Supporting Information

Hydrogen bond, as a temporary protecting group, enables the photocatalytic [2+2] cycloaddition of redox-active aliphatic amine-containing indole derivatives

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Contents

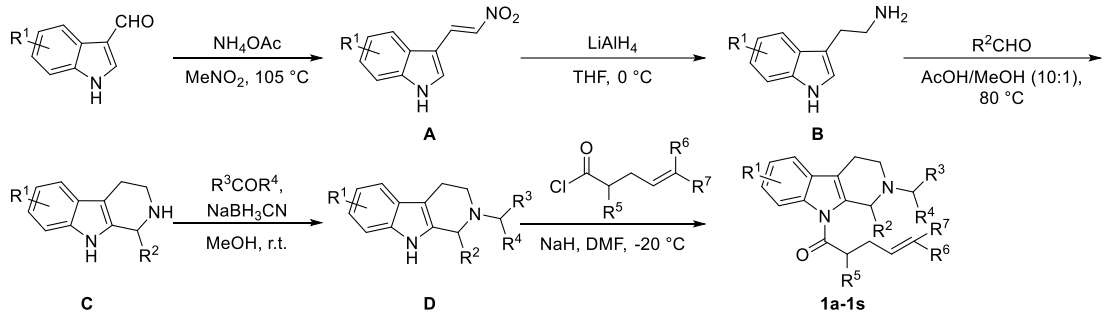
1. General information

All reactions were carried out under Argon atmosphere in Schlenk tubes. Anhydrous solvents (including DCM, MeCN, DMSO, MeOH, DMF, Water < 0.005%) were purchased from Energy and used as received. Solvent (including TFE, HFIP, Acetone and EtOH, reagent grade) and commercially available compounds were purchased from Adamas-beta®, Aldrich, Energy, J&K and TCI Chemical Company as reagent grade and used without further purification unless otherwise stated.

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were obtained with a Bruker AV II-400 spectrometer (^{1}H: 400 MHz, ^{13}C: 101 MHz, ^{19}F: 376 MHz). The chemical shifts (δ) were expressed in ppm and *J* values were given in Hz using tetramethylsilane as the internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets ddt = doublet of doublets of triplets and br = broad. TLC was performed using commercially prepared silica gel plates (GF_{254}), and visualized under UV light 254 nm. Flash column chromatography was performed on silica gel (100-200 mesh). All mixed solvent eluents are reported as v/v solutions. UV/Vis spectra were obtained using an Agilent Cary 60 spectrometer. Emission intensities were recorded using PerkinElmer LS55 Fluorescence Spectrometer. Cyclic voltammetry tests were carried out with a CHI700E electrochemical workstation. Mass analysis data were acquired on a SCIEX UPLC (EXion) – Q-TOF (X500R). Melting points were measured using a Hanon MP470 apparatus.

2. The general synthetic route of substrates

2.1 Synthetic route of substrates 1a-1s



Synthesis of substrates A[1]: The compounds were synthesized according to the procedures in the literature. Aldehyde (10 mmol, 1.0 equiv) and ammonium acetate (30 mmol, 3.0 equiv) were refluxed in nitromethane (20 mL/g of aldehyde) for 2 h. The solvent was removed in vacuo and the solid residue washed with water, filtered and concentrated in vacuo to furnish the desired nitro olefin. No further purification was required and the crude nitroolefin **A** was used directly for further transformation.

Synthesis of substrates B: $LiAlH_4$ (30 mmol, 3.0 equiv) was dissolved in anhydrous THF (70 mL/g of $LiAlH_4$) and the corresponding nitroolefin **A** was added gradually at 0 °C. The reaction mixture was refluxed for 2 h, then cooled to room temperature. After that, 1 mL H_2O, 2 mL 10% NaOH, and 3 mL H_2O were added in sequence for each gram of $LiAlH_4$ at 0 °C. The resulting mixture was filtered over celite, washed with ethyl acetate and concentrated under reduced pressure. The crude material was purified by chromatography on silica gel (DCM : MeOH : Et_3N = 15 : 1 : 0.1 - 5 : 1 : 0.1) to obtain the corresponding amine **B**.

Synthesis of substrates C[2]: To a solution of substituted tryptamine **B** (5 mmol, 1.0 equiv) in a mixed solution (AcOH : MeOH = 10 : 1, 15 mL) was added aldehyde (6 mmol, 1.2 equiv). The mixture was heated to 80 °C for 1 h, then the mixture was cooled to room temperature. The reaction mixture was basified to pH 9-10 using NH_3•H_2O (aq.) and extracted with DCM. The combined organic layers were washed with saturated brine, dried over Na_2SO_4, filtered and the solvent was evaporated to give the crude amine **C**. It was used directly without further purification.

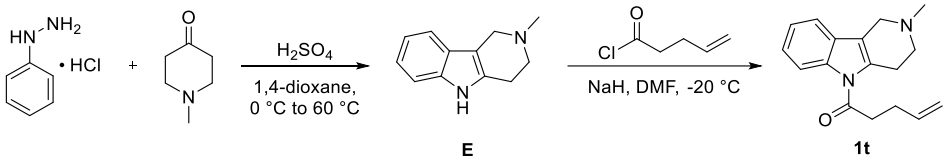
Synthesis of substrates D[3]: The crude amine **C** was added to $NaBH_3CN$ (12.5 mmol, 2.5 equiv) in MeOH, and then aldehyde or ketone (50 mmol, 10.0 equiv) was added. This mixture was stirred for 2 h. After the completion of the reaction, 2N HCl (100 mL, 20 mL/mmol of substituted tryptamine) was added and the mixture was stirred for 15 min. Subsequently, the mixture was adjusted to pH 11 by the addition of concentrated, aqueous NaOH and extracted with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated. The crude material was purified by chromatography on silica gel (DCM : MeOH : Et_3N = 30 : 1 : 0.1 - 10 : 1 : 0.1) to obtain the derivatives of 2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole **D**.

Synthesis of substrates 1a–1s: A round bottom flask containing the derivatives of 2,3,4,9-

tetrahydro-1*H*-pyrido[3,4-*b*]indole **D** (2 mmol, 1.0 equiv) was vacuum purged, filled with argon and followed by addition of DMF to dissolve it completely. Sodium hydride (3 mmol, 120 mg, 60% by wt. in mineral oil, 1.5 equiv) was added to the mixture at -20 °C. After stirring this mixture for 1 h. 4-pentenoyl chloride (2.4 mmol, 264 μL, 1.2 equiv) was added. Subsequently, the mixture was removed to room temperature and stirred for another 1 h. The reaction was quenched by the addition of water and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by chromatography on silica gel (DCM : MeOH : Et_3N = 30 : 1 : 0.1 - 15 : 1 : 0.1) to obtain the derivatives of 4-pentenoyl substituted 2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole (**1a**–**1s**).

The products **1a-1d** and **1k-1s** are synthesized from tryptamine hydrochloride, 5-methyltryptamine hydrochloride, 5-methoxytryptamine hydrochloride and 5-chlorotryptamine hydrochloride.

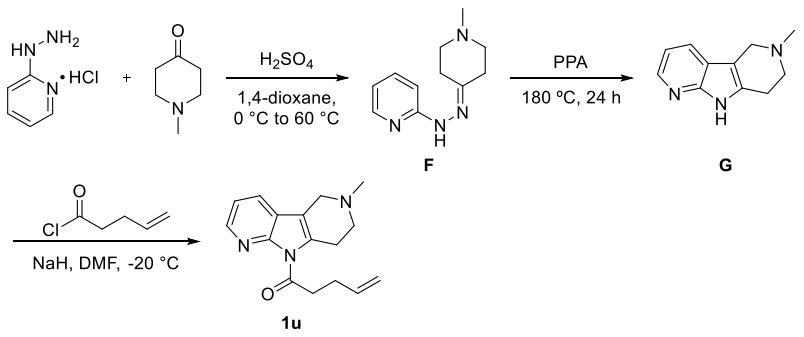
2.2 Synthetic route of substrate 1t



Synthesis of substrates E[4]: Phenyl hydrazine hydrochloride (5 mmol, 718 mg, 1.0 equiv) and 1-methyl-piperidin-4-one (5 mmol, 556 mg, 1.0 equiv) were dissolved in 1,4-dioxane and cooled to 0 °C. Concentrated sulfuric acid (50 mmol, 2.7 mL, 10.0 equiv) was added dropwise to the reaction with stirring. Then, the reaction was heated at 60 °C for 1 h. After cooling to room temperature, the mixture was adjusted to approximately pH = 12 with the addition of saturated aqueous sodium bicarbonate solution and small portions of solid sodium hydroxide. The organic products were extracted with chloroform and the combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatography (DCM : MeOH : Et_3N = 10 : 1 : 0.1) to obtain a white solid **E** with a yield of 72%.

Synthesis of substrates 1t: The synthetic method of substrate **1t** is the same as the synthetic route of substrate **D** to **1a**. The product **1t** was a white solid with a yield of 40%.

2.3 Synthetic route of substrate 1u

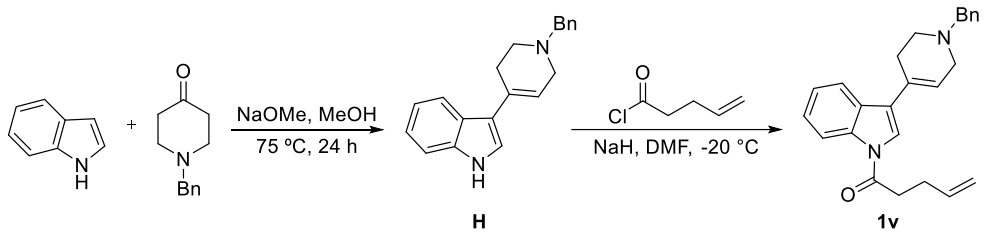


Synthesis of substrates F: The synthetic method of substrate **F** is the same as the synthetic route of substrate **E**. The product **F** was obtained in 98% yield as a white solid.

Synthesis of substrates G[5]: The compounds were synthesized by the procedure in the literature. Polyphosphoric acid (4.4 g, 2.2 g/mmol of **F**) was added to 2-(2-(1-methylpiperidin-4-ylidene)hydrazineyl)pyridine **F** (2 mmol, 409 mg, 1.0 equiv) and stirred gently at 180 °C for 24 h. The mixture was cooled to room temperature and ice was added to break up the gum. Subsequently, the reaction mixture was basified with 2 M NaOH (aq.) and extracted with EtOAc. The combined organic extracts were treated with brine, dried over Na_2SO_4, concentrated in vacuo and purified by flash silica gel column chromatography (DCM : MeOH : Et_3N = 8 : 1 : 0.1) to furnish the desired compound **G**. The product **G** was an off-white solid with a yield of 80%.

Synthesis of substrates 1u: The synthetic method of substrate **1u** is the same as the synthetic route of substrate **D** to **1a**. The product **1u** was obtained in 52% yield as a yellow solid.

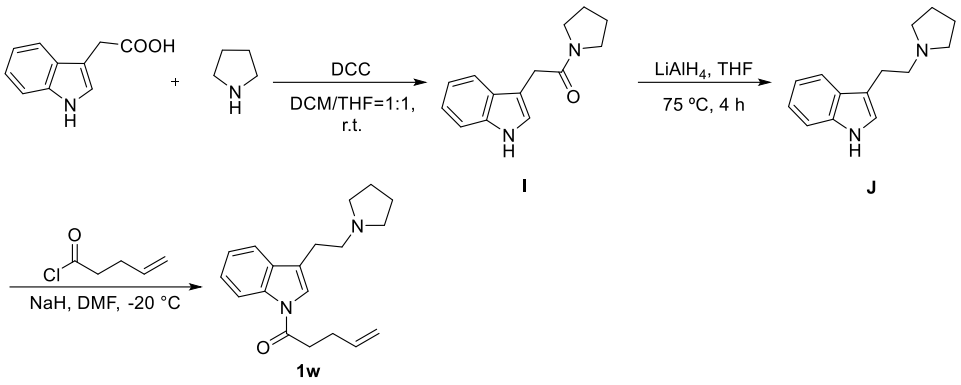
2.4 Synthetic route of substrate 1v



Synthesis of substrates H[6]: The compounds were synthesized by the procedure in the literature. A solution of indole (5 mmol, 586 mg, 1.0 equiv), piperidone (15 mmol, 2839 mg, 3.0 equiv) and sodium methoxide (30 mmol, 973 mg, 6.0 equiv) in anhydrous methanol (20 mL) was refluxed under argon for 24 h. After cooling to room temperature, methanol was evaporated under reduced pressure until precipitation occurred. The pure product **H** was collected by filtration, washed with cold methanol and dried under vacuum. The product **H** was obtained as a white solid with a yield of 81%.

Synthesis of substrates 1v: The synthetic method of substrate **1v** is the same as the synthetic route of substrate **D** to **1a**. The product **1v** was a yellow solid with a yield of 50%.

2.5 Synthetic route of substrate 1w

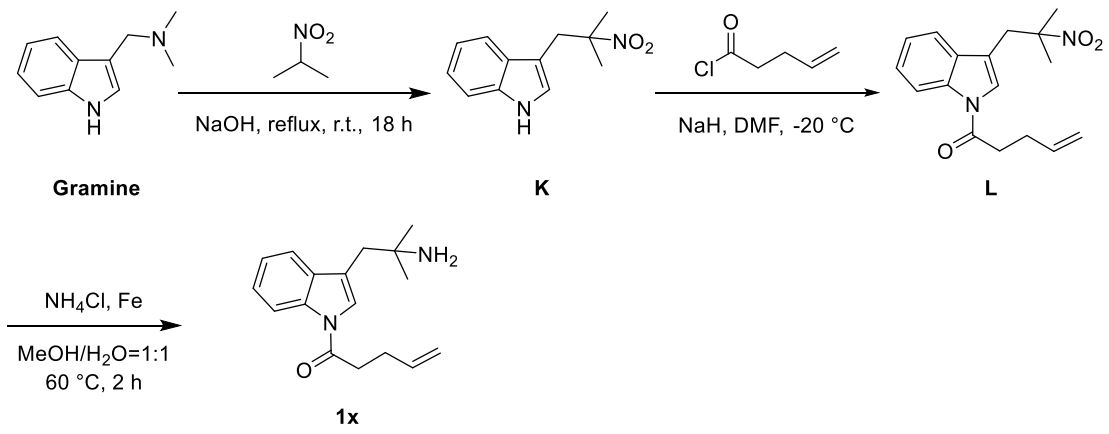


Synthesis of substrates I[7]: The compounds were synthesized according to the procedure in the literature. Under the argon atmosphere, 2-(1*H*-indol-3-yl)acetic acid (3 mmol, 526 mg, 1 equiv) in a mixed solution (DCM : THF = 1 : 1, 10 mL) was added with DCC (3.45 mmol, 712 mg, 1.2 equiv). The mixture was stirred for 1 h at room temperature, then pyrrolidine (3.9 mmol, 278 mg, 1.3 equiv) was added and the mixture was stirred for another 3 h. After the addition of water, the mixture was extracted with DCM, and the combined organic phases were dried over Na_2SO_4, concentrated under vacuum. The residue was purified by silica gel column chromatography to give **I**. The product **I** was obtained as a white solid with a yield of 48%.

Synthesis of substrates J[8]: The compounds were synthesized according to the procedure in the literature. Under the argon atmospheres, a solution of **I** (2 mmol, 457 mg, 1.0 equiv) in anhydrous THF was slowly added with $LiAlH_4$ (3 mmol, 114 mg, 1.5 equiv) and the reaction was refluxed for 4 h. Afterwards, the reaction mixture was added with 1 mL H_2O, 2 mL 10% NaOH, and 3 ml H_2O for each gram of $LiAlH_4$ at 0 °C, then stirred for 10 min. The formed solid was filtered off and washed with THF. The filtrate was concentrated under vacuum and the crude material was purified by chromatography on silica gel (DCM : MeOH : Et_3N = 15 : 1 : 0.1 – 5 : 1 : 0.1) to obtain 3-(2-(pyrrolidin-1-yl)ethyl)-1*H*-indole **J**. The product **J** was a white solid with a yield of 90%.

Synthesis of substrate 1w: The synthetic method of substrate **1w** is the same as the synthetic route of substrate **D** to **1a**. The product **1w** was a white solid with a yield of 58%.

2.6 Synthetic route of substrate 1x

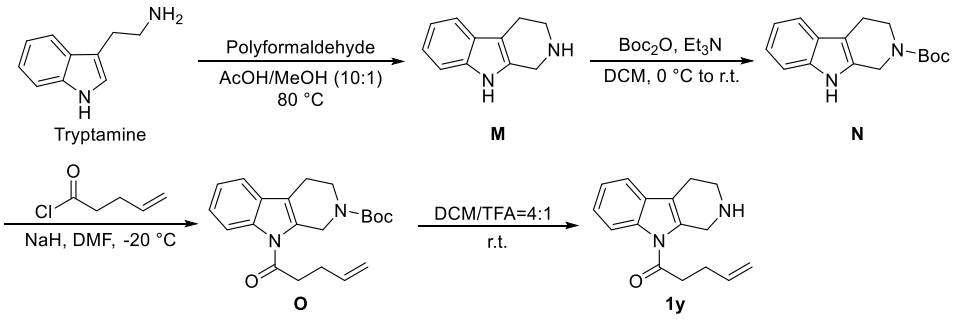


Synthesis of substrate K[7]: The compounds were synthesized according to the procedure in the literature. A mixture of gramine (5 mmol, 872 mg, 1.0 equiv), 2-nitropropane (35.5 mmol, 3.36 mL, 7.1 equiv) and NaOH pellets (5.25 mmol, 210 mg, 1.1 equiv) was stirred and refluxed for 18 h. After the mixture was cooled to room temperature, 10% AcOH (5 mL, 1 mL/mmol of NaOH) was added and stirred for another 1 h. The mixture was partitioned between Et_2O and water to afford an organic layer, which was washed three times with water and dried over Na_2SO_4. The crude mixture was purified by silica gel column chromatography (PE : EtOAc=10 : 1) to afford the final product 3-(2-methyl-2-nitropropyl)-1*H*-indole **K**. The product **K** was a white solid with a yield of 62%.

Synthesis of substrate L: The synthetic method of substrate **L** is the same as the synthetic route of substrate **D** to **1a**. The product **L** was a white solid with a yield of 58%.

Synthesis of substrate 1x[8]: The compounds were synthesized according to the procedure in the literature. To a suspension of **L** (1.34 mmol, 400 mg, 1.0 equiv) in a mixed solution (MeOH : H_2O = 1 : 1) was added NH_4Cl (13.4 mmol, 728 mg, 10.0 equiv) followed by Fe powder (6.66 mmol, 372 mg, 5.0 equiv). The solution was refluxed for 2 h. After cooling to room temperature, the mixture was filtrated and concentrated in vacuo. The residue was extracted with EtOAc, washed with brine, dried over Na_2SO_4 and evaporated under vacuum. The crude material was purified by flash chromatography on silica gel (DCM : MeOH : Et_3N = 20 : 1 : 0.1) to obtain the corresponding amine **1x**. The product **1x** was a yellow liquid with a yield of 60%.

2.7 Synthetic route of substrate 1y



Synthesis of substrate M: The synthetic method of substrate **M** is the same as the synthetic route of substrate **B** to **C1**. The product **M** was a white solid with a yield of 83%.

Synthesis of substrate N[2a]: This compound was synthesized according to a known literature procedure with slight modifications. To a solution of **M** (2 mmol, 345 mg, 1.0 equiv) in DCM was slowly added Boc_2O (5 mmol, 1092 mg, 2.5 equiv) and Et_3N (2.4 mmol, 250 μL, 1.2 equiv) at 0 °C. After the addition was completed, the reaction mixture was allowed to reach room temperature and stirred for 16 h. The crude material was purified by flash chromatography on silica gel (PE : EtOAc = 10 : 1) to obtain the derivatives of *tert*-butyl 1,3,4,9-tetrahydro-2*H*-pyrido[3,4-*b*]indole-2-carboxylate (**N**). The product **N** was a white solid with a yield of 86%.

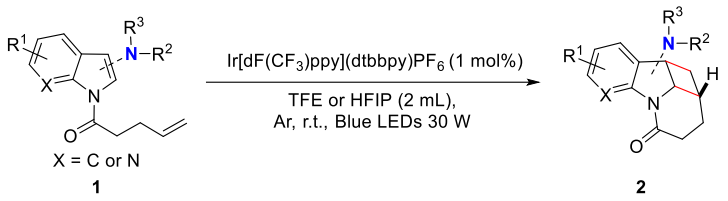
Synthesis of substrate O: The synthetic method of substrate **O** is the same as the synthetic route of substrate **D** to **1a**. The product **O** was a white solid with a yield of 53%.

Synthesis of substrate 1y: The compound **O** was added to the mixed solution (DCM : TFA = 4 : 1). After the mixture was stirred for 3 h at room temperature, it was concentrated in vacuo. The crude material was purified by flash chromatography on silica gel (DCM : MeOH : Et_3N = 20 : 1 : 0.1) to obtain the derivatives of **1y**. The product **1y** was a white solid with a yield of 96%.

2.8 Synthetic route of substrates 1z, 1aa, 1ab and 1ac

The synthetic method of substrates **1z**, **1aa**, **1ab** and **1ac** are the same as the synthetic route of substrate **D** to **1a**. The product **1z** was obtained as a yellow solid with a yield of 20%. The product **1aa** was a yellow solid with a yield of 64%. The product **1ab** was a white solid with a yield of 52%. The product **1ac** was a white solid with a yield of 32%.

3. Typical experimental procedure for the [2+2] cycloaddition



An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the substrates **1** (0.2 mmol) and photosensitizer (1 mol %). Then, the Schlenk tube was connected to a vacuum line where it was evacuated and back-filled with argon for 3 times. Afterwards, trifluoroethanol or hexafluoroisopropanol (2 mL), which was bubbled with argon for 5 minutes, was added under argon flow. Finally, the reaction mixture in a sealed tube was placed at a distance of 2 – 3 cm from a 30 W blue LED and stirred at room temperature for 3 – 12 h. After finishing the reaction, the mixture was concentrated in vacuo and purified by silica gel flash chromatography (EtOAc or DCM : MeOH = 30 : 1 – 10 : 1) to afford the corresponding products **2**.

3.1 The reaction involves the potential and triplet energy of the photosensitizer structure

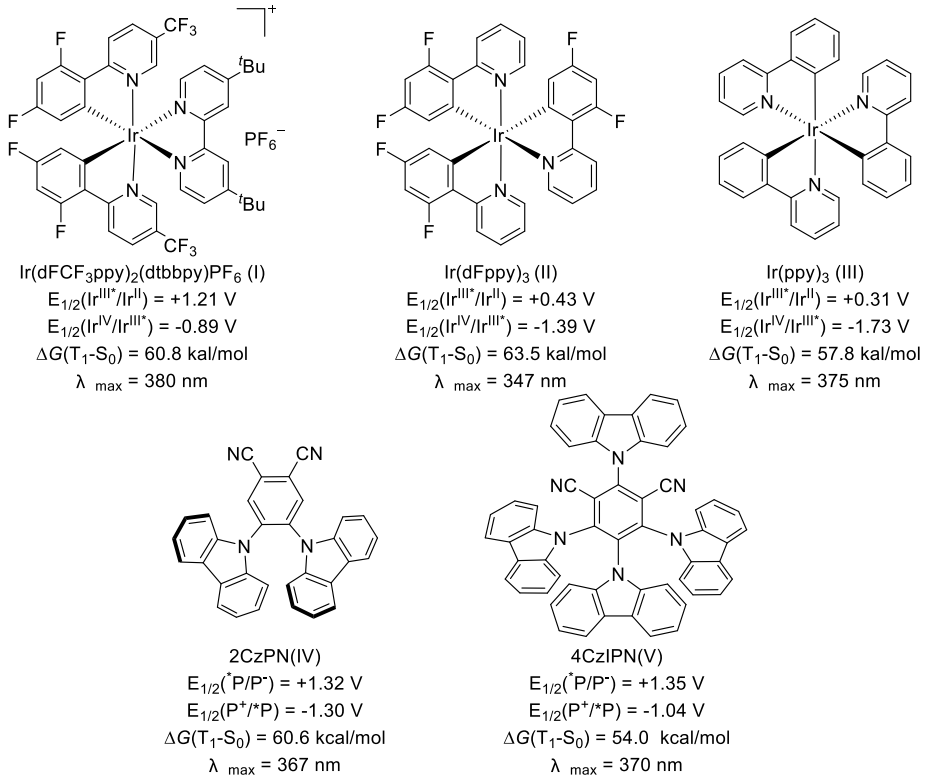
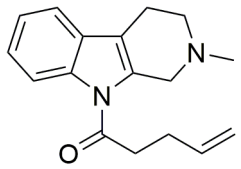


Figure S1. The structures and photophysical properties of PC-(I-V)

4. Characterization data for substrates

1-(2-methyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indol-9-yl)pent-4-en-1-one (1a)



Physical State: Light yellow solid.

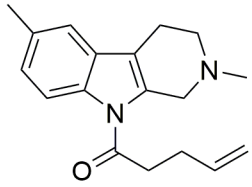
Melting Point: 57.9-58.9 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.72 (m, 1H), 7.44 (dd, *J* = 6.3, 2.6 Hz, 1H), 7.33 – 7.26 (m, 2H), 5.96 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.22 – 5.03 (m, 2H), 3.95 (s, 2H), 3.11 (t, *J* = 7.3 Hz, 2H), 3.83 – 2.77 (m, 4H), 2.64 – 2.56 (m, 2H), 2.55 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 136.7, 135.0, 134.5, 130.2, 123.8, 122.9, 118.4, 115.9, 115.8, 114.7, 55.1, 51.4, 45.5, 37.7, 28.5, 21.5.

HRMS (ESI): calcd for $C_{17}H_{21}N_2O$ $[M+H]^+$ *m/z* 269.1648, found 269.1639.

1-(2,6-dimethyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indol-9-yl)pent-4-en-1-one (1b)



Physical State: Light yellow solid.

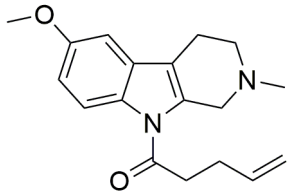
Melting Point: 93.6-94.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.5 Hz, 1H), 7.24 – 7.22 (m, 1H), 7.09 (dd, *J* = 8.5, 1.2 Hz, 1H), 5.96 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.20 – 5.04 (m, 2H), 3.94 (s, 2H), 3.09 (t, *J* = 7.3 Hz, 2H), 2.80 – 2.75 (m, 4H), 2.63 – 2.56 (m, 2H), 2.55 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 136.7, 134.6, 133.2, 132.5, 130.4, 125.0, 118.5, 115.9, 115.6, 114.3, 55.1, 51.4, 45.5, 37.5, 28.5, 21.5, 21.2.

HRMS (ESI): calcd for $C_{18}H_{23}N_2O$ $[M+H]^+$ *m/z* 283.1805, found 283.1801.

1-(6-methoxy-2-methyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indol-9-yl)pent-4-en-1-one (1c)



Physical State: Light yellow solid.

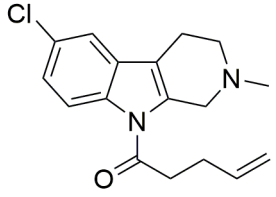
Melting Point: 106.7-107.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.9 Hz, 1H), 6.98 – 6.78 (m, 2H), 5.95 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.18 – 5.05 (m, 2H), 3.93 (s, 2H), 3.87 (s, 3H), 3.06 (t, *J* = 7.3 Hz, 2H), 2.84 – 2.71 (m, 4H), 2.62 – 2.54 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 156.0, 136.7, 135.2, 131.3, 129.6, 115.9, 115.8, 115.5, 111.7, 101.5, 55.7, 55.2, 51.3, 45.5, 37.4, 28.5, 21.5.

HRMS (ESI): calcd for $C_{18}H_{23}N_2O_2$ $[M+H]^+$ *m/z* 299.1754, found 299.1751.

1-(6-chloro-2-methyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indol-9-yl)pent-4-en-1-one (1d)



Physical State: Off-white solid.

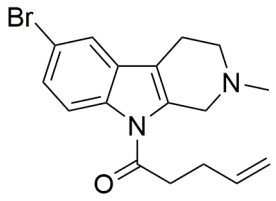
Melting Point: 112.9-113.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.9 Hz, 1H), 7.38 (d, *J* = 2.1 Hz, 1H), 7.21 (dd, *J* = 8.9, 2.1 Hz, 1H), 5.94 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.21 – 4.98 (m, 2H), 3.90 (s, 2H), 3.03 (t, *J* = 7.3 Hz, 2H), 2.80 – 2.70 (m, 4H), 2.62 – 2.55 (m, 2H), 2.55 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 136.5, 135.7, 133.5, 131.4, 128.7, 123.8, 118.1, 116.1, 115.8, 115.3, 55.0, 51.2, 45.5, 37.5, 28.4, 21.3.

HRMS (ESI): calcd for $C_{17}H_{20}ClN_2O$ $[M+H]^+$ *m/z* 303.1259, found 303.1252.

1-(6-bromo-2-methyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indol-9-yl)pent-4-en-1-one (1e)



Physical State: Yellow solid.

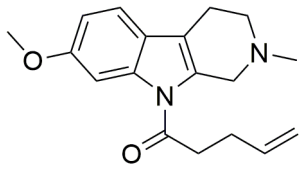
Melting Point: 110.3-113.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.9 Hz, 1H), 7.55 (d, *J* = 1.7 Hz, 1H), 7.36 (dd, *J* = 8.8, 1.8 Hz, 1H), 5.94 (ddt, *J* = 16.8, 10.3, 6.5 Hz, 1H), 5.21 – 5.02 (m, 2H), 3.91 (s, 2H), 3.04 (t, *J* = 7.3 Hz, 2H), 2.83 – 2.71 (m, 4H), 2.63 – 2.56 (m, 2H), 2.55 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 136.5, 135.6, 133.9, 131.9, 126.5, 121.2, 116.4, 116.2, 116.1, 115.3, 55.1, 51.3, 45.5, 37.6, 28.5, 21.4.

HRMS (ESI): calcd for $C_{17}H_{20}BrN_2O$ $[M+H]^+$ *m/z* 347.0754, found 347.0743.

1-(7-methoxy-2-methyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indol-9-yl)pent-4-en-1-one (1f)



Physical State: Light yellow solid.

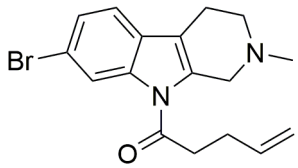
Melting Point: 79.2-81.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 1.8 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 6.89 (dd, *J* = 8.5, 2.1 Hz, 1H), 5.95 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.19 – 5.05 (m, 2H), 3.90 (s, 2H), 3.88 (s, 3H), 3.03 (t, *J* = 7.3 Hz, 2H), 2.81 – 2.73 (m, 4H), 2.64 – 2.56 (m, 2H), 2.55 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 157.4, 136.7, 136.2, 132.7, 124.1, 118.5, 115.95, 115.87, 110.3, 101.5, 55.9, 55.2, 51.4, 45.6, 37.4, 28.5, 21.6.

HRMS (ESI): calcd for $C_{18}H_{23}N_2O_2$ $[M+H]^+$ *m/z* 299.1754, found 299.1754.

1-(7-bromo-2-methyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indol-9-yl)pent-4-en-1-one (1g)



Physical State: White solid.

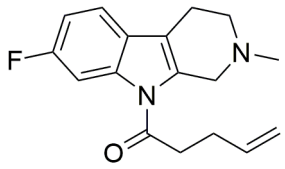
Melting Point: 127.0-128.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 1.1 Hz, 1H), 7.37 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 5.95 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.24 – 5.04 (m, 2H), 3.87 (s, 2H), 3.02 (t, *J* = 7.2 Hz, 2H), 2.80 – 2.73 (m, 4H), 2.65 – 2.56 (m, 2H), 2.55 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 136.5, 135.9, 134.7, 128.9, 126.2, 119.3, 118.1, 117.4, 116.2, 115.7, 55.0, 51.3, 45.6, 37.5, 28.5, 21.4.

HRMS (ESI): calcd for $C_{17}H_{20}BrN_2O$ $[M+H]^+$ *m/z* 347.0754, found 347.0754.

1-(7-fluoro-2-methyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indol-9-yl)pent-4-en-1-one (1h)



Physical State: Yellow solid.

Melting Point: 83.6-88.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 10.9, 2.1 Hz, 1H), 7.34 (dd, *J* = 8.5, 5.6 Hz, 1H), 7.02 (td, *J* = 8.8, 2.2 Hz, 1H), 5.95 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.19 – 5.06 (m, 2H), 3.90 (s, 2H), 3.06 – 2.99 (m, 2H), 2.80 – 2.75 (m, 4H), 2.64 – 2.57 (m, 2H), 2.55 (s, 3H).

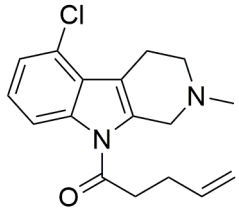
^{19}F NMR (376 MHz, $CDCl_3$) δ -117.57.

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 160.6 (d, *J* = 239.2 Hz), 136.5, 135.3 (d, *J* = 11.8 Hz), 134.2

(d, *J* = 4.0 Hz), 126.4 (d, *J* = 1.3 Hz), 118.7 (d, *J* = 9.9 Hz), 116.1, 115.7, 110.9 (d, *J* = 23.7 Hz), 102.9 (d, *J* = 29.2 Hz), 55.1, 51.3, 45.5, 37.4, 28.4, 21.5.

HRMS (ESI): calcd for $C_{17}H_{20}FN_2O$ $[M+H]^+$ *m/z* 287.1554, found 287.1545.

1-(5-chloro-2-methyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indol-9-yl)pent-4-en-1-one (1i)



Physical State: White solid.

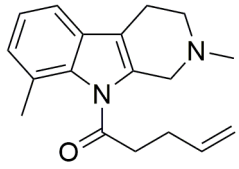
Melting Point: 55.4-55.9 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.63 (m, 1H), 7.19 – 7.07 (m, 2H), 5.92 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.18 – 5.04 (m, 2H), 3.83 (s, 2H), 3.16 – 3.08 (m, 2H), 3.01 (t, *J* = 7.3 Hz, 2H), 2.70 (t, *J* = 5.8 Hz, 2H), 2.61 – 2.53 (m, 2H), 2.51 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 136.5, 136.3, 135.2, 127.2, 126.4, 124.1, 123.8, 116.1, 115.6, 113.2, 55.2, 51.7, 45.6, 37.8, 28.6, 24.1.

HRMS (ESI): calcd for $C_{17}H_{20}ClN_2O$ $[M+H]^+$ *m/z* 303.1259, found 303.1259.

1-(2,8-dimethyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indol-9-yl)pent-4-en-1-one (1j)



Physical State: Yellow solid.

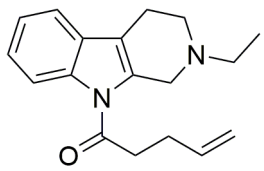
Melting Point: 44.8-45.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.3 Hz, 1H), 5.80 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.09 – 4.99 (m, 2H), 3.72 (s, 2H), 2.83 (dd, *J* = 8.3, 6.7 Hz, 2H), 2.80 – 2.75 (m, 4H), 2.58 – 2.50 (m, 5H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 136.2, 135.9, 133.0, 130.9, 126.8, 124.4, 123.2, 116.2, 115.8, 114.2, 53.9, 51.7, 45.7, 38.8, 30.2, 21.5, 21.2.

HRMS (ESI): calcd for $C_{18}H_{23}N_2O$ $[M+H]^+$ *m/z* 283.1805, found 283.1805.

1-(2-ethyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indol-9-yl)pent-4-en-1-one (1k)



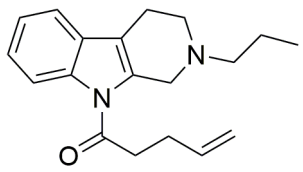
Physical State: Yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.7 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.32 – 7.22 (m, 2H), 5.96 (ddt, *J* = 16.9, 10.2, 6.5 Hz, 1H), 5.26 – 4.94 (m, 2H), 4.00 (s, 2H), 3.11 (t, *J* = 7.3 Hz, 2H), 2.88 – 2.82 (m, 2H), 2.82 – 2.76 (m, 2H), 2.72 (q, *J* = 7.2 Hz, 2H), 2.61 (dd, *J* = 13.6, 6.7 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 136.7, 135.0, 134.7, 130.2, 123.8, 122.9, 118.4, 116.3, 115.9, 114.6, 52.9, 51.5, 49.1, 37.7, 28.5, 21.5, 12.6.

HRMS (ESI): calcd for $C_{18}H_{23}N_2O$ $[M+H]^+$ *m/z* 283.1805, found 283.1793.

1-(2-propyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indol-9-yl)pent-4-en-1-one (1l)



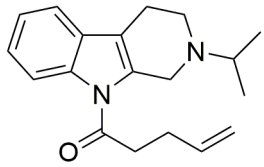
Physical State: Yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.66 (m, 1H), 7.39 – 7.33 (m, 1H), 7.24 – 7.14 (m, 2H), 5.88 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.12 – 4.94 (m, 2H), 3.90 (s, 2H), 3.01 (t, *J* = 7.3 Hz, 2H), 2.77 – 2.73 (m, 2H), 2.72 – 2.66 (m, 2H), 2.58 – 2.47 (m, 4H), 1.63 – 1.51 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 135.7, 134.0, 133.7, 129.2, 122.7, 121.9, 117.3, 115.3, 114.9, 113.6, 58.7, 52.3, 48.4, 36.6, 27.5, 20.4, 19.5, 10.9.

HRMS (ESI): calcd for $C_{19}H_{25}N_2O$ $[M+H]^+$ *m/z* 297.1961, found 297.1954.

1-(2-isopropyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indol-9-yl)pent-4-en-1-one (1m)



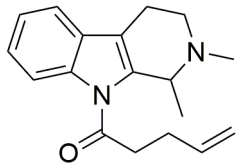
Physical State: Red liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 1H), 7.46 – 7.39 (m, 1H), 7.30 – 7.21 (m, 2H), 5.96 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.21 – 5.04 (m, 2H), 4.08 – 1.04 (m, 2H), 3.14 – 3.00 (m, 3H), 2.84 (t, *J* = 5.4 Hz, 2H), 2.79 – 2.73 (m, 2H), 2.64 – 2.57 (m, 2H), 1.18 (d, *J* = 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 136.7, 135.4, 135.1, 130.4, 123.7, 122.9, 118.4, 116.5, 115.9, 114.6, 54.1, 49.2, 44.8, 37.7, 28.5, 22.2, 18.5.

HRMS (ESI): calcd for $C_{19}H_{25}N_2O$ $[M+H]^+$ *m/z* 297.1961, found 297.1950.

1-(1,2-dimethyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indol-9-yl)pent-4-en-1-one (1n)



Physical State: Light yellow solid.

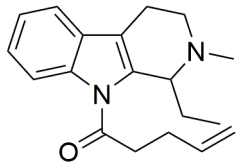
Melting Point: 54.3-56.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.0, 1.7 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.32 – 7.24 (m, 2H), 5.96 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.18 – 5.05 (m, 2H), 4.51 (q, *J* = 6.4 Hz, 1H), 3.24 – 3.13 (m, 3H), 2.94 – 2.83 (m, 2H), 2.67 – 2.54 (m, 3H), 2.53 (s, 3H), 1.39 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 139.8, 136.7, 135.0, 130.5, 123.8, 122.9, 118.6, 115.9, 114.61, 114.55, 55.8, 43.6, 41.7, 38.2, 28.6, 18.3, 18.1.

HRMS (ESI): calcd for $C_{18}H_{23}N_2O$ $[M+H]^+$ *m/z* 283.1805, found 283.1795.

1-(1-ethyl-2-methyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indol-9-yl)pent-4-en-1-one (1o)



Physical State: White solid.

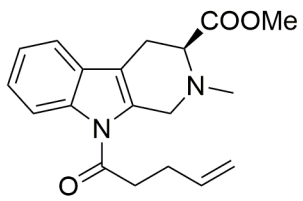
Melting Point: 81.5-82.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 6.9, 1.9 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.32 – 7.22 (m, 2H), 5.96 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.18 – 5.05 (m, 2H), 4.11 (d, *J* = 9.1 Hz, 1H), 3.30 – 3.17 (m, 1H), 3.17 – 3.11 (m, 2H), 2.97 – 2.81 (m, 2H), 2.71 – 2.55 (m, 2H), 2.52 (s, 3H), 2.50 – 2.42 (m, 1H), 1.77 (dqd, *J* = 14.6, 7.3, 2.3 Hz, 1H), 1.62 – 1.45 (m, 1H), 1.09 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 139.0, 136.7, 135.0, 130.5, 123.8, 122.8, 118.5, 115.9, 114.7, 114.5, 62.5, 43.2, 42.1, 38.2, 28.7, 27.5, 16.5, 11.9.

HRMS (ESI): calcd for $C_{19}H_{25}N_2O$ $[M+H]^+$ *m/z* 297.1961, found 297.1950.

Methyl-(*S*)-2-methyl-9-(pent-4-enoyl)-2,3,4,9-tetrahydro-1*H*-pyrido[3,4-*b*]indole-3-carboxylate (1p)



Physical State: White solid.

Melting Point: 144.3-146.0 °C.

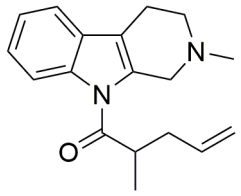
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.3 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.31 – 7.22 (m, 2H), 5.95 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.20 – 5.03 (m, 2H), 4.27 (dd, *J* = 80.4, 17.3 Hz, 2H), 3.77 – 3.66 (m,

4H), 3.14 – 2.98 (m, 4H), 2.66 – 2.53 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 171.8, 136.7, 135.0, 133.9, 129.9, 124.0, 123.0, 118.4, 116.0, 114.9, 113.6, 60.2, 52.1, 51.9, 42.1, 37.7, 28.5, 23.2.

HRMS (ESI): calcd for $C_{19}H_{23}N_2O_3$ $[M+H]^+$ *m/z* 327.1703, found 327.1703.

2-methyl-1-(2-methyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indol-9-yl)pent-4-en-1-one (1q)



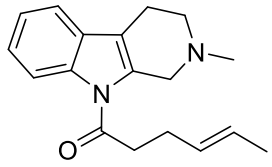
Physical State: Yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.7 Hz, 1H), 7.45 (dd, *J* = 6.5, 2.2 Hz, 1H), 7.27 (pd, *J* = 7.2, 3.9 Hz, 2H), 5.81 (ddt, *J* = 17.1, 10.1, 7.0 Hz, 1H), 5.15 – 5.03 (m, 2H), 3.91 (s, 2H), 3.55 – 3.43 (m, 1H), 2.87 – 2.72 (m, 4H), 2.67 (dt, *J* = 13.4, 6.7 Hz, 1H), 2.55 (s, 3H), 2.32 (dt, *J* = 14.2, 7.1 Hz, 1H), 1.37 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 135.0, 134.9, 134.6, 130.3, 123.9, 122.9, 118.5, 117.6, 115.8, 114.5, 55.1, 51.5, 45.6, 40.1, 38.2, 21.6, 17.2.

HRMS (ESI): calcd for $C_{18}H_{23}N_2O$ $[M+H]^+$ *m/z* 283.1805, found 283.1805.

1-(2-methyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indol-9-yl)hex-4-en-1-one (1r)



Physical State: Light yellow solid.

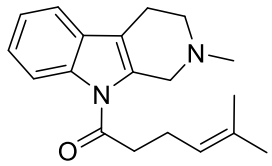
Melting Point: 77.7-78.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.3 Hz, 1H), 7.45 (d, *J* = 6.4 Hz, 1H), 7.34 – 7.20 (m, 2H), 5.65 – 5.49 (m, 2H), 3.94 (s, 2H), 3.06 (t, *J* = 7.1 Hz, 2H), 2.89 – 2.72 (m, 4H), 2.64 – 2.46 (m, 5H), 1.68 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 135.1, 134.6, 130.2, 129.2, 126.7, 123.8, 122.9, 118.4, 115.8, 114.8, 55.2, 51.4, 45.6, 38.5, 27.5, 21.5, 18.0.

HRMS (ESI): calcd for $C_{18}H_{23}N_2O$ $[M+H]^+$ *m/z* 283.1805, found 283.1805.

5-methyl-1-(2-methyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indol-9-yl)hex-4-en-1-one (1s)



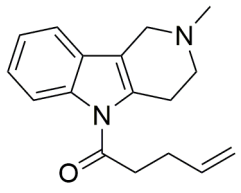
Physical State: Yellow liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 6.6 Hz, 1H), 7.25 – 7.14 (m, 2H), 5.24 – 5.04 (m, 1H), 3.87 (s, 2H), 2.94 (t, *J* = 7.3 Hz, 2H), 2.79 – 2.66 (m, 4H), 2.54 – 2.40 (m, 5H), 1.65 (s, 3H), 1.59 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 135.1, 134.6, 133.5, 130.2, 123.8, 122.9, 122.3, 118.4, 115.7, 114.8, 55.2, 51.4, 45.6, 38.6, 25.8, 23.3, 21.5, 17.8.

HRMS (ESI): calcd for $C_{19}H_{25}N_2O$ $[M+H]^+$ *m/z* 297.1961, found 283.1959.

1-(2-methyl-1,2,3,4-tetrahydro-5*H*-pyrido[4,3-*b*]indol-5-yl)pent-4-en-1-one (1t)



Physical State: White solid.

Melting Point: 66.6-67.3 °C.

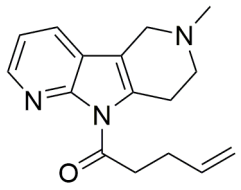
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.29 – 7.20 (m, 2H), 5.93 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.17 – 5.01 (m, 2H), 3.58 (s, 2H), 3.18 – 3.12 (m, 2H), 3.00 (t, *J* = 7.4 Hz, 2H), 2.76 (t, *J* = 5.7 Hz, 2H), 2.61 – 2.55 (m, 2H), 2.53 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 136.8, 135.9, 133.2, 128.4, 124.1, 123.1, 117.6, 116.7, 115.9,

115.7, 52.9, 51.4, 45.8, 37.6, 28.7, 27.8.

HRMS (ESI): calcd for $C_{17}H_{21}N_2O$ $[M+H]^+$ *m/z* 269.1648, found 269.1648.

1-(6-methyl-5,6,7,8-tetrahydro-9*H*-pyrrolo[2,3-*b*:4,5-*c*′]dipyridin-9-yl)pent-4-en-1-one (1u)



Physical State: Yellow solid.

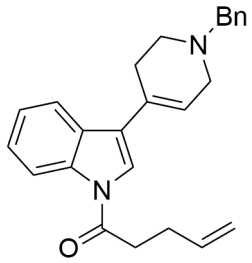
Melting Point: 42.1-43.8 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 4.6, 1.0 Hz, 1H), 7.64 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.15 (dd, *J* = 7.7, 4.8 Hz, 1H), 5.98 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.17 – 5.00 (m, 2H), 3.69 (t, *J* = 7.4 Hz, 2H), 3.56 (s, 2H), 3.33 – 3.26 (m, 2H), 2.78 (t, *J* = 5.7 Hz, 2H), 2.62 – 2.50 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 148.6, 142.6, 137.4, 135.7, 125.4, 120.9, 118.4, 115.4, 113.1, 52.8, 50.9, 45.9, 38.3, 28.7, 27.2.

HRMS (ESI): calcd for $C_{16}H_{20}N_3O$ $[M+H]^+$ *m/z* 270.1601, found 270.1601.

1-(3-(1-benzyl-1,2,3,6-tetrahydropyridin-4-yl)-1*H*-indol-1-yl)pent-4-en-1-one (1v)



Physical State: Yellow solid.

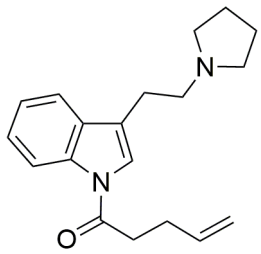
Melting Point: 85.9-86.7 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.42 – 7.36 (m, 3H), 7.35 – 7.32 (m, 3H), 7.31 – 7.25 (m, 2H), 6.30 – 6.23 (m, 1H), 5.92 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.19 – 5.03 (m, 2H), 3.66 (s, 2H), 3.26 – 3.20 (m, 2H), 2.97 (t, *J* = 7.4 Hz, 2H), 2.74 (t, *J* = 5.7 Hz, 2H), 2.61 – 2.53 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 138.2, 136.6, 136.5, 129.3, 128.5, 128.43, 128.37, 127.2, 125.3, 123.8, 123.6, 123.5, 120.7, 120.6, 116.8, 116.1, 62.9, 53.2, 49.8, 35.2, 29.1, 28.4.

HRMS (ESI): calcd for $C_{25}H_{27}N_2O$ $[M+H]^+$ *m/z* 371.2118, found 371.2118.

2-(3-(2-(pyrrolidin-1-yl)ethyl)-1*H*-indol-1-yl)pent-4-en-1-one (1w)



Physical State: White solid.

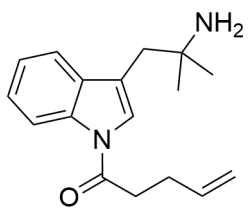
Melting Point: 49.9-50.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 7.8 Hz, 1H), 7.59 – 7.52 (m, 1H), 7.38 – 7.33 (m, 1H), 7.31 – 7.26 (m, 2H), 5.94 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.18 – 5.04 (m, 2H), 3.02 – 2.97 (m, 2H), 2.97 – 2.90 (m, 2H), 2.84 – 2.77 (m, 2H), 2.68 – 2.55 (m, 6H), 1.86 – 1.81 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 136.7, 136.0, 130.6, 125.3, 123.4, 121.3, 121.2, 118.9, 116.8, 115.9, 56.1, 54.3, 35.1, 28.5, 25.0, 23.5.

HRMS (ESI): calcd for $C_{19}H_{25}N_2O$ $[M+H]^+$ *m/z* 297.1961, found 297.1961.

1-(3-(2-amino-2-methylpropyl)-1*H*-indol-1-yl)pent-4-en-1-one (1x)



Physical State: Yellow liquid.

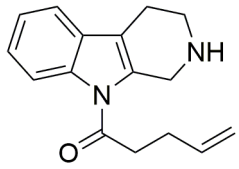
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.31 – 7.25 (m, 2H), 7.24 – 7.18 (m, 1H), 5.87 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.17 – 4.94 (m, 2H), 2.95 (t, *J* = 7.5 Hz, 2H), 2.72 (s, 2H), 2.58 – 2.47 (m, 2H), 1.79 (s, 2H), 1.14 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 136.6, 135.8, 131.5, 125.2, 123.5,

123.3, 119.6, 119.2, 116.6, 116.0, 50.5, 39.5, 35.2, 30.7, 28.5.

HRMS (ESI): calcd for $C_{17}H_{23}N_2O$ $[M+H]^+$ *m/z* 271.1805, found 271.1784.

1-(1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indol-9-yl)pent-4-en-1-one (1y)



Physical State: White solid.

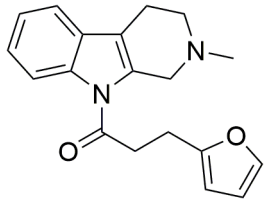
Melting Point: 99.5-100.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 1H), 7.46 – 7.39 (m, 1H), 7.31 – 7.22 (m, 2H), 5.94 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.17 – 5.04 (m, 2H), 4.29 – 4.21 (m, 2H), 3.12 (t, *J* = 5.7 Hz, 2H), 3.04 – 2.97 (m, 2H), 2.70 – 2.64 (m, 2H), 2.61 – 2.53 (m, 2H), 1.89 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 136.7, 135.7, 134.8, 130.5, 124.0, 123.0, 118.2, 116.4, 115.9, 114.9, 46.2, 42.5, 37.6, 28.5, 22.7.

HRMS (ESI): calcd for $C_{16}H_{19}N_2O$ $[M+H]^+$ *m/z* 255.1492, found 255.1492.

3-(furan-2-yl)-1-(2-methyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indol-9-yl)propan-1-one (1z)



Physical State: Yellow solid.

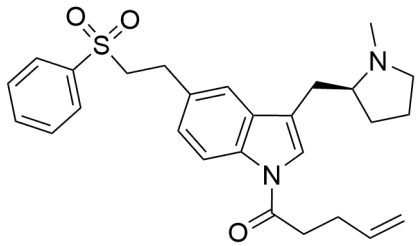
Melting Point: 54.8-55.9 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 1H), 7.47 – 7.40 (m, 1H), 7.36 – 7.31 (m, 1H), 7.30 – 7.22 (m, 2H), 6.31 (dd, *J* = 3.0, 1.9 Hz, 1H), 6.14 – 6.07 (m, 1H), 3.93 (s, 2H), 3.34 (t, *J* = 7.3 Hz, 2H), 3.18 (t, *J* = 7.3 Hz, 2H), 2.79 – 2.76 (m, 4H), 2.54 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 154.0, 141.4, 135.0, 134.6, 130.2, 123.9, 123.1, 118.4, 116.0, 114.7, 110.4, 105.8, 55.1, 51.4, 45.6, 36.9, 23.1, 21.5.

HRMS (ESI): calcd for $C_{19}H_{21}N_2O_2$ $[M+H]^+$ *m/z* 309.1598, found 309.1597.

(*S*)-1-(3-((1-methylpyrrolidin-2-yl)methyl)-5-(2-(phenylsulfonyl)ethyl)-1*H*-indol-1-yl)pent-4-en-1-one (1aa)



Physical State: Yellow solid.

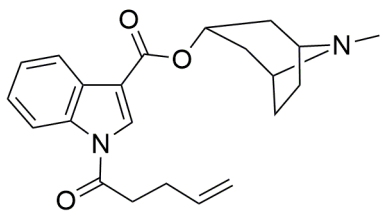
Melting Point: 86.6-87.8 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.1 Hz, 1H), 8.00 – 7.93 (m, 2H), 7.72 – 7.65 (m, 1H), 7.65 – 7.55 (m, 2H), 7.32 (s, 1H), 7.27 (s, 1H), 7.08 (dd, *J* = 8.5, 1.4 Hz, 1H), 5.93 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.19 – 5.03 (m, 2H), 3.47 – 3.38 (m, 2H), 3.24 – 3.13 (m, 3H), 3.11 – 3.05 (m, 1H), 2.99 (t, *J* = 7.4 Hz, 2H), 2.65 – 2.53 (m, 4H), 2.47 (s, 3H), 2.36 – 2.27 (m, 1H), 1.92 – 1.77 (m, 2H), 1.76 – 1.64 (m, 1H), 1.61 – 1.50 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 138.9, 136.5, 134.9, 133.9, 132.6, 131.1, 129.4, 128.1, 125.5, 122.6, 120.0, 118.5, 117.1, 116.1, 65.7, 58.0, 57.5, 40.9, 35.0, 31.4, 29.6, 28.8, 28.4, 21.9.

HRMS (ESI): calcd for $C_{27}H_{33}N_2O_3S$ $[M+H]^+$ *m/z* 465.2206, found 465.2206.

(1*R*,3r,5*S*)-8-methyl-8-azabicyclo[3.2.1]octan-3-yl-1-(pent-4-enoyl)-1*H*-indole-3-carboxylate (1ab)



Physical State: White solid.

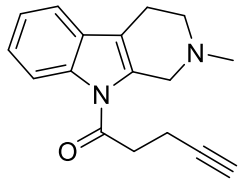
Melting Point: 104.8-105.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 – 8.42 (m, 1H), 8.25 – 8.18 (m, 1H), 8.13 (s, 1H), 7.46 – 7.37 (m, 2H), 5.95 (ddt, *J* = 16.8, 10.2, 6.5 Hz, 1H), 5.29 (t, *J* = 5.4 Hz, 1H), 5.23 – 5.07 (m, 2H), 3.24 – 3.16 (m, 2H), 3.09 (t, *J* = 7.3 Hz, 2H), 2.69 – 2.58 (m, 2H), 2.33 (s, 3H), 2.31 – 2.23 (m, 2H), 2.18 – 2.00 (m, 4H), 1.92 (d, *J* = 15.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 163.4, 136.1, 136.0, 130.2, 127.3, 126.0, 124.8, 121.4, 116.6, 116.5, 114.5, 68.0, 59.8, 40.5, 36.8, 35.1, 28.4, 25.9.

HRMS (ESI): calcd for $C_{22}H_{27}N_2O_3$ $[M+H]^+$ *m/z* 367.2016, found 367.2004.

1-(2-methyl-1,2,3,4-tetrahydro-9*H*-pyrido[3,4-*b*]indol-9-yl)pent-4-yn-1-one (1ac)



Physical State: White solid.

Melting Point: 120.3-121.3 °C.

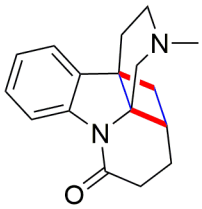
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.71 (m, 1H), 7.44 (dd, *J* = 6.2, 2.5 Hz, 1H), 7.33 – 7.23 (m, 2H), 3.93 (s, 2H), 3.29 – 3.18 (m, 2H), 2.82 – 2.75 (m, 4H), 2.75 – 2.69 (m, 2H), 2.55 (s, 3H), 2.04 (t, *J* = 2.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 134.9, 134.5, 130.3, 124.0, 123.2, 118.5, 116.2, 114.7, 82.7, 69.4, 55.1, 51.4, 45.6, 37.5, 21.5, 14.1.

HRMS (ESI): calcd for $C_{17}H_{19}N_2O$ $[M+H]^+$ *m/z* 267.1492, found 267.1489.

5. Characterization data for products

(4a*R*,5*S*,13b*S*)-3-methyl-1,2,3,4,6,7-hexahydro-5,13b-methanodipyrido[1,2-*a*:3',4'-*b*]indol-8(5*H*)-one (2a)



Physical State: Yellow liquid.

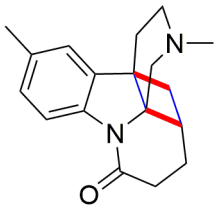
Yield: 72%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1H), 7.26 – 7.17 (m, 1H), 7.09 – 6.93 (m, 2H), 3.30 – 3.19 (m, 1H), 2.97 (dd, *J* = 11.9, 1.1 Hz, 1H), 2.70 – 2.63 (m, 1H), 2.50 – 2.41 (m, 2H), 2.40 – 2.30 (m, 3H), 2.27 (s, 3H), 2.13 (td, *J* = 13.6, 4.6 Hz, 1H), 1.95 (d, *J* = 11.9 Hz, 1H), 1.87 (dd, *J* = 11.4, 9.0 Hz, 1H), 1.76 – 1.58 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 144.8, 136.8, 127.7, 124.5, 121.8, 118.2, 70.5, 60.2, 51.7, 46.5, 43.0, 42.2, 32.8, 31.3, 28.8, 26.3.

HRMS (ESI): calcd for $C_{17}H_{21}N_2O$ $[M+H]^+$ *m/z* 269.1648, found 269.1637.

(4a*R*,5*S*,13b*S*)-3,12-dimethyl-1,2,3,4,6,7-hexahydro-5,13b-methanodipyrido[1,2-*a*:3',4'-*b*]indol-8(5*H*)-one (2b)



Physical State: Yellow solid.

Yield: 91%.

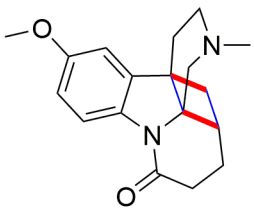
Melting Point: 129.0-132.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.87 (s, 1H), 3.31 – 3.18 (m, 1H), 3.01 (d, *J* = 11.9 Hz, 1H), 2.75 – 2.64 (m, 1H), 2.51 – 2.33 (m, 5H), 2.32 (s, 3H), 2.30 (s, 3H), 2.14 (td, *J* = 13.7, 4.5 Hz, 1H), 1.98 (d, *J* = 11.9 Hz, 1H), 1.85 (dd, *J* = 11.3, 9.0 Hz, 1H), 1.79 – 1.60 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 142.4, 136.7, 134.2, 128.1, 122.6, 117.9, 70.4, 59.9, 51.6, 46.3, 42.9, 42.2, 32.6, 31.0, 28.8, 26.3, 21.2.

HRMS (ESI): calcd for $C_{18}H_{23}N_2O$ $[M+H]^+$ *m/z* 283.1805, found 283.1803.

(4a*R*,5*S*,13b*S*)-12-methoxy-3-methyl-1,2,3,4,6,7-hexahydro-5,13b-methanodipyrido[1,2-*a*:3',4'-*b*]indol-8(5*H*)-one (2c)



Physical State: Yellow solid.

Yield: 80%.

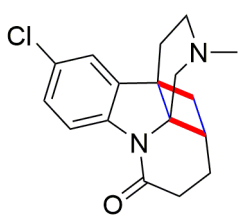
Melting Point: 148.9-151.6 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.6 Hz, 1H), 6.72 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.63 (d, *J* = 2.5 Hz, 1H), 3.79 (s, 3H), 3.30 – 3.19 (m, 1H), 2.98 (d, *J* = 11.9 Hz, 1H), 2.72 – 2.65 (m, 1H), 2.47 – 2.30 (m, 5H), 2.28 (s, 3H), 2.13 (td, *J* = 13.7, 4.5 Hz, 1H), 1.96 (d, *J* = 11.9 Hz, 1H), 1.87 (dd, *J* = 11.3, 9.1 Hz, 1H), 1.76 – 1.60 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 157.1, 138.5, 138.3, 118.6, 111.2, 108.9, 70.7, 59.9, 55.7, 51.6, 46.4, 42.8, 42.2, 32.5, 31.1, 28.8, 26.4.

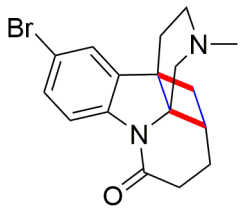
HRMS (ESI): calcd for $C_{18}H_{23}N_2O_2$ $[M+H]^+$ *m/z* 299.1754, found 299.1745.

(4a*R*,5*S*,13b*S*)-12-chloro-3-methyl-1,2,3,4,6,7-hexahydro-5,13b-methanodipyrido[1,2-*a*:3',4'-*b*]indol-8(5*H*)-one (2d)



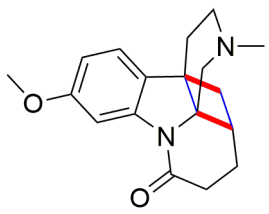
Physical State: Yellow solid.
Yield: 87%.
Melting Point: 133.7-134.4 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 1H), 7.18 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.02 (d, *J* = 1.8 Hz, 1H), 3.30 – 3.20 (m, 1H), 2.98 (d, *J* = 11.9 Hz, 1H), 2.72 – 2.65 (m, 1H), 2.56 – 2.40 (m, 2H), 2.39 – 2.31 (m, 3H), 2.28 (s, 3H), 2.13 (td, *J* = 13.7, 4.5 Hz, 1H), 1.94 (d, *J* = 11.9 Hz, 1H), 1.87 (dd, *J* = 11.3, 9.2 Hz, 1H), 1.76 – 1.60 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 143.4, 138.9, 129.4, 127.5, 122.4, 119.0, 70.9, 60.1, 51.6, 46.4, 42.9, 42.3, 32.6, 31.1, 28.9, 26.2.
HRMS (ESI): calcd for $C_{17}H_{20}ClN_2O$ $[M+H]^+$ *m/z* 303.1259, found 303.1257.

(4a*R*,5*S*,13b*S*)-12-bromo-3-methyl-1,2,3,4,6,7-hexahydro-5,13b-methanodipyrido[1,2-*a*:3',4'-*b*]indol-8(5*H*)-one (2e)



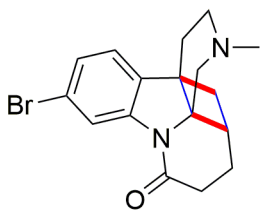
Physical State: White solid.
Yield: 74%.
Melting Point: 159.0-159.5 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 1H), 7.32 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.16 (d, *J* = 2.0 Hz, 1H), 3.29 – 3.20 (m, 1H), 2.96 (d, *J* = 11.9 Hz, 1H), 2.75 – 2.61 (m, 1H), 2.47 – 2.29 (m, 5H), 2.27 (s, 3H), 2.12 (td, *J* = 13.6, 4.6 Hz, 1H), 1.93 (d, *J* = 11.9 Hz, 1H), 1.87 (dd, *J* = 11.4, 9.0 Hz, 1H), 1.75 – 1.62 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 143.9, 139.3, 130.5, 125.3, 119.5, 117.0, 70.9, 60.2, 51.6, 46.4, 43.0, 42.3, 32.6, 31.1, 28.9, 26.2.
HRMS (ESI): calcd for $C_{17}H_{20}BrN_2O$ $[M+H]^+$ *m/z* 347.0754, found 347.0742.

(4a*R*,5*S*,13b*S*)-11-methoxy-3-methyl-1,2,3,4,6,7-hexahydro-5,13b-methanodipyrido[1,2-*a*:3',4'-*b*]indol-8(5*H*)-one (2f)



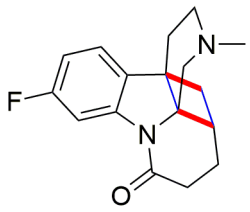
Physical State: Yellow liquid.
Yield: 67%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 2.4 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.60 (dd, *J* = 8.2, 2.4 Hz, 1H), 3.83 (s, 3H), 3.27 – 3.15 m, 1H), 2.97 (d, *J* = 11.8 Hz, 1H), 2.73 – 2.61 (m, 1H), 2.48 – 2.29 (m, 5H), 2.27 (s, 3H), 2.10 (td, *J* = 13.6, 4.6 Hz, 1H), 1.95 (d, *J* = 11.9 Hz, 1H), 1.84 (dd, *J* = 11.3, 9.0 Hz, 1H), 1.74 – 1.62 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 159.6, 146.0, 128.7, 122.1, 110.0, 104.6, 71.1, 60.1, 55.7, 51.6, 46.4, 43.3, 41.6, 32.9, 31.3, 28.7, 26.4.
HRMS (ESI): calcd for $C_{18}H_{23}N_2O_2$ $[M+H]^+$ *m/z* 299.1754, found 299.1754.

(4a*R*,5*S*,13b*S*)-11-bromo-3-methyl-1,2,3,4,6,7-hexahydro-5,13b-methanodipyrido[1,2-*a*:3',4'-*b*]indol-8(5*H*)-one (2g)



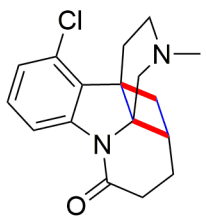
Physical State: White solid.
Yield: 89%.
Melting Point: 146.9-148.9 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 1.7 Hz, 1H), 7.19 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.91 (d, *J* = 7.9 Hz, 1H), 3.29 – 3.17 (m, 1H), 2.97 (d, *J* = 11.9 Hz, 1H), 2.73 – 2.62 (m, 1H), 2.49 – 2.29 (m, 5H), 2.27 (s, 3H), 2.11 (td, *J* = 13.7, 4.6 Hz, 1H), 1.92 (d, *J* = 11.9 Hz, 1H), 1.85 (dd, *J* = 11.4, 9.0 Hz, 1H), 1.74 – 1.59 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 146.0, 136.1, 127.3, 123.1, 121.3, 121.1, 70.9, 60.2, 51.6, 46.5, 43.0, 42.0, 32.7, 31.1, 28.8, 26.2.
HRMS (ESI): calcd for $C_{17}H_{20}BrN_2O$ $[M+H]^+$ *m/z* 347.0754, found 347.0754.

(4a*R*,5*S*,13b*S*)-11-fluoro-3-methyl-1,2,3,4,6,7-hexahydro-5,13b-methanodipyrido[1,2-*a*:3',4'-*b*]indol-8(5*H*)-one (2h)



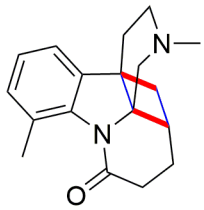
Physical State: White solid.
Yield: 81%.
Melting Point: 136.1-137.0 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 9.6, 2.4 Hz, 1H), 6.96 (dd, *J* = 8.2, 5.4 Hz, 1H), 6.81 – 6.68 (m, 1H), 3.28 – 3.18 (m, 1H), 2.97 (d, *J* = 11.9 Hz, 1H), 2.72 – 2.61 (m, 1H), 2.50 – 2.29 (m, 5H), 2.28 (s, 3H), 2.12 (td, *J* = 13.6, 4.6 Hz, 1H), 1.94 (d, *J* = 11.9 Hz, 1H), 1.85 (dd, *J* = 11.4, 9.0 Hz, 1H), 1.75 – 1.62 (m, 2H).
^{19}F NMR (376 MHz, $CDCl_3$) δ -114.0.
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 162.4 (d, *J* = 243.8 Hz), 146.0 (d, *J* = 12.2 Hz), 132.3 (d, *J* = 2.5 Hz), 122.2 (d, *J* = 10.0 Hz), 110.6 (d, *J* = 22.8 Hz), 106.6 (d, *J* = 27.7 Hz), 71.2, 60.2, 51.6, 46.4, 43.2 (d, *J* = 0.9 Hz), 41.7, 32.7, 31.3, 28.8, 26.3.
HRMS (ESI): calcd for $C_{17}H_{20}FN_2O$ $[M+H]^+$ *m/z* 287.1554, found 287.1544.

(4a*R*,5*S*,13b*S*)-13-chloro-3-methyl-1,2,3,4,6,7-hexahydro-5,13b-methanodipyrido[1,2-*a*:3',4'-*b*]indol-8(5*H*)-one (2i)



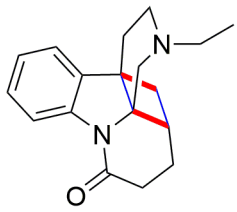
Physical State: Yellow solid.
Yield: 83%.
Melting Point: 109.3-109.9 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 3.41 (dt, *J* = 14.7, 2.5 Hz, 1H), 3.30 – 3.20 (m, 1H), 2.98 (dd, *J* = 11.9, 0.9 Hz, 1H), 2.74 – 2.64 (m, 1H), 2.48 – 2.30 (m, 4H), 2.28 (s, 3H), 2.08 – 1.99 (m, 1H), 1.97 (d, *J* = 11.9 Hz, 1H), 1.91 (dd, *J* = 11.5, 8.9 Hz, 1H), 1.78 – 1.61 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 146.6, 133.0, 129.8, 128.9, 126.0, 116.5, 70.0, 60.6, 52.0, 46.5, 43.9, 42.4, 32.7, 29.9, 28.9, 26.1.
HRMS (ESI): calcd for $C_{17}H_{20}ClN_2O$ $[M+H]^+$ *m/z* 303.1259, found 303.1259.

(4a*R*,5*S*,13b*S*)-3,10-dimethyl-1,2,3,4,6,7-hexahydro-5,13b-methanodipyrido[1,2-*a*:3',4'-*b*]indol-8(5*H*)-one (2j)



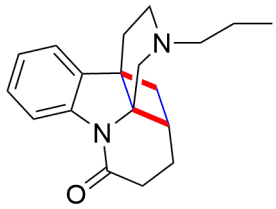
Physical State: Yellow solid.
Yield: 98%.
Melting Point: 140.5-141.9 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 – 7.01 (m, 2H), 6.90 – 6.85 (m, 1H), 3.33 – 3.20 (m, 1H), 3.04 (d, *J* = 11.9 Hz, 1H), 2.64 – 2.56 (m, 1H), 2.49 – 2.33 (m, 4H), 2.38 (s, 3H), 2.30 – 2.25 (m, 1H), 2.25 (s, 3H), 2.07 (td, *J* = 13.6, 4.5 Hz, 1H), 1.94 (d, *J* = 11.9 Hz, 1H), 1.92 – 1.85 (m, 1H), 1.84 – 1.72 (m, 1H), 1.54 (td, *J* = 13.0, 2.5 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 144.1, 138.2, 130.1, 129.9, 125.7, 119.0, 74.4, 59.7, 51.5, 46.4, 43.2, 41.0, 32.5, 31.5, 28.5, 26.4, 20.7.
HRMS (ESI): calcd for $C_{18}H_{23}N_2O$ $[M+H]^+$ *m/z* 283.1805, found 283.1805.

(4a*R*,5*S*,13b*S*)-3-ethyl-1,2,3,4,6,7-hexahydro-5,13b-methanodipyrido[1,2-*a*:3',4'-*b*]indol-8(5*H*)-one (2k)



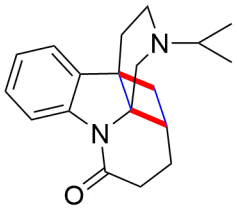
Physical State: White solid.
Yield: 93%.
Melting Point: 83.2-85.4 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1H), 7.26 – 7.15 (m, 1H), 7.15 – 6.98 (m, 2H), 3.30 – 3.20 (m, 1H), 3.02 (dd, *J* = 11.8, 1.2 Hz, 1H), 2.80 – 2.70 (m, 1H), 2.51 – 2.39 (m, 4H), 2.39 – 2.26 (m, 3H), 2.10 (td, *J* = 13.6, 4.6 Hz, 1H), 1.98 (d, *J* = 11.8 Hz, 1H), 1.86 (dd, *J* = 11.3, 9.0 Hz, 1H), 1.76 – 1.62 (m, 2H), 1.06 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 144.8, 137.0, 127.6, 124.4, 121.8, 118.1, 70.5, 57.7, 52.3, 49.3, 43.00, 42.97, 32.7, 31.4, 28.7, 26.4, 11.9.
HRMS (ESI): calcd for $C_{18}H_{23}N_2O$ $[M+H]^+$ *m/z* 283.1805, found 283.1795.

(4a*R*,5*S*,13b*S*)-3-propyl-1,2,3,4,6,7-hexahydro-5,13b-methanodipyrido[1,2-*a*:3',4'-*b*]indol-8(5*H*)-one (2l)



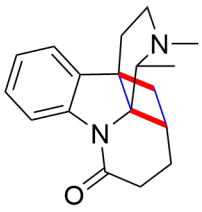
Physical State: Colorless liquid.
Yield: 89%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.16 (m, 1H), 7.12 – 7.01 (m, 2H), 3.33 – 3.19 (m, 1H), 2.99 (d, *J* = 11.7 Hz, 1H), 2.76 – 2.68 (m, 1H), 2.50 – 2.22 (m, 7H), 2.10 (td, *J* = 13.5, 4.4 Hz, 1H), 1.99 (d, *J* = 11.8 Hz, 1H), 1.85 (dd, *J* = 11.1, 9.2 Hz, 1H), 1.76 – 1.61 (m, 2H), 1.57 – 1.43 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 144.8, 137.0, 127.6, 124.4, 121.8, 118.1, 70.5, 60.4, 58.2, 49.7, 43.1, 43.0, 32.8, 31.5, 28.7, 26.4, 20.0, 11.9.
HRMS (ESI): calcd for $C_{19}H_{25}N_2O$ $[M+H]^+$ *m/z* 297.1961, found 297.1947.

(4a*R*,5*S*,13b*S*)-3-isopropyl-1,2,3,4,6,7-hexahydro-5,13b-methanodipyrido[1,2-*a*:3',4'-*b*]indol-8(5*H*)-one (2m)



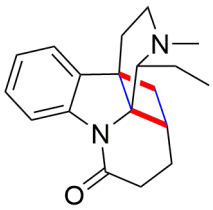
Physical State: Yellow liquid.
Yield: 45%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.11 – 7.01 (m, 2H), 3.35 – 3.21 (m, 1H), 2.92 – 2.77 (m, 2H), 2.70 – 2.62 (m, 1H), 2.48 – 2.22 (m, 6H), 2.10 – 2.02 (m, 1H), 1.91 – 1.80 (m, 2H), 1.73 – 1.63 (m, 1H), 0.98 (d, *J* = 6.6 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 144.9, 137.2, 127.6, 124.4, 121.9, 118.1, 70.8, 54.8, 53.4, 45.4, 43.4, 43.1, 32.8, 32.0, 28.4, 26.5, 18.0 (d, *J* = 5.9 Hz).
HRMS (ESI): calcd for $C_{19}H_{25}N_2O$ $[M+H]^+$ *m/z* 297.1961, found 297.1954.

(4a*R*,5*S*,13b*S*)-3,4-dimethyl-1,2,3,4,6,7-hexahydro-5,13b-methanodipyrido[1,2-*a*:3',4'-*b*]indol-8(5*H*)-one (2n)



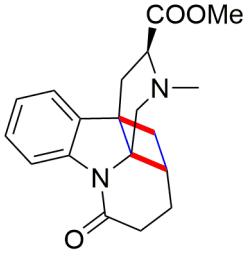
Physical State: Yellow solid.
Yield: 56%, dr=1:11.11.
Melting Point: 118.2-119.9 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.8 Hz, 1H), 7.23 – 7.15 (m, 1H), 7.02 (d, *J* = 4.1 Hz, 2H), 3.40 – 3.29 (m, 1H), 3.12 (q, *J* = 6.9 Hz, 1H), 2.49 – 2.41 (m, 2H), 2.38 (s, 3H), 2.36 – 2.26 (m, 5H), 2.19 – 2.09 (m, 1H), 1.83 (dd, *J* = 11.2, 9.1 Hz, 1H), 1.72 – 1.61 (m, 1H), 0.73 (d, *J* = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 146.2, 138.4, 127.5, 124.0, 121.2, 117.4, 73.4, 59.2, 44.1, 43.4, 42.5, 42.2, 33.0, 31.2, 29.3, 26.1, 5.3.
HRMS (ESI): calcd for $C_{18}H_{23}N_2O$ $[M+H]^+$ *m/z* 283.1805, found 283.1794.

(4a*R*,5*S*,13b*S*)-4-ethyl-3-methyl-1,2,3,4,6,7-hexahydro-5,13b-methanodipyrido[1,2-*a*:3',4'-*b*]indol-8(5*H*)-one (2o)



Physical State: Yellow solid.
Yield: 12%, (The yield using HFIP instead of TFE is 64%, dr=1:2.23).
Melting Point: 139.7-140.4 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.8 Hz, 1H), 7.23 – 7.15 (m, 1H), 7.09 – 6.96 (m, 2H), 3.33 – 3.13 (m, 1H), 2.71 – 2.61 (m, 1H), 2.47 (s, 3H), 2.44 – 2.28 (m, 6H), 2.21 – 2.08 (m, 1H), 1.84 (dd, *J* = 11.3, 9.0 Hz, 1H), 1.69 – 1.61 (m, 2H), 1.33 – 1.26 (m, 1H), 1.21 – 1.09 (m, 1H), 0.85 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 146.3, 138.8, 127.5, 124.1, 121.3, 117.2, 73.4, 66.2, 44.0, 43.8, 43.7, 42.4, 33.1, 30.3, 30.2, 26.5, 17.3, 14.0.
HRMS (ESI): calcd for $C_{19}H_{25}N_2O$ $[M+H]^+$ *m/z* 297.1961, found 297.1950.

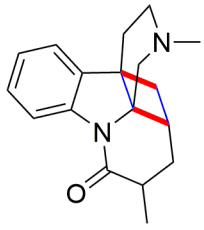
Methyl-(2*S*,4a*R*,5*S*,13b*S*)-3-methyl-8-oxo-1,2,3,4,5,6,7,8-octahydro-5,13b-methanodipyrido[1,2-*a*:3',4'-*b*]indole-2-carboxylate (2p)



Physical State: Yellow solid.
Yield: 97%, dr=1:1.24.
Melting Point: 134.6-138.7 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.8 Hz, 1H), 7.22 – 7.13 (m, 1H), 7.04 – 6.94 (m, 2H), 3.50 – 3.42 (m, 1H), 3.28 (d, *J* = 12.0 Hz, 1H), 3.22 – 3.10 (m, 4H), 2.95 (dd, *J* = 14.3, 1.9 Hz, 1H), 2.80 (d, *J* = 12.0 Hz,

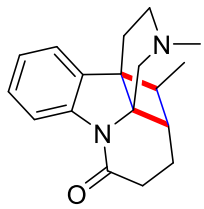
1H), 2.52 (s, 3H), 2.48 – 2.29 (m, 5H), 1.87 (dd, *J* = 11.3, 9.2 Hz, 1H), 1.74 – 1.62 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 170.4, 144.7, 136.2, 127.8, 123.9, 121.9, 118.2, 69.4, 58.3, 53.5, 50.6, 43.7, 43.6, 41.1, 33.1, 32.9, 29.5, 26.2.
HRMS (ESI): calcd for $C_{19}H_{23}N_2O_3$ $[M+H]^+$ *m/z* 327.1703, found 327.1703.

(4a*R*,5*S*,13b*S*)-3,7-dimethyl-1,2,3,4,6,7-hexahydro-5,13b-methanodipyrido[1,2-*a*:3',4'-*b*]indol-8(5*H*)-one (2q)



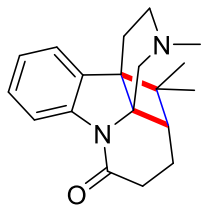
Physical State: Yellow solid.
Yield: 76%, dr>20:1.
Melting Point: 166.8-168.6 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.18 (m, 1H), 7.05 (d, *J* = 4.4 Hz, 2H), 3.31 – 3.19 (m, 1H), 3.04 (d, *J* = 11.9 Hz, 1H), 2.73 – 2.62 (m, 1H), 2.55 – 2.41 (m, 2H), 2.37 – 2.24 (m, 5H), 2.12 (td, *J* = 13.6, 4.6 Hz, 1H), 1.95 (d, *J* = 11.9 Hz, 1H), 1.86 (dd, *J* = 11.3, 9.0 Hz, 1H), 1.68 (td, *J* = 13.1, 2.4 Hz, 1H), 1.43 (td, *J* = 13.5, 4.5 Hz, 1H), 1.20 (d, *J* = 6.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 145.0, 137.1, 127.7, 124.3, 121.8, 118.3, 70.4, 60.1, 51.7, 46.5, 43.2, 42.5, 35.8, 35.5, 31.3, 28.9, 14.6.
HRMS (ESI): calcd for $C_{18}H_{23}N_2O$ $[M+H]^+$ *m/z* 283.1805, found 283.1804.

(4a*R*,5*S*,13b*R*)-3,14-dimethyl-1,2,3,4,6,7-hexahydro-5,13b-methanodipyrido[1,2-*a*:3',4'-*b*]indol-8(5*H*)-one (2r)



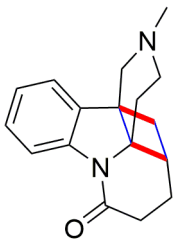
Physical State: Yellow viscous liquid.
Yield: 74%, dr = 4.7:1 (The yield using HFIP instead of TFE is 68%, dr=18.3:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.7 Hz, 1H), 7.22 (t, *J* = 7.0 Hz, 1H), 7.12 – 7.00 (m, 2H), 3.02 (d, *J* = 11.6 Hz, 1H), 2.73 (d, *J* = 8.3 Hz, 2H), 2.51 – 2.19 (m, 7H), 2.17 – 2.05 (m, 2H), 2.01 (d, *J* = 11.7 Hz, 1H), 1.75 (t, *J* = 11.8 Hz, 1H), 1.70 – 1.57 (m, 1H), 1.06 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 144.6, 137.6, 127.6, 124.4, 121.6, 118.5, 68.4, 60.1, 51.3, 47.3, 46.4, 45.9, 37.2, 32.5, 24.6, 23.8, 13.8.
HRMS (ESI): calcd for $C_{18}H_{23}N_2O$ $[M+H]^+$ *m/z* 283.1805, found 283.1804.

(4a*R*,5*S*,13b*R*)-3,14,14-trimethyl-1,2,3,4,6,7-hexahydro-5,13b-methanodipyrido[1,2-*a*:3',4'-*b*]indol-8(5*H*)-one (2s)



Physical State: Light yellow solid.
Yield: 28%, (The yield using HFIP instead of TFE).
Melting Point: 164.6-166.0 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.7 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 7.2 Hz, 1H), 7.03 (d, *J* = 7.1 Hz, 1H), 3.02 (d, *J* = 11.7 Hz, 1H), 2.86 (dd, *J* = 10.0, 3.5 Hz, 1H), 2.75 – 2.65 (m, 1H), 2.59 – 2.47 (m, 1H), 2.46 – 2.30 (m, 2H), 2.26 (s, 3H), 2.17 – 2.03 (m, 2H), 1.96 (d, *J* = 11.7 Hz, 1H), 1.85 – 1.64 (m, 2H), 1.17 (s, 3H), 0.52 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 145.5, 135.2, 127.8, 124.5, 123.4, 117.9, 67.1, 61.9, 51.9, 49.4, 46.5, 41.6, 40.2, 32.7, 27.3, 26.5, 22.6, 18.8.
HRMS (ESI): calcd for $C_{19}H_{25}N_2O$ $[M+H]^+$ *m/z* 297.1961, found 297.1980.

(4a*R*,5*S*,13b*R*)-2-methyl-1,2,3,4,6,7-hexahydro-5,13b-methanodipyrido[1,2-*a*:4',3'-*b*]indol-8(5*H*)-one (2t)



Physical State: White solid.

Yield: 79%.

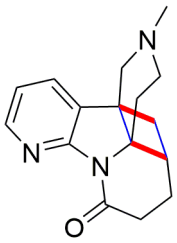
Melting Point: 127.3-128.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.8 Hz, 1H), 7.20 (td, *J* = 7.8, 1.5 Hz, 1H), 7.08 (dtd, *J* = 8.1, 7.3, 1.0 Hz, 2H), 3.54 (dd, *J* = 12.3, 1.6 Hz, 1H), 3.04 – 2.93 (m, 1H), 3.82 – 2.73 (m, 1H), 2.49 – 2.26 (m, 8H), 2.10 (td, *J* = 12.3, 3.4 Hz, 1H), 1.98 – 1.80 (m, 3H), 1.73 – 1.62 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.3, 144.2, 136.8, 127.8, 124.7, 121.3, 118.2, 68.8, 60.6, 51.9, 46.7, 44.7, 41.2, 32.8, 31.7, 28.8, 26.4.

HRMS (ESI): calcd for $C_{17}H_{21}N_2O$ $[M+H]^+$ *m/z* 269.1648, found 269.1648.

(4a*R*,5*S*,13b*R*)-2-methyl-1,2,3,4,6,7-hexahydro-5,13b-methanodipyrido[3,2-*b*:4',3'-*i*]indolizin-8(5*H*)-one (2u)



Physical State: White solid.

Yield: 57%.

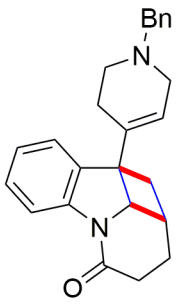
Melting Point: 153.2-155.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.09 (m, 1H), 7.36 – 7.30 (m, 1H), 6.90 (dd, *J* = 7.2, 5.3 Hz, 1H), 3.48 – 3.38 (m, 1H), 3.02 – 2.92 (m, 1H), 2.77 – 2.66 (m, 1H), 2.51 – 2.42 (m, 1H), 2.37 – 2.22 (m, 7H), 2.05 (td, *J* = 12.4, 3.3 Hz, 1H), 1.97 – 1.79 (m, 3H), 1.72 – 1.60 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.7, 158.4, 147.2, 130.7, 130.1, 119.5, 67.7, 60.2, 51.7, 46.6, 43.0, 40.7, 33.5, 32.3, 29.3, 26.1.

HRMS (ESI): calcd for $C_{16}H_{20}N_3O$ $[M+H]^+$ *m/z* 270.1601, found 270.1601.

(1a*S*,1a^1*R*,9b*S*)-9b-(1-benzyl-1,2,3,6-tetrahydropyridin-4-yl)-1,1a,1a^1,2,3,9b-hexahydro-4*H*-benzo[*b*]cyclobuta[*hi*]indolizin-4-one (2v)



Physical State: Yellow liquid.

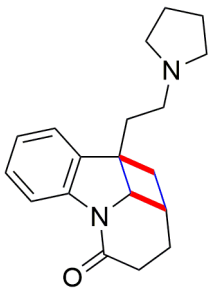
Yield: 32%, (The yield using HFIP instead of TFE is 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.30 (m, 4H), 7.30 – 7.26 (m, 1H), 7.19 (td, *J* = 7.8, 1.2 Hz, 1H), 7.04 – 6.95 (m, 1H), 6.94 – 6.88 (m, 1H), 5.96 – 5.80 (m, 1H), 4.53 – 4.42 (m, 1H), 3.70 – 3.58 (m, 2H), 3.31 – 3.20 (m, 1H), 3.15 – 3.05 (m, 1H), 3.01 – 2.85 (m, 2H), 2.72 – 2.63 (m, 1H), 2.51 – 2.39 (m, 2H), 2.29 – 2.09 (m, 3H), 2.07 – 1.96 (m, 1H), 1.94 – 1.85 (m, 1H), 1.61 – 1.46 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 145.6, 138.03, 137.96, 133.8, 129.2, 128.3, 127.6, 127.2, 124.2, 122.9, 122.3, 117.2, 65.8, 62.7, 53.3, 53.1, 49.7, 39.3, 35.0, 28.6, 26.3, 26.1.

HRMS (ESI): calcd for $C_{25}H_{27}N_2O$ $[M+H]^+$ *m/z* 371.2118, found 371.2118.

(1a*S*,1a^1*R*,9b*S*)-9b-(2-(pyrrolidin-1-yl)ethyl)-1,1a,1a^1,2,3,9b-hexahydro-4*H*-benzo[*b*]cyclobuta[*hi*]indolizin-4-one (2w)



Physical State: Yellow liquid.

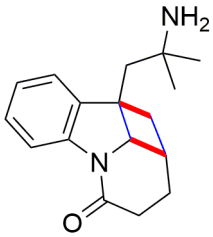
Yield: 36%, (The yield using HFIP instead of TFE is 98%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.9 Hz, 1H), 7.12 (ddd, *J* = 7.9, 6.6, 2.3 Hz, 1H), 6.99 – 6.92 (m, 2H), 4.31 (dd, *J* = 6.1, 3.3 Hz, 1H), 3.02 – 2.89 (m, 1H), 2.51 – 2.28 (m, 8H), 2.25 – 2.04 (m, 4H), 1.93 (dd, *J* = 12.0, 8.9 Hz, 1H), 1.81 – 1.64 (m, 4H), 1.51 – 1.39 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 145.5, 137.6, 127.5, 124.1, 121.8, 117.2, 64.9, 54.3, 52.4, 46.9, 42.4, 35.0, 32.5, 28.2, 26.2, 23.4.

HRMS (ESI): calcd for $C_{19}H_{25}N_2O$ $[M+H]^+$ *m/z* 297.1961, found 297.1961.

(1a*S*,1a^1*R*,9b*S*)-9b-(2-amino-2-methylpropyl)-1,1a,1a^1,2,3,9b-hexahydro-4*H*-benzo[*b*]cyclobuta[*hi*]indolizin-4-one (2x)



Physical State: Yellow solid.

Yield: 77% (The yield using HFIP instead of TFE).

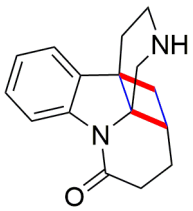
Melting Point: 110.0-113.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.9 Hz, 1H), 7.15 – 7.04 (m, 2H), 6.93 (t, *J* = 7.4 Hz, 1H), 4.77 (dd, *J* = 5.9, 3.2 Hz, 1H), 4.15 (s, 2H), 3.13 – 3.00 (m, 1H), 2.46 (d, *J* = 15.2 Hz, 1H), 2.41 – 2.28 (m, 2H), 2.24 (d, *J* = 15.3 Hz, 1H), 2.21 – 2.09 (m, 2H), 1.91 (dd, *J* = 11.8, 9.2 Hz, 1H), 1.45 – 1.34 (m, 1H), 1.15 (d, *J* = 4.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 145.2, 137.7, 127.5, 123.8, 122.4, 117.2, 64.5, 53.5, 47.3, 46.1, 44.0, 35.1, 30.7 (d, *J* = 150.2 Hz), 28.0, 25.8.

HRMS (ESI): calcd for $C_{17}H_{23}N_2O$ $[M+H]^+$ *m/z* 271.1805, found 271.1783.

(4a*R*,5*S*,13b*S*)-1,2,3,4,6,7-hexahydro-5,13b-methanodipyrido[1,2-*a*:3',4'-*b*]indol-8(5*H*)-one (2y)



Physical State: Yellow solid.

Yield: 90%, (The yield using HFIP instead of TFE is 91%).

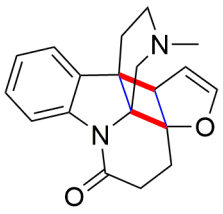
Melting Point: 141.0-144.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1H), 7.26 – 7.18 (m, 1H), 7.12 – 7.01 (m, 2H), 3.31 – 3.20 (m, 1H), 3.16 (d, *J* = 12.8 Hz, 1H), 3.00 – 2.91 (m, 1H), 2.67 (d, *J* = 12.8 Hz, 1H), 2.49 – 2.39 (m, 2H), 2.38 – 2.21 (m, 4H), 2.01 – 1.84 (m, 3H), 1.75 – 1.62 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 144.8, 136.9, 127.7, 124.4, 121.8, 118.2, 69.2, 50.7, 43.5, 43.4, 42.4, 32.8, 31.8, 28.0, 26.3.

HRMS (ESI): calcd for $C_{16}H_{19}N_2O$ $[M+H]^+$ *m/z* 255.1492, found 255.1492.

(3a*R*,3a^1*R*,6a*R*,6b*R*)-14-methyl-2,3-dihydro-1*H*,6a*H*-6b,3a^1-(ethanoiminomethano)benzo[*b*]furo[2',3':1,4]cyclobuta[1,2,3-*hi*]indolizin-1-one (2z)



Physical State: Yellow solid.

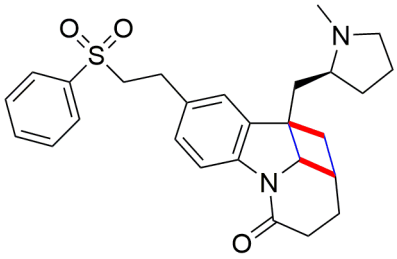
Yield: 29% (The yield using HFIP instead of TFE).

Melting Point: 146.1-149.4 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.9 Hz, 1H), 7.26 – 7.19 (m, 1H), 7.13 – 7.06 (m, 2H), 6.70 (d, *J* = 2.7 Hz, 1H), 5.00 (t, *J* = 3.1 Hz, 1H), 3.46

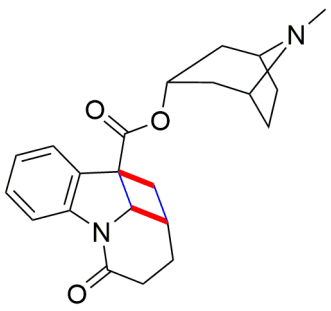
(d, *J* = 12.1 Hz, 1H), 3.27 (d, *J* = 3.5 Hz, 1H), 2.69 – 2.56 (m, 2H), 2.52 – 2.41 (m, 2H), 2.28 – 2.14 (m, 5H), 2.09 (d, *J* = 12.1 Hz, 1H), 1.92 (dt, *J* = 13.8, 3.0 Hz, 1H), 1.75 (td, *J* = 11.8, 3.0 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 150.1, 143.8, 136.6, 128.1, 124.7, 122.4, 117.1, 99.9, 89.0, 71.2, 58.71, 58.69, 50.5, 47.4, 46.9, 33.7, 32.9, 25.8.
HRMS (ESI): calcd for $C_{19}H_{21}N_2O_2$ $[M+H]^+$ *m/z* 309.1598, found 309.1598.

(1a*S*,1a^1*R*,9b*S*)-9b-(((*S*)-1-methylpyrrolidin-2-yl)methyl)-8-(2-(phenylsulfonyl)ethyl)-1,1a,1a^1,2,3,9b-hexahydro-4*H*-benzo[*b*]cyclobuta[*hi*]indolizin-4-one (2aa)



Physical State: Yellow solid.
Yield: 55%, dr=1:1.53.
Melting Point: 126.3-130.9 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (t, *J* = 7.4 Hz, 3H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 2H), 7.02 (dd, *J* = 8.1, 1.4 Hz, 1H), 6.96 (s, 1H), 4.43 (dd, *J* = 6.1, 3.0 Hz, 1H), 3.71 – 3.54 (m, 1H), 3.43 – 3.27 (m, 2H), 3.27 – 3.18 (m, 1H), 3.17 – 3.00 (m, 3H), 2.86 (s, 3H), 2.71 – 2.61 (m, 2H), 2.57 – 2.43 (m, 3H), 2.34 – 2.25 (m, 1H), 2.18 (td, *J* = 14.2, 5.4 Hz, 1H), 2.12 – 2.00 (m, 2H), 1.99 – 1.78 (m, 3H), 1.55 – 1.44 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 144.6, 139.6, 135.8, 134.0, 133.6, 129.5, 127.9, 127.7, 123.0, 117.8, 65.5, 65.1, 57.7, 55.0, 46.5, 43.5, 38.6, 34.9, 32.9, 30.2, 28.3, 27.7, 26.0, 21.1.
HRMS (ESI): calcd for $C_{27}H_{33}N_2O_3S$ $[M+H]^+$ *m/z* 465.2206, found 465.2206.

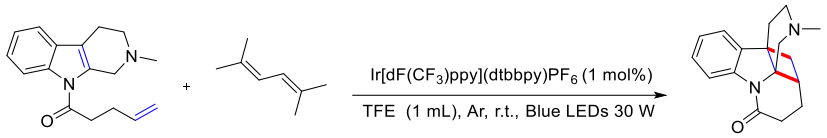
(1*R*,3*r*,5*S*)-8-methyl-8-azabicyclo[3.2.1]octan-3-yl-(1a*S*,1a^1*R*,9b*S*)-4-oxo-1a,2,3,4-tetrahydro-1*H*-benzo[*b*]cyclobuta[*hi*]indolizine-9b(1a^1*H*)-carboxylate (2ab)



Physical State: Yellow liquid.
Yield: 54%, (The yield using HFIP instead of TFE is 98%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.9 Hz, 1H), 7.31 – 7.22 (m, 2H), 7.05 (t, *J* = 7.5 Hz, 1H), 5.17 (t, *J* = 5.2 Hz, 1H), 4.81 (dd, *J* = 5.8, 3.7 Hz, 1H), 3.25 – 3.07 (m, 4H), 2.54 – 2.45 (m, 1H), 2.34 – 2.19 (m, 8H), 2.08 – 1.88 (m, 2H), 1.88 – 1.69 (m, 3H), 1.67 – 1.51 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 171.0, 145.3, 133.1, 128.4, 124.3, 123.0, 117.5, 68.8, 65.1, 59.70, 59.67, 52.2, 40.7, 40.4, 36.6, 36.5, 34.8, 29.2, 26.3, 25.7, 25.4.
HRMS (ESI): calcd for $C_{22}H_{27}N_2O_3$ $[M+H]^+$ *m/z* 367.2016, found 367.2014.

6. Preliminary mechanistic studies

6.1 Control experiment with triplet quencher



1a, 0.1 mmol **3a**, 0.1 mmol **2a**, 7%

An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the indole derivative **1a** (27.0 mg, 0.1 mmol) and **PC-I** (1.2 mg, 1 mol%). The Schlenk tube was then connected to a vacuum line where it was evacuated and back-filled with argon for 3 times. Then TFE (1 mL), which bubbled with argon for 5 minutes, and 2,5-dimethylhexa-2,4-diene (known as a triplet quencher, 14.3 μL, 0.1 mmol), were added to the reaction in sequence under argon flow. Finally, the reaction mixture in a sealed tube was placed at a distance of 2 ~ 3 cm from a 30 W blue LED and stirred at room temperature for 12 h. Then, the mixture was concentrated in vacuo. The yield of the product was determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol) as internal standard. The model reaction was significantly inhibited in the presence of 1.0 equivalent of 2,5-dimethylhexa-2,4-diene.

6.2 Stern-Volmer quenching studies

Stern-Volmer experiments were conducted on a PerkinElmer LS55 Fluorescence Spectrophotometer. Before each set of experiments, each component was prepared in TFE and DCM. The solutions were irradiated at 440 nm and the luminescence was measured at 467 nm. Linear regression of I_0/I against concentration was performed in Origin.

Species	Solvent	Concentration (mM)
$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DCM	0.1
1a	DCM	Varied
$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	TFE	0.1
1a	TFE	Varied

Substrate (mM)	0.000	0.250	0.500	0.750	1.000	1.250	1.500
I_0/I in DCM	1.000	1.145	1.513	1.765	1.918	2.062	2.213
I_0/I in TFE	1.000	1.031	1.049	1.062	1.084	1.108	1.125

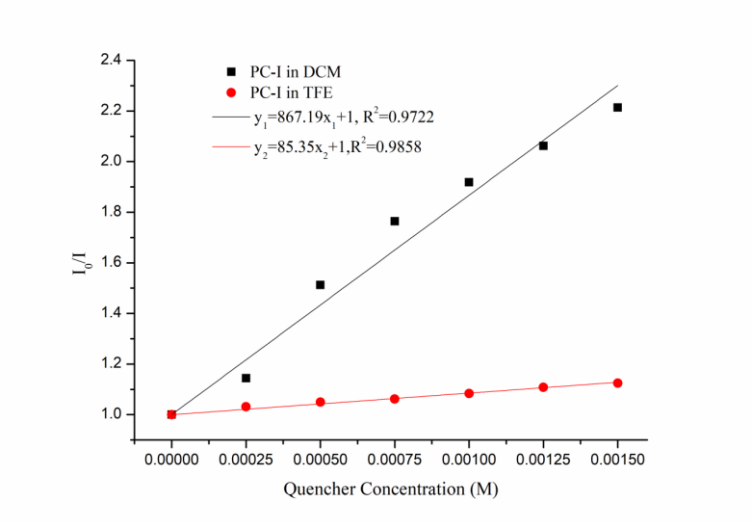


Figure S2. Stern-Volmer quenching experiments with **PC-I** in DCM and TFE (0.1 mM, λ_{ex} = 440 nm, λ_{em} = 467 nm)

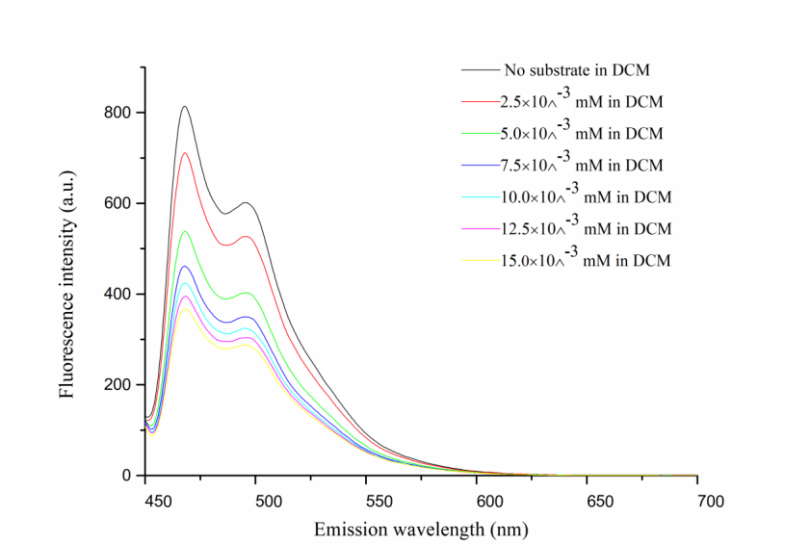


Figure S3. Emission spectra of **PC-I** (0.1 mM, DCM, λ_{ex} = 440 nm) in the presence of **1a**.

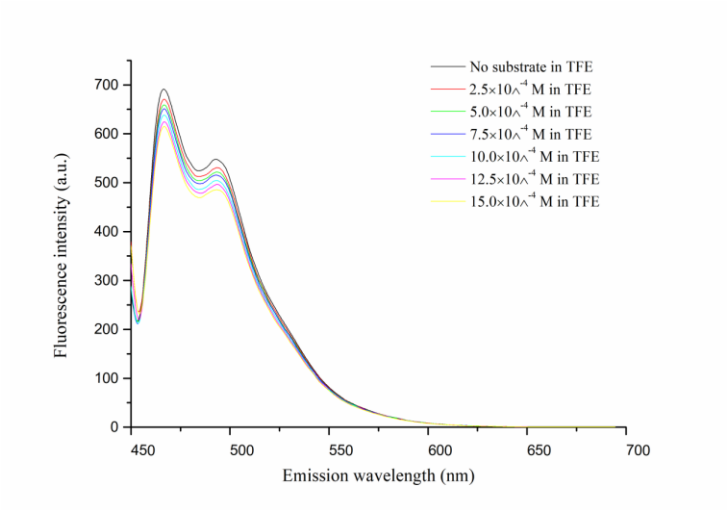


Figure S4. Emission spectra of **PC-I** (0.1 mM, TFE, λ_{ex} = 440 nm) in the presence of **1a**.

6.3 Cyclic voltammetry test

Cyclic voltammetry test was performed in a three-electrode cell under argon at room temperature. All cyclic voltammograms were measured using Ag/Ag^+ (0.01 M $AgNO_3$ in MeCN) reference electrode, a platinum (Pt) wire counter electrode and a glassy carbon working electrode. The conditions of the experiments were as follows: testing compounds are in solution of 0.1 M Tetrabutylammonium hexafluorophosphate ($^nBu_4NPF_6$) in DCM, TFE or HFIP at a scan rate of 50 mV/s; Prior to each measurement, solutions were purged with argon (Ar) for 10 minutes to ensure the oxygen-free conditions.

Under our experimental conditions, the oxidation peaks of the substrate **1a** in DCM, TFE and HFIP were measured as shown in the figure below.

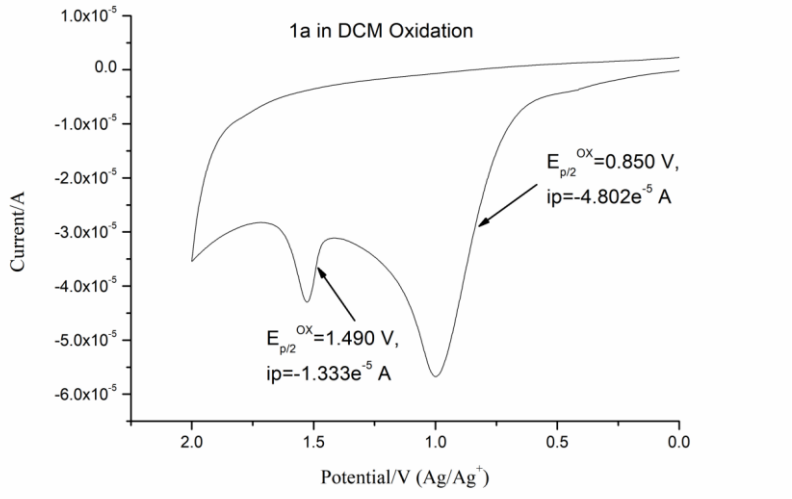


Figure S5. Cyclic voltammetry of **1a** (0.005 M) in DCM (vs Ag/Ag^+) with $^nBu_4NPF_6$ (0.1 M) under argon at a glassy carbon electrode at a scan rate of 50 mV/s.

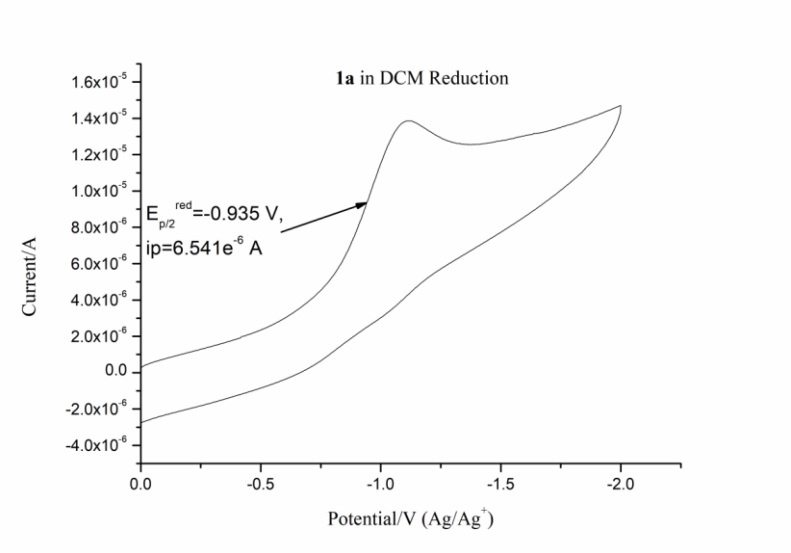


Figure S6. Cyclic voltammetry of **1a** (0.005 M) in DCM (vs Ag/Ag^+) with $^nBu_4NPF_6$ (0.1 M) under argon at a glassy carbon electrode at a scan rate of 50 mV/s.

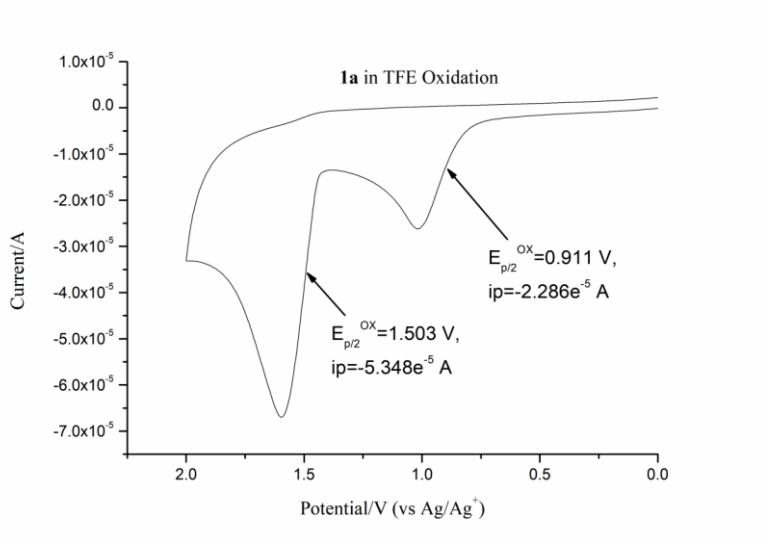


Figure S7. Cyclic voltammetry of **1a** (0.005 M) in TFE (vs Ag/Ag^+) with $^nBu_4NPF_6$ (0.1 M) under argon at a glassy carbon electrode at a scan rate of 50 mV/s.

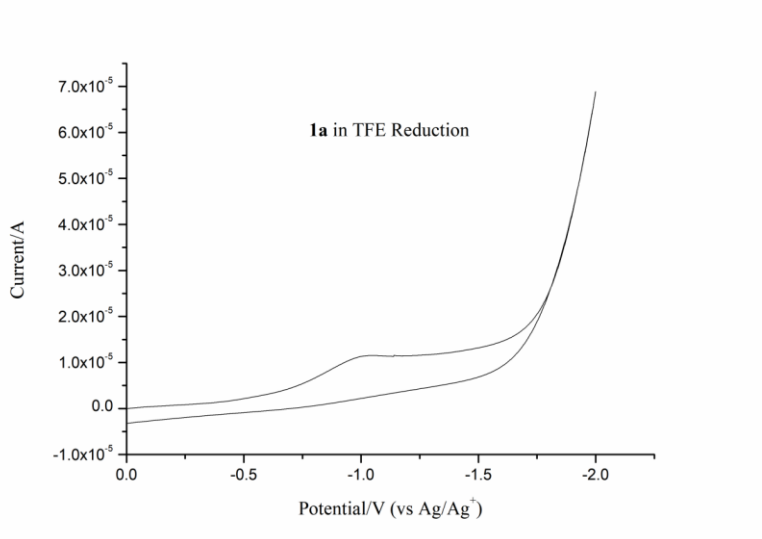


Figure S8. Cyclic voltammetry of **1a** (0.005 M) in TFE (vs Ag/Ag^+) with $^nBu_4NPF_6$ (0.1 M) under argon at a glassy carbon electrode at a scan rate of 50 mV/s.

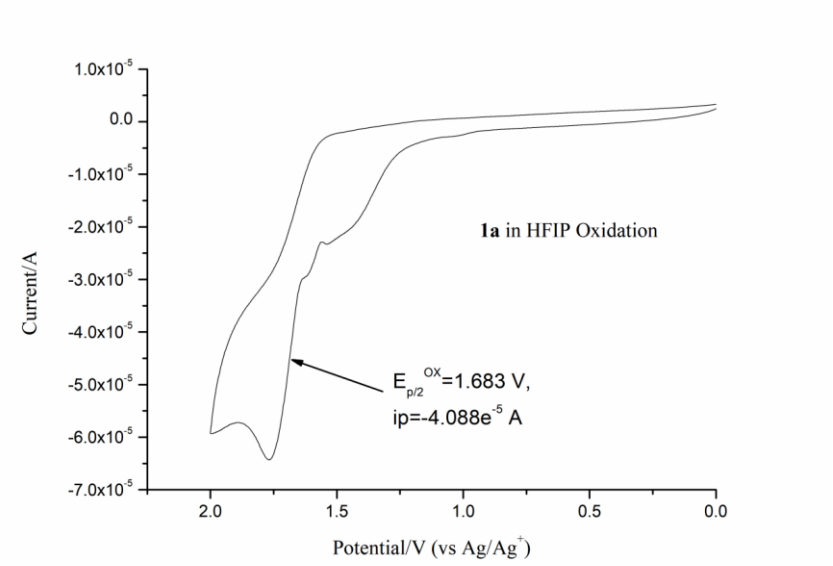


Figure S9. Cyclic voltammetry of **1a** (0.005 M) in HFIP (vs Ag/Ag^+) with $^nBu_4NPF_6$ (0.1 M) under argon at a glassy carbon electrode at a scan rate of 50 mV/s.

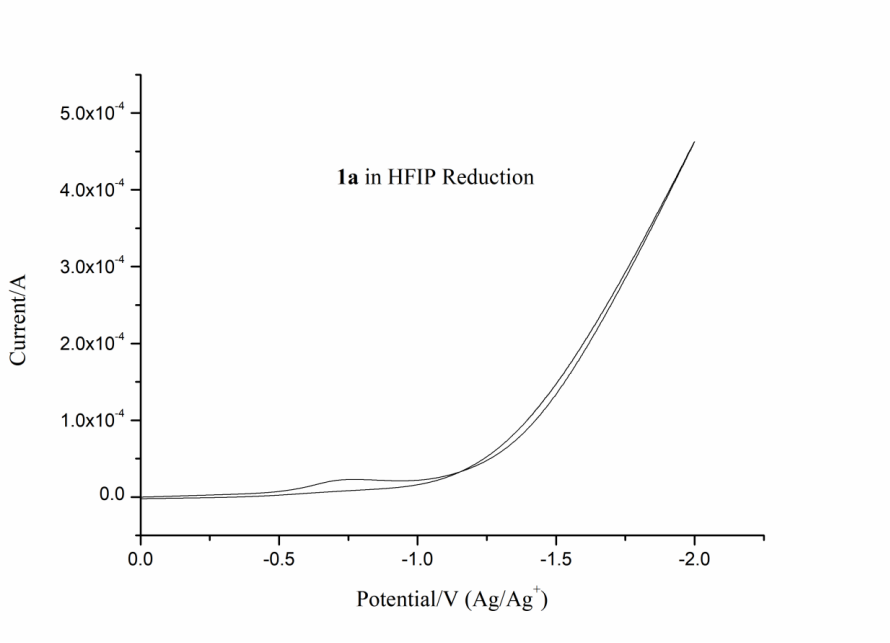


Figure S10. Cyclic voltammetry of **1a** (0.005 M) in HFIP (vs Ag/Ag^+) with $^nBu_4NPF_6$ (0.1 M) under argon at a glassy carbon electrode at a scan rate of 50 mV/s.

6.4 Computational studies

All calculations were performed with the Gaussian 16 C.01 version[9] and GaussView 6.1.1 was used to build up input structure, if not otherwise stated. The hydrogen bond effect has been investigated at the (U)B3LYP-D3(BJ)/def2-SVP level.[10] The HOMO molecular orbitals of **1a** and **1a**-alcohol H-bonded complexes were generated by Gaussview 6.1.1. The solvent effect was taken into account for the investigation of the bond lengths of H-bonded complexes by the Polarizable Continuum Model.[11] All the optimized structures were confirmed to have no imaginary frequency.

6.4.1 The calculated results of different H-bonded complexes

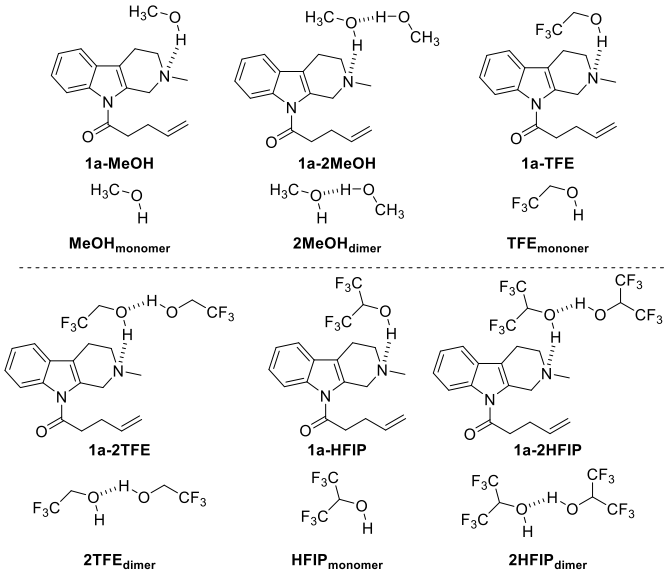


Figure S11. Proposed structures of H-bonded complexes and monomer or dimer of solvents.

Table S1. Calculated thermal enthalpy correction for electronic energy in vacuum and binding energies of different H-bonded complexes of **1a**.[1]

	$H_{complexes}$[2]	H_{mono} *or* H_{dimer}[3]	E_{BSSE}[4]	ΔH / eV	ΔH[5]/kcal mol^{-1}
1a	-843.682463				
1a-MeOH	-959.279681	-115.579726	0.007341529	-0.010150	-6.36952
1a-2MeOH	-1074.887324	-231.17249	0.013568305	-0.018803	-11.7989
1a-TFE	-1296.075124	-452.364962	0.010648244	-0.017051	-10.6995
1a-2TFE	-1748.47662	-904.752977	0.019952716	-0.021227	-13.3203
1a-HFIP	-1632.858092	-789.146803	0.011693479	-0.017133	-10.7508
1a-2HFIP	-2422.033483	-1578.313198	0.014676414	-0.023146	-14.5241

[1] Computational method: (U)B3LYP-D3(BJ)/def2-SVP. [2] Thermal enthalpy correction for electronic energy of **1a** and H-bonded complexes. [3] Thermal enthalpy correction for electronic energy of monomers or dimers of solvents. [4] Basis set superposition error. [5] Binding energies of H-bonded complexes.

6.4.2 The calculated results for HOMO molecular orbitals of 1a and H-bonded complexes

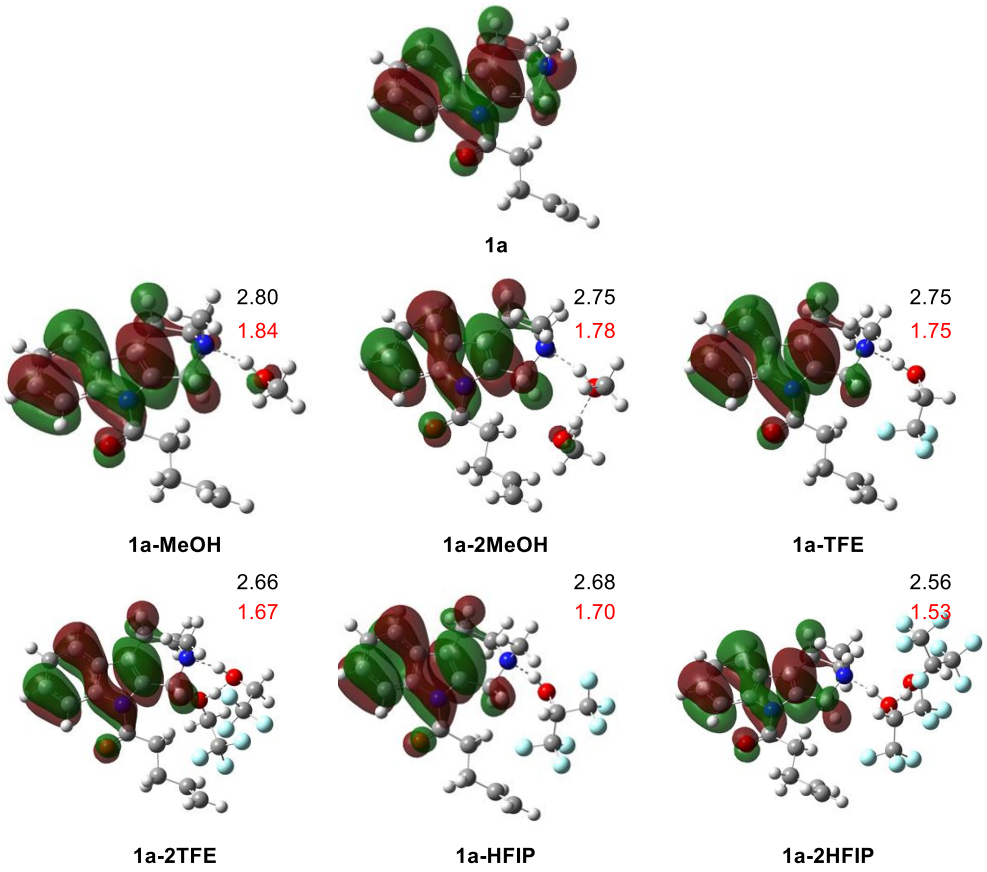
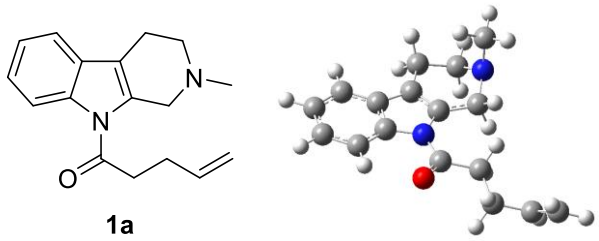


Figure S12. The HOMO molecular orbitals of **1a** and H-bonded complexes of **1a** with alcohol solvents. The bond lengths of N···H in red color, and the distances of N-atom and O-atom in black color. Computational method: (U)B3LYP-D3(BJ)/def2-SVP/PCM (Solvent).

6.4.3 Cartesian coordinates and energies of all optimized structures

(1) At (U)B3LYP-D3(BJ) / def2-SVP level of theory



1a

SCF Done: E(RB3LYP) = -844.000878235 A.U.

Zero-point correction = 0.339069 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -843.748372

C,0,2.3809745908,-0.2395180256,-0.1519118268

C,0,1.3900337737,-1.2497320671,-0.2327074535

C,0,1.7341303799,-2.606051566,-0.2213771062

C,0,3.0909565102,-2.9277525643,-0.1288867693

C,0,4.0830271574,-1.9354557392,-0.0492784022

C,0,3.7359699263,-0.585836309,-0.0594008063

C,0,1.7012850193,1.033669392,-0.1855881664

C,0,0.3581702217,0.7953741994,-0.292226947

H,0,0.9709230489,-3.3752198425,-0.2879460725

H,0,3.3829112284,-3.9806225255,-0.121916853

H,0,5.1337283087,-2.2268623893,0.0199899478

H,0,4.5014887995,0.1911671525,0.0028453317

N,0,0.1265420511,-0.6084756873,-0.3009761791

C,0,-1.0839807441,-1.3173615885,-0.2870198816

O,0,-1.0939623987,-2.5279117071,-0.3730932033

C,0,-2.3790109884,-0.5370772605,-0.127744414

H,0,-2.5535151712,0.0631013117,-1.0344394984

C,0,-3.5790524696,-1.4602821703,0.1084137834

H,0,-3.3780822394,-2.0745485063,1.002941888

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H,0,-4.8831377751,-0.0025744811,1.1492853907

C,0,-5.919451543,-0.762672967,-0.5102025432

H,0,-5.9332021244,-1.429937601,-1.3786145012

H,0,-2.2768546436,0.1833876412,0.6982202761

H,0,-3.6694927764,-2.1656580308,-0.7306680281

H,0,-6.8192637618,-0.1695371923,-0.3256422474

C,0,2.2969841207,2.4069884662,-0.1414576448

H,0,3.028885163,2.4856630504,0.6807794092

H,0,2.8646350619,2.6040333494,-1.0693868029

C,0,1.1742953911,3.4451245714,0.0427866858

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H,0,1.541503744,4.4603445396,-0.1760565722

C,0,-0.643517233,1.9236253292,-0.4232832625

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H,0,-1.1920797434,2.06769043,0.5261418011
N,0,0.0064078888,3.1747455077,-0.7867430237
C,0,0.2558383764,3.302845856,-2.2118410949
H,0,-0.6974920939,3.2587619856,-2.7622391887
H,0,0.7129101489,4.28371204,-2.4162475217
H,0,0.9232817151,2.521963884,-2.6350907975

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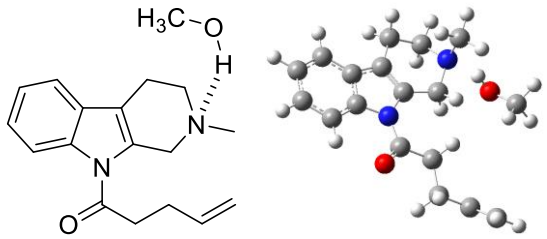
(2) At (U)B3LYP-D3(BJ) / def2-SVP / PCM (MeOH) level of theory



1a-MeOH

SCF Done: E(RB3LYP) = -959.684001421 A.U.
Zero-point correction = 0.392797 (Hartree/Particle)
Sum of electronic and thermal Free Energies = -959.357579

C,0,-2.463041453,-0.7000381213,-0.0552923796
C,0,-1.288610263,-1.4653081778,0.1569299356
C,0,-1.3466016389,-2.8540277661,0.3184618427
C,0,-2.6054066596,-3.4582283863,0.2645507474
C,0,-3.7771893532,-2.7106560317,0.0557664654
C,0,-3.7150706122,-1.3280574513,-0.10629131
C,0,-2.0584528199,0.6797613825,-0.1842108248
C,0,-0.6990988054,0.7368880104,-0.0443302465
H,0,-0.4439395146,-3.4339538601,0.4844330368
H,0,-2.6752525793,-4.5411215947,0.3916963109
H,0,-4.7432188942,-3.219724461,0.0214024511
H,0,-4.6218072603,-0.7409862921,-0.2700206666
N,0,-0.1854095319,-0.574104044,0.1456087014
C,0,1.1479235981,-1.011623345,0.214826115
O,0,1.4053131854,-2.173171461,0.4510629623
C,0,2.2526261947,-0.0011104229,-0.0455064079
H,0,2.2748355507,0.7296857391,0.7779455735
C,0,3.6283443118,-0.664071008,-0.166946755
H,0,3.5883377715,-1.4113596325,-0.9778825856
C,0,4.7042868163,0.3459324315,-0.44622377
H,0,4.6090521825,0.9029777931,-1.3881299319
C,0,5.7319090099,0.6172384486,0.3624604191
H,0,5.8650905318,0.0875562147,1.3118592468

H,0,2.0202549069,0.5738753499,-0.9546425012
H,0,3.8493281277,-1.2237433463,0.7538736314
H,0,6.4813841235,1.3704238397,0.1046857342
C,0,-2.9130157537,1.887431938,-0.4137105343
H,0,-3.6245367226,1.7076020611,-1.2374061546
H,0,-3.5321413241,2.0946812228,0.4782495706
C,0,-2.0195407093,3.0913869365,-0.7505465642
H,0,-1.6553613194,3.0047852469,-1.7872440221
H,0,-2.5831995972,4.0343083797,-0.6823992855
C,0,0.0568951088,2.0405146994,-0.052342154
H,0,0.798162118,2.0818330679,0.7563150825
H,0,0.6176777068,2.1899993456,-0.990747538
C,0,-1.1646708708,3.4632516483,1.5124742526
H,0,-0.2415873638,3.6929814607,2.0663628588
H,0,-1.8197418572,4.3457590132,1.5669700345
H,0,-1.6711357899,2.6230802714,2.0271319128
C,0,2.166529946,4.8861364651,-0.4470017644
H,0,2.5282798383,3.953192933,0.0379649042
O,0,1.0619028935,4.6837848096,-1.2832735015
H,0,3.0013750373,5.2761858385,-1.0522025666
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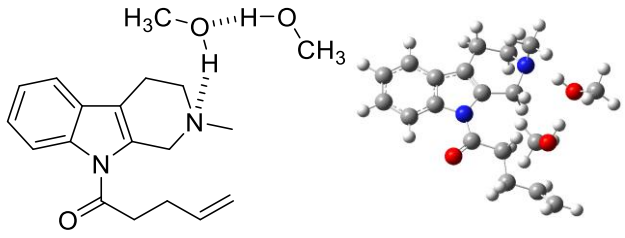

1a-2MeOH

SCF Done: E(RB3LYP) = -1075.37244352 A.U.

Zero-point correction = 0.446213 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1074.986723

C,0,-2.9716327711,-0.5392694098,0.205361958
C,0,-2.6068388577,0.8144492961,-0.0181627321
C,0,-3.5600297575,1.8381208638,0.0355855995
C,0,-4.8831222897,1.4810295791,0.3155168856
C,0,-5.2554714857,0.143862572,0.5393321912
C,0,-4.3037706104,-0.8744791171,0.4866917381
C,0,-1.7713718263,-1.3335512614,0.0850256164
C,0,-0.7384256204,-0.4901955114,-0.2146239232
H,0,-3.2785750577,2.8721538909,-0.1373044881
H,0,-5.6429748401,2.2650893003,0.3580869946

H,0,-6.2991041395,-0.0973261525,0.7546554667
H,0,-4.5858705482,-1.9155690801,0.6598736484
N,0,-1.2101187391,0.8499412995,-0.2593316497
C,0,-0.4801222072,2.0454104108,-0.3706557305
O,0,-1.0605548358,3.1143259354,-0.4159816585
C,0,1.0315116407,1.9650694709,-0.4059275675
H,0,1.3353312523,1.5065448124,-1.3607254885
C,0,1.7050065365,3.3320046892,-0.2580687634
H,0,1.3588224868,3.7886727662,0.6861562763
C,0,3.2013765328,3.1920050513,-0.2314931039
H,0,3.5948421561,2.487709522,0.5131763779
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H,0,1.4004348943,1.2945490272,0.3823773538
H,0,1.3899239119,4.0085495561,-1.0668056087
H,0,5.1294925945,3.6809720047,-0.9770702087
C,0,-1.592216654,-2.8087812776,0.2690935415
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H,0,-2.0214383052,-3.3660695077,-0.5825408077
C,0,-0.0962124726,-3.118598562,0.4247124727
H,0,0.2459208476,-2.7843383024,1.4178557659
H,0,0.0929373979,-4.1999776239,0.3577517457
C,0,0.6638652272,-0.973561359,-0.4555746144
H,0,1.0826555625,-0.5438642563,-1.3753453393
H,0,1.3328741868,-0.659592872,0.3578768861
C,0,0.4891557586,-2.9080409314,-1.9428678667
H,0,1.2493131138,-2.489014502,-2.6182953346
H,0,0.5734452771,-4.0042495278,-1.9691802415
H,0,-0.5071637457,-2.6257068289,-2.3319518369
C,0,4.1593010892,-2.3151390506,-0.9881787996
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H,0,4.1355548538,-3.264884793,-1.5534910112
H,0,2.4151375884,-2.5505450322,-0.1053858279
N,0,0.7342300535,-2.4375735136,-0.5792538756
C,0,2.7484744035,-0.4019977721,2.873253941
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H,0,2.5836630702,0.5185125792,3.455207061
H,0,1.8061516835,-0.9850899801,2.8992047508
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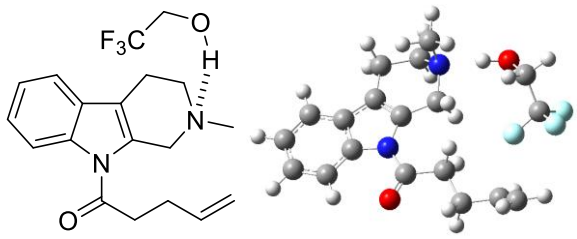
(3) At (U)B3LYP-D3(BJ) / def2-SVP / PCM (CF_3CH_2OH) level of theory



1a-TFE

SCF Done: E(RB3LYP) = -1296.51295449 A.U.

Zero-point correction = 0.398560 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1296.173595

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C,0,3.1509024188,0.7025808416,-0.0818822942
C,0,4.153895603,1.6765518842,-0.1553876948
C,0,5.4727916378,1.2407461225,-0.3180502655
C,0,5.7941515833,-0.1251203056,-0.4075069493
C,0,4.7934238219,-1.0936706144,-0.335028433
C,0,2.2229835234,-1.4092964209,-0.0655852069
C,0,1.2140936271,-0.5018209703,0.0958388469
H,0,3.9132279915,2.7326471598,-0.0862652346
H,0,6.2703021047,1.9854411128,-0.375306825
H,0,6.8362977185,-0.4276464374,-0.5340353037
H,0,5.0350108574,-2.1567876931,-0.4038954014
N,0,1.7456903121,0.8172808417,0.0710899448
C,0,1.0757017118,2.0508701204,0.1033706019
O,0,1.7044875288,3.0921439956,0.0815216836
C,0,-0.4387343671,2.0467052918,0.1587619749
H,0,-0.7517116997,1.6273236124,1.1278950449
C,0,-1.0496488932,3.4405187139,-0.0088171131
H,0,-0.7322973497,3.8481183649,-0.9845197669
C,0,-2.5499953994,3.3809454193,0.0578075358
H,0,-3.0357602701,2.7225198966,-0.6731750673
C,0,-3.3072182,4.033778535,0.944176391
H,0,-2.8643998373,4.6903885496,1.7011223556
H,0,-0.8367882077,1.3728469549,-0.6111693627
H,0,-0.6541708045,4.1206723643,0.7602430474
H,0,-4.3966358986,3.9364715194,0.9451005344
C,0,1.996231785,-2.8887762743,-0.1216371342
H,0,2.5595258093,-3.3347154057,-0.9578623096
H,0,2.3820999436,-3.3727333325,0.7931933533
C,0,0.4975104732,-3.1736396721,-0.2994016892
H,0,0.2002142169,-2.9583708984,-1.3382665841
H,0,0.271297953,-4.2320783588,-0.1045542627
C,0,-0.2226696766,-0.9184420189,0.2605305622
H,0,-0.7171240931,-0.3614905735,1.0643578901

H,0,-0.795556296,-0.7200994711,-0.6582308601
C,0,-0.1591563843,-2.6370467631,1.9989676064
H,0,-0.9167411856,-2.0994718534,2.5874786861
H,0,-0.2947088526,-3.7149724561,2.1679309791
H,0,0.8379190749,-2.3456664769,2.3775732079
C,0,-4.0705373896,-0.5636355923,-0.4603850307
C,0,-3.6736280493,-1.6529143872,0.5255677846
H,0,-3.1177337013,-1.1556319239,1.3406767253
H,0,-4.6193281957,-2.0257008336,0.959773252
F,0,-4.7524934469,0.4187825216,0.1586392905
F,0,-4.8455850726,-1.0353588254,-1.4495602973
F,0,-2.9977683186,0.014736134,-1.0506841725
O,0,-2.9659441038,-2.677442519,-0.091571697
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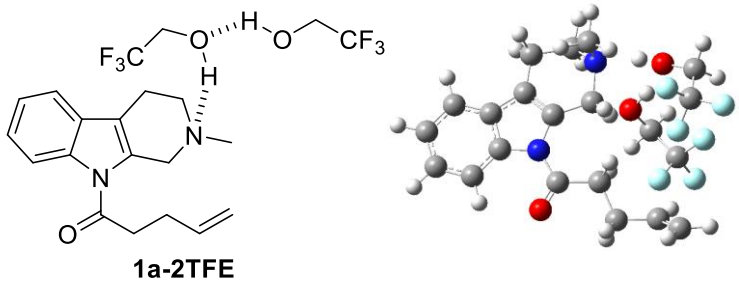

1a-2TFE

SCF Done: E(RB3LYP) = -1748.98033335 A.U.

Zero-point correction = 0.458465 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1748.589180

C,0,3.9879419271,-0.6862034793,-0.2729839501
C,0,3.7293963695,0.6909250613,-0.0441243417
C,0,4.7382157692,1.6500119772,-0.1908537093
C,0,6.0092402714,1.2045092716,-0.5682018079
C,0,6.2768934237,-0.1567069601,-0.7965784004
C,0,5.2694798512,-1.110496985,-0.6519437607
C,0,2.752825981,-1.3993603316,-0.044646954
C,0,1.803348299,-0.4869998952,0.3196260332
H,0,4.5383147111,2.7020981166,-0.0130988061
H,0,6.8115864923,1.9371078932,-0.6841701203
H,0,7.2826958243,-0.4677256349,-1.0886631416
H,0,5.4700784082,-2.1697000901,-0.8287414357
N,0,2.3613346132,0.8197620748,0.3059377607
C,0,1.7246338691,2.0605067652,0.4713383537
O,0,2.378531049,3.0866583186,0.4824633704
C,0,0.2138325126,2.0859183519,0.6018405701
H,0,-0.0734067001,1.5931141819,1.5423176336

C,0,-0.3541055408,3.5083213103,0.5844158323
H,0,-0.0733835727,3.985499166,-0.3707464352
C,0,-1.8497040094,3.5073809026,0.7322540911
H,0,-2.4043508313,2.9551399606,-0.0353320564
C,0,-2.5208976576,4.1027320852,1.722527019
H,0,-2.0019116032,4.6549657535,2.5137746185
H,0,-0.2355273211,1.490564515,-0.205628711
H,0,0.111559245,4.1058996906,1.3824607863
H,0,-3.6125186408,4.0619072003,1.7787613227
C,0,2.469077324,-2.8639701427,-0.1729681168
H,0,2.8958209867,-3.2587767117,-1.1098424727
H,0,2.956456662,-3.4285585056,0.6417668501
C,0,0.9510847658,-3.0907274337,-0.165349927
H,0,0.5216191282,-2.765365662,-1.1252540224
H,0,0.7112398498,-4.1560089307,-0.0340074858
C,0,0.3997946486,-0.8736764645,0.6876871594
H,0,0.0735017763,-0.381466737,1.6097482063
H,0,-0.2988310829,-0.57583205,-0.1066286502
C,0,0.6465362854,-2.7460238523,2.2453624047
H,0,-0.0254731357,-2.2736477278,2.9744690858
H,0,0.5366709572,-3.8369528064,2.3288089627
H,0,1.6869402139,-2.4785021148,2.5047788095
C,0,-3.061080671,-0.7537082044,1.6765425375
C,0,-3.3209022927,-2.0421575236,0.9095932988
H,0,-3.5834649668,-2.8064925814,1.6636793349
H,0,-4.2069818243,-1.8639442647,0.2826574094
F,0,-4.1733612708,-0.3492659003,2.3074678012
F,0,-2.6498724631,0.2501671119,0.8824819245
F,0,-2.1031712621,-0.9145446406,2.6194832669
O,0,-2.263169423,-2.4343737242,0.0894555049
H,0,-1.3647817825,-2.4980870282,0.5691793223
N,0,0.265449564,-2.3268992155,0.8941770602
C,0,-2.9718679858,0.4240133334,-2.5300448784
C,0,-2.1069104649,-0.7048985304,-3.0644782348
H,0,-2.7933390635,-1.4417807728,-3.5226724148
H,0,-1.4852088107,-0.2802936306,-3.8677363427
F,0,-3.6816364177,0.9951176226,-3.517000424
F,0,-2.2361866523,1.3918545853,-1.9475238733
F,0,-3.8510086016,-0.0139224416,-1.6054312469
O,0,-1.2764979906,-1.246045629,-2.0881431332
H,0,-1.80529039,-1.6829372466,-1.3759062274

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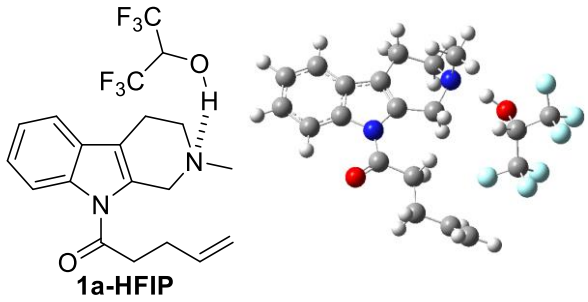
(4) At (U)B3LYP-D3(BJ) / def2-SVP / PCM (HFIP) level of theory



1a-HFIP

SCF Done: E(RB3LYP) = -1633.30411470 A.U.

Zero-point correction = 0.403578 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1632.964260

C,0,-4.060728547,-1.0399946465,0.150053164

C,0,-3.9698673869,0.356161099,-0.0880097442

C,0,-5.1195754798,1.1475057383,-0.1955965891

C,0,-6.3588141118,0.513671328,-0.062268145

C,0,-6.4606244432,-0.8687976217,0.1733811917

C,0,-5.3139202551,-1.6547699771,0.2819975195

C,0,-2.712571818,-1.5545220131,0.2115018862

C,0,-1.8562800882,-0.5102655434,0.0049906564

H,0,-5.0479820665,2.2149087468,-0.3794017751

H,0,-7.268594781,1.1128787816,-0.1462197815

H,0,-7.4467819024,-1.3286300471,0.2711285468

H,0,-5.3850088848,-2.7292027421,0.4658724359

N,0,-2.5946108002,0.6928993068,-0.1631394577

C,0,-2.1318129659,2.0137742219,-0.2830416998

O,0,-2.9158525427,2.9270043081,-0.4557119019

C,0,-0.6407086272,2.2633100986,-0.1718096144

H,0,-0.1402568596,1.8026273682,-1.0371130423

C,0,-0.2784021376,3.7499902869,-0.1190285089

H,0,-0.7927245556,4.2086502512,0.7429667505

C,0,1.2081858769,3.9288382909,0.012323125

H,0,1.6664233569,3.4825641508,0.9038317864

C,0,1.9920718438,4.5430252046,-0.8783365849

H,0,1.580648869,4.99123498,-1.7893640407

H,0,-0.2489060642,1.7530756877,0.7187944792

H,0,-0.6530125136,4.2599400261,-1.0191199004

H,0,3.0727357005,4.6200708841,-0.7289567979

C,0,-2.2487910877,-2.9570481902,0.4568617664

H,0,-2.7973575011,-3.4031661,1.302542068

H,0,-2.4690641905,-3.5963168507,-0.4164228935

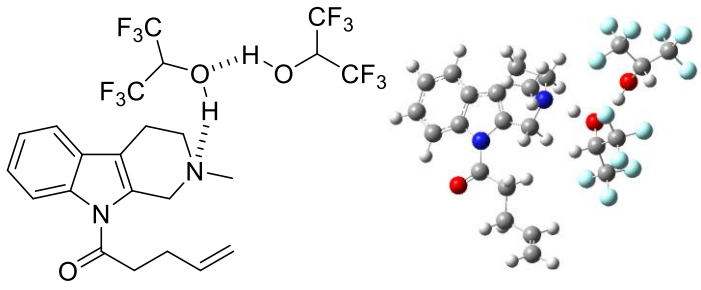
C,0,-0.7455977305,-2.9530383427,0.7652160836

H,0,-0.5757883041,-2.5650574099,1.7822019711

H,0,-0.3297405334,-3.9699831392,0.7262250827

C,0,-0.3647348637,-0.6870173624,-0.0493043349

H,0,0.065271688,-0.1619854209,-0.9109793378
H,0,0.1181209297,-0.272832355,0.8501123307
C,0,0.0145430263,-2.5944059362,-1.5409247558
H,0,0.749162908,-2.033584426,-2.1362608272
H,0,0.3100366263,-3.6530514274,-1.5457408433
H,0,-0.9722275937,-2.5018261886,-2.0289661411
C,0,3.3719847092,0.4746981021,0.9761524594
C,0,3.0056354338,-0.7019531863,0.0613888739
H,0,2.3123014271,-0.2860912925,-0.6908195817
F,0,3.8921555502,1.5039261289,0.2905845469
F,0,4.2473488264,0.1259279619,1.9249208482
F,0,2.2617734156,0.9240350274,1.593935123
O,0,2.4581755058,-1.7145988961,0.8247168578
H,0,1.5621086635,-1.9782479422,0.4273365532
C,0,4.1970576278,-1.2446505915,-0.7414025644
F,0,5.1535407323,-1.7475331259,0.0480248802
F,0,4.7560173294,-0.3038639681,-1.5184749027
F,0,3.7666965387,-2.2320786631,-1.5438668561
N,0,0.0233291609,-2.1019877642,-0.1601553347



1a-2HFIP

SCF Done: E(RB3LYP) = -2422.55600914 A.U.

Zero-point correction = 0.466678 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -2422.170522

C,0,4.0435832024,-2.8033186067,-0.0296046926
C,0,4.9141921686,-1.6828556821,-0.0592861241
C,0,6.2975466427,-1.8447281417,-0.198741927
C,0,6.7905273377,-3.1488964906,-0.3041251724
C,0,5.9376182226,-4.2664925348,-0.2744587537
C,0,4.5595927491,-4.1024955345,-0.1383035319
C,0,2.6981967572,-2.2984011451,0.1167593631
C,0,2.7688838284,-0.9359017238,0.1840109099
H,0,6.9612550116,-0.9859356932,-0.2191235007
H,0,7.8677783274,-3.297932636,-0.4093445511
H,0,6.3602658895,-5.2703814838,-0.3581746079
H,0,3.8911090653,-4.9661157641,-0.1158528313
N,0,4.1189586763,-0.5146434946,0.0548474749

C,0,4.6378841596,0.7849400423,-0.0720782976
O,0,5.8391814073,0.9643998655,-0.1206793454
C,0,3.6602563772,1.9398207082,-0.1742249129
H,0,3.1460122158,2.0557001422,0.7921559914
C,0,4.33281126,3.264055159,-0.5462406957
H,0,4.8482353626,3.1371118669,-1.5140595213
C,0,3.3218198145,4.3718191269,-0.6454399736
H,0,2.5119914521,4.2180925655,-1.3702540905
C,0,3.327629149,5.4867318322,0.0908897954
H,0,4.1093263408,5.6764385269,0.8345640709
H,0,2.8823094771,1.6965614152,-0.911023538
H,0,5.1084434474,3.5122027321,0.1935261862
H,0,2.5540925498,6.2513188944,-0.024370306
C,0,1.4087401658,-3.0554521161,0.1912151059
H,0,1.362607716,-3.8190746255,-0.6021614423
H,0,1.3364392316,-3.6074668287,1.1448284498
C,0,0.2315188856,-2.0882388429,0.0300720486
H,0,0.1437540692,-1.7710059393,-1.0205840114
H,0,-0.7183135189,-2.5620840808,0.3085990778
C,0,1.563382814,-0.071868847,0.4120923016
H,0,1.7501610577,0.681789091,1.1872517389
H,0,1.2774221848,0.4732039799,-0.50058257
C,0,0.3636842673,-1.1201524155,2.2873866496
H,0,0.3201860082,-0.1648946506,2.8287016717
H,0,-0.5411335738,-1.6937744588,2.5260322637
H,0,1.2484627099,-1.6792692502,2.6349306727
C,0,-0.9393491537,3.0213460642,-0.7106191853
C,0,-1.241914833,2.0348057291,0.4262301253
H,0,-0.4209549182,2.148936021,1.156302886
F,0,-0.851938507,4.2838099766,-0.2738551185
F,0,-1.8701575819,2.9748327948,-1.6702362289
F,0,0.2418440473,2.7028791813,-1.2728025943
O,0,-1.3202226024,0.7594425285,-0.0959021151
H,0,-0.6775036452,0.0665359334,0.3976588973
C,0,-2.5335821448,2.3529779724,1.1937246179
F,0,-3.6167661323,2.2495059589,0.4016993663
F,0,-2.5266698932,3.5825575274,1.7202436141
F,0,-2.6797598296,1.4730347814,2.1928501101
N,0,0.3917133689,-0.8608281237,0.8410613463
C,0,-5.3048205762,-1.4305275571,-1.3189489814
C,0,-4.1300003409,-0.9396268226,-0.4667500981
H,0,-4.4530409803,0.0150596109,-0.0166072356
F,0,-6.4161418784,-1.5917417658,-0.5841898137
F,0,-5.0367100124,-2.5991616996,-1.9171107693

F,0,-5.5745674307,-0.5343589584,-2.2759104141
O,0,-3.0310715517,-0.816062335,-1.3016965268
H,0,-2.444561601,-0.1046060666,-0.9472253703
C,0,-3.8110862608,-1.8788583979,0.7084861239
F,0,-3.4338097919,-3.0977966653,0.2963684633
F,0,-4.8487567738,-2.0260841618,1.5415952761
F,0,-2.7897116459,-1.3667664077,1.4225688702

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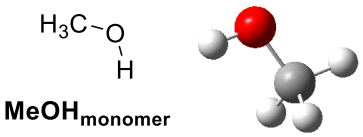
(5) At (U)B3LYP-D3(BJ) / def2-SVP level of theory



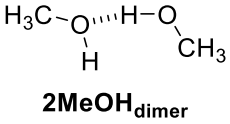
MeOH$_{monomer}$

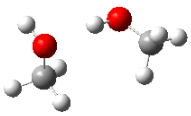
SCF Done: E(RB3LYP) = -115.631277615 A.U.

Zero-point correction = 0.051030 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -115.606682

C,0,0.4341048427,6.2051774377,-0.3749797908
H,0,0.7372012043,6.002451325,0.6728603419
O,0,0.7632223785,5.161695159,-1.2593252486
H,0,0.9761946055,7.1051767285,-0.7054203875
H,0,-0.647482821,6.4523608492,-0.3733330905
H,0,0.2913393557,4.3685477654,-0.975855378





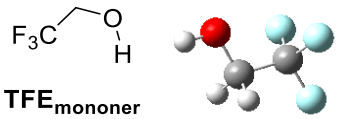
2MeOH$_{dimer}$

SCF Done: E(RB3LYP) = -231.283380567 A.U.

Zero-point correction = 0.104924 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -231.212831

C,0,4.1405748968,-2.2680172738,-0.5217045853
H,0,4.1614572101,-1.1850065236,-0.7360163699
O,0,2.8966029247,-2.6744838393,0.0321678856
H,0,4.9150739966,-2.4814487864,0.2291846906
H,0,4.3898037506,-2.8318342265,-1.4383038476
H,0,2.217475051,-2.5936024854,-0.6511950805
C,0,3.4192982433,-0.2584447846,2.5569715358
H,0,4.4370967858,-0.6808903232,2.4188599929
O,0,2.6584450661,-0.2506737784,1.3795390935
H,0,3.5439088431,0.7824225651,2.8978011422
H,0,2.9399361687,-0.8197999391,3.3856776043
H,0,2.5757640631,-1.1708786049,1.0700499385



TFE$_{mononer}$

SCF Done: E(RB3LYP) = -452.428392992 A.U.

Zero-point correction = 0.057332 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -452.401896

C,0,-5.8070026246,-0.3914326579,-0.1234591193

C,0,-4.4473688865,-0.8377132106,0.3811595998

H,0,-4.3801648612,-0.5131298851,1.4376309717

H,0,-4.4518850873,-1.9448360213,0.3646837871

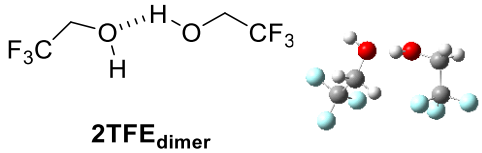
F,0,-6.76762743,-0.9261741362,0.6544527238

F,0,-6.0292228412,-0.7910943004,-1.3816410268

F,0,-5.9424474512,0.939821984,-0.0846712303

O,0,-3.4655090361,-0.2724437546,-0.4387312051

H,0,-2.5993337819,-0.5526370178,-0.121211501



2TFE$_{dimer}$

SCF Done: E(RB3LYP) = -904.878201700 A.U.

Zero-point correction = 0.117673 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -904.811221

C,0,-2.8830094718,-0.8424377401,1.6872943134

C,0,-3.4437167446,-1.95229606,0.8145136079

H,0,-3.9364252797,-2.6850543445,1.4771453868

H,0,-4.1918350763,-1.5213181132,0.1389483677

F,0,-3.8394217301,-0.3308498558,2.4718275934

F,0,-2.3499025062,0.1471221423,0.9669221436

F,0,-1.9071822884,-1.3337756182,2.4839260066

O,0,-2.4372071605,-2.5393258241,0.0230392108

H,0,-1.7658705258,-2.9257766773,0.6051275508

C,0,-3.0746053239,0.3378989151,-2.6255286227

C,0,-1.9771847084,-0.6763754463,-2.912851936

H,0,-2.4834949846,-1.593555176,-3.274106247

H,0,-1.3870649761,-0.2713552674,-3.7507995747

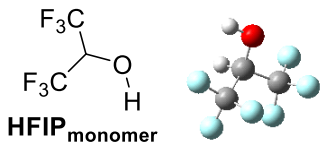
F,0,-3.8391366184,0.5273820262,-3.7155495778

F,0,-2.5927123385,1.5235647172,-2.2464014045

F,0,-3.8963479385,-0.0936784516,-1.6356419899

O,0,-1.1372964833,-0.8839282272,-1.8275421818

H,0,-1.610621845,-1.4213939991,-1.1655496465



HFIP$_{monomer}$

SCF Done: E(RB3LYP) = -789.216344032 A.U.

Zero-point correction = 0.062837 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -789.191911

C,0,3.3987180873,0.5494055926,1.0651487236

C,0,2.9279559862,-0.5587384636,0.1161253275

H,0,2.255430551,-0.0704990729,-0.6158385567

F,0,4.0913127013,1.4772409486,0.3877013225

F,0,4.1715939936,0.0785305922,2.0424294071

F,0,2.3386806335,1.1465789584,1.6194660756

O,0,2.2954250662,-1.5219425984,0.8970129901

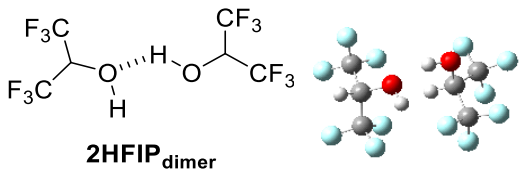
H,0,1.9628580448,-2.2194051107,0.3162366844

C,0,4.0665040836,-1.1831656007,-0.7068059195

F,0,5.0833801326,-1.6012491029,0.0452781077

F,0,4.5351557459,-0.3340340299,-1.6246177061

F,0,3.5666349739,-2.2577711126,-1.3561414564



2HFIP$_{dimer}$

SCF Done: E(RB3LYP) = -1578.44934551 A.U.

Zero-point correction = 0.127385 (Hartree/Particle)

Sum of electronic and thermal Free Energies = -1578.386175

C,0,-1.5636003697,2.6599985554,-0.967080063

C,0,-1.2328433849,2.0600462048,0.4063525714

H,0,-0.3212162629,2.5725891207,0.7647692444

F,0,-1.8592709234,3.9575044358,-0.8520867355

F,0,-2.6033109491,2.0362466972,-1.5345837078

F,0,-0.5123329193,2.5331177894,-1.777434622

O,0,-1.0308197141,0.6902670583,0.2127099931

H,0,-1.0292820817,0.2279220325,1.0653457765

C,0,-2.3140719553,2.3202888637,1.4688236628

F,0,-3.5369751916,1.9585907528,1.0628362706

F,0,-2.3471760724,3.6030536217,1.8204668731

F,0,-2.0123028031,1.5898815151,2.558215293

C,0,-4.8876118534,-1.4374321232,-1.5641846088

C,0,-3.7997800855,-0.9030344278,-0.6252235856

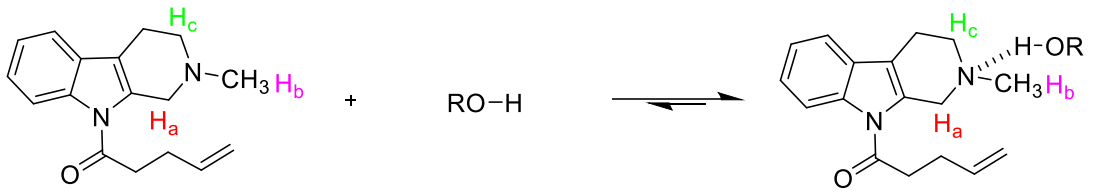
H,0,-4.0250668633,0.1660751053,-0.4757017565

F,0,-6.1014679692,-1.3260300945,-1.0005416885

F,0,-4.6932975583,-2.7181744373,-1.8819067485
F,0,-4.8922782509,-0.7225708428,-2.6943674162
O,0,-2.5726951529,-1.1299649985,-1.2314821395
H,0,-1.951516141,-0.449637001,-0.9188518675
C,0,-3.8455730935,-1.5470512474,0.7711926166
F,0,-3.7679141496,-2.87562829,0.731269551
F,0,-4.9476681395,-1.2046594013,1.4441474504
F,0,-2.7844011155,-1.1058468889,1.4978786363

6.5 Investigation of H-bond between TFE(HFIP) and N-atom of tertiary amine functionality of substrate 1a

6.5.1 ^{1}H NMR titration experiments



1a, 1 eq. **ROH=TFE** or **HFIP**, x eq. **Hydrogen bonded complexes**

Substrate **1a** was dissolved in 0.5 mL CD_3Cl, then TFE or HFIP (0, 0.2, 0.5, 0.8, 1.0, 1.5, 2.0, 3.0, 4.0 equiv.) was added sequentially, and the ^{1}H NMR of the obtained hydrogen bonded additives were recorded at 298 K on a Bruker AV II-400 spectrometer, respectively. As outlined in Figure S13 and S14, H_a、H_b and H_c of compound **1a** shows an obvious downfield shift with the increasing of the concentration of TFE(HFIP).

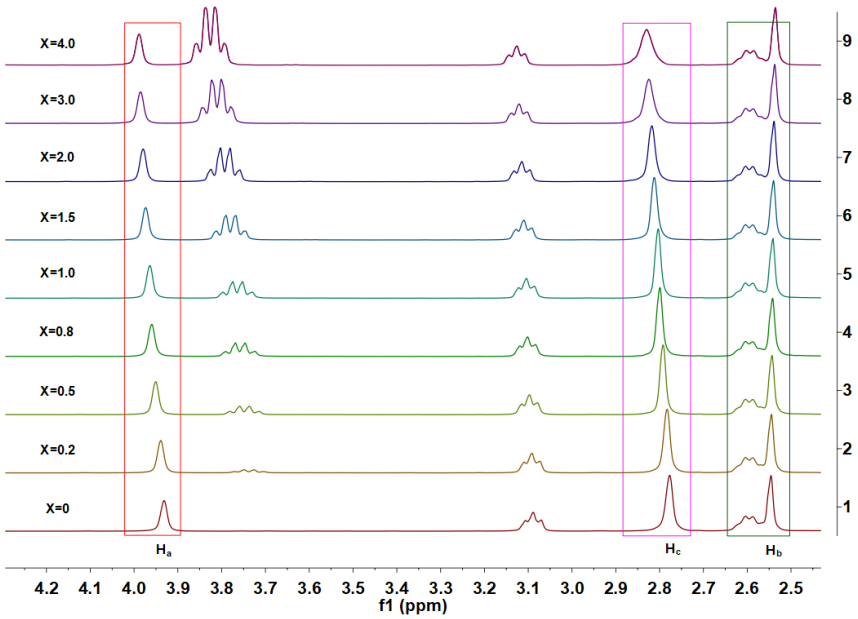


Figure S13. ^{1}H NMR titration of **1a** with increasing amounts of **TFE**

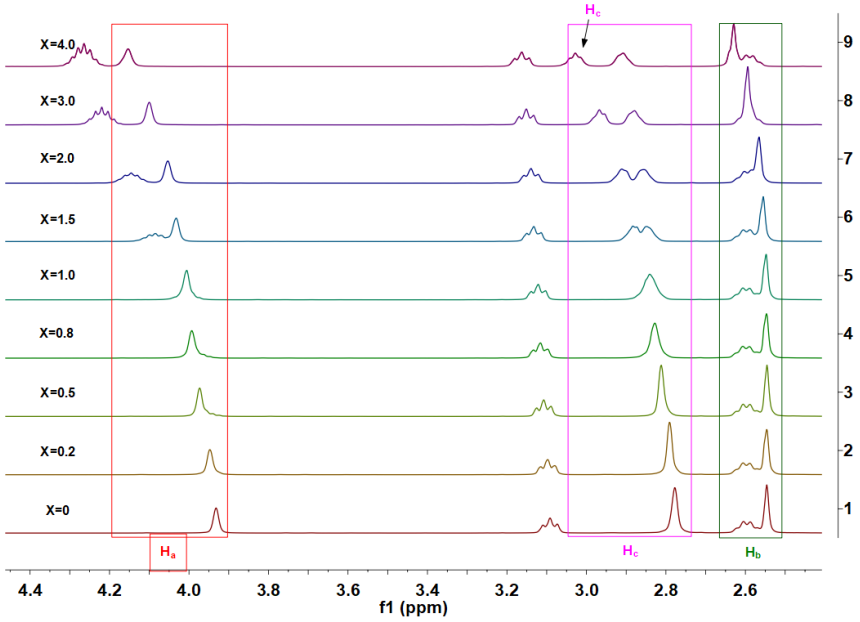
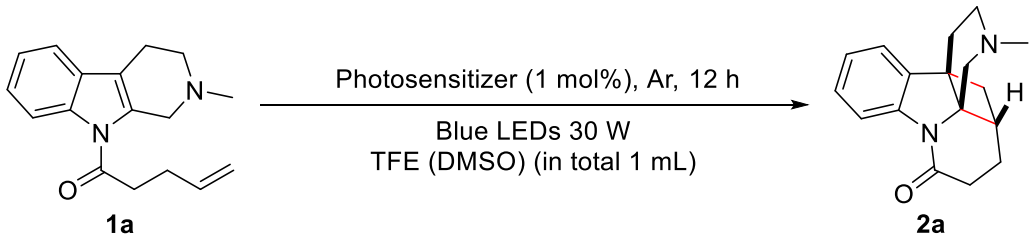


Figure S14. ^{1}H NMR titration of **1a** with increasing amounts of **HFIP**

6.5.2 The correlation between the percentage of DMSO or TFE and the product yield / conversion rate with TFE or DCM as solvent

To further demonstrate that hydrogen bonding is in fact occurring, control experiments were performed by conducting the reaction of **1a** under standard conditions with different amounts of DMSO in TFE solvent or with different amounts of TFE in DCM solvent. When DMSO was used as co-solvent, the yield and conversion decreased with the increasing proportion of DMSO. When TFE was used as co-solvent, the yield and conversion rate increased with the increasing of the proportion of TFE.

6.5.2.1 Control experiments with different percentage of DMSO as hydrogen bonding acceptor co-solvents



1a **2a**

An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the substrates **1a** (0.1 mmol) and **PC-I** (1 mol %). Then, the Schlenk tube was connected to a vacuum line where it was evacuated and back-filled with argon for 3 times. Afterwards, DMSO and TFE (in total 1 mL), which was bubbled with argon for 5 minutes, was added under argon flow. Finally, the reaction mixture in a sealed tube was placed at a distance of 2 – 3 cm from a 30 W blue LED and stirred at room temperature for 12 h. Then, the mixture was concentrated in vacuo. The yield and conversion rate of the product were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol) as internal standard.

Table S2. The yield and conversion rate of the reaction of substrate **1a** with different percentage of DMSO in TFE

Entry	TFE (μL)	DMSO (μL)	Conversion rate (%)	**2a** Yield (%)
1	1000	0	100	82
2	950	50	93	67
3	900	100	89	58
4	850	150	83	46
5	800	200	73	26
6	600	400	72	5
7	400	600	67	trace
8	200	800	63	trace
9	0	1000	54	trace

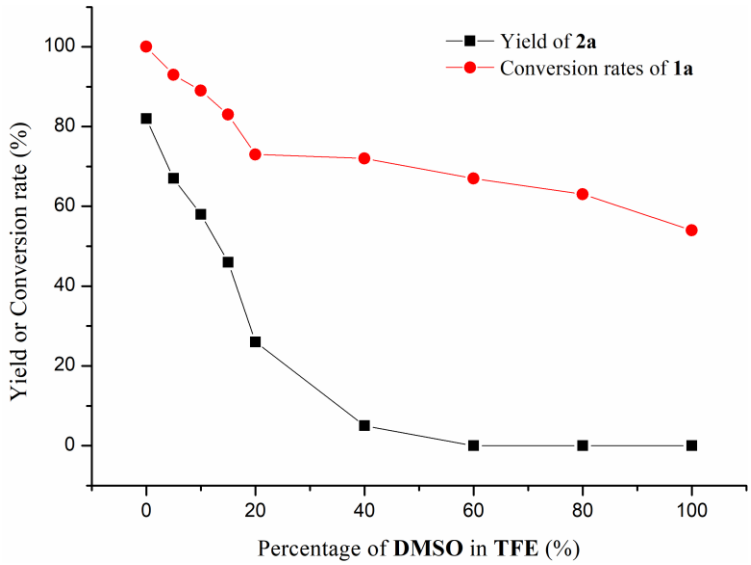
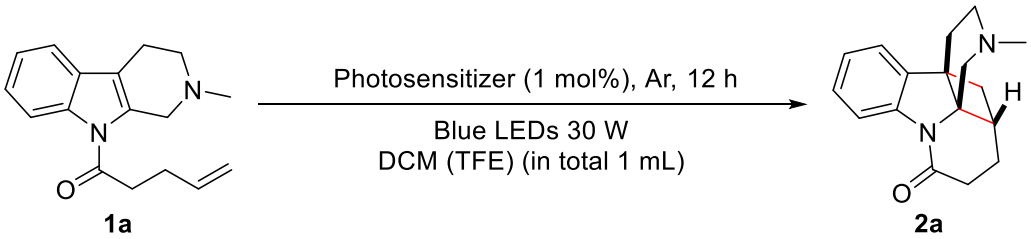


Figure S15. The yield and conversion rate with different percentage of DMSO in TFE

6.5.2.2 Control experiments with different percentage of TFE in DCM



An oven-dried Schlenk tube (10 mL) containing a stirring bar was charged with the substrates **1a** (0.1 mmol) and **PC-I** (1 mol %). Then, the Schlenk tube was connected to a vacuum line where it was evacuated and back-filled with argon for 3 times. Afterwards, DCM and TFE (in total 1 mL), which was bubbled with argon for 5 minutes, was added under argon flow. Finally, the reaction mixture in a sealed tube was placed at a distance of 2 – 3 cm from a 30 W blue LED and stirred at

room temperature for 12 h. Then, the mixture was concentrated in vacuo. The yield and conversion rate of the product were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene (8.4 mg, 0.05 mmol) as internal standard.

Table S3. The yield and conversion rate of the reaction of substrate **1a** with different percentage of TFE in DCM

Entry	DCM (μL)	TFE (μL)	Conversion rate (%)	**2a** Yield (%)
1	1000	0	60	16
2	950	50	63	23
3	900	100	73	30
4	800	200	87	43
5	600	400	100	55
6	400	600	100	74
7	200	800	100	81
8	0	1000	100	82

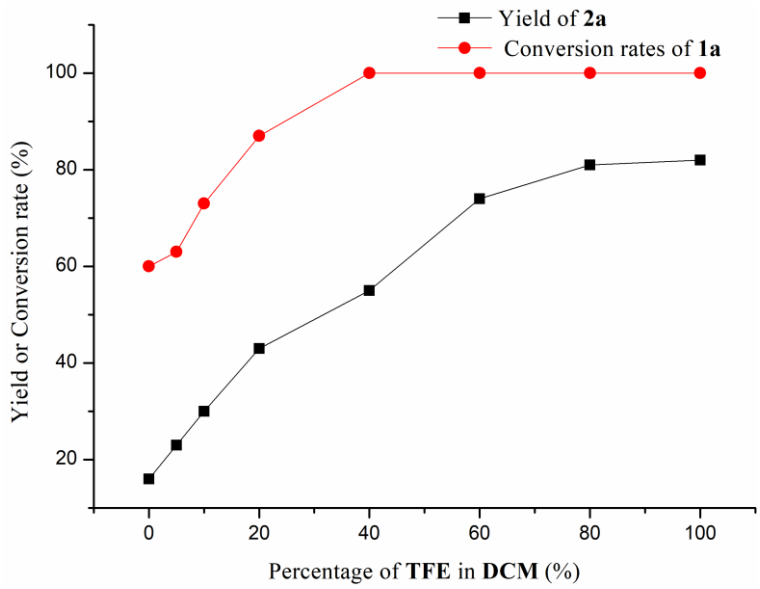


Figure S16. The yield and conversion rate with different percentage of TFE in DCM

7. X-ray crystal data of 2c

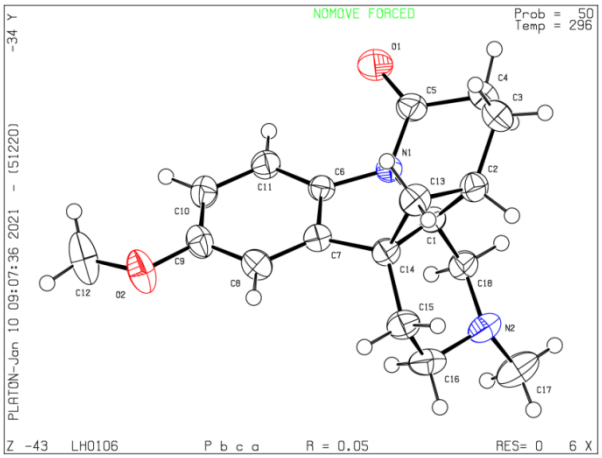


Figure S17. X-Ray crystal structure of **2c** (The crystal was obtained by slow evaporation of the solution of DCM and hexane) (CCDC 2100009):

Bond precision:	C-C = 0.0018 Å		Wavelength=0.710 73
Cell:	a=15.223 (3)	b=10.344 (2)	c = 19.924 (4)
	alpha=90	beta=90	gamma=90
Temperature:	296 K		
	Calculated		Reported
Volume	3137.4 (11)		3137.3 (10)
Space group	P b c a		P b c a
Hall group	-P 2ac 2ab		-P 2ac 2ab
Moiety formula	$C_{18}H_{22}N_2O_2$		$C_{18}H_{22}N_2O_2$
Sum formula	$C_{18}H_{22}N_2O_2$		$C_{18}H_{22}N_2O_2$
Mr	298.38		298.37
Dx, g cm^{-3}	1.263		1.263
Z	8		8
Mu (mm^{-1})	0.083		0.083
F000	1280.0		1280.0
F000′	1280.52		
h, k, l_{max}	19, 13, 25		19, 13, 25
Nref	3613		3611
T_{min}, T_{max}	0.985, 0.988		0.985, 0.988
$T_{min'}$	0.985		
Correction method = # Reported	T Limits: T_{min}=0.985 T_{max}=0.988		
AbsCorr = MULTI-SCAN			
Data completeness = 0.999	Theta(max) = 27.529		
R(reflections) = 0.0472 (2822)	wR2(reflections) = 0.1509 (3611)		
S = 1.086	Npar = 201		

8. References

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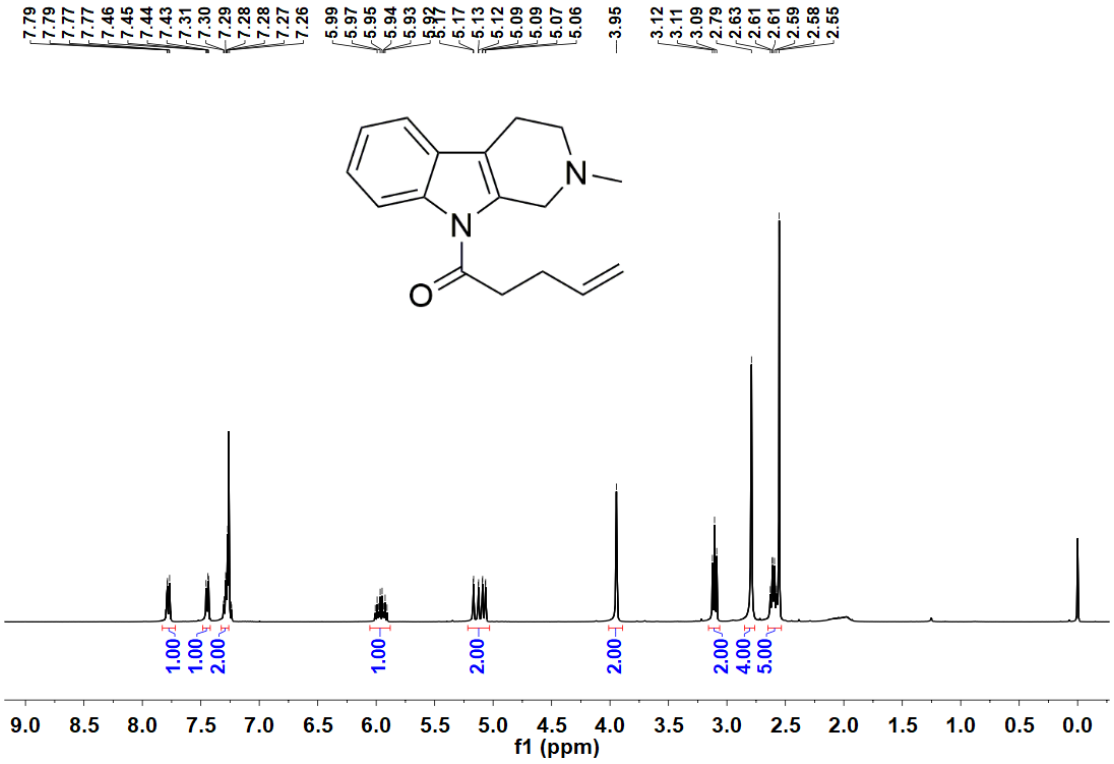
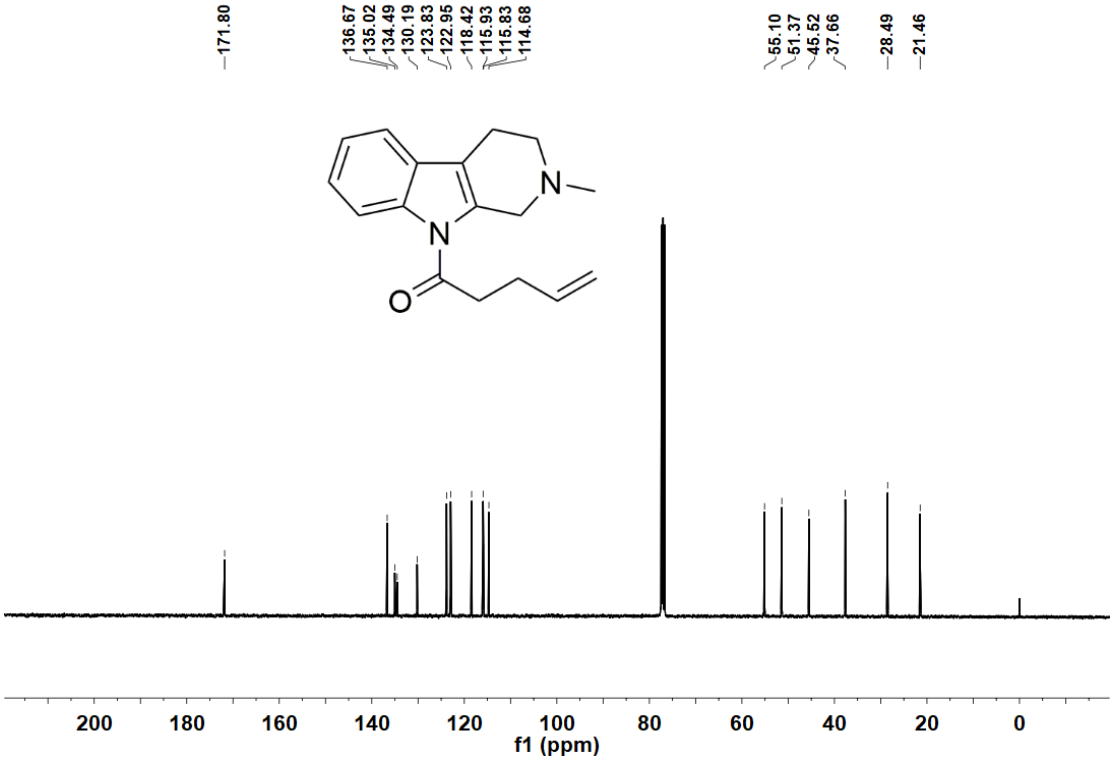
9. Copies of NMR spectra for substrates

^{1}H NMR spectrum of **1a**



^{13}C NMR spectrum of **1a**



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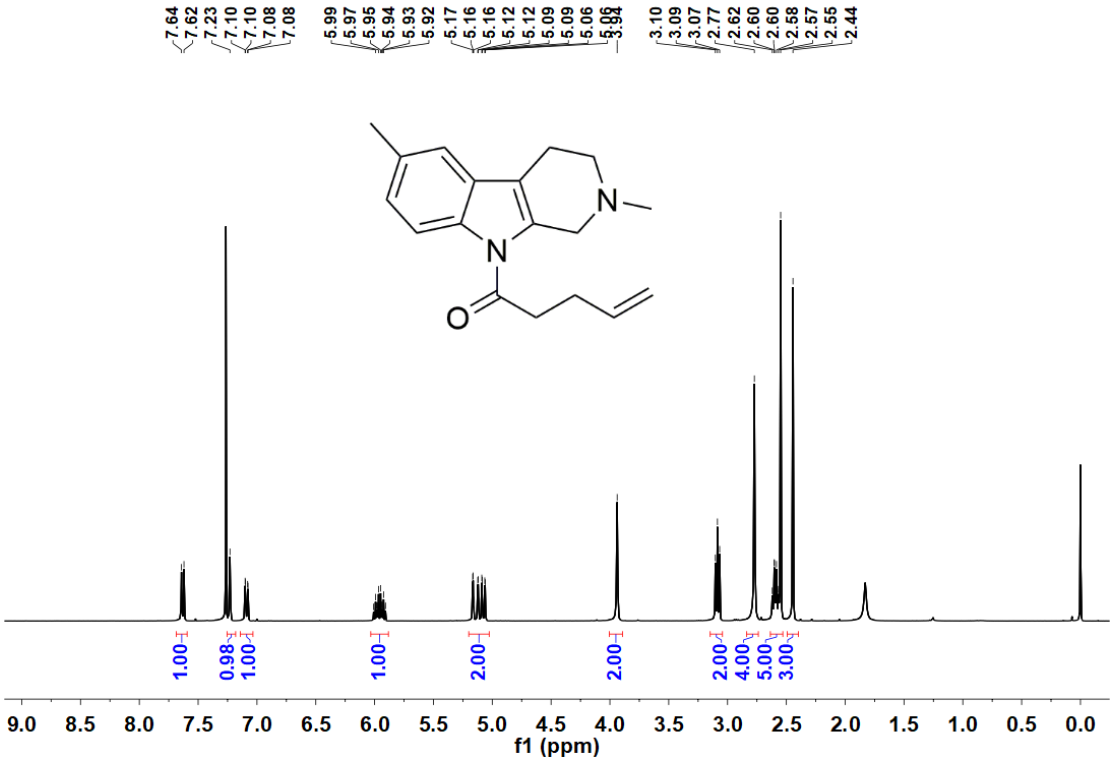

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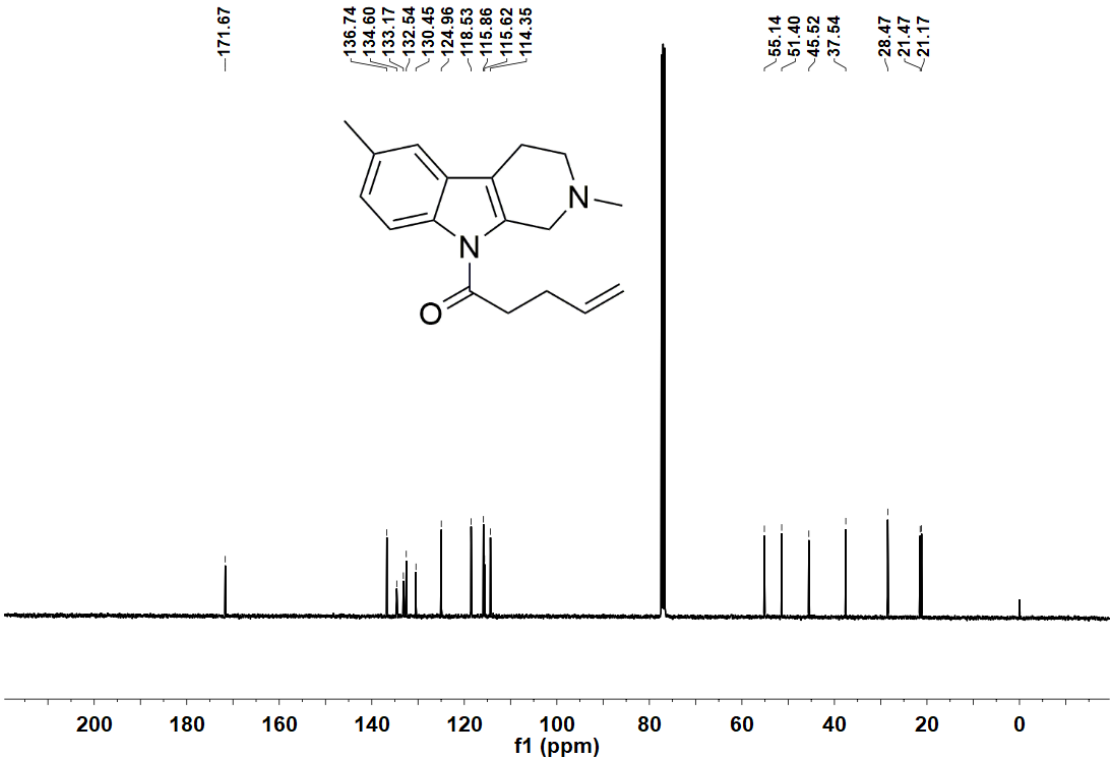
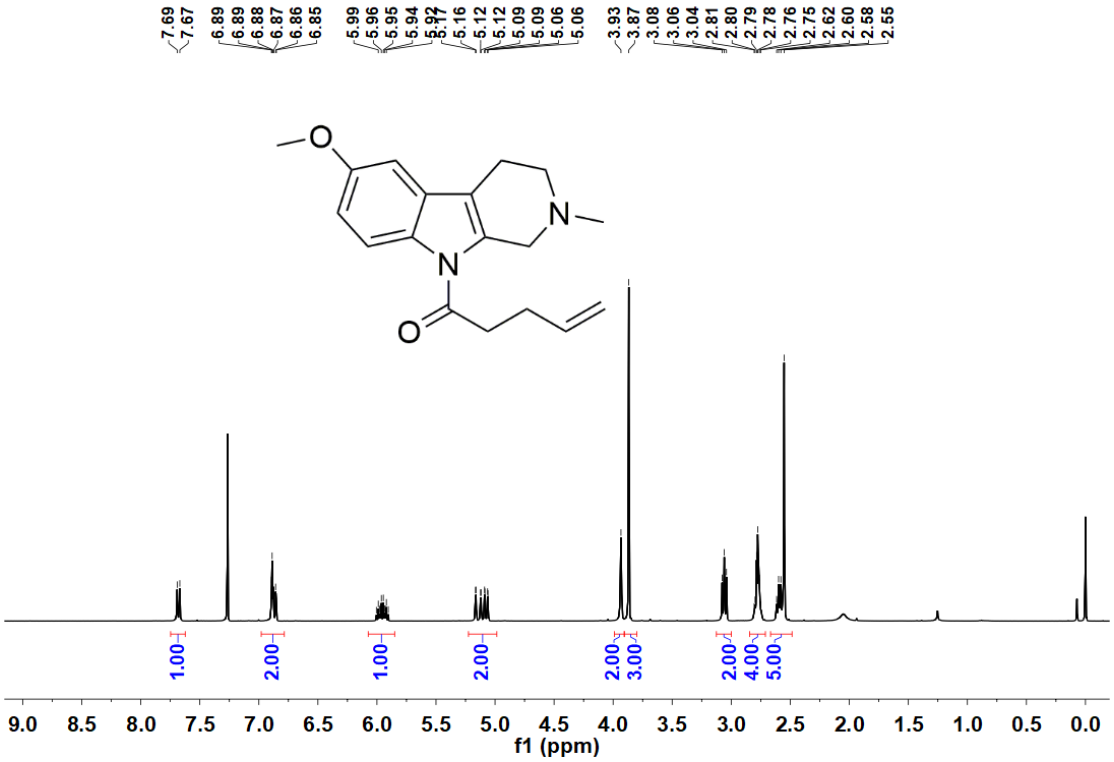


^{1}H NMR spectrum of **1c**



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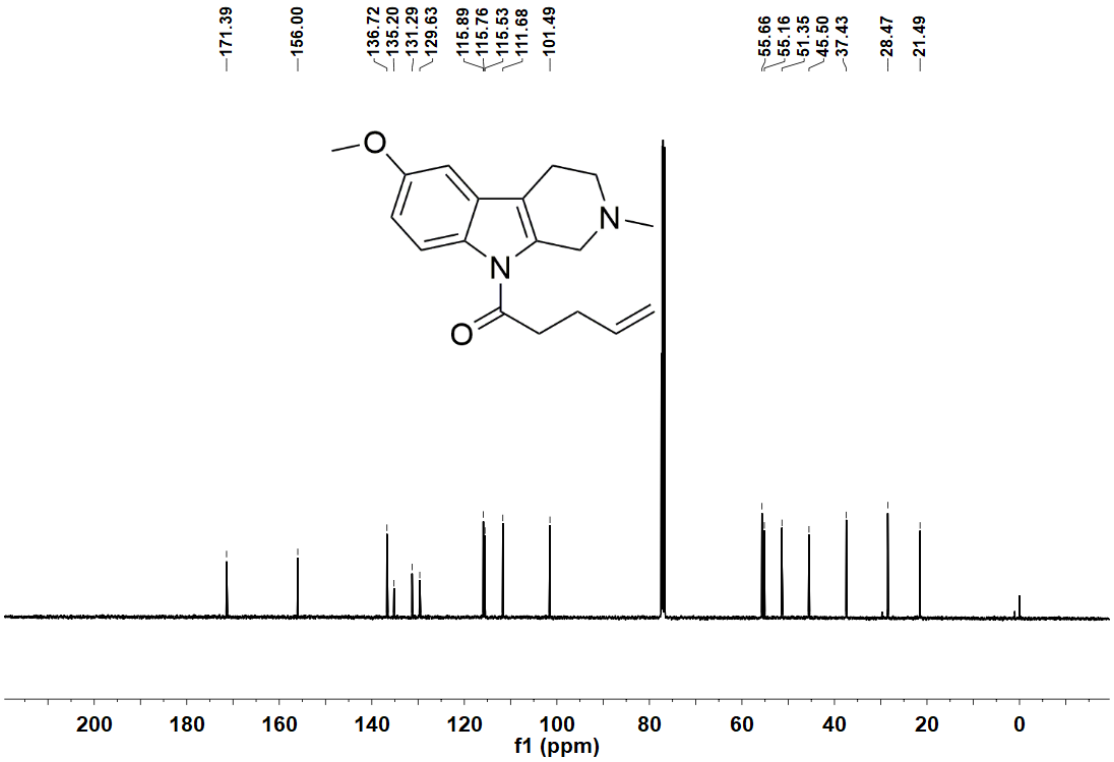

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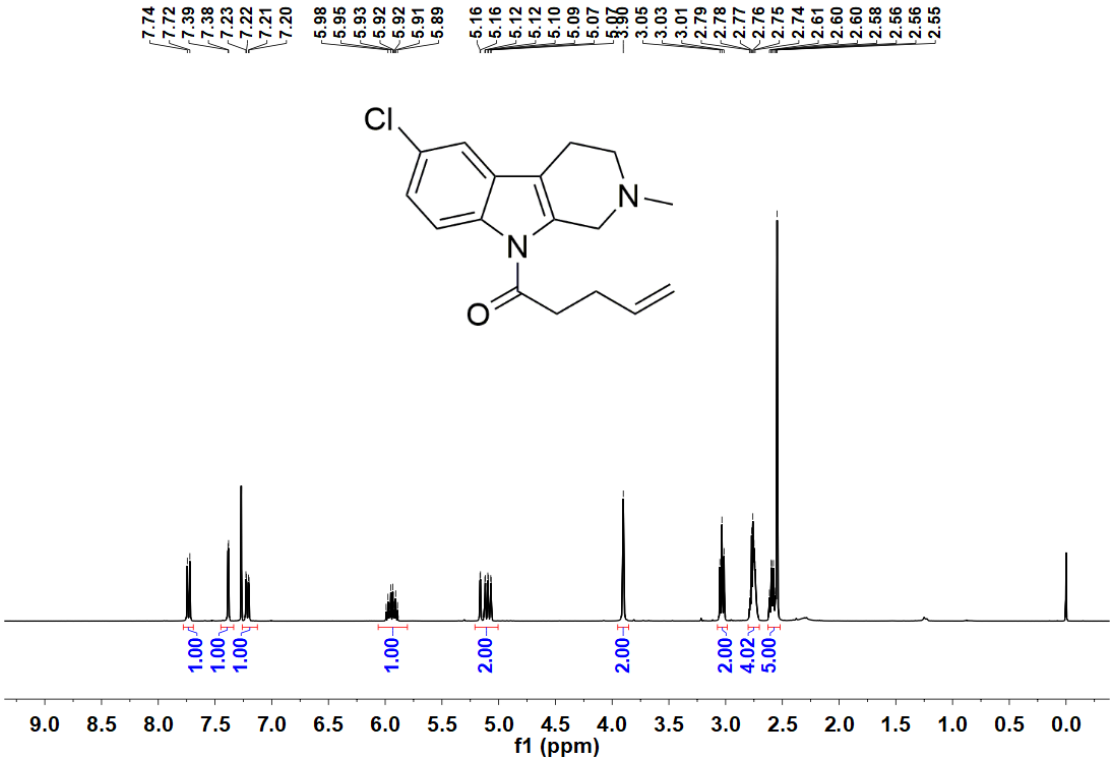
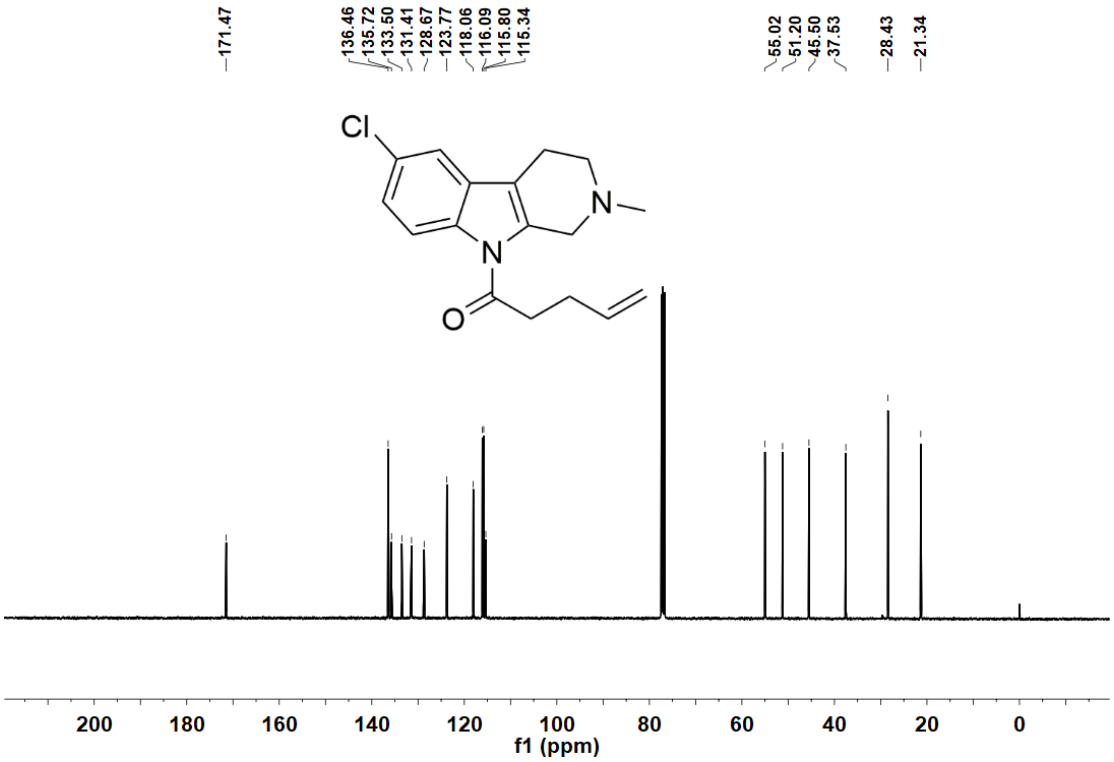


^{13}C NMR spectrum of **1d**



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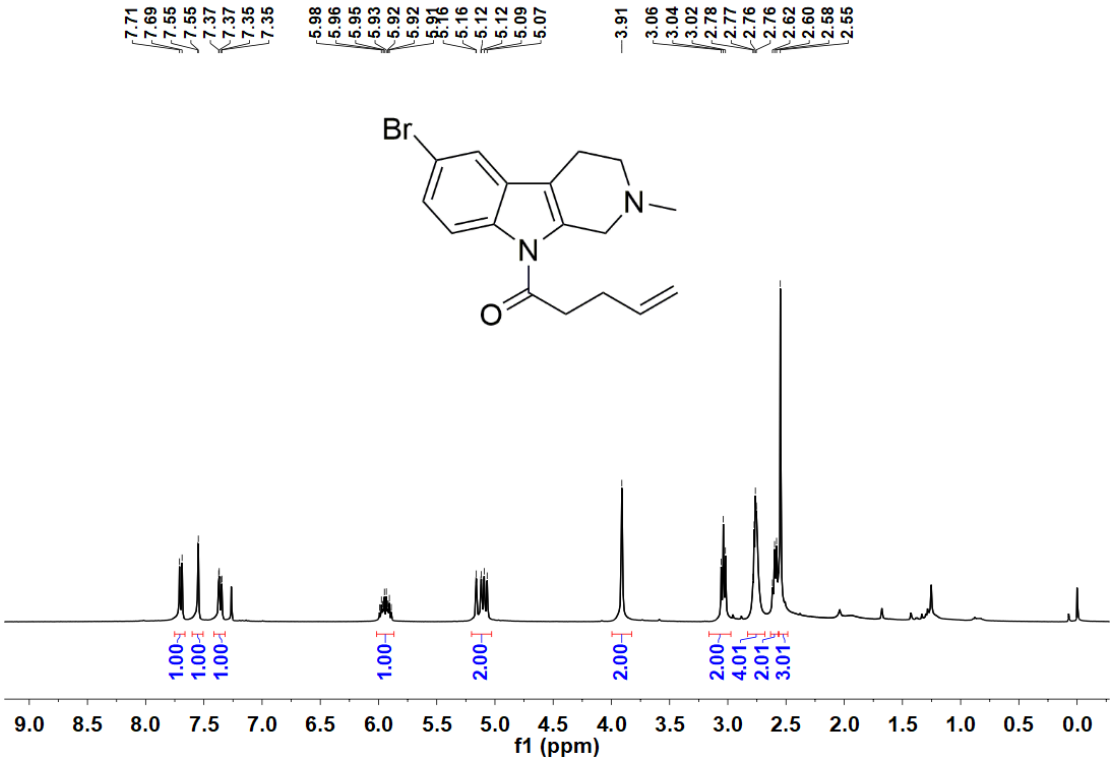

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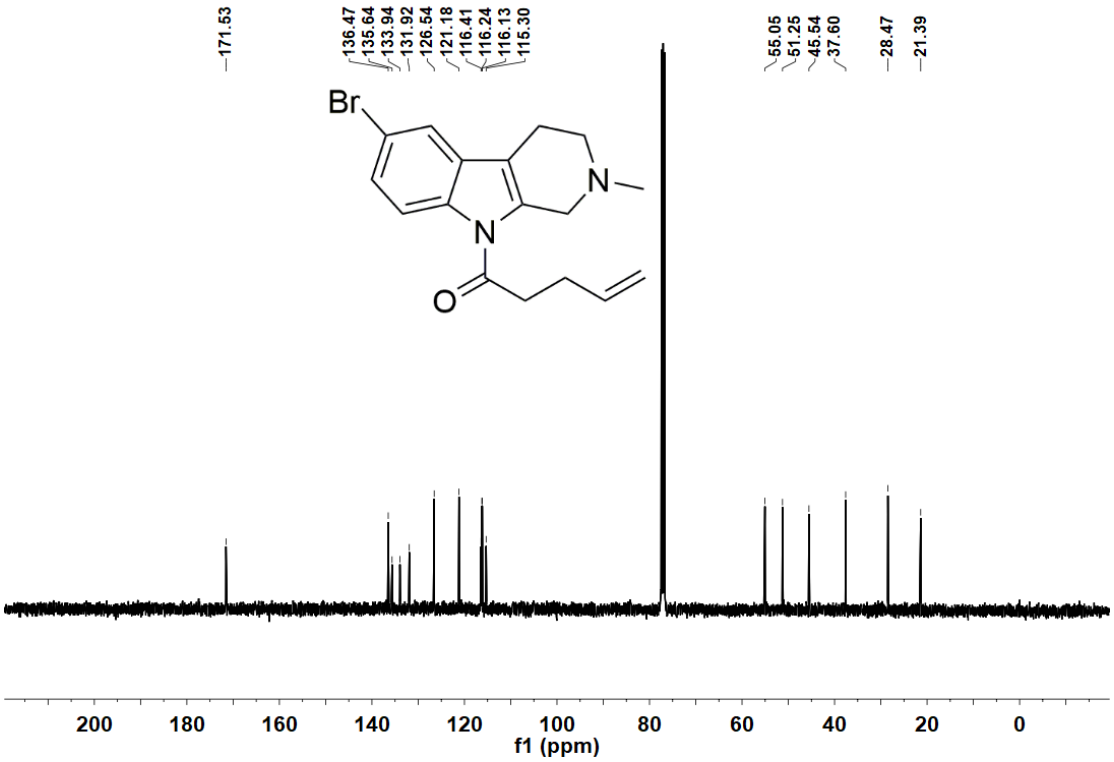

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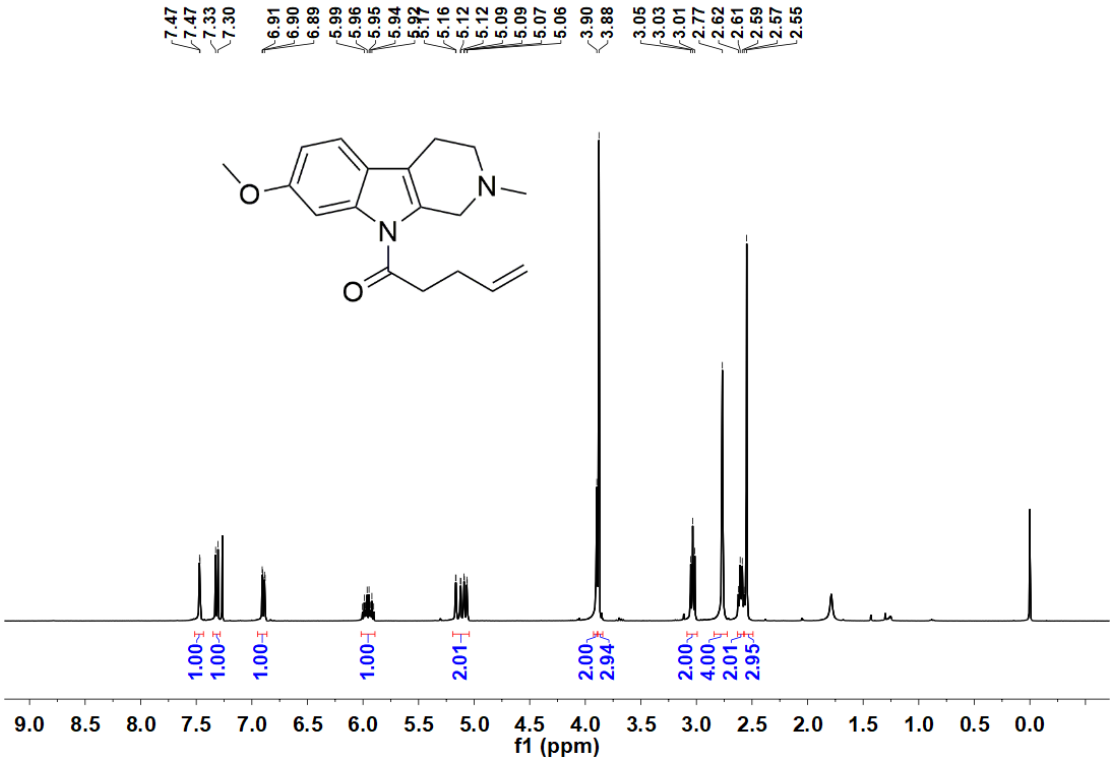

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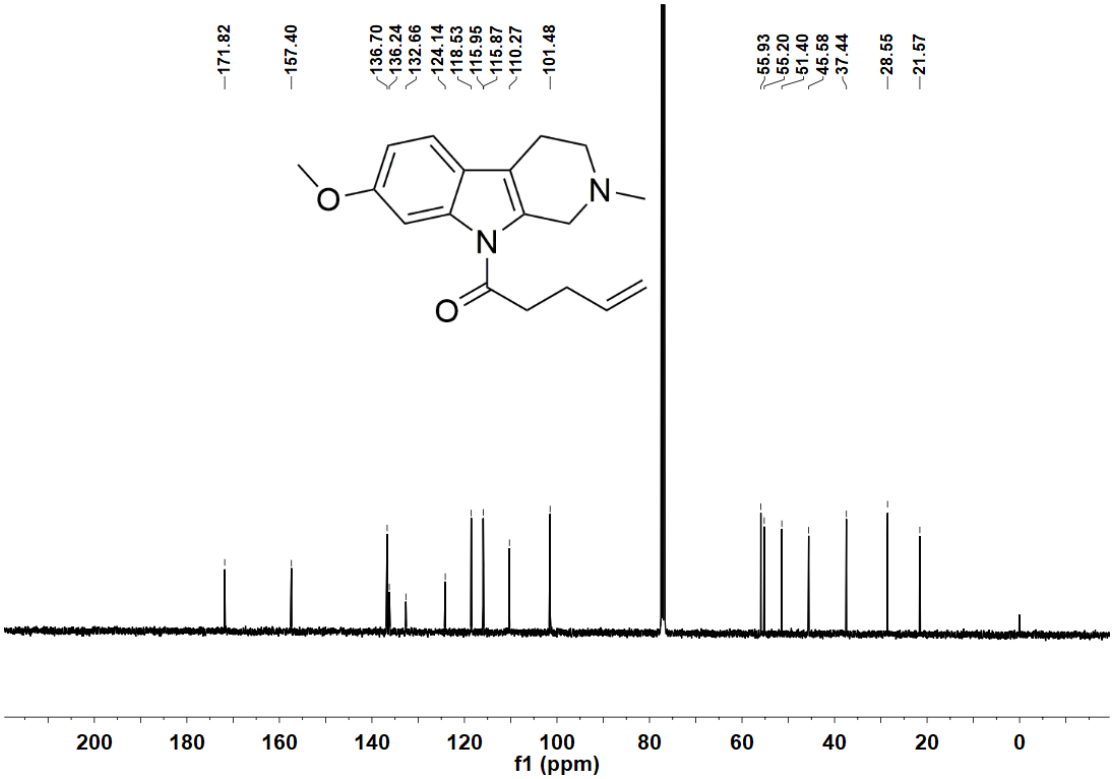
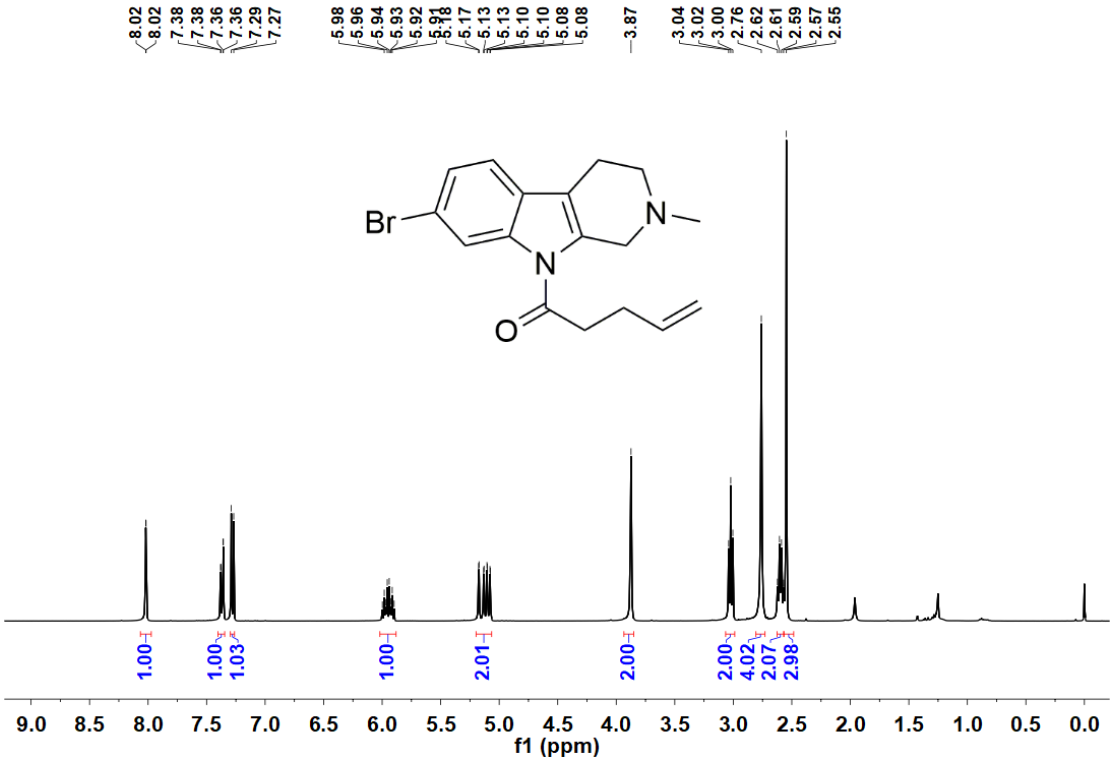


^{1}H NMR spectrum of **1g**



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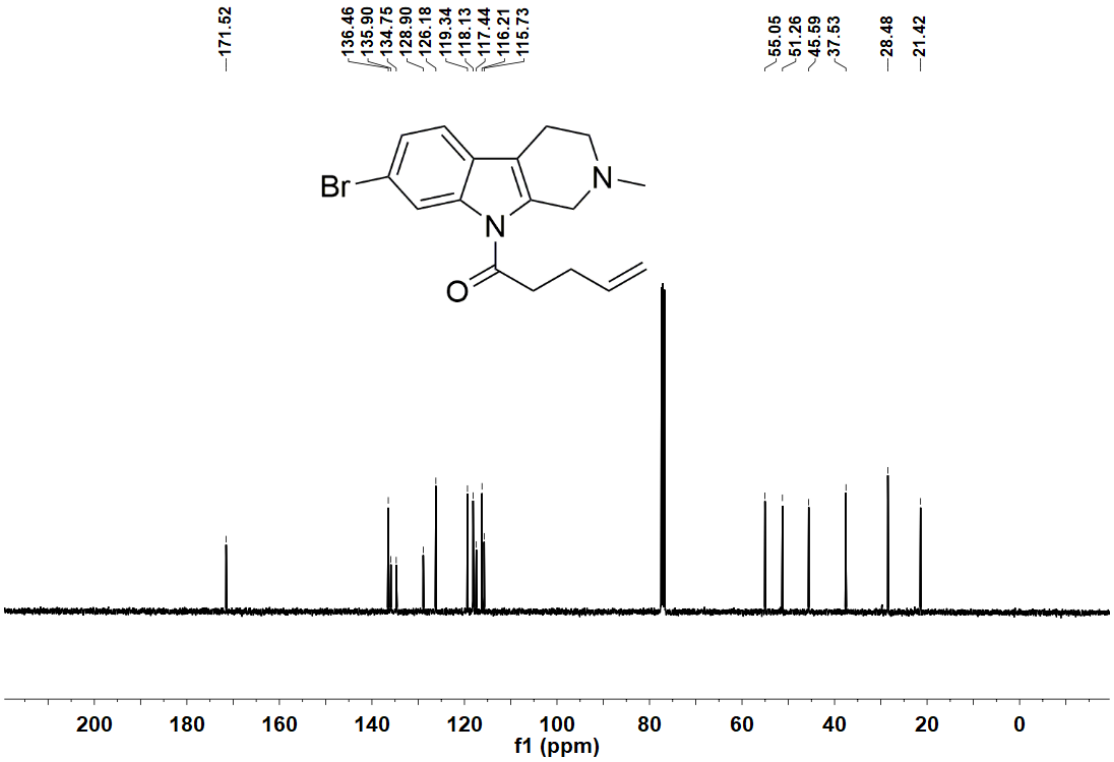

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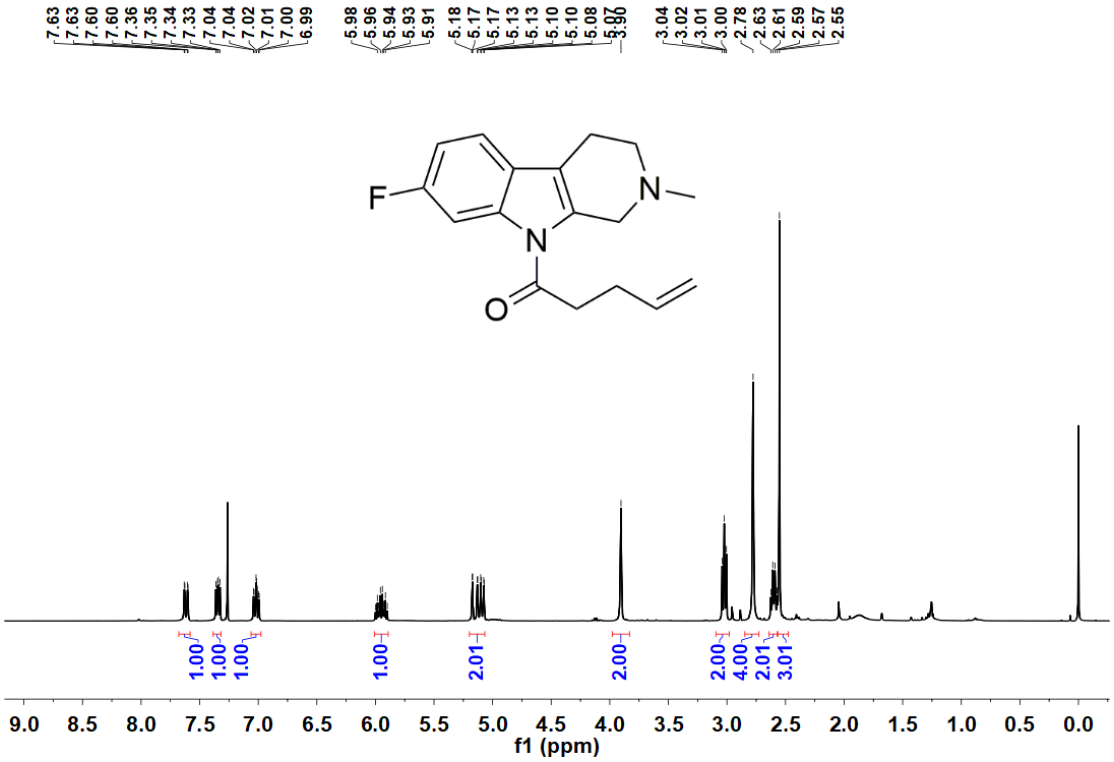

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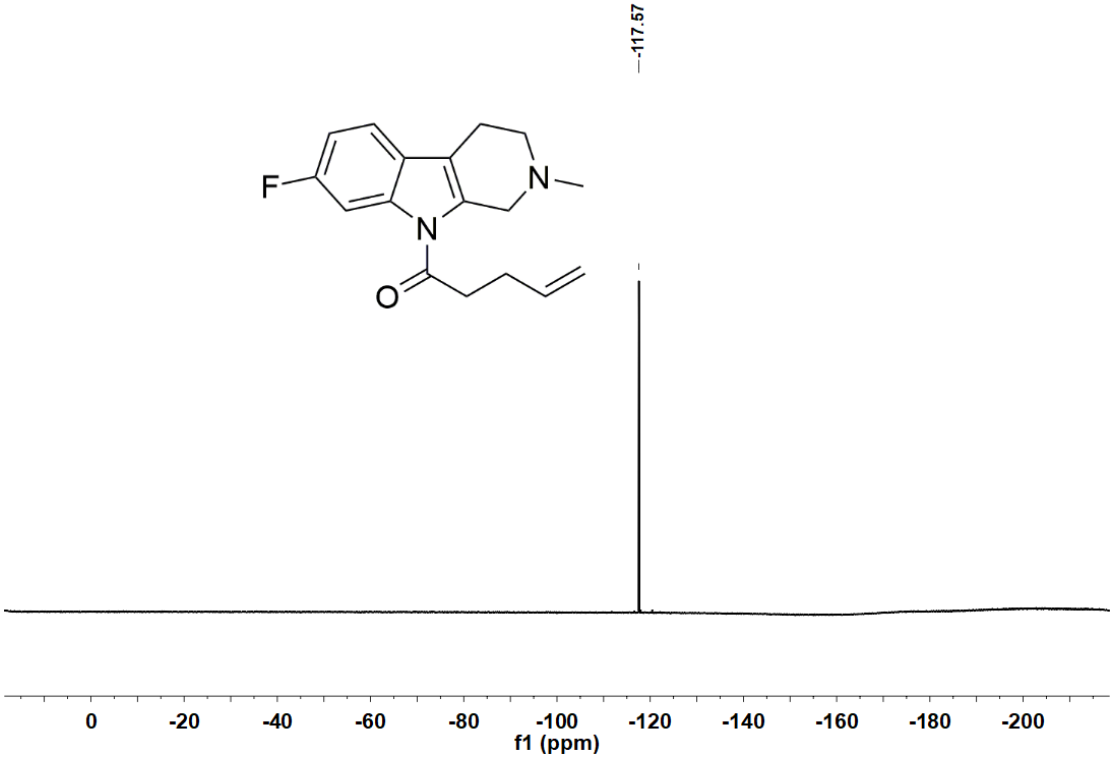

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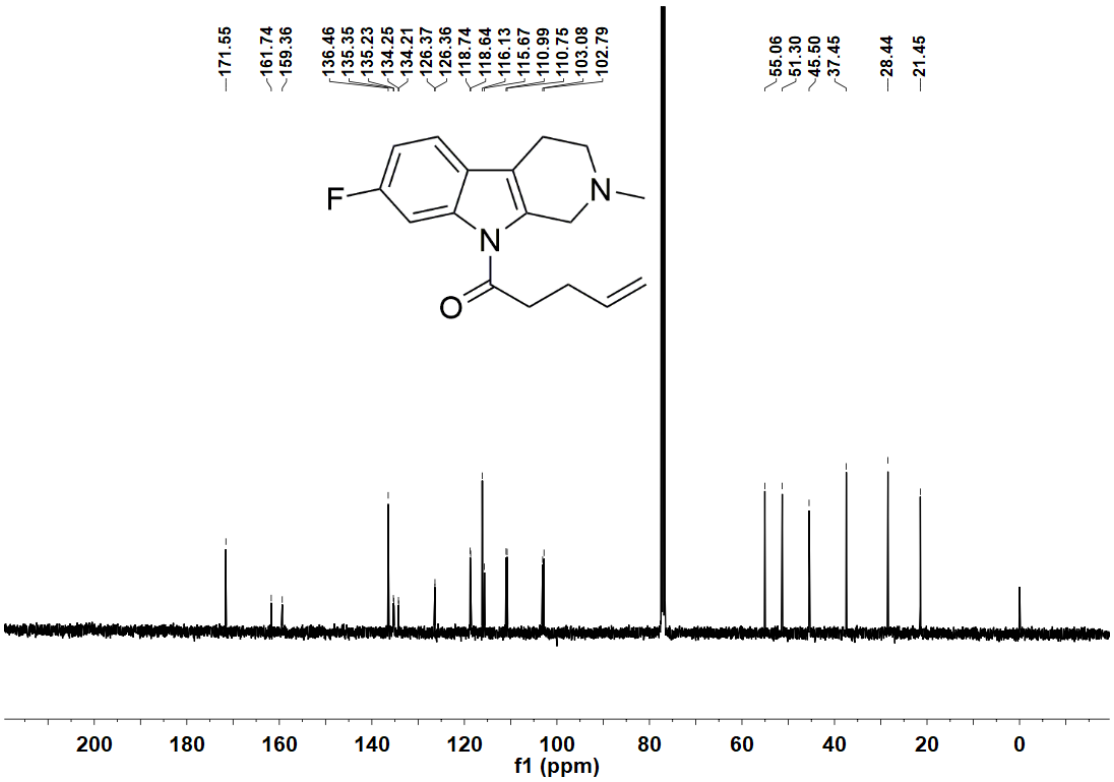
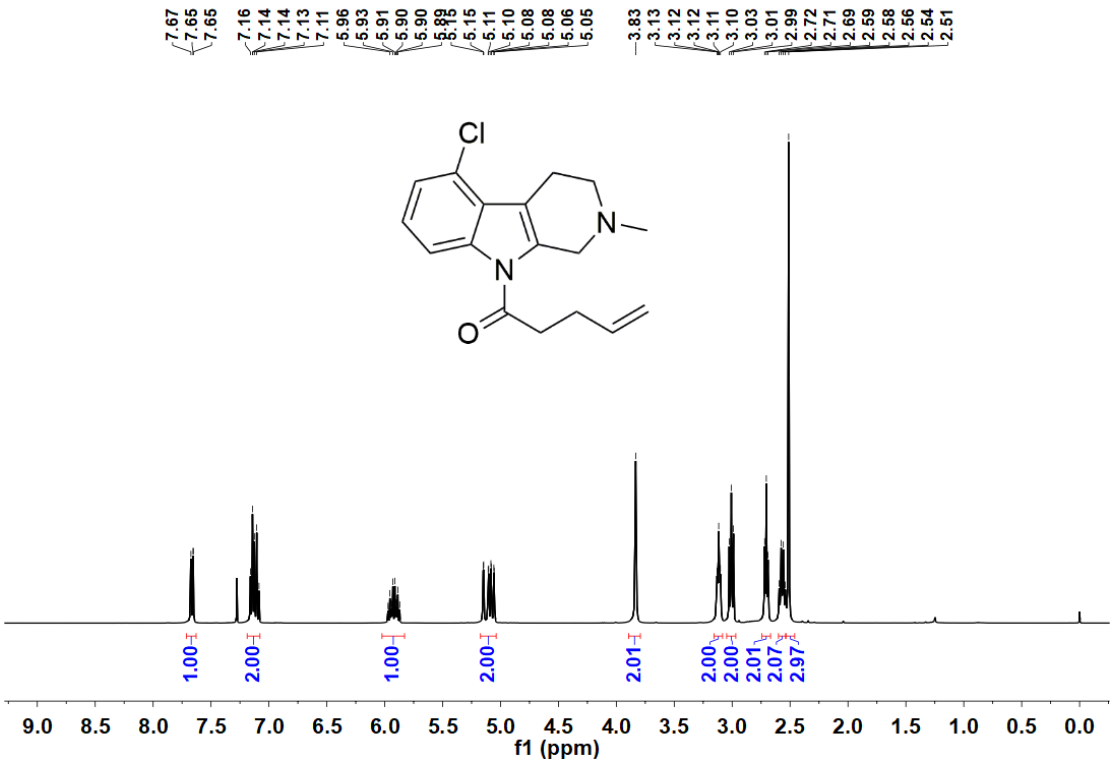


^{1}H NMR spectrum of **1i**



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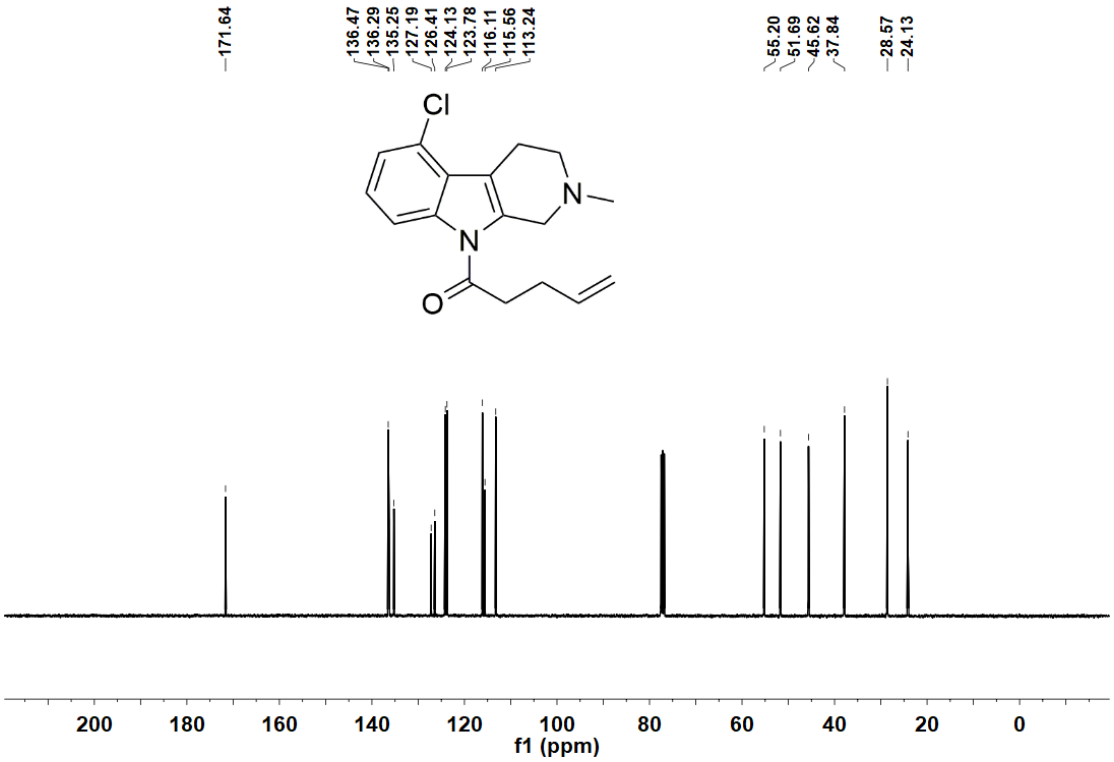

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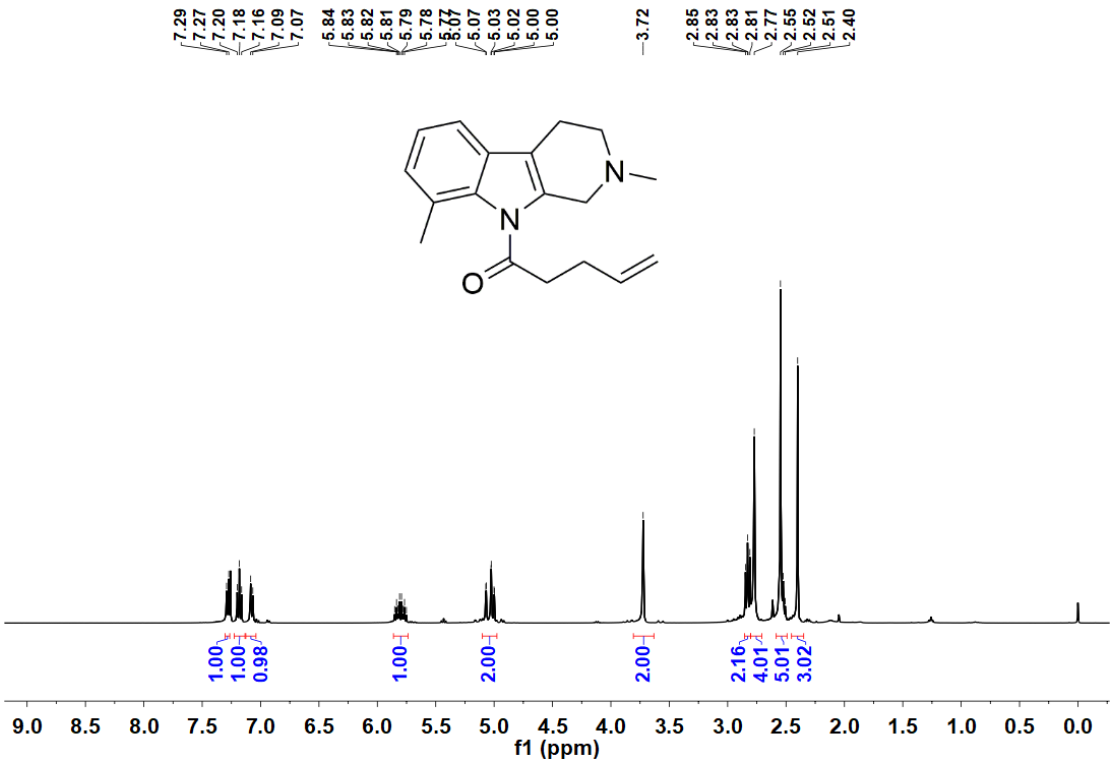

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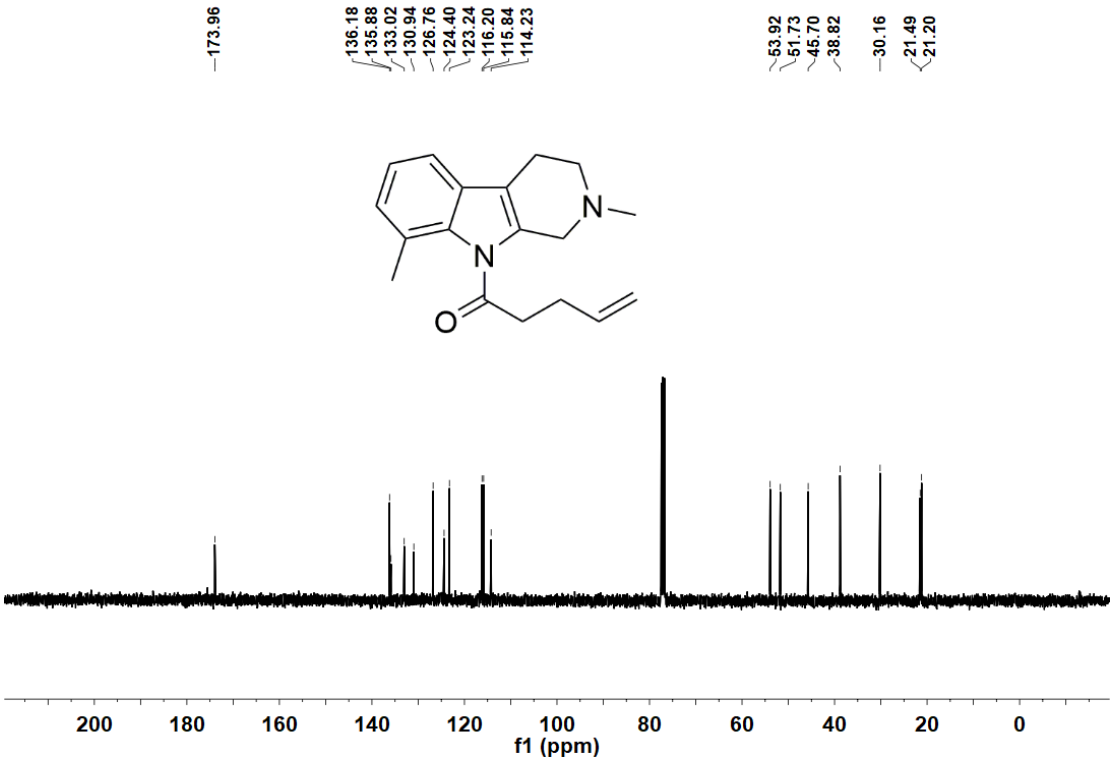

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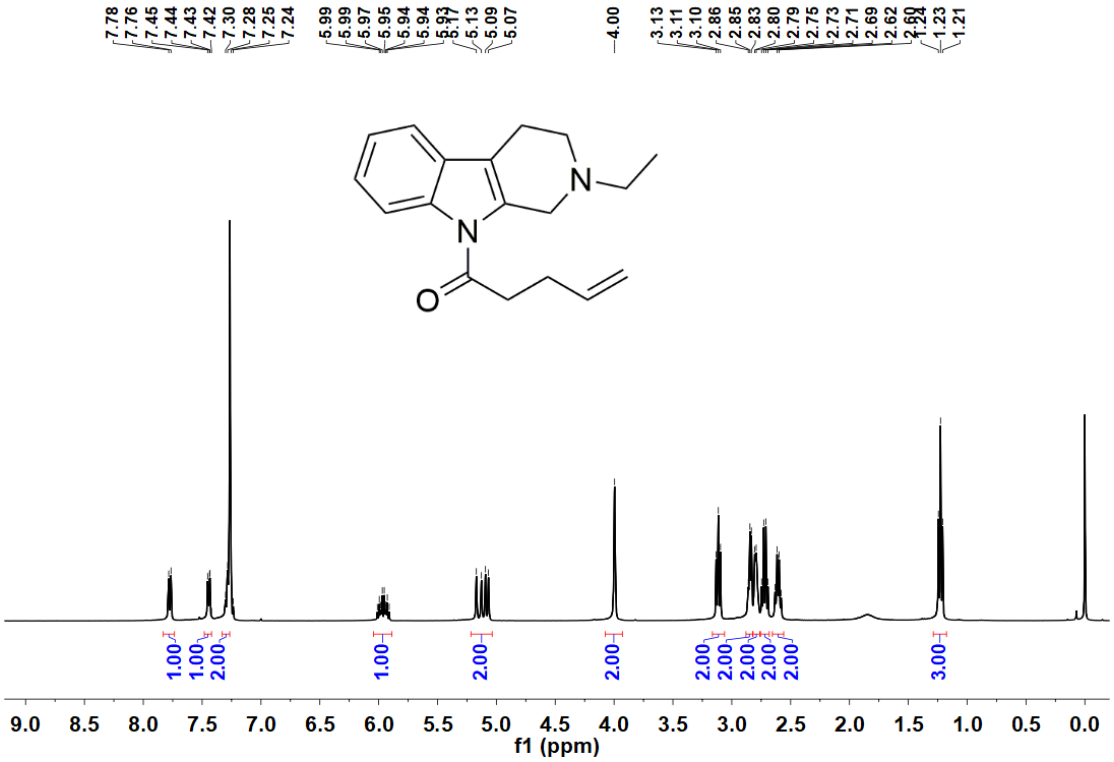

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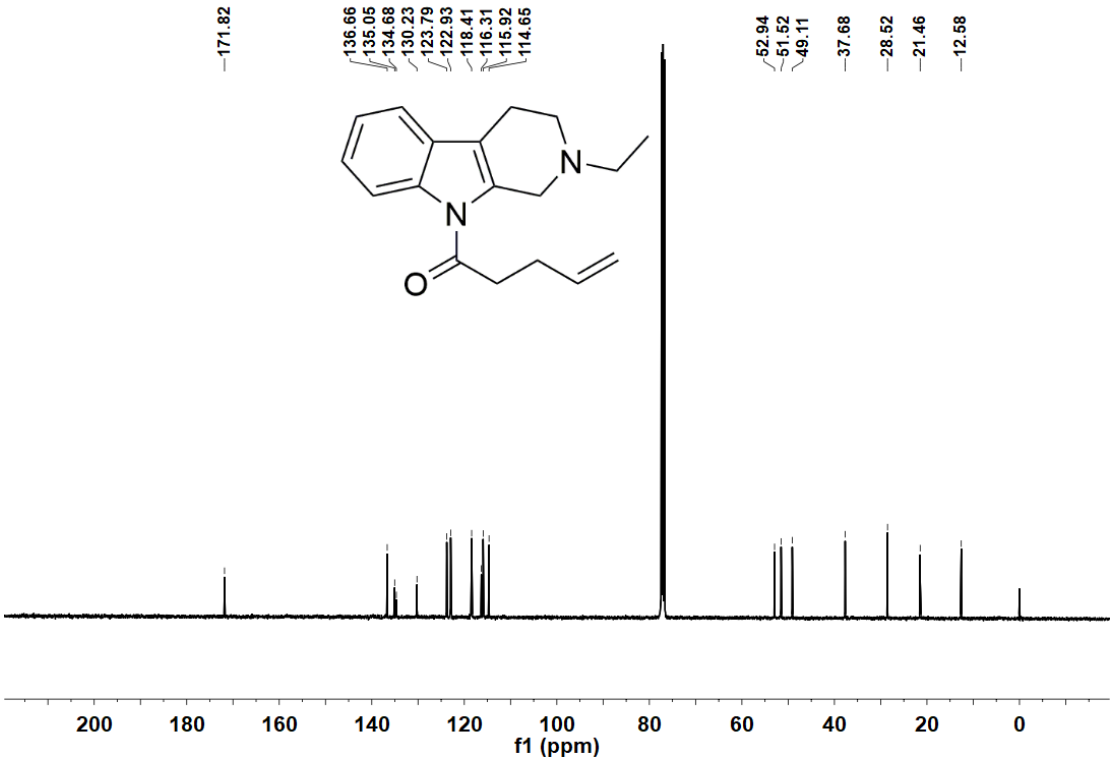
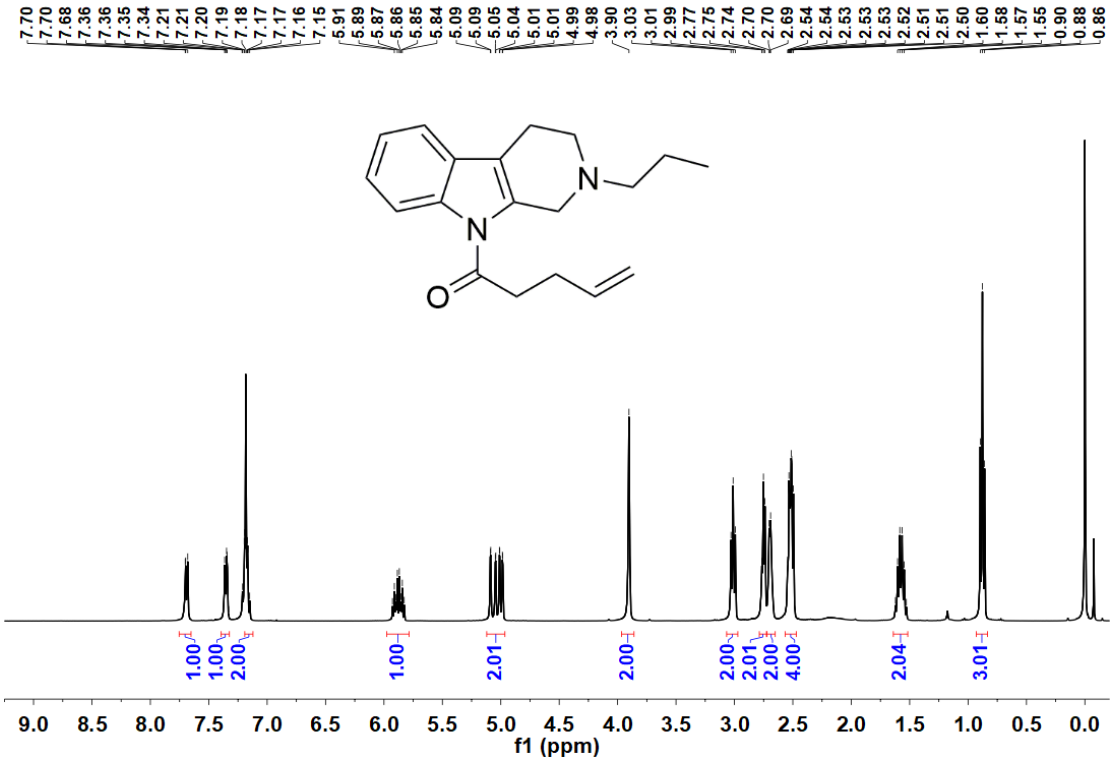
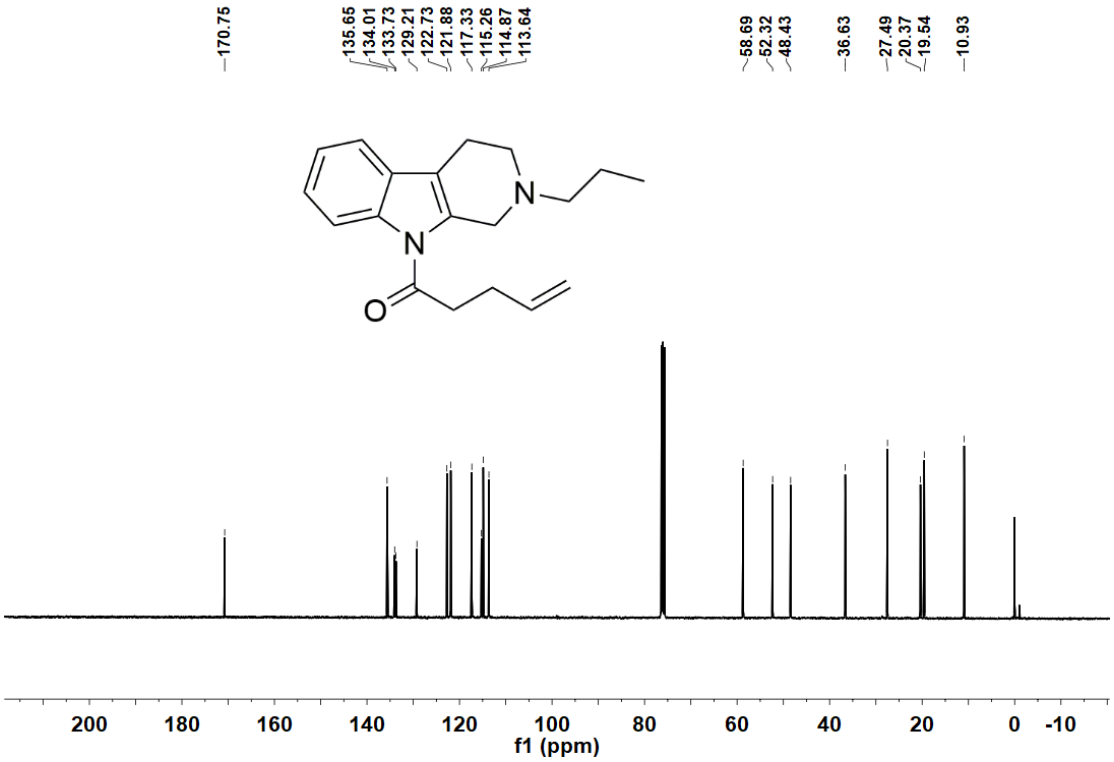


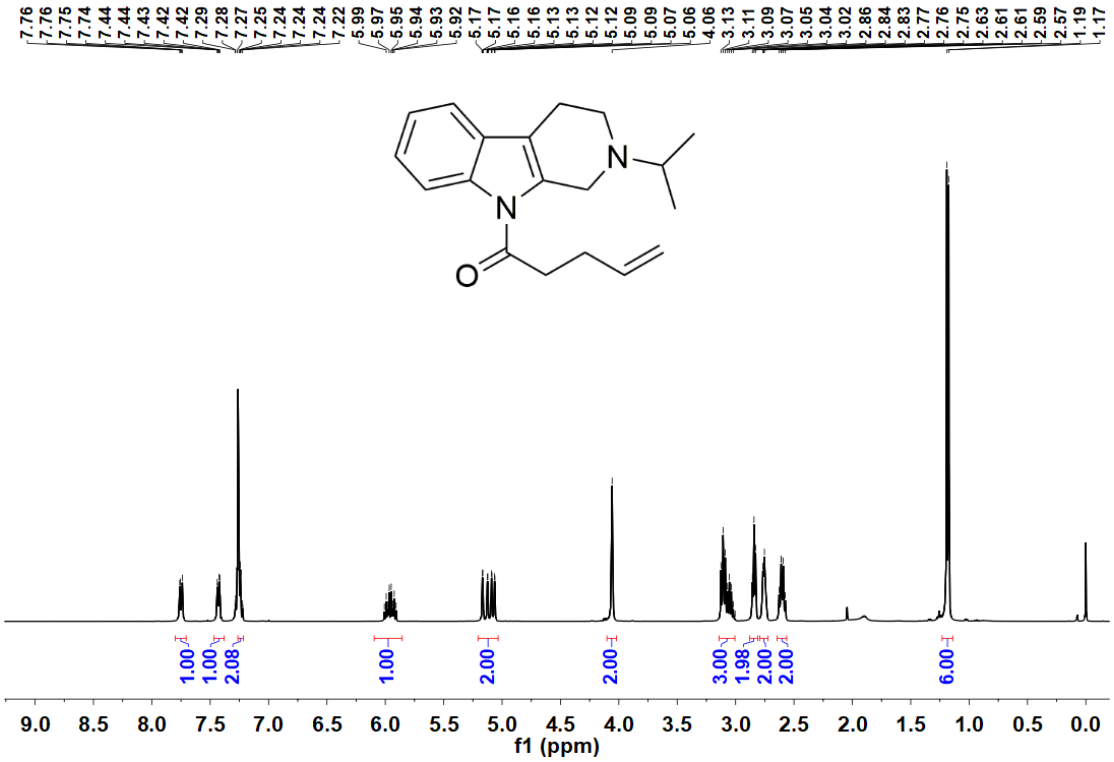
^{1}H NMR spectrum of **1l**



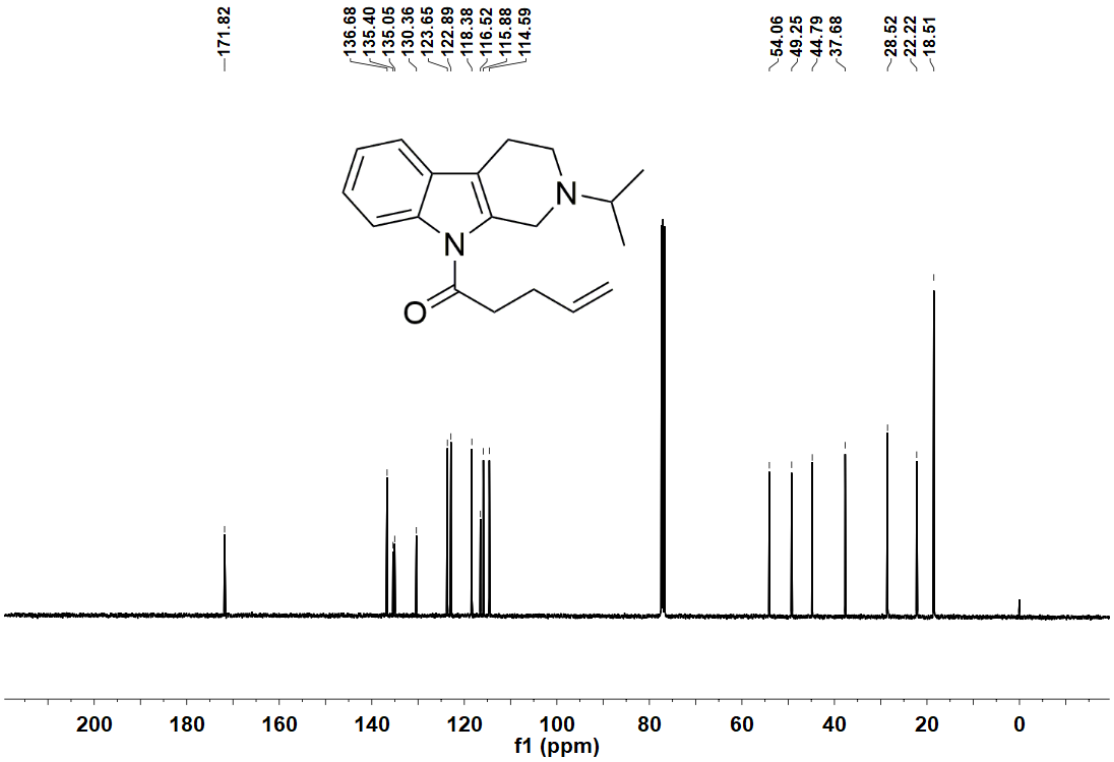
^{13}C NMR spectrum of **1l**



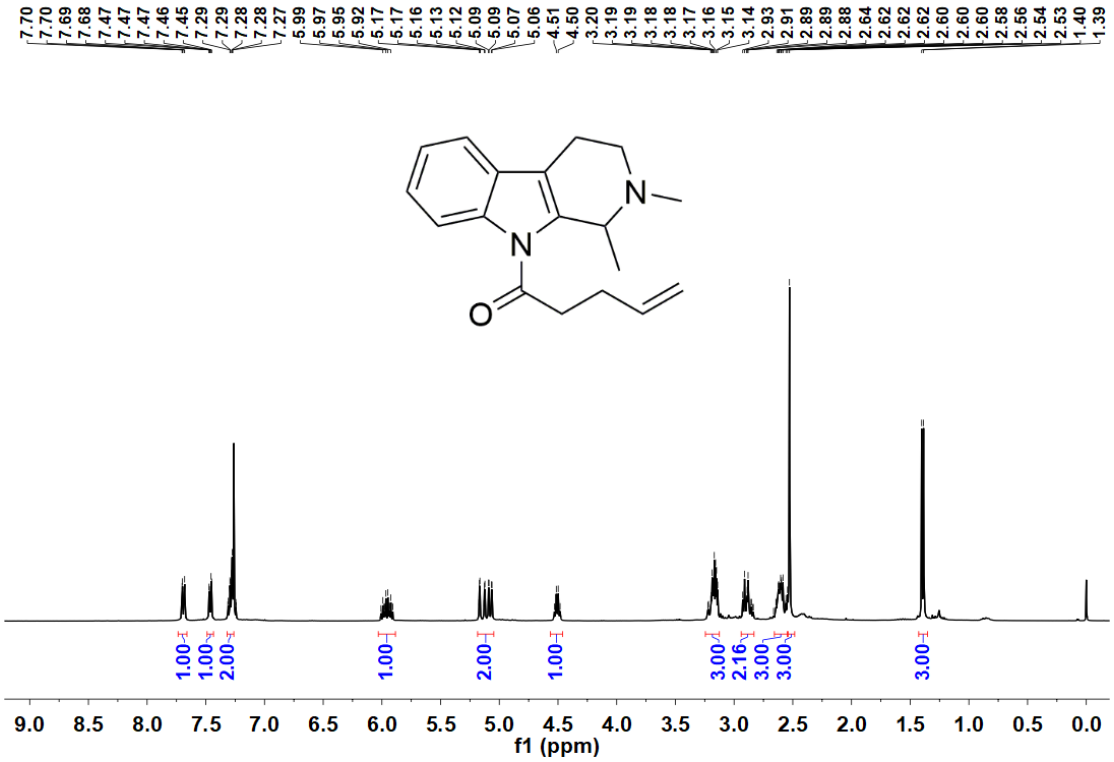
^{1}H NMR spectrum of **1m**



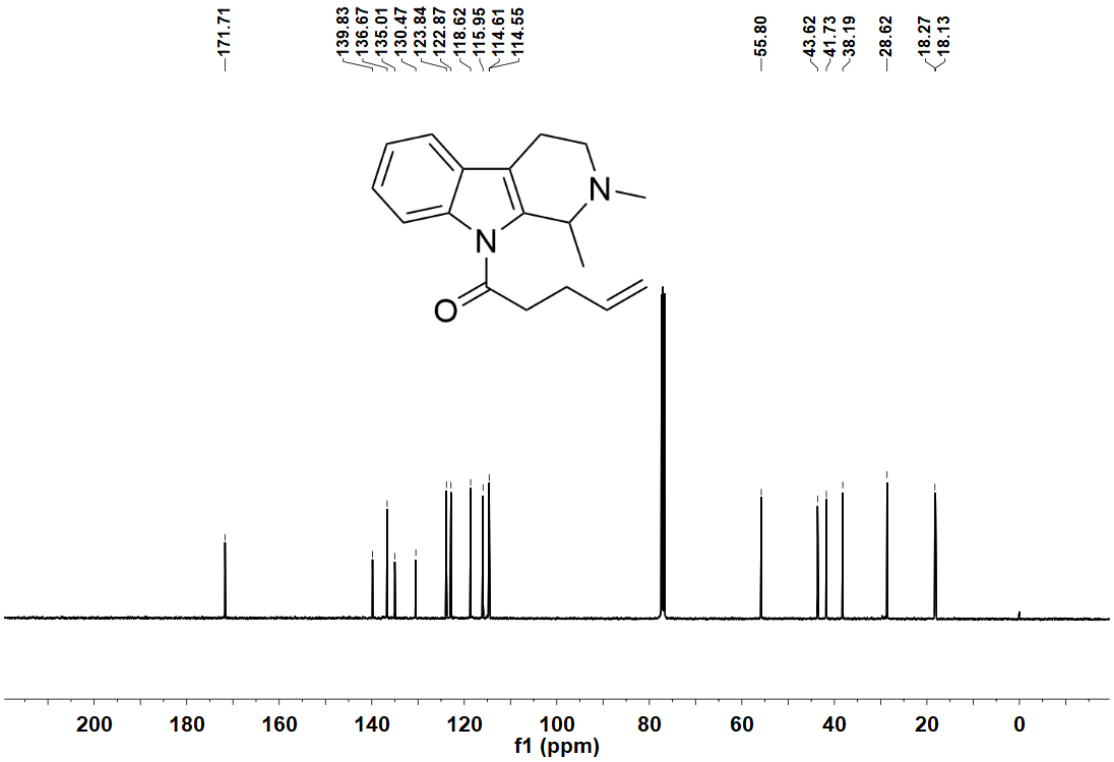
^{13}C NMR spectrum of **1m**



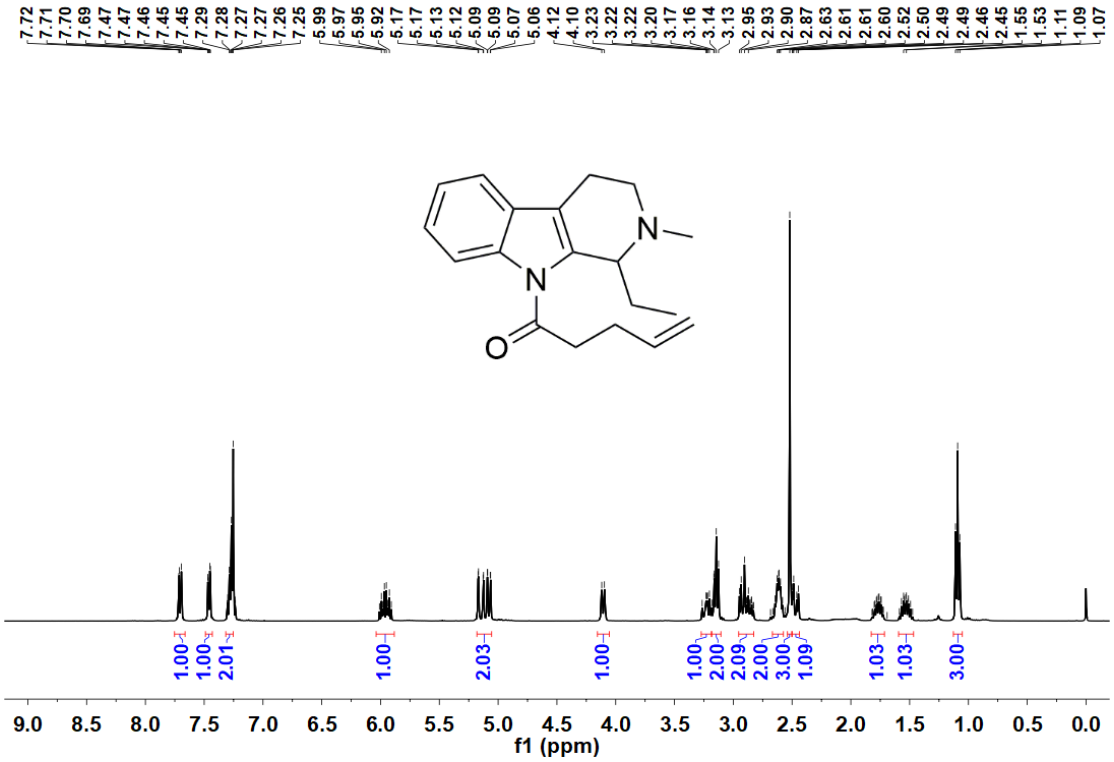
^{1}H NMR spectrum of **1n**



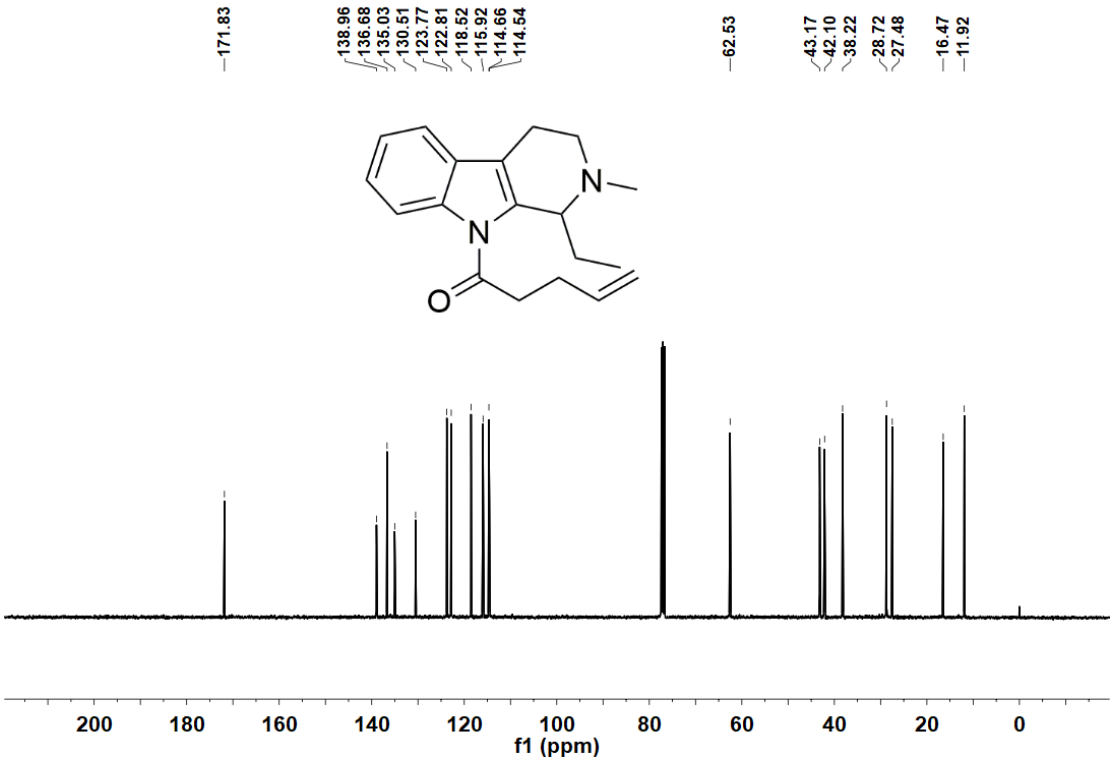
^{13}C NMR spectrum of **1n**



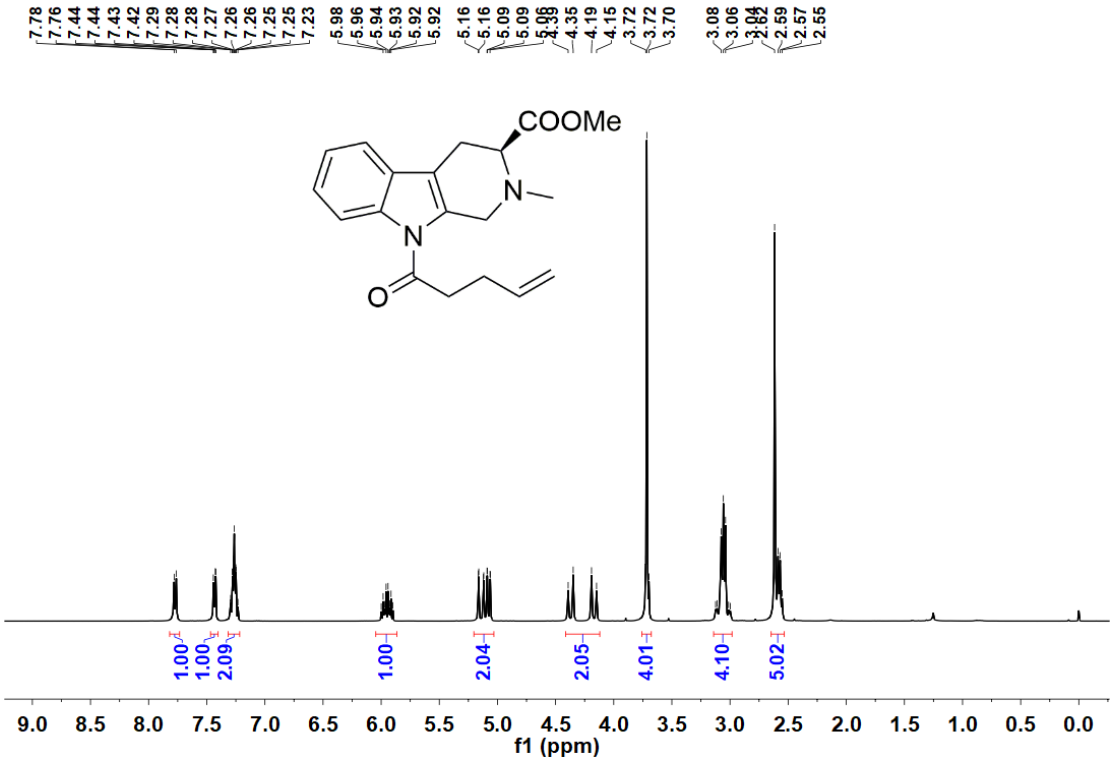
^{1}H NMR spectrum of **1o**



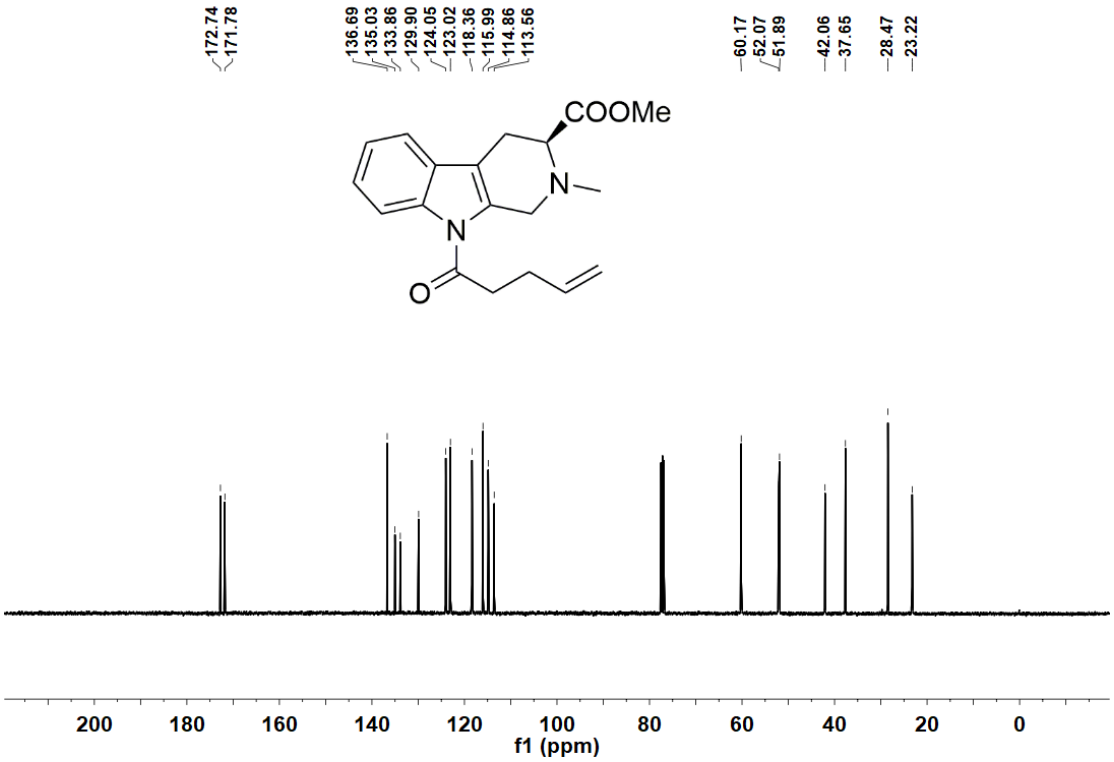
^{13}C NMR spectrum of **1o**



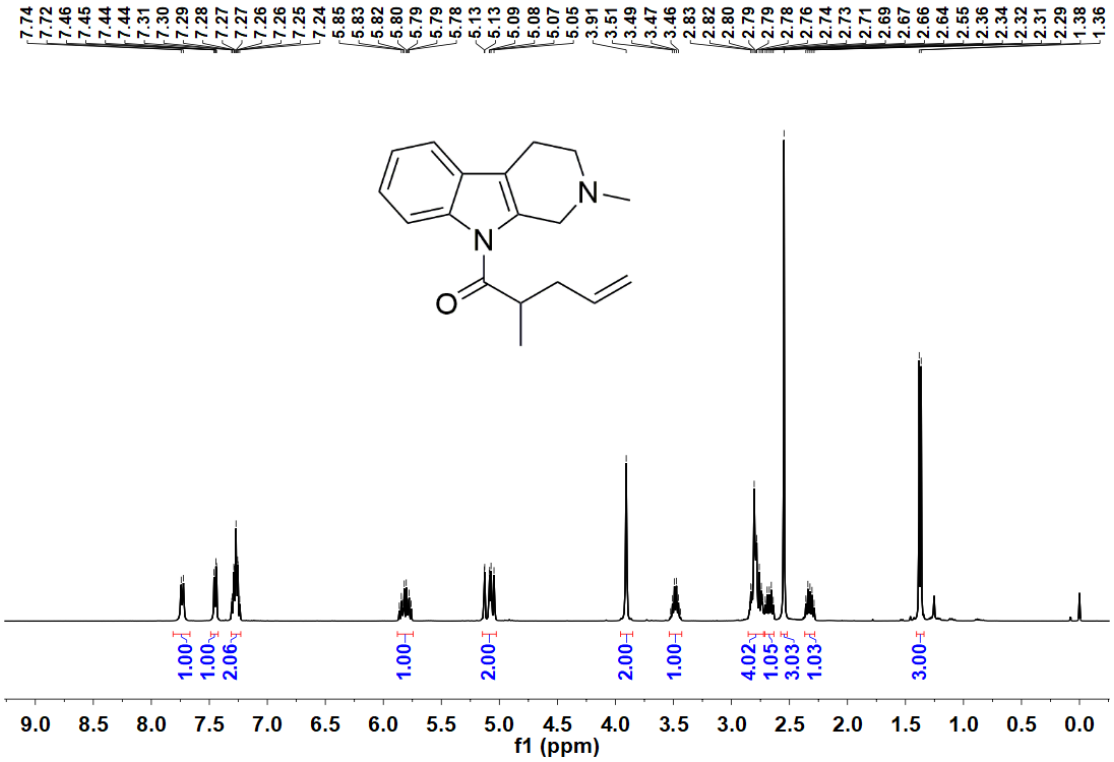
^{1}H NMR spectrum of **1p**



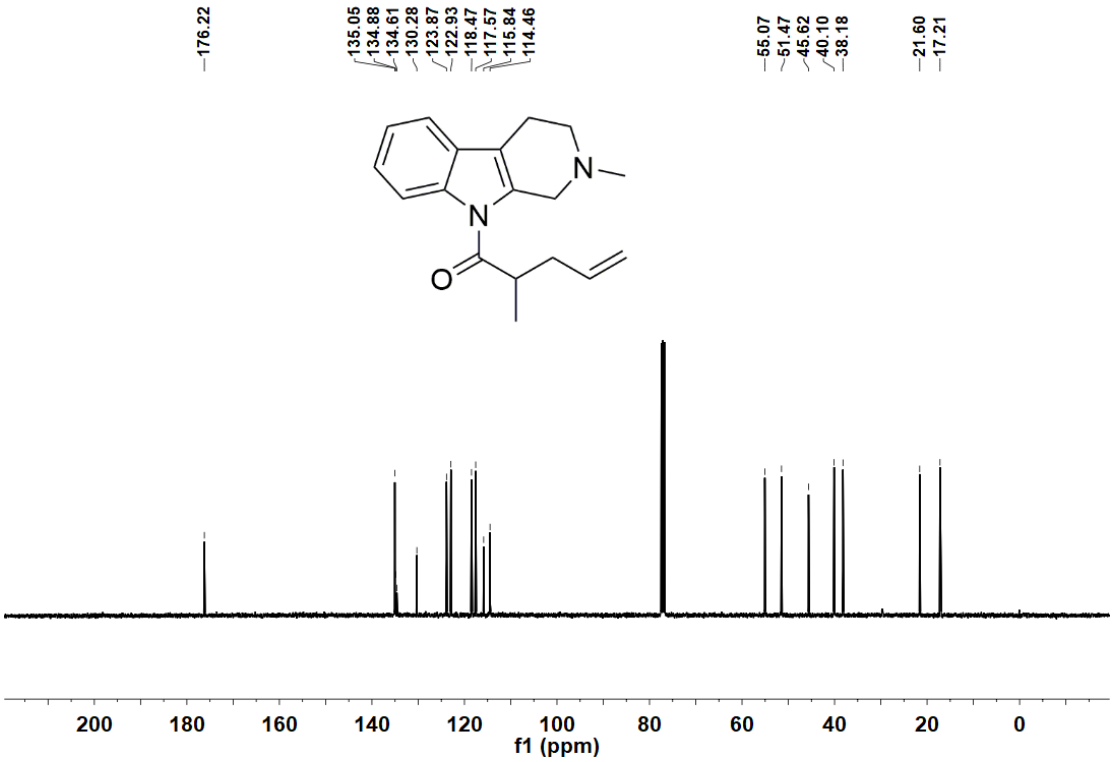
^{13}C NMR spectrum of **1p**



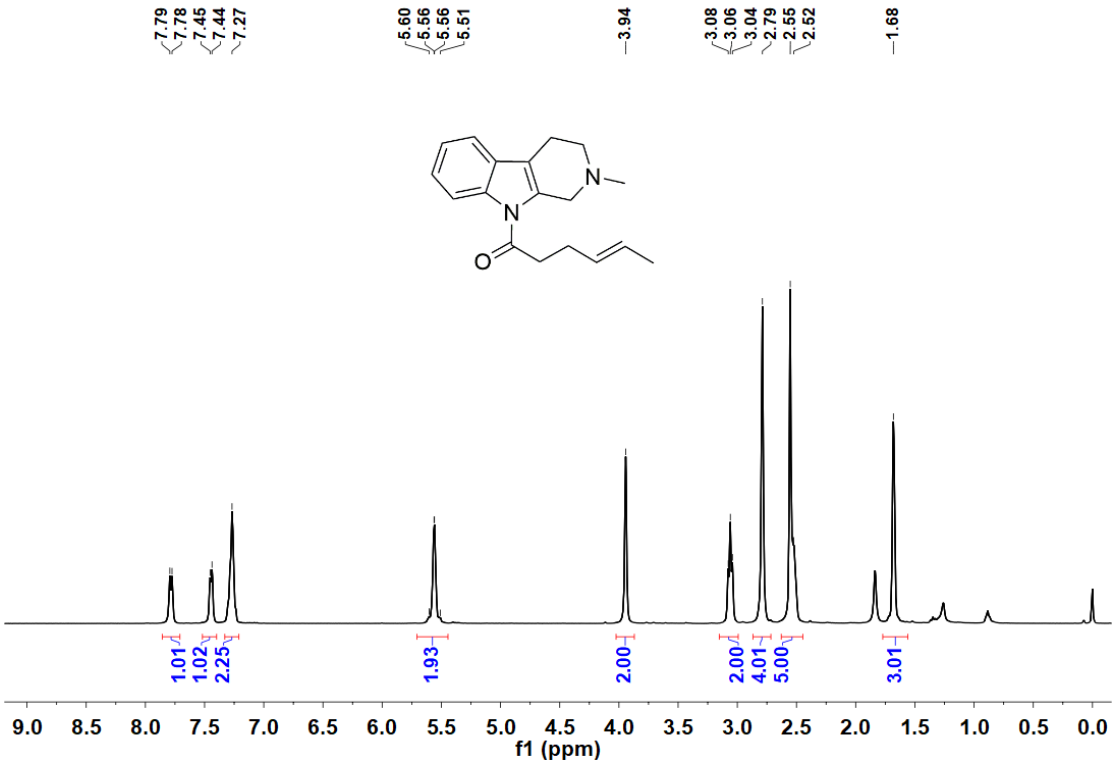
^{1}H NMR spectrum of **1q**



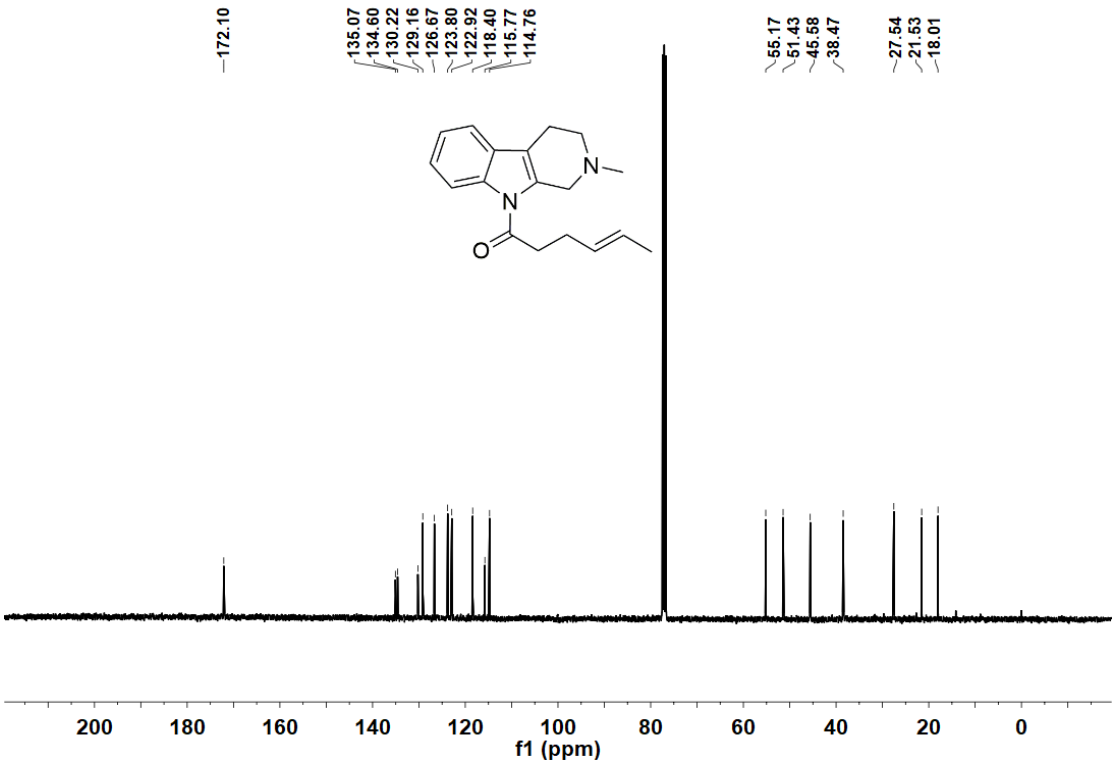
^{13}C NMR spectrum of **1q**



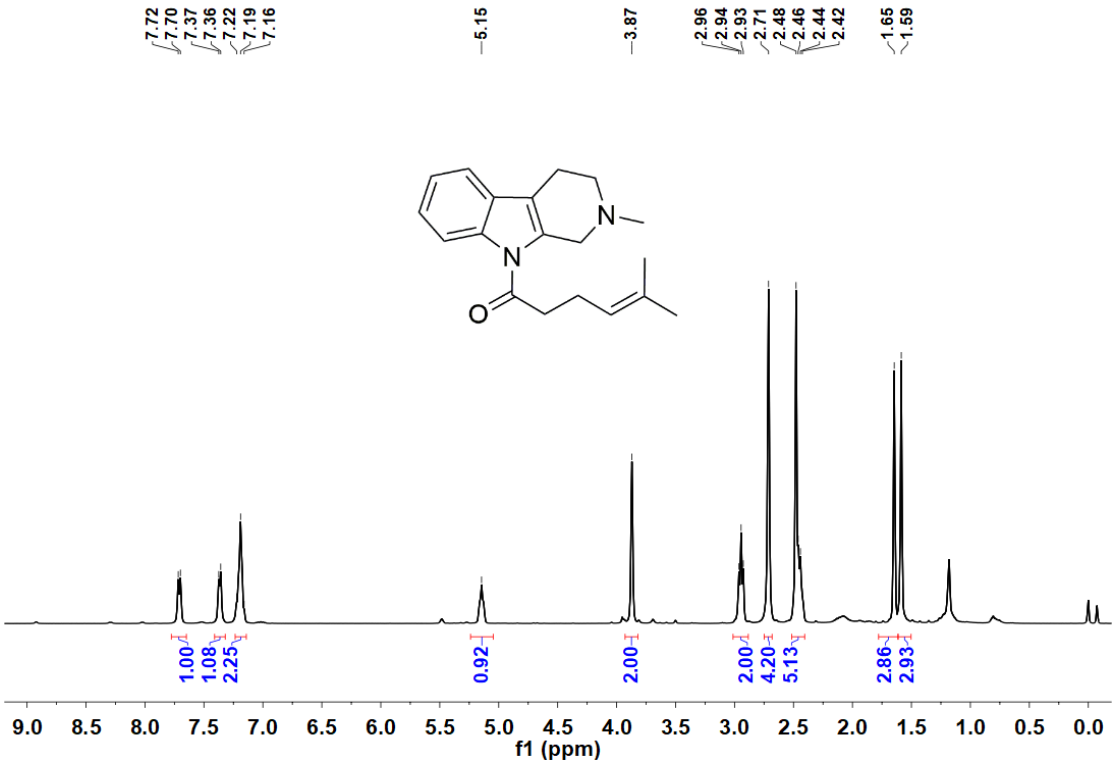
^{1}H NMR spectrum of **1r**



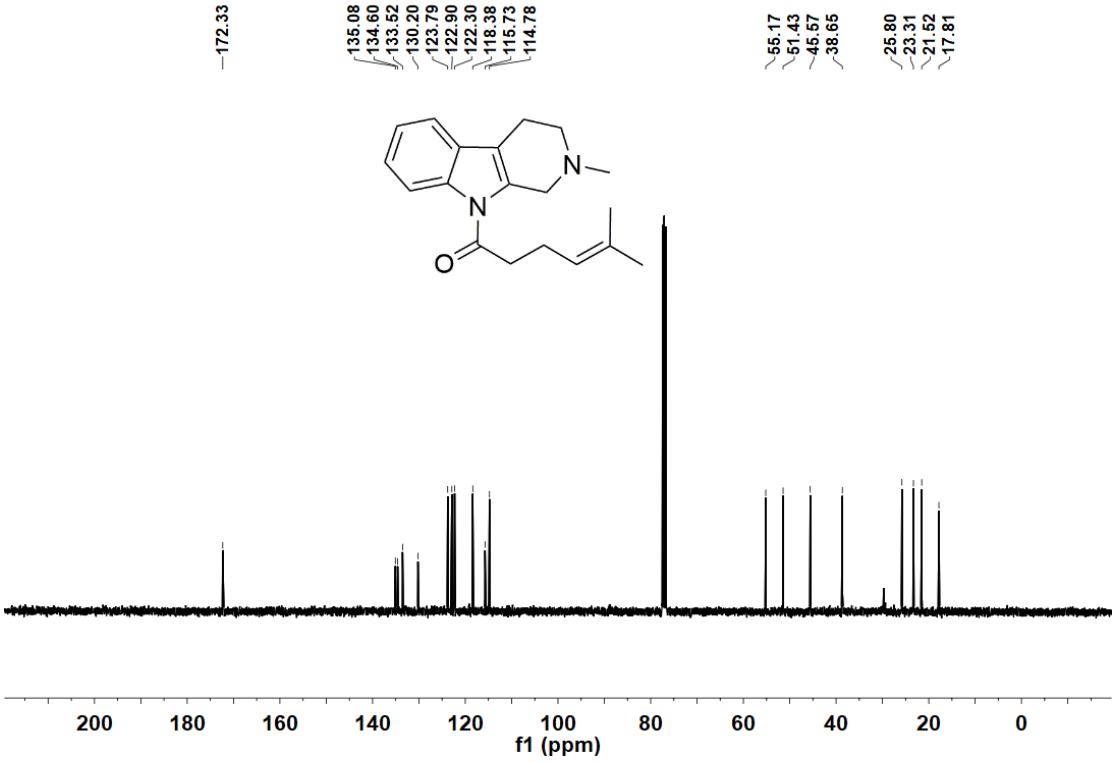
^{13}C NMR spectrum of **1r**



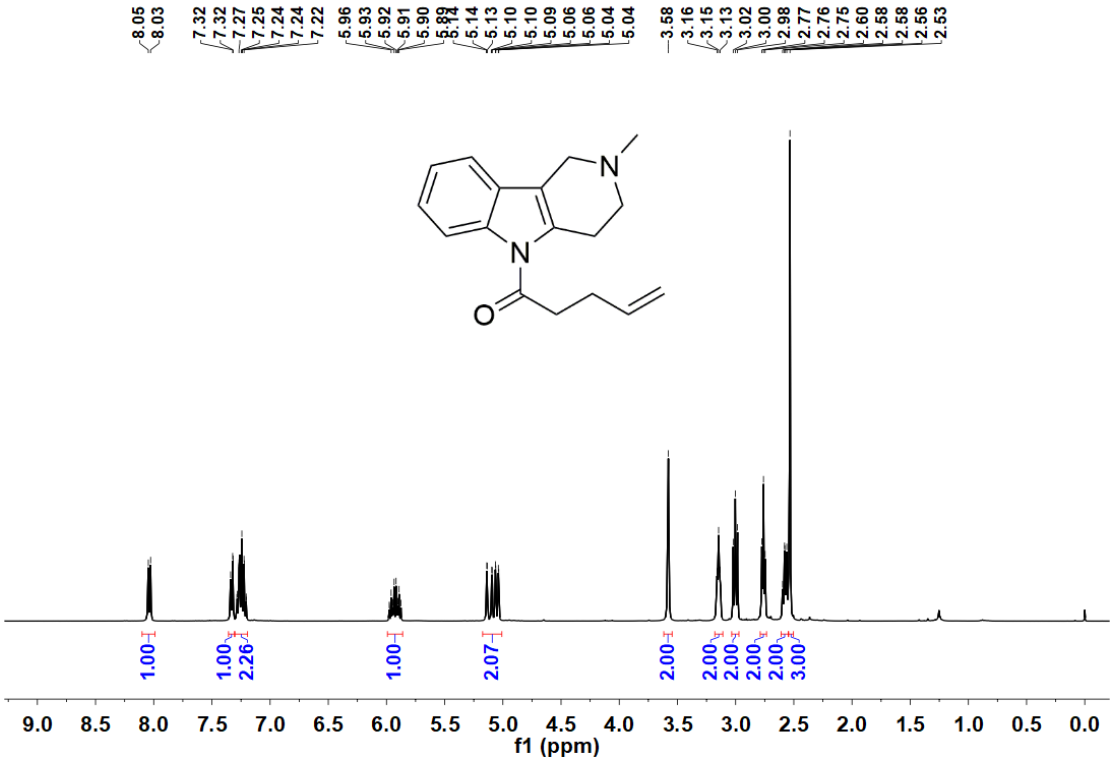
^{1}H NMR spectrum of **1s**



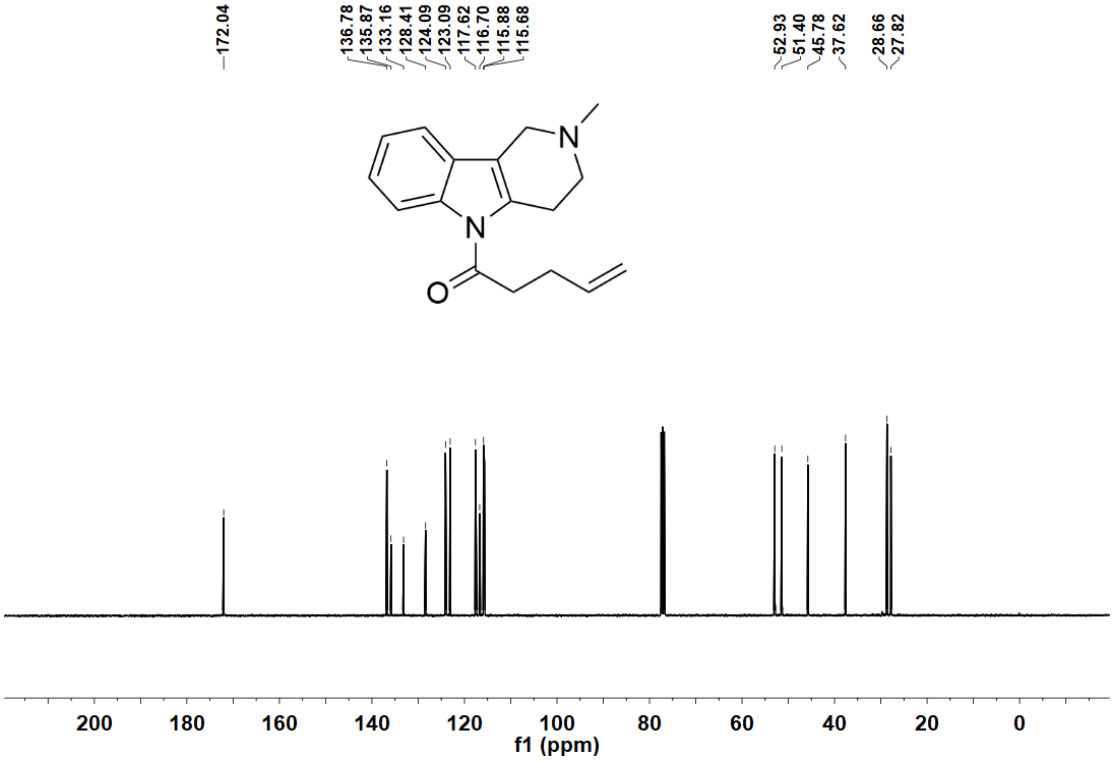
^{13}C NMR spectrum of **1s**



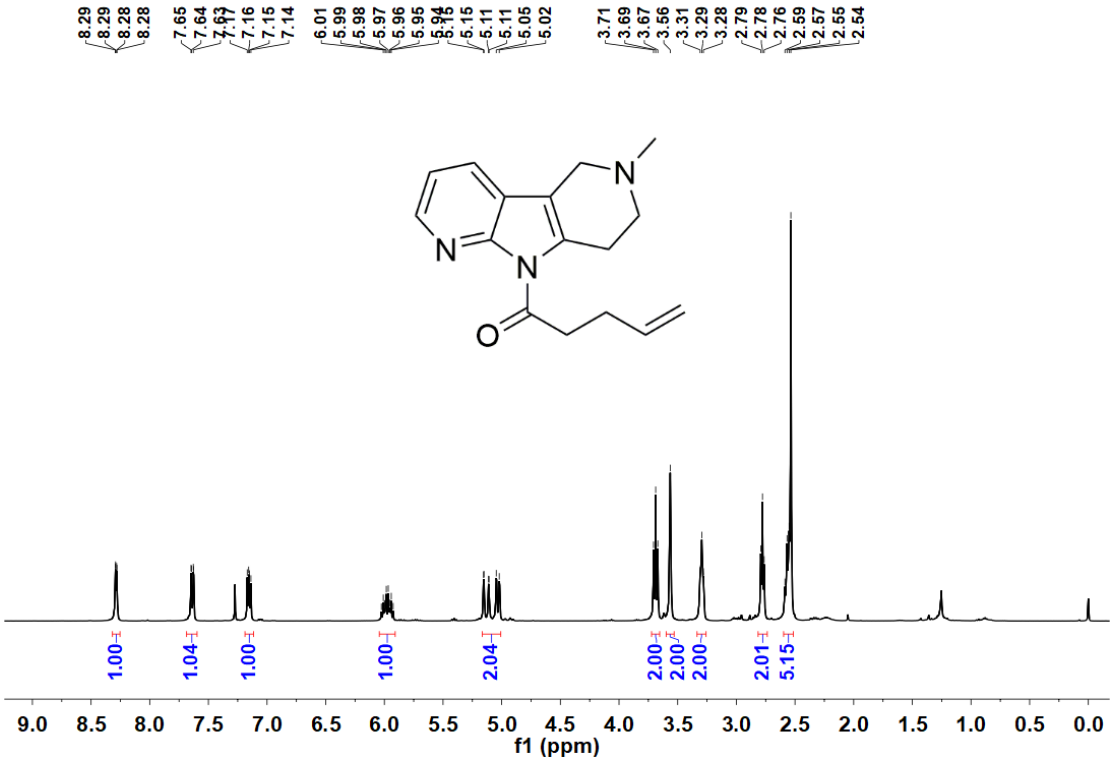
^{1}H NMR spectrum of **1t**



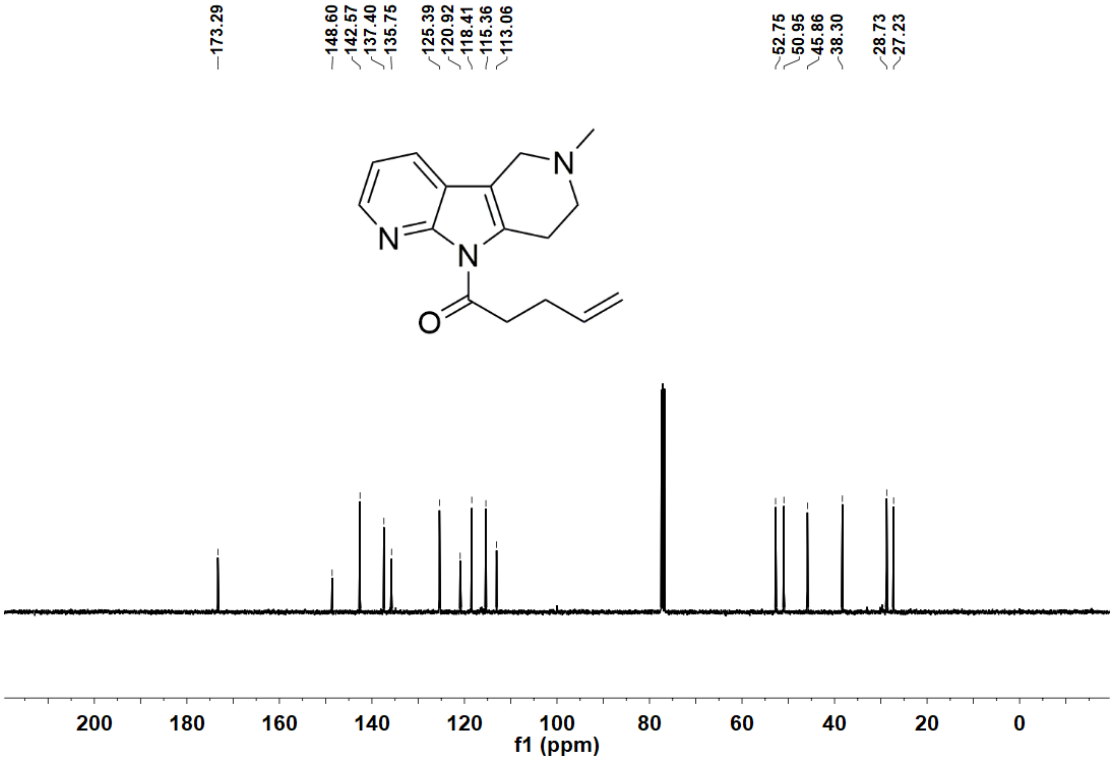
^{13}C NMR spectrum of **1t**



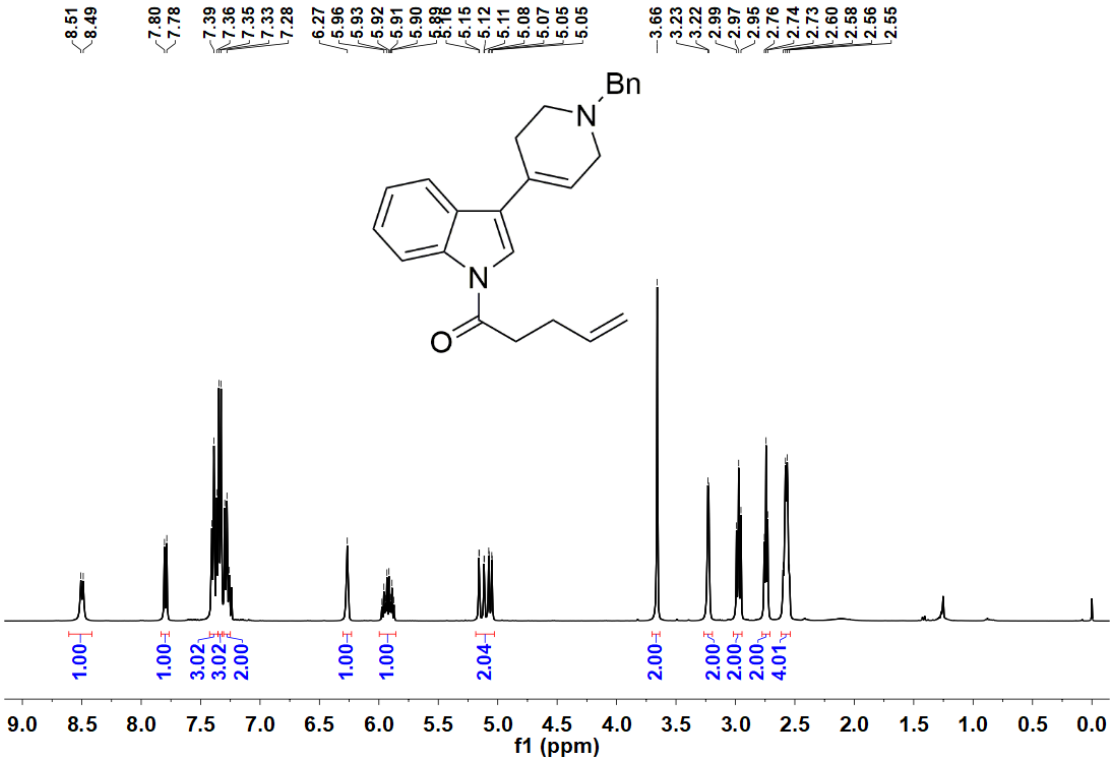
^{1}H NMR spectrum of **1u**



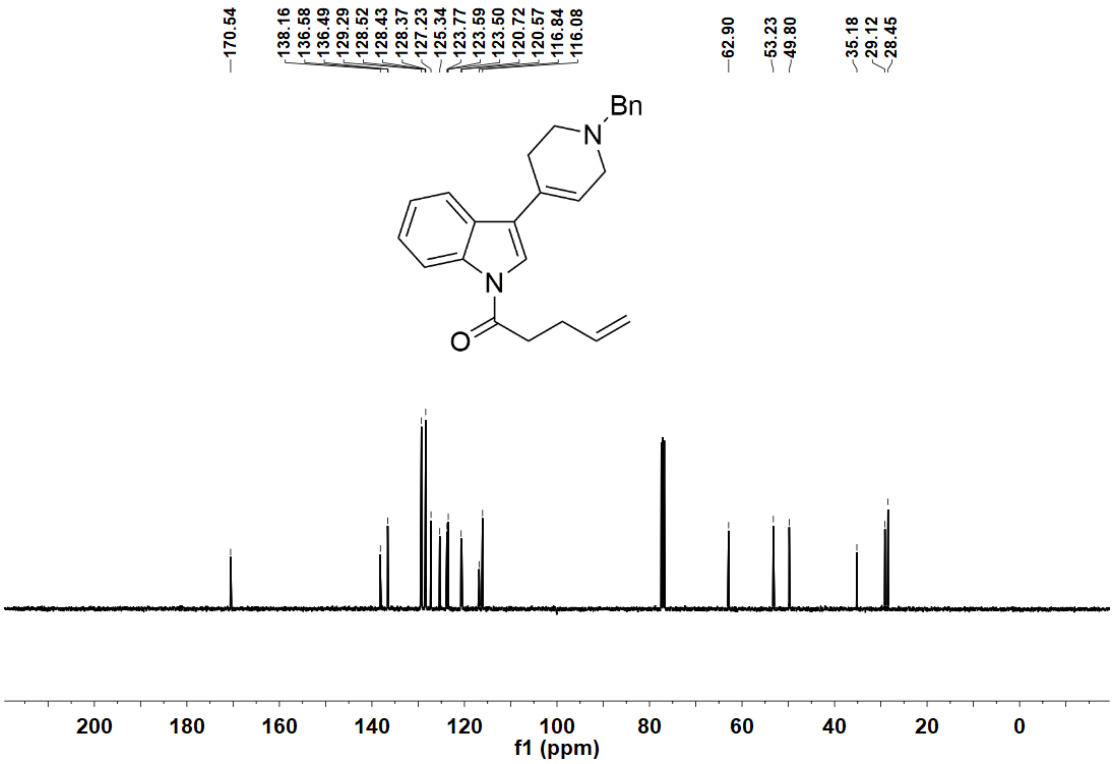
^{13}C NMR spectrum of **1u**



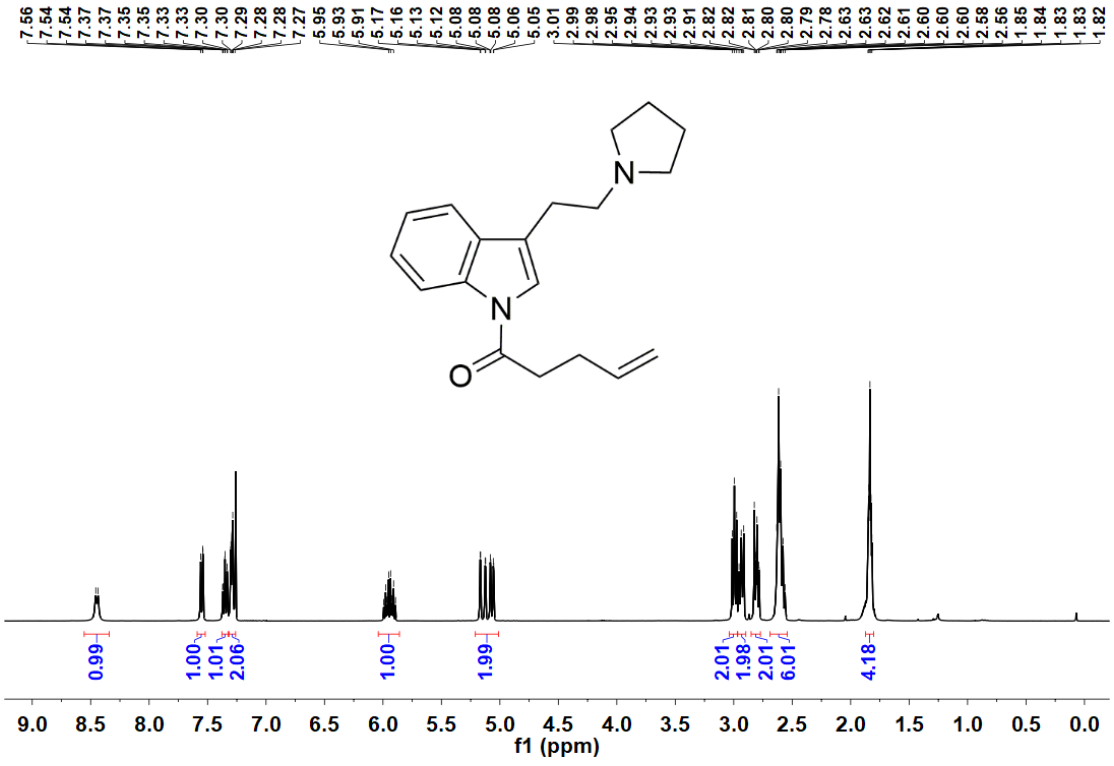
^{1}H NMR spectrum of **1v**



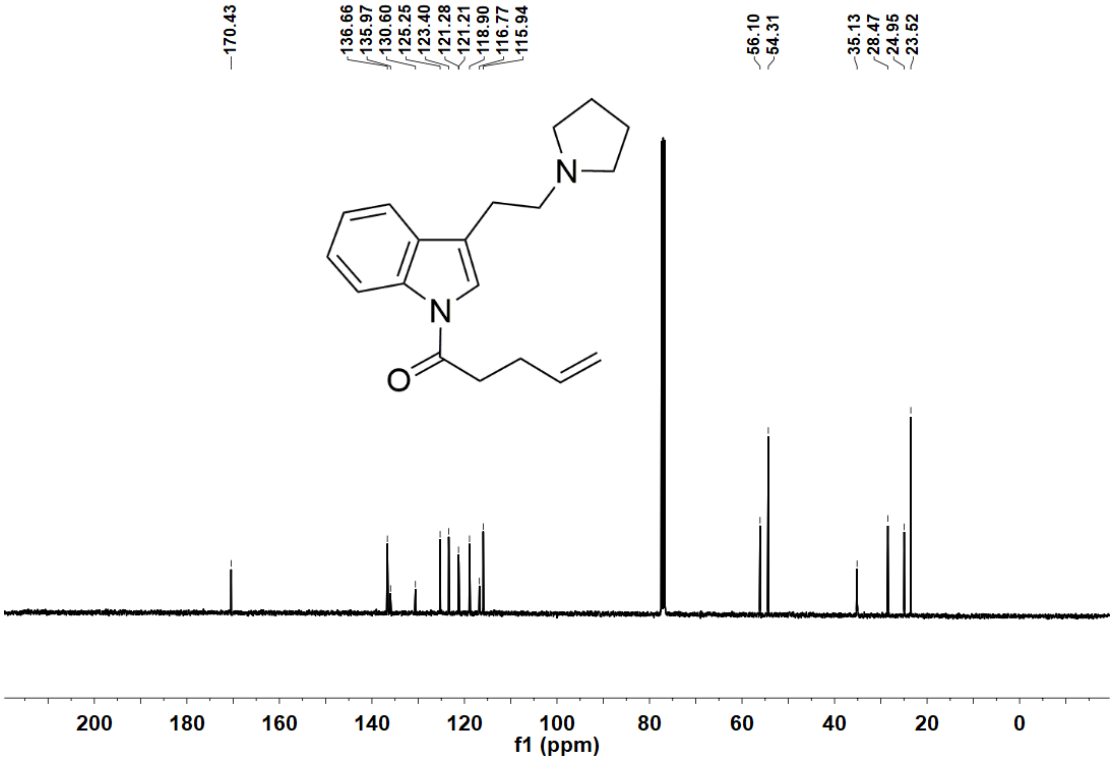
^{13}C NMR spectrum of **1v**



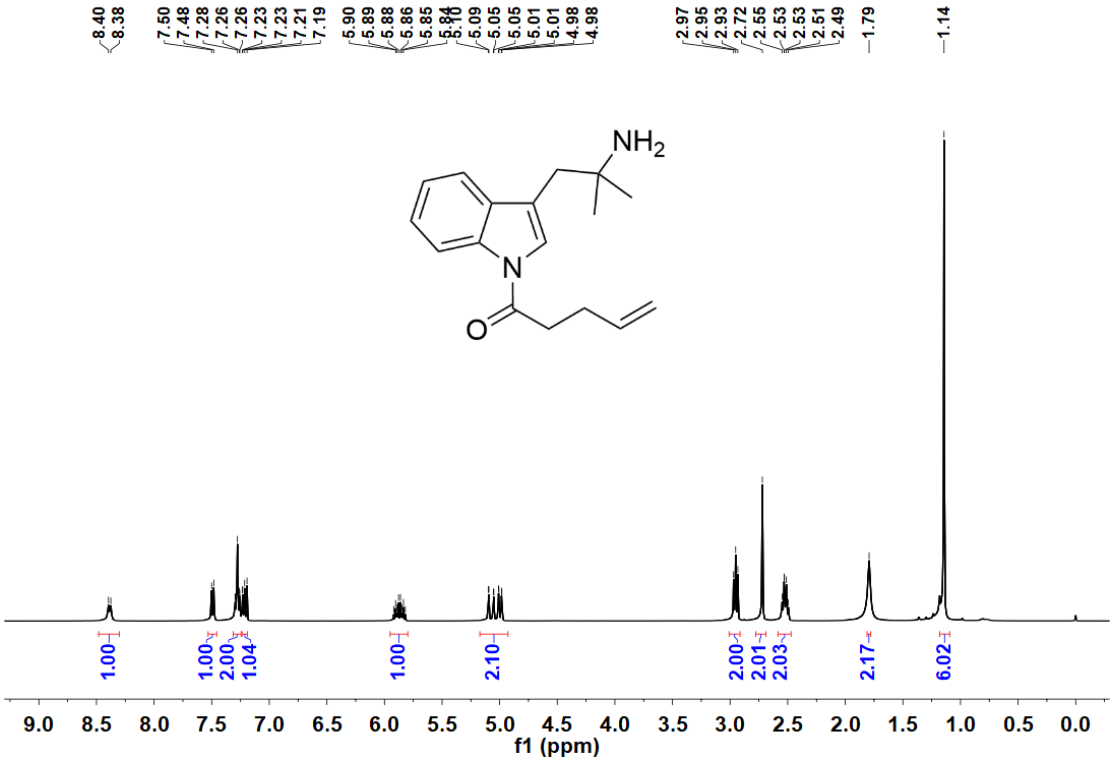
^{1}H NMR spectrum of **1w**



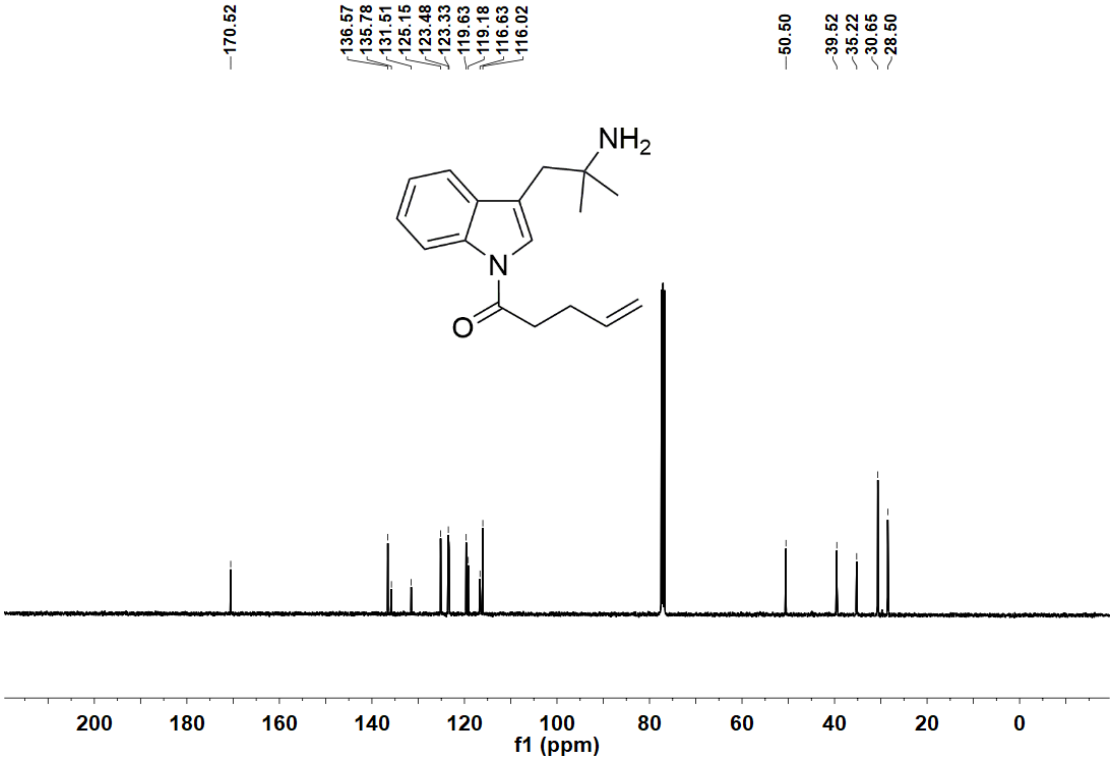
^{13}C NMR spectrum of **1w**



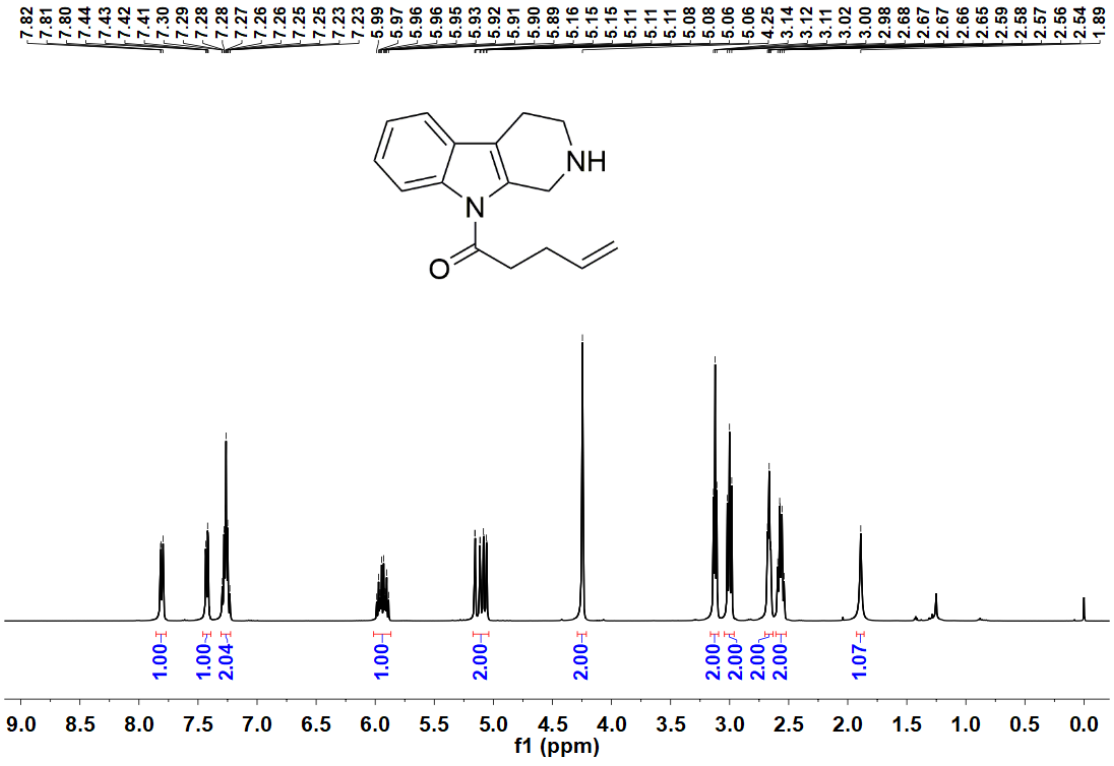
^{1}H NMR spectrum of **1x**



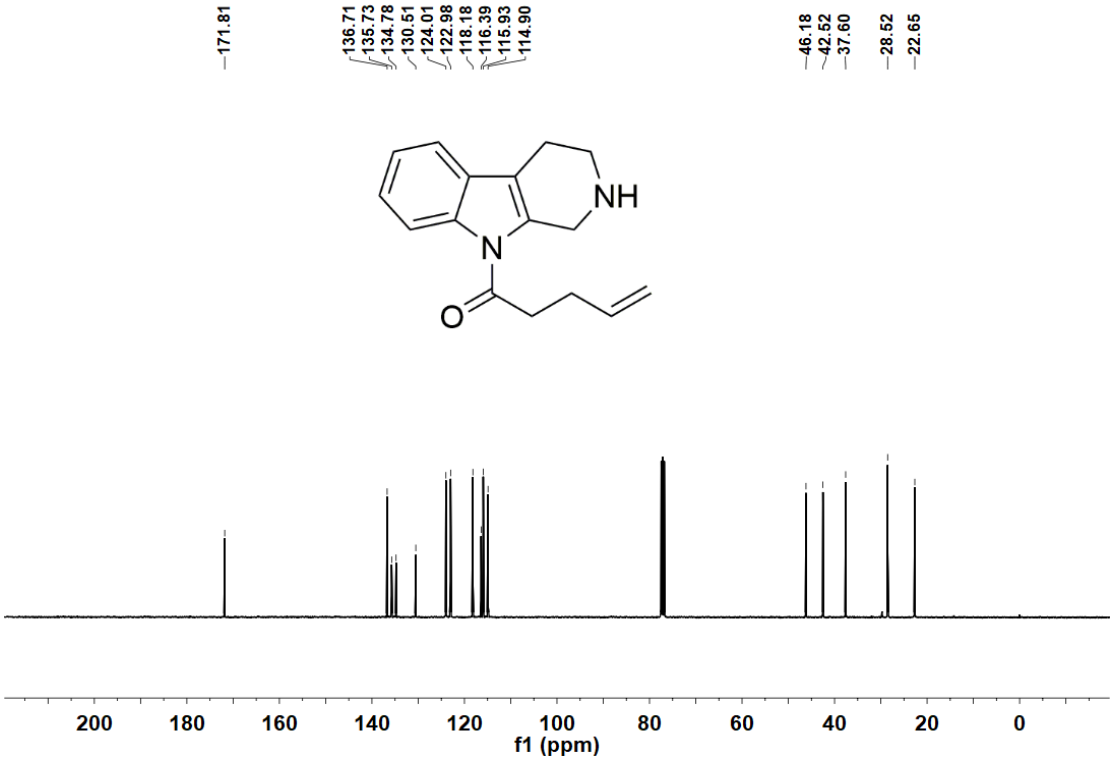
^{13}C NMR spectrum of **1x**



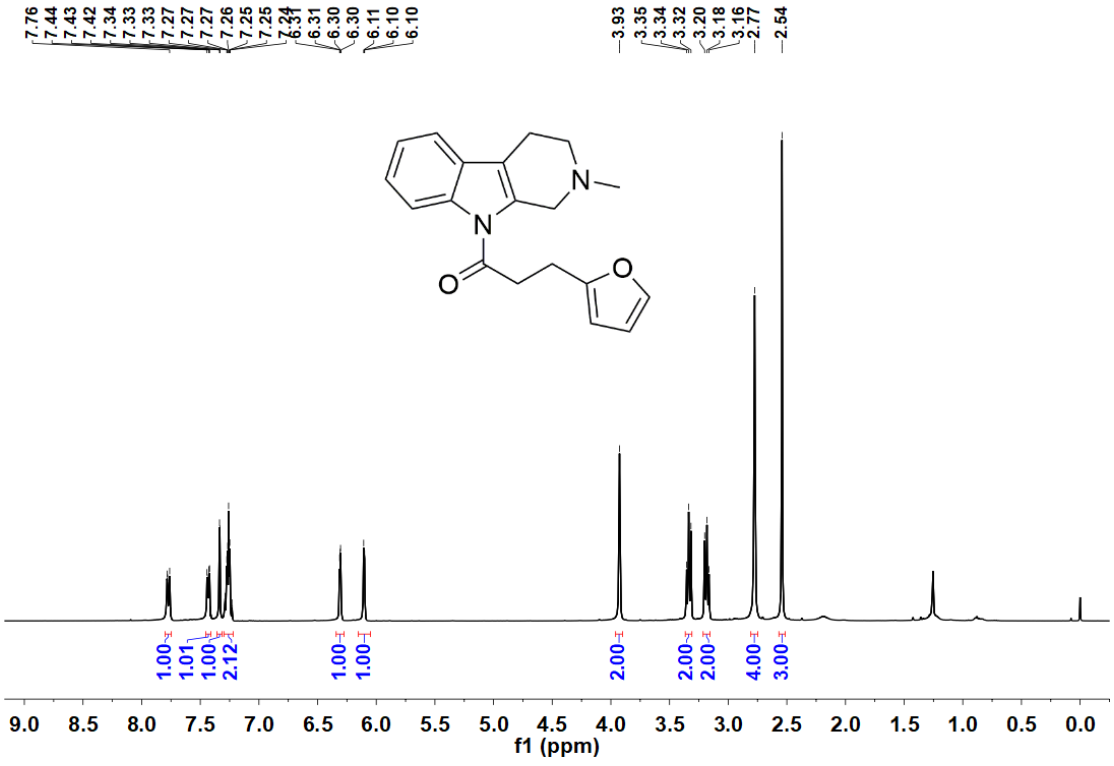
^{1}H NMR spectrum of **1y**



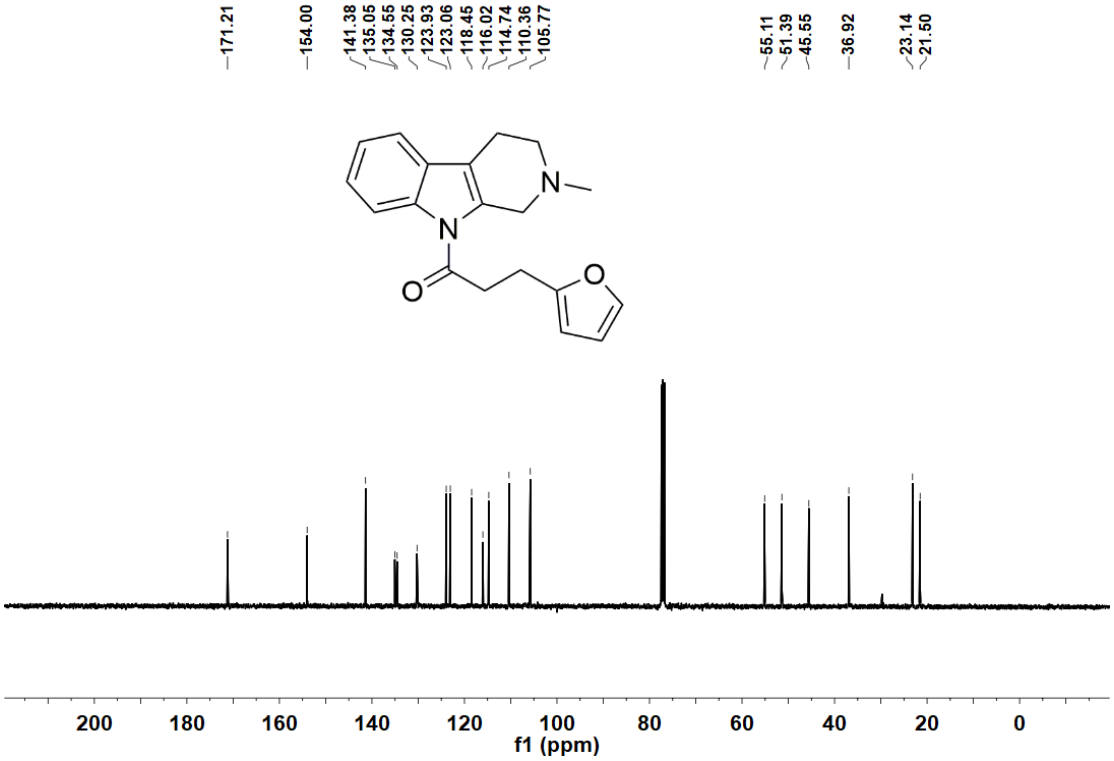
^{13}C NMR spectrum of **1y**



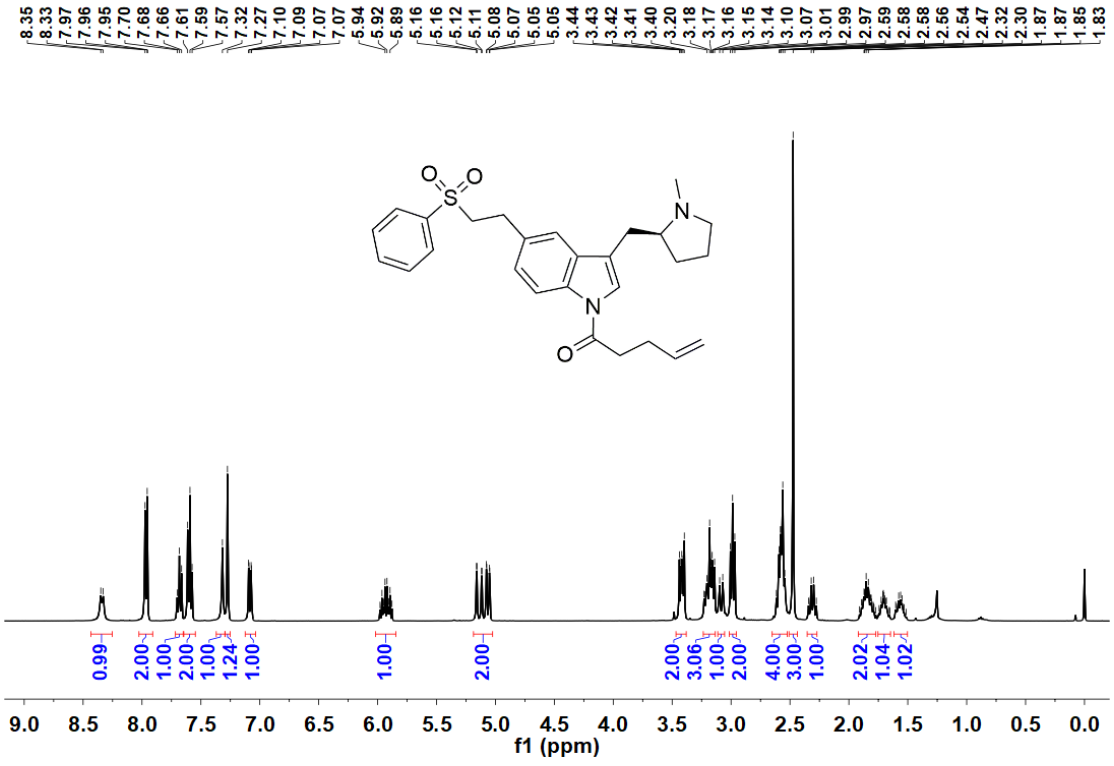
^{1}H NMR spectrum of **1z**



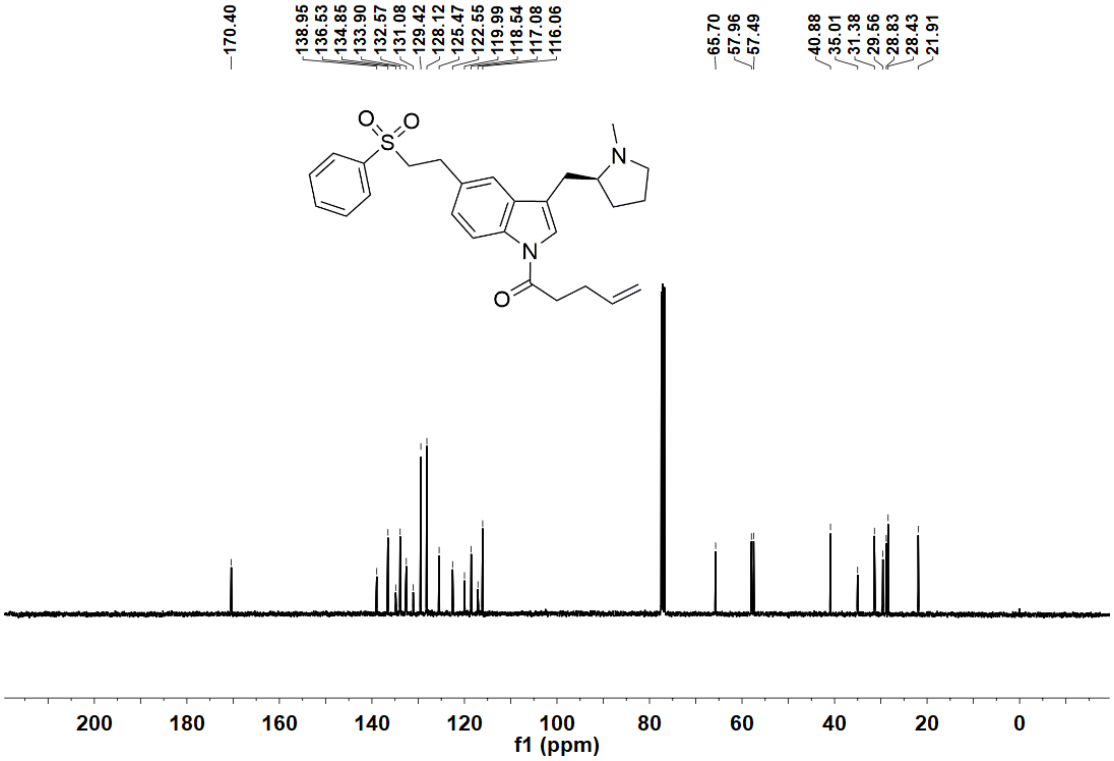
^{13}C NMR spectrum of **1z**



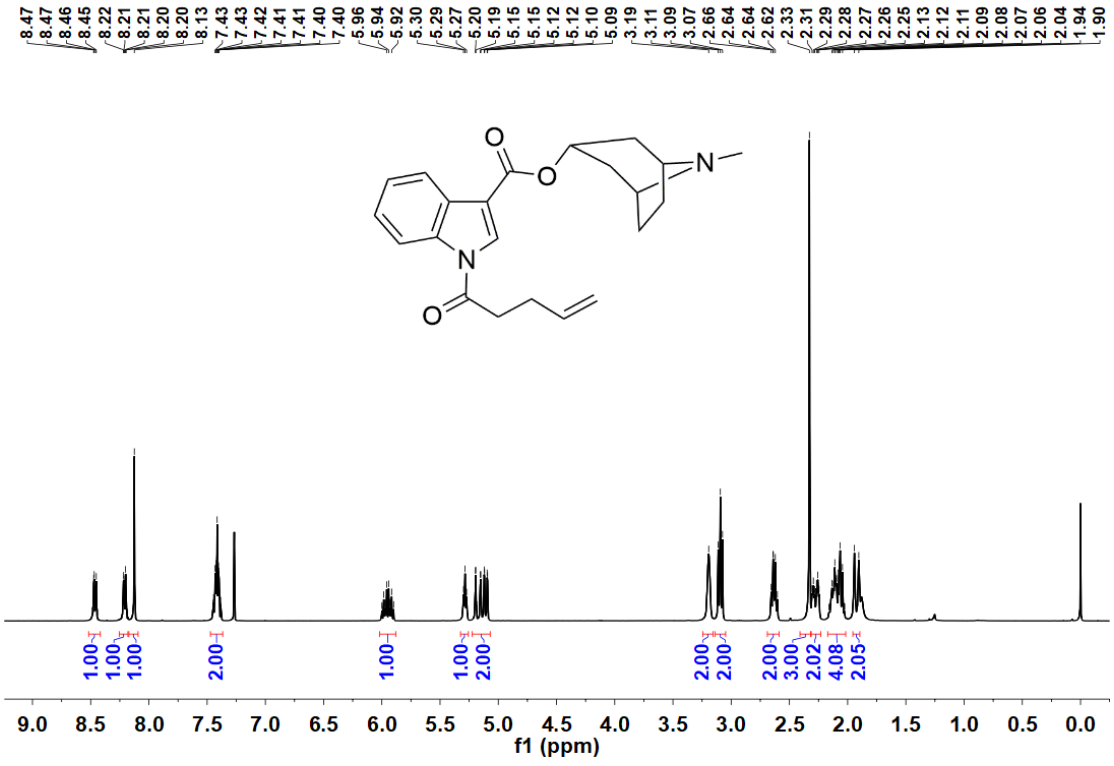
^{1}H NMR spectrum of **1aa**



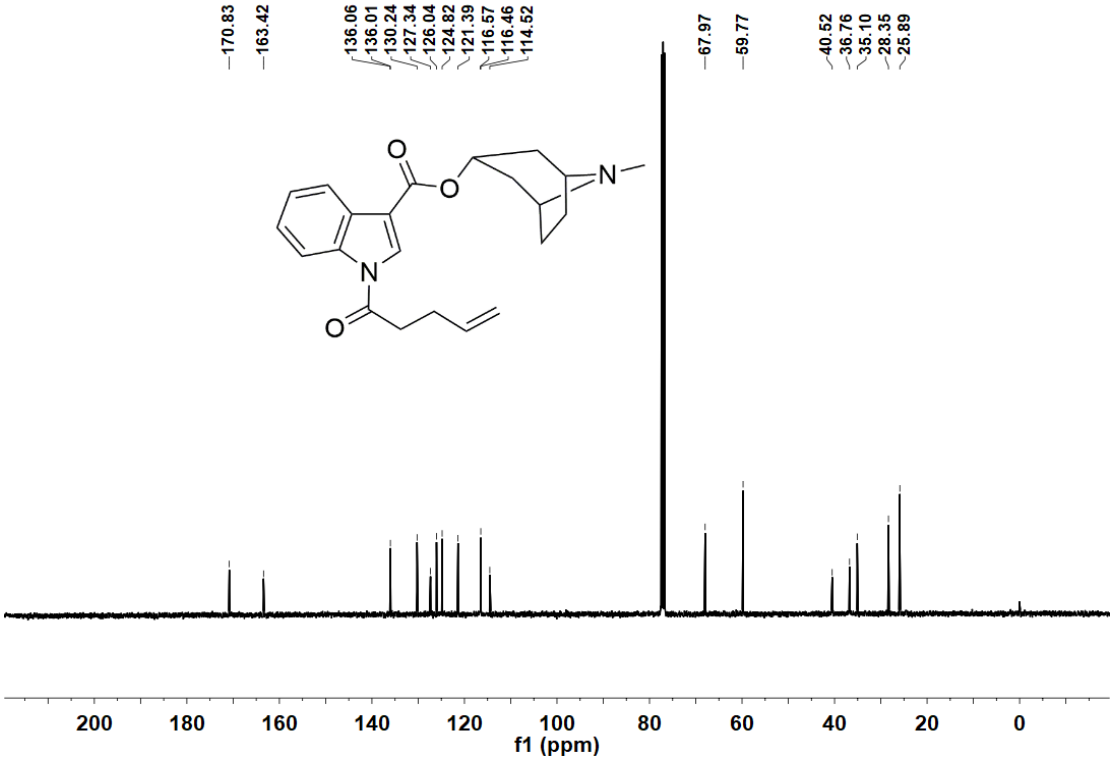
^{13}C NMR spectrum of **1aa**



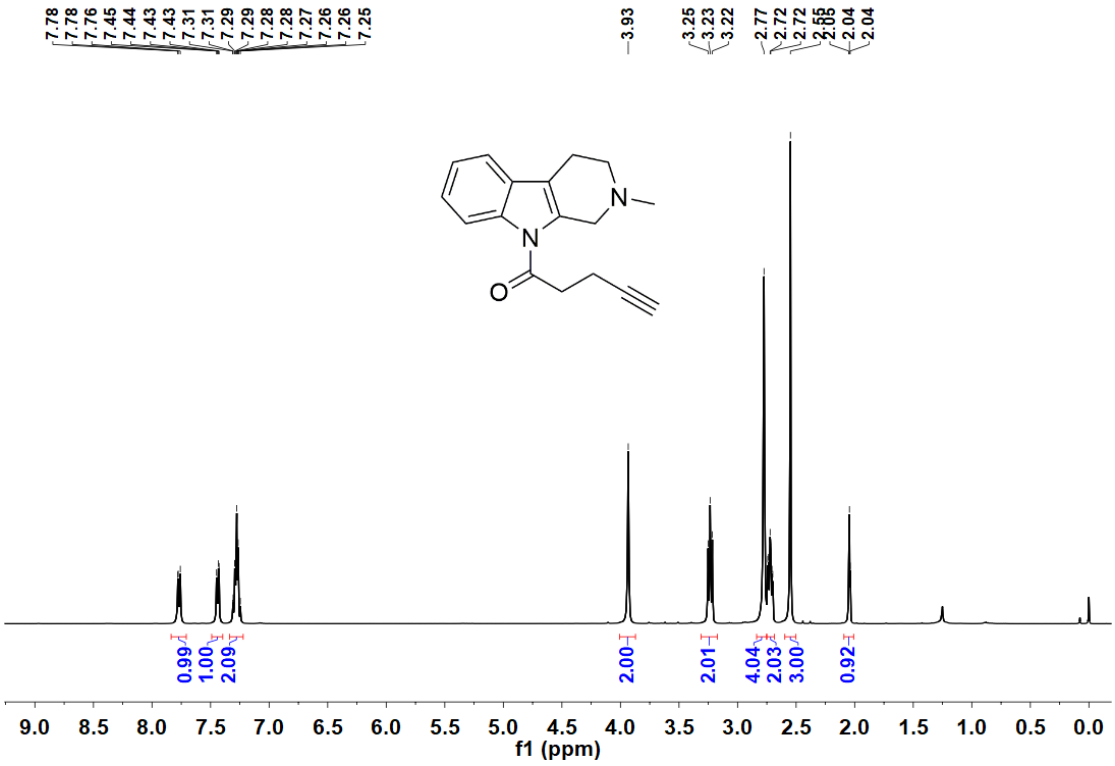
^{1}H NMR spectrum of **1ab**



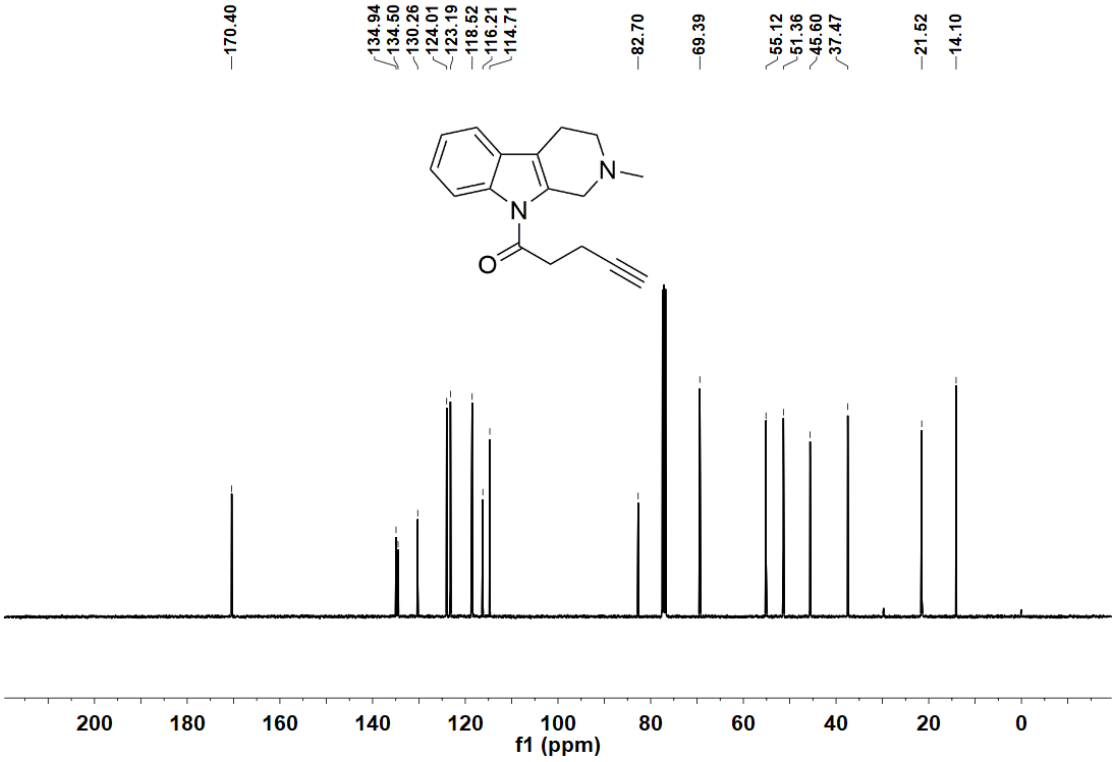
^{13}C NMR spectrum of **1ab**



^{1}H NMR spectrum of **1ac**

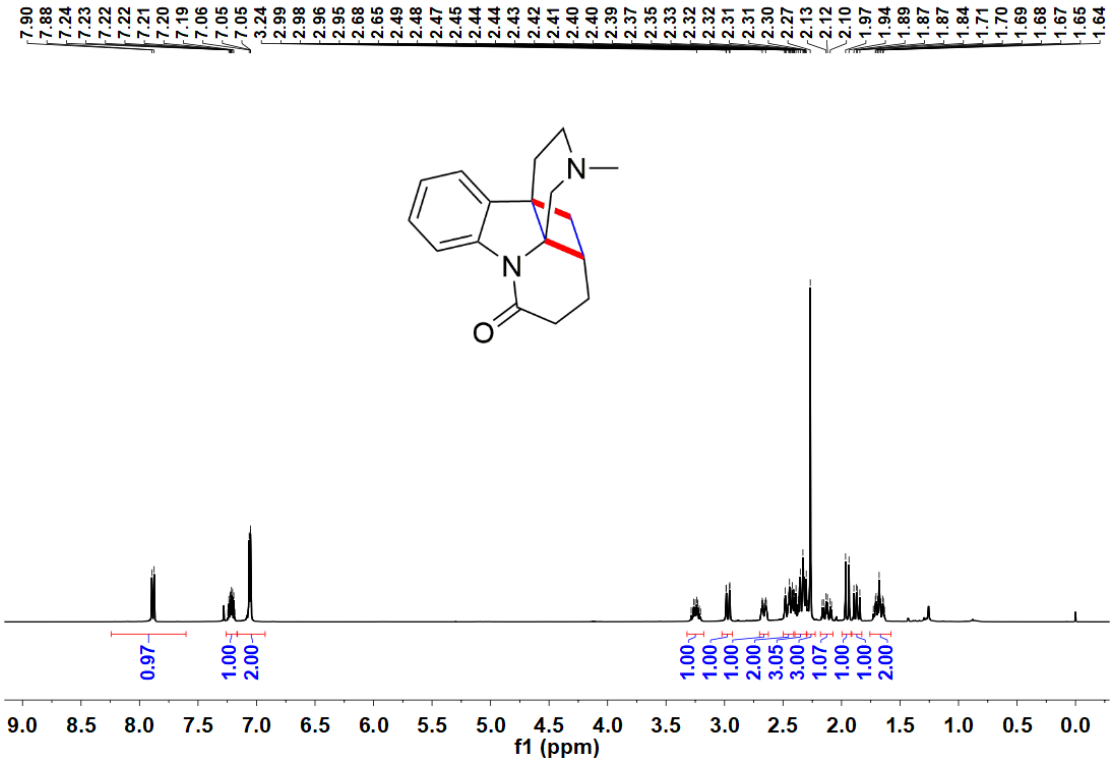


^{13}C NMR spectrum of **1ab**

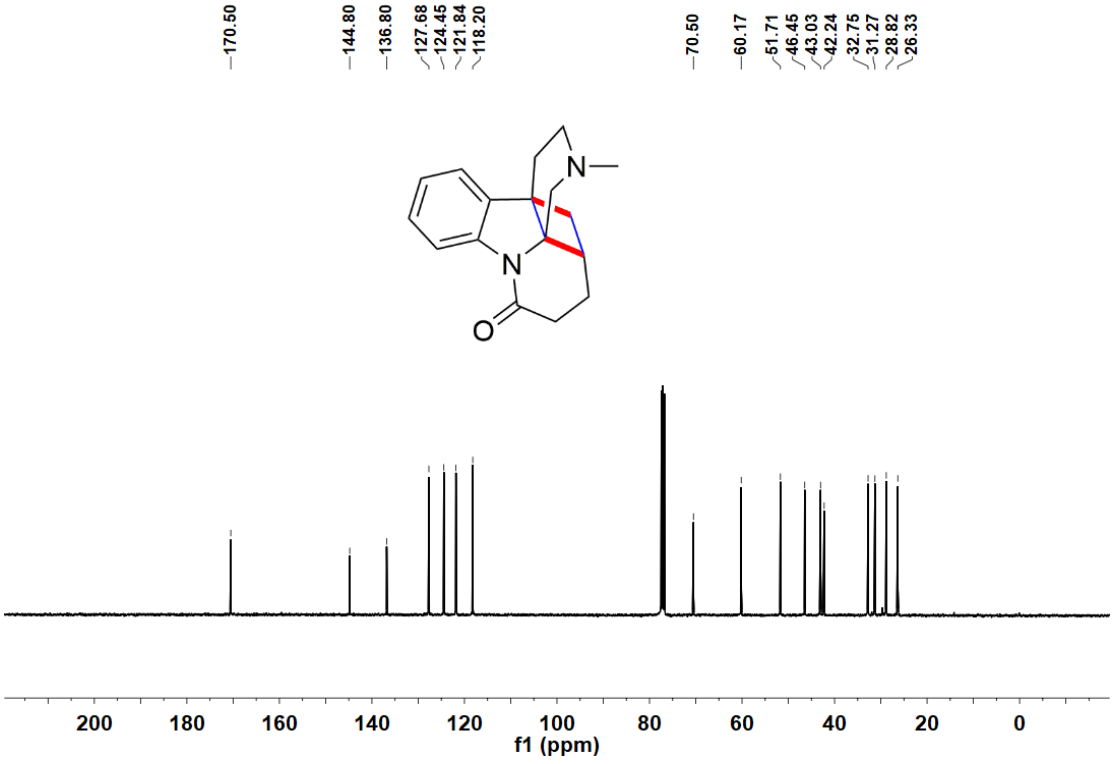


10. Copies of NMR spectra for products

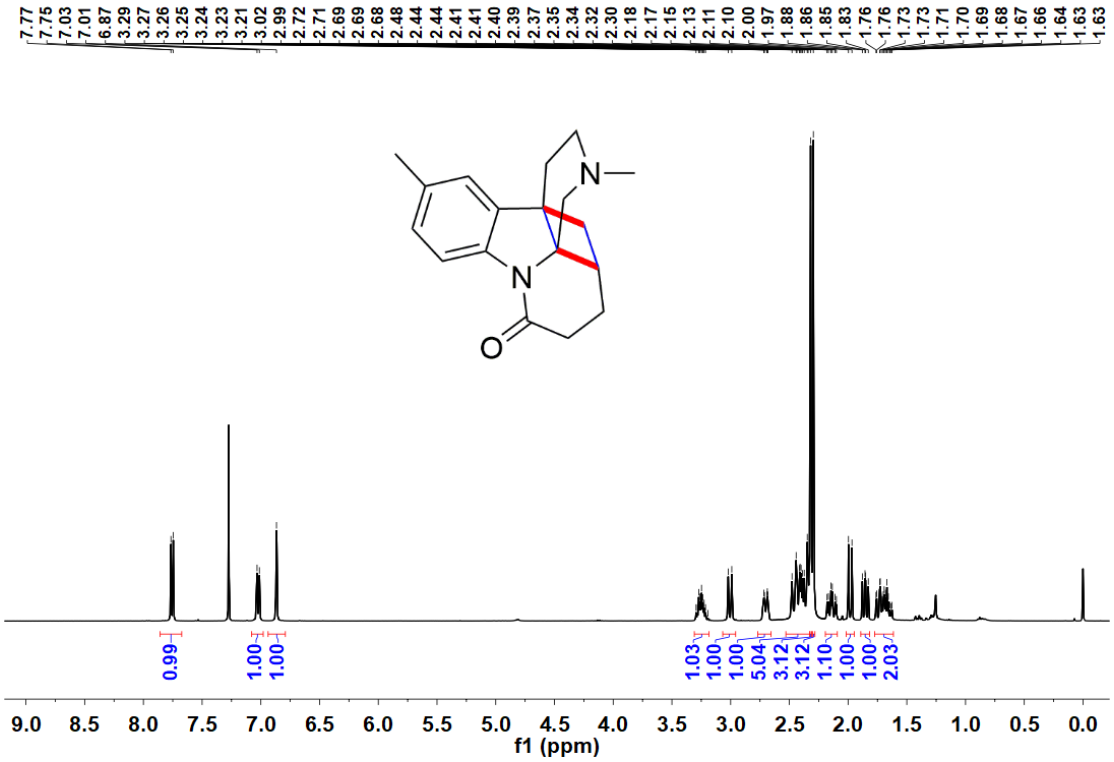
^{1}H NMR spectrum of **2a**



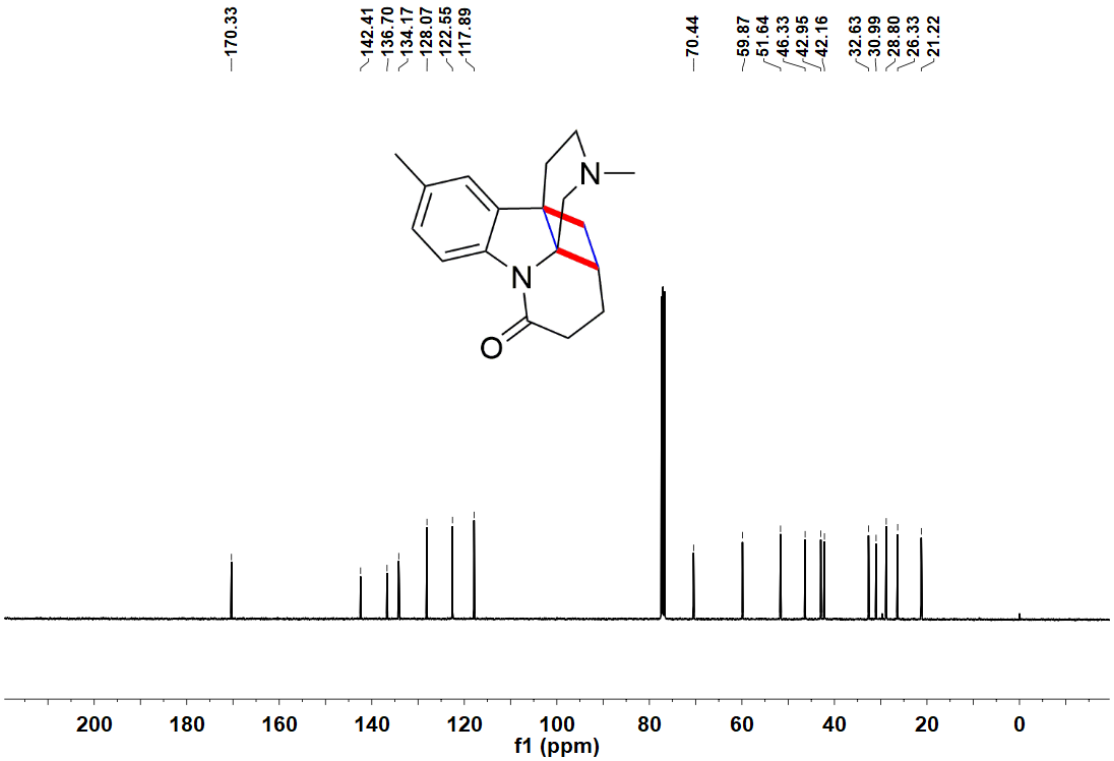
^{13}C NMR spectrum of **2a**



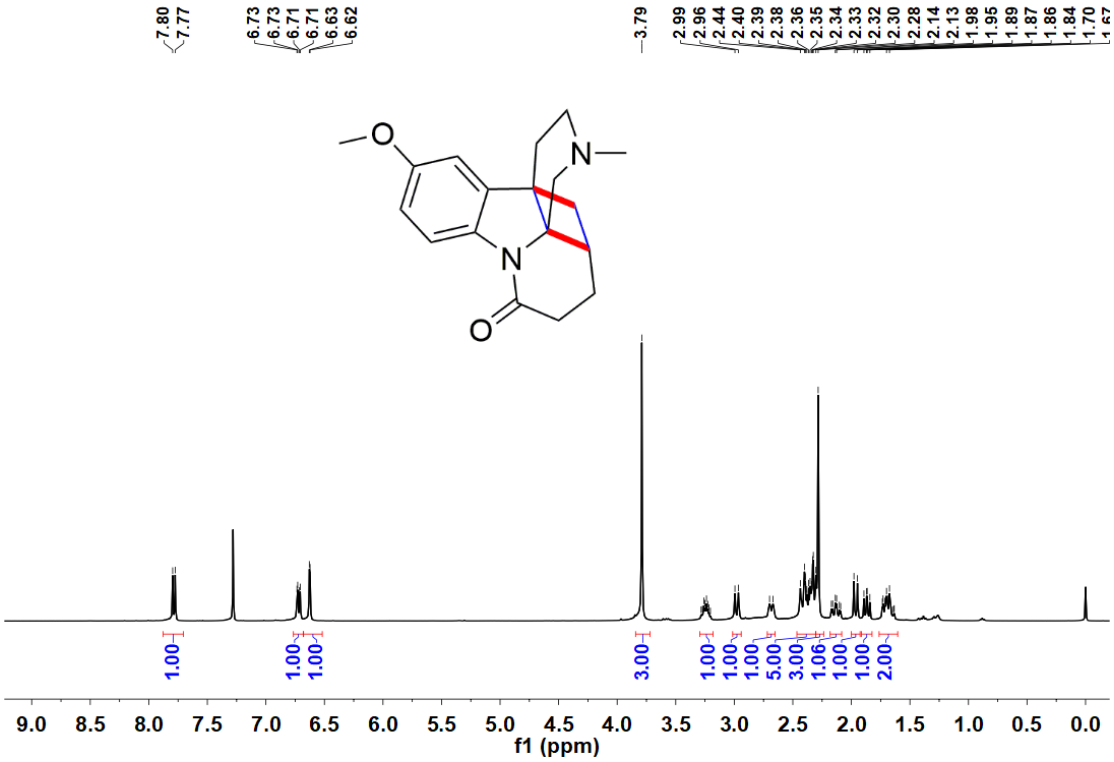
^{1}H NMR spectrum of **2b**



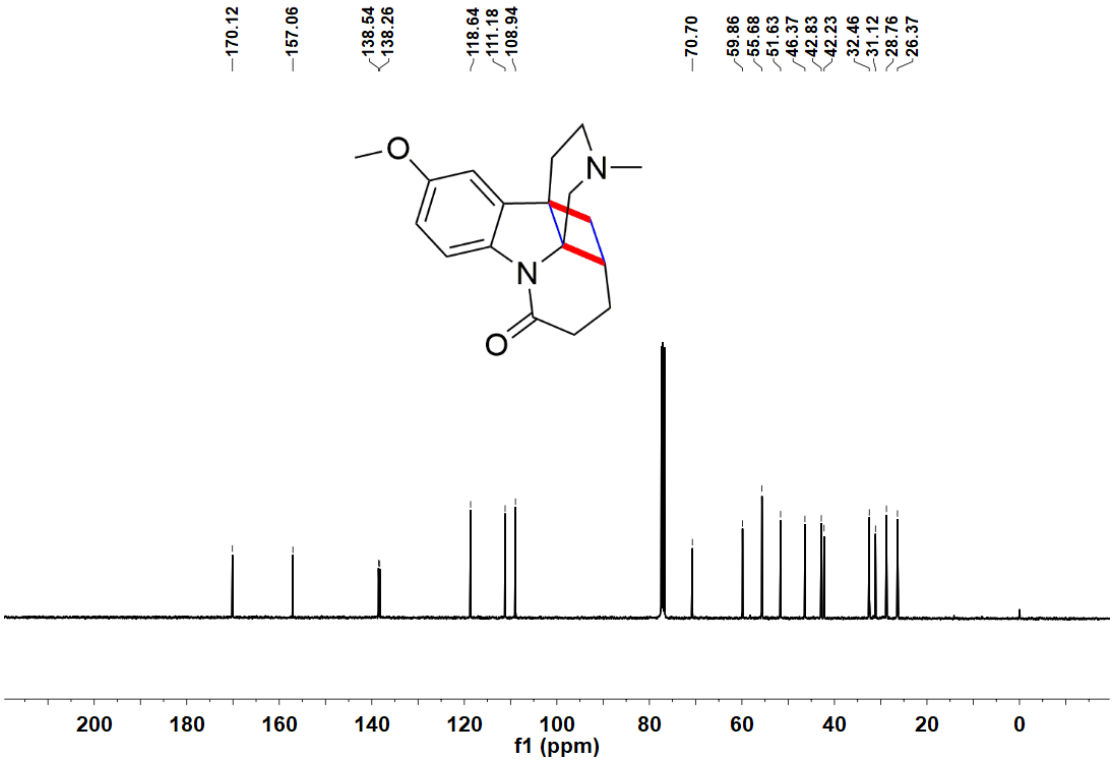
^{13}C NMR spectrum of **2b**



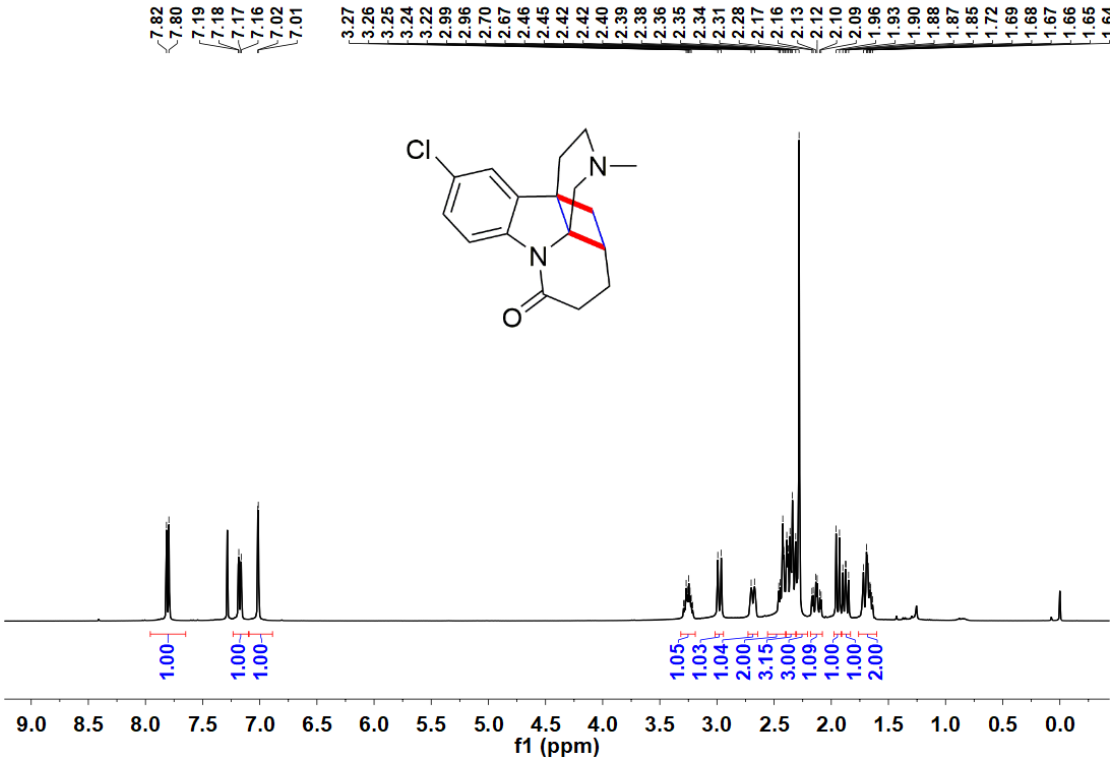
^{1}H NMR spectrum of **2c**



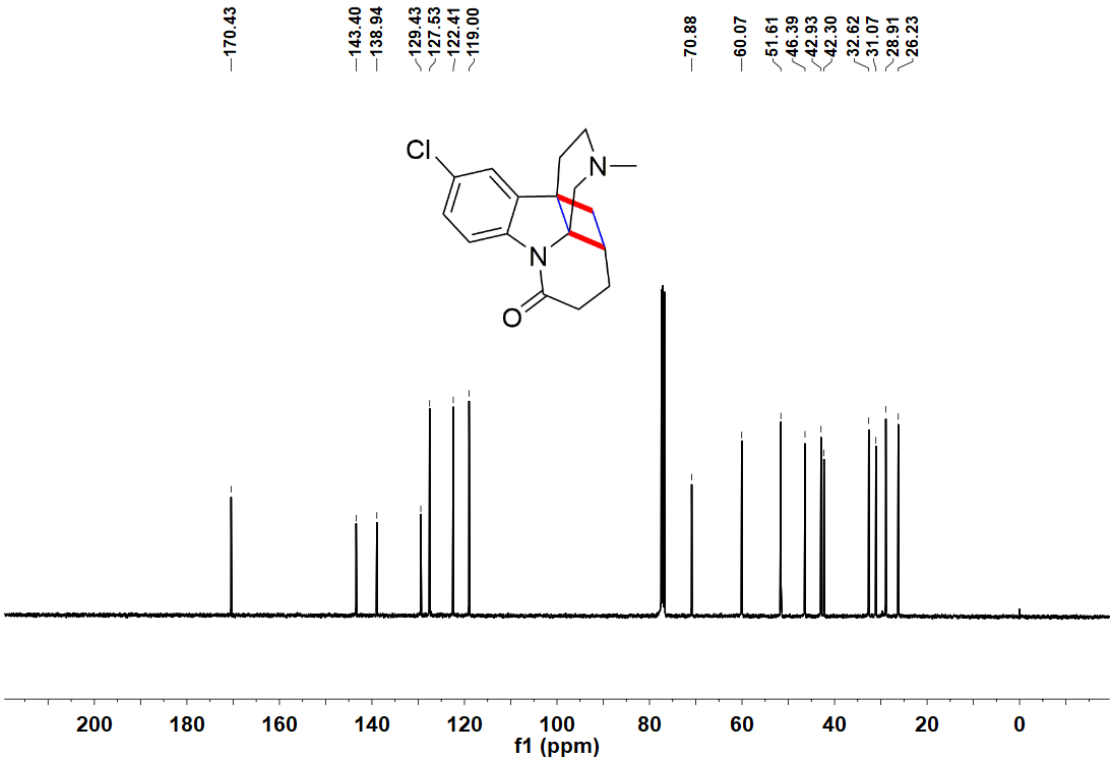
^{13}C NMR spectrum of **2c**



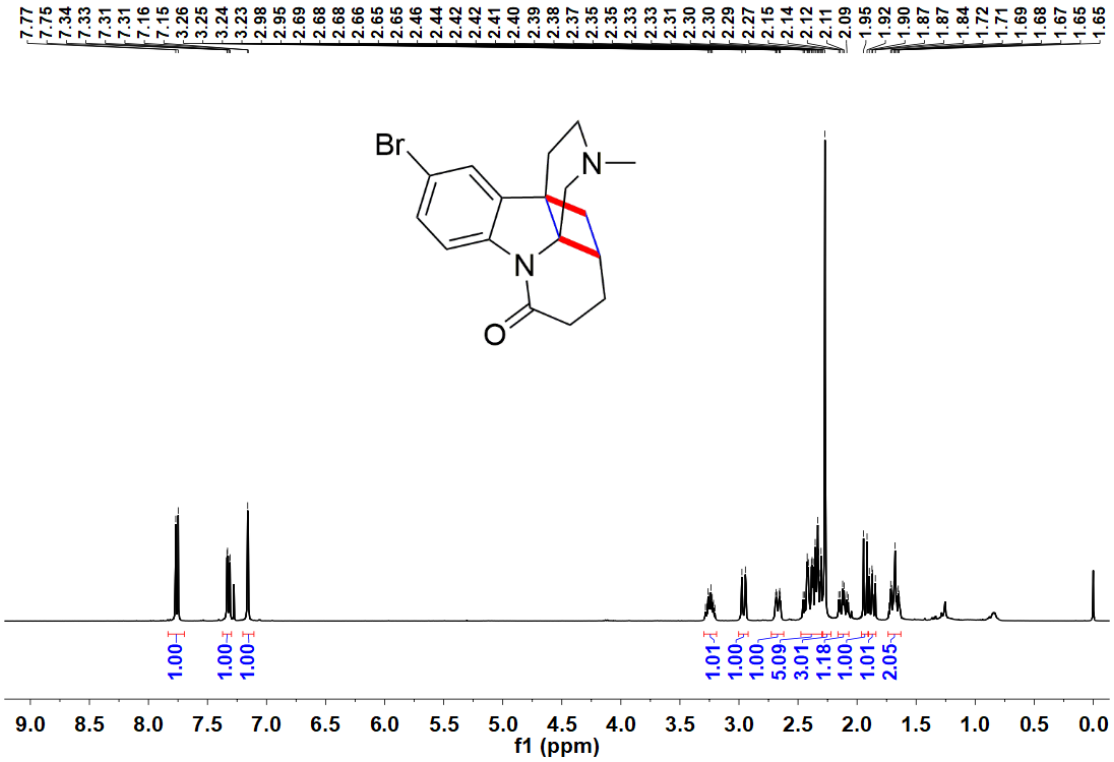
^{1}H NMR spectrum of **2d**



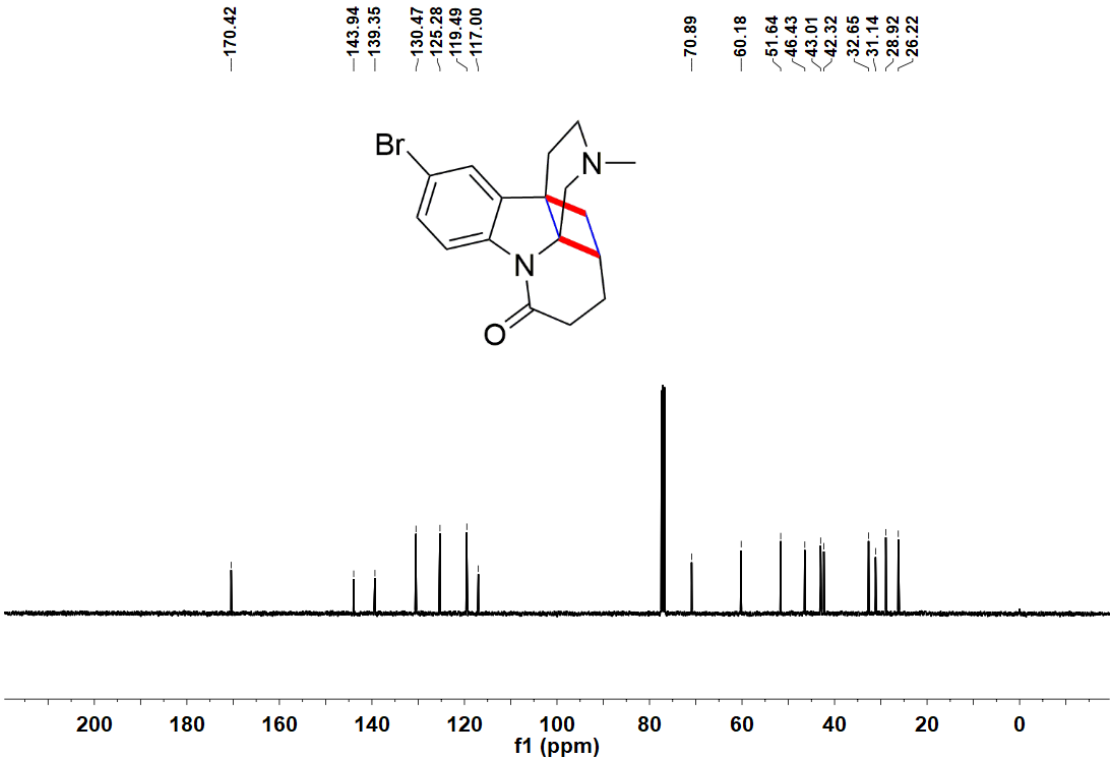
^{13}C NMR spectrum of **2d**



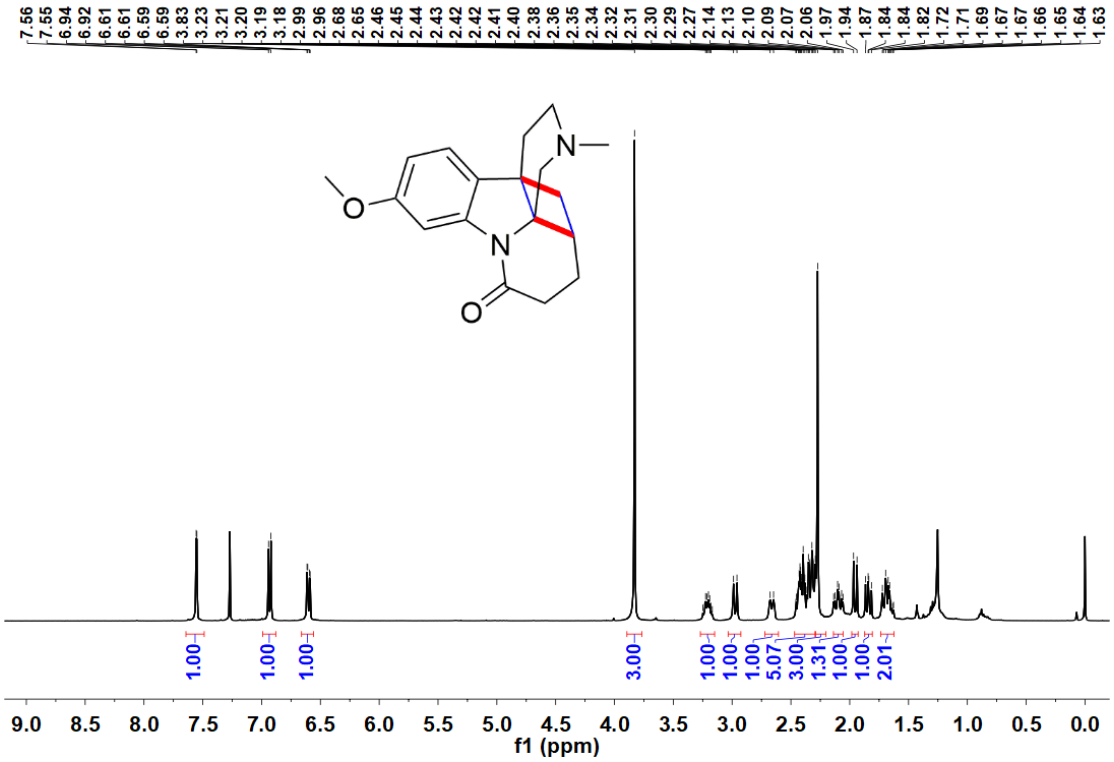
^{1}H NMR spectrum of **2e**



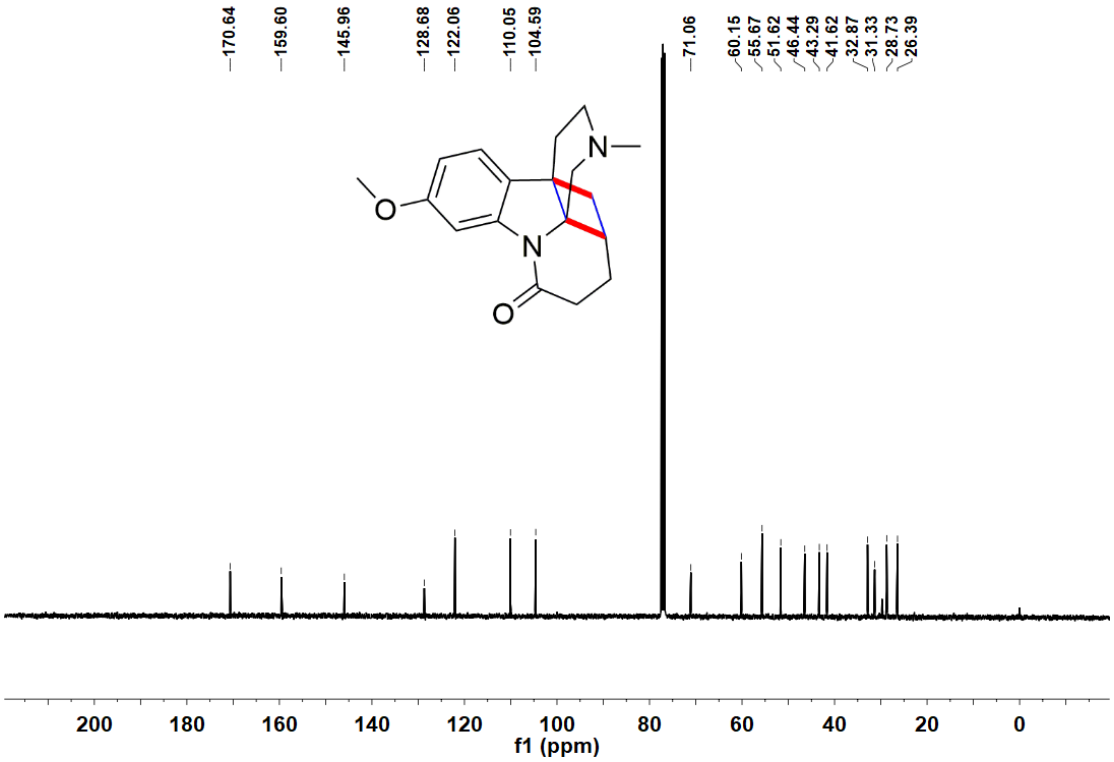
^{13}C NMR spectrum of **2e**



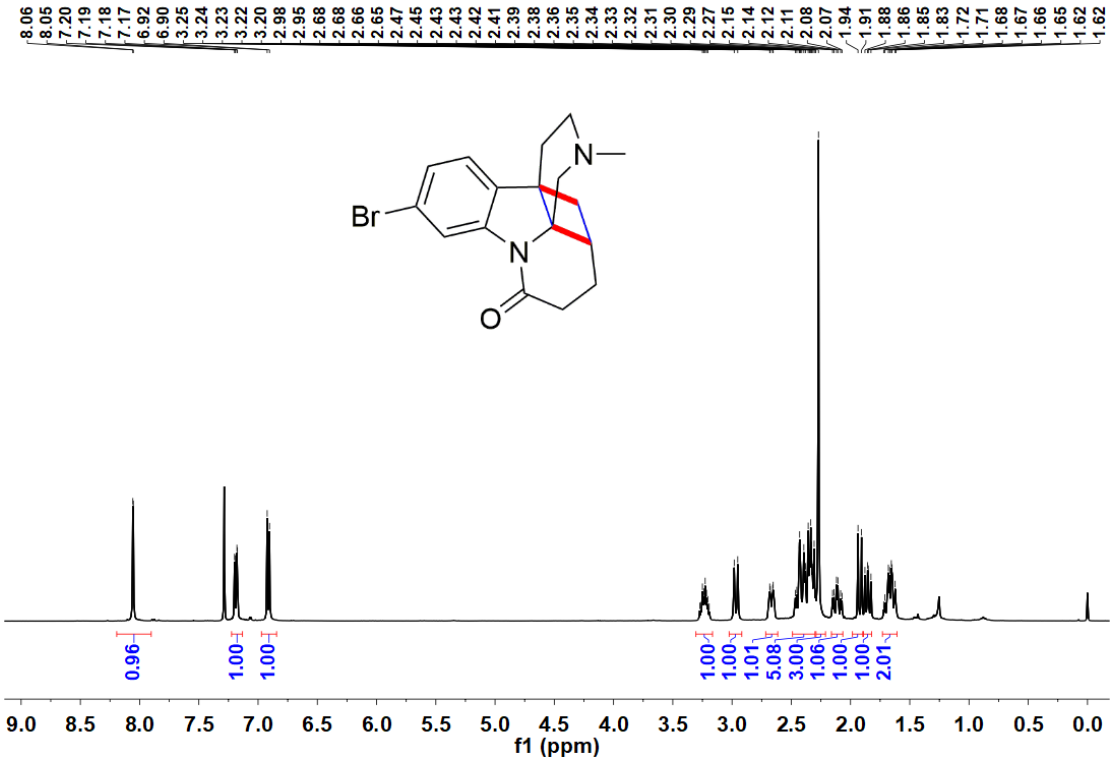
^{1}H NMR spectrum of **2f**



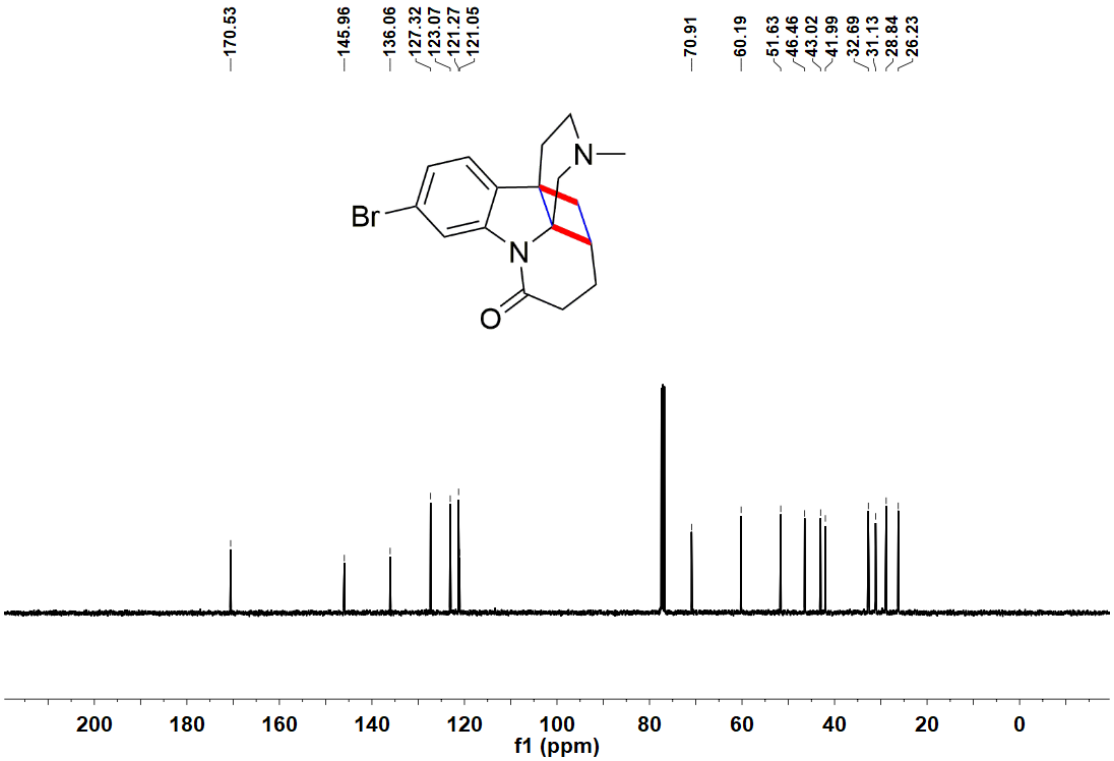
^{13}C NMR spectrum of **2f**



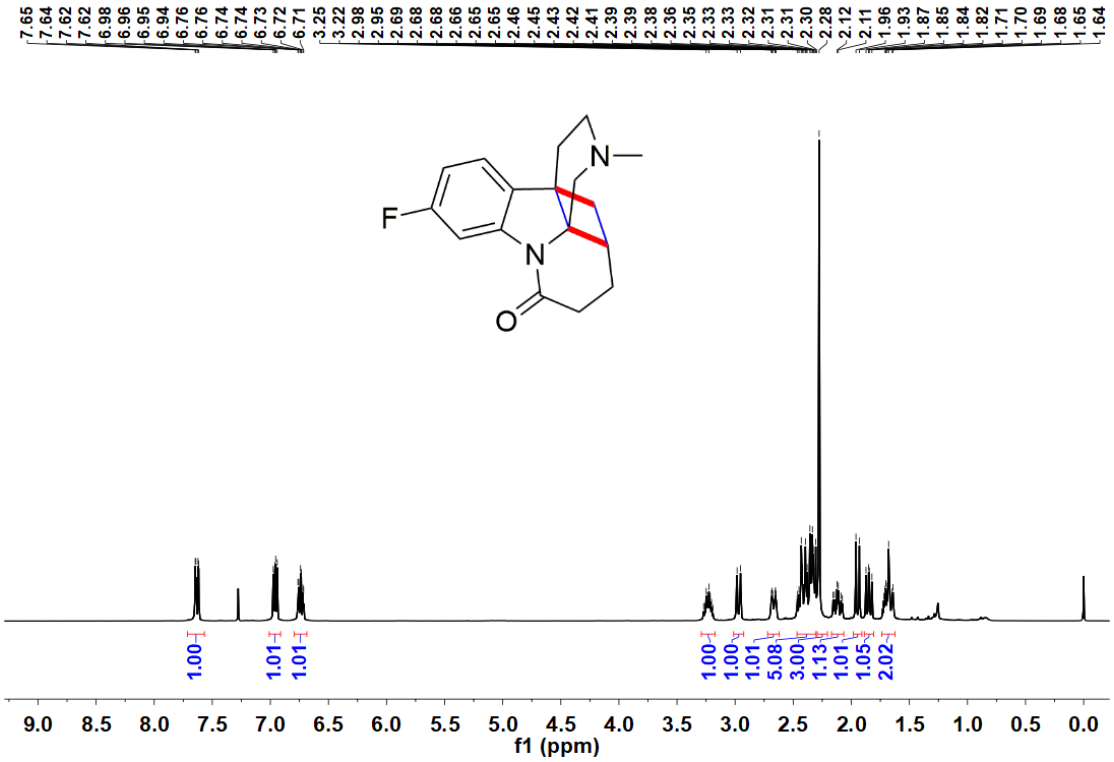
^{1}H NMR spectrum of **2g**



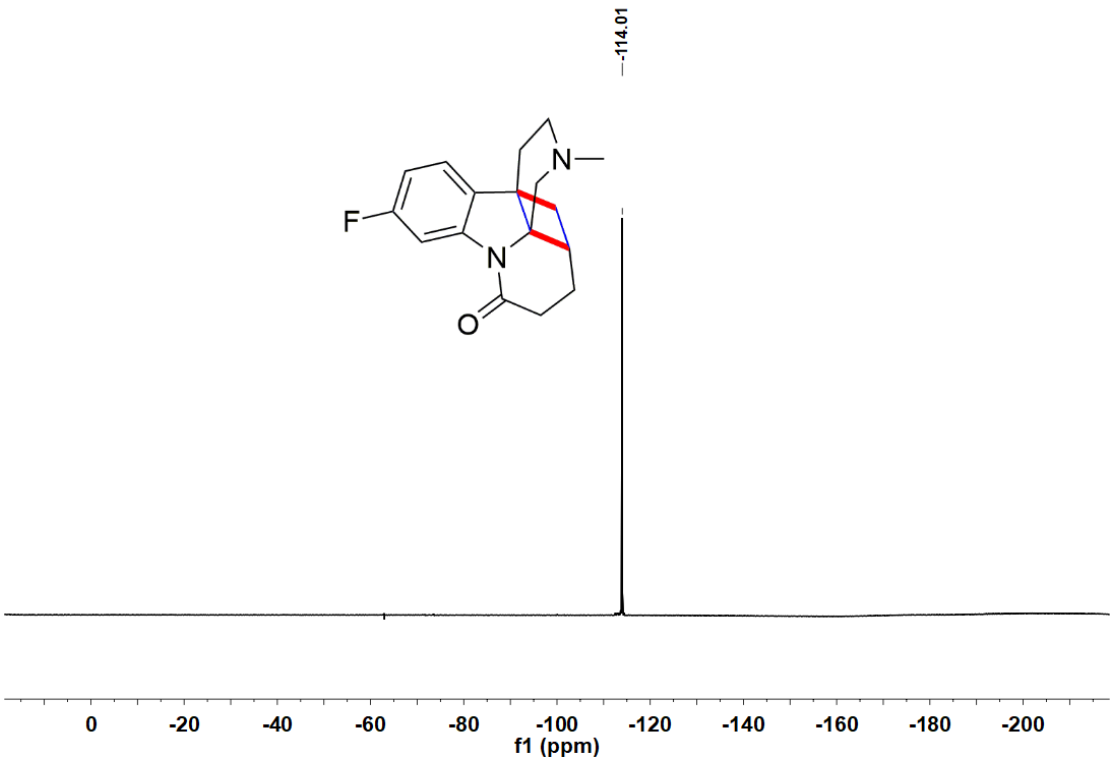
^{13}C NMR spectrum of **2g**



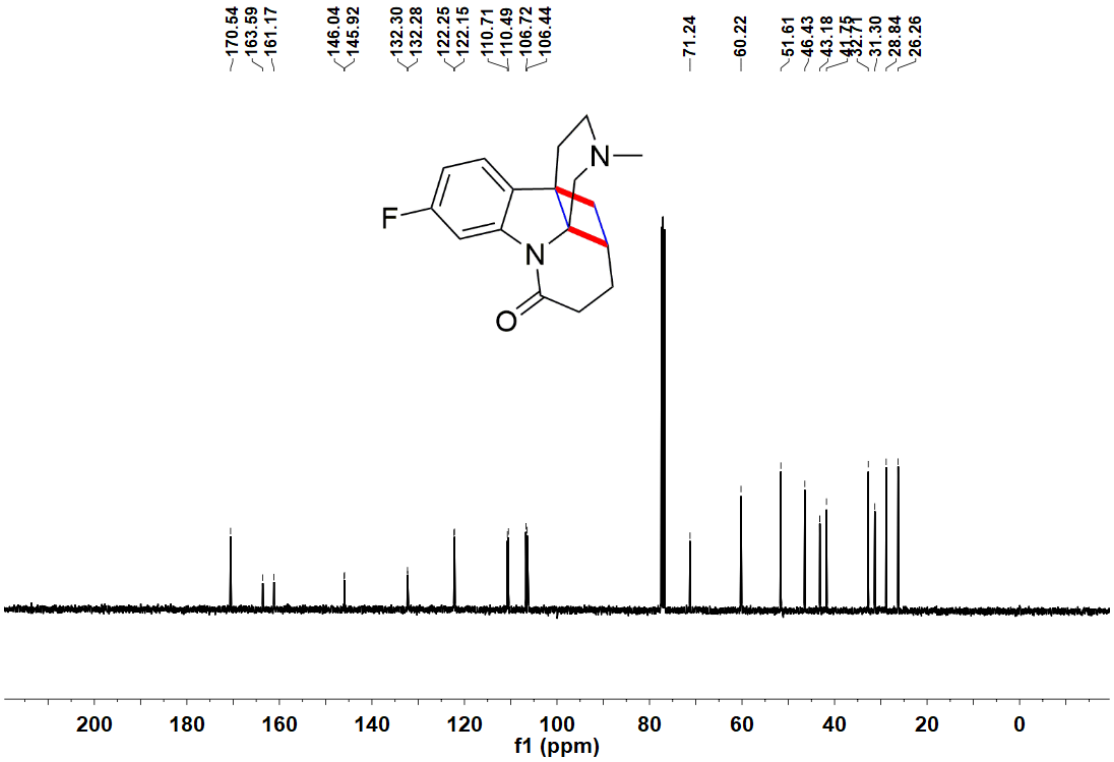
^{1}H NMR spectrum of **2h**



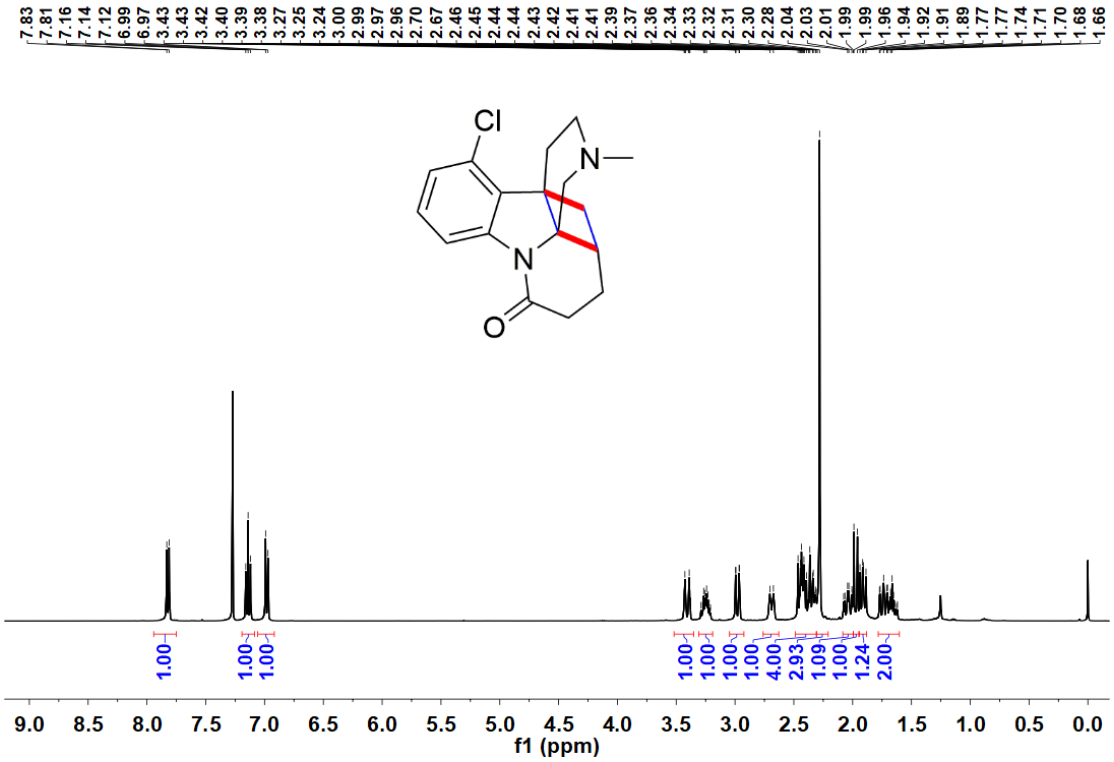
^{19}F NMR spectrum of **2h**



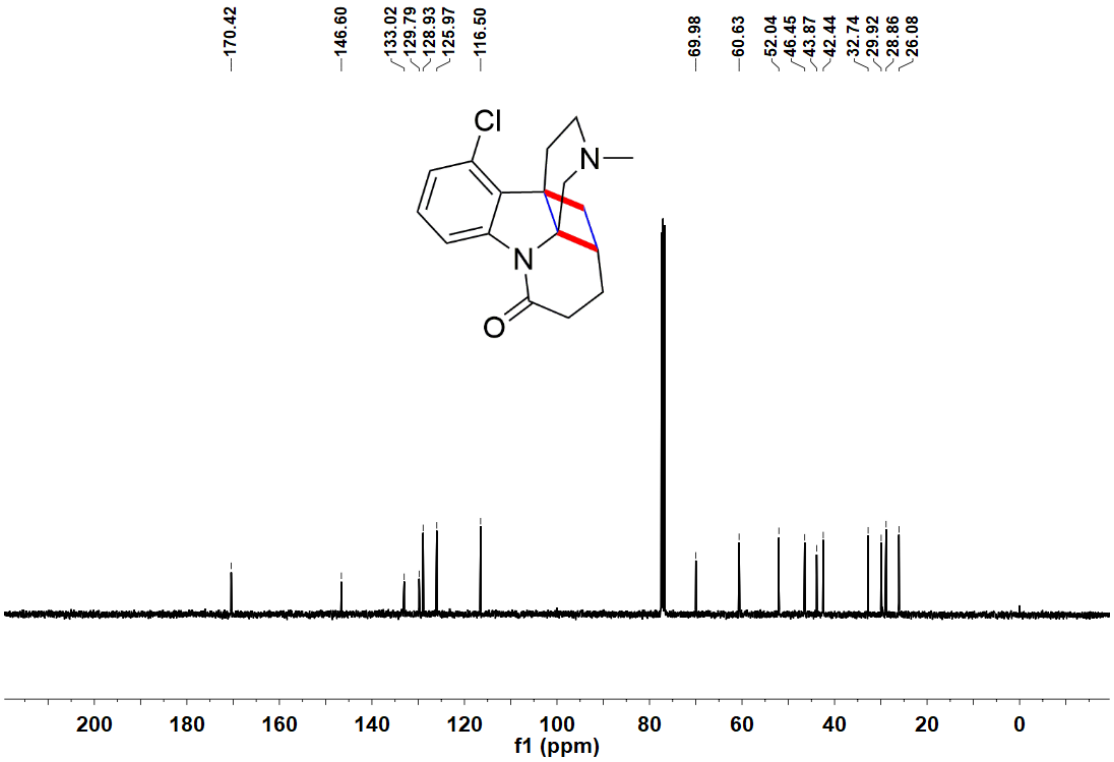
^{13}C NMR spectrum of **2h**



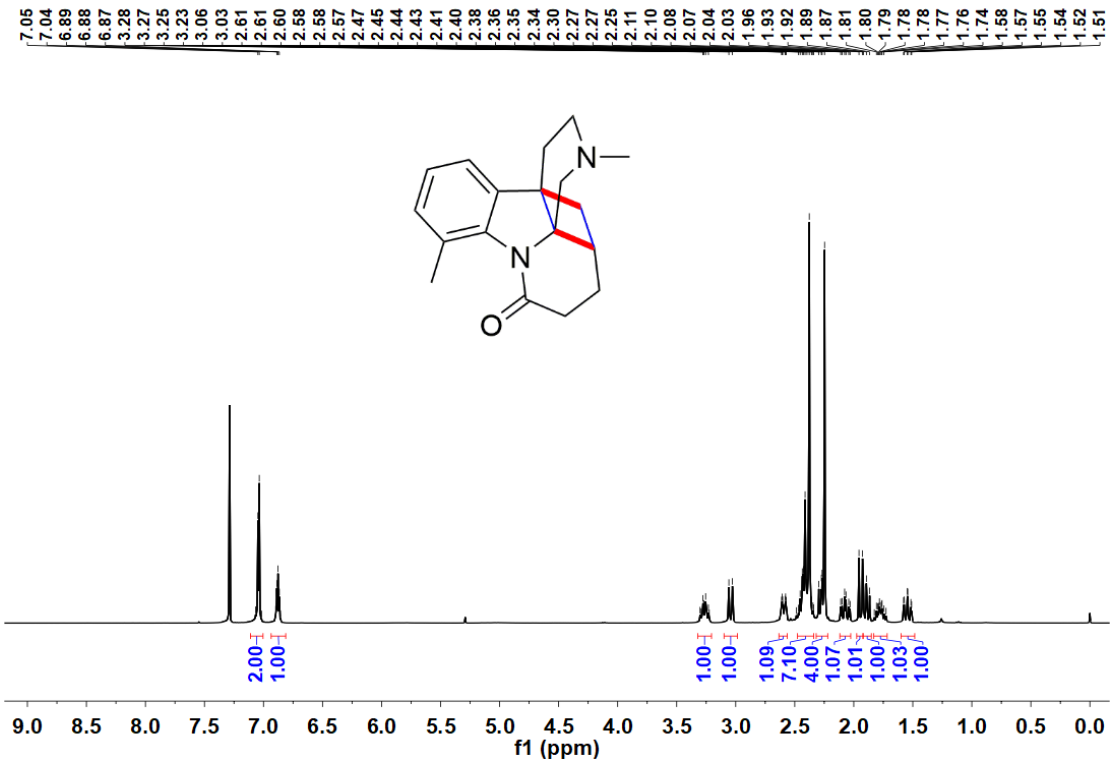
^{1}H NMR spectrum of **2i**



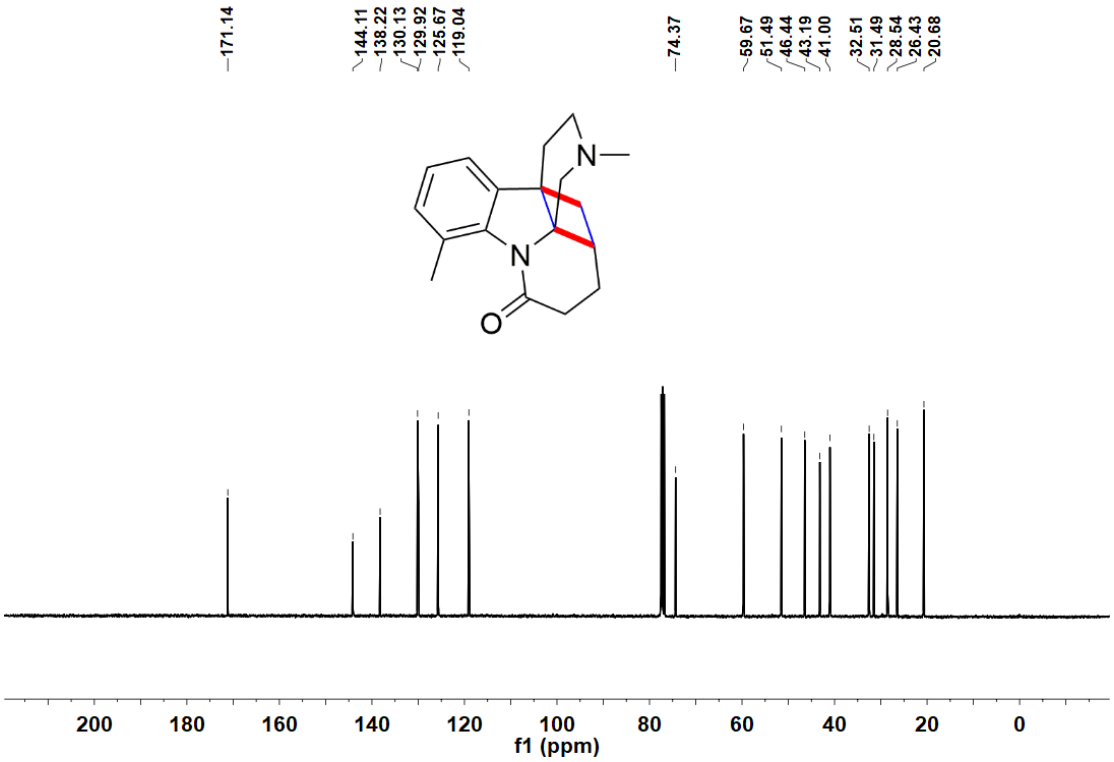
^{13}C NMR spectrum of **2i**



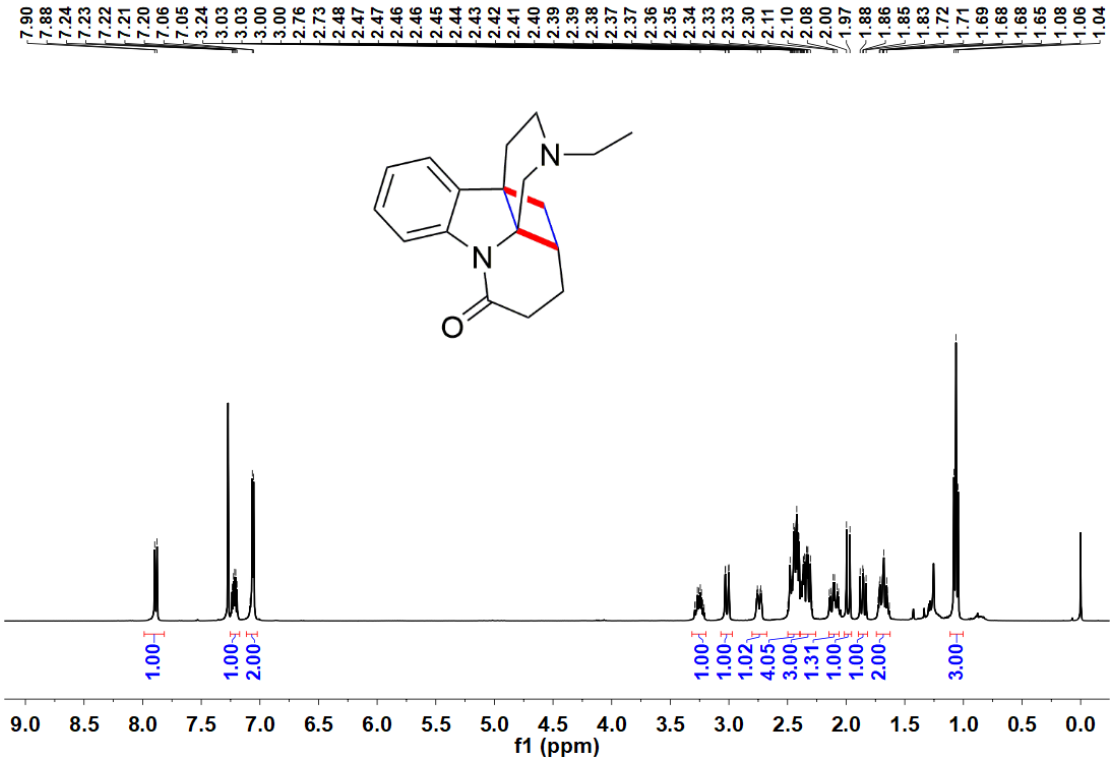
^{1}H NMR spectrum of **2j**



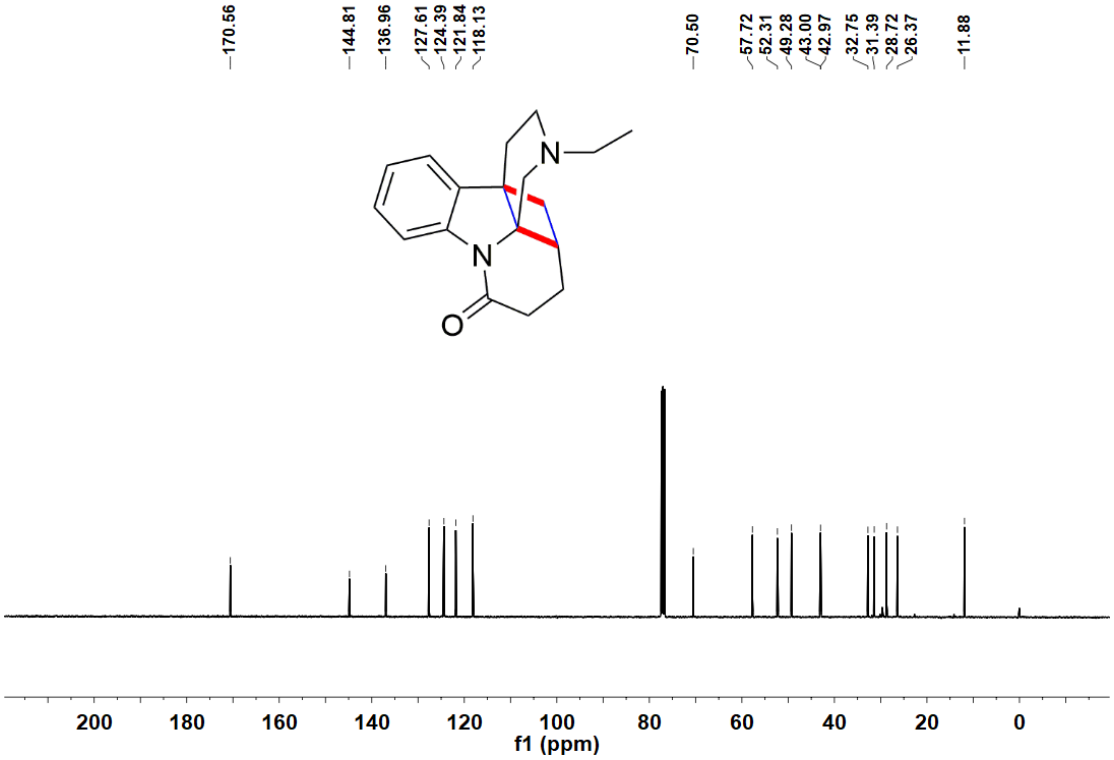
^{13}C NMR spectrum of **2j**



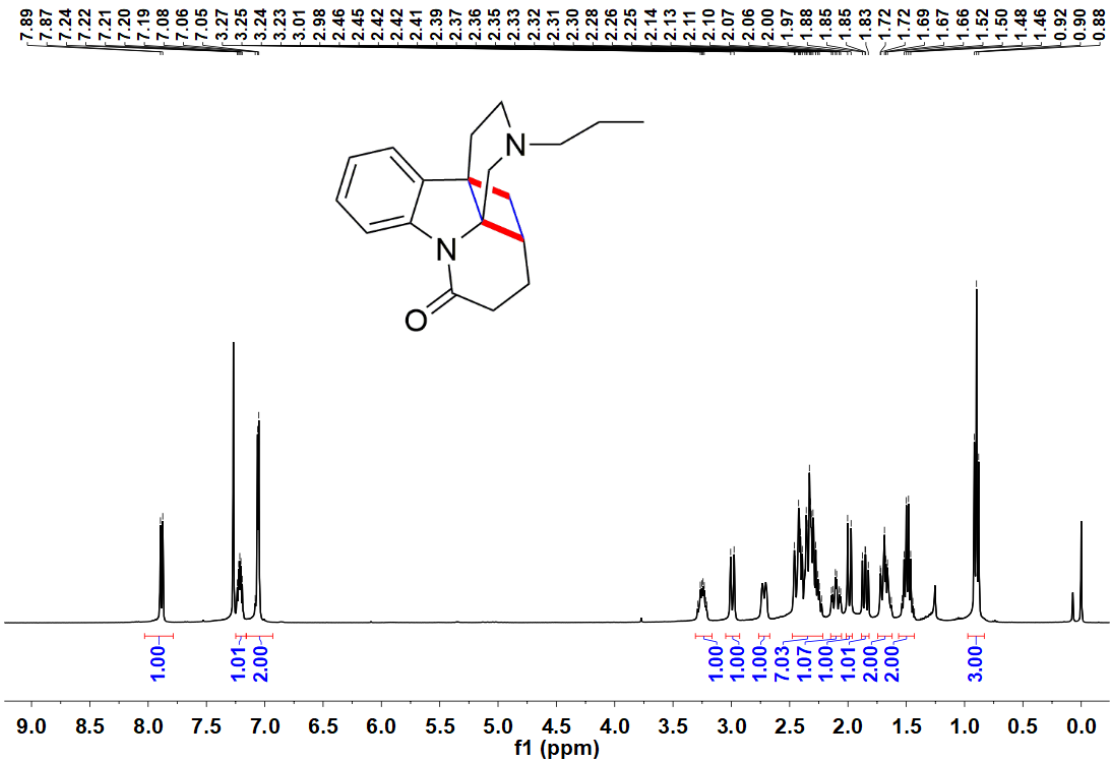
^{1}H NMR spectrum of **2k**



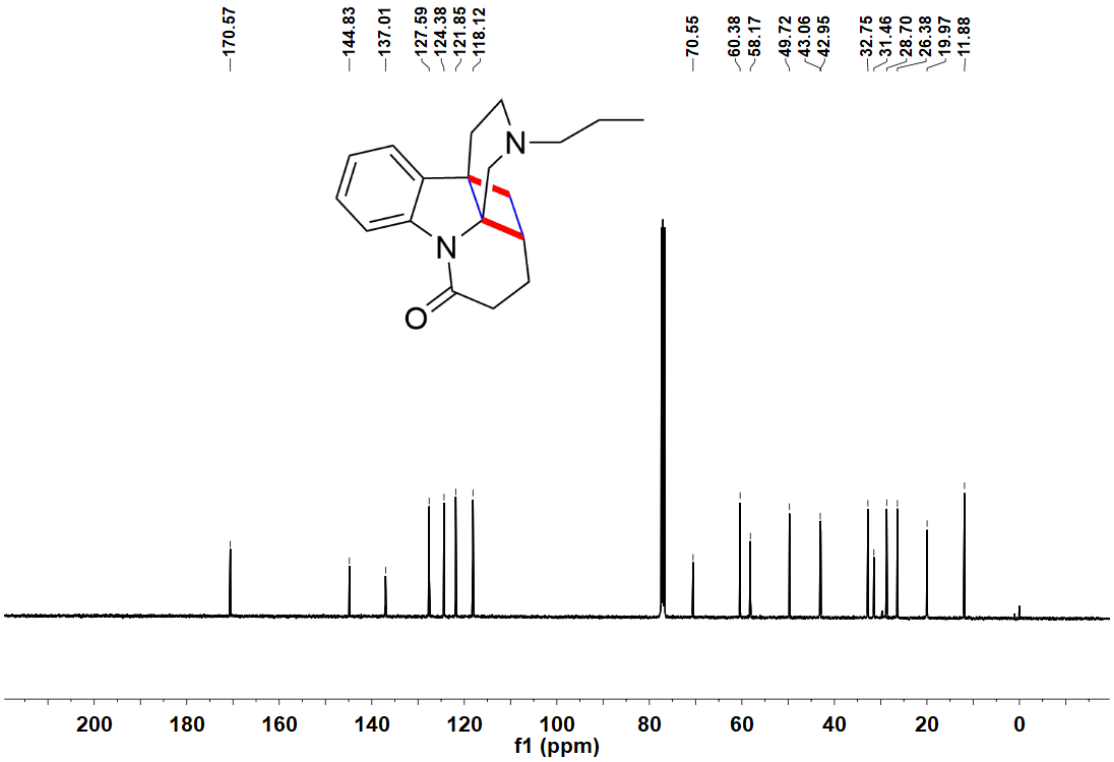
^{13}C NMR spectrum of **2k**



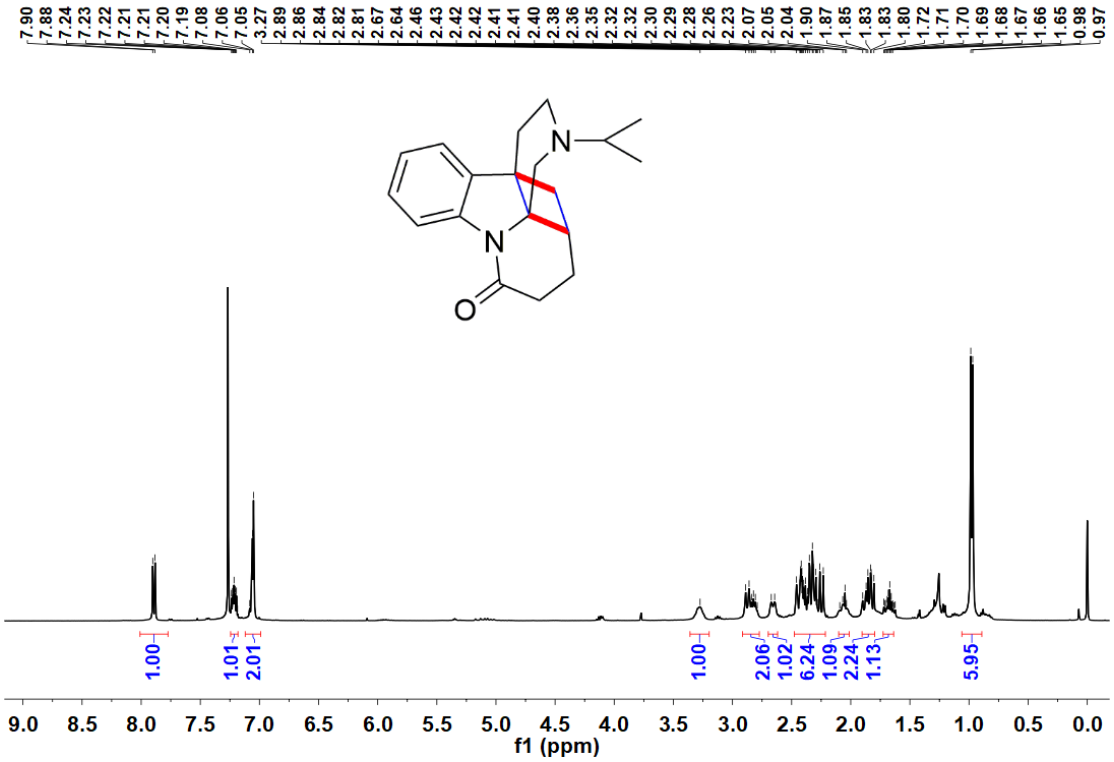
^{1}H NMR spectrum of **2l**



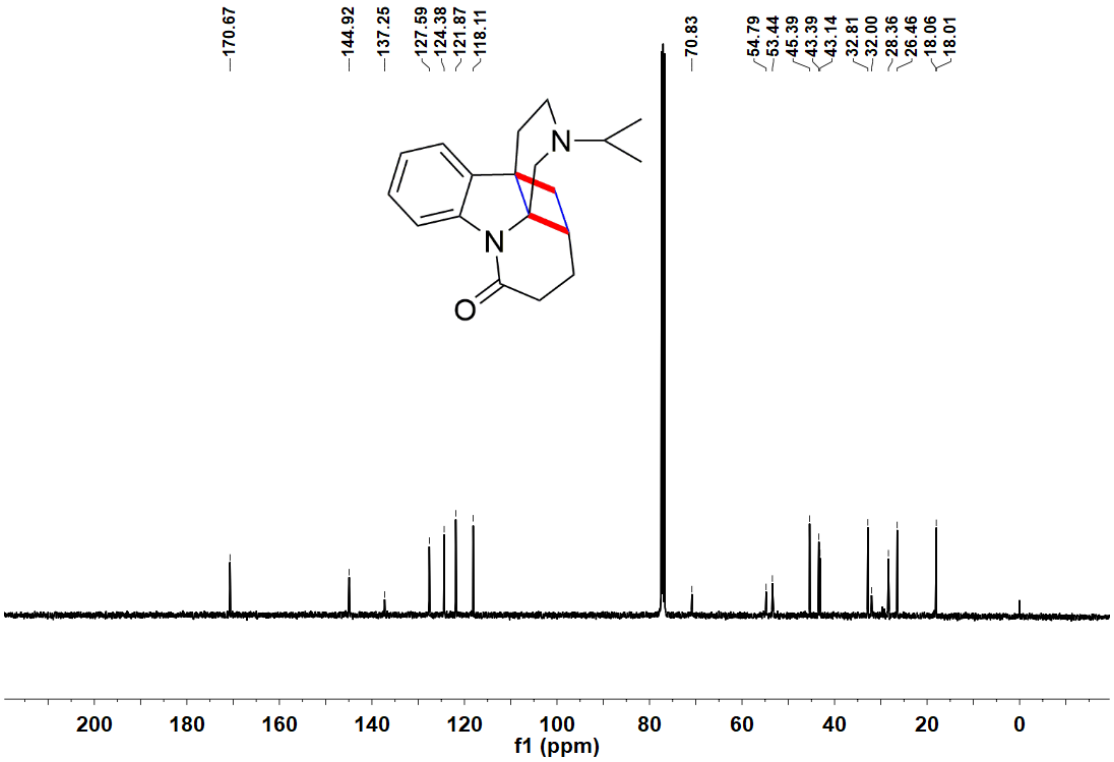
^{13}C NMR spectrum of **2l**



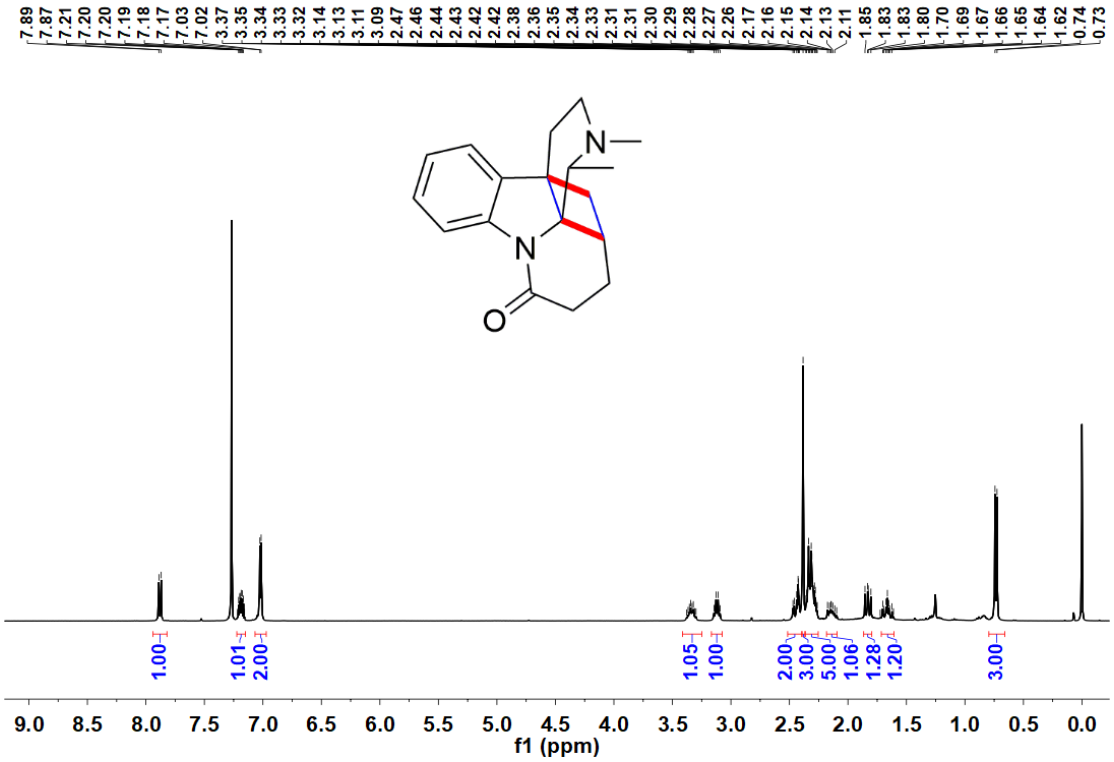
^{1}H NMR spectrum of **2m**



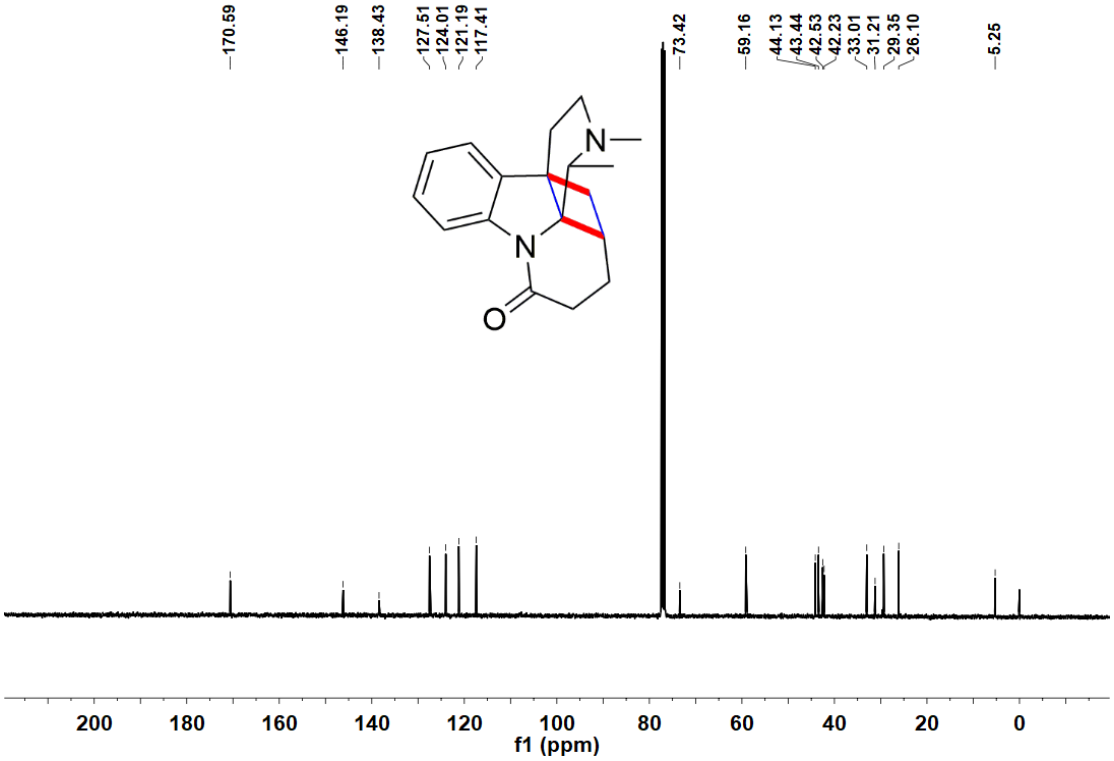
^{13}C NMR spectrum of **2m**



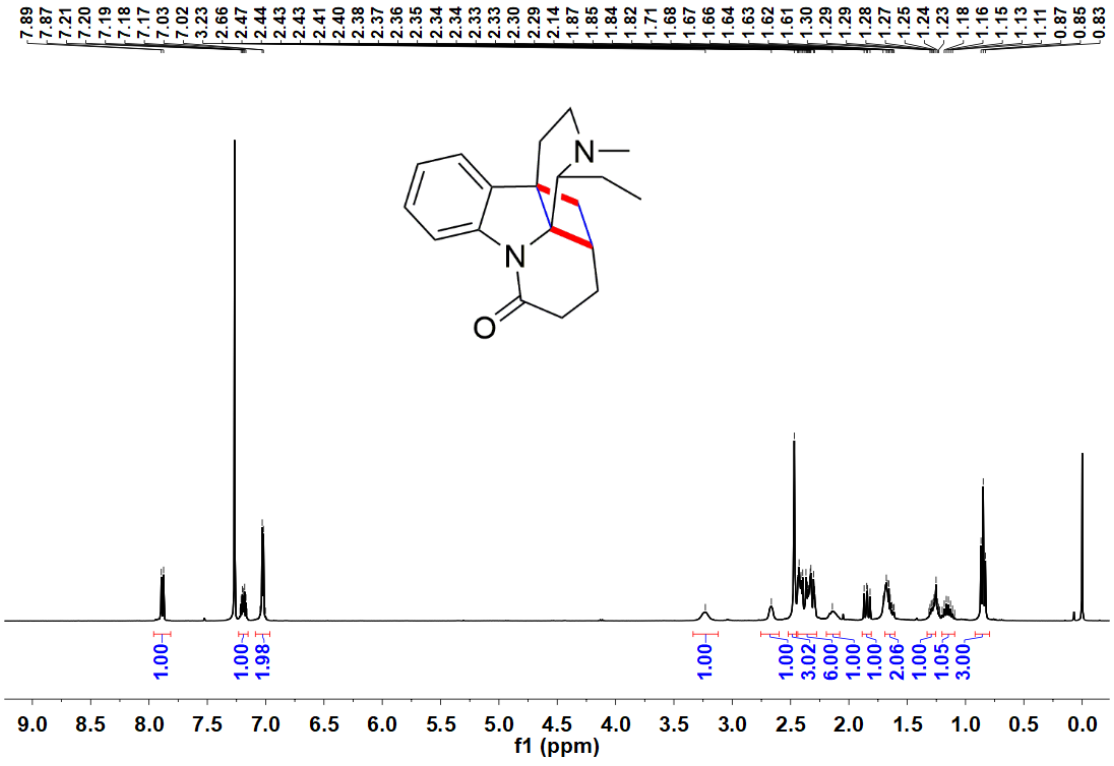
^{1}H NMR spectrum of **2n**



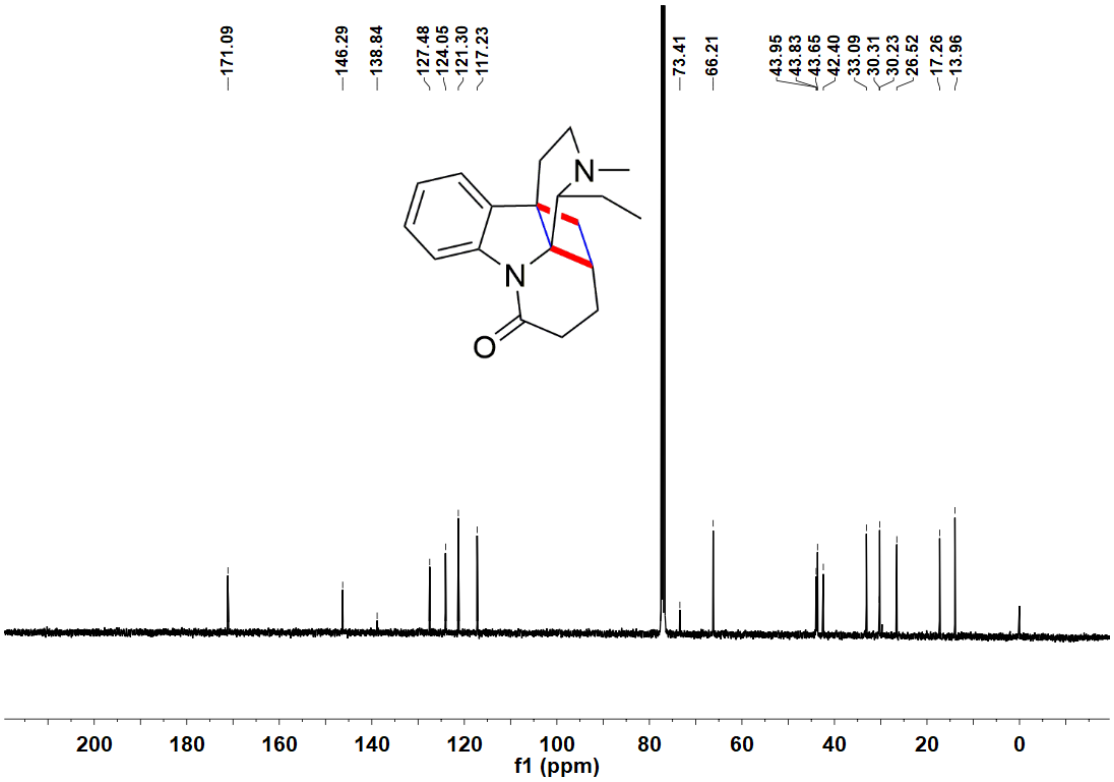
^{13}C NMR spectrum of **2n**



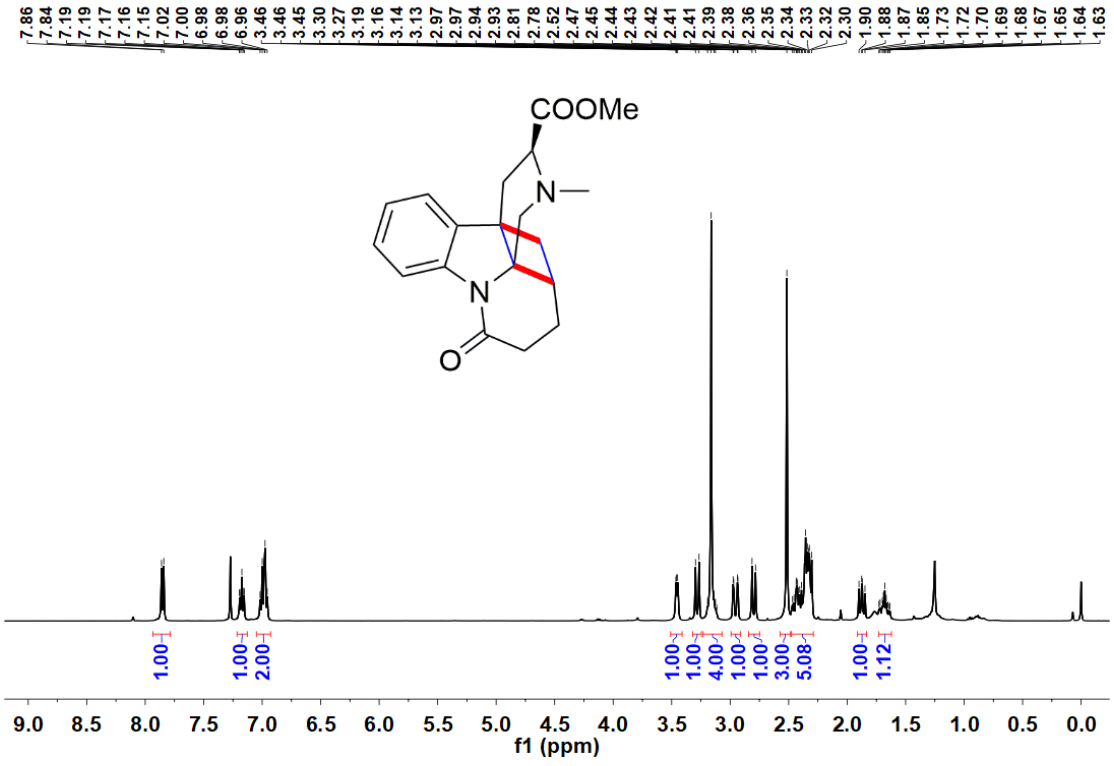
^{1}H NMR spectrum of **2o**



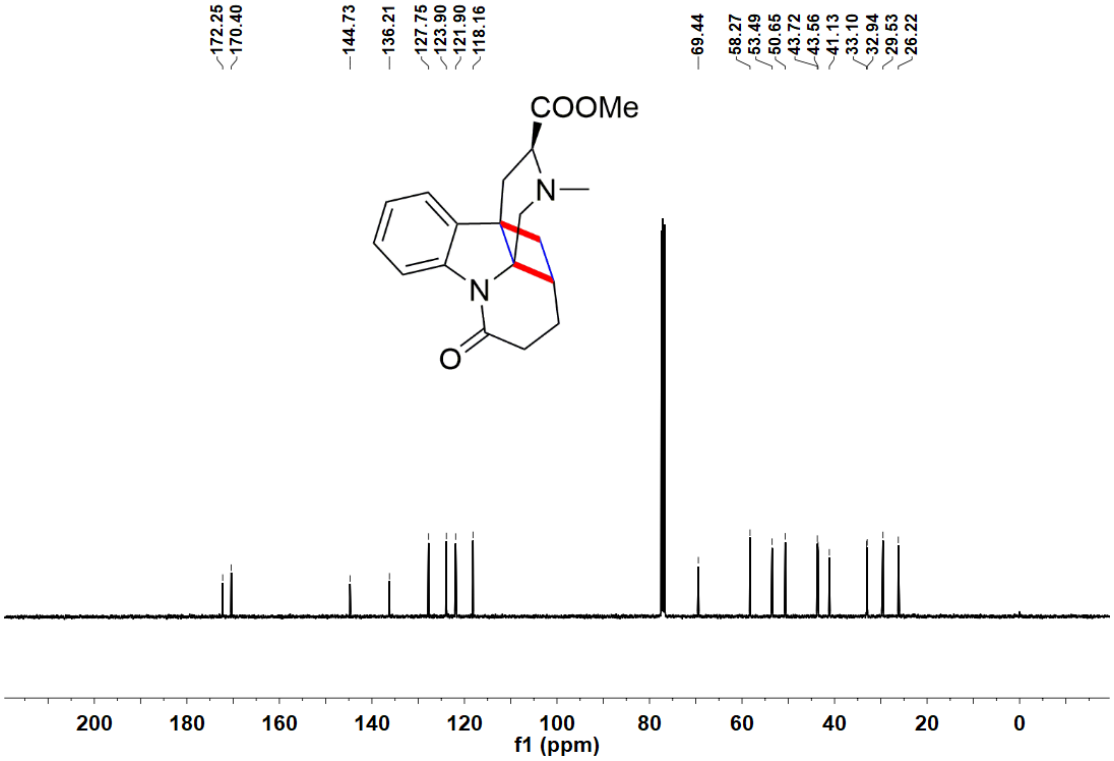
^{13}C NMR spectrum of **2o**



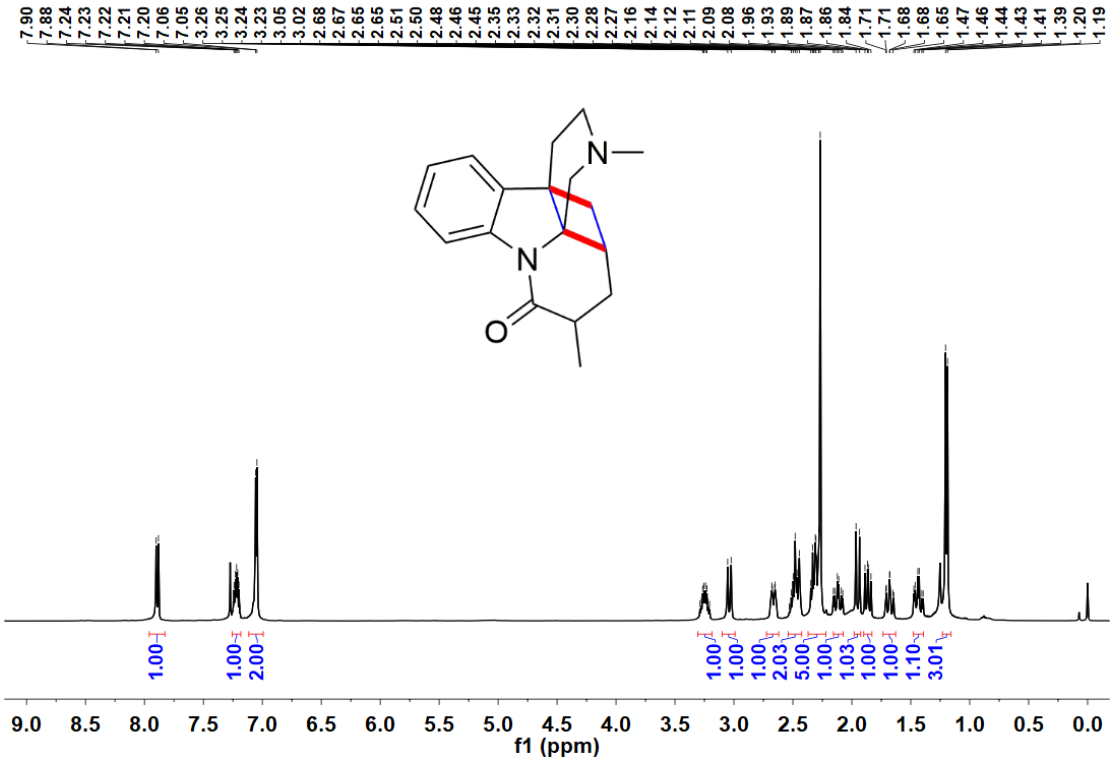
^{1}H NMR spectrum of **2p**



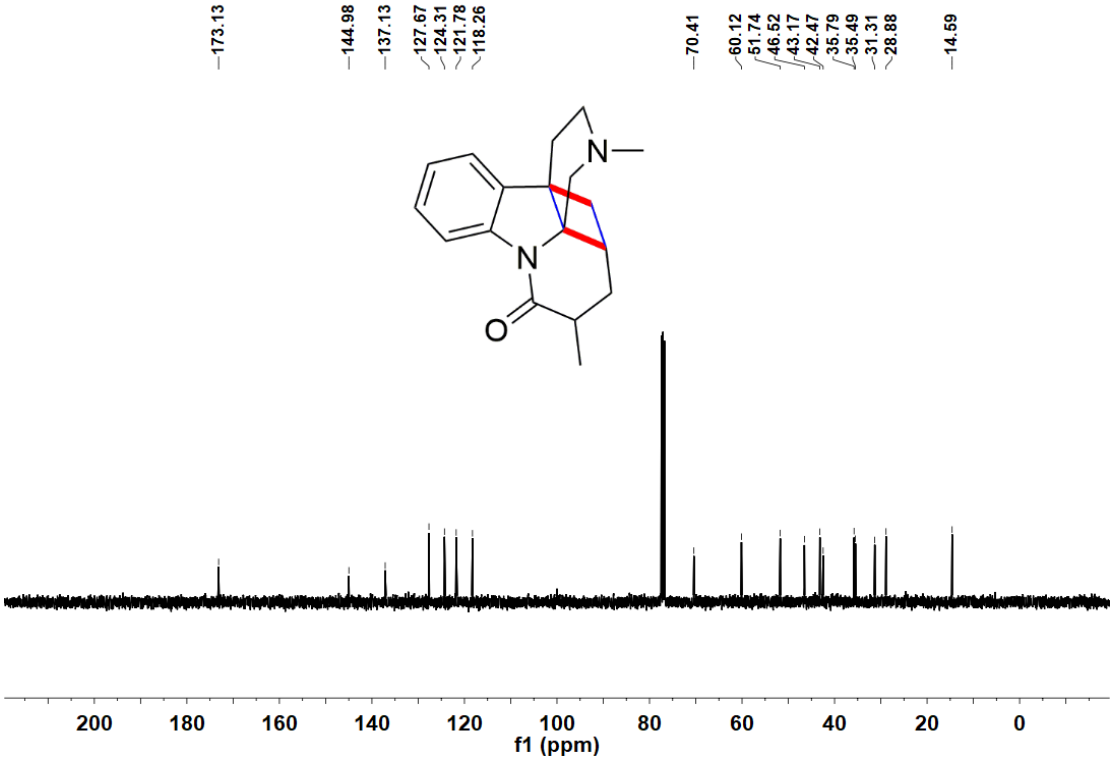
^{13}C NMR spectrum of **2p**



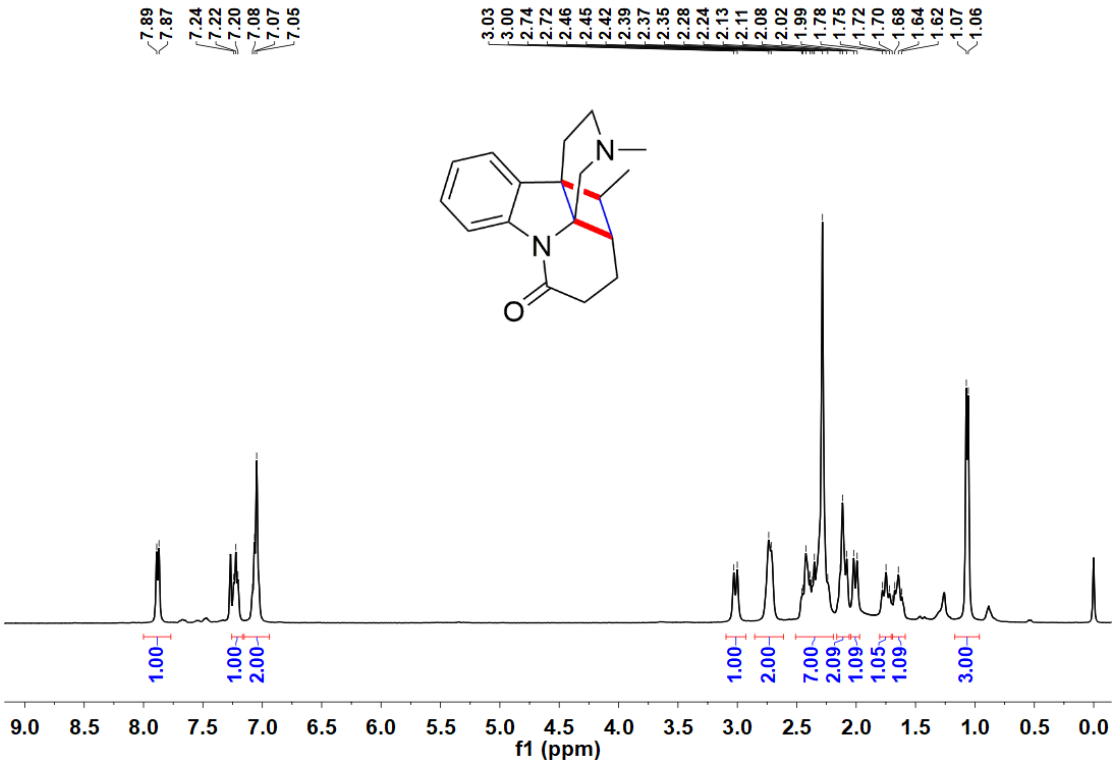
^{1}H NMR spectrum of **2q**



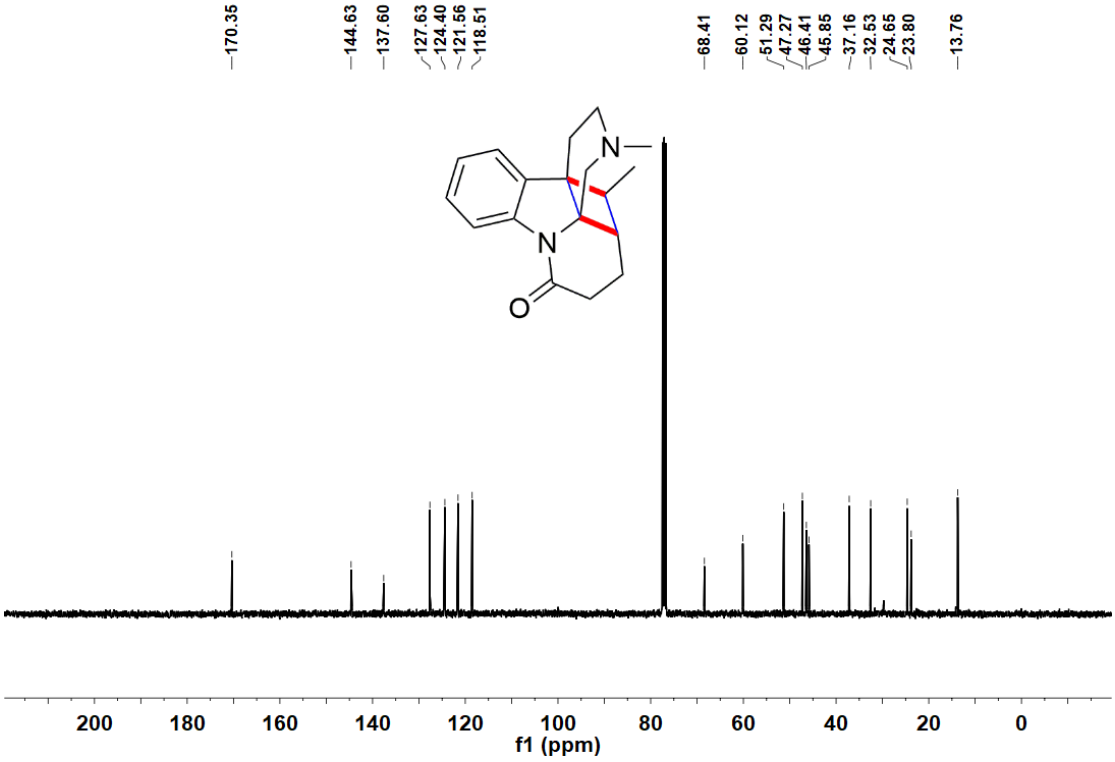
^{13}C NMR spectrum of **2q**



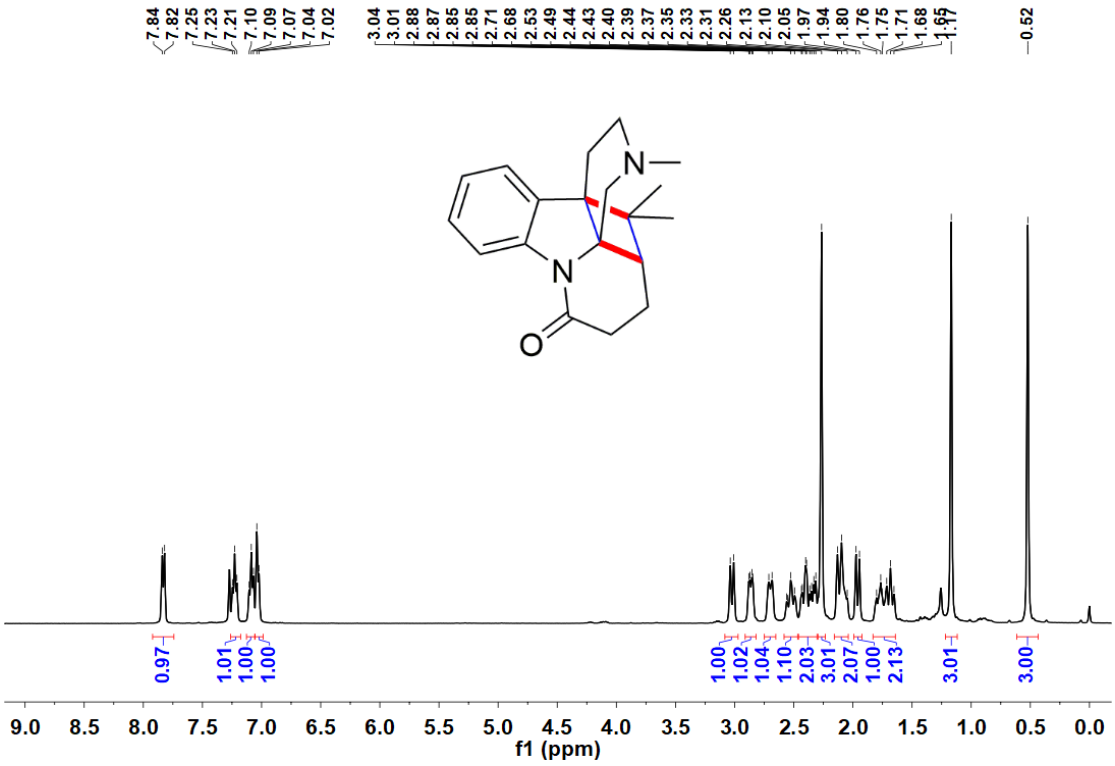
^{1}H NMR spectrum of **2r**



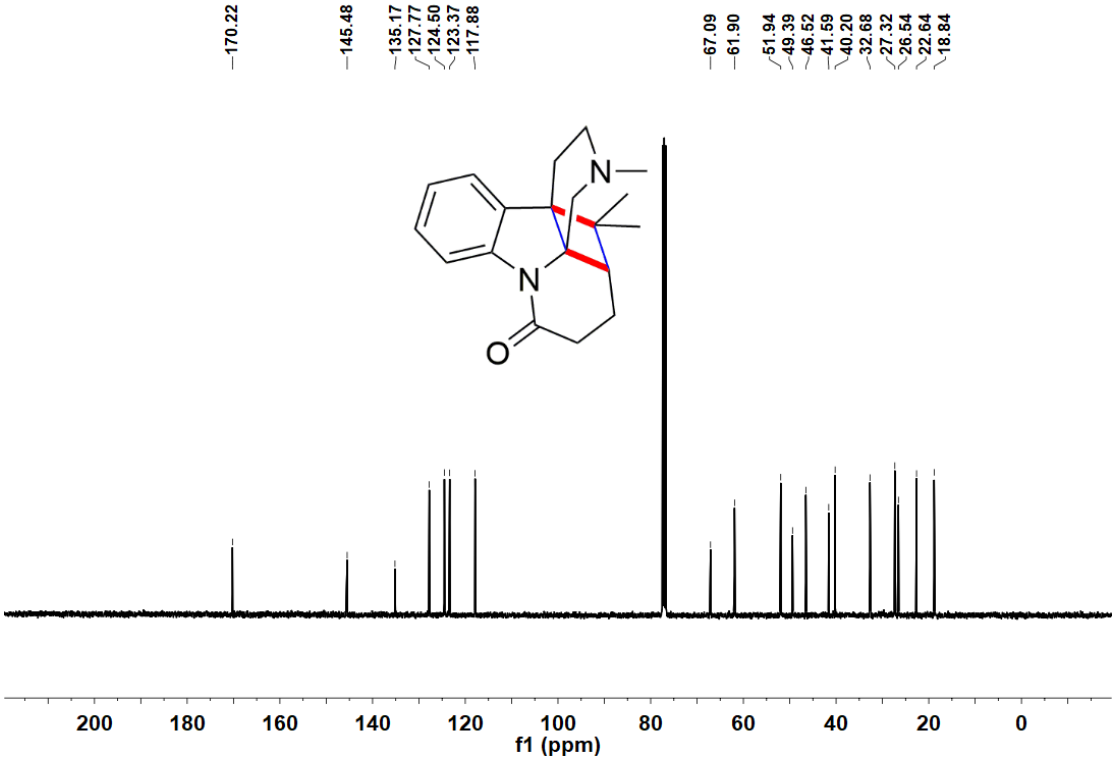
^{13}C NMR spectrum of **2r**



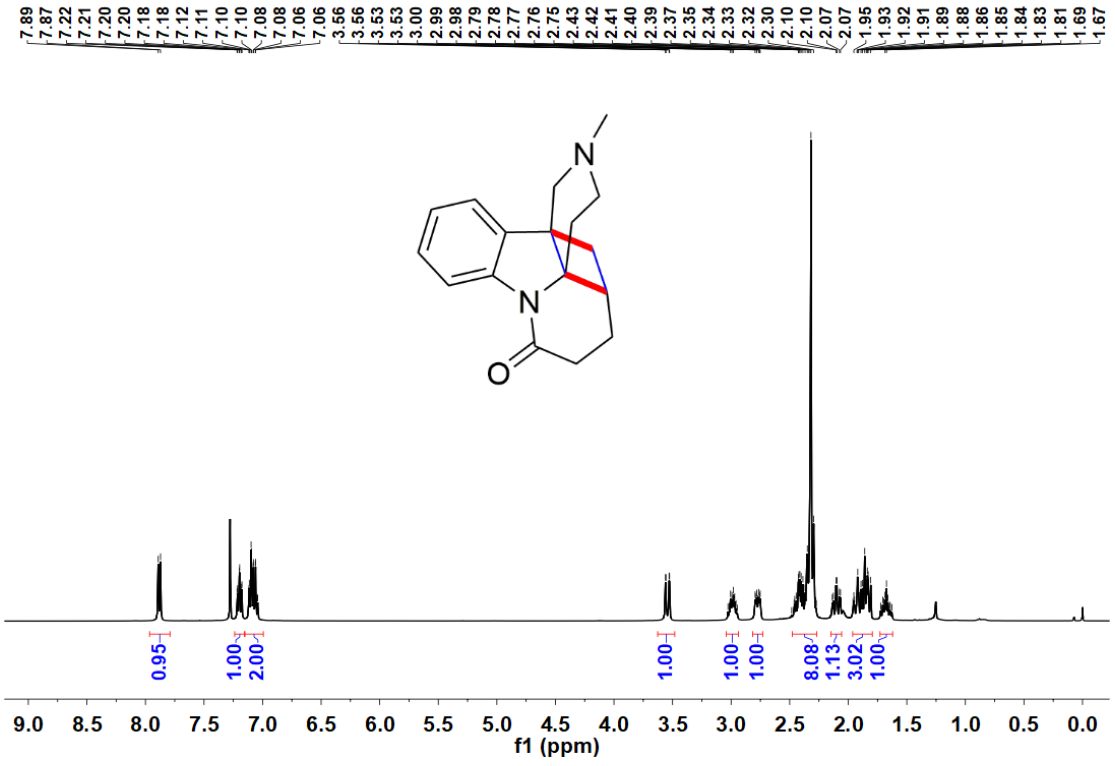
^{1}H NMR spectrum of **2s**



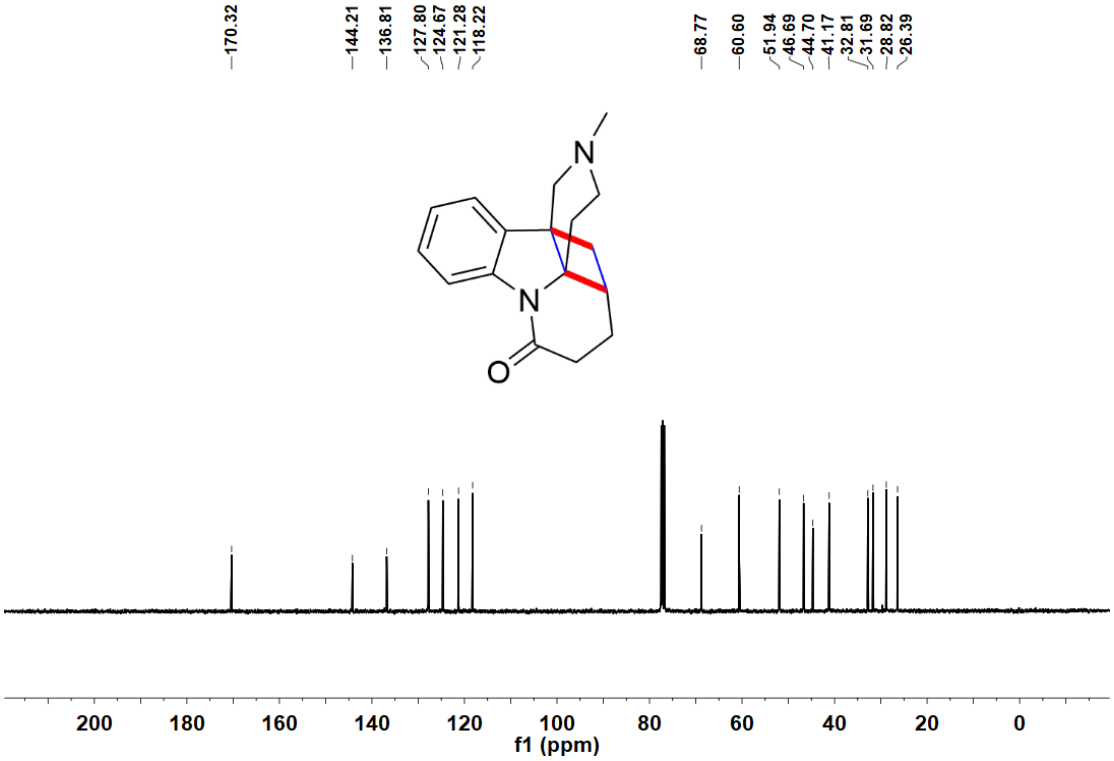
^{13}C NMR spectrum of **2s**



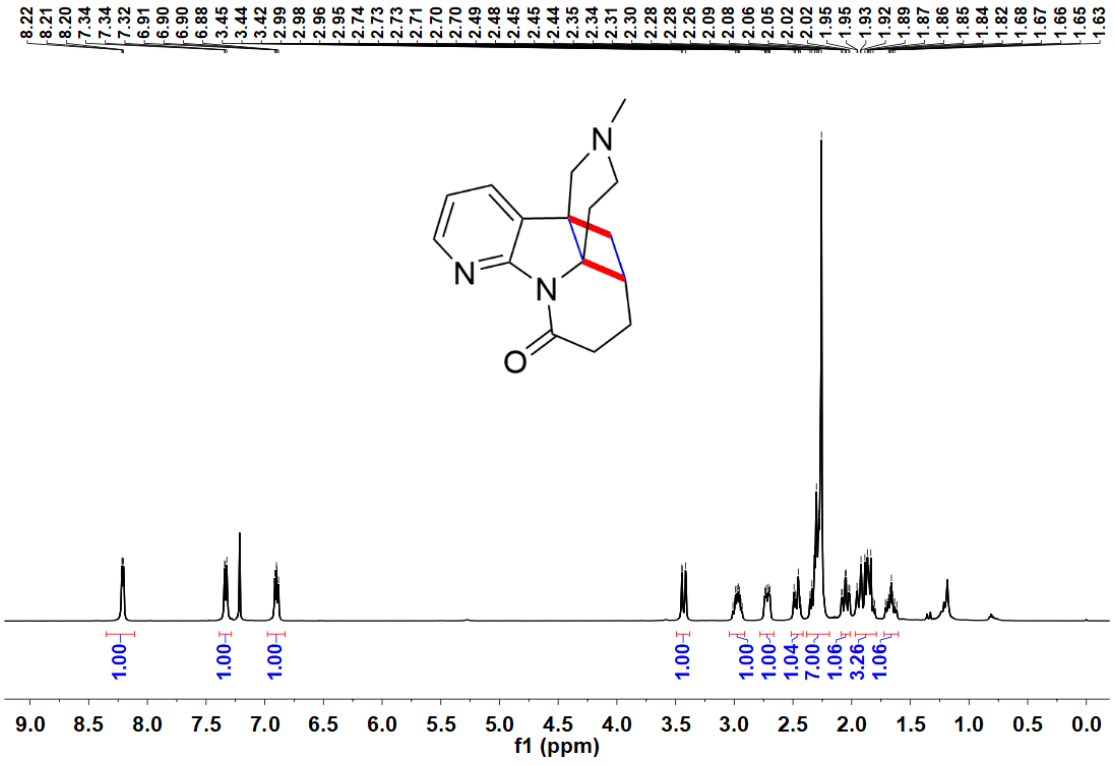
^{1}H NMR spectrum of **2t**



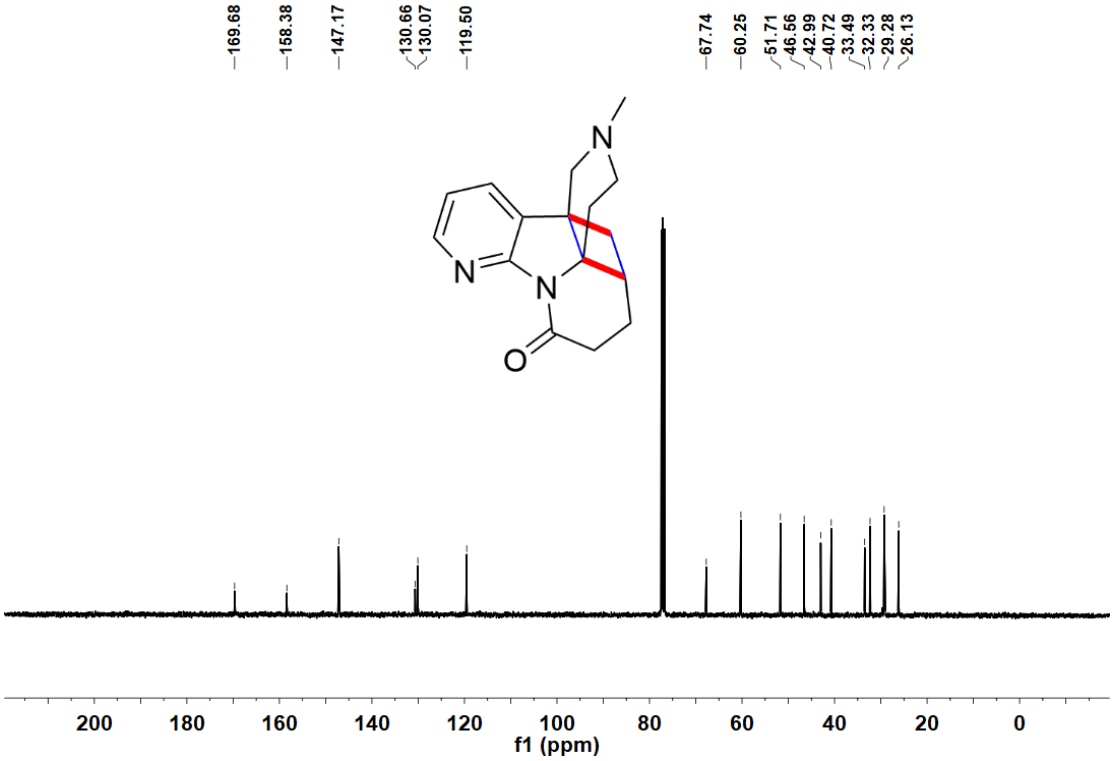
^{13}C NMR spectrum of **2t**



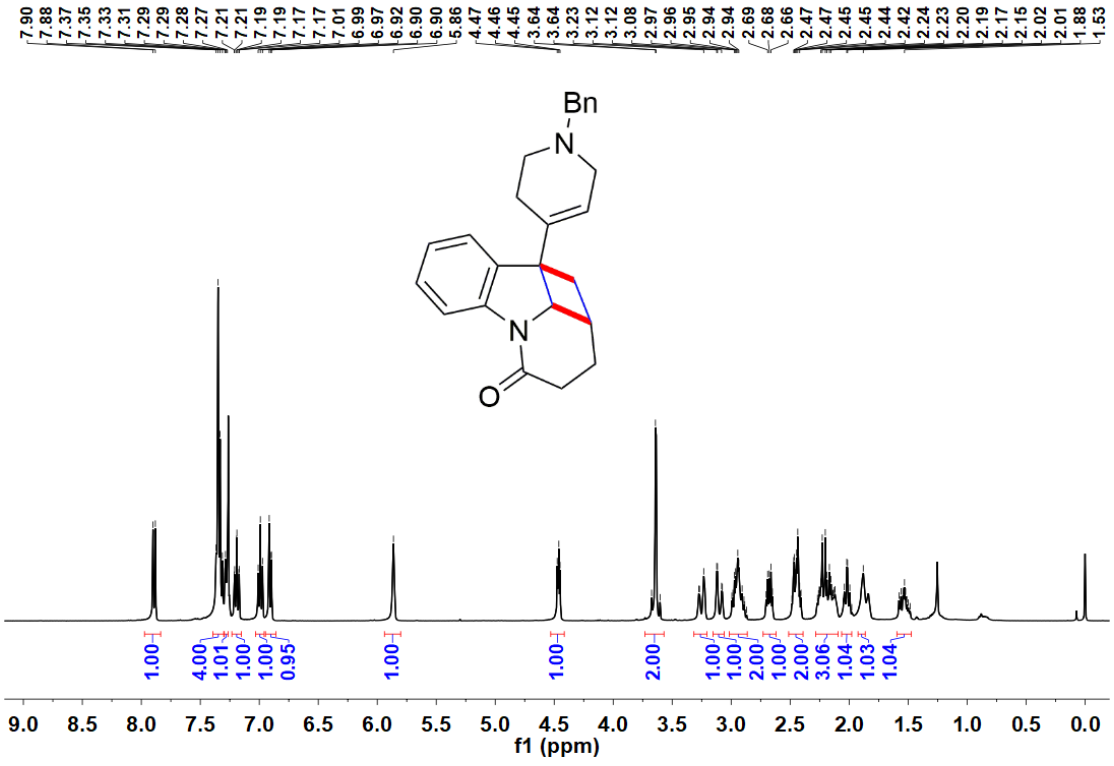
^{1}H NMR spectrum of **2u**



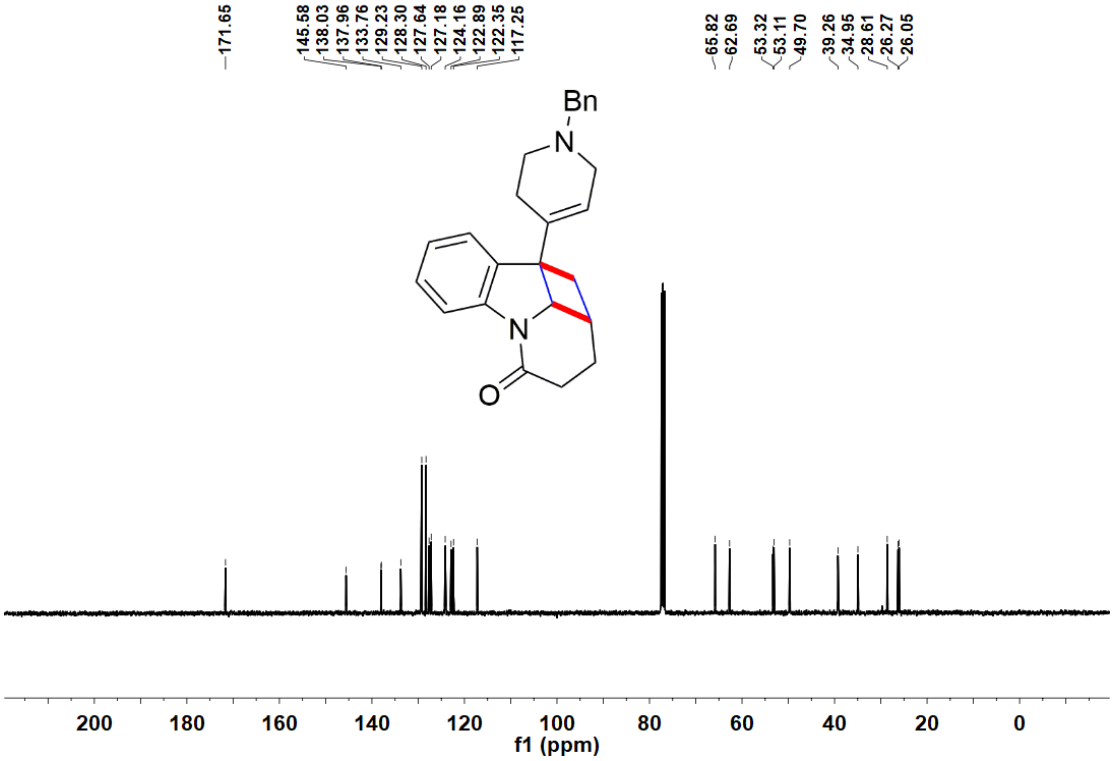
^{13}C NMR spectrum of **2u**



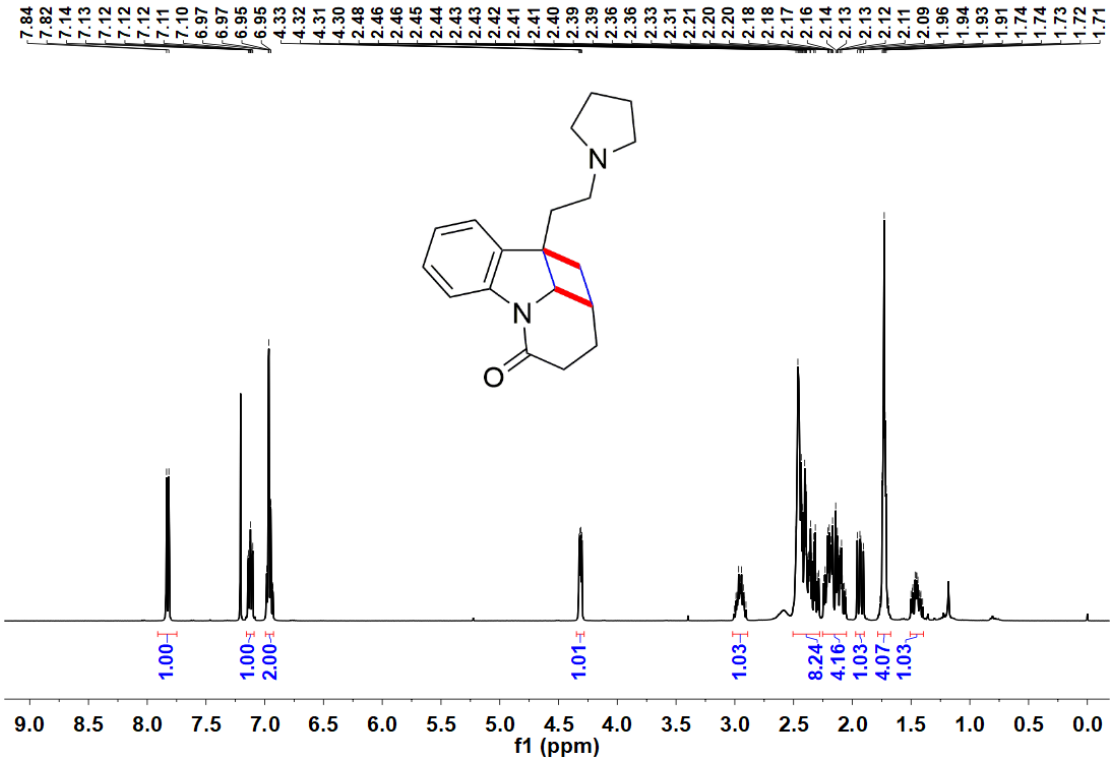
^{1}H NMR spectrum of **2v**



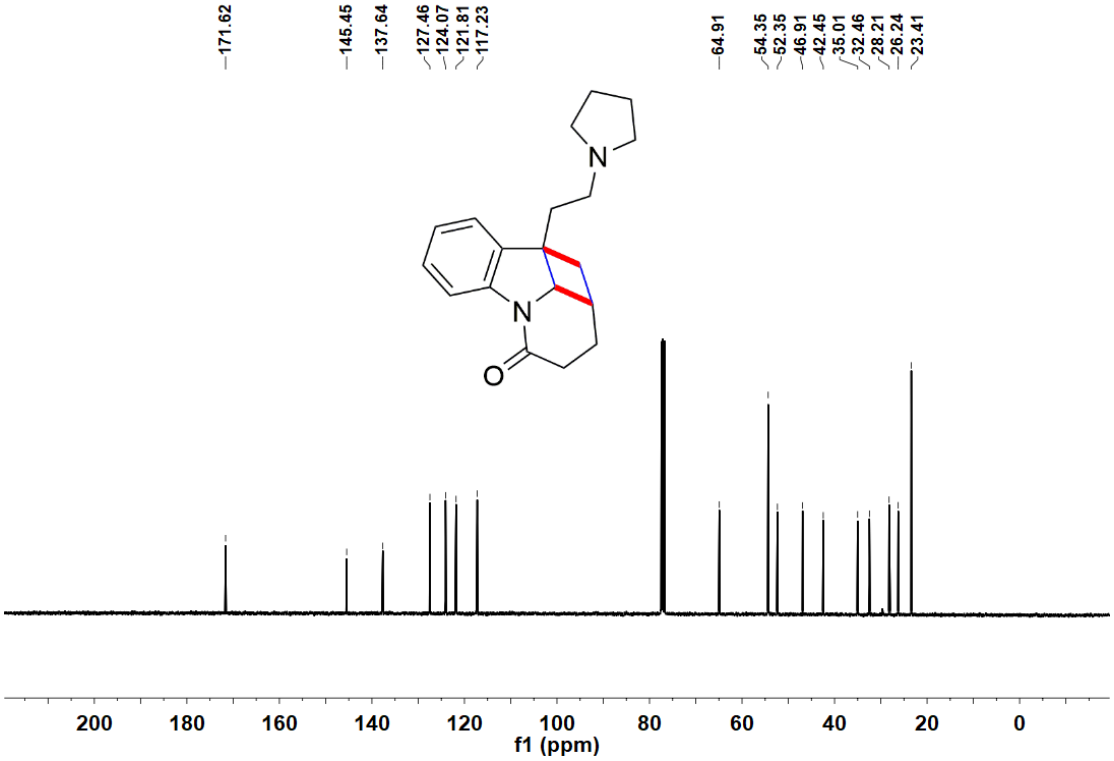
^{13}C NMR spectrum of **2v**



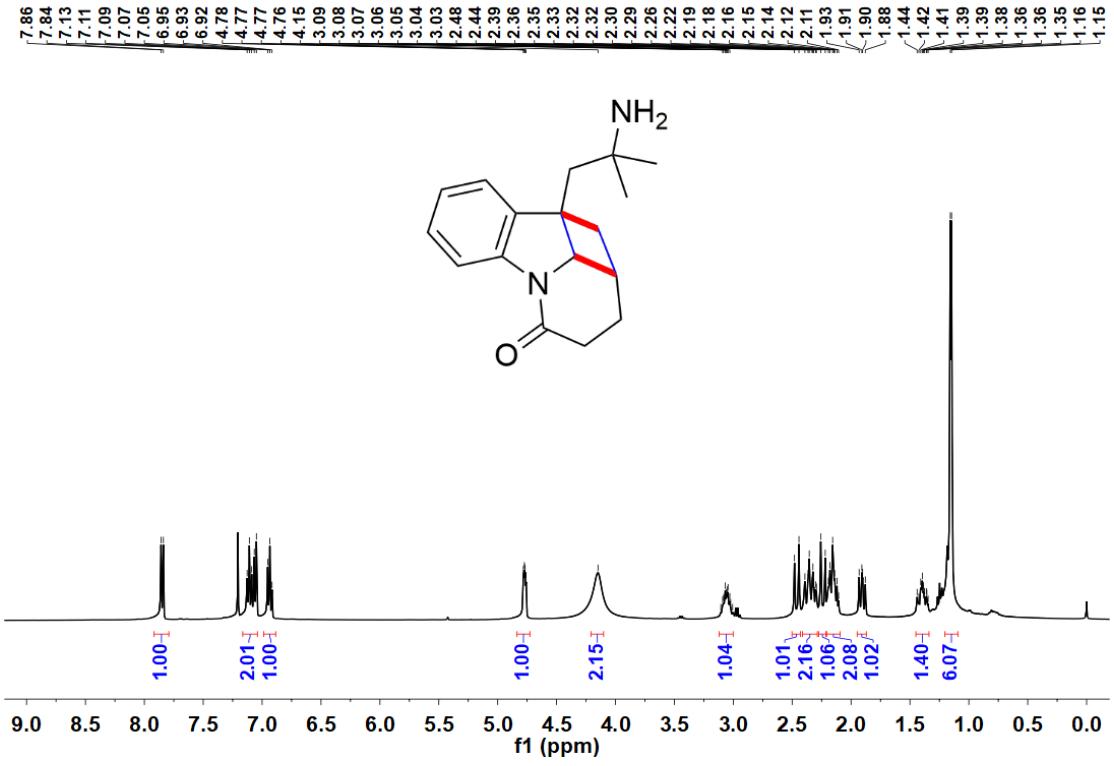
^{1}H NMR spectrum of **2w**



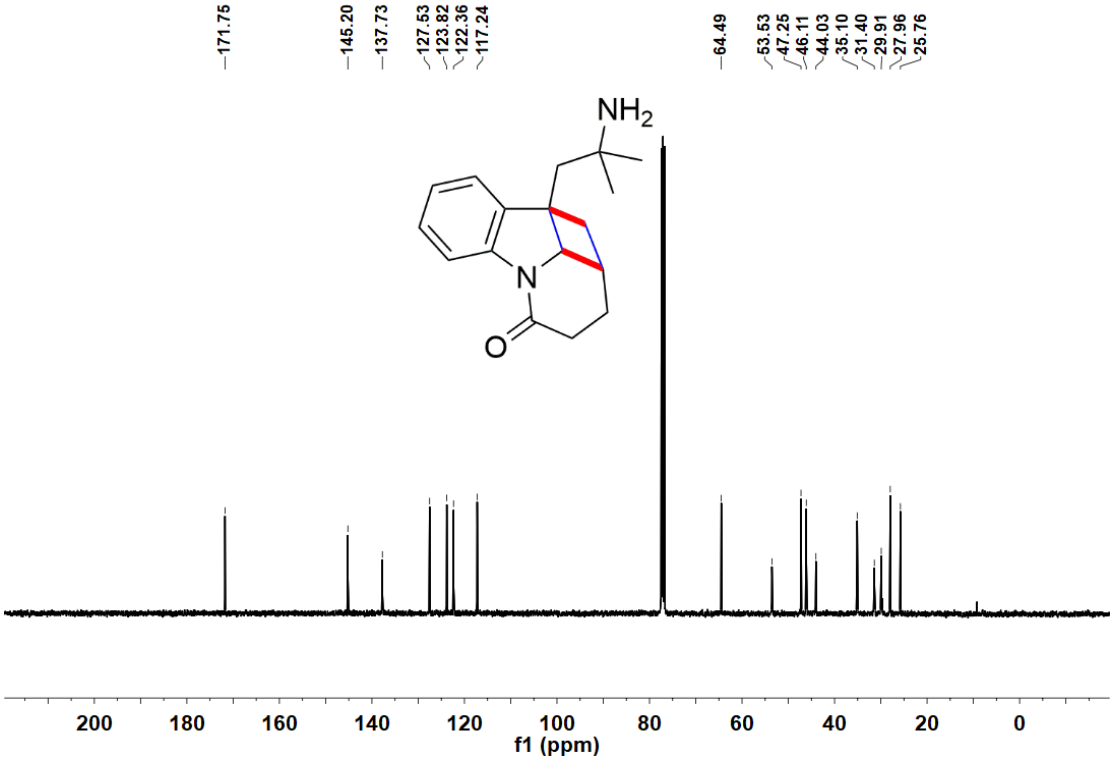
^{13}C NMR spectrum of **2w**



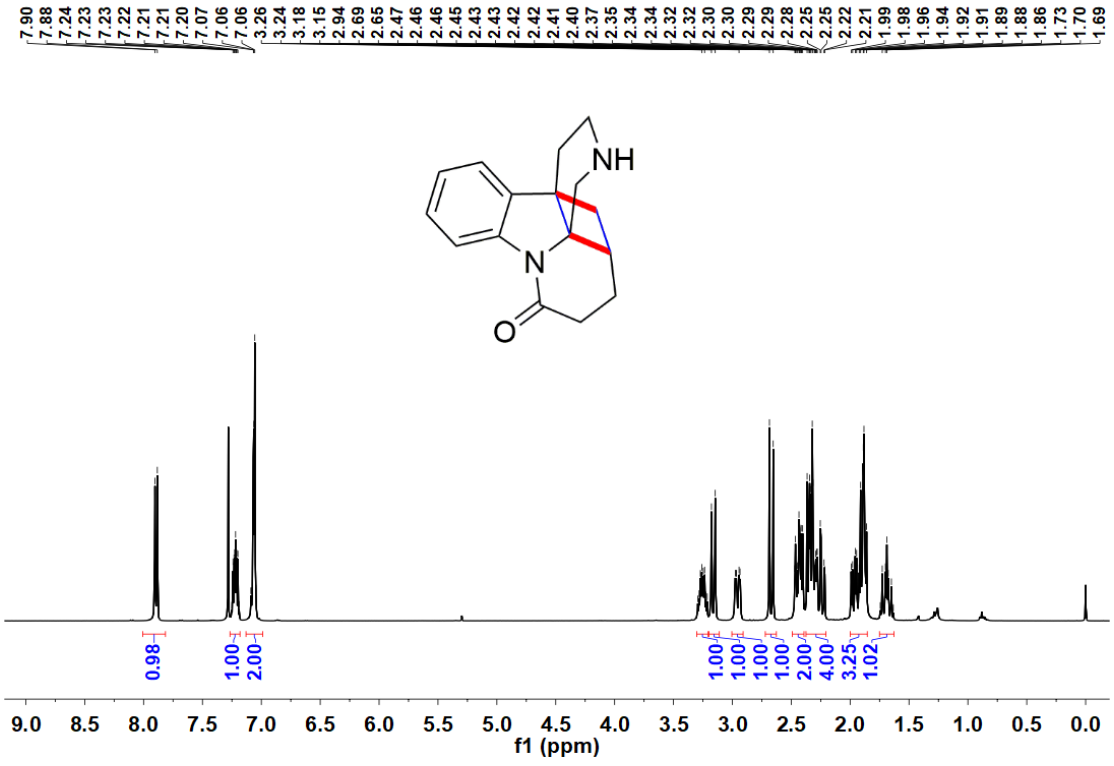
^{1}H NMR spectrum of **2x**



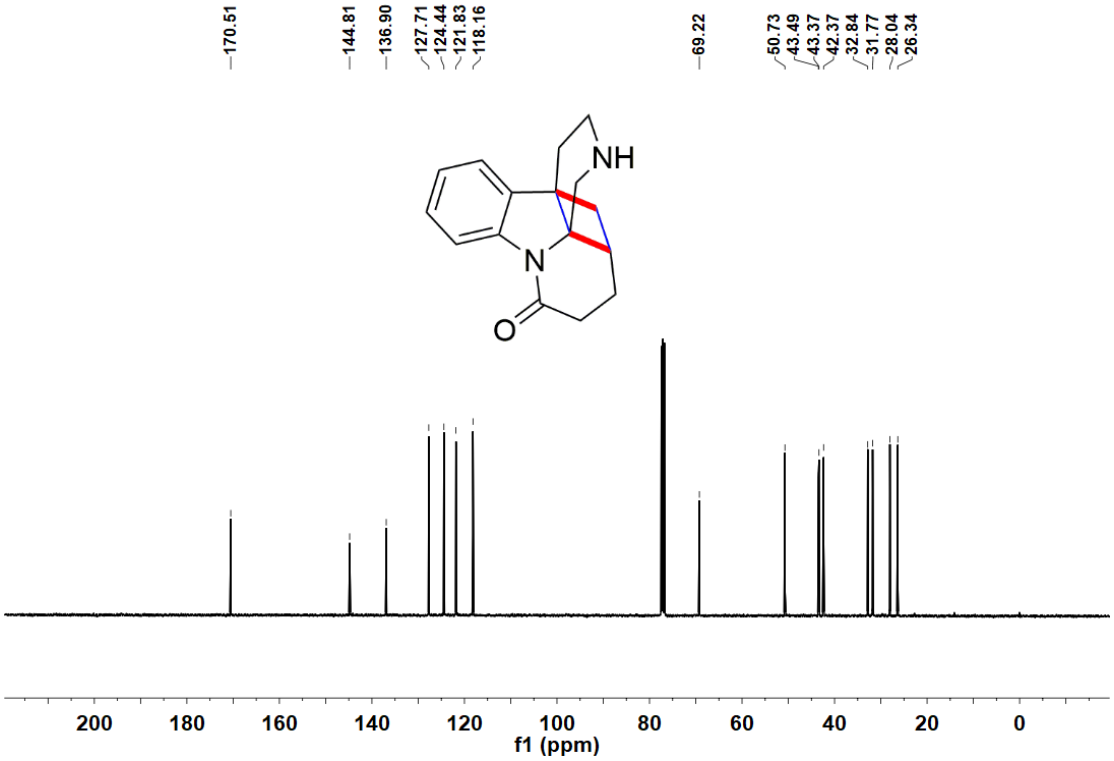
^{13}C NMR spectrum of **2x**



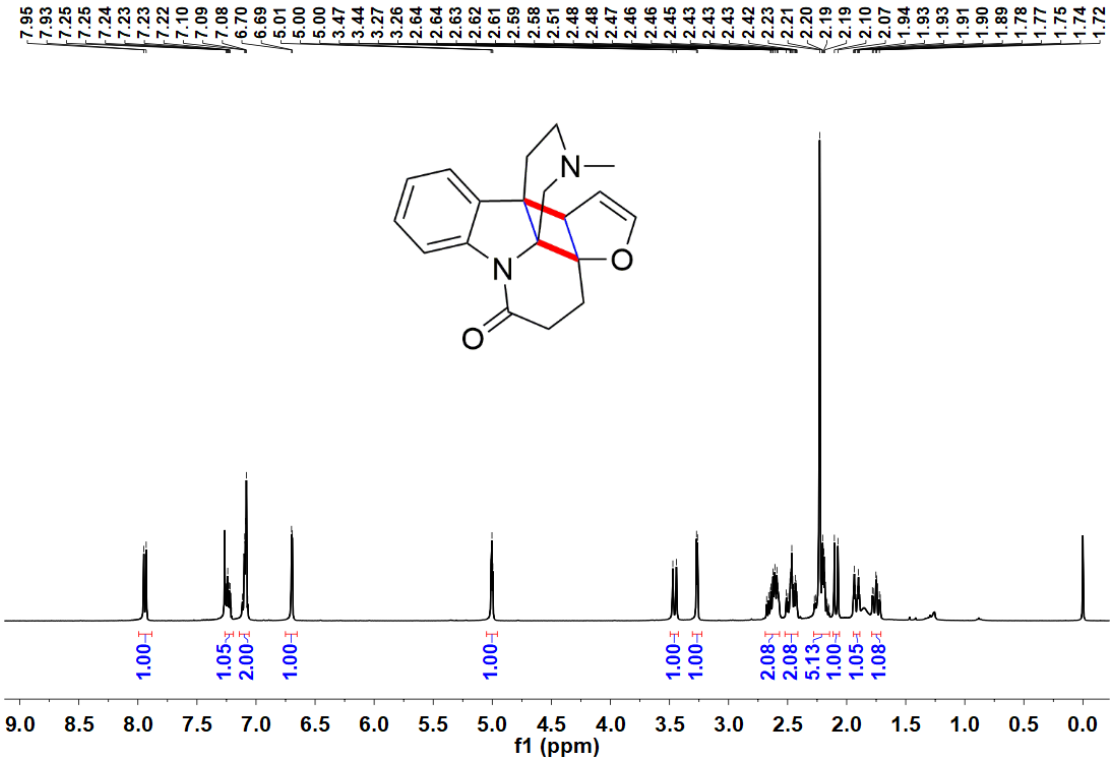
^{1}H NMR spectrum of **2y**



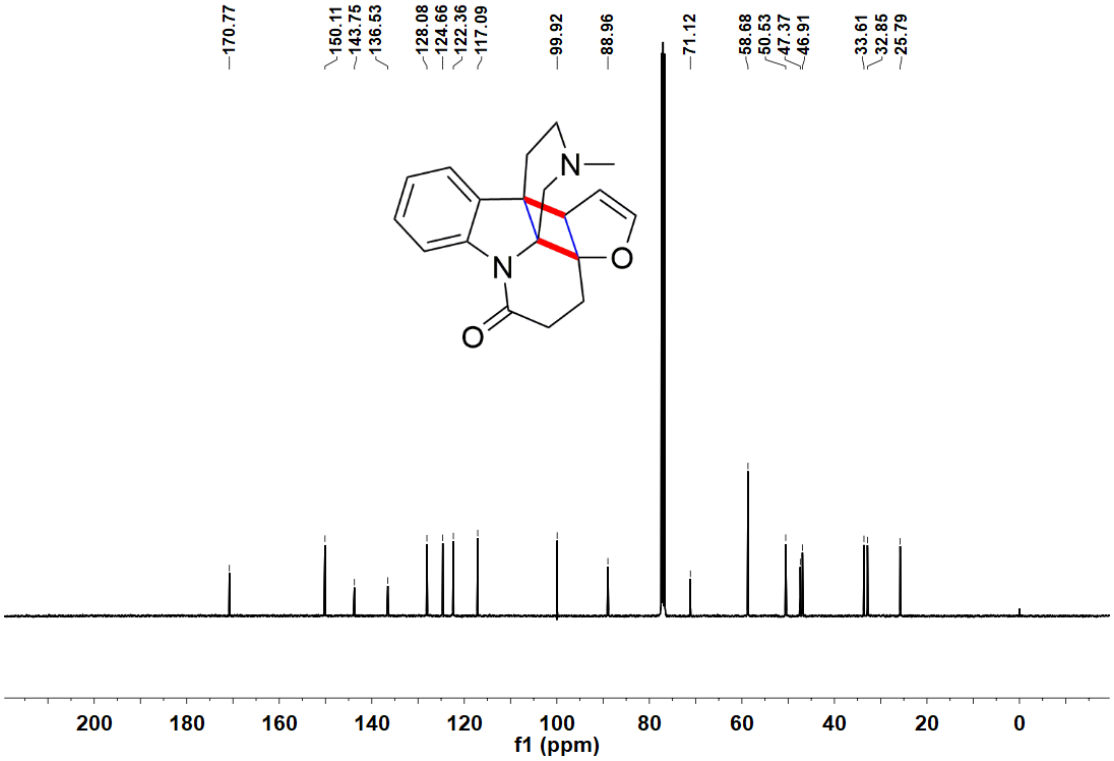
^{13}C NMR spectrum of **2y**



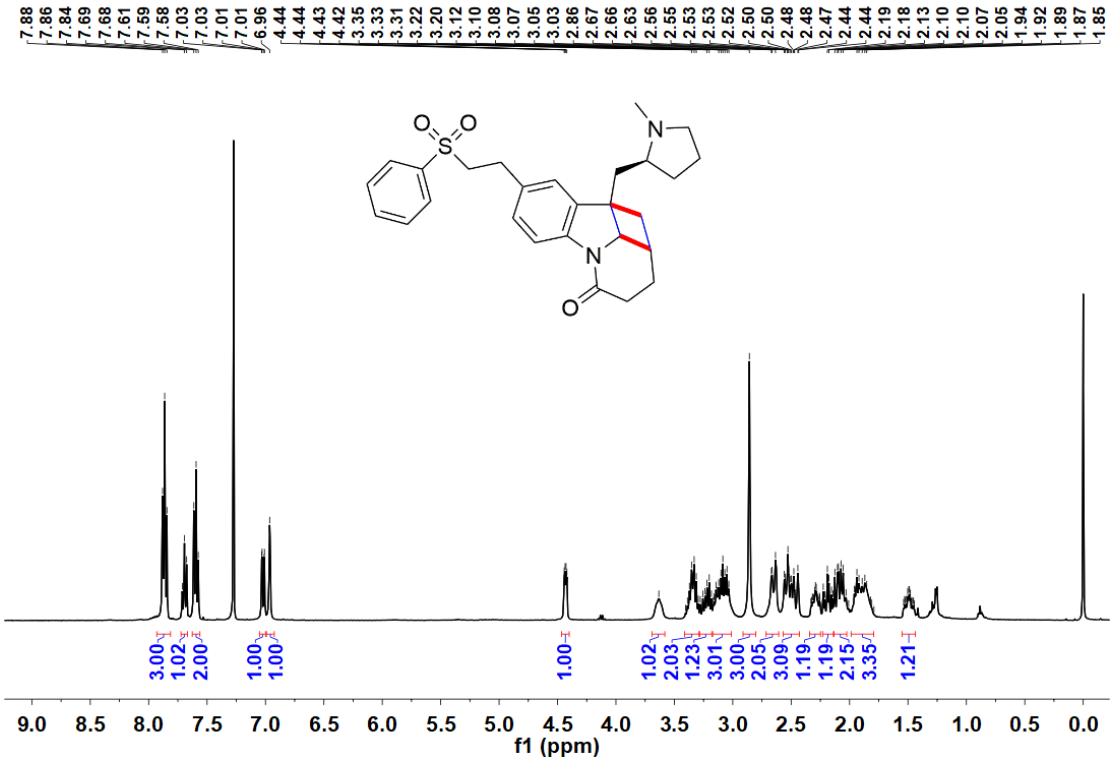
^{1}H NMR spectrum of **2z**



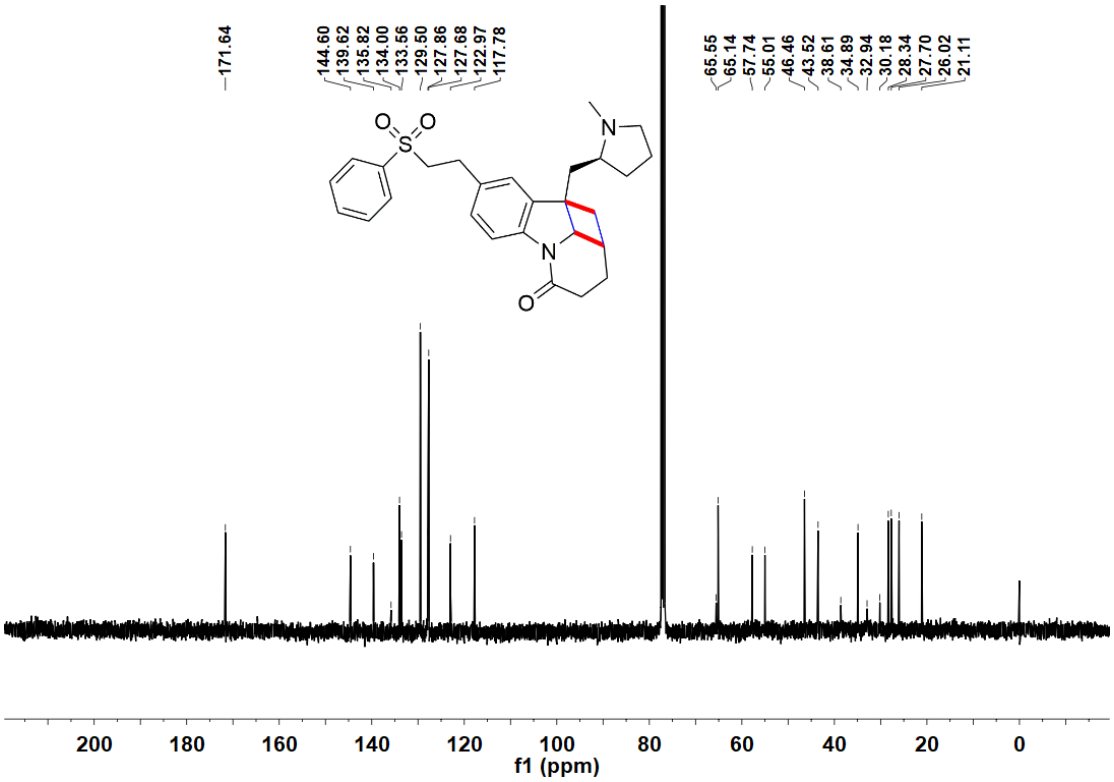
^{13}C NMR spectrum of **2z** (Two carbons in 58.68 ppm)



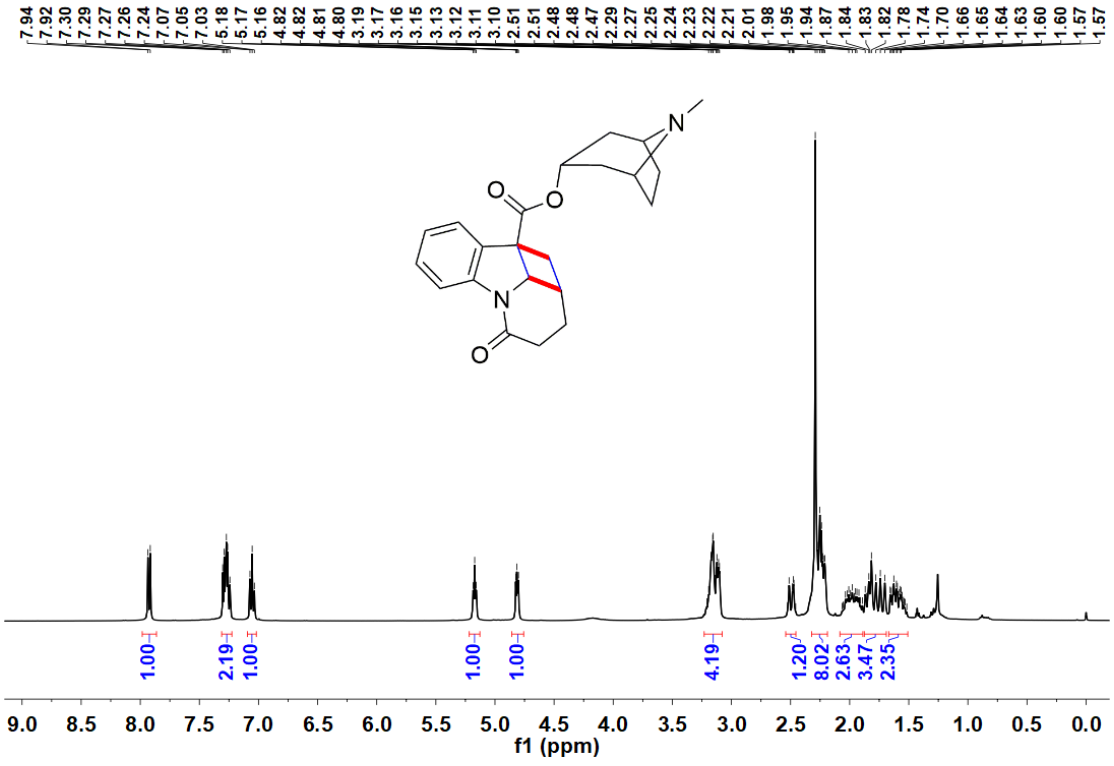
^{1}H NMR spectrum of **2aa**



^{13}C NMR spectrum of **2aa**



^{1}H NMR spectrum of **2ab**



^{13}C NMR spectrum of **2ab**