Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Support Information

Metal-Free Phosphine-Catalyzed Visible-Light-Induced Radical Cyclization of Alkenes: Access to Cyclic *gem*-Difluoroacyl Scaffolds

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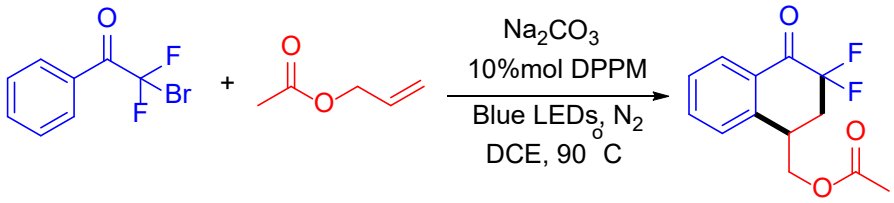
1 General Information

All reagents were commercially available and used without further purification unless indicated otherwise. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatorgraphy (TLC) carried out on GF254 plates (0.25mm layer thickness) using UV light or 5% molybdophosphoric acid solution as visualizing agent. Flash chromatography was performed with 200-300 mesh silica gels. All NMR spectra were recorded on a Quantun-IPlusNMR 400 (model: Qone AS400, resonance frequencies 400MHz for 1H and 100 MHz for ^{13}C and 376 MHz for ^{19}F) or Bruker AVANCE III 500 MHz. The samples were dissolved in 0.6 mL $CDCl_3$ (99.8 % D.TMS). Chemical shifts were given in values of δ H and δ C referenced to residual solvent signals (δ H 7.26 for ^{1}H, δ C 77.0 for ^{13}C in $CDCl_3$). Data are presented in the following space: chemical shift, multiplicity, coupling constantin hertz (Hz), and signal area integration in natural numbers. ^{1}H, ^{13}C and ^{19}F multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of doublets of doublets (ddd), and multiplet (m). High resolution mass spectra (HRMS) were recorded on a Bruker solan X 70 FT-MS (samples was dissolved in CH_3OH and the ion source was ESI). Blue LEDs (40 W) were used as the irradiation light.

2 Experimental procedures

2.1 Typical synthesis methods of 3aa



Take a 25 ml dry reaction tube and add a suitable size magneton, then add dppm (38.4 mg, 10 mol%) and Na_2CO_3 (265.0 mg, 2.5 eq) in turn. After N_2 is replaced for three times, add allyl acetate (100.1 mg, 1 mmol) and $BrCF_2COC_6H_5$ (470.1 mg, 2.0 eq) under the N_2 stream. Finally, the reaction was stirred for 24 hours under blue LEDs (the light source is 5 cm away from the reaction device). After the completion of the reaction, add 60 mL of water and ethyl acetate to extract three times, dry with anhydrous Na_2SO_4 for 30 minutes, filter and concentrate. The residue was purified by silica gel column chromatography using a petroleum ether/AcOEt (30:1) as the eluent to give the corresponding products.

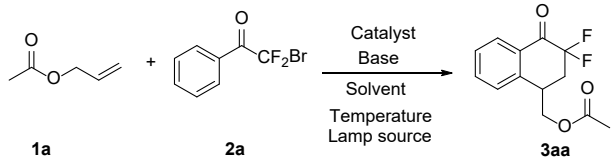
2.2 Typical synthesis methods of 4aa

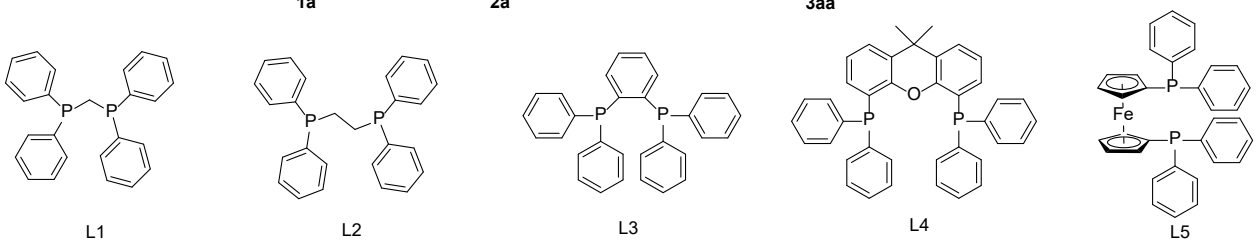
Take a 25 ml dry reaction tube and add a suitable size magneton, then add dppm (38.4 mg, 10 mol%) and Na_2CO_3 (265.0 mg, 2.5 eq) in turn. After N_2 is replaced for three times, add allyl acetate (100.1 mg, 1 mmol) and $ICF_2COC_6H_5$ (564.1 mg, 2.0 eq) under the N_2 stream. Finally, the reaction was stirred for 24 hours under blue LEDs (the light source is 5 cm away from the reaction device). After the completion of the reaction, add 60 mL of water and ethyl acetate to extract three times, dry with anhydrous Na_2SO_4 for 30 minutes, filter and concentrate. The residue was purified by silica gel column chromatography using a petroleum ether/AcOEt (30:1) as the eluent to give the corresponding products.

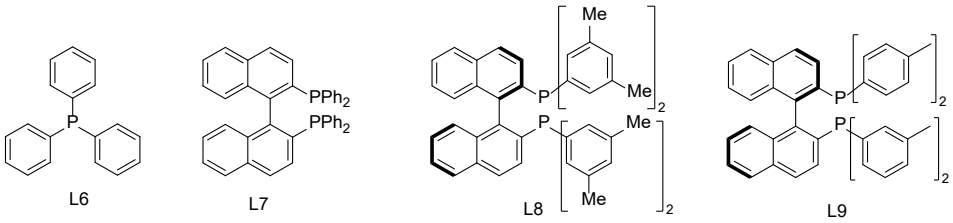
2.3 Experimental setup

Spot Lamp 460-470 nm. (For more details: [taobao] https://item.taobao.com/item.htm?spm=2013.1.w4004l5722417492.24.21f6209ekm032z&id=597700668537). The seal tube was positioned on a stir plate approximately 5 cm away from the LED.

3 Optimization details of the reaction conditions







Entry	Phosphine	Base	Solvent	Temperature	Yield[c] (%)
1	L1	Na_2CO_3	DCE	90 °C	81
2	L2	Na_2CO_3	DCE	90 °C	8
3	L3	Na_2CO_3	DCE	90 °C	32
4	L4	Na_2CO_3	DCE	90 °C	31
5	L5	Na_2CO_3	DCE	90 °C	36
6	L6	Na_2CO_3	DCE	90 °C	33
7	L7	Na_2CO_3	DCE	90 °C	57
8	L8	Na_2CO_3	DCE	90 °C	51
9	L9	Na_2CO_3	DCE	90 °C	55
10	——	Na_2CO_3	DCE	90 °C	7
11	L1	K_2CO_3	DCE	90 °C	57

12	L1	Cs_2CO_3	DCE	90 °C	23
13	L1	KOH	DCE	90 °C	Trace
14	L1	NaOH	DCE	90 °C	Trace
15	L1	^tBuOK	DCE	90 °C	Trace
16	L1	KOAc	DCE	90 °C	32
17	L1	Et_3N	DCE	90 °C	44
18	L1	TMEDA	DCE	90 °C	22
19	L1	——	DCE	90 °C	Trace
20	L1	Na_2CO_3	CH_3CN	90 °C	69
21	L1	Na_2CO_3	DMF	90 °C	23
22	L1	Na_2CO_3	DMSO	90 °C	N.D.
23	L1	Na_2CO_3	THF	90 °C	40
24	L1	Na_2CO_3	DME	90 °C	15
25	L1	Na_2CO_3	DCM	R.T.	48
26	L1	Na_2CO_3	DCE	100 °C	69
27	L1	Na_2CO_3	DCE	60 °C	48
28	L1	Na_2CO_3	DCE	30 °C	45
29[b]	L1	Na_2CO_3	DCE	90 °C	60

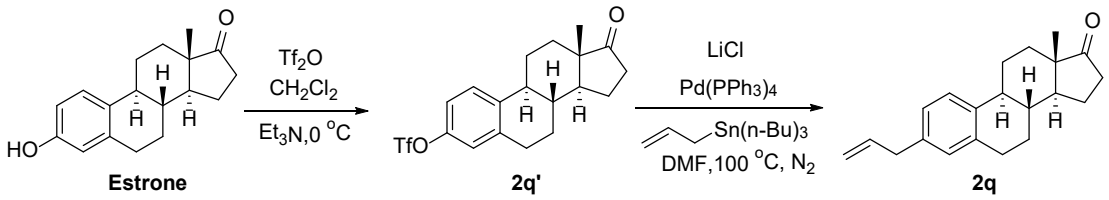
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4mmol), phosphine (10 mol%), Base (0.5mmol), solvent (2.0 mL), blue LED 40 W, 90 °C, N_2, 24 h. [b] Blue LED 18W instead of blue LED 40W. [c]Yields determined by ^{19}F NMR analysis using Benzotrifluoride as the intemal standard.

4 Synthesis of raw materials

4.1 Preparation of 2-bromo-2,2-difluoroketones

The 2-bromo-2,2-difluoroacetophenones **1a-1q** were prepared according to the reported procedure.[1] As shown above, the intermediates enols were obtained from the reaction of ethyl 2,2,2-trifluoroacetate and ketones. The enols reacted with Selectfluor® to form fluorinated gem-diols, which then reacted with N-Bromosuccinimide to afford 2-bromo-2,2 difluoroacetophenones **1a-1q** using the trifluoroacetate release conditions.

4.2 Synthesis of complex olefins

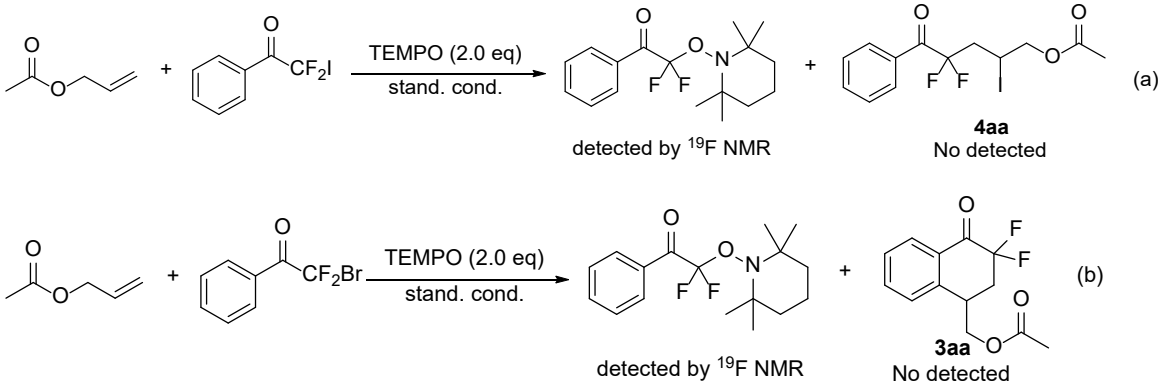


The Estra-1,3,5(10)-trien-17-one, 3-(2-propen-1-yl) **2q** were prepared according to the reported procedure.[2] To an oven-dried round-bottom flask with a stir bar was added Estrone starting material (1.0 equiv), CH_2Cl_2 (0.2 M), Et_3N (2.0 equiv). The reaction was cooled to 0℃. Trifluoromethanesulfonic anhydride Tf_2O (1.2 equiv) was added dropwise and the reaction was stirred at 0℃ for 30 min. After warming up to room temperature, the reaction was quenched with addition of cold water. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (20 mL x 3). The organic layers were combined and concen trated under reduced pressure. The crude mixture was purified by flash column chromatography to the **2q'**.

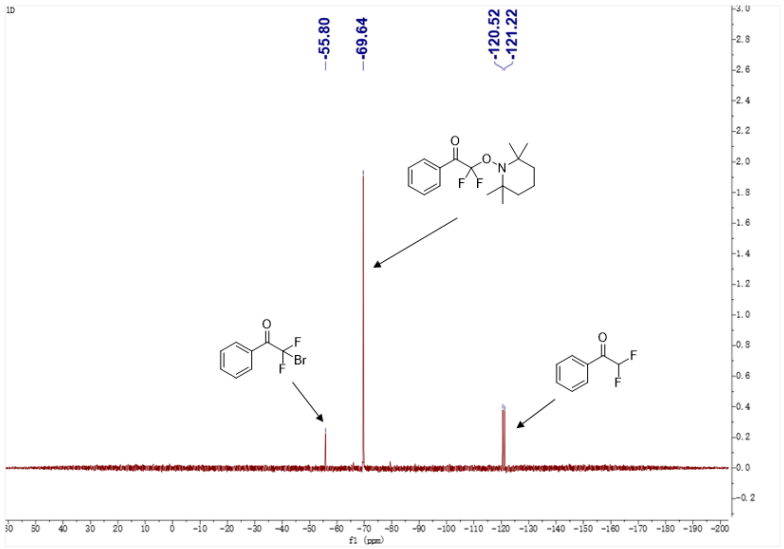
To an oven-dried round bottom flask equipped with condenser was added a stir bar, LiCl (4.0 equiv), DMF (0.25 M), allyltributylstannane (1.1 equiv), **2q'** (1.0 equiv) and $Pd(PPh_3)_4$ (0.03 equiv). The reaction was heated to 100° C. and stirred for 12 hours. Upon completion, the reaction was cooled to room temperature, transferred into a separatory funnel with iced 10% NH_4OH solution (1:1 to DMF) and shake vigorously. Layers were separated, aqueous layer was extracted with ethyl acetate (30 mL x 3). The organic layers were combined and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography to give allylated olefin product **2q**.

5 Mechanistic Studies

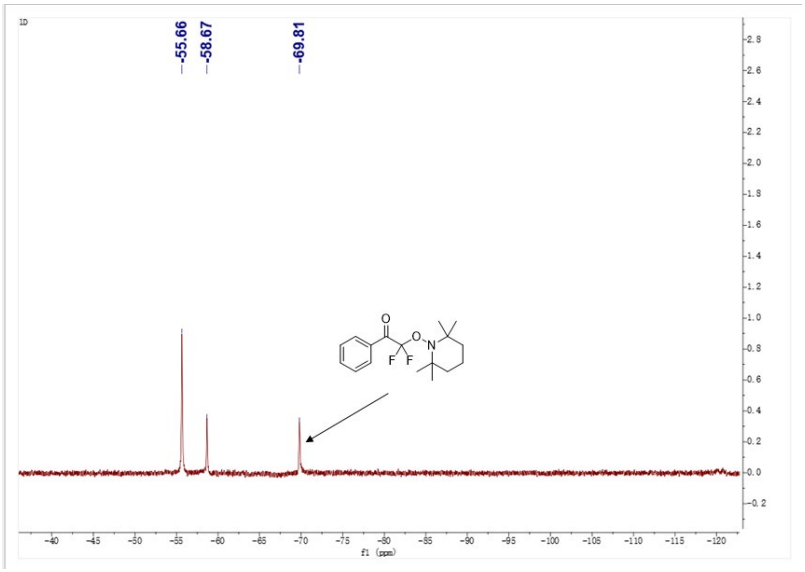
5.1 Trapping experiment with TEMPO



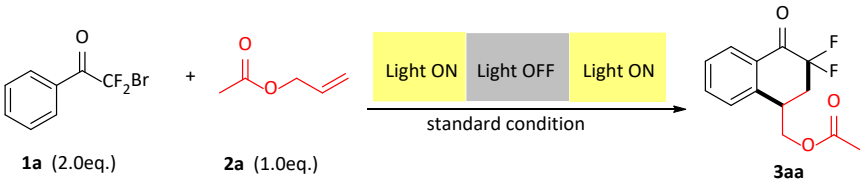
(a)



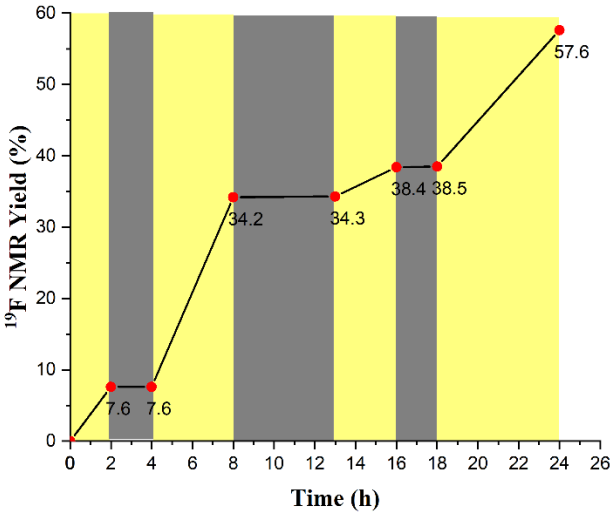
(b)



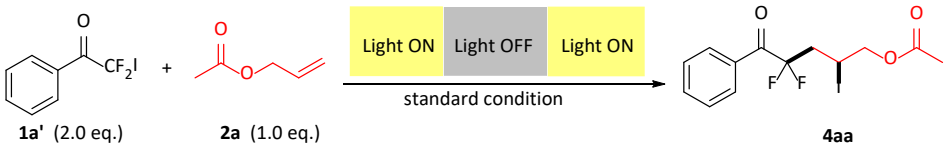
5.2 Switch on and off the light experiment

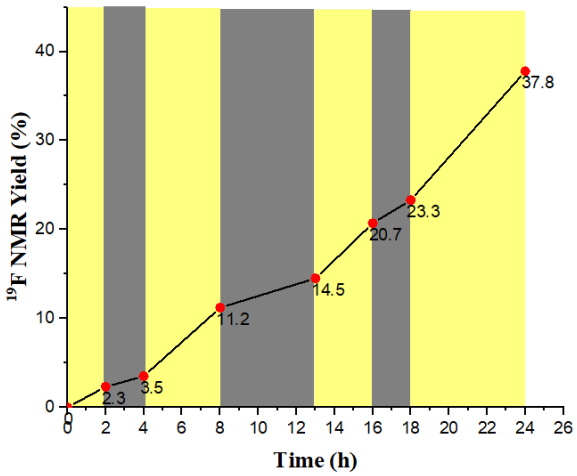


1a (2.0eq.) **2a** (1.0eq.) **3aa**



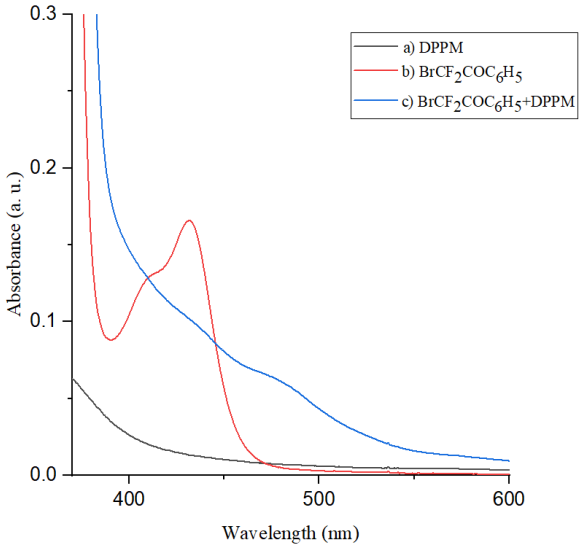
The results of the on-off lamp experiment of the phosphine-catalyzed radical cyclization of 2-bromo-2,2-difluoroacetophenone (**1a**) and allyl acetate (**2a**) show that there is no product formation in the dark, which suggested that an extended radical chain process is unlikely.





In addition, we also performed an on-off lamp experiment of the addition reaction of iododifluoroacyl to allyl acetate, the reaction was found to proceed continuously when the light was turned off, but with a slower rate, which indicated that a radical-chain process might be involved in this reaction.

5.3 UV-Vis absorption experiment



UV-Vis absorption were recorded using Shimadzu UV-1800 spectrophotometer for all experiments. Four solutions were prepared:

a) DPPM (0.5 mmol) in DCE (5.0 mL).

b) 2-bromo-2,2-difluoroacetophenone **1a** (0.5 mmol) in DCE (5.0 mL).

c) 2-bromo-2,2-difluoroacetophenone **1a** (0.5 mmol) and DPPM (0.5 mmol) in DCE (5.0 mL).

As shown in Figure above, DPPM has no absorption in the visible-light region (curve **a**). A medium visible-light absorption of 2-bromo-2,2-difluoroacetophenone (**1a**) was detected at 280-430 nm (curve **b**). The mixture of DPPM with **1a** shows a red shift and a new absorption band (curve **c**) in the visible region (416-520 nm). This redshift may support the formation of an electron donor-acceptor complex (EDA complex) between 2-bromo-2,2-difluoroacetophenone and DPPM in the reaction mixture.

5.4 DFT calculations

5.4.1 Computational Details

Structures of the reactants, intermediates, transition states, and products were optimized in dichloroethane at the M06-2X/def2-tzvp level using Gaussian16. The solvation effect was introduced via SMD model. At the same computational level, vibrational frequencies were calculated to confirm the local minima with all positive frequencies and transition states with only one imaginary frequency. Intrinsic reaction coordinate (IRC) calculations were performed at the M06-2X/def2-tzvp level to verify that the optimized geometry is truly a transition state, which connects the designated intermediates. The electronic energies (Gibbs free energies and Enthalpies) of all the complexes are listed in Table S1.

Table S1. The electronic energies, Gibbs free energies and Enthalpies of all the complexes

(Hartree)	Electronic	Free Energy	Enthalpy

	Energy		
IV + II	-5151.3038	-5150.7786	-5150.6227
TS1 + II	-5151.2870	-5150.7559	-5150.6065
V + II	-5151.3239	-5150.7905	-5150.6413
VII + dppm + (Br-)	-5151.2905	-5150.7667	-5150.6074
3aa + HBr + dppm	-5151.3794	-5150.8628	-5150.7001
VI + dppm	-5151.3722	-5150.8375	-5150.6882
2FBrPh	-3156.9762	-3156.9014	-3156.8514
dppm	-1648.5676	-1648.2256	-1648.1462
2FBrPh-dppm	-4805.5466	-4805.1131	-4804.9985

5.4.2 Cartesian Coordinate

IV			
C	4.40139500	2.33610000	0.16159800
C	4.95138400	1.17212200	-0.36534500
C	4.17258500	0.03560100	-0.48685800
C	2.83700300	0.04605100	-0.07600400
C	2.29166200	1.21620600	0.45570400
C	3.07448500	2.35634100	0.56805600
H	5.00909400	3.22730400	0.25569000
H	5.98640900	1.15403300	-0.68097200
H	4.58746100	-0.87512800	-0.89817300
H	1.26395400	1.25524300	0.78659200
H	2.64529800	3.26113400	0.97824100
C	2.06968700	-1.21631800	-0.26027700
O	2.51861100	-2.16611400	-0.84953900
C	0.62175300	-1.33703600	0.26923000
F	0.35059400	-2.65675000	0.43288200
F	0.53755800	-0.79230900	1.51757200
C	-0.40567300	-0.72490900	-0.66276800
C	-1.78537300	-0.85257800	-0.12565200
H	-0.29008400	-1.24236700	-1.62535800
H	-0.14656600	0.32199400	-0.83703300
C	-2.82709200	0.09729400	-0.57314300
H	-2.10142400	-1.78279300	0.32812400
H	-2.44987300	1.12433600	-0.54418900
H	-3.13709200	-0.11539700	-1.60536600
O	-3.95414600	-0.04279700	0.29900900
C	-5.07176100	0.67600400	0.10371700
O	-5.99069600	0.51107200	0.86253300
C	-5.10128100	1.63961100	-1.04493800
H	-4.29448600	2.36803300	-0.95487200
H	-4.96991300	1.11029100	-1.98964800
H	-6.05894100	2.15063400	-1.04307700

II			
C	4.13800200	-0.48716300	0.61657700
C	5.23258600	-1.23253300	1.04141900
C	5.23354700	-2.61373300	0.91215800
C	4.13640500	-3.24961300	0.34179700
C	3.04829500	-2.50666100	-0.09006100
C	3.02729600	-1.11626400	0.05622200
H	4.15793500	0.58982600	0.72549900
H	6.08565100	-0.72714400	1.47711200
H	6.08533800	-3.19241600	1.24644100
H	4.13112500	-4.32622700	0.22512400
H	2.21091000	-3.01613400	-0.55524600
P	1.59808800	-0.19751400	-0.64707800
C	1.76871800	1.45517200	0.12921600
C	1.90691100	2.54881700	-0.72195200
C	1.76805200	1.66964200	1.50934500
C	2.03570600	3.83565700	-0.20860400
H	1.90542000	2.39445200	-1.79515700
C	1.89233900	2.95123700	2.02309600
H	1.68086200	0.83178300	2.19169800
C	2.02493000	4.03782300	1.16321200
H	2.13677700	4.67675800	-0.88320000
H	1.88966400	3.10514300	3.09505600
H	2.12029600	5.03857100	1.56582300
C	0.25171500	-0.95052000	0.39542700
H	0.32931700	-0.64039300	1.43937600
H	0.37101000	-2.03465100	0.34545700
P	-1.41611900	-0.58725300	-0.23946600
C	-2.56045700	-0.83599900	1.12462800
C	-2.26246300	-1.72959100	2.15644200
C	-3.81927800	-0.22608200	1.08609300
C	-3.19925400	-1.98441600	3.14820400
H	-1.30054300	-2.22569900	2.19232000
C	-4.74714800	-0.48279900	2.08190200
H	-4.06834100	0.45372200	0.27966200
C	-4.43957400	-1.36089300	3.11593200
H	-2.95683100	-2.67168900	3.94878400
H	-5.71472700	0.00172300	2.05011800
H	-5.16731600	-1.56035200	3.89208800
C	-1.48152300	1.16816600	-0.67328800
C	-1.36446500	1.53862200	-2.01079900
C	-1.59748200	2.15025100	0.31463800
C	-1.36087200	2.88437400	-2.35990600
H	-1.27629200	0.77560600	-2.77489800
C	-1.59391800	3.48955900	-0.03987300
H	-1.68389400	1.86598200	1.35696800
C	-1.47651600	3.85679600	-1.37761900
H	-1.27056000	3.16862100	-3.40052500

H	-1.67754800	4.24891400	0.72749700
H	-1.47381000	4.90476300	-1.65035500
Br	-1.38895100	-2.19282100	-2.42304800
IV_TS			
C	-1.49856500	3.17266700	0.20246400
C	-2.77334900	2.65489300	-0.06914200
C	-2.99086300	1.29098100	0.00666400
C	-1.94750400	0.42622700	0.33131200
C	-0.63924900	0.93476900	0.55006300
C	-0.45778400	2.33671100	0.53775500
H	-1.33946500	4.24350000	0.16995800
H	-3.58517300	3.32127100	-0.32874300
H	-3.96684400	0.87267100	-0.20616300
H	0.51265100	2.74540600	0.79009900
C	-2.16754800	-1.01883500	0.21343700
O	-3.24885300	-1.55837100	0.18529400
C	-0.89298000	-1.84885700	-0.03789600
F	-0.14175300	-1.85848700	1.10531200
F	-1.24049100	-3.13856900	-0.25539300
C	-0.06295200	-1.35966300	-1.22132700
C	0.28627300	0.10635700	-1.23878600
H	-0.64154400	-1.61831100	-2.11079000
H	0.84178100	-1.97330400	-1.21396500
C	1.71876700	0.49543200	-1.12284500
H	2.27109700	0.14453300	-2.00343700
H	1.81599500	1.58107600	-1.06468100
O	2.25812100	-0.11906500	0.05258500
C	3.55063200	0.04074000	0.39192000
O	3.94477800	-0.50725300	1.38660400
C	4.40998200	0.89532500	-0.49043400
H	4.45053600	0.48256200	-1.49929700
H	4.00305100	1.90503500	-0.55886800
H	5.41006600	0.93088800	-0.06978100
H	0.09565400	0.33722600	1.07145900
H	-0.26912500	0.71796600	-1.94003200
V			
C	-1.17009500	2.84964000	0.37536400
C	-0.22981400	3.17181900	-0.65115700
C	0.86062300	2.35576800	-0.88646200
C	1.09545200	1.22530200	-0.11458500
C	0.25381500	0.93911600	1.09842700
C	-0.97176600	1.78682100	1.18026400
H	-2.05098100	3.46716400	0.49594800
H	-0.40023900	4.03714200	-1.27762200
H	1.52639000	2.56247000	-1.71525000
H	-1.67994300	1.54722400	1.96401100

O	3.02501900	0.58736600	-1.33003600
C	1.36784100	-1.26824700	1.37718800
C	0.00937200	-0.57090800	1.30848100
C	-0.90177800	-1.17941400	0.25248700
H	-0.48147800	-0.70499100	2.27453700
H	-0.62105200	-0.85664400	-0.75151800
H	-0.85684700	-2.26968700	0.29914400
O	-2.23364600	-0.74646000	0.54882800
C	-3.24204600	-0.95207800	-0.31467300
O	-4.33903200	-0.56709800	-0.00463500
C	-2.93242200	-1.64071100	-1.60986700
H	-2.29810000	-1.00065700	-2.22600000
H	-2.39801900	-2.57564600	-1.44000100
H	-3.86484600	-1.83333500	-2.13137900
H	0.85633900	1.23578700	1.97845300
H	1.94281500	-0.83760400	2.19939800
H	1.26638200	-2.34049800	1.55478200
C	2.17017000	0.33381500	-0.49852800
C	2.17625700	-1.08024400	0.12134300
F	3.46233900	-1.46297500	0.33342700
F	1.70735000	-1.91983200	-0.86314400
VII			
C	-1.37574200	2.66340100	0.37294000
C	-0.54506800	2.96255700	-0.69928400
C	0.65669500	2.25930300	-0.95590600
C	1.01588500	1.24569500	-0.13143400
C	0.20581100	0.88302600	1.04119600
C	-1.02566400	1.64016600	1.22009100
H	-2.28276500	3.22821600	0.53439600
H	-0.81987600	3.76961100	-1.36825300
H	1.26852200	2.52551800	-1.80761500
H	-1.63005800	1.40556500	2.08759800
O	3.21996300	0.95329600	-0.95061300
C	1.46874800	-1.28979100	1.28654700
C	0.08188200	-0.65146200	1.28693900
C	-0.87470200	-1.28263300	0.28459400
H	-0.34614100	-0.77827200	2.28179300
H	-0.55655800	-1.10727600	-0.74349300
H	-0.93027100	-2.35703500	0.46990100
O	-2.14337500	-0.67125700	0.50839600
C	-3.20115900	-0.92167400	-0.29729000
O	-4.21663000	-0.31969400	-0.08342300
C	-3.01794000	-1.92990600	-1.38774400
H	-2.28548400	-1.56725400	-2.11133400
H	-2.65050000	-2.87306400	-0.98222400
H	-3.97167000	-2.08381300	-1.88255600
H	0.80884300	1.22821700	1.91843600

H	2.04453100	-0.90176900	2.12871000
H	1.39601700	-2.37366500	1.39306400
C	2.27201600	0.47462000	-0.40015900
C	2.26315600	-1.00641800	0.03685800
F	3.53538200	-1.42528600	0.17599900
F	1.74597800	-1.69638700	-1.02682000
dppm			
P	1.00213800	0.71973600	0.37380100
C	2.78178200	1.02931300	0.02911200
C	3.31291100	1.36708400	-1.21378900
C	3.64743700	0.94740600	1.12466500
C	4.67570300	1.61103800	-1.35871200
H	2.67592100	1.43940600	-2.08568700
C	5.00589400	1.17907200	0.97911600
H	3.24975200	0.69572200	2.10263600
C	5.52522500	1.51510500	-0.26704800
H	5.07067800	1.87282900	-2.33265900
H	5.66001800	1.10540000	1.83907100
H	6.58514000	1.70375100	-0.38252900
C	1.05151600	-1.09920100	0.64616700
C	0.23327200	-1.64095800	1.63537500
C	1.87005600	-1.95270000	-0.09443200
C	0.21902300	-3.01095800	1.87260400
H	-0.39803800	-0.98730700	2.22706200
C	1.86130500	-3.31942300	0.14297200
H	2.52135600	-1.54647700	-0.86102800
C	1.03395000	-3.85122100	1.12703800
H	-0.42610400	-3.41861500	2.64105000
H	2.50170600	-3.97188700	-0.43793500
H	1.02798500	-4.91832800	1.31180300
C	0.27722400	0.84449100	-1.32101100
H	0.52135800	1.84831500	-1.68269300
H	0.74491700	0.13854000	-2.01332900
P	-1.55696500	0.73853900	-1.58546100
C	-1.99947600	-0.93837200	-0.99737100
C	-3.13886400	-1.19377500	-0.23499500
C	-1.26529500	-2.02519400	-1.48191500
C	-3.51199300	-2.49903100	0.06755700
H	-3.74667900	-0.37444200	0.12783800
C	-1.63678300	-3.32583600	-1.18044800
H	-0.39086000	-1.85574400	-2.09972600
C	-2.76043200	-3.56840900	-0.39721000
H	-4.39615400	-2.67608200	0.66759400
H	-1.04624600	-4.15263300	-1.55588600
H	-3.04933300	-4.58414000	-0.15798300
C	-2.21595600	1.87155700	-0.30430300
C	-2.69421300	3.10342400	-0.75061000

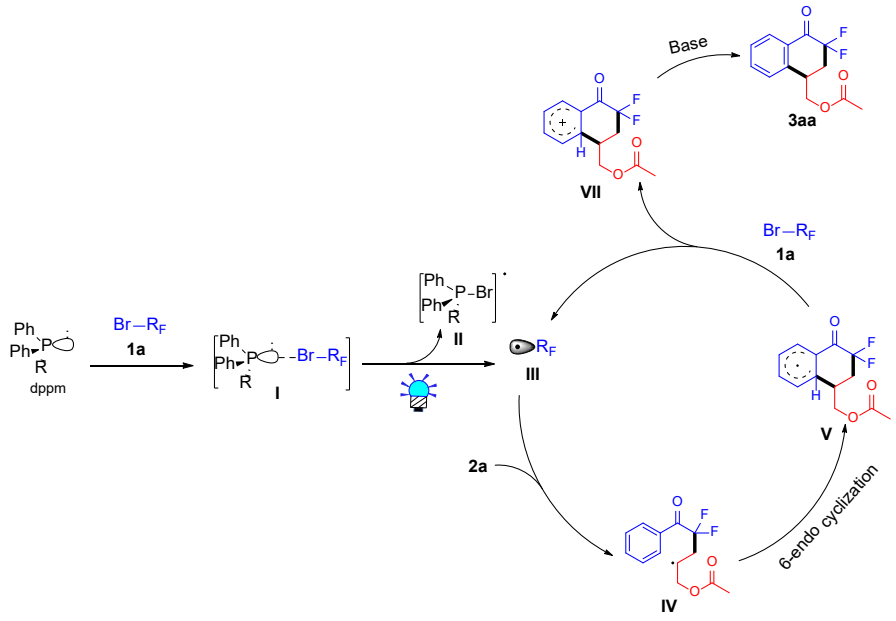
C	-2.23974100	1.60104200	1.06638300
C	-3.17368500	4.05058800	0.14750000
H	-2.69305900	3.32335900	-1.81233500
C	-2.72695500	2.53965200	1.96324900
H	-1.88008800	0.64825500	1.43499600
C	-3.19197000	3.76826000	1.50526100
H	-3.53843400	5.00281900	-0.21662600
H	-2.74043200	2.31516500	3.02254600
H	-3.57060200	4.50024000	2.20777200
Br-			
Br	0.00000000	0.00000000	0.00000000
3aa			
C	0.04825400	3.28826300	-0.30094300
C	-1.09243700	3.35864800	0.49529400
C	-1.82785100	2.21426400	0.72922900
C	-1.42605900	0.99409900	0.17901000
C	-0.27340400	0.91395400	-0.61520600
C	0.45062300	2.08094600	-0.84969200
H	0.62541400	4.18318300	-0.49753700
H	-1.40322600	4.30363500	0.92102900
H	-2.72473300	2.24215300	1.33460100
H	1.33713400	2.03650600	-1.46903900
O	-3.28133100	-0.17889300	1.08992600
C	-0.94735400	-1.37906300	-1.40036200
C	0.20793700	-0.40144200	-1.18466000
C	1.30873400	-1.00688300	-0.31084900
H	0.66142000	-0.20847300	-2.15853600
H	1.01626200	-1.02148500	0.73835900
H	1.52526300	-2.02569500	-0.64061200
O	2.46995900	-0.19088800	-0.48532700
C	3.56169600	-0.36280600	0.27961900
O	4.51596400	0.33839800	0.06865000
C	3.51197900	-1.40988300	1.35105500
H	2.78871400	-1.12011900	2.11558900
H	3.20092300	-2.37244100	0.94486700
H	4.49711600	-1.49522300	1.79893000
H	-1.59878000	-0.99691800	-2.18856800
H	-0.58902500	-2.36631900	-1.69679500
C	-2.26943100	-0.19286400	0.43675300
C	-1.79307400	-1.52832600	-0.16991000
F	-2.87322900	-2.30431900	-0.42368300
F	-1.09687000	-2.17581300	0.82098400
H			
Br	0.00000000	0.00000000	0.03954600
H	0.00000000	0.00000000	-1.38412300

VI			
C	-4.68065400	-1.13380400	-0.65613900
C	-5.97606800	-0.78715300	-0.31788600
C	-6.20247800	0.23285300	0.60065500
C	-5.13195100	0.90317600	1.17653800
C	-3.83049900	0.56124400	0.83896200
C	-3.59854900	-0.46290600	-0.08105100
H	-4.48954000	-1.92545700	-1.36863800
H	-6.81062200	-1.30880400	-0.76804900
H	-7.21621700	0.50484400	0.86686000
H	-5.30825300	1.69649700	1.89109500
H	-3.01156800	1.09603400	1.29760900
C	-2.23808800	-0.89539400	-0.49331400
O	-2.04429200	-1.80376100	-1.26127900
C	-1.00481400	-0.15123800	0.07881200
C	0.30865800	-0.69081000	-0.42850400
C	1.52899200	-0.01784100	0.18241400
H	0.32667300	-1.75020400	-0.16240100
H	0.32274600	-0.63149000	-1.51628600
C	2.73499000	-0.92342000	0.06486800
H	1.36635800	0.23991100	1.22699200
H	2.49544800	-1.87426300	0.54930300
H	2.97069700	-1.10490900	-0.98516800
F	-1.14218500	1.17303900	-0.20238600
F	-1.04459300	-0.25186000	1.44227400
Br	1.92889100	1.69155800	-0.70472500
O	3.82242500	-0.30740800	0.74242800
C	5.07260500	-0.79483600	0.63732700
O	5.94043300	-0.26146200	1.27482000
C	5.30090100	-1.96085000	-0.27722800
H	4.62311500	-2.78267800	-0.04508600
H	5.12377300	-1.66021500	-1.31169900
H	6.33041600	-2.28746000	-0.16863100
2FBrPh			
C	2.44035200	-1.33514900	-0.00690800
C	3.79426200	-1.05554800	-0.01549600
C	4.22897300	0.26591500	-0.00955000
C	3.30758200	1.30389400	0.00441500
C	1.94794800	1.03049300	0.01180300
C	1.50782300	-0.29424300	0.00656600
H	2.08783600	-2.35800500	-0.01128000
H	4.51244200	-1.86500300	-0.02693400
H	5.28914200	0.48577000	-0.01599000
H	3.64594400	2.33156700	0.00941500
H	1.25168100	1.85660000	0.02268700
C	0.07538000	-0.68519400	0.01582100

O	-0.30552500	-1.82132100	0.03188000
C	-0.97704100	0.46786500	0.00239100
F	-0.80832300	1.24792200	1.08039600
F	-0.79229400	1.23850600	-1.07952900
Br	-2.79682800	-0.18418300	-0.00842800
2FBrPh-dppm			
P	3.73192800	0.67653900	0.76671300
C	4.34168700	2.39759100	0.54987300
C	3.53939000	3.50612800	0.28822500
C	5.71895600	2.59040800	0.69922900
C	4.10061300	4.77469700	0.17263100
H	2.46949900	3.39698300	0.16658300
C	6.27983300	3.85128900	0.57326400
H	6.35787900	1.73973500	0.91418400
C	5.46900900	4.95111500	0.31106300
H	3.46135500	5.62503600	-0.03087500
H	7.34927000	3.97886400	0.68685700
H	5.90359300	5.93848700	0.21881300
C	4.36266100	-0.07491200	-0.78923300
C	4.84315700	-1.38206900	-0.74412300
C	4.37418200	0.60698000	-2.00642100
C	5.31208900	-2.00497000	-1.89541200
H	4.85017000	-1.91953200	0.19767200
C	4.84712800	-0.00989500	-3.15535100
H	4.01305700	1.62875500	-2.05681900
C	5.31573600	-1.31867900	-3.10169200
H	5.67628300	-3.02375800	-1.84722900
H	4.85254900	0.53007500	-4.09429400
H	5.68397800	-1.79991300	-3.99930400
C	1.93292800	0.87820200	0.39824800
H	1.55154000	1.60435900	1.12331800
H	1.76976000	1.30880300	-0.59406800
P	0.75967200	-0.54725000	0.57447200
C	1.36473700	-1.79006800	-0.62476800
C	1.44817500	-3.14961000	-0.32654900
C	1.58025500	-1.38261000	-1.94514100
C	1.77742600	-4.07271100	-1.31365000
H	1.25489800	-3.50001500	0.67948300
C	1.91039500	-2.30205600	-2.92770200
H	1.49547100	-0.33470400	-2.20989000
C	2.01585100	-3.65321400	-2.61402900
H	1.84412200	-5.12370300	-1.06043800
H	2.08607300	-1.96347700	-3.94145800
H	2.27585000	-4.37205100	-3.38087800
C	1.18209700	-1.23309200	2.21928000
C	0.26566100	-0.99851100	3.24419600

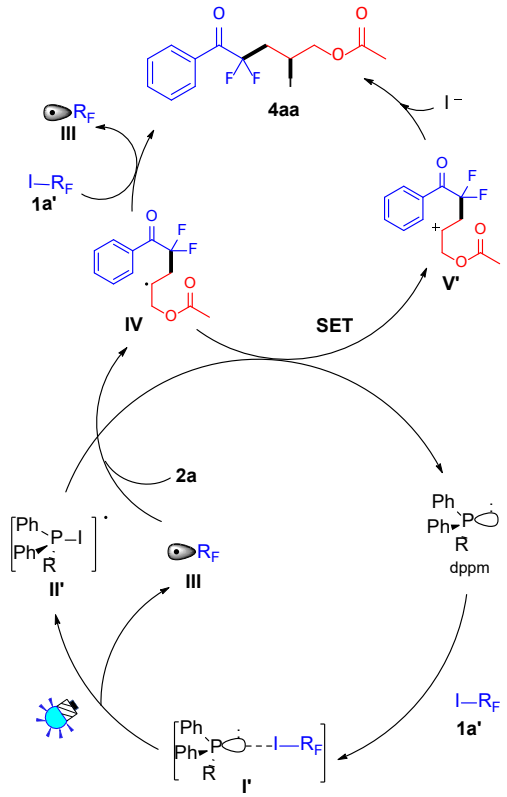
C	2.35209900	-1.93789400	2.51494100
C	0.51361600	-1.44287200	4.53827100
H	-0.65331400	-0.46510000	3.02743100
C	2.59759000	-2.38977800	3.80260800
H	3.07282200	-2.14031500	1.73228900
C	1.67972600	-2.13968700	4.81772500
H	-0.20800600	-1.25021100	5.32210400
H	3.50807700	-2.93544900	4.01700500
H	1.87422900	-2.49261700	5.82287500
C	-7.31607200	0.94927400	-1.23445400
C	-8.67099300	1.15104700	-1.45213600
C	-9.59005600	0.86325800	-0.45259900
C	-9.15741200	0.37028600	0.77418100
C	-7.80810700	0.16690600	0.99737500
C	-6.87776100	0.45474300	-0.00478000
H	-6.62076800	1.18102000	-2.02820100
H	-9.00773900	1.53425200	-2.40637500
H	-10.64641700	1.02303500	-0.62859400
H	-9.87347900	0.14594200	1.55388700
H	-7.45742000	-0.21583700	1.94666100
C	-5.44869100	0.20682200	0.32117700
O	-5.07505800	-0.21572700	1.37936600
C	-4.39665500	0.52170200	-0.78493300
F	-4.67429200	-0.20210000	-1.88435100
F	-4.49198500	1.81809900	-1.13307300
Br	-2.58045300	0.15419700	-0.23492900

5.5 Another possible reaction mechanism



First, an EDA complex **I**, is assembled from 2-bromo-2,2-difluoro-1-phenyl-ethanone

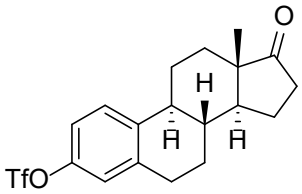
(**1a**) and phosphine, which then undergoes visible light irradiation to generate a difluoroalkyl radical (•CF_2R) **III** and the intermediate **II**. Subsequently, the difluoroalkyl radical is captured by alkenes to afford radical addition and migration intermediate **IV**， which is well suited for a 6-endo cyclization to give a stabilized radical adduct **V**. Aryl cation **VII** is then formed through a radical exchange with RCF_2Br (**1a**) to generate a difluoromethyl radical, which then enters the radical chain process. The final product **3aa** is obtained by deprotonation with a base.



First, an EDA complex **I'**, is assembled from 2,2-difluoro-2-iodo-1-phenylethan-1-one (**1a'**) and phosphine, which then undergoes visible light irradiation to generate a difluoroalkyl radical (•CF_2R) **III** and the intermediate **II'**. Subsequently, the difluoroalkyl radical is captured by alkenes to afford radical addition and migration intermediate **IV**. The final product **4aa** is then formed through a radical exchange with RCF_2I (**1a'**) to generate a difluoromethyl radical, which then enters the radical chain process. Or the **IV** is a SET oxidation by intermediate II to recover the phosphine catalyst to give a stabilized radical adduct **V'**, which is well captures I^- to get **4aa**.

6 Characterization data of all products

(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl trifluoromethanesulfonate(2q')

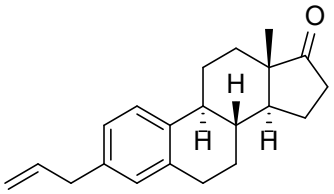


^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31(d, *J* = 8.0 Hz, 1H), 7.01 - 6.95 (m, 2H), 2.93 - 2.89 (m, 2H), 2.50 - 2.27 (m, 3H), 2.15 - 1.93 (m, 4H), 1.64 - 1.42 (m, 6H), 0.89 (d, *J* = 8.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 220.3, 174.6, 140.4, 139.4, 127.3, 121.2, 118.8 (q, $^{1}J_{C\text{-}F}$ = 636.0, 318.0 Hz), 118.3, 50.4, 47.9, 44.1, 37.8, 35.8, 31.5, 29.4, 26.4 (d, $^{2}J_{C\text{-}F}$ = 39.0 Hz), 21.6, 13.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -73.07 (s, 3F).

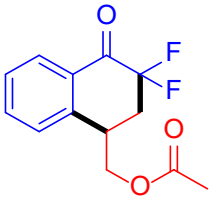
(8R,9S,13S,14S)-3-allyl-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one(2q)



^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 (d, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 7.02 (s, 1H), 6.09 - 5.99 (m, 1H), 5.16 (t, *J* = 16.0 Hz, 2H), 3.42 (d, *J* = 4.0 Hz, 2H), 2.97 (t, *J* = 4.0 Hz, 2H), 2.61 - 2.48 (m, 2H), 2.39 - 2.32 (m, 1H), 2.26 - 2.03 (m, 4H), 1.75 - 1.49 (m, 6H), 0.98 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 220.9, 137.7, 137.6, 137.6, 137.6, 136.6, 129.3, 126.1, 125.6, 115.8, 50.6, 48.1, 44.4, 39.9, 38.3, 36.0, 31.7, 29.5, 26.7, 25.9, 21.7.

(3,3-difluoro-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)methyl acetate (3aa)



A light yellow oily (81% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

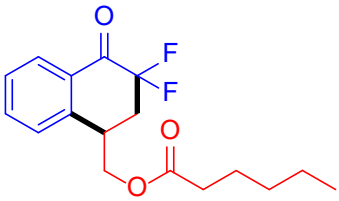
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.14 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 16.0 Hz, 1H), 7.49 - 7.46 (m, 2H), 4.50 - 4.37 (m, 2H), 3.64 - 3.58 (m, 1H), 2.74 - 2.60 (m, 2H), 2.09 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 184.8 (t, $^{2}J_{C\text{-}F}$ = 26.0 Hz), 170.8, 142.0, 135.5, 130.1, 129.1, 128.4, 128.2, 113.3 (t, $^{1}J_{C\text{-}F}$ = 246.0 Hz), 68.08 (d, $^{4}J_{C\text{-}F}$ = 2.0 Hz), 35.5 (t, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 34.5 (d, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 20.82.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -104.87 (ddd, *J* = 274.5, 18.8, 11.3, Hz, 1F), δ = -107.65 (ddd, *J* = 274.5, 18.8, 11.3 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{13}H_{12}O_3F_2Na$: 277.0647; found: 278.0608.

(3,3-difluoro-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)methyl hexanoate(3ab)



A light yellow oily (65% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

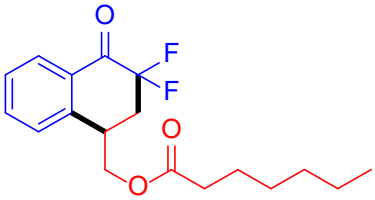
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10 (d, *J* = 8.0 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 4.41 (t, *J* = 4.0 Hz, 2H), 3.57 (p, *J* = 8.0 Hz, 1H), 2.74 - 2.53 (m, 2H), 2.30 (t, *J* = 8.0 Hz, 2H), 1.58 (p, *J* = 8.0 Hz, 2H), 1.27 - 1.24 (m, 4H), 0.85 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 184.8 (t, $^2J_{C\text{-}F}$ = 26.0 Hz), 173.5, 142.1, 135.4, 130.2, 129.1, 128.3, 128.1, 113.2 (t, $^1J_{C\text{-}F}$ = 246.0 Hz), 65.83 (d, $^2J_{C\text{-}F}$ = 3.0 Hz), 35.6 (t, $^2J_{C\text{-}F}$ = 5.0 Hz), 34.6 (t, $^2J_{C\text{-}F}$ = 22.0 Hz), 34.1, 31.2, 24.6, 22.3, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -105.11 (ddd, *J* = 274.5, 22.6, 11.3 Hz, 1F), -107.68 (ddd, *J* = 274.5, 18.8, 11.3 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{17}H_{20}O_3F_2Na$: 333.1273; found: 333.1278.

(3,3-difluoro-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)methyl heptanoate(3ac)



A light yellow oily (72% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

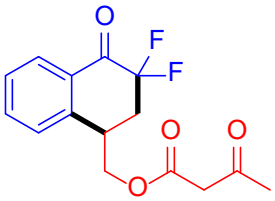
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.13 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 4.45 (s, 2H), 3.61 (s, 1H), 2.77 - 2.59 (m, 2H), 2.33 (t, *J* = 8.0 Hz, 2H), 1.60 (s, 2H), 1.27 (s, 6H), 0.88 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 184.8 (t, $^2J_{C\text{-}F}$ = 26.0 Hz), 173.5, 142.1, 135.3, 130.2, 129.0, 128.3, 128.1, 113.2 (t, $^1J_{C\text{-}F}$ = 246.0 Hz), 65.81 (d, $^2J_{C\text{-}F}$ = 3.0 Hz), 35.5 (t, $^2J_{C\text{-}F}$ = 5.0 Hz), 34.6 (t, $^2J_{C\text{-}F}$ = 22.0 Hz), 34.1, 31.4, 28.7, 24.8, 22.5, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -105.10 (ddd, *J* = 274.5, 18.8, 11.3 Hz, 1F), -107.67 (ddd, *J* = 274.5, 18.8, 11.3 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{18}H_{22}O_3F_2Na$: 347.1429; found: 347.1434.

(3,3-difluoro-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)methyl 3-oxobutanoate (3ad)



A light yellow oily (35% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.15 (d, J = 8.0 Hz, 1H), 7.67 (t, J = 8.0 Hz, 1H), 7.47

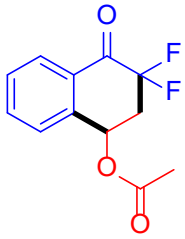
(t, J = 8.0 Hz, 2H), 4.57-4.44 (m, 2H), 3.67-3.61 (m, 1H), 3.52 (s, 2H), 2.75-2.63 (m, 2H), 2.25 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.5 (t, $^2J_{C\text{-}F}$ = 26.0 Hz), 166.1, 147.0, 135.1, 129.7, 128.6, 128.4, 128.0, 127.4, 113.6 (t, $^1J_{C\text{-}F}$ = 246.0 Hz), 37.4 (d, $^2J_{C\text{-}F}$ = 2.0 Hz), 36.1 (t, $^2J_{C\text{-}F}$ = 20.0 Hz), 35.4 (t, $^2J_{C\text{-}F}$ = 1.0 Hz), 19.77, 13.92.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -104.82 (d, *J* = 274.5Hz, 1F), -106.37 (d, *J* = 274.5Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{15}H_{14}O_4F_2Na$: 319.0954; found: 319.1012.

3,3-difluoro-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl acetate(3ae)



A light yellow oily (60% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

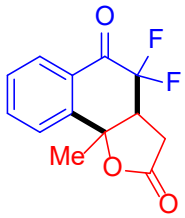
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.14 (d, *J* = 8.0 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 6.30 (q, *J* = 4.0 Hz, 1H), 3.07 - 2.95 (m, 1H), 2.75 - 2.62 (m, 1H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 184.2 (t, $^2J_{C\text{-}F}$ = 26.0 Hz), 170.2, 140.6, 135.7, 129.6, 129.2, 128.6, 127.9, 132.2 (t, $^1J_{C\text{-}F}$ = 246.0 Hz), 66.2 (t, $^2J_{C\text{-}F}$ = 5.0 Hz), 38.0 (t, $^2J_{C\text{-}F}$ = 22.0 Hz), 21.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -105.36 (ddd, *J* = 282.0, 18.8, 11.3 Hz, 1F), -107.48 (ddd, *J* = 274.5, 22.6, 11.3 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{12}H_{10}O_3F_2Na$: 263.0490; found: 263.0495.

4,4-difluoro-9b-methyl-3a,9b-dihydronaphtho[1,2-b]furan-2,5(3H,4H)-dione (3af)



A light yellow oily (50% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

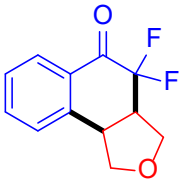
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.11 (d, *J* = 8.0 Hz, 1H), 7.82 (t, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 3.57 - 3.46 (m, 1H), 2.89 (q, *J* = 8.0 Hz, 1H), 2.49 (q, *J* = 12.0 Hz, 1H), 1.97 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 183.1 (t, $^2J_{C\text{-}F}$ = 26.0 Hz), 171.8, 142.0, 136.8, 130.2, 128.8, 127.9, 127.3, 112.3 (t, $^1J_{C\text{-}F}$ = 246.0 Hz), 49.1 (t, $^2J_{C\text{-}F}$ = 24.0 Hz), 30.8 (d, $^2J_{C\text{-}F}$ = 6.0 Hz), 29.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -99.31 (dd, *J* = 282.0, 11.3 Hz, 1F), -113.07 (dd, *J* = 282.0, 7.5 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{13}H_{10}O_3F_2Na$: 275.0490; found: 275.0496.

4,4-difluoro-1,3a,4,9b-tetrahydronaphtho[1,2-c]furan-5(3H)-one (3ag)



A light yellow oily (65% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

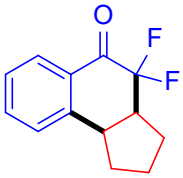
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 4.28 - 4.24 (m, 1H), 4.16 (t, *J* = 8.0 Hz, 1H), 4.06 (q, *J* = 4.0 Hz, 1H), 3.94 - 3.88 (m, 2H), 3.45 - 3.33 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.2 (t, $^{2}J_{C\text{-}F}$ = 26.0 Hz), 141.5, 135.7, 130.2, 129.0, 128.3, 128.1, 113.7 (t, $^{1}J_{C\text{-}F}$ = 246.0 Hz), 75.1, 66.5 (t, $^{2}J_{C\text{-}F}$ = 4.0 Hz), 44.9 (t, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 42.2 (t, $^{2}J_{C\text{-}F}$ = 4.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -104.20 (dd, *J* = 282.0, 11.3 Hz, 1F), -113.4 (dd, *J* = 282.0, 11.3 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{12}H_{10}O_2F_2Na$: 247.0541; found: 247.0546.

4,4-difluoro-1,2,3,3a,4,9b-hexahydro-5H-cyclopenta[a]naphthalen-5-one (3ah)



A light yellow oily (40% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

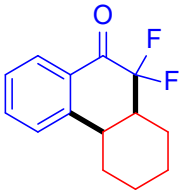
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.0 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 2H), 3.62 (q, *J* = 8.0 Hz, 1H), 3.07 - 2.94 (m, 1H), 2.28 - 2.19 (m, 1H), 2.08 - 1.91 (m, 2H), 1.88 - 1.81 (m, 1H), 1.78 - 1.70 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 186.3 (t, $^{2}J_{C\text{-}F}$ = 45.0 Hz), 144.8, 138.4, 133.6, 130.4(t, $^{2}J_{C\text{-}F}$ = 49.0 Hz) 128.9, 125.9, 113.7 (t, $^{1}J_{C\text{-}F}$ = 246.0 Hz), 44.91 (t, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 42.4, 35.0, 24.4, 24.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -106.19 (dd, *J* = 267.0, 11.3 Hz, 1F), -113.81 (dd, *J* = 267.0, 11.3 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{13}H_{12}OF_2Na$: 245.0754; found: 245.0752.

10,10-difluoro-2,3,4,4a,10,10a-hexahydrophenanthren-9(1H)-one (3ai)

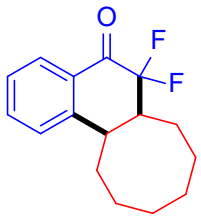


A light yellow oily (63% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.12 - 8.10 (m, 1H), 7.66 - 7.62 (m, 1H), 7.42 - 7.36 (m, 2H), 3.50 - 3.46 (m, 1H), 2.75 - 2.59 (m, 1H), 2.40 - 2.36 (m, 1H), 1.71 - 1.68 (m,

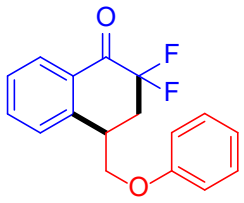
2H), 1.58 - 1.51 (m, 1H), 1.47 - 1.41 (m, 2H), 1.37 - 1.27 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.7 (t, $^2J_{C\text{-}F}$ = 26.0 Hz), 135.5, 133.3, 129.8, 128.5, 127.6, 127.2, 115.5 (t, $^1J_{C\text{-}F}$ = 248.0 Hz), 64.5, 47.7, 29.0, 24.2, 21.7, 21.6 (t, $^2J_{C\text{-}F}$ = 4.0 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ = -120.76 (d, *J* = 270.7Hz, 1F), -122.59 (d, *J* = 2667.0 Hz, 1F).
HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{14}H_{14}OF_2Na$: 259.0905; found: 259.0911.

6,6-difluoro-6a,7,8,9,10,11,12,12a-octahydrocycloocta[a]naphthalen-5(6H)-one (3aj)



A light yellow oily (70% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.11- 8.08 (m, 1H), 7.63 - 7.58 (m, 1H), 7.40 - 7.36 (m, 2H), 3.25 - 3.19 (m, 1H), 2.68 - 2.55 (m, 1H), 2.47 - 2.34 (m, 1H), 1.90 - 1.81 (m, 1H), 1.77 - 1.63 (m, 2H), 1.50 - 1.39 (m, 1H), 1.35 - 1.22 (m, 5H), 0.89 - 0.85 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.5 (t, $^2J_{C\text{-}F}$ = 26.0 Hz), 147.1, 135.1, 128.7, 128.0, 127.4, 127.2, 113.6 (t, $^1J_{C\text{-}F}$ = 246.0 Hz), 36.1 (t, $^2J_{C\text{-}F}$ = 21.0 Hz), 35.6 (t, $^2J_{C\text{-}F}$ = 5.0 Hz), 31.7, 29.2, 26.5, 22.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ = -104.78 (ddd, *J* = 278.2, 22.6, 15.0 Hz, 1F), -106.25 (ddd, *J* = 274.5, 18.8, 11.3 Hz, 1F).
HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{16}H_{18}OF_2Na$: 287.1218; found: 287.1215.

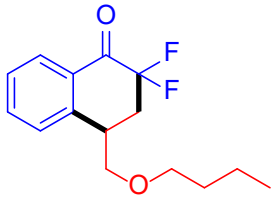
2,2-difluoro-4-(phenoxymethyl)-3,4-dihydronaphthalen-1(2H)-one(3ak)



A light yellow oily (58% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.13 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 2H), 6.95 (t, *J* = 4.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 2H), 4.31 - 4.21 (m, 2H), 3.69 (s, 1H), 2.81 - 2.66 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.1 (t, $^2J_{C\text{-}F}$ = 26.0 Hz), 158.4, 142.8, 135.4, 130.4, 130.2, 129.7, 129.1, 129.0, 128.5, 128.3, 121.5, 114.7, 113.6 (t, $^1J_{C\text{-}F}$ = 246.0 Hz), 70.15 (d, $^2J_{C\text{-}F}$ = 3.0 Hz), 36.3 (t, $^2J_{C\text{-}F}$ = 5.0 Hz), 34.6 (t, $^2J_{C\text{-}F}$ = 22.0 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ = -104.54 (ddd, *J* = 274.5, 22.6, 11.3 Hz, 1F), -107.38 (ddd, *J* = 274.5, 22.6, 11.3 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{17}H_{14}O_2F_2Na$: 311.0854; found: 311.0859.

4-(butoxymethyl)-2,2-difluoro-3,4-dihydronaphthalen-1(2H)-one(3al)



A light yellow oily (77% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

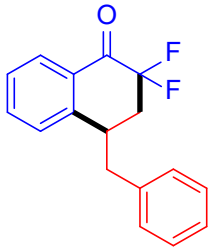
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.12 (d, *J* = 8.0 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 3.73 (s, 2H), 3.49 (s, 3H), 2.66 (t, *J* = 8.0 Hz, 2H), 1.57 (s, 2H), 1.37 (d, *J* = 8.0 Hz, 2H), 0.92 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.4 (t, $^2J_{C\text{-}F}$ = 26.0 Hz), 143.7, 135.1, 130.2, 128.8, 128.4, 127.9, 113.2 (t, $^1J_{C\text{-}F}$ = 246.0 Hz), 73.4, 71.2, 36.6 (t, $^2J_{C\text{-}F}$ = 5.0 Hz), 34.6 (t, $^2J_{C\text{-}F}$ = 22.0 Hz), 31.7, 19.4, 13.9.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -104.95 (dt, *J* = 274.5, 15.0 Hz, 1F), -107.40 (dt, *J* = 274.5, 15.0 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{15}H_{18}O_2F_2Na$: 291.1167; found: 291.1172.

4-benzyl-2,2-difluoro-3,4-dihydronaphthalen-1(2H)-one(3am)



A light yellow oily (53% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

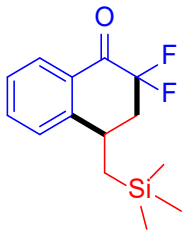
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 4.0 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 4.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 3.47 (s, 1H), 3.27 (d, *J* = 12.0 Hz, 1H), 2.85 (t, *J* = 12.0 Hz, 1H), 2.46 - 2.27 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.4 (t, $^2J_{C\text{-}F}$ = 26.0 Hz), 146.2, 138.7, 135.4, 129.6, 129.4, 129.0, 128.9, 128.5, 127.9, 126.9, 113.8 (t, $^1J_{C\text{-}F}$ = 246.0 Hz), 42.23 (d, $^2J_{C\text{-}F}$ = 3.0 Hz), 38.02 (q, $^2J_{C\text{-}F}$ = 3.0 Hz), 35.4 (t, $^2J_{C\text{-}F}$ = 22.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ = -102.80 (ddd, *J* = 278.2, 22.6, 11.3 Hz, 1F), -106.38 (ddd, *J* = 278.2, 18.8, 11.3 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{17}H_{14}OF_2Na$: 295.0905; found: 295.0909.

2,2-difluoro-4-((trimethylsilyl)methyl)-3,4-dihydronaphthalen-1(2H)-one(3an)



A light yellow oily (94% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

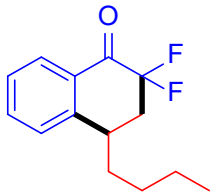
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.31 (t, *J* = 8.0 Hz, 1H), 7.88 - 7.83 (m, 1H), 7.67 (q, *J* = 4.0 Hz, 1H), 7.63 - 7.58 (m, 1H), 3.62 (s, 1H), 2.98 - 2.85 (m, 1H), 2.65 - 2.50 (m, 1H), 1.52 (d, *J* = 16.0 Hz, 1H), 1.30 (t, *J* = 12.0 Hz, 1H), 0.37 (d, *J* = 4.0 Hz, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.5 (t, $^{2}J_{C\text{-}F}$ = 26.0 Hz), 149.4, 135.4, 129.3, 128.6, 128.0, 127.3, 113.5 (t, $^{1}J_{C\text{-}F}$ = 246.0 Hz), 64.5, 44.8, 39.1 (t, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 32.4 (t, $^{2}J_{C\text{-}F}$ = 5.0 Hz), 24.1, 0.55.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -105.41 (ddd, *J* = 274.5, 18.8, 11.3 Hz, 1F), -106.34 (ddd, *J* = 278.2, 26.3, 11.3 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{14}H_{18}OF_2SiNa$: 291.0987; found: 291.0992.

4-butyl-2,2-difluoro-3,4-dihydronaphthalen-1(2H)-one(3ao)



A light yellow oily (83% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

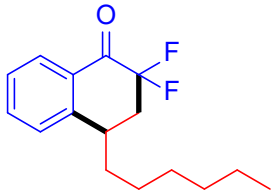
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10 (t, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.44 -7.36 (m, 2H), 3.23 (m, 1H), 2.71 - 2.56 (m, 1H), 2.49 - 2.36 (m, 1H), 1.88 (s, 1H), 1.79 (s, 1H), 1.38 (t, *J* = 8.0 Hz, 4H), 0.94 (d, *J* = 8.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.6 (t, $^{2}J_{C\text{-}F}$ = 26.0 Hz), 148.7, 135.2, 129.8, 128.8, 128.0, 127.4, 113.7 (t, $^{1}J_{C\text{-}F}$ = 246.0 Hz), 36.2 (t, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 35.6, 35.0, 28.8, 22.7, 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -104.97 (ddd, *J* = 274.5, 22.6, 11.3 Hz, 1F), -106.43 (ddd, *J* = 278.2, 18.8, 11.3 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{14}H_{16}OF_2Na$: 261.1061; found: 261.1067.

2,2-difluoro-4-hexyl-3,4-dihydronaphthalen-1(2H)-one(3ap)



A light yellow oily (80% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.09 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.42

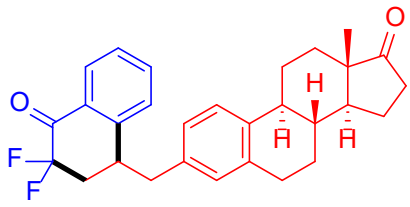
(q, J = 8.0 Hz, 2H), 3.24 (m, 1H), 2.69 - 2.56 (m, 1H), 2.49 - 2.36 (m, 1H), 1.91 - 1.72 (m, 2H), 1.36 - 1.32 (d, J = 16.0 Hz, 8H), 0.89 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.6 (t, $^2J_{C\text{-}F}$ = 26.0 Hz), 147.1, 135.2, 129.7, 128.8, 128.0, 127.4, 113.7 (t, $^1J_{C\text{-}F}$ = 246.0 Hz), 36.2 (t, $^2J_{C\text{-}F}$ = 21.0 Hz), 35.7 (t, $^2J_{C\text{-}F}$ = 4.0 Hz), 35.3, 31.2, 29.3, 26.6, 22.7, 14.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -104.95 (ddd, J = 274.5, 18.8, 11.3 Hz, 1F), -106.42 (ddd, J = 274.5, 15.0, 11.3 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{16}H_{20}OF_2Na$: 289.1380; found: 289.1379.

(8R,9S,13S,14S)-3-((3,3-difluoro-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)methyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one(3aq)



A white solid (55% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1). m. p. (174.2 °C-176.3°C)

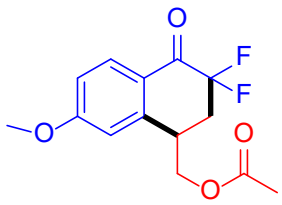
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (d, J = 8.0 Hz, 1H), 7.80 - 7.71 (m, 2H), 7.54 (t, J = 8.0 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H), 7.09 - 7.05 (m, 2H), 2.87 (s, 2H), 2.71 (t, J = 6.0 Hz, 1H), 2.52 (s, 3H), 2.45 - 2.39 (m, 2H), 2.27 (t, J = 8.0 Hz, 1H), 2.11 - 1.96 (m, 2H), 1.80 (d, J = 6.0 Hz, 1H), 1.62 - 1.37 (m, 6H), 1.22 (d, J = 10.0 Hz, 2H), 0.86 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 220.3, 185.3, 147.0, 138.3, 136.8, 135.4, 136.2, 130.1, 129.5, 129.3, 128.4, 127.2, 125.9, 114.7, 50.2, 47.9, 44.3, 41.2, 38.2, 37.3, 35.9, 31.2, 29.4, 26.6, 25.8, 21.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -102.63 (dd, J = 270.7, 26.3 Hz, 1F), -105.56 (d, J = 270.7Hz, 1F).

HRMS (ESI-TOF): m/z $[M+H]^+$ calcd for $C_{29}H_{30}O_2F_2$: 449.2292; found: 449.2289.

(3,3-difluoro-7-methoxy-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)methyl acetate (3ba)



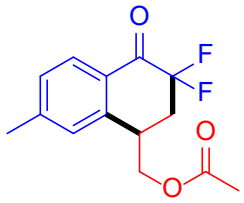
A light yellow oily (67% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 - 8.02 (m, 1H), 6.90 - 6.87 (m, 1H), 6.80 (t, J = 4.0 Hz, 1H), 4.39 - 4.27 (m, 2H), 3.82 (s, 3H), 3.48 - 3.42 (m, 1H), 2.63 -2.49 (m, 2H), 2.02 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 183.4 (t, $^2J_{C\text{-}F}$ = 24.0 Hz), 170.8, 165.3, 144.6, 131.8, 123.4, 114.6, 113.2 (t, $^1J_{C\text{-}F}$ = 253.0 Hz), 112.7, 66.1 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 55.8, 35.7 (t,

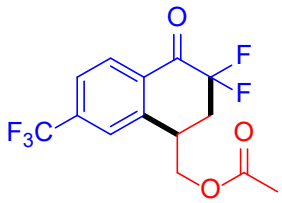
$^{3}J_{C\text{-}F}$ = 5.0 Hz), 34.6 (t, $^{2}J_{C\text{-}F}$ = 23.0 Hz), 20.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ = -104.43 (ddd, *J* = 274.5, 18.8, 11.3 Hz, 1F), -107.25 (ddd, *J* = 274.5, 18.8, 11.3 Hz, 1F).
HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{14}H_{14}O_4F_2Na$: 307.0752; found: 307.0757.

(3,3-difluoro-7-methyl-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)methyl acetate(3ca)



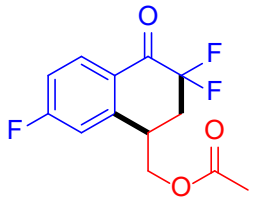
A light yellow oily (77% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, J = 8.0 Hz, 1H), 7.26 (t, J = 8.0 Hz, 2H), 4.52 - 4.48 (m, 1H), 4.36 - 4.30 (m, 1H), 3.54 (q, J = 8.0 Hz, 1H), 2.74 - 2.57 (m, 2H), 2.44 (s, 3H), 2.10 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 184.4 (t, $^{2}J_{C\text{-}F}$ = 26.0 Hz), 170.7, 146.9, 142.0, 129.4, 129.1, 128.7, 127.7, 113.3 (t, $^{1}J_{C\text{-}F}$ = 246.0 Hz), 66.1, 35.4, 34.3 (t, $^{2}J_{C\text{-}F}$ = 23.0 Hz), 22.0, 20.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ = -104.43 (ddd, *J* = 267.0, 22.6, 11.3 Hz, 1F), -107.38 (ddd, *J* = 228.2, 22.6, 11.3 Hz, 1F).
HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{14}H_{14}O_3F_2Na$: 291.0803; found: 291.0809.

(3,3-difluoro-4-oxo-7-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalen-1-yl)methyl acetate(3da)



A light yellow oily (70% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.17 (d, *J* = 8.0 Hz, 1H), 7.67 - 7.63 (m, 2H), 4.43 - 4.32 (m, 2H), 3.62 - 3.56 (m, 1H), 2.74 -2.52 (m, 2H), 2.01 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 184.0 (t, $^{2}J_{C\text{-}F}$ = 26.0 Hz), 170.6, 142.8, 136.1 (q, $^{2}J_{C\text{-}F}$ = 33.0 Hz), 132.6, 129.8, 125.5 (d, $^{2}J_{C\text{-}F}$ = 4.0 Hz), 125.1 (d, $^{2}J_{C\text{-}F}$ = 4.0 Hz), 122.5 (q, $^{1}J_{C\text{-}F}$ = 273.0 Hz), 112.9 (t, $^{1}J_{C\text{-}F}$ = 246.0 Hz), 65.8 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 35.6 (t, $^{3}J_{C\text{-}F}$ = 5.0 Hz), 34.4 (t, $^{2}J_{C\text{-}F}$ = 23.0 Hz), 20.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ = -63.52(s, 3F), -105.09 (ddd, *J* = 274.5, 18.8, 11.3 Hz, 1F), -108.04 (ddd, *J* = 274.5, 18.8, 11.3 Hz, 1F).
HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{14}H_{11}O_3F_5Na$: 345.0526; found: 345.0527.

(3,3,7-trifluoro-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)methyl acetate(3ea)



A light yellow solid (73% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1). m. p. (72.2 ºC-73.7 ºC)

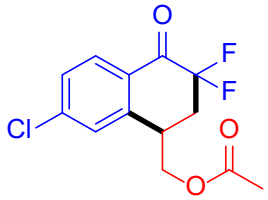
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.17 - 8.04 (m, 1H), 7.18 - 7.13 (m, 2H), 4.45 - 4.40 (m, 2H), 3.62 - 3.56 (m, 1H), 2.76 - 2.53 (m, 2H), 2.08 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 183.4 (t, $^{2}J_{C\text{-}F}$ = 26.0 Hz), 170.7, 166.9 (d, $^{1}J_{C\text{-}F}$ = 257.0 Hz), 145.5 (d, $^{2}J_{C\text{-}F}$ = 9.0 Hz), 132.3 (d, $^{2}J_{C\text{-}F}$ = 10.0 Hz), 126.8, 116.2 (d, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 115.0 (d, $^{2}J_{C\text{-}F}$ = 23.0 Hz), 113.1 (t, $^{1}J_{C\text{-}F}$ = 246.0 Hz), 65.7, 35.4, 34.6 (t, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 20.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -100.07(t, *J* = 6.0 Hz, 1F), -105.64 (ddd, *J* = 274.5, 18.8, 11.3 Hz, 1F), -107.82 (ddd, *J* = 274.5, 18.8, 11.3 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{13}H_{11}O_3F_3Na$: 295.0558; found: 295.0551.

(7-chloro-3,3-difluoro-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)methyl acetate(3fa)



A light yellow solid (70% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1). m. p. (88.1ºC-88.8 ºC)

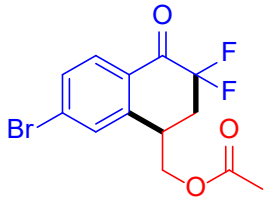
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (d, *J* = 8.0 Hz, 1H), 7.45 - 7.38 (m, 2H), 4.46 - 4.32 (m, 2H), 3.58 - 3.52 (m, 1H), 2.75 - 2.53 (m, 2H), 2.06 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 183.8 (t, $^{2}J_{C\text{-}F}$ = 26.0 Hz), 170.6, 143.7, 142.1, 130.6, 128.9, 128.5, 128.3, 113.0 (t, $^{1}J_{C\text{-}F}$ = 246.0 Hz), 65.7 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 35.3 (t, $^{3}J_{C\text{-}F}$ = 4.0 Hz), 34.4 (d, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 20.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -105.21 (ddd, *J* = 278.2, 22.6, 11.3 Hz, 1F), -107.72 (ddd, *J* = 278.2, 22.6, 11.3 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{13}H_{11}O_3F_2ClNa$: 311.0262; found: 311.0261.

(7-bromo-3,3-difluoro-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)methyl acetate(3ga)



A light yellow solid (60% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1). m. p. (108.2 ºC-108.8 ºC)

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (d, *J* = 8.0 Hz, 1H), 7.63 - 7.56 (m, 2H), 4.47 -

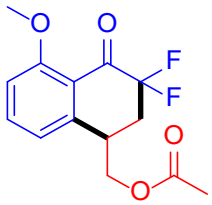
4.32 (m, 2H), 3.59 -3.53 (m, 1H), 2.75 - 2.53 (m, 2H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 184.0 (t, $^2J_{C\text{-}F}$ = 26.0 Hz), 170.6, 143.7, 131.9, 131.3, 131.1, 131.0, 129.0, 113.0 (t, $^1J_{C\text{-}F}$ = 246.0 Hz), 65.7 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 35.3 (t, $^3J_{C\text{-}F}$ = 4.0 Hz), 34.3 (d, $^2J_{C\text{-}F}$ = 22.0 Hz), 20.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -105.05 (ddd, *J* = 274.5, 22.6, 11.3 Hz, 1F), -107.67 (ddd, *J* = 274.5, 18.8, 11.3 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{13}H_{11}BrO_3F_2Na$: 354.9757; found: 354.9760.

(3,3-difluoro-5-methoxy-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)methyl acetate(3ha)



A light yellow oily (66% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

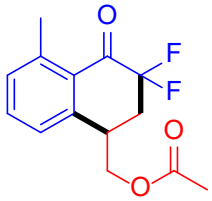
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 - 7.51 (m, 1H), 6.94 (d, *J* = 8.0 Hz, 2H), 4.40 - 4.35 (m, 1H), 4.27 - 4.22 (m, 1H), 3.89 (s, 3H), 3.49(s, 1H), 2.63 - 2.52 (m, 2H), 2.02 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 183.4 (t, $^2J_{C\text{-}F}$ = 26.0 Hz), 170.8, 161.8, 144.1, 136.3, 120.2, 119.4, 113.1 (t, $^1J_{C\text{-}F}$ = 246.0 Hz), 111.3, 68.7, 56.2, 35.8, 33.7 (t, $^2J_{C\text{-}F}$ = 23.0 Hz), 20.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ=-103.27 (ddd, *J* = 259.4, 33.8, 18.8 Hz, 1F), -104.62 (ddd, *J* = 259.4, 33.8, 18.8 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{14}H_{14}O_4F_2Na$: 307.0752; found: 307.0757.

(3,3-difluoro-5-methyl-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)methyl acetate(3ia)



A light yellow oily (80% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

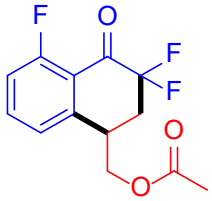
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 (t, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.0Hz, 1H), 4.47 - 4.42 (m, 1H), 3.33 - 3.28 (m, 1H), 3.58 - 3.55 (m, 1H), 2.70 - 2.59 (m, 5H), 2.07 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 186.3 (t, $^2J_{C\text{-}F}$ = 26.0 Hz), 170.7, 143.7, 143.0, 134.2, 131.9, 128.6, 128.5, 113.2 (t, $^1J_{C\text{-}F}$ = 246.0 Hz), 66.8 (d, $^2J_{C\text{-}F}$ = 3.0 Hz), 36.0 (q, $^2J_{C\text{-}F}$ = 3.0 Hz), 33.8 (t, $^2J_{C\text{-}F}$ = 23.0 Hz), 23.0, 20.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -103.27 (ddd, *J* = 274.5, 18.8, 11.3 Hz,F), -105.14 (ddd, *J* = 274.5, 18.8, 11.3 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{14}H_{14}O_3F_2Na$: 291.0803; found: 291.0809.

(3,3,5-trifluoro-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)methyl acetate(3ja)



A light yellow oily (84% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

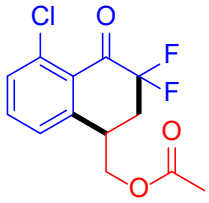
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 - 7.63 (m, 1H), 7.31 - 7.27 (m, 1H), 7.19 - 7.12 (m, 1H), 4.49 - 4.43 (m, 2H), 3.66 - 3.61 (m, 1H), 2.75 - 2.61 (m, 2H), 2.08 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 186.4 (t, $^2J_{C\text{-}F}$ = 26.0 Hz), 170.7, 163.0 (d, $^1J_{C\text{-}F}$ = 267.0 Hz), 144.0, 136.7 (d, $^2J_{C\text{-}F}$ = 10.0 Hz), 124.1, 119.2, 116.5 (d, $^2J_{C\text{-}F}$ = 20.0 Hz), 112.7 (t, $^1J_{C\text{-}F}$ = 246.0 Hz), 66.2, 35.7, 34.0 (t, $^2J_{C\text{-}F}$ = 23.0 Hz), 20.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -104.97 (ddd, *J* = 270.1, 18.8, 11.3 Hz, 1F), -106.79 (ddd, *J* = 270.1, 18.8, 11.3 Hz, 1F), -108.55 (s, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{13}H_{11}O_3F_3Na$: 295.0553; found: 295.0557.

(5-chloro-3,3-difluoro-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)methyl acetate(3ka)



A light yellow oily (60% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

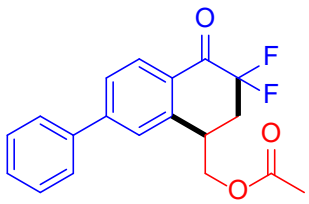
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.49 (t, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 4.39 - 4.25 (m, 2H), 3.59 - 3.53 (m, 1H), 2.73 - 2.53 (m, 2H), 2.00 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 183.4 (t, $^2J_{C\text{-}F}$ = 26.0 Hz), 170.6, 144.6, 135.9, 134.8, 131.6, 127.6, 127.4, 113.0 (d, $^1J_{C\text{-}F}$ = 246.0 Hz), 66.5, 35.8 (t, $^2J_{C\text{-}F}$ = 5.0 Hz), 33.6 (t, $^2J_{C\text{-}F}$ = 23.0 Hz), 20.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -104.07 (ddd, *J* = 267.0, 22.6, 15.0 Hz, 1F), -105.13 (ddd, *J* = 267.0, 22.6, 15.0 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{13}H_{11}O_3F_2ClNa$: 311.0257; found: 311.0262.

(3,3-difluoro-4-oxo-7-phenyl-1,2,3,4-tetrahydronaphthalen-1-yl)methyl acetate(3la)



A light yellow solid (74% yield), purified by flash column chromatography on silica

gel (petroleum ether/ethyl acetate = 80:1). m.p. (101.0 ºC-103.1ºC)

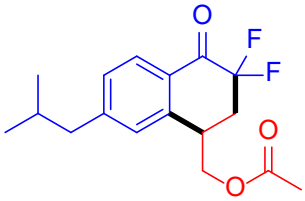
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.20 (d, *J* = 8.0 Hz, 1H), 7.68 - 7.63 (m, 4H), 7.52 - 7.43 (m, 3H), 4.57 - 4.45 (m, 2H), 3.70 - 3.64 (m, 1H), 2.79 - 2.66 (m, 2H), 2.11 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 184.5 (t, $^{2}J_{C\text{-}F}$ = 26.0 Hz), 170.8, 148.1, 142.6, 139.1, 129.8, 129.2, 129.0, 128.9, 127.4, 127.1, 126.7, 113.4 (t, $^{1}J_{C\text{-}F}$ = 246.0 Hz), 65.1 (d, $^{4}J_{C\text{-}F}$ = 2.0 Hz), 35.7 (q, $^{3}J_{C\text{-}F}$ = 3.0 Hz), 34.5 (d, $^{2}J_{C\text{-}F}$ = 23.0 Hz), 20.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -104.41 (ddd, *J* = 278.2, 18.8, 11.3 Hz, 1F), -107.24 (ddd, *J* = 278.2, 18.8, 11.3 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{19}H_{16}O_3F_2Na$: 353.0560; found: 353.0964.

(3,3-difluoro-7-isobutyl-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)methyl acetate(3ma)



A light yellow oily (79% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

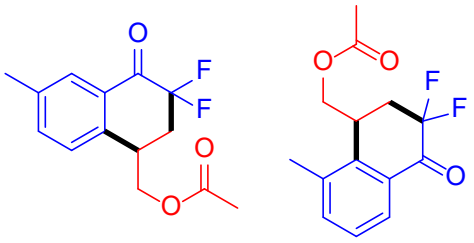
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 - 8.02 (m, 1H), 7.25 - 7.20 (m, 2H), 4.48 - 4.36 (m, 2H), 3.58 – 3.53 (m, 1H), 2.72 - 2.50 (m, 4H), 2.07 (s, 3H), 1.94 - 1.86 (m, 1H), 0.93 - 0.89 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 184.4 (t, $^{2}J_{C\text{-}F}$ = 26.0 Hz), 170.7, 150.5, 141.8, 129.4, 129.1, 128.7, 128.0, 113.3 (t, $^{1}J_{C\text{-}F}$ = 246.0 Hz), 66.1 (d, $^{2}J_{C\text{-}F}$ = 3.0 Hz), 45.6, 34.5 (t, $^{2}J_{C\text{-}F}$ = 5.0 Hz), 34.6 (t, $^{2}J_{C\text{-}F}$ = 23.0 Hz), 30.1, 22.4, 22.2, 20.7.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -104.43 (ddd, *J* = 274.5, 22.6, 11.3 Hz, 1F), -107.44 (ddd, *J* = 274.5, 22.6, 11.3 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{17}H_{20}O_3F_2Na$: 333.1273; found: 333.1278.

(3,3-difluoro-6-methyl-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)methyl acetate and (3,3-difluoro-8-methyl-4-oxo-1,2,3,4-tetrahydronaphthalen-1-yl)methyl acetate (3na:3na'=4:5)



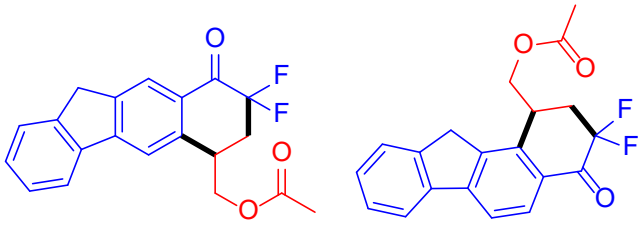
A light yellow oily (75% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 - 7.84 (m, 1H), 7.51 - 7.41 (m, 1H), 7.36 - 7.28 (m, 1H), 4.44 - 3.92 (m, 2H), 3.71 - 3.49 (m, 1H), 2.98 - 2.33 (m, 5H), 2.09 - 2.02 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.0 (t, $^{2}J_{C\text{-}F}$ = 27.0 Hz), 170.7, 140.1, 139.2, 138.3, 137.7, 137.4, 136.5, 113.4 (t, $^{1}J_{C\text{-}F}$ = 246.0 Hz), 64.7, 34.5, 33.5 (d, t, $^{2}J_{C\text{-}F}$ = 11.0 Hz), 32.9 (t, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 20.7.

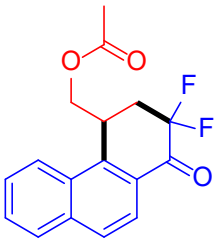
^{19}F NMR (376 MHz, $CDCl_3$) δ = -96.81 (ddd, *J* = 285.8, 26.32, 15.0 Hz, 1F), -103.16 (dd, *J* = 289.5, 26.32 Hz, 1F).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 - 7.84 (m, 1H), 7.51 - 7.41 (m, 1H), 7.36 - 7.28 (m, 1H), 4.44 - 3.92 (m, 2H), 3.71 - 3.49 (m, 1H), 2.98 - 2.33 (m, 5H), 2.09 - 2.02 (m, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.0 (t, $^{2}J_{C\text{-}F}$ = 27.0 Hz), 170.7, 130.7, 129.9, 129.0, 128.3, 128.1, 127.2, 112.7 (t, $^{1}J_{C\text{-}F}$ = 246.0 Hz), 66.1, 35.1, 34.5 (t, $^{2}J_{C\text{-}F}$ = 20.0 Hz), 32.9 (t, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 18.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ = -104.76 (ddd, *J* = 274.5, 18.8, 11.3 Hz, 1F), -107.55 (ddd, *J* = 274.5, 18.8, 11.3 Hz, 1F).
HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{14}H_{14}O_3F_2Na$: 291.0803; found: 291.0809.

(8,8-difluoro-9-oxo-7,8,9,11-tetrahydro-6H-benzo[b]fluoren-6-yl)methyl acetate and (3,3-difluoro-4-oxo-2,3,4,11-tetrahydro-1H-benzo[a]fluoren-1-yl)methyl acetate (3oa:3oa'=1:1.4)



A light yellow oily (79% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 4.0 Hz, 2H), 7.46 - 7.43 (m, 3H), 4.63 (t, *J* = 12.0 Hz, 1H), 4.19 - 4.15 (m, 1H), 3.92 (d, *J* = 8.0 Hz, 1H), 3.76 (s, 1H), 3.02 (t, *J* = 12.0 Hz, 1H), 2.76 - 2.63 (m, 1H), 2.18 (d, *J* = 4.0 Hz, 3H), 1.29 (t, *J* = 12.0 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 184.5 (t, $^{2}J_{C\text{-}F}$ = 24.0 Hz), 170.9, 149.0, 144.4, 142.0, 139.6, 138.1, 129.2, 129.0, 128.4, 127.4, 125.5, 121.4, 120.2, 113.0 (t, $^{1}J_{C\text{-}F}$ = 249.0 Hz), 65.1 (d, $^{2}J_{C\text{-}F}$ = 5.0 Hz), 35.78 (d, $^{2}J_{C\text{-}F}$ = 3.0 Hz), 35.6, 33.0 (t, $^{2}J_{C\text{-}F}$ = 22.0 Hz), 20.94 (d, $^{2}J_{C\text{-}F}$ = 8.0 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ = -96.70 (ddd, *J* = 270.7, 37.6, 15.0 Hz, 1F), -103.84 (ddd, *J* = 278.2, 18.8, 11.3 Hz, 1F), -103.93 (d, *J* = 285.8 Hz, 1F).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.28 (s, 1H), 7.85 (d, *J* = 4.0 Hz, 2H), 7.84 (d, *J* = 4.0 Hz, 1H), 7.79 (s, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 4.44 (t, *J* = 8.0 Hz, 1H), 4.13 (d, *J* = 4.0 Hz, 1H), 3.97 (s, 1H), 3.76 (s, 1H), 3.02 (t, *J* = 12.0 Hz, 1H), 2.58 - 2.50 (m, 1H), 2.15 (d, *J* = 4.0 Hz, 3H), 2.07 (d, *J* = 4.0 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.0 (t, $^{2}J_{C\text{-}F}$ = 26.0 Hz), 170.9, 148.9, 145.1, 246.0, 141.3, 140.0, 138.1, 129.2, 127.4, 125.5, 125.4, 121.4, 118.9, 113.4 (t, $^{1}J_{C\text{-}F}$ = 123.0 Hz), 66.3 (d, $^{2}J_{C\text{-}F}$ = 8.0 Hz), 36.6, 35.7 (d, $^{2}J_{C\text{-}F}$ = 4.0 Hz), 34.7 (d, $^{2}J_{C\text{-}F}$ = 10.0 Hz), 34.5 (t, $^{2}J_{C\text{-}F}$ = 19.0 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ = -103.88 (ddd, *J* = 274.5, 18.8, 15.0 Hz, 1F), -106.93 (ddd, *J* = 278.2, 18.8, 11.3 Hz, 1F).
HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{20}H_{16}O_3F_2Na$: 365.0960; found: 365.0963.

(2,2-difluoro-1-oxo-1,2,3,4-tetrahydrophenanthren-4-yl)methyl acetate (3pa)



A light yellow oily (79% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

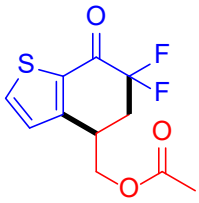
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.43 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.92 - 7.86 (m, 2H), 7.73 - 7.67 (m, 2H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.37 (s, 1H), 4.14 (t, *J* = 8.0 Hz, 1H), 3.16 - 3.08 (m, 1H), 2.70 - 2.53 (m, 1H), 2.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.0 (t, $^2J_{C\text{-}F}$ = 26.0 Hz), 171.1, 141.2, 136.7, 130.3, 129.5(t, $^2J_{C\text{-}F}$ = 26.0 Hz), 129.0, 128.2, 125.3, 124.5 (t, $^2J_{C\text{-}F}$ = 4.0 Hz), 123.9, 123.1, 112.7 (t, $^1J_{C\text{-}F}$ = 246.0 Hz), 66.0 (d, $^2J_{C\text{-}F}$ = 5.0 Hz), 33.0 (t, $^2J_{C\text{-}F}$ = 11.0 Hz), 32.7, 19.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -97.75 (ddd, *J* = 285.8, 37.6 15.0 Hz, 1F), -104.59 (dd, *J* = 282.0, 7.52 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{17}H_{14}O_3F_2Na$: 327.0803; found: 327.0808.

(6,6-difluoro-7-oxo-4,5,6,7-tetrahydrobenzo[b]thiophen-4-yl)methyl acetate(3qa)



A light yellow oily (30% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

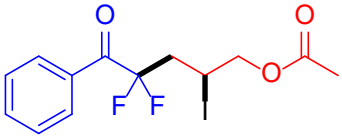
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 - 7.89 (m, 1H), 7.19 - 7.17 (m, 1H), 4.44 (d, *J* = 8.0 Hz, 2H), 3.63 - 3.56 (m, 1H), 2.28 - 2.71 (m, 1H), 2.60 - 2.45 (m, 1H), 2.11 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.3 (t, $^2J_{C\text{-}F}$ = 26.0 Hz), 170.7, 151.9, 138.3, 134.5, 127.3, 114.2 (t, $^1J_{C\text{-}F}$ = 246.0 Hz), 65.2, 36.3 (t, $^2J_{C\text{-}F}$ = 23.0 Hz), 34.1 (q, $^3J_{C\text{-}F}$ =83.0 Hz), 20.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ = -106.77 (ddd, *J* = 274.5, 26.3, 11.3 Hz, 1F), -108.29 (ddd, *J* = 278.2, 15.0, 7.52 Hz, 1F).

HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{11}H_{10}O_3F_2SNa$: 283.0211; found: 283.0219.

4,4-difluoro-2-iodo-5-oxo-5-phenylpentyl acetate(4aa)

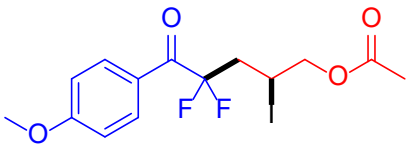


A light yellow oily (80% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.12 (d, *J* = 8.0 Hz, 2H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 2H), 4.52 - 4.42 (m, 2H), 4.31 (q, *J* = 8.0 Hz, 1H), 3.16 - 2.91(m, 2H),

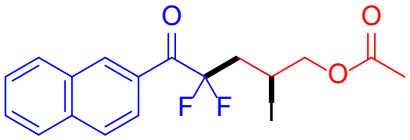
2.09 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 185.2 (t, $^2J_{C\text{-}F}$ = 30.0 Hz), 170.2, 143.7, 131.5, 130.3 (t, $^1J_{C\text{-}F}$ = 3.0 Hz), 128.9, 118.6(t, $^1J_{C\text{-}F}$ = 254.0 Hz), 68.9, 41.0 (t, $^2J_{C\text{-}F}$ = 22.0 Hz), 20.8, 15.1 (t, $^2J_{C\text{-}F}$ = 3.0 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ = -98.58 (dd, *J* = 33.84, 18.8 Hz, 2F).
HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{13}H_{13}O_3F_2INa$: 404.9770; found: 404.9771.

4,4-difluoro-2-iodo-5-(4-methoxyphenyl)-5-oxopentyl acetate(4ba)



A light yellow oily (80% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.11 (d, *J* = 6.0 Hz, 2H), 6.99 (d, *J* = 4.0 Hz, 1H), 6.97 (d, *J* = 4.0 Hz, 1H), 4.52 - 4.40 (m, 2H), 4.30 (q, *J* = 4.0 Hz, 1H), 3.90(s, 3H), 3.13 - 2.88 (m, 2H), 2.09 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 186.6 (t, $^2J_{C\text{-}F}$ = 30.0 Hz), 170.2, 164.8, 132.9(t, $^2J_{C\text{-}F}$ = 3.0 Hz), 124.3, 118.8 (t, $^1J_{C\text{-}F}$ = 254.0 Hz), 114.2, 68.9, 55.7, 41.1 (t, $^2J_{C\text{-}F}$ = 22.0 Hz), 20.8, 15.4 (t, $^2J_{C\text{-}F}$ = 4.0 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ = -98.14 (dd, *J* = 33.84, 15.0 Hz, 2F).
HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{14}H_{15}O_4F_2INa$: 434.9875; found: 434.9873.

4,4-difluoro-2-iodo-5-(naphthalen-2-yl)-5-oxopentyl acetate(4ca)



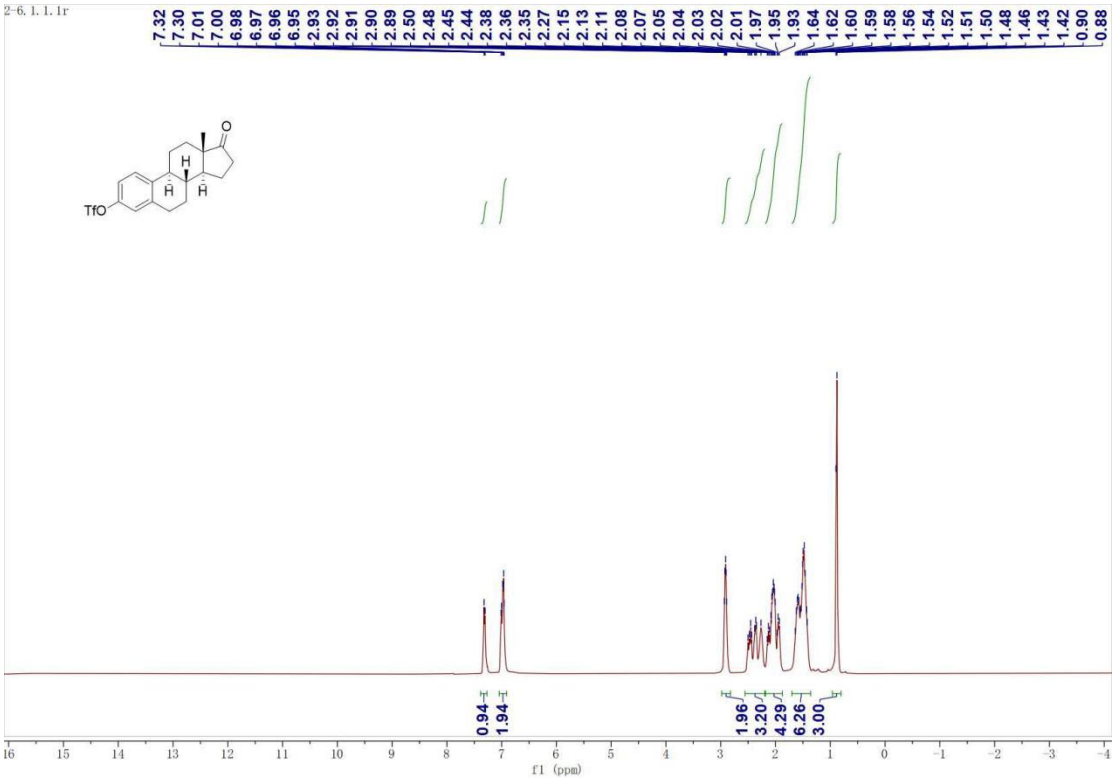
A light yellow oily (80% yield), purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 80:1).
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.73 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.92 (q, *J* = 8.0 Hz, 2H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 4.58 - 4.46 (m, 2H), 4.38 - 4.33 (m, 1H), 3.23 - 2.99 (m, 2H), 2.10 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ = 188.1 (t, $^2J_{C\text{-}F}$ = 31.0 Hz), 170.3, 136.2, 133.1, 132.3, 130.2, 129.7, 128.8, 128.6, 127.9, 127.2, 124.8, 118.8 (t, $^1J_{C\text{-}F}$ = 254.0 Hz), 68.9, 41.1 (t, $^2J_{C\text{-}F}$ = 23.0 Hz), 20.8, 15.2.
^{19}F NMR (376 MHz, $CDCl_3$) δ = -97.85 (dd, *J* = 37.60, 18.8 Hz, 2F).
HRMS (ESI-TOF): m/z $[M+Na]^+$ calcd for $C_{17}H_{15}O_3F_2INa$:454.9926; found: 454.9921.

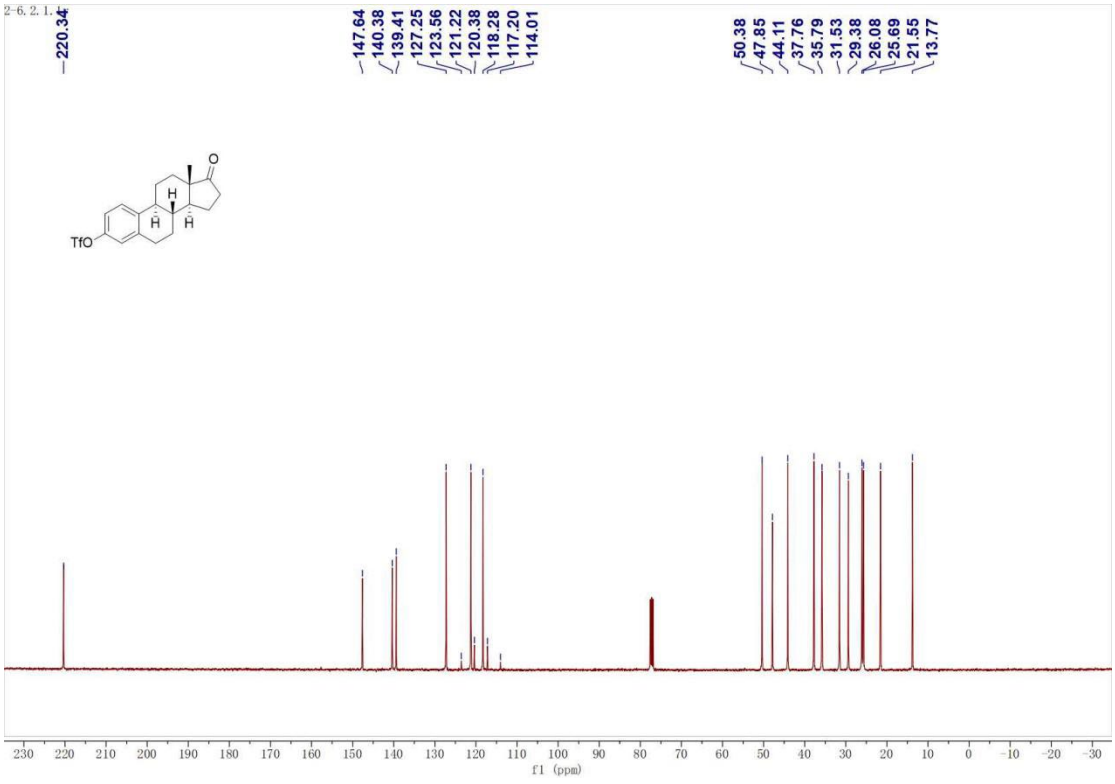
7 References

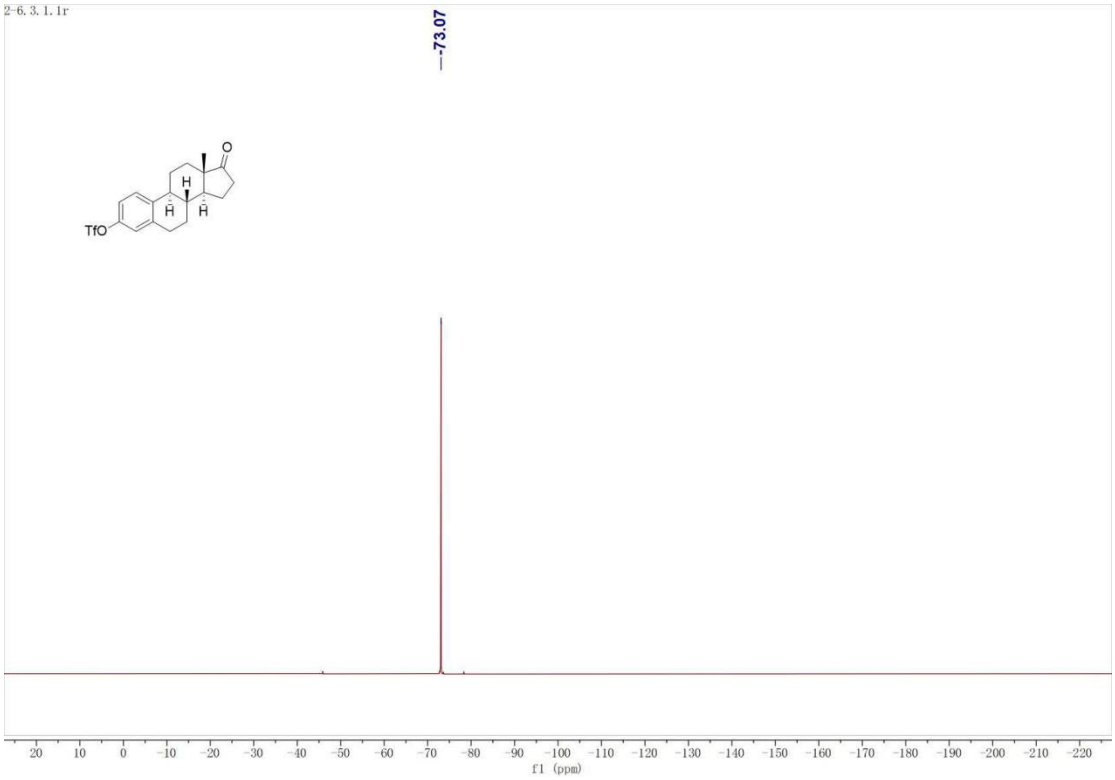
[1] a) I. Saidalimu, X. Fang, F. H. Wu, *Angew. Chem. Int. Ed.* **2013**, *52*, 5566-5570; b) H. Chen, J. X. Wang, J. J. Wu, Y. J. Kuang, F. H. Wu, *J. Fluor. Chem.* **2017**, *200*, 41-46; c) J. X. Wang, J. J. Wu, H. Chen, S. W. Zhang, F. H. Wu, *Chin. Chem. Lett.* **2019**, 26, 1381-1384.
[2] White, M. C., W. Liu, R. L. Ma: Sulfoxide Ligand Metal Catalyzed: *US 10266503*

Bl [P]. 2019-4-23.

8 NMR spectra (^{1}H, ^{13}C and ^{19}F)



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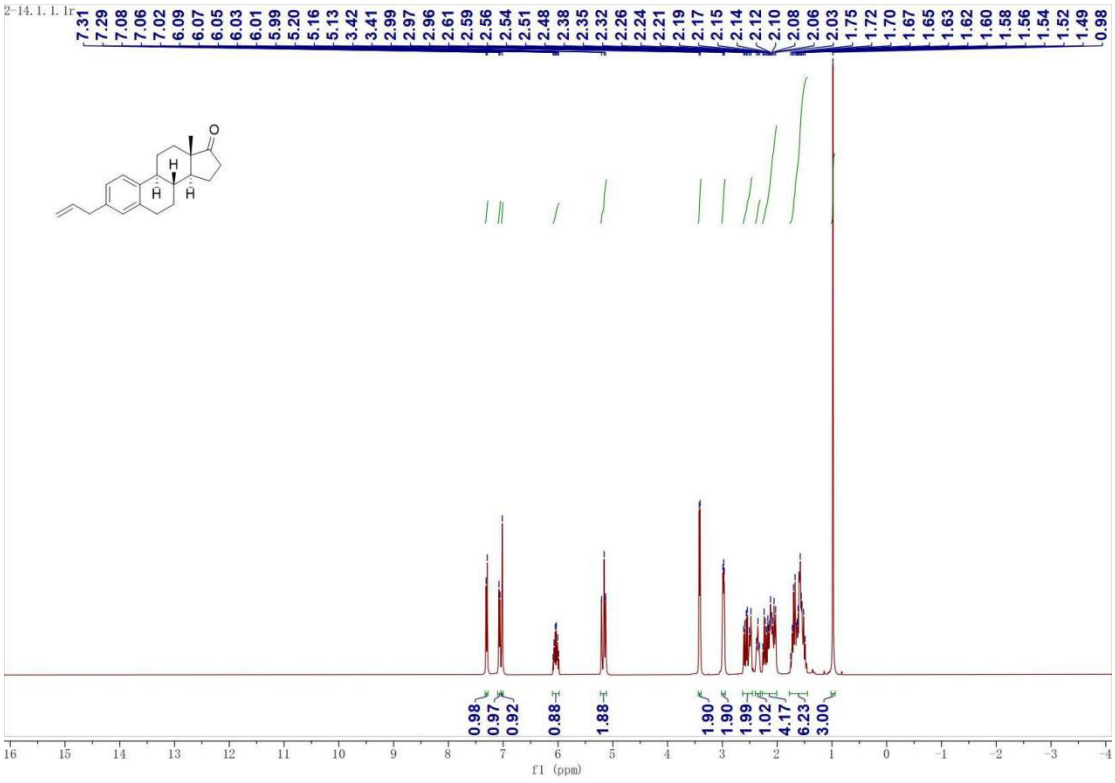
TfO
f1 (ppm)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7.29
7.08
7.06
7.02
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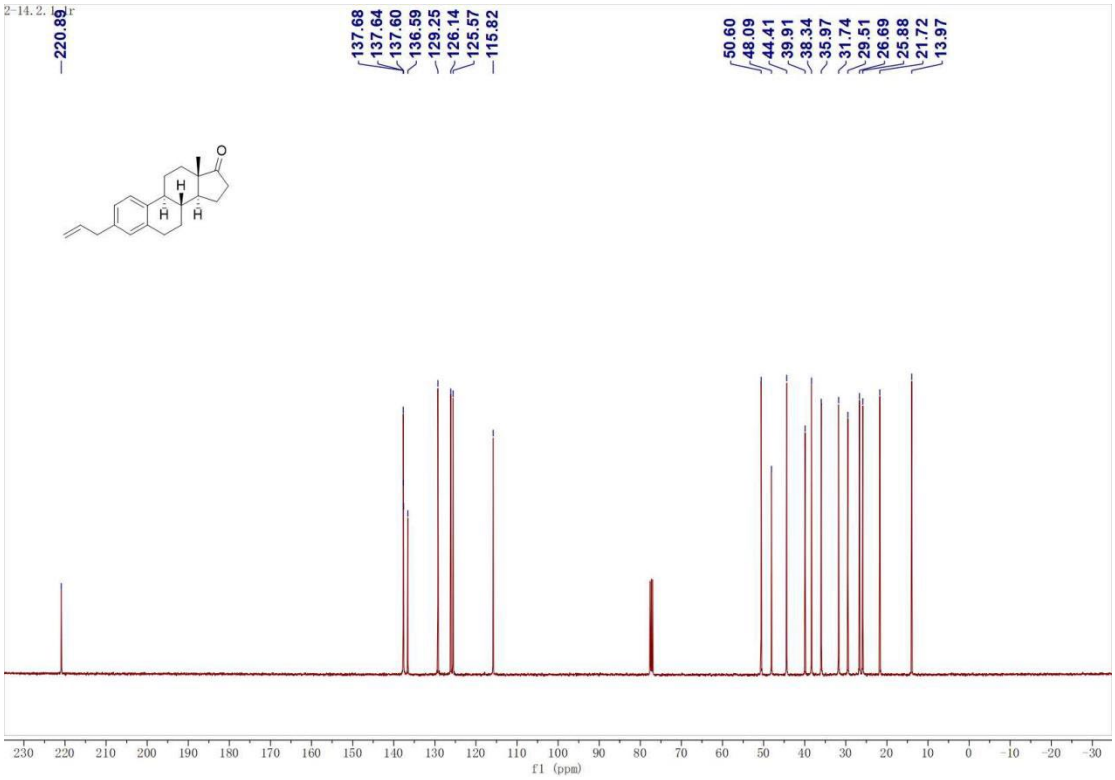
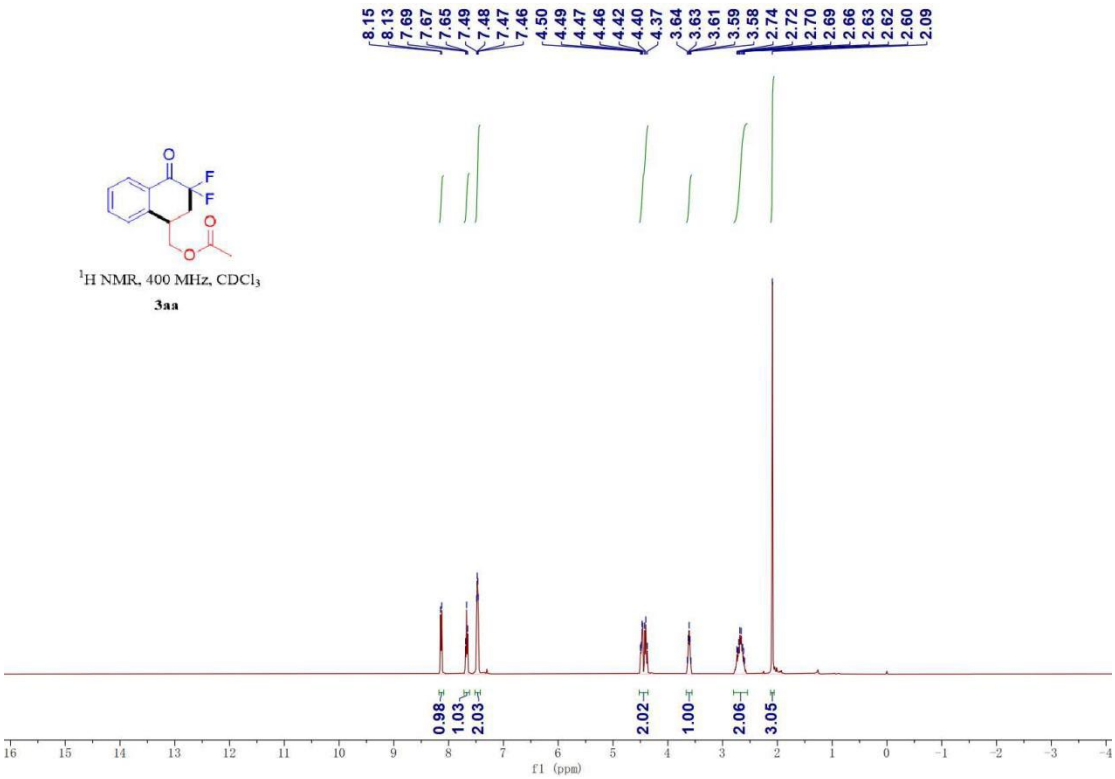
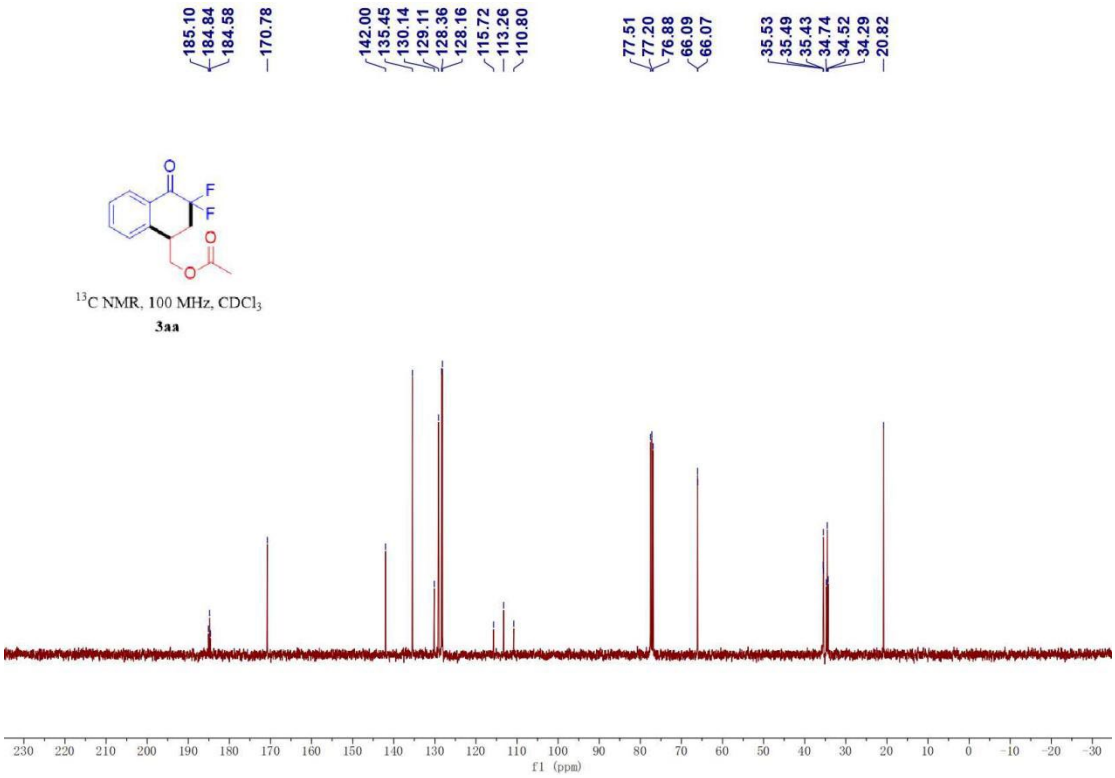
6.05
6.03
6.01
5.99
5.20
5.16
5.13
3.42
3.41
2.99
2.97
2.96
2.61
2.59
2.56
2.54
2.51
2.48
2.38
2.35
2.32
2.26
2.24
2.21
2.19
2.17
2.15
2.14
2.12
2.10
2.08
2.06
2.03
1.75
1.72
1.70
1.67
1.65
1.63
1.62
1.60
1.58
1.56
1.54
1.52
1.49
0.98
0.98
0.97
0.92
0.88
1.88
1.90
1.90
1.99
1.02
4.17
6.23
3.00
f1 (ppm)





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

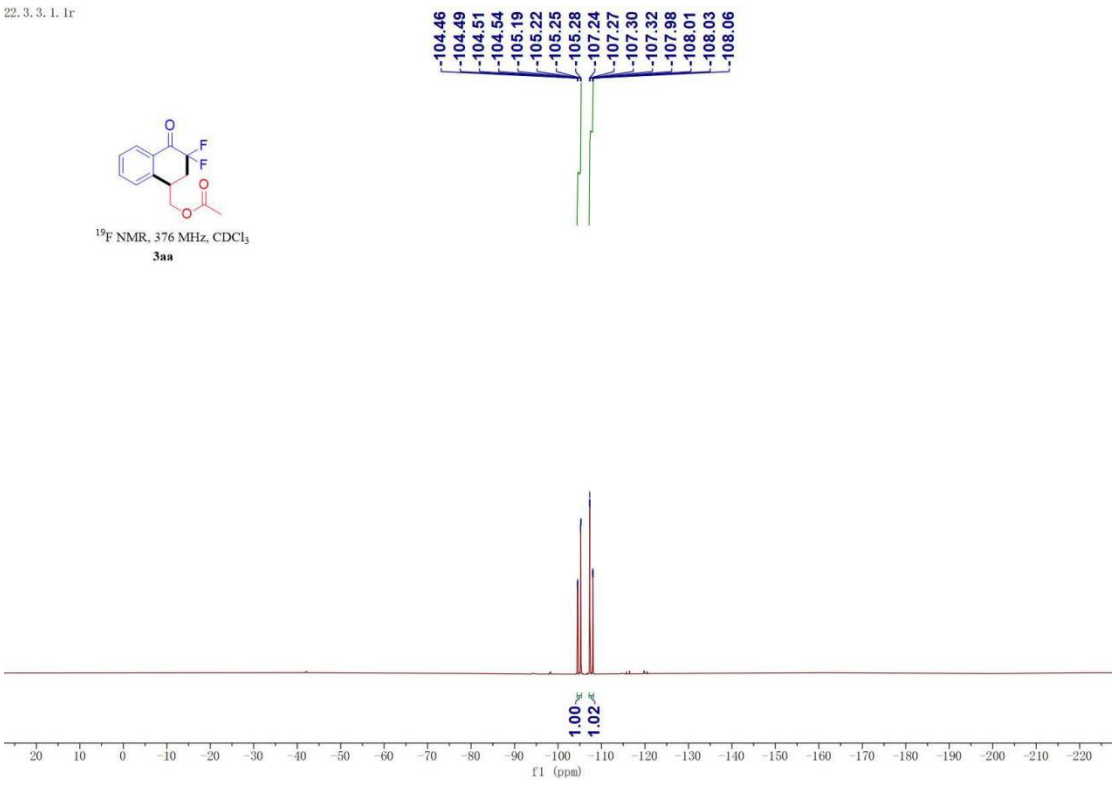
3aa



^{13}C NMR, 100 MHz, $CDCl_3$

3aa

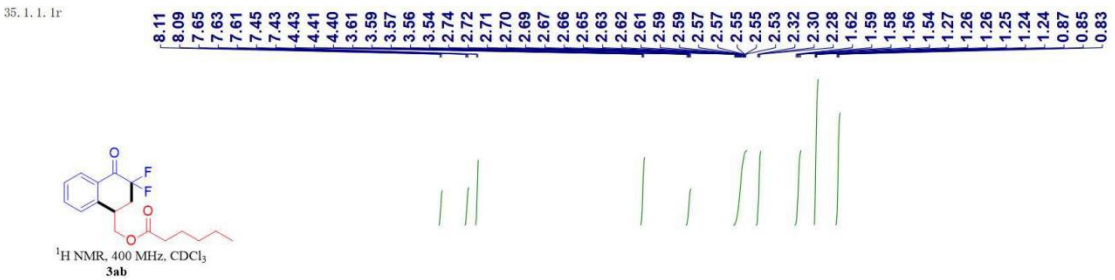
22. 3. 3. 1. 1r



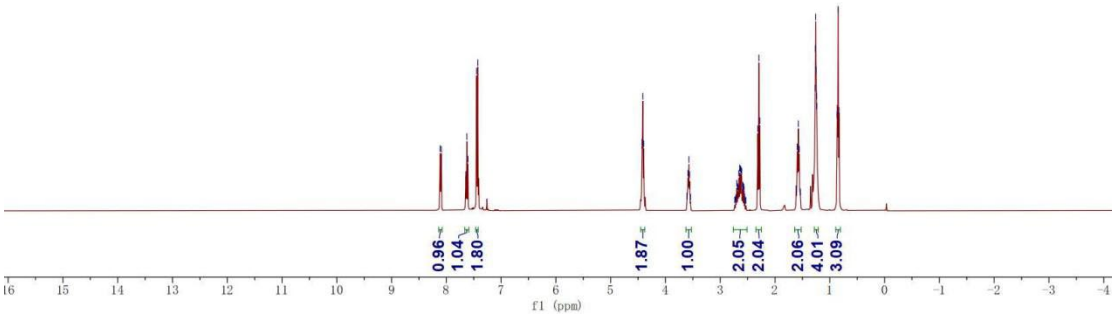
^{19}F NMR, 376 MHz, $CDCl_3$

3aa

35. 1. 1. 1r

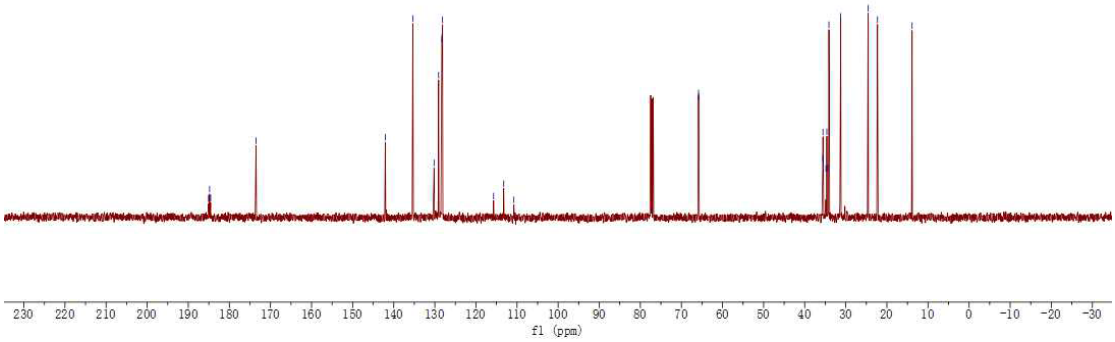


^{1}H NMR, 400 MHz, $CDCl_3$
3ab

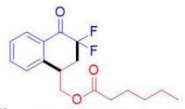


35. 2. 1. 1r

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



35. 3. 1. 1r



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

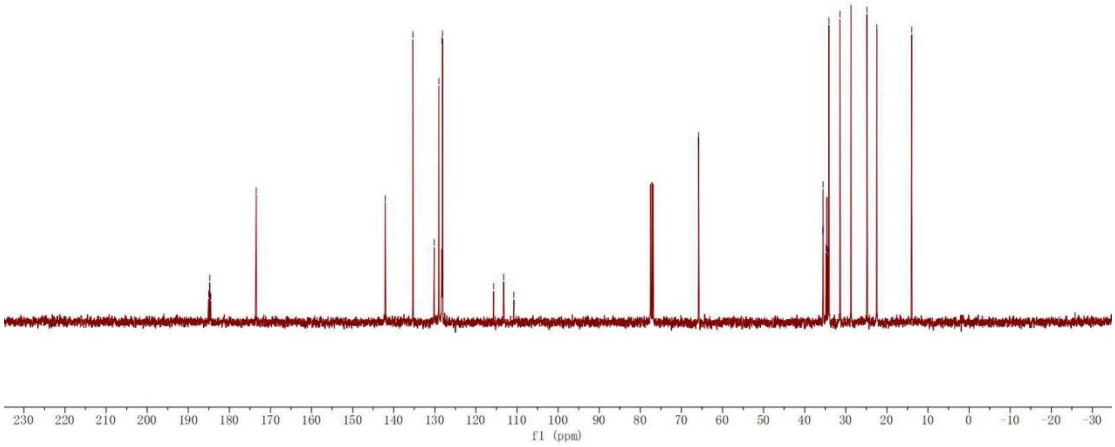
1-5. 1. 1. 1r

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

1-5. 2. 1. 1r

185.03
184.77
184.52
173.46
142.07
135.33
130.15
129.03
128.26
128.13
115.71
113.24
110.78
65.82
65.79
35.58
35.54
35.49
34.81
34.36
34.12
31.40
28.74
24.84
22.45
13.98

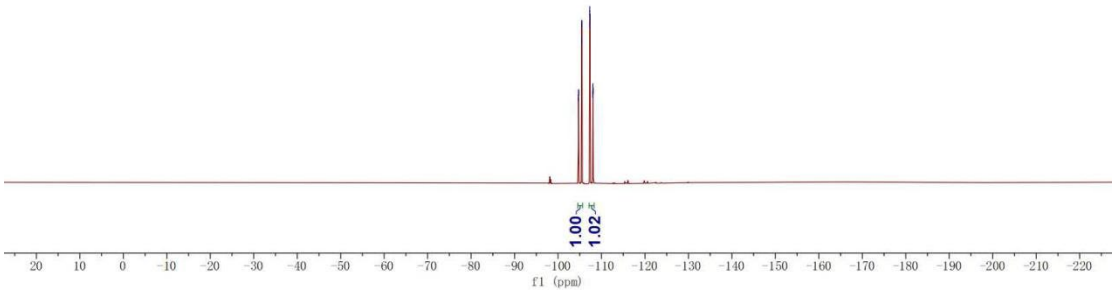
^{13}C NMR, 100 MHz, $CDCl_3$
3ac

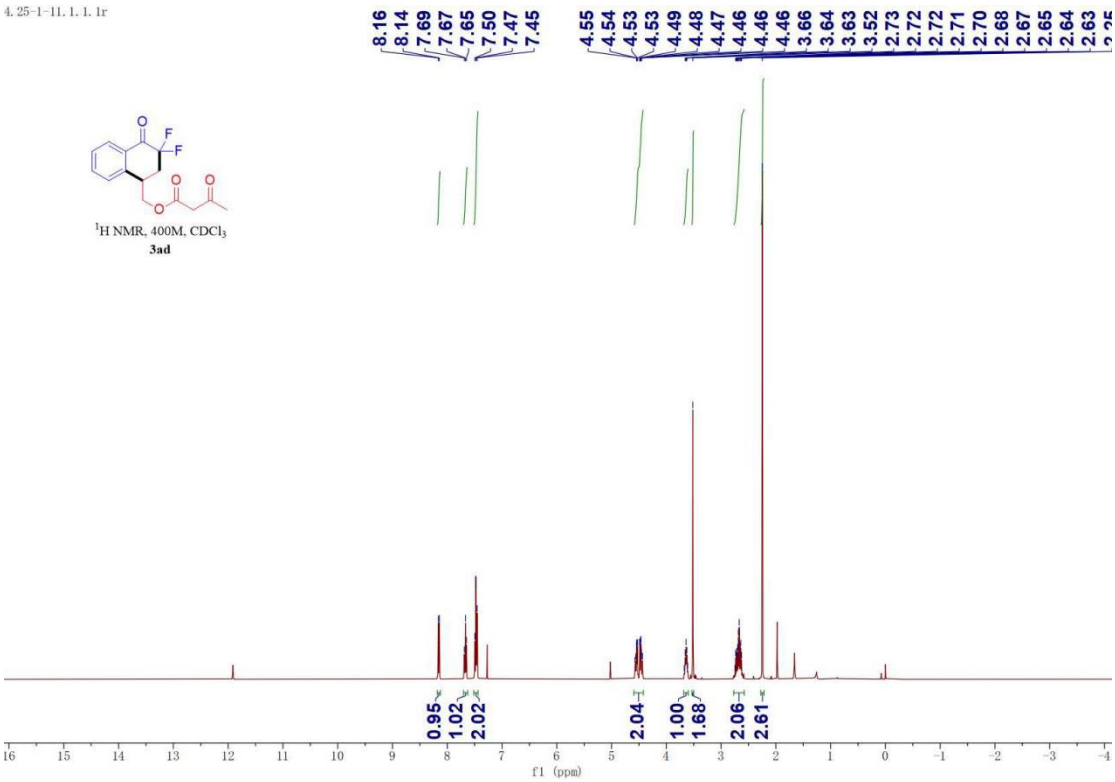


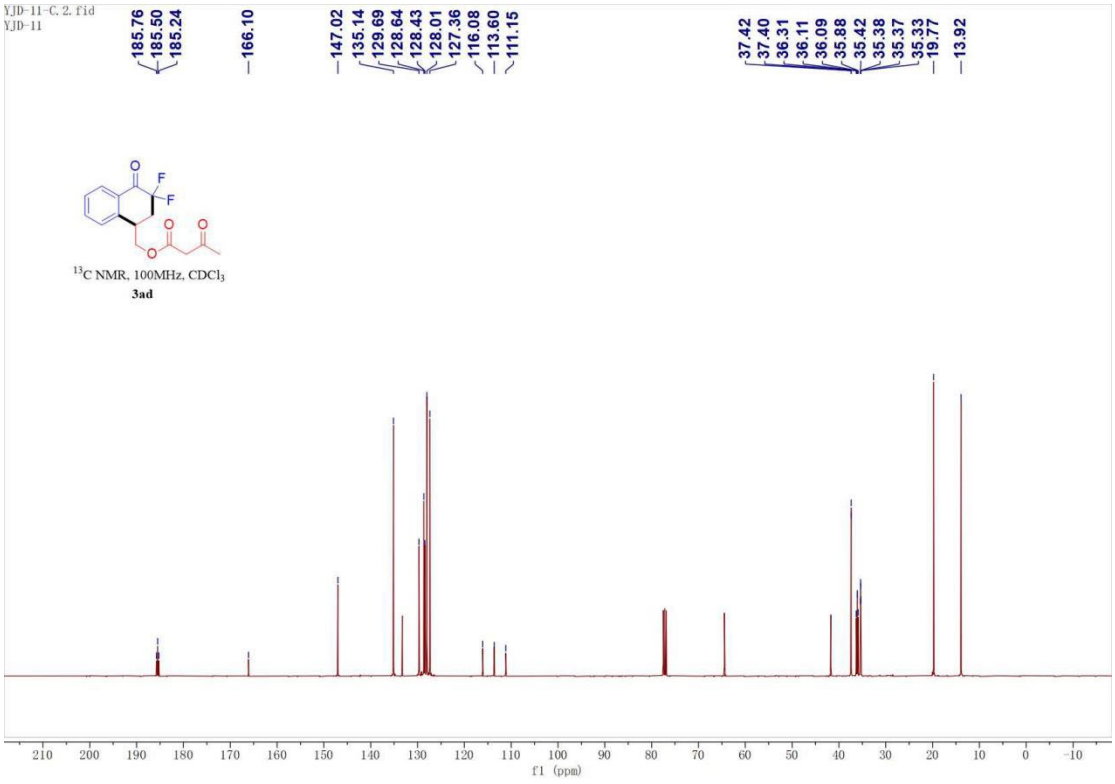
1-5. 3. 1. 1r

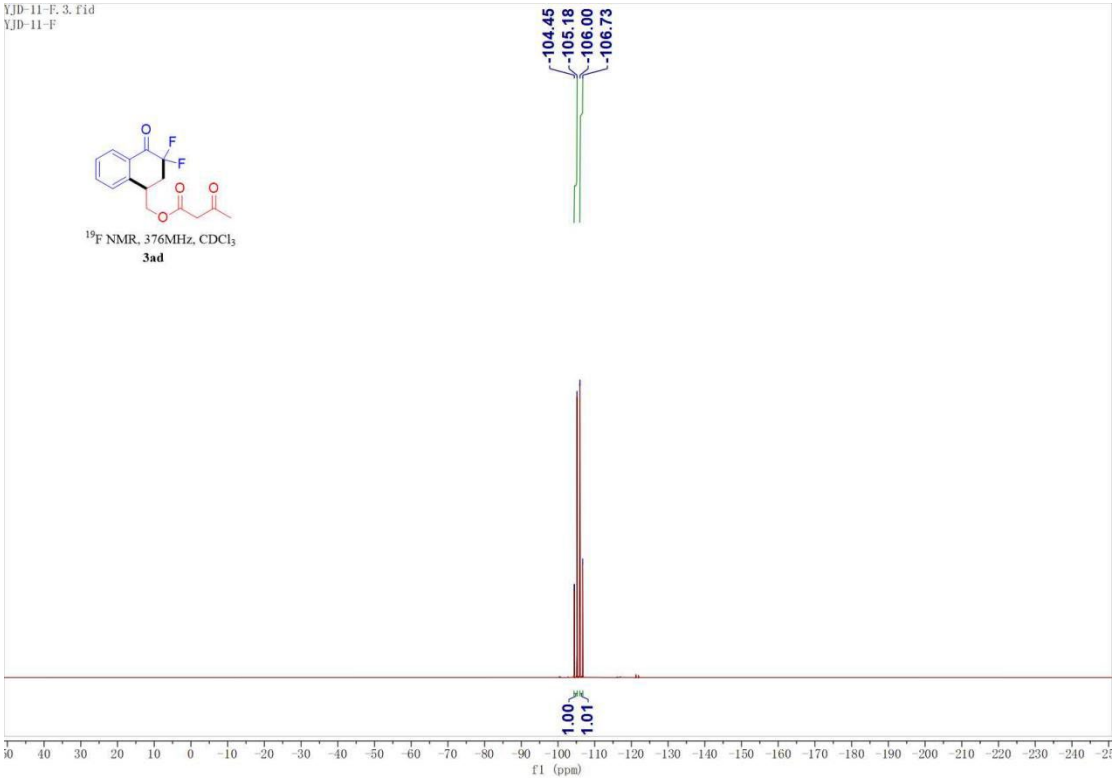
-104.69
-104.72
-104.74
-104.77
-105.42
-105.45
-105.48
-105.50
-107.26
-107.28
-107.31
-107.34
-107.99
-108.02
-108.04
-108.07

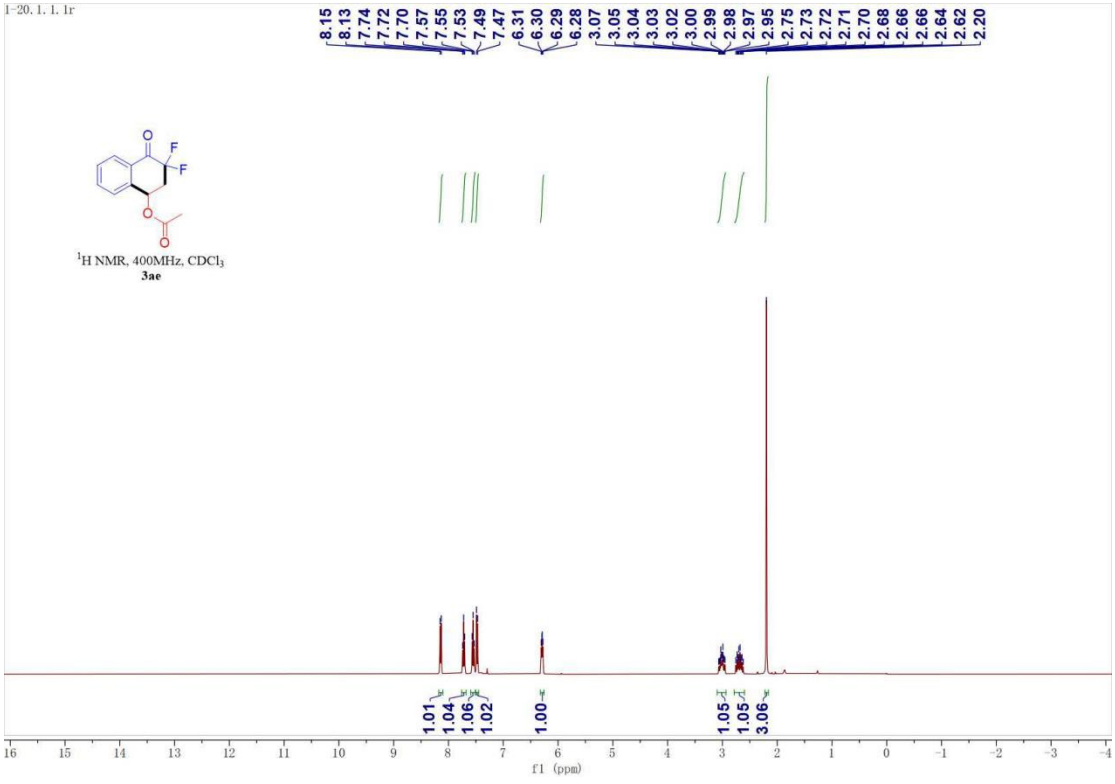
^{19}F NMR, 376 MHz, $CDCl_3$
3ac

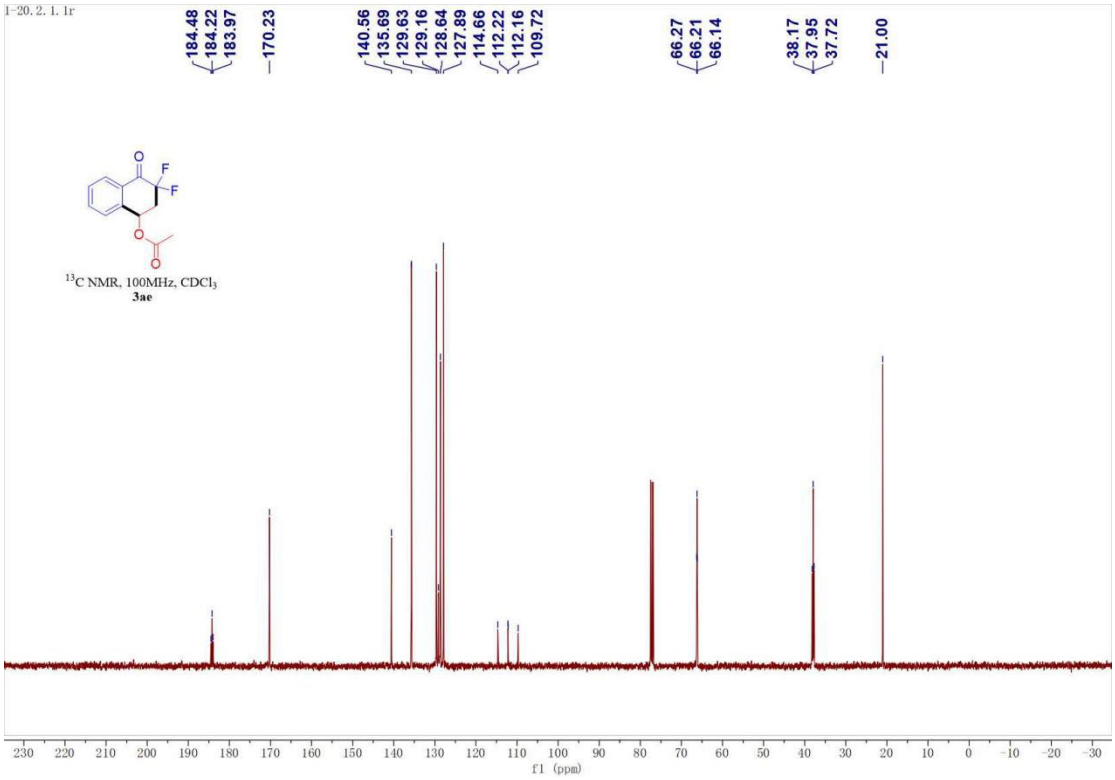


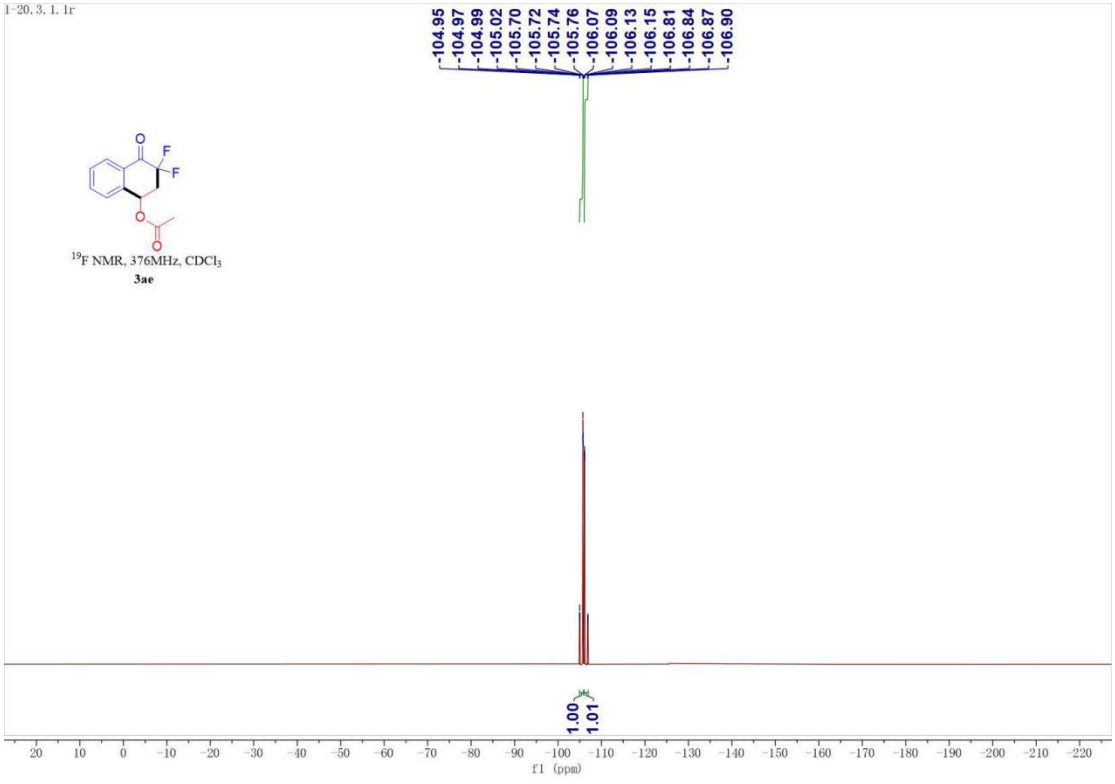

4. 25-1-11. 1. 1. 1r
8.16
8.14
7.69
7.67
7.65
7.50
7.47
7.45
4.55
4.54
4.53
4.53
4.49
4.48
4.47
4.46
4.46
4.46
3.66
3.64
3.63
3.52
2.73
2.72
2.72
2.71
2.70
2.68
2.67
2.65
2.64
2.63
F
F
O
O
O
O
^{1}H NMR, 400M, CDCl$_3$
3ad
0.95
1.02
2.02
2.04
1.00
1.68
2.06
2.61
f1 (ppm)


YJD-11-C. 2. fid
YJD-11
185.76
185.50
185.24
166.10
147.02
135.14
129.69
128.64
128.43
128.01
127.36
116.08
113.60
111.15
37.42
37.40
36.31
36.11
36.09
35.88
35.42
35.38
35.37
35.33
19.77
13.92
F
F
O
O
O
O
^{13}C NMR, 100MHz, CDCl$_3$
3ad
f1 (ppm)

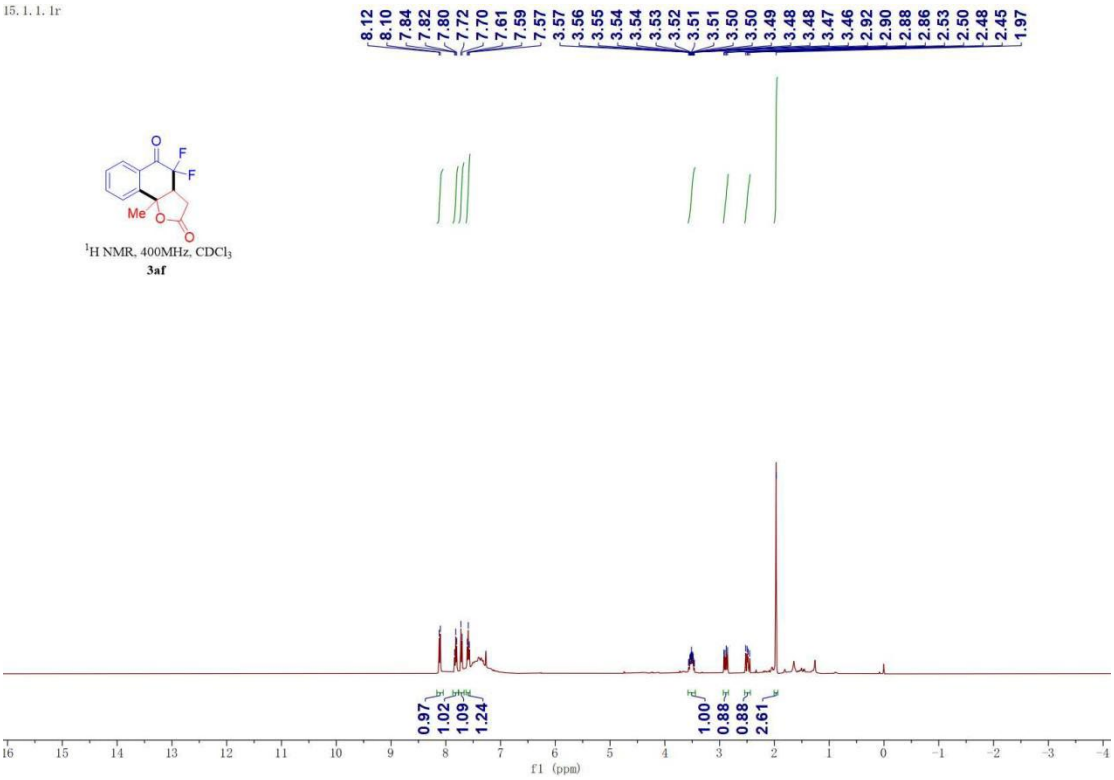

YJD-11-F. 3. fid
YJD-11-F
-104.45
-105.18
-106.00
-106.73
F
F
O
O
O
O
^{19}F NMR, 376MHz, CDCl$_3$
3ad
1.00
1.01
f1 (ppm)


1-20. 1. 1. 1r
8.15
8.13
7.74
7.72
7.70
7.57
7.55
7.53
7.49
7.47
6.31
6.30
6.29
6.28
3.07
3.05
3.04
3.03
3.02
3.00
2.99
2.98
2.97
2.95
2.75
2.73
2.72
2.71
2.70
2.68
2.66
2.66
2.64
2.62
2.20
F
F
O
O
^{1}H NMR, 400MHz, CDCl$_3$
3ae
1.01
1.04
1.06
1.02
1.00
1.05
1.05
3.06
f1 (ppm)


1-20.2.1.1r
184.48
184.22
183.97
170.23
140.56
135.69
129.63
129.16
128.64
127.89
114.66
112.22
112.16
109.72
66.27
66.21
66.14
38.17
37.95
37.72
21.00
F
F
O
O
O
13C NMR, 100MHz, CDCl3
3ae
f1 (ppm)


1-20.3.1.1r
-104.95
-104.97
-104.99
-105.02
-105.70
-105.72
-105.74
-105.76
-106.07
-106.09
-106.13
-106.15
-106.81
-106.84
-106.87
-106.90
F
F
O
O
O
19F NMR, 376MHz, CDCl3
3ae
1.00
1.01
f1 (ppm)

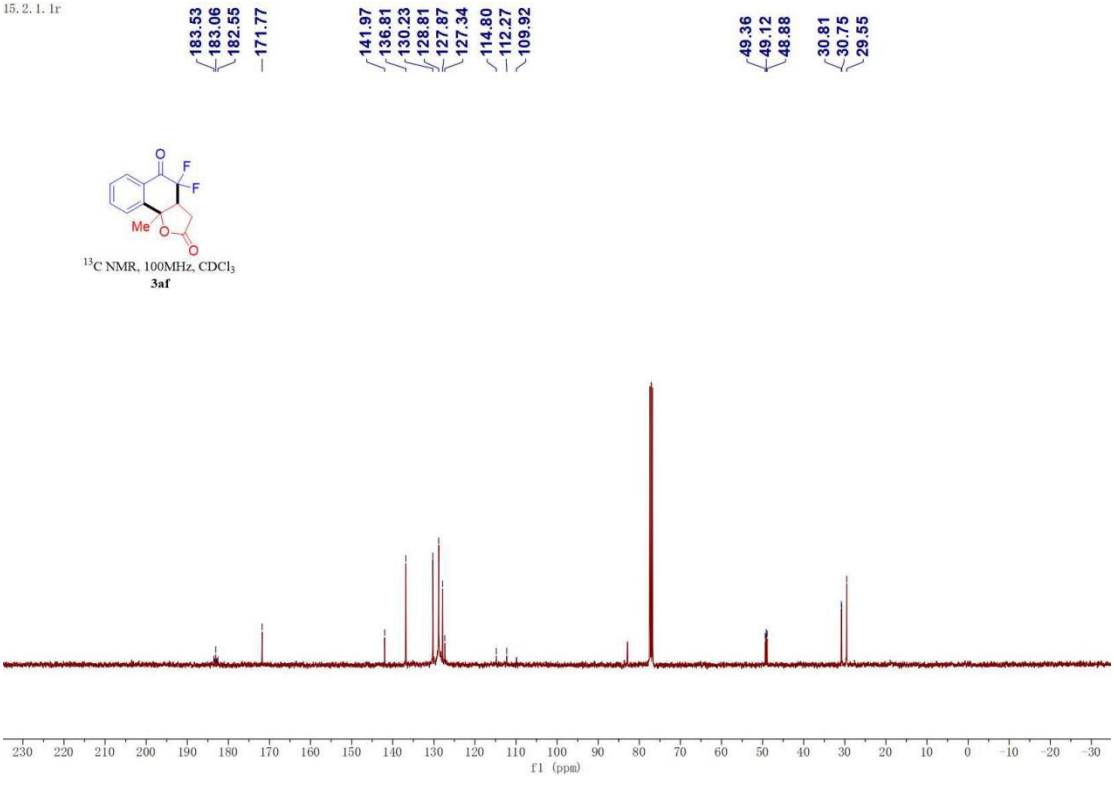
15. 1. 1. 1r



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

3af

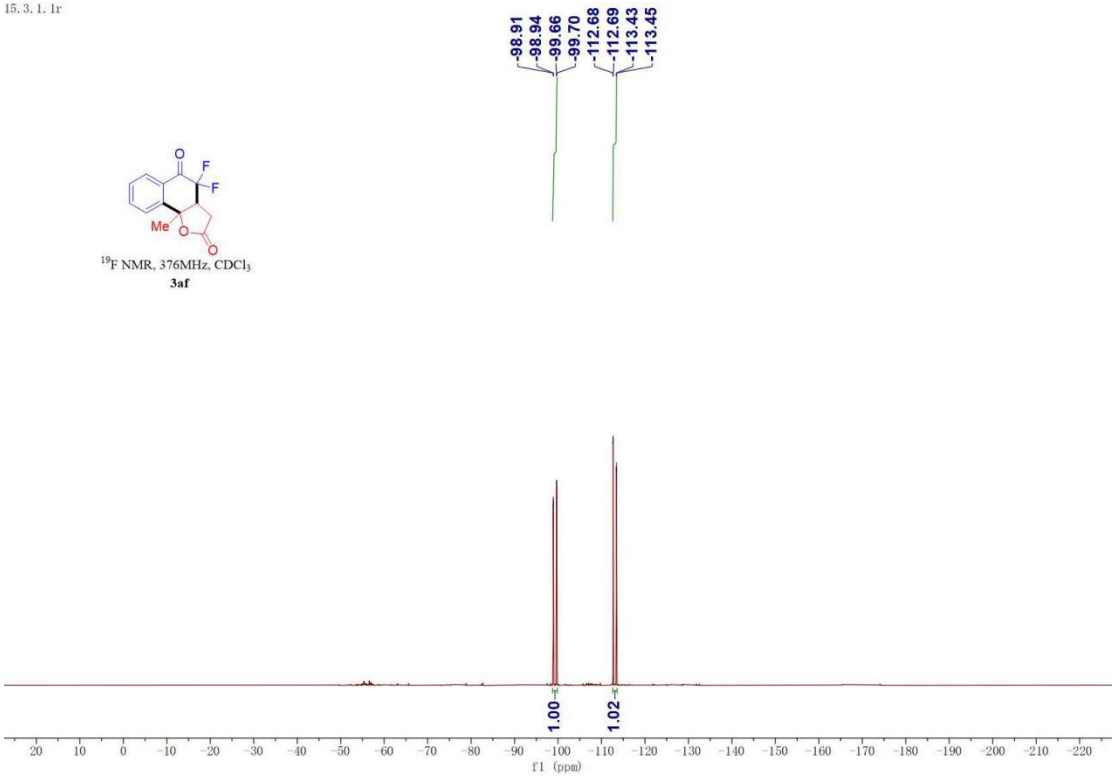
15. 2. 1. 1r



^{13}C NMR, 100MHz, $CDCl_3$

3af

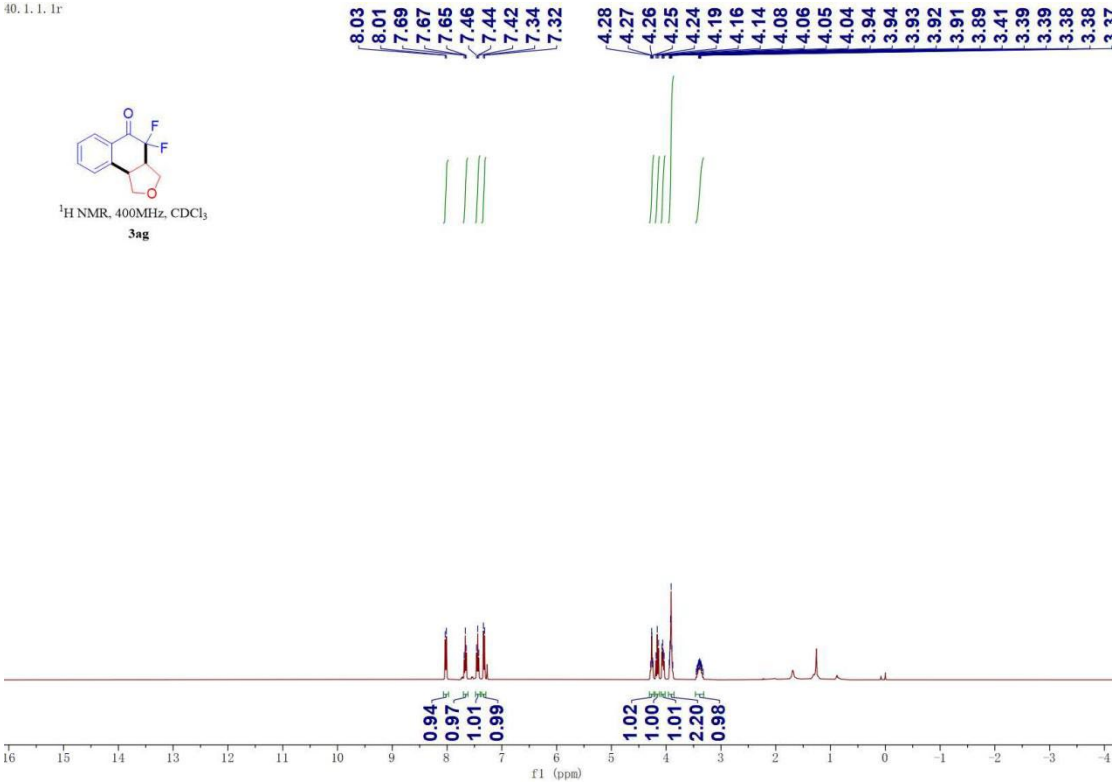
15. 3. 1. 1r



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

3af

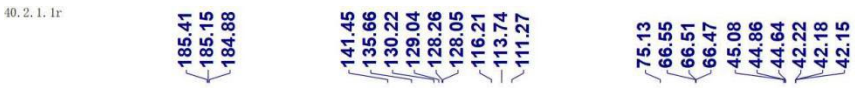
40. 1. 1. 1r



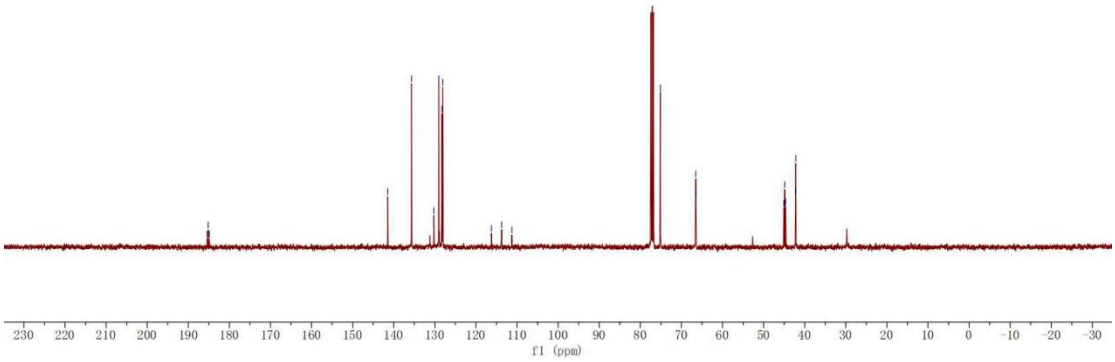
^{1}H NMR, 400MHz, $CDCl_3$

3ag

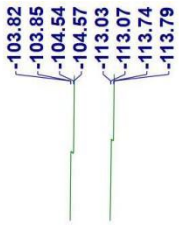
40. 2. 1. 1r



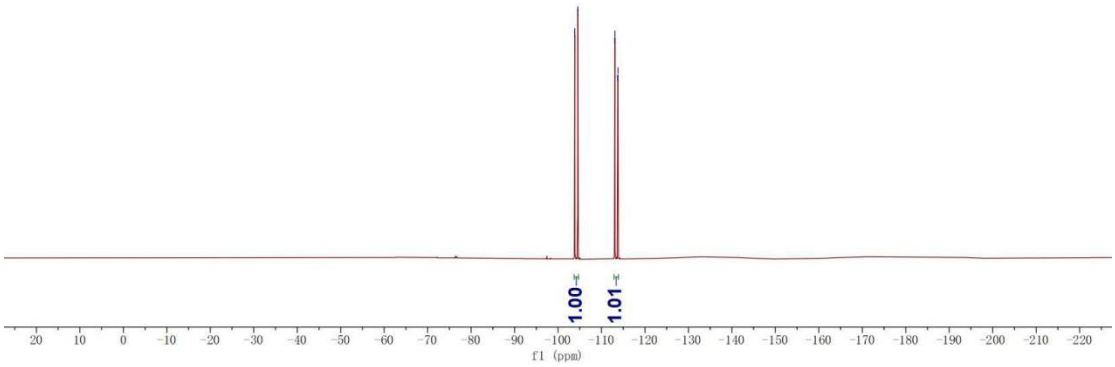
^{13}C NMR, 100MHz, $CDCl_3$
3ag

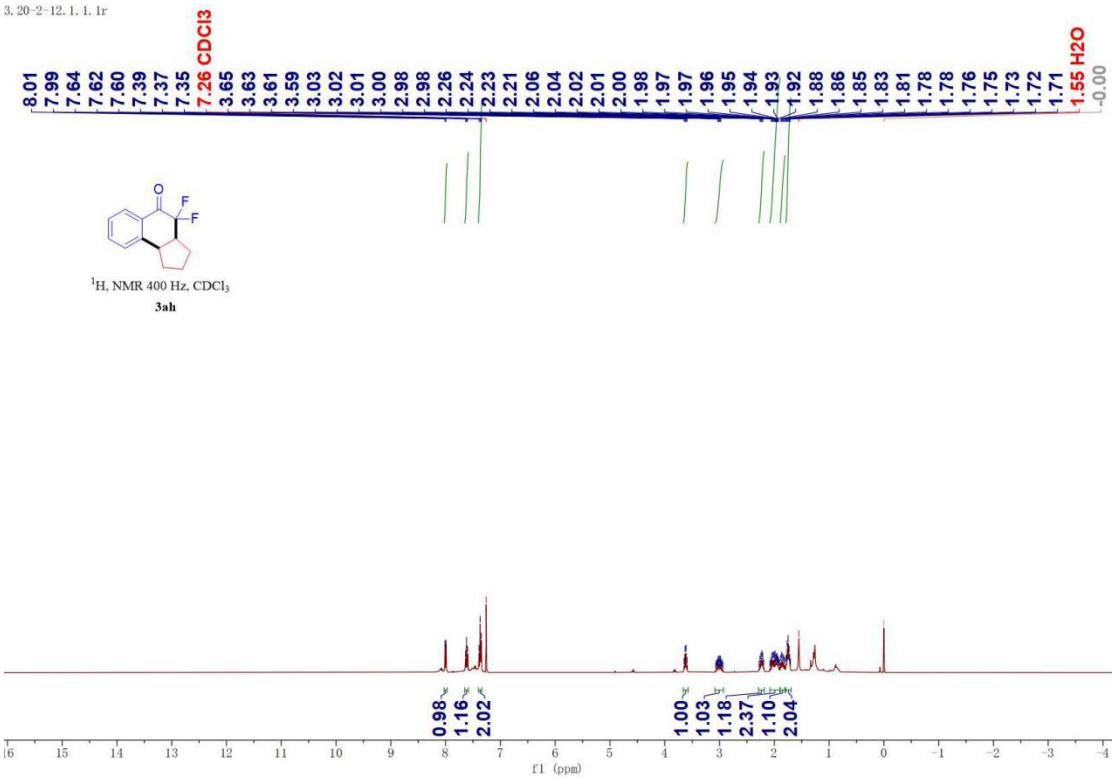


40. 3. 1. 1r



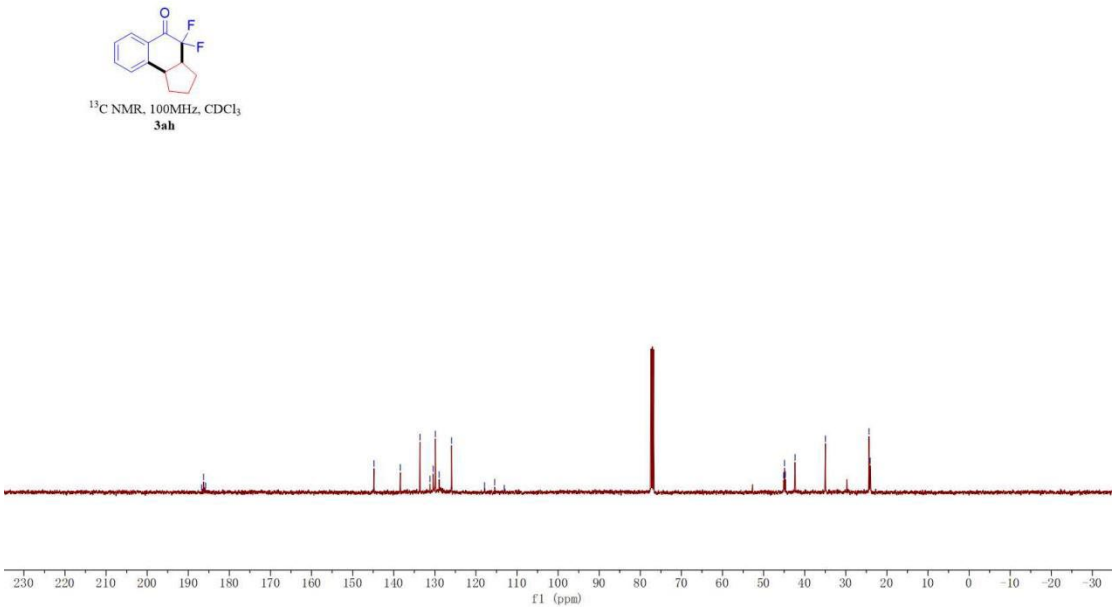
^{19}F NMR, 376MHz, $CDCl_3$
3ag





^{1}H, NMR 400 Hz, $CDCl_3$

3ah

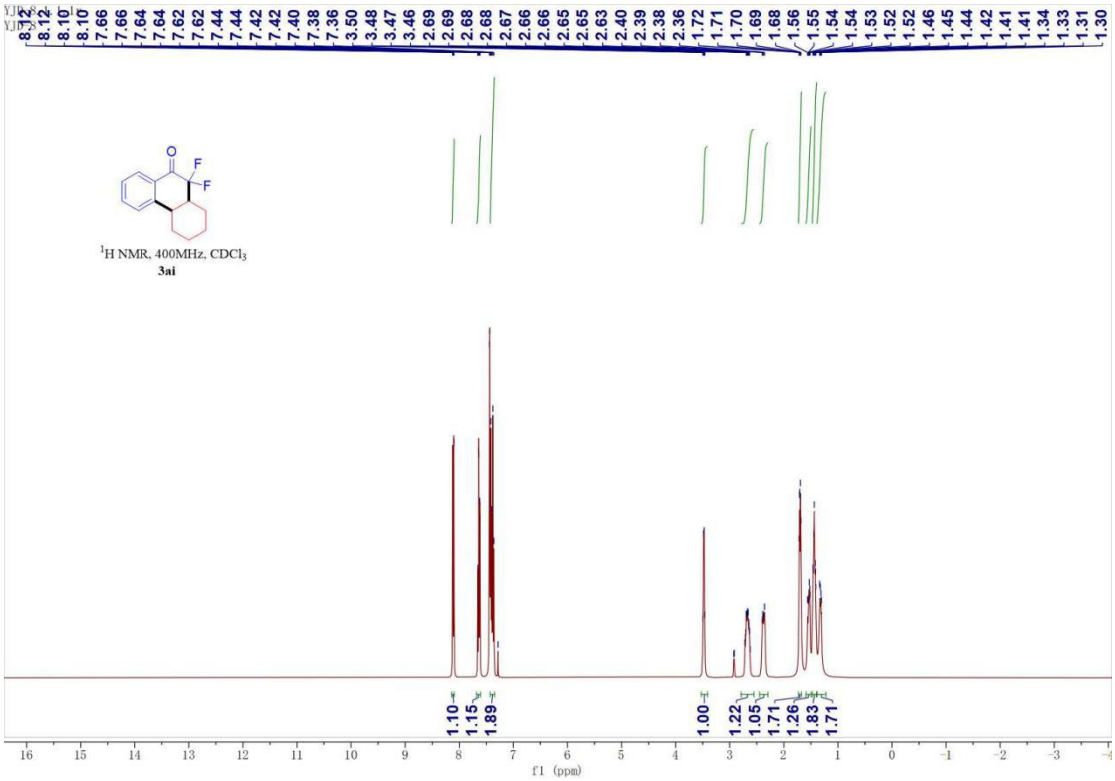


^{13}C NMR, 100MHz, $CDCl_3$

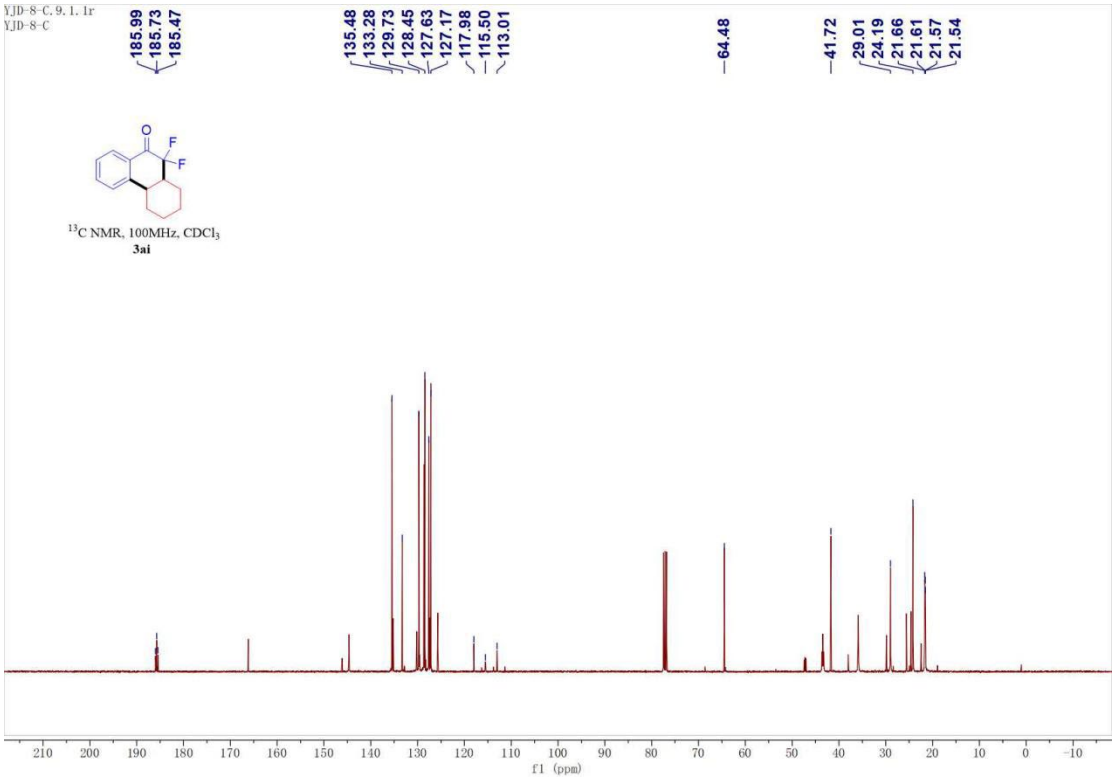
3ah

3.20-2-12.3.1.1r

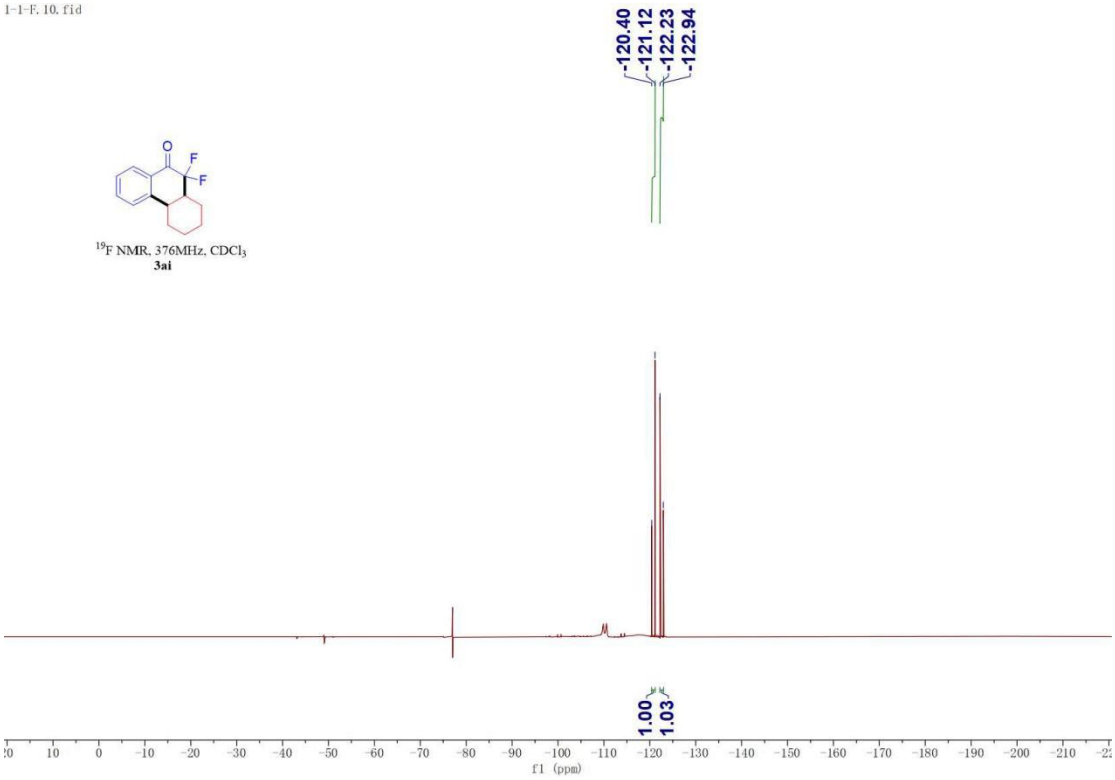
^{19}F NMR, 376MHz, $CDCl_3$
3ah



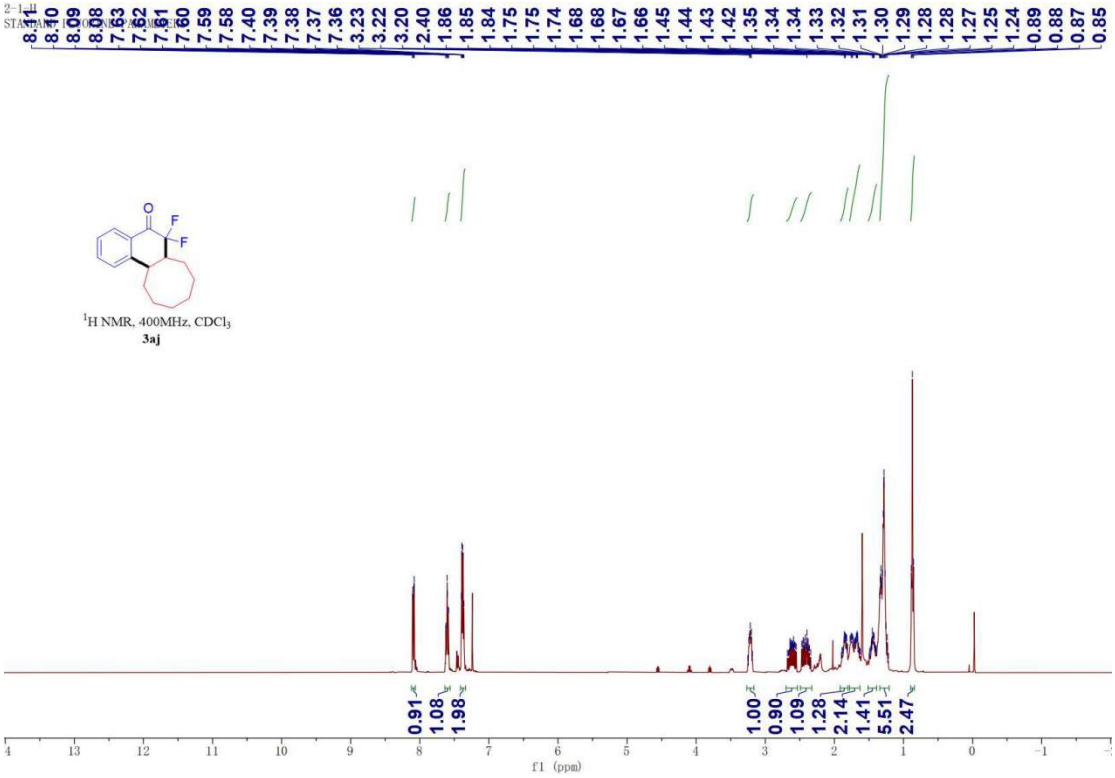
^{1}H NMR, 400MHz, $CDCl_3$
3ai



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

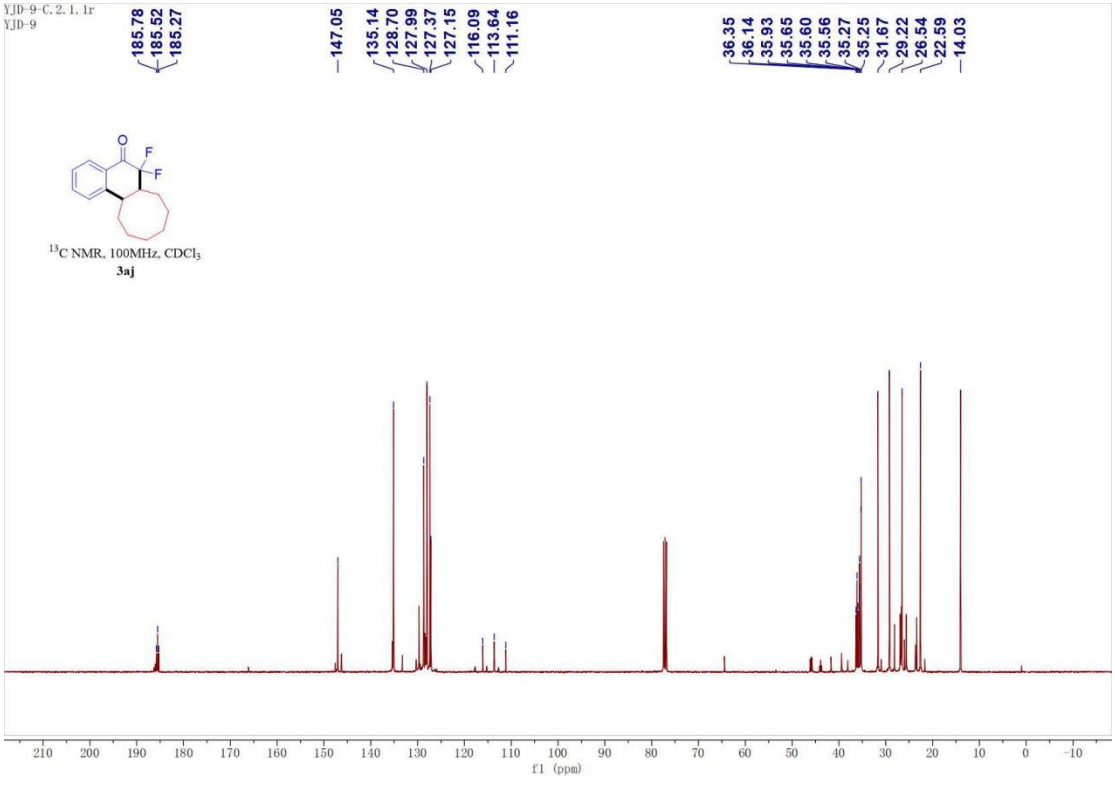


^{19}F NMR, 376MHz, $CDCl_3$
3ai



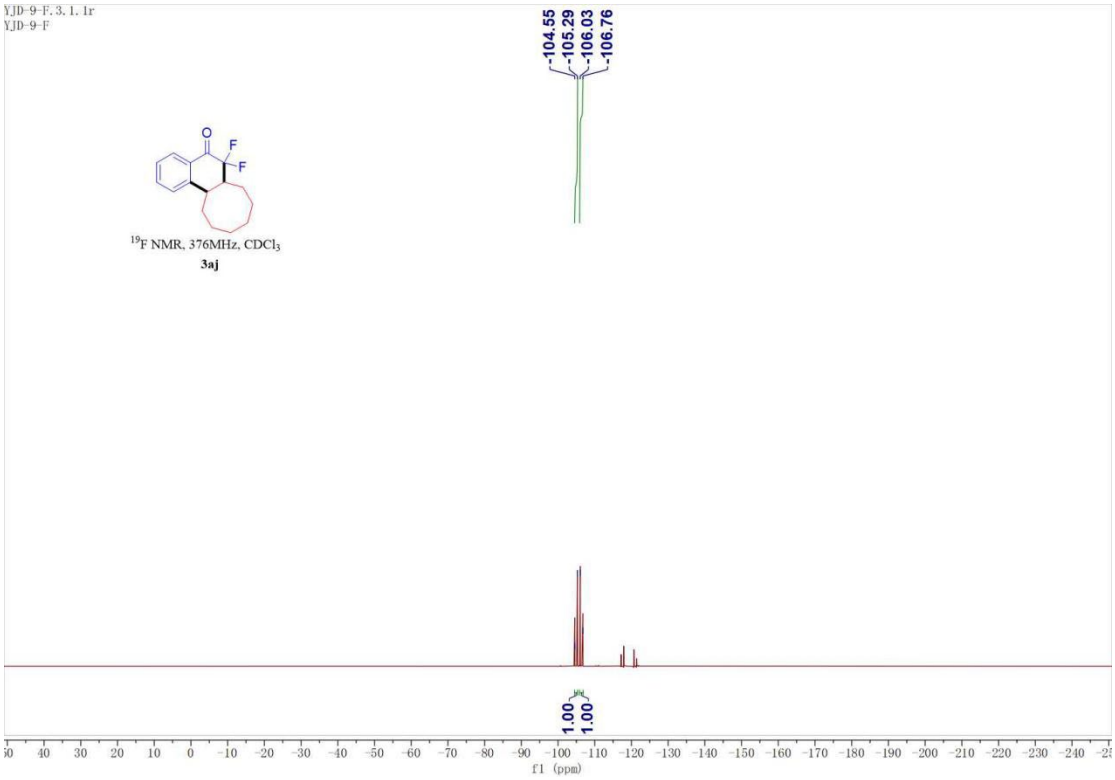
^{1}H NMR, 400MHz, $CDCl_3$

3aj



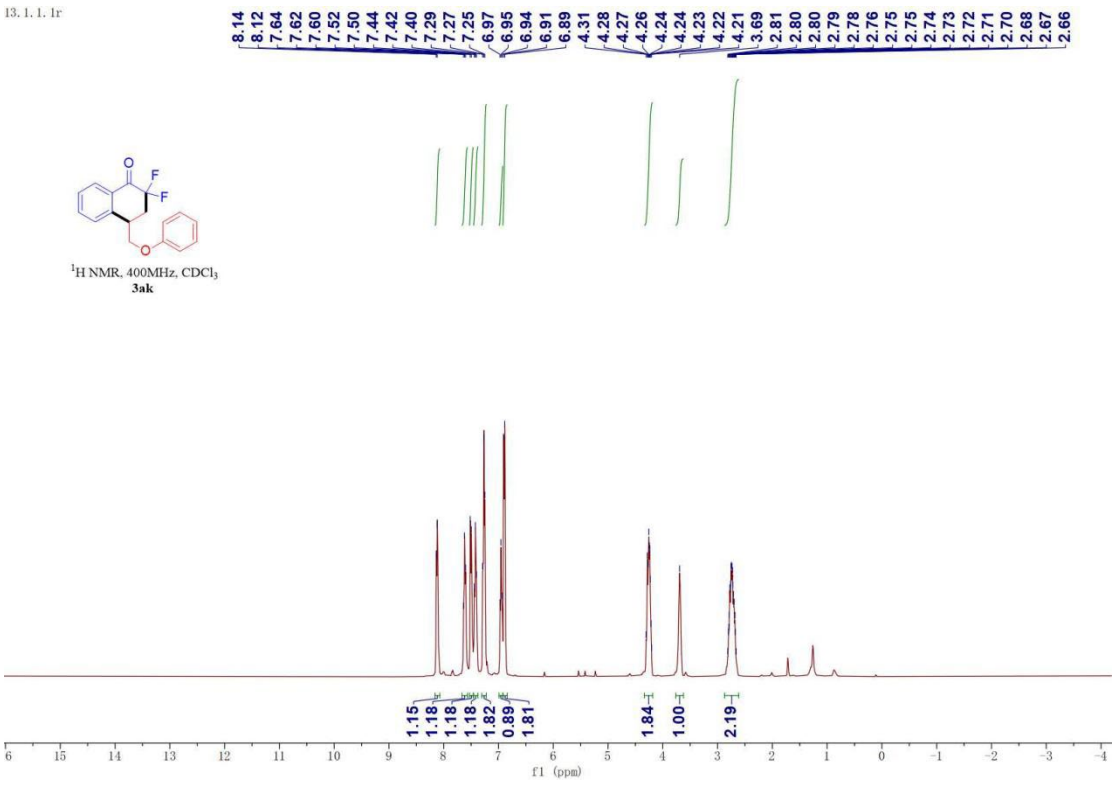
^{13}C NMR, 100MHz, $CDCl_3$

3aj



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

3aj



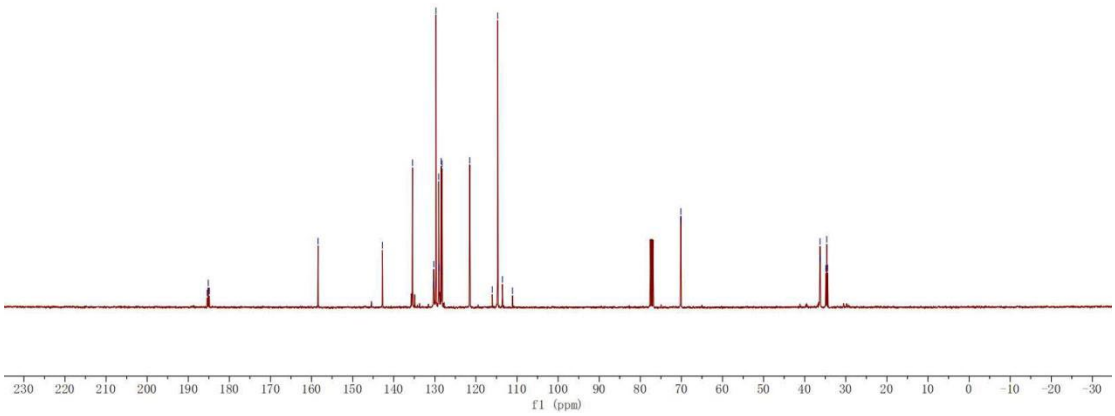
^{1}H NMR, 400MHz, $CDCl_3$

3ak

13. 2. 2. 1. 1r

185.39
185.13
184.87
158.40
142.76
135.42
130.36
130.24
129.73
129.06
128.99
128.47
128.27
121.52
116.03
114.69
113.57
111.10
70.16
70.13
36.33
36.28
36.23
34.87
34.64
34.42

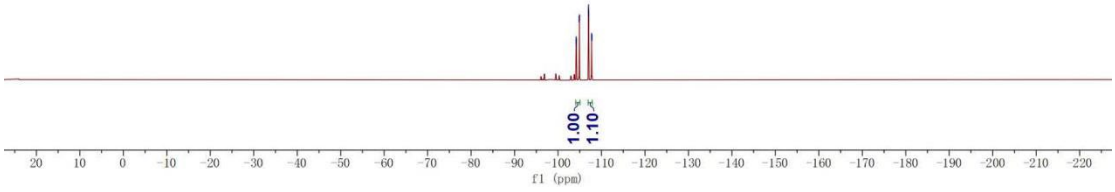
^{13}C NMR, 100MHz, $CDCl_3$
3ak



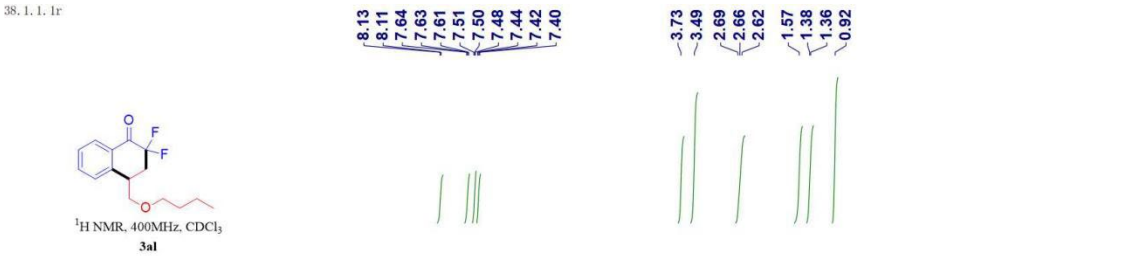
13. 3. 3. 1. 1r

-104.13
-104.16
-104.19
-104.22
-104.86
-104.89
-104.92
-104.95
-106.96
-106.99
-107.02
-107.05
-107.70
-107.72
-107.75
-107.78

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

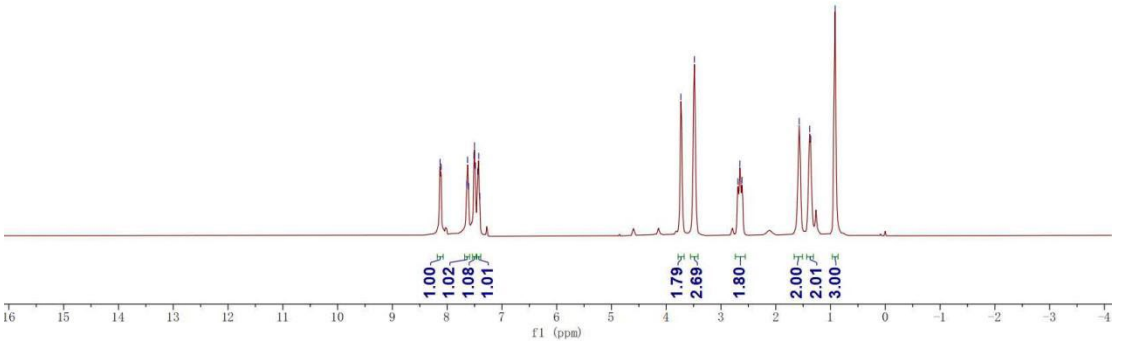


38. 1. 1. 1r



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

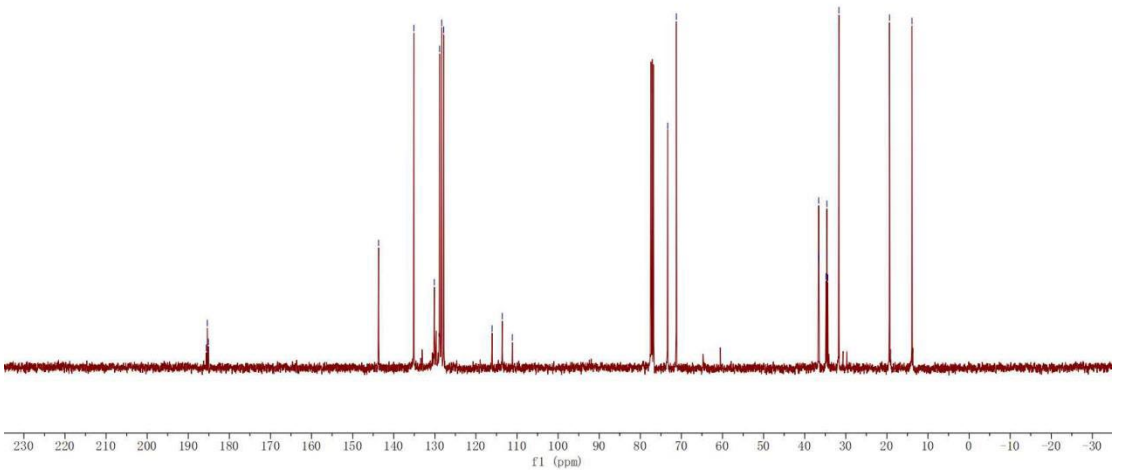
3al



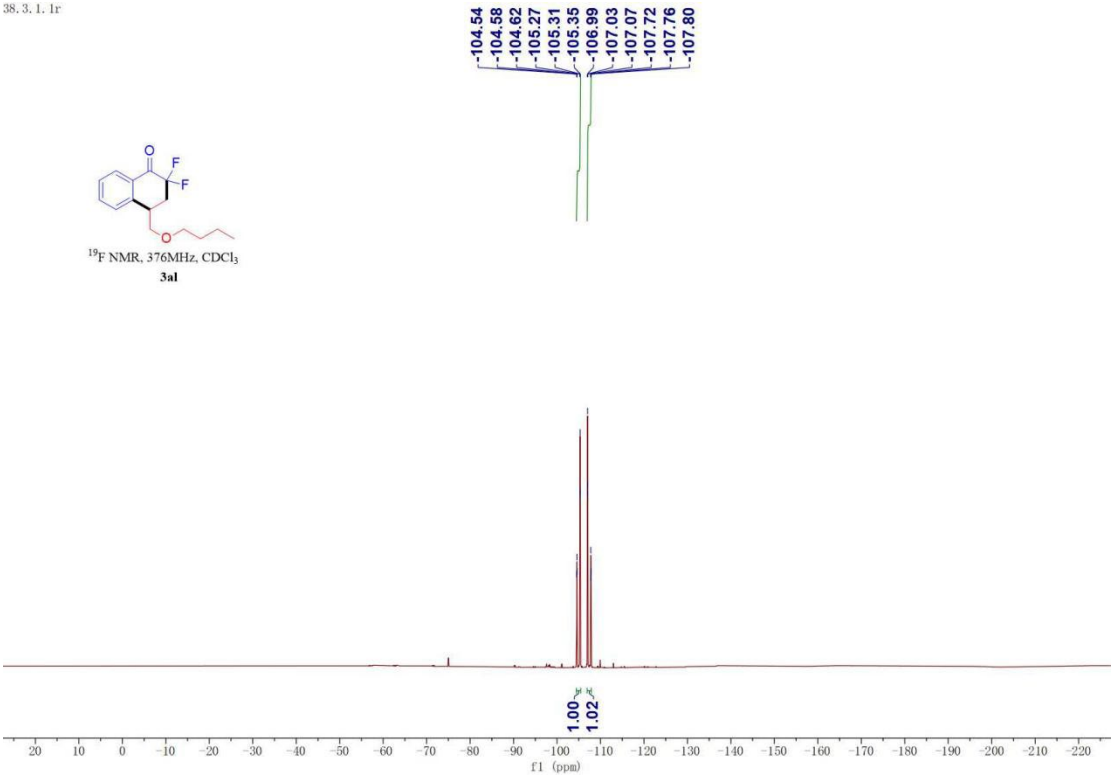
38. 2. 1. 1r

^{13}C NMR, 100MHz, $CDCl_3$

3al



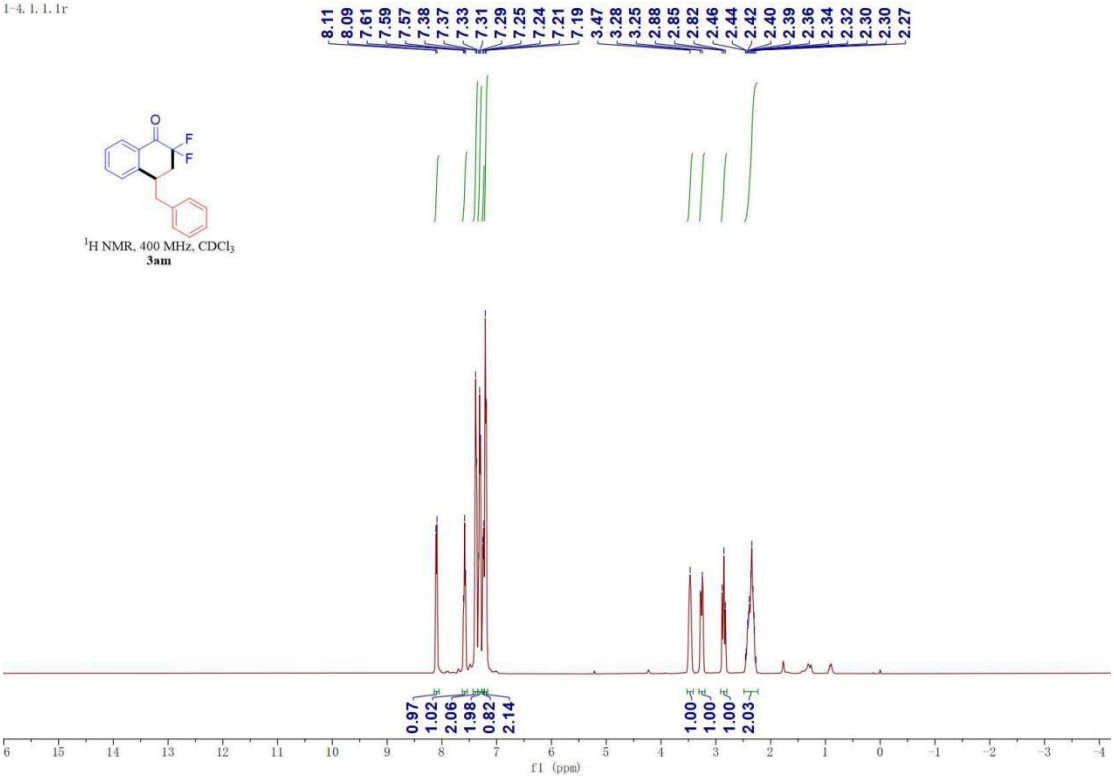
38. 3. 1. 1r



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

3al

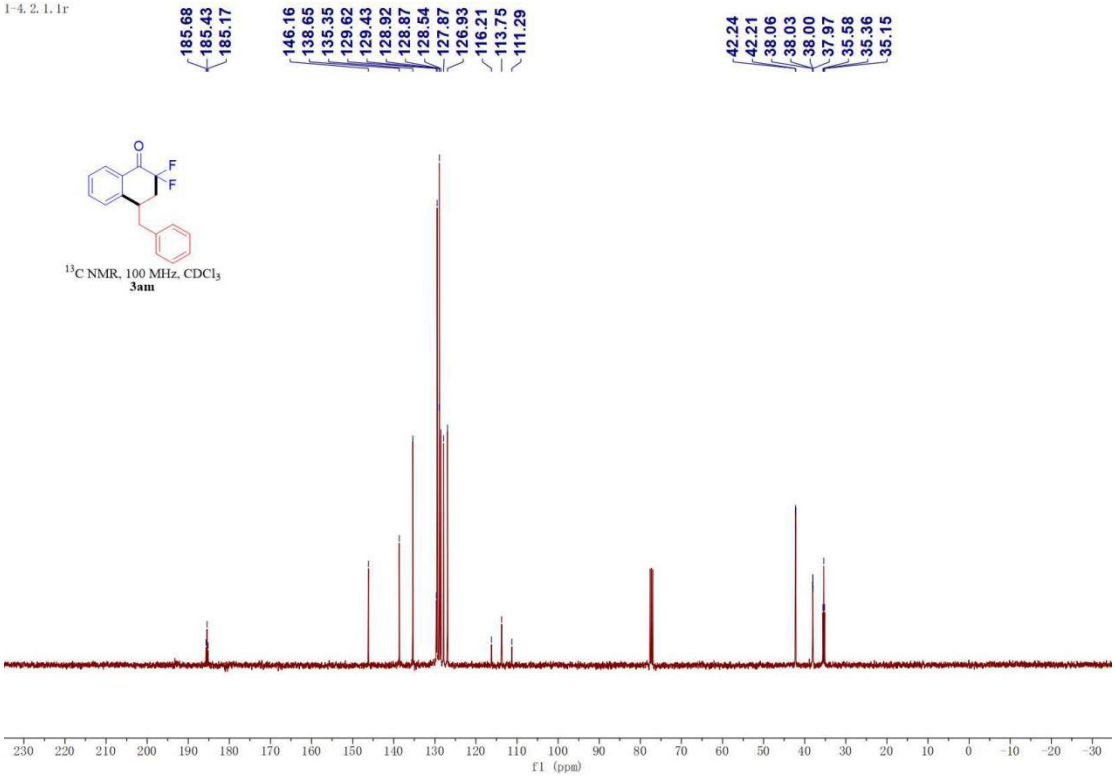
1-4. 1. 1. 1r



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

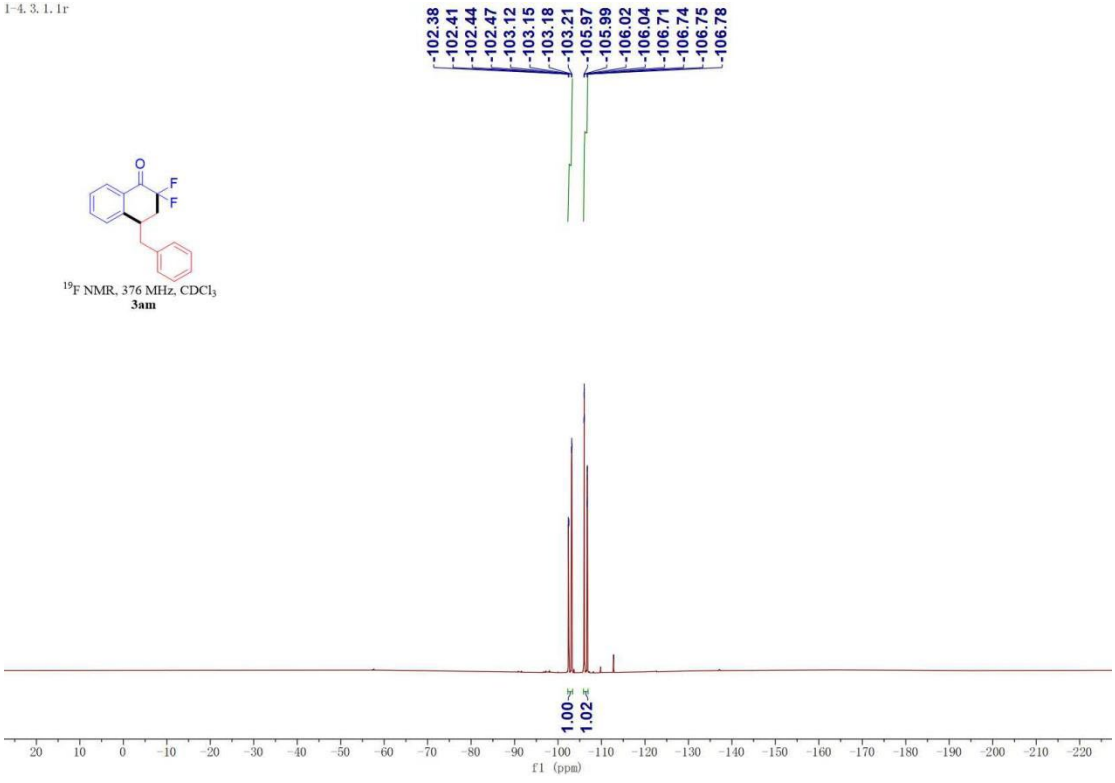
3am

1-4. 2. 1. 1r

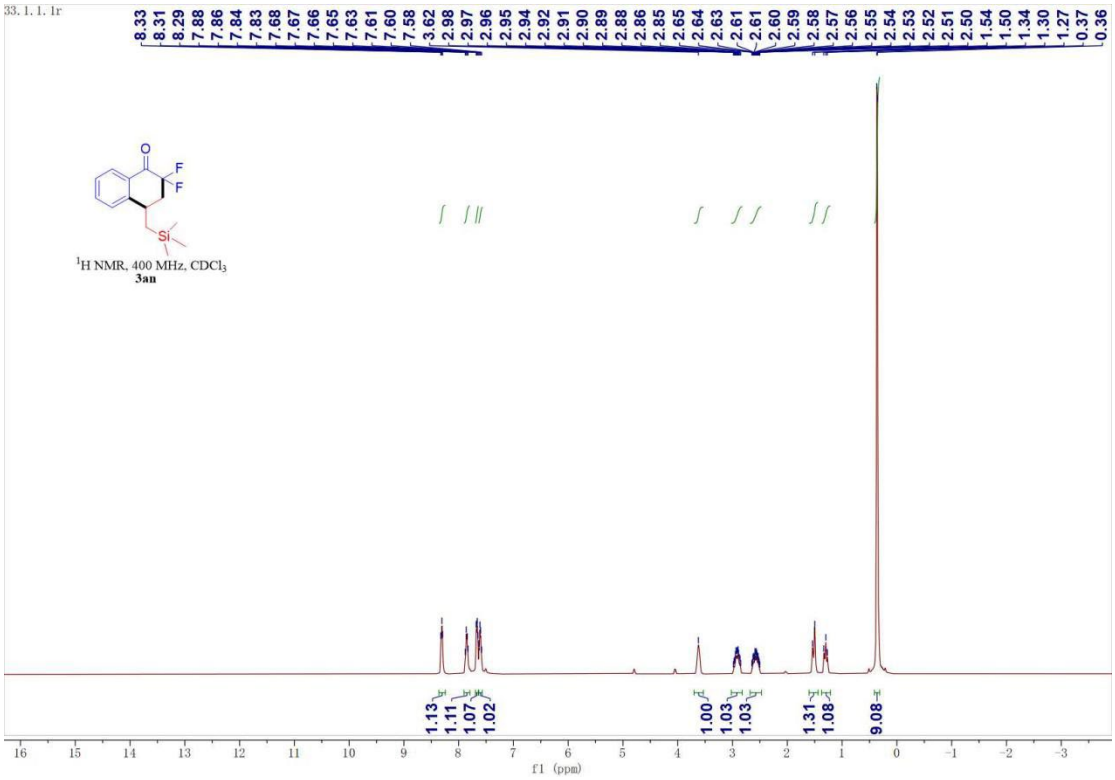


^{13}C NMR, 100 MHz, $CDCl_3$
3am

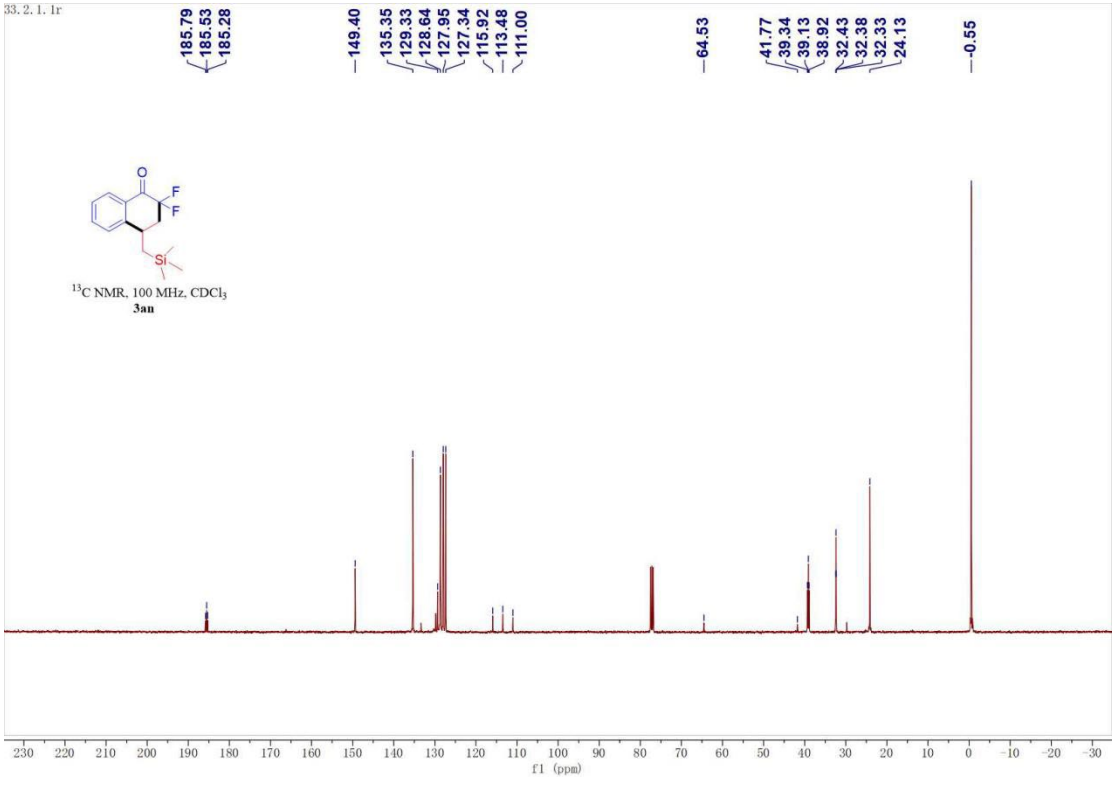
1-4. 3. 1. 1r



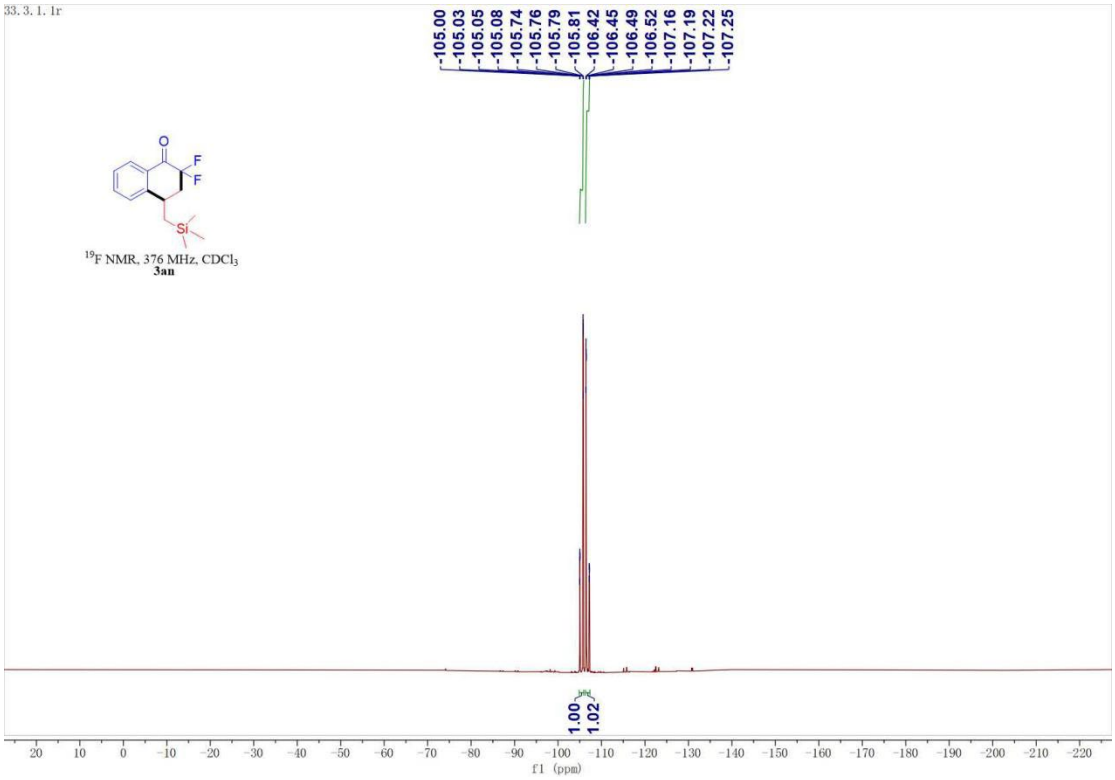
^{19}F NMR, 376 MHz, $CDCl_3$
3am



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

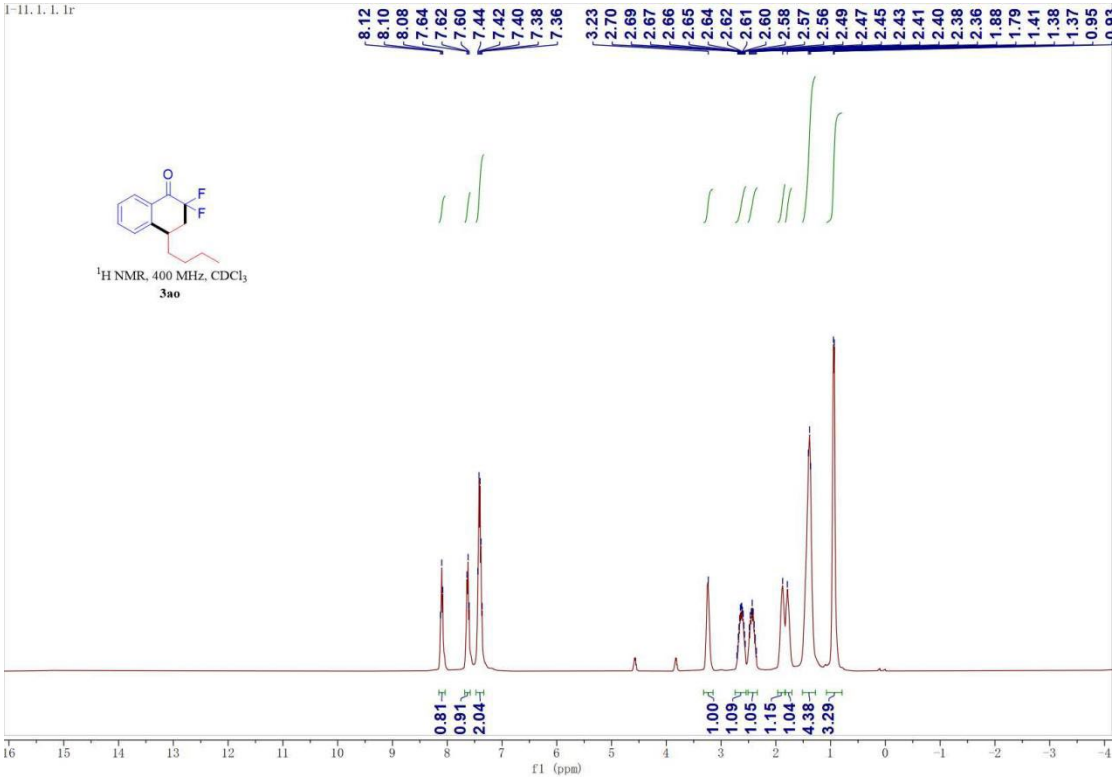


^{13}C NMR, 100 MHz, $CDCl_3$
3an



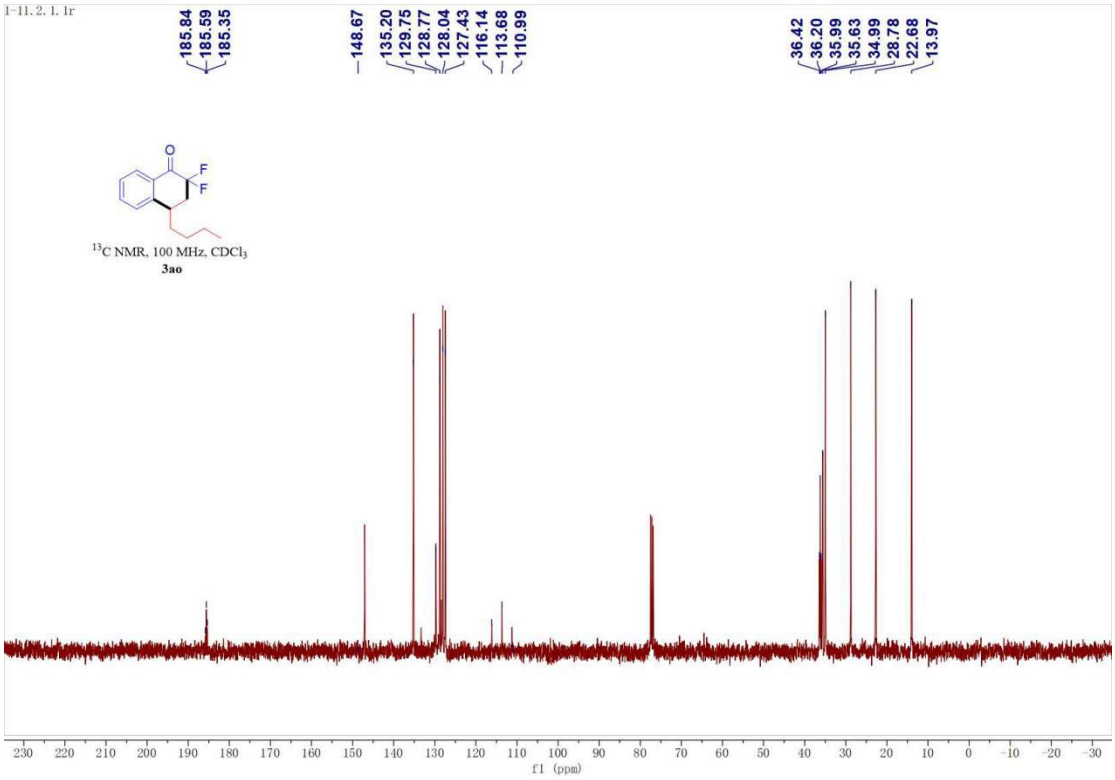
^{19}F NMR, 376 MHz, $CDCl_3$

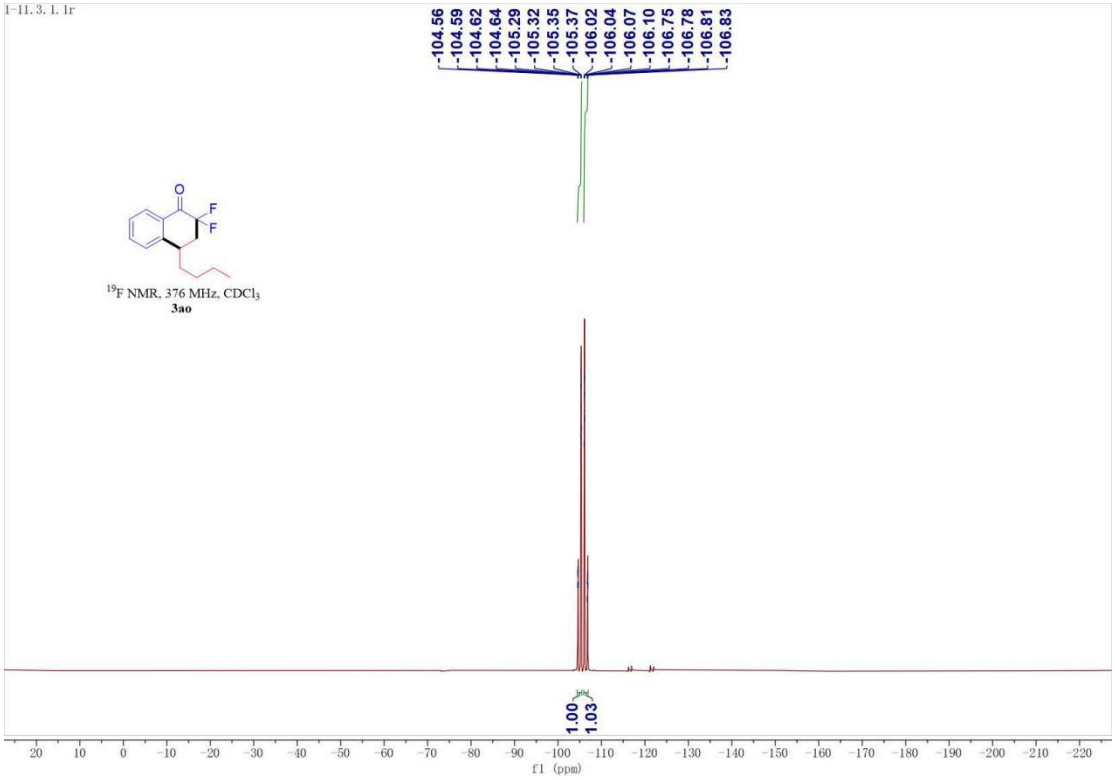
3au

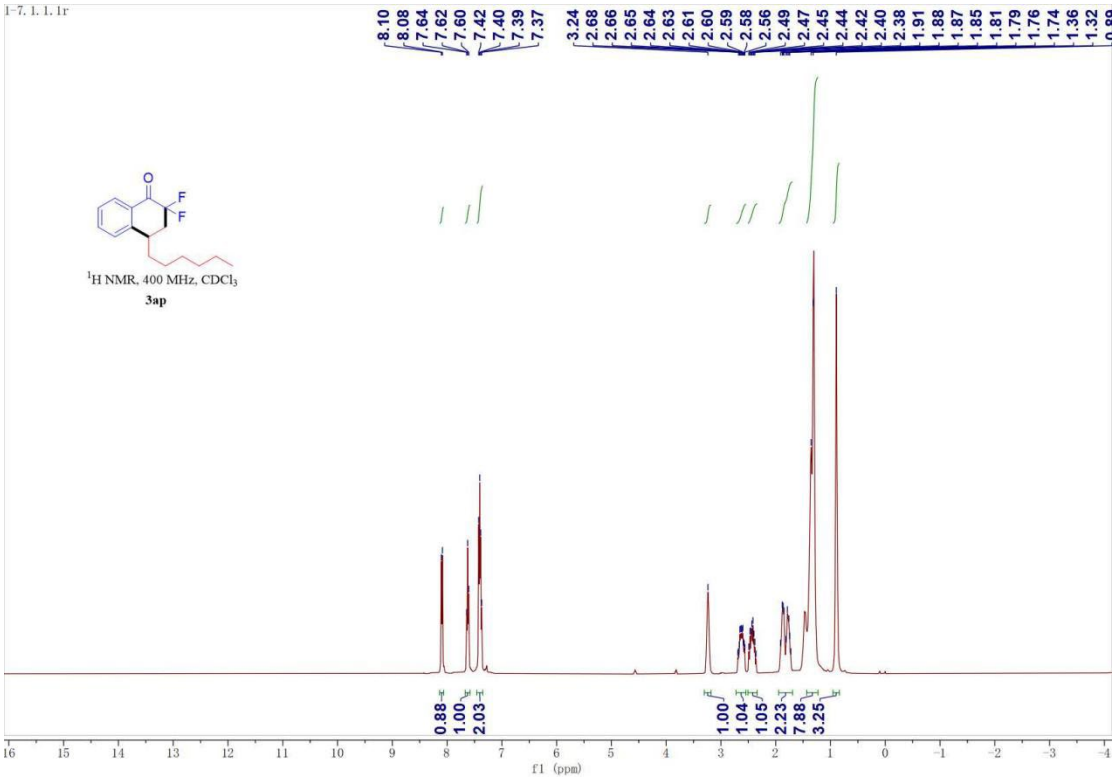


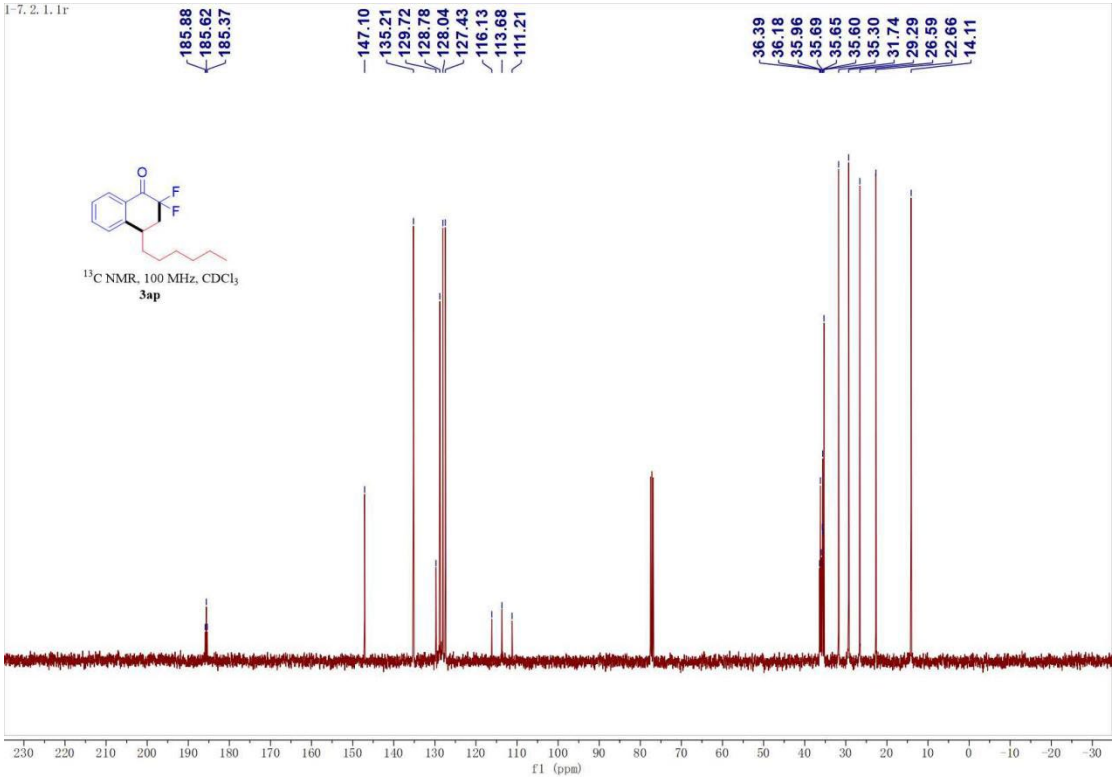
^{1}H NMR, 400 MHz, $CDCl_3$

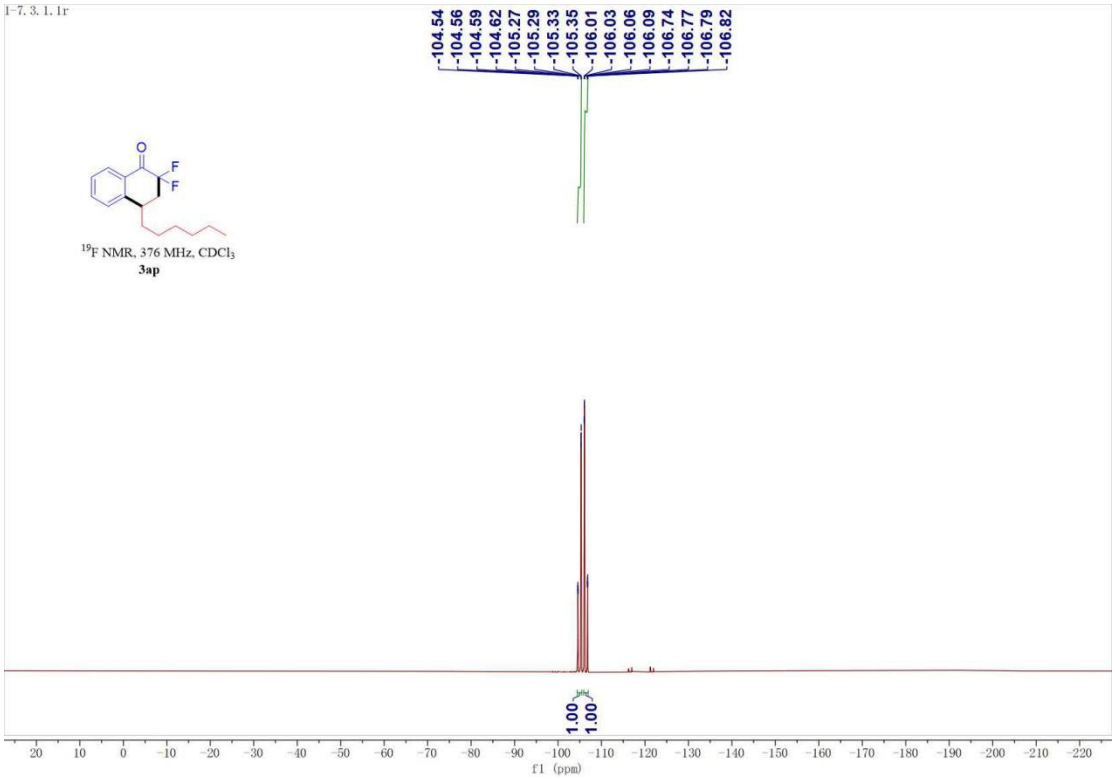
3ao


185.84
185.59
185.35
148.67
135.20
129.75
128.77
128.04
127.43
116.14
113.68
110.99
36.42
36.20
35.99
35.63
34.99
28.78
22.68
13.97
F
F
O
^{13}C NMR, 100 MHz, $CDCl_3$
3ao
f1 (ppm)


-104.56
-104.59
-104.62
-104.64
-105.29
-105.32
-105.35
-105.37
-106.02
-106.04
-106.07
-106.10
-106.75
-106.78
-106.81
-106.83
1.00
1.03
F
F
O
^{19}F NMR, 376 MHz, $CDCl_3$
3ao
f1 (ppm)

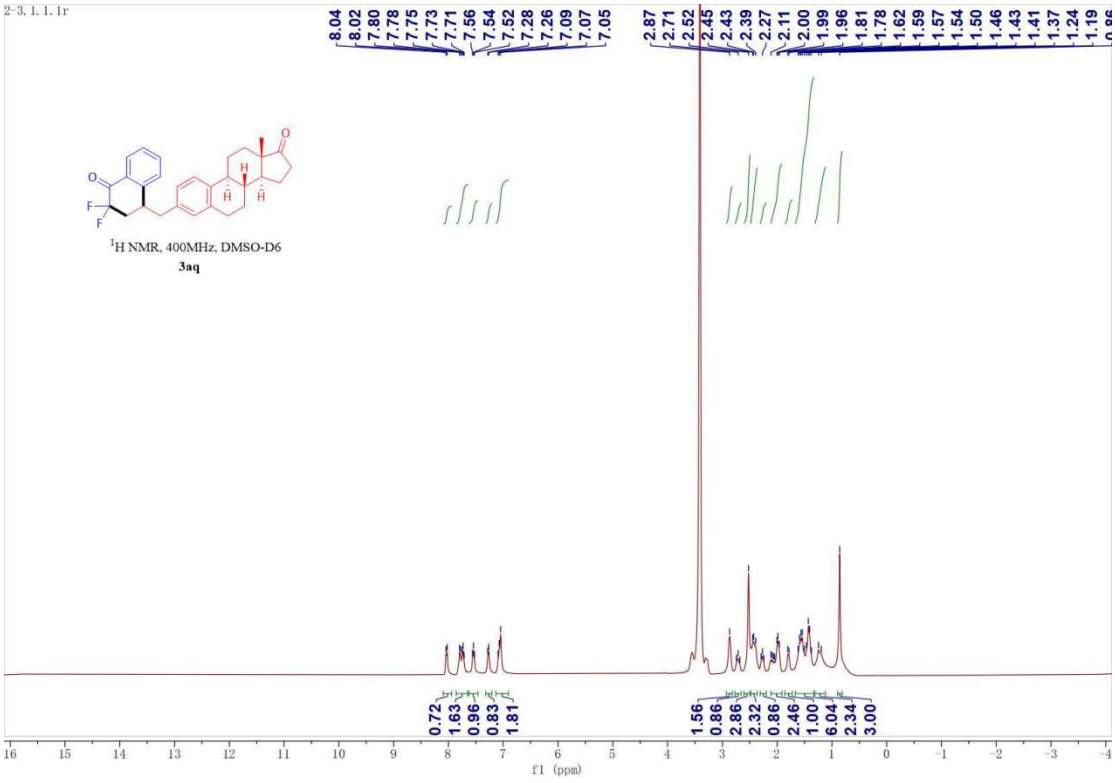

1-7. 1. 1. 1r
8.10
8.08
7.64
7.62
7.60
7.42
7.40
7.39
7.37
3.24
2.68
2.66
2.65
2.64
2.63
2.61
2.60
2.59
2.58
2.56
2.49
2.47
2.45
2.44
2.42
2.40
2.38
1.91
1.88
1.87
1.85
1.81
1.79
1.76
1.74
1.36
1.32
F
F
O
^{1}H NMR, 400 MHz, CDCl$_3$
3ap
0.88
1.00
2.03
1.00
1.04
1.05
2.23
7.88
3.25
f1 (ppm)


1-7. 2. 1. 1r
185.88
185.62
185.37
147.10
135.21
129.72
128.78
128.04
127.43
116.13
113.68
111.21
36.39
36.18
35.96
35.69
35.65
35.60
35.30
31.74
29.29
26.59
22.66
14.11
F
F
O
^{13}C NMR, 100 MHz, CDCl$_3$
3ap
f1 (ppm)



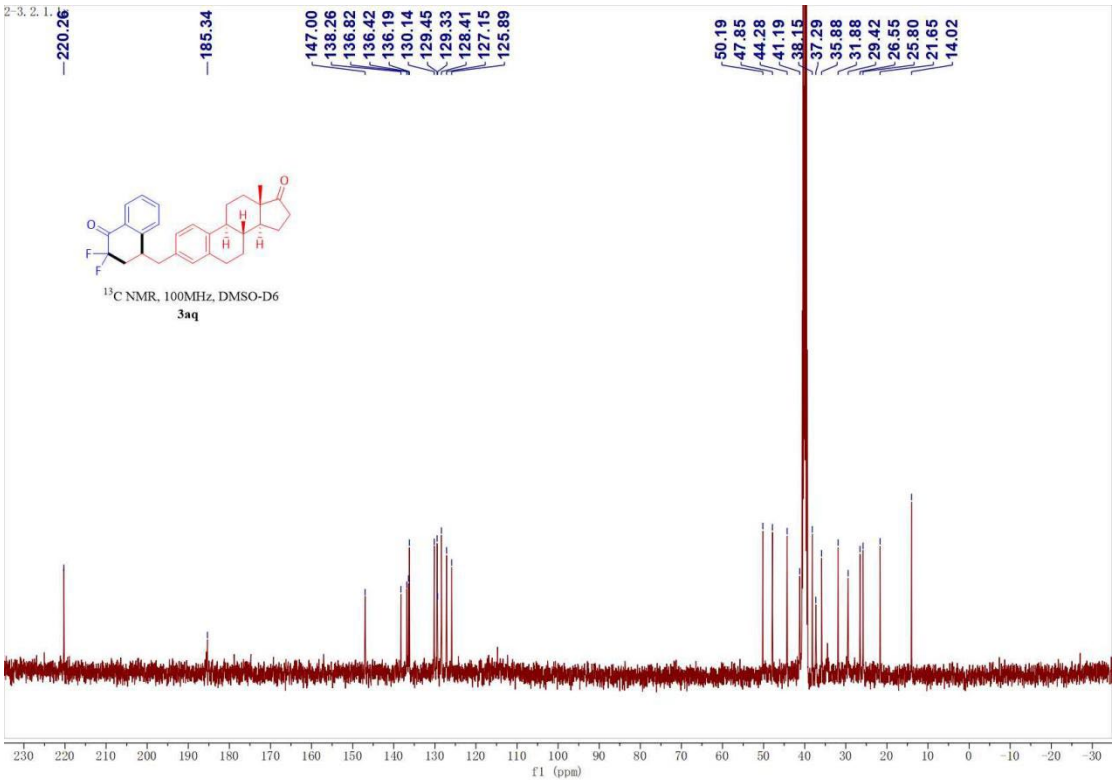
^{19}F NMR, 376 MHz, $CDCl_3$

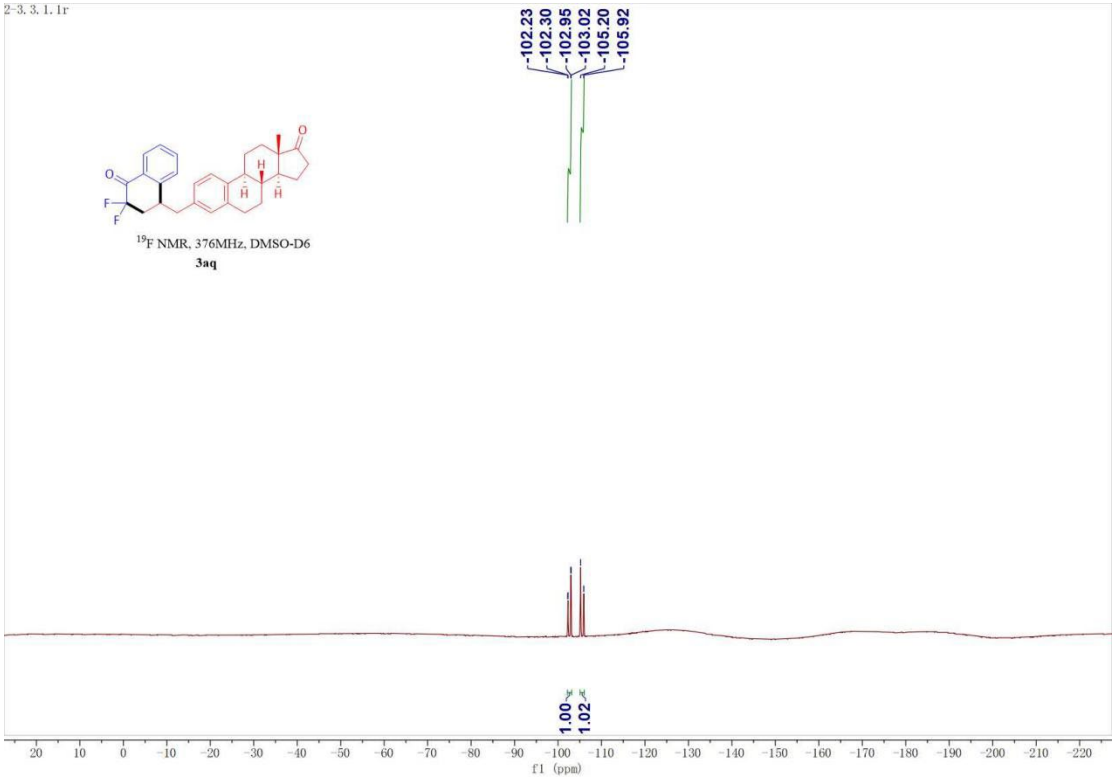
3ap

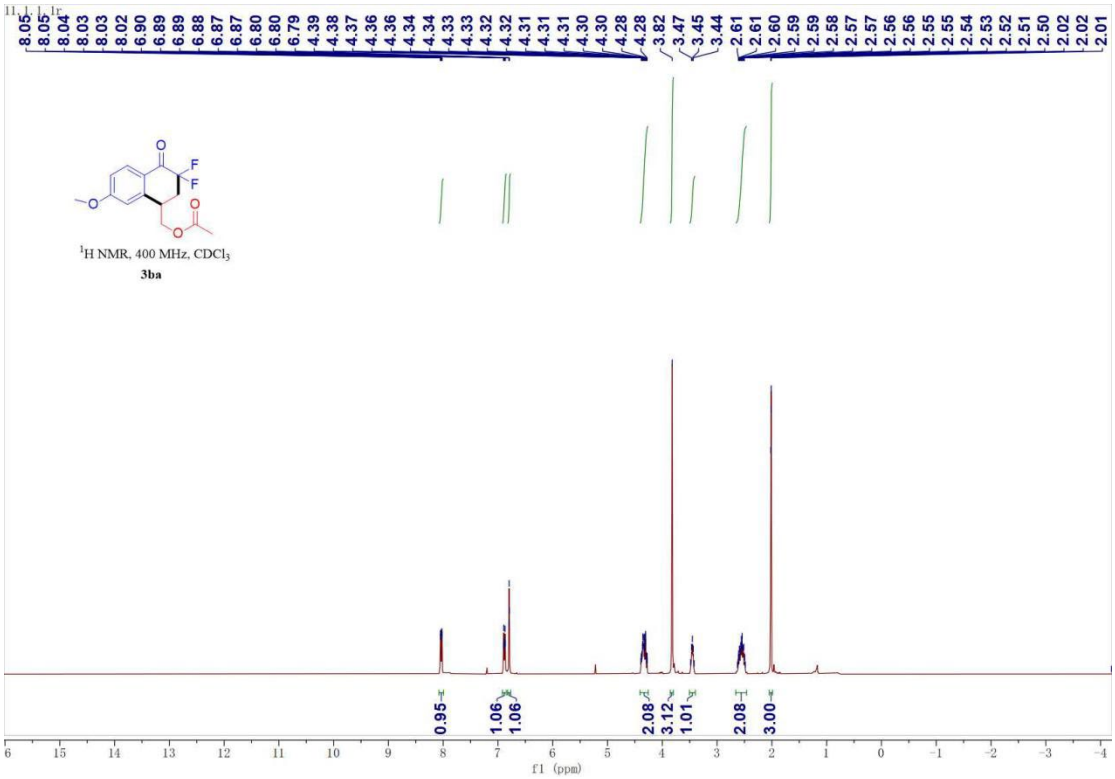


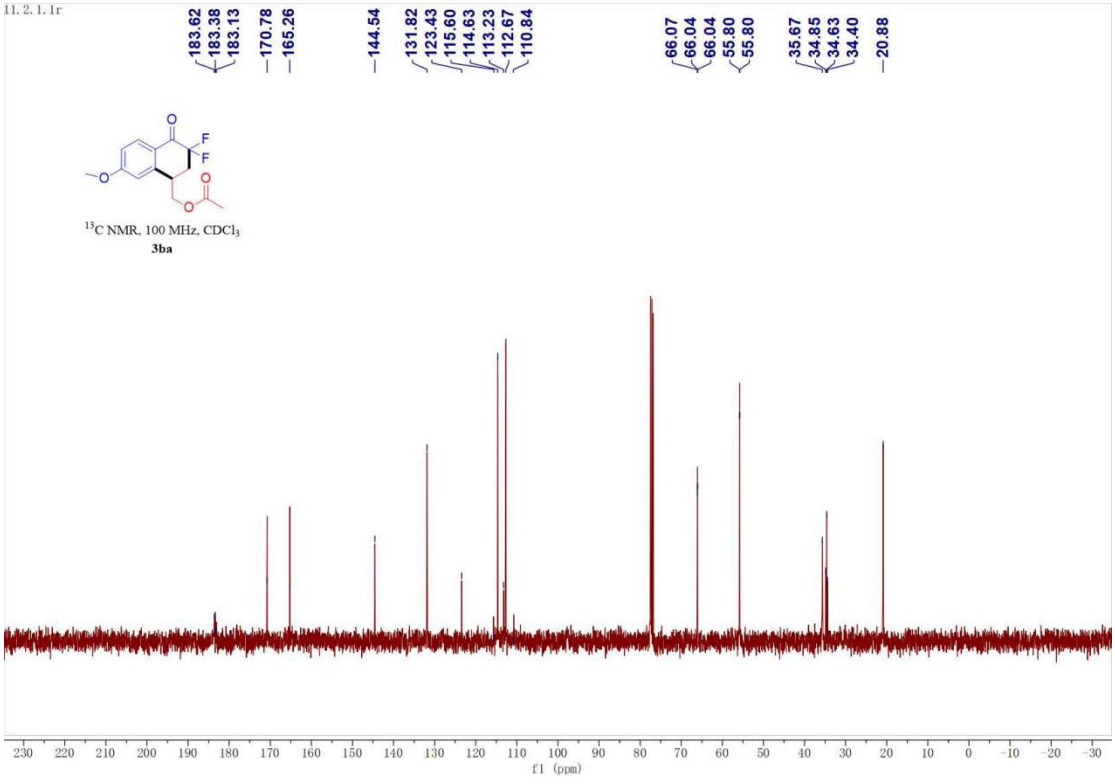
^{1}H NMR, 400MHz, DMSO-D6

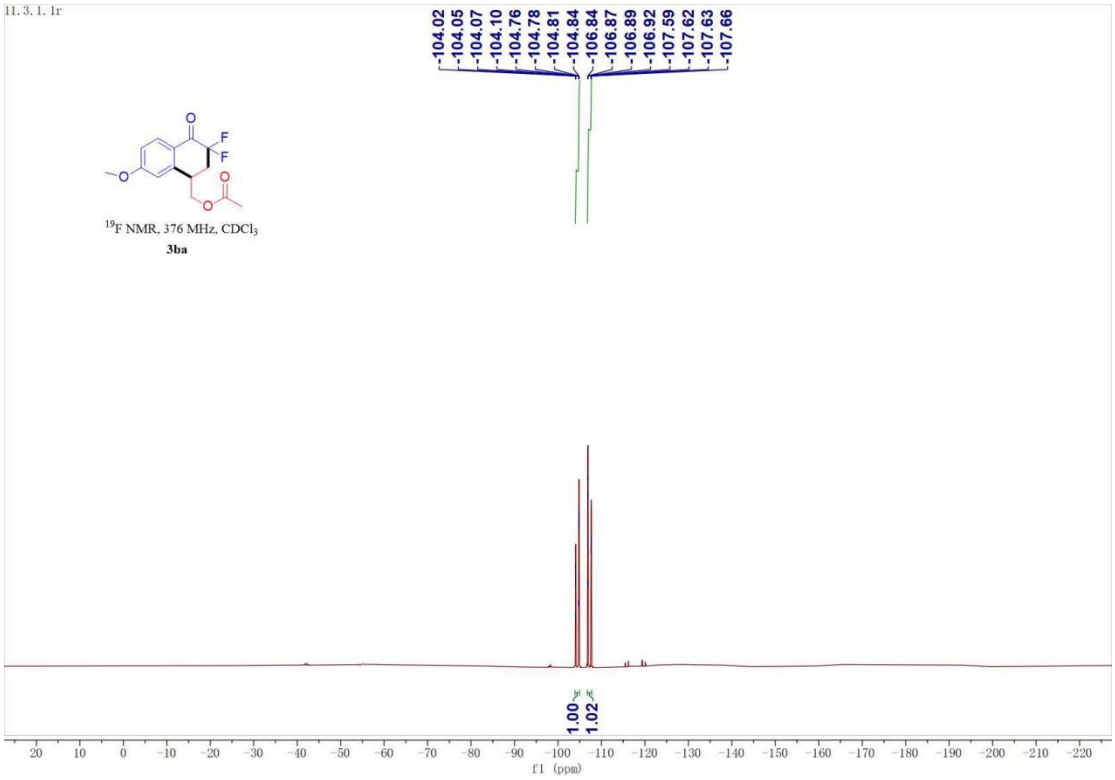
3aq


2-3. 2. 1. 1r
220.26
185.34
147.00
138.26
136.82
136.42
136.19
130.14
129.45
129.33
128.41
127.15
125.89
50.19
47.85
44.28
41.19
38.15
37.29
35.88
31.88
29.42
26.55
25.80
21.65
14.02
O
O
F
F
H
H
H
^{13}C NMR, 100MHz, DMSO-D6
3aq
f1 (ppm)


2-3. 3. 1. 1r
-102.23
-102.30
-102.95
-103.02
-105.20
-105.92
O
O
F
F
H
H
H
^{19}F NMR, 376MHz, DMSO-D6
3aq
1.00
1.02
f1 (ppm)

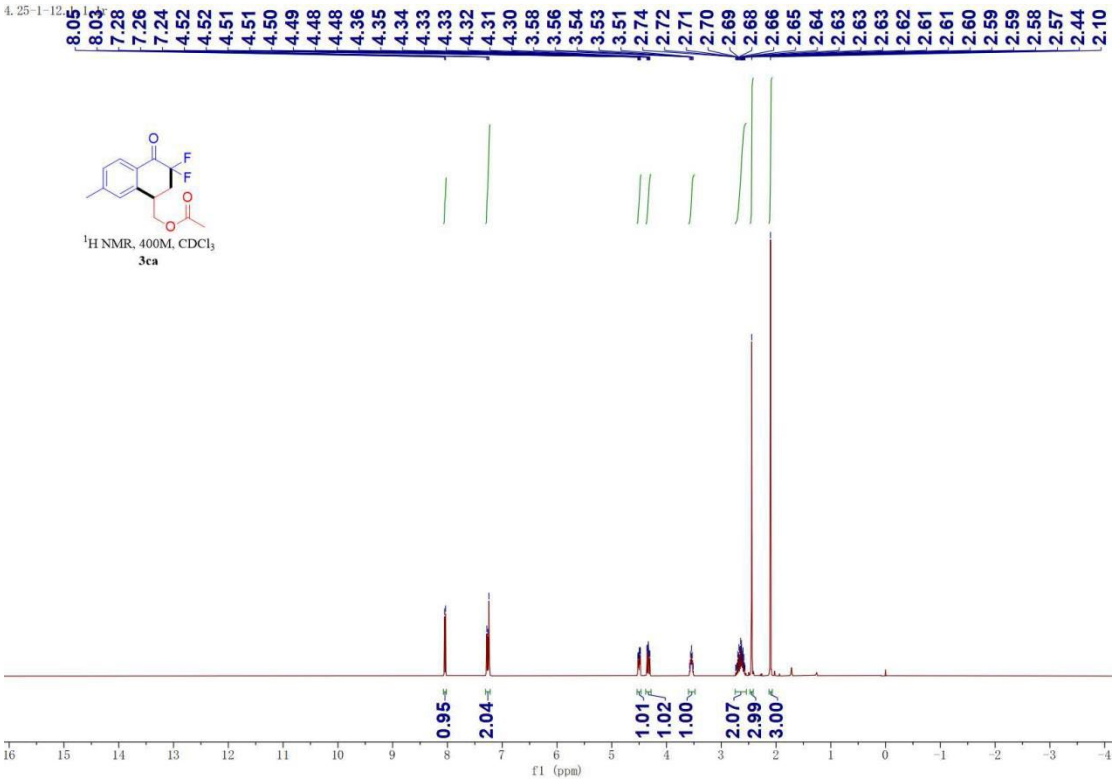

11. 1. 1r
8.05
8.05
8.04
8.03
8.03
8.02
6.90
6.89
6.89
6.88
6.87
6.87
6.80
6.80
6.79
4.39
4.38
4.37
4.36
4.36
4.34
4.34
4.33
4.33
4.32
4.32
4.31
4.31
4.31
4.30
4.30
4.28
4.28
3.82
3.47
3.45
3.44
2.61
2.61
2.60
2.59
2.59
2.58
2.57
2.57
2.56
2.56
2.55
2.55
2.54
2.53
2.52
2.51
2.50
2.02
2.02
2.01
F
F
O
O
O
^{1}H NMR, 400 MHz, CDCl$_3$
3ba
0.95
1.06
1.06
2.08
3.12
1.01
2.08
3.00
f1 (ppm)


11. 2. 1. 1r
183.62
183.38
183.13
170.78
165.26
144.54
131.82
123.43
115.60
114.63
113.23
112.67
110.84
66.07
66.04
66.04
55.80
55.80
35.67
34.85
34.63
34.40
20.88
F
F
O
O
O
^{13}C NMR, 100 MHz, CDCl$_3$
3ba
f1 (ppm)



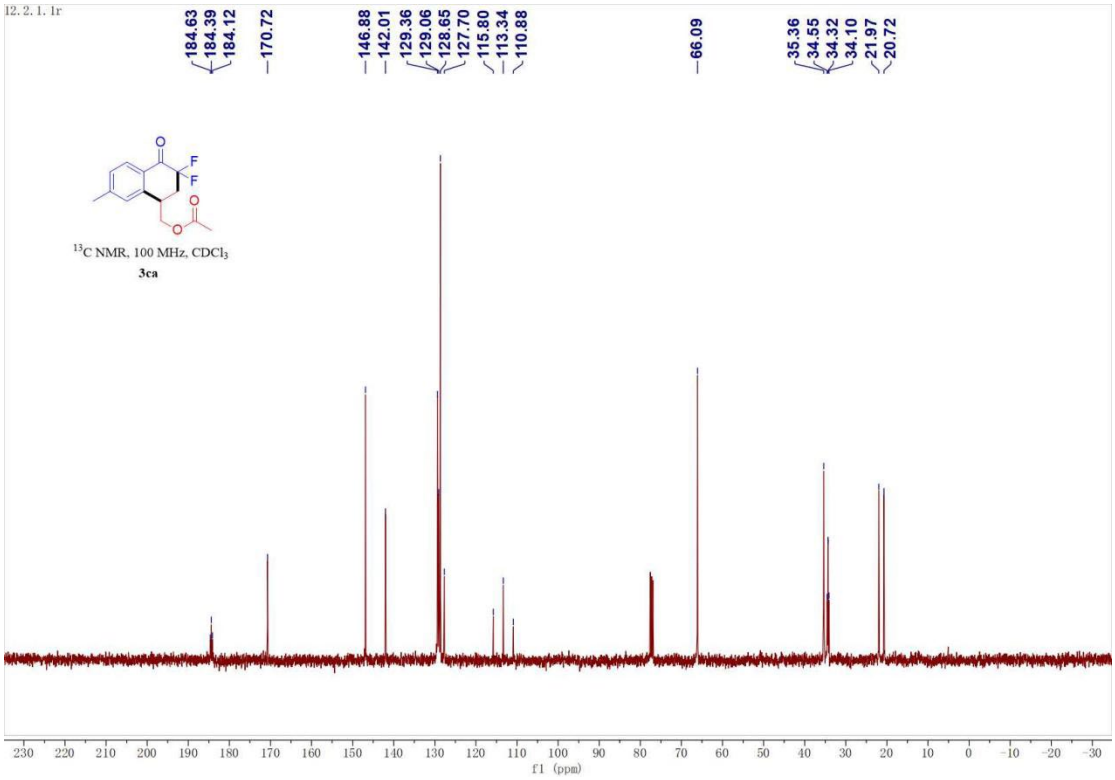
^{19}F NMR, 376 MHz, $CDCl_3$

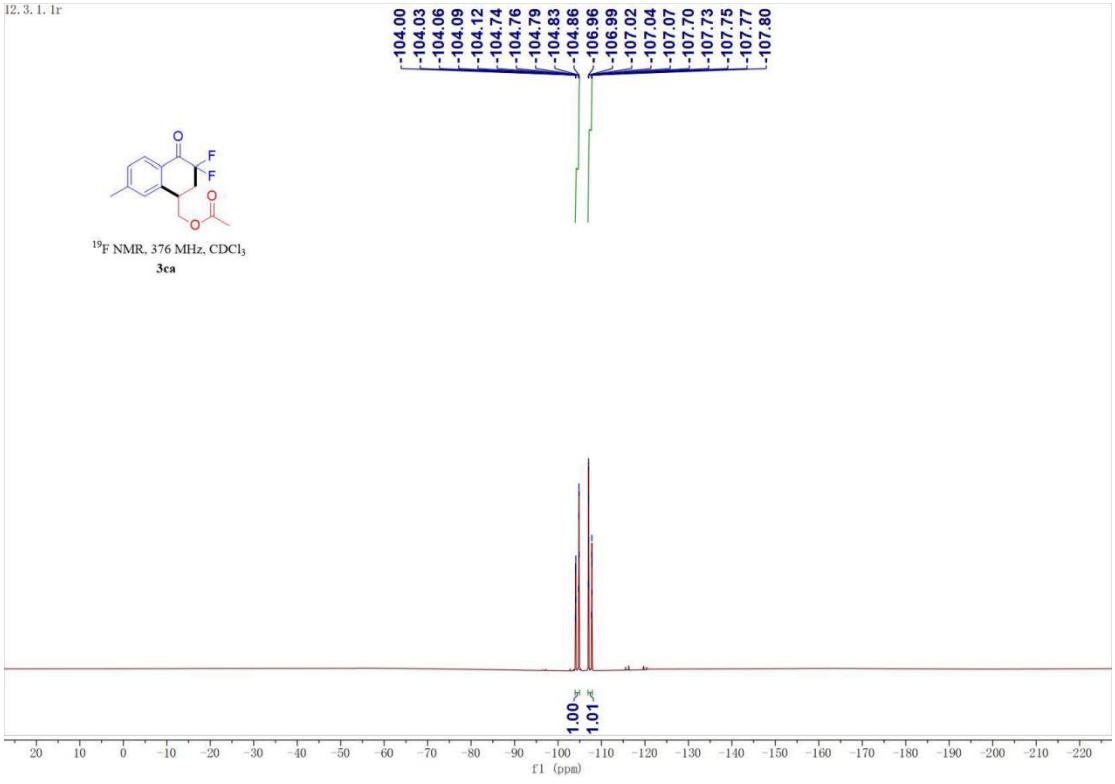
3ba

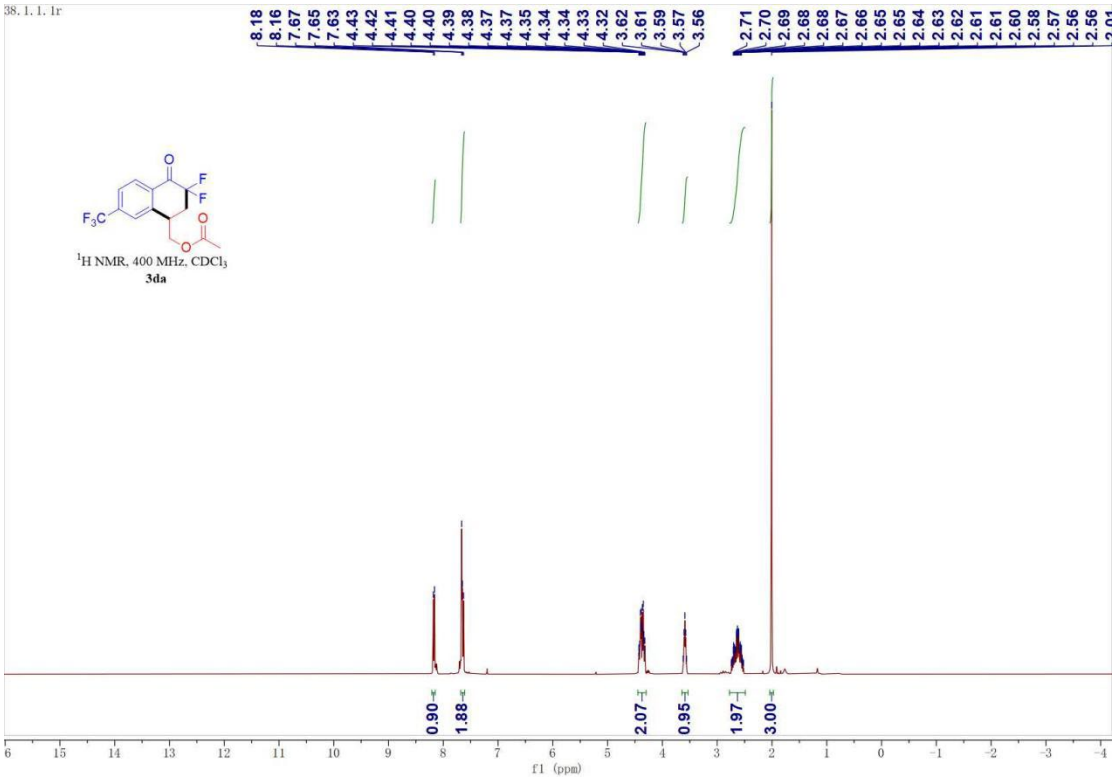


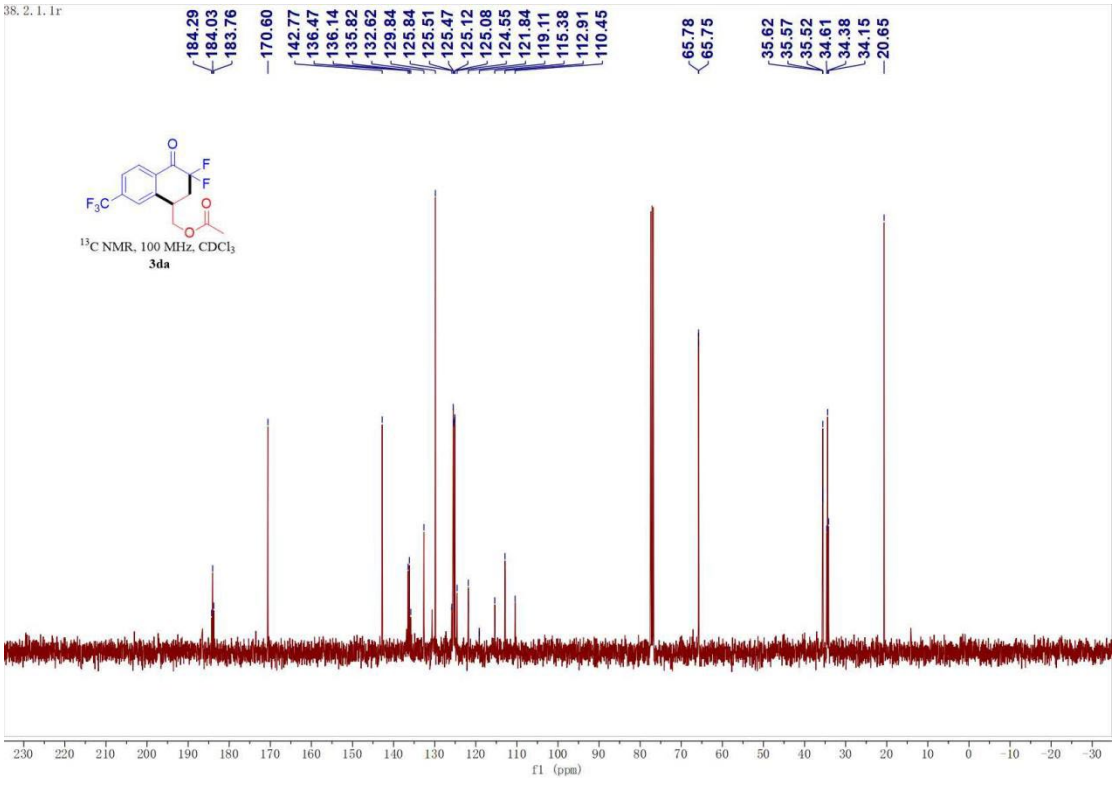
^{1}H NMR, 400M, $CDCl_3$

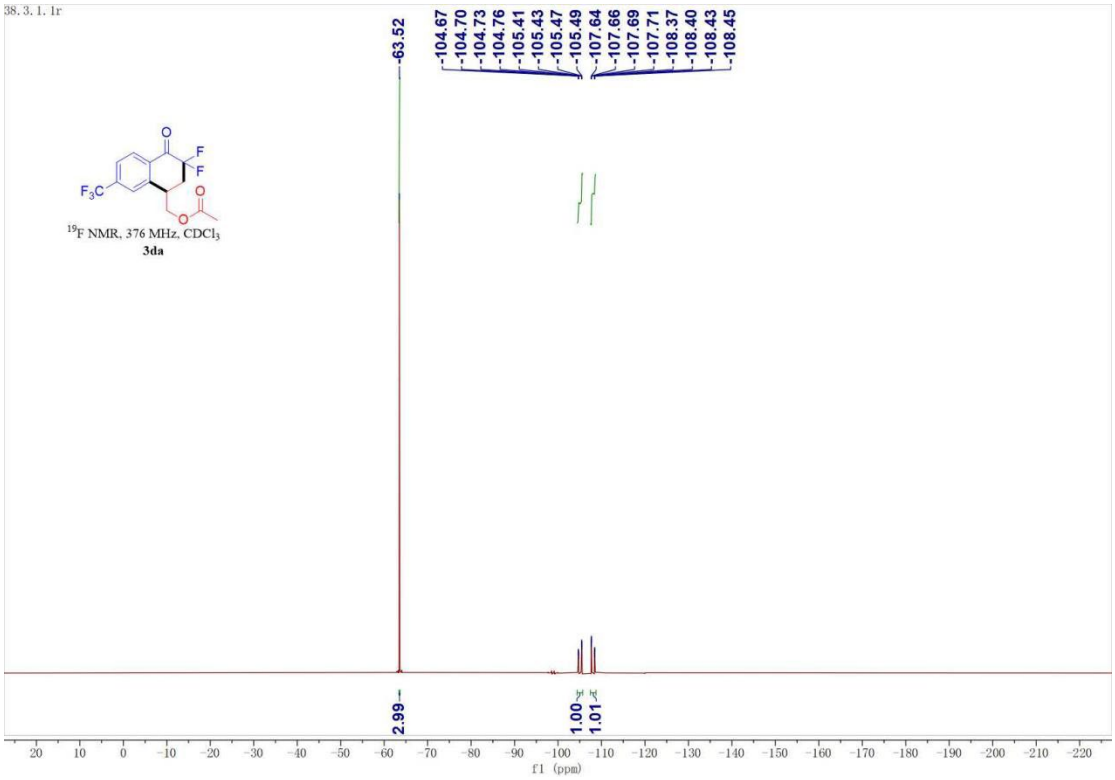
3ca

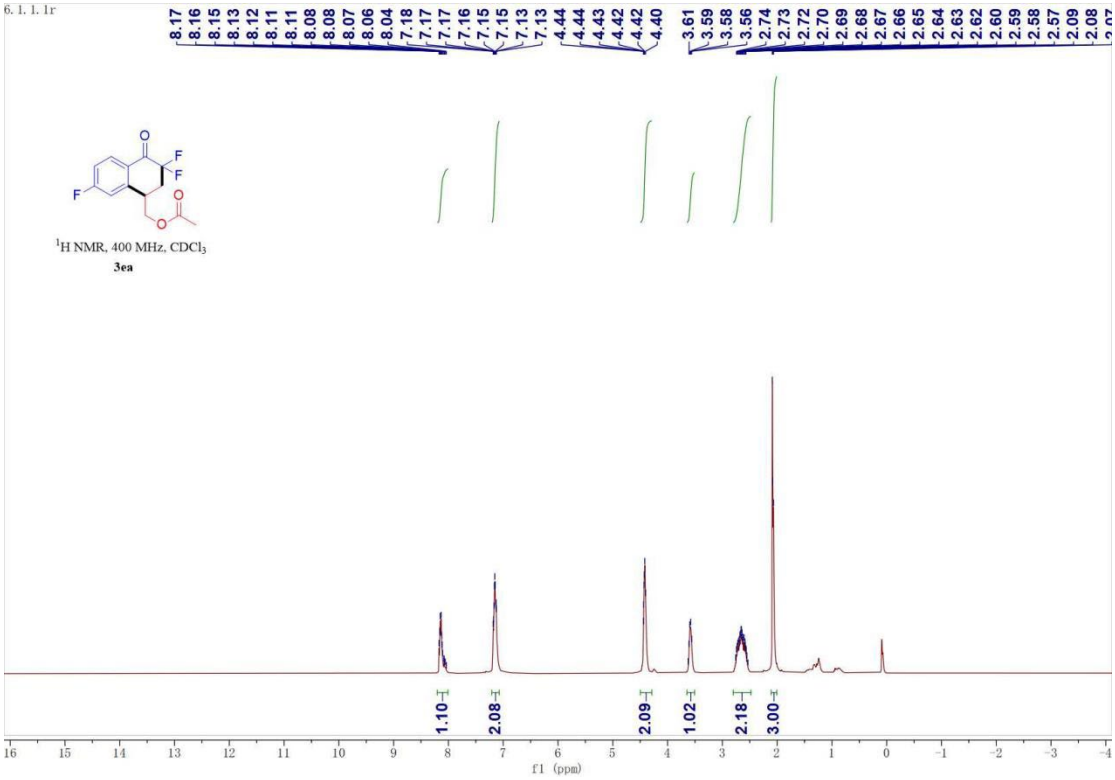

12. 2. 1. 1r
184.63
184.39
184.12
170.72
146.88
142.01
129.36
129.06
128.65
127.70
115.80
113.34
110.88
66.09
35.36
34.55
34.32
34.10
21.97
20.72
F
F
O
O
O
13C NMR, 100 MHz, CDCl3
3ca
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30
f1 (ppm)

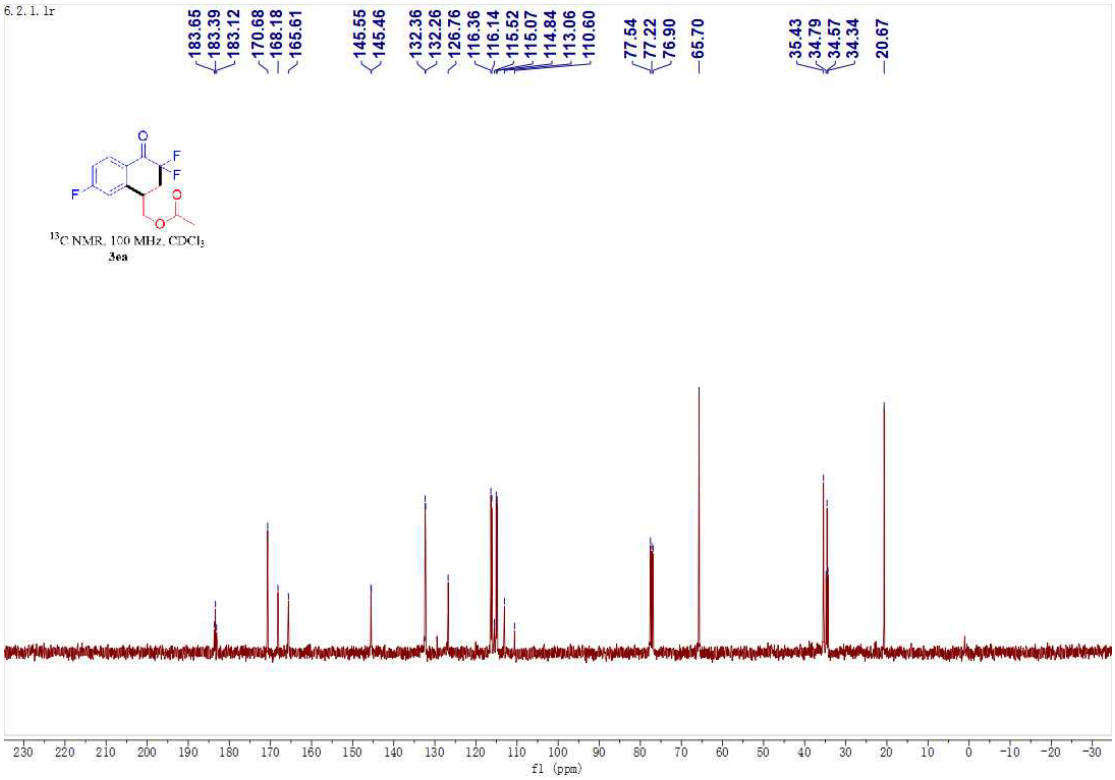

12. 3. 1. 1r
-104.00
-104.03
-104.06
-104.09
-104.12
-104.74
-104.76
-104.79
-104.83
-104.86
-106.96
-106.99
-107.02
-107.04
-107.07
-107.70
-107.73
-107.75
-107.77
-107.80
F
F
O
O
O
19F NMR, 376 MHz, CDCl3
3ca
1.00
1.01
20 10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210 −220
f1 (ppm)

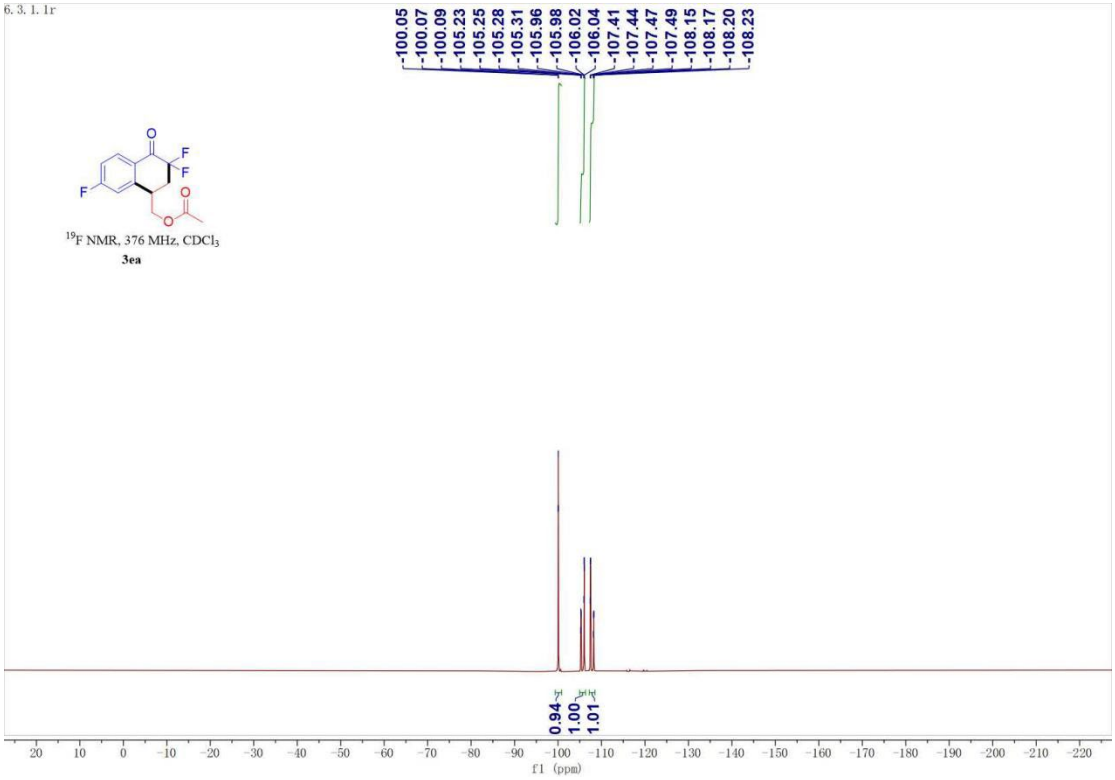

38. 1. 1. 1r
8.18
8.16
7.67
7.65
7.63
4.43
4.42
4.41
4.40
4.40
4.39
4.38
4.37
4.37
4.35
4.34
4.34
4.33
4.32
3.62
3.61
3.59
3.57
3.56
2.71
2.70
2.69
2.68
2.68
2.67
2.66
2.65
2.65
2.64
2.63
2.62
2.61
2.61
2.60
2.58
2.57
2.56
2.56
F
F
O
O
F3C
1H NMR, 400 MHz, CDCl3
3da
0.90
1.88
2.07
0.95
1.97
3.00
f1 (ppm)

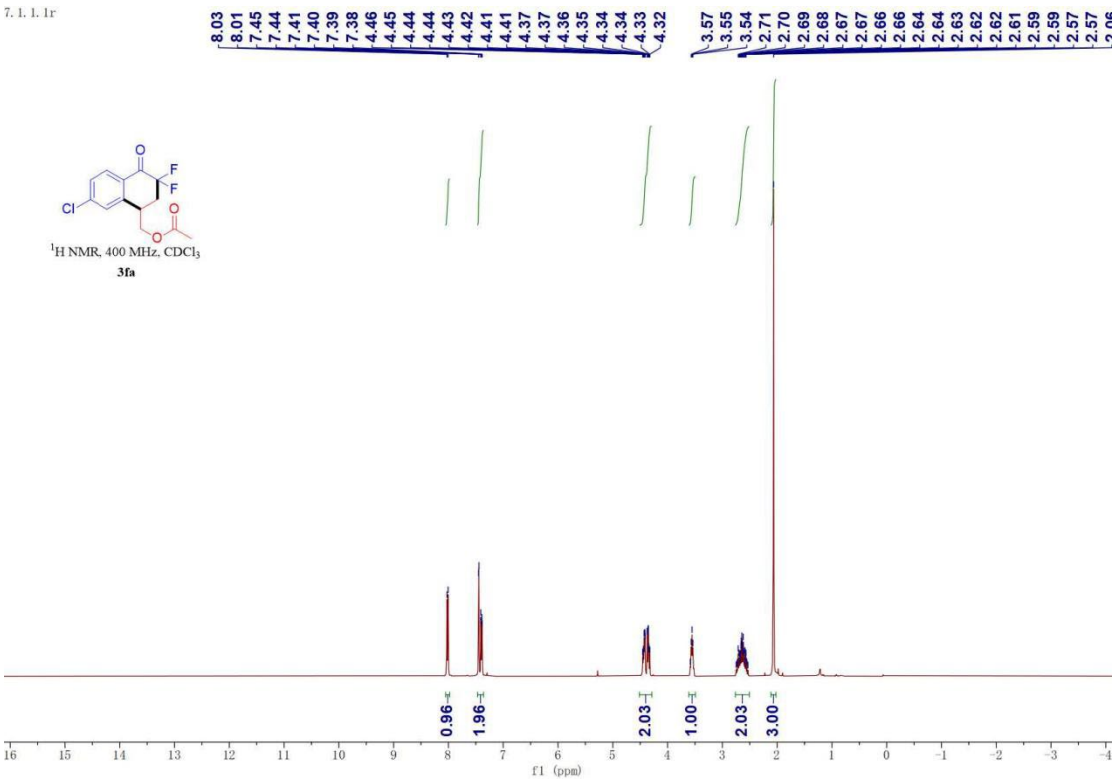

38. 2. 1. 1r
184.29
184.03
183.76
170.60
142.77
136.47
136.14
135.82
132.62
129.84
125.84
125.51
125.47
125.12
125.08
124.55
121.84
119.11
115.38
112.91
110.45
65.78
65.75
35.62
35.57
35.52
34.61
34.38
34.15
20.65
F
F
O
O
F3C
13C NMR, 100 MHz, CDCl3
3da
f1 (ppm)

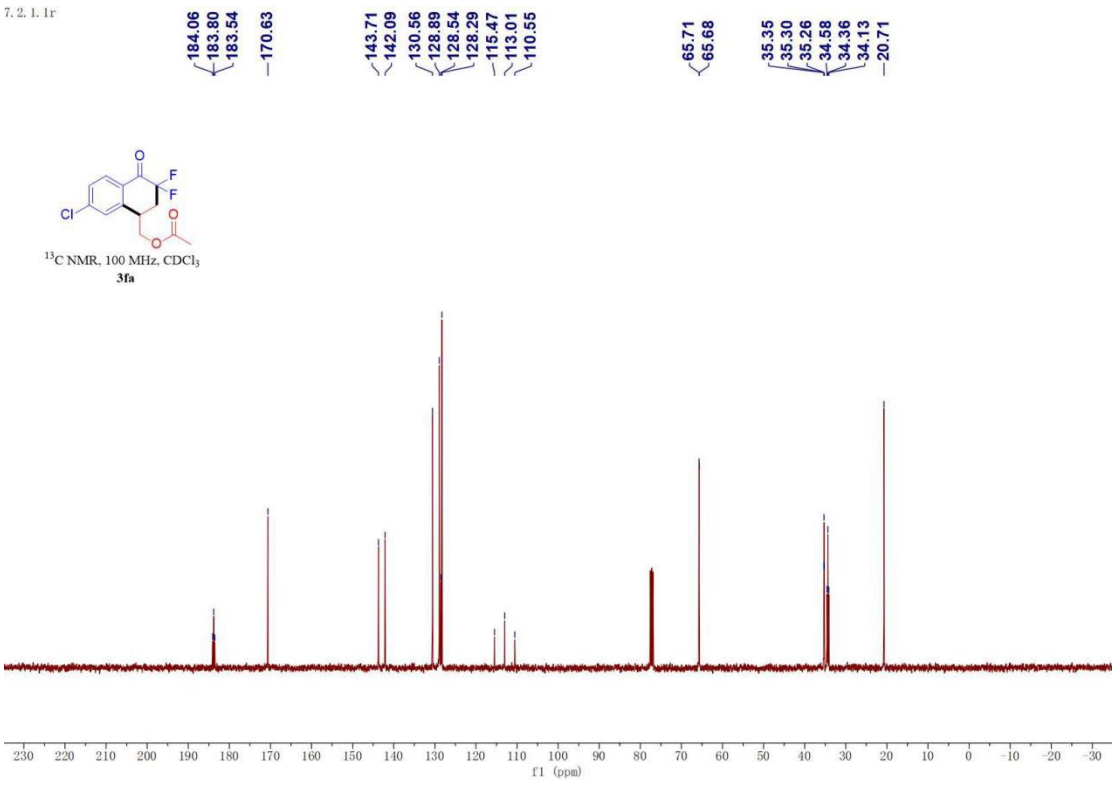

38. 3. 1. 1r
-63.52
-104.67
-104.70
-104.73
-104.76
-105.41
-105.43
-105.47
-105.49
-107.64
-107.66
-107.69
-107.71
-108.37
-108.40
-108.43
-108.45
F
F
F_3C
O
O
^{19}F NMR, 376 MHz, $CDCl_3$
3da
2.99
1.00
1.01
f1 (ppm)


6. 1. 1. 1r
8.17
8.16
8.15
8.13
8.12
8.11
8.11
8.08
8.08
8.07
8.06
8.04
7.18
7.17
7.17
7.16
7.15
7.15
7.13
7.13
4.44
4.44
4.43
4.42
4.42
4.40
3.61
3.59
3.58
3.56
2.74
2.73
2.72
2.70
2.69
2.68
2.67
2.66
2.65
2.64
2.63
2.62
2.60
2.59
2.58
2.57
2.09
2.08
F
F
F
O
O
^{1}H NMR, 400 MHz, $CDCl_3$
3ea
1.10
2.08
2.09
1.02
2.18
3.00
f1 (ppm)

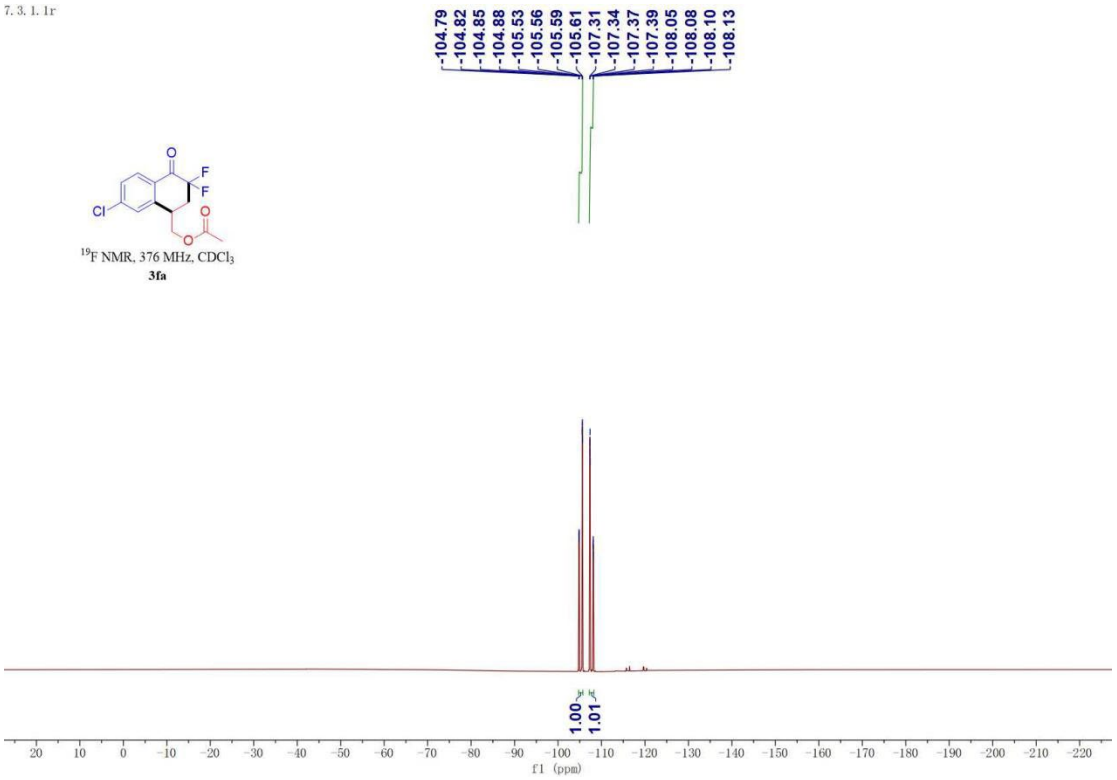

6.2.1.1r
183.65
183.39
183.12
170.68
168.18
165.61
145.55
145.46
132.36
132.26
126.76
116.36
116.14
115.52
115.07
114.84
113.06
110.60
77.54
77.22
76.90
65.70
35.43
34.79
34.57
34.34
20.67
F
F
F
O
O
O
13C NMR, 100 MHz, CDCl3
3ea
f1 (ppm)


6.3.1.1r
-100.05
-100.07
-100.09
-105.23
-105.25
-105.28
-105.31
-105.96
-105.98
-106.02
-106.04
-107.41
-107.44
-107.47
-107.49
-108.15
-108.17
-108.20
-108.23
F
F
F
O
O
19F NMR, 376 MHz, CDCl3
3ea
0.94
1.00
1.01
f1 (ppm)


7. 1. 1. 1r
8.03
8.01
7.45
7.44
7.41
7.40
7.39
7.38
4.46
4.45
4.44
4.44
4.43
4.42
4.41
4.41
4.37
4.37
4.36
4.35
4.34
4.34
4.33
4.32
3.57
3.55
3.54
2.71
2.70
2.69
2.68
2.67
2.67
2.66
2.66
2.64
2.64
2.63
2.62
2.62
2.61
2.59
2.59
2.57
2.57
O
F
F
Cl
O
O
1H NMR, 400 MHz, CDCl3
3fa
0.96
1.96
2.03
1.00
2.03
3.00
f1 (ppm)


7. 2. 1. 1r
184.06
183.80
183.54
170.63
143.71
142.09
130.56
128.89
128.54
128.29
115.47
113.01
110.55
65.71
65.68
35.35
35.30
35.26
34.58
34.36
34.13
20.71
O
F
F
Cl
O
O
13C NMR, 100 MHz, CDCl3
3fa
f1 (ppm)

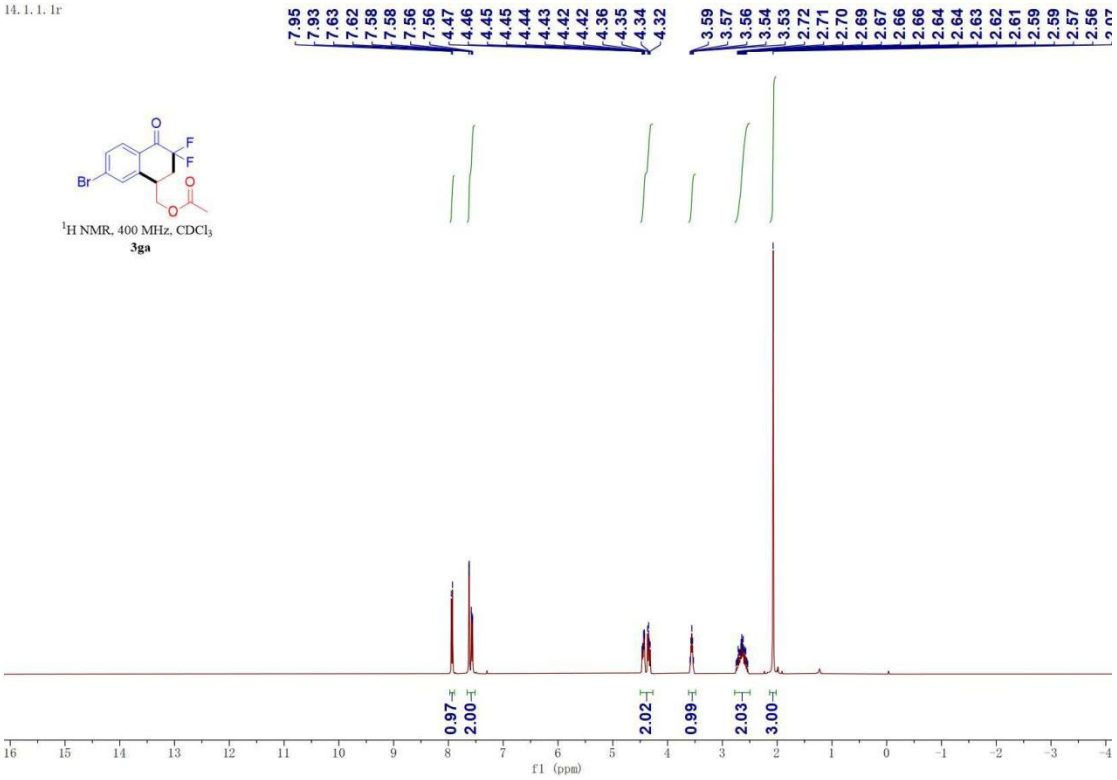
7. 3. 1. 1r



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

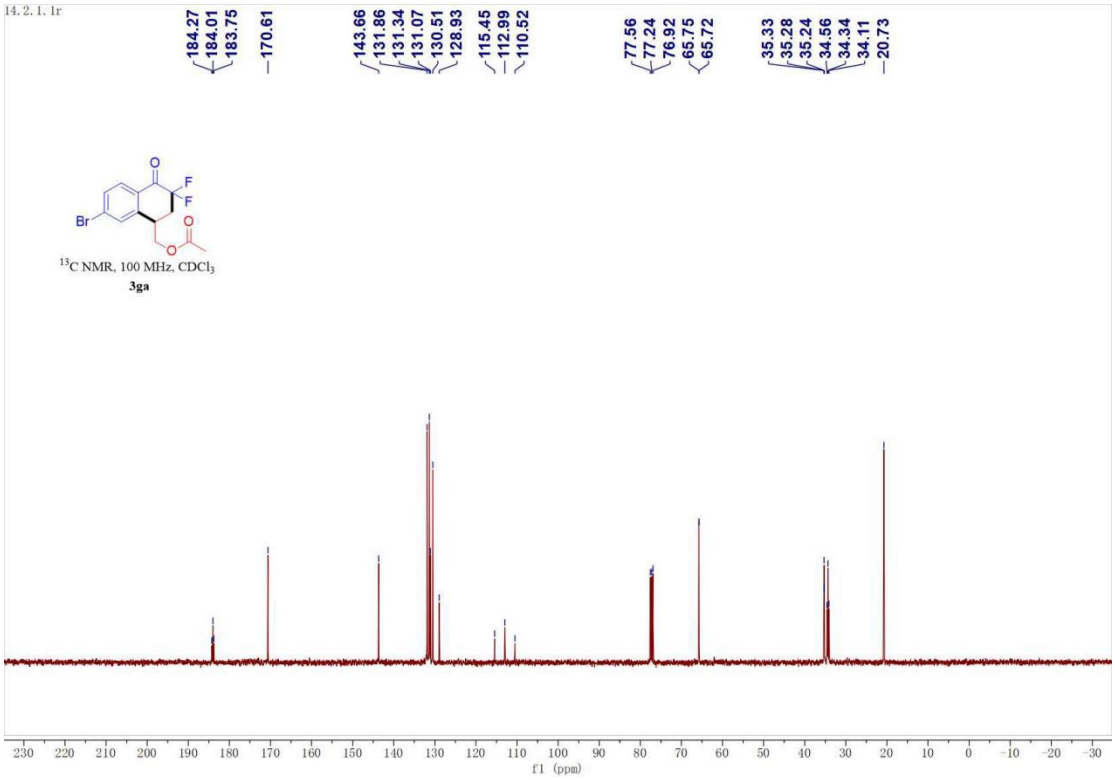
3fa

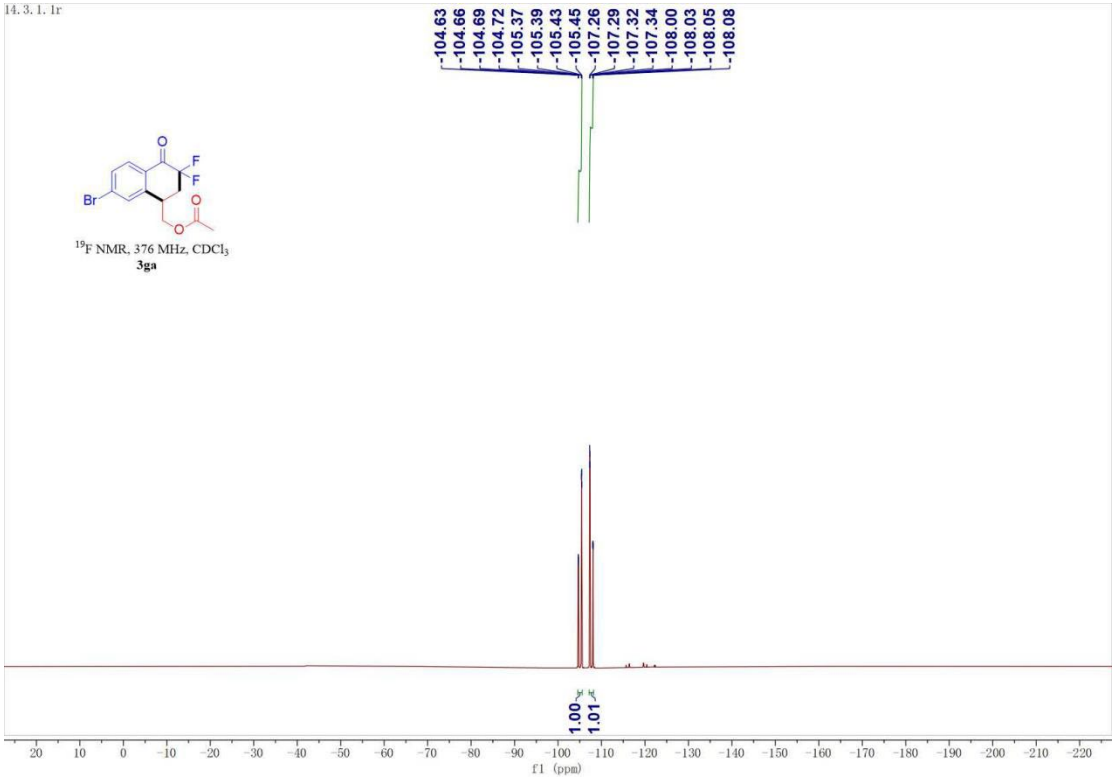
14. 1. 1. 1r

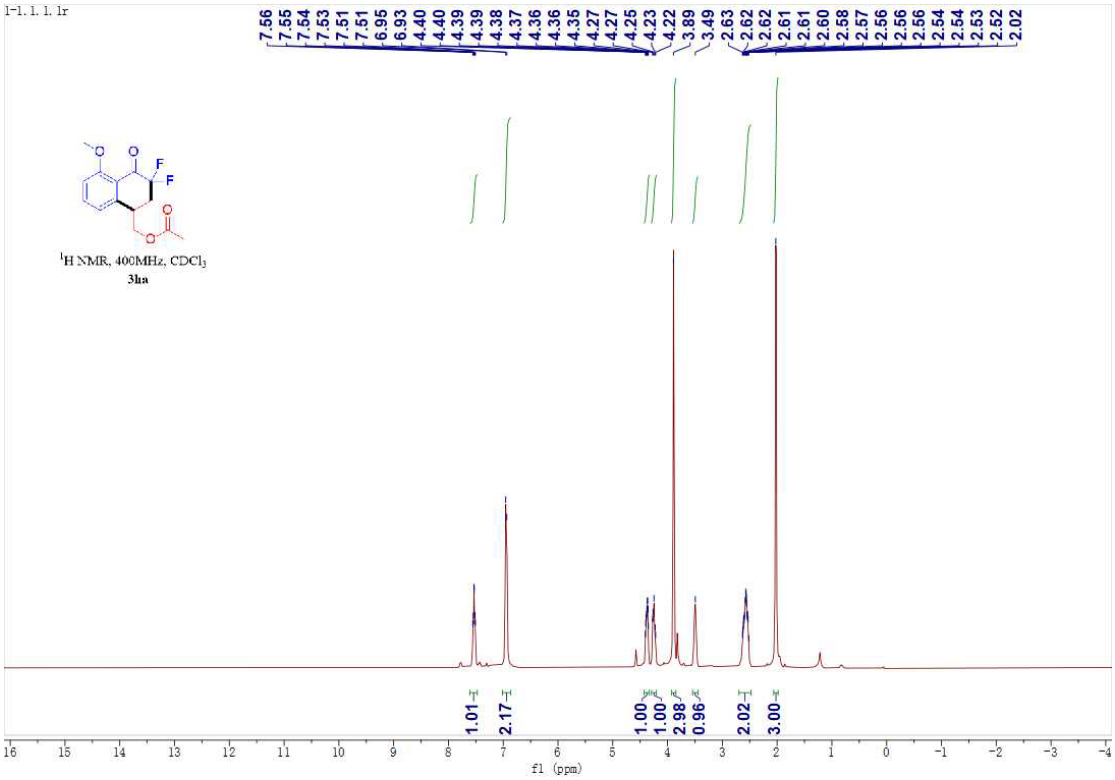


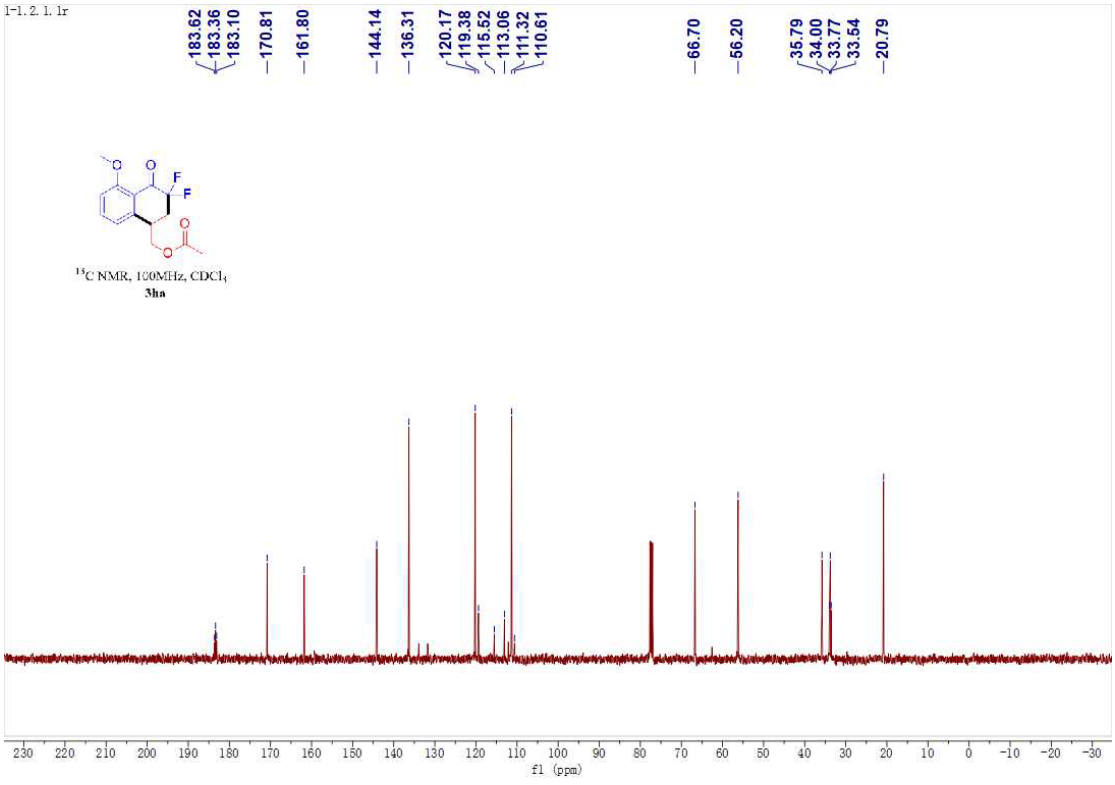
^{1}H NMR, 400 MHz, $CDCl_3$

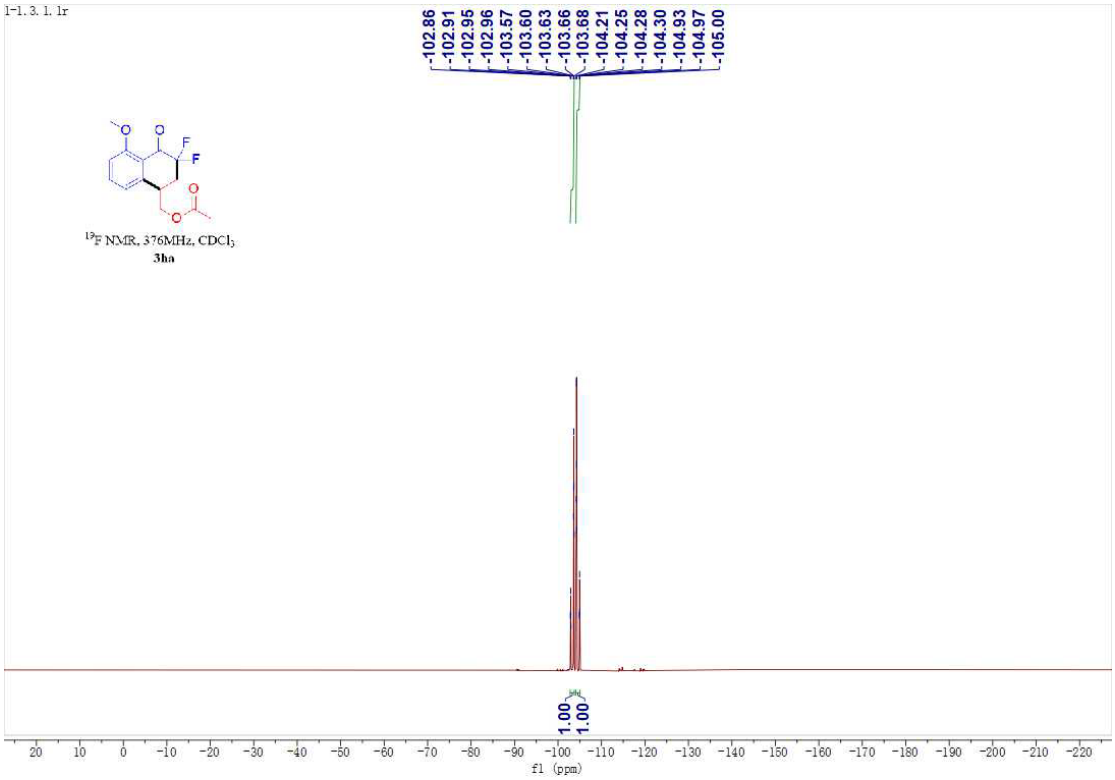
3ga


14.2.1.1r
184.27
184.01
183.75
170.61
143.66
131.86
131.34
131.07
130.51
128.93
115.45
112.99
110.52
77.56
77.24
76.92
65.75
65.72
35.33
35.28
35.24
34.56
34.34
34.11
20.73
O
F
F
Br
O
O
13C NMR, 100 MHz, CDCl3
3ga
f1 (ppm)


14.3.1.1r
-104.63
-104.66
-104.69
-104.72
-105.37
-105.39
-105.43
-105.45
-107.26
-107.29
-107.32
-107.34
-108.00
-108.03
-108.05
-108.08
O
F
F
Br
O
O
19F NMR, 376 MHz, CDCl3
3ga
1.00
1.01
f1 (ppm)

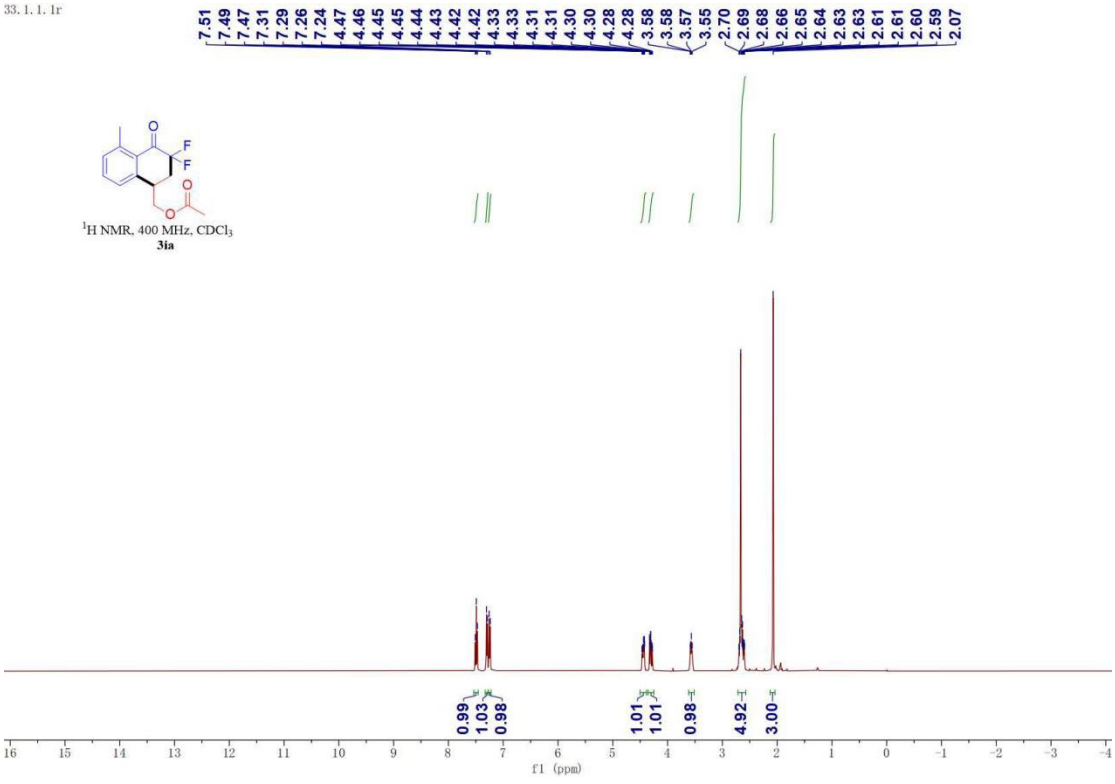

1-1. 1. 1. 1r
7.56
7.55
7.54
7.53
7.51
7.51
6.95
6.93
4.40
4.40
4.39
4.39
4.38
4.37
4.36
4.36
4.35
4.27
4.27
4.25
4.23
4.22
3.89
3.49
2.63
2.62
2.62
2.61
2.61
2.60
2.58
2.57
2.56
2.56
2.56
2.54
2.54
2.53
2.52
2.02
O
F
F
O
O
^{1}H NMR, 400MHz, CDCl$_3$
3ha
1.01
2.17
1.00
1.00
2.98
0.96
2.02
3.00
f1 (ppm)


1-1. 2. 1. 1r
183.62
183.36
183.10
170.81
161.80
144.14
136.31
120.17
119.38
115.52
113.06
111.32
110.61
66.70
56.20
35.79
34.00
33.77
33.54
20.79
O
F
F
O
O
^{13}C NMR, 100MHz, CDCl$_3$
3ha
f1 (ppm)



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

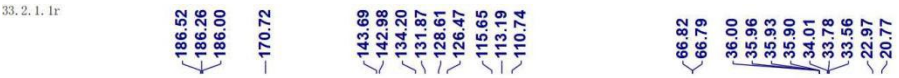
3ha



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

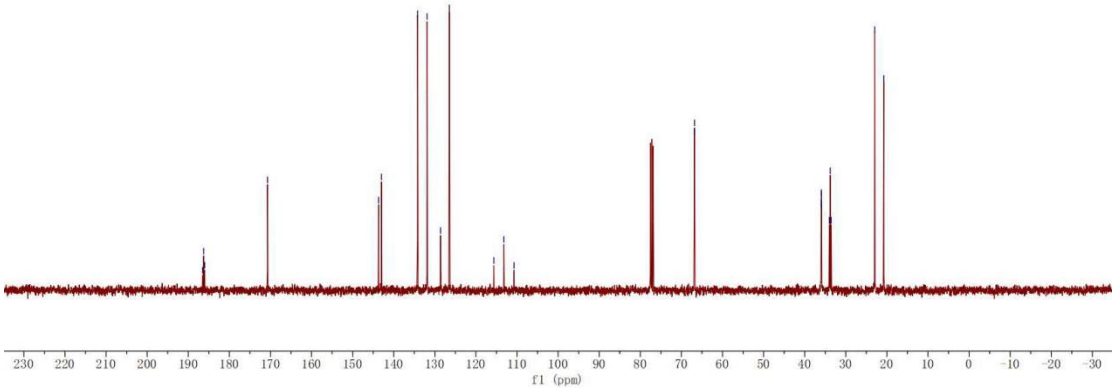
3ia

33. 2. 1. 1r

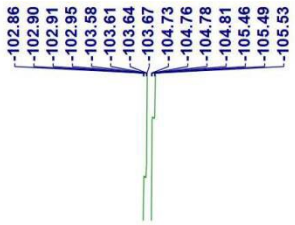


^{13}C NMR, 100 MHz, $CDCl_3$

3ia

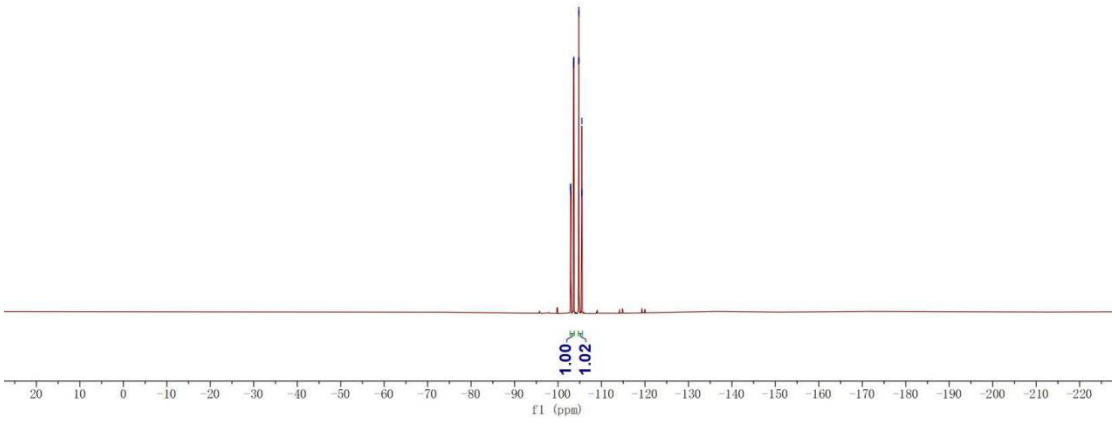


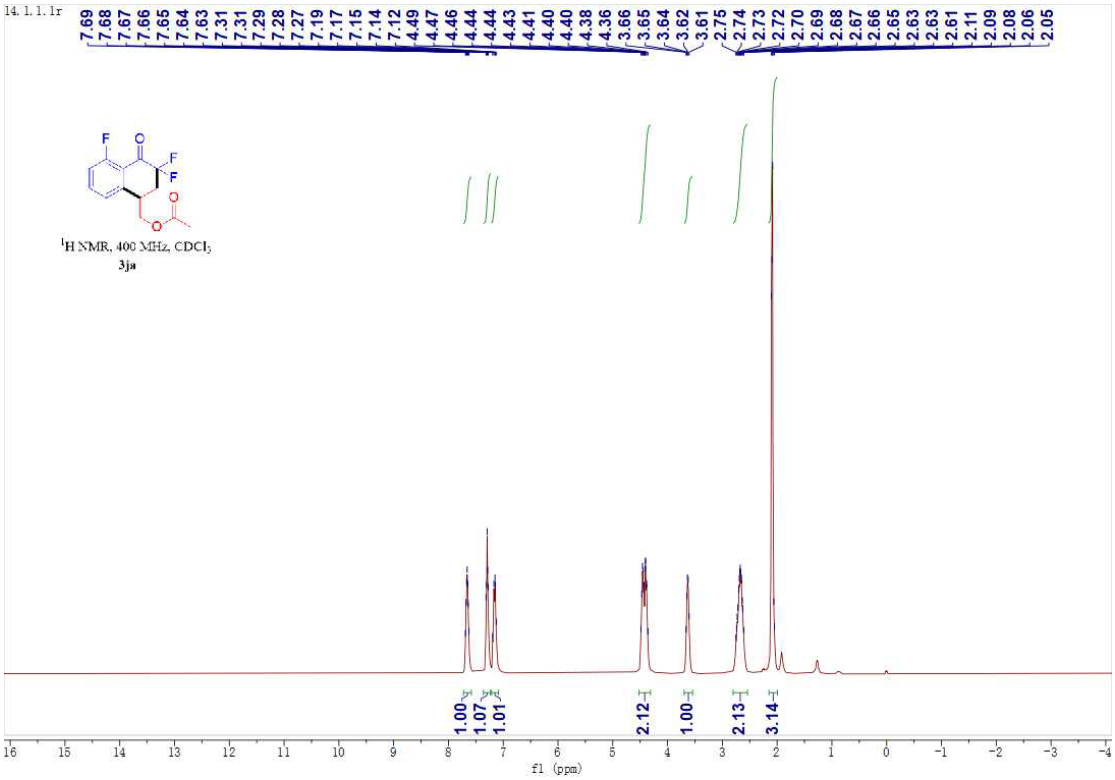
33. 3. 1. 1r

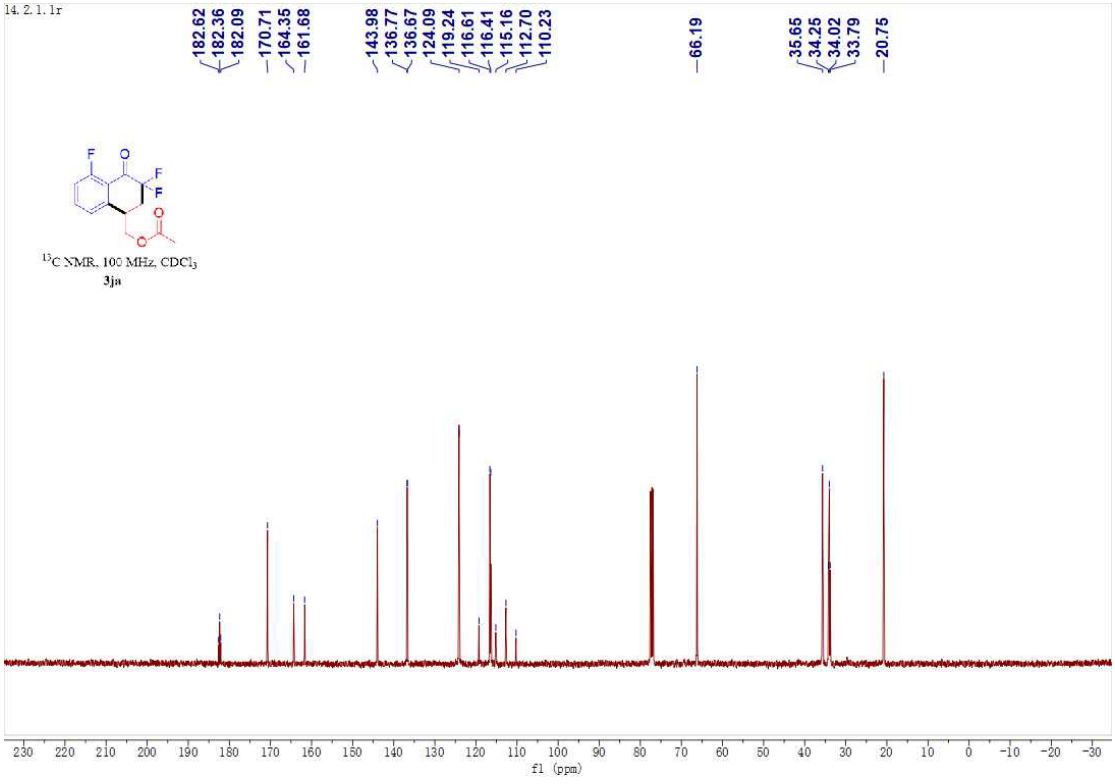


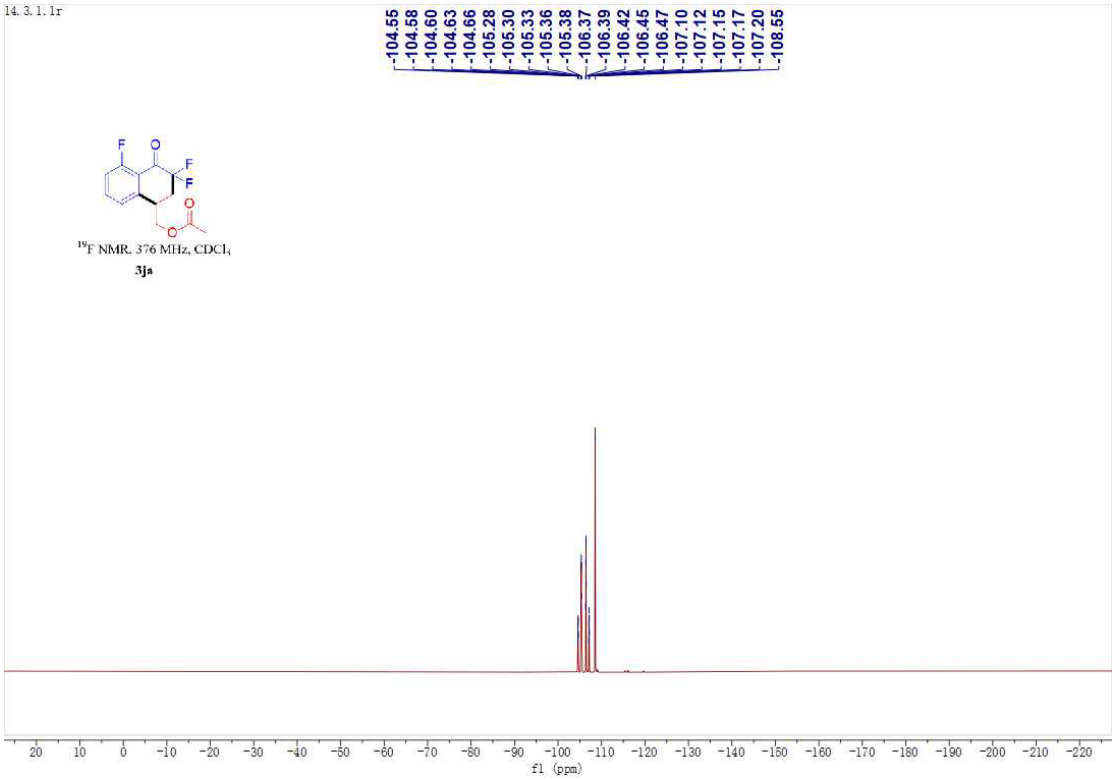
^{19}F NMR, 376 MHz, $CDCl_3$

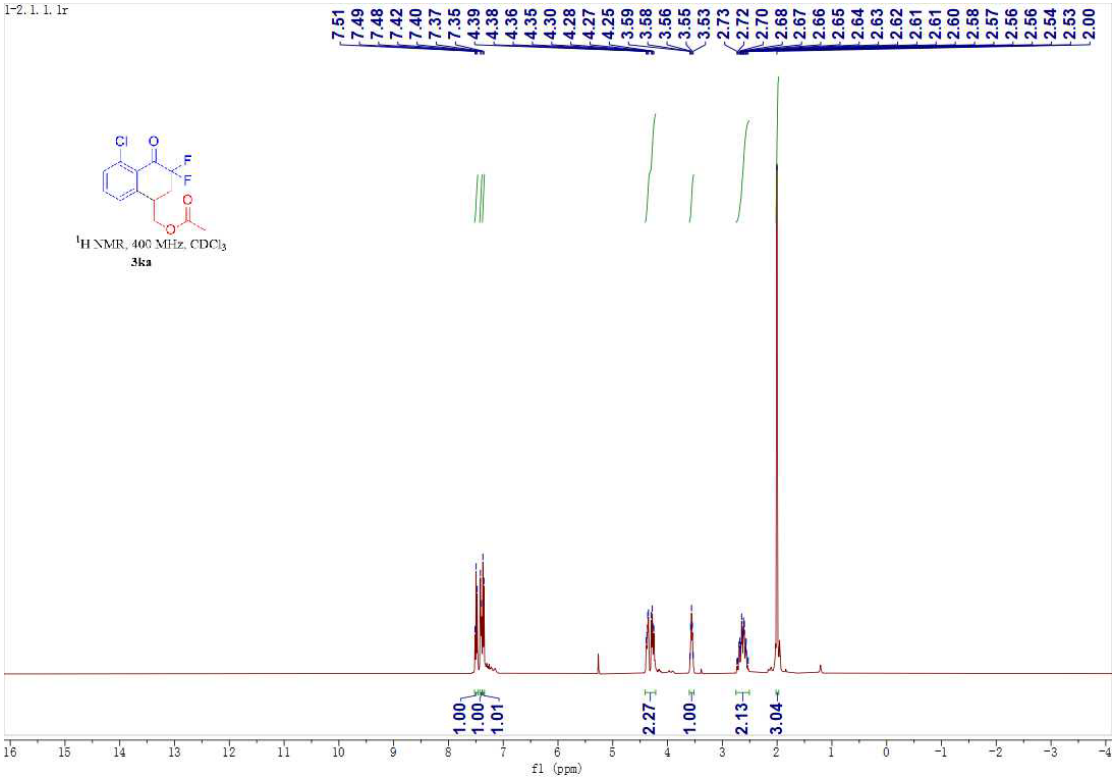
3ia

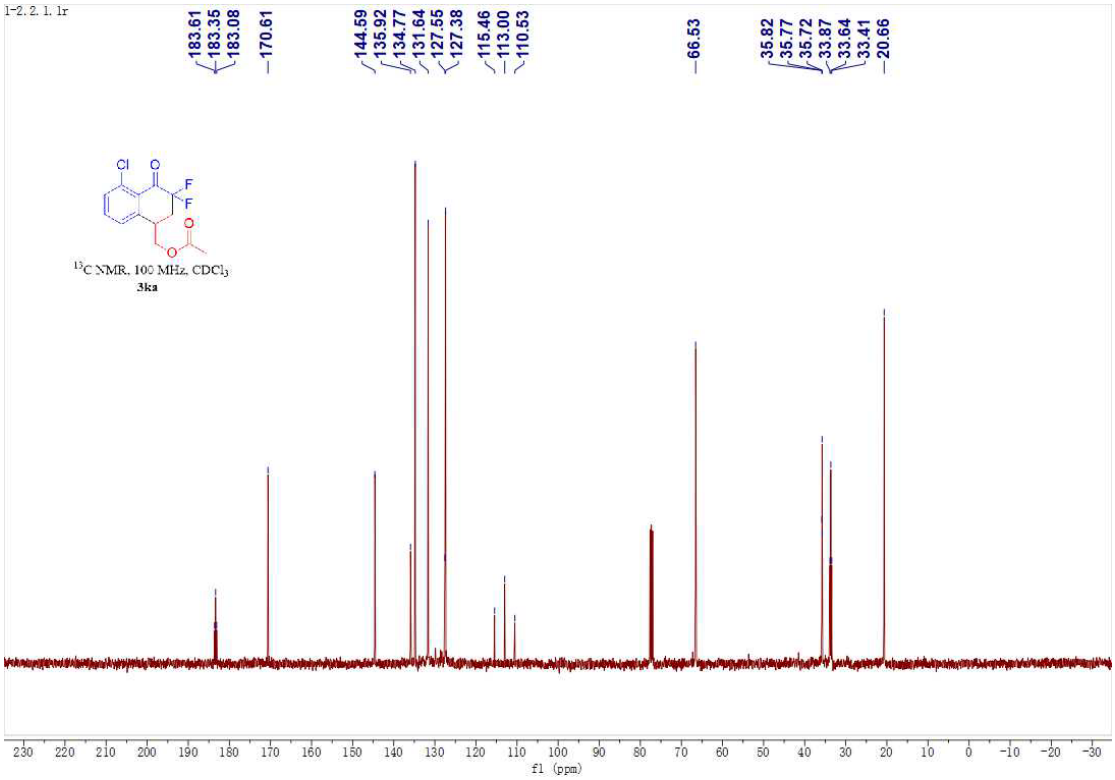


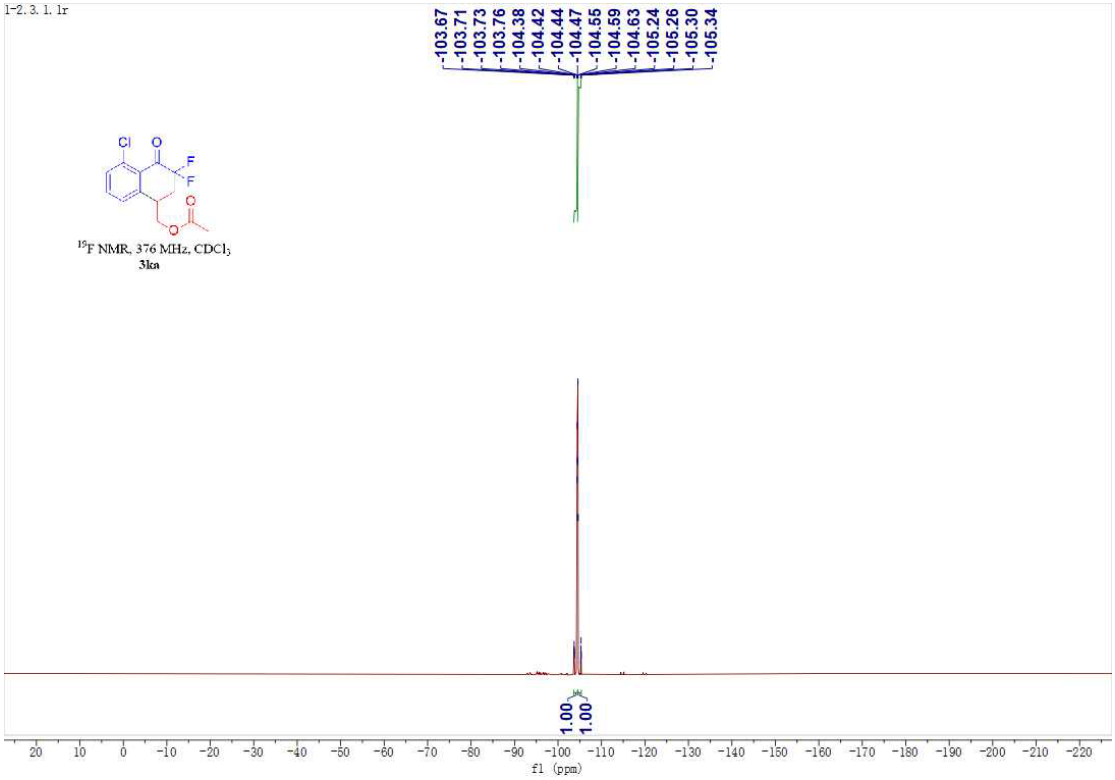

14.1.1.1r
7.69 7.68 7.67 7.66 7.65 7.64 7.63 7.31 7.31 7.29 7.28 7.27 7.19 7.17 7.15 7.14 7.12 4.49 4.47 4.46 4.44 4.44 4.43 4.41 4.40 4.40 4.38 4.36 3.66 3.65 3.64 3.62 3.61 2.75 2.74 2.73 2.72 2.70 2.69 2.68 2.67 2.66 2.65 2.63 2.63 2.61 2.11 2.09 2.08 2.06 2.05
1.00 1.07 1.01 2.12 1.00 2.13 3.14
f1 (ppm)
^{1}H NMR, 400 MHz, CDCl$_3$
3ja

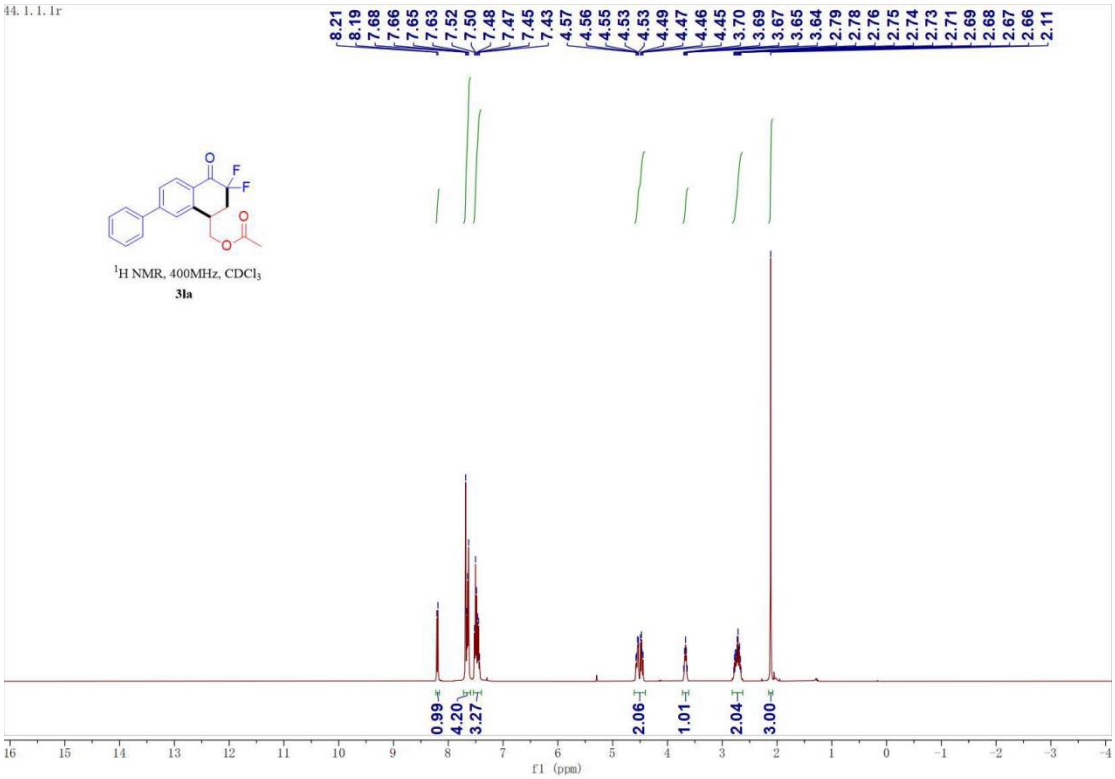

14.2.1.1r
182.62 182.36 182.09 170.71 164.35 161.68 143.98 136.77 136.67 124.09 119.24 116.61 116.41 115.16 112.70 110.23 66.19 35.65 34.25 34.02 33.79 20.75
f1 (ppm)
^{13}C NMR, 100 MHz, CDCl$_3$
3ja


14. 3. 1. 1r
-104.55
-104.58
-104.60
-104.63
-104.66
-105.28
-105.30
-105.33
-105.36
-105.38
-106.37
-106.39
-106.42
-106.45
-106.47
-107.10
-107.12
-107.15
-107.17
-107.20
-108.55
F
O
F
F
O
O
^{19}F NMR, 376 MHz, CDCl$_3$
3ja
f1 (ppm)


1-2. 1. 1. 1r
7.51
7.49
7.48
7.42
7.40
7.37
7.35
4.39
4.38
4.36
4.35
4.30
4.28
4.27
4.25
3.59
3.58
3.56
3.55
3.53
2.73
2.72
2.70
2.68
2.67
2.66
2.65
2.64
2.63
2.62
2.61
2.61
2.60
2.58
2.57
2.56
2.56
2.54
2.53
2.00
Cl
O
F
F
O
O
^{1}H NMR, 400 MHz, CDCl$_3$
3ka
1.00
1.00
1.01
2.27
1.00
2.13
3.04
f1 (ppm)

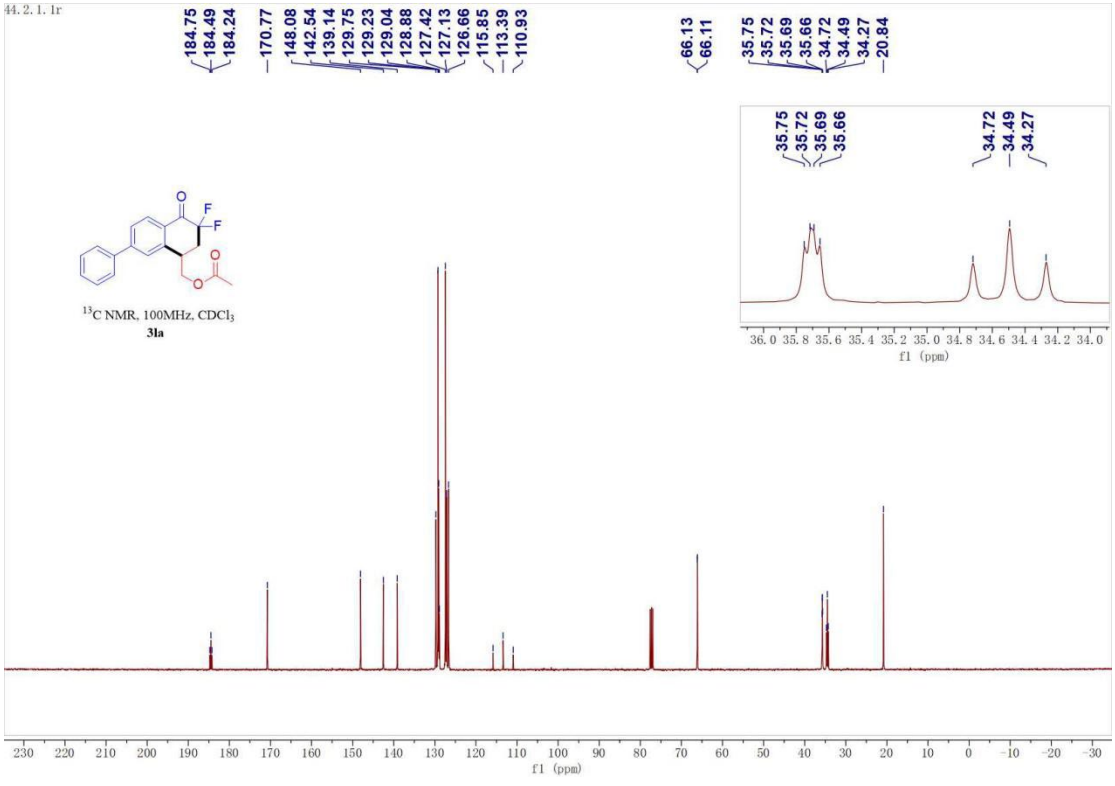

1-2. 2. 1. 1r
183.61
183.35
183.08
170.61
144.59
135.92
134.77
131.64
127.55
127.38
115.46
113.00
110.53
66.53
35.82
35.77
35.72
33.87
33.64
33.41
20.66
Cl
O
F
F
O
O
^{13}C NMR, 100 MHz, $CDCl_3$
3ka
f1 (ppm)


1-2. 3. 1. 1r
-103.67
-103.71
-103.73
-103.76
-104.38
-104.42
-104.44
-104.47
-104.55
-104.59
-104.63
-105.24
-105.26
-105.30
-105.34
Cl
O
F
F
O
O
^{19}F NMR, 376 MHz, $CDCl_3$
3ka
1.00
1.00
f1 (ppm)



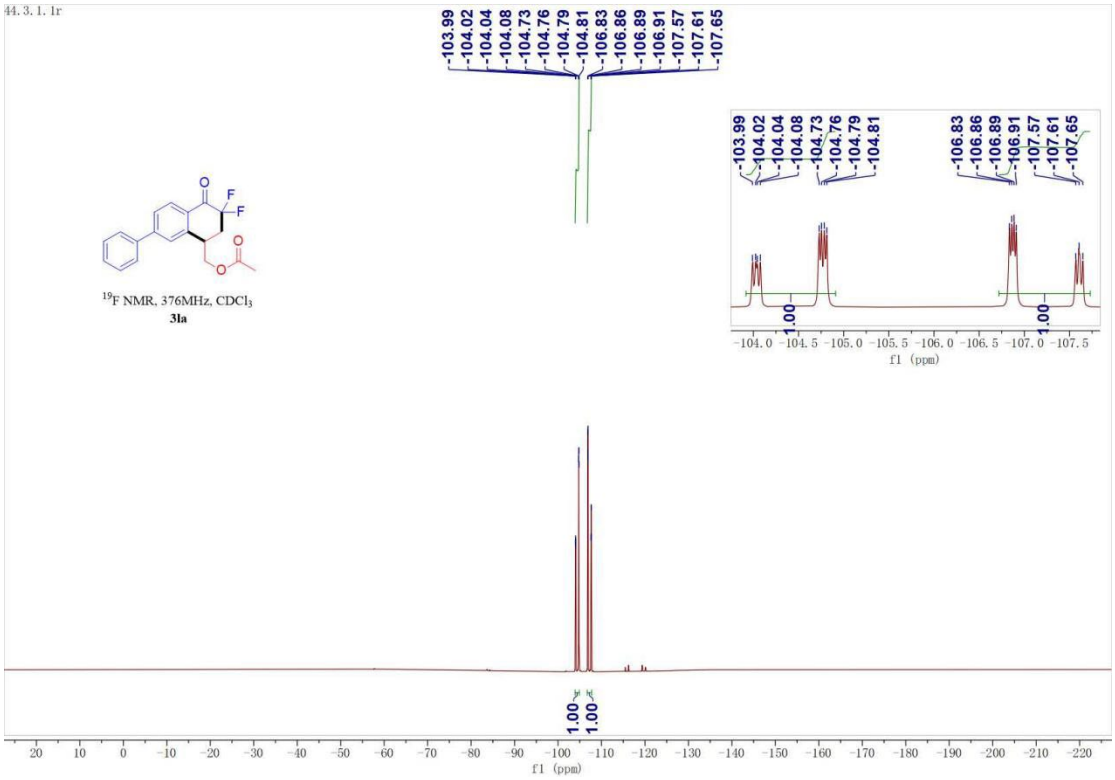
^{1}H NMR, 400MHz, $CDCl_3$

3la



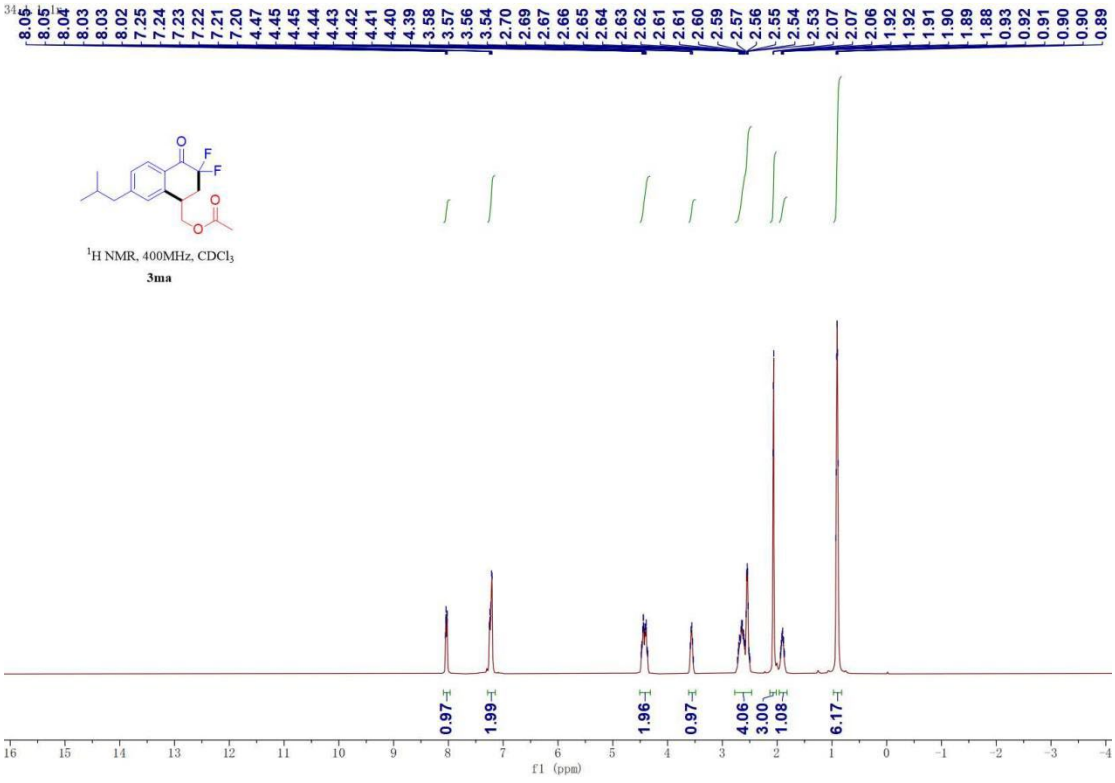
^{13}C NMR, 100MHz, $CDCl_3$

3la



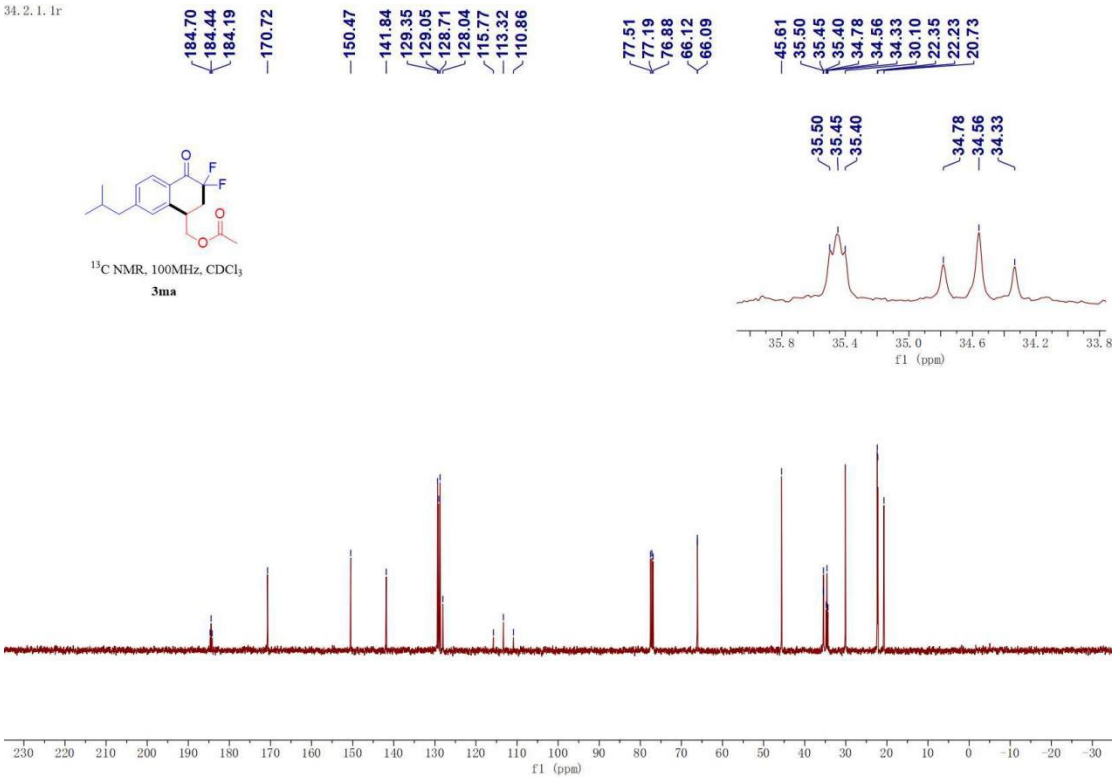
^{19}F NMR, 376MHz, $CDCl_3$

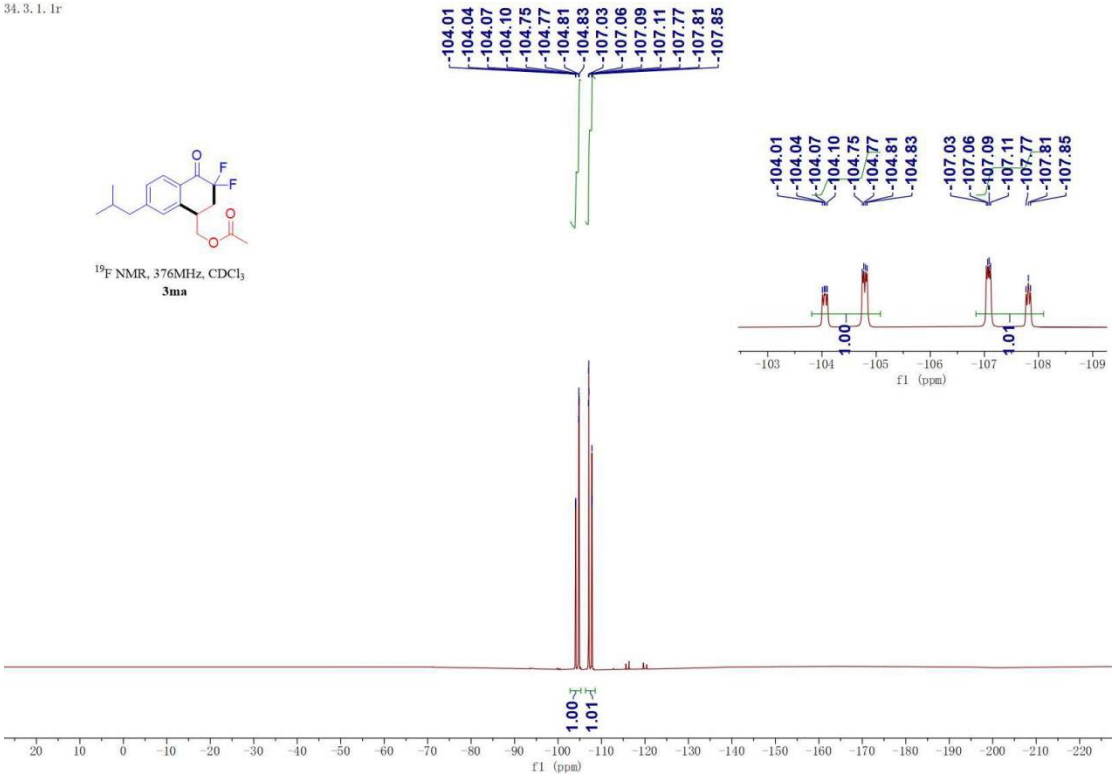
3la

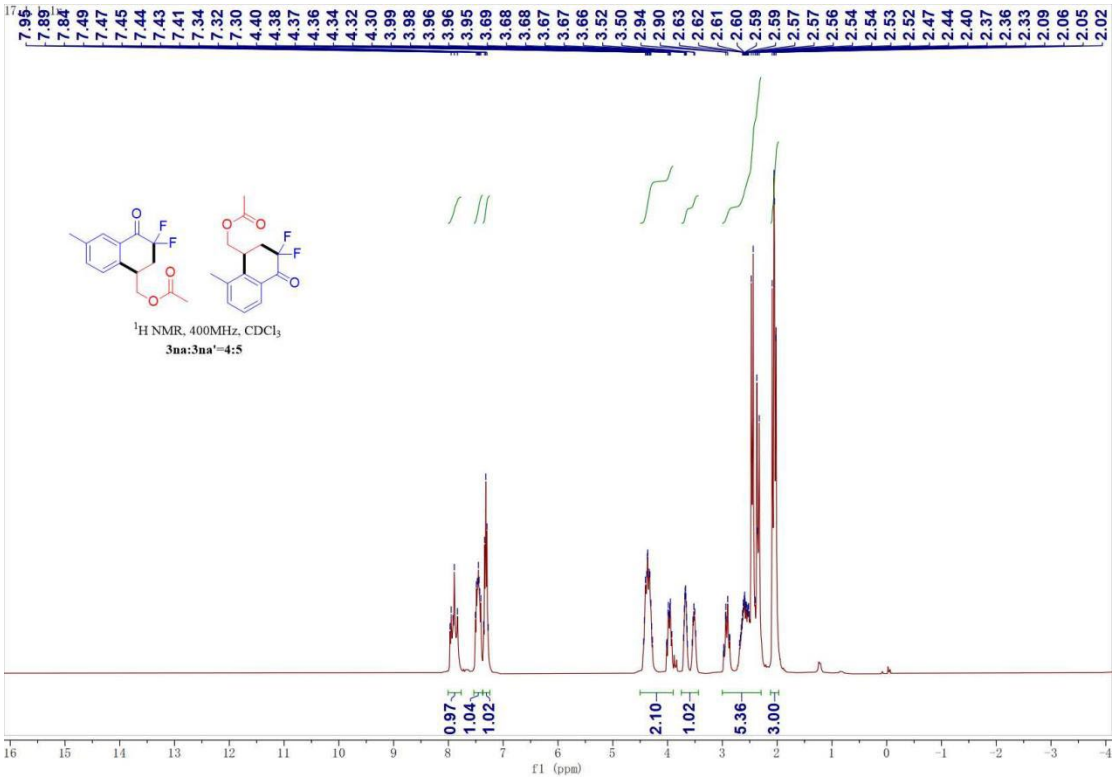


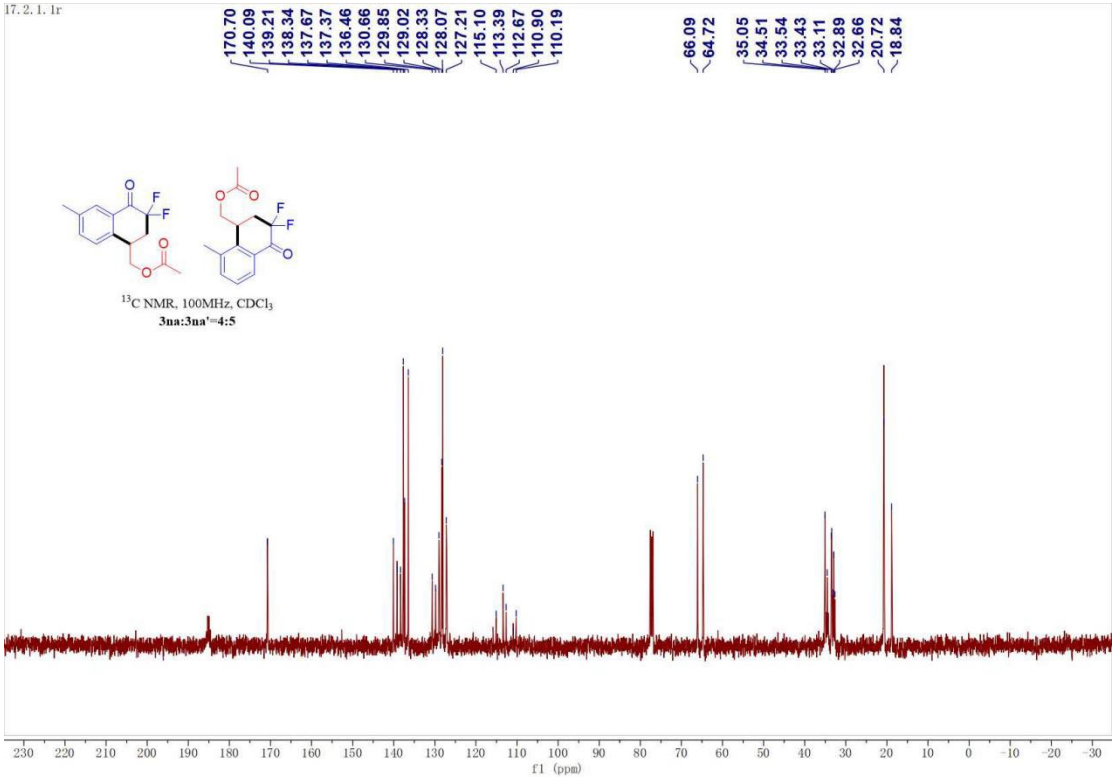
^{1}H NMR, 400MHz, $CDCl_3$

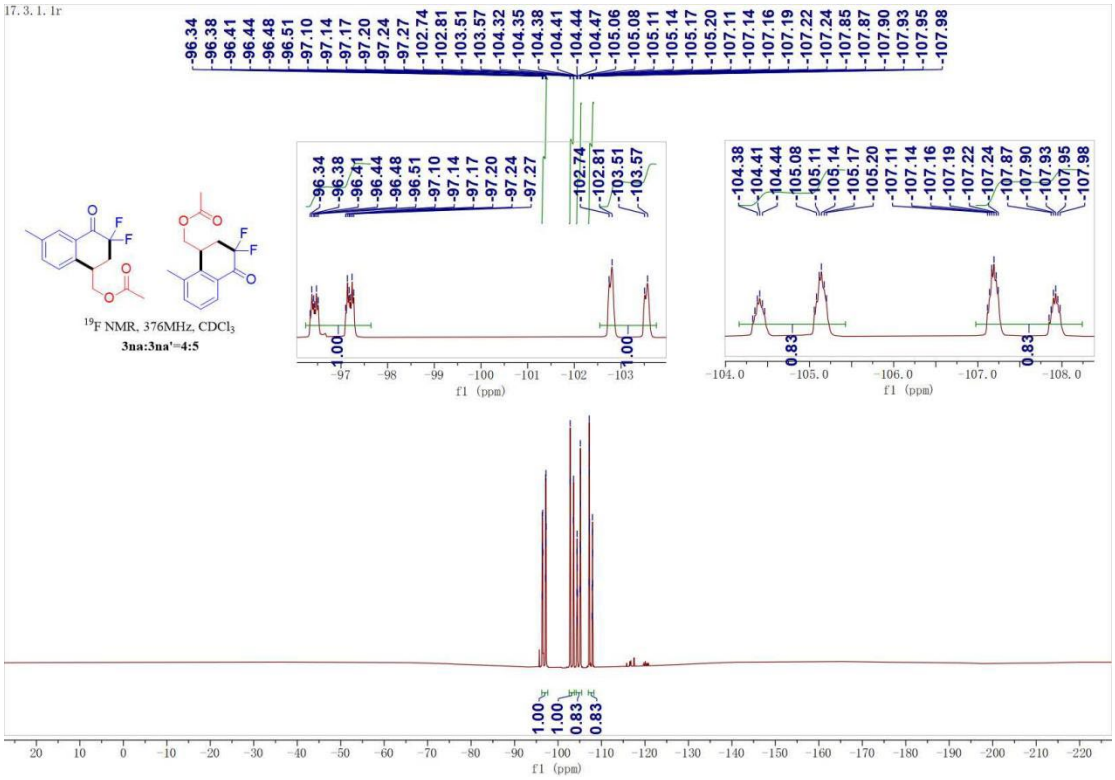
3ma


34.2.1.1r
184.70
184.44
184.19
170.72
150.47
141.84
129.35
129.05
128.71
128.04
115.77
113.32
110.86
77.51
77.19
76.88
66.12
66.09
45.61
35.50
35.45
35.40
34.78
34.56
34.33
30.10
22.35
22.23
20.73
F
F
O
O
O
13C NMR, 100MHz, CDCl3
3ma
35.50
35.45
35.40
34.78
34.56
34.33
35.8
35.4
35.0
34.6
34.2
33.8
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)


34.3.1.1r
-104.01
-104.04
-104.07
-104.10
-104.75
-104.77
-104.81
-104.83
-107.03
-107.06
-107.09
-107.11
-107.77
-107.81
-107.85
F
F
O
O
O
19F NMR, 376MHz, CDCl3
3ma
1.00
1.01
-103
-104
-105
-106
-107
-108
-109
f1 (ppm)
1.00
1.01
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

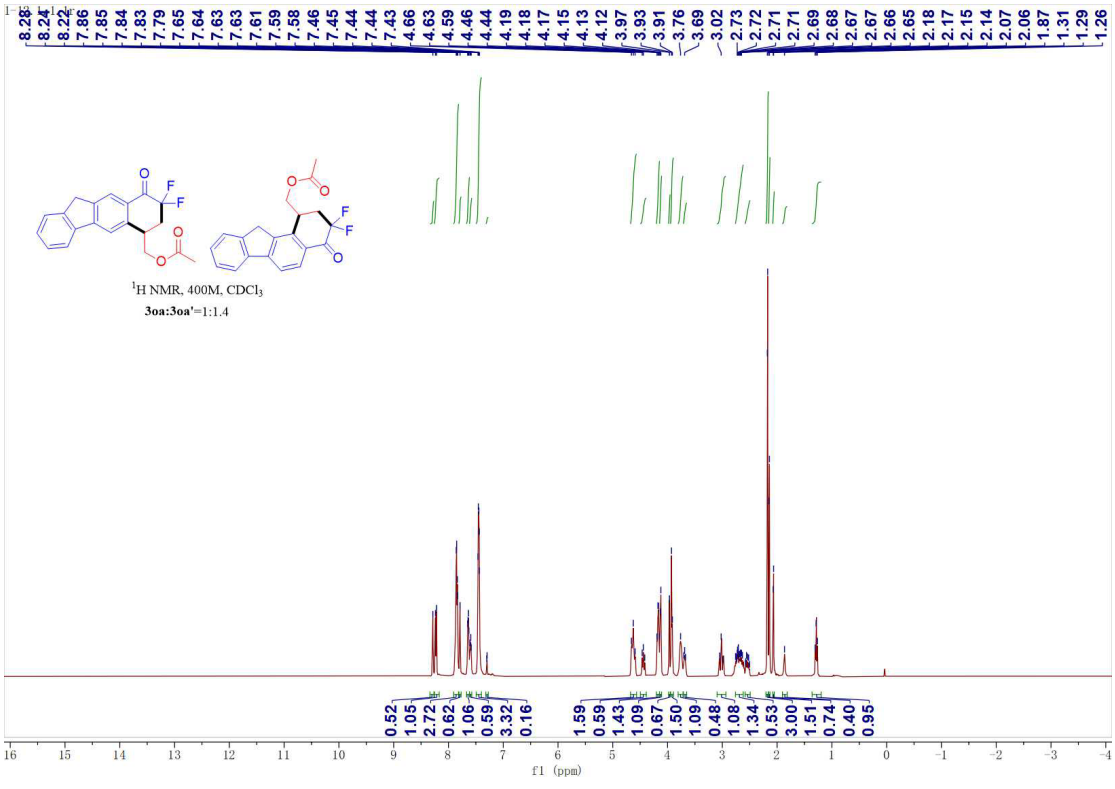

^{1}H NMR, 400MHz, $CDCl_3$
3na:3na'=4:5
f1 (ppm)


^{13}C NMR, 100MHz, $CDCl_3$
3na:3na'=4:5
f1 (ppm)



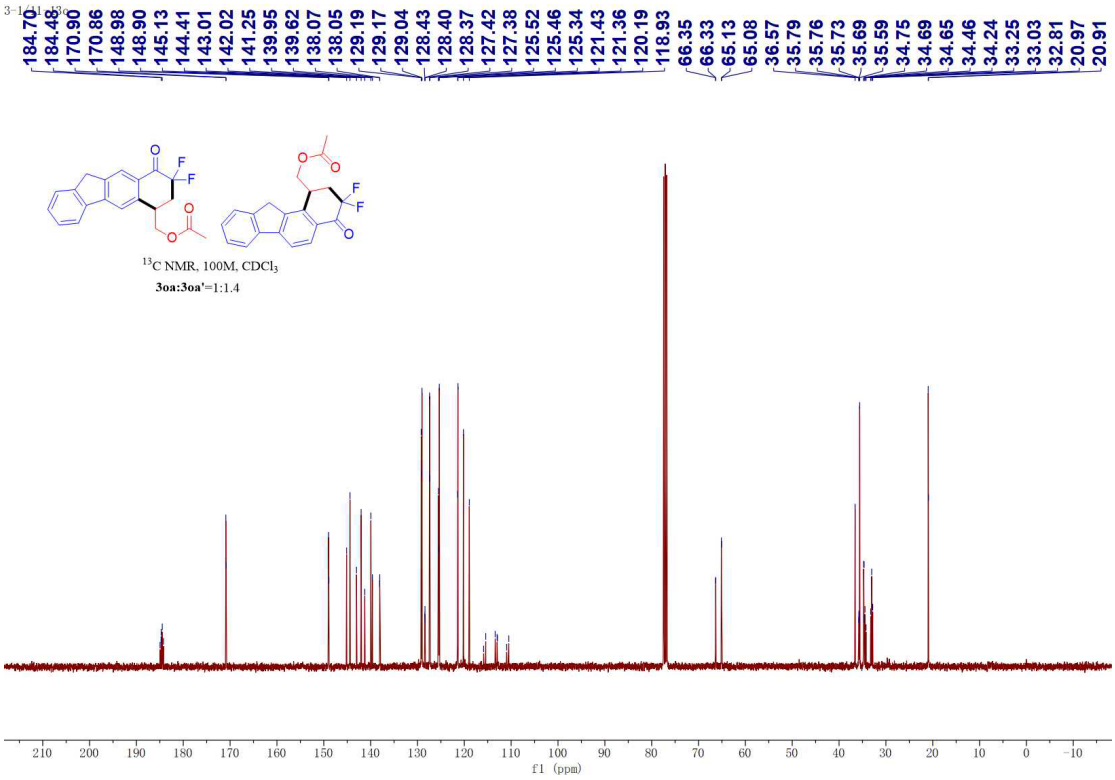
^{19}F NMR, 376MHz, $CDCl_3$

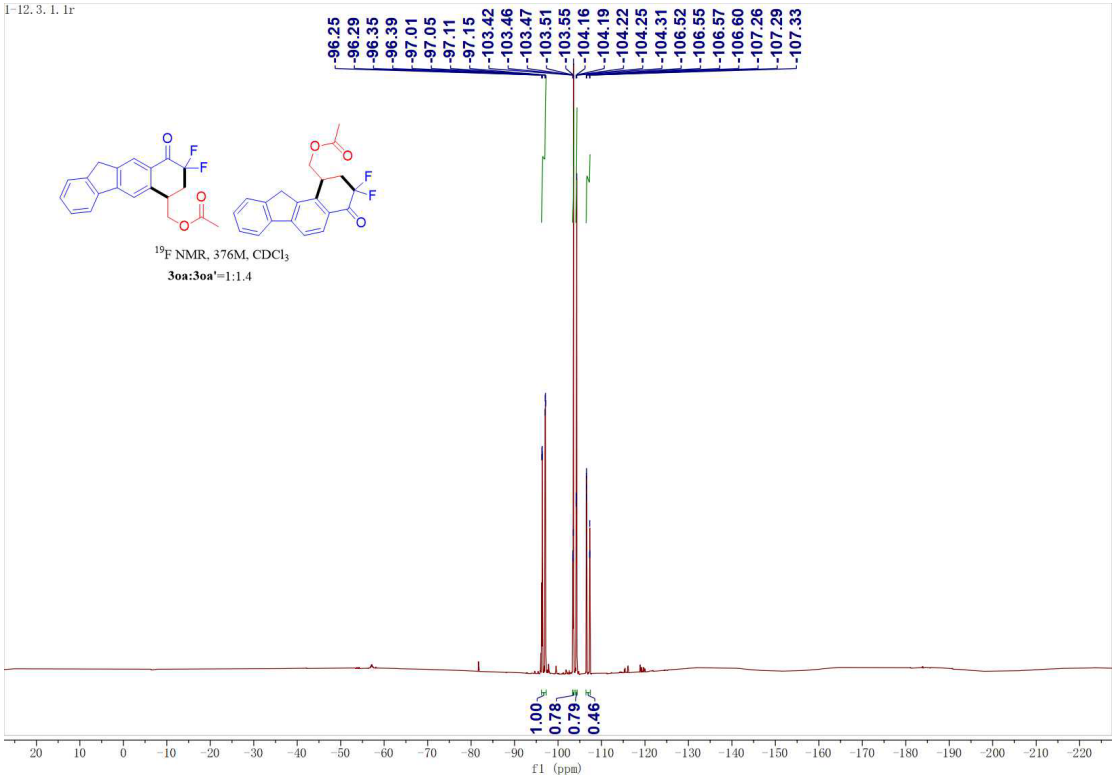
3na:3na'=4:5

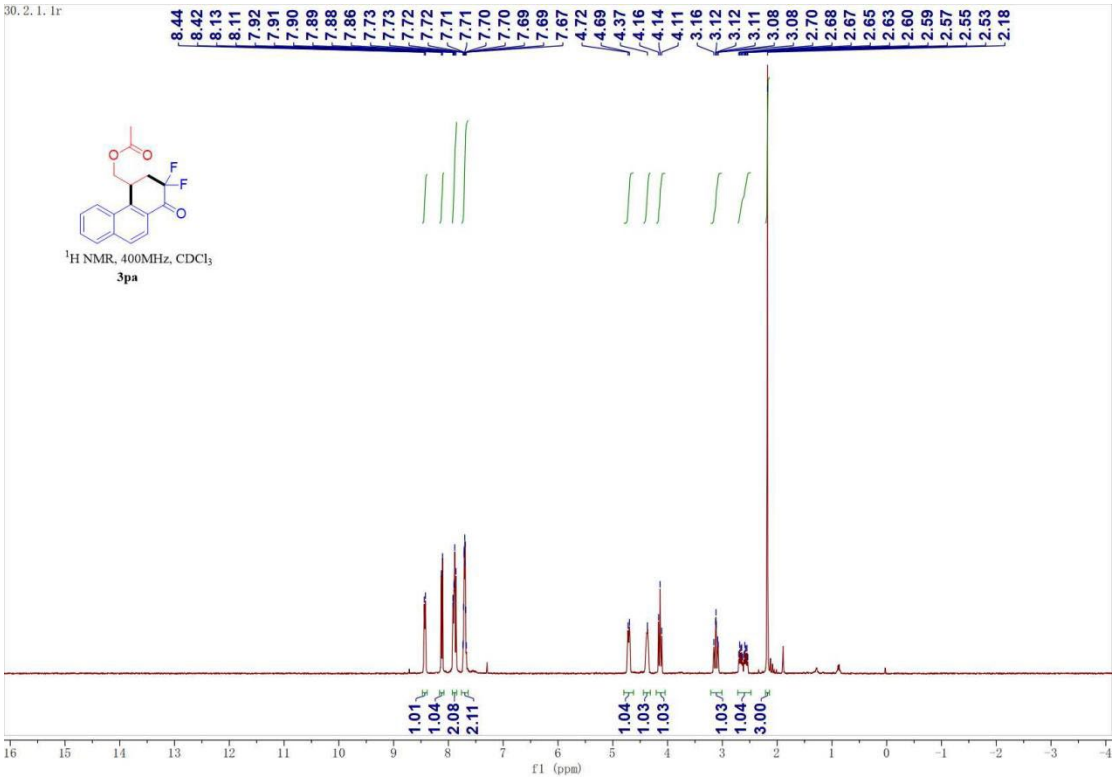


^{1}H NMR, 400M, $CDCl_3$

3oa:3oa'=1:1.4

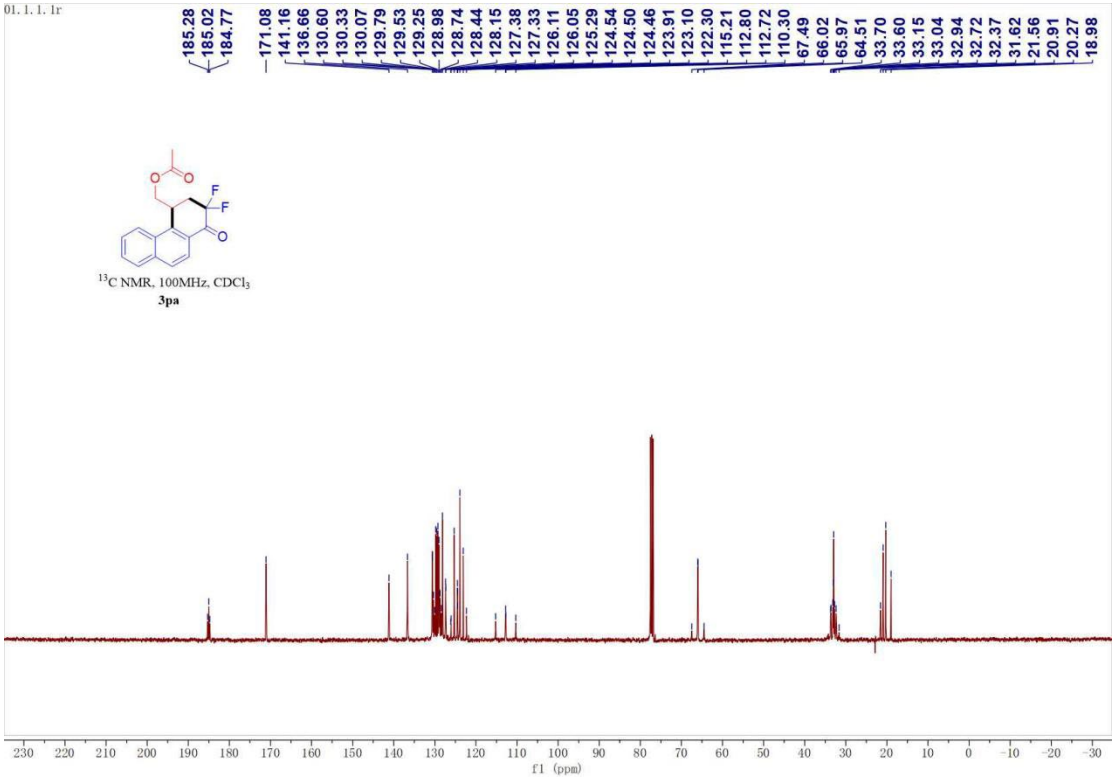

184.70
184.48
170.90
170.86
148.98
148.90
145.13
144.41
143.01
142.02
141.25
139.95
139.62
138.07
138.05
129.19
129.17
129.04
128.43
128.40
128.37
127.42
127.38
125.52
125.46
125.34
121.43
121.36
120.19
118.93
66.35
66.33
65.13
65.08
36.57
35.79
35.76
35.73
35.69
35.59
34.75
34.69
34.65
34.46
34.24
33.25
33.03
32.81
20.97
20.91
F
F
O
O
O
O
F
F
O
^{13}C NMR, 100M, CDCl$_3$
3oa:3oa'=1:1.4
f1 (ppm)


-96.25
-96.29
-96.35
-96.39
-97.01
-97.05
-97.11
-97.15
-103.42
-103.46
-103.47
-103.51
-103.55
-104.16
-104.19
-104.22
-104.25
-104.31
-106.52
-106.55
-106.57
-106.60
-107.26
-107.29
-107.33
1.00
0.78
0.79
0.46
F
F
O
O
O
O
F
F
O
^{19}F NMR, 376M, CDCl$_3$
3oa:3oa'=1:1.4
f1 (ppm)



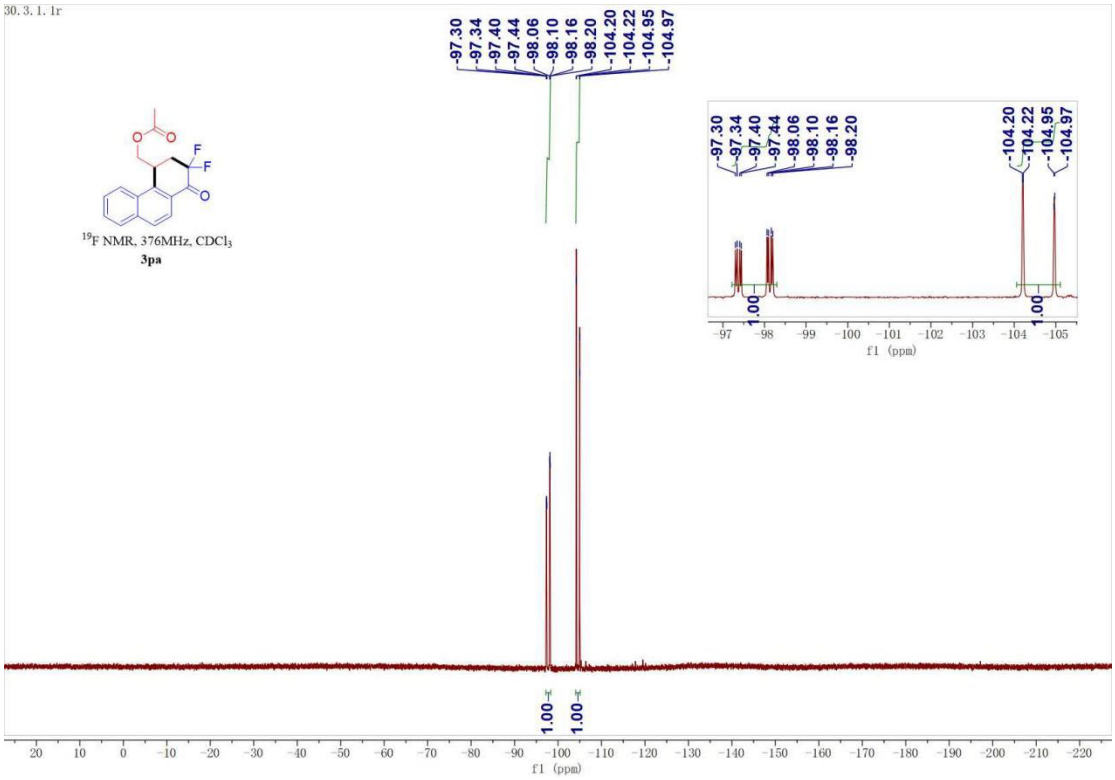
^{1}H NMR, 400MHz, $CDCl_3$

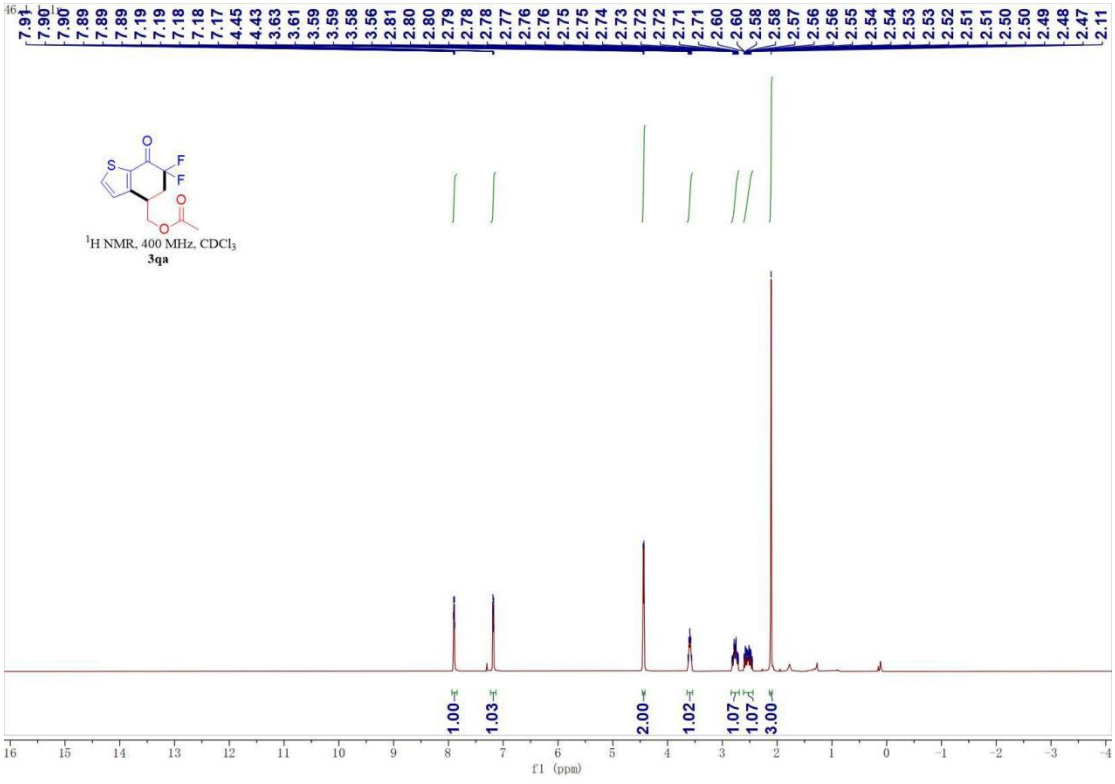
3pa

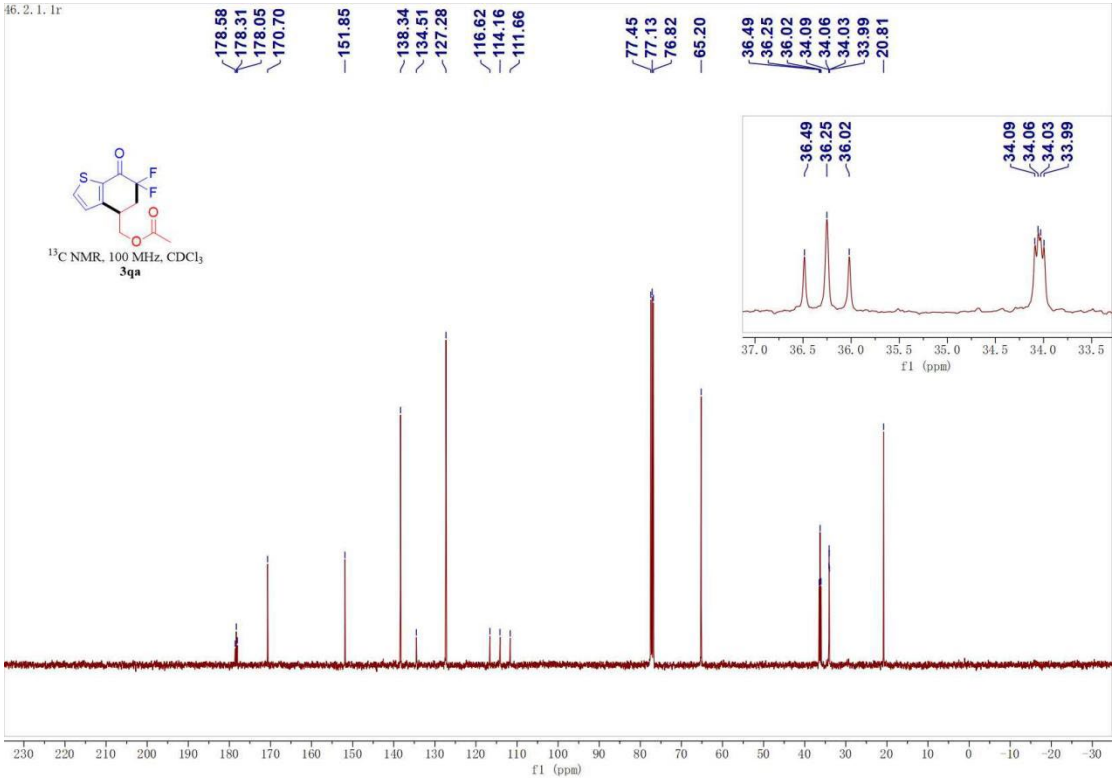


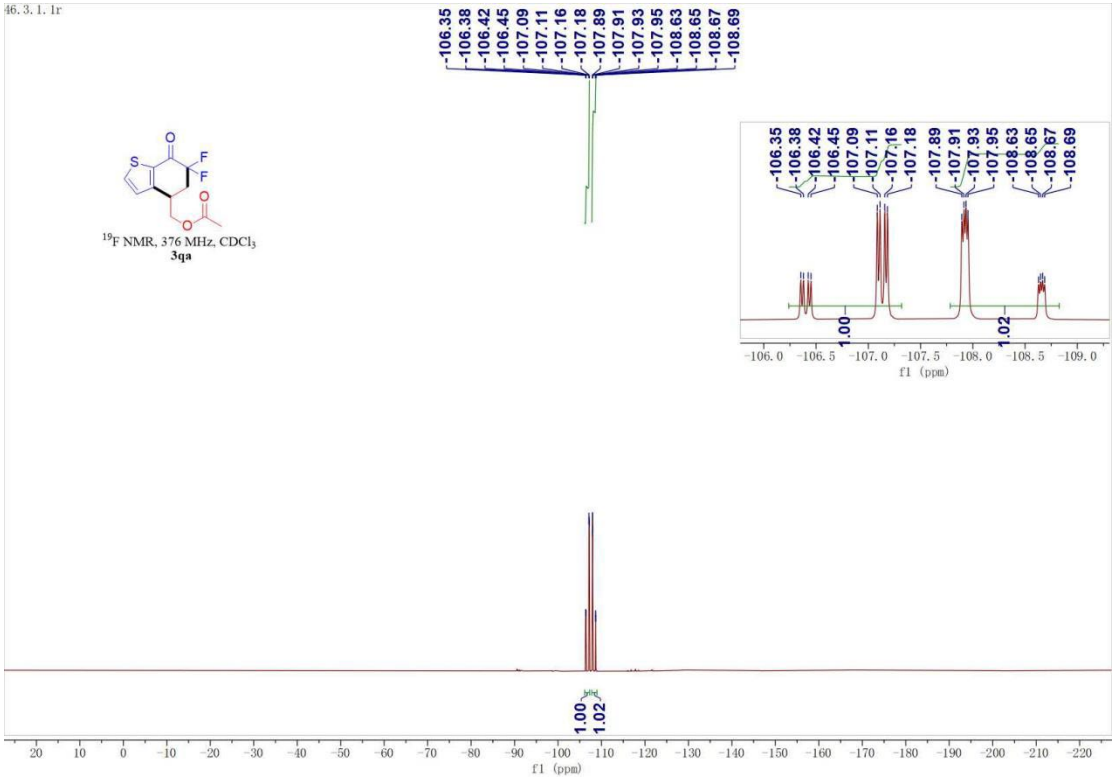
^{13}C NMR, 100MHz, $CDCl_3$

3pa

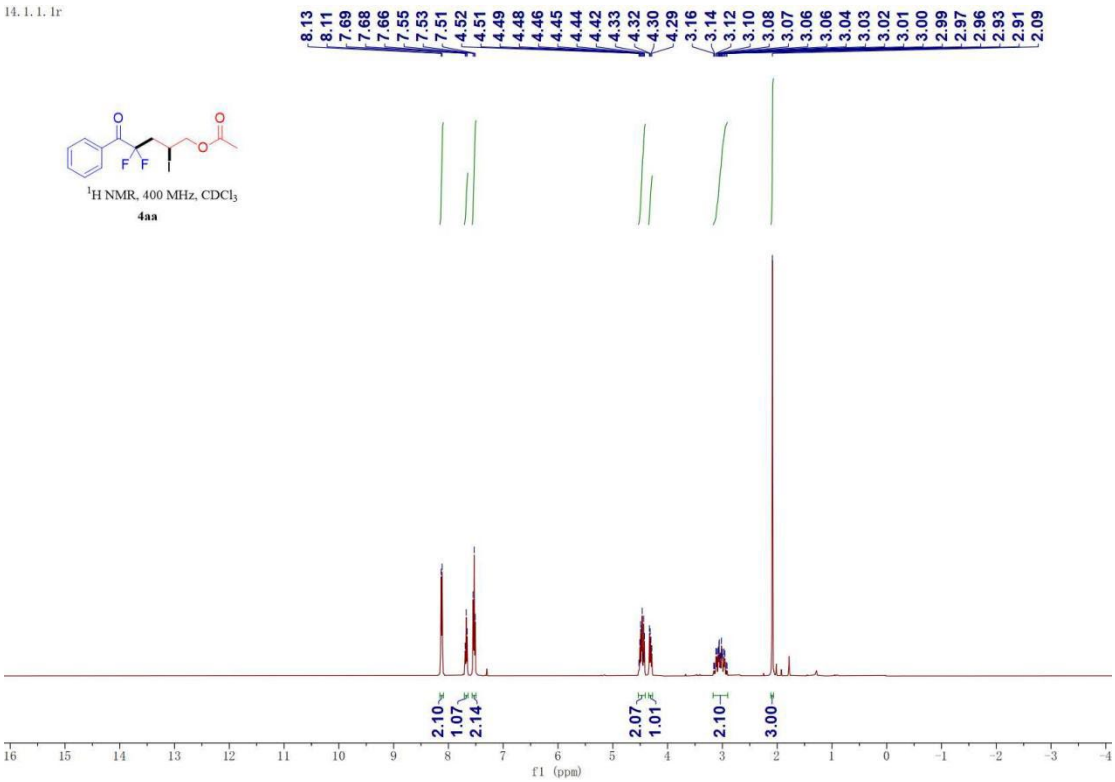

30. 3. 1. 1r
-97.30
-97.34
-97.40
-97.44
-98.06
-98.10
-98.16
-98.20
-104.20
-104.22
-104.95
-104.97
F
F
O
O
^{19}F NMR, 376MHz, CDCl$_3$
3pa
1.00
1.00
f1 (ppm)


7.91
7.90
7.89
7.19
7.18
7.17
4.45
4.43
3.63
3.61
3.59
3.58
3.56
2.81
2.80
2.79
2.78
2.77
2.76
2.75
2.74
2.73
2.72
2.71
2.60
2.58
2.57
2.56
2.55
2.54
2.53
2.52
2.51
2.50
2.49
2.48
2.47
2.11
S
O
F
F
O
O
^{1}H NMR, 400 MHz, CDCl$_3$
3qa
1.00
1.03
2.00
1.02
1.07
1.07
3.00
f1 (ppm)

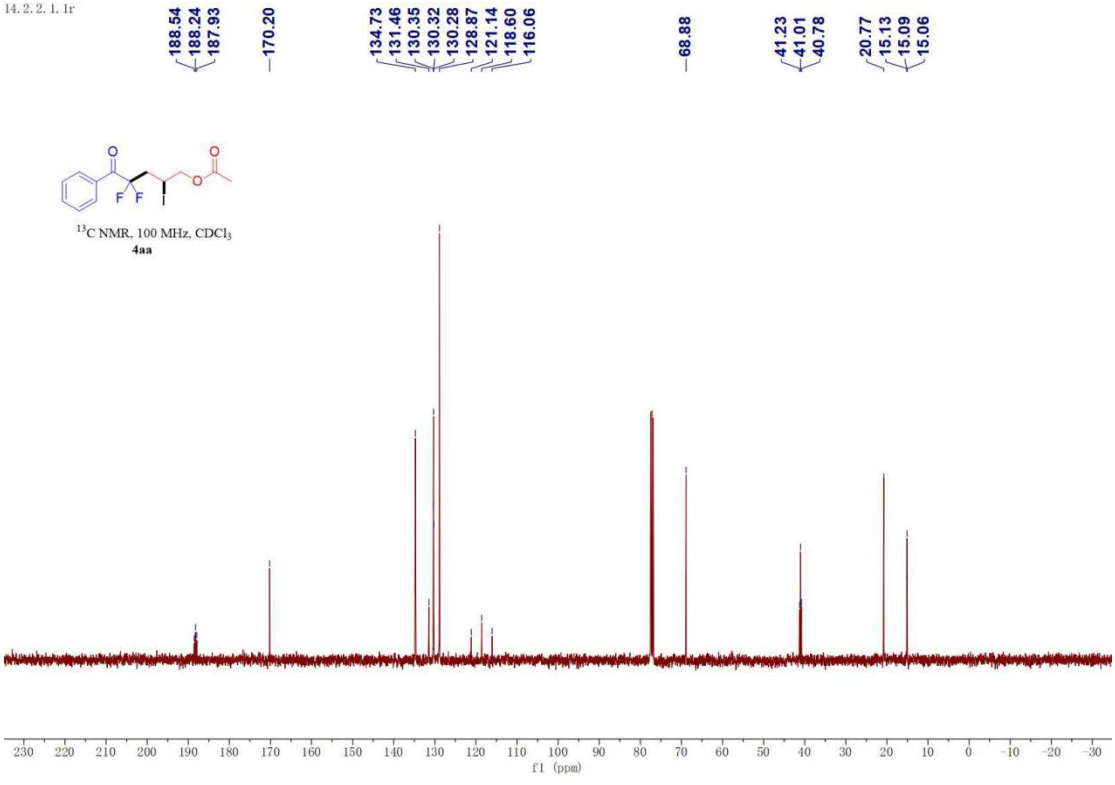

46.2.1.1r
178.58
178.31
178.05
170.70
151.85
138.34
134.51
127.28
116.62
114.16
111.66
77.45
77.13
76.82
65.20
36.49
36.25
36.02
34.09
34.06
34.03
33.99
20.81
^{13}C NMR, 100 MHz, CDCl$_3$
3qa
f1 (ppm)


46.3.1.1r
-106.35
-106.38
-106.42
-106.45
-107.09
-107.11
-107.16
-107.18
-107.89
-107.91
-107.93
-107.95
-108.63
-108.65
-108.67
-108.69
1.00
1.02
^{19}F NMR, 376 MHz, CDCl$_3$
3qa
f1 (ppm)

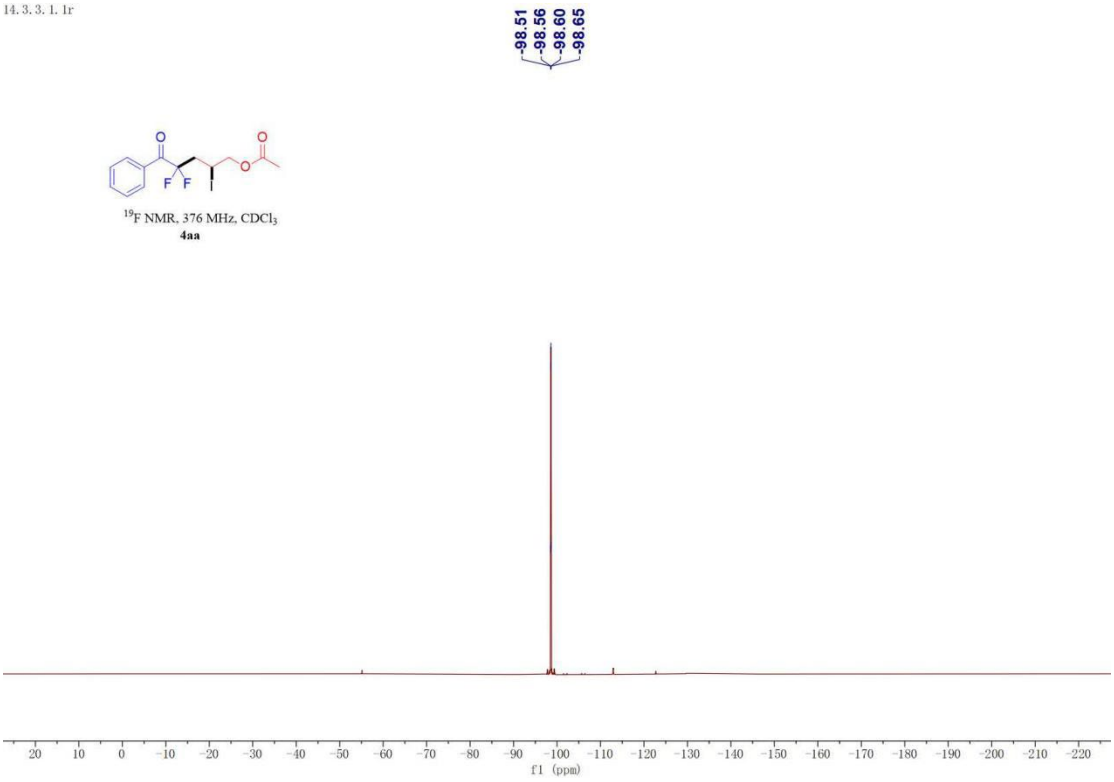
14. 1. 1. 1r



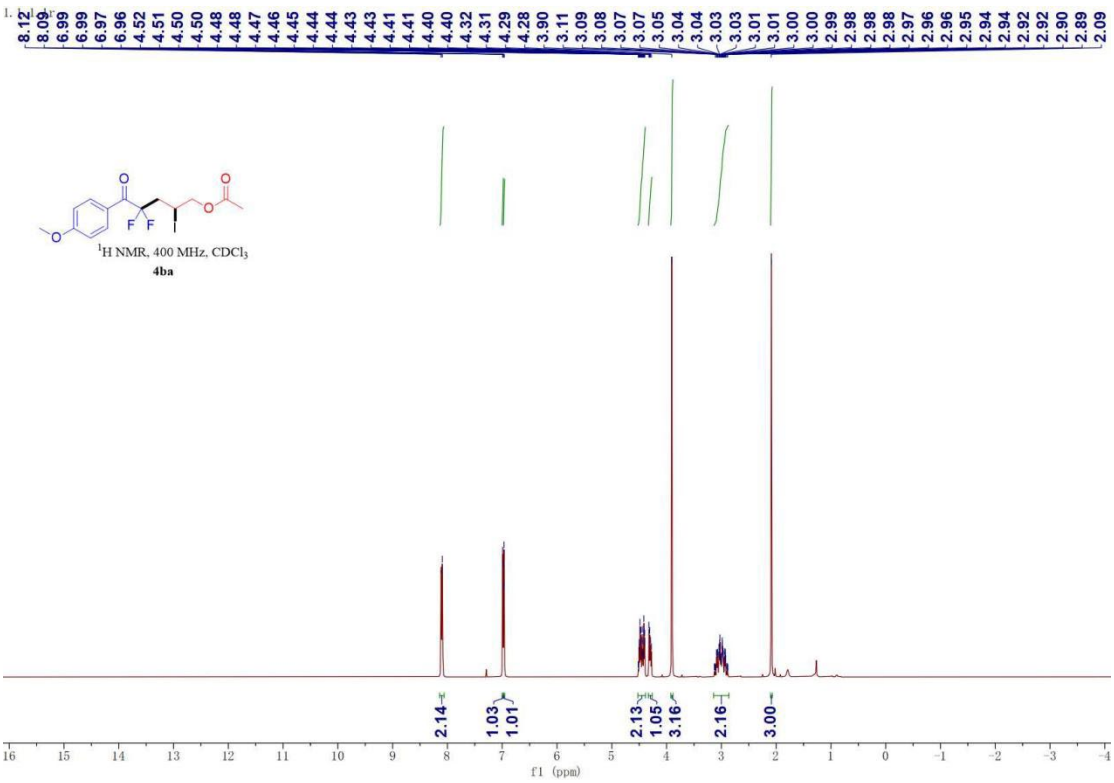
14. 2. 2. 1. 1r



14.3.3.1.1r

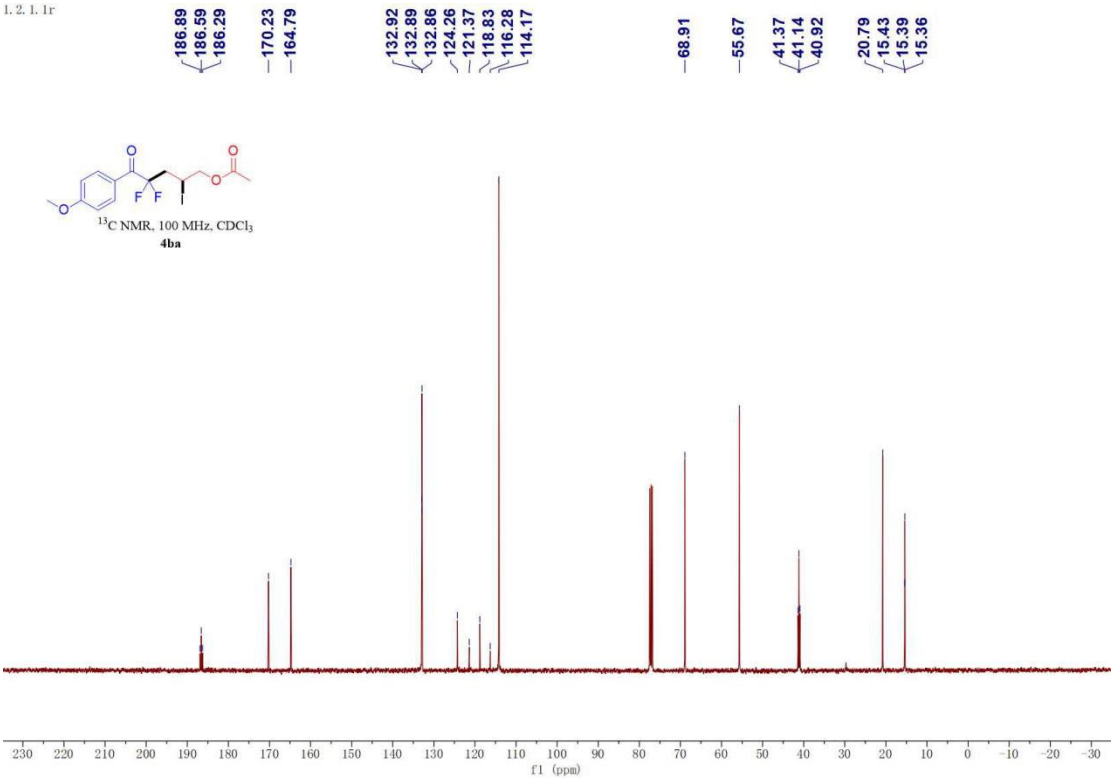


^{19}F NMR, 376 MHz, $CDCl_3$
4aa



^{1}H NMR, 400 MHz, $CDCl_3$
4ba

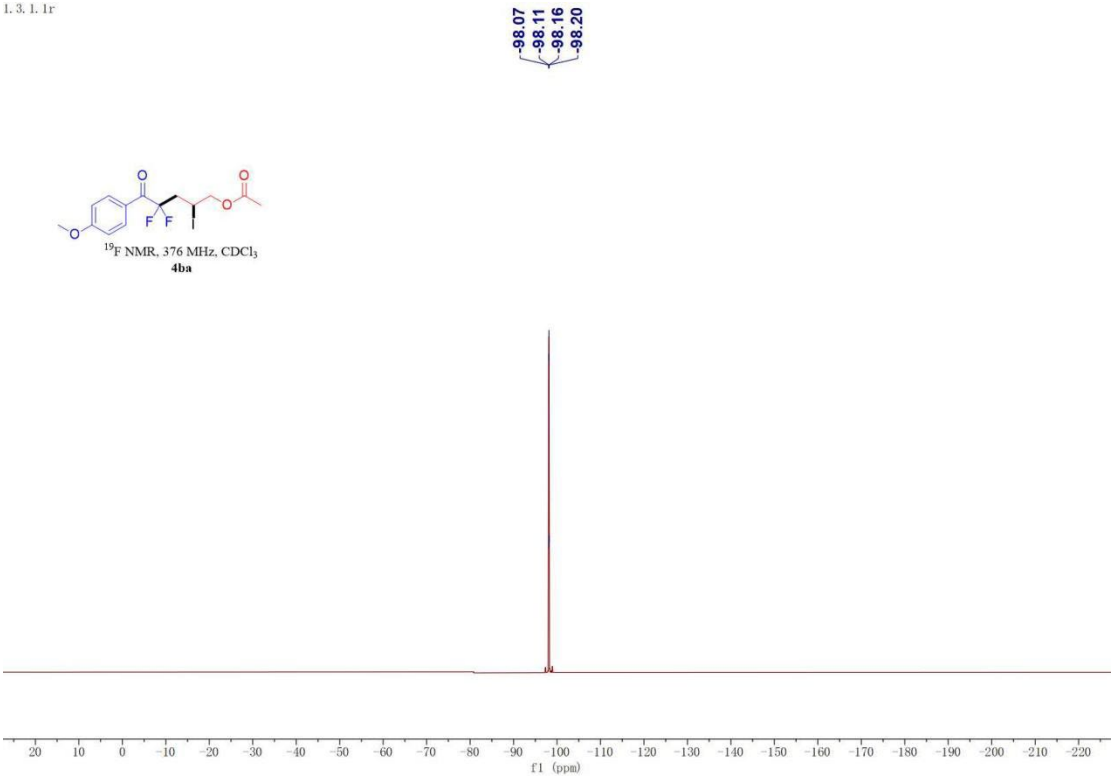
1. 2. 1. 1r



^{13}C NMR, 100 MHz, $CDCl_3$

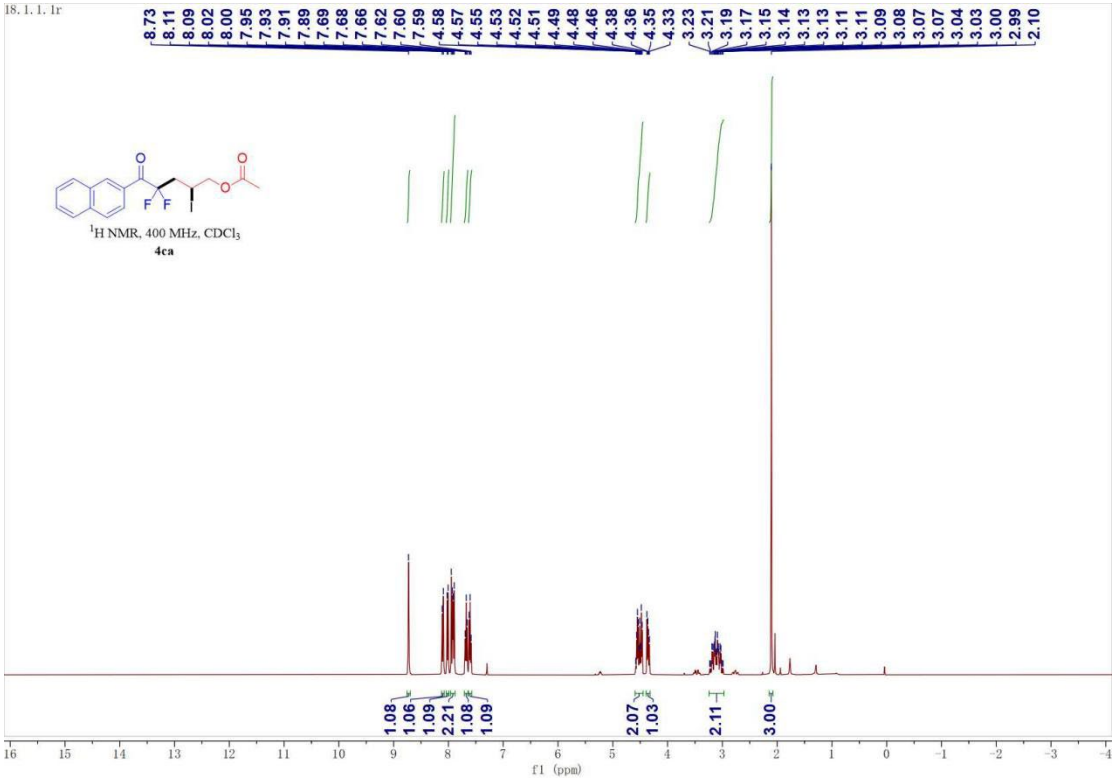
4ba

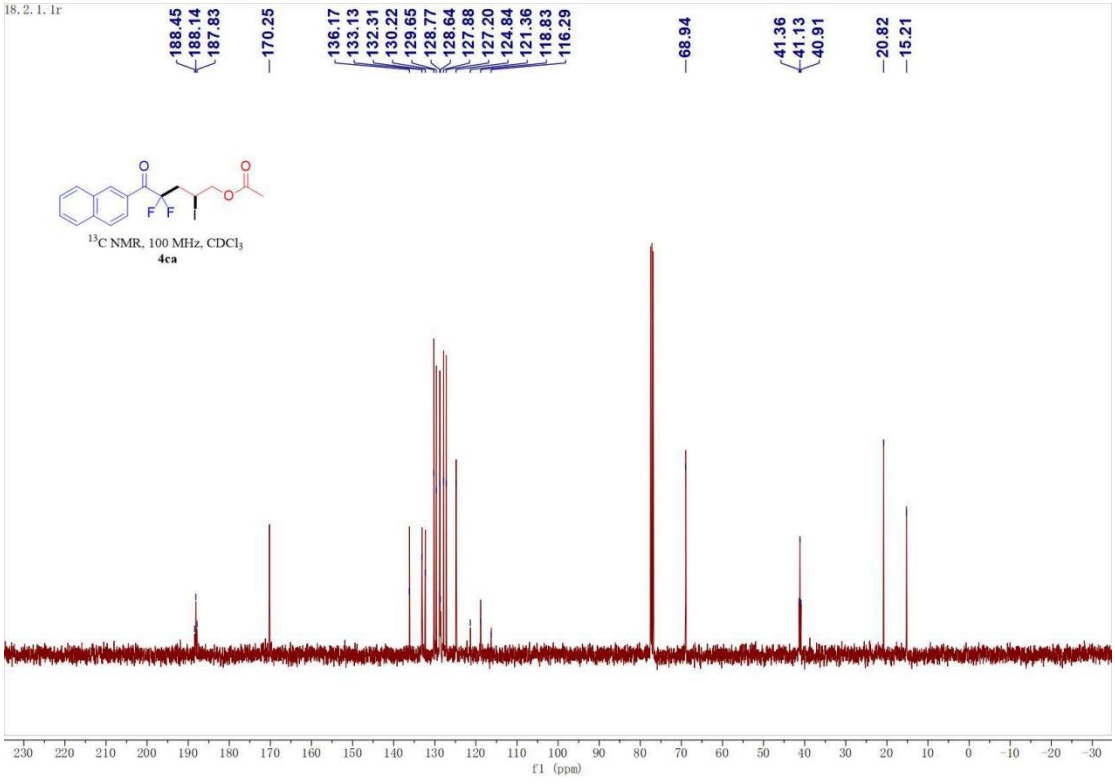
1. 3. 1. 1r

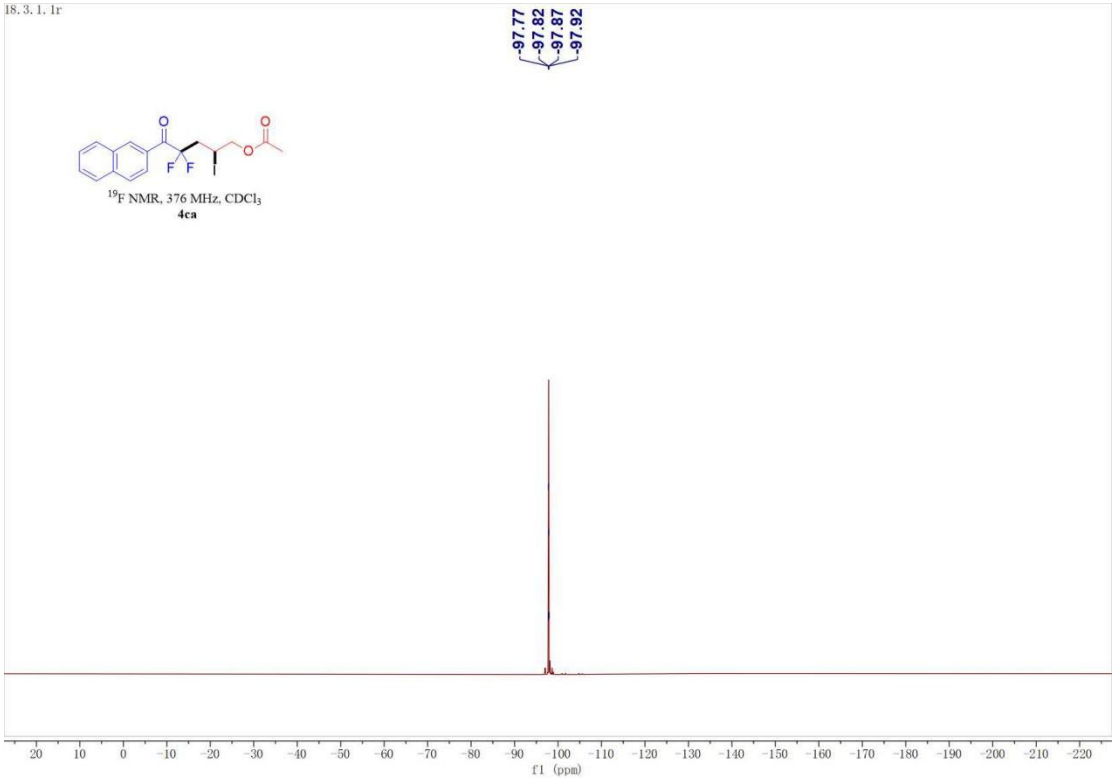


^{19}F NMR, 376 MHz, $CDCl_3$

4ba


18. 1. 1. 1r
8.73
8.11
8.09
8.02
8.00
7.95
7.93
7.91
7.89
7.69
7.68
7.66
7.62
7.60
7.59
4.58
4.57
4.55
4.53
4.52
4.51
4.49
4.48
4.46
4.38
4.36
4.35
4.33
3.23
3.21
3.19
3.17
3.15
3.14
3.13
3.13
3.11
3.11
3.09
3.08
3.07
3.07
3.04
3.03
3.00
2.99
2.10
F F
1H NMR, 400 MHz, CDCl3
4ca
1.08
1.06
1.09
2.21
1.08
1.09
2.07
1.03
2.11
3.00
f1 (ppm)


18. 2. 1. 1r
188.45
188.14
187.83
170.25
136.17
133.13
132.31
130.22
129.65
128.77
128.64
127.88
127.20
124.84
121.36
118.83
116.29
68.94
41.36
41.13
40.91
20.82
15.21
F F
13C NMR, 100 MHz, CDCl3
4ca
f1 (ppm)



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

4ca

9 X-Ray structures