Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Rh(III)-Catalyzed C-H Allylation/Annulative Markovnikov Addition with 5-Methylene-1,3-dioxan-2-one: Formation of Isoquinolilones Containing C3 Quaternary Centre

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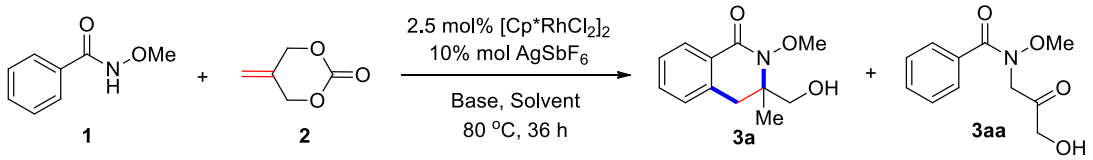
I. General Information

All reactions were performed under Argon. The reagents used for experiments were purchased from Adamas, Aladdin, Accela, Sigma-Aldrich, Acros Organics, TCI, and Alfa Aesar and used as received unless otherwise noted. CH_3CN, DCM and DMF were distilled from CaH_2 under Argon. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker Avance 400 MHz, JNM-ECS 400 MHz and Bruker Avance 600 MHz spectrometer. Chemical shifts were reported in the scale relative to TMS (0.00 ppm). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration. High resolution mass spectroscopy (HRMS) was recorded on a TOF MS mass spectrometer. Column chromatography was carried out on silica gel (300-400 mesh). *N*-methoxybenzamides[1-5] and 5-methylene-1,3-dioxan-2-one[6] were prepared according to the literature procedures.

II. Optimization of the reaction conditions

Table S1. Optimization of reaction conditions[a]



Entry	Additive	Solvent	**3a**/**3aa**, Yield (%)[b]
1	-	TFE	30/0
2	-	THF	0/0
3	-	HFIP	13/0
4	-	DCM	23/0
5	-	CH_3CN	0/0
6	-	DMF	0/0
10	HOAc	TFE	10/0
11	HOPiv	TFE	20/0
12	LiOAc	TFE	52/0
13	NaOAc	TFE	32/0
14	KOAc	TFE	31/0
15	**Li_2CO_3**	**TFE**	**87**/0
16	Na_2CO_3	TFE	＜10/0
17	K_2CO_3	TFE	＜10/0
18	PivONa	TFE	34/0
19[c]	Li_2CO_3	TFE	0/21
20[d]	Li_2CO_3	TFE	0/0
21[e]	Li_2CO_3	TFE	0/0

[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), additive (0.2 mmol), 2 mL of solvent, 80 °C, 36 h. [b]Isolated yield. [c]2.5 mol% of $[Cp^*IrCl_2]_2$ was used instead of $[Cp^*RhCl_2]_2$. [d]5 mol% of $[Cp^*Co(Co)I_2]$ was used instead of $[Cp^*RhCl_2]_2$. [e]In the absence of $[Cp^*RhCl_2]_2$.

III. General Procedure

Method I

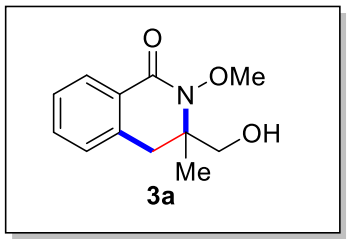
An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with $[Cp^*RhCl_2]_2$ (2.5 mol%, 0.0031 g), $AgSbF_6$ (10 mol%, 0.0069 g), Li_2CO_3 (0.2 mmol, 0.0148 g), *N*-methoxybenzamides (0.2 mmol), 5-methylene-1,3-dioxan-2-one (0.3 mmol, 0.0342 g) and TFE (2 mL) under Argon, and was evacuated and refilled with Argon for three times. Then, the septum was replaced by a Teflon screwcap under Argon flow. The reaction mixture was stirred at 80 °C for 36 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with ethyl acetate (30 mL). The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to provide the corresponding product.

(**Note:** In some cases, the product isolated according to Method I was always accompanied with unidentified byproduct, therefore Method II was applied.)

Method II

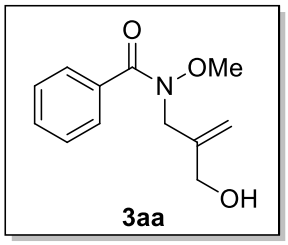
An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with $[Cp^*RhCl_2]_2$ (2.5 mol%, 0.0031 g), $AgSbF_6$ (10 mol%, 0.0069 g), Li_2CO_3 (0.2 mmol, 0.0148 g), *N*-methoxybenzamides (0.2 mmol), 5-methylene-1,3-dioxan-2-one (0.3 mmol, 0.0342 g), TFE (2 mL) under Argon, and was evacuated and refilled with Argon for three times. Then, the septum was replaced by a Teflon screwcap under Argon flow. The reaction mixture was stirred at 80 °C for 36 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with ethyl acetate (30 mL). The filtrate was concentrated under reduced pressure. Then 2M HCl (1 mL) and TFE (1 mL) were added to the crude product. The mixture was stirred at 80 °C for 2 h. Upon completion, the mixture was extracted with DCM (10 mL) for three times. The DCM layer was concentrated and the residue was purified by chromatography on silica gel to provide the corresponding product.

IV. Characterization data for the annulation products



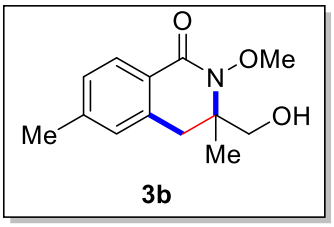
3a

3-(Hydroxymethyl)-2-methoxy-3-methyl-3,4-dihydroisoquinolin-1(2*H*)-one (3a): The title compound was prepared according to the general procedure (Method I). White solid (38.4 mg, 87%; eluent: 10%-40% ethyl acetate/hexane). Mp: 98-100 ^oC. ^1H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 3.95 (s, 3H), 3.77 (d, *J* = 11.2 Hz, 1H), 3.65 (d, *J* = 11.2 Hz, 1H), 3.40 (d, *J* = 16.4 Hz, 1H), 2.96 (d, *J* = 16.4 Hz, 1H), 1.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.98, 135.79, 132.62, 127.93, 127.79, 127.71, 126.91, 66.23, 65.33, 64.43, 37.97, 20.38. HRMS (ESI): calcd for $C_{12}H_{16}NO_3$ $[M+H]^+$: 222.1130, found 222.1108.



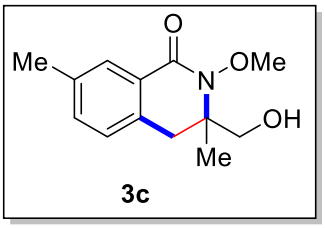
3aa

***N*-(2-(Hydroxymethyl)allyl)-*N*-methoxybenzamide (3aa):** The title compound was prepared according to the general procedure (Method I) using 2.5 mol% of $[Cp^*IrCl_2]_2$ instead of $[Cp^*RhCl_2]_2$. Colorless oil (9.3 mg, 21%; eluent: 10%-30% ethyl acetate/hexane). ^{1}H NMR (400 MHz,) δ 7.70 (d, *J* = 7.3 Hz, 2H), 7.47-7.44 (m, 1H), 7.41-7.37 (m, 2H), 5.19 (d, *J* = 18.4 Hz, 2H), 4.45 (s, 2H), 4.13 (s, 2H), 3.52 (s, 3H). ^{13}C NMR (101 MHz,) δ 170.27, 143.71, 133.43, 131.08, 128.38, 128.20, 115.08, 63.88, 62.27, 49.34. HRMS (ESI): calcd for $C_{12}H_{16}NO_3$ $[M+H]^+$: 222.1130, found 222.1114.



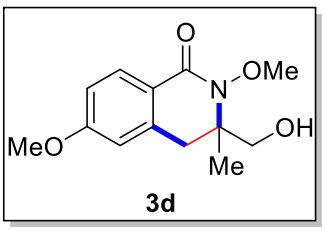
3b

3-(Hydroxymethyl)-2-methoxy-3,6-dimethyl-3,4-dihydroisoquinolin-1(*2H*)-one (3b): The title compound was prepared according to the general procedure (Method I). White solid (40.4 mg, 86%; eluent: 10%-40% ethyl acetate/hexane). Mp: 66-68 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 1H), 6.95 (s, 1H), 3.94 (s, 3H), 3.76 (d, *J* = 11.2 Hz, 1H), 3.65 (d, *J* = 11.2 Hz, 1H), 3.34 (d, *J* = 16.4 Hz, 1H), 2.91 (d, *J* = 16.4 Hz, 1H), 2.35 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.24, 143.26, 135.75, 128.29, 128.03, 127.79, 125.20, 66.30, 65.32, 64.43, 37.95, 21.57, 20.28. HRMS (ESI): calcd for $C_{13}H_{18}NO_3$ $[M+H]^+$: 236.1287, found 236.1283.



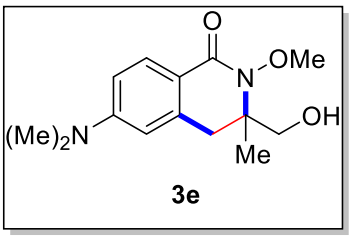
3c

3-(Hydroxymethyl)-2-methoxy-3,7-dimethyl-3,4-dihydroisoquinolin-1(*2H*)-one (3c): The title compound was prepared according to the general procedure (Method I). White solid (33.9 mg, 72%; eluent: 10%-40% ethyl acetate/hexane). Mp: 134-136°C. ^{1}H NMR (400 MHz, DMSO) δ 7.70 (d, *J* = 0.8 Hz, 1H), 7.29 (d, *J* = 1.3 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 5.09 (t, *J* = 5.3 Hz, 1H), 3.81 (s, 3H), 3.53-3.49 (m, 1H), 3.37 (d, *J* = 5.1 Hz, 1H), 3.30 (d, *J* = 16.5 Hz, 1H), 2.87 (d, *J* = 16.5 Hz, 1H), 2.31 (s, 3H), 1.20 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 164.12, 136.24, 133.70, 133.55, 128.48, 128.08, 127.64, 65.30, 64.35, 63.96, 36.98, 21.06, 20.46. HRMS (ESI): calcd for $C_{13}H_{18}NO_3$ $[M+H]^+$: 236.1287, found 236.1274.



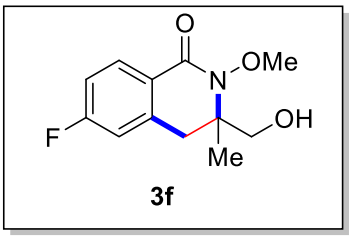
3d

3-(Hydroxymethyl)-2,6-dimethoxy-3-methyl-3,4-dihydroisoquinolin-1(*2H*)-one (3d): The title compound was prepared according to the general procedure (Method I). White solid (40.2 mg, 80%; eluent: 10%-30% ethyl acetate/hexane). Mp: 98-100°C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 1H), 6.82-6.80 (m, 1H), 6.63 (s, 1H), 3.92 (s, 3H), 3.81 (s, 3H), 3.76 (d, *J* = 11.1 Hz, 1H), 3.63 (d, *J* = 11.3 Hz, 1H), 3.36 (d, *J* = 16.4 Hz, 1H), 2.90 (d, *J* = 16.3 Hz, 1H), 1.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.29, 163.02, 138.10, 130.04, 120.48, 112.61, 112.54, 65.82, 65.28, 64.38, 55.37, 38.05, 20.17. HRMS (ESI): calcd for $C_{13}H_{18}NO_4$ $[M+H]^+$: 252.1236, found 252.1219.



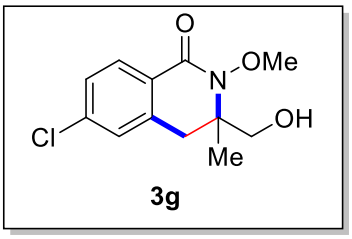
3e

6-(Dimethylamino)-3-(hydroxymethyl)-2-methoxy-3-methyl-3,4-dihydroisoquinolin-1(*2H*)-one (3e): The title compound was prepared according to the general procedure (Method II). Yellow solid (24.3 mg, 46%; eluent: 10%-40% ethyl acetate/hexane). Mp: 84-86 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.8 Hz, 1H), 6.59 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.33 (d, *J* = 2.4 Hz, 1H), 3.94 (s, 3H), 3.72 (dd, *J* = 25.9, 11.2 Hz, 2H), 3.28 (d, *J* = 16.2 Hz, 1H), 3.01 (s, 6H), 2.86 (d, *J* = 16.0 Hz, 1H), 1.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.31, 153.16, 137.42, 129.80, 115.28, 110.15, 109.32, 66.81, 65.16, 64.53, 40.06, 38.69, 19.88. HRMS (ESI): calcd for $C_{14}H_{21}N_2O_3$ $[M+H]^+$: 265.1552, found 265.1542.



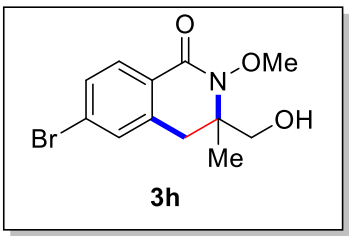
3f

6-Fluoro-3-(hydroxymethyl)-2-methoxy-3-methyl-3,4-dihydroisoquinolin-1(*2H*)-one (3f): The title compound was prepared according to the general procedure (Method I). White solid (33.5 mg, 70%; eluent: 10%-40% ethyl acetate/hexane). Mp: 118-120 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.2, 6.2 Hz, 1H), 7.01-6.98 (m, 1H), 6.86 (d, *J* = 8.6 Hz, 1H), 3.93 (s, 3H), 3.79 (d, *J* = 11.0 Hz, 1H), 3.63 (d, *J* = 11.1 Hz, 1H), 3.39 (d, *J* = 16.5 Hz, 1H), 2.97 (d, *J* = 16.5 Hz, 1H), 1.38 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 165.31 (d, *J* = 253.9 Hz), 164.29, 138.79 (d, *J* = 8.7 Hz), 130.74 (d, *J* = 9.6 Hz), 124.18 (d, *J* = 2.4 Hz), 114.48 (d, *J* = 22.6 Hz), 114.26 (d, *J* = 21.9 Hz), 66.05, 65.26, 64.45, 37.92, 20.44. ^{19}F NMR (565 MHz, $CDCl_3$) δ -106.55. HRMS (ESI): calcd for $C_{12}H_{15}FNO_3$ $[M+H]^+$: 240.1036, found 240.1018.



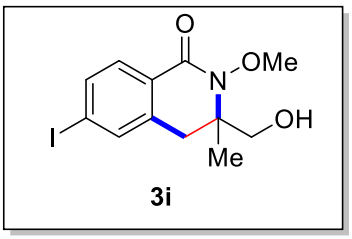
3g

6-Chloro-3-(hydroxymethyl)-2-methoxy-3-methyl-3,4-dihydroisoquinolin-1(*2H*)-one (3g): The title compound was prepared according to the general procedure (Method II). White solid (32.7 mg, 64%; eluent: 10%-40% ethyl acetate/hexane). Mp: 95-97°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.31-7.29 (m, 1H), 7.16 (d, *J* = 1.6 Hz, 1H), 3.95 (s, 3H), 3.79 (d, *J* = 11.2 Hz, 1H), 3.63 (d, *J* = 11.2 Hz, 1H), 3.36 (d, *J* = 16.5 Hz, 1H), 2.97-2.92 (m, 1H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.17, 138.73, 137.52, 129.57, 127.64, 127.36, 126.44, 66.31, 65.28, 64.50, 37.80, 20.49. HRMS (ESI): calcd for $C_{12}H_{15}ClNO_3$ $[M+H]^+$: 256.0740, found 256.0723.



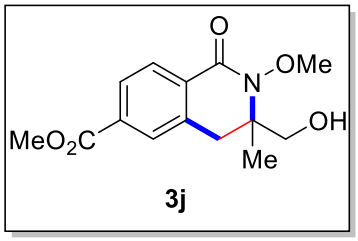
3h

6-Bromo-3-(hydroxymethyl)-2-methoxy-3-methyl-3,4-dihydroisoquinolin-1(*2H*)-one (3h): The title compound was prepared according to the general procedure (Method II). White solid (31.2 mg, 52%; eluent: 10%-40% ethyl acetate/hexane). Mp: 68-70 °C. ^{1}H NMR (400 MHz, CDCl3) δ 7.88 (d, *J* = 8.3 Hz, 1H), 7.44 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.32 (s, 1H), 3.92 (s, 3H), 3.77 (d, *J* = 11.2 Hz, 1H), 3.60 (d, *J* = 11.2 Hz, 1H), 3.38 (d, *J* = 16.6 Hz, 1H), 2.95 (d, *J* = 16.6 Hz, 1H), 1.36 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 173.65, 164.29, 137.82, 130.61, 130.23, 129.53, 127.32, 126.83, 65.83, 65.35, 64.42, 37.61, 20.54. HRMS (ESI): calcd for C12H15BrNO3 $[M+H]^+$: 300.0235, found 300.0220.



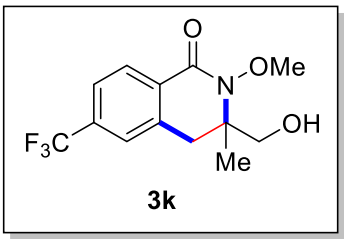
3i

3-(Hydroxymethyl)-6-iodo-2-methoxy-3-methyl-3,4-dihydroisoquinolin-1(*2H*)-one (3i): The title compound was prepared according to the general procedure (Method I). White solid (56.9 mg, 82%; 10%-40% ethyl acetate/hexane). Mp: 82-84 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 1H), 7.69 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.56 (s, 1H), 3.95 (s, 3H), 3.79 (d, *J* = 11.2 Hz, 1H), 3.63 (d, *J* = 11.2 Hz, 1H), 3.33 (d, *J* = 16.5 Hz, 1H), 2.93 (d, *J* = 16.5 Hz, 1H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.41, 137.49, 136.55, 136.34, 129.51, 127.48, 100.05, 66.44, 65.29, 64.52, 37.59, 20.51. HRMS (ESI): calcd for $C_{12}H_{15}INO_3$ $[M+H]^+$: 348.0097, found 348.0086.



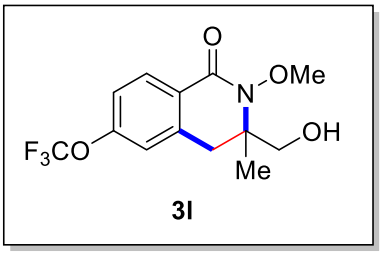
3j

Methyl-3-(hydroxymethyl)-2-methoxy-3-methyl-1-oxo-1,2,3,4-tetrahydroisoquinoline-6-carboxylate (3j): The title compound was prepared according to the general procedure (Method I) and then recrystallized from CH_2Cl_2/ hexane. White solid (34.1 mg, 61%; eluent: 10%-40% ethyl acetate/hexane). Mp: 88-90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.1 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.84 (s, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 3.81 (d, *J* = 11.2 Hz, 1H), 3.64 (d, *J* = 11.2 Hz, 1H), 3.46 (d, *J* = 16.5 Hz, 1H), 3.03 (d, *J* = 16.5 Hz, 2H), 1.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.32, 163.89, 135.96, 133.44, 131.63, 128.88, 128.00, 127.83, 66.09, 65.32, 64.41, 52.44, 37.87, 20.59. HRMS (ESI): calcd for $C_{14}H_{18}NO_5$ $[M+H]^+$: 280.1185, found 280.1171.



3k

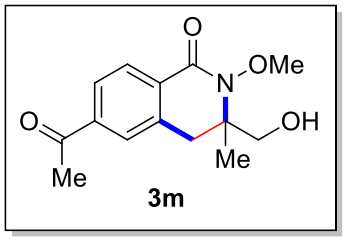
3-(Hydroxymethyl)-2-methoxy-3-methyl-6-(trifluoromethyl)-3,4-dihydroisoquinolin-1(*2H*)-one (3k): The title compound was prepared according to the general procedure (Method I). White solid (49.2 mg, 85%; eluent: 10%-40% ethyl acetate/hexane). Mp: 68-70 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.41 (s, 1H), 3.93 (s, 3H), 3.80 (dd, *J* = 11.2, 5.9 Hz, 1H), 3.61 (dd, *J* = 11.3, 5.3 Hz, 1H), 3.44 (d, *J* = 16.6 Hz, 1H), 3.03 (d, *J* = 16.6 Hz, 1H), 2.79 (t, *J* = 5.7 Hz, 1H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.57, 136.58, 134.02 (q, *J* = 32.6 Hz), 131.04, 128.49, 124.58 (q, *J* = 3.75 Hz), 123.74 (q, *J* = 3.77 Hz), 123.57 (q, *J* = 271.6 Hz), 66.24, 65.27, 64.47, 37.97, 20.68. ^{19}F NMR (565 MHz, $CDCl_3$) δ -63.07. HRMS (ESI): calcd for $C_{13}H_{15}F_3NO_3$ $[M+H]^+$: 290.1004, found 290.0996.



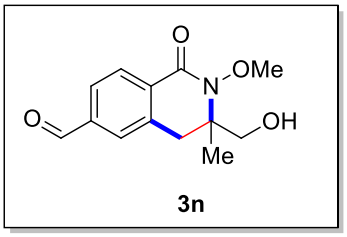
3l

3-(Hydroxymethyl)-2-methoxy-3-methyl-6-(trifluoromethoxy)-3,4-dihydroisoquinolin-1(*2H*)-one (3l): The title compound was prepared according to the general procedure (Method II). Colorless oil (47.6 mg, 78%; eluent: 10%-40% ethyl acetate/hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.6 Hz, 1H), 7.16 (dd, *J* = 19.8, 9.0 Hz, 1H), 6.99 (s, 1H), 3.93 (s, 3H), 3.80 (d, *J* = 11.2 Hz, 1H), 3.62 (d, *J* = 11.2 Hz, 1H), 3.41 (d, *J* = 16.7 Hz, 1H), 2.99 (d, *J* = 16.6 Hz, 1H), 1.37 (s, 3H). ^{13}C NMR (101 MHz,

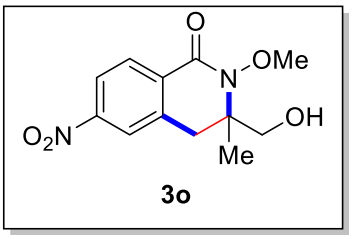
$CDCl_3$) δ 163.88, 152.20, 138.19, 130.22, 126.33, 120.26 (q, *J* = 259.6 Hz), 119.21, 118.86, 66.34, 65.26, 64.48, 37.98, 20.52. ^{19}F NMR (377 MHz, $CDCl_3$) δ -57.58. HRMS (ESI): calcd for $C_{13}H_{15}F_3NO_4$ $[M+H]^+$: 306.0953, found 306.0957.



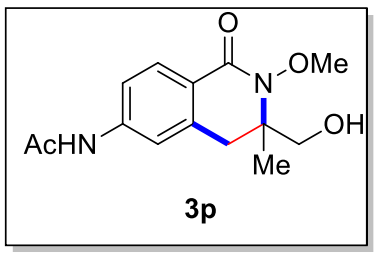
6-Acetyl-3-(hydroxymethyl)-2-methoxy-3-methyl-3,4-dihydroisoquinolin-1(*2H*)-one (3m): The title compound was prepared according to the general procedure (Method I). Yellow solid (47.4 mg, 90%; eluent: 10%-50% ethyl acetate/hexane). Mp: 89-91 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.1 Hz, 1H), 7.87 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.75 (s, 1H), 3.98 (s, 3H), 3.82 (d, *J* = 11.3 Hz, 1H), 3.65 (d, *J* = 11.3 Hz, 1H), 3.46 (d, *J* = 16.6 Hz, 1H), 3.05 (d, *J* = 16.5 Hz, 1H), 2.62 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.75, 163.84, 139.89, 136.19, 131.71, 128.31, 127.35, 126.80, 66.33, 65.31, 64.48, 38.06, 26.86, 20.66. HRMS (ESI): calcd for $C_{14}H_{18}NO_4$ $[M+H]^+$: 264.1236, found 264.1234.



3-(Hydroxymethyl)-2-methoxy-3-methyl-1-oxo-1,2,3,4-tetrahydroisoquinoline-6-carbaldehyde (3n): The title compound was prepared according to the general procedure (Method II). White solid (21.4 mg, 43%; eluent: 10%-50% ethyl acetate/hexane). Mp: 54-56 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 10.05 (s, 1H), 8.26 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.70 (s, 1H), 3.99 (s, 3H), 3.84 (d, *J* = 11.3 Hz, 1H), 3.66 (d, *J* = 11.3 Hz, 1H), 3.48 (d, *J* = 16.5 Hz, 1H), 3.08 (d, *J* = 16.5 Hz, 1H), 1.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.69, 163.61, 138.87, 136.59, 132.91, 128.76, 128.54, 128.18, 66.53, 65.22, 64.53, 38.01, 20.70.HRMS (ESI): calcd for $C_{13}H_{16}NO_4$ $[M+H]^+$: 250.1079, found 250.1071.

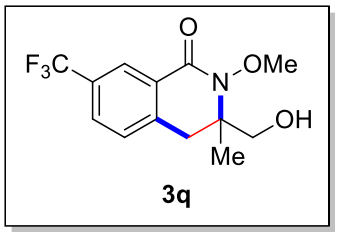


3-(Hydroxymethyl)-2-methoxy-3-methyl-6-nitro-3,4-dihydroisoquinolin-1(*2H*)-one (3o): The title compound was prepared according to the general procedure (Method II).Yellow solid (38.3 mg, 72%; eluent: 10%-40% ethyl acetate/hexane). Mp: 130-132 °C. ^1H NMR (400 MHz, DMSO) δ 8.17-8.14 (m, 2H), 8.10 (dd, *J* = 7.7, 1.4 Hz, 1H), 5.16 (t, *J* = 5.3 Hz, 1H), 3.86 (s, 3H), 3.56 (dd, *J* = 11.0, 5.5 Hz, 1H), 3.46 (d, *J* = 17.0 Hz, 1H), 3.38 (dd, *J* = 9.5, 3.6 Hz, 1H), 3.19 (d, *J* = 17.0 Hz, 1H), 1.28 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 162.10, 149.97, 138.93, 133.88, 128.85, 123.30, 121.91, 65.34, 64.89, 64.13, 37.53, 20.98. HRMS (ESI): calcd for $C_{12}H_{15}N_2O_5$ $[M+H]^+$: 267.0981, found 267.0973.



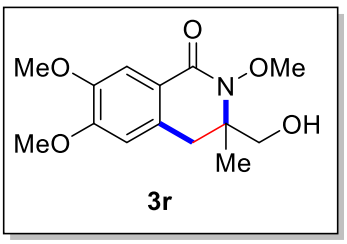
N-(3-(hydroxymethyl)-2-methoxy-3-methyl-1-oxo-1,2,3,4-tetrahydroisoquinolin-6-yl)acetamide (3p): The title compound was prepared according to the general procedure (Method I). White solid (50.1 mg, 90%; eluent: 1%-5% MeOH/CH_2Cl_2). Mp: 176-178 °C. ^1H NMR (400 MHz, DMSO) δ 10.20 (s, 1H), 7.80 (d, *J* = 8.5 Hz, 1H), 7.55 (s, 1H), 7.49 (dd, *J* = 8.5, 1.9 Hz, 1H), 5.10 (t, *J* = 5.4 Hz, 1H), 3.80 (s,

3H), 3.51 (dd, *J* = 10.7, 5.6 Hz, 1H), 3.39 (d, *J* = 5.4 Hz, 1H), 3.30 (d, *J* = 16.6 Hz, 1H), 2.89 (d, *J* = 16.6 Hz, 1H), 2.07 (s, 3H), 1.21 (s, 3H). ^{13}C NMR NMR (101 MHz,) δ 169.37, 164.05, 143.43, 137.81, 128.64, 122.85, 117.68, 117.24, 100.00, 65.27, 64.02, 31.85, 29.60, 29.58, 29.54, 29.27, 24.70, 22.66, 20.47, 14.52. HRMS (ESI): calcd for $C_{14}H_{19}N_2O_4$ $[M+H]^+$: 279.1345, found 279.1343.



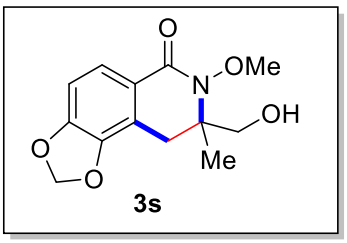
3q

3-(Hydroxymethyl)-2-methoxy-3-methyl-7-(trifluoromethyl)-3,4-dihydroisoquinolin-1(*2H*)-one (3q): The title compound was prepared according to the general procedure (Method I). White solid (32.4 mg, 56%; eluent: 10%-40% ethyl acetate/hexane). Mp: 127-129 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.67 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 3.95 (s, 3H), 3.83 (d, *J* = 11.3 Hz, 1H), 3.63 (d, *J* = 11.3 Hz, 1H), 3.46 (d, *J* = 16.7 Hz, 1H), 3.06 (d, *J* = 16.7 Hz, 1H), 1.39 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.63, 139.75, 129.56 (q, *J* = 33.2 Hz), 128.93 (q, *J* = 3.75 Hz), 128.66, 128.26, 124.99 (q, *J* = 3.62 Hz), 123.77 (q, *J* = 272.5 Hz), 66.31, 65.24, 64.46, 38.10, 20.72. ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.64. HRMS (ESI): calcd for $C_{13}H_{15}F_3NO_3$ $[M+H]^+$: 290.1004, found 290.1003.



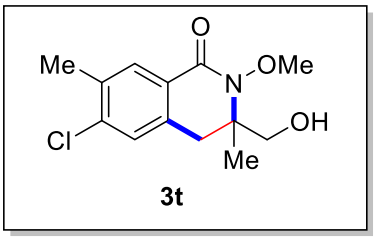
3r

3-(Hydroxymethyl)-2,6,7-trimethoxy-3-methyl-3,4-dihydroisoquinolin-1(*2H*)-one (3r): The title compound was prepared according to the general procedure (Method I). White solid (34.9 mg, 62%; eluent: 10%-40% ethyl acetate/hexane). Mp: 117-119 °C. ^{1}H NMR (400 MHz, CDCl3) δ 7.54 (s, 1H), 6.61 (s, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 3.89 (s, 3H), 3.78 (d, *J* = 11.0 Hz, 1H), 3.66 (d, *J* = 11.1 Hz, 1H), 3.34 (d, *J* = 16.3 Hz, 1H), 2.89 (d, *J* = 16.3 Hz, 1H), 1.38 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 165.34, 152.60, 147.93, 129.67, 120.11, 109.93, 109.86, 65.90, 65.50, 64.35, 56.04, 55.99, 37.48, 20.16. HRMS (ESI): calcd for $C_{14}H_{20}NO_5$ $[M+H]^+$: 282.1341, found 282.1337.



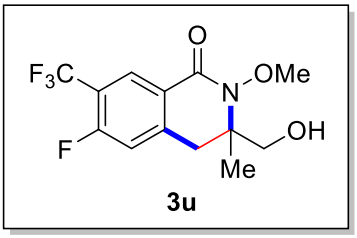
3s

8-(Hydroxymethyl)-7-methoxy-8-methyl-8,9-dihydro-[1,3]dioxolo[4,5-*f*]isoquinolin-6(*7H*)-one (3s): The title compound was prepared according to the general procedure (Method I). White solid 44.0 mg, 83%; eluent: 10%-40% ethyl acetate/hexane). Mp: 132-134 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.01 (dd, *J* = 4.7, 1.2 Hz, 2H), 3.92 (s, 3H), 3.78 (d, *J* = 11.2 Hz, 1H), 3.64 (d, *J* = 11.2 Hz, 1H), 3.29 (d, *J* = 16.6 Hz, 1H), 2.85 (d, *J* = 16.6 Hz, 1H), 1.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 164.99, 150.81, 144.39, 123.38, 122.17, 116.82, 106.97, 102.00, 66.12, 65.06, 64.37, 31.43, 20.55. HRMS (ESI): calcd for $C_{13}H_{16}NO_5$ $[M+H]^+$: 266.1028, found 266.1025.



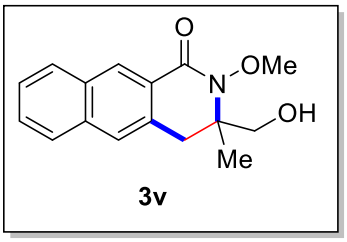
3t

6-Chloro-3-(hydroxymethyl)-2-methoxy-3,7-dimethyl-3,4-dihydroisoquinolin-1(*2H*)-one (3t): The title compound was prepared according to the general procedure (Method II). White solid (41.0 mg, 76%; eluent: 10%-50% ethyl acetate/hexane). Mp: 87-89 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.14 (s, 1H), 3.93 (s, 3H), 3.77 (d, *J* = 11.2 Hz, 1H), 3.62 (d, *J* = 11.2 Hz, 1H), 3.34 (d, *J* = 16.4 Hz, 1H), 2.90 (d, *J* = 16.4 Hz, 1H), 2.37 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.44, 138.84, 134.89, 134.69, 130.22, 128.08, 126.25, 66.03, 65.41, 64.41, 37.25, 20.44, 19.63. HRMS (ESI): calcd for $C_{13}H_{16}ClNO_3$ $[M+H]^+$: 270.0897, found 270.0899.



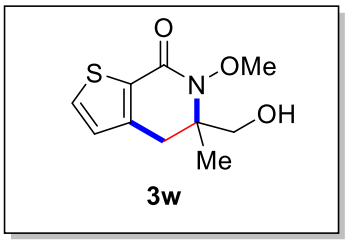
3u

6-Fluoro-3-(hydroxymethyl)-2-methoxy-3-methyl-7-(trifluoromethyl)-3,4-dihydroisoquinolin-1(*2H*)-one (3u): The title compound was prepared according to the general procedure (Method II). White solid (47.3 mg, 77%; eluent: 10%-40% ethyl acetate/hexane). Mp: 127-129 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 21.8, 7.3 Hz, 1H), 7.02 (d, *J* = 10.1 Hz, 1H), 3.93 (s, 3H), 3.86 (d, *J* = 11.3 Hz, 1H), 3.59 (d, *J* = 11.3 Hz, 1H), 3.43 (d, *J* = 17.0 Hz, 1H), 3.07 (d, *J* = 17.0 Hz, 1H), 1.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.04, 161.88 (d, *J* = 263.9 Hz), 143.03 (d, *J* = 9.4 Hz), 127.87-127.80 (m), 124.60 (d, *J* = 3.2 Hz), 122.19 (q, *J* = 272.7 Hz), 118.14, 117.92-117.04 (m), 115.92 (d, *J* = 21.6 Hz), 66.31, 65.23, 64.48, 38.19, 20.85. ^{19}F NMR (377 MHz, $CDCl_3$) δ -61.38 (d, *J* = 12.6 Hz), -108.66 (q, *J* = 12.9 Hz). HRMS (ESI): calcd for $C_{13}H_{13}F_4NO_3$ $[M+H]^+$: 308.0910, found 308.0904.



3v

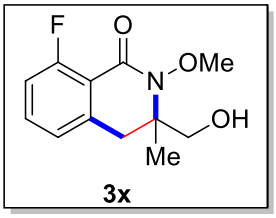
3-(Hydroxymethyl)-2-methoxy-3-methyl-3,4-dihydrobenzo[*g*]isoquinolin-1(*2H*)-one (3v): The title compound was prepared according to the general procedure (Method I). White solid (36.3 mg, 67%; eluent: 10%-40% ethyl acetate/hexane). Mp: 156-158 ^{o}C. ^{1}H NMR (400 MHz, DMSO) δ 8.55 (s, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.73 (s, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 5.16 (s, 1H), 3.89 (s, 3H), 3.56 (d, *J* = 10.5 Hz, 1H), 3.48 (d, *J* = 16.8 Hz, 1H), 3.45 (d, *J* = 12.4 Hz, 1H), 3.11 (d, *J* = 16.2 Hz, 1H), 1.27 (s, 3H). ^{13}C NMR (101 MHz,) δ 163.11, 134.67, 132.24, 131.14, 129.03, 127.99, 127.87, 126.83, 126.43, 125.95, 125.89, 64.69, 64.11, 63.52, 37.29, 20.17. HRMS (ESI): calcd for $C_{16}H_{18}NO_3$ $[M+H]^+$: 272.1287, found 272.1279.



3w

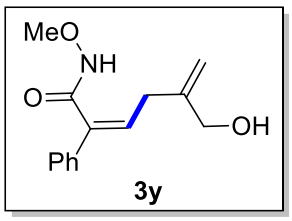
5-(Hydroxymethyl)-6-methoxy-5-methyl-5,6-dihydrothieno[2,3-*c*]pyridin-7(*4H*)-one (3w): The title compound was prepared according to the general procedure (Method I). Yellow oil (19.1 mg, 42%; eluent: 10%-40% ethyl acetate/hexane). ^{1}H NMR (400 MHz, CDCl3) δ 7.51 (d, *J* = 4.9 Hz, 1H), 6.88 (d, *J* = 4.9 Hz, 1H), 3.91 (s, 3H), 3.81 (d, *J* = 11.1 Hz, 1H), 3.66 (d, *J* = 11.1 Hz, 1H), 3.37 (d, *J* = 16.7 Hz, 1H), 2.87 (d, *J* = 16.7 Hz, 1H), 1.39 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 162.83, 141.81, 132.42, 129.54, 127.24, 77.43, 77.11, 76.79,

67.37, 65.79, 64.59, 34.21, 20.15. HRMS (ESI): calcd for $C_{10}H_{14}NO_3S$ $[M+H]^+$: 228.0694, found 228.0688.



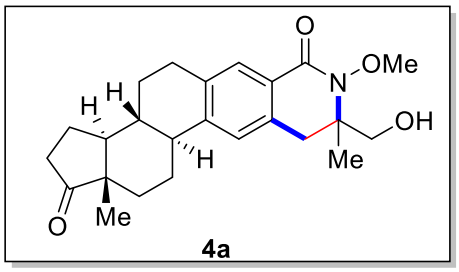
3x

8-Fluoro-3-(hydroxymethyl)-2-methoxy-3-methyl-3,4-dihydroisoquinolin-1(2*H*)-one (3x): The title compound was prepared according to the general procedure (Method II). White solid (8.1 mg, 7%; eluent: 10%-40% ethyl acetate/hexane). Mp: 160-162 °C. ^{1}H NMR (400 MHz, CDCl3) δ 7.40 (td, *J* = 8.0, 4.9 Hz, 1H), 7.02 (dd, *J* = 11.2, 8.5 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 3.97 (s, 3H), 3.83 (dd, *J* = 11.3, 3.5 Hz, 1H), 3.65 (dd, *J* = 11.2, 2.9 Hz, 1H), 3.41 (d, *J* = 16.3 Hz, 1H), 2.93 (d, *J* = 16.3 Hz, 1H), 1.37 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 162.34 (d, *J* = 262.7 Hz), 161.83 (d, *J* = 4.2 Hz), 161.03, 138.56, 133.77 (d, *J* = 10.1 Hz), 123.53 (d, *J* = 4.1 Hz), 115.81 (d, *J* = 22.4 Hz), 66.70, 64.69, 64.57, 38.40, 38.37, 20.38. ^{19}F NMR (377 MHz, CDCl3) δ -111.20. HRMS (ESI): calcd for $C_{12}H_{14}FNO_3$ $[M+H]^+$: 240.1036, found 240.1031.



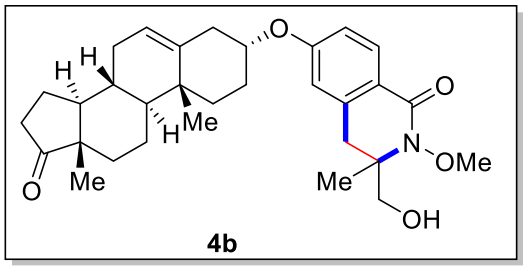
3y

(Z)-5-(hydroxymethyl)-*N*-methoxy-2-phenylhexa-2,5-dienamide (3y): The title compound was prepared according to the general procedure (Method I) on 1 mmol scale at rt. Pale yellow oil (152.7 mg, 61%; eluent: 10%-50% ethyl acetate/hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H), 7.50-7.09 (m, 5H), 6.00 (t, *J* = 8.2 Hz, 1H), 4.97 (s, 1H), 4.89 (s, 1H), 3.98 (s, 2H), 3.70 (s, 3H), 3.02 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.55, 145.95, 136.57, 135.75, 131.78, 128.60, 128.07, 126.21, 113.11, 65.46, 64.00, 34.21. HRMS (ESI): calcd for $C_{14}H_{18}NO_3$ $[M+H]^+$: 248.1287, found 248.1281.



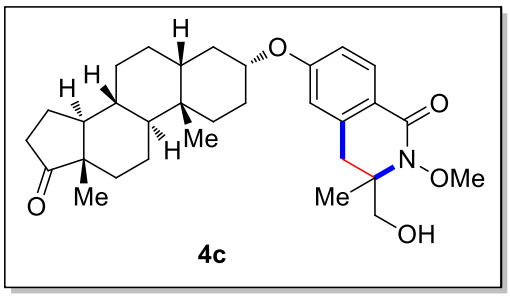
4a

(*3aS,3bR,9S,11bS,13aS*)-9-(Hydroxymethyl)-8-methoxy-9,13a-dimethyl-3,3a,3b,4,5,8,9,10,11b,12,13,13a-dodecahydro-1*H*-cyclopenta[5,6]naphtho[1,2-*g*]isoquinoline-1,7(2*H*)-dione (4a): The title compound was prepared according to the general procedure (Method II). White solid (62.8 mg, 79%; eluent: 10%-40% ethyl acetate/hexane). Mp: 230-232 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.08 (s, 1H), 3.95 (s, 3H), 3.77 (dd, *J* = 11.2, 3.6 Hz, 1H), 3.67 (dd, *J* = 11.2, 4.6 Hz, 1H), 3.33 (dd, *J* = 16.2, 5.4 Hz, 1H), 2.94-2.88 (m, 3H), 2.51 (dd, *J* = 18.6, 8.7 Hz, 1H), 2.43-2.36 (m, 1H), 2.33-2.22 (m, 1H), 2.21-2.00 (m, 3H), 1.97 (d, *J* = 12.1 Hz, 1H), 1.71-1.40 (m, 7H), 1.38 (d, *J* = 5.4 Hz, 3H), 0.91 (d, *J* = 1.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.16, 144.89, 135.39, 135.37, 132.82, 128.36, 125.38, 125.35, 124.63, 66.55, 66.47, 65.42, 64.44, 50.54, 47.87, 44.59, 37.93, 37.78, 35.83, 31.54, 28.89, 26.31, 25.64, 25.60, 21.58, 20.36, 20.28, 13.81. HRMS (ESI): calcd for $C_{24}H_{32}NO_4$ $[M+H]^+$: 398.2331, found 398.2315.



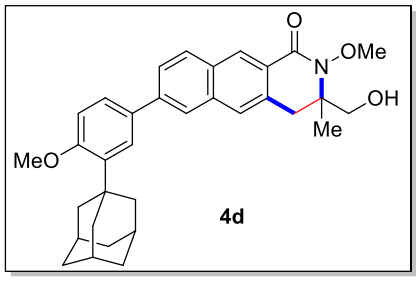
4b

6-(((*3R,8R,9S,10R,13S,14S*)-10,13-Dimethyl-17-oxo-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)-3-(hydroxymethyl)-2-methoxy-3-methyl-3,4-dihydroisoquinolin-1(*2H*)-one (4b): The title compound was prepared according to the general procedure (Method II). Mp: 195-197 °C. White solid (37.5 mg, 37%; eluent: 10%-40% ethyl acetate/hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.7 Hz, 1H), 6.81 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.63 (d, *J* = 2.2 Hz, 1H), 5.28 (d, *J* = 4.2 Hz, 1H), 4.60 (s, 1H), 3.95 (s, 3H), 3.77 (d, *J* = 11.2 Hz, 1H), 3.67 (d, *J* = 11.2 Hz, 1H), 3.32 (d, *J* = 16.4 Hz, 1H), 2.88 (d, *J* = 16.4 Hz, 1H), 2.47 (ddd, *J* = 41.5, 32.8, 15.1 Hz, 4H), 2.17-2.03 (m, 2H), 1.98-1.93 (m, 3H), 1.83 (ddd, *J* = 16.4, 6.1, 2.5 Hz, 2H), 1.77-1.61 (m, 4H), 1.58-1.42 (m, 3H), 1.37 (s, 3H), 1.31 (dd, *J* = 12.9, 4.2 Hz, 2H), 1.26 (s, 1H), 1.19 (dd, *J* = 11.3, 4.0 Hz, 1H), 1.07 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.27, 161.35, 138.45, 137.78, 130.15, 121.74, 120.25, 114.76, 114.20, 72.74, 66.57, 65.21, 64.49, 51.79, 49.98, 47.58, 38.19, 37.07, 36.22, 36.20, 35.87, 33.08, 31.43, 30.74, 29.70, 25.76, 25.73, 21.87, 20.14, 20.07, 19.04, 13.56. HRMS (ESI): calcd for $C_{31}H_{42}NO_5$ $[M+H]^+$: 508.3063, found 508.3056.



4c

6-(((*3R,5R,8R,9S,10S,13S,14S*)-10,13-Dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)-3-(hydroxymethyl)-2-methoxy-3-methyl-3,4-dihydroisoquinolin-1(*2H*)-one (4c): The title compound was prepared according to the general procedure (Method II). White solid (55.0 mg, 54%; eluent: 10%-40% ethyl acetate/hexane). Mp: 185-187 °C. ^{1}H NMR (400 MHz, CDCl3) δ 7.95 (d, *J* = 8.7 Hz, 1H), 6.77 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.61 (d, *J* = 1.9 Hz, 1H), 4.56 (s, 1H), 3.90 (s, 3H), 3.73 (dd, *J* = 11.1, 2.4 Hz, 1H), 3.63 (d, *J* = 11.1 Hz, 1H), 3.33 (d, *J* = 16.3 Hz, 1H), 3.04 (s, 1H), 2.86 (d, *J* = 16.1 Hz, 1H), 2.40 (dd, *J* = 19.2, 8.7 Hz, 1H), 2.11-1.98 (m, 1H), 1.89 (ddd, *J* = 20.1, 13.1, 9.1 Hz, 2H), 1.76 (d, *J* = 11.1 Hz, 2H), 1.71-1.58 (m, 4H), 1.55 (d, *J* = 4.2 Hz, 1H), 1.53-1.44 (m, 3H), 1.34 (dd, *J* = 9.4, 2.9 Hz, 4H), 1.28 (d, *J* = 5.4 Hz, 1H), 1.26-1.18 (m, 4H), 0.99 (qd, *J* = 12.0, 5.7 Hz, 1H), 0.83 (s, 3H), 0.82 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 165.31, 165.29, 161.36, 138.01, 130.13, 120.06, 114.29, 113.86, 72.07, 66.09, 66.07, 65.23, 64.41, 54.23, 51.45, 47.81, 39.60, 38.08, 35.92, 35.84, 35.00, 32.57, 31.52, 30.73, 28.06, 25.62, 25.58, 21.73, 20.15, 20.10, 20.06, 13.82, 11.41. HRMS (ESI): calcd for $C_{31}H_{44}NO_5$ $[M+H]^+$: 510.3219, found 510.3217.



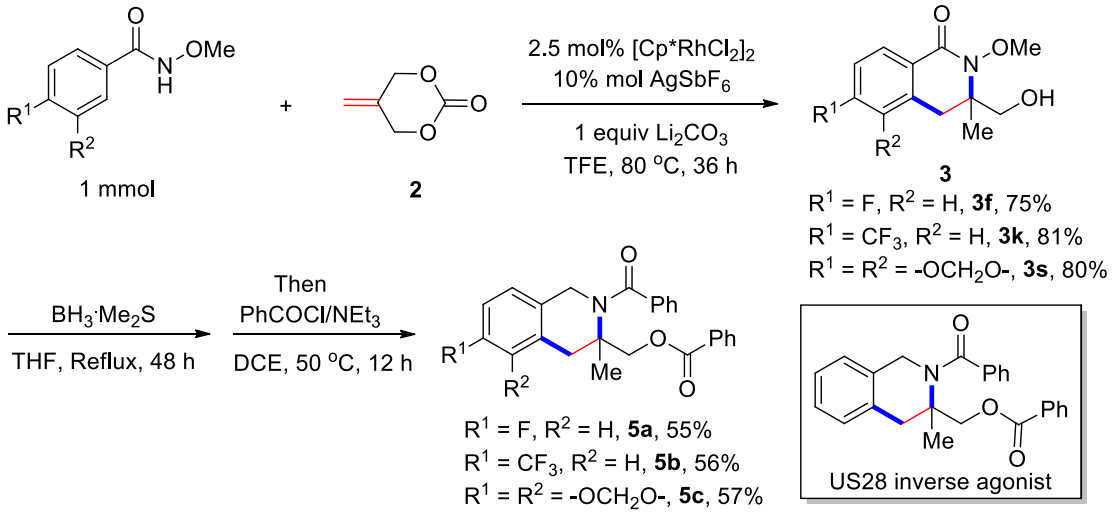
4d

7-(3-((3S,5S,7S)-Adamantan-1-yl)-4-methoxyphenyl)-3-(hydroxymethyl)-2-methoxy-3-methyl-3,4-dihydrobenzo[*g*]isoquinolin-1(2*H*)-one (4d): The title compound was prepared according to the general procedure (Method II). White solid (76.6 mg, 77%; eluent: 10%-50% ethyl acetate/hexane). Mp: 225-227 °C. ^{1}H NMR (400 MHz, DMSO) δ 8.52 (s, 1H), 8.10 (d, *J* = 7.8 Hz, 2H), 7.81 (s,

1H), 7.78 (dd, *J* = 8.8, 1.3 Hz, 1H), 7.60 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.54 (d, *J* = 2.1 Hz, 1H), 7.09 (d, *J* = 8.6 Hz, 1H), 5.15 (t, *J* = 5.3 Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 3.63-3.53 (m, 1H), 3.51 (s, 1H), 3.47 (s, 1H), 3.11 (d, *J* = 16.4 Hz, 1H), 2.12 (s, 6H), 2.04 (s, 3H), 1.74 (s, 6H), 1.27 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 163.77, 159.02, 140.54, 138.49, 135.79, 133.12, 132.16, 130.53, 130.16, 128.18, 126.76, 126.60, 126.13, 125.71, 125.54, 123.89, 113.16, 65.27, 64.70, 64.11, 55.79, 37.95, 37.06, 37.02, 28.88, 20.71. HRMS (ESI): calcd for $C_{33}H_{38}NO_4$ $[M+H]^+$: 512.2801, found 512.2781.

V. Synthetic applications

Synthesis of the analogs of US28 inverse agonist[7-8]:



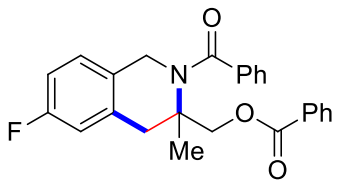
Step 1:

An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), Li_2CO_3 (1 mmol), **1f** or **1k** or **1s** (1 mmol), 5-methylene-1,3-dioxan-2-one (1.5 mmol) and TFE (5 mL) under Argon, and was evacuated and refilled with Argon for three times. Then, the septum was replaced by a Teflon screwcap under Argon flow. The reaction mixture was stirred at 80 °C for 36 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (30 mL). The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to provide the corresponding product **3f** or **3k** or **3s**.

Step 2:

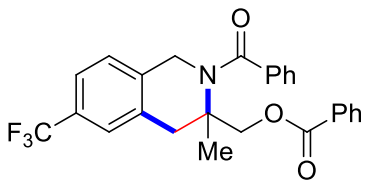
To a solution of **3f** or **3k** or **3s** (0.3 mmol) in dried THF (4 mL) was added $BH_3{\cdot}Me_2S$ (2.0 M in THF, 0.9 mL, 1.8 mmol) dropwise in an ice-bath. The mixture was warmed to room temperature and stirred for 2.5 h, then heated to reflux for 48 h. After cooling to 0 ℃ , 10% HCl was added slowly to quench the reaction, and the resulting solution was refluxed for 1.5 h. The mixture was cooled to 0 ℃ again, and 12 N NaOH was added until pH > 10. The mixture was extracted with Et_2O for three times, and the combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was used without further purification. The crude product obtained above was dissolved in a mixture of

1,2-dichloroethane (15 mL) and triethylamine (1.2 mmol) under argon atmosphere. The acid chloride (1.2 mmol) was added dropwise at room temperature and the reaction mixture was stirred at 50 ℃ for 12 h. Afterwards, 1,2-dichloroethane was removed under reduced pressure. The residue was acidified to pH 1 with 3M HCl, extracted with ethyl acetate and washed with saturated Na_2CO_3 solution and brine. The organic phase was dried over anhydrous sodium sulfate and the solvent was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to provide the corresponding product 5**a-c**.



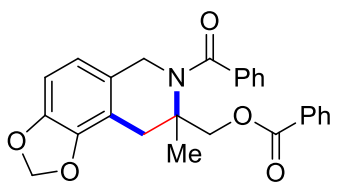
5a

(2-Benzoyl-6-fluoro-3-methyl-1,2,3,4-tetrahydroisoquinolin-3-yl)methyl benzoate (5a): White solid (66.5 mg, 55%; eluent: 5%-20% ethyl acetate/hexane). Mp: 130-132^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.4 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.42-7.40 (m, 5H), 7.38-7.36 (m, 2H), 6.96-6.91 (m, 2H), 6.85 (td, *J* = 8.7, 2.3 Hz, 1H), 5.18 (d, *J* = 10.9 Hz, 1H), 4.68 (d, *J* = 11.0 Hz, 1H), 4.37 (q, *J* = 14.6 Hz, 2H), 3.28 (d, *J* = 15.0 Hz, 1H), 2.78 (d, *J* = 15.0 Hz, 1H), 1.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.44, 166.03, 162.54 (d, *J* = 246.3 Hz), 138.05 (d, *J* = 1.8 Hz), 137.96, 133.10, 130.93 (d, *J* = 3.0 Hz), 130.03, 129.65, 129.49, 128.66, 128.44, 126.57, 126.42 (d, *J* = 8.5 Hz), 114.99 (d, *J* = 22.0 Hz), 113.40 (d, *J* = 21.7 Hz), 67.55, 59.05, 49.72, 40.75, 21.94. ^{19}F NMR (377 MHz, $CDCl_3$) δ -113.80. HRMS (ESI): calcd for $C_{25}H_{23}FNO_3$ $[M+H]^+$: 404.1662, found 404.1643.



5b

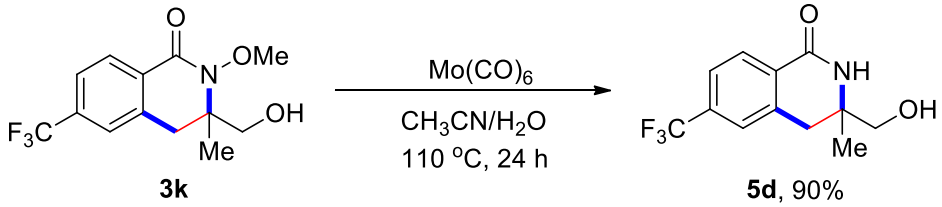
(2-Benzoyl-3-methyl-6-(trifluoromethyl)-1,2,3,4-tetrahydroisoquinolin-3-yl)methyl benzoate (5b): White solid (76.2 mg, 56%; eluent: 5%-20% ethyl acetate/hexane). Mp: 105-109 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.4 Hz, 2H), 7.58-7.52 (m, 1H), 7.50 (s, 1H), 7.487.35 (m, 8H), 7.10 (d, *J* = 7.8 Hz, 1H), 5.27 (d, *J* = 11.1 Hz, 1H), 4.67 (d, *J* = 11.1 Hz, 1H), 4.52-4.39 (m, 2H), 3.35 (d, *J* = 15.1 Hz, 1H), 2.88 (d, *J* = 15.1 Hz, 1H), 1.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.50, 165.99, 138.96, 137.87, 136.82, 133.10, 130.51 (q, *J* = 35.5 Hz), 129.88, 129.77, 129.43, 128.72, 128.42, 126.57, 125.27, 124.41 (q, *J* = 3.6 Hz), 123.92 (q, *J* = 269.3 Hz), 123.83 (q, *J* = 3.7 Hz), 123.82, 67.66, 59.19, 49.94, 40.76, 22.09. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.41. HRMS (ESI): calcd for $C_{26}H_{23}F_3NO_3$ $[M+H]^+$: 454.1630, found 454.1617.



5c

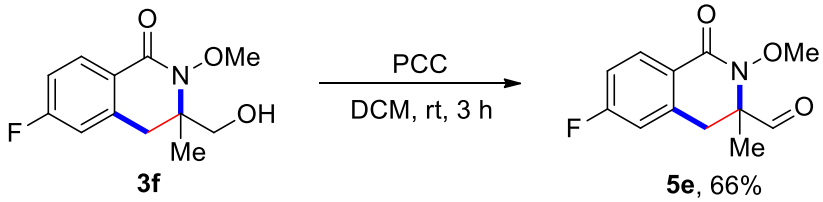
(7-Benzoyl-8-methyl-6,7,8,9-tetrahydro-[1,3]dioxolo[4,5-f]isoquinolin-8-yl)methyl benzoate (5c): White solid (73.4 mg, 57%; eluent: 5%-20% ethyl acetate/hexane). Mp: 98-100 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91-7.87 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43-7.40 (m, 4H), 7.39-7.36 (m, 3H), 6.62 (d, *J* = 7.7 Hz, 1H), 6.46 (d, *J* = 7.7 Hz, 1H), 5.91 (d, *J* = 1.4 Hz, 1H), 5.72 (d, *J* = 1.4 Hz, 1H), 5.19 (d, *J* = 11.0 Hz, 1H), 4.67 (d, *J* = 11.0 Hz, 1H), 4.34 (s, 2H), 3.22 (d, *J* = 15.2 Hz, 1H), 2.83 (d, *J* = 15.2 Hz, 1H), 1.69 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.57, 166.02, 147.22, 144.92, 138.07, 133.02, 130.07, 129.62, 129.57, 129.48, 128.60, 128.40, 126.65, 117.61, 116.68, 106.17, 101.23, 67.74, 58.99, 49.79, 33.98, 22.09. HRMS (ESI): calcd for $C_{26}H_{24}NO_5$ $[M+H]^+$: 430.1654, found 430.1634.

Transformations of 3[9]:



3k **5d**, 90%

Procedure: An oven dried 35 mL Schlenk tube equipped with a stir bar was charged with **3k** (0.2 mmol), $Mo(CO)_6$ (0.4 mmol), CH_3CN/H_2O (15:1, 2 mL). The reaction mixture was stirred at 110 ^oC for 24 h, whereupon the black reaction mixture was cooled to room temperature, opened to the atmosphere, and stirred for 24 h. Then, the mixture was concentrated. The residue was diluted with ethyl acetate (100 mL), filtered and concentrated under reduced pressure and was purified by chromatography on silica gel to afford **5d** as white solid (46.6 mg, 90%, eluent: 10-50% ethyl acetate/hexane). Mp: 112-114 ^oC. ^1H NMR (400 MHz, DMSO) δ 8.02 (d, *J* = 7.2 Hz, 2H), 7.67 (s, 1H), 7.66 (s, 1H), 5.03 (s, 1H), 3.22 (s, 2H), 3.14 (d, *J* = 16.3 Hz, 1H), 2.86 (d, *J* = 16.3 Hz, 1H), 1.18 (s, 3H). ^{13}C NMR (101 MHz,) δ 162.74, 138.77, 131.95, 131.94, 131.53 (q, *J* = 31.4 Hz), 131.38, 127.61, 124.99 (q, *J* = 3.8 Hz), 123.87 (q, *J* = 271.2 Hz), 123.21 (q, *J* = 3.8 Hz), 66.72, 54.79, 35.06, 23.85. ^{19}F NMR (376 MHz,) δ -61.91. HRMS (ESI): calcd for $C_{12}H_{13}F_3NO_2$ $[M+H]^+$: 260.0898, found 260.0883.



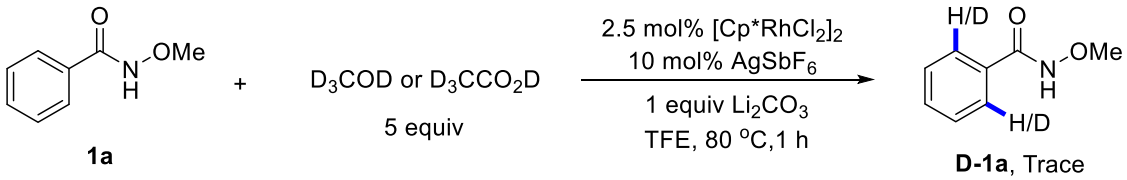
3f **5e**, 66%

Procedure: An oven dried 35 mL Schlenk tube equipped with a stir bar was added with PCC (0.4 mmol) and DCM (2 mL). Then, **3f** (0.2 mmol) was added in one portion. The reaction mixture was stirred at rt for 3 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (30 mL). The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel to provide the corresponding product **5e** as light yellow sticky oil (31.2 mg, 66%, eluent: 10%-30% ethyl acetate/hexane). ^1H NMR (400 MHz, $CDCl_3$) δ 9.68 (s, 1H), 8.15 (dd, *J* = 8.7, 5.7 Hz, 1H), 7.06 (td, *J* = 8.5, 2.5 Hz, 1H), 6.87 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.99 (s, 3H), 3.40 (d, *J* = 16.5 Hz, 1H), 3.08 (d, *J* = 16.5 Hz, 1H), 1.58 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.52, 165.40 (d, *J* = 253.4 Hz), 164.66, 136.84 (d, *J* = 9.1 Hz), 131.33 (d, *J* = 9.8 Hz), 124.10 (d, *J* = 2.8 Hz), 115.14 (d, *J* = 21.9 Hz), 114.45 (d, *J* = 22.5 Hz), 71.39, 64.96, 36.71, 18.08. ^{19}F NMR (377 MHz, $CDCl_3$) δ -105.36. HRMS (ESI): calcd for $C_{12}H_{13}FNO_3$ $[M+H]^+$: 238.0879, found 238.0864.

Note: 5e was found to be apt to decompose at a temperature higher than 40 ^oC, all the procedures above were conducted at rt.

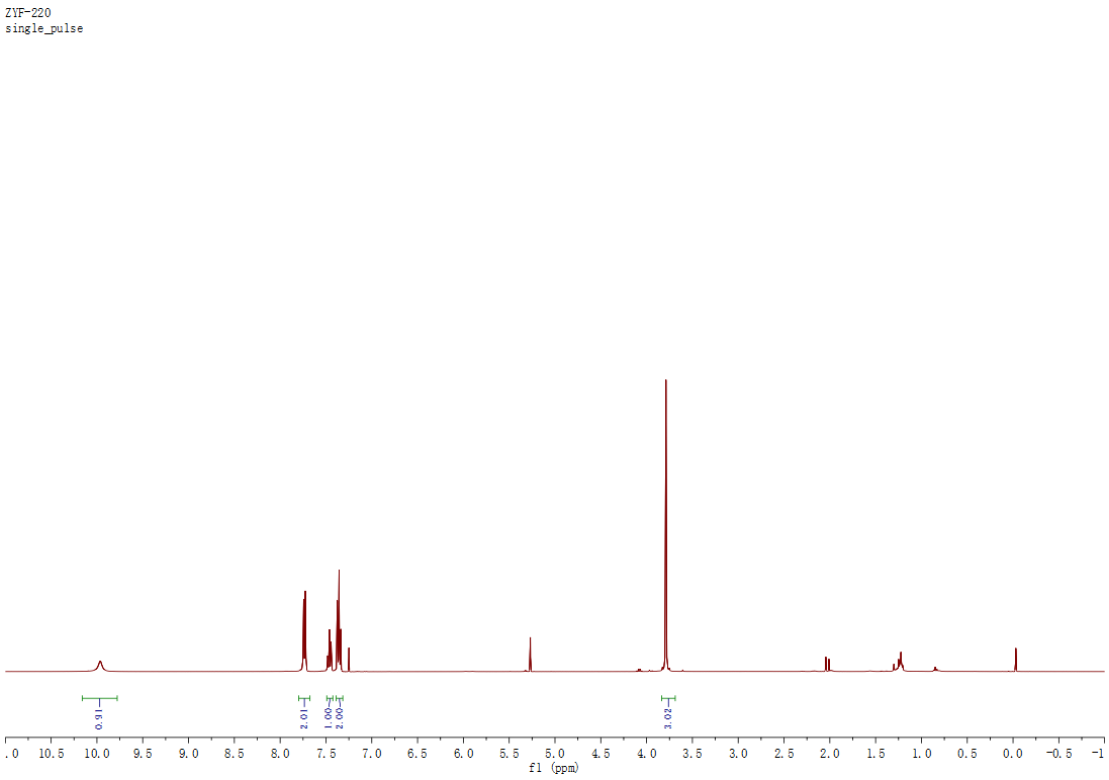
VI. Mechanistic studies

H/D exchange experiment

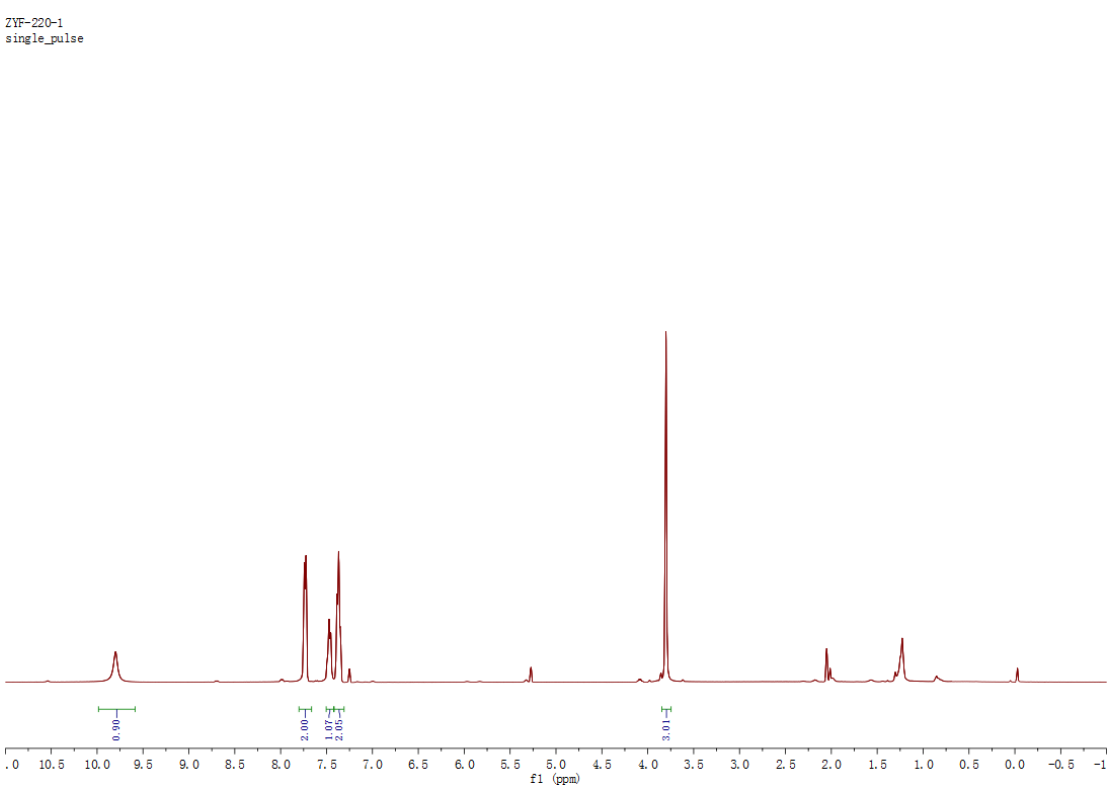


Procedure: An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), Li_2CO_3 (0.2 mmol), **1a** (0.2 mmol), CD_3OD (1.0 mmol) or CD_3CO_2D (1.0 mmol) and TFE (2 mL) under Argon, and was evacuated and refilled with Argon for three times. Then, the septum was replaced by a Teflon screwcap under Argon flow. The reaction mixture was stirred at 80 °C for 1 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (30 mL). The filtrate was concentrated under reduced pressure. The residue was then purified by chromatography on silica gel. ^{1}H NMR showed that D did not incorporate into **1a**.

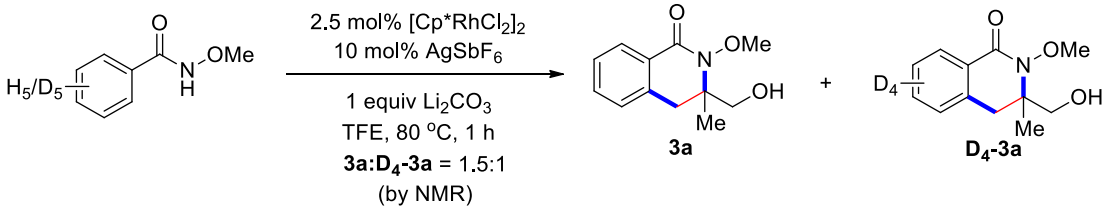
CD_3OD:



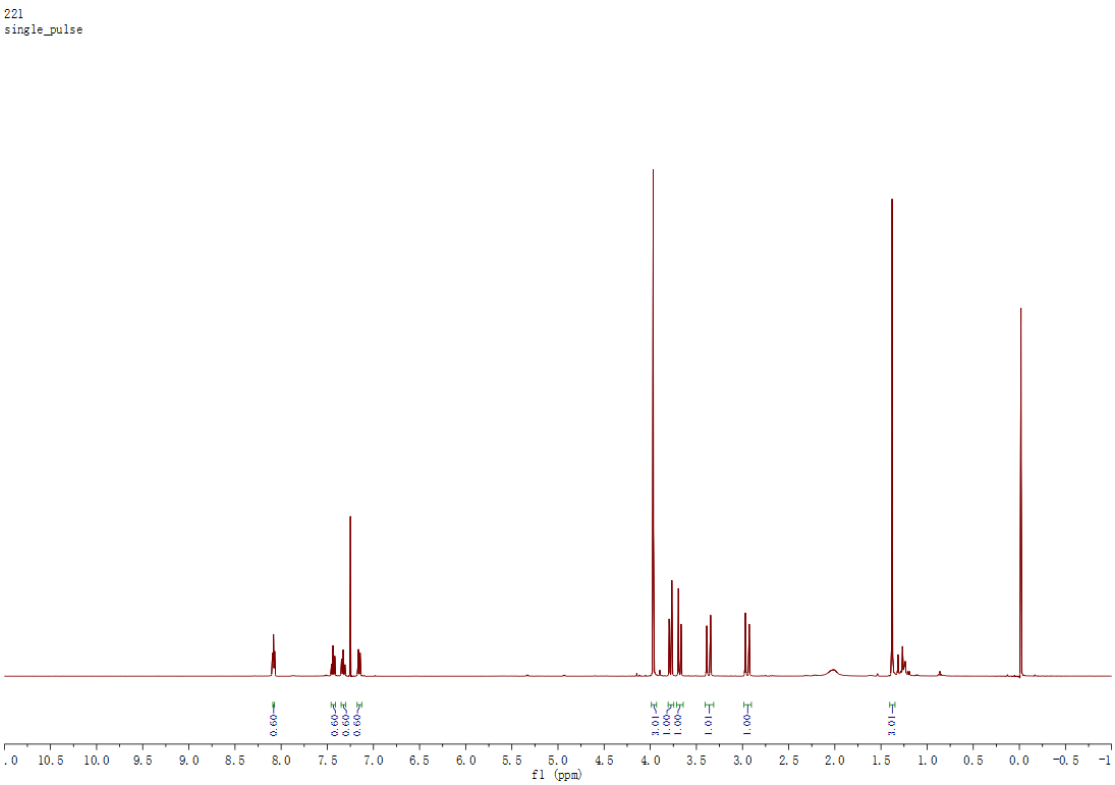
CD_3CO_2D:



KIE experiment

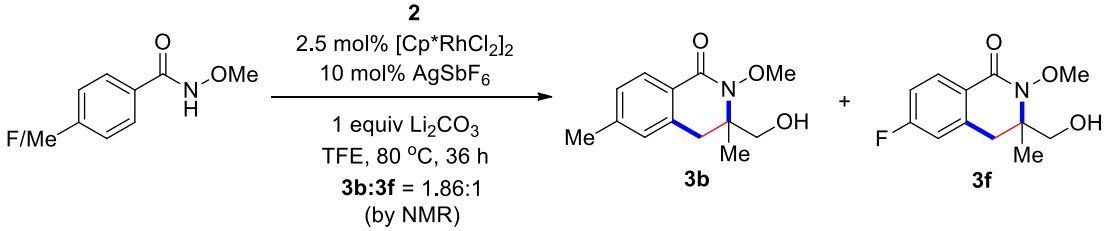


Procedure: An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), Li_2CO_3 (0.2 mmol), **1a** (0.2 mmol), **D_4-1a** (0.2 mmol), **2** (0.3 mmol) and TFE (2 mL) under Argon, and was evacuated and refilled with Argon for three times. The reaction mixture was stirred at 80 °C for 1 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (30 mL). The filtrate was concentrated under reduced pressure and the residue was then purified by chromatography on silica gel to afford a mixture of **3a** and **D_4-3a** (26.6 mg). ^{1}H NMR was measured to determine the ratio of **3a** and **D_4-3a**.

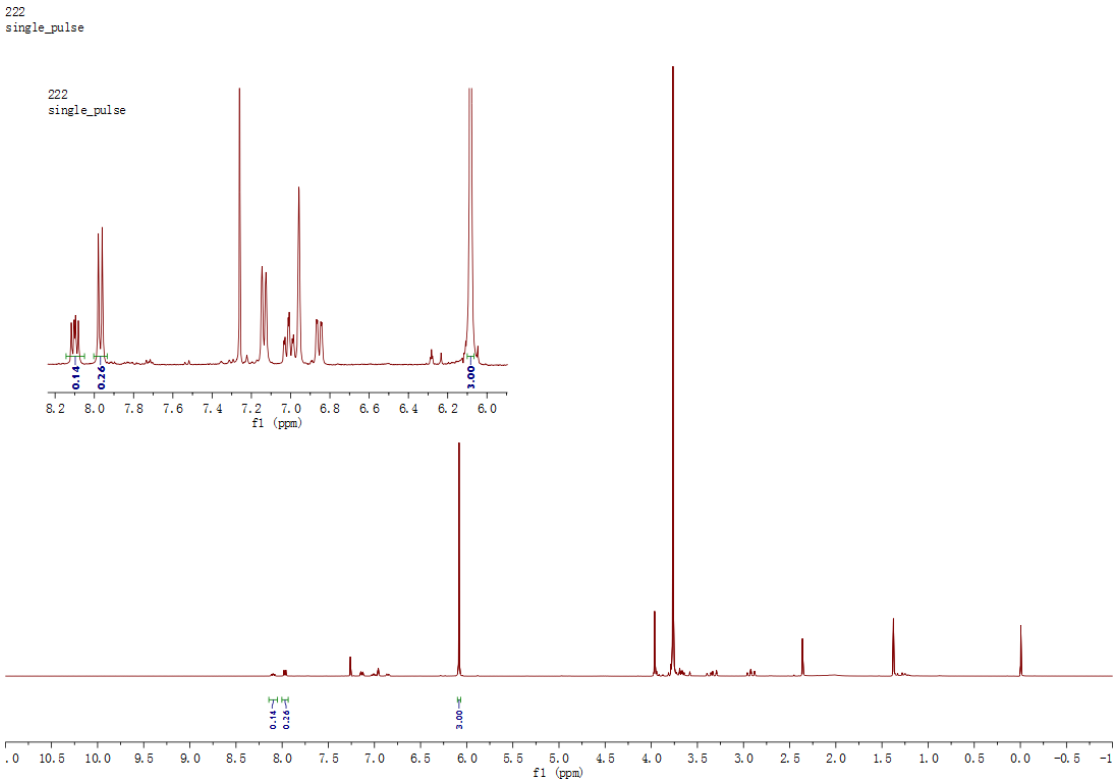


3a : **D_4-3a = 0.6 : 0.4 = 1.5**

Competition experiment between *N*-methoxybenzamides

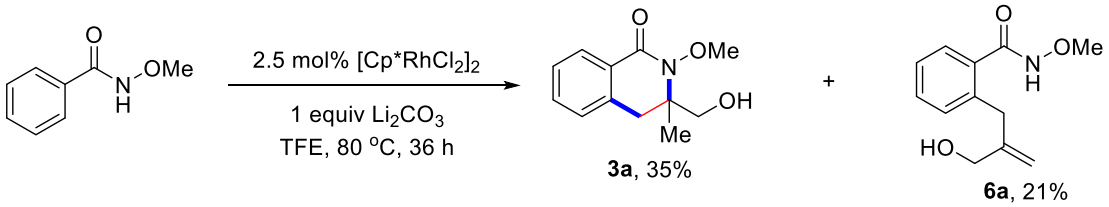


Procedure: An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), Li_2CO_3 (0.2 mmol), **1b** (0.2 mmol), **1f** (0.2 mmol), **2** (0.2 mmol), TFE (2 mL) under Argon, and was evacuated and refilled with Argon for three times. The reaction mixture was stirred at 80°C for 36 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (30 mL). The filtrate was concentrated under reduced pressure and the residue was then purified by chromatography on silica gel. The crude ^1H NMR was measured to determine the conversions to the products **3b** (26%) and **3f** (14%) using 1,3,5-trimethoxybenzene as the internal standard.

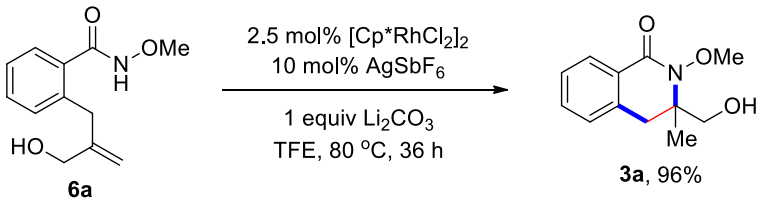


3b : **3f = 0.26 : 0.14 = 1.86 : 1**

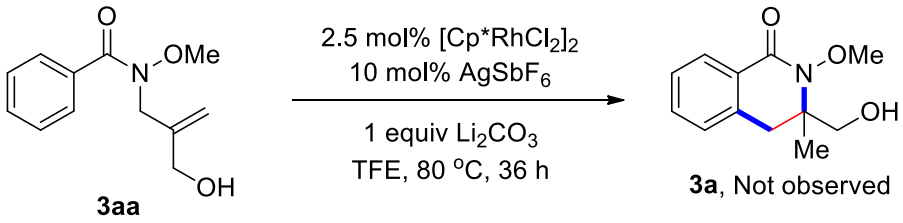
Control experiment



Procedure: An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with $[Cp^*RhCl_2]_2$ (2.5 mol%), Li_2CO_3 (0.2 mmol), **1a** (0.2 mmol), **2** (0.3 mmol) and TFE (2 mL) under Argon, and was evacuated and refilled with Argon for three times. The reaction mixture was stirred at 80°C for 36 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (30 mL). The filtrate was concentrated under reduced pressure and the residue was then purified by chromatography on silica gel to afford **3a** (15.5 mg, 35%) and **6a** (9.3 mg, 21%). ***N*-(2-(hydroxymethyl)allyl)-*N*-methoxybenzamide (6a)**: Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (bs, 1H), 7.45-7.34 (m, 2H), 7.29-7.22 (m, 2H), 5.06 (s, 1H), 4.89 (s, 1H), 3.95 (s, 2H), 3.85 (s, 3H), 3.56 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.06, 148.01, 137.75, 132.74, 130.83, 130.79, 127.86, 126.57, 113.40, 65.27, 64.52, 36.45. HRMS (ESI): calcd for $C_{12}H_{16}NO_3$ $[M+H]^+$: 222.1130, found 222.1120.

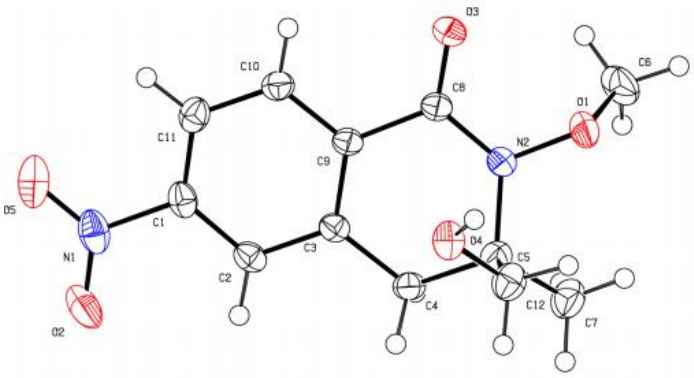


Procedure: An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), Li_2CO_3 (0.2 mmol), **6a** (0.2 mmol) and TFE (2 mL) under Argon, and was evacuated and refilled with Argon for three times. The reaction mixture was stirred at 80 °C for 36 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl acetate, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl acetate (30 mL). The filtrate was concentrated under reduced pressure and the residue was then purified by chromatography on silica gel to afford **3a** (42.5 mg, 96%).



Procedure: An oven dried 35 mL Schlenk tube equipped with a stir bar was fitted with a rubber septum and cooled under vacuum. After cooling, the tube was charged with $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), Li_2CO_3 (0.2 mmol), **3aa** (0.2 mmol) and TFE (2 mL) under Argon, and was evacuated and refilled with Argon for three times. The reaction mixture was stirred at 80 °C for 36 h. **3a** was not observed by TLC.

VII. X-ray crystallographic analysis of 3o (CCDC: 2103476)



Identification code	**3o**
Empirical formula	$C_{12}H_{14}N_2O_5$
Formula Mass	266.25
Temperature / K	150(2)
Wavelength / Å	0.71073

Crystal system	orthorhombic
Space group	*Pbca*
a / Å	12.7365(14)
b / Å	7.8148(9)
c / Å	24.702(3)
V / Å^3	2458.6(5)
Z	8
μ / mm^{-1}	0.113
F(000)	1120
Crystal size / mm	0.25 x 0.1 x 0.08
Theta range for data collection / °	3.168 to 30.821
Index ranges	-18<=h<=17, -11<=k<=10, -33<=l<=35
ρ_{calcd} /g cm^{-3}	1.439
Measured refls.	43727
Independent refls.	3855
Completeness to theta = 25.242 °	99.9%
Absorption correction	None
Ratio of min. to max. transmission	0.8791
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3855 / 0 / 175
R_{int}	0.0627
[a]R indices [$I > 2\sigma(I)$] R_1, $wR2$	0.0703, 0.1651
R indices (all data) R_1, $wR2$	0.0968, 0.1794
GOF	1.116
Largest diff. peak and hole / e.Å^{-3}	0.645 and -0.313
CCDC reference numbers	2103476

VIII. References

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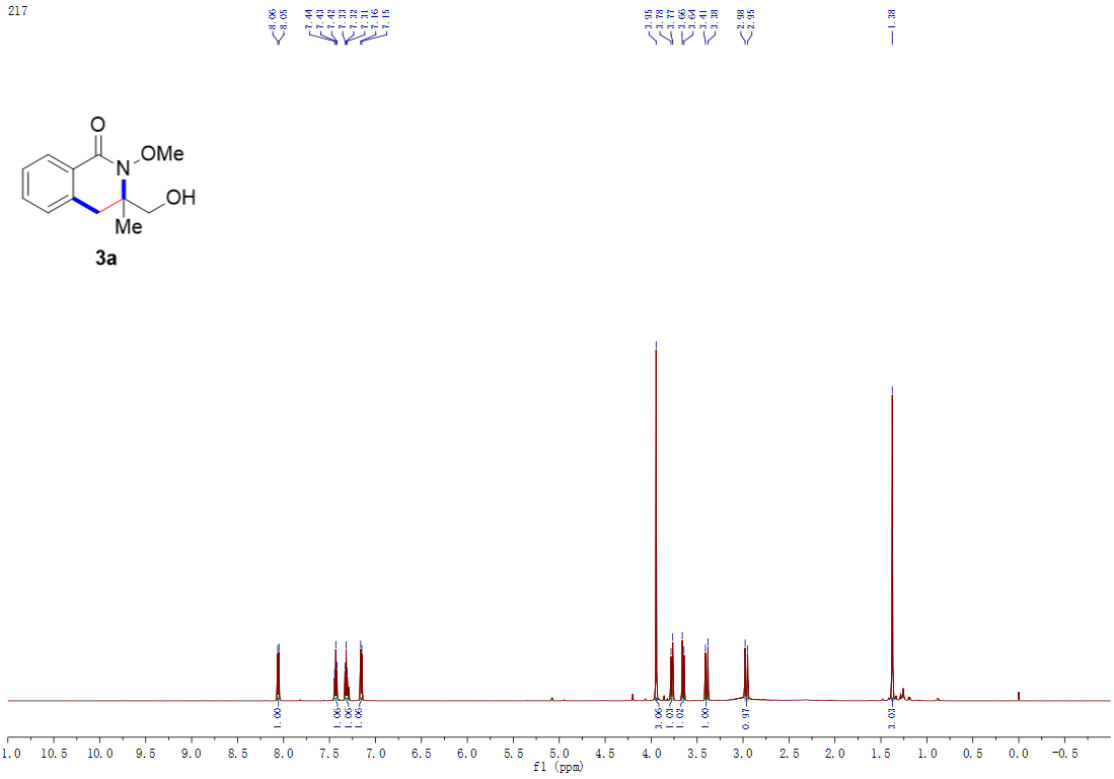
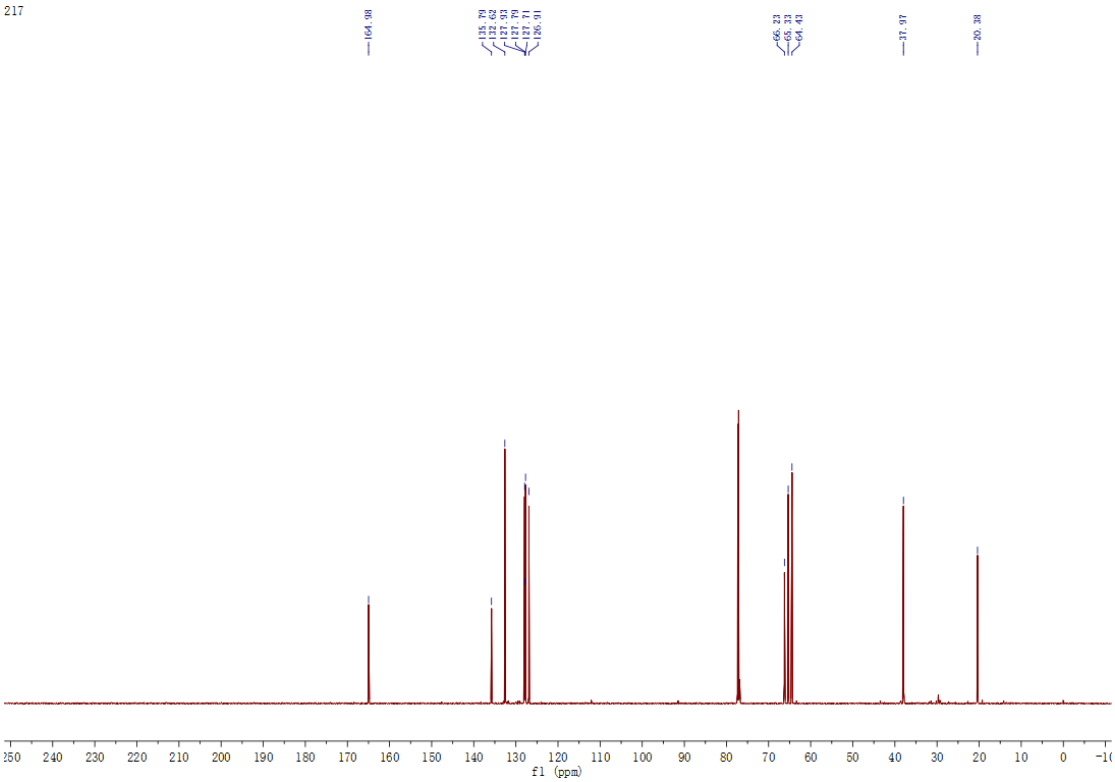
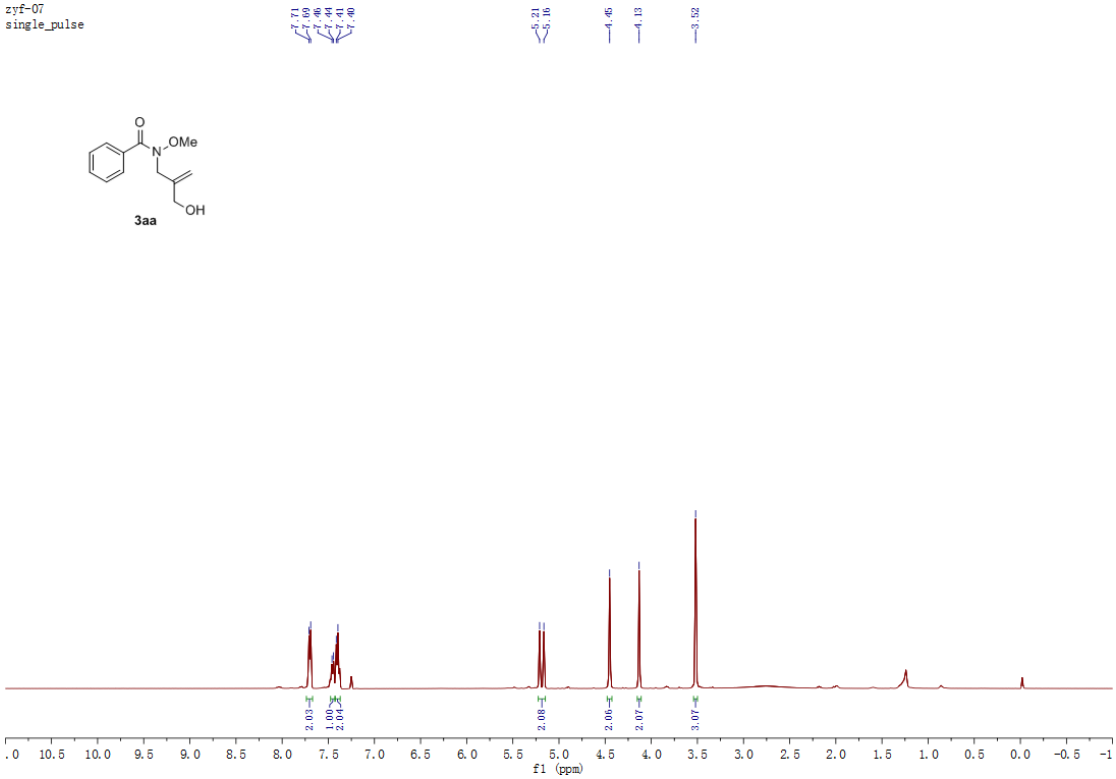
IX. ^{1}H, ^{13}C and ^{19}F NMR spectra



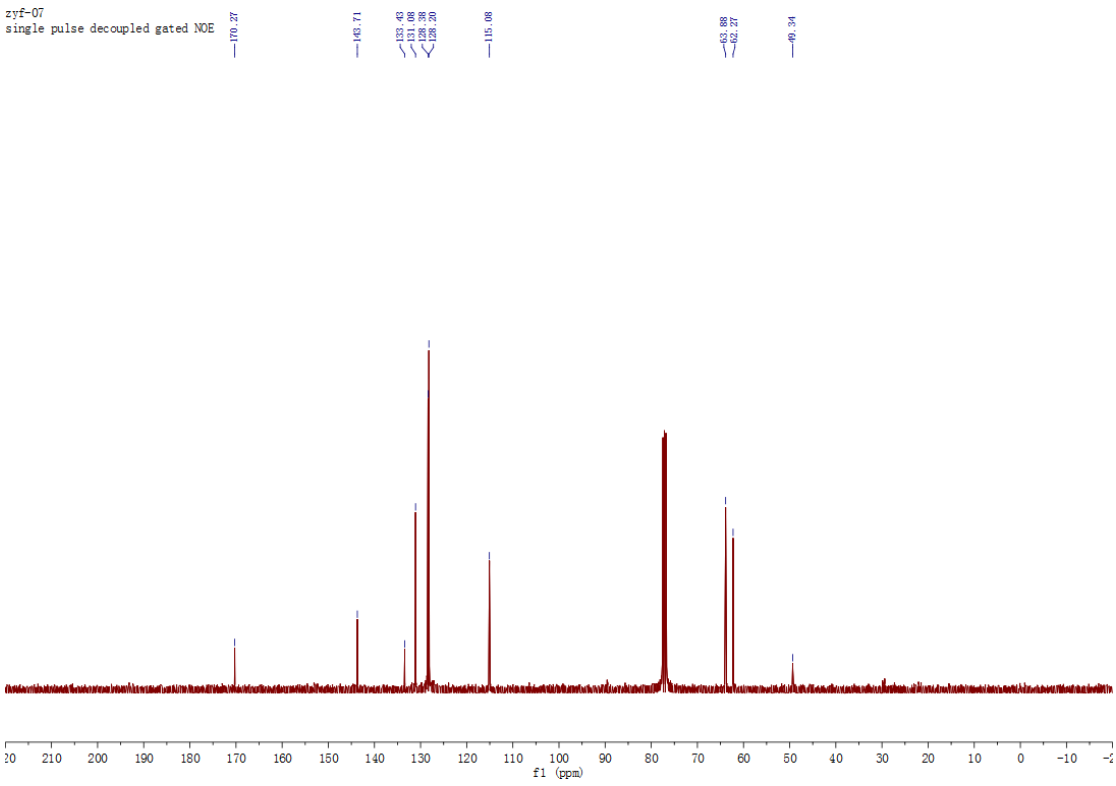
^{1}H NMR spectra of 3a ($CDCl_3$)



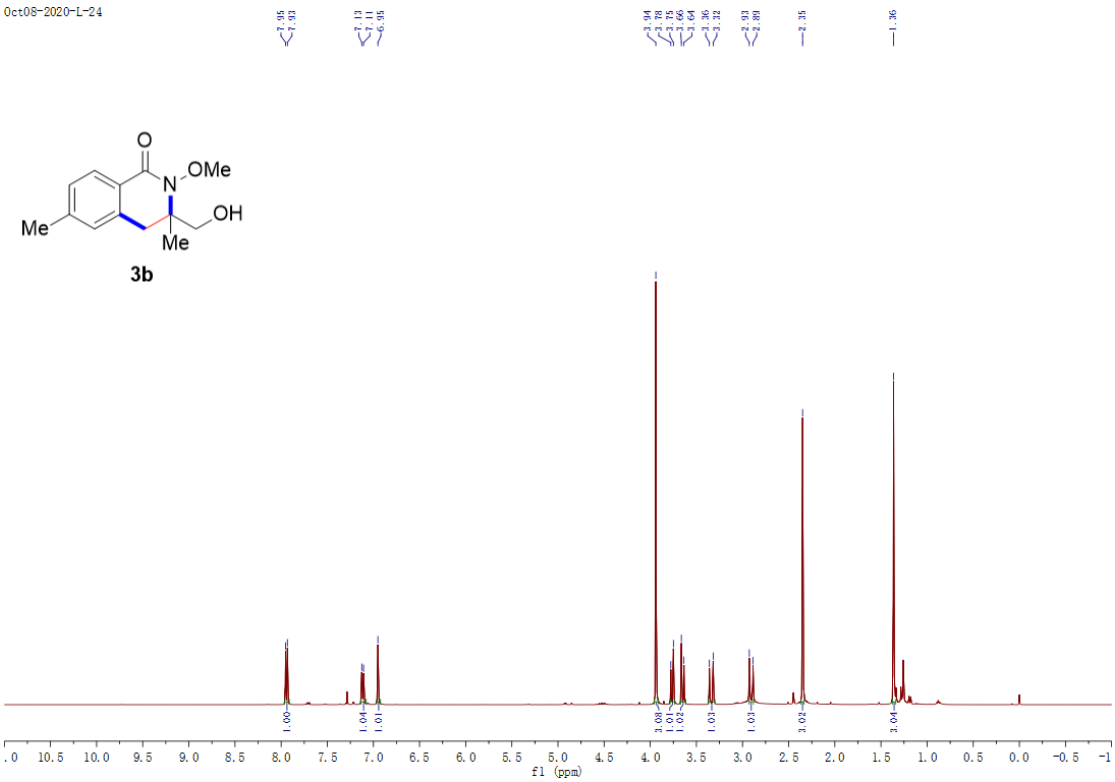
^{13}C NMR spectra of 3a ($CDCl_3$)



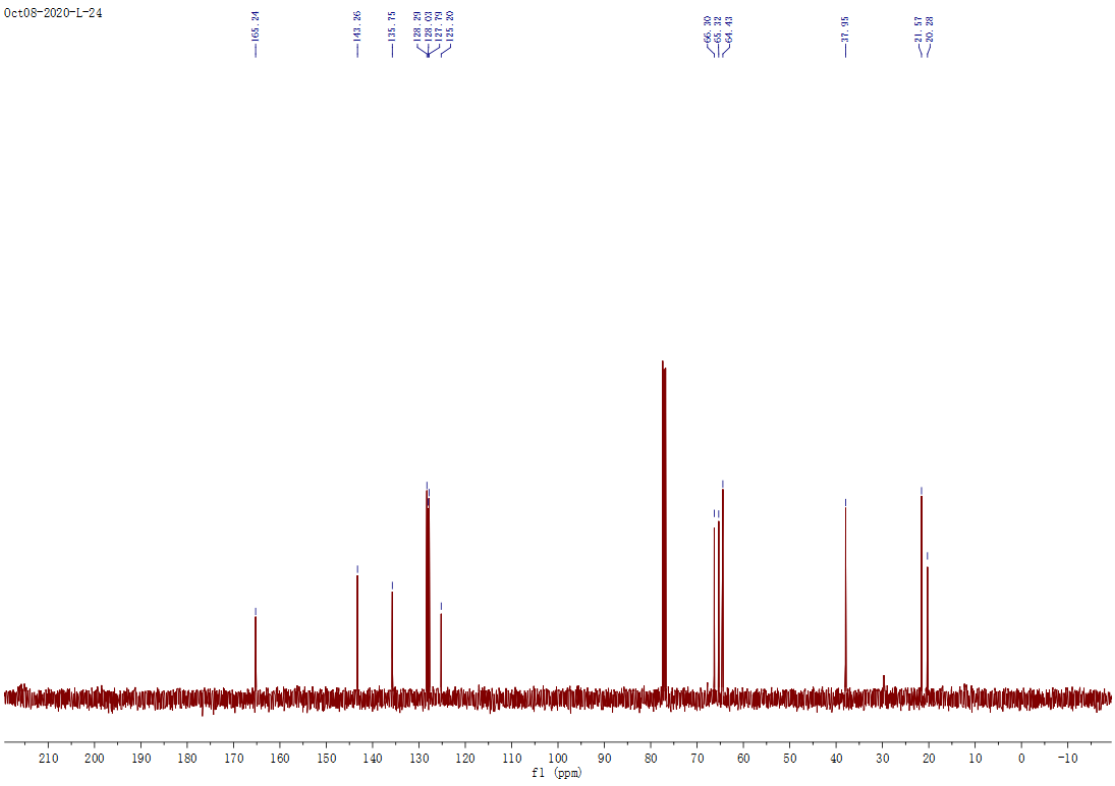
^{1}H NMR spectra of 3aa ($CDCl_3$)



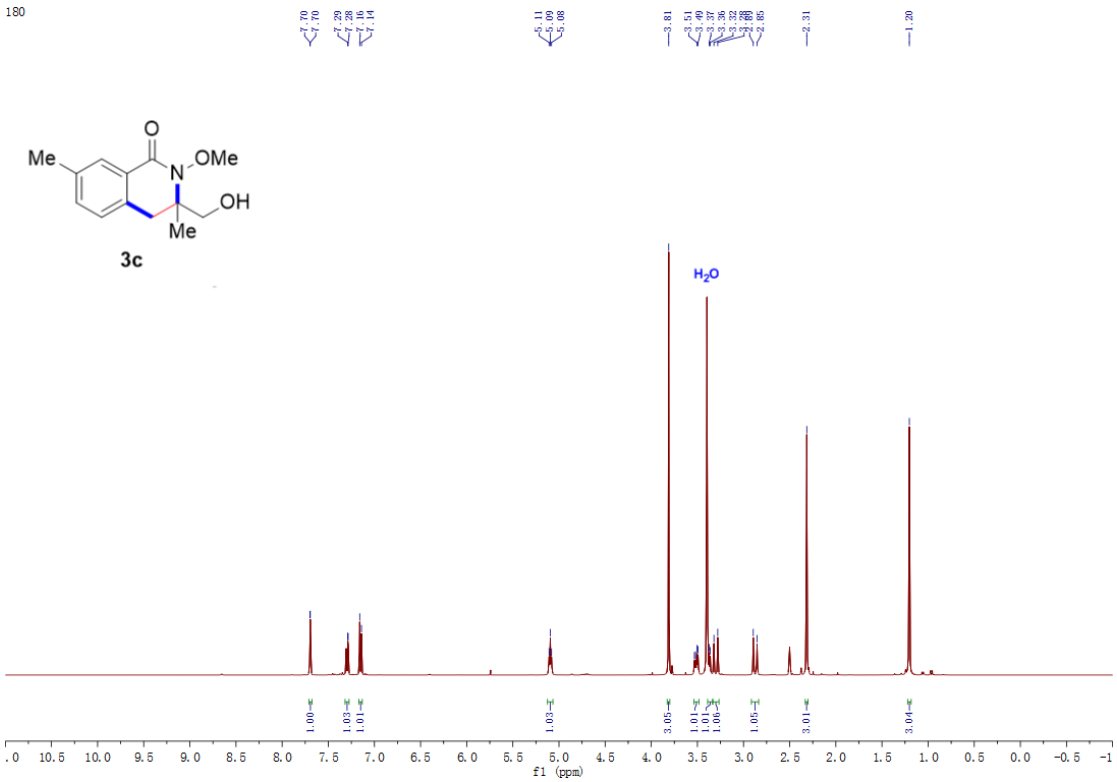
^{13}C NMR spectra of 3aa ($CDCl_3$)



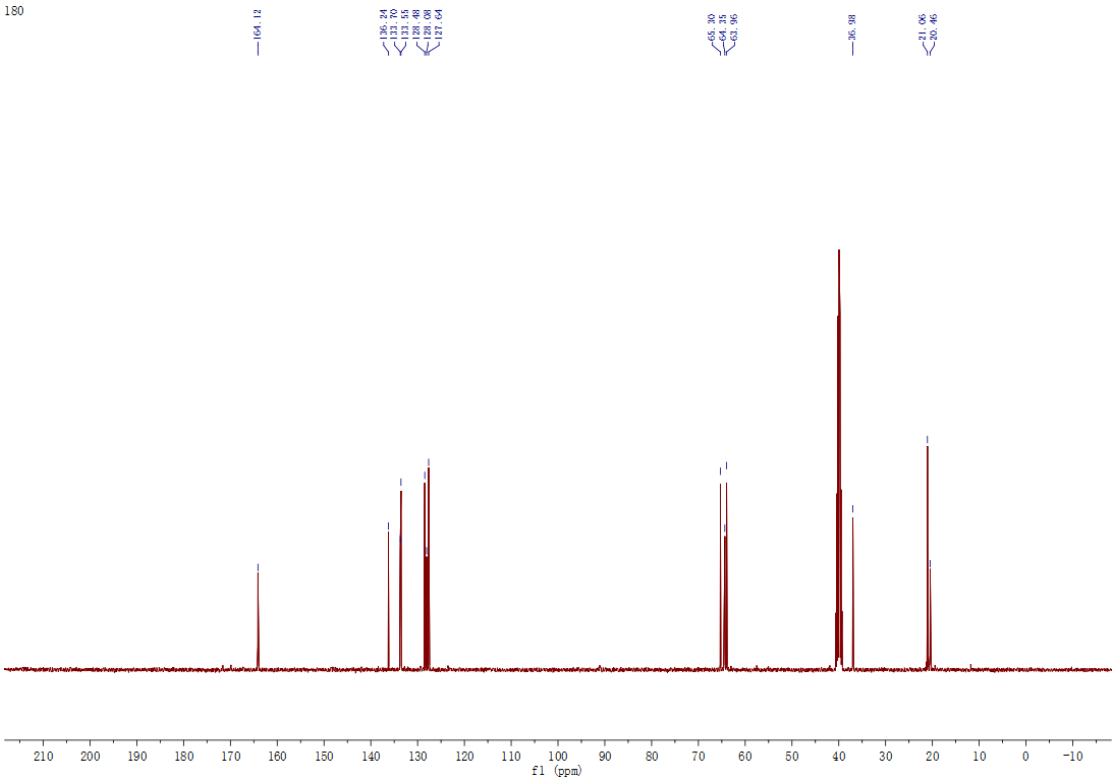
^{1}H NMR spectra of 3b ($CDCl_3$)



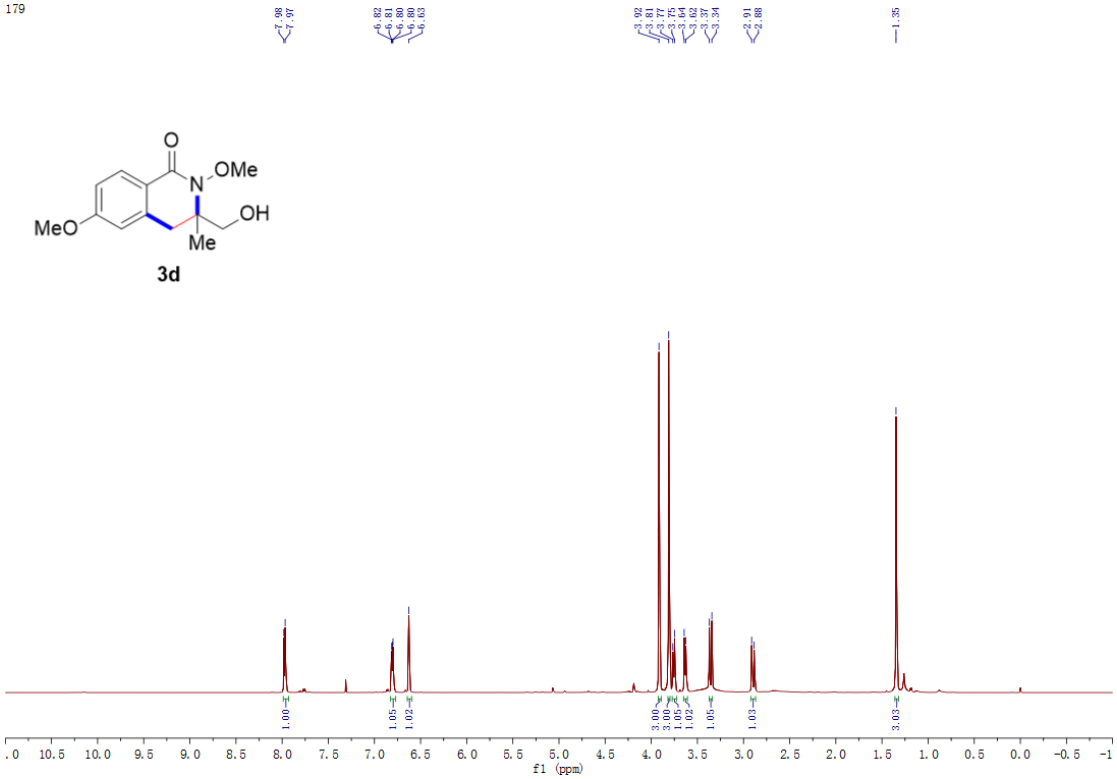
^{13}C NMR spectra of 3b ($CDCl_3$)



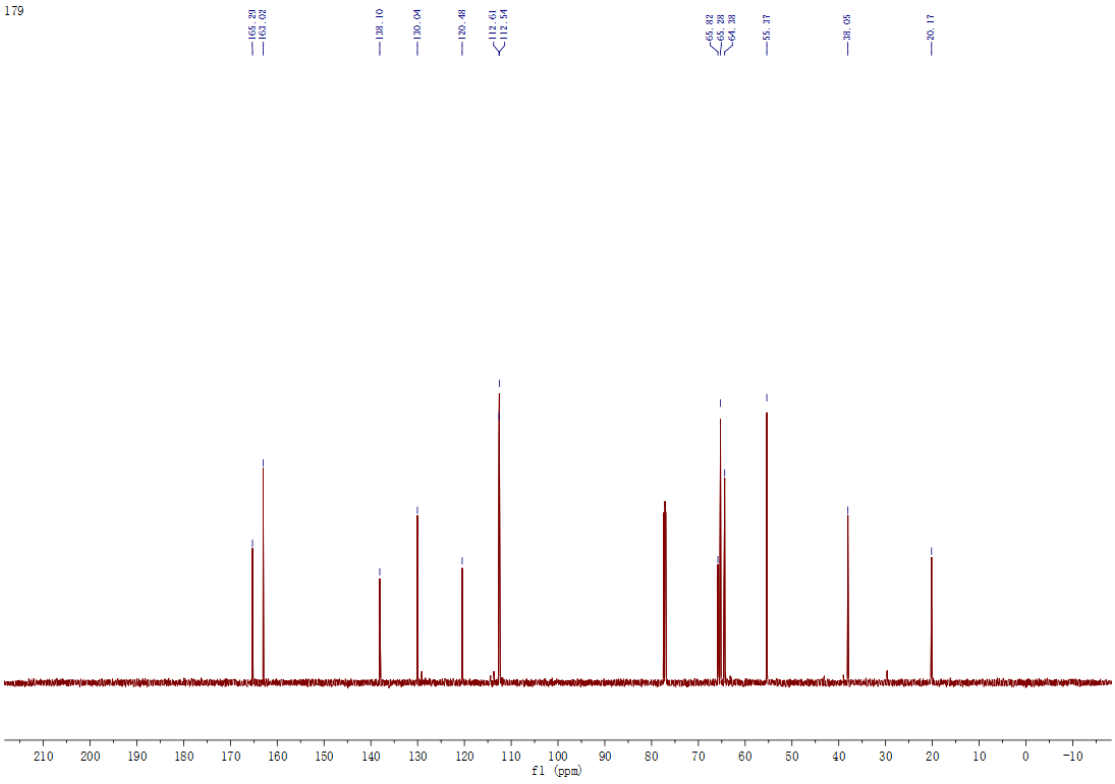
^{1}H NMR spectra of 3c ($(CD_3)_2SO$)



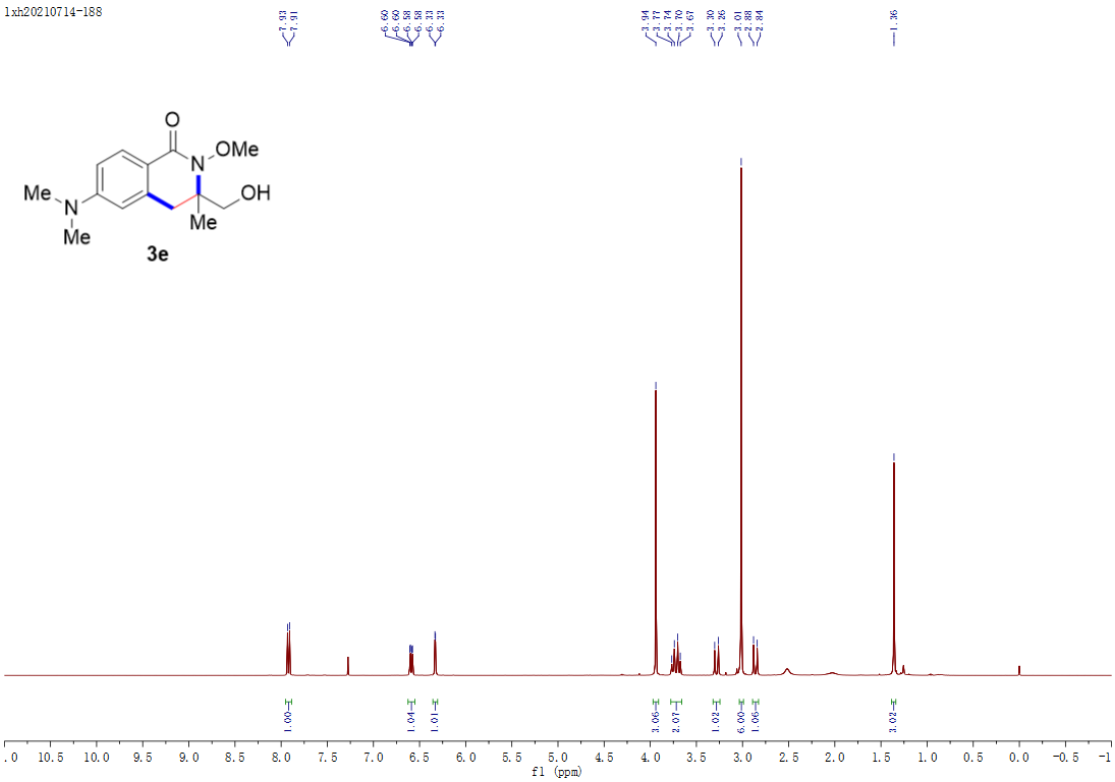
^{13}C NMR spectra of 3c ($(CD_3)_2SO$)



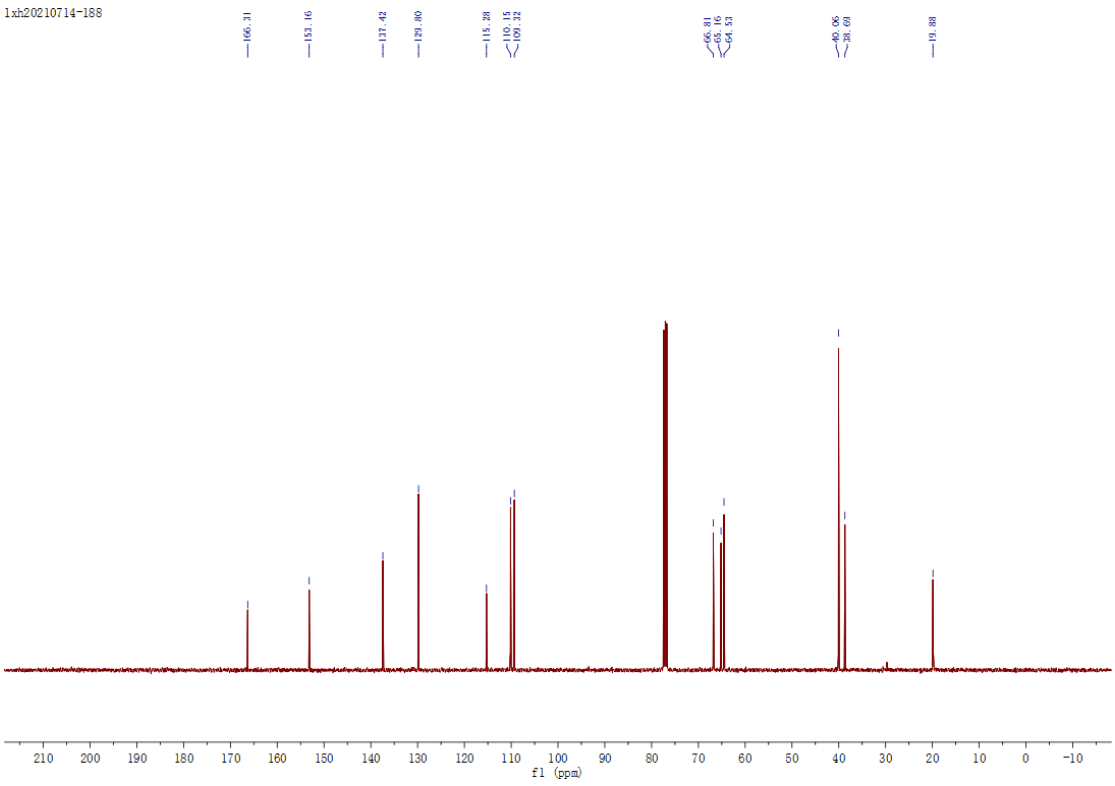
^{1}H NMR spectra of 3d ($CDCl_3$)



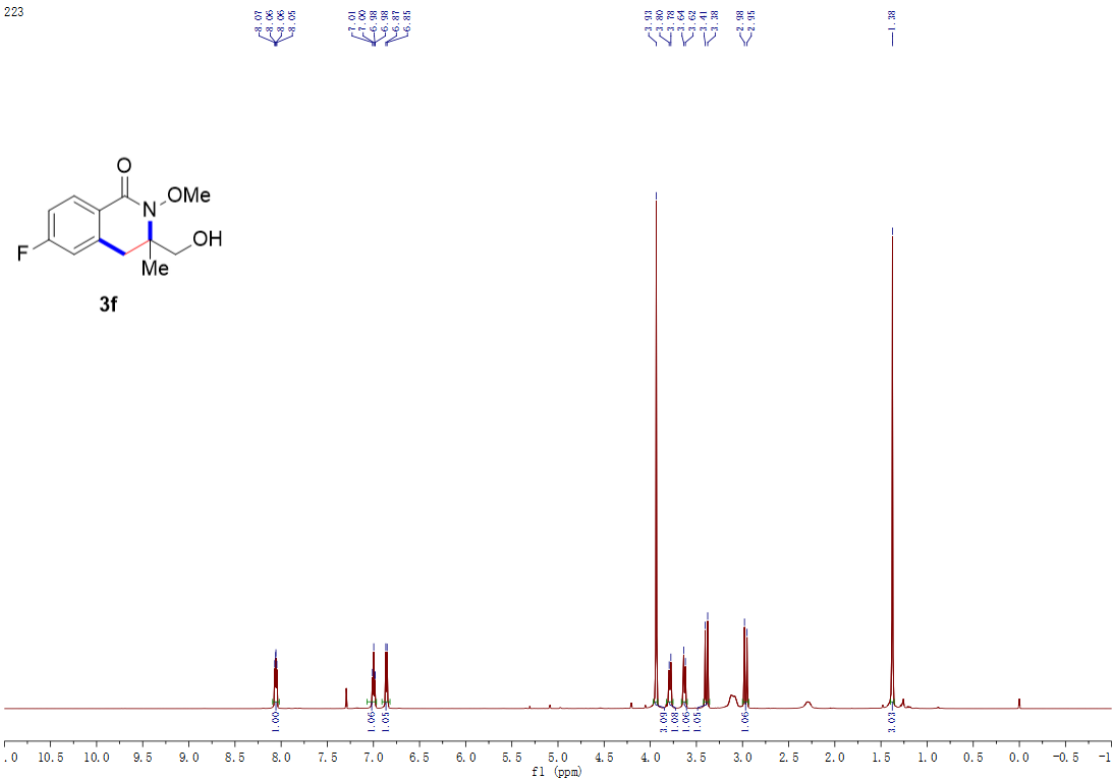
^{13}C NMR spectra of 3d ($CDCl_3$)



^{1}H NMR spectra of 3e ($CDCl_3$)

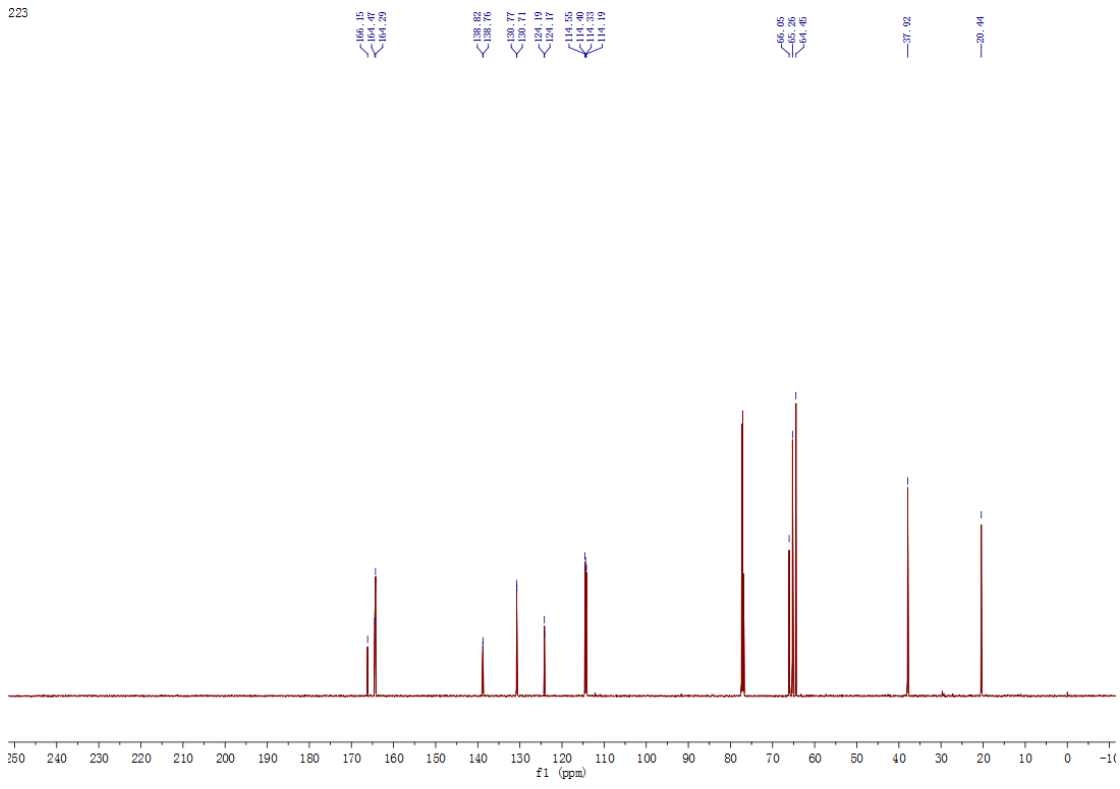


^{13}C NMR spectra of 3e ($CDCl_3$)

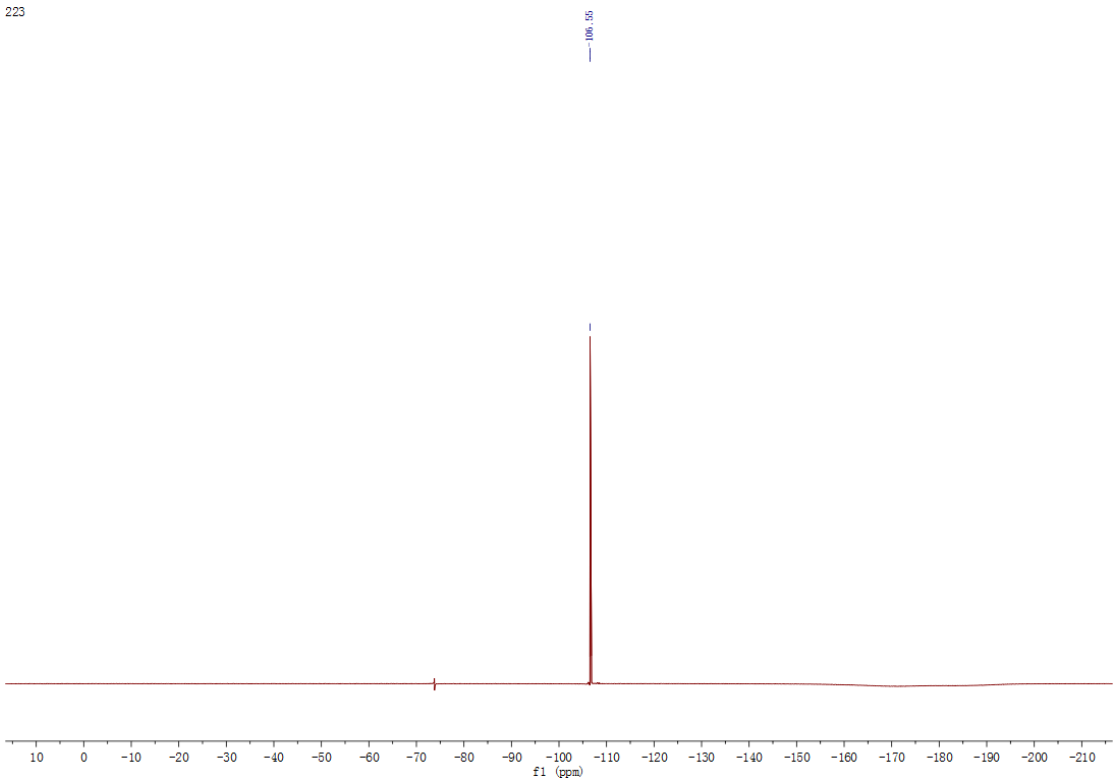


3f

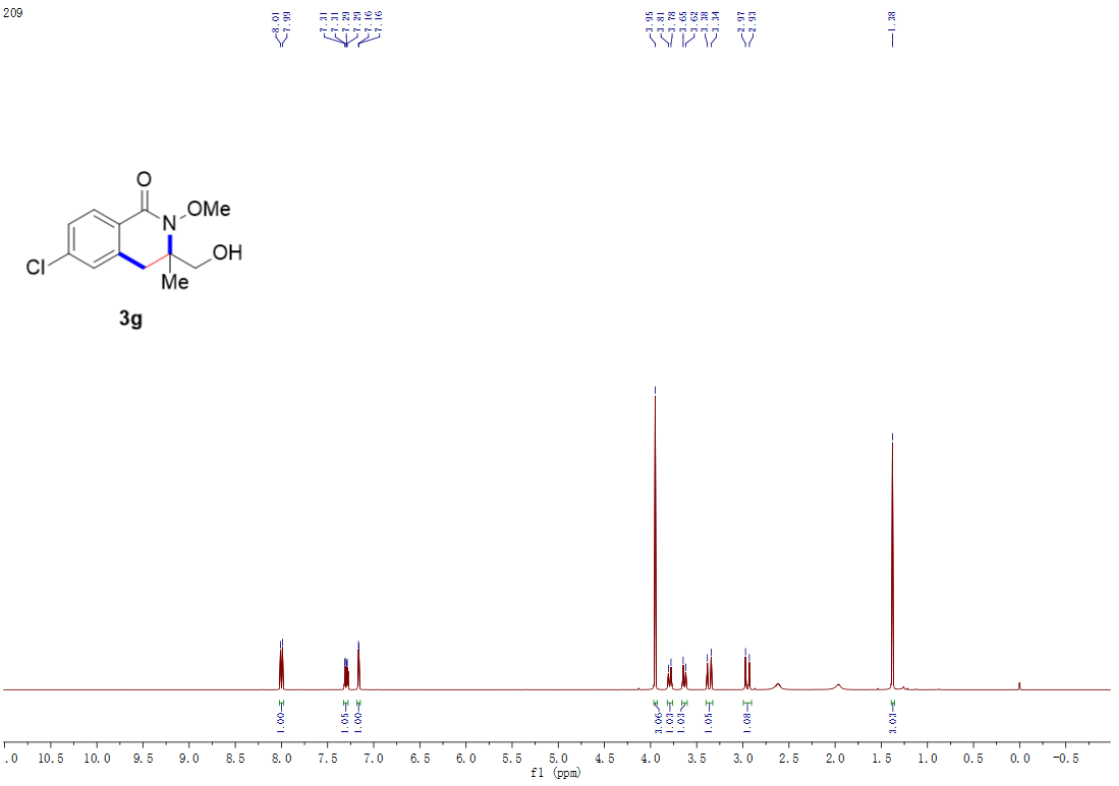
^{1}H NMR spectra of 3f ($CDCl_3$)



^{13}C NMR spectra of 3f ($CDCl_3$)

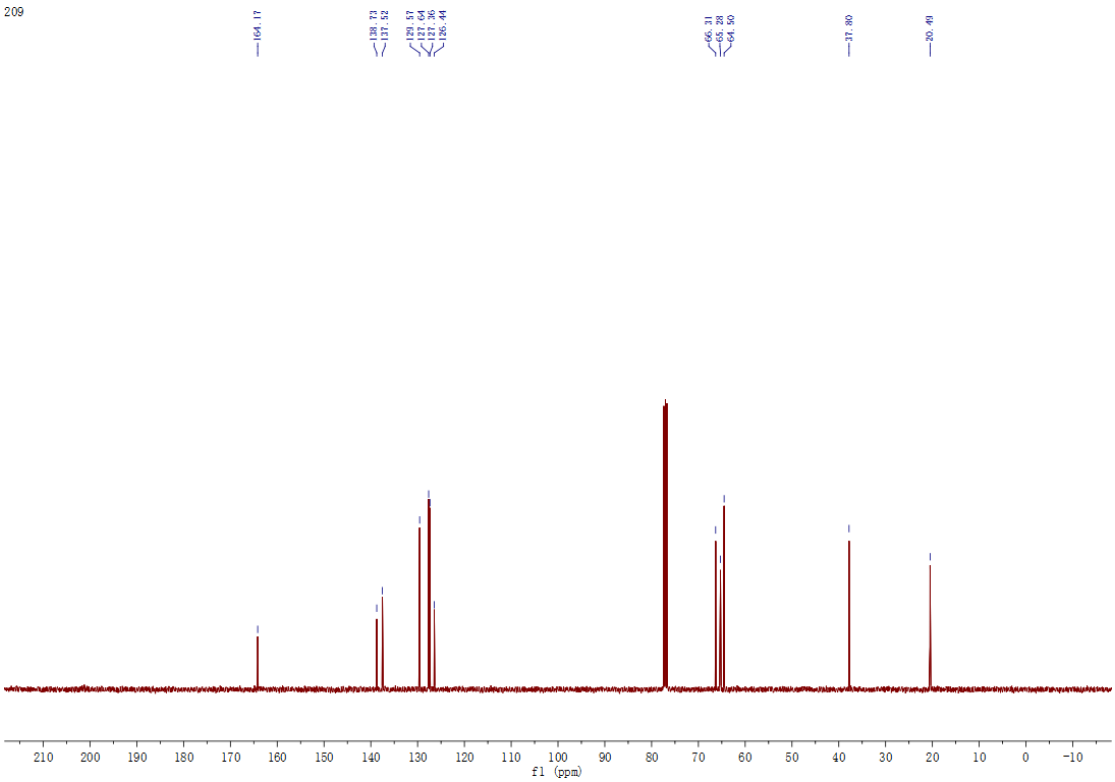


^{19}F NMR spectra of 3f ($CDCl_3$)

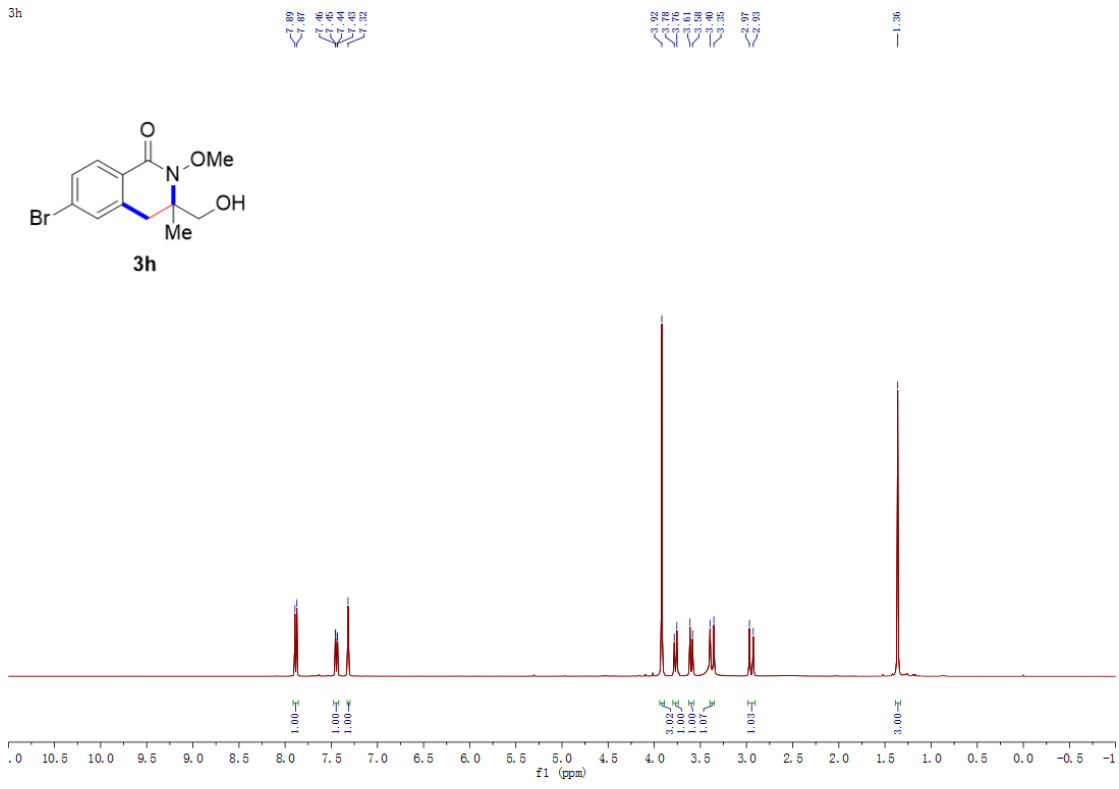


3g

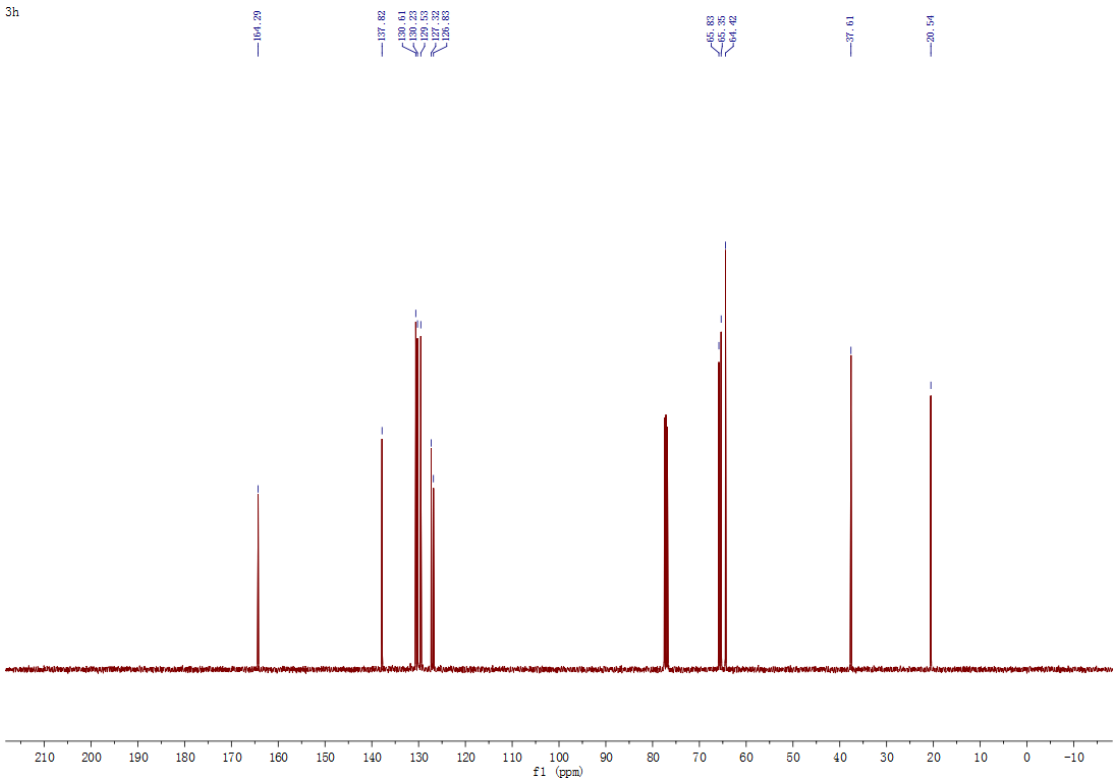
^{1}H NMR spectra of 3g ($CDCl_3$)



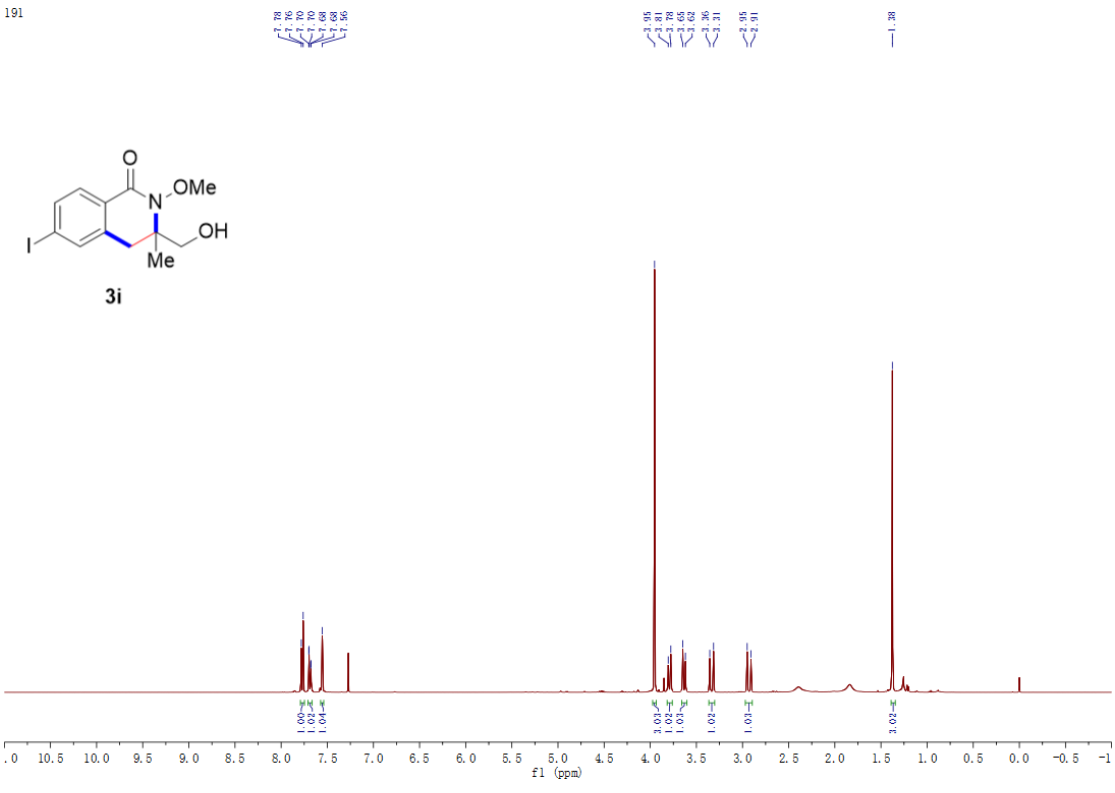
^{13}C NMR spectra of 3g ($CDCl_3$)



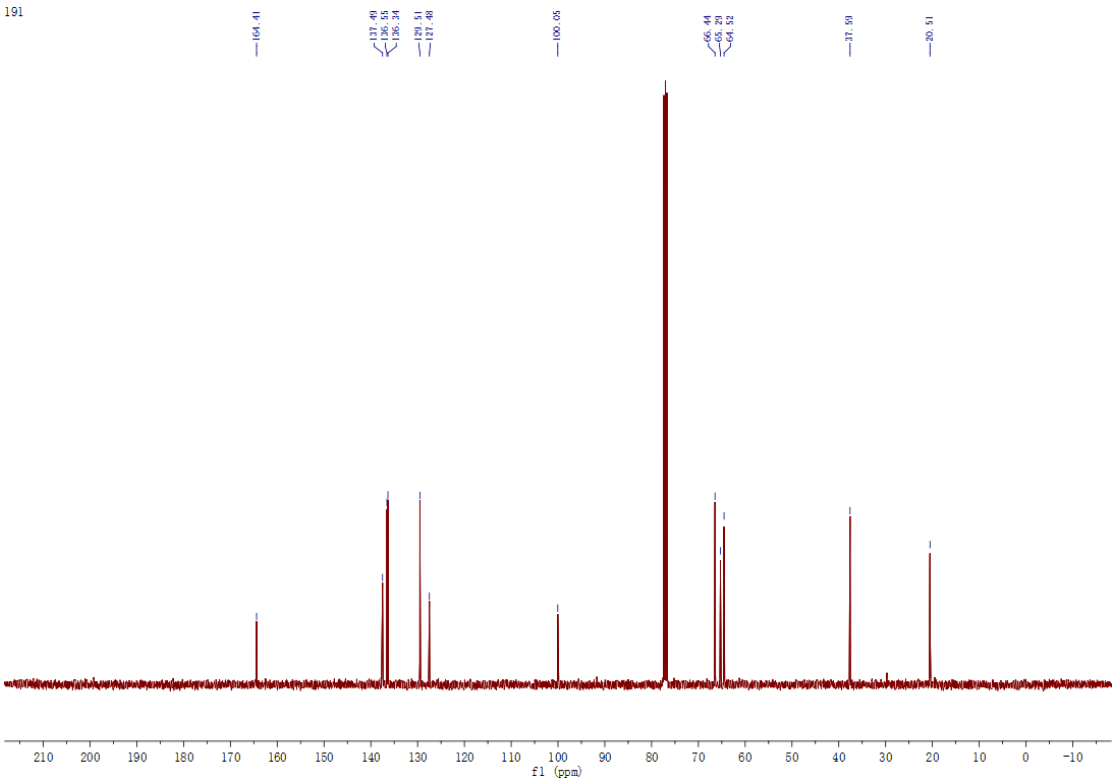
^{1}H NMR spectra of 3h ($CDCl_3$)



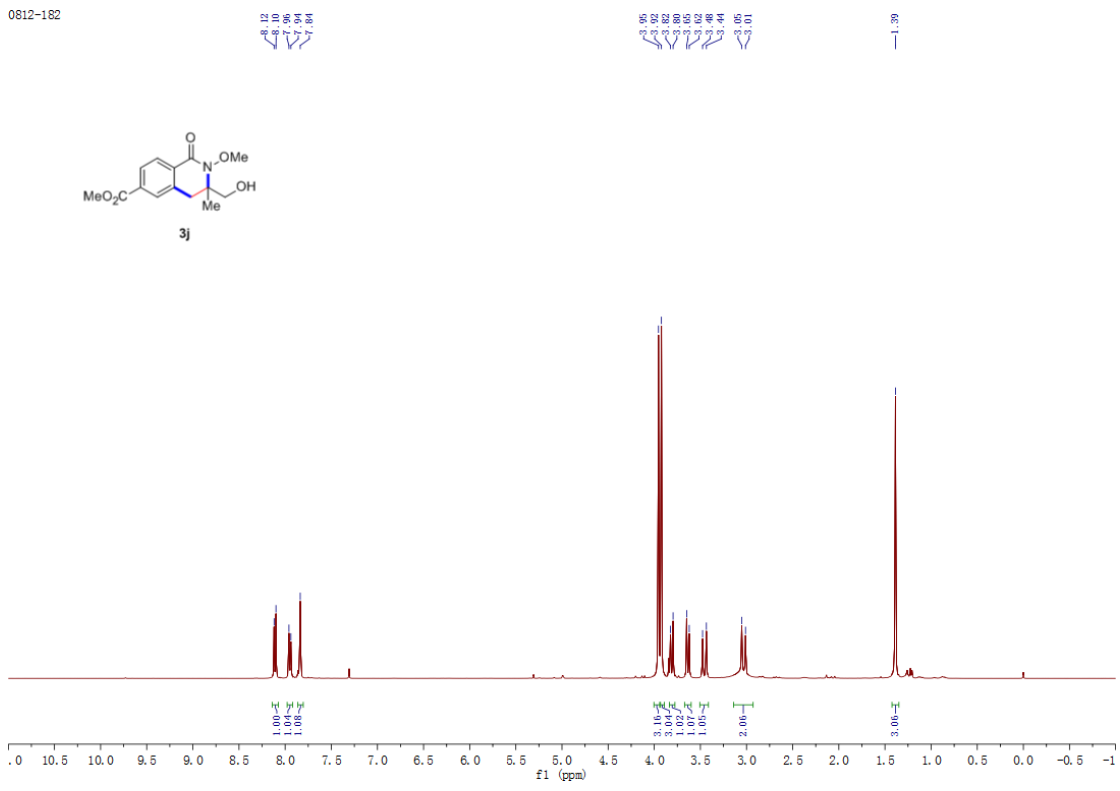
^{13}C NMR spectra of 3h ($CDCl_3$)



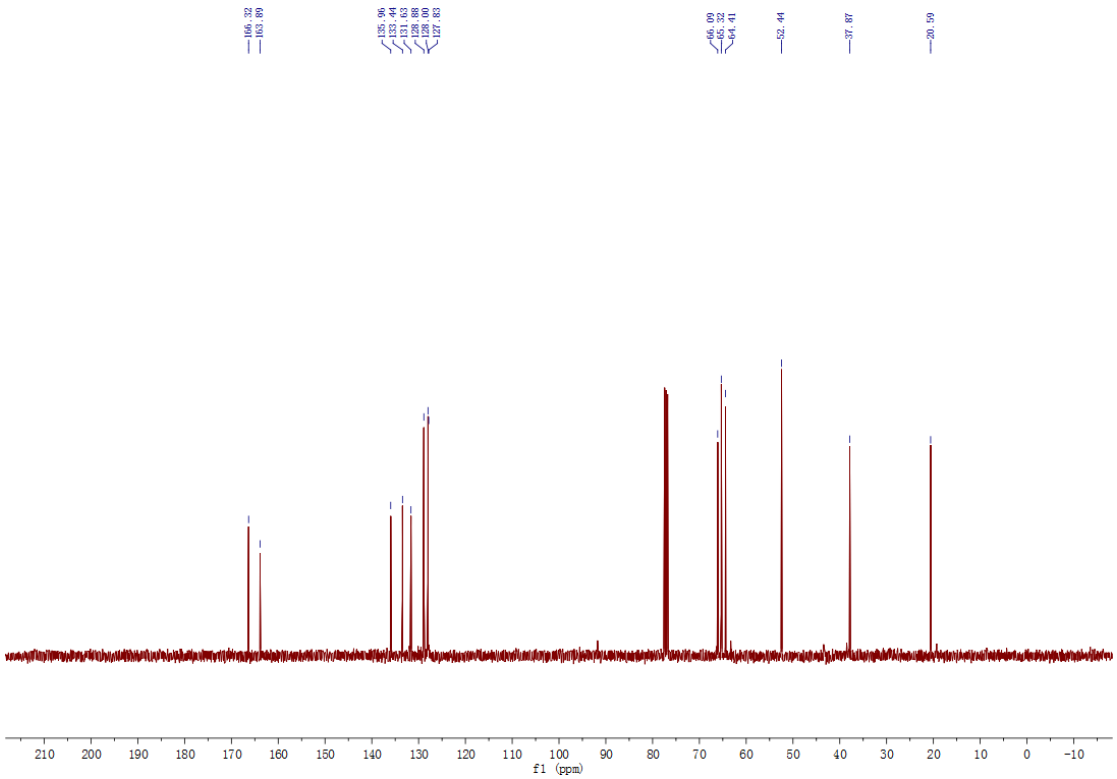
^{1}H NMR spectra of 3i ($CDCl_3$)



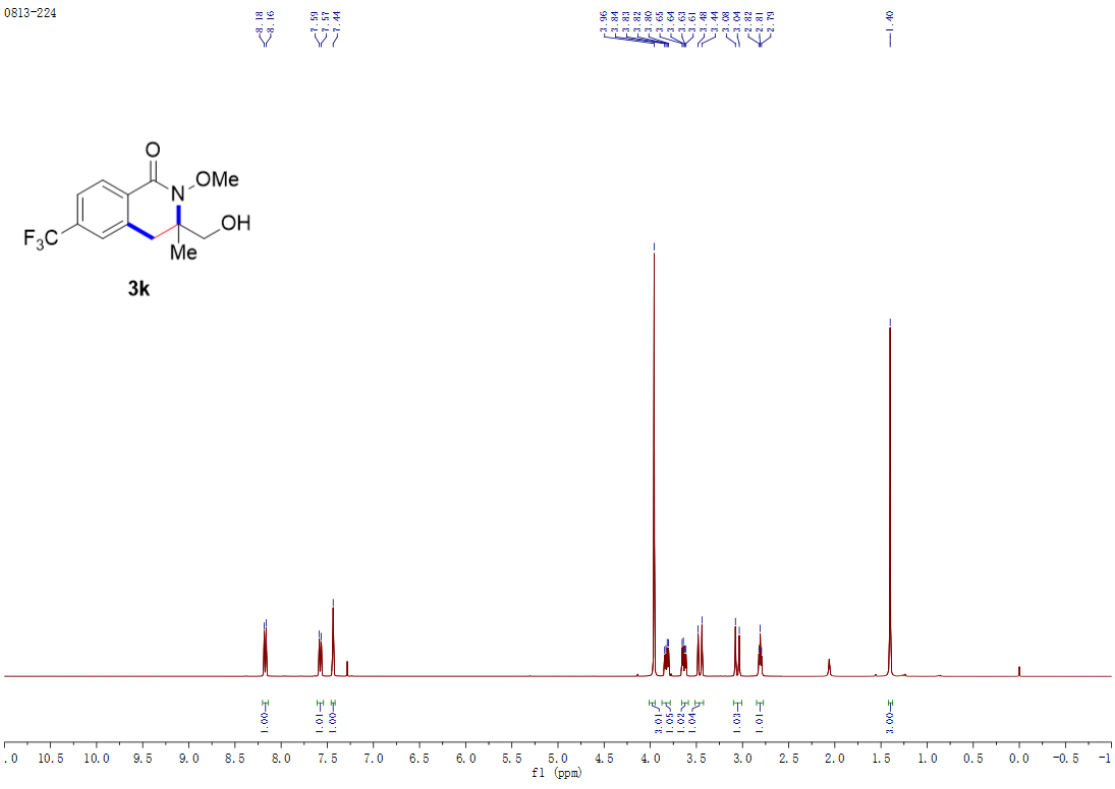
^{13}C NMR spectra of 3i ($CDCl_3$)



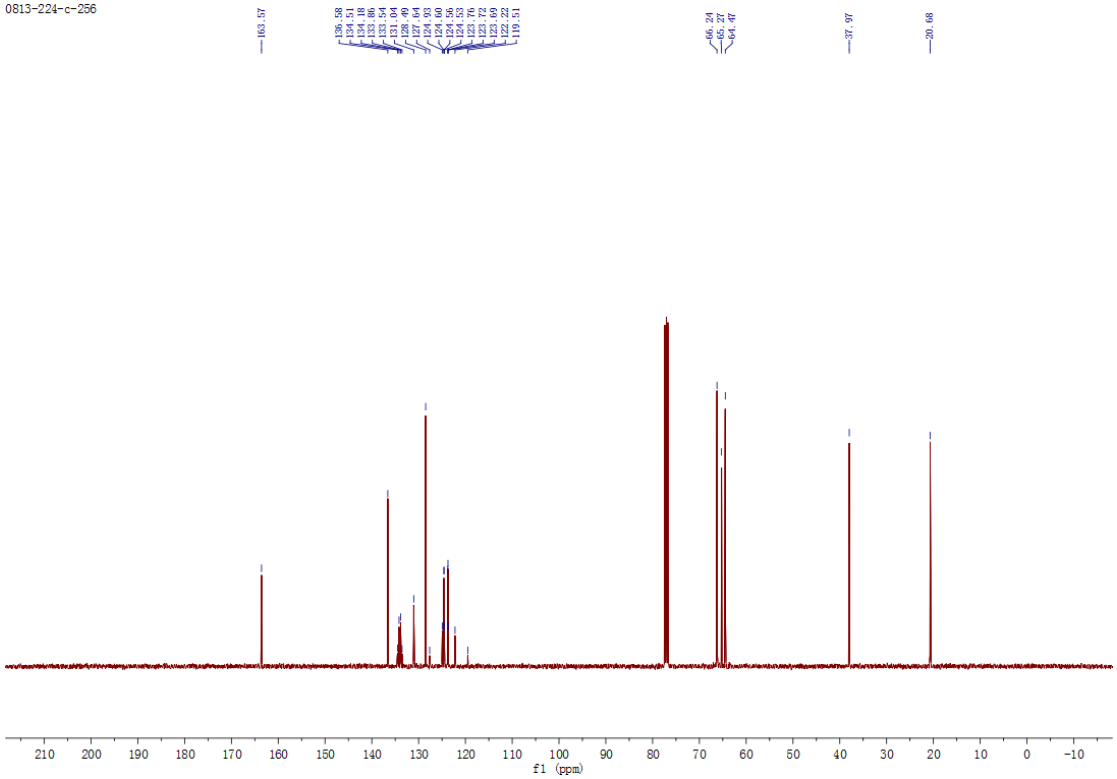
^{1}H NMR spectra of 3j ($CDCl_3$)



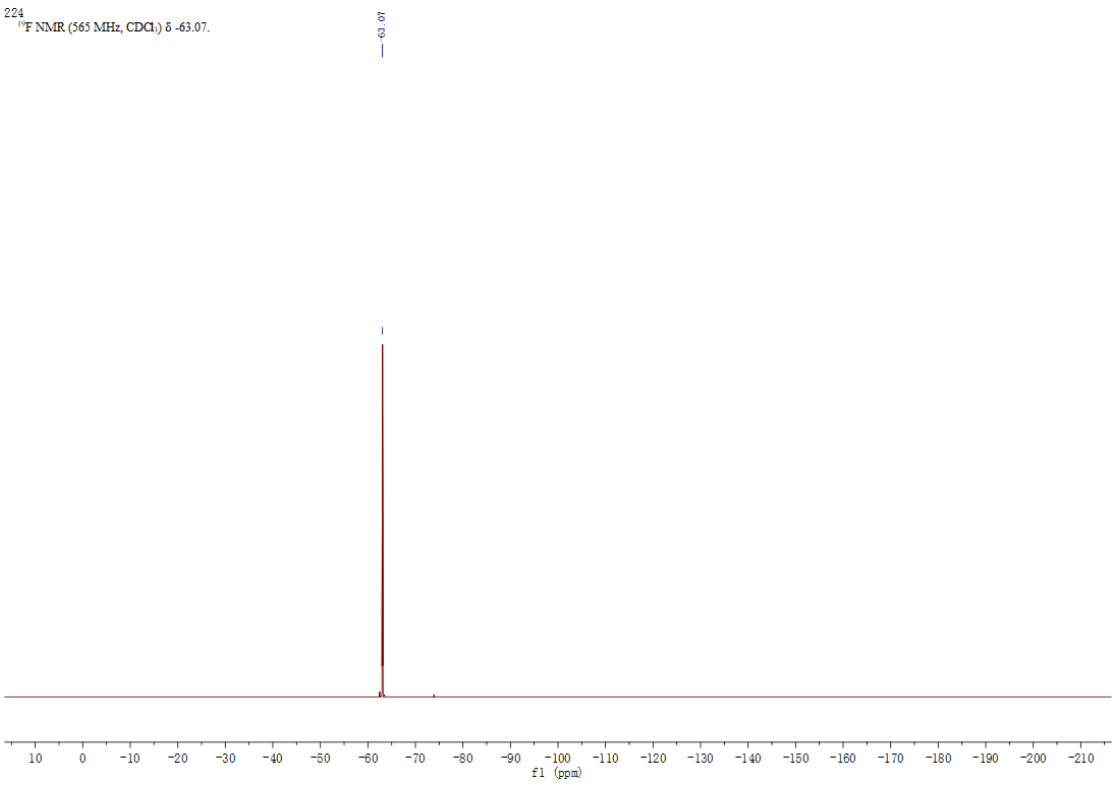
^{13}C NMR spectra of 3j ($CDCl_3$)



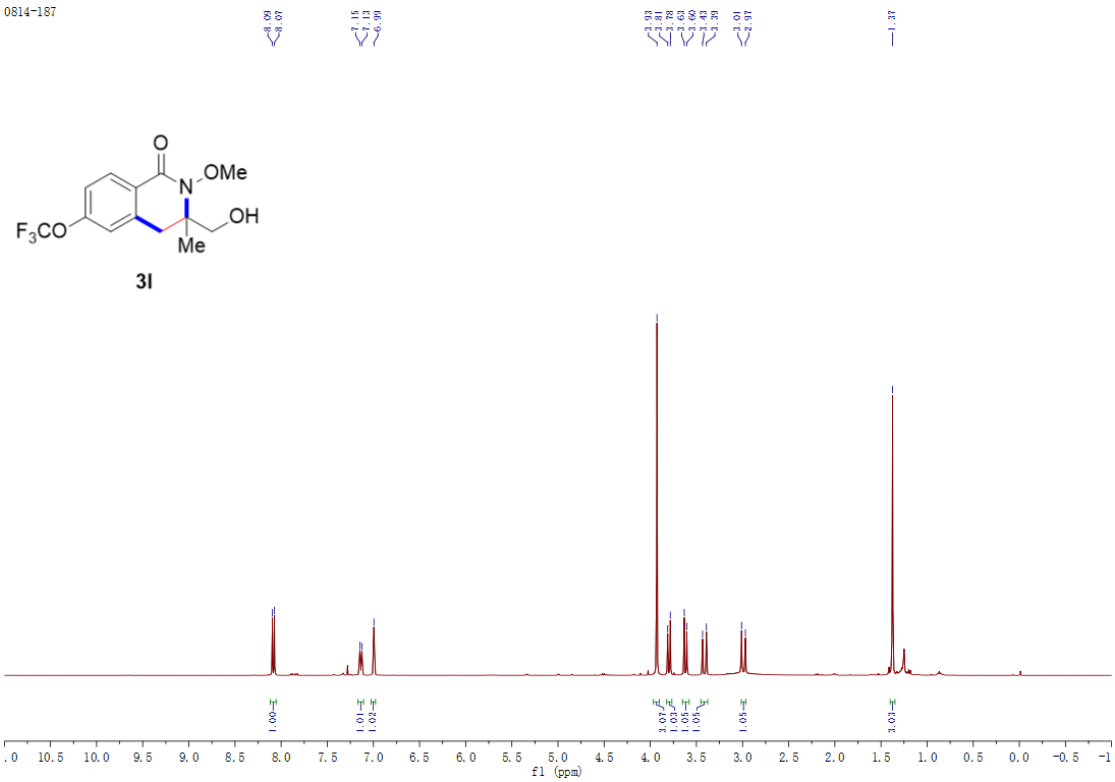
^{1}H NMR spectra of 3k ($CDCl_3$)



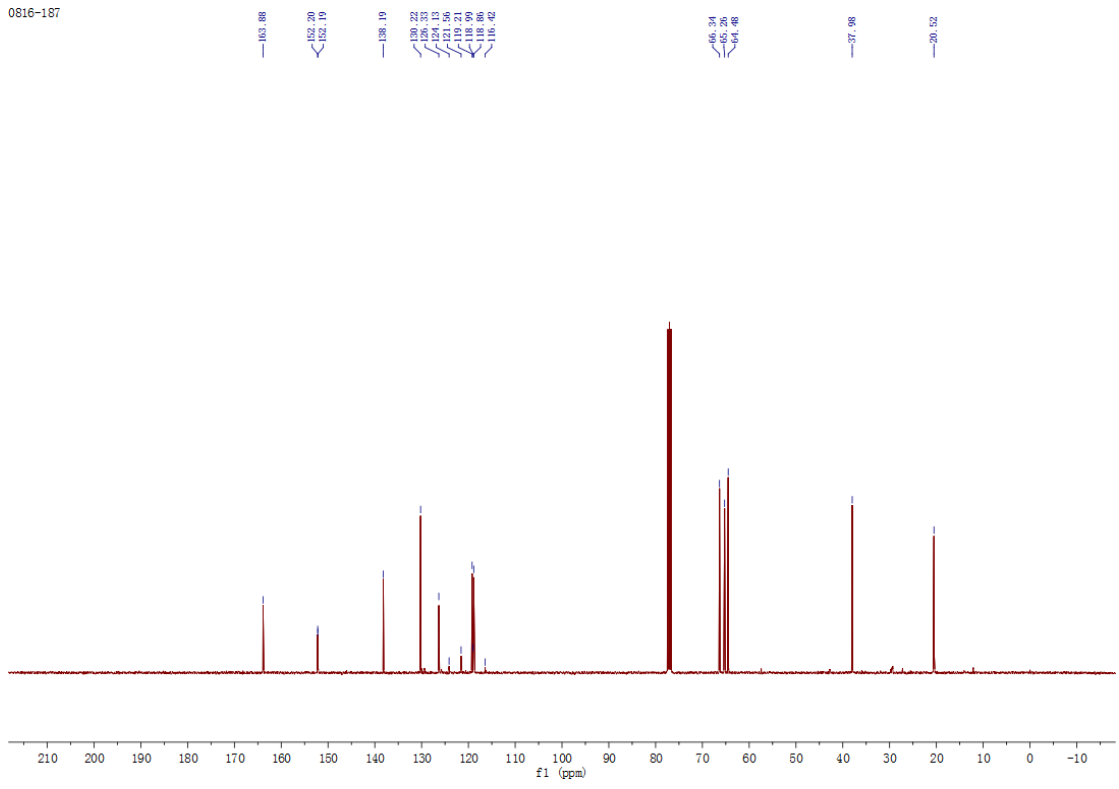
^{13}C NMR spectra of 3k ($CDCl_3$)



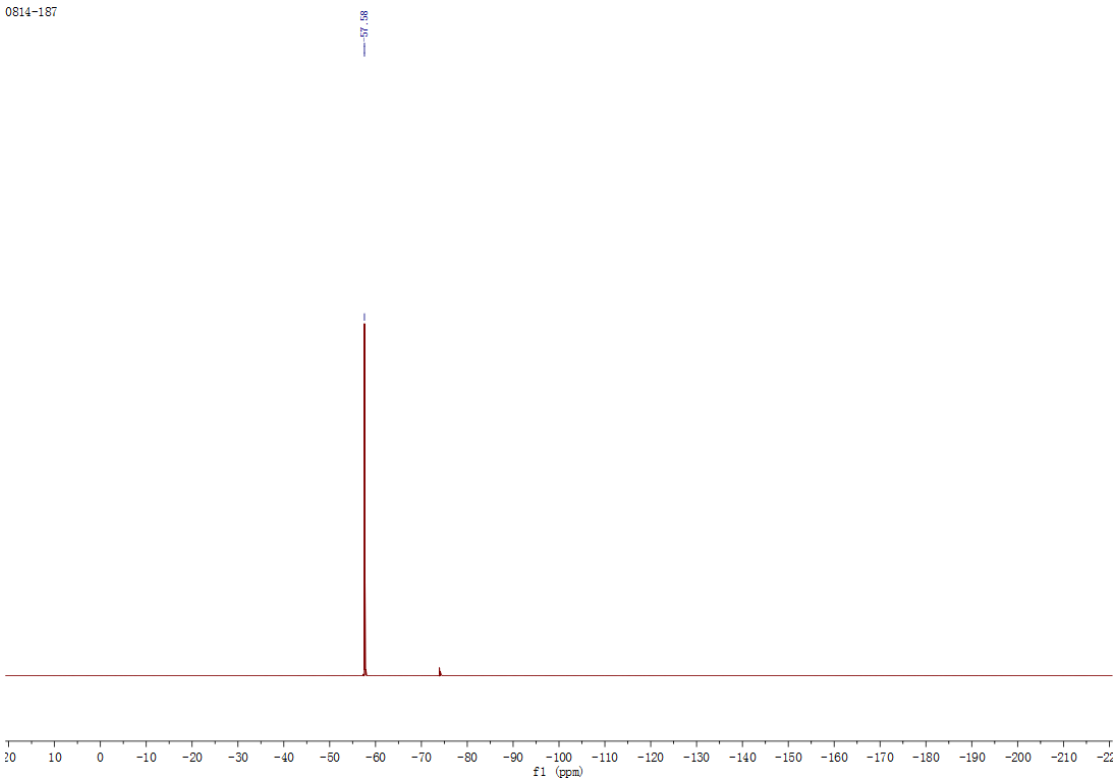
^{19}F NMR spectra of 3k ($CDCl_3$)



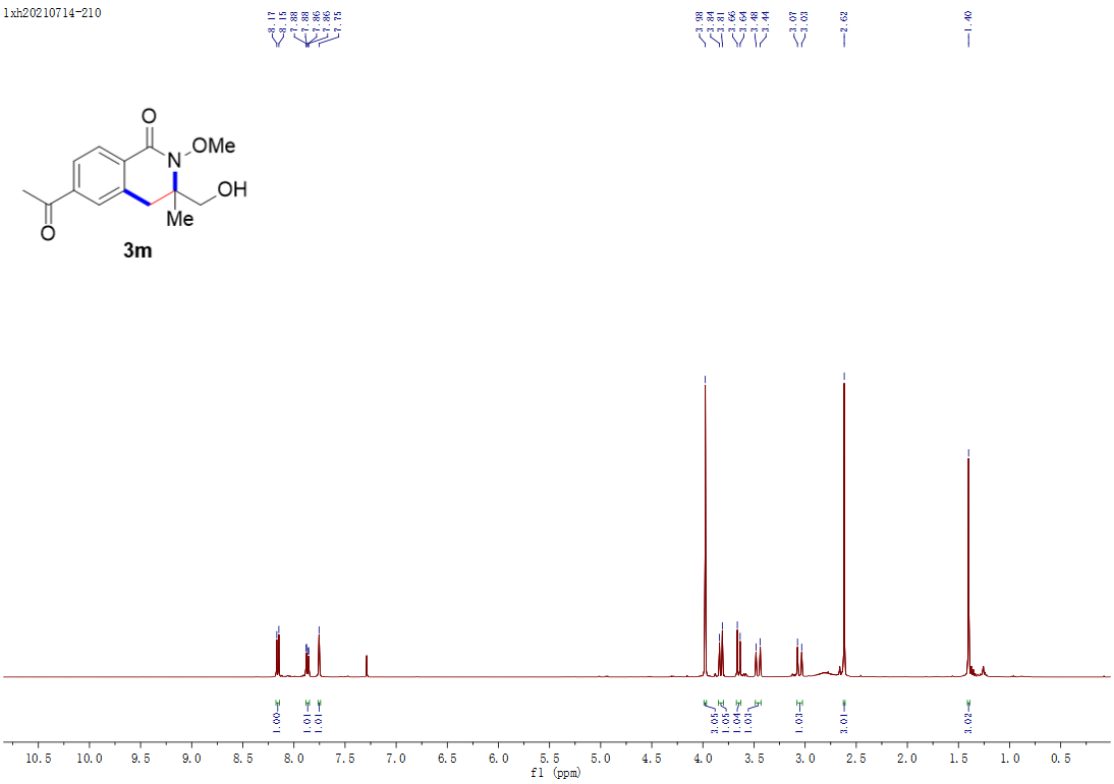
^{1}H NMR spectra of 3l ($CDCl_3$)



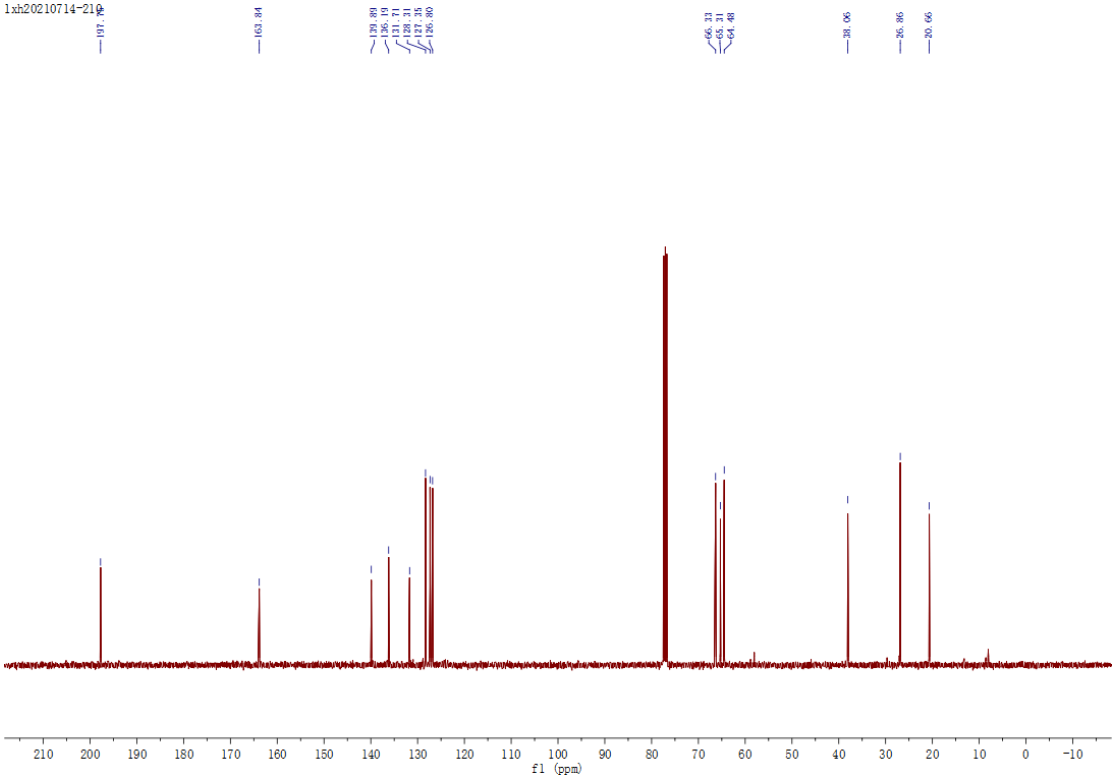
^{13}C NMR spectra of 3l ($CDCl_3$)



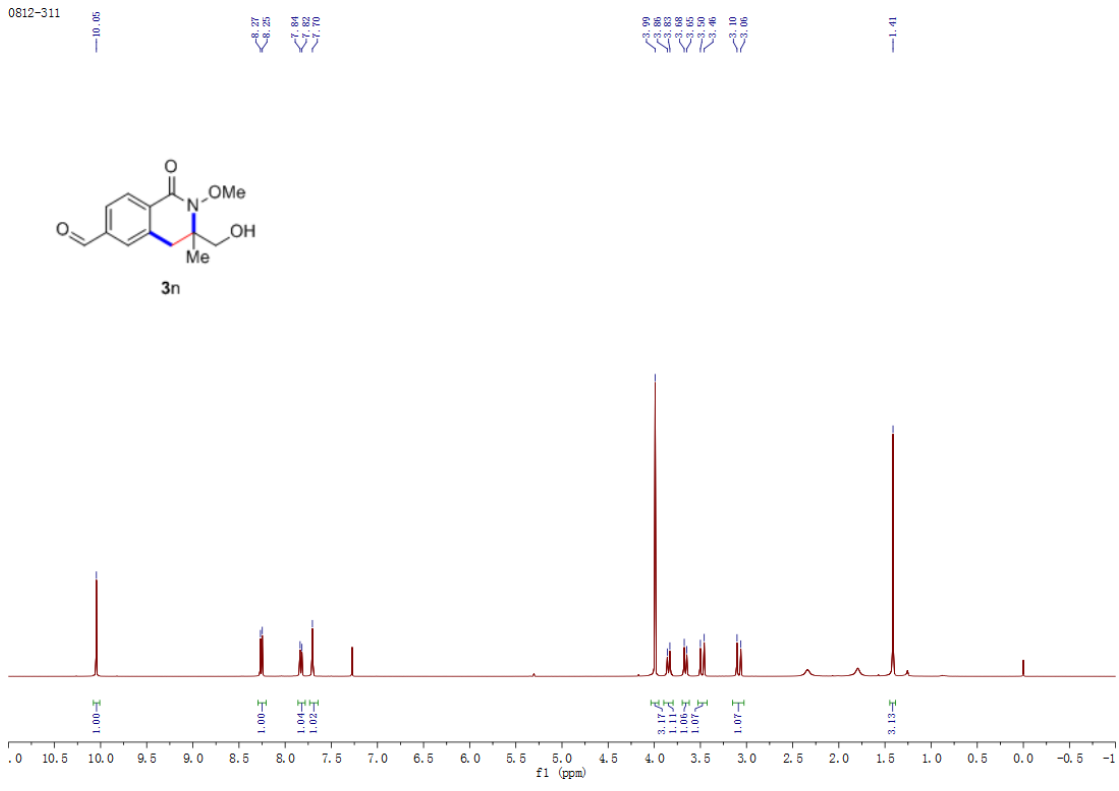
^{19}F NMR spectra of 3l ($CDCl_3$)



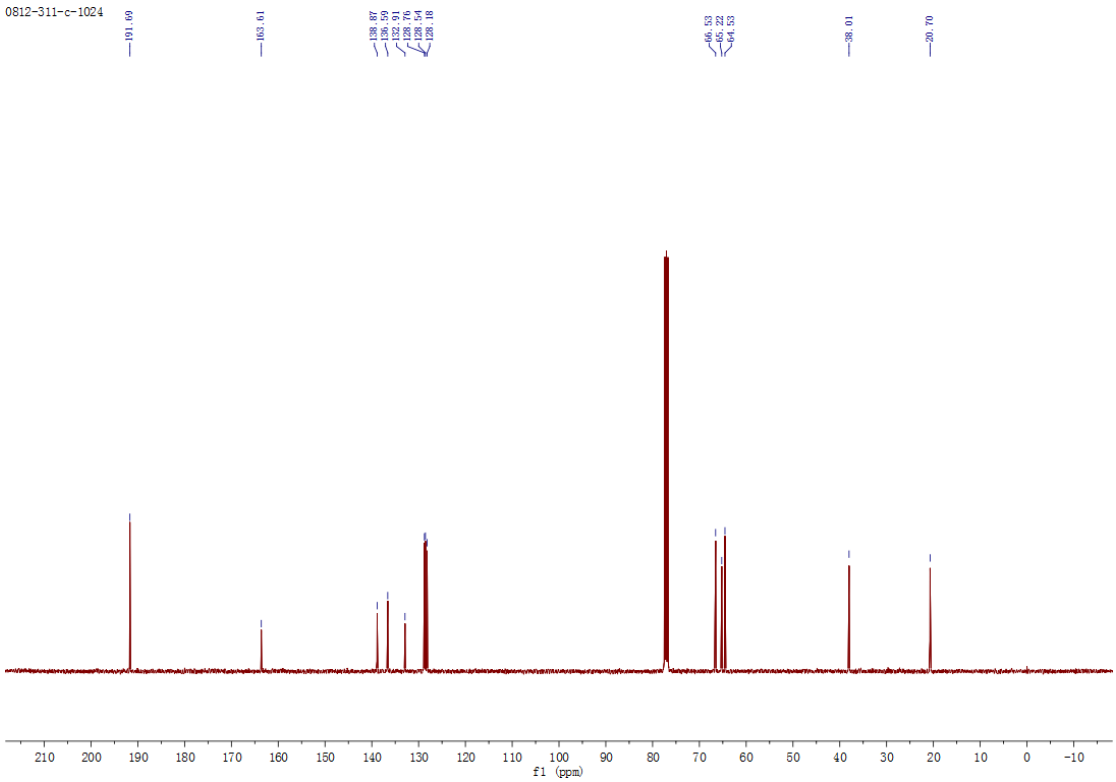
^{1}H NMR spectra of 3m ($CDCl_3$)



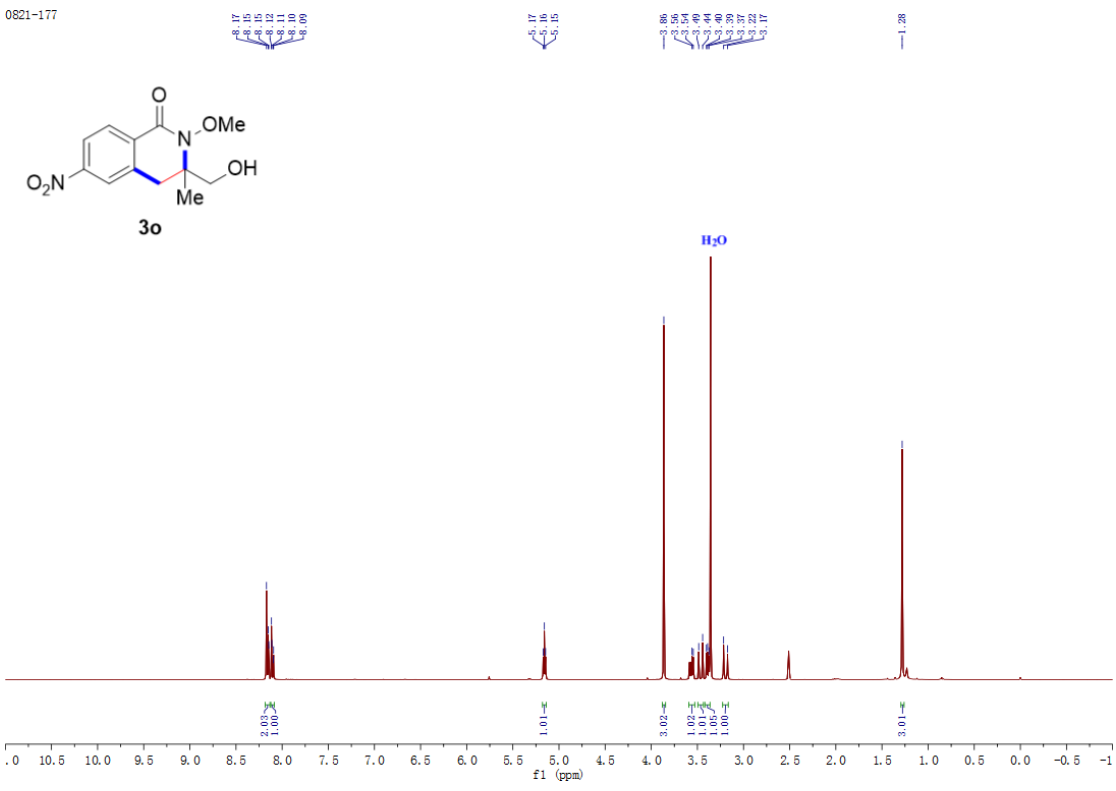
^{13}C NMR spectra of 3m ($CDCl_3$)



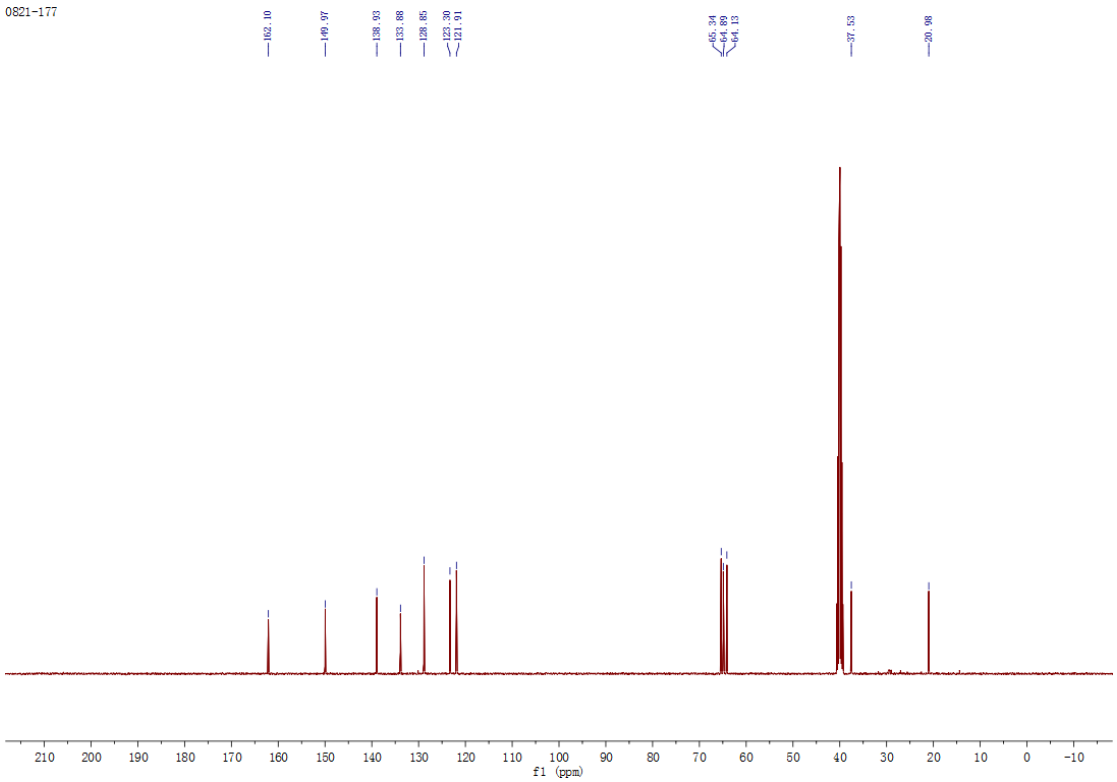
^{1}H NMR spectra of 3n ($CDCl_3$)



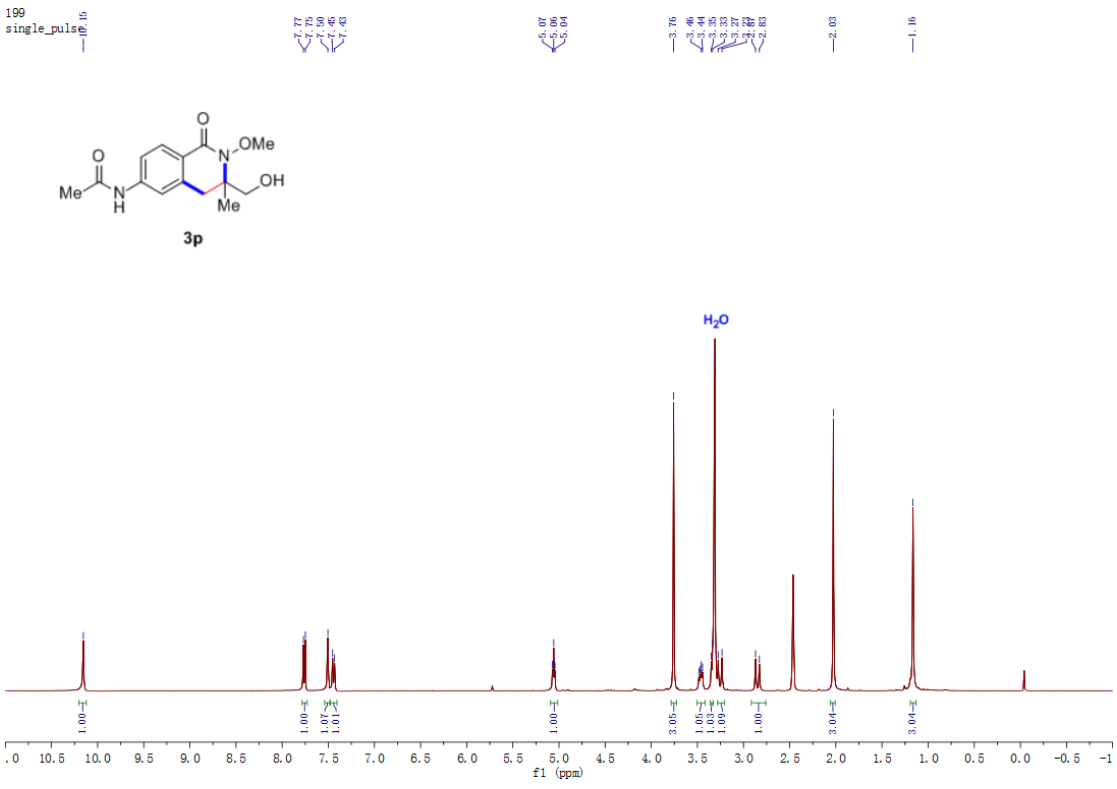
^{13}C NMR spectra of 3n ($CDCl_3$)



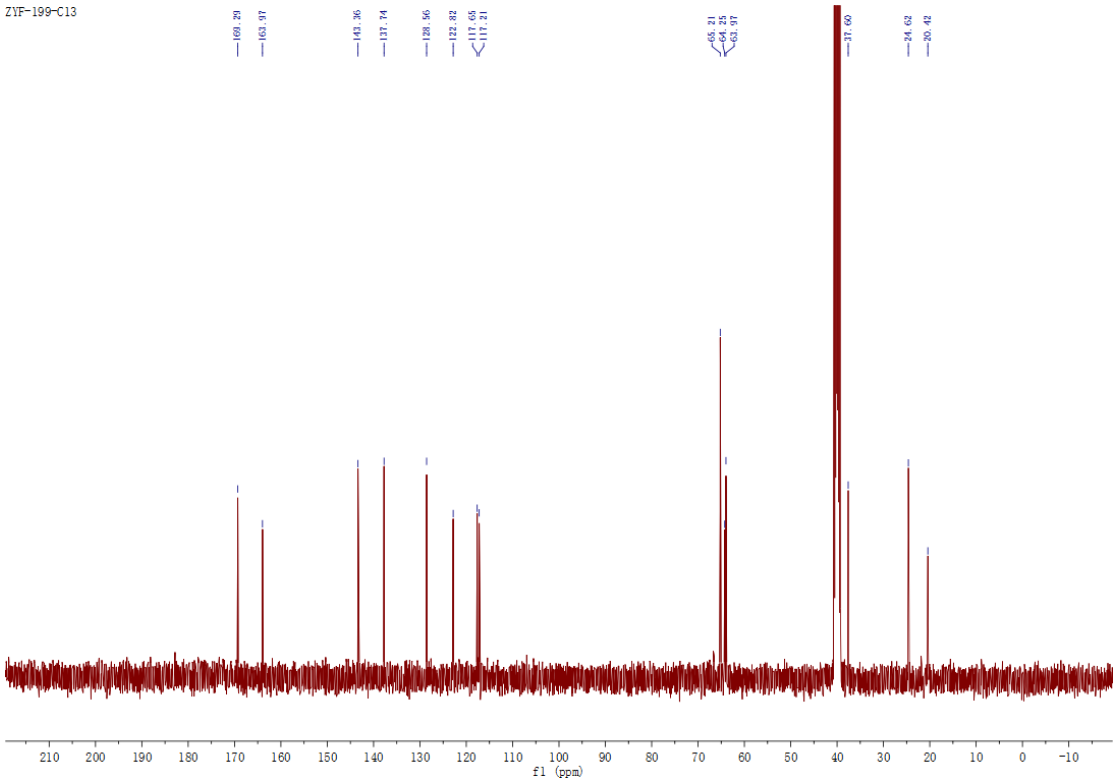
^{1}H NMR spectra of 3o ($(CD_3)_2SO$)



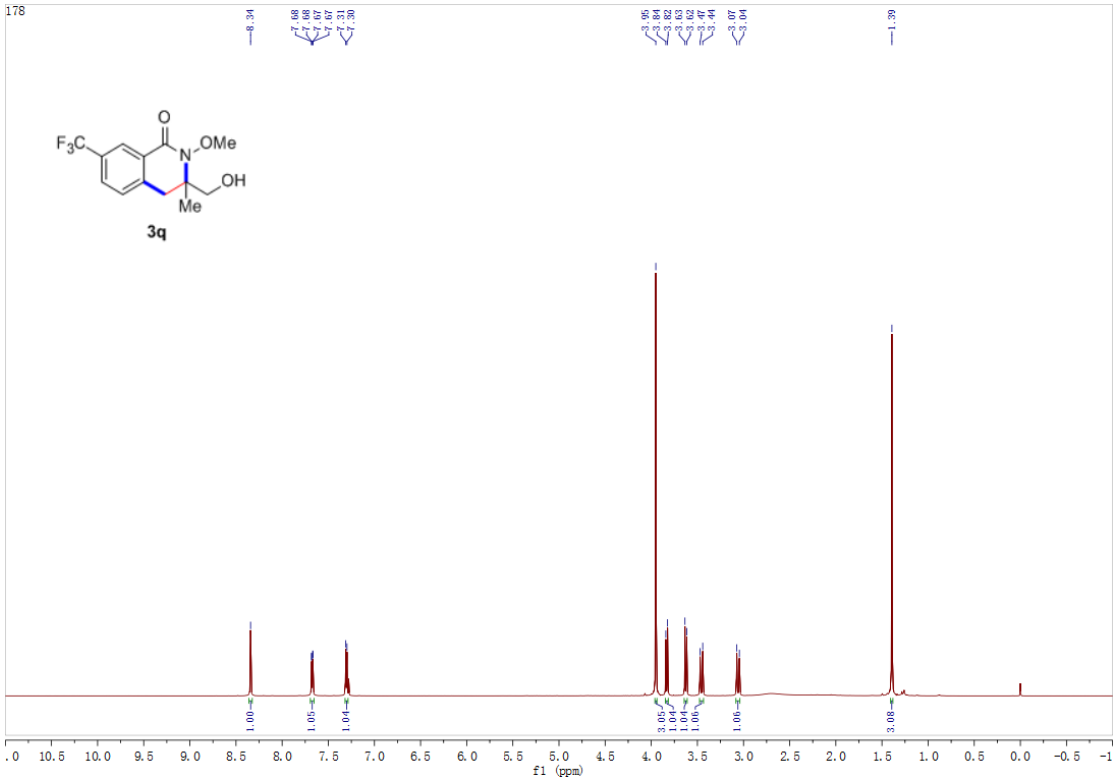
^{13}C NMR spectra of 3o ($(CD_3)_2SO$)



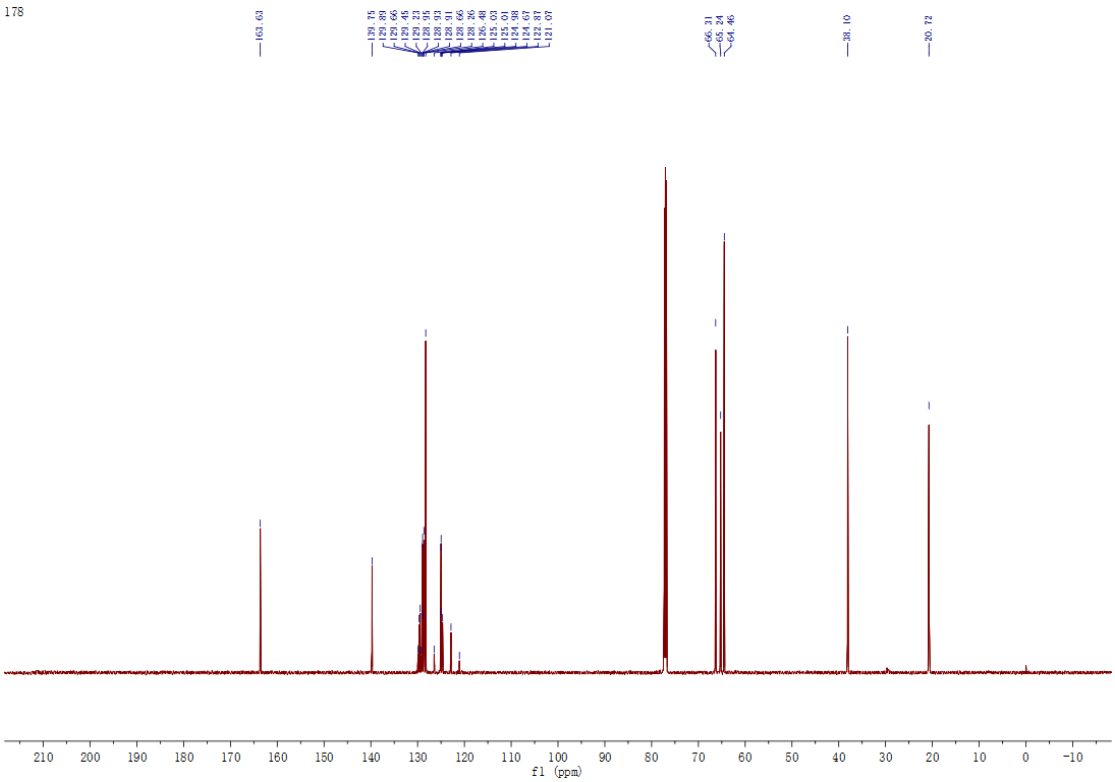
^{1}H NMR spectra of 3p ($(CD_3)_2SO$)



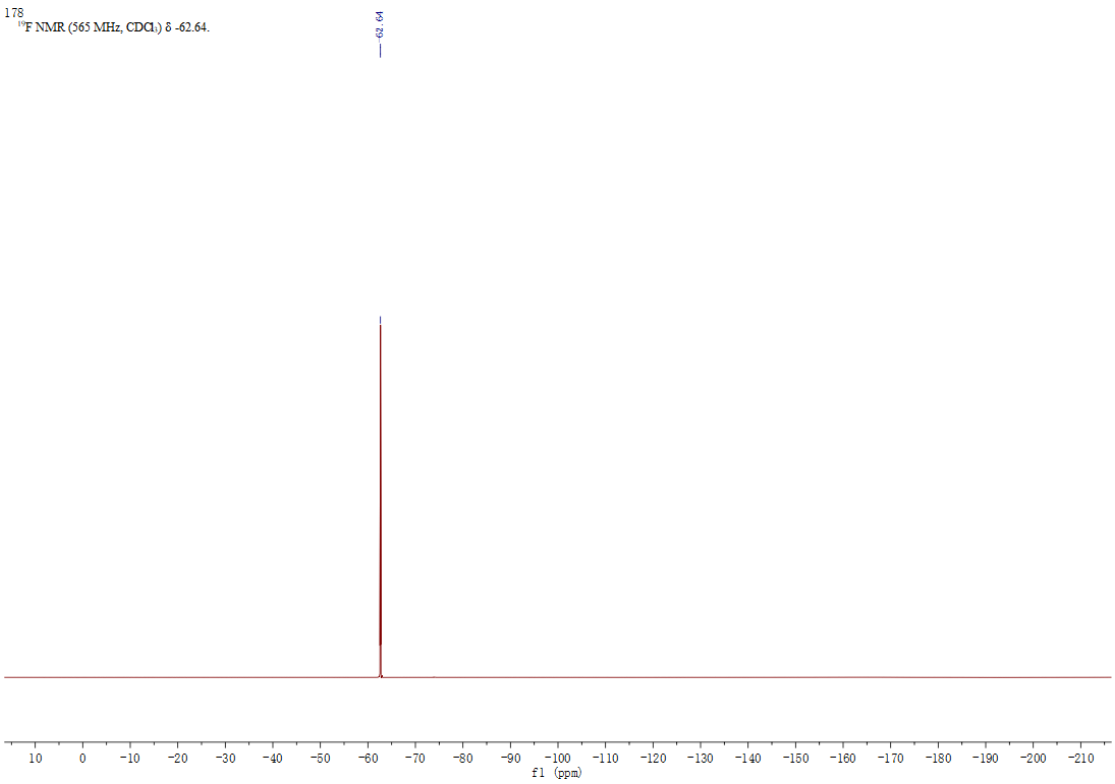
^{13}C NMR spectra of 3p ($(CD_3)_2SO$)



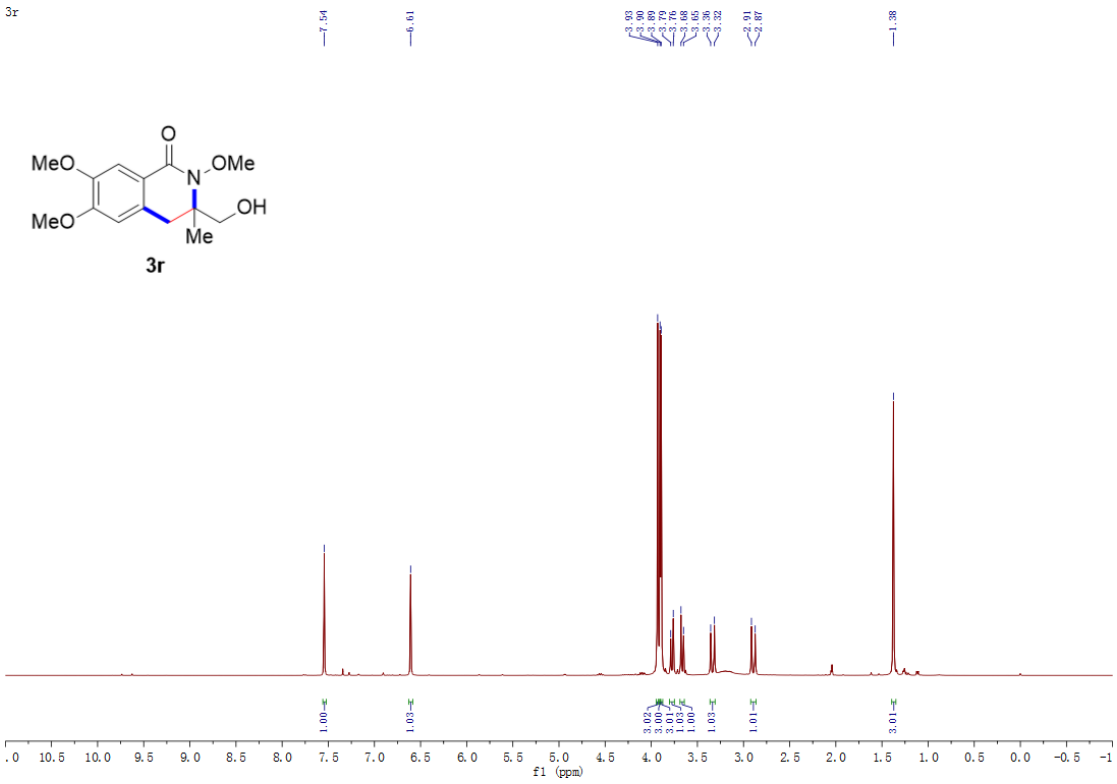
^{1}H NMR spectra of 3q ($CDCl_3$)



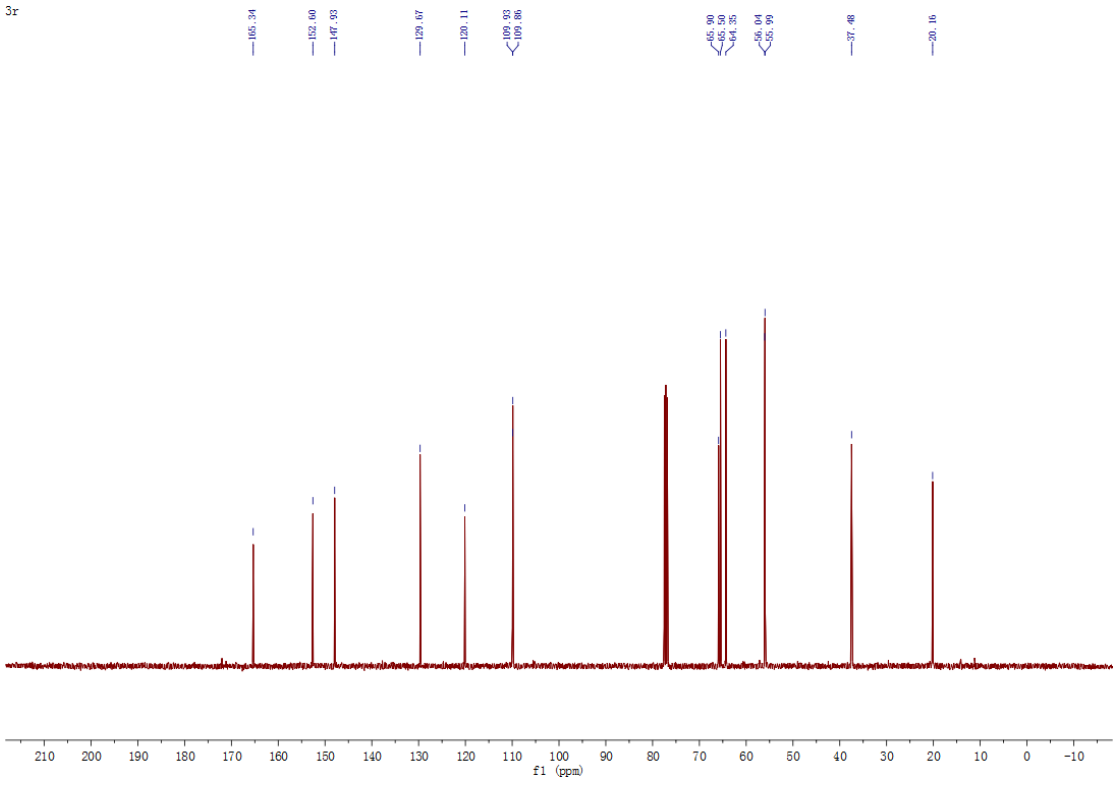
^{13}C NMR spectra of 3q ($CDCl_3$)



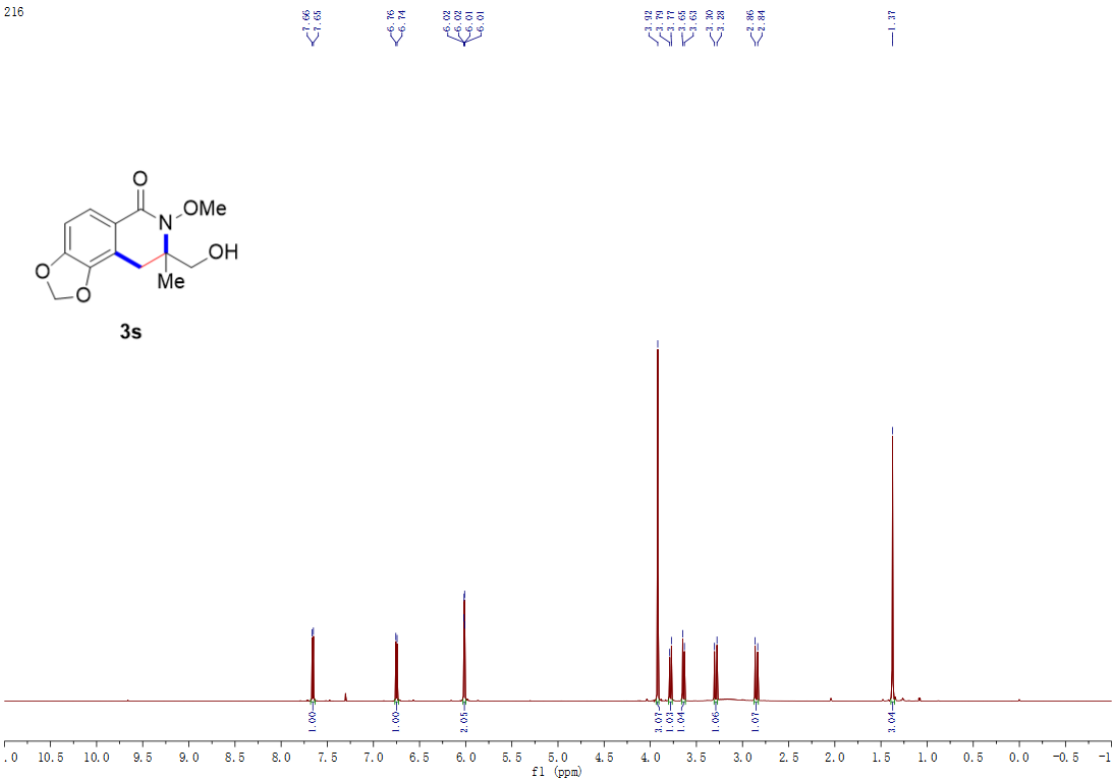
^{19}F NMR spectra of 3q ($CDCl_3$)



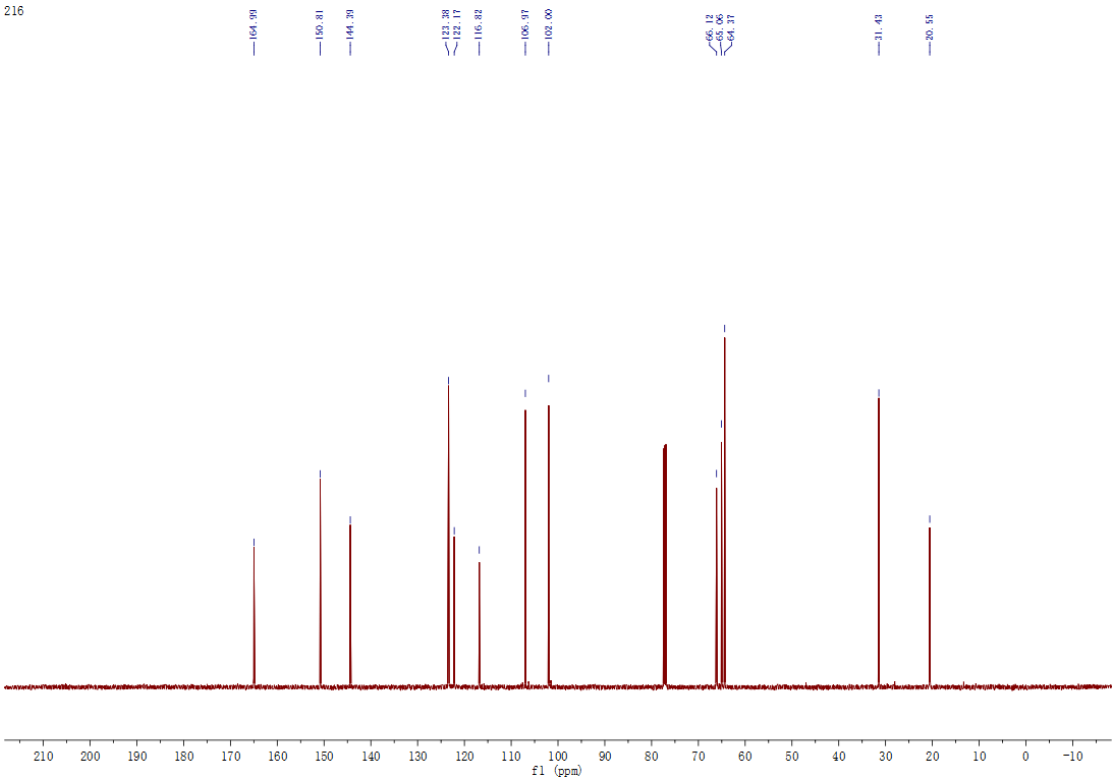
^{1}H NMR spectra of 3r ($CDCl_3$)



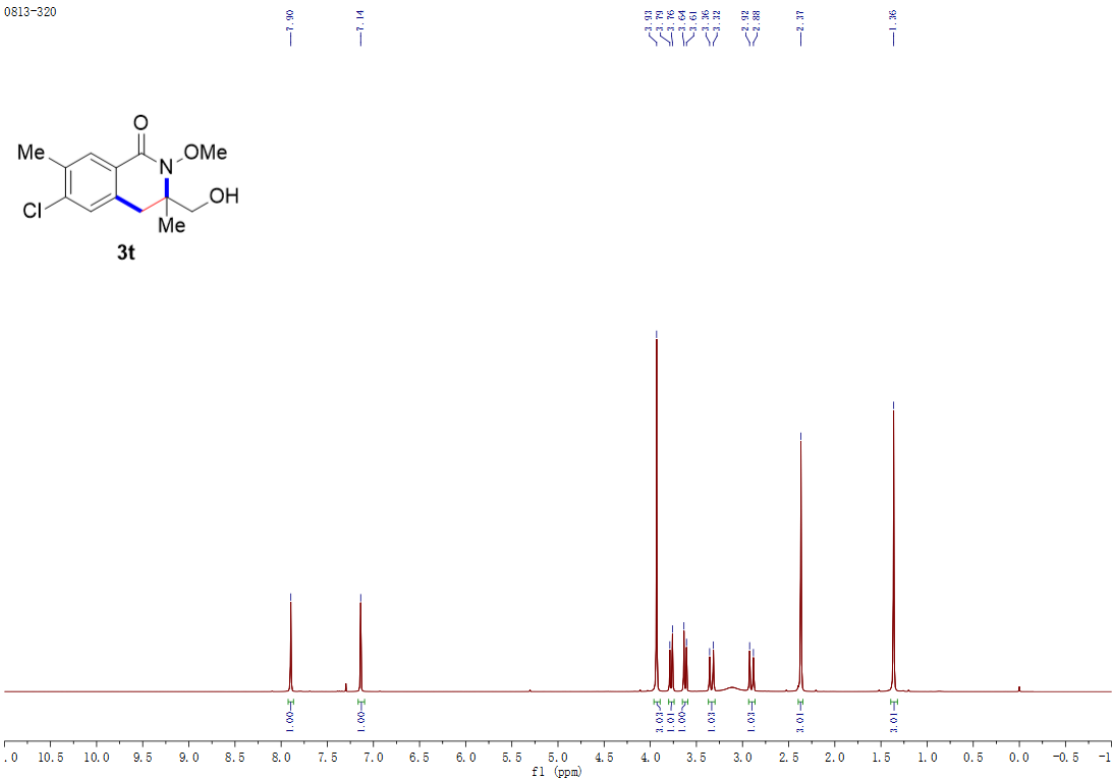
^{13}C NMR spectra of 3r ($CDCl_3$)



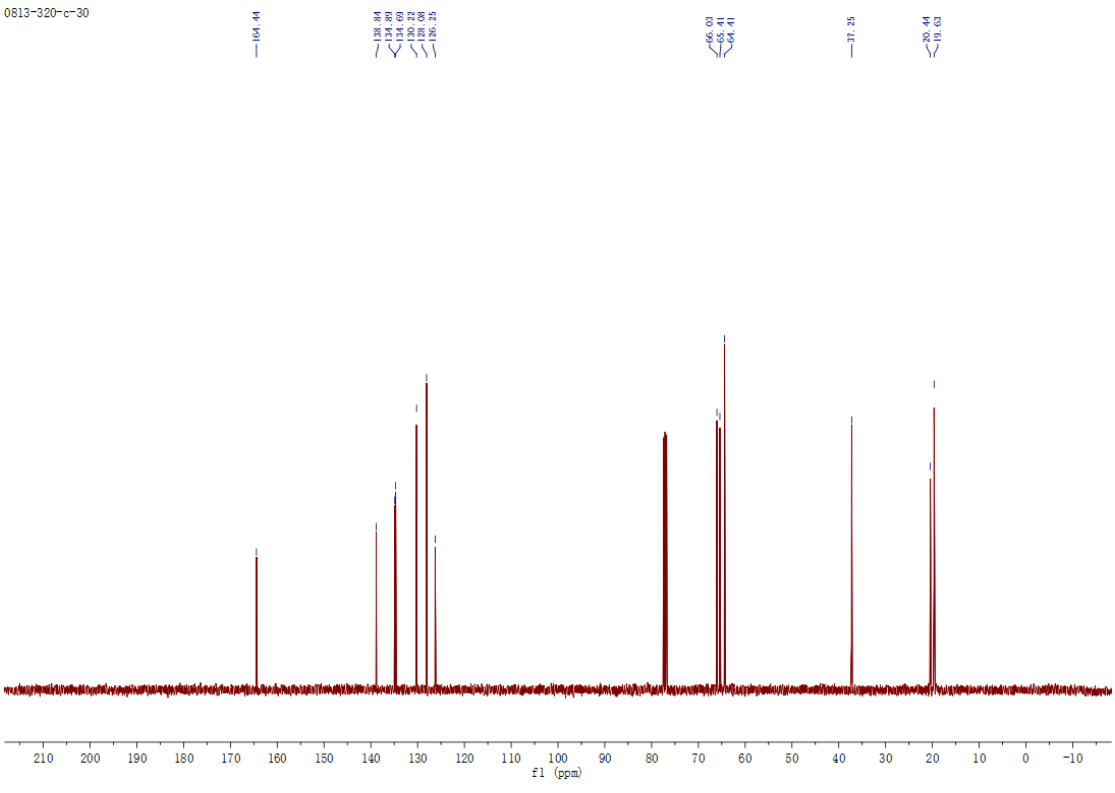
^{1}H NMR spectra of 3s ($CDCl_3$)



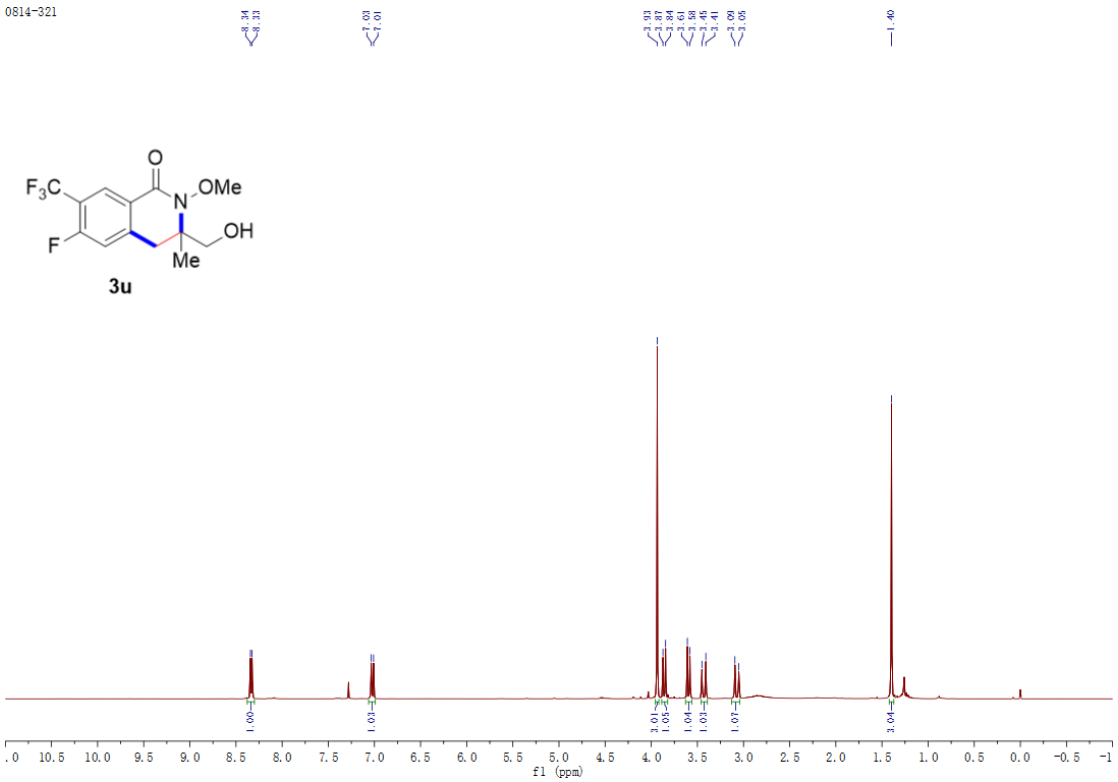
^{13}C NMR spectra of 3s ($CDCl_3$)



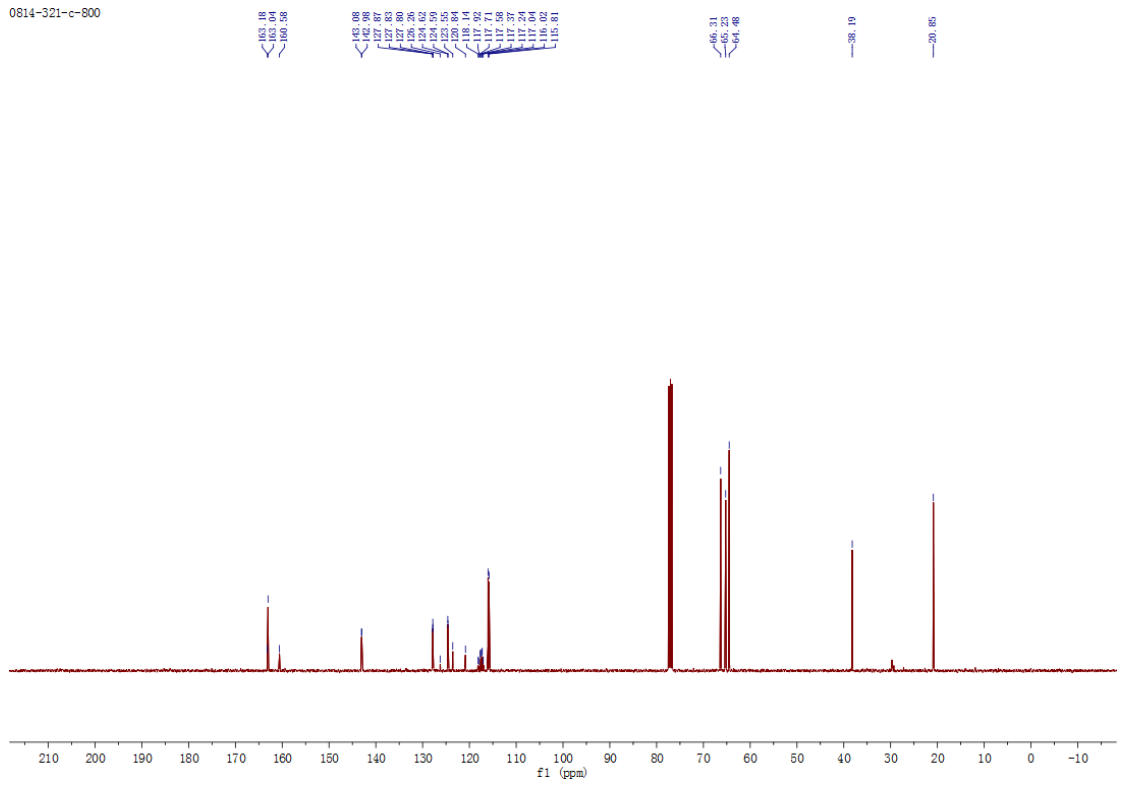
^{1}H NMR spectra of 3t ($CDCl_3$)



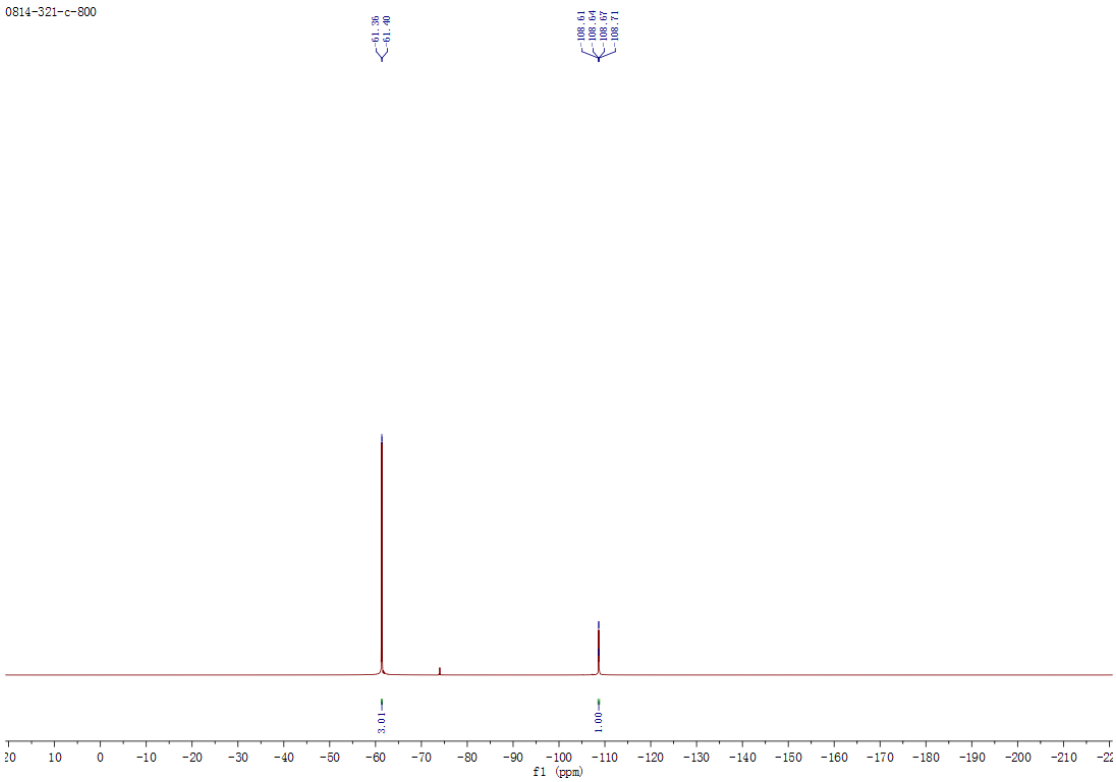
^{13}C NMR spectra of 3t ($CDCl_3$)



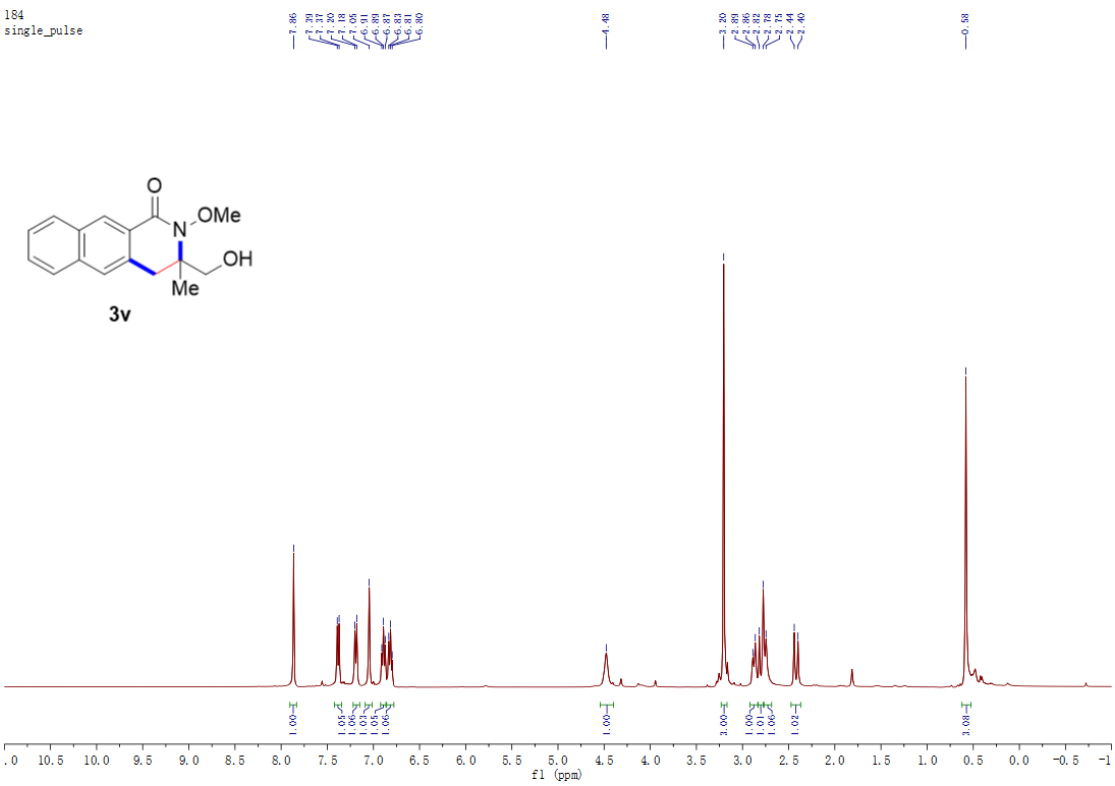
^{1}H NMR spectra of 3u ($CDCl_3$)



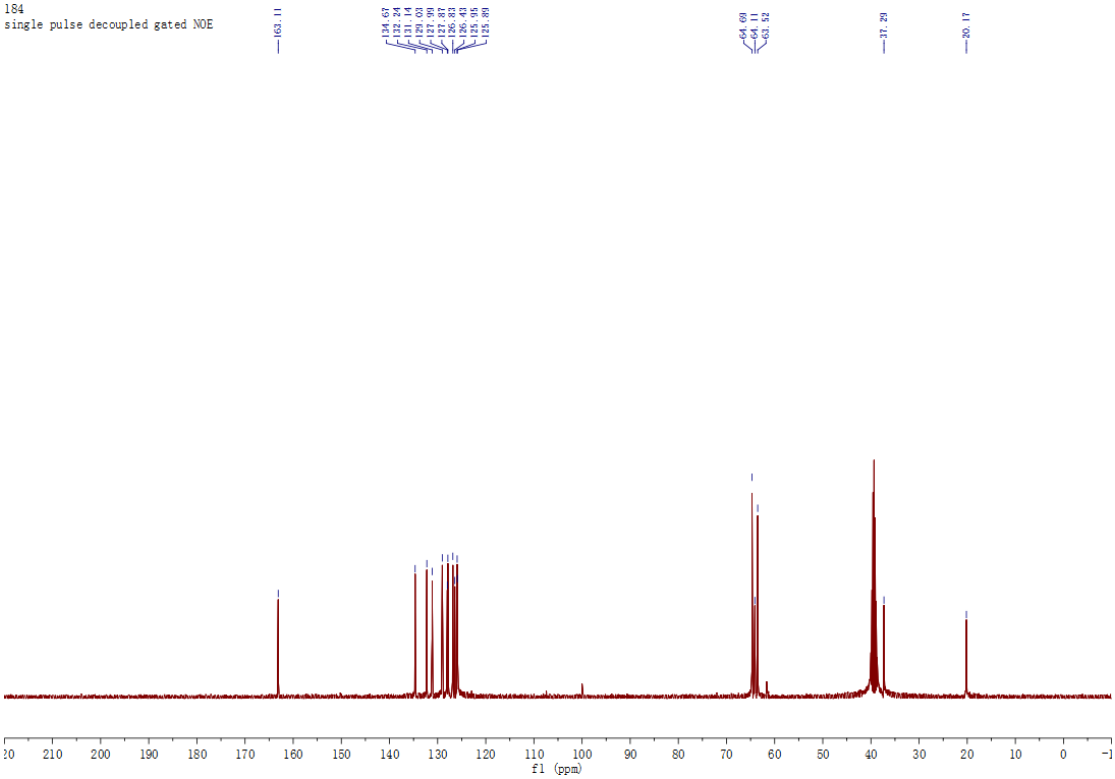
^{13}C NMR spectra of 3u ($CDCl_3$)



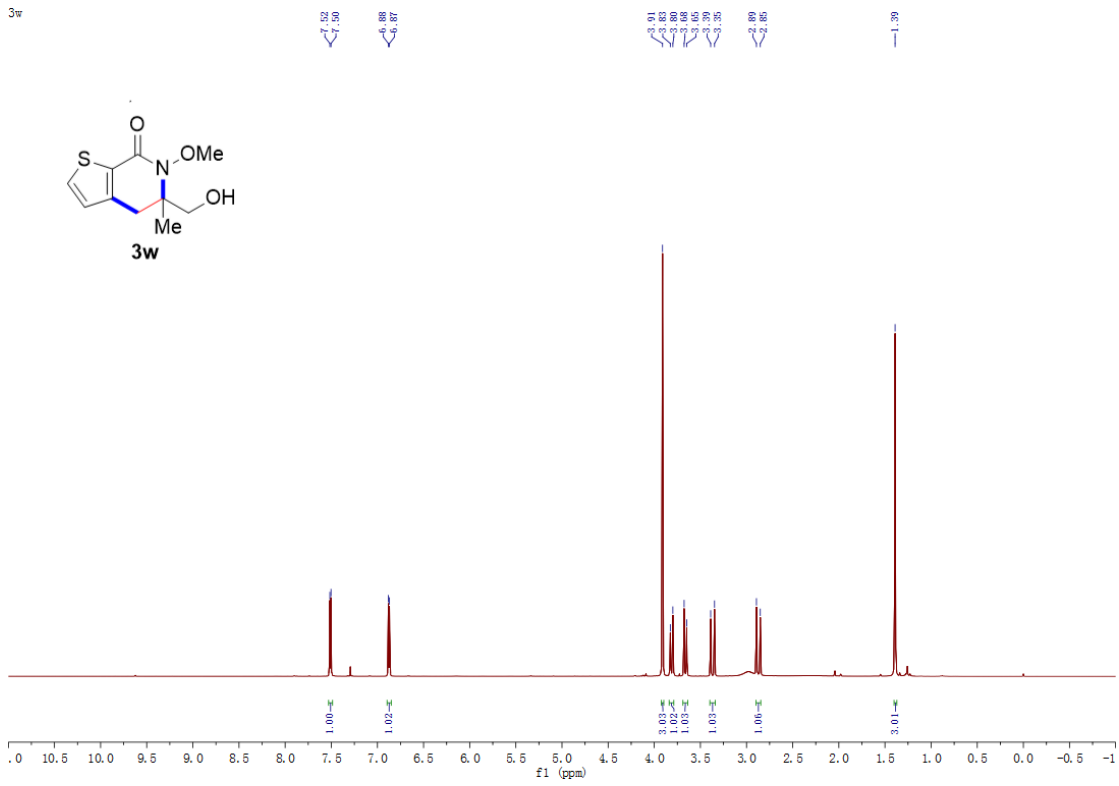
^{19}F NMR spectra of 3u ($CDCl_3$)



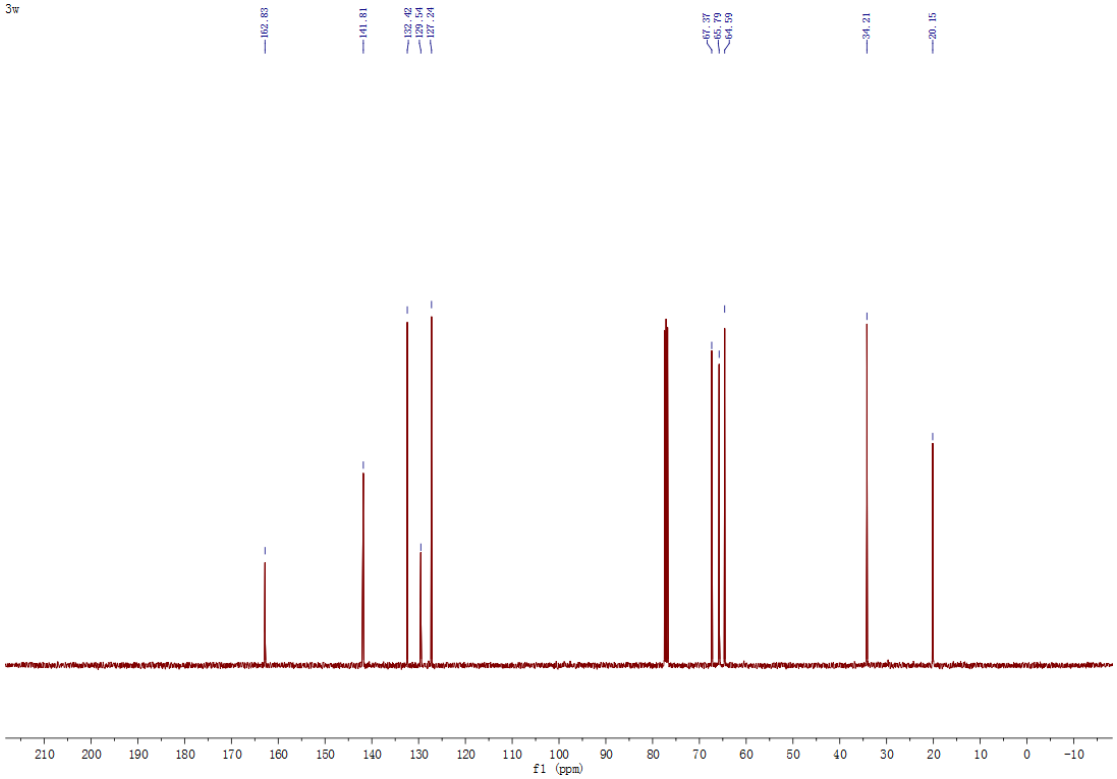
^{1}H NMR spectra of 3v($(CD_3)_2SO$)



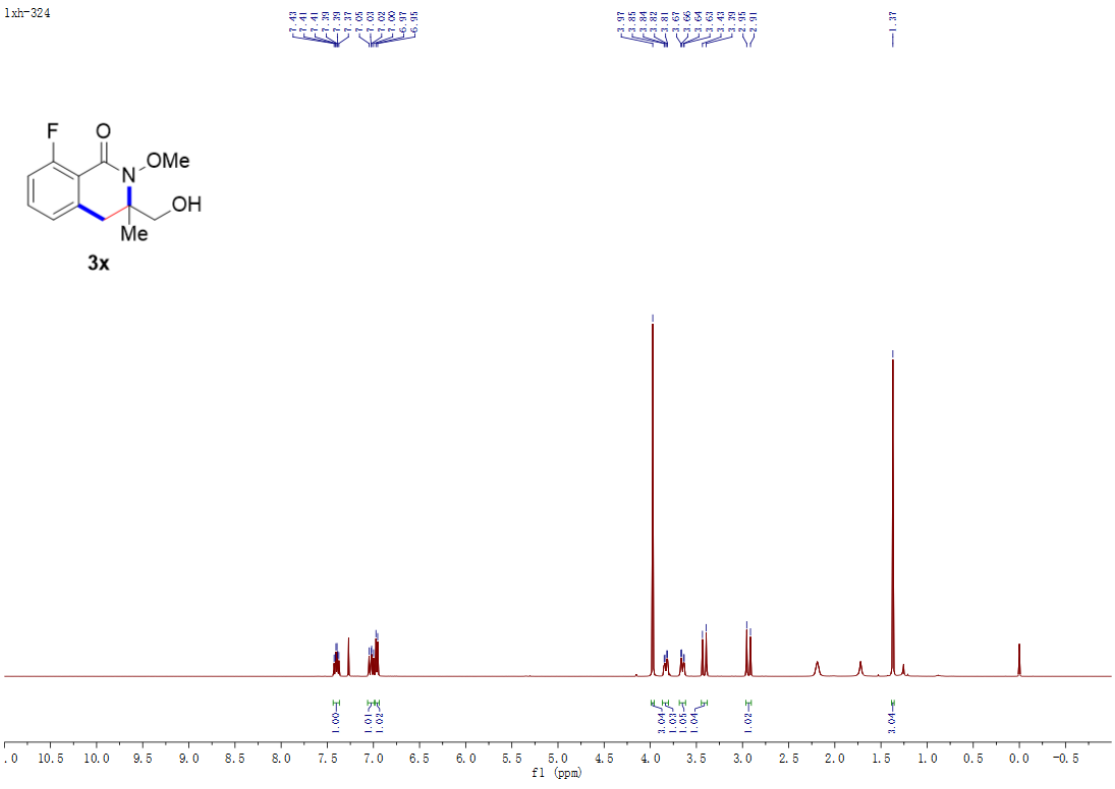
^{13}C NMR spectra of 3v ($(CD_3)_2SO$)



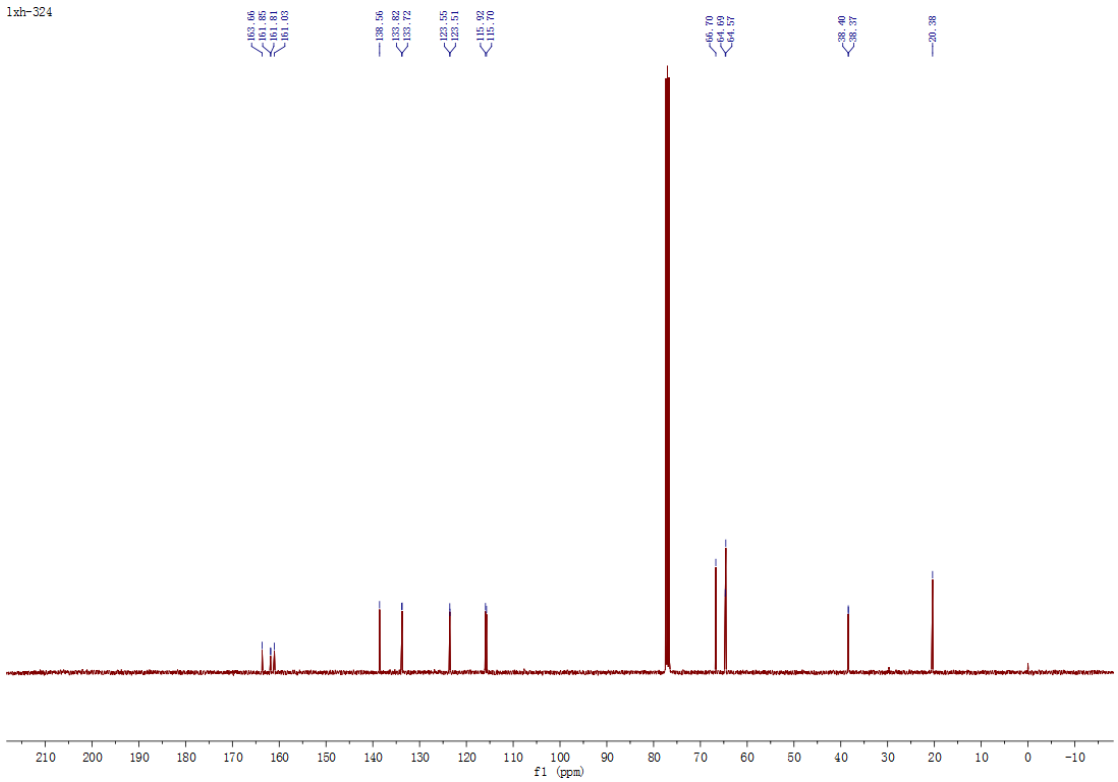
^{1}H NMR spectra of 3w ($CDCl_3$)



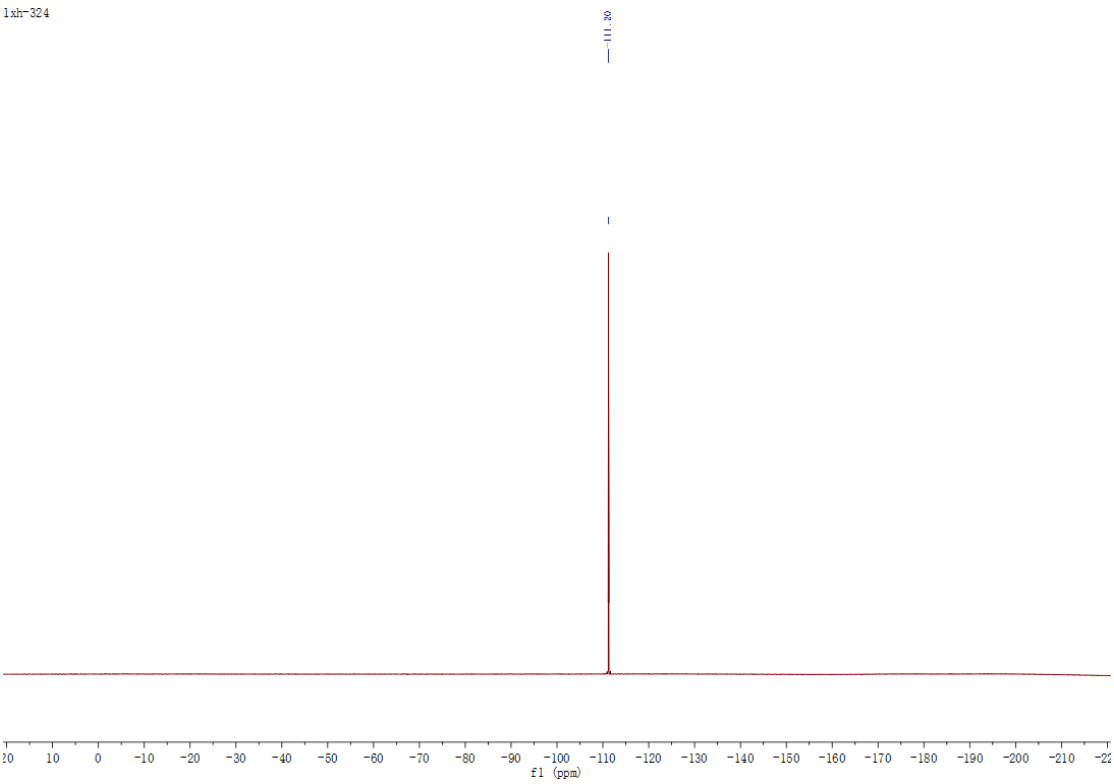
^{13}C NMR spectra of 3w ($CDCl_3$)



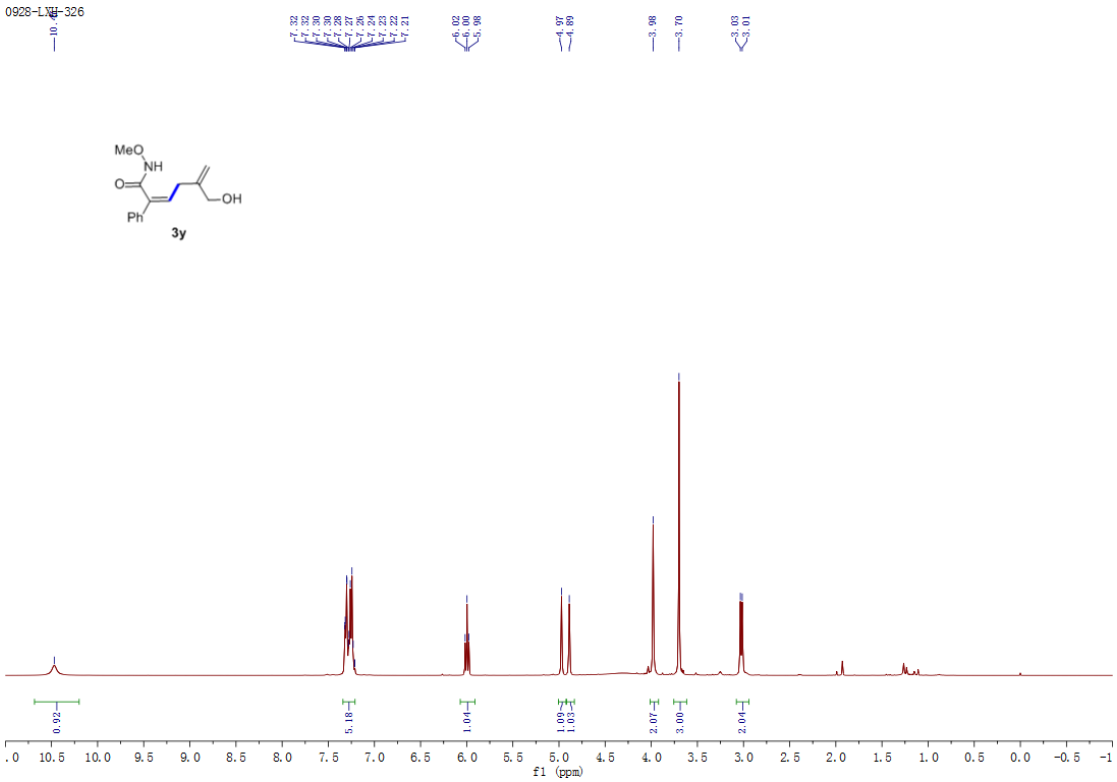
^{1}H NMR spectra of 3x ($CDCl_3$)



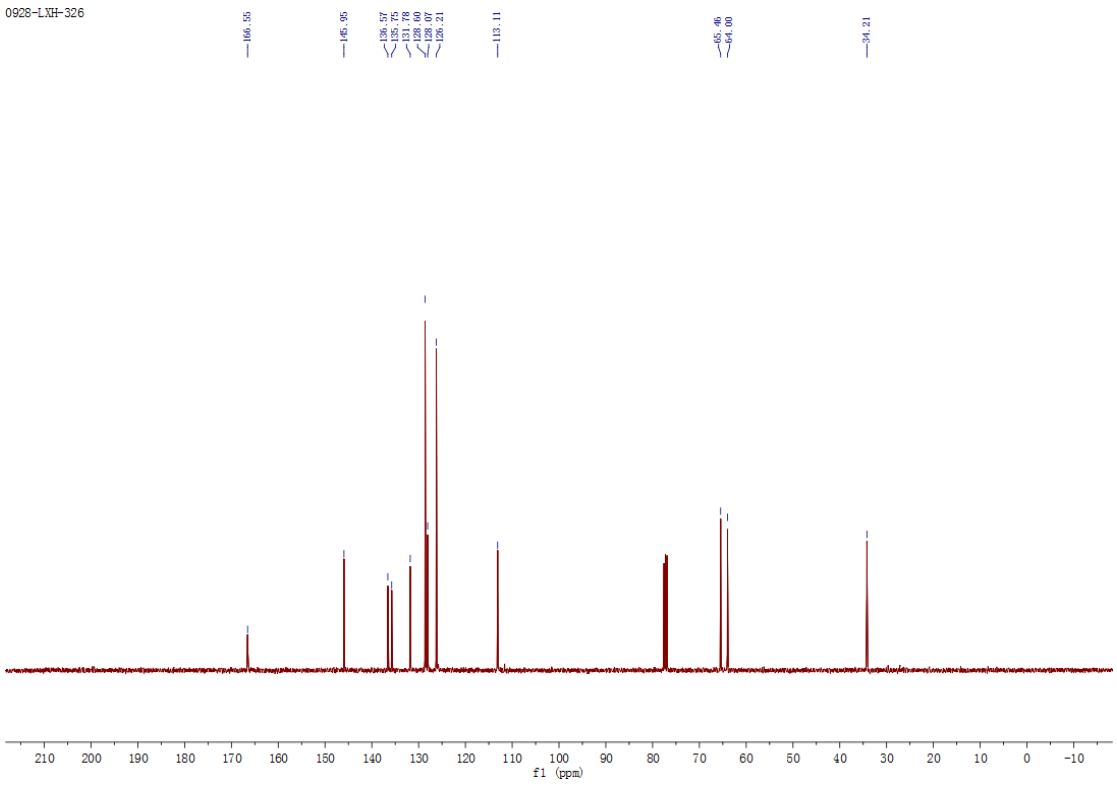
^{13}C NMR spectra of 3x ($CDCl_3$)



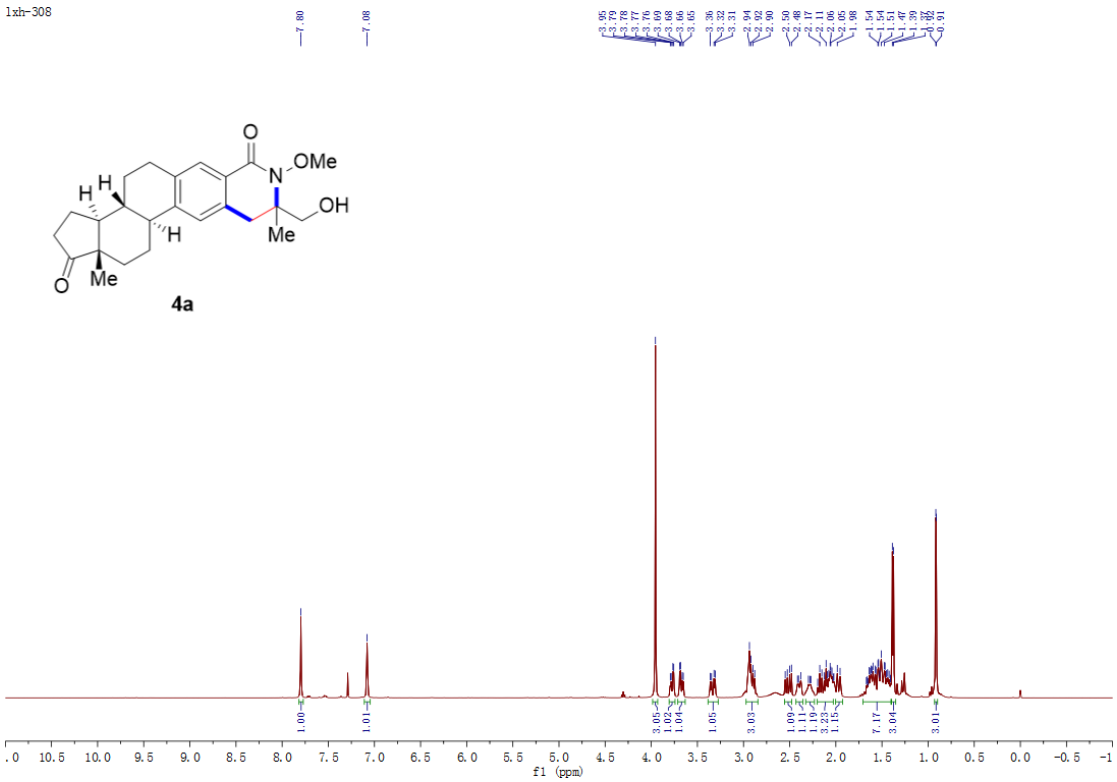
^{19}F NMR spectra of 3x ($CDCl_3$)



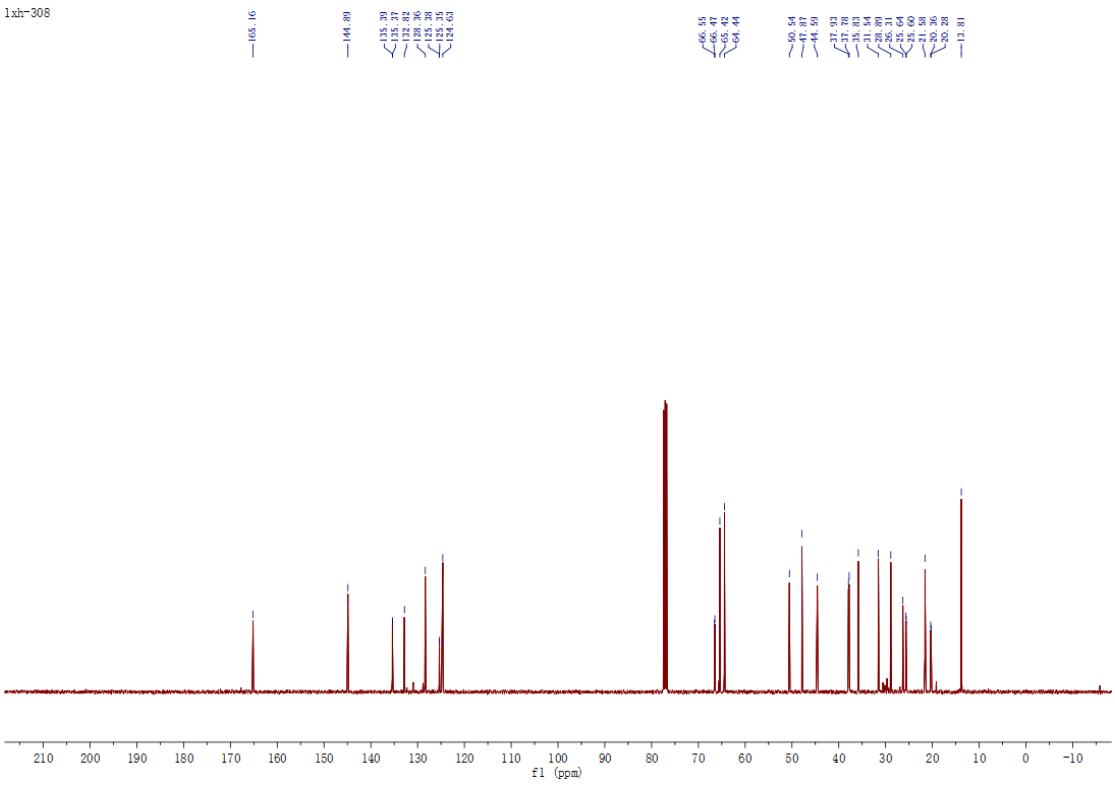
^{1}H NMR spectra of 3y ($CDCl_3$)



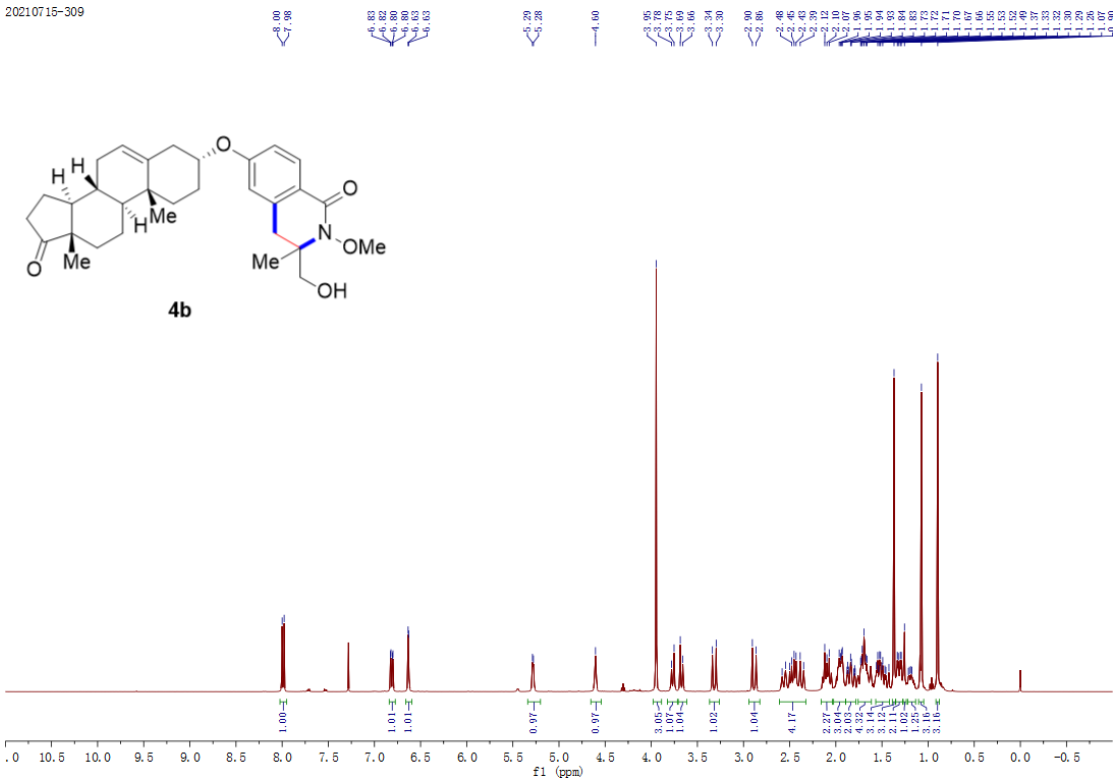
^{13}C NMR spectra of 3x ($CDCl_3$)



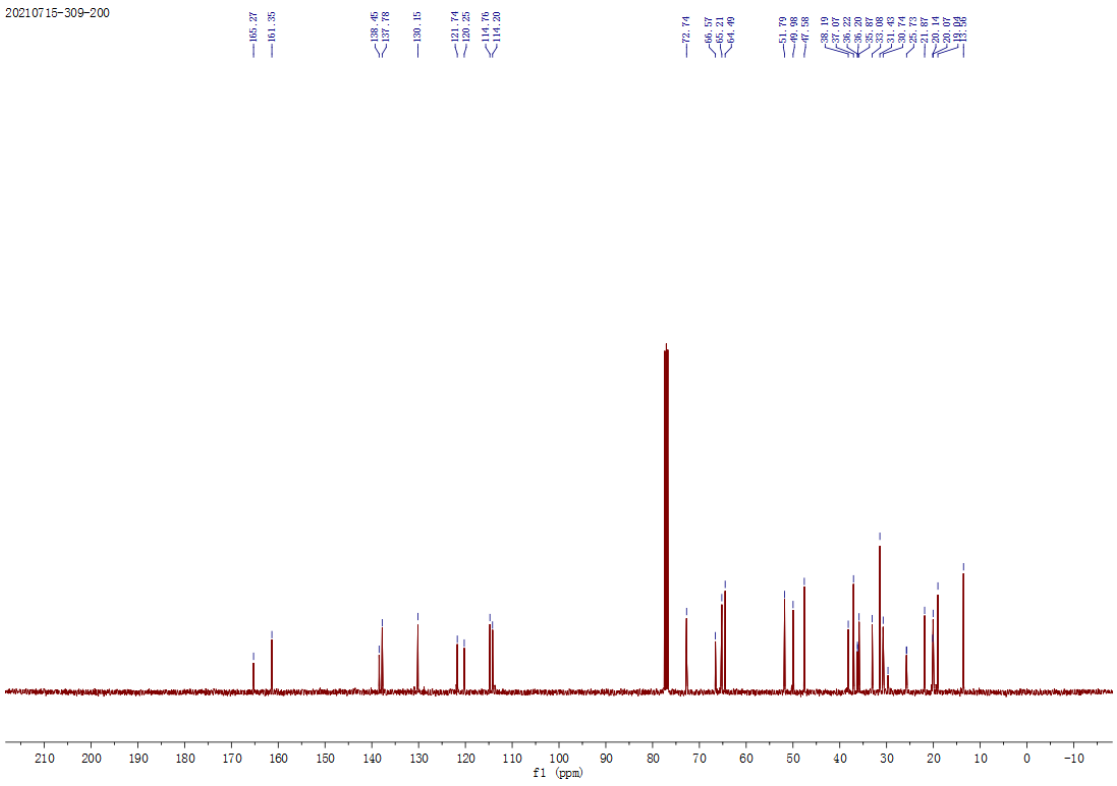
^{1}H NMR spectra of 4a ($CDCl_3$)



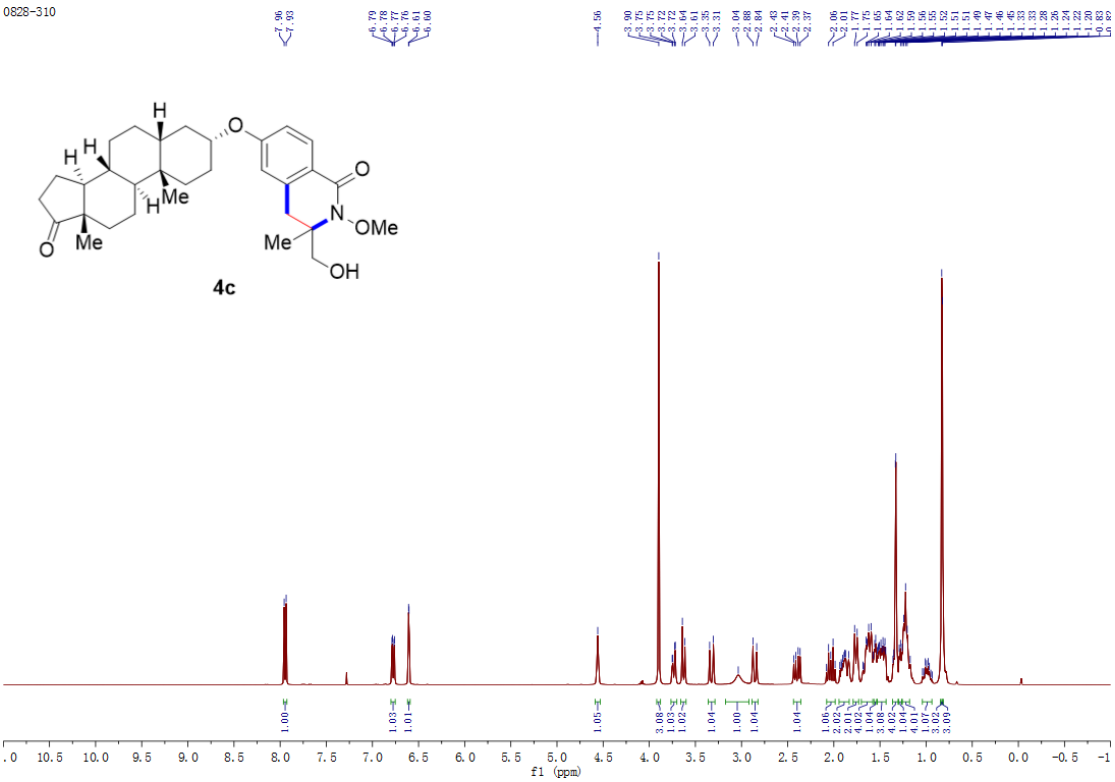
^{13}C NMR spectra of 4a ($CDCl_3$)



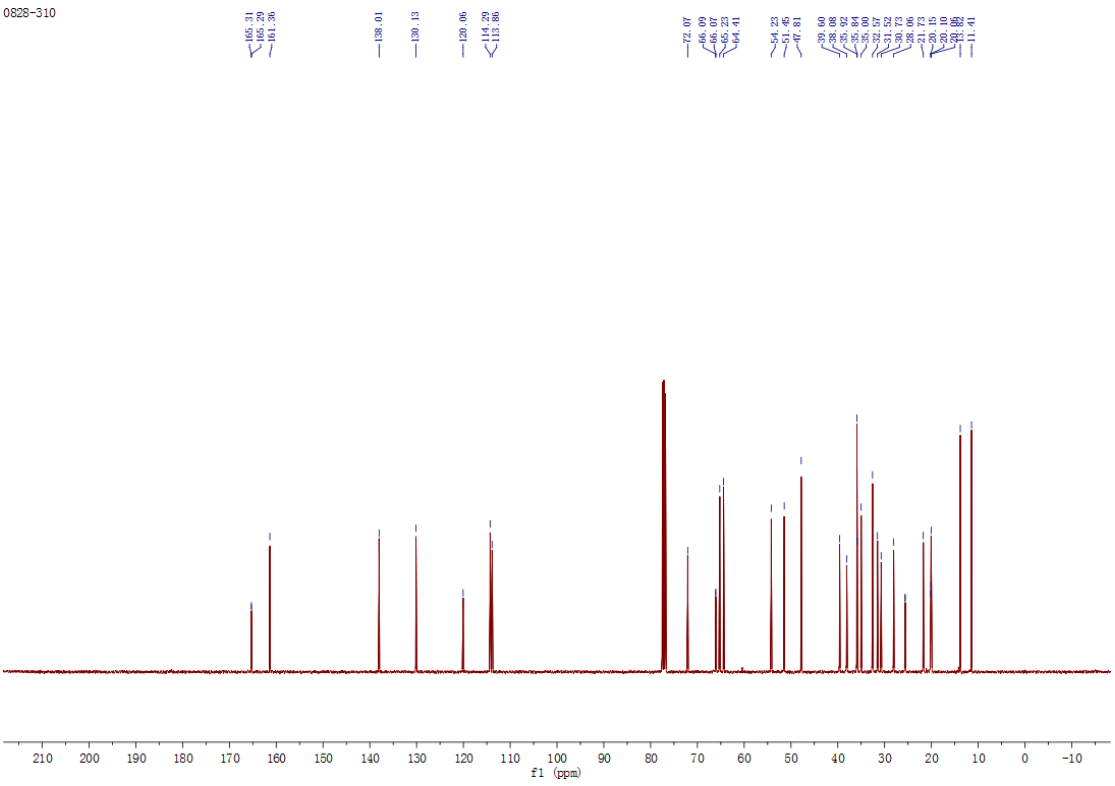
^{1}H NMR spectra of 4b ($CDCl_3$)



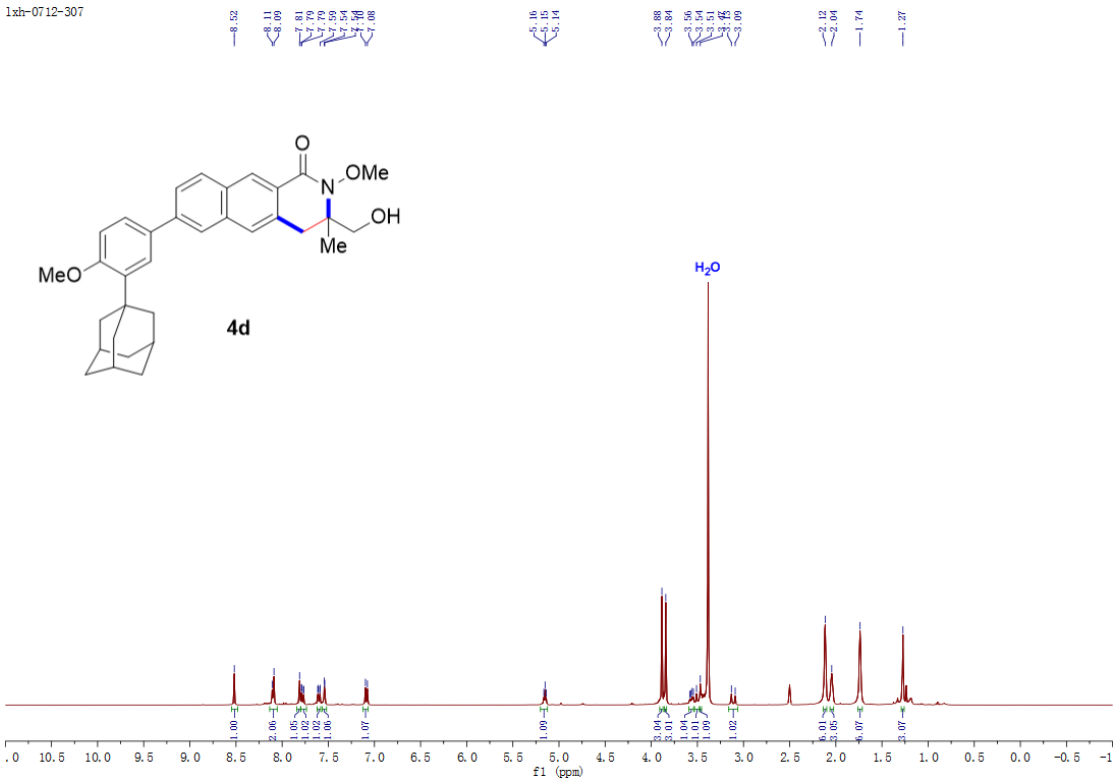
^{13}C NMR spectra of 4b ($CDCl_3$)



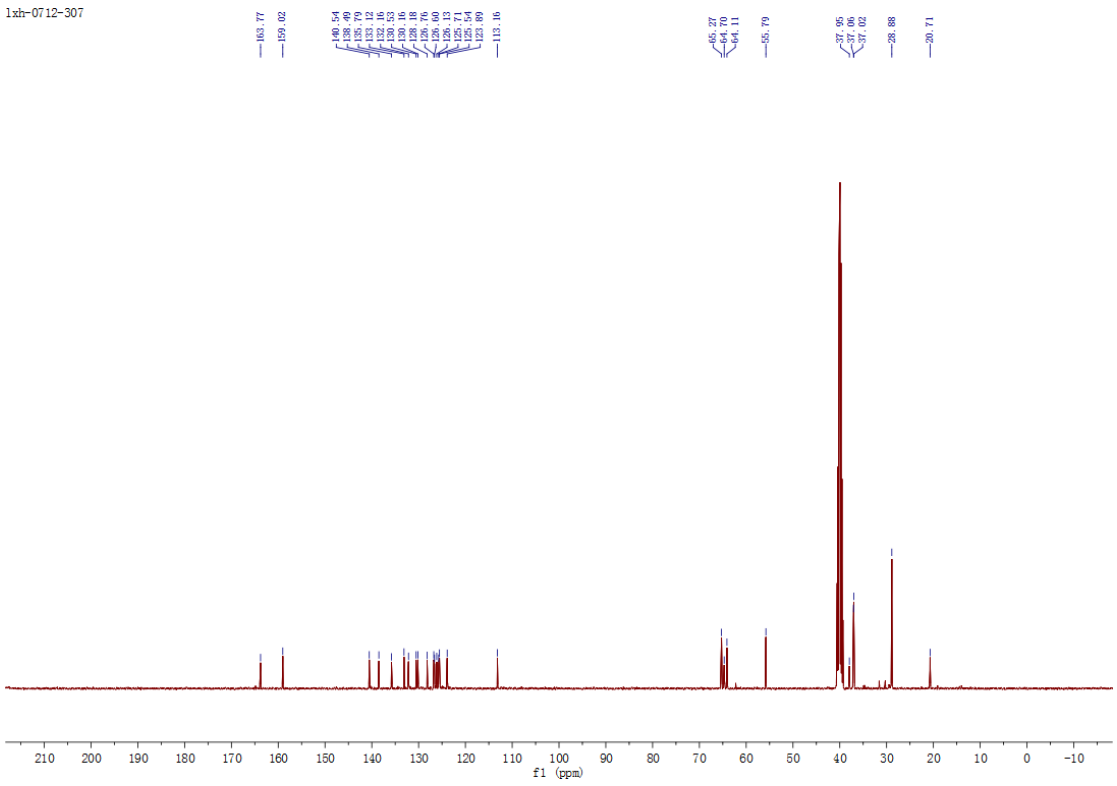
^{1}H NMR spectra of 4c ($CDCl_3$)



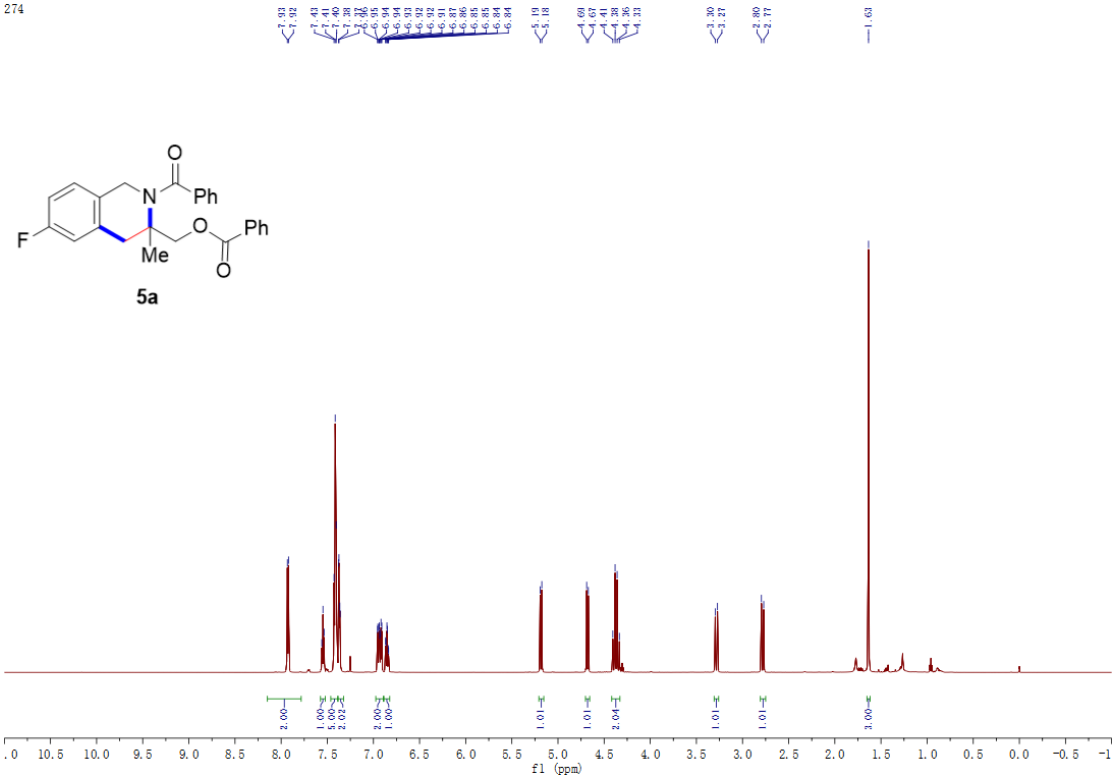
^{13}C NMR spectra of 4c ($CDCl_3$)



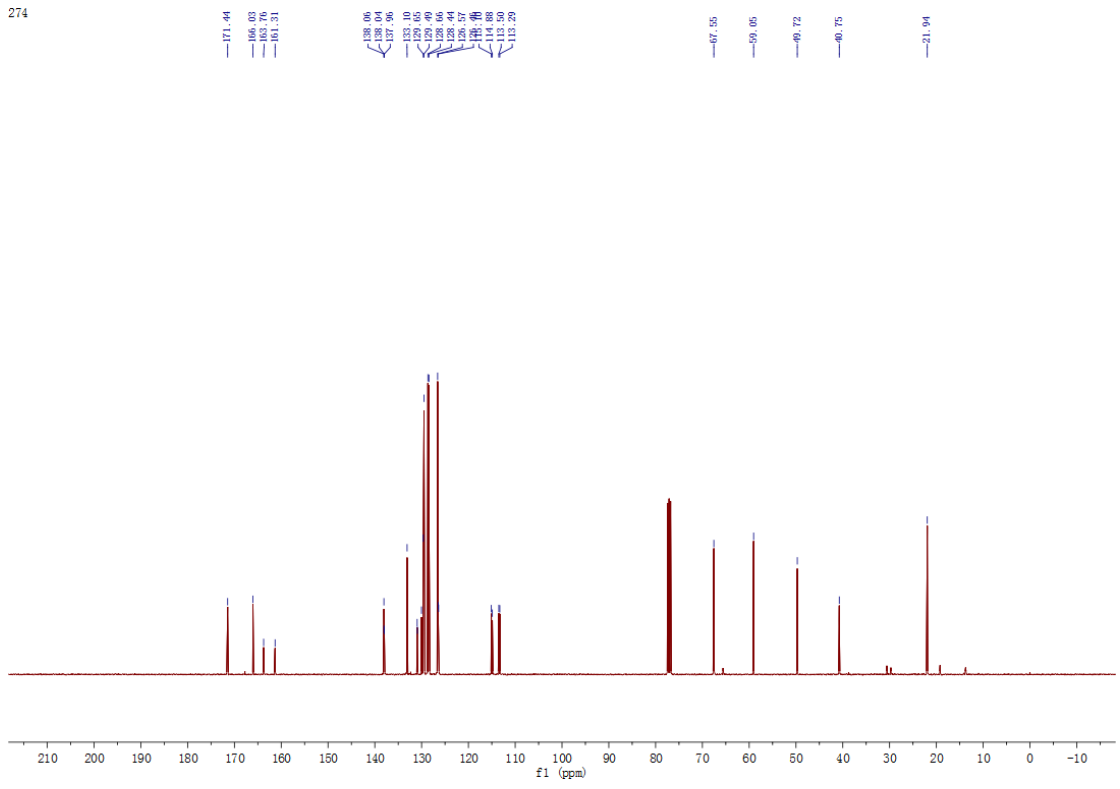
^{1}H NMR spectra of 4d ($(CD_3)_2SO$)



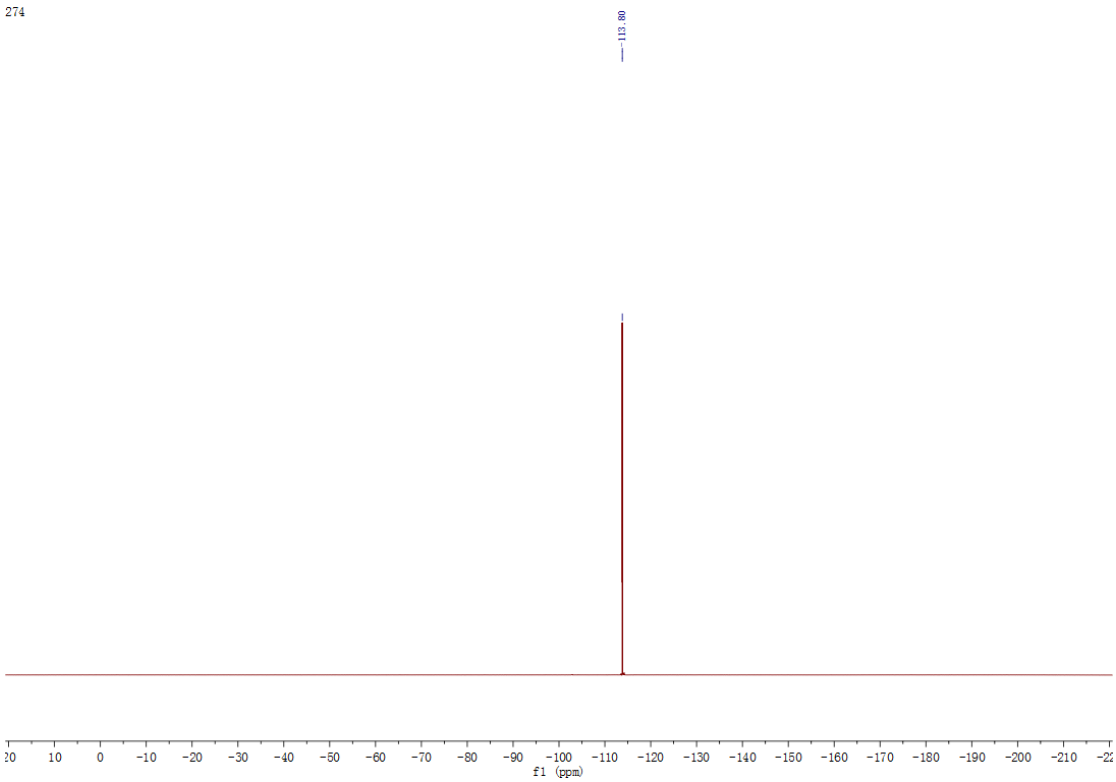
^{13}C NMR spectra of 4d ($(CD_3)_2SO$)



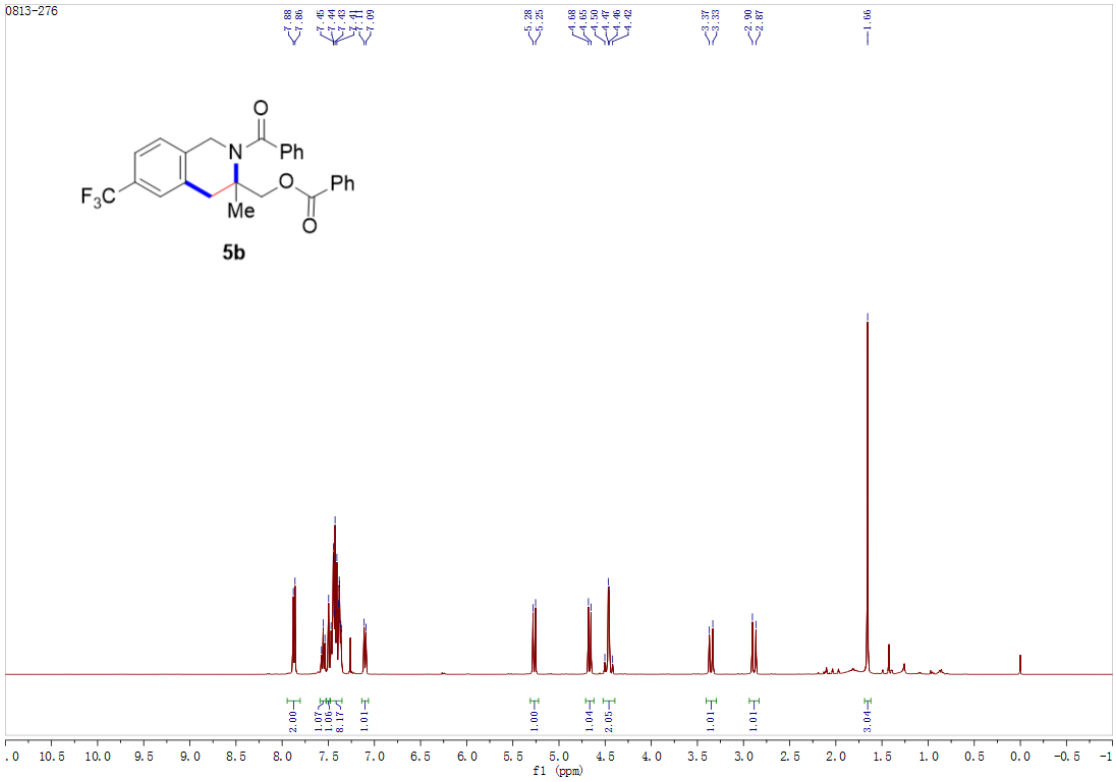
^{1}H NMR spectra of 5a ($CDCl_3$)



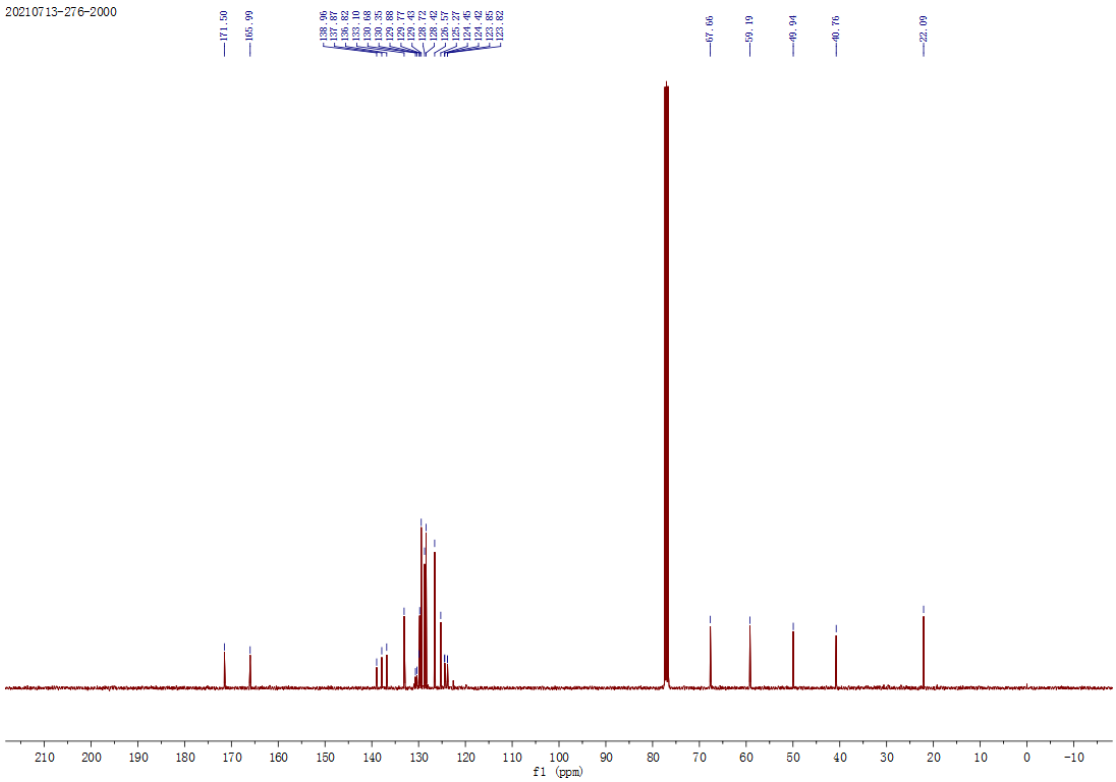
^{13}C NMR spectra of 5a ($CDCl_3$)



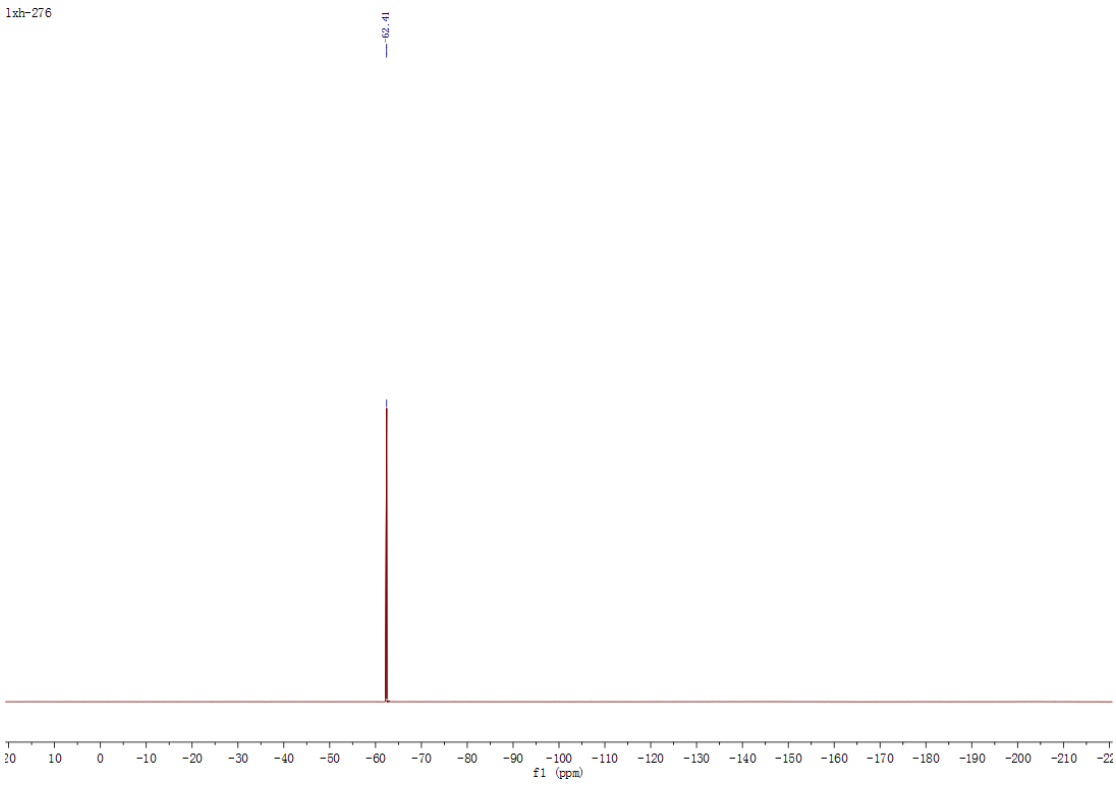
^{19}F NMR spectra of 5a ($CDCl_3$)



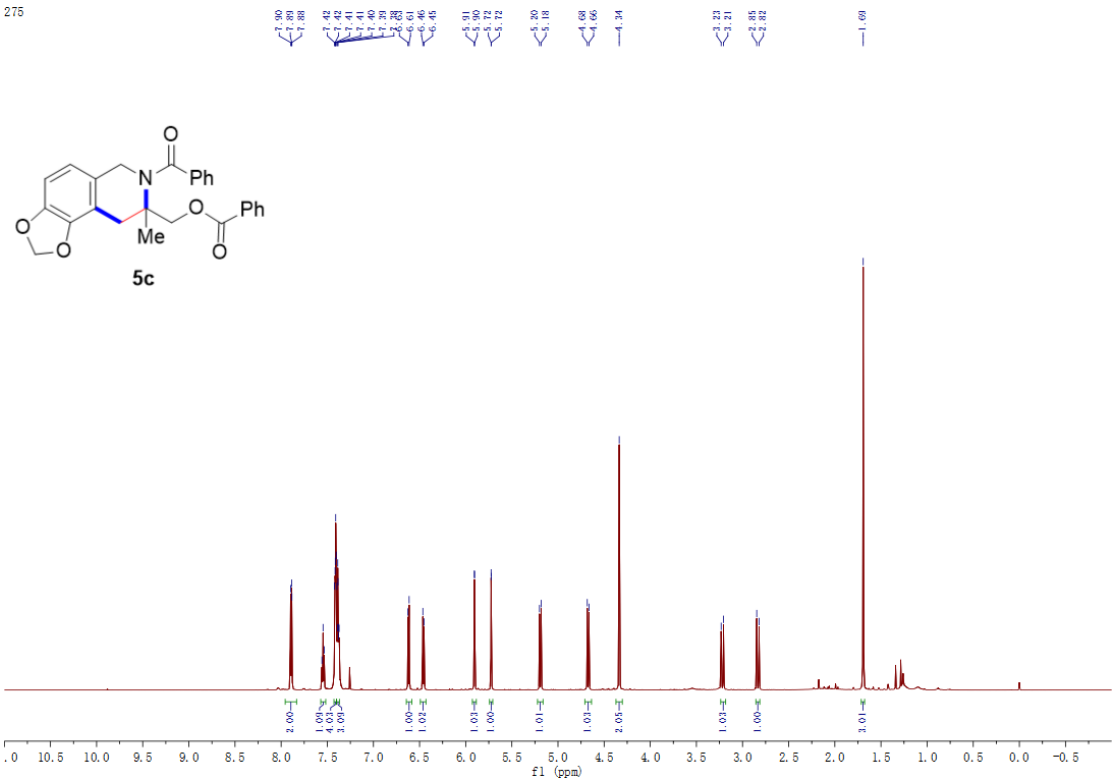
^{1}H NMR spectra of 5b ($CDCl_3$)



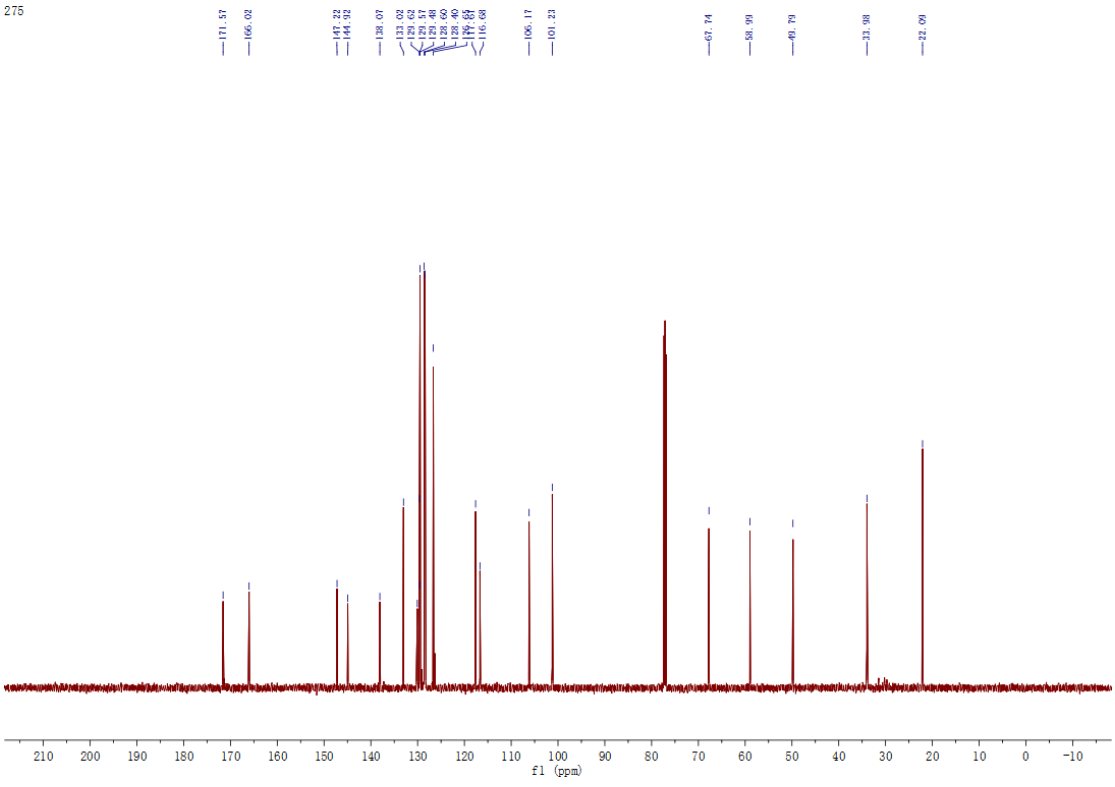
^{13}C NMR spectra of 5b ($CDCl_3$)



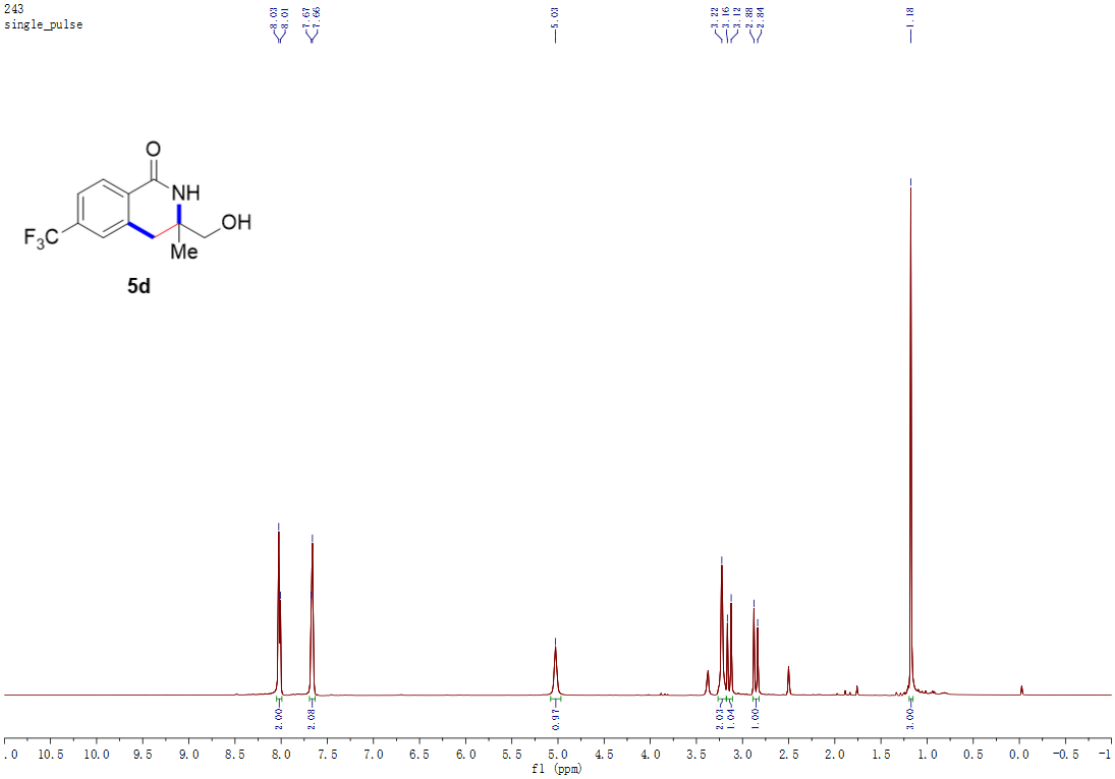
^{19}F NMR spectra of 5b($CDCl_3$)



^{1}H NMR spectra of 5c ($CDCl_3$)

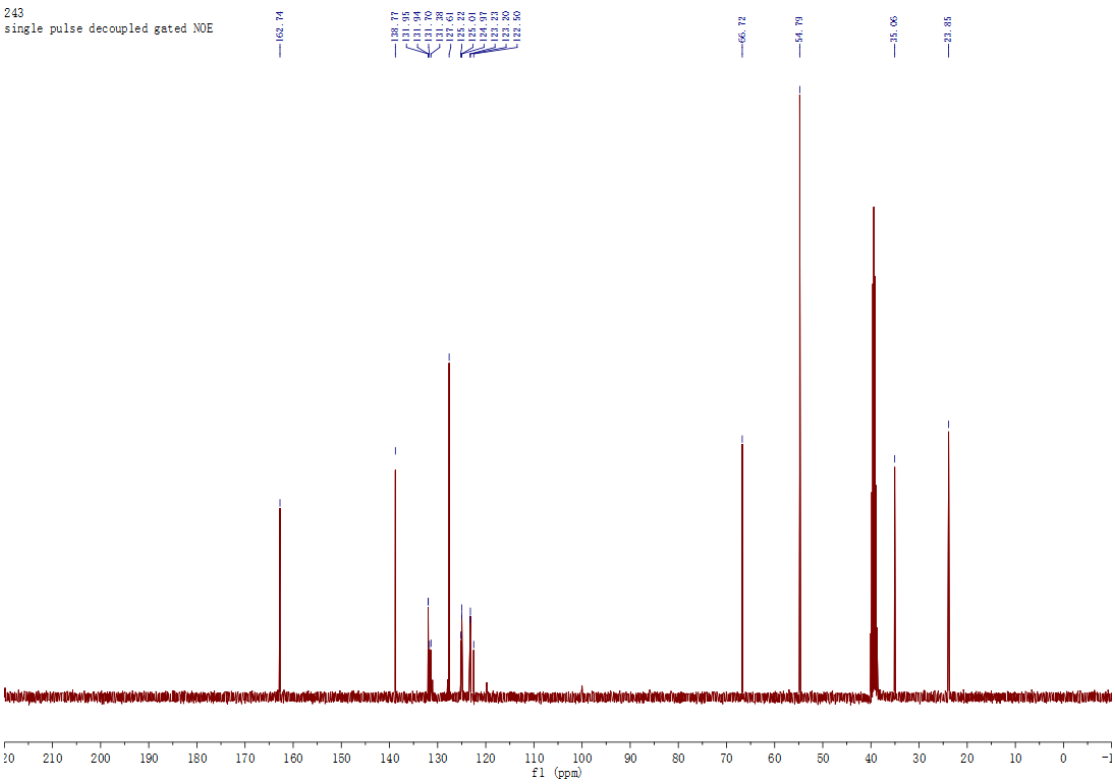


^{13}C NMR spectra of 5c ($CDCl_3$)

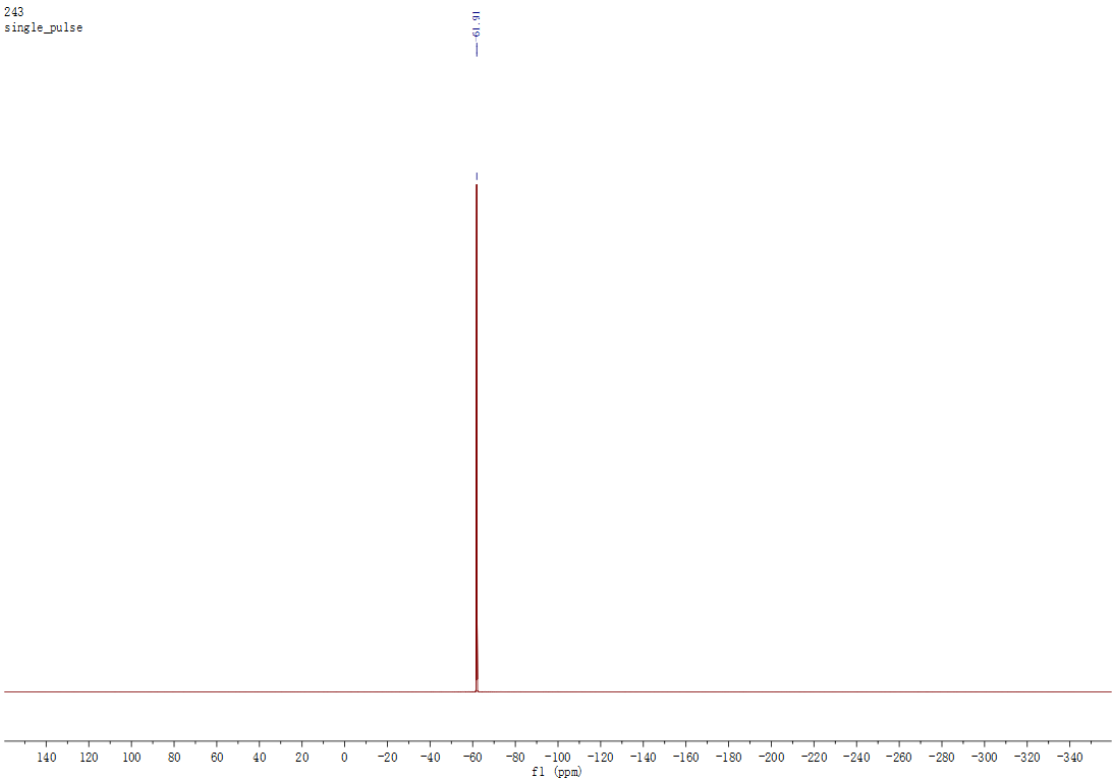


5d

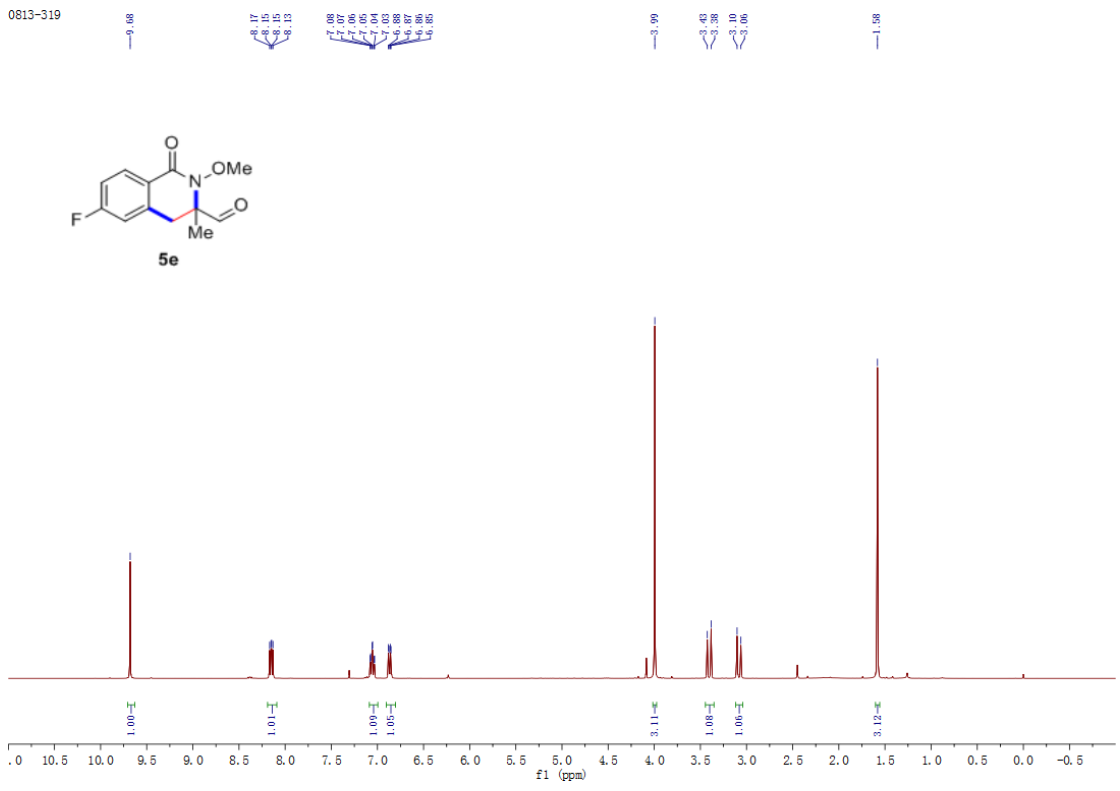
^{1}H NMR spectra of 5d ($(CD_3)_2SO$)



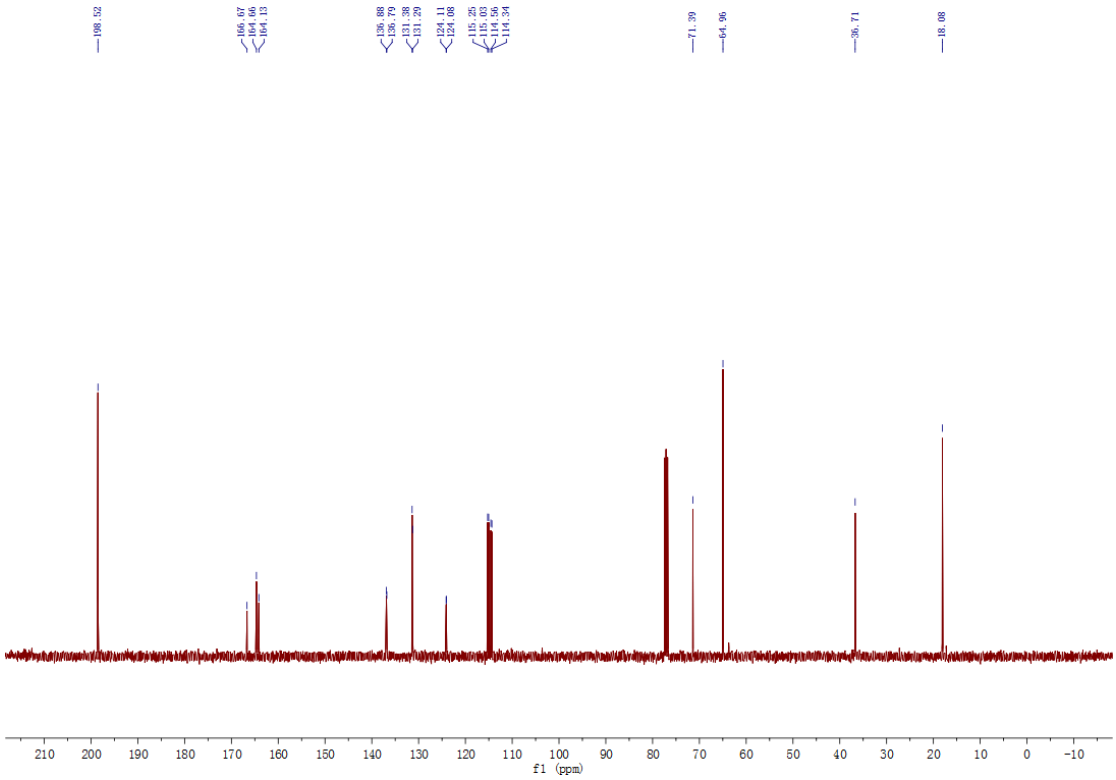
^{13}C NMR spectra of 5d ($(CD_3)_2SO$)



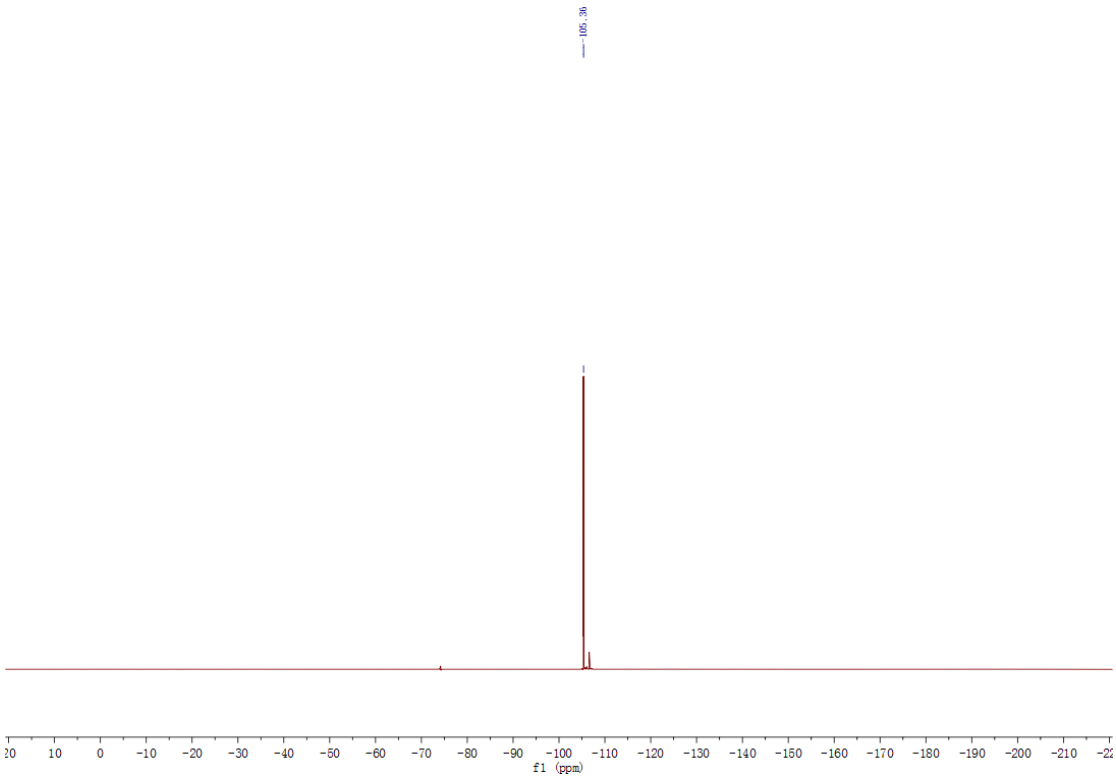
^{19}F NMR spectra of 5d ($(CD_3)_2SO$)



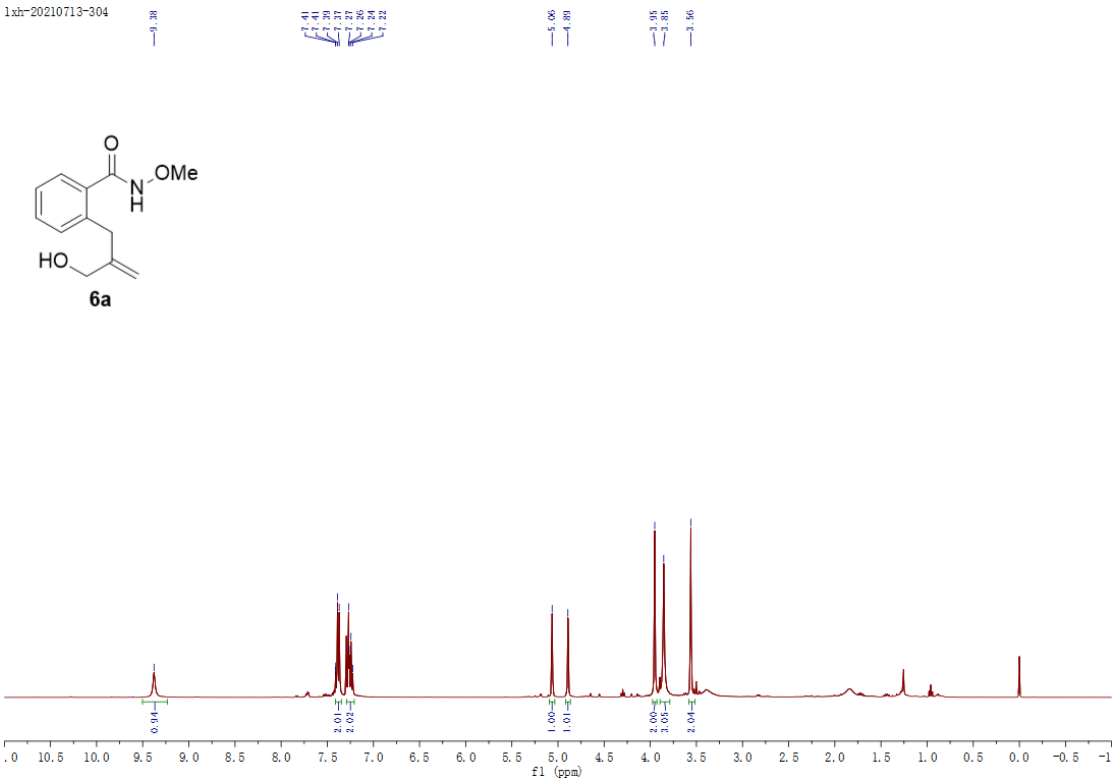
^{1}H NMR spectra of 5e ($CDCl_3$)



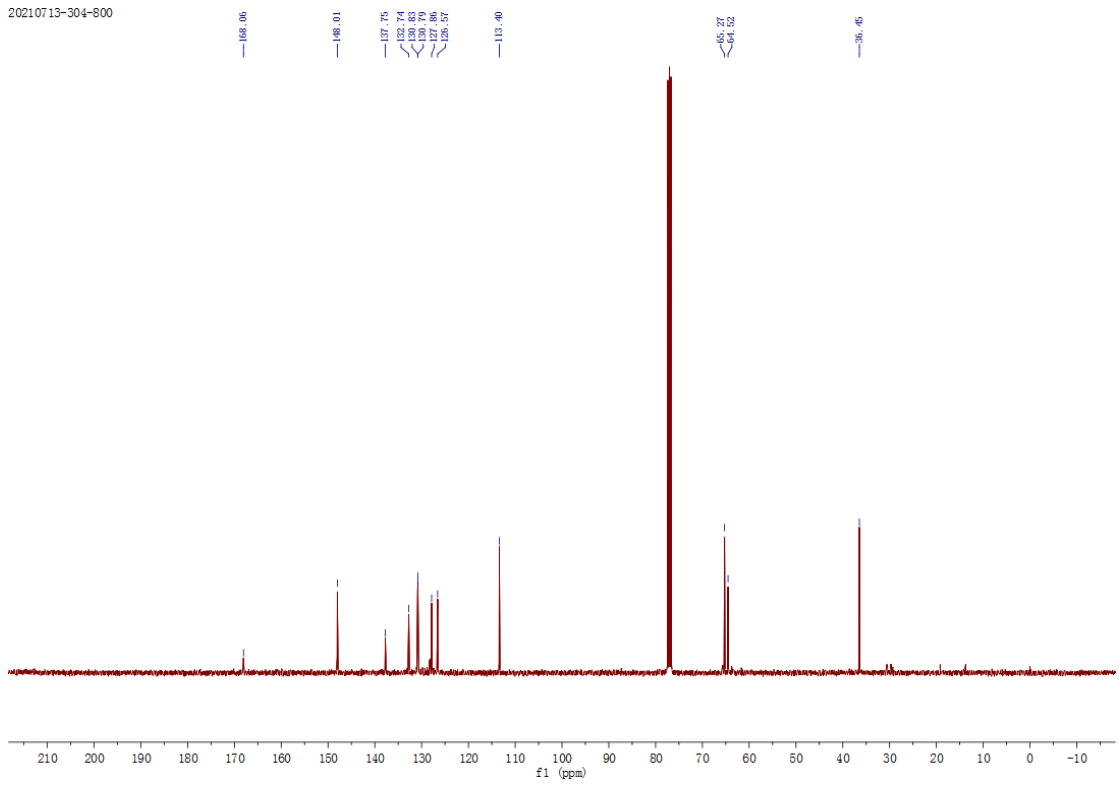
^{13}C NMR spectra of 5e ($CDCl_3$)



^{19}F NMR spectra of 5e ($CDCl_3$)



^{1}H NMR spectra of 6a ($CDCl_3$)



^{13}C NMR spectra of 6a ($CDCl_3$)