Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Synthesis of *gem*-Difluorinated Pentacyclic Indenopyrazolopyrazolones via Rh(III)-Catalyzed Cascade C-H Functionalization/[3+2] Dipolar Cycloaddition

Fu-Xiaomin Liu,[a,b,+] Weijie Chen,[b,+] Ying Cai,[b] Zhi Zhou,[b,*] Wei Yi[b,*] and Kui Cheng[a,*]

[a]Guangdong Provincial Key Laboratory of New Drug Screening and Guangzhou Key Laboratory of Drug Research for Emerging Virus Prevention and Treatment, School of Pharmaceutical Sciences, Southern Medical University, Guangzhou, Guangdong 510515, China.

[b]Key Laboratory of Molecular Target & Clinical Pharmacology and the State Key Laboratory of Respiratory Disease, School of Pharmaceutical Sciences and The Fifth Affiliated Hospital, Guangzhou Medical University, Guangzhou, Guangdong 511436, China

[+]These authors contributed equally.

* E-mail: zhouzhi@gzhmu.edu.cn, yiwei@gzhmu.edu.cn and Chengk@smu.edu.cn

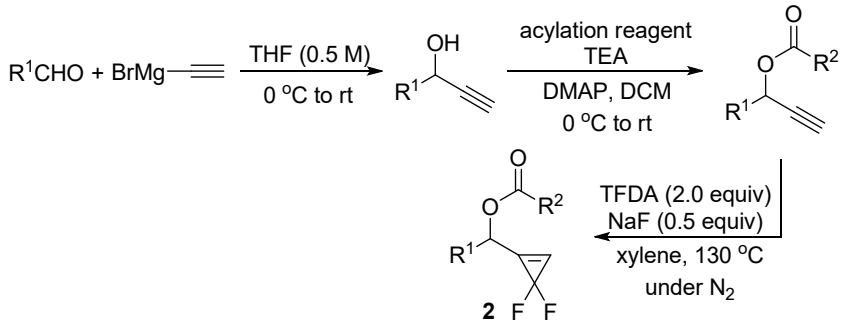
Table of Contents

I. General

NMR spectra were recorded on JEOL 400 NMR (^{1}H 400 MHz; ^{13}C 100 MHz) in $CDCl_3$, CD_3OD or CD_2Cl_2. Abbreviations for data quoted are s, singlet; brs, broad singlet; d, doublet; t, triplet; dd, doublet of doublets; m, multiplet. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; CD_3OD: δ_H = 3.31 ppm, δ_C = 49.00 ppm; CD_2Cl_2: δ_H = 5.32 ppm, δ_C = 53.84 ppm). Mass spectra and high-resolution mass spectra (HRMS) were measured on an agilent TOF-G6230B mass spectrometer and Thermo-DFS mass spectrometer. X-ray single-crystal diffraction was conducted on HyPix diffractometer. Thin-layer chromatographies were done on pre-coated silica gel 60 F254 plates (Merck). Silica gel 60H (200-300 mesh) and preparative TLC (200x200 mm, 0.2-0.25 mm in thickness) manufactured by Qingdao Haiyang Chemical Group Co. (China) were used for general chromatography. $[Cp^*IrCl_2]_2$, $[Cp^*RhCl_2]_2$ and $[Ru(p\text{-cymene})Cl_2]_2$ were purchased from Aldrich and used without further purification. Substrates azomethine imines[S1] and *gem*-difluorocyclopropenes[S2] were synthesized according to published procedures. Other chemicals were purchased from commercial suppliers and were dried and purified when necessary. No attempts were made to optimize yields for substrate synthesis.

II. Experimental Information and Characterization Data

General procedure for the synthesis of *gem*-difluorocyclopropenes:



Procedure A (Following a published procedure):[S2] The solution of aldehyde (36 mmol, 1.0 equiv) in dry THF (72 mL, 0.5 M) was added into an oven dried 250 mL round-bottom flask. Then the reaction mixture was cooled to 0 °C in an ice bath, and

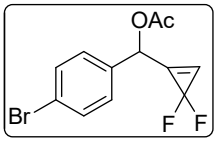
the ethynylmagnesium bromide (0.5 M in THF, 1.1 equiv) was added dropwise over 10 min. After completion of the addition, the solution was stirred for 10 min and allowed to warm to room temperature for another 3 hours. Afterwards, the reaction mixture was quenched with saturated ammonium chloride solution (60 mL) and diluted with H_2O (50 mL). The organic phase was separated, and the aqueous phase was extracted with ethyl acetate (3x50 mL). The combined organic phase was washed with brine (50 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to obtain the crude propargyl alcohol product.

To a solution of propargyl alcohol (10 mmol), acetic acid (11 mmol) and *N*, *N*-dimethylpyridin-4-amine (DMAP, 1 mmol) in DCM (20 mL) was added a solution of dicyclohexylmethanediimine (DCC, 11 mmol) in DCM (10 mL) at 0 °C. Afterwards, the reaction was allowed to warm to room temperature and monitored by TLC. Then the reaction mixture was filtrated and concentrated. The crude product was purified by silica gel column chromatography (PE/EA = 20/1) to afford the desired propargylic acetates in 60-90% yield as a pale yellow oil.

The mixture of propargylic acetate (4 mmol, 1.0 equiv), NaF (2 mmol) and xylene (1.6 mL) was added into a 10 mL Schlenk flask at room temperature under an atmosphere of N_2. Then the mixture was heated at 130 °C in an oil bath for 10 min. Afterwards, TFDA (8 mmol, 2.0 equiv) was added dropwise over 30 min. Then the mixture was stirred for an additional 30 min to ensure the substrate was consumed completely. After that, the reaction mixture was cooled to room temperature and the solvent was removed under the reduced pressure. The crude product was purified by silica gel column chromatography (PE/EA = 80/1) to provide the corresponding *gem*-difluorocyclopropenyl acetates **2**.

The *gem*-difluorocyclopropenyl acetates **2b**, **2e**, **2g**, **2h**, **2j-2l** were known compounds and the characteristic data were in line with the literature precedents.[S2]

(4-bromophenyl)(3,3-difluorocycloprop-1-en-1-yl)methyl acetate (2a)



This compound was obtained in 42% yield (509 mg) as pale yellow oil. Eluent: PE/EA = 10/1, R_f = 0.5.

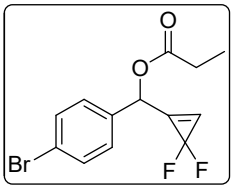
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.53 (m, 2H), 7.52 (dd, *J* = 3.1, 1.7 Hz, 1H), 7.31-7.27 (m, 2H), 6.66 (s, 1H), 2.16 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 136.1 (t, *J* = 11.3 Hz), 133.8, 132.4, 129.4, 123.8, 119.8 (t, *J* = 12.0 Hz), 101.1 (t, *J* = 272.1 Hz), 69.1, 20.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ -102.89 – -103.84 (m).

HRMS (ESI) calculated for $C_{12}H_8BrF_2O_2$ ([M-H]$^-$): 300.9681; found: 300.9689.

(4-bromophenyl)(3,3-difluorocycloprop-1-en-1-yl)methyl propionate (2ab)



This compound was obtained in 27% yield (337 mg) as pale yellow oil. Eluent: PE/EA = 10/1, R_f = 0.6.

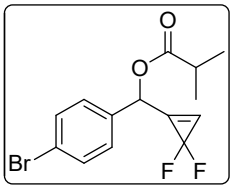
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.53 (m, 2H), 7.52-7.49 (m, 1H), 7.30-7.26 (m, 2H), 6.67 (s, 1H), 2.50-2.39 (m, 2H), 1.18 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.2, 136.1 (t, *J* = 11.4 Hz), 133.9, 132.3, 129.3, 123.7, 119.7 (t, *J* = 11.9 Hz), 101.1 (t, *J* = 272.0 Hz), 68.9, 27.5, 9.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ -102.81 – -103.78 (m).

HRMS (ESI) calculated for $C_{13}H_{10}BrF_2O_2$ ([M-H]$^-$): 314.9838; found: 314.9838.

(4-bromophenyl)(3,3-difluorocycloprop-1-en-1-yl)methyl isobutyrate (2ac)



This compound was obtained in 26% yield (350 mg) as pale yellow oil. Eluent: PE/EA = 10/1, R_f = 0.6.

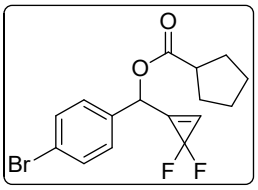
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 7.8 Hz, 2H), 7.51-7.48 (m, 1H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.66 (s, 1H), 2.68-2.64 (m, 1H), 1.23 (d, *J* = 7.0 Hz, 3H), 1.19 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.8, 136.2 (t, *J* = 11.3 Hz), 134.0, 132.3, 131.8, 129.8, 129.2, 123.7, 119.6 (t, *J* = 11.9 Hz), 101.1 (t, *J* = 272.1 Hz), 68.8, 34.0, 19.0, 18.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ -102.78 – -103.76 (m).

HRMS (ESI) calculated for $C_{14}H_{12}BrF_2O_2$ ($[M-H]^-$): 328.9994; found: 328.9999.

(4-bromophenyl)(3,3-difluorocycloprop-1-en-1-yl)methyl cyclopentane carboxylate (2ad)



This compound was obtained in 47% yield (678 mg) as pale yellow oil. Eluent: PE/EA = 10/1, R_f = 0.6.

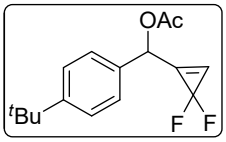
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.52 (m, 2H), 7.50-7.47 (m, 1H), 7.30-7.26 (m, 2H), 6.66 (s, 1H), 2.89-2.79 (m, 1H), 1.95-1.59 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 175.5, 136.3 (t, *J* = 11.5 Hz), 134.1, 132.3, 129.2, 123.7, 119.5 (t, *J* = 11.9 Hz), 101.1 (t, *J* = 272.0 Hz), 68.8, 43.6, 30.2, 29.9, 25.93, 25.91.

^{19}F NMR (376 MHz, $CDCl_3$): δ -102.81 – -103.78 (m).

HRMS (ESI) calculated for $C_{16}H_{14}BrF_2O_2$ ($[M-H]^-$): 355.0151; found: 355.0157.

(4-(*tert*-butyl)phenyl)(3,3-difluorocycloprop-1-en-1-yl)methyl acetate (2c)



This compound was obtained in 42% yield (468 mg) as pale yellow oil. Eluent: PE/EA = 10/1, R_f = 0.5.

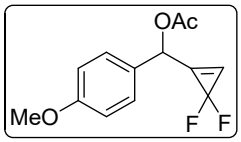
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.46 (m, 1H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 6.69 (s, 1H), 2.15 (s, 3H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 152.7, 136.6 (t, *J* = 11.4 Hz), 131.7, 127.6, 126.1, 119.3 (t, *J* = 11.9 Hz), 101.4 (t, *J* = 271.7 Hz), 69.7, 34.8, 31.3, 21.0.

^{19}F NMR (376 MHz, $CDCl_3$): δ -100.72 – -108.39 (m).

HRMS (ESI) calculated for $C_{16}H_{19}F_2O_2$ ($[M+H]^+$): 281.1348; found: 281.1346.

(3,3-difluorocycloprop-1-en-1-yl)(4-methoxyphenyl)methyl acetate (2d)



This compound was obtained in 16% yield (167 mg) as pale yellow oil. Eluent: PE/EA = 10/1, R_f = 0.3.

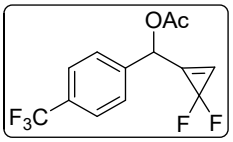
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (dd, *J* = 3.0, 1.7 Hz, 1H), 7.35-7.31 (m, 2H), 6.94-6.91 (m, 2H), 6.66 (s, 1H), 3.81 (s, 3H), 2.14 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 160.5, 136.6 (t, *J* = 11.2 Hz), 129.5, 126.8, 119.2 (t, *J* = 11.9 Hz), 114.4, 101.4 (t, *J* = 271.7 Hz), 69.5, 55.4, 21.0.

^{19}F NMR (376 MHz, $CDCl_3$): δ -84.58 – -132.01 (m).

HRMS (ESI) calculated for $C_{13}H_{13}F_2O_3$ ($[M+H]^+$): 255.0827; found: 255.0827.

(3,3-difluorocycloprop-1-en-1-yl)(4-(trifluoromethyl)phenyl)methyl acetate (2f)



This compound was obtained in 49% yield (568 mg) as pale yellow oil. Eluent: PE/EA = 10/1, R_f = 0.5.

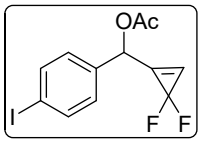
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.56-7.52 (m, 3H), 6.76 (s, 1H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 138.7, 135.9 (t, *J* = 11.5 Hz), 131.6 (q, *J* = 32.6 Hz), 128.0, 126.2 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 272.2 Hz), 120.1 (t, *J* = 11.9 Hz), 101.0 (t, *J* = 272.2 Hz), 69.0, 20.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.27 – -63.86 (m), -89.74 – -124.91 (m).

HRMS (ESI) calculated for $C_{13}H_{10}F_5O_2$ ($[M+H]^+$): 293.0595; found: 293.0590.

(3,3-difluorocycloprop-1-en-1-yl)(4-iodophenyl)methyl acetate (2i)



This compound was obtained in 51% yield (718 mg) as pale yellow oil. Eluent: PE/EA = 10/1, R_f = 0.5.

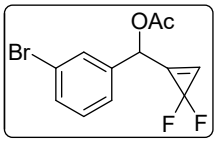
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78-7.73 (m, 2H), 7.53-7.49 (m, 1H), 7.18-7.12 (m, 2H), 6.64 (s, 1H), 2.16 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 138.3, 136.0 (t, *J* = 11.5 Hz), 134.5, 129.5, 119.8 (t, *J* = 12.0 Hz), 101.1 (t, *J* = 272.1 Hz), 95.7, 69.2, 20.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ -86.54 – -131.92 (m).

HRMS (ESI) calculated for $C_{12}H_{10}F_2IO_2$ ($[M+H]^+$): 350.9688; found: 350.9680.

(3-bromophenyl)(3,3-difluorocycloprop-1-en-1-yl)methyl acetate (2m)



This compound was obtained in 35% yield (428 mg) as pale yellow oil. Eluent: PE/EA = 10/1, R_f = 0.5.

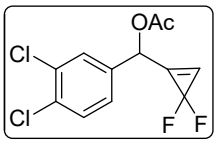
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.51 (m, 3H), 7.34 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 6.66 (s, 1H), 2.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 136.9, 136.0 (t, *J* = 11.5 Hz), 132.7, 130.7, 130.6, 126.3, 123.1, 119.9 (t, *J* = 12.0 Hz), 101.0 (t, *J* = 272.2 Hz), 68.9, 20.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ -102.91 – -103.70 (m).

HRMS (ESI) calculated for $C_{12}H_8BrF_2O_2$ ([M-H]$^-$): 300.9681; found: 300.9685.

(3,4-dichlorophenyl)(3,3-difluorocycloprop-1-en-1-yl)methyl acetate (2n)



This compound was obtained in 35% yield (411 mg) as pale yellow oil. Eluent: PE/EA = 10/1, R_f = 0.5.

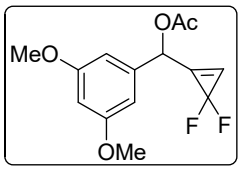
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.54 (m, 1H), 7.39 (t, *J* = 1.8 Hz, 1H), 7.29 (d, *J* = 1.8 Hz, 2H), 6.63 (s, 1H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5, 138.0, 135.8, 135.6 (t, *J* = 11.6 Hz), 129.7, 126.0, 120.4 (t, *J* = 12.0 Hz), 100.8 (t, *J* = 272.6 Hz), 68.3, 20.8.

^{19}F NMR (376 MHz, $CDCl_3$): -102.85 – -103.72 (m)

HRMS (ESI) calculated for $C_{12}H_7ClF_2O_2$ ([M-H]$^-$): 290.9797; found: 290.9799.

(3,3-difluorocycloprop-1-en-1-yl)(3,5-dimethoxyphenyl)methyl acetate (2o)



This compound was obtained in 20% yield (226 mg) as pale yellow oil. Eluent: PE/EA = 10/1, R_f = 0.3.

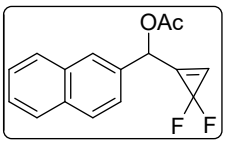
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.46 (m, 1H), 6.63 (s, 1H), 6.54 (d, *J* = 2.2 Hz, 2H), 6.47 (t, *J* = 2.2 Hz, 1H), 3.80 (s, 6H), 2.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 161.3, 136.8, 136.4 (t, *J* = 11.3 Hz), 119.4 (t, *J* = 12.0 Hz), 105.6, 101.3, 101.3 (t, *J* = 271.9 Hz), 69.6, 55.6, 20.9.

^{19}F NMR (376 MHz, $CDCl_3$): δ -102.62 – -103.76 (m)

HRMS (ESI) calculated for $C_{14}H_{15}F_2O_4$ ([M+H]$^+$): 285.0933; found: 285.0930.

(3,3-difluorocycloprop-1-en-1-yl)(naphthalen-2-yl)methyl acetate (2p)



This compound was obtained in 18% yield (198 mg) as brown solid, m.p.: 91-93 °C. Eluent: PE/EA = 10/1, R_f = 0.5.

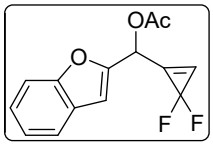
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90-7.84 (m, 4H), 7.54-7.50 (m, 3H), 7.47 (dd, *J* = 8.6, 1.6 Hz, 1H), 6.87 (s, 1H), 2.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.8, 136.6 (t, *J* = 11.4 Hz), 133.7, 133.2, 132.1, 129.2, 128.4, 127.9, 127.4, 127.1, 126.8, 124.7, 119.6 (t, *J* = 11.9 Hz), 101.3 (t, *J* = 271.9 Hz), 69.9, 20.9.

^{19}F NMR (376 MHz, $CDCl_3$): -102.48 – -103.69 (m)

HRMS (ESI) calculated for $C_{16}H_{13}F_2O_2$ ($[M+H]^+$): 275.0878; found: 275.0875.

benzofuran-2-yl(3,3-difluorocycloprop-1-en-1-yl)methyl acetate (2q)



This compound was obtained in 12% yield (127 mg) as brown oil. Eluent: PE/EA = 20/1, R_f = 0.4.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68-7.65 (m, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.37-7.32 (m, 1H), 7.29-7.24 (m, 1H), 6.93 (s, 1H), 6.88 (s, 1H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.6, 155.5, 149.3, 134.0 (t, *J* = 11.9 Hz), 127.5, 125.7, 123.5, 121.9, 121.4 (t, *J* = 11.9 Hz), 111.8, 107.6, 100.7 (t, *J* = 272.6 Hz), 63.1, 20.8.

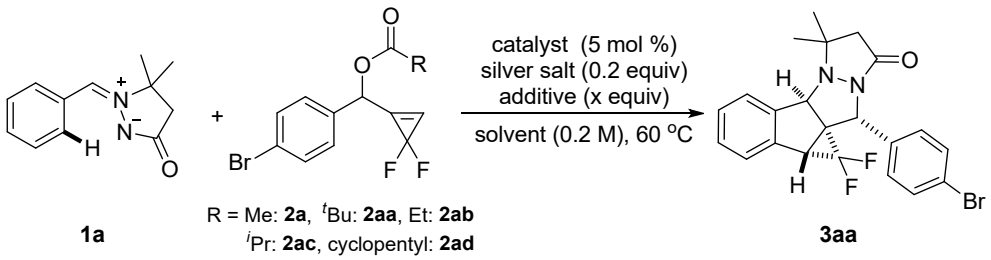
^{19}F NMR (376 MHz, $CDCl_3$): -102.65 – -103.14 (m)

HRMS (ESI) calculated for $C_{14}H_{11}F_2O_3$ ($[M+H]^+$): 265.0671; found: 265.0668.

Optimization studies:

The mixture of azomethine imine **1a** (0.1 mmol, 1.0 equiv), *gem*-difluorocyclopropenyl ester **2** (0.1 mmol, 1.0 equiv), catalyst (5 mol %), $AgSbF_6$ (20 mol %) and additive in the solvent (0.5 mL) was stirred at the specified temperature in an oil bath for 24 h without exclusion of air or moisture. Afterwards, the solvent was removed under reduced pressure and the crude product was purified by preparative TLC (eluent: DCM/MeOH = 40/1) to afford the corresponding indenopyrazolopyrazolones derivative **3aa**.

Table S1 Conditions Screening for the Synthesis of Indenopyrazolopyrazolone **3aa**[a]

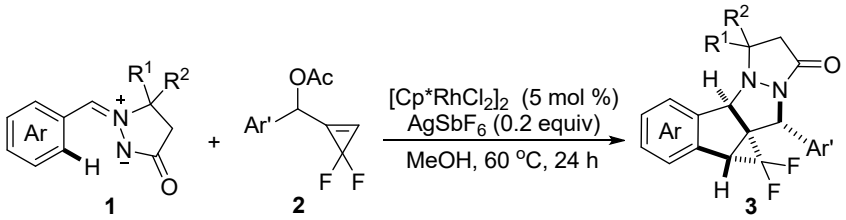


entry	R	catalyst (5 mol %)	additives (x equiv)	solvent	tem. (°C)	yield (%)[b]
1	Me	$[Cp^*RhCl_2]_2$	$AgSbF_6$ (0.2)	MeOH	60	63
2	^{t}Bu	$[Cp^*RhCl_2]_2$	$AgSbF_6$ (0.2)	MeOH	60	22
3	Et	$[Cp^*RhCl_2]_2$	$AgSbF_6$ (0.2)	MeOH	60	59
4	^{i}Pr	$[Cp^*RhCl_2]_2$	$AgSbF_6$ (0.2)	MeOH	60	43
5	cyclopentyl	$[Cp^*RhCl_2]_2$	$AgSbF_6$ (0.2)	MeOH	60	25
6	Me	$[Ru(p\text{-cymene})Cl_2]_2$	$AgSbF_6$ (0.2)	MeOH	60	trace
7	Me	$[Cp^*IrCl_2]_2$	$AgSbF_6$ (0.2)	MeOH	60	n.d.
8[c]	Me	$[Cp^*Co(CO)I_2]$	$AgSbF_6$ (0.2)	MeOH	60	n.d.
9	Me	$[Os(p\text{-cymene})Cl_2]_2$	$AgSbF_6$ (0.2)	MeOH	60	trace
10[c]	Me	$Cp^*Rh(MeCN)_3(SbF_6)_2$	-	MeOH	60	61
11	Me	$[Cp^*RhCl_2]_2$	$AgSbF_6$ (0.2)	TFE	60	42

12	Me	$[Cp^*RhCl_2]_2$	$AgSbF_6$ (0.2)	TCE	60	39
13	Me	$[Cp^*RhCl_2]_2$	$AgSbF_6$ (0.2)	dioxane	60	42
14	Me	$[Cp^*RhCl_2]_2$	$AgSbF_6$ (0.2)	DCE	60	42
15	Me	$[Cp^*RhCl_2]_2$	$AgSbF_6$ (0.2)	EtOH	60	43
16	Me	$[Cp^*RhCl_2]_2$	$AgSbF_6$ (0.2)	THF	60	37
17	Me	$[Cp^*RhCl_2]_2$	$AgSbF_6$ (0.2)	HFIP	60	13
18	Me	$[Cp^*RhCl_2]_2$	$AgSbF_6$ (0.2)	MeCN	60	trace
19	Me	$[Cp^*RhCl_2]_2$	AgOTf (0.2)	MeOH	60	44
20	Me	$[Cp^*RhCl_2]_2$	$AgNTf_2$ (0.2)	MeOH	60	48
21	Me	$[Cp^*RhCl_2]_2$	$AgBF_4$ (0.2)	MeOH	60	46
22	Me	$[Cp^*RhCl_2]_2$	AgF_2 (0.2)	MeOH	60	33
23	Me	$[Cp^*RhCl_2]_2$	AgF (0.2)	MeOH	60	27
24	Me	$[Cp^*RhCl_2]_2$	$AgSbF_6$ (0.2) $Zn(OAc)_2$ (1)	MeOH	60	43
25	Me	$[Cp^*RhCl_2]_2$	$AgSbF_6$ (0.2) HOAc (1)	MeOH	60	61
26	Me	$[Cp^*RhCl_2]_2$	$AgSbF_6$ (0.2) HOPiv (1)	MeOH	60	62
27[d]	Me	$[Cp^*RhCl_2]_2$	$AgSbF_6$ (0.2)	MeOH	60	60
28[e]	Me	$[Cp^*RhCl_2]_2$	$AgSbF_6$ (0.2)	MeOH	60	80 (75)[f]
29[e]	Me	$[Cp^*RhCl_2]_2$	$AgSbF_6$ (0.2)	MeOH	80	58
30[e]	Me	$[Cp^*RhCl_2]_2$	$AgSbF_6$ (0.2)	MeOH	100	50

[a]Reaction conditions: **1a** (0.1 mmol), **2** (0.1 mmol), catalyst (5 mol %), silver salt (0.2 equiv) and other additives (1.0 equiv) in solvent (0.2 M) for 24 h without exclusion of air or moisture. [b]^{1}H-NMR yields were reported. [c]10 mol % of catalyst was used. [d]**2a** (0.12 mmol) was used. [e]**1a** (0.12 mmol) was used. [f]Isolated yields were reported. n.d.: not detected.

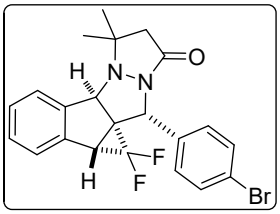
General procedure:



The mixture of azomethine imines **1** (0.24 mmol, 1.2 equiv), *gem*-difluorocyclopropenyl acetates **2** (0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (5 mol %) and $AgSbF_6$ (20 mol %) in MeOH (1.0 mL) was stirred at 60 °C in an oil bath for 24 h without exclusion of air or moisture. Afterwards, the solvent was removed under reduced pressure and the crude product was purified by preparative TLC (eluent: DCM/MeOH = 40/1) to afford the desired indenopyrazolopyrazolone products **3**.

Characterization of products 3:

11-(4-bromophenyl)-1,1-difluoro-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3aa)



This compound was obtained in 75% yield (66.5 mg) as white solid, m.p.: 228-230 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.6.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.51 (m, 2H), 7.43-7.31 (m, 6H), 4.91-4.85 (m, 2H), 3.44 (d, *J* = 13.1 Hz, 1H), 2.76 (d, *J* = 16.2 Hz, 1H), 2.42 (d, *J* = 16.2 Hz, 1H), 1.60 (s, 3H), 1.42 (s, 3H).

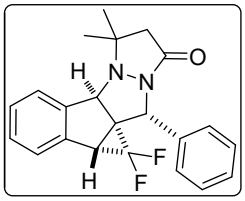
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 139.8, 137.2, 135.9, 132.1, 129.60, 129.56, 127.9, 126.13, 126.10, 122.8, 110.9 (dd, *J* = 302.5, 283.5 Hz), 63.9, 60.9, 56.9, 50.8, 48.7 (dd, *J* = 14.1, 7.9 Hz), 38.9 (t, *J* = 12.5 Hz), 27.5, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.20 (dd, J_{FF} = 165.0 Hz, J_{HF} = 14.0 Hz), -144.46 (d, *J* = 164.4 Hz).

HRMS (ESI) calculated for $C_{22}H_{20}BrF_2N_2O$ ($[M+H]^+$): 445.0722; found: 445.0723.

Another batch of **3aa** was obtained via three component, one-pot synthesis from the benzaldehyde substrate in 68% yield (60.3 mg).

1,1-difluoro-7,7-dimethyl-11-phenyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ab)



This compound was obtained in 75% yield (54.9 mg) as white solid, m.p.: 210-212 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.5.

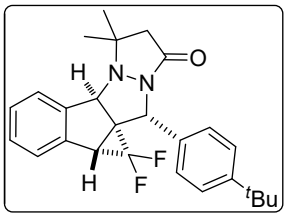
^{1}H NMR (**400 MHz**, **$CDCl_3$**): δ 7.53-7.48 (m, 2H), 7.44-7.32 (m, 7H), 4.95-4.90 (m, 2H), 3.44 (d, *J* = 13.1 Hz, 1H), 2.77 (d, *J* = 16.1 Hz, 1H), 2.41 (d, *J* = 16.1 Hz, 1H), 1.61 (s, 3H), 1.42 (s, 3H).

^{13}C NMR (**100 MHz**, **$CDCl_3$**): δ 162.7, 140.0, 137.4, 136.8, 129.5, 128.8, 128.6, 127.8, 127.8, 126.1, 111.0 (dd, *J* = 302.1, 283.7 Hz), 63.8, 60.9, 57.5, 50.8, 48.9 (dd, *J* = 13.9, 7.9 Hz), 38.9 (t, *J* = 12.5 Hz), 27.5, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.55 (dd, J_{FF} = 164.0, J_{HF} = 14.9 Hz), -144.50 (d, *J* = 161.6 Hz).

HRMS (ESI) calculated for $C_{22}H_{21}F_2N_2O$ ($[M+H]^+$): 367.1616; found: 367.1613.

11-(4-(*tert*-butyl)phenyl)-1,1-difluoro-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ac)



This compound was obtained in 73% yield (61.6 mg) as light yellow solid, m.p.: 171-173 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.5.

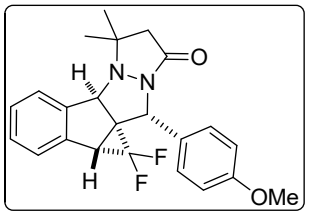
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.31 (m, 8H), 4.92 (d, *J* = 5.0 Hz, 1H), 4.90 (s, 1H), 3.42 (d, *J* = 13.1 Hz, 1H), 2.76 (d, *J* = 16.0 Hz, 1H), 2.41 (d, *J* = 16.1 Hz, 1H), 1.60 (s, 3H), 1.41 (s, 3H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6, 151.2, 140.1, 137.4, 133.6, 129.5, 127.7, 127.5, 126.1, 125.7, 111.1 (dd, *J* = 301.8, 283.7 Hz), 63.7, 60.9, 57.2, 50.9, 48.8 (dd, *J* = 13.9, 8.0 Hz), 38.9 (t, *J* = 12.5 Hz), 34.7, 31.4, 27.5, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.58 (dd，J_{FF} = 161.6 Hz, J_{HF} = 14.0 Hz), -144.50 (d, J_{FF} = 166.0 Hz, J_{HF} = 6.9 Hz).

HRMS (ESI) calculated for $C_{26}H_{29}F_2N_2O$ ($[M+H]^+$): 423.2242; found: 423.2243.

1,1-difluoro-11-(4-methoxyphenyl)-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ad)



This compound was obtained in 68% yield (53.8 mg) as yellow solid, m.p.: 187-189 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.4.

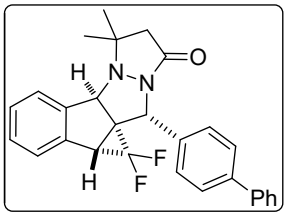
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.30 (m, 6H), 6.96-6.91 (m, 2H), 4.92 (d, *J* = 5.0 Hz, 1H), 4.89 (s, 1H), 3.80 (s, 3H), 3.43 (d, *J* = 13.1 Hz, 1H), 2.76 (d, *J* = 16.1 Hz, 1H), 2.40 (d, *J* = 16.1 Hz, 1H), 1.59 (s, 3H), 1.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7, 159.6, 140.0, 137.4, 129.5, 129.0, 128.9, 127.8, 126.1, 114.2, 111.1 (dd, *J* = 301.9, 283.6 Hz), 63.7, 60.9, 57.0, 55.3, 50.9, 48.7 (dd, *J* = 14.0, 7.8 Hz), 38.8 (t, *J* = 12.5 Hz), 27.5, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.20 (dd, J_{FF} = 163.8 Hz, J_{HF} = 13.8 Hz), -143.88 – -145.86 (m).

HRMS (ESI) calculated for $C_{23}H_{23}F_2N_2O_2$ ($[M+H]^+$): 397.1722; found: 397.1720.

11-([1,1'-biphenyl]-4-yl)-1,1-difluoro-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ae)



This compound was obtained in 76% yield (67.2 mg) as white solid, m.p.: 206-208 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.5.

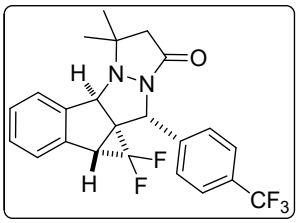
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64-7.56 (m, 6H), 7.44-7.32 (m, 7H), 4.98 (d, *J* = 4.9 Hz, 1H), 4.93 (s, 1H), 3.45 (d, *J* = 13.0 Hz, 1H), 2.77 (d, *J* = 16.1 Hz, 1H), 2.42 (d, *J* = 16.1 Hz, 1H), 1.62 (s, 3H), 1.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.8, 141.4, 140.7, 140.0, 137.3, 135.8, 129.5, 128.8, 128.3, 127.8, 127.6, 127.5, 127.2, 126.1, 111.1 (dd, *J* = 302.1, 283.5 Hz), 63.8, 60.9, 57.2, 50.9, 48.8 (dd, *J* = 13.9, 8.0 Hz), 38.9 (t, *J* = 12.5 Hz), 27.5, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.28 (dd, J_{FF} = 163.8 Hz, J_{HF} = 13.9 Hz), -143.47 – -145.30 (m).

HRMS (ESI) calculated for $C_{28}H_{25}F_2N_2O$ ($[M+H]^+$):443.1929; found: 443.1933.

1,1-difluoro-7,7-dimethyl-11-(4-(trifluoromethyl)phenyl)-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3af)



This compound was obtained in 53% yield (46.1 mg) as white solid, m.p.: 228-230 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.6.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.44-7.32 (m, 4H), 4.97 (d, *J* = 5.0 Hz, 1H), 4.90 (s, 1H), 3.47 (d, *J* = 13.1 Hz, 1H), 2.77 (d, *J* = 16.1 Hz, 1H), 2.43 (d, *J* = 16.2 Hz, 1H), 1.62 (s, 3H), 1.43 (s, 3H).

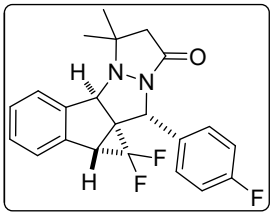
^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1, 140.7, 139.7, 137.2, 130.7 (q, *J* = 32.4 Hz), 129.7, 128.3, 128.0, 126.2 (q, *J* = 4.1 Hz), 126.0 (q, *J* = 3.5 Hz), 124.1 (q, *J* = 272.2

Hz), 110.9 (dd, J = 302.6, 283.2 Hz), 63.9, 60.9, 57.0, 50.7, 48.8 (dd, J = 14.1, 8.0 Hz), 39.0 (t, J = 12.5 Hz), 27.5, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.39 – -62.51 (m), -129.00 (dd, J_{FF} = 164.7, J_{HF} = 13.0 Hz), -144.50 (d, J = 160.0 Hz).

HRMS (ESI) calculated for $C_{23}H_{20}F_5N_2O$ ($[M+H]^+$): 435.1490; found: 435.1489.

1,1-difluoro-11-(4-fluorophenyl)-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ag)



This compound was obtained in 74% yield (56.8 mg) as white solid, m.p.: 154-155 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.5.

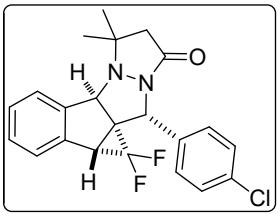
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.46 (m, 2H), 7.43-7.31 (m, 4H), 7.10 (t, J = 8.6 Hz, 2H), 4.92 (d, J = 4.9 Hz, 1H), 4.88 (s, 1H), 3.44 (d, J = 13.1 Hz, 1H), 2.76 (d, J = 16.1 Hz, 1H), 2.41 (d, J = 16.1 Hz, 1H), 1.60 (s, 3H), 1.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 162.7(d, J = 248.5 Hz), 139.9, 137.2, 132.7, 129.62, 129.56, 129.53, 127.9, 126.1 (d, J = 2.1 Hz), 115.9 (d, J = 21.7 Hz), 111.0 (dd, J = 302.3, 283.4 Hz), 63.8, 60.8, 56.8, 50.8, 48.8 (dd, J = 13.9, 7.9 Hz), 38.9 (t, J = 12.5 Hz), 27.5, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -113.15 – -113.26 (m), -129.50 (dd, J_{FF} = 162.9 Hz, J_{HF} = 14.6 Hz), -144.16 – -144.75 (m).

HRMS (ESI) calculated for $C_{22}H_{20}F_3N_2O$ ($[M+H]^+$): 385.1522; found: 385.1517.

11-(4-chlorophenyl)-1,1-difluoro-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ah)



This compound was obtained in 74% yield (59.2 mg) as white solid, m.p.: 213-214 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.5.

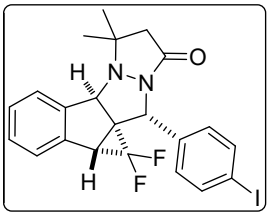
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.42 (m, 2H), 7.41-7.30 (m, 6H), 4.90 (d, *J* = 5.0 Hz, 1H), 4.87 (s, 1H), 3.44 (d, *J* = 13.1 Hz, 1H), 2.75 (d, *J* = 16.0 Hz, 1H), 2.41 (d, *J* = 16.2 Hz, 1H), 1.59 (s, 3H), 1.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 139.8, 137.2, 135.3, 134.5, 129.6, 129.2, 129.1, 127.9, 126.12, 126.09, 110.9 (dd, *J* = 302.4, 283.4 Hz), 63.8, 60.9, 56.8, 50.8, 48.7 (dd, *J* = 14.1, 7.9 Hz), 38.9 (t, *J* = 12.5 Hz), 27.5, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.24 (dd, J_{FF} = 161.4 Hz, J_{HF} = 13.8 Hz), -143.54 – -145.20 (m).

HRMS (ESI) calculated for $C_{22}H_{20}ClF_2IN_2O$ ($[M+H]^+$): 401.1227; found: 401.1226.

1,1-difluoro-11-(4-iodophenyl)-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ai)



This compound was obtained in 75% yield (73.6 mg) as white solid, m.p.: 239-241 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.6.

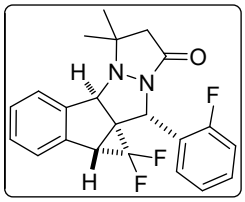
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.43-7.31 (m, 4H), 7.25 (d, *J* = 8.4 Hz, 2H), 4.88-4.85 (m, 2H), 3.44 (d, *J* = 13.1 Hz, 1H), 2.75 (d, *J* = 16.1 Hz, 1H), 2.41 (d, *J* = 16.2 Hz, 1H), 1.59 (s, 3H), 1.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 139.8, 138.0, 137.2, 136.5, 129.7, 129.6, 127.9, 126.13, 126.07, 110.9 (dd, *J* = 302.5, 283.5 Hz), 94.6, 63.8, 60.9, 57.0, 50.8, 48.6 (dd, *J* = 14.1, 7.9 Hz), 38.9 (t, *J* = 12.5 Hz), 27.5, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.12 (dd, J_{FF} = 162.4 Hz, J_{HF} = 14.5 Hz), -144.18 – -144.62 (m).

HRMS (ESI) calculated for $C_{22}H_{20}F_2IN_2O$ ($[M+H]^+$): 493.0583; found: 493.0582.

1,1-difluoro-11-(2-fluorophenyl)-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3aj)



This compound was obtained in 51% yield (39.1 mg) as white solid, m.p.: 196-198 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.6.

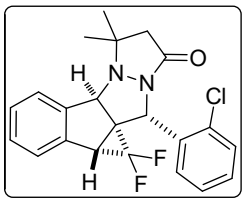
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (td, *J* = 7.5, 1.4 Hz, 1H), 7.43-7.32 (m, 5H), 7.21-7.16 (m, 1H), 7.14-7.08 (m, 1H), 5.09 (d, *J* = 3.5 Hz, 1H), 4.95 (s, 1H), 3.42 (d, *J* = 13.2 Hz, 1H), 2.77 (d, *J* = 16.1 Hz, 1H), 2.46 (d, *J* = 16.2 Hz, 1H), 1.63 (s, 3H), 1.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 160.7 (d, *J* = 247.9 Hz), 140.0, 137.5, 130.6 (d, *J* = 8.5 Hz), 129.5, 127.8, 126.1 (d, *J* = 5.6 Hz), 124.5 (d, *J* = 3.1 Hz), 123.2 (d, *J* = 11.6 Hz), 116.1 (d, *J* = 21.4 Hz), 111.0 (dd, *J* = 302.8, 283.7 Hz), 63.93, 63.91, 60.6, 50.9, 48.4 (dd, *J* = 13.9, 7.9 Hz), 38.7 (t, *J* = 12.6 Hz), 27.9, 21.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ -116.76 (d, *J* = 18.4 Hz), -131.26 (dd, J_{FF} = 162.1 Hz, J_{HF} = 14.7 Hz), -144.73 (d, *J* = 162.4 Hz).

HRMS (ESI) calculated for $C_{22}H_{20}F_3N_2O$ ($[M+H]^+$): 385.1522; found: 385.1520.

11-(2-chlorophenyl)-1,1-difluoro-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ak)



This compound was obtained in 37% yield (24.9 mg) as white solid, m.p.: 198-199 °C.

Eluent: DCM/MeOH = 40/1, R_f = 0.7.

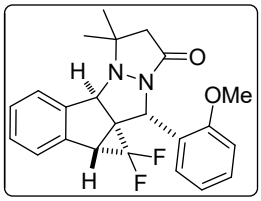
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 7.2 Hz, 1H), 7.42-7.28 (m, 7H), 5.49 (s, 1H), 4.92 (s, 1H), 3.45 (d, *J* = 12.4 Hz, 1H), 2.78 (d, *J* = 16.3 Hz, 1H), 2.50 (d, *J* = 16.2 Hz, 1H), 1.69 (s, 3H), 1.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.1, 139.8, 137.8, 130.1, 129.7, 129.5, 128.5, 127.8, 127.5, 126.5, 126.2, 110.9 (dd, *J* = 302.2, 285.2 Hz), 64.5, 64.4, 60.3, 51.0, 48.9 (dd, *J* = 13.8, 4.1 Hz), 38.5 (t, *J* = 12.5 Hz), 28.0, 21.8.

^{19}F NMR (376 MHz, $CDCl_3$): δ -131.61 (d, J_{FF} = 171.4 Hz), -143.89 (d, J_{FF} = 164.5 Hz).

HRMS (ESI) calculated for $C_{22}H_{20}ClF_2IN_2O$ ($[M+H]^+$): 401.1227; found: 401.1226.

1,1-difluoro-11-(2-methoxyphenyl)-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3al)



This compound was obtained in 32% yield (25.3 mg) as light yellow solid, m.p.: 199-200 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.5.

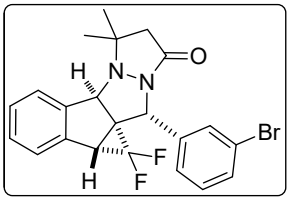
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.29 (m, 6H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 5.12 (s, 1H), 4.94 (s, 1H), 3.90 (s, 3H), 3.33 (d, *J* = 13.1 Hz, 1H), 2.76 (d, *J* = 16.1 Hz, 1H), 2.45 (d, *J* = 16.1 Hz, 1H), 1.64 (s, 3H), 1.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6, 157.1, 140.4, 138.0, 130.2, 129.3, 127.6, 126.14, 126.08, 120.8, 111.3 (dd, *J* = 302.1, 284.8 Hz), 111.0, 64.3, 60.5, 55.2, 51.2, 48.6 (dd, *J* = 13.5, 7.6 Hz), 38.4 (t, *J* = 12.4 Hz), 28.0, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -132.26 (dd, J_{FF} = 160.3 Hz, J_{HF} = 12.0 Hz), -144.86 (d, *J* = 156.2 Hz).

HRMS (ESI) calculated for $C_{23}H_{23}F_2N_2O_2$ ($[M+H]^+$): 397.1722; found: 397.1720.

11-(3-bromophenyl)-1,1-difluoro-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3am)



This compound was obtained in 71% yield (63.0 mg) as white solid, m.p.: 211-212 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.6.

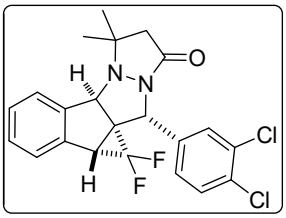
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (t, *J* = 1.7 Hz, 1H), 7.50-7.27 (m, 7H), 4.90-4.84 (m, 2H), 3.44 (d, *J* = 13.1 Hz, 1H), 2.76 (d, *J* = 16.2 Hz, 1H), 2.44 (d, *J* = 16.2 Hz, 1H), 1.62 (s, 3H), 1.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0, 139.8, 139.1, 137.2, 131.8, 130.9, 130.4, 129.6, 127.9, 126.5, 126.1, 122.8, 110.9 (dd, *J* = 302.6, 283.4 Hz), 63.8, 60.9, 56.9, 50.8, 48.8 (dd, *J* = 14.0, 8.0 Hz), 38.9 (t, *J* = 12.5 Hz), 27.5, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.26 (dd, J_{FF} = 164.1 Hz, J_{HF} = 13.6 Hz), -144.33 (dd, J_{FF} = 164.0 Hz, J_{HF} = 6.6 Hz).

HRMS (ESI) calculated for $C_{22}H_{20}BrF_2N_2O$ ($[M+H]^+$): 445.0722; found: 445.0718.

11-(3,4-dichlorophenyl)-1,1-difluoro-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3an)



This compound was obtained in 68% yield (59.0 mg) as white solid, m.p.: 210-212 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.7.

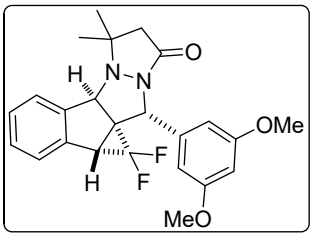
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.32 (m, 7H), 4.86 (s, 1H), 4.83 (d, *J* = 5.0 Hz, 1H), 3.45 (d, *J* = 13.1 Hz, 1H), 2.76 (d, *J* = 16.2 Hz, 1H), 2.46 (d, *J* = 16.3 Hz, 1H), 1.63 (s, 3H), 1.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3, 140.2, 139.6, 137.1, 135.4, 129.7, 129.0, 128.0, 126.5, 126.2, 126.1, 110.8 (dd, *J* = 302.8, 283.2 Hz), 63.8, 60.9, 56.5, 50.7, 48.7 (dd, *J* = 14.2, 8.1 Hz), 39.0 (t, *J* = 12.5 Hz), 27.6, 21.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.08 (dd, J_{FF} = 161.7 Hz, J_{HF} = 14.0 Hz), -144.21 (dd, J_{FF} = 164.3 Hz, J_{HF} = 7.0 Hz).

HRMS (ESI) calculated for $C_{22}H_{19}Cl_2F_2N_2O$ ($[M+H]^+$): 435.0837; found: 435.0846.

11-(3,5-dimethoxyphenyl)-1,1-difluoro-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ao)



This compound was obtained in 71% yield (60.5 mg) as light yellow solid, m.p.: 203-205 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.4.

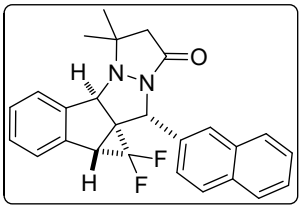
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.29 (m, 4H), 6.65 (d, *J* = 2.2 Hz, 2H), 6.44 (t, *J* = 2.2 Hz, 1H), 4.87 (s, 1H), 4.85 (d, *J* = 4.9 Hz, 1H), 3.80 (s, 6H), 3.43 (d, *J* = 13.0 Hz, 1H), 2.76 (d, *J* = 16.1 Hz, 1H), 2.42 (d, *J* = 16.2 Hz, 1H), 1.62 (s, 3H), 1.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7, 160.9, 139.9, 139.2, 137.3, 129.5, 127.7, 126.1, 111.0 (dd, *J* = 301.8, 283.6 Hz), 106.2, 100.1, 63.7, 60.9, 57.5, 55.4, 50.9, 48.8 (dd, *J* = 14.0, 8.1 Hz) 38.9 (t, *J* = 12.4 Hz), 27.5, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.66 (dd, J_{FF} = 163.9 Hz, J_{HF} = 13.7 Hz), -144.58 (dd, J_{FF} = 164.8 Hz, J_{HF} = 6.3 Hz).

HRMS (ESI) calculated for $C_{24}H_{25}F_2N_2O_3$ ($[M+H]^+$): 427.1828; found: 427.1830.

1,1-difluoro-7,7-dimethyl-11-(naphthalen-2-yl)-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ap)



This compound was obtained in 65% yield (54.1 mg) as light yellow solid, m.p.: 215-

217 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.6.

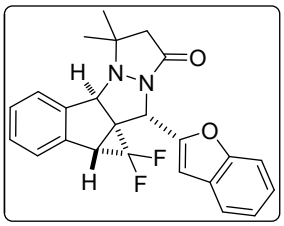
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.88-7.81 (m, 2H), 7.63 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.51-7.46 (m, 2H), 7.43-7.31 (m, 4H), 5.11 (d, *J* = 5.0 Hz, 1H), 4.99 (s, 1H), 3.47 (d, *J* = 13.0 Hz, 1H), 2.77 (d, *J* = 16.2 Hz, 1H), 2.41 (d, *J* = 16.2 Hz, 1H), 1.64 (s, 3H), 1.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 140.0, 137.4, 134.0, 133.4, 133.3, 129.5, 129.0, 128.3, 128.0, 127.9, 127.8, 126.5, 126.4, 126.1, 124.5, 111.0 (dd, *J* = 302.1, 284.0 Hz), 64.0, 60.8, 57.8, 50.9, 48.9 (dd, *J* = 13.9, 8.0 Hz), 38.9 (t, *J* = 12.5 Hz), 27.6, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.60 (dd, J_{FF} = 162.8 Hz, J_{HF} = 14.5 Hz), -144.08 – -144.63 (m).

HRMS (ESI) calculated for $C_{26}H_{23}F_2N_2O$ ($[M+H]^+$): 417.1773; found: 417.1772.

11-(benzofuran-2-yl)-1,1-difluoro-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3aq)



This compound was obtained in 79% yield (64.1 mg) as yellow solid, m.p.: 199-201 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.5.

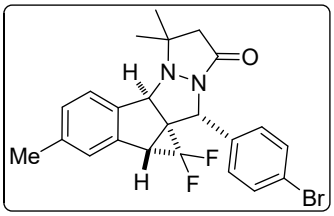
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.2 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.44-7.33 (m, 4H), 7.32-7.27 (m, 1H), 7.25-7.20 (m, 1H), 6.91 (s, 1H), 5.19 (d, *J* = 3.9 Hz, 1H), 5.05 (s, 1H), 3.49 (d, *J* = 13.0 Hz, 1H), 2.80 (d, *J* = 16.0 Hz, 1H), 2.40 (d, *J* = 16.0 Hz, 1H), 1.65 (s, 3H), 1.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0, 155.3, 150.5, 140.3, 137.1, 129.5, 128.0, 127.9, 126.1, 124.8, 123.1, 121.7, 111.5, 110.7 (dd, *J* = 302.5, 282.6 Hz), 107.1, 63.4, 62.1, 50.8, 50.7, 46.9 (dd, *J* = 14.3, 8.3 Hz), 38.8 (t, *J* = 12.5 Hz), 27.5, 21.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ -131.72 (dd, J_{FF} = 164.1 Hz, J_{HF} = 14.8 Hz), -145.88 (d, J_{FF} = 163.4 Hz).

HRMS (ESI) calculated for $C_{24}H_{21}F_2N_2O_2$ ($[M+H]^+$): 407.1566; found: 407.1561.

11-(4-bromophenyl)-1,1-difluoro-3,7,7-trimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ba)



This compound was obtained in 71% yield (65.0 mg) as white solid, m.p.: 172-174 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.5.

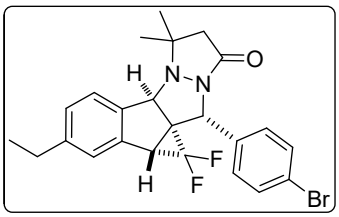
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.52 (m, 2H), 7.40-7.35 (m, 2H), 7.27-7.22 (m, 2H), 7.14 (d, *J* = 7.8 Hz, 1H), 4.88 (d, *J* = 4.9 Hz, 1H), 4.83 (s, 1H), 3.39 (d, *J* = 13.2 Hz, 1H), 2.76 (d, *J* = 16.1 Hz, 1H), 2.44-2.36 (m, 4H), 1.59 (s, 3H), 1.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 139.8, 137.3, 136.9, 136.0, 132.1, 129.6, 128.8, 126.7, 125.8, 122.7, 111.1 (dd, *J* = 302.4, 283.4 Hz), 63.5, 60.8, 56.9, 50.8, 49.0 (dd, *J* = 14.0, 7.9 Hz), 38.8 (t, *J* = 12.4 Hz), 27.5, 21.5, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$):δ -129.10 (dd, J_{FF} = 163.9, J_{HF} = 14.7 Hz), -144.53 (d, *J* = 162.7 Hz).

HRMS (ESI) calculated for $C_{23}H_{22}BrF_2N_2O$ ($[M+H]^+$): 459.0878; found: 459.0881.

11-(4-bromophenyl)-3-ethyl-1,1-difluoro-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ca)



This compound was obtained in 60% yield (56.4 mg) as yellow solid, m.p.: 125-127 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.6.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.52 (m, 2H), 7.40-7.35 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.24 (s, 1H), 7.16 (dd, *J* = 7.8, 1.4 Hz, 1H), 4.88 (d, *J* = 5.0 Hz, 1H),

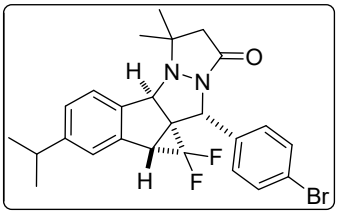
4.84 (s, 1H), 3.40 (d, J = 13.2 Hz, 1H), 2.76 (d, J = 16.1 Hz, 1H), 2.67 (q, J = 7.6 Hz, 2H), 2.40 (d, J = 16.1 Hz, 1H), 1.58 (s, 3H), 1.42 (s, 3H), 1.24 (t, J = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 146.1, 137.3, 137.1, 135.9, 132.0, 129.6, 127.7, 125.8, 125.5, 122.7, 111.0 (dd, J = 302.5, 283.3 Hz), 63.6, 60.9, 56.9, 50.8, 49.0 (dd, J = 14.1, 7.8 Hz), 38.9 (t, J = 12.4 Hz), 28.9, 27.5, 21.4, 15.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.03 (dd, J_{FF} = 161.6, J_{HF} = 14.0 Hz), -144.48 (dd, J_{FF} = 163.6, J_{HF} = 5.9 Hz).

HRMS (ESI) calculated for $C_{24}H_{24}BrF_2N_2O$ ($[M+H]^+$): 473.1035; found: 473.1035.

11-(4-bromophenyl)-1,1-difluoro-3-isopropyl-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3da)



This compound was obtained in 61% yield (59.3 mg) as yellow solid, m.p.: 173-175 ^{o}C. Eluent: DCM/MeOH = 40/1, R_f = 0.6.

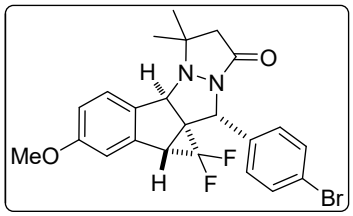
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.52 (m, 2H), 7.38 (d, J = 8.5 Hz, 2H), 7.29-7.26 (m, 2H), 7.20-7.17 (m, 1H), 4.88 (d, J = 4.9 Hz, 1H), 4.84 (s, 1H), 3.41 (d, J = 13.2 Hz, 1H), 2.91-2.87 (m, 1H), 2.76 (d, J = 16.1 Hz, 1H), 2.40 (d, J = 16.2 Hz, 1H), 1.58 (s, 3H), 1.43 (s, 3H), 1.25 (d, J = 7.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 150.7, 137.2, 134.0, 132.0, 129.6, 126.3, 125.8, 124.15, 122.7, 111.0 (dd, J = 302.5, 283.5 Hz), 63.6, 60.9, 57.0, 50.8, 49.1 (dd, J = 13.9, 7.9 Hz), 38.9 (t, J = 12.4 Hz), 34.2, 27.5, 24.1, 24.0, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -128.95 (dd, J_{FF} = 163.2, J_{HF} = 14.4 Hz), -143.01 – -146.13 (m).

HRMS (ESI) calculated for $C_{25}H_{26}BrF_2N_2O$ ($[M+H]^+$): 487.1191; found: 487.1188.

11-(4-bromophenyl)-1,1-difluoro-3-methoxy-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-c]pyrazolo[1,2-a]pyrazol-9-one (3ea)



This compound was obtained in 53% yield (50.5 mg) as light yellow solid, m.p.: 156-158 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.4.

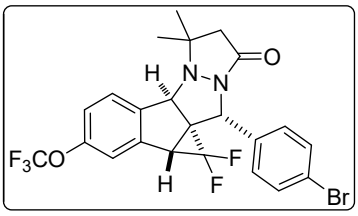
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.52 (m, 2H), 7.40-7.35 (m, 2H), 7.25 (d, *J* = 8.4 Hz, 1H), 6.92 (d, *J* = 2.3 Hz, 1H), 6.86 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.87 (d, *J* = 4.9 Hz, 1H), 4.81 (s, 1H), 3.82 (s, 3H), 3.39 (d, *J* = 13.2 Hz, 1H), 2.75 (d, *J* = 16.1 Hz, 1H), 2.40 (d, *J* = 16.1 Hz, 1H), 1.57 (s, 3H), 1.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0, 160.9, 138.9, 135.9, 132.0, 131.8, 129.5, 126.8, 122.7, 114.0, 111.2, 111.0 (dd, *J* = 304.2, 284.3 Hz), 63.2, 60.7, 56.9, 55.6, 50.8, 49.5 (dd, *J* = 13.9, 7.8 Hz), 38.9 (t, *J* = 12.5 Hz), 27.5, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.02 (dd, J_{FF} = 163.5, J_{HF} = 14.1 Hz), -143.65 – -145.36 (m).

HRMS (ESI) calculated for $C_{23}H_{22}BrF_2N_2O_2$ ($[M+H]^+$): 475.0827; found: 475.0823.

11-(4-bromophenyl)-1,1-difluoro-7,7-dimethyl-3-(trifluoromethoxy)-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3fa)



This compound was obtained in 48% yield (50.7 mg) as light yellow solid, m.p.: 176-178 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.6.

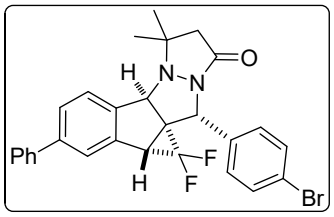
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.1 Hz, 2H), 7.42-7.34 (m, 3H), 7.30-7.26 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 4.89 (d, *J* = 4.8 Hz, 1H), 4.85 (s, 1H), 3.45 (d, *J* = 12.7 Hz, 1H), 2.76 (d, *J* = 16.2 Hz, 1H), 2.42 (d, *J* = 16.2 Hz, 1H), 1.59 (s, 3H), 1.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 150.1, 139.5, 138.5, 135.5, 132.2, 129.5, 127.2, 122.9, 120.6, 120.4 (q, J = 257.8 Hz), 118.8, 110.6 (dd, J = 302.6, 284.1 Hz), 63.1, 61.0, 56.9, 50.7, 49.6 (dd, J = 13.9, 8.0 Hz), 38.6 (t, J = 12.7 Hz), 27.6, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -57.51 – -57.83 (m), -129.40 (dd, J_{FF} = 165.1, J_{HF} = 13.3 Hz), -143.62 – -144.12 (m).

HRMS (ESI) calculated for $C_{23}H_{19}BrF_5N_2O_2$ ($[M+H]^+$): 529.0545; found: 529.0550.

11-(4-bromophenyl)-1,1-difluoro-7,7-dimethyl-3-phenyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ga)



This compound was obtained in 66% yield (68.8 mg) as light yellow solid, m.p.: 213-215 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.5.

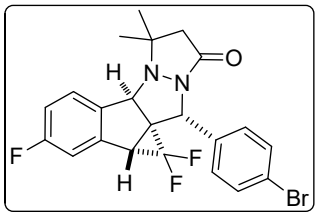
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.52 (m, 6H), 7.48-7.35 (m, 6H), 4.94-4.88 (m, 2H), 3.49 (d, J = 13.0 Hz, 1H), 2.78 (d, J = 16.2 Hz, 1H), 2.43 (d, J = 16.2 Hz, 1H), 1.61 (s, 3H), 1.45 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0, 143.0, 140.3, 138.7, 138.1, 135.8, 132.1, 129.6, 129.0, 127.9, 127.4, 127.0, 126.3, 124.8, 122.8, 111.0 (dd, J = 302.2, 283.8 Hz), 63.6, 61.0, 57.0, 50.8, 49.2 (dd, J = 14.0, 7.9 Hz), 38.9 (t, J = 12.5 Hz), 27.6, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.10 (dd, J_{FF} = 162.9 Hz, J_{HF} = 14.1 Hz), -144.12 (dd, J_{FF} = 162.9 Hz, J_{HF} = 5.9 Hz).

HRMS (ESI) calculated for $C_{28}H_{24}BrF_2N_2O$ ($[M+H]^+$): 521.1035; found: 521.1032.

11-(4-bromophenyl)-1,1,3-trifluoro-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ha)



This compound was obtained in 60% yield (55.4 mg) as white solid, m.p.: 218-220 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.5.

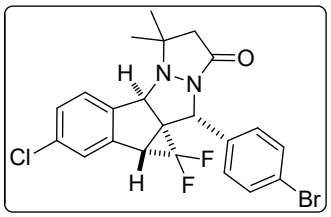
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.52 (m, 2H), 7.39-7.35 (m, 2H), 7.32 (dd, *J* = 8.4, 4.9 Hz, 1H), 7.11 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.03 (td, *J* = 8.6, 2.4 Hz, 1H), 4.88 (d, *J* = 4.9 Hz, 1H), 4.82 (s, 1H), 3.41 (d, *J* = 12.9 Hz, 1H), 2.75 (d, *J* = 16.2 Hz, 1H), 2.41 (d, *J* = 16.2 Hz, 1H), 1.58 (s, 3H), 1.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.5 (d, *J* = 247.7 Hz), 162.9, 139.6 (d, *J* = 9.2 Hz), 135.6, 132.1, 129.5, 127.3 (d, *J* = 9.3 Hz), 122.9, 115.2 (d, *J* = 22.8 Hz), 113.5 (d, *J* = 23.5 Hz), 110.7 (dd, *J* = 304.0, 284.9 Hz), 63.0, 60.9, 56.8, 50.7, 49.6 (dd, *J* = 13.8, 7.9 Hz), 38.6 (t, *J* = 11.7 Hz), 27.6, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -111.43 (s), -129.35 (dd, J_{FF} = 162.2 Hz, J_{HF} = 10.9 Hz), -144.11 (d, *J* = 163.0 Hz).

HRMS (ESI) calculated for $C_{22}H_{19}BrF_3N_2O$ ($[M+H]^+$): 463.0627; found:463.0623.

11-(4-bromophenyl)-3-chloro-1,1-difluoro-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ia)



This compound was obtained in 68% yield (65.0 mg) as white solid, m.p.: 198-200 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.6.

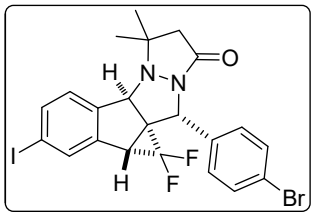
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.52 (m, 2H), 7.41 (d, *J* = 1.3 Hz, 1H), 7.38-7.35 (m, 2H), 7.34-7.28 (m, 2H), 4.88 (d, *J* = 4.9 Hz, 1H), 4.82 (s, 1H), 3.42 (d, *J* = 12.9 Hz, 1H), 2.75 (d, *J* = 16.2 Hz, 1H), 2.42 (d, *J* = 16.2 Hz, 1H), 1.58 (s, 3H), 1.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 139.2, 138.4, 135.5, 132.1, 129.5, 128.2, 127.1, 126.4, 122.9, 110.6 (dd, J = 302.4, 284.0 Hz), 63.2, 60.9, 56.8, 50.7, 49.3 (dd, J = 13.8, 8.0 Hz), 38.5 (t, J = 12.7 Hz), 27.6, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.43 (dd, J_{FF} = 161.2 Hz, J_{HF} = 12.1 Hz), -143.97 (d, J = 164.0 Hz).

HRMS (ESI) calculated for $C_{22}H_{19}BrClF_2N_2O$ ($[M+H]^+$): 479.0332; found: 479.0334.

11-(4-bromophenyl)-1,1-difluoro-3-iodo-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ja)



This compound was obtained in 66% yield (75.2 mg) as white solid, m.p.: 214-215 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.6.

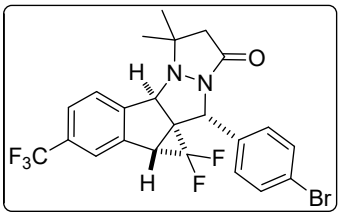
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.67 (d, J = 7.1 Hz, 1H), 7.54 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 7.9 Hz, 1H), 4.87 (d, J = 5.0 Hz, 1H), 4.80 (s, 1H), 3.41 (d, J = 12.8 Hz, 1H), 2.75 (d, J = 16.2 Hz, 1H), 2.41 (d, J = 16.2 Hz, 1H), 1.58 (s, 3H), 1.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 139.6, 137.0, 135.6, 135.2, 132.1, 129.5, 127.6, 122.9, 110.6 (dd, J = 302.4, 284.2 Hz), 95.1, 63.4, 60.9, 56.8, 50.7, 49.0 (dd, J = 13.8, 7.8 Hz), 38.3 (t, J = 12.6 Hz), 27.6, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.39 (dd, J_{FF} = 166.9 Hz, J_{HF} = 11.4 Hz), -143.93 (d, J = 164.1 Hz).

HRMS (ESI) calculated for $C_{22}H_{19}BrF_2IN_2O$ ($[M+H]^+$): 570.9688; found: 570.9686.

11-(4-bromophenyl)-1,1-difluoro-7,7-dimethyl-3-(trifluoromethyl)-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ka)



This compound was obtained in 47% yield (48.1 mg) as white solid, m.p.: 191-193 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.6.

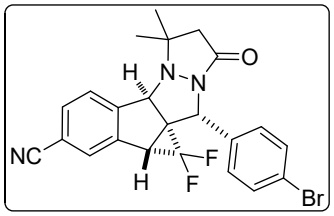
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 1H), 7.63-7.60 (m, 1H), 7.57-7.53 (m, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.39-7.36 (m, 2H), 4.92-4.88 (m, 2H), 3.50 (d, *J* = 10.9 Hz, 1H), 2.76 (d, *J* = 16.1 Hz, 1H), 2.43 (d, *J* = 16.2 Hz, 1H), 1.61 (s, 3H), 1.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 143.7, 138.3, 135.4, 132.2, 129.5, 126.5, 125.1, 123.8 (q, *J* = 274.2 Hz), 123.2 (q, *J* = 2.5 Hz), 123.0, 110.5 (dd, *J* = 301.6, 284.6 Hz), 63.4, 61.1, 56.8, 50.7, 49.1 (dd, *J* = 13.8, 7.6 Hz), 38.6 (t, *J* = 12.7 Hz), 27.6, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.61 (dd, J_{FF} = 164.2 Hz, J_{HF} = 11.5 Hz), -143.75 (d, *J* = 164.2 Hz).

HRMS (ESI) calculated for $C_{23}H_{19}BrF_5N_2O$ ($[M+H]^+$): 513.0595; found: 513.0594.

11-(4-bromophenyl)-1,1-difluoro-7,7-dimethyl-9-oxo-1a,5b,8,9-tetrahydro-1*H*,7*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazole-3-carbonitrile (3la)



This compound was obtained in 31% yield (29.1 mg) as white solid, m.p.: 197-199 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.4.

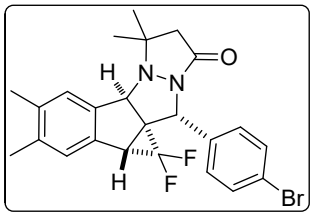
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 4.93-4.85 (m, 2H), 3.49 (d, *J* = 12.5 Hz, 1H), 2.75 (d, *J* = 16.2 Hz, 1H), 2.43 (d, *J* = 16.3 Hz, 1H), 1.60 (s, 3H), 1.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0, 144.9, 138.9, 135.2, 132.2, 131.9, 129.7, 129.5, 127.0, 123.1, 118.1, 113.8, 110.3 (dd, J = 302.1, 285.1 Hz), 63.6, 61.1, 56.8, 50.7, 49.1 (dd, J = 13.7, 8.2 Hz), 38.4 (t, J = 12.6 Hz), 27.7, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.67 (dd, J_{FF} = 164.3 Hz, J_{HF} = 15.1 Hz), -143.42 (d, J_{FF} = 165.4 Hz).

HRMS (ESI) calculated for $C_{23}H_{19}BrF_2N_3O$ ($[M+H]^+$): 470.0674; found: 470.0673.

11-(4-bromophenyl)-1,1-difluoro-3,4,7,7-tetramethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ma)



This compound was obtained in 49% yield (46.2 mg) as light yellow solid, m.p.: 178-180 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.5.

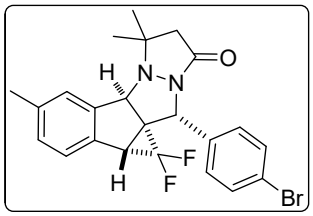
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.51 (m, 2H), 7.38 (d, J = 8.2 Hz, 2H), 7.18 (s, 1H), 7.11 (s, 1H), 4.87 (d, J = 4.8 Hz, 1H), 4.80 (s, 1H), 3.37 (d, J = 13.0 Hz, 1H), 2.76 (d, J = 16.1 Hz, 1H), 2.41 (d, J = 16.1 Hz, 1H), 2.30-2.25 (m, 6H), 1.59 (s, 3H), 1.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 138.4, 137.5, 136.5, 136.0, 134.7, 132.1, 129.6, 127.1, 127.0, 122.7, 111.2 (dd, J = 302.4, 284.0 Hz), 63.7, 60.9, 57.0, 50.8, 49.0 (dd, J = 13.9, 7.9 Hz), 38.7 (t, J = 12.4 Hz), 27.6, 21.4, 20.2, 20.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.09 (dd，J_{FF} = 163.3 Hz, J_{HF} = 14.2 Hz), -144.79 (d, J = 162.5 Hz).

HRMS (ESI) calculated for $C_{24}H_{24}BrF_2N_2O$ ($[M+H]^+$): 473.1035; found: 473.1032.

11-(4-bromophenyl)-1,1-difluoro-4,7,7-trimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3na)



This compound was obtained in 59% yield (54.0 mg) as light yellow solid, m.p.: 189-191 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.5.

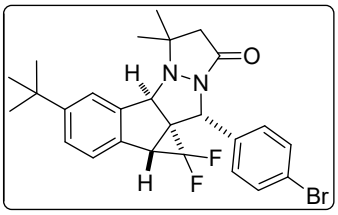
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.52 (m, 2H), 7.40-7.36 (m, 2H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.20-7.16 (m, 2H), 4.88 (d, *J* = 5.0 Hz, 1H), 4.82 (s, 1H), 3.39 (d, *J* = 13.0 Hz, 1H), 2.76 (d, *J* = 16.1 Hz, 1H), 2.44-2.38 (m, 4H), 1.59 (s, 3H), 1.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 140.0, 137.9, 135.9, 134.2, 132.1, 130.4, 129.6, 126.8, 125.9, 122.7, 111.0 (dd, *J* = 302.3, 283.6 Hz), 63.8, 60.9, 56.9, 50.8, 48.8 (dd, *J* = 13.9, 8.0 Hz), 38.6 (t, *J* = 12.5 Hz), 27.6, 21.6, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.27 (dd, J_{FF} = 162.3 Hz, J_{HF} = 13.6 Hz), -144.70 (d, *J* = 167.2 Hz).

HRMS (ESI) calculated for $C_{23}H_{22}BrF_2N_2O$ ($[M+H]^+$): 459.0878; found: 459.0880.

11-(4-bromophenyl)-4-(tert-butyl)-1,1-difluoro-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3oa)



This compound was obtained in 52% yield (52.0 mg) as light yellow solid, m.p.: 227-229 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.6.

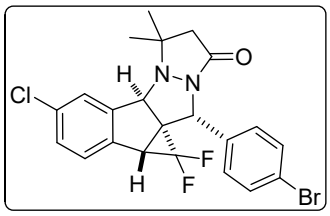
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.52 (m, 2H), 7.43-7.35 (m, 4H), 7.32 (d, *J* = 8.0 Hz, 1H), 4.91-4.84 (m, 2H), 3.39 (d, *J* = 12.9 Hz, 1H), 2.76 (d, *J* = 16.1 Hz, 1H), 2.41 (d, *J* = 16.2 Hz, 1H), 1.61 (s, 3H), 1.43 (s, 3H), 1.32 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 151.2, 139.8, 136.0, 134.1, 132.1, 129.6, 126.7, 125.5, 123.2, 122.7, 111.1 (dd, J = 302.8, 283.2 Hz), 64.0, 61.0, 57.0, 50.8, 49.1 (dd, J = 14.2, 7.7 Hz), 38.7 (t, J = 12.4 Hz), 34.9, 31.5, 27.4, 21.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ -128.93 (dd, J_{FF} = 162.0, J_{HF} = 13.4 Hz), -144.37 (d, J = 162.0 Hz).

HRMS (ESI) calculated for $C_{26}H_{28}BrF_2N_2O$ ($[M+H]^+$): 501.1348; found: 501.1347.

11-(4-bromophenyl)-4-chloro-1,1-difluoro-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3pa)



This compound was obtained in 53% yield (50.6 mg) as light yellow solid, m.p.: 238-240 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.5.

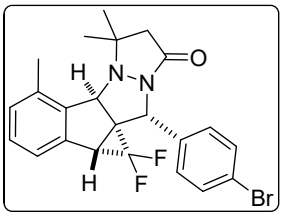
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, J = 8.4 Hz, 2H), 7.39-7.32 (m, 5H), 4.88 (d, J = 4.9 Hz, 1H), 4.81 (s, 1H), 3.41 (d, J = 12.7 Hz, 1H), 2.76 (d, J = 16.2 Hz, 1H), 2.42 (d, J = 16.2 Hz, 1H), 1.58 (s, 3H), 1.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 141.7, 135.8, 135.6, 133.8, 132.1, 129.9, 129.5, 127.2, 126.5, 122.9, 110.6 (dd, J = 302.4, 284.4 Hz), 63.5, 61.0, 56.9, 50.8, 49.2 (dd, J = 13.9, 8.1 Hz), 38.3 (t, J = 12.7 Hz), 27.7, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.46 (dd, J_{FF} = 161.8, J_{HF} = 12.3 Hz), -144.11 (d, J = 163.4 Hz).

HRMS (ESI) calculated for $C_{22}H_{19}BrClF_2N_2O$ ($[M+H]^+$): 479.0332; found: 479.0332.

11-(4-bromophenyl)-1,1-difluoro-5,7,7-trimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3qa)



This compound was obtained in 47% yield (43.0 mg) as yellow solid, m.p.: 174-176 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.5.

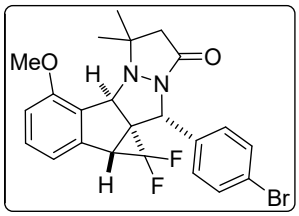
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57-7.52 (m, 2H), 7.45-7.40 (m, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 4.92 (d, *J* = 3.6 Hz, 1H), 4.87 (s, 1H), 3.44 (d, *J* = 13.0 Hz, 1H), 2.69 (d, *J* = 16.0 Hz, 1H), 2.51 (s, 3H), 2.41 (d, *J* = 16.1 Hz, 1H), 1.61 (s, 3H), 1.26 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.7, 137.8, 137.4, 136.6, 134.7, 132.1, 130.3, 130.0, 129.5, 123.8, 122.7, 111.7 (dd, *J* = 303.3, 281.6 Hz), 62.6, 60.9, 56.6, 51.8, 45.4 (dd, *J* = 14.5, 8.9 Hz), 39.3 (t, *J* = 12.3 Hz), 25.5, 21.1, 20.7.

^{19}F NMR (376 MHz, $CDCl_3$): δ -130.34 (dd, J_{FF} = 164.6 Hz, J_{HF} = 13.5 Hz), -145.86 (d, *J* = 164.2 Hz).

HRMS (ESI) calculated for $C_{23}H_{22}BrF_2N_2O$ ($[M+H]^+$): 459.0878; found: 459.0876.

11-(4-bromophenyl)-1,1-difluoro-5-methoxy-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ra)



This compound was obtained in 65% yield (61.6 mg) as light yellow solid, m.p.: 220-222 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.6.

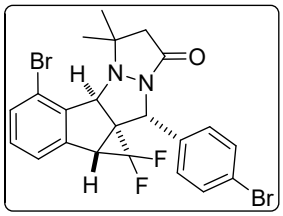
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.42-7.33 (m, 3H), 7.02 (d, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 4.92 (s, 1H), 4.86 (d, *J* = 4.5 Hz, 1H), 3.89 (s, 3H), 3.43 (d, *J* = 13.2 Hz, 1H), 2.74 (d, *J* = 16.3 Hz, 1H), 2.42 (d, *J* = 16.3 Hz, 1H), 1.63 (s, 3H), 1.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.3, 155.9, 139.2, 136.4, 132.0, 131.6, 129.5, 127.0, 122.7, 118.4, 111.2 (dd, *J* = 303.2, 281.8 Hz), 110.0, 61.3, 60.8, 56.6, 54.8, 51.3, 47.6 (dd, *J* = 14.3, 8.0 Hz), 39.0 (t, *J* = 12.2 Hz), 25.6, 20.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.81 (dd, J_{FF} = 162.9, J_{HF} = 14.1 Hz), -145.34 (d, *J* = 163.3 Hz).

HRMS (ESI) calculated for $C_{23}H_{22}BrF_2N_2O_2$ ($[M+H]^+$): 475.0827; found: 475.0834.

5-bromo-11-(4-bromophenyl)-1,1-difluoro-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3sa)



This compound was obtained in 35% yield (36.5 mg) as light yellow solid, m.p.: 218-220 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.4.

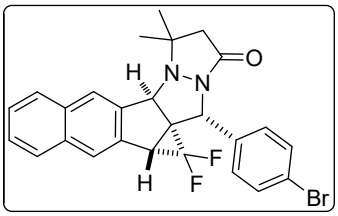
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.53 (m, 2H), 7.51-7.46 (m, 1H), 7.44-7.37 (m, 3H), 7.30-7.25 (m, 1H), 4.92-4.89 (m, 2H), 3.51 (d, *J* = 12.7 Hz, 1H), 2.70 (d, *J* = 16.1 Hz, 1H), 2.40 (d, *J* = 16.1 Hz, 1H), 1.72 (s, 3H), 1.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.7, 139.5, 139.4, 136.2, 132.6, 132.2, 131.6, 129.5, 125.5, 122.9, 119.9, 111.3 (dd, *J* = 303.7, 282.6 Hz), 64.3, 61.2, 56.3, 51.7, 44.9 (dd, *J* = 14.6, 9.1 Hz), 39.6 (t, *J* = 12.5 Hz), 25.7, 20.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ -130.71 (dd, J_{FF} = 164.5, J_{HF} = 15.1 Hz), -145.23 (d, *J* = 164.6 Hz).

HRMS (ESI) calculated for $C_{22}H_{19}Br_2F_2N_2O$ ($[M+H]^+$): 522.9827; found: 522.9835.

2-(4-bromophenyl)-1,1-difluoro-6,6-dimethyl-5,6,7a,13b-tetrahydro-1*H*,2*H*,4*H*-benzo[5,6]cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-4-one (3ta)



This compound was obtained in 40% yield (36.0 mg) as yellow solid, m.p.: 201-203 ^{o}C. Eluent: DCM/MeOH = 40/1, R_f = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89-7.84 (m, 3H), 7.81 (s, 1H), 7.58-7.51 (m, 4H), 7.44-7.40 (m, 2H), 5.03 (s, 1H), 4.95 (d, *J* = 4.8 Hz, 1H), 3.57 (d, *J* = 13.0 Hz, 1H), 2.76 (d, *J* = 16.1 Hz, 1H), 2.44 (d, *J* = 16.2 Hz, 1H), 1.68 (s, 3H), 1.43 (s, 3H).

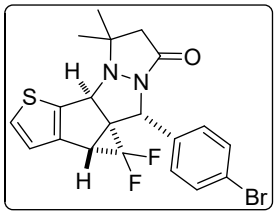
^{13}C NMR (100 MHz, $CDCl_3$): δ 162.9, 137.9, 135.9, 135.0, 134.0, 132.8, 132.1, 129.6, 128.2, 128.0, 127.0, 126.5, 125.8, 125.1, 122.8, 111.1 (dd, *J* = 302.6, 284.1 Hz), 63.4, 61.0, 57.0, 50.9, 49.4 (dd, *J* = 13.8, 7.8 Hz), 38.6 (t, *J* = 12.4 Hz), 27.7, 21.6.

^{19}F NMR (376 MHz, $CDCl_3$): δ -128.83 (dd, J_{FF} = 164.0 Hz, J_{HF} = 15.0 Hz), -143.11 (d, *J* = 165.4 Hz).

HRMS (ESI) calculated for $C_{20}H_{18}BrF_2N_2OS$ ($[M+H]^+$): 451.0286; found: 451.0282.

Another batch of **3ta** was obtained via three component, one-pot synthesis from the 2-naphthaldehyde substrate in 33% yield (29.7 mg).

10-(4-bromophenyl)-1,1-difluoro-6,6-dimethyl-1a,4b,6,7-tetrahydro-1*H*,8*H*,10*H*-cyclopropa[2,3]thieno[3',2':4,5]cyclopenta[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-8-one (3ua)



This compound was obtained in 26% yield (23.4 mg) as yellow solid, m.p.: 211-213 ^{o}C. Eluent: DCM/MeOH = 40/1, R_f = 0.5.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 5.0 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 5.0 Hz, 1H), 4.92 (d, *J* = 5.3 Hz, 1H), 4.78 (d, *J*

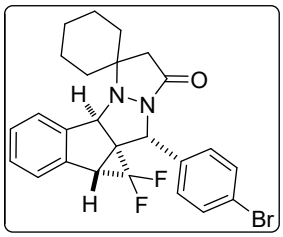
= 1.1 Hz, 1H), 3.31 (d, *J* = 12.3 Hz, 1H), 2.77 (d, *J* = 16.0 Hz, 1H), 2.40 (d, *J* = 16.1 Hz, 1H), 1.53 (s, 3H), 1.51 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 141.9, 135.6, 132.1, 131.8, 129.5, 122.9, 122.3, 110.8 (dd, *J* = 303.9, 285.8 Hz), 60.9, 59.0, 57.5, 55.7 (dd, *J* = 14.0, 7.7 Hz), 50.4, 34.9 (t, *J* = 13.4 Hz), 27.1, 21.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ -128.80 (dd, J_{FF} = 160.9 Hz, J_{HF} = 12.5 Hz), -144.97 (d, J_{FF} = 161.3 Hz).

HRMS (ESI) calculated for $C_{20}H_{18}BrF_2N_2OS$ ($[M+H]^+$): 451.0286; found: 451.0282.

11'-(4-bromophenyl)-1',1'-difluoro-1a',5b'-dihydro-1'*H*,11'*H*-spiro[cyclohexane-1,7'-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol]-9'(8'*H*)-one (3va)



This compound was obtained in 34% yield (32.9 mg) as white solid, m.p.: 245-247 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.5.

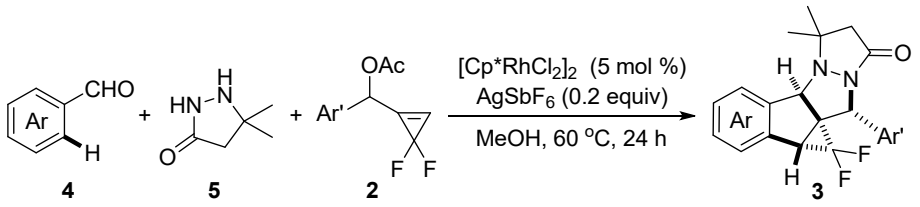
^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 7.0 Hz, 1H), 7.35-7.25 (m, 5H), 4.94 (s, 1H), 4.78 (d, *J* = 5.2 Hz, 1H), 3.38 (d, *J* = 13.3 Hz, 1H), 2.68 (d, *J* = 16.5 Hz, 1H), 2.41 (d, *J* = 16.5 Hz, 1H), 2.14-2.05 (m, 1H), 1.97-1.85 (m, 2H), 1.71-1.61 (m, 3H), 1.45-1.35 (m, 1H), 1.21-1.10 (m, 2H), 0.83-0.70 (m, 1H).

^{13}C NMR (100 MHz, CD_2Cl_2): δ 162.8, 140.5, 138.0, 137.1, 132.3, 130.1, 129.9, 128.2, 127.0, 126.4, 122.8, 111.8 (dd, *J* = 302.0, 283.2 Hz), 64.2, 63.6, 56.9, 49.0 (dd, *J* = 13.9, 7.8 Hz), 46.1, 39.1 (t, *J* = 12.5 Hz), 38.8, 30.0, 26.4, 24.6, 23.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.27 (dd，J_{FF} = 161.8 Hz, J_{HF} = 14.1 Hz), -144.70 (dd，J_{FF} = 165.6 Hz, J_{HF} = 7.3 Hz).

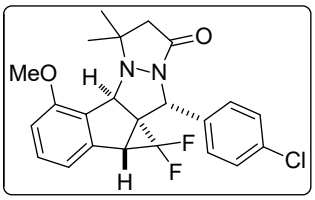
HRMS (ESI) calculated for $C_{25}H_{24}BrF_2N_2O$ ($[M+H]^+$): 485.1035; found: 485.1032.

Three component, one-pot synthesis of products 3:



The mixture of benzaldehyde (0.24 mmol, 1.2 equiv), 5,5-dimethylpyrazolidin-3-one (0.24 mmol, 1.2 equiv), *gem*-difluorocyclopropenyl acetate **2** (0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (5 mol %) and $AgSbF_6$ (20 mol %) in MeOH (1.0 mL) was stirred at 60 °C in an oil bath for 24 h without exclusion of air or moisture. Afterwards, the solvent was removed under reduced pressure and the crude product was purified by preparative TLC (eluent: DCM/MeOH = 40/1) to afford the corresponding indenopyrazolopyrazolones products **3**.

11-(4-chlorophenyl)-1,1-difluoro-5-methoxy-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3wa)



This compound was obtained in 52% yield (45.2 mg) as white solid, m.p.: 240-242 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.4.

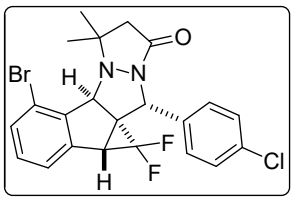
^{1}H NMR (**400 MHz, $CDCl_3$**): δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.40-7.33 (m, 3H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 4.92 (s, 1H), 4.88 (d, *J* = 4.5 Hz, 1H), 3.89 (s, 3H), 3.43 (d, *J* = 13.3 Hz, 1H), 2.74 (d, *J* = 16.3 Hz, 1H), 2.41 (d, *J* = 16.2 Hz, 1H), 1.62 (s, 3H), 1.31 (s, 3H).

^{13}C NMR (**100 MHz**, **$CDCl_3$**): δ 163.3, 156.0, 139.2, 135.9, 134.4, 131.6, 129.2, 129.1, 127.1, 118.4, 111.2 (dd, *J* = 303.1, 281.8 Hz), 110.0, 61.3, 60.7, 56.6, 54.8, 51.3, 47.7 (dd, *J* = 14.1, 8.1 Hz), 39.0 (t, *J* = 12.3 Hz), 25.6, 20.5.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.81 (dd, J_{FF} = 163.0 Hz, J_{HF} = 14.2 Hz), -145.31 (d, J_{FF} = 163.5 Hz).

HRMS (ESI) calculated for $C_{23}H_{22}ClF_2N_2O_2$ ($[M+H]^+$): 431.1332; found: 431.1331.

5-bromo-11-(4-chlorophenyl)-1,1-difluoro-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3xa)



This compound was obtained in 39% yield (37.2 mg) as white solid, m.p.: 168-170 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.4.

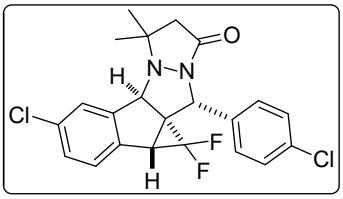
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.44 (m, 3H), 7.42-7.35 (m, 3H), 7.30-7.27 (m, 1H), 4.91-4.89 (m, 2H), 3.51 (d, *J* = 12.7 Hz, 1H), 2.70 (d, *J* = 16.1 Hz, 1H), 2.40 (d, *J* = 16.1 Hz, 1H), 1.72 (s, 3H), 1.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8, 139.6, 135.7, 134.7, 132.6, 131.6, 129.24, 129.18, 125.5, 119.9, 111.3 (dd, *J* = 303.6, 283.6 Hz), 64.3, 61.2, 56.3, 51.7, 44.9 (dd, *J* = 14.6, 9.1 Hz), 39.6 (t, *J* = 12.5 Hz), 25.7, 20.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ -130.71 (dd, J_{FF} = 164.8 Hz, J_{HF} = 15.5 Hz), -145.22 (d, J_{FF} = 165.7 Hz).

HRMS (ESI) calculated for $C_{22}H_{19}BrClF_2N_2O$ ($[M+H]^+$): 479.0332; found: 479.0329.

5-chloro-11-(4-chlorophenyl)-1,1-difluoro-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ya)



This compound was obtained in 37% yield (32.1 mg) as white solid, m.p.: 210-212 °C. Eluent: DCM/MeOH = 40/1, R_f = 0.5.

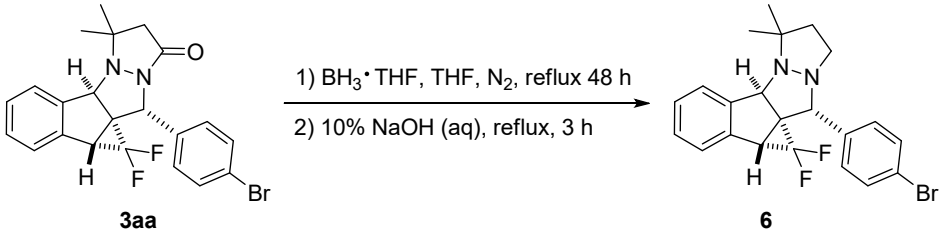
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.32 (m, 7H), 4.89 (d, *J* = 4.9 Hz, 1H), 4.81 (s, 1H), 3.40 (d, *J* = 12.7 Hz, 1H), 2.75 (d, *J* = 16.2 Hz, 1H), 2.42 (d, *J* = 16.2 Hz, 1H), 1.58 (s, 3H), 1.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.0, 141.8, 135.9, 135.1, 134.7, 133.8, 129.9, 129.2, 127.2, 126.5, 110.7 (dd, J = 302.0, 284.5 Hz), 63.5, 61.0, 56.9, 50.8, 49.3 (dd, J = 13.8, 8.1 Hz), 38.4 (t, J = 12.7 Hz), 27.7, 21.4.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.47 (dd, J_{FF} = 166.3 Hz, J_{HF} = 12.2 Hz), -144.08 (d, J_{FF} = 163.2 Hz).

HRMS (ESI) calculated for $C_{22}H_{19}Cl_2F_2N_2O$ ($[M+H]^+$): 435.0837; found: 435.0833.

Derivatizations of the product 3aa:



3aa **6**

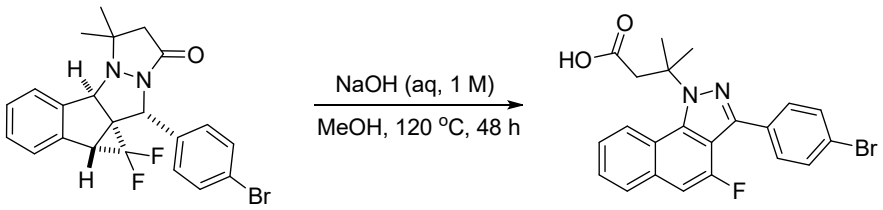
To an ice-cooled solution of **3aa** in dry THF (0.25 mL) was added the 1 M solution of boran-tetrahydrofuran complex (BH_3•THF, 1.0 mL, 1 mmol) in THF slowly under an atmosphere of N_2. Then the resulted mixture was refluxed in an oil bath for 48 h. Afterwards, the mixture was concentrated under the reduced pressure followed by the addition of 10% aqueous NaOH (1 mL). The resulted solution was refluxed for 3 h and the solvent was removed under reduced pressure. The crude product was purified by preparative TLC (eluent: PE/EA = 5/1) to give the desired product **6** in 51% isolated yield (21.8 mg) as yellow solid (m.p.: 103-105 ^oC).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 8.6 Hz, 2H), 7.40-7.33 (m, 4H), 7.31-7.24 (m, 2H), 4.55 (s, 1H), 3.71 (d, J = 7.8 Hz, 1H), 3.17 (d, J = 13.3 Hz, 1H), 2.79-2.68 (m, 1H), 2.36-2.24 (m, 1H), 2.19-2.05 (m, 2H), 1.52 (s, 3H), 1.30 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 140.8, 138.6, 137.7, 131.5, 130.3, 128.8, 127.2, 126.6, 126.1, 122.0, 111.8 (dd, J = 302.3, 286.2 Hz), 68.3, 64.9, 56.3, 52.1 (dd, J = 12.9, 7.2 Hz), 47.1, 46.0, 37.6 (t, J = 13.0 Hz), 29.3, 23.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ -129.71 (dd, J_{FF} = 157.7 Hz, J_{HF} = 15.2 Hz), -141.56 (d, J_{FF} = 164.8 Hz, J_{HF} = 10.5 Hz).

HRMS (ESI) calculated for $C_{22}H_{22}BrF_2N_2$ ($[M+H]^+$): 431.0929; found: 431.0925.



3aa **7**

Compound **3aa** (0.1 mmol, 1.0 eq) was dissolved in MeOH (0.5 mL) in a 10 mL Schlenk flask, followed by the addition of NaOH queous solution (1 M, 0.5 mL), and the resulted mixture was stirred at 120 °C in an oil bath for 48 h. Afterwards, the reaction mixture was re-cooled to room temperature and diluted with EA, neutralized by 1 M HCl solution and concentrated. The crude product was purified by preparative TLC (eluent: DCM/MeOH = 30/1) to afford the corresponding product **7** in 58% isolated yield (21.5 mg) as white solid (m.p.: 184-186 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.72-7.61 (m, 4H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.23 (d, *J* = 11.3 Hz, 1H), 3.44 (s, 2H), 2.16 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 154.2 (d, *J* = 250.9 Hz), 140.9 (d, *J* = 2.5 Hz), 139.5 (d, *J* = 8.8 Hz), 134.7 (d, *J* = 9.5 Hz), 131.6, 131.4, 131.0 (d, *J* = 4.8 Hz), 129.4 (d, *J* = 5.2 Hz), 127.0, 126.0, 125.4, 123.0, 118.6, 112.7 (d, *J* = 23.6 Hz), 106.3 (d, *J* = 19.2 Hz), 63.4, 49.6, 29.8, 27.8.

^{19}F NMR (376 MHz, $CDCl_3$): -116.81 (d, J_{HF} = 13.0 Hz)

HRMS (ESI) calculated for $C_{22}H_{19}BrFN_2O_2$ ($[M+H]^+$): 441.0608; found: 441.0608.

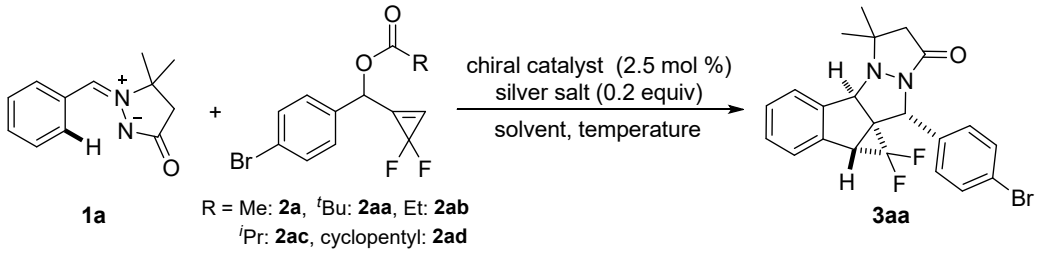
Asymmetric synthesis with chiral catalyst:

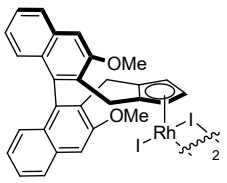
Optimization studies:

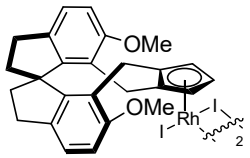
The mixture of azomethine imine **1a** (0.1 mmol, 1.0 equiv), *gem*-difluorocyclopropenyl acetate **2a** (0.1 mmol, 1.0 equiv), catalyst (2.5 mol %), and silver salt (20 mol %) in the solvent was stirred at room temperature (25 °C) for 24 h

without exclusion of air or moisture. Afterwards, the solvent was removed under reduced pressure and the crude product was purified by preparative TLC (eluent: DCM/MeOH = 40/1) to afford the corresponding indenopyrazolopyrazolone derivative **3aa**.

Table S2 Chiral $Cp^XRh(III)$ Enabled Enantioselective Synthesis of Indenopyrazolopyrazolone **3aa**[a]




(*R*)-**Rh1**

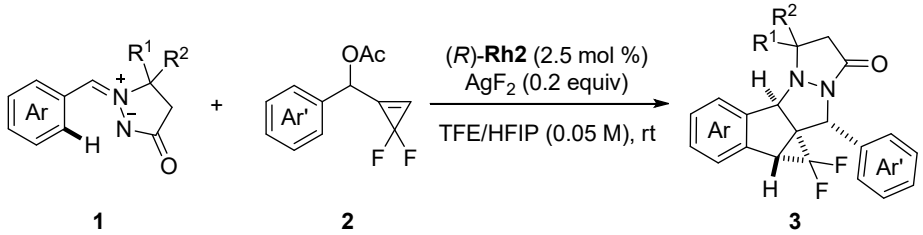

(*R*)-**Rh2**

entry	catalyst (2.5 mol %)	additives (0.2 equiv)	solvent (x M)	Tem. (°C)	yield (%)	e.r.[b]
1	(*R*)-**Rh1**	$AgSbF_6$	MeOH (0.2)	60	trace	-
2	(*R*)-**Rh2**	$AgSbF_6$	MeOH (0.2)	60	22	32:68
3	(*R*)-**Rh2**	$AgSbF_6$	EtOH (0.2)	60	<10	49:51
4	(*R*)-**Rh2**	$AgSbF_6$	THF (0.2)	60	n.d.	-
5	(*R*)-**Rh2**	$AgSbF_6$	MeCN (0.2)	60	n.d.	-
6	(*R*)-**Rh2**	$AgSbF_6$	HFIP (0.2)	60	<10	23:77
7	(*R*)-**Rh2**	$AgSbF_6$	TFE (0.2)	60	45	26:74
8	(*R*)-**Rh2**	$AgSbF_6$	dioxane (0.2)	60	n.d.	-
9[c]	(*R*)-**Rh2**	$AgSbF_6$	TFE (0.2)	60	18	28:72
10[d]	(*R*)-**Rh2**	$AgSbF_6$	TFE (0.2)	60	49	36:64
11[e]	(*R*)-**Rh2**	$AgSbF_6$	TFE (0.2)	60	37	26:74

12[f]	(*R*)-**Rh2**	$AgSbF_6$	TFE (0.2)	60	30	25:75
13	(*R*)-**Rh2**	AgOTf	TFE (0.2)	60	44	26:74
14	(*R*)-**Rh2**	$AgNTF_2$	TFE (0.2)	60	55	27:73
15	(*R*)-**Rh2**	$AgBF_4$	TFE (0.2)	60	43	25:75
16	(*R*)-**Rh2**	AgF_2	TFE (0.2)	60	29	18:82
17	(*R*)-**Rh2**	AgF_2	TFE (0.2)	rt	22	20:80
18	(*R*)-**Rh2**	AgF_2	TFE/HFIP=1/1 (0.2)	rt	62	28:72
19[e]	(*R*)-**Rh2**	AgF_2	TFE/HFIP=1/1 (0.05)	rt	34	15:85
20[f]	(*R*)-**Rh2**	AgF_2	TFE/HFIP=1/1 (0.05)	rt	22	24:76
21	(*R*)-**Rh2**	AgF_2	TFE/HFIP=1/3 (0.05)	rt	33	12:88
22	(*R*)-**Rh2**	AgF_2	TFE/HFIP=3/1 (0.05)	rt	38	19:81
23[g]	(*R*)-**Rh2**	AgF_2	MeOH (0.05)	rt	<10	29:71

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), chiral catalyst (2.5 mol %), silver salt (0.2 equiv) in solvent for 24 h without exclusion of air or moisture, isolated yield were reported. [b]Determined by HPLC analysis with a chiral stationary phase. [c]**2aa** was used instead of **2a**. [d]**2ab** was used instead of **2a**. [e]**2ac** was used instead of **2a**. [f]**2ad** was used instead of **2a**. [g]The reaction was conducted starting from three-component raw materials. n.d.: not detected.

General Procedure:

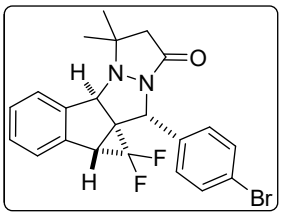


1 **2** **3**

The mixture of azomethine imine **1** (0.1 mmol, 1.0 equiv), *gem*-difluorocyclopropenyl acetate **2** (0.1 mmol, 1.0 equiv), (*R*)-**Rh2** (2.5 mol %), and AgF_2 (20 mol %) in the TFE/HFIP (1:3, 2.0 mL) was stirred at room temperature (25 °C) for 24 h without exclusion of air or moisture. Afterwards, the solvent was removed under reduced pressure and the crude product was purified by preparative TLC (eluent: DCM/MeOH

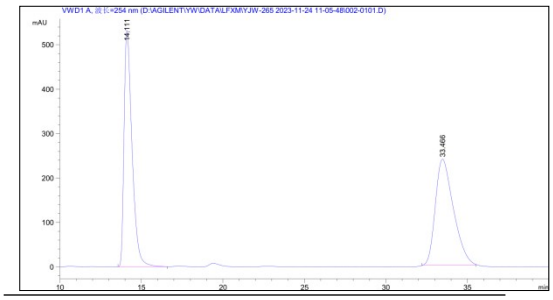
= 40/1) to afford the corresponding indenopyrazolopyrazolones derivative **3**.

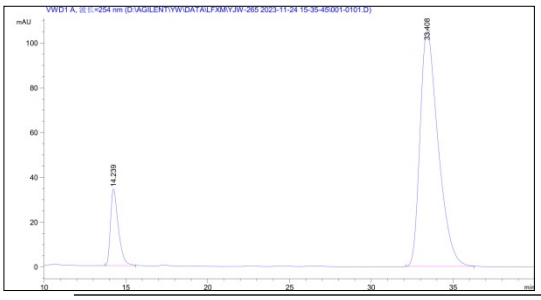
11-(4-bromophenyl)-1,1-difluoro-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3aa)



HPLC conditions: Daicel Chiralpak IC-3 column (80:20 hexane: 2-propanol, 1.0 mL/min, 30 °C, 254 nm); tr (minor) = 14.24 min, tr (major) = 33.41 min, 12:88 er.

$[\alpha]_D^{25}$ = 75.4° (c = 0.06, CH_2Cl_2).

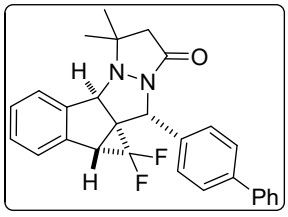




No.	Time	Area	Area(%)
1	14.111	1.81309e4	49.6608
2	33.466	1.83786e4	50.3392

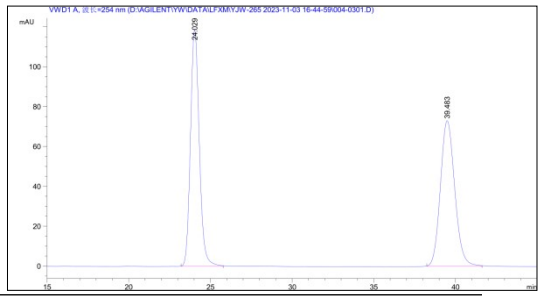
No.	Time	Area	Area(%)
1	14.239	1141.86243	12.3135
2	33.408	8131.39111	87.6865

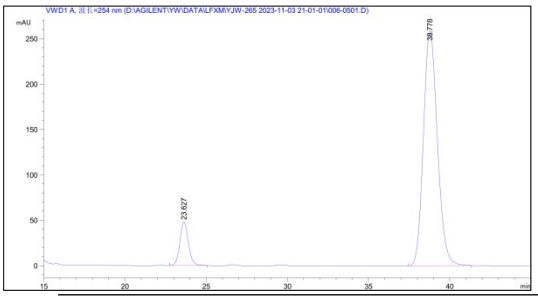
11-([1,1'-biphenyl]-4-yl)-1,1-difluoro-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ae)



HPLC conditions: Daicel Chiralpak IC-3 column (80:20 hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); tr (minor) = 23.63 min, tr (major) = 38.78 min, 10:90 er.

$[\alpha]_D^{25}$ = 171.7° (c = 0.04, CH_2Cl_2).

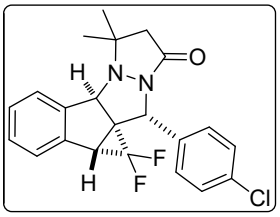




No.	Time	Area	Area(%)
1	24.029	4462.82764	49.9523
2	39.483	4471.35303	50.0477

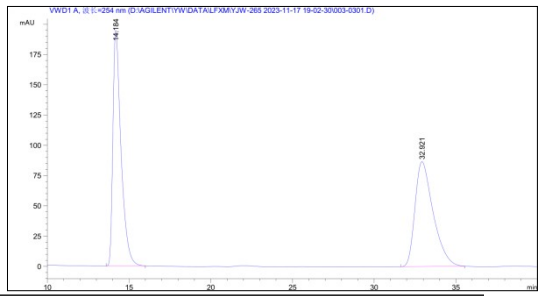
No.	Time	Area	Area(%)
1	23.627	1778.46716	10.2841
2	38.778	1.55150e4	89.7159

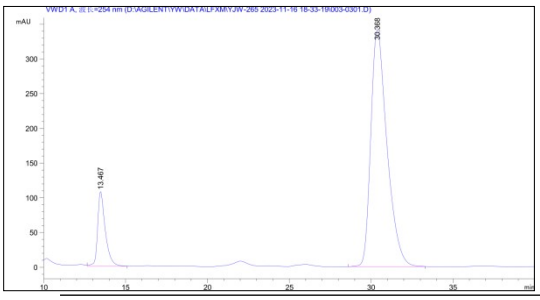
11-(4-chlorophenyl)-1,1-difluoro-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ah)



HPLC conditions: Daicel Chiralpak IC-3 column (80:20 hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); tr (minor) = 13.47 min, tr (major) = 30.37 min, 13:87 er.

$[\alpha]_D^{25}$ = 113.3° (c = 0.08, CH_2Cl_2).

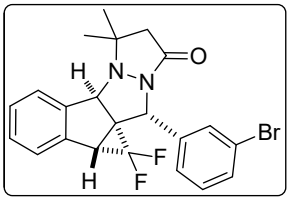




No.	Time	Area	Area(%)
1	14.184	6739.50488	50.1478
2	32.921	6699.78955	49.8522

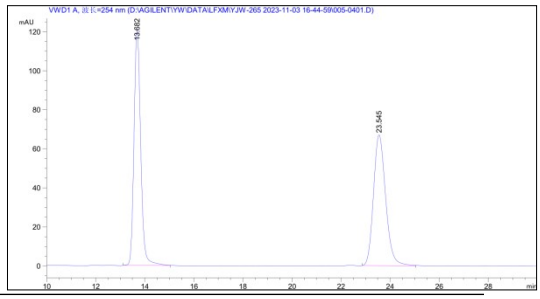
No.	Time	Area	Area(%)
1	13.467	3535.89551	13.0765
2	30.368	2.35041e4	86.9235

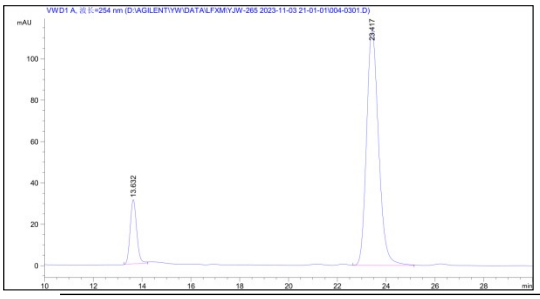
11-(3-bromophenyl)-1,1-difluoro-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3am)



HPLC conditions: Daicel Chiralpak IC-3 column (80:20 hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); tr (minor) = 13.63 min, tr (major) = 23.42 min, 13:87 er.

$[\alpha]_D^{25}$ = 43.6° (c = 0.06, CH_2Cl_2).

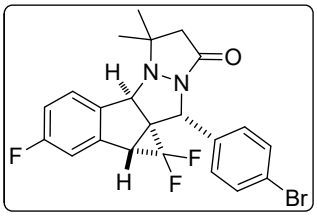




No.	Time	Area	Area(%)
1	13.682	2298.44653	49.8927
2	23.545	2308.32837	50.1073

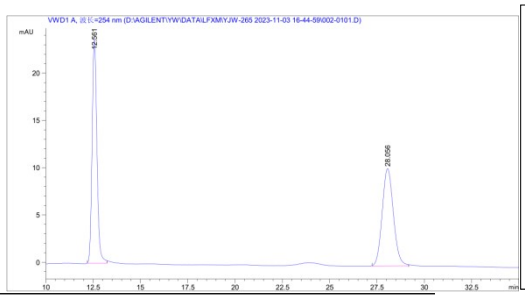
No.	Time	Area	Area(%)
1	13.632	575.99774	12.8455
2	23.417	3908.05176	87.1545

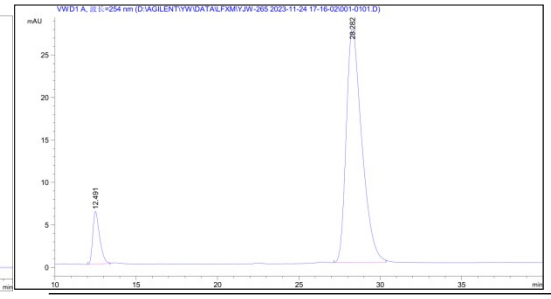
11-(4-bromophenyl)-1,1,3-trifluoro-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ha)



HPLC conditions: Daicel Chiralpak IC-3 column (80:20 hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); tr (minor) = 12.49 min, tr (major) = 28.28 min, 9:91 er.

$[\alpha]_D^{25}$ = 233.3° (c = 0.01, CH_2Cl_2).



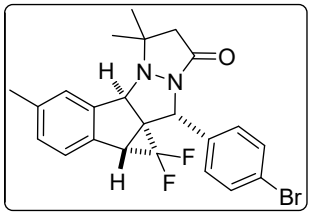


No.	Time	Area	Area(%)

No.	Time	Area	Area(%)

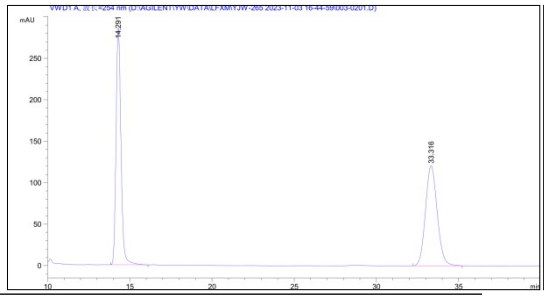
1	12.561	419.97964	49.7081	1	12.491	182.38930	9.0644
2	28.056	424.91202	50.2919	2	28.282	1829.75452	90.9356

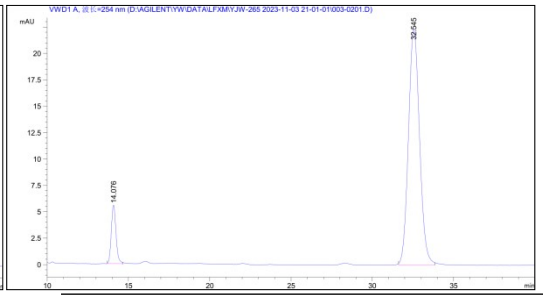
11-(4-bromophenyl)-1,1-difluoro-4,7,7-trimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3na)



HPLC conditions: Daicel Chiralpak IC-3 column (80:20 hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); tr (minor) = 14.08 min, tr (major) = 32.55 min, 10:90 er.

$[\alpha]_D^{25}$ = 125.3° (c = 0.03, CH_2Cl_2).

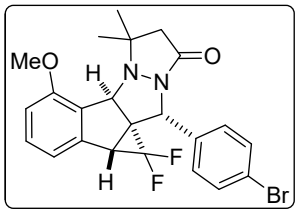




No.	Time	Area	Area(%)
1	14.291	5962.27979	49.8460
2	33.316	5999.10986	50.1540

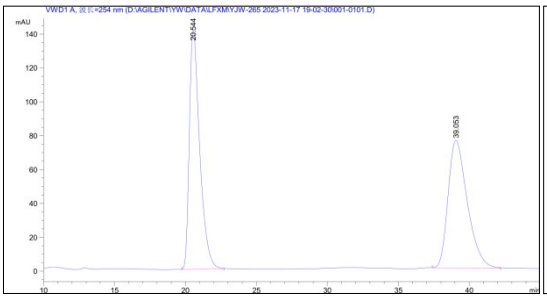
No.	Time	Area	Area(%)
1	14.076	111.46470	9.5353
2	32.545	1057.50696	90.4647

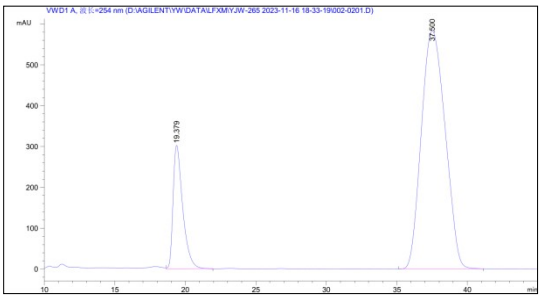
11-(4-bromophenyl)-1,1-difluoro-5-methoxy-7,7-dimethyl-1a,5b,7,8-tetrahydro-1*H*,9*H*,11*H*-cyclopropa[2,3]indeno[1,2-*c*]pyrazolo[1,2-*a*]pyrazol-9-one (3ra)



HPLC conditions: Daicel Chiralpak IC-3 column (80:20 hexane: 2-propanol, 1.0 mL/min, 30°C, 254 nm); tr (minor) = 19.38 min, tr (major) = 37.50 min, 17:83 er.

$[\alpha]_D^{25}$ = 104.3° (c = 0.19, CH_2Cl_2).





No.	Time	Area	Area(%)
1	20.544	7179.37500	50.2579
2	39.053	7105.69336	49.7421

No.	Time	Area	Area(%)
1	19.379	1.43623e4	17.3134
2	37.500	6.85924e4	82.6866

III. X-Ray Crystallographic Data

Experimental: The sample was dissolved in appropriate amount of ethyl acetate followed by the addition of petroleum ether to furnish a saturated solution. Afterwards, the mixture was allowed to stand at room temperature to form the crystals. A suitable crystal was selected and measured on a XtaLAB AFC12 (RINC): Kappa single diffractometer. The crystal was kept at 200.00(10) K during data collection. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation.

Crystal structure determination: Crystal Data for $C_{22}H_{19}BrF_2N_2O$ (M = 445.30 g/mol): triclinic, space group P-1 (no. 2), a = 9.26640(10) Å, b = 11.0963(2) Å, c = 11.4001(2) Å, α = 65.9180(10)°, β = 89.2430(10)°, γ = 69.2100(10)°, V = 988.52(3)Å^3, Z = 2, T = 200.00(10) K, μ(Cu Kα) = 3.123 mm^{-1},D_{calc} = 1.496g/cm^3, 9231 reflections measured (8.598° ≤ 2Θ ≤ 142.634°), 3711 unique (R_{int} = 0.0143, R_{sigma} = 0.0141) which were used in all calculations. The final R_1 was 0.0456 (I > 2σ(I)) and wR_2 was 0.1125 (all data).

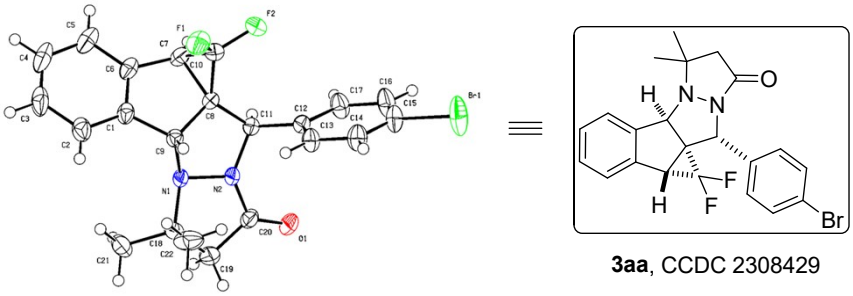
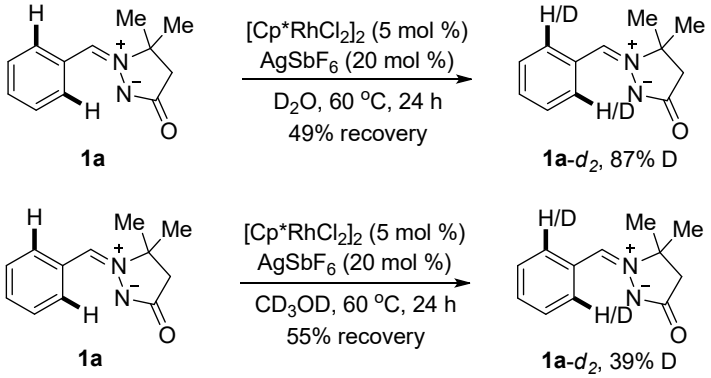


Table S3. Crystal data and structure refinement for **3aa**

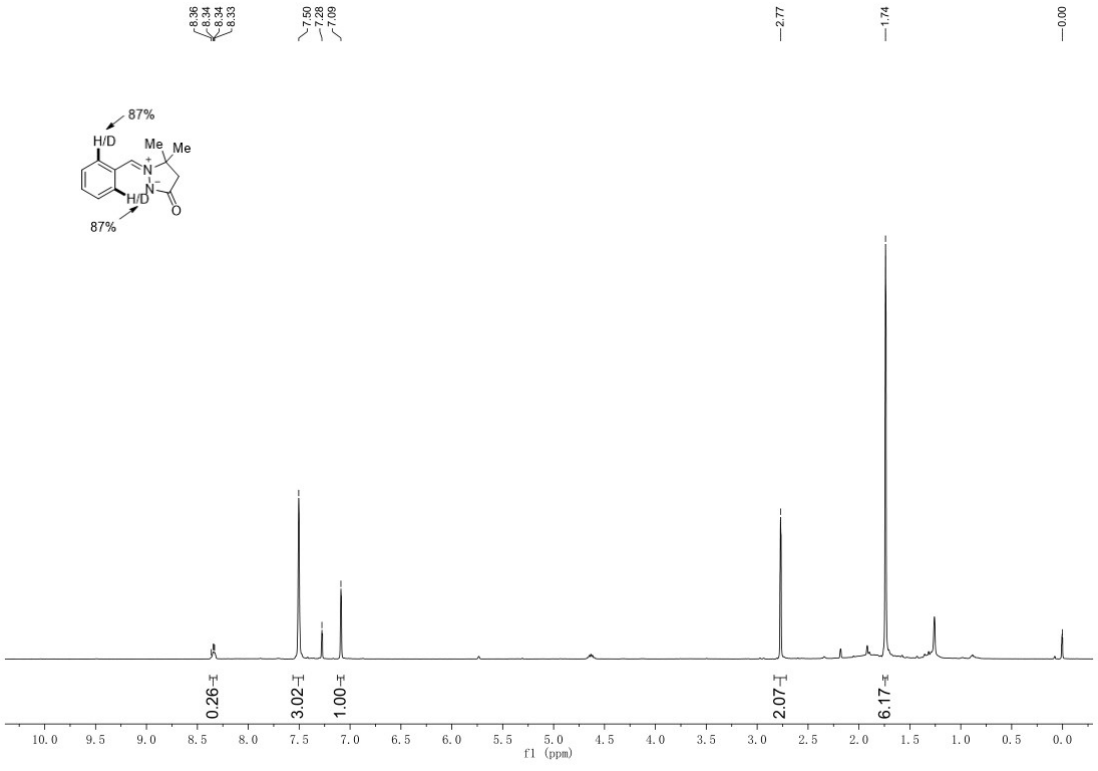
Identification code	1900_2
Empirical formula	$C_{22}H_{19}BrF_2N_2O$
Formula weight	445.30
Temperature/K	200.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.26640(10)
b/Å	11.0963(2)
c/Å	11.4001(2)
α/°	65.9180(10)
β/°	89.2430(10)
γ/°	69.2100(10)
Volume/Å^3	988.52(3)
Z	2
ρ_{calc}g/cm^3	1.496
μ/mm^{-1}	3.123
F(000)	452.0
Crystal size/mm^3	0.13 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.598 to 142.634
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -8 ≤ l ≤ 13
Reflections collected	9231
Independent reflections	3711 [R_{int} = 0.0143, R_{sigma} = 0.0141]
Data/restraints/parameters	3711/0/255
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0456, wR_2 = 0.1118
Final R indexes [all data]	R_1 = 0.0466, wR_2 = 0.1125
Largest diff. peak/hole / e Å^{-3}	1.39/-1.49

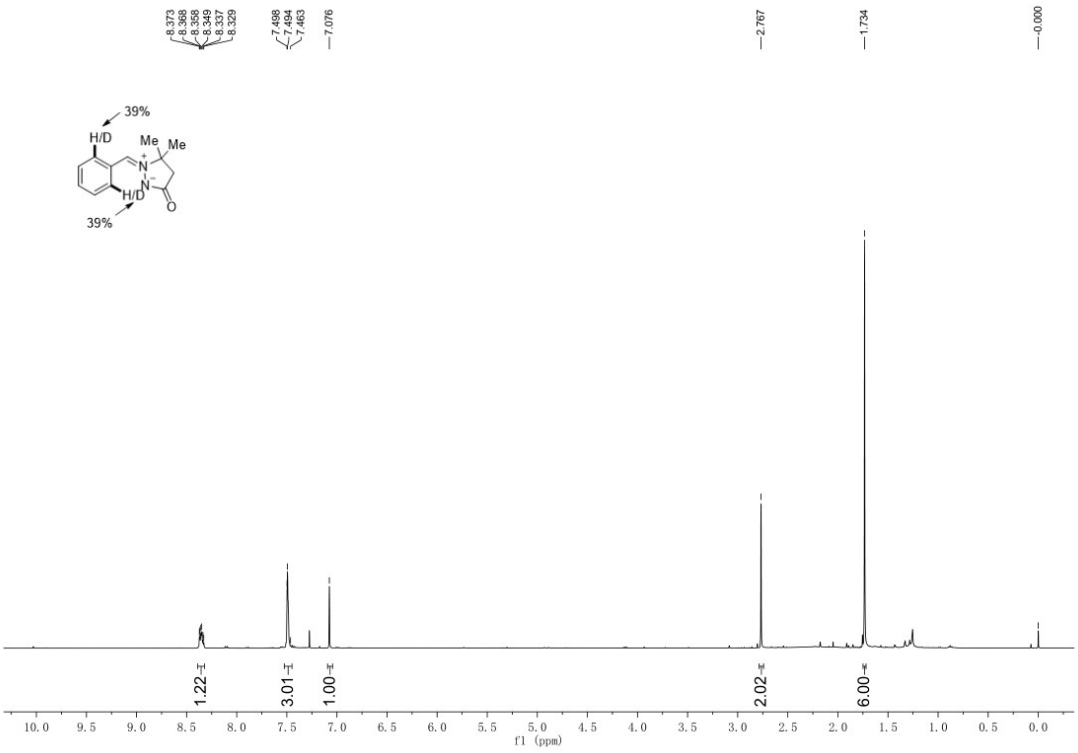
IV. Experimental Mechanistic Studies

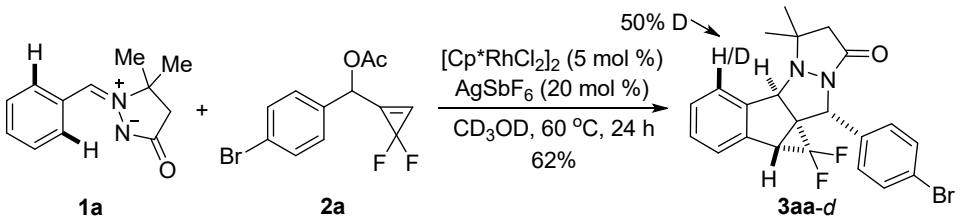
Deuterium-labeling experiments:



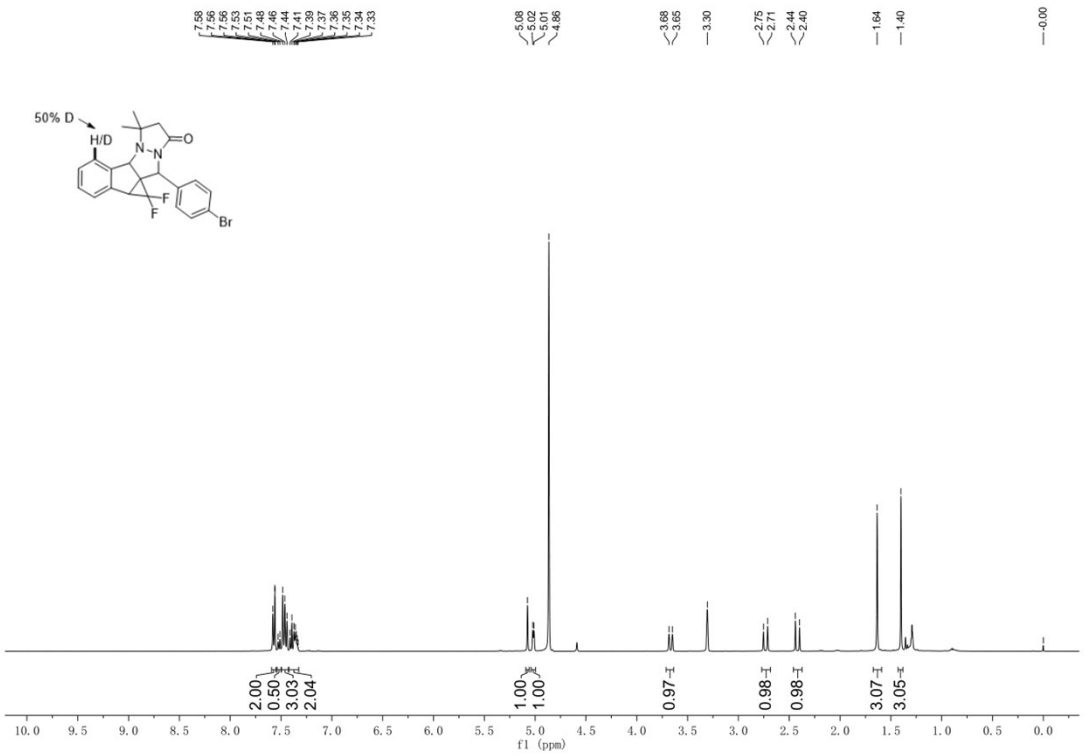
1a (0.2 mmol, 1.0 equiv) was dissolved in D_2O or CD_3OD (1.0 mL) in the presence of $[Cp^*RhCl_2]_2$ (5.0 mol %) and $AgSbF_6$ (20 mol %). The reactions were conducted under the standard conditions for 24 h. Afterwards, **1a** was recovered by preparative TLC (eluent: DCM/MeOH = 40/1) and analyzed by ^{1}H-NMR spectroscopy. The results showed that 87% (in D_2O) and 39% (in CD_3OD) deuterium incorporation was observed at the *ortho* position of the directing group.



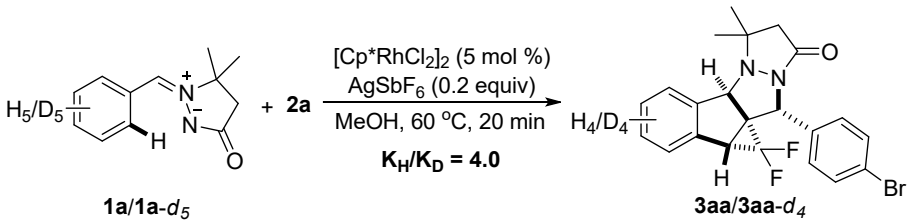




The mixture of azomethine imine **1a** (0.12 mmol, 1.0 equiv), *gem*-difluorocyclopropenyl acetate **2a** (0.1 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (5 mol %) and $AgSbF_6$ (20 mol %) in CD_3OD (1.0 mL) was stirred at 60 °C in an oil bath for 24 h without exclusion of air or moisture. Afterwards, the solvent was removed under the reduced pressure, and the resulted mixture was purified by preparative TLC to afford the corresponding product **3aa**-*d*. The deuterium incorporation was analyzed by ^{1}H-NMR spectroscopy. The results showed that 50% deuterium incorporation was observed at the *ortho* position of the directing group.

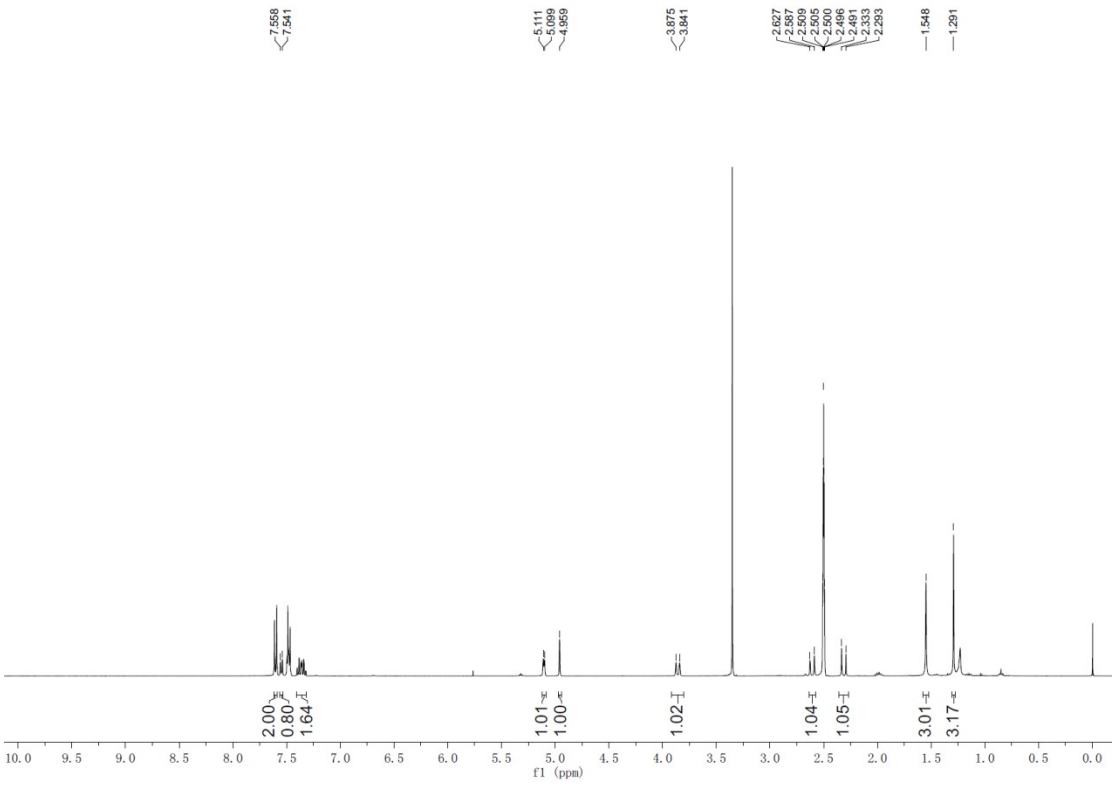


General procedure for estimation of the KIE:

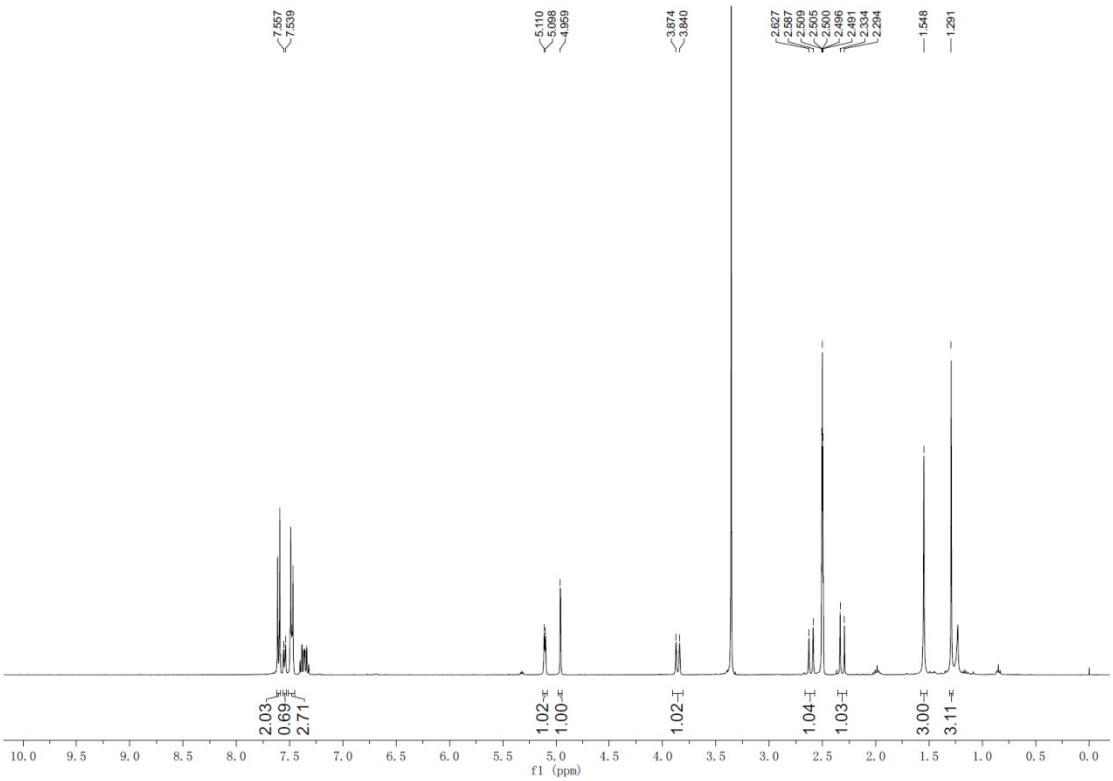


1a/**1a**-d_5 **3aa**/**3aa**-d_4

An equimolar mixture of **1a** (0.12 mmol, 1.2 equiv) and **1a**-d_5 (0.12 mmol, 1.2 equiv) was allowed to react with **2a** (0.1 mmol, 1.0 equiv) in MeOH (1.0 mL) in the presence of $[Cp^*RhCl_2]_2$ (5 mol %) and $AgSbF_6$ (20 mol %) under the standard conditions. The reaction was stopped after 20 min, and the product was isolated by preparative TLC and analyzed by ^{1}H-NMR spectroscopy (DMSO-d_6, 400 MHz). The double doublet at δ: 7.54 (0.80H) were used for calculation and an average value of k_H/k_D = 4.0 was obtained.



Another two parallel KIE experiments were performed by treating 1.2 equiv of **1a** or 1.2 equiv of **1a**-d_5 with 1.0 equiv of **2a** separately under the standard conditions for 20 min. Afterwards, the two reactions were mixed and the solvent was removed under reduce pressure, the resulted mixture was purified by preparative TLC to afford the corresponding product **3aa**. The double doublet at δ: 7.54 (0.69H) were used for calculation and an average value of k_H/k_D = 2.2 was obtained.



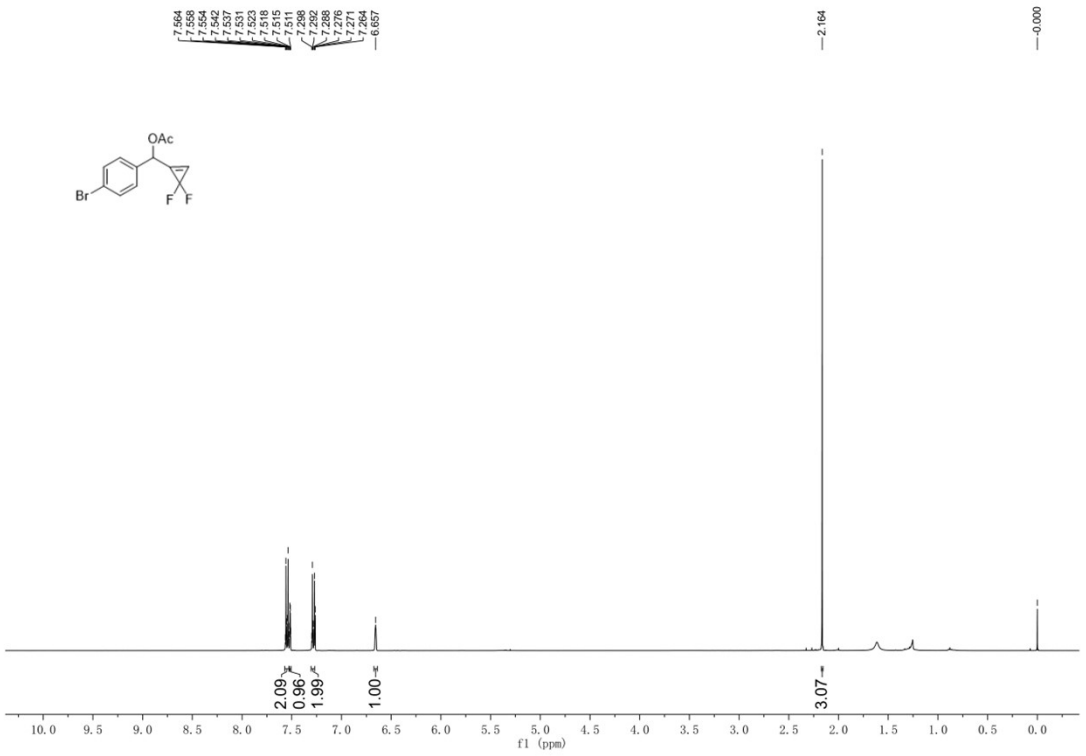
V. References

[S1] (a) M. Wu, R. Wang, F. Chen, W. Chen, Z. Zhou and W. Yi, *Org. Lett.*, 2020, **22**, 7152; (b) M. Zhang, F. Wu, H. Wang, J. Wu and W. Chen, *Adv. Catal. Synth.,* 2017, **359**, 2768; (c) R. Shintani and G. C. Fu, *J. Am. Chem. Soc*., 2003, **125**, 10778.

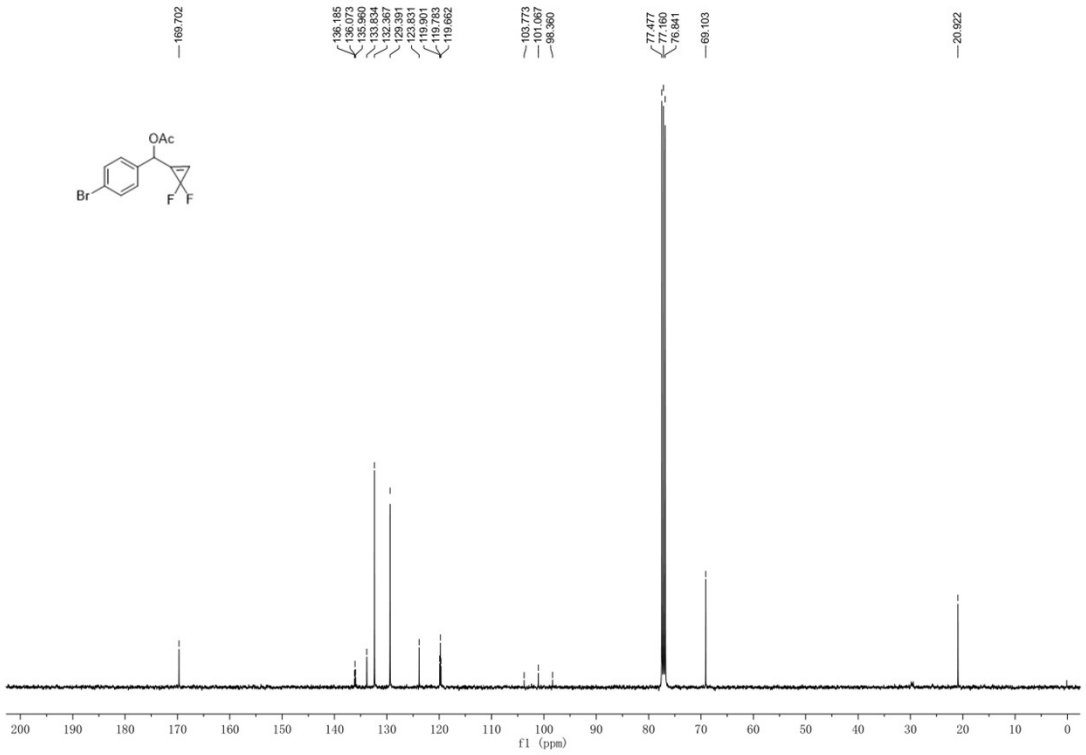
[S2] (a) L. Burroughs, L. Eccleshare, J. Ritchie, O. Kulkarni, B. Lygo, S. Woodward and W. Lewis, *Angew. Chem., Int. Ed*., 2015, **54**, 10648; (b) L. Eccleshare, L. Lozada-Rodríguez, P. Cooper, L. Burroughs, J. Ritchie, W. Lewis and S. Woodward, *Chem. Eur. J*., 2016, **22**, 12542; (c) R. Shen, B. Luo, J. Yang, L. Zhang and L.-B. Han, *Chem. Commun.,* 2016, **52**, 6451; (d) X.-C. Hang, W.-P. Gu, Q.-Y. Chen and J.-C. Xiao, *Tetrahedron,* 2009, **65**, 6320.

VI. Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra

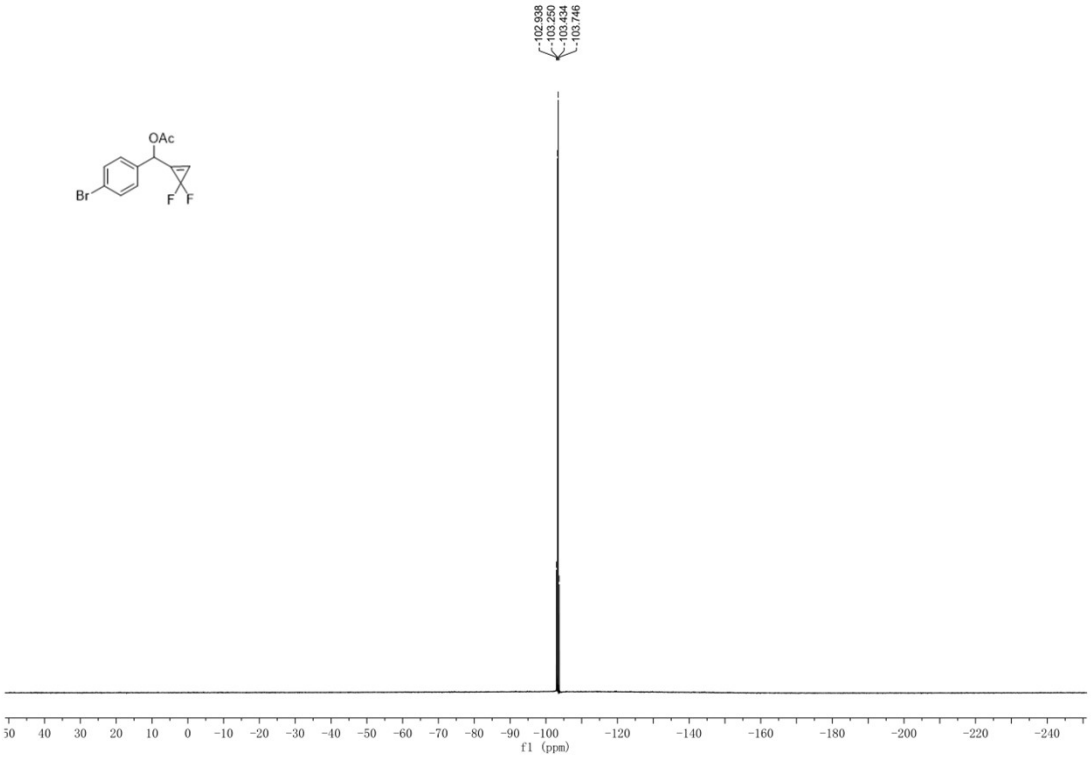
2a-^{1}H NMR (400 MHz, $CDCl_3$)



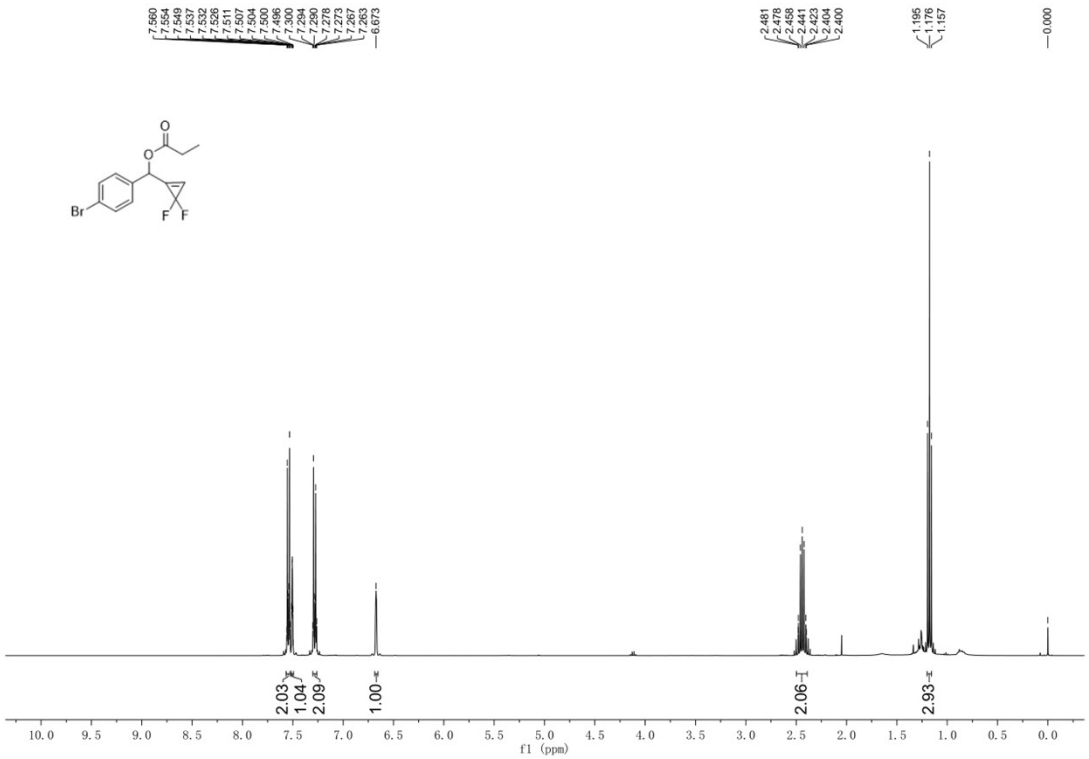
2a-^{13}C NMR (100 MHz, $CDCl_3$)



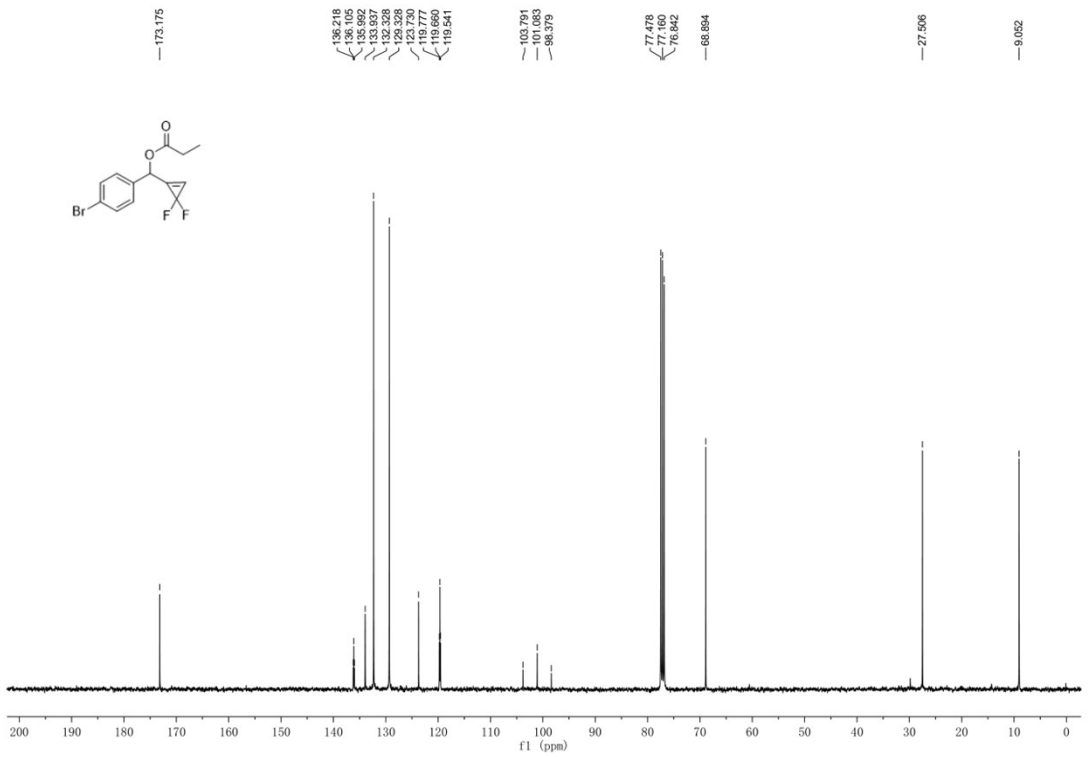
2a-^{19}F NMR (376 MHz, $CDCl_3$)



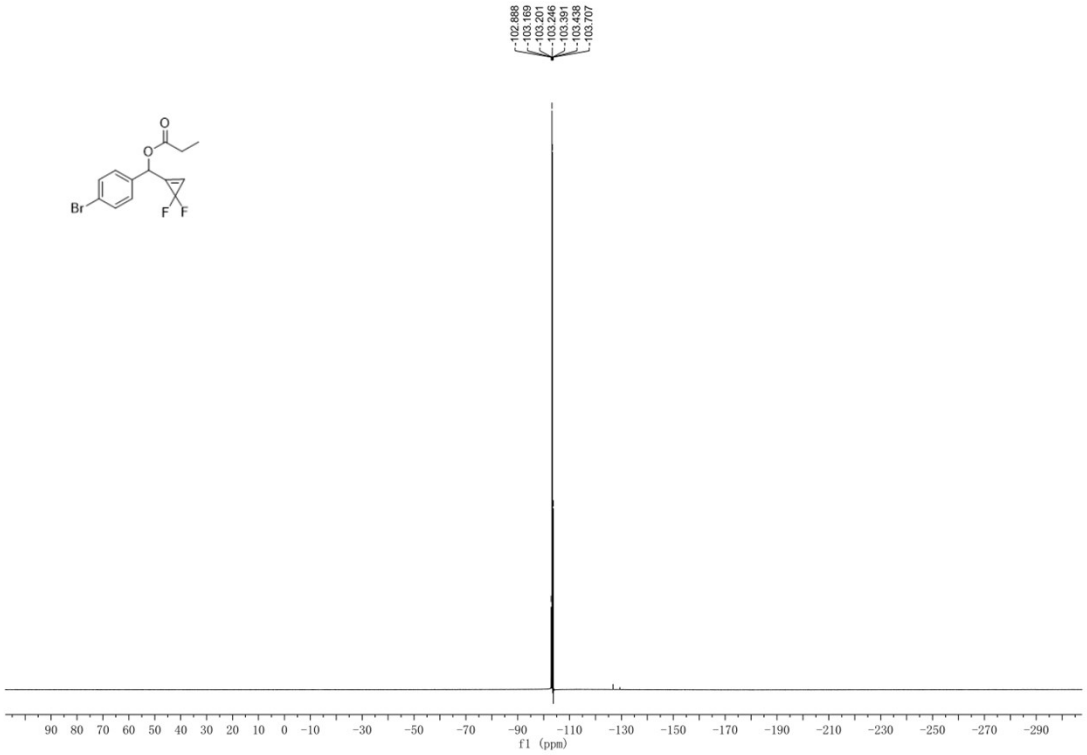
2ab-^{1}H NMR (400 MHz, $CDCl_3$)



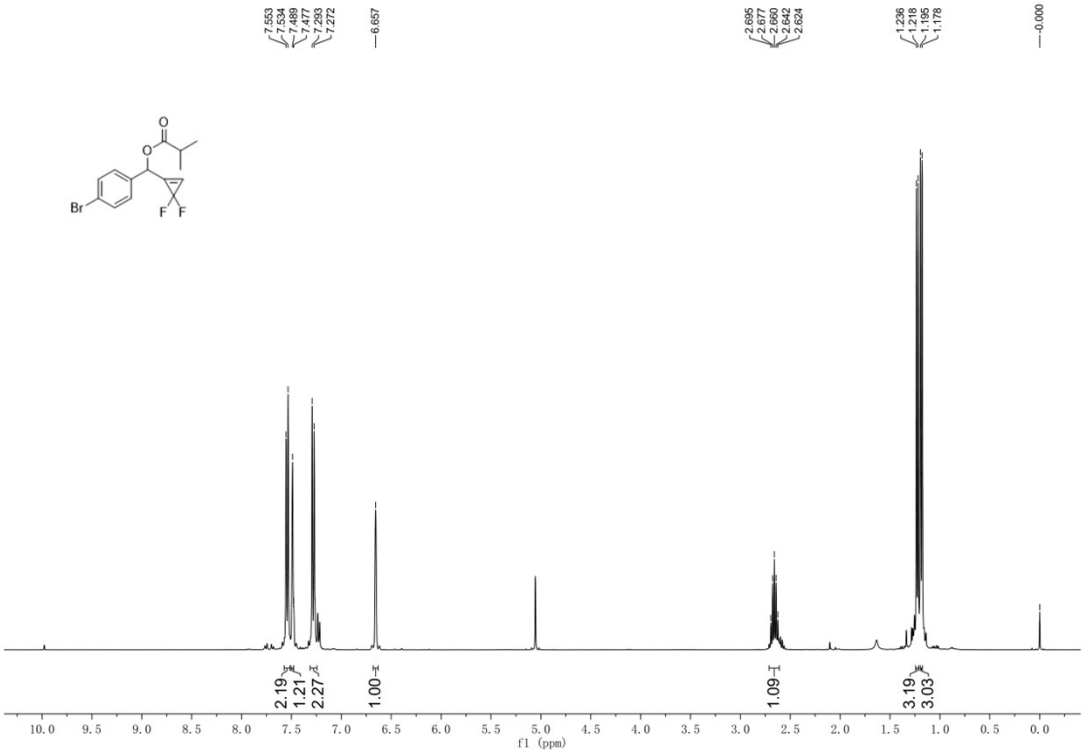
2ab-^{13}C NMR (100 MHz, $CDCl_3$)



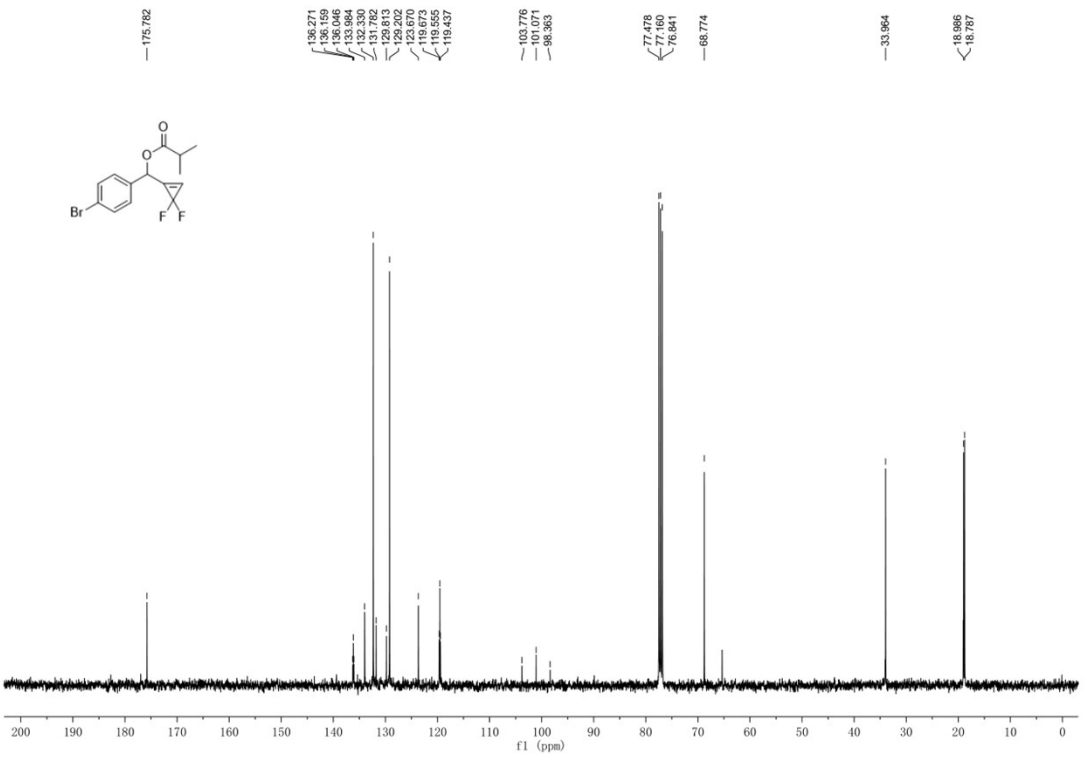
2ab-^{19}F NMR (376 MHz, $CDCl_3$)



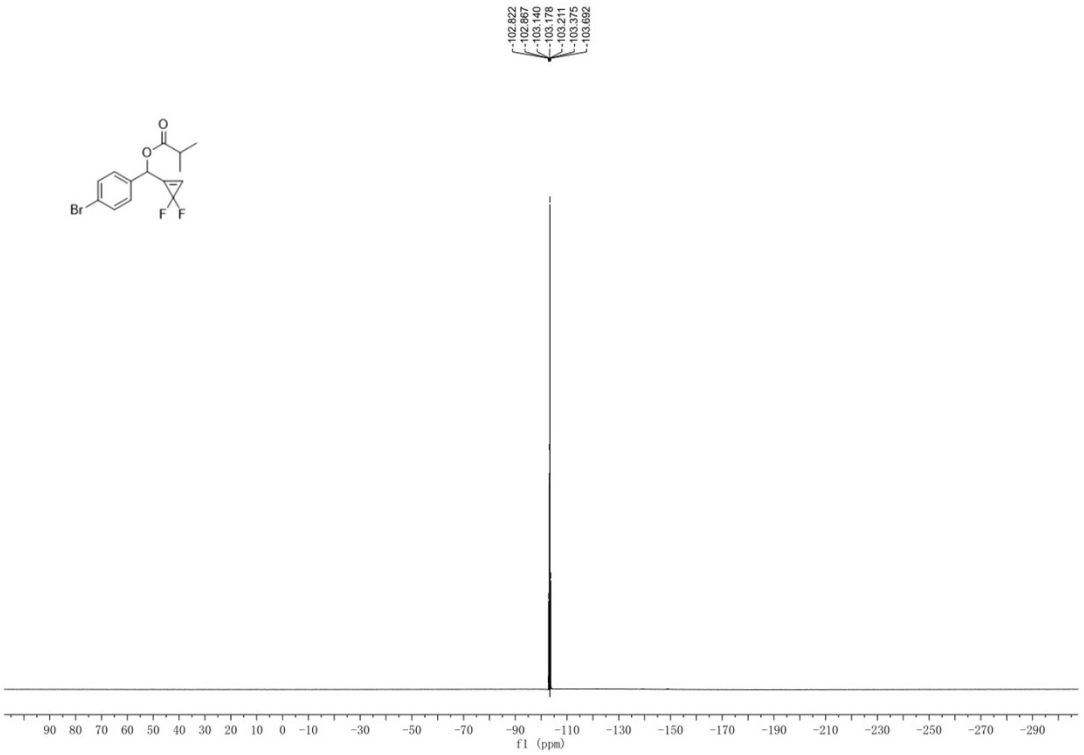
2ac-^{1}H NMR (400 MHz, $CDCl_3$)



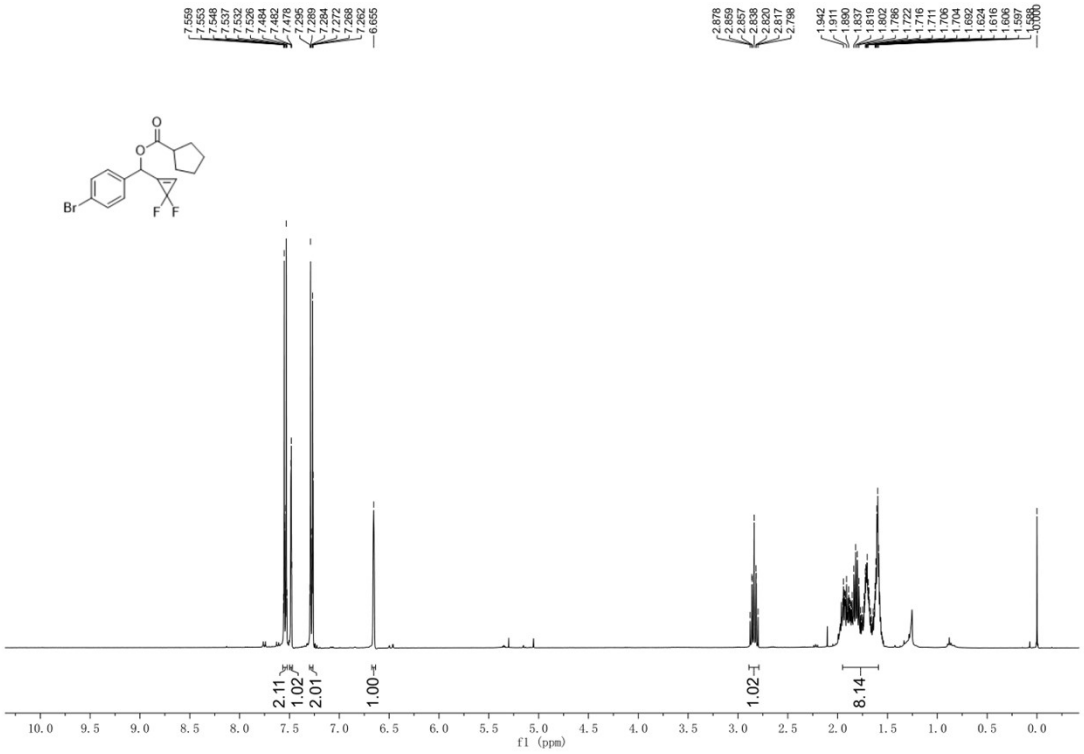
2ac-^{13}C NMR (100 MHz, $CDCl_3$)



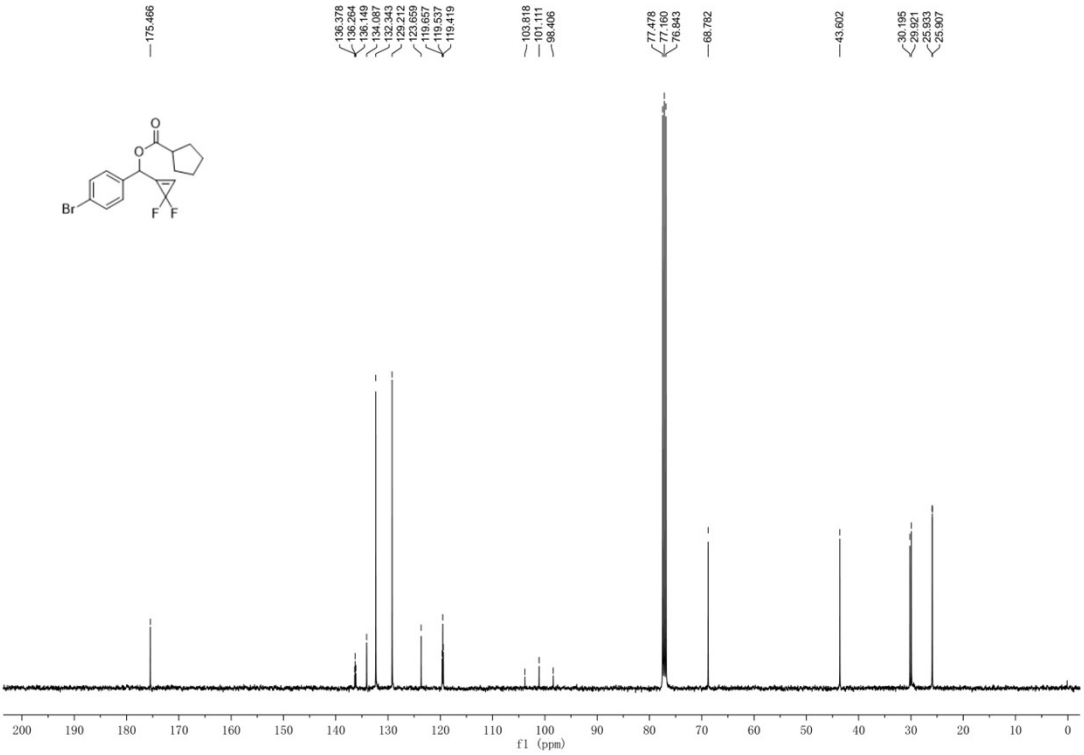
2ac-^{19}F NMR (376 MHz, $CDCl_3$)



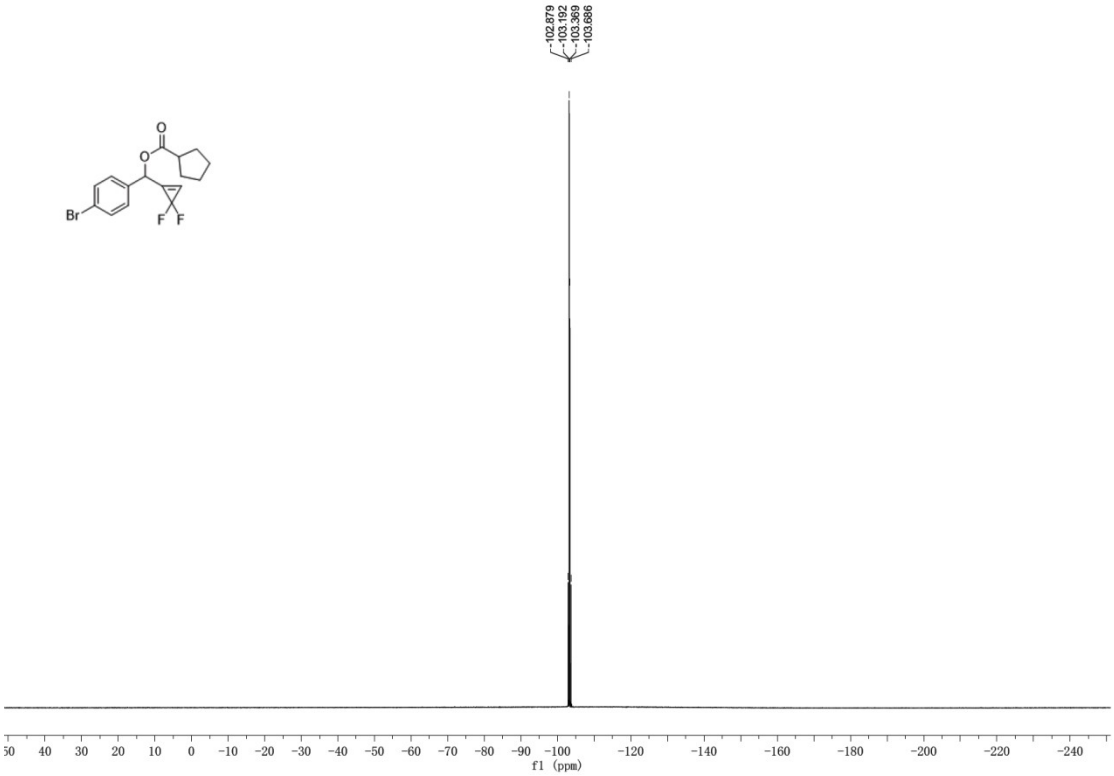
2ad-^{1}H NMR (400 MHz, $CDCl_3$)



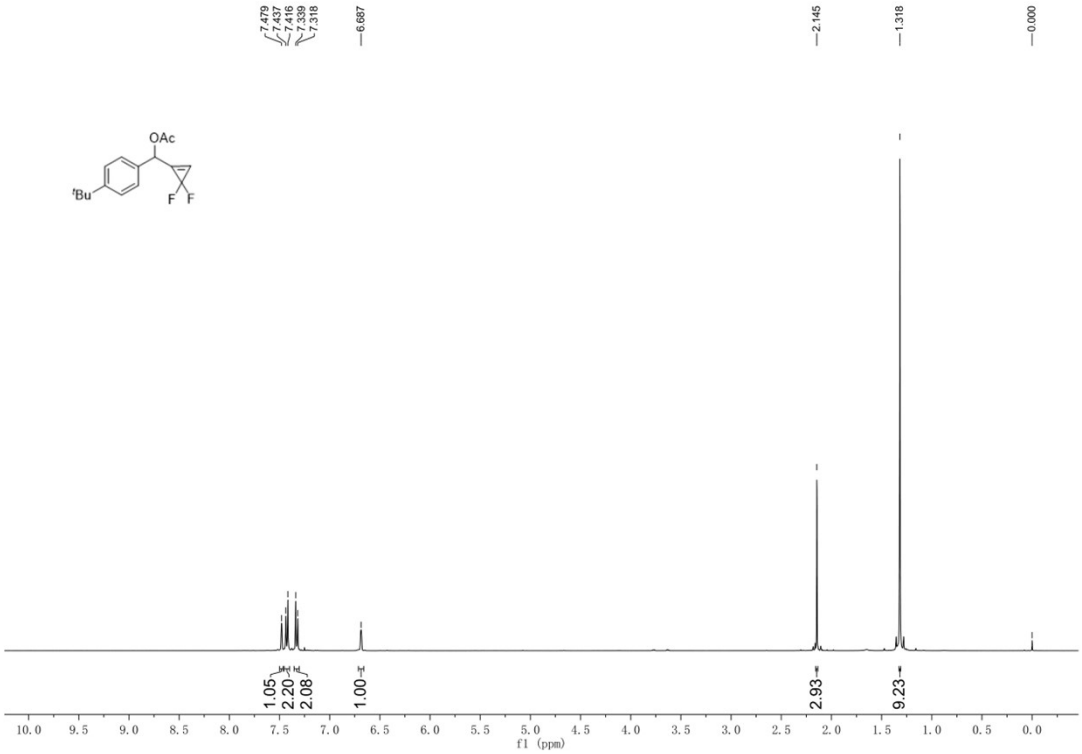
2ad-^{13}C NMR (100 MHz, $CDCl_3$)



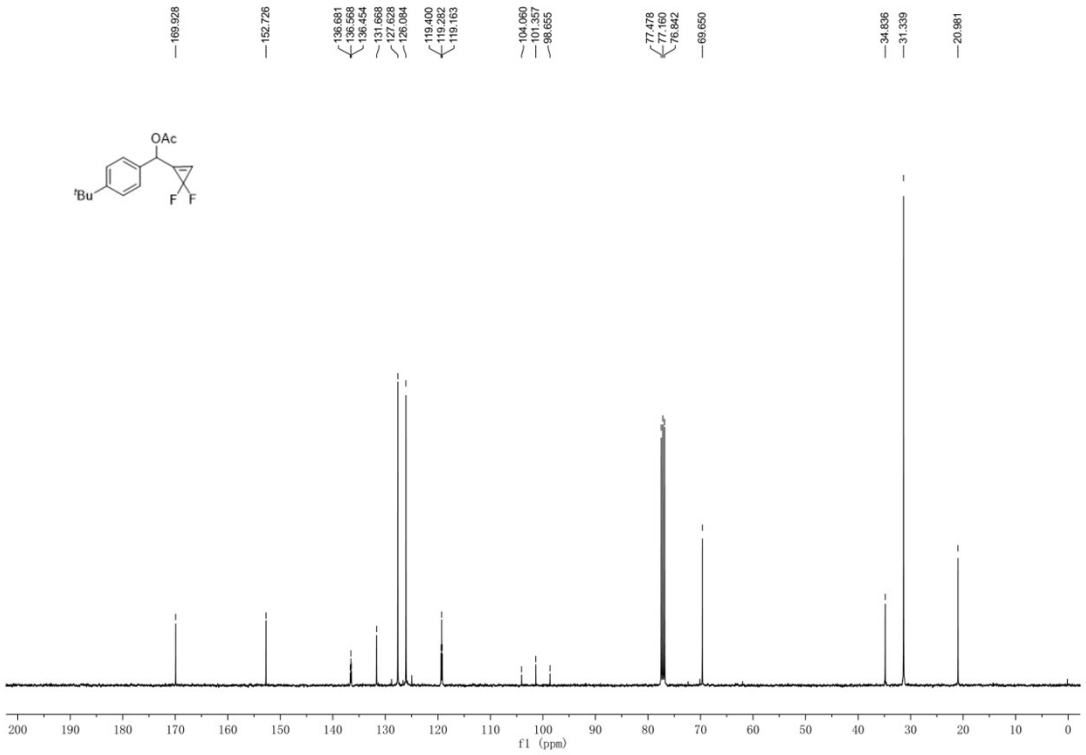
2ad-^{19}F NMR (376 MHz, $CDCl_3$)



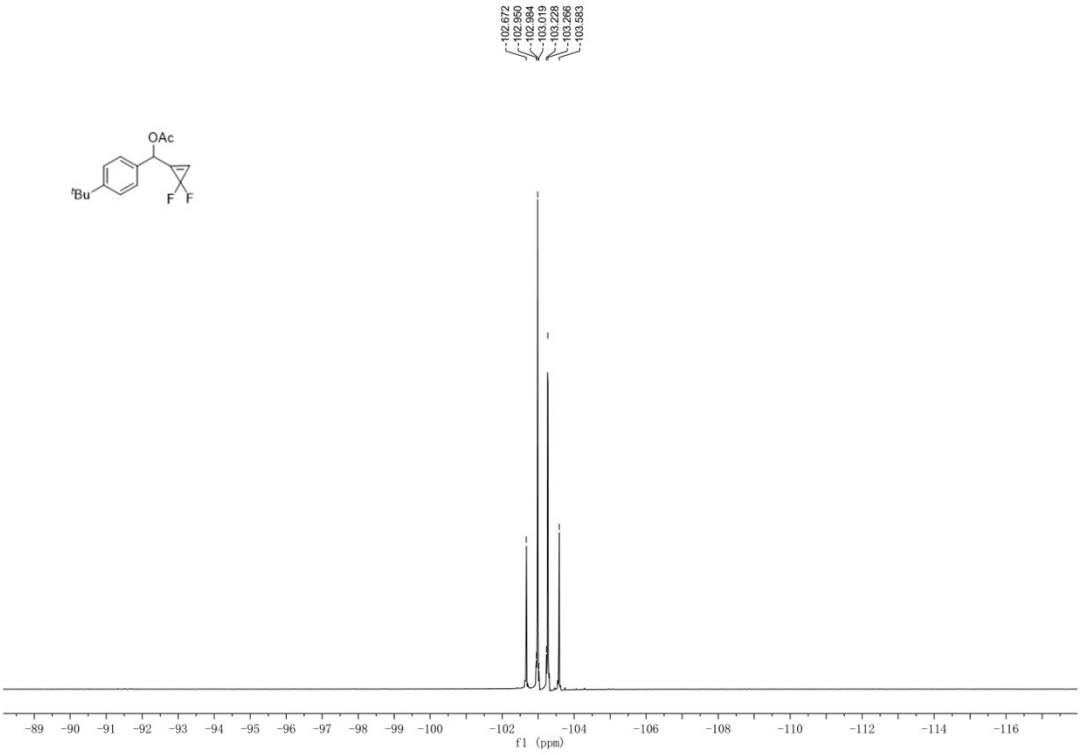
2c-^{1}H NMR (400 MHz, $CDCl_3$)



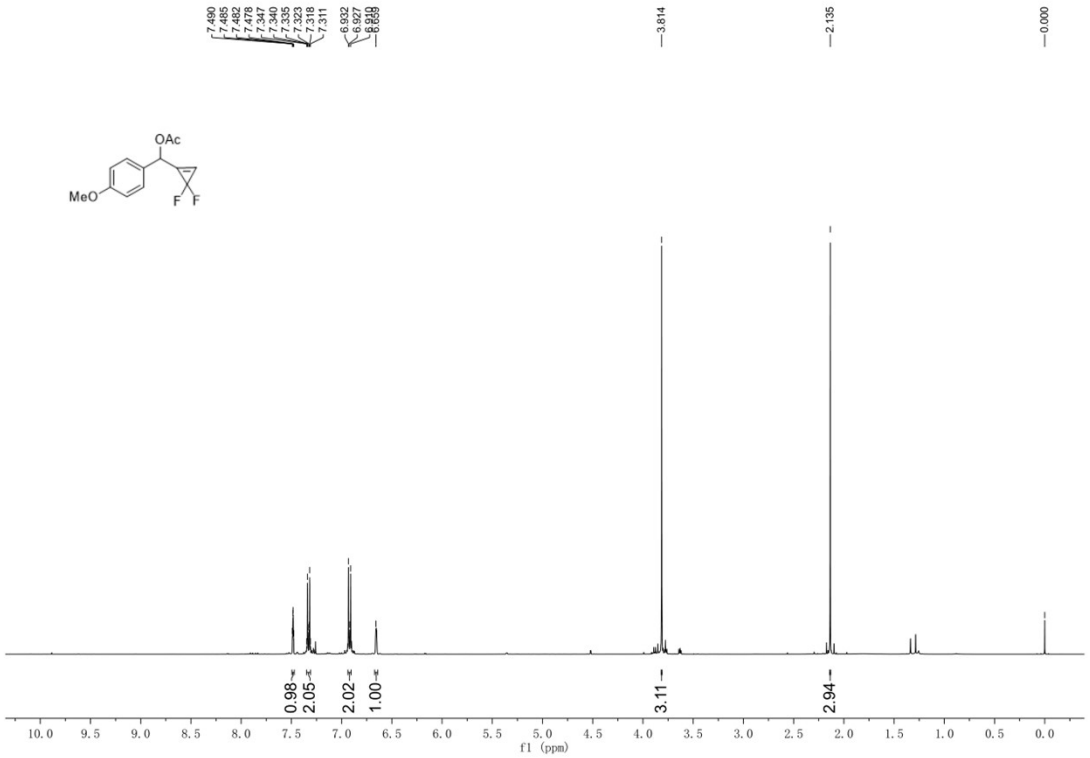
2c-^{13}C NMR (100 MHz, $CDCl_3$)



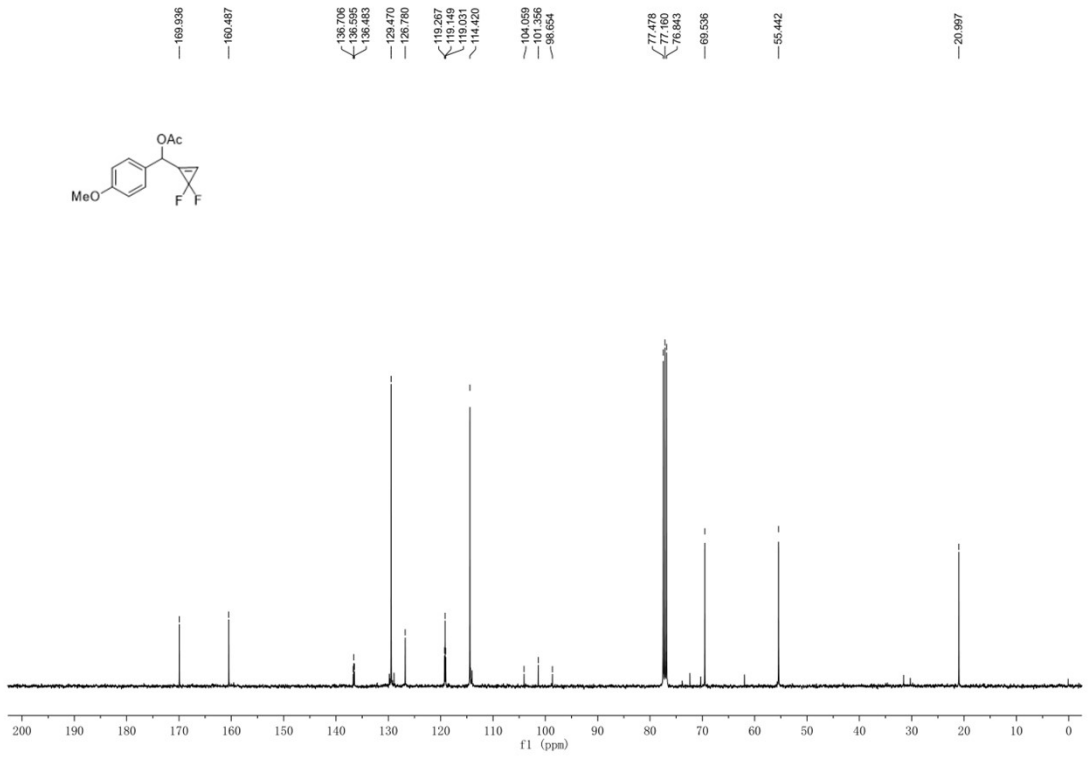
2c-^{19}F NMR (376 MHz, $CDCl_3$)



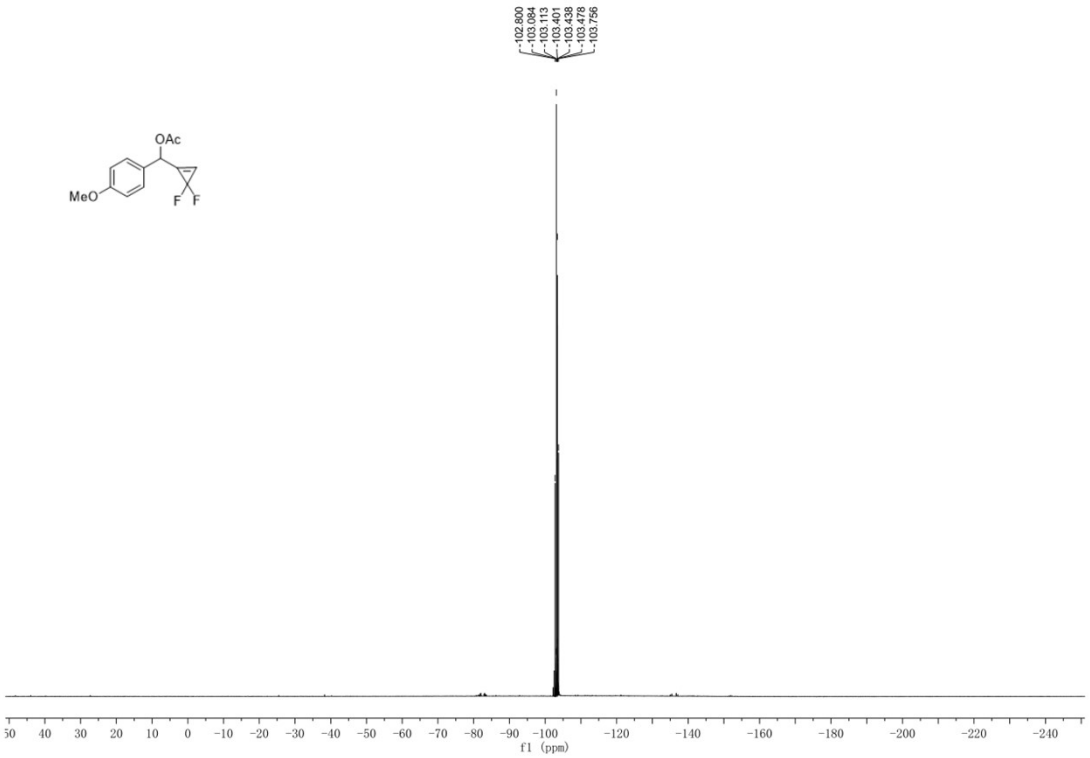
2d-^{1}H NMR (400 MHz, $CDCl_3$)



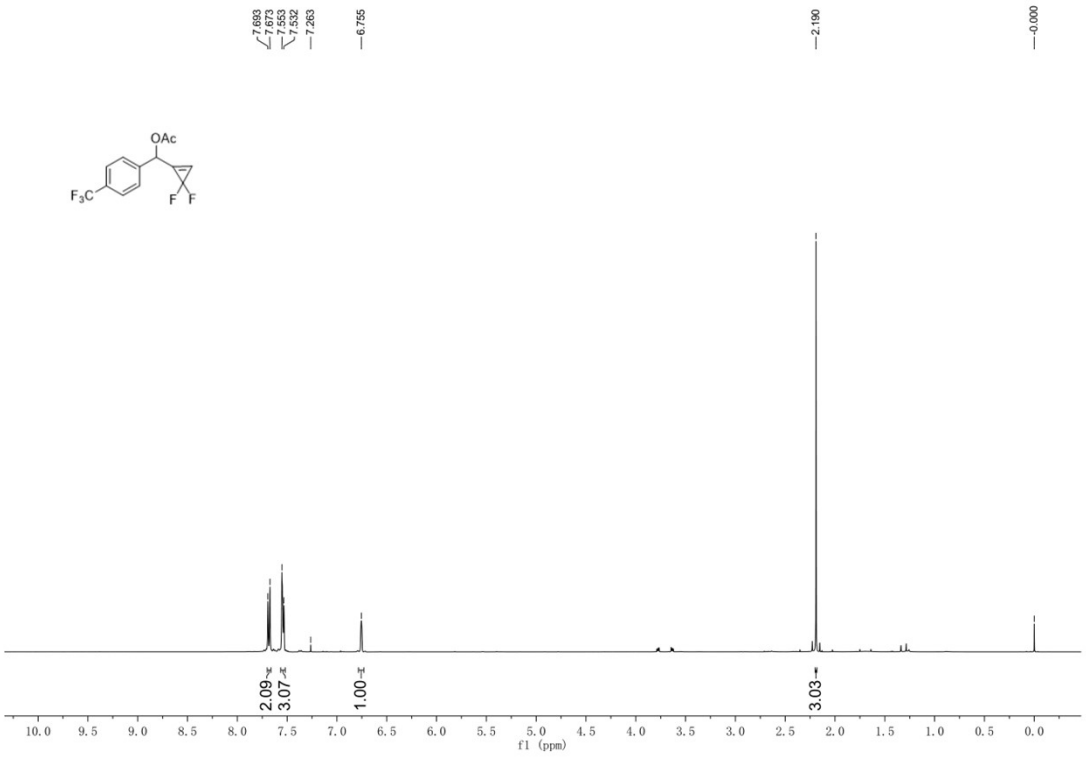
2d-^{13}C NMR (100 MHz, $CDCl_3$)



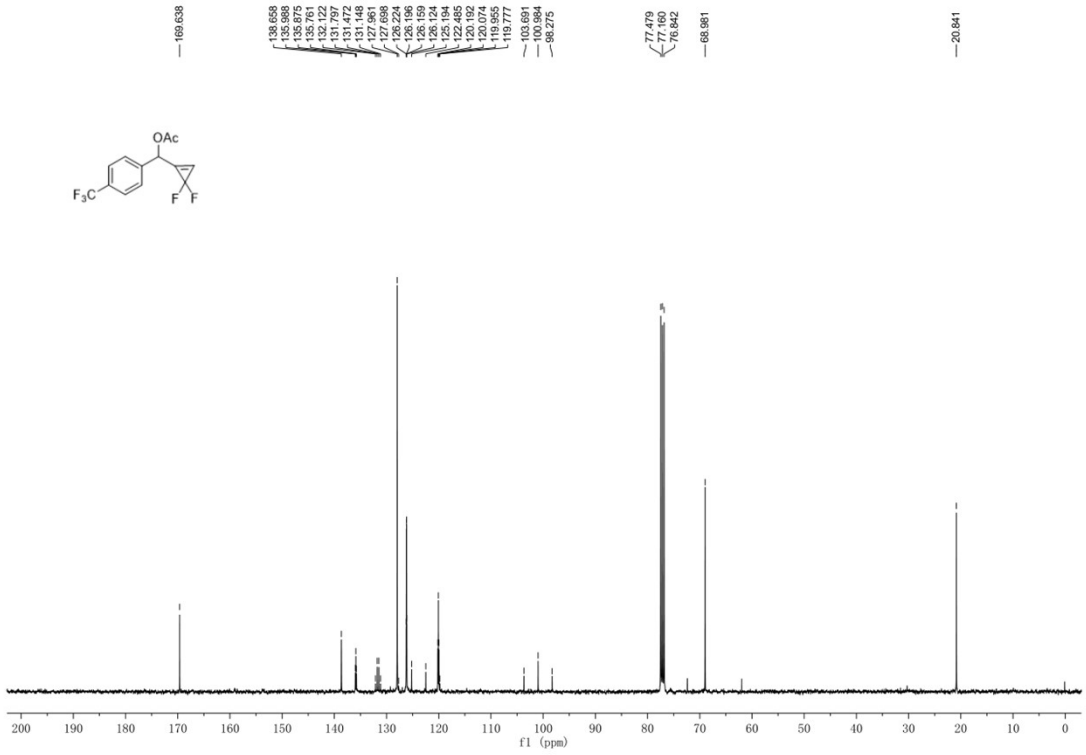
2d-^{19}F NMR (376 MHz, $CDCl_3$)



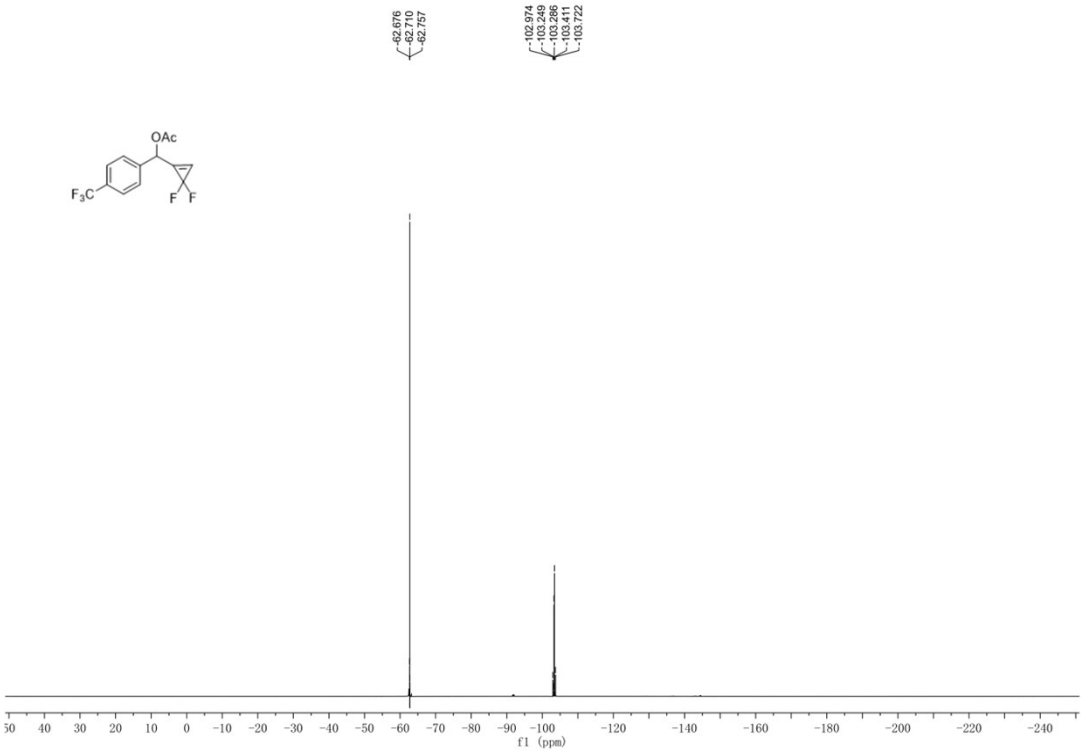
2f-^{1}H NMR (400 MHz, $CDCl_3$)



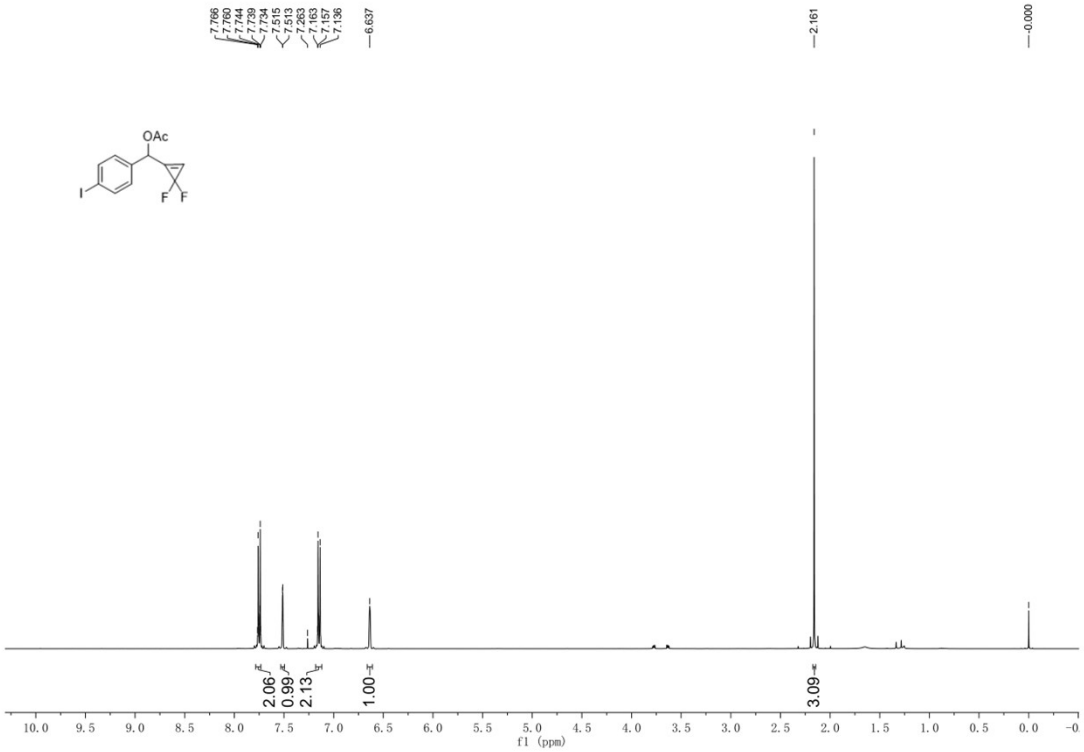
2f-^{13}C NMR (100 MHz, $CDCl_3$)



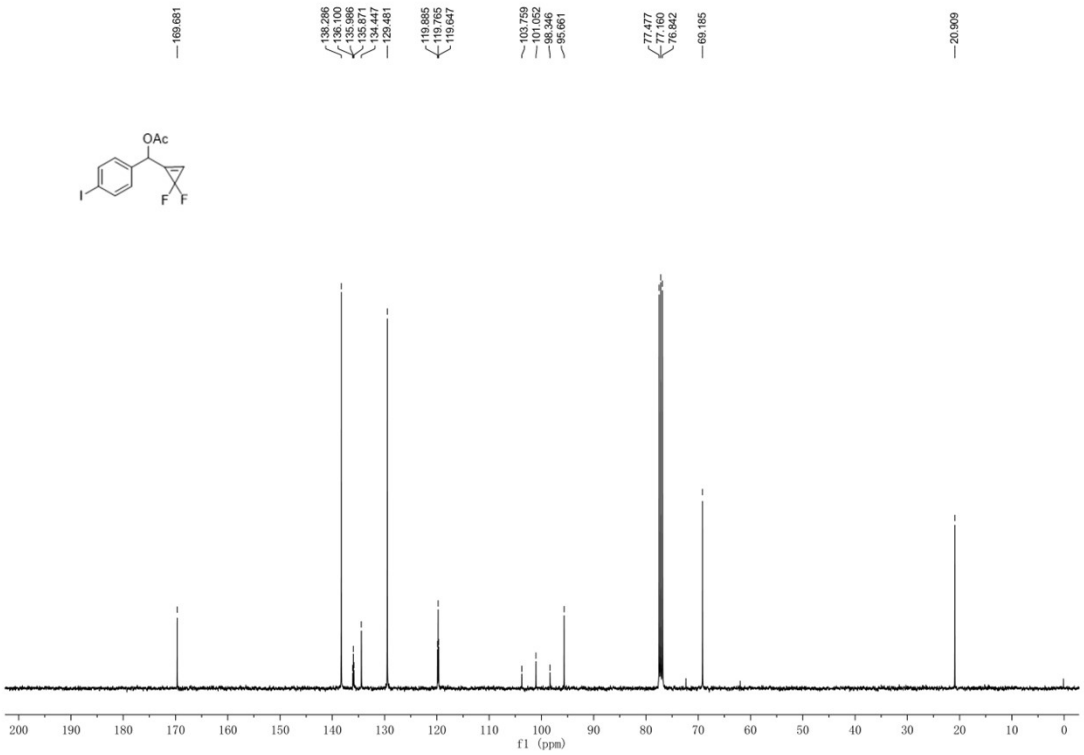
2f-^{19}F NMR (376 MHz, $CDCl_3$)



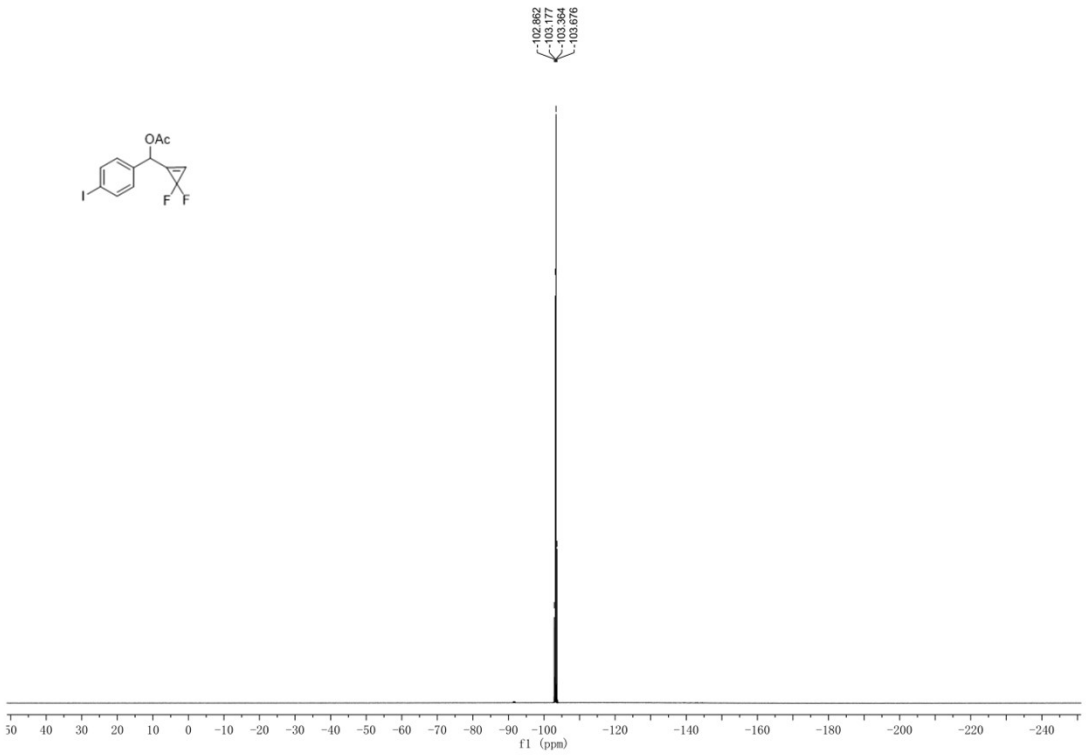
2i-^{1}H NMR (400 MHz, $CDCl_3$)



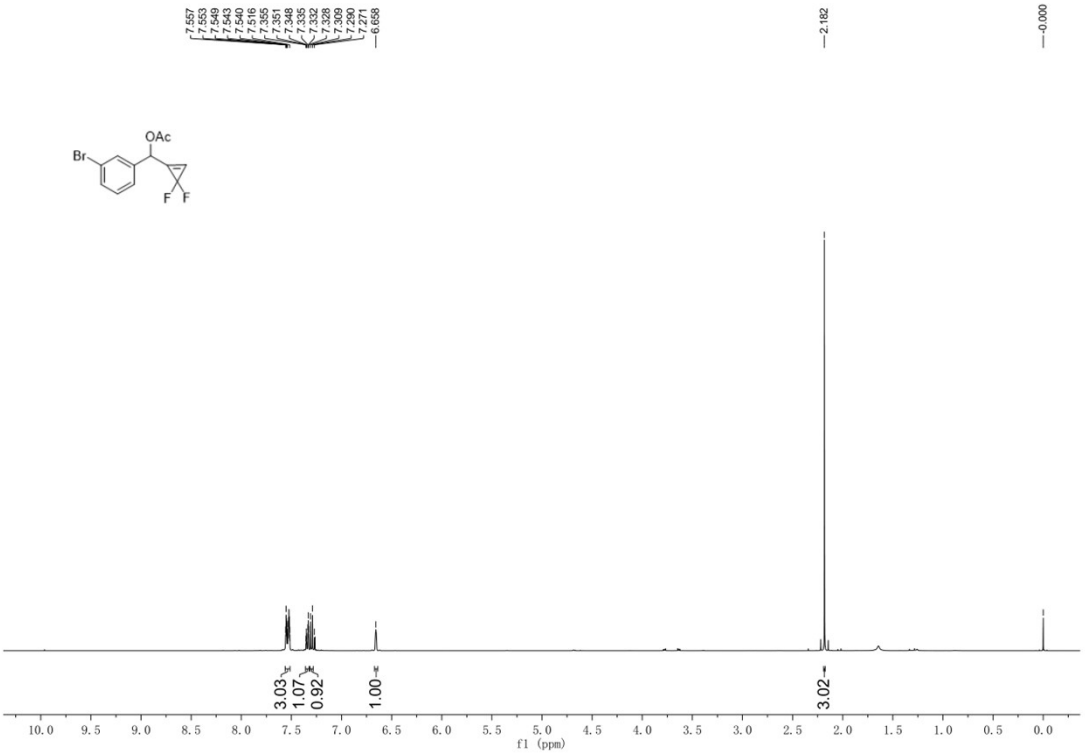
2i-^{13}C NMR (100 MHz, $CDCl_3$)



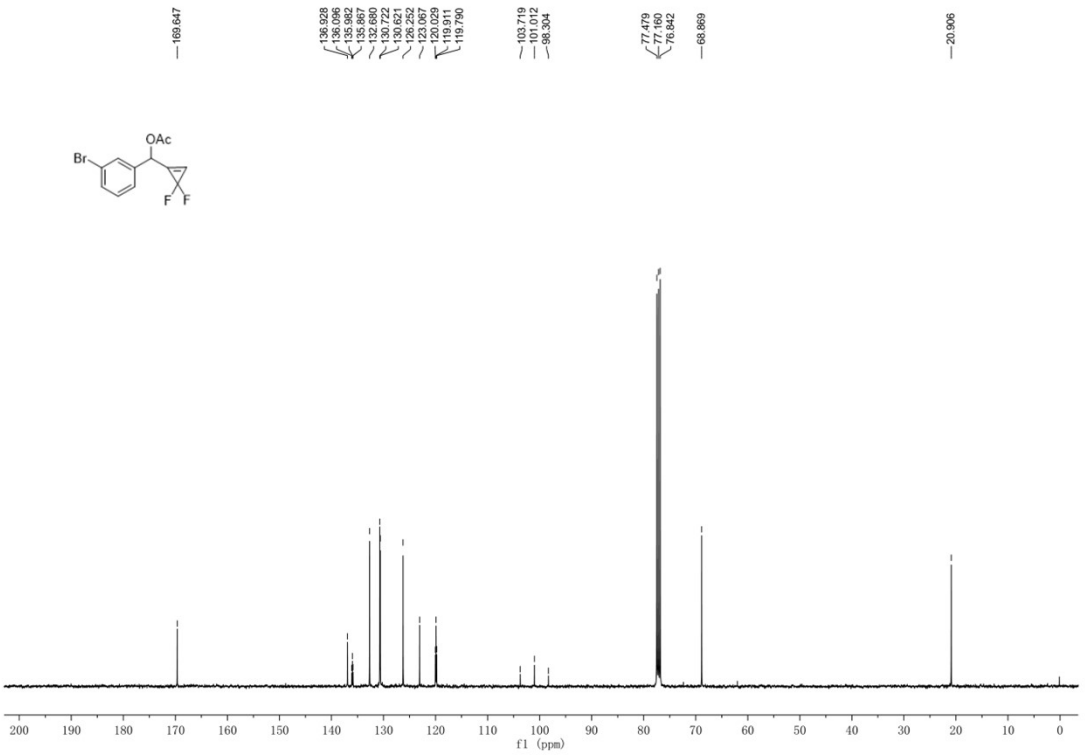
2i-^{19}F NMR (376 MHz, $CDCl_3$)



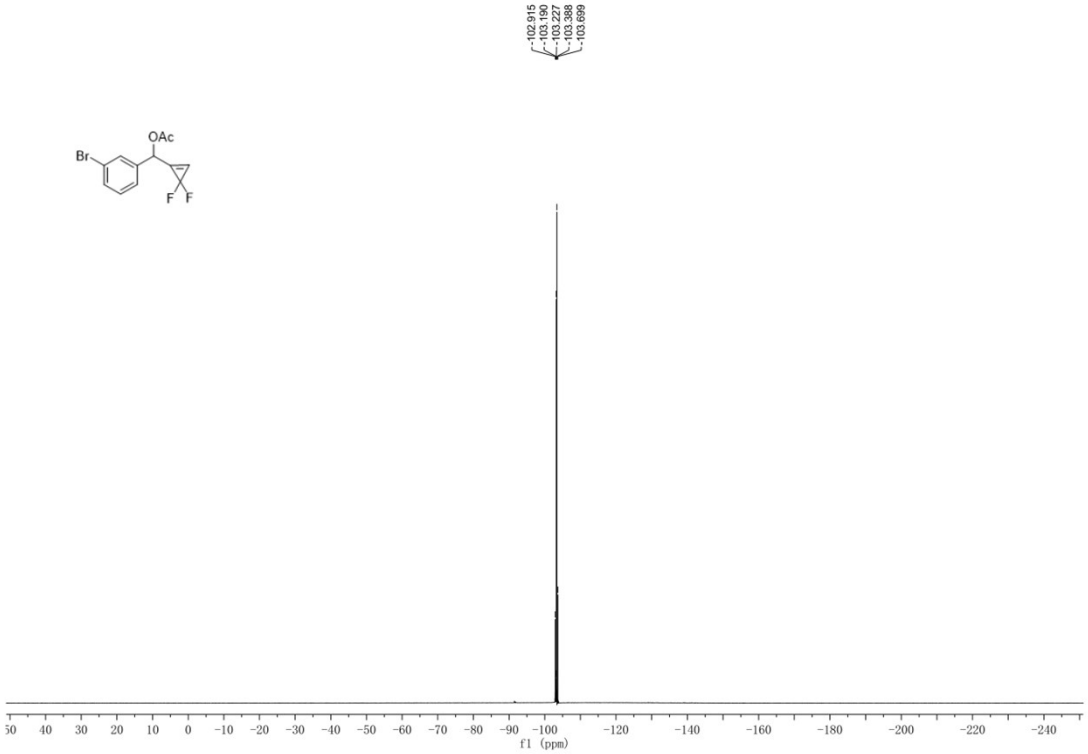
2m-^{1}H NMR (400 MHz, $CDCl_3$)



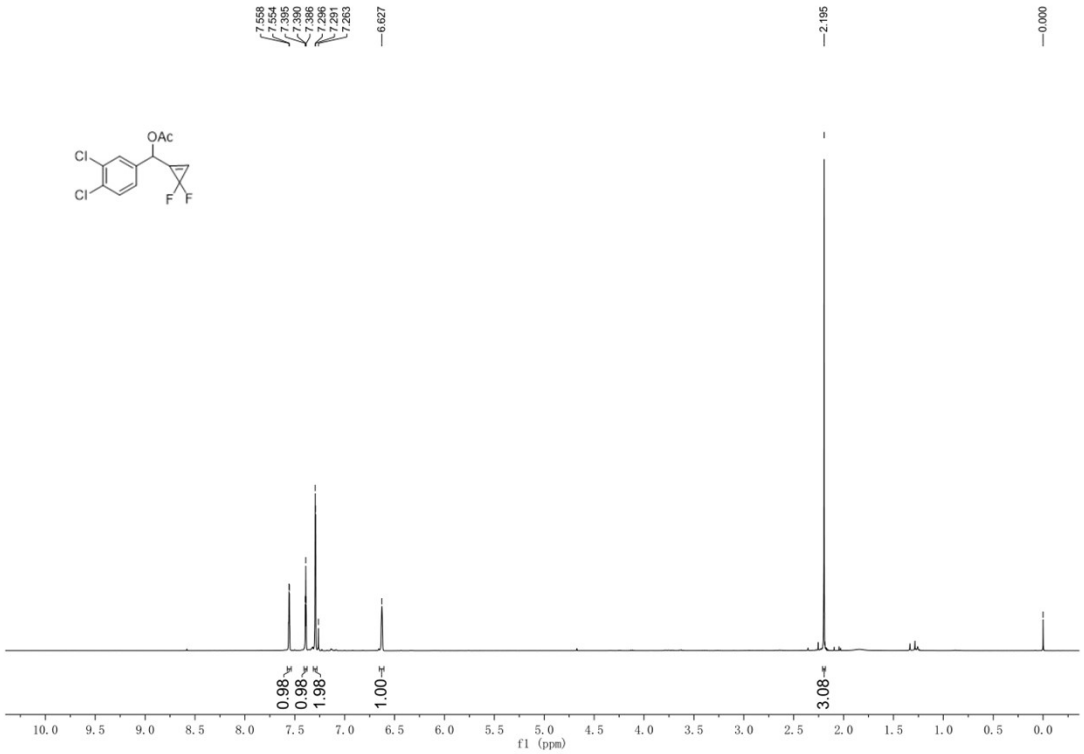
2m-^{13}C NMR (100 MHz, $CDCl_3$)



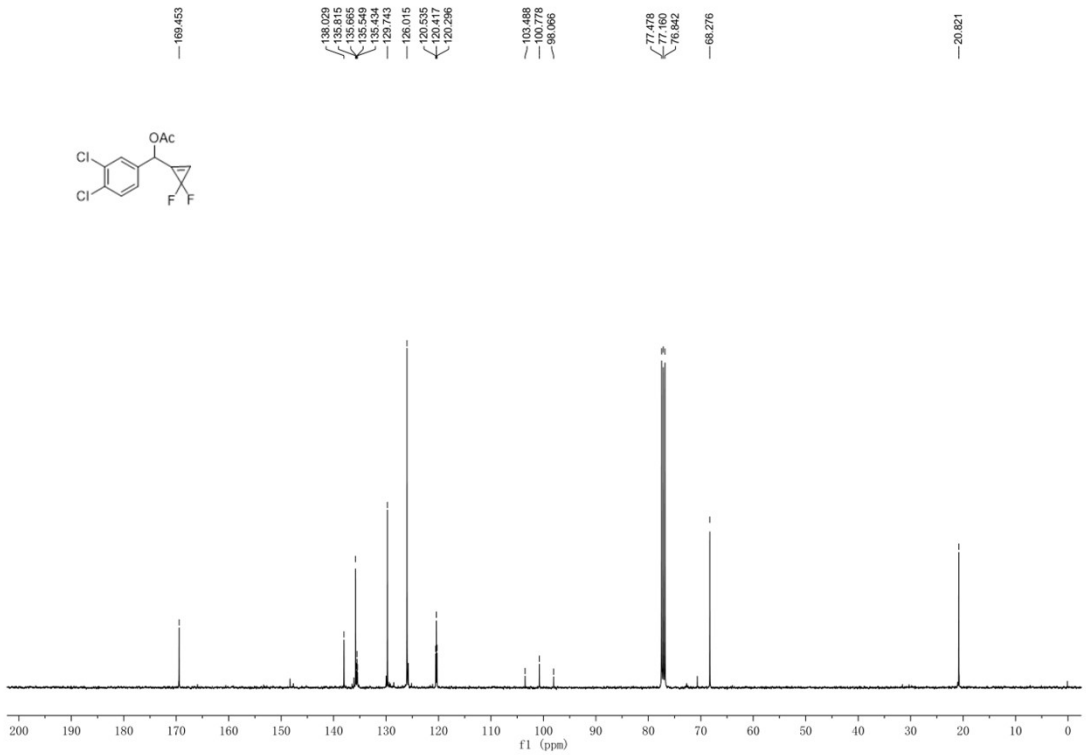
2m-^{19}F NMR (376 MHz, $CDCl_3$)



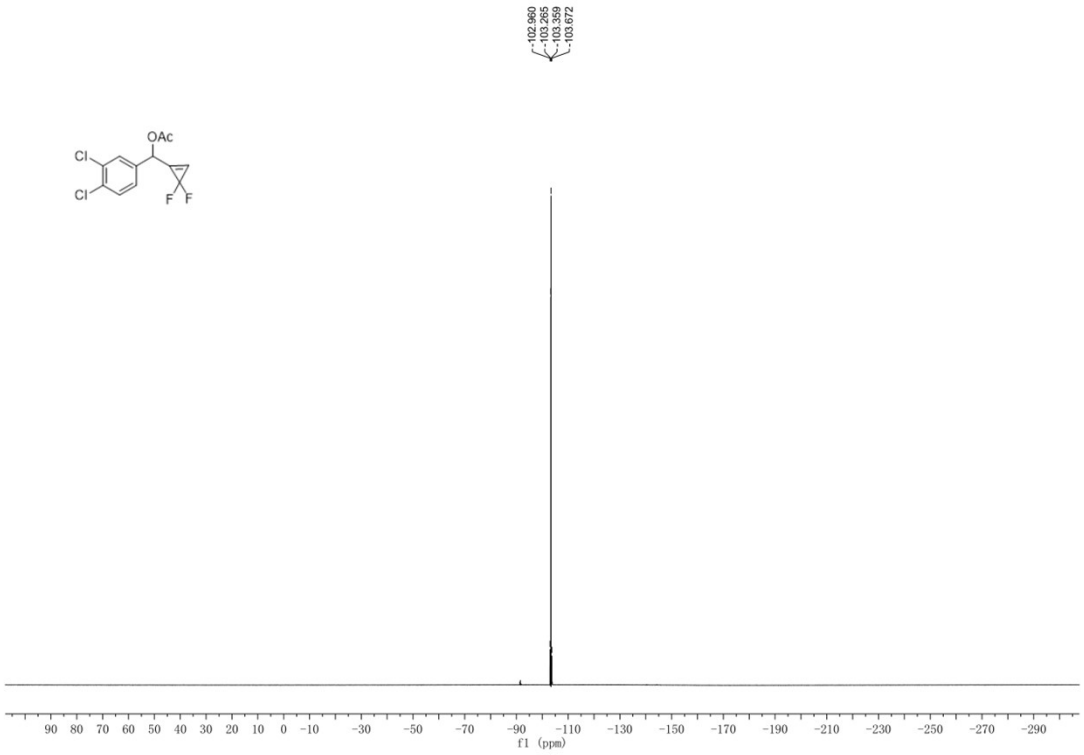
2n-^{1}H NMR (400 MHz, $CDCl_3$)



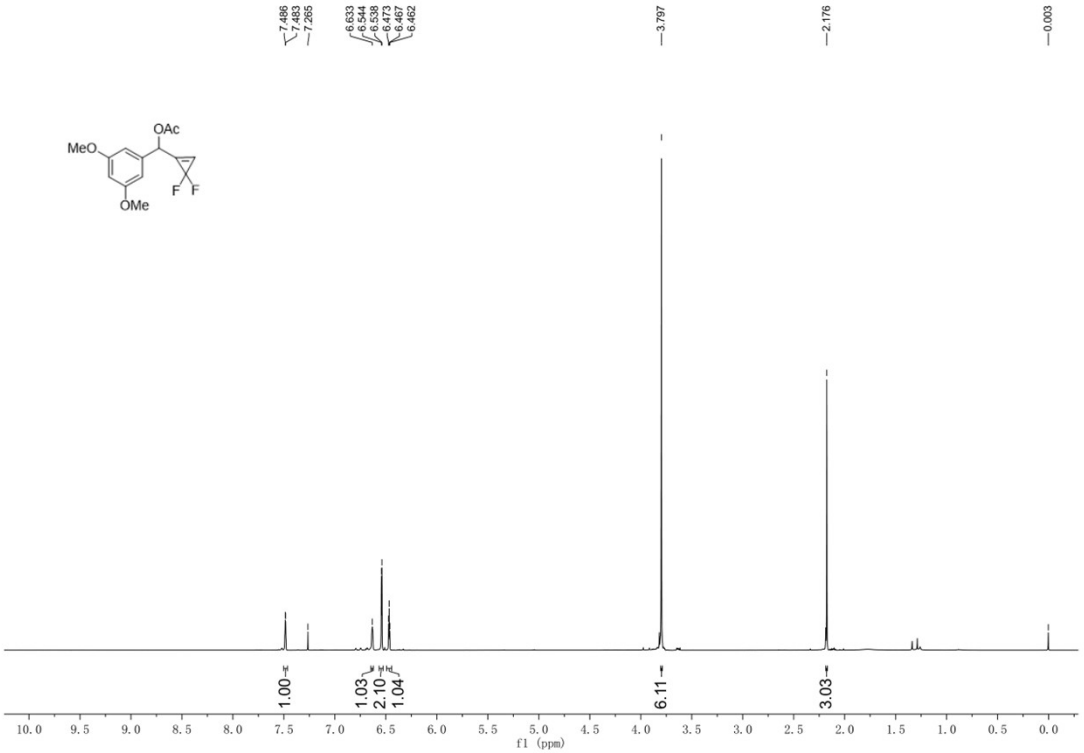
2n-^{13}C NMR (100 MHz, $CDCl_3$)



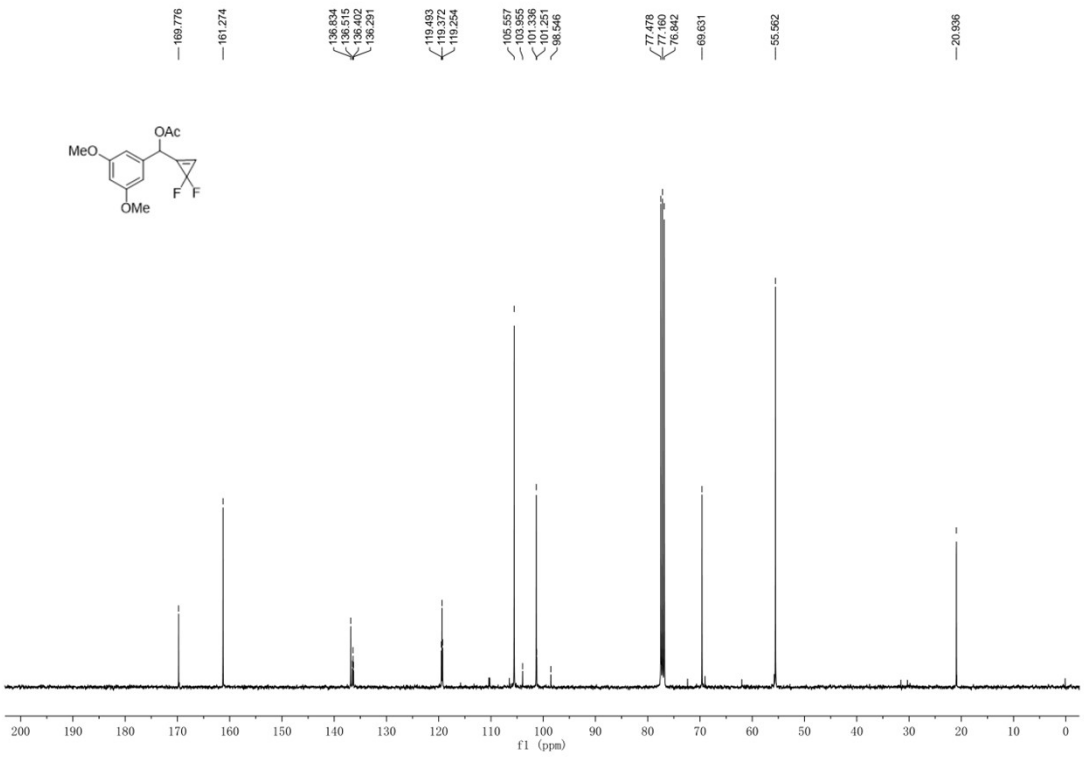
2n-^{19}F NMR (376 MHz, $CDCl_3$)



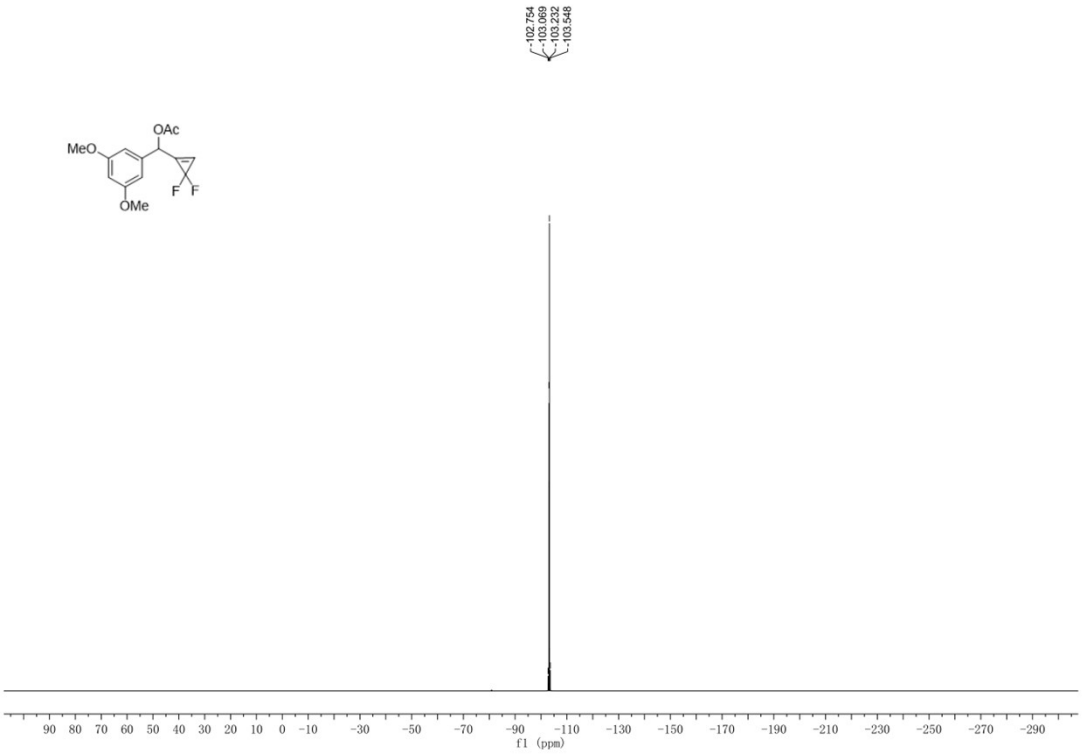
2o-^{1}H NMR (400 MHz, $CDCl_3$)



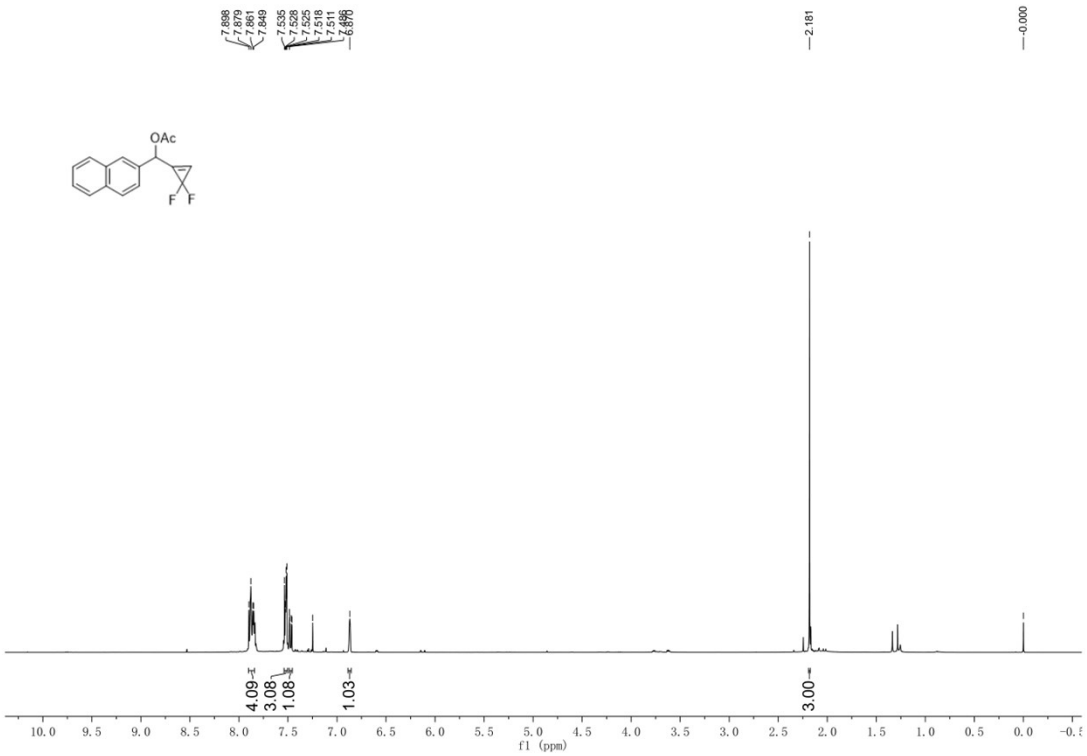
2o-^{13}C NMR (100 MHz, $CDCl_3$)



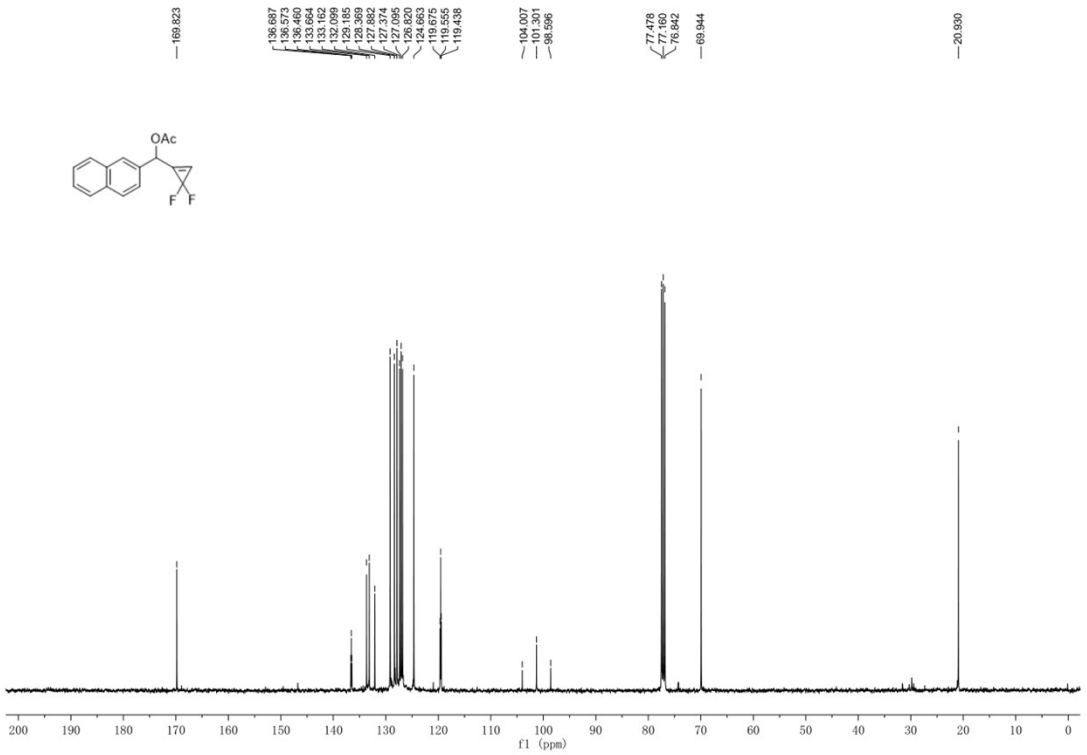
2o-^{19}F NMR (376 MHz, $CDCl_3$)



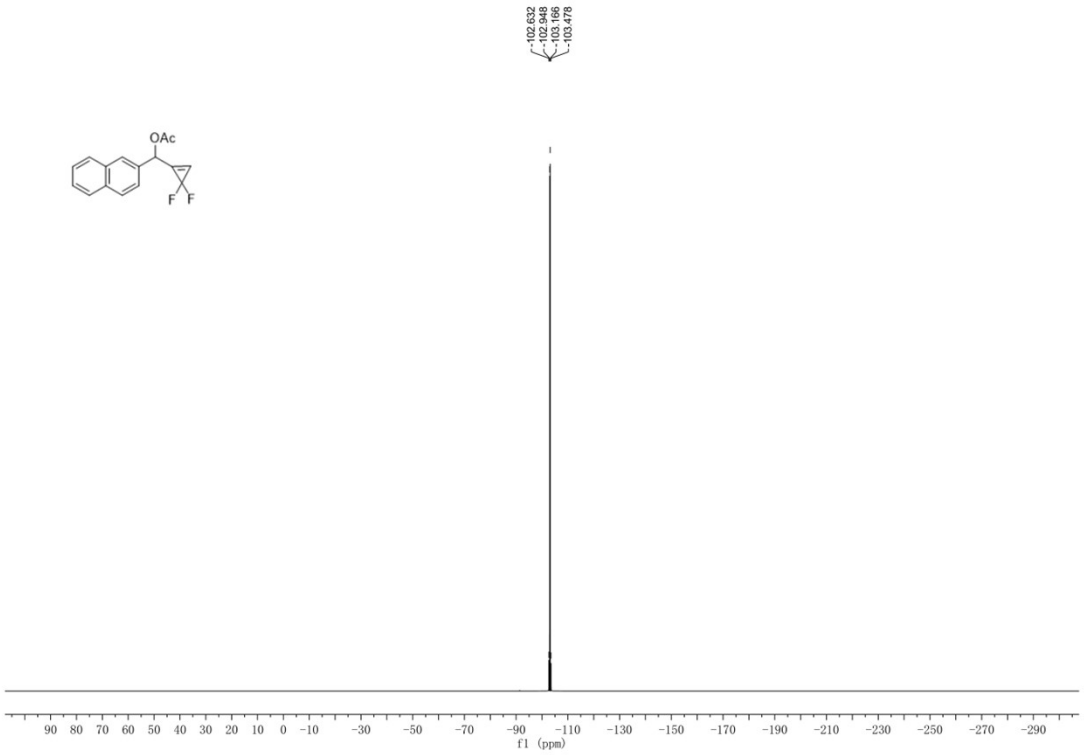
2p-^{1}H NMR (400 MHz, $CDCl_3$)



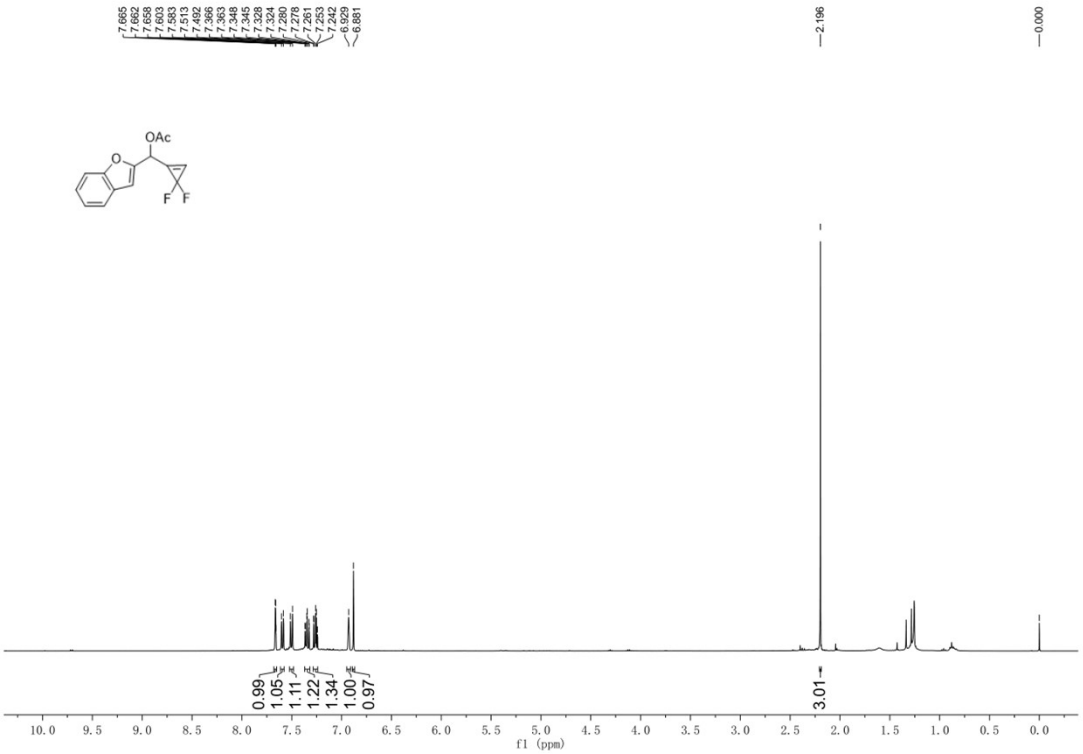
2p-^{13}C NMR (100 MHz, $CDCl_3$)



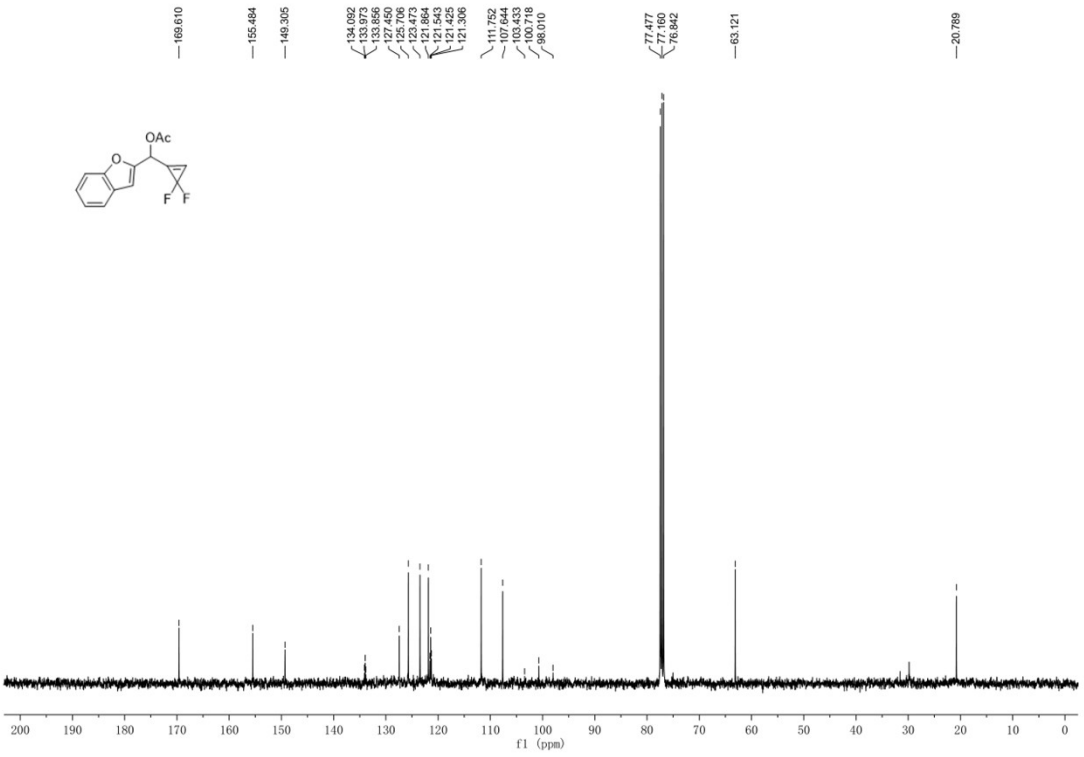
2p-^{19}F NMR (376 MHz, $CDCl_3$)



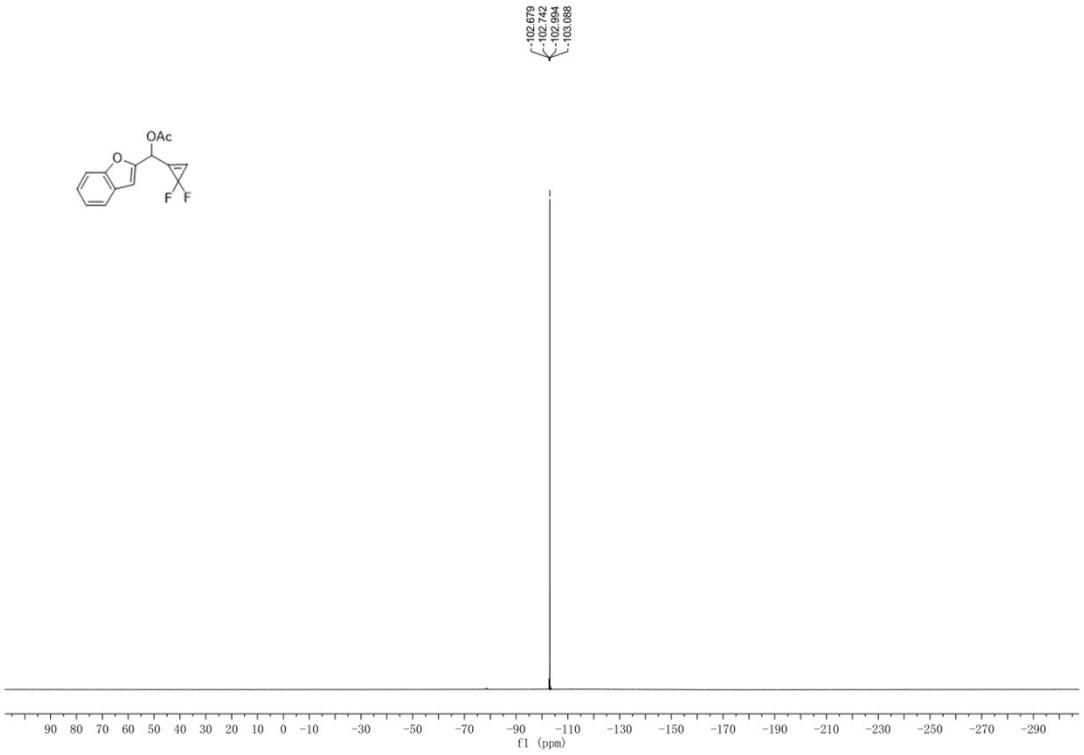
2q-^{1}H NMR (400 MHz, $CDCl_3$)



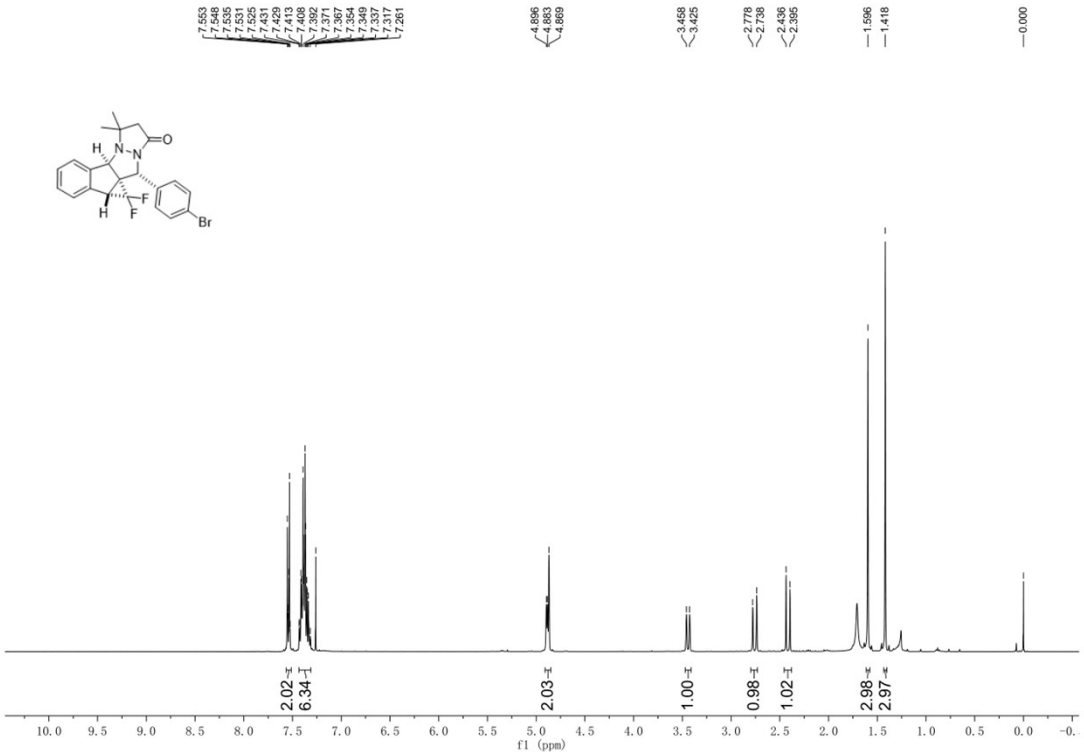
2q-^{13}C NMR (100 MHz, $CDCl_3$)



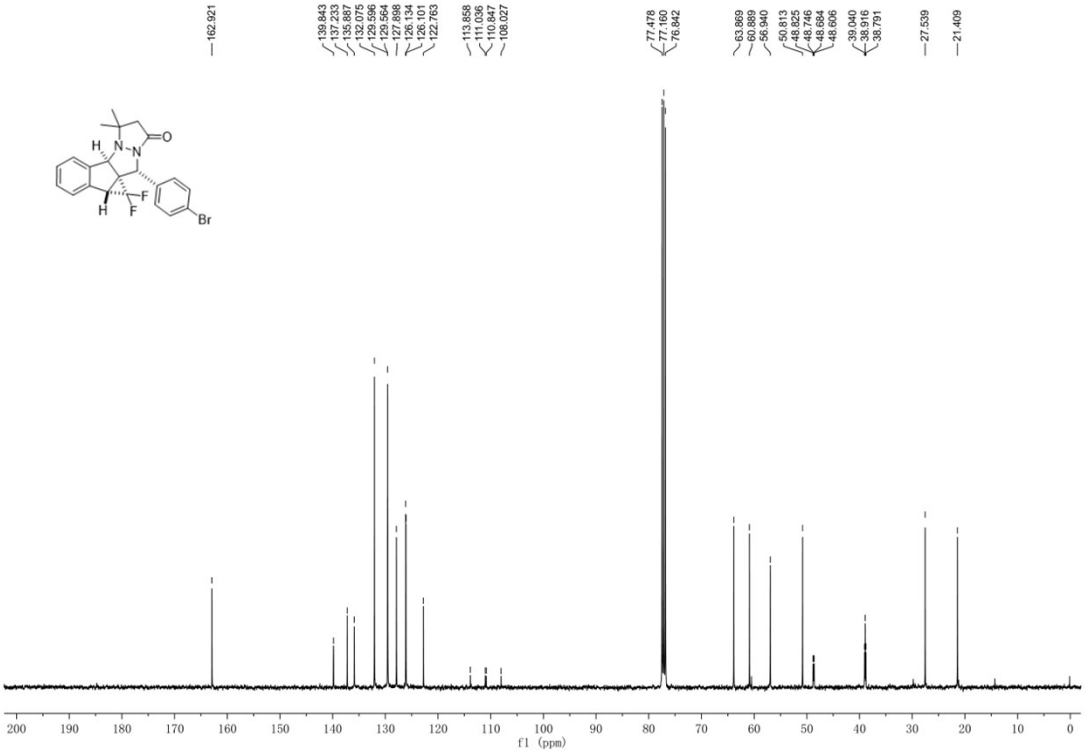
2q-^{19}F NMR (376 MHz, $CDCl_3$)



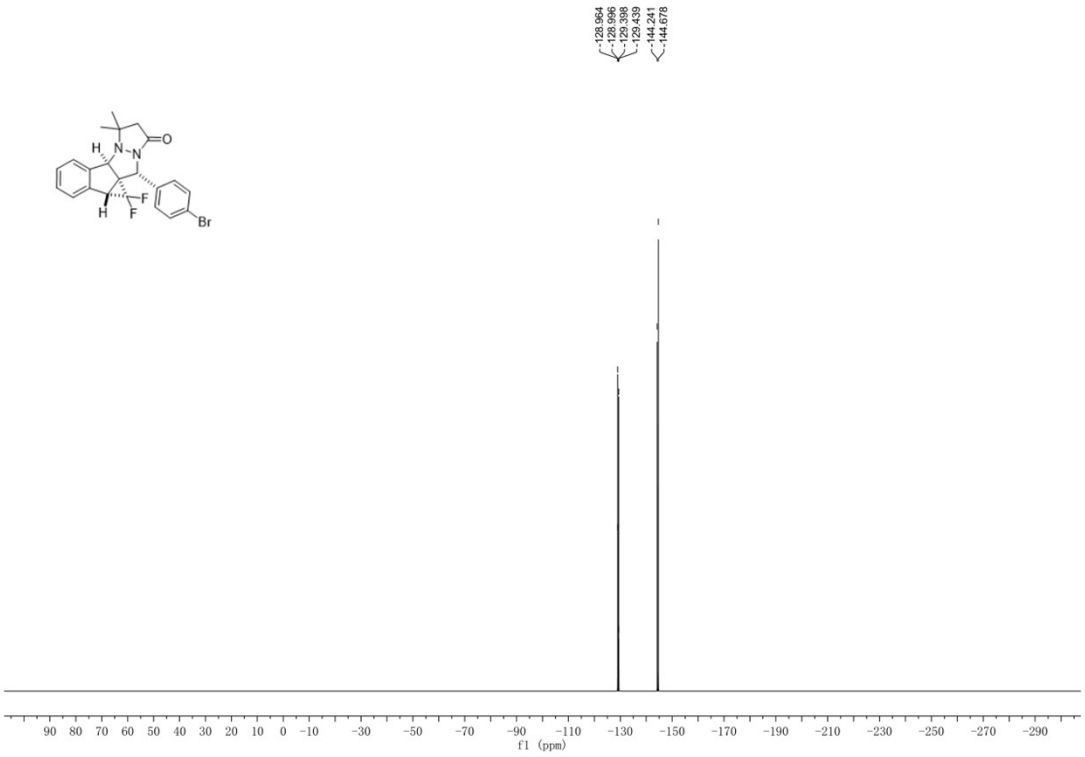
3aa-^{1}H NMR (400 MHz, $CDCl_3$)



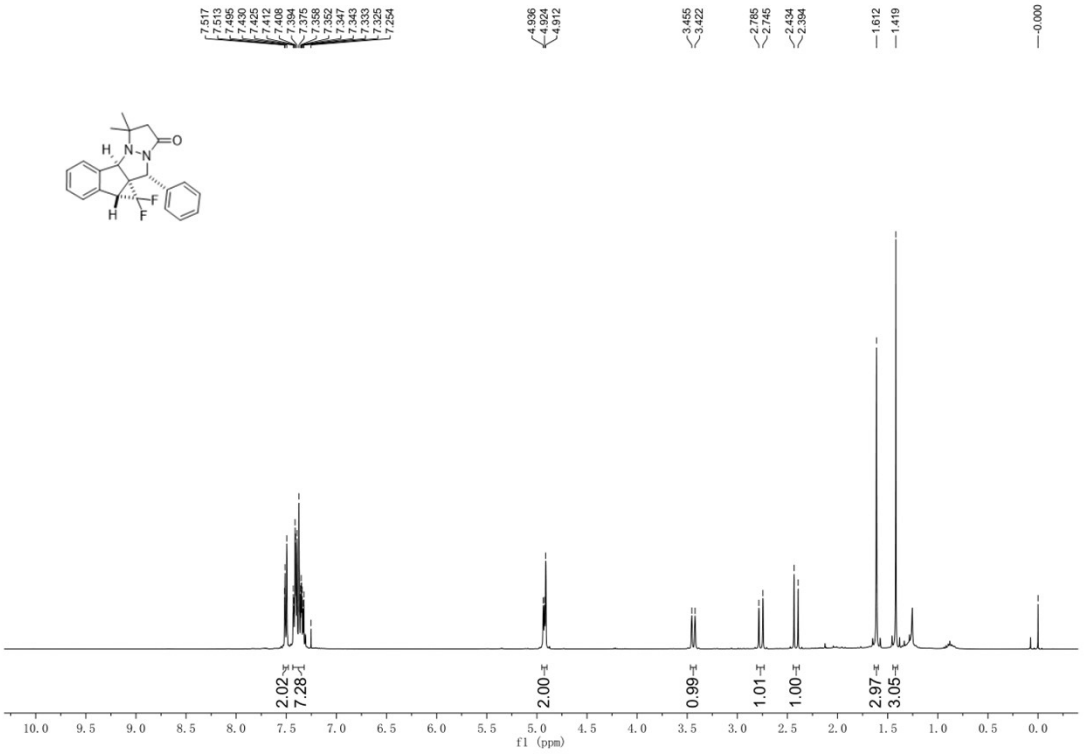
3aa-^{13}C NMR (100 MHz, $CDCl_3$)



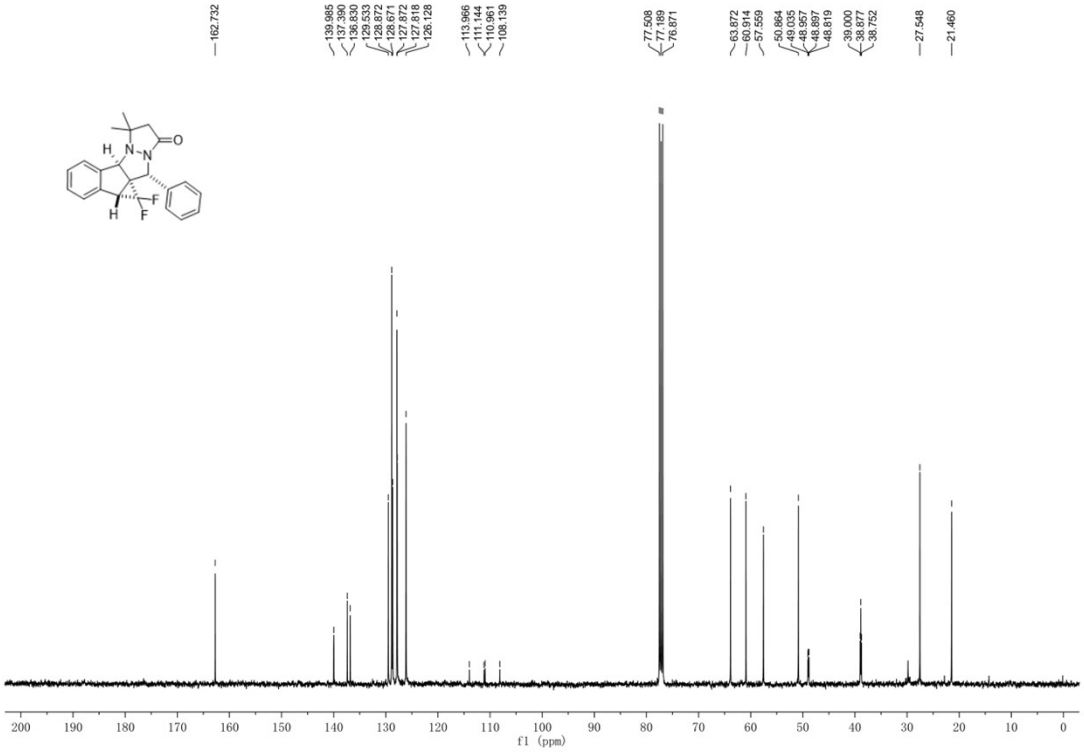
3aa-^{19}F NMR (376 MHz, $CDCl_3$)



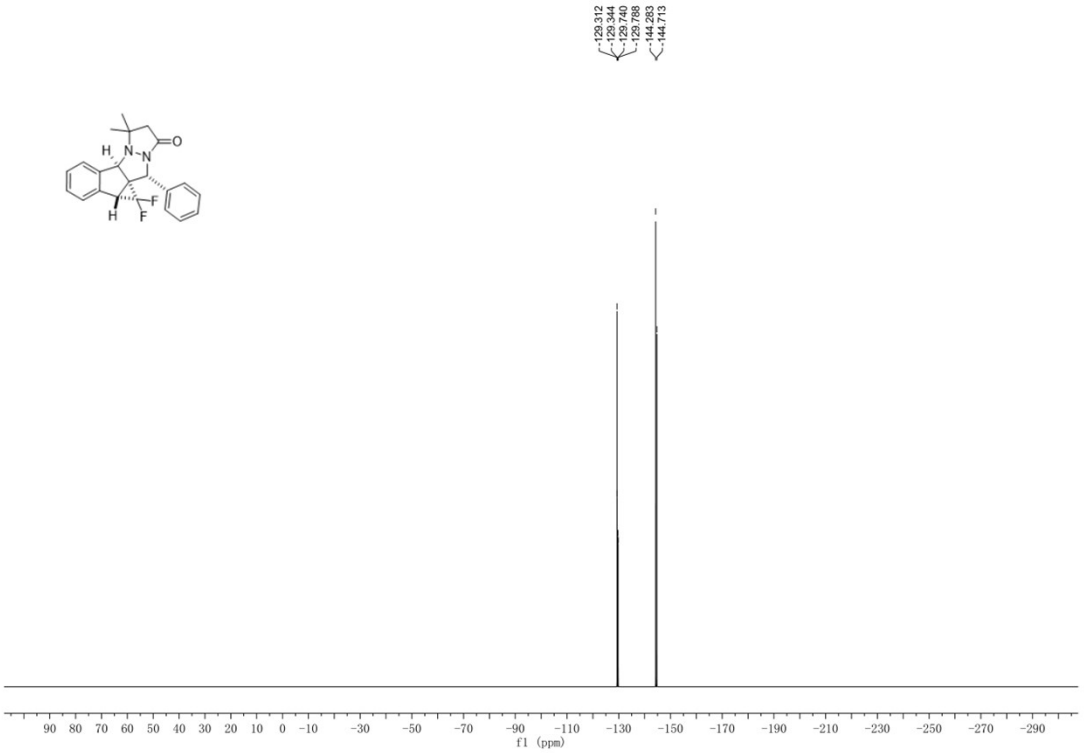
3ab-^{1}H NMR (400 MHz, $CDCl_3$)



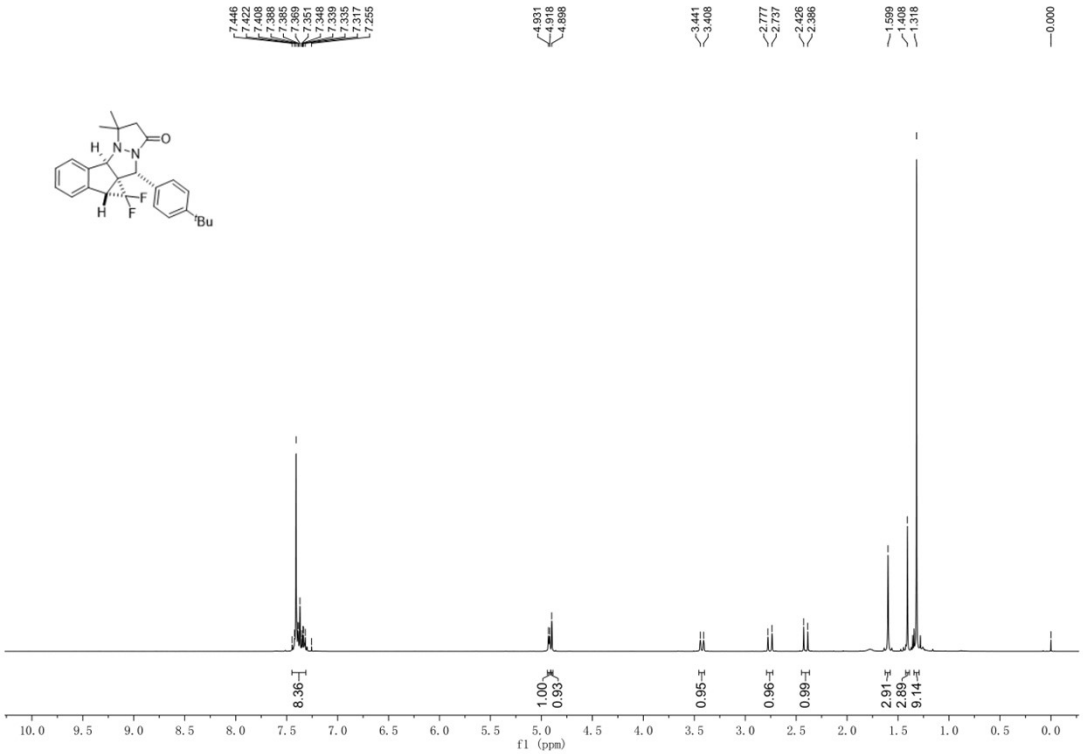
3ab-^{13}C NMR (100 MHz, $CDCl_3$)



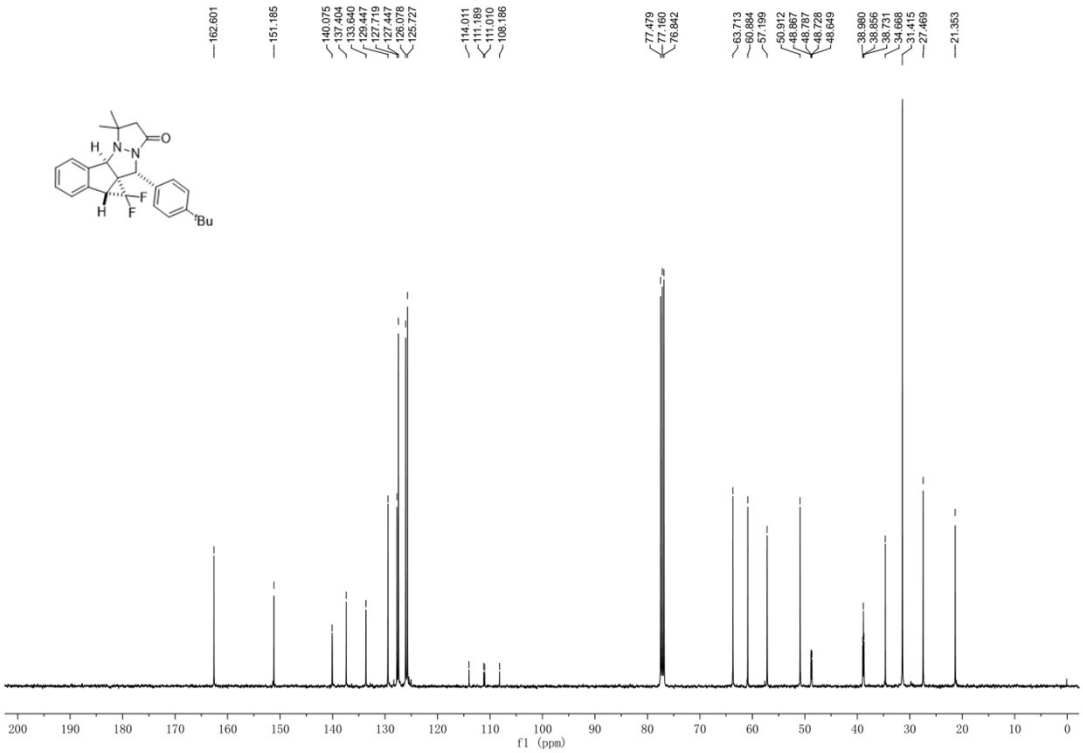
3ab-^{19}F NMR (376 MHz, $CDCl_3$)



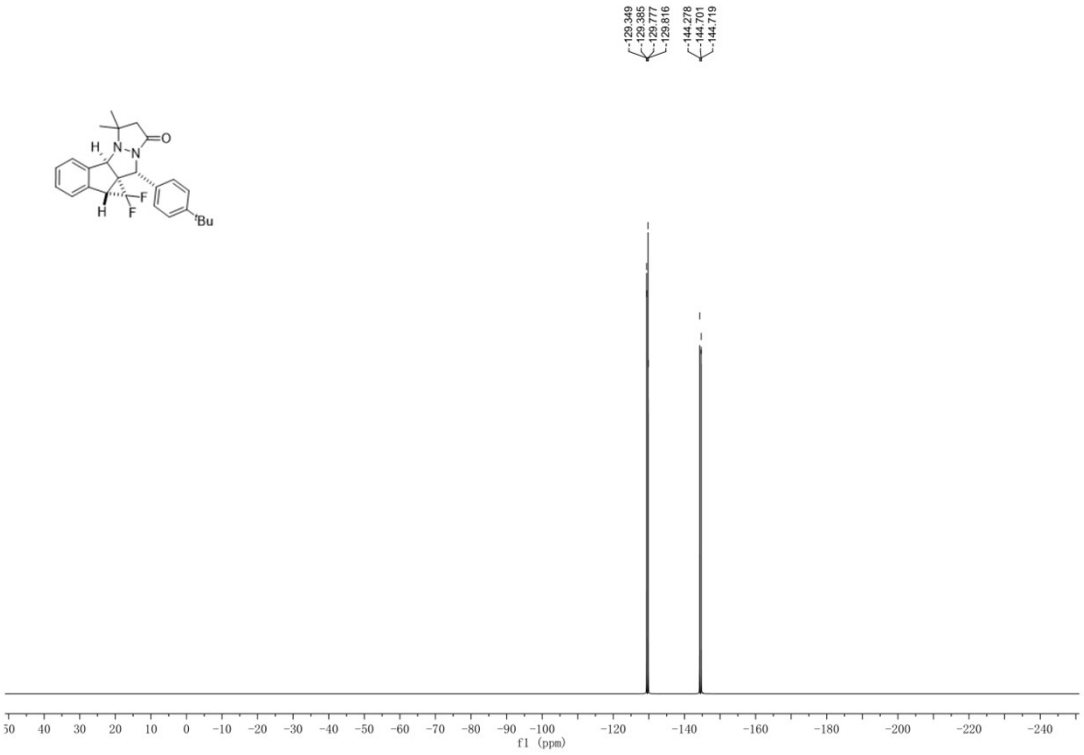
3ac-^{1}H NMR (400 MHz, $CDCl_3$)



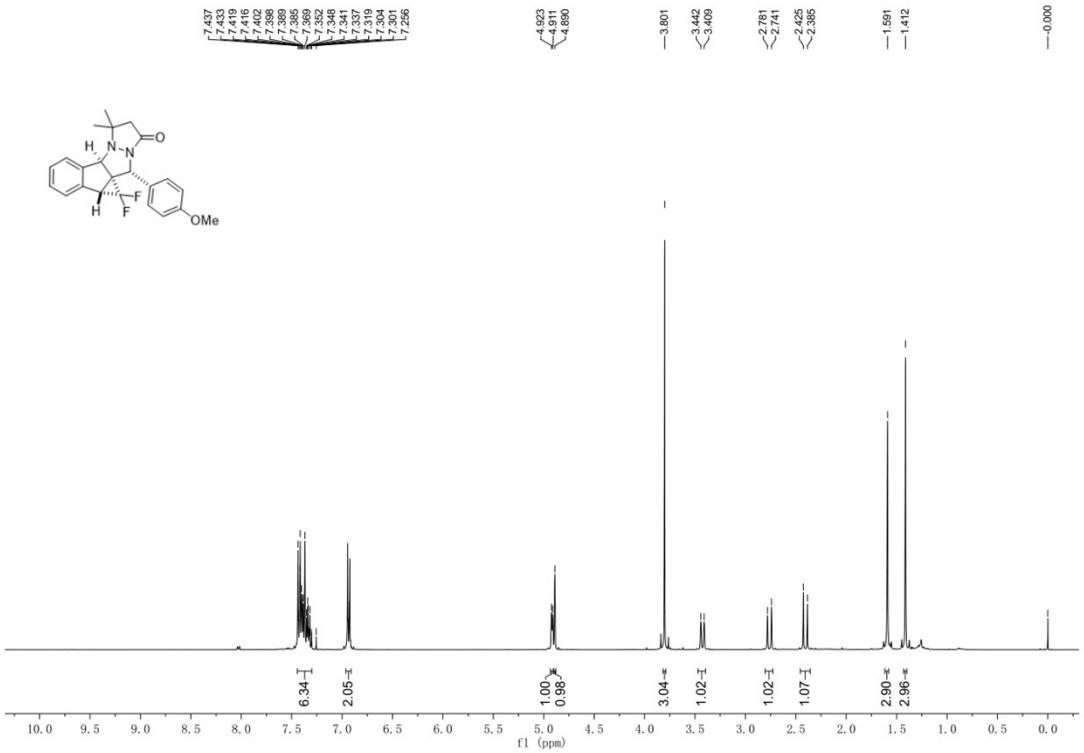
3ac-^{13}C NMR (100 MHz, $CDCl_3$)



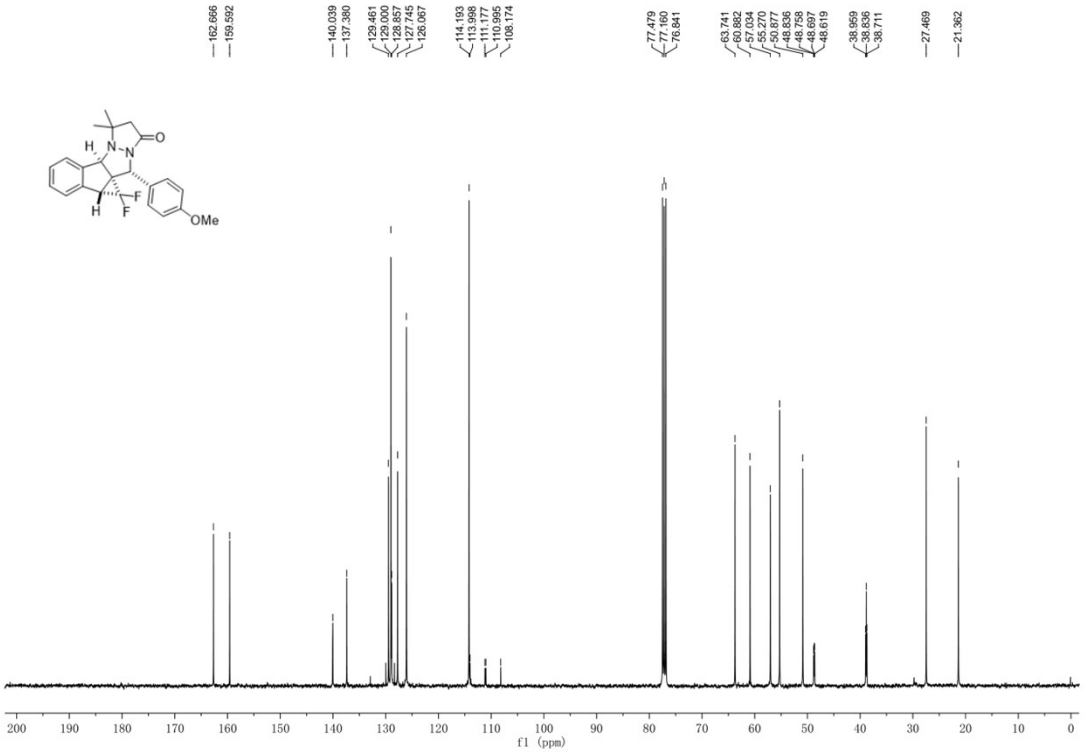
3ac-^{19}F NMR (376 MHz, $CDCl_3$)



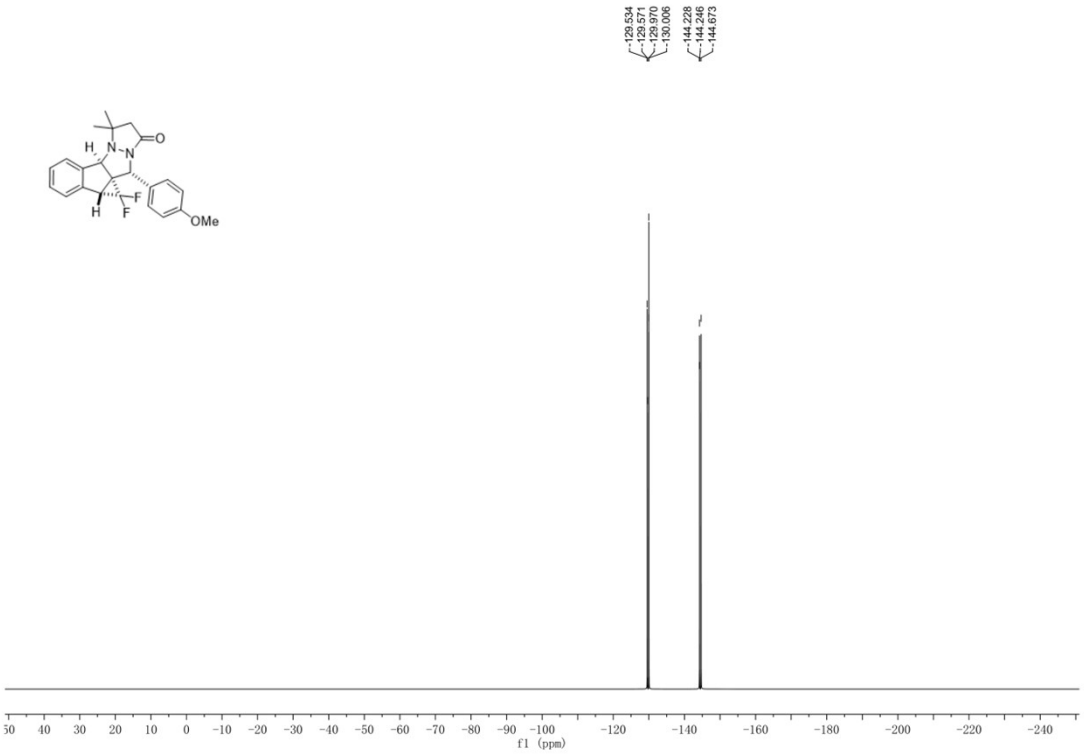
3ad-^{1}H NMR (400 MHz, $CDCl_3$)



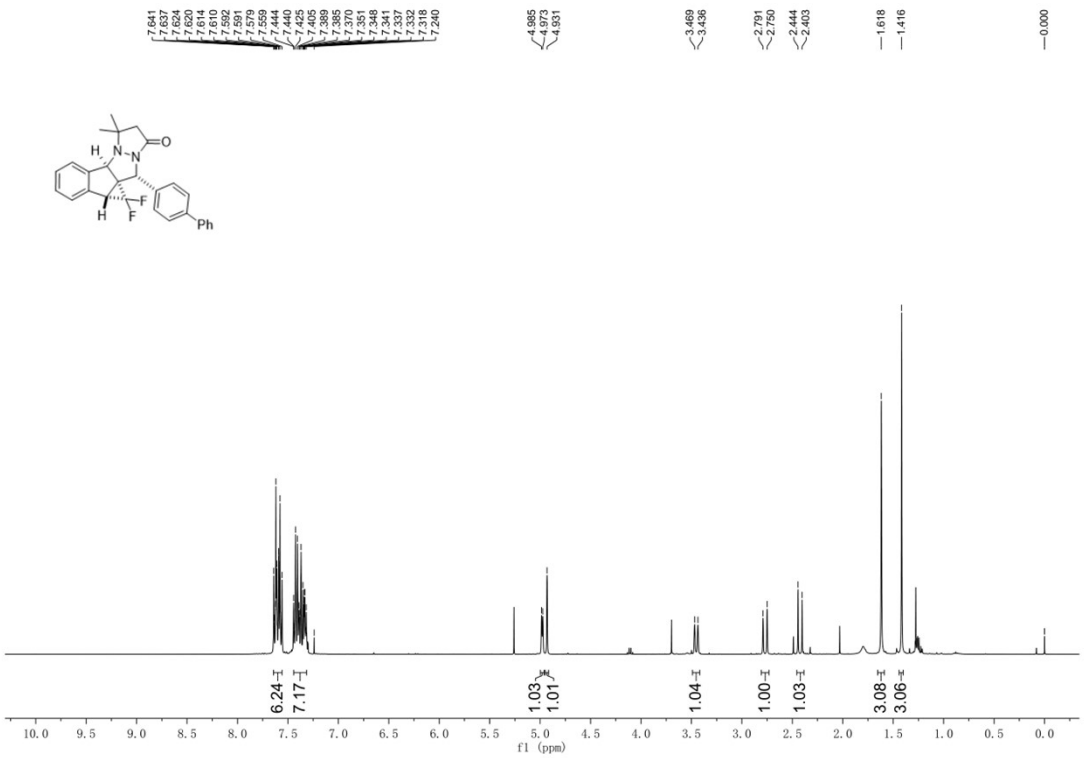
3ad-^{13}C NMR (100 MHz, $CDCl_3$)



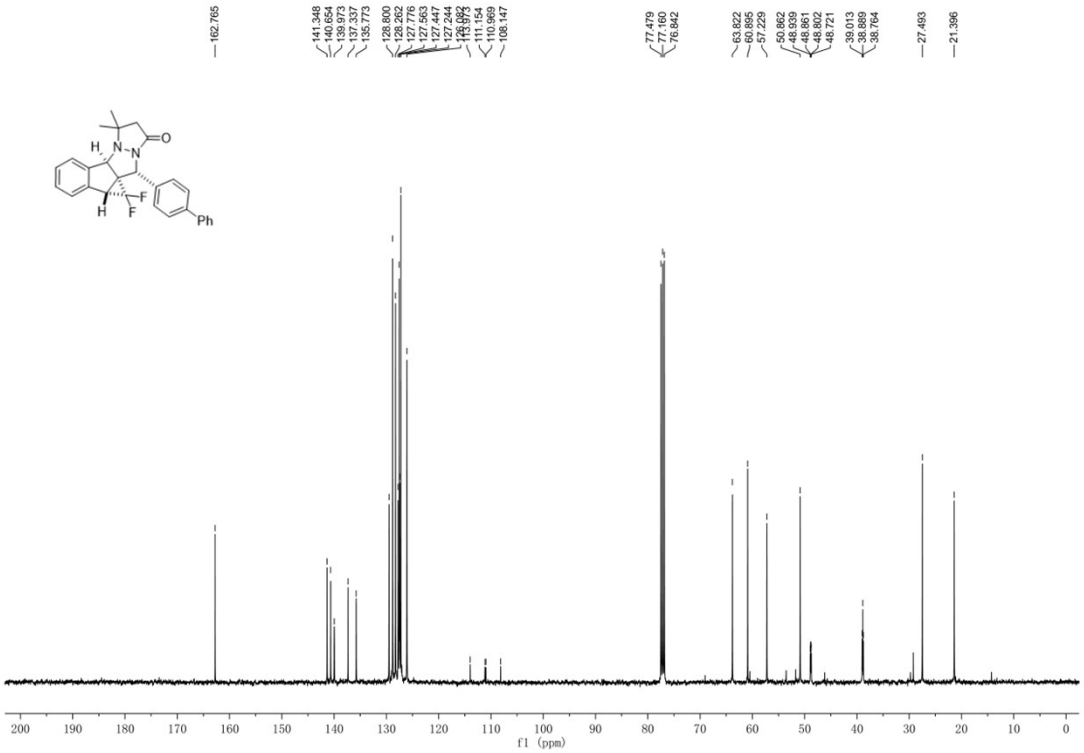
3ad-^{19}F NMR (376 MHz, $CDCl_3$)



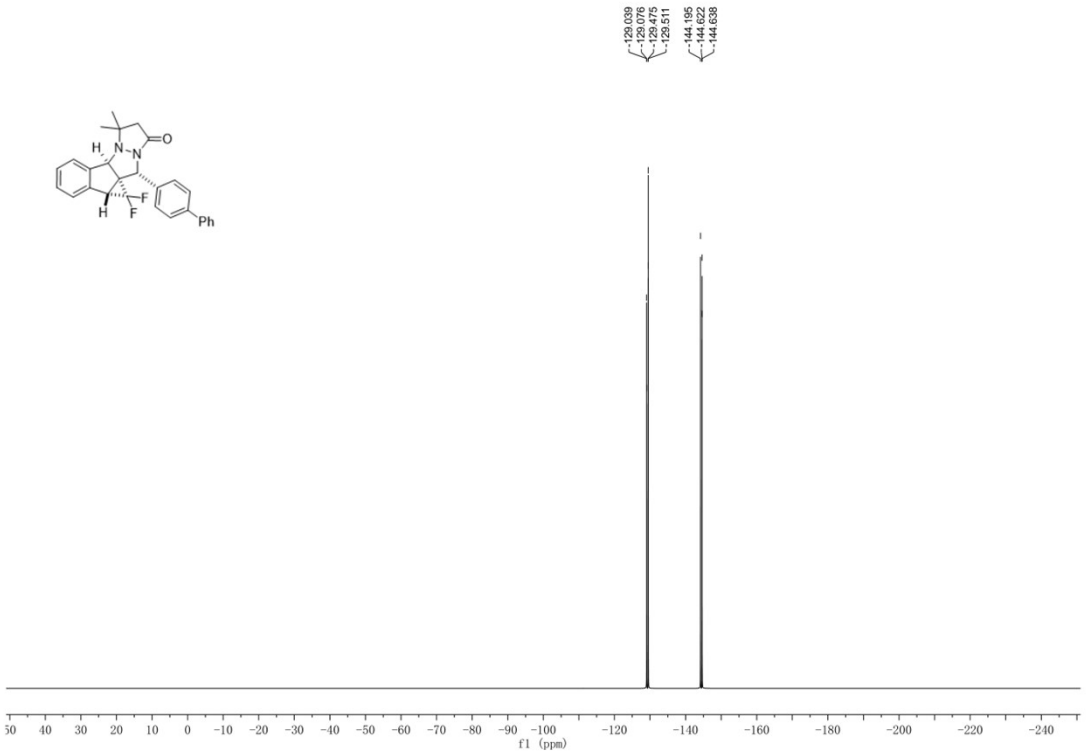
3ae-^{1}H NMR (400 MHz, $CDCl_3$)



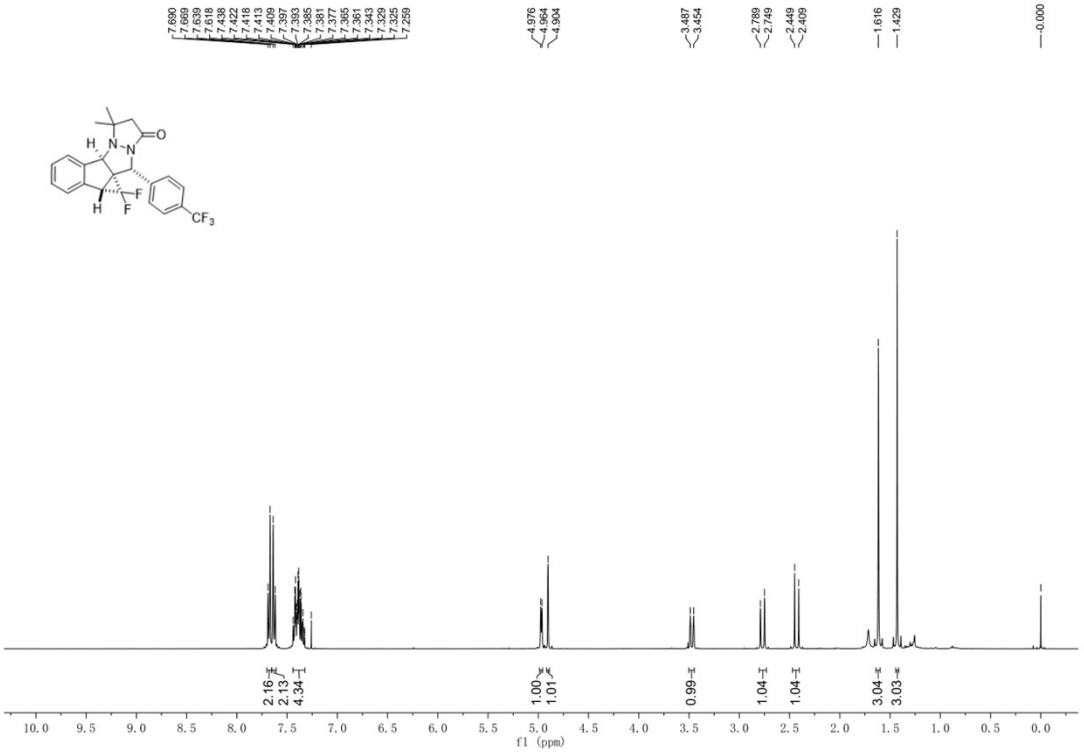
3ae-^{13}C NMR (100 MHz, $CDCl_3$)



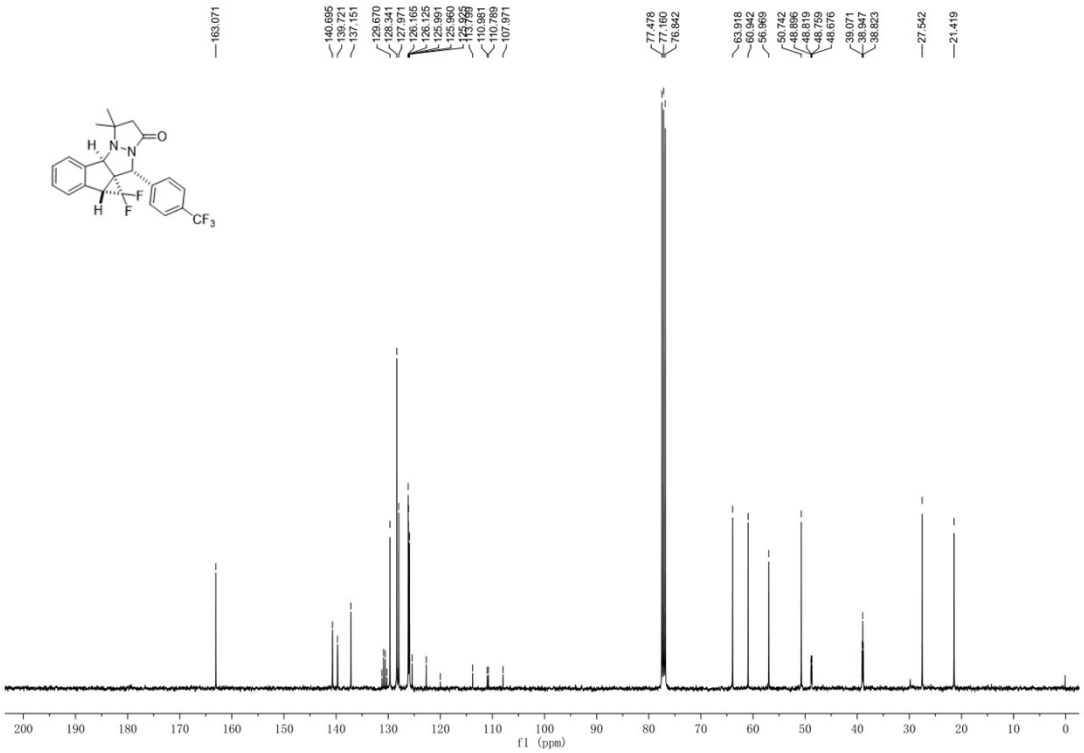
3ae-^{19}F NMR (376 MHz, $CDCl_3$)



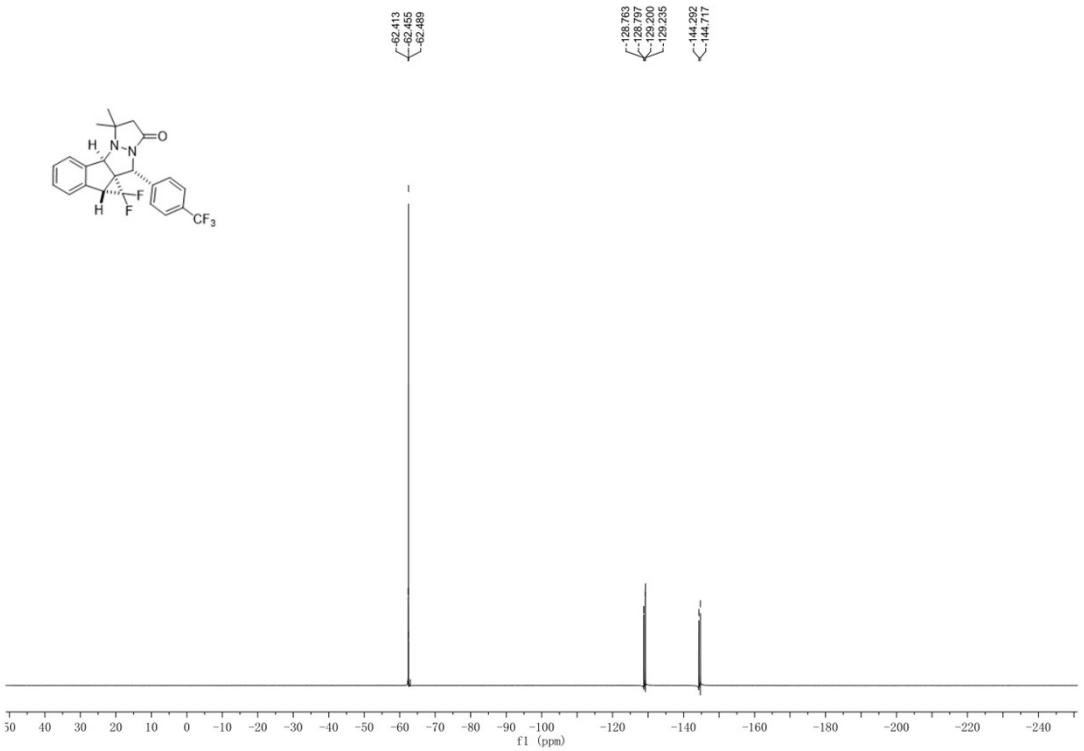
3af-^{1}H NMR (400 MHz, $CDCl_3$)



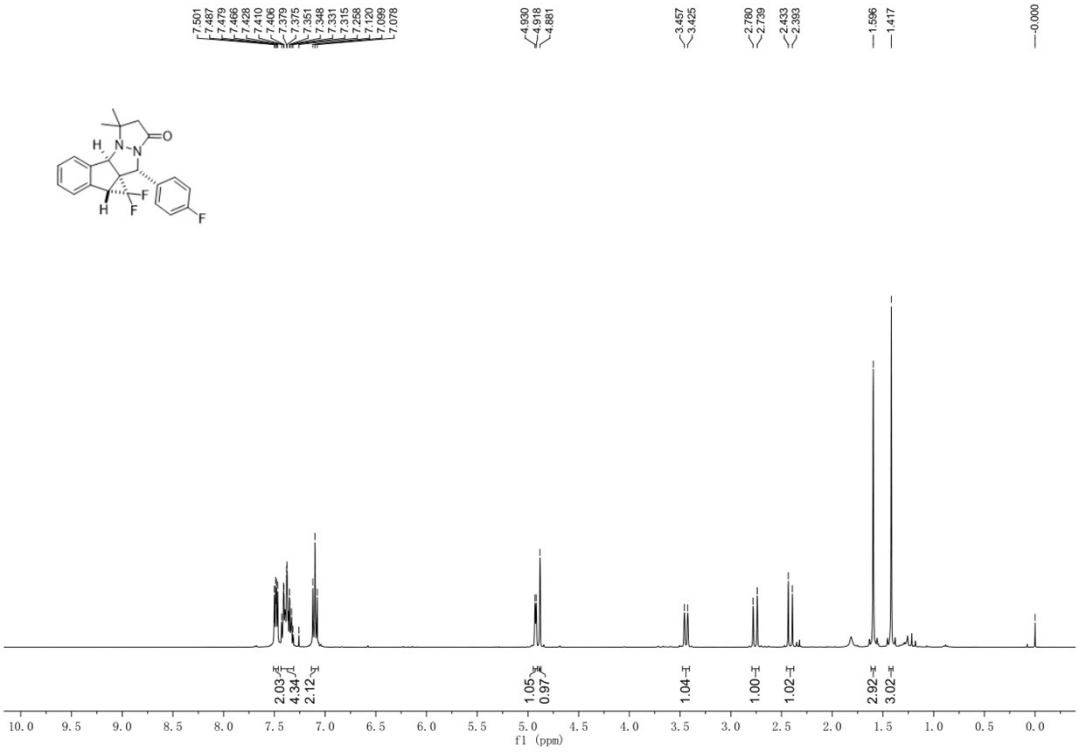
3af-^{13}C NMR (100 MHz, $CDCl_3$)



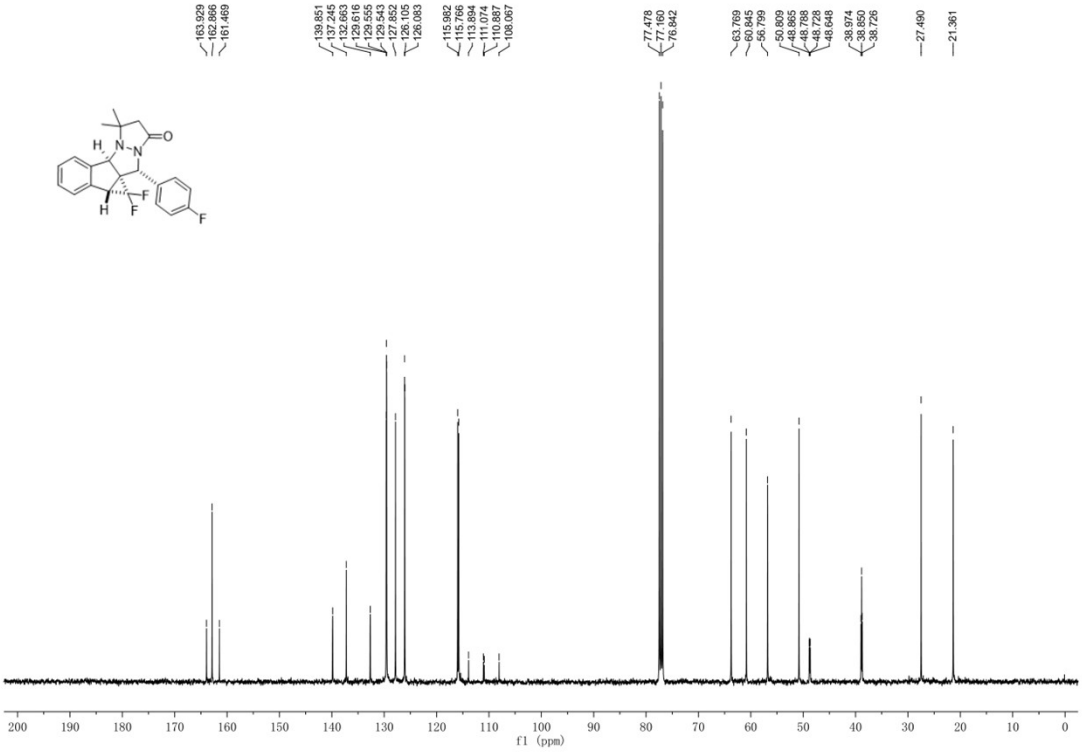
3af-^{19}F NMR (376 MHz, $CDCl_3$)



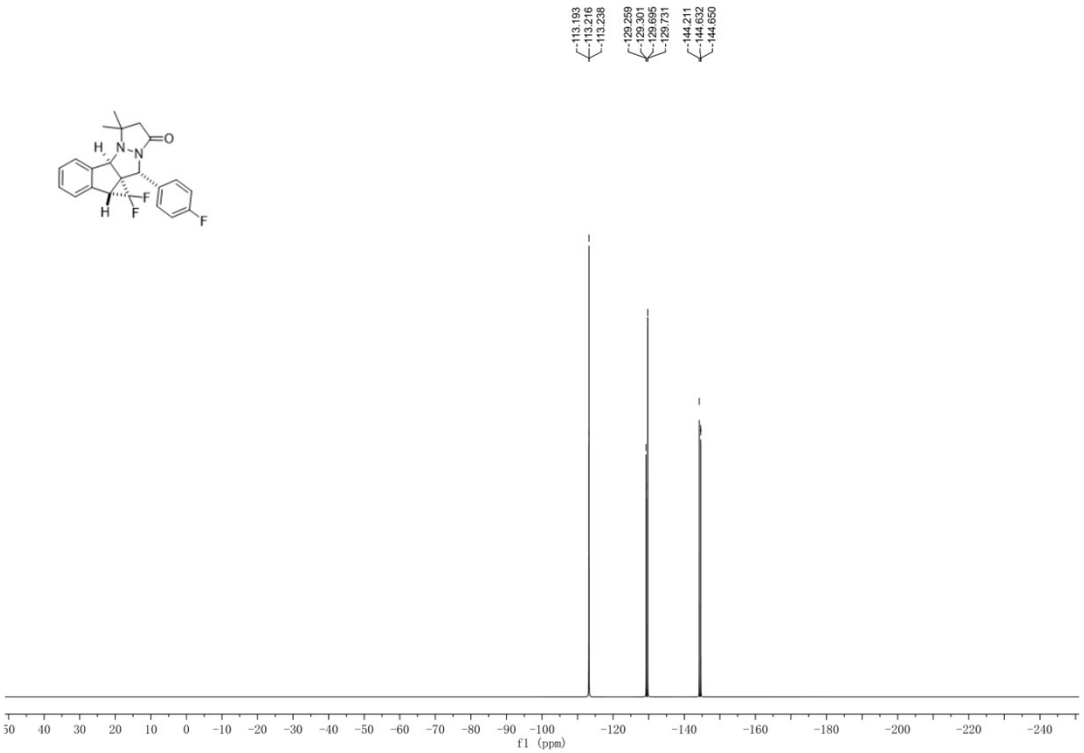
3ag-^{1}H NMR (400 MHz, $CDCl_3$)



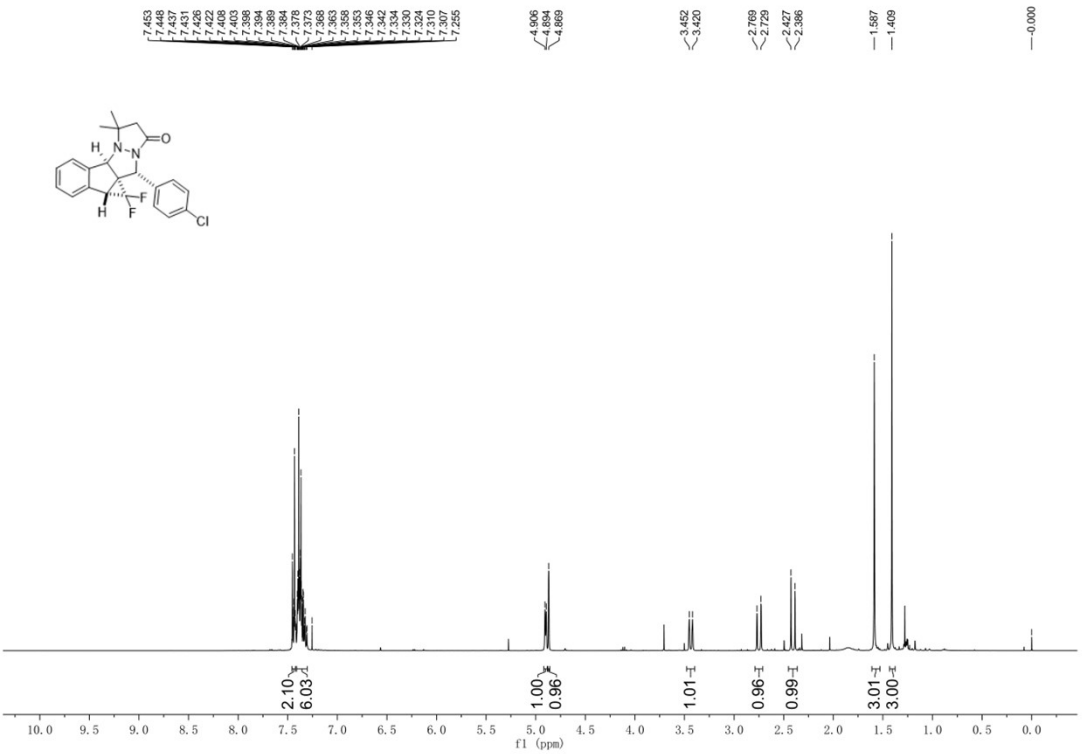
3ag-^{13}C NMR (100 MHz, $CDCl_3$)



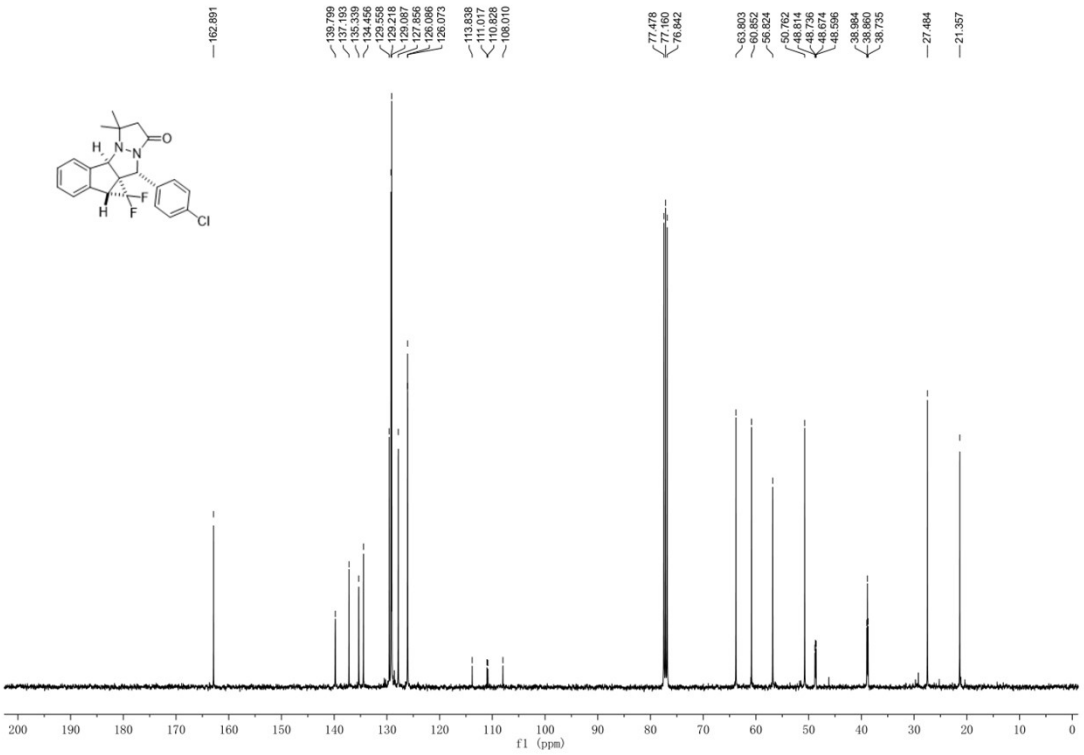
3ag-^{19}F NMR (376 MHz, $CDCl_3$)



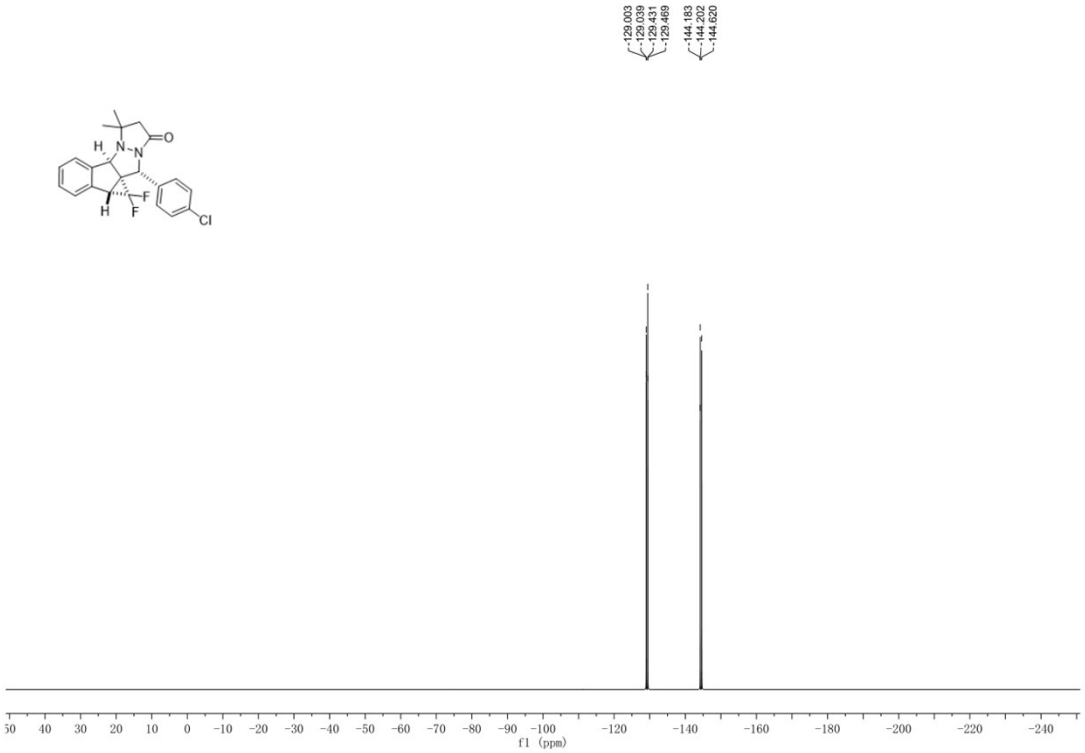
3ah-^{1}H NMR (400 MHz, $CDCl_3$)



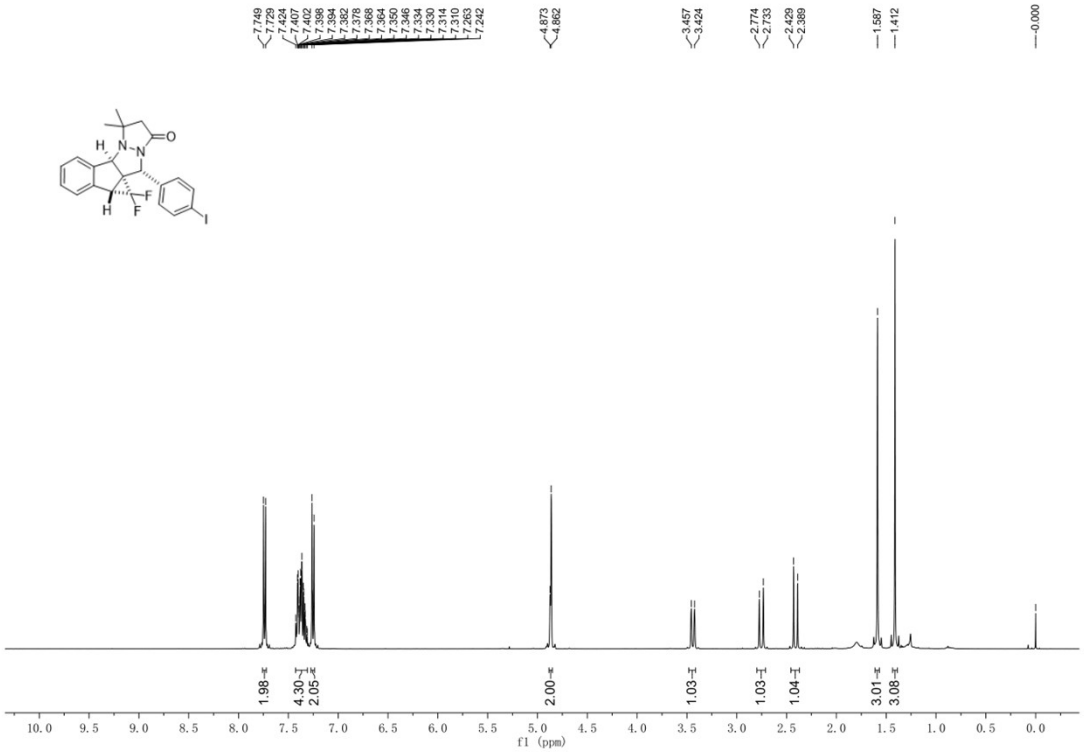
3ah-^{13}C NMR (100 MHz, $CDCl_3$)



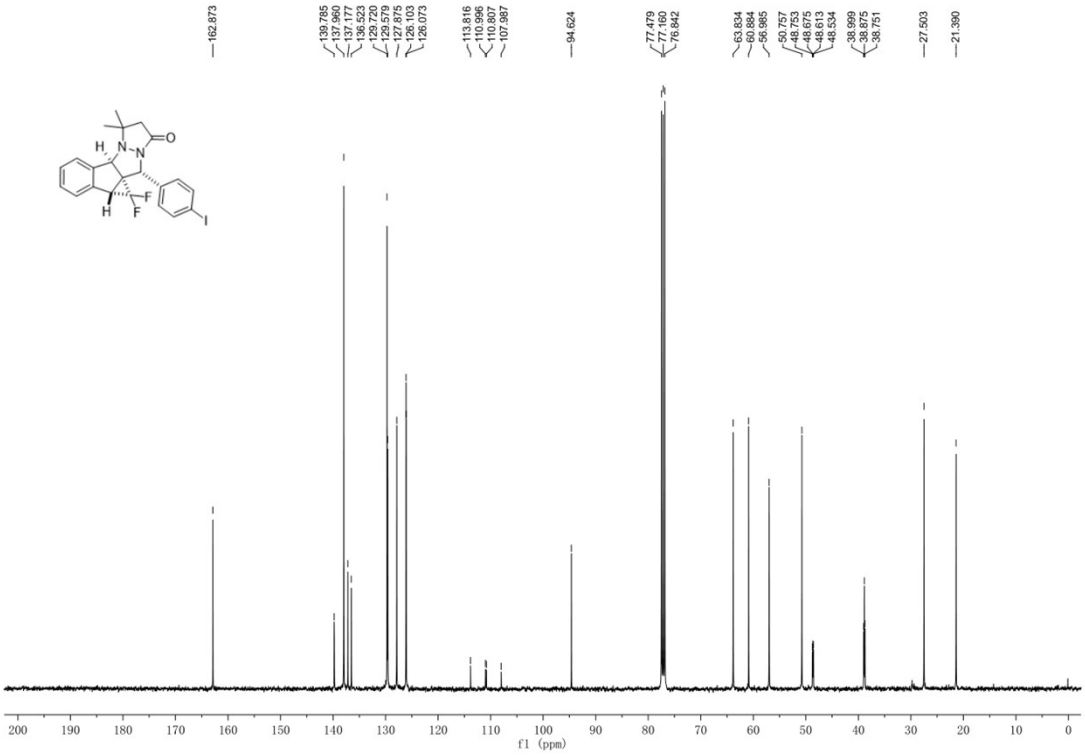
3ah-^{19}F NMR (376 MHz, $CDCl_3$)



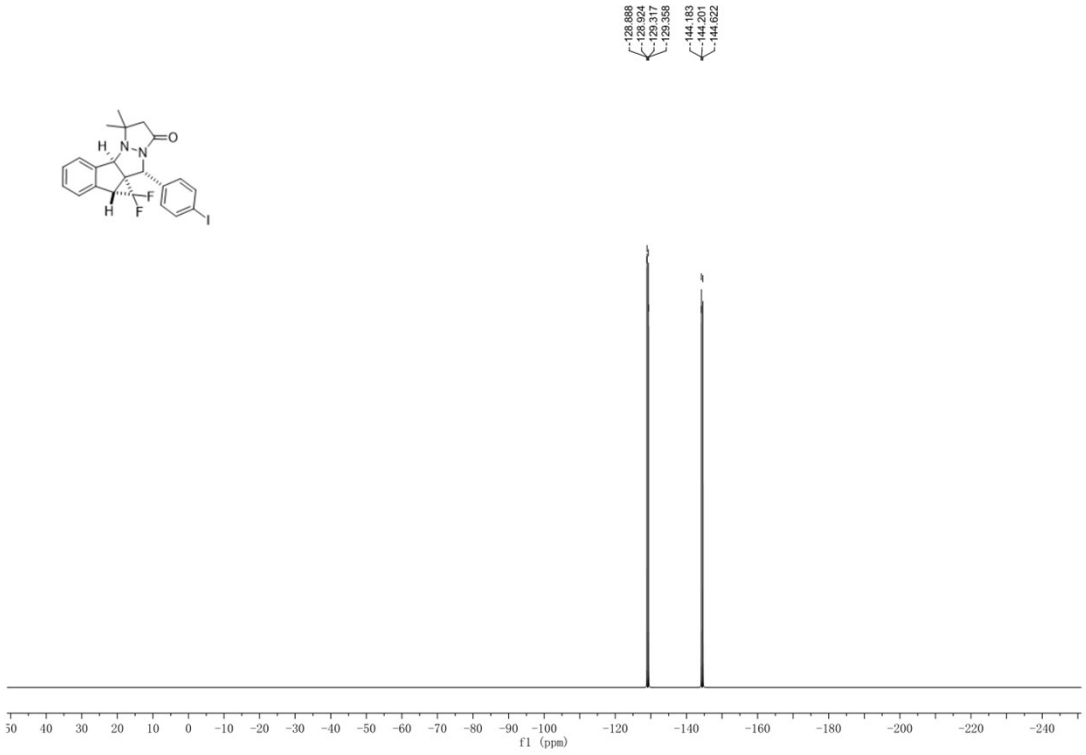
3ai-^{1}H NMR (400 MHz, $CDCl_3$)



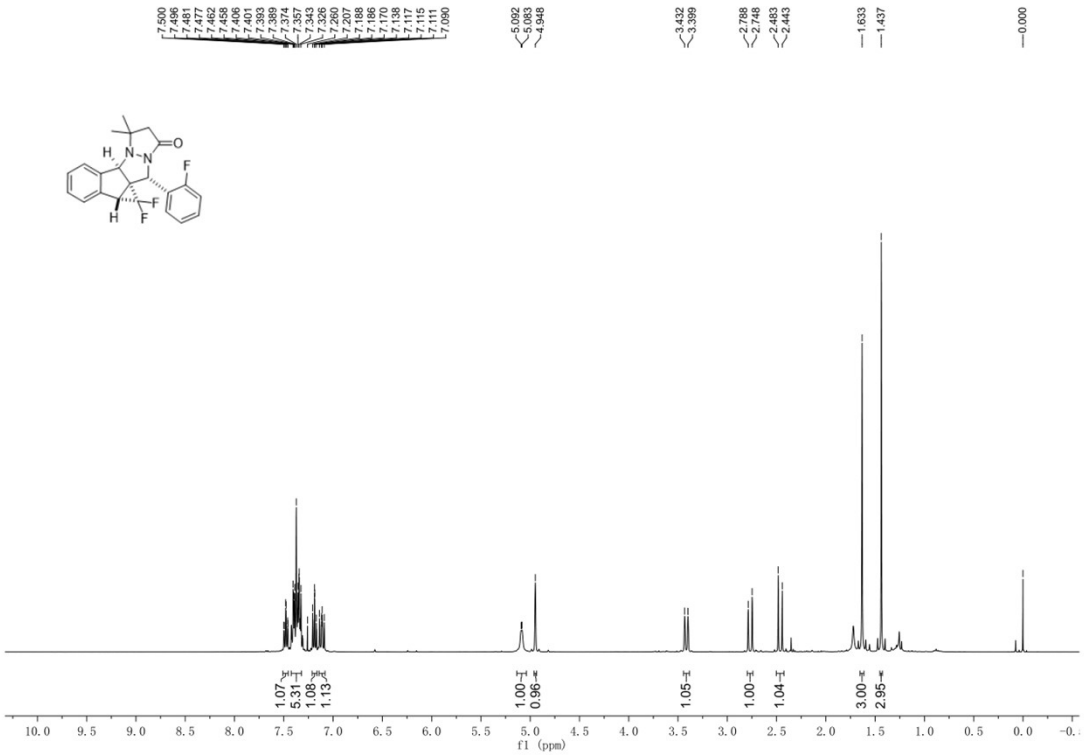
3ai-^{13}C NMR (100 MHz, $CDCl_3$)



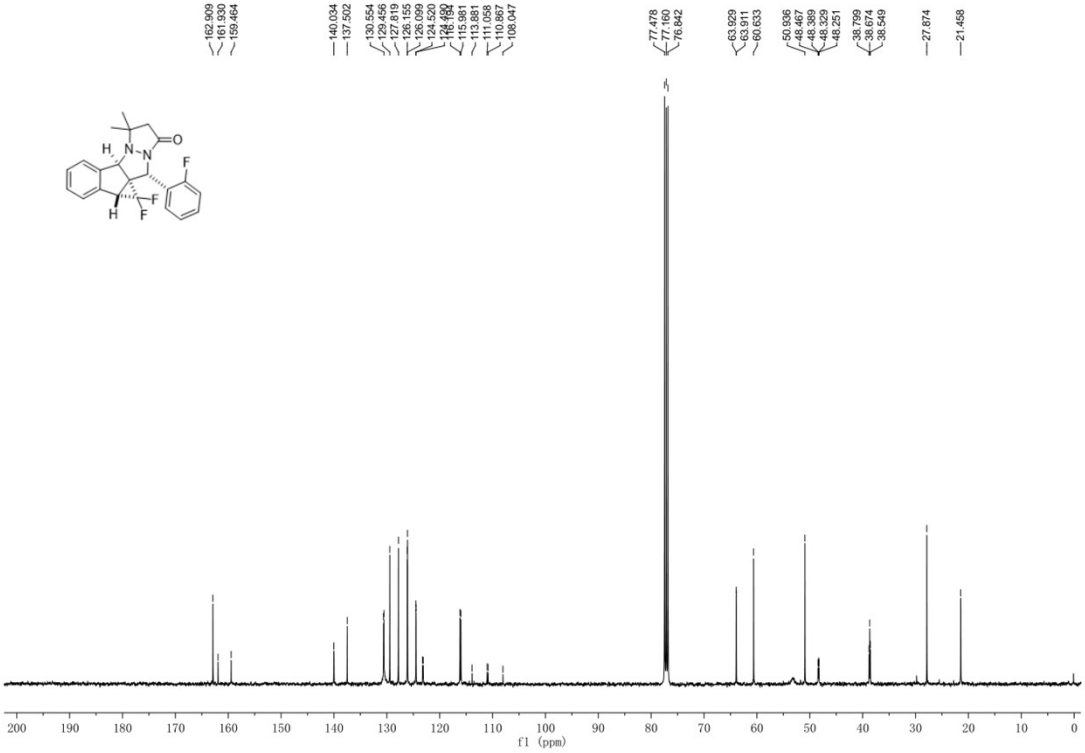
3ai-^{19}F NMR (376 MHz, $CDCl_3$)



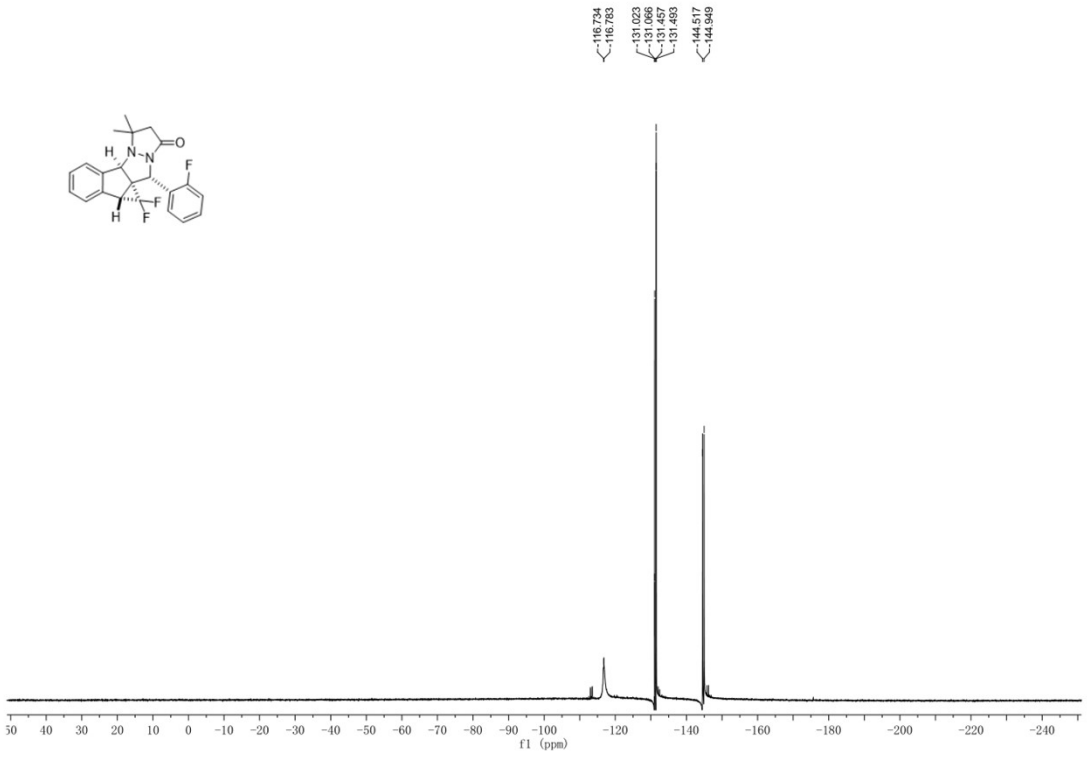
3aj-^{1}H NMR (400 MHz, $CDCl_3$)



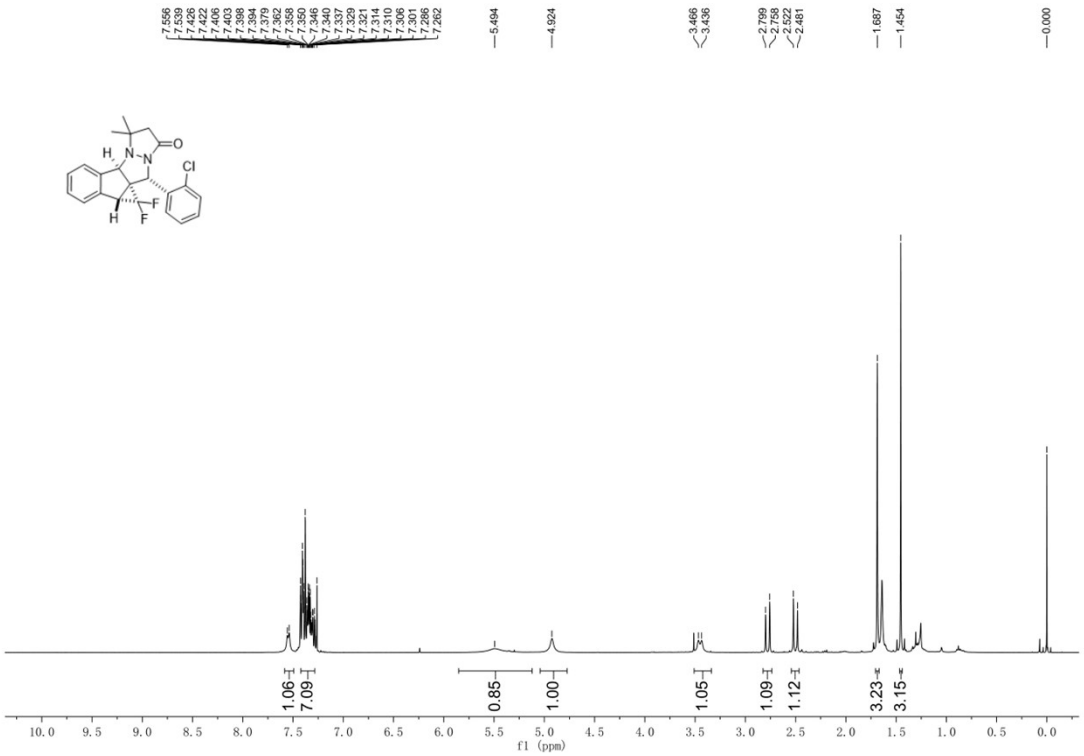
3aj-^{13}C NMR (100 MHz, $CDCl_3$)



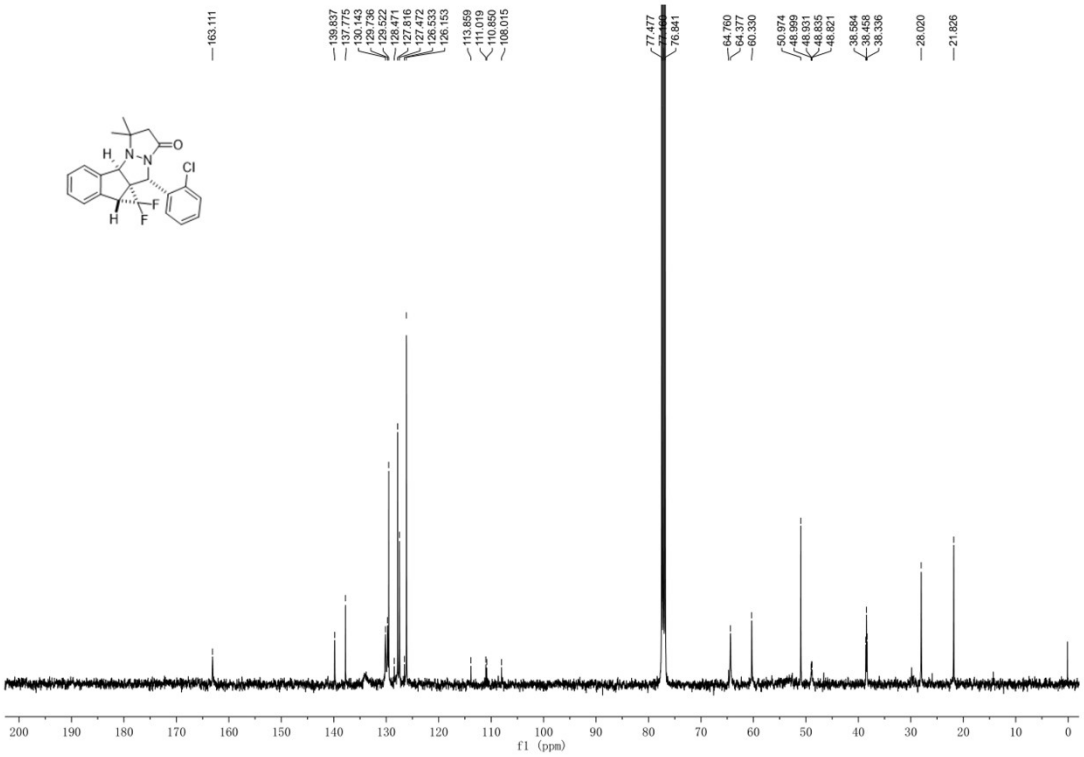
3aj-^{19}F NMR (376 MHz, $CDCl_3$)



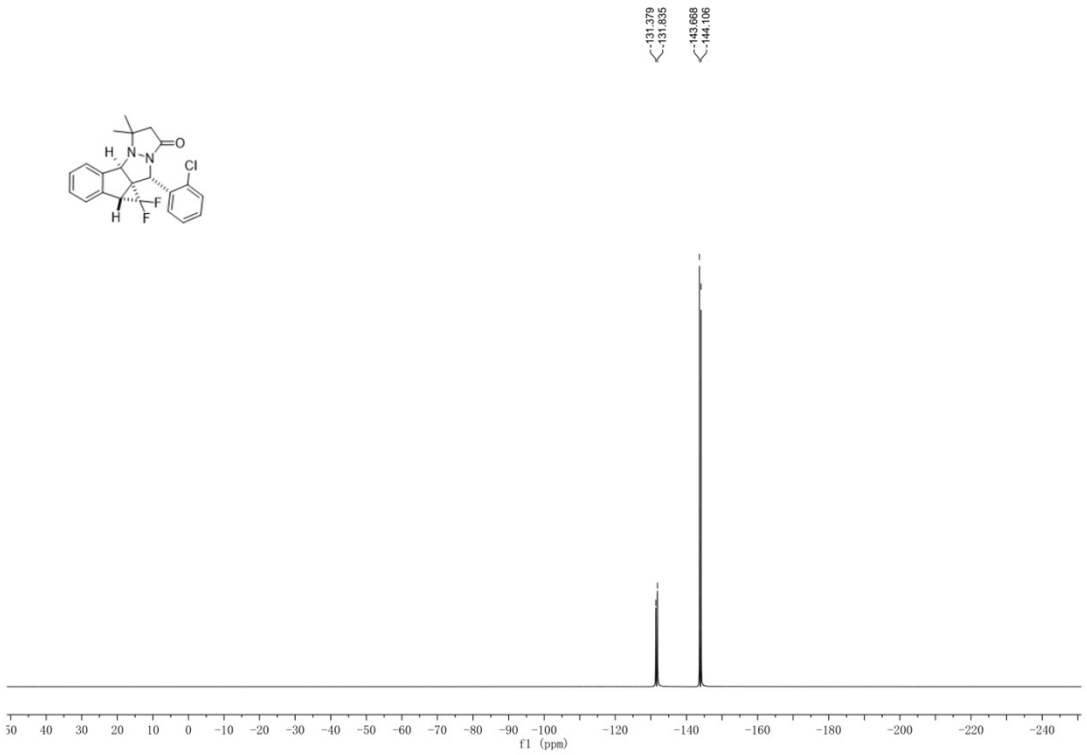
3ak-^{1}H NMR (400 MHz, $CDCl_3$)



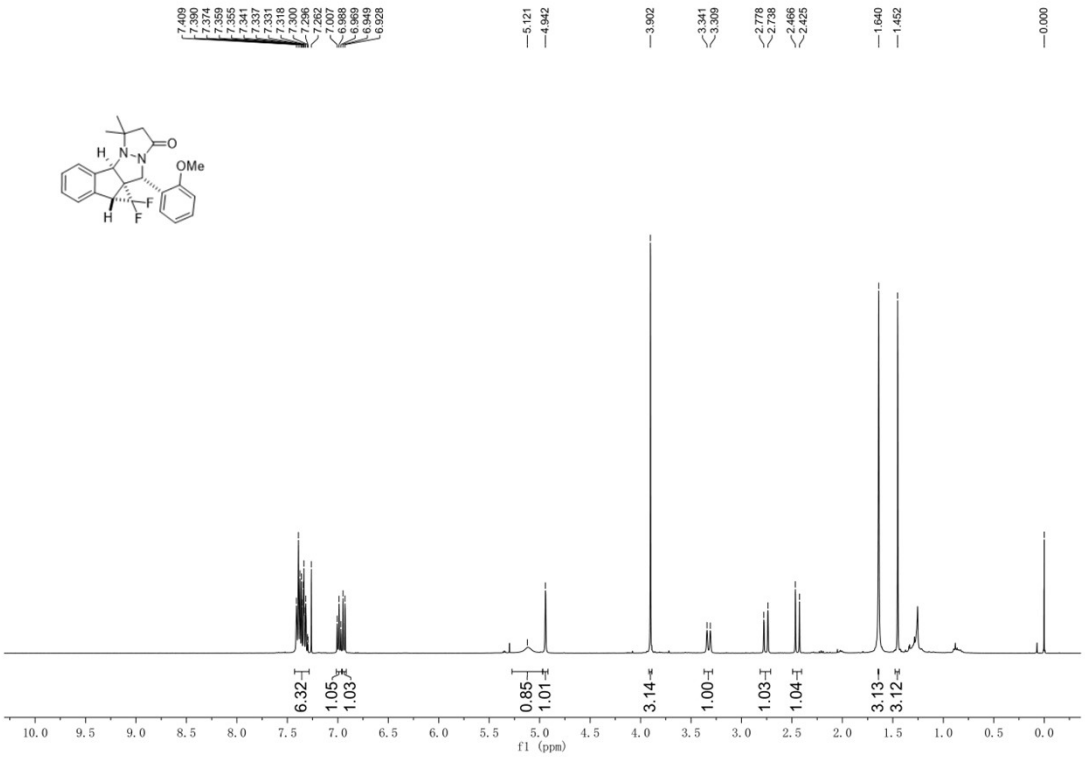
3ak-^{13}C NMR (100 MHz, $CDCl_3$)



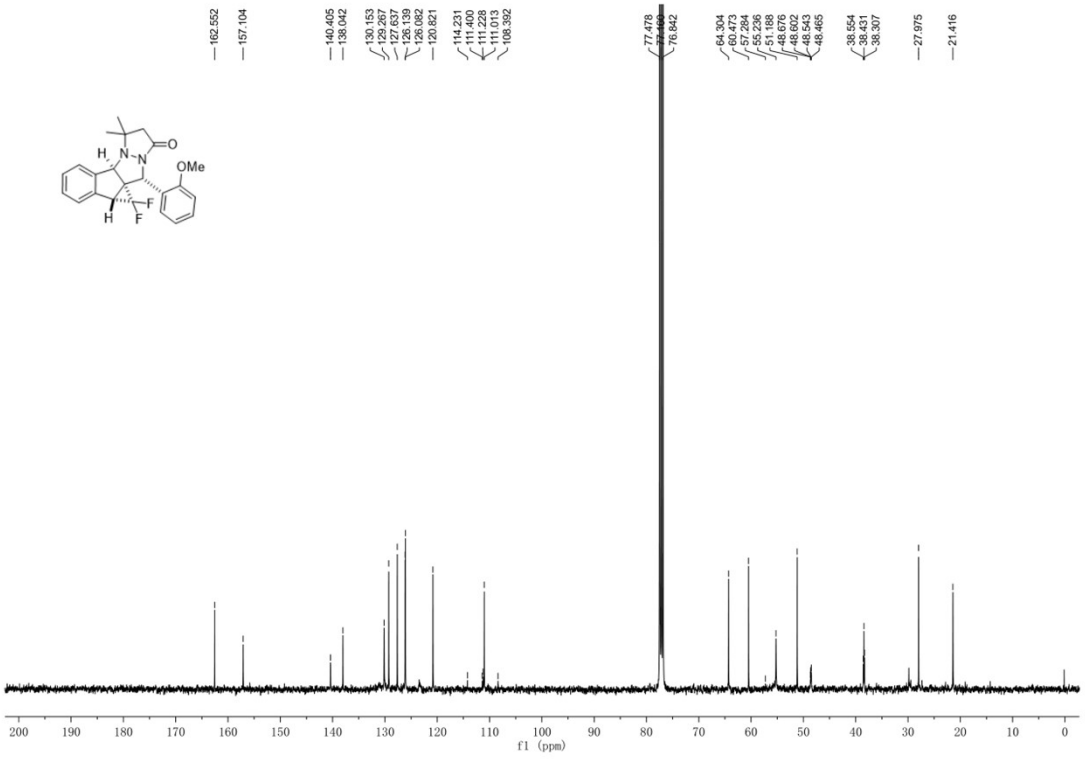
3ak-^{19}F NMR (376 MHz, $CDCl_3$)



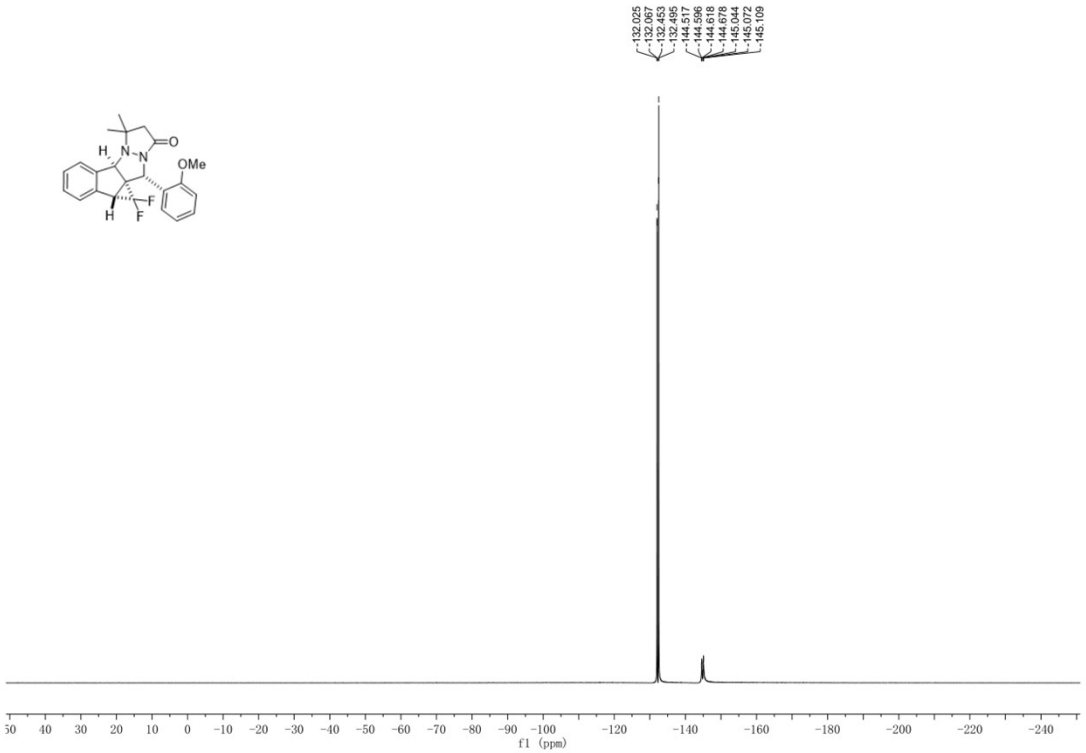
3al-^{1}H NMR (400 MHz, $CDCl_3$)



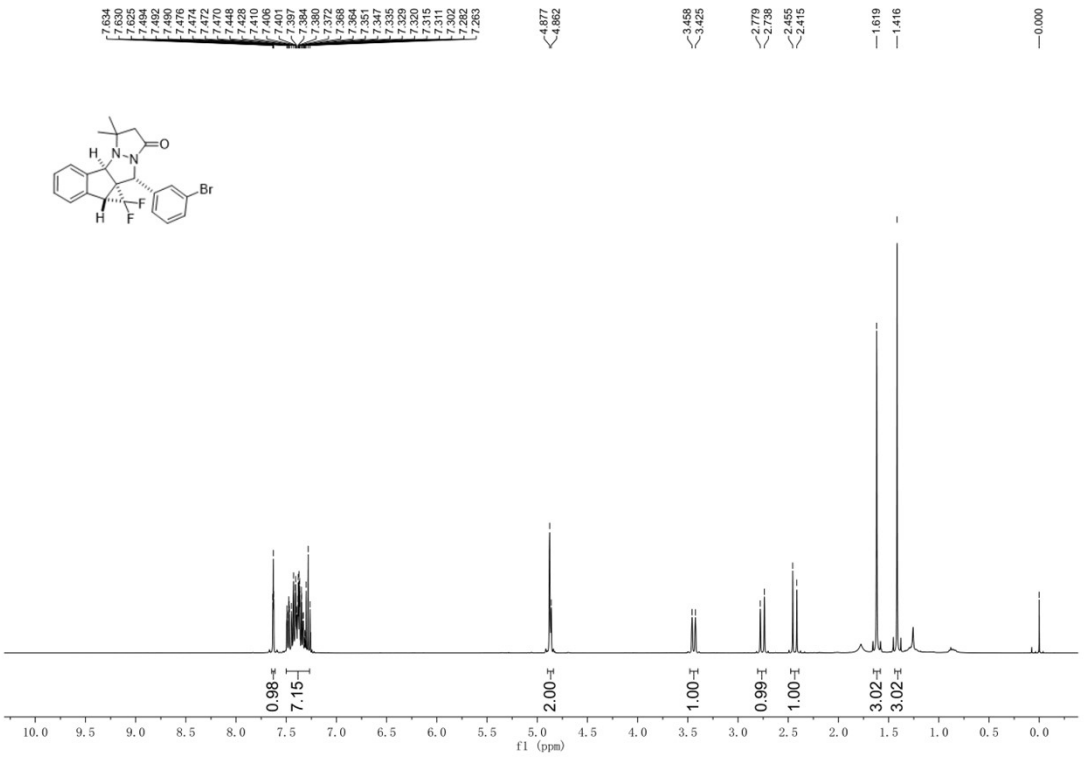
3al-^{13}C NMR (100 MHz, $CDCl_3$)



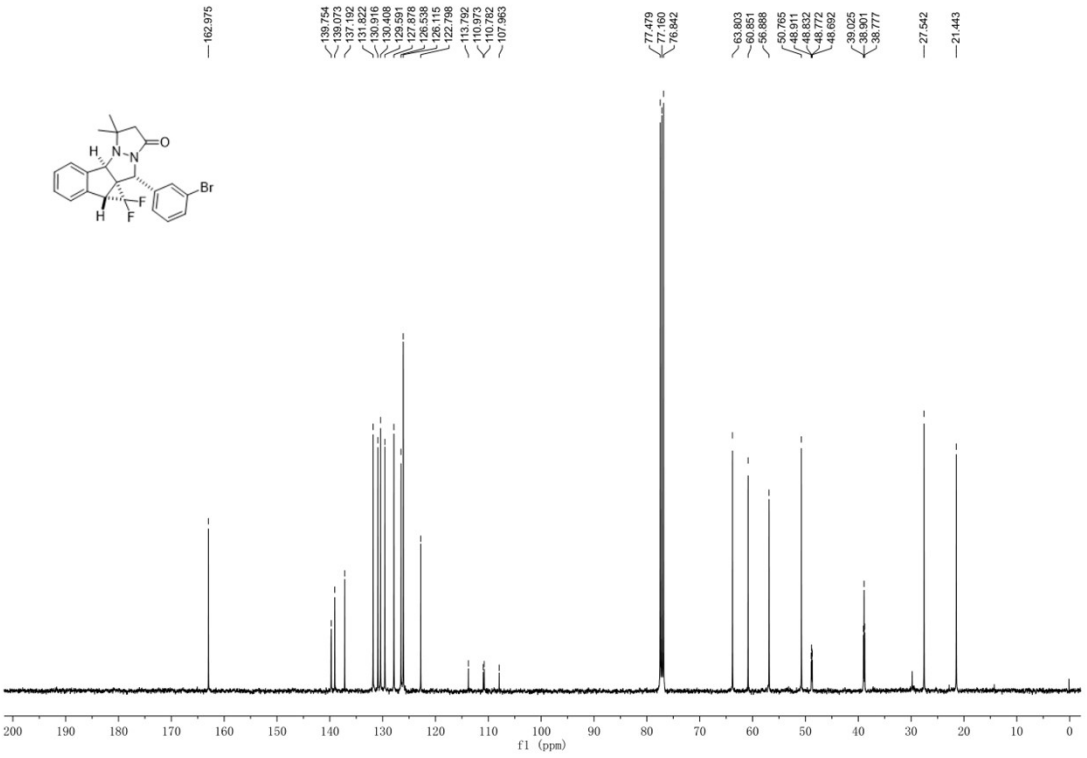
3al-^{19}F NMR (376 MHz, $CDCl_3$)



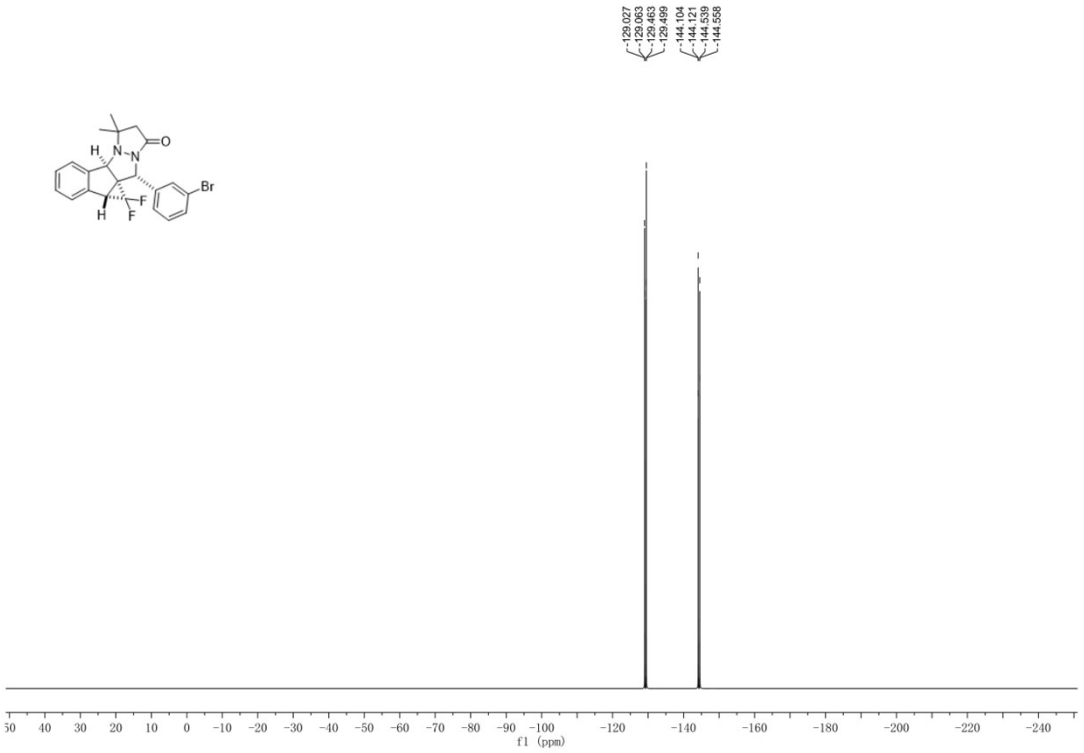
3am-^{1}H NMR (400 MHz, $CDCl_3$)



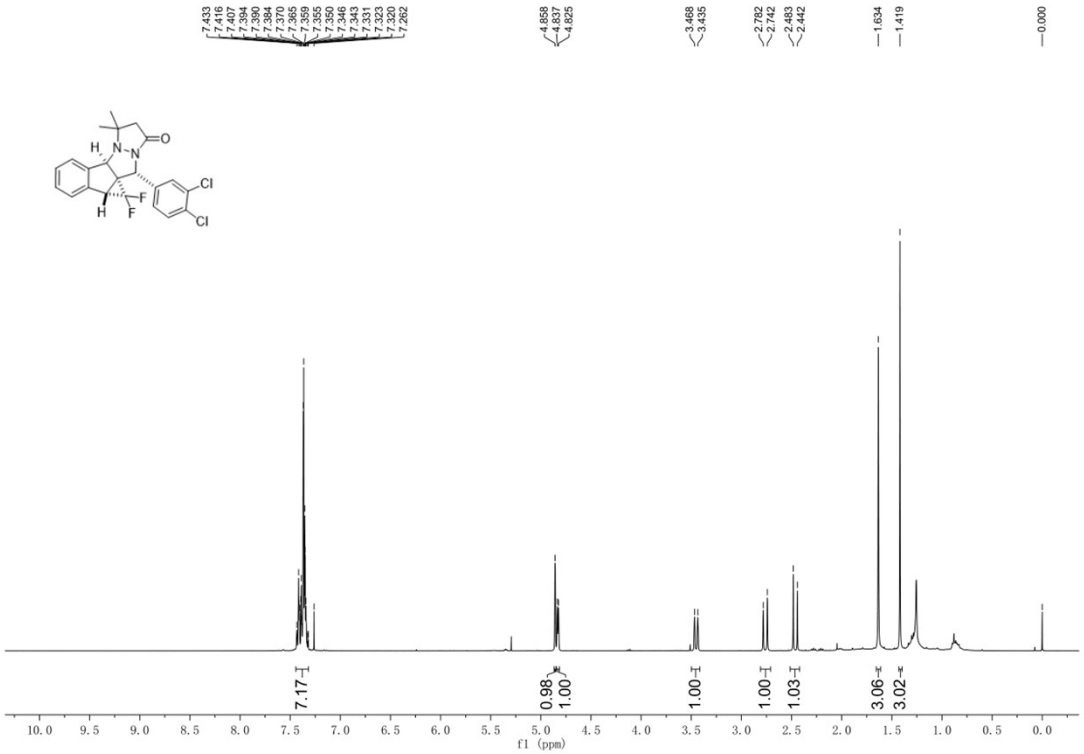
3am-^{13}C NMR (100 MHz, $CDCl_3$)



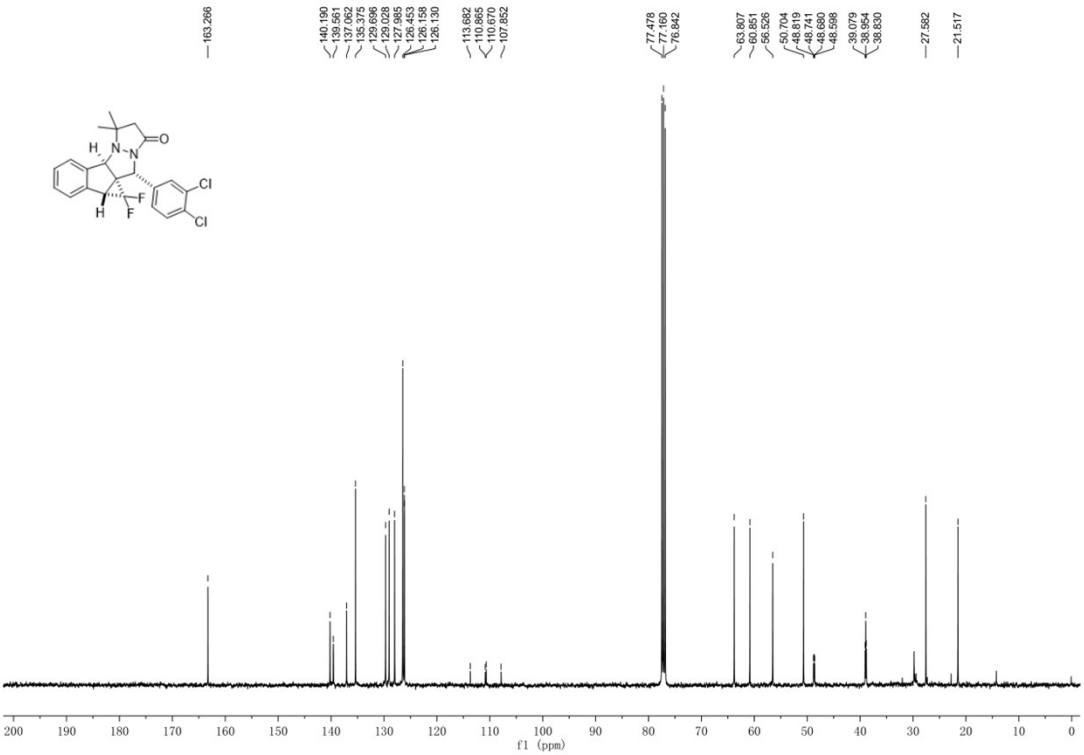
3am-^{19}F NMR (376 MHz, $CDCl_3$)



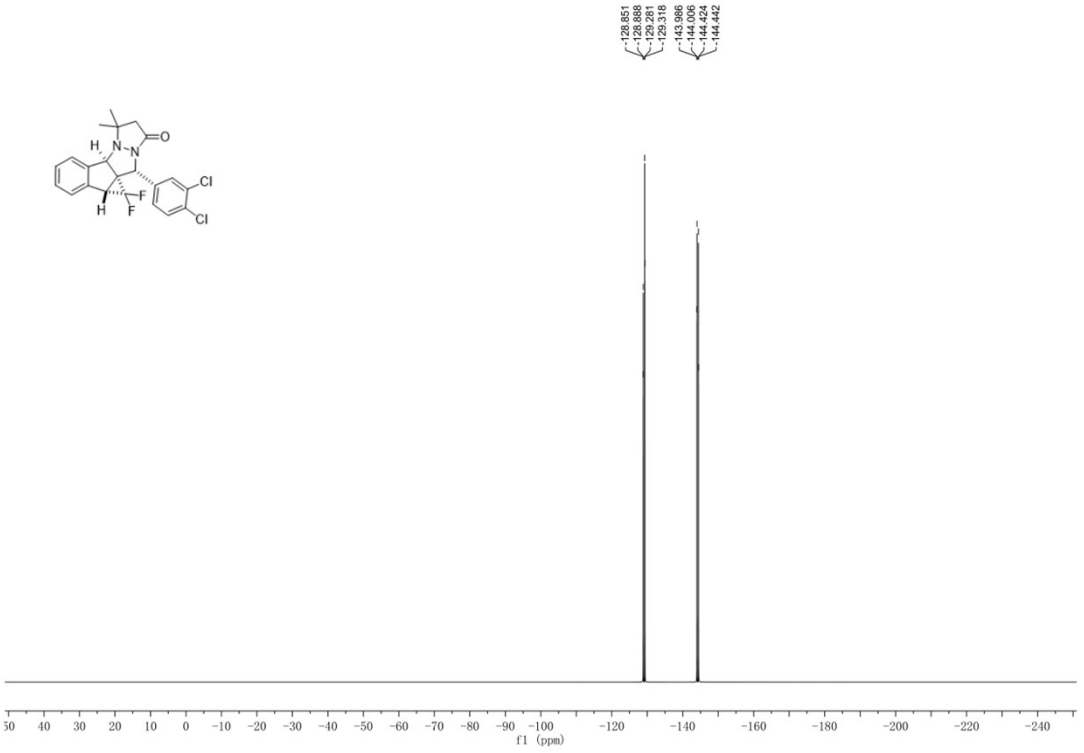
3an-^{1}H NMR (400 MHz, $CDCl_3$)



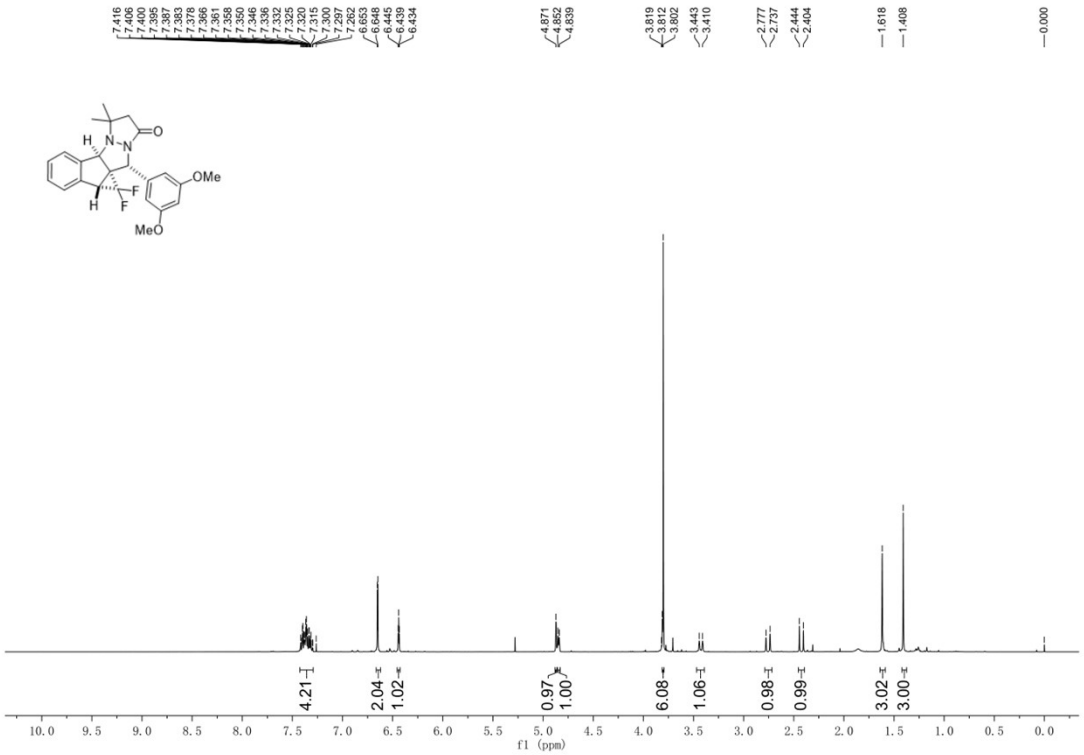
3an-^{13}C NMR (100 MHz, $CDCl_3$)



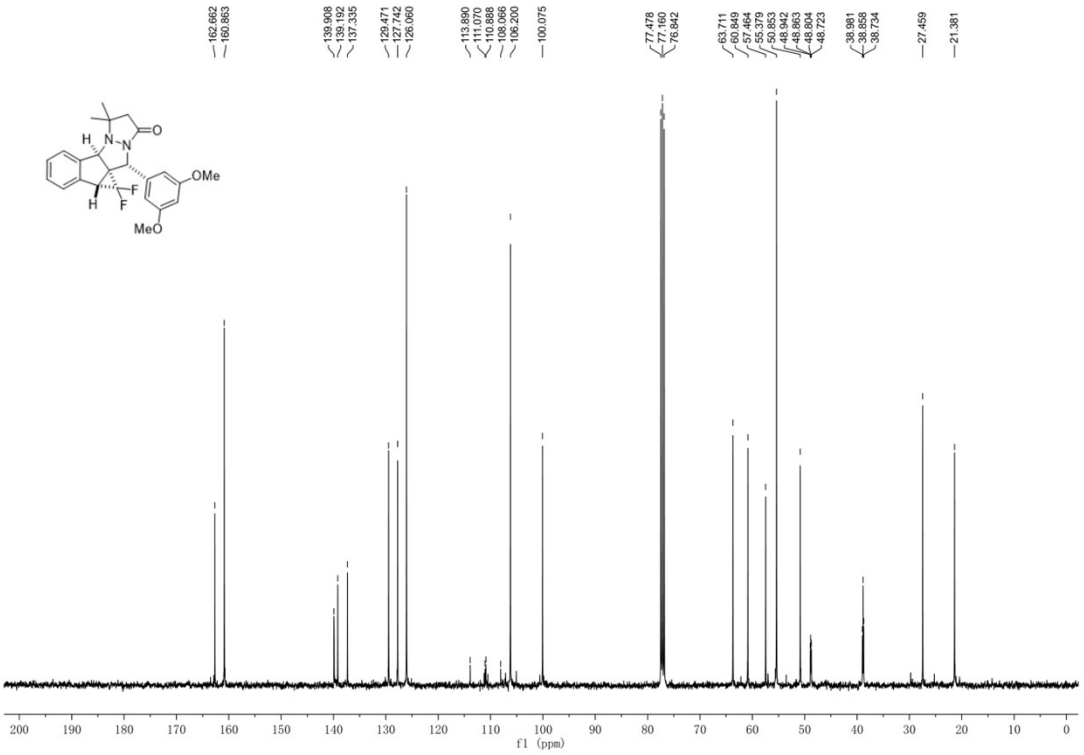
3an-^{19}F NMR (376 MHz, $CDCl_3$)



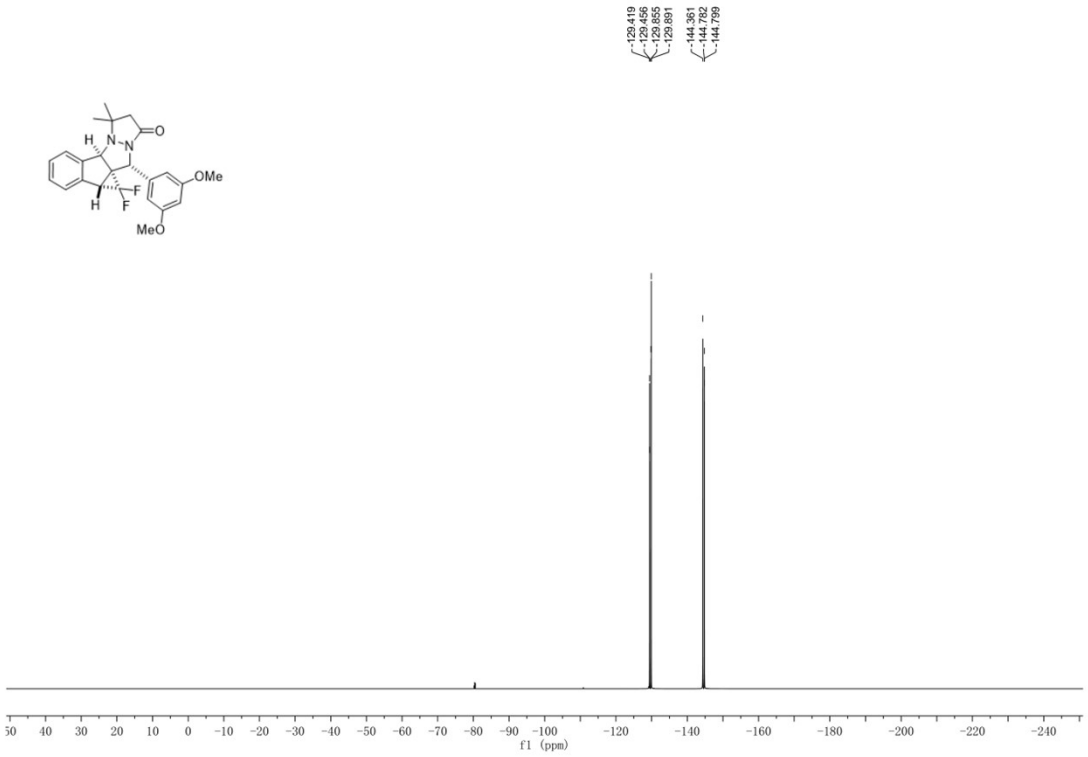
3ao-^{1}H NMR (400 MHz, $CDCl_3$)



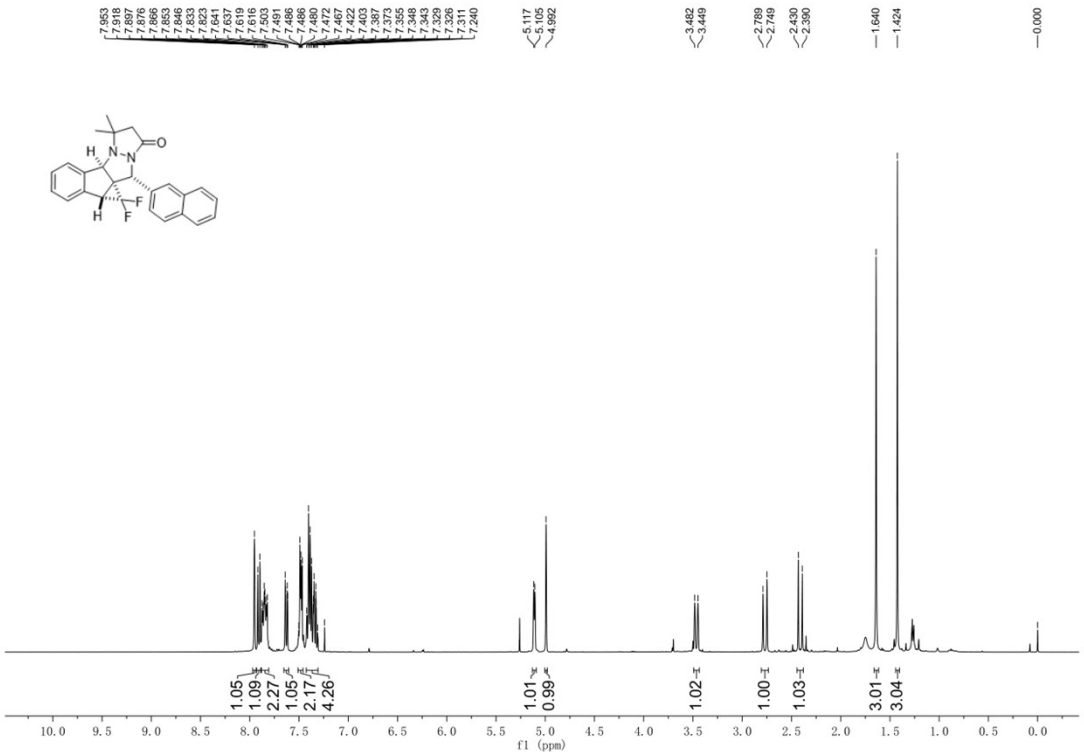
3ao-^{13}C NMR (100 MHz, $CDCl_3$)



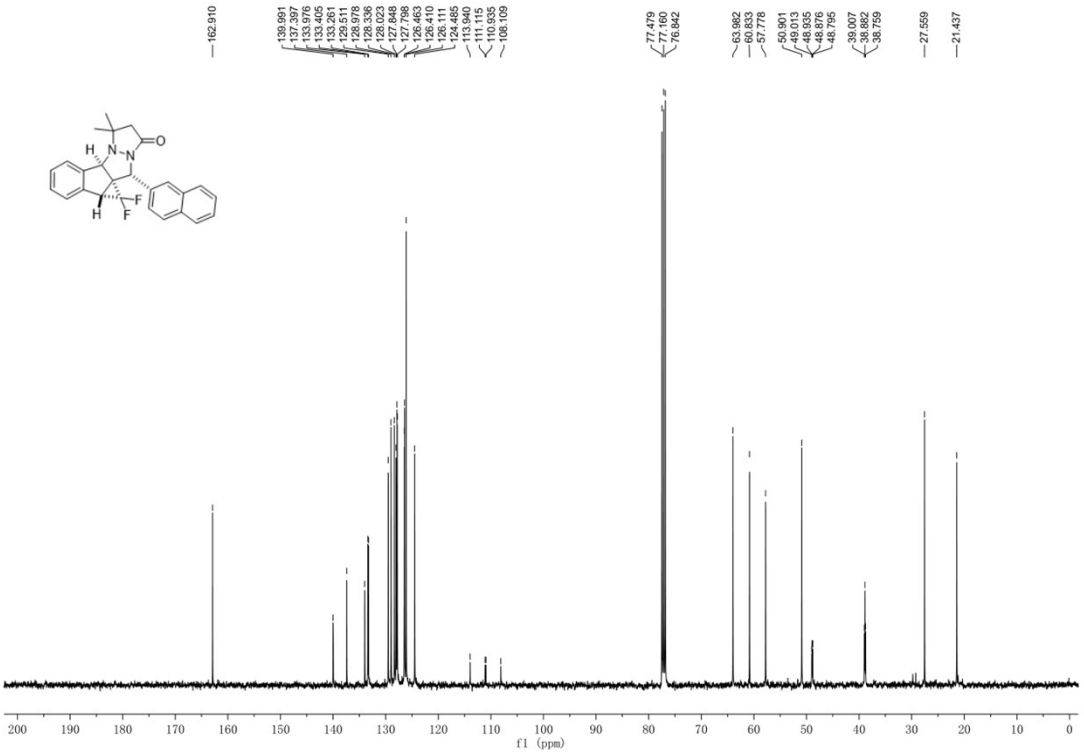
3ao-^{19}F NMR (376 MHz, $CDCl_3$)



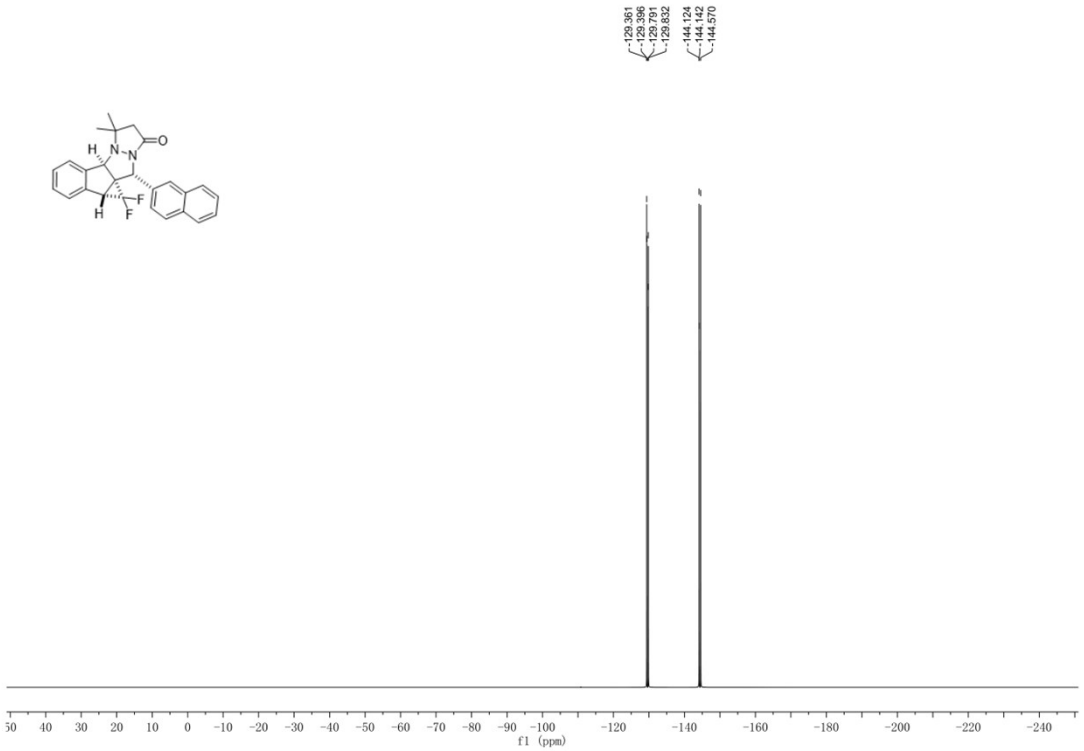
3ap-^{1}H NMR (400 MHz, $CDCl_3$)



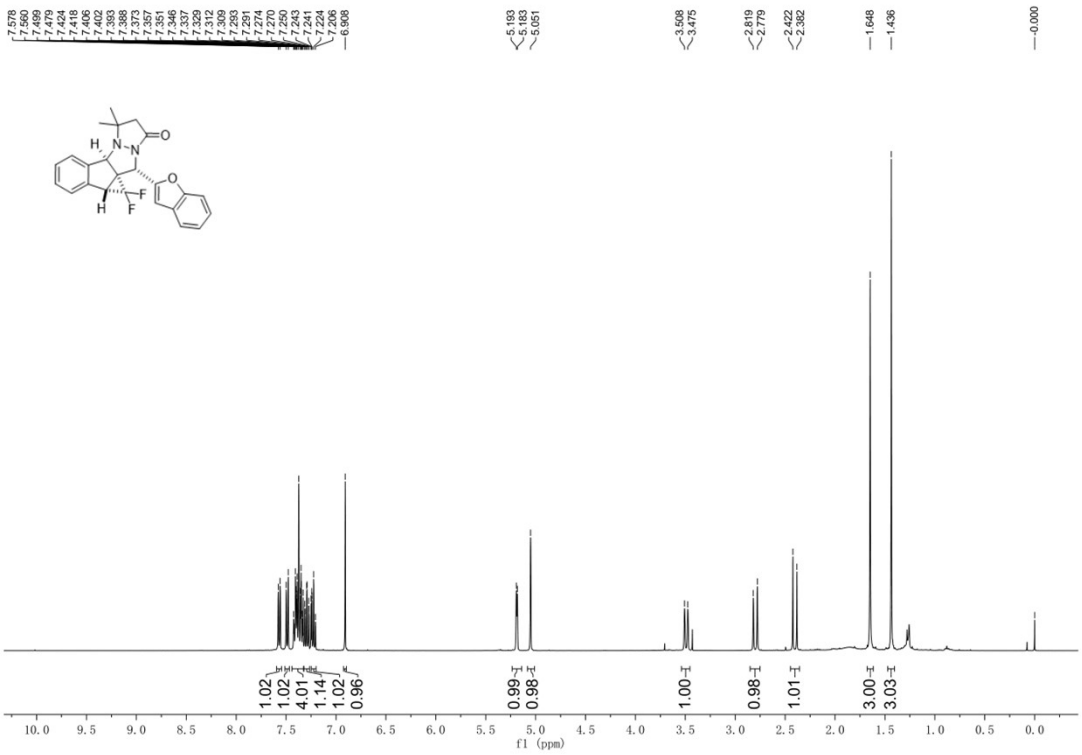
3ap-^{13}C NMR (100 MHz, $CDCl_3$)



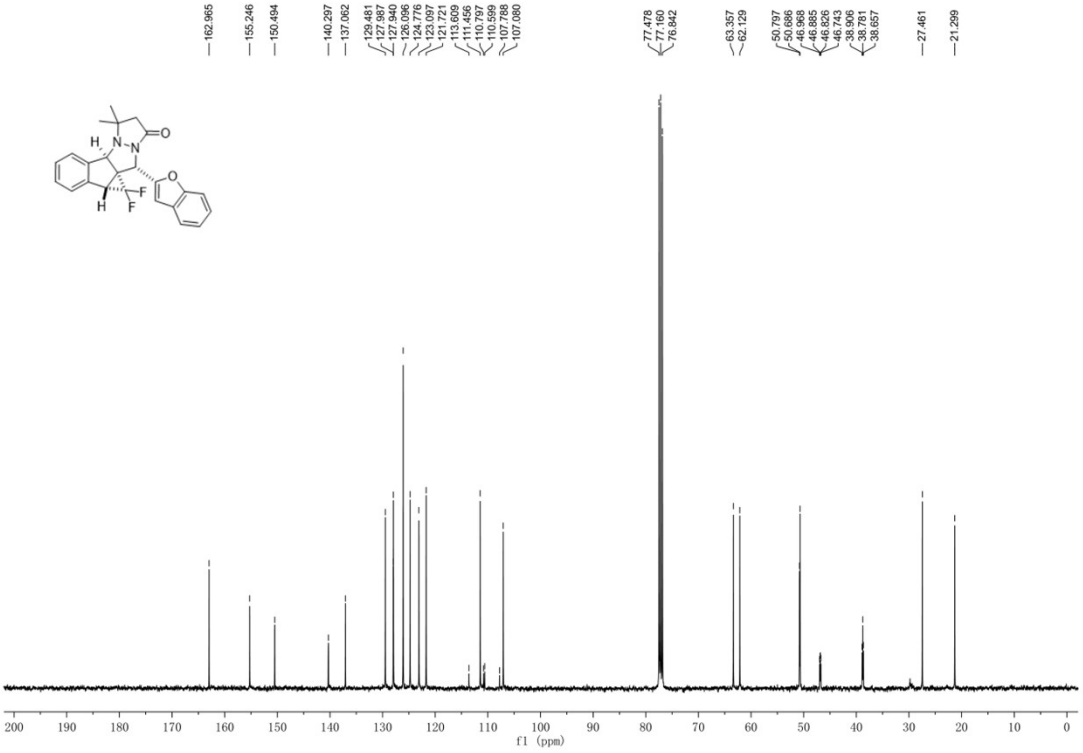
3ap-^{19}F NMR (376 MHz, $CDCl_3$)



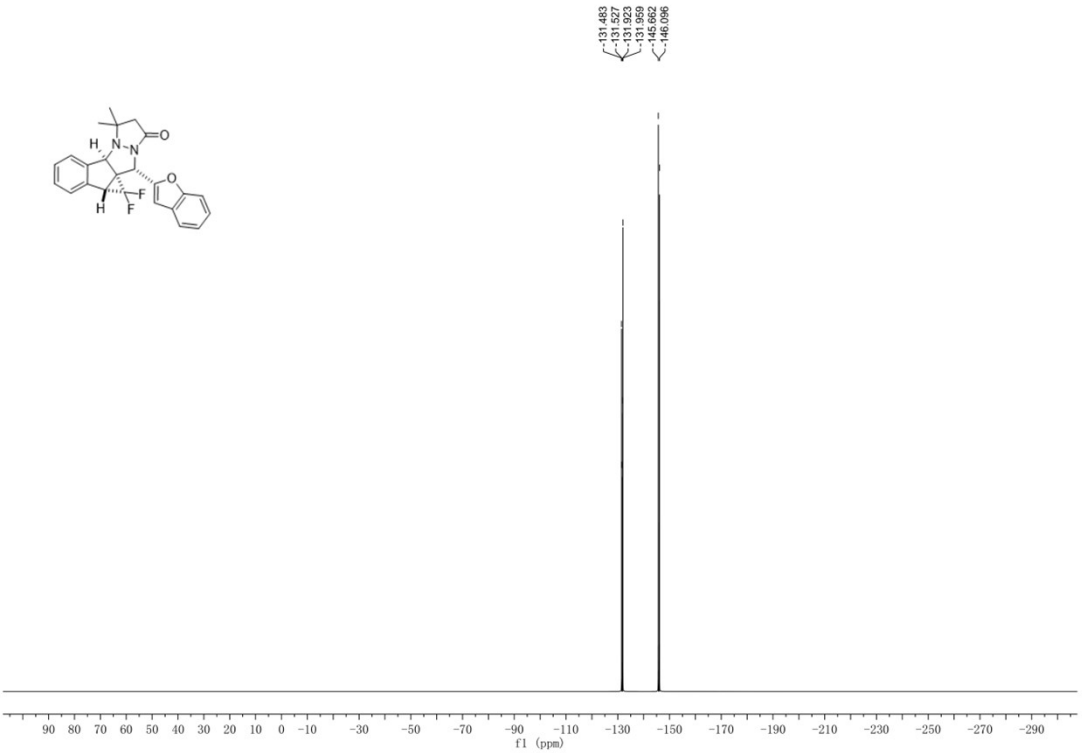
3aq-^{1}H NMR (400 MHz, $CDCl_3$)



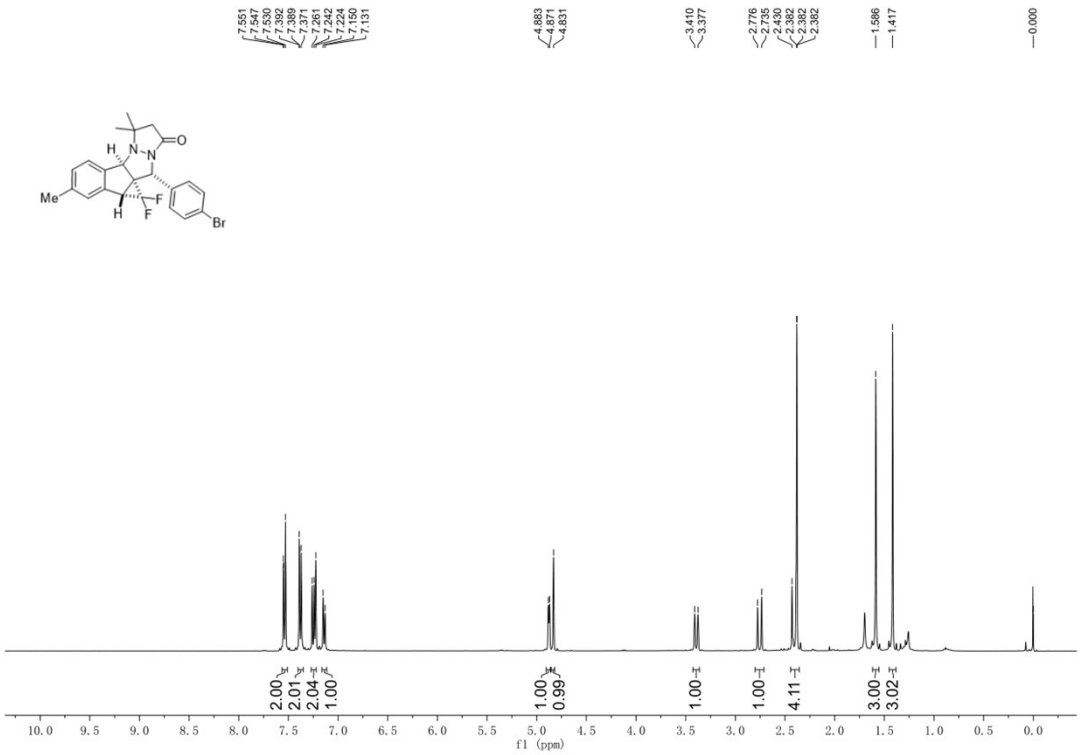
3aq-^{13}C NMR (100 MHz, $CDCl_3$)



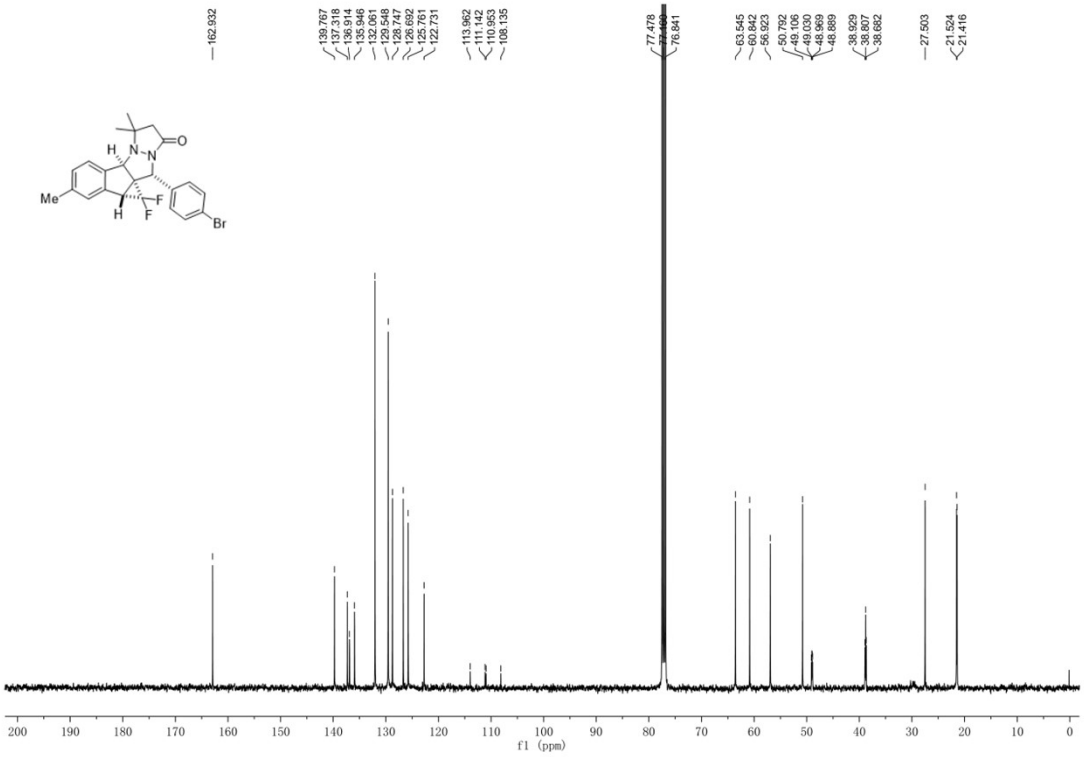
3aq-^{19}F NMR (376 MHz, $CDCl_3$)



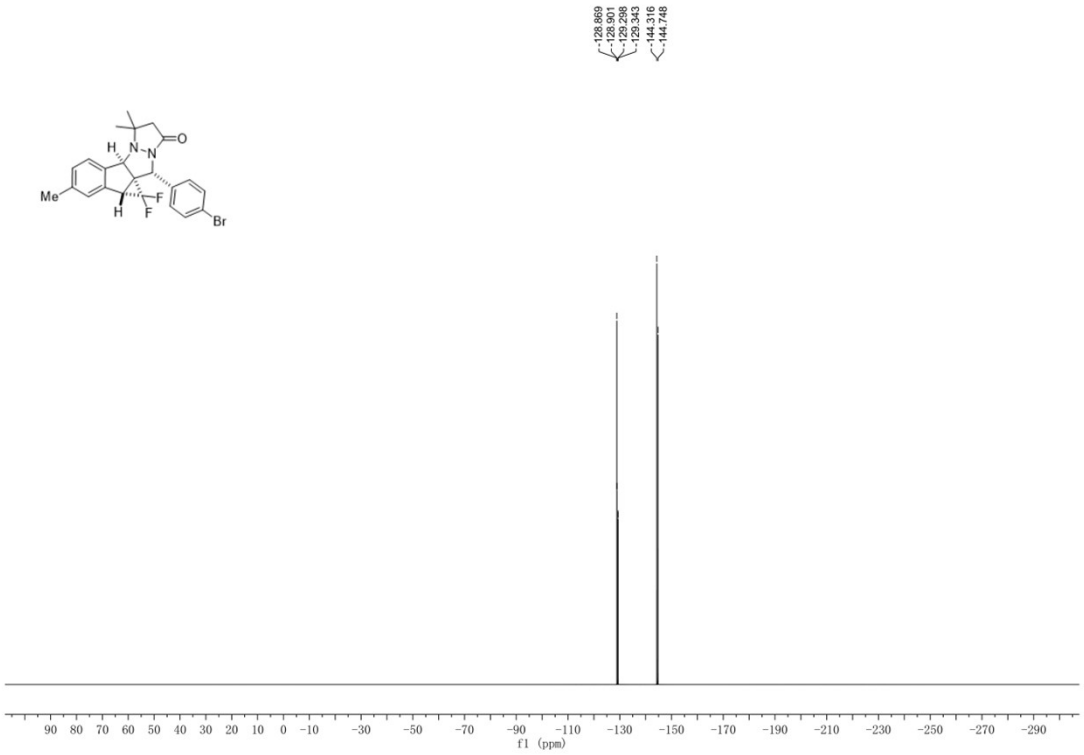
3ba-^{1}H NMR (400 MHz, $CDCl_3$)



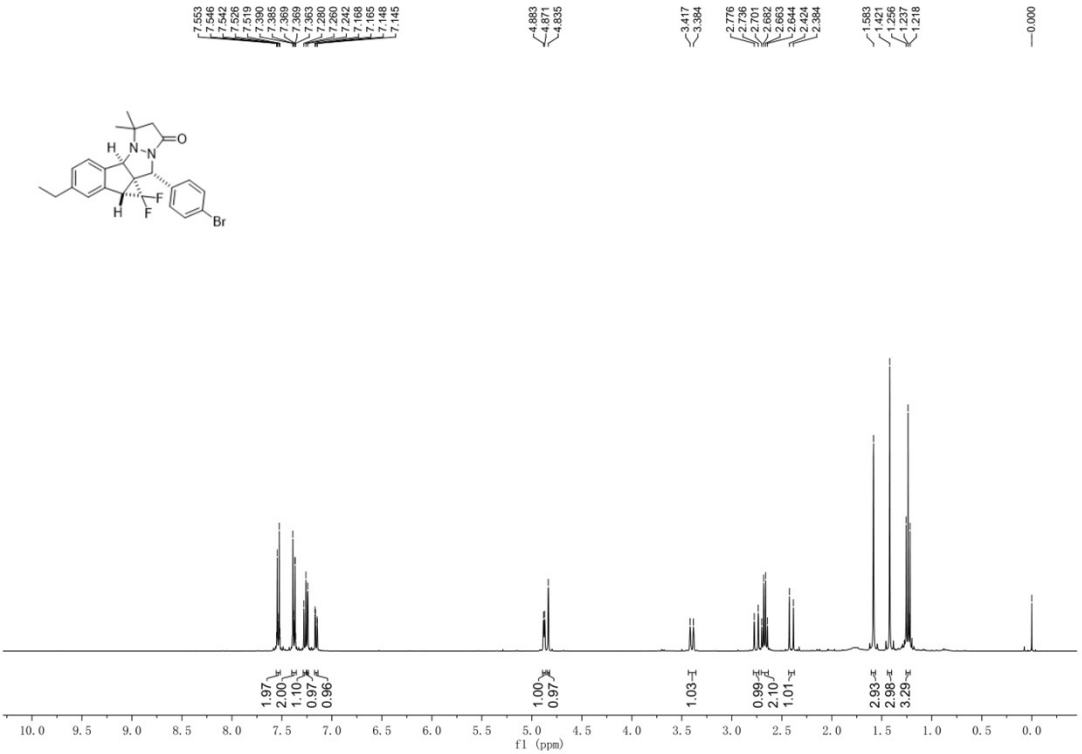
3ba-^{13}C NMR (100 MHz, $CDCl_3$)



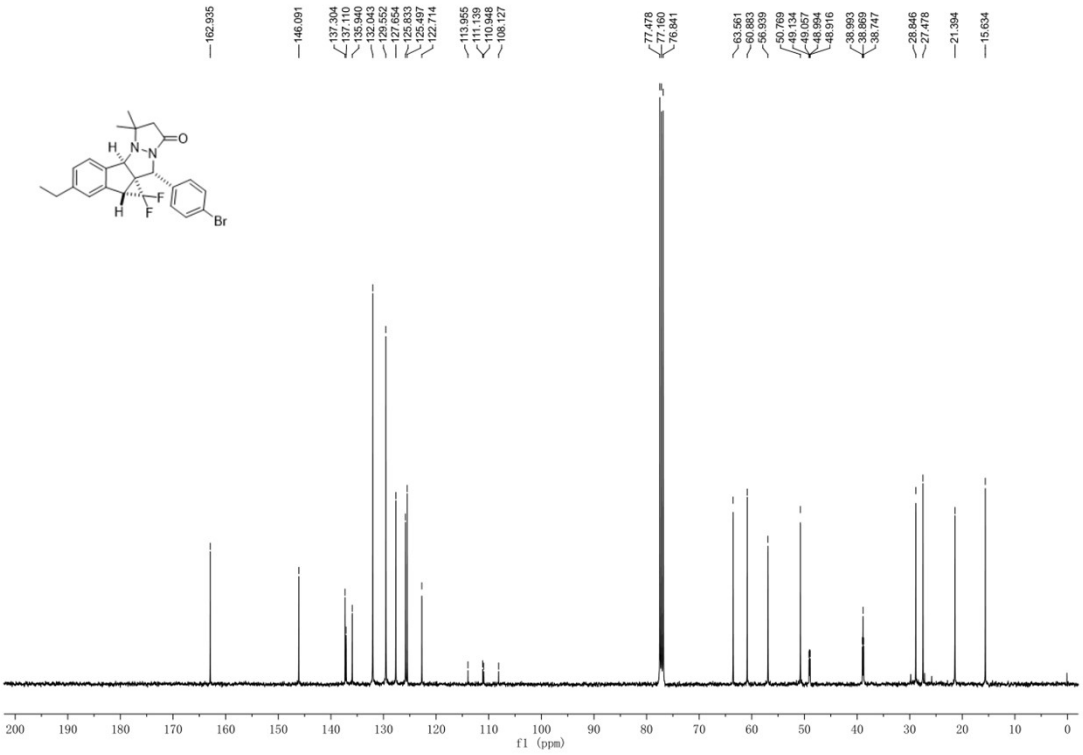
3ba-^{19}F NMR (376 MHz, $CDCl_3$)



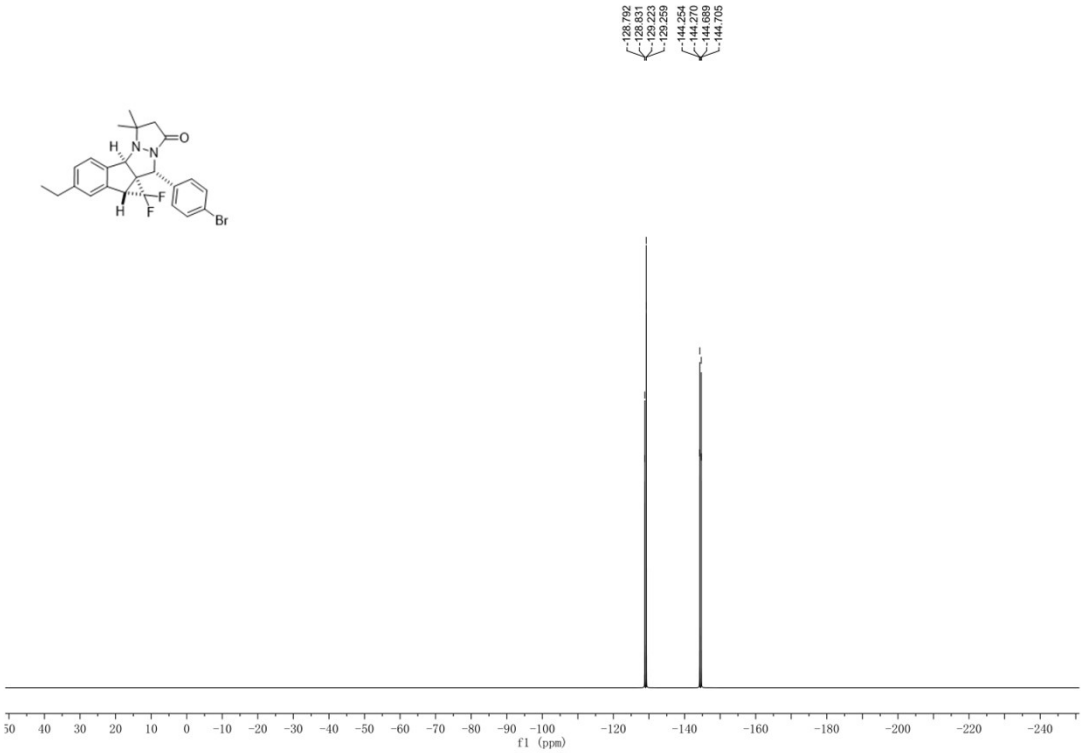
3ca-^{1}H NMR (400 MHz, $CDCl_3$)



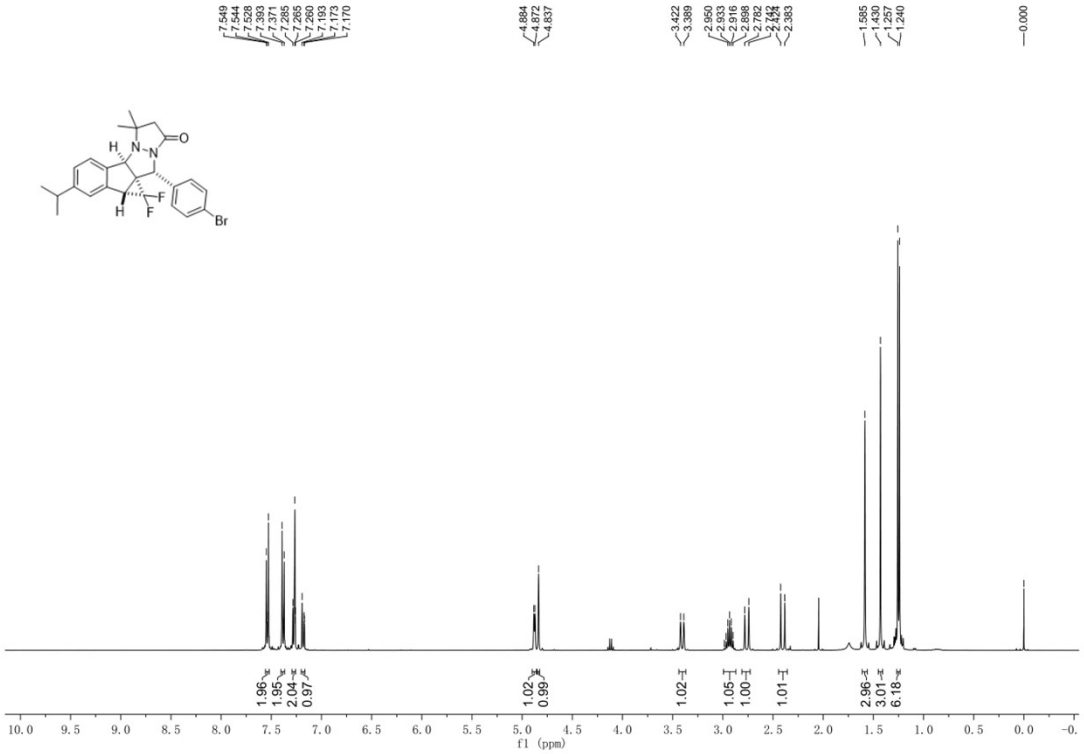
3ca-^{13}C NMR (100 MHz, $CDCl_3$)



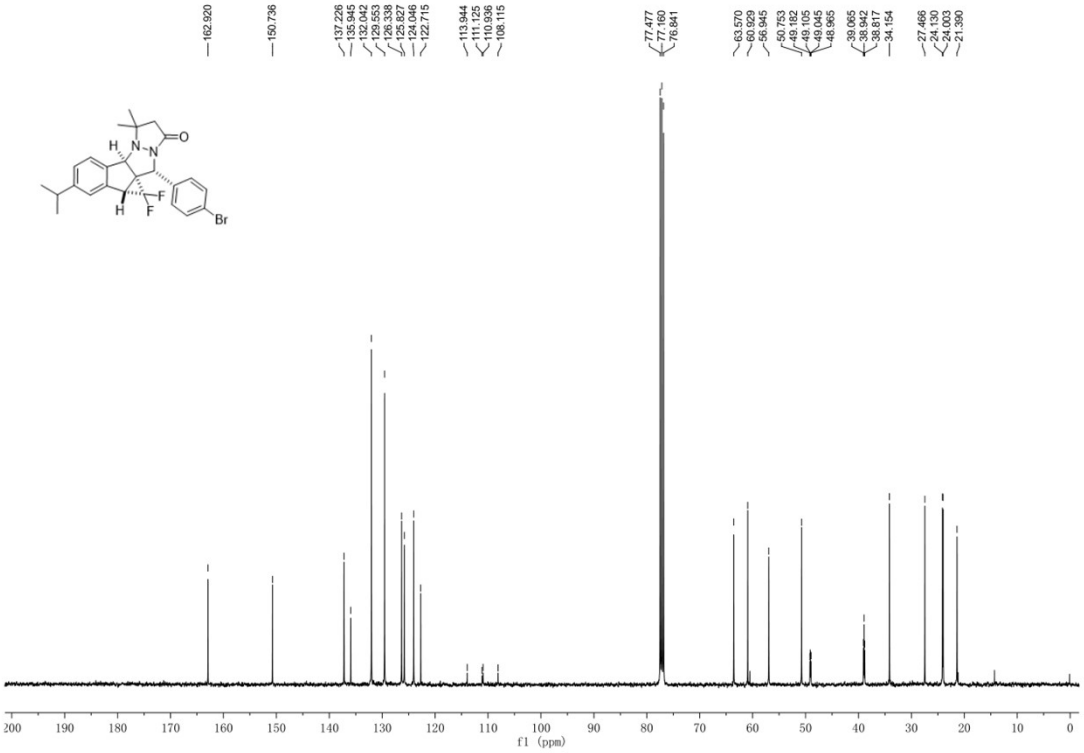
3ca-^{19}F NMR (376 MHz, $CDCl_3$)



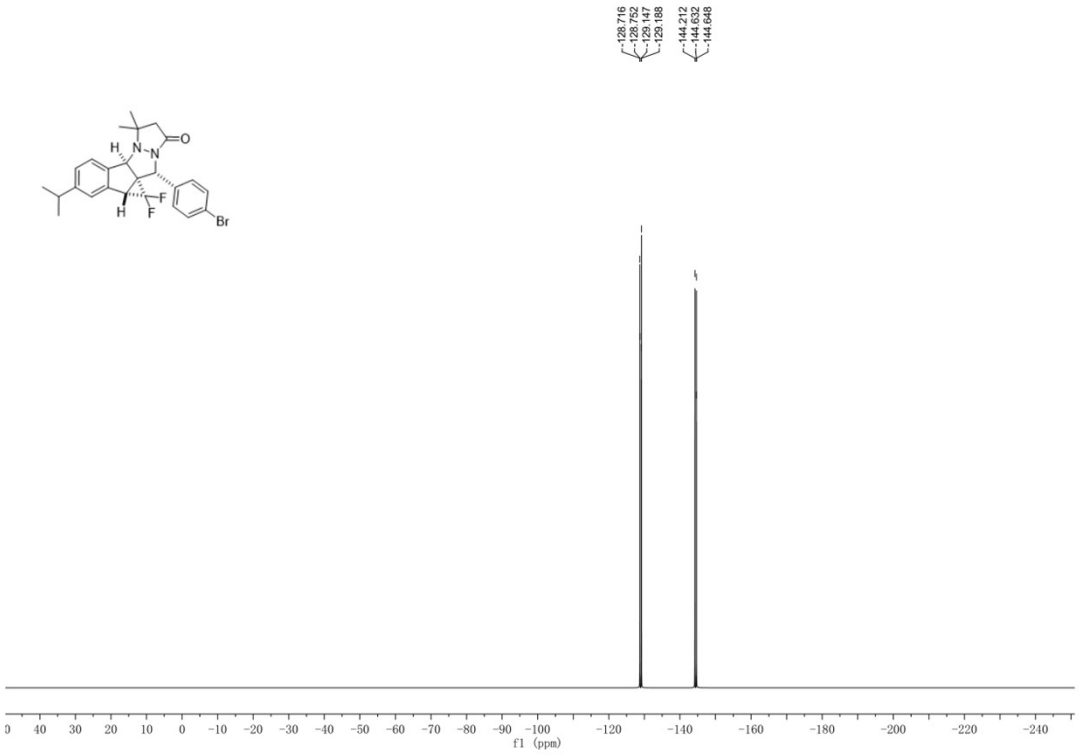
3da-^{1}H NMR (400 MHz, $CDCl_3$)



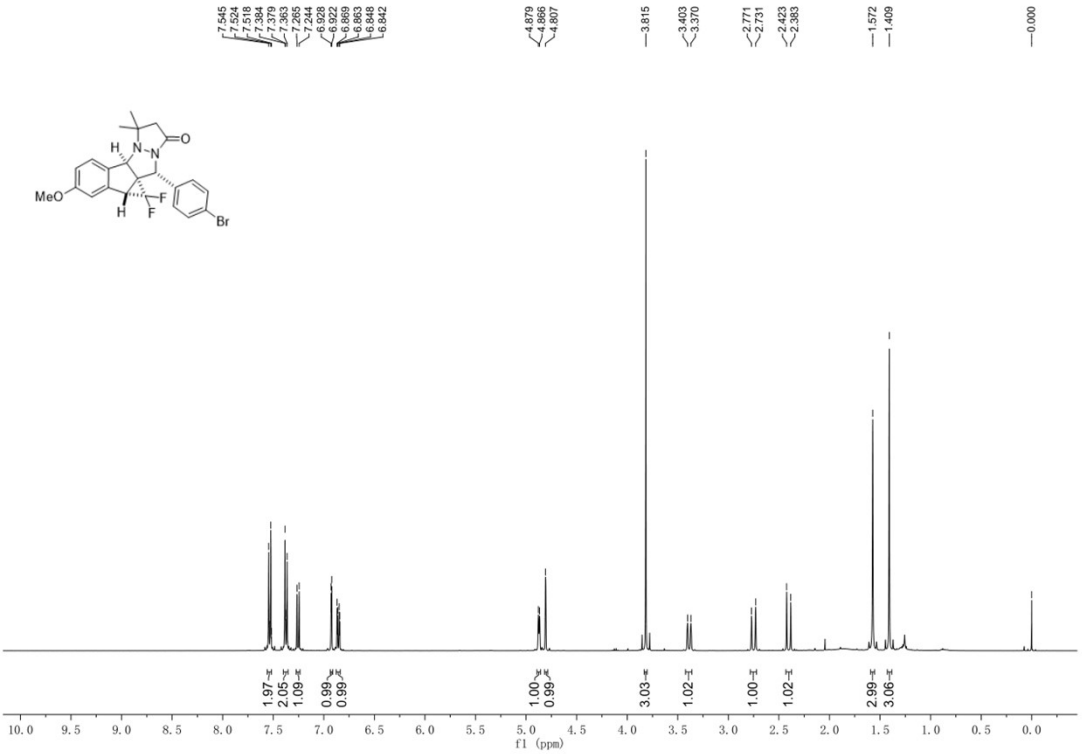
3da-^{13}C NMR (100 MHz, $CDCl_3$)



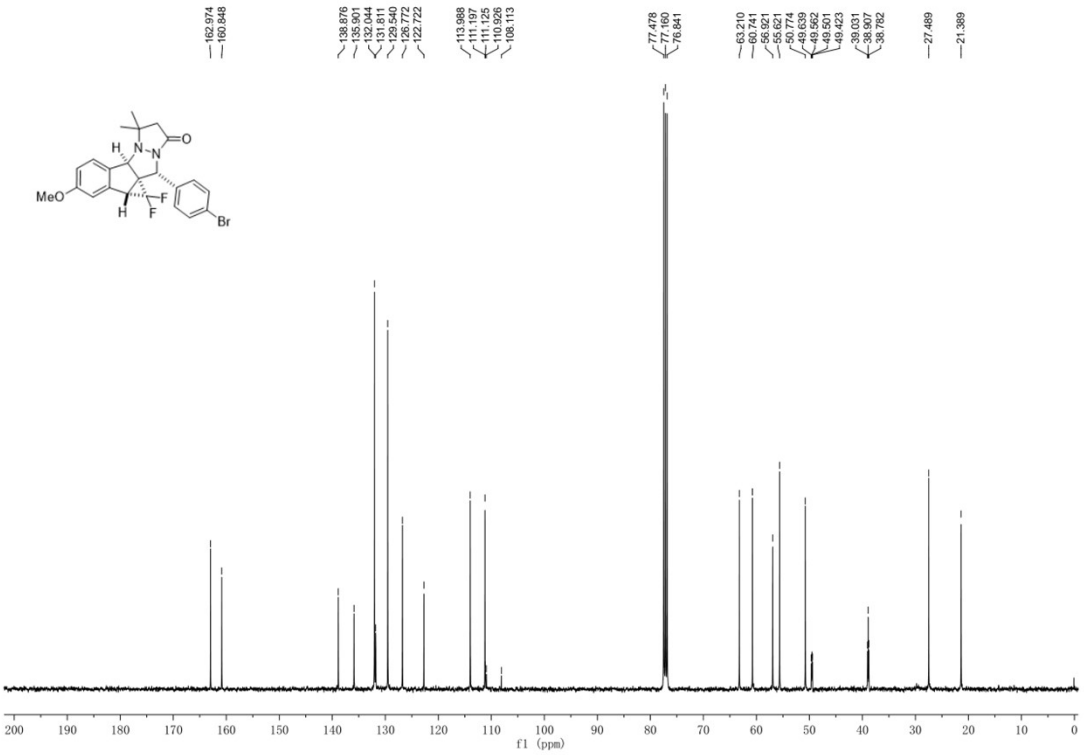
3da-^{19}F NMR (376 MHz, $CDCl_3$)



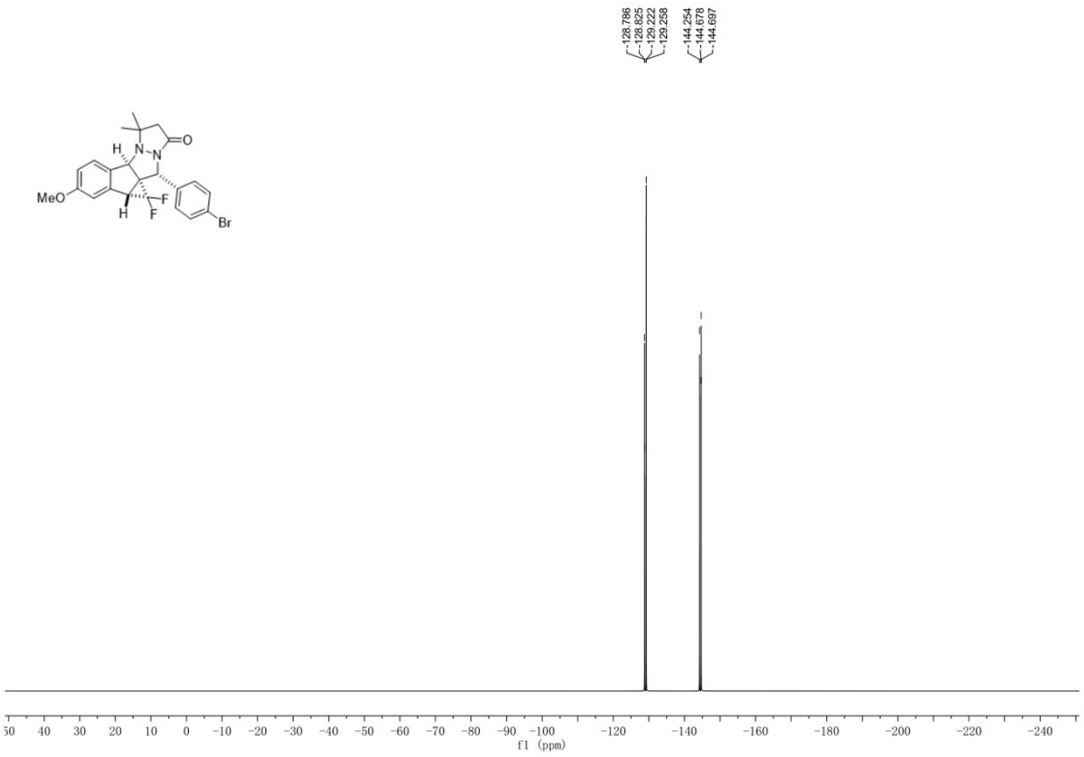
3ea-^{1}H NMR (400 MHz, $CDCl_3$)



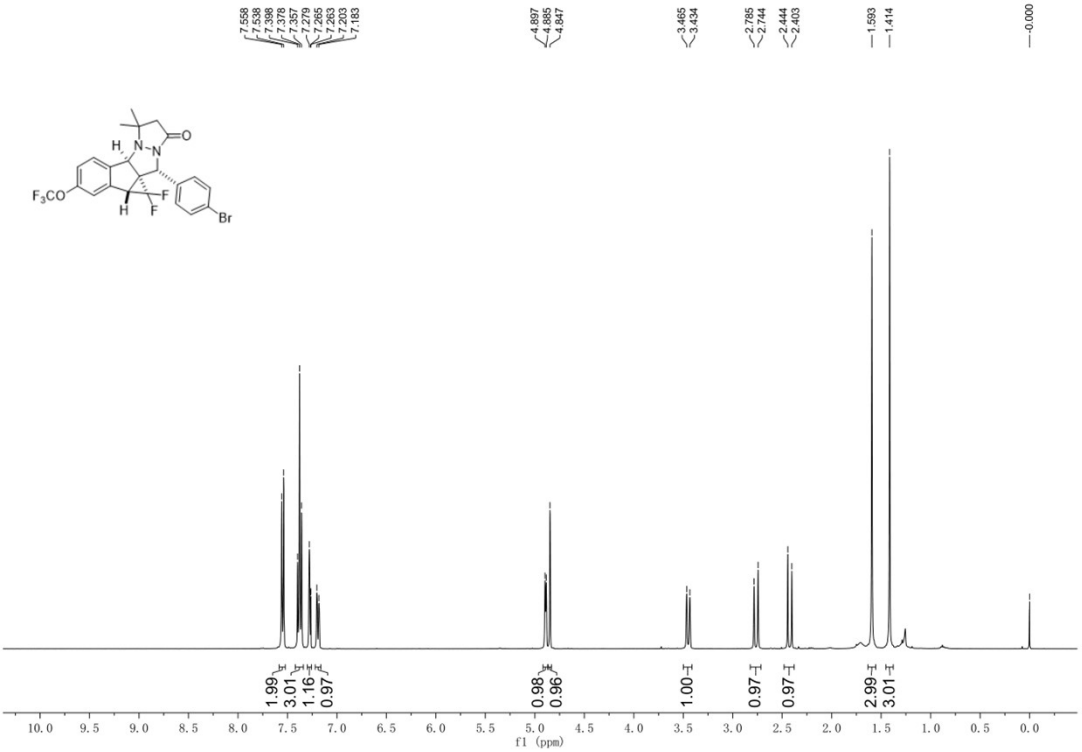
3ea-^{13}C NMR (100 MHz, $CDCl_3$)



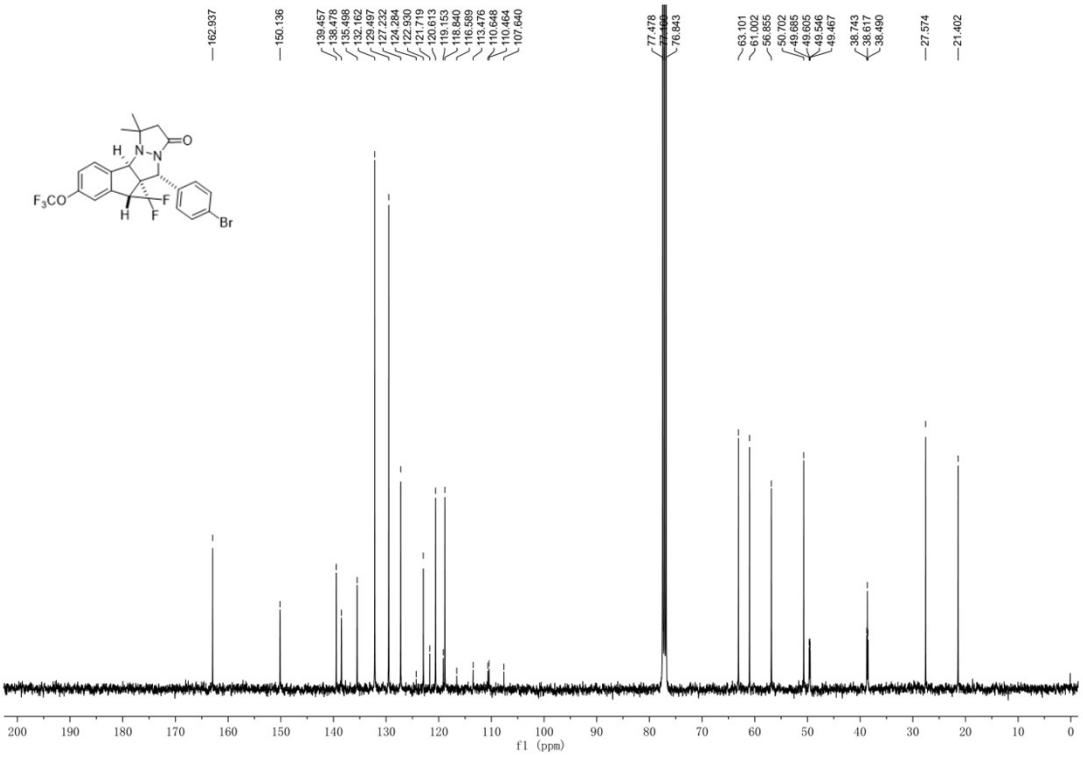
3ea-^{19}F NMR (376 MHz, $CDCl_3$)



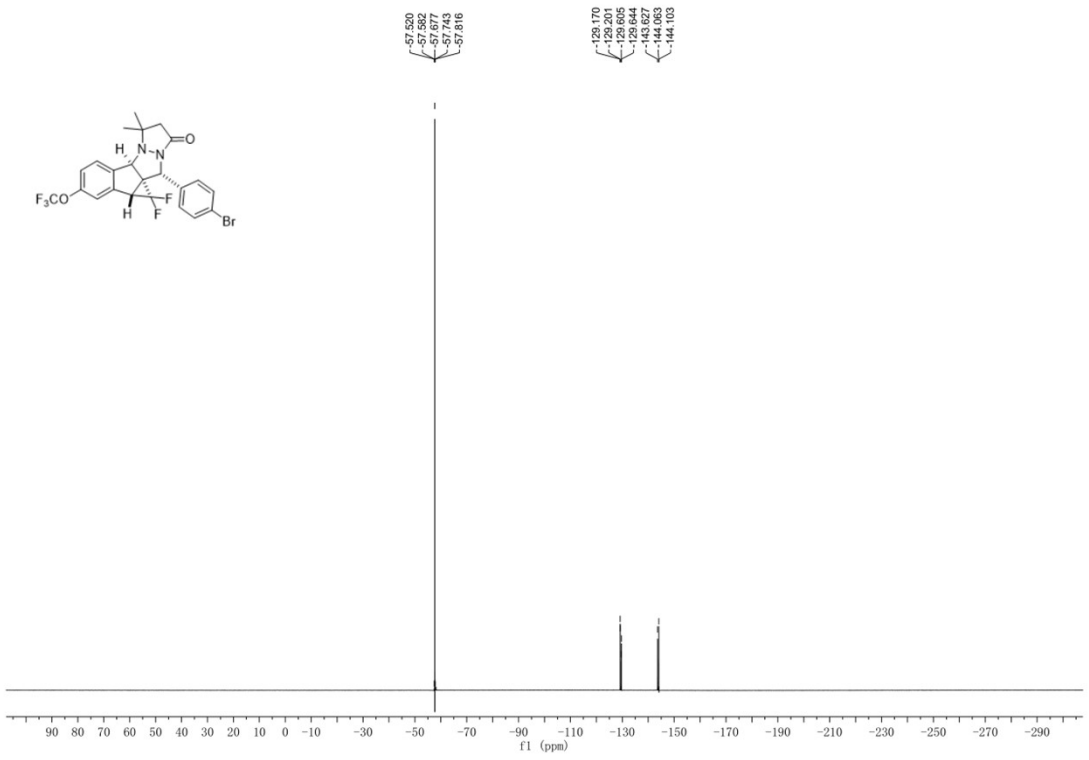
3fa-^{1}H NMR (400 MHz, $CDCl_3$)



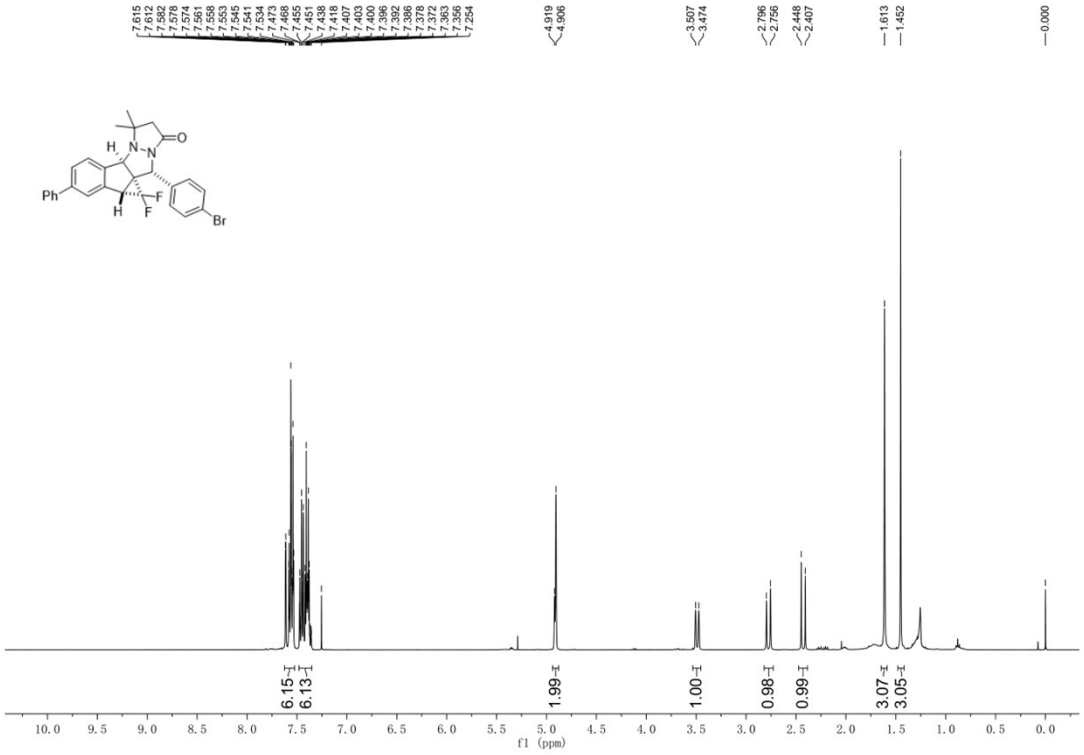
3fa-^{13}C NMR (100 MHz, $CDCl_3$)



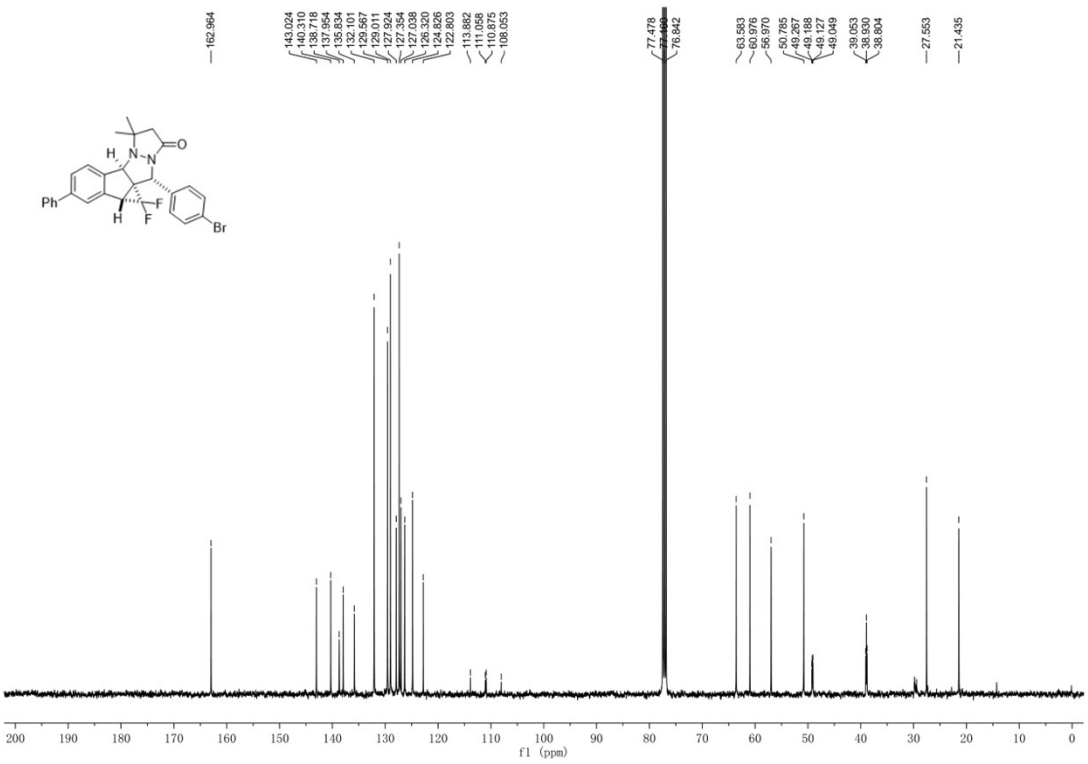
3fa-^{19}F NMR (376 MHz, $CDCl_3$)



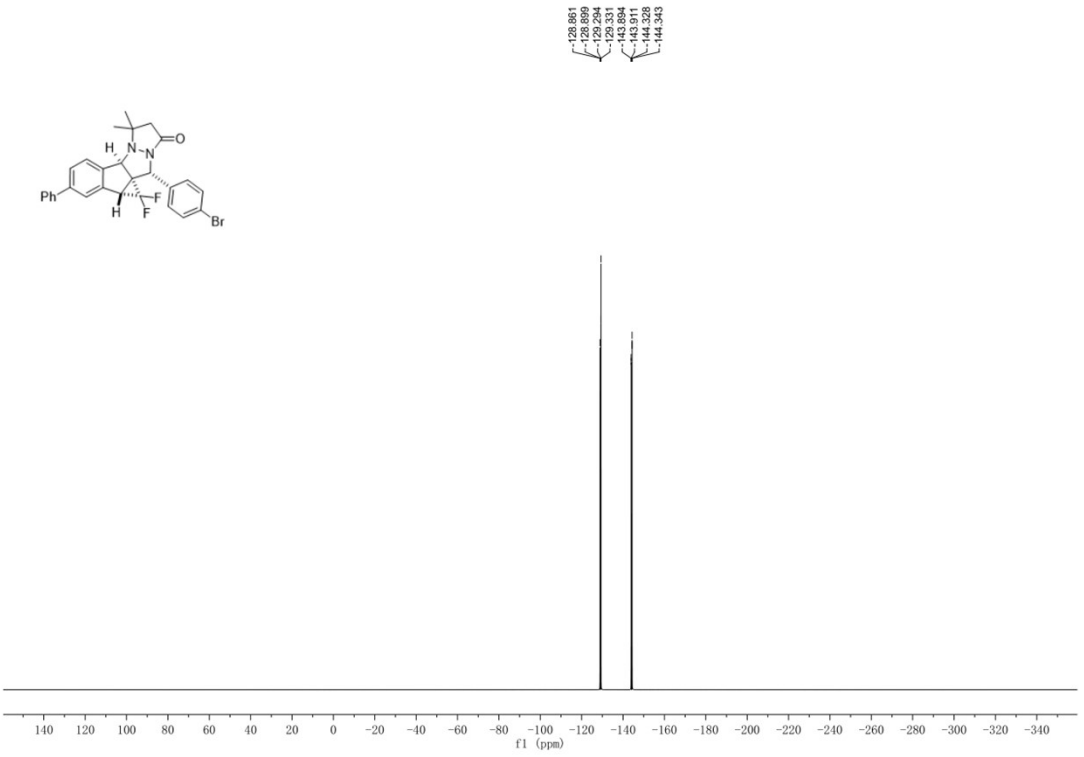
3ga-^{1}H NMR (400 MHz, $CDCl_3$)



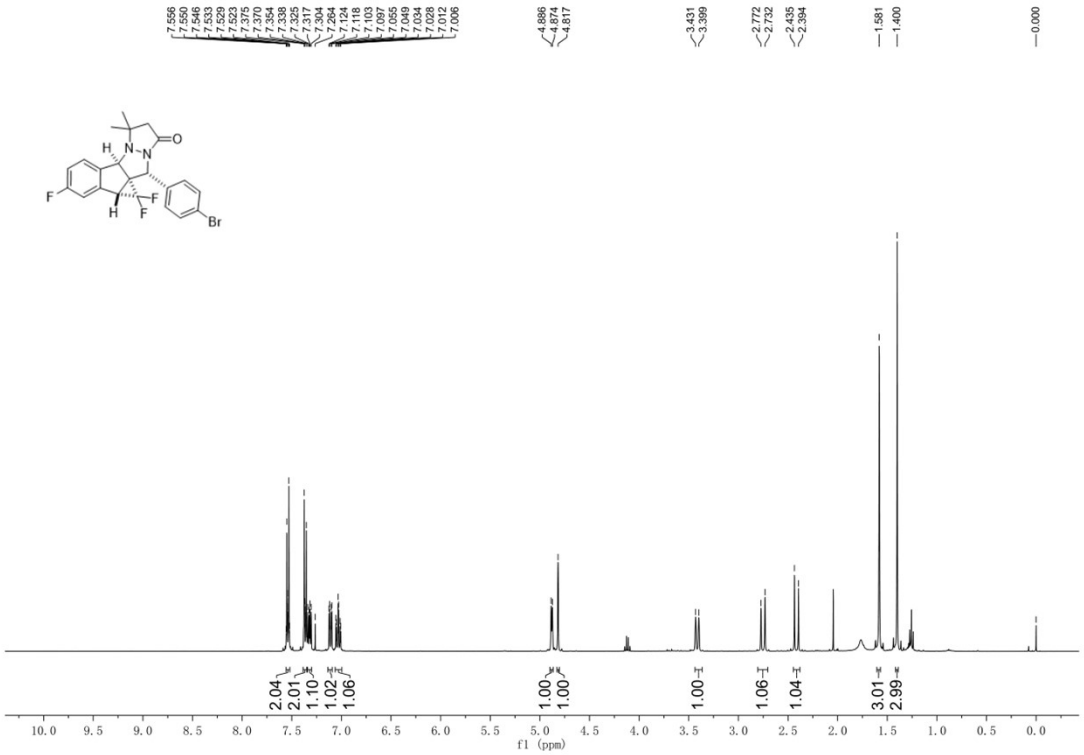
3ga-^{13}C NMR (100 MHz, $CDCl_3$)



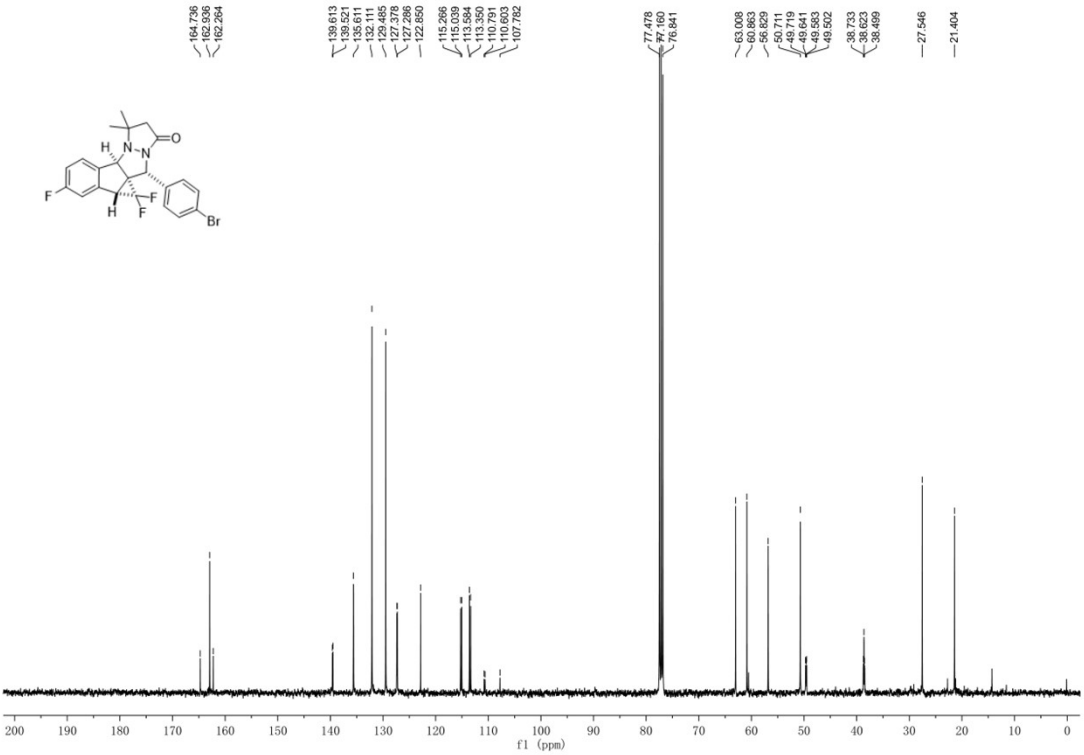
3ga-^{19}F NMR (376 MHz, $CDCl_3$)



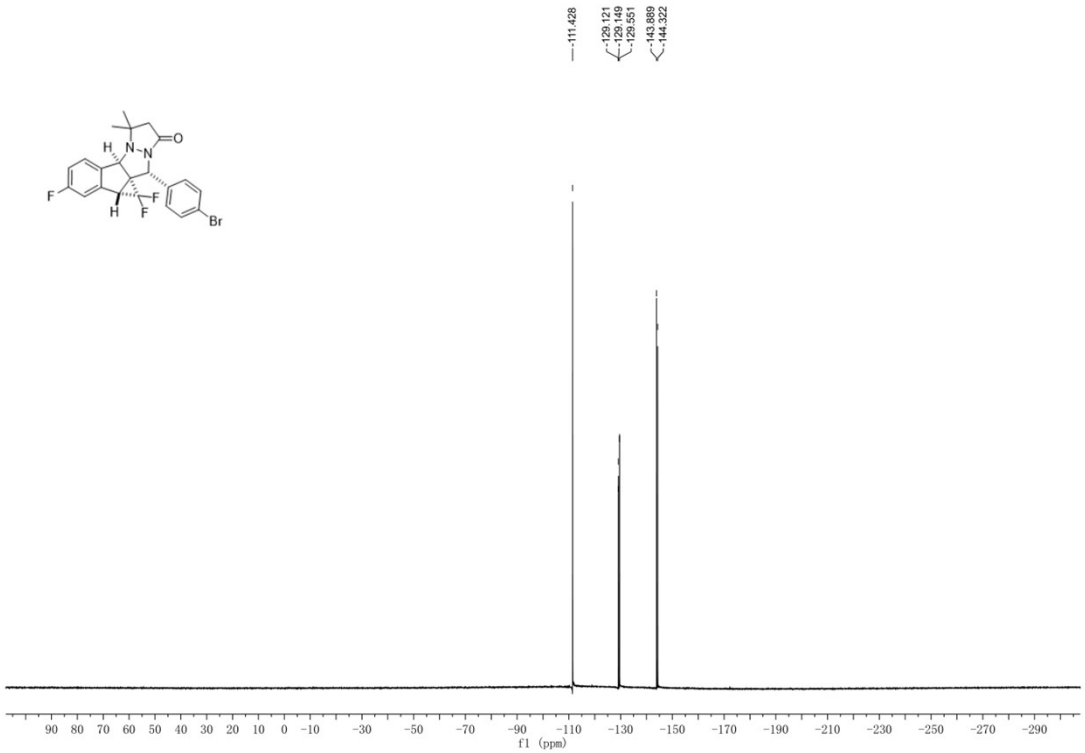
3ha-^{1}H NMR (400 MHz, $CDCl_3$)



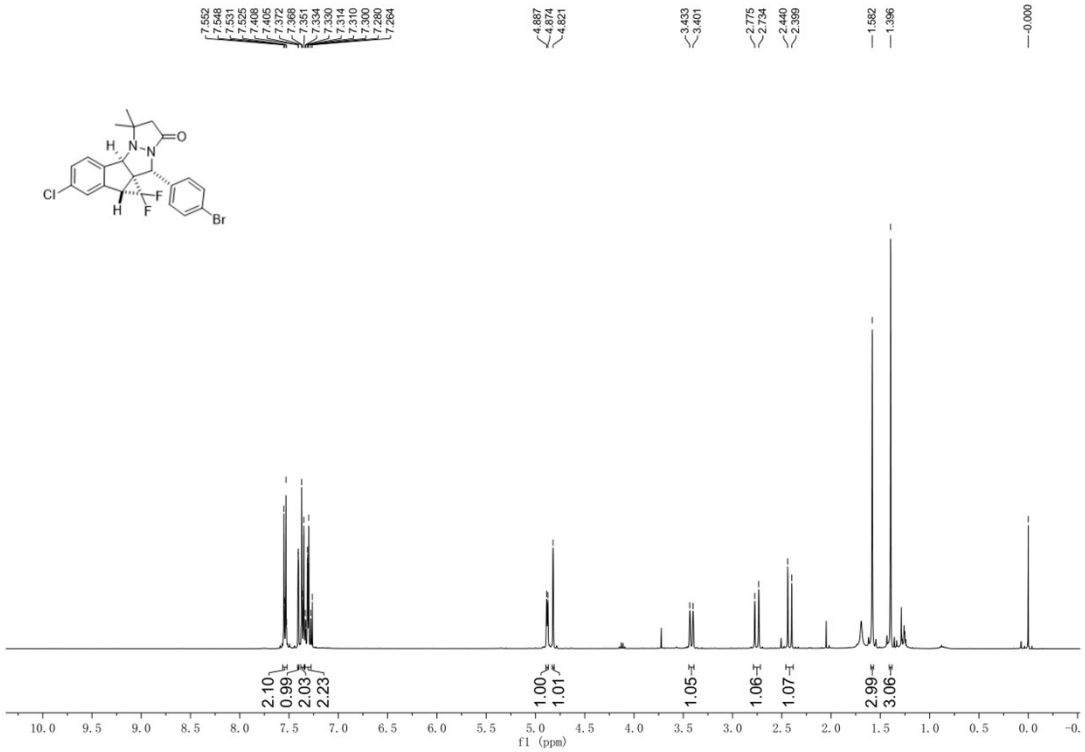
3ha-^{13}C NMR (100 MHz, $CDCl_3$)



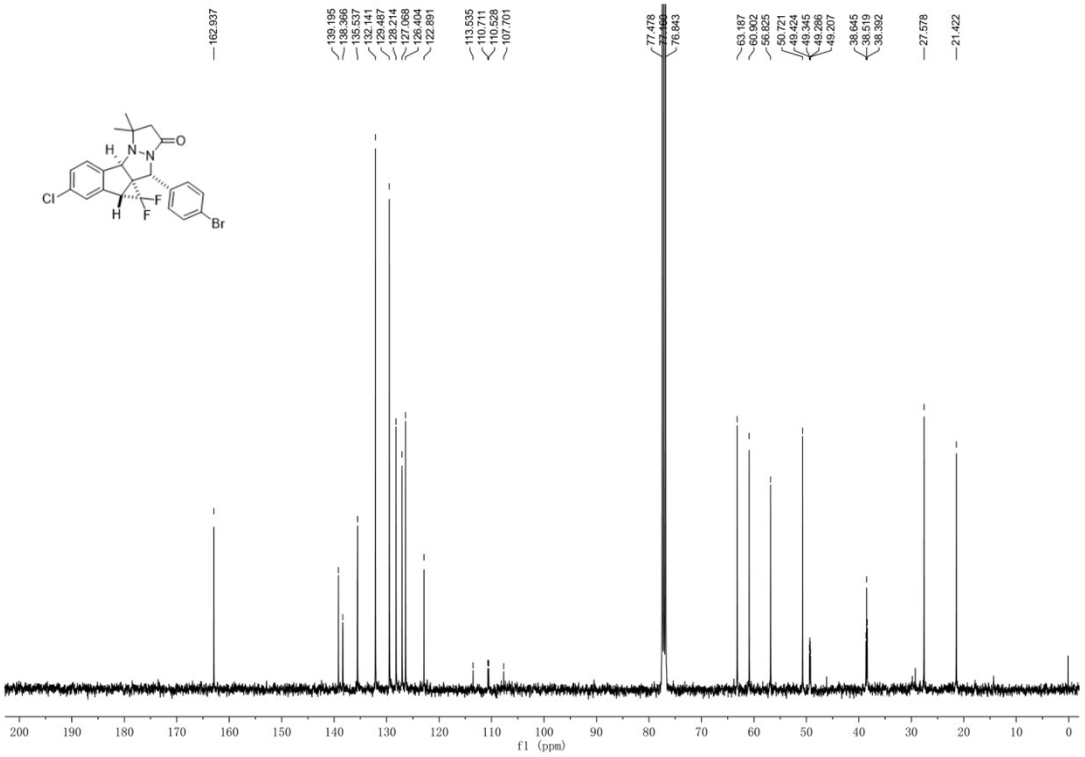
3ha-^{19}F NMR (376 MHz, $CDCl_3$)



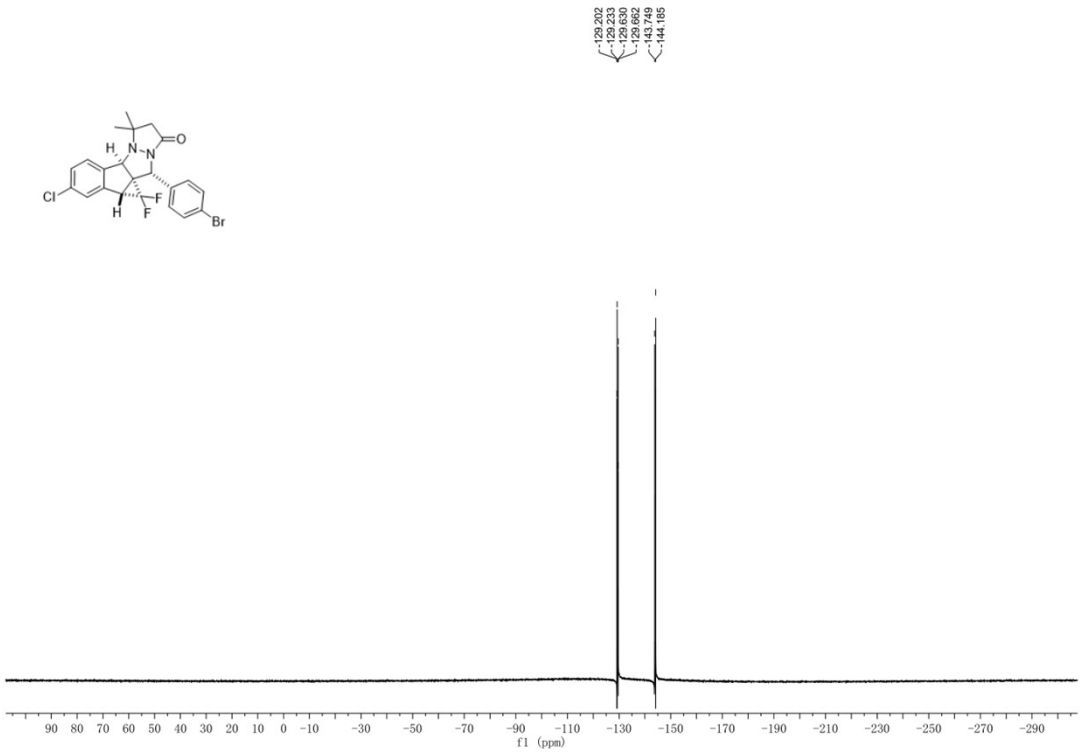
3ia-^{1}H NMR (400 MHz, $CDCl_3$)



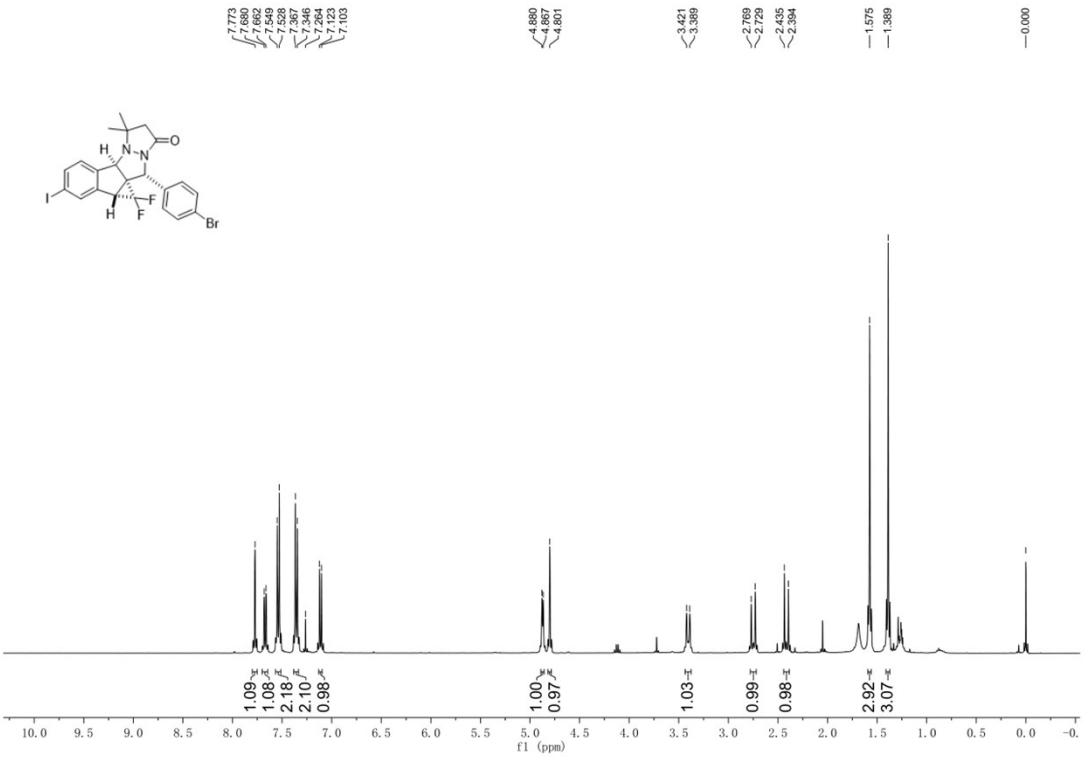
3ia-^{13}C NMR (100 MHz, $CDCl_3$)



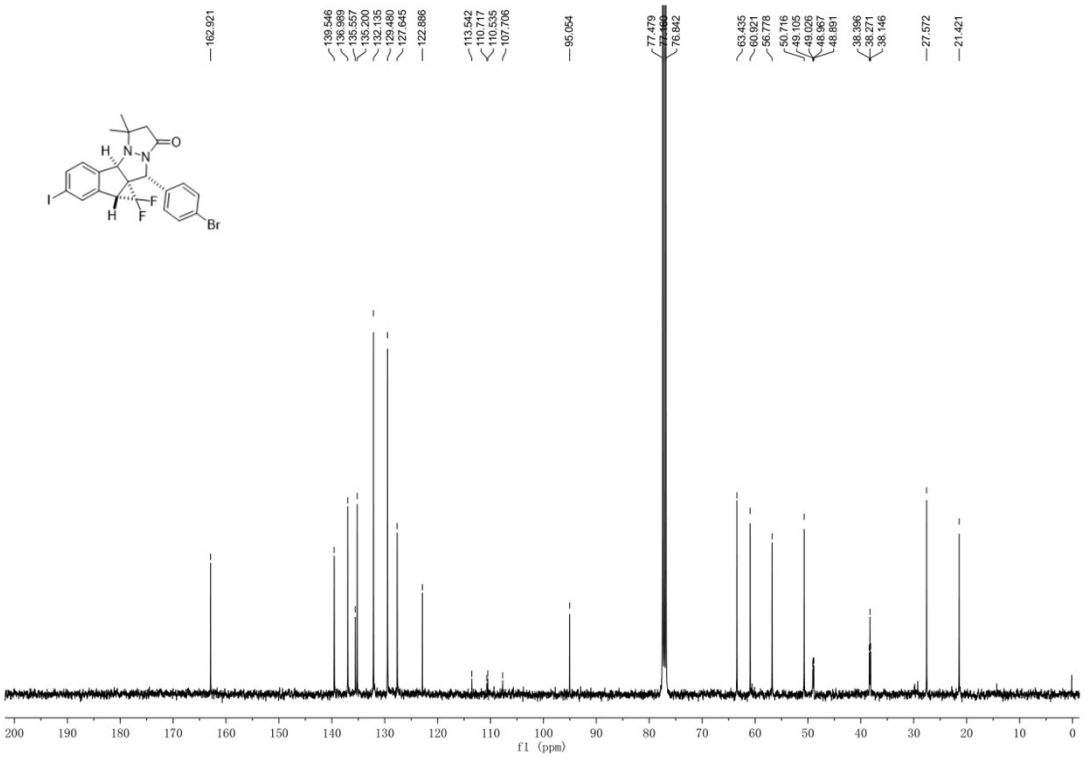
3ia-^{19}F NMR (376 MHz, $CDCl_3$)



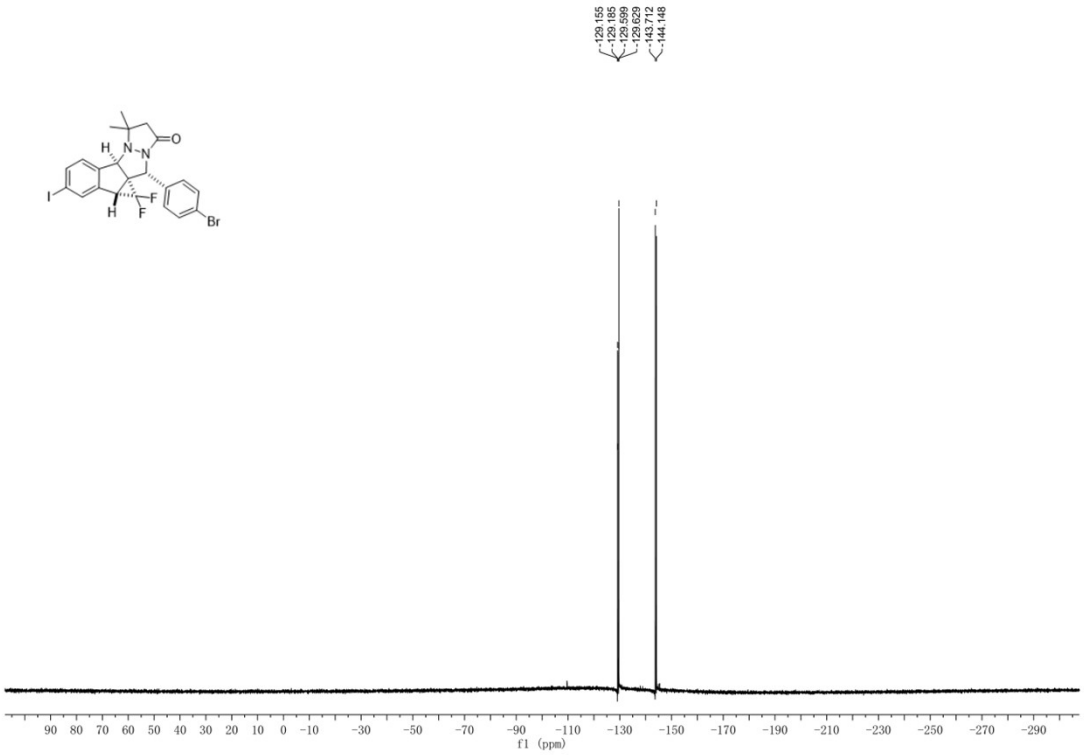
3ja-^{1}H NMR (400 MHz, $CDCl_3$)



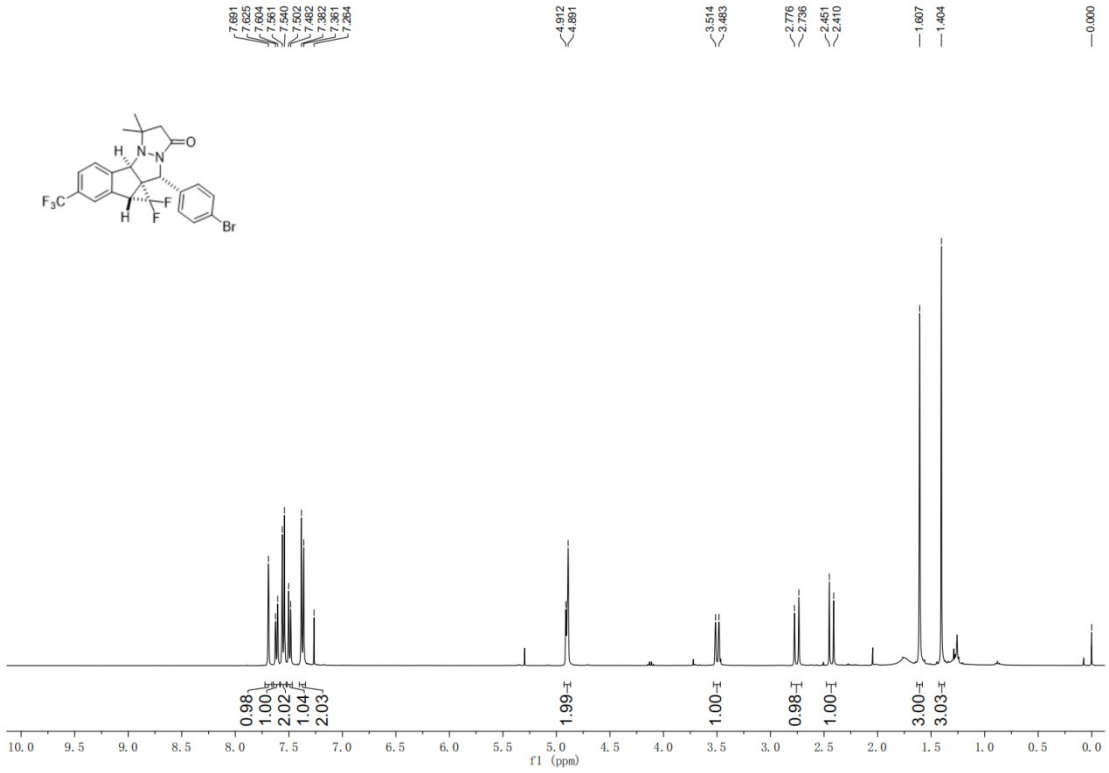
3ja-^{13}C NMR (100 MHz, $CDCl_3$)



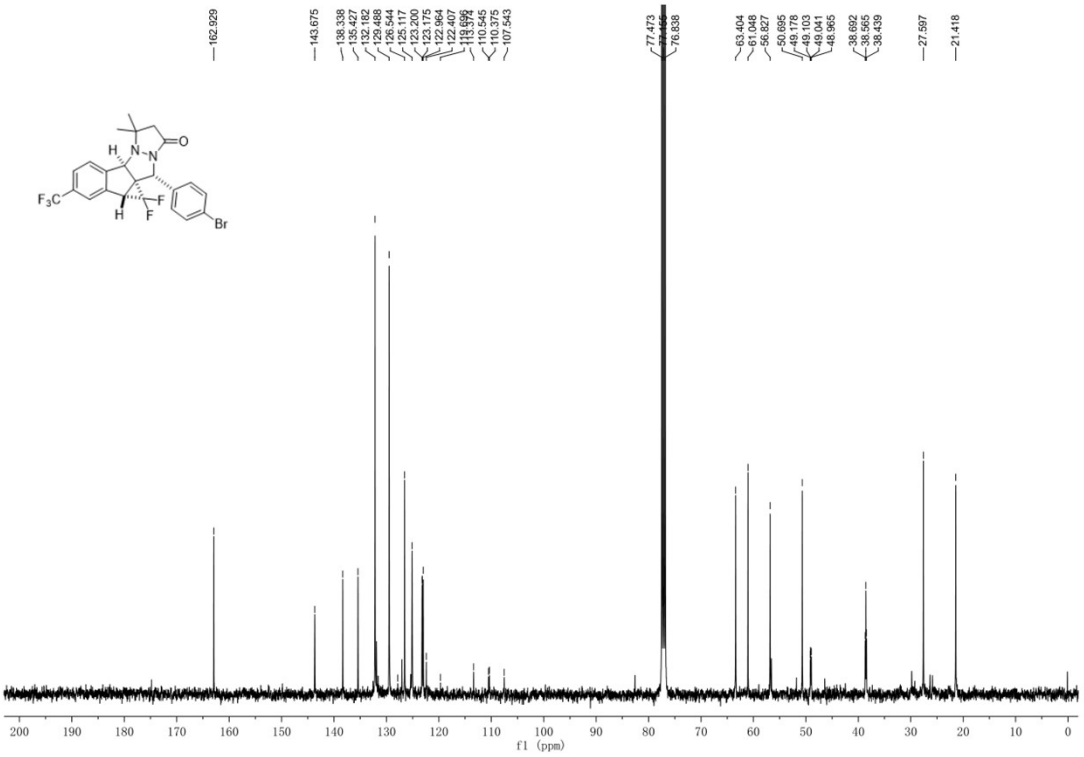
3ja-^{19}F NMR (376 MHz, $CDCl_3$)



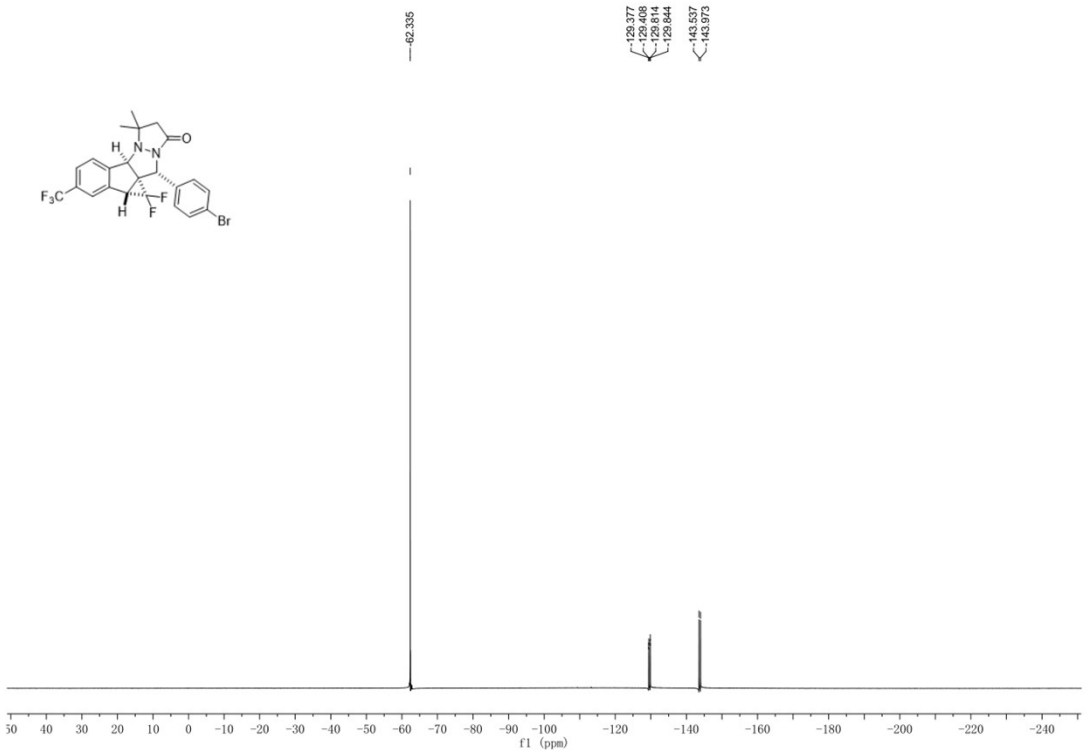
3ka-^{1}H NMR (400 MHz, $CDCl_3$)



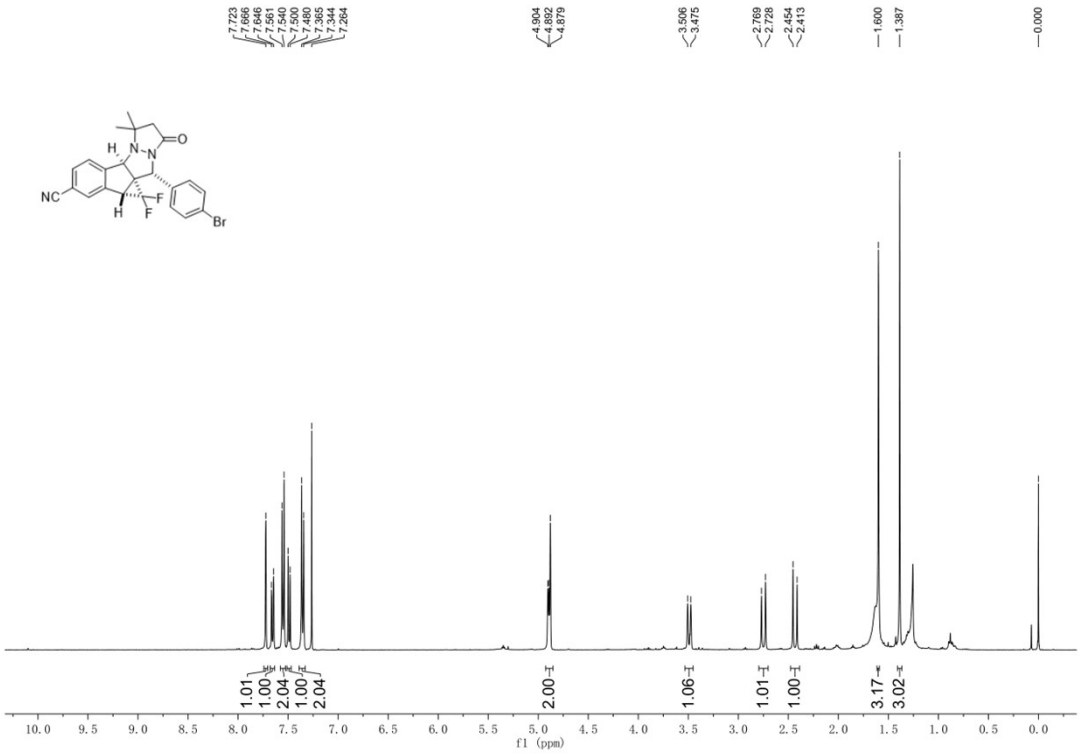
3ka-^{13}C NMR (100 MHz, $CDCl_3$)



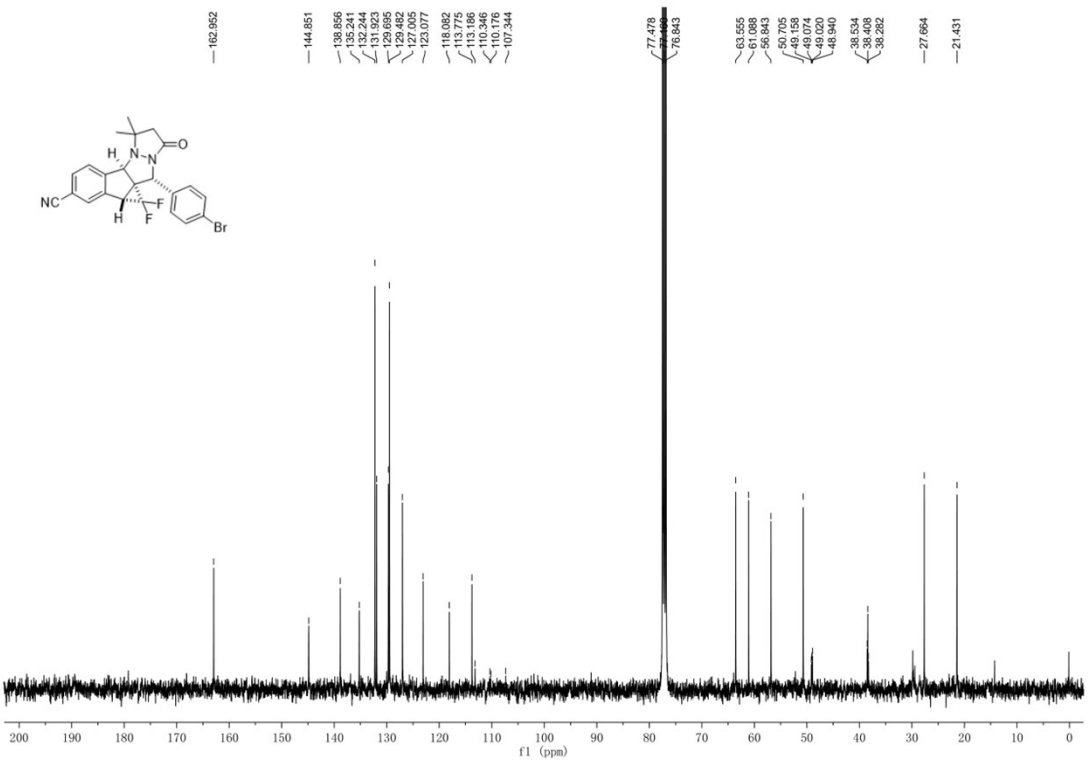
3ka-^{19}F NMR (376 MHz, $CDCl_3$)



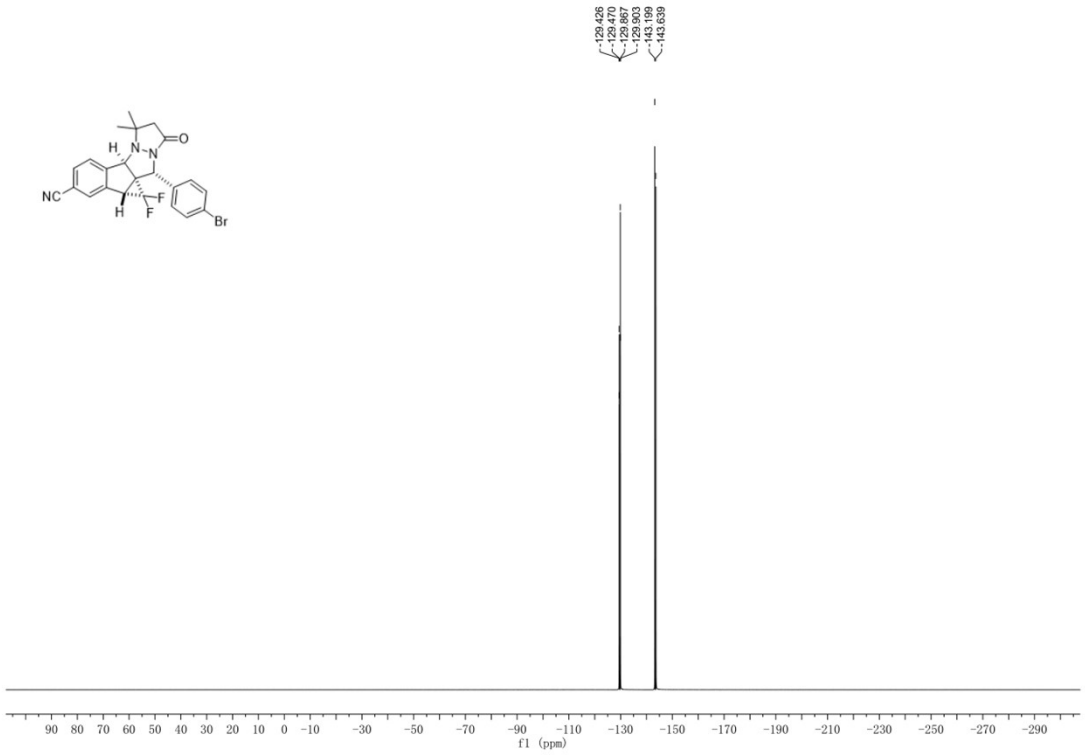
3la-^{1}H NMR (400 MHz, $CDCl_3$)



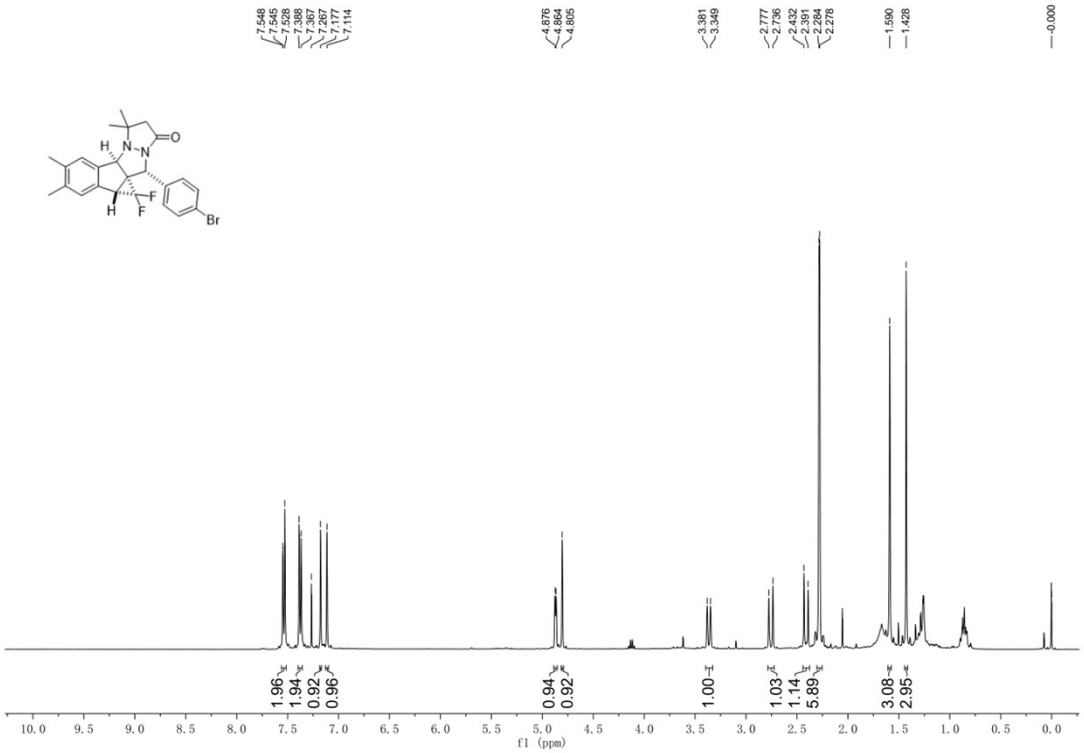
3la-^{13}C NMR (100 MHz, $CDCl_3$)



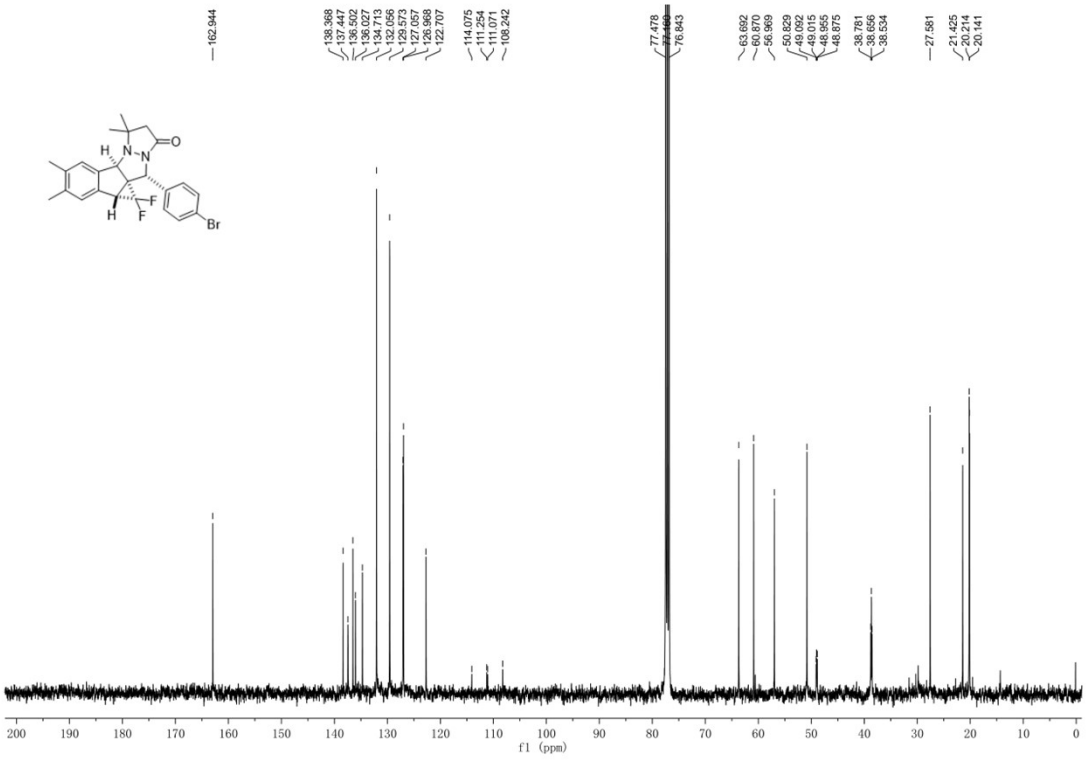
3la-^{19}F NMR (376 MHz, $CDCl_3$)



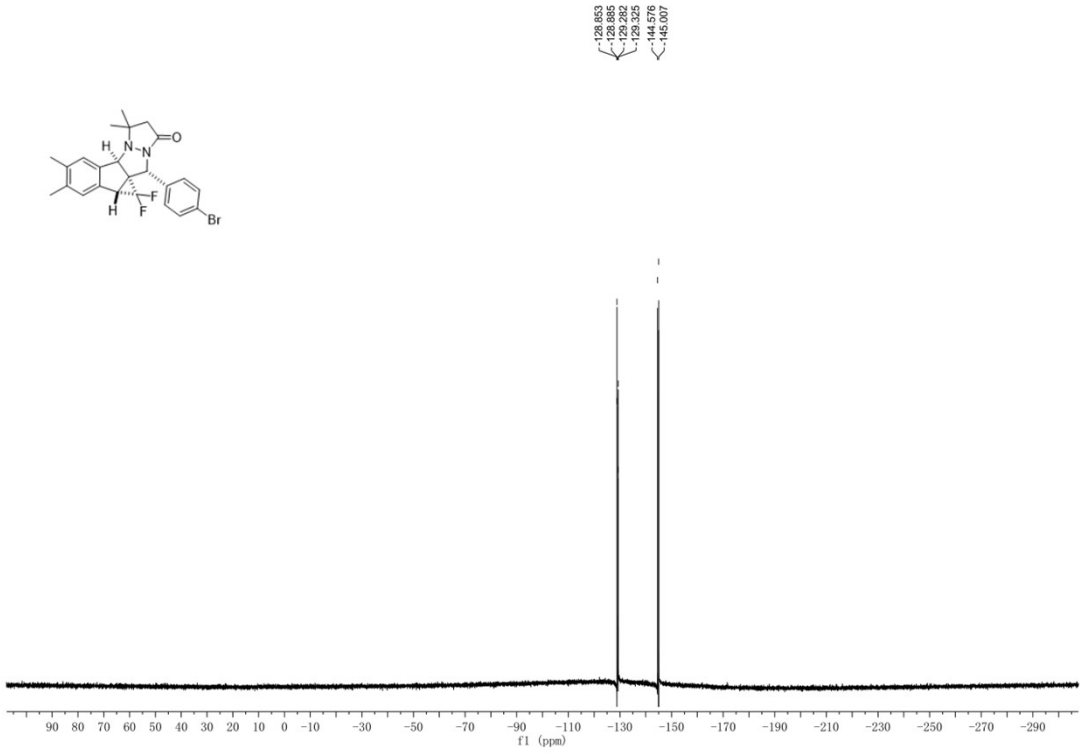
3ma-^{1}H NMR (400 MHz, $CDCl_3$)



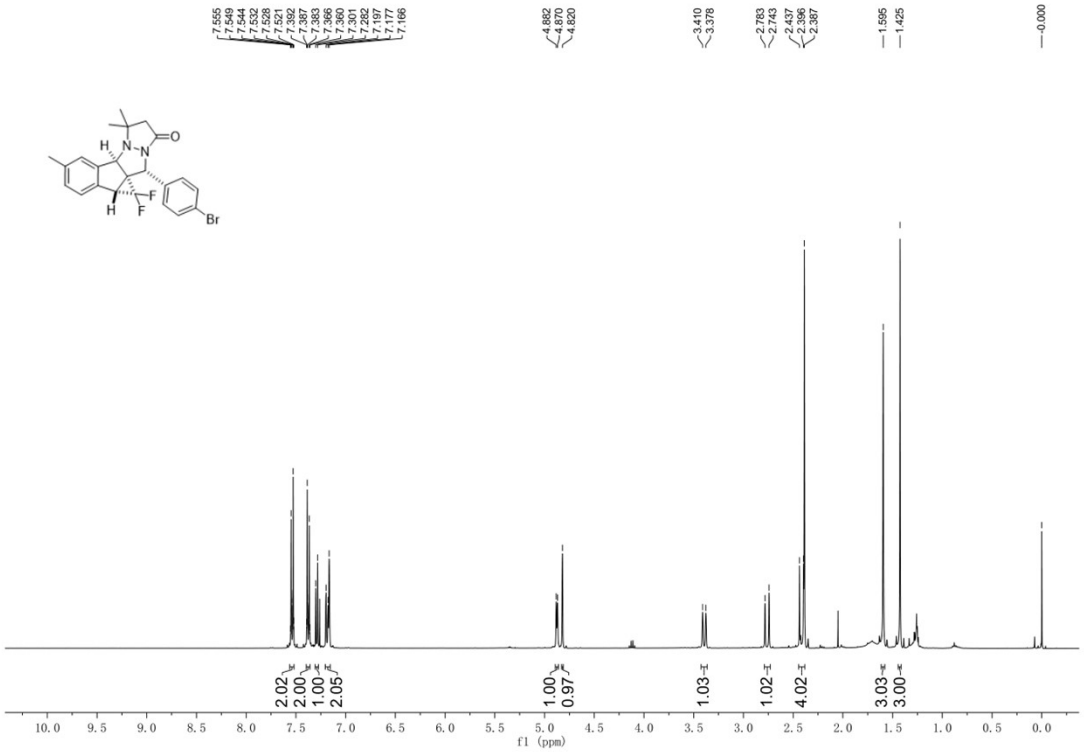
3ma-^{13}C NMR (100 MHz, $CDCl_3$)



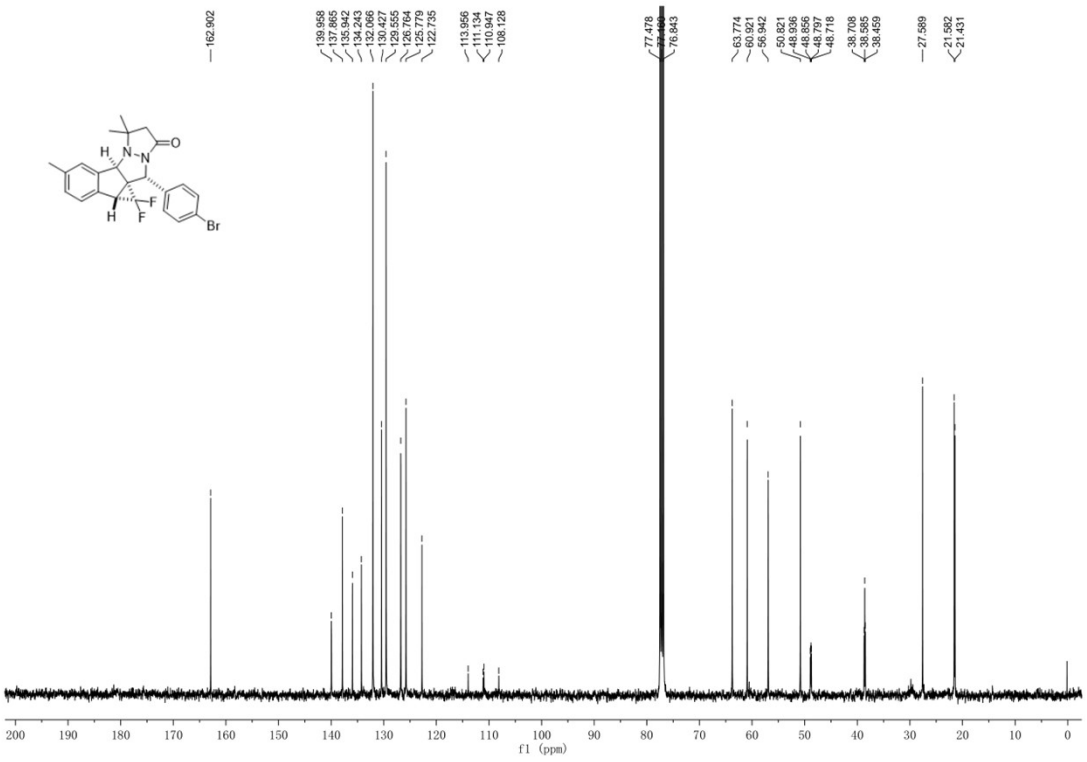
3ma-^{19}F NMR (376 MHz, $CDCl_3$)



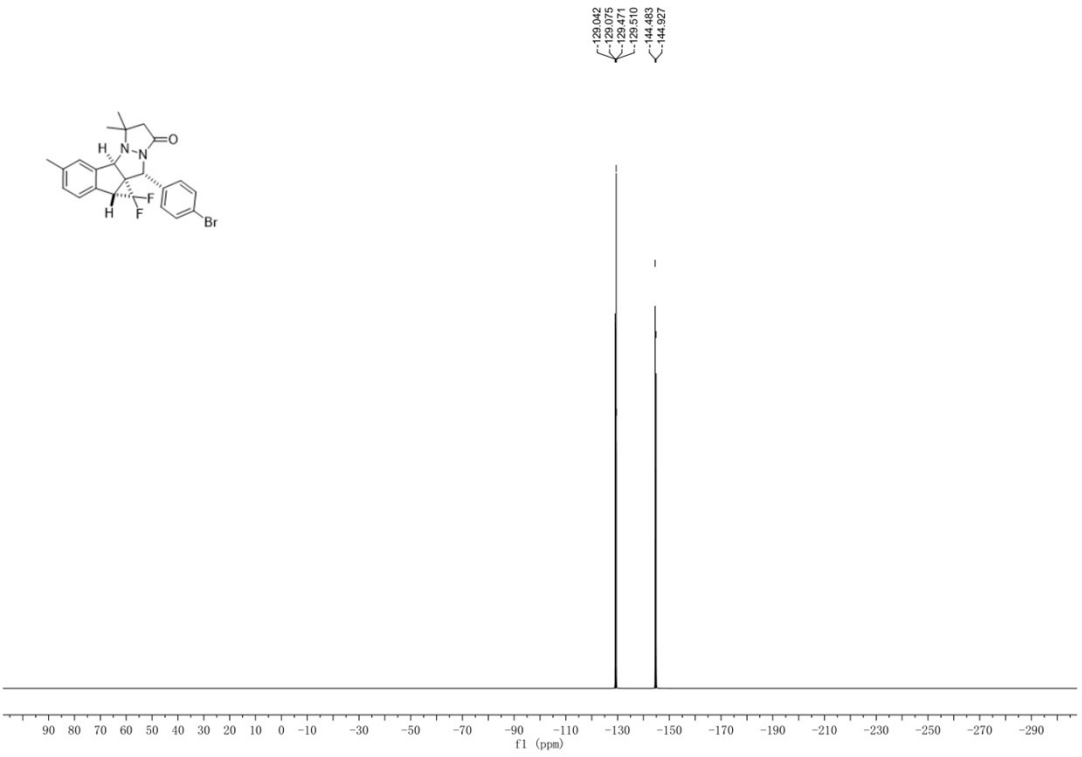
3na-^{1}H NMR (400 MHz, $CDCl_3$)



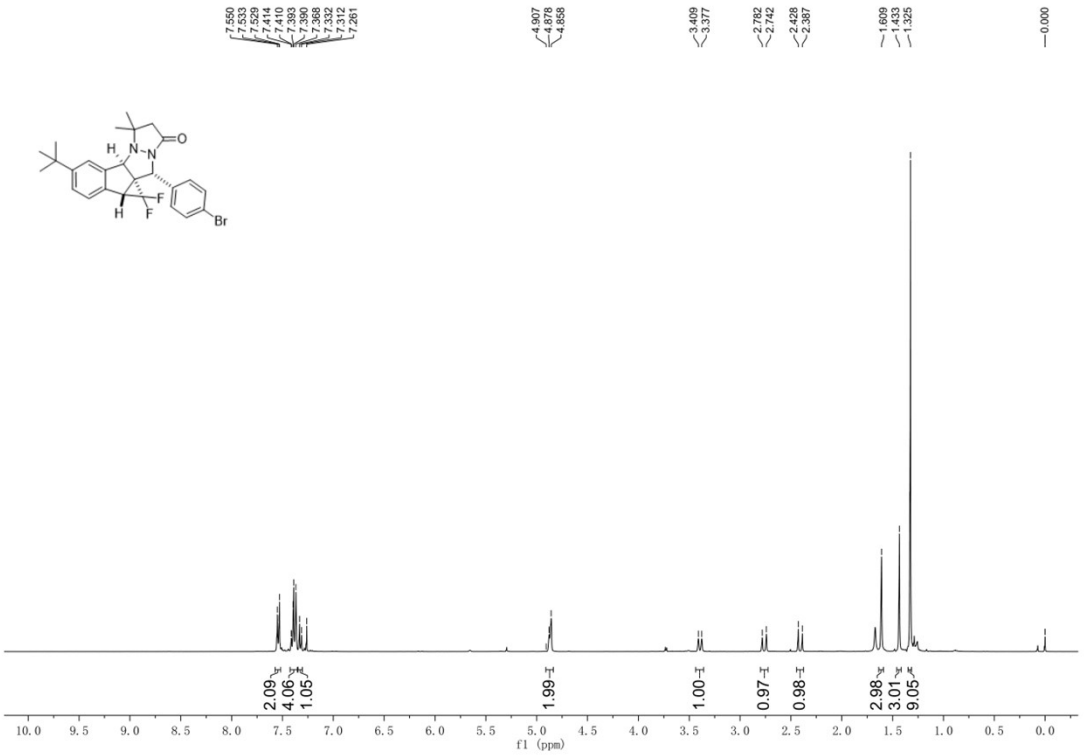
3na-^{13}C NMR (100 MHz, $CDCl_3$)



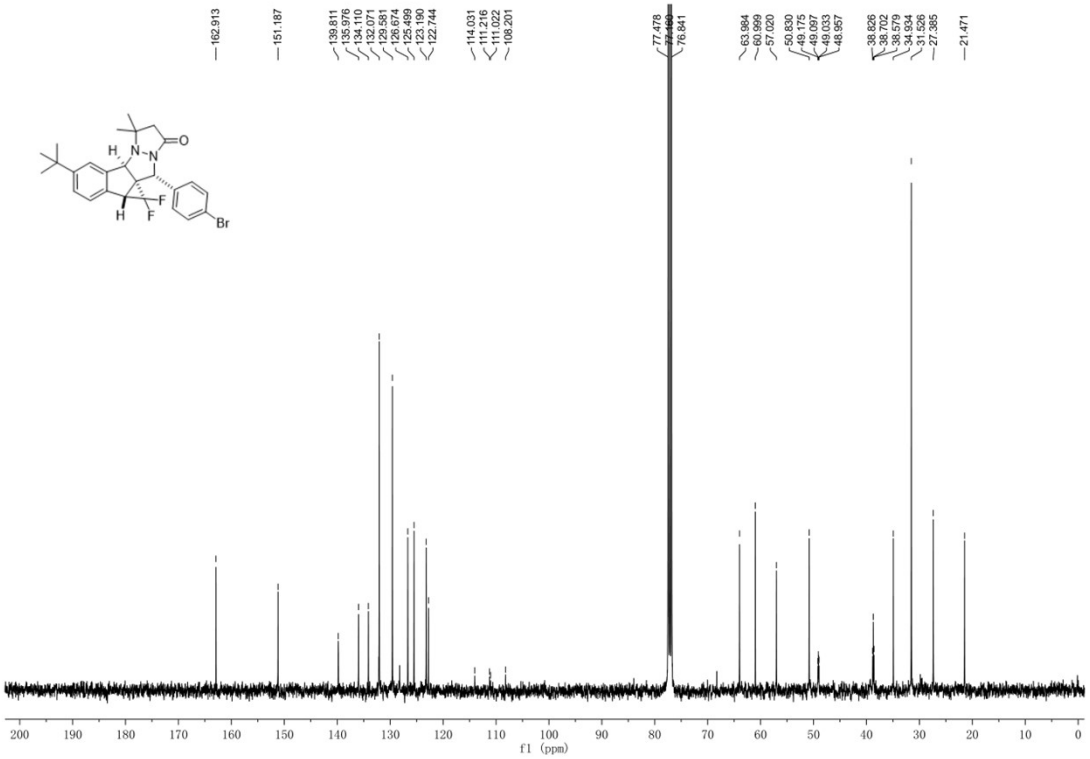
3na-^{19}F NMR (376 MHz, $CDCl_3$)



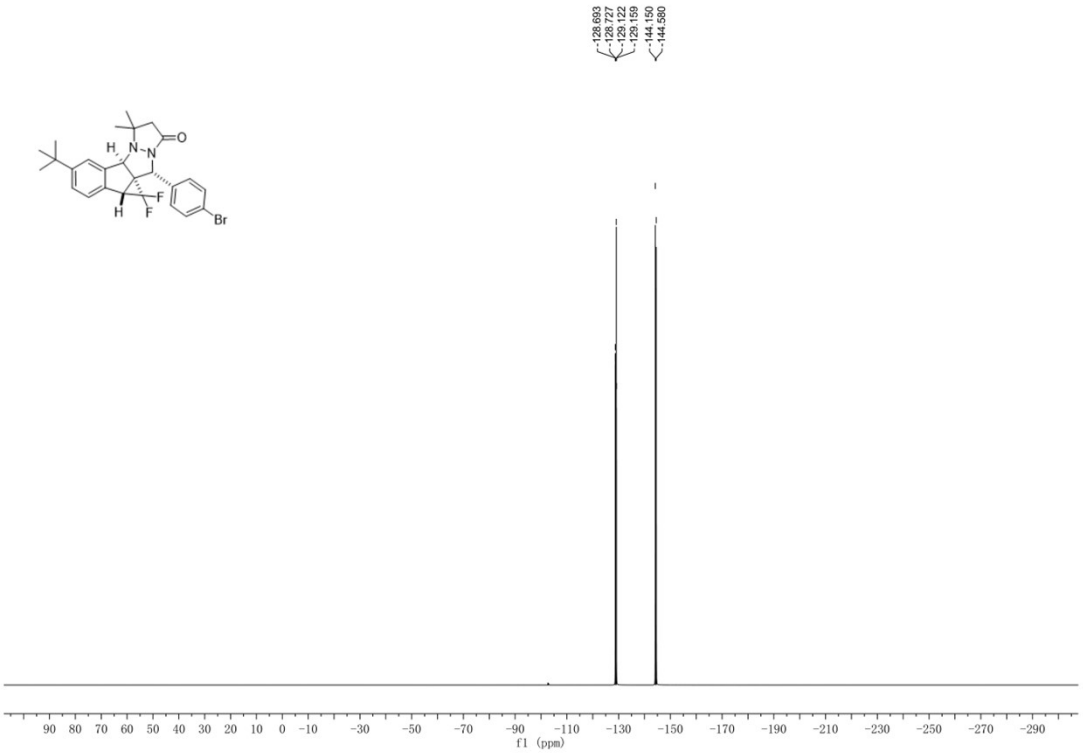
3oa-^{1}H NMR (400 MHz, $CDCl_3$)



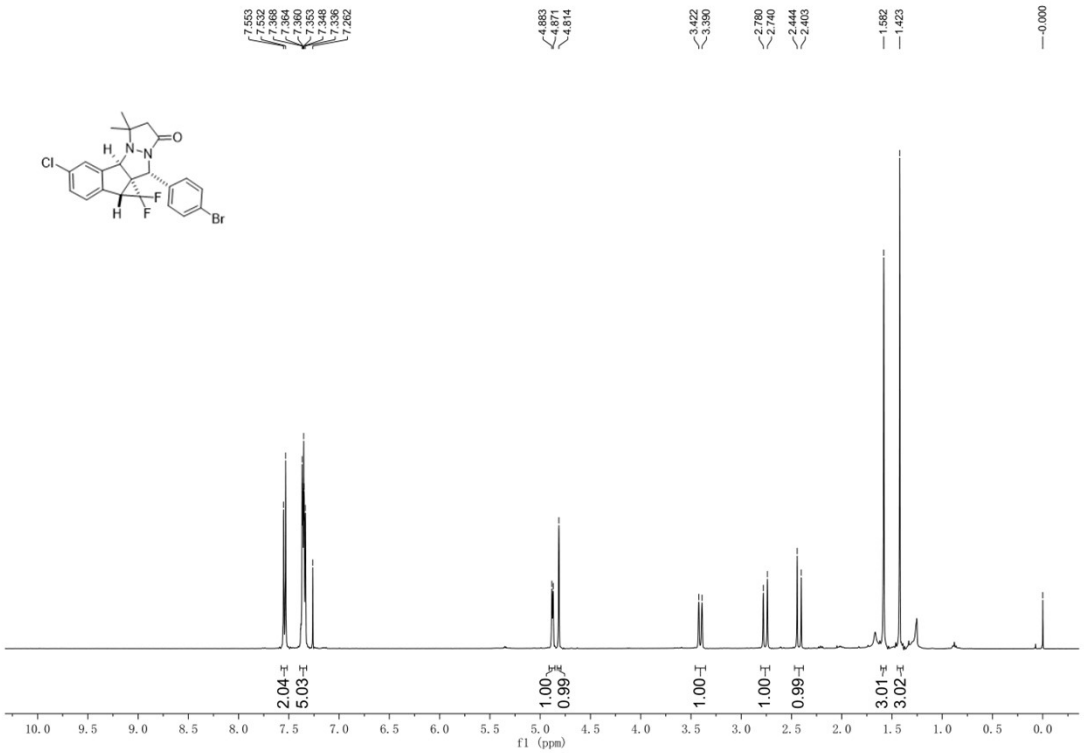
3oa-^{13}C NMR (100 MHz, $CDCl_3$)



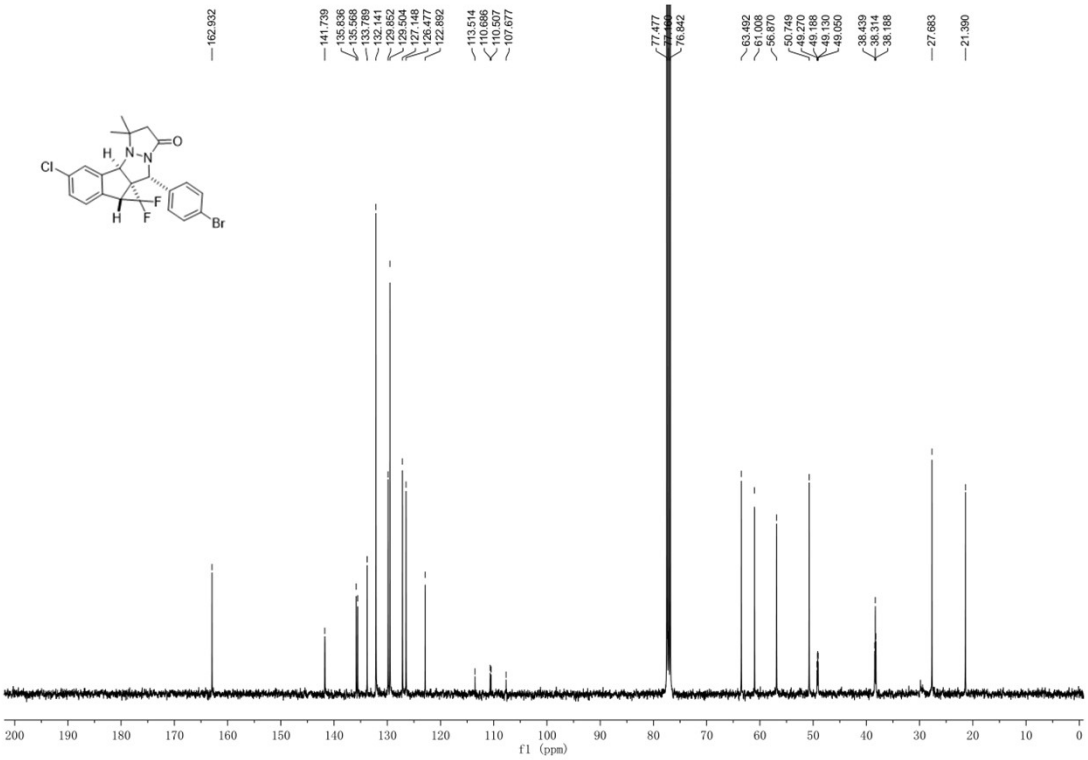
3oa-^{19}F NMR (376 MHz, $CDCl_3$)



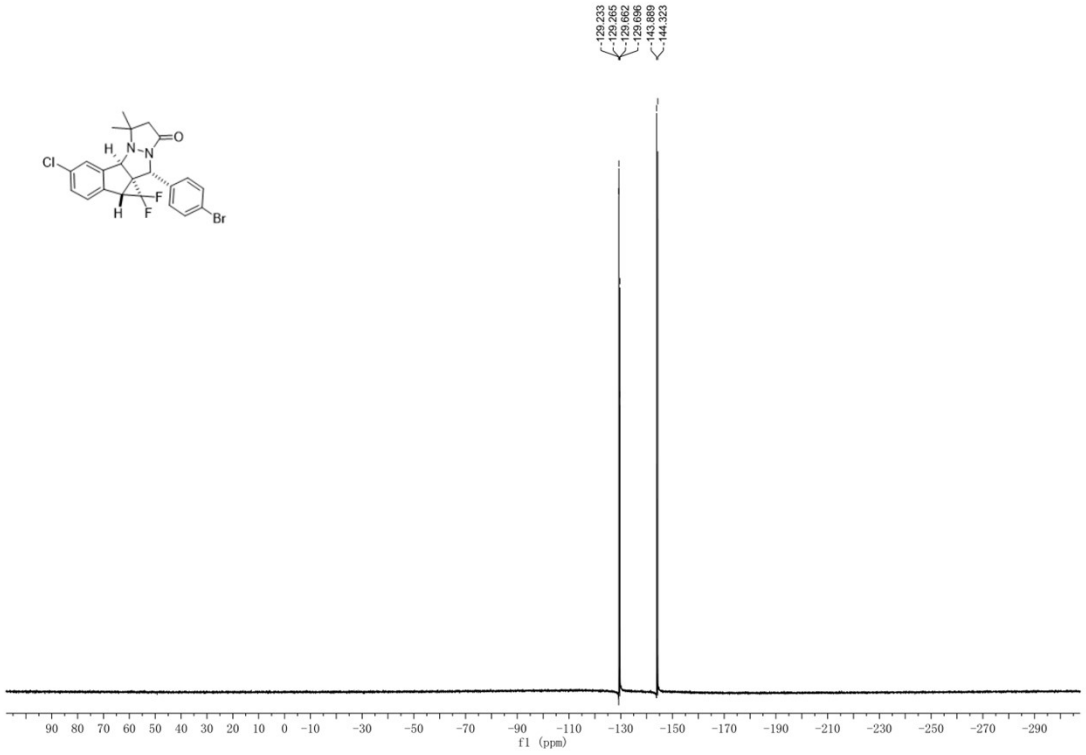
3pa-^{1}H NMR (400 MHz, $CDCl_3$)



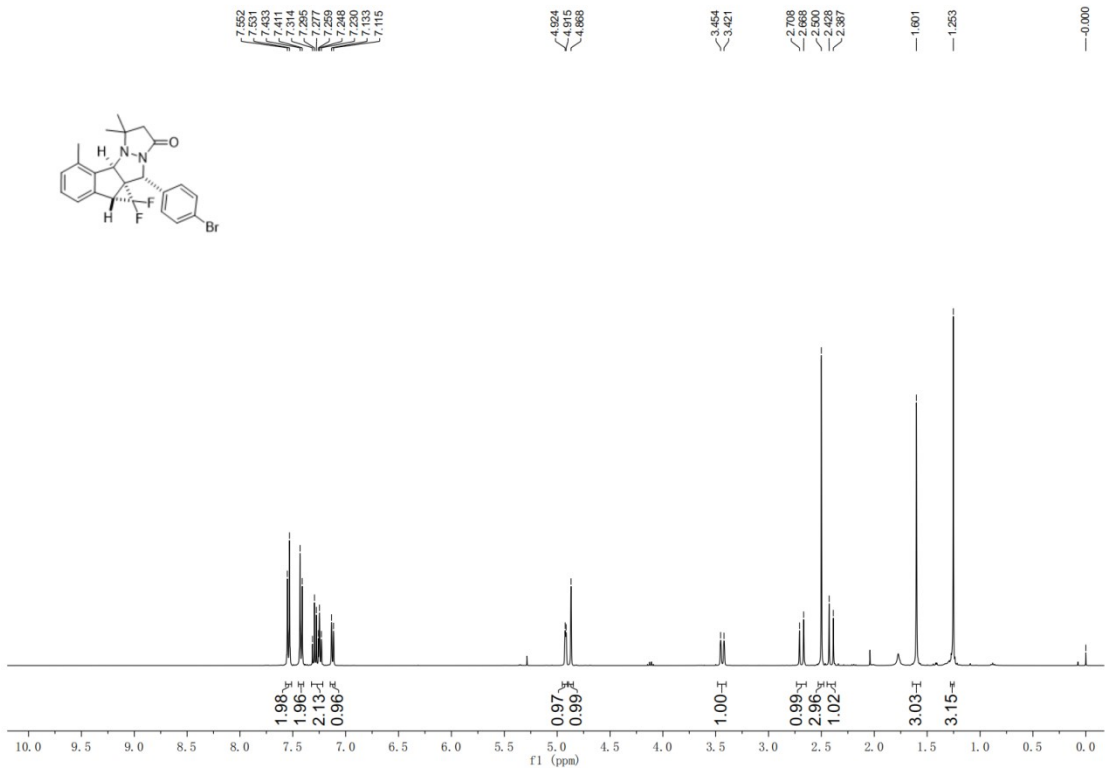
3pa-^{13}C NMR (100 MHz, $CDCl_3$)



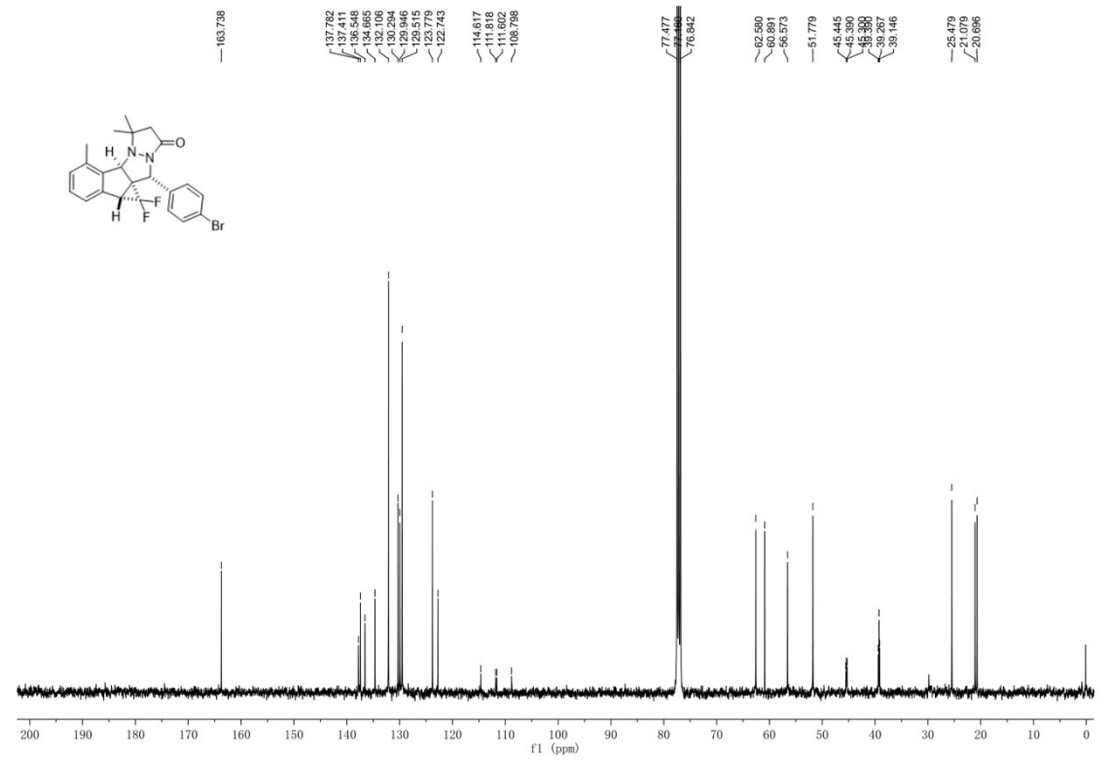
3pa-^{19}F NMR (376 MHz, $CDCl_3$)



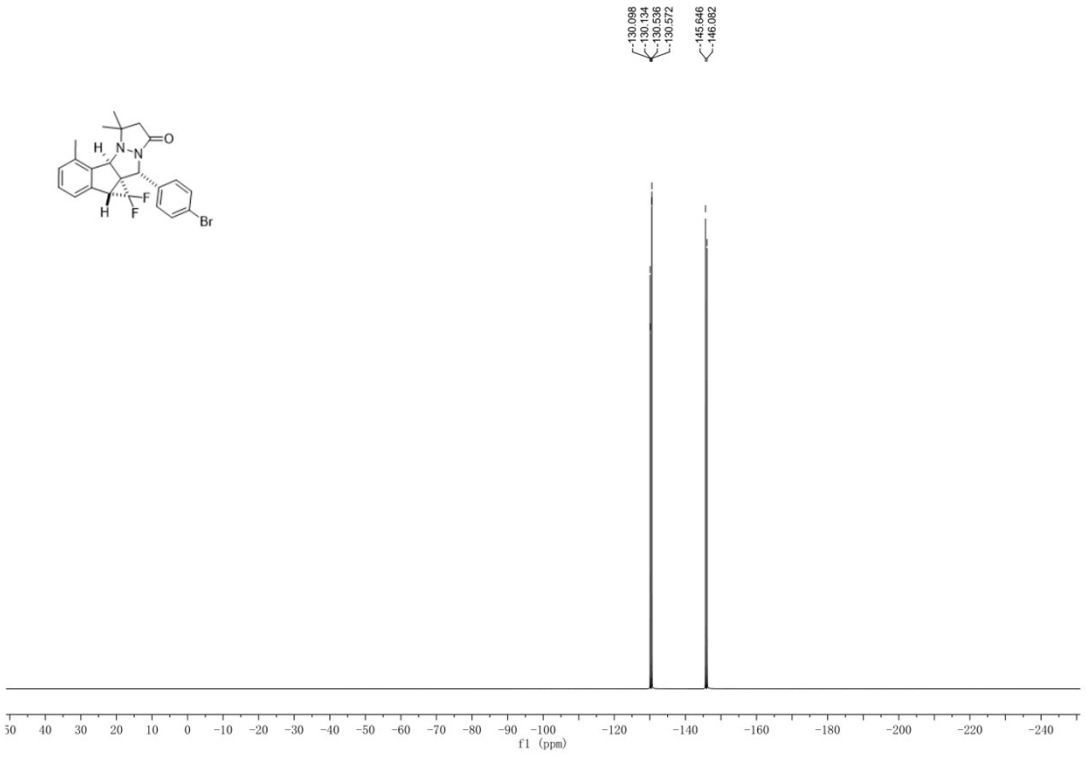
3qa-^{1}H NMR (400 MHz, $CDCl_3$)



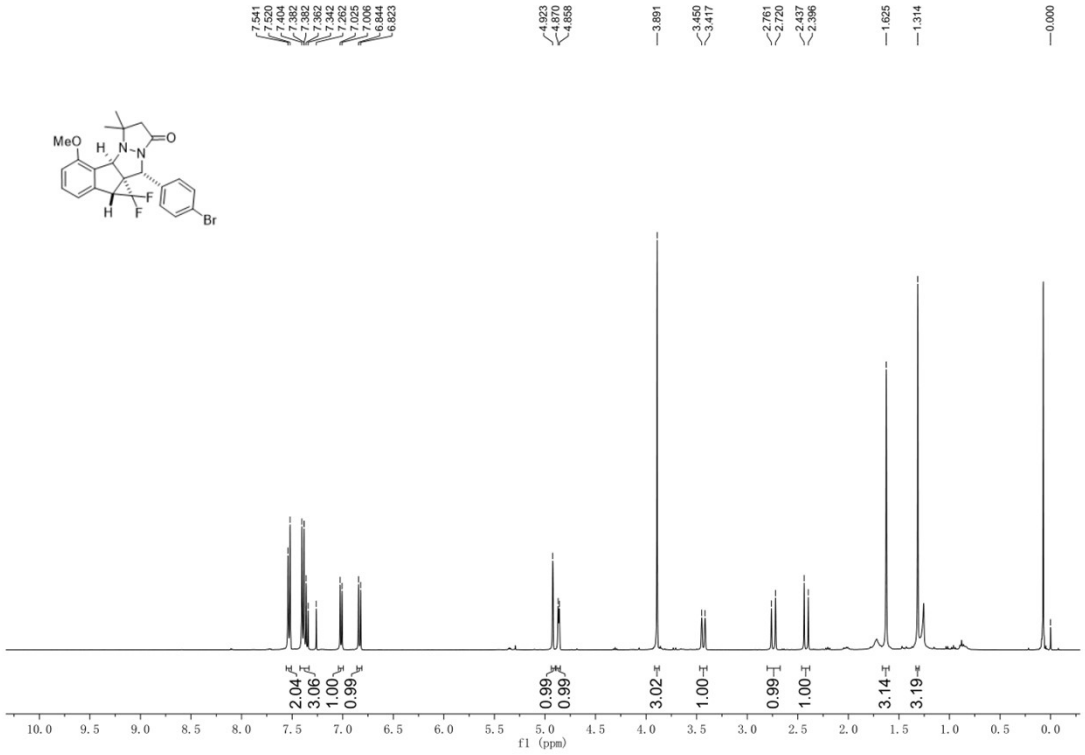
3qa-^{13}C NMR (100 MHz, $CDCl_3$)



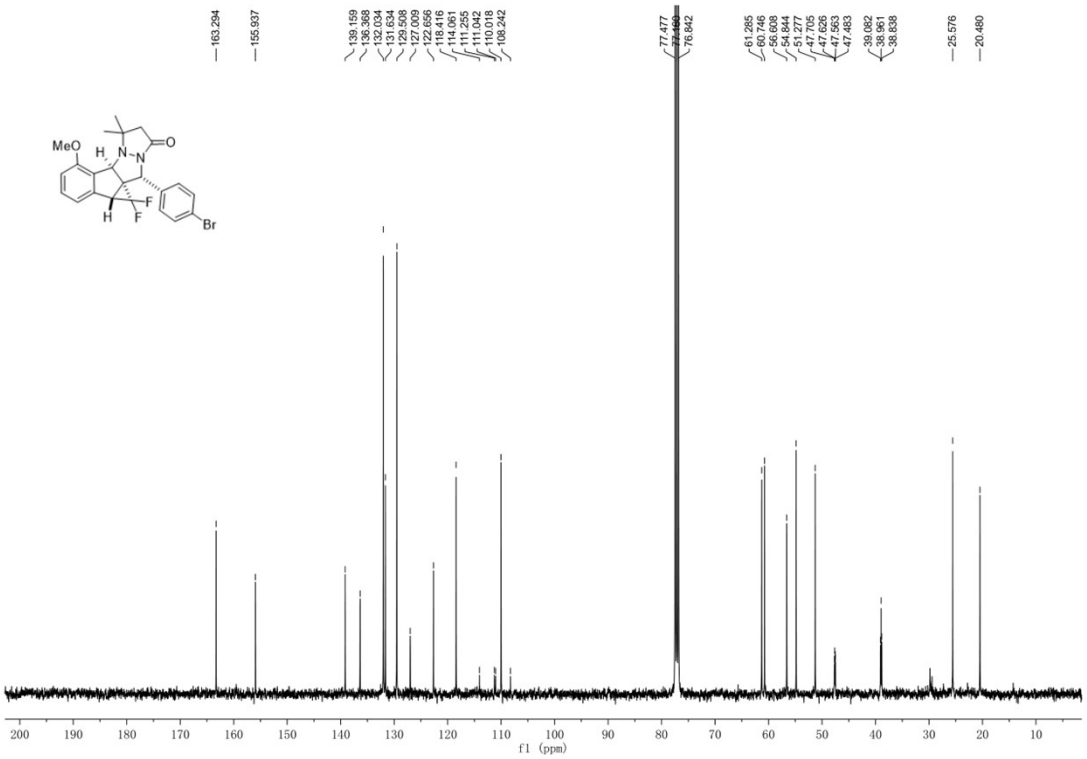
3qa-^{19}F NMR (376 MHz, $CDCl_3$)



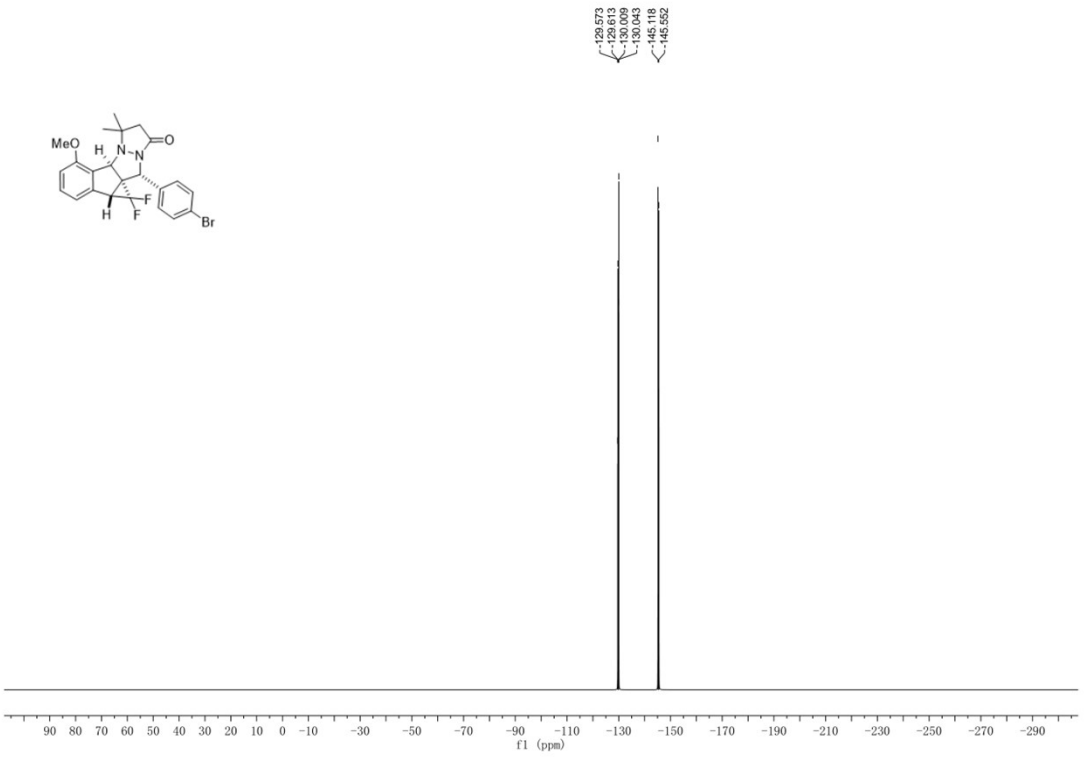
3ra-^{1}H NMR (400 MHz, $CDCl_3$)



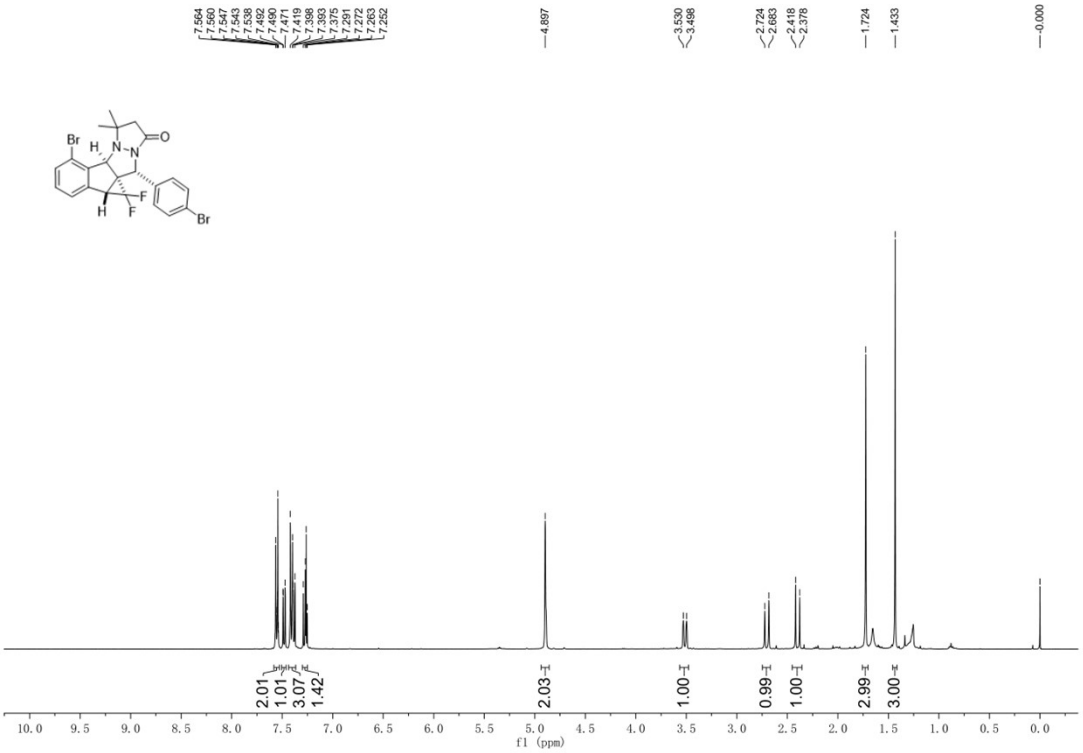
3ra-^{13}C NMR (100 MHz, $CDCl_3$)



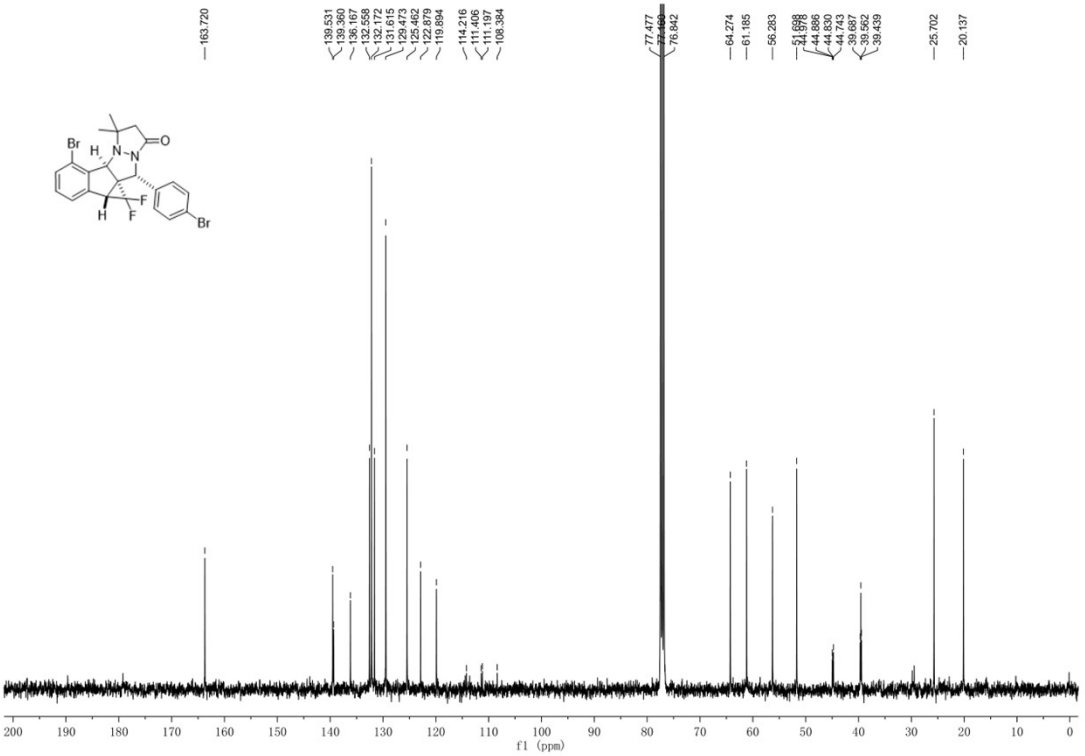
3ra-^{19}F NMR (376 MHz, $CDCl_3$)



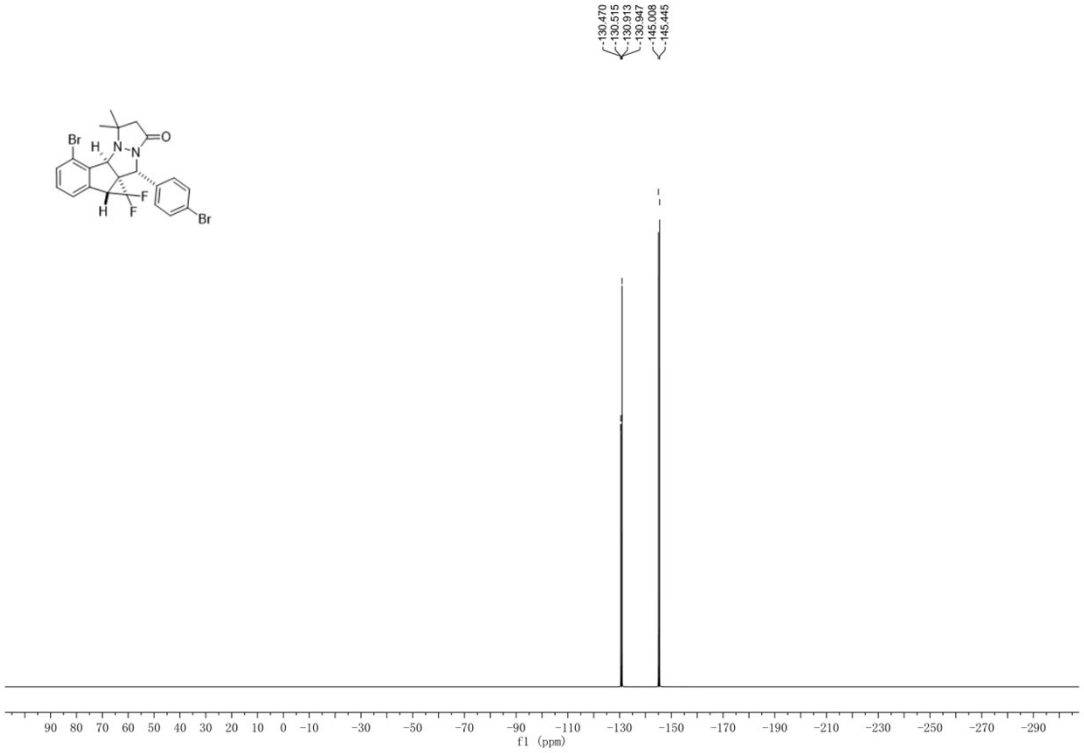
3sa-^{1}H NMR (400 MHz, $CDCl_3$)



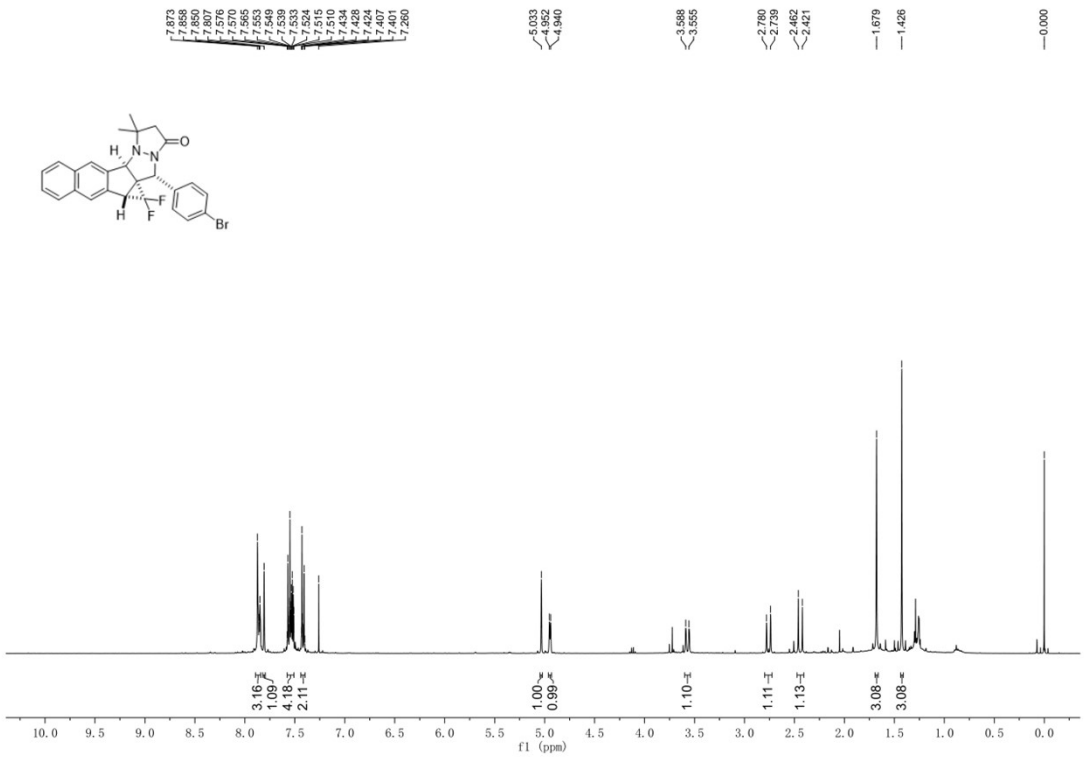
3sa-^{13}C NMR (100 MHz, $CDCl_3$)



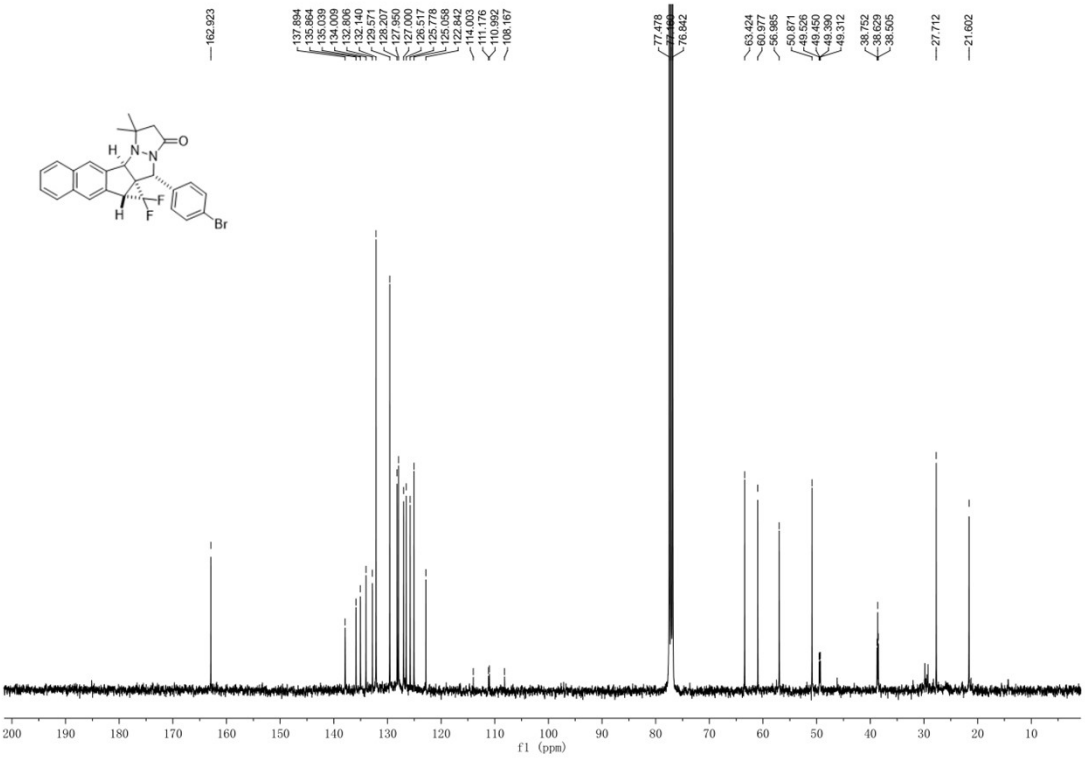
3sa-^{19}F NMR (376 MHz, $CDCl_3$)



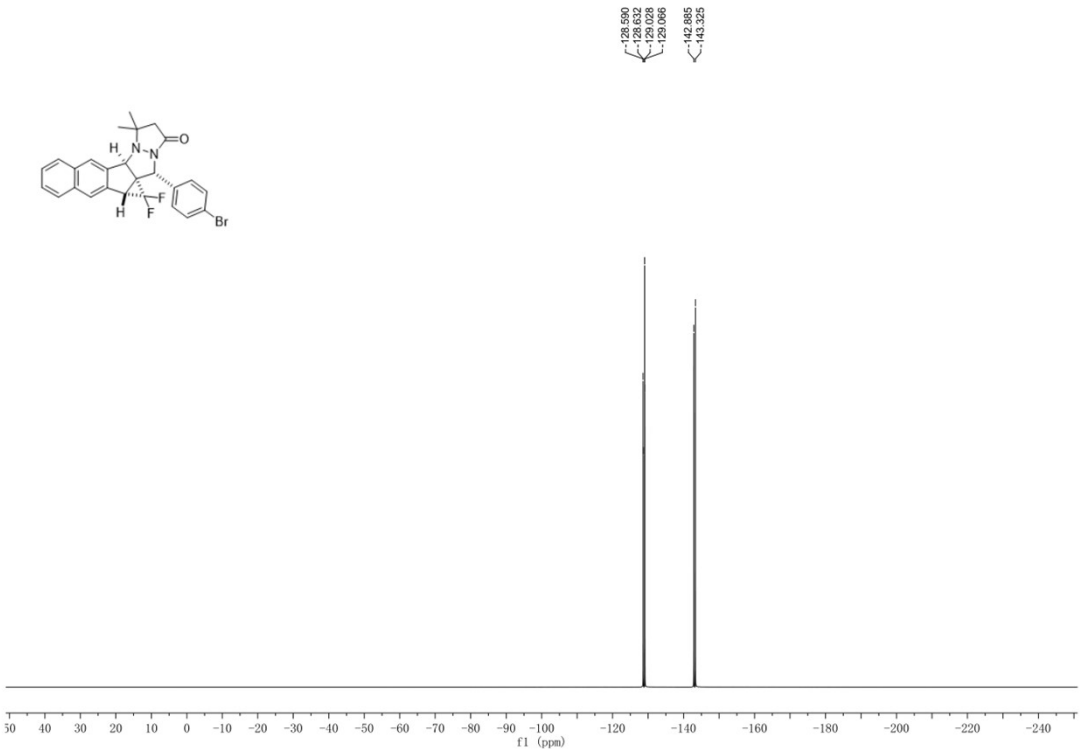
3ta-^{1}H NMR (400 MHz, $CDCl_3$)



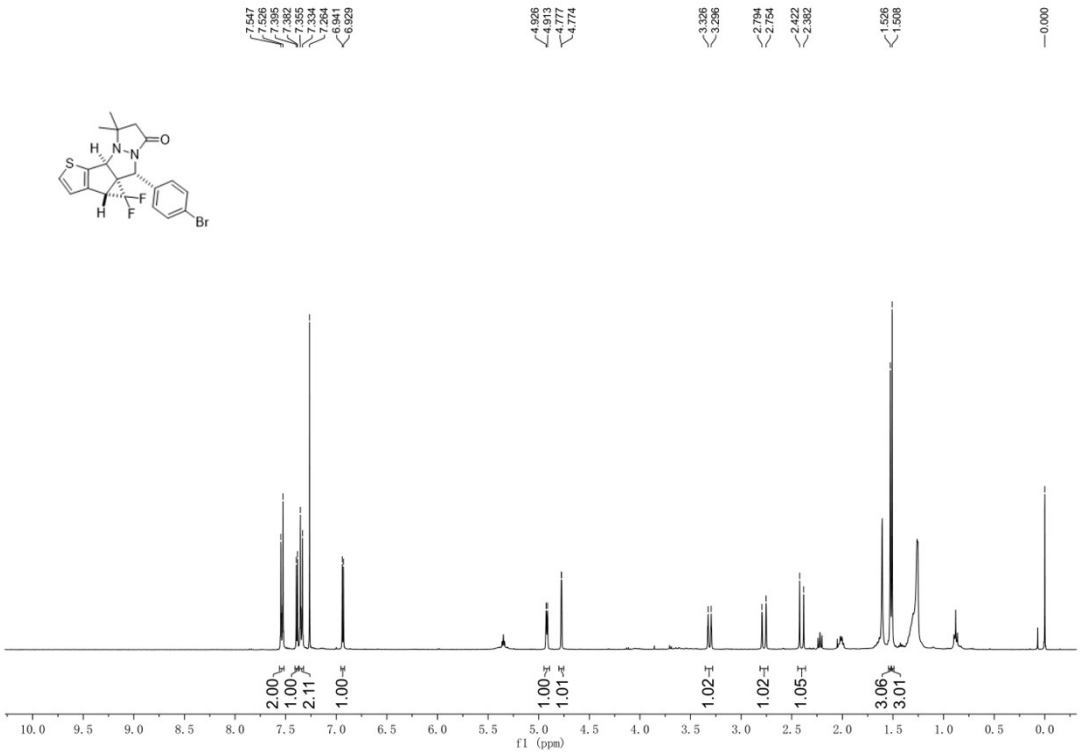
3ta-^{13}C NMR (100 MHz, $CDCl_3$)



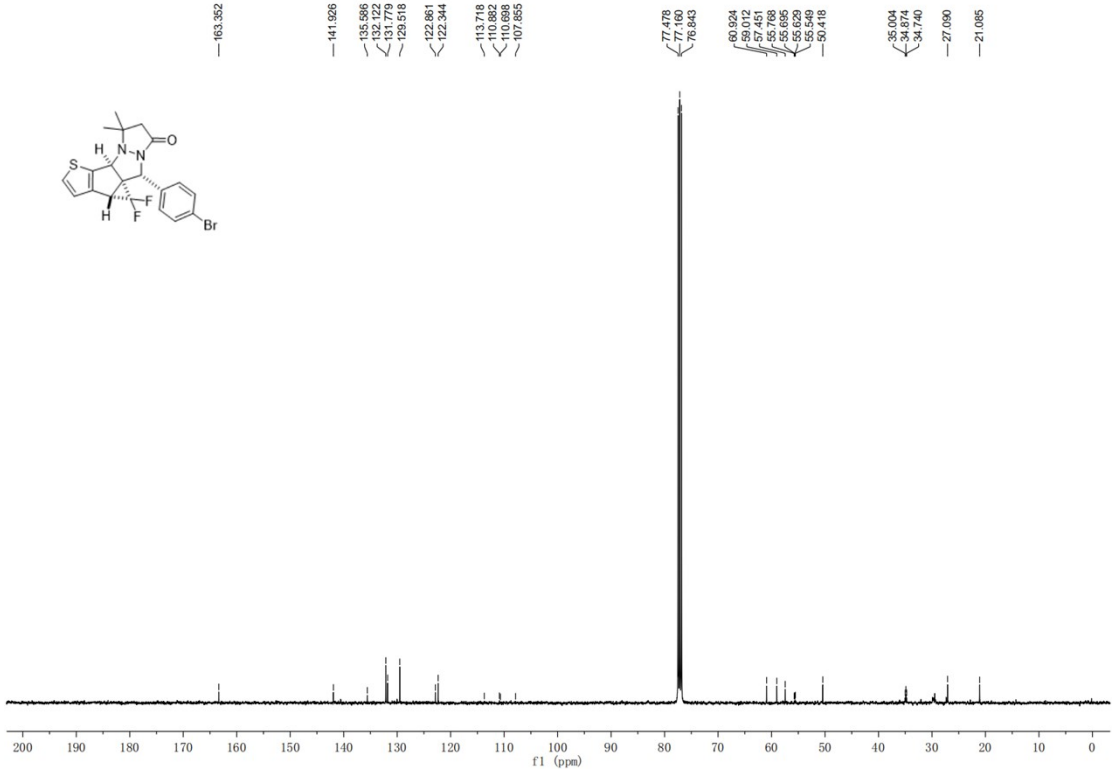
3ta-^{19}F NMR (376 MHz, $CDCl_3$)



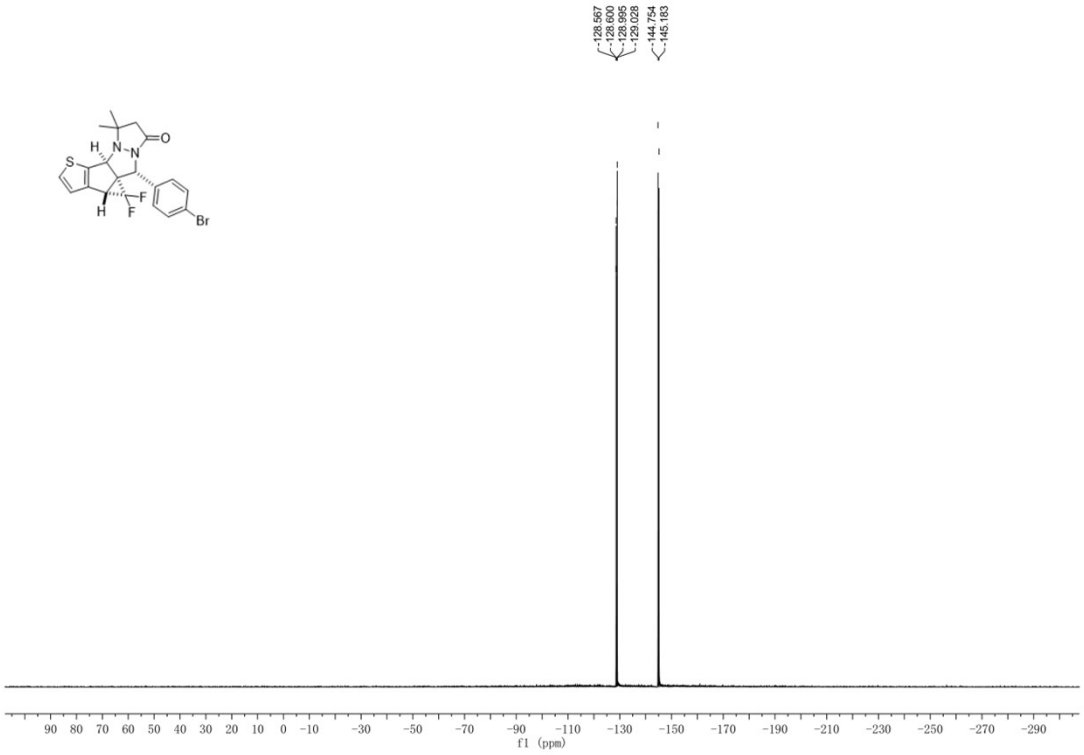
3ua-^{1}H NMR (400 MHz, $CDCl_3$)



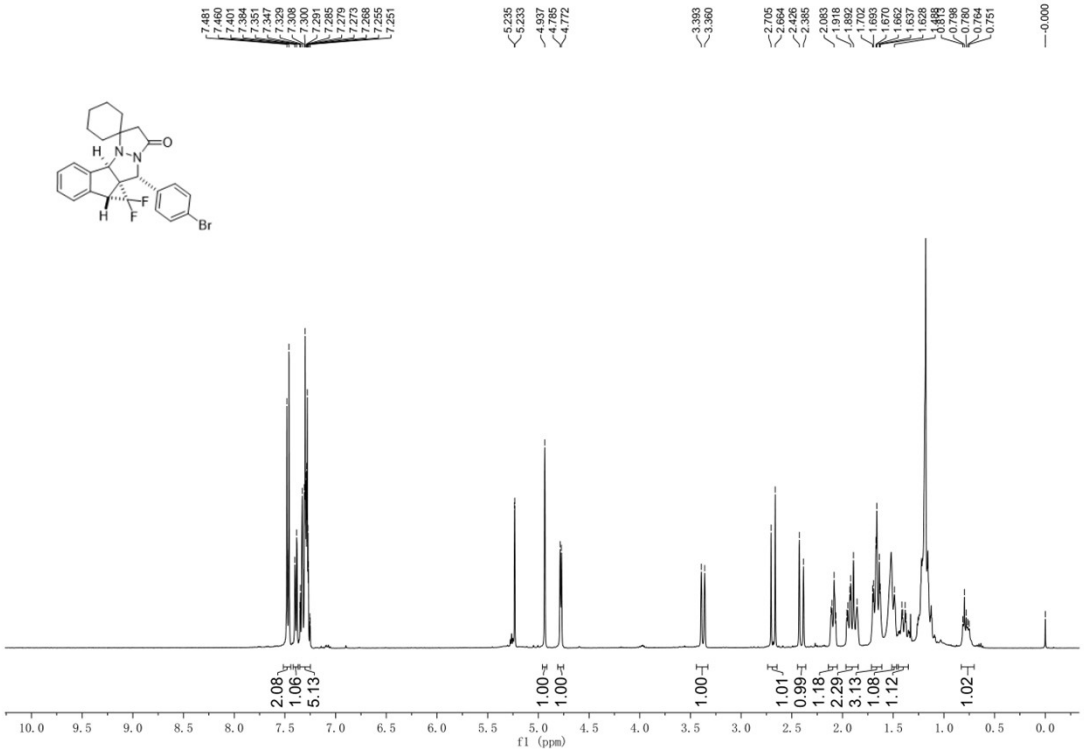
3ua-^{13}C NMR (100 MHz, $CDCl_3$)



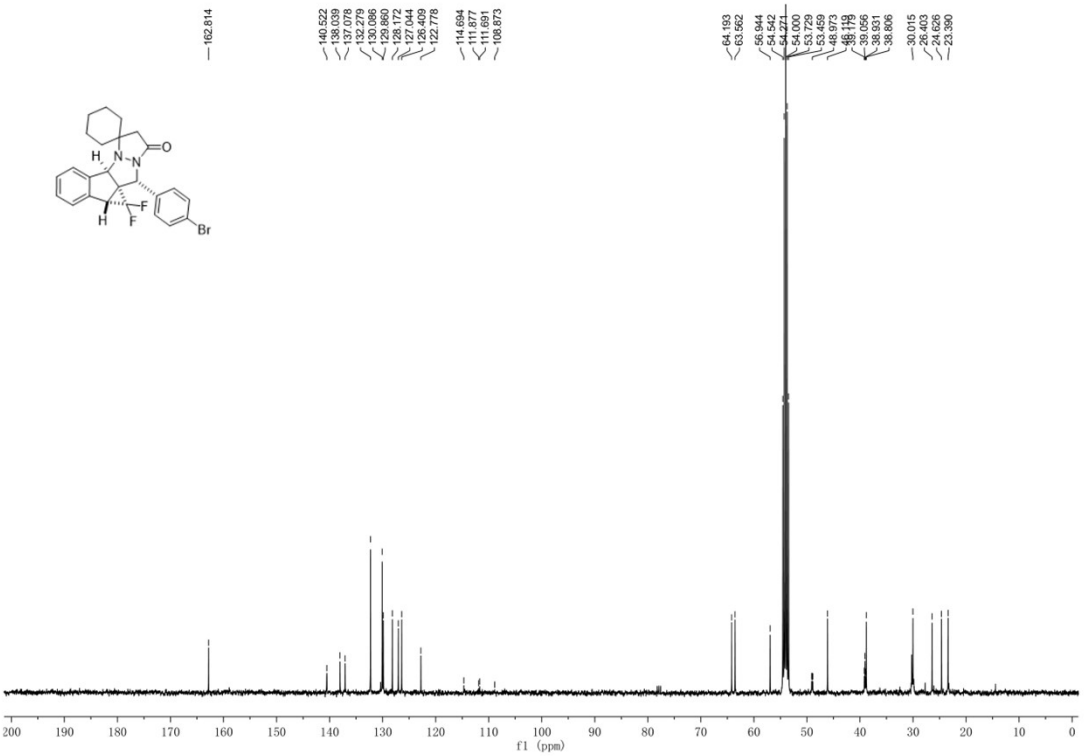
3ua-^{19}F NMR (376 MHz, $CDCl_3$)



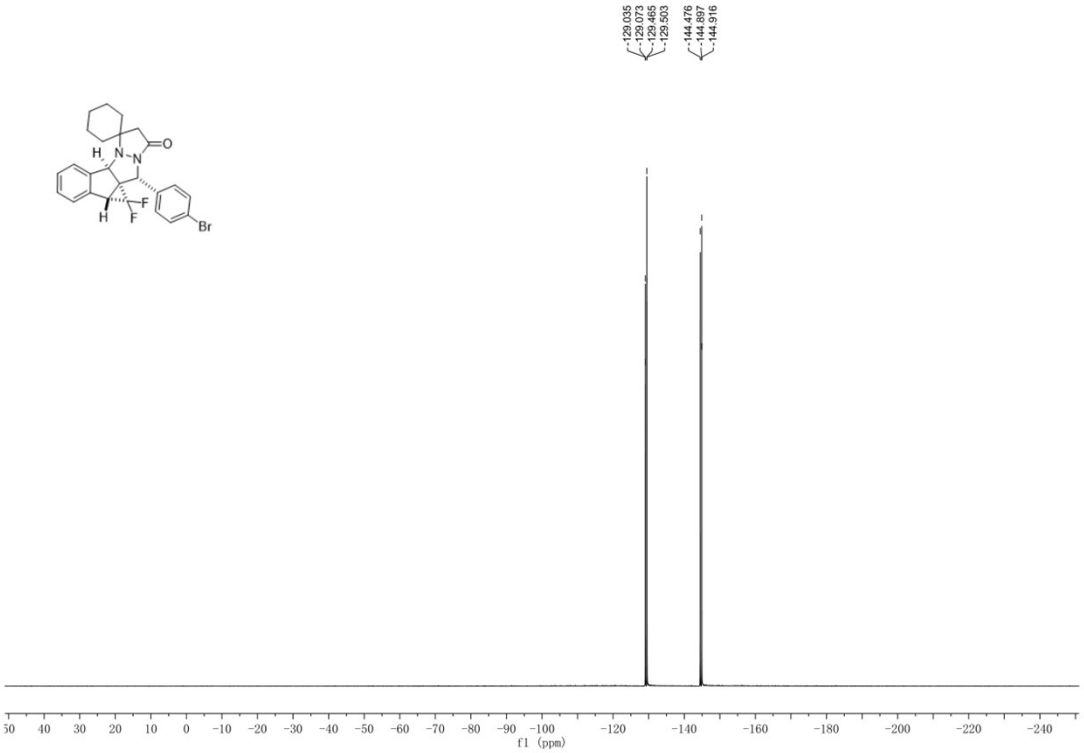
3va-^{1}H NMR (400 MHz, CD_2Cl_2)



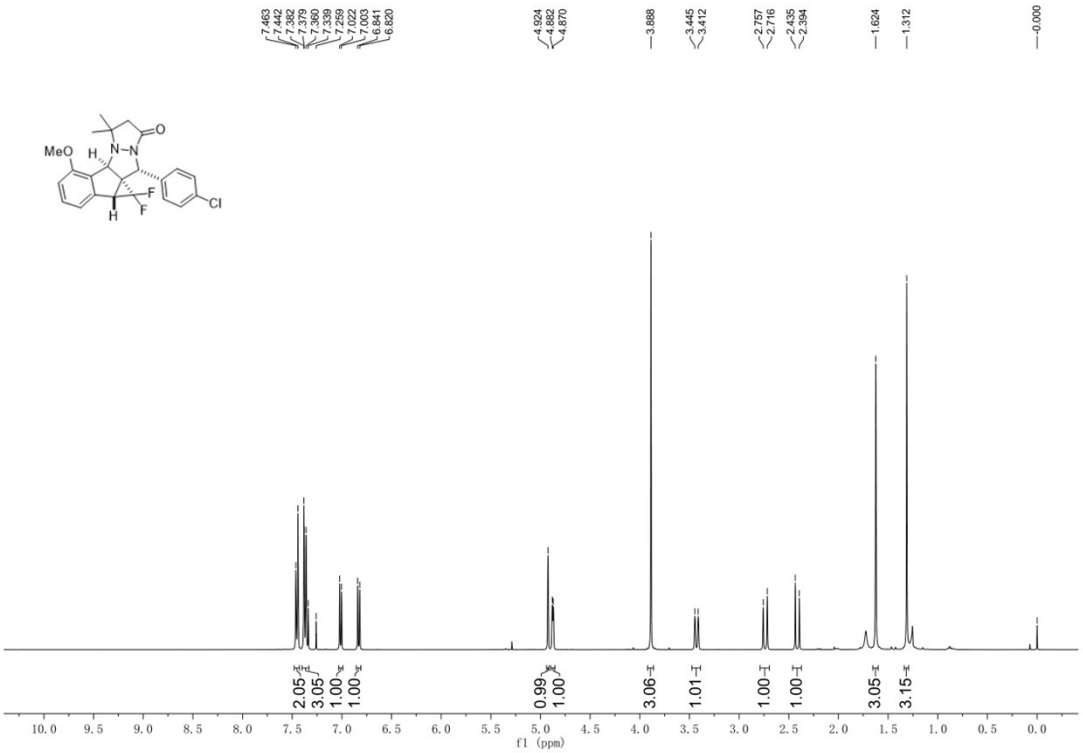
3va-^{13}C NMR (100 MHz, CD_2Cl_2)



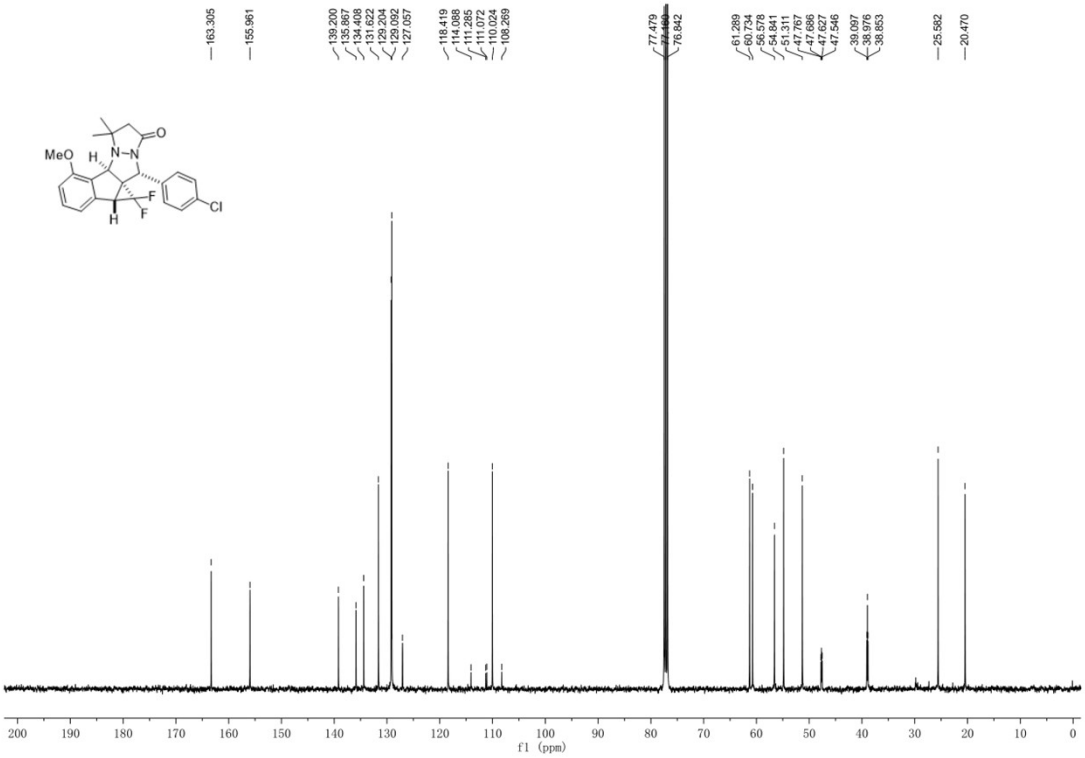
3va-^{19}F NMR (376 MHz, $CDCl_3$)



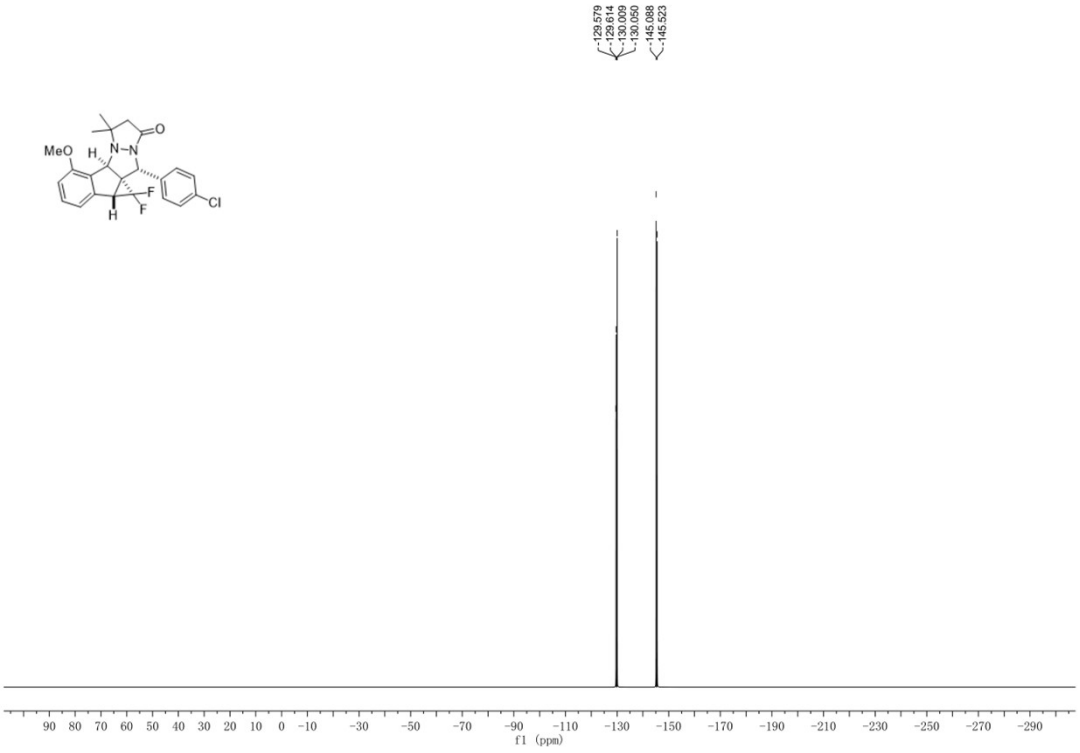
3wa-^{1}H NMR (400 MHz, $CDCl_3$)



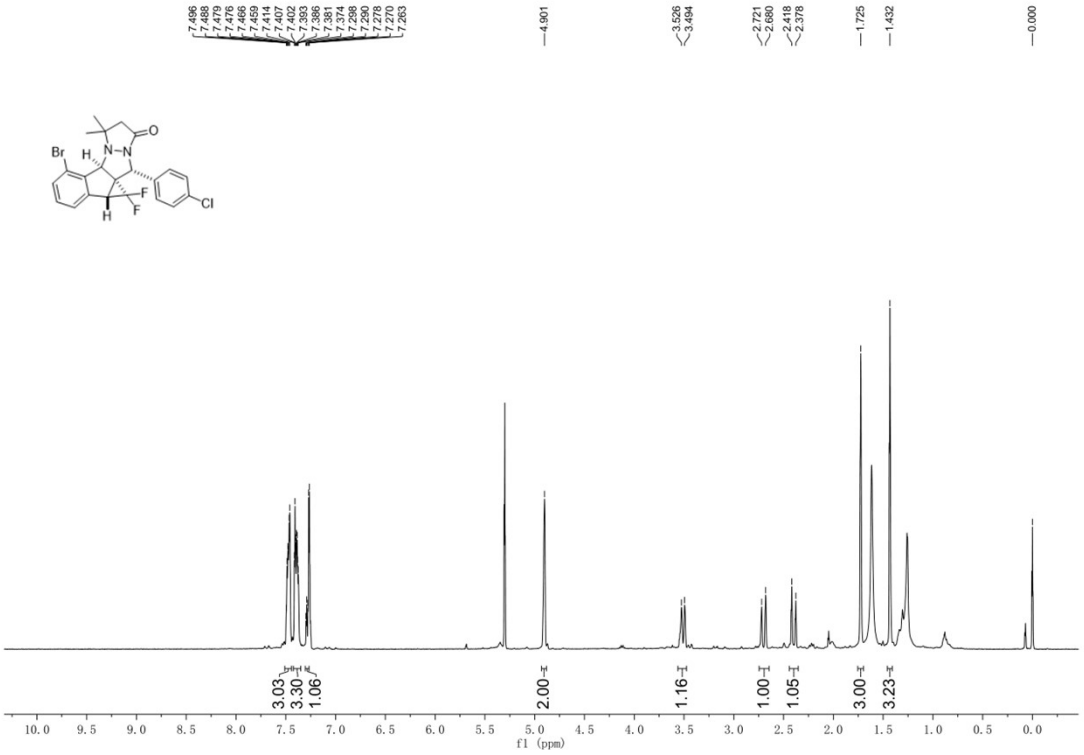
3wa-^{13}C NMR (100 MHz, $CDCl_3$)



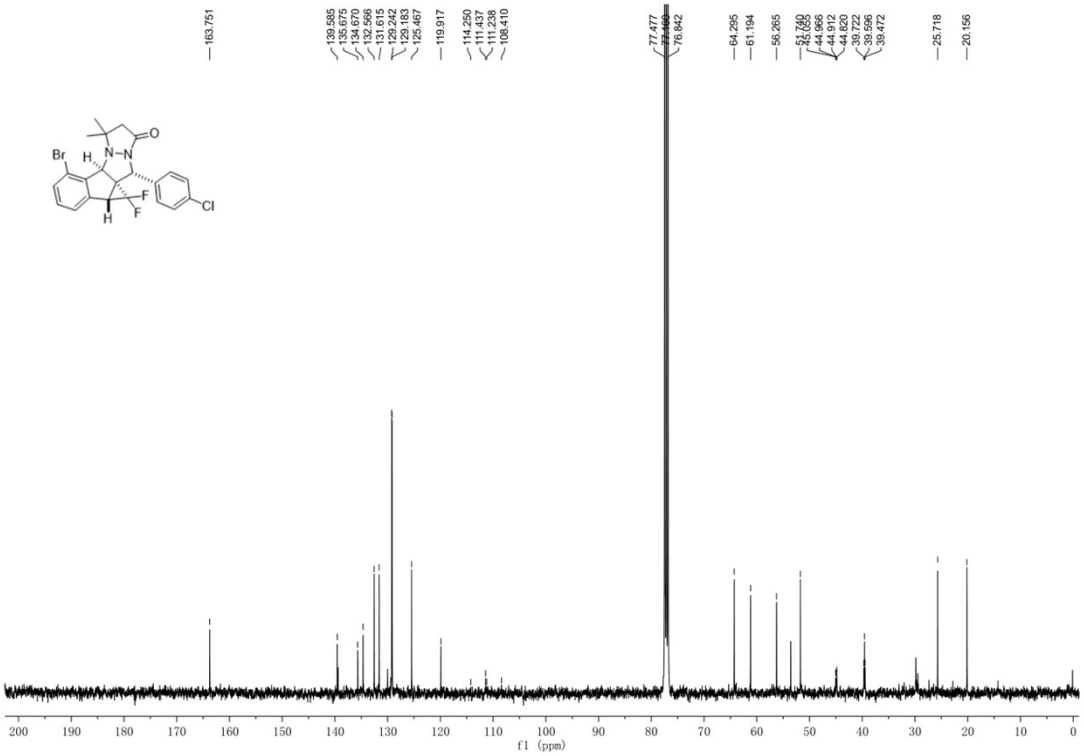
3wa-^{19}F NMR (376 MHz, $CDCl_3$)



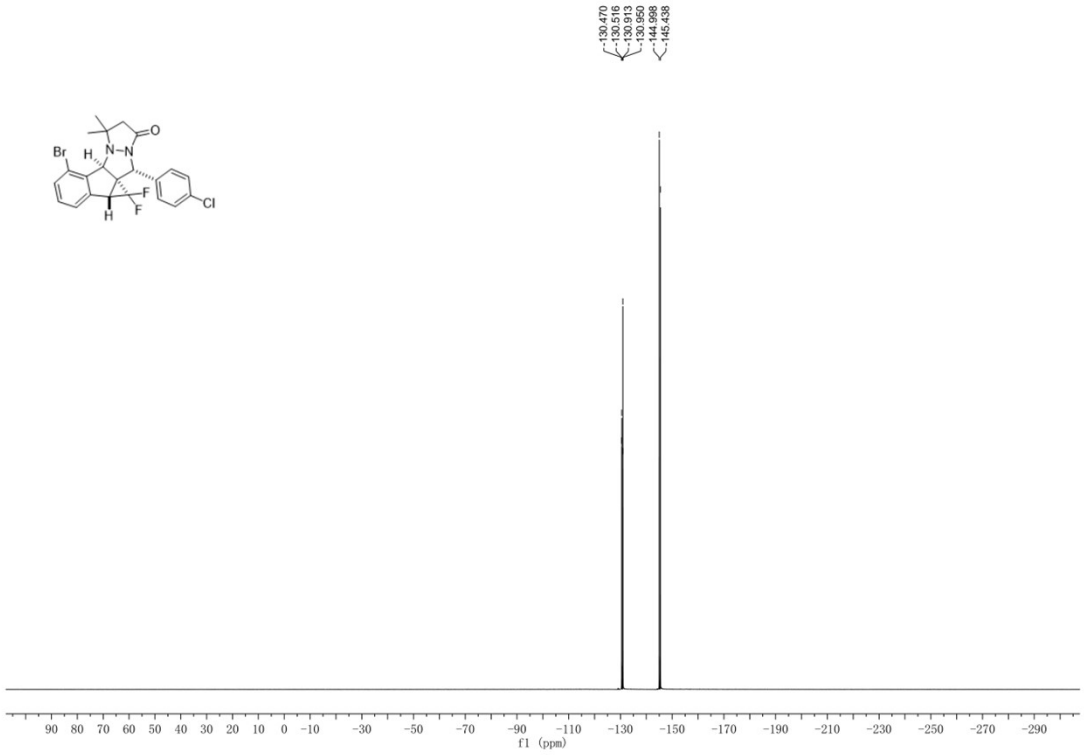
3xa-^{1}H NMR (400 MHz, $CDCl_3$)



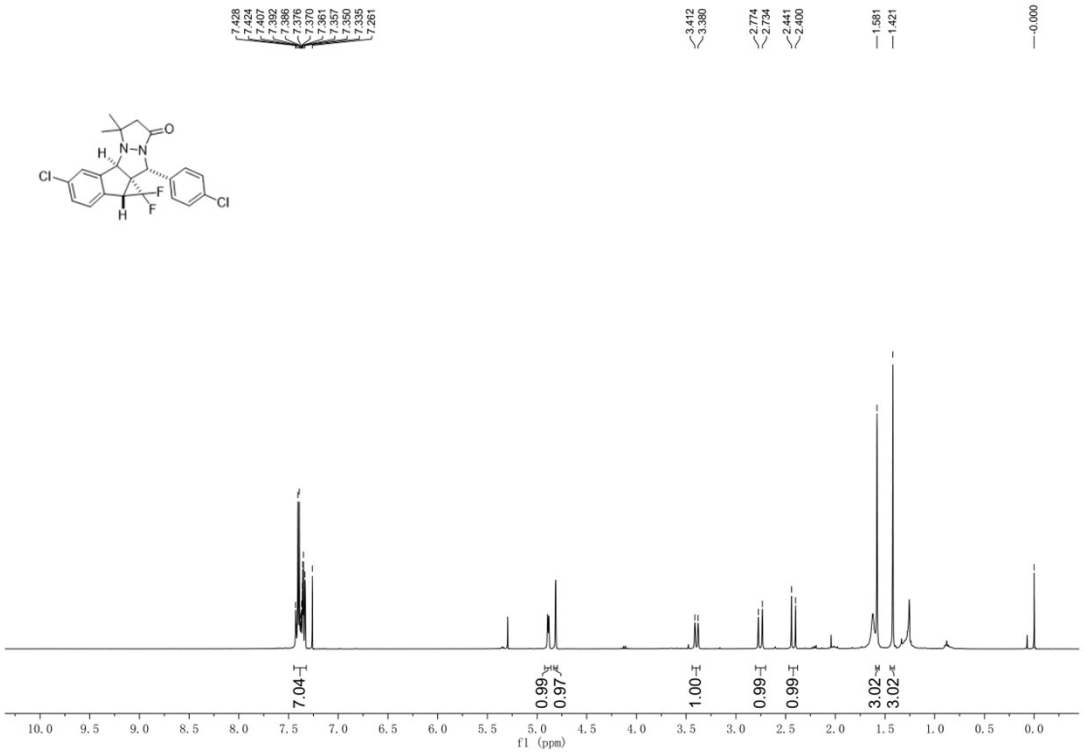
3xa-^{13}C NMR (100 MHz, $CDCl_3$)



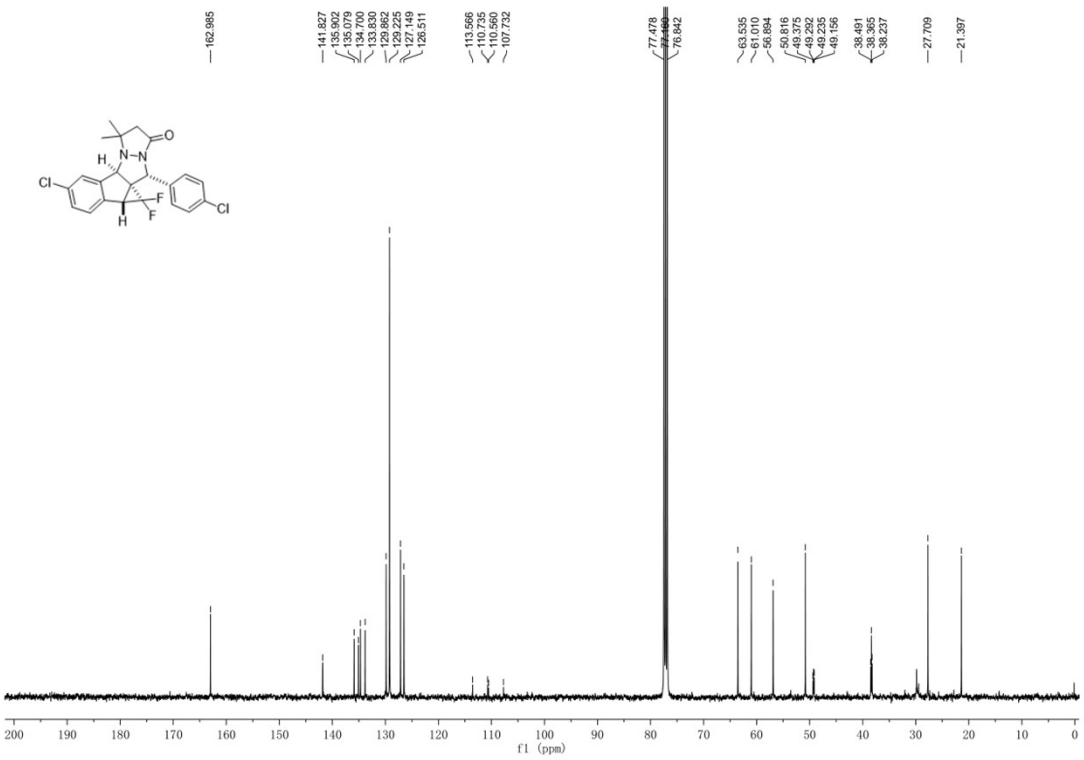
3xa-^{19}F NMR (376 MHz, $CDCl_3$)



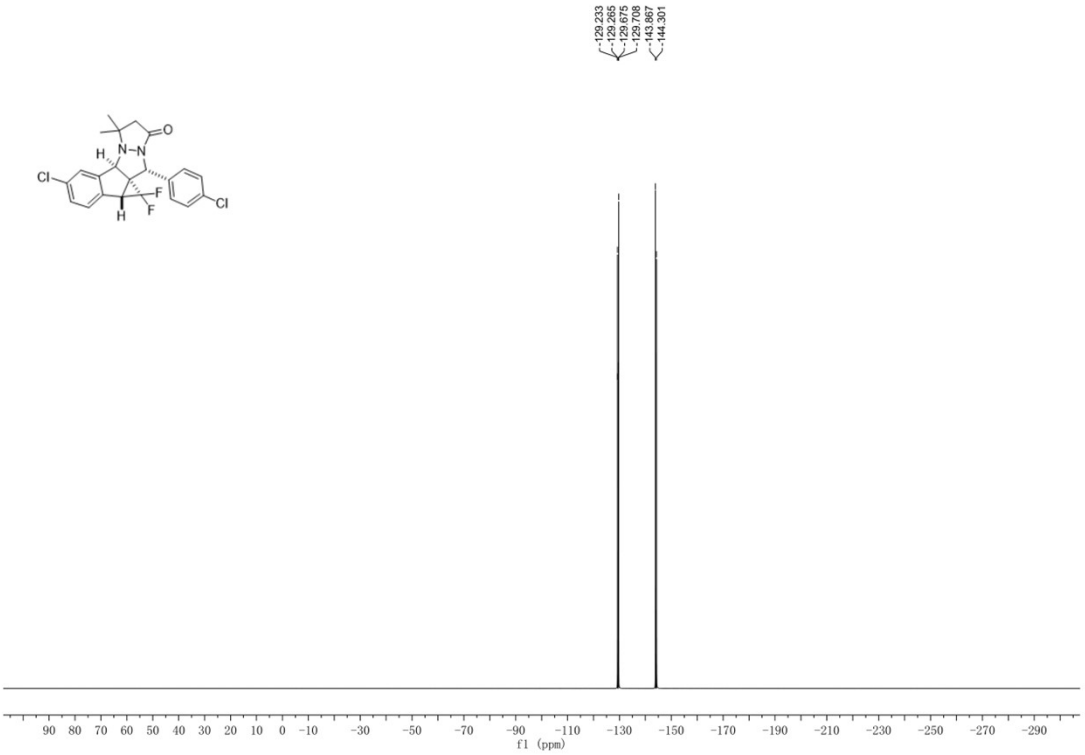
3ya-^{1}H NMR (400 MHz, $CDCl_3$)



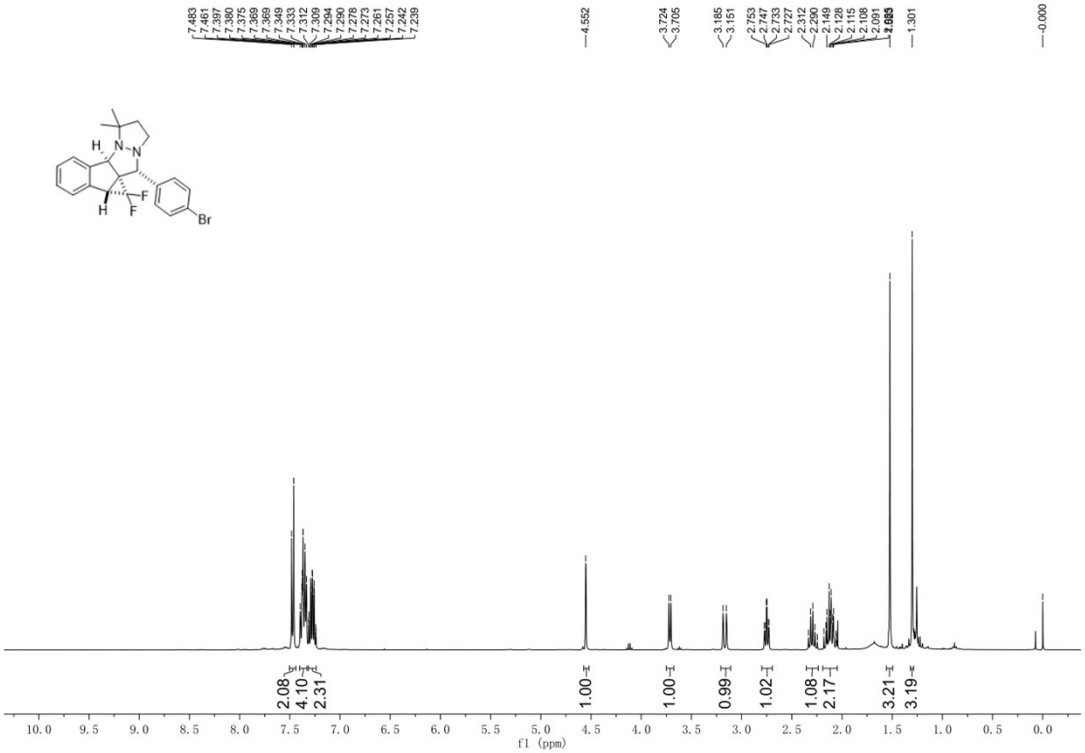
3ya-^{13}C NMR (100 MHz, $CDCl_3$)



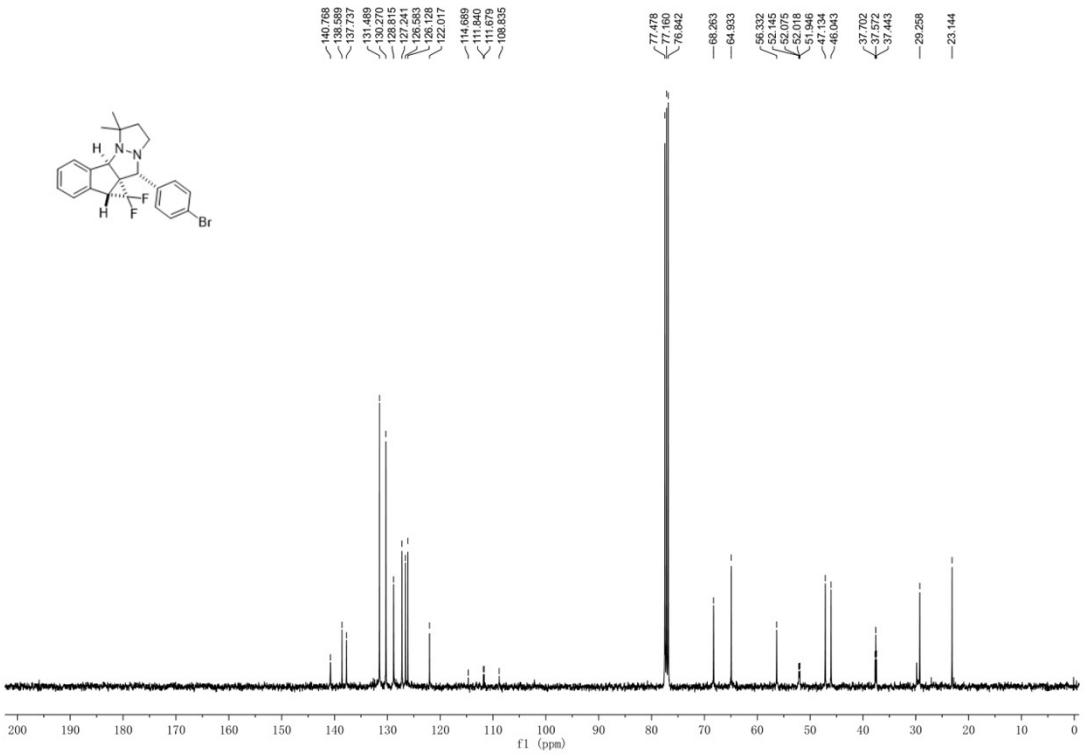
3ya-^{19}F NMR (376 MHz, $CDCl_3$)



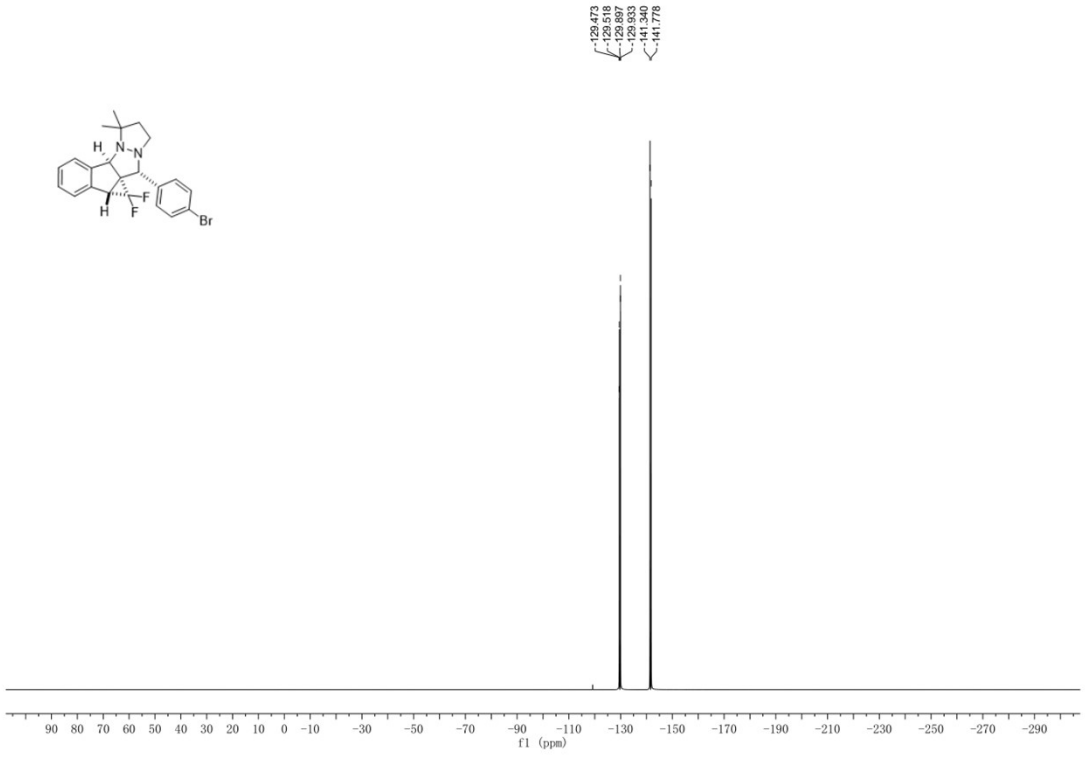
6-^{1}H NMR (400 MHz, $CDCl_3$)



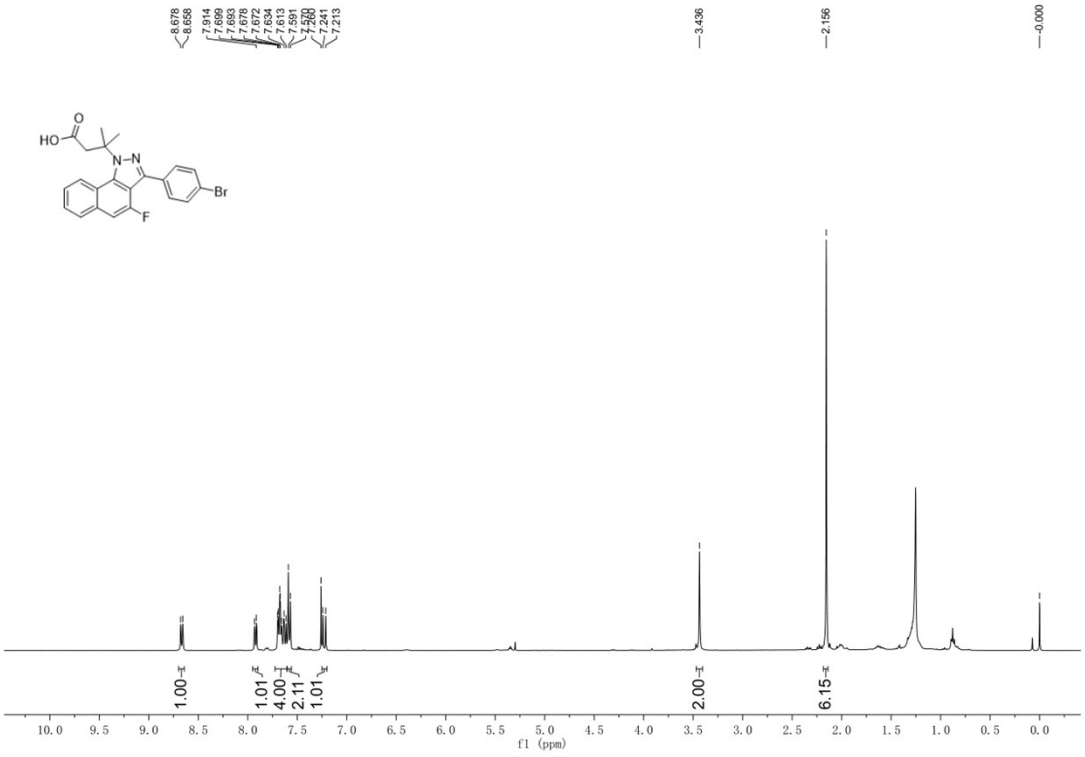
6-^{13}C NMR (100 MHz, $CDCl_3$)



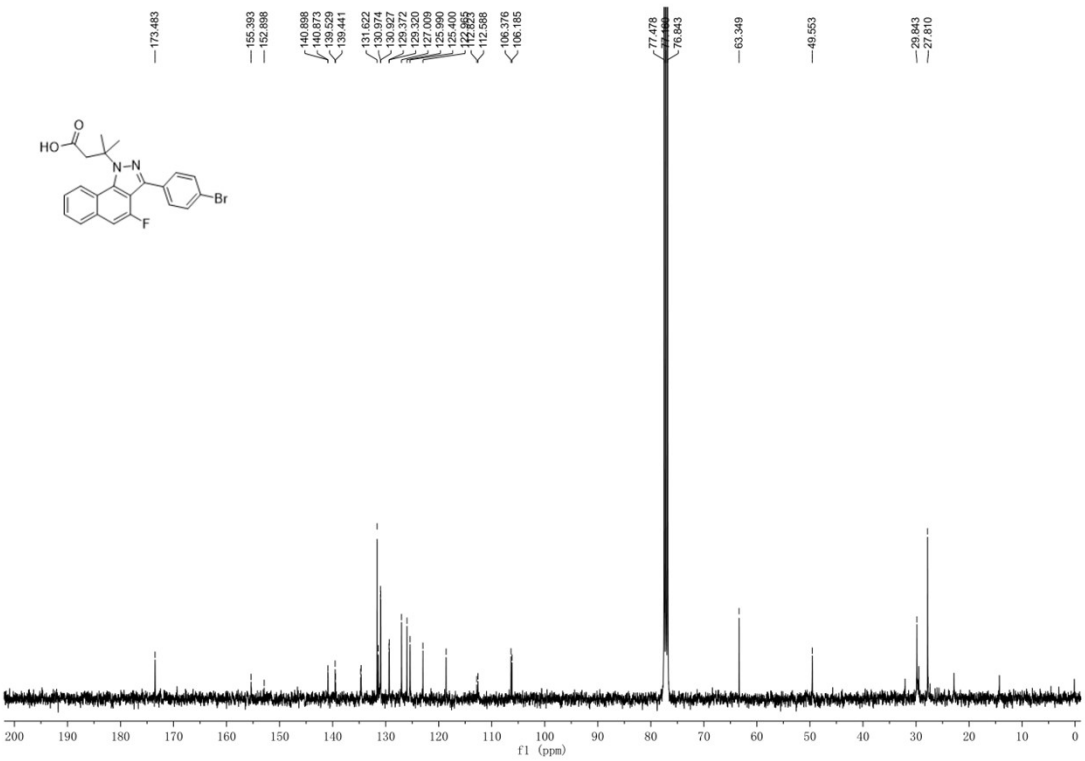
6-^{19}F NMR (376 MHz, $CDCl_3$)



7-^{1}H NMR (400 MHz, $CDCl_3$)



7-^{13}C NMR (100 MHz, $CDCl_3$)



7-^{19}F NMR (376 MHz, $CDCl_3$)