Supplementary Information

Concise synthesis of (±)-fortuneicyclidins and (±)-cephalotine B enabled by Pd-catalyzed dearomative spirocyclization

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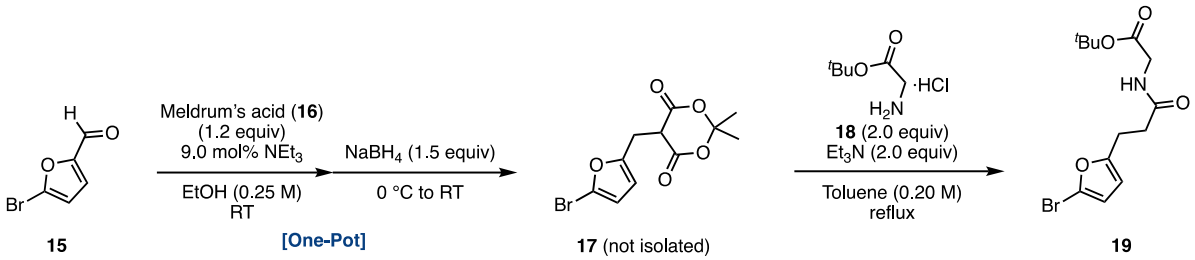
1. General

Unless otherwise noted, all reactions were performed with reagent-grade solvents under air in dried glassware using standard vacuum-line techniques. All work-up and purification procedures were carried out with reagent-grade solvents under air. CH_2Cl_2 and THF were purified by a Glass Contour Ultimate Solvent System. 5-Bromofuran-2-carbaldehyde (**15**), Meldrum's acid (**16**), *tert*-butyl glycinate hydrochloride (**18**), piperonal (**S1**), 4-methylbenzenesulfonohydrazide, bis[2-(diphenylphosphino)phenyl] ether (DPEphos), trifluoroacetic anhydride (TFAA), triisopropylsilyl trifluoromethanesulfonate (TIPSOTf), Karstedt catalyst, triisopropylsilane, $Ru_3(CO)_{12}$, polymethylhydrosiloxane (PMHS) were obtained from Tokyo Chemical Industry (TCI). Et_3N, $NaBH_4$, trifluoroacetic acid (TFA), 2,6-lutidine, hydrogen chloride, and L-selectride were obtained from KANTO Chemical. *m*-Chloroperoxybenzoic acid (*m*CPBA) and HF·pyridine were obtained from Sigma-Aldrich. Cesium carbonate was obtained from Iwatani Corporation. $Pd_2(dba)_3{\cdot}CHCl_3$[1] was synthesized according to a procedure and the spectra matched with those of the compound reported in the literature.

Analytical thin-layer chromatography (TLC) was performed using Silica-gel 70 TLC Plate-Wako (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm). Flash column chromatography was performed with Biotage Isolera® equipped with Biotage Sfär Cartridge Silica D columns. Preparative thin-layer chromatography (PTLC) was performed using Wakogel B5-F silica coated plates (0.75 mm) prepared in our laboratory. Preparative recycling gel permeation chromatography (GPC) was performed with a JAI LaboACE LC-5060 instrument equipped with two JAIGEL-2HR columns using $CHCl_3$ as an eluent. High-resolution mass spectra were conducted on Thermo Fisher Scientific ExactivePlus Orbitrap (ESI) and Bruker Compact QTOF (ESI and APCI). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECS-400, JNM-ECZ-400 (^{1}H 400 MHz, ^{13}C 101 MHz), and a Bruker AVANCE600 (^{1}H 600 MHz, ^{13}C NMR 151 MHz) spectrometer. Chemical shifts for ^{1}H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm) in $CDCl_3$, CHD_2CN (δ 1.94 ppm) in acetonitrile-d_3, CHD_2SOCD_3 (δ 2.50 ppm) in DMSO-d_6, and CHD_2COCD_3 (δ 2.05 ppm) in acetone-d_6. Chemical shifts for ^{13}C NMR are expressed in ppm relative to $CDCl_3$ (δ 77.0 ppm), DMSO-d_6 (δ 39.5 ppm), and acetone-d_6 (δ 29.8 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublets of doublets, t = triplet, m = multiplet, brs = broad singlet), coupling constant (Hz), and integration.

2. Total Synthesis of Fortuneicyclidin A and B

Synthesis of *tert*-Butyl (3-(5-bromofuran-2-yl)propanoyl)glycinate (19)

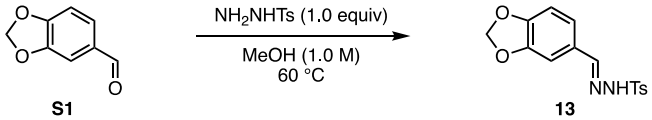


To a round-bottom flask containing 5-bromofuran-2-carbaldehyde (**15**: 1.40 g, 8.00 mmol, 1.0 equiv) and Meldrum's acid (**16**: 1.38 g, 9.60 mmol, 1.2 equiv), and EtOH (32 mL) was added Et_3N (100 µL, 0.720 mmol, 9.0 mol%). The mixture was stirred at room temperature for 8 h with monitoring reaction progress with TLC. The mixture was cooled to 0 °C and then $NaBH_4$ (455.2 mg, 12.0 mmol, 1.5 equiv) was added portionwise at room temperature. After stirring the mixture for 1 h with monitoring reaction progress with ^{1}H NMR, the mixture was concentrated *in vacuo*. To the mixture was added 3 M HCl aq. to adjust pH to 2. The mixture was extracted three times with EtOAc. The combined organic layer was washed twice with brine, dried over Na_2SO_4, filtrated, and concentrated *in vacuo*. The crude mixture of bromofuran **17** was used for the next step without further purification.

Following to the literature procedure,[2] amide **19** was prepared. To a crude of bromofuran **17** (1.0 equiv) in a round-bottom flask were added *tert*-butyl glycinate hydrochloride (**18**: 2.68 g, 16.0 mmol, 2.0 equiv), Et_3N (2.24 mL, 16.0 mmol, 2.0 equiv), and toluene (40 mL). The mixture was refluxed for 8 h with monitoring reaction progress with TLC. After cooling the mixture to room temperature, the mixture was concentrated *in vacuo*. To the mixture was added $NaHCO_3$ aq. and the mixture was extracted three times with EtOAc. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated *in vacuo*. The residue was purified by Isolera® (hexane/$CHCl_3$ = 50:50 to 0:100) to afford amide **19** (2.32 g, 87% yield over 2 steps) as a brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 (d, *J* = 3.2 Hz, 1H), 6.03 (d, *J* = 3.2 Hz, 1H), 5.93 (brs, 1H), 3.93 (d, *J* = 4.8 Hz, 2H), 2.97 (t, *J* = 7.6 Hz, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.47 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 169.0, 156.4, 119.5, 111.7, 108.3, 82.3, 42.0, 34.2, 27.9, 23.9. HRMS (ESI) *m/z* calcd for $C_{13}H_{18}BrNO_4Na$ $[M+Na]^+$: 354.0311 found 354.0313.

Synthesis of (*E*)-*N*'-(Benzo[*d*][1,3]dioxol-5-ylmethylene)-4-methylbenzenesulfonohydrazide (13)

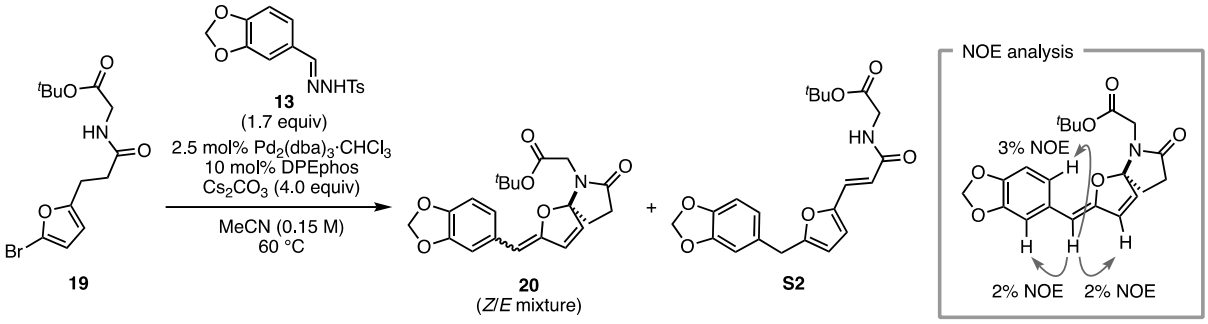


N-Tosylhydrazone **13** was prepared according to literature procedure.[3] To a 100 mL round-bottom flask containing piperonal (**S1**: 7.62 g, 50.7 mmol, 1.0 equiv) were added 4-methylbenzenesulfonohydrazide (9.44 g, 50.7 mmol, 1.0 equiv) and MeOH (50 mL). The mixture was

stirred at 60 °C for 2 h with monitoring reaction progress with TLC. After cooling the mixture to room temperature, the mixture was concentrated *in vacuo* to afford **13** (16.0 g, 50.1 mmol, 99% yield) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.66 (s, 1H), 7.59 (brs, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 1.6 Hz, 1H), 6.92 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.99 (s, 2H), 2.42 (s, 3H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 148.2, 148.0, 144.2, 135.2, 129.7, 127.9, 127.7, 123.8, 108.1, 105.7, 101.5, 21.6;. HRMS (ESI) *m/z* calcd for $C_{15}H_{14}N_2O_4SNa$ $[M+Na]^+$: 341.0567 found 341.0567. The spectra are in accordance with those reported in the literature.[4]

Synthesis of *tert*-Butyl 2-(2-(benzo[*d*][1,3]dioxol-5-ylmethylene)-7-oxo-1-oxa-6-azaspiro[4.4]non-3-en-6-yl)acetate (20)

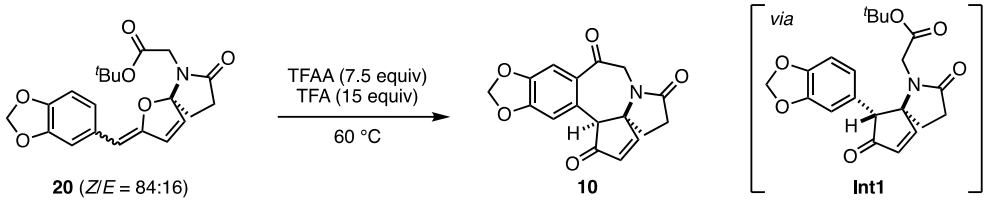


Following a literature procedure,[5] **20** was synthesized. A 200-mL two-necked round-bottom with a rubber septum flask containing a magnetic stirring bar and Cs_2CO_3 (7.85 g, 24.1 mmol, 4.0 equiv) was dried with a heat-gun *in vacuo* and N_2 gas was filled after cooling to room temperature. To this flask were added $Pd_2(dba)_3$·$CHCl_3$ (187.0 mg, 180 µmol, 2.5 mol%), DPEphos (323.8 mg, 602 µmol, 10 mol%), **19** (2.00 g, 6.02 mmol, 1.0 equiv), and **13** (3.26 g, 10.2 mmol, 1.7 equiv). The flask was placed under vacuum and N_2 gas was refilled three times. To this flask was added MeCN (40 mL). The flask was sealed with rubber septa. After stirring the mixture at 60 °C for 12 h, the mixture was passed through a pad of Celite® with EtOAc as an eluent. The filtrate was concentrated *in vacuo*. The residue was purified by Isolera® ($CHCl_3$/MeOH = 98:2 to 90:10), and further purified by Isolera® (hexane/acetone = 90:10 to 75:25) to afford a mixture of **20** and **S2** as a brown solid (1.65 g, *Z*-**20**:*E*-**20**:**S2** = 74:14:12; ^{1}H NMR peaks at 5.37 ppm (s, 0.74H, *Z*-**20**), 6.19 ppm (dd, 0.16H, *E*-**20**), and 6.26 ppm (d, 0.10H, **S2**), were used) and the yield of **10** was determined as 62%. Further purification by GPC was performed for the characterization of *Z*-**20**.

For *Z*-**20**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 2.0 Hz, 1H), 6.96 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.36 (d, *J* = 5.6 Hz, 1H), 6.03 (d, *J* = 5.6 Hz, 1H), 5.96–5.93 (m, 2H), 5.37 (s, 1H), 4.12 (d, *J* = 17.6 Hz, 1H), 3.36 (d, *J* = 17.6 Hz, 1H), 2.84–2.71 (m, 1H), 2.61–2.50 (m, 1H), 2.44–2.37 (m, 2H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 167.8, 154.4, 147.5, 145.9, 130.3,

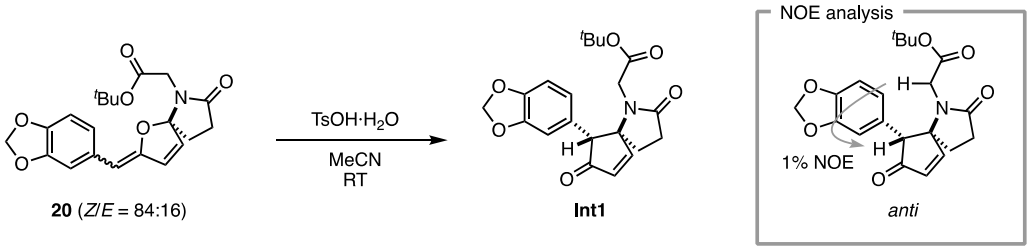
130.1, 129.7, 122.2, 108.2, 107.7, 101.7, 100.8, 81.9, 40.8, 31.1, 28.5, 27.9 (One peak is missing due to overlapping). HRMS (ESI) *m*/*z* calcd for $C_{21}H_{23}NO_6Na$ $[M+Na]^+$: 408.1418 found 408.1420.

Synthesis of (3a*S,14b*S**)-4,5-Dihydro-6*H*-[1,3]dioxolo[4',5':4,5]benzo[1,2-*d*]cyclopenta[*b*]pyrrolo[1,2-a]azepine-1,6,9(8*H*,14b*H*)-trione (10)**



Following procedure was performed in parallel 12 batches. To twelve 8-mL glass tubes equipped with a screw cap containing a magnetic stirring bar were added **20** (*Z*/*E* = 84:16: 452.3 mg (37.7 mg in each tube), 1.17 mmol, 1.0 equiv), TFAA (1.22 mL (0.10 mL in each tube), 8.80 mmol, 7.5 equiv), and TFA (1.35 mL (0.11 mL in each tube), 17.6 mmol, 15 equiv). After stirring the mixture at 60 °C for 24 h, the combined mixture was poured into 6 M NaOH aq. at 0 °C and extracted three times with EtOAc. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated *in vacuo*. The residue was purified by Isolera® ($CHCl_3$/MeOH = 100:0 to 90:10) and further purified by PTLC ($CHCl_3$/MeOH = 20:1) to afford **10** (110.6 mg, 30% yield) as a brown solid.

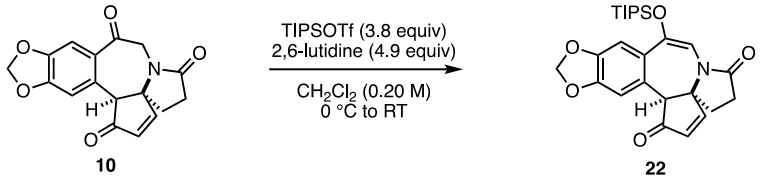
^{1}H NMR (400 MHz, CD_3CN) δ 7.42 (d, *J* = 5.6 Hz, 1H), 7.14 (s, 1H), 6.82 (s, 1H), 6.51 (d, *J* = 5.6 Hz, 1H), 6.11–6.00 (m, 2H), 4.45 (d, *J* = 19.2 Hz, 1H), 3.91 (s, 1H), 3.32 (d, *J* = 19.2 Hz, 1H), 2.55–2.42 (m, 2H), 2.40–2.26 (m, 1H), 2.26–2.17 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.6, 199.1, 173.9, 157.3, 151.7, 148.3, 135.9, 130.0, 128.1, 112.9, 110.1, 102.2, 70.4, 63.6, 47.0, 29.3, 28.4. HRMS (ESI) *m*/*z* calcd for $C_{17}H_{13}NO_5Na$ $[M+Na]^+$: 334.0686 found 334.0677.



To confirm the stereochemistry of **Int1**, following experiment was conducted. To a glass tube equipped with a screw cap containing a magnetic stirring bar were added **20** (*Z*/*E* = 84:16: 47.6 mg, 0.123 mmol, 1.0 equiv), TsOH·H_2O (4.7 mg, 25μmol, 0.20 mol%) and MeCN (0.62 mL). The mixture was stirred for 4 h at room temperature. NaHCO3 aq. was added to the mixture to quench the reaction. The mixture was extracted for three times with EtOAc. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated *in vacuo*. The residue was purified by PTLC (hexane/acetone = 2:1) to afford **Int1** (42.5 mg, 89% yield, dr = 92:8) as a brown solid. NOE analysis indicated that the major product was *anti*-product. Compound **Int1** did not isomerize under TFA (7.5 equiv) conditions.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 6.0 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.70–6.65 (m, 2H), 6.43 (dd, *J* = 6.0 Hz, 1H), 5.99–5.92 (m, 2H), 3.97 (d, *J* = 17.2 Hz, 1H), 3.77 (d, *J* = 17.2 Hz, 1H), 3.70 (s, 1H), 2.18 (ddd, *J* = 16.0, 8.8, 2.8 Hz, 1H), 2.06–1.89 (m, 2H), 1.85 (dd, *J* = 16.0, 8.8 Hz, 1H), 1.49 (s, 9H).

Synthesis of (3a*S,14b*S**)-9-((Triisopropylsilyl)oxy)-4,5-dihydro-6*H*-[1,3]dioxolo'[4'',5'':4,5]benzo[1,2-*d*]cyclopenta[*b*]pyrrolo[1,2-*a*]azepine-1,6(14b*H*)-dione (22)**

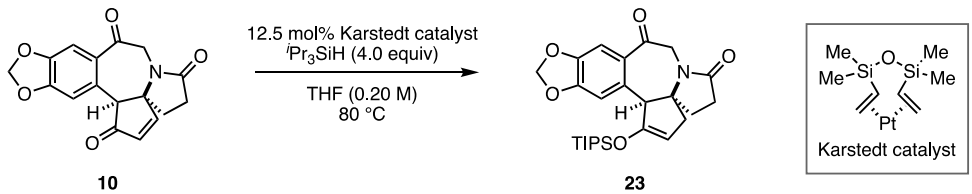


10 **22**

An 8-mL tube equipped with a screw cap containing a magnetic stirring bar, **10** (15.2 mg, 48.8 μmol, 1.0 equiv) and CH_2Cl_2 (0.33 mL) was filled with N_2. To this tube were added 2,6-lutidine (11.9 mg, 97.7 μmol, 2.0 equiv), TIPSOTf (23.8 mg, 73.2 μmol, 1.5 equiv) at 0 °C. After stirring the mixture for 3 h at room temperature, 2,6-lutidine (15.3 mg, 142.8 μmol, 2.9 equiv), TIPSOTf (33.5 mg, 29.4 μmol, 2.3 equiv) were further added at 0 °C. After stirring the mixture at room temperature for 40 h, NH_4Cl aq. was added to the mixture. The mixture was extracted three times with EtOAc. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated *in vacuo*. Purification by PTLC ($CHCl_3$/MeOH = 50:1) afforded **22** (11.7 mg, 51%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 5.6 Hz, 1H), 7.04 (s, 1H), 6.64 (s, 1H), 6.37 (d, *J* = 5.6 Hz, 1H), 6.00 (d, *J* = 1.6 Hz, 1H), 5.99 (d, *J* = 1.6 Hz, 1H), 5.50 (s, 1H), 3.16 (s, 1H), 2.65–2.37 (m, 3H), 2.36–2.27 (m, 1H), 1.29–1.17 (m, 3H), 1.11 (d, *J* = 7.2 Hz, 9H), 1.07 (d, *J* = 7.2 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.7, 173.0, 156.0, 152.1, 147.9, 147.8, 134.3, 130.1, 125.8, 112.5, 108.7, 103.7, 101.6, 83.5, 61.7, 30.1, 27.5, 17.98, 17.95, 12.6. HRMS (ESI) *m*/*z* calcd for $C_{26}H_{33}NO_5SiNa$ $[M+Na]^+$: 490.2020 found 490.2022.

Synthesis of (3a*S,14b*S**)-1-((Triisopropylsilyl)oxy)-3,4,5,14b-tetrahydro-6*H*-[1,3]dioxolo'[4'',5':4,5]benzo[1,2-*d*]cyclopenta[*b*]pyrrolo[1,2-*a*]azepine-6,9(8*H*)-dione (23)**



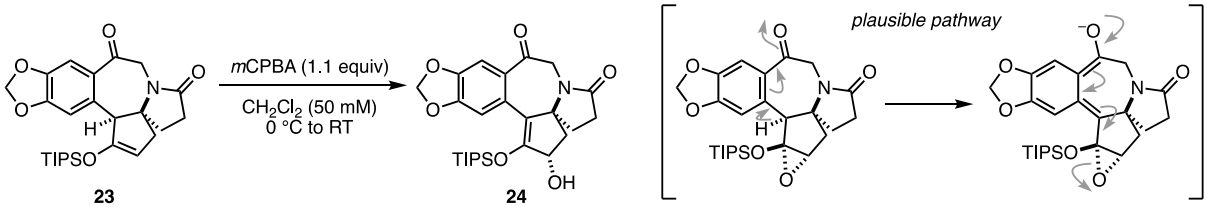
10 **23**

An 8-mL tube equipped with a screw cap containing a magnetic stirring bar was dried with a heat-gun *in vacuo* and filled with N_2 after cooling to room temperature. To this tube were added Karstedt catalyst (20.0 μL, 26.0 μmol, 12.5 mol%) and ^{i}Pr$_3$SiH (124.8 mg, 0.80 mmol, 4.0 equiv) under a stream of N_2 gas. After stirring the mixture at room temperature for 30 min, to the mixture was added a solution

of **10** (62.3 mg, 0.20 mmol, 1.0 equiv) in THF (1.0 mL). After stirring the mixture at 80 °C for 7 h, the mixture was passed through a pad of Celite® with EtOAc as an eluent and the solvent was removed *in vacuo*. Purification by PTLC ($CHCl_3$/MeOH = 40:1) afforded **23** (66.0 mg, 70% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 1H), 6.64 (s, 1H), 6.00 (s, 2H), 4.73 (d, *J* = 18.8 Hz, 1H), 4.63 (dd, *J* = 4.8, 2.4 Hz, 1H), 3.86 (s, 1H), 3.80 (d, *J* = 18.8 Hz, 1H), 2.74 (dt, *J* = 16.4, 2.4 Hz, 1H), 2.49 (dt, *J* = 16.4, 1.6 Hz, 1H), 2.42–2.32 (m, 1H), 2.32–2.14 (m, 3H), 1.07–0.97 (m, 3H), 0.89 (d, *J* = 4.0 Hz, 12H), 0.87 (d, *J* = 4.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.2, 174.6, 152.8, 150.8, 147.5, 131.7, 131.6, 111.9, 109.9, 101.8, 97.8, 69.5, 62.9, 49.7, 40.6, 31.2, 30.1, 17.7, 17.5, 12.1. HRMS (ESI) *m*/*z* calcd for $C_{26}H_{35}NO_5SiNa$ $[M+Na]^+$: 492.2177 found 492.2177.

Synthesis of (2*S,3a*S**)-2-Hydroxy-1-((triisopropylsilyl)oxy)-2,3,4,5-tetrahydro-6*H*-[1,3]dioxolo'[4'',5':4,5]benzo[1,2-*d*]cyclopenta[*b*]pyrrolo[1,2-*a*]azepine-6,9(8*H*)-dione (24)**

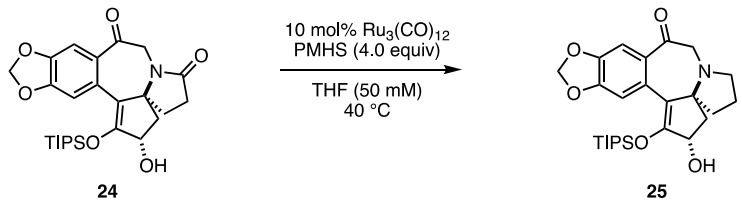


23 24

To a solution of **23** (96.2 mg, 0.205 mmol, 1.0 equiv) in CH_2Cl_2 (4.0 mL) was added *m*-chloroperbenzoic acid (*m*CPBA: 50.7 mg, 0.225 mmol, 1.1 equiv, purity 77%) at 0 °C. After stirring the mixture at room temperature for 1.5 h with monitoring reaction progress with TLC, the reaction was quenched with $Na_2S_2O_3$ aq. and saturated $NaHCO_3$ aq. The mixture was extracted three times with EtOAc. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated *in vacuo*. Purification by PTLC ($CHCl_3$/MeOH = 30:1) afforded **24** (84.3 mg, 85% yield) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 6.90 (s, 1H), 6.06–6.03 (m, 2H), 4.72–4.62 (m, 2H), 3.44 (d, *J* = 17.6 Hz, 1H), 2.59–2.45 (m, 1H), 2.31–2.06 (m, 4H), 2.01–1.90 (m, 1H), 1.01–0.89 (m, 21H) (The peak of O–H was not observed); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 174.4, 154.3, 151.6, 147.9, 130.6, 129.0, 122.0, 110.8, 109.6, 102.0, 74.2, 71.9, 47.7, 40.6, 33.1, 30.1, 17.50, 17.47, 12.6. HRMS (ESI) *m*/*z* calcd for $C_{26}H_{35}NO_6SiNa$ $[M+Na]^+$: 508.2126 found 508.2129.

Synthesis of (2*S,3a*S**)-2-Hydroxy-1-((triisopropylsilyl)oxy)-2,3,5,6-tetrahydro-4*H*-[1,3]dioxolo[4',5':4,5]benzo[1,2-*d*]cyclopenta[*b*]pyrrolo[1,2-*a*]azepin-9(8*H*)-one (25)**

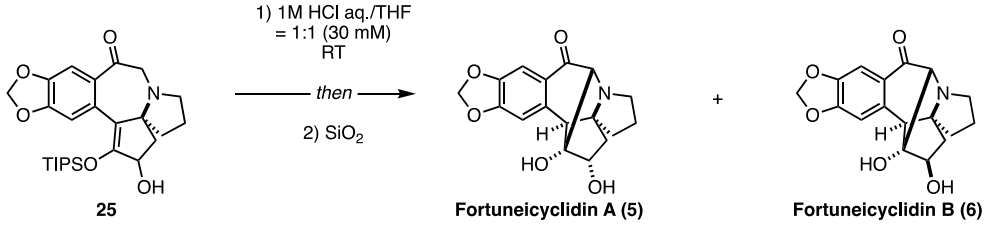


24 25

Following a literature procedure with a modification,[6] **20** was synthesized. A spitz tube equipped with a screw cap containing a magnetic stirring bar was dried with a heat-gun *in vacuo* and filled with N_2 after cooling to room temperature. To this tube were added $Ru_3(CO)_{12}$ (1.5 mg, 2.47 μmol, 10 mol%) and **24** (12.1 mg, 24.7 μmol, 1.0 equiv). The tube was placed under vacuum and N_2 gas was refilled three times. To this tube were added THF (0.48 mL) and poly(methylhydrosiloxane) (PMHS: 8.2 μL). After stirring the mixture at room temperature for 10 min, the mixture was stirred at 40 °C for 9 h with monitoring reaction progress with TLC. After cooling the mixture to room temperature, the mixture was passed through a pad of silica-gel with EtOAc as an eluent and the solvent was removed *in vacuo*. Purification by PTLC ($CHCl_3$/MeOH = 50:1) afforded **25** (6.1 mg, 52% yield) as a yellow solid and recovered **24** (3.2 mg, 27% recovery).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.05 (s, 1H), 6.05 (d, *J* = 1.2 Hz, 1H), 6.03 (d, *J* = 1.2 Hz, 1H), 4.62 (d, *J* = 6.0 Hz, 1H), 3.74–3.61 (m, 2H), 2.95 (dd, *J* = 7.6, 6.0 Hz, 1H), 2.60–2.51 (m, 1H), 2.12–1.96 (m, 3H), 1.84–1.57 (m, 3H), 1.06–0.93 (m, 21H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.8, 152.2, 151.5, 147.5, 132.7, 130.9, 126.4, 111.5, 108.0, 102.0, 74.7, 73.8, 57.7, 50.9, 47.1, 39.8, 24.0, 17.63, 17.59, 12.7; HRMS (ESI) *m*/*z* calcd for $C_{26}H_{38}NO_5Si$ $[M+H]^+$: 472.2514 found 472.2537.

Synthesis of Fortuneicyclidin A (5) and B (6)



To a spitz tube containing a magnetic stirring bar and **25** (3.7 mg, 7.8 μmol, 1.0 equiv) were added THF (0.13 mL) and 1 M HCl aq. (0.13 mL) at room temperature. After stirring the mixture at room temperature for 3.5 hours, the reaction was quenched with saturated $NaHCO_3$ aq. The mixture was extracted three times with EtOAc. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated *in vacuo*. The obtained mixture was treated with silica-gel in $CHCl_3$ and stirred for 1 h. Silica-gel was removed by a filtration and the mixture was concentrated *in vacuo*. Purification by PTLC (EtOAc/$CHCl_3$ = 3:1, three times) afforded fortuneicyclidin A (**5**: 1.0 mg, 40% yield) as a pale yellow solid and fortuneicyclidin B (**6**: 0.2 mg, 8% yield) as a white solid.

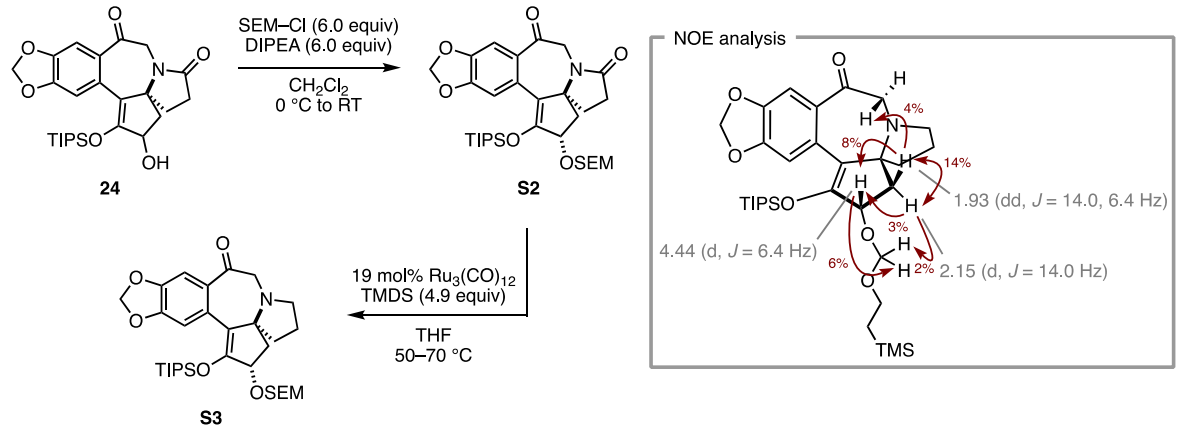
For fortuneicyclidin A (**5**): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (s, 1H), 6.72 (s, 1H), 6.06 (d, *J* = 1.2 Hz, 1H), 6.05 (d, *J* = 1.2 Hz, 1H), 4.03 (dd, *J* = 7.2, 3.6 Hz, 1H), 3.48 (s, 1H), 3.10 (s, 1H), 2.82–2.76 (m, 1H), 2.50 (dd, *J* = 12.0, 7.2 Hz, 1H), 2.25 (dd, *J* = 15.0, 7.2 Hz, 1H), 1.84 (dd, *J* = 12.0, 3.6 Hz, 1H), 1.75–1.58 (m, 4H); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 7.24 (s, 1H), 7.01 (s, 1H), 6.121 (d, *J* = 6.0 Hz, 1H), 6.120 (d, *J* = 6.0 Hz, 1H), 5.21 (s, 1H), 5.01 (d, *J* = 4.8 Hz, 1H), 3.68–3.64 (m, 1H), 3.14 (s, 1H), 3.08 (s, 1H), 2.64–2.59 (m, 1H), 2.26 (dd, *J* = 12.0, 7.8 Hz, 1H), 2.10–2.05 (m, 1H), 1.67 (dd,

J = 11.4, 3.6 Hz, 1H), 1.60–1.53 (m, 3H), 1.13–1.09 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 152.7, 147.8, 136.9, 127.7, 109.9, 105.7, 101.9, 90.0, 74.4, 72.2, 71.3, 54.4, 48.8, 47.7, 26.6, 26.5; ^{13}C NMR (151 MHz, DMSO-d_6) δ 197.3, 151.9, 146.9, 138.2, 127.5, 110.1, 103.9, 101.8, 90.3, 73.9, 71.8, 71.2, 53.6, 48.7, 47.2, 26.3, 26.2; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{18}NO_5$ $[M+H]^+$: 316.1179 found 316.1177.

For fortuneicyclidin B (**6**): ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.23 (s, 1H), 6.94 (s, 1H), 6.114 (d, *J* = 7.2 Hz, 1H), 6.112 (d, *J* = 7.2 Hz, 1H), 5.42 (s, 1H), 4.86 (d, *J* = 4.8 Hz, 1H), 4.01 (ddd, *J* = 10.2, 4.8, 2.4 Hz, 1H), 3.70 (s, 1H), 2.95 (s, 1H), 2.66–2.59 (m, 1H), 2.23 (dd, *J* = 11.4, 10.2 Hz, 1H), 2.12–2.06 (m, 1H), 1.58 (dd, *J* = 12.0, 2.4 Hz, 1H), 1.57–1.51 (m, 3H), 1.11–1.07 (m, 1H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 197.6, 151.7, 146.8, 137.5, 127.9, 109.7, 104.0, 101.8, 92.5, 75.1, 72.9, 68.8, 56.9, 47.3, 45.7, 26.8, 25.8; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{18}NO_5$ $[M+H]^+$: 316.1179 found 316.1182.

The spectra are in accordance with those reported in the literature.[7]

Determination of relative stereochemistry at C2–OH after Rubottom oxidation



To a spitz tube equipped with a screw cap containing a magnetic stirring bar were added **24** (43.6 mg, 90 µmol, 1.0 equiv) and CH_2Cl_2 (0.89 mL). The mixture was cooled to 0 °C in an ice bath. To this tube were added trimethylsilylethoxymethylchrolide (SEM–Cl: 94.5 µL, 0.54 mmol, 6.0 equiv) and diisopropylethylamine (93.8 µL, 0.54 mmol, 6.0 equiv) at 0 °C. After stirring the mixture for 16 h at room temperature, sat. $NaHCO_3$ aq. was added to the mixture. The mixture was extracted three times with EtOAc. The combined organic layer was dried over Na_2SO_4, filtrated, and then concentrated *in vacuo*. Purification by Isolera (hexane/EtOAc = 90:10 to 25:75) afforded (2*S*,3a*S*)-1-((triisopropylsilyl)oxy)-2-((2-(trimethylsilyl)ethoxy)methoxy)-2,3,4,5-tetrahydro-6*H*-[1,3]dioxolo[4',5':4,5]benzo[1,2-*d*]cyclopenta[*b*]pyrrolo[1,2-*a*]azepine-6,9(8*H*)-dione (**S2**: 44.6 mg, 81% yield).

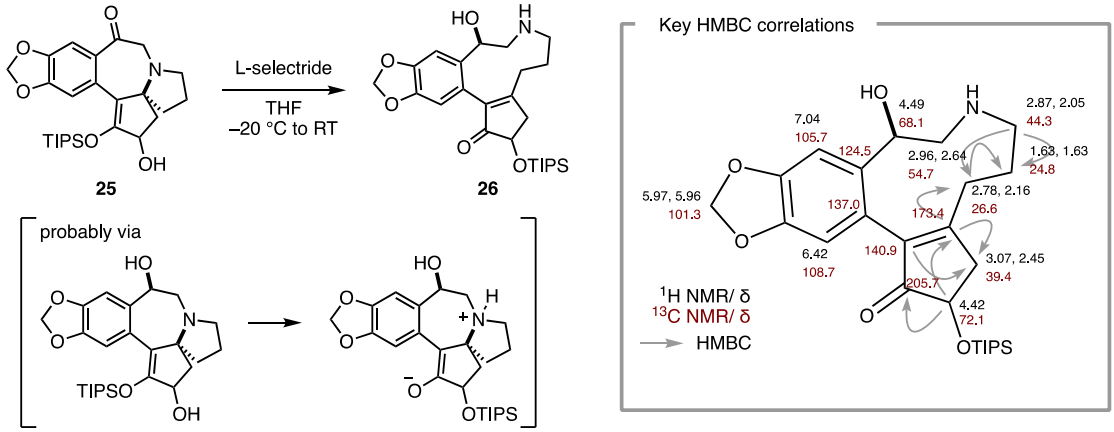
A spitz tube equipped with a screw cap containing a magnetic stirring bar was dried with a heat-gun *in vacuo* and filled with N_2 after cooling to room temperature. To this tube were added $Ru_3(CO)_{12}$ (1.1 mg, 1.7 µmol, 19 mol%) and **S2** (5.7 mg, 9.3 µmol, 1.0 equiv). The tube was placed under vacuum and refilled with N_2 gas three times. To this tube were added THF (0.10 mL) and tetramethyldisiloxane

(TMDS: 6.1 mg, 45 μmol, 4.9 equiv). After stirring the mixture at room temperature for 10 min, the mixture was stirred at 50 °C for 1 h, 60 °C for 4 h, and them 70 °C for 5 h. After cooling the mixture to room temperature, the mixture was passed through a pad of Celite with EtOAc as an eluent and the solvent was removed *in vacuo*. Purification by PTLC ($CHCl_3$/MeOH = 50:1) afforded **S3** (2.7 mg, 49% yield) as a yellow oil and recovered **S2** (1.3 mg, 23% recovery).

S3: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.09 (s, 1H), 6.04 (d, *J* = 1.2 Hz, 1H), 6.03 (d, *J* = 1.2 Hz, 1H), 4.87 (d, *J* = 7.2 Hz, 1H), 4.82 (d, *J* = 7.2 Hz, 1H), 4.44 (d, *J* = 6.4 Hz, 1H), 3.82 (ddd, *J* = 11.2, 9.6, 6.0 Hz, 1H), 3.71 (d, *J* = 16.4 Hz, 1H), 3.66 (d, *J* = 16.4 Hz, 1H), 3.60 (ddd, *J* = 11.2, 9.6, 6.0 Hz, 1H), 2.94 (dd, *J* = 8.4, 5.2 Hz, 1H), 2.62–2.52 (m, 1H), 2.15 (d, *J* = 14.0 Hz, 1H), 2.02 (d, *J* = 6.0 Hz, 1H), 1.95 (dd, *J* = 14.0, 6.4 Hz, 1H), 1.78–1.71 (m, 2H), 1.62–1.57 (m, 1H), 1.00–0.95 (s, 23H), 0.03 (s, 9H). According to NOE analysis, relative stereochemistry at the C2-OH was assigned as follows.

3. Total Synthesis of Cephalotine B

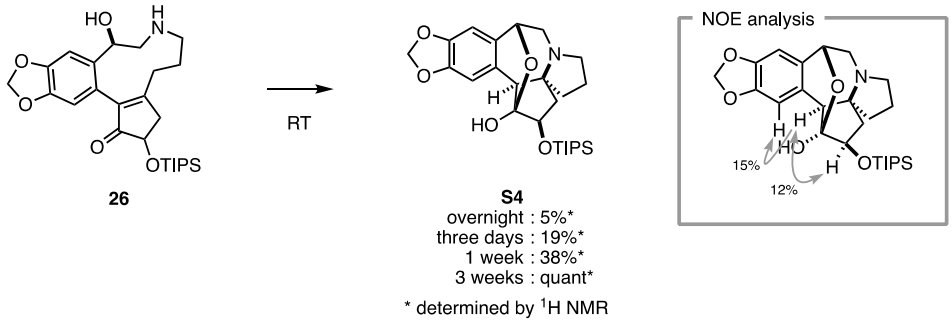
Synthesis of (9*R**)-9-Hydroxy-2-((triisopropylsilyl)oxy)-2,3,4,5,6,7,8,9-octahydro-1*H*-[1,3]dioxolo[4',5':4,5]benzo[1,2-*d*]cyclopenta[*f*]azecin-1-one (26)



To a spitz tube equipped with a screw cap containing a magnetic stirring bar and **25** (7.2 mg, 15 μmol, 1.0 equiv) in THF (0.50 mL) was added L-selectride (1.0 M, 31 μL, 30 μmol, 2.0 equiv) at –20 °C (in an ice brine bath). After stirring the mixture at 0 °C for 1 h, to the mixture was added NH_4Cl aq. and stirred for 5 min (color of solution changed from yellow to colorless). The mixture was extracted four times with EtOAc. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated *in vacuo*. Purification by PTLC ($CHCl_3$/MeOH = 20:1) afforded **26** (4.2 mg, 58% yield) as a colorless oil. Although **26** was obtained as a single isomer, stereochemistry at the C2 position was not determined.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (s, 1H), 6.42 (s, 1H), 5.97 (d, *J* = 6.4 Hz, 1H), 5.96 (d, *J* = 6.4 Hz, 1H), 4.49 (dd, *J* = 10.8, 4.4 Hz, 1H), 4.42 (dd, *J* = 6.4, 2.0 Hz, 1H), 3.07 (dd, *J* = 18.0, 6.4 Hz, 1H), 2.96 (dd, *J* = 12.8, 4.4 Hz, 1H), 2.91–2.74 (m, 2H), 2.64 (dd, *J* = 12.8, 10.8 Hz, 1H), 2.45 (dd, *J* = 18.0, 2.0 Hz, 1H), 2.21–2.02 (m, 2H), 1.22–1.04 (m, 21H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.7, 173.4, 148.4, 147.2, 140.9, 137.0, 125.1, 108.7, 105.7, 101.3, 72.0, 68.1, 54.7, 44.3, 39.4, 26.6, 24.8, 17.9, 17.8, 12.2; HRMS (ESI) *m*/*z* calcd for $C_{26}H_{40}NO_5Si$ $[M+H]^+$: 474.2670 found 474.2668.

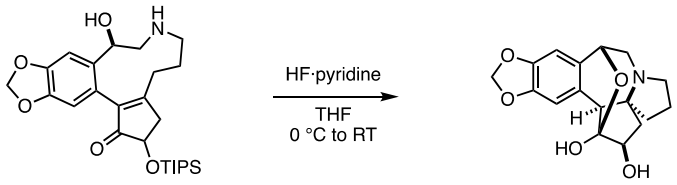
Note: Compound **26** was gradually converted to TIPS–cephalotine B (**S4**) at room temperature.



S4: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (s, 1H), 6.70 (s, 1H), 5.95 (d, *J* = 1.6 Hz, 1H), 5.94 (d, *J* = 1.6 Hz, 1H), 4.94 (d, *J* = 3.2 Hz, 1H), 4.33 (t, *J* = 8.8 Hz, 1H), 3.08 (s, 1H), 2.84 (dd, *J* = 12.4, 4.0 Hz, 1H), 2.82–2.75 (m, 2H), 2.35–2.29 (m, 1H), 1.88 (dd, *J* = 13.4, 9.2 Hz, 1H), 1.75–1.65 (m, 5H), 1.22–

1.04 (m, 21H) ^{1}H NMR (400 MHz, acetone-d_6) δ 6.74 (s, 1H), 6.73 (s, 1H), 5.99 (d, *J* = 1.2 Hz, 1H), 5.94 (d, *J* = 1.2 Hz, 1H), 4.85 (dd, *J* = 4.0, 1.2 Hz, 1H), 4.38 (t, *J* = 8.8 Hz, 1H), 4.05 (s, 1H), 3.08 (s, 1H), 2.74 (dd, *J* = 12.0, 4.0 Hz, 1H), 2.67 (dd, *J* = 12.0, 1.2 Hz, 1H), 2.64–2.58 (m, 1H), 2.35–2.25 (m, 1H), 1.86 (dd, *J* = 14.4, 8.8 Hz, 1H), 1.80 (dd, *J* = 14.4, 8.8 Hz, 1H), 1.75–1.51 (m, 4H), 1.22–1.08 (m, 21H); ^{13}C NMR (101 MHz, acetone-d_6) δ 147.3, 147.0, 132.8, 128.3, 110.1, 105.9, 104.2, 101.5, 77.6, 75.6, 65.1, 55.2, 55.0, 50.2, 38.7, 34.4, 20.6, 18.49, 18.46, 13.2; HRMS (ESI) *m/z* calcd for $C_{26}H_{40}NO_5Si$ $[M+H]^+$: 474.2670 found 474.2670.

Synthesis of Cephalotine B (8)

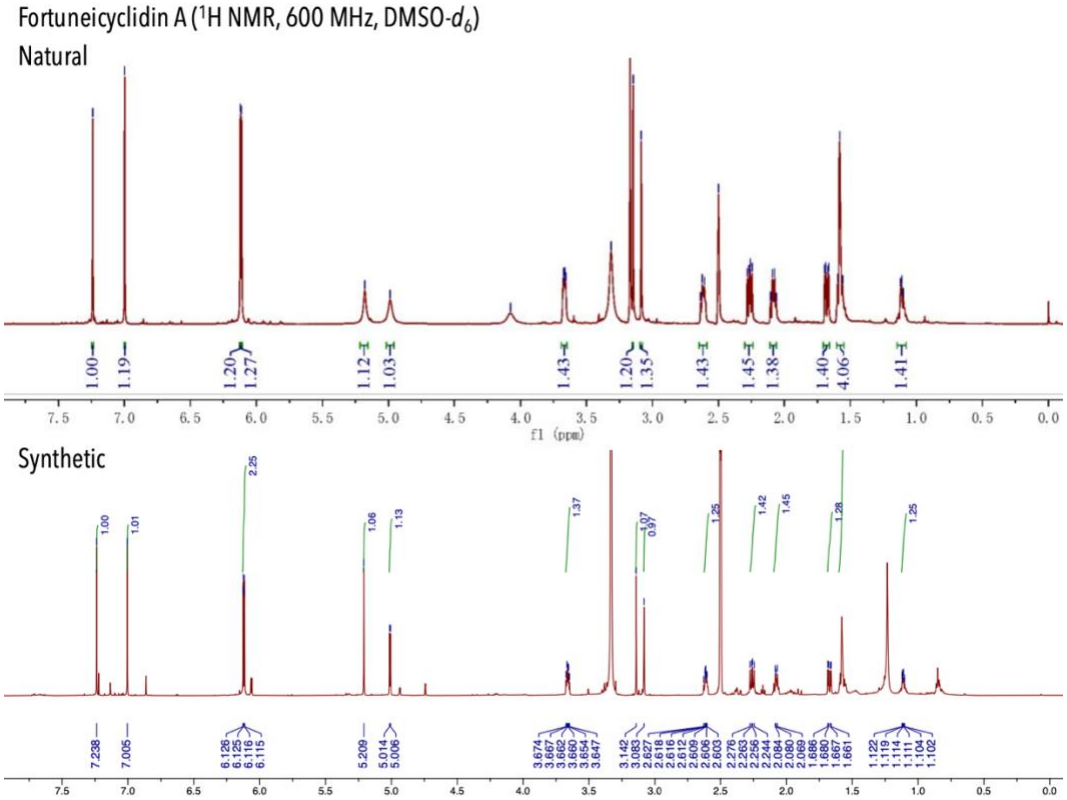


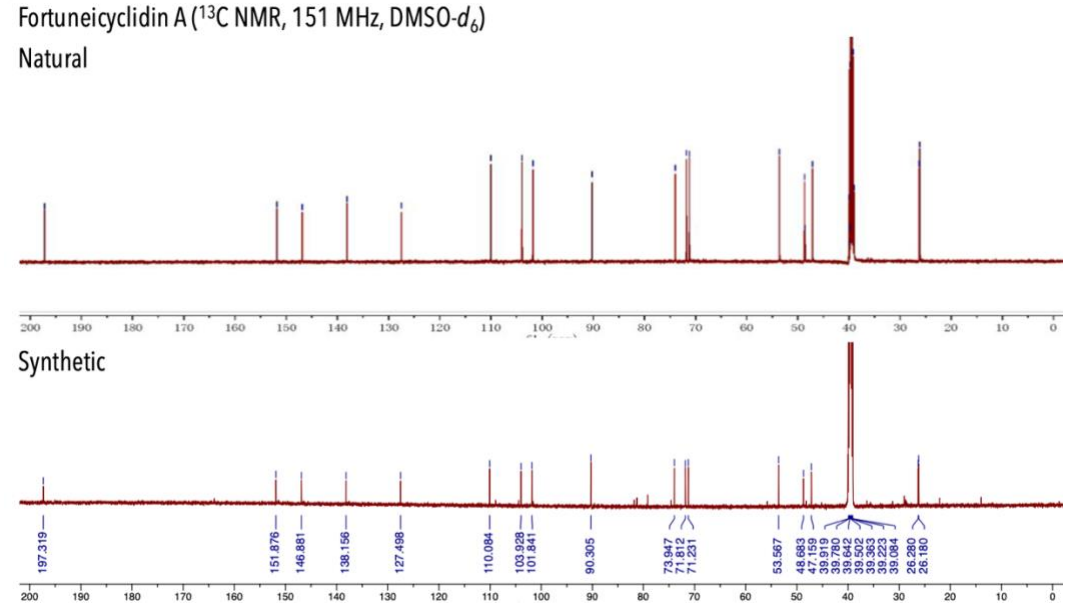
25 cephalotine B (**8**)

In a polypropylene tube, HF·pyridine (HF 70% weight, 100 µL, 24 equiv) was added to a solution of **25** (2.2 mg, 4.6 µmol, 1.0 equiv) in THF (0.50 mL) at 0 °C. The solution was gradually allowed to warm to RT. After stirring for 6 h, $NaHCO_3$ aq. was slowly added to the solution. The mixture was extracted five times with EtOAc. The combined organic layer was dried over Na_2SO_4, filtrated, and then concentrated *in vacuo*. Purification by PTLC ($CHCl_3$/MeOH = 9:1) afforded **8** (0.7 mg, 47% yield) as a white solid. The spectra are in accordance with those reported in the literature.[8]

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (s, 1H), 6.72 (s, 1H), 5.97 (d, *J* = 2.8 Hz, 1H), 5.95 (d, *J* = 2.8 Hz, 1H), 4.95 (d, *J* = 4.0 Hz, 1H), 4.21 (t, *J* = 8.8 Hz, 1H), 3.16 (s, 1H), 2.89 (dd, *J* = 12.8, 4.0 Hz, 1H), 2.82–2.76 (m, 1H), 2.68 (d, *J* = 12.8 Hz, 1H), 2.33–2.27 (m, 2H), 1.94 (dd, *J* = 14.8, 9.6 Hz, 1H), 1.76–1.66 (m, 6H). ^{1}H NMR (600 MHz, acetone-d_6) δ 6.75 (s, 1H), 6.74 (s, 1H), 5.98 (d, *J* = 1.2 Hz, 1H), 5.94 (d, *J* = 1.2 Hz, 1H), 4.89 (d, *J* = 3.6 Hz, 1H), 4.48 (brs, 1H), 4.05 (t, *J* = 9.0 Hz, 1H), 3.30 (brs, *J* = 9.6 Hz, 1H), 3.11 (s, 1H), 2.74 (dd, *J* = 12.6, 4.2 Hz, 1H), 2.66 (d, *J* = 12.6 Hz, 1H), 2.63–2.58 (m, 1H), 2.31–2.26 (m, 1H), 1.83 (dd, *J* = 14.4, 9.6 Hz, 1H), 1.71 (dd, *J* = 14.4, 8.4 Hz, 1H), 1.69–1.66 (m, 1H), 1.64–1.57 (m, 3H); ^{13}C NMR (151 MHz, acetone-d_6) δ 147.4, 146.9, 132.4, 128.6, 110.0, 106.0, 104.1, 101.6, 77.1, 76.2, 65.6, 55.2, 55.0, 50.1, 38.7, 34.4, 20.7; HRMS (ESI) *m/z* calcd for $C_{17}H_{20}NO_5$ $[M+H]^+$: 318.1339 found 318.1336.

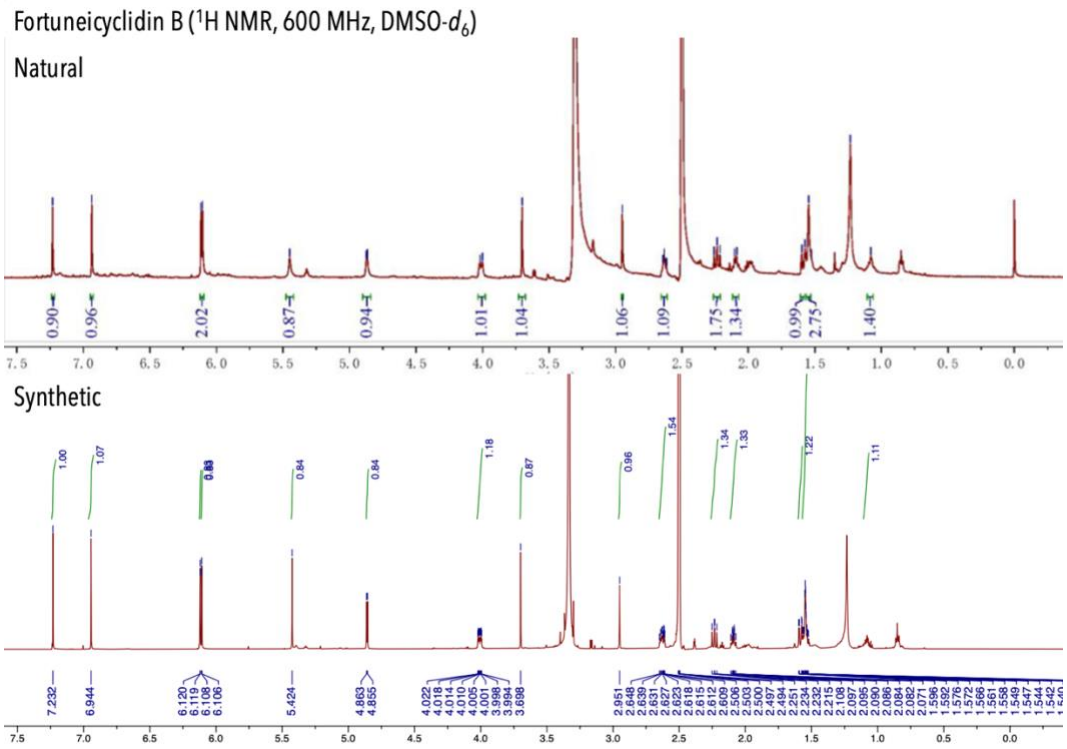
4. Comparison of NMR Spectra of the Natural Products 5, 6, and 8



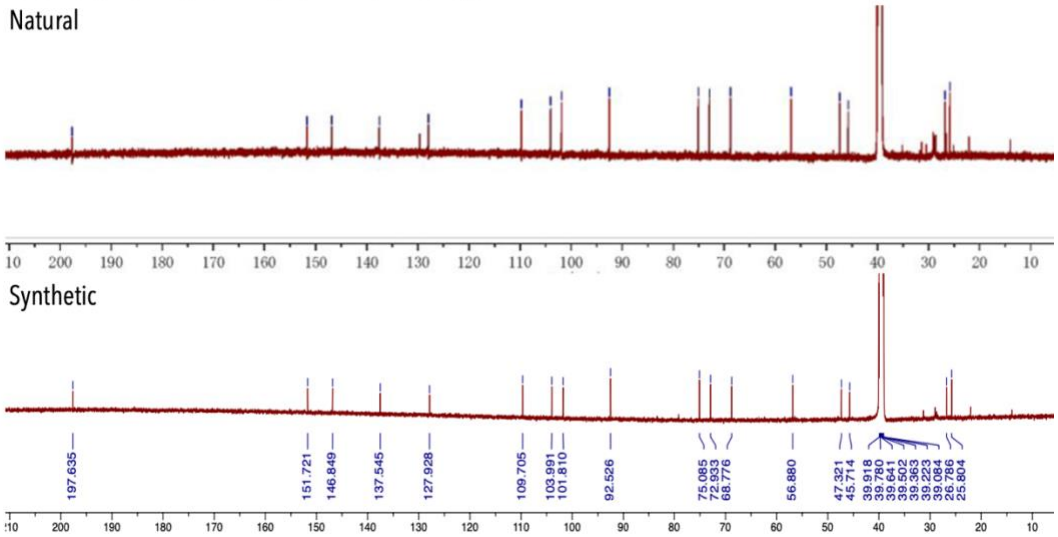


Natural (isolated by Kong, Luo)			Synthetic		
^{1}H NMR	7.24 (s, 1H)	^{13}C NMR 197.2	^{1}H NMR	7.24 (s, 1H)	^{13}C NMR 197.3
	7.00 (s, 1H)	151.8		7.01 (s, 1H)	151.9
	6.12 (d, *J* = 5.9 Hz, 1H)	146.9		6.121 (d, *J* = 6.0 Hz, 1H)	146.9
	6.11 (d, *J* = 5.9 Hz, 1H)	138.1		6.120 (d, *J* = 6.0 Hz, 1H)	138.2
	5.18 (br s)	127.5		5.21 (s, 1H)	127.5
	4.99 (br s)	110.0		5.01 (d, *J* = 4.8 Hz, 1H)	110.1
	3.67 (dd, *J* = 7.5, 4.0 Hz, 1H)	104.0		3.68–3.64 (m, 1H)	103.9
	3.15 (s, 1H)	103.9		3.14 (s, 1H)	101.8
	3.09 (s, 1H)	90.3		3.08 (s, 1H)	90.3
	2.62 (m, 1H)	73.9		2.64–2.59 (m, 1H)	73.9
	2.26 (dd, *J* = 11.5, 7.5 Hz, 1H)	71.8		2.26 (dd, *J* = 12.0, 7.8 Hz, 1H)	71.8
	2.08 (m, 1H)	71.2		2.10–2.05 (m, 1H)	71.2
	1.67 (dd, *J* = 11.5, 4.0 Hz, 1H)	53.6		1.67 (dd, *J* = 11.4, 3.6 Hz, 1H)	53.6
	1.61–1.55 (m, 3H)	48.7		1.60–1.53 (m, 3H)	48.7
	1.11 (m, 1H)	47.1		1.13–1.09 (m, 1H)	47.2
		26.3			26.3
		26.2			26.2

Fortuneicyclidin B (^{1}H NMR, 600 MHz, DMSO-d_6)

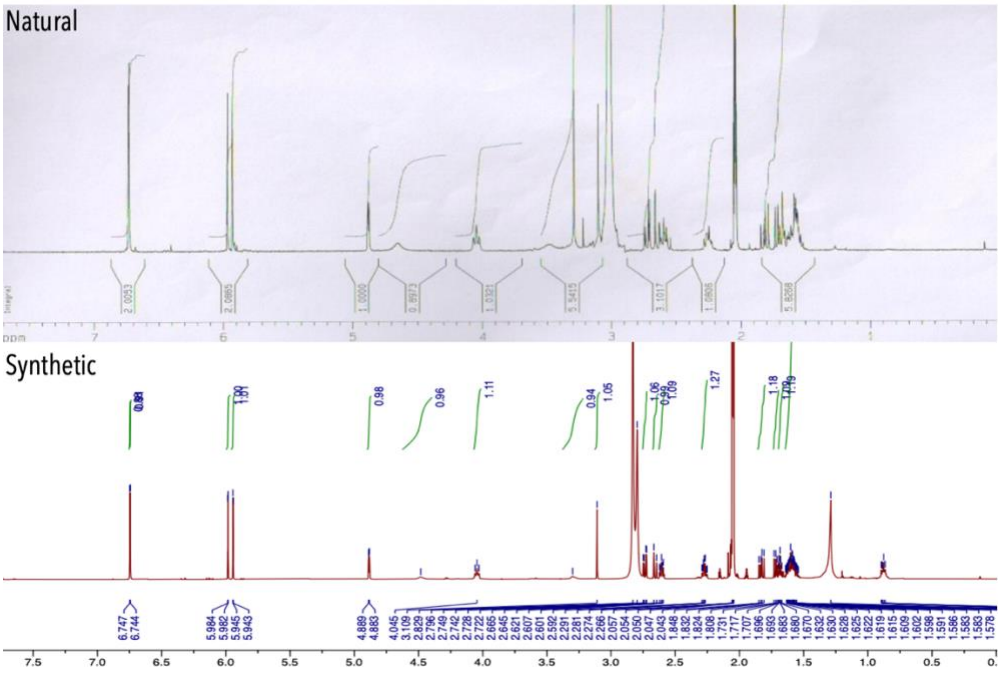


Fortuneicyclidin B (^{13}C NMR, 151 MHz, DMSO-d_6)

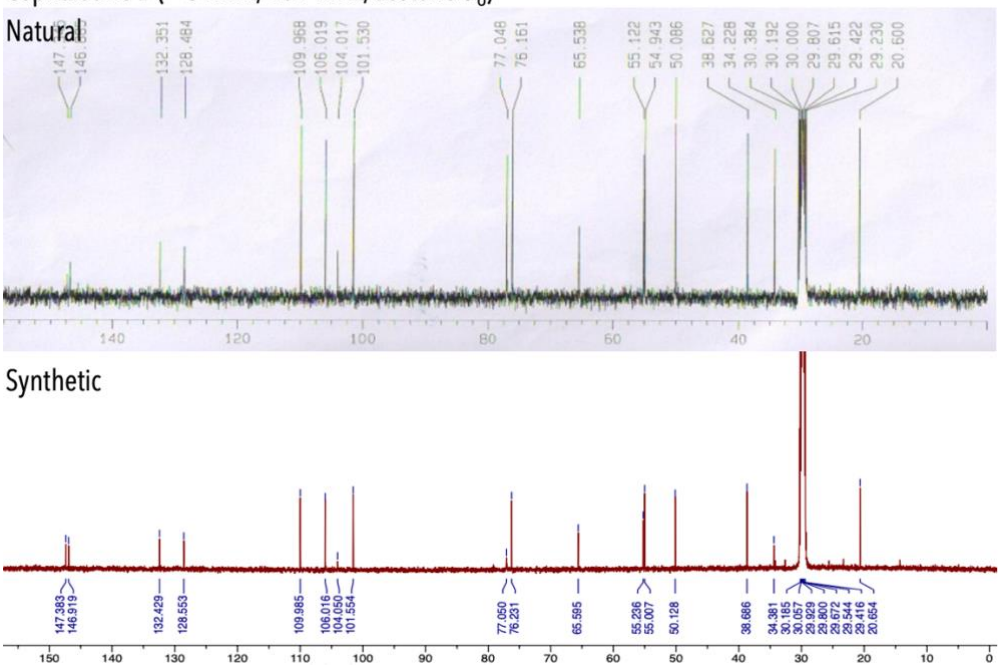


Natural (isolated by Kong, Luo)		Synthetic	
^{1}H NMR	^{13}C NMR	^{1}H NMR	^{13}C NMR
7.23 (s, 1H)	197.6	7.23 (s, 1H)	197.6
6.95 (s, 1H)	151.7	6.94 (s, 1H)	151.7
6.12 (d, *J* = 6.5 Hz, 1H)	146.6	6.114 (d, *J* = 7.2 Hz, 1H)	146.8
6.11 (d, *J* = 6.5 Hz, 1H)	137.5	6.112 (d, *J* = 7.2 Hz, 1H)	137.5
5.43 (br s)	127.9	5.42 (s, 1H)	127.9
4.86 (d, *J* = 4.2 Hz, 1H)	109.7	4.86 (d, *J* = 4.8 Hz, 1H)	109.7
4.01 (ddd, *J* = 10.4, 4.2, 2.4 Hz, 1H)	104.0	4.01 (ddd, *J* = 10.2, 4.8, 2.4 Hz, 1H)	104.0
3.70 (s, 1H)	101.8	3.70 (s, 1H)	101.8
2.95 (s, 1H)	92.5	2.95 (s, 1H)	92.5
2.63 (m, 1H)	75.1	2.66–2.59 (m, 1H)	75.1
2.23 (dd, *J* = 12.0, 10.4 Hz, 1H)	72.9	2.23 (dd, *J* = 11.4, 10.2 Hz, 1H)	72.9
2.09 (m, 1H)	68.8	2.12–2.06 (m, 1H)	68.8
1.58 (dd, *J* = 12.0, 2.4 Hz, 1H)	56.9	1.58 (dd, *J* = 12.0, 2.4 Hz, 1H)	56.9
1.57–1.52 (m, 3H)	47.3	1.57–1.51 (m, 3H)	47.3
1.08 (m, 1H)	45.7	1.11–1.07 (m, 1H)	45.7
	26.9		26.8
	25.8		25.8

Cephalotine B (^{1}H NMR, 600 MHz, acetone-d_6)



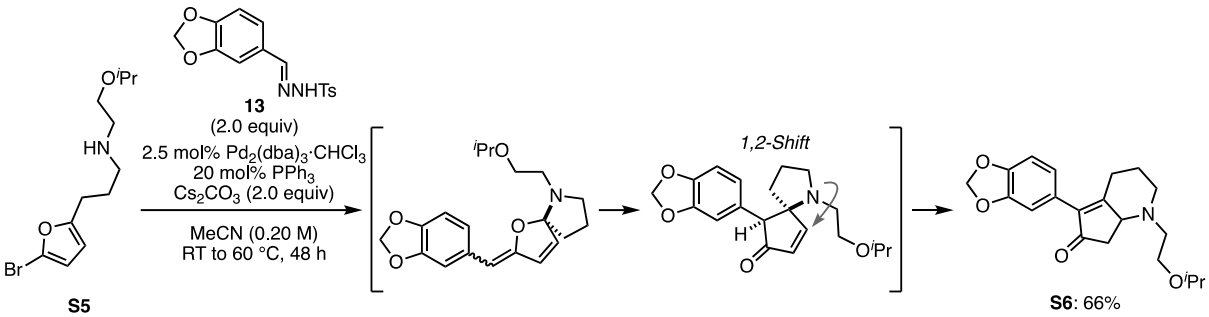
Cephalotine B (^{13}C NMR, 151 MHz, acetone-d_6)



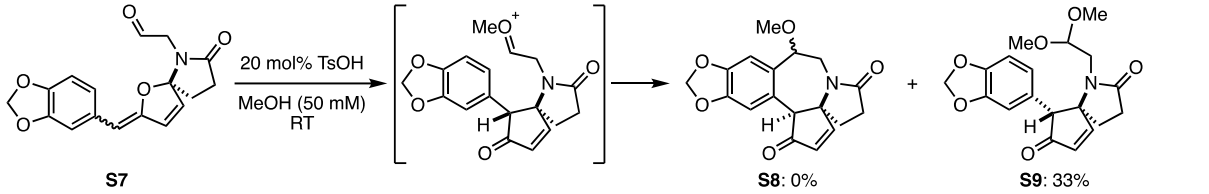
Natural (isolated by Cai)		Synthetic	
^{1}H NMR	^{13}C NMR	^{1}H NMR	^{13}C NMR
6.74 (s, 1H)	147.3	6.747 (s, 1H)	147.4
6.73 (s, 1H)	146.8	6.744 (s, 1H)	146.9
5.97 (d, J = 1.1 Hz, 1H)	132.4	5.98 (d, J = 1.2 Hz, 1H)	132.4
5.93 (d, J = 1.1 Hz, 1H)	128.5	5.94 (d, J = 1.2 Hz, 1H)	128.6
4.87 (d, J = 3.8 Hz, 1H)	110.0	4.89 (d, J = 3.6 Hz, 1H)	110.0
4.65 (br, 1H)	106.0	4.48 (brs, 1H)	106.0
4.05 (t, J = 8.9 Hz, 1H)	104.0	4.05 (t, J = 9.0 Hz, 1H)	104.1
3.45 (br, 1H)	101.5	3.30 (br d, J = 9.6 Hz, 1H)	101.6
3.10 (s, 1H)	77.0	3.11 (s, 1H)	77.1
2.71 (dd, J = 12.2, 4.0 Hz,1H)	76.2	2.74 (dd, J = 12.6, 4.2 Hz, 1H)	76.2
2.65 (d, J = 12.2 Hz, 1H)	65.5	2.66 (d, J = 12.6 Hz, 1H)	65.6
2.59 (m, 1H)	55.1	2.63–2.58 (m, 1H)	55.2
2.25 (m, 1H)	54.9	2.31–2.26 (m, 1H)	55.0
1.82 (dd, J = 14.4, 9.6 Hz, 1H)	50.1	1.83 (dd, J = 14.4, 9.6 Hz, 1H)	50.1
1.70 (dd, J = 14.4, 9.6 Hz, 1H)	38.6	1.71 (dd, J = 14.4, 8.4 Hz, 1H)	38.7
1.68 (m, 1H)	34.2	1.69–1.66 (m, 1H)	34.4
1.58–1.56 (m, 3H)	20.1	1.64–1.57 (m, 3H)	20.7

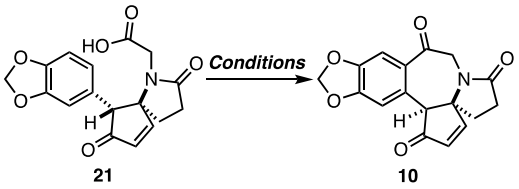
5. Other Attempts toward the Synthesis of 5, 6, and 8

· Attempts for the Dearomative Azaspirocyclization Using Dialkylamine S5.



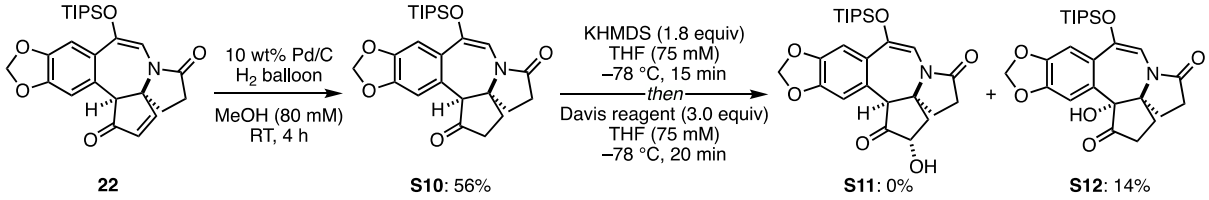
· Attempts Seven-membered Ring Formation



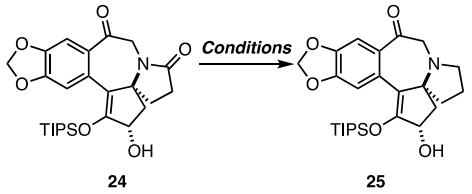


entry	*Conditions*	Yield of **10** (%)
1	1) $(COCl)_2$ (2.0 equiv), cat. DMF, 1,2-DCE (0.20 M), 0 °C to RT 2) $AlCl_3$ (3.0 equiv), 1,2-DCE (0.10 M), RT to 60 °C	n.d.
2	TfOH (0.10 M), RT	n.d.
3	TFAA (5.0 equiv), TFA (10 equiv), RT to 50 °C	3
4	**TFAA (10 equiv), TFA (20 equiv), 60 °C**	**46**

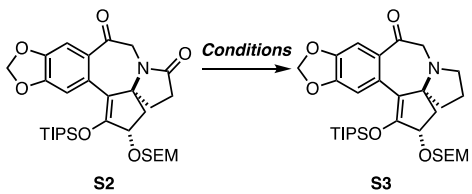
· Attempts for the C2-Oxygenation of Cyclopentanone 22



· Condition Screening for the Deoxygenation of Lactam



entry	*Conditions*	Yield/ % **24**	**25**
1	Hantzsch ester (2.5 equiv), Tf_2O (1.1 equiv), CH_2Cl_2 (50 mM), RT, 10 min	complex	
2	10 mol% $H_2PtCl_6·6H_2O$, TMDS (1.5 equiv), THF (0.10 M), 50 °C, 8 h	74	0
3	15 mol% $RhH(CO)(PPh_3)_3$, $PhSiH_3$ (5.0 equiv), THF (50 mM), RT, 1.5 h	complex	
4	10 mol% $Ru_3(CO)_{12}$, TMDS (4.0 equiv), THF (50 mM), 60 °C, 2.5 h	30	43
5	10 mol% $Ru_3(CO)_{12}$, PMHS (3.0 M), THF (50 mM), 40 °C, 9 h	27	52



entry	*Conditions*	Yield/ % **S2**	**S3**
1	15 mol% $RhH(CO)(PPh_3)_3$, $PhSiH_3$ (5.0 equiv), THF (30 mM), RT, 1.5 h	no reaction	
2	15 mol% $RhH(CO)(PPh_3)_3$, Ph_2SiH_2 (5.0 equiv), THF (50 mM), RT, 4 h	complex	
3	Hantzsch ester (2.5 equiv), Tf_2O (1.1 equiv), CH_2Cl_2 (0.10 M), 0 °C, 15 min	0	n.d.
4	65 mol% Karstedt cat., TMDS (2.5 equiv), THF (50 mM), 50 °C, 6 h	no reaction	
5	10 mol% $IrCl(CO)(PPh_3)_2$, TMDS (2.5 equiv), CH_2Cl_2 (50 mM), RT, 5 h	no reaction	
6	10 mol% $Ru_3(CO)_{12}$, TMDS (4.0 equiv), THF (50 mM), 60 °C, 13 h	0	45

6. X-ray Crystal Structure Analysis of 22

Recrystallization from acetone/hexane solution (vapor diffusion) gave crystals of **22** suitable for X-ray analysis. A suitable crystal was mounted with Immersion oil viscosity 1,250 cSt (lit.) (SIGMA–ALDRICH) on a MiTeGen MicroMounts and transferred to Rigaku XtaLAB Synergy-S diffractometer equipped with a HyPix-6000HE Hybrid Photon Counting detector and dual Mo and Cu microfocus sealed tube. Cell parameters were determined and refined, and raw frame data were integrated using CrysAlis^{Pro} (1.171.42.49, Rigaku Oxford Diffraction, 2021).[9] The structures were solved by direct methods with (SHELXT)[10] and refined by full-matrix least-squares techniques against F^2 (SHELXL-2018/3)[11] by using Olex2 software package.[12] The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions.

Table S1. Crystallographic Data and Structure Refinement Details for **22**

Compound	**22**
Empirical formula	$C_{26}H_{33}NO_5Si$
Formula weight	467.62
T / K	100.15
Crystal system	orthorhombic
Space group	*P*bca
a / Å	9.40630(10)
b / Å	21.6190(2)
c / Å	24.4354(3)
α / °	90
β / °	90
γ / °	90
V / Å^3	4969.06(9)
Z	8
D_{calc}, /g cm^{-3}	1.250
μ / mm^{-1}	1.131
F(000)	2000.0
Crystal size / mm	0.21 × 0.15 × 0.03
λ / Å	1.54184
2θ range / °	7.236 to 150.304
Reflns collected	26121
Indep reflns/R_{int}	4951/0.0368
Params	304
GOF on F^2	1.035

R_1, wR_2 [I>2σ(I)]	0.0566, 0.1567
R_1, wR_2 [all data]	0.0633, 0.1638
Max./Mini. Peak / e Å^{-3}	1.33/–0.57

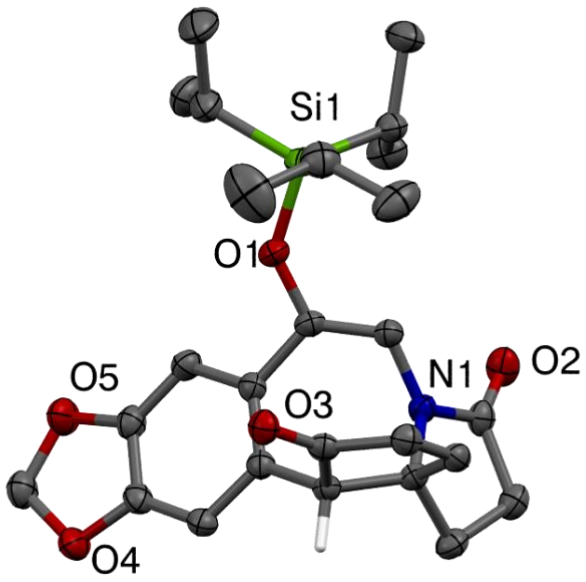


Figure S1. ORTEP drawing of **22** with 50% thermal ellipsoid. All hydrogen atoms expect benzyl H are omitted for clarity.

7. References

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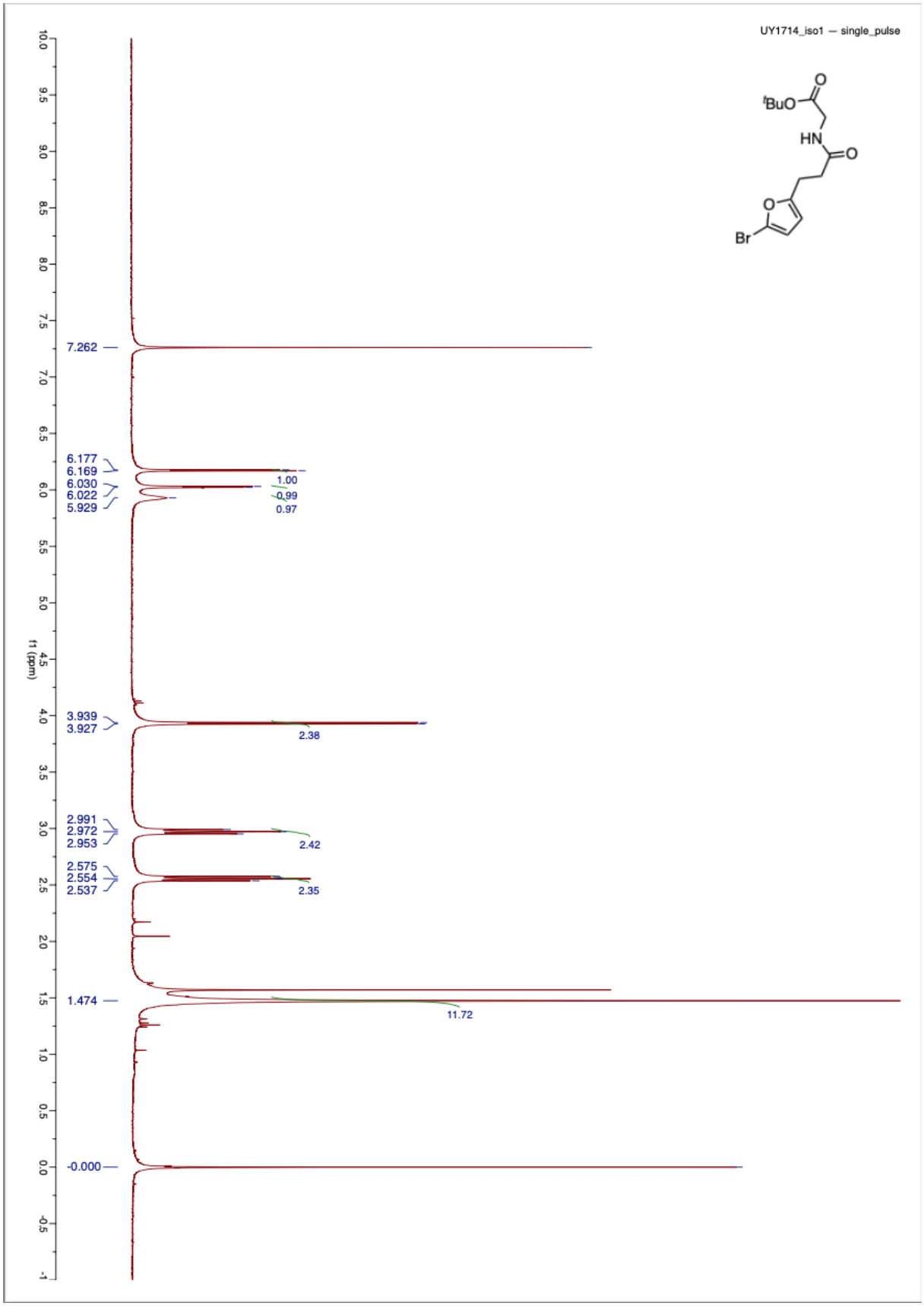
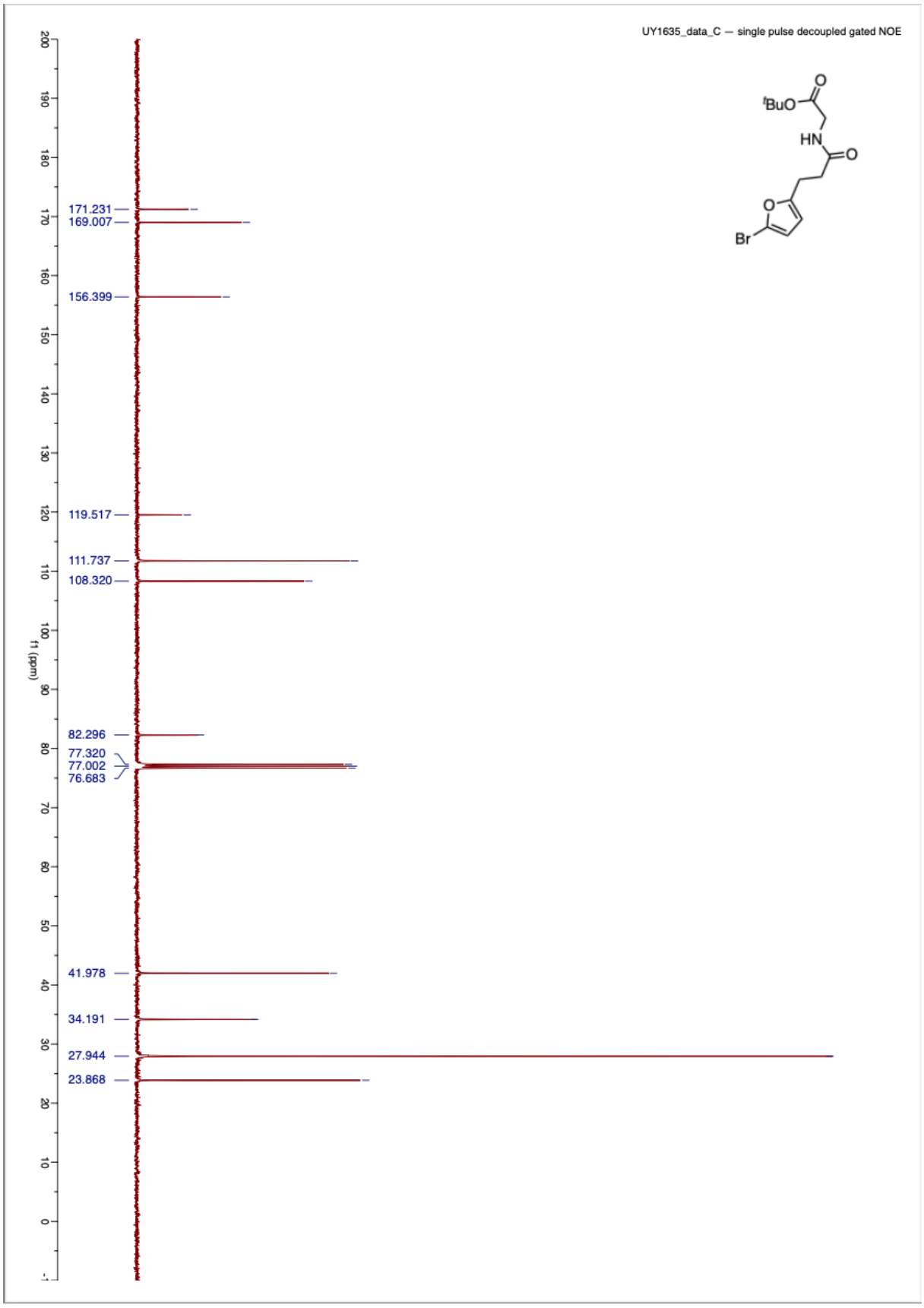
8. ^{1}H NMR, and ^{13}C NMR Spectra

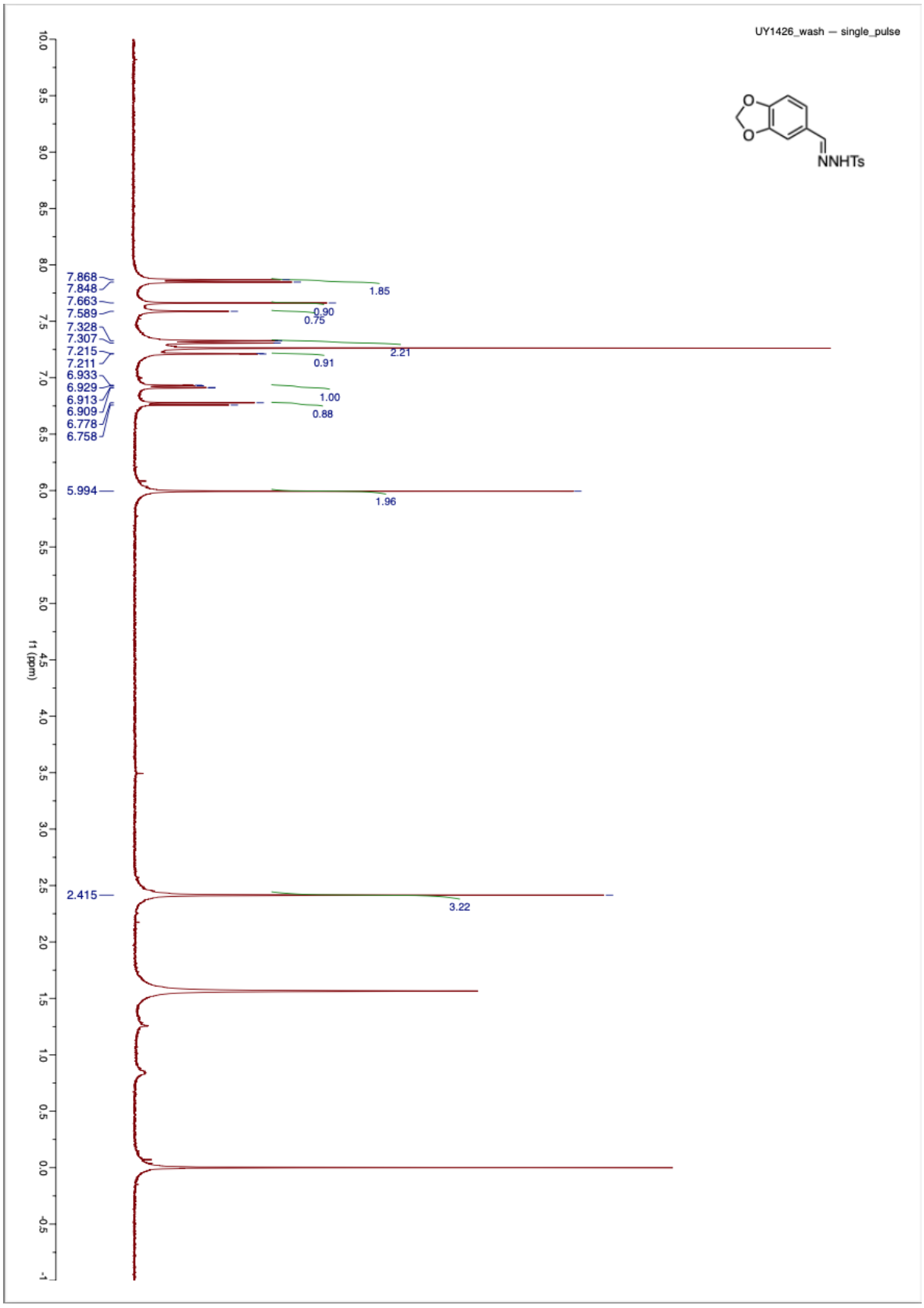
^{1}H NMR of 19 (400 MHz, $CDCl_3$)



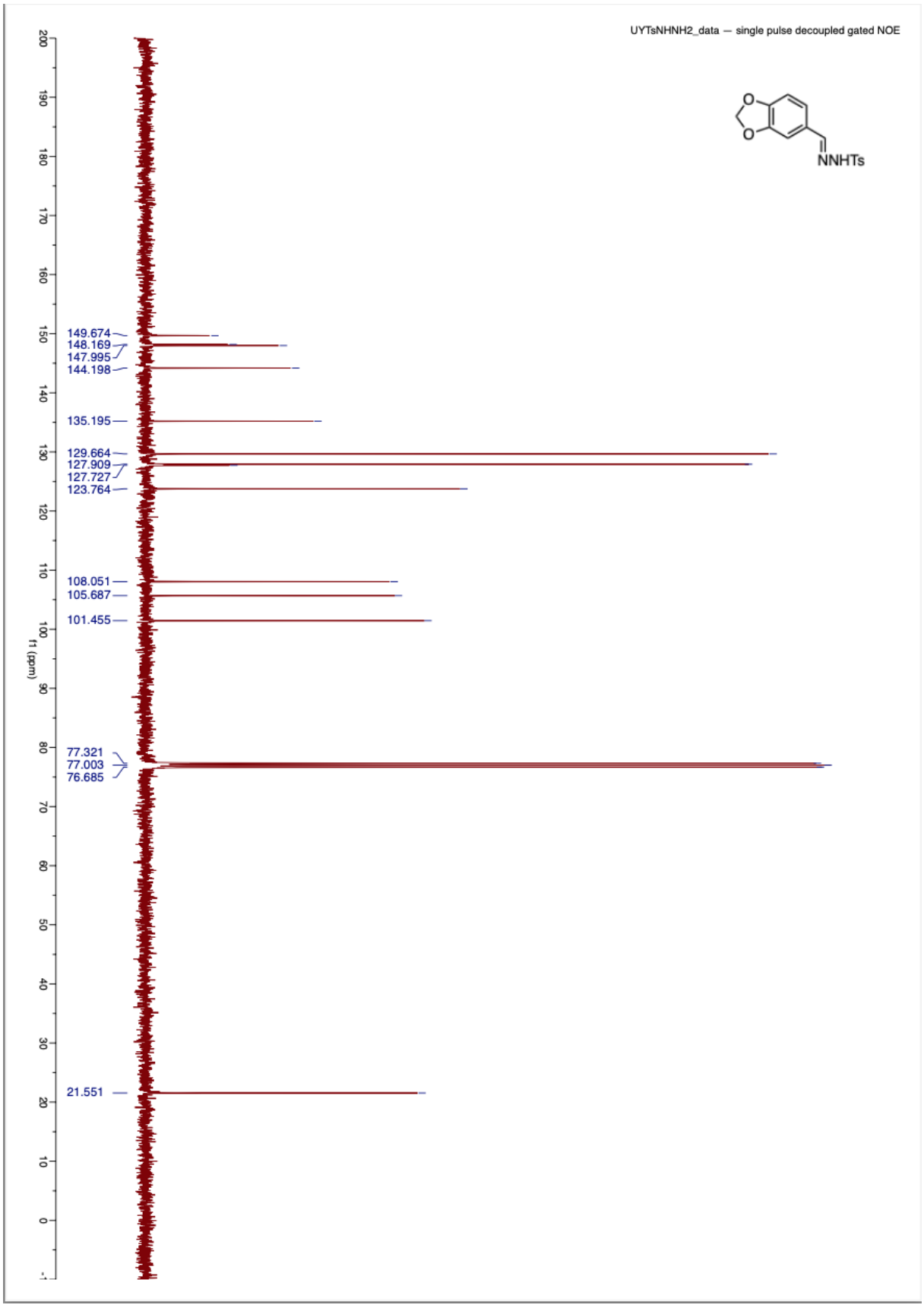
^{13}C NMR of 19 (101 MHz, $CDCl_3$)



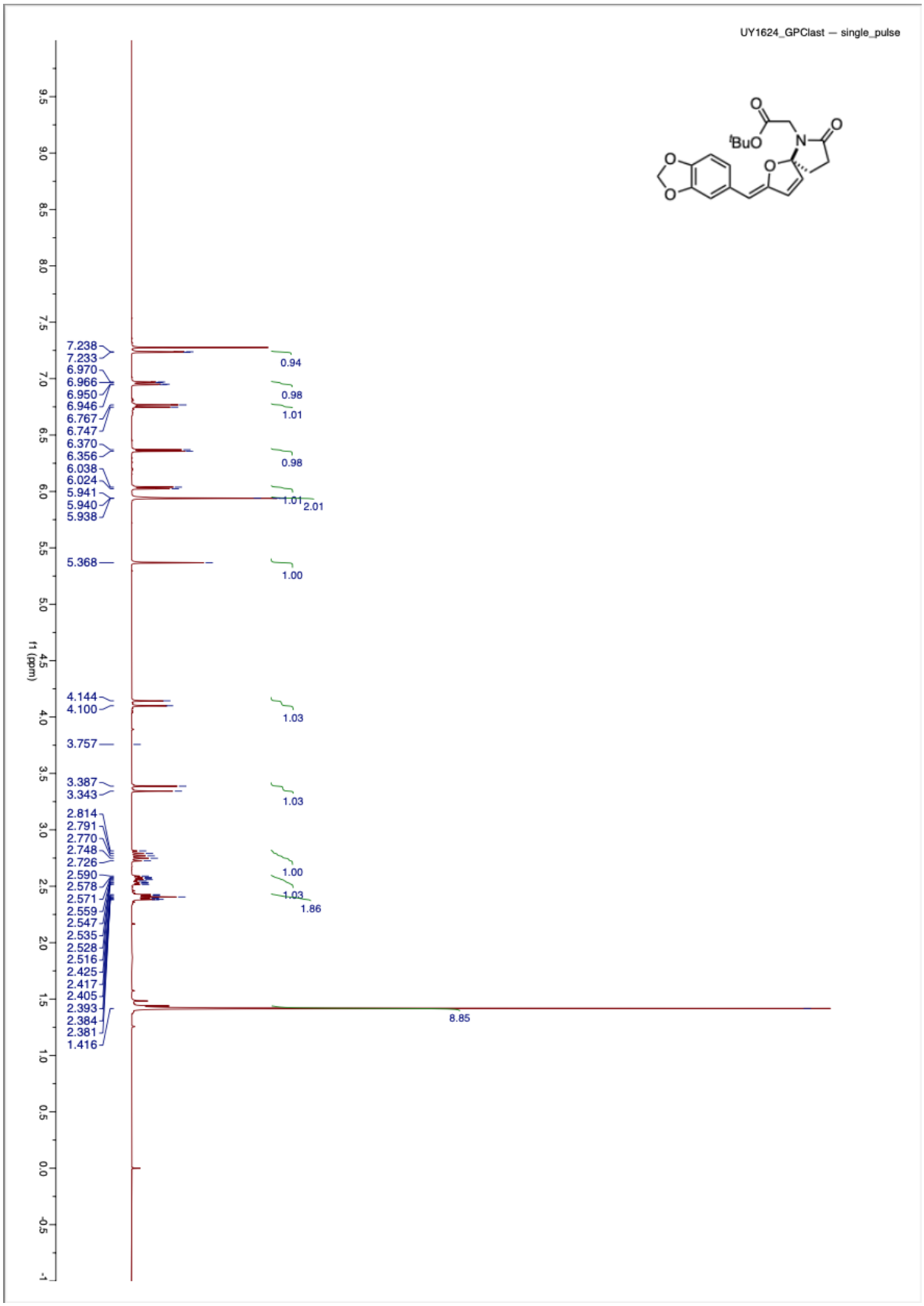
^{1}H NMR of 13 (400 MHz, $CDCl_3$)



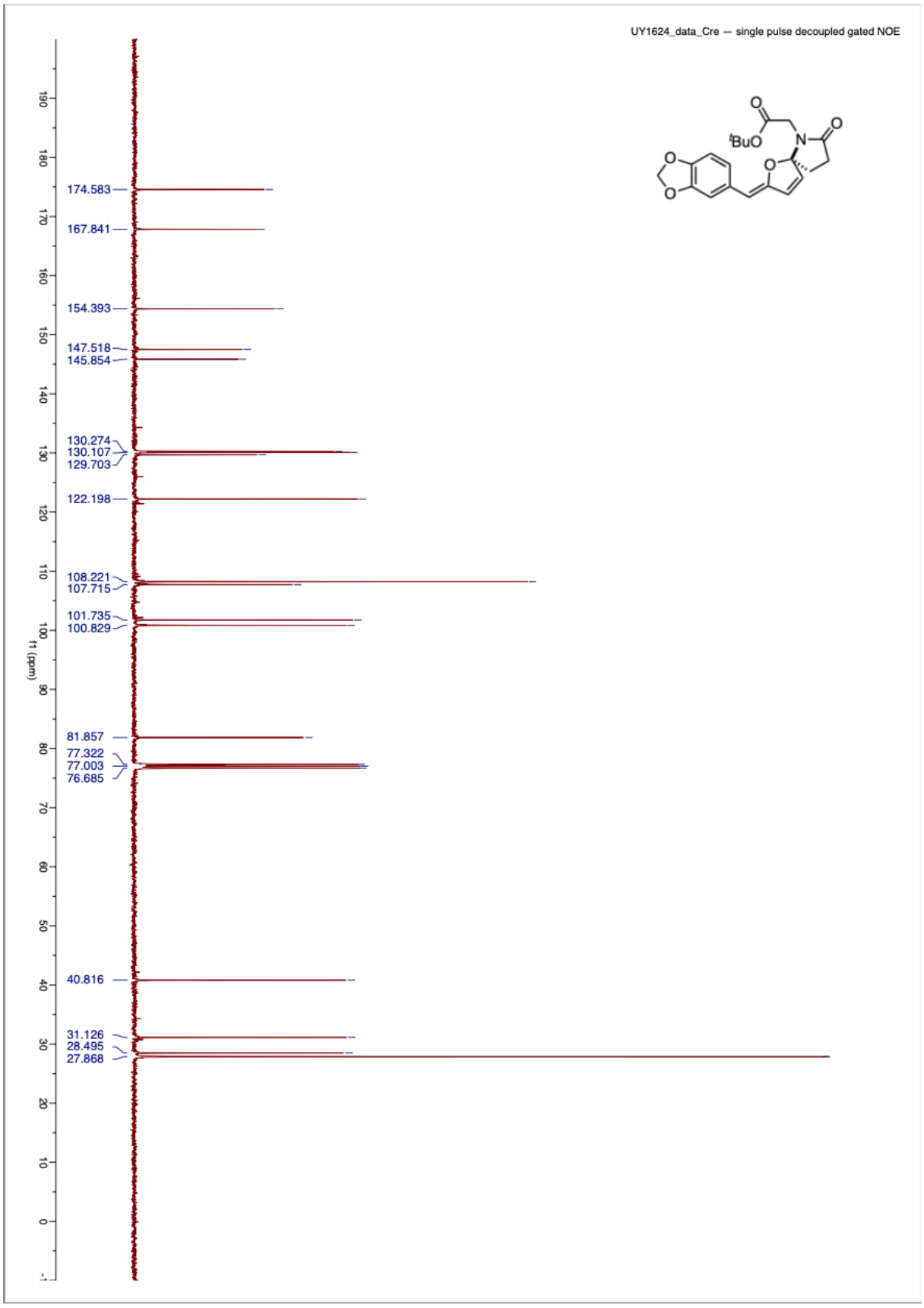
^{13}C NMR of 13 (101 MHz, $CDCl_3$)



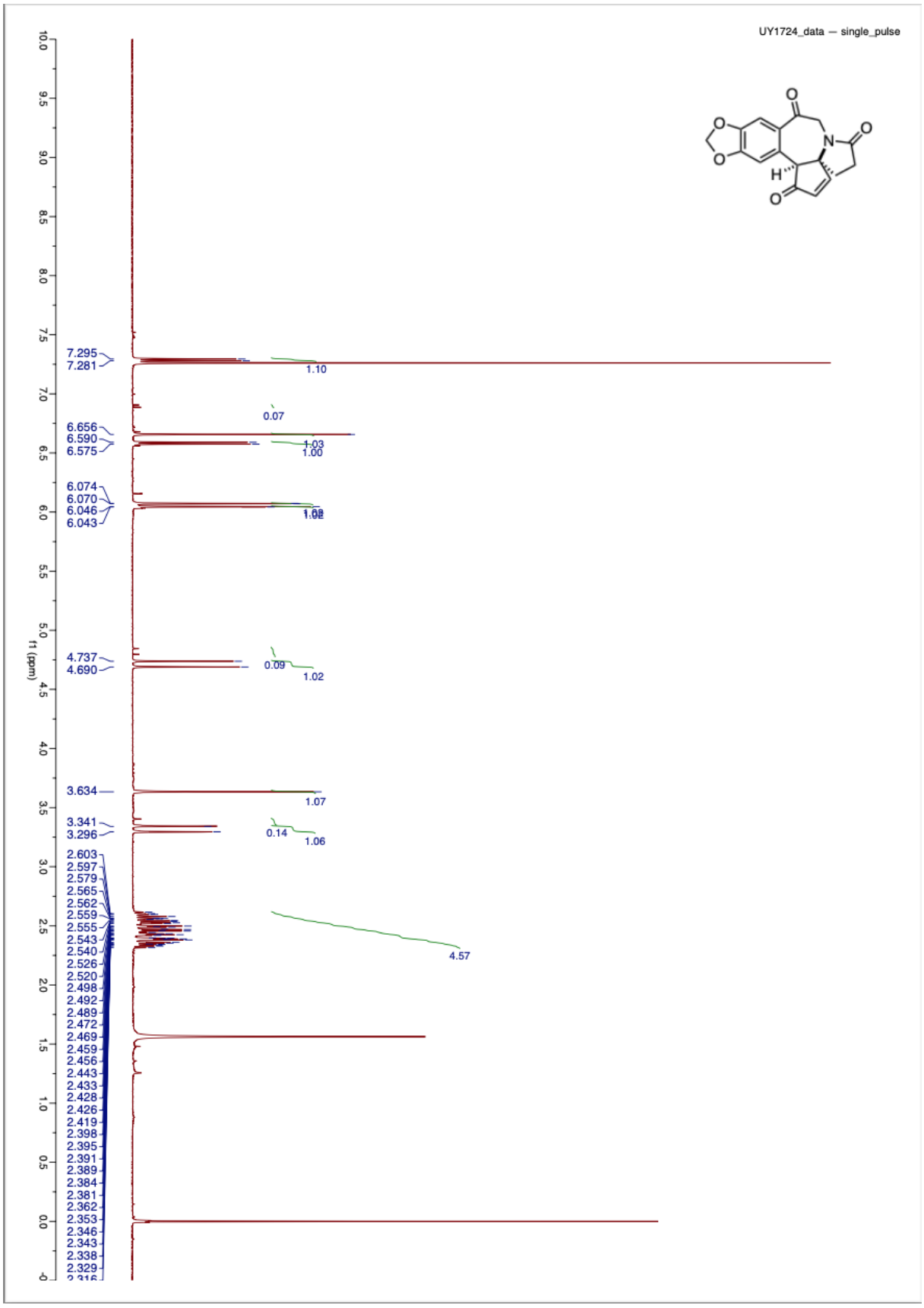
^{1}H NMR of *Z*-20 (400 MHz, $CDCl_3$)



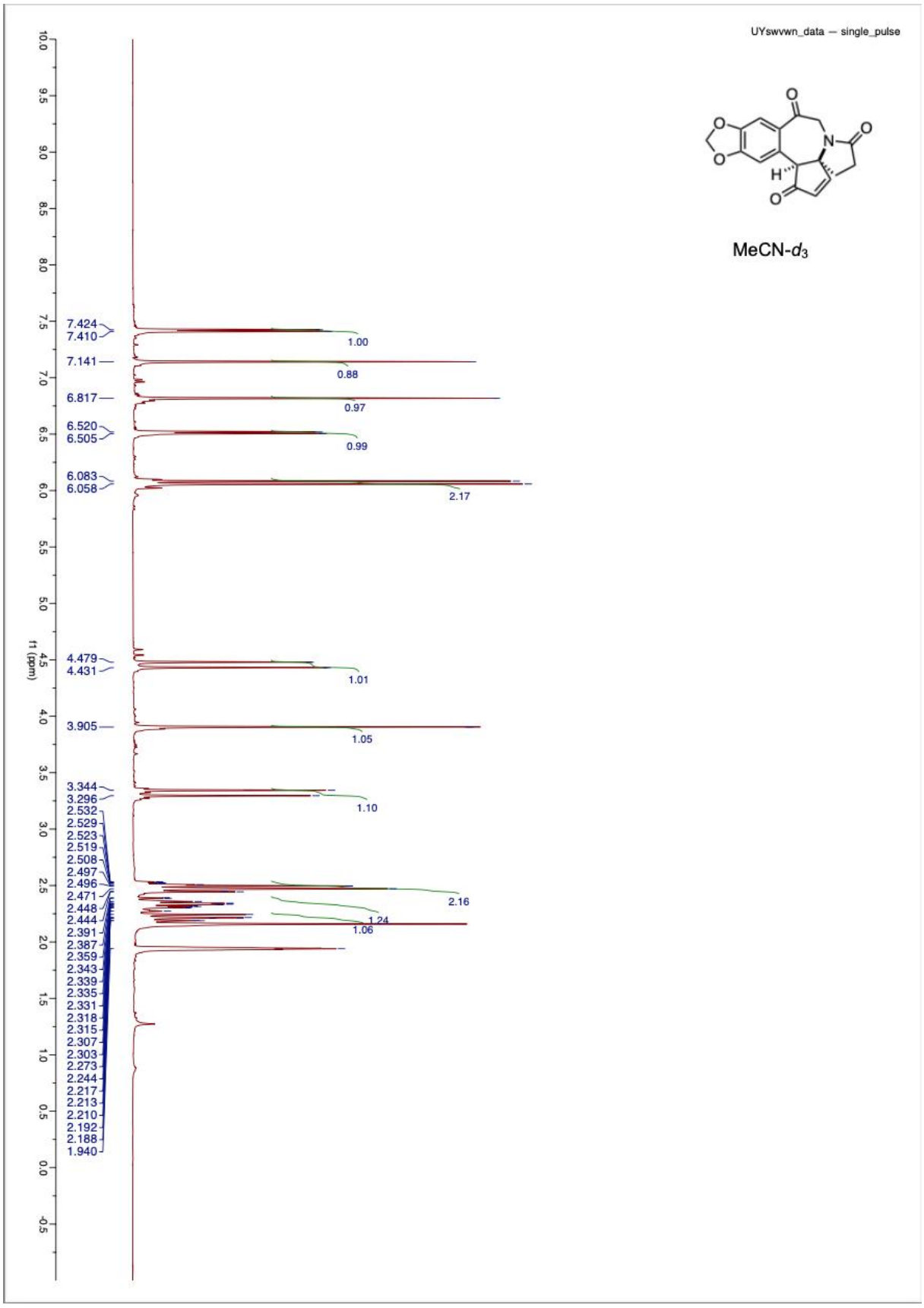
^{13}C NMR of *Z*-20 (101 MHz, $CDCl_3$)



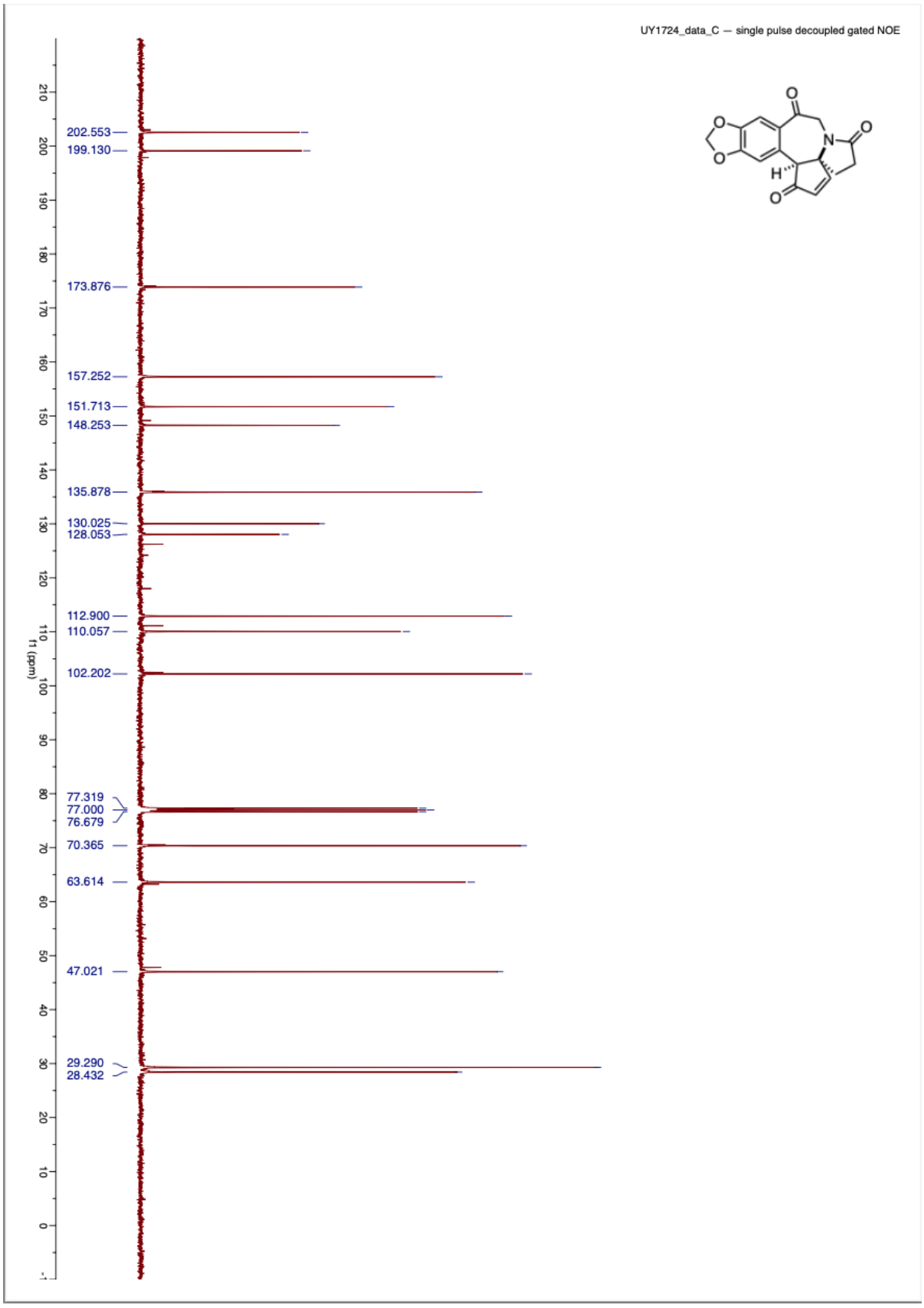
^{1}H NMR of 10 (400 MHz, $CDCl_3$)



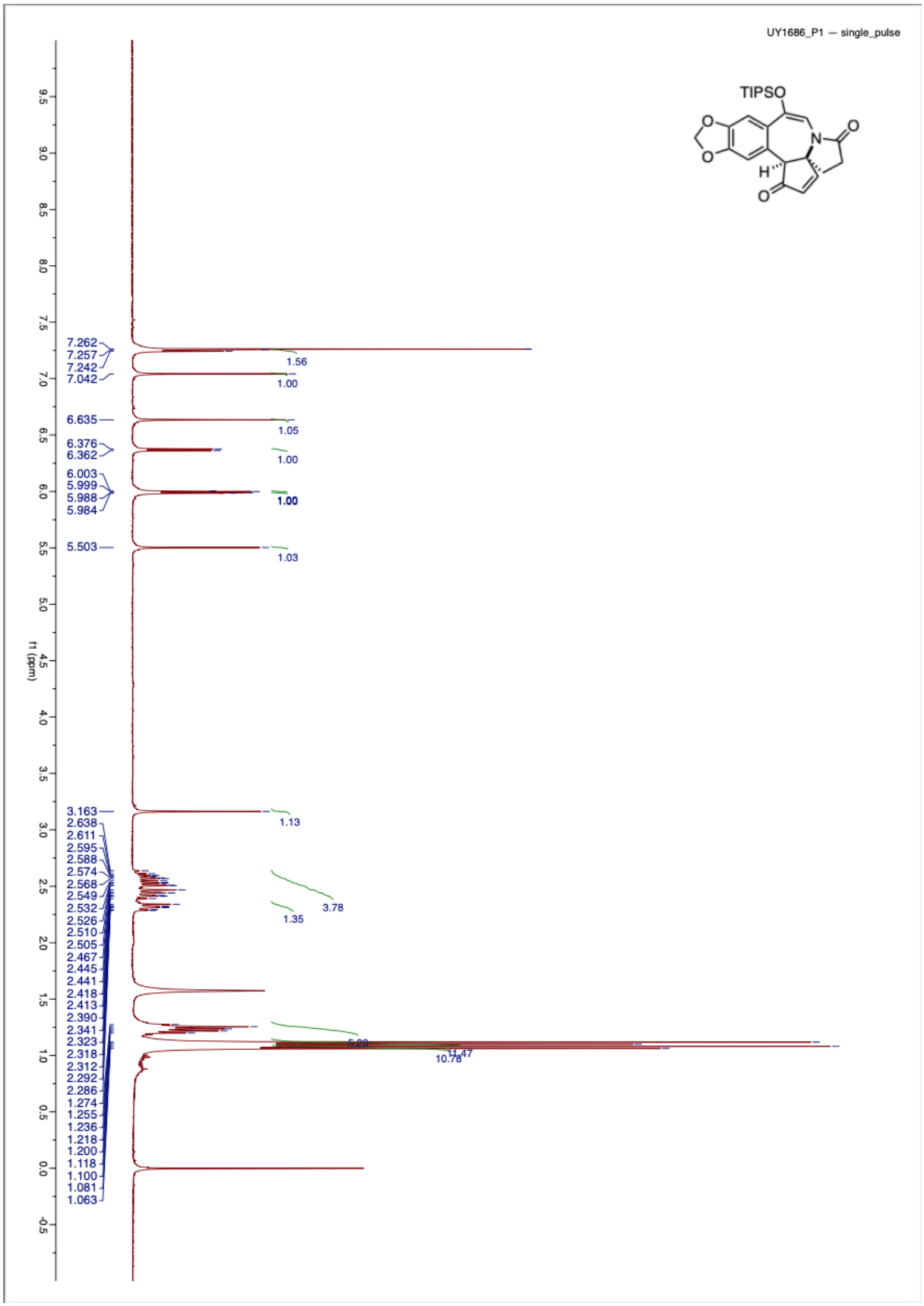
^{1}H NMR of 10 (400 MHz, MeCN-d_3)



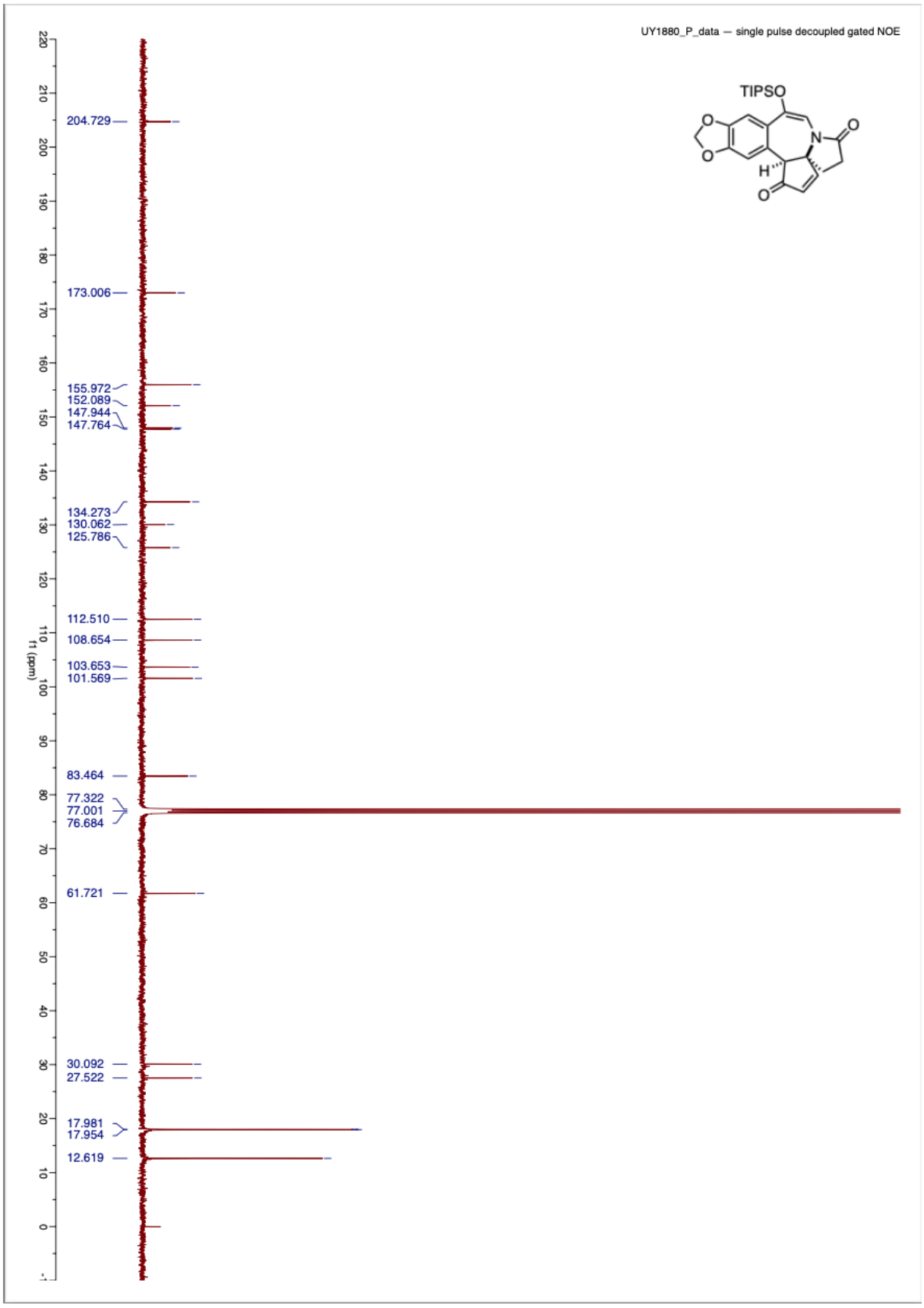
^{13}C NMR of 10 (101 MHz, $CDCl_3$)



^{1}H NMR of 22 (400 MHz, $CDCl_3$)



^{13}C NMR of 22 (101 MHz, $CDCl_3$)



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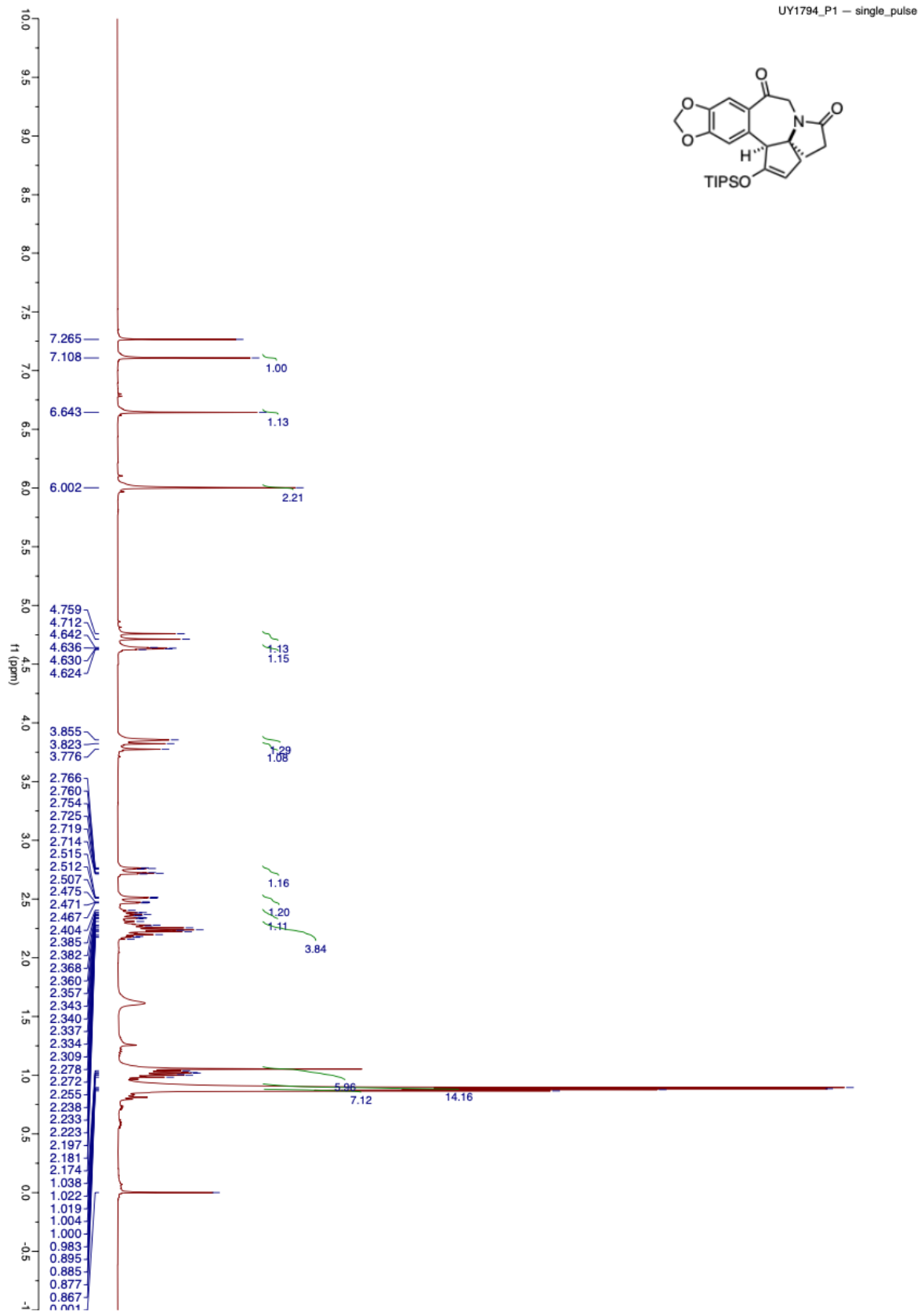

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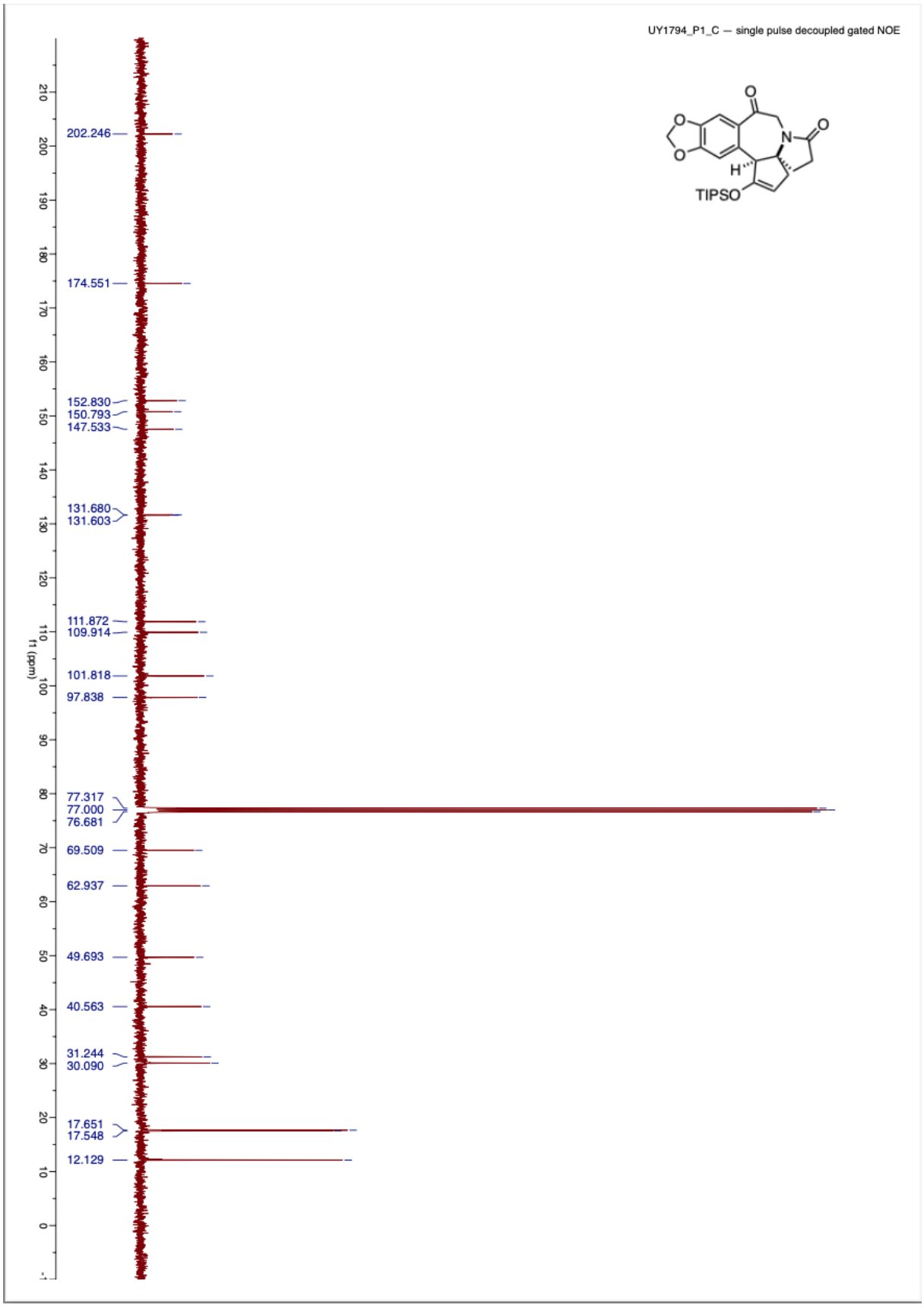
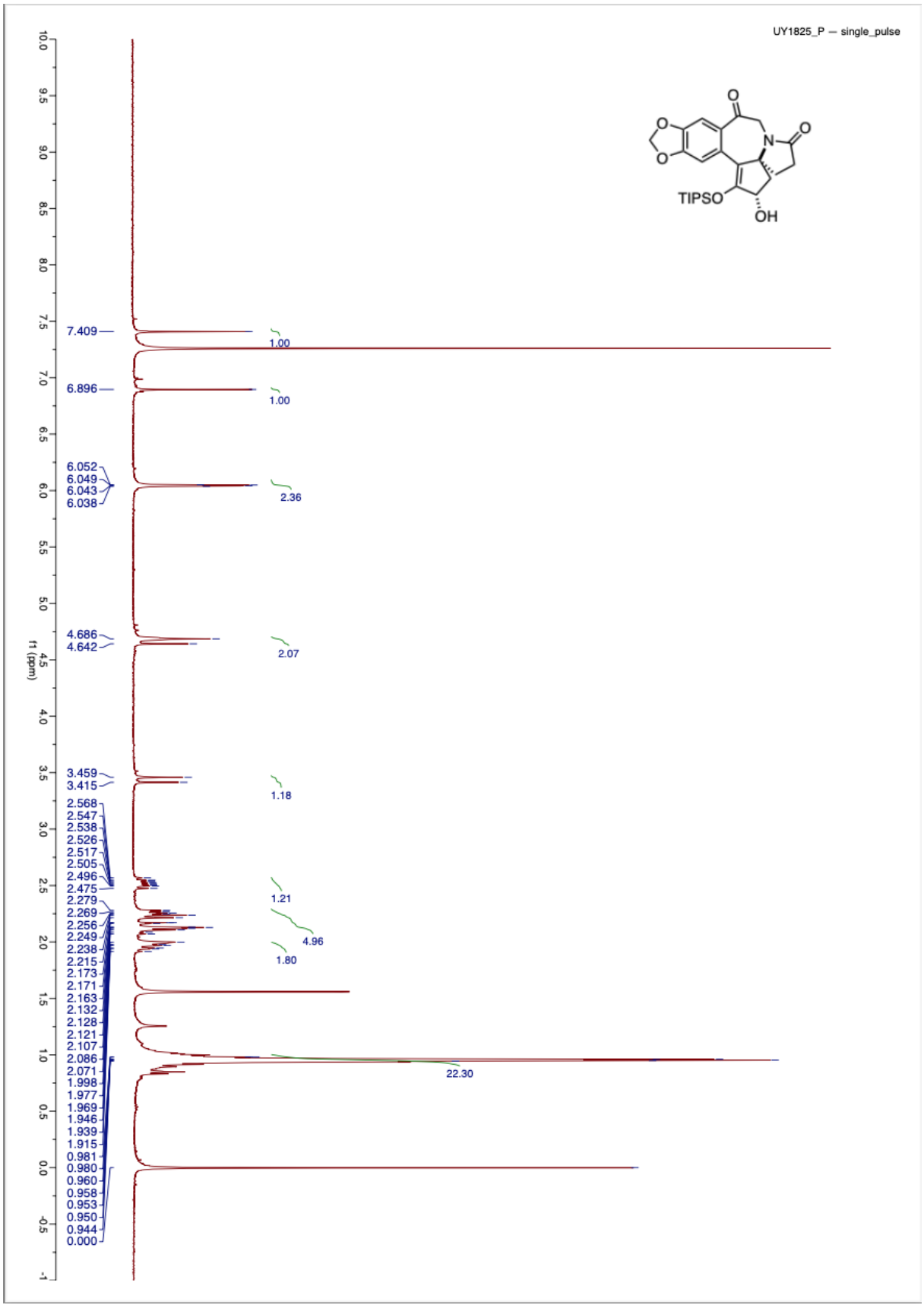
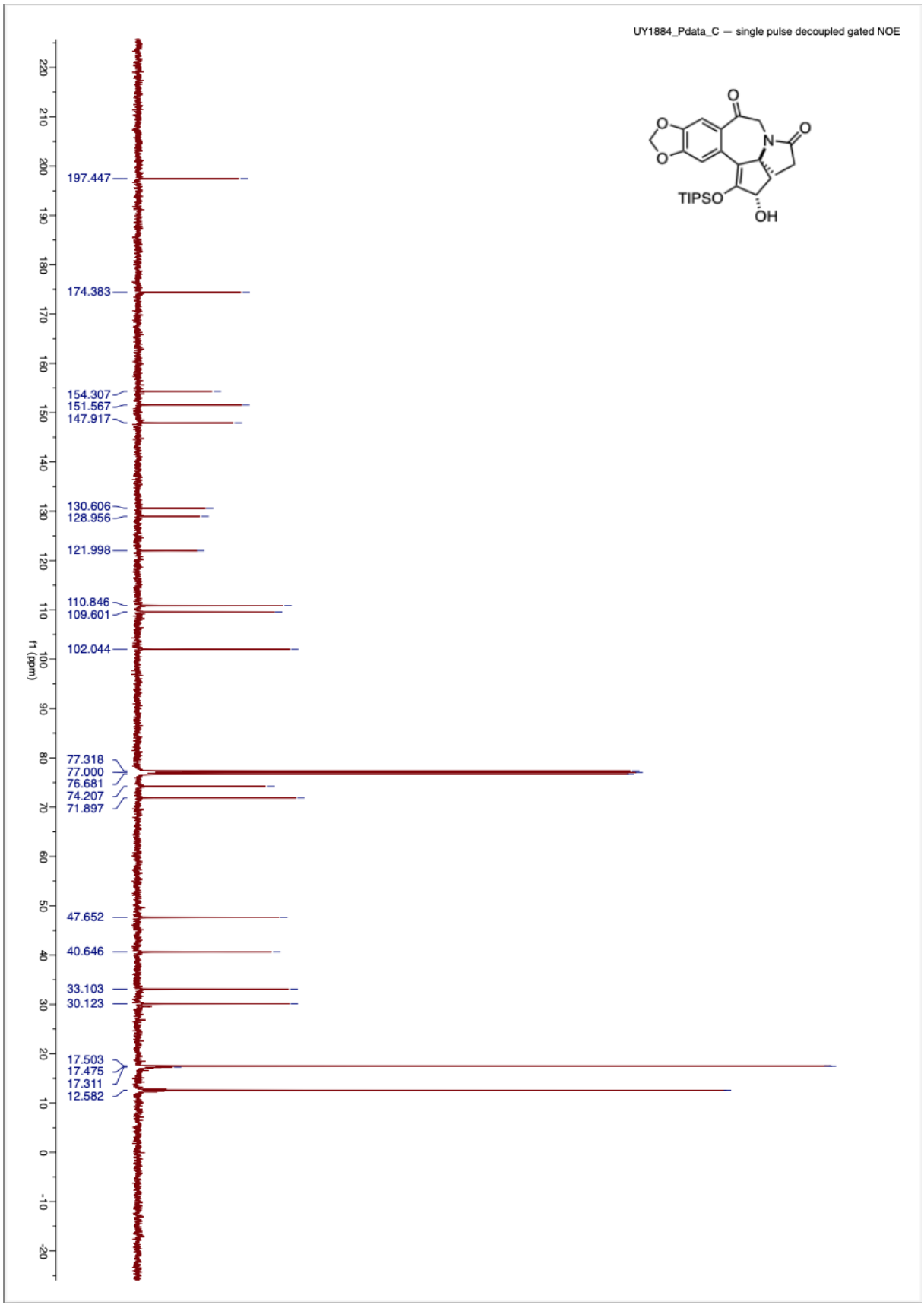


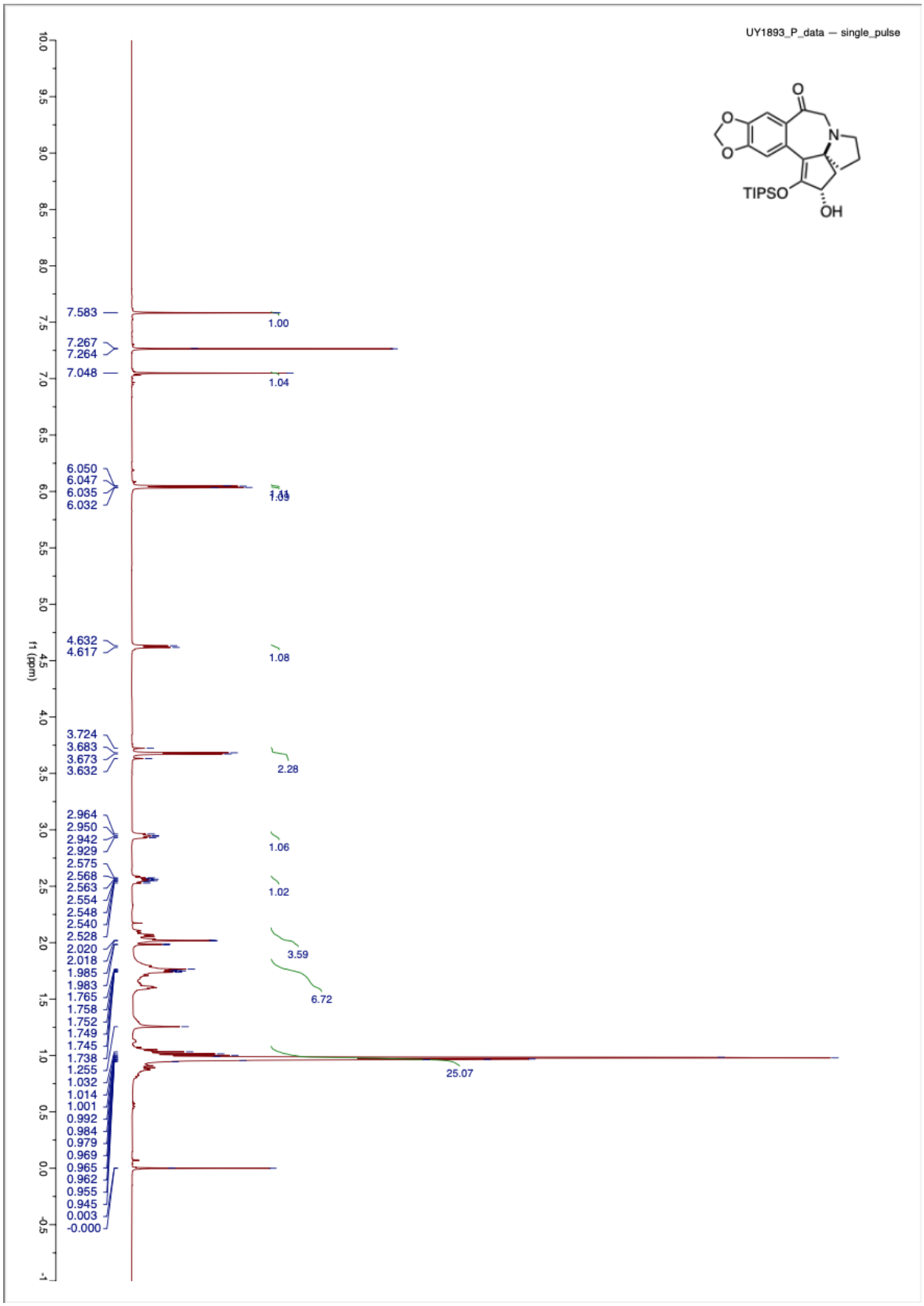
^{1}H NMR of 24 (400 MHz, $CDCl_3$)



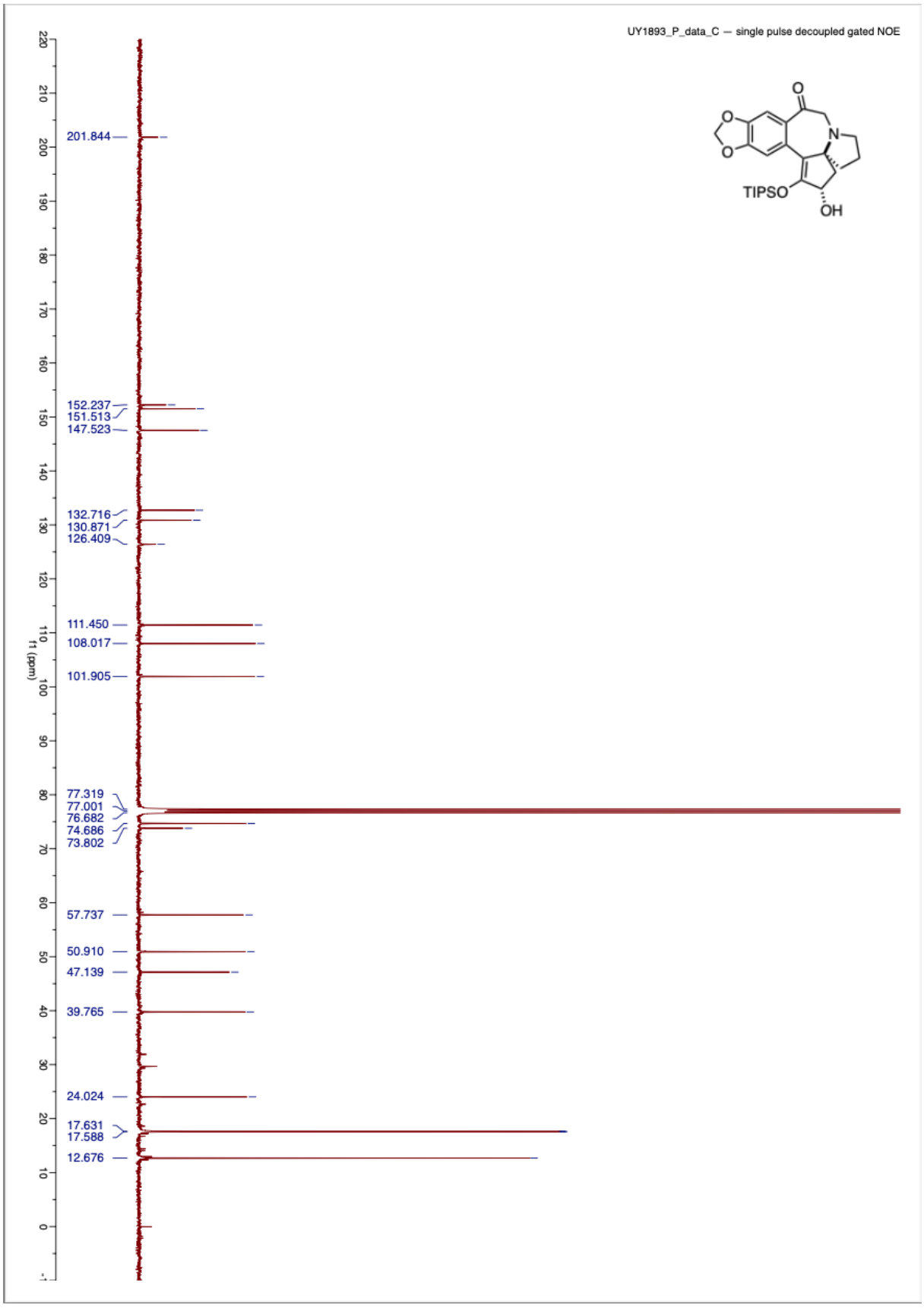
^{13}C NMR of 24 (101 MHz, $CDCl_3$)



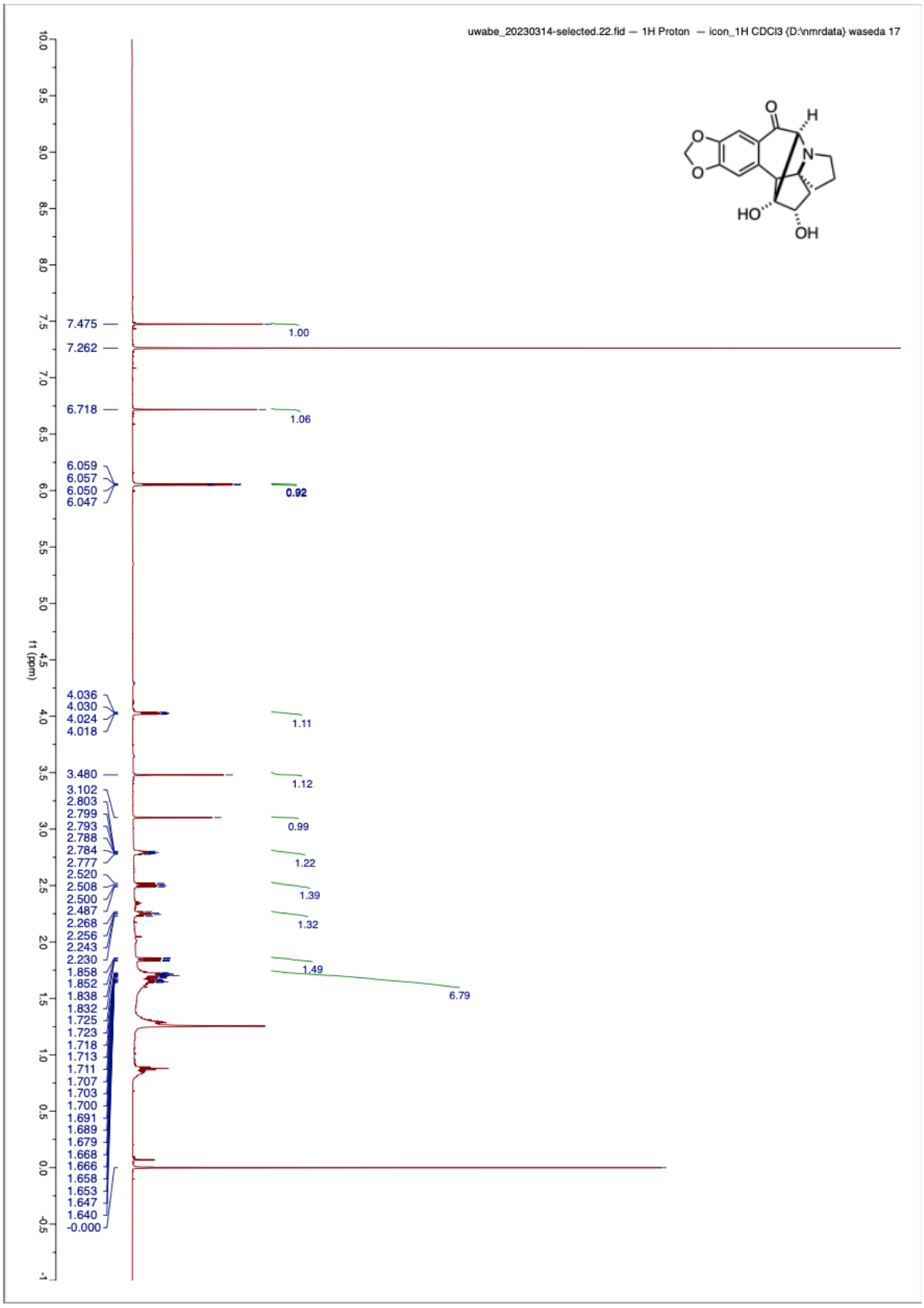
^{1}H NMR of 25 (400 MHz, $CDCl_3$)



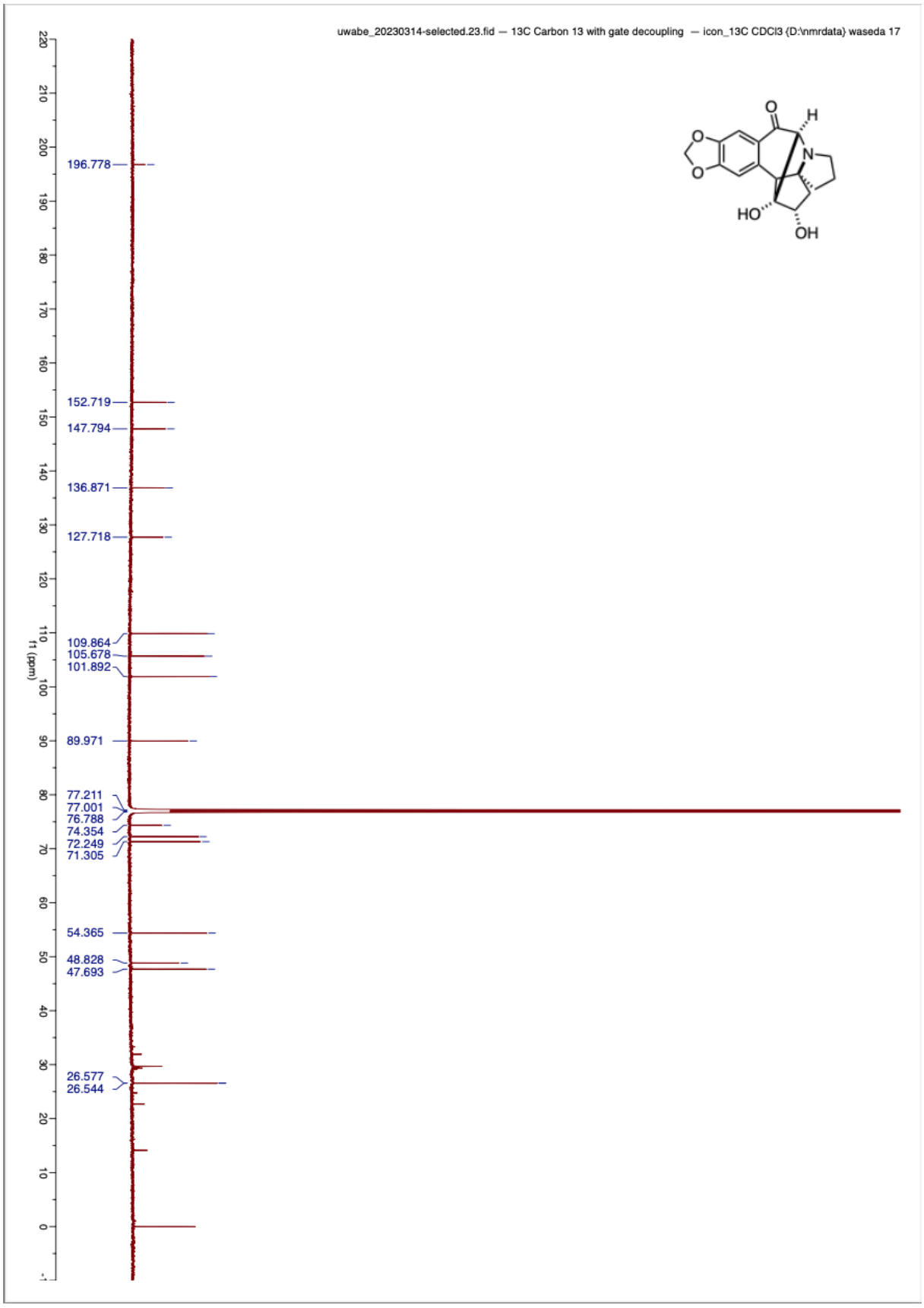
^{13}C NMR of 25 (101 MHz, $CDCl_3$)



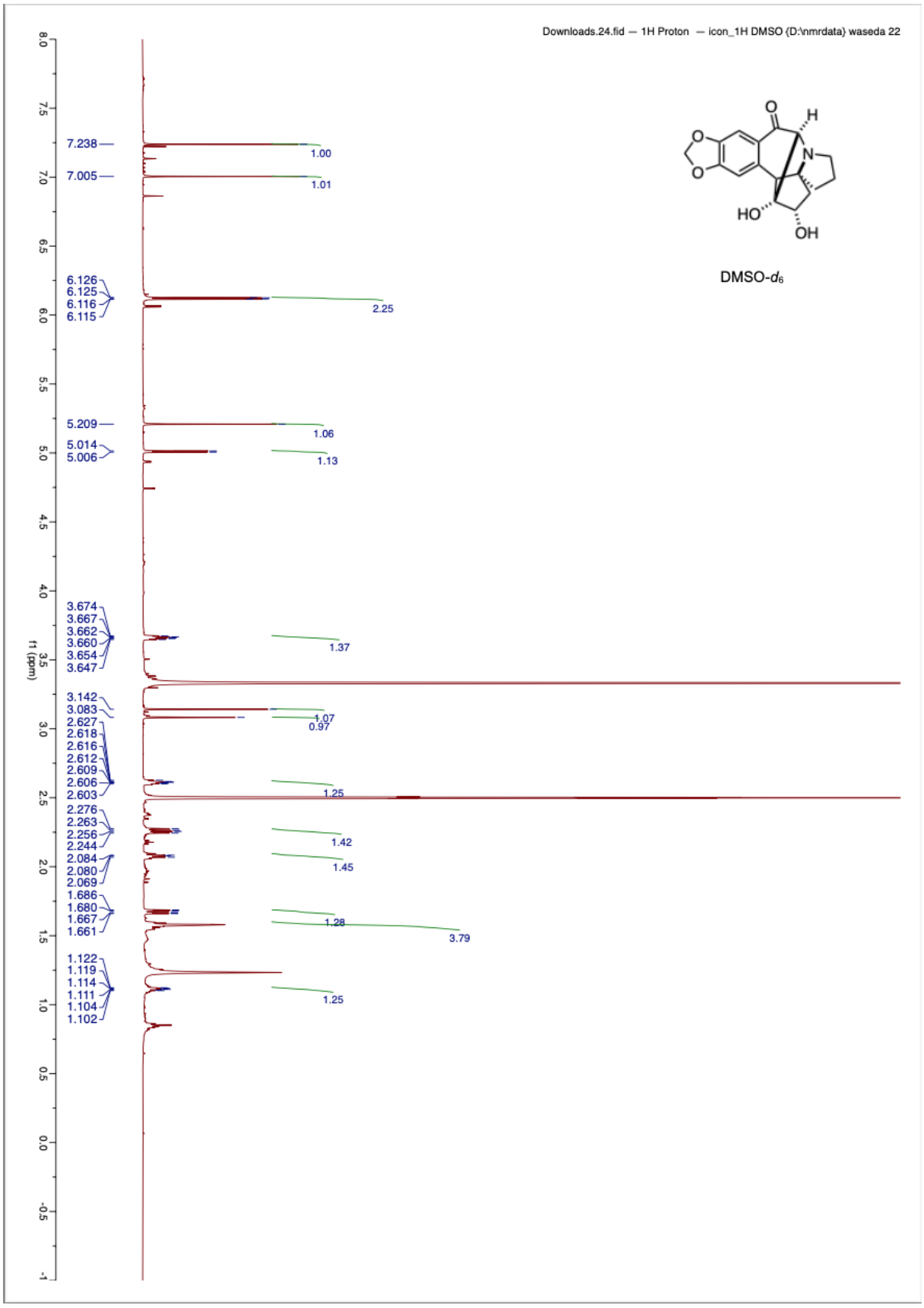
^{1}H NMR of fortuneicyclidin A (5) (400 MHz, $CDCl_3$)



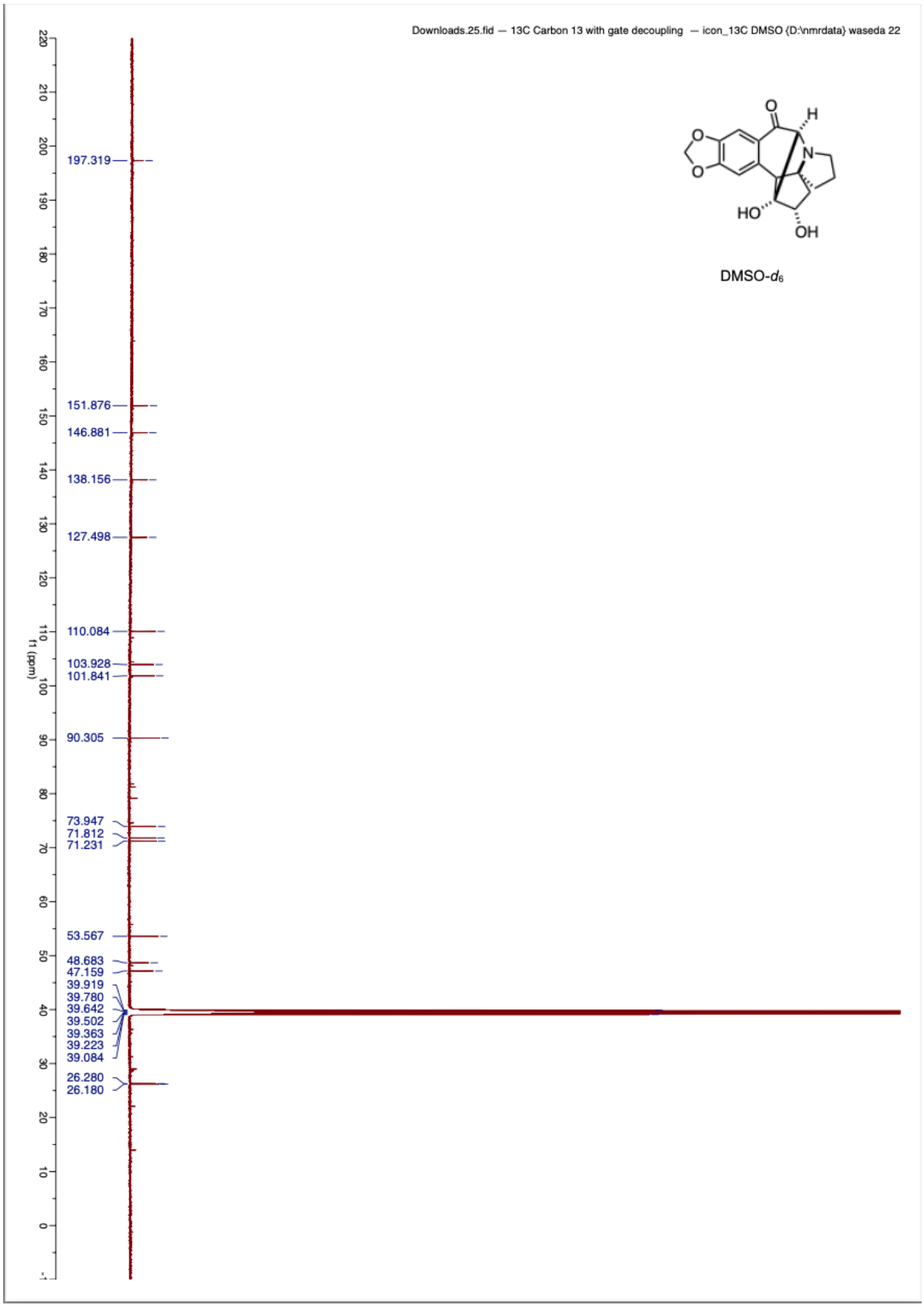
^{13}C NMR of fortuneicyclidin A (5) (101 MHz, $CDCl_3$)



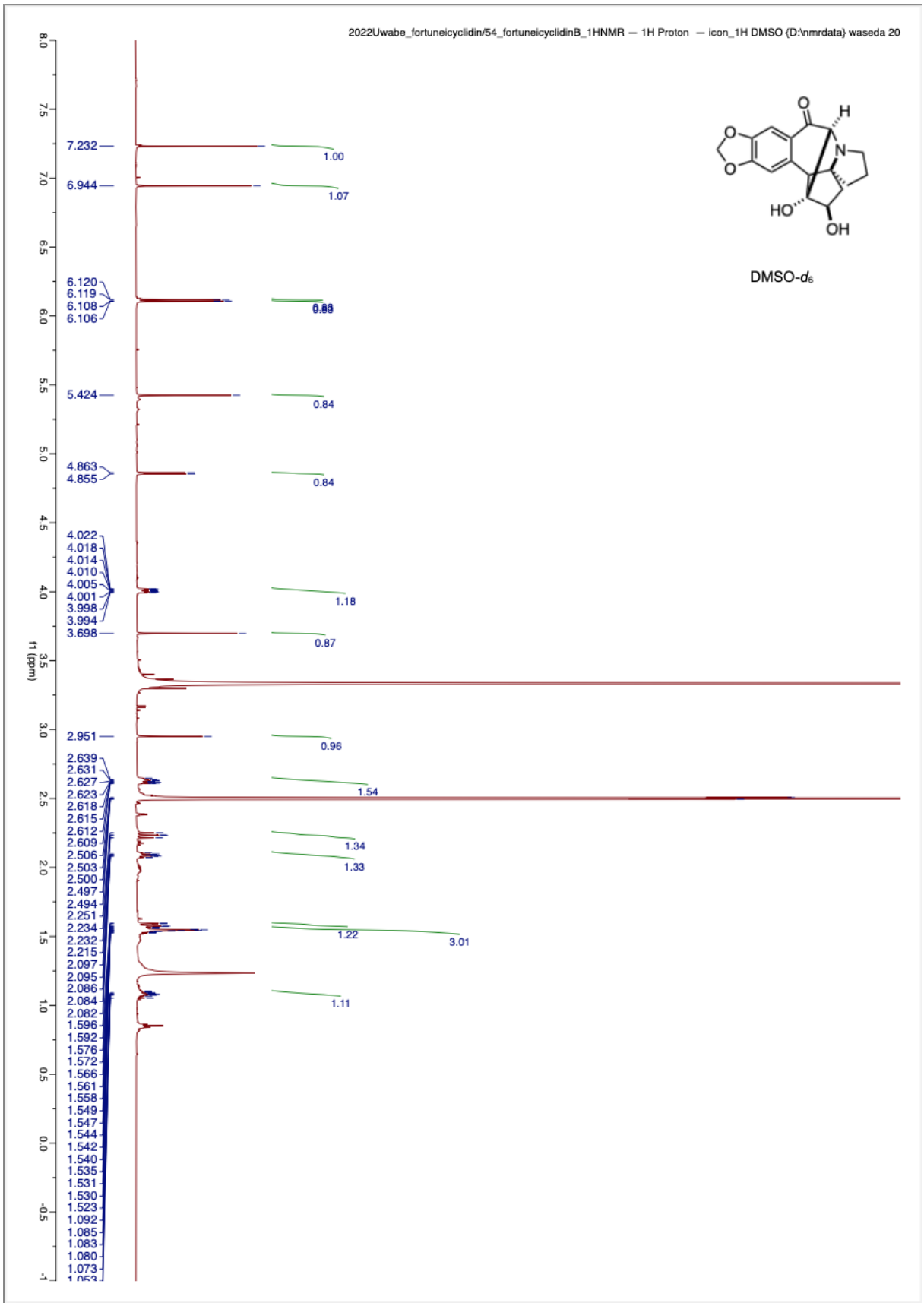
^{1}H NMR of fortuneicyclidin A (5) (600 MHz, DMSO-d_6)



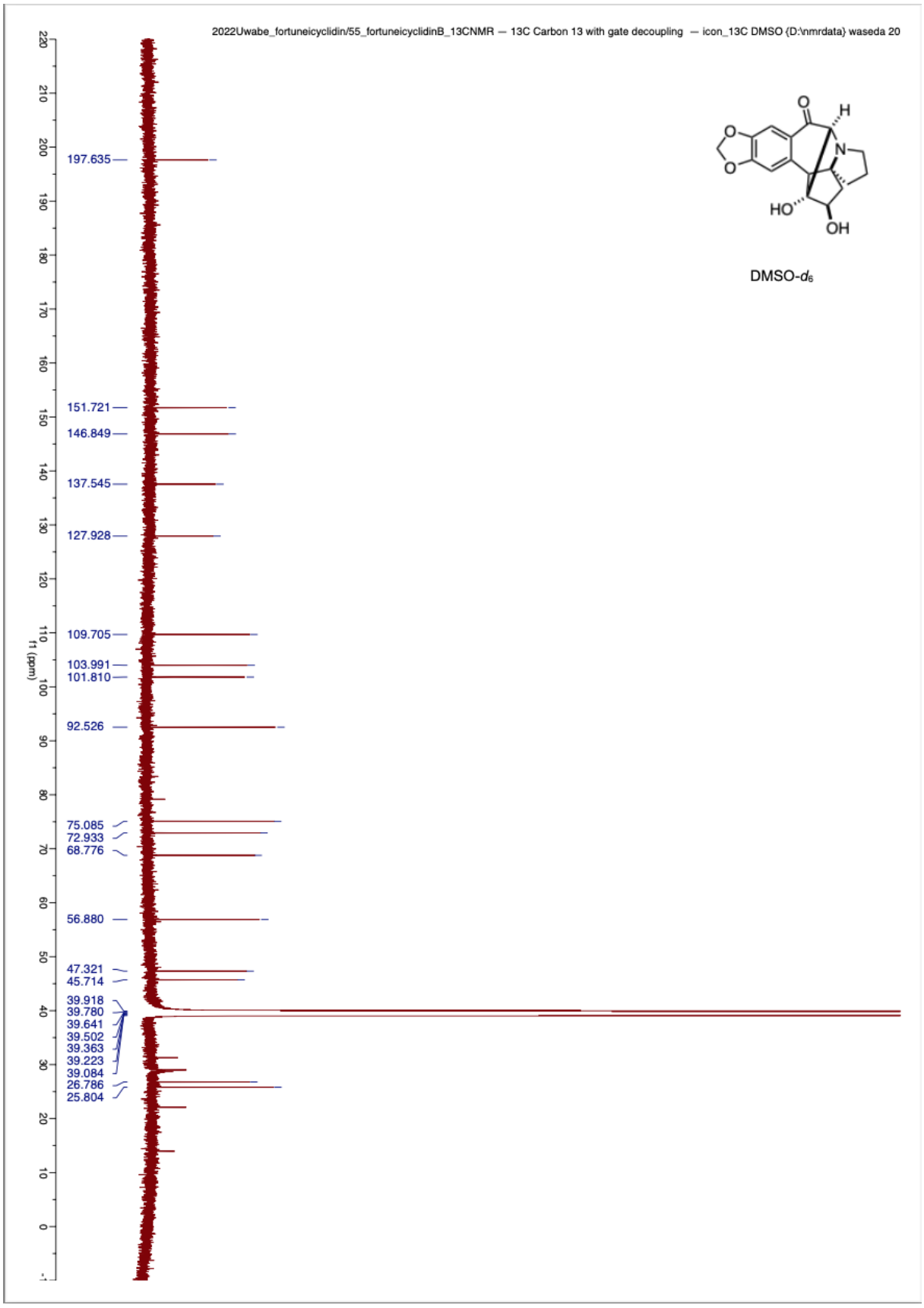
^{13}C NMR of fortuneicyclidin A (5) (151 MHz, DMSO-d_6)



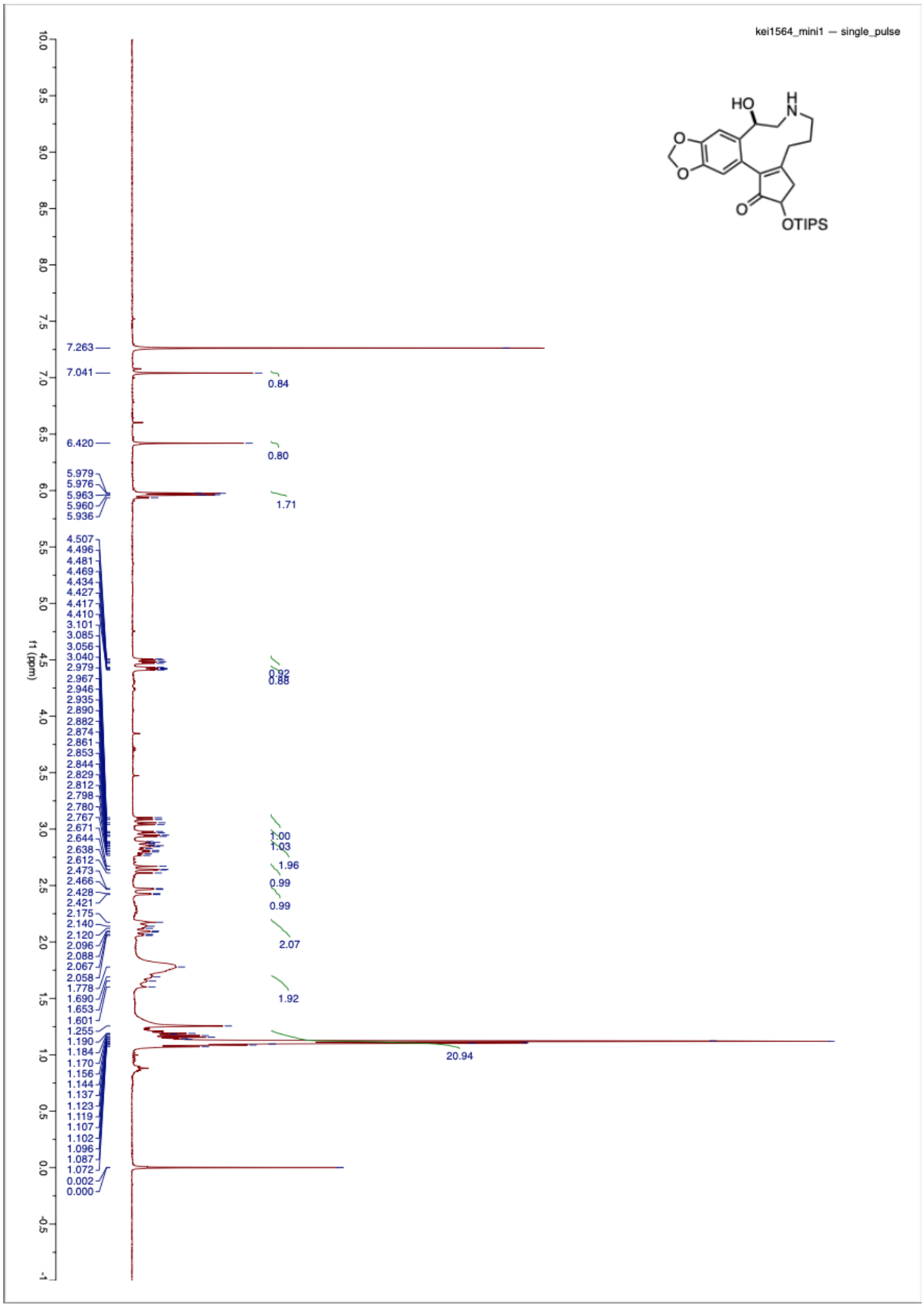
^{1}H NMR of fortuneicyclidin B (6) (600 MHz, DMSO-d_6)



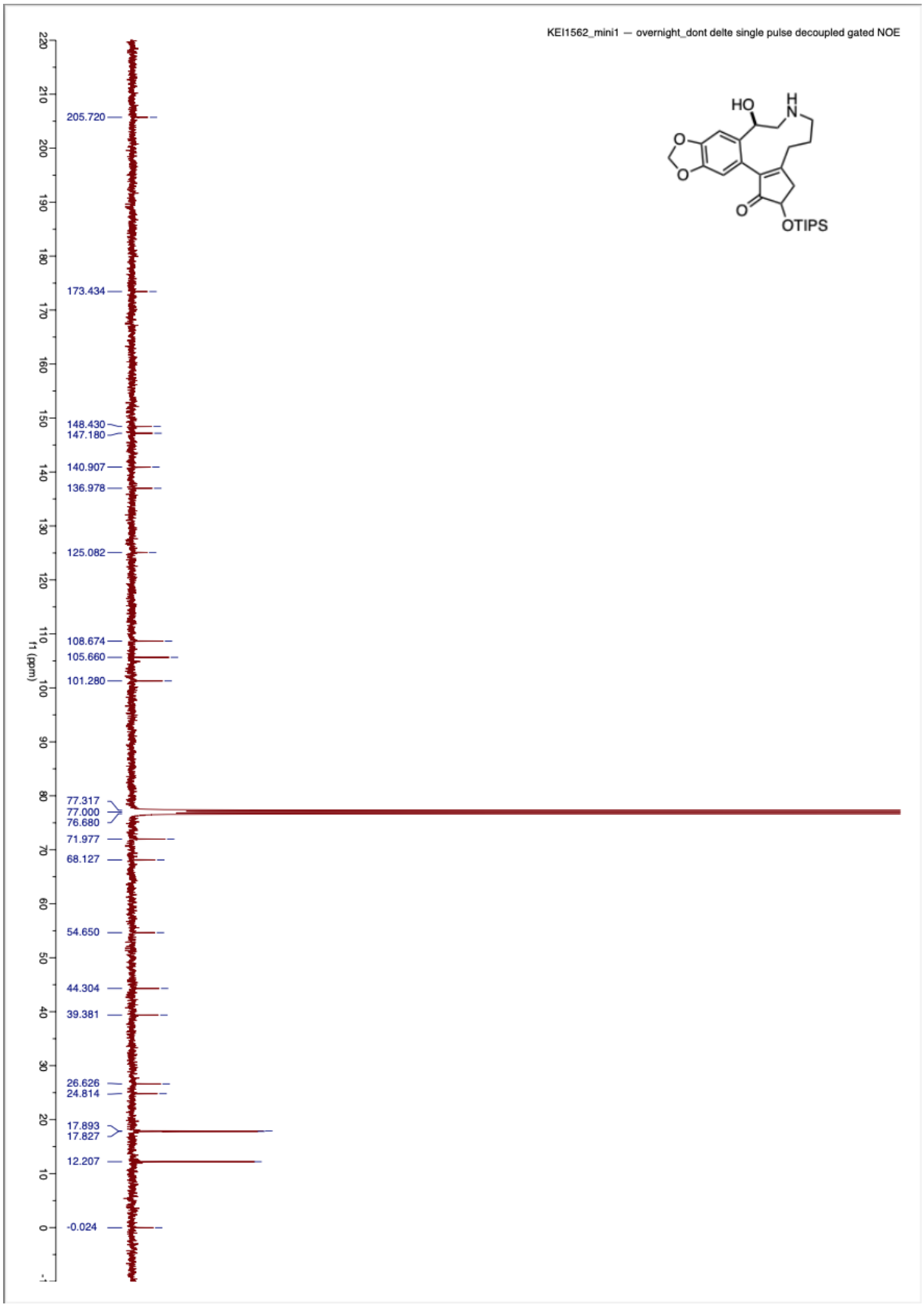
^{13}C NMR of fortuneicyclidin B (6) (151 MHz, DMSO-d_6)



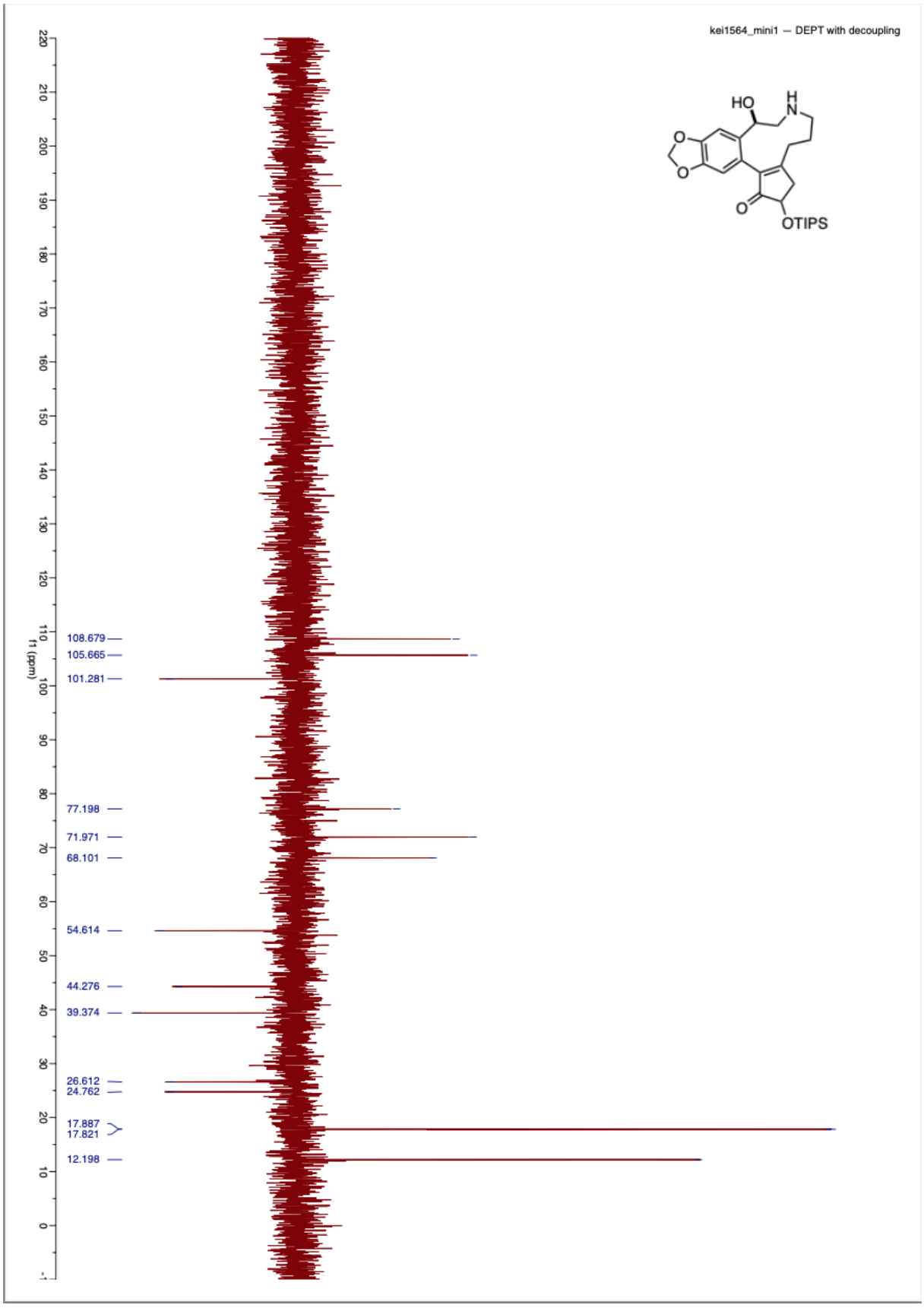
^{1}H NMR of 26 (400 MHz, $CDCl_3$)



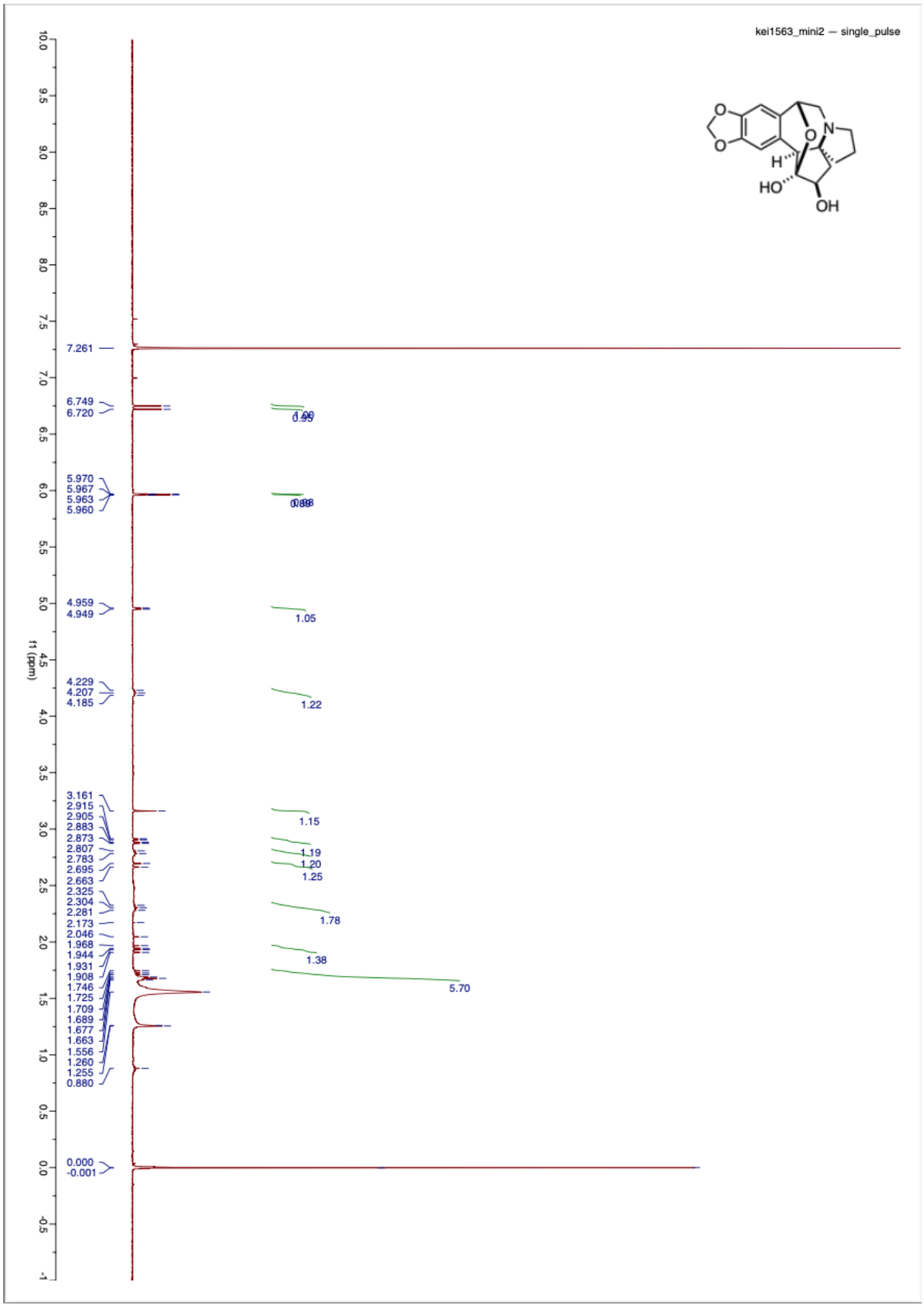
^{13}C NMR of 26 (101 MHz, $CDCl_3$)



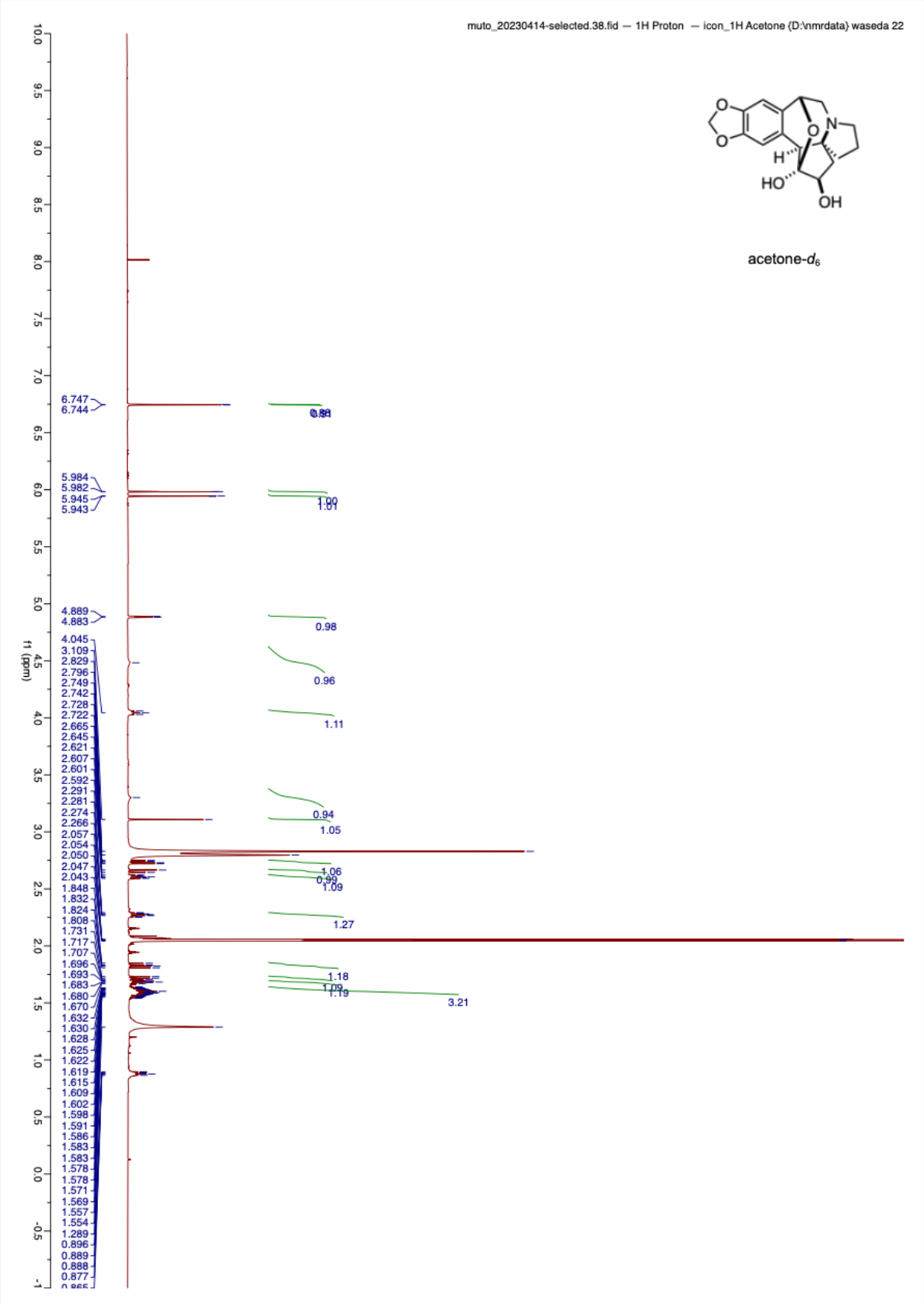
DEPT135 of 26 (101 MHz, $CDCl_3$)



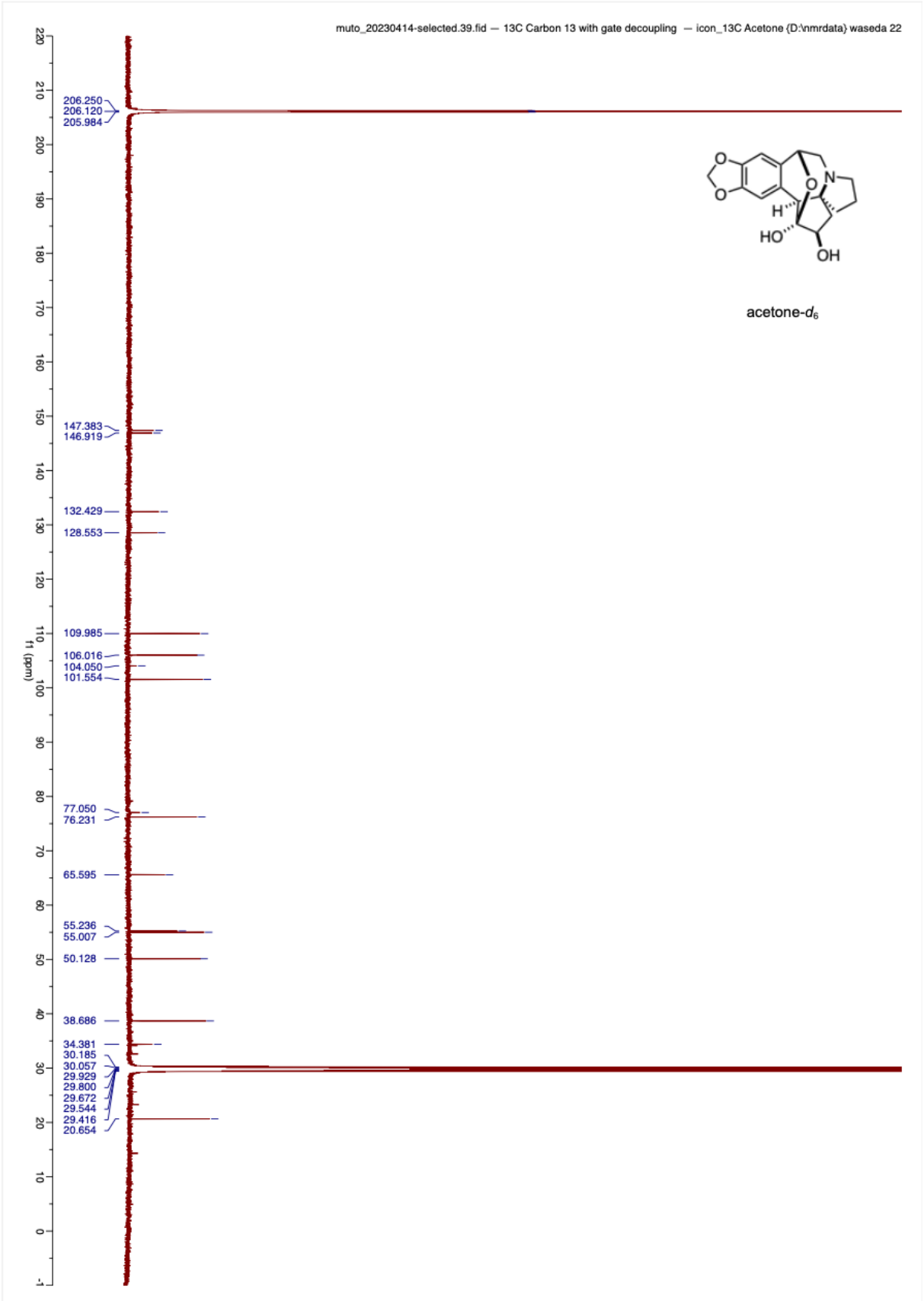
^{1}H NMR of cephalotine B (8) (400 MHz, $CDCl_3$)



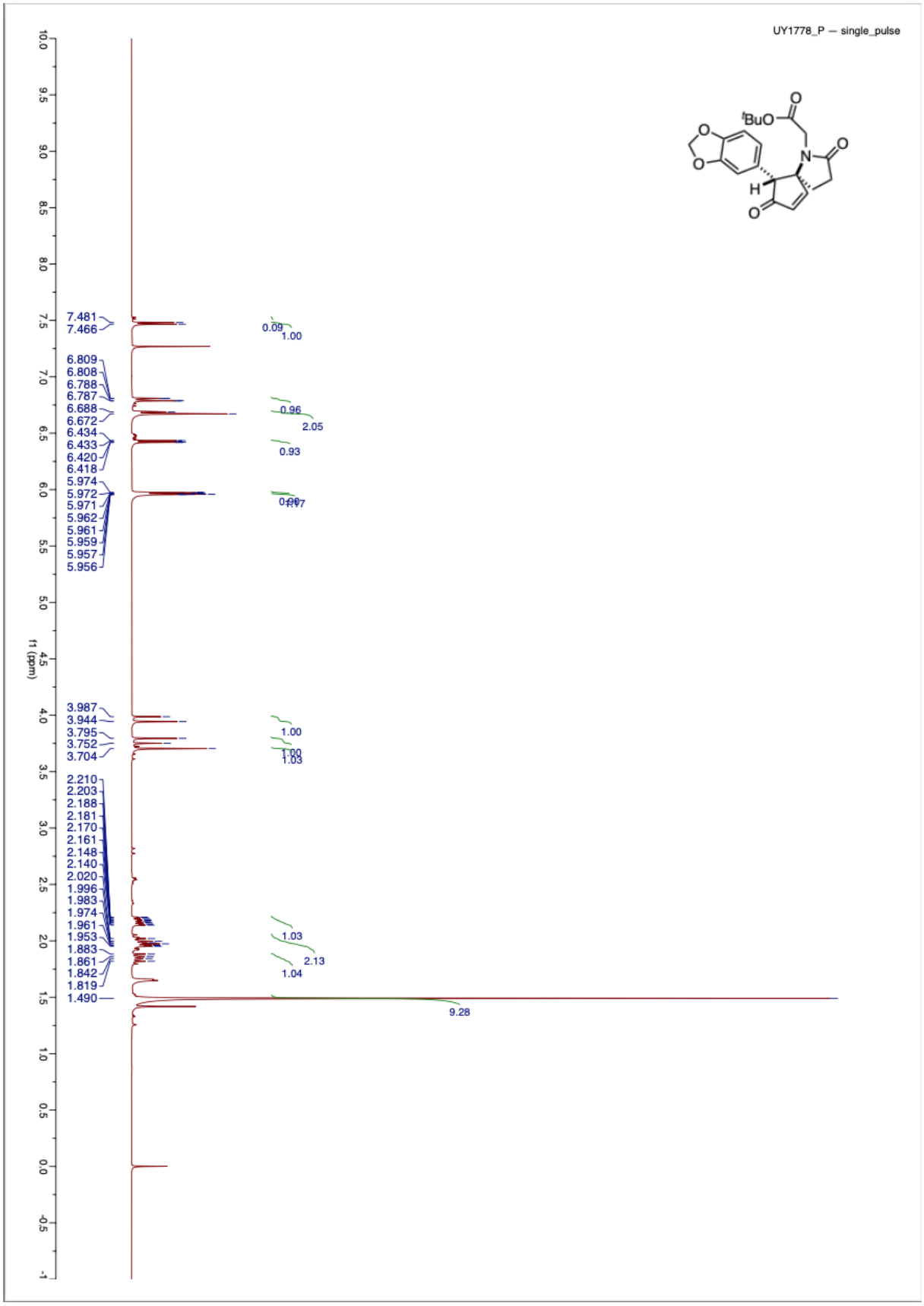
^{1}H NMR of cephalotine B (8) (400 MHz, acetone-d_6)



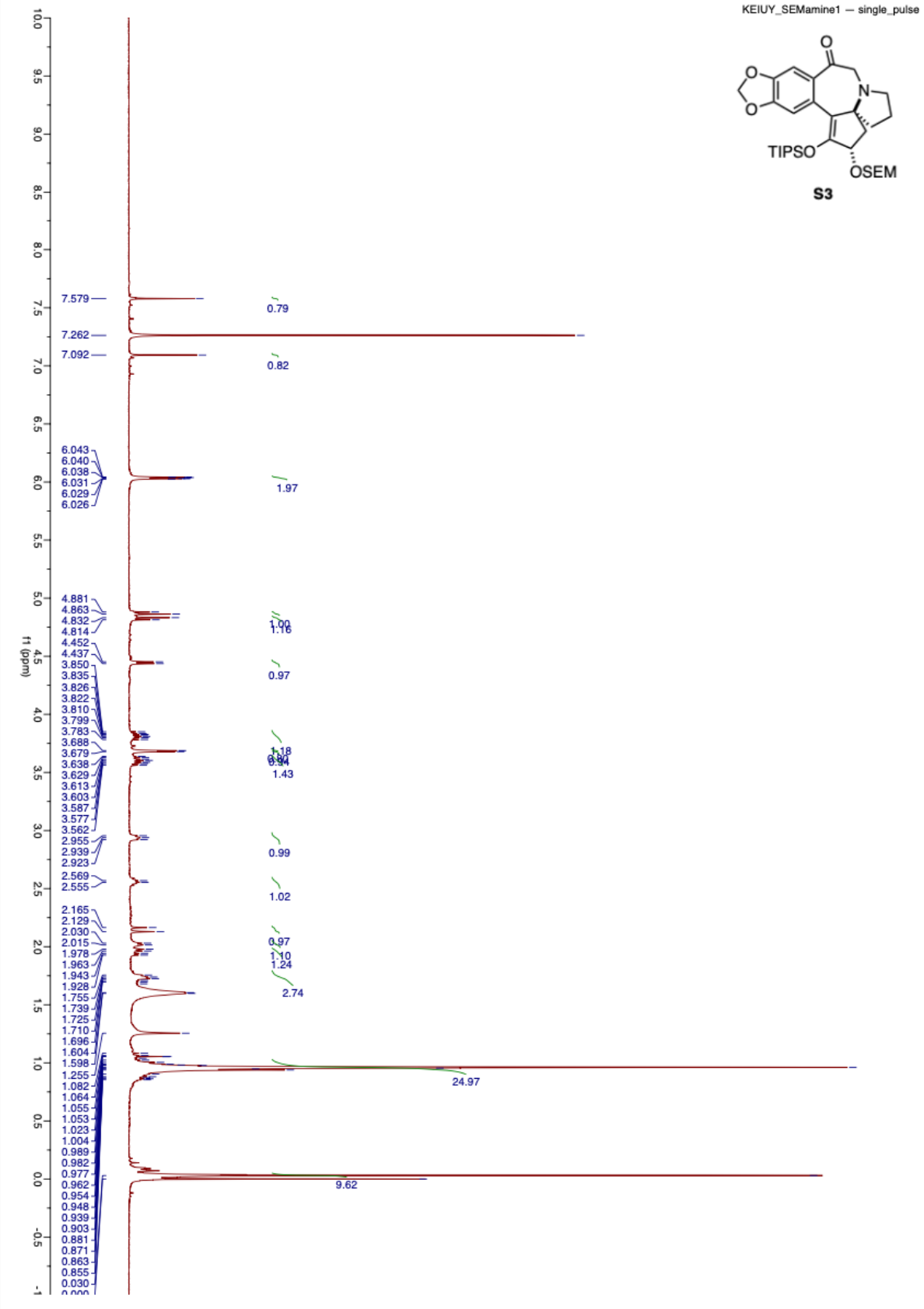
^{13}C NMR of cephalotine B (8) (151 MHz, acetone-d_6)



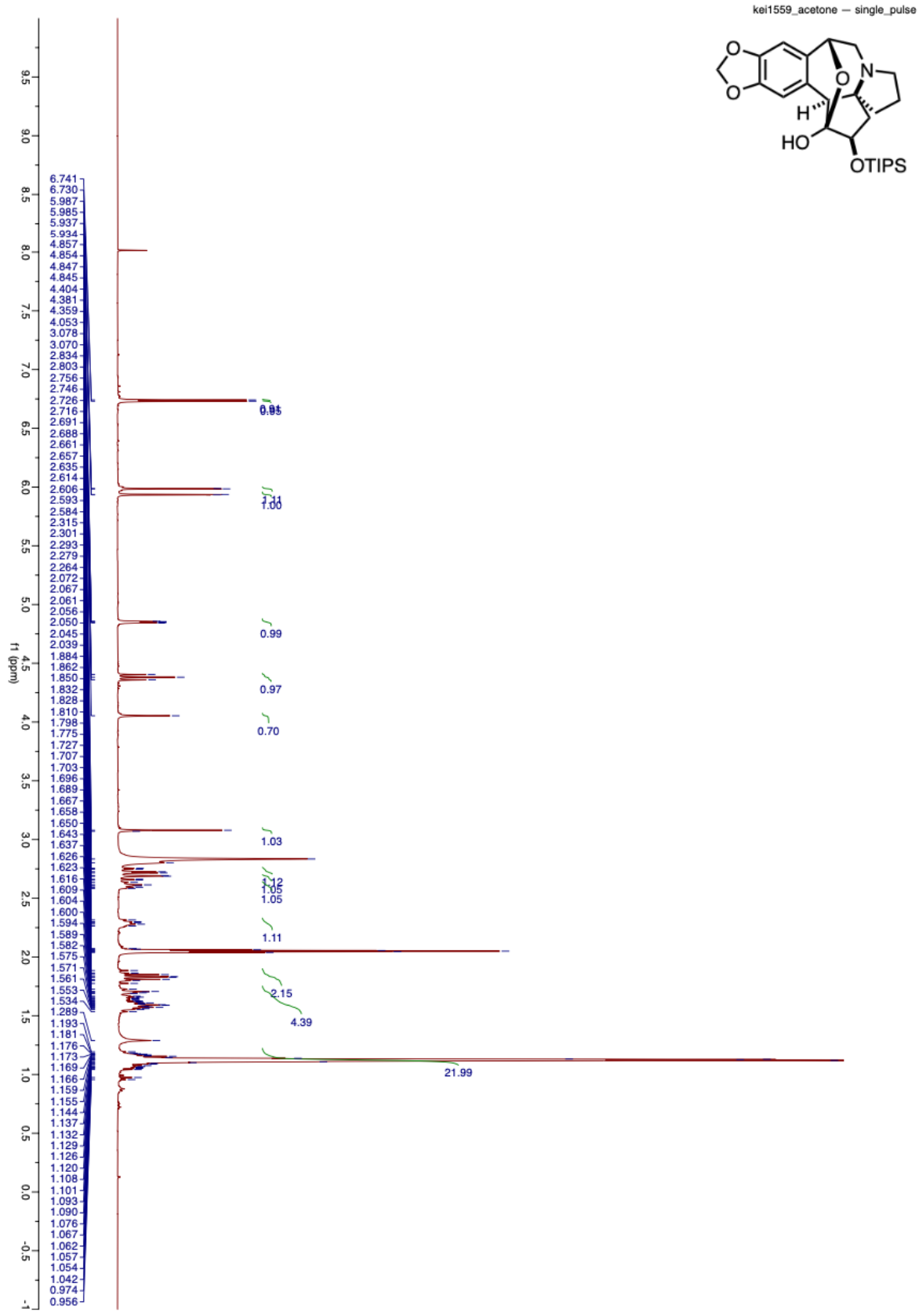
^{1}H NMR of Int1 (400 MHz, $CDCl_3$)



^{1}H NMR of S3 (400 MHz, $CDCl_3$)



^{1}H NMR of TIPS–cephalotine B (S4) (400 MHz, acetone-d_6)



^{13}C NMR of TIPS–cephalotine B (S4) (101 MHz, acetone-d_6)