Supporting Information

Selective Access to Fused Tetrahydroquinolines via a Copper-Catalysed Oxidative Three-Component Annulation Reaction

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1. General Information

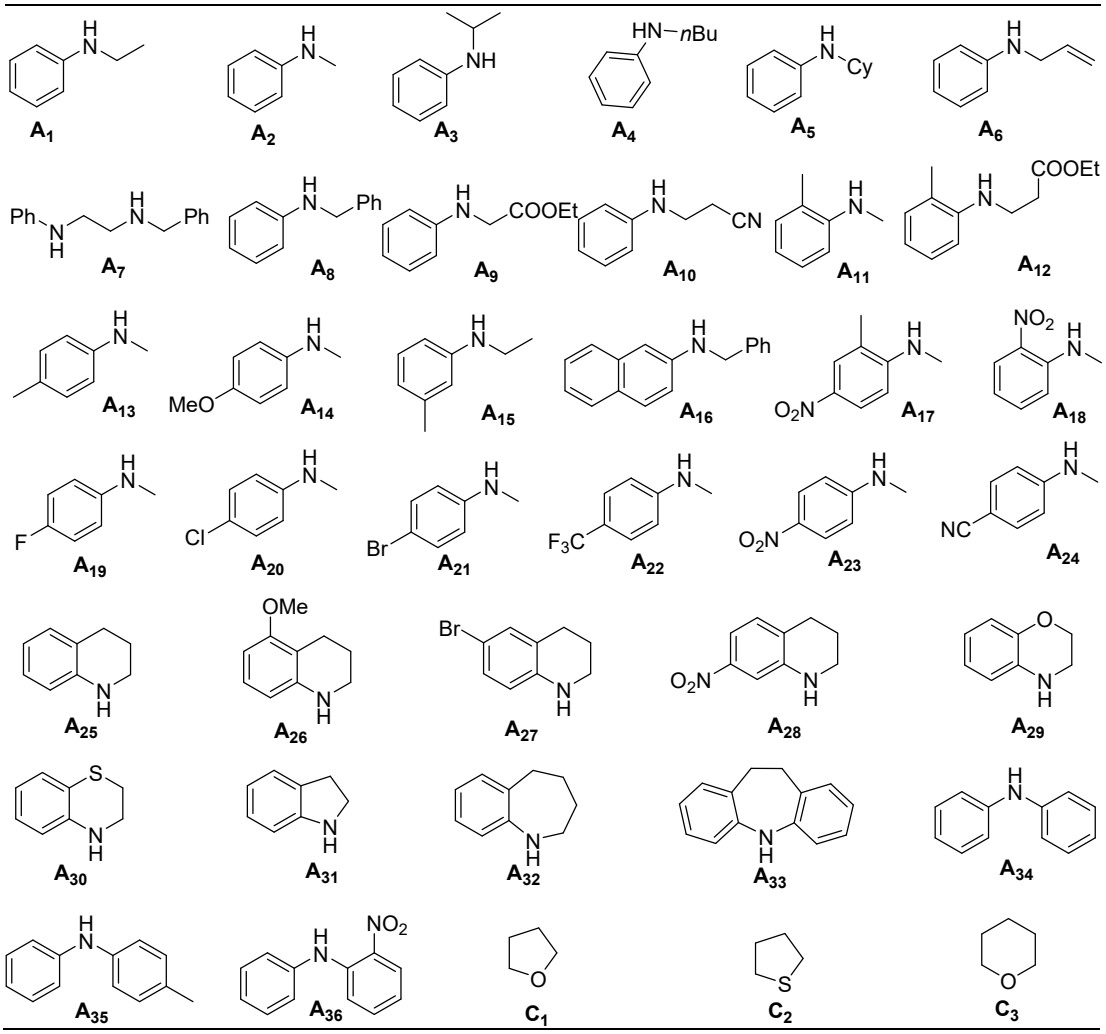
All the reactions were carried out using oven dried glassware and under air unless otherwise stated. All the obtained products were characterized by melting points (m.p.), ^{1}H-NMR, ^{13}C-NMR, and mass spectra (MS), the NMR spectra of the known compounds were found to be identical with the ones reported in the literatures. Additionally, all the new compounds were further characterized by high resolution mass spectra (HRMS). Melting points were measured on a BUCHI Melting Point M-565. ^{1}H-NMR, ^{13}C-NMR spectra were obtained on Bruker-500 MHz or 400 MHz. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-600 spectrometer. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m). TLC was performed using commercially prepared 1600-2000 mesh silica gel plates (GF254), and visualization was effected with short wavelength UV light (254 nm).

All the reagents were purchased from Bide Pharmatech Ltd. and Energy Chemical. All solvents were purchased from Greagent (Shanghai Titansci incorporated company) and used without further purification. All reactions were heated by metal sand bath (WATTCAS, LAB500, https://www.wattcas.com).

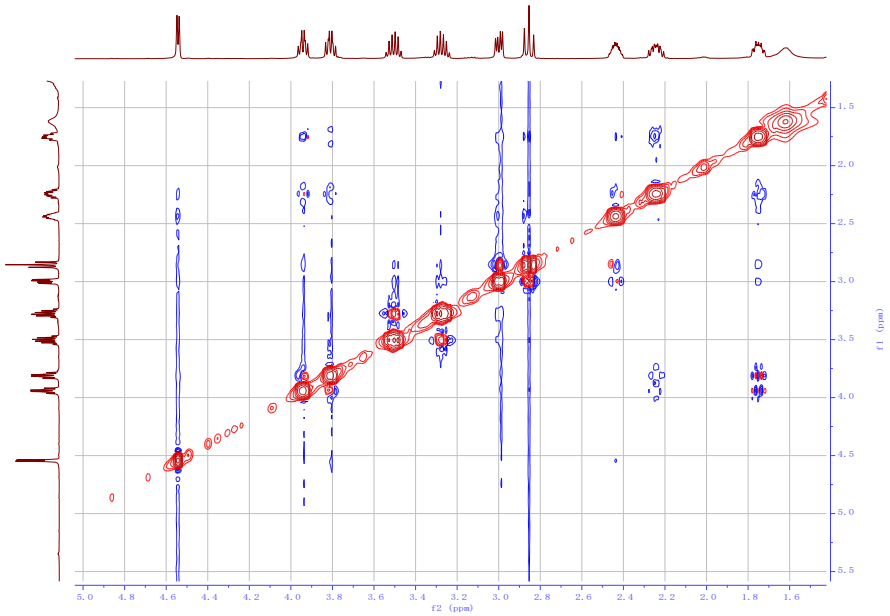
2. Typical procedure for the synthesis of product D_1

Under air atmosphere, $Cu(OTf)_2$ (0.02 mmol, 7.22 mg), *p*-nitrobenzoic acid (0.06 mmol,10.1 mg) and paraformaldehyde **B** (0.6 mmol,18.0 mg) were introduced into a dried Schlenk tube (50 mL) at room temperature. Then, THF $\mathbf{C_1}$ (1.0 mL), *N*-ethyl aniline $\mathbf{A_1}$ (0.2 mmol, 24.2 mg) and tert-Butyl hydroperoxide (70 % in water, 0.4 mmol, 51.4 mg) were added, and the Schlenk tube was then sealed. After stirring for 16 hours at 80 ºC, the reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica, eluting with petroleum ether (PE, 60-90 ºC) and ethyl acetate (EA) (v/v = 8 : 1) to give the desired yellow oily product $\mathbf{D_1}$ (30.5 mg, 75 %).

3.Substrate employed for the synthesis of tetrahydroquinoline derivatives



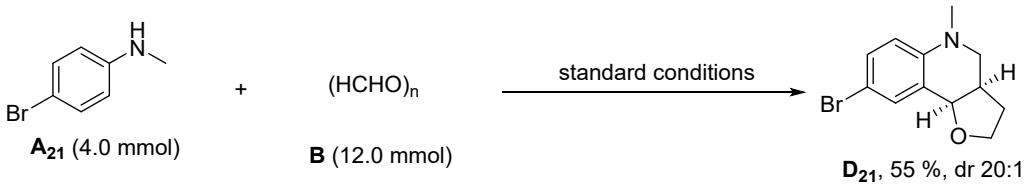
3. NOESY Spectrum of Compound D_1



NOESY Spectrum of Compound **D_1**

4. Synthetic utility

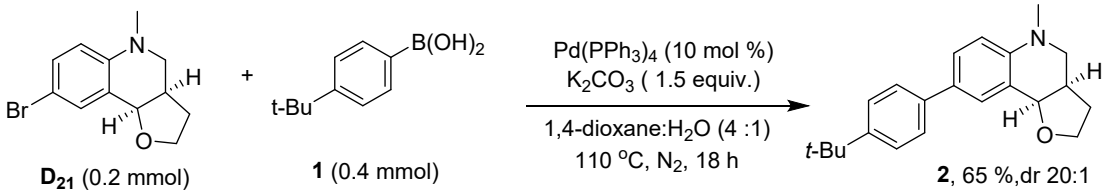
(1) Large-scale experiments synthesis of **D_{21}**



A_{21} (4.0 mmol) **B** (12.0 mmol) **D_{21}**, 55 %, dr 20:1

Under air atmosphere, $Cu(OTf)_2$ (0.4 mmol, 0.144 g), *p*-nitrobenzoic acid (1.2 mmol, 0.202 g) and Paraformaldehyde **B** (12.0 mmol, 0.36 g) were introduced into a dried Schlenk tube (100 mL) at room temperature. Then, THF **C_1** (15.0 mL), *N*-ethylaniline **A_1** (4.0 mmol, 0.484 g) and tert-butyl hydroperoxide (70 % in water, 8.0 mmol, 1.028 g) were added and the Schlenk tube was sealed. After stirring for 16 hours at 80 °C, the reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica, eluting with petroleum ether and ethyl acetate (v/v = 8 : 1) to give the desired product **D_{21}** as a yellow oil (0.587 g, 55 %).

(2) Synthesis of compound 2

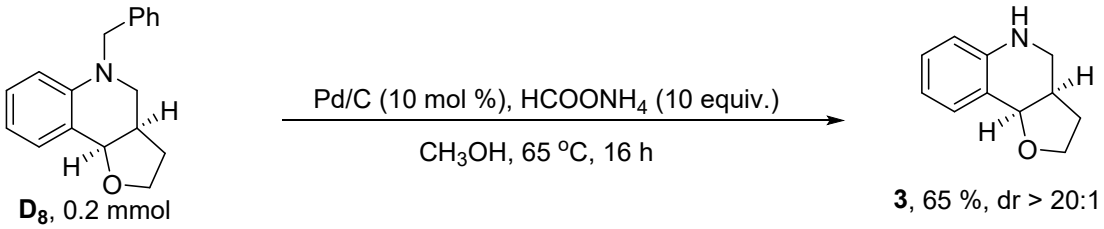


D_{21} (0.2 mmol) **1** (0.4 mmol) **2**, 65 %,dr 20:1

Under nitrogen atmosphere, $Pd(PPh_3)_4$ (0.02 mmol, 23.1 mg), K_2CO_3 (0.3 mmol, 41.4 mg), 4-tert-

butylphenylboronic acid **1** (0.4 mmol, 71.2 mg) and $\mathbf{D_{21}}$ (0.2 mmol, 53.4 mg) were introduced into a dried Schlenk tube (50 mL) at room temperature. Then, 1,4-dioxane and H_2O (v : v = 4 : 1, 1.5 mL) were added into the Schreck tube via injection. After that, the reaction mixture was stirred at 110 °C for 18 h. The reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica, eluting with PE : EA = 10 : 1 (v/v) to give the desired yellow oily product **2** (41.7 mg, 65 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 5.0 Hz, 1H), 7.48 – 7.44 (m, 3H), 7.43 – 7.40 (m, 2H), 6.75 – 6.70 (m, 1H), 5.43 (dd, *J* = 4.7, 1.4 Hz, 1H), 3.92 – 3.80 (m, 2H), 3.06 – 3.01 (m, 0.5H), 2.93 (s, 1H), 2.89 (s, 3H), 2.86 – 2.80 (m, 0.5H), 1.98 – 1.91 (m, 1H), 1.87 – 1.79 (m, 2H), 1.35 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1, 138.3, 129.8, 127.8, 126.0, 126.0, 125.6, 125.5, 113.3, 100.0, 67.0, 52.6, 39.4, 36.0, 34.4, 32.3, 31.4, 23.4; HRMS (ESI): Calcd. for $C_{22}H_{28}NO$ $[M+H]^+$: 322.2165; found: 322.2162.

(3) Synthesis of compound 3



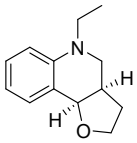
$\mathbf{D_8}$, 0.2 mmol

3, 65 %, dr > 20:1

Under nitrogen atmosphere, Pd/C (0.02 mmol,2.1 mg), $\mathbf{D_8}$ (0.2 mmol, 53 mg), $HCOONH_4$ (2 mmol, 136 mg), and methanol (0.5 mL) were introduced into a Schlenk tube, successively. Then the Schlenk tube was closed and the resulting mixture was stirred at 65 °C for 16 h. After cooling down to room temperature, the resulting mixture was extracting with ethyl acetate, washed with H_2O, dried with anhydrous sodium sulfate, and then concentrated by removing the solvent under vacuum. Finally, the residue was purified by preparative TLC on silica, eluting with PE : EA = 4 : 1 (v/v) to give the desired white solid product **3** (22.8 mg, 65 % yield)[1]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.08 (td, *J* = 7.6, 1.6 Hz, 1H), 6.74 (td, *J* = 7.4, 1.2 Hz, 1H), 6.60 (dd, *J* = 8.0, 1.1 Hz, 1H), 4.58 (d, *J* = 5.4 Hz, 1H), 3.98 – 3.93 (m, 1H), 3.86 – 3.78 (m, 1H), 3.15 (dd, *J* = 11.0, 5.2 Hz, 1H), 2.87 (t, *J* = 11.0 Hz, 1H), 2.49 – 2.40 (m, 1H), 2.30 – 2.18 (m, 1H), 1.81 – 1.72 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 131.4, 128.8, 120.6, 118.2, 114.8, 75.5, 65.3, 43.2, 36.1, 29.8.

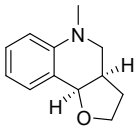
5. Analytical data of the obtained compounds

(1) 5-ethyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_1)[2] CAS: 2380351-17-5



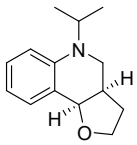
Yellow oil liquid (30.5 mg, 75 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.5 Hz, 1H), 7.17 (m, 1H), 6.74 – 6.67 (m, 2H), 4.54 (d, *J* = 5.0 Hz, 1H), 3.94 (td, *J* = 8.4, 5.8 Hz, 1H), 3.81 (td, *J* = 8.9, 6.1 Hz, 1H), 3.57 – 3.44 (m, 1H), 3.32 – 3.21 (m, 1H), 3.03 – 2.96 (m, 1H), 2.86 (t, *J* = 12.5 Hz, 1H), 2.48 – 2.39 (m, 1H), 2.32 – 2.19 (m, 1H), 1.78 – 1.71 (m, 1H), 1.13 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.4, 131.7, 129.0, 121.2, 116.6, 111.6, 76.1, 65.0, 49.2, 45.3, 35.6, 30.0, 10.6.

(2) 5-methyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_2)[2] CAS: 143771-30-6



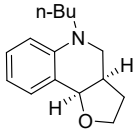
Yellow oil liquid (27 mg, 72 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 5.0 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.76 (t, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 5.0 Hz, 1H), 4.59 (d, *J* = 5.0 Hz, 1H), 3.98 – 3.90 (m, 1H), 3.85 – 3.77 (m, 1H), 3.01 (dd, *J* = 11.2, 5.2 Hz, 1H), 2.89 (s, 3H), 2.79 (t, *J* = 11.0 Hz, 1H), 2.57 – 2.50 (m, 1H), 2.30 – 2.21 (m, 1H), 1.80 – 1.73 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.2, 131.2, 129.1, 121.7, 117.5, 111.9, 75.9, 65.2, 52.6, 39.4, 36.0, 30.1.

(3) 5-isopropyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_3)[2] CAS: 1683587-11-2



Yellow oil liquid (29.9 mg, 69 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.19 – 7.14 (m, 1H), 6.78 (d, *J* = 5.0 Hz, 1H), 6.70 (t, *J* = 7.5 Hz, 1H), 4.54 (d, *J* = 5.0 Hz, 1H), 4.14 – 4.04 (m, 1H), 3.95 – 3.86 (m, 1H), 3.78 (td, *J* = 8.7, 6.5 Hz, 1H), 3.08 (dd, *J* = 11.5, 4.8 Hz, 1H), 2.51 (t, *J* = 11.2 Hz, 1H), 2.41 – 2.30 (m, 1H), 2.28 – 2.18 (m, 1H), 1.80 – 1.72 (m, 1H), 1.24 (d, *J* = 5.0 Hz, 3H), 1.12 (d, *J* = 5.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2, 131.8, 128.9, 122.1, 116.6, 111.6, 76.2, 65.1, 46.3, 41.2, 36.3, 30.3, 20.4, 17.7.

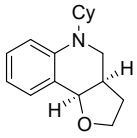
(4) 5-butyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_4)[2] CAS: 1683587-12-3



Yellow oil liquid (30 mg, 65 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 5.0 Hz, 1H), 7.16 (t, *J* = 10.0 Hz, 1H), 6.69 (t, *J* = 7.5 Hz, 2H), 4.54 (d, *J* = 5.0 Hz, 1H), 3.98 – 3.90 (m, 1H), 3.85 – 3.77 (m, 1H), 3.38 – 3.28 (m, 1H), 3.27 – 3.17 (m, 1H), 3.02 (dd, *J* = 11.6, 5.3 Hz, 1H), 2.87 (t, *J* = 10.0 Hz, 1H), 2.45 – 2.36 (m, 1H), 2.30 – 2.17 (m, 1H), 1.81 – 1.69 (m, 1H), 1.56 – 1.51 (m, 2H), 1.41 – 1.33 (m, 2H), 0.95 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.7, 131.7, 129.0, 120.9, 116.3, 111.5, 76.1, 65.0, 51.2, 50.2, 35.6, 30.0, 28. 2,

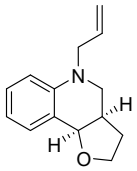
20.5, 14.0.

(5) 5-cyclohexyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_5)



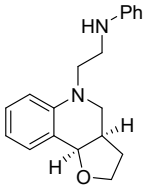
Yellow oil liquid (31.8 mg, 62 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 5.0 Hz, 1H), 7.16 (t, *J* = 10.0 Hz, 1H), 6.76 (d, *J* = 10.0 Hz, 1H), 6.69 (t, *J* = 7.5 Hz, 1H), 4.54 (d, *J* = 5.0 Hz, 1H), 3.98 – 3.87 (m, 1H), 3.82 – 3.71 (m, 1H), 3.62 – 3.54 (m, 1H), 3.14 (dd, *J* = 11.7, 4.8 Hz, 1H), 2.56 (t, *J* = 11.2 Hz, 1H), 2.37 – 2.31 (m, 1H), 2.27 – 2.17 (m, 1H), 1.90 – 1.81 (m, 3H), 1.79 – 1.68 (m, 2H), 1.62 – 1.53 (m, 2H), 1.43 – 1.29 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.1, 131.9, 128.9, 122.0, 116.4, 111.6, 76.2, 65.1, 55.8, 42.7, 36.4, 30.9, 30.2, 28.7, 26.5, 26.1, 26.1; HRMS (ESI): Calcd. for $C_{17}H_{24}NO$ $[M+H]^+$: 258.1852; found: 258.1852.

(6) 5-allyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_6)



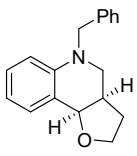
Yellow oil liquid (19.4 mg, 45 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 10.0, 1.7 Hz, 1H), 7.18 – 7.12 (m, 1H), 6.75 – 6.67 (m, 2H), 5.92 – 5.80 (m, 1H), 5.25 – 5.13 (m, 2H), 4.57 (d, *J* = 5.0Hz, 1H), 4.01 – 3.91 (m, 2H), 3.87 – 3.78 (m, 2H), 3.03 (dd, *J* = 11.5, 5.3 Hz, 1H), 2.87 (t, *J* = 10.0 Hz, 1H), 2.52 – 2.41 (m, 1H), 2.28 – 2.16 (m, 1H), 1.80 – 1.68 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.7, 133.5, 131.6, 129.0, 125.2, 117.0, 116.7, 112.1, 76.0, 65.1, 53.9, 50.0, 35.7, 29.7; HRMS (ESI): Calcd. for $C_{14}H_{18}NO$ $[M+H]^+$: 216.1383; found: 216.1381.

(7) N-(2-(2,3,3a,9b-tetrahydrofuro[3,2-c]quinolin-5(4H)-yl)ethyl)aniline (D_7)



Yellow oil liquid (20 mg, 34 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.43 – 7.38 (m, 2H), 7.33 – 7.29 (m, 2H), 7.16 – 7.09 (m, 3H), 6.74 – 6.67 (m, 2H), 4.48 (d, *J* = 5.0 Hz, 1H), 4.06 – 4.00 (m, 1H), 3.99 – 3.94 (m, 1H), 3.93 – 3.87 (m, 1H), 3.81 – 3.77 (m, 1H), 3.54 – 3.49 (m, 2H), 3.04 (dd, *J* = 11.5, 5.2 Hz, 1H), 2.87 (t, *J* = 11.1 Hz, 1H), 2.32 – 2.26 (m, 1H), 2.23 – 2.15 (m, 1H), 1.70 – 1.66 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.6, 145.1, 141.1, 131.8, 129.8, 129.3, 127.0, 124.0, 117.1, 111.30, 75.9, 65.0, 50.2, 48.4, 42.7, 35.4, 29.8. HRMS (ESI): Calcd. for $C_{19}H_{23}N_2O$ $[M+H]^+$: 316.1696; found: 316.1694.

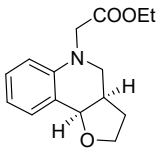
(8) 5-benzyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_8)[3] CAS: 1269006-20-3



Gray oily liquid (30.6 mg, 58 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 1H), 7.34 – 7.26 (m, 4H), 7.25 – 7.22 (m, 1H), 7.13 – 7.08 (m, 1H), 6.75 – 6.70 (m, 1H), 6.67 – 6.61 (m, 1H), 4.61 (d, *J* = 5.0 Hz, 1H), 4.54 – 4.44 (m, 2H), 3.99 – 3.93 (m,

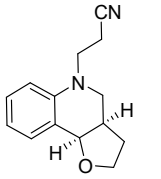
1H), 3.88 – 3.80 (m, 1H), 3.09 (dd, *J* = 11.6, 5.3 Hz, 1H), 2.96 (t, *J* = 12.5 Hz, 1H), 2.55 – 2.44 (m, 1H), 2.28 – 2.14 (m, 1H), 1.78 – 1.67 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.0, 138.6, 131.6, 129.1, 128.6, 126.9, 126.9, 121.0, 117.1, 112.1, 76.0, 65.1, 55.2, 50.5, 35.7, 29.9.

(9) ethyl 2-(2,3,3a,9b-tetrahydrofuro[3,2-c]quinolin-5(4H)-yl)acetate (D_9)



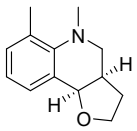
Yellow oil liquid (24 mg, 46 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 5.0 Hz, 1H), 6.70 (t, *J* = 7.5 Hz, 1H), 6.45 (d, *J* = 5.0 Hz, 1H), 4.54 (d, *J* = 10.0 Hz, 1H), 4.14 – 4.07 (m, 2H), 4.07 – 3.98 (m, 1H), 3.93 – 3.84 (m, 1H), 3.83 – 3.71 (m, 2H), 3.06 (d, *J* = 5.0 Hz, 2H), 2.49 – 2.39 (m, 1H), 2.21 – 2.12 (m, 1H), 1.88 – 1.82 (m, 1H), 1.17 (t, *J* = 12.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 145.0, 131.6, 129.0, 121.7, 117.9, 111.2, 75.7, 65.2, 61.0, 53.3, 51.4, 36.0, 29.8, 14.2; HRMS (ESI): Calcd. for $C_{15}H_{20}NO_3$ $[M+H]^+$: 262.1437; found: 262.1436.

(10) 3-(2,3,3a,9b-tetrahydrofuro[3,2-c]quinolin-5(4H)-yl)propanenitrile (D_{10})



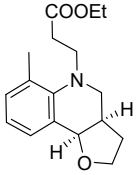
Gray oily liquid (22 mg, 48 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.5 Hz, 1H), 7.20 (d, *J* = 10.0 Hz, 1H), 6.79 (t, *J* = 7.5 Hz, 1H), 6.60 (d, *J* = 10.0 Hz, 1H), 4.54 (d, *J* = 5.0 Hz, 1H), 4.00 – 3.91 (m, 1H), 3.86 – 3.78 (m, 1H), 3.72 (d, *J* = 7.5 Hz, 1H), 3.62 (d, *J* = 7.8 Hz, 1H), 3.12 (dd, *J* = 11.4, 5.3 Hz, 1H), 2.97 (t, *J* = 11.2 Hz, 1H), 2.67 – 2.59 (m, 1H), 2.57 – 2.53 (m, 1H), 2.51 – 2.46 (m, 1H), 2.30 – 2.21 (m, 1H), 1.80 – 1.70 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 132.3, 129.4, 121.7, 118.5, 118.0, 110.8, 75.7, 65.1, 50.6, 47.4, 35.6, 29.8, 15.0; HRMS (ESI): Calcd. for $C_{14}H_{17}N_2O$ $[M+H]^+$: 229.1335; found: 229.1334.

(11) 5,6-dimethyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_{11})[4] CAS: 2033096-59-0



Gray oily liquid (24.8 mg, 61 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 4.55 (d, *J* = 5.4 Hz, 1H), 4.03 – 3.89 (m, 1H), 3.85 – 3.77 (m, 1H), 2.97 (dd, *J* = 13.0, 4.4 Hz, 1H), 2.76 (d, *J* = 12.9 Hz, 1H), 2.73 (s, 3H), 2.69 – 2.63 (m, 1H), 2.31 (s, 4H), 1.64 – 1.56 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.2, 131.7, 130.6, 128.6, 127.8, 122.5, 76.0, 66.0, 53.5, 41.5, 30.2, 30.1, 18.3.

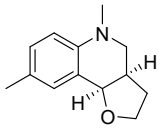
(12) ethyl 3-(6-methyl-2,3,3a,9b-tetrahydrofuro[3,2-c]quinolin-5(4H)-yl)propanoate (D_{12})



Yellow oil liquid (32.4 mg, 56 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, *J* = 10.0 Hz, 1H), 7.11 (d, *J* = 10.0 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 4.55 (d, *J* = 5.0 Hz, 1H), 4.13 (q, *J* = 7.5 Hz, 2H), 3.99 – 3.91 (m, 1H), 3.83 – 3.77 (m, 1H), 3.27 – 3.18 (m,

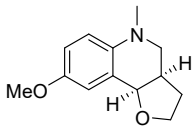
1H), 3.13 – 3.05 (m, 2H), 2.77 – 2.66 (m, 2H), 2.61 (d, *J* = 11.1 Hz, 2H), 2.36 – 2.29 (m, 1H), 2.28 (s, 3H), 1.62 – 1.51 (m, 1H), 1.26 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2, 146.7, 131.7, 130.7, 128.4, 128.0, 122.6, 75.9, 66.0, 60.6, 48.7, 48.3, 34.6, 30.9, 30.2, 18.6, 14.2; HRMS (ESI): Calcd. for $C_{17}H_{24}NO_3$ $[M+H]^+$: 290.1750; found: 290.1749.

(13) 5,8-dimethyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_{13})[4] CAS: 143771-28-2



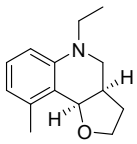
Yellow oil liquid (30.5 mg, 75 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (s, 1H), 7.01 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.63 (d, *J* = 5.0 Hz, 1H), 4.57 (d, *J* = 5.0 Hz, 1H), 3.97 – 3.89 (m, 1H), 3.84 – 3.75 (m, 1H), 2.97 (dd, *J* = 11.1, 5.1 Hz, 1H), 2.85 (s, 3H), 2.72 (t, *J* = 10.0 Hz, 1H), 2.57 – 2.50 (m, 1H), 2.28 – 2.21 (m, 4H), 1.80 – 1.72 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.2, 131.5, 129.6, 126.8, 122.0, 112.1, 75.9, 65.3, 53.0, 39.5, 36.3, 30.2, 20.2.

(14) 8-methoxy-5-methyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_{14})[3] CAS: 143771-29-3



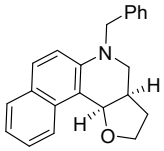
Yellow oil liquid (35.5 mg, 81 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 (d, *J* = 5.0 Hz, 1H), 6.81 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.67 (d, *J* = 9.0 Hz, 1H), 4.59 (d, *J* = 5.8 Hz, 1H), 3.97 – 3.91 (m, 1H), 3.84 – 3.78 (m, 1H), 3.76 (s, 3H), 2.97 (dd, *J* = 11.0, 5.1 Hz, 1H), 2.84 (s, 3H), 2.68 (t, *J* = 10.8 Hz, 1H), 2.60 – 2.55 (m, 1H), 2.29 – 2.20 (m, 1H), 1.80 – 1.76(m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.0, 141.9, 123.2, 115.8, 115.6, 113.3, 76.0, 65.5, 55.8, 53.4, 39.9, 36.6, 30.2.

(15) 5-ethyl-9-methyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_{15})



Gray oily liquid (23 mg, 53%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.18 (m, 1H), 6.53 (d, *J* = 10.0 Hz, 2H), 4.52 (d, *J* = 5.0 Hz, 1H), 3.97 – 3.89 (m, 1H), 3.83 – 3.75 (m, 1H), 3.55 – 3.44 (m, 1H), 3.31 – 3.22 (m, 1H), 2.98 (dd, *J* = 11.4, 5.3 Hz, 1H), 2.84 (t, *J* = 12.5 Hz, 1H), 2.46 – 2.37 (m, 1H), 2.29 (s, 3H), 2.25 – 2.17 (m, 1H), 1.77 – 1.69 (m, 1H), 1.13 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.3, 138.8, 131.6, 118.5, 117.6, 112.1, 76.0, 65.0, 49.3, 45.2, 35.7, 30.0, 21.9, 10.7. HRMS (ESI): Calcd. for $C_{14}H_{20}NO$ $[M+H]^+$: 218.1539; found: 218.1539.

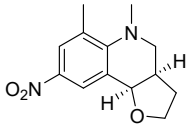
(16) 5-benzyl-2,3,3a,4,5,11c-hexahydrobenzo[f]furo[3,2-c]quinoline (D_{16})



Red solid (26 mg, 41 %); m.p.: 115-116 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 10.0 Hz, 1H), 7.64 (d, *J* = 10.0 Hz, 1H), 7.60 (d, *J* = 10.0 Hz, 1H), 7.46 (t,

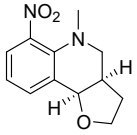
J = 75 Hz, 1H), 7.33 – 7.25 (m, 5H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 5.0 Hz, 1H), 5.03 (d, *J* = 5.0 Hz, 1H), 4.74 – 4.59 (m, 2H), 4.06 – 4.00 (m, 1H), 3.98 – 3.94 (m, 1H), 3.17 – 3.04 (m, 2H), 2.54 – 2.46 (m, 1H), 2.40 – 2.29 (m, 1H), 1.80 – 1.71 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 138.7, 134.8, 129.8, 128.7, 128.0, 127.1, 127.0, 127.0, 126.7, 122.7, 122.0, 115.1, 111.5, 73.6, 64.8, 55.6, 50.9, 34.7, 29.8; HRMS (ESI): Calcd. for $C_{22}H_{22}NO$ $[M+H]^+$: 316.1696; found: 316.1694.

(17) 5,6-dimethyl-8-nitro-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_{17})



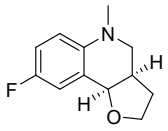
Yellow oily liquid (24.8 mg, 50 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, *J* = 2.7 Hz, 1H), 7.96 (d, *J* = 2.6 Hz, 1H), 4.52 (d, *J* = 5.0 Hz, 1H), 4.01 – 3.95 (m, 1H), 3.88 – 3.80 (m, 1H), 3.04 (dd, *J* = 13.4, 4.8 Hz, 1H), 2.92 (s, 3H), 2.77 (t, *J* = 13.0 Hz, 1H), 2.58 – 2.51 (m, 1H), 2.37 (s, 3H), 2.35 – 2.30 (m, 1H), 1.73 – 1.63 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.6, 141.1, 130.8, 126.9, 126.1, 125.0, 75.6, 65.8, 53.1, 41.8, 31.6, 29.6, 19.7. HRMS (ESI): Calcd. for $C_{13}H_{17}N_2O_3$ $[M+H]^+$: 249.1234; found: 249.1231.

(18) 5-methyl-6-nitro-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_{18})



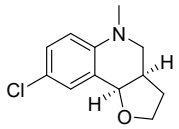
Yellow solid (20 mg, 43 %); m.p.: 118-122 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 10.0 Hz, 1H), 7.51 (d, *J* = 10.0 Hz, 1H), 6.79 (t, *J* = 7.5 Hz, 1H), 4.56 (d, *J* = 5.0 Hz, 1H), 4.05 – 3.97 (m, 1H), 3.91 – 3.83 (m, 1H), 3.16 (dd, *J* = 12.8, 5.3 Hz, 1H), 3.02 – 2.95 (m, 1H), 2.83 (s, 3H), 2.53 – 2.47 (m, 1H), 2.32 – 2.23 (m, 1H), 1.78 – 1.72 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.3, 138.5, 135.6, 126.8, 126.1, 116.8, 75.2, 65.4, 52.2, 42.8, 33.7, 29.4. HRMS (ESI): Calcd. for $C_{12}H_{15}N_2O_3$ $[M+H]^+$: 235.1077; found: 235.1076.

(19) 8-fluoro-5-methyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_{19})[1] CAS: 1683587-07-6



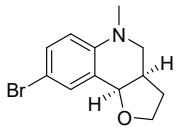
Yellow oil liquid (26.1 mg, 63 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.92 – 6.86 (m, 1H), 6.62 (dd, *J* = 9.0, 4.6 Hz, 1H), 4.55 (d, *J* = 5.0 Hz, 1H), 3.96 – 3.88 (m, 1H), 3.83 – 3.76 (m, 1H), 2.99 (dd, *J* = 11.2, 5.1 Hz, 1H), 2.85 (s, 3H), 2.71 (t, *J* = 10.0 Hz, 1H), 2.60 – 2.48 (m, 1H), 2.30 – 2.18 (m, 1H), 1.80 – 1.70 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ155.6 (d, *J* = 236.3 Hz), 143.8 (d, *J* = 1.8 Hz), 123.4 (d, *J* = 6.4 Hz), 117.1 (d, *J* = 21.9 Hz), 115.5 (d, *J* = 22.1 Hz), 112.8 (d, *J* = 7.4 Hz), 75.6, 65.4, 53.0, 39.8, 36.4, 30.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ -128.05.

(20) 8-chloro-5-methyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_{20})[2] CAS: 192223-77-1



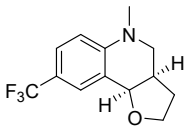
Yellow oil liquid (23.2 mg, 52 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 5.0 Hz, 1H), 7.13 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.60 (d, *J* = 10.0 Hz, 1H), 4.53 (d, *J* = 5.0 Hz, 1H), 3.93 (td, *J* = 8.4, 5.8 Hz, 1H), 3.80 (td, *J* = 8.8, 6.2 Hz, 1H), 3.01 (dd, *J* = 11.3, 5.2 Hz, 1H), 2.86 (s, 3H), 2.76 (t, *J* = 11.0 Hz, 1H), 2.55 – 2.47 (m, 1H), 2.29 – 2.20 (m, 1H), 1.79 – 1.71 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.8, 130.7, 128.8, 123.3, 122.2, 113.1, 75.4, 65.3, 52.5, 39.4, 36.0, 30.0.

(21) 8-bromo-5-methyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_{21})[2] CAS: 1683587-08-7



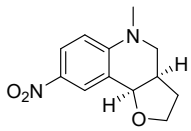
Gray oil liquid (29.5 mg, 55 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 2.5 Hz, 1H), 7.27 – 7.22 (m, 1H), 6.55 (d, *J* = 10.0 Hz, 1H), 4.53 (d, *J* = 5.0 Hz, 1H), 3.97 – 3.89 (m, 1H), 3.83 – 3.76 (m, 1H), 3.01 (dd, *J* = 11.4, 5.3 Hz, 1H), 2.86 (s, 3H), 2.76 (t, *J* = 11.0 Hz, 1H), 2.56 – 2.45 (m, 1H), 2.28 – 2.18 (m, 1H), 1.81 – 1.67 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2, 133.5, 131.7, 123.8, 113.5, 109.3, 75.4, 65.3, 52.4, 39.3, 36.0, 29.9.

(22) 5-methyl-8-(trifluoromethyl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_{22})[2] CAS: 2242742-73-8



White solid (24.2 mg, 47 %); m.p.: 69-71 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 2.3 Hz, 1H), 7.41 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.69 (d, *J* = 8.7 Hz, 1H), 4.56 (d, *J* = 5.2 Hz, 1H), 3.98 – 3.91 (m, 1H), 3.87 – 3.79 (m, 1H), 3.08 (dd, *J* = 11.4, 5.5 Hz, 1H), 2.95 (s, 3H), 2.87 (t, *J* = 11.2 Hz, 1H), 2.54 – 2.43 (m, 1H), 2.33 – 2.21 (m, 1H), 1.81 – 1.72 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.2, 128.4 (q, *J* = 3.7 Hz), 126.2 (q, *J* = 3.6 Hz), 123.8, 120.9, 118.6 (q, *J* = 32.5 Hz), 111.2, 75.4, 65.1, 51.9, 39.2, 35.4, 29.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -61.06.

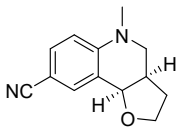
(23) 5-methyl-8-nitro-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_{23})[2] CAS: 2242742-74-7



Yellow solid (28.1 mg, 60 %); m.p.: 123-125°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 2.6 Hz, 1H), 8.06 (dd, *J* = 9.2, 2.7 Hz, 1H), 6.61 (d, *J* = 10.0 Hz, 1H), 4.56 (d, *J* = 5.0 Hz, 1H), 3.96 (td, *J* = 8.6, 6.1 Hz, 1H), 3.87 (td, *J* = 9.0, 5.9 Hz, 1H), 3.19 (dd, *J* = 12.0, 5.6 Hz, 1H), 3.06 (s, 3H), 3.02 (t, *J* = 12.5 Hz, 1H), 2.53 – 2.46 (m,

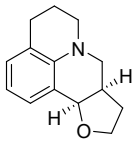
1H), 2.33 – 2.24 (m, 1H), 1.81 – 1.72 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.3, 137.3, 127.9, 125.8, 119.9, 110.4, 75.1, 65.1, 51.4, 39.3, 34.8, 29.5.

(24) 5-methyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline-8-carbonitrile (D_{24})



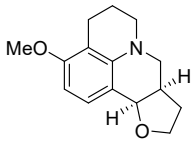
Gray oil liquid (24 mg, 56 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.43 (dd, *J* = 8.8, 1.4 Hz, 1H), 6.64 (d, *J* = 10.0 Hz, 1H), 4.51 (d, *J* = 5.0 Hz, 1H), 3.95 (td, *J* = 8.4, 5.9 Hz, 1H), 3.84 (td, *J* = 8.8, 5.9 Hz, 1H), 3.13 (dd, *J* = 11.8, 5.5 Hz, 1H), 2.98 (s, 3H), 2.93 (t, *J* = 12.5 Hz, 1H), 2.50 – 2.41 (m, 1H), 2.36 – 2.24 (m, 1H), 1.80 – 1.71 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6, 135.3, 133.2, 121.2, 120.3, 111.5, 98.5, 74.9, 65.1, 51.5, 39.0, 35.0, 29.6; HRMS (ESI): Calcd. for $C_{13}H_{15}N_2O$ $[M+H]^+$: 215.1179; found: 215.1177.

(25) 5,6,8a,9,10,11a-hexahydro-4H,8H-furo[3,2-c]pyrido[3,2,1-ij]quinoline (D_{25})



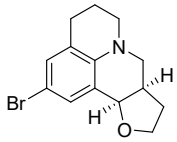
Yellow oil liquid (29.2 mg, 68 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.90 (dd, *J* = 7.2, 1.5 Hz, 1H), 6.64 (t, *J* = 7.5 Hz, 1H), 4.56 (d, *J* = 5.0 Hz, 1H), 3.98 – 3.90 (m, 1H), 3.83 – 3.76 (m, 1H), 3.21 – 3.13 (m, 1H), 3.06 (td, *J* = 10.5, 3.4 Hz, 1H), 2.92 (dd, *J* = 11.1, 5.2 Hz, 1H), 2.87 – 2.75 (m, 2H), 2.70 (t, *J* = 12.5 Hz, 1H), 2.53 – 2.43 (m, 1H), 2.28 – 2.18 (m, 1H), 2.11 – 1.94 (m, 2H), 1.80 – 1.72 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6, 129.1, 129.0, 122.7, 120.9, 117.2, 76.1, 65.1, 51.3, 50.4, 35.5, 30.2, 27.6, 22.1; HRMS (ESI): Calcd. for $C_{14}H_{18}NO$ $[M+H]^+$: 216.1383; found: 216.1380.

(26) 3-methoxy-5,6,8a,9,10,11a-hexahydro-4H,8H-furo[3,2-c]pyrido[3,2,1-ij]quinoline (D_{26})



Gray oil liquid (36.7 mg, 75 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (d, *J* = 5.0 Hz, 1H), 6.32 (d, *J* =10.0 Hz, 1H), 4.55 (d, *J* = 5.0 Hz, 1H), 3.96 – 3.90 (m, 1H), 3.82 – 3.79 (m, 1H), 3.78 (s, 3H), 3.17 – 3.08 (m, 1H), 3.02 – 2.97 (m, 1H), 2.89 (dd, *J* = 11.1, 5.2 Hz, 1H), 2.80 – 2.74 (m, 1H), 2.68 (t, *J* = 15.0 Hz, 1H), 2.59 – 2.44 (m, 2H), 2.28 – 2.17 (m, 1H), 2.02 – 1.97 (m, 2H), 1.81 – 1.71 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 144.6, 129.2, 114.3, 110.6, 100.3, 76.1, 65.1, 55.4, 51.6, 50.0, 35.7, 30.2, 21.7, 21.3; HRMS (ESI): Calcd. for $C_{15}H_{20}NO_2$ $[M+H]^+$: 246.1489; found: 246.1485.

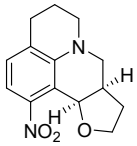
(27) 2-bromo-5,6,8a,9,10,11a-hexahydro-4H,8H-furo[3,2-c]pyrido[3,2,1-ij]quinoline (D_{27})



Gray solid (39 mg, 67 %); m.p.: 87-90 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (s, 1H), 7.00 (s, 1H), 4.49 (d, *J* = 5.0 Hz, 1H), 3.97 – 3.89 (m, 1H), 3.84 – 3.75 (m, 1H), 3.18 – 3.12 (m, 1H), 3.07 – 2.99 (m, 1H), 2.92 (dd, *J* = 11.3, 5.2 Hz, 1H), 2.79 – 2.70 (m, 2H), 2.67 (t, *J* = 10.0 Hz, 1H), 2.51 – 2.42 (m, 1H), 2.29 – 2.17 (m, 1H), 2.02 – 1.93

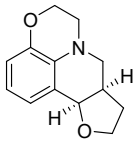
(m, 2H), 1.79 – 1.69 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.6, 131.4, 131.3, 124.9, 122.9, 108.8, 75.5, 65.2, 51.0, 50.1, 35.4, 30.0, 27.4, 21.7; HRMS (ESI): Calcd. for $C_{14}H_{17}NBrO$ $[M+H]^+$: 294.0488; found: 294.0483.

(28) 1-nitro-5,6,8a,9,10,11a-hexahydro-4H,8H-furo[3,2-c]pyrido[3,2,1-ij]quinoline (D_{28})



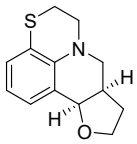
Yellow oil liquid (25 mg, 48 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 – 6.93 (m, 2H), 5.19 (d, *J* = 5.0 Hz, 1H), 3.90 – 3.82 (m, 1H), 3.81 – 3.74 (m, 1H), 3.28 – 3.21 (m, 1H), 3.17 – 3.10 (m, 1H), 3.06 (dd, *J* = 11.6, 5.0 Hz, 1H), 2.84 – 2.76 (m, 3H), 2.53 – 2.44 (m, 1H), 2.25 – 2.15 (m, 1H), 2.05 – 1.96 (m, 2H), 1.82 – 1.73 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.2, 144.1, 128.5, 127.3, 113.5, 112.3, 71.1, 65.3, 50.3, 50.2, 35.0, 29.4, 28.1, 21.2; HRMS (ESI): Calcd. for $C_{14}H_{17}N_2O_3$ $[M+H]^+$: 261.1234; found: 261.1231.

(29) 5,6,8a,9,10,11a-hexahydro-8H-furo[3,2-c][1,4]oxazino[2,3,4-ij]quinoline (D_{29})



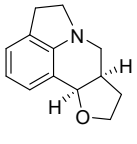
Yellow oil liquid (19.1 mg, 44 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (dd, *J* = 6.7, 2.3 Hz, 1H), 6.72 – 6.66 (m, 2H), 4.61 (d, *J* = 5.0 Hz, 1H), 4.39 – 4.29 (m, 2H), 4.00 – 3.94 (m, 1H), 3.85 – 3.78 (m, 1H), 3.24 – 3.14 (m, 2H), 2.95 (dd, *J* = 10.6, 4.9 Hz, 1H), 2.65 (t, *J* = 12.5 Hz, 1H), 2.59 – 2.54 (m, 1H), 2.30 – 2.18 (m, 1H), 1.82 – 1.75 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.2, 127.8, 123.1, 122.5, 118.9, 115.4, 75.2, 65.4, 64.8, 50.7, 48.0, 35.7, 30.1; HRMS (ESI): Calcd. for $C_{15}H_{16}NO_2$ $[M+H]^+$: 218.1176; found: 218.1175.

(30) 5,6,8a,9,10,11a-hexahydro-8H-furo[3,2-c][1,4]thiazino[2,3,4-ij]quinoline (D_{30})



Yellow solid (25 mg, 53 %); m.p.: 38-40 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.95 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.64 (t, *J* = 7.6 Hz, 1H), 4.55 (d, *J* = 5.0 Hz, 1H), 3.99 – 3.90 (m, 1H), 3.85 – 3.76 (m, 1H), 3.56 – 3.44 (m, 2H), 3.34 – 3.26 (m, 1H), 3.00 – 2.93 (m, 2H), 2.81 (t, *J* = 12.5 Hz, 1H), 2.51 – 2.42 (m, 1H), 2.28 – 2.18 (m, 1H), 1.79 – 1.70 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.2, 128.2, 127.0, 121.9, 118.0, 117.8, 76.3, 65.2, 52.0, 50.8, 35.3, 30.0, 25.5; HRMS (ESI): Calcd. for $C_{13}H_{16}NOS$ $[M+H]^+$: 234.0947; found: 234.0945.

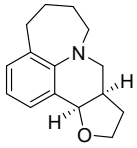
(31) 4,5,7a,8,9,10a-hexahydro-7H-furo[3,2-c]pyrrolo[3,2,1-ij]quinoline (D_{31})[3] CAS: 355394-0204



Yellow oil liquid (25 mg, 62 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (d, *J* = 5.0 Hz, 1H), 7.04 (d, *J* =5.0 Hz, 1H), 6.73 (t, *J* = 7.5 Hz, 1H), 4.66 (d, *J* = 5.0 Hz, 1H), 4.02 – 3.93 (m, 1H), 3.88 – 3.81 (m, 1H), 3.51 – 3.37 (m, 1H), 3.10 – 3.02 (m, 2H), 3.00

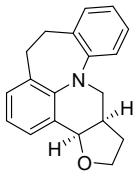
– 2.92 (m, 1H), 2.72 – 2.63 (m, 1H), 2.47 (t, *J* = 10.0 Hz, 1H), 2.31 – 2.23 (m, 1H), 1.96 – 1.87 (m, 1H), 1.84 – 1.76 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.8, 152.8, 127.308, 123.9, 119.4, 113.9, 74.3, 66.0, 57.3, 55.3, 50.0, 38.0, 29.0.

(32) 4,5,6,7,9a,10,11,12a-octahydro-9H-azepino[3,2,1-ij]furo[3,2-c]quinoline (D_{32})



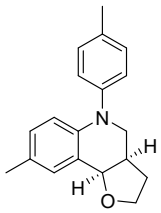
Yellow oil (31 mg, 68 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.05 (dd, *J* = 7.3, 1.6 Hz, 1H), 6.89 (t, *J* = 7.5 Hz, 1H), 4.52 (d, *J* = 5.2 Hz, 1H), 4.02 – 3.91 (m, 1H), 3.85 – 3.77 (m, 1H), 3.26 – 3.15 (m, 1H), 3.00 (dd, *J* = 13.3, 4.5 Hz, 1H), 2.91 – 2.81 (m, 3H), 2.74 – 2.64 (m, 1H), 2.48 – 2.37 (m, 1H), 2.33 – 2.22 (m, 1H), 1.92 – 1.84 (m, 1H), 1.84 – 1.70 (m, 2H), 1.64 – 1.54 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 136.2, 129.3, 129.1, 126.0, 121.3, 76.1, 65.7, 55.9, 55.7, 34.9, 32.33, 30.7, 29.9, 25.8; HRMS (ESI): Calcd. for $C_{15}H_{20}NO$ $[M+H]^+$: 230.1539; found: 230.1538.

(33) 5,6,9b,11,12,12a-hexahydro-13H-benzo[6,7]azepino[3,2,1-ij]furo[3,2-c]quinoline (D_{33})



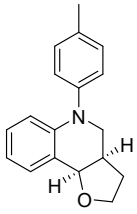
Yellow oil (20 mg, 36 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.16 – 7.11 (m, 2H), 7.10 – 7.07 (m, 1H), 7.05 – 7.02 (m, 1H), 6.94 – 6.88 (m, 2H), 4.63 (d, *J* = 6.0 Hz, 1H), 4.06 – 3.94 (m, 1H), 3.87 – 3.75 (m, 2H), 3.41 – 3.32 (m, 2H), 3.14 – 3.08 (m, 1H), 2.96 – 2.85 (m, 3H), 2.42 – 2.31 (m, 1H), 1.74 – 1.66 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.6, 132.4, 131.2, 129.9, 129.3, 129.1, 128.8, 126.7, 121.9, 121.5, 119.2, 116.7, 76.3, 65.8, 52.1, 35.6, 33.3, 33.3, 30.3; HRMS (ESI): Calcd. for $C_{19}H_{20}N_2O$ $[M+H]^+$: 278.1539; found: 278.1539.

(34) 8-methyl-5-(p-tolyl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_{34})



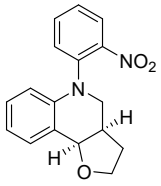
Gray solid (29.6 mg, 53 %); m.p.: 88-89 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 10.0Hz, 1H), 7.14 (d, *J* = 10.0 Hz, 2H), 7.09 – 7.05 (m, 2H), 6.84 (d, *J* = 5.0 Hz, 1H), 6.68 (d, *J* = 10.0 Hz, 1H), 4.62 (d, *J* = 5.0 Hz, 1H), 4.02 – 3.95 (m, 1H), 3.85 – 3.78 (m, 1H), 3.47 (dd, *J* = 11.8, 5.0 Hz, 1H), 3.17 (t, *J* = 12.5 Hz, 1H), 2.58 – 2.51 (m, 1H), 2.33 (s, 3H), 2.25 (s, 3H), 2.21 (d, *J* = 8.4 Hz, 1H), 1.80 – 1.70 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.1, 142.7, 133.2, 131.5, 130.0, 129.2, 128.2, 124.1, 123.0, 115.7, 75.8, 65.5, 51.5, 36.3, 29.9, 20.9, 20.4; HRMS (ESI): Calcd. for $C_{19}H_{22}NO$ $[M+H]^+$: 280.1696; found: 280.1693.

(35) 5-(p-tolyl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_{35})



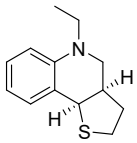
Yellow oil (24 mg, 45 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.12 – 7.02 (m, 2H), 7.02 – 6.92 (m, 1H), 6.87 (d, *J* = 8.4 Hz, 0.7H), 6.78 (t, *J* = 6.7 Hz, 1H), 6.72 (d, *J* = 8.3 Hz, 0.3H), 4.64 (dd, *J* = 10.9, 5.6 Hz, 1H), 4.02 – 3.95 (m, 1H), 3.86 – 3.79 (m, 1H), 3.57 – 3.52 (m, 0.7H), 3.46 (dd, *J* = 11.8, 5.1 Hz, 0.3H), 3.20 (q, *J* = 11.9 Hz, 1H), 2.60 – 2.51 (m, 1H), 2.35 (s, 1H), 2.32 – 2.27 (m, 1H), 2.26 (s, 2H), 1.81 – 1.69 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 142.1, 131.5, 130.1, 129.3, 128.4, 124.8, 123.6, 123.1, 116.2, 75.7, 65.6, 51.2, 36.4, 29.9, 20.4; HRMS (ESI): Calcd. for $C_{18}H_{20}NO$ $[M+H]^+$: 266.1539; found: 266.1537.

(36) 5-(2-nitrophenyl)-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_{36})



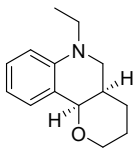
Yellow oil (12.5 mg, 21 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 5.0 Hz, 1H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.30 (d, *J* =5.0 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.87 (t, *J* = 7.5 Hz, 1H), 6.48 (s, 1H), 4.68 (d, *J* = 5.5 Hz, 1H), 4.04 – 3.97 (m, 1H), 3.90 – 3.81 (m, 1H), 3.40 (s, 1H), 3.24 (t, *J* = 12.5 Hz, 1H), 2.68 (s, 1H), 2.32 – 2.22 (m, 1H), 1.79 – 1.72 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.2, 143.3, 140.8, 137.2, 133.8, 131.5, 128.9, 128.7, 125.6, 125.2, 120.2, 112.1, 75.4, 65.5, 51.5, 35.9, 29.6; HRMS (ESI): Calcd. for $C_{17}H_{17}N_2O_3$ $[M+H]^+$: 297.1234; found: 297.1231.

(37) 5-ethyl-2,3,3a,4,5,9b-hexahydrothieno[3,2-c]quinoline (D_{37})



Yellow oil (18.9 mg, 43 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 – 7.04 (m, 2H), 6.72 – 6.53 (m, 2H), 4.61 (d, *J* = 5.0 Hz, 1H), 3.50 – 3.42 (m, 1H), 3.33 – 3.22 (m, 2H), 3.00 – 2.94 (m, 3H), 2.68 – 2.61 (m, 1H), 2.24 – 2.18 (m, 1H), 2.11 – 2.05 (m, 1H), 1.15 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 130.8, 128.0, 122.6, 116.2, 111.4, 49.0, 48.0, 45.4, 39.8, 34.2, 30.0, 10.7; HRMS (ESI): Calcd. for $C_{13}H_{18}NS$ $[M+H]^+$: 220.1154; found: 220.1153.

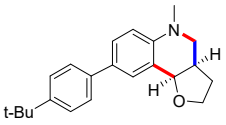
(38) 6-ethyl-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline (D_{38})



Yellow oil (16.5 mg, 38 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 – 7.18 (m, 1H), 7.15 – 7.09 (m, 1H), 6.63 – 6.59 (m, 2H), 4.40 (d, *J* = 5.0 Hz, 1H), 3.99 – 3.91 (m, 1H), 3.70 – 3.62 (m, 1H), 3.57 (t, *J* = 11.1 Hz, 1H), 3.48 – 3.40 (m, 1H), 3.31 – 3.20 (m,

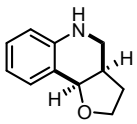
1H), 2.96 (dd, J = 11.1, 4.0 Hz, 1H), 2.12 – 2.07 (m, 1H), 1.93 – 1.85 (m, 1H), 1.81 – 1.71 (m, 2H), 1.50 – 1.41 (m, 1H), 1.13 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 131.0, 129.3, 121.3, 115.7, 110.9, 74.3, 67.2, 48.2, 45.3, 32.15, 25.5, 22.6, 10.9; HRMS (ESI): Calcd. for $C_{14}H_{20}NO$ $[M+H]^+$: 218.1539; found: 218.1538. HRMS (ESI): Calcd. for $C_{14}H_{20}NO$ $[M+H]^+$: 218.1539; found: 218.1538.

(39) 8-(4-(tert-butyl)phenyl)-5-methyl-2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_{39}).



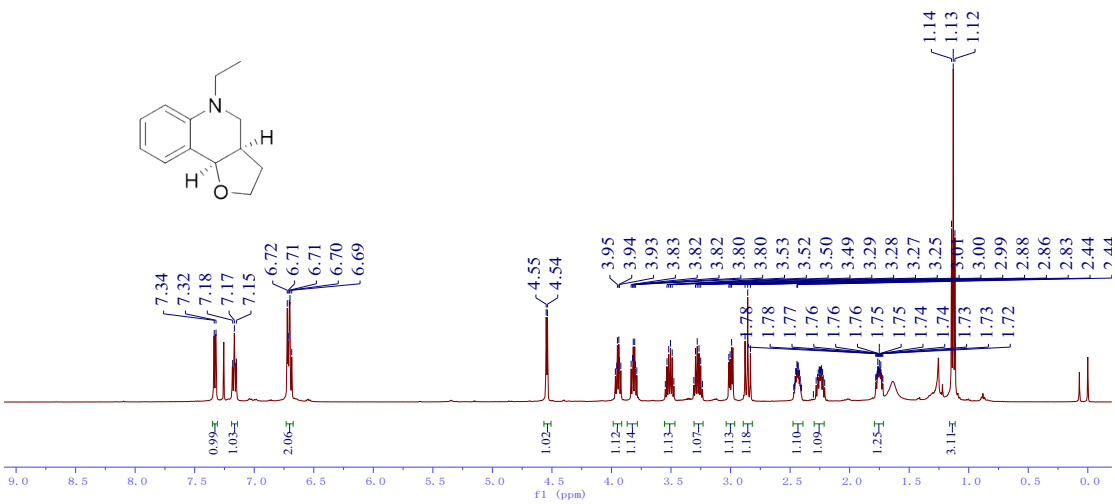
Brown liquid (41.7 mg, 65 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, J = 5.0 Hz, 1H), 7.48 – 7.44 (m, 3H), 7.43 – 7.40 (m, 2H), 6.75 – 6.70 (m, 1H), 5.43 (dd, J = 4.7, 1.4 Hz, 1H), 3.92 – 3.80 (m, 2H), 3.06 – 3.01 (m, 0.5H), 2.93 (s, 1H), 2.89 (s, 3H), 2.86 – 2.80 (m, 0.5H), 1.98 – 1.91 (m, 1H), 1.87 – 1.79 (m, 2H), 1.35 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.1, 138.3, 129.8, 127.8, 126.0, 126.0, 125.6, 125.5, 113.3, 100.0, 67.0, 52.6, 39.4, 36.0, 34.4, 32.3, 31.4, 23.4; HRMS (ESI): Calcd. for $C_{22}H_{28}NO$ $[M+H]^+$: 322.2165; found: 322.2162.

(40) 2,3,3a,4,5,9b-hexahydrofuro[3,2-c]quinoline (D_{40}).

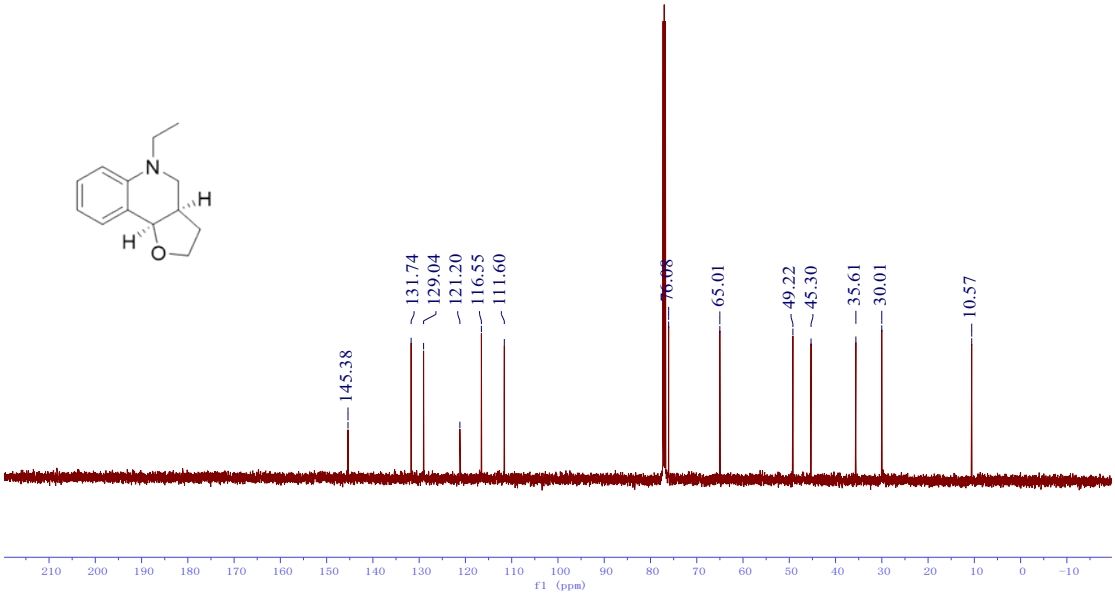


Brown liquid (22.8 mg, 65 %); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (dd, J = 5.0 Hz, 1H), 7.06 – 7.09 (m, 1H), 7.72 – 7.76 (m, 1H), 6.59 – 6.61 (m, 1H), 4.58 (d, J = 5.0 Hz, 1H), 3.95 – 3.97 (m, 1H), 3.82 – 3.83 (m, 1H), 3.15 – 3.17 (m, 1H), 2.86 (t, J = 10.0 Hz, 1H), 2.28 – 2.50 (m, 2H), 1.73 – 1.80 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.4, 131.4, 128.8, 120.6, 118.2, 114.8, 75.4, 65.3, 43.2, 36.1, 29.8; HRMS (ESI): Calcd. for $C_{11}H_{14}NO$ $[M+H]^+$: 176.1162; found: 176.0921.

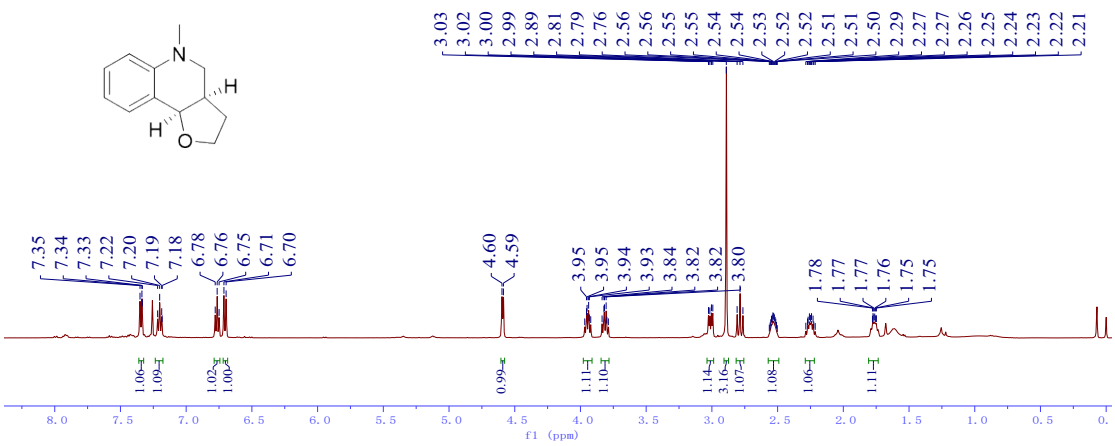
5. NMR spectra of the obtained compounds



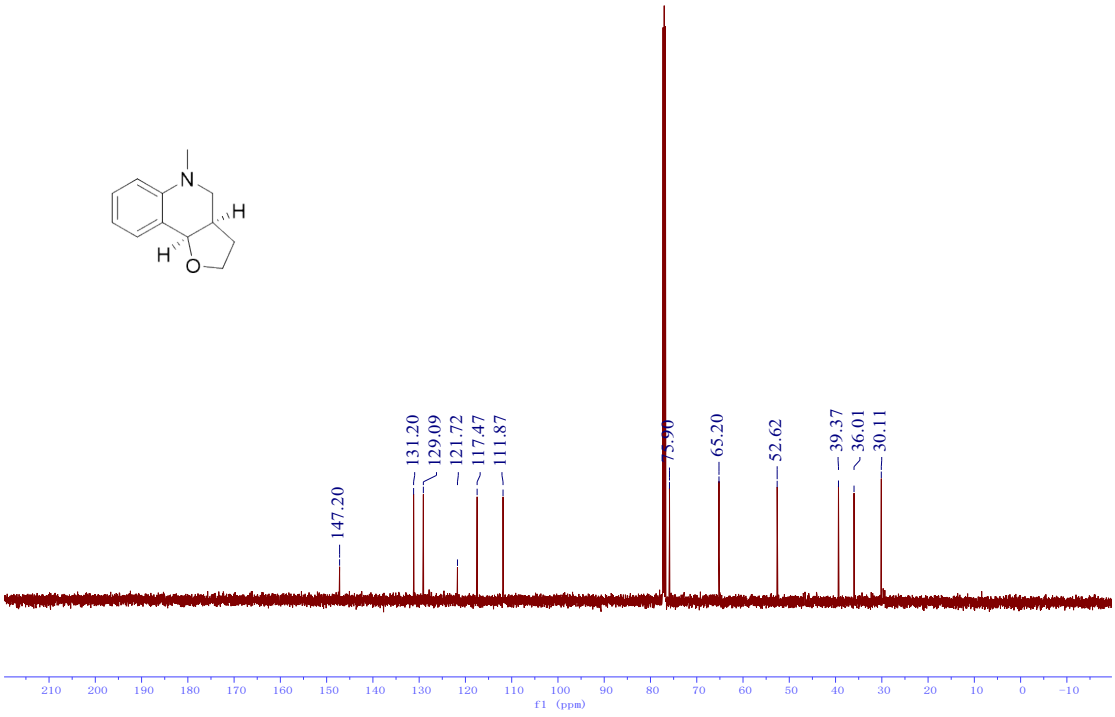
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_1



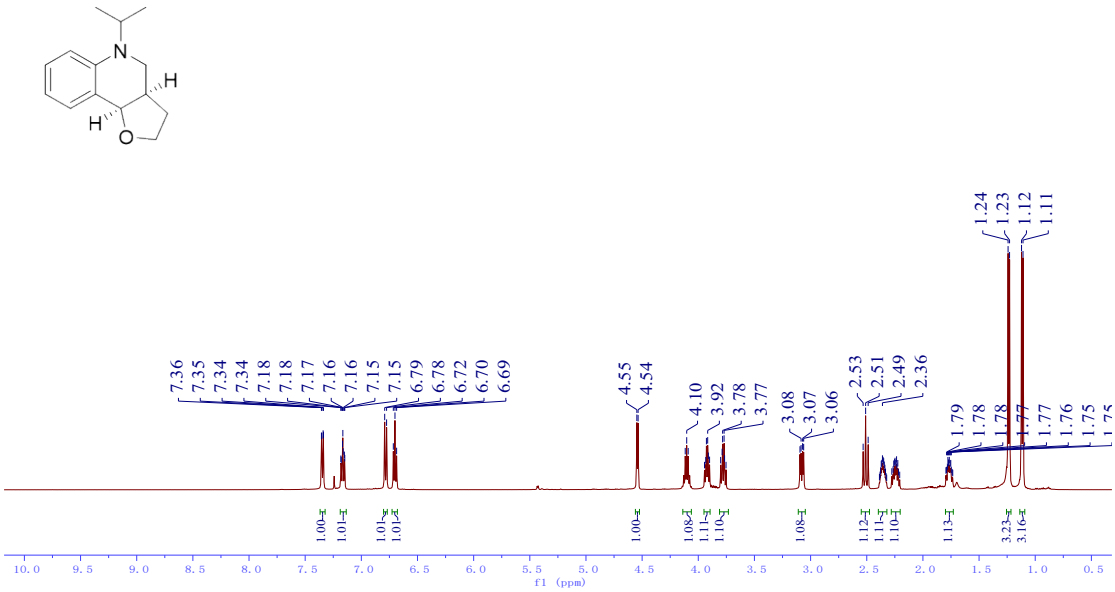
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_1



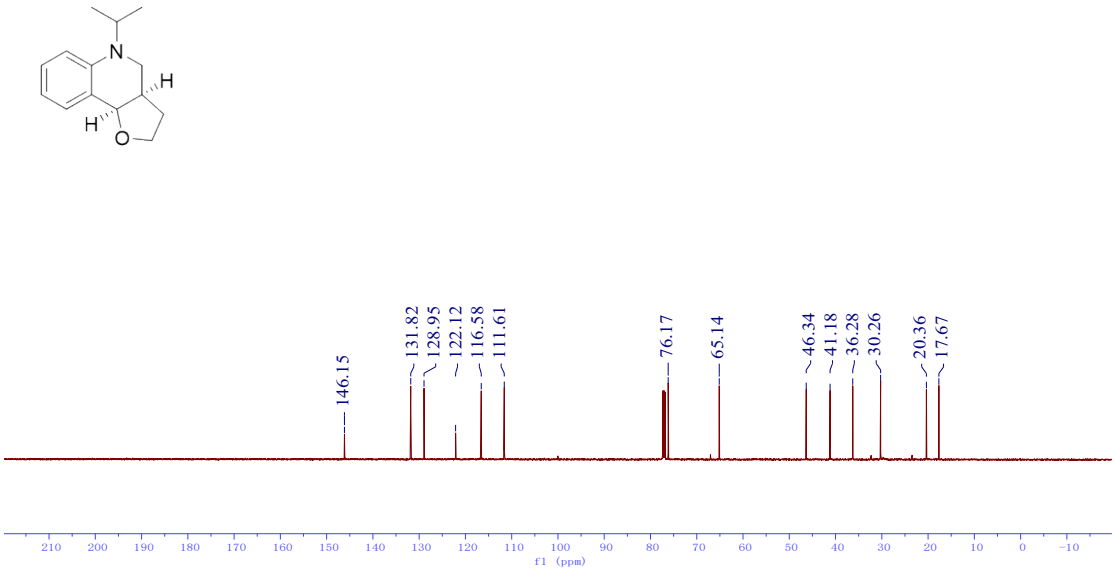
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_2



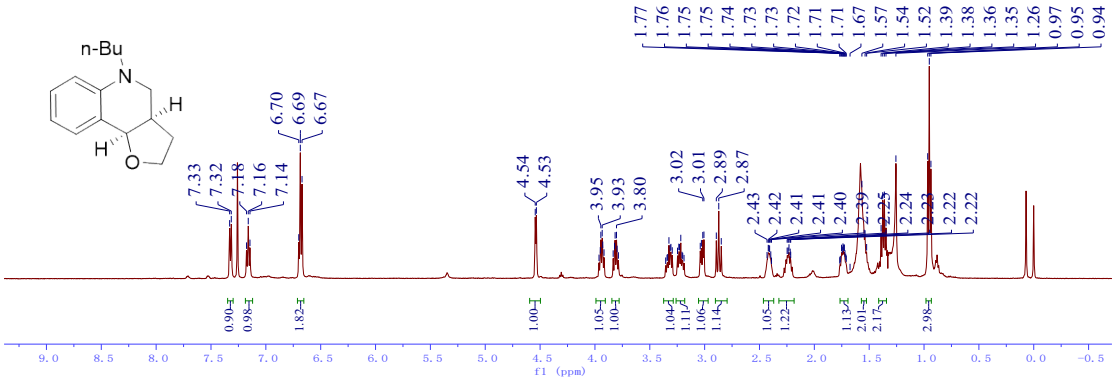
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_2



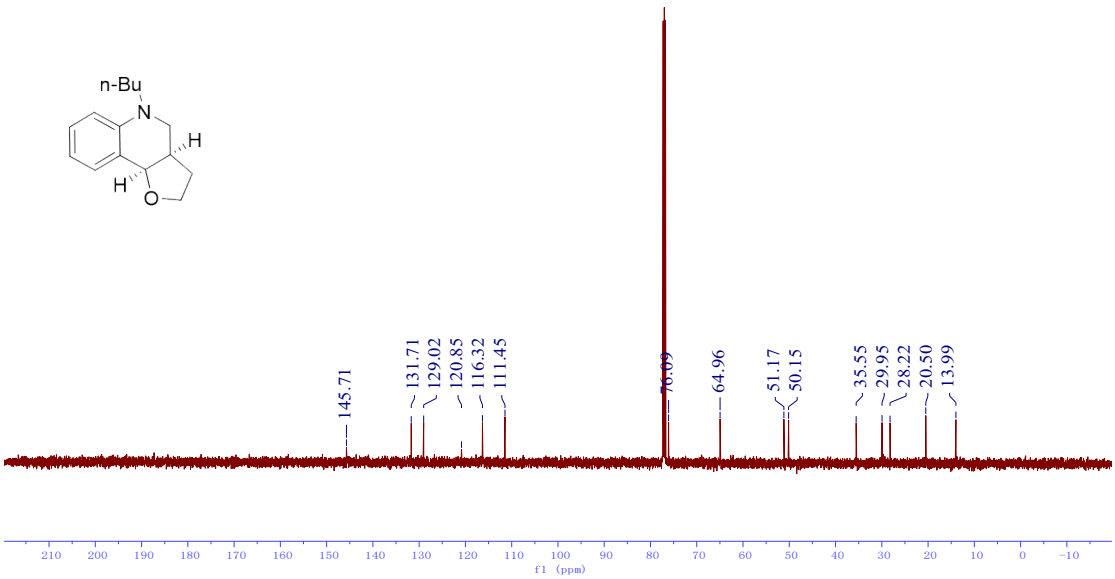
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_3



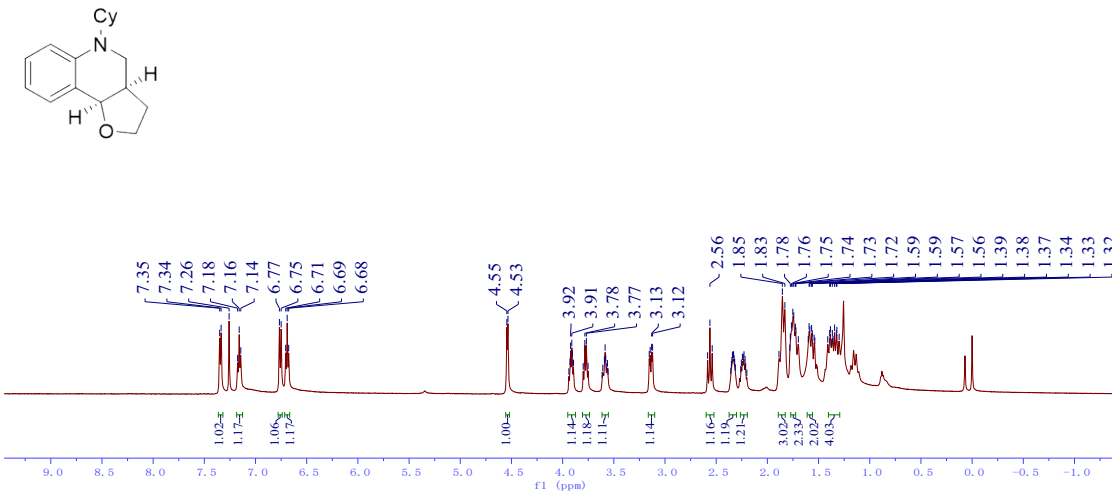
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_3



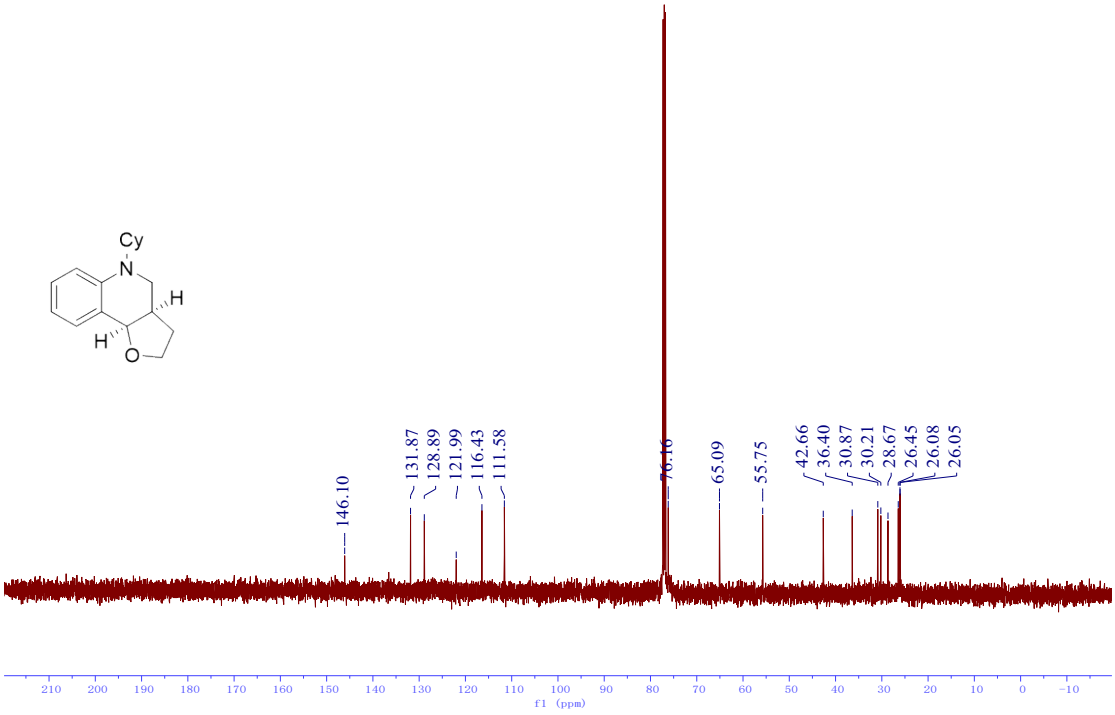
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_4



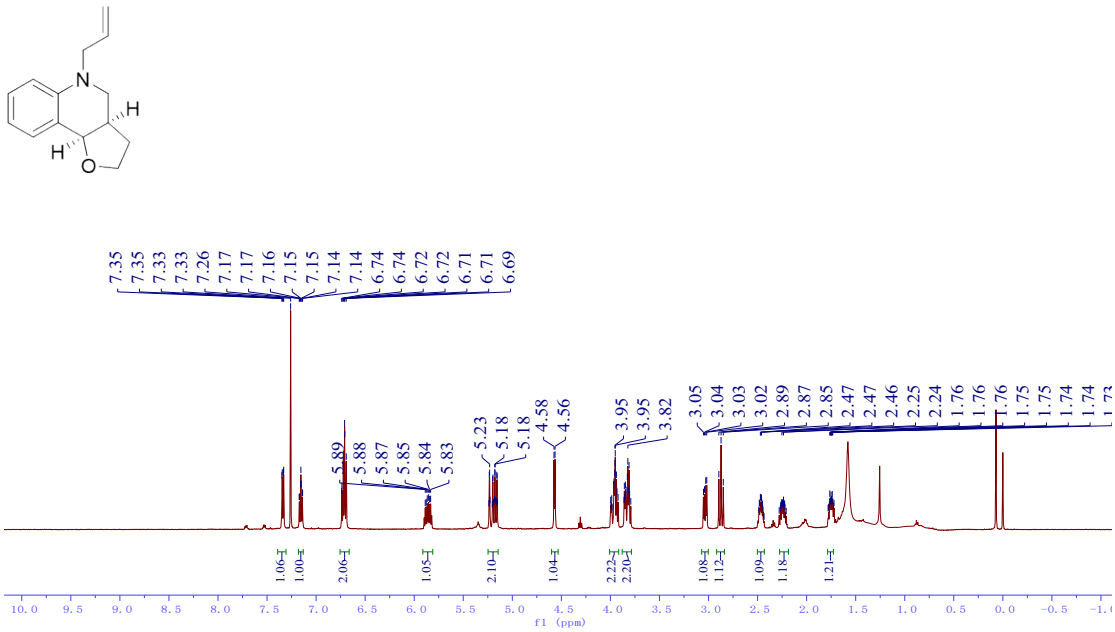
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_4



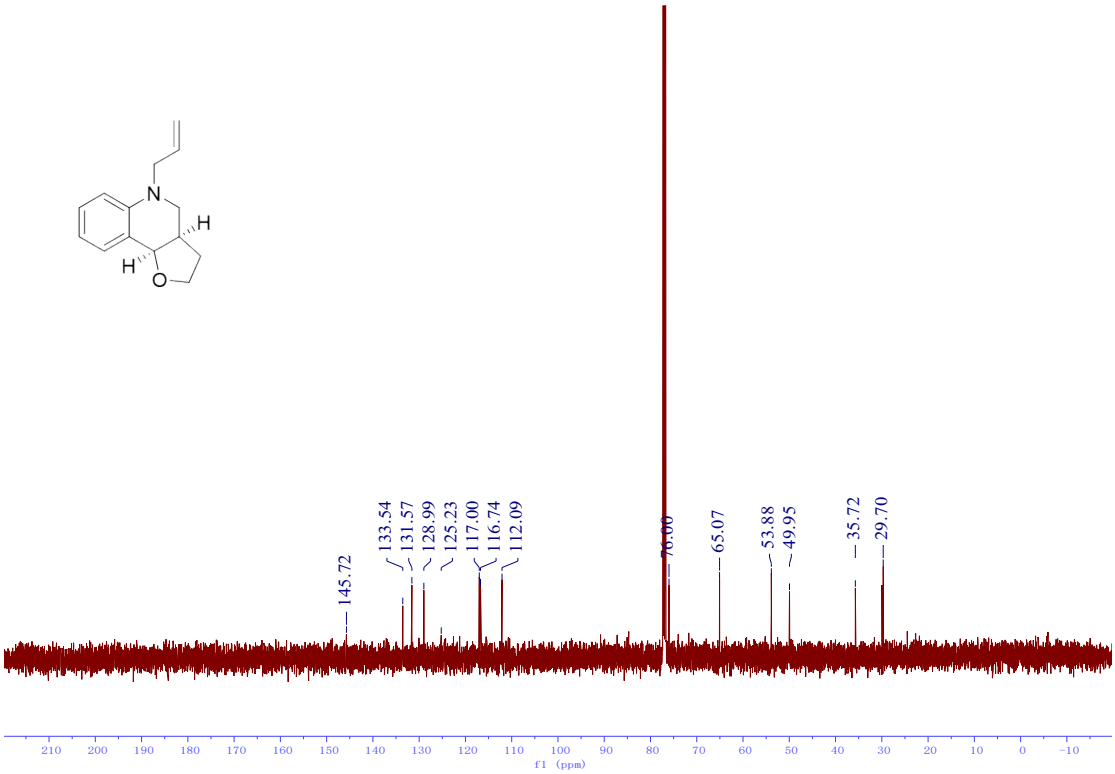
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_5



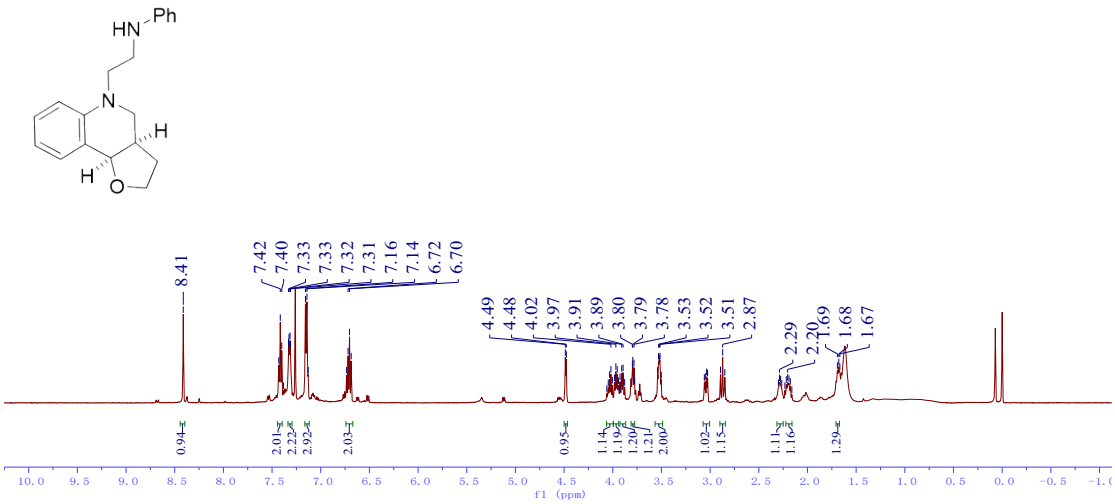
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_5



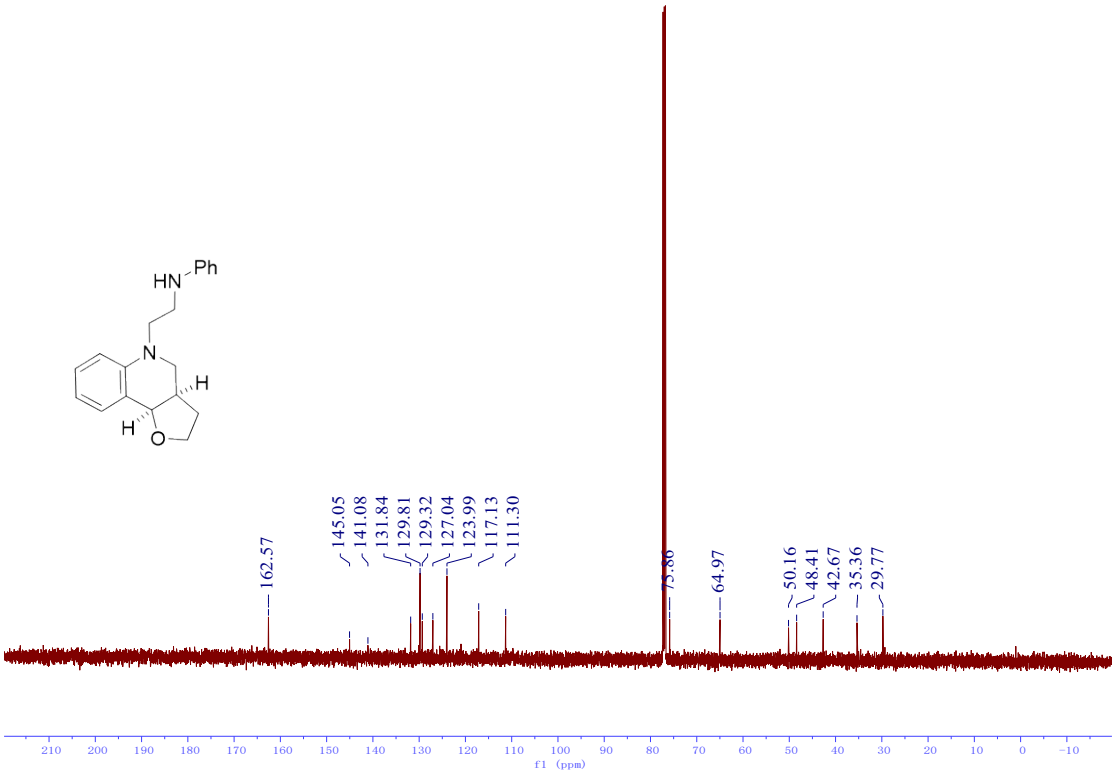
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_6



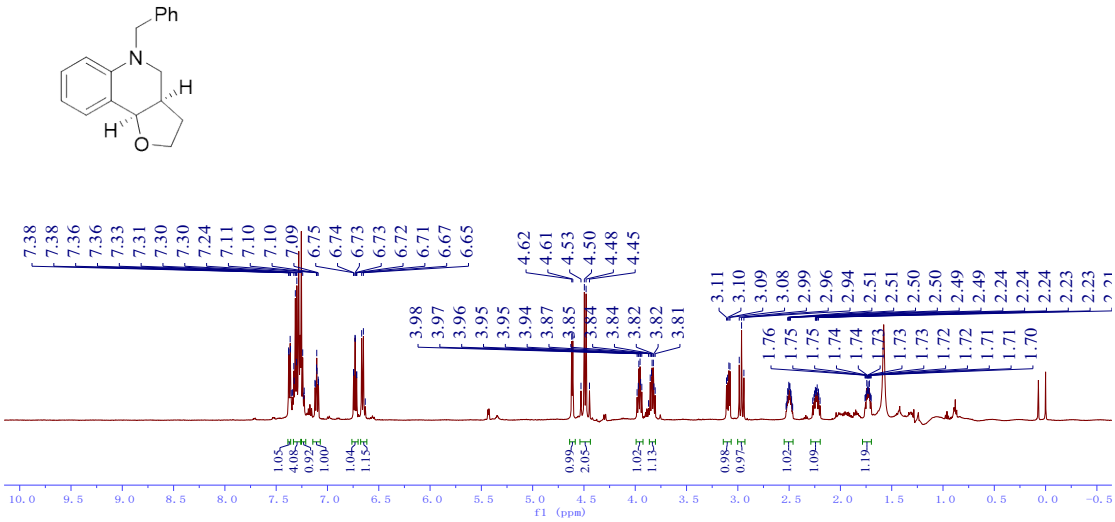
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_6



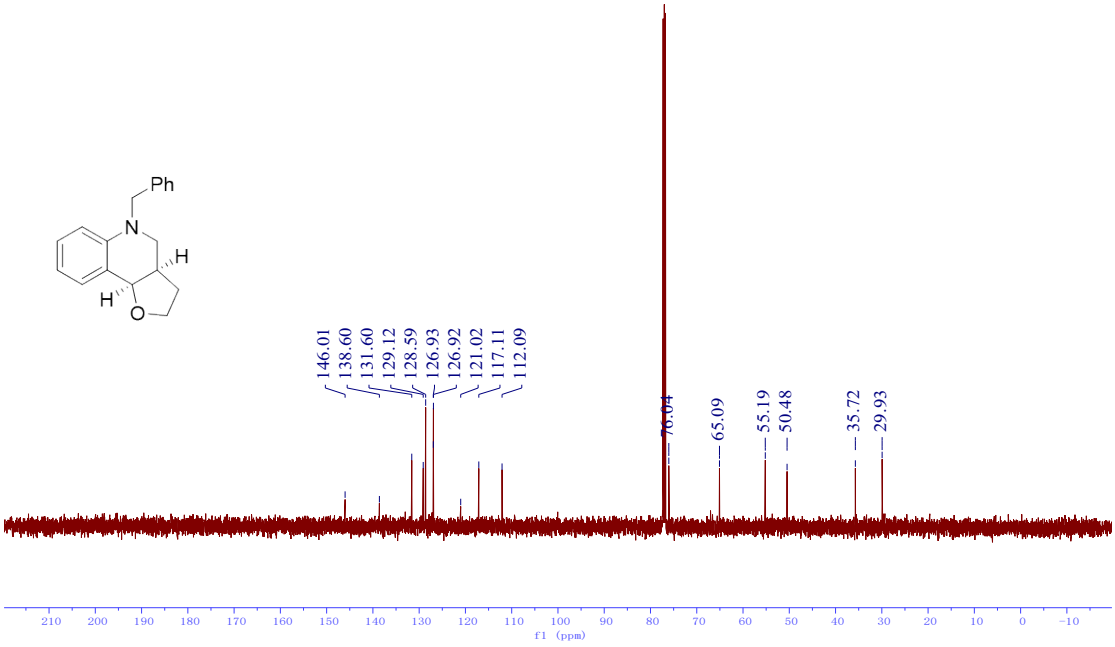
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_7



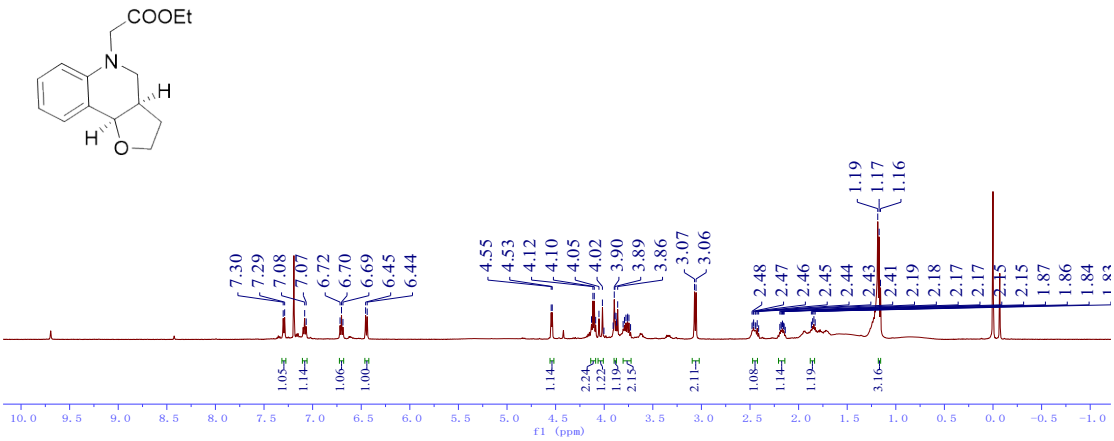
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_7



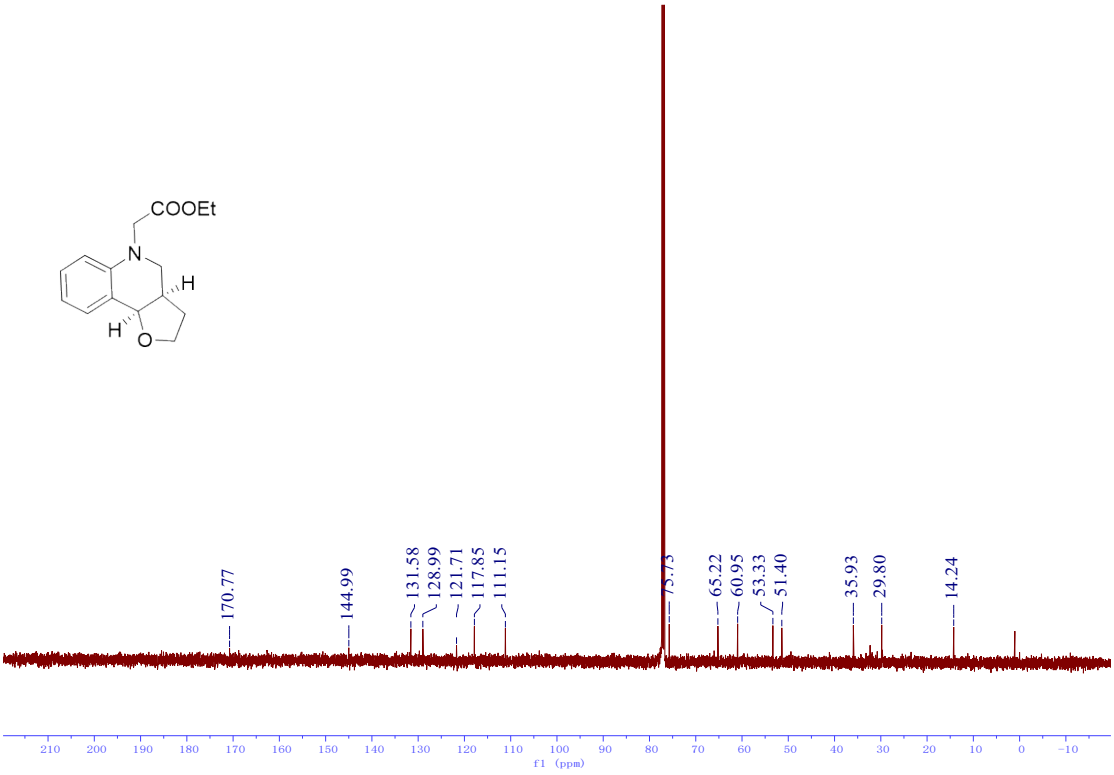
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_8



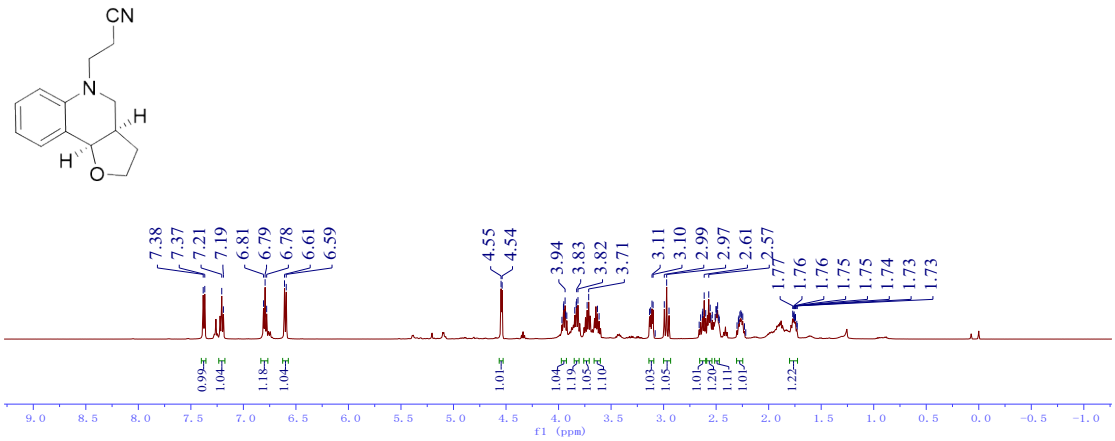
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_8



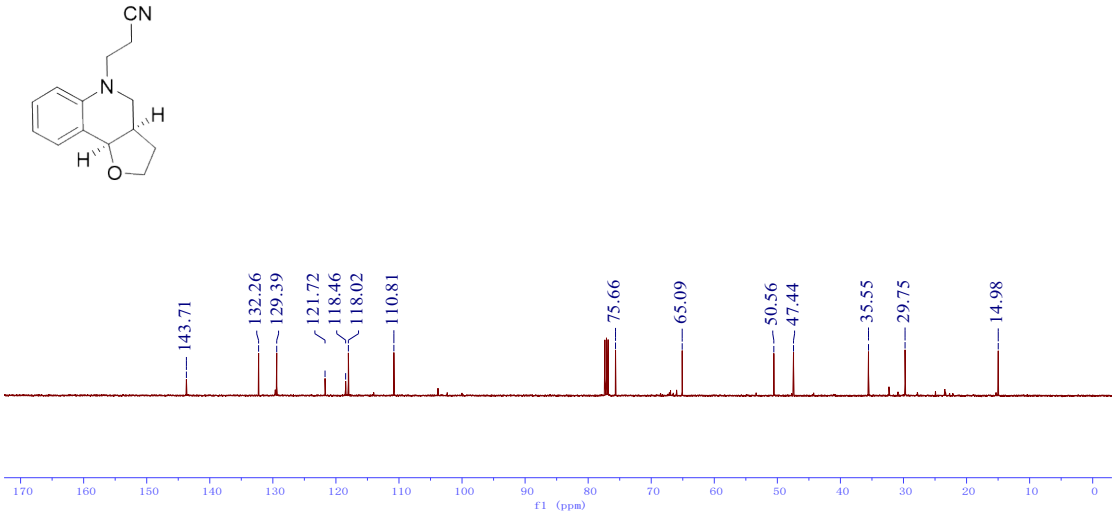
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_9



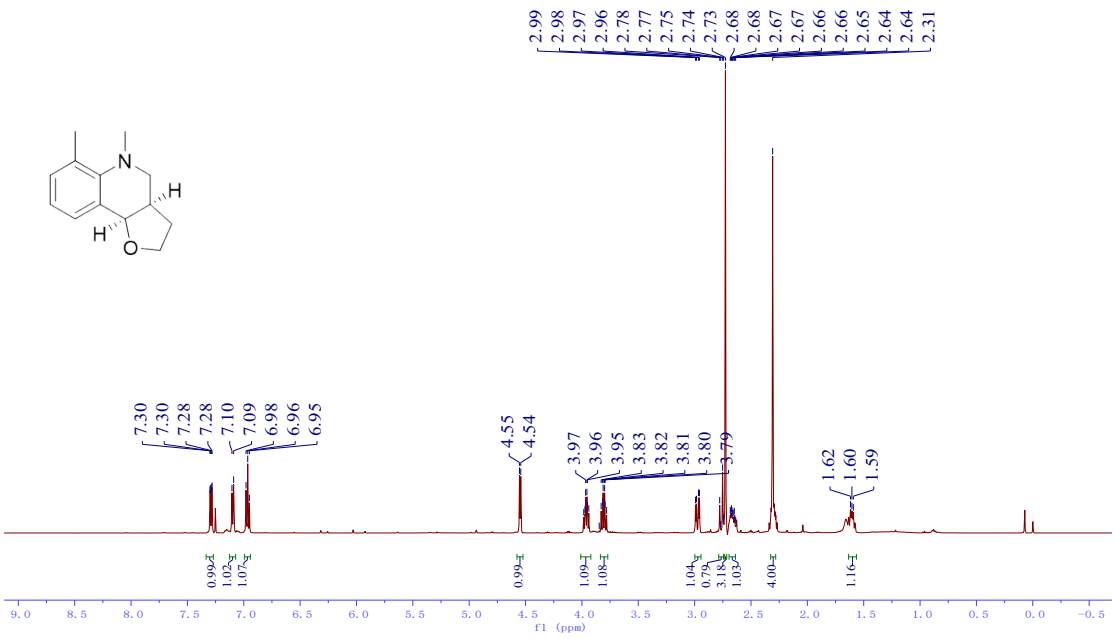
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_9



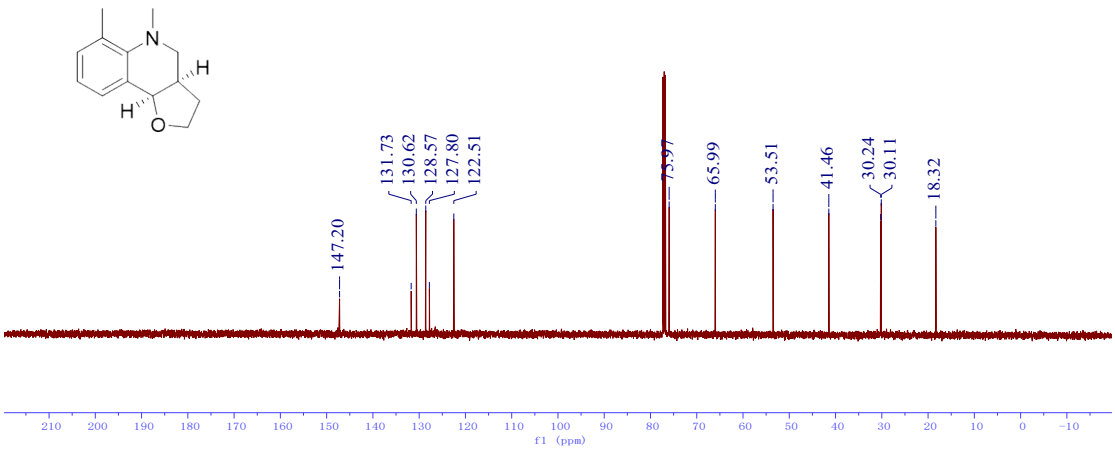
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{10}



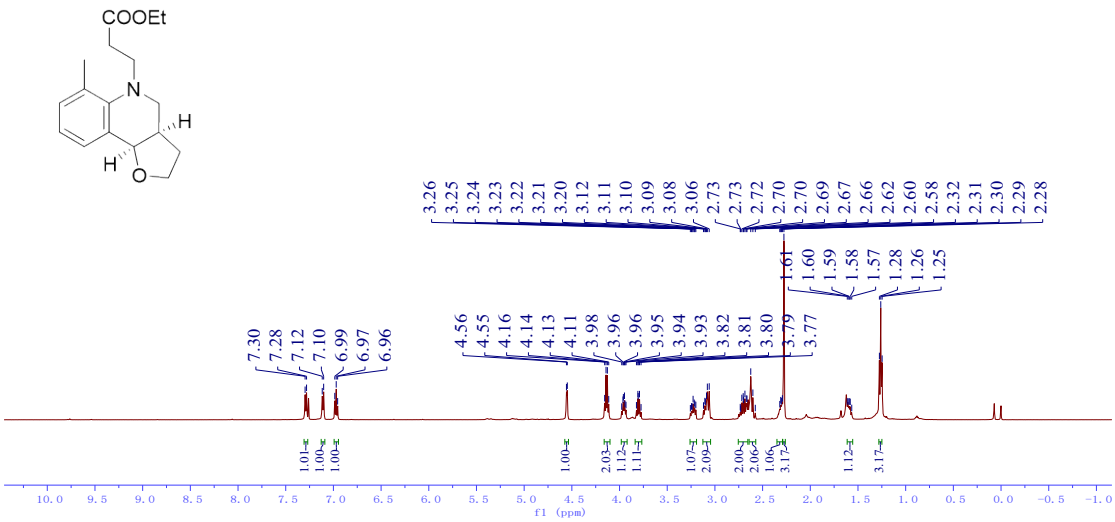
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{10}



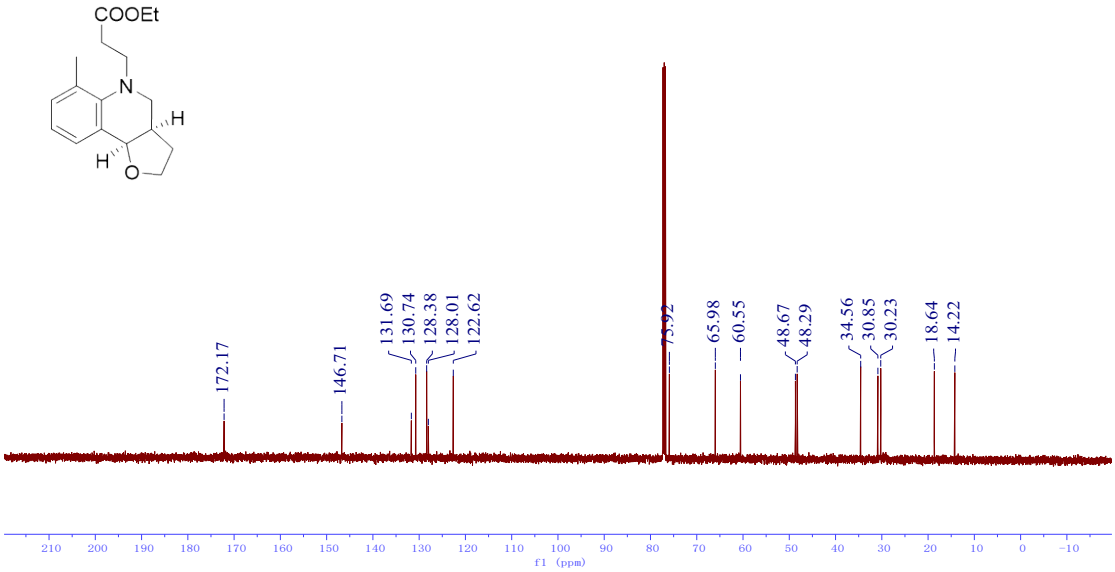
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{11}



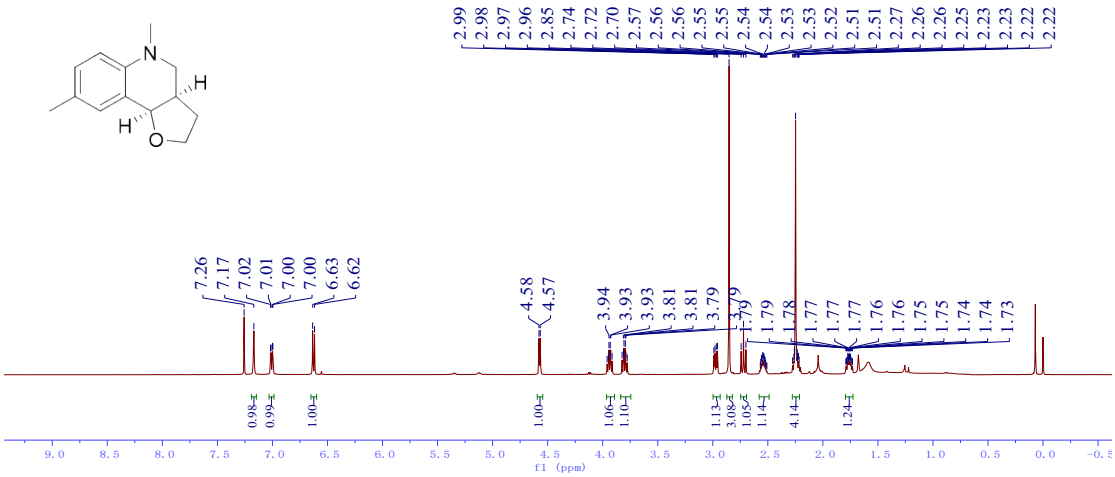
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{11}



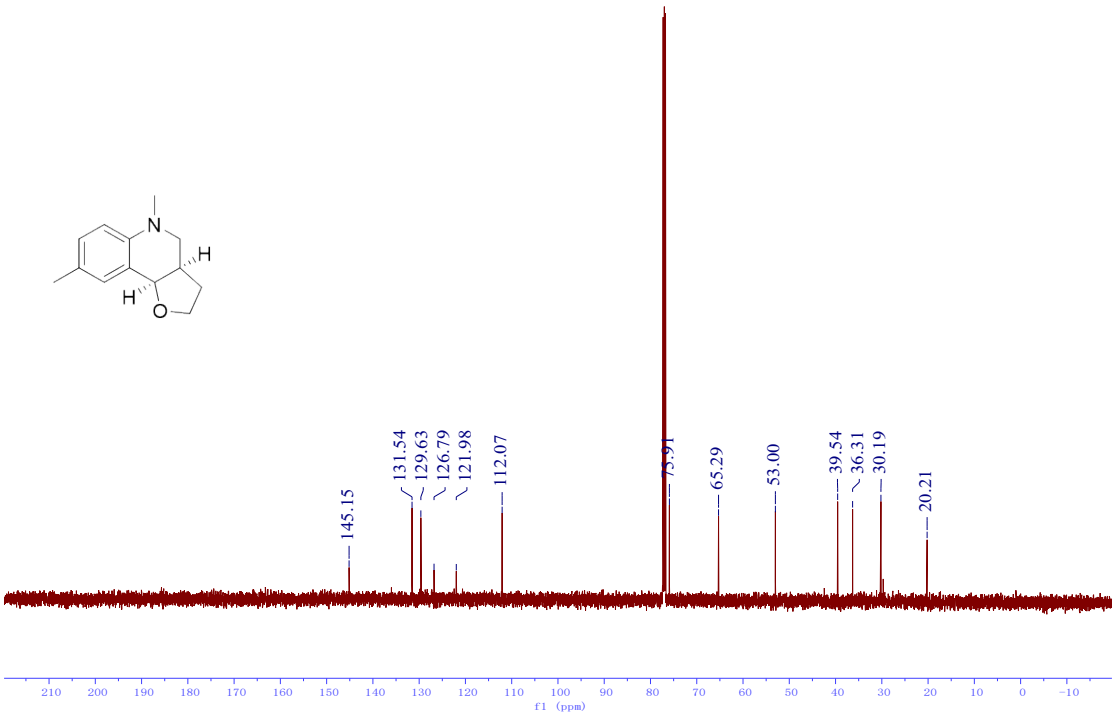
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{12}



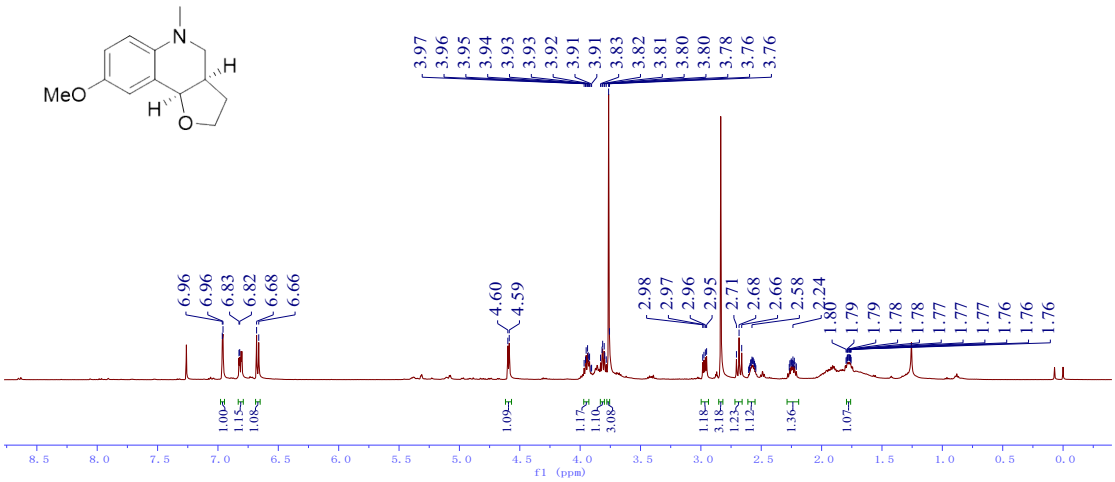
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{12}



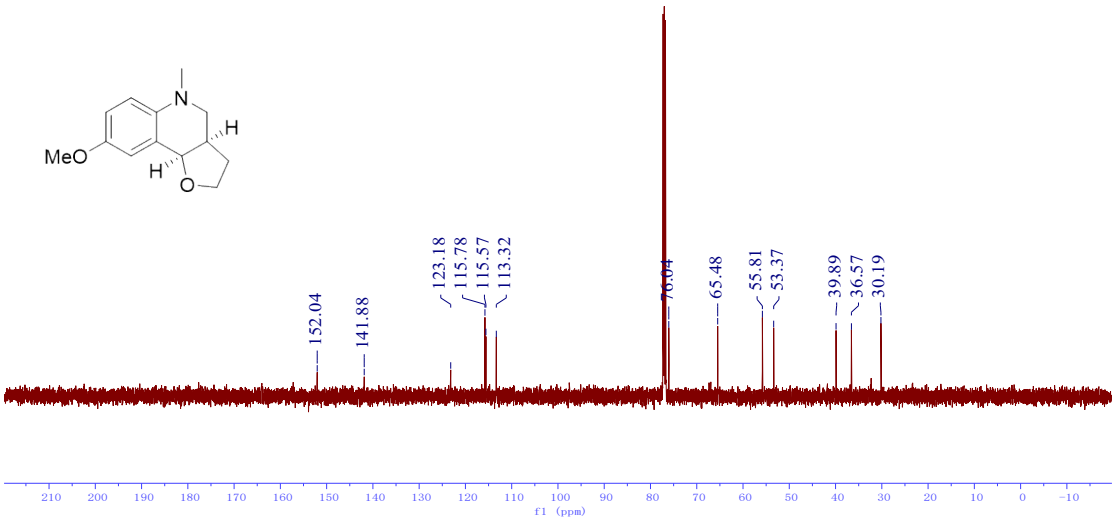
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{13}



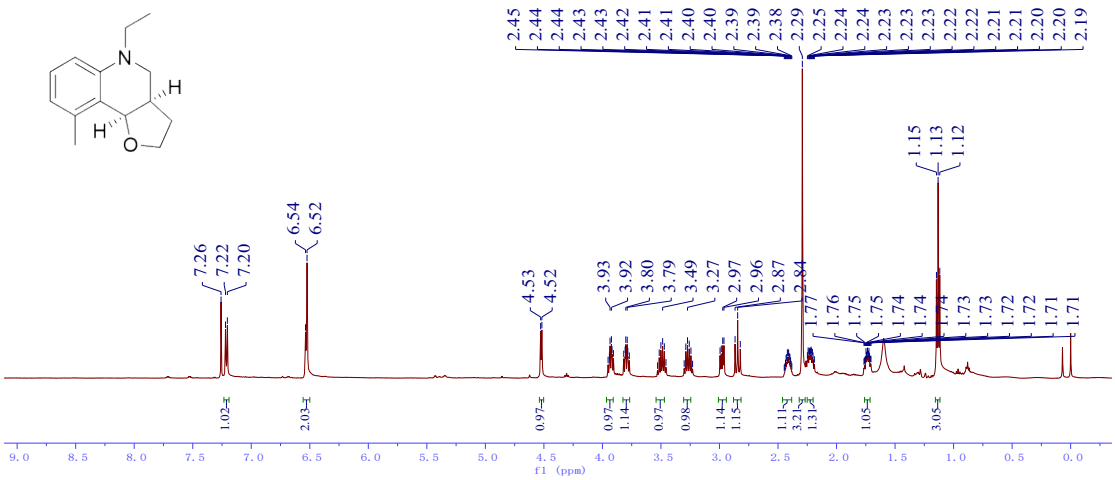
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{13}



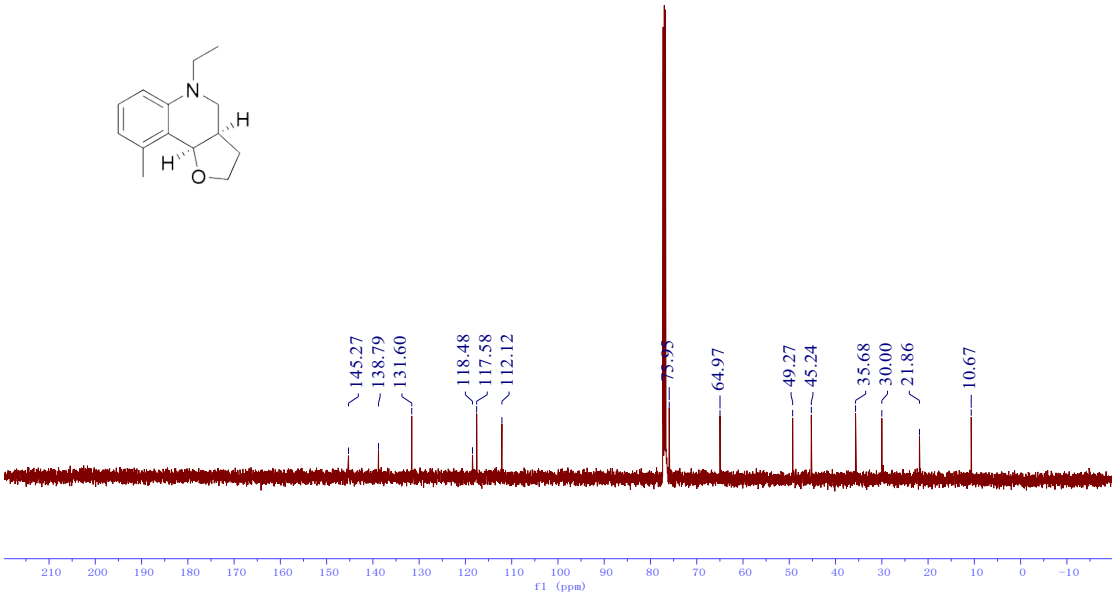
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{14}



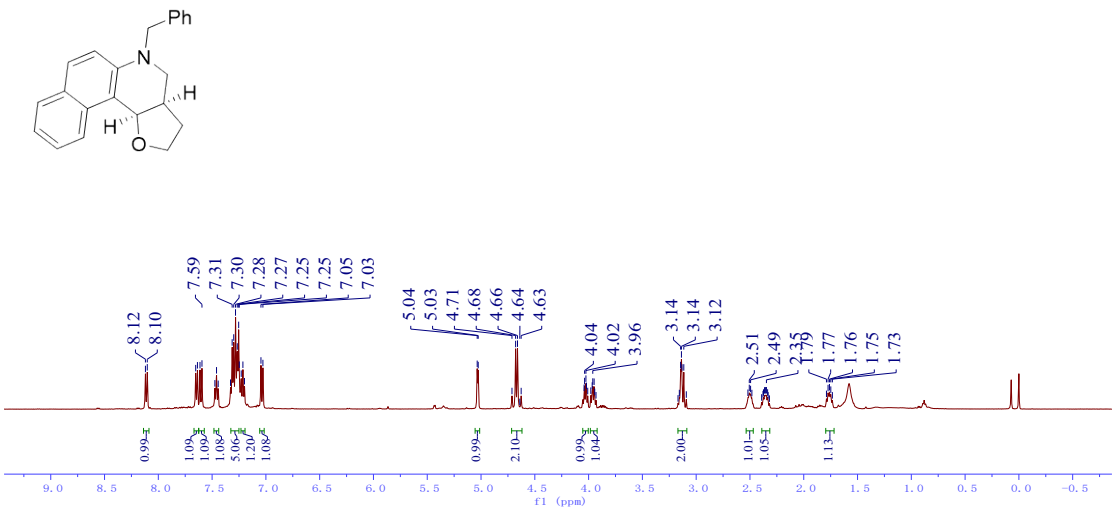
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{14}



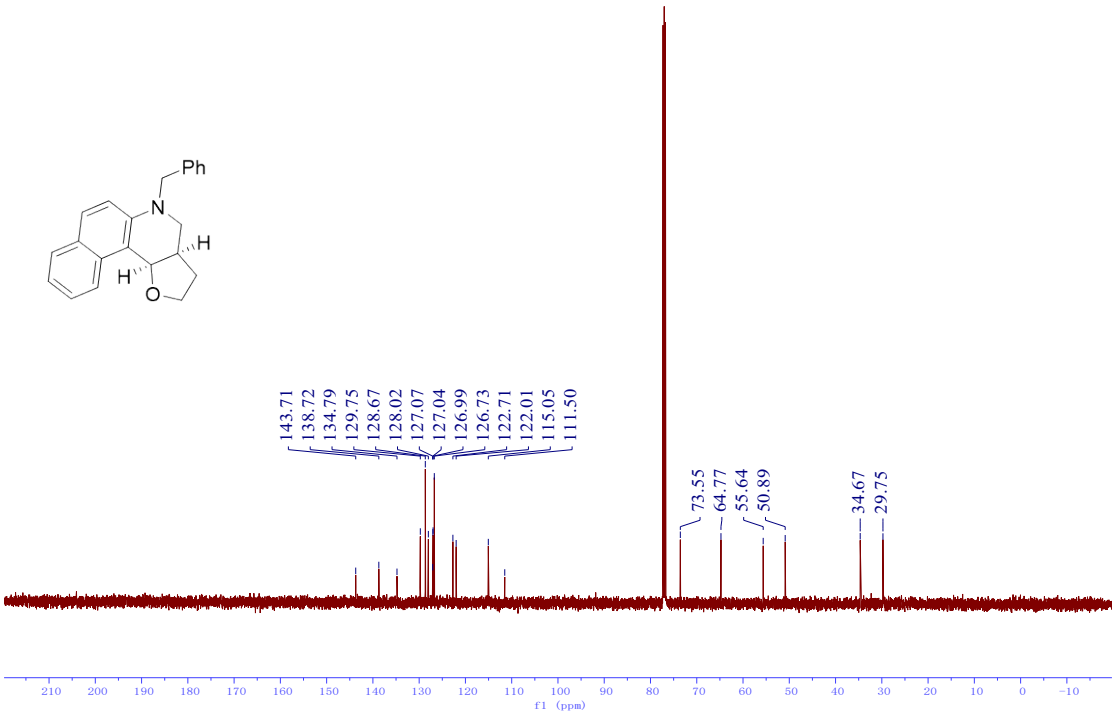
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{15}



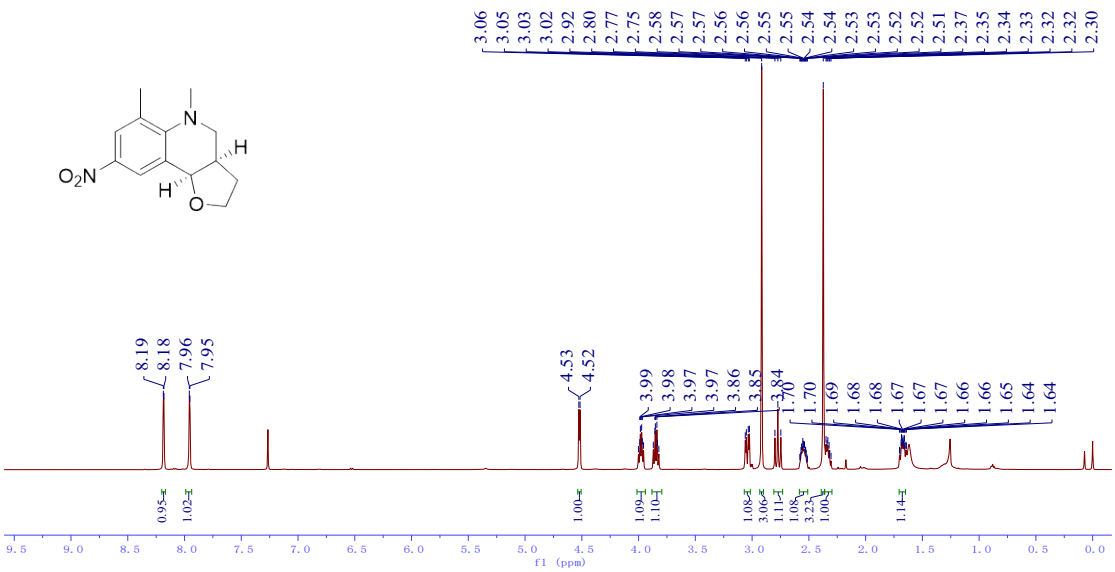
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{15}



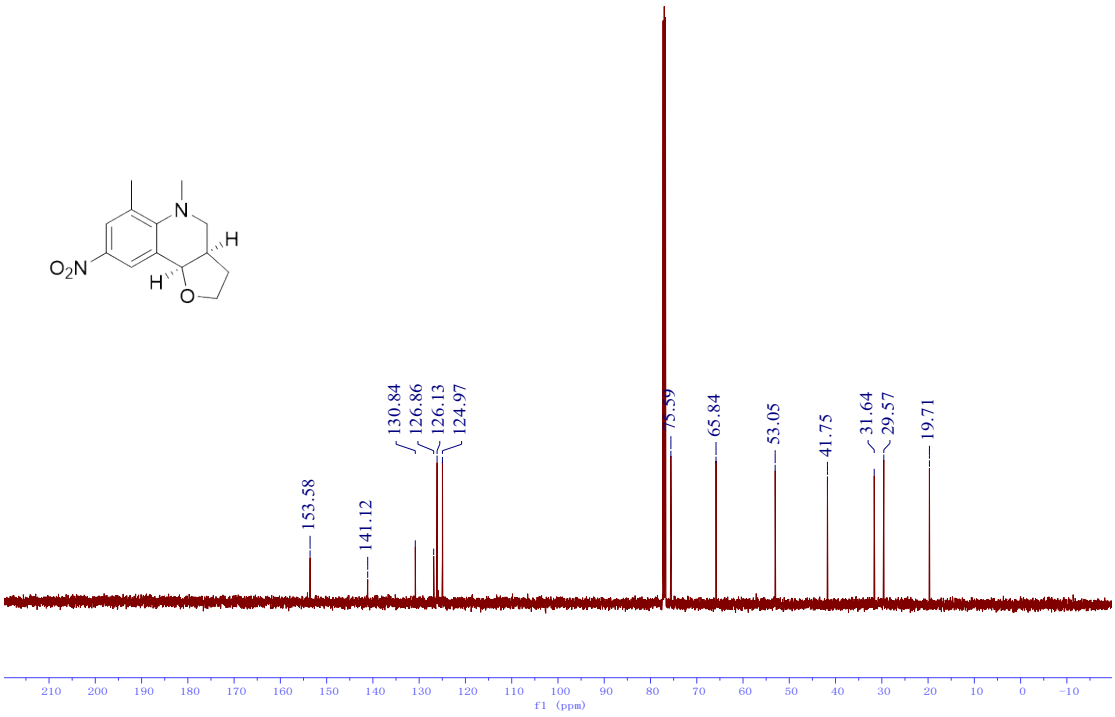
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{16}



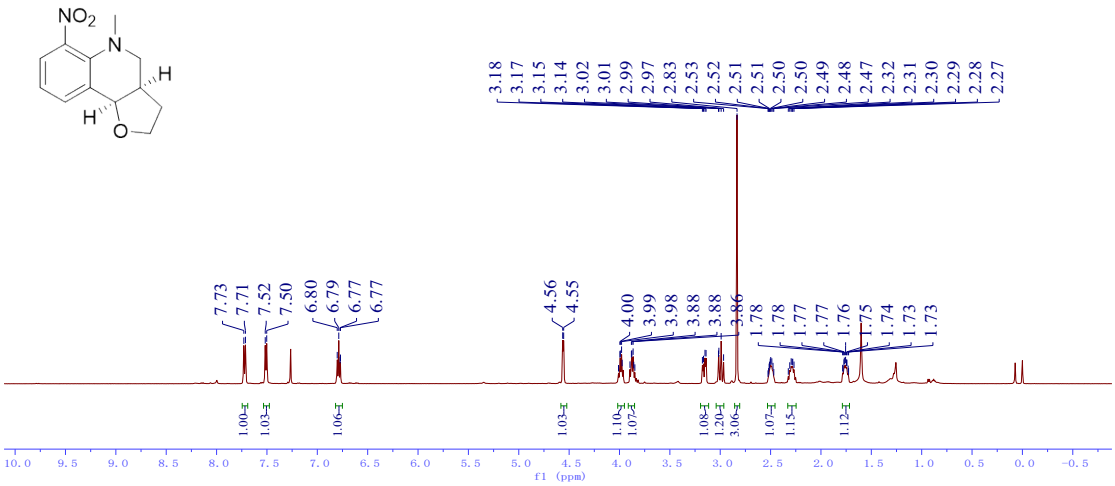
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{16}



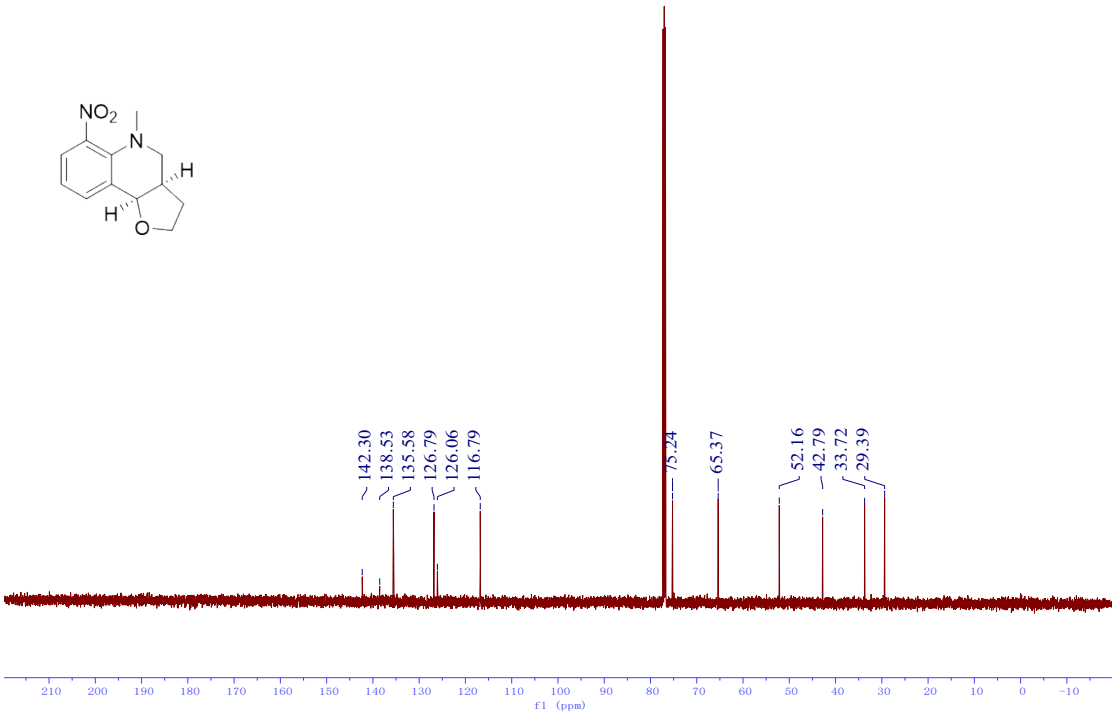
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{17}



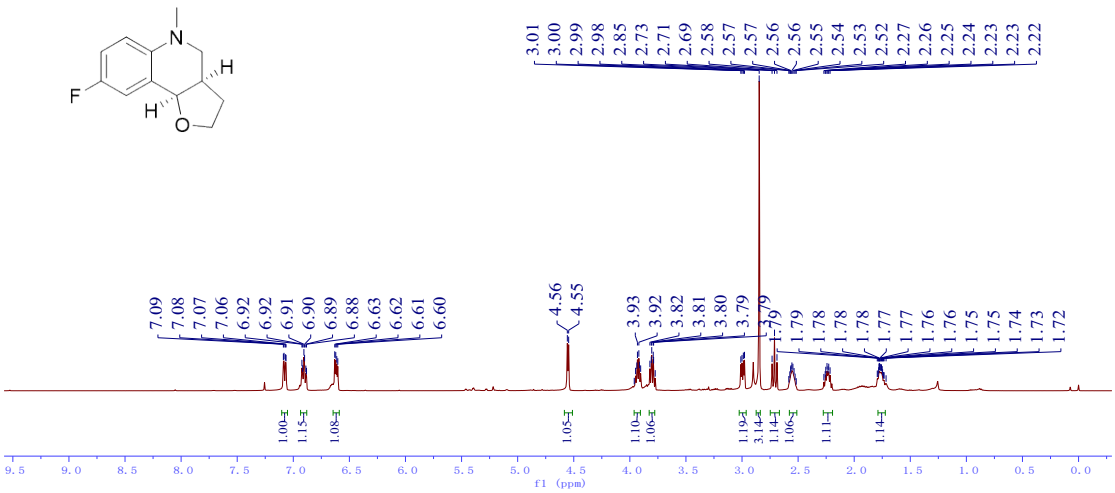
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{17}



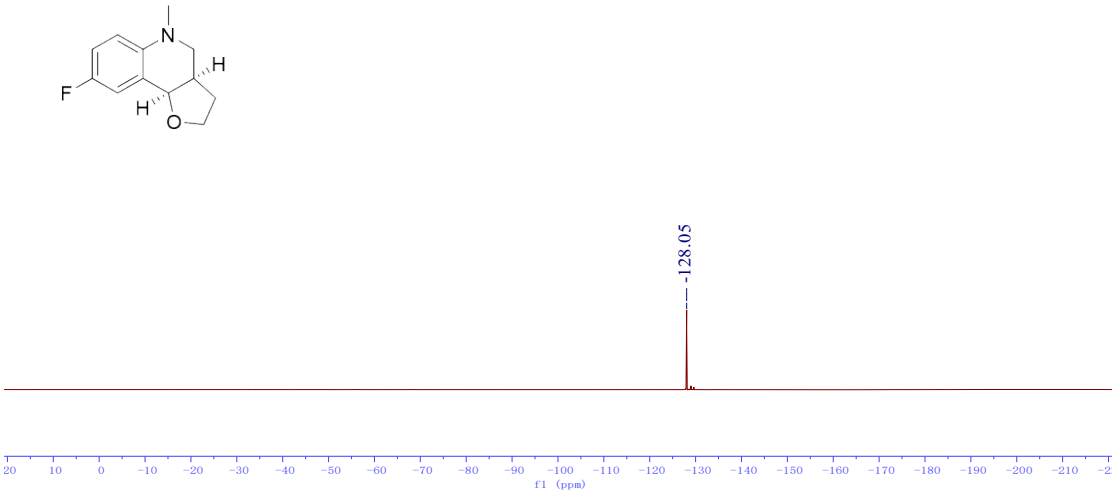
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{18}



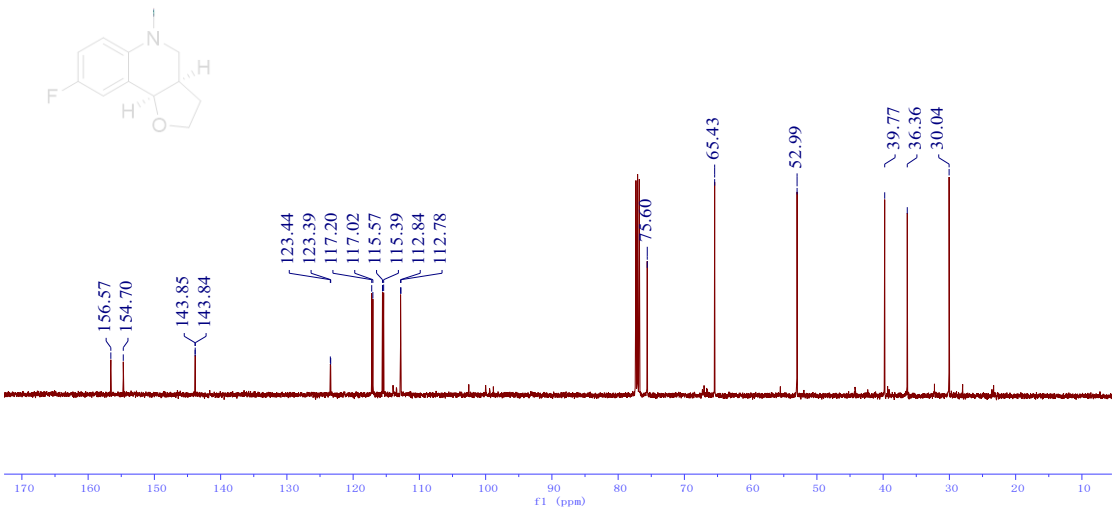
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{18}



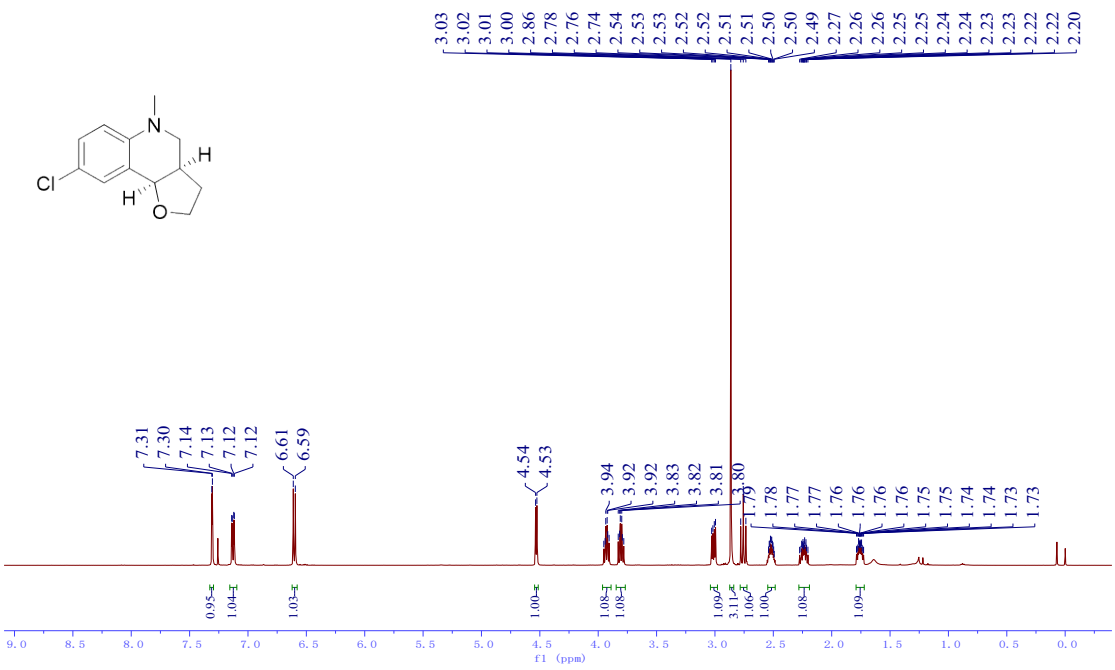
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{19}



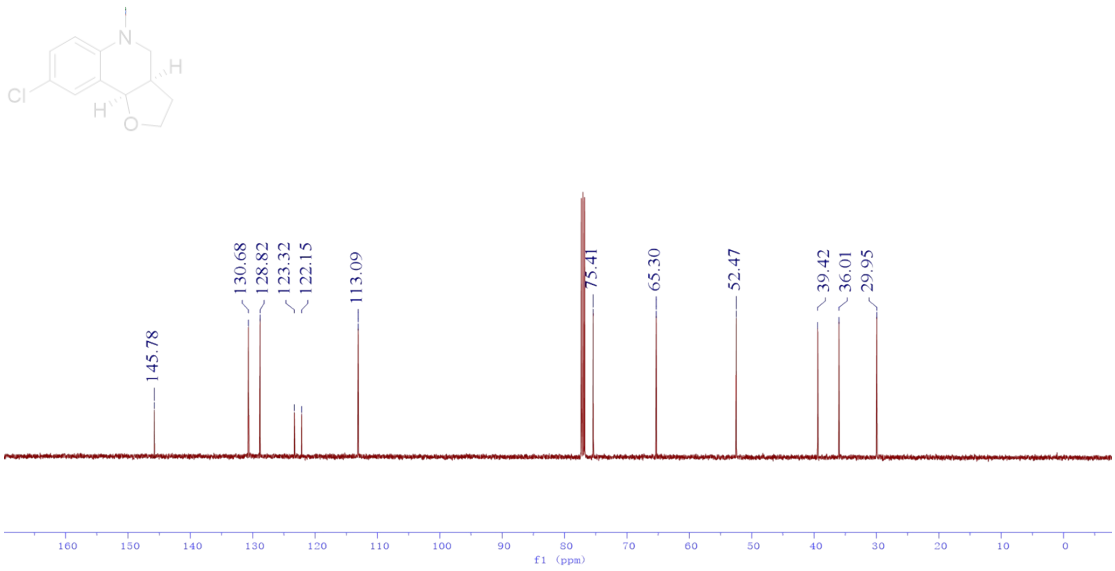
^{19}F-NMR (471 MHz, $CDCl_3$) spectrum of D_{19}



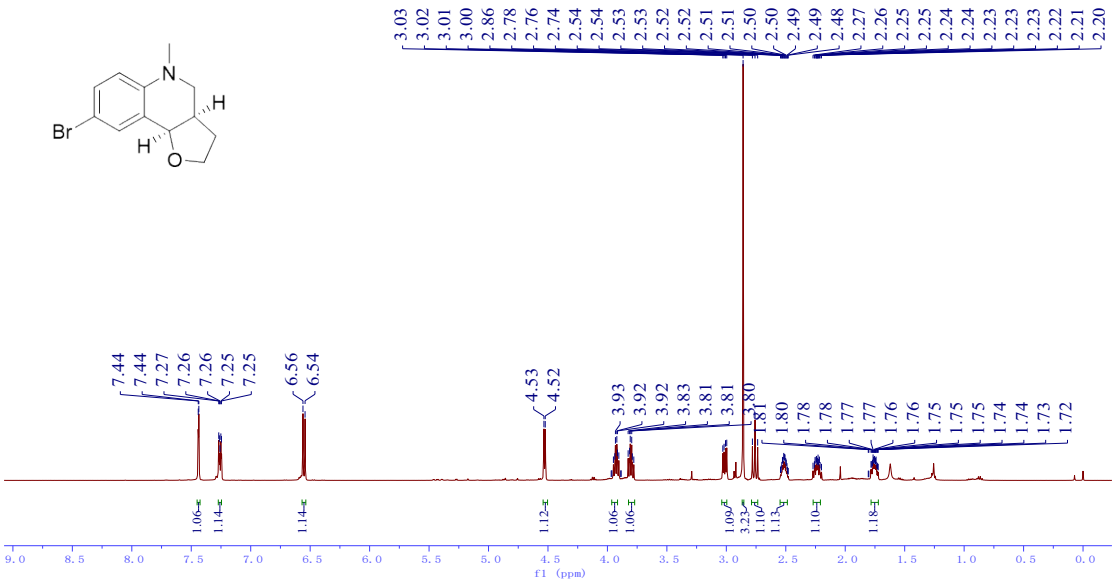
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{19}



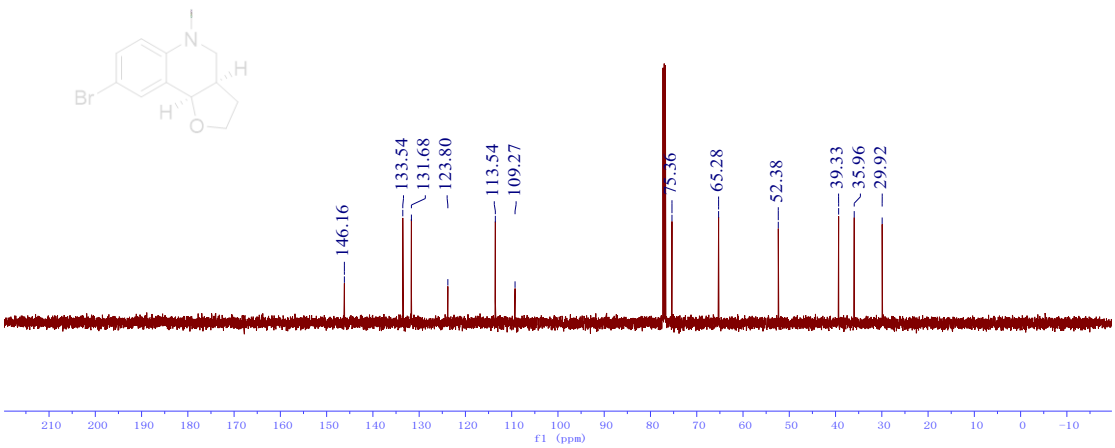
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{20}



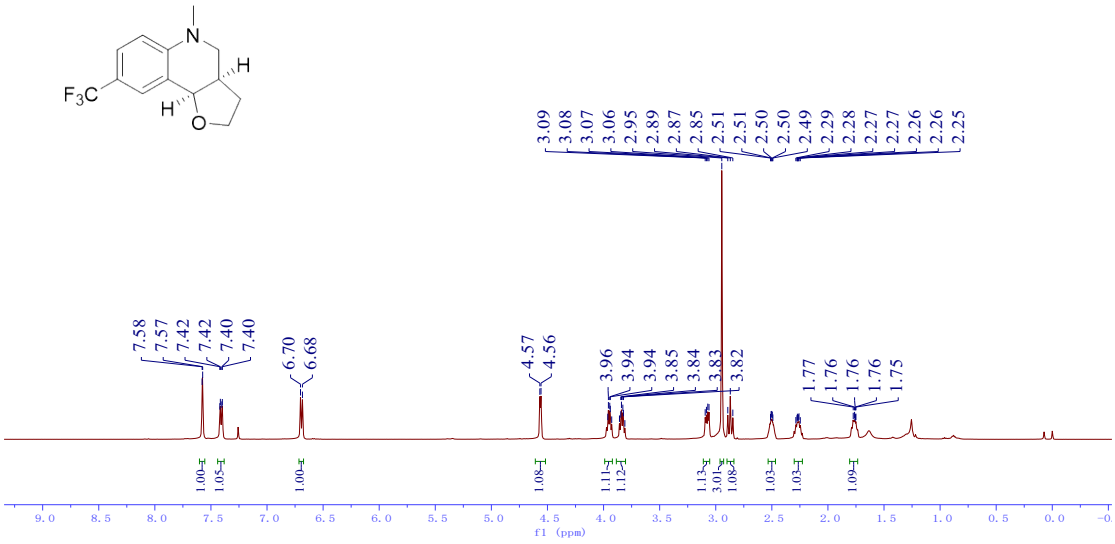
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{20}



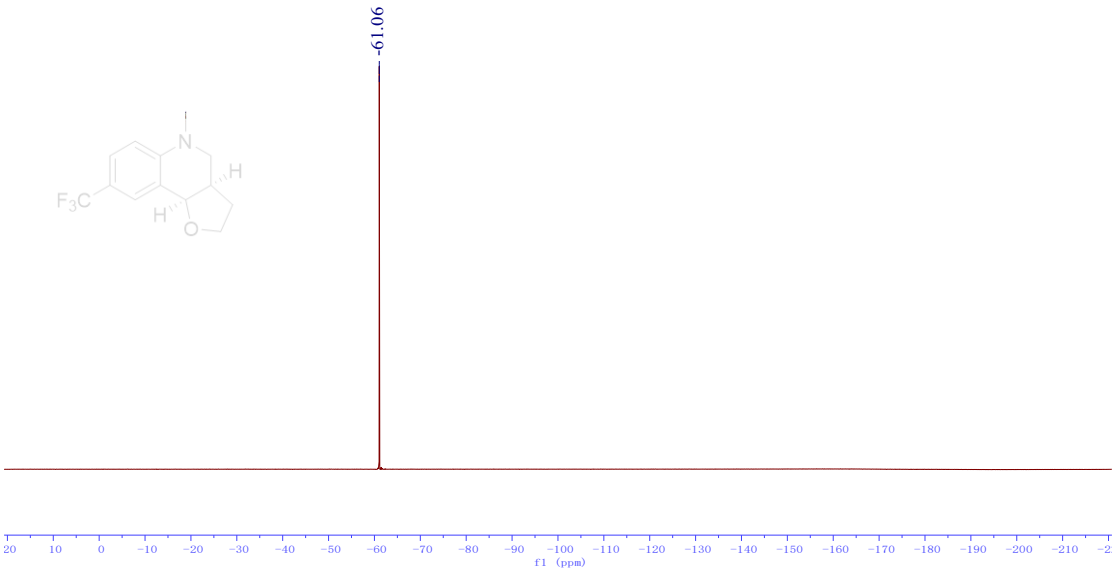
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{21}



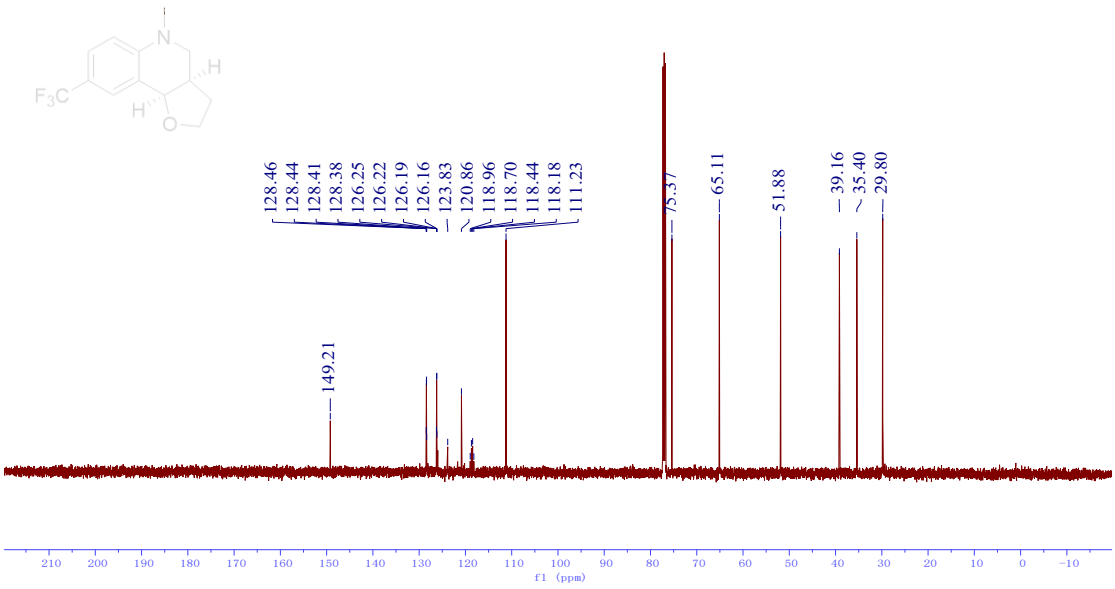
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{21}



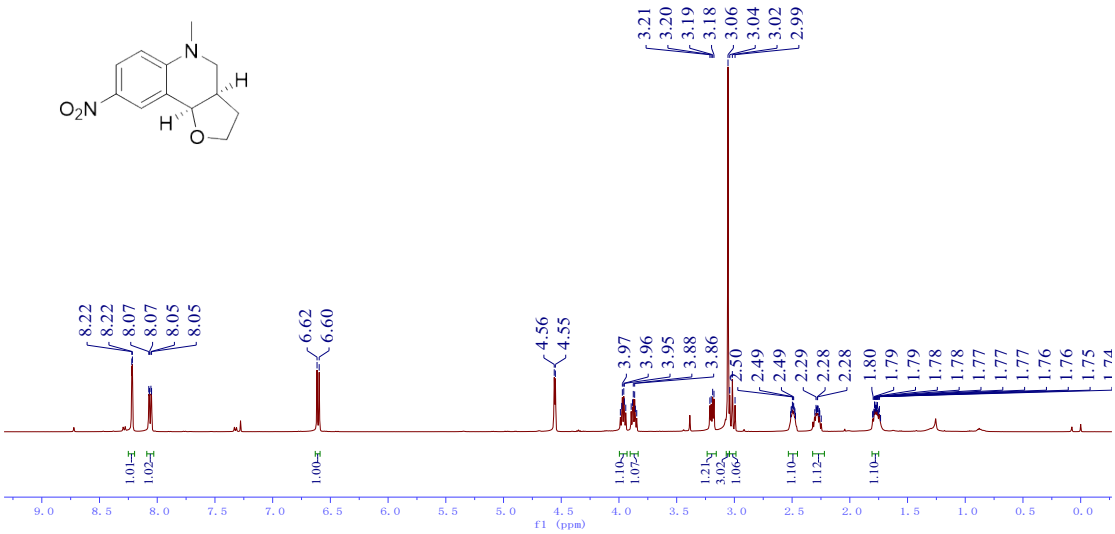
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{22}



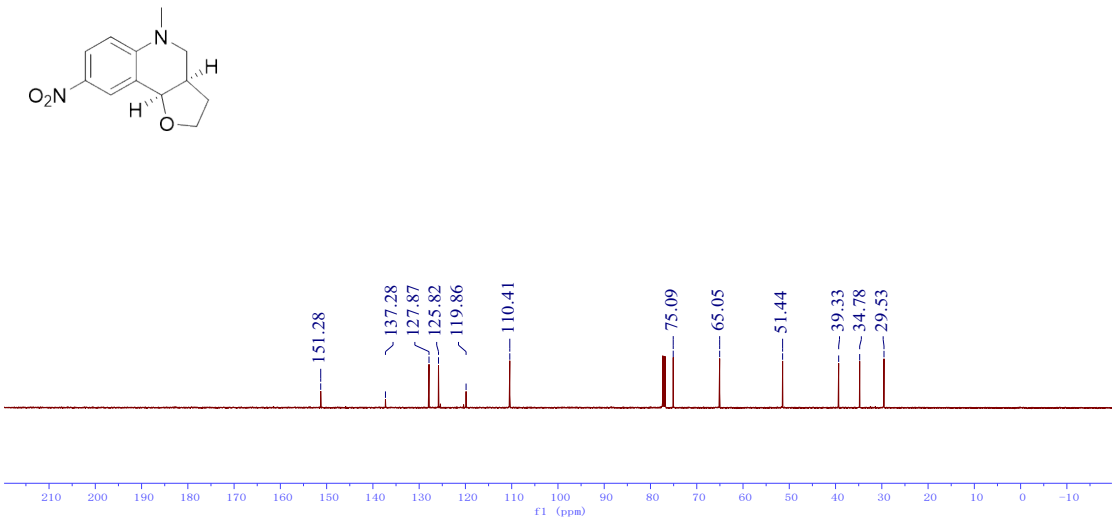
^{19}F-NMR (471 MHz, $CDCl_3$) spectrum of D_{22}



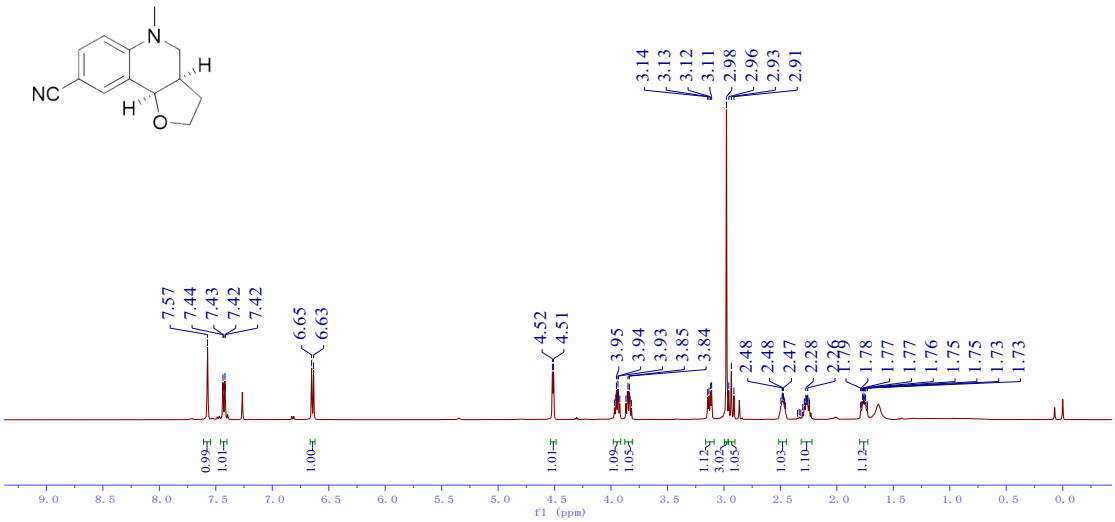
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{22}



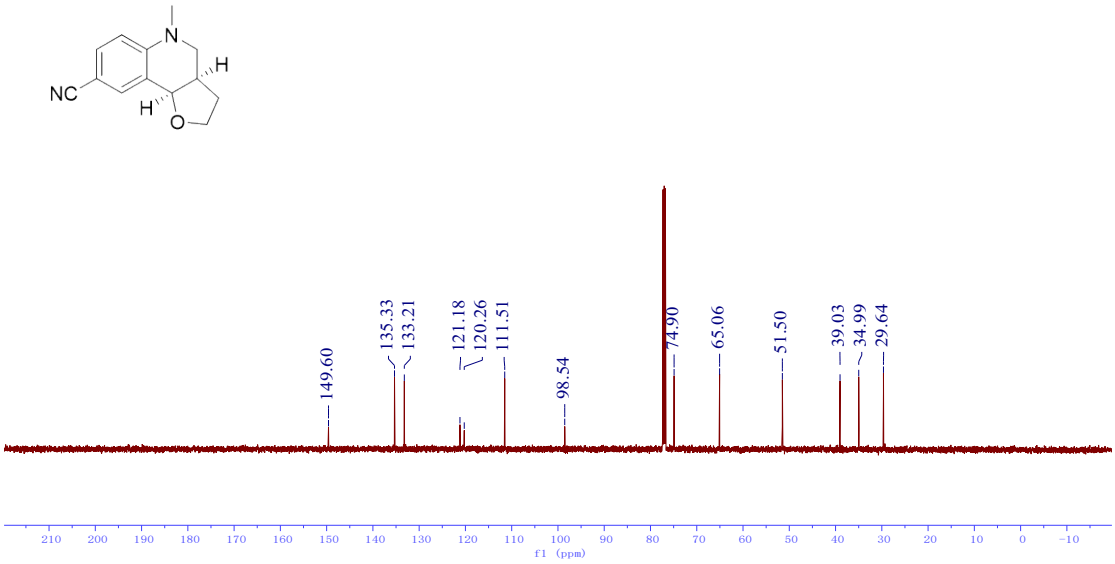
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{23}



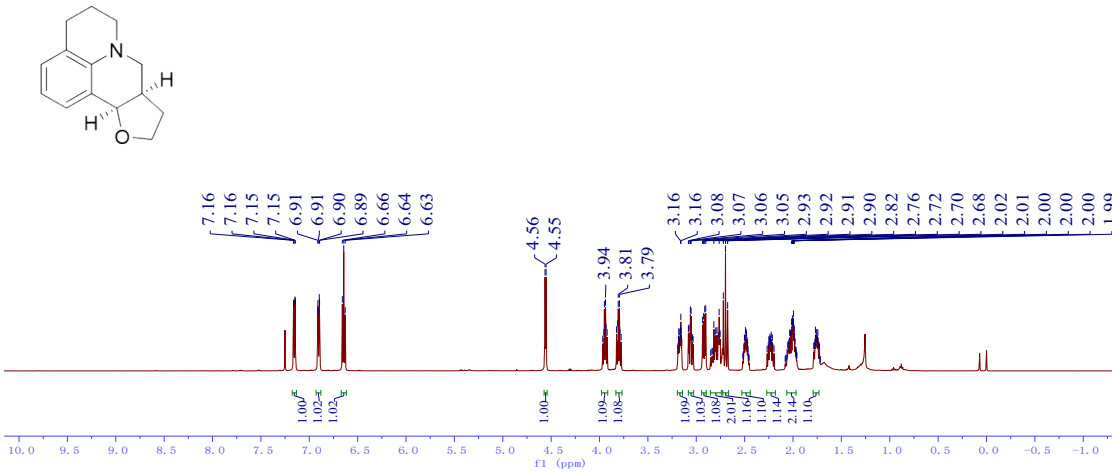
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{23}



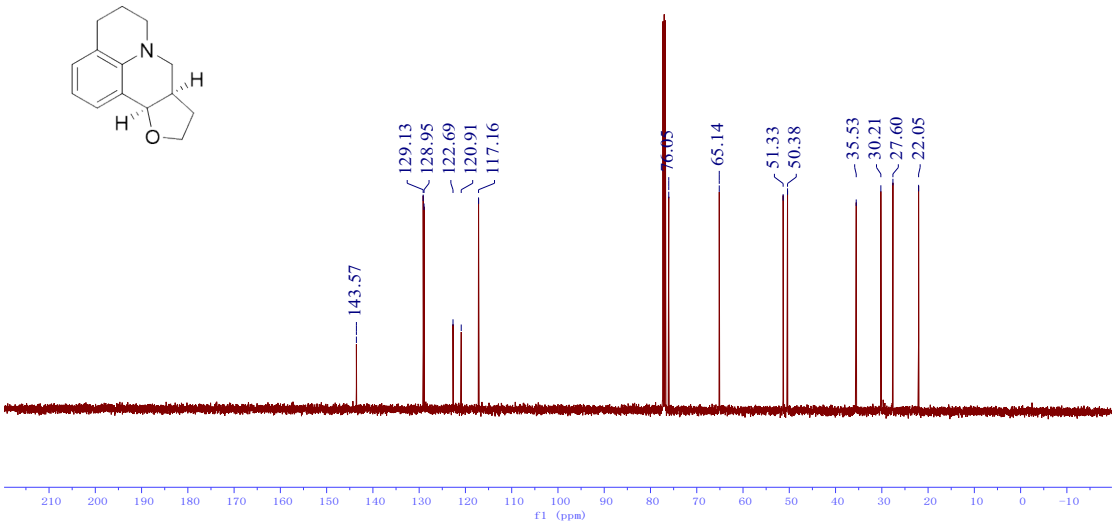
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{24}



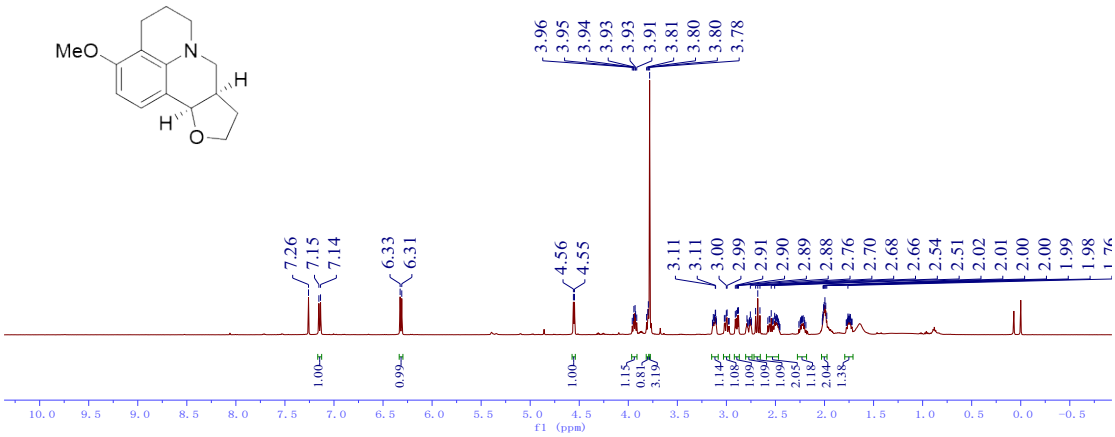
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{24}



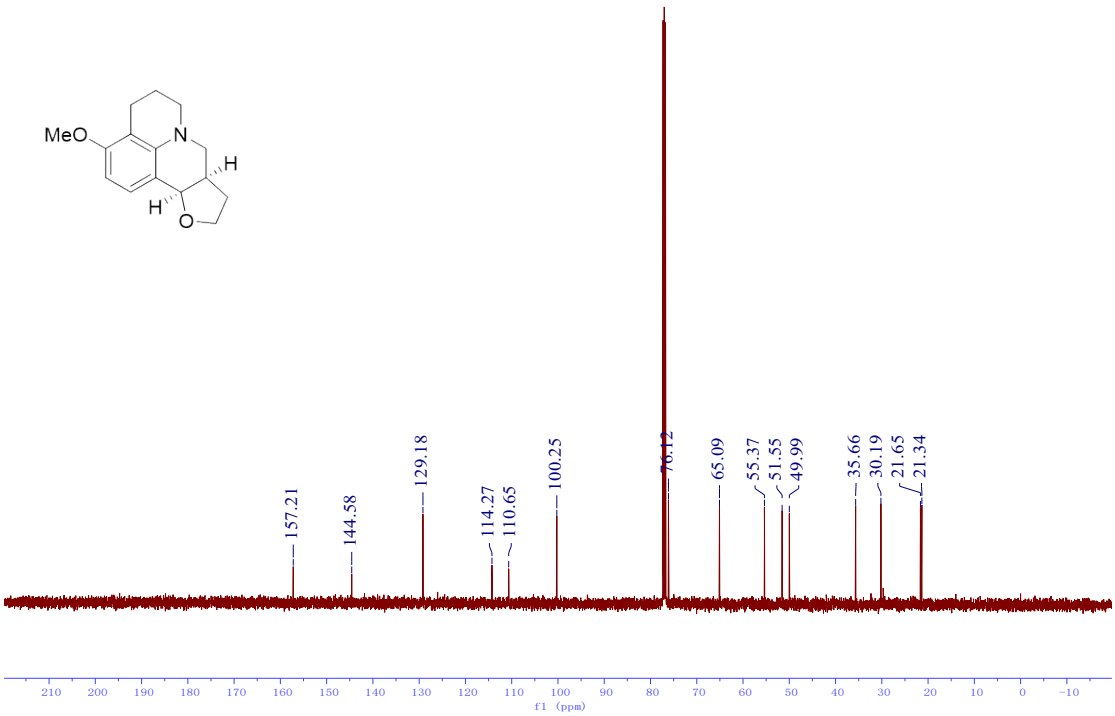
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{25}



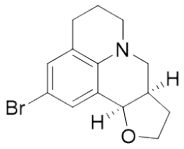
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{25}

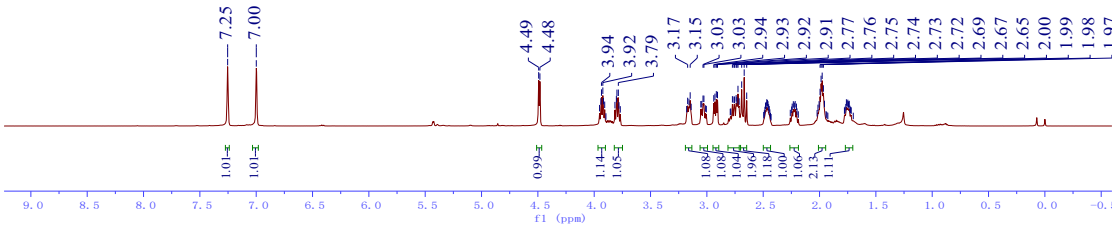


^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{26}

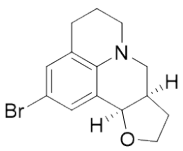


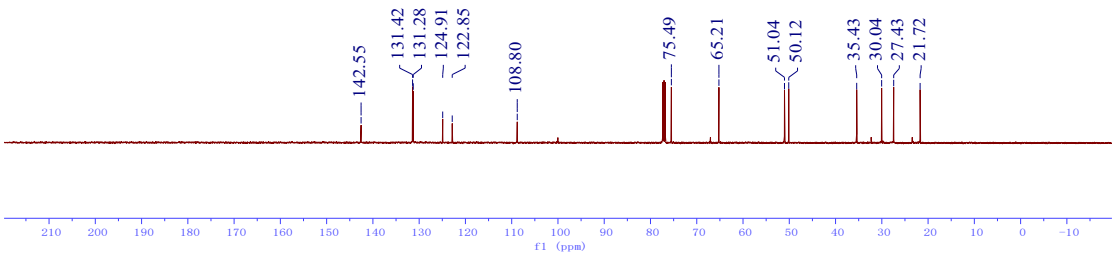
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{26}



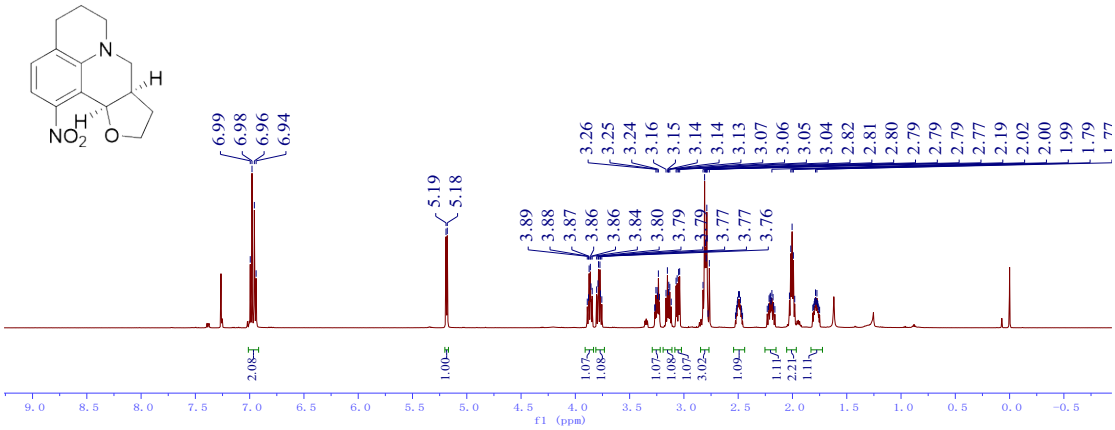


^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{27}

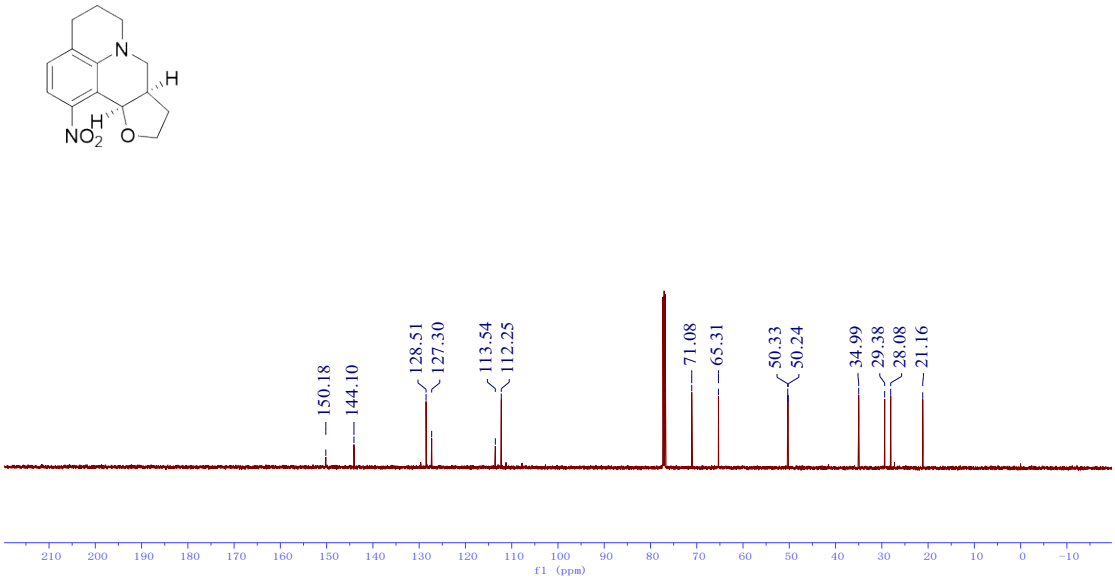




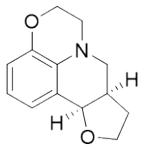
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{27}

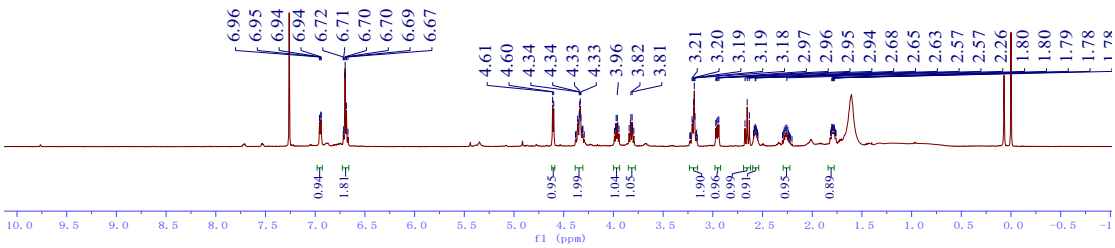


^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{28}

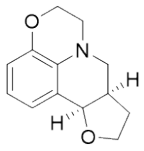


^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{28}

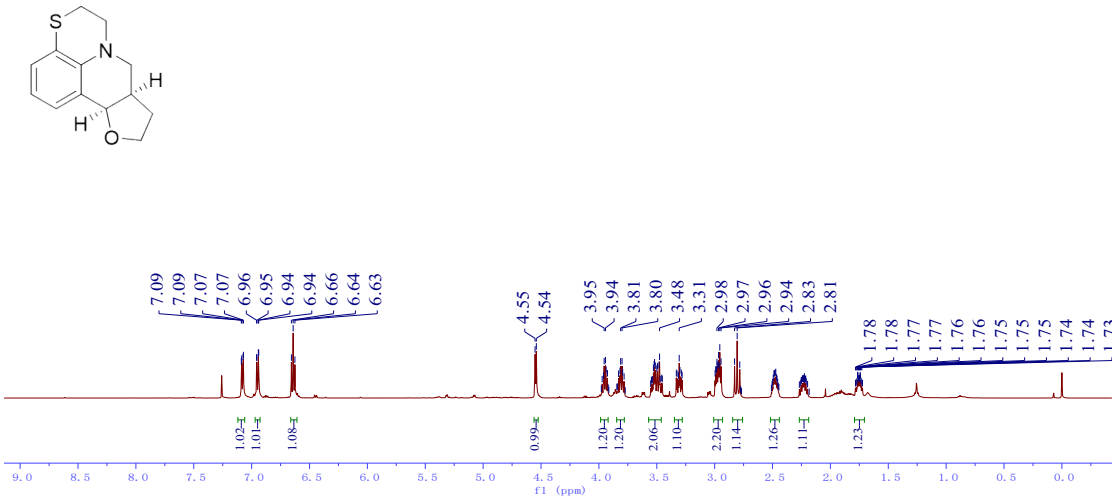




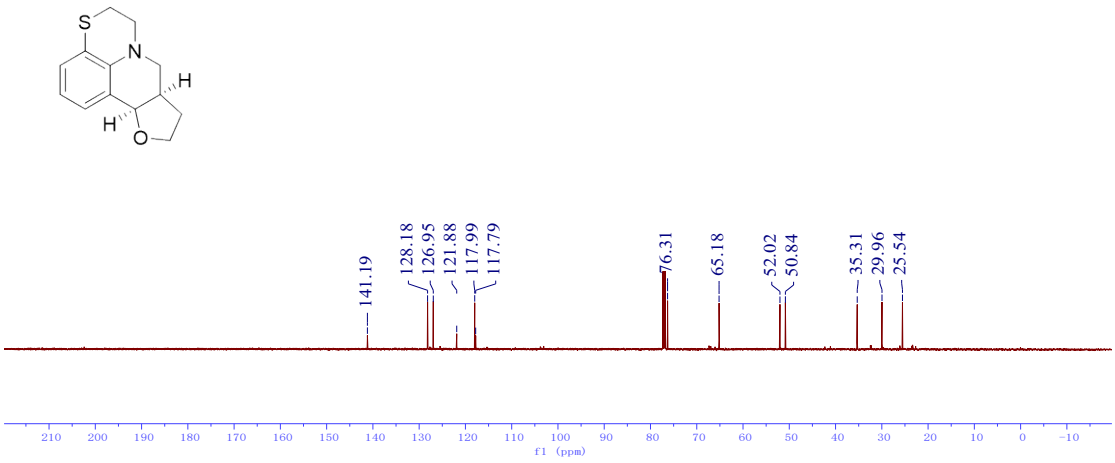
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{29}



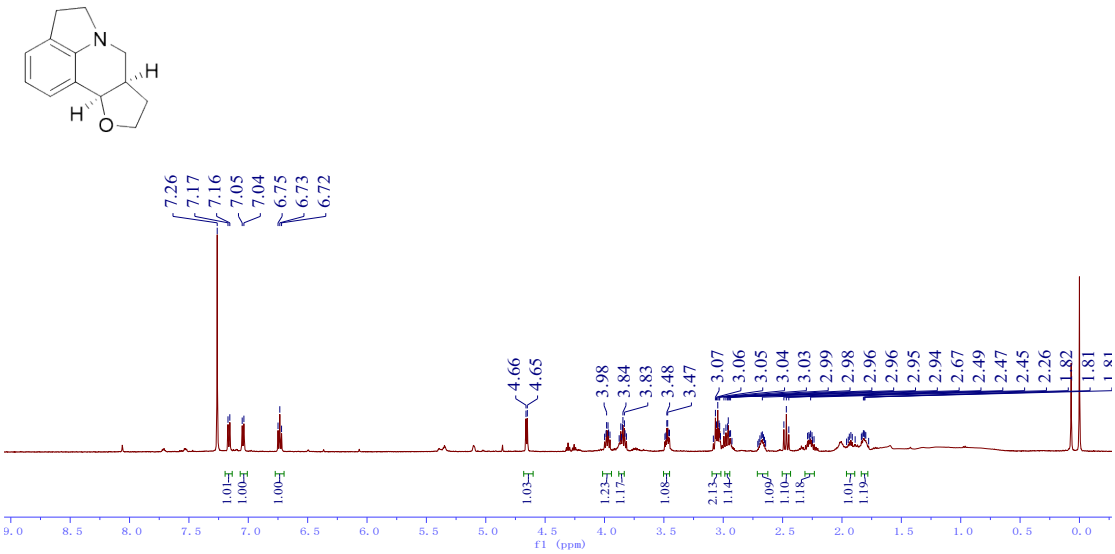
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{29}



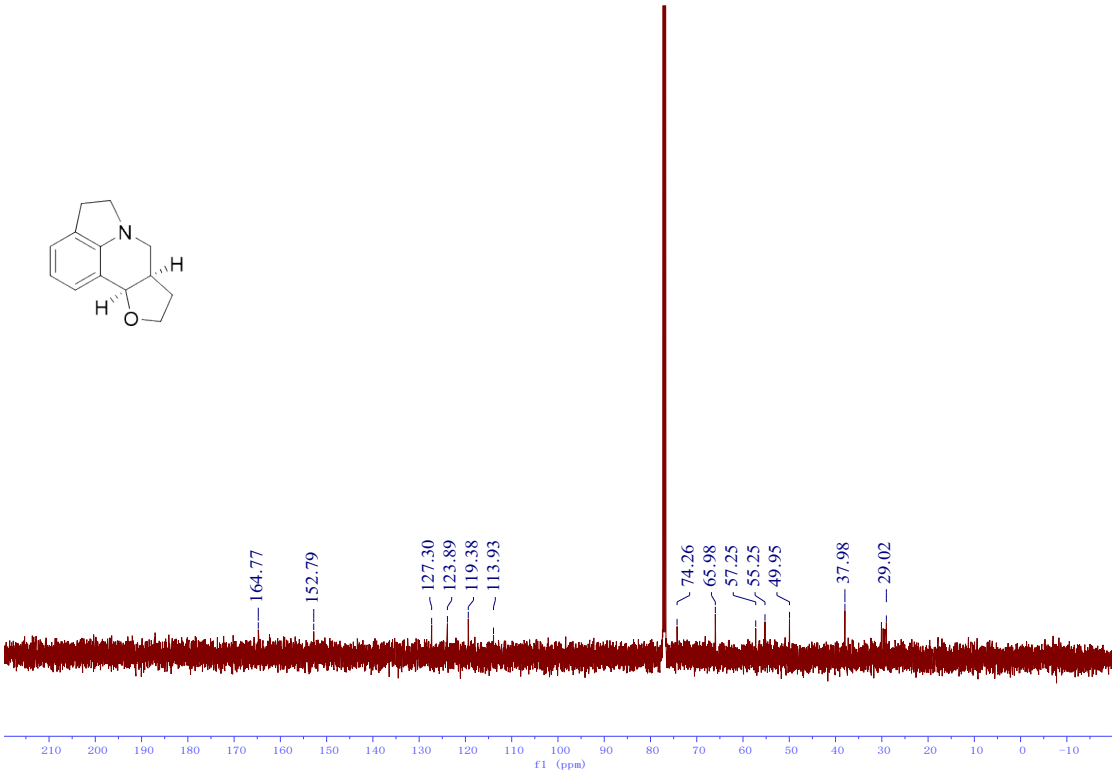
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{30}



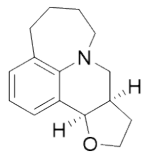
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{30}

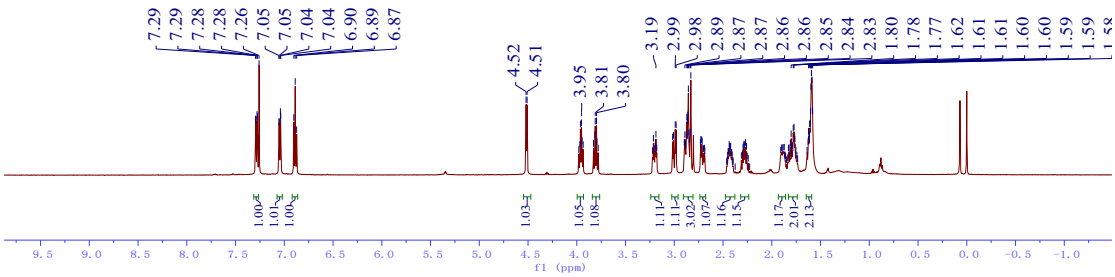


^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{31}

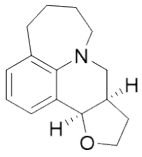


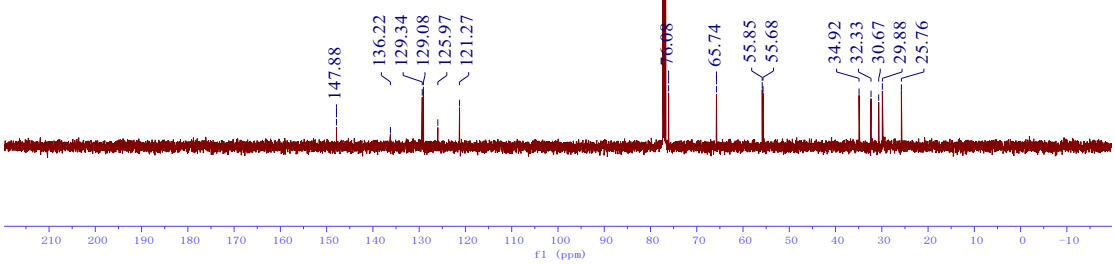
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{31}



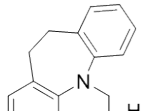


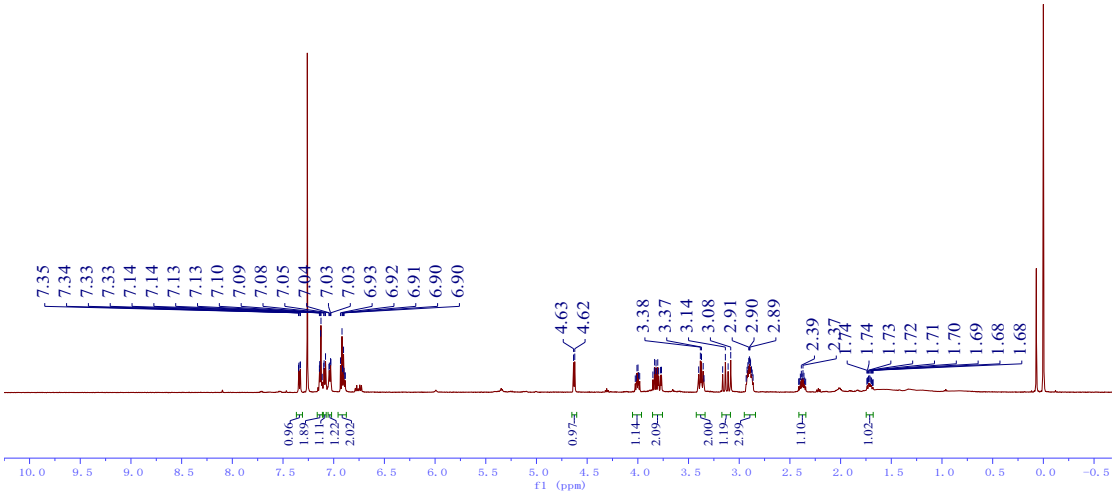
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{32}



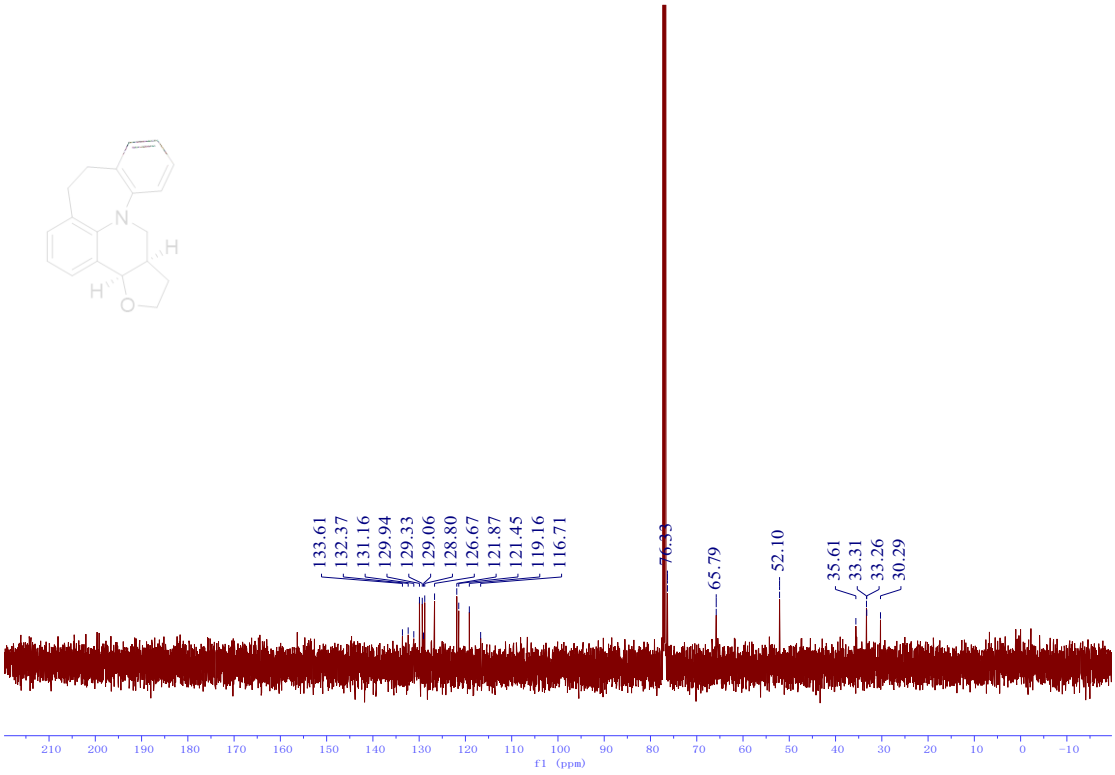


^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{32}

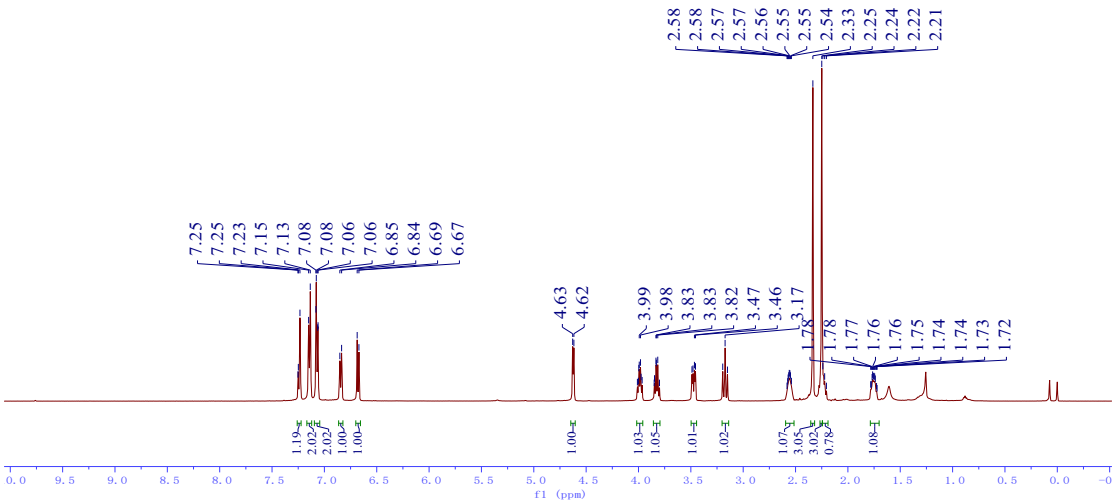




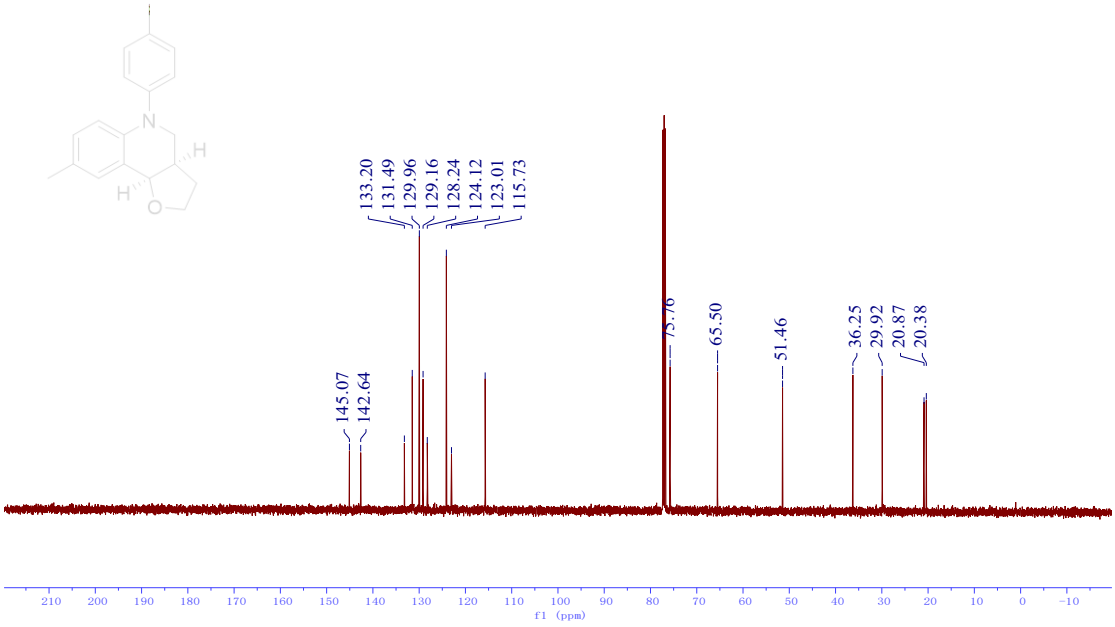
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{33}



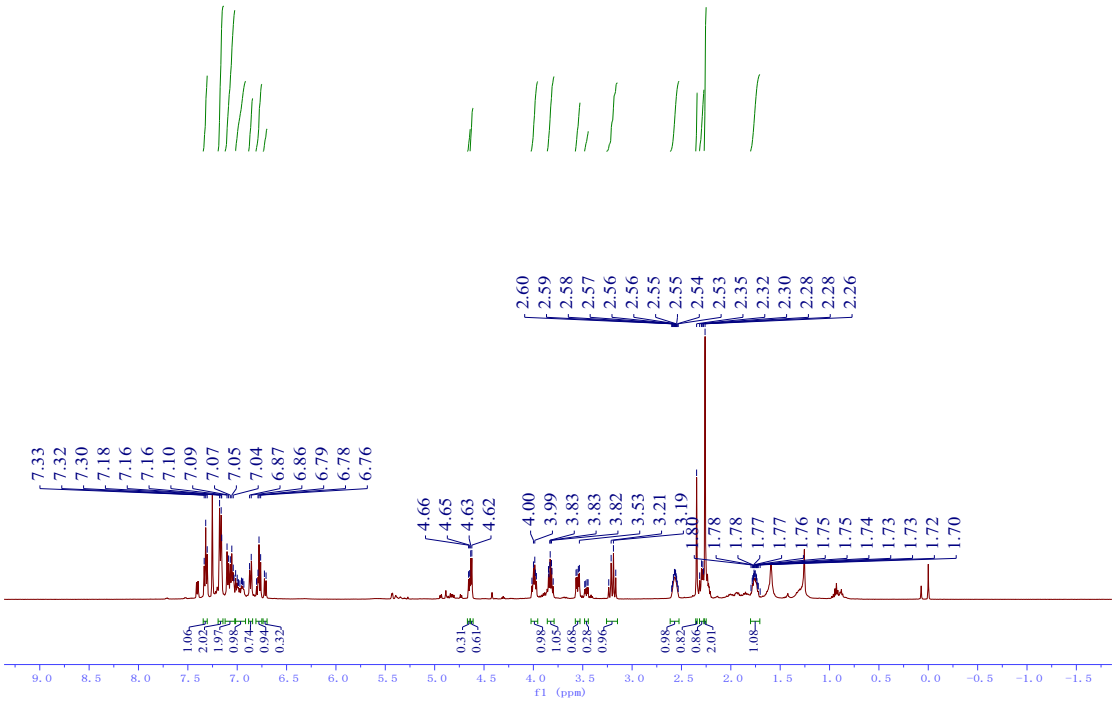
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{33}



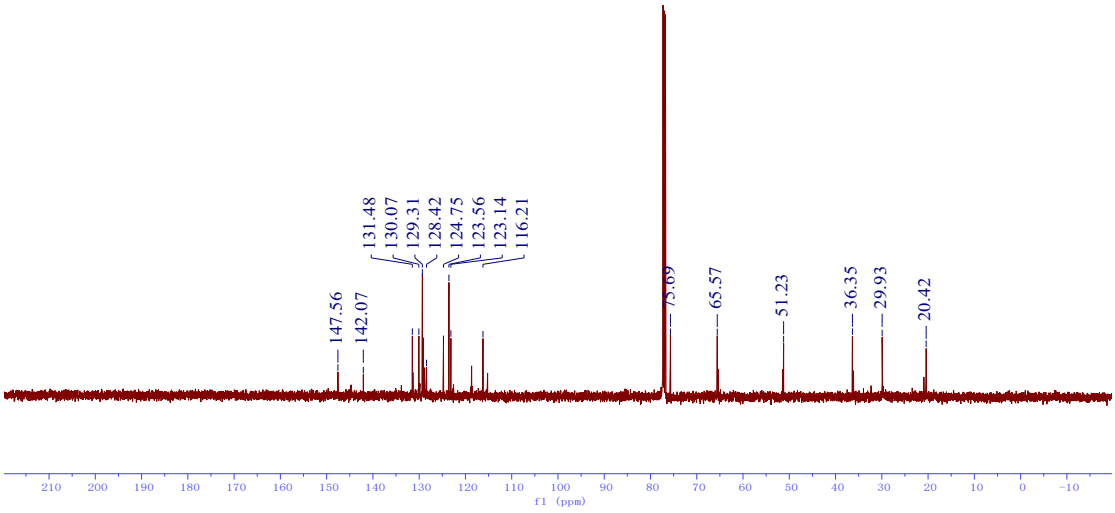
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{34}



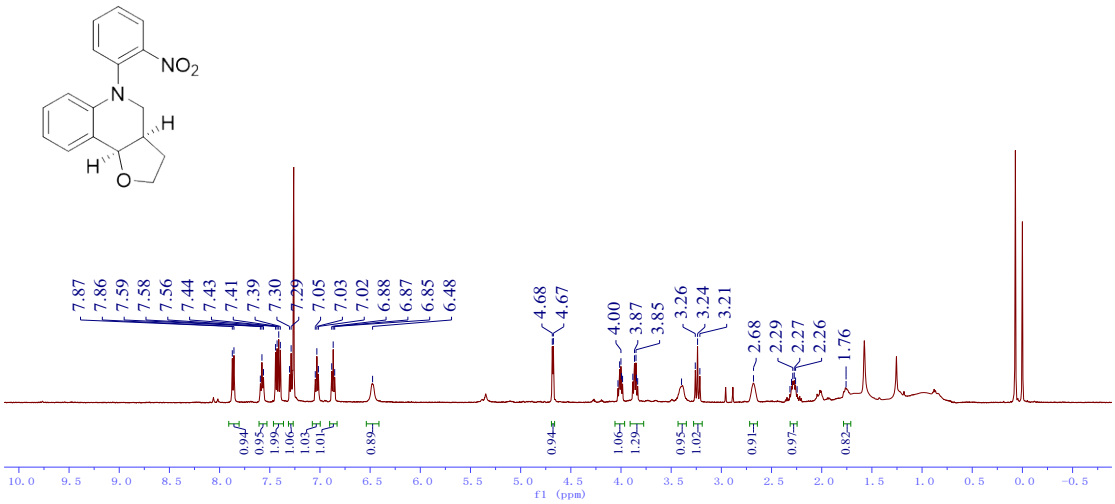
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{34}



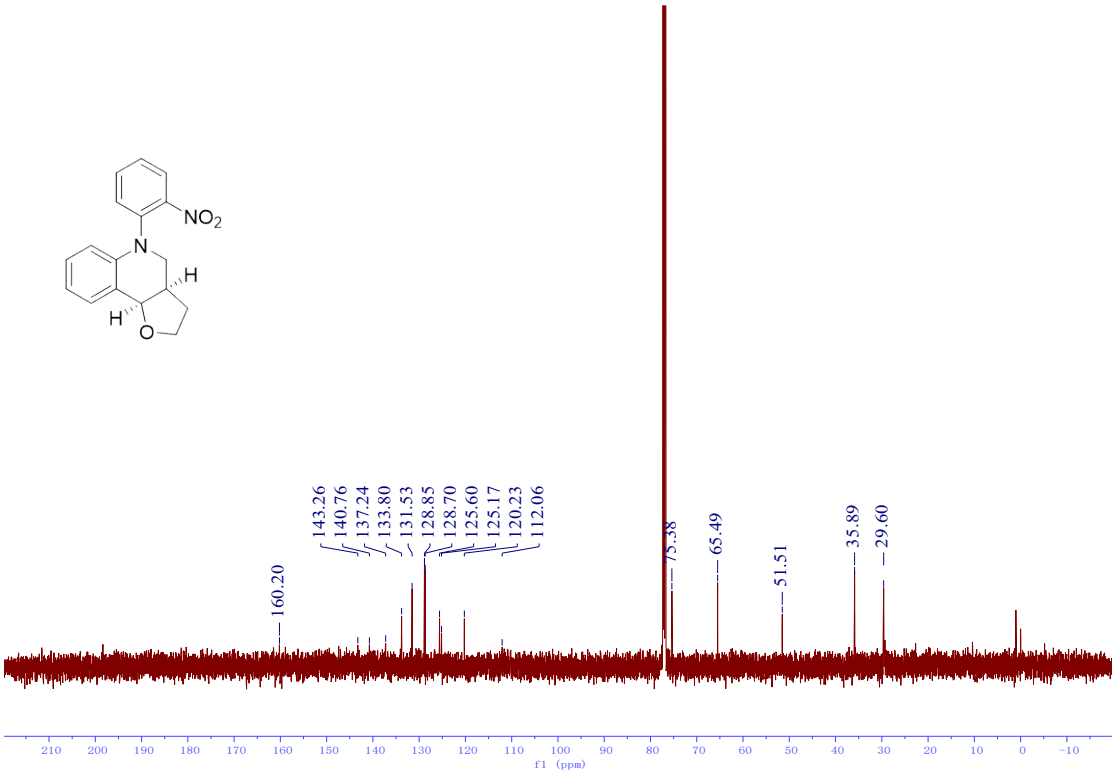
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{35}



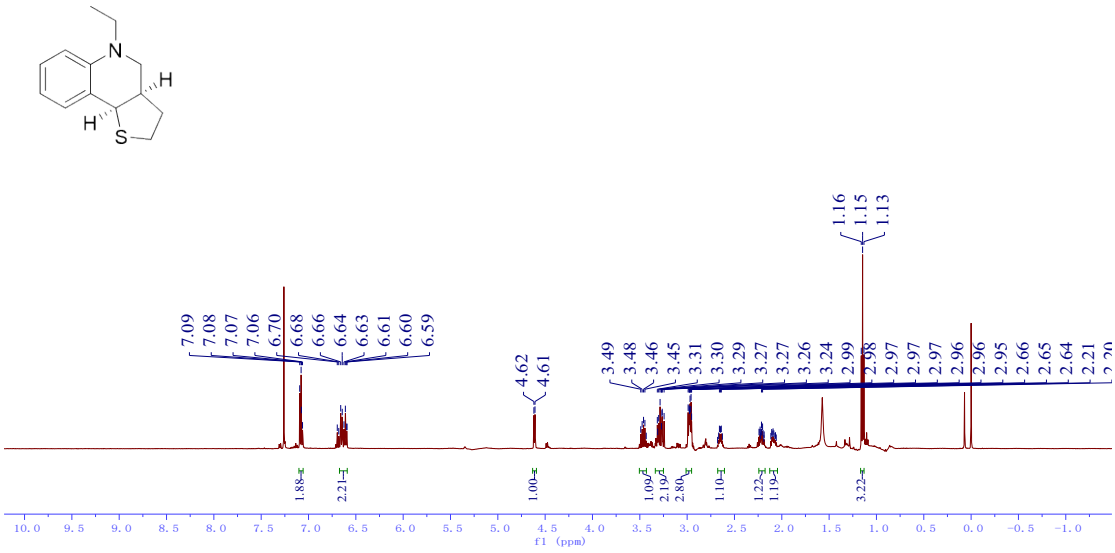
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{35}



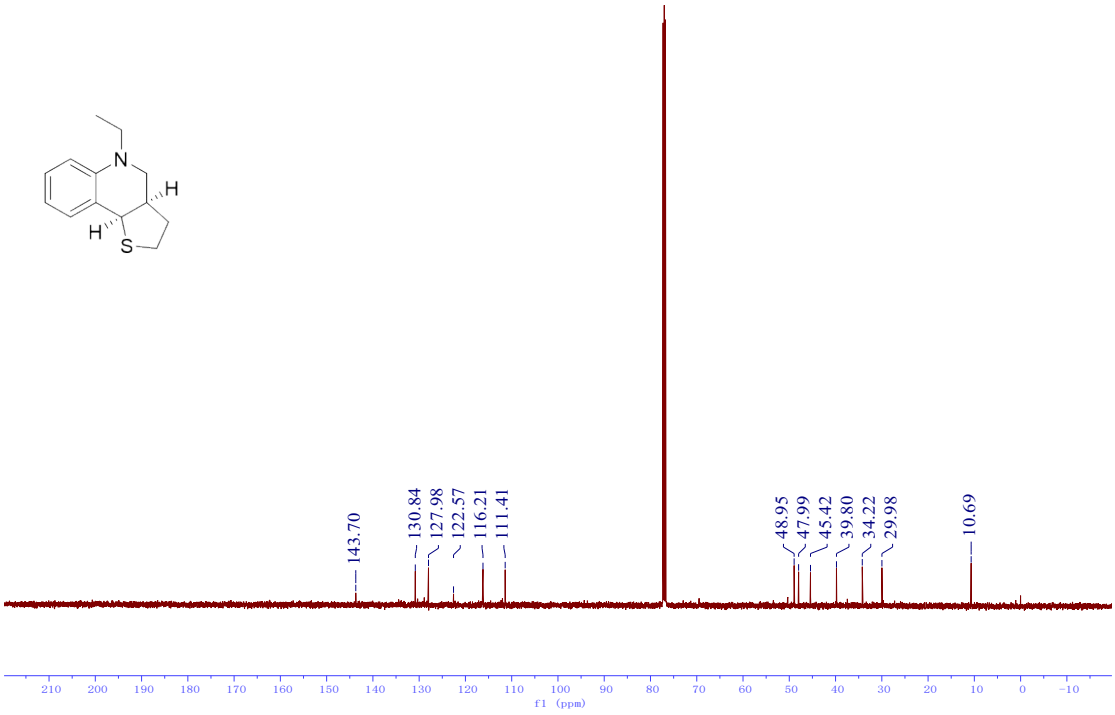
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{36}



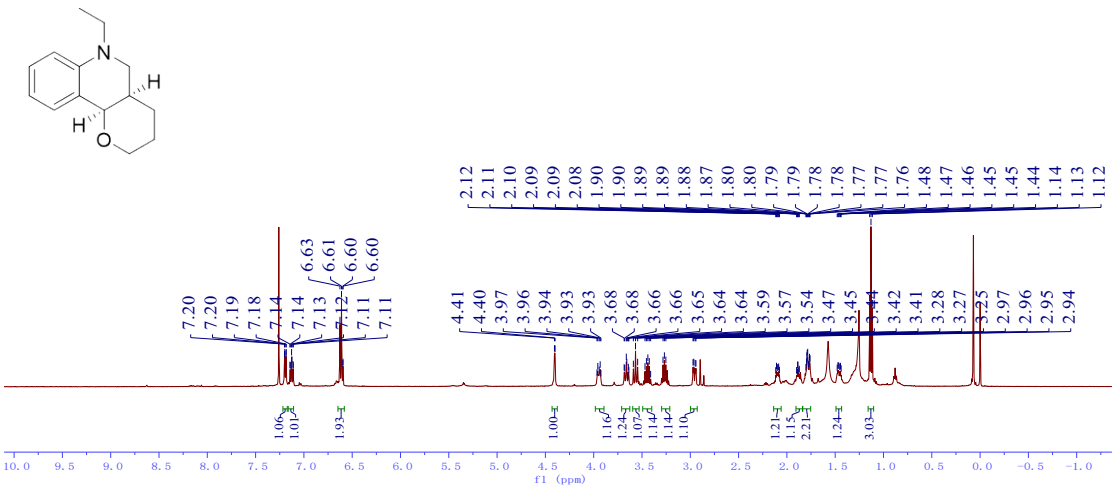
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{36}



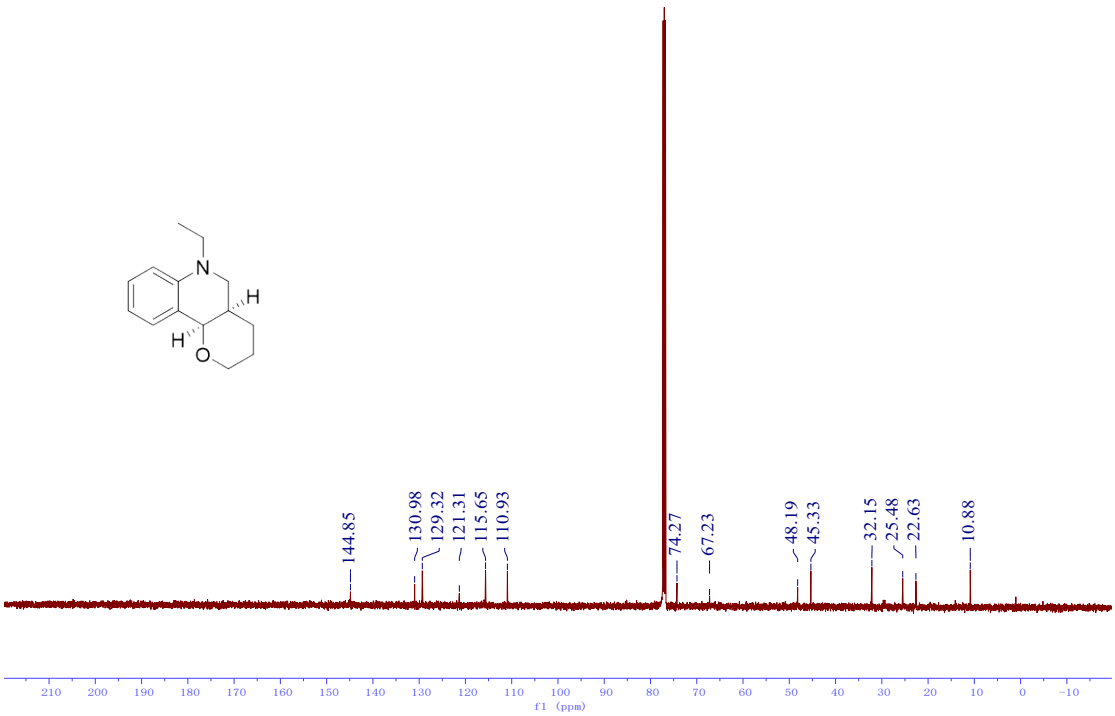
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{37}



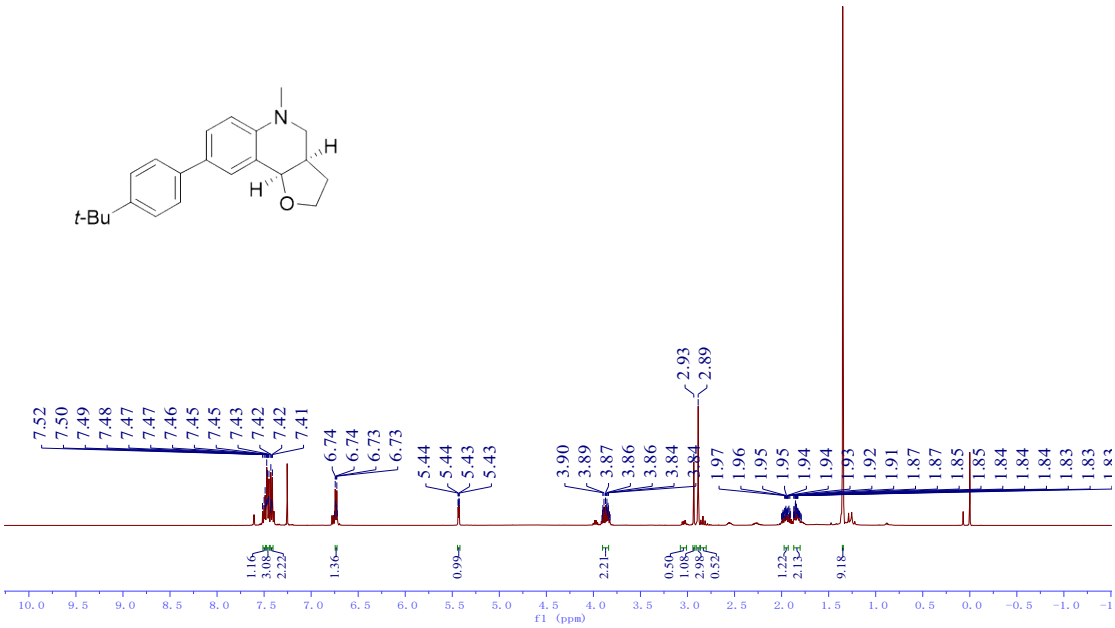
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{37}



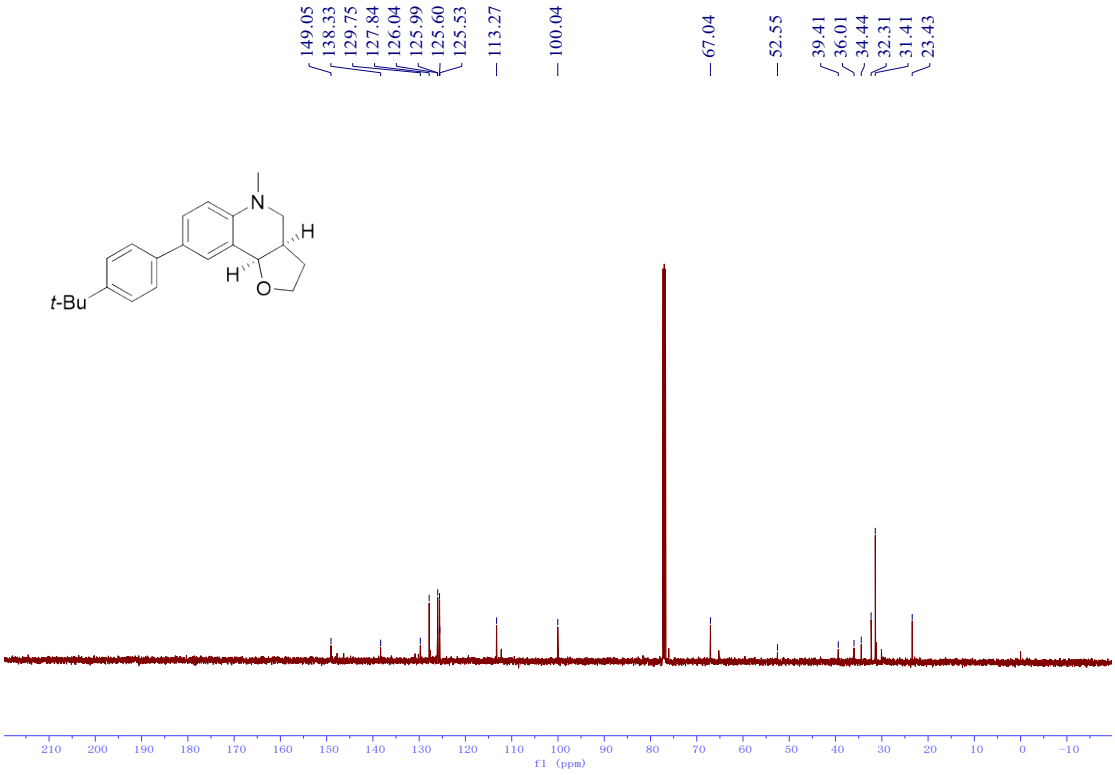
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{38}



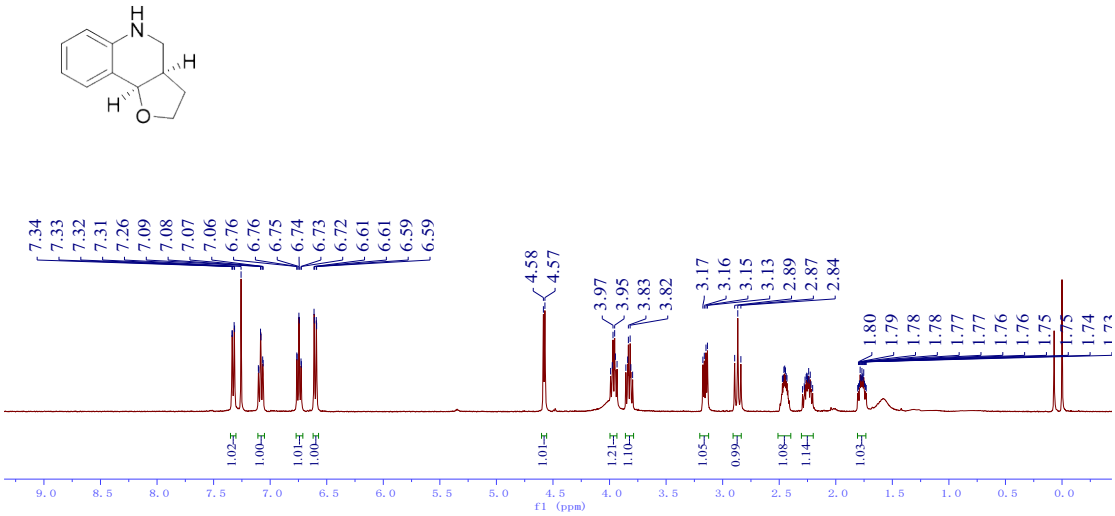
^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{38}



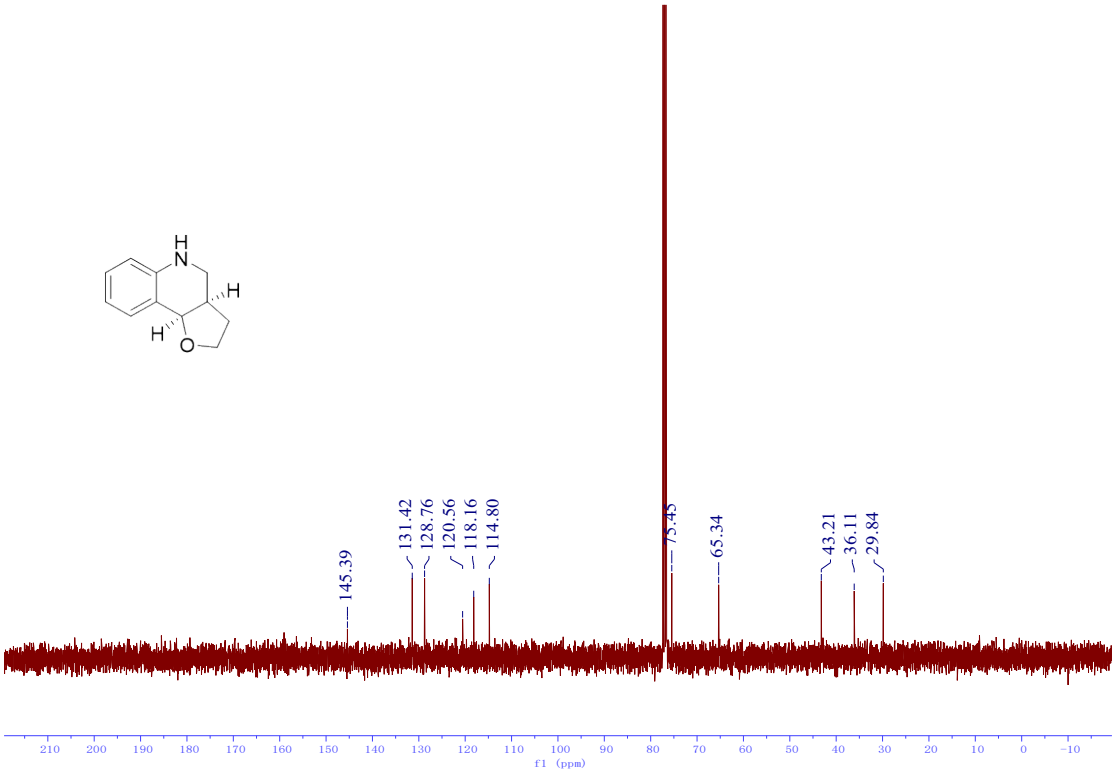
^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of D_{39}



^{13}C-NMR (126 MHz, $CDCl_3$) spectrum of D_{39}



^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of D_{40}



^{13}C-NMR (101 MHz, $CDCl_3$) spectrum of D_{40}

6. References

1. Zhao H.; Wu Y.; Ci C. G.; Tan Z. D.; Yang J.; Jiang H. F.; Dixneuf P. H.; Zhang M. Intermolecular Diastereoselective Annulation of Azaarenes into Fused N-heterocycles by Ru(II) Reductive Catalysis. *Nat. Commun*., DOI:10.1038/s41467-022-29985-z.

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