Rh(III)-Catalyzed Tandem C(sp^2)-H Allylation/*N*-Alkylation Annulation of Arene Amides with 2-Alkylidenetrimethylene Carbonates

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Supporting Information

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1. General information

Unless otherwise noted, all reactions were carried out at room temperature under an atmosphere of nitrogen with flame-dried glassware. If reaction was not conducted at room temperature, reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The dry solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under nitrogen: THF (Na-benzophenone), 1,2-dichloroethane (CaH_2), dichloromethane (CaH_2). Anhydrous CF_3CH_2OH, CH_3CN, DMF and MeOH were purchased from Acros Organics and stored under nitrogen atmosphere. Commercially available chemicals were obtained from commercial suppliers and used without further purification unless otherwise stated.

Proton NMR (^1H) were recorded at 400 MHz, and Carbon NMR (^{13}C) at 101 MHz NMR spectrometer unless otherwise stated. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br s: broad singlet for proton spectra. Coupling constants (*J*) are reported in Hertz (Hz).

High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI and ESI mode unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV_{254} plates. Visualization was accomplished with short wave UV light, or $KMnO_4$ staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use.

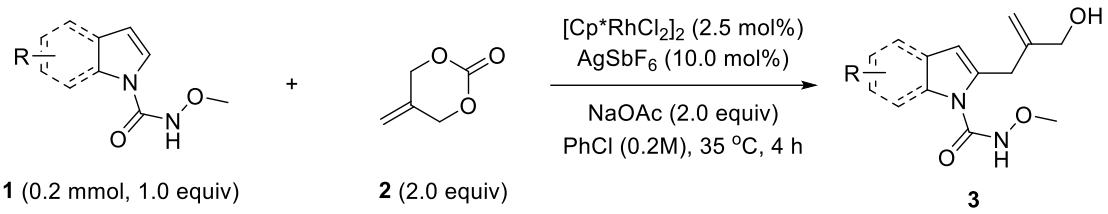
No attempts were made to optimize yields for substrate synthesis.

2. Synthesis of substrates 1, 2

The substrates of *N*-methoxy-1*H*-indole-1-carboxamide **1** and 5-methylene-1,3-dioxan-2-one **2** were prepared accroding to the previous procedure.[1-2] All the characteristic data are consistent with the data reported before.[1-2]

3. General procedure and characterization of products

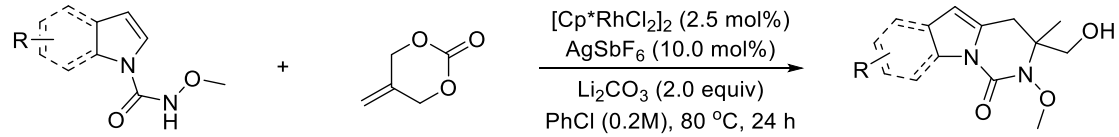
(1) General procedure A



1 (0.2 mmol, 1.0 equiv) **2** (2.0 equiv) **3**

In an oven-dried Schlenk tube under air, a mixture of *N*-methoxy-1*H*-indole-1-carboxamide derivatives **1** (0.2 mmol, 1.0 equiv), 5-methylene-1,3-dioxan-2-one **2** (0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mmol%), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10.0 mmol%), NaOAc (32.8 mg, 0.4 mmol, 2.0 equiv), and PhCl (1.0 mL) was stirred at 35 °C for 4 h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **3**.

(2) General procedure B

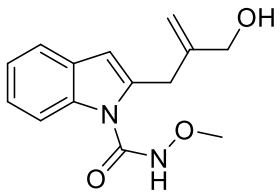


1 (0.2 mmol, 1.0 equiv) **2** (1.2 equiv) **4**

In an oven-dried Schlenk tube under air, a mixture of *N*-methoxy-1*H*-indole-1-carboxamide derivatives **1** (0.2 mmol, 1.0 equiv), 5-methylene-1,3-dioxan-2-one **2** (0.24 mmol, 1.2 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mmol%), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10.0 mmol%), Li_2CO_3 (29.5 mg, 0.4 mmol, 2.0 equiv), and PhCl (1.0 mL) was stirred at 80 °C for 24 h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **4**.

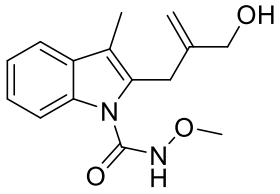
Characterization of products

2-(2-(hydroxymethyl)allyl)-*N*-methoxy-1*H*-indole-1-carboxamide (3a)



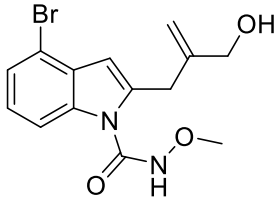
Following the general procedure A, the product **3a** was obtained in 92% yield (47.7 mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.18. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.15 (m, 2H), 6.45 (s, 1H), 5.16 (s, 1H), 4.87 (s, 1H), 4.15 (s, 2H), 3.90 (s, 3H), 3.75 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.56, 146.21, 137.19, 136.04, 128.97, 123.28, 122.35, 120.38, 112.87, 112.84, 108.01, 65.46, 64.69, 31.66. ESI-MS: calculated $C_{14}H_{16}N_2O_3Na$ $[M+Na]^+$ 283.1053; Found 283.1055.

2-(2-(hydroxymethyl)allyl)-*N*-methoxy-3-methyl-1*H*-indole-1-carboxamide (3b)



Following the general procedure A, the product **3b** was obtained in 79% yield (43.4 mg, 0.20 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.75 (m, 1H), 7.53 – 7.41 (m, 1H), 7.30 – 7.05 (m, 2H), 5.11 (s, 1H), 4.74 (s, 1H), 4.09 (s, 2H), 3.86 (s, 3H), 3.71 (s, 2H), 2.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.83, 146.23, 135.28, 131.83, 130.23, 123.57, 122.11, 118.67, 115.43, 112.99, 112.50, 65.76, 64.77, 29.24, 8.68. ESI-MS: calculated $C_{15}H_{18}N_2O_3Na$ $[M+Na]^+$ 297.1209; Found 297.1210.

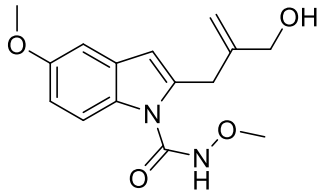
4-bromo-2-(2-(hydroxymethyl)allyl)-*N*-methoxy-1*H*-indole-1-carboxamide (3c)



Following the general procedure A, the product **3c** was obtained in 58% yield (39.2 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.19. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 7.06 (t, *J* = 8.0 Hz, 1H), 6.48 (s, 1H), 5.15 (s, 1H), 4.90 (s, 1H), 4.11 (s, 2H), 3.86 (s, 3H), 3.70 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.96, 145.65, 137.81, 136.36, 129.55, 125.24, 124.22, 114.15, 113.73, 111.98, 107.69, 65.61,

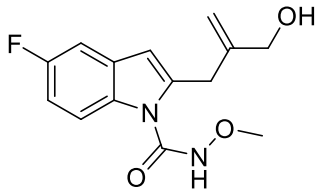
64.80, 31.66. ESI-MS: calculated $C_{14}H_{15}BrN_2O_3Na$ $[M+Na]^+$ 361.0158; Found 361.0157.

2-(2-(hydroxymethyl)allyl)-*N*,5-dimethoxy-1*H*-indole-1-carboxamide (3d)



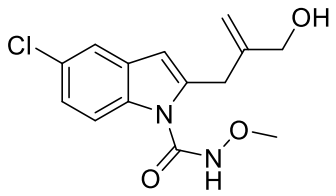
Following the general procedure A, the product **3d** was obtained in 88% yield (50.8 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.16. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.6 Hz, 1H), 6.94 (s, 1H), 6.83 (d, *J* = 9.0 Hz, 1H), 6.35 (s, 1H), 5.12 (s, 1H), 4.81 (s, 1H), 4.05 (s, 2H), 3.84 (dd, *J* = 12.3, 2.8 Hz, 6H), 3.68 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.52, 152.87, 146.45, 137.99, 130.85, 129.74, 113.75, 112.32, 112.13, 107.92, 102.64, 65.25, 64.53, 55.76, 31.75. ESI-MS: calculated $C_{15}H_{18}N_2O_4Na$ $[M+Na]^+$ 313.1159; Found 313.1162.

5-fluoro-2-(2-(hydroxymethyl)allyl)-*N*-methoxy-1*H*-indole-1-carboxamide (3e)



Following the general procedure A, the product **3e** was obtained in 70% yield (39.1 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.18. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 7.70 (dd, *J* = 9.0, 4.4 Hz, 1H), 7.13 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.95 (td, *J* = 9.1, 2.5 Hz, 1H), 6.39 (s, 1H), 5.16 (s, 1H), 4.87 (s, 1H), 4.14 (s, 2H), 3.87 (s, 3H), 3.72 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.09 (d, *J* = 238.5 Hz), 152.36, 146.02, 138.60, 132.59, 129.75 (d, *J* = 10.1 Hz), 114.04 (d, *J* = 9.3 Hz), 113.51, 111.24 (d, *J* = 25.5 Hz), 108.05 (d, *J* = 4.0 Hz), 105.67 (d, *J* = 23.7 Hz), 65.68, 64.81, 31.80. ^{19}F NMR (471 MHz, $CDCl_3$) δ -121.37. ESI-MS: calculated $C_{14}H_{15}FN_2O_3Na$ $[M+Na]^+$ 301.0959; Found 301.0960.

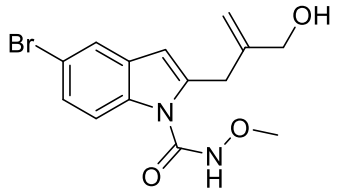
5-chloro-2-(2-(hydroxymethyl)allyl)-*N*-methoxy-1*H*-indole-1-carboxamide (3f)



Following the general procedure A, the product **3f** was obtained in 58% yield (34.3 mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ

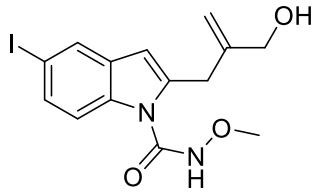
9.25 (s, 1H), 7.66 (d, *J* = 8.8 Hz, 1H), 7.43 (d, *J* = 2.0 Hz, 1H), 7.16 (dd, *J* = 8.8, 2.1 Hz, 1H), 5.15 (s, 1H), 4.86 (s, 1H), 4.11 (s, 2H), 3.86 (s, 3H), 3.70 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.56, 146.21, 137.19, 136.04, 128.97, 123.28, 122.35, 120.38, 112.87, 112.84, 108.01, 65.46, 64.69, 31.66. ESI-MS: calculated $C_{14}H_{15}ClN_2O_3Na$ $[M+Na]^+$ 317.0663; Found 317.0665.

5-bromo-2-(2-(hydroxymethyl)allyl)-*N*-methoxy-1*H*-indole-1-carboxamide (3g)



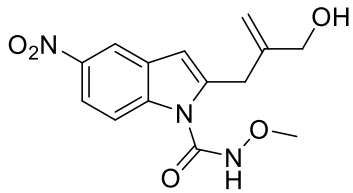
Following the general procedure A, the product **3g** was obtained in 53% yield (36.2 mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (s, 1H), 7.61 (dd, *J* = 6.7, 5.4 Hz, 2H), 7.29 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.36 (s, 1H), 5.16 (s, 1H), 4.87 (s, 1H), 4.12 (s, 2H), 3.87 (s, 3H), 3.71 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.09, 145.90, 138.24, 134.91, 130.66, 126.13, 122.93, 115.64, 114.50, 113.61, 107.36, 65.67, 64.84, 31.68. ESI-MS: calculated $C_{14}H_{15}BrN_2O_3Na$ $[M+Na]^+$ 361.0158; Found 361.0157.

2-(2-(hydroxymethyl)allyl)-5-iodo-*N*-methoxy-1*H*-indole-1-carboxamide (3h)



Following the general procedure A, the product **3h** was obtained in 54% yield (41.9 mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.25. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.26 (s, 1H), 7.80 (s, 1H), 7.48 (dd, *J* = 19.8, 8.6 Hz, 2H), 6.34 (s, 1H), 5.14 (s, 1H), 4.85 (s, 1H), 4.10 (s, 2H), 3.85 (s, 3H), 3.69 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.05, 145.92, 137.87, 135.46, 131.76, 131.32, 129.18, 114.94, 113.64, 107.11, 86.25, 65.71, 64.87, 31.64. ESI-MS: calculated $C_{14}H_{15}IN_2O_3Na$ $[M+Na]^+$ 409.0019; Found 409.0024.

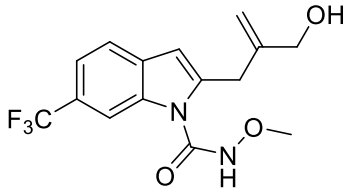
2-(2-(hydroxymethyl)allyl)-*N*-methoxy-5-nitro-1*H*-indole-1-carboxamide (3i)



Following the general procedure A, the product **3i** was obtained in 49% yield (30.0 mg, 0.20 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF

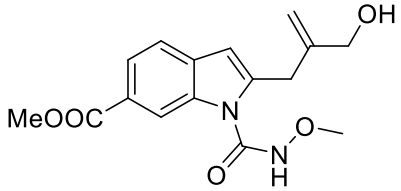
(Petroleum ether/EtOAc 2:1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (s, 1H), 8.36 (d, *J* = 2.2 Hz, 1H), 8.07 (dd, *J* = 9.1, 2.3 Hz, 1H), 7.82 (d, *J* = 9.1 Hz, 1H), 6.57 (s, 1H), 5.23 (d, *J* = 0.9 Hz, 1H), 4.97 (s, 1H), 4.19 (s, 2H), 3.93 (s, 3H), 3.78 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.10, 145.27, 143.42, 140.06, 139.44, 128.45, 118.70, 116.77, 114.64, 113.19, 108.49, 65.80, 64.99, 31.71. ESI-MS: calculated $C_{14}H_{15}N_3O_5Na$ $[M+Na]^+$ 328.0904; Found 328.0908.

2-(2-(hydroxymethyl)allyl)-*N*-methoxy-6-(trifluoromethyl)-1*H*-indole-1-carboxamide (3j)



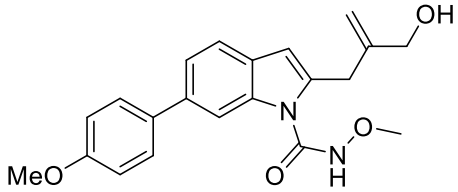
Following the general procedure A, the product **3j** was obtained in 44% yield (28.8 mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.16. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 8.07 (d, *J* = 0.7 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.42 (dd, *J* = 8.2, 1.0 Hz, 1H), 6.49 (d, *J* = 0.5 Hz, 1H), 5.19 (d, *J* = 1.1 Hz, 1H), 4.91 (s, 1H), 4.16 (s, 2H), 3.90 (s, 3H), 3.77 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.76, 145.75, 139.61, 135.41, 131.40, 125.43 (q, *J* = 32.0 Hz), 124.93 (q, *J* = 271.9 Hz), 120.68, 119.23 (q, *J* = 3.4 Hz), 114.00, 110.65 (q, *J* = 4.4 Hz), 107.87, 65.77, 64.93, 31.76. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.85. ESI-MS: calculated $C_{15}H_{15}F_3N_2O_3Na$ $[M+Na]^+$ 351.0927; Found 351.0935.

methyl 2-(2-(hydroxymethyl)allyl)-1-(methoxycarbamoyl)-1*H*-indole-6-carboxylate (3k)



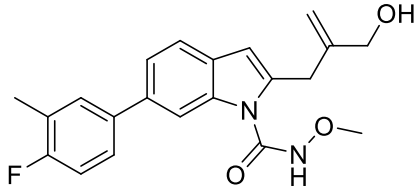
Following the general procedure A, the product **3k** was obtained in 68% yield (43.3 mg, 0.20 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 1:1 v/v). RF (Petroleum ether/EtOAc 1:1): 0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.41 (s, 1H), 7.83 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 6.48 (s, 1H), 5.17 (d, *J* = 0.9 Hz, 1H), 4.88 (s, 1H), 4.14 (s, 2H), 3.93 (s, 3H), 3.88 (s, 3H), 3.76 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.98, 151.77, 145.81, 140.93, 135.47, 132.76, 124.80, 123.52, 120.05, 114.64, 113.51, 107.86, 65.75, 64.92, 52.30, 31.78. ESI-MS: calculated $C_{16}H_{18}N_2O_5Na$ $[M+Na]^+$ 341.1108; Found 341.1115.

2-(2-(hydroxymethyl)allyl)-*N*-methoxy-6-(4-methoxyphenyl)-1*H*-indole-1-carboxamide (3l)



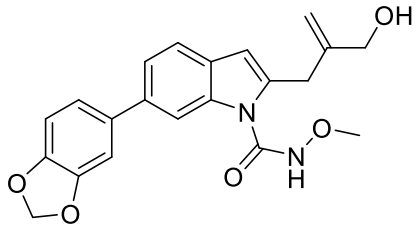
Following the general procedure A, the product **3l** was obtained in 84% yield (61.2 mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 7.90 (s, 1H), 7.50 (m, *J* = 13.4, 8.5 Hz, 3H), 7.36 (dd, *J* = 8.1, 1.5 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.40 (s, 1H), 5.12 (s, 1H), 4.86 (s, 1H), 4.09 (s, 2H), 3.85 (s, 3H), 3.83 (s, 3H), 3.67 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.98, 152.47, 146.25, 137.42, 136.73, 136.48, 134.34, 128.39, 127.78, 121.77, 120.53, 114.32, 113.04, 111.06, 107.89, 65.61, 64.77, 55.45, 31.72. ESI-MS: calculated $C_{21}H_{22}N_2O_4Na$ $[M+Na]^+$ 389.1472; Found 389.1471.

6-(4-fluoro-3-methylphenyl)-2-(2-(hydroxymethyl)allyl)-*N*-methoxy-1*H*-indole-1-carboxamide (3m)



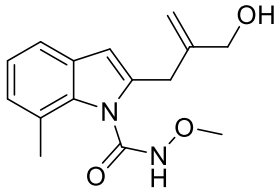
Following the general procedure A, the product **3m** was obtained in 84% yield (62.1 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.19. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 7.92 (s, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.44 – 7.32 (m, 3H), 7.08 – 7.00 (m, 1H), 6.42 (s, 1H), 5.15 (s, 1H), 4.88 (s, 1H), 4.12 (s, 2H), 3.86 (s, 3H), 3.70 (s, 2H), 2.33 (d, *J* = 1.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.98 (d, *J* = 244.8 Hz), 152.38, 146.23, 137.62 (d, *J* = 3.6 Hz), 137.39, 136.77, 136.16, 130.46 (d, *J* = 5.1 Hz), 128.08, 126.18 (d, *J* = 8.0 Hz), 125.16 (d, *J* = 17.4 Hz), 121.99, 120.55, 115.34 (d, *J* = 22.4 Hz), 113.35, 111.49, 107.97, 65.71, 64.82, 31.78, 14.83 (d, *J* = 3.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.47. ESI-MS: calculated $C_{21}H_{21}FN_2O_3Na$ $[M+Na]^+$ 391.1428; Found 391.1433.

6-(benzo[d][1,3]dioxol-5-yl)-2-(2-(hydroxymethyl)allyl)-*N*-methoxy-1*H*-indole-1-carboxamide (3n)



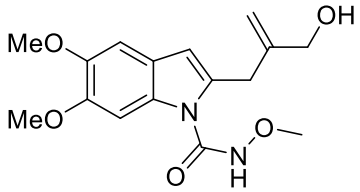
Following the general procedure A, the product **3n** was obtained in 80% yield (61.1 mg, 0.20 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.18. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (s, 1H), 7.85 (s, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.31 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.10 – 7.00 (m, 2H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.38 (s, 1H), 5.96 (s, 2H), 5.11 (s, 1H), 4.84 (s, 1H), 4.07 (s, 2H), 3.83 (s, 3H), 3.66 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.41, 148.16, 146.91, 146.22, 137.51, 136.66, 136.58, 136.20, 127.96, 121.89, 120.83, 120.51, 113.11, 111.25, 108.68, 107.94, 107.88, 101.23, 65.62, 64.79, 31.73. ESI-MS: calculated $C_{21}H_{20}N_2O_5Na$ $[M+Na]^+$ 403.1264; Found 403.1268.

2-(2-(hydroxymethyl)allyl)-*N*-methoxy-7-methyl-1*H*-indole-1-carboxamide (3o)



Following the general procedure A, the product **3o** was obtained in 74% yield (40.4 mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.18. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.35 (s, 1H), 5.15 (s, 1H), 4.98 (s, 1H), 4.09 (s, 2H), 3.87 (s, 3H), 3.58 (s, 2H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.59, 145.49, 138.13, 136.89, 129.46, 125.37, 121.98, 118.12, 113.96, 109.00, 105.67, 65.36, 64.13, 31.03, 18.55. ESI-MS: calculated $C_{15}H_{18}N_2O_3Na$ $[M+Na]^+$ 297.1209; Found 297.1210.

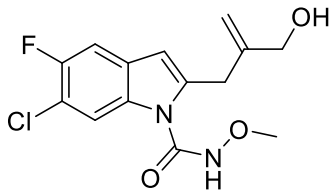
2-(2-(hydroxymethyl)allyl)-*N*,5,6-trimethoxy-1*H*-indole-1-carboxamide (3p)



Following the general procedure A, the product **3p** was obtained in 80% yield (51.1 mg, 0.20 mmol) as a pale yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.19. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.36 (s, 1H), 7.38 (s, 1H), 6.87 (s, 1H), 6.27 (s, 1H), 5.12 (s, 1H), 4.85 (s, 1H), 4.09 (s, 2H), 3.85 – 3.79 (m, 9H), 3.64 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.82, 147.07, 146.57, 146.26, 134.57, 130.53, 121.64, 113.20, 108.25, 101.77, 97.60, 65.53, 64.60, 56.25, 56.18, 31.82.

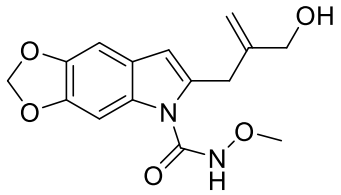
ESI-MS: calculated $C_{16}H_{20}N_2O_5Na$ $[M+Na]^+$ 343.1264; Found 343.1269.

6-chloro-5-fluoro-2-(2-(hydroxymethyl)allyl)-*N*-methoxy-1*H*-indole-1-carboxamide (3q)



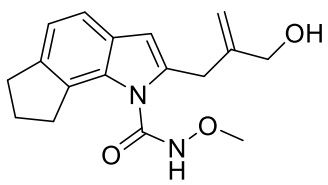
Following the general procedure A, the product **3q** was obtained in 29% yield (18.0 mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.17. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 6.3 Hz, 1H), 7.18 (d, *J* = 9.1 Hz, 1H), 6.34 (s, 1H), 5.13 (s, 1H), 4.83 (s, 1H), 4.06 (s, 2H), 3.86 (s, 3H), 3.69 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.27 (d, *J* = 240.9 Hz), 151.98, 145.84, 139.11, 132.49, 127.96 (d, *J* = 9.3 Hz), 116.53 (d, *J* = 20.6 Hz), 114.70, 113.34, 107.45, 106.42 (d, *J* = 23.4 Hz), 65.30, 64.67, 31.71. ^{19}F NMR (376 MHz, $CDCl_3$) δ -123.69. ESI-MS: calculated $C_{14}H_{14}ClFN_2O_3Na$ $[M+Na]^+$ 335.0569; Found 335.0567.

6-(2-(hydroxymethyl)allyl)-*N*-methoxy-5*H*-[1,3]dioxolo[4,5-f]indole-5-carboxamide (3r)



Following the general procedure A, the product **3r** was obtained in 68% yield (41.5 mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 1:1 v/v). RF (Petroleum ether/EtOAc 1:1): 0.18. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 1H), 6.80 (s, 1H), 6.23 (s, 1H), 5.88 (s, 2H), 5.08 (s, 1H), 4.79 (s, 1H), 4.02 (s, 2H), 3.81 (s, 3H), 3.61 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.71, 146.56, 145.34, 144.14, 135.36, 130.92, 122.83, 112.60, 108.10, 101.01, 99.02, 94.90, 65.25, 64.55, 31.76. ESI-MS: calculated $C_{15}H_{16}N_2O_5Na$ $[M+Na]^+$ 327.0951; Found 327.0952.

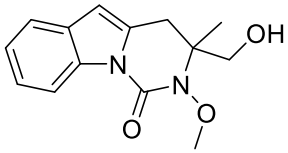
2-(2-(hydroxymethyl)allyl)-*N*-methoxy-7,8-dihydrocyclopenta[g]indole-1(6*H*)-carboxamide (3s)



Following the general procedure A, the product **3s** was obtained in 87% yield (52.2 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.1 Hz, 1H), 7.07 (d,

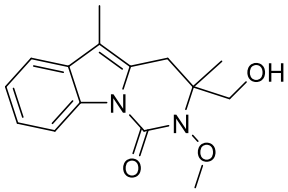
J = 7.8 Hz, 1H), 6.33 (s, 1H), 5.12 (s, 1H), 4.89 (s, 1H), 4.02 (s, 2H), 3.85 (s, 3H), 3.59 (s, 2H), 3.05 (t, *J* = 7.1 Hz, 2H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.17 – 2.07 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.56, 146.21, 137.19, 136.04, 128.97, 123.28, 122.35, 120.38, 112.87, 112.84, 108.01, 65.46, 64.69, 31.66. ESI-MS: calculated $C_{17}H_{20}N_2O_3Na$ $[M+Na]^+$ 323.1366; Found 323.1369.

3-(hydroxymethyl)-2-methoxy-3-methyl-3,4-dihydropyrimido[1,6-a]indol-1(2*H*)-one (4a)



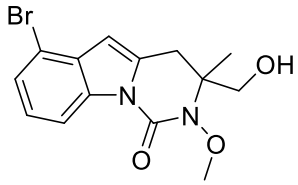
Following the general procedure B, the product **4a** was obtained in 77% yield (40.0 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.21. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, J = 8.1 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.28 (dd, J = 11.0, 3.9 Hz, 1H), 7.21 (t, J = 7.1 Hz, 1H), 6.29 (s, 1H), 3.96 (s, 3H), 3.81 (d, J = 11.3 Hz, 1H), 3.66 (d, J = 11.3 Hz, 1H), 3.38 (d, J = 16.1 Hz, 1H), 3.04 (d, J = 16.1 Hz, 1H), 1.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.27, 135.54, 131.94, 130.04, 124.01, 123.27, 120.08, 115.49, 104.57, 66.50, 65.03, 32.31, 19.91. ESI-MS: calculated $C_{14}H_{16}N_2O_3Na$ $[M+Na]^+$ 283.1053; Found 283.1055.

3-(hydroxymethyl)-2-methoxy-3,5-dimethyl-3,4-dihydropyrimido[1,6-a]indol-1(2*H*)-one (4b)



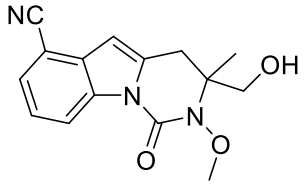
Following the general procedure B, the product **4b** was obtained in 63% yield (34.7 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.20. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, J = 7.8 Hz, 1H), 7.42 (d, J = 7.2 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.24 (td, J = 7.4, 1.1 Hz, 1H), 3.95 (s, 3H), 3.80 (d, J = 11.2 Hz, 1H), 3.69 (d, J = 11.2 Hz, 1H), 3.29 (d, J = 16.1 Hz, 1H), 2.94 (d, J = 16.0 Hz, 1H), 2.16 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.39, 134.95, 131.12, 127.19, 124.15, 122.98, 118.20, 115.38, 112.21, 66.68, 65.01, 64.73, 30.49, 19.87, 8.36. ESI-MS: calculated $C_{15}H_{18}N_2O_3Na$ $[M+Na]^+$ 297.1209; Found 297.1214.

6-bromo-3-(hydroxymethyl)-2-methoxy-3-methyl-3,4-dihydropyrimido[1,6-a]indol-1(2*H*)-one (4c)



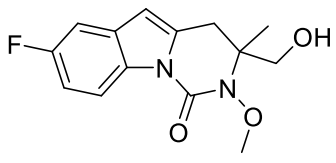
Following the general procedure B, the product **4c** was obtained in 87% yield (59.5 mg, 0.20 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.20. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, J = 8.2 Hz, 1H), 7.37 (d, J = 7.8 Hz, 1H), 7.13 (t, J = 8.0 Hz, 1H), 6.38 (s, 1H), 3.97 (s, 3H), 3.84 (d, J = 10.8 Hz, 1H), 3.66 (d, J = 11.1 Hz, 1H), 3.40 (d, J = 16.2 Hz, 1H), 3.07 (d, J = 16.2 Hz, 1H), 1.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.99, 135.81, 132.87, 130.68, 126.14, 125.03, 114.54, 113.77, 104.33, 66.41, 65.10, 65.04, 32.37, 20.12. ESI-MS: calculated $C_{14}H_{15}BrN_2O_3Na$ $[M+Na]^+$ 361.0158; Found 361.0158.

3-(hydroxymethyl)-2-methoxy-3-methyl-1-oxo-1,2,3,4-tetrahydropyrimido[1,6-a]indole-6-carbonitrile (4d)



Following the general procedure B, the product **4d** was obtained in 56% yield (32.0 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.21. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, J = 8.3 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.24 (d, J = 8.4 Hz, 1H), 6.46 (s, 1H), 3.90 (s, 3H), 3.77 (d, J = 11.2 Hz, 1H), 3.52 (d, J = 11.3 Hz, 1H), 3.40 (d, J = 16.5 Hz, 1H), 3.09 (d, J = 16.5 Hz, 1H), 1.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.91, 135.68, 135.25, 132.05, 127.57, 123.74, 119.93, 118.09, 102.57, 102.30, 65.80, 65.36, 64.95, 32.50, 20.45. ESI-MS: calculated $C_{15}H_{15}N_3O_3Na$ $[M+Na]^+$ 308.1005; Found 308.1010.

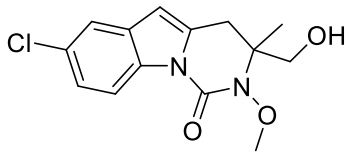
7-fluoro-3-(hydroxymethyl)-2-methoxy-3-methyl-3,4-dihydropyrimido[1,6-a]indol-1(2*H*)-one (4e)



Following the general procedure B, the product **4e** was obtained in 79% yield (40.9 mg, 0.20 mmol) as a pale yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.20. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (dd, J = 9.0, 4.8 Hz, 1H), 7.08 (dd, J = 8.9, 2.5 Hz, 1H), 6.95 (td, J = 9.2, 2.6 Hz, 1H), 6.22 (s, 1H), 3.92 (s, 3H), 3.77 (d, J =

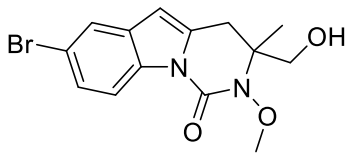
11.3 Hz, 1H), 3.58 (d, J = 11.3 Hz, 1H), 3.35 (d, J = 16.3 Hz, 1H), 3.03 (d, J = 16.3 Hz, 1H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.61 (d, *J* = 238.8 Hz), 153.28, 133.88, 131.78, 130.96 (d, *J* = 10.1 Hz), 116.18 (d, *J* = 9.2 Hz), 111.45 (d, *J* = 24.9 Hz), 105.69 (d, *J* = 24.1 Hz), 104.03 (d, *J* = 3.9 Hz), 65.95, 65.23, 64.94, 32.38, 20.16. ^{19}F NMR (471 MHz, $CDCl_3$) δ -120.49. ESI-MS: calculated $C_{14}H_{15}FN_2O_3Na$ $[M+Na]^+$ 301.0959; Found 301.0965.

7-chloro-3-(hydroxymethyl)-2-methoxy-3-methyl-3,4-dihydropyrimido[1,6-a]indol-1(2*H*)-one (4f)



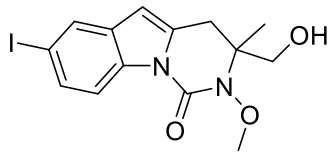
Following the general procedure B, the product **4f** was obtained in 65% yield (38.0 mg, 0.20 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.19. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, J = 8.8 Hz, 1H), 7.42 (d, J = 2.0 Hz, 1H), 7.21 (dd, J = 8.8, 2.1 Hz, 1H), 6.22 (s, 1H), 3.95 (s, 3H), 3.82 (d, J = 11.3 Hz, 1H), 3.64 (d, J = 11.3 Hz, 1H), 3.37 (dd, J = 16.3, 0.8 Hz, 1H), 3.04 (dd, J = 16.2, 1.0 Hz, 1H), 1.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.00, 133.84, 133.51, 131.25, 128.81, 124.07, 119.70, 116.38, 103.72, 66.39, 65.13, 65.02, 32.34, 20.11. ESI-MS: calculated $C_{14}H_{15}ClN_2O_3Na$ $[M+Na]^+$ 317.0663; Found 317.0668.

7-bromo-3-(hydroxymethyl)-2-methoxy-3-methyl-3,4-dihydropyrimido[1,6-a]indol-1(2*H*)-one (4g)



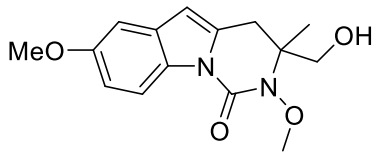
Following the general procedure B, the product **4g** was obtained in 74% yield (50.3 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.8 Hz, 1H), 7.59 (s, 1H), 7.35 (d, *J* = 8.7 Hz, 1H), 6.23 (s, 1H), 3.96 (s, 3H), 3.84 (d, *J* = 7.3 Hz, 1H), 3.65 (d, *J* = 11.0 Hz, 1H), 3.38 (d, *J* = 16.3 Hz, 1H), 3.05 (d, *J* = 16.3 Hz, 1H), 2.17 (s, 1H), 1.71 (s, 2H), 1.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.19, 134.16, 133.56, 131.79, 127.82, 126.66, 122.71, 116.71, 103.46, 65.95, 65.23, 64.95, 32.36, 20.25. ESI-MS: calculated $C_{14}H_{15}BrN_2O_3Na$ $[M+Na]^+$ 314.0158; Found 314.0153.

3-(hydroxymethyl)-7-iodo-2-methoxy-3-methyl-3,4-dihydropyrimido[1,6-a]indol-1(2*H*)-one (4h)



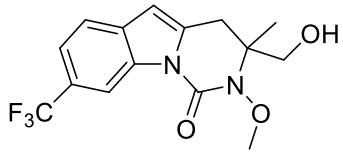
Following the general procedure B, the product **4h** was obtained in 60% yield (46.5 mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.21. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, J = 8.6 Hz, 1H), 7.72 (s, 1H), 7.45 (d, J = 8.7 Hz, 1H), 6.15 (s, 1H), 3.86 (d, J = 3.6 Hz, 3H), 3.69 (d, J = 11.3 Hz, 1H), 3.49 (d, J = 11.3 Hz, 1H), 3.32 (d, J = 16.3 Hz, 1H), 2.98 (d, J = 16.3 Hz, 1H), 1.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.26, 134.60, 133.28, 132.35, 132.16, 128.77, 116.98, 103.19, 87.08, 65.19, 65.14, 64.72, 31.95, 19.88. ESI-MS: calculated $C_{14}H_{16}IN_2O_3$ $[M+H]^+$ 387.0200; Found 387.0206.

3-(hydroxymethyl)-2,7-dimethoxy-3-methyl-3,4-dihydropyrimido[1,6-a]indol-1(2*H*)-one (4i)



Following the general procedure B, the product **4i** was obtained in 50% yield (29.0 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.9 Hz, 1H), 6.95 (d, *J* = 2.3 Hz, 1H), 6.89 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.23 (s, 1H), 3.97 (s, 3H), 3.84 (s, 3H), 3.81 (s, 1H), 3.68 (d, *J* = 11.2 Hz, 1H), 3.37 (d, *J* = 16.1 Hz, 1H), 3.02 (d, *J* = 16.2 Hz, 1H), 2.00 (s, 1H), 1.64 (s, 2H), 1.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.25, 153.36, 132.79, 130.96, 130.17, 116.01, 112.15, 104.30, 103.21, 66.14, 65.17, 64.96, 55.80, 32.34, 19.98. ESI-MS: calculated $C_{15}H_{18}N_2O_4Na$ $[M+Na]^+$ 313.1159; Found 313.1161.

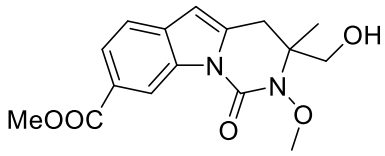
3-(hydroxymethyl)-2-methoxy-3-methyl-8-(trifluoromethyl)-3,4-dihydropyrimido[1,6-a]indol-1(2*H*)-one (4j)



Following the general procedure B, the product **4j** was obtained in 43% yield (43.4 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.54 (d, *J* = 8.2 Hz,

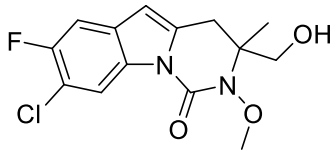
1H), 7.46 (d, *J* = 8.2 Hz, 1H), 6.35 (s, 1H), 3.97 (s, 3H), 3.88 (dd, *J* = 11.2, 5.6 Hz, 1H), 3.66 (dd, *J* = 11.3, 4.6 Hz, 1H), 3.43 (d, *J* = 16.3 Hz, 1H), 3.11 (d, *J* = 16.4 Hz, 1H), 2.13 (t, *J* = 5.5 Hz, 1H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.17, 135.17, 134.59, 132.61, 125.78 (q, *J* = 31.9 Hz), 124.93 (q, *J* = 271.8 Hz), 120.27, 119.95 (q, *J* = 3.6 Hz), 112.82 (q, *J* = 4.3 Hz), 103.85, 65.89, 65.26, 64.93, 32.52, 20.38. ^{19}F NMR (471 MHz, $CDCl_3$) δ -60.97. ESI-MS: calculated $C_{15}H_{15}F_3N_2O_3Na$ $[M+Na]^+$ 351.0927; Found 351.0930.

methyl 3-(hydroxymethyl)-2-methoxy-3-methyl-1-oxo-1,2,3,4-tetrahydropyrimido[1,6-a]indole-8-carboxylate (4k)



Following the general procedure B, the product **4k** was obtained in 42% yield (27.0 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.21. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, J = 8.2 Hz, 1H), 7.37 (d, J = 7.8 Hz, 1H), 7.13 (t, J = 8.0 Hz, 1H), 6.38 (s, 1H), 3.97 (s, 3H), 3.84 (d, J = 10.8 Hz, 1H), 3.66 (d, J = 11.1 Hz, 1H), 3.40 (d, J = 16.2 Hz, 1H), 3.07 (d, J = 16.2 Hz, 1H), 1.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.88, 152.90, 135.56, 134.91, 133.86, 125.57, 124.60, 119.71, 117.15, 104.29, 66.30, 65.11, 64.96, 52.15, 32.49, 20.18. ESI-MS: calculated $C_{16}H_{18}N_2O_5Na$ $[M+Na]^+$ 341.1108; Found 341.1107.

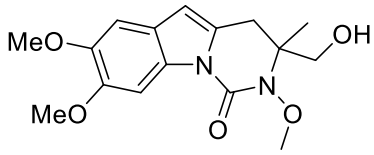
8-chloro-7-fluoro-3-(hydroxymethyl)-2-methoxy-3-methyl-3,4-dihydropyrimido[1,6-a]indol-1(2*H*)-one (4l)



Following the general procedure B, the product **4l** was obtained in 37% yield (23.3 mg, 0.20 mmol) as a yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.21. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, J = 6.6 Hz, 1H), 7.15 (d, J = 9.1 Hz, 1H), 6.20 (s, 1H), 3.91 (s, 3H), 3.77 (d, J = 11.3 Hz, 1H), 3.54 (d, J = 11.3 Hz, 1H), 3.34 (d, J = 16.4 Hz, 1H), 3.03 (d, J = 16.4 Hz, 1H), 1.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.83 (d, *J* = 241.7 Hz), 153.06, 134.39, 131.43, 129.28 (d, *J* = 9.0 Hz), 116.91 (d, *J* = 19.9 Hz), 116.85, 106.55 (d, *J* = 23.9 Hz), 103.62 (d, *J* = 3.7 Hz), 65.87, 65.30, 64.92, 32.44, 20.34 . ^{19}F NMR (471

MHz, $CDCl_3$) δ -122.03. ESI-MS: calculated $C_{14}H_{14}ClFN_2O_3Na$ $[M+Na]^+$ 335.0569; Found 335.0579.

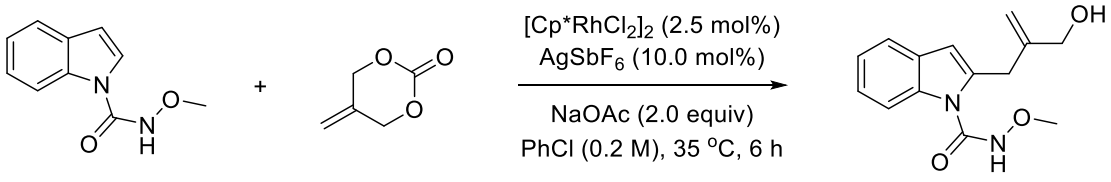
3-(hydroxymethyl)-2,7,8-trimethoxy-3-methyl-3,4-dihydropyrimido[1,6-a]indol-1(2*H*)-one (4m)



Following the general procedure B, the product **4m** was obtained in 97% yield (61.8 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.23. ^1H NMR (500 MHz, $CDCl_3$) δ 7.96 (s, 1H), 6.91 (s, 1H), 6.16 (s, 1H), 3.93 (d, J = 6.5 Hz, 6H), 3.88 (s, 3H), 3.78 (d, J = 11.2 Hz, 1H), 3.64 (d, J = 11.2 Hz, 1H), 3.32 (d, J = 16.0 Hz, 1H), 2.98 (d, J = 16.0 Hz, 1H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.51, 147.29, 146.63, 130.17, 129.59, 122.52, 112.42, 104.28, 101.96, 99.14, 66.37, 65.15, 64.98, 64.78, 56.25, 56.23, 32.23, 19.84. ESI-MS: calculated $C_{16}H_{20}N_2O_5Na$ $[M+Na]^+$ 343.1264; Found 343.1266.

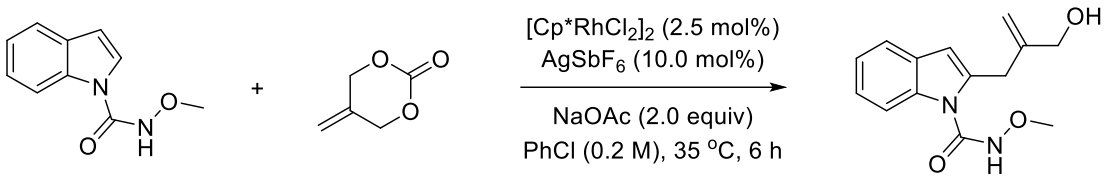
4. Synthetic application of the product

4.1 Gram- Scale Synthesis



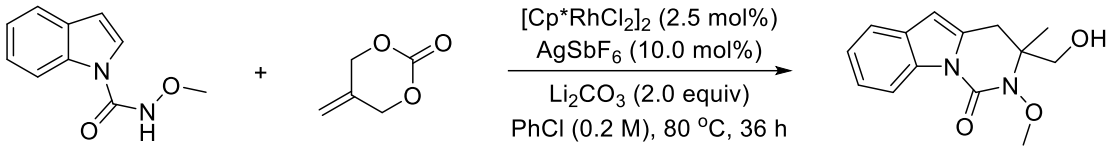
1a, 1.0 mmol **2** **3a**, 235.8 mg, 91%

In an oven-dried Schlenk tube under air, a mixture of *N*-methoxy-1*H*-indole-1-carboxamide **1a** (1.0 mmol, 1.0 equiv), 5-methylene-1,3-dioxan-2-one **2** (2.0 mmol, 2.0 equiv), $(Cp^*RhCl_2)_2$ (0.025 mmol, 2.5 mmol%), $AgSbF_6$ (0.1 mmol, 10.0 mmol%), NaOAc (2.0 mmol, 2.0 equiv), and PhCl (5.0 mL) was stirred at 35 °C for 6 h. The reaction mixture was then diluted with DCM (50.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 2:1) to give **3a** (235.8 mg, 91%).



1a, 5.0 mmol **2** **3a**, 986.3 mg, 76%

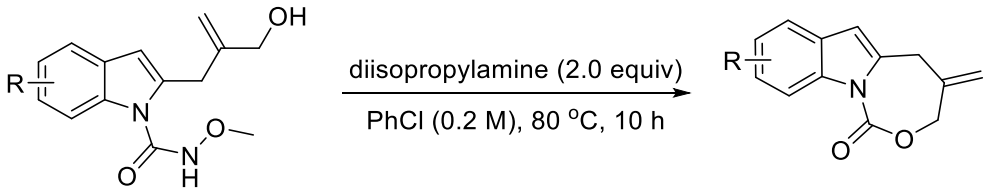
In an oven-dried Schlenk tube under air, a mixture of *N*-methoxy-1*H*-indole-1-carboxamide **1a** (5.0 mmol, 1.0 equiv), 5-methylene-1,3-dioxan-2-one **2** (10.0 mmol, 2.0 equiv), $(Cp^*RhCl_2)_2$ (0.125 mmol, 2.5 mmol%), $AgSbF_6$ (0.5 mmol, 10.0 mmol%), NaOAc (10.0 mmol, 2.0 equiv), and PhCl (25.0 mL) was stirred at 35 °C for 6 h. The reaction mixture was then diluted with DCM (250.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 2:1) to give **3a** (986.3 mg, 76%).



1a, 1.0 mmol **2** **4a**, 192.8 mg, 74%

In an oven-dried Schlenk tube under air, a mixture of *N*-methoxy-1*H*-indole-1-carboxamide **1a** (1.0 mmol, 1.0 equiv), 5-methylene-1,3-dioxan-2-one **2** (1.2 mmol, 1.2 equiv), $(Cp^*RhCl_2)_2$ (0.025 mmol, 2.5 mmol%), $AgSbF_6$ (0.1 mmol, 10.0 mmol%), Li_2CO_3 (2.0 mmol, 2.0 equiv), and PhCl (5.0 mL) was stirred at 80 °C for36 h. The reaction mixture was then diluted with DCM (50.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 3:1) to give **4a** (192.8 mg, 74%).

4.2 Application of the product 3



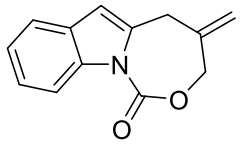
3 **5**

General procedure C

In an oven-dried Schlenk tube under air, a mixture of 2-(2-(hydroxymethyl)allyl)-*N*-methoxy-1*H*-indole-1-carboxamide derivatives **3** (0.1 mmol, 1.0 equiv), diisopropylamine (0.2 mmol, 2.0 equiv), and PhCl (0.5 mL) was stirred at 80 °C for10 h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **5**.

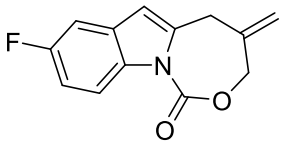
4-methylene-4,5-dihydro-1*H*,3*H*-[1,3]oxazepino[3,4-a]indol-1-one (5a)

Following the general procedure C, the product **5a** was obtained in 44% yield (9.4 mg, 0.10 mmol) as a pale yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v).



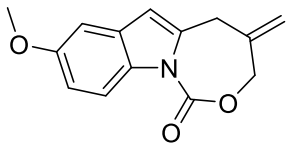
RF (Petroleum ether/EtOAc 16:1): 0.21. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.2 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.30 – 7.26 (m, 1H), 6.44 (s, 1H), 5.13 (s, 1H), 5.05 (s, 1H), 4.83 (s, 2H), 3.84 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.86, 141.11, 137.14, 134.68, 129.47, 124.48, 123.72, 120.36, 114.91, 111.14, 107.16, 73.51, 33.05. ESI-MS: calculated $C_{13}H_{12}NO_2$ $[M+H]^+$ 214.0863; Found 214.0866.

8-fluoro-4-methylene-4,5-dihydro-1*H*,3*H*-[1,3]oxazepino[3,4-a]indol-1-one (5b)



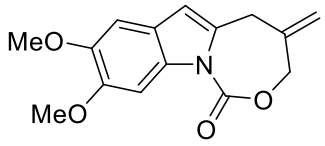
Following the general procedure C, the product **5b** was obtained in 27% yield (6.2 mg, 0.10 mmol) as a pale yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.20. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 9.0, 4.6 Hz, 1H), 7.15 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.03 (td, *J* = 9.1, 2.6 Hz, 1H), 6.39 (s, 1H), 5.12 (s, 1H), 5.04 (s, 1H), 4.82 (s, 2H), 3.82 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.89 (d, *J* = 240.0 Hz), 151.74, 140.80, 136.36, 133.42, 130.36 (d, *J* = 10.3 Hz), 115.95 (d, *J* = 9.1 Hz), 112.23 (d, *J* = 25.0 Hz), 111.43, 106.91 (d, *J* = 3.9 Hz), 106.02 (d, *J* = 24.1 Hz), 73.57, 33.17. ^{19}F NMR (471 MHz, $CDCl_3$) δ -119.65. ESI-MS: calculated $C_{13}H_{11}FNO_2$ $[M+H]^+$ 232.0769; Found 232.0772.

8-methoxy-4-methylene-4,5-dihydro-1H,3H-[1,3]oxazepino[3,4-a]indol-1-one (5c)



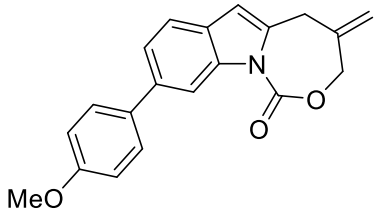
Following the general procedure C, the product **5c** was obtained in 32% yield (7.7 mg, 0.10 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.20. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 9.0 Hz, 1H), 6.96 (d, *J* = 2.4 Hz, 1H), 6.92 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.35 (s, 1H), 5.09 (s, 1H), 5.01 (s, 1H), 4.80 (s, 2H), 3.85 (s, 3H), 3.80 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.69, 151.90, 141.25, 135.39, 131.72, 130.34, 115.69, 112.89, 111.03, 107.12, 103.32, 73.53, 55.87, 33.19. ESI-MS: calculated $C_{14}H_{14}NO_3$ $[M+H]^+$ 244.0968; Found 244.0968.

8,9-dimethoxy-4-methylene-4,5-dihydro-1*H*,3*H*-[1,3]oxazepino[3,4-a]indol-1-one (5d)



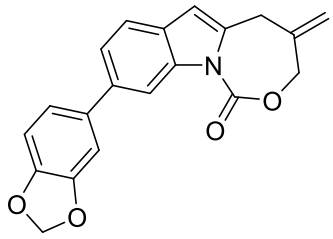
Following the general procedure C, the product **5d** was obtained in 86% yield (23.6 mg, 0.10 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 4:1 v/v). RF (Petroleum ether/EtOAc 4:1): 0.22. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (s, 1H), 6.94 (s, 1H), 6.31 (s, 1H), 5.08 (s, 1H), 5.00 (s, 1H), 4.80 (s, 2H), 3.95 (s, 3H), 3.91 (s, 3H), 3.78 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.16, 147.92, 147.16, 141.46, 133.09, 131.27, 121.96, 110.86, 107.02, 102.12, 98.79, 73.69, 56.39, 56.35, 33.07. ESI-MS: calculated $C_{15}H_{16}NO_4$ $[M+H]^+$ 274.1074; Found 274.1070.

9-(4-methoxyphenyl)-4-methylene-4,5-dihydro-1H,3H-[1,3]oxazepino[3,4-a]indol-1-one (5e)



Following the general procedure C, the product **5e** was obtained in 39% yield (12.5 mg, 0.10 mmol) as a pale yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.22. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.60 (d, J = 8.8 Hz, 2H), 7.52 (d, J = 8.1 Hz, 1H), 7.47 (d, J = 8.1 Hz, 1H), 6.99 (d, J = 8.8 Hz, 2H), 6.43 (s, 1H), 5.11 (s, 1H), 5.03 (s, 1H), 4.83 (s, 2H), 3.86 (s, 3H), 3.84 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.19, 151.88, 141.11, 137.85, 137.72, 134.94, 134.21, 128.59, 128.21, 122.97, 120.48, 114.35, 113.06, 111.16, 107.00, 73.53, 55.51, 33.15. ESI-MS: calculated $C_{20}H_{18}NO_3$ $[M+H]^+$ 320.1281; Found 320.1277.

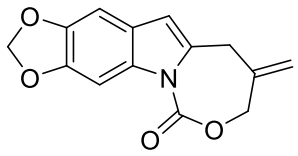
9-(benzo[d][1,3]dioxol-5-yl)-4-methylene-4,5-dihydro-1H,3H-[1,3]oxazepino[3,4-a]indol-1-one (5f)



Following the general procedure C, the product **5f** was obtained in 40% yield (13.4 mg, 0.10 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.24. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.51 (d, J = 8.1 Hz, 1H), 7.43 (d, J = 8.1 Hz, 1H), 7.13 (d, J = 9.7 Hz, 2H), 6.89 (d, J = 7.9 Hz, 1H), 6.42 (s, 1H), 6.00 (s, 2H), 5.11 (s, 1H), 5.03 (s, 1H), 4.82 (s, 2H), 3.83 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.83, 148.24, 147.09, 141.06, 137.81, 137.76, 136.06, 135.11, 128.41,

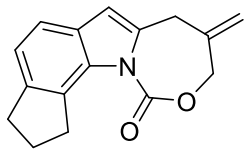
123.09, 121.09, 120.48, 113.27, 111.20, 108.69, 108.14, 106.96, 101.26, 73.53, 33.15. ESI-MS: calculated $C_{20}H_{16}NO_4$ $[M+H]^+$ 334.1074; Found 334.1070.

9-methylene-9,10-dihydro-6H,8H-[1,3]dioxolo[4,5-f][1,3]oxazepino[3,4-a]indol-6-one (5g)



Following the general procedure C, the product **5g** was obtained in 36% yield (9.3 mg, 0.10 mmol) as a pale yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.23. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (s, 1H), 6.86 (s, 1H), 6.28 (s, 1H), 5.97 (s, 2H), 5.08 (s, 1H), 5.00 (s, 1H), 4.79 (s, 2H), 3.76 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.97, 146.20, 145.19, 141.38, 133.35, 131.85, 123.34, 110.91, 107.25, 101.30, 99.31, 96.88, 73.66, 33.10. ESI-MS: calculated $C_{14}H_{12}NO_4$ $[M+H]^+$ 258.0761; Found 258.0760.

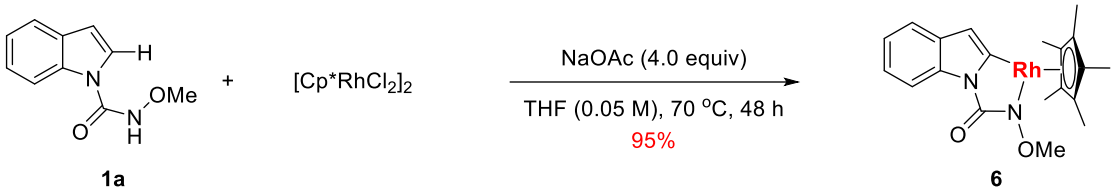
8-methylene-1,2,3,7,8,9-hexahydro-11*H*-cyclopenta[g][1,3]oxazepino[3,4-a]indol-11-one (5h)



Following the general procedure C, the product **5h** was obtained in 95% yield (24.1 mg, 0.10 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 2:1 v/v). RF (Petroleum ether/EtOAc 2:1): 0.20. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, J = 7.9 Hz, 1H), 7.01 (d, J = 7.9 Hz, 1H), 6.30 (s, 1H), 5.18 (s, 1H), 5.07 (s, 1H), 4.11 (s, 2H), 3.58 (s, 2H), 3.02 (dt, J = 10.6, 7.4 Hz, 4H), 2.21 (dd, J = 14.7, 7.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.40, 138.03, 135.34, 133.44, 127.40, 125.03, 118.08, 116.71, 112.70, 101.66, 65.57, 33.22, 32.97, 30.03, 25.62. ESI-MS: calculated $C_{16}H_{16}NO_2$ $[M+H]^+$ 254.1176; Found 254.1182.

5. Mechanistic experiments

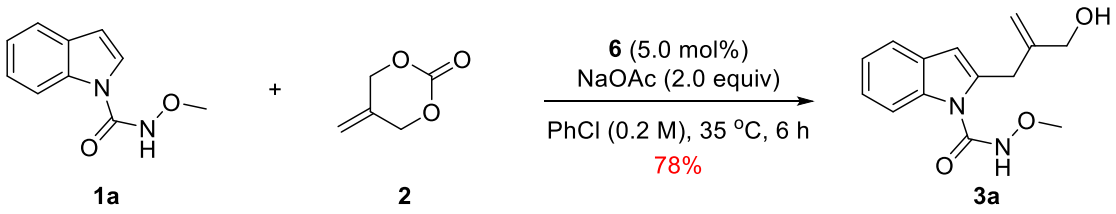
(1) Preparation of Rhodium Complex



1a **6**

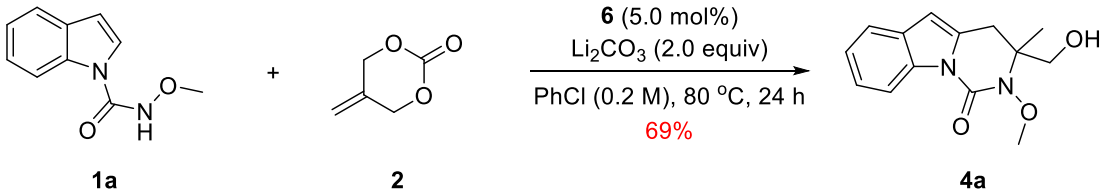
The intermediate **6** was prepared from the *N*-methoxy-1*H*-indole-1-carboxamide **1a** and $(Cp^*RhCl_2)_2$ according to the reported procedure.[1]

(2) Mechanistic experiments



1a **2** **3a**

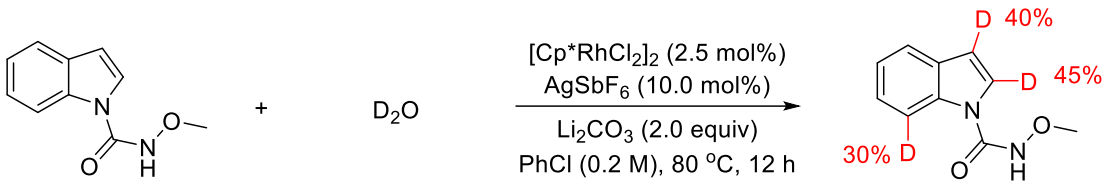
In an oven-dried Schlenk tube under air, a mixture of *N*-methoxy-1*H*-indole-1-carboxamide **1a** (0.2 mmol, 1.0 equiv), 5-methylene-1,3-dioxan-2-one **2** (0.4 mmol, 2.0 equiv), rhodium complex **6** (4.3 mg, 0.01 mmol, 5 mmol%), NaOAc (32.8 mg, 0.4 mmol, 2.0 equiv), and PhCl (1.0 mL) was stirred at 35 °C for 6 h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 2:1) to give **3a** (40.8 mg, 78%).



1a **2** **4a**

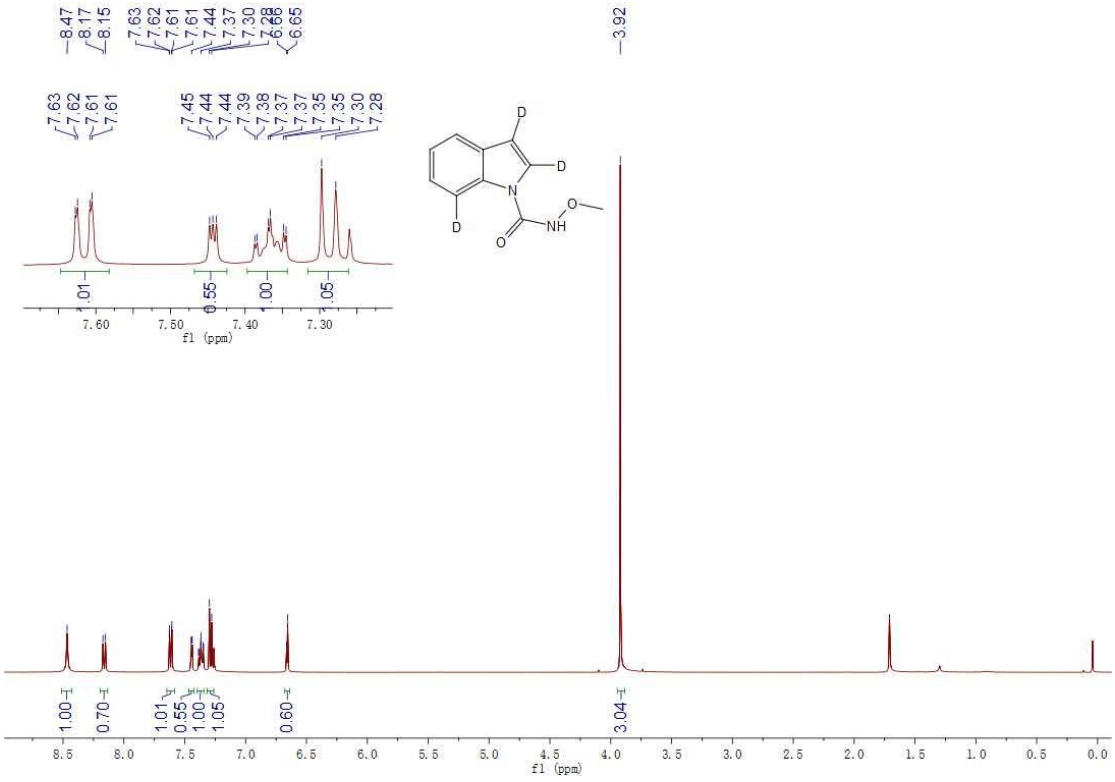
In an oven-dried Schlenk tube under air, a mixture of *N*-methoxy-1*H*-indole-1-carboxamide **1a** (0.2 mmol, 1.0 equiv), 5-methylene-1,3-dioxan-2-one **2** (0.24 mmol, 1.2 equiv), rhodium complex **6** (4.3 mg, 0.01 mmol, 5 mmol%), Li_2CO_3 (29.5 mg, 0.4 mmol, 2.0 equiv), and PhCl (1.0 mL) was stirred at 80 °C for 24 h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined,

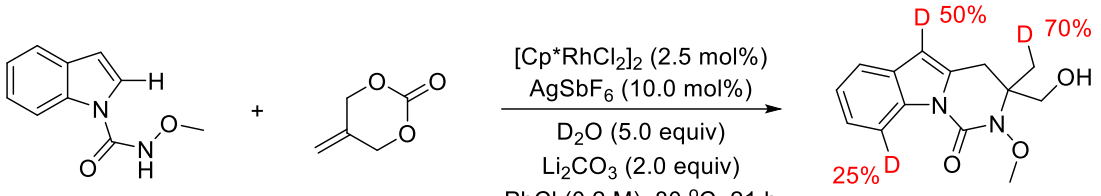
washed with brine and dried over Na_2SO_4. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 3:1) to give **4a** (36.0 mg, 69%).



1a, 0.2 mmol　　5.0 equiv　　[D]-**1a**, 24.7 mg, 65%

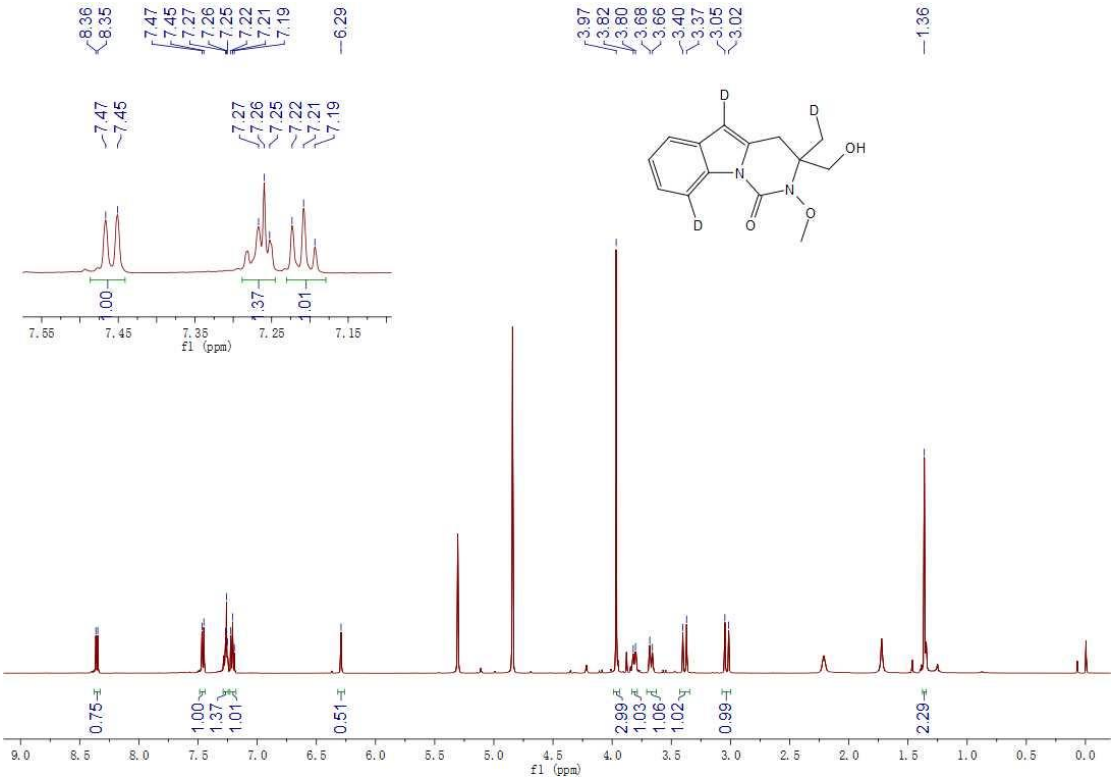
In an oven-dried Schlenk tube under air, a mixture of *N*-methoxy-1*H*-indole-1-carboxamide **1a** (0.2 mmol, 1.0 equiv),D_2O (1.0 mmol, 5.0 equiv), $(Cp^*RhCl_2)_2$ (0.005 mmol, 2.5 mmol%), $AgSbF_6$ (0.02 mmol, 10.0 mmol%), Li_2CO_3 (0.4 mmol, 2.0 equiv), and PhCl (1.0 mL) was stirred at 80 °C for 12 h. The reaction mixture was then diluted with DCM (50.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 4:1) to give [D]-**1a** (24.7 mg, 65%).

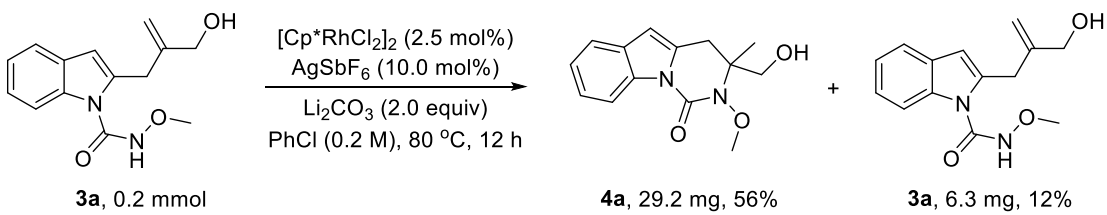




1a, 0.2 mmol　　**2**　　[D]-**4a**, 31.6 mg

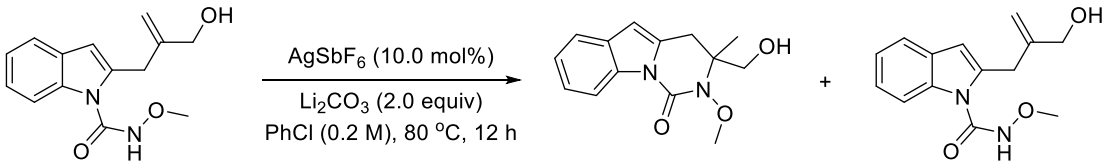
In an oven-dried Schlenk tube under air, a mixture of *N*-methoxy-1*H*-indole-1-carboxamide **1a** (0.2 mmol, 1.0 equiv), 5-methylene-1,3-dioxan-2-one **2** (0.24 mmol, 1.2 equiv), $(Cp^*RhCl_2)_2$ (0.005 mmol, 2.5 mmol%), $AgSbF_6$ (0.02 mmol, 10.0 mmol%), D_2O (1.0 mmol, 5.0 equiv) Li_2CO_3 (0.4 mmol, 2.0 equiv), and PhCl (1.0 mL) was stirred at 80 °C for 21 h. The reaction mixture was then diluted with DCM (50.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 3:1) to give [D]-**4a** (31.6 mg).





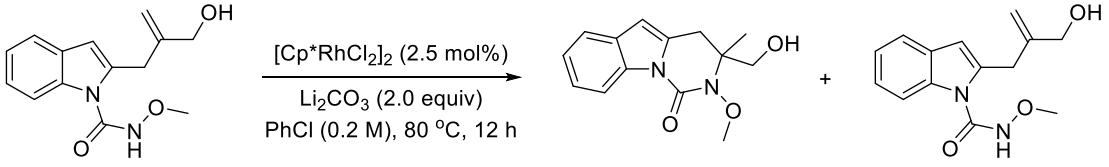
3a, 0.2 mmol　　**4a**, 29.2 mg, 56%　　**3a**, 6.3 mg, 12%

In an oven-dried Schlenk tube under air, a mixture of 2-(2-(hydroxymethyl)allyl)-*N*-methoxy-1*H*-indole-1-carboxamide **3a** (0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mmol%), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10.0 mmol%), Li_2CO_3 (29.5 mg, 0.4 mmol, 2.0 equiv), and PhCl (1.0 mL) was stirred at 80 °C for 12 h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 3:1) to give **4a** (29.2 mg, 56%). The raw material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 2:1) to give **3a** (6.3 mg, 12%).



3a, 0.2 mmol **4a**, 0% **3a**, 24.5mg, 47%

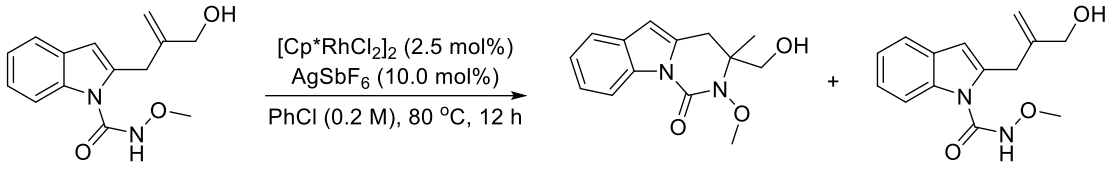
In an oven-dried Schlenk tube under air, a mixture of 2-(2-(hydroxymethyl)allyl)-*N*-methoxy-1*H*-indole-1-carboxamide **3a** (0.2 mmol, 1.0 equiv), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10.0 mmol%), Li_2CO_3 (29.5 mg, 0.4 mmol, 2.0 equiv), and PhCl (1.0 mL) was stirred at 80 °C for 12 h. No product **4a** can be detected by TLC. The raw material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 2:1) to give **3a** (24.5 mg, 47%).



3a, 0.2 mmol **4a**, 8.3 mg, 16% **3a**, 16.6 mg, 32%

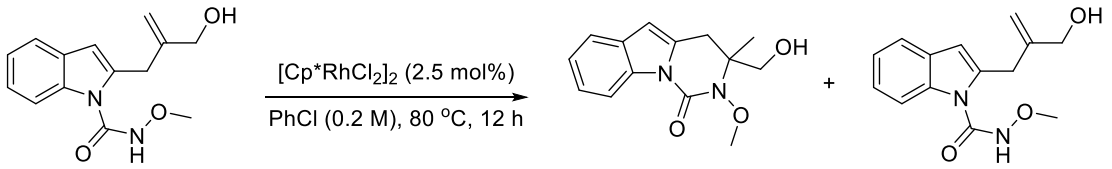
In an oven-dried Schlenk tube under air, a mixture of 2-(2-(hydroxymethyl)allyl)-*N*-methoxy-1*H*-indole-1-carboxamide **3a** (0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mmol%), Li_2CO_3 (29.5 mg, 0.4 mmol, 2.0 equiv), and PhCl (1.0 mL) was stirred at 80 °C for 12 h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and

dried over Na_2SO_4. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 3:1) to give **4a** (8.3 mg, 16%). The raw material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 2:1) to give **3a** (16.6 mg, 32%).



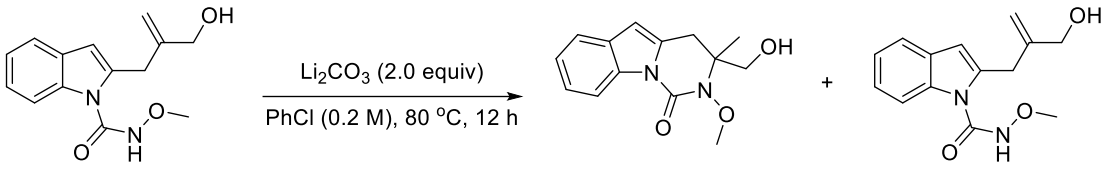
3a, 0.2 mmol **4a**, 10.5 mg, 20% **3a**, 5.2 mg, 10%

In an oven-dried Schlenk tube under air, a mixture of 2-(2-(hydroxymethyl)allyl)-*N*-methoxy-1*H*-indole-1-carboxamide **3a** (0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mmol%), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10.0 mmol%), and PhCl (1.0 mL) was stirred at 80 °C for 12 h. The organic layers were combined, washed with brine and dried over Na_2SO_4. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 3:1) to give **4a** (10.5 mg, 20%). The raw material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 2:1) to give **3a** (5.2 mg, 10%).



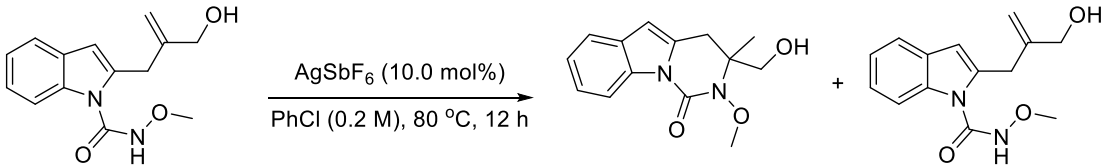
3a, 0.2 mmol **4a**, 9.4 mg, 18% **3a**, 27.6 mg, 53%

In an oven-dried Schlenk tube under air, a mixture of 2-(2-(hydroxymethyl)allyl)-*N*-methoxy-1*H*-indole-1-carboxamide **3a** (0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 2.5 mmol%), and PhCl (1.0 mL) was stirred at 80 °C for 12 h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 3:1) to give **4a** (9.4 mg, 18%). The raw material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 2:1) to give **3a** (27.6 mg, 53%).



3a, 0.2 mmol **4a**, 0% **3a**, 30.5 mg, 59%

In an oven-dried Schlenk tube under air, a mixture of 2-(2-(hydroxymethyl)allyl)-*N*-methoxy-1*H*-indole-1-carboxamide **3a** (0.2 mmol, 1.0 equiv), Li_2CO_3 (29.5 mg, 0.4 mmol, 2.0 equiv), and PhCl (1.0 mL) was stirred at 80 °C for 12 h. No product **4a** can be detected by TLC. The raw material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 2:1) to give **3a** (30.5 mg, 59%).

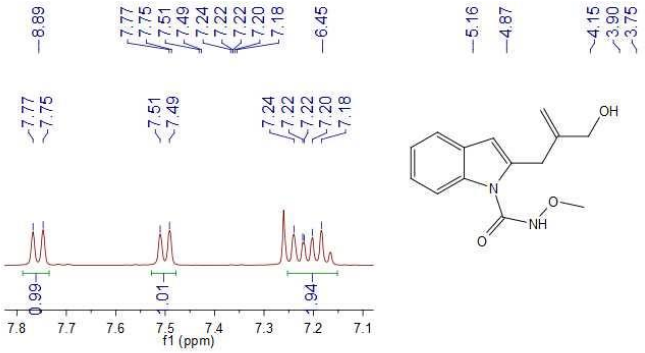


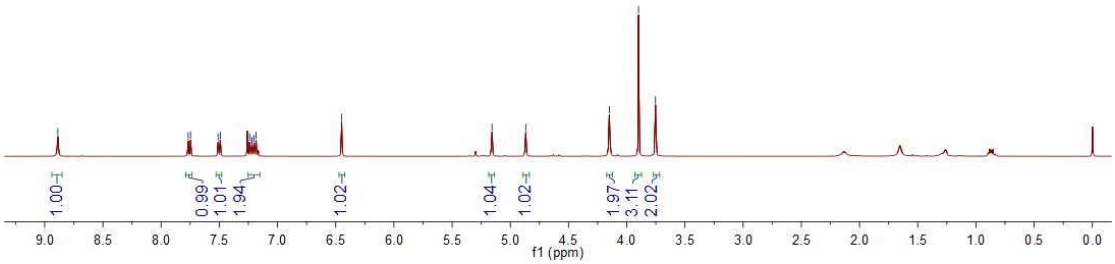
3a, 0.2 mmol **4a**, 0% **3a**, 0%

In an oven-dried Schlenk tube under air, a mixture of 2-(2-(hydroxymethyl)allyl)-*N*-methoxy-1*H*-indole-1-carboxamide **3a** (0.2 mmol, 1.0 equiv), $AgSbF_6$ (6.9 mg, 0.02 mmol, 10.0 mmol%), and PhCl (1.0 mL) was stirred at 80 °C for 12 h. No product **4a** and **3a** can be detected by TLC.

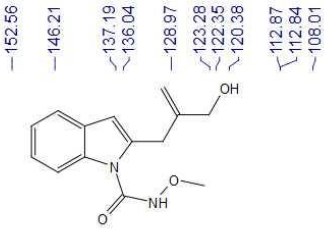
6. NMR Spectra for New Compounds

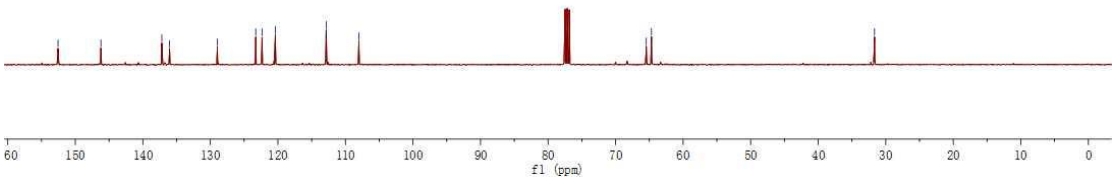
3a





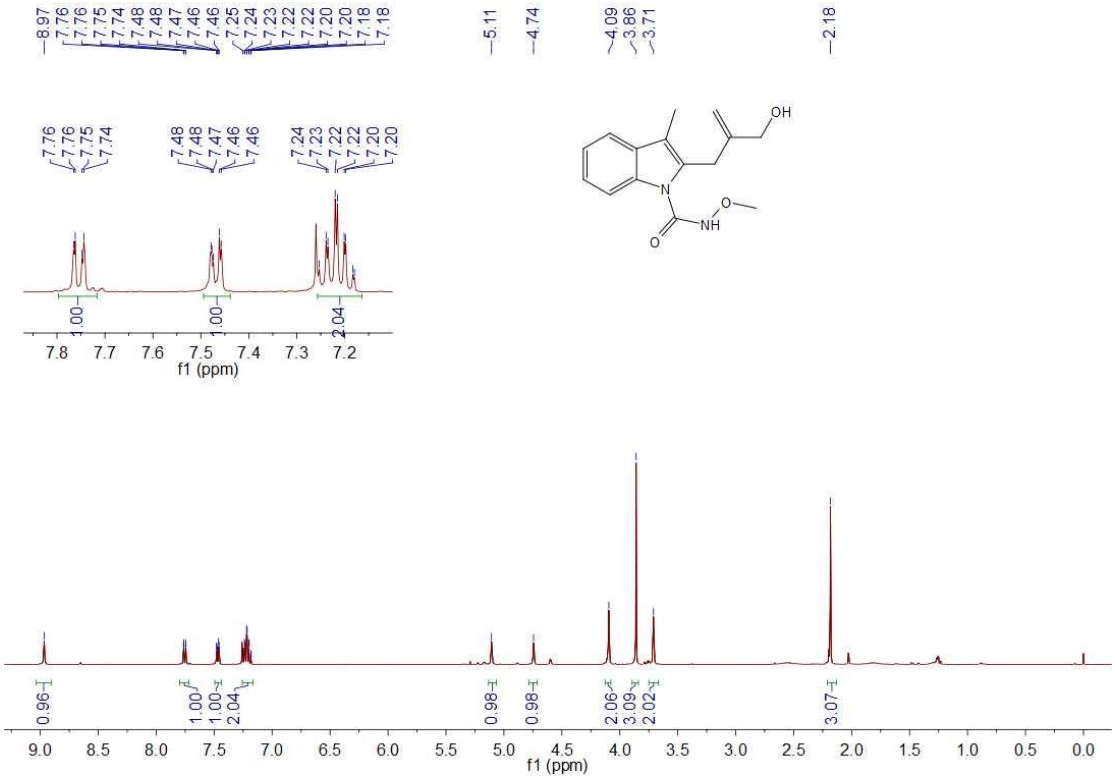
^{1}H NMR (400 MHz, $CDCl_3$)



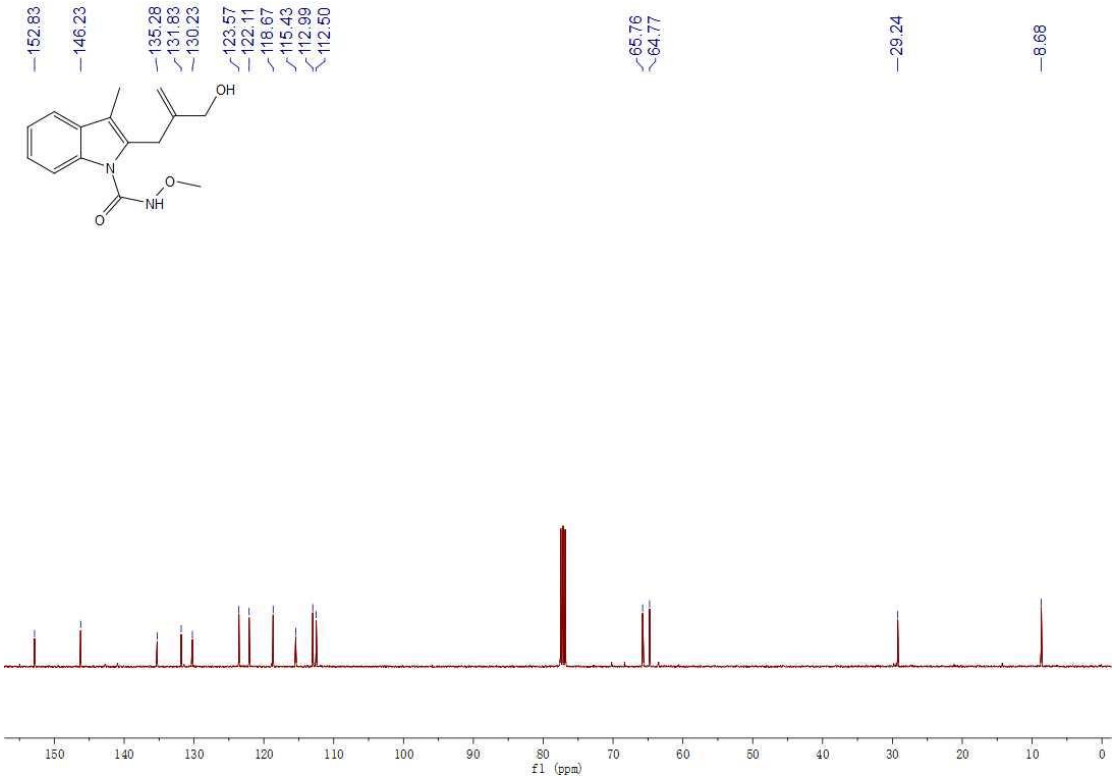


^{13}C NMR (101 MHz, $CDCl_3$)

3b

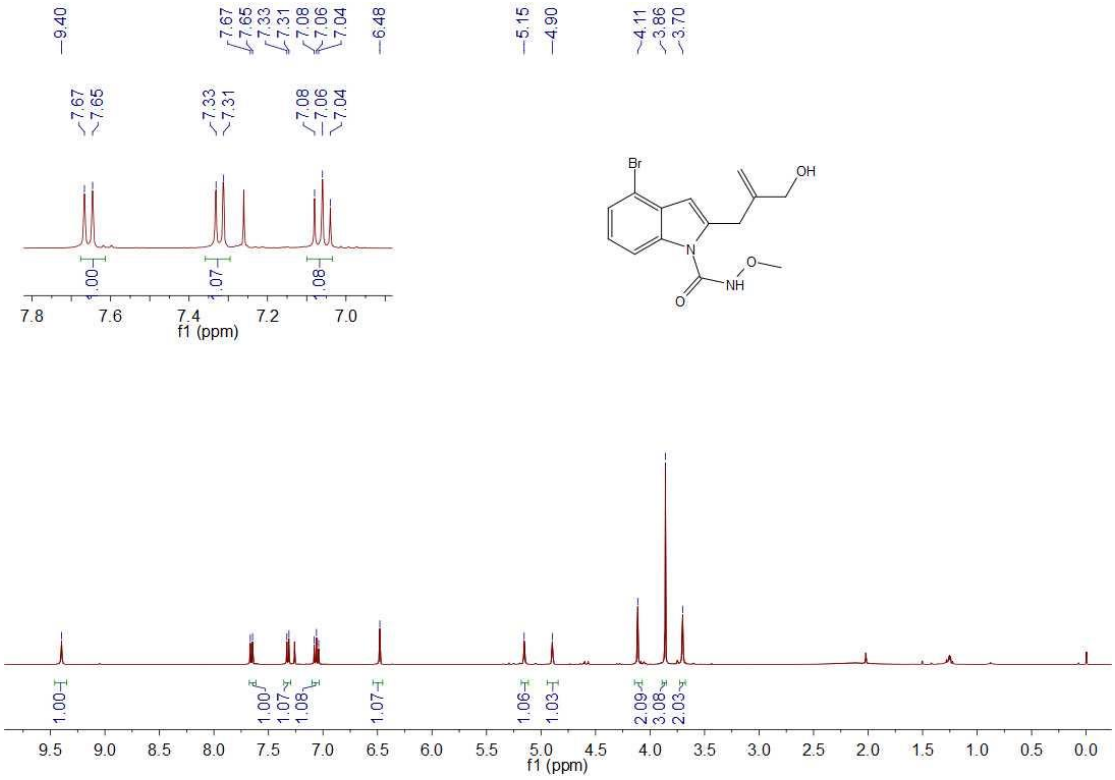


^{1}H NMR (400 MHz, $CDCl_3$)

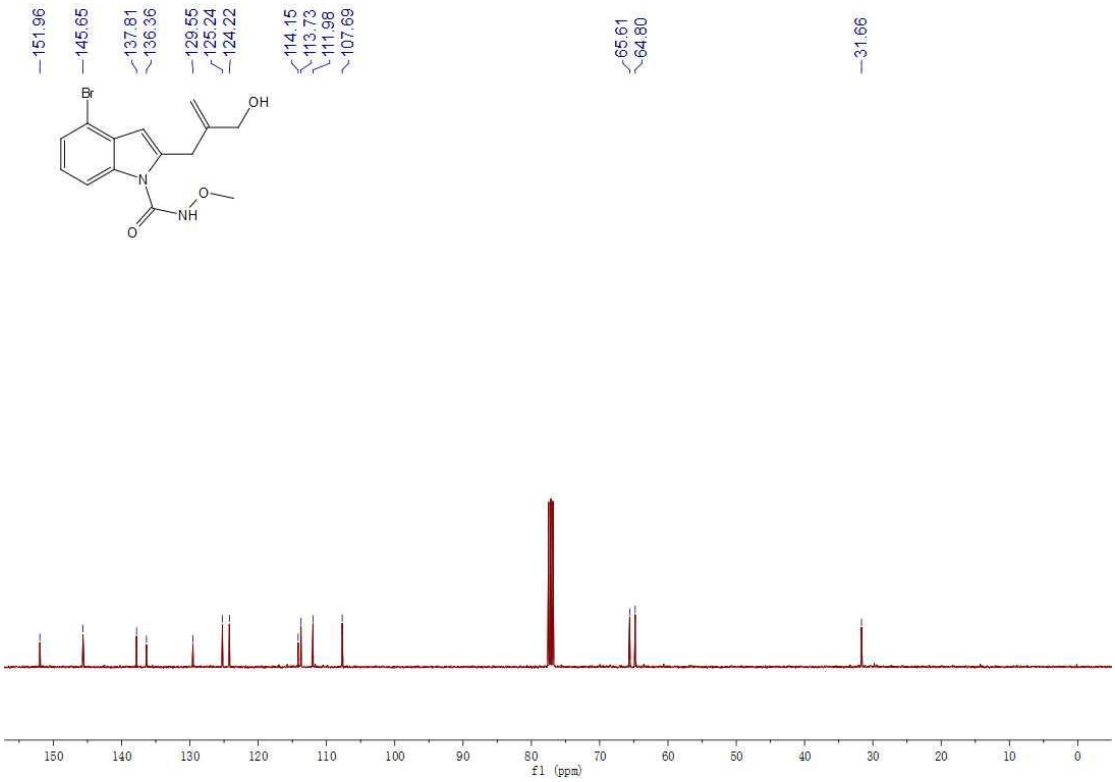


^{13}C NMR (101 MHz, $CDCl_3$)

3c

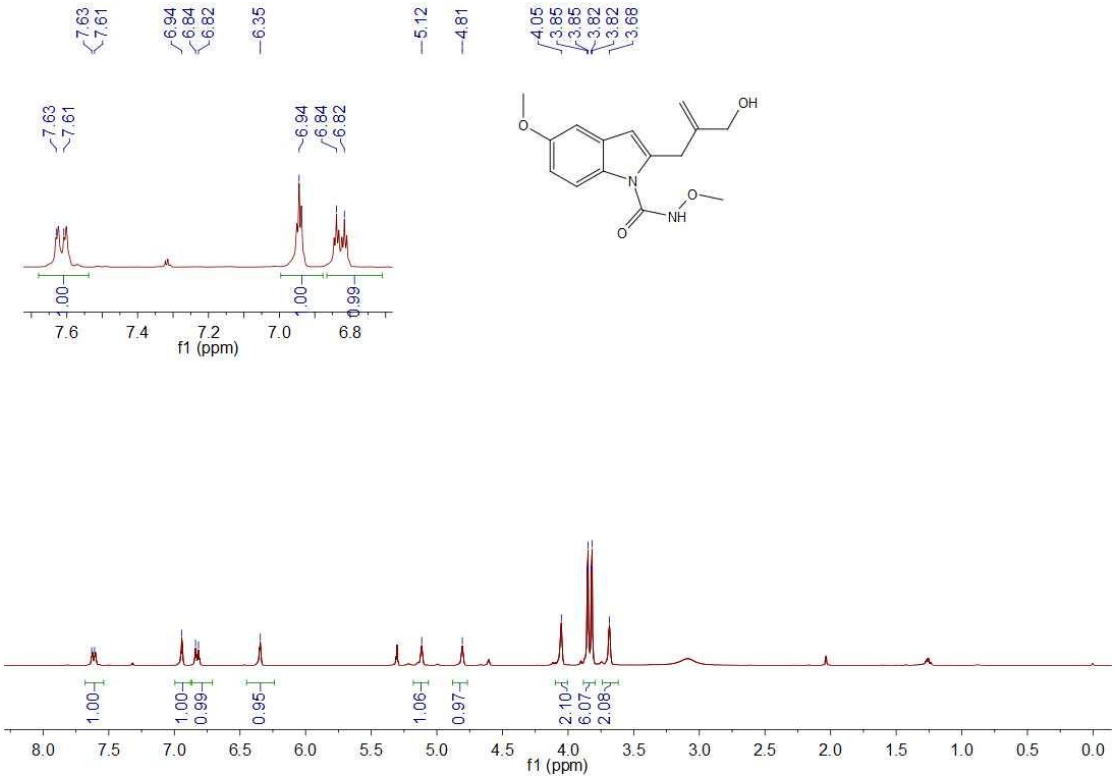


^{1}H NMR (400 MHz, $CDCl_3$)

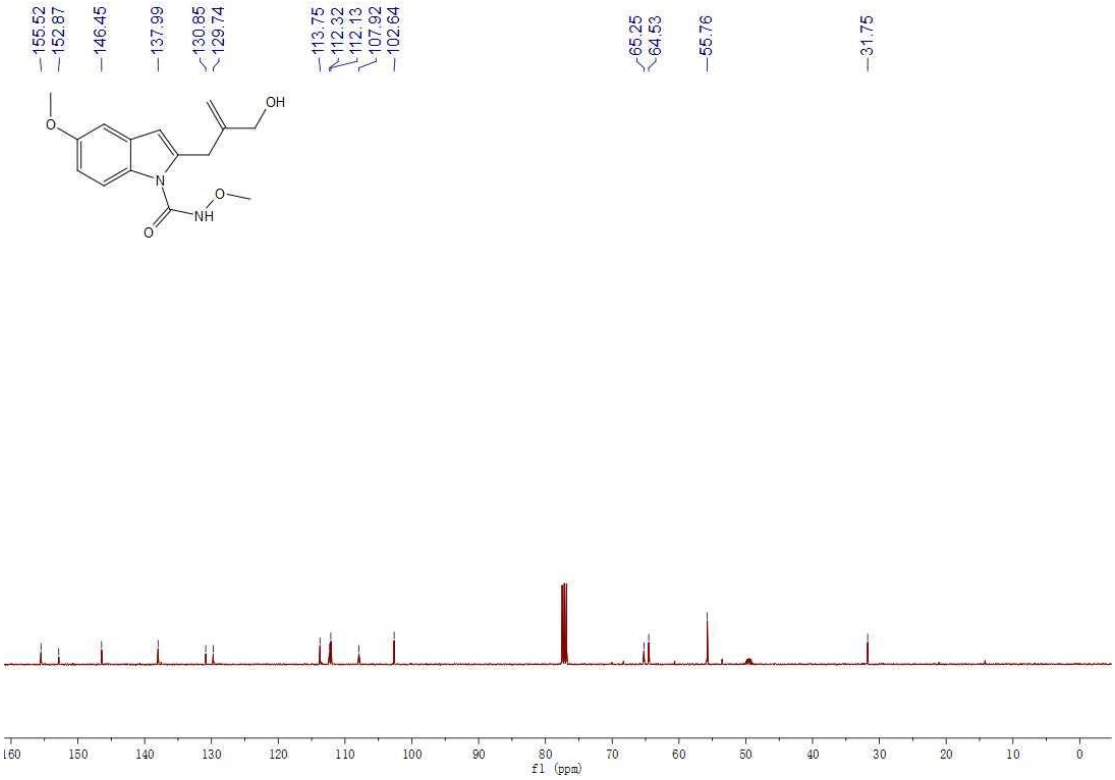


^{13}C NMR (101 MHz, $CDCl_3$)

3d

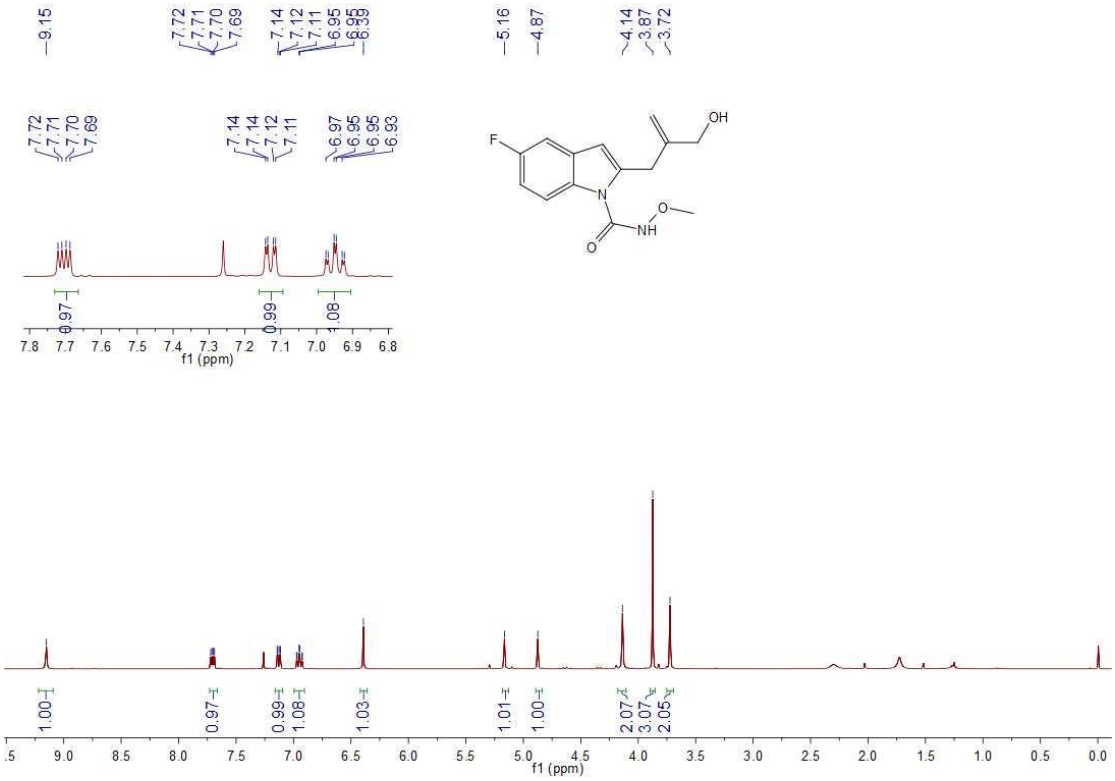


^{1}H NMR (400 MHz, $CDCl_3$)

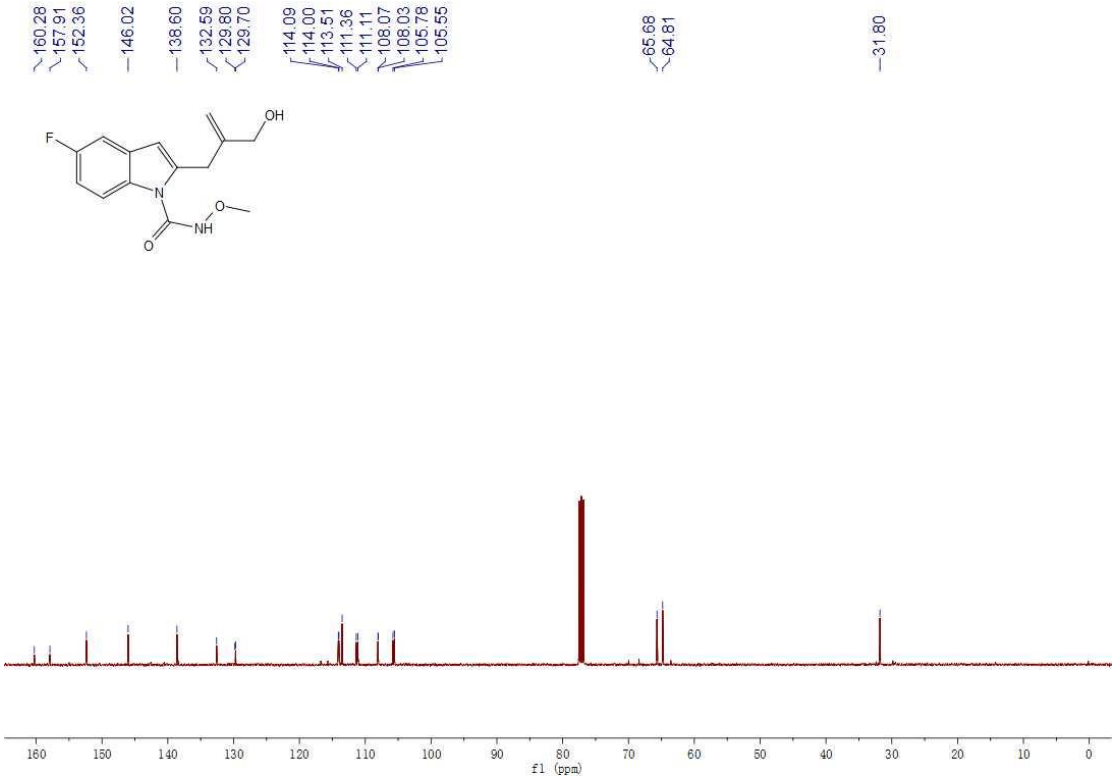


^{13}C NMR (101 MHz, $CDCl_3$)

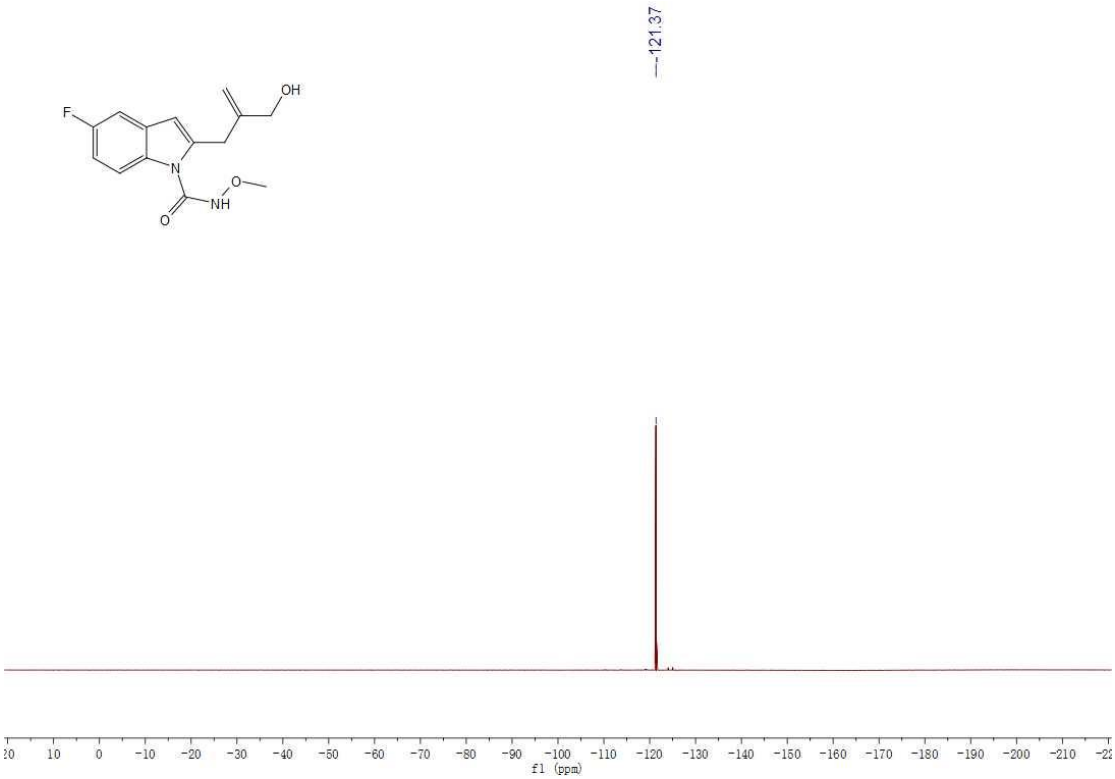
3e



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

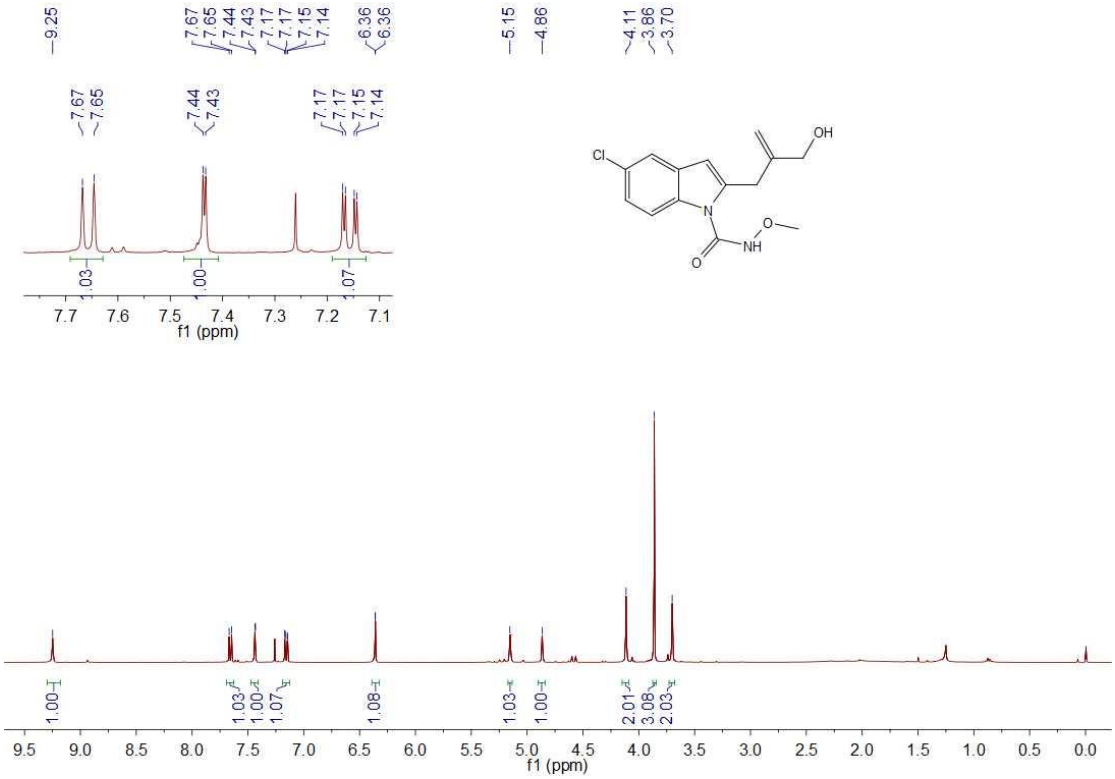


^{13}C NMR (101 MHz, $CDCl_3$)

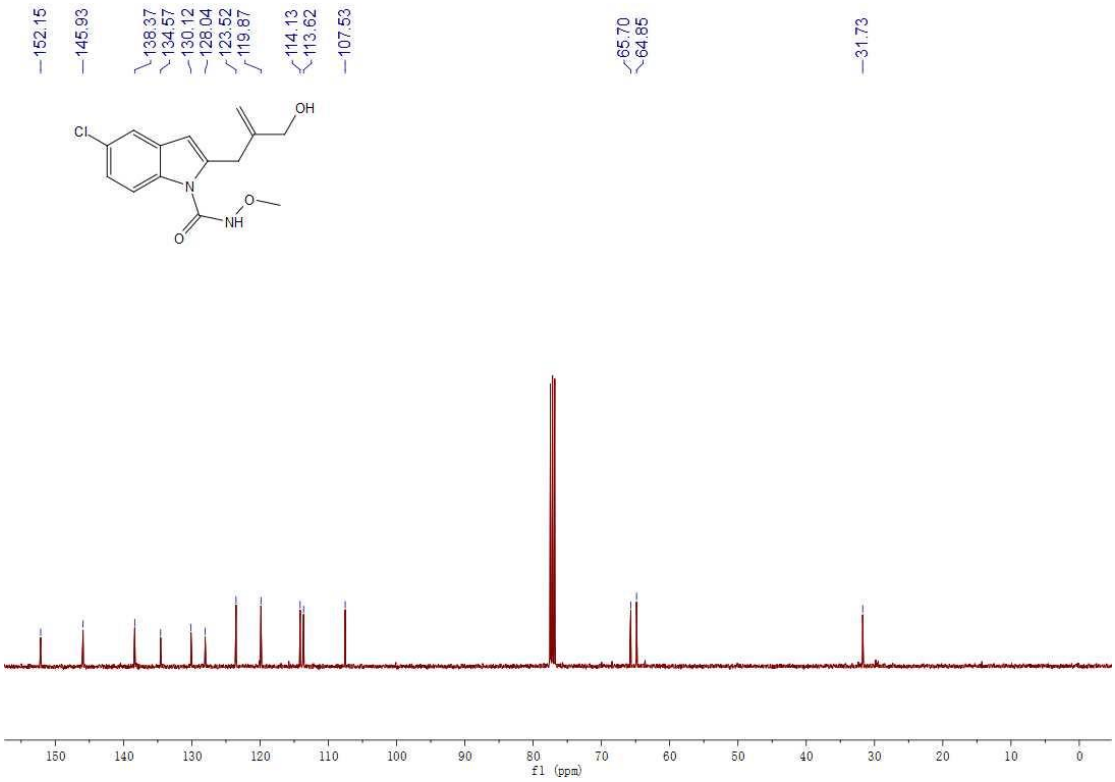


^{19}F NMR (471 MHz, $CDCl_3$)

3f

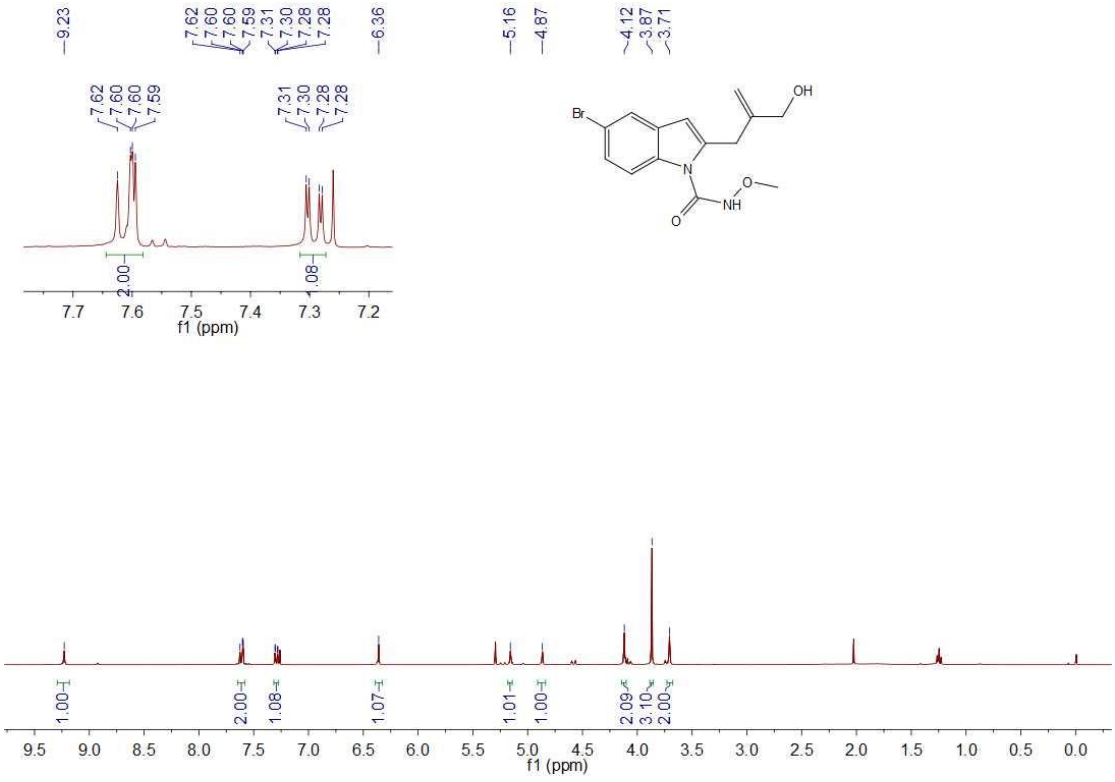


^{1}H NMR (400 MHz, $CDCl_3$)

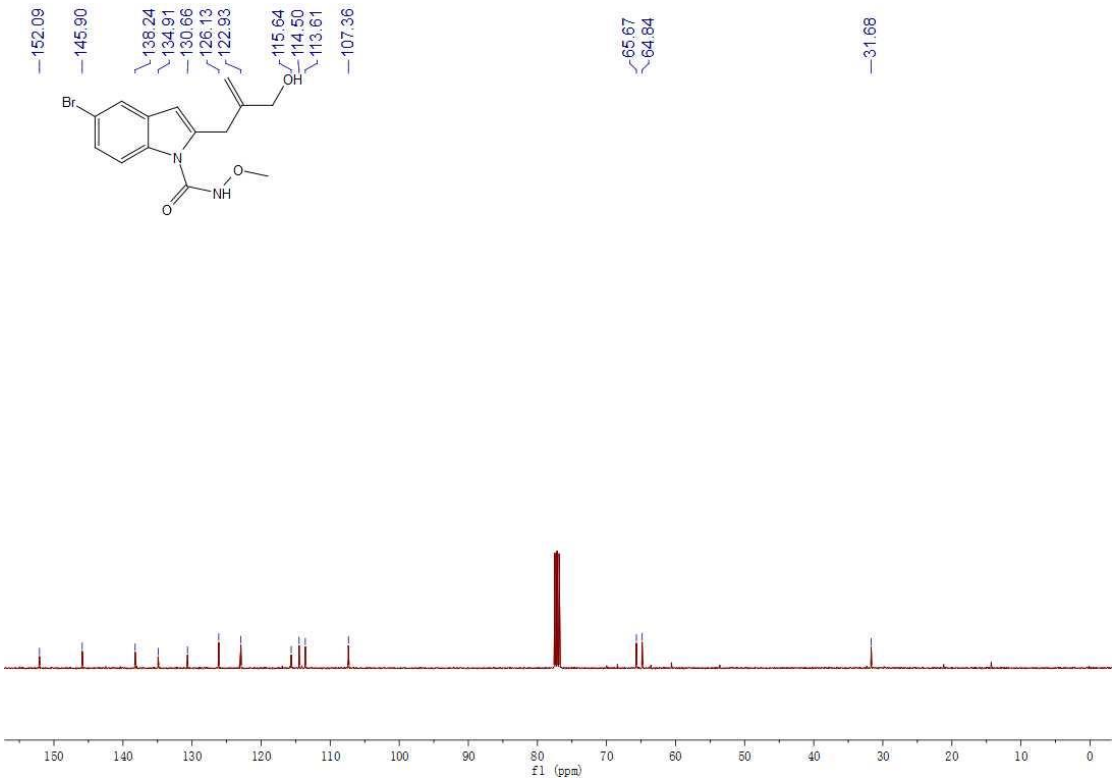


^{13}C NMR (101 MHz, $CDCl_3$)

3g

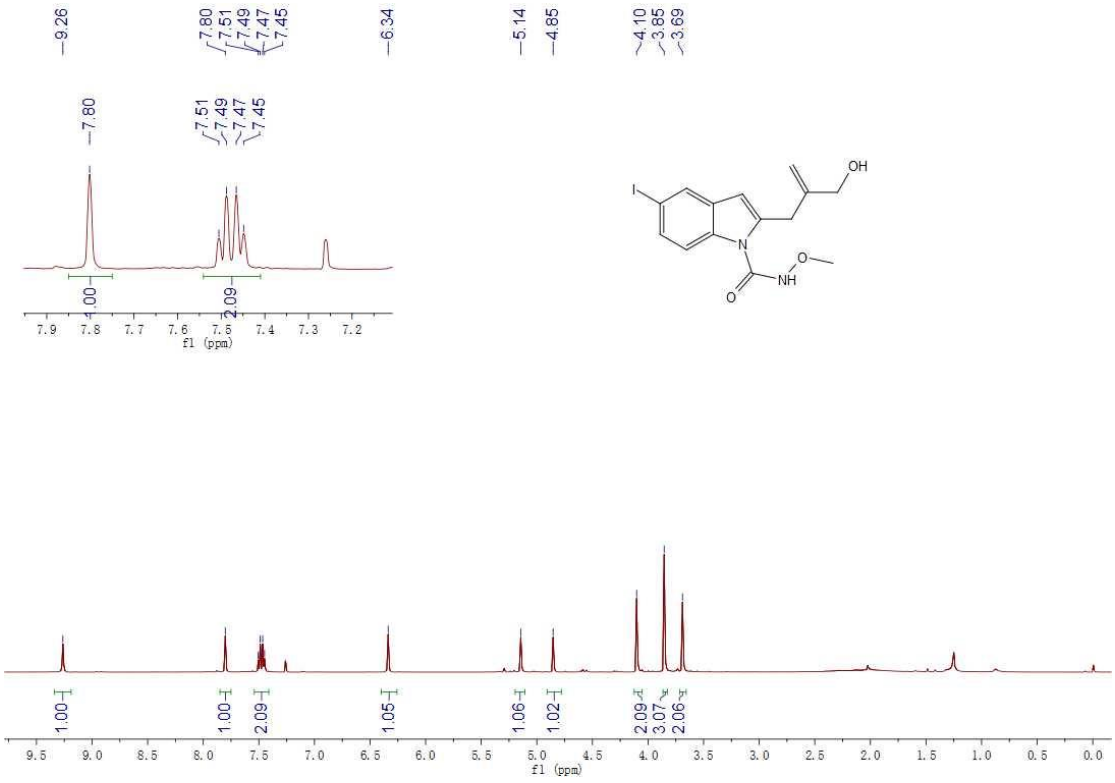


^{1}H NMR (400 MHz, $CDCl_3$)

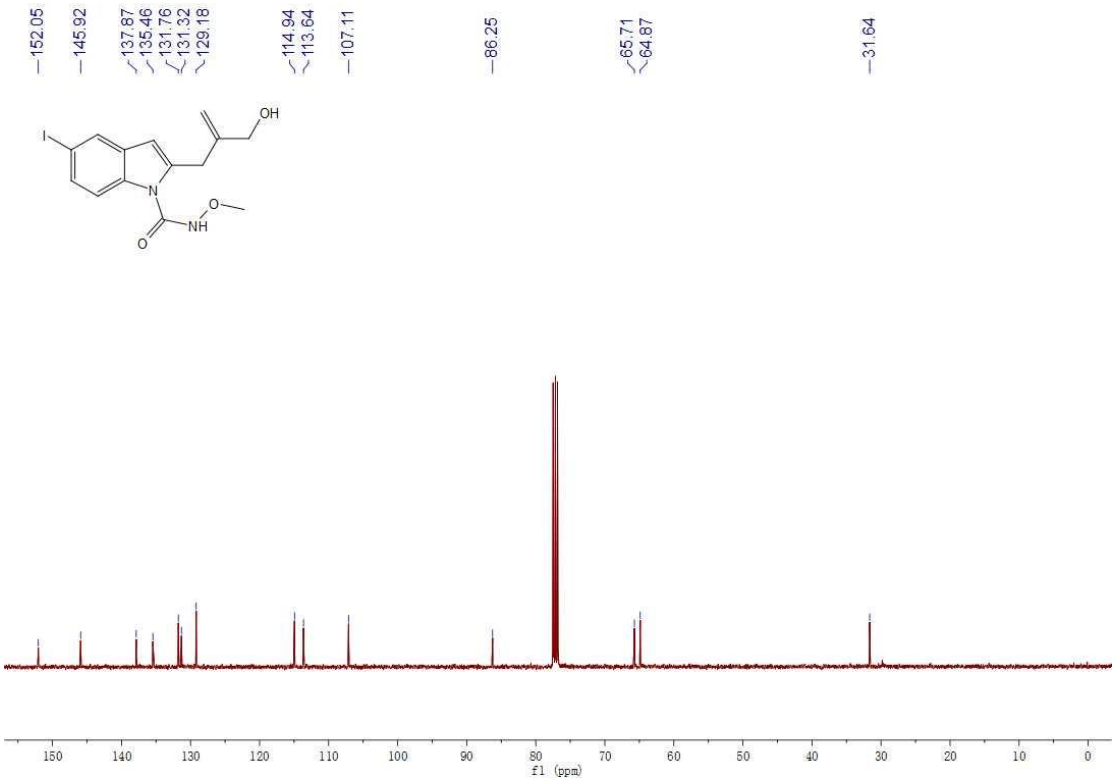


^{13}C NMR (101 MHz, $CDCl_3$)

3h

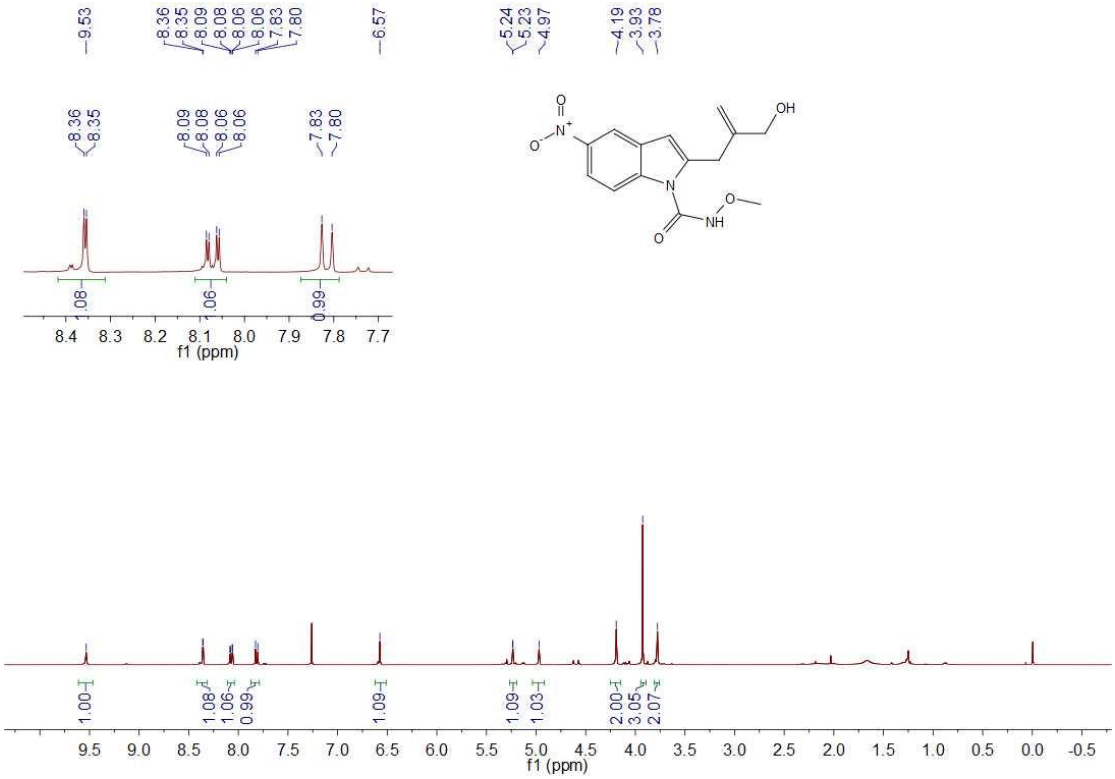


^{1}H NMR (500 MHz, $CDCl_3$)

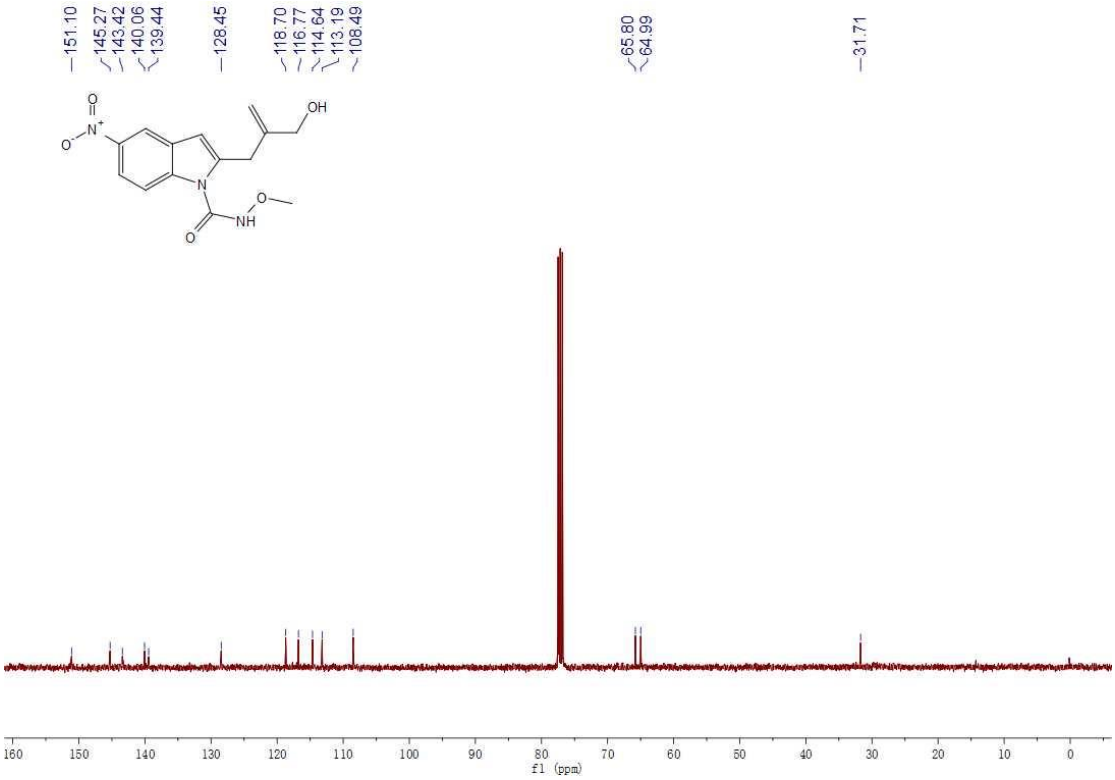


^{13}C NMR (101 MHz, $CDCl_3$)

3i

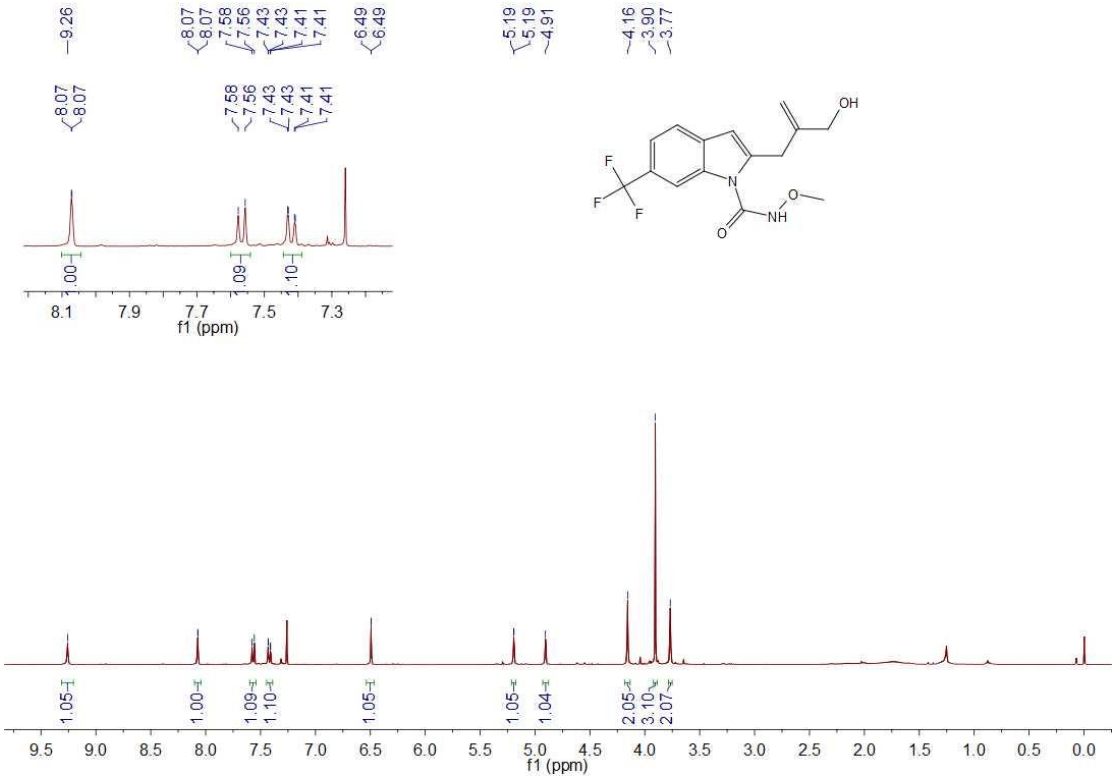


^{1}H NMR (400 MHz, $CDCl_3$)

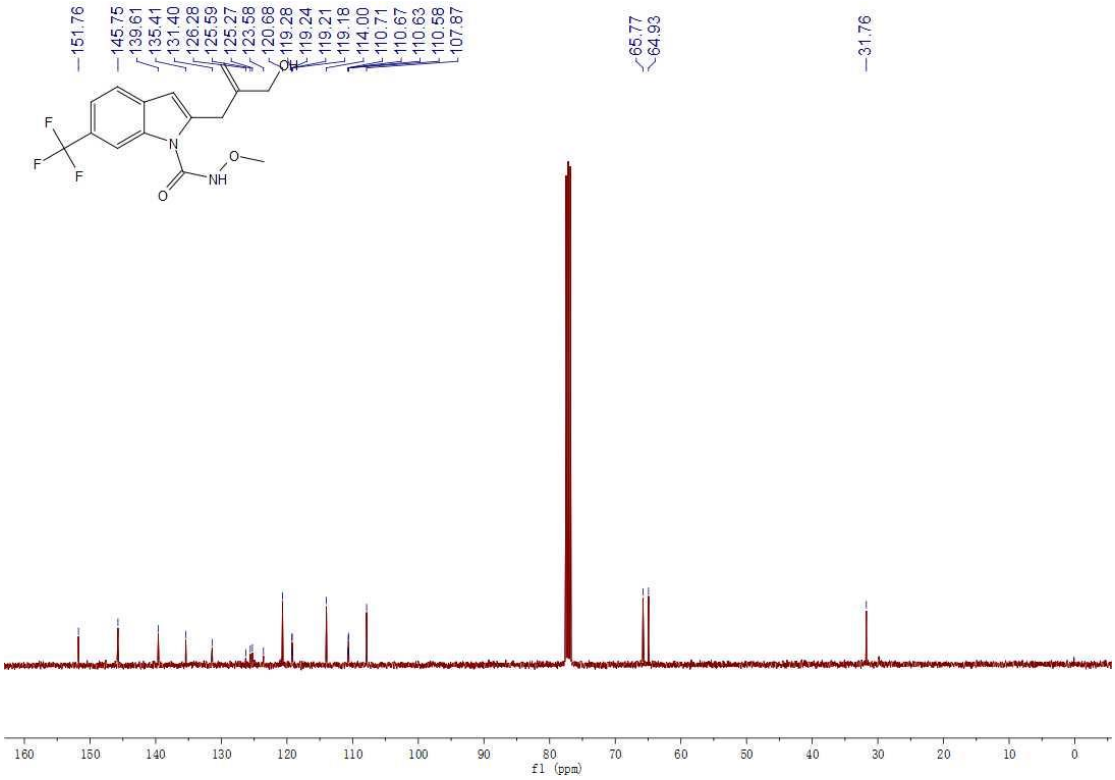


^{13}C NMR (101 MHz, $CDCl_3$)

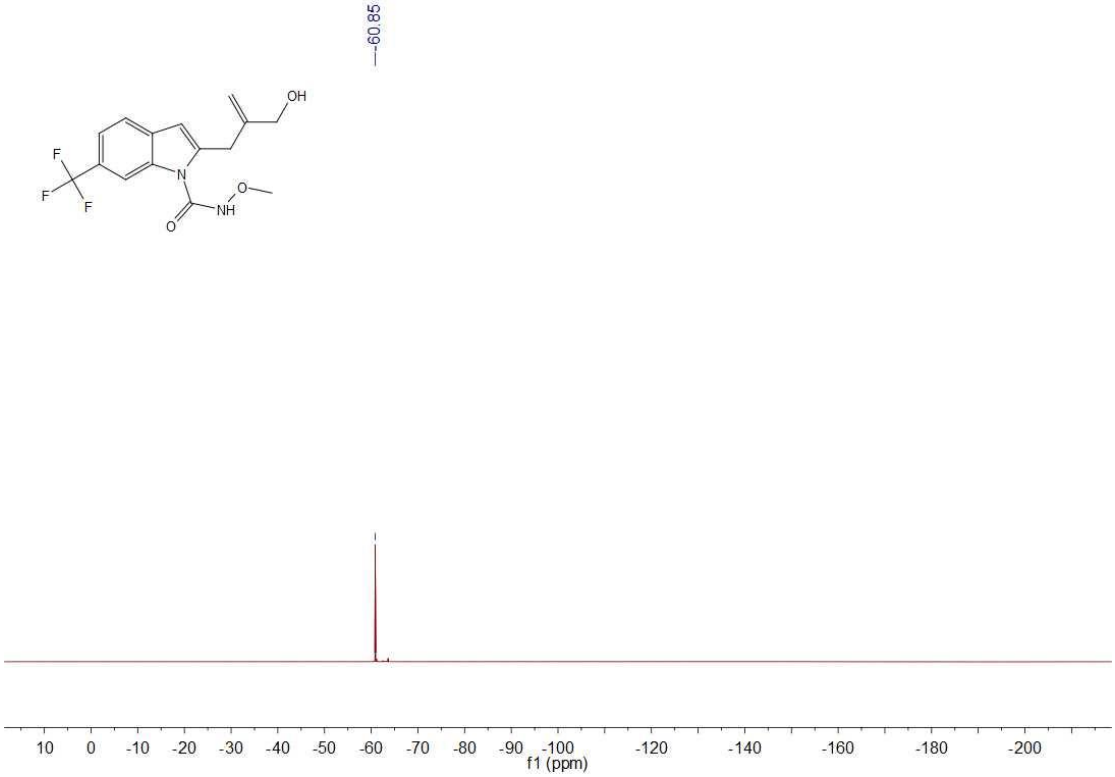
3j



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

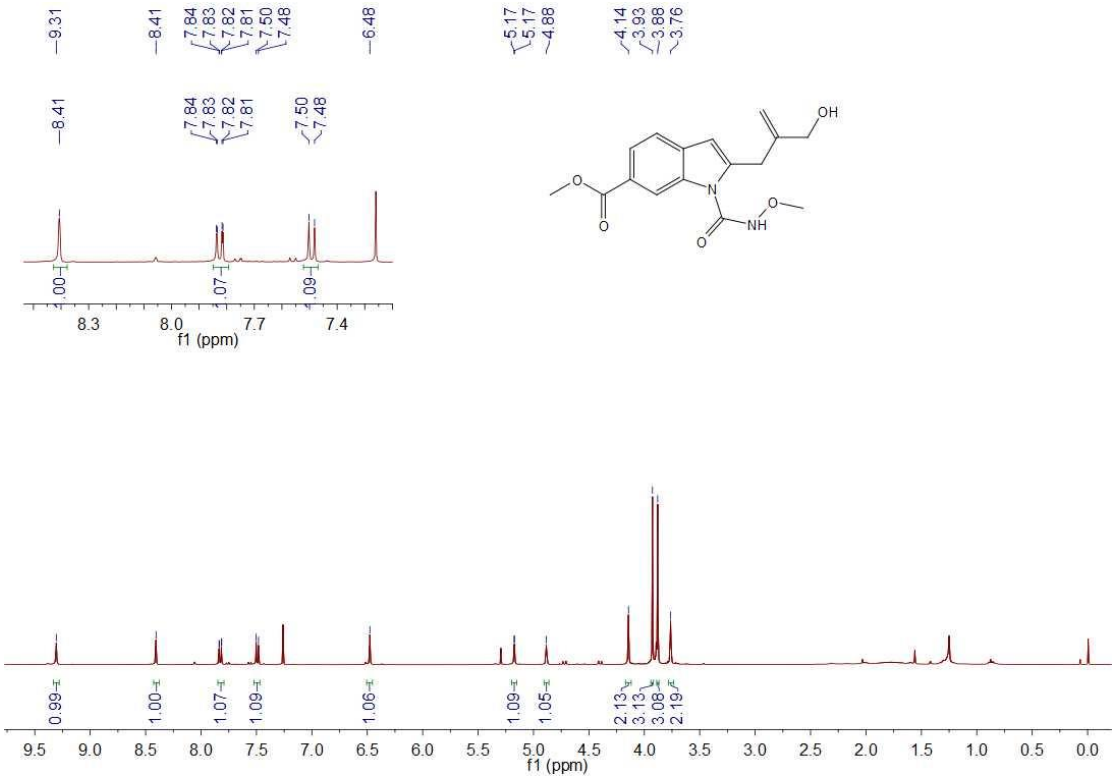


^{13}C NMR (101 MHz, $CDCl_3$)

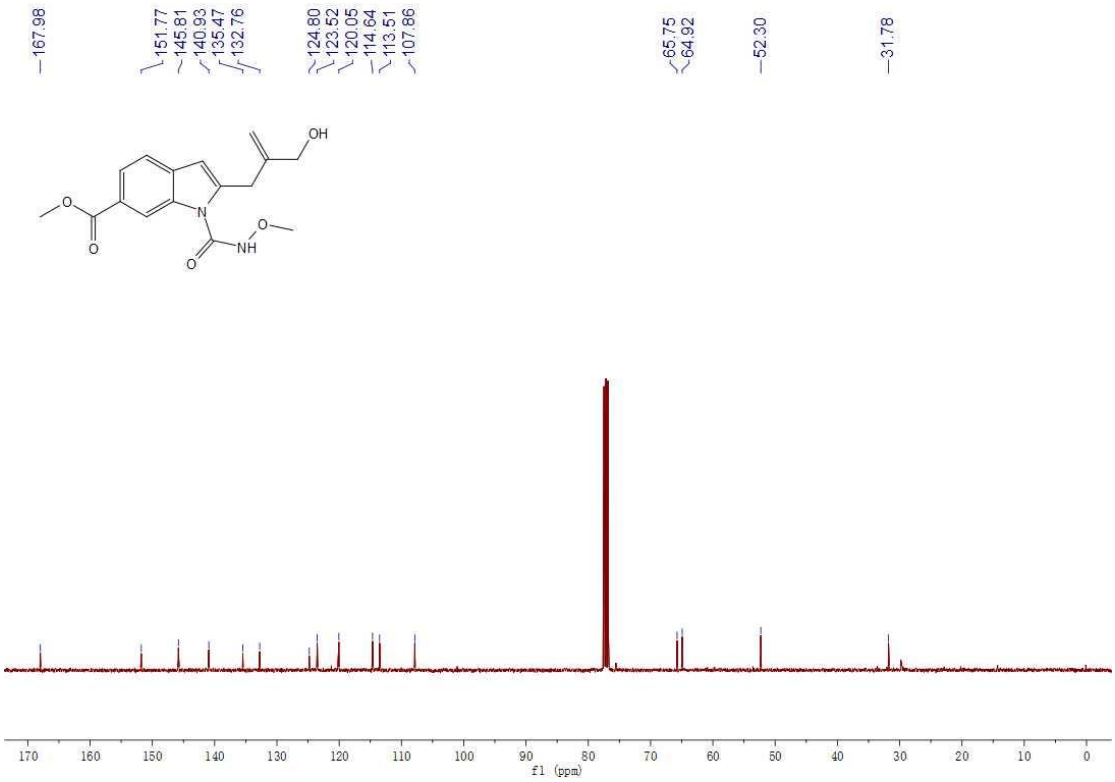


^{19}F NMR (376 MHz, $CDCl_3$)

3k

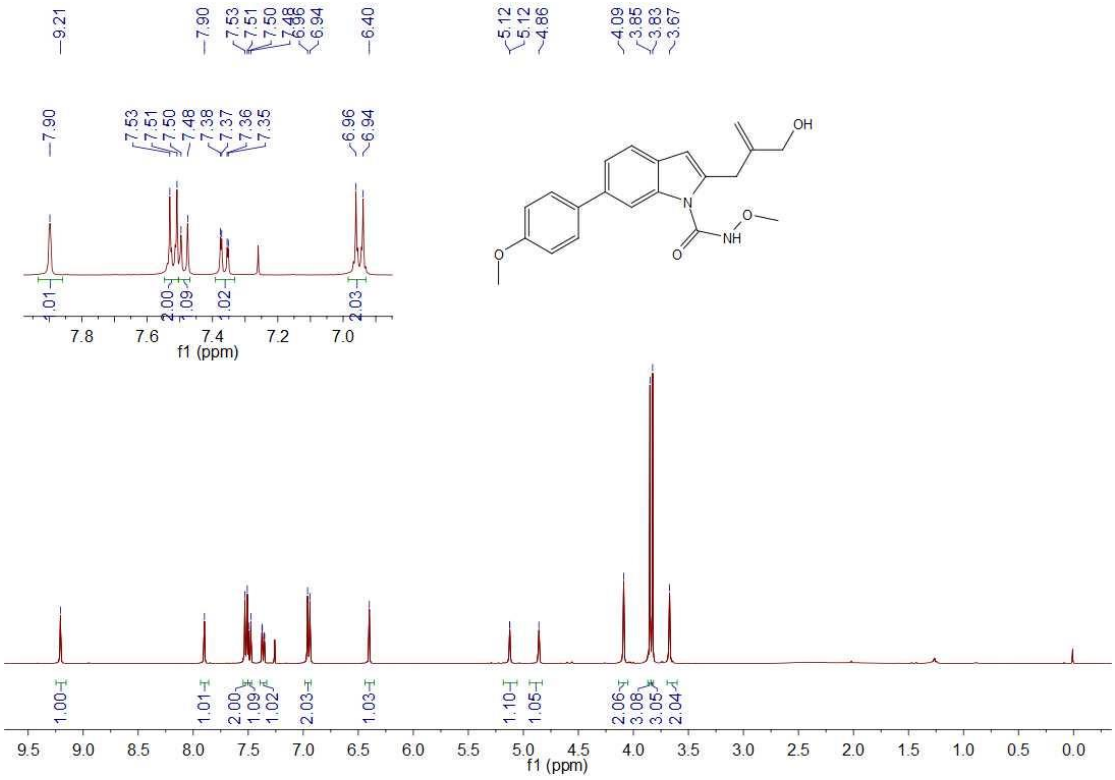


^{1}H NMR (400 MHz, $CDCl_3$)

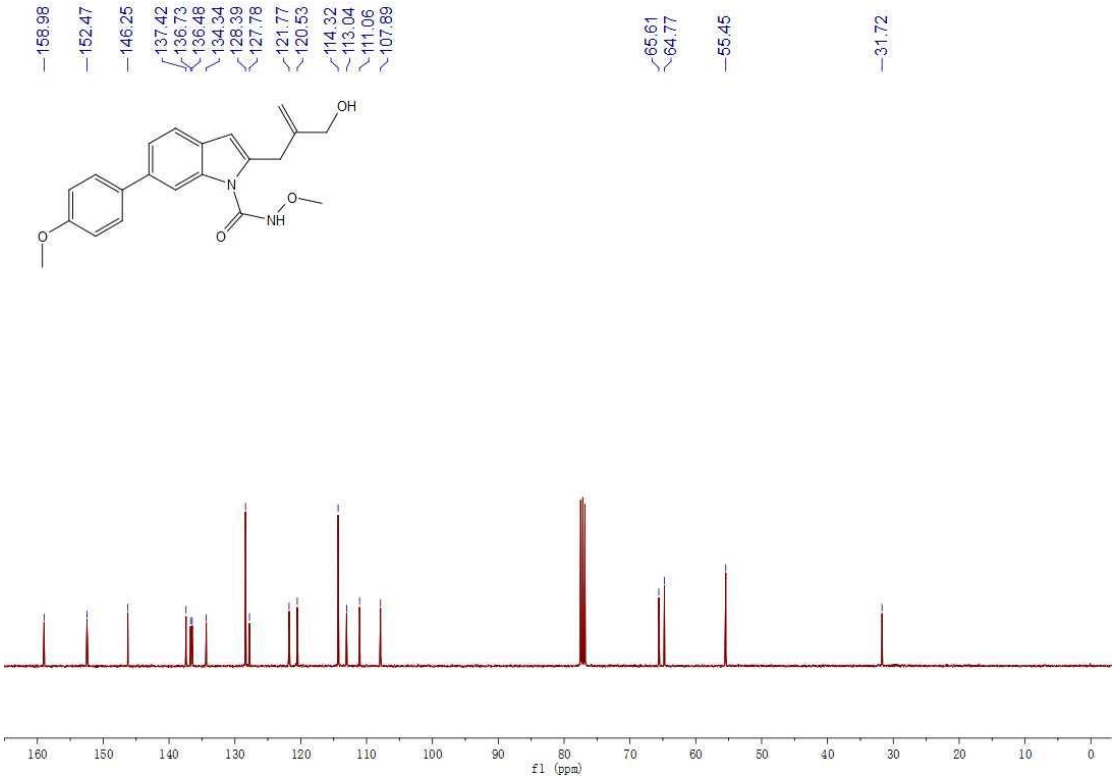


^{13}C NMR (101 MHz, $CDCl_3$)

3l

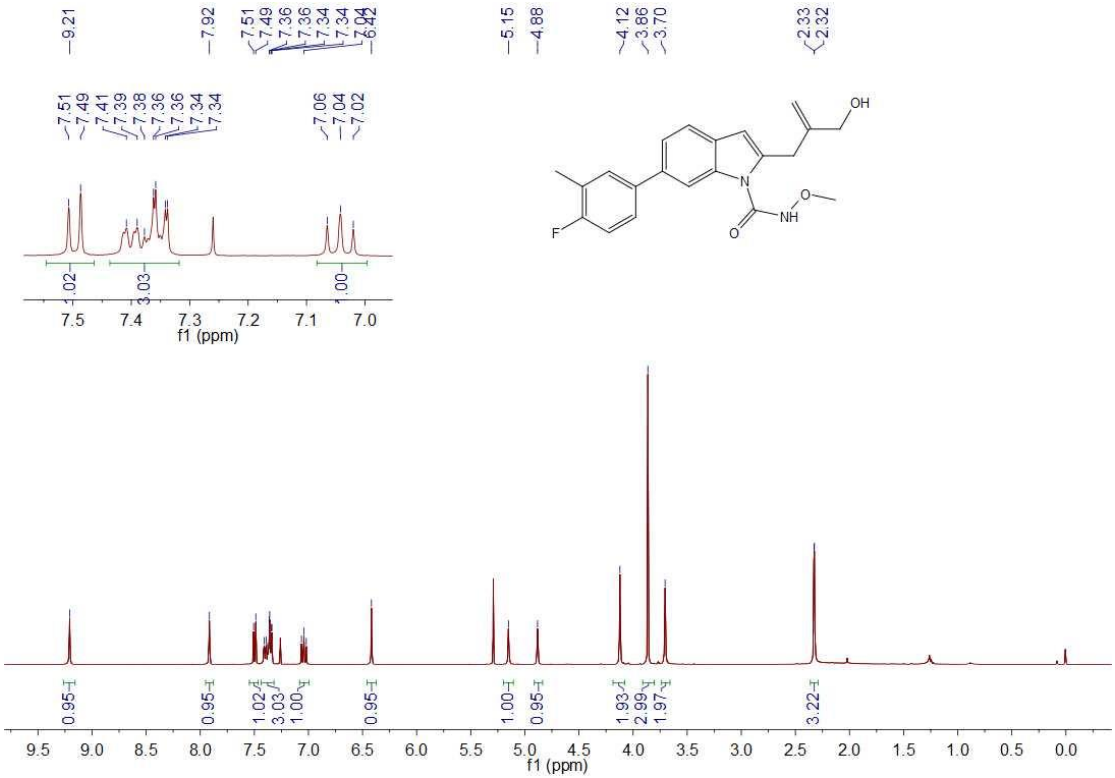


^{1}H NMR (400 MHz, $CDCl_3$)

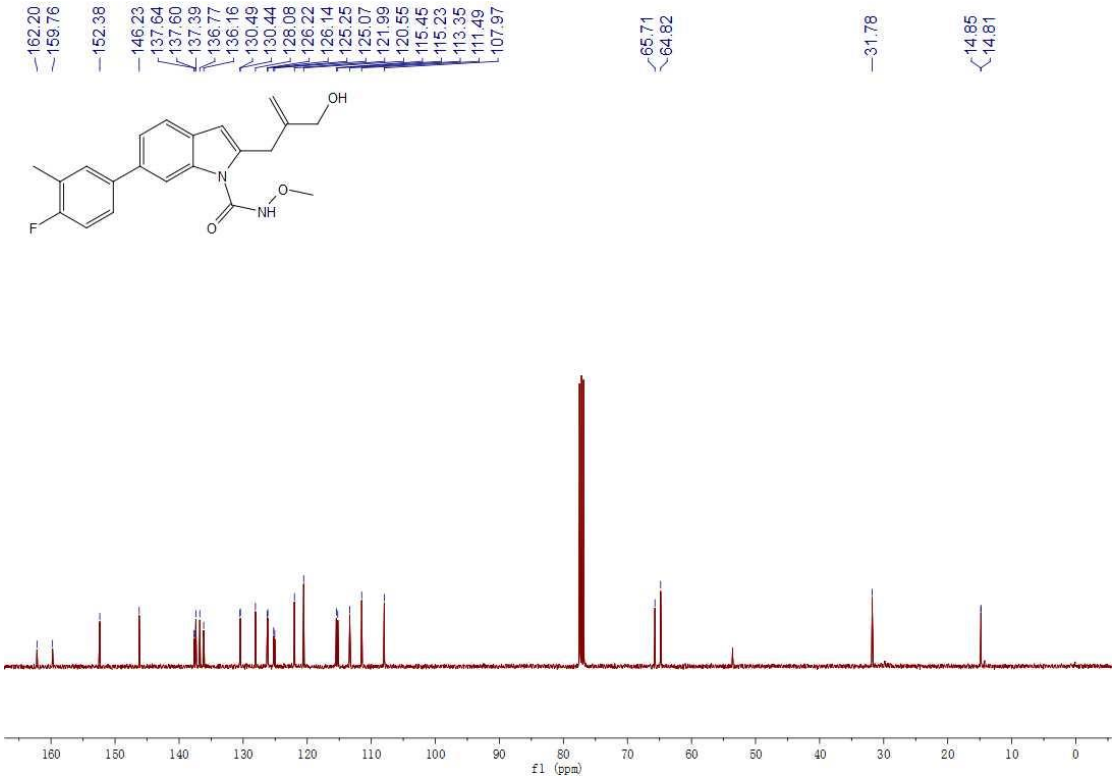


^{13}C NMR (101 MHz, $CDCl_3$)

3m

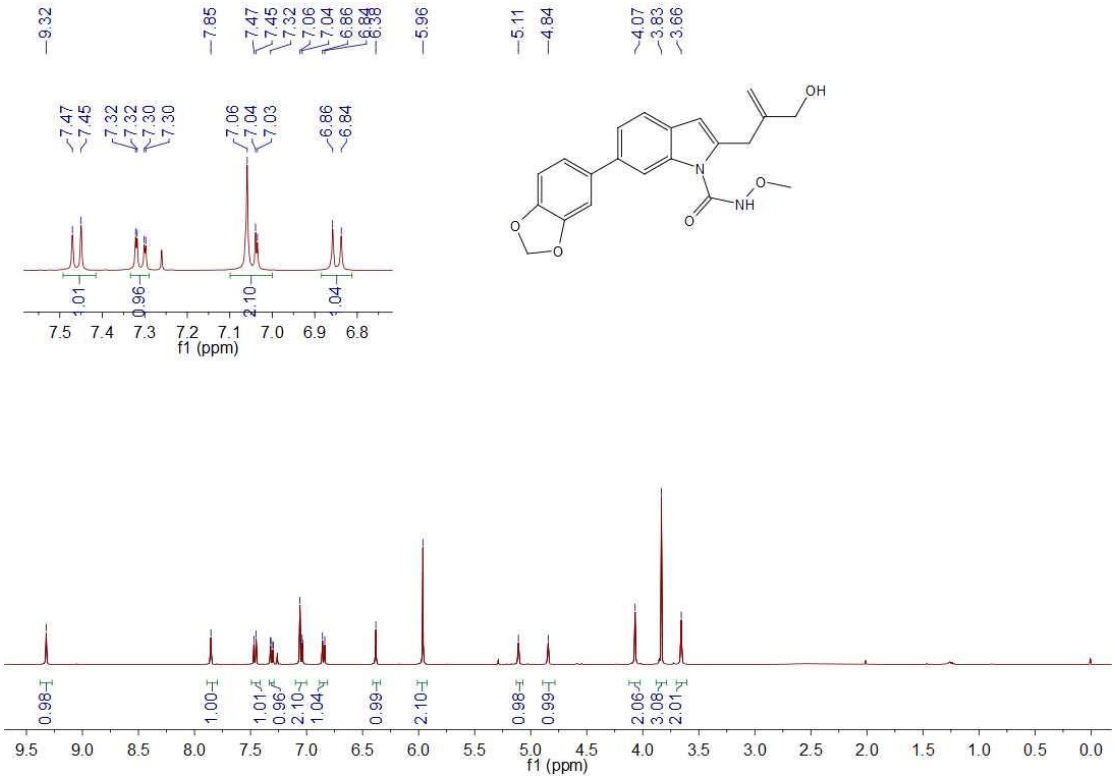


^{1}H NMR (400 MHz, $CDCl_3$)

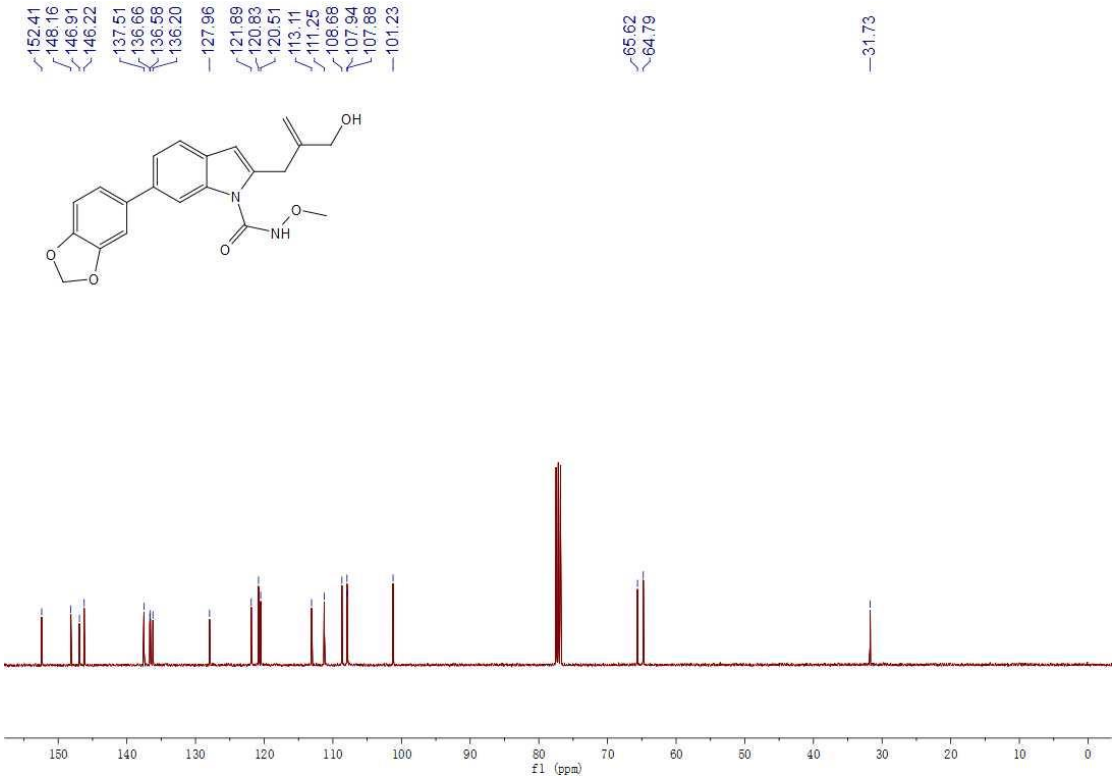


^{13}C NMR (101 MHz, $CDCl_3$)

3n

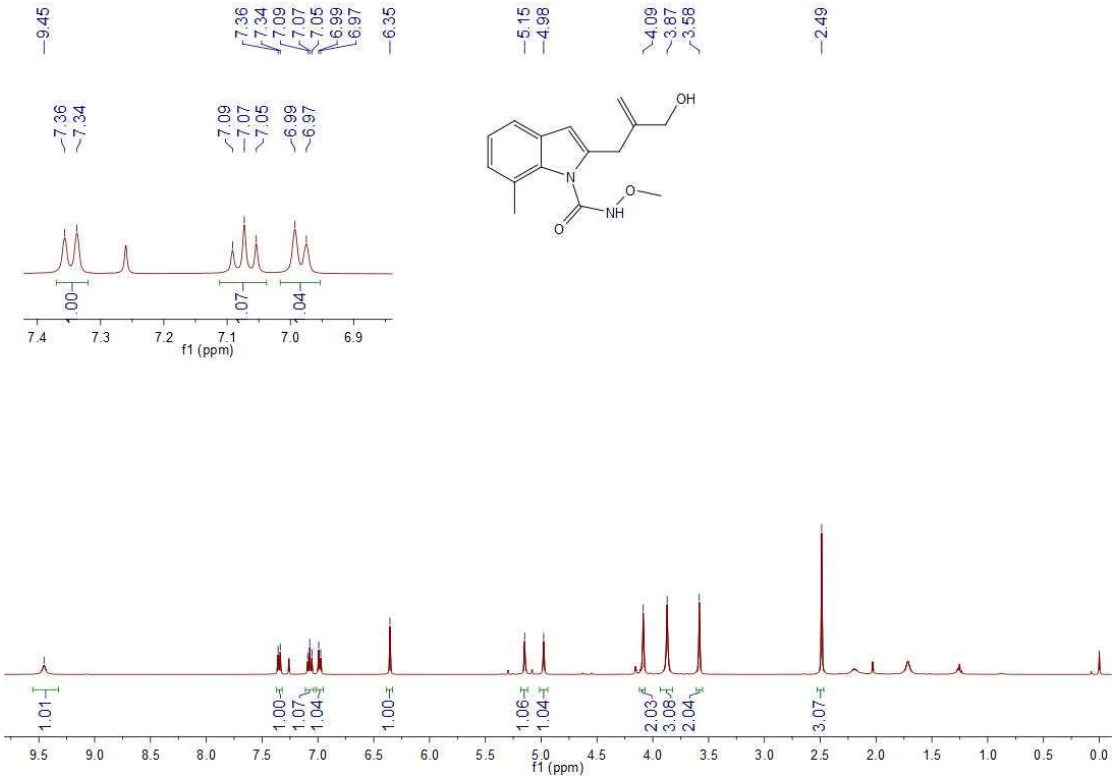


^{1}H NMR (400 MHz, $CDCl_3$)

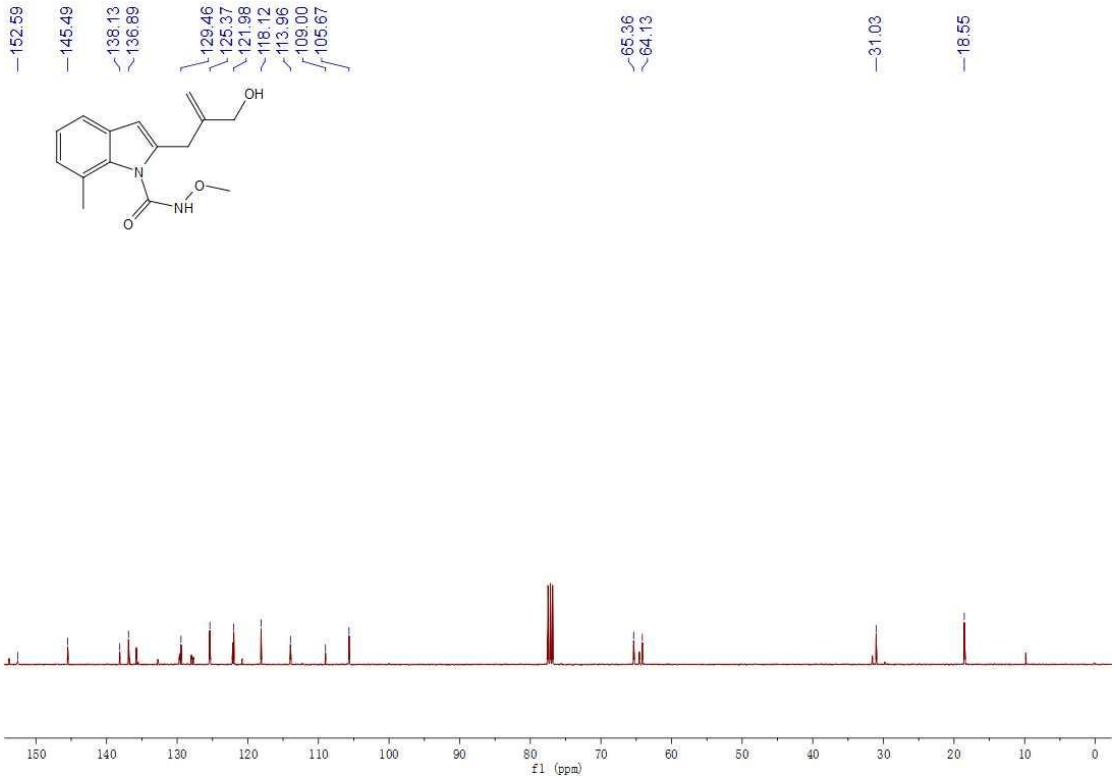


^{13}C NMR (101 MHz, $CDCl_3$)

3o

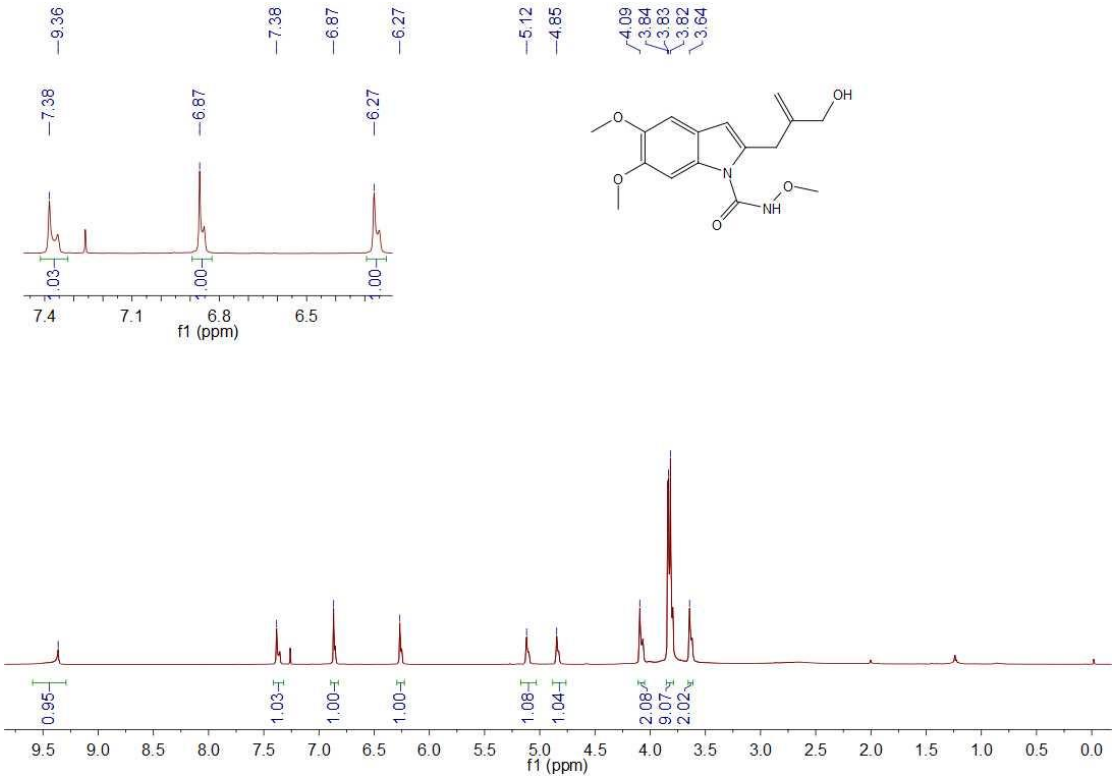


^{1}H NMR (400 MHz, $CDCl_3$)

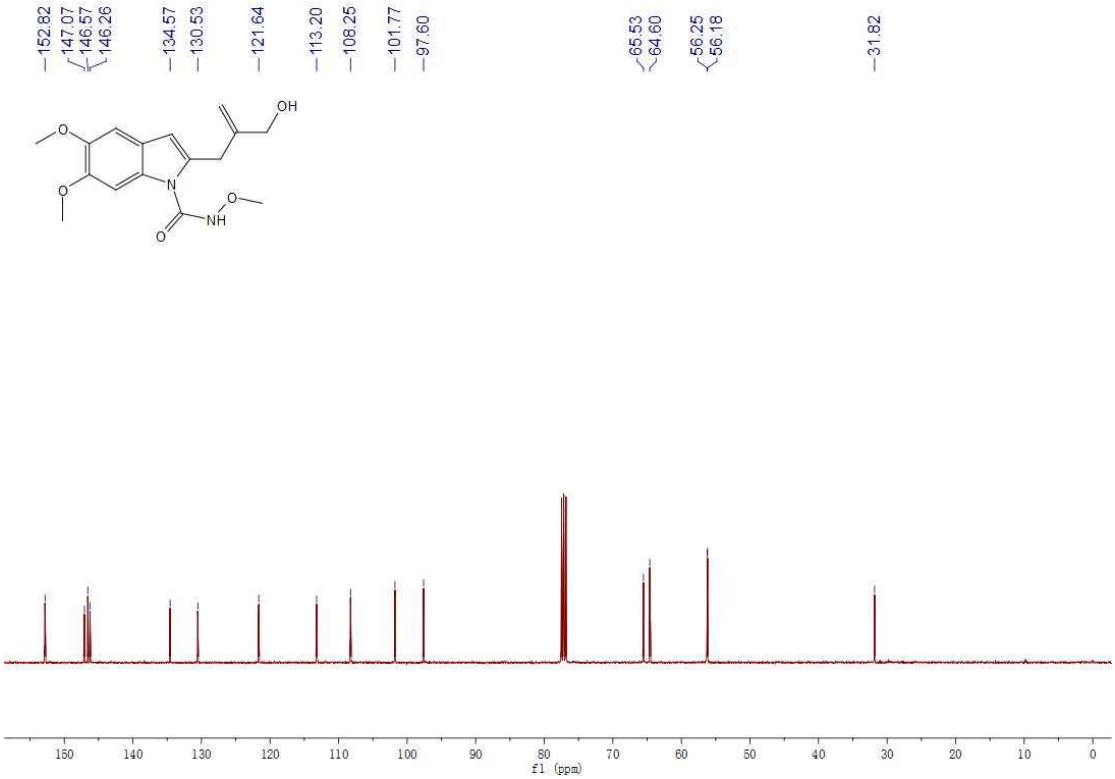


^{13}C NMR (101 MHz, $CDCl_3$)

3p

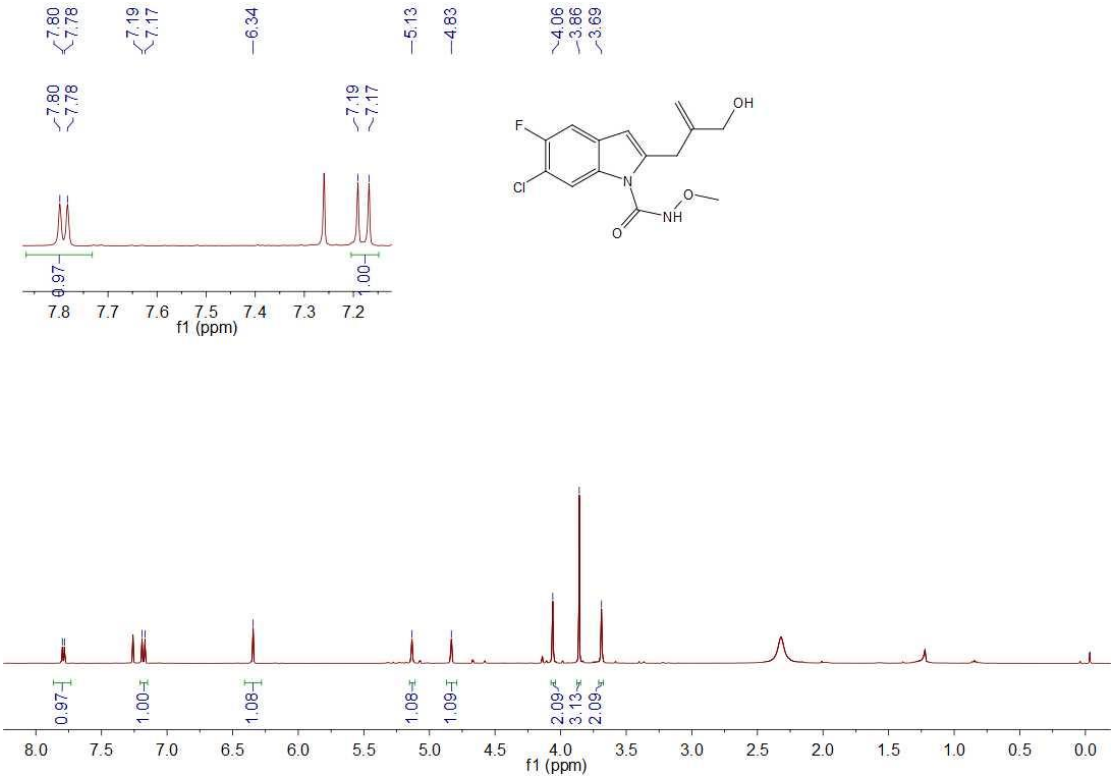


^{1}H NMR (400 MHz, $CDCl_3$)

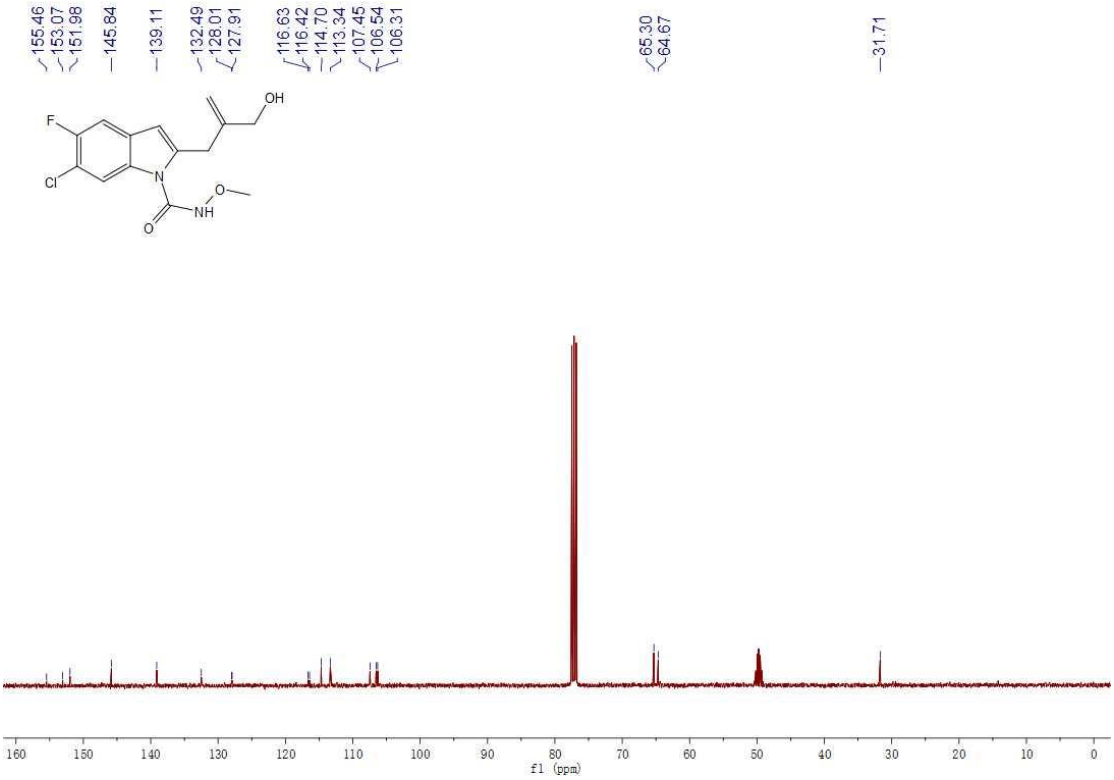


^{13}C NMR (101 MHz, $CDCl_3$)

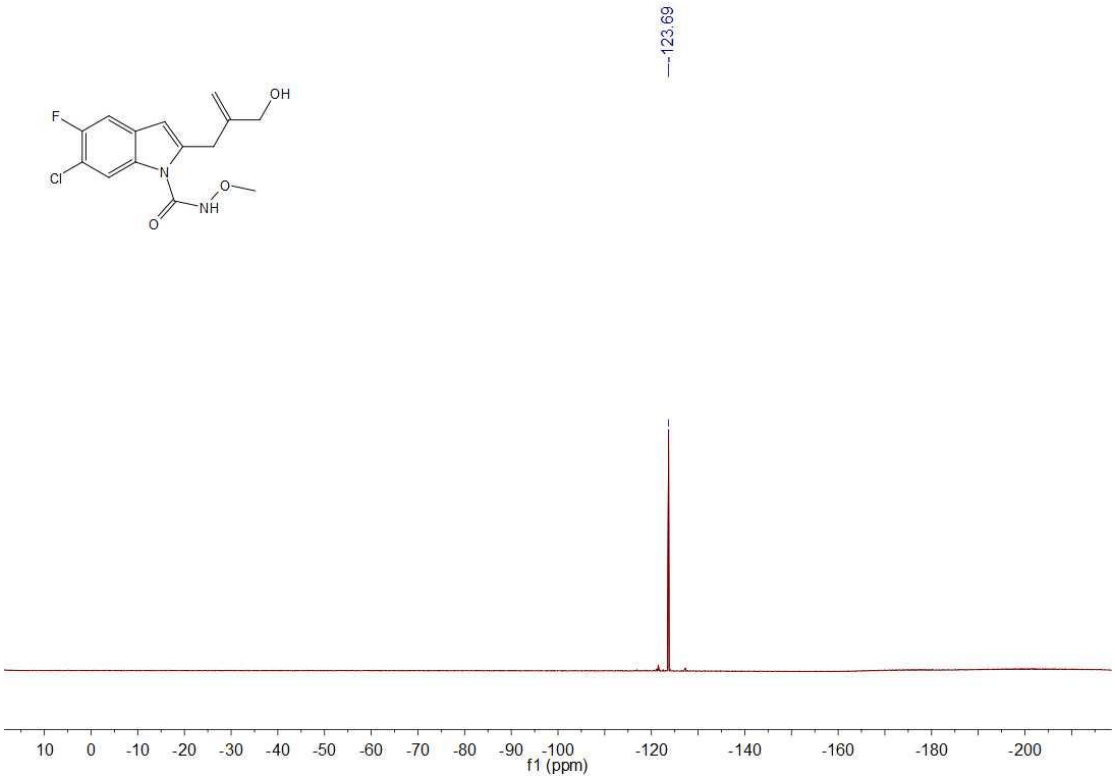
3q



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

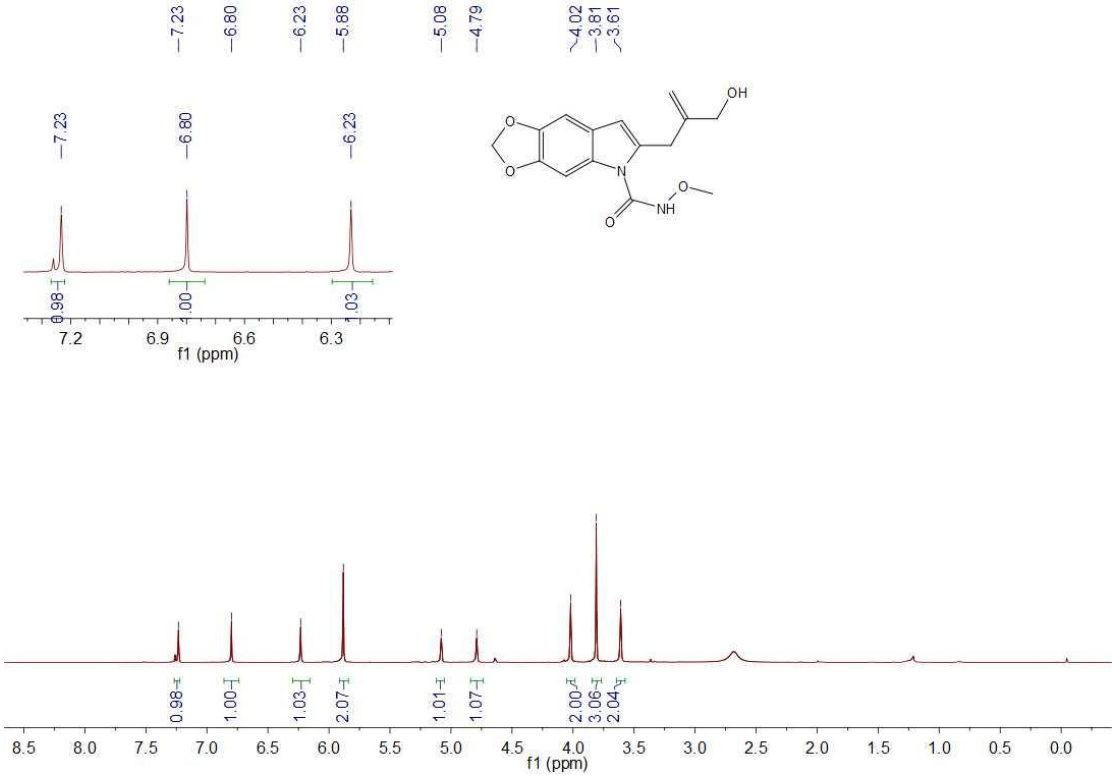


^{13}C NMR (101 MHz, $CDCl_3$)

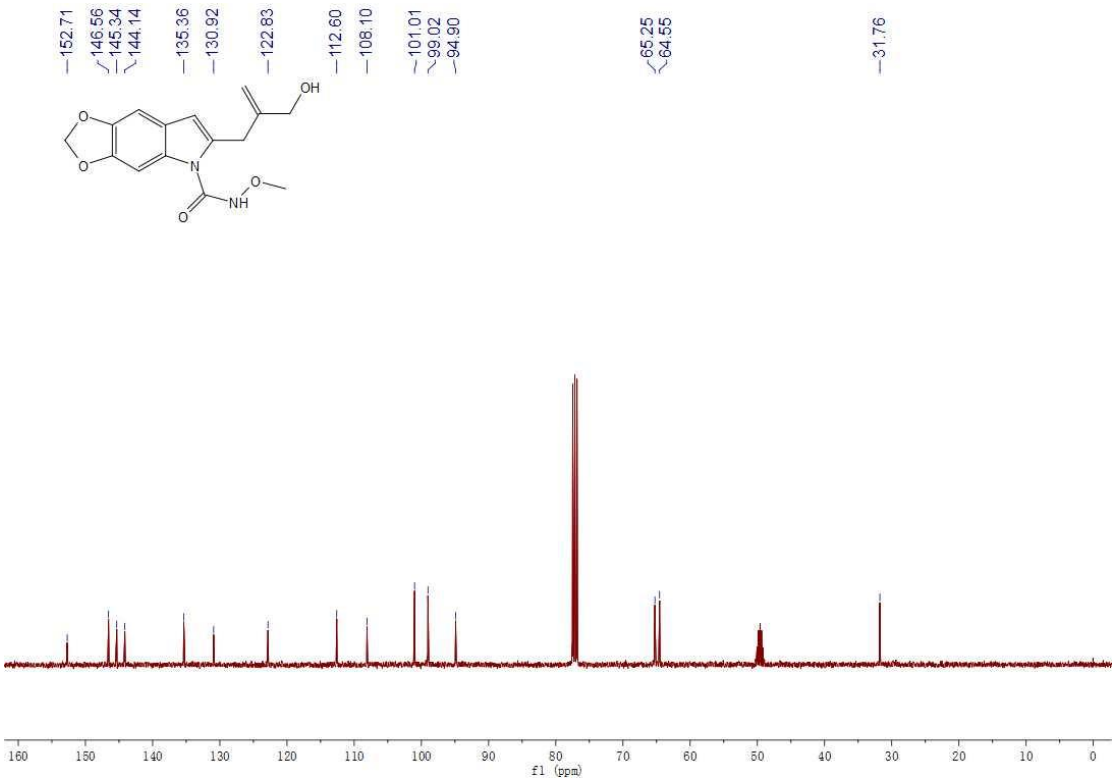


^{19}F NMR (376 MHz, $CDCl_3$)

3r

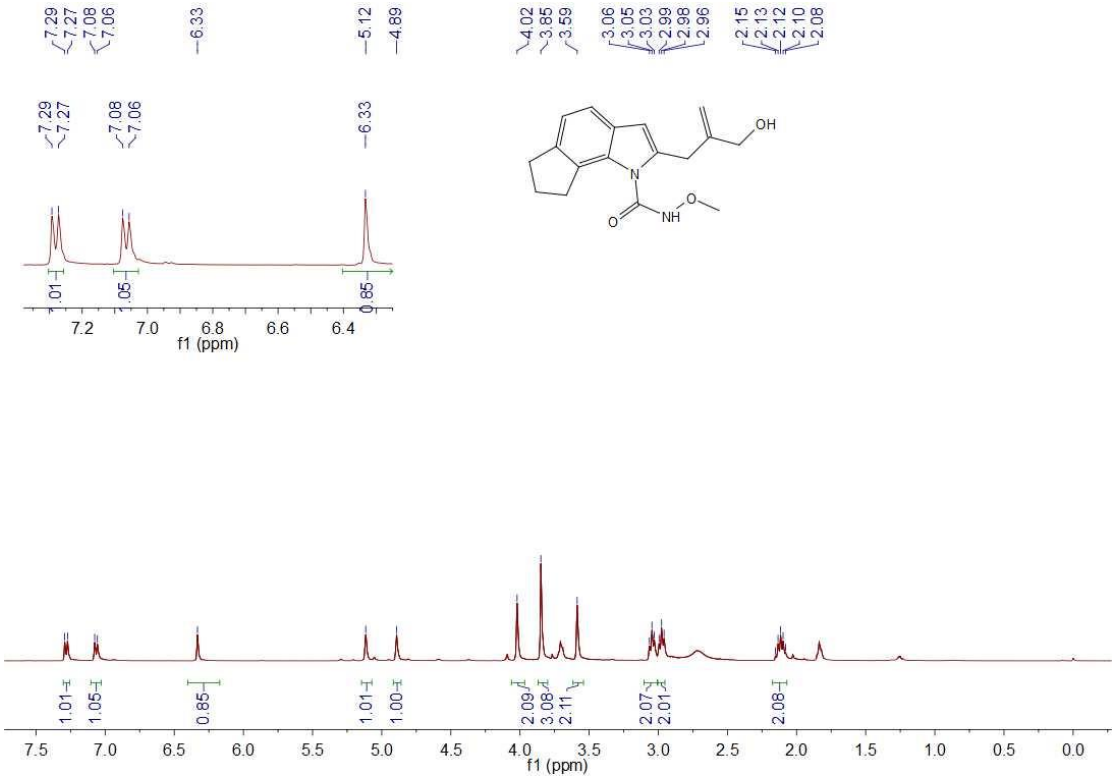


^{1}H NMR (400 MHz, $CDCl_3$)

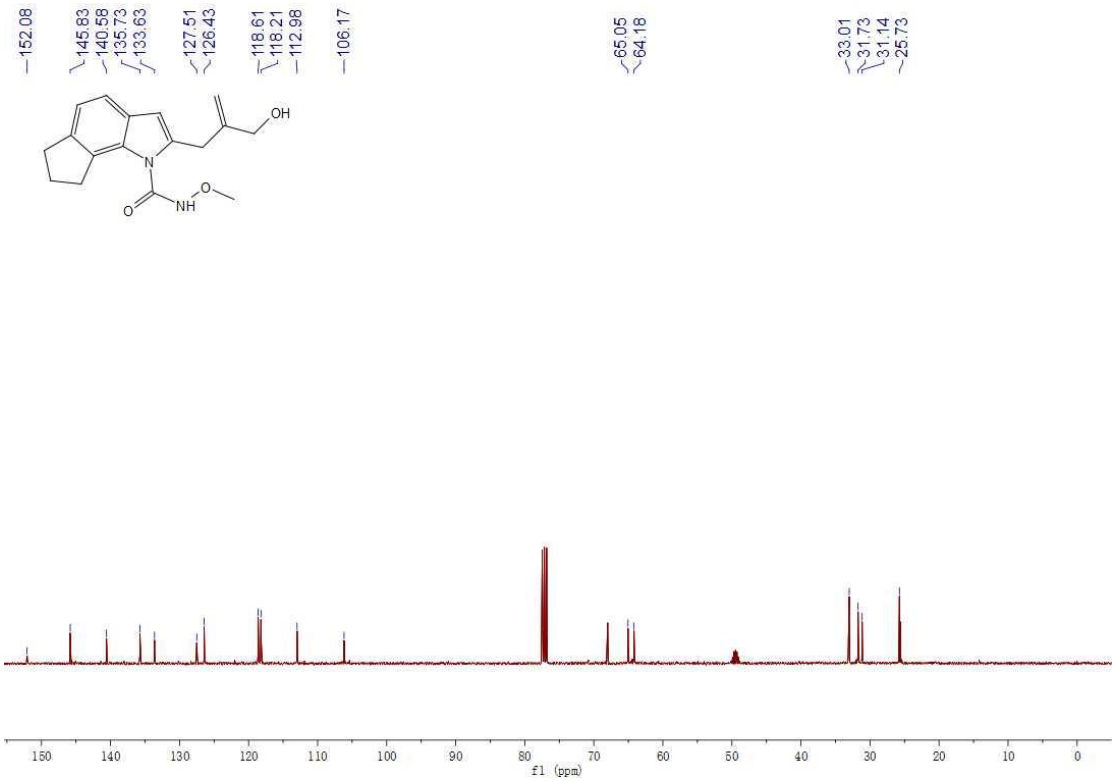


^{13}C NMR (101 MHz, $CDCl_3$)

3s

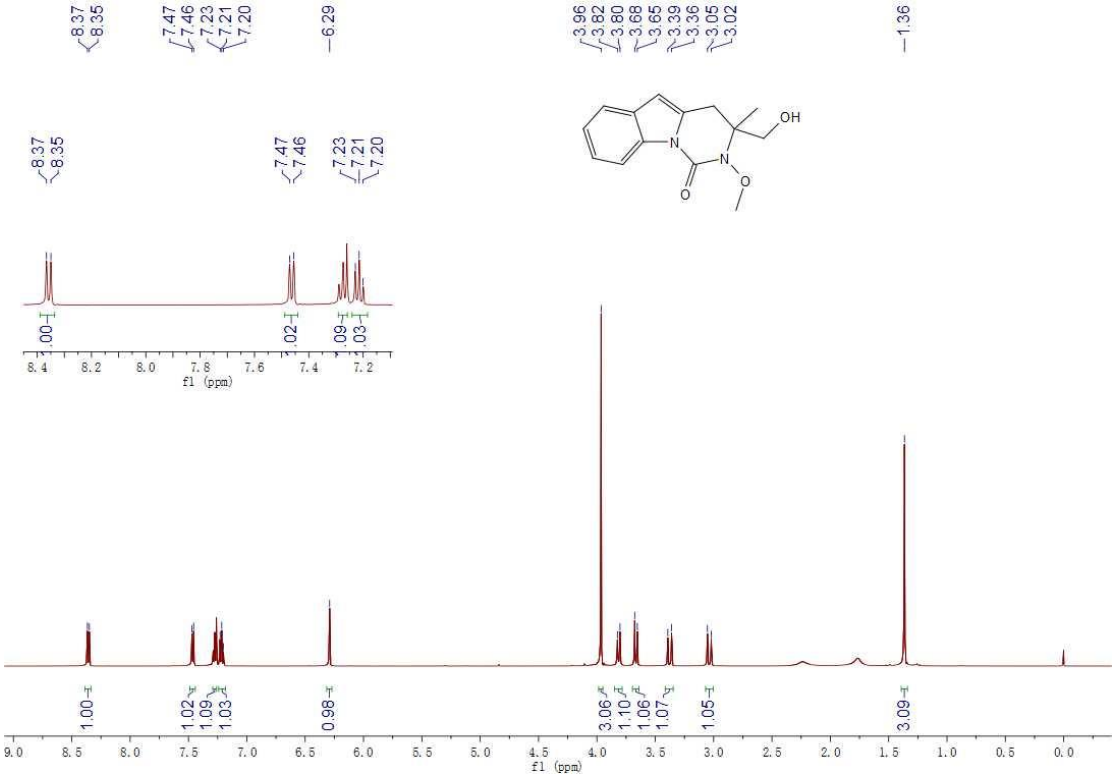


^{1}H NMR (400 MHz, $CDCl_3$)

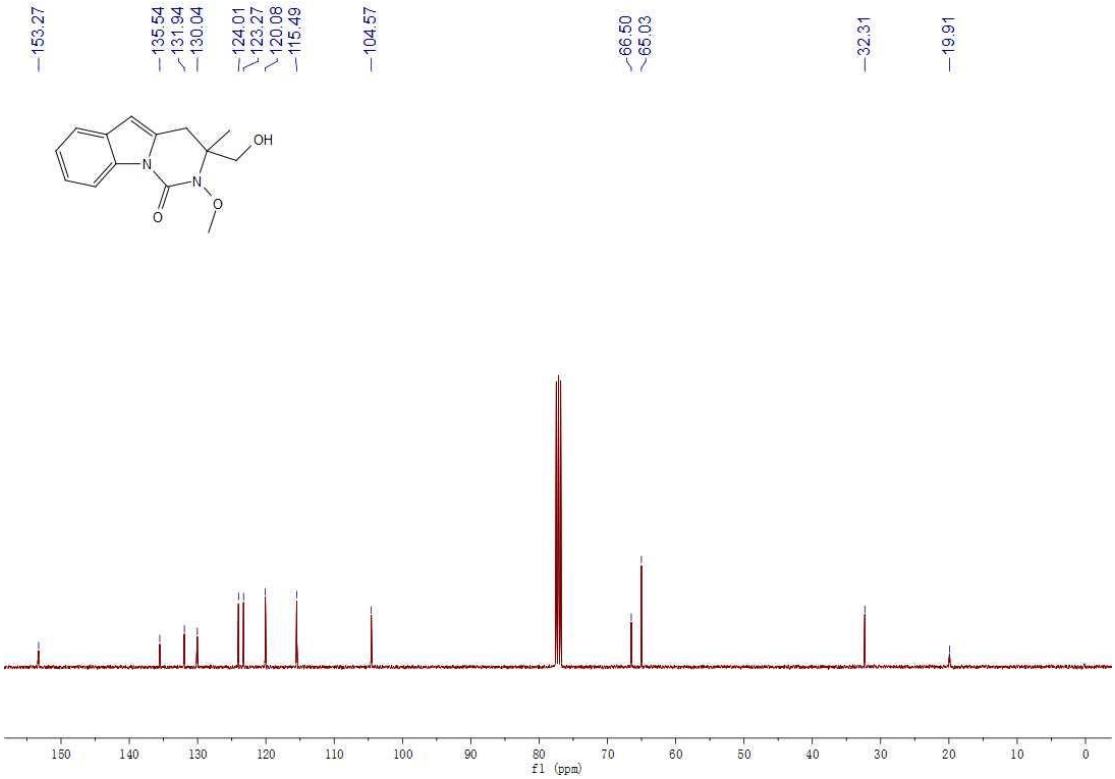


^{13}C NMR (101 MHz, $CDCl_3$)

4a

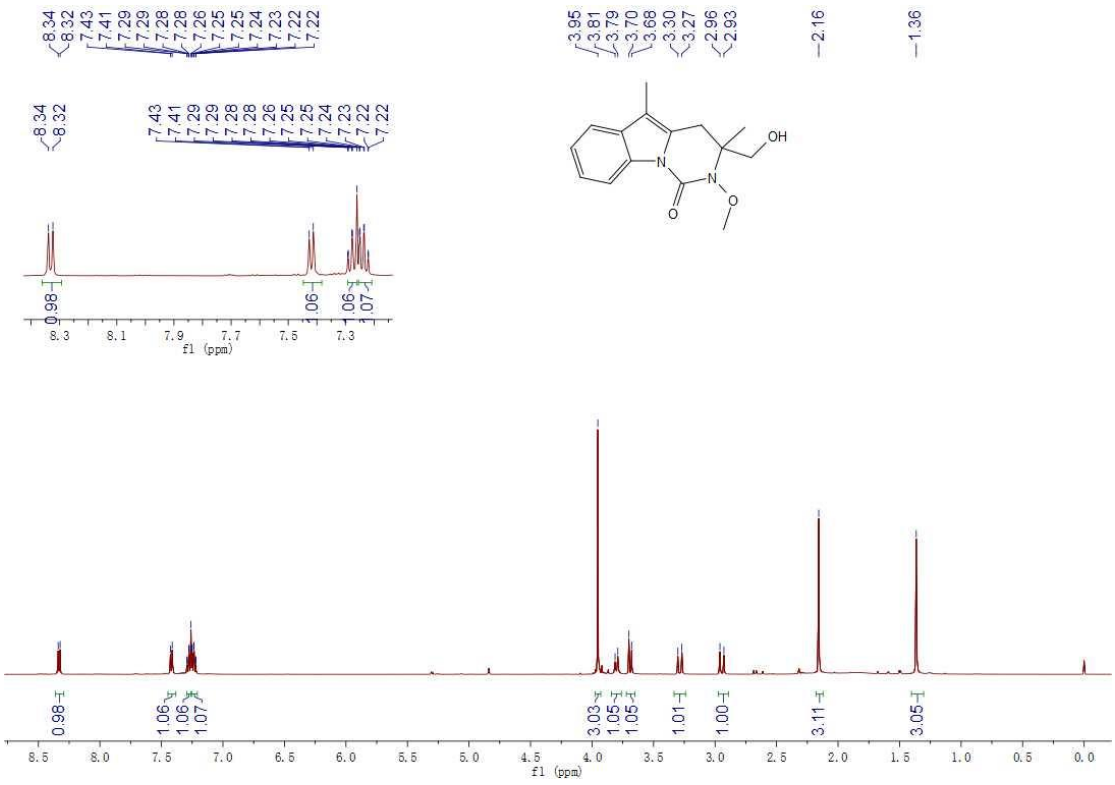


^{1}H NMR (500 MHz, $CDCl_3$)

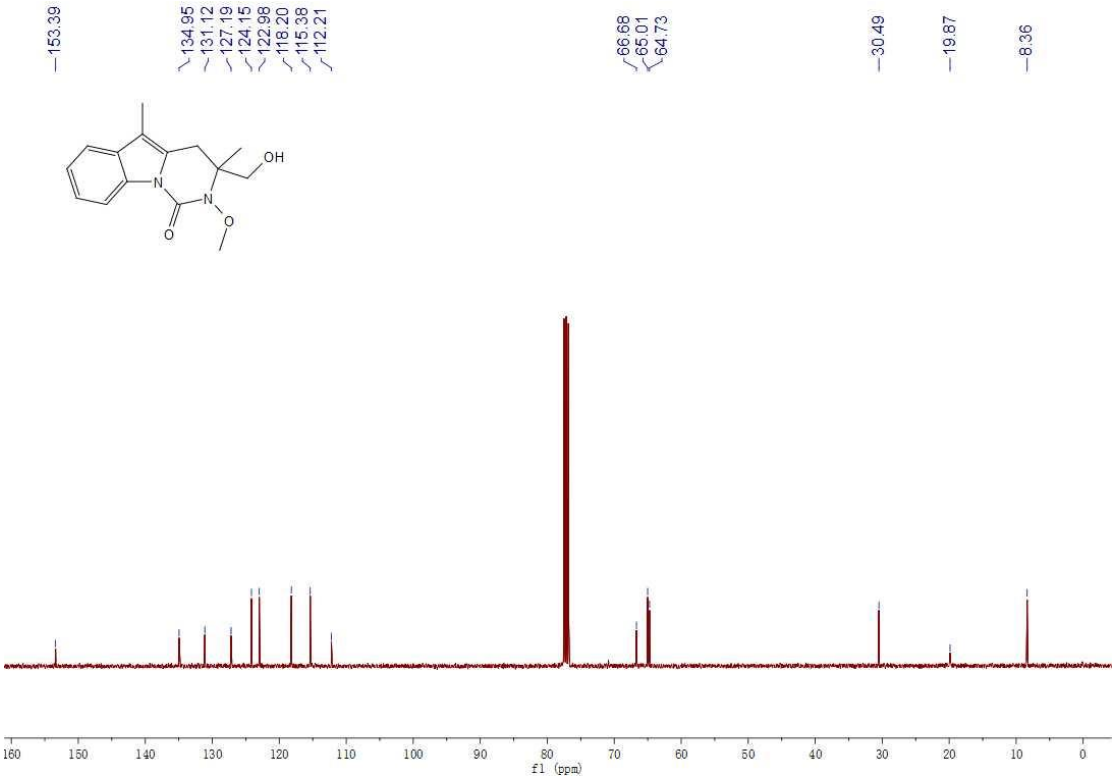


^{13}C NMR (101 MHz, $CDCl_3$)

4b

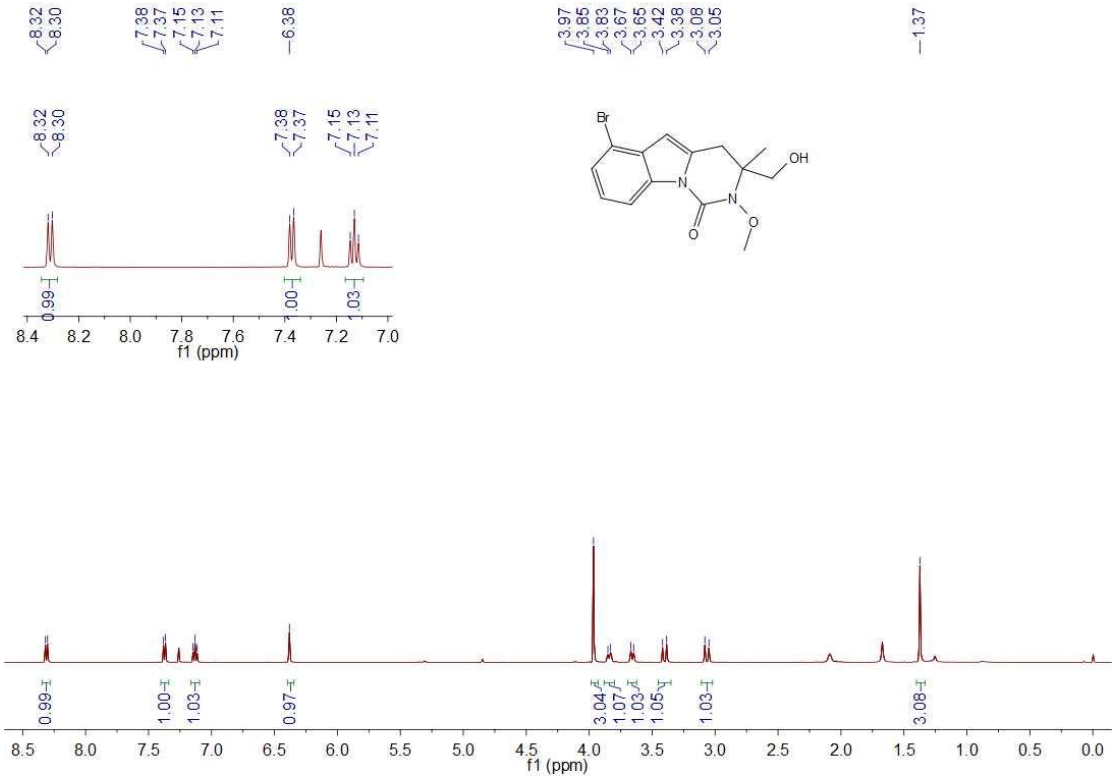


^{1}H NMR (500 MHz, $CDCl_3$)

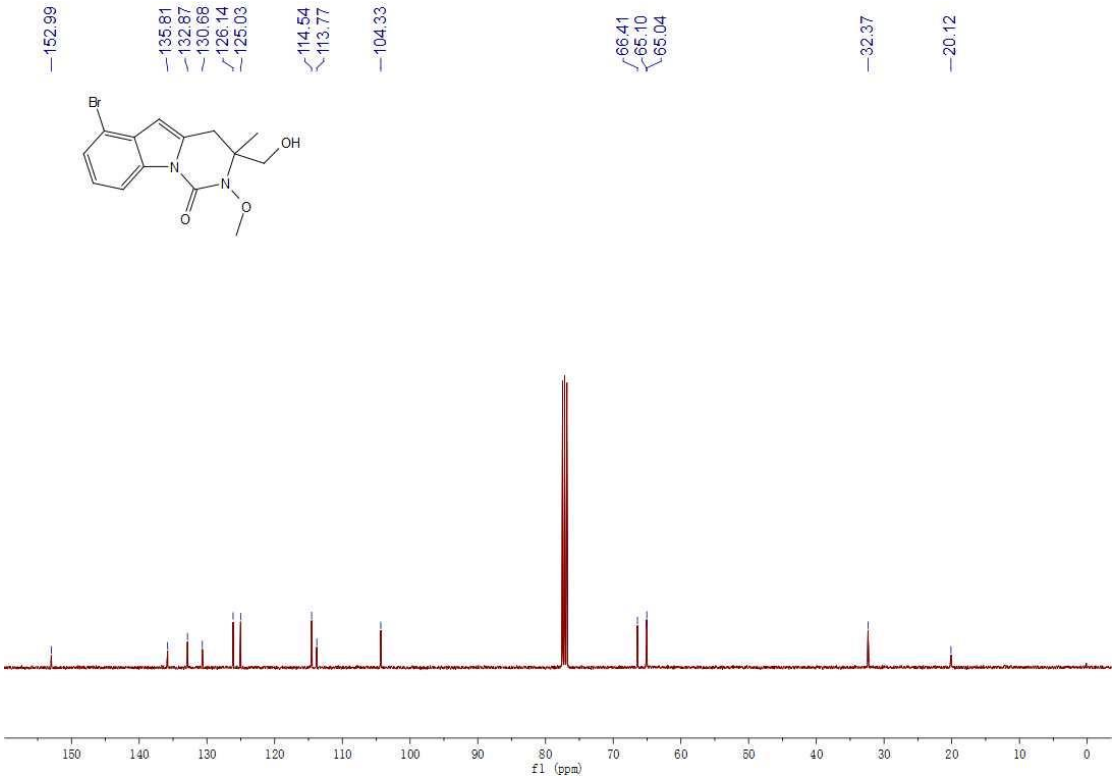


^{13}C NMR (101 MHz, $CDCl_3$)

4c

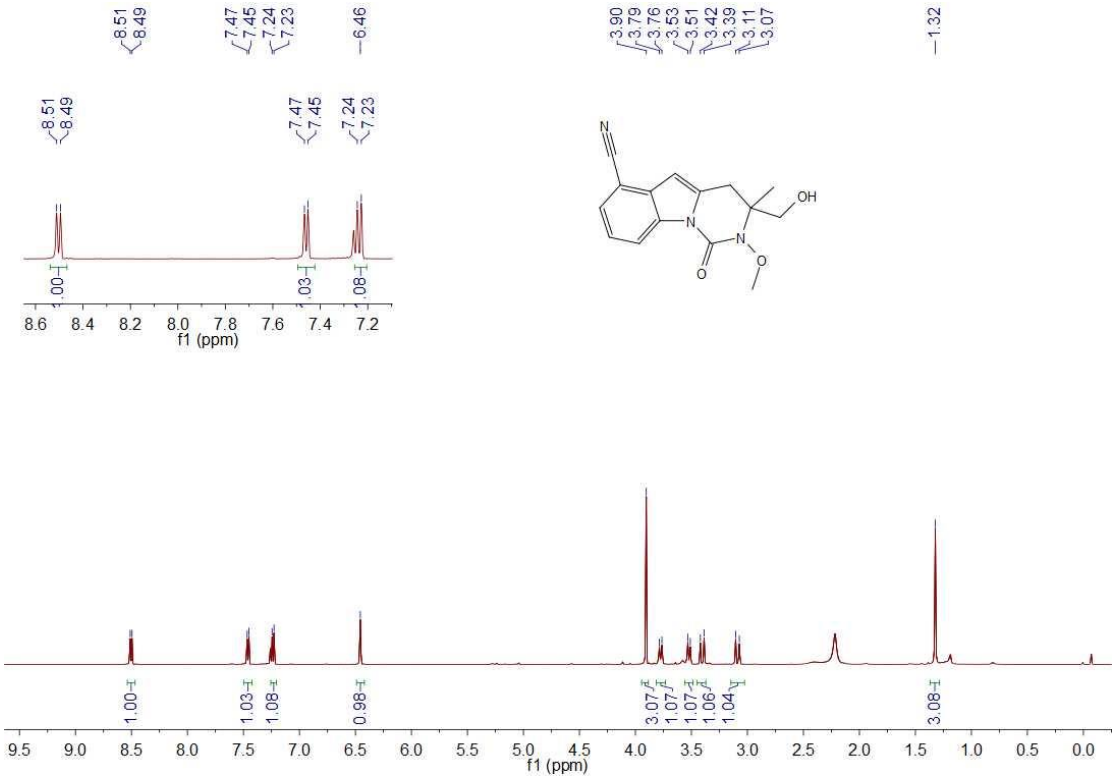


^{1}H NMR (500 MHz, $CDCl_3$)

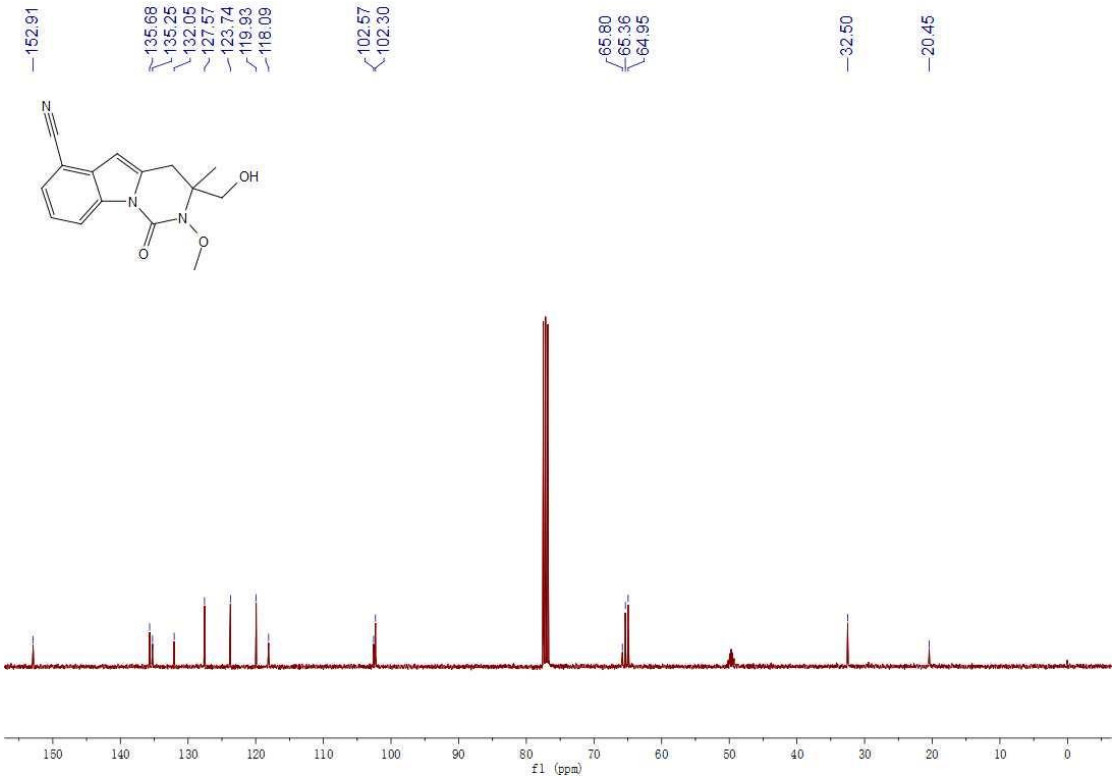


^{13}C NMR (101 MHz, $CDCl_3$)

4d

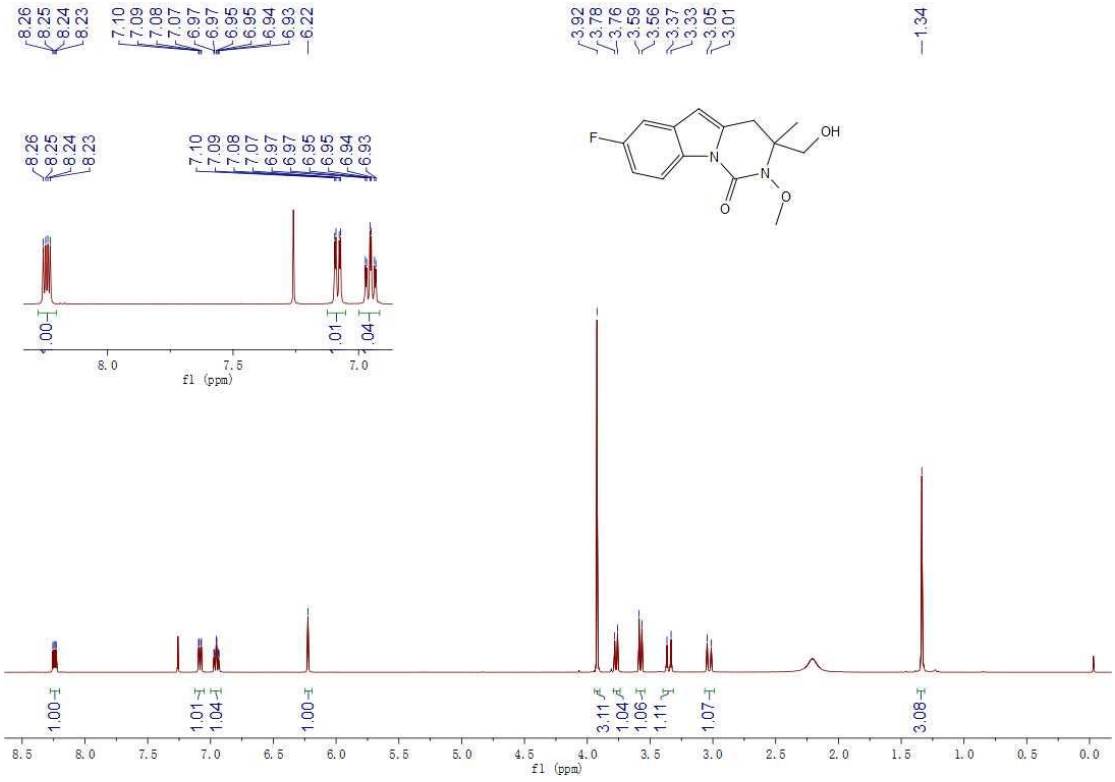


^{1}H NMR (500 MHz, $CDCl_3$)

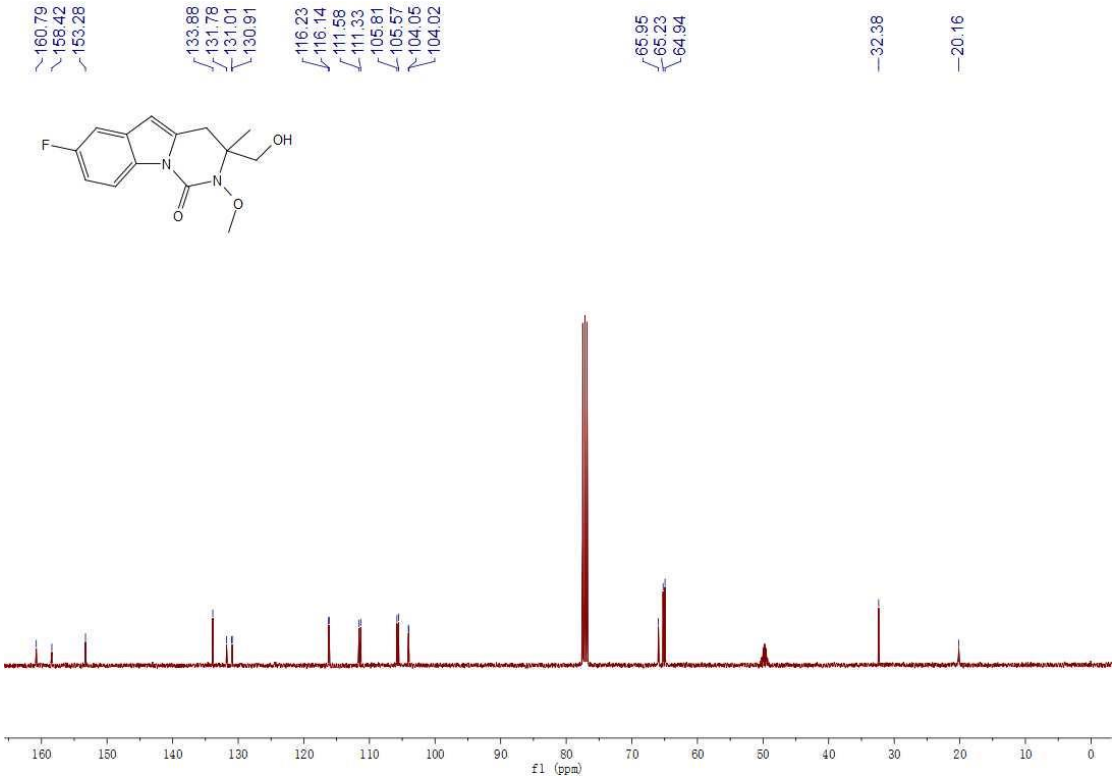


^{13}C NMR (101 MHz, $CDCl_3$)

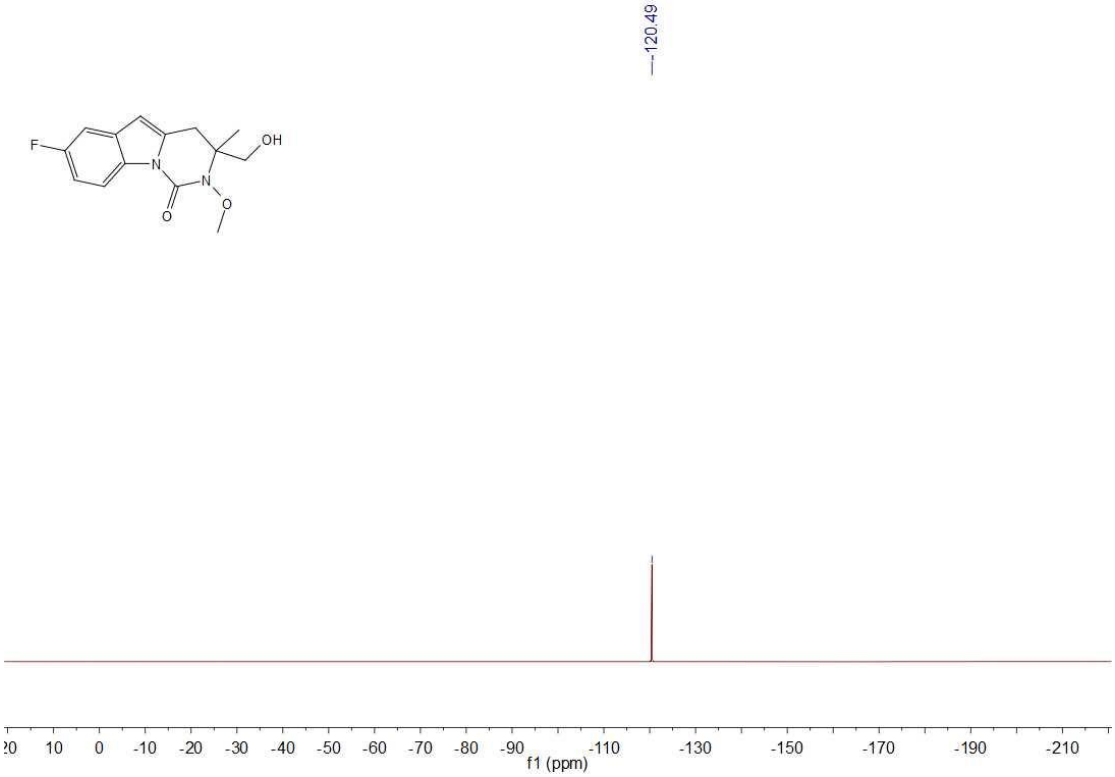
4e



^{1}H NMR (500 MHz, $CDCl_3$)

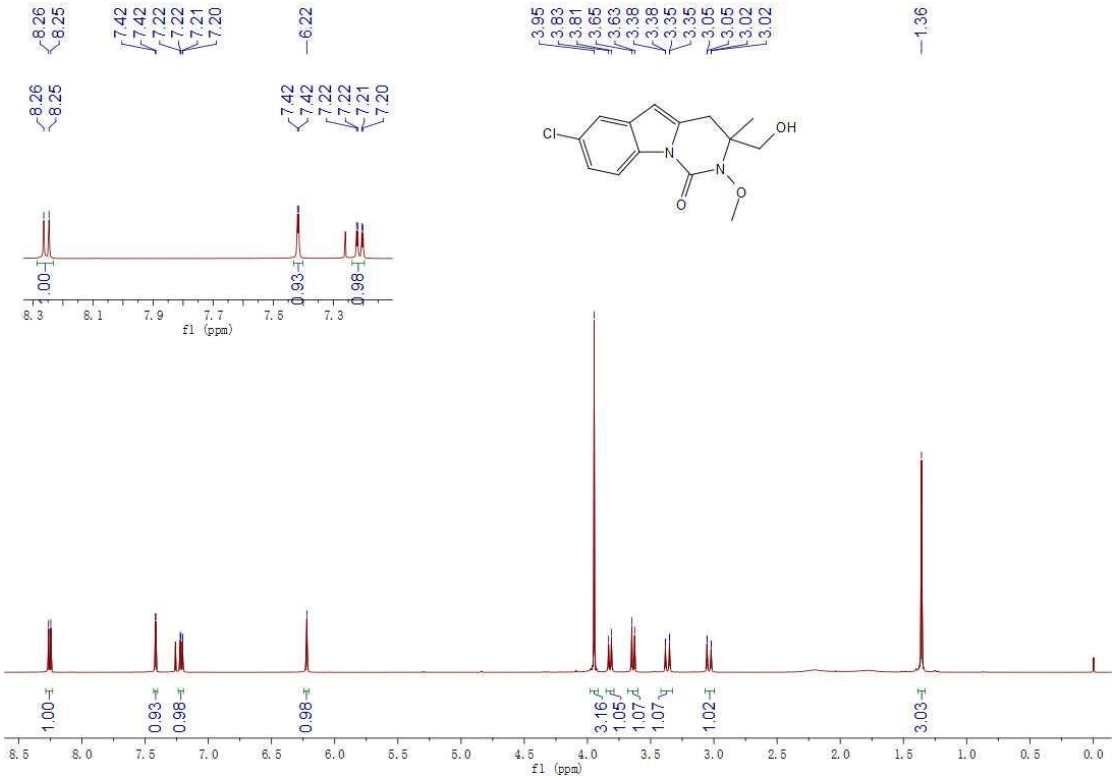


^{13}C NMR (101 MHz, $CDCl_3$)

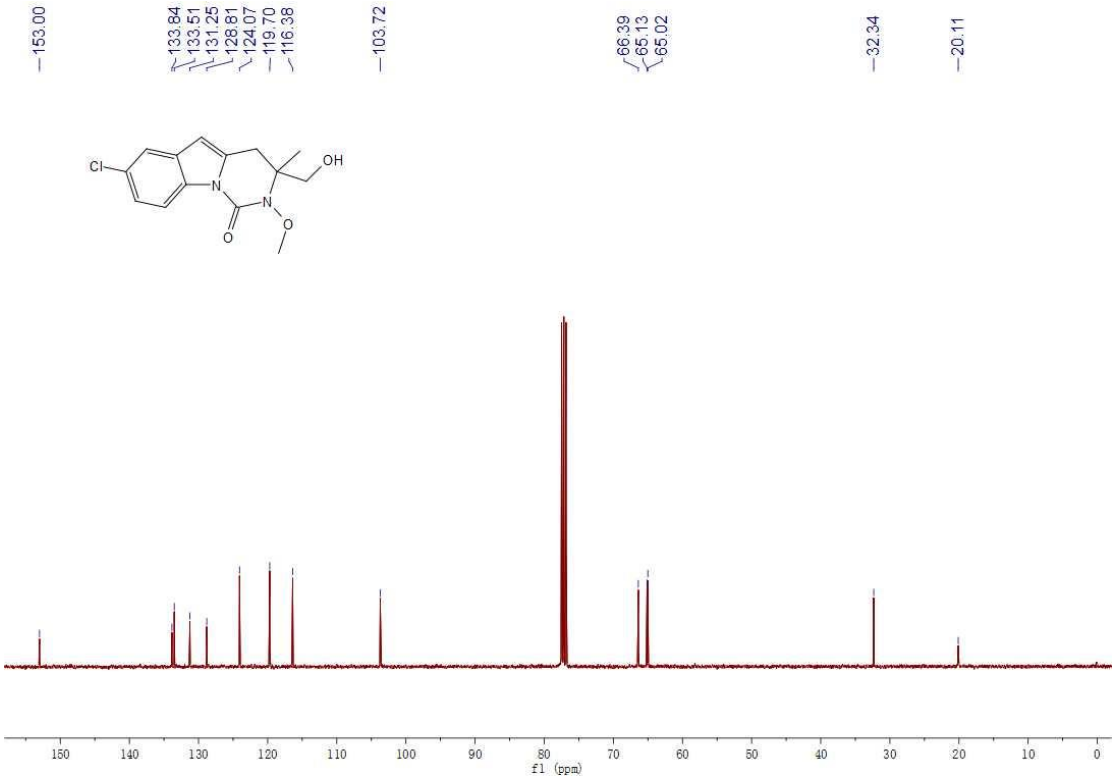


^{19}F NMR (471 MHz, $CDCl_3$)

4f

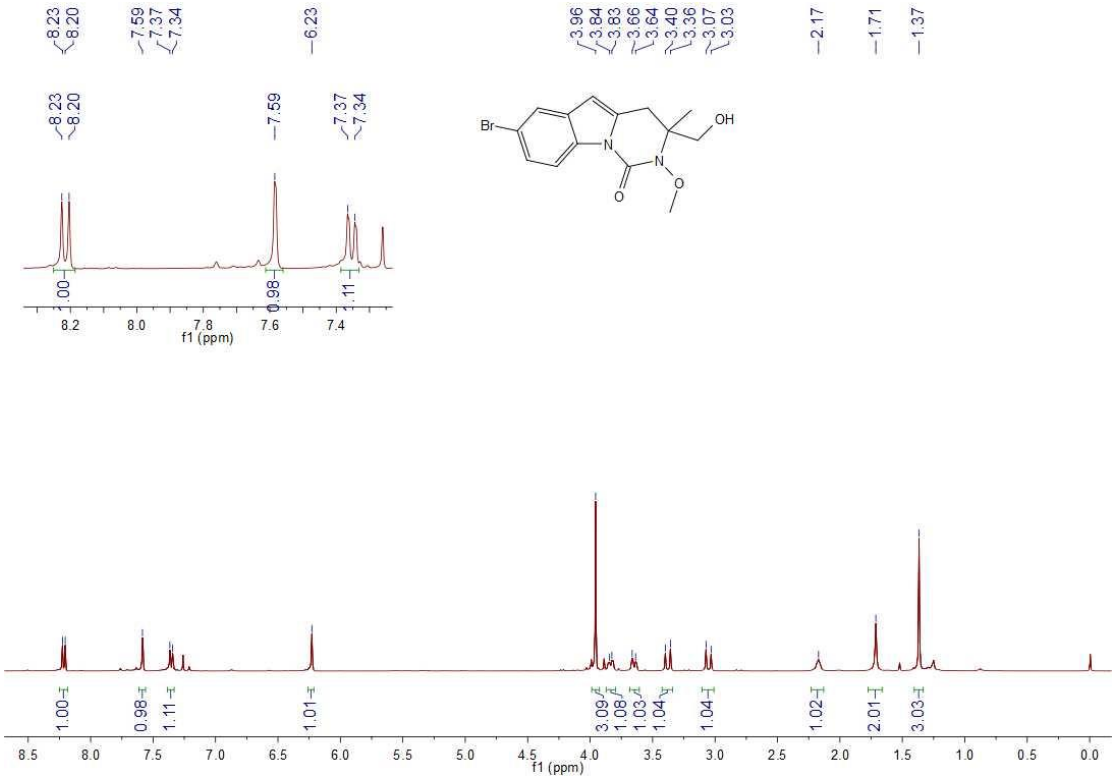


^{1}H NMR (500 MHz, $CDCl_3$)

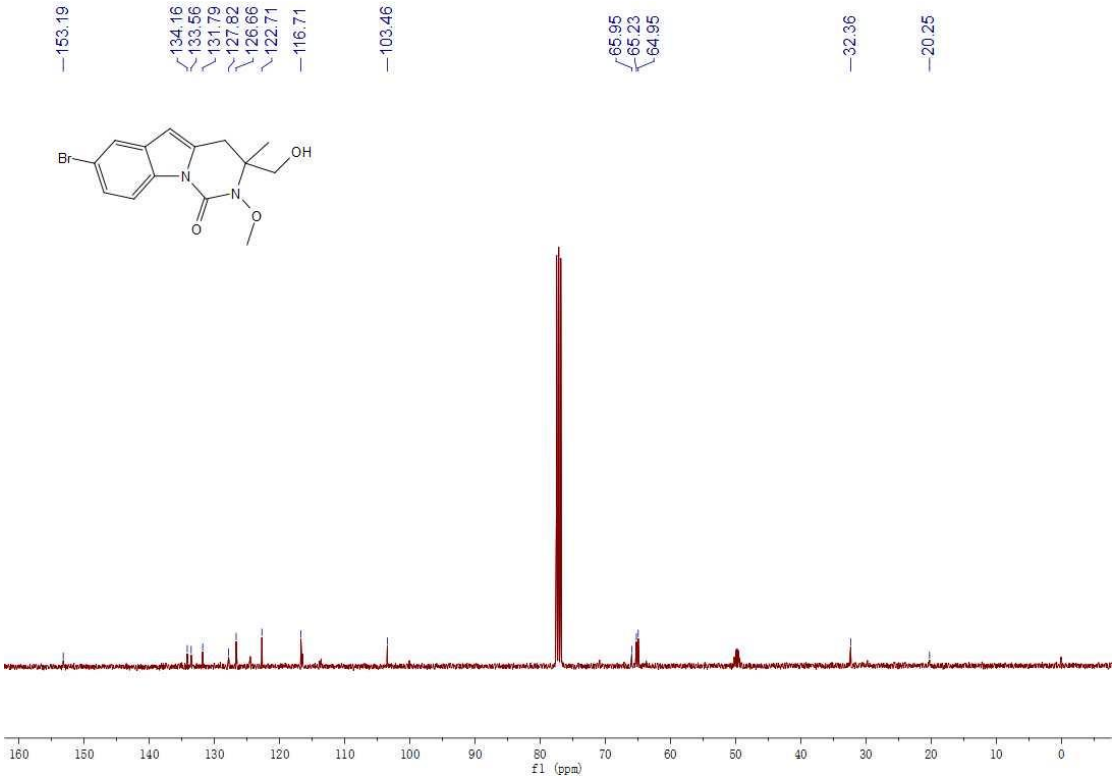


^{13}C NMR (101 MHz, $CDCl_3$)

4g

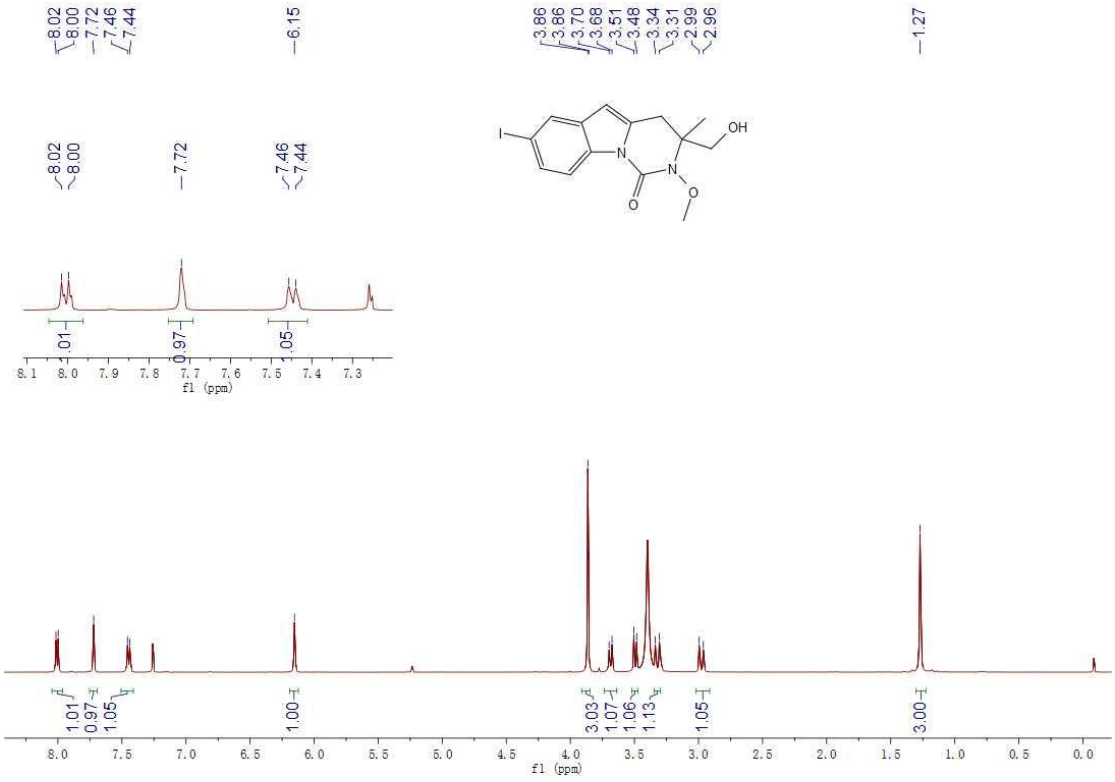


^{1}H NMR (400 MHz, $CDCl_3$)

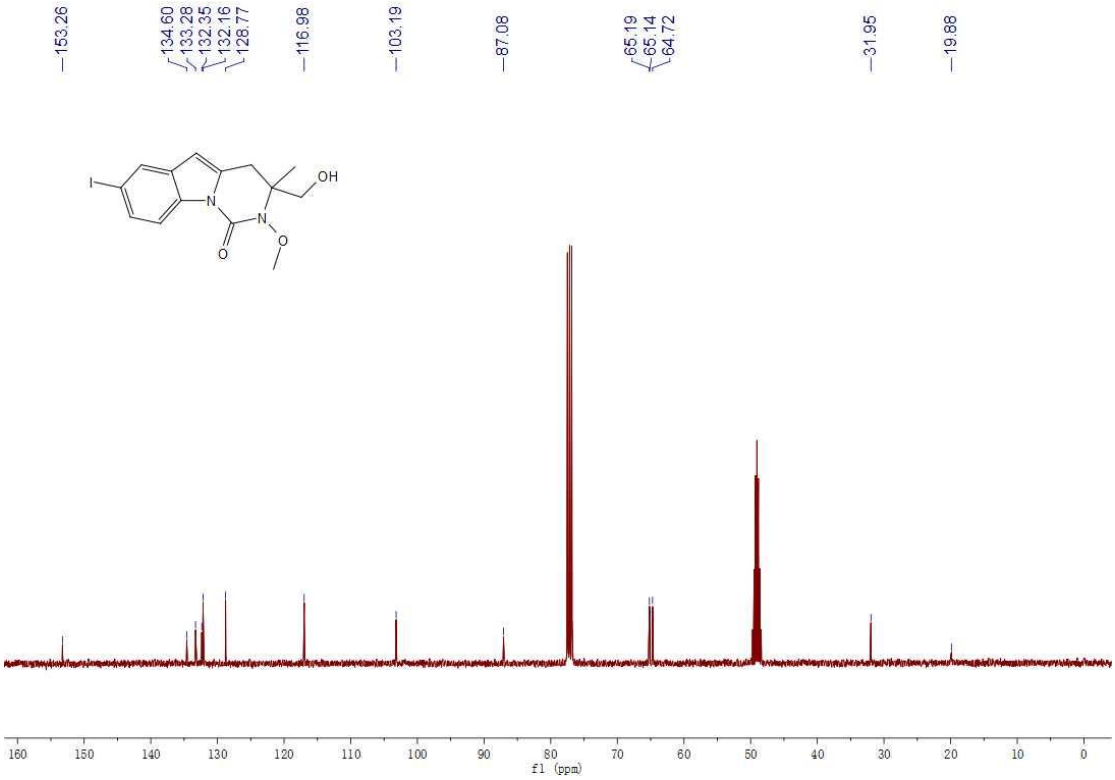


^{13}C NMR (101 MHz, $CDCl_3$)

4h

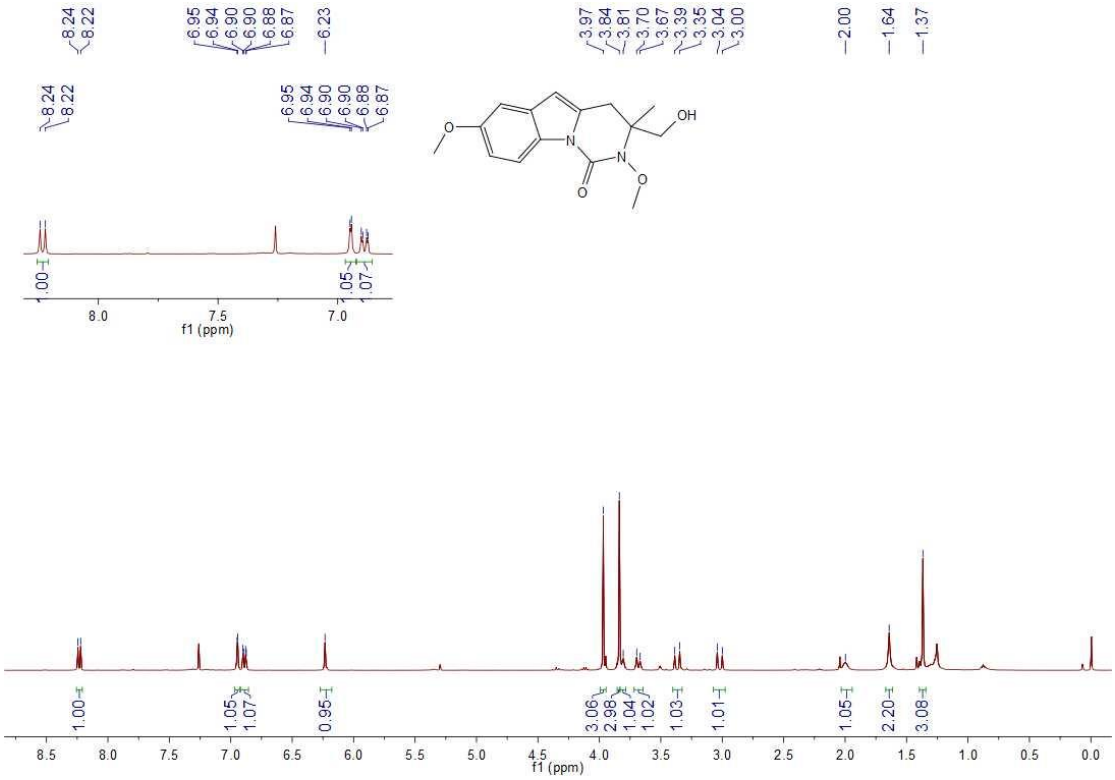


^{1}H NMR (500 MHz, $CDCl_3$)

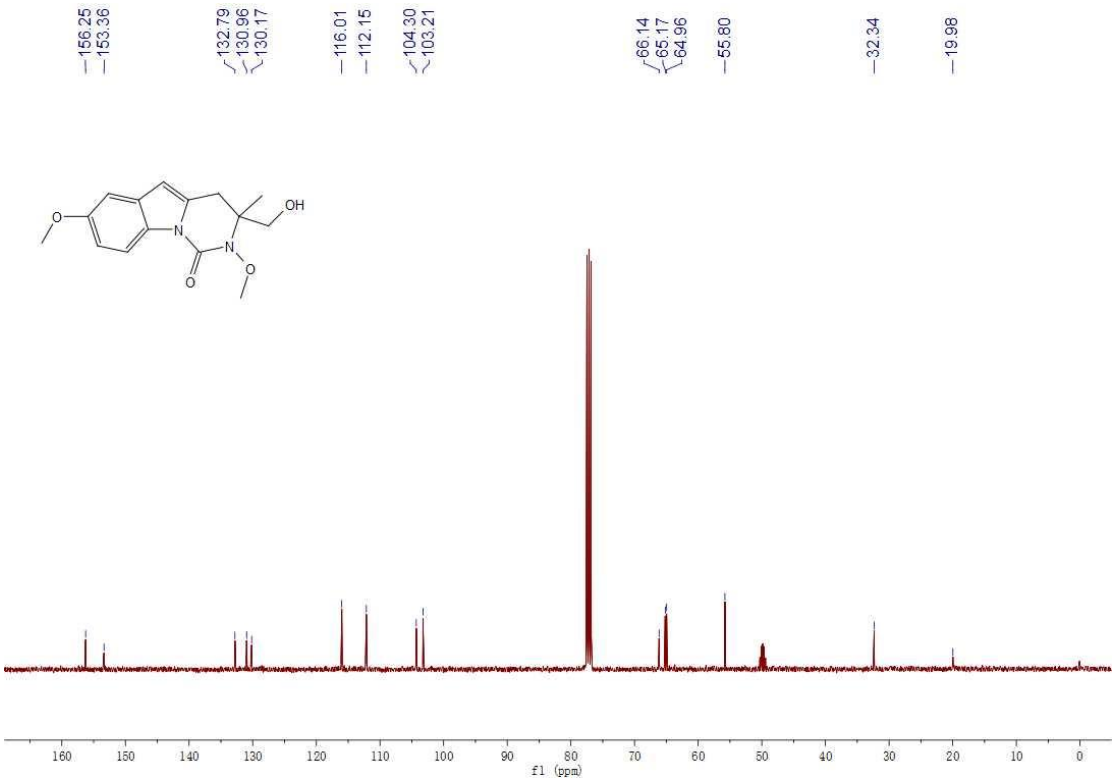


^{13}C NMR (101 MHz, $CDCl_3$)

4i

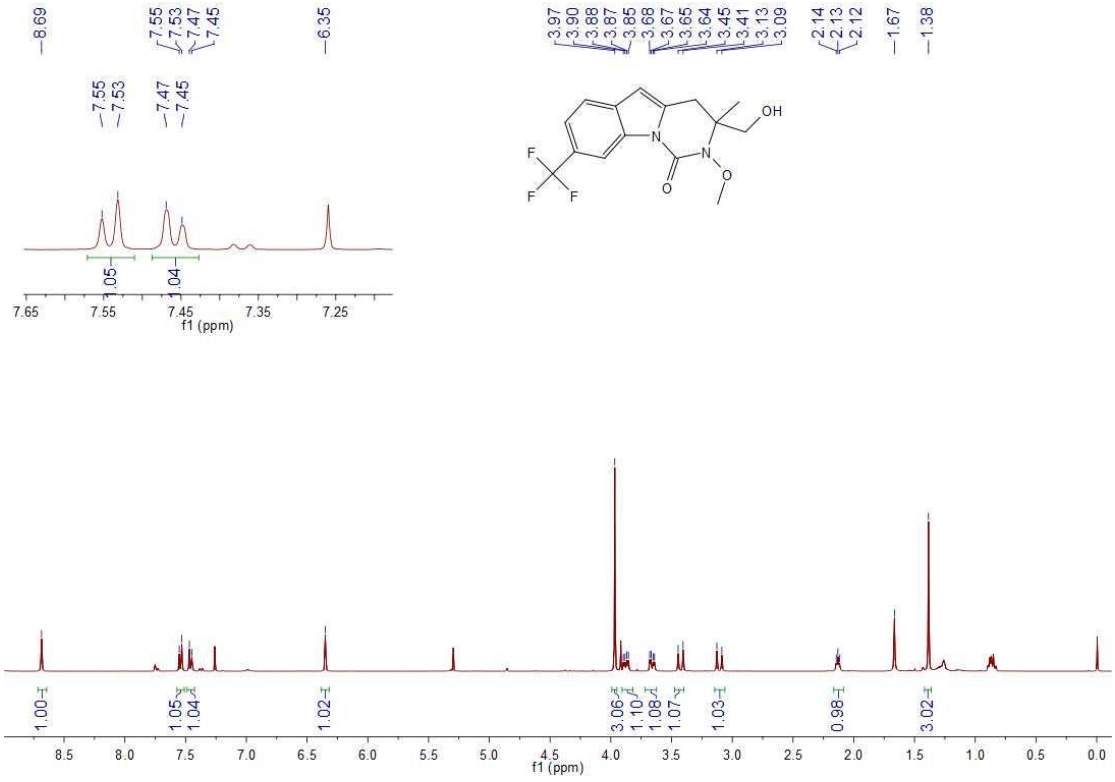


^{1}H NMR (400 MHz, $CDCl_3$)

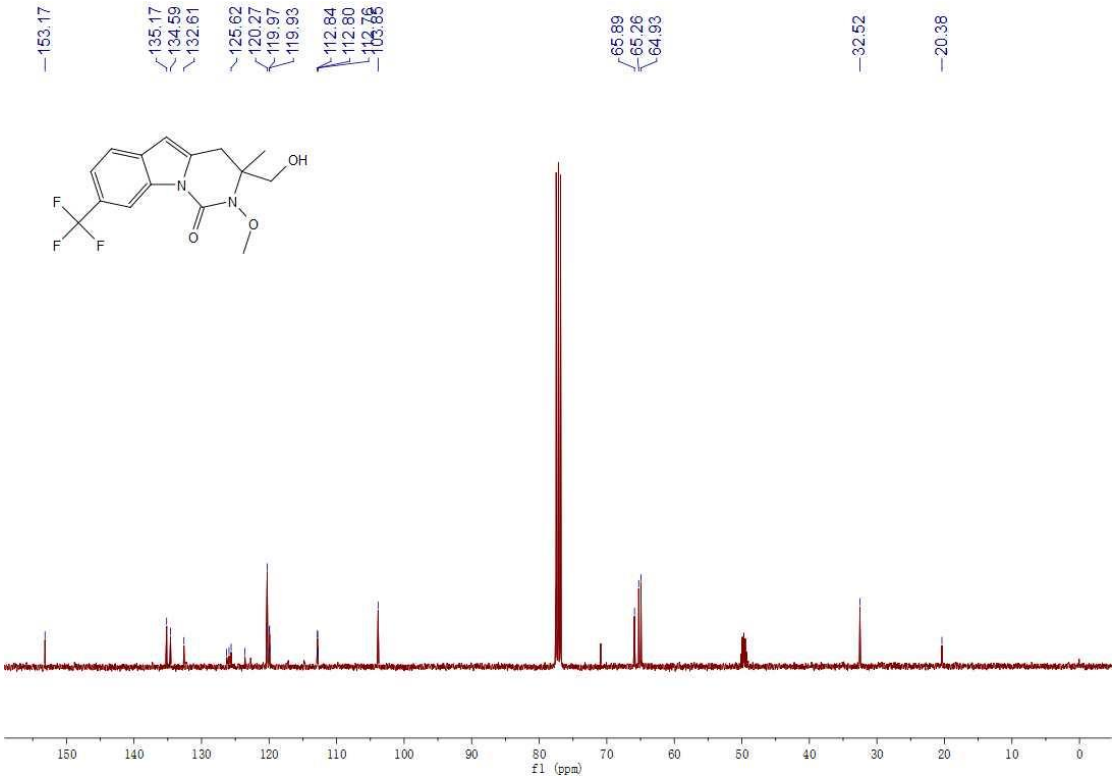


^{13}C NMR (101 MHz, $CDCl_3$)

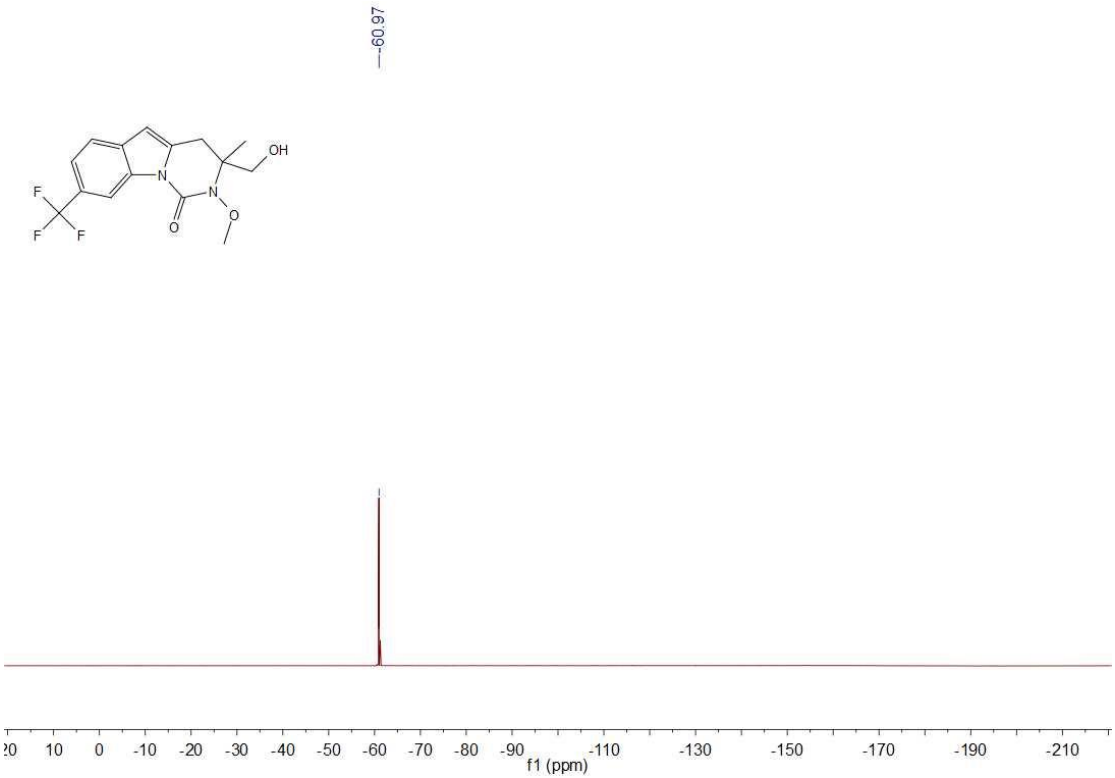
4j



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

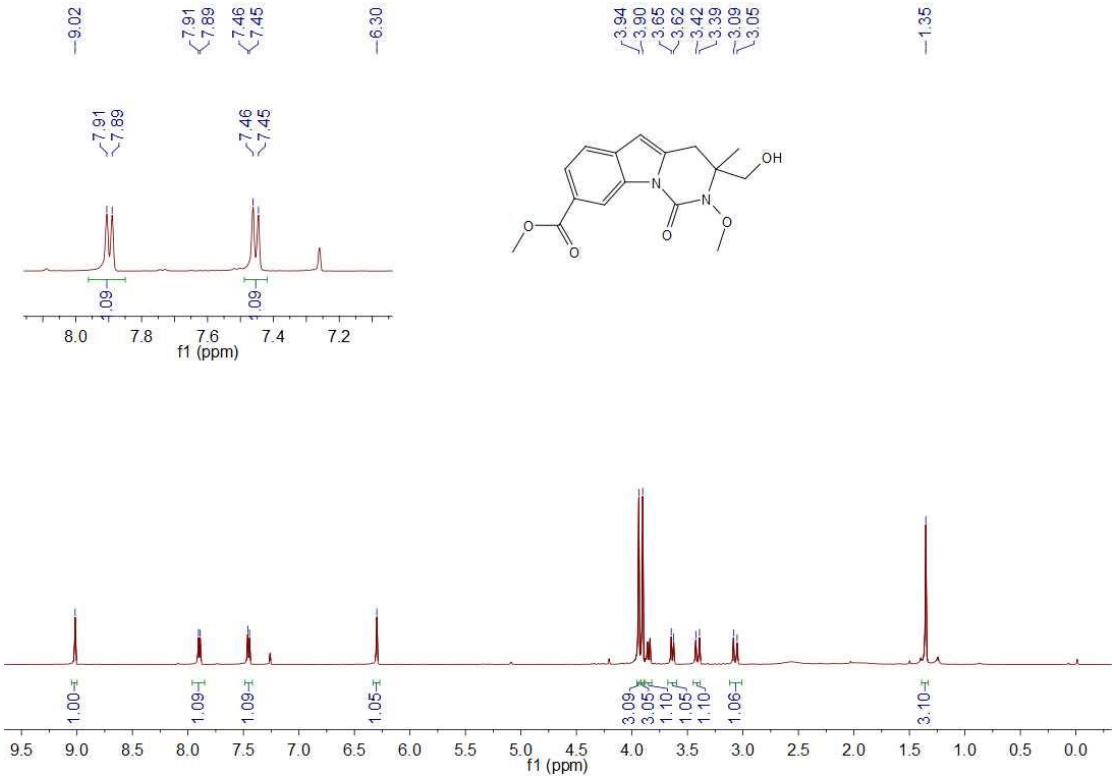


^{13}C NMR (101 MHz, $CDCl_3$)

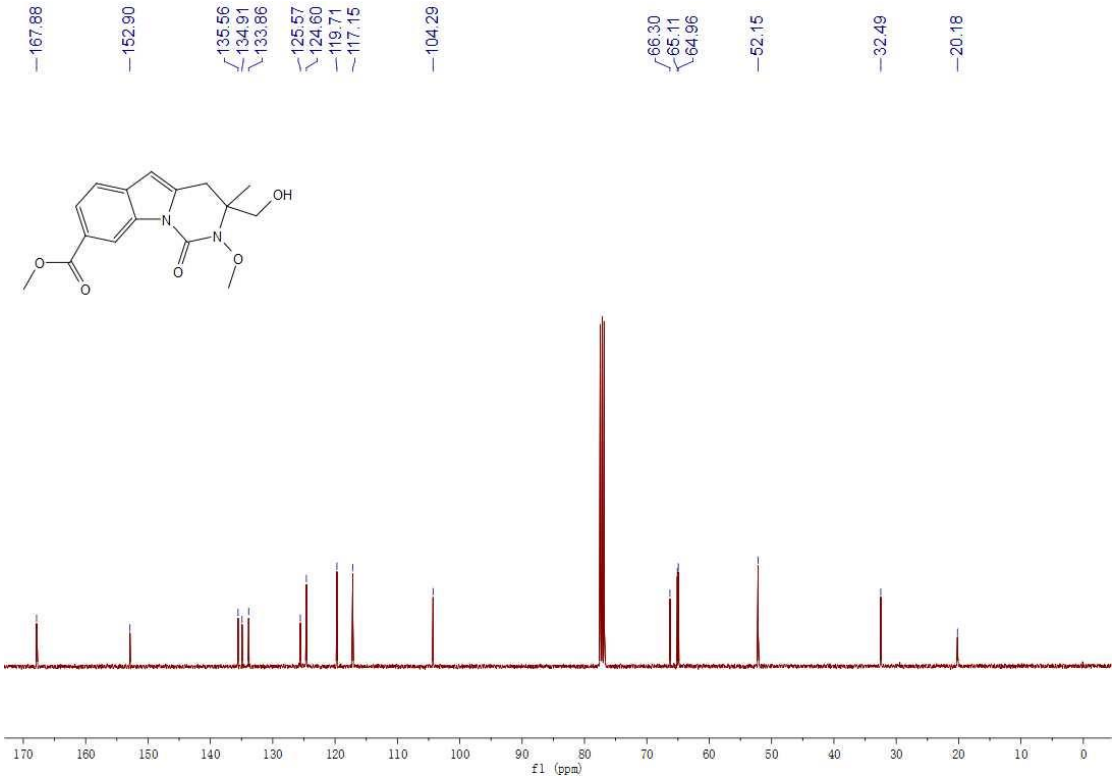


^{19}F NMR (471 MHz, $CDCl_3$)

4k

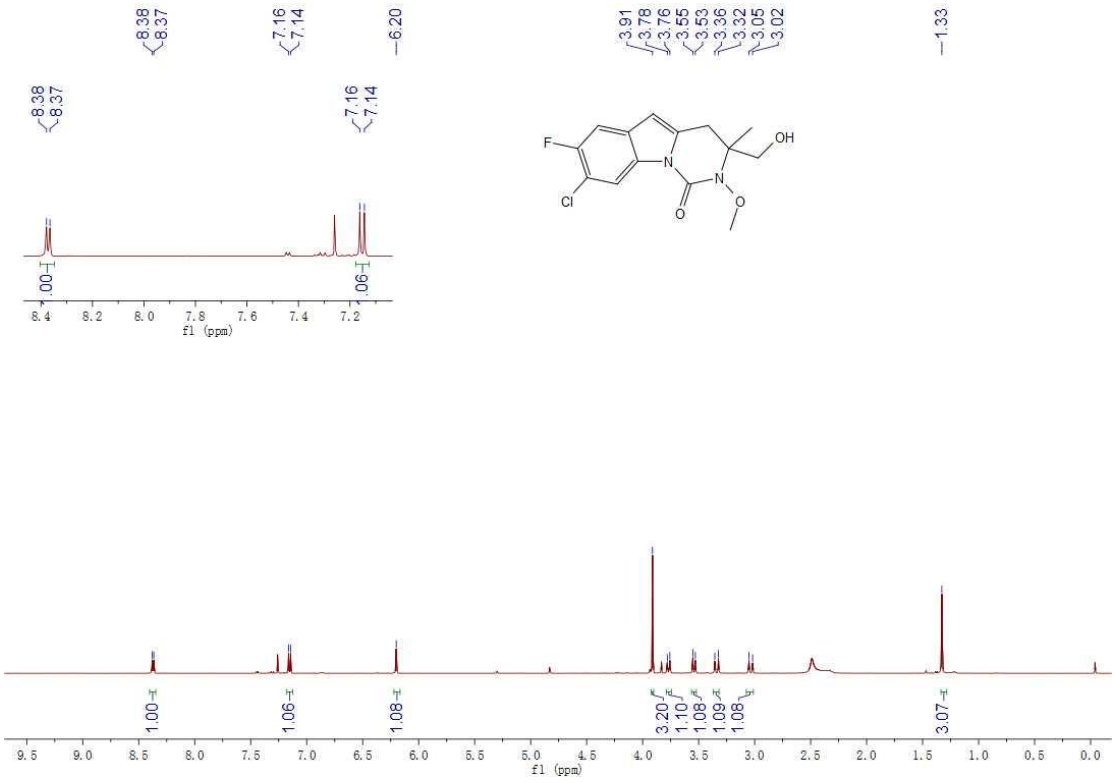


^{1}H NMR (500 MHz, $CDCl_3$)

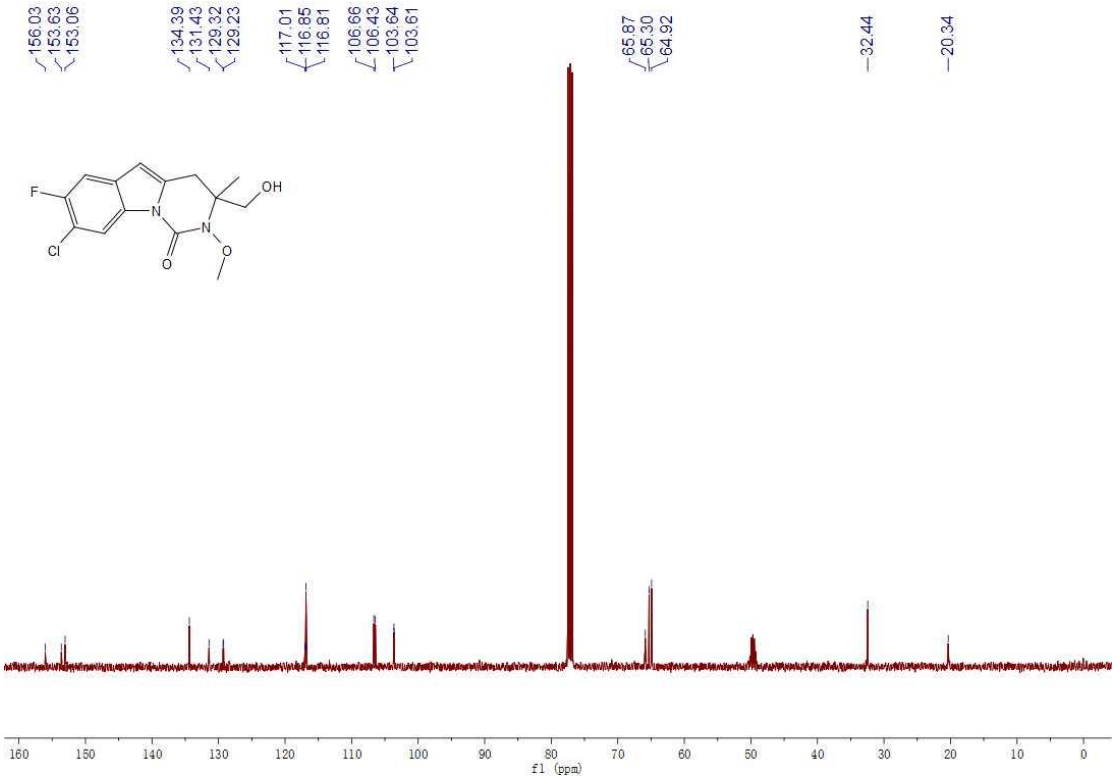


^{13}C NMR (101 MHz, $CDCl_3$)

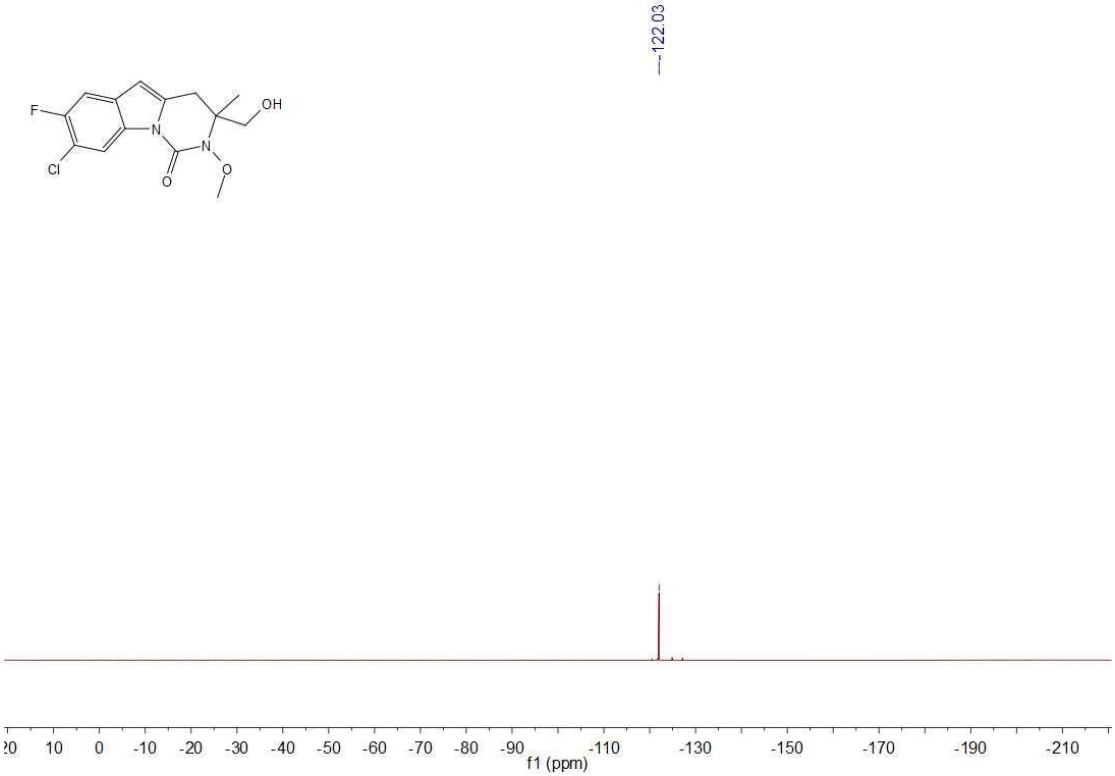
4l



^{1}H NMR (500 MHz, $CDCl_3$)

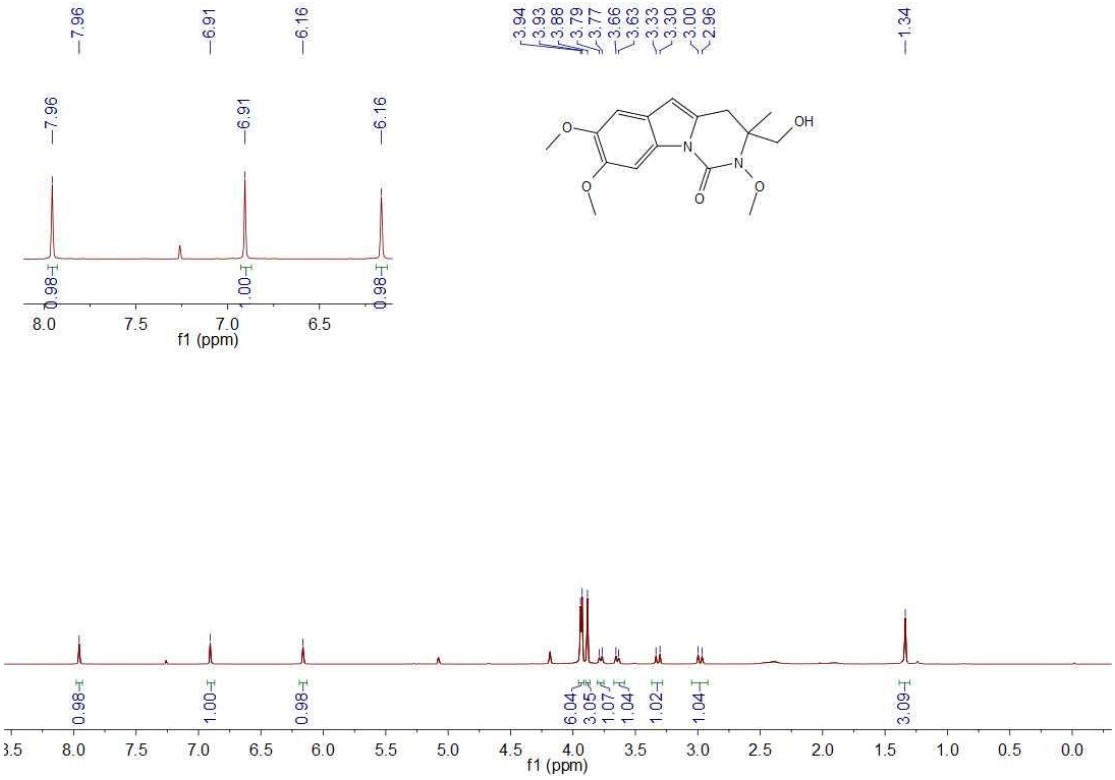


^{13}C NMR (101 MHz, $CDCl_3$)

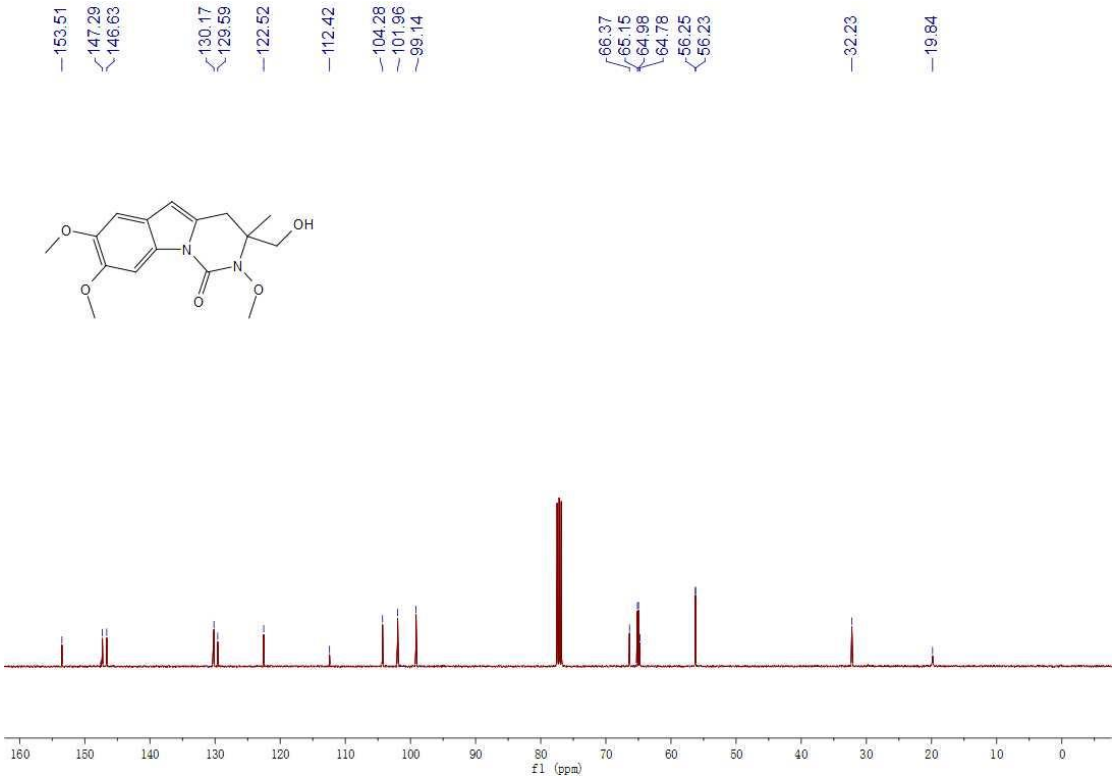


^{19}F NMR (471 MHz, $CDCl_3$)

4m

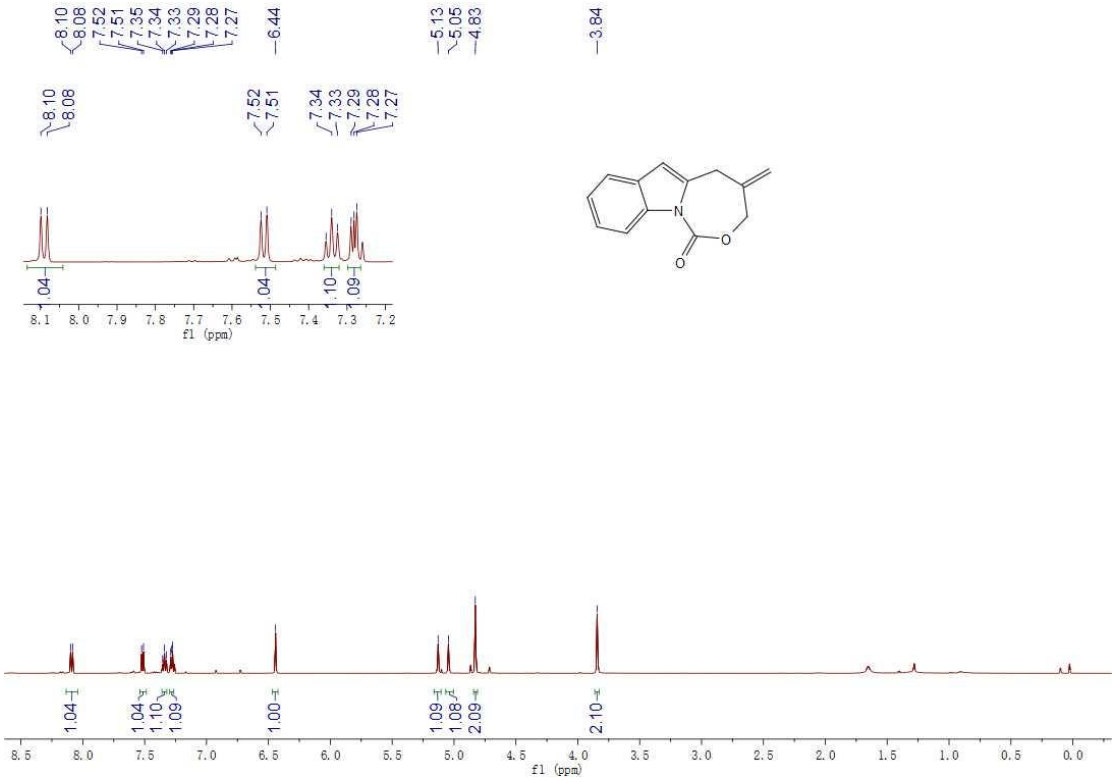


^{1}H NMR (500 MHz, $CDCl_3$)

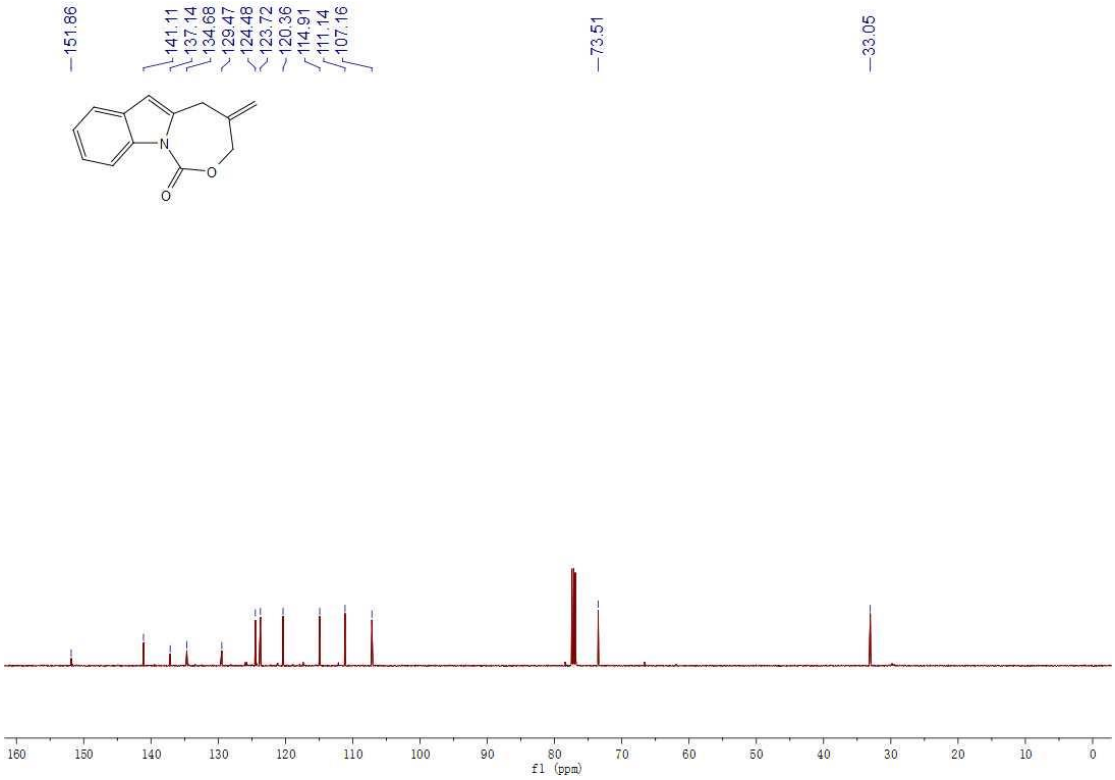


^{13}C NMR (101 MHz, $CDCl_3$)

5a

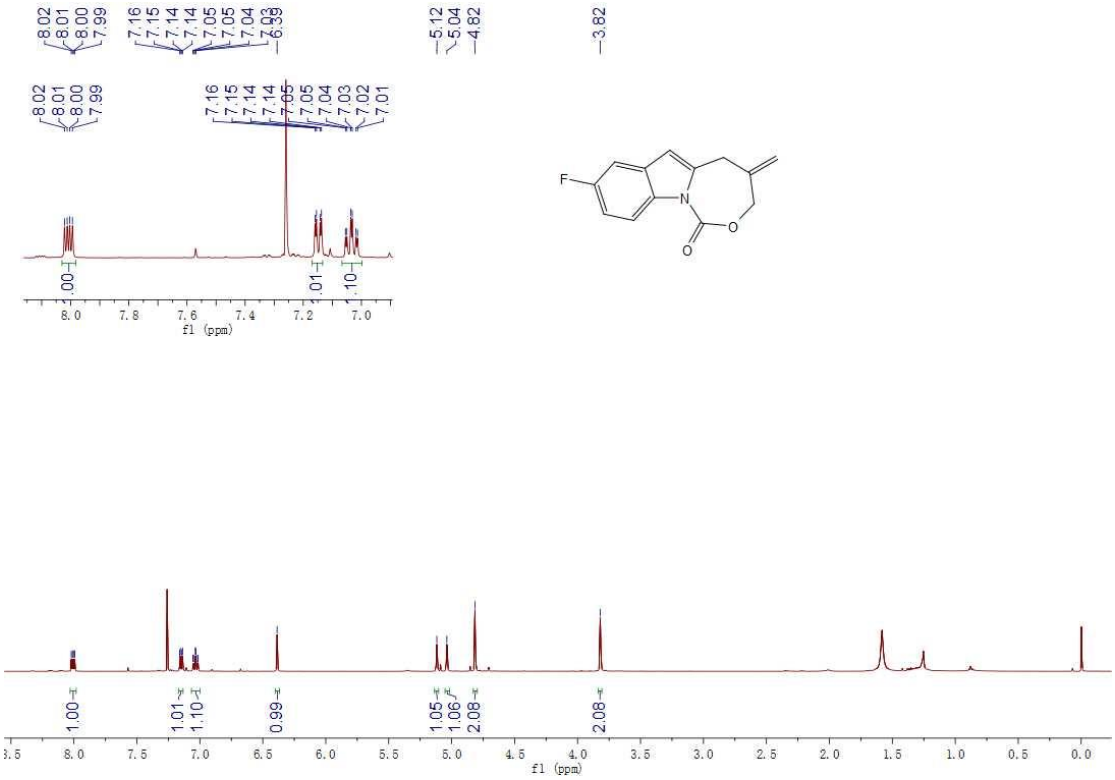


^{1}H NMR (500 MHz, $CDCl_3$)

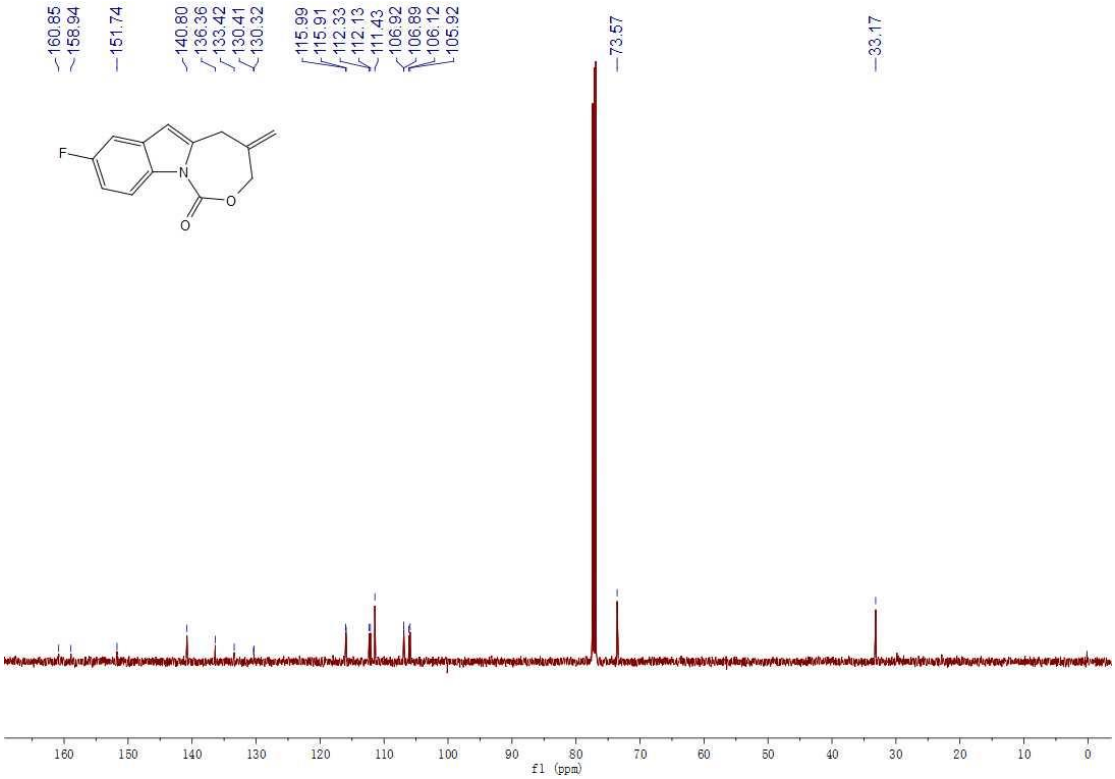


^{13}C NMR (126 MHz, $CDCl_3$)

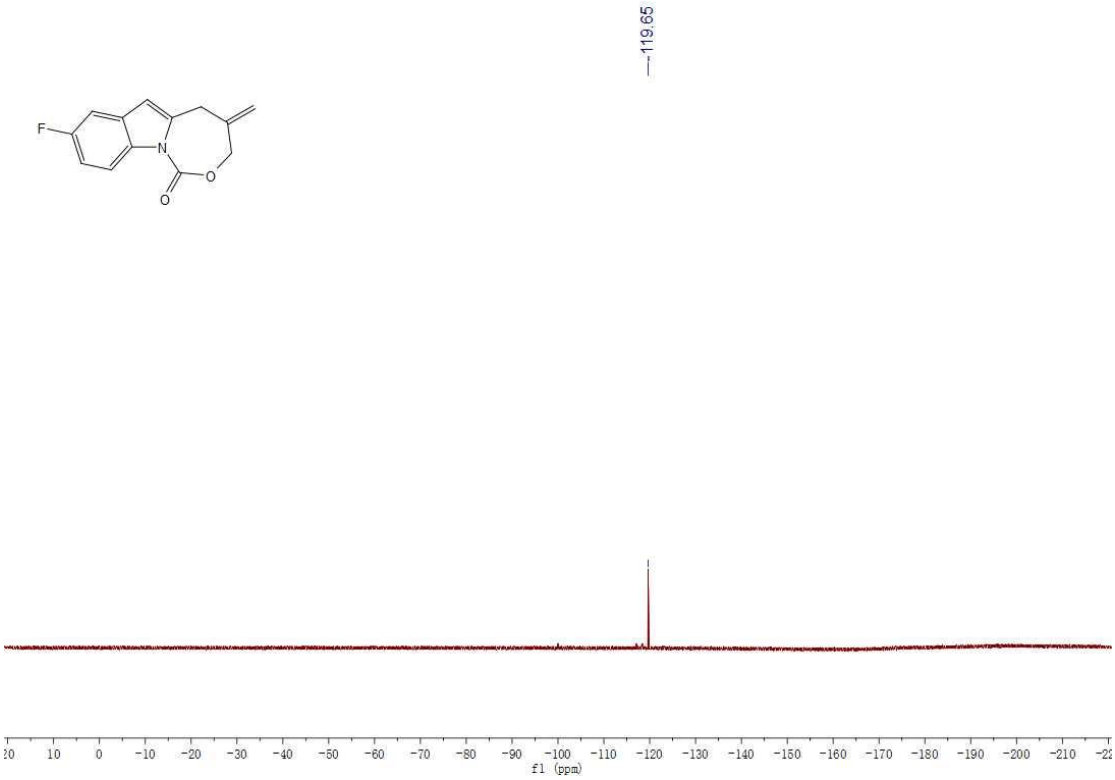
5b



^{1}H NMR (500 MHz, $CDCl_3$)

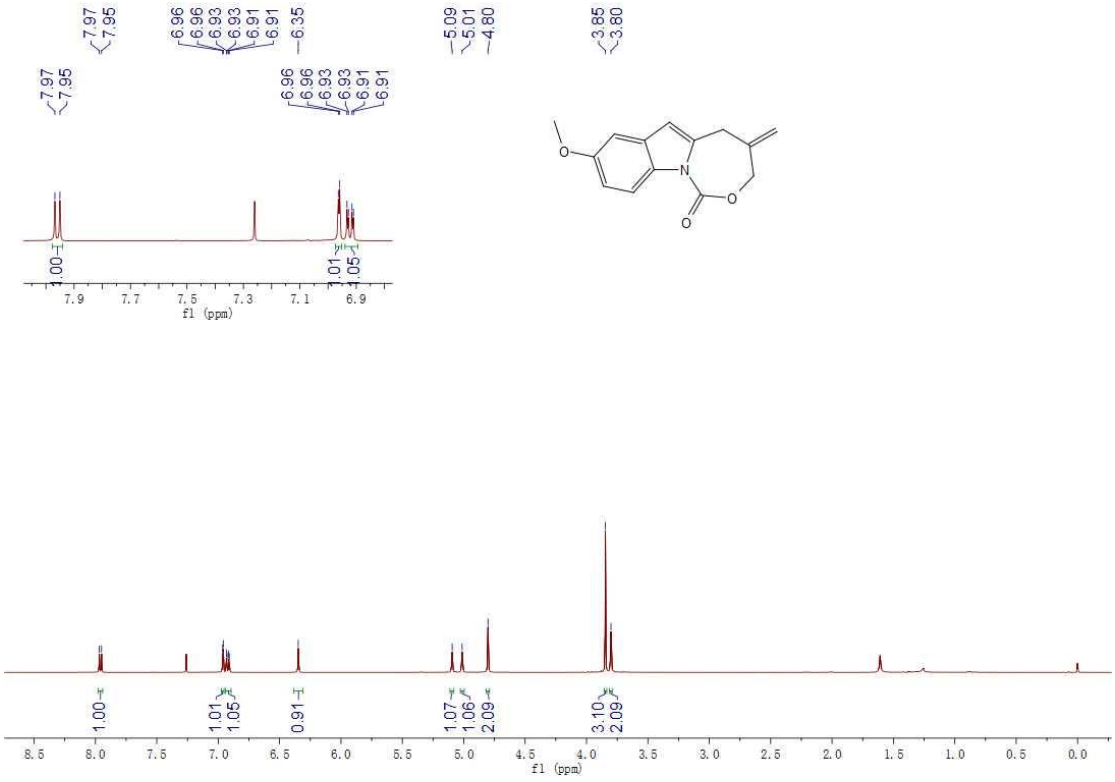


^{13}C NMR (126 MHz, $CDCl_3$)

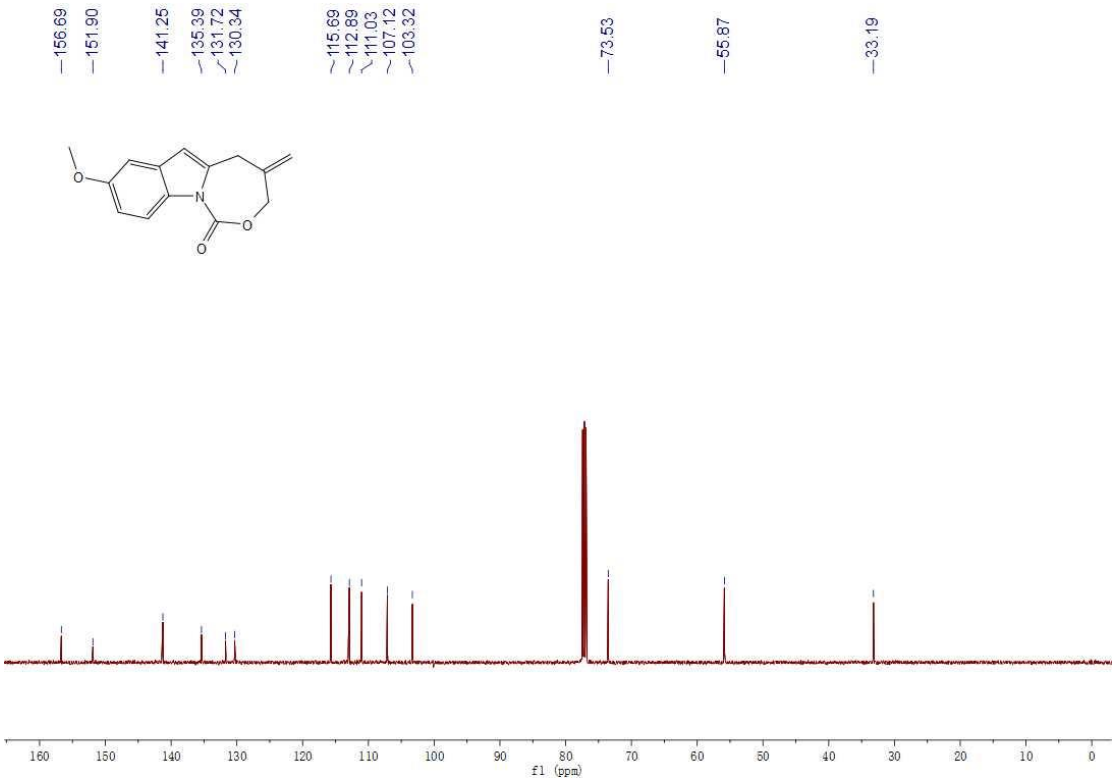


^{19}F NMR (471 MHz, $CDCl_3$)

5c

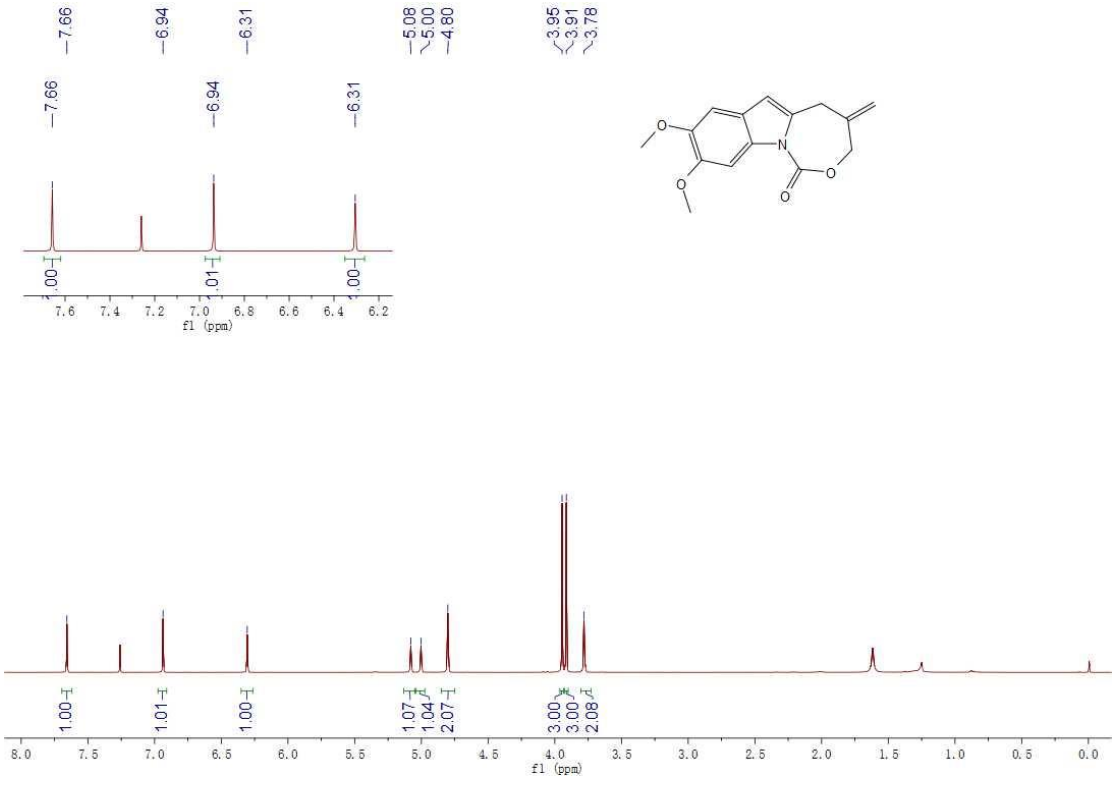


^{1}H NMR (500 MHz, $CDCl_3$)

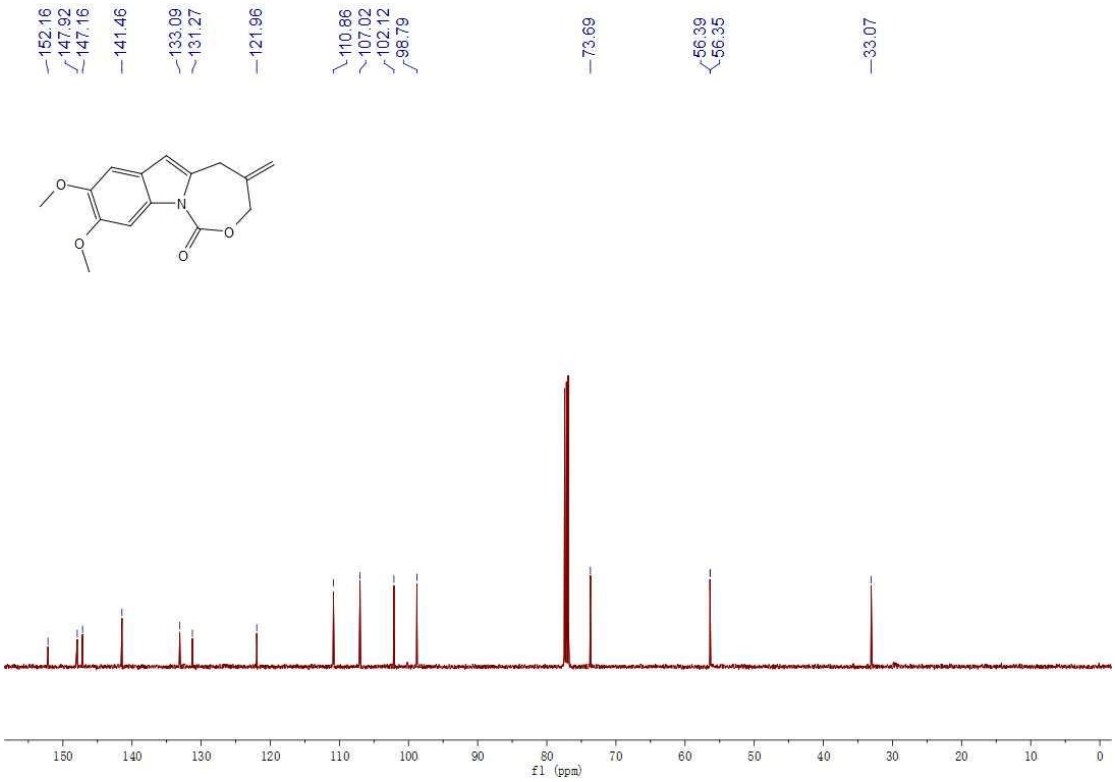


^{13}C NMR (126 MHz, $CDCl_3$)

5d

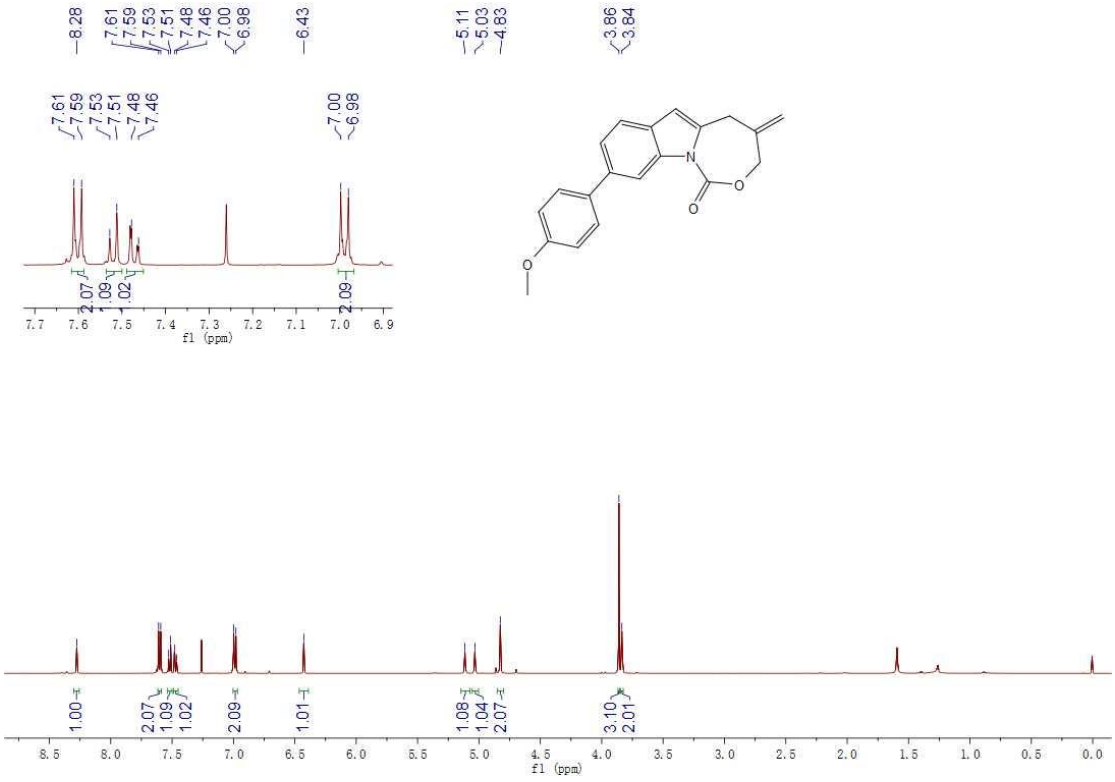


^{1}H NMR (500 MHz, $CDCl_3$)

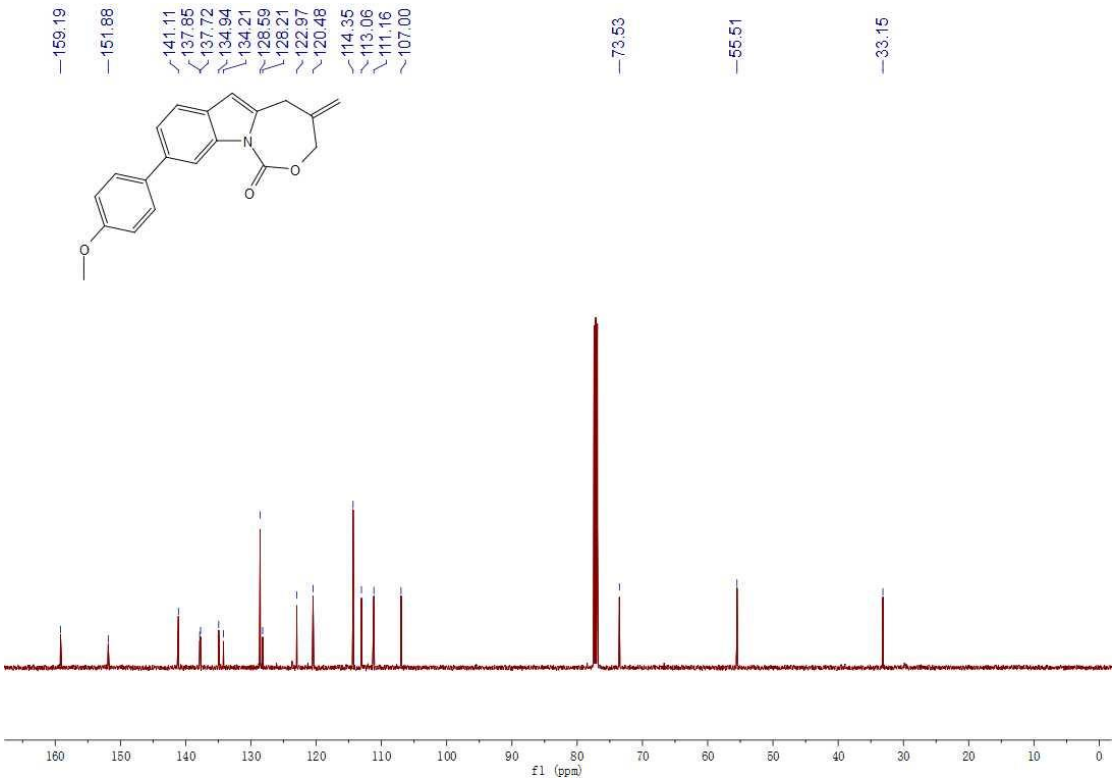


^{13}C NMR (126 MHz, $CDCl_3$)

5e

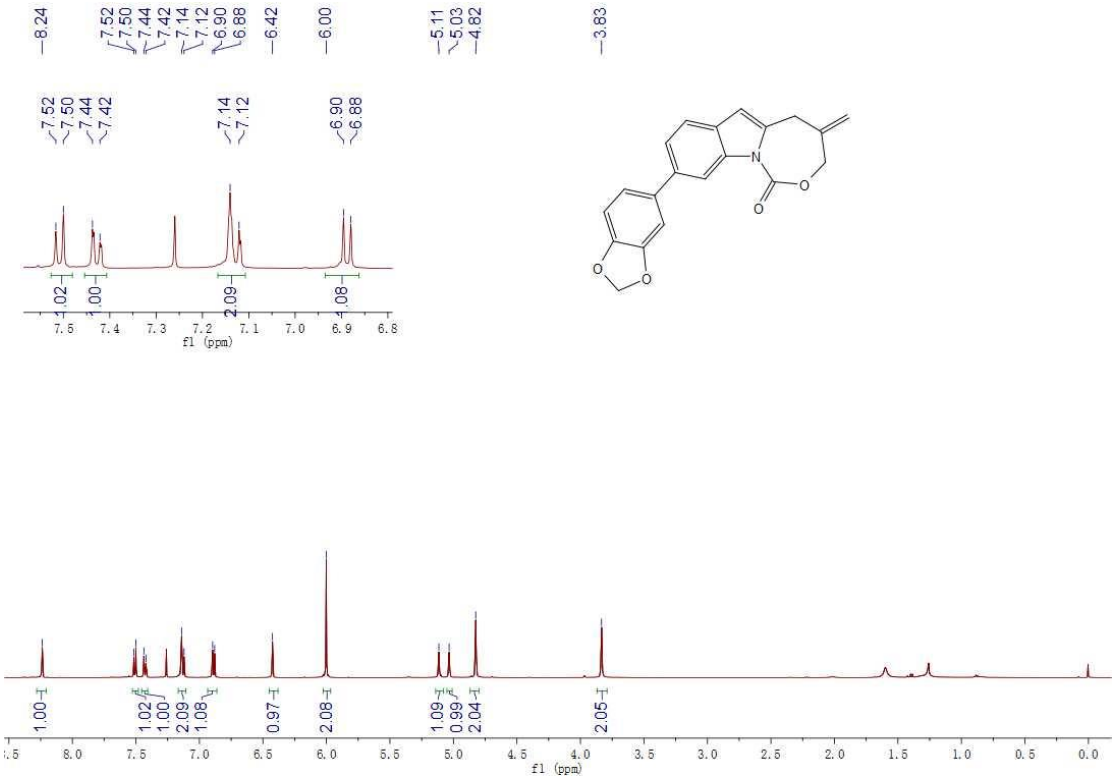


^{1}H NMR (500 MHz, $CDCl_3$)

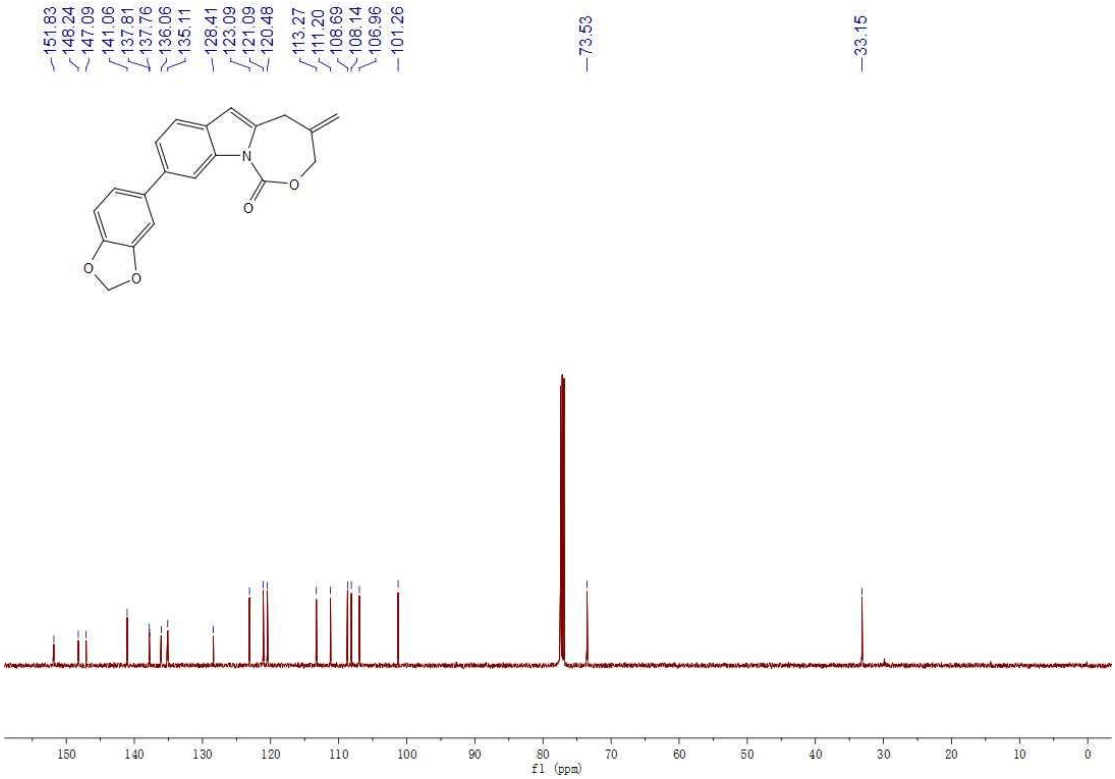


^{13}C NMR (126 MHz, $CDCl_3$)

5f

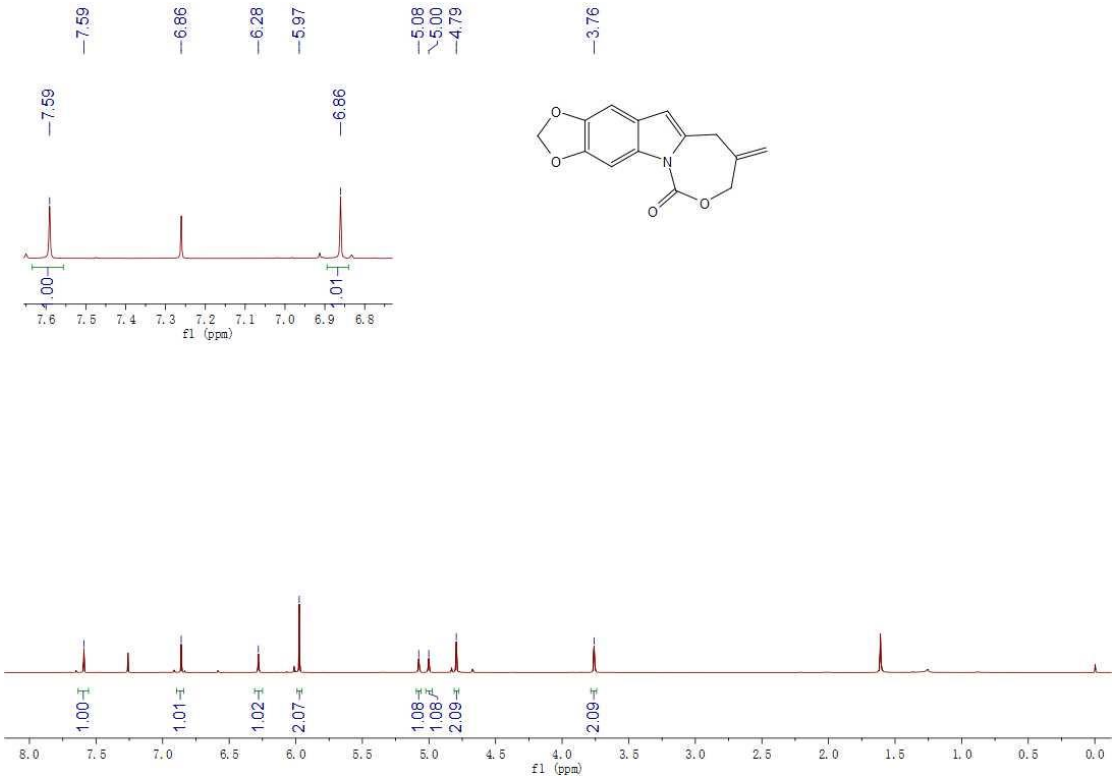


^{1}H NMR (500 MHz, $CDCl_3$)

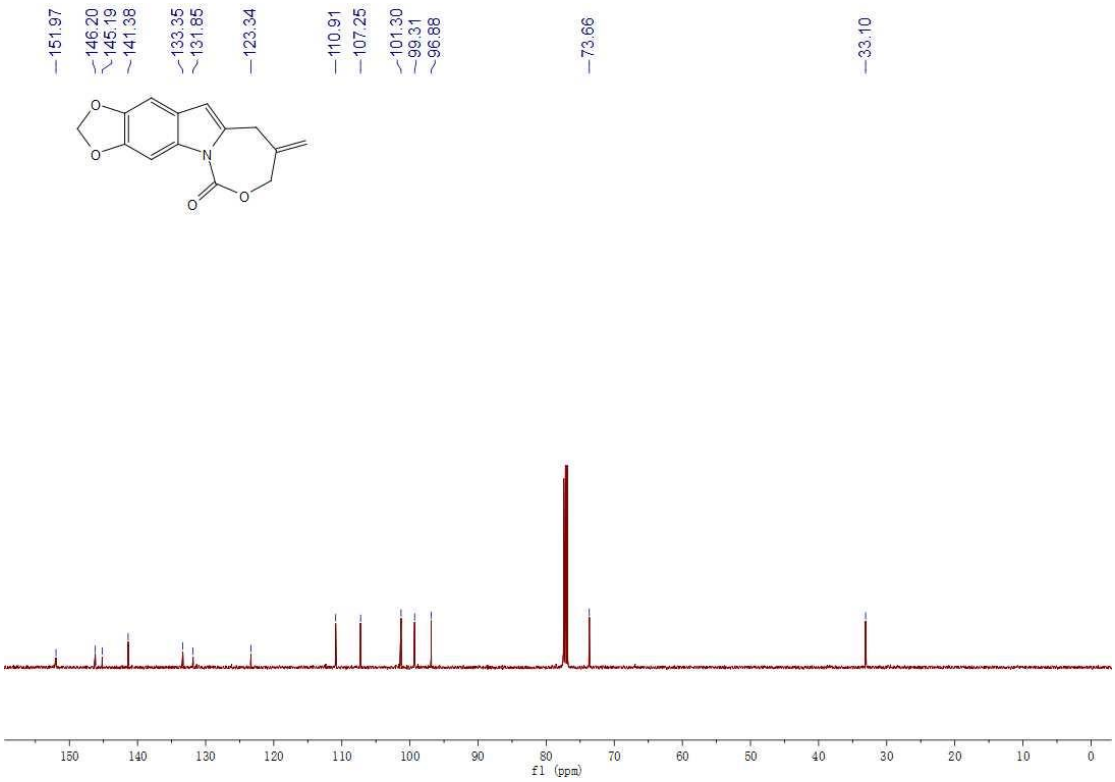


^{13}C NMR (126 MHz, $CDCl_3$)

5g

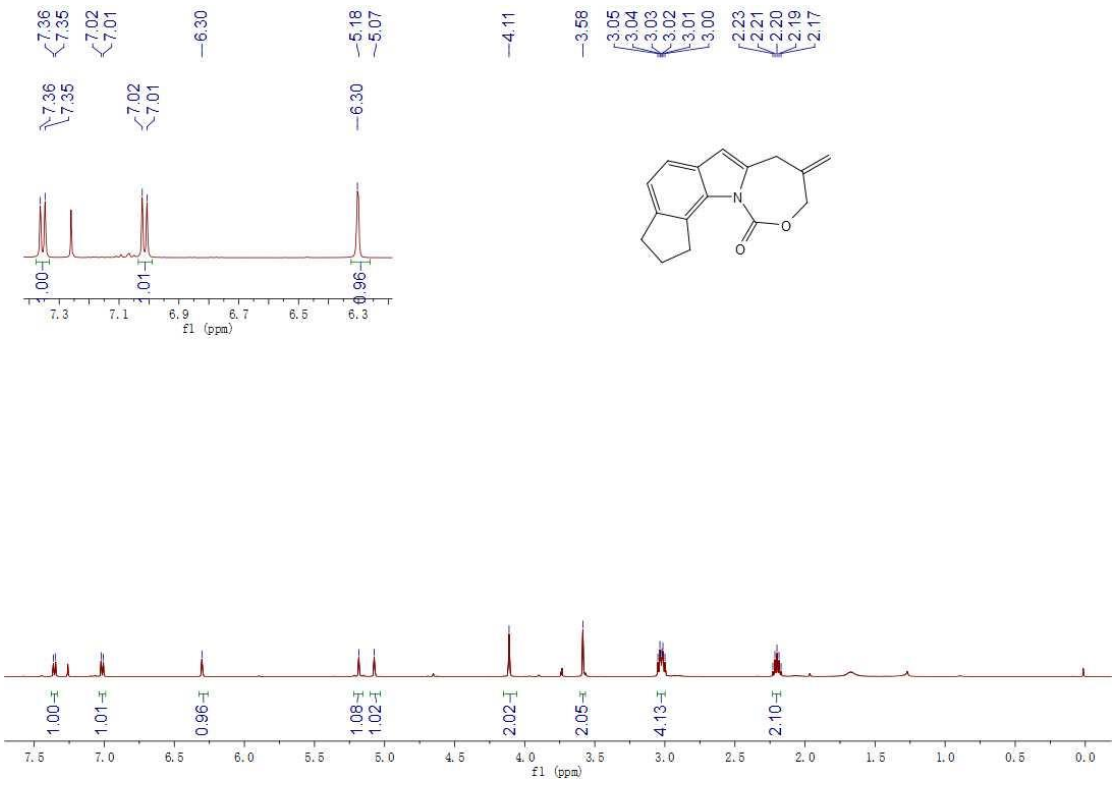


^{1}H NMR (500 MHz, $CDCl_3$)

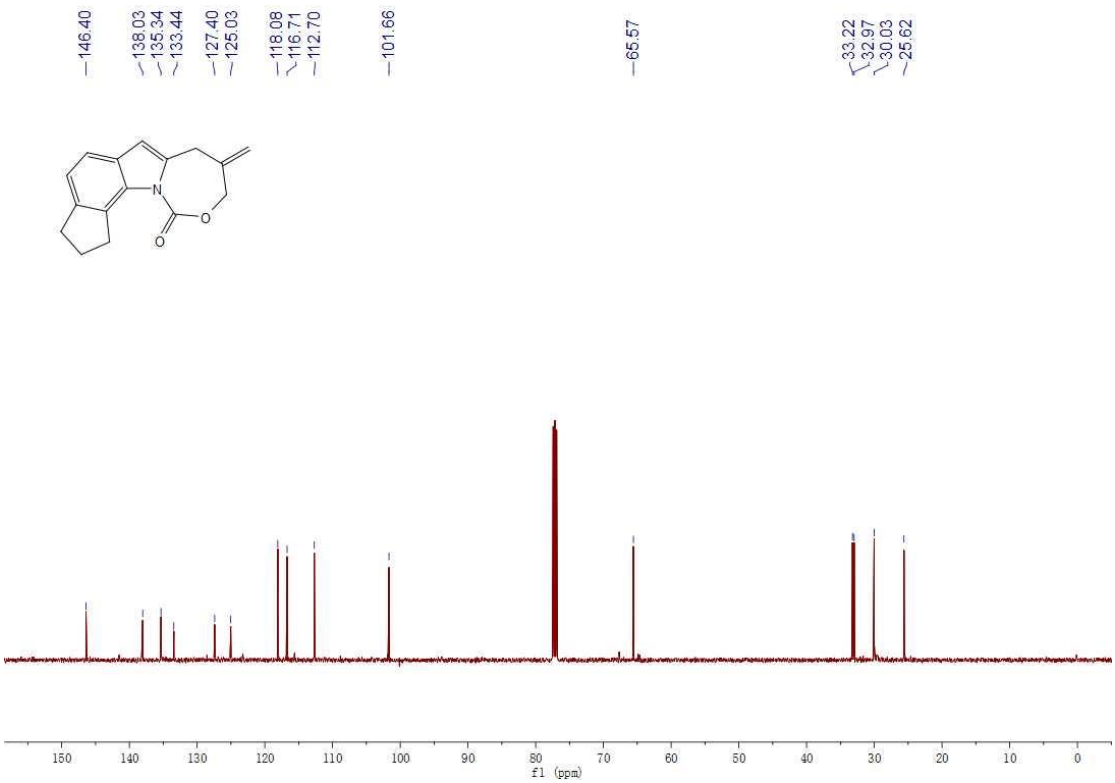


^{13}C NMR (126 MHz, $CDCl_3$)

5h



^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

7. Reference

[1] J. Zhang, H. Xie, H. Zhu, S. Zhang, M. R. Lonka, H. Zou, *ACS Catal*. **2019**, *9*, 10233-10244.

[2] Ryo Shintani, Kohei Moriya, Tamio Hayashi. *Chem. Commun.*, **2011**, *47*, 3057-3059.