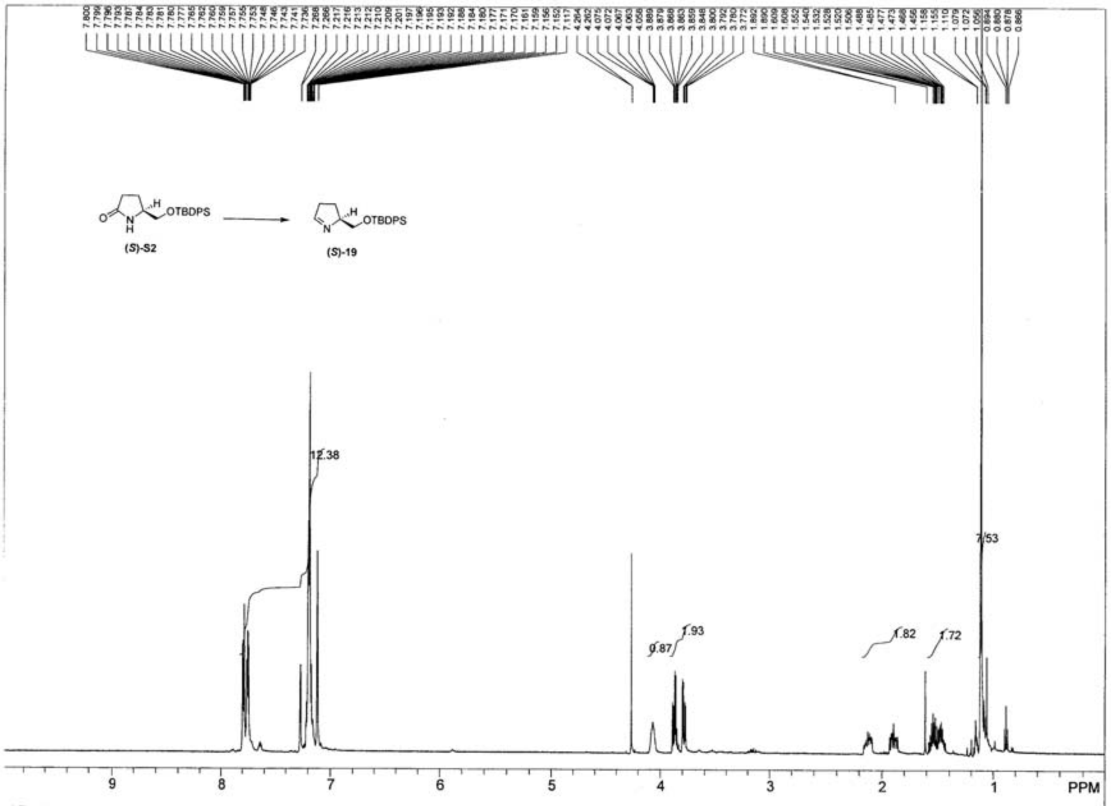

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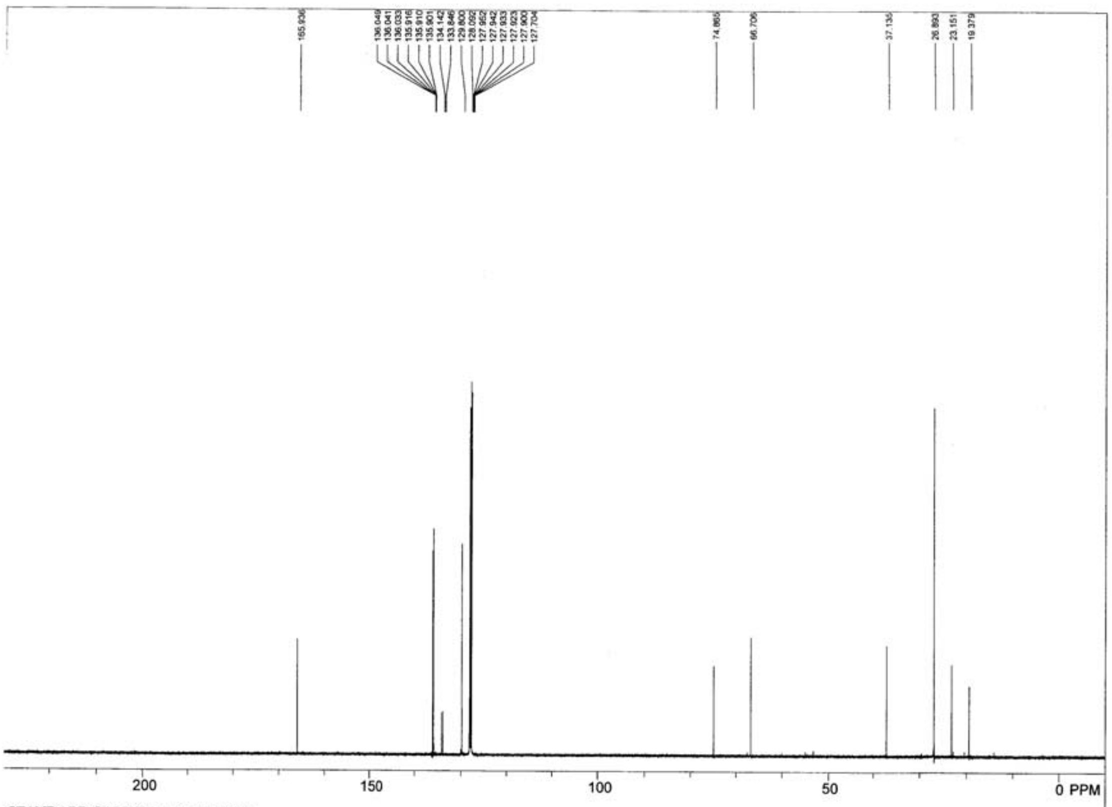

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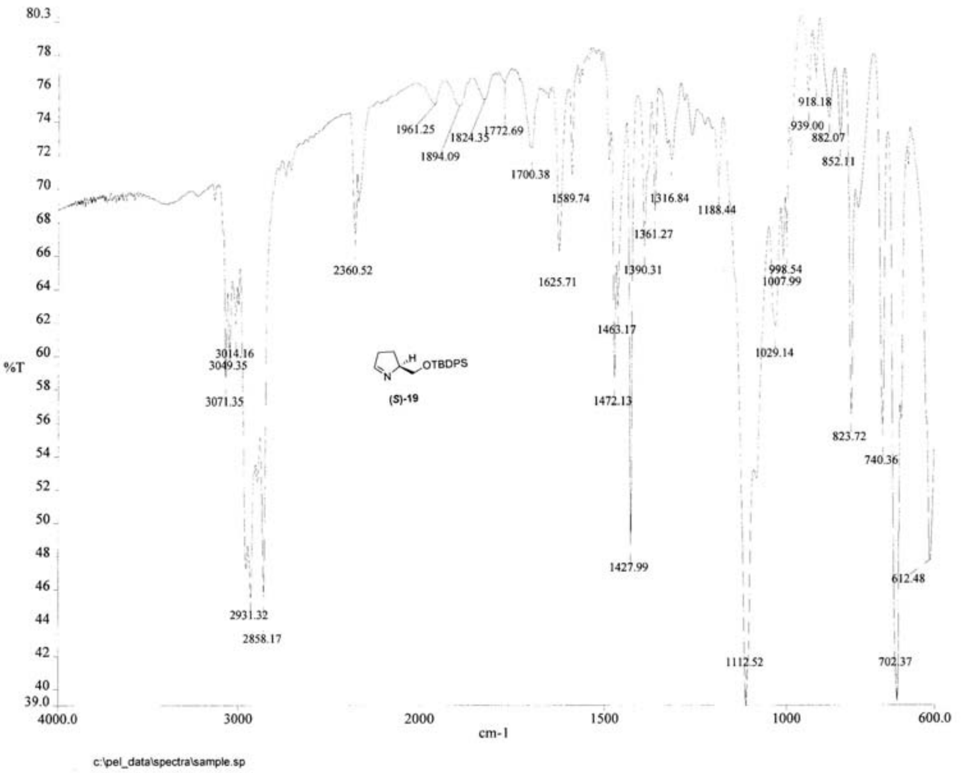
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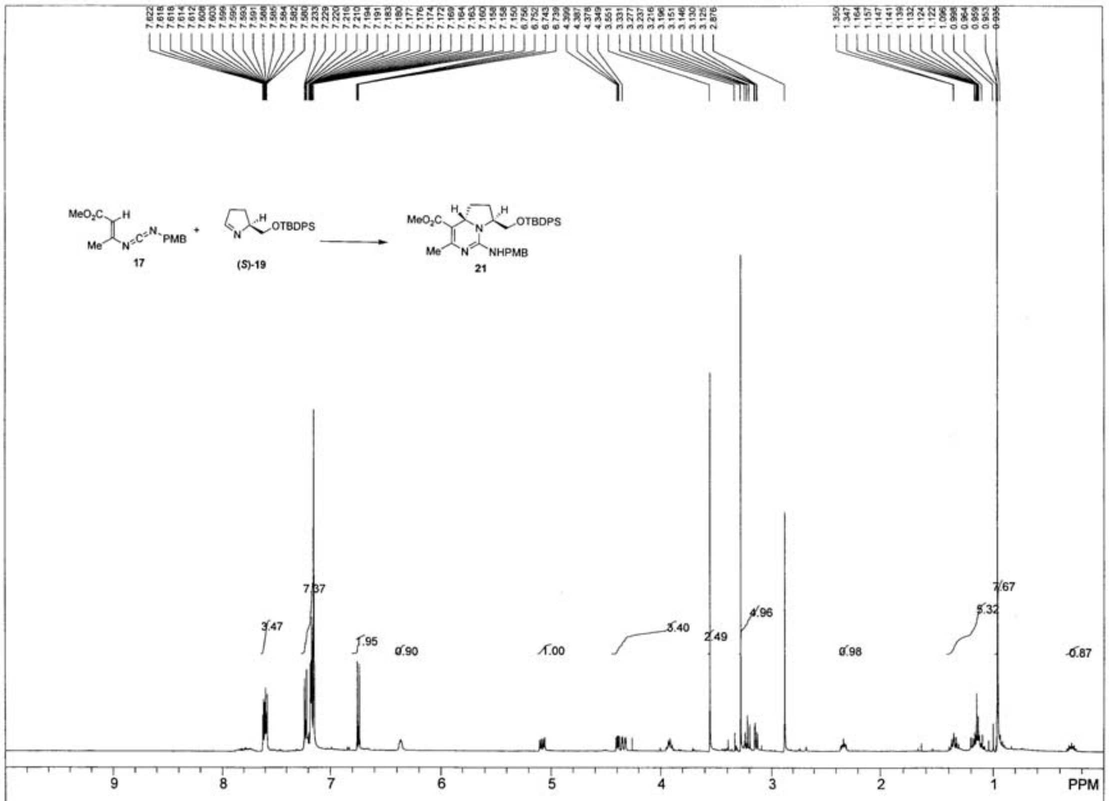

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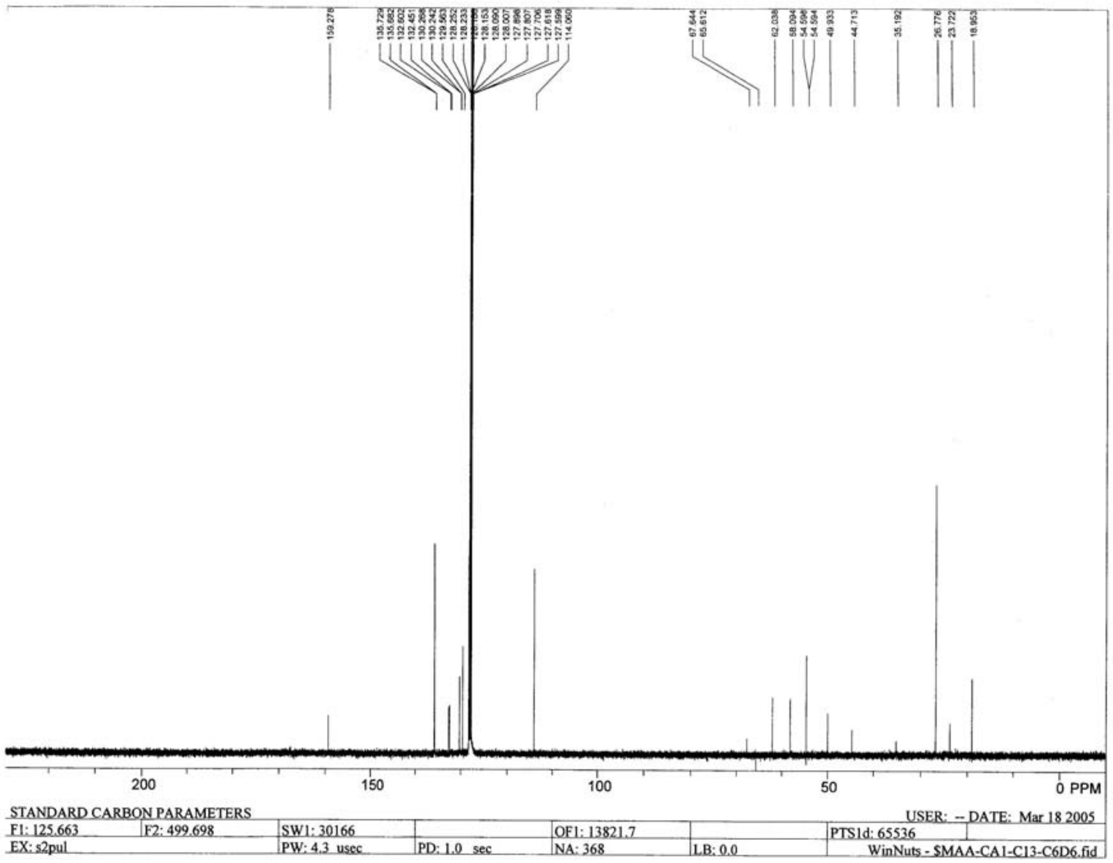
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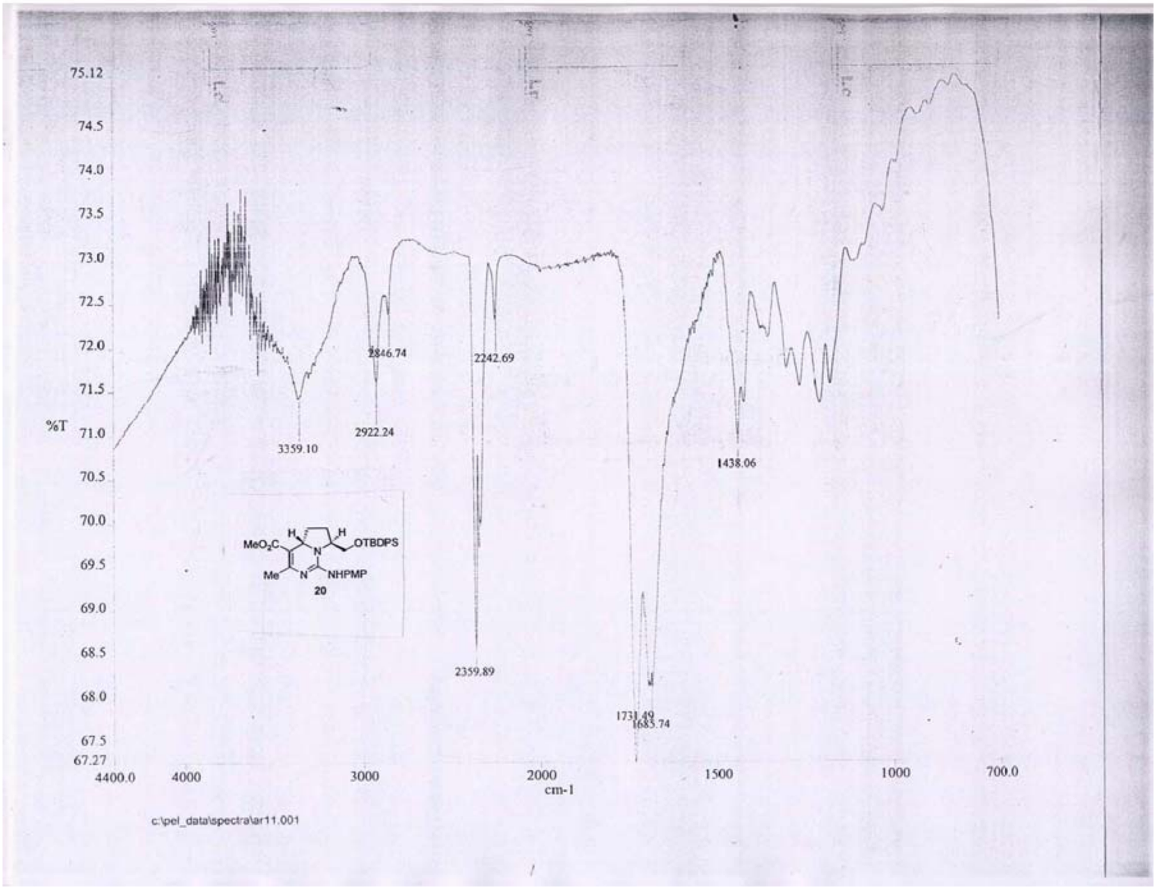
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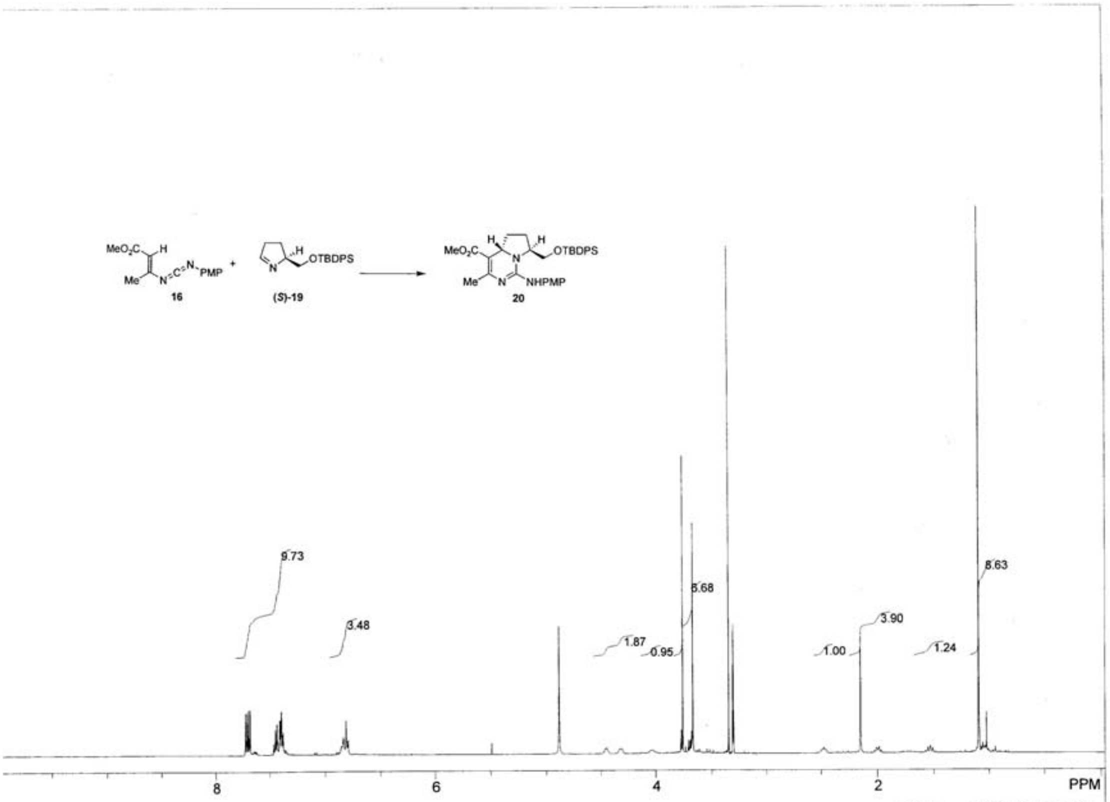

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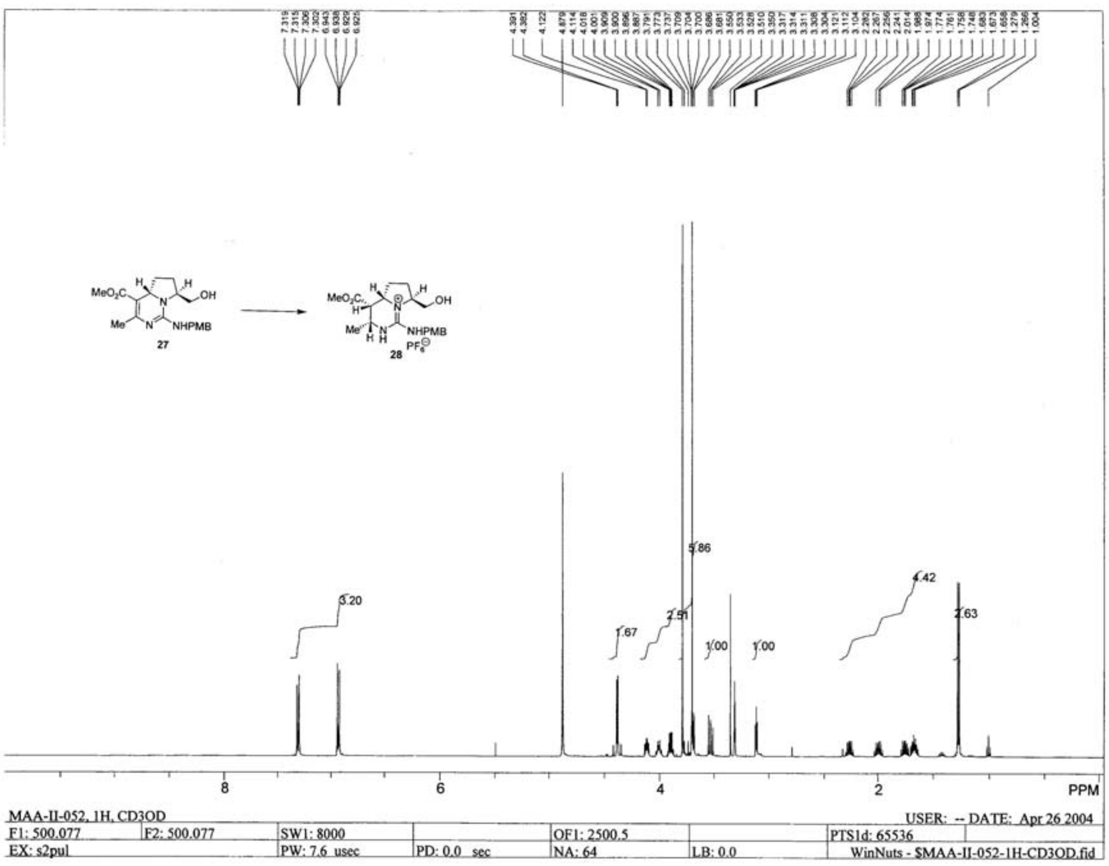
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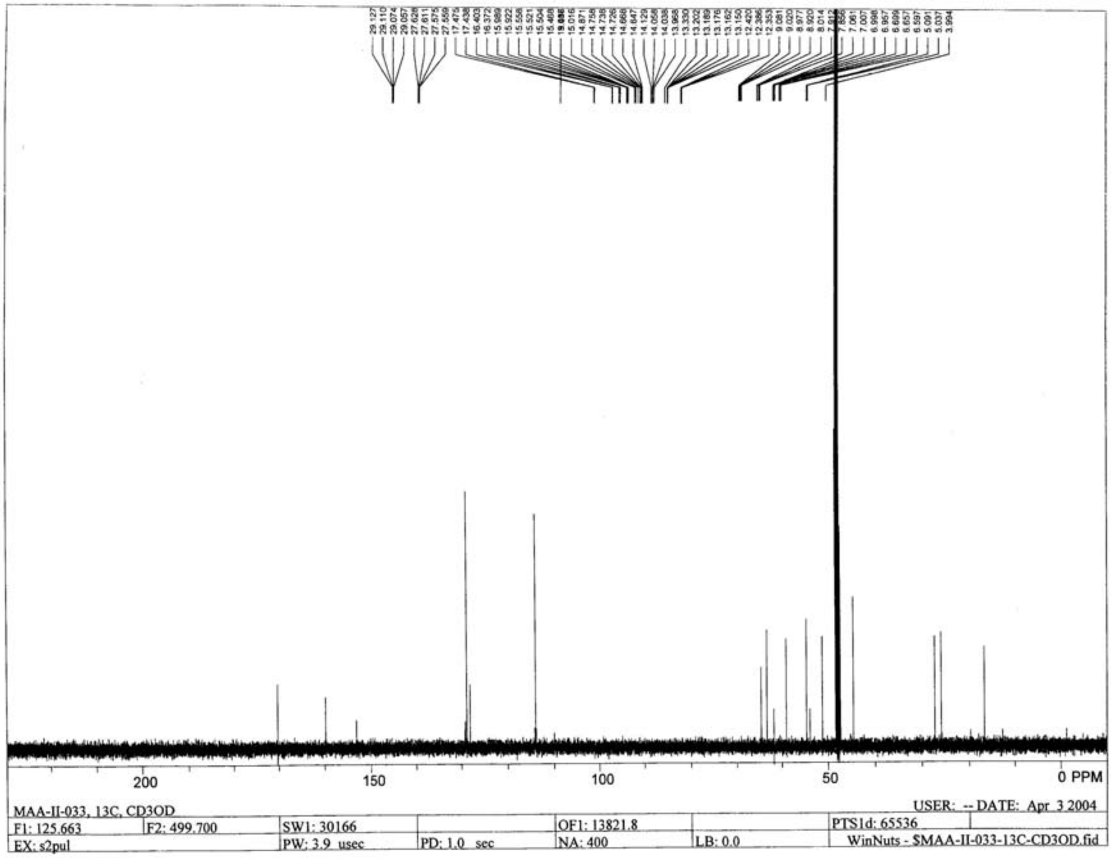
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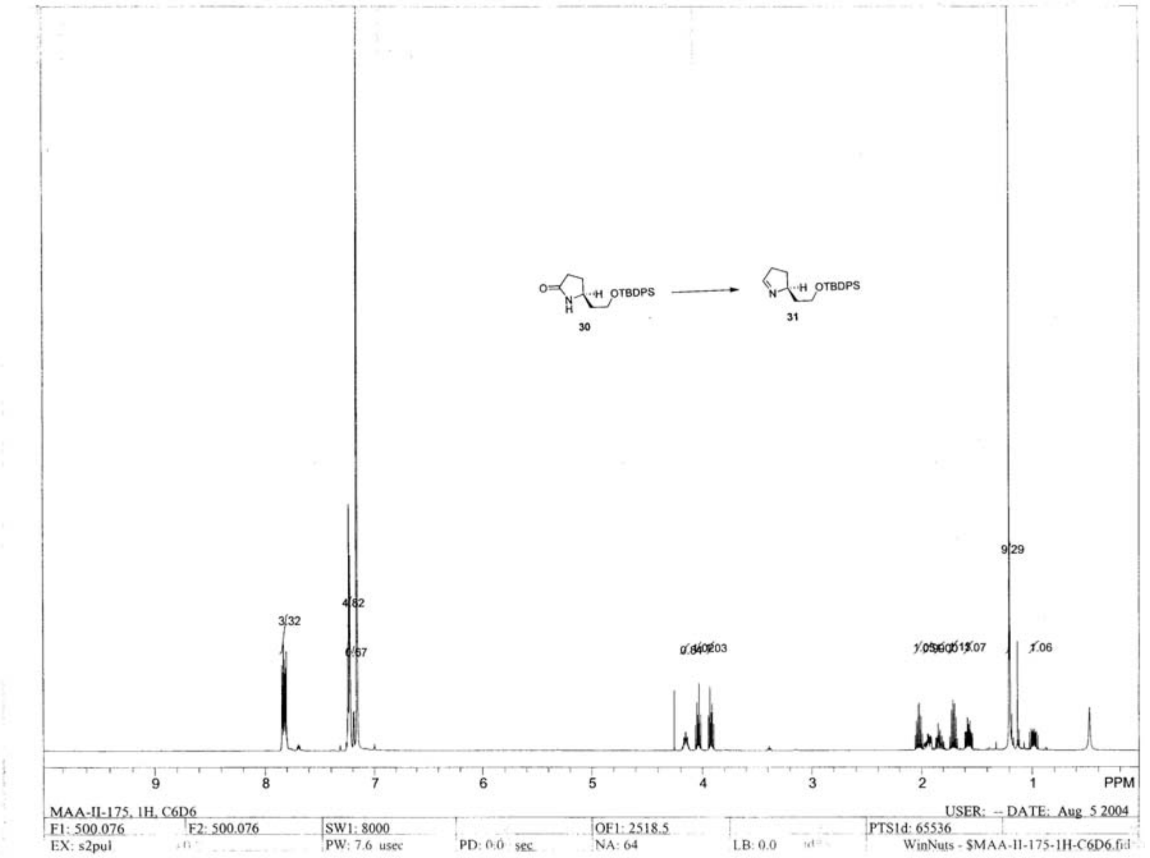
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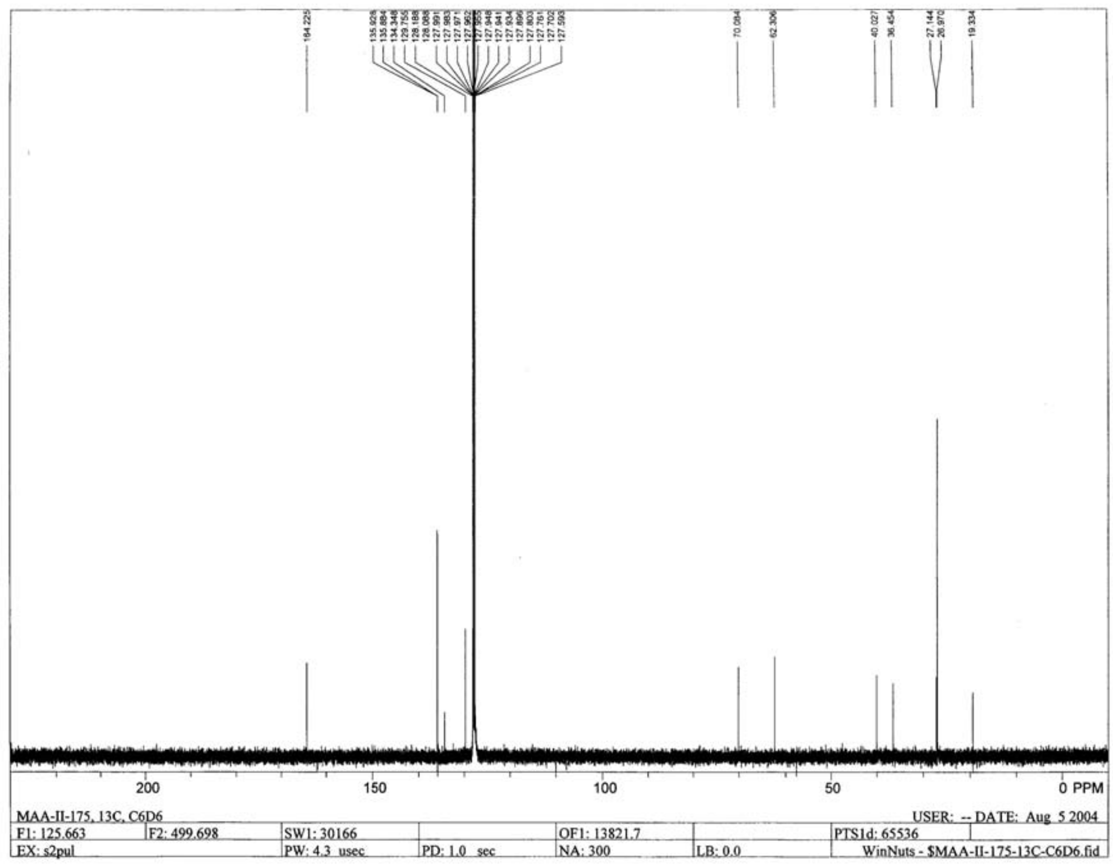
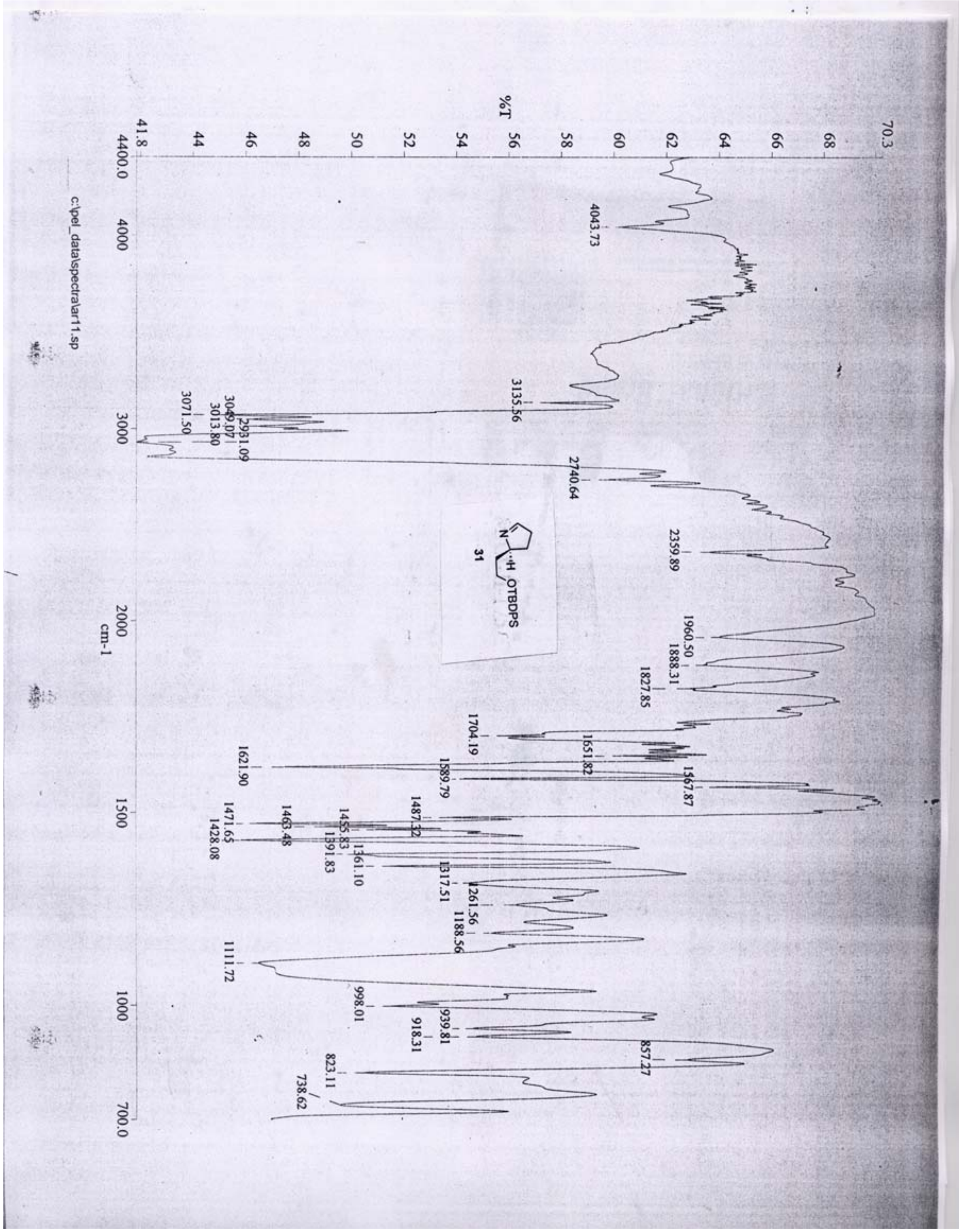
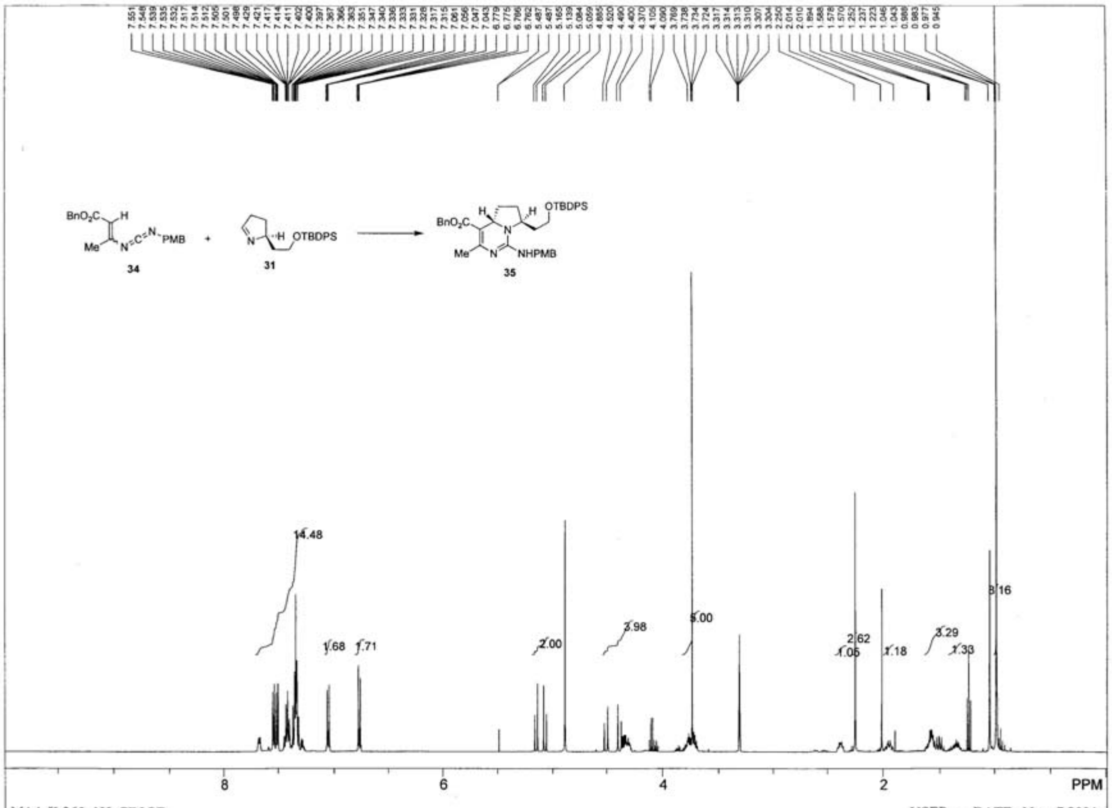
LB: 0.0
WinNuts - $MAA-II-175-1H-C6D6.fid

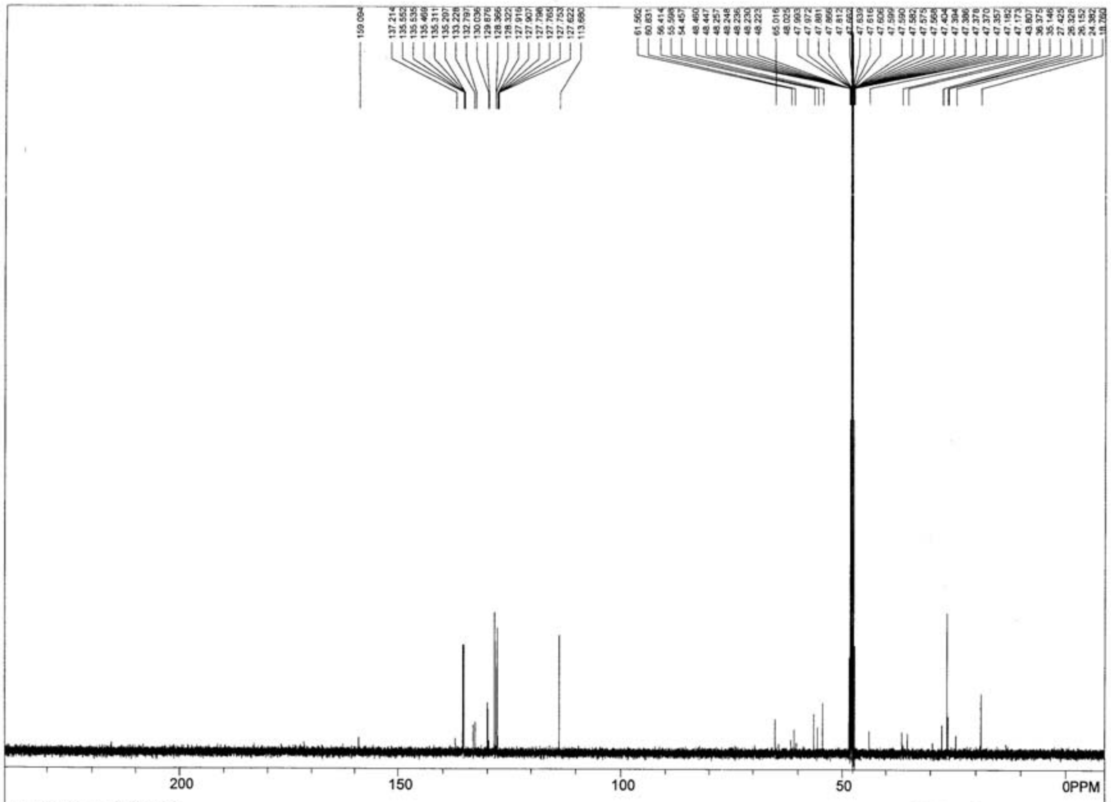

164.225
135.928
135.884
134.348
129.755
128.188
128.088
127.991
127.983
127.971
127.962
127.955
127.948
127.941
127.934
127.896
127.803
127.761
127.702
127.593
70.084
62.306
40.027
36.454
27.144
26.970
19.334
200
150
100
50
0 PPM
MAA-II-175, 13C, C6D6
USER: -- DATE: Aug 5 2004
F1: 125.663
F2: 499.698
SW1: 30166
OF1: 13821.7
PTS1d: 65536
EX: s2pul
PW: 4.3 usec
PD: 1.0 sec
NA: 300
LB: 0.0
WinNuts - $MAA-II-175-13C-C6D6.fid


%T
70.3
68
66
64
62
60
58
56
54
52
50
48
46
44
41.8
4400.0
4000
3000
2000
1500
1000
700.0
cm-1
4043.73
3135.56
3071.50
3049.07
3013.80
2931.09
2740.64
2359.89
1960.50
1888.31
1827.85
1704.19
1651.82
1621.90
1589.79
1567.87
1487.32
1471.65
1463.48
1455.83
1428.08
1391.83
1361.10
1317.51
1261.56
1188.56
1111.72
998.01
939.81
918.31
857.27
823.11
738.62
N
H
OTBDPS
31
c:\pel_data\spectra\ar11.sp



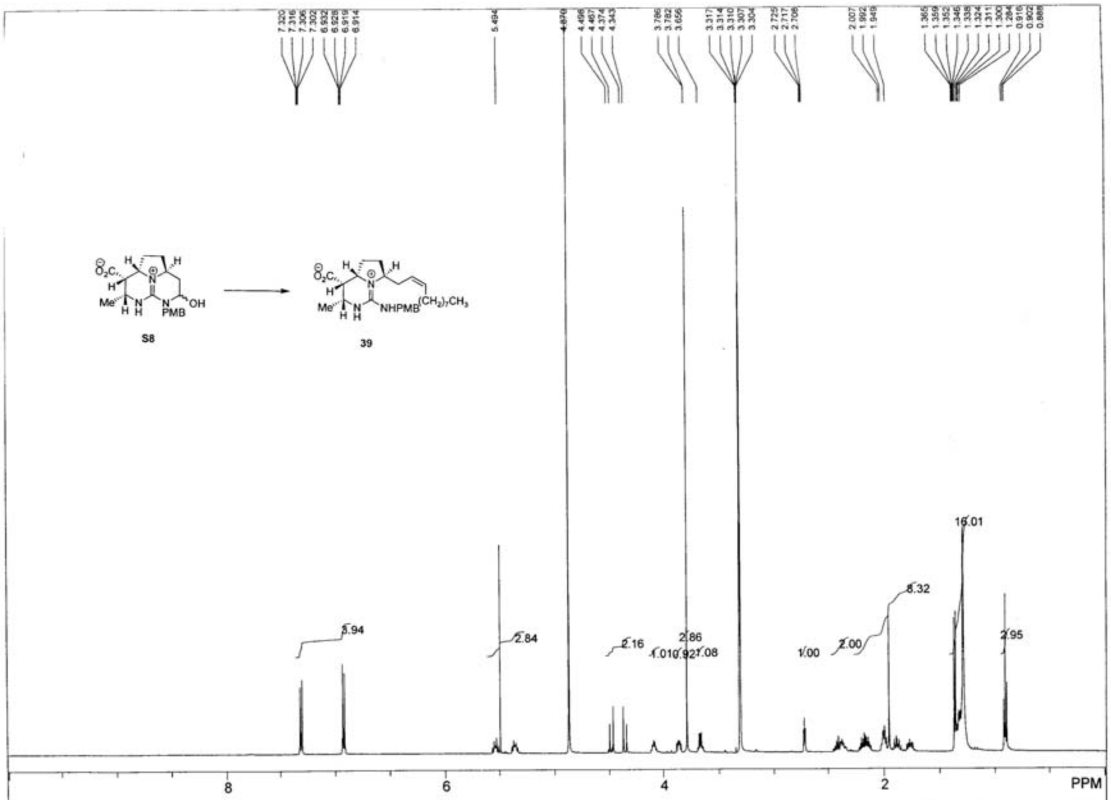
MAA-II-265, 1H, CD3OD USER: -- DATE: Nov 7 2004

F1: 500.077	F2: 500.077	SW1: 8000		OF1: 2500.5		PTS1d: 65536	
EX: s2pul		PW: 7.6 usec	PD: 0.0 sec	NA: 64	LB: 0.0	WinNuts - $MAA-II-265-1H-CD3OD.fid	



MAA-III-050, 13C, CD3OD USER: -- DATE: Jan 15 2005

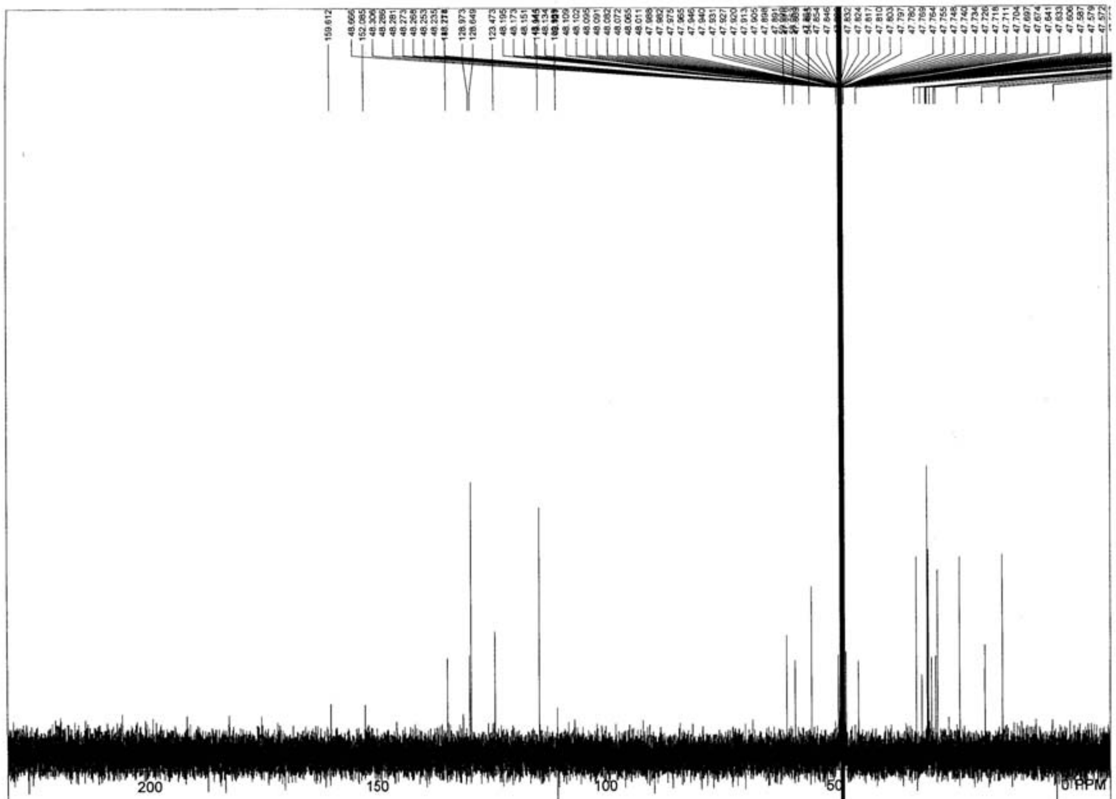
F1: 100.579	F2: 399.952	SW1: 25000		OF1: 11589.9		PTS1d: 65536	
EX: s2pul		PW: 7.1 usec	PD: 1.0 sec	NA: 500	LB: 0.0	WinNuts - $MAA-III-050-13C-CD3OD.fid	



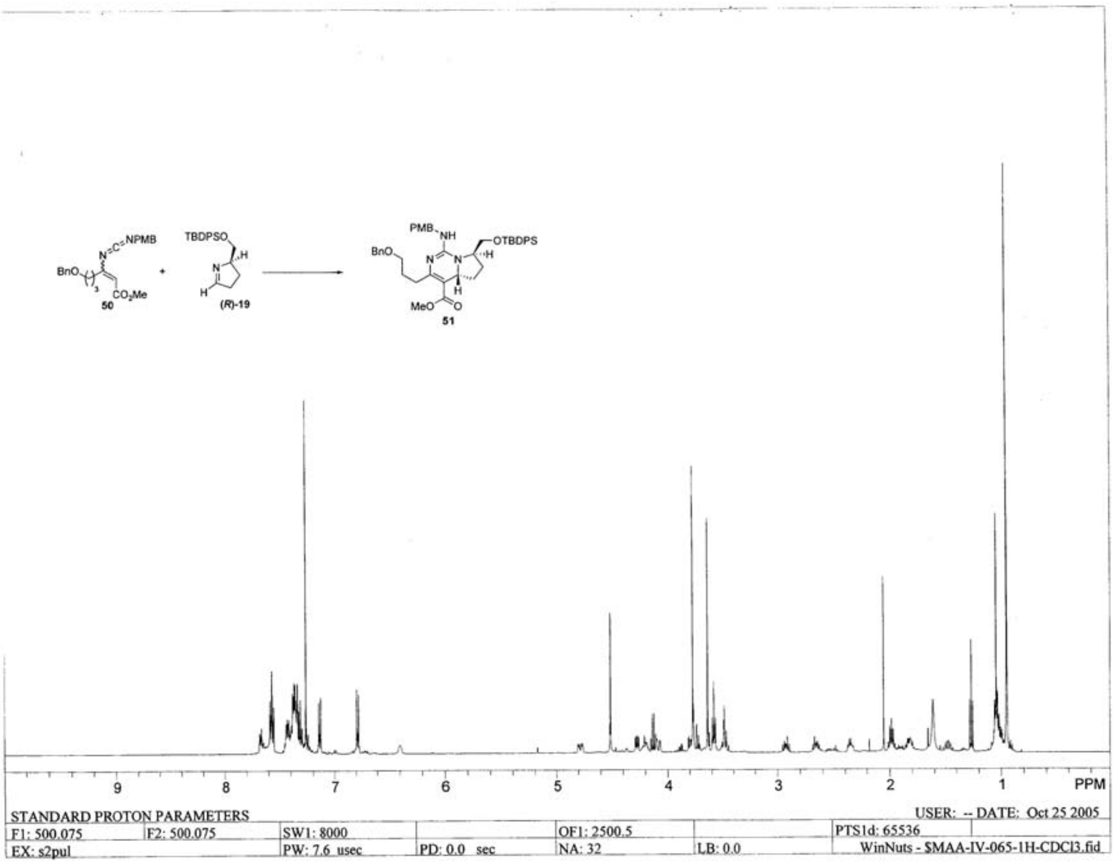
MAA-III-114, 1H, CD3OD

USER: -- DATE: Mar 14 2005

F1: 500.077	F2: 500.077	SW1: 8000		OF1: 2500.5		PTS1d: 65536	
EX: s2pul		PW: 7.6 usec	PD: 0.0 sec	NA: 16	LB: 0.0	WinNuts - $MAA-III-114-1H-CD3OD.fid	



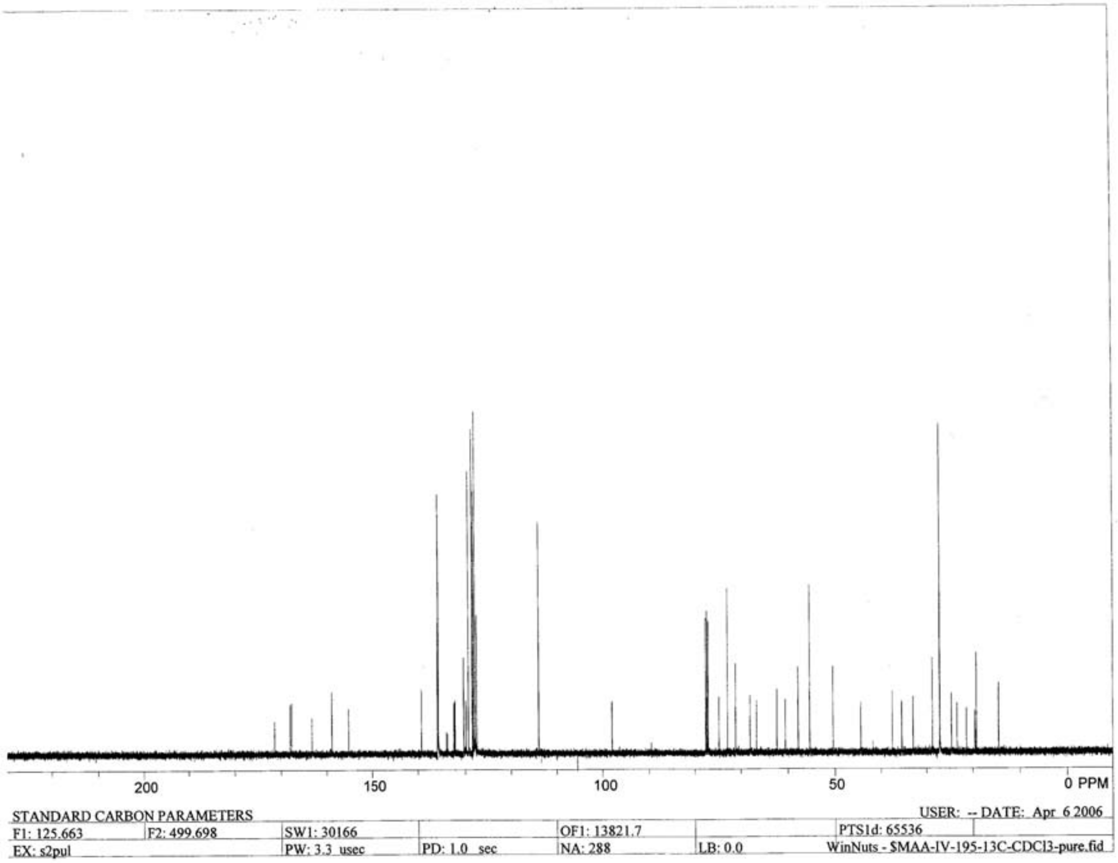
STANDARD CARBON PARAMETERS							USER: -- DATE: Feb 5 2005
F1: 125.663	F2: 499.700	SW1: 30166		OF1: 13821.8		FTS1d: 65536	
EX: s2pul		PW: 4.3 usec	PD: 1.0 sec	NA: 1408	LB: 0.0	WinNuts - $MAA-III-073-13C-CD3OD.fid	



STANDARD PROTON PARAMETERS

USER: -- DATE: Oct 25 2005

F1: 500.075	F2: 500.075	SW1: 8000		OF1: 2500.5		PTS1d: 65536
EX: s2pul		PW: 7.6 usec	PD: 0.0 sec	NA: 32	LB: 0.0	WinNuts - $MAA-IV-065-1H-CDCl3.fid



STANDARD CARBON PARAMETERS

USER: -- DATE: Apr 6 2006

F1: 125.663	F2: 499.698	SW1: 30166		OF1: 13821.7		PTS1d: 65536
EX: s2pul		PW: 3.3 usec	PD: 1.0 sec	NA: 288	LB: 0.0	WinNuts - $MAA-IV-195-13C-CDCl3-pure.fid