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Supporting Information

Concise Syntheses of bis-Strychnos Alkaloids (–)-Sungucine, (–)-Isosungucine, and (–)-Strychnogucine B from (–)-Strychnine

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Michael J. Zdilla, Graham E. Dobereiner, and Rodrigo B. Andrade*^[a]

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SUPPORTING INFORMATION

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General Methods. All reactions containing moisture or air sensitive reagents were performed in oven-dried glassware under nitrogen or argon. Tetrahydrofuran, toluene and dichloromethane were passed through two columns of neutral alumina prior to use. Pyridine, acetone, *i*-Pr₂NEt, and Et₃N were all distilled from CaH₂ prior to use. All other reagents were purchased from commercial sources and used without further purification. All solvents for work-up procedures were used as received. Silica gel column chromatography was performed according to the procedure of Still (Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923) using ICN Silitech 32-63 D 60Å silica gel with the indicated solvents. Thin layer chromatography was performed on Analtech 60F₂₅₄ silica gel plates. Detection was performed using UV light, KMnO₄ stain, PMA stain and subsequent heating. ¹H and ¹³C NMR spectra were recorded on a 500 MHz or 400 MHz instrument in CDCl₃ at 298K. Chemical shifts are indicated in parts per million (ppm) and internally referenced to residual solvent signals. Splitting patterns are abbreviated as follows: s (singlet), d (doublet), bs (broad singlet), bd (broad doublet), t (triplet), q (quartet) and m (multiplet). Single crystal X-ray diffraction was performed using a Bruker KAPPA APEX II DUO diffractometer with a Mo K α radiation obtained from a sealed molybdenum tube with a TRIUMPH™ monochromator. The sample was mounted on a MiTeGen™ loop with paratone N oil, and cooled to 173K using an oxford cryostream low temperature device. The structure was solved using direct methods and refined using full-matrix least squares (SHELXTL). Additional experimental and sample details are given in the crystallographic tables.

Computational Methods. Density functional theory (DFT) calculations were performed using Gaussian 09, Revision C.01¹ (keywords in parenthesis below). The mpw1pw91² functional (mPW1PW91) and cc-pvdz³ basis set (CC-pVDZ) were used for all atoms. Justification of the above method for calculating relative energies is provided by Reinscheid and coworkers,⁴ who

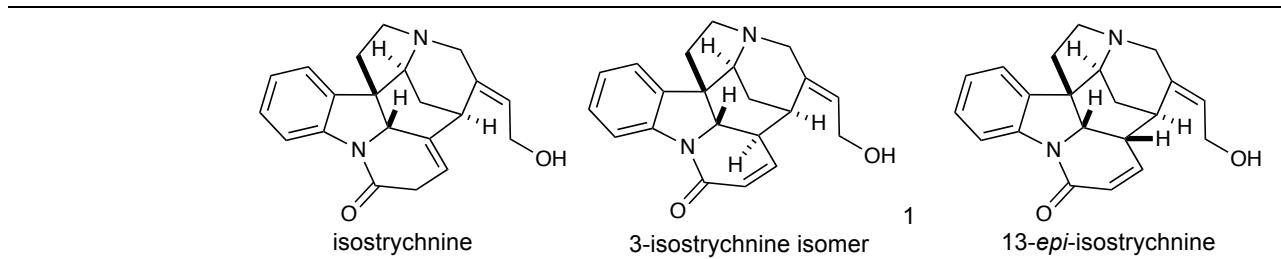
showed the mpw1pw91/cc-pvdz level of theory to best reproduce the bond lengths of crystal structures and ^{13}C NMR chemical shifts of strychnine•HCl. Calculations on all structures were performed using the IEFPCM (scrf=iefpcm) solvation model. Isostrychnine isomers were minimized with dimethylacetamide chosen as solvent (solvent=dimethylacetamide) given its similarity to the *N*-methyl-2-pyrrolidone used experimentally. The iminium and acylimonium structures were minimized with dicholoromethane (solvent=dichloromethane).

Optimized geometries, obtained using standard convergence criteria and a standard grid, were used in frequency calculations to ensure the absence of imaginary frequencies and to provide thermochemistry (enthalpy and free energy corrections) at 298.15 K and 1 atm. The natural population analysis was performed using NBO version 6.0⁵ in stand-alone GenNBO mode, using the NBO3 ARCHIVE (0.47) files generated from Gaussian 09 calculations. The 3D representations of the DFT minimized structures were generated using CYLview 1.0b.⁶

Cartesian coordinates of DFT structures. The supplemental file **cartesian.xyz** contains the computed Cartesian coordinates of all of the molecules reported in this study. The file may be opened as a text file to read the coordinates, or opened directly by a molecular modeling program such as Mercury (version 3.3 or later, <http://www.ccdc.cam.ac.uk/pages/Home.aspx>) for visualization and analysis.

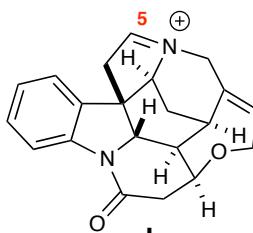
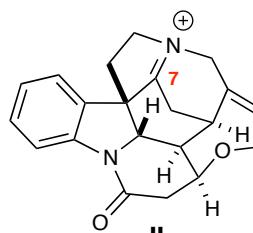
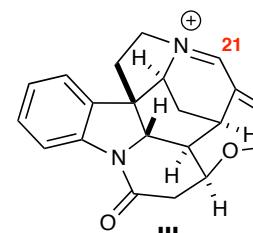
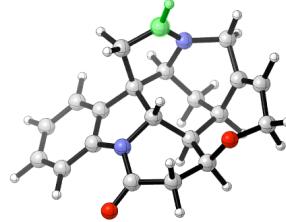
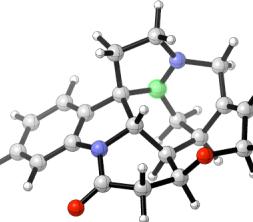
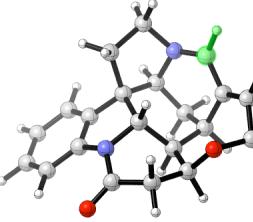
Single point energies (E) and free energies (G) for DFT structures.

Table S1. Energies of isostrychnine isomers 1-3.

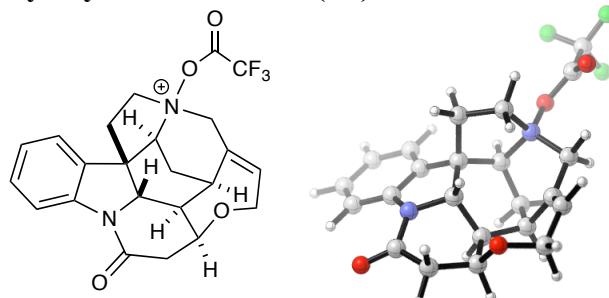


E (Hartrees)	-1073.256992	-1073.248627	-1073.259865
ΔE_{rel} (kcal/mol)	0	+5.2	-1.8
G (Hartrees)	-1072.906991	-1072.896591	-1072.907754
ΔG_{rel} (kcal/mol)	0	+6.5	-0.5

Table S2. Energies of iminium ions I-III (positive charge on nitrogen not shown).

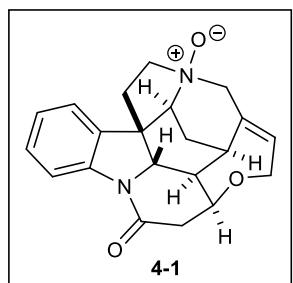
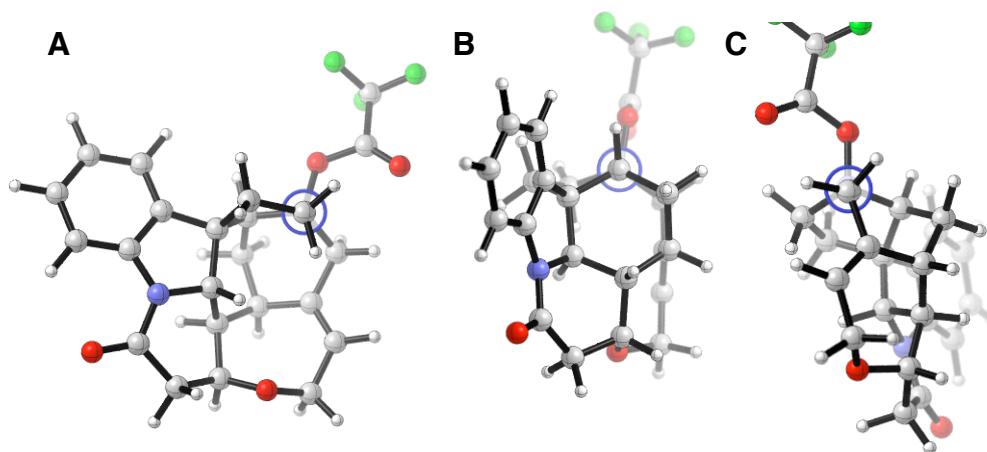
			
			
E (Hartrees)	-1072.499781	-1072.494528	-1072.503371
ΔE_{rel} (kcal/mol)	0	+3.3	-2.3
G (Hartrees)	-1072.152161	-1072.147402	-1072.155078
ΔG_{rel} (kcal/mol)	0	+3.0	-1.8

DFT-minimized structure of acyloxyammonium ion (IV).

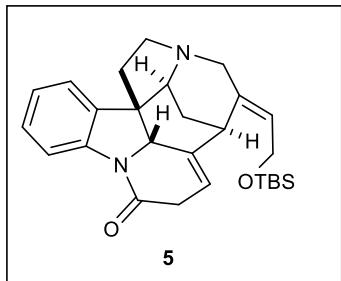


Energy (E): -1599.1489922 hartrees
Free energy (G): -1598.768892 hartrees

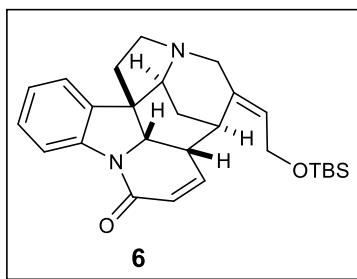
Figure S1. Newman projections along (A) C5-N4, (B) C7-N4, and (C) C21-N4 bonds of IV to give iminiums I, II, III, respectively.



Strychnine N-oxide (4-1): To a suspension of (-)-strychnine (5.00 g, 14.95 mmol) in acetonitrile (30 mL) and water (30 mL) was added aq. H_2O_2 [(30% w/w in H_2O), 1.8 mL, 18 mmol]. After stirring at rt for 48 h, the resulting mixture was concentrated under reduced pressure. The residue was washed with cold water and dried under vacuum to afford 5.14 g (98%) of **4-1** as a white solid. mp = 205–206 °C; $[\alpha]^{20}_{\text{D}} -12.0$ (c 0.86, CHCl_3); IR (neat) 3213, 2162, 1602, 1481, 1463, 1410, 1383, 1289, 1109, 992, 761 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.09 (d, J = 8.1 Hz, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.32 (t, J = 7.8 Hz, 1H), 7.16 (t, J = 7.5 Hz, 1H), 6.30 (t, J = 6.3 Hz, 1H), 4.44 (s, 1H), 4.33 – 4.30 (m, 1H), 4.25 (dd, J = 14.0, 7.0 Hz, 1H), 4.16 (d, J = 13.5 Hz, 1H), 4.08 (dd, J = 14.0, 5.9 Hz, 1H), 3.99 (d, J = 10.5 Hz, 1H), 3.98 – 3.91 (m, 1H), 3.89 (d, J = 13.5 Hz, 1H), 3.75 – 3.71 (m, 1H), 3.25 (s, 1H), 3.16 (dd, J = 17.7, 8.4 Hz, 1H), 2.79 (dt, J = 15.2, 4.1 Hz, 1H), 2.71 – 2.64 (m, 2H), 2.03 (dd, J = 13.2, 5.7 Hz, 1H), 1.66 (d, J = 15.2 Hz, 1H), 1.37 (dt, J = 10.5, 2.7 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 169.2, 142.0, 136.1, 133.9, 130.2, 129.8, 125.2, 122.7, 116.9, 83.8, 77.7, 72.3, 68.7, 64.6, 58.8, 53.6, 47.9, 42.6, 39.7, 30.8, 25.6; HRMS (ESI) calc'd for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_3 + \text{H} = 351.1709$, found 351.1701.

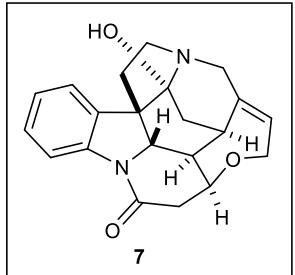


TBS-protected Isostrychnine 5: A stirred suspension of (-)-strychnine (**4**) (4.0 g, 11.96 mmol) and DBU (18.2 g, 17.88 mL, 119.6 mmol) in *N*-methyl-2-pyrrolidone (100 mL) was deaerated by bubbling argon (1 min/mL) for 2h. The reaction mixture was stirred at 200 °C for 40 min under inert atmosphere. The resultant reaction mixture was cooled to rt, followed by addition of imidazole (3.26 g, 47.84 mmol) and TBSCl (5.4 g, 35.88 mmol). The stirring was continued at rt for 12 h. The reaction was quenched with adding water (80 mL) and the resulting mixture was extracted with EtOAc (3x 160 mL). The combined organic layers were washed with brine (5x 160 mL), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography eluting with MeOH/DCM (1:100 to 3:100) to afford 2.69 g (50% over 2 steps) of **5** as a white foam. [α]²⁰_D−18.4 (c 1.13, CHCl₃); IR (neat) 2928, 2854, 2162, 1980, 1662, 1596, 1481, 1461, 1393, 1251, 1093, 1047, 992, 832, 774, 760, 681 cm^{−1}; ¹H NMR (500 MHz, CDCl₃) δ 8.15 (d, *J* = 7.8 Hz, 1H), 8.26 – 8.22 (m, 1H), 7.20 – 7.19 (m, 1H), 7.09 (td, *J* = 7.5, 1.0 Hz, 1H), 5.79 (dt, *J* = 6.4, 2.5 Hz, 1H), 5.49 (t, *J* = 5.5 Hz, 1H), 4.33 – 4.25 (m, 3H), 3.68 (d, *J* = 2.0 Hz, 1H), 3.59 (d, *J* = 14.4 Hz, 1H), 3.50 (s, 1H), 3.22 – 3.17 (m, 1H), 3.11 (dd, *J* = 17.4, 6.7 Hz, 1H), 3.04 – 2.99 (m, 1H), 2.93 – 2.86 (m, 2H), 2.29 – 2.23 (m, 1H), 2.19 – 2.14 (m, 2H), 1.45 (dt, *J* = 14.0, 2.1 Hz, 1H), 0.91 (s, 9H), 0.08 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 168.4, 142.1, 141.4, 135.9, 134.7, 128.2, 127.4, 124.1, 122.5, 120.2, 114.6, 67.1, 63.2, 59.1, 53.9, 52.8, 52.3, 46.1, 36.8, 34.8, 25.9, 25.6, 18.3, -5.1, -5.2; HRMS (ESI) calc'd for C₂₇H₃₆N₂O₂Si + H = 449.2624, found 449.2612.



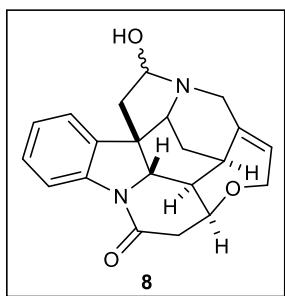
TBS-protected Isostrychnine Isomer 6: The procedure used to prepare **5** was applied toward the synthesis of **6**. The residue was

purified by flash chromatography eluting with MeOH/DCM (1:100 to 3:100) to afford 1.40 g (26% over 2 steps) of **6** as a white foam. $[\alpha]^{20}_D -331.0$ (*c* 0.78, CHCl₃); IR (neat) 2927, 2856, 2162, 1665, 1616, 1594, 1481, 1413, 1250, 1144, 1080, 1059, 1045, 832, 818, 776, 758, 592 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.25 (d, *J* = 7.9 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.12 (td, *J* = 7.5, 1.0 Hz, 1H), 6.75 (dd, *J* = 9.8, 6.5 Hz, 1H), 6.02 (dd, *J* = 9.8, 1.1 Hz, 1H), 5.44 (t, *J* = 6.3 Hz, 1H), 4.25 (d, *J* = 6.8 Hz, 1H), 4.24 – 4.16 (m, 2H), 3.62 (d, *J* = 15.1 Hz, 1H), 3.30 – 3.21 (m, 3H), 3.08 – 3.03 (m, 1H), 2.70 (d, *J* = 2.7 Hz, 1H), 2.61 – 2.53 (m, 2H), 2.15 (dt, *J* = 13.2, 5.8 Hz, 1H), 1.87 – 1.81 (m, 1H), 1.78 – 1.74 (m, 1H), 0.91 (s, 9H), 0.09 (d, *J* = 2.2 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 162.0, 142.9, 142.9, 141.7, 135.9, 128.8, 124.8, 124.6, 124.1, 122.7, 116.8, 65.7, 64.9, 59.0, 54.3, 52.9, 52.4, 38.4, 37.5, 31.8, 26.3, 23.6, 18.7, -4.6, -4.7; HRMS (ESI) calc'd for C₂₇H₃₆N₂O₂Si + H = 449.2624, found 449.2616.

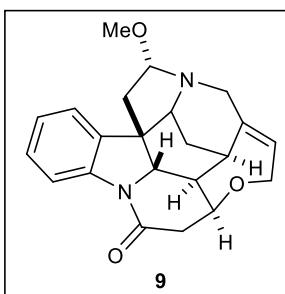


Pseudostrychnine (7): To a stirred clear solution of strychnine *N*-oxide **4-1** (2.0 g, 5.7 mmol) in CH₂Cl₂ (80 mL) was added TFAA (2.39 g, 1.60 mL, 11.4 mmol) at 0 °C. The resulting mixture was stirred at 0 °C for 1 h. Then the cooling bath was removed and the reaction mixture was stirred at rt for 4h. A solution of KOH (3.2 g, 57 mmol) in water (40 mL) was added and stirring was continued at rt for 20 h. The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (2 x 40 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography eluting with acetone/EtOAc (50% to 100%) to afford 0.804 g (40%) of pseudostrychnine (**7**) as a white solid. mp = 235–236 °C; $[\alpha]^{20}_D -79.3$ (*c* 0.76, CHCl₃); IR (neat) 3401, 2871, 2162, 1666, 1593, 1476, 1384, 1063, 866, 785 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.07 (t, *J* = 7.5 Hz, 1H),

5.95 – 5.92 (m, 1H), 4.33 – 4.22 (m, 1H), 4.15 (dd, J = 13.8, 6.8 Hz, 1H), 4.06 (dd, J = 13.8, 6.0 Hz, 1H), 3.92 – 3.80 (m, 2H), 3.28 (s, 1H), 3.23 – 3.09 (m, 2H), 2.88 – 2.81 (m, 2H), 2.64 (dd, J = 17.3, 3.5 Hz, 1H), 2.35 – 2.20 (m, 2H), 1.87 – 1.79 (m, 2H), 1.40 – 1.36 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.4, 142.6, 139.1, 132.1, 128.8, 127.4, 127.4, 124.6, 116.1, 92.2, 77.8, 65.1, 60.3, 56.9, 52.7, 48.4, 48.2, 42.8, 39.9, 35.4, 33.7; HRMS (ESI) calc'd for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_3 + \text{H}$ = 351.1709, found 351.1699.



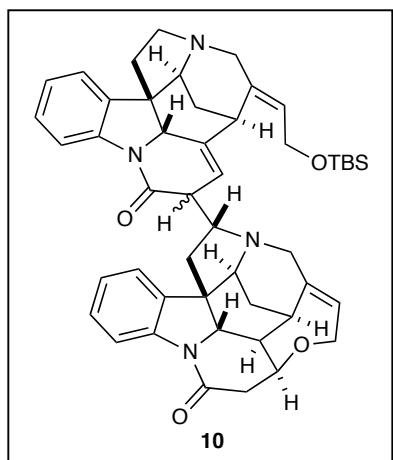
Carbinolamine 8: The same procedure was followed as the one for the synthesis of the tertiary alcohol **7**. The residue was purified by flash chromatography eluting with acetone/EtOAc (50% to 100%) to afford 1.05 g (52%) of carbinolamine **8** as a mixture of epimers, which was used in next step without further purification.



N,O-acetal 9: A solution of secondary amino alcohols **8** (1.05 g, 2.99 mmol) in $\text{MeOH}/\text{CH}_2\text{Cl}_2$ (1:4, 30 mL) was stirred at rt for 1h. The resulting mixture was concentrated under reduced pressure to afford 1.09 g (100%) of **9** as a white foam. $[\alpha]^{20}_{\text{D}} -60.5$ (c 1.4, CHCl_3); IR (neat) 2941, 2858, 2360, 2341, 2161, 1979, 1665, 1596, 1478, 1460, 1389, 1282, 1106, 1072, 1048, 754, 726 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.08 (d, J = 8.0 Hz, 1H), 7.27 – 7.20 (m, 2H), 7.12 – 7.07 (m, 1H), 5.91 (t, J = 6.2 Hz, 1H), 4.45 (dd, J = 8.1, 5.9 Hz, 1H), 4.28 (dt, J = 8.4, 3.4 Hz, 1H), 4.23 – 4.21 (m, 1H), 4.14 (dd, J = 13.8, 6.9 Hz, 1H), 4.08 – 4.04 (m, 1H), 3.91 (d, J = 10.5 Hz, 1H), 3.84 (dd, J = 15.1, 1.3 Hz, 1H), 3.32 (s, 3H), 3.18 (s, 1H), 3.12 (dd, J = 17.4, 8.5 Hz, 1H), 3.00 (d, J = 15.2 Hz, 1H), 2.65 (dd, J = 17.4, 3.4 Hz, 1H), 2.37 – 2.32 (m, 2H), 1.89 (dd, J = 13.2, 8.1 Hz, 1H), 1.42 (d, J = 14.5 Hz, 1H), 1.28 – 1.25 (m,

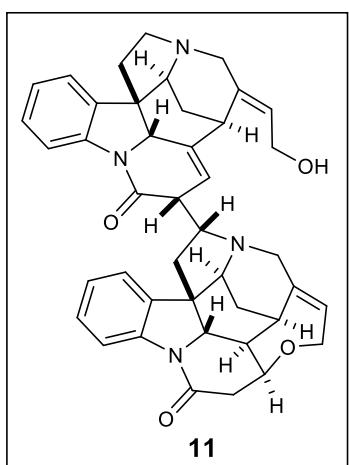
1H). ^{13}C NMR (126 MHz, CDCl_3) δ 169.3, 142.1, 141.4, 131.7, 128.7, 125.9, 124.3, 122.3, 116.2, 96.6, 77.5, 64.4, 60.8, 58.9, 54.3, 52.8, 52.4, 48.6, 47.8, 42.3, 31.2, 26.9; HRMS (ESI) calc'd for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_3 + \text{H} = 365.1865$, found 365.1853.

Studies of acylating agents and temperature on the formation of 7 and 8 (from Table 1): To a stirred solution of strychnine *N*-oxide **4-1** (50 mg, 0.143 mmol) in CH_2Cl_2 (1.5 mL) was added TFAA (60 mg, 40 μL , 0.285 mmol) or Ac_2O (29 mg, 27 μL , 0.285 mmol) at either 0 °C, 23 °C, 35 °C. The resulting mixture was stirred at the respective temperature for 2 or 4 h. The reaction mixture was cooled or warmed to rt followed by the addition of KOH (80 mg, 1.43 mmol) in water (1 mL). The reaction mixture was stirred at rt for an additional 16 h. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 3 mL). The combined organic layers were dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. Crude ^1H NMR samples were used to determine the percent of conversion and ratio of product formation (Table 1). The crude products were purified by flash chromatography eluting with acetone/EtOAc (50% to 100%) to corroborate product ratios.



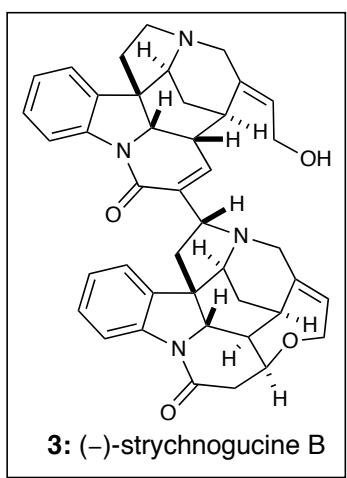
Mannich Products 10: To a stirred solution of $(i\text{-Pr})_2\text{NH}$ (0.075 mL, 0.54 mmol) in THF (4 mL) was added *n*-BuLi (2.35M solution in hexanes, 0.21 mL, 0.49 mmol) at 0 °C. The mixture was stirred at 0 °C for 30 min, followed by addition of a solution of northern fragment **5** (200 mg, 0.45 mmol) in THF (4 mL). The mixture was stirred at 0 °C for 1 h and then a solution of southern fragment **9** (292 mg, 0.80 mmol) in THF (4 mL) was added, followed by addition of $\text{BF}_3\bullet\text{Et}_2\text{O}$ (0.44 mL, 3.56 mmol). Stirring was continued at 0 °C

for 4 h. The reaction was quenched with saturated aq. NaHCO₃ (5 mL). The cooling bath was removed and the resultant mixture was stirred at rt for 2h. The mixture was extracted with CH₂Cl₂ (2 x 20 mL) and the combined organic layers were dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography eluting with isopropanol/CH₂Cl₂ (3% to 8%) to afford 236 mg (67%) of the Mannich products **10** as a mixture of epimers, which were used in next step without further purification.



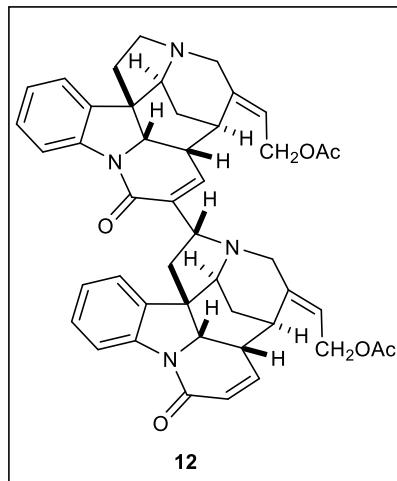
Strychnogucine B Precursor 11: Pyridine (1.5 mL, 18.6 mmol) was added to a solution of the mixture of the Mannich products **10** (408 mg, 0.52 mmol) in THF (15 mL) in a Nalgene container at 0 °C, followed by dropwise addition of HF•Pyridine (70% HF, 0.4 mL, 15.4 mmol). The cooling bath was removed and the reaction mixture was stirred at rt for 12 h. The reaction was quenched with slow addition of sat. aq. NaHCO₃ (25 mL) at 0 °C and the resulting mixture was extracted with CH₂Cl₂ (2x 60 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography eluting with CH₂Cl₂/MeOH/29% aq. NH₄OH (97:3:0.1) → CH₂Cl₂/MeOH/29% aq. NH₄OH (92:8:0.1) to afford 306 mg (88 %) of TBS-deprotected product **11** as an off-white solid. mp = 270–271.8 °C; [α]²⁰_D –108.5 (*c* 1.2, CHCl₃); IR (neat) 3200, 2932, 2876, 1668, 1596, 1481, 1460, 1389, 1329, 1282, 1109, 1091, 1078, 919, 754, 729 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.07 (d, *J* = 8.4 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.25 – 7.16 (m, 4H), 7.07 – 7.03 (m, 2H), 5.92 – 5.89 (m, 2H), 5.63 (t, *J* = 6.5 Hz, 1H), 4.40 – 4.32 (m, 2H), 4.30 – 4.25 (m, 2H), 4.14 – 4.08 (m, 2H), 4.03 – 3.98 (m, 2H), 3.85 – 3.81 (m, 1H), 3.66 – 3.54 (m, 4H), 3.24 – 3.08 (m, 4H), 2.97 – 2.91 (m, 2H), 2.74 – 2.69 (m, 2H), 2.38 – 2.34 (m, 2H), 2.28 (t,

$J = 7.6$ Hz, 2H), 2.16 – 2.11 (m, 1H), 1.54 – 1.46 (m, 3H), 1.25 (dt, $J = 10.4, 3.2$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 169.4, 169.2, 142.2, 142.2, 141.2, 140.6, 138.5, 134.9, 132.5, 128.5, 128.3, 127.3, 125.6, 124.2, 123.9, 122.5, 122.4, 121.9, 116.3, 114.5, 77.3, 67.8, 64.2, 63.8, 61.0, 60.5, 59.6, 58.3, 54.4, 53.2, 52.1, 52.0, 50.9, 47.9, 47.5, 46.8, 45.9, 42.3, 34.9, 31.4, 27.2, 26.4; HRMS (ESI) calc'd for $\text{C}_{42}\text{H}_{42}\text{N}_4\text{O}_4 + \text{Na} = 689.3104$, found 689.3109.

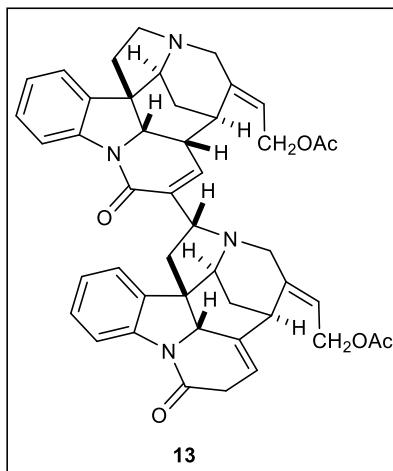


(-)-Strychnogucine B (3): A mixture of strychnogucine B precursor **11** (204 mg, 0.3 mmol), Cs_2CO_3 (997 mg, 3 mmol) and *t*-BuOH (6 g) was deaerated by bubbling Argon (1 min/mL) for 30 min. The reaction mixture was then heated at 85 °C for 3 h under inert atmosphere. The resultant reaction mixture was cooled to rt, diluted with CH_2Cl_2 and filtered through a short pad of Celite. The filter cake was washed with CH_2Cl_2 . The combined filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography eluting with EtOAc/MeCN/29% aq. NH_4OH (70:30:0.5) to afford 143 mg (70%) of strychnogucine B (**3**) as a white foam. $[\alpha]^{20}_{\text{D}} -167.5$ (c 0.65, CHCl_3); IR (neat) 3213, 2162, 1662, 1596, 1480, 1463, 1410, 1383, 1289, 1274, 1109, 1097, 1050, 1037, 992, 761 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.22 (d, $J = 7.9$ Hz, 1H), 8.09 (dd, $J = 8.3, 0.8$ Hz, 1H), 7.25 – 7.22 (m, 4H), 7.11 – 7.05 (m, 3H), 5.87 – 5.84 (m, 1H), 5.53 (t, $J = 6.7$ Hz, 1H), 4.36 – 4.27 (m, 4H), 4.13 – 4.09 (m, 3H), 4.04 (dd, $J = 13.7, 6.0$ Hz, 1H), 3.97 (dd, $J = 11.2, 5.7$ Hz, 1H), 3.65 – 3.60 (m, 2H), 3.31 (d, $J = 15.2$ Hz, 1H), 3.26 – 3.22 (m, 2H), 3.16 (s, 1H), 3.12 (dd, $J = 17.3, 8.4$ Hz, 1H), 3.09 – 3.04 (m, 1H), 2.72 (dd, $J = 17.3, 3.5$ Hz, 1H), 2.69 – 2.52 (m, 5H), 2.39 (dt, $J = 14.2, 4.2$ Hz, 1H), 2.17 – 2.12 (m, 1H), 1.83 (dd, $J = 14.2, 2.3$ Hz, 1H), 1.75 – 1.71 (m, 2H), 1.49 (d, $J = 14.3$ Hz, 1H), 1.28 (dt, $J = 10.5, 3.2$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 169.4, 162.2,

143.9, 142.1, 141.3, 140.7, 136.8, 135.8, 135.1, 132.4, 128.5, 128.4, 127.2, 124.4, 123.9, 123.5, 122.3, 122.2, 116.4, 116.2, 77.4, 65.3, 64.5, 64.3, 61.1, 60.4, 60.0, 58.3, 53.9, 52.9, 52.3, 52.1, 51.2, 50.6, 48.0, 42.4, 37.6, 36.9, 31.8, 31.5, 27.2, 23.3; HRMS (ESI) calc'd for C₄₂H₄₂N₄O₄ + H = 667.3284, found 667.3289.

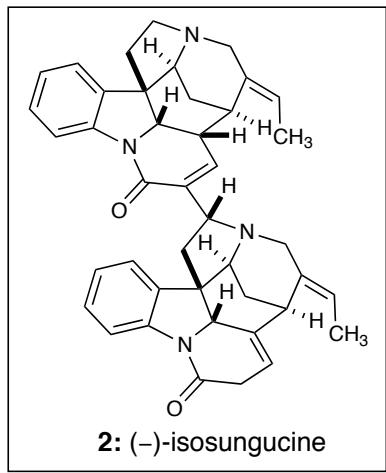


Bis-acetate 12: A stirred suspension of (-)-strychnogucine B (**3**) (177 mg, 0.265 mmol) and DBU (404 mg, 0.397 mL, 2.65 mmol) in *N*-methyl-2-pyrrolidone (3 mL) was deaerated by bubbling Argon (1 min/mL) for 30 min. The reaction mixture was stirred at 200 °C for 40 min under inert atmosphere. The resultant reaction mixture was cooled to rt, followed by addition of Ac₂O (271 mg, 0.25 mL, 2.65 mmol) and 4-dimethylaminopyridine (32.4 mg, 0.265 mmol). The stirring was continued at rt for 20 h. The resulting reaction mixture was directly loaded onto a silica gel column and purified by flash chromatography eluting with CH₂Cl₂/MeOH/29% aq. NH₄OH (100:2:0.1) to afford 140 mg (70% over 2 steps) of a mixture of the acetates (Ratio of **12** to **13** = 1:2, as determined by ¹H NMR). The mixture was used in the next reaction without further purification.

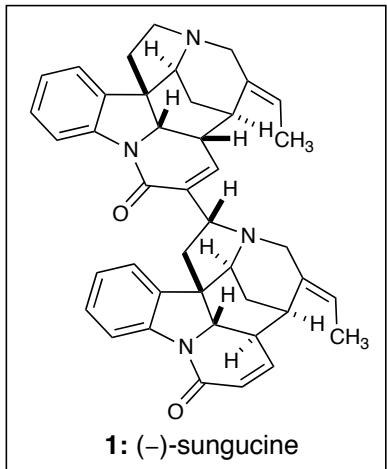


Bis-acetate 13: The same procedure for the synthesis of the bis-acetate **12** was followed. The resulting reaction mixture was directly loaded onto a silica gel column and purified by flash chromatography eluting with CH₂Cl₂/MeOH/29% aq. NH₄OH (100:2:0.1) to afford 140 mg (70% over 2 steps) of a mixture of

the acetates (Ratio of **13** to **12** = 2:1, as determined by ^1H NMR). The mixture was used in the next reaction without further purification.

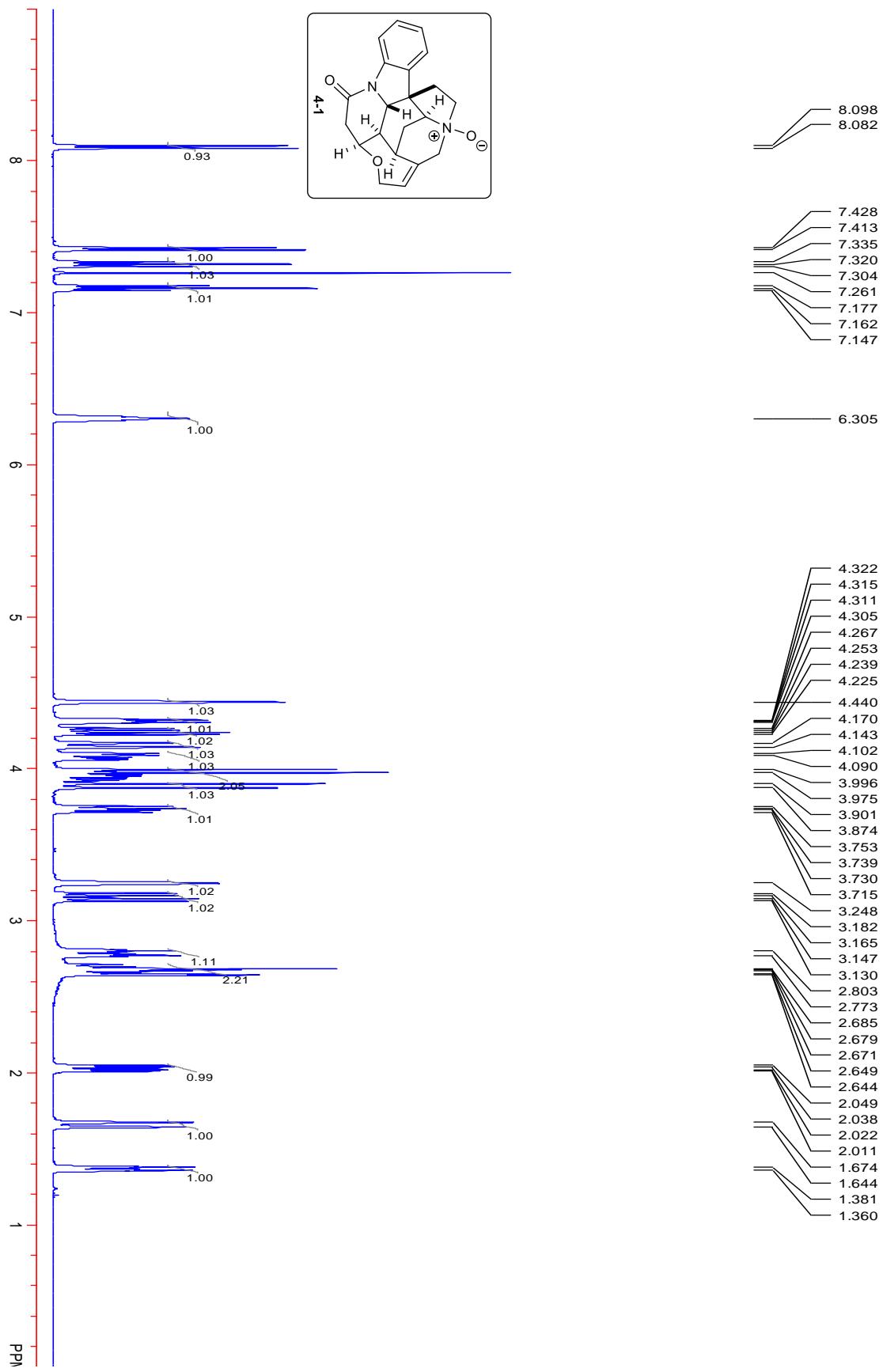


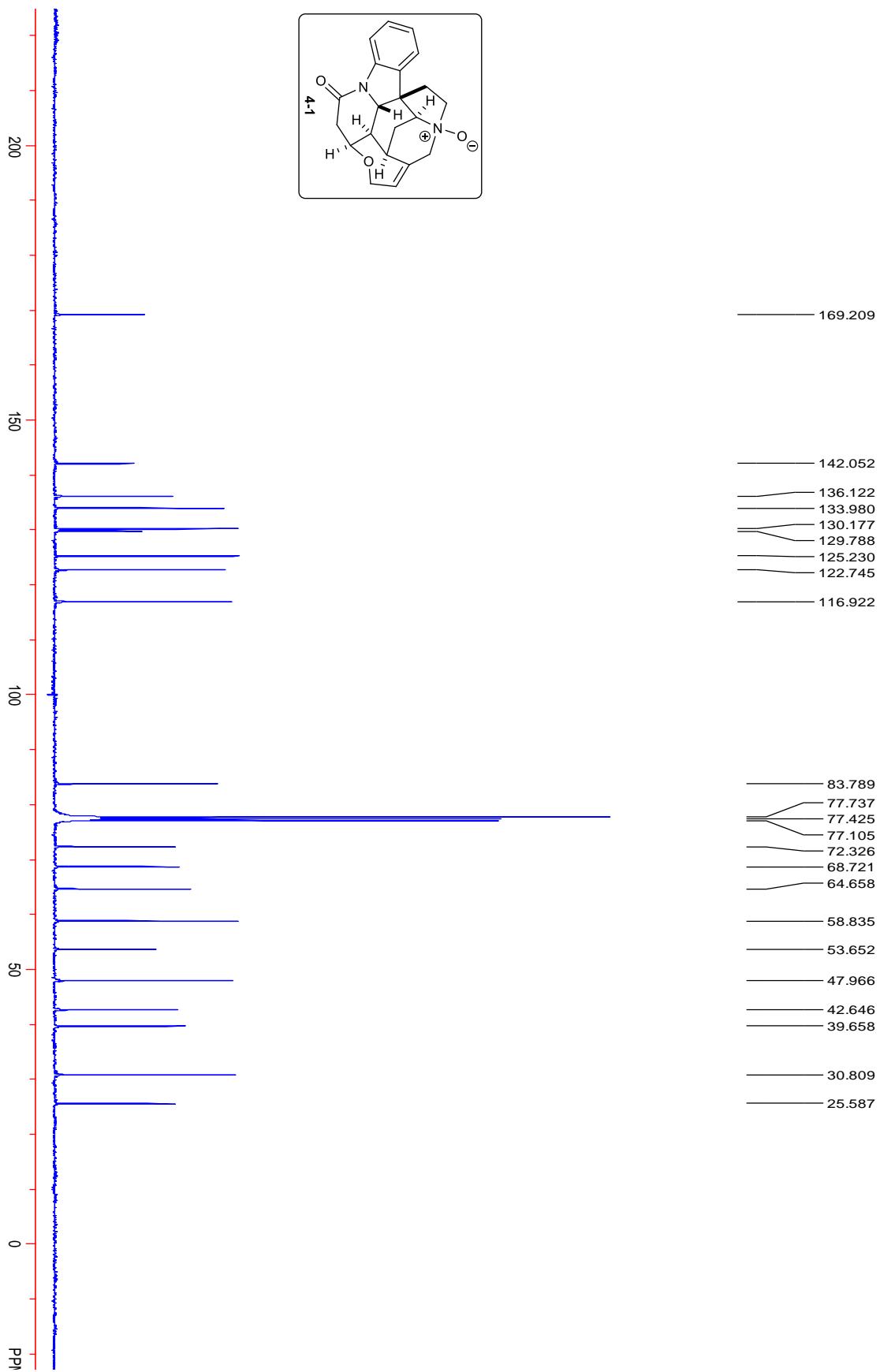
(-)-Isosungucine (2): The same procedure was followed as the one for the synthesis of (-)-sungucine (**1**). The residue was first purified by preparative thin layer chromatography eluting with $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (100:4), then by flash chromatography eluting with $\text{CH}_2\text{Cl}_2/\text{MeOH}/29\%$ aq. NH_4OH (100:4:0.2) to afford 25 mg (34% over two steps) of (-)-isosungucine (**2**) as a white solid. mp = 195–202 °C; $[\alpha]^{20}_{\text{D}} -214.9$ (c 1.0, CHCl_3); IR (neat) 3471, 3044, 2930, 2858, 1664, 1627, 1595, 1480, 1418, 1392, 1274, 753, 733 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.20 (d, J = 7.6 Hz, 1H), 8.18 (d, J = 7.9 Hz, 1H), 7.24 – 7.21 (m, 4H), 7.12 – 7.03 (m, 3H), 5.88– 5.85 (m, 1H), 5.40 – 5.35 (m, 2H), 4.46 (s, 1H), 4.30 (d, J = 6.8 Hz, 1H), 4.04 (d, J = 4.1 Hz, 1H), 3.97 (dd, J = 11.3, 4.9 Hz, 1H), 3.68 – 3.54 (m, 3H), 3.26 – 3.19 (m, 3H), 3.11 – 3.04 (m, 3H), 2.72 – 2.67 (m, 3H), 2.60 (dd, J = 12.4, 5.0 Hz, 1H), 2.57 – 2.51 (m, 1H), 2.24 (dt, J = 14.2, 4.0 Hz, 1H), 2.17 – 2.12 (m, 1H), 1.93 (t, J = 11.9 Hz, 1H), 1.82 (dd, J = 14.1, 1.8 Hz, 1H), 1.75 (d, J = 6.8 Hz, 4H), 1.61 (d, J = 6.8 Hz, 3H), 1.41 (d, J = 14.2 Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 168.8, 162.5, 141.9, 141.3, 140.9, 140.7, 137.5, 136.2, 135.1, 134.3, 133.3, 128.3, 128.2, 124.4, 124.0, 123.6, 122.6, 122.3, 120.3, 118.9, 116.3, 114.8, 65.6, 64.9, 64.7, 61.3, 60.9, 53.7, 53.3, 52.5, 52.4, 52.1, 51.2, 37.7, 37.1, 36.6, 34.3, 31.3, 24.6, 23.4, 13.1, 13.1; HRMS (ESI) calc'd for $\text{C}_{42}\text{H}_{42}\text{N}_4\text{O}_2 + \text{H} = 635.3386$, found 635.3371.

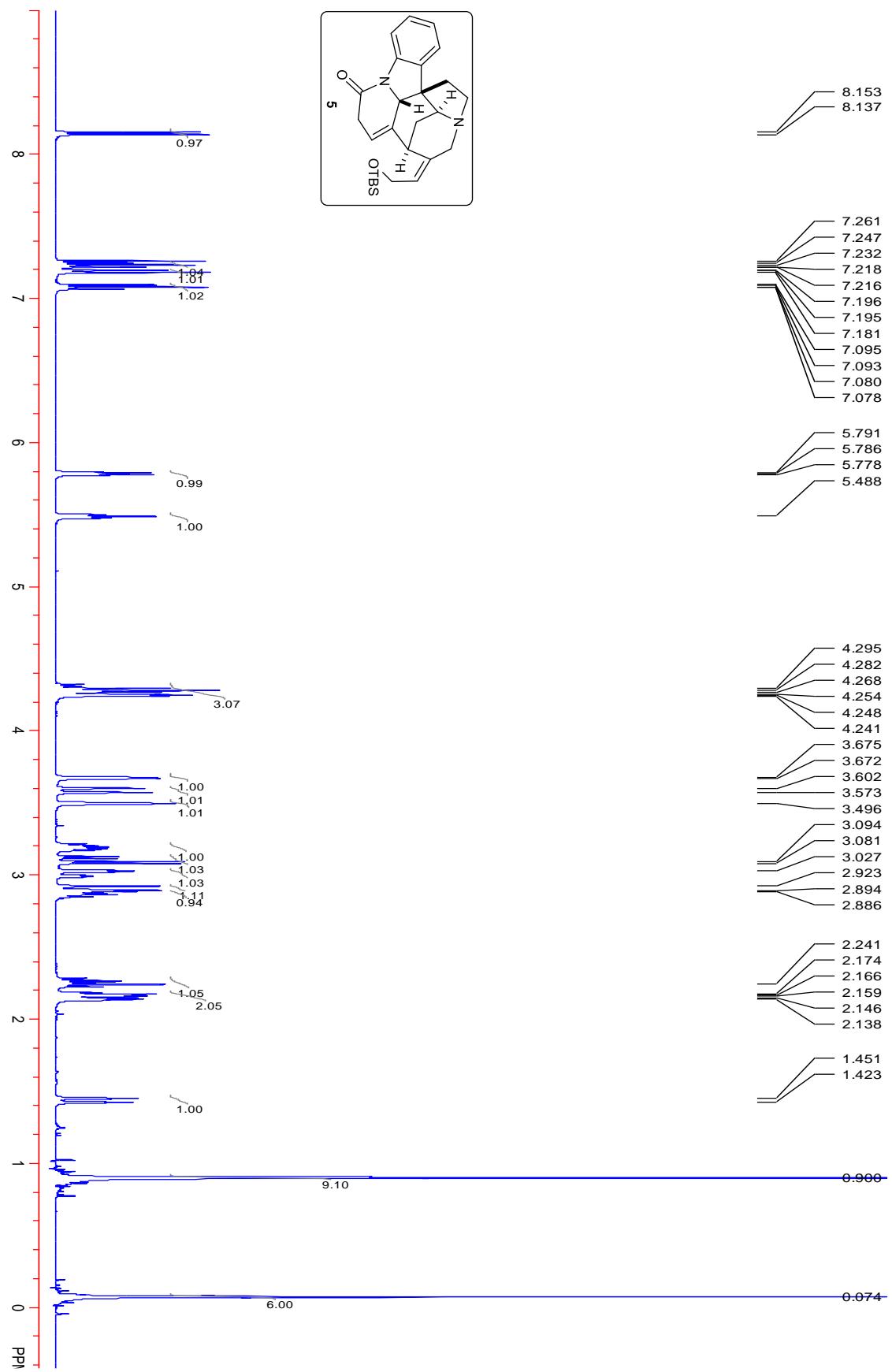


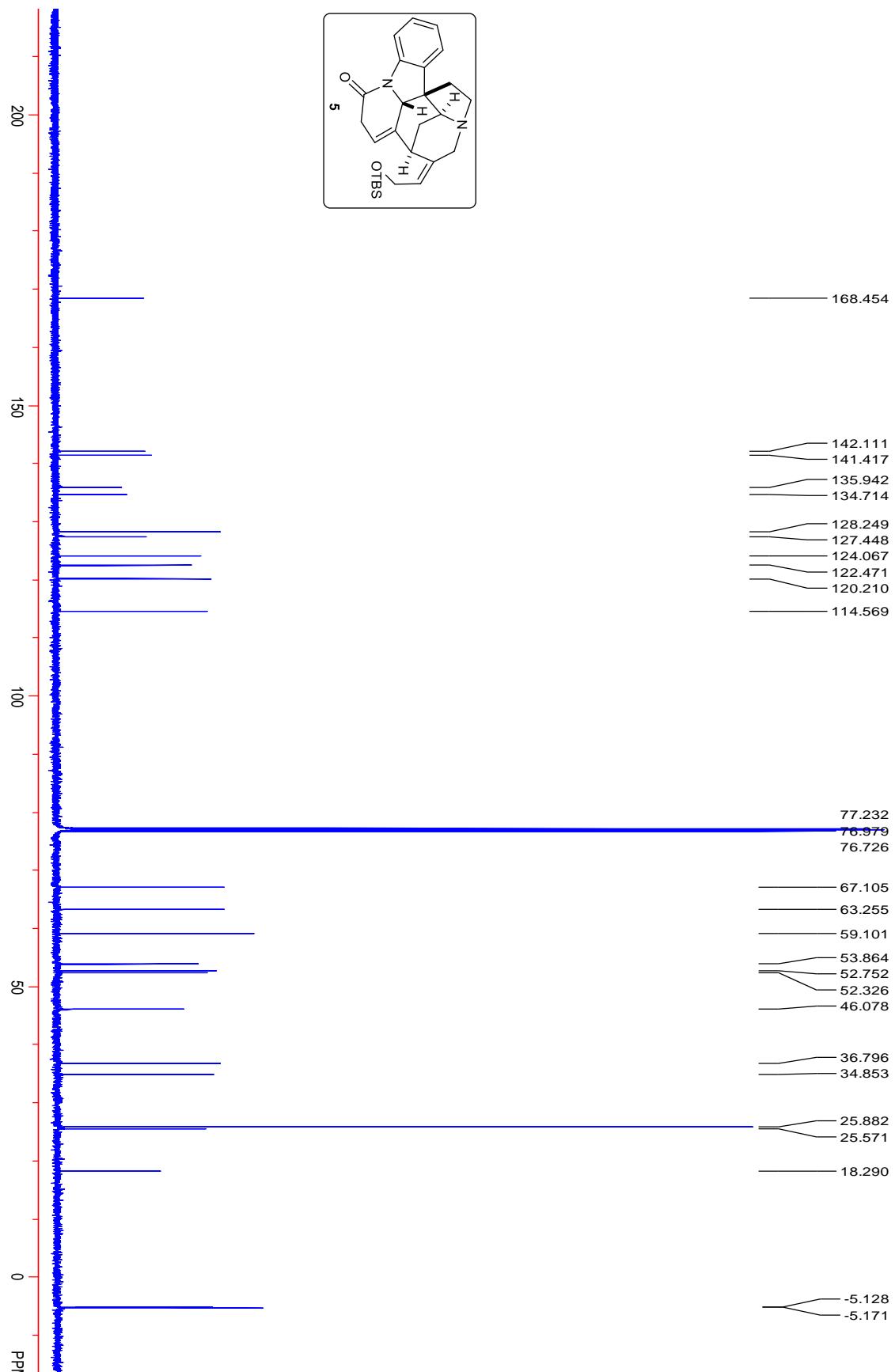
(-)-Sungucine (1): To a stirred solution of a mixture of bis-acetates **12** and **13** (2:1, 88 mg, 0.117 mmol) in HOAc (4 mL) was added HBr (33% in HOAc, 0.4 mL) at 10 °C. The cooling bath was removed and the reaction mixture was stirred at rt for 24 h. The solvent was then removed under reduced pressure. The residue was dissolved in DMF (2 mL) followed by addition of NaBH₃CN (44 mg, 0.7 mmol). The reaction mixture was stirred at rt for 24 h and quenched with MeOH (2 mL) at 0 °C. After stirring at rt for 30 min, the mixture was basified with sat. aq. NaHCO₃ (2 mL), followed by extraction with EtOAc (2x 6 mL). The combined organic layers were washed with brine (1x 6 mL), dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was first purified by preparative TLC eluting with CH₂Cl₂/MeOH (100:4), then by flash chromatography eluting with CH₂Cl₂/MeOH/29% aq. NH₄OH (100:4:0.2) to afford 12 mg (16% over two steps) of sungucine (**1**) as a white solid. mp > 350 °C; [α]²⁰_D -261.0 (c 1.17, CHCl₃); IR (neat) 3496, 3042, 2931, 2857, 1666, 1627, 1594, 1480, 1462, 1418, 1280, 1144, 818, 754, 734 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.28 (d, *J* = 7.9 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 7.31 – 7.25 (m, 4H), 7.12 – 7.09 (m, 2H), 7.06 (d, *J* = 6.3 Hz, 1H), 6.86 (dd, *J* = 9.8, 6.5 Hz, 1H), 6.02 (d, *J* = 9.8 Hz, 1H), 5.37 (q, *J* = 6.6 Hz, 1H), 5.21 (q, *J* = 6.5 Hz, 1H), 4.38 (d, *J* = 6.8 Hz, 1H), 4.31 (d, *J* = 6.7 Hz, 1H), 4.21 (dd, *J* = 11.2, 5.2 Hz, 1H), 3.64 – 3.56 (m, 3H), 3.28 – 3.20 (m, 3H), 3.10 – 3.05 (m, 1H), 2.89 (d, *J* = 16.3 Hz, 1H), 2.80 – 2.76 (m, 1H), 2.70 (m, 3H), 2.66 (dd, *J* = 12.9, 5.3 Hz, 1H), 2.57 – 2.53 (m, 1H), 2.30 (t, *J* = 12 Hz, 1H), 2.20 – 2.12 (m, 1H), 1.90 – 1.79 (m, 4H), 1.75 (d, *J* = 6.7 Hz, 3H), 1.65 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 162.6, 161.7, 143.4, 142.4, 141.7, 141.3, 140.7, 137.1, 136.2, 135.1, 134.1, 128.4, 128.3, 124.4, 124.1, 123.4, 122.4, 122.3,

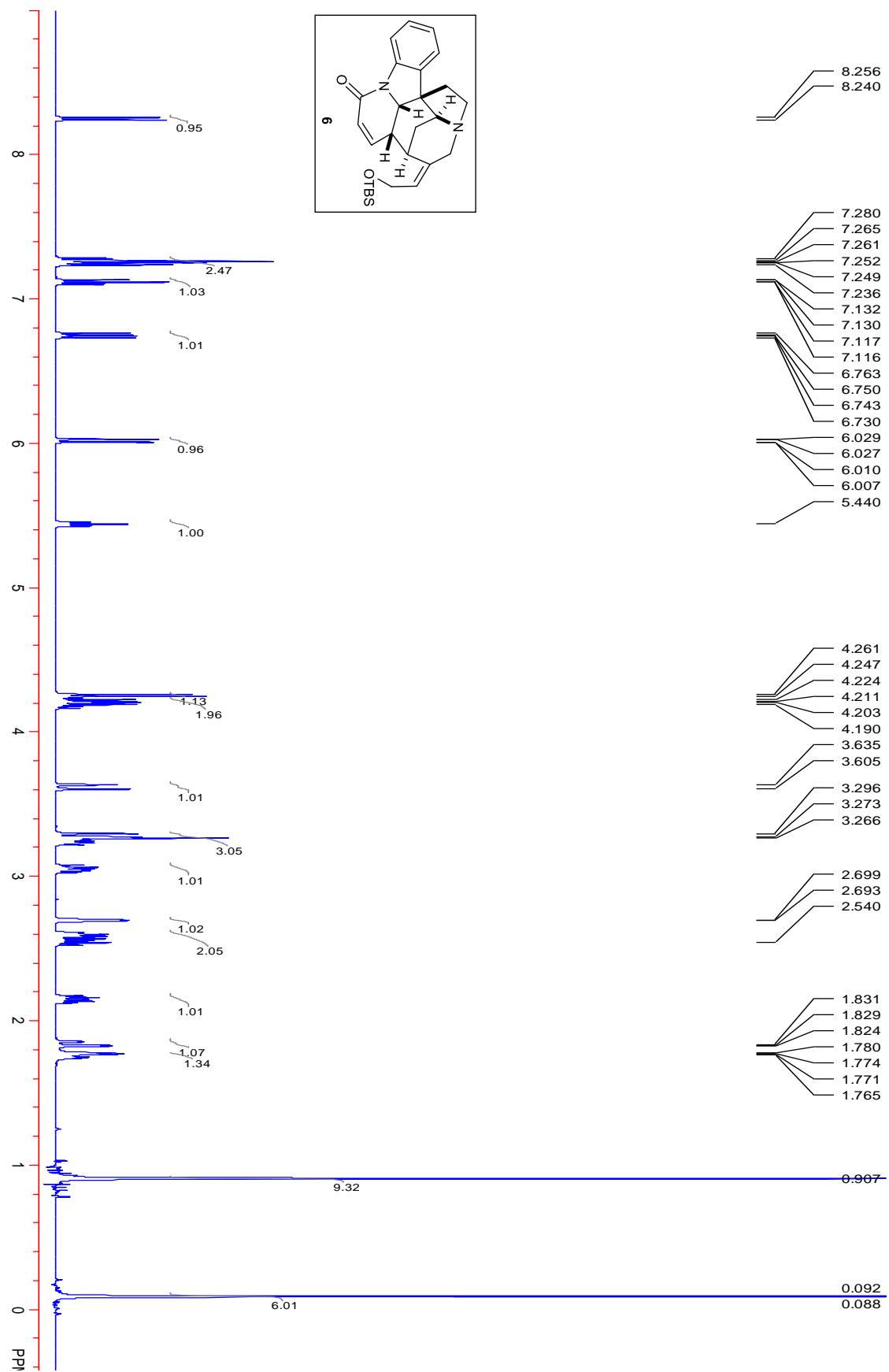
119.5, 118.9, 116.5, 116.2, 65.6, 64.8, 64.8, 64.2, 62.0, 53.7, 52.6, 52.5, 52.4, 50.1, 45.6, 40.3, 37.6, 37.1, 31.3, 31.1, 23.4, 22.4, 13.1, 12.9; HRMS (ESI) calc'd for C₄₂H₄₂N₄O₂+ H = 635.3386, found 635.3380.

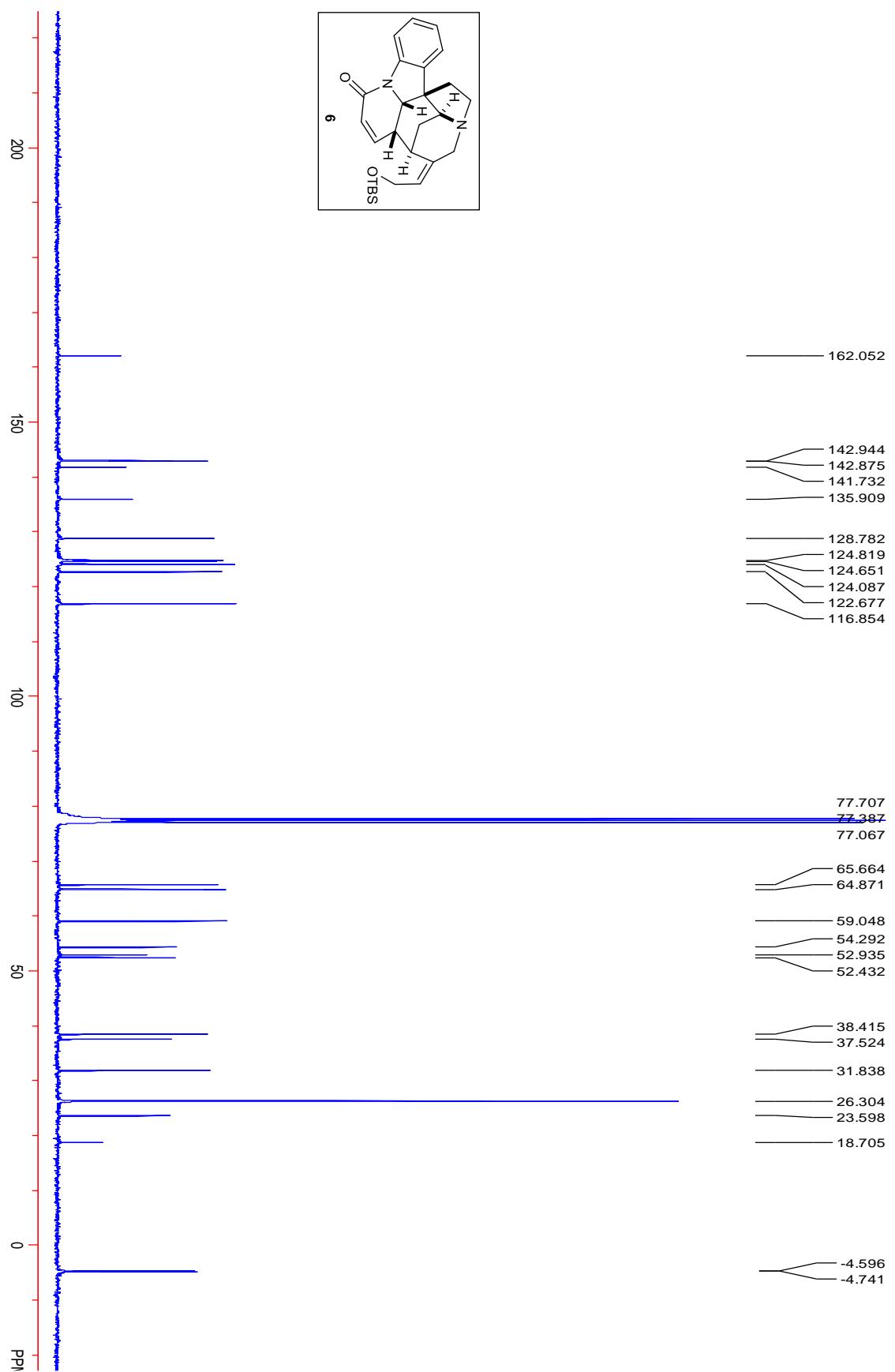


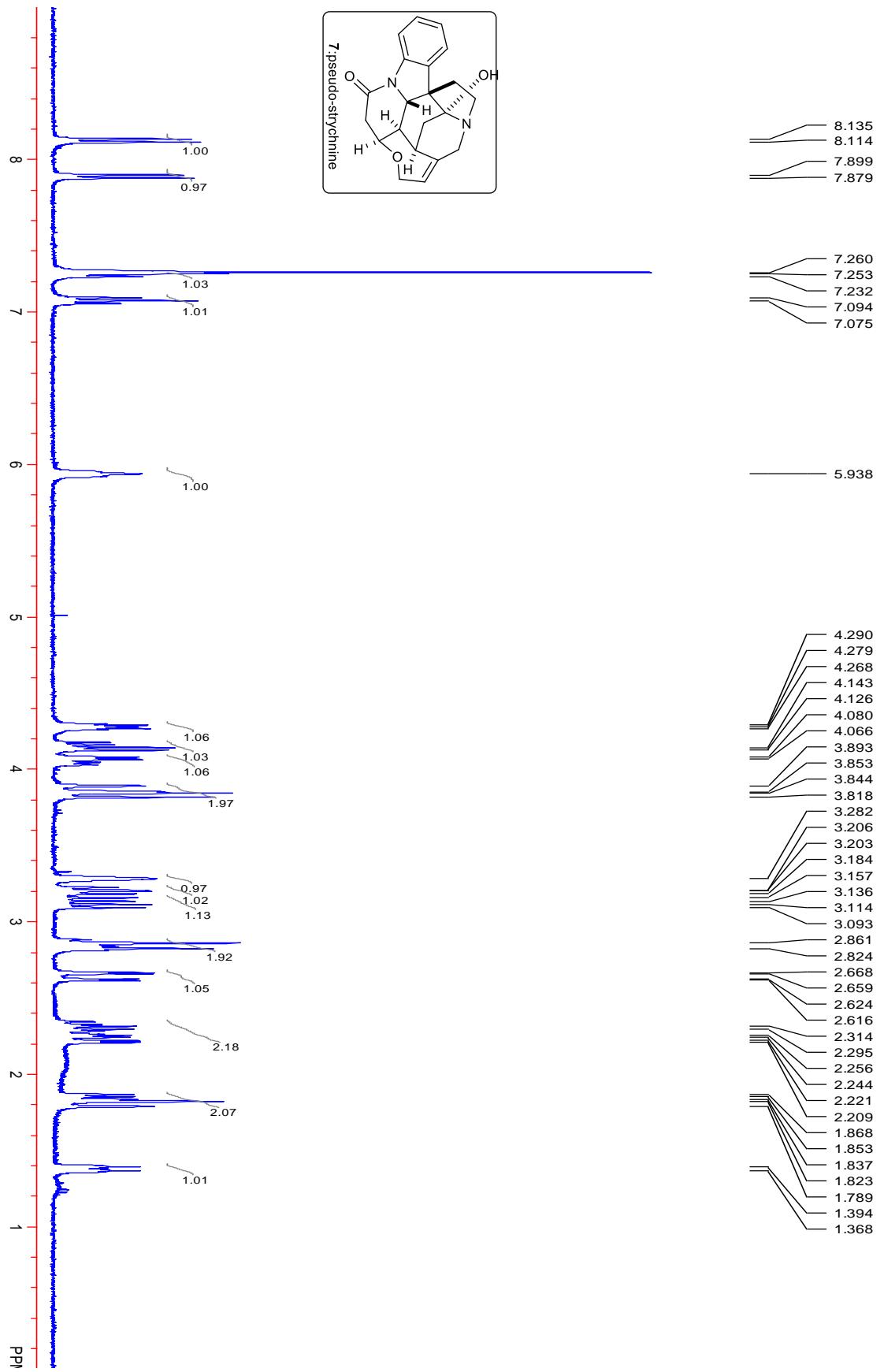


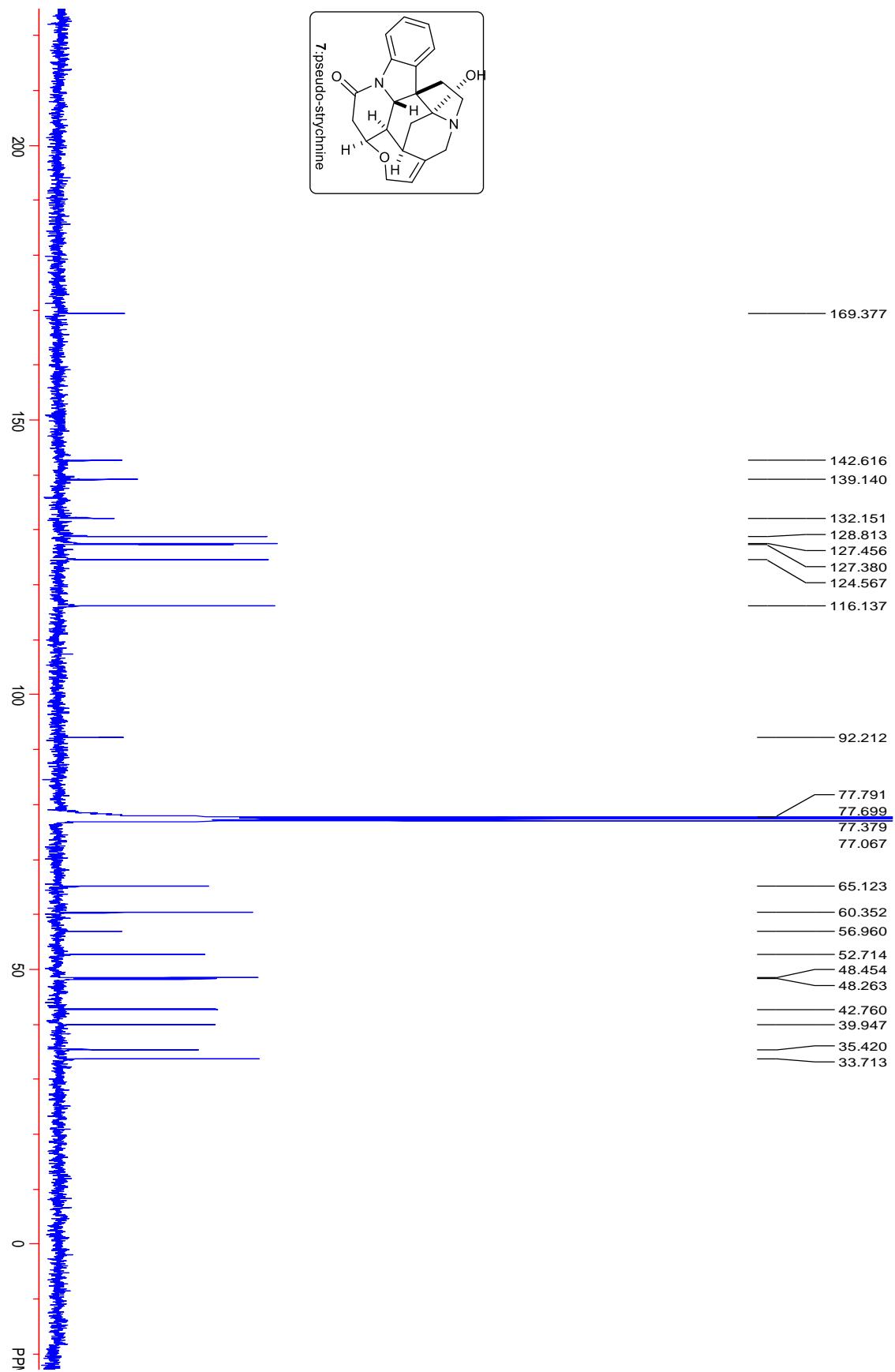


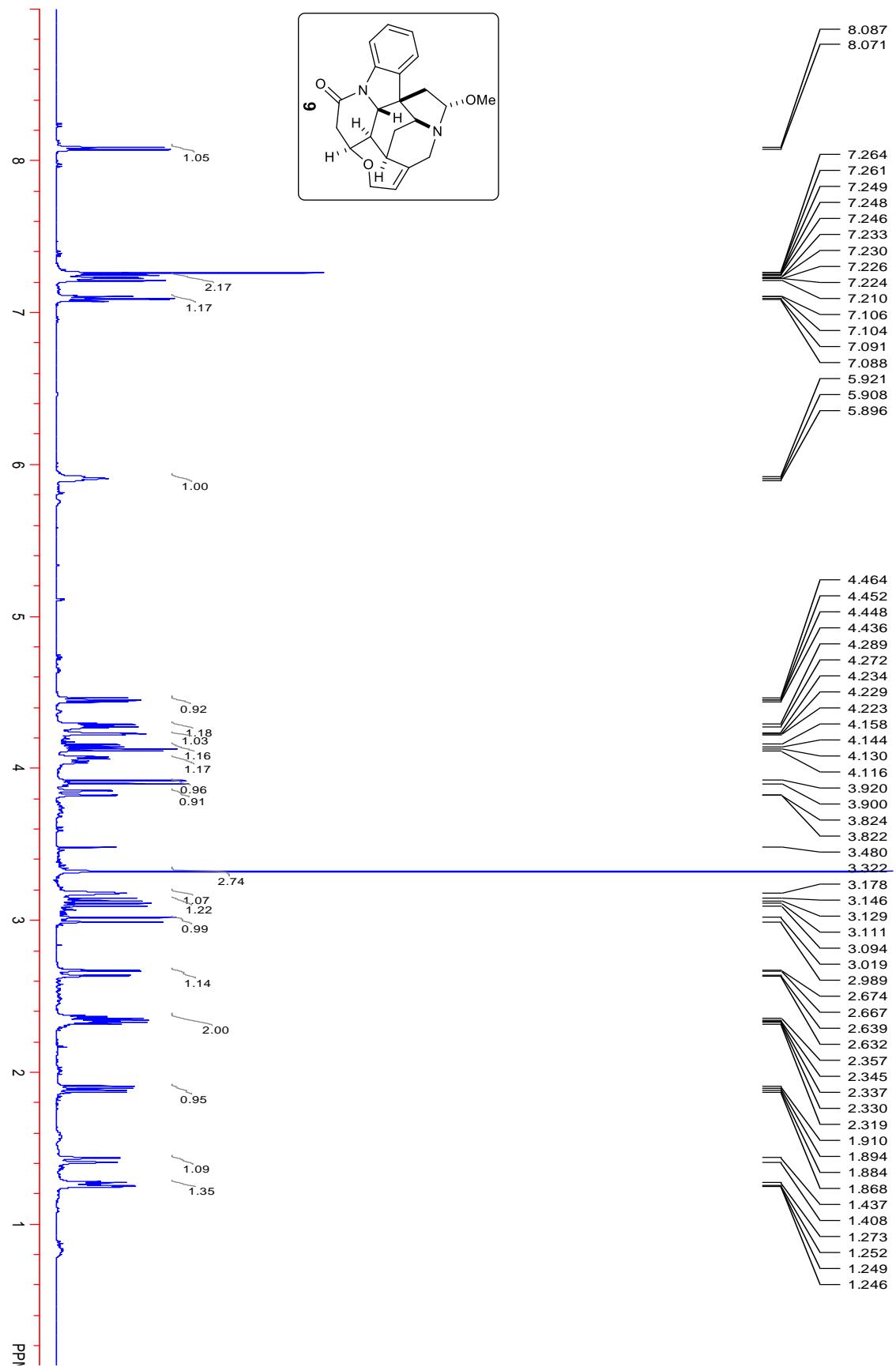


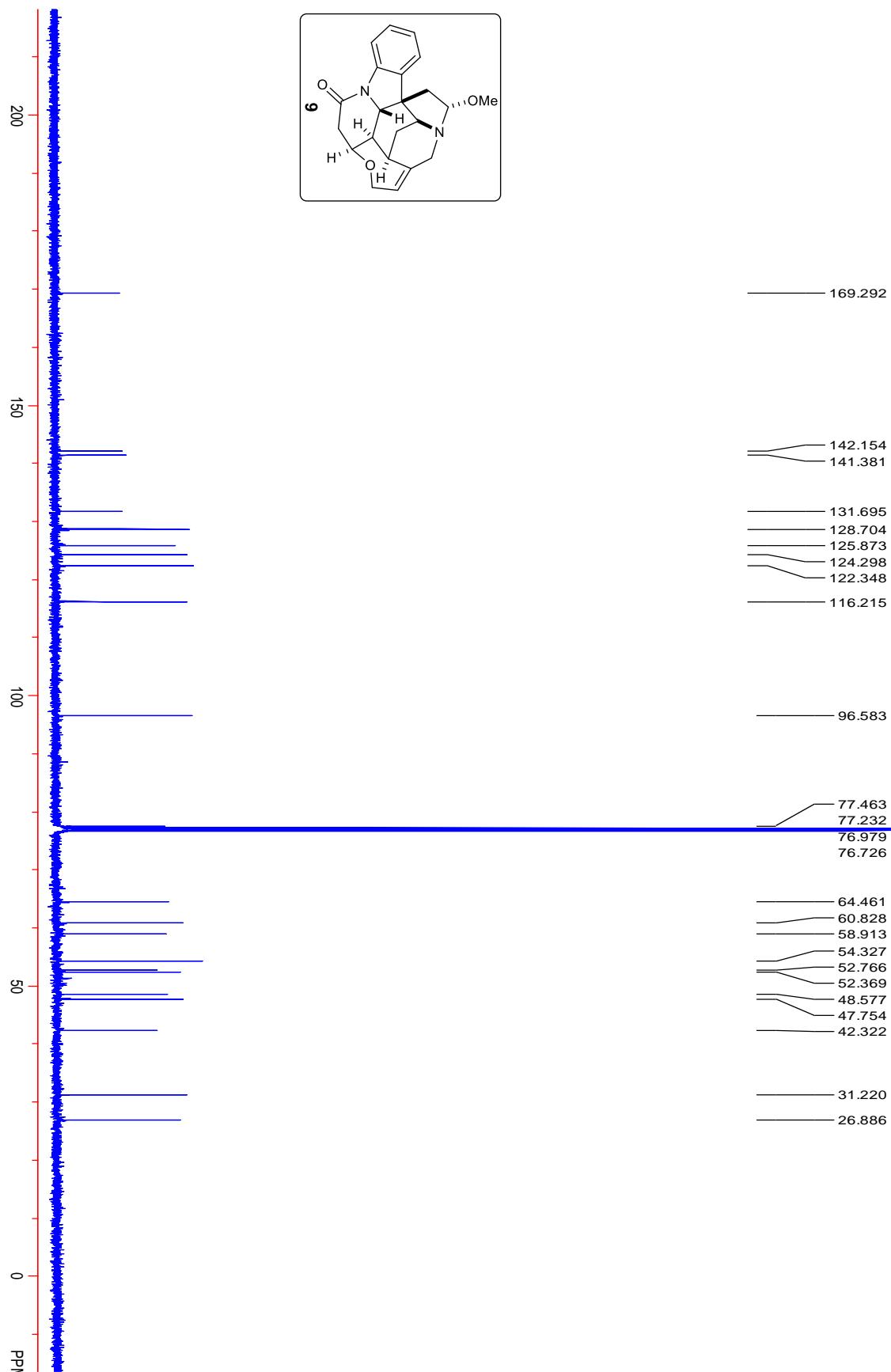


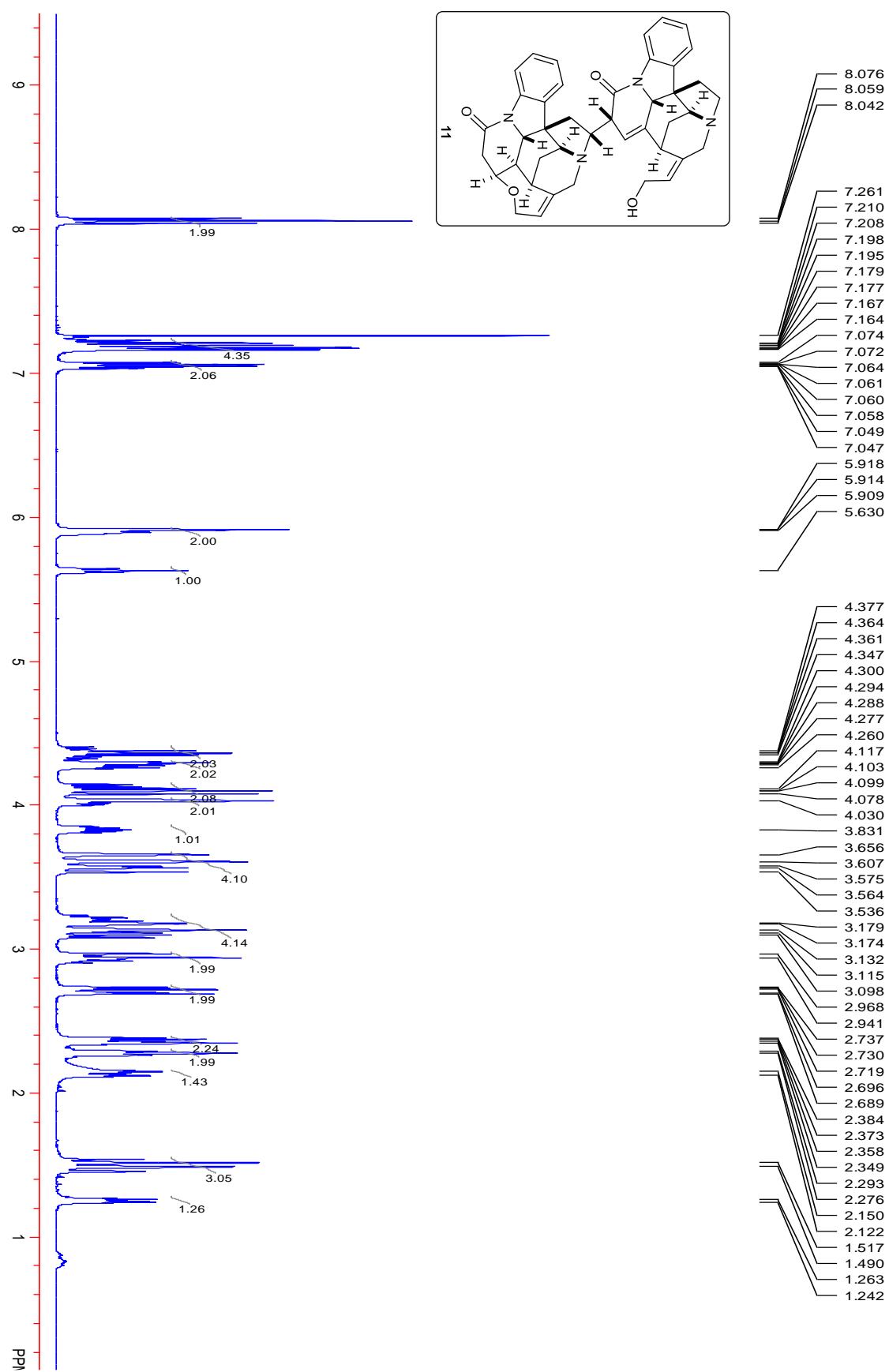


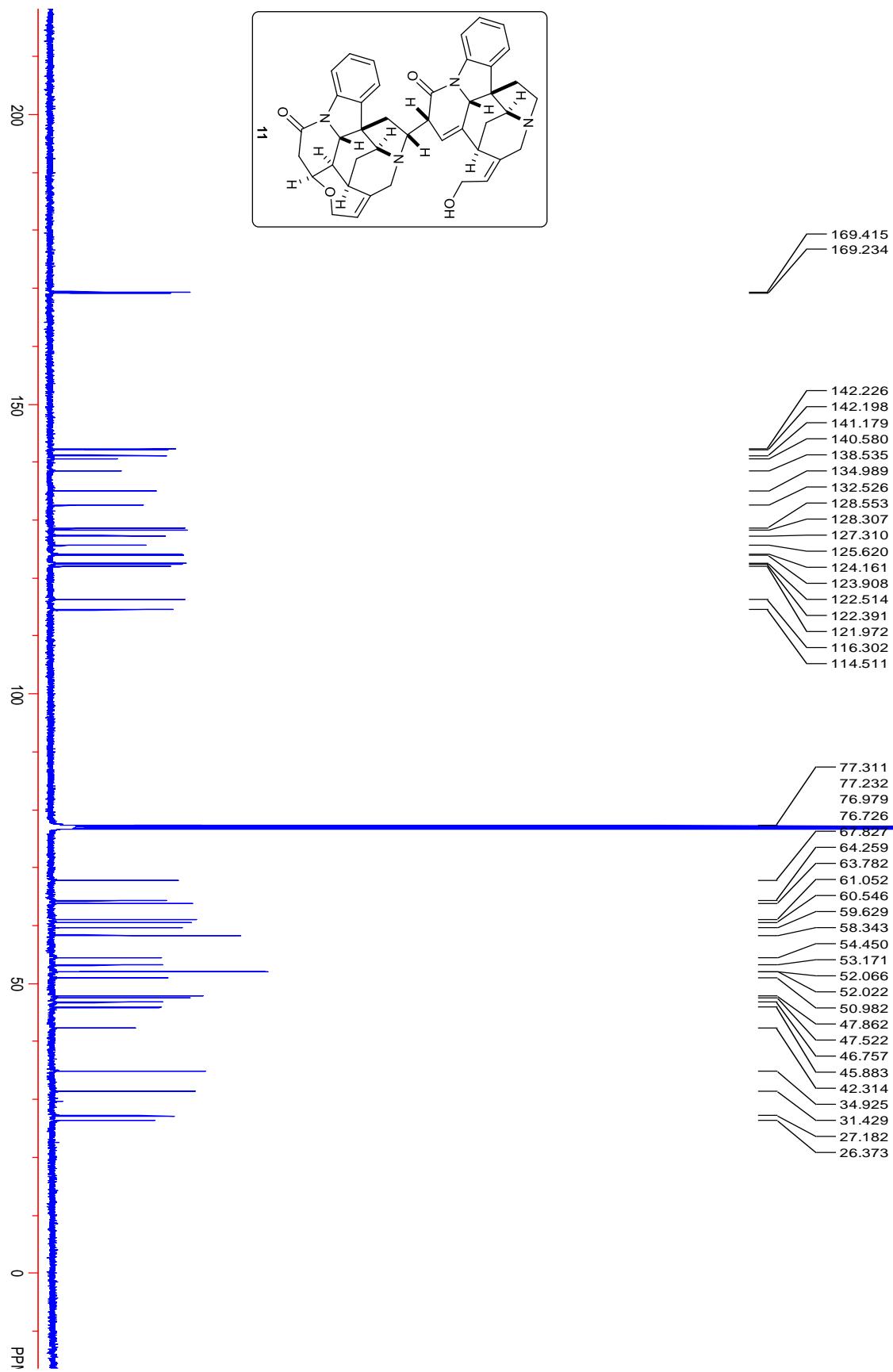


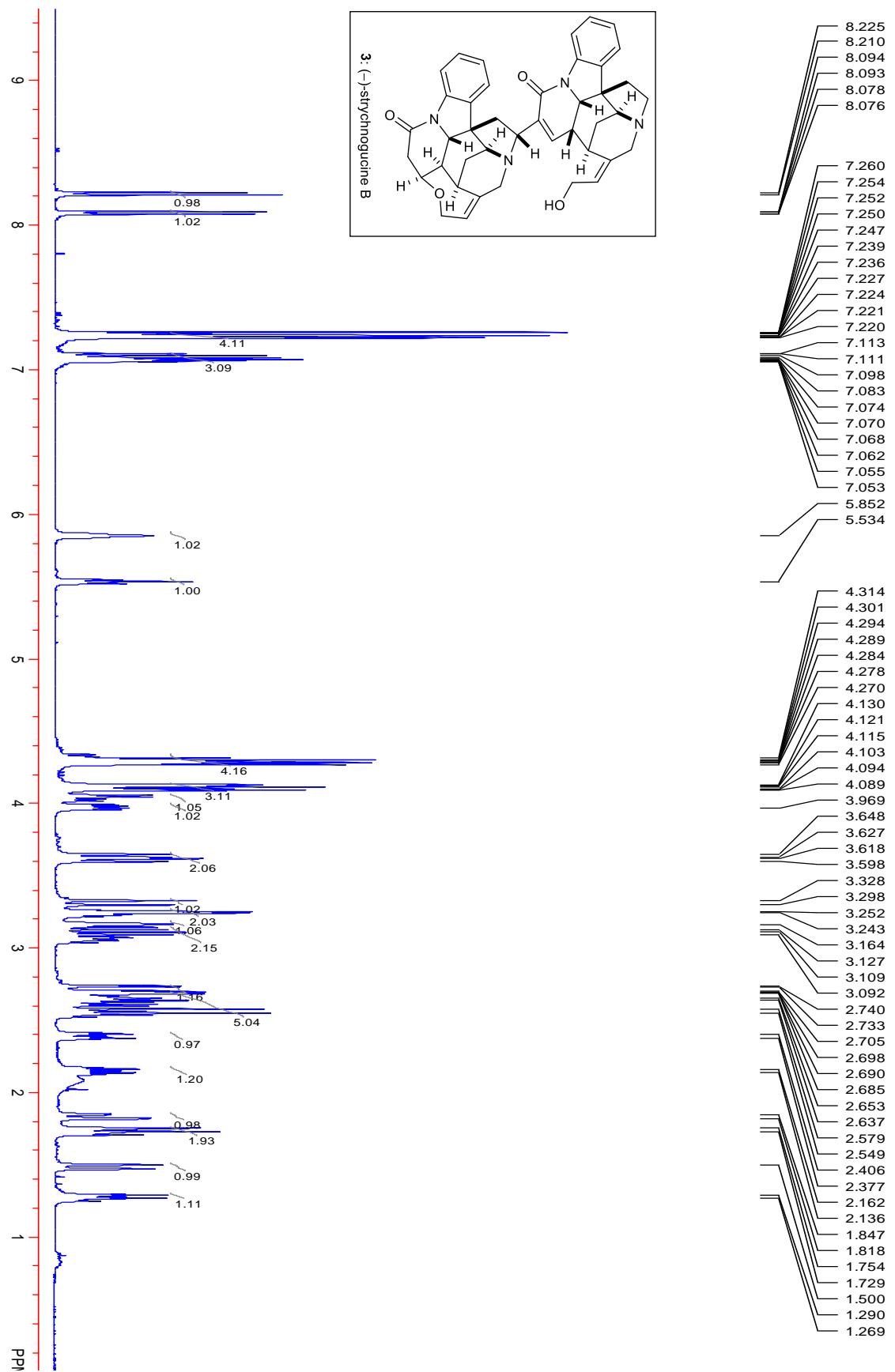


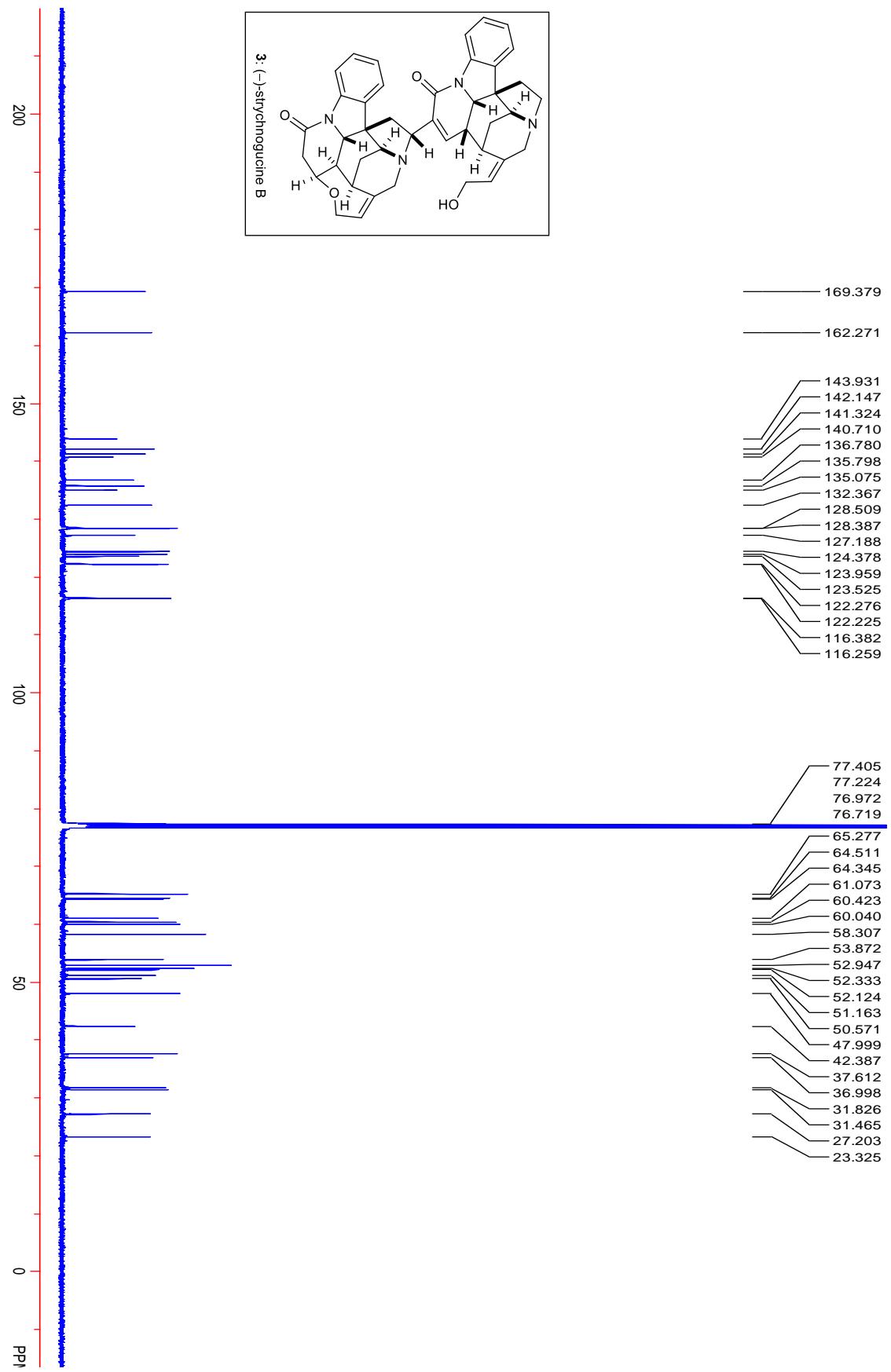


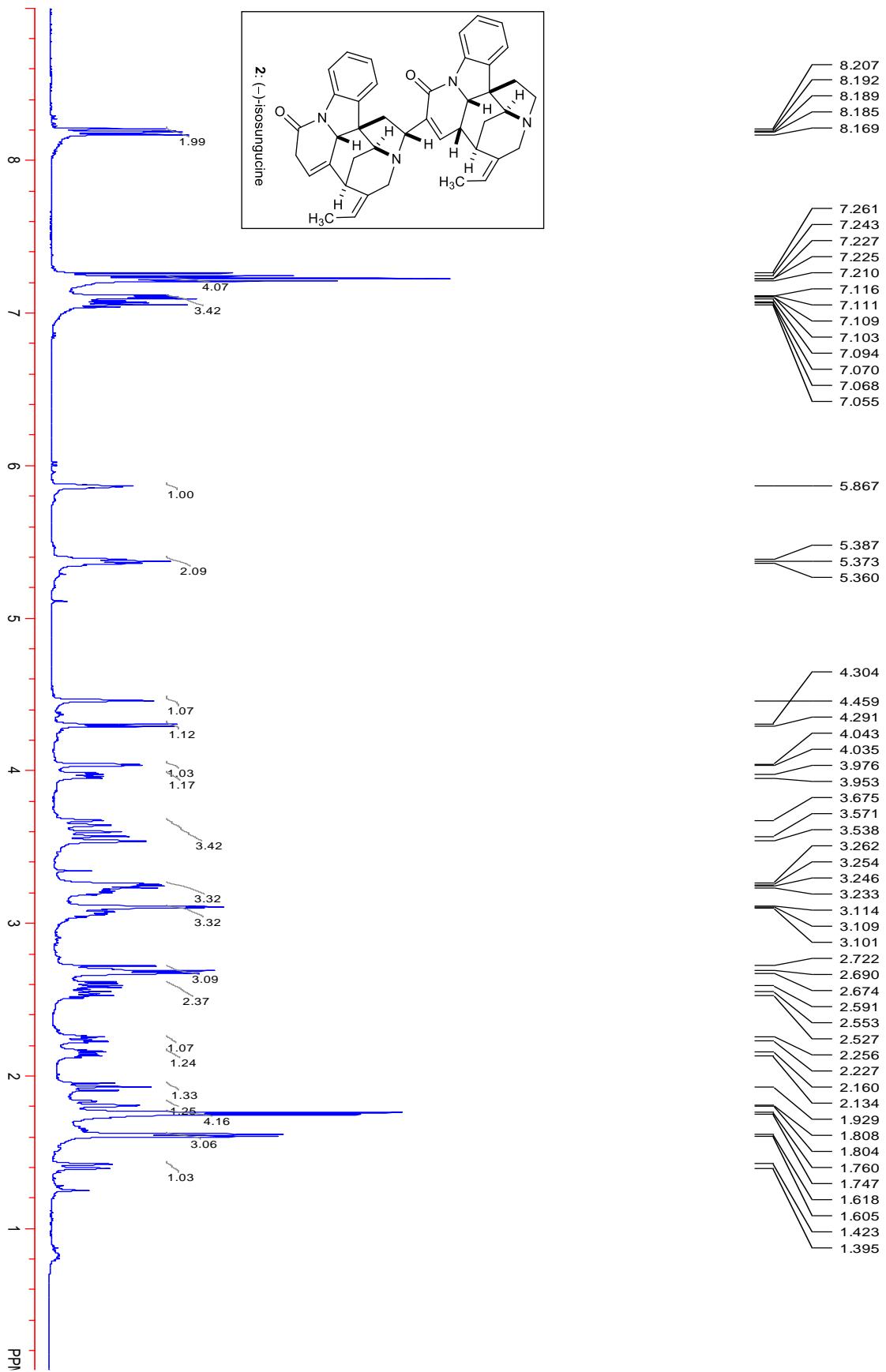


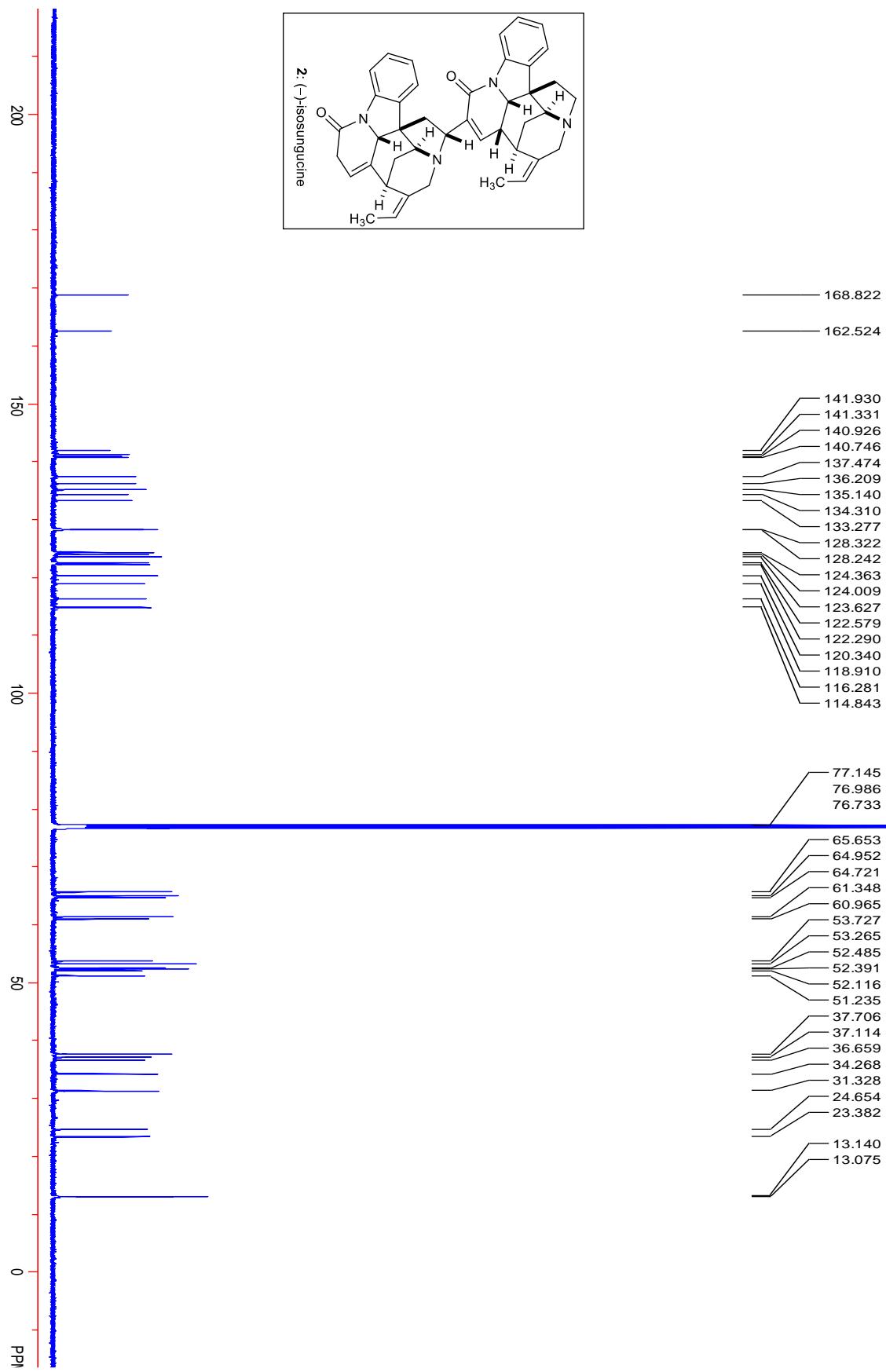


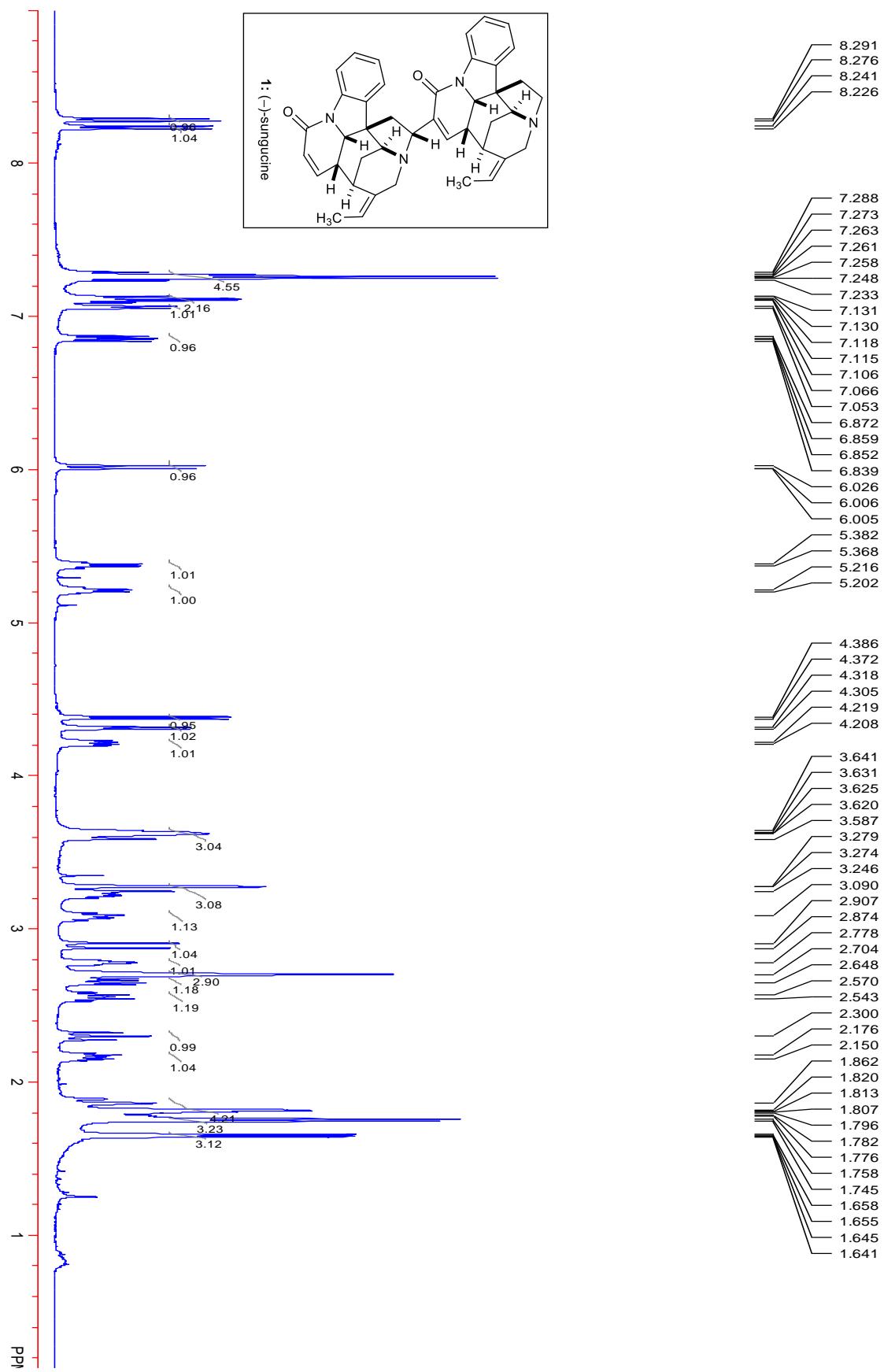


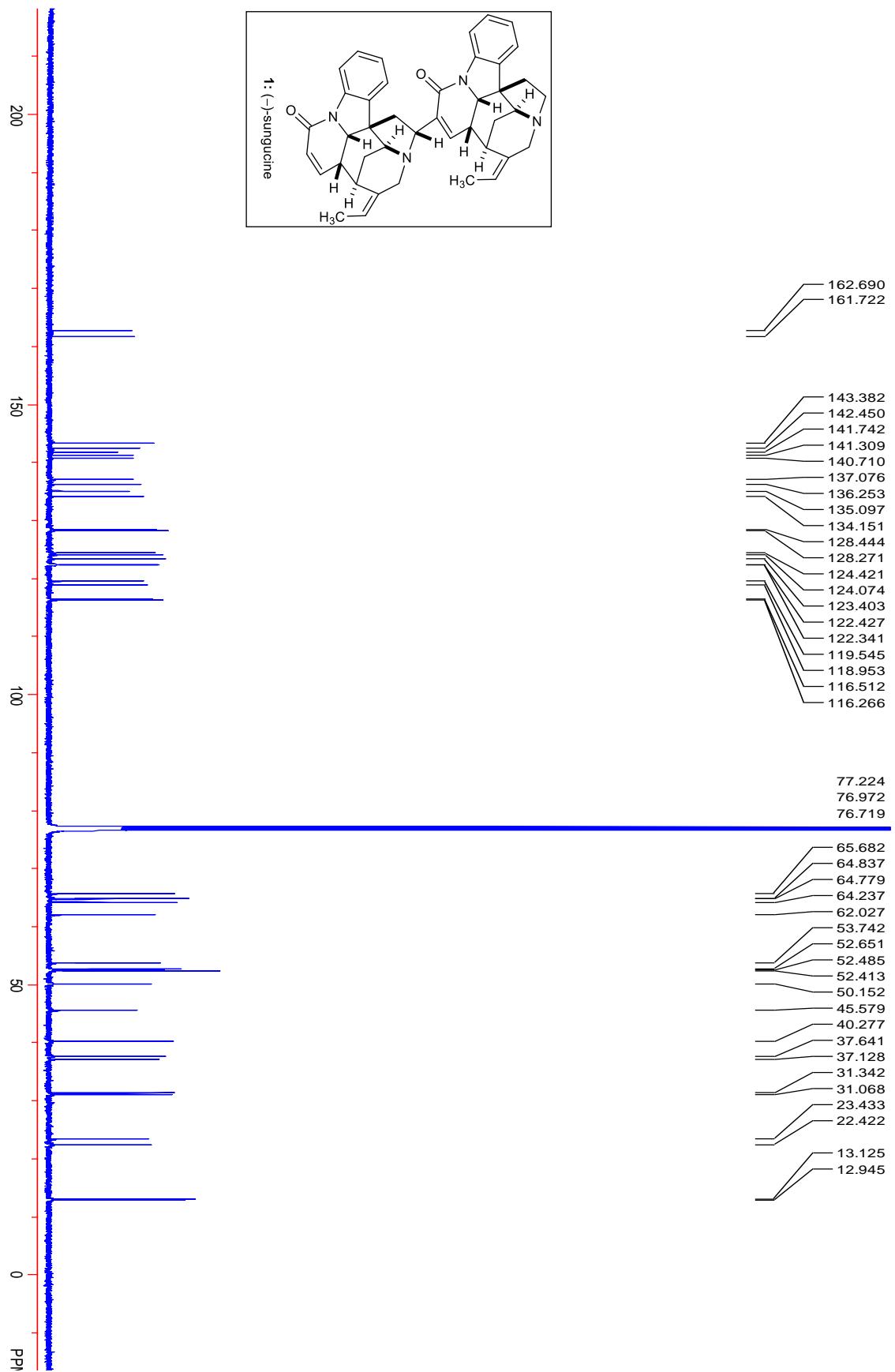












Crystal Structure Report for 7

A specimen of $C_{21}H_{22}N_2O_3$, approximate dimensions $0.030\text{ mm} \times 0.080\text{ mm} \times 0.240\text{ mm}$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 4.91 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 12003 reflections to a maximum θ angle of 27.95° (0.76 \AA resolution), of which 3832 were independent (average redundancy 3.132, completeness = 98.4%, $R_{\text{int}} = 5.40\%$, $R_{\text{sig}} = 7.05\%$) and 2951 (77.01%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 11.757(3)\text{ \AA}$, $b = 11.796(3)\text{ \AA}$, $c = 11.987(3)\text{ \AA}$, volume = $1662.4(7)\text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 3282 reflections above $20\sigma(I)$ with $4.844^\circ < 2\theta < 54.43^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.808. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6014 and 0.7439.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P\bar{1}\bar{1}\bar{1}\bar{1}\bar{1}\bar{1}$, with $Z = 4$ for the formula unit, $C_{21}H_{22}N_2O_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 236 variables converged at $R1 = 3.77\%$, for the observed data and $wR2 = 7.41\%$ for all data. The goodness-of-fit was 0.915. The largest peak in the final difference electron density synthesis was $0.232\text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.185\text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.043\text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.400 g/cm^3 and $F(000)$, 744 e^- .

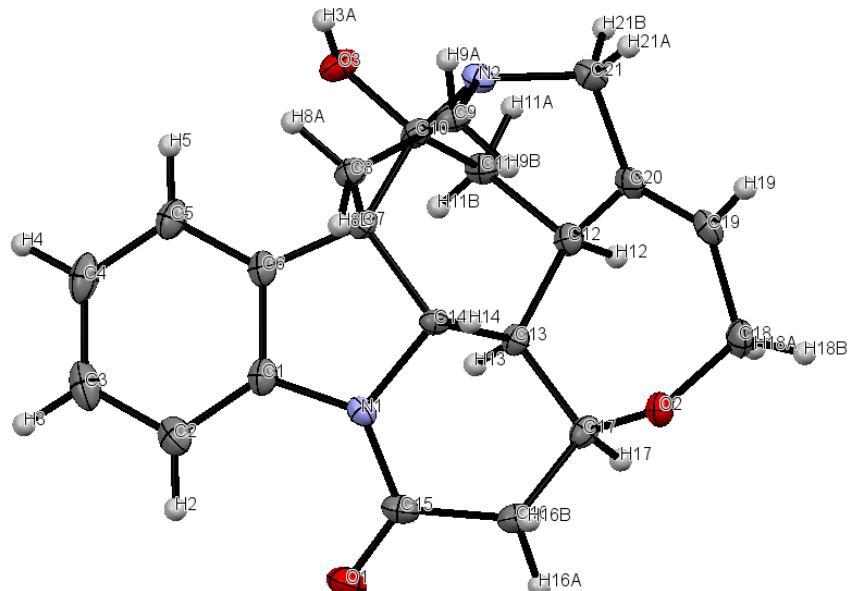


Table 1. Sample and crystal data for 7.

Identification code	7	
Chemical formula	C ₂₁ H ₂₂ N ₂ O ₃	
Formula weight	350.40 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.030 x 0.080 x 0.240 mm	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 11.757(3) Å b = 11.796(3) Å c = 11.987(3) Å	α = 90° β = 90° γ = 90°
Volume	1662.4(7) Å ³	
Z	4	
Density (calculated)	1.400 g/cm ³	
Absorption coefficient	0.094 mm ⁻¹	
F(000)	744	

Table 2. Data collection and structure refinement for 7.

Theta range for data collection	2.42 to 27.95°
Index ranges	-15<=h<=13, -15<=k<=15, -15<=l<=15
Reflections collected	12003
Independent reflections	3832 [R(int) = 0.0540]
Coverage of independent reflections	98.4%
Absorption correction	multi-scan
Max. and min. transmission	0.7439 and 0.6014
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	3832 / 0 / 236
Goodness-of-fit on F²	0.915
Final R indices	2951 data; I>2σ(I) R1 = 0.0377, wR2 = 0.0700 all data R1 = 0.0560, wR2 = 0.0741
Weighting scheme	w=1/[σ ² (F _o ²)+(0.0314P) ²] where P=(F _o ² +2F _c ²)/3

Absolute structure parameter	0.0(7)
Largest diff. peak and hole	0.232 and -0.185 eÅ ⁻³
R.M.S. deviation from mean	0.043 eÅ ⁻³

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for 7.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
O2	0.25102(13)	0.25628(12)	0.73015(13)	0.0173(4)
C21	0.42816(19)	0.56300(18)	0.6081(2)	0.0182(6)
C9	0.5911(2)	0.46766(17)	0.6980(2)	0.0174(6)
C8	0.62255(18)	0.45851(17)	0.8202(2)	0.0161(5)
C12	0.28646(19)	0.51643(17)	0.7613(2)	0.0160(5)
C16	0.2717(2)	0.22588(18)	0.9233(2)	0.0185(6)
O1	0.32267(14)	0.24473(13)	0.11603(16)	0.0256(4)
C17	0.23344(19)	0.31258(17)	0.8347(2)	0.0164(5)
C14	0.42429(18)	0.39336(16)	0.8743(2)	0.0133(5)
N1	0.42609(15)	0.34406(14)	0.98824(17)	0.0153(5)
C1	0.48434(18)	0.41730(18)	0.0621(2)	0.0167(5)
C20	0.33288(19)	0.48682(17)	0.6471(2)	0.0174(5)
N2	0.51741(15)	0.56925(14)	0.69391(17)	0.0163(5)
C6	0.52904(18)	0.50946(17)	0.0035(2)	0.0156(5)
C15	0.3404(2)	0.27153(18)	0.0193(2)	0.0175(6)
C18	0.2087(2)	0.31740(19)	0.6348(2)	0.0207(6)
C13	0.30021(17)	0.42353(17)	0.8497(2)	0.0146(5)
C2	0.50113(18)	0.4039(2)	0.1759(2)	0.0212(6)
C3	0.5615(2)	0.4871(2)	0.2324(2)	0.0258(6)
C19	0.29657(19)	0.39721(18)	0.5897(2)	0.0186(5)
C7	0.51195(17)	0.49319(16)	0.8799(2)	0.0145(5)
C11	0.34905(19)	0.62068(17)	0.8070(2)	0.0168(6)
C10	0.47559(19)	0.59702(17)	0.8068(2)	0.0161(5)
C4	0.60484(19)	0.5805(2)	0.1759(2)	0.0252(6)
C5	0.59041(19)	0.5911(2)	0.0612(2)	0.0206(6)
O3	0.52938(14)	0.69754(12)	0.84606(16)	0.0211(4)

Table 4. Bond lengths (Å) for 7.

O2-C17	1.433(3)	O2-C18	1.440(3)
C21-N2	1.471(3)	C21-C20	1.510(3)
C21-H21A	0.99	C21-H21B	0.99
C9-N2	1.480(3)	C9-C8	1.514(3)
C9-H9A	0.99	C9-H9B	0.99
C8-C7	1.539(3)	C8-H8A	0.99
C8-H8B	0.99	C12-C20	1.515(3)
C12-C11	1.534(3)	C12-C13	1.533(3)
C12-H12	1.0	C16-C15	1.506(3)
C16-C17	1.541(3)	C16-H16A	0.99
C16-H16B	0.99	O1-C15	1.220(3)
C17-C13	1.537(3)	C17-H17	1.0
C14-N1	1.484(3)	C14-C13	1.530(3)
C14-C7	1.566(3)	C14-H14	1.0
N1-C15	1.373(3)	N1-C1	1.414(3)
C1-C2	1.388(3)	C1-C6	1.397(3)
C20-C19	1.331(3)	N2-C10	1.477(3)
C6-C5	1.388(3)	C6-C7	1.507(3)
C18-C19	1.499(3)	C18-H18A	0.99
C18-H18B	0.99	C13-H13	1.0
C2-C3	1.388(3)	C2-H2	0.95
C3-C4	1.390(4)	C3-H3	0.95
C19-H19	0.95	C7-C10	1.565(3)
C11-C10	1.514(3)	C11-H11A	0.99
C11-H11B	0.99	C10-O3	1.424(2)
C4-C5	1.392(4)	C4-H4	0.95
C5-H5	0.95	O3-H3A	0.84

Table 5. Bond angles (°) for 7.

C17-O2-C18	114.32(16)	N2-C21-C20	110.03(19)
N2-C21-H21A	109.7	C20-C21-H21A	109.7
N2-C21-H21B	109.7	C20-C21-H21B	109.7
H21A-C21-H21B	108.2	N2-C9-C8	103.48(18)
N2-C9-H9A	111.1	C8-C9-H9A	111.1
N2-C9-H9B	111.1	C8-C9-H9B	111.1
H9A-C9-H9B	109.0	C9-C8-C7	102.95(18)
C9-C8-H8A	111.2	C7-C8-H8A	111.2

C9-C8-H8B	111.2	C7-C8-H8B	111.2
H8A-C8-H8B	109.1	C20-C12-C11	109.54(19)
C20-C12-C13	114.96(18)	C11-C12-C13	106.02(18)
C20-C12-H12	108.7	C11-C12-H12	108.7
C13-C12-H12	108.7	C15-C16-C17	116.48(18)
C15-C16-H16A	108.2	C17-C16-H16A	108.2
C15-C16-H16B	108.2	C17-C16-H16B	108.2
H16A-C16-H16B	107.3	O2-C17-C13	115.06(19)
O2-C17-C16	104.66(17)	C13-C17-C16	109.59(18)
O2-C17-H17	109.1	C13-C17-H17	109.1
C16-C17-H17	109.1	N1-C14-C13	106.39(18)
N1-C14-C7	104.25(18)	C13-C14-C7	117.42(16)
N1-C14-H14	109.5	C13-C14-H14	109.5
C7-C14-H14	109.5	C15-N1-C1	124.5(2)
C15-N1-C14	118.88(19)	C1-N1-C14	110.10(17)
C2-C1-C6	122.0(2)	C2-C1-N1	127.9(2)
C6-C1-N1	110.0(2)	C19-C20-C21	123.4(2)
C19-C20-C12	122.3(2)	C21-C20-C12	114.19(19)
C21-N2-C10	114.48(18)	C21-N2-C9	113.60(17)
C10-N2-C9	110.11(17)	C5-C6-C1	119.0(2)
C5-C6-C7	130.3(2)	C1-C6-C7	110.20(19)
O1-C15-N1	123.0(2)	O1-C15-C16	122.8(2)
N1-C15-C16	114.2(2)	O2-C18-C19	111.26(19)
O2-C18-H18A	109.4	C19-C18-H18A	109.4
O2-C18-H18B	109.4	C19-C18-H18B	109.4
H18A-C18-H18B	108.0	C14-C13-C12	113.59(18)
C14-C13-C17	108.15(17)	C12-C13-C17	118.29(18)
C14-C13-H13	105.2	C12-C13-H13	105.2
C17-C13-H13	105.2	C3-C2-C1	118.1(2)
C3-C2-H2	120.9	C1-C2-H2	120.9
C2-C3-C4	120.7(3)	C2-C3-H3	119.6
C4-C3-H3	119.6	C20-C19-C18	122.2(2)
C20-C19-H19	118.9	C18-C19-H19	118.9
C6-C7-C8	112.20(18)	C6-C7-C14	103.01(19)
C8-C7-C14	109.65(17)	C6-C7-C10	119.13(18)
C8-C7-C10	100.29(19)	C14-C7-C10	112.64(17)
C10-C11-C12	108.86(17)	C10-C11-H11A	109.9
C12-C11-H11A	109.9	C10-C11-H11B	109.9

C12-C11-H11B	109.9	H11A-C11-H11B	108.3
O3-C10-N2	109.85(18)	O3-C10-C11	106.41(17)
N2-C10-C11	111.67(19)	O3-C10-C7	110.21(18)
N2-C10-C7	104.38(17)	C11-C10-C7	114.34(19)
C3-C4-C5	120.5(2)	C3-C4-H4	119.7
C5-C4-H4	119.7	C6-C5-C4	119.6(2)
C6-C5-H5	120.2	C4-C5-H5	120.2
C10-O3-H3A	109.5		

Table 6. Torsion angles (°) for 7.

N2-C9-C8-C7	38.0(2)	C18-O2-C17-C13	-66.3(2)
C18-O2-C17-C16	173.34(17)	C15-C16-C17-O2	138.0(2)
C15-C16-C17-C13	14.1(3)	C13-C14-N1-C15	40.5(2)
C7-C14-N1-C15	165.27(17)	C13-C14-N1-C1	-112.40(19)
C7-C14-N1-C1	12.3(2)	C15-N1-C1-C2	26.6(3)
C14-N1-C1-C2	177.7(2)	C15-N1-C1-C6	-155.2(2)
C14-N1-C1-C6	-4.1(2)	N2-C21-C20-C19	-124.2(2)
N2-C21-C20-C12	52.1(2)	C11-C12-C20-C19	177.6(2)
C13-C12-C20-C19	58.3(3)	C11-C12-C20-C21	1.2(2)
C13-C12-C20-C21	-118.0(2)	C20-C21-N2-C10	-50.8(2)
C20-C21-N2-C9	76.9(2)	C8-C9-N2-C21	-147.73(19)
C8-C9-N2-C10	-17.8(2)	C2-C1-C6-C5	-1.2(3)
N1-C1-C6-C5	-179.49(19)	C2-C1-C6-C7	171.8(2)
N1-C1-C6-C7	-6.5(2)	C1-N1-C15-O1	-16.6(3)
C14-N1-C15-O1	-165.4(2)	C1-N1-C15-C16	164.66(19)
C14-N1-C15-C16	15.9(3)	C17-C16-C15-O1	135.4(2)
C17-C16-C15-N1	-45.9(3)	C17-O2-C18-C19	88.3(2)
N1-C14-C13-C12	156.23(17)	C7-C14-C13-C12	40.0(3)
N1-C14-C13-C17	-70.4(2)	C7-C14-C13-C17	173.43(19)
C20-C12-C13-C14	61.9(3)	C11-C12-C13-C14	-59.3(2)
C20-C12-C13-C17	-66.5(3)	C11-C12-C13-C17	172.34(19)
O2-C17-C13-C14	-76.0(2)	C16-C17-C13-C14	41.6(3)
O2-C17-C13-C12	54.9(3)	C16-C17-C13-C12	172.48(19)
C6-C1-C2-C3	1.9(3)	N1-C1-C2-C3	179.9(2)
C1-C2-C3-C4	-0.7(3)	C21-C20-C19-C18	174.7(2)
C12-C20-C19-C18	-1.3(3)	O2-C18-C19-C20	-66.3(3)
C5-C6-C7-C8	67.7(3)	C1-C6-C7-C8	-104.3(2)

C5-C6-C7-C14	-174.5(2)	C1-C6-C7-C14	13.6(2)
C5-C6-C7-C10	-48.9(3)	C1-C6-C7-C10	139.1(2)
C9-C8-C7-C6	-170.27(17)	C9-C8-C7-C14	75.9(2)
C9-C8-C7-C10	-42.8(2)	N1-C14-C7-C6	-15.13(19)
C13-C14-C7-C6	102.2(2)	N1-C14-C7-C8	104.5(2)
C13-C14-C7-C8	-138.1(2)	N1-C14-C7-C10	-144.75(18)
C13-C14-C7-C10	-27.4(3)	C20-C12-C11-C10	-55.5(2)
C13-C12-C11-C10	69.1(2)	C21-N2-C10-O3	-121.62(19)
C9-N2-C10-O3	108.94(19)	C21-N2-C10-C11	-3.8(2)
C9-N2-C10-C11	-133.24(17)	C21-N2-C10-C7	120.23(18)
C9-N2-C10-C7	-9.2(2)	C12-C11-C10-O3	178.01(19)
C12-C11-C10-N2	58.1(2)	C12-C11-C10-C7	-60.1(3)
C6-C7-C10-O3	36.6(3)	C8-C7-C10-O3	-86.1(2)
C14-C7-C10-O3	157.36(18)	C6-C7-C10-N2	154.50(18)
C8-C7-C10-N2	31.8(2)	C14-C7-C10-N2	-84.7(2)
C6-C7-C10-C11	-83.2(2)	C8-C7-C10-C11	154.1(2)
C14-C7-C10-C11	37.6(3)	C2-C3-C4-C5	-1.3(3)
C1-C6-C5-C4	-0.9(3)	C7-C6-C5-C4	-172.3(2)
C3-C4-C5-C6	2.1(3)		

Table 7. Anisotropic atomic displacement parameters (\AA^2) for 7.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	0.0181(9)	0.0182(7)	0.0157(10)	-0.0022(7)	-0.0016(8)	0.0001(7)
C21	0.0196(12)	0.0184(10)	0.0168(15)	0.0025(10)	0.0008(11)	0.0022(9)
C9	0.0166(12)	0.0144(10)	0.0213(15)	0.0003(10)	0.0035(11)	0.0002(9)
C8	0.0125(12)	0.0156(10)	0.0202(16)	0.0006(10)	0.0011(11)	0.0001(8)
C12	0.0125(11)	0.0165(11)	0.0189(15)	0.0013(10)	-0.0013(11)	0.0026(9)
C16	0.0187(13)	0.0152(11)	0.0216(15)	0.0013(10)	0.0038(12)	-0.0015(9)
O1	0.0265(10)	0.0287(9)	0.0216(11)	0.0084(9)	0.0024(9)	-0.0023(8)
C17	0.0126(12)	0.0172(10)	0.0194(15)	-0.0030(10)	0.0010(11)	-0.0010(9)
C14	0.0144(11)	0.0114(9)	0.0142(14)	0.0008(10)	0.0014(11)	0.0006(8)
N1	0.0157(11)	0.0166(9)	0.0134(12)	0.0016(9)	-0.0010(9)	0.0019(8)
C1	0.0113(11)	0.0196(11)	0.0191(16)	-0.0029(11)	-0.0011(11)	0.0044(9)
C20	0.0154(12)	0.0187(11)	0.0181(15)	0.0064(10)	-0.0038(11)	0.0041(9)
N2	0.0157(10)	0.0166(9)	0.0168(12)	0.0026(9)	0.0014(9)	0.0026(8)

	U₁₁	U₂₂	U₃₃	U₂₃	U₁₃	U₁₂
C6	0.0098(11)	0.0191(10)	0.0177(15)	-0.0014(10)	-0.0010(11)	0.0048(9)
C15	0.0165(13)	0.0159(11)	0.0200(16)	0.0042(11)	0.0047(12)	0.0034(9)
C18	0.0191(13)	0.0230(11)	0.0199(16)	-0.0004(11)	-0.0077(12)	0.0014(10)
C13	0.0125(11)	0.0147(10)	0.0166(14)	-0.0012(10)	-0.0006(11)	0.0014(9)
C2	0.0133(13)	0.0291(12)	0.0211(16)	0.0020(12)	0.0007(11)	0.0058(10)
C3	0.0183(14)	0.0421(15)	0.0170(15)	-0.0063(13)	-0.0020(12)	0.0102(12)
C19	0.0189(12)	0.0236(12)	0.0135(14)	0.0027(10)	-0.0034(11)	0.0046(9)
C7	0.0118(11)	0.0141(10)	0.0177(14)	-0.0007(10)	-0.0013(11)	0.0000(8)
C11	0.0164(12)	0.0141(10)	0.0198(15)	0.0011(10)	0.0009(11)	0.0031(9)
C10	0.0156(12)	0.0124(10)	0.0203(15)	0.0001(10)	-0.0008(11)	-0.0018(9)
C4	0.0156(13)	0.0317(13)	0.0282(18)	-0.0135(13)	-0.0049(12)	0.0053(11)
C5	0.0143(13)	0.0225(12)	0.0249(17)	-0.0058(11)	-0.0012(11)	0.0017(10)
O3	0.0193(9)	0.0161(7)	0.0279(12)	-0.0028(7)	0.0042(9)	-0.0034(7)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (\AA^2) for 7.

	x/a	y/b	z/c	U(eq)
H21A	0.4607	0.5329	0.5379	0.022
H21B	0.3981	0.6399	0.5930	0.022
H9A	0.6596	0.4778	0.6511	0.021
H9B	0.5495	0.3994	0.6727	0.021
H8A	0.6857	0.5106	0.8392	0.019
H8B	0.6448	0.3801	0.8399	0.019
H12	0.2038	0.5351	0.7540	0.019
H16A	0.2029	0.1888	0.9540	0.022
H16B	0.3172	0.1666	0.8856	0.022
H17	0.1504	0.3282	0.8443	0.02
H14	0.4512	0.3354	0.8194	0.016
H18A	0.1401	0.3608	0.6566	0.025
H18B	0.1865	0.2629	0.5759	0.025
H13	0.2705	0.4575	0.9204	0.017
H2	0.4721	0.3395	1.2141	0.025
H3	0.5733	0.4801	1.3105	0.031
H19	0.3274	0.3834	0.5177	0.022
H11A	0.3324	0.6876	0.7598	0.02
H11B	0.3230	0.6371	0.8838	0.02

	x/a	y/b	z/c	U(eq)
H4	0.6446	0.6376	1.2160	0.03
H5	0.6224	0.6538	1.0226	0.025
H3A	0.5936	0.7040	0.8160	0.032

Crystal Structure Report for 9

A specimen of $C_{23}H_{26}Cl_2N_2O_3$, approximate dimensions 0.042 mm x 0.086 mm x 0.120 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The integration of the data using an orthorhombic unit cell yielded a total of 9426 reflections to a maximum θ angle of 27.91° (0.76 Å resolution), of which 4599 were independent (average redundancy 2.050, completeness = 99.3%, $R_{\text{int}} = 4.69\%$, $R_{\text{sig}} = 10.46\%$) and 2951 (64.17%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 7.6514(10)$ Å, $b = 10.5279(14)$ Å, $c = 25.339(3)$ Å, volume = 2041.1(5) Å³, are based upon the refinement of the XYZ-centroids of reflections above 20 $\sigma(I)$. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6319 and 0.7456.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 21 21 21, with Z = 4 for the formula unit, $C_{23}H_{26}Cl_2N_2O_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 272 variables converged at $R1 = 6.69\%$, for the observed data and $wR2 = 16.93\%$ for all data. The goodness-of-fit was 1.020. The largest peak in the final difference electron density synthesis was 0.779 e⁻/Å³ and the largest hole was -0.544 e⁻/Å³ with an RMS deviation of 0.081 e⁻/Å³. On the basis of the final model, the calculated density was 1.462 g/cm³ and $F(000)$, 944 e⁻.

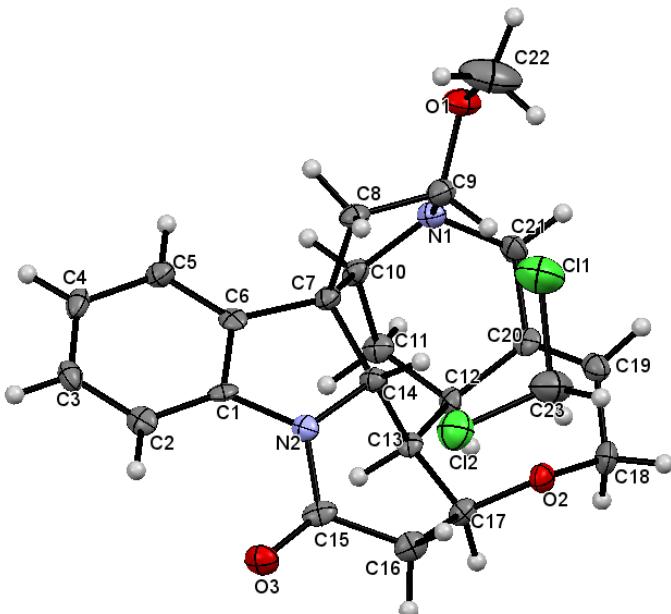


Table 1. Sample and crystal data for 9.

Identification code	9	
Chemical formula	C ₂₃ H ₂₆ Cl ₂ N ₂ O ₃	
Formula weight	449.36 g/mol	
Temperature	99(2) K	
Wavelength	0.71073 Å	
Crystal size	0.042 x 0.086 x 0.120 mm	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 7.6514(10) Å b = 10.5279(14) Å c = 25.339(3) Å	α = 90° β = 90° γ = 90°
Volume	2041.1(5) Å ³	
Z	4	
Density (calculated)	1.462 g/cm ³	
Absorption coefficient	0.348 mm ⁻¹	
F(000)	944	

Table 2. Data collection and structure refinement for 9.

Theta range for data collection	1.61 to 27.91°
Index ranges	-8<=h<=10, -13<=k<=9, -33<=l<=32
Reflections collected	9426
Independent reflections	4599 [R(int) = 0.0469]
Max. and min. transmission	0.7456 and 0.6319
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014 (Sheldrick, 2014)
Function minimized	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	4599 / 0 / 272
Goodness-of-fit on F²	1.020
Final R indices	2951 data; I>2σ(I) R1 = 0.0669, wR2 = 0.1445 all data R1 = 0.1219, wR2 = 0.1693
Weighting scheme	w=1/[σ ² (F _o ²)+(0.0795P) ² +0.8615P] where P=(F _o ² +2F _c ²)/3
Absolute structure parameter	0.1(1)
Largest diff. peak and hole	0.779 and -0.544 eÅ ⁻³

R.M.S. deviation from mean 0.081 e\AA^{-3}

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (\AA^2) for 9.

$U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C8	0.2815(8)	0.5825(6)	0.4369(2)	0.0192(13)
O1	0.3812(6)	0.5419(4)	0.52868(16)	0.0294(11)
O3	0.3222(6)	0.5125(4)	0.21581(15)	0.0245(10)
O2	0.7364(5)	0.3513(4)	0.33468(15)	0.0205(9)
C21	0.7367(8)	0.6094(6)	0.4731(2)	0.0210(13)
C5	0.1539(8)	0.8288(6)	0.3667(2)	0.0202(13)
C4	0.0359(8)	0.8755(6)	0.3290(2)	0.0207(14)
C3	0.0149(8)	0.8099(6)	0.2814(2)	0.0214(14)
C2	0.1099(8)	0.7019(6)	0.2700(2)	0.0205(13)
Cl2	0.2661(2)	0.17274(17)	0.31486(7)	0.0368(5)
C17	0.7031(8)	0.4591(5)	0.3013(2)	0.0184(13)
C14	0.4564(7)	0.5496(6)	0.3521(2)	0.0164(12)
C19	0.8476(8)	0.4301(6)	0.4188(2)	0.0219(14)
C20	0.7906(7)	0.5472(6)	0.4217(2)	0.0187(13)
C10	0.5126(7)	0.7283(6)	0.4212(2)	0.0184(13)
C11	0.6797(7)	0.7575(6)	0.3906(2)	0.0202(13)
C12	0.7628(8)	0.6318(5)	0.3735(2)	0.0159(12)
C6	0.2504(8)	0.7202(5)	0.3556(2)	0.0164(12)
C1	0.2274(7)	0.6583(5)	0.3071(2)	0.0158(12)
C16	0.5600(8)	0.4159(6)	0.2619(2)	0.0220(14)
C13	0.6433(7)	0.5768(5)	0.3316(2)	0.0148(12)
C7	0.3763(7)	0.6483(6)	0.3905(2)	0.0170(12)

C9	0.4300(8)	0.5494(6)	0.4740(2)	0.0220(14)
C15	0.3983(8)	0.4968(6)	0.2579(2)	0.0193(13)
N2	0.3413(6)	0.5521(5)	0.30431(18)	0.0179(11)
C18	0.8878(8)	0.3642(6)	0.3673(2)	0.0236(14)
N1	0.5529(6)	0.6536(5)	0.46926(18)	0.0188(11)
C23	0.4185(11)	0.1404(7)	0.3659(3)	0.0386(19)
Cl1	0.3362(3)	0.1908(2)	0.42696(7)	0.0592(7)
C22	0.2920(13)	0.4295(8)	0.5409(3)	0.060(3)

Table 4. Bond lengths (Å) for 9.

C8-C9	1.516(8)	C8-C7	1.544(8)
C8-H8A	0.99	C8-H8B	0.99
O1-C22	1.401(9)	O1-C9	1.436(7)
O3-C15	1.226(7)	O2-C18	1.429(7)
O2-C17	1.438(7)	C21-N1	1.484(8)
C21-C20	1.515(8)	C21-H21A	0.99
C21-H21B	0.99	C5-C6	1.389(8)
C5-C4	1.403(8)	C5-H5	0.95
C4-C3	1.400(9)	C4-H4	0.95
C3-C2	1.381(9)	C3-H3	0.95
C2-C1	1.381(8)	C2-H2	0.95
C12-C23	1.773(8)	C17-C13	1.528(8)
C17-C16	1.549(8)	C17-H17	1.0
C14-N2	1.497(7)	C14-C13	1.548(8)
C14-C7	1.552(8)	C14-H14	1.0
C19-C20	1.310(8)	C19-C18	1.509(8)
C19-H19	0.95	C20-C12	1.526(8)
C10-N1	1.483(8)	C10-C11	1.526(8)
C10-C7	1.549(8)	C10-H10	1.0
C11-C12	1.531(8)	C11-H11A	0.99
C11-H11B	0.99	C12-C13	1.516(8)
C12-H12	1.0	C6-C1	1.401(7)
C6-C7	1.511(8)	C1-N2	1.420(7)
C16-C15	1.506(9)	C16-H16A	0.99
C16-H16B	0.99	C13-H13	1.0
C9-N1	1.451(8)	C9-H9	1.0
C15-N2	1.383(7)	C18-H18A	0.99
C18-H18B	0.99	C23-C11	1.754(7)
C23-H23A	0.99	C23-H23B	0.99
C22-H22A	0.98	C22-H22B	0.98
C22-H22C	0.98		

Table 5. Bond angles (°) for 9.

C9-C8-C7	102.9(5)	C9-C8-H8A	111.2
C7-C8-H8A	111.2	C9-C8-H8B	111.2
C7-C8-H8B	111.2	H8A-C8-H8B	109.1
C22-O1-C9	112.7(5)	C18-O2-C17	114.1(4)
N1-C21-C20	109.7(5)	N1-C21-H21A	109.7
C20-C21-H21A	109.7	N1-C21-H21B	109.7
C20-C21-H21B	109.7	H21A-C21-H21B	108.2
C6-C5-C4	119.5(5)	C6-C5-H5	120.3
C4-C5-H5	120.3	C3-C4-C5	119.2(6)
C3-C4-H4	120.4	C5-C4-H4	120.4
C2-C3-C4	121.8(6)	C2-C3-H3	119.1
C4-C3-H3	119.1	C3-C2-C1	118.2(6)
C3-C2-H2	120.9	C1-C2-H2	120.9
O2-C17-C13	113.4(4)	O2-C17-C16	105.8(5)
C13-C17-C16	110.5(5)	O2-C17-H17	109.0
C13-C17-H17	109.0	C16-C17-H17	109.0
N2-C14-C13	105.6(4)	N2-C14-C7	105.3(4)
C13-C14-C7	116.8(5)	N2-C14-H14	109.6
C13-C14-H14	109.6	C7-C14-H14	109.6
C20-C19-C18	123.3(6)	C20-C19-H19	118.4
C18-C19-H19	118.4	C19-C20-C21	123.1(5)
C19-C20-C12	123.4(5)	C21-C20-C12	113.4(5)
N1-C10-C11	110.4(5)	N1-C10-C7	105.3(5)
C11-C10-C7	114.8(5)	N1-C10-H10	108.7
C11-C10-H10	108.7	C7-C10-H10	108.7
C10-C11-C12	108.5(5)	C10-C11-H11A	110.0
C12-C11-H11A	110.0	C10-C11-H11B	110.0
C12-C11-H11B	110.0	H11A-C11-H11B	108.4
C13-C12-C20	114.9(5)	C13-C12-C11	106.1(5)
C20-C12-C11	109.6(5)	C13-C12-H12	108.7
C20-C12-H12	108.7	C11-C12-H12	108.7
C5-C6-C1	119.6(5)	C5-C6-C7	129.2(5)
C1-C6-C7	111.1(5)	C2-C1-C6	121.7(5)
C2-C1-N2	128.8(5)	C6-C1-N2	109.5(5)
C15-C16-C17	117.3(5)	C15-C16-H16A	108.0
C17-C16-H16A	108.0	C15-C16-H16B	108.0

C17-C16-H16B	108.0	H16A-C16-H16B	107.2
C12-C13-C17	118.8(5)	C12-C13-C14	113.2(4)
C17-C13-C14	107.1(5)	C12-C13-H13	105.6
C17-C13-H13	105.6	C14-C13-H13	105.6
C6-C7-C8	111.8(4)	C6-C7-C10	116.7(5)
C8-C7-C10	100.3(4)	C6-C7-C14	102.7(4)
C8-C7-C14	111.3(5)	C10-C7-C14	114.4(4)
O1-C9-N1	106.9(5)	O1-C9-C8	114.6(5)
N1-C9-C8	105.1(5)	O1-C9-H9	110.0
N1-C9-H9	110.0	C8-C9-H9	110.0
O3-C15-N2	122.2(6)	O3-C15-C16	121.7(5)
N2-C15-C16	116.1(5)	C15-N2-C1	124.6(5)
C15-N2-C14	119.6(5)	C1-N2-C14	109.6(4)
O2-C18-C19	112.2(5)	O2-C18-H18A	109.2
C19-C18-H18A	109.2	O2-C18-H18B	109.2
C19-C18-H18B	109.2	H18A-C18-H18B	107.9
C9-N1-C10	109.6(4)	C9-N1-C21	111.8(5)
C10-N1-C21	114.6(5)	C11-C23-C12	110.4(4)
C11-C23-H23A	109.6	C12-C23-H23A	109.6
C11-C23-H23B	109.6	C12-C23-H23B	109.6
H23A-C23-H23B	108.1	O1-C22-H22A	109.5
O1-C22-H22B	109.5	H22A-C22-H22B	109.5
O1-C22-H22C	109.5	H22A-C22-H22C	109.5
H22B-C22-H22C	109.5		

Table 6. Torsion angles (°) for 9.

C6-C5-C4-C3	1.5(9)	C5-C4-C3-C2	-1.4(9)
C4-C3-C2-C1	0.4(9)	C18-O2-C17-C13	-69.9(6)
C18-O2-C17-C16	168.8(4)	C18-C19-C20-C21	175.0(6)
C18-C19-C20-C12	-1.7(9)	N1-C21-C20-C19	-122.4(6)
N1-C21-C20-C12	54.6(6)	N1-C10-C11-C12	61.6(6)
C7-C10-C11-C12	-57.2(6)	C19-C20-C12-C13	55.4(8)
C21-C20-C12-C13	-121.6(5)	C19-C20-C12-C11	174.8(5)
C21-C20-C12-C11	-2.2(7)	C10-C11-C12-C13	69.7(6)
C10-C11-C12-C20	-54.9(6)	C4-C5-C6-C1	-0.6(8)
C4-C5-C6-C7	-176.1(5)	C3-C2-C1-C6	0.5(8)
C3-C2-C1-N2	-178.7(5)	C5-C6-C1-C2	-0.4(8)

C7-C6-C1-C2	175.9(5)	C5-C6-C1-N2	178.9(5)
C7-C6-C1-N2	-4.8(6)	O2-C17-C16-C15	126.4(5)
C13-C17-C16-C15	3.2(7)	C20-C12-C13-C17	-66.6(7)
C11-C12-C13-C17	172.1(5)	C20-C12-C13-C14	60.3(6)
C11-C12-C13-C14	-61.0(6)	O2-C17-C13-C12	59.4(7)
C16-C17-C13-C12	178.1(5)	O2-C17-C13-C14	-70.3(6)
C16-C17-C13-C14	48.4(6)	N2-C14-C13-C12	155.9(5)
C7-C14-C13-C12	39.3(7)	N2-C14-C13-C17	-71.3(5)
C7-C14-C13-C17	172.1(5)	C5-C6-C7-C8	68.0(8)
C1-C6-C7-C8	-107.8(5)	C5-C6-C7-C10	-46.6(8)
C1-C6-C7-C10	137.6(5)	C5-C6-C7-C14	-172.6(6)
C1-C6-C7-C14	11.6(6)	C9-C8-C7-C6	-164.8(5)
C9-C8-C7-C10	-40.4(5)	C9-C8-C7-C14	81.1(5)
N1-C10-C7-C6	152.1(5)	C11-C10-C7-C6	-86.3(6)
N1-C10-C7-C8	31.1(5)	C11-C10-C7-C8	152.8(5)
N1-C10-C7-C14	-88.0(6)	C11-C10-C7-C14	33.6(7)
N2-C14-C7-C6	-13.5(5)	C13-C14-C7-C6	103.3(5)
N2-C14-C7-C8	106.2(5)	C13-C14-C7-C8	-137.0(5)
N2-C14-C7-C10	-141.0(5)	C13-C14-C7-C10	-24.2(7)
C22-O1-C9-N1	-167.4(6)	C22-O1-C9-C8	76.6(8)
C7-C8-C9-O1	152.5(5)	C7-C8-C9-N1	35.5(6)
C17-C16-C15-O3	144.4(6)	C17-C16-C15-N2	-35.5(8)
O3-C15-N2-C1	-19.3(9)	C16-C15-N2-C1	160.6(5)
O3-C15-N2-C14	-168.7(5)	C16-C15-N2-C14	11.1(8)
C2-C1-N2-C15	22.7(9)	C6-C1-N2-C15	-156.6(5)
C2-C1-N2-C14	174.7(5)	C6-C1-N2-C14	-4.6(6)
C13-C14-N2-C15	41.1(7)	C7-C14-N2-C15	165.3(5)
C13-C14-N2-C1	-112.6(5)	C7-C14-N2-C1	11.7(6)
C17-O2-C18-C19	87.0(6)	C20-C19-C18-O2	-62.7(8)
O1-C9-N1-C10	-138.0(5)	C8-C9-N1-C10	-15.8(6)
O1-C9-N1-C21	93.8(5)	C8-C9-N1-C21	-144.0(5)
C11-C10-N1-C9	-134.7(5)	C7-C10-N1-C9	-10.3(6)
C11-C10-N1-C21	-8.0(7)	C7-C10-N1-C21	116.4(5)
C20-C21-N1-C9	76.4(6)	C20-C21-N1-C10	-49.0(6)

Crystal Structure Report for 11

A specimen of $C_{45}H_{50}N_4O_5$, approximate dimensions 0.010 mm x 0.060 mm x 0.250 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 21.73 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 10585 reflections to a maximum θ angle of 27.48° (0.77 \AA resolution), of which 6813 were independent (average redundancy 1.554, completeness = 99.8%, $R_{\text{int}} = 2.82\%$, $R_{\text{sig}} = 5.15\%$) and 5834 (85.63%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 7.2191(6) \text{ \AA}$, $b = 15.8176(15) \text{ \AA}$, $c = 16.0421(15) \text{ \AA}$, $\beta = 102.217(2)^\circ$, volume = $1790.3(3) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 3838 reflections above $20 \sigma(I)$ with $5.155^\circ < 2\theta < 55.77^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.922. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6874 and 0.7456.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21 1, with $Z = 2$ for the formula unit, $C_{45}H_{50}N_4O_5$. The final anisotropic full-matrix least-squares refinement on F^2 with 497 variables converged at $R1 = 4.21\%$, for the observed data and $wR2 = 9.82\%$ for all data. The goodness-of-fit was 1.040. The largest peak in the final difference electron density synthesis was $0.301 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.231 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.048 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.348 g/cm^3 and $F(000)$, 776 e^- .

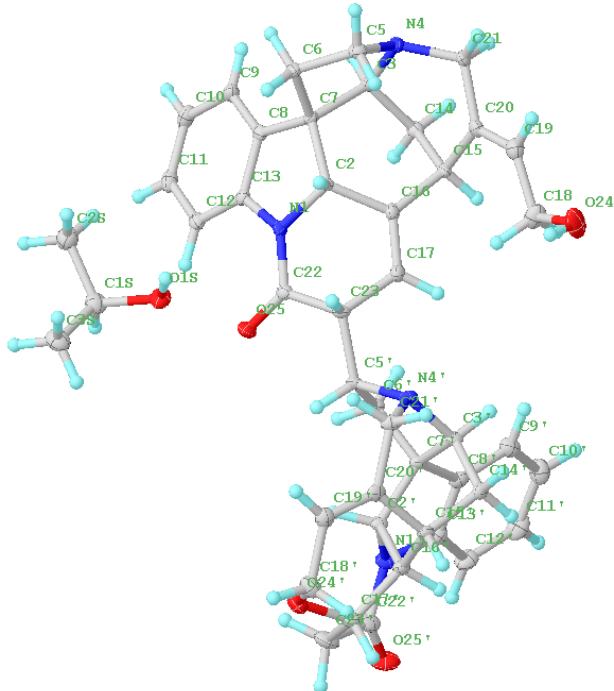


Table 1. Sample and crystal data for 11.

Identification code	11	
Chemical formula	C ₄₅ H ₅₀ N ₄ O ₅	
Formula weight	726.89 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.010 x 0.060 x 0.250 mm	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 7.2191(6) Å b = 15.8176(15) Å c = 16.0421(15) Å	α = 90° β = 102.217(2)° γ = 90°
Volume	1790.3(3) Å ³	
Z	2	
Density (calculated)	1.348 g/cm ³	
Absorption coefficient	0.088 mm ⁻¹	
F(000)	776	

Table 2. Data collection and structure refinement for 11.

Theta range for data collection	1.83 to 27.48°
Index ranges	-6<=h<=9, -20<=k<=17, -20<=l<=20
Reflections collected	10585
Independent reflections	6813 [R(int) = 0.0282]
Coverage of independent reflections	99.8%
Absorption correction	multi-scan
Max. and min. transmission	0.7456 and 0.6874
Structure solution technique	direct methods
Structure solution program	SHELXL-2014/6 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2014/6 (Sheldrick, 2014), Olex2 (Olexsys)
Function minimized	Σ w(F _o ² - F _c ²) ²
Data / restraints / parameters	6813 / 1 / 497
Goodness-of-fit on F²	1.040
Final R indices	5834 data; I>2σ(I) R1 = 0.0421, wR2 = 0.0926 all data R1 = 0.0557, wR2 = 0.0982
Weighting scheme	w=1/[σ ² (F _o ²)+(0.0491P) ² +0.2776P]

	where $P = (F_o^2 + 2F_c^2)/3$
Absolute structure parameter	-0.4(6)
Largest diff. peak and hole	0.301 and -0.231 eÅ ⁻³
R.M.S. deviation from mean	0.048 eÅ ⁻³

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for 11.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
O24	0.7753(4)	0.24945(17)	0.35081(18)	0.0378(7)
O25	0.8023(3)	0.49980(15)	0.15474(12)	0.0211(5)
N1	0.9810(3)	0.51541(16)	0.28931(13)	0.0126(5)
N4	0.4695(3)	0.53506(16)	0.52836(14)	0.0148(5)
C2	0.1434(4)	0.48473(19)	0.35664(16)	0.0124(6)
C3	0.3717(4)	0.5897(2)	0.45572(17)	0.0132(6)
C5	0.3313(4)	0.4730(2)	0.54737(17)	0.0176(6)
C6	0.1411(4)	0.5152(2)	0.51378(16)	0.0156(6)
C7	0.1672(4)	0.55355(19)	0.42866(16)	0.0124(6)
C8	0.0248(4)	0.6202(2)	0.39082(17)	0.0143(6)
C9	0.9937(4)	0.6983(2)	0.42405(18)	0.0179(6)
C10	0.8605(4)	0.7525(2)	0.37658(19)	0.0208(7)
C11	0.7561(4)	0.7274(2)	0.29705(19)	0.0205(7)
C12	0.7825(4)	0.6485(2)	0.26346(18)	0.0164(6)
C13	0.9193(4)	0.5954(2)	0.31096(17)	0.0140(6)
C14	0.4776(4)	0.5932(2)	0.38325(17)	0.0159(6)
C15	0.5046(4)	0.5031(2)	0.35322(16)	0.0147(6)
C16	0.3104(4)	0.46840(19)	0.31386(16)	0.0141(6)
C17	0.2676(4)	0.4277(2)	0.24021(17)	0.0163(6)
C18	0.6842(5)	0.3294(2)	0.3373(2)	0.0258(7)
C19	0.6910(4)	0.3759(2)	0.41960(19)	0.0208(7)
C20	0.6160(4)	0.4510(2)	0.42790(18)	0.0163(6)
C21	0.6442(4)	0.4952(2)	0.51337(17)	0.0161(6)
C22	0.9344(4)	0.4764(2)	0.21138(16)	0.0150(6)
C23	0.0651(4)	0.4028(2)	0.20195(17)	0.0150(6)
O24'	0.6629(3)	0.22886(14)	0.85459(13)	0.0226(5)
O25'	0.9324(4)	0.42198(16)	0.69020(13)	0.0327(6)
N1'	0.0116(4)	0.41434(17)	0.83617(15)	0.0189(6)

	x/a	y/b	z/c	U(eq)
N4'	0.1660(3)	0.29980(16)	0.10606(14)	0.0151(5)
C2'	0.0008(4)	0.35827(19)	0.91017(17)	0.0148(6)
C3'	0.2734(4)	0.31283(19)	0.03721(16)	0.0142(6)
C5'	0.0413(4)	0.37321(19)	0.10853(17)	0.0139(6)
C6'	0.1028(4)	0.43906(19)	0.04987(17)	0.0153(6)
C7'	0.1719(4)	0.38630(19)	0.98196(17)	0.0147(6)
C8'	0.2935(4)	0.4357(2)	0.93326(17)	0.0171(6)
C9'	0.4766(4)	0.4654(2)	0.96159(19)	0.0200(6)
C10'	0.5599(4)	0.5123(2)	0.9058(2)	0.0249(7)
C11'	0.4591(5)	0.5295(2)	0.8237(2)	0.0272(7)
C12'	0.2746(5)	0.5000(2)	0.79457(19)	0.0246(7)
C13'	0.1949(4)	0.4527(2)	0.85049(18)	0.0177(6)
C14'	0.2870(4)	0.23193(19)	0.98758(17)	0.0157(6)
C15'	0.0859(4)	0.2026(2)	0.94581(17)	0.0157(6)
C16'	0.0076(4)	0.2678(2)	0.87612(17)	0.0159(6)
C17'	0.8166(4)	0.2493(2)	0.81480(18)	0.0202(7)
C18'	0.6896(4)	0.1516(2)	0.9031(2)	0.0235(7)
C19'	0.7890(4)	0.1680(2)	0.99437(19)	0.0193(6)
C20'	0.9678(4)	0.19317(19)	0.01361(17)	0.0156(6)
C21'	0.0706(4)	0.21746(19)	0.10284(17)	0.0172(6)
C22'	0.9055(5)	0.3925(2)	0.75730(19)	0.0247(7)
C23'	0.7506(5)	0.3293(2)	0.76114(19)	0.0254(7)
O1S	0.4658(3)	0.14811(15)	0.33864(13)	0.0223(5)
C1S	0.2841(4)	0.1891(2)	0.3260(2)	0.0231(7)
C2S	0.2647(5)	0.2393(2)	0.4046(2)	0.0270(8)
C3S	0.1245(5)	0.1250(2)	0.3016(2)	0.0274(8)

Table 4. Bond lengths (Å) for 11.

O24-C18	1.420(4)	O24-H24	0.89(4)
O25-C22	1.226(3)	N1-C22	1.370(3)
N1-C13	1.409(4)	N1-C2	1.497(3)
N4-C21	1.474(4)	N4-C5	1.476(4)
N4-C3	1.502(4)	C2-C16	1.530(4)
C2-C7	1.570(4)	C2-H2	1.0
C3-C14	1.522(4)	C3-C7	1.557(4)
C3-H3	1.0	C5-C6	1.519(4)

C5-H5A	0.99	C5-H5B	0.99
C6-C7	1.542(4)	C6-H6A	0.99
C6-H6B	0.99	C7-C8	1.507(4)
C8-C9	1.384(4)	C8-C13	1.401(4)
C9-C10	1.388(4)	C9-H9	0.95
C10-C11	1.395(4)	C10-H10	0.95
C11-C12	1.389(5)	C11-H11	0.95
C12-C13	1.394(4)	C12-H12	0.95
C14-C15	1.530(4)	C14-H14A	0.99
C14-H14B	0.99	C15-C16	1.514(4)
C15-C20	1.534(4)	C15-H15	1.0
C16-C17	1.324(4)	C17-C23	1.513(4)
C17-H17	0.95	C18-C19	1.504(4)
C18-H18A	0.99	C18-H18B	0.99
C19-C20	1.324(4)	C19-H19	0.95
C20-C21	1.514(4)	C21-H21A	0.99
C21-H21B	0.99	C22-C23	1.527(4)
C23-C5'	1.545(4)	C23-H23	1.0
O24'-C17'	1.429(4)	O24'-C18'	1.440(4)
O25'-C22'	1.226(4)	N1'-C22'	1.377(4)
N1'-C13'	1.430(4)	N1'-C2'	1.497(4)
N4'-C21'	1.469(4)	N4'-C5'	1.475(4)
N4'-C3'	1.492(3)	C2'-C16'	1.536(4)
C2'-C7'	1.564(4)	C2'-H2'	1.0
C3'-C14'	1.521(4)	C3'-C7'	1.549(4)
C3'-H3'	1.0	C5'-C6'	1.531(4)
C5'-H5'	1.0	C6'-C7'	1.537(4)
C6'-H6'A	0.99	C6'-H6'B	0.99
C7'-C8'	1.511(4)	C8'-C9'	1.386(4)
C8'-C13'	1.394(4)	C9'-C10'	1.393(5)
C9'-H9'	0.95	C10'-C11'	1.390(5)
C10'-H10'	0.95	C11'-C12'	1.395(5)
C11'-H11'	0.95	C12'-C13'	1.383(4)
C12'-H12'	0.95	C14'-C15'	1.536(4)
C14'-H14C	0.99	C14'-H14D	0.99
C15'-C20'	1.525(4)	C15'-C16'	1.538(4)
C15'-H15'	1.0	C16'-C17'	1.543(4)
C16'-H16'	1.0	C17'-C23'	1.548(5)

C17'-H17'	1.0	C18'-C19'	1.510(4)
C18'-H18C	0.99	C18'-H18D	0.99
C19'-C20'	1.323(4)	C19'-H19'	0.95
C20'-C21'	1.516(4)	C21'-H21C	0.99
C21'-H21D	0.99	C22'-C23'	1.511(5)
C23'-H23A	0.99	C23'-H23B	0.99
O1S-C1S	1.439(4)	O1S-H1S	0.98(4)
C1S-C2S	1.520(5)	C1S-C3S	1.523(5)
C1S-H1SA	1.0	C2S-H2SA	0.98
C2S-H2SB	0.98	C2S-H2SC	0.98
C3S-H3SA	0.98	C3S-H3SB	0.98
C3S-H3SC	0.98		

Table 5. Bond angles (°) for 11.

C18-O24-H24	105.(3)	C22-N1-C13	126.8(2)
C22-N1-C2	121.1(2)	C13-N1-C2	110.7(2)
C21-N4-C5	112.9(2)	C21-N4-C3	113.4(2)
C5-N4-C3	108.4(2)	N1-C2-C16	107.6(2)
N1-C2-C7	104.7(2)	C16-C2-C7	118.2(2)
N1-C2-H2	108.7	C16-C2-H2	108.7
C7-C2-H2	108.7	N4-C3-C14	112.6(2)
N4-C3-C7	105.5(2)	C14-C3-C7	113.6(2)
N4-C3-H3	108.3	C14-C3-H3	108.3
C7-C3-H3	108.3	N4-C5-C6	103.6(2)
N4-C5-H5A	111.0	C6-C5-H5A	111.0
N4-C5-H5B	111.0	C6-C5-H5B	111.0
H5A-C5-H5B	109.0	C5-C6-C7	102.5(2)
C5-C6-H6A	111.3	C7-C6-H6A	111.3
C5-C6-H6B	111.3	C7-C6-H6B	111.3
H6A-C6-H6B	109.2	C8-C7-C6	115.5(2)
C8-C7-C3	112.4(2)	C6-C7-C3	100.6(2)
C8-C7-C2	103.2(2)	C6-C7-C2	111.3(2)
C3-C7-C2	114.2(2)	C9-C8-C13	120.1(3)
C9-C8-C7	128.5(3)	C13-C8-C7	111.4(3)
C8-C9-C10	119.3(3)	C8-C9-H9	120.3
C10-C9-H9	120.3	C9-C10-C11	120.2(3)
C9-C10-H10	119.9	C11-C10-H10	119.9

C12-C11-C10	121.2(3)	C12-C11-H11	119.4
C10-C11-H11	119.4	C11-C12-C13	118.0(3)
C11-C12-H12	121.0	C13-C12-H12	121.0
C12-C13-C8	121.1(3)	C12-C13-N1	129.1(3)
C8-C13-N1	109.8(2)	C3-C14-C15	108.9(2)
C3-C14-H14A	109.9	C15-C14-H14A	109.9
C3-C14-H14B	109.9	C15-C14-H14B	109.9
H14A-C14-H14B	108.3	C16-C15-C14	107.5(2)
C16-C15-C20	114.6(3)	C14-C15-C20	109.6(2)
C16-C15-H15	108.3	C14-C15-H15	108.3
C20-C15-H15	108.3	C17-C16-C15	124.7(3)
C17-C16-C2	115.2(2)	C15-C16-C2	120.0(2)
C16-C17-C23	120.8(3)	C16-C17-H17	119.6
C23-C17-H17	119.6	O24-C18-C19	111.9(3)
O24-C18-H18A	109.2	C19-C18-H18A	109.2
O24-C18-H18B	109.2	C19-C18-H18B	109.2
H18A-C18-H18B	107.9	C20-C19-C18	126.1(3)
C20-C19-H19	116.9	C18-C19-H19	116.9
C19-C20-C21	121.8(3)	C19-C20-C15	124.2(3)
C21-C20-C15	114.0(3)	N4-C21-C20	112.9(2)
N4-C21-H21A	109.0	C20-C21-H21A	109.0
N4-C21-H21B	109.0	C20-C21-H21B	109.0
H21A-C21-H21B	107.8	O25-C22-N1	122.9(3)
O25-C22-C23	123.8(2)	N1-C22-C23	113.3(2)
C17-C23-C22	109.0(2)	C17-C23-C5'	111.8(2)
C22-C23-C5'	112.5(2)	C17-C23-H23	107.7
C22-C23-H23	107.7	C5'-C23-H23	107.7
C17'-O24'-C18'	113.9(2)	C22'-N1'-C13'	124.8(3)
C22'-N1'-C2'	117.9(3)	C13'-N1'-C2'	109.0(2)
C21'-N4'-C5'	114.5(2)	C21'-N4'-C3'	114.2(2)
C5'-N4'-C3'	109.1(2)	N1'-C2'-C16'	105.0(2)
N1'-C2'-C7'	104.5(2)	C16'-C2'-C7'	116.5(2)
N1'-C2'-H2'	110.1	C16'-C2'-H2'	110.1
C7'-C2'-H2'	110.1	N4'-C3'-C14'	111.9(2)
N4'-C3'-C7'	105.7(2)	C14'-C3'-C7'	114.0(2)
N4'-C3'-H3'	108.4	C14'-C3'-H3'	108.4
C7'-C3'-H3'	108.4	N4'-C5'-C6'	105.1(2)
N4'-C5'-C23	108.8(2)	C6'-C5'-C23	113.8(2)

N4'-C5'-H5'	109.7	C6'-C5'-H5'	109.7
C23-C5'-H5'	109.7	C5'-C6'-C7'	104.2(2)
C5'-C6'-H6'A	110.9	C7'-C6'-H6'A	110.9
C5'-C6'-H6'B	110.9	C7'-C6'-H6'B	110.9
H6'A-C6'-H6'B	108.9	C8'-C7'-C6'	113.4(2)
C8'-C7'-C3'	115.3(2)	C6'-C7'-C3'	100.8(2)
C8'-C7'-C2'	102.7(2)	C6'-C7'-C2'	110.6(2)
C3'-C7'-C2'	114.4(2)	C9'-C8'-C13'	120.4(3)
C9'-C8'-C7'	128.6(3)	C13'-C8'-C7'	110.9(2)
C8'-C9'-C10'	118.8(3)	C8'-C9'-H9'	120.6
C10'-C9'-H9'	120.6	C11'-C10'-C9'	120.2(3)
C11'-C10'-H10'	119.9	C9'-C10'-H10'	119.9
C10'-C11'-C12'	121.6(3)	C10'-C11'-H11'	119.2
C12'-C11'-H11'	119.2	C13'-C12'-C11'	117.5(3)
C13'-C12'-H12'	121.2	C11'-C12'-H12'	121.2
C12'-C13'-C8'	121.6(3)	C12'-C13'-N1'	128.5(3)
C8'-C13'-N1'	109.9(3)	C3'-C14'-C15'	108.8(2)
C3'-C14'-H14C	109.9	C15'-C14'-H14C	109.9
C3'-C14'-H14D	109.9	C15'-C14'-H14D	109.9
H14C-C14'-H14D	108.3	C20'-C15'-C14'	109.8(2)
C20'-C15'-C16'	114.1(2)	C14'-C15'-C16'	106.4(2)
C20'-C15'-H15'	108.8	C14'-C15'-H15'	108.8
C16'-C15'-H15'	108.8	C2'-C16'-C15'	113.6(2)
C2'-C16'-C17'	108.2(2)	C15'-C16'-C17'	118.5(3)
C2'-C16'-H16'	105.1	C15'-C16'-H16'	105.1
C17'-C16'-H16'	105.1	O24'-C17'-C16'	115.6(2)
O24'-C17'-C23'	104.9(2)	C16'-C17'-C23'	109.1(3)
O24'-C17'-H17'	109.0	C16'-C17'-H17'	109.0
C23'-C17'-H17'	109.0	O24'-C18'-C19'	111.1(3)
O24'-C18'-H18C	109.4	C19'-C18'-H18C	109.4
O24'-C18'-H18D	109.4	C19'-C18'-H18D	109.4
H18C-C18'-H18D	108.0	C20'-C19'-C18'	121.2(3)
C20'-C19'-H19'	119.4	C18'-C19'-H19'	119.4
C19'-C20'-C21'	123.7(3)	C19'-C20'-C15'	121.9(3)
C21'-C20'-C15'	114.4(2)	N4'-C21'-C20'	113.0(2)
N4'-C21'-H21C	109.0	C20'-C21'-H21C	109.0
N4'-C21'-H21D	109.0	C20'-C21'-H21D	109.0
H21C-C21'-H21D	107.8	O25'-C22'-N1'	123.4(3)

O25'-C22'-C23'	122.9(3)	N1'-C22'-C23'	113.6(3)
C22'-C23'-C17'	114.9(3)	C22'-C23'-H23A	108.5
C17'-C23'-H23A	108.5	C22'-C23'-H23B	108.5
C17'-C23'-H23B	108.5	H23A-C23'-H23B	107.5
C1S-O1S-H1S	113.(2)	O1S-C1S-C2S	111.1(2)
O1S-C1S-C3S	110.7(3)	C2S-C1S-C3S	111.3(3)
O1S-C1S-H1SA	107.9	C2S-C1S-H1SA	107.9
C3S-C1S-H1SA	107.9	C1S-C2S-H2SA	109.5
C1S-C2S-H2SB	109.5	H2SA-C2S-H2SB	109.5
C1S-C2S-H2SC	109.5	H2SA-C2S-H2SC	109.5
H2SB-C2S-H2SC	109.5	C1S-C3S-H3SA	109.5
C1S-C3S-H3SB	109.5	H3SA-C3S-H3SB	109.5
C1S-C3S-H3SC	109.5	H3SA-C3S-H3SC	109.5
H3SB-C3S-H3SC	109.5		

Table 6. Torsion angles (°) for 11.

C22-N1-C2-C16	45.1(3)	C13-N1-C2-C16	-122.2(2)
C22-N1-C2-C7	171.7(2)	C13-N1-C2-C7	4.3(3)
C21-N4-C3-C14	-1.2(3)	C5-N4-C3-C14	-127.4(2)
C21-N4-C3-C7	123.2(2)	C5-N4-C3-C7	-2.9(3)
C21-N4-C5-C6	-150.4(2)	C3-N4-C5-C6	-23.9(3)
N4-C5-C6-C7	41.6(3)	C5-C6-C7-C8	-163.5(2)
C5-C6-C7-C3	-42.2(3)	C5-C6-C7-C2	79.1(3)
N4-C3-C7-C8	151.3(2)	C14-C3-C7-C8	-84.9(3)
N4-C3-C7-C6	27.8(3)	C14-C3-C7-C6	151.7(2)
N4-C3-C7-C2	-91.5(3)	C14-C3-C7-C2	32.3(3)
N1-C2-C7-C8	-4.6(3)	C16-C2-C7-C8	115.1(3)
N1-C2-C7-C6	120.0(2)	C16-C2-C7-C6	-120.3(3)
N1-C2-C7-C3	-126.9(2)	C16-C2-C7-C3	-7.2(3)
C6-C7-C8-C9	63.3(4)	C3-C7-C8-C9	-51.4(4)
C2-C7-C8-C9	-174.9(3)	C6-C7-C8-C13	-118.2(3)
C3-C7-C8-C13	127.1(3)	C2-C7-C8-C13	3.5(3)
C13-C8-C9-C10	-1.5(4)	C7-C8-C9-C10	176.8(3)
C8-C9-C10-C11	1.5(4)	C9-C10-C11-C12	-0.1(5)
C10-C11-C12-C13	-1.1(4)	C11-C12-C13-C8	1.1(4)
C11-C12-C13-N1	-175.8(3)	C9-C8-C13-C12	0.3(4)
C7-C8-C13-C12	-178.3(3)	C9-C8-C13-N1	177.6(3)

C7-C8-C13-N1	-1.0(3)	C22-N1-C13-C12	8.4(5)
C2-N1-C13-C12	174.8(3)	C22-N1-C13-C8	-168.7(3)
C2-N1-C13-C8	-2.3(3)	N4-C3-C14-C15	56.2(3)
C7-C3-C14-C15	-63.7(3)	C3-C14-C15-C16	66.3(3)
C3-C14-C15-C20	-58.9(3)	C14-C15-C16-C17	133.7(3)
C20-C15-C16-C17	-104.2(3)	C14-C15-C16-C2	-42.0(3)
C20-C15-C16-C2	80.1(3)	N1-C2-C16-C17	-44.6(3)
C7-C2-C16-C17	-162.8(3)	N1-C2-C16-C15	131.5(3)
C7-C2-C16-C15	13.3(4)	C15-C16-C17-C23	-174.0(3)
C2-C16-C17-C23	1.9(4)	O24-C18-C19-C20	-178.8(3)
C18-C19-C20-C21	-175.2(3)	C18-C19-C20-C15	1.1(5)
C16-C15-C20-C19	71.4(4)	C14-C15-C20-C19	-167.6(3)
C16-C15-C20-C21	-112.0(3)	C14-C15-C20-C21	9.0(3)
C5-N4-C21-C20	73.7(3)	C3-N4-C21-C20	-50.0(3)
C19-C20-C21-N4	-137.5(3)	C15-C20-C21-N4	45.9(3)
C13-N1-C22-O25	-14.9(4)	C2-N1-C22-O25	180.0(3)
C13-N1-C22-C23	164.0(3)	C2-N1-C22-C23	-1.2(4)
C16-C17-C23-C22	43.0(4)	C16-C17-C23-C5'	168.1(3)
O25-C22-C23-C17	136.9(3)	N1-C22-C23-C17	-41.9(3)
O25-C22-C23-C5'	12.2(4)	N1-C22-C23-C5'	-166.6(2)
C22'-N1'-C2'-C16'	42.6(3)	C13'-N1'-C2'-C16'	-107.2(3)
C22'-N1'-C2'-C7'	165.8(3)	C13'-N1'-C2'-C7'	15.9(3)
C21'-N4'-C3'-C14'	-9.5(3)	C5'-N4'-C3'-C14'	-139.0(2)
C21'-N4'-C3'-C7'	115.1(2)	C5'-N4'-C3'-C7'	-14.4(3)
C21'-N4'-C5'-C6'	-139.5(2)	C3'-N4'-C5'-C6'	-10.2(3)
C21'-N4'-C5'-C23	98.3(3)	C3'-N4'-C5'-C23	-132.4(2)
C17-C23-C5'-N4'	59.4(3)	C22-C23-C5'-N4'	-177.4(2)
C17-C23-C5'-C6'	-57.4(3)	C22-C23-C5'-C6'	65.8(3)
N4'-C5'-C6'-C7'	31.0(3)	C23-C5'-C6'-C7'	149.9(2)
C5'-C6'-C7'-C8'	-162.4(2)	C5'-C6'-C7'-C3'	-38.6(3)
C5'-C6'-C7'-C2'	82.8(3)	N4'-C3'-C7'-C8'	155.0(2)
C14'-C3'-C7'-C8'	-81.7(3)	N4'-C3'-C7'-C6'	32.5(3)
C14'-C3'-C7'-C6'	155.8(2)	N4'-C3'-C7'-C2'	-86.2(3)
C14'-C3'-C7'-C2'	37.1(3)	N1'-C2'-C7'-C8'	-16.5(3)
C16'-C2'-C7'-C8'	98.8(3)	N1'-C2'-C7'-C6'	104.8(3)
C16'-C2'-C7'-C6'	-139.9(3)	N1'-C2'-C7'-C3'	-142.3(2)
C16'-C2'-C7'-C3'	-26.9(3)	C6'-C7'-C8'-C9'	70.9(4)
C3'-C7'-C8'-C9'	-44.6(4)	C2'-C7'-C8'-C9'	-169.7(3)

C6'-C7'-C8'-C13'	-107.1(3)	C3'-C7'-C8'-C13'	137.5(3)
C2'-C7'-C8'-C13'	12.3(3)	C13'-C8'-C9'-C10'	-0.2(5)
C7'-C8'-C9'-C10'	-177.9(3)	C8'-C9'-C10'-C11'	0.9(5)
C9'-C10'-C11'-C12'	-0.8(5)	C10'-C11'-C12'-C13'	0.0(5)
C11'-C12'-C13'-C8'	0.7(5)	C11'-C12'-C13'-N1'	-178.9(3)
C9'-C8'-C13'-C12'	-0.6(5)	C7'-C8'-C13'-C12'	177.5(3)
C9'-C8'-C13'-N1'	179.0(3)	C7'-C8'-C13'-N1'	-2.8(3)
C22'-N1'-C13'-C12'	23.7(5)	C2'-N1'-C13'-C12'	170.9(3)
C22'-N1'-C13'-C8'	-156.0(3)	C2'-N1'-C13'-C8'	-8.7(3)
N4'-C3'-C14'-C15'	60.7(3)	C7'-C3'-C14'-C15'	-59.2(3)
C3'-C14'-C15'-C20'	-55.3(3)	C3'-C14'-C15'-C16'	68.7(3)
N1'-C2'-C16'-C15'	154.2(2)	C7'-C2'-C16'-C15'	39.2(3)
N1'-C2'-C16'-C17'	-71.9(3)	C7'-C2'-C16'-C17'	173.0(2)
C20'-C15'-C16'-C2'	62.1(3)	C14'-C15'-C16'-C2'	-59.1(3)
C20'-C15'-C16'-C17'	-66.6(3)	C14'-C15'-C16'-C17'	172.2(2)
C18'-O24'-C17'-C16'	-64.3(3)	C18'-O24'-C17'-C23'	175.6(2)
C2'-C16'-C17'-O24'	-78.6(3)	C15'-C16'-C17'-O24'	52.6(4)
C2'-C16'-C17'-C23'	39.2(3)	C15'-C16'-C17'-C23'	170.4(3)
C17'-O24'-C18'-C19'	89.6(3)	O24'-C18'-C19'-C20'	-67.7(4)
C18'-C19'-C20'-C21'	174.9(3)	C18'-C19'-C20'-C15'	-3.2(5)
C14'-C15'-C20'-C19'	-179.5(3)	C16'-C15'-C20'-C19'	61.1(4)
C14'-C15'-C20'-C21'	2.2(3)	C16'-C15'-C20'-C21'	-117.1(3)
C5'-N4'-C21'-C20'	82.0(3)	C3'-N4'-C21'-C20'	-44.7(3)
C19'-C20'-C21'-N4'	-129.3(3)	C15'-C20'-C21'-N4'	48.9(3)
C13'-N1'-C22'-O25'	-19.2(5)	C2'-N1'-C22'-O25'	-163.9(3)
C13'-N1'-C22'-C23'	161.5(3)	C2'-N1'-C22'-C23'	16.8(4)
O25'-C22'-C23'-C17'	129.4(3)	N1'-C22'-C23'-C17'	-51.3(4)
O24'-C17'-C23'-C22'	144.2(3)	C16'-C17'-C23'-C22'	19.8(4)

Crystal Structure Report for 3

A specimen of $C_{42}H_{42}N_4O_4$, approximate dimensions $0.042\text{ mm} \times 0.100\text{ mm} \times 0.220\text{ mm}$, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The integration of the data using an orthorhombic unit cell yielded a total of 17765 reflections to a maximum θ angle of 27.88° (0.76 \AA resolution), of which 8013 were independent (average redundancy 2.217, completeness = 99.9%, $R_{\text{int}} = 4.37\%$, $R_{\text{sig}} = 7.46\%$) and 5241 (65.41%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 7.3442(12)\text{ \AA}$, $b = 15.617(2)\text{ \AA}$, $c = 29.319(5)\text{ \AA}$, volume = $3362.7(9)\text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of reflections above $20\sigma(I)$. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6763 and 0.7456.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P\bar{1}\bar{1}\bar{1}\bar{1}\bar{1}\bar{1}$, with $Z = 4$ for the formula unit, $C_{42}H_{42}N_4O_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 452 variables converged at $R1 = 5.11\%$, for the observed data and $wR2 = 10.45\%$ for all data. The goodness-of-fit was 1.008. The largest peak in the final difference electron density synthesis was $0.196\text{ e}^{-}/\text{\AA}^3$ and the largest hole was $-0.194\text{ e}^{-}/\text{\AA}^3$ with an RMS deviation of $0.040\text{ e}^{-}/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.317 g/cm^3 and $F(000)$, 1416 e^{-} .

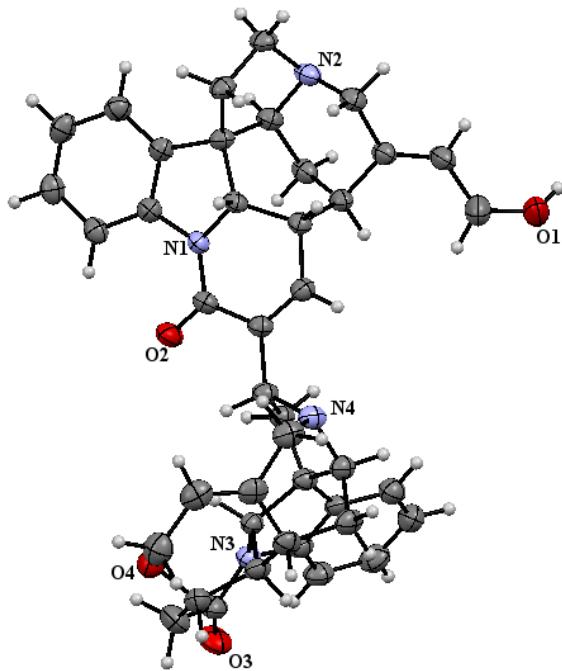


Table 1. Sample and crystal data for 3.

Identification code	2443_1	
Chemical formula	C ₄₂ H ₄₂ N ₄ O ₄	
Formula weight	666.79 g/mol	
Wavelength	0.71073 Å	
Crystal size	0.042 x 0.100 x 0.220 mm	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 7.3442(12) Å b = 15.617(2) Å c = 29.319(5) Å	$\alpha = 90^\circ$ $\beta = 90^\circ$ $\gamma = 90^\circ$
Volume	3362.7(9) Å ³	
Z	4	
Density (calculated)	1.317 g/cm ³	
Absorption coefficient	0.085 mm ⁻¹	
F(000)	1416	

Table 2. Data collection and structure refinement for 3.

Theta range for data collection	1.91 to 27.88°	
Index ranges	-9<=h<=4, -14<=k<=20, -38<=l<=33	
Reflections collected	17765	
Independent reflections	8013 [R(int) = 0.0437]	
Max. and min. transmission	0.7456 and 0.6763	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	XL (Sheldrick, 2008)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	8013 / 0 / 452	
Goodness-of-fit on F²	1.008	
Final R indices	5241 data; I>2σ(I) R1 = 0.0511, wR2 = 0.0899 all data R1 = 0.0980, wR2 = 0.1045	
Weighting scheme	w=1/[σ ² (F _o ²)+(0.0406P) ² +0.1359P] where P=(F _o ² +2F _c ²)/3	
Absolute structure parameter	0.5(8)	
Largest diff. peak and hole	0.196 and -0.194 eÅ ⁻³	
R.M.S. deviation from mean	0.040 eÅ ⁻³	

Table 3. Bond lengths (Å) for 3.

C1-C2	1.383(4)	C1-C6	1.392(4)
C1-N1	1.408(4)	C2-H2	0.95
C2-C3	1.380(4)	C3-H3	0.95
C3-C4	1.386(5)	C4-H4	0.95
C4-C5	1.384(5)	C5-H5	0.95
C5-C6	1.376(4)	C6-C7	1.515(4)
C7-C8	1.544(4)	C7-C14	1.570(4)
C7-C15	1.557(4)	C8-H8A	0.99
C8-H8B	0.99	C8-C9	1.534(4)
C9-H9A	0.99	C9-H9B	0.99
C9-N2	1.468(4)	C10-H10A	0.99
C10-H10B	0.99	C10-C11	1.508(4)
C10-N2	1.489(4)	C11-C12	1.513(4)
C11-C20	1.323(4)	C12-H12	1.0
C12-C13	1.523(5)	C12-C19	1.573(4)
C13-H13A	0.99	C13-H13B	0.99
C13-C14	1.514(4)	C14-H14	1.0
C14-N2	1.491(4)	C15-H15	1.0
C15-C19	1.522(4)	C15-N1	1.492(4)
C16-C17	1.486(5)	C16-N1	1.359(4)
C16-O2	1.227(4)	C17-C18	1.329(4)
C17-C30	1.505(4)	C18-H18	0.95
C18-C19	1.499(4)	C19-H19	1.0
C20-H20	0.95	C20-C21	1.501(5)
C21-H21A	0.99	C21-H21B	0.99
C21-O1	1.408(4)	C22-C23	1.384(4)
C22-C27	1.384(4)	C22-N3	1.422(4)
C23-H23	0.95	C23-C24	1.397(5)
C24-H24	0.95	C24-C25	1.376(5)
C25-H25	0.95	C25-C26	1.379(5)
C26-H26	0.95	C26-C27	1.380(4)
C27-C28	1.509(4)	C28-C29	1.532(4)
C28-C35	1.552(4)	C28-C37	1.557(4)
C29-H29A	0.99	C29-H29B	0.99
C29-C30	1.531(4)	C30-H30	1.0

C30-N4	1.475(4)	C31-H31A	0.99
C31-H31B	0.99	C31-C32	1.512(5)
C31-N4	1.472(4)	C32-C33	1.529(5)
C32-C42	1.315(5)	C33-H33	1.0
C33-C34	1.525(5)	C33-C36	1.538(5)
C34-H34A	0.99	C34-H34B	0.99
C34-C35	1.519(4)	C35-H35	1.0
C35-N4	1.495(4)	C36-H36	1.0
C36-C37	1.526(4)	C36-C40	1.525(4)
C37-H37	1.0	C37-N3	1.490(4)
C38-C39	1.510(5)	C38-N3	1.373(4)
C38-O3	1.220(4)	C39-H39A	0.99
C39-H39B	0.99	C39-C40	1.538(5)
C40-H40	1.0	C40-O4	1.431(4)
C41-H41A	0.99	C41-H41B	0.99
C41-C42	1.503(5)	C41-O4	1.424(4)
C42-H42	0.95	O1-H1	0.84

Table 4. Bond angles (°) for 3.

C2-C1-C6	121.8(3)	C2-C1-N1	129.2(3)
C6-C1-N1	108.9(3)	C1-C2-H2	121.1
C3-C2-C1	117.7(3)	C3-C2-H2	121.1
C2-C3-H3	119.3	C2-C3-C4	121.3(3)
C4-C3-H3	119.3	C3-C4-H4	120.0
C5-C4-C3	120.0(3)	C5-C4-H4	120.0
C4-C5-H5	120.2	C6-C5-C4	119.7(3)
C6-C5-H5	120.2	C1-C6-C7	111.0(3)
C5-C6-C1	119.4(3)	C5-C6-C7	129.3(3)
C6-C7-C8	113.5(3)	C6-C7-C14	112.6(2)
C6-C7-C15	101.2(2)	C8-C7-C14	102.9(2)
C8-C7-C15	115.2(2)	C15-C7-C14	111.9(2)
C7-C8-H8A	110.8	C7-C8-H8B	110.8
H8A-C8-H8B	108.9	C9-C8-C7	104.5(2)
C9-C8-H8A	110.8	C9-C8-H8B	110.8

C8-C9-H9A	110.7	C8-C9-H9B	110.7
H9A-C9-H9B	108.8	N2-C9-C8	105.3(2)
N2-C9-H9A	110.7	N2-C9-H9B	110.7
H10A-C10-H10B	107.8	C11-C10-H10A	109.1
C11-C10-H10B	109.1	N2-C10-H10A	109.1
N2-C10-H10B	109.1	N2-C10-C11	112.4(3)
C10-C11-C12	113.0(3)	C20-C11-C10	122.0(3)
C20-C11-C12	125.0(3)	C11-C12-H12	109.3
C11-C12-C13	107.1(2)	C11-C12-C19	110.4(2)
C13-C12-H12	109.3	C13-C12-C19	111.4(3)
C19-C12-H12	109.3	C12-C13-H13A	109.8
C12-C13-H13B	109.8	H13A-C13-H13B	108.3
C14-C13-C12	109.3(3)	C14-C13-H13A	109.8
C14-C13-H13B	109.8	C7-C14-H14	108.1
C13-C14-C7	112.8(2)	C13-C14-H14	108.1
N2-C14-C7	106.2(2)	N2-C14-C13	113.3(3)
N2-C14-H14	108.1	C7-C15-H15	107.4
C19-C15-C7	119.0(2)	C19-C15-H15	107.4
N1-C15-C7	103.3(2)	N1-C15-H15	107.4
N1-C15-C19	111.9(2)	N1-C16-C17	115.8(3)
O2-C16-C17	122.4(3)	O2-C16-N1	121.8(3)
C16-C17-C30	113.8(3)	C18-C17-C16	120.8(3)
C18-C17-C30	125.1(3)	C17-C18-H18	117.8
C17-C18-C19	124.4(3)	C19-C18-H18	117.8
C12-C19-H19	106.9	C15-C19-C12	114.9(2)
C15-C19-H19	106.9	C18-C19-C12	110.1(2)
C18-C19-C15	110.7(2)	C18-C19-H19	106.9
C11-C20-H20	116.8	C11-C20-C21	126.4(3)
C21-C20-H20	116.8	C20-C21-H21A	109.2
C20-C21-H21B	109.2	H21A-C21-H21B	107.9
O1-C21-C20	112.2(3)	O1-C21-H21A	109.2
O1-C21-H21B	109.2	C23-C22-N3	128.7(3)
C27-C22-C23	121.5(3)	C27-C22-N3	109.7(3)
C22-C23-H23	121.5	C22-C23-C24	117.0(3)
C24-C23-H23	121.5	C23-C24-H24	119.0
C25-C24-C23	122.0(3)	C25-C24-H24	119.0
C24-C25-H25	120.1	C24-C25-C26	119.8(3)
C26-C25-H25	120.1	C25-C26-H26	120.3

C25-C26-C27	119.5(3)	C27-C26-H26	120.3
C22-C27-C28	110.8(3)	C26-C27-C22	120.2(3)
C26-C27-C28	128.9(3)	C27-C28-C29	111.7(2)
C27-C28-C35	117.2(3)	C27-C28-C37	102.7(2)
C29-C28-C35	100.8(2)	C29-C28-C37	110.7(2)
C35-C28-C37	114.0(3)	C28-C29-H29A	111.2
C28-C29-H29B	111.2	H29A-C29-H29B	109.1
C30-C29-C28	102.9(2)	C30-C29-H29A	111.2
C30-C29-H29B	111.2	C17-C30-C29	112.6(2)
C17-C30-H30	108.8	C29-C30-H30	108.8
N4-C30-C17	113.7(3)	N4-C30-C29	104.0(2)
N4-C30-H30	108.8	H31A-C31-H31B	108.0
C32-C31-H31A	109.4	C32-C31-H31B	109.4
N4-C31-H31A	109.4	N4-C31-H31B	109.4
N4-C31-C32	111.3(3)	C31-C32-C33	113.7(3)
C42-C32-C31	123.3(3)	C42-C32-C33	122.8(3)
C32-C33-H33	108.6	C32-C33-C36	114.7(3)
C34-C33-C32	109.5(3)	C34-C33-H33	108.6
C34-C33-C36	106.7(3)	C36-C33-H33	108.6
C33-C34-H34A	110.0	C33-C34-H34B	110.0
H34A-C34-H34B	108.3	C35-C34-C33	108.6(3)
C35-C34-H34A	110.0	C35-C34-H34B	110.0
C28-C35-H35	108.5	C34-C35-C28	114.0(3)
C34-C35-H35	108.5	N4-C35-C28	105.4(2)
N4-C35-C34	111.9(3)	N4-C35-H35	108.5
C33-C36-H36	105.8	C37-C36-C33	112.1(2)
C37-C36-H36	105.8	C40-C36-C33	119.4(3)
C40-C36-H36	105.8	C40-C36-C37	107.0(3)
C28-C37-H37	109.2	C36-C37-C28	117.7(3)
C36-C37-H37	109.2	N3-C37-C28	104.3(2)
N3-C37-C36	106.9(2)	N3-C37-H37	109.2
N3-C38-C39	115.9(3)	O3-C38-C39	122.2(3)
O3-C38-N3	121.8(3)	C38-C39-H39A	107.8
C38-C39-H39B	107.8	C38-C39-C40	118.1(3)
H39A-C39-H39B	107.1	C40-C39-H39A	107.8
C40-C39-H39B	107.8	C36-C40-C39	110.6(3)
C36-C40-H40	109.2	C39-C40-H40	109.2
O4-C40-C36	114.0(3)	O4-C40-C39	104.6(3)

O4-C40-H40	109.2	H41A-C41-H41B	107.8
C42-C41-H41A	109.0	C42-C41-H41B	109.0
O4-C41-H41A	109.0	O4-C41-H41B	109.0
O4-C41-C42	112.9(3)	C32-C42-C41	124.3(3)
C32-C42-H42	117.9	C41-C42-H42	117.9
C1-N1-C15	108.8(2)	C16-N1-C1	126.1(3)
C16-N1-C15	124.2(3)	C9-N2-C10	109.4(3)
C9-N2-C14	101.3(2)	C10-N2-C14	115.2(2)
C22-N3-C37	109.6(2)	C38-N3-C22	124.6(3)
C38-N3-C37	119.5(3)	C30-N4-C35	108.9(2)
C31-N4-C30	111.6(3)	C31-N4-C35	113.0(2)
C21-O1-H1	109.5	C41-O4-C40	113.8(3)

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