Supplementary Information

$TMSCFX_2$ (X = Cl, Br) as halofluorocarbene sources for the synthesis of halofluorocyclopropanes

Dingben Chen[a,b], Zili Fan[a], Ling Huang[b], Kaili Gao[b], Pan Xiao[a,c], Chuanfa Ni[a] and Jinbo Hu[a,c*]

[a.] *Key Laboratory of Organofluorine Chemistry, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai, 200032, China.*

[b.] *School of Pharmaceutical and Materials Engineering, Taizhou University, Taizhou, Zhejiang, China.*

[c.] *School of Physical Science and Technology, ShanghaiTech University, 100 Haike Road, Shanghai 201210, China.*

*E-mail：jinbohu@sioc.ac.cn

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1. General Information

Commercially available reagents were used without further purification. The solvent toluene was distilled from CaH_2. $CFBr_3$ was synthesized according to the literature.[1] Column chromatography was performed with 300-400 mesh silica gel. All melting points are uncorrected. ^1H, ^{13}C and ^{19}F NMR spectra were recorded on a 400 MHz NMR spectrometer. ^1H NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ at δ 0.00 ppm. ^{19}F NMR chemical shifts were reported relative to $CFCl_3$ at δ 0.00 ppm. ^{13}C NMR chemical shifts were determined relative to the signal of internal $(CH_3)_4Si$ at δ 0.00 ppm. TLC was carried out with 0.2-mm-thick silica gel plates (GF254). Visualization was accomplished by UV light. Mass spectra were obtained on a mass spectrometer. High-resolution mass data were recorded on a high-resolution mass spectrometer in the EI or ESI mode.

2. Experimental Procedures

2.1 General procedures for the synthesis of chlorofluorocyclopropanes with $TMSCFCl_2$

Under argon atmosphere, *n*-Bu_4NBr (8.0 mg，0.025 mmol, 5 mol%), alkene **1** (0.5 mmol, 1.0 equiv), $TMSCFCl_2$ (130.0 mg, 0.75 mmol, 1.5 equiv) and toluene (2.0 mL) were added into an oven-dried pressure tube. The tube was sealed and the mixture was heated at 110 ℃ for 4 h . Then it was cooled to room temperature and poured into water (5 mL), followed by extraction with methyl *tert*-butyl ether (3 × 15 mL). The organic layers were combined and dried over anhydrous $MgSO_4$. After filtration and evaporation under vacuum, the residue was subjected to silica gel column chromatography using hexane as eluent to give product **2**.

2.2 General procedures for the synthesis of bromofluorocyclopropanes with $TMSCFBr_2$

Alkene **1** (0.25 mmol, 1.0 equiv.), benzyl triethylammonium chloride (5.5 mg, 10

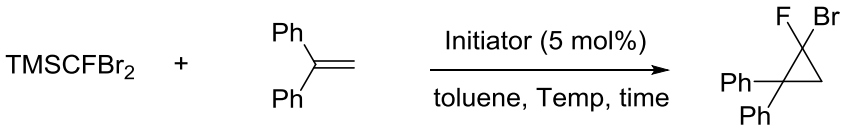
mol%), $TMSCFBr_2$ (141 mg, 0.5 mmol, 2.0 equiv.) and dichloromethane (2.0 mL) were added into a reaction tube. NaOH (120 mg, 3.0 mmol, 12.0 equiv.) formulated into 50 wt% aqueous NaOH solution (about 0.4 mL) was slowly dripped into the reaction tube, and then the mixture was stirred for 4 h at room temperature. After the reaction was finished, the water (10.0 mL) was added, followed by extraction with dichloromethane (3 × 15 mL). The organic layers were combined and dried over anhydrous Na_2SO_4. After filtration and evaporation under vacuum, the residue was subjected to silica gel column chromatography using hexane as eluent to give product **3**.

2.3 Experimental procedures for the synthesis of $TMSCFCl_2$ and $TMSCFBr_2$[2]

Under argon atmosphere, chlorotrimethylsilane (100.0 mmol), $CFCl_3$ (13.6 g, 100.0 mmol) or $CFBr_3$ (26.8 g, 100.0 mmol) in CH_2Cl_2 (50.0 mL) were added to a dry three-necked flask. Then tris(*N*,*N*-diethylamino)phosphine ($(Et_2N)_3P$, 24.7g, 100.0 mmol) in CH_2Cl_2 (50.0 mL) was slowly injected into the flask by a syringe pump in three hours at –70 ^oC. The reaction was gradually warmed to room temperature and stirred overnight. The product and the solvent CH_2Cl_2 were directly pumped into a cold trap by an oil pump, followed by distillation to remove dichloromethane and vacuum distillation (water pump) to obtain $TMSCFCl_2$ (10.9 g, 63% yield) or $TMSCFBr_2$ (22.3 g, 85% yield) in 60–80 ^oC.

3. Screening of Reaction Conditions Using $TMSCFBr_2$ and 1,1-Diphenylethylene in A Non-aqueous Medium

Table S1 Screening of reaction conditions using $TMSCFBr_2$ and 1,1-diphenylethylene 1,1-diphenylethylene (**1a**) in a non-aqueous medium[a]

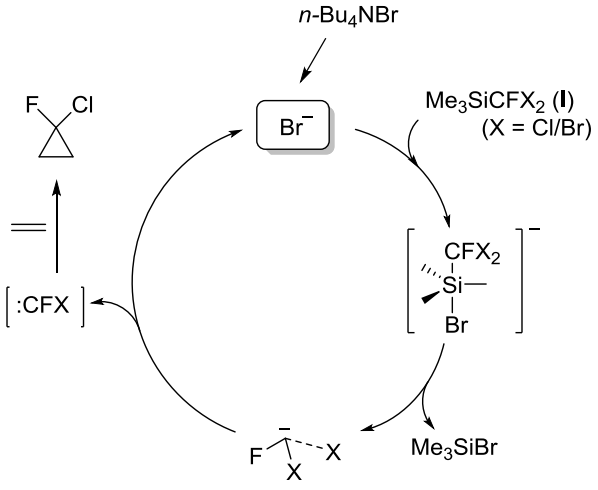


1a **3a**

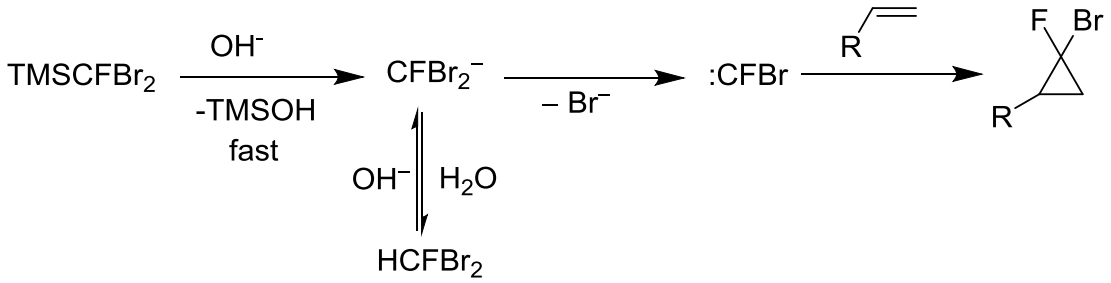
Entry	Initiator[b]	Temp (°C)	Time (h)	Yield[c] (%)
1	*n*-Bu_4NBr	110	4	65
2	*n*-Bu_4NBr	110	8	62
3	*n*-Bu_4NBr	80	8	33
4	*n*-Bu_4NCl	110	8	25
5	*n*-Bu_4NF	110	8	55
6	None	110	8	0

[a] $TMSCFBr_2$ (0.3 mmol, 1.5 equiv) and **1a** (0.2 mmol, 1.0 equiv) were used. [b] The amount of initiator was calculated on the basis of the amount of reagent **1a** used. [c] All yields were determined using ^{19}F NMR spectroscopy with $PhCF_3$ as an internal standard.

4. Proposed Mechanism of the [2+1] Cycloaddition Reactions between $TMSCFX_2$ and Alkenes in Non-aqueous or Aqueous Medium



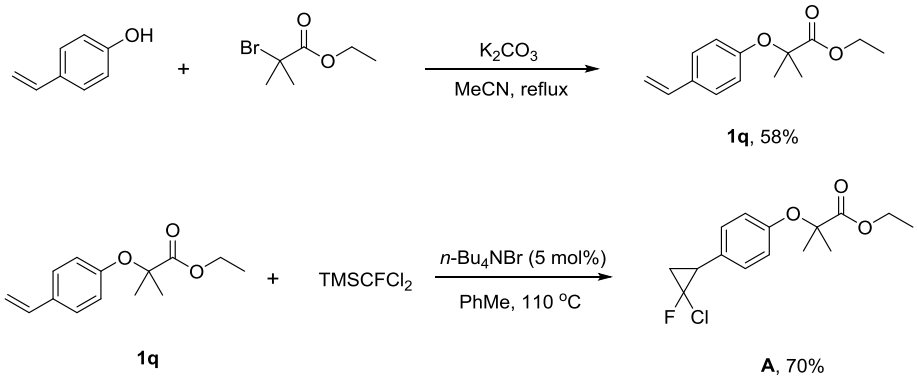
Scheme S1 The proposed mechanism of the [2+1] cycloaddition reaction between $TMSCFX_2$ and alkene in a non-aqueous medium



Scheme S2 The proposed mechanism of the [2+1] cycloaddition reactions between $TMSCFBr_2$ and alkene in an aqueous medium.

Further discussion： In the non-aqueous medium, TBAB (as a Lewis base initiator) attacks the silicon atom of $TMSCFX_2$ to produce a pentacoordinate silicate species, which releases a halofluoromethanide anion. The halofluoromethanide anion undergoes alpha-elimination of a halide anion to give halofluorocarbene under heating, which reacts with alkenes to give halofluorocyclopropanes. The activity of three different carbene reagents (towards the reaction with Lewis base TBAB) is different, as their Lewis acidities are different. Indeed, we found that $TMSCFBr_2$ (with the lowest Lewis acidity among three carbene precursors) could not be fully consumed after heating in toluene for 4 hours in the presence of catalytic amount of TBAB, and 28% of unreacted $TMSCFBr_2$ remained. However, in aqueous medium, NaOH (as a strong nucleophile) can attack all three halofluorocarbene reagents ($TMSCF_2Br$, $TMSCFCl_2$, and $TMSCFBr_2$) readily to produce halofluorocarbene species. Because the intrinsic reactivity of chlorofluorocarbene and bromofluorocarbene towards alkenes are higher than that of difluorocarbene, as evidenced by the fact that the [2+1] cyclopropanations can be achieved in aqueous solution with $TMSCFCl_2$ and $TMSCFBr_2$. Note that such [2+1] reaction with difluorocarbene (from $TMSCF_2Br$) could not be efficiently accomplished in aqueous NaOH solution because NaOH competes with alkene to react with difluorocarbene. These results are indeed consistent with the previous literature.[18]

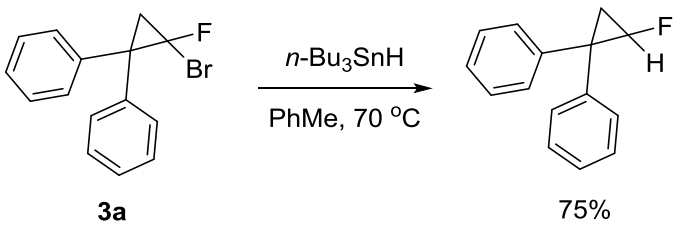
5. Synthesis of Chlorofluorocyclopropane-Containing Hypolipemic Agent A



4-Vinylphenol (1.2 g, 10.0 mmol), ethyl 2-bromo-2-methylpropanoate (2.34 g, 12.0 mmol) and K_2CO_3 (2.76 g, 20.0 mmol) in MeCN (30 mL) was stirred at reflux for 5 hours. Then the mixture was filtered and the filtrate was evaporated under vacuum. The residue was subjected to silica gel column chromatography using ethyl acetate and n-hexane as eluent to give ethyl 2-methyl-2-(4-vinylphenoxy)propanoate (**1q**) (1.35 g, 58% yield).

The hypolipemic agent **A** was synthesized from **1q** and $TMSCFCl_2$ according to the general procedures for the synthesis of chlorofluorocyclopropane products **2**. The yield of **A** was 70%.

6. Debromination of Fluorobromocyclopropane 3a with *n*-Bu_3SnH

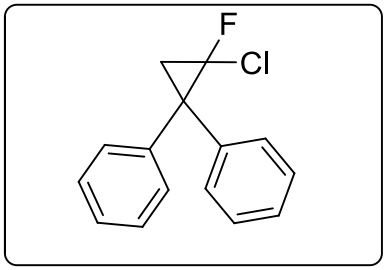


To a stirred solution of fluorobromocyclopropane **3a** (291.0 mg, 1.0 mmol) and AIBN (16.4 mg, 0.1 mmol) in benzene (5.0 mL) at 70 °C under argon atmosphere was

slowly added (ca. 0.5 h) a solution of tributyltin hydride (1.0 mL, 3.7 mmol) in benzene (3.0 mL). The reaction mixture was further stirred at 70 ^{o}C for 4 h. After the removal of benzene under reduced pressure, acetonitrile (10.0 mL) was added, and the mixture was washed with *n*-hexane (3 × 5.0 mL). Acetonitrile was removed under reduced pressure, and the residue was subject to flash chromatography to give the pure product in 75% yield (159.0 mg).

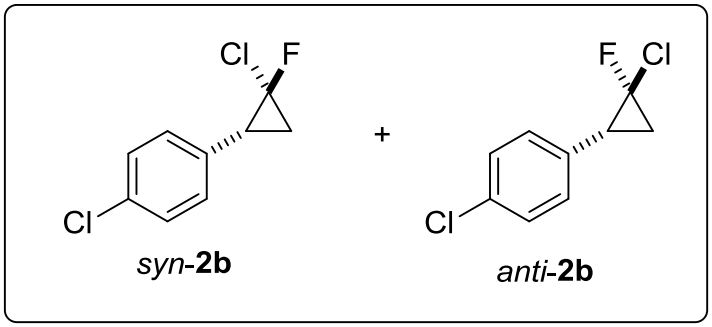
7. Characterization Data of Isolated Products

(2-Chloro-2-fluorocyclopropane-1,1-diyl)dibenzene (**2a**)[3]



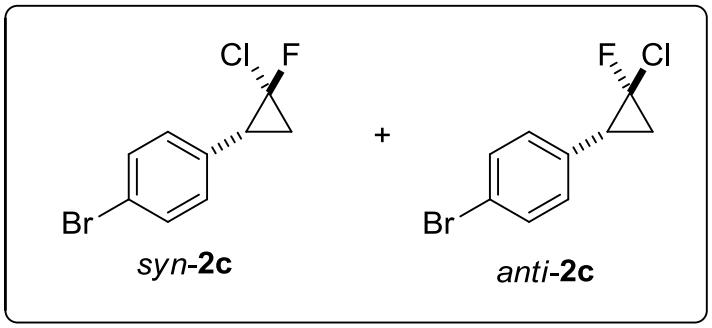
Yield: 119 mg (97%), Yellow solid. M.p.: 76 − 77 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.46 – 7.42 (m, 4H, CH, Ar), 7.35 – 7.27 (m, 4H, CH, Ar), 7.26 – 7.18 (m, 2H, CH, Ar), 2.23 [dd, J = 16.4, 7.6 Hz, 1H, CH_2 (*cis*- to F)], 2.09 [t, J = 7.2 Hz, 1H, CH_2 (*trans*- to F)]. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -131.59 (ddd, J = 16.3, 6.7, 3.3 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 140.2 (d, J_{CF} = 2.5 Hz) (C, Ar), 139.3 (d, J = 2.5 Hz) (C, Ar), 129.2 (CH, Ar), 128.8 (CH, Ar), 128.9 (CH, Ar), 128.6 (CH, Ar), 128.5 (CH, Ar), 127.4 (CH, Ar), 95.5 (d, J_{CF} = 291.1 Hz) (CF), 43.0 (d, J_{CF} = 10.6 Hz) (CAr), 28.0 (d, J_{CF} = 10.4 Hz) (CH_2). **MS** (**EI**, *m/z*, %): 246 (M^+, 24.63), 211 (100.00). **HRMS (EI)**: *m/z* calcd. for $C_{15}H_{12}ClF$ (M^+), 246.0612; found, 246.0607.

1-Chloro-4-(2-chloro-2-fluorocyclopropyl)benzene **(2b)**



Yield: 97 mg (95%, *syn*/*anti* = 77/23). Light yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39 – 7.27 (m, 2H, CH, Ar), 7.16 (dd, J = 10.9, 8.5 Hz, 2H, CH, Ar), 2.84 (ddd, J = 16.8, 11.5, 8.6 Hz, 0.77×1H, C<u>H</u>Ar, *syn*-isomer), 2.72 – 2.59 (m, 0.23×1H, C<u>H</u>Ar, *anti*-isomer), 2.00 (ddd, J = 15.6, 11.6, 7.8 Hz, 0.77×1H, CH_2 (*cis*- to F), *syn*-isomer), 1.87 – 1.73 (m, 0.46H, CH_2 (*cis*- and *trans*- to F), *anti*-isomer), 1.63 – 1.56 (m, 0.77×1H, CH_2 (*trans*- to F), *syn*-isomer). **^{19}F NMR** (377 MHz, $CDCl_3$): δ -128.76 (dt, J = 13.9, 4.9 Hz, 0.77×1F, *syn*-isomer), -148.71 (dd, J = 14.0, 8.6 Hz, 0.23×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 133.4/133.3(C, Ar), 133.0/132.1 (d, J_{CF} = 1.2 Hz) (CH, Ar), 129.8 (d, J_{CF} = 2.0 Hz)/129.6(CH, Ar), 128.6/128.5(C, Ar), 94.3 (d, J_{CF} = 288.2 Hz)/91.6 (d, J_{CF} = 286.9 Hz) (CF), 31.6 (d, J = 11.1 Hz)/29.7 (d, J_{CF} = 11.9 Hz) (CHAr), 21.7 (d, J_{CF} = 11.0 Hz), 21.0 (d, J_{CF} = 11.3 Hz) (CH_2). **HRMS (EI)**: *m/z* calcd. for $C_9H_7Cl_2F$ (M^+), 203.9909; found, 203.9907.

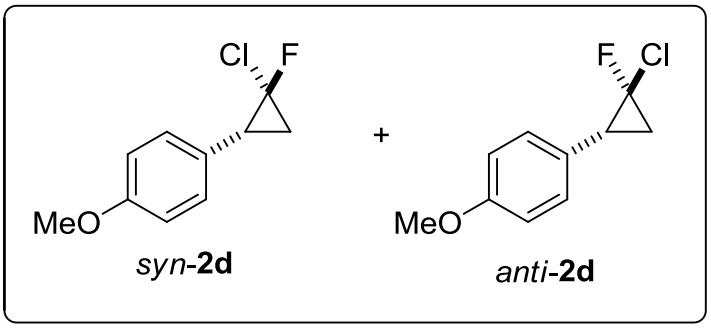
1-Bromo-4-(2-chloro-2-fluorocyclopropyl)benzene **(2c)**



Yield: 88 mg (71%, *syn*/*anti* = 54/46). Light yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53 – 7.42 (m, 2H, CH, Ar), 7.11 (dd, J = 11.0, 8.4 Hz, 2H, CH, Ar), 2.83 (ddd, J = 16.8, 11.6, 8.5 Hz, 0.54×1H, C<u>H</u>Ar, *syn*-isomer), 2.72 – 2.57 (m, 0.46×1H, C<u>H</u>Ar, *anti*-isomer), 2.01 [ddd, J = 15.6, 11.6, 7.8 Hz, 0.54×1H, CH_2 (*cis*- to F), *syn*-isomer], 1.88 – 1.74 [m, 0.92H, CH_2 (*cis*- and *trans*- to F), *anti*-isomer], 1.66 –

1.54 [m, 0.54×1H, CH_2 (*trans*- to F), *syn*-isomer]. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -127.14 (d, J = 13.6 Hz, 0.54×1F, *syn*-isomer), -133.63 (dd, J = 15.3, 7.7 Hz, 0.46×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 133.5/132.7 (d, J_{CF} = 1.5 Hz) (C, Ar), 131.6/131.5 (CH, Ar), 130.2 (d, J_{CF} = 2.0 Hz)/130.0 (d, J_{CF} = 1.1 Hz) (CH, Ar), 121.4/121.3 (C, Ar), 94.3 (d, J_{CF} = 288.3 Hz)/91.6 (d, J_{CF} = 287.4 Hz) (CF), 31.7 (d, J_{CF} = 11.2 Hz)/29.8 (d, J_{CF} = 12.0 Hz) (CHAr), 21.7 (d, J_{CF} = 10.9 Hz)/21.0 (d, J_{CF} = 11.2 Hz) (CH_2). **HRMS (EI)**: *m/z* calcd. for C_9H_7BrClF (M^+), 247.9404; found, 247.9403.

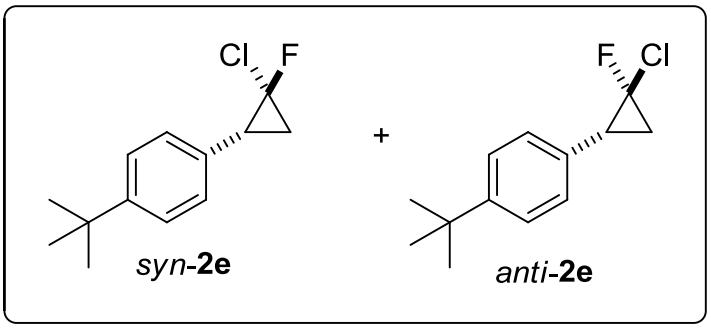
1-(2-Chloro-2-fluorocyclopropyl)-4-methoxybenzene (**2d**) [4]



Yield: 96 mg (96%, *syn*/*anti* = 55/45). Light yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.17 – 7.11 (m, 2H, CH, Ar), 6.88 – 6.85 (m, 2H, CH, Ar), 3.79 (s, 0.55×3H, CH_3, *syn*-isomer), 3.78 (s, 0.45×3H, CH_3, *anti*-isomer), 2.81 (ddd, J = 17.0, 11.6, 8.5 Hz, 0.55×1H, CHAr, *syn*-isomer), 2.73 – 2.58 (m, 0.45×1H, CHAr, *anti*-isomer), 1.93 [ddd, J = 15.9, 11.6, 7.7 Hz, 0.55×1H, CH_2 (*cis*- to F), *syn*-isomer], 1.82 – 1.65 [m, 0.90H, CH_2 (*cis*- and *trans*- to F), *anti*-isomer], 1.54 [ddd, J = 8.4, 7.7, 6.2 Hz, 0.55×1H, CH_2 (*trans*- to F), *syn*-isomer]. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -127.3 – -130.3 (m, 0.55×1F, *syn*-isomer), -147.6 – -150.9 (m, 0.45×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 158.9 (MeOC, Ar), 129.6 (d, J_{CF} = 2.0 Hz)/129.4 (CH, Ar), 126.6/125.5 (C, Ar), 113.9/113.8 (CH, Ar), 95.0 (d, J_{CF} = 287.7 Hz)/92.0 (d, J_{CF} = 287.1 Hz) (CF), 55.30/55.27 (CH_3), 31.6 (d, J_{CF} = 11.3 Hz)/29.6 (d, J_{CF} = 11.7 Hz) (CHAr), 21.4 (d, J_{CF} = 10.9 Hz)/20.8 (d, J_{CF} = 11.2 Hz) (CH_2). MS (ESI) *m/z*: 201 ($[M+H]^+$). **HRMS (ESI)**: *m/z* calcd. for $C_{10}H_9ClFO$ ($[M-H]^+$), 199.0326; found,

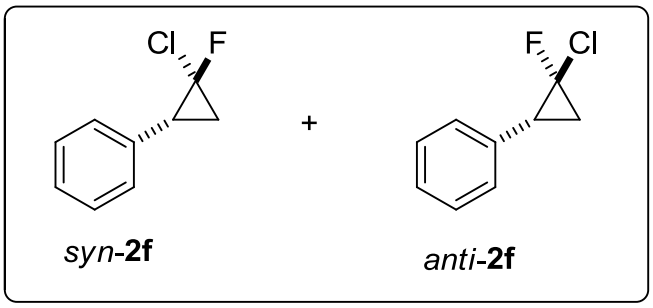
199.0328.

1-Tert-butyl-4-(2-chloro-2-fluorocyclopropyl)benzene **(2e)**



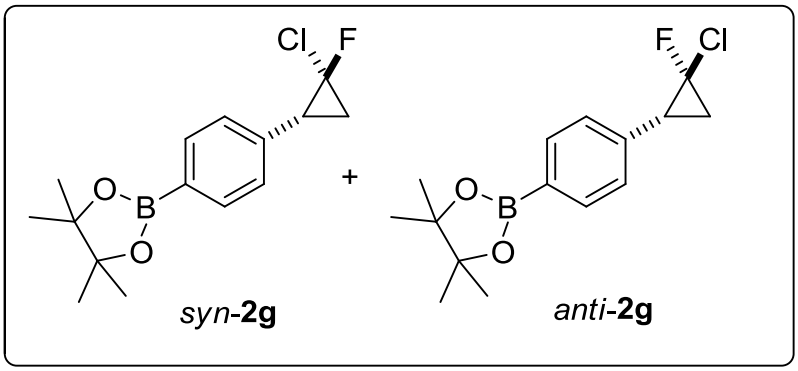
Yield: 100 mg (88%, *syn*/*anti* = 57/43). Light yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.37 (d, J = 7.2 Hz, 2H, CH, Ar), 7.17 (dd, J = 12.5, 8.3 Hz, 2H CH, Ar), 2.85 (ddd, J = 17.2, 11.6, 8.6 Hz, 0.57×1H, CHAr, *syn*-isomer), 2.74 – 2.61 (m, 1H, 0.43×1H, CHAr, *anti*-isomer), 1.97 [ddd, J = 15.9, 11.6, 7.7 Hz, 0.57×1H, CH_2 (*cis*- to F), *syn*-isomer] , 1.79 [ddt, J = 26.5, 11.1, 7.8 Hz, 0.86H, CH_2 (*cis*- and *trans*- to F), *anti*-isomer], 1.66 – 1.55 [m, 1H, 0.57×1H, CH_2 (*trans*- to F), *syn*-isomer], 1.33 (s, 0.57×9H, CH_3, *syn*-isomer), 1.32 (s, 0.43×9H, CH_3, *anti*-isomer). **^{19}F NMR** (376 MHz, $CDCl_3$): δ -127.88 – -128.86 (m, 0.57×1F, *syn*-isomer), -148.8 (ddd, J = 15.9, 7.5, 1.2 Hz, 0.43×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.3 (C, Ar), 131.5/130.6 (d, J_{CF} = 1.4 Hz) (C, Ar), 128.1 (d, J_{CF} = 1.9 Hz)/127.9 (d, J_{CF} = 1.9 Hz) (CH, Ar), 125.4/125.3 (CH, Ar), 94.9 (d, J_{CF} = 287.7 Hz)/92.1 (d, J_{CF} = 288.0 Hz) (CF), 34.55 /34.54 [$C(CH_3)_3$], 32.0 (d, J_{CF} = 11.2 Hz)/30.0 (d, J_{CF} = 11.7 Hz) (CHAr), 31.4/31.3 (CH_3), 21.6 (d, J_{CF} = 10.9 Hz)/20.9 (d, J_{CF} = 11.1 Hz) (CH_2). **MS** (**EI**, *m/z*, %): 211 (100), 226 (M^+, 7.31). **HRMS (EI)**: *m/z* calcd. for $C_{13}H_{16}ClF$ (M^+), 226.0925; found, 226.0919.

(2-Chloro-2-fluorocyclopropyl)benzene (**2f**) [5]



Yield: 47 mg (94%, *syn*/*anti* = 52/48). Light yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31 (dddd, J = 27.9, 19.1, 9.3, 4.4 Hz, 5H, CH, Ar), 2.89 (ddd, J = 17.2, 11.5, 8.6 Hz, 0.52×1H, CHAr, *syn*-isomer), 2.81 – 2.55 (m, 0.48×1H, CHAr, *anti*-isomer), 1.99 [ddd, J = 15.8, 11.6, 7.7 Hz, 0.52×1H, CH_2 (*cis*- to F), *syn*-isomer], 1.92 – 1.72 [m, 0.96H, CH_2 (*cis*- and *trans*- to F), *anti*-isomer], 1.63 [dt, J = 7.7, 7.0 Hz, 0.52×1H, CH_2 (*trans*- to F), *syn*-isomer]. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -128.39 (td, J = 16.6, 5.8 Hz, 0.52×1F, *syn*-isomer), -148.79 (dd, J = 16.1, 7.6 Hz, 0.48×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 134.5/133.6 (C, Ar), 128.5 (d, J_{CF} = 2.0 Hz)/128.47 (CH, Ar), 128.4/128.3 (CH, Ar), 127.4/127.3 (C, Ar), 94.8 (d, J_{CF} = 287.8 Hz)/91.9 (d, J_{CF} = 287.6 Hz) (CF), 32.4 (d, J_{CF} = 11.2 Hz)/30.4 (d, J_{CF} = 11.6 Hz) (CHAr), 21.5 (d, J_{CF} = 11.0 Hz)/20.8 (d, J_{CF} = 11.1 Hz) (CH_2). **MS** (**EI**, *m/z*, %): 115 (59.58), 135 (100), 170 (M^+, 21.83). **HRMS (EI)**: *m/z* calcd. for C_9H_8ClF (M^+), 170.0299; found, 170.0292.

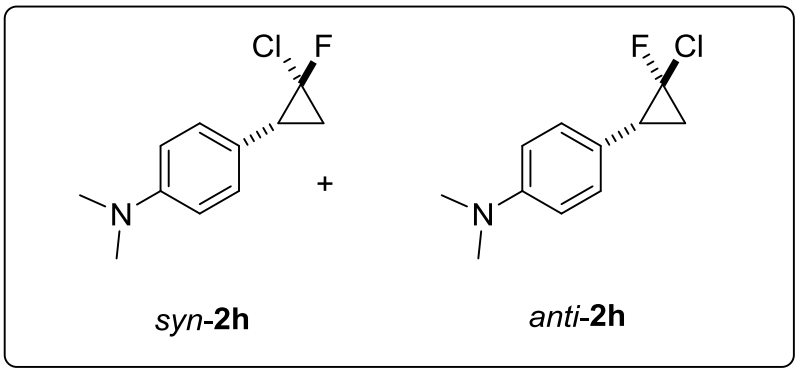
2-(4-(2-Chloro-2-fluorocyclopropyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2g**)



Yield: 88 mg (89%, *syn*/*anti* = 60/40). Yellow solid. M.p.: 55−56 ^{o}C. **^{1}H NMR** (400

MHz, $CDCl_3$): δ 7.78 (dd, J = 7.5, 5.3 Hz, 2H, CH, Ar), 7.23 (dd, J = 11.5, 8.0 Hz, 2H, CH, Ar), 2.88 (ddd, J = 17.1, 11.5, 8.7 Hz, 0.60×1H, CHAr, *syn*-isomer), 2.76 – 2.56 (m, 0.40×1H, CHAr, *anti*-isomer), 1.98 [ddd, J = 15.7, 11.6, 7.8 Hz, 0.60×1H, CH_2 (*cis*- to F), *syn*-isomer], 1.92 –1.74 [m, 0.80H, CH_2 (*cis*- and *trans*- to F), *anti*-isomer], 1.65 [dd, J = 14.4, 8.1 Hz, 0.60×1H, CH_2 (*trans*- to F), *syn*-isomer], 1.33 (s, 12H, CH_3). **^{19}F NMR** (376 MHz, $CDCl_3$): δ -128.15 (ddd, J = 15.9, 11.5, 4.5 Hz, 0.60×1F, *syn*-isomer), -148.64 (dd, J = 16.1, 7.6 Hz, 0.40×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 137.5/136.70 (d, J_{CF} = 1.4 Hz) (C, Ar), 134.9 (CH, Ar), 134.80 (CH, Ar), 127.8 (d, J_{CF} = 1.9 Hz)/127.6, 94.7 (d, J_{CF} = 288.1 Hz)/91.9 (d, J_{CF} = 288.0 Hz) (CF), 83.85/83.84 (C-O), 32.4 (d, J_{CF} = 11.2 Hz)/30.54 (d, J_{CF} = 11.7 Hz) (CHAr), 24.88/24.86 (CH_3), 21.59 (d, J_{CF} = 10.9 Hz)/20.81 (d, J_{CF} = 11.1 Hz) (CH_2). **MS** (**EI**, *m/z*, %): 161(89.34), 197(100), 261(84.62), 296 (M^+, 10.58). **HRMS (EI)**: *m/z* calcd. for $C_{15}H_{18}BClFO_2$ ($^{10B}[M-H]^+$), 294.1109; found, 294.1098.

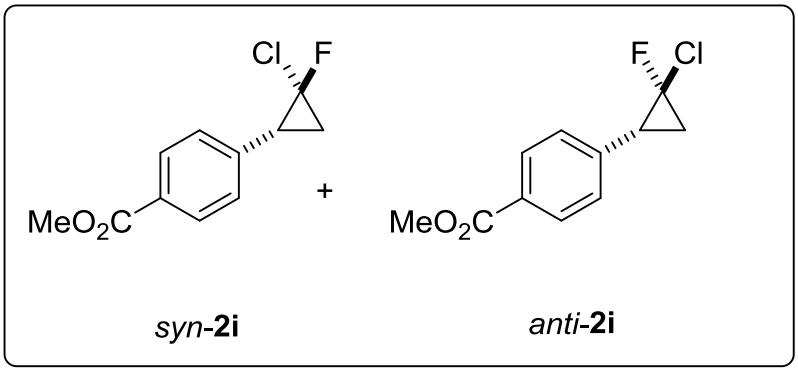
4-(2-Chloro-2-fluorocyclopropyl)-N,N-dimethylaniline (**2h**)



Yield: 53 mg (50%, *syn*/*anti* = 69/31). Light yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.10 (dd, J = 13.7, 8.7 Hz, 2H, CH, Ar), 6.71 (d, J = 8.7 Hz, 2H, CH, Ar), 2.94 (s, 0.69×6H, CH_3, *syn*-isomer), 2.93 (s, 0.31×6H, CH_3, *anti*-isomer), 2.78 (ddd, J = 17.2, 11.6, 8.6 Hz, 0.69×1H, CHAr, *syn*-isomer), 2.69 – 2.47 (m, 0.31×1H, CHAr, *anti*-isomer), 1.90 (ddd, J = 16.0, 11.7, 7.6 Hz, 0.69×1H, CH_2 (*cis*- to F), *syn*-isomer), 1.81 – 1.63 (m, 0.62×1H, CH_2 (*cis*- and *trans*- to F), *anti*-isomer), 1.59 – 1.47 (m, 0.69×1H, CH_2 (*trans*- to F), *syn*-isomer). **^{19}F NMR** (377 MHz, $CDCl_3$): δ -128.76 (td, J = 16.9, 5.5 Hz, 0.69×1F, *syn*-isomer), -148.91 (dd, J = 15.8, 7.2 Hz, 0.31×1F,

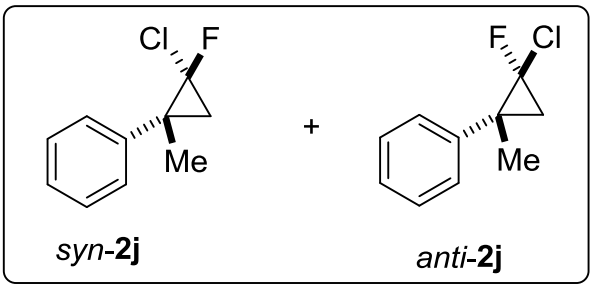
anti-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 149.8/149.7(Me_2NC, Ar), 129.2 (d, J_{CF} = 1.9 Hz)/129.0 (CH, Ar), 122.2/122.1 (C, Ar), 112.6/112.4 (CH, Ar), 95.5 (d, J_{CF} = 287.8 Hz)/92.3 (d, J_{CF} = 287.2 Hz) (CF), 40.7/40.6 (s, CH_3), 31.6 (d, J_{CF} = 11.2 Hz)/29.6 (d, J_{CF} = 11.4 Hz) (CHAr), 21.2 (d, J_{CF} = 10.7 Hz)/20.7 (d, J_{CF} = 11.1 Hz) (CH_2). **HRMS (ESI)**: *m/z* calcd. for $C_{11}H_{14}ClFN$ ($[M+H]^+$), 214.0799; found, 214.0795.

Methyl 4-(2-chloro-2-fluorocyclopropyl)benzoate (**2i**)



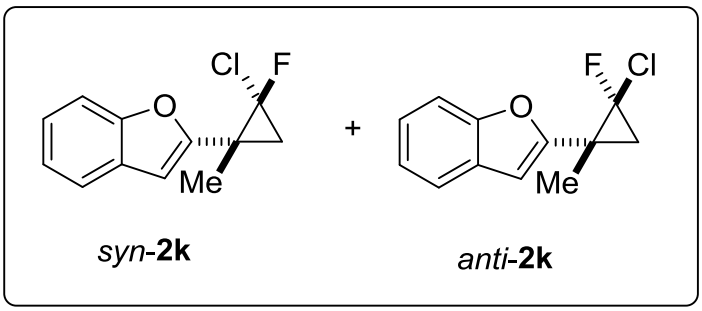
Yield: 82 mg (72%, *syn*/*anti* = 50/50). Light yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.31 – 7.73 (m, 2H, CH, Ar), 7.29 (dd, *J* = 16.2, 7.6 Hz, 2H, CH, Ar), 3.92 (s, 0.50×3H, CH_3, *syn*-isomer), 3.91 (s, 0.50×3H, CH_3, *anti*-isomer), 2.92 (ddd, *J* = 16.8, 11.5, 8.7 Hz, 0.50×1H, CHAr, *syn*-isomer), 2.75 (dd, *J* = 14.2, 5.1 Hz, 0.50×1H, CHAr, *anti*-isomer), 2.05 (ddd, *J* = 15.6, 11.5, 7.9 Hz, 0.50×1H, CH_2 (*cis*- to F), *syn*-isomer), 1.94 – 1.79 (m, 1H, CH_2 (*cis*- and *trans*- to F), *anti*-isomer), 1.69 (td, *J* = 8.2, 6.3 Hz, 0.50×1H, CH_2 (*trans*- to F), *syn*-isomer). **^{19}F NMR** (377 MHz, $CDCl_3$): δ -128.15 (td, *J* = 16.9, 7.5 Hz, 0.50×1F, *syn*-isomer), -148.58 (dd, *J* = 15.7, 7.6 Hz, 0.50×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 165.7 (COOMe), 138.6/137.8 (d, J_{CF} = 1.1 Hz) (C, Ar), 128.7/128.6 (CH, Ar), 128.3/128.2 (C, Ar), 127.5 (d, J_{CF} = 2.0 Hz)/127.2 (d, J_{CF} = 1.2 Hz) (CH, Ar), 93.2 (d, J_{CF} = 288.8 Hz)/90.7 (d, J_{CF} = 287.7 Hz) (CF), 51.1 (s, CH_3), 31.2 (d, J_{CF} = 11.1 Hz)/29.3 (d, J_{CF} = 12.0 Hz) (CHAr), 21.0 (d, J_{CF} = 11.0 Hz)/ 20.1 (d, J_{CF} = 11.1 Hz) (CH_2). **HRMS (ESI)**: *m/z* calcd. for $C_{11}H_9ClFO_2$ ($[M-H]^+$), 227.0275; found, 227.0257.

(2-Chloro-2-fluoro-1-methylcyclopropyl)benzene (**2j**) [5]



Yield: 89 mg (96%, *syn*/*anti* = 50/50). Light yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 – 6.78 (m, 5H, CH, Ar), 1.91 [dd, J = 17.4, 7.5 Hz, 0.50×1H, CH_2 (*cis*- to F), *syn*-isomer], 1.72 – 1.61 [m, 1H, CH_2 (*cis*- and *trans*- to F), *anti*-isomer], 1.60 (d, J = 2.2 Hz, 0.5×3H, CH_3, *syn*-isomer), 1.58 (d, J = 2.2 Hz, 0.5×3H, CH_3, *anti*-isomer), 1.36 [t, J = 7.6 Hz, 0.50×1H, CH_2 (*trans*- to F), *syn*-isomer]. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -133.36 (dd, J = 17.3, 6.6 Hz, 0.50×1F, *syn*-isomer), -140.94 (dd, J = 15.8, 3.2 Hz, 0.50×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 140.9 (d, J_{CF} = 1.8 Hz)/139.2 (d, J_{CF} = 3.9 Hz) (C, Ar), 128.58 /128.55 (CH, Ar), 128.48 (CH, Ar), 128.42 (d, J_{CF} = 1.8 Hz)/127.27 (d, J_{CF} = 4.7 Hz) (CH, Ar), 97.1 (d, J_{CF} = 286.9 Hz)/96.9 (d, J_{CF} = 291.7 Hz) (CF), 34.3 (d, J_{CF} = 10.8 Hz)/33.7 (d, J_{CF} = 9.8 Hz) (CAr), 27.1 (d, J_{CF} = 10.5 Hz)/26.9 (d, J_{CF} = 10.3 Hz) (CH_2), 25.1 (d, J_{CF} = 2.3 Hz)/21.8 (d, J_{CF} = 8.1 Hz) (CH_3). **MS** (**EI**, *m/z*, %): 149 (100), 179 (39.13), 184 (M^+, 21.04). **HRMS (EI)**: *m/z* calcd. for $C_{10}H_{10}ClF$ (M^+), 184.0455; found, 184.0456.

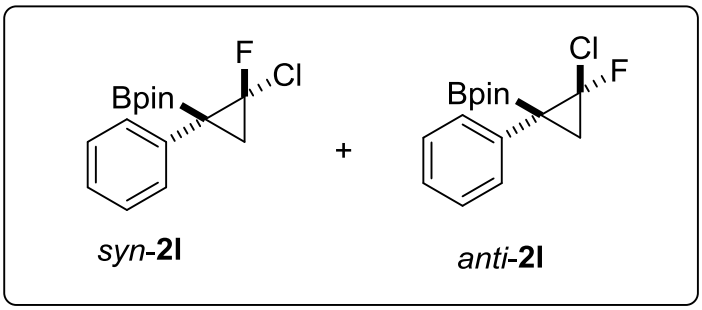
2-(2-Chloro-2-fluoro-1-methylcyclopropyl)benzofuran (**2k**)



Yield: 90 mg (80%, *syn*/*anti* = 52/48), Light yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53 (dd, J = 7.5, 4.2 Hz, 1H, CH, Ar), 7.45 (dd, J = 8.0, 4.5 Hz, 1H, CH, Ar), 7.34 – 7.17 (m, 2H, CH, Ar), 6.59 (s, 0.52×1H, CH=C, *syn*-isomer), 6.57 (s,

0.48×1H, *anti*-isomer), 2.27 [dd, J = 17.2, 7.8 Hz, 0.52×1H, CH_2 (*cis*- to F), *syn*-isomer], 2.05 [t, J = 7.6 Hz, 0.48×1H, CH_2 (*cis*- to F), *anti*-isomer], 1.70 (s, 0.52×3H, CH_3, *syn*-isomer), 1.69 (s, 0.48×3H, CH_3, *anti*-isomer), 1.71 – 1.65 [m, 0.48×1H, CH_2 (*trans*- to F), *anti*-isomer], 1.45 [t, J = 7.9 Hz, 0.52×1H, CH_2 (*trans*- to F), *syn*-isomer]. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -138.42 (dd, J = 17.1, 7.7 Hz, 0.52×1F, *syn*-isomer), -140.03 (dd, J = 15.8, 5.8 Hz, 0.48×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 156.35 (d, J = 2.5 Hz)/154.82 (d, J = 3.9 Hz) (O-C=), 154.7/154.6 (O-C, Ar), 128.4/128.3 (C, Ar), 124.1/124.0 (CH, Ar), 122.9/122.8 (CH, Ar), 120.8/120.7 (CH, Ar), 111.1/111.0 (CH, Ar), 104.15 (d, J_{CF} = 1.6 Hz)/104.08 (d, J_{CF} = 0.9 Hz) (HC=), 96.4 (d, J_{CF} = 289.8 Hz)/95.8 (d, J_{CF} = 294.2 Hz) (CF), 28.6 (d, J_{CF} = 12.5 Hz)/27.8 (d, J_{CF} = 9.6 Hz) (CAr), 27.1 (d, J = 11.1 Hz)/26.6 (d, J_{CF} = 9.9 Hz) (CH_2), 20.21 (d, J_{CF} = 2.0 Hz)/17.03 (d, J_{CF} = 6.5 Hz) (CH_3). **MS** (**EI**, *m/z*, %): 189 (100), 224 (M^+, 31.84). **HRMS (EI)**: *m/z* calcd. for $C_{12}H_{10}ClFO$ (M^+), 224.0404; found, 224.0397.

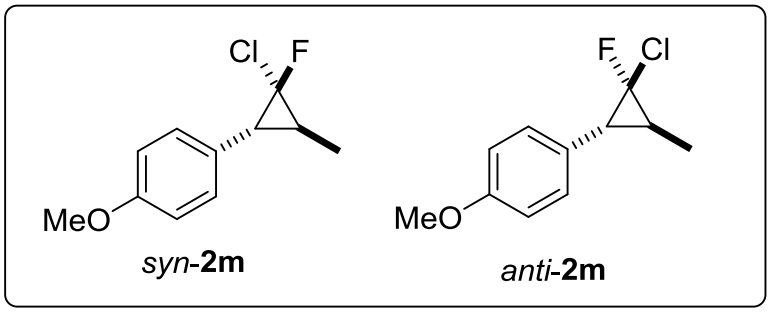
2-(2-Chloro-2-fluoro-1-phenylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2l**)



Yield: 118mg (80%, *syn*/*anti* = 52/48). Colorless liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39 – 7.14 (m, 5H, CH, Ar), 2.25 [dd, J = 13.9, 6.6 Hz, 0.52×1H, CH_2 (*cis*- to F), *syn*-isomer], 1.98 – 1.84 [m, 0.96×H, CH_2 (*cis*- and *trans*- to F), *anti*-isomer], 1.70 – 1.67 [m, 0.52×1H, CH_2 (*trans*- to F), *syn*-isomer], 1.24 –1.23 (m, 0.52×12H, CH_3, *syn*-isomer), 1.18 (s, 0.48×12H, CH_3, *anti*-isomer). **^{19}F NMR** (376 MHz, $CDCl_3$): δ -127.14 (d, J = 13.6 Hz, 0.52×1F, *syn*-isomer), -133.63 (dd, J = 15.3, 7.7 Hz, 0.48×1F,

anti-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 137.8/136.2 (d, J_{CF} = 3.8 Hz) (C, Ar), 129.4/129.3 (d, J_{CF} = 2.3 Hz) (CH, Ar), 128.2/128.1 (CH, Ar), 126.7/126.6 (CH, Ar) 97.48 (d, J_{CF} = 286.2 Hz)/94.46 (d, J = 289.6 Hz) (CF), 84.6/84.5 (C-O), 24.77/24.74 (CH_3), 24.7/24.6 (d, J_{CF} = 2.3 Hz) (CH_2), 24.5/24.4 (CH_3). **MS** (**ESI**, *m/z*, %): 319 ($[M+Na]^+$). **HRMS (ESI)**: *m/z* calcd. for $C_{15}H_{19}BClFNaO_2$ $[M+Na]^+$, 319.1048; found, 319.1039.

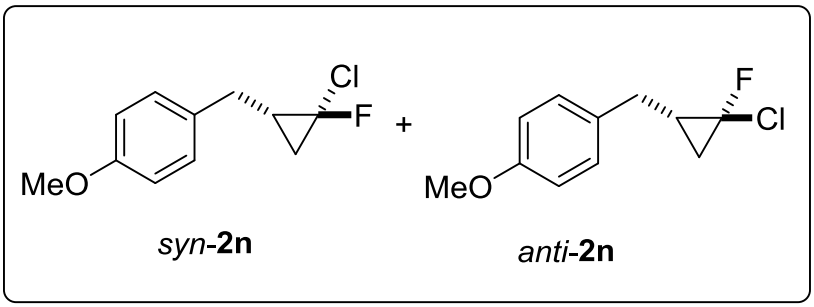
1-(2-Chloro-2-fluoro-3-methylcyclopropyl)-4-methoxybenzene (**2m**)



syn-**2m** *anti*-**2m**

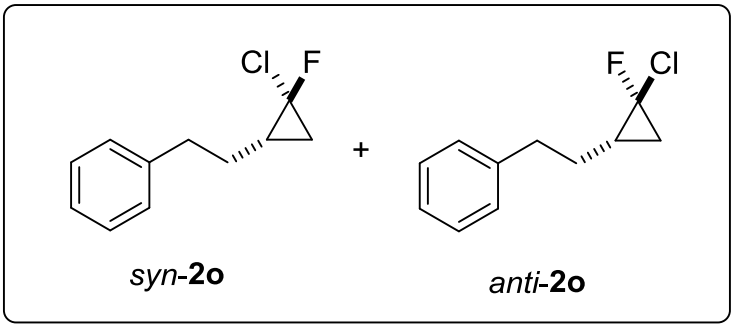
Yield: 84 mg (78%, *syn*/*anti* = 58/42). Light yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.10 – 6.93 (m, 2H, CH, Ar), 6.75 (dd, J = 8.8, 3.0 Hz, 2H, CH, Ar), 3.68 (s, 0.42×3H, CH_3, *anti*-isomer), 3.67 (s, 0.58×3H, CH_3, *syn*-isomer), 2.24 (dd, J = 18.1, 8.1 Hz, 0.42×1H, CHAr, *anti*-isomer), 2.05 (d, J = 8.0 Hz, 0.58×1H, CHAr, *syn*-isomer), 1.85 – 1.70 (m, 1H, 0.57×1H, CHMe, *syn*-isomer), 1.70 – 1.58 (m, 0.42×1H, CHMe, *anti*-isomer), 1.28 (d, J = 6.3 Hz, 0.42×3H, CH_3, *anti*-isomer), 1.24 (dd, J = 6.3, 1.9 Hz, 0.58×3H, CH_3, *syn*-isomer). **^{19}F NMR** (376 MHz, $CDCl_3$): δ -142.03 (d, J = 19.7 Hz, 0.58×1F, *syn*-isomer), -142.64 (d, J = 18.1 Hz, 0.42×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 158.7 (MeOC, Ar), 129.4 (d, J = 1.8 Hz)/129.2 ((d, J = 0.6 Hz) (CH, Ar), 127.0/126.1 (d, J = 1.8 Hz) (C, Ar), 113.9/113.7 (CH, Ar), 97.57 (d, J_{CF} = 292.1 Hz)/97.48 (d, J = 289.1 Hz) (CF), 55.31/55.28 (CH_3), 38.18 (d, J_{CF} = 11.3 Hz)/36.04 (d, J_{CF} = 10.6 Hz) (CHAr), 27.66 (d, J_{CF} = 11.1 Hz)/26.02 (d, J_{CF} = 9.6 Hz) (CHMe), 14.5 /11.8 (d, J_{CF} = 6.4 Hz) (CH_3). **HRMS (EI)**: *m/z* calcd. for $C_{11}H_{11}ClFO$ ($[M-H]^+$), 213.0483; found, 213.0482.

1-((2-Chloro-2-fluorocyclopropyl)methyl)-4-methoxybenzene (**2n**)



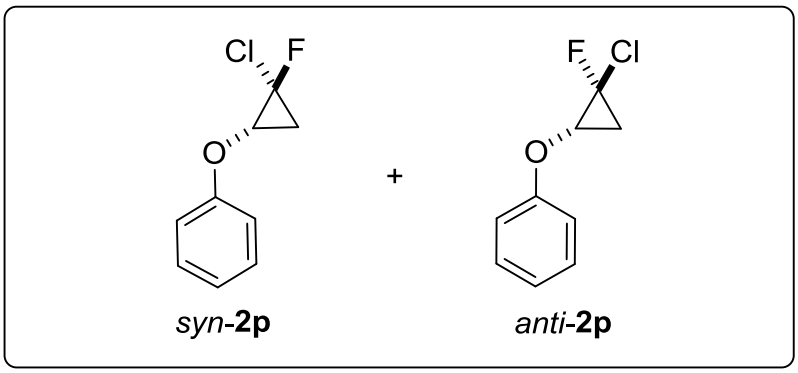
Yield: 78 mg (73%, *syn*/*anti* = 52/48). Yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.19 (t, J = 8.4 Hz, 2H, CH, Ar), 6.90 – 6.86 (m, 2H, CH, Ar), 3.81 (s, 3H, CH_3), 2.87 – 2.63 (m, 2H, *syn*-isomer and *anti*-isomer, C$\underline{H_2}$Ar), 1.95 – 1.76 (m, 1H, 0.52×1H, C$\underline{H}$CH_2Ar, *syn*-isomer), 1.75 – 1.69 (m, 0.48×1H, C$\underline{H}$CH_2Ar, *anti*-isomer), 1.68 – 1.62 [m, 0.52×1H, CH_2 (*cis*- to F), *syn*-isomer], 1.49 – 1.38 [m, 0.48×1H, CH_2 (*cis*- to F), *anti*-isomer], 1.35 – 1.20 [m, 0.48×1H, CH_2 (*trans*- to F), *anti*-isomer], 1.01 [td, J = 7.6, 6.1 Hz, 0.52×1H, CH_2 (*trans*- to F), *syn*-isomer]. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -129.77 – -131.77 (m, 0.52×1F, *syn*-isomer), -149.39 – -150.59 (m, 0.48×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 158.27/158.26 (MeOC, Ar), 131.7/131.4 (d, J_{CF} = 1.3 Hz) (C, Ar), 129.22/129.18 (CH, Ar), 114.03/114.01 (CH, Ar), 96.0 (d, J_{CF} = 285.4 Hz)/93.4 (d, J_{CF} = 287.0 Hz) (CF), 55.3 (CH_3), 34.6/32.4 (d, J_{CF} = 5.2 Hz) (Ar$\underline{C}H_2$), 28.9 (d, J_{CF} = 11.2 Hz)/26.4 (d, J_{CF} = 10.2 Hz) ($\underline{C}$HCH_2Ar), 21.4 (d, J_{CF} = 7.1 Hz)/21.3 (d, J_{CF} = 6.6 Hz) (CH$\underline{C}H_2$CFCl). **MS** (**EI**, *m/z*, %): 179 (100), 214 (M^+, 67.82). **HRMS (EI)**: *m/z* calcd. for $C_{11}H_{12}ClFO$ (M^+), 214.0561; found, 214.0559.

(2-(2-Chloro-2-fluorocyclopropyl)ethyl)benzene (**2o**)



Yield: 84 mg (85%, *syn*/*anti* = 51/49). Light yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43 – 6.95 (m, 5H, CH, Ar), 2.90 – 2.63 (m, 2H, C$\underline{H_2}$Ar, *syn*-isomer and *anti*-isomer), 1.96 – 1.67 (m, 2H, C$\underline{H_2}CH_2$Ar, *syn*-isomer and *anti*-isomer), 1.65 – 1.50 (m, 1H, CFClC$\underline{H}CH_2$, *syn*-isomer and *anti*-isomer), 1.45 [dd, *J* = 16.3, 8.6 Hz, 1H, 0.51×1H, CH_2 (*cis*- to F), *syn*-isomer], 1.32 [dt, *J* = 17.8, 9.1 Hz, 0.49×1H , CH_2 (*cis*- to F), *anti*-isomer], 1.11 [dt, *J* = 15.3, 7.5 Hz, 0.49×1H, CH_2 (*trans*- to F), *anti*-isomer], 0.85 [d, *J* = 5.7 Hz, 0.51×1H, CH_2 (*trans*- to F), *syn*-isomer]. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -130.50 (td, *J* = 17.7, 2.8 Hz, 0.51×1F, *syn*-isomer), -151.63 (dd, *J* = 16.3, 5.6 Hz, 0.49×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 141.3 (C, Ar), 128.52/128.50 (CH, Ar), 128.48/128.47 (CH, Ar), 126.11/126.10 (CH, Ar), 96.2 (d, J_{CF}= 284.7 Hz)/93.5 (d, J_{CF} = 287.0 Hz) (CF), 35.2/34.8 (d, J_{CF} = 1.3 Hz) (C$\underline{H_2}$Ar), 31.8 (d, *J* = 0.8 Hz)/29.3 (d, J_{CF} = 4.5 Hz) (C$\underline{H_2}CH_2$Ar), 27.4 (d, J_{CF} = 11.2 Hz)/24.9 (d, J_{CF} = 10.1 Hz) (CFCl$\underline{C}HCH_2$), 21.4 (d, J_{CF} = 6.6 Hz)/21.3 (d, J_{CF} = 5.9 Hz) (CH$\underline{C}H_2$CFCl). **HRMS (EI)**: *m/z* calcd. for $C_{11}H_{12}ClF$ (M^+), 198.0612; found, 198.0612.

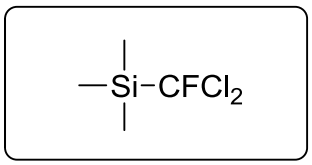
(2-chloro-2-fluorocyclopropoxy)benzene (**2p**)



Yield: 87 mg (94%, *syn*/*anti* = 40/60). Light yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43 – 7.28 (m, 2H, CH, Ar), 7.11 – 6.92 (m, 3H, CH, Ar), 4.09 (ddd, *J* = 12.0, 8.8, 5.0 Hz, 0.40×1H, CHOAr, *syn*-isomer), 3.94 – 3.72 (m, 0.60×1H, CHOAr, *anti*-isomer), 2.10 – 1.90 (m, 0.40×1H, CH_2 (*cis*- to F), *syn*-isomer), 1.84 (ddd, *J* = 18.7, 9.2, 4.6 Hz, 0.60×1H, CH_2 (*cis* to F), *anti*-isomer), 1.72 (dd, *J* = 17.6, 9.2 Hz,

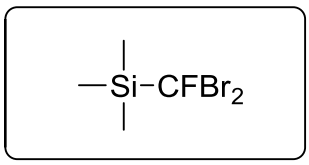
0.60×1H, CH_2 (*trans*- to F), *anti*-isomer), 1.56 (ddd, J = 8.9, 7.4, 5.2 Hz, 0.40×1H, CH_2 (*trans*- to F), *syn*-isomer). **^{19}F NMR** (377 MHz, $CDCl_3$): δ -137.44 – -140.63 (m, 0.40×1F, *syn*-isomer), -155.75 – -160.20 (m, 0.60×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 157.8/157.3 (C, Ar), 129.8/129.7 (CH, Ar), 122.4 (C, Ar), 115.0/114.9 (CH, Ar), 92.1 (d, J_{CF} = 290.4 Hz)/89.6 (d, J_{CF} = 292.4 Hz) (CF), 58.2 (d, J_{CF} = 9.6 Hz)/56.3 (d, J_{CF} = 14.2 Hz) (CHOAr) , 23.31 (d, J_{CF} = 11.9 Hz), 22.54 (d, J_{CF} = 10.9 Hz) (CH_2). **HRMS (ESI)**: *m/z* calcd. for C_9H_7ClFO ($[M-H]^+$), 185.0170; found, 185.0163.

(Dichlorofluoromethyl)trimethylsilane[7]



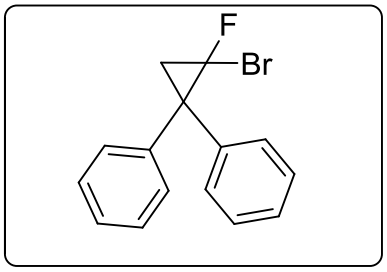
White solid. M.p.: 42−43 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.32 (s, 9H, CH_3). **^{19}F NMR** (376 MHz, $CDCl_3$,): δ -75.73 (1F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 123.65 (d, J = 321.7 Hz) (CF), -4.29 (CH_3).

(Dibromofluoromethyl)trimethylsilane[8]



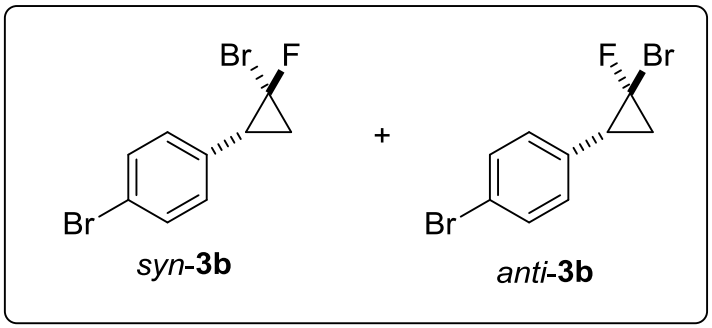
Yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.31 (s, 9H, CH_3). **^{19}F NMR** (376 MHz, $CDCl_3$): δ -76.29 (1F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 103.93 (d, J = 339.6 Hz) (CF), -4.74 (CH_3). **MS** (**ESI**, *m/z*, %): 264 (M^+), 266 ($[M+2]^+$).

(2-Bromo-2-fluorocyclopropane-1,1-diyl)dibenzene (**3a**) [9]



Yield: 139 mg (96%), Light yellow solid. M.p.: 78 - 79 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.44 (dd, J = 12.7, 7.6 Hz, 4H, CH, Ar), 7.31 (dd, J = 4.4, 1.8 Hz, 4H, CH, Ar), 7.26 – 7.19 (m, 2H, CH, Ar), 2.27 [dd, J = 17.6, 7.7 Hz, 1H, CH_2 (*cis*- to F)], 2.16 [dd, J = 10.7, 4.9 Hz, 1H, CH_2 (*trans*- to F)]. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -123.51 (dd, J = 16.7, 7.6 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 141.3 (d, J_{CF} = 2.6 Hz) (C, Ar), 139.1 (d, J_{CF} = 2.8 Hz) (C, Ar), 129.3 (CH, Ar), 128.8 (CH, Ar), 128.79 (CH, Ar), 128.6 (CH, Ar), 128.5 (CH, Ar), 127.4 (CH, Ar), 86.6 (d, J_{CF} = 305.0 Hz) (CF), 43.08 (d, J_{CF} = 10.1 Hz) (CAr), 29.11 (d, J_{CF} = 9.8 Hz) (CH_2). **MS** (**EI**, *m/z*, %): 290 (M^+, 3.32), 211 (100.00). **HRMS (EI)**: *m/z* calcd for $C_{15}H_{12}FBr$ (M^+), 290.0106; found, 290.0115.

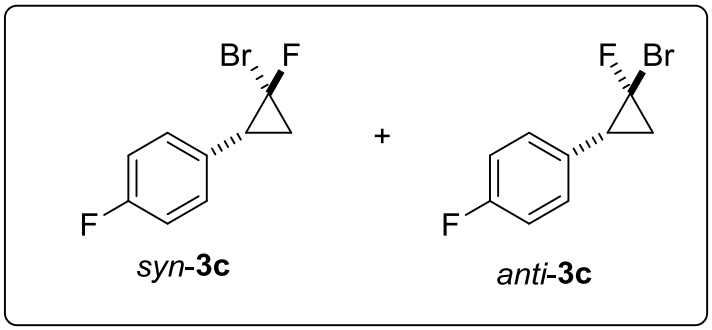
1-Bromo-4-(2-bromo-2-fluorocyclopropyl)benzene (**3b**) [10]



Yield: 112 mg (76%, *syn*/*anti* = 38/62). Light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.47 (dd, J = 8.3, 6.6 Hz, 2H, CH, Ar), 7.10 (dd, J = 14.6, 8.3 Hz, 2H, CH, Ar), 2.98 – 2.55 (m, 1H, *syn*-isomer and *anti*-isomer), 2.06 [ddd, J = 17.0, 11.6, 8.0 Hz, 0.38×1H, CH_2 (*cis*- to F), *syn*-isomer], 1.95 – 1.74 [m, 1H, 1.24H, CH_2 (*cis*- and *trans*- to F), *anti*-isomer], 1.64 [dd, J = 15.9, 8.0 Hz, 0.38×1H, CH_2 (*trans*- to F), *syn*-isomer]. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -125.45 (td, J = 17.4, 7.3 Hz, 0.38×1F,

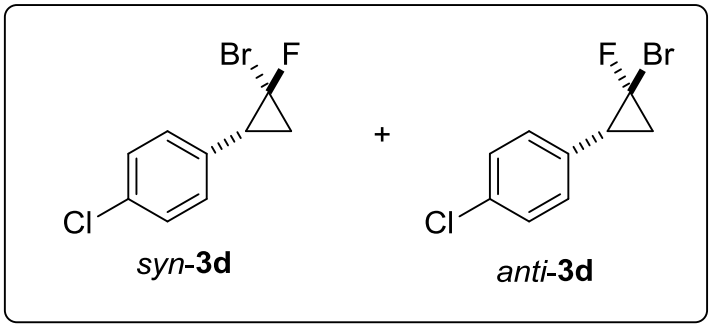
syn-isomer), -145.77 – -147.48 (m, 0.62×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 134.5/132.6 (d, J_{CF} = 1.8 Hz) (C, Ar), 131.6/131.5 (CH, Ar), 130.3 (d, J_{CF} = 2.0 Hz)/130.1 (d, J_{CF} = 1.1 Hz) (CH, Ar), 121.5/121.4 (C, Ar), 85.5 (d, J_{CF} = 302.0 Hz)/79.9 (d, J_{CF} = 301.7 Hz) (CF), 32.7 (d, J_{CF} = 10.7 Hz)/30.1 (d, J_{CF} = 11.3 Hz) (CHAr), 22.8 (d, J_{CF} = 10.4 Hz)/ 22.2 (d, J_{CF} = 10.6 Hz) (CH_2). **MS** (**EI**, *m/z*, %): 292 (M^+, 0.21), 134 (100.00). **HRMS (EI)**: *m/z* calcd for $C_9H_7FBr_2$ (M^+): 291.8899; found: 291.8912.

1-(2-Bromo-2-fluorocyclopropyl)-4-fluorobenzene (**3c**) [11]



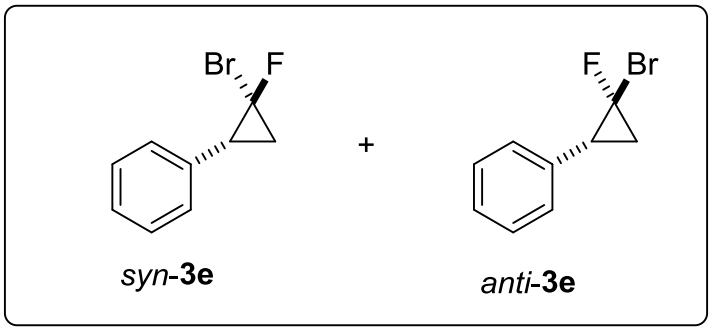
Yield: 81 mg (70%, *syn*/*anti* = 42/58), Light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.20 (ddd, *J* = 8.4, 7.0, 3.7 Hz, 2H, CH, Ar), 7.09 – 6.98 (m, 2H, CH, Ar), 2.81 – 2.69 (m, 1H, *syn*-isomer and *anti*-isomer), 2.05 [ddd, *J* = 17.0, 11.6, 7.9 Hz, 0.42×1H, CH_2 (*cis*- to F), *syn*-isomer], 1.86 – 1.80 [m, 1H, 1.16H, CH_2 (*cis*- and *trans*- to F), *anti*-isomer], 1.63 [dd, *J* = 15.7, 8.0 Hz, 0.42×1H, CH_2 (*trans*- to F), *syn*-isomer]. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -114.84 – -115.1 (m, F-Ar), -125.67 (td, *J* = 17.4, 7.1 Hz, 0.42×1F, *syn*-isomer), -146.46 – -146.61 (m, 0.58×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 162.3 (d, J_{CF} = 246.2 Hz)/162.1 (d, J_{CF} = 246.0 Hz), 131.2 (d, J_{CF} = 3.3 Hz)/129.3, 130.2 (d, J_{CF} = 8.2 Hz)/129.9 (d, J_{CF} = 8.1 Hz), 115.4 (d, J_{CF} = 21.6 Hz)/115.3 (d, J_{CF} = 21.5 Hz), 85.9 (d, J_{CF} = 301.4 Hz)/80.1 (d, J_{CF} = 301.5 Hz), 32.5 (d, J_{CF} = 10.8 Hz)/29.8 (d, J_{CF} = 11.2 Hz), 22.8 (d, J_{CF} = 10.3 Hz)/22.1 (d, J_{CF} = 10.6 Hz). **MS** (**EI**, *m/z*, %): 232 (M^+, 0.19), 153(100.00). **HRMS (EI)**: *m/z* calcd for $C_9H_7F_2Br$ (M^+), 231.9699; found, 231.9693.

1-(2-Bromo-2-fluorocyclopropyl)-4-chlorobenzene(**3d)** [4]



Yield:112 mg (90%, *syn*/*anti* = 43/57). Light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31 (t, J = 6.8 Hz, 2H, CH, Ar), 7.16 (dd, J = 14.3, 8.1 Hz, 2H, CH, Ar), 2.75 (t, J = 18.1 Hz, 1H, *syn*-isomer and *anti*-isomer), 2.19 – 1.92 [m, 0.43×1H, CH_2 (*cis*- to F), *syn*-isomer], 1.84 [t, J = 11.3 Hz, 1H, 1.14H, CH_2 (*cis*- and *trans*- to F), *anti*-isomer], 1.65 [dd, J = 15.7, 7.8 Hz, 0.43×1H, CH_2 (*trans*- to F), *syn*-isomer]. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -125.50 (dd, J = 16.5, 7.5 Hz, 0.43×1F, *syn*-isomer), -146.47 (d, J = 7.6 Hz, 0.57×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 134.0/133.4 (C, Ar), 133.3/132.1 (d, J_{CF} = 1.7 Hz), 129.9 (d, J_{CF} = 1.9 Hz) (CH, Ar)/129.7 (d, J_{CF} = 0.8 Hz) (CH, Ar), 128.7/128.6 (s) (CH, Ar), 85.6 (d, J = 301.5 Hz)/79.9 (d, J_{CF} = 301.2 Hz) (CF), 32.6 (d, J_{CF} = 10.8 Hz)/29.9 (d, J_{CF} = 11.3 Hz) (CHAr), 22.82 (d, J_{CF} = 10.3 Hz)/22.08 (d, J_{CF} = 10.7 Hz) (CH_2). **MS** (**EI**, *m/z*, %): 248 (M^+, 1.3), 169 (100.00); **HRMS (EI)**: *m/z* calcd for C_9H_7FClBr (M^+); 247.9404, found, 247.9411.

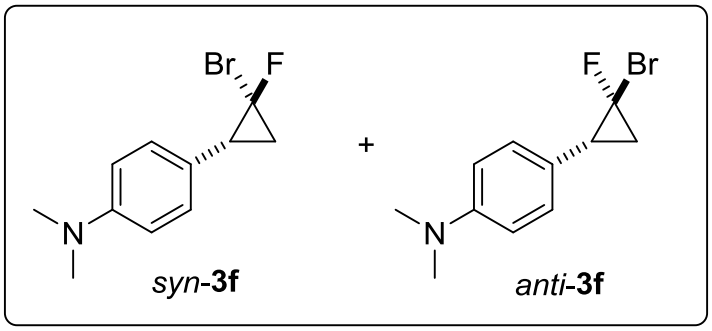
(2-Bromo-2-fluorocyclopropyl)benzene (**3e**) [12]



Yield: 97 mg (90%, *syn*/*anti* = 43/57). Light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35 – 7.20 (m, 5H, CH, Ar), 2.83-2.75 (m, 1H, CHAr, *syn*-isomer and *anti*-isomer),

2.07 – 1.98 [m, 0.43×1H, CH_2 (*cis*- to F), *syn*-isomer], 1.93 – 1.78 [m, 1.14H, CH_2 (*cis*- and *trans*- to F), *anti*-isomer], 1.70 – 1.65 [m, 0.43×1H, CH_2 (*trans*- to F), *syn*-isomer]. **^{19}F NMR** (376 MHz, $CDCl_3$/TMS): δ -124.98 (td, J = 17.6, 7.3 Hz, 0.43×1F, *syn*-isomer), δ-146.33 (dd, J = 17.1, 8.8 Hz, 0.57×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 135.4/133.5 (d, J_{CF} = 1.7 Hz) (C, Ar), 128.52 (d, J_{CF} = 2.1 Hz)/ 128.48 (CH, Ar), 128.36/128.34 (d, J_{CF} = 1.4 Hz) (CH, Ar), 127.5/127.4 (CH, Ar), 86.13 (d, J_{CF} = 301.4 Hz)/80.41 (d, J_{CF} = 302.1 Hz) (CF), 33.23 (d, J_{CF} = 10.8 Hz)/30.57 (d, J_{CF} = 11.0 Hz) (CHAr), 22.64 (d, J_{CF} = 10.3 Hz)/21.88 (d, J_{CF} = 10.6 Hz) (CH_2). **MS** (**EI**, *m/z*, %): 248 (M^+, 1.3), 169 (100.00), **HRMS (EI)**: *m/z* calcd for C_9H_8FBr (M^+), 213.9793; found, 213.9797.

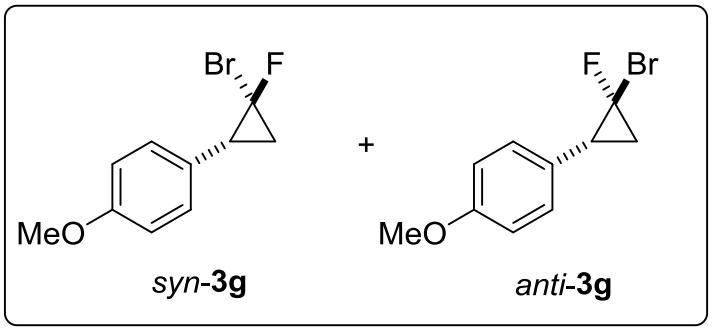
4-(2-Bromo-2-fluorocyclopropyl)-N,N-dimethylaniline (**3f**)



Yield:103 mg (80%, *syn*/*anti* = 61/39), White solid, M.p. 72-73 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.09 (dd, J = 18.3, 8.4 Hz, 2H, CH, Ar), 6.71 (d, J = 8.5 Hz, 2H, CH, Ar), 2.94 (s, 0.61×6H, CH_3, *syn*-isomer), 2.93 (s, 0.39×6H, CH_3, *anti*-isomer), 2.76 – 2.56 (m, 1H, CHAr, *syn*-isomer and *anti*-isomer), 2.03 – 1.87 [m, 0.61×1H, CH_2 (*cis*- to F), *syn*-isomer], 1.78 [dt, J = 17.5, 9.2 Hz, 0.78H, CH_2 (*cis*- and *trans*- to F), *anti*-isomer], 1.59 [dd, J = 15.8, 7.7 Hz, 0.61×1H, CH_2 (*trans*- to F), *syn*-isomer]. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -145.50 (0.61×1F, *syn*-isomer). δ -125.29 (0.39×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 149.4 (C, Ar), 129.3 (C, Ar), 129.2/129.1 (CH, Ar), 113.0/112.7 (CH, Ar), 87.3 (d, J_{CF} = 301.7 Hz)/81.0 (d, J_{CF} = 301.7 Hz) (CF), 41.0/40.9 (CH_3), 32.6 (d, J_{CF} = 10.8 Hz)/29.9 (d, J_{CF} = 10.9 Hz) (CHAr), 22.4 (d, J_{CF} = 10.3 Hz)/21.8 (d, J_{CF} = 10.5 Hz) (CH_2). **MS** (**EI**, *m/z*, %): 257

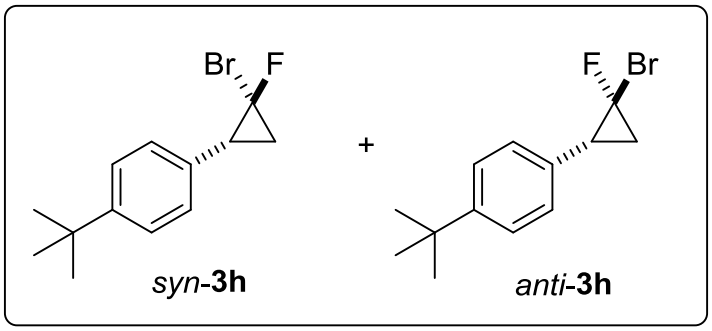
(M^+, 0.5), 178(100.00). **HRMS (ESI)**: *m/z* calcd for $C_{11}H_{14}BrFN$ ($[M+H]^+$), 258.0294; found, 258.0301.

1-(2-Bromo-2-fluorocyclopropyl)-4-methoxybenzene(**3g**) [13]



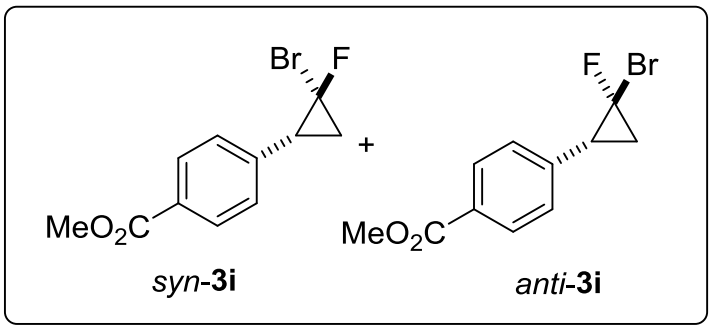
Yield: 119 mg (97%, *syn*/*anti* = 48/52), Light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.15 (dd, J = 16.8, 8.2 Hz, 2H, CH, Ar), 6.87 (dd, J = 4.5, 1.9 Hz, 2H, CH, Ar), 3.79 (s, 3H, CH_3), 2.71 (dd, J = 19.5, 9.9 Hz, 1H, CHAr, *syn*-isomer and *anti*-isomer), 2.07 – 1.89 [m, 0.48×1H, CH_2 (*cis*- to F), *syn*-isomer], 1.80 [dd, J = 18.1, 9.2 Hz, 1.04H, CH_2 (*cis*- and *trans*- to F), *anti*-isomer], 1.61 [dd, J = 17.4, 9.8 Hz, 0.48×1H, CH_2 (*trans*- to F), *syn*-isomer]. **^{19}F NMR** (376 MHz, $CDCl_3$/TMS): δ -125.43 (td, J = 17.7, 7.3 Hz, 0.48×1F, *syn*-isomer), -146.47 (dd, J = 15.3, 10.1 Hz, 0.52×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 158.9 (MeOC, Ar), 129.6 (d, J_{CF} = 2.0 Hz)/129.4 (d, J_{CF} = 0.8 Hz) (CH, Ar), 127.6/125.5 (d, J_{CF} = 2.0 Hz) (C, Ar), 113.93/113.75 (CH, Ar), 86.7 (d, J_{CF} = 301.7 Hz)/ 80.6 (d, J_{CF} = 301.7 Hz) (CF), 55.3/55.3 (CH_3), 32.6 (d, J_{CF} = 10.8 Hz)/29.9 (d, J_{CF} = 11.0 Hz) (CHAr), 22.5 (d, J_{CF} = 10.3 Hz)/21.9 (d, J_{CF} = 10.6 Hz) (CH_2). **MS** (**EI**, *m/z*, %): 244 (M^+, 1.09), 165 (100.00); HRMS(EI): *m/z* calcd for $C_{10}H_{10}OFBr(M^+)$, 243.9899; found, 243.9904.

1-(2-Bromo-2-fluorocyclopropyl)-4-tert-butylbenzene(**3h**)



Yield: 95 mg (70%, *syn*/*anti* = 22/78), Light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36 (dd, *J* = 8.3, 1.6 Hz, 2H, CH, Ar), 7.16 (dd, *J* = 16.6, 8.3 Hz, 2H, CH, Ar), 2.83 – 2.66 (m,1H, CHAr, *syn*-isomer and *anti*-isomer), 2.01 [ddd, *J* = 17.2, 11.7, 7.8 Hz, 0.22×1H, CH_2 (*cis*- to F), *syn*-isomer], 1.92 – 1.72 [m, 1.56 H, CH_2 (*cis*- and *trans*- to F), *anti*-isomer], 1.65 [dd, *J* = 16.2, 7.7 Hz, 0.22×1H, CH_2 (*trans*- to F), *syn*-isomer], 1.32 (s, 0.22×9H),1.31 (s, 0.78×9H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ -124.79 (td, *J* = 17.5, 7.5 Hz, 0.22×1F, *syn*-isomer), -145.82 – -147.35 (0.78×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.35/150.33 (C, Ar), 132.4/130.5 (d, J_{CF} = 1.7 Hz) (C, Ar), 128.1 (d, J_{CF} = 2.0 Hz)/127.9 (d, J_{CF} = 1.1 Hz) (CH, Ar), 125.4/125.2 (CH, Ar), 86.4 (d, J_{CF} = 301.3 Hz)/80.6 (d, J_{CF} = 302.2 Hz) (CF), 34.54/34.52 ($\underline{C}(CH_3)_3$), 32.9 (d, J_{CF} = 10.8 Hz)/30.2 (d, J_{CF} = 11.0 Hz) (CHAr), 31.33/31.31 [$C(\underline{C}H_3)_3$], 22.7 (d, J_{CF} = 10.3 Hz)/22.0 (d, J_{CF} = 10.5 Hz) (CH_2). **MS** (**EI**, *m/z*, %): 270 (M^+, 0.13), 57 (100.00). **HRMS (EI)**: *m/z* calcd for $C_{10}H_{16}FBr$ (M^+), 270.0419; found, 270.0406.

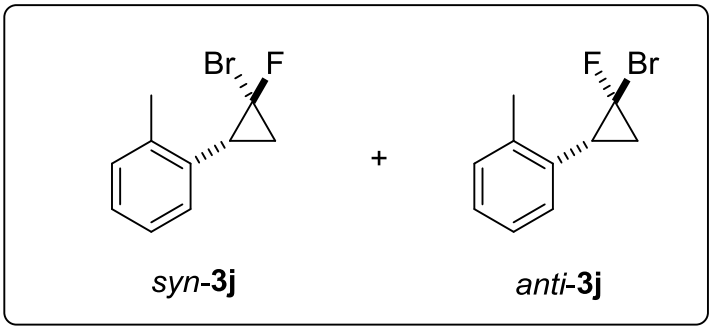
Methyl 4-(2-bromo-2-fluorocyclopropyl)benzoate(**3i**)



Yield: 60 mg (44%, *syn*/*anti* = 46/54). Light yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.01 (t, *J* = 8.3 Hz, 2H, CH, Ar), 7.48 – 7.06 (m, 2H, CH, Ar), 3.92 (s, 0.46×3H, CH_3, *syn*-isomer), 3.91 (s, 0.54×3H, CH_3, *anti*-isomer), 2.91 – 2.73 (m, 1H,

CHAr, *syn*-isomer and *anti*-isomer), 2.10 (ddd, J = 16.9, 11.5, 8.0 Hz, 0.46×1H, CH_2 (*cis*- to F), *syn*-isomer), 2.00 – 1.81 (m, 1.08H, CH_2 (*cis*- and *trans*- to F), *anti*-isomer), 1.74 (dd, J = 16.0, 8.1 Hz, 0.46×1H, CH_2 (*trans*- to F), *syn*-isomer). **^{19}F NMR** (377 MHz, $CDCl_3$): δ -124.84 (dd, J = 17.1, 11.2 Hz, 0.46×1F, *syn*-isomer), -146.28 (dd, J = 16.9, 8.7 Hz, 0.54×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.8 (COOMe),, 140.6/138.8 (C, Ar), 129.7/129.6 (CH, Ar), 129.3/129.2 (C, Ar), 128.5 (d, J = 1.9 Hz)/128.3 (CH, Ar), 85.23 (d, J = 302.2 Hz)/79.91 (d, J = 302.2 Hz) (CF), 52.2 (CH_3), 33.2 (d, J = 10.7 Hz)/30.5 (d, J = 11.4 Hz) (CHAr), 23.2 (d, J = 10.4 Hz)/22.2 (d, J = 10.4 Hz) (CH_2). **HRMS (ESI)**: *m/z* calcd. for $C_{11}H_{11}O_2FBr$ ($[M+H]^+$), 272.9926; found, 272.9946.

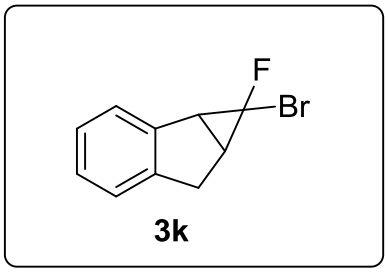
1-(2-Bromo-2-fluorocyclopropyl)-2-methylbenzene (**3j**) [13]



Yield: 83 mg (73%, *syn*/*anti* = 52/48), Light yellow oil. **^{1}H NMR** (376 MHz, $CDCl_3$): δ 7.25-6.96 (m, 4H, CH, Ar), 2.74 (ddd, J = 17.4, 11.2, 8.8 Hz, 1H, CHAr, *syn*-isomer and *anti*-isomer), 2.46 (s, 0.52×3H, CH_3, *syn*-isomer), 2.44 (s, 0.48×3H, CH_3, *anti*-isomer), 2.04 [ddd, J = 16.6, 11.5, 7.8 Hz, 0.52×1H, CH_2 (*cis*- to F), *syn*-isomer], 1.98 – 1.78 [m, 0.96 H, CH_2 (*cis*- and *trans*- to F), *anti*-isomer], 1.77 – 1.64 [m, 0.52×1H, CH_2 (*trans*- to F), *syn*-isomer]. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -127.75 (t, J = 17.3 Hz, 0.52×1F, *syn*-isomer), -145.79 (dd, J = 17.2, 7.8 Hz, 0.48×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 139.0/138.6 (C, Ar), 134.27/132.23 (d, J_{CF} = 2.3 Hz) (C, Ar), 129.9/129.8 (CH, Ar), 127.9/127.7 (CH, Ar), 127.7/127.3 (d, J = 4.3 Hz) (CH, Ar), 125.9 (CH, Ar), 86.2 (d, J_{CF} = 302.4 Hz)/80.8 (d, J_{CF} = 300.2 Hz) (CF), 32.3 (d, J_{CF} = 11.3 Hz)/29.7 (d, J_{CF} = 10.6 Hz) (CHAr), 21.4 (d, J_{CF} = 4.4 Hz)/21.3 (d, J_{CF} = 4.7 Hz) (CH_2), 20.1/19.8 (CH_3). **MS** (**EI**, *m/z*, %): 228 (M^+, 0.44), 189 (100.00).

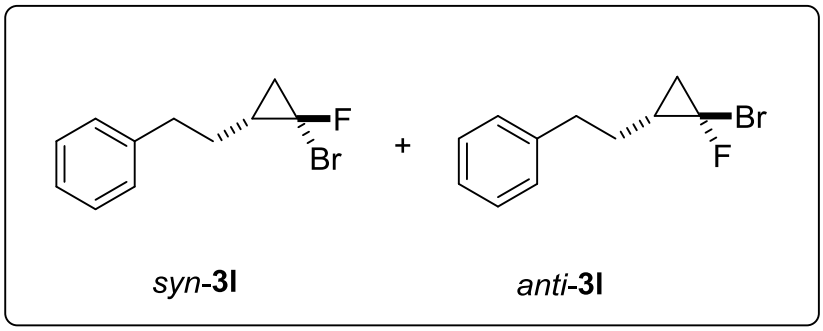
HRMS (EI): *m/z* calcd for $C_{10}H_{10}FBr(M^+)$, 227.9950; found, 227.9948.

1-Bromo-1-fluoro-1,1a,6,6a-tetrahydro-cycloprop[a]indene (**3k**) [14]



Yield: 79.5 mg (70%), White solid, M.p.: 70-71 ^oC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36 (dd, J = 5.1, 3.5 Hz, 1H, CH, Ar), 7.21 – 7.12 (m, 3H, CH, Ar), 3.26 – 3.17 (m, 3H), 2.58 – 2.51 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ -160.1. **^{13}C NMR** (101 MHz, $CDCl_3$): δ 143.53 (d, J_{CF} = 2.2 Hz) (C, Ar), 137.10 (d, J_{CF} = 2.6 Hz) (C, Ar), 127.32 (CH, Ar), 126.71 32 (CH, Ar), 125.30 32 (CH, Ar), 124.38 32 (CH, Ar), 82.57 (d, J_{CF} = 315.1 Hz) (CF), 41.30 (d, J_{CF} = 12.3 Hz) (CH), 34.04 (d, J_{CF} = 13.0 Hz) (CH), 32.26 (d, J_{CF} = 3.8 Hz) (CH_2). **MS** (**EI**, *m/z*, %): 226 (M^+, 0.27), 147(100.00). **HRMS (EI)**: *m/z* calcd for $C_{10}H_7FBr$ ($[M-H]^+$), 224.9715; found, 224.9722.

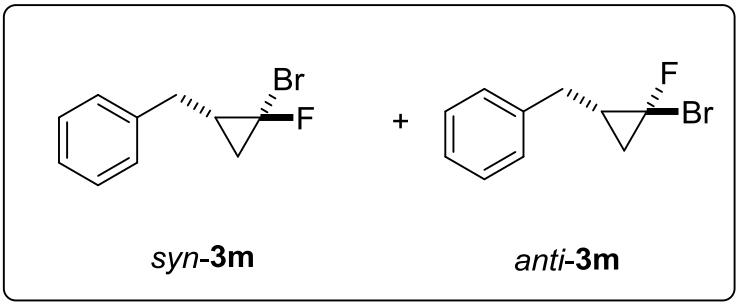
(2-(2-Bromo-2-fluorocyclopropyl)ethyl)benzene (**3l**)



Yield: 49 mg (40%，*syn*/*anti* = 42/58), Light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31-7.27 (m, 2H, CH, Ar), 7.23 – 7.16 (m, 3H, CH, Ar), 2.90 – 2.64 (m, 2H, CH_2Ar, *syn*-isomer and *anti*-isomer), 1.96 – 1.67 (m, 2H, *syn*-isomer and *anti*-isomer), 1.66-1.53 (m, 1H, C<u>H</u>CFBr, *syn*-isomer and *anti*-isomer), 1.53 – 1.44 [m, 0.42×1H, CH_2 (*cis*- to F), *syn*-isomer], 1.47 – 1.30 [m, 0.58×1H, CH_2 (*cis*- to F), *anti*-isomer], 1.12 [dt, J = 17.6, 7.6 Hz, 0.58×1H, CH_2 (*trans*- to F), *anti*-isomer], 0.90 [dd, J = 15.0,

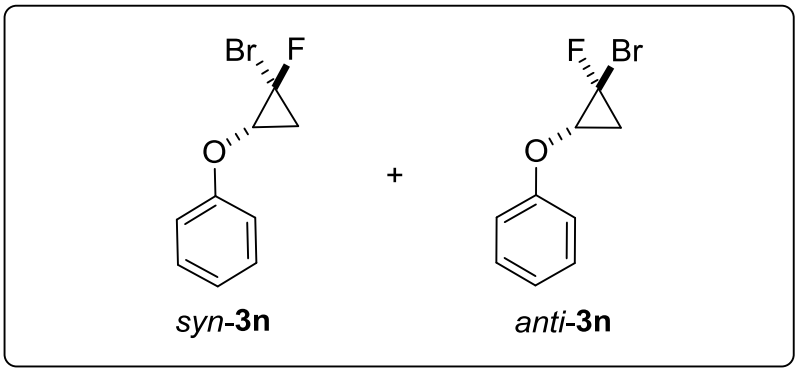
7.4 Hz, 0.42×1H, CH_2 (*trans*- to F), *syn*-isomer]. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -122.99 (ddd, J = 17.4, 12.0, 3.9 Hz, 0.42×1F, *syn*-isomer), -145.20 (dd, J = 17.6, 7.0 Hz, 0.58×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 141.23/141.22 (C, Ar), 128.51/128.49 (CH, Ar), 128.47/128.46 (CH, Ar), 126.10/126.09 (CH, Ar), 87.5 (d, J_{CF} = 298.0 Hz)/82.3 (d, J_{CF} = 301.3 Hz) (CF), 35.1/34.5 (d, J_{CF} = 0.7 Hz) (Ar$\underline{C}H_2$), 33.6 (d, J_{CF} = 0.8 Hz)/29.3 (d, J_{CF} = 4.7 Hz) (ArCH$_2\underline{C}H_2$), 28.4 (d, J_{CF} = 10.7 Hz)/25.1 (d, J_{CF} = 9.3 Hz) ($\underline{C}$HCFBr), 22.6 (d, J_{CF} = 10.8 Hz)/22.3 (d, J_{CF} = 10.1 Hz) ($\underline{C}H_2$CFBr). **HRMS (EI)**: *m/z* calcd for $C_{11}H_{12}BrF$ (M^+), 242.0106; found, 242.0103.

((2-Bromo-2-fluorocyclopropyl)methyl)benzene（**3m**）[15]



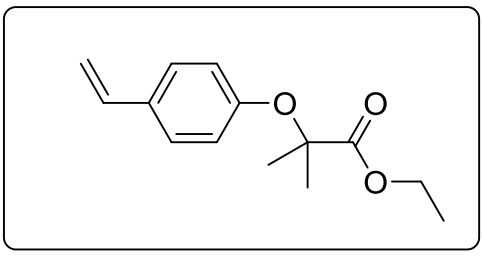
Yield: 46 mg (40%, *syn*/*anti* = 40/60), Light yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 – 6.93 (m, 5H, CH, Ar), 2.97 – 2.64 (m, 1H, Ar$\underline{CH_2}$), 2.79 (dd, J = 15.1, 6.8 Hz, 0.6×1H, Ar$\underline{CH_2}$), 2.68 (ddd, J = 15.2, 6.5, 2.9 Hz, 0.4×1H, Ar$\underline{CH_2}$), 1.89 – 1.73 (m, 1H, $\underline{C}$HCFBr, *syn*-isomer and *anti*-isomer), 1.72 –1.67 [m, 0.40×1H, CFBr$\underline{CH_2}$ (*cis*- to F), *syn*-isomer], 1.52 – 1.42 [m, 0.6×1H, CFBr$\underline{CH_2}$ (*cis*- to F), *anti*-isomer], 1.31 [dt, J = 17.5, 7.7 Hz, 0.6×1H, CH_2 (*trans*- to F), *anti*-isomer], 1.15 – 1.00 [m, 1H, 0.40×1H, CH_2 (*trans*- to F), *syn*-isomer]. **^{19}F NMR** (376 MHz, $CDCl_3$): δ -127.12 (d, J = 11.5 Hz, 0.40×1F, *syn*-isomer), -147.53 (s, 0.60×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 139.6/139.2 (d, J_{CF} = 1.1 Hz) (C, Ar), 128.64/128.62 (CH, Ar), 128.34/128.29 (CH, Ar), 126.53/126.49 (CH, Ar), 87.2 (d, J_{CF} = 298.6 Hz)/82.0 (d, J_{CF} = 301.4 Hz) (CF), 37.2 (d, J_{CF} = 0.7 Hz)/33.2 (d, J_{CF} = 5.4 Hz) ($\underline{C}H_2$Ar), 29.6 (d, J_{CF} = 10.7 Hz)/26.4 (d, J_{CF} = 9.6 Hz) ($\underline{C}$HCFBr), 22.8 (d, J_{CF} = 10.8 Hz)/22.5 (d, J_{CF} = 10.3 Hz) ($\underline{C}H_2$CFBr). **HRMS (EI)**: *m/z* calcd for $C_{10}H_{10}FBr$ (M^+), 227.9950; found, 227.9941.

(2-bromo-2-fluorocyclopropoxy)benzene（**3n**）



Yield: 110 mg (96%, *syn*/*anti* = 32/68). Light yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.34 (td, J = 7.6, 1.0 Hz, 2H, CH, Ar), 7.10 – 6.98 (m, 3H, CH, Ar), 4.10 – 3.90 (m, 1H, CHOAr, *syn*-isomer and *anti*-isomer), 2.03 (dt, J = 19.4, 9.2 Hz, 0.32×1H, CH_2 (*cis*- to F), *syn*-isomer), 1.90 (dddd, J = 20.3, 9.5, 4.9, 0.5 Hz, 0.68×1H, CH_2 (*cis* to F), *anti*-isomer), 1.80 (dt, J = 18.1, 9.2 Hz, 0.68×1H, CH_2 (*trans*- to F), *anti*-isomer), 1.67 – 1.57 (m, 0.32×1H, CH_2 (*trans*- to F), *syn*-isomer). **^{19}F NMR** (377 MHz, $CDCl_3$): δ -136.41 – -138.15 (m, 0.32×1F, *syn*-isomer), -155.90 – -157.50 (m, 0.68×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 157.8/157.1 (C, Ar), 129.7/129.6 (CH, Ar), 122.3 (C, Ar), 115.1/114.9 (CH, Ar), 82.4 (d, J_{CF} = 303.7 Hz)/78.4 (d, J_{CF} = 306.6 Hz) (CF), 58.9 (d, J_{CF} = 9.4 Hz)/56.3 (d, J_{CF} = 13.8 Hz) (CHOAr), 24.8 (d, J_{CF} = 11.4 Hz)/23.5 (d, J_{CF} = 10.5 Hz) (CH_2). **HRMS (ESI)**: *m/z* calcd. for C_9H_7BrFO ($[M-H]^+$), 228.9665; found, 228.9670.

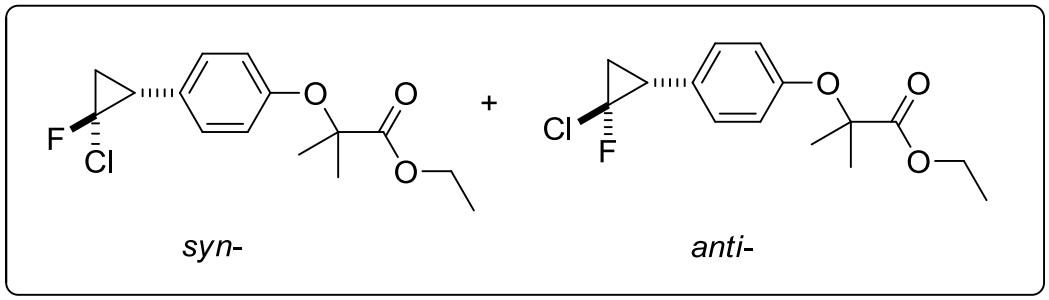
Ethyl 2-methyl-2-(4-vinylphenoxy)propanoate **(6a)**[6]



Light yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.29 (d, J = 8.6 Hz, 2H, CH, Ar), 6.80 (d, J = 8.7 Hz, 2H, CH, Ar), 6.64 (dd, J = 17.6, 10.9 Hz, 1H, C<u>H</u>=CH_2), 5.62 (dd, J = 17.6, 0.8 Hz, 1H, CH=C<u>H</u>$_2$), 5.14 (dd, J = 10.9, 0.7 Hz, 1H, CH=C<u>H</u>$_2$), 4.23 (q, J

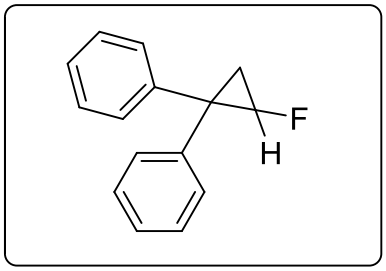
= 7.1 Hz, 2H, OC<u>H</u>$_2$), 1.60 (s, 6H, 2CH$_3$), 1.25 (t, *J* = 7.1 Hz, 3H, CH$_2$<u>CH</u>$_3$). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 174.3 (C=O), 155.2 (Ar<u>C</u>-O), 136.1 (<u>C</u>H=CH$_2$), 131.7 (C, Ar), 127.0 (CH, Ar), 119.0 (CH, Ar), 112.2 (CH=<u>C</u>H$_2$), 79.2 (<u>C</u>(CH$_3$)$_2$), 61.5 (O<u>C</u>H$_2$CH$_3$), 25.4 (C(<u>C</u>H$_3$)$_2$), 14.1 (OCH$_2$<u>C</u>H$_3$). **HRMS (ESI)**: *m/z* calcd. for $C_{14}H_{18}NaO_3$ $[M+Na]^+$, 257.1154; found, 257.1156.

Ethyl 2-(4-(2-chloro-2-fluorocyclopropyl)phenoxy)-2-methylpropanoate **(A)**[6]



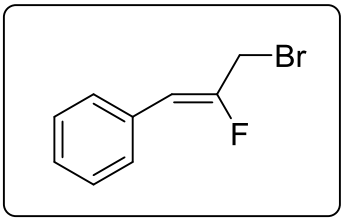
Yield: 92 mg (60%, *syn*/*anti* = 1.1:1). Yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.09 (dd, *J* = 12.2, 8.6 Hz, 2H, CH, Ar), 6.81 (dd, *J* = 8.7, 2.0 Hz, 2H, CH, Ar), 4.22 (tt, *J* = 7.1, 3.6 Hz, 2H, OC<u>H</u>$_2$CH$_3$), 2.80 (ddd, *J* = 17.1, 11.6, 8.6 Hz, 0.52×1H, CHAr, *syn*-isomer), 2.63 (t, *J* = 9.7 Hz, 1H, 0.48×1H, CHAr, *anti*-isomer), 1.94 [ddd, *J* = 15.9, 11.6, 7.7 Hz, 0.52×1H, CH$_2$ (*cis*- to F), *syn*-isomer], 1.80 – 1.72 [m, 0.96H, CH$_2$ (*cis*- and *trans*- to F), *anti*-isomer], 1.59 (s, 0.52×6H, 2CH$_3$, *syn*-isomer), 1.58 (s, 0.48×6H, 2CH$_3$, *anti*-isomer), 1.55 – 1.50 [m, 0.52×1H, CH$_2$ (*trans*- to F), *syn*-isomer], 1.23 (td, *J* = 7.1, 4.5 Hz, 3H, OCH$_2$C<u>H</u>$_3$). **^{19}F NMR** (376 MHz, $CDCl_3$): δ -128.71 (td, *J* = 16.4, 5.9 Hz, 0.52×1F, *syn*-isomer), -148.95 (dd, *J* = 15.7, 8.0 Hz,0.48×1F, *anti*-isomer). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 174.2 (C=O), 154.8/154.7 (ArC-O), 129.2 (d, J_{CF} = 2.0 Hz)/129.0 (d, J_{CF} = 0.6 Hz) (CH, Ar), 128.0/ 127.1 (d, J_{CF} = 1.6 Hz) (C, Ar), 119.0/118.8 (CH, Ar), 94.8 (d, J_{CF} = 293.6 Hz)/92.0 (d, J_{CF} = 293.4 Hz) (CF), 79.2 [O<u>C</u>(CH$_3$)$_2$], 61.4 (O<u>C</u>H$_2$CH$_3$), 31.6 (d, J_{CF} = 11.3 Hz)/29.7 (d, J_{CF} = 11.7 Hz) (CHAr), 25.39/25.36 (C(<u>C</u>H$_3$)$_2$), 21.5 (d, J_{CF} = 10.9 Hz)/20.9 (d, J_{CF} = 11.1 Hz) (FClC<u>C</u>H$_2$), 14.1(OCH$_2$<u>C</u>H$_3$). **HRMS (ESI)**: *m/z* calcd. for $C_{15}H_{18}ClFNaO_3$ $[M+Na]^+$, 323.0826; found, 323.0827.

(2-Fluorocyclopropane-1,1-diyl)dibenzene [16]



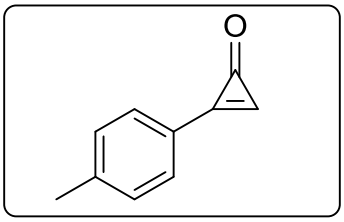
Yield: 76 mg (72%), Light yellow viscous oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.42 (d, J = 7.4 Hz, 2H, CH, Ar), 7.33 (t, J = 7.4 Hz, 2H, CH, Ar), 7.25 (d, J = 5.7 Hz, 3H, CH, Ar), 7.17 (d, J = 7.3 Hz, 3H, CH, Ar), 5.00 (dd, J = 65.0, 3.3 Hz, 1H, CF<u>H</u>), 1.87 – 1.72 (m, 1H, C<u>H</u>$_2$), 1.63 – 1.47 (m, 1H, C<u>H</u>$_2$). **^{19}F NMR** (376 MHz, $CDCl_3$): δ -207.04 (ddd, J = 65.1, 22.7, 11.3 Hz, 1F). **^{13}C NMR** (101 MHz, $CDCl_3$) δ: 143.4 (d, J_{CF} = 2.0 Hz), 139.0 (d, J_{CF} = 3.1 Hz), 130.4, 128.6, 128.4, 127.6 (d, J_{CF} = 1.4 Hz), 127.0, 126.6, 77.0 (d, J_{CF} = 229.5 Hz) (CF), 35.1 (d, J_{CF} = 10.5 Hz) ($C(Ph)_2$), 20.7 (d, J_{CF} = 9.6 Hz) (CH_2). **MS** (**EI**, *m/z*, %): 212 (M^+, 88.93), 165 (100.00). **HRMS (EI)**: *m/z* calcd for $C_{10}H_{13}F$ (M^+), 212.1001; found, 212.0995.

(Z)-(3-Bromo-2-fluoroprop-1-en-1-yl)benzene [17]



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 7.3 Hz, 2H), 7.29 (ddd, J = 11.1, 9.4, 6.1 Hz, 3H), 5.85 (d, J = 36.0 Hz, 1H), 4.10 (d, J = 20.1 Hz, 2H). **^{19}F NMR** (376 MHz, $CDCl_3$): δ -107.73 (dt, J = 36.1, 20.1 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 154.5 (d, J = 262.8 Hz), 132.4, 129.0 (d, J = 7.6 Hz), 128.7, 128.2, 110.5 (d, J = 8.2 Hz), 29.7 (d, J = 31.3 Hz). **MS** (**EI**, *m/z*, %): 214 (M^+, 7.44), 216 ($[M+2]^+$, 7.70), 135 (100.00), 115 (54.04).

2-(p-Tolyl)cycloprop-2-en-1-one



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1H), 7.76 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 7.9 Hz, 2H), 2.45 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 161.6, 155.4, 144.7, 139.1, 131.3, 130.1, 120.5, 22.0. **HRMS (ESI)**: *m/z* calcd. for $C_{10}H_9O$ $[M+H]^+$, 145.0653; found, 146.0654.

8. Full List of Ref. 6(b)

$FSO_2CF_2CO_2R$ (R = $SiMe_3$, Me)

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$Ph_3P^+CF_2CO_2^-$

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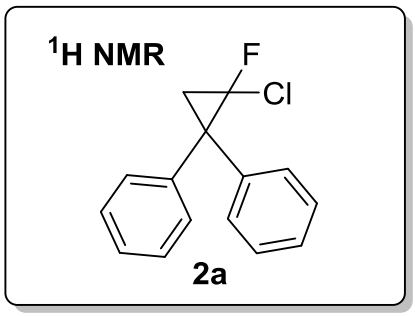
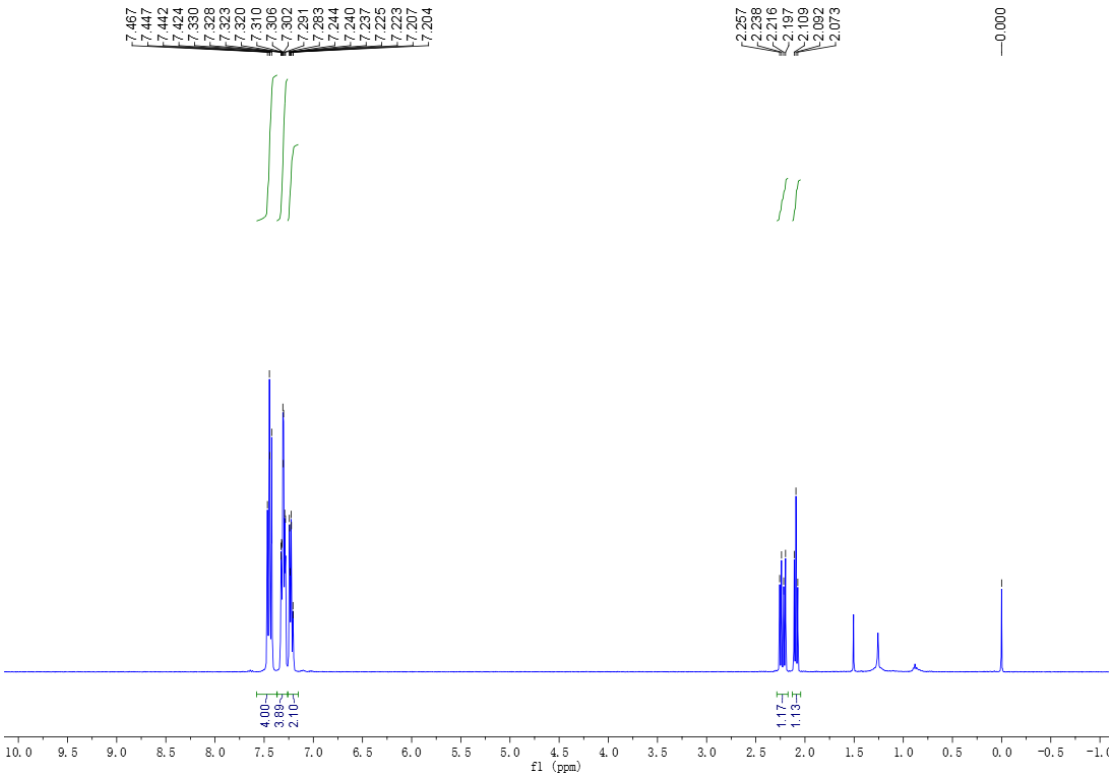
10. ^{1}H, ^{13}C and ^{19}F NMR Spectra

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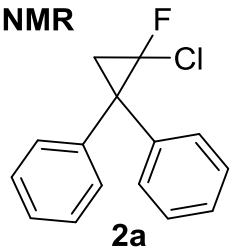
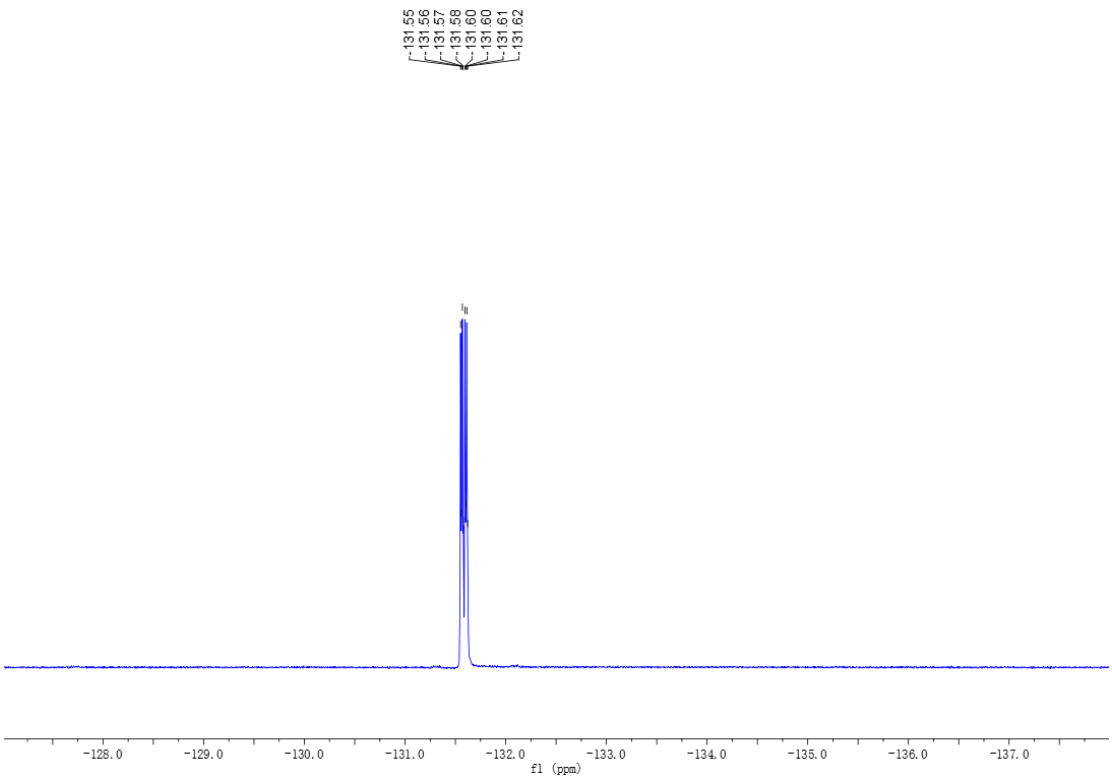
7.447
7.442
7.424
7.330
7.328
7.323
7.320
7.310
7.306
7.302
7.291
7.283
7.244
7.240
7.237
7.225
7.223
7.207
7.204
2.257
2.238
2.216
2.197
2.109
2.092
2.073
0.000
4.00
3.89
2.10
1.17
1.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

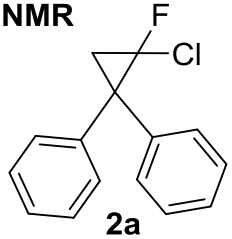
^{19}F NMR


F
Cl

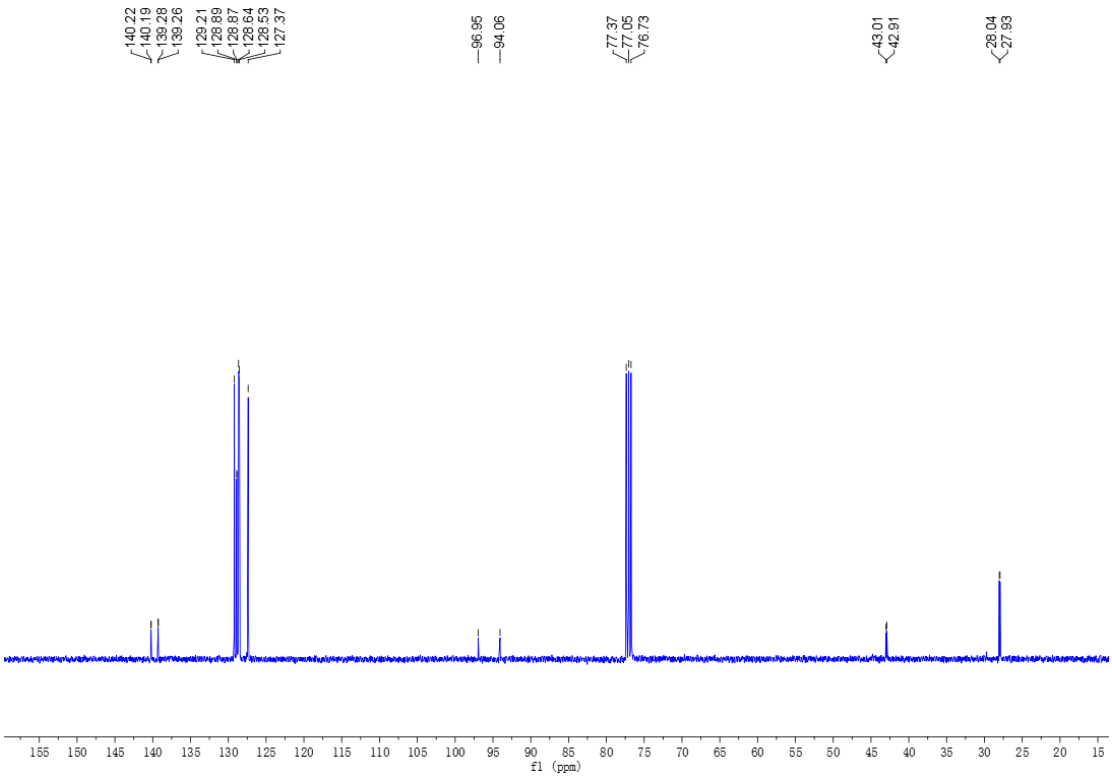
2a


131.55
131.56
131.57
131.58
131.60
131.60
131.61
131.62
-128.0
-129.0
-130.0
-131.0
-132.0
-133.0
-134.0
-135.0
-136.0
-137.0
f1 (ppm)

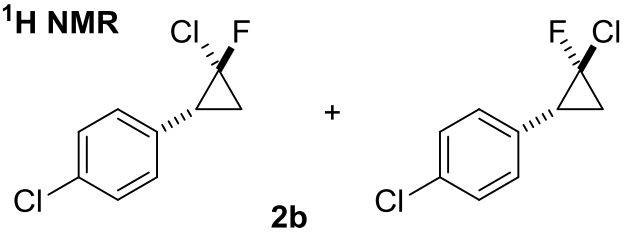
^{13}C NMR


F
Cl

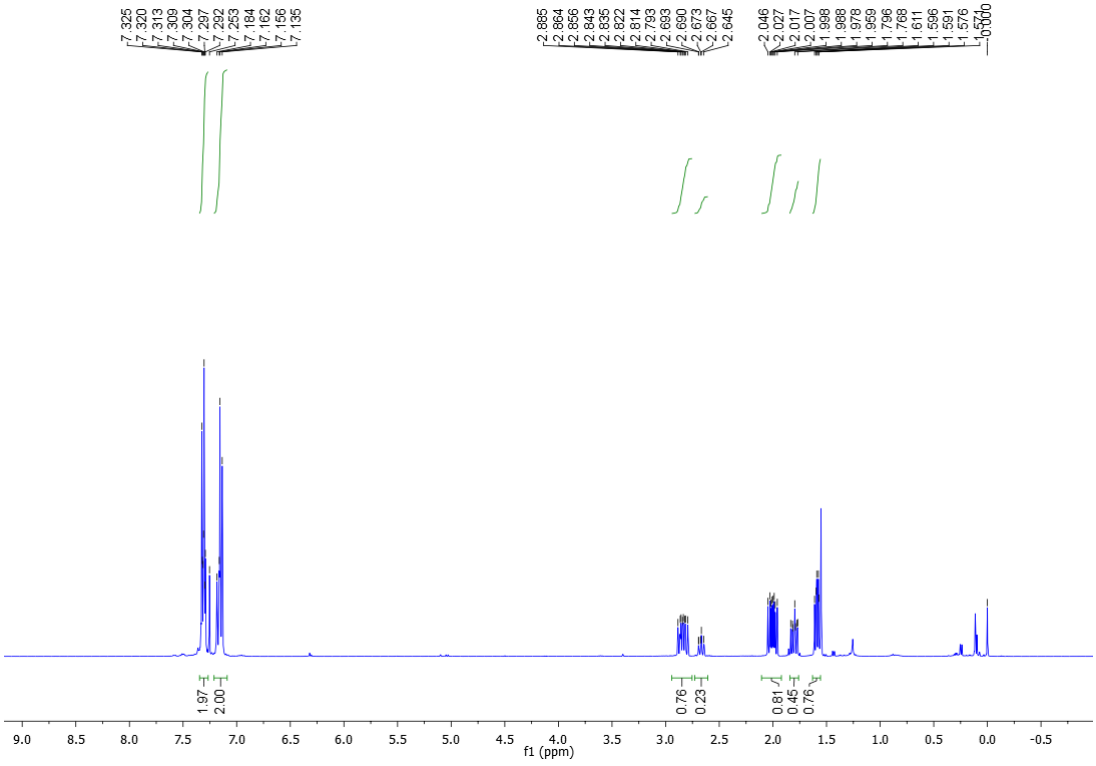
2a

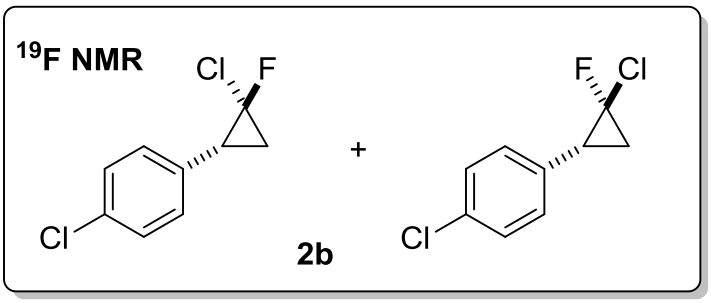

140.22
140.19
139.28
139.26
129.21
128.89
128.87
128.64
128.53
127.37
96.95
94.06
77.37
77.05
76.73
43.01
42.91
28.04
27.93
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)

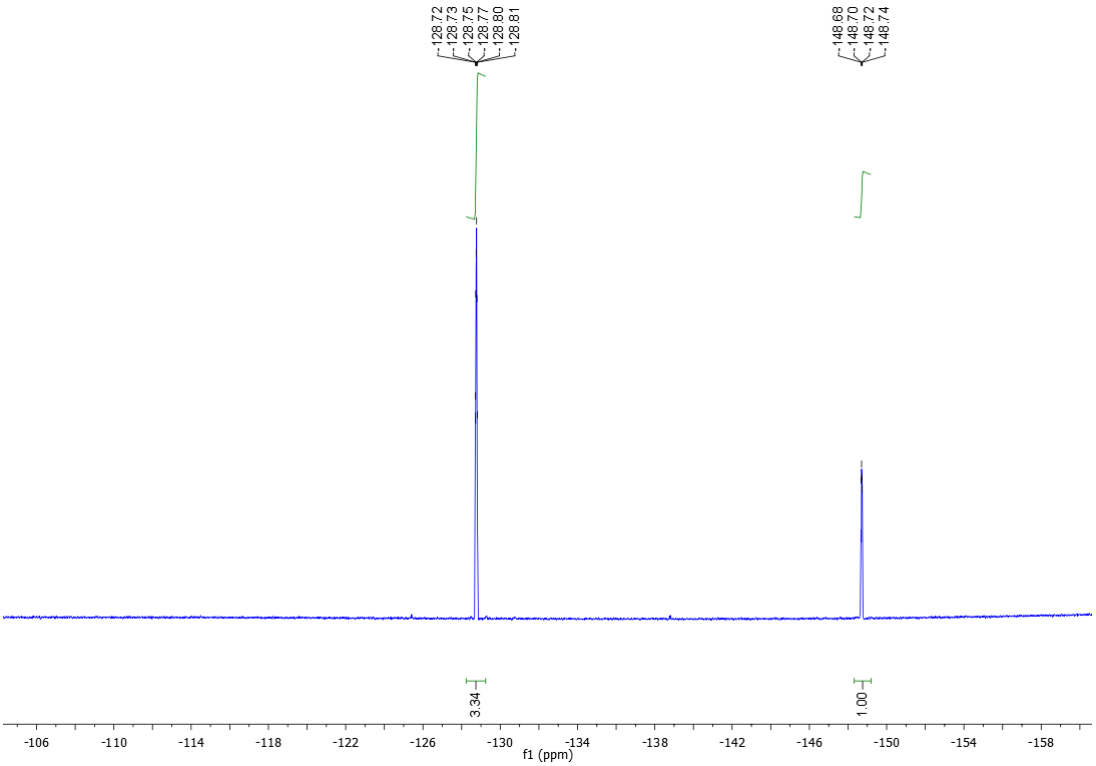
^{1}H NMR


Cl
F
Cl
+
F
Cl
Cl

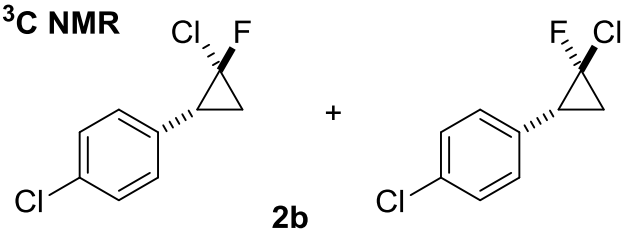
2b


7.325
7.320
7.313
7.309
7.304
7.297
7.292
7.253
7.184
7.162
7.156
7.135
2.885
2.864
2.856
2.843
2.835
2.822
2.814
2.793
2.693
2.690
2.673
2.667
2.645
2.046
2.027
2.017
2.007
1.998
1.988
1.978
1.959
1.796
1.768
1.611
1.596
1.591
1.576
1.571
0.000
1.97
2.00
0.76
0.23
0.81
0.45
0.76
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

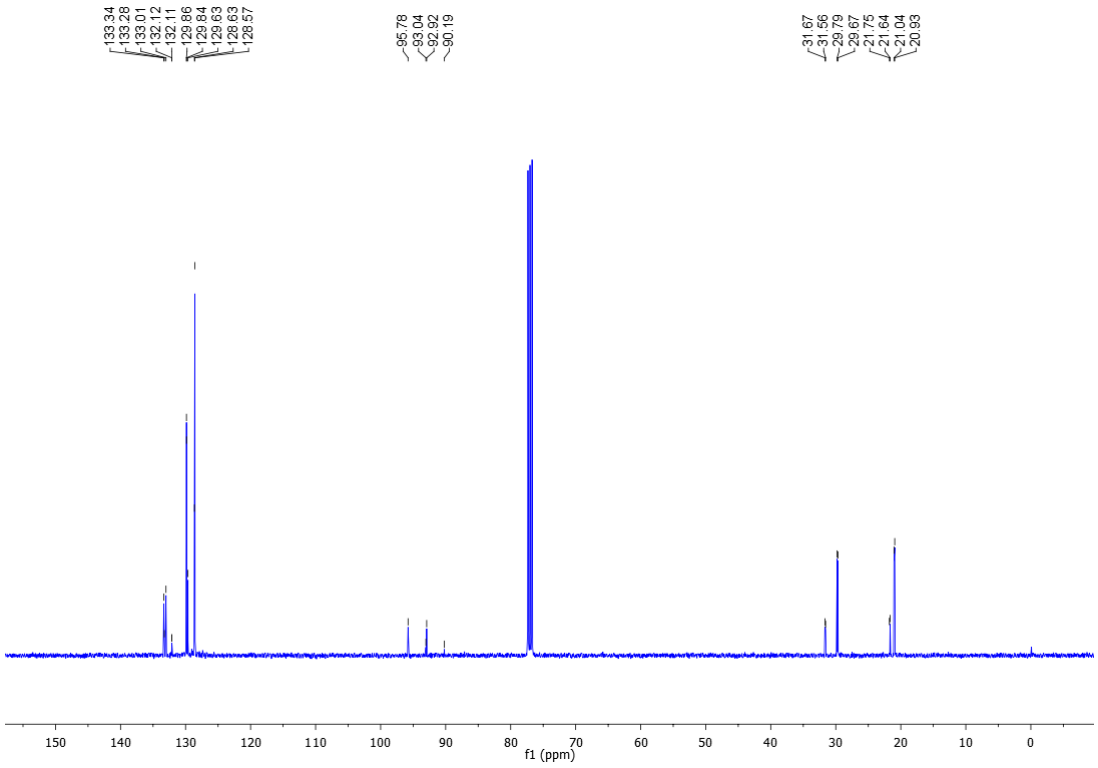

19F NMR
Cl
F
Cl
+
F
Cl
Cl
2b


128.72
128.73
128.75
128.77
128.80
128.81
148.68
148.70
148.72
148.74
3.34
1.00
-106
-110
-114
-118
-122
-126
-130
-134
-138
-142
-146
-150
-154
-158
f1 (ppm)

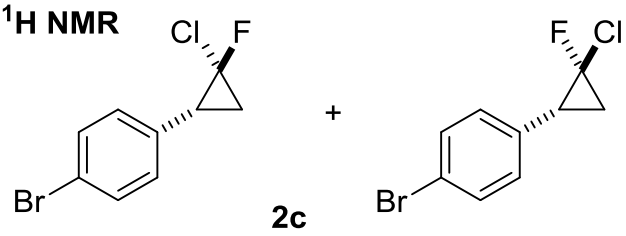
^{13}C NMR


Cl
F
Cl
+
F
Cl
Cl

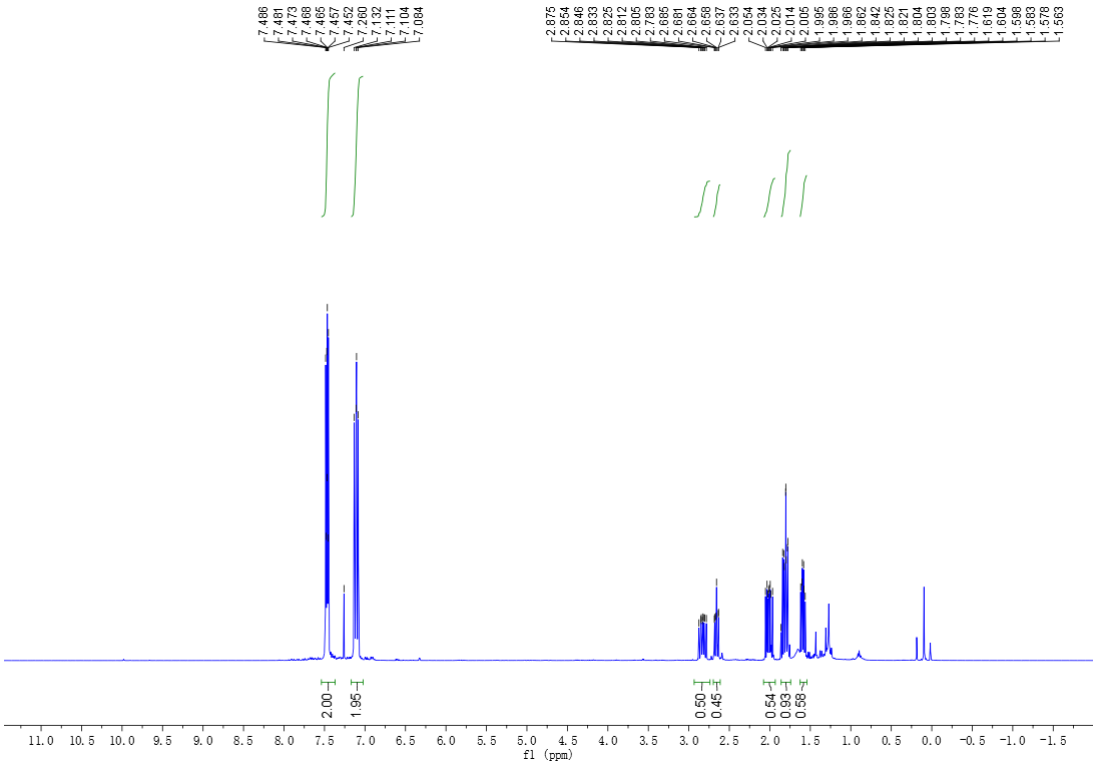
2b


133.34
133.28
133.01
132.12
132.11
129.86
129.84
129.63
128.63
128.57
95.78
93.04
92.92
90.19
31.67
31.56
29.79
29.67
21.75
21.64
21.04
20.93
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H NMR


Cl
F
Br
+
F
Cl
Br

2c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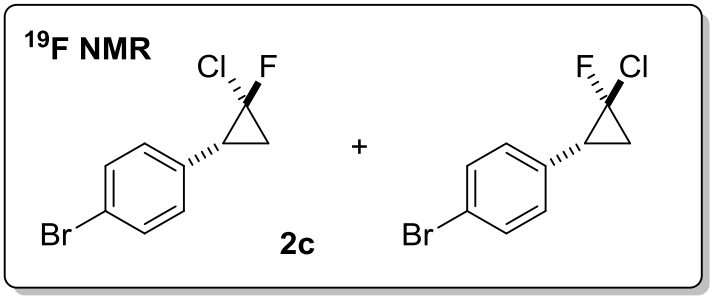
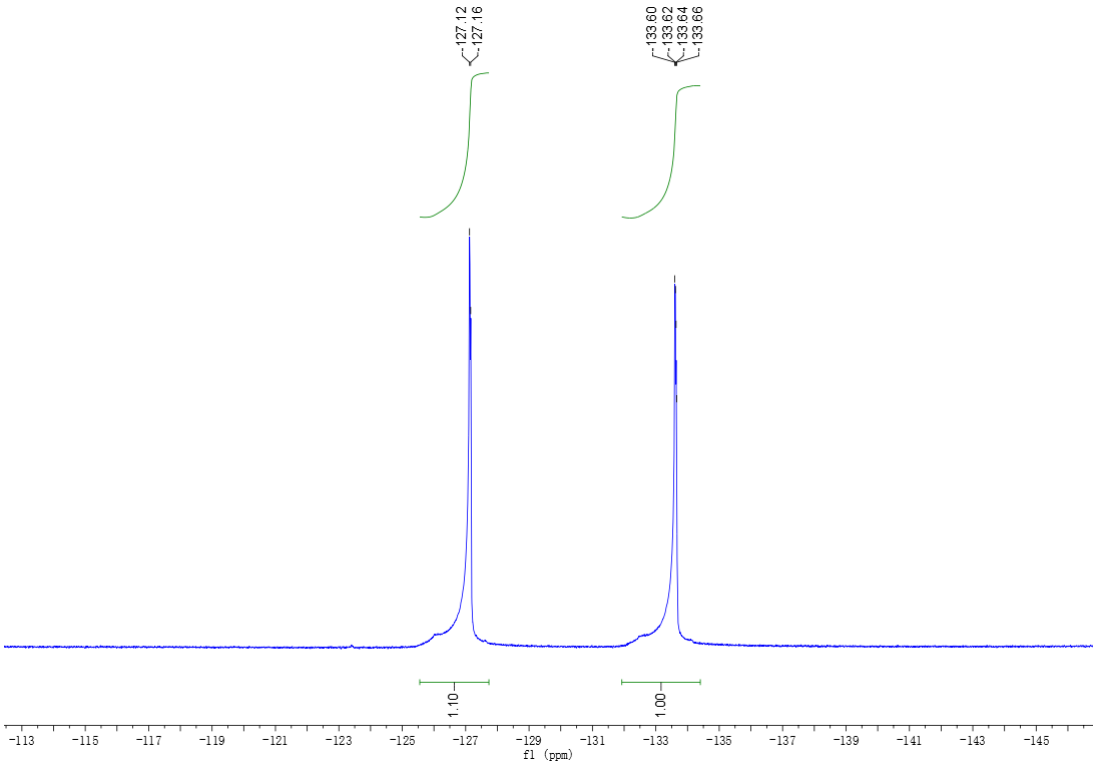
7.481
7.473
7.468
7.465
7.457
7.452
7.260
7.132
7.111
7.104
7.084
2.875
2.854
2.846
2.833
2.825
2.812
2.805
2.783
2.685
2.681
2.664
2.658
2.637
2.633
2.054
2.034
2.025
2.014
2.005
1.995
1.986
1.966
1.862
1.842
1.825
1.821
1.804
1.803
1.798
1.783
1.776
1.619
1.604
1.598
1.583
1.578
1.563
2.00
1.95
0.50
0.45
0.54
0.93
0.58
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)


19F NMR
Cl
F
Br
+
F
Cl
Br
2c


127.12
127.16
133.60
133.62
133.64
133.66
1.10
1.00
-113
-115
-117
-119
-121
-123
-125
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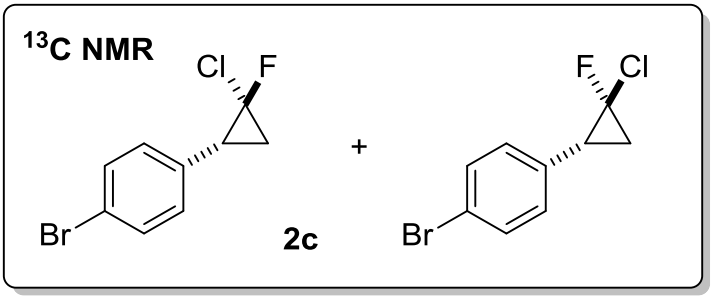
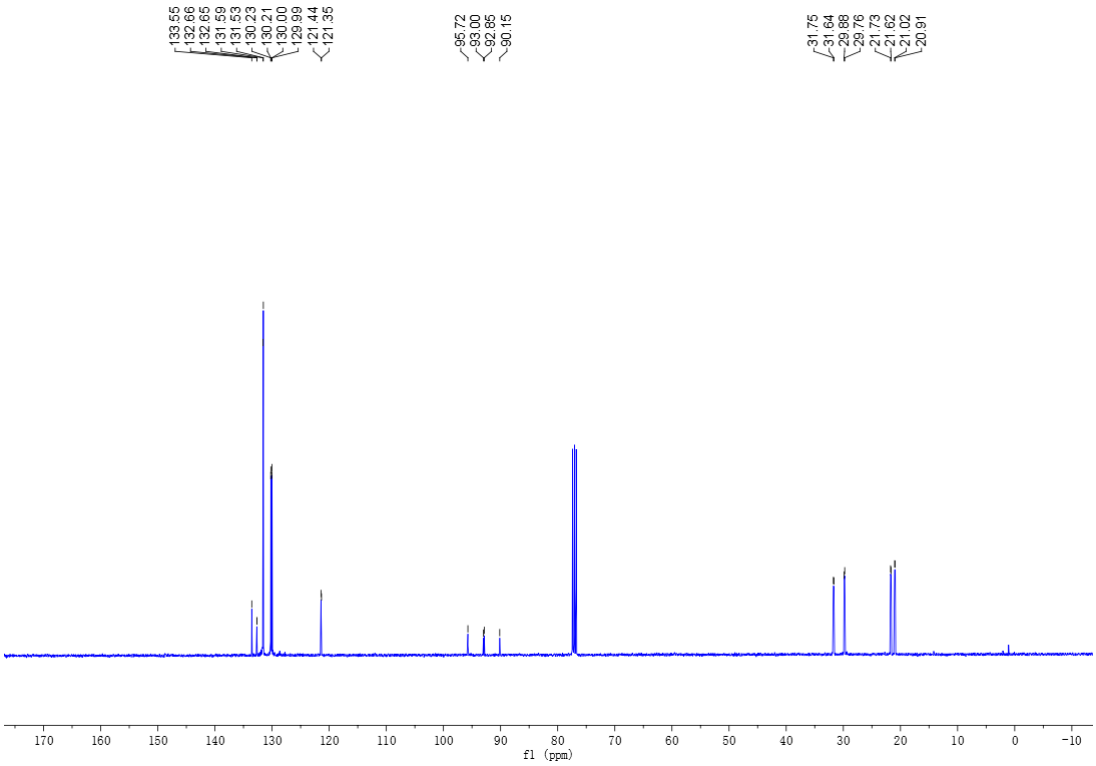
-129
-131
-133
-135
-137
-139
-141
-143
-145
f1 (ppm)

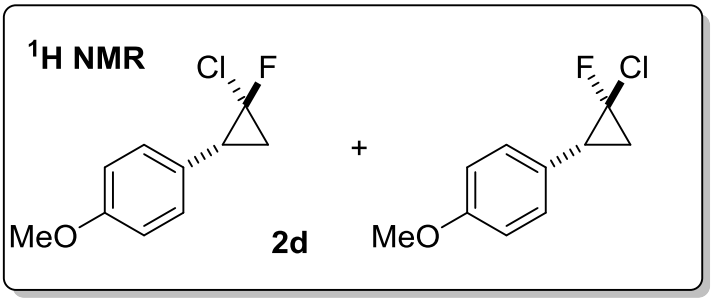
^{13}C NMR


Cl
F
Br
+
F
Cl
Br

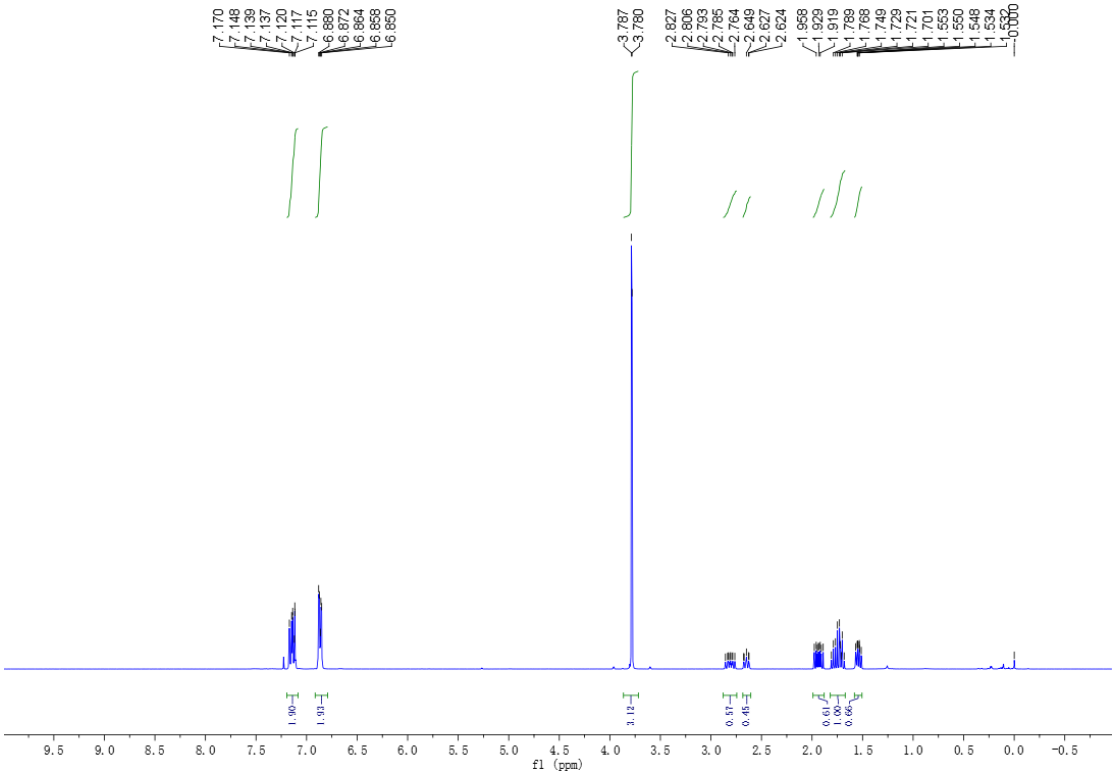
2c

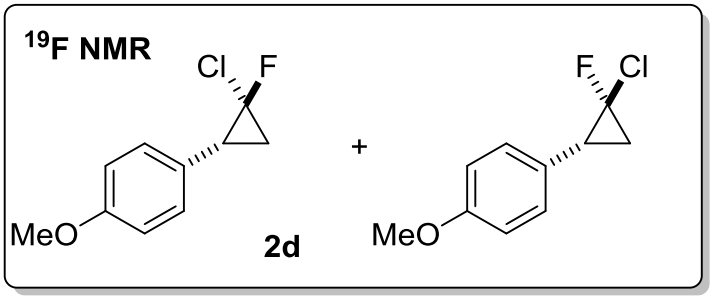

133.55
132.66
132.65
131.59
131.53
130.23
130.21
130.00
129.99
121.44
121.35
95.72
93.00
92.85
90.15
31.75
31.64
29.88
29.76
21.73
21.62
21.02
20.91
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

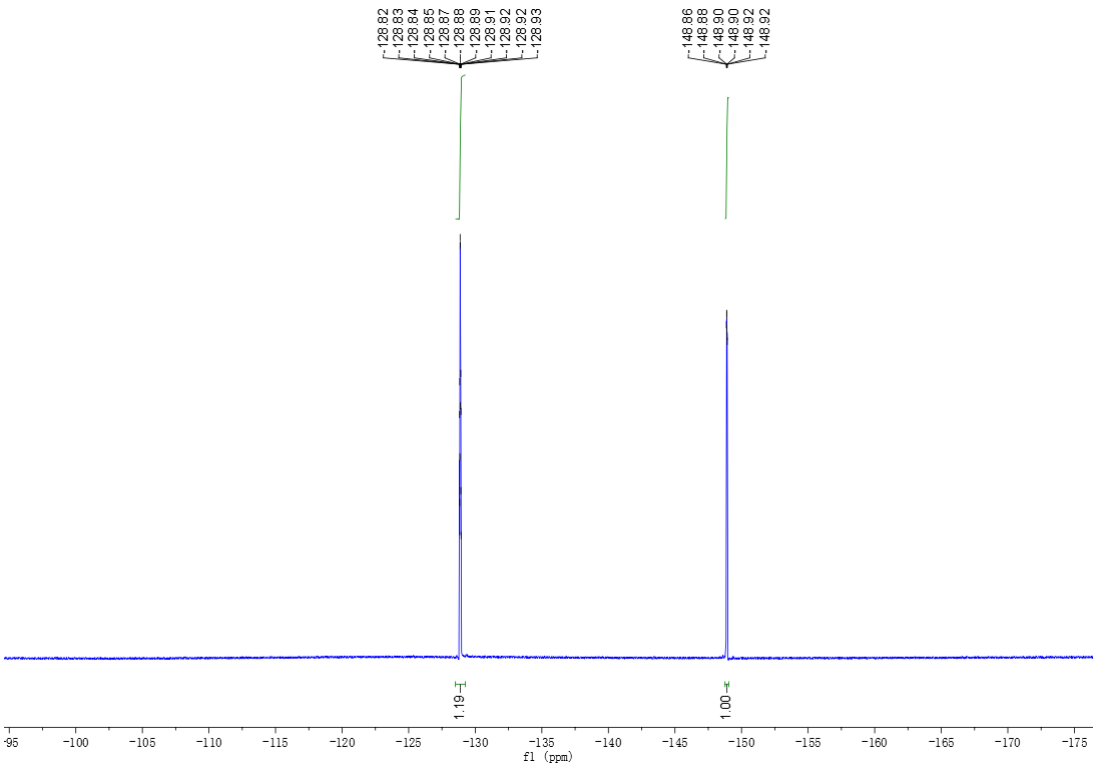
^{1}H NMR


Cl
F
MeO
+
F
Cl
MeO

2d


7.170
7.148
7.139
7.137
7.120
7.117
7.115
6.880
6.872
6.864
6.858
6.850
3.787
3.780
2.827
2.806
2.793
2.785
2.764
2.649
2.627
2.624
1.958
1.929
1.919
1.789
1.788
1.749
1.729
1.721
1.701
1.553
1.550
1.548
1.534
1.532
0.000
1.90
1.93
3.12
0.57
0.45
0.61
1.00
0.66
f1 (ppm)


19F NMR
Cl
F
MeO
2d
+
F
Cl
MeO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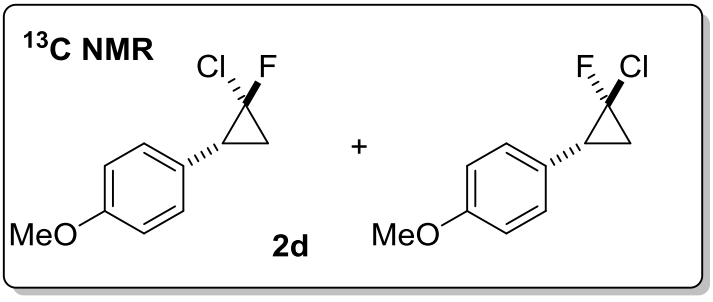
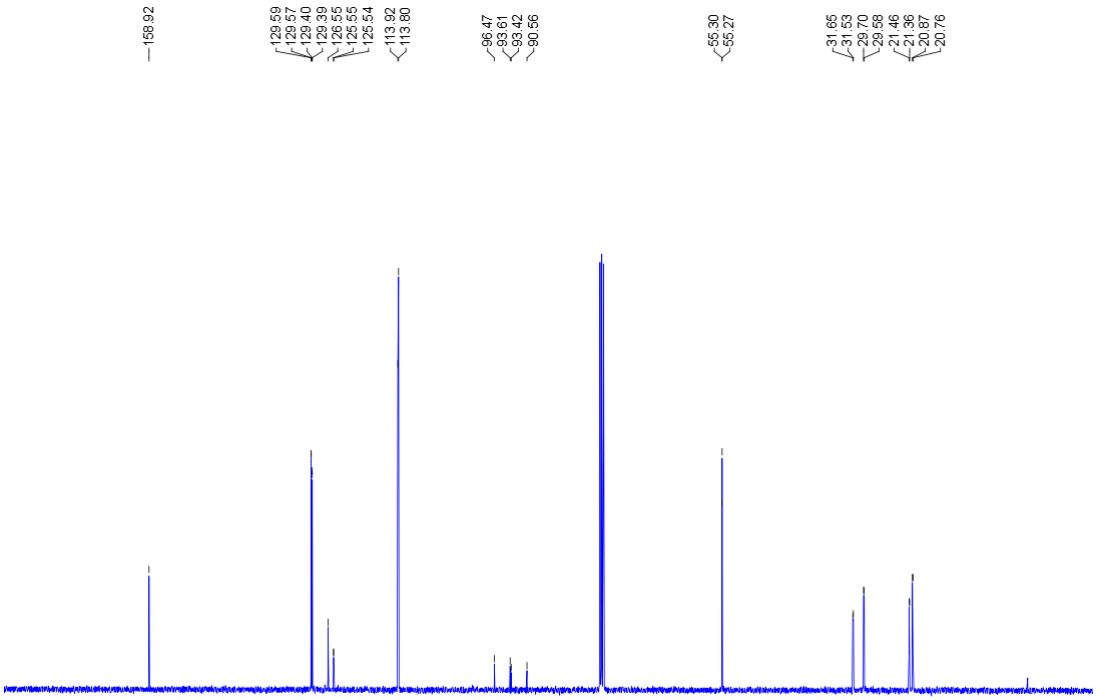
128.88
128.89
128.91
128.92
128.92
128.93
148.86
148.88
148.90
148.90
148.92
148.92
1.19
1.00
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
f1 (ppm)

^{13}C NMR


Cl
F
MeO
+
F
Cl
MeO

2d


158.92
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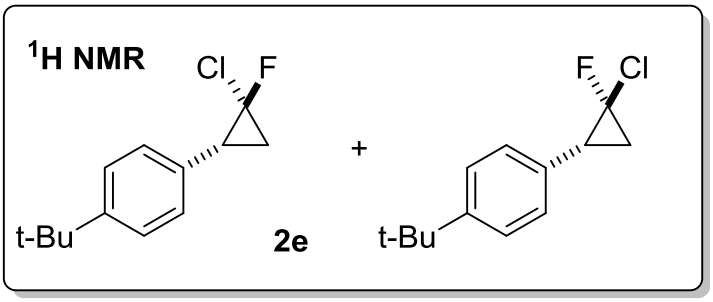
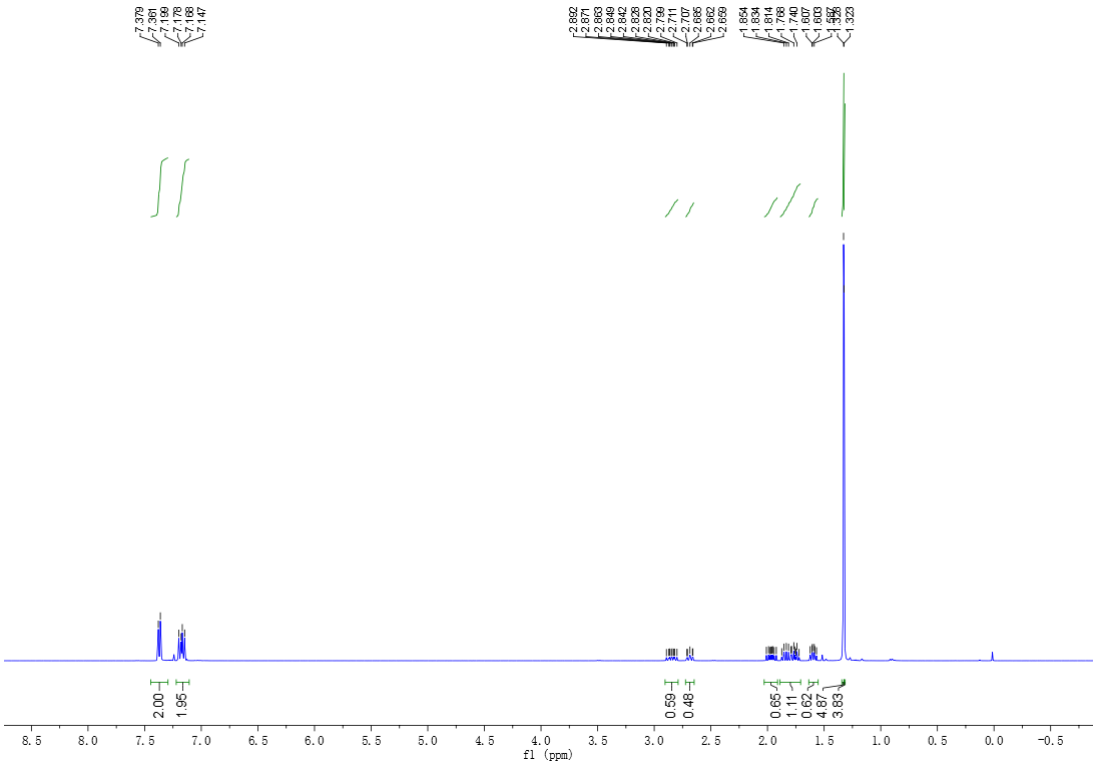
129.57
129.40
129.39
126.55
125.55
125.54
113.92
113.80
96.47
93.61
93.42
90.56
55.30
55.27
31.65
31.53
29.70
29.58
21.46
21.36
20.87
20.76

^{1}H NMR


Cl
F
t-Bu
+
F
Cl
t-Bu

2e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7.166
7.147
2.882
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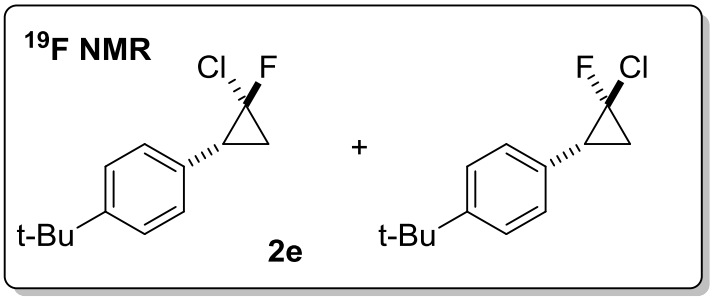
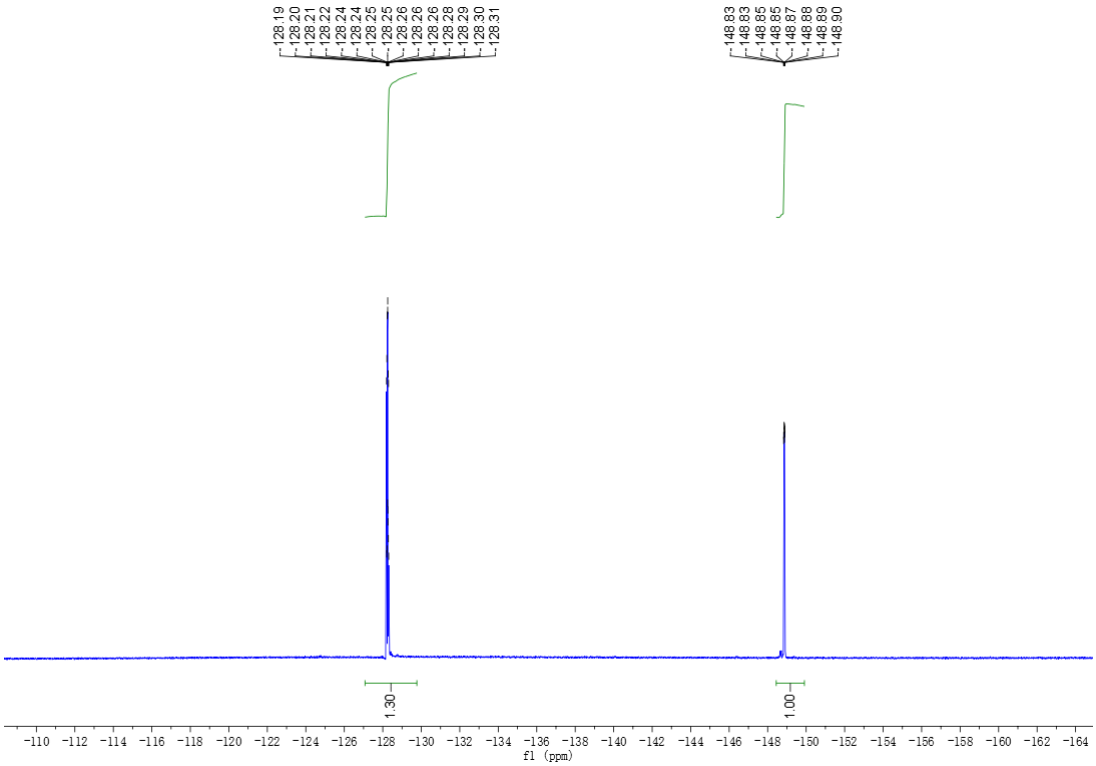
2.842
2.828
2.820
2.799
2.711
2.707
2.685
2.662
2.659
1.854
1.834
1.814
1.788
1.740
1.607
1.603
1.323
2.00
1.95
0.59
0.48
0.65
1.11
0.62
4.87
3.83
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

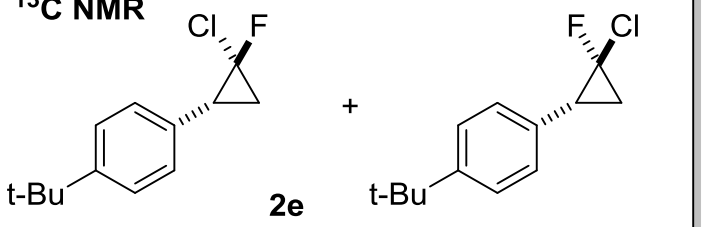
^{19}F NMR


Cl
F
t-Bu
+
F
Cl
t-Bu

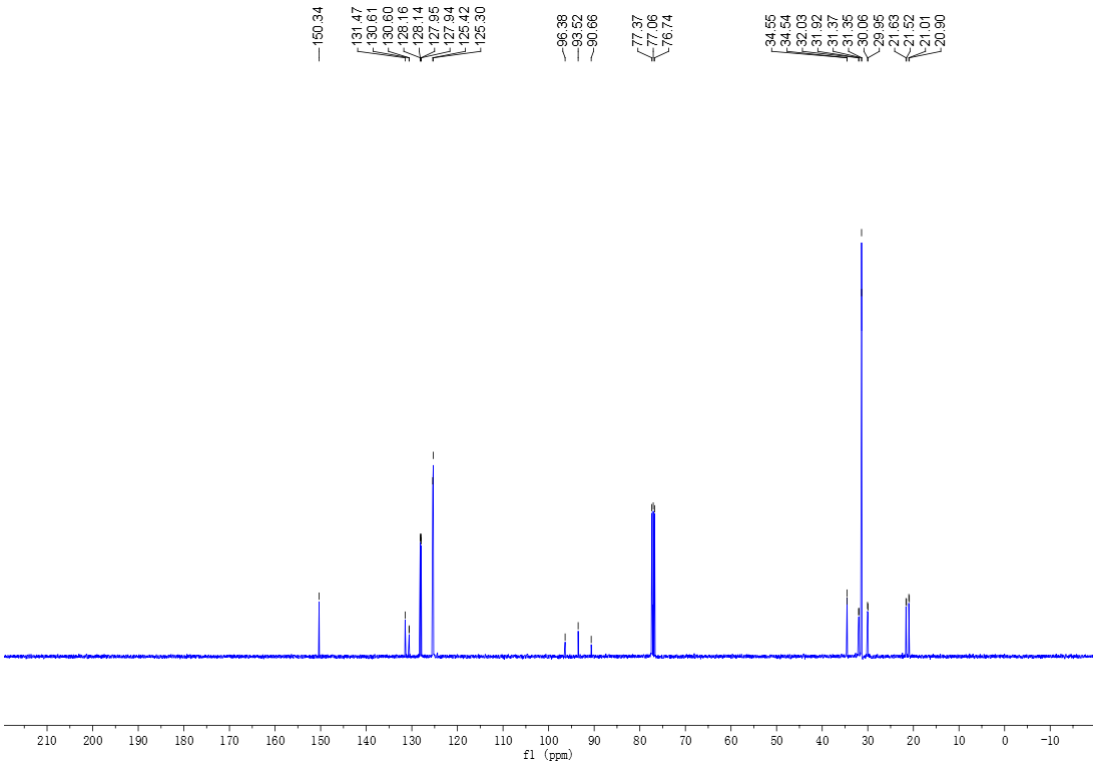
2e


128.19
128.20
128.21
128.22
128.24
128.24
128.25
128.25
128.26
128.26
128.26
128.28
128.29
128.30
128.31
148.83
148.83
148.85
148.85
148.87
148.88
148.89
148.90
1.30
1.00
-110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150 -152 -154 -156 -158 -160 -162 -164
f1 (ppm)

^{13}C NMR


Cl
F
t-Bu
+
F
Cl
t-Bu

2e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127.94
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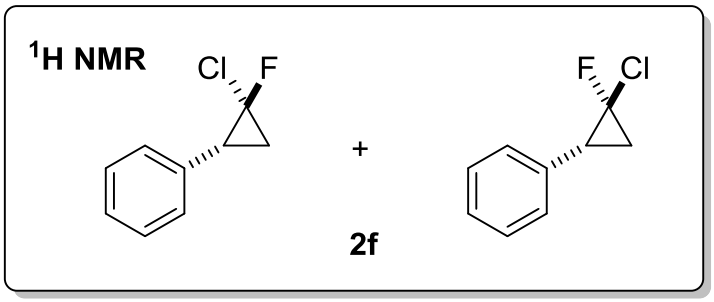
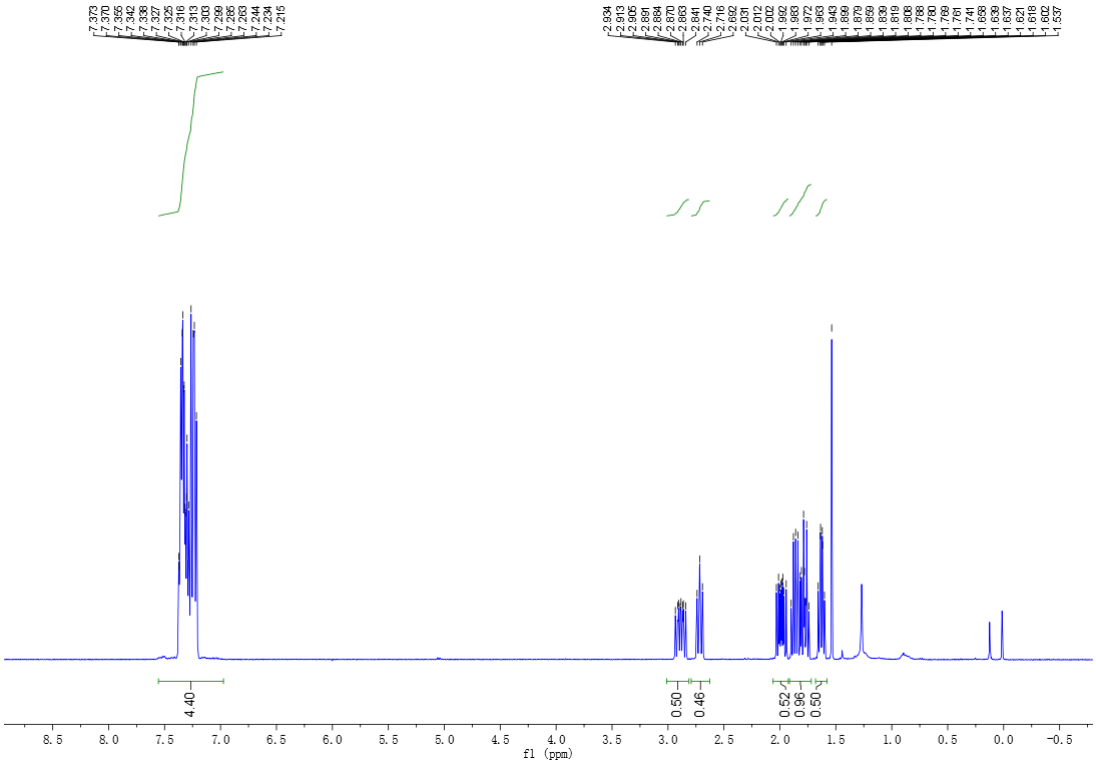
125.30
96.38
93.52
90.66
77.37
77.06
76.74
34.55
34.54
32.03
31.92
31.37
31.35
30.06
29.95
21.63
21.52
21.01
20.90
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


1H NMR
Cl
F
+
F
Cl
2f


7.373
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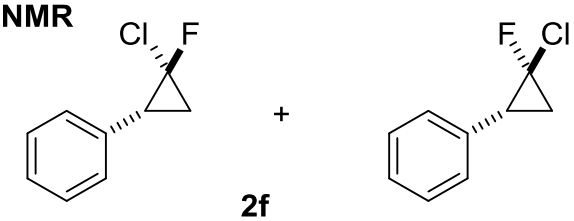
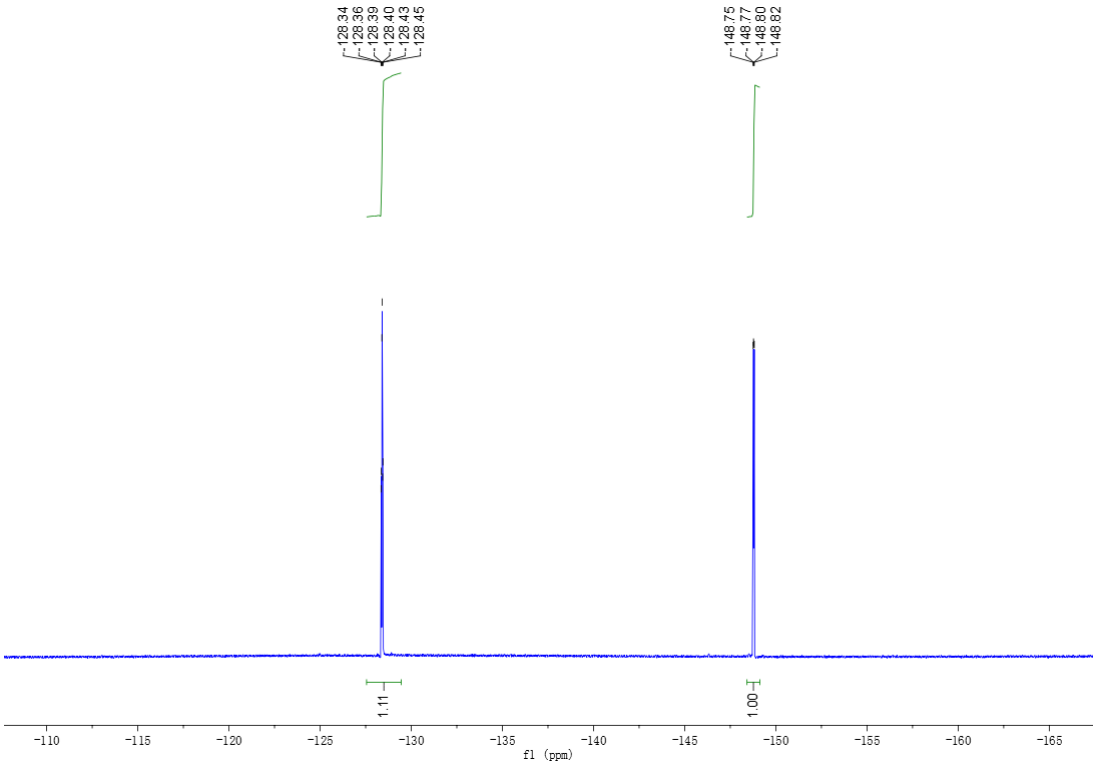
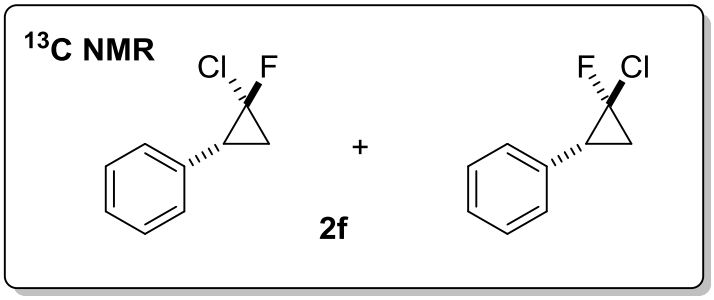
7.303
7.299
7.285
7.263
7.244
7.234
7.215
2.934
2.913
2.895
2.891
2.884
2.870
2.863
2.841
2.740
2.716
2.692
2.071
2.012
2.002
1.992
1.983
1.972
1.963
1.943
1.899
1.879
1.869
1.838
1.819
1.808
1.788
1.780
1.761
1.741
1.698
1.689
1.637
1.621
1.618
1.602
1.537
4.40
0.50
0.46
0.52
0.96
0.50
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

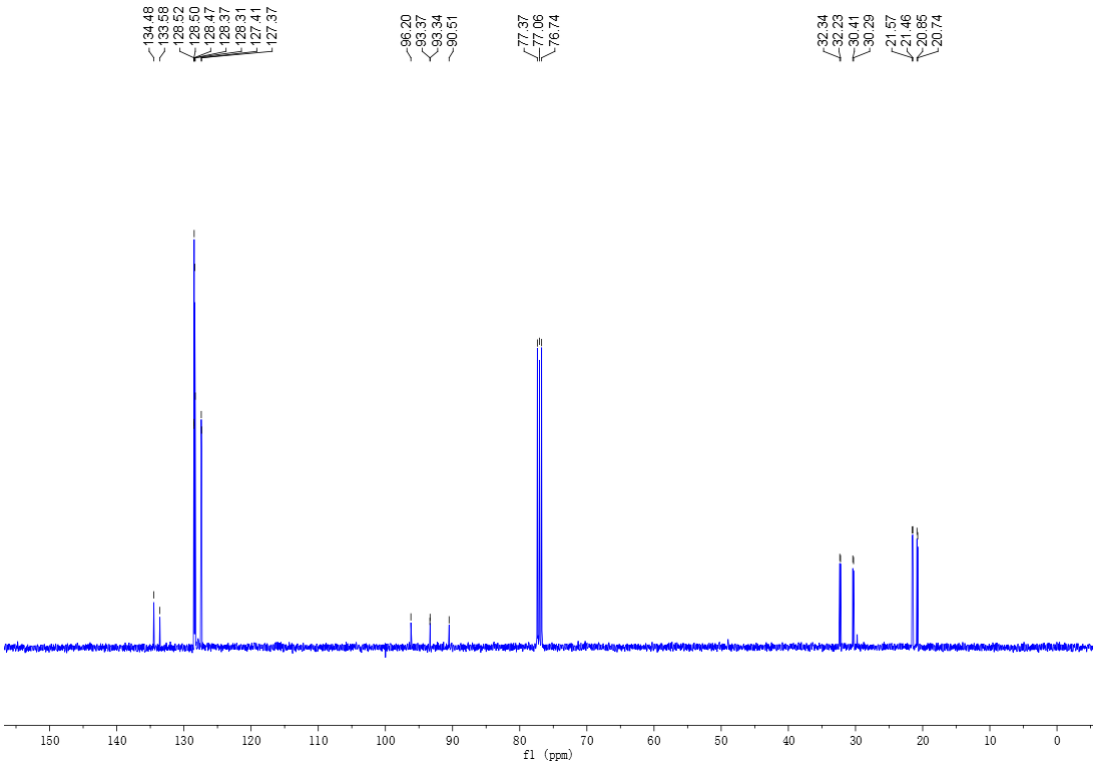
^{19}F NMR

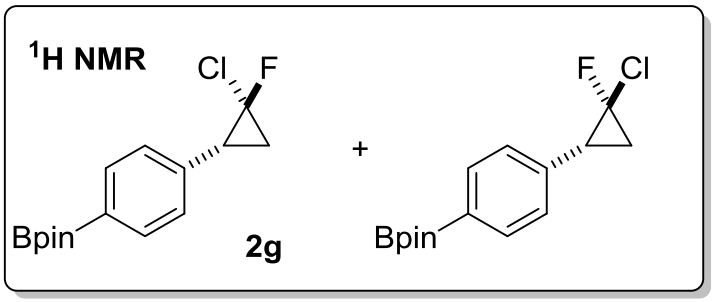


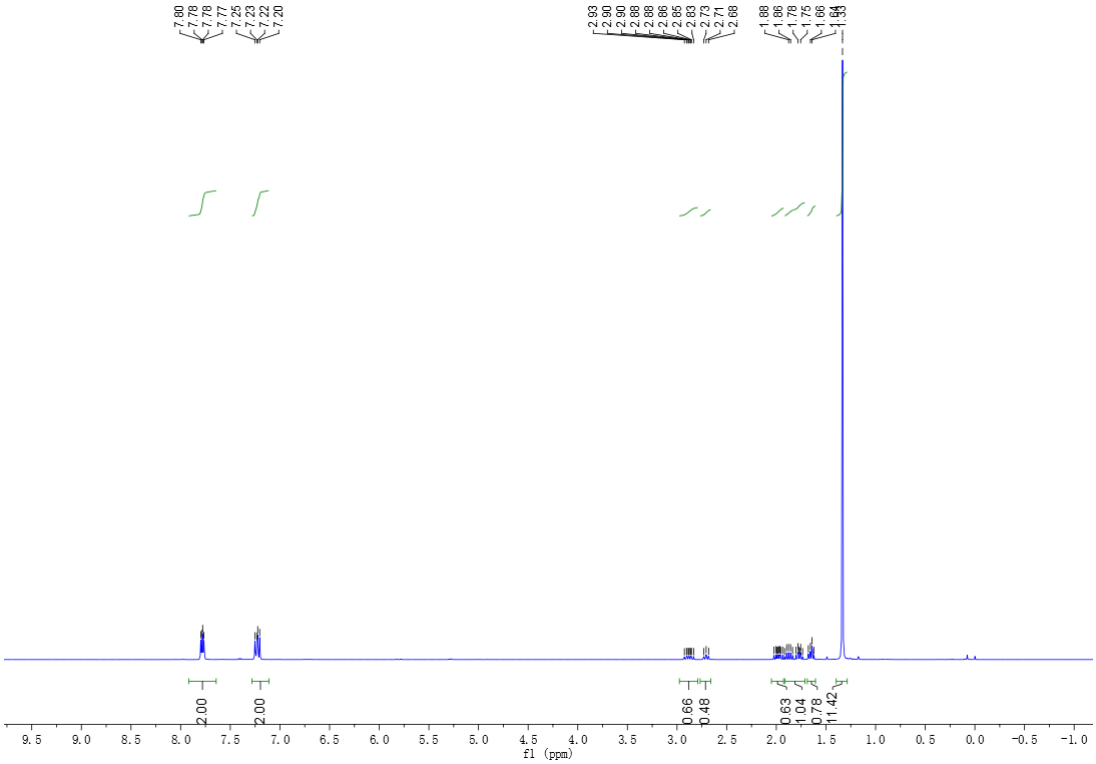
2f


128.34
128.36
128.39
128.40
128.43
128.45
148.75
148.77
148.80
148.82
1.11
1.00
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
f1 (ppm)

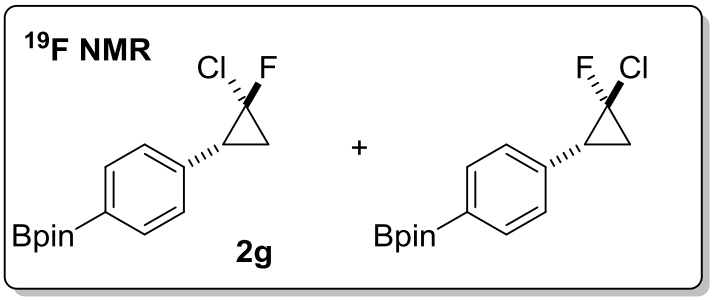

13C NMR
Cl
F
+
F
Cl
2f


134.48
133.58
128.52
128.50
128.47
128.37
128.31
127.41
127.37
96.20
93.37
93.34
90.51
77.37
77.06
76.74
32.34
32.23
30.41
30.29
21.57
21.46
20.85
20.74
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

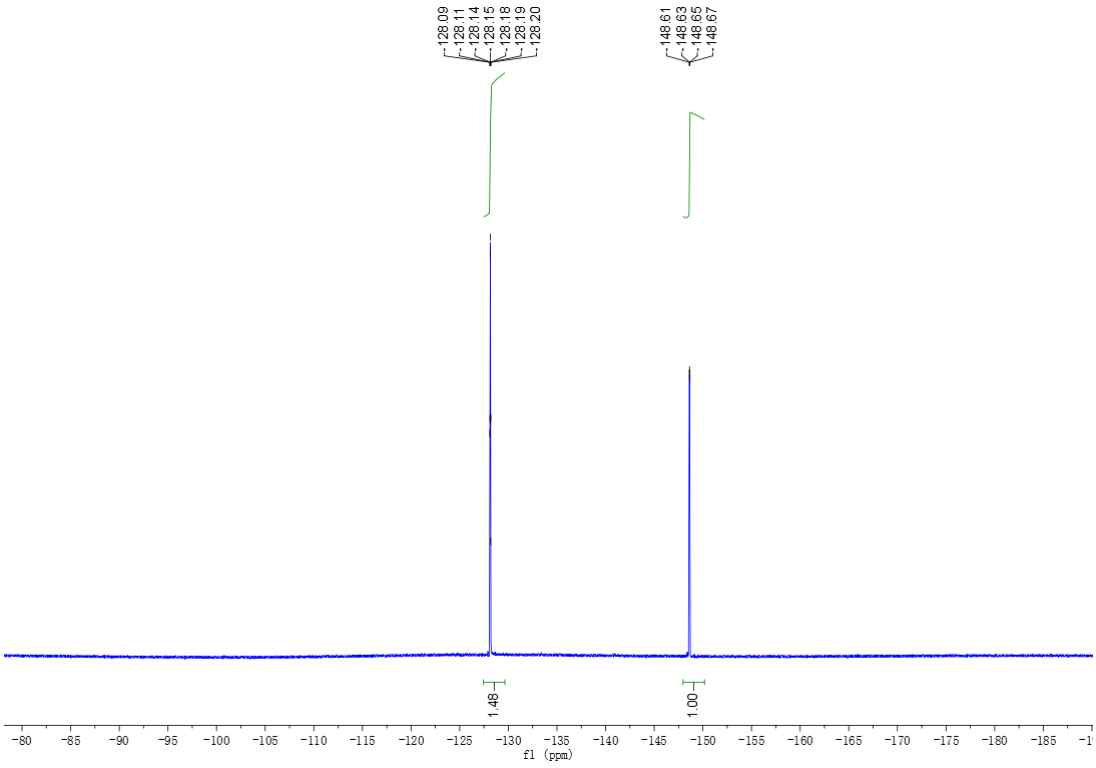

1H NMR
Cl
F
Bpin
2g
+
F
Cl
Bpin

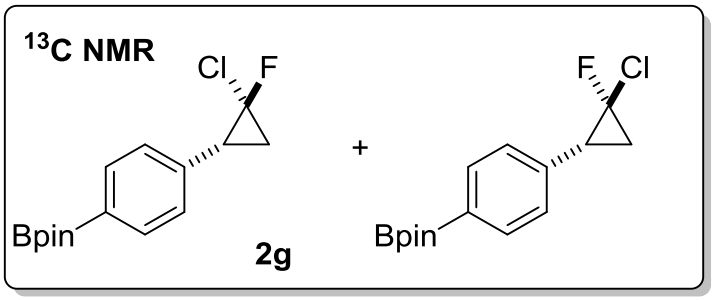

7.80
7.78
7.78
7.77
7.25
7.23
7.22
7.20
2.93
2.90
2.90
2.88
2.88
2.86
2.85
2.83
2.73
2.71
2.68
1.88
1.86
1.78
1.75
1.66
1.64
1.53
2.00
2.00
0.66
0.48
0.63
1.04
0.78
11.42
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

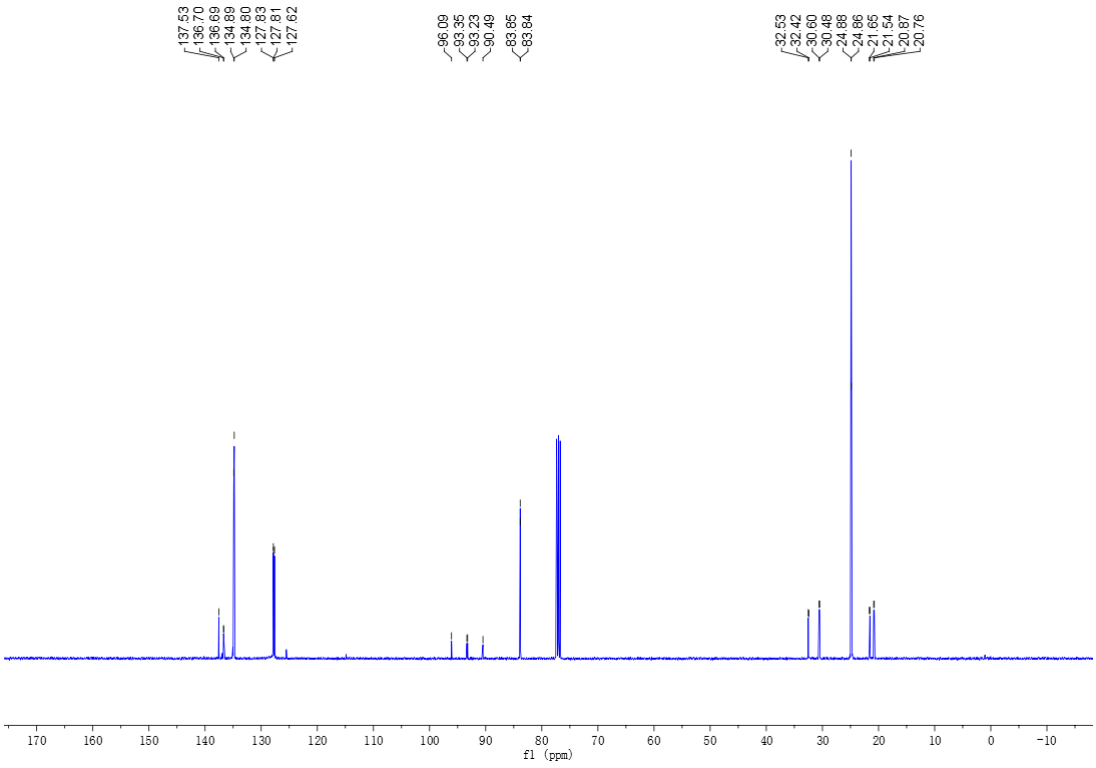
^{19}F NMR

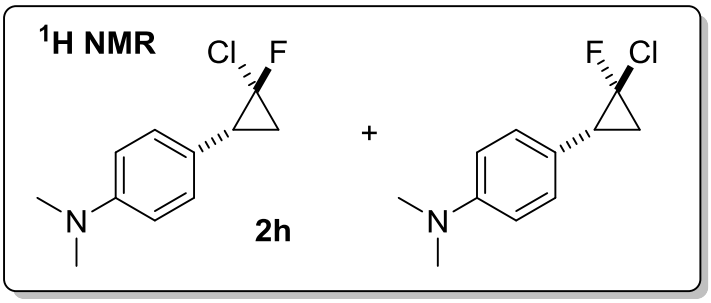

Cl
F
Bpin
+
F
Cl
Bpin

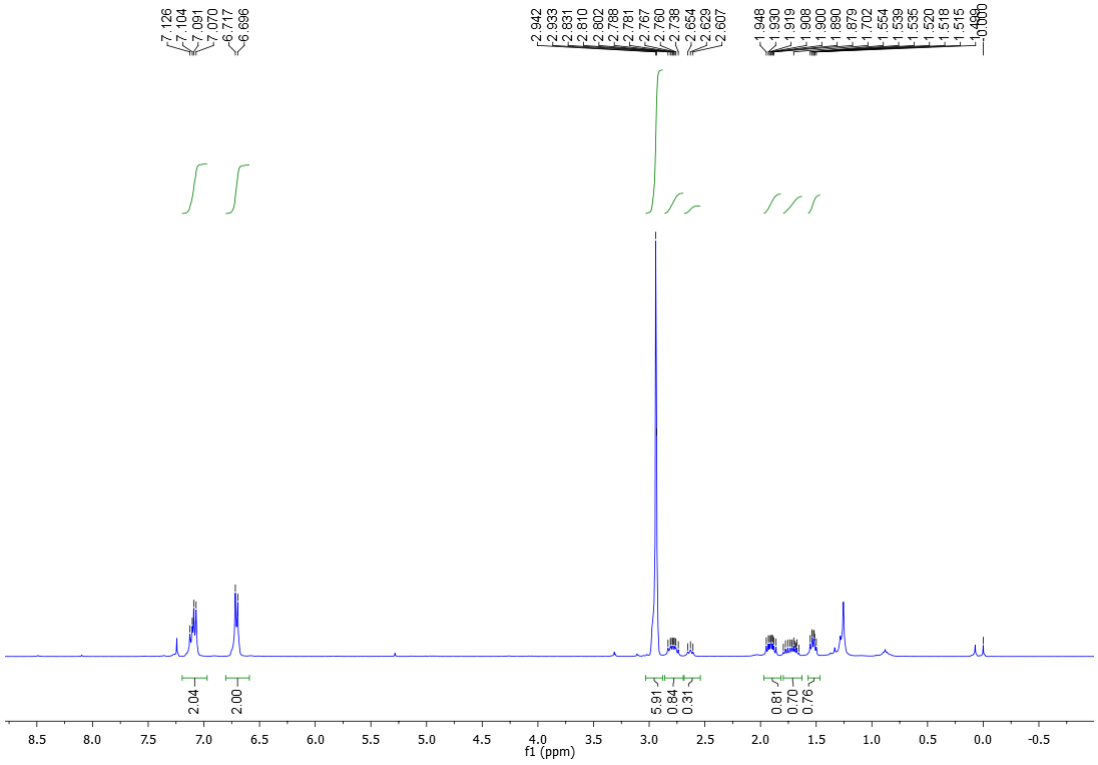
2g


128.09
128.11
128.14
128.15
128.18
128.19
128.20
148.61
148.63
148.65
148.67
1.48
1.00
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
-180
-185
f1 (ppm)

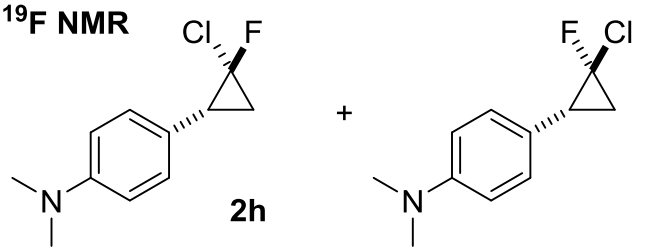

13C NMR
Cl
F
Bpin
2g
+
F
Cl
Bpin

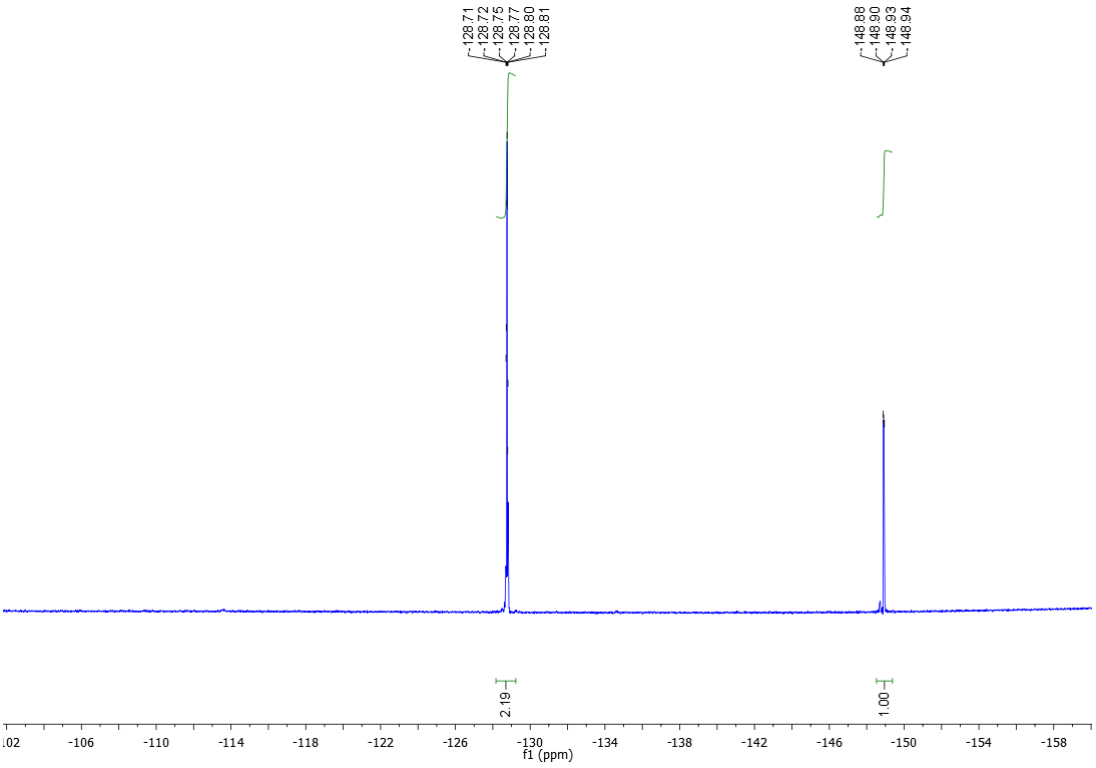

137.53
136.70
136.69
134.89
134.80
127.83
127.81
127.62
96.09
93.35
93.23
90.49
83.85
83.84
32.53
32.42
30.60
30.48
24.88
24.86
21.65
21.54
20.87
20.76
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

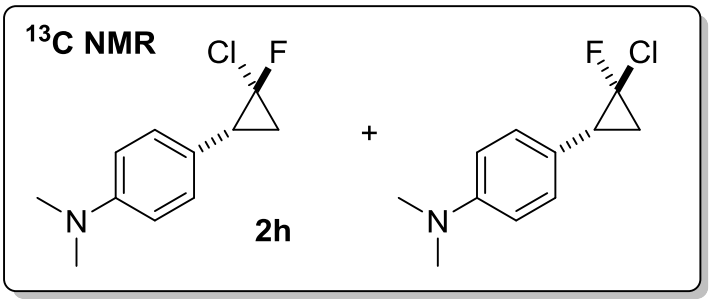

1H NMR
Cl
F
N
2h
+
F
Cl
N

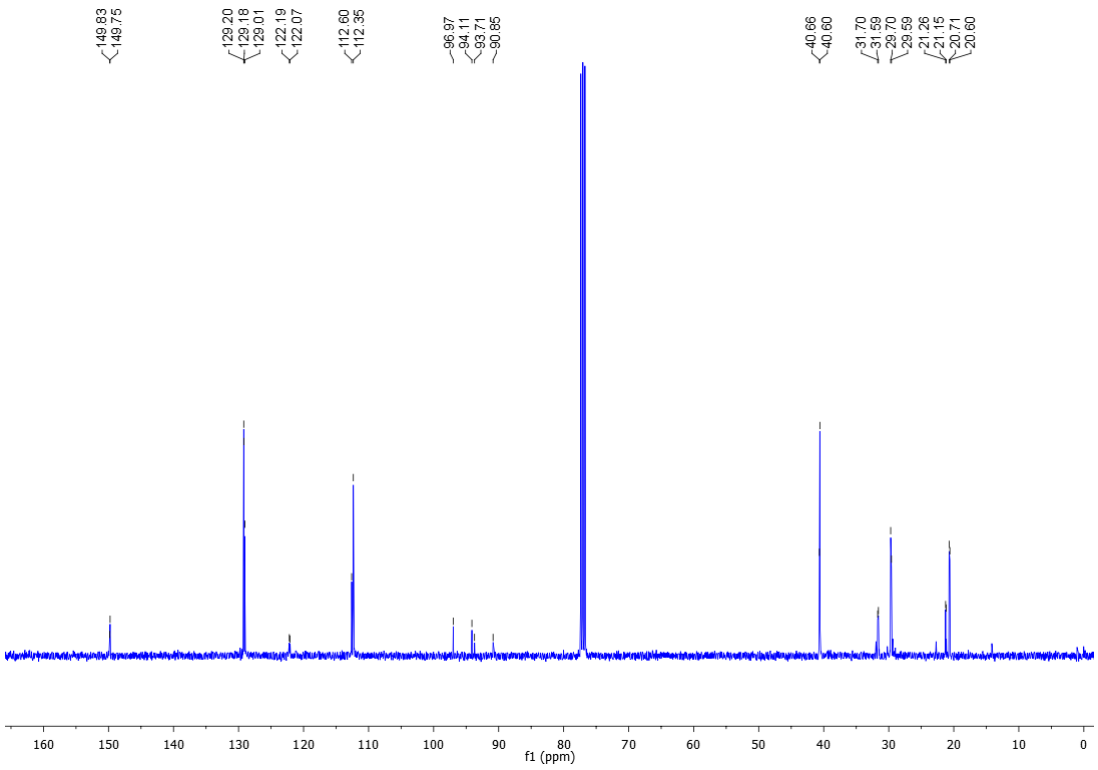

7.126
7.104
7.091
7.070
6.717
6.696
2.942
2.933
2.831
2.810
2.802
2.788
2.781
2.767
2.760
2.738
2.654
2.629
2.607
1.948
1.930
1.919
1.908
1.900
1.890
1.879
1.702
1.554
1.539
1.535
1.520
1.518
1.515
0.000
2.04
2.00
5.91
0.84
0.31
0.81
0.70
0.76
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

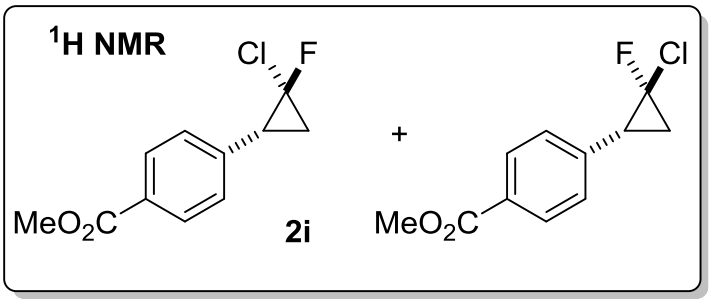
^{19}F NMR

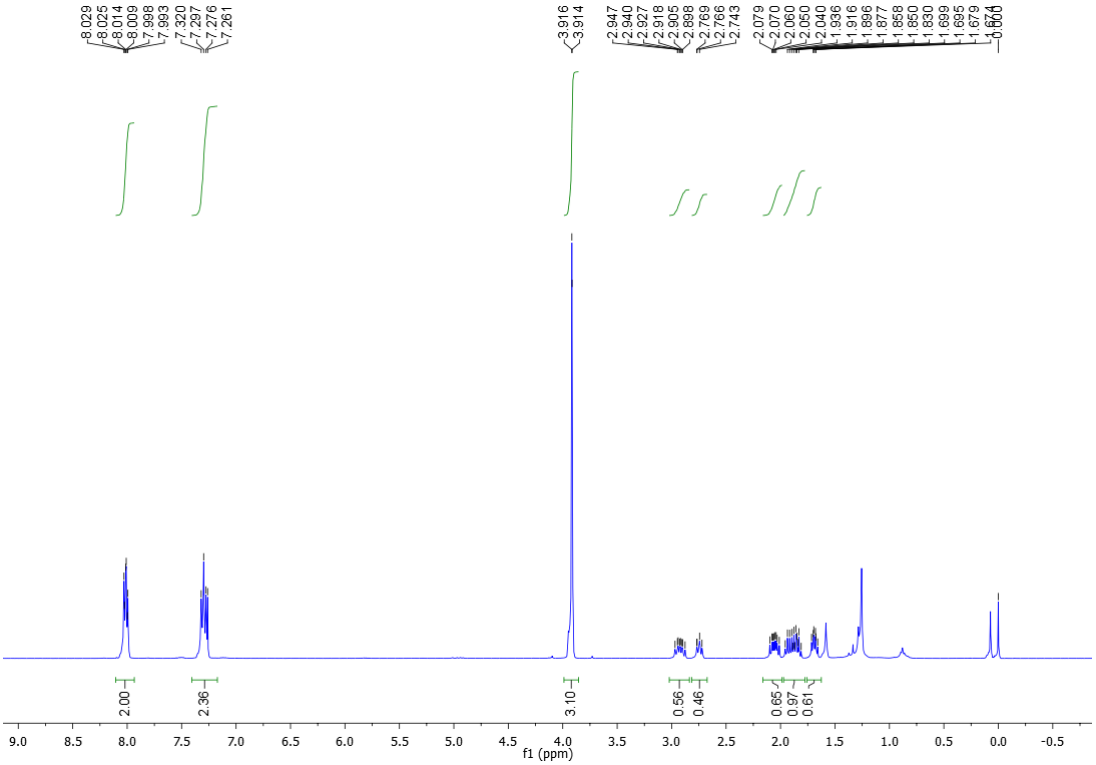

Cl
F
N
2h
+
F
Cl
N

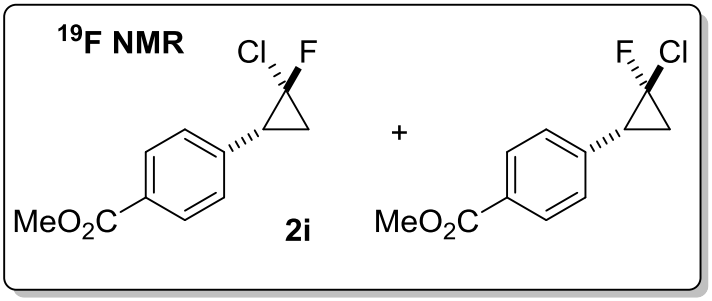

-128.71
-128.72
-128.75
-128.77
-128.80
-128.81
-148.88
-148.90
-148.93
-148.94
2.19
1.00
-102
-106
-110
-114
-118
-122
-126
-130
-134
-138
-142
-146
-150
-154
-158
f1 (ppm)

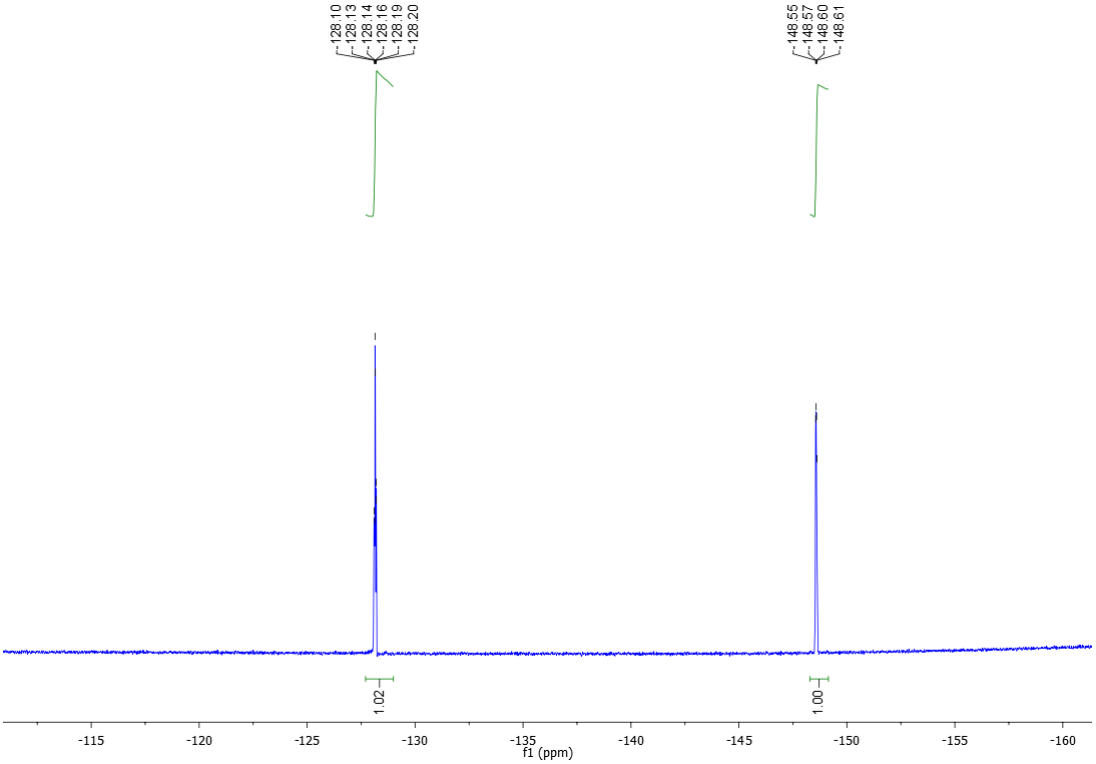

13C NMR
Cl
F
N
2h
+
F
Cl
N


149.83
149.75
129.20
129.18
129.01
122.19
122.07
112.60
112.35
96.97
94.11
93.71
90.85
40.66
40.60
31.70
31.59
29.70
29.59
21.26
21.15
20.71
20.60
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

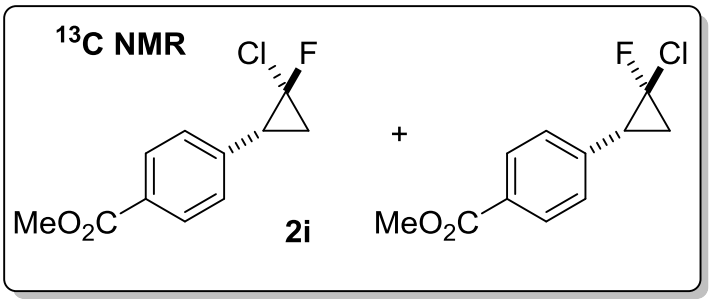

1H NMR
Cl
F
MeO2C
2i
+
F
Cl
MeO2C

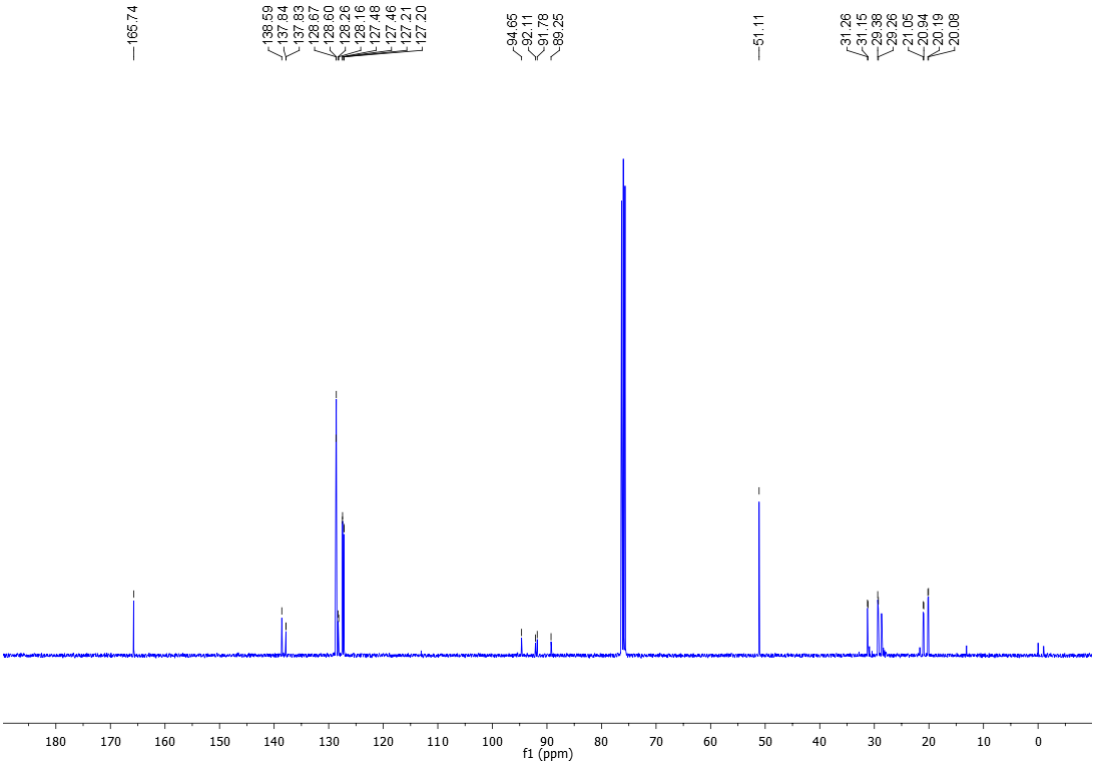

8.029
8.025
8.014
8.009
7.998
7.993
7.320
7.297
7.276
7.261
3.916
3.914
2.947
2.940
2.927
2.918
2.905
2.898
2.769
2.766
2.743
2.079
2.070
2.060
2.050
2.040
1.936
1.916
1.896
1.877
1.858
1.850
1.830
1.699
1.695
1.679
0.000
2.00
2.36
3.10
0.56
0.46
0.65
0.97
0.61
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


19F NMR
Cl
F
MeO2C
2i
+
F
Cl
MeO2C

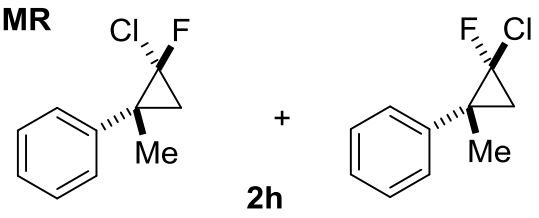

128.10
128.13
128.14
128.16
128.19
128.20
148.55
148.57
148.60
148.61
1.02
1.00
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
f1 (ppm)

^{13}C NMR

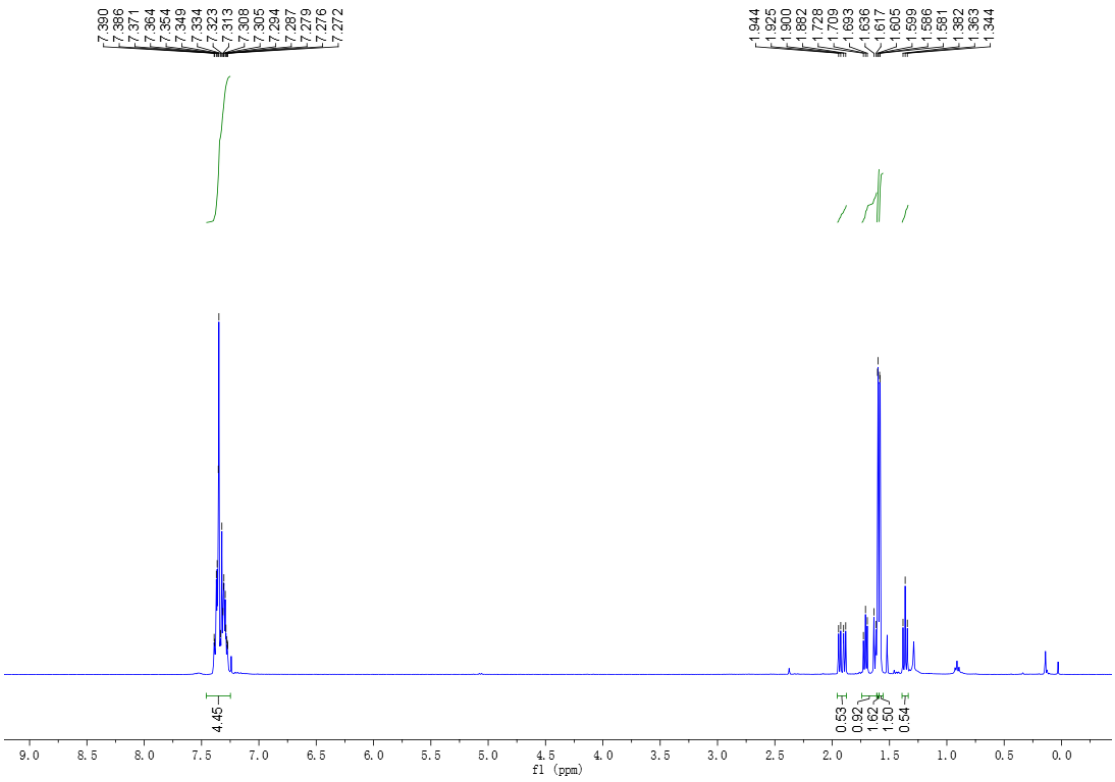

Cl
F
MeO2C
2i
+
F
Cl
MeO2C


165.74
138.59
137.84
137.83
128.67
128.60
128.26
128.16
127.48
127.46
127.21
127.20
94.65
92.11
91.78
89.25
51.11
31.26
31.15
29.38
29.26
21.05
20.94
20.19
20.08
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H NMR


Cl
F
Me
+
F
Cl
Me

2h


7.390
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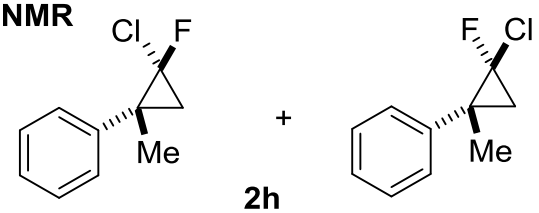
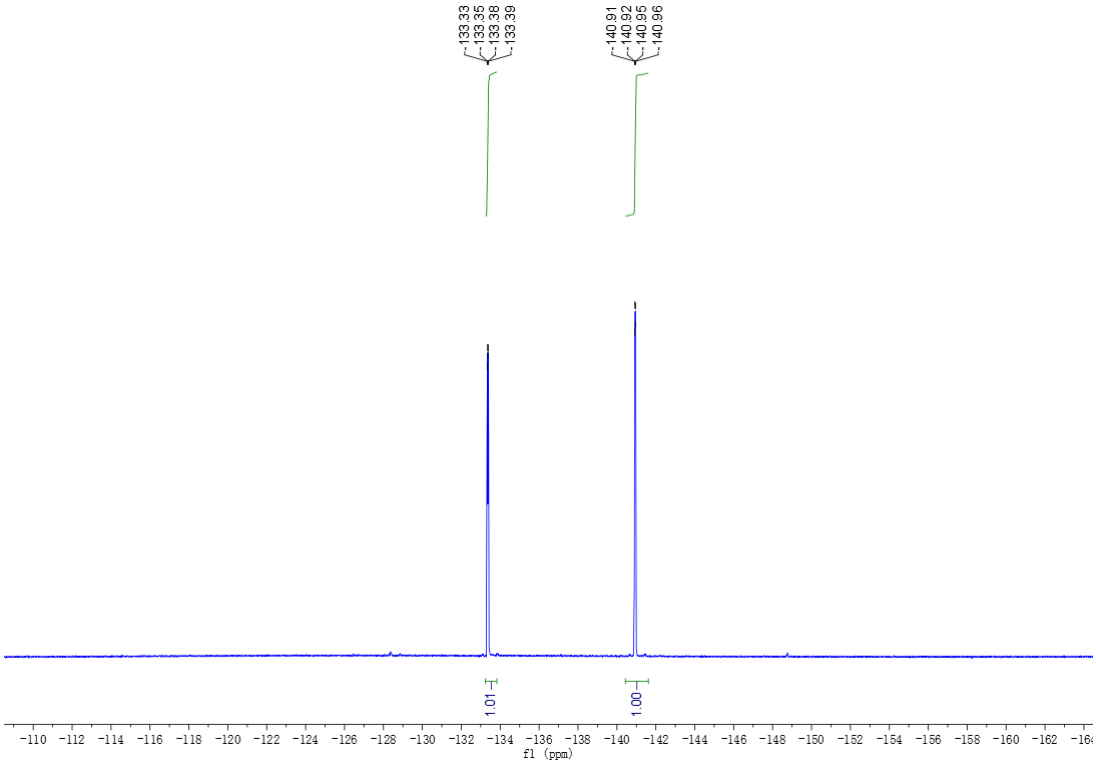
7.364
7.354
7.349
7.334
7.323
7.313
7.308
7.305
7.294
7.287
7.279
7.276
7.272
1.944
1.925
1.900
1.882
1.728
1.709
1.693
1.636
1.617
1.605
1.599
1.586
1.581
1.382
1.363
1.344
4.45
0.53
0.92
1.62
1.50
0.54
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

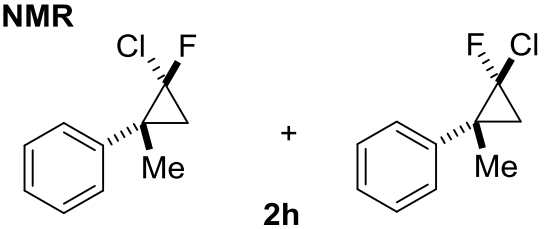
^{19}F NMR


Cl
F
Me
+
F
Cl
Me

2h

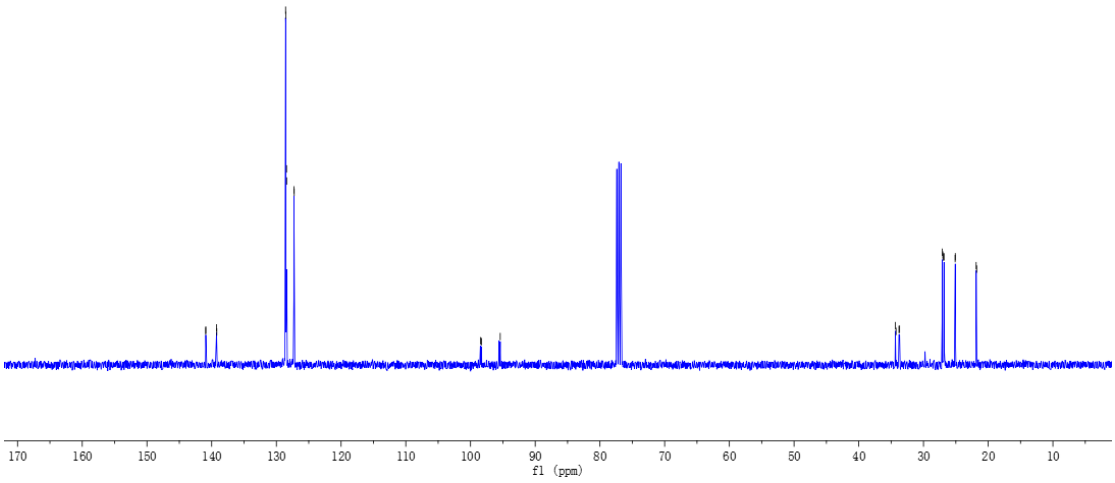

133.33
133.35
133.38
133.39
140.91
140.92
140.95
140.96
1.01
1.00
-110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150 -152 -154 -156 -158 -160 -162
f1 (ppm)

^{13}C NMR

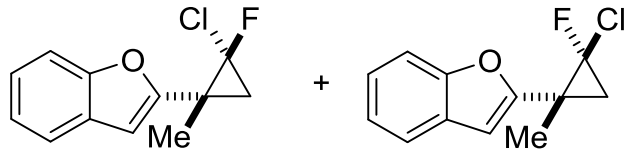

Cl
F
Me
+
F
Cl
Me

2h

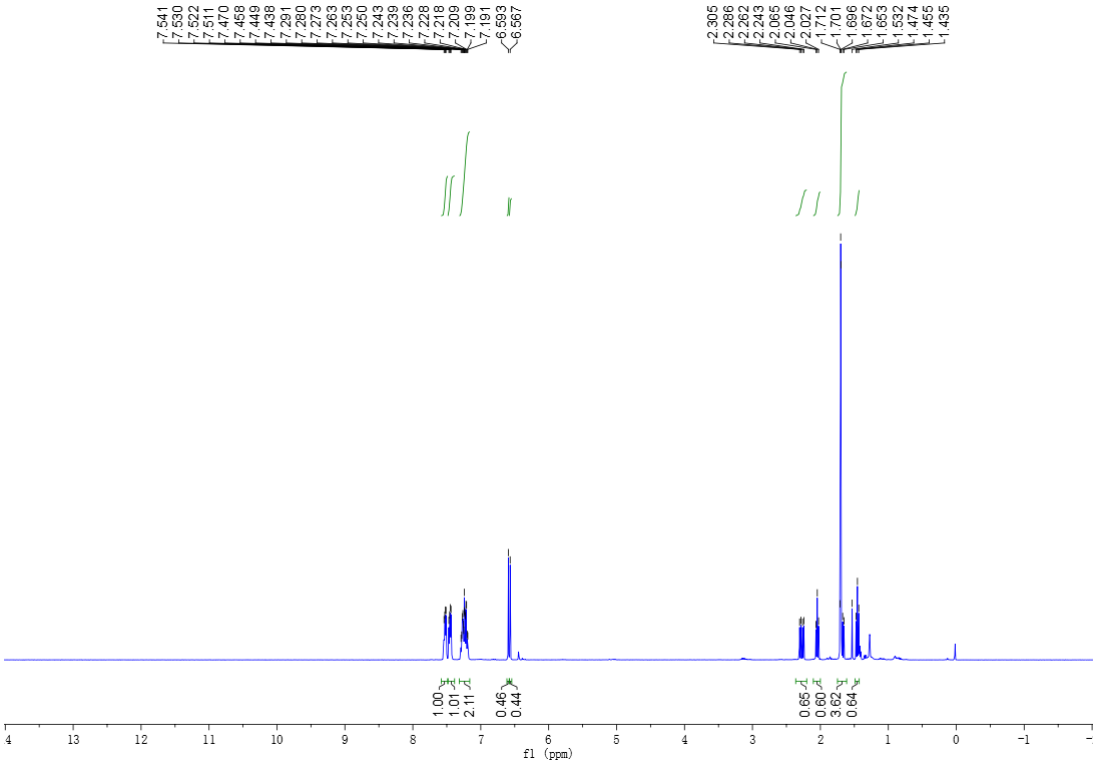

140.92
140.91
139.25
139.21
128.58
128.55
128.43
128.41
127.29
127.24
98.47
98.31
95.41
34.34
34.24
33.79
33.69
27.12
27.01
26.92
26.82
25.11
25.09
21.86
21.78


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{1}H NMR


Cl
F
O
Me
+
F
Cl
O
Me

2i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7.470
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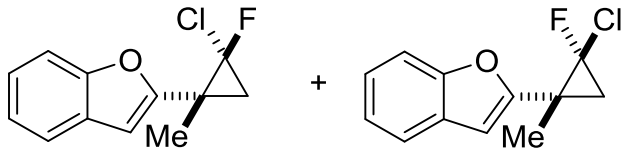
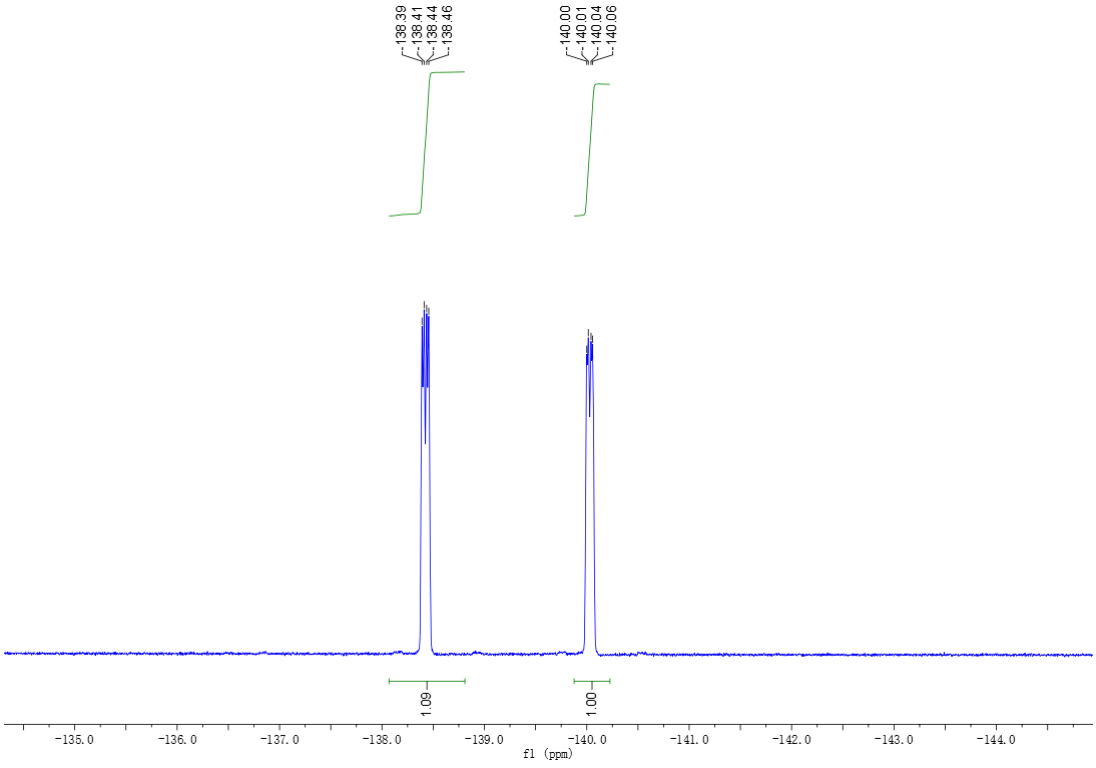
7.449
7.438
7.291
7.280
7.273
7.263
7.253
7.250
7.243
7.239
7.236
7.228
7.218
7.209
7.199
7.191
6.593
6.567
2.305
2.286
2.262
2.243
2.065
2.046
2.027
1.712
1.701
1.696
1.672
1.653
1.532
1.474
1.455
1.435
1.00
1.01
2.11
0.46
0.44
0.65
0.60
3.62
0.64
f1 (ppm)

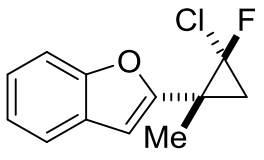
^{19}F NMR


Cl
F
O
Me
+
F
Cl
O
Me

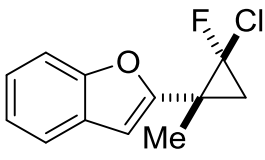
2i


138.39
138.41
138.44
138.46
140.00
140.01
140.04
140.06
1.09
1.00
-135.0
-136.0
-137.0
-138.0
-139.0
-140.0
-141.0
-142.0
-143.0
-144.0
f1 (ppm)

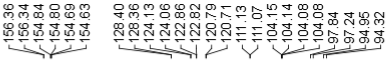
^{13}C NMR

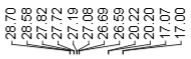

Cl
F
O
Me

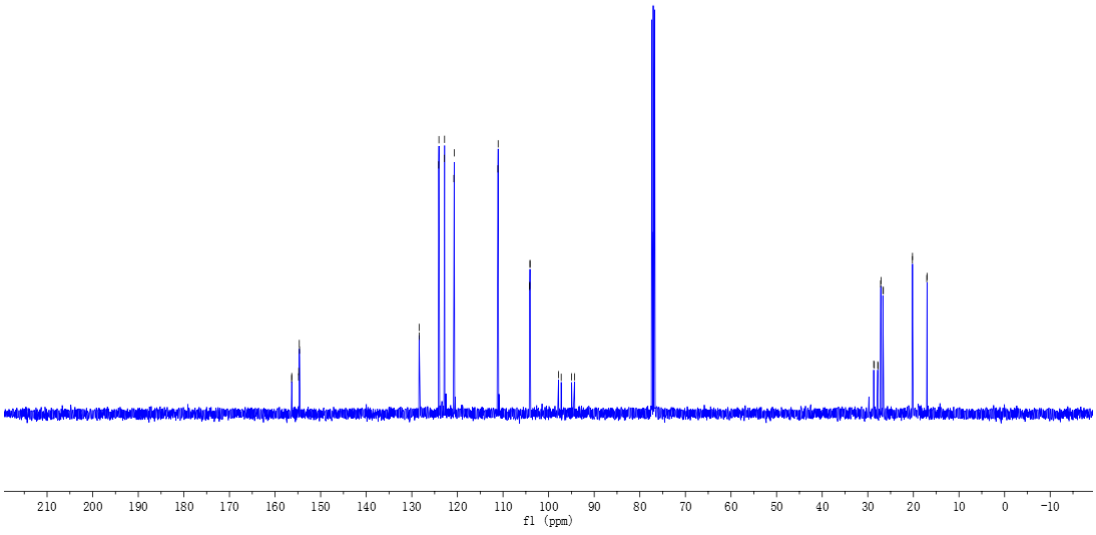
+


F
Cl
O
Me

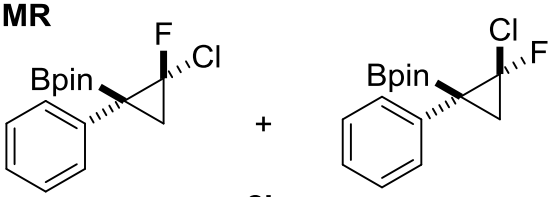
2i


156.36
156.34
154.84
154.80
154.69
154.63
128.40
128.36
124.13
124.06
122.86
122.82
120.79
120.71
111.13
111.07
104.15
104.14
104.08
104.08
97.84
97.24
94.95
94.32

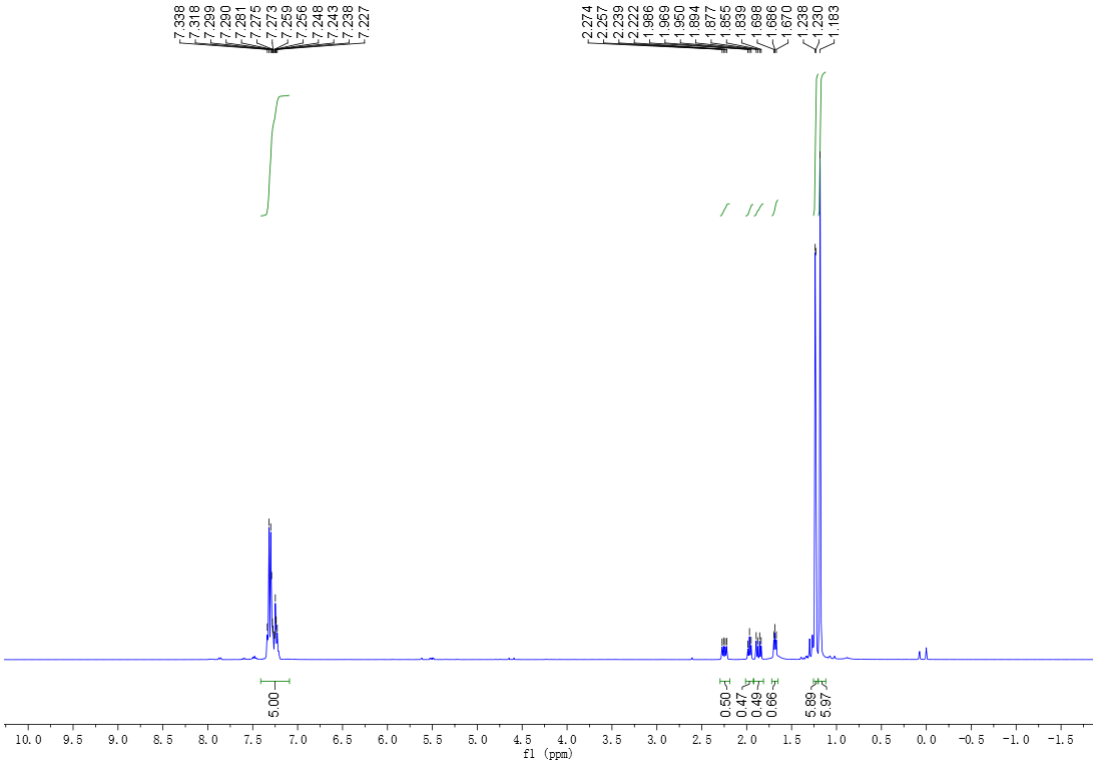

28.70
28.58
27.82
27.72
27.19
27.08
26.69
26.59
20.22
20.20
17.07
17.00


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

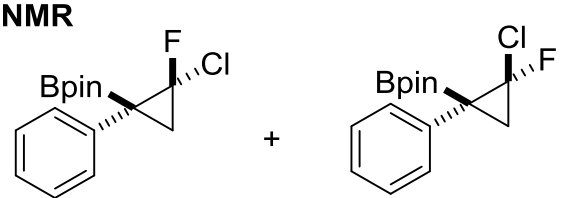
^{1}H NMR


F
Cl
Bpin
+
Cl
F
Bpin

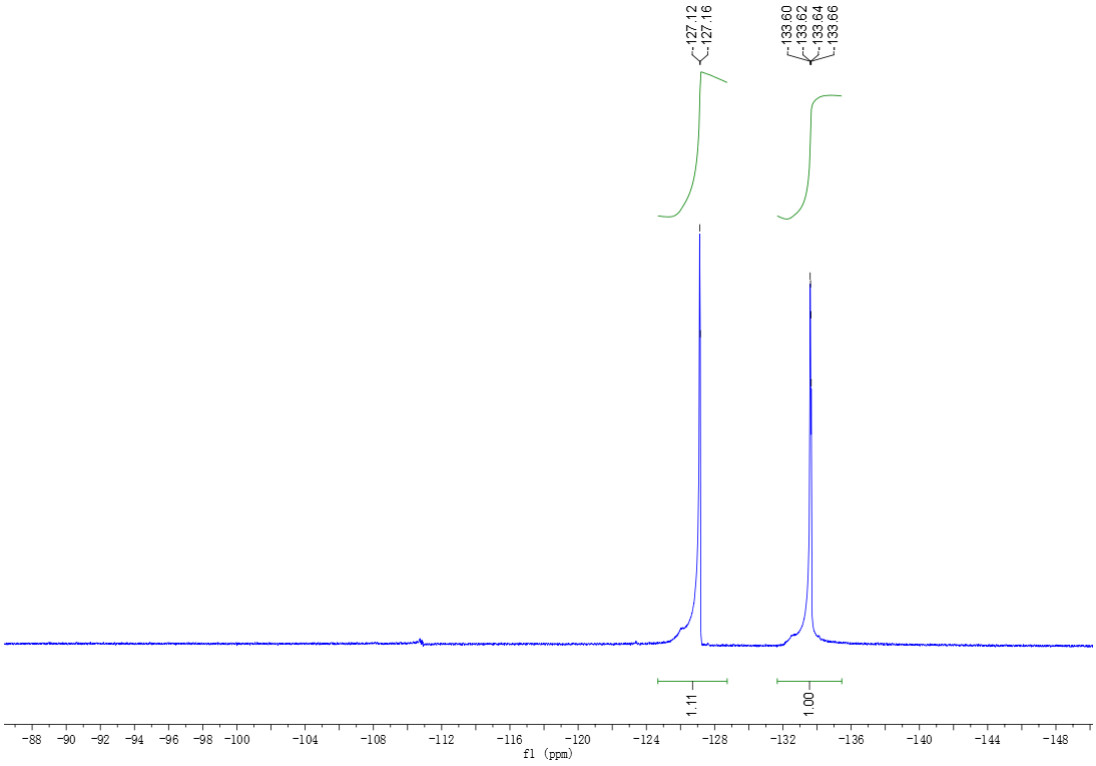
2j


7.338
7.318
7.299
7.290
7.281
7.275
7.273
7.259
7.256
7.248
7.243
7.238
7.227
2.274
2.257
2.239
2.222
1.986
1.969
1.950
1.894
1.877
1.855
1.839
1.698
1.686
1.670
1.238
1.230
1.183
5.00
0.50
0.47
0.49
0.66
5.89
5.97
f1 (ppm)

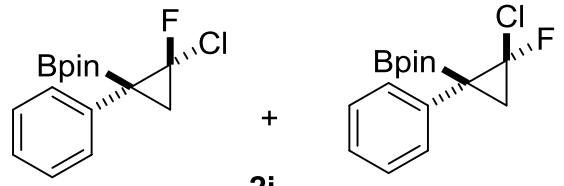
^{19}F NMR


F
Cl
Bpin
+
Cl
F
Bpin

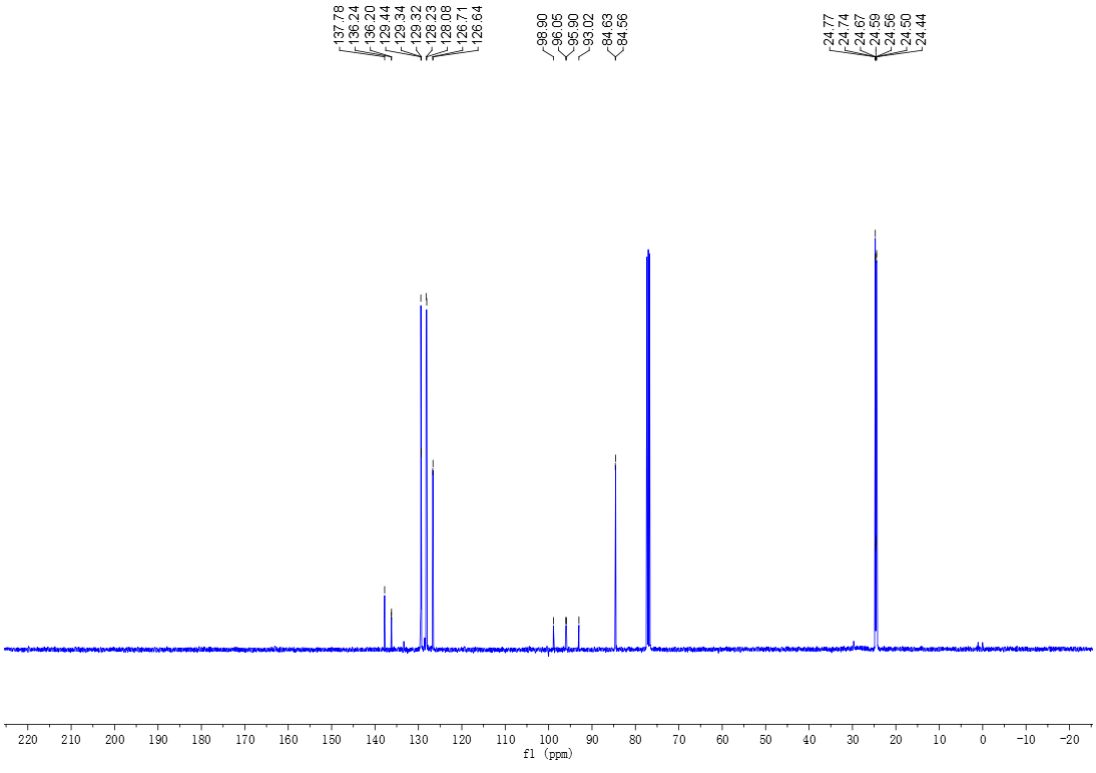
2j

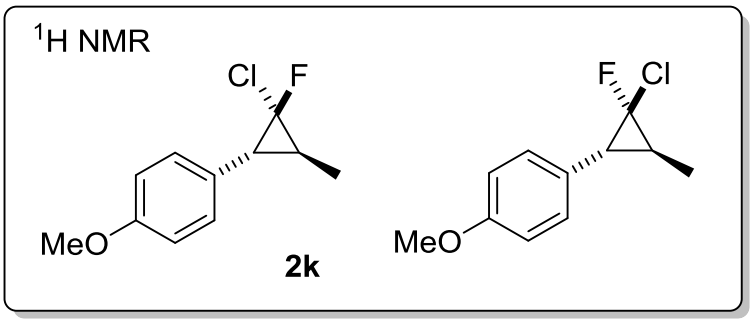

127.12
127.16
133.60
133.62
133.64
133.66
1.11
1.00
-88 -90 -92 -94 -96 -98 -100 -104 -108 -112 -116 -120 -124 -128 -132 -136 -140 -144 -148
f1 (ppm)

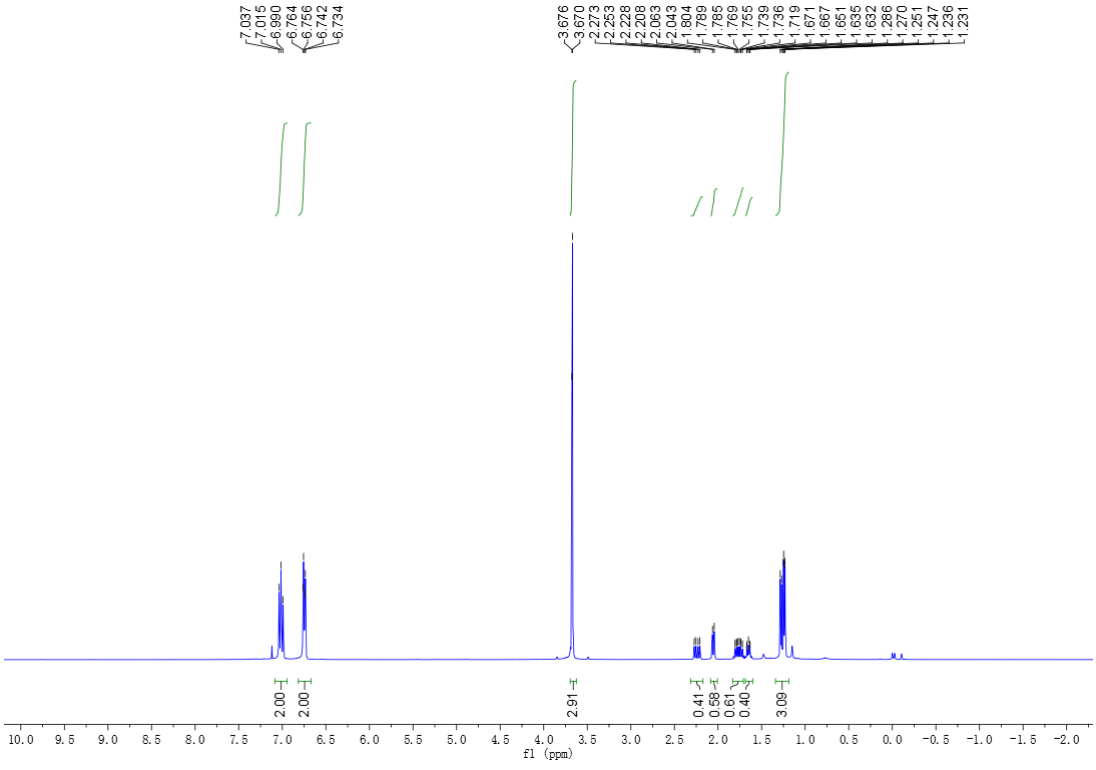
^{13}C NMR


F
Cl
Bpin
+
Cl
F
Bpin

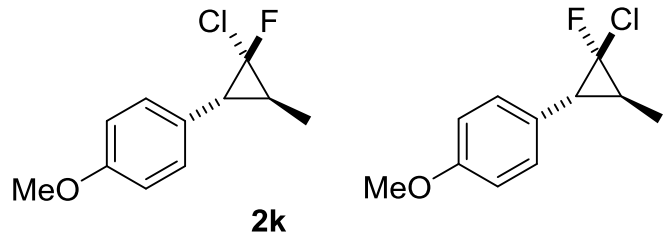
2j


137.78
136.24
136.20
129.44
129.34
129.32
128.23
128.08
126.71
126.64
98.90
96.05
95.90
93.02
84.63
84.56
24.77
24.74
24.67
24.59
24.56
24.50
24.44
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
f1 (ppm)

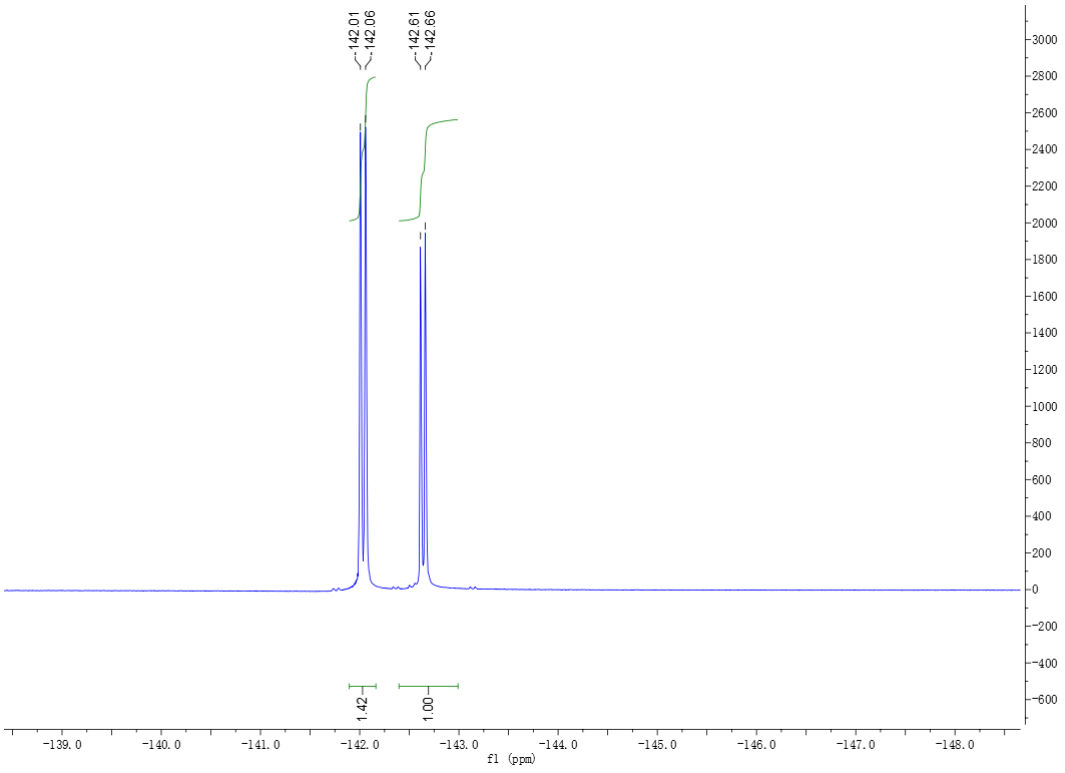

1H NMR
Cl
F
MeO
2k
F
Cl
MeO

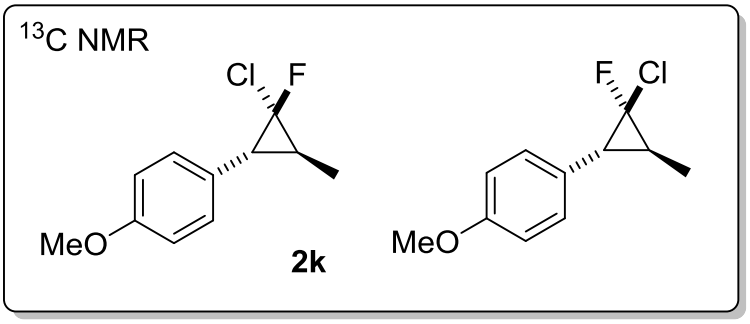

7.037
7.015
6.990
6.764
6.756
6.742
6.734
3.676
3.670
2.273
2.253
2.228
2.208
2.063
2.043
1.804
1.789
1.785
1.769
1.755
1.739
1.736
1.719
1.671
1.667
1.651
1.635
1.632
1.286
1.270
1.251
1.247
1.236
1.231
2.00
2.00
2.91
0.41
0.58
0.61
0.40
3.09
f1 (ppm)

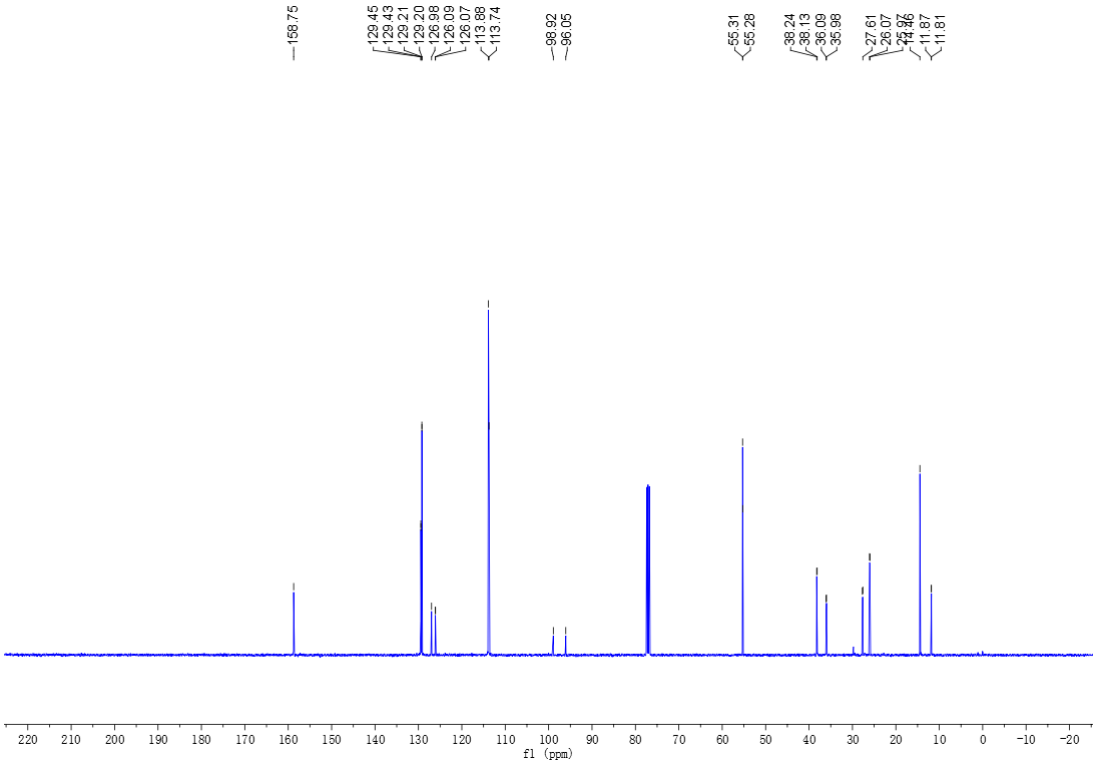
^{19}F NMR


Cl
F
MeO
F
Cl
MeO

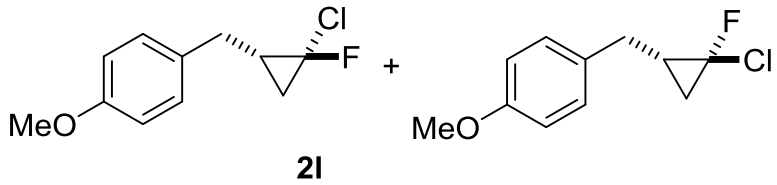
2k


142.01
142.06
142.61
142.66
1.42
1.00
-139.0
-140.0
-141.0
-142.0
-143.0
-144.0
-145.0
-146.0
-147.0
-148.0
f1 (ppm)
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
-600

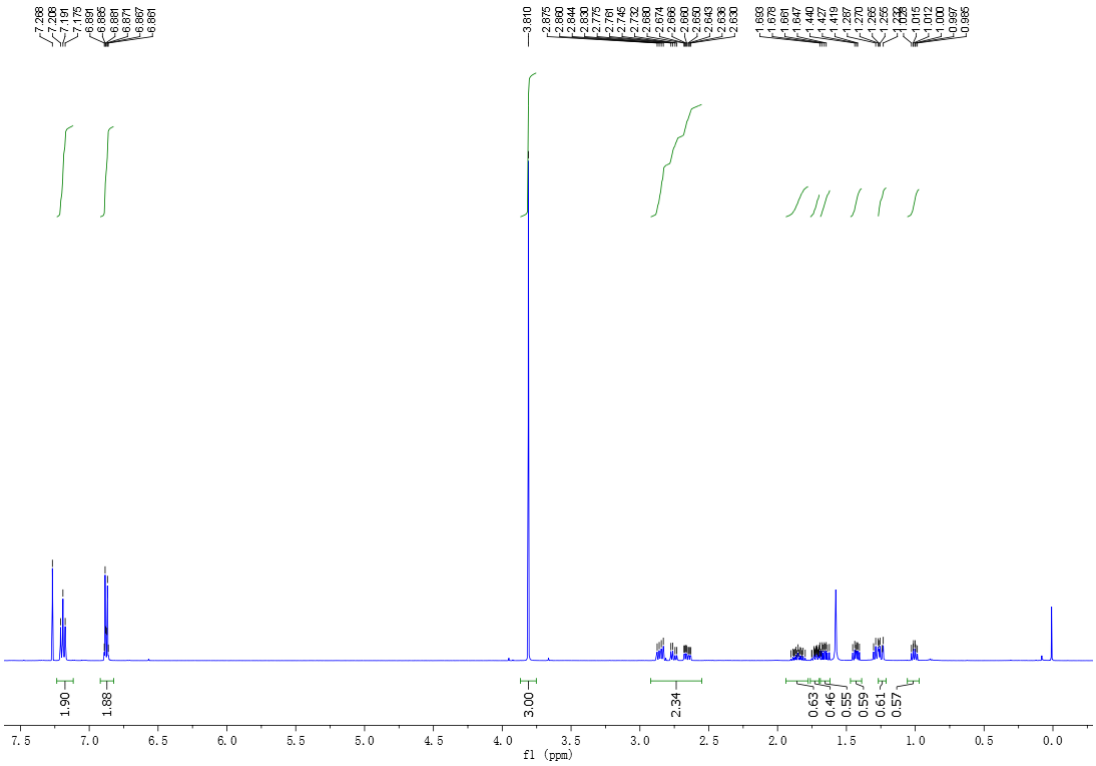

^{13}C NMR
Cl
F
MeO
2k
F
Cl
MeO


158.75
129.45
129.43
129.21
129.20
126.98
126.09
126.07
113.88
113.74
98.92
96.05
55.31
55.28
38.24
38.13
36.09
35.98
27.61
26.07
11.87
11.81
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
f1 (ppm)

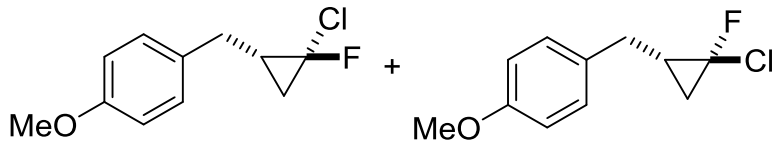
^{1}H NMR


Cl
F
MeO
+
F
Cl
MeO

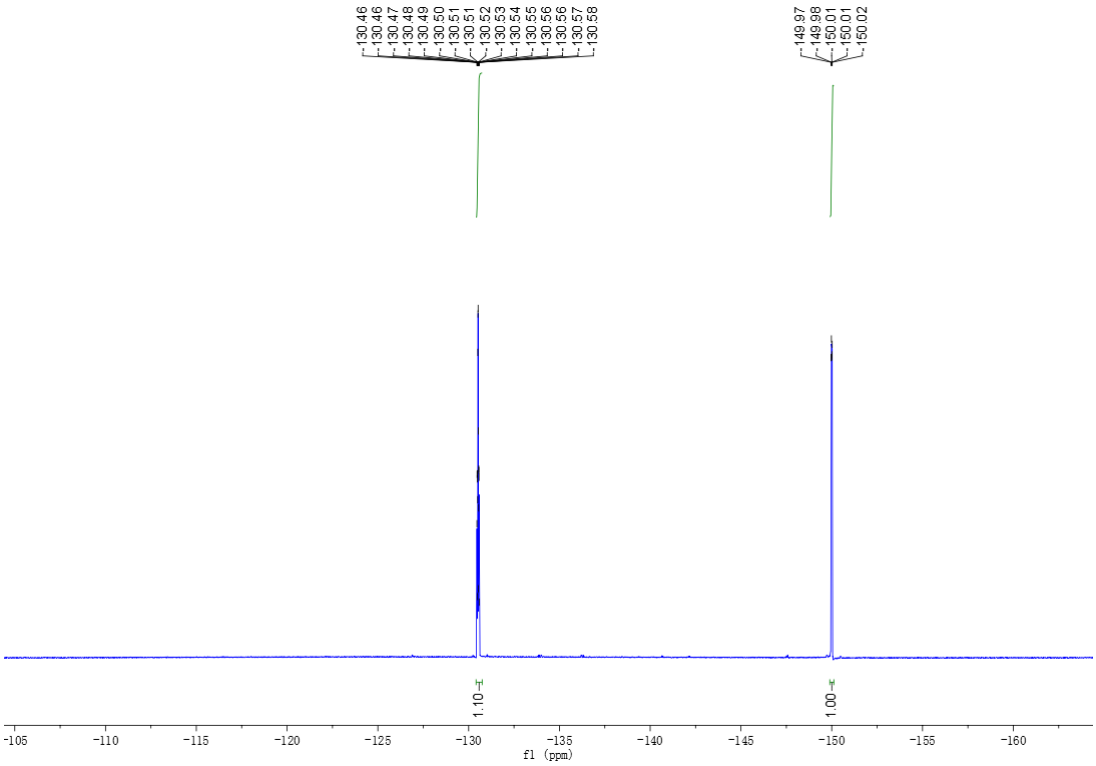
2l


7.288
7.208
7.191
7.175
6.891
6.885
6.871
6.867
6.861
3.810
2.875
2.860
2.844
2.830
2.775
2.761
2.745
2.732
2.690
2.674
2.664
2.660
2.650
2.643
2.636
2.630
1.693
1.678
1.661
1.647
1.440
1.427
1.419
1.287
1.270
1.265
1.255
1.028
1.015
1.012
1.000
0.997
0.985
1.90
1.88
3.00
2.34
0.63
0.46
0.55
0.59
0.61
0.57
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

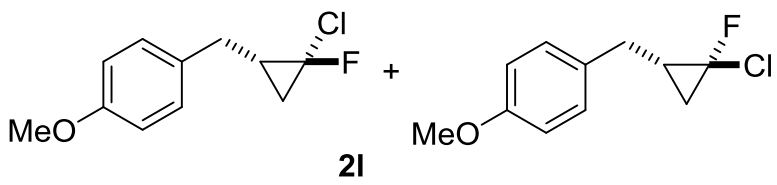
^{19}F NMR


Cl
F
MeO
+
F
Cl
MeO

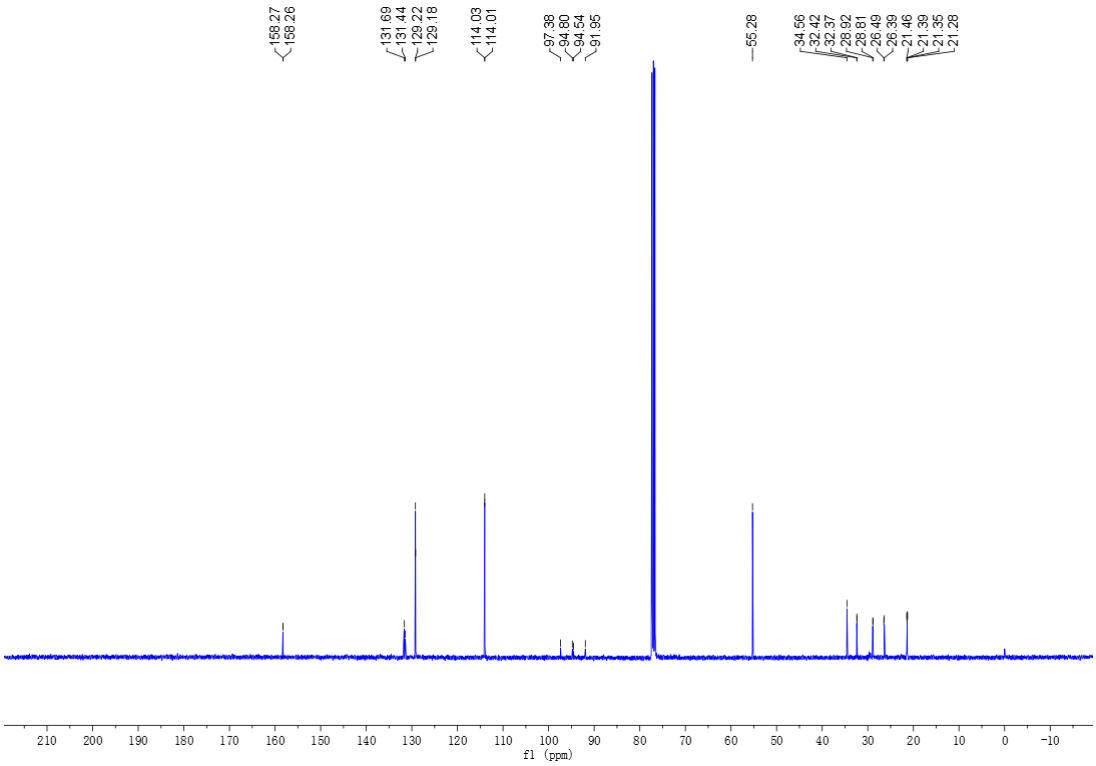
2l


-130.46
-130.46
-130.47
-130.48
-130.49
-130.50
-130.51
-130.51
-130.52
-130.53
-130.54
-130.55
-130.56
-130.56
-130.57
-130.58
-149.97
-149.98
-150.01
-150.01
-150.02
1.10
1.00
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
f1 (ppm)

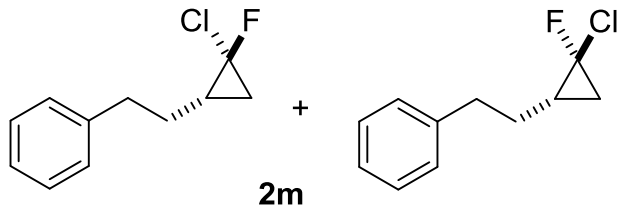
^{13}C NMR


Cl
F
MeO
+
F
Cl
MeO

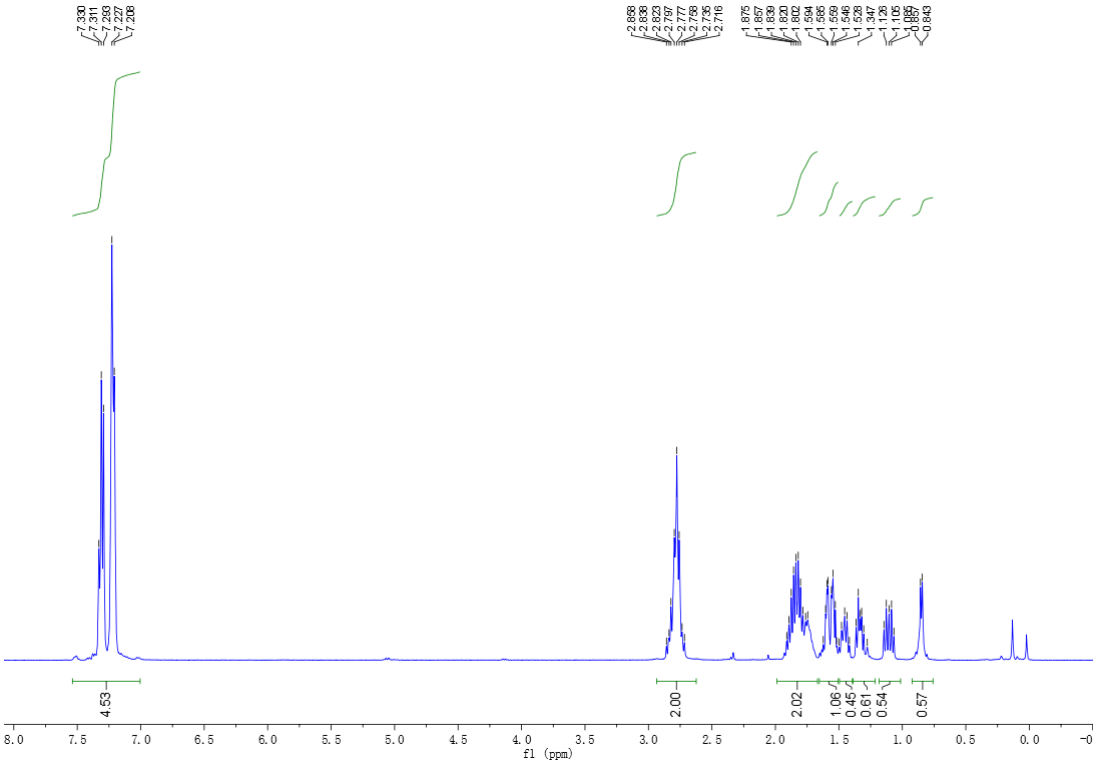
2l


158.27
158.26
131.69
131.44
129.22
129.18
114.03
114.01
97.38
94.80
94.54
91.95
55.28
34.56
32.42
32.37
28.92
28.81
26.49
26.39
21.46
21.39
21.35
21.28
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

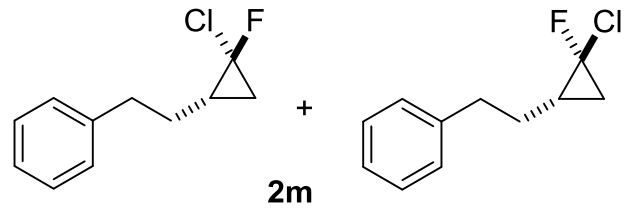
^{1}H NMR


Cl
F
+
F
Cl

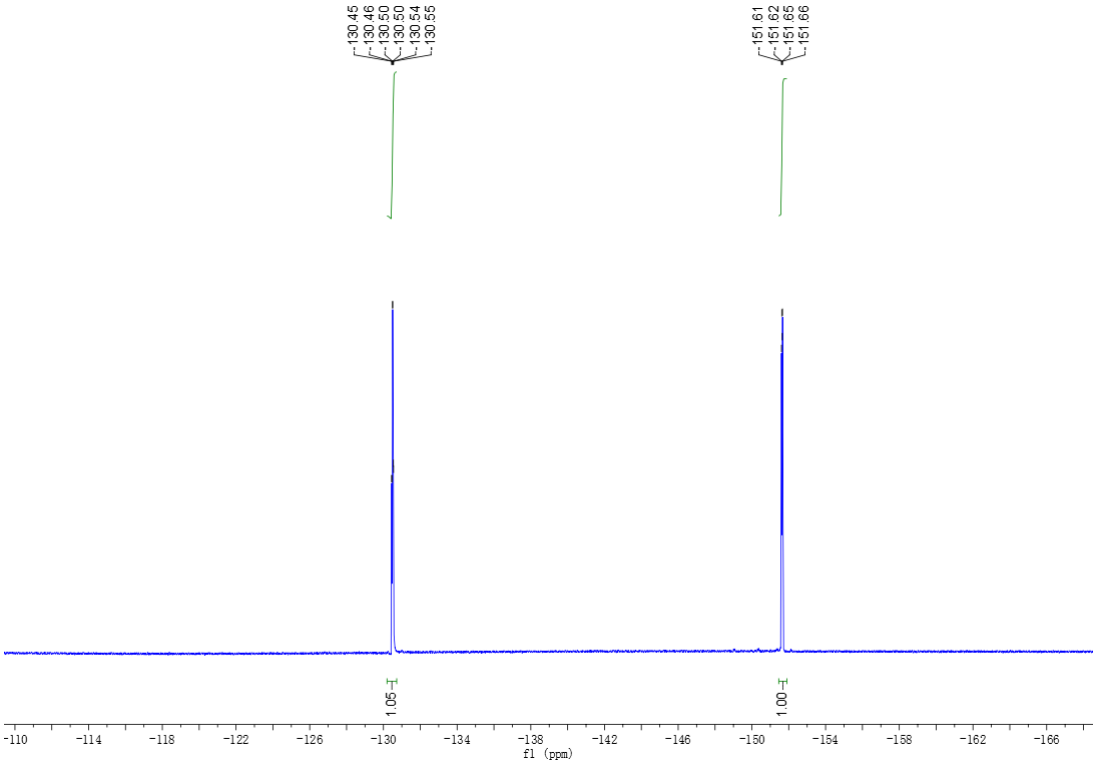
2m


7.330
7.311
7.293
7.227
7.208
2.868
2.838
2.823
2.797
2.777
2.758
2.735
2.716
1.875
1.857
1.839
1.820
1.802
1.594
1.585
1.559
1.546
1.528
1.347
1.326
1.105
1.085
0.897
0.843
4.53
2.00
2.02
1.06
0.45
0.61
0.54
0.57
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

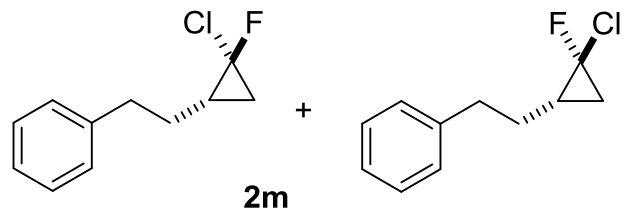
^{19}F NMR


Cl
F
+
F
Cl

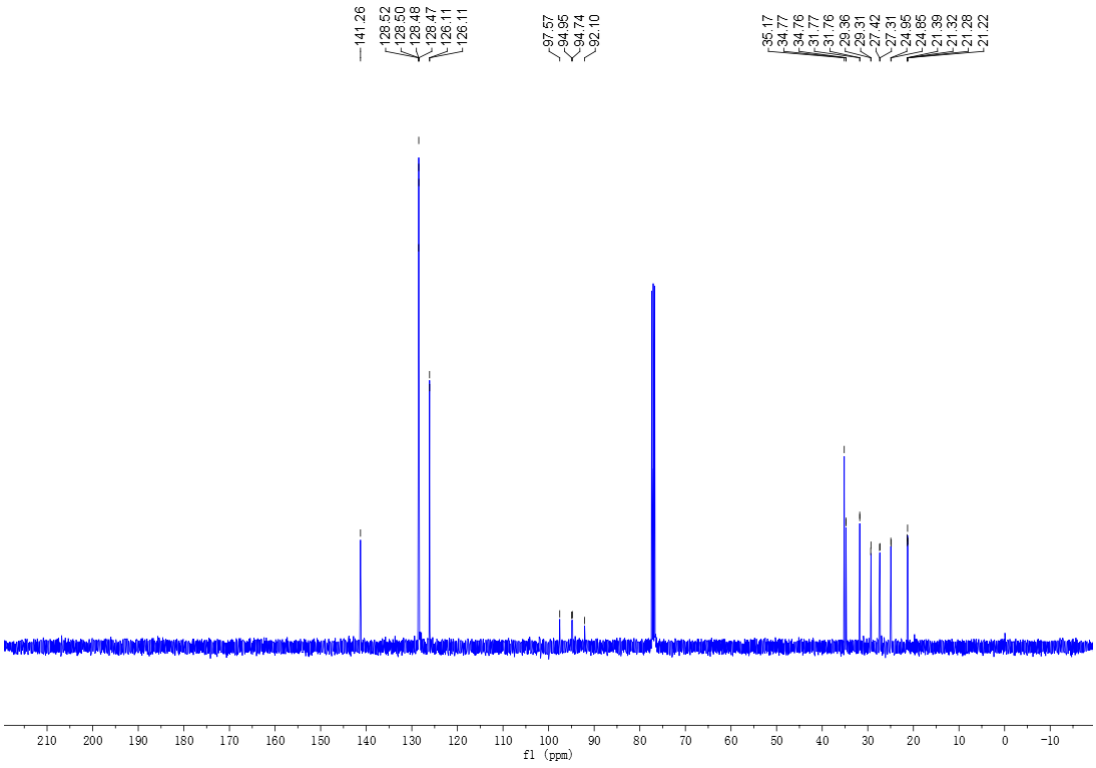
2m

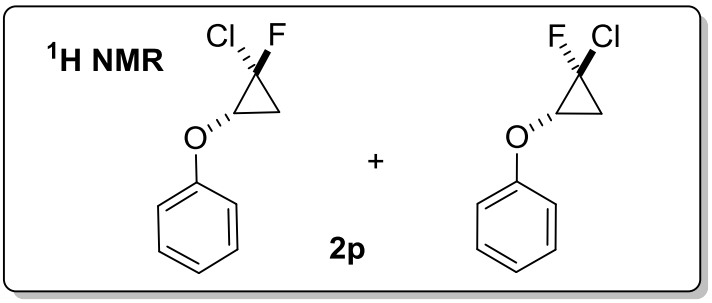

130.45
130.46
130.50
130.50
130.54
130.55
151.61
151.62
151.65
151.66
1.05
1.00
-110
-114
-118
-122
-126
-130
-134
-138
-142
-146
-150
-154
-158
-162
-166
f1 (ppm)

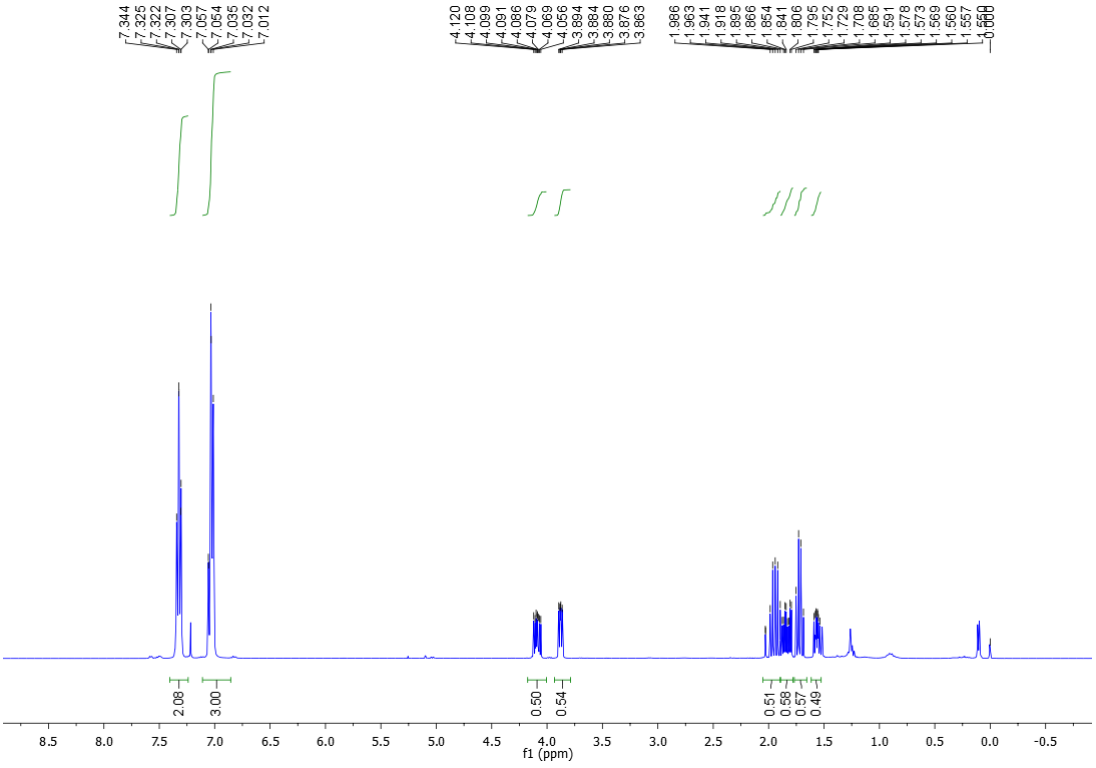
^{13}C NMR

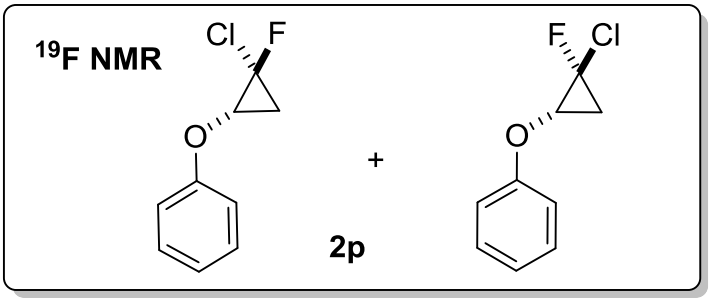

Cl
F
+
F
Cl

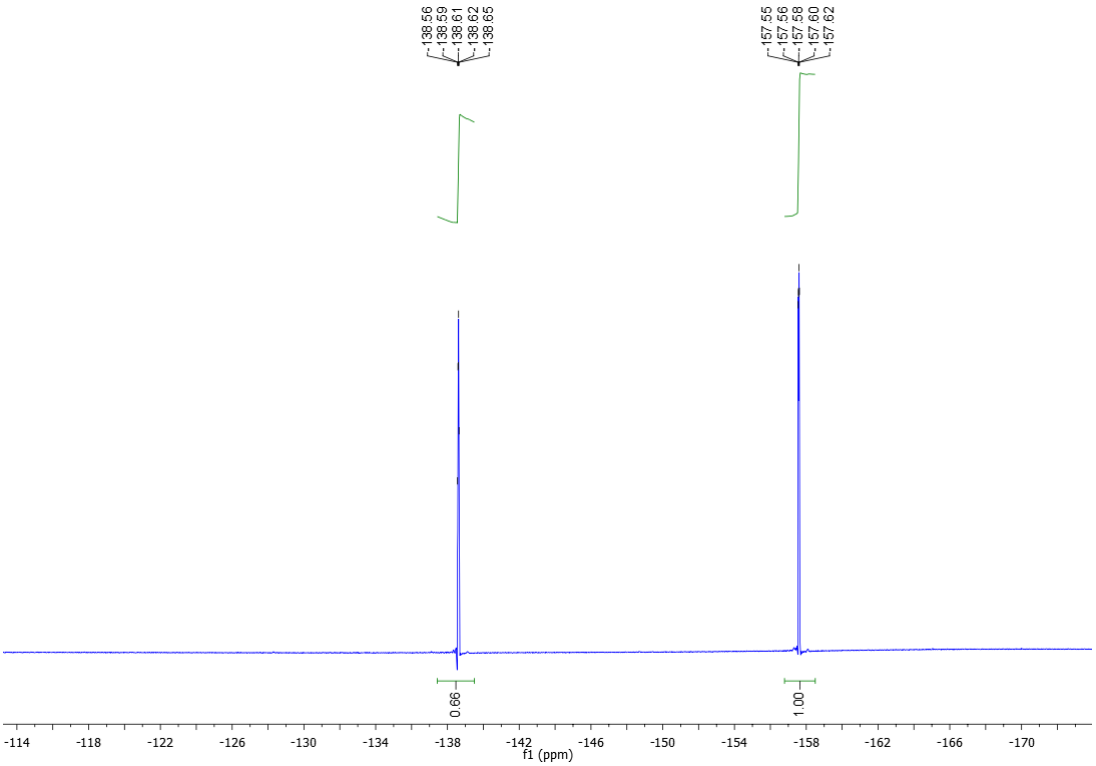
2m

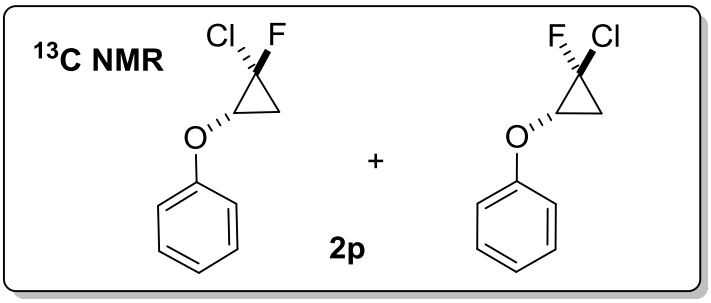

141.26
128.52
128.50
128.48
128.47
126.11
126.11
97.57
94.95
94.74
92.10
35.17
34.77
34.76
31.77
31.76
29.36
29.31
27.42
27.31
24.95
24.85
21.39
21.32
21.28
21.22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

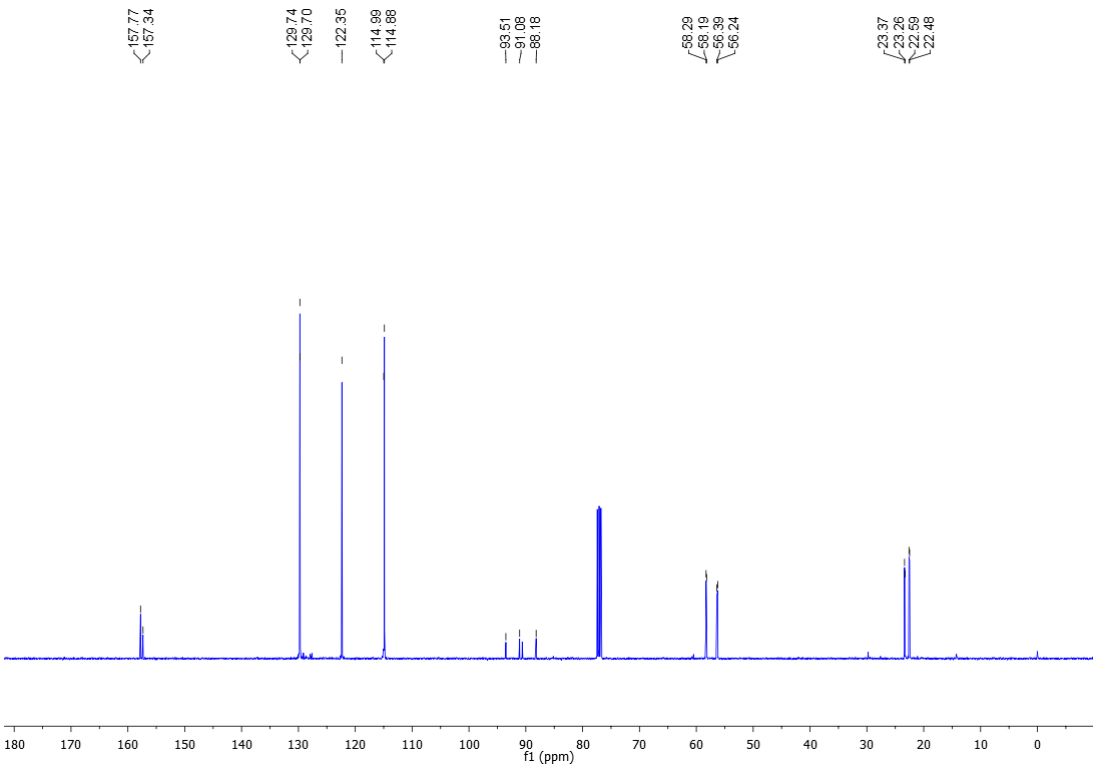

1H NMR
Cl
F
O
+
F
Cl
O
2p


7.344
7.325
7.322
7.307
7.303
7.057
7.054
7.035
7.032
7.012
4.120
4.108
4.099
4.091
4.086
4.079
4.069
4.056
3.894
3.884
3.880
3.876
3.863
1.986
1.963
1.941
1.918
1.895
1.866
1.854
1.841
1.806
1.795
1.752
1.729
1.708
1.685
1.591
1.578
1.573
1.569
1.560
1.557
2.08
3.00
0.50
0.54
0.51
0.58
0.57
0.49
f1 (ppm)

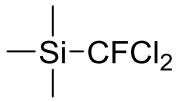

19F NMR
Cl
F
O
+
F
Cl
O
2p

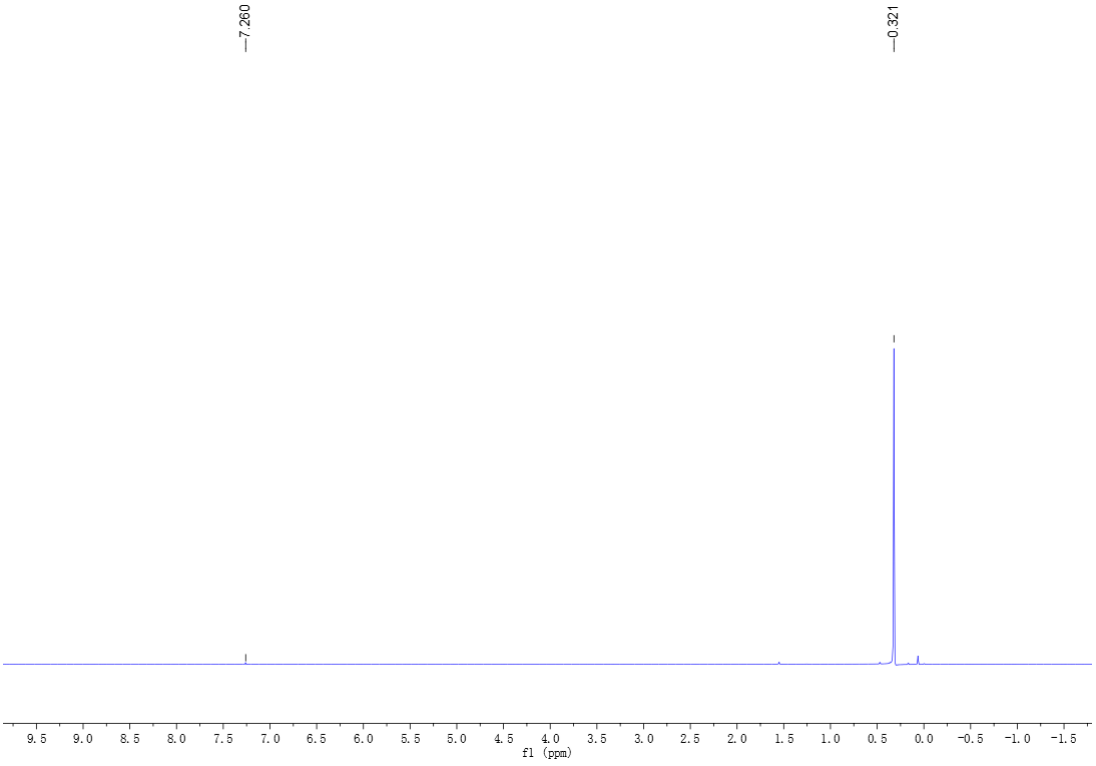

-138.56
-138.59
-138.61
-138.62
-138.65
-157.55
-157.56
-157.58
-157.60
-157.62
0.66
1.00
-114
-118
-122
-126
-130
-134
-138
-142
-146
-150
-154
-158
-162
-166
-170
f1 (ppm)


13C NMR
Cl
F
O
+
F
Cl
O
2p

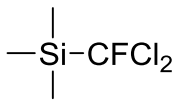

157.77
157.34
129.74
129.70
122.35
114.99
114.88
93.51
91.08
88.18
58.29
58.19
56.39
56.24
23.37
23.26
22.59
22.48
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

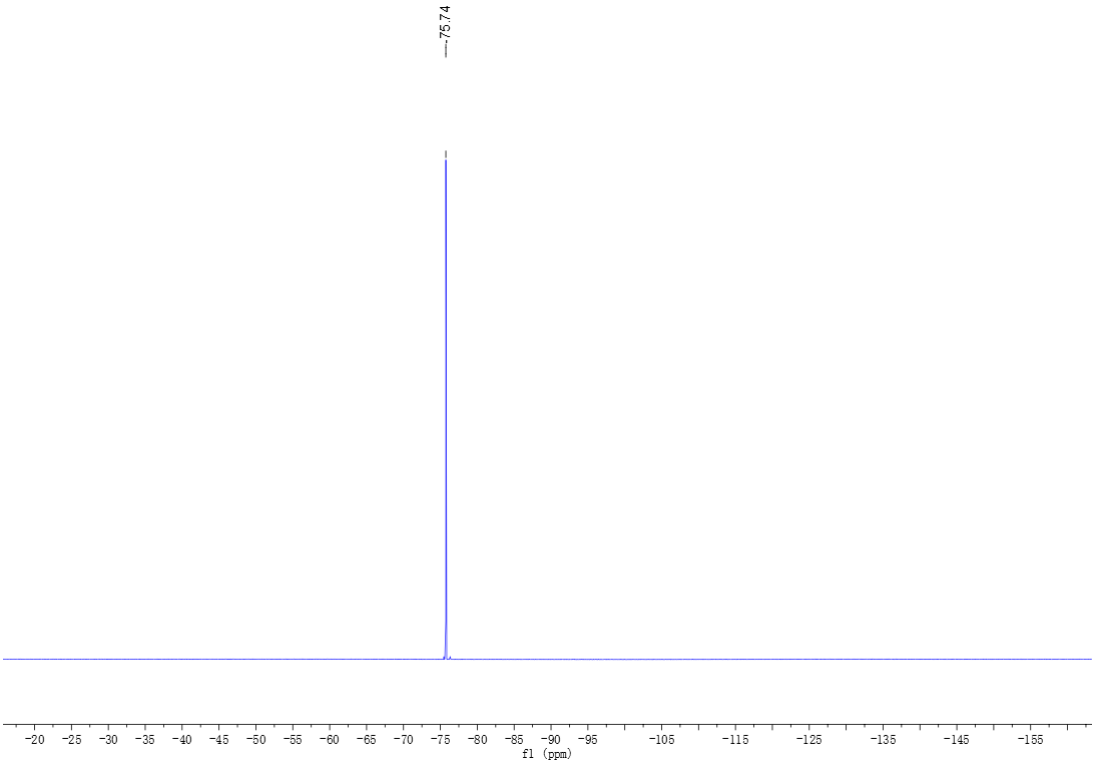
^{1}H NMR



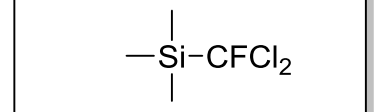

7.260
0.321
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)

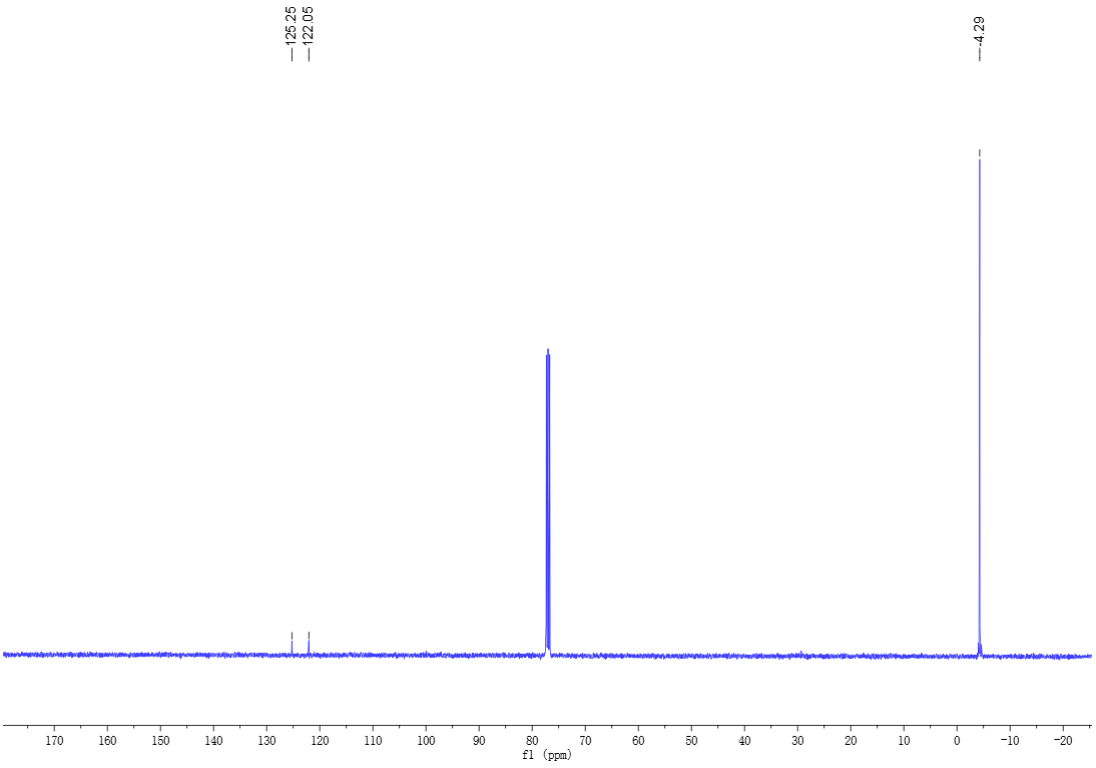
^{19}F NMR



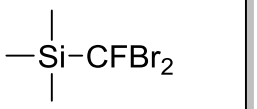

-75.74
-20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -105 -115 -125 -135 -145 -155
f1 (ppm)

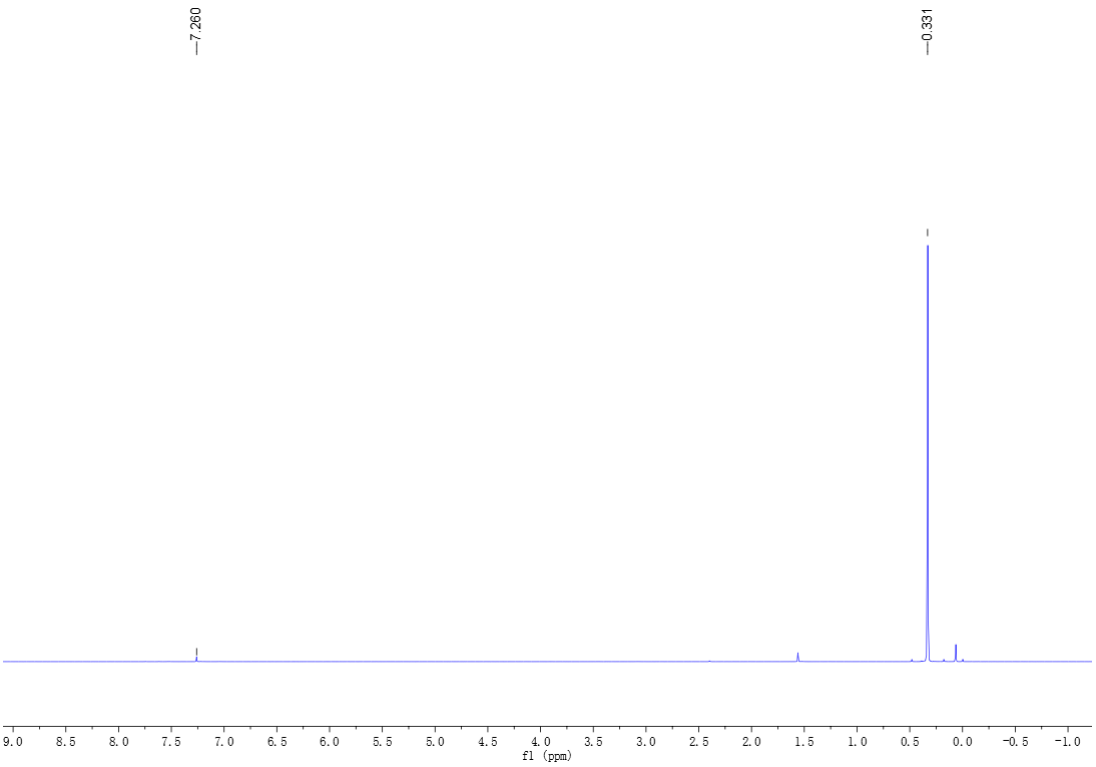
^{13}C NMR



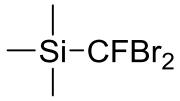

125.25
122.05
4.29
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

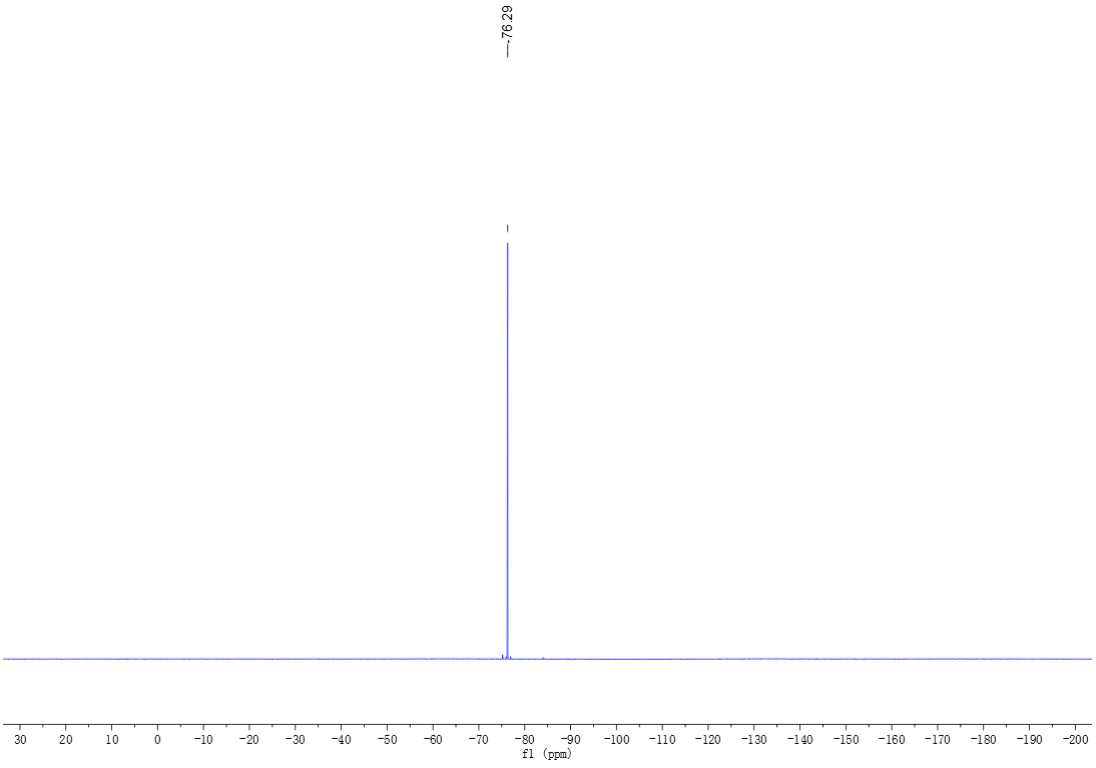
^{1}H NMR


Si
CFBr2

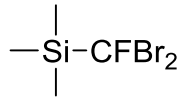

7.260
0.331
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

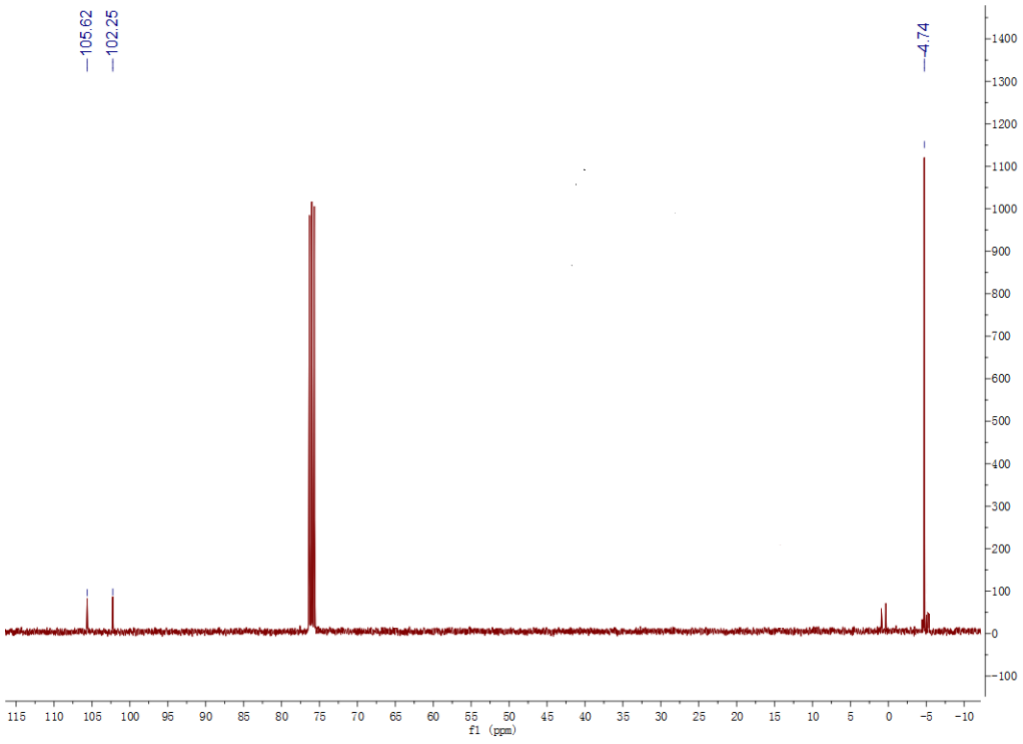
^{19}F NMR

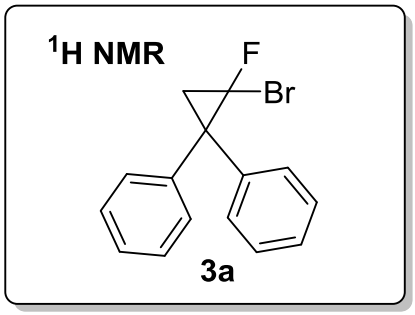


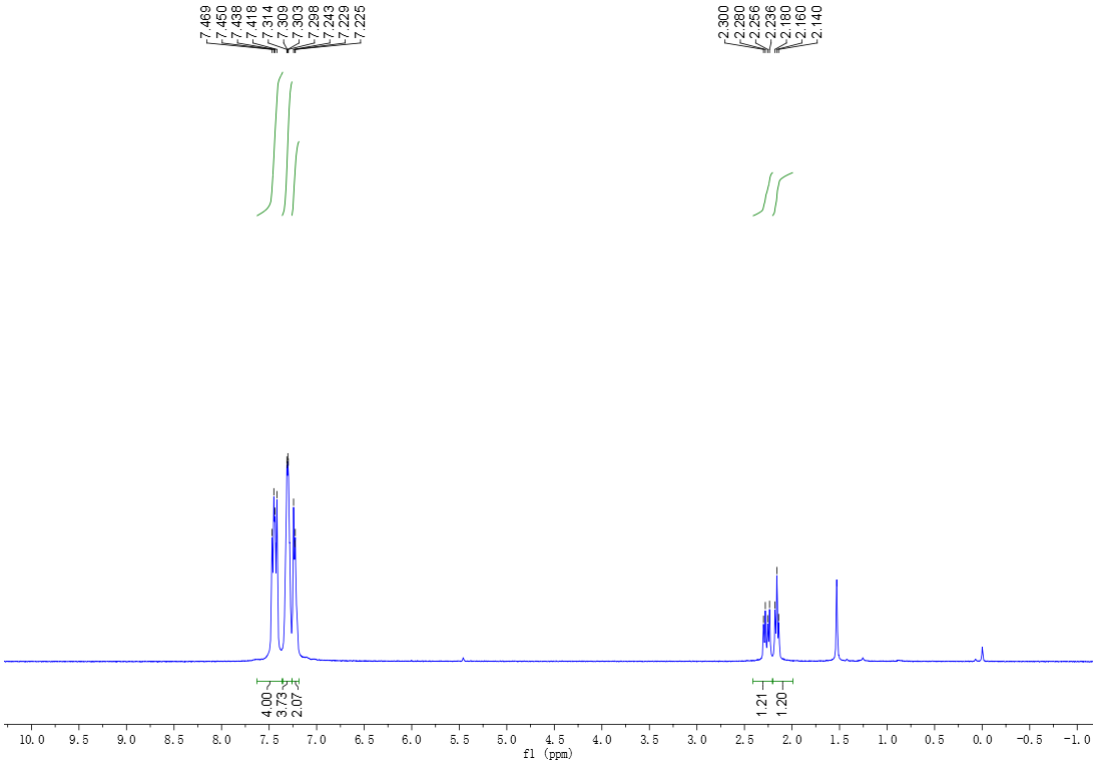

-76.29
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

^{13}C NMR

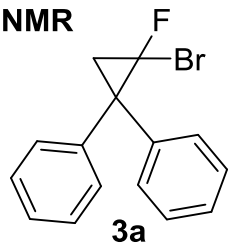





1H NMR
F
Br
3a

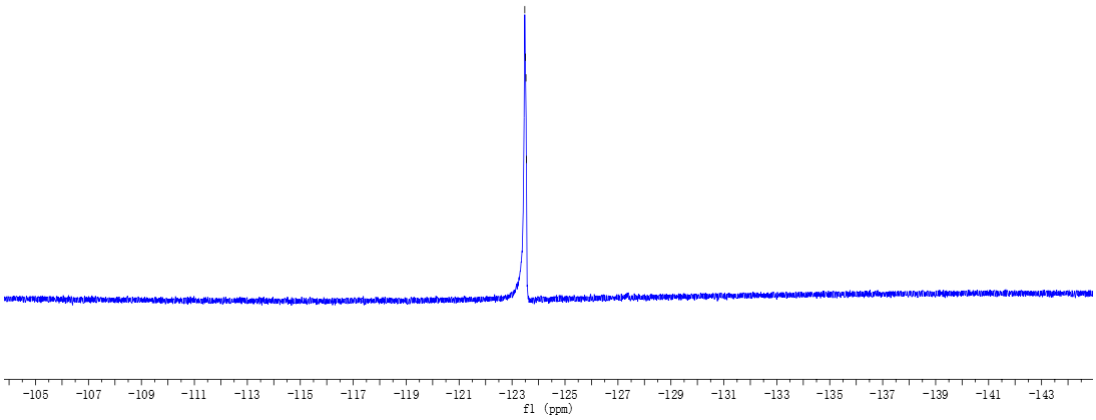

7.469
7.450
7.438
7.418
7.314
7.309
7.303
7.298
7.243
7.229
7.225
2.300
2.280
2.256
2.236
2.180
2.160
2.140
4.00
3.73
2.07
1.21
1.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

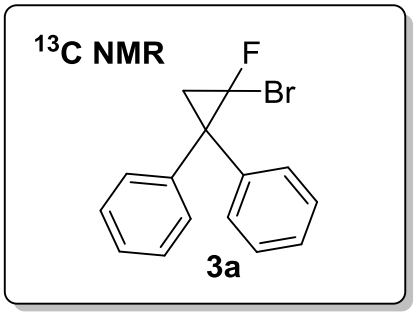
^{19}F NMR

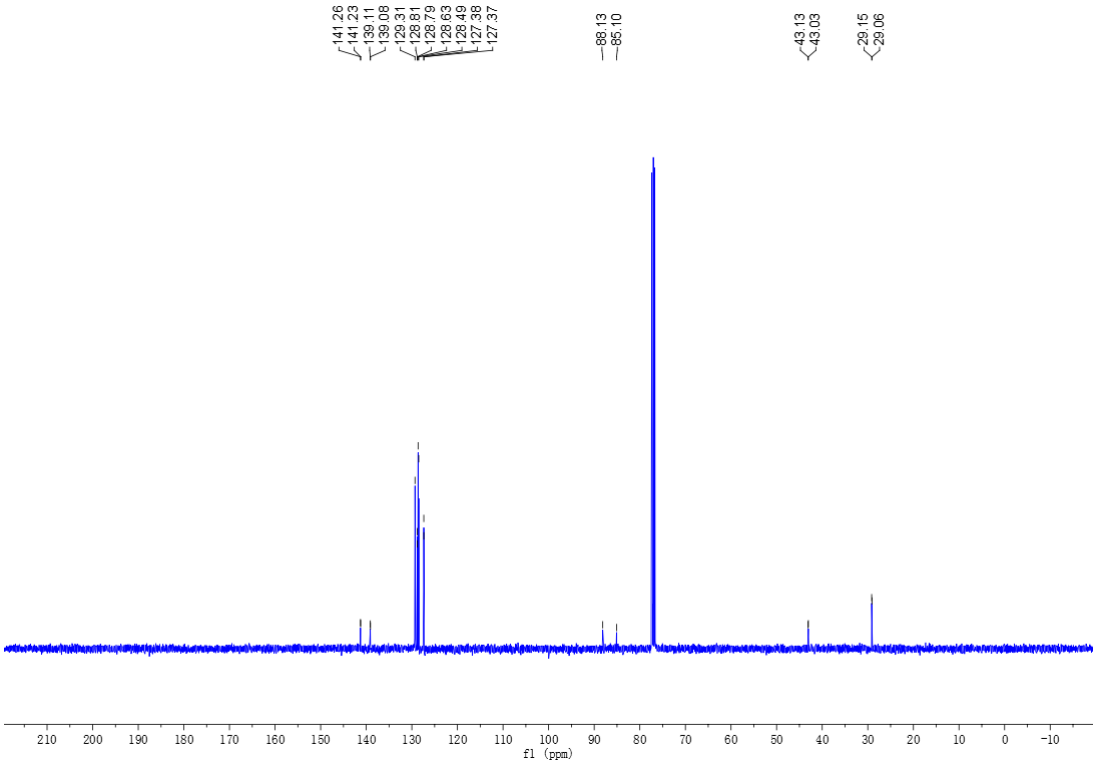

F
Br

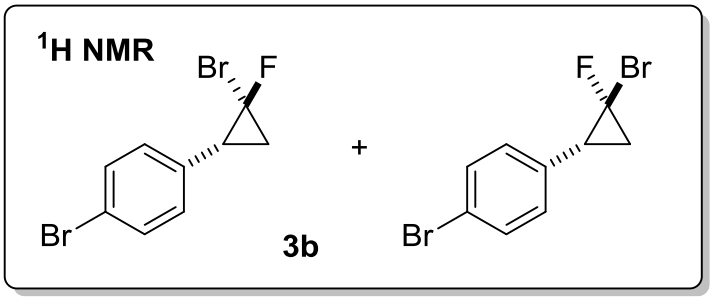
3a

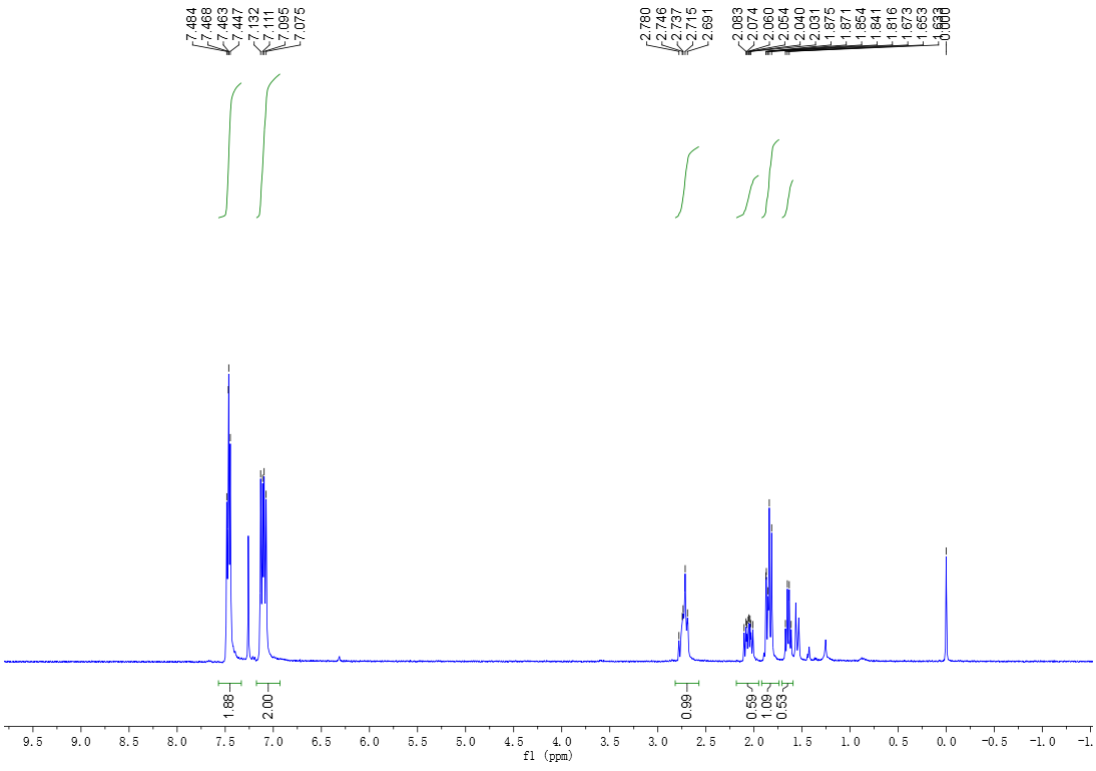

-123.48
-123.50
-123.53
-123.54


-105
-107
-109
-111
-113
-115
-117
-119
-121
-123
-125
-127
-129
-131
-133
-135
-137
-139
-141
-143
f1 (ppm)

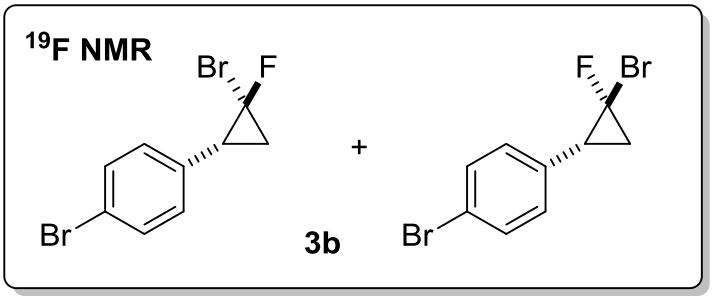

13C NMR
F
Br
3a


141.26
141.23
139.11
139.08
129.31
128.81
128.79
128.63
128.49
127.38
127.37
88.13
85.10
43.13
43.03
29.15
29.06
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

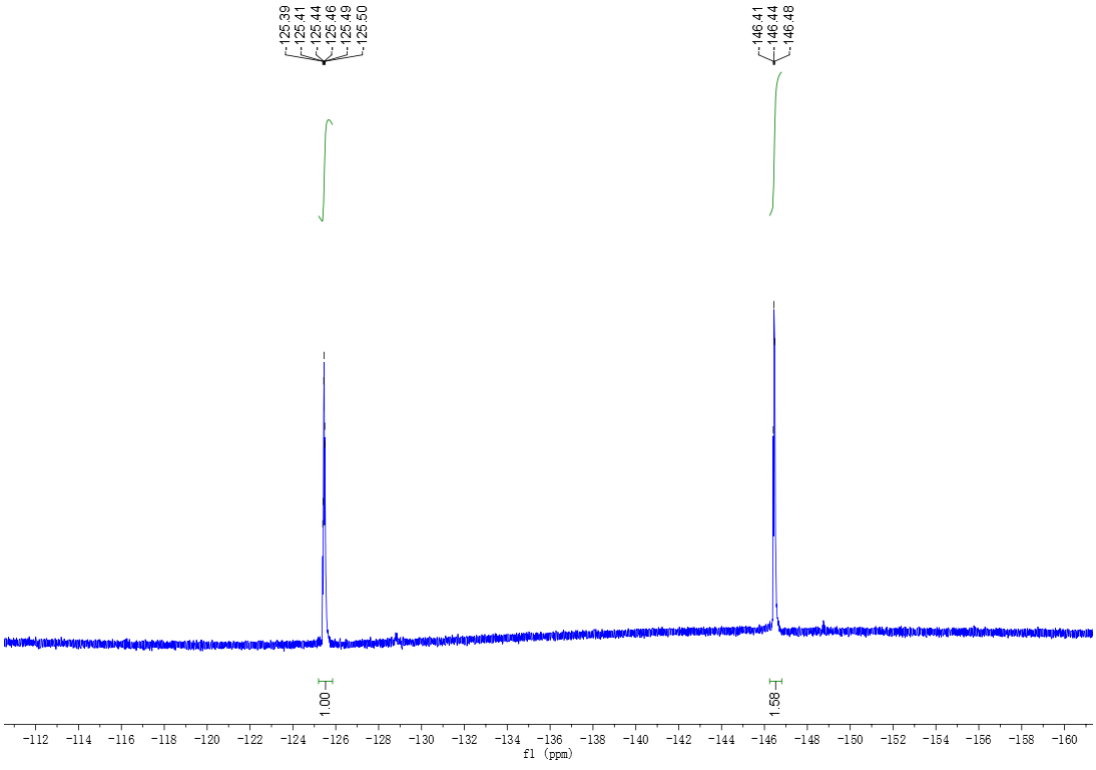

1H NMR
Br
F
Br
3b
+
F
Br
Br

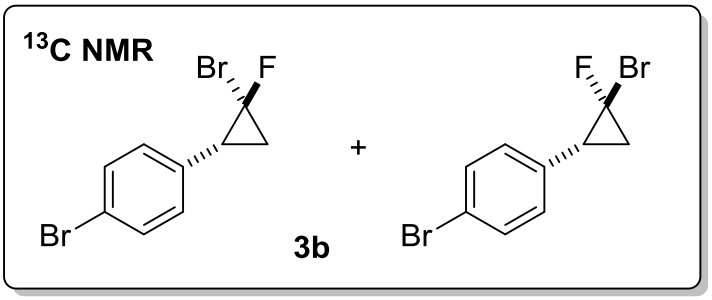

7.484
7.468
7.463
7.447
7.132
7.111
7.095
7.075
2.780
2.746
2.737
2.715
2.691
2.083
2.074
2.060
2.054
2.040
2.031
1.875
1.871
1.854
1.841
1.816
1.673
1.653
1.633
0.000
1.88
2.00
0.99
0.59
1.09
0.53
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.
f1 (ppm)

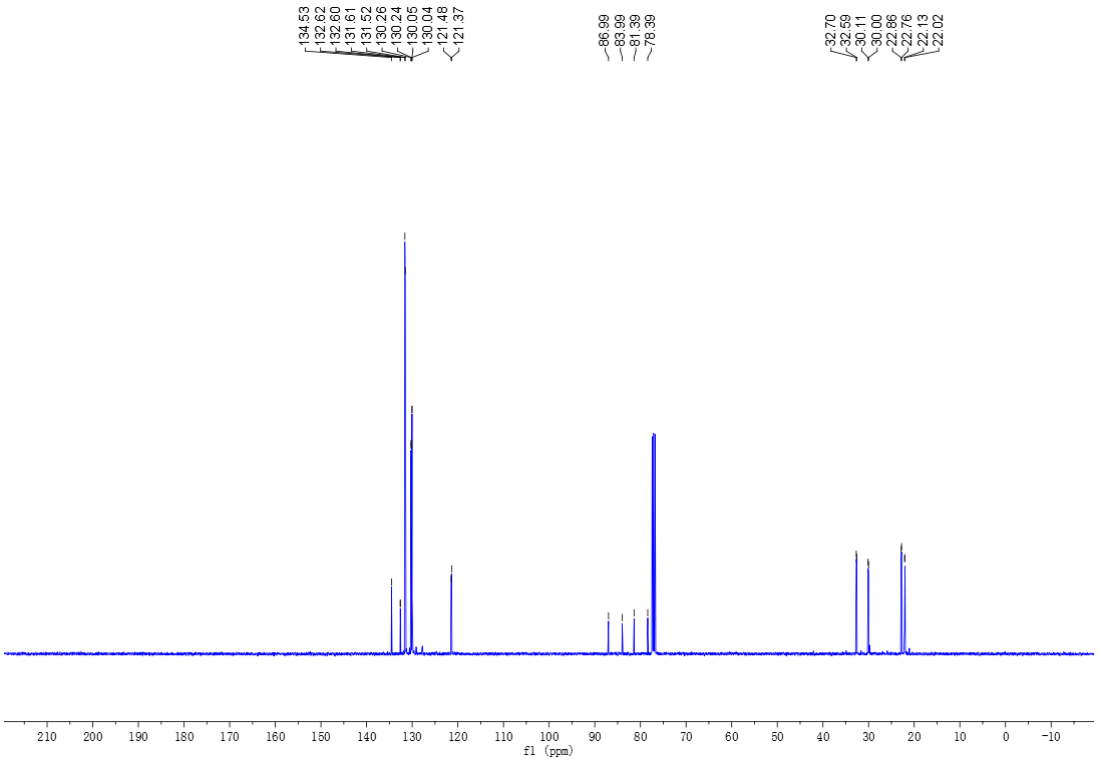
^{19}F NMR

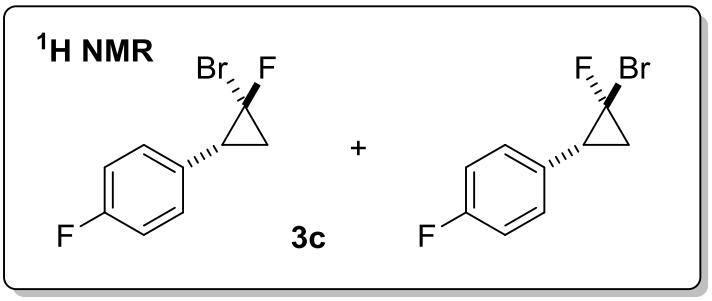

Br
F
Br
+
F
Br
Br

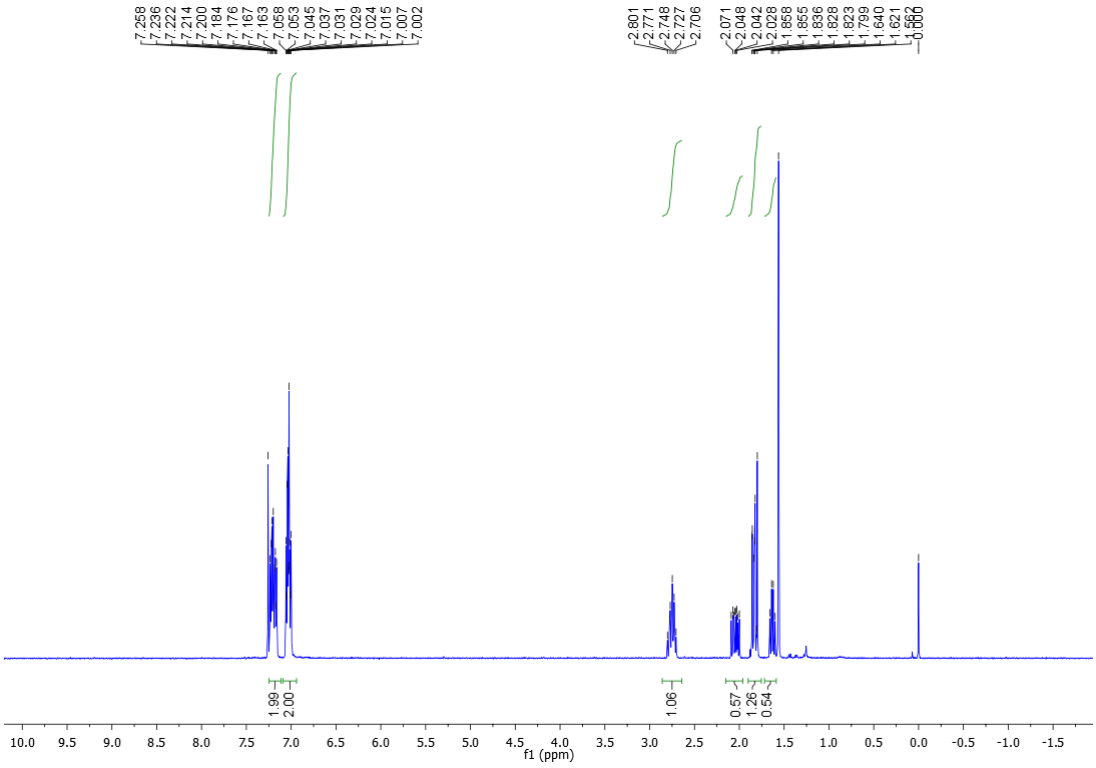
3b


125.39
125.41
125.44
125.46
125.49
125.50
146.41
146.44
146.48
1.00
1.58
-112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150 -152 -154 -156 -158 -160
f1 (ppm)

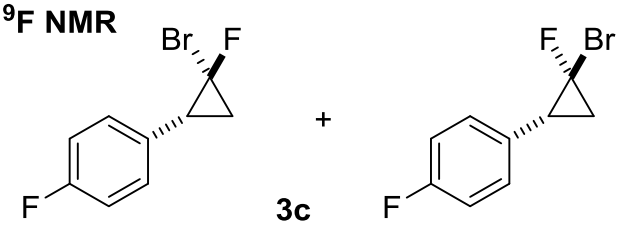

13C NMR
Br
F
+
F
Br
Br
Br
3b


134.53
132.62
132.60
131.61
131.52
130.26
130.24
130.05
130.04
121.48
121.37
86.99
83.99
81.39
78.39
32.70
32.59
30.11
30.00
22.86
22.76
22.13
22.02
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

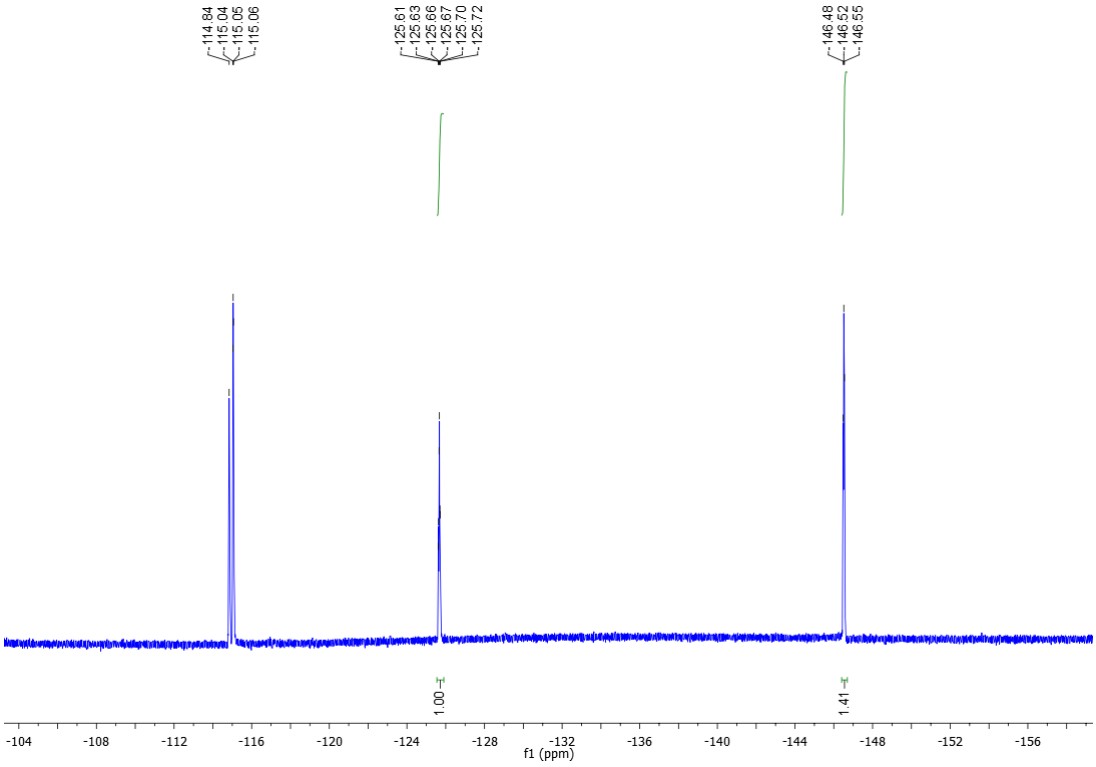

1H NMR
Br
F
F
3c
+
F
Br
F

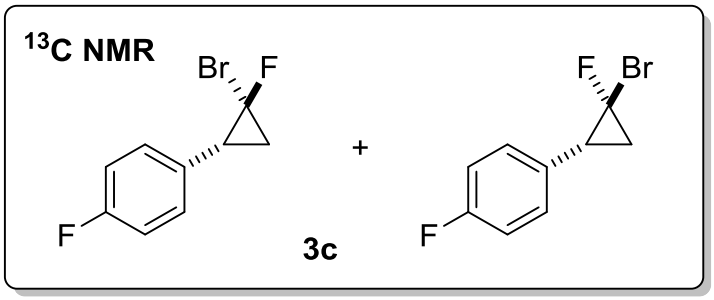

7.258
7.236
7.222
7.214
7.200
7.184
7.176
7.167
7.163
7.058
7.053
7.045
7.037
7.031
7.029
7.024
7.015
7.007
7.002
2.801
2.771
2.748
2.727
2.706
2.071
2.048
2.042
2.028
1.858
1.855
1.836
1.828
1.823
1.799
1.640
1.621
1.562
0.000
1.99
2.00
1.06
0.57
1.26
0.54
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)

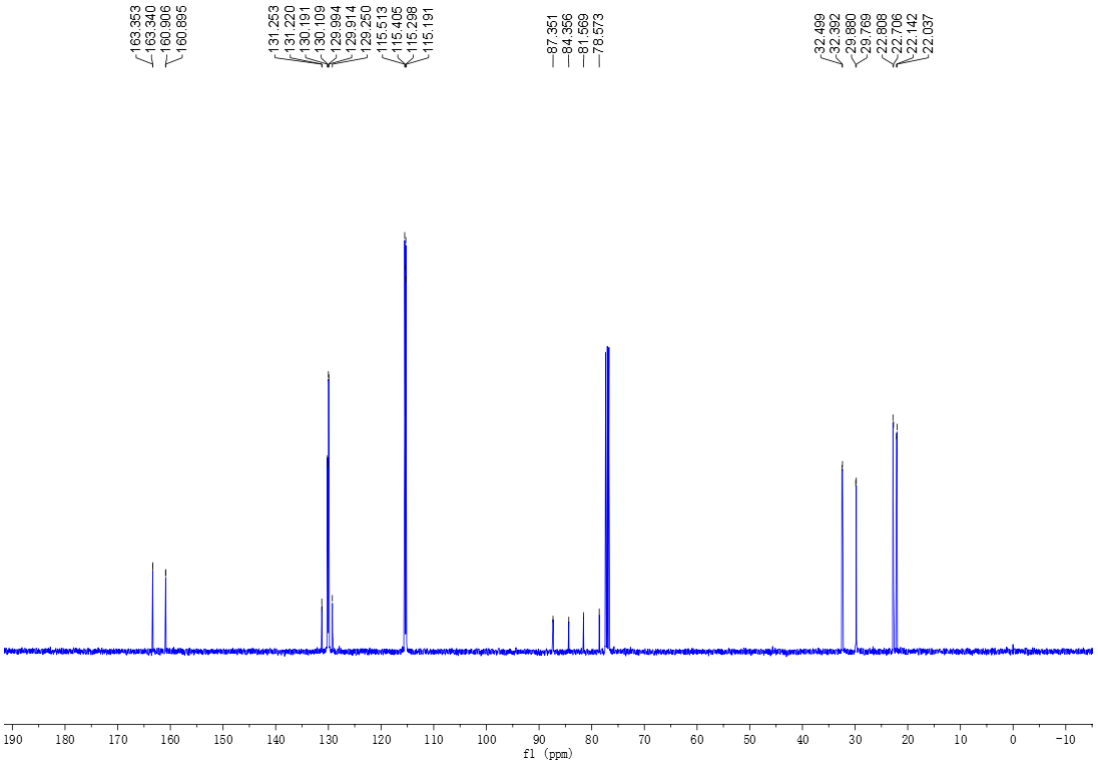
^{19}F NMR


Br
F
F
+
F
Br
F

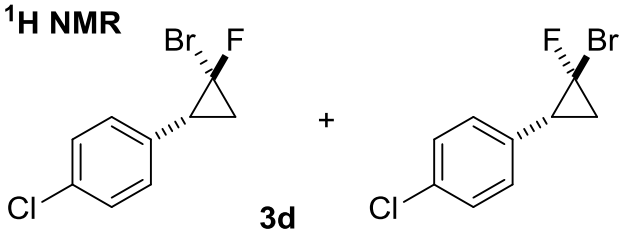
3c


114.84
115.04
115.05
115.06
125.61
125.63
125.66
125.67
125.70
125.72
146.48
146.52
146.55
1.00
1.41
-104
-108
-112
-116
-120
-124
-128
-132
-136
-140
-144
-148
-152
-156
f1 (ppm)

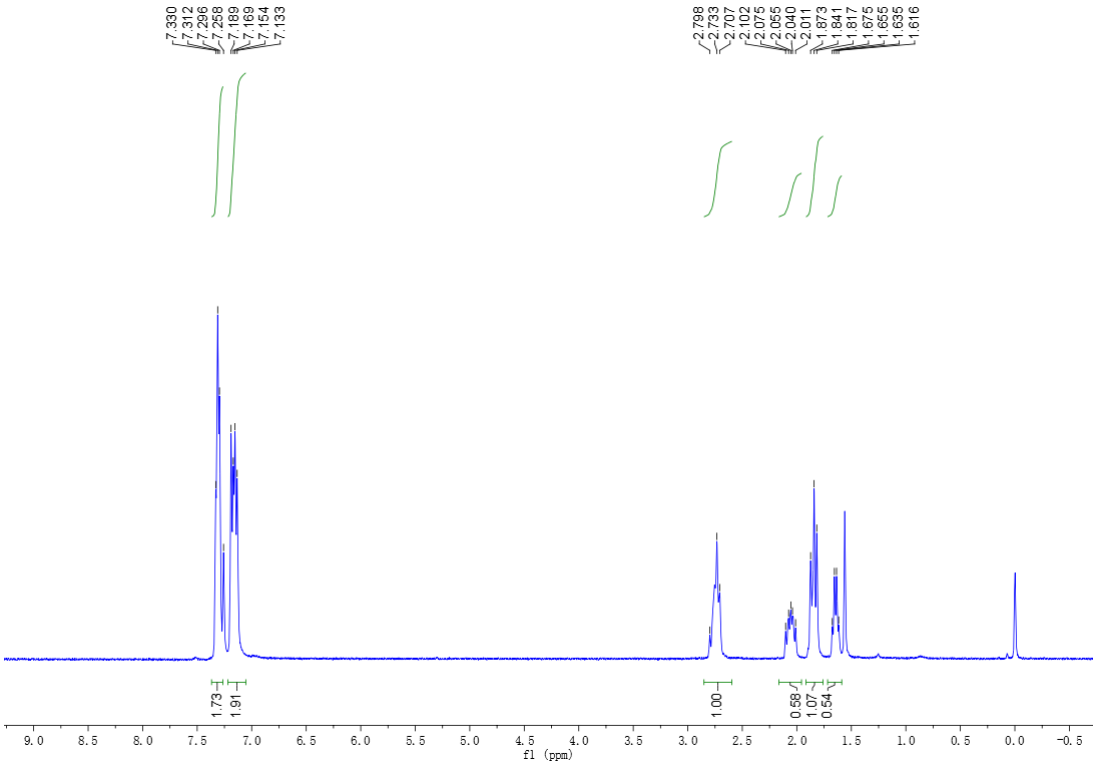

13C NMR
Br
F
F
+
F
Br
F
3c


163.353
163.340
160.906
160.895
131.253
131.220
130.191
130.109
129.994
129.914
129.250
115.513
115.405
115.298
115.191
87.351
84.356
81.569
78.573
32.499
32.392
29.880
29.769
22.808
22.706
22.142
22.037
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

^{1}H NMR


Br
F
Cl
+
F
Br
Cl

3d


7.330
7.312
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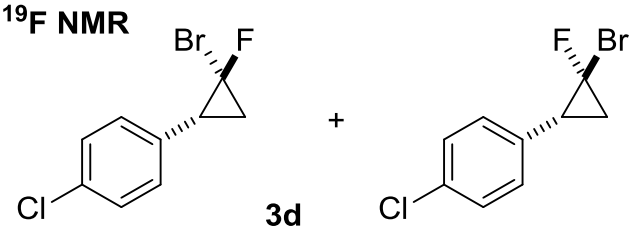
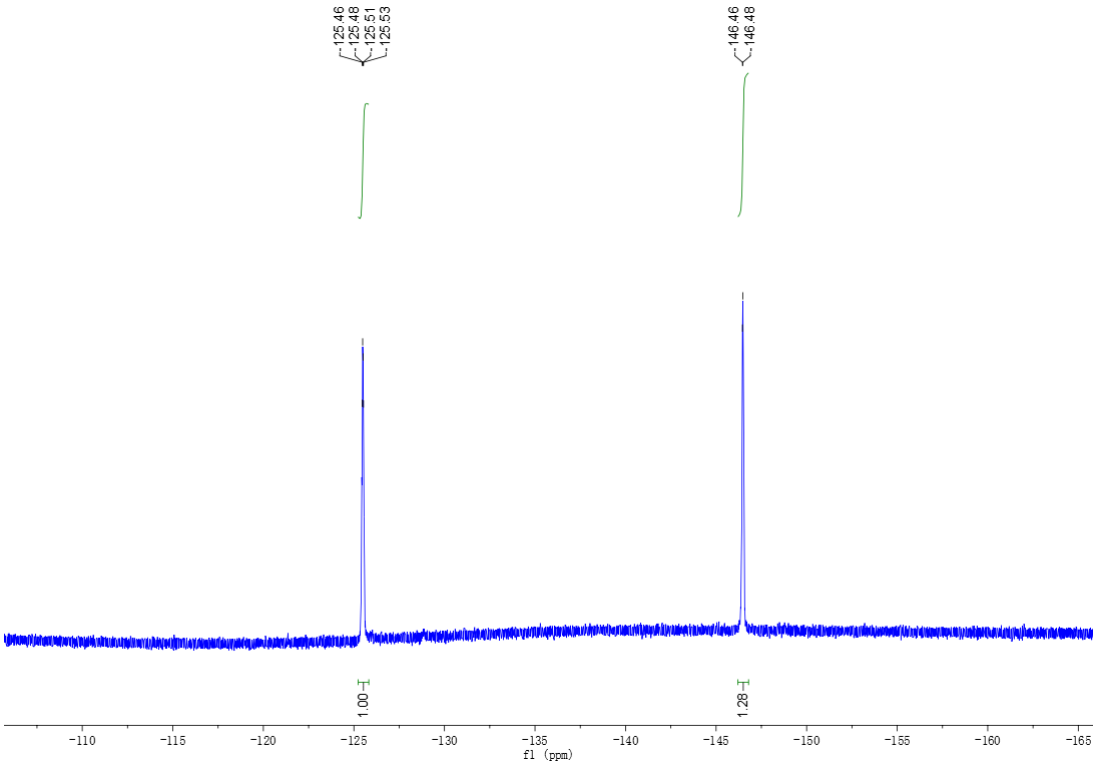
7.258
7.189
7.169
7.154
7.133
2.798
2.733
2.707
2.102
2.075
2.055
2.040
2.011
1.873
1.841
1.817
1.675
1.655
1.635
1.616
1.73
1.91
1.00
0.58
1.07
0.54
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

^{19}F NMR


Br
F
Cl
+
F
Br
Cl

3d


125.46
125.48
125.51
125.53
146.46
146.48
1.00
1.28
-110
-115
-120
-125
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-135
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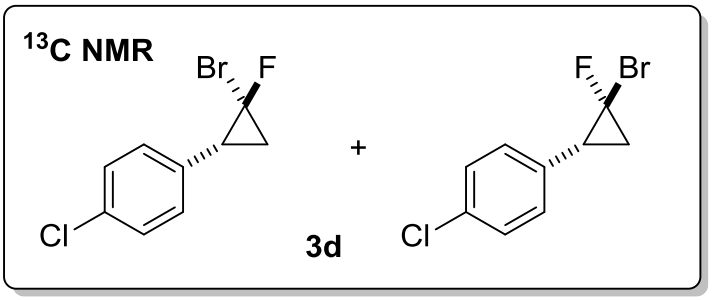
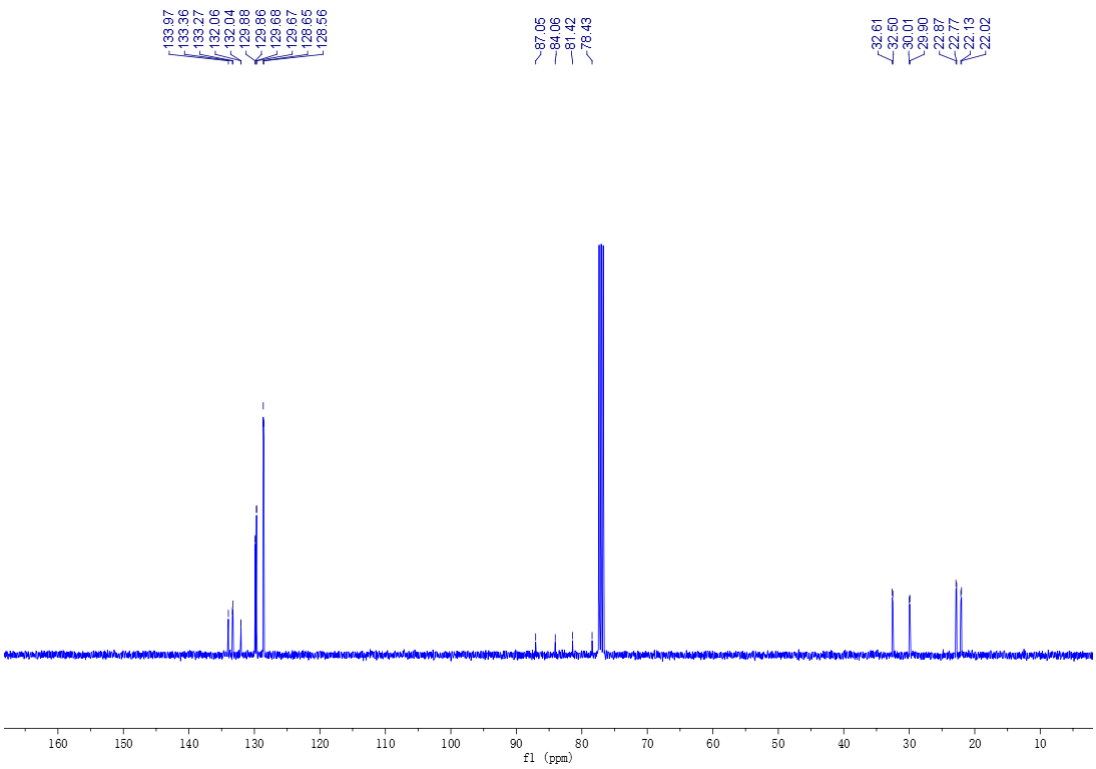
-145
-150
-155
-160
-165
f1 (ppm)


13C NMR
Br
F
Cl
+
F
Br
Cl
3d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133.36
133.27
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132.04
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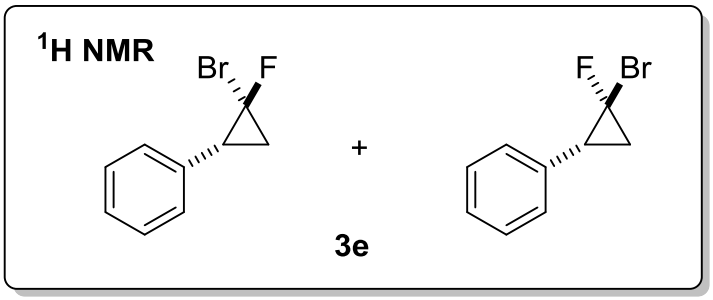
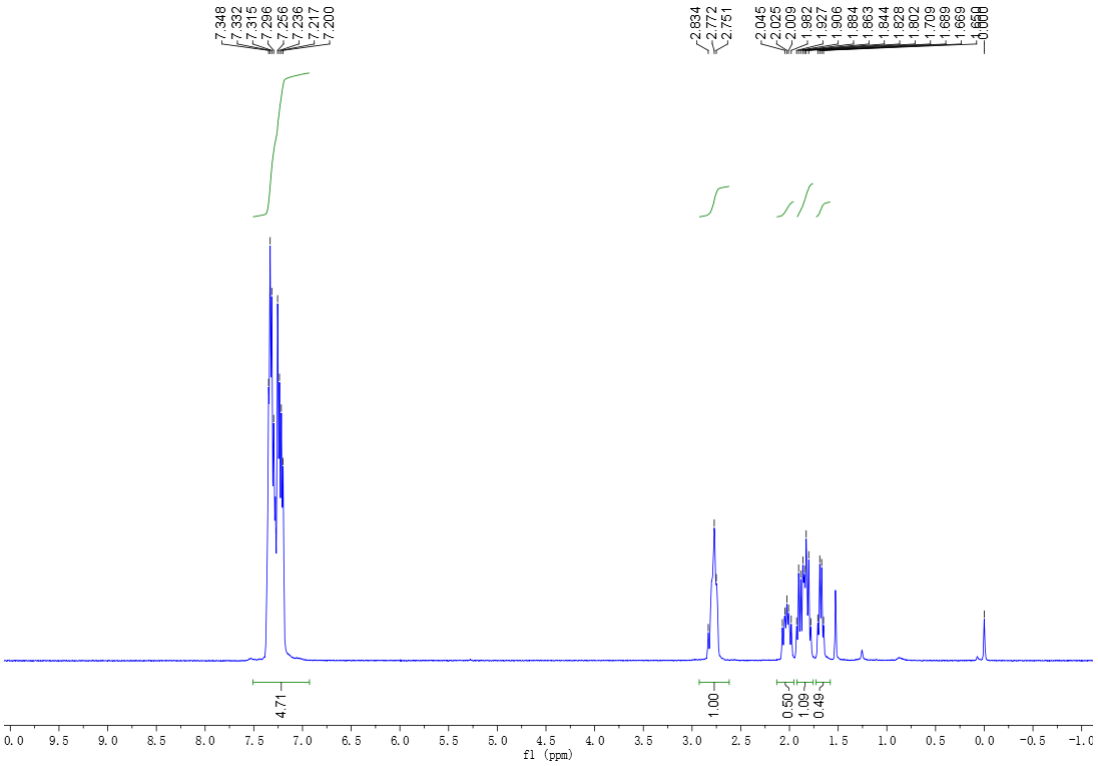
129.68
129.67
128.65
128.56
87.05
84.06
81.42
78.43
32.61
32.50
30.01
29.90
22.87
22.77
22.13
22.02
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


1H NMR
Br
F
+
F
Br
3e


7.348
7.332
7.315
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7.256
7.236
7.217
7.200
2.834
2.772
2.751
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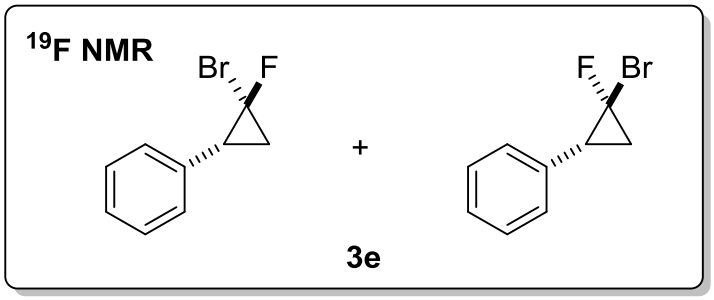
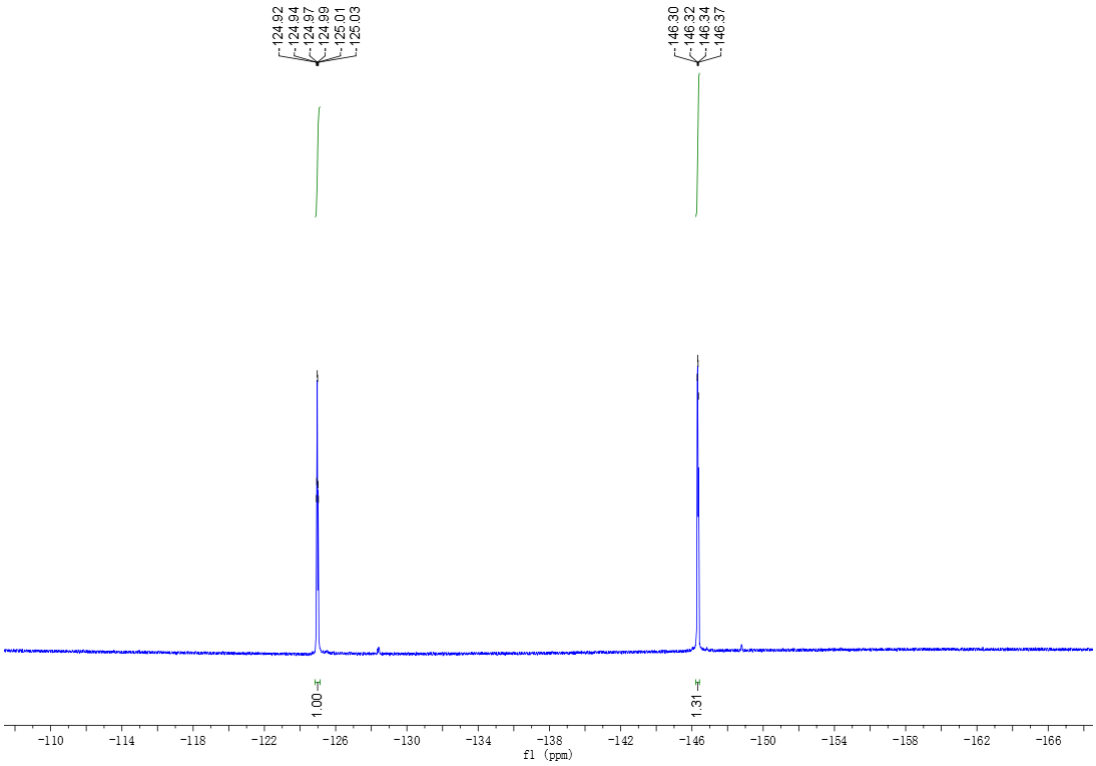
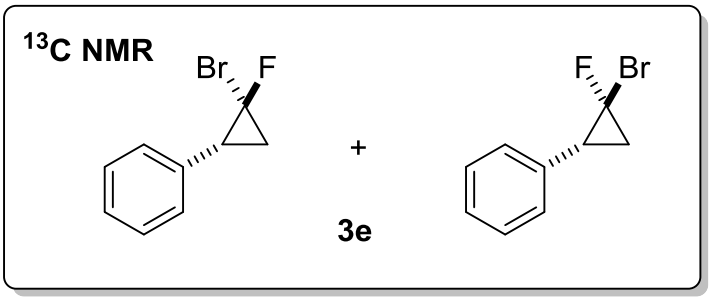
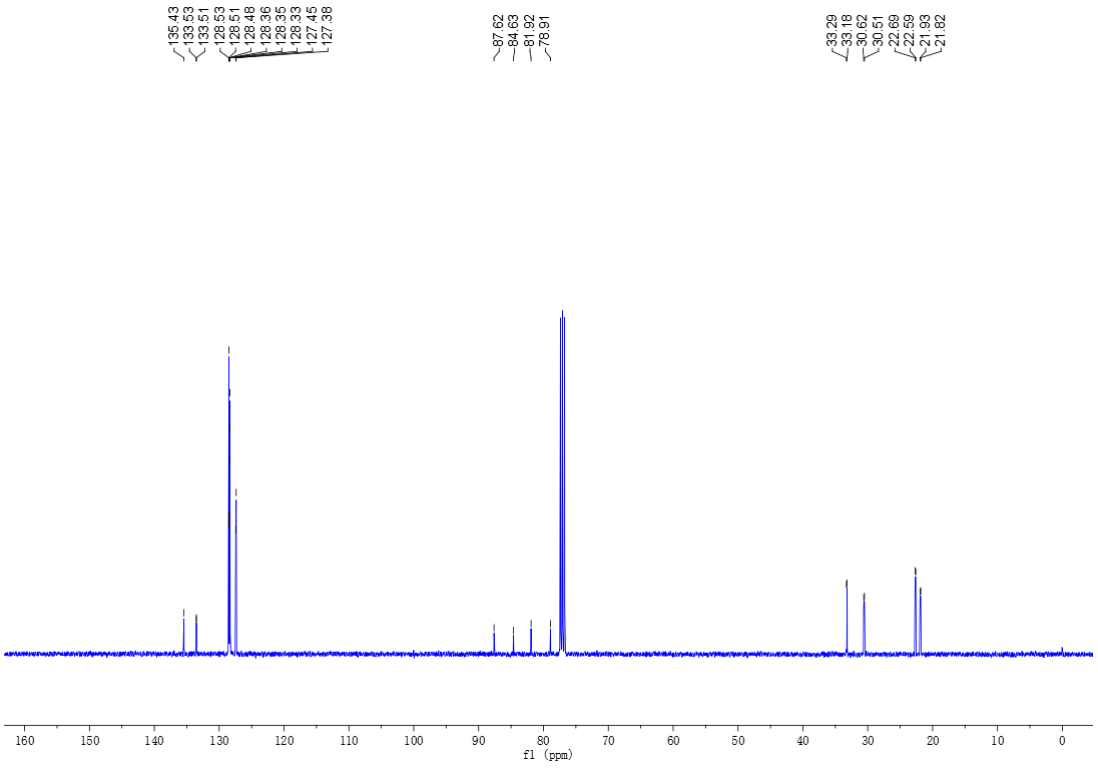
2.025
2.009
1.982
1.927
1.906
1.884
1.863
1.844
1.828
1.802
1.709
1.689
1.669
1.650
0.000
4.71
1.00
0.50
1.09
0.49
f1 (ppm)

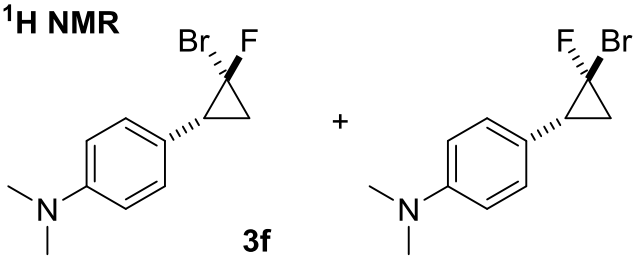

19F NMR
Br
F
+
F
Br
3e


124.92
124.94
124.97
124.99
125.01
125.03
146.30
146.32
146.34
146.37
1.00
1.31
-110
-114
-118
-122
-126
-130
-134
-138
-142
-146
-150
-154
-158
-162
-166
f1 (ppm)

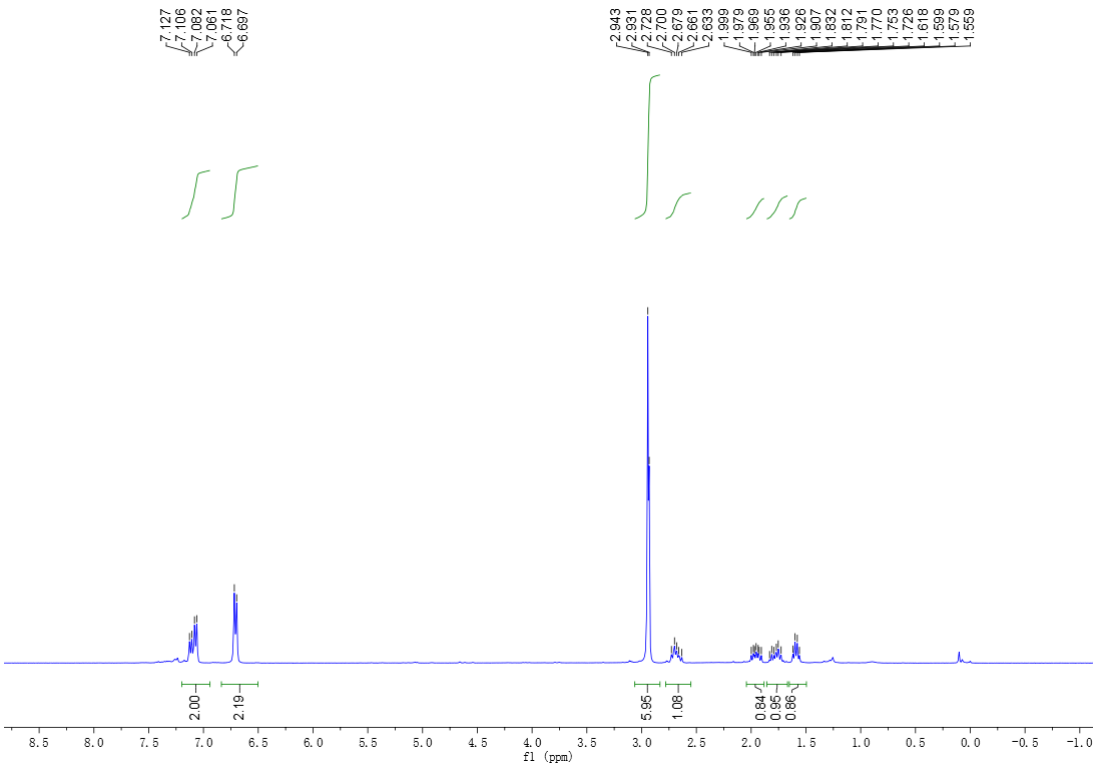

13C NMR
Br
F
+
F
Br
3e


135.43
133.53
133.51
128.53
128.51
128.48
128.36
128.35
128.33
127.45
127.38
87.62
84.63
81.92
78.91
33.29
33.18
30.62
30.51
22.69
22.59
21.93
21.82
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

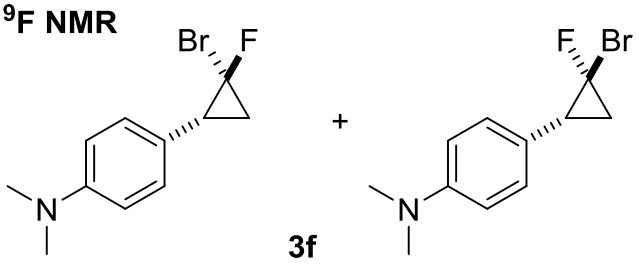
^{1}H NMR


Br
F
N
+
F
Br
N

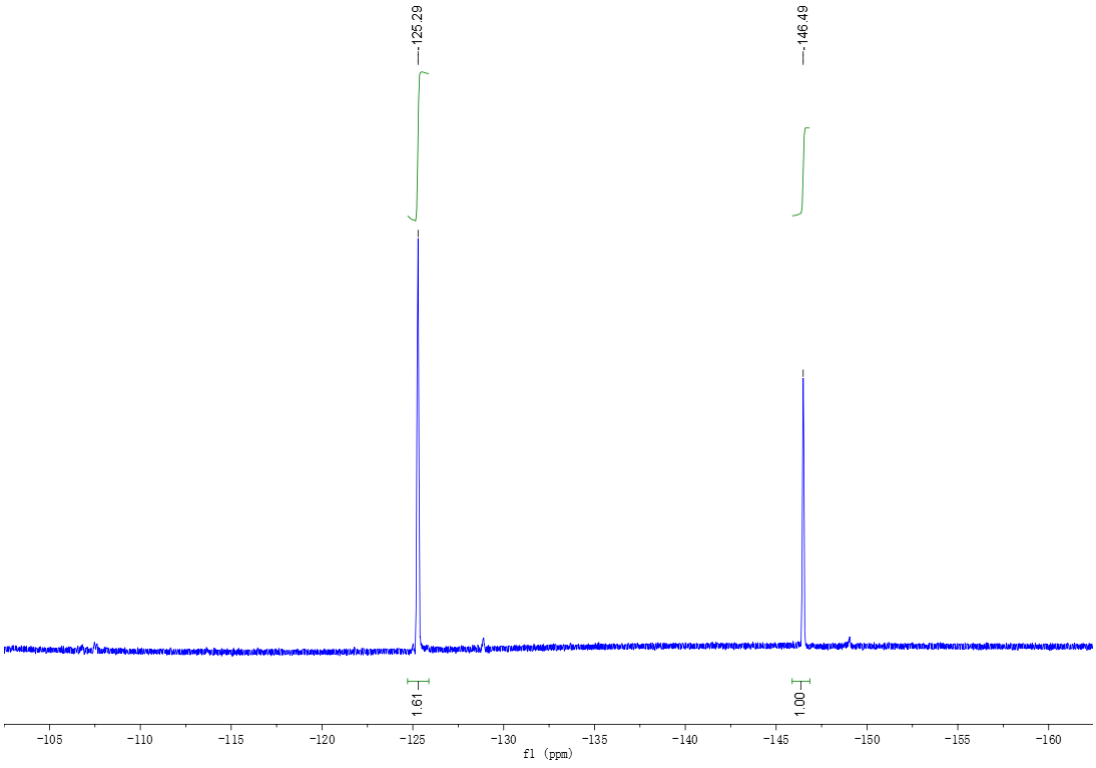
3f

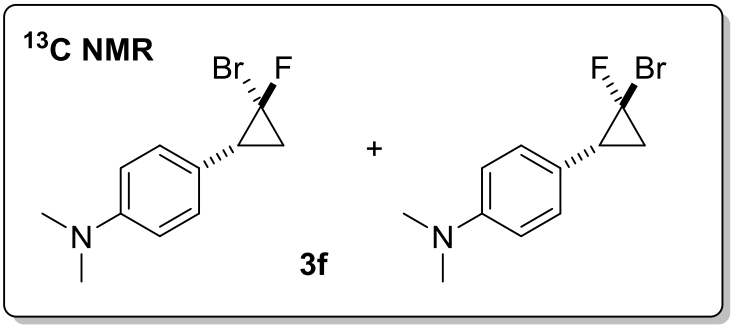

7.127
7.106
7.082
7.061
6.718
6.697
2.943
2.931
2.728
2.700
2.679
2.661
2.633
1.999
1.979
1.969
1.955
1.936
1.926
1.907
1.832
1.812
1.791
1.770
1.753
1.726
1.618
1.599
1.579
1.559
2.00
2.19
5.95
1.08
0.84
0.95
0.86
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

^{19}F NMR

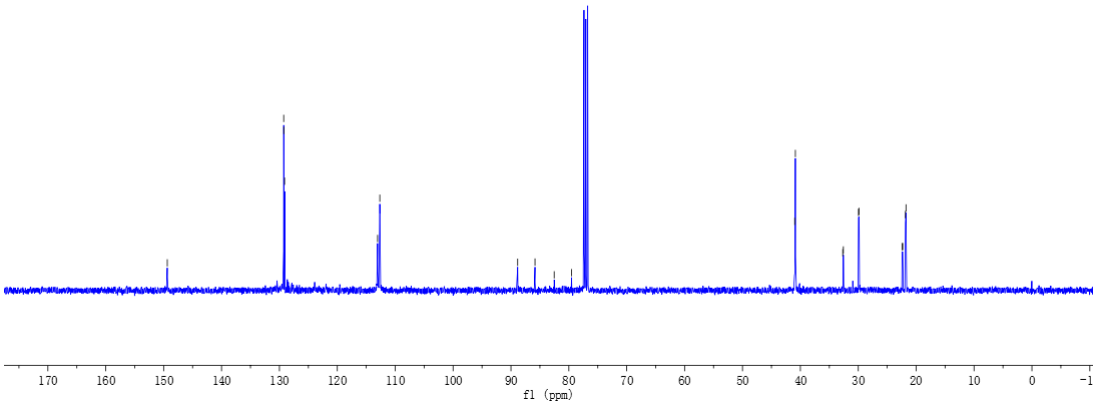

Br
F
N
+
F
Br
N

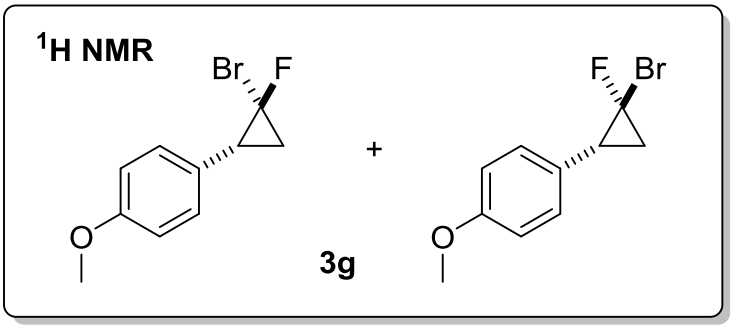
3f

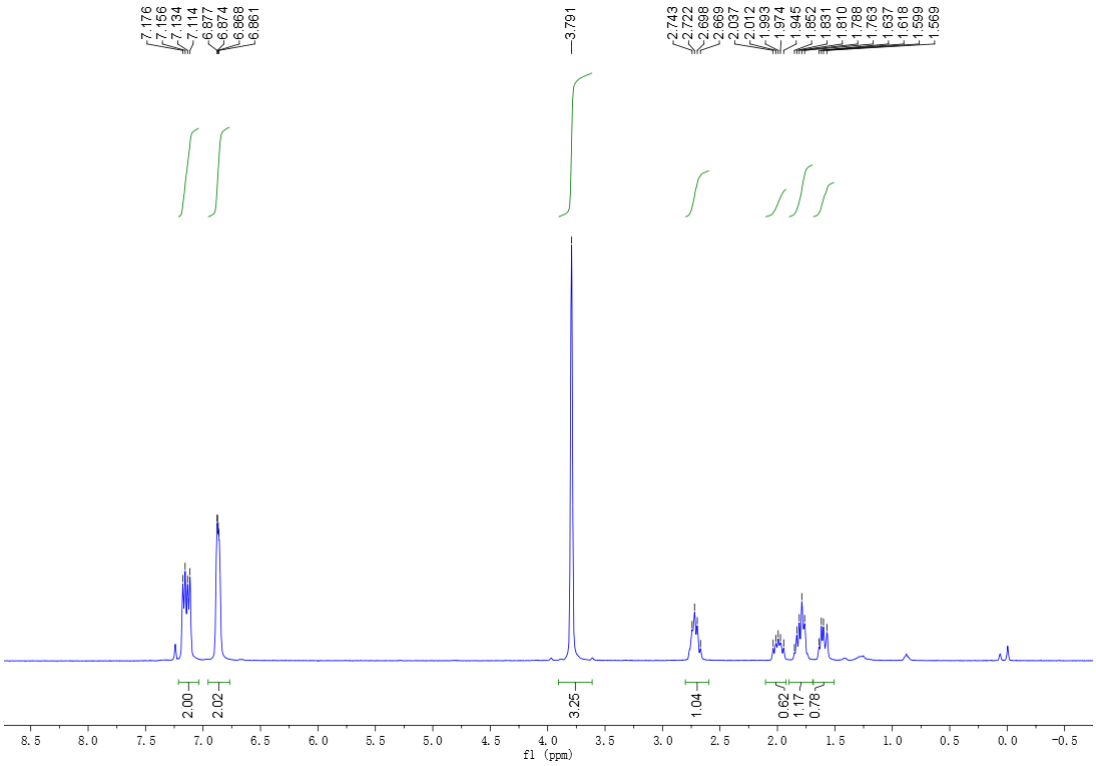

-125.29
-146.49
1.61
1.00
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
f1 (ppm)


13C NMR
Br
F
+
F
Br
N
N
3f


149.37
129.26
129.24
129.11
113.04
112.66
88.84
85.84
82.53
79.53
40.98
40.87
32.68
32.58
29.96
29.86
22.42
22.32
21.86
21.76


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


1H NMR
Br
F
+
F
Br
O
O
3g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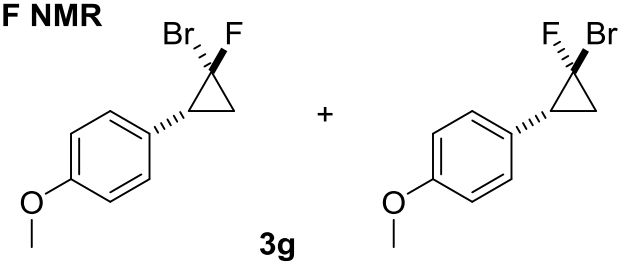
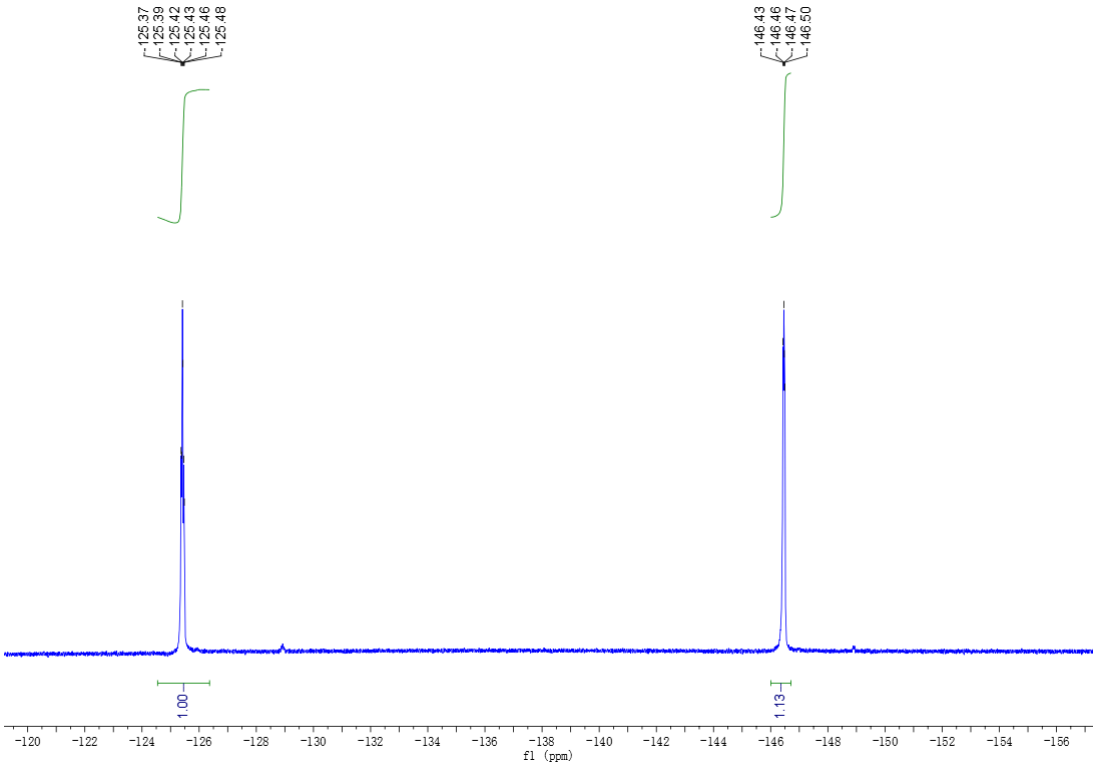
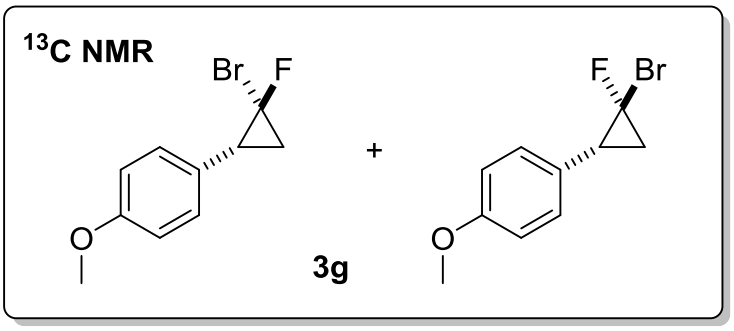
7.156
7.134
7.114
6.877
6.874
6.868
6.861
3.791
2.743
2.722
2.698
2.669
2.037
2.012
1.993
1.974
1.945
1.852
1.831
1.810
1.788
1.763
1.637
1.618
1.599
1.569
2.00
2.02
3.25
1.04
0.62
1.17
0.78
f1 (ppm)

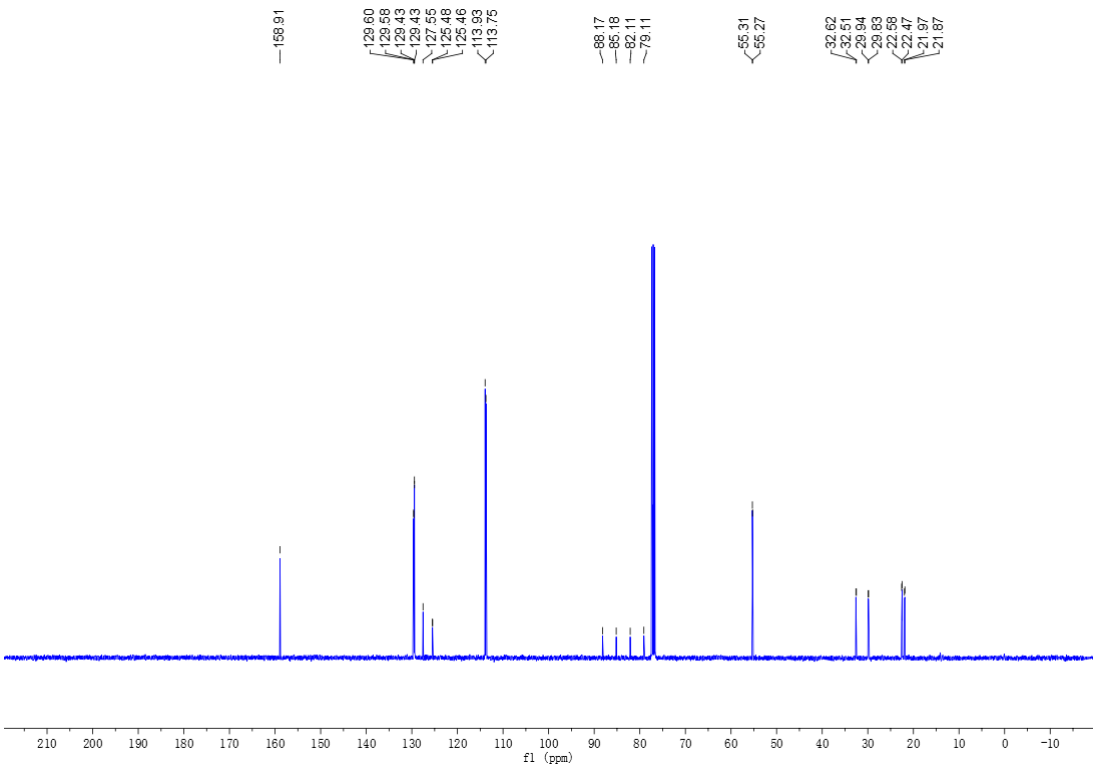
^{19}F NMR

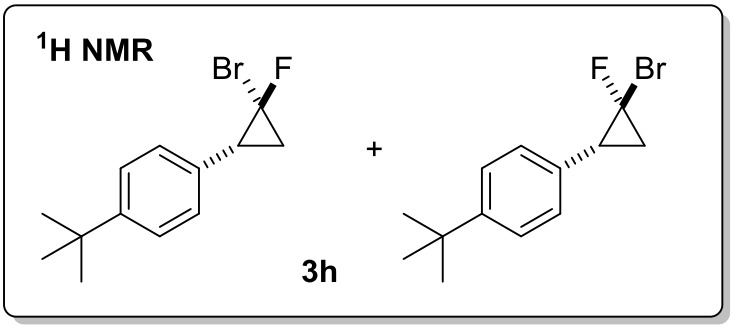

Br
F
+
F
Br
O
O

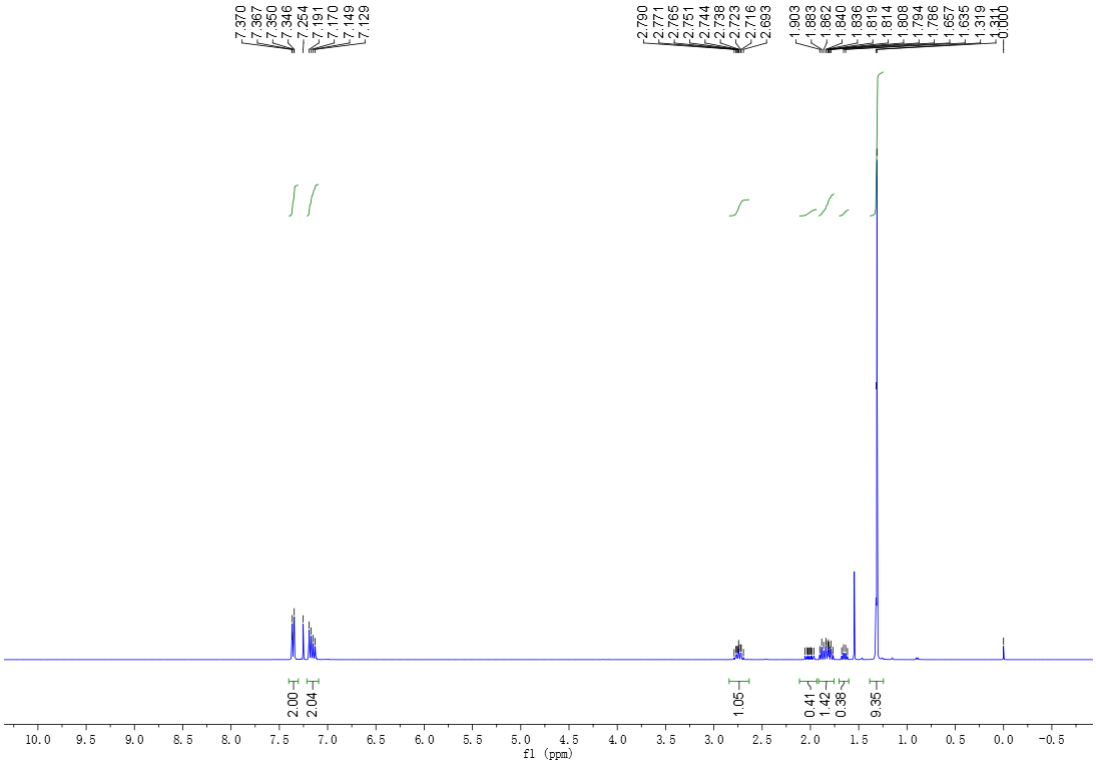
3g

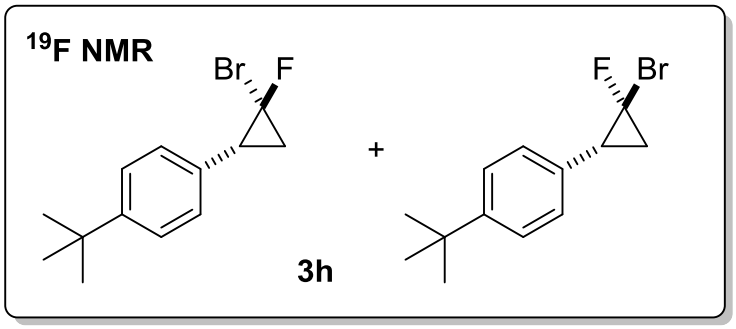

125.37
125.39
125.42
125.43
125.46
125.48
146.43
146.46
146.47
146.50
1.00
1.13
-120
-122
-124
-126
-128
-130
-132
-134
-136
-138
-140
-142
-144
-146
-148
-150
-152
-154
-156
f1 (ppm)

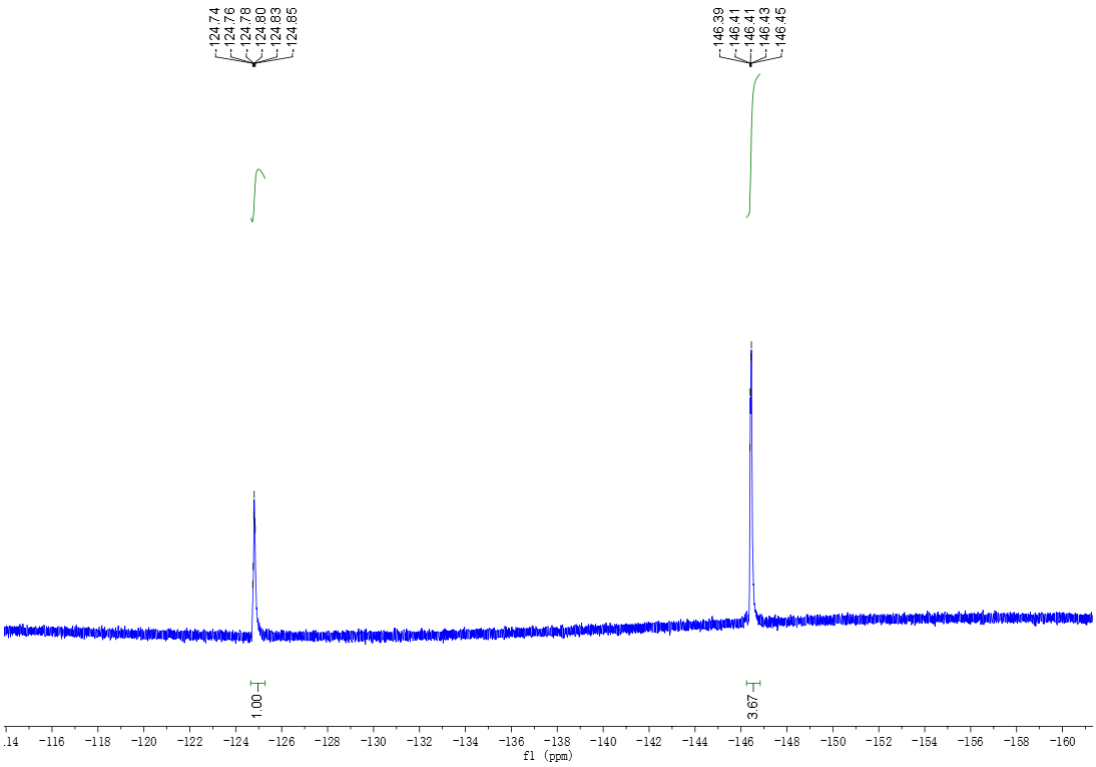

13C NMR
Br
F
+
F
Br
O
O
3g

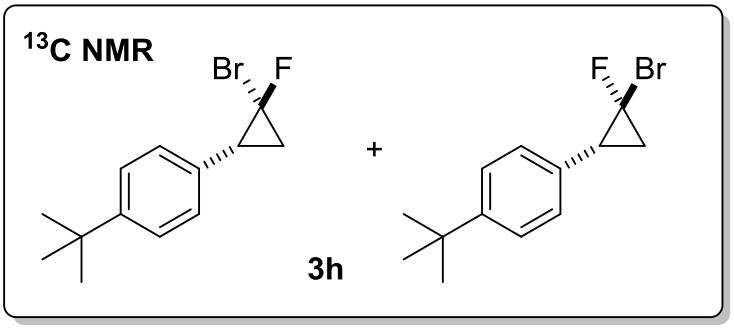

158.91
129.60
129.58
129.43
129.43
127.55
125.48
125.46
113.93
113.75
88.17
85.18
82.11
79.11
55.31
55.27
32.62
32.51
29.94
29.83
22.58
22.47
21.97
21.87
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

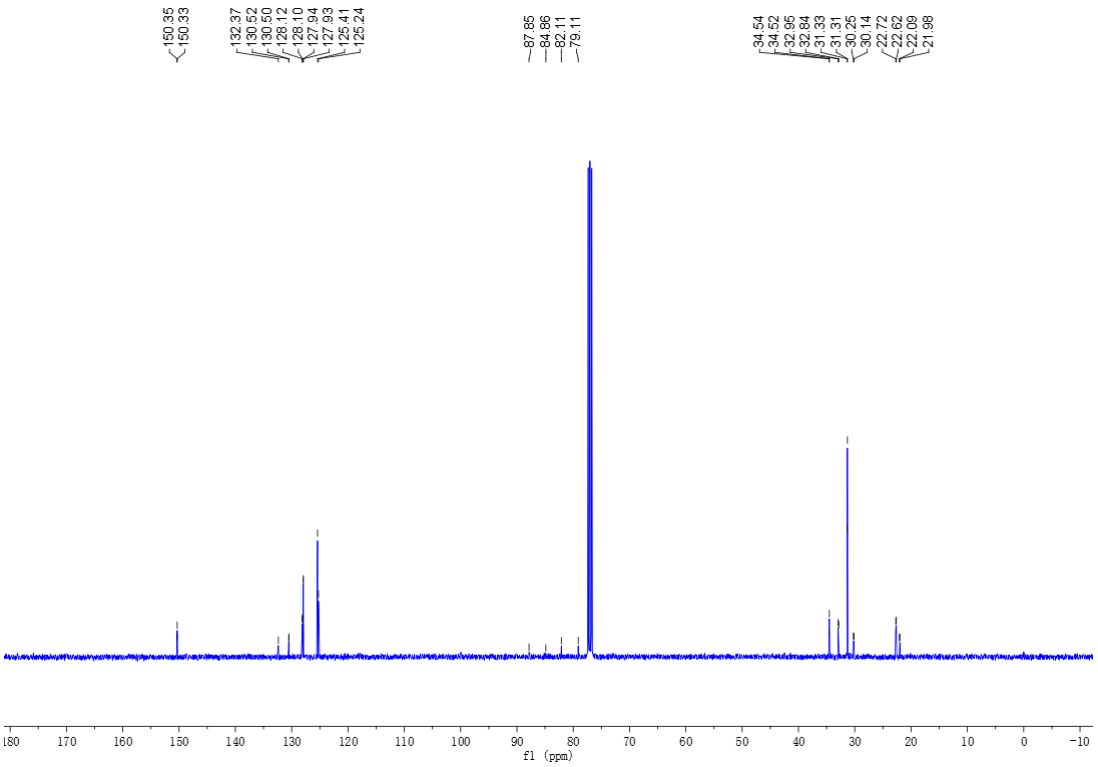

1H NMR
Br
F
+
F
Br
3h

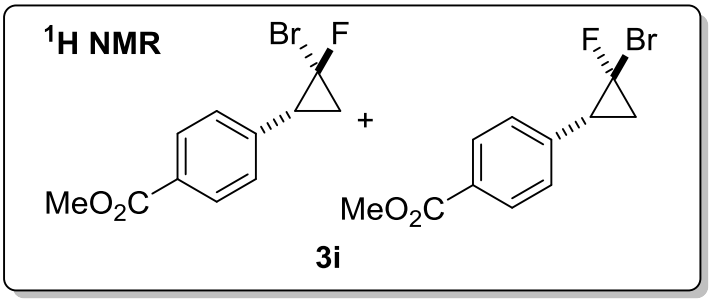

7.370
7.367
7.350
7.346
7.254
7.191
7.170
7.149
7.129
2.790
2.771
2.765
2.751
2.744
2.738
2.723
2.716
2.693
1.903
1.883
1.862
1.840
1.836
1.819
1.814
1.808
1.794
1.786
1.657
1.635
1.319
1.311
0.000
2.00
2.04
1.05
0.41
1.42
0.38
9.35
f1 (ppm)

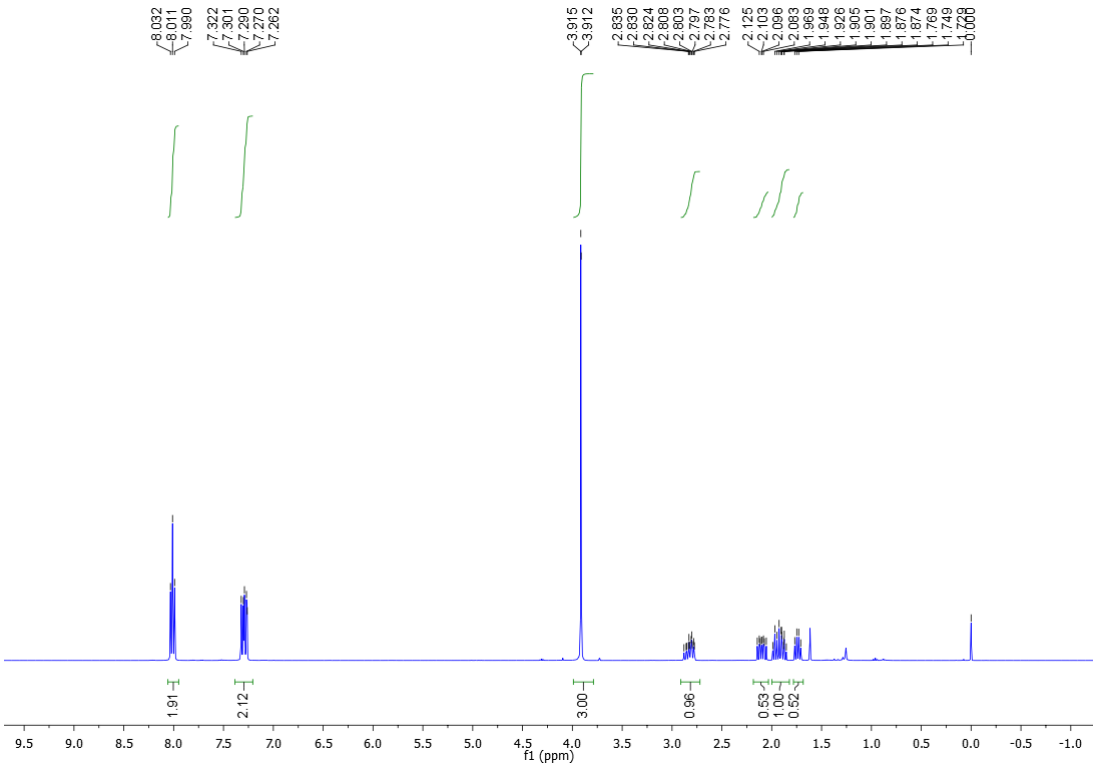

19F NMR
Br
F
+
F
Br
3h


124.74
124.76
124.78
124.80
124.83
124.85
146.39
146.41
146.41
146.43
146.45
1.00
3.67
-114
-116
-118
-120
-122
-124
-126
-128
-130
-132
-134
-136
-138
-140
-142
-144
-146
-148
-150
-152
-154
-156
-158
-160
f1 (ppm)


13C NMR
Br
F
+
F
Br
3h


150.35
150.33
132.37
130.52
130.50
128.12
128.10
127.94
127.93
125.41
125.24
87.85
84.86
82.11
79.11
34.54
34.52
32.95
32.84
31.33
31.31
30.25
30.14
22.72
22.62
22.09
21.98
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


1H NMR
Br
F
+
F
Br
MeO2C
MeO2C
3i


8.032
8.011
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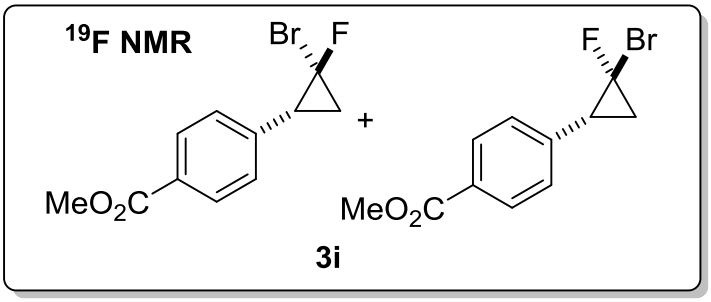
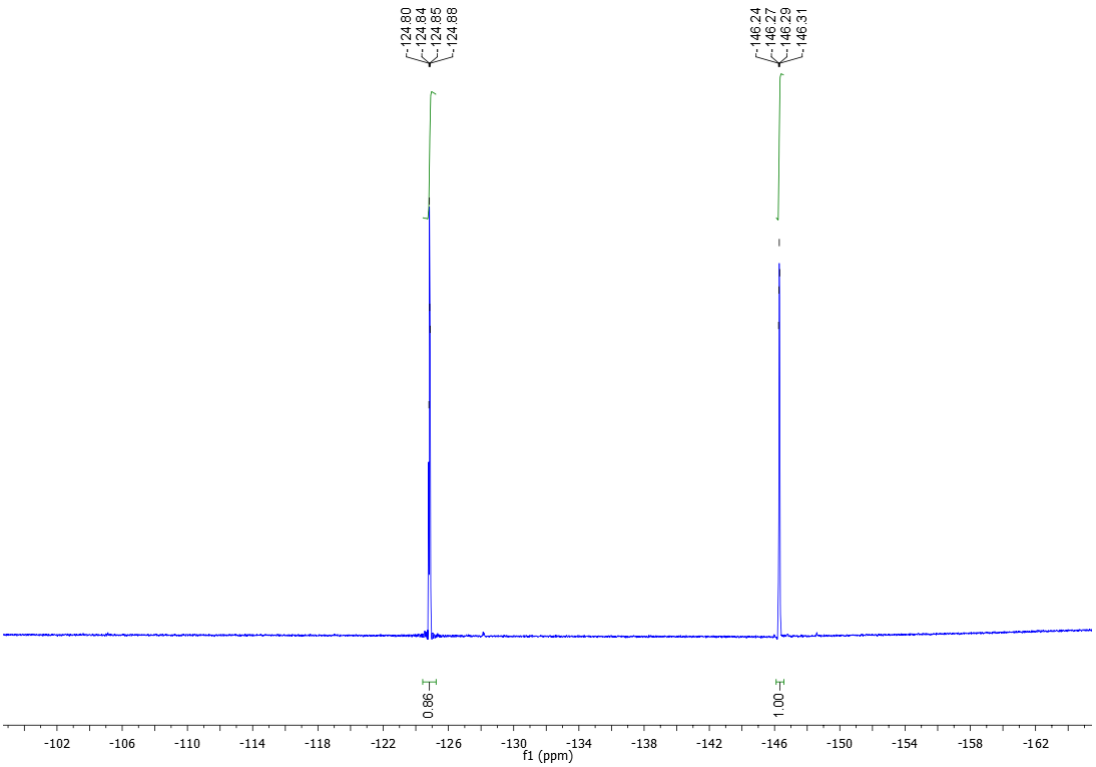
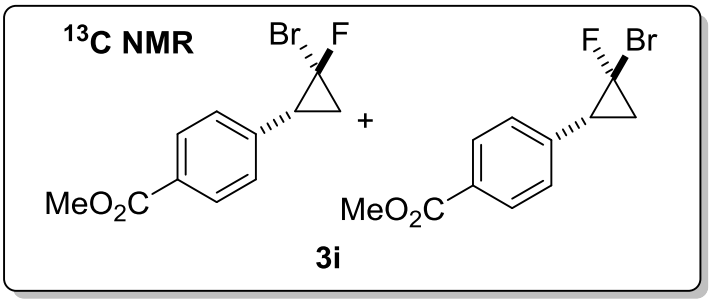
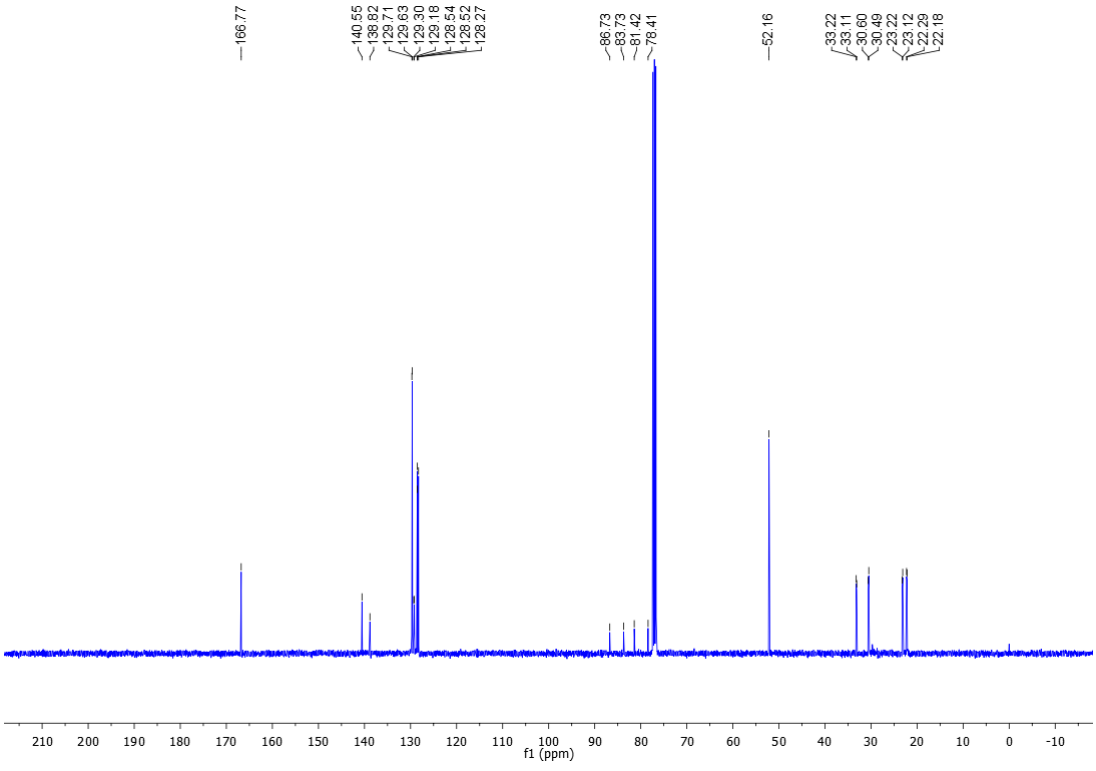
7.322
7.301
7.290
7.270
7.262
3.915
3.912
2.835
2.830
2.824
2.808
2.803
2.797
2.783
2.776
2.125
2.103
2.096
2.083
1.969
1.948
1.926
1.905
1.901
1.897
1.876
1.874
1.769
1.749
1.728
0.000
1.91
2.12
3.00
0.96
0.53
1.00
0.52
f1 (ppm)

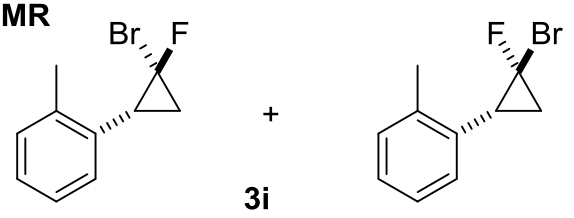

19F NMR
Br
F
+
MeO2C
F
Br
MeO2C
3i


-124.80
-124.84
-124.85
-124.88
-146.24
-146.27
-146.29
-146.31
0.86
1.00
-102
-106
-110
-114
-118
-122
-126
-130
-134
-138
-142
-146
-150
-154
-158
-162
f1 (ppm)

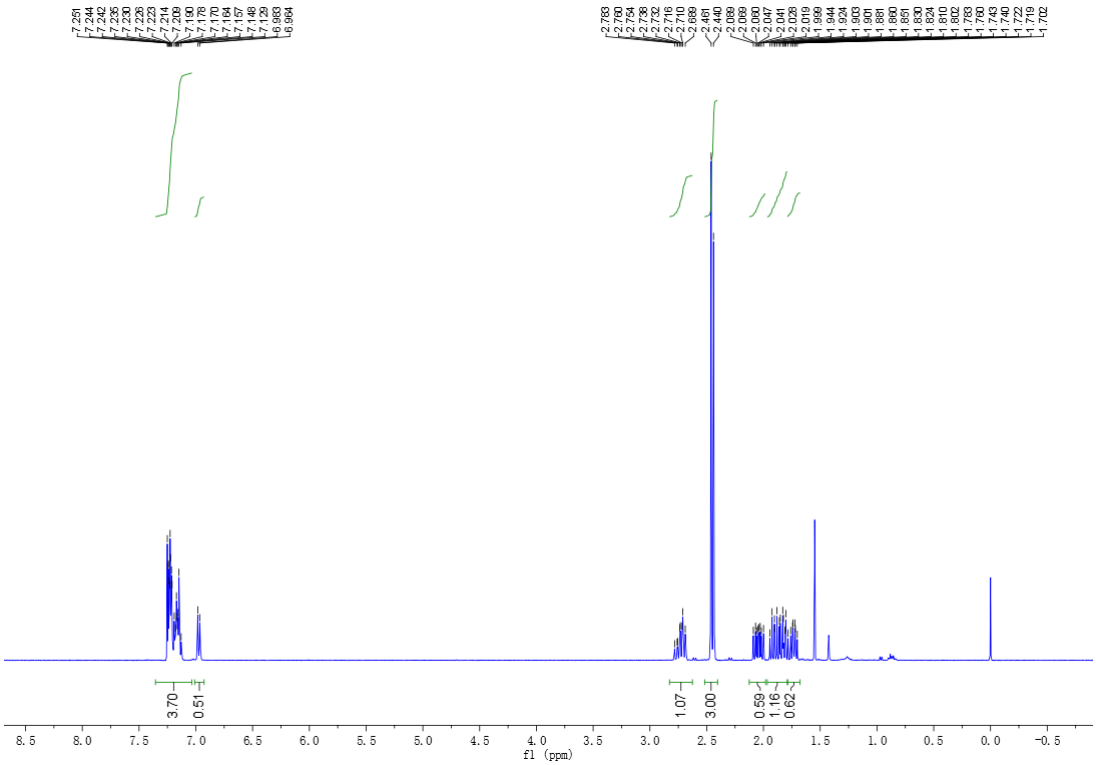

13C NMR
Br
F
+
F
Br
MeO2C
MeO2C
3i


166.77
140.55
138.82
129.71
129.63
129.30
129.18
128.54
128.52
128.27
86.73
83.73
81.42
78.41
52.16
33.22
33.11
30.60
30.49
23.22
23.12
22.29
22.18
f1 (ppm)

^{1}H NMR


Br
F
+
F
Br

3i


7.251
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7.242
7.235
7.230
7.223
7.214
7.209
7.190
7.178
7.170
7.164
7.157
7.148
7.129
6.983
6.964
2.763
2.760
2.754
2.738
2.732
2.716
2.710
2.689
2.461
2.440
2.089
2.069
2.047
2.041
2.028
2.019
1.999
1.944
1.924
1.903
1.901
1.881
1.880
1.851
1.830
1.824
1.810
1.802
1.783
1.778
1.743
1.740
1.722
1.719
1.702
3.70
0.51
1.07
3.00
0.59
1.16
0.62
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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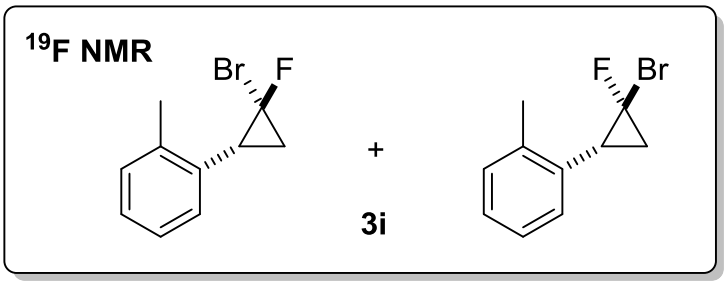
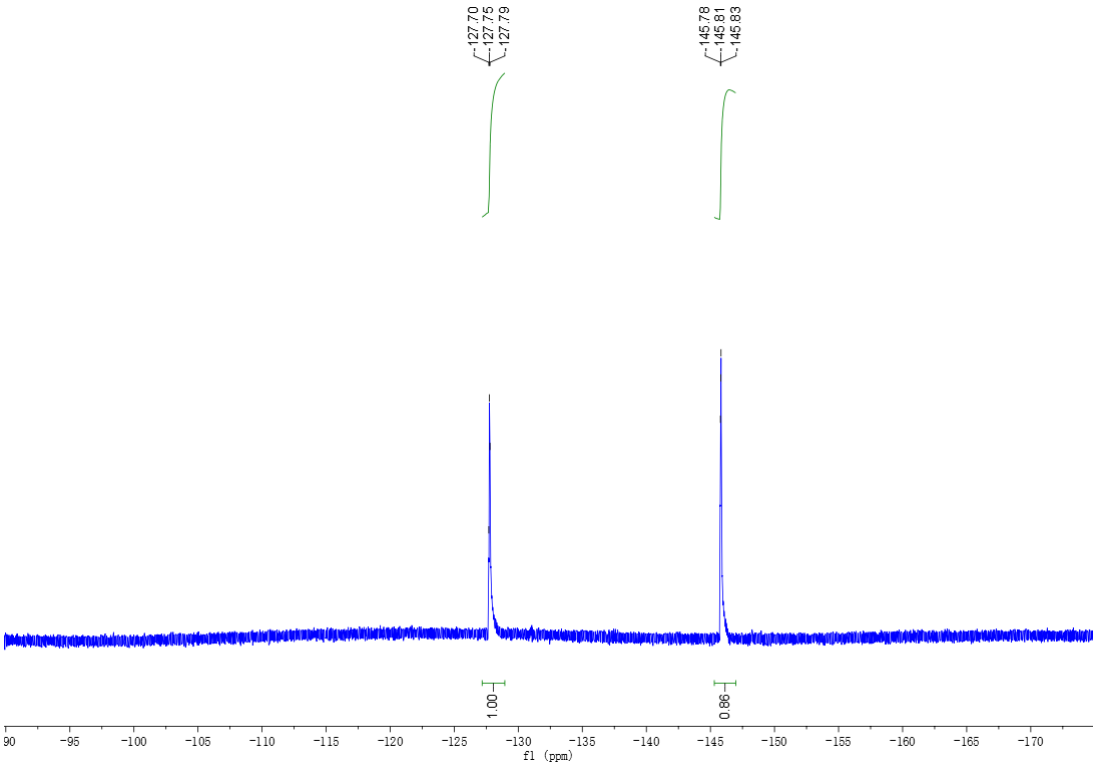
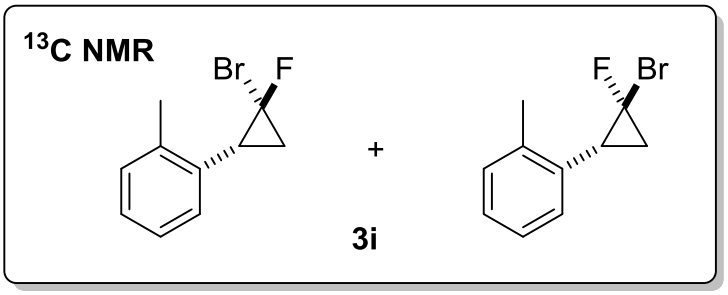
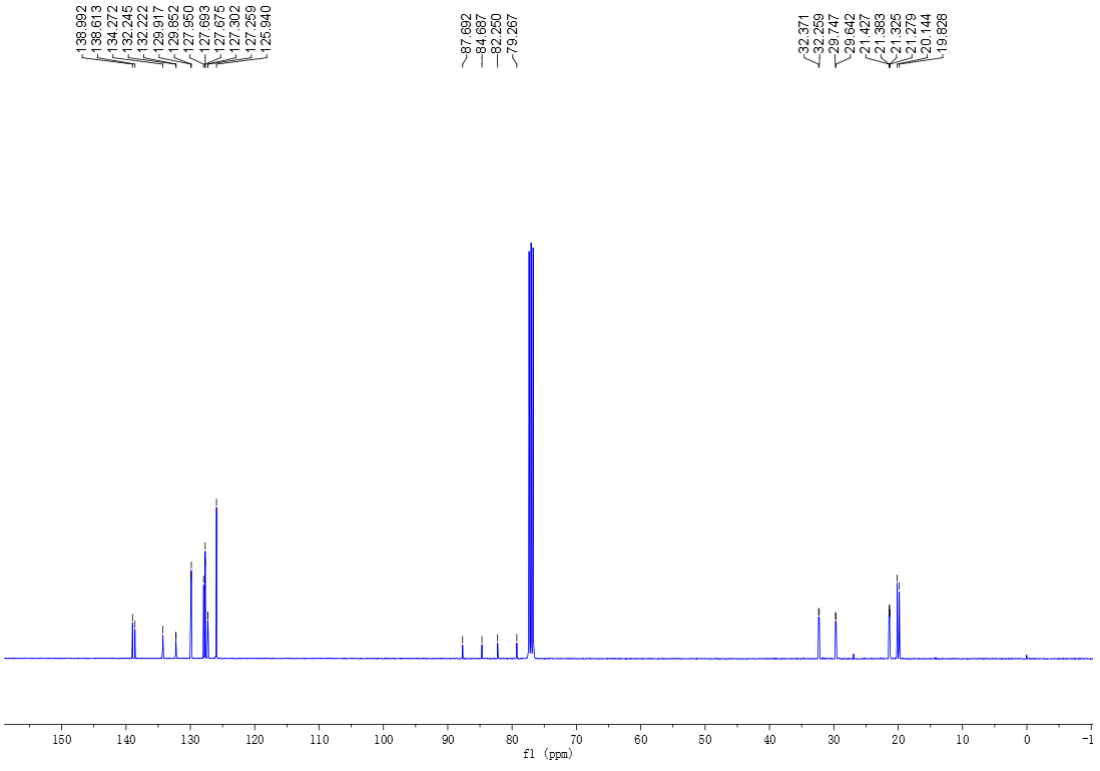
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


19F NMR
Br
F
+
3i
F
Br


127.70
127.75
127.79
145.78
145.81
145.83
1.00
0.86
90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
-170
f1 (ppm)


13C NMR
Br
F
+
F
Br
3i


138.992
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134.272
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129.917
129.852
127.950
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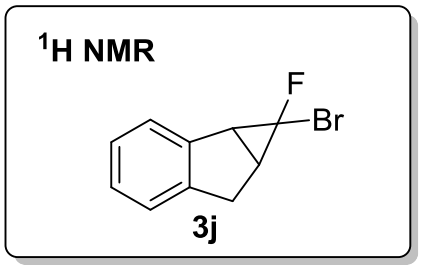
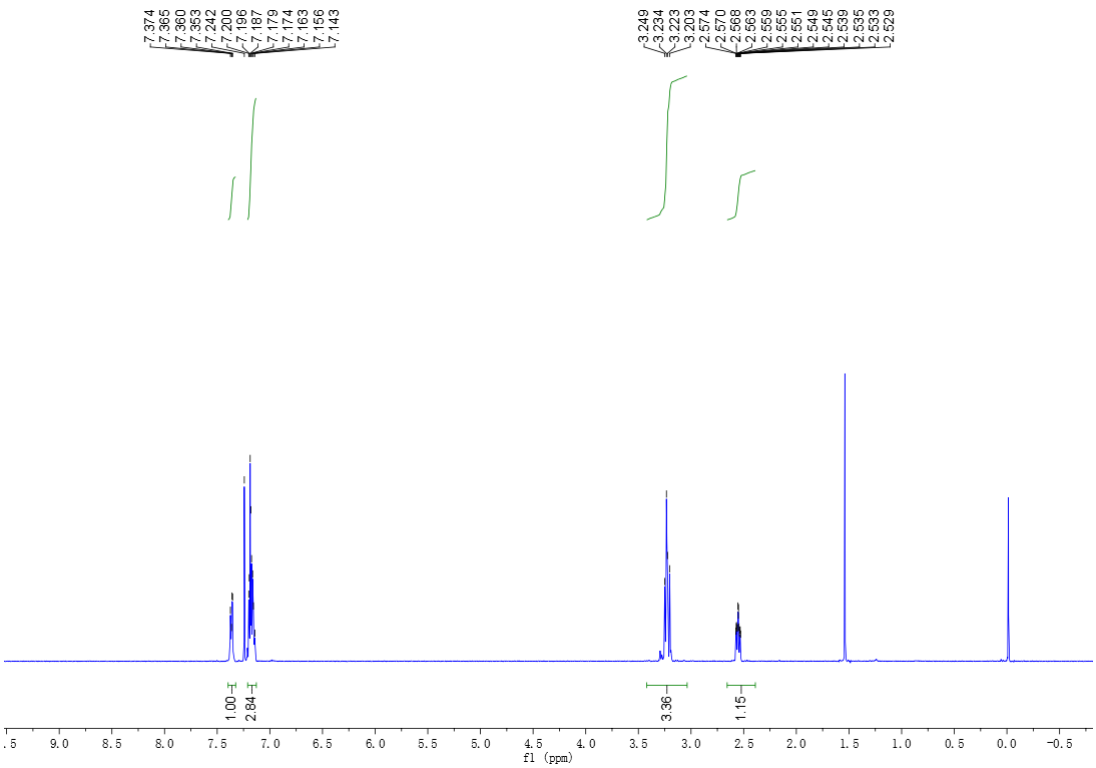
127.675
127.302
127.259
125.940
87.692
84.687
82.250
79.267
32.371
32.259
29.747
29.642
21.427
21.383
21.325
21.279
20.144
19.828
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


1H NMR
F
Br
3j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7.242
7.200
7.196
7.187
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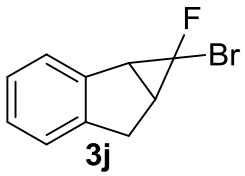
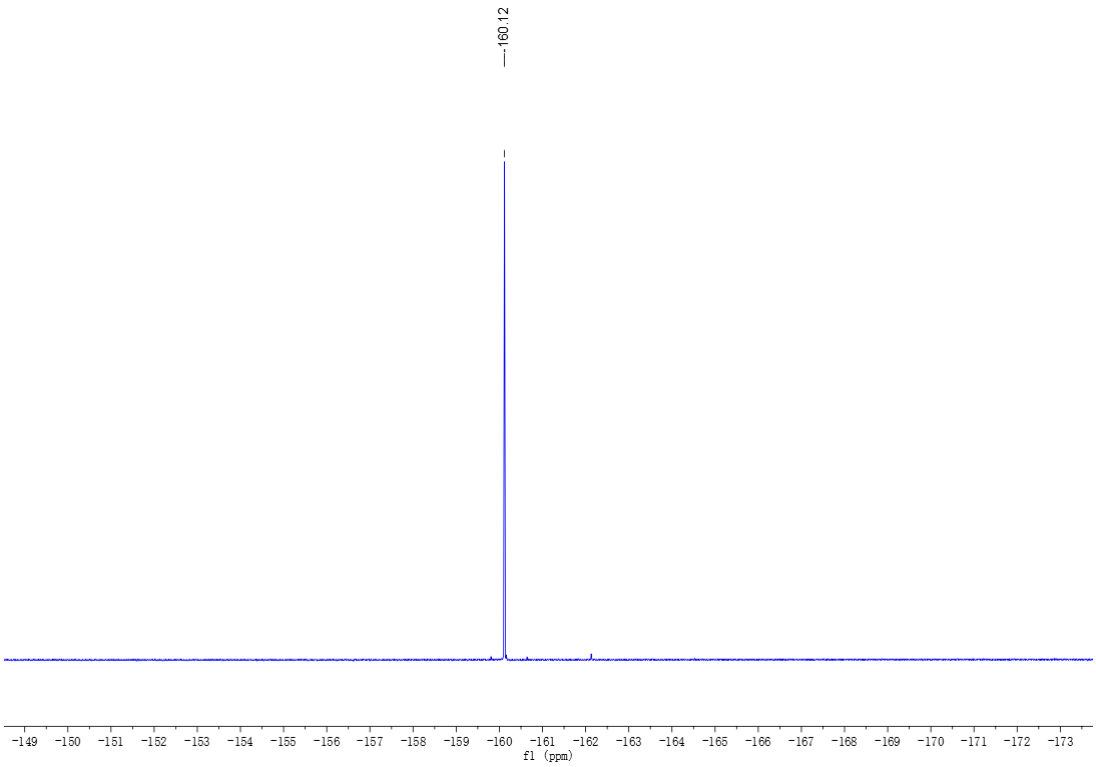
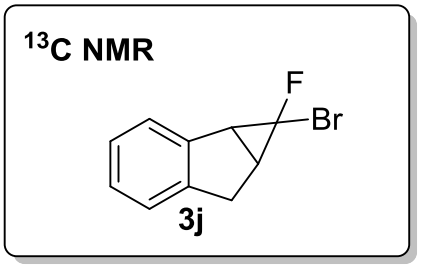
7.174
7.163
7.156
7.143
3.249
3.234
3.223
3.203
2.574
2.570
2.568
2.563
2.559
2.555
2.551
2.549
2.545
2.539
2.535
2.533
2.529
1.00
2.84
3.36
1.15
f1 (ppm)

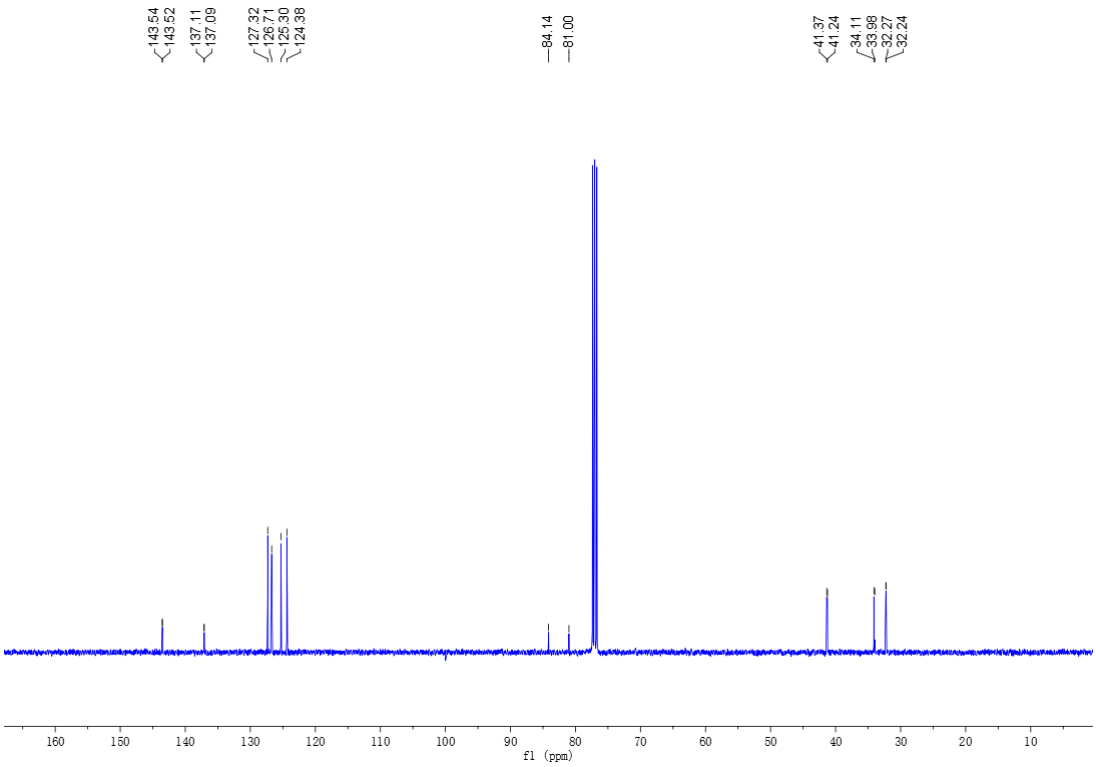
^{19}F NMR


F
Br

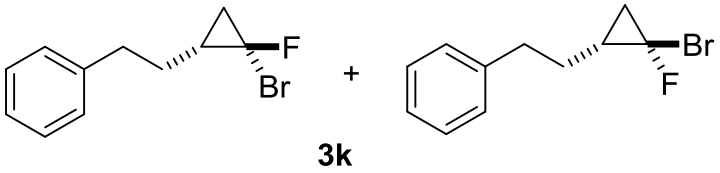
3j


-160.12
-149 -150 -151 -152 -153 -154 -155 -156 -157 -158 -159 -160 -161 -162 -163 -164 -165 -166 -167 -168 -169 -170 -171 -172 -173
f1 (ppm)

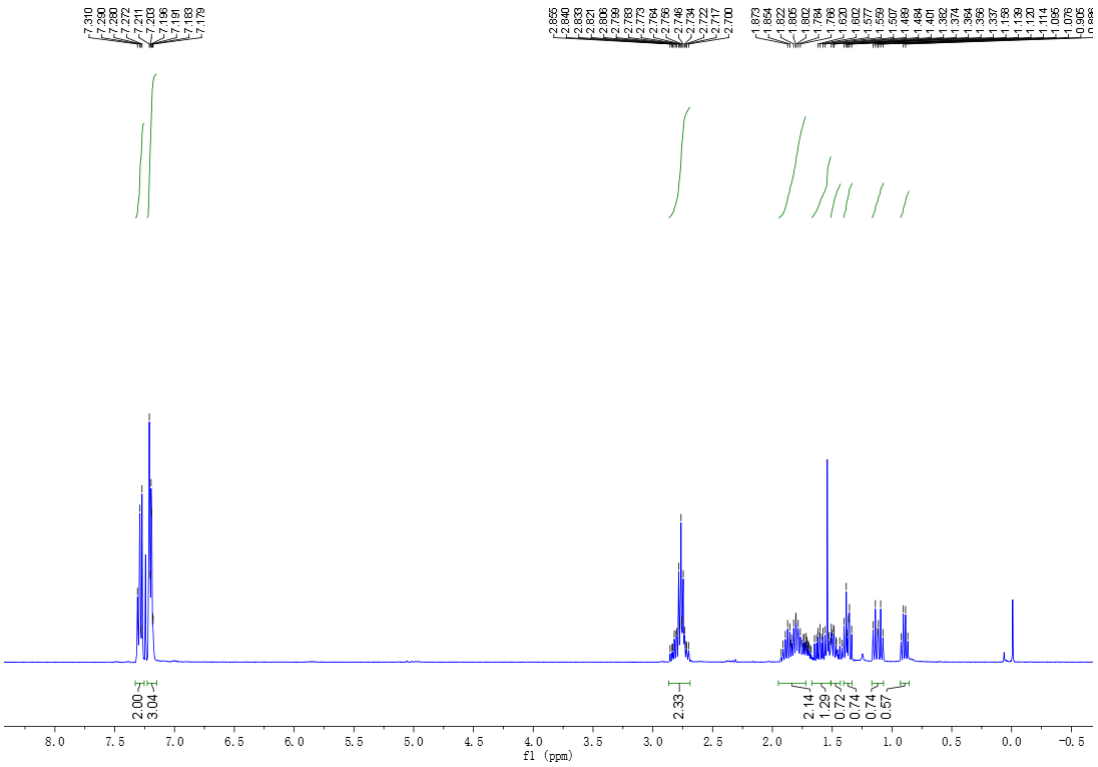

13C NMR
F
Br
3j


143.54
143.52
137.11
137.09
127.32
126.71
125.30
124.38
84.14
81.00
41.37
41.24
34.11
33.98
32.27
32.24
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{1}H NMR


F
Br
+
Br
F

3k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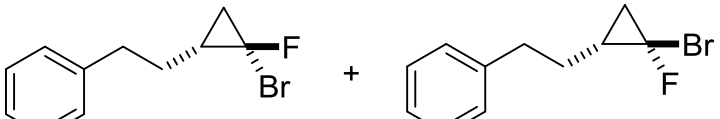
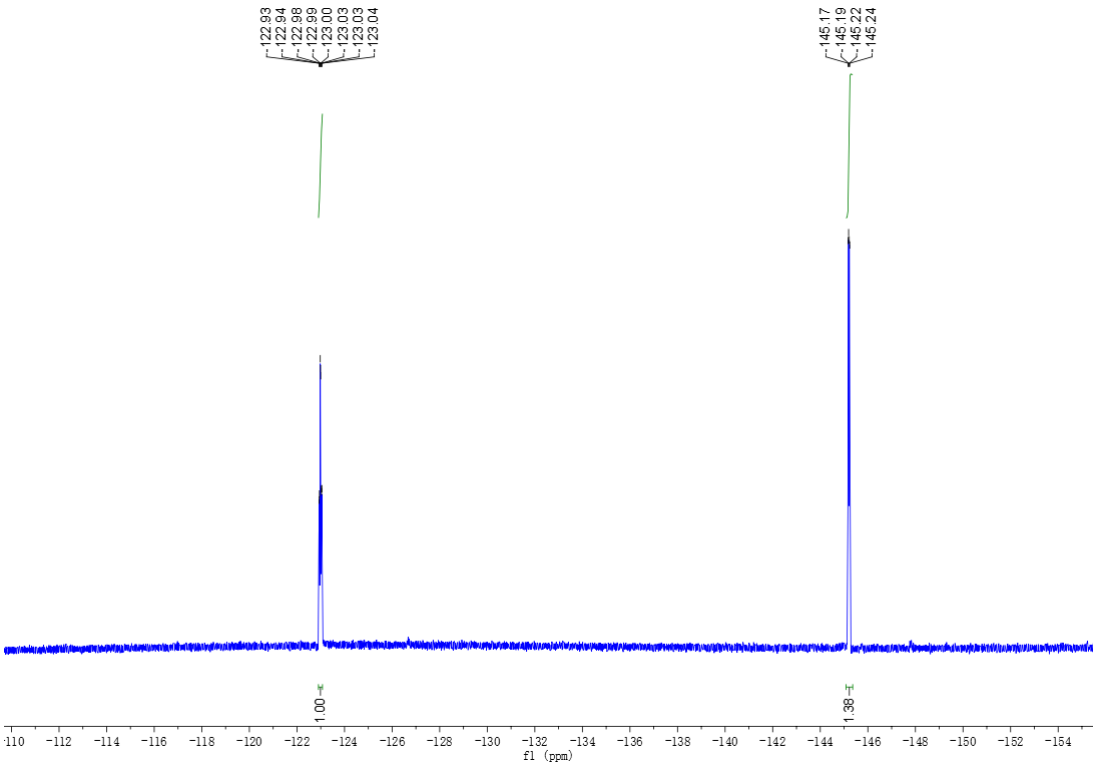
7.290
7.280
7.272
7.211
7.203
7.196
7.191
7.183
7.179
2.855
2.840
2.833
2.821
2.805
2.796
2.783
2.773
2.764
2.756
2.746
2.734
2.722
2.717
2.700
1.873
1.854
1.822
1.805
1.802
1.794
1.786
1.620
1.602
1.577
1.559
1.507
1.489
1.484
1.401
1.382
1.374
1.364
1.356
1.337
1.158
1.139
1.120
1.114
1.096
1.076
1.065
0.884
2.00
3.04
2.33
2.14
1.29
0.72
0.74
0.74
0.57
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

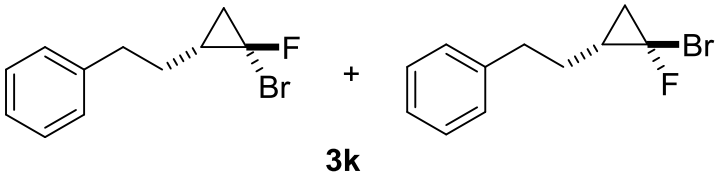
^{19}F NMR


F
Br
+
Br
F

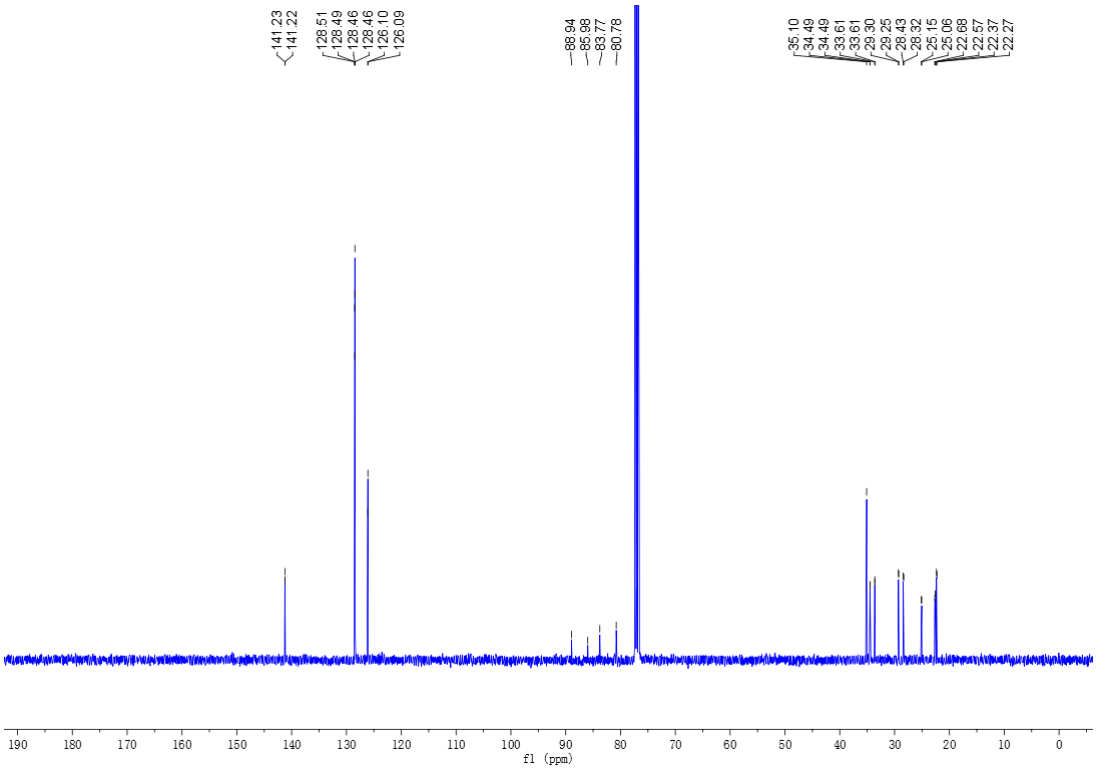
3k


122.93
122.94
122.98
122.99
123.00
123.03
123.03
123.04
145.17
145.19
145.22
145.24
1.00
1.38
f1 (ppm)

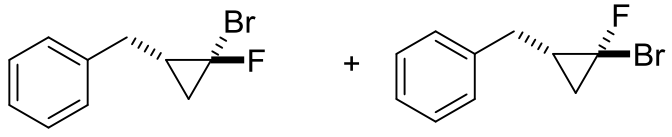
^{13}C NMR


F
Br
+
Br
F

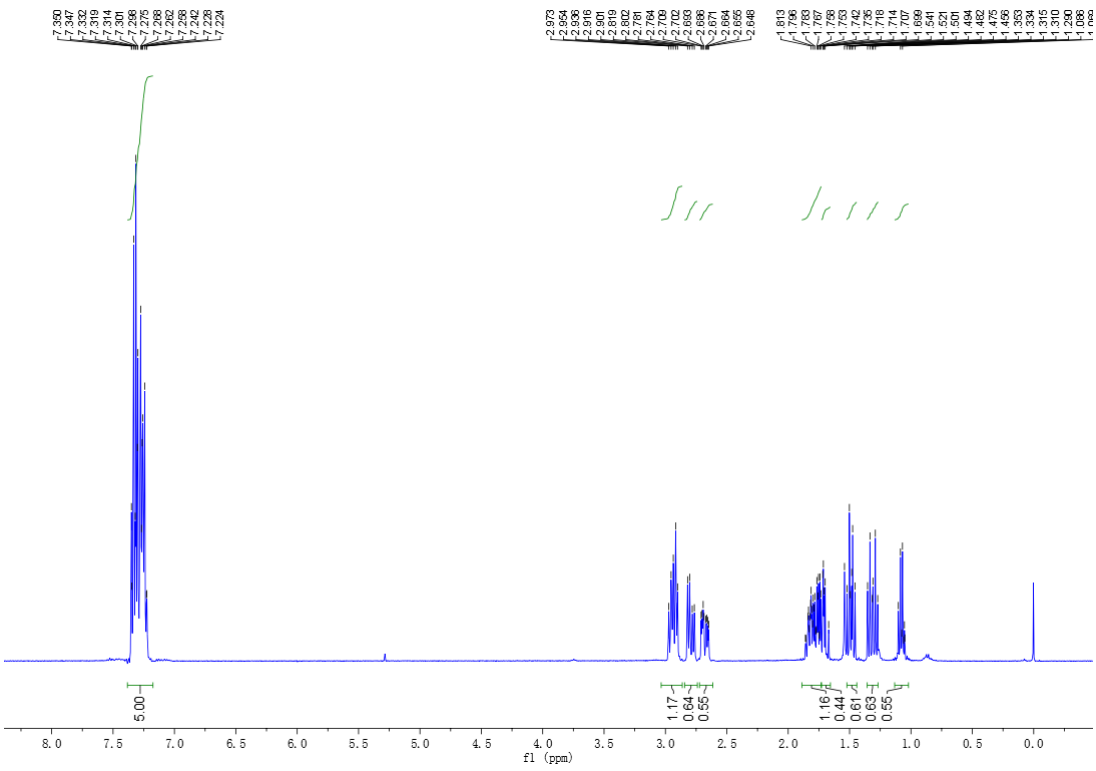
3k


141.23
141.22
128.51
128.49
128.46
128.46
126.10
126.09
88.94
85.98
83.77
80.78
35.10
34.49
34.49
33.61
33.61
29.30
29.25
28.43
28.32
25.15
25.06
22.68
22.57
22.37
22.27
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H NMR


Br
F
+
F
Br

3l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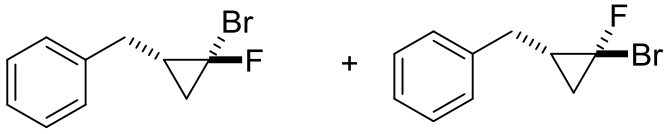
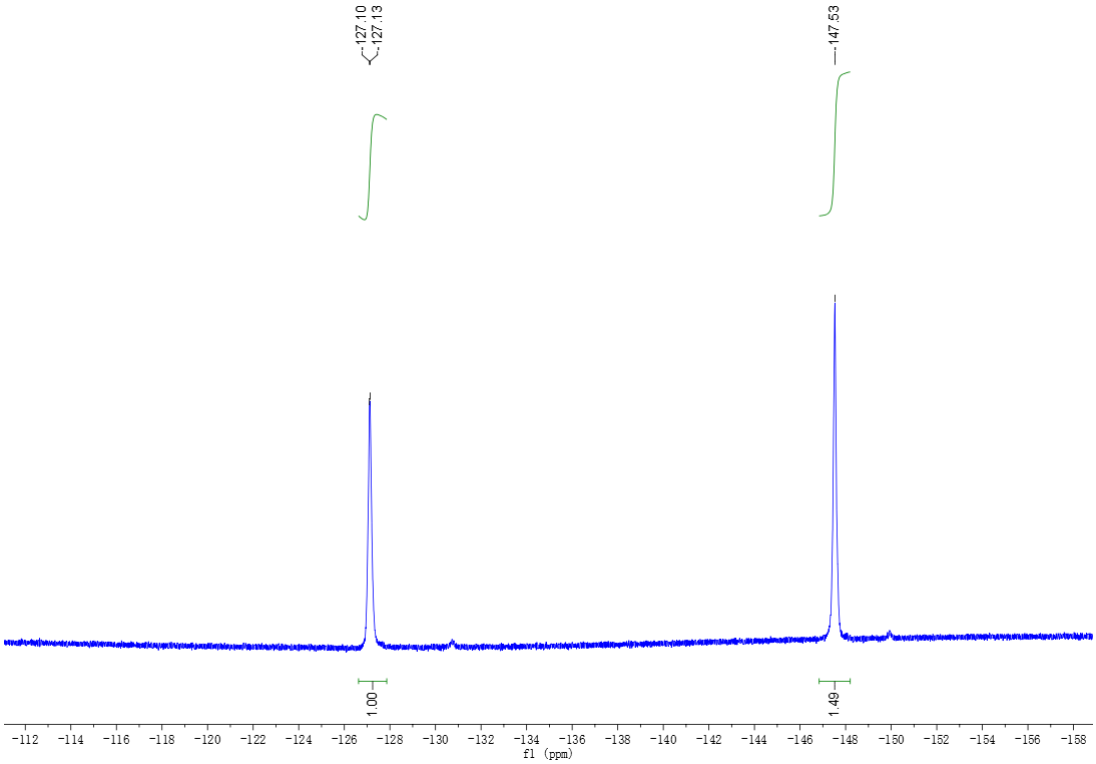
7.347
7.332
7.319
7.314
7.301
7.298
7.275
7.268
7.262
7.256
7.242
7.228
7.224
2.973
2.954
2.935
2.916
2.901
2.819
2.802
2.781
2.764
2.709
2.702
2.686
2.671
2.664
2.655
2.648
1.813
1.796
1.783
1.767
1.758
1.753
1.742
1.735
1.718
1.714
1.707
1.699
1.541
1.521
1.501
1.494
1.482
1.475
1.456
1.353
1.334
1.315
1.310
1.290
1.265
1.164
5.00
1.17
0.64
0.55
1.16
0.44
0.61
0.63
0.55
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

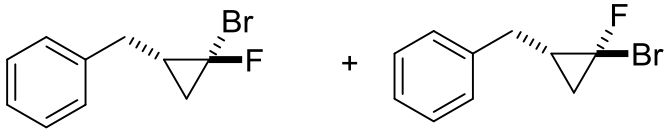
^{19}F NMR


Br
F
+
F
Br

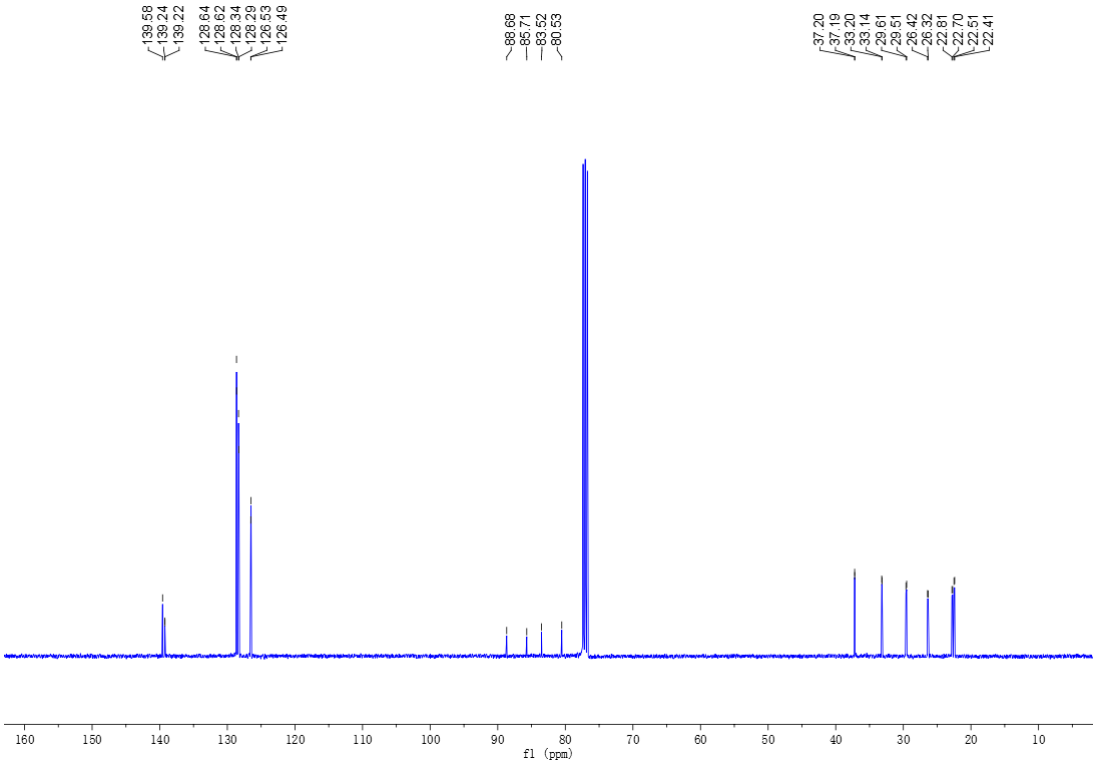
3l

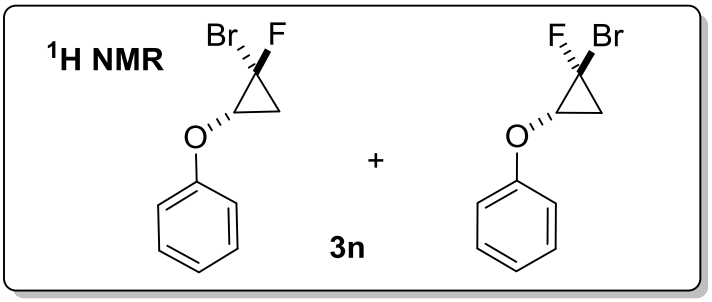

127.10
127.13
147.53
1.00
1.49
-112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150 -152 -154 -156 -158
f1 (ppm)

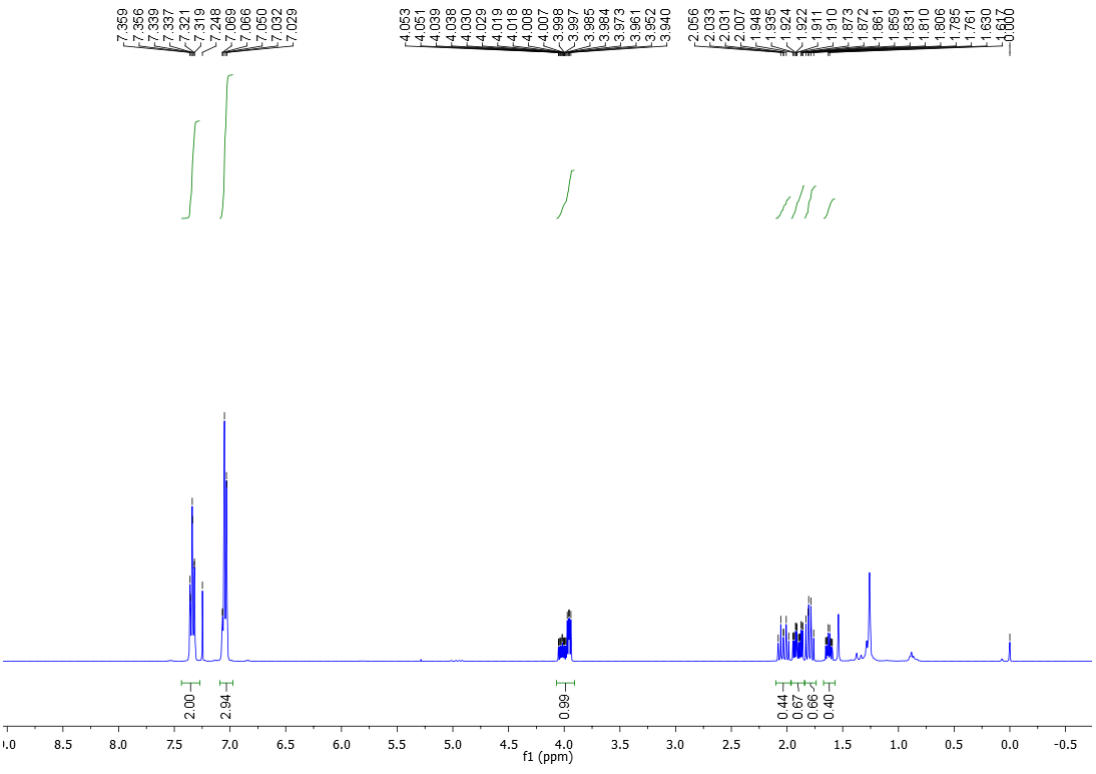
^{13}C NMR

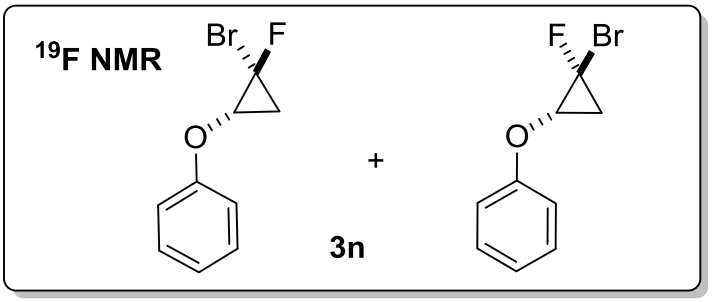

Br
F
+
F
Br

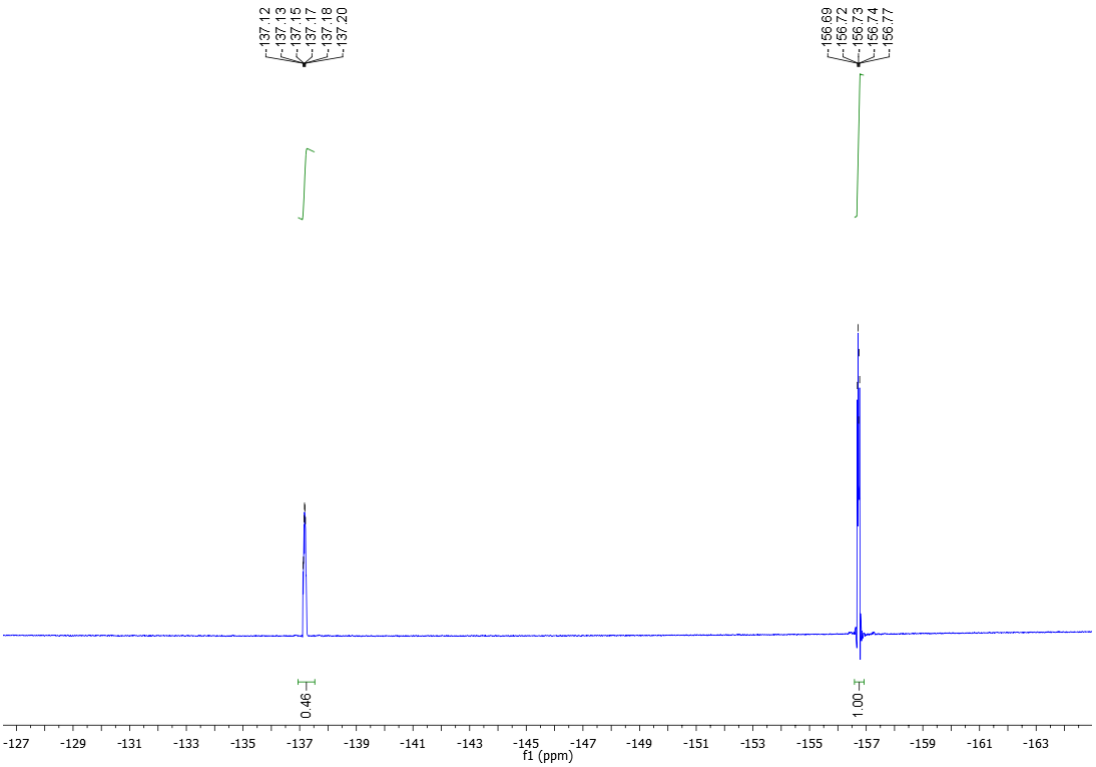
3l

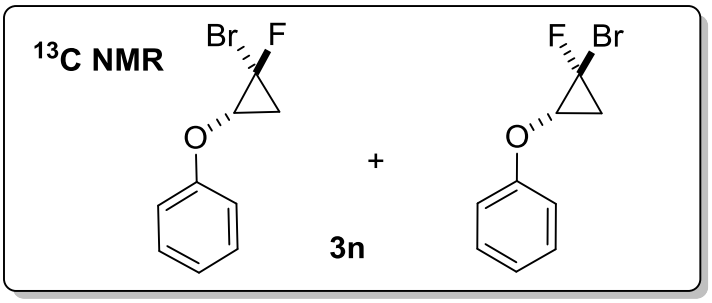

139.58
139.24
139.22
128.64
128.62
128.34
128.29
126.53
126.49
88.68
85.71
83.52
80.53
37.20
37.19
33.20
33.14
29.61
29.51
26.42
26.32
22.81
22.70
22.51
22.41
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

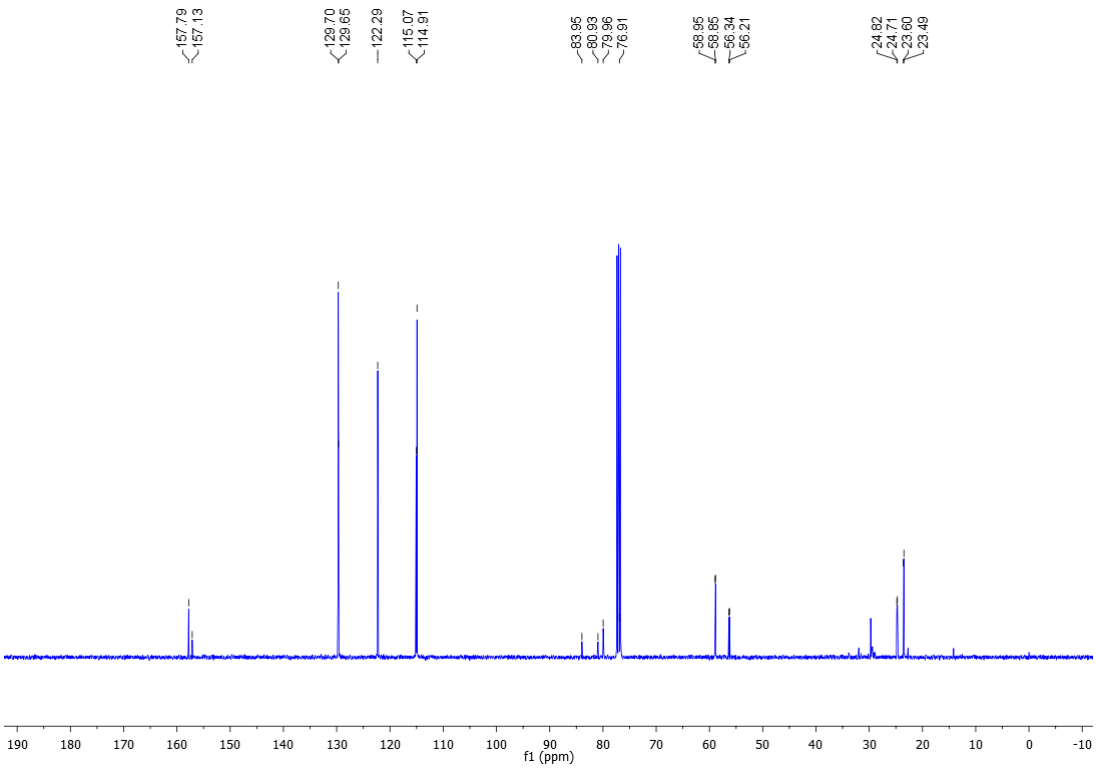

^{1}H NMR
Br
F
O
+
F
Br
O
3n

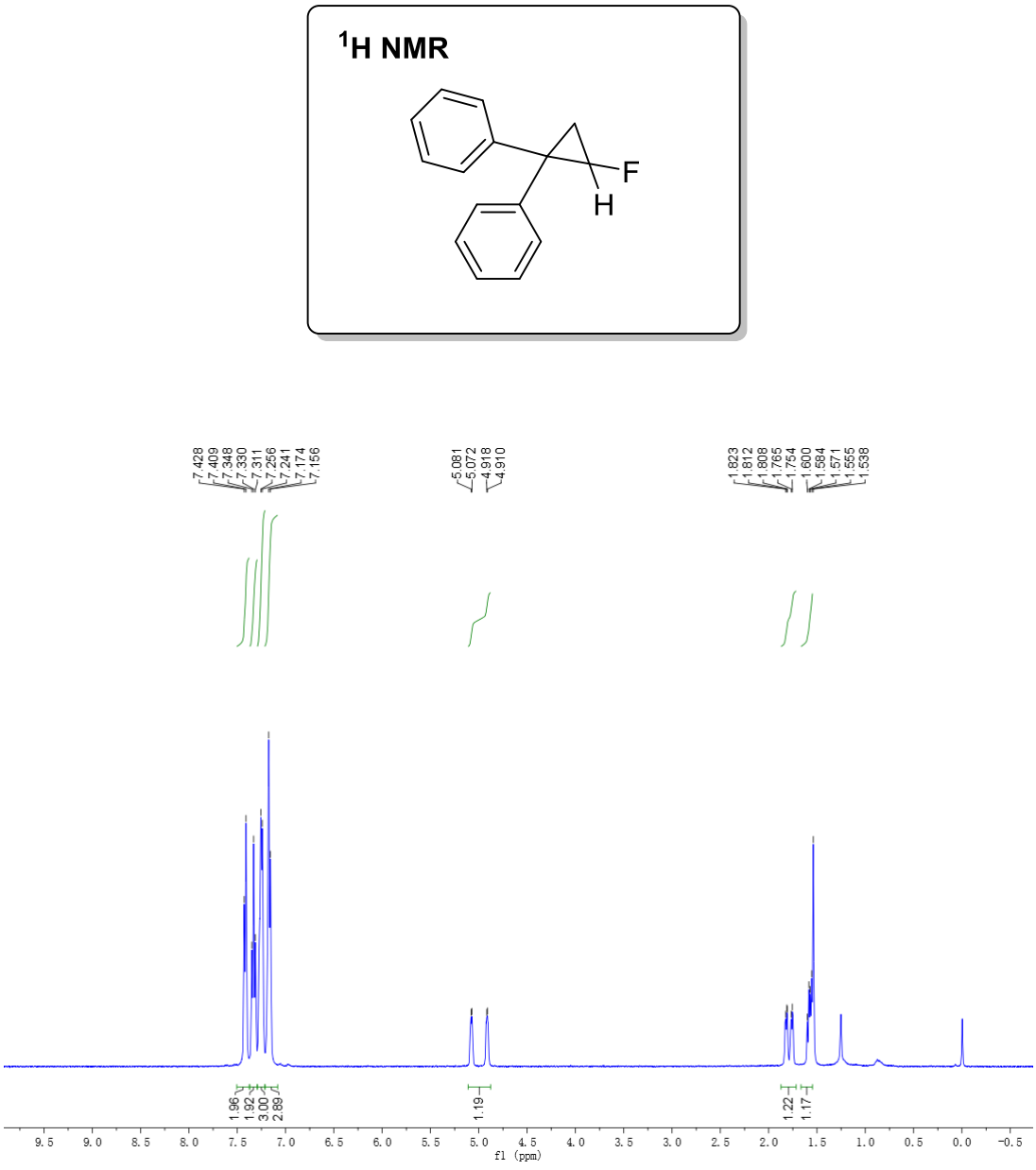

7.359
7.356
7.339
7.337
7.321
7.319
7.248
7.069
7.066
7.050
7.032
7.029
4.053
4.051
4.039
4.038
4.030
4.029
4.019
4.018
4.008
4.007
3.998
3.997
3.985
3.984
3.973
3.961
3.952
3.940
2.056
2.033
2.031
2.007
1.948
1.935
1.924
1.922
1.911
1.910
1.873
1.872
1.861
1.859
1.831
1.810
1.806
1.785
1.761
1.690
0.807
0.000
2.00
2.94
0.99
0.44
0.67
0.66
0.40
f1 (ppm)

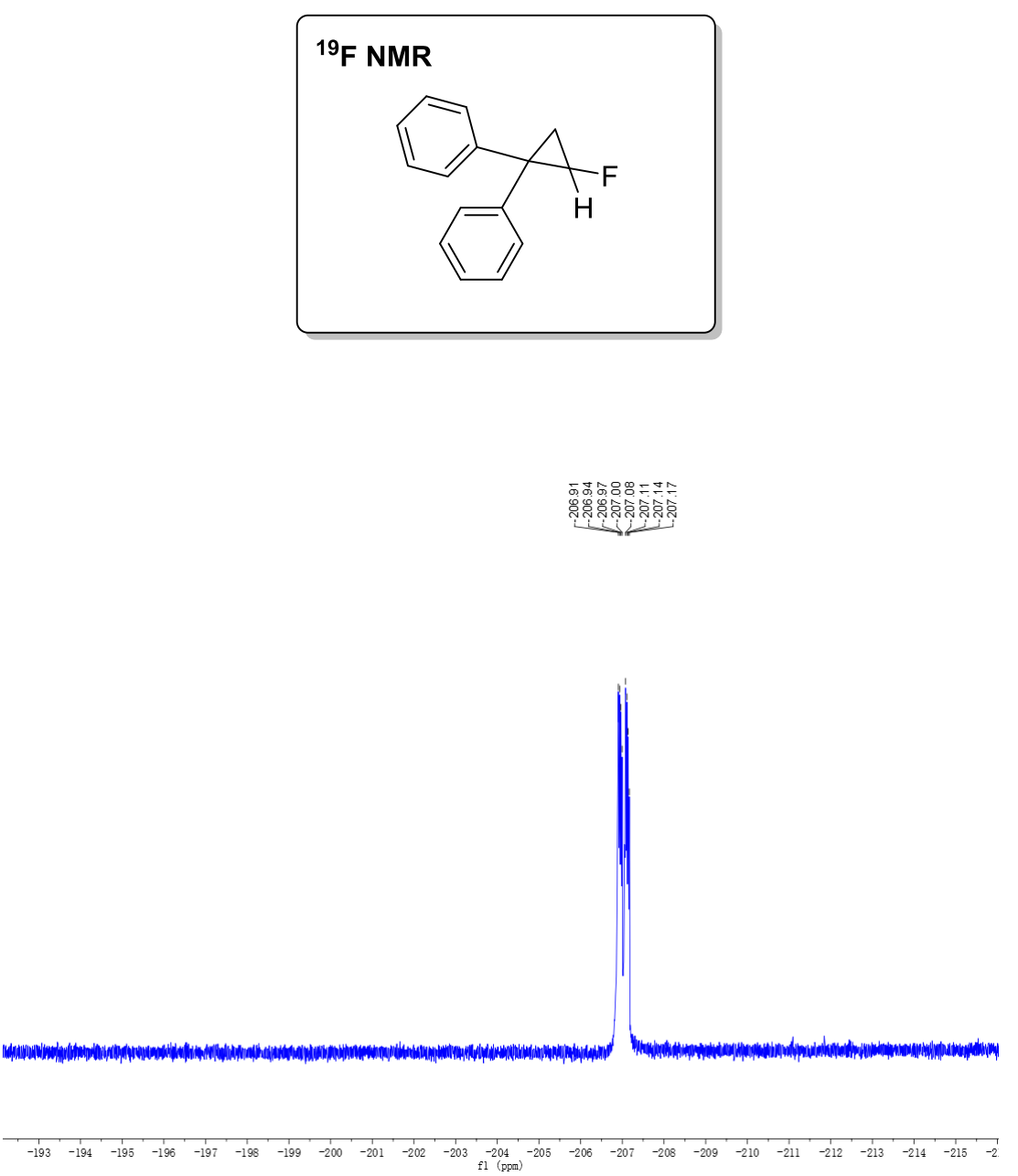

19F NMR
Br
F
O
+
F
Br
O
3n


137.12
137.13
137.15
137.17
137.18
137.20
156.69
156.72
156.73
156.74
156.77
0.46
1.00
-127
-129
-131
-133
-135
-137
-139
-141
-143
-145
-147
-149
-151
-153
-155
-157
-159
-161
-163
f1 (ppm)

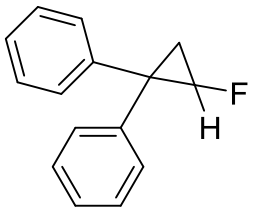

13C NMR
Br
F
O
+
F
Br
O
3n

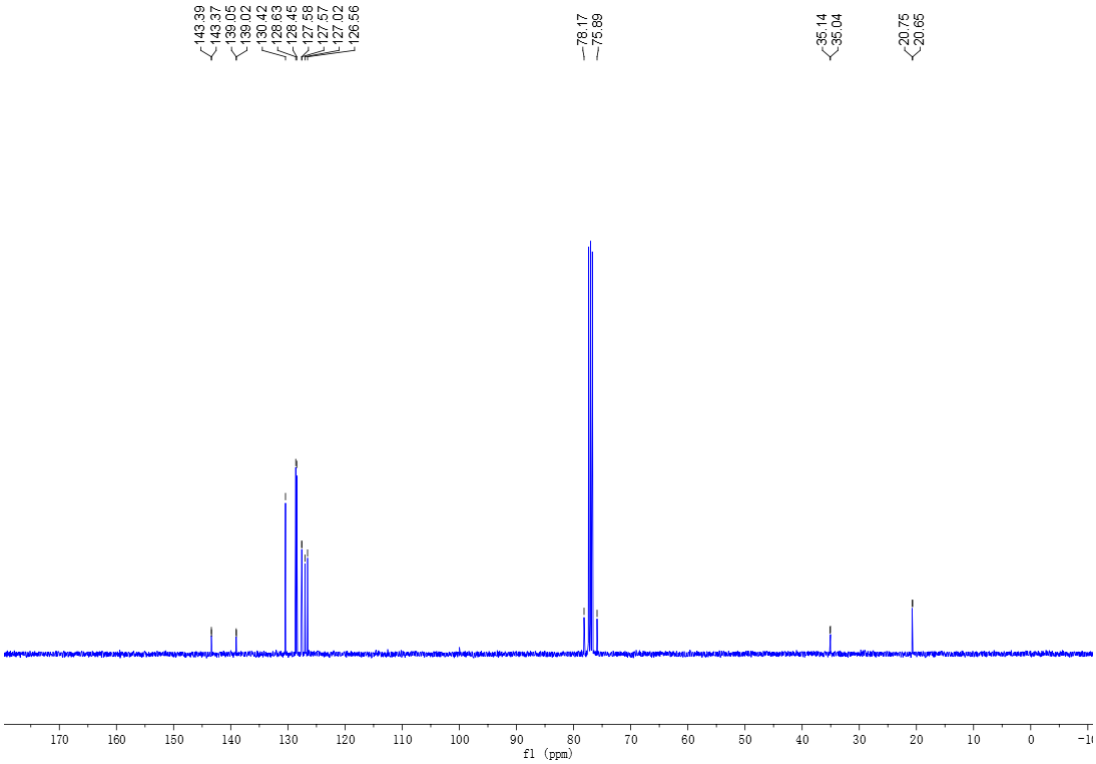

157.79
157.13
129.70
129.65
122.29
115.07
114.91
83.95
80.93
79.96
76.91
58.95
58.85
56.34
56.21
24.82
24.71
23.60
23.49
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

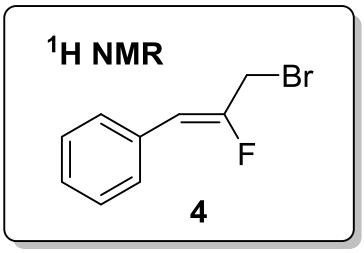

1H NMR
F
H
7.428
7.409
7.348
7.330
7.311
7.256
7.241
7.174
7.156
5.081
5.072
4.918
4.910
1.823
1.812
1.808
1.765
1.754
1.600
1.584
1.571
1.555
1.538
1.96
1.92
3.00
2.89
1.19
1.22
1.17
f1 (ppm)

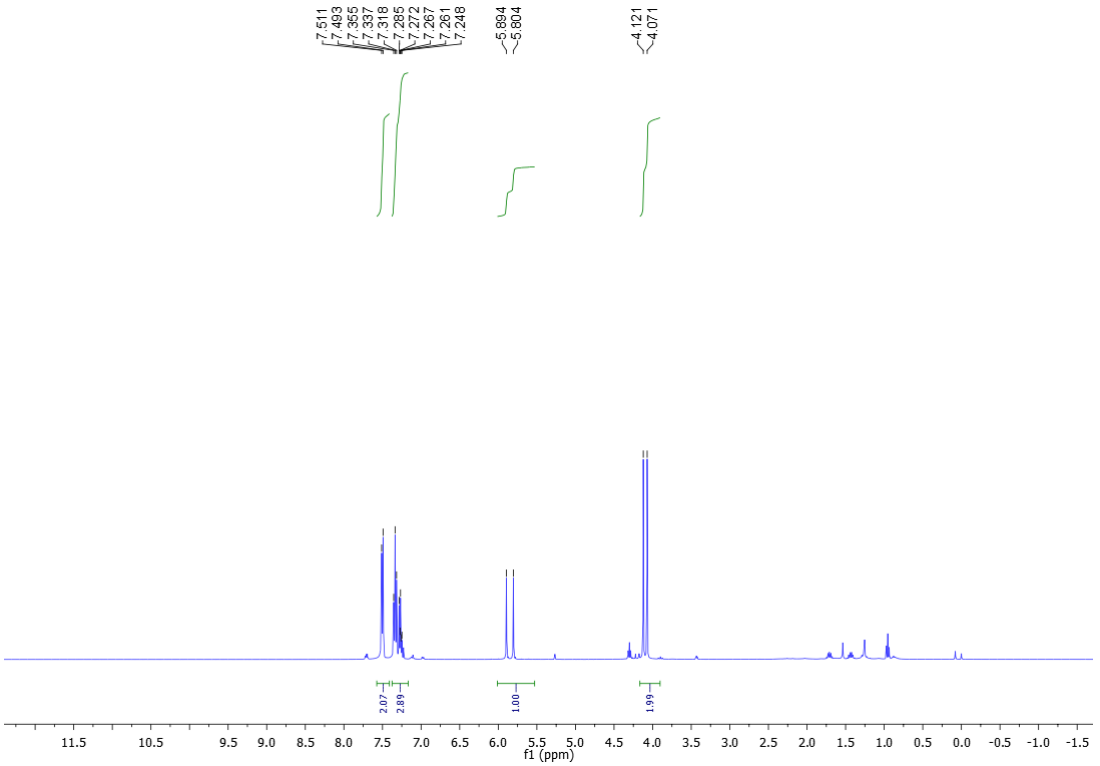

19F NMR
F
H
206.91
206.94
206.97
207.00
207.08
207.11
207.14
207.17
-193
-194
-195
-196
-197
-198
-199
-200
-201
-202
-203
-204
-205
-206
-207
-208
-209
-210
-211
-212
-213
-214
-215
f1 (ppm)

^{13}C NMR


F
H


143.39
143.37
139.05
139.02
130.42
128.63
128.45
127.58
127.57
127.02
126.56
78.17
75.89
35.14
35.04
20.75
20.65
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


^{1}H NMR
Br
F
4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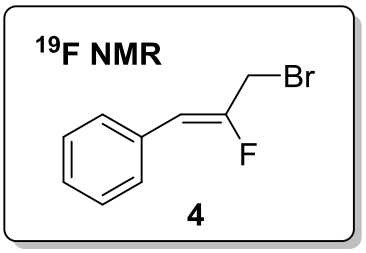
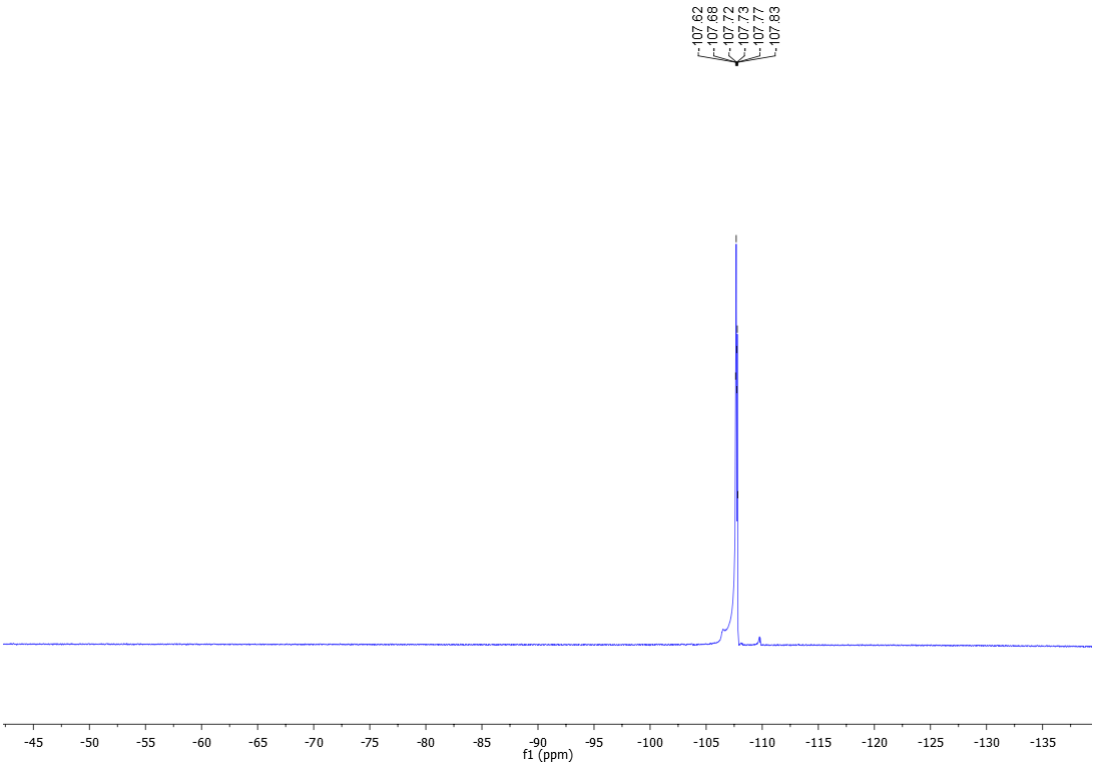
7.285
7.272
7.267
7.261
7.248
5.894
5.804
4.121
4.071
2.07
2.89
1.00
1.99
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)


19F NMR
Br
F
4


-107.62
-107.68
-107.72
-107.73
-107.77
-107.83
-45
-50
-55
-60
-65
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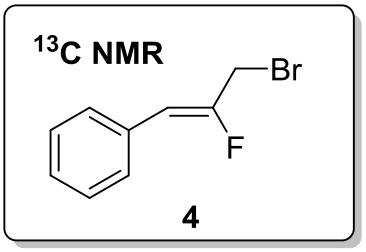
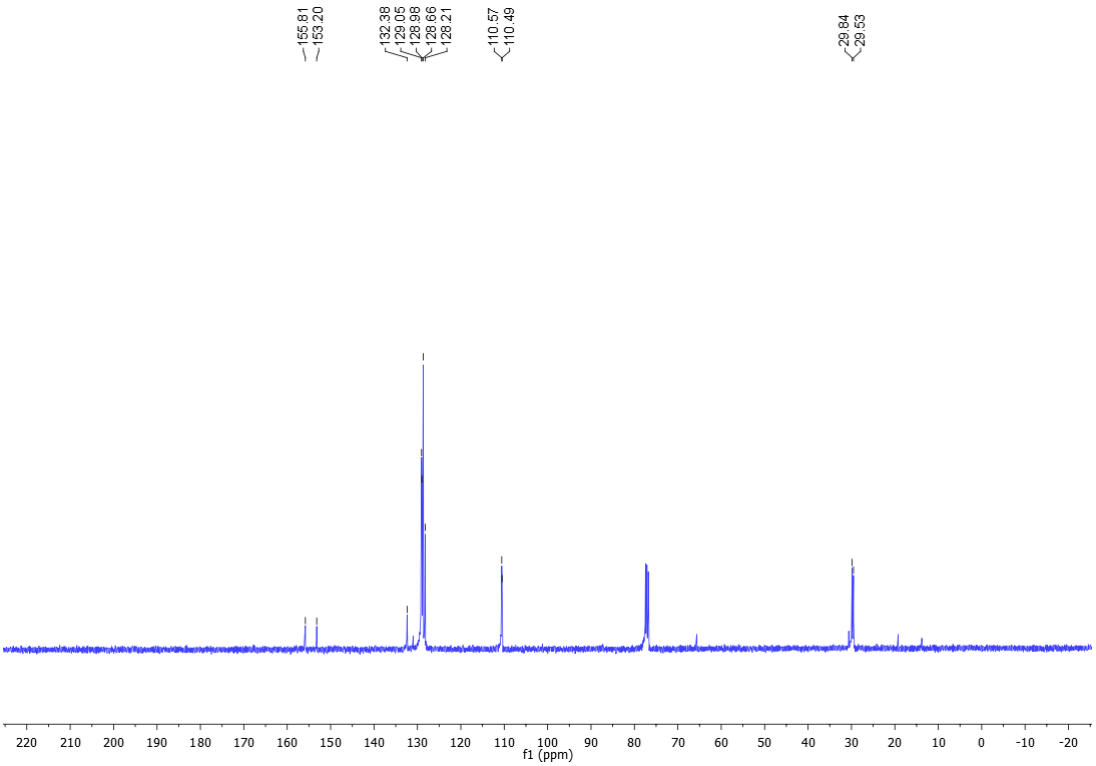
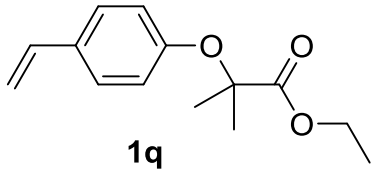
-110
-115
-120
-125
-130
-135
f1 (ppm)

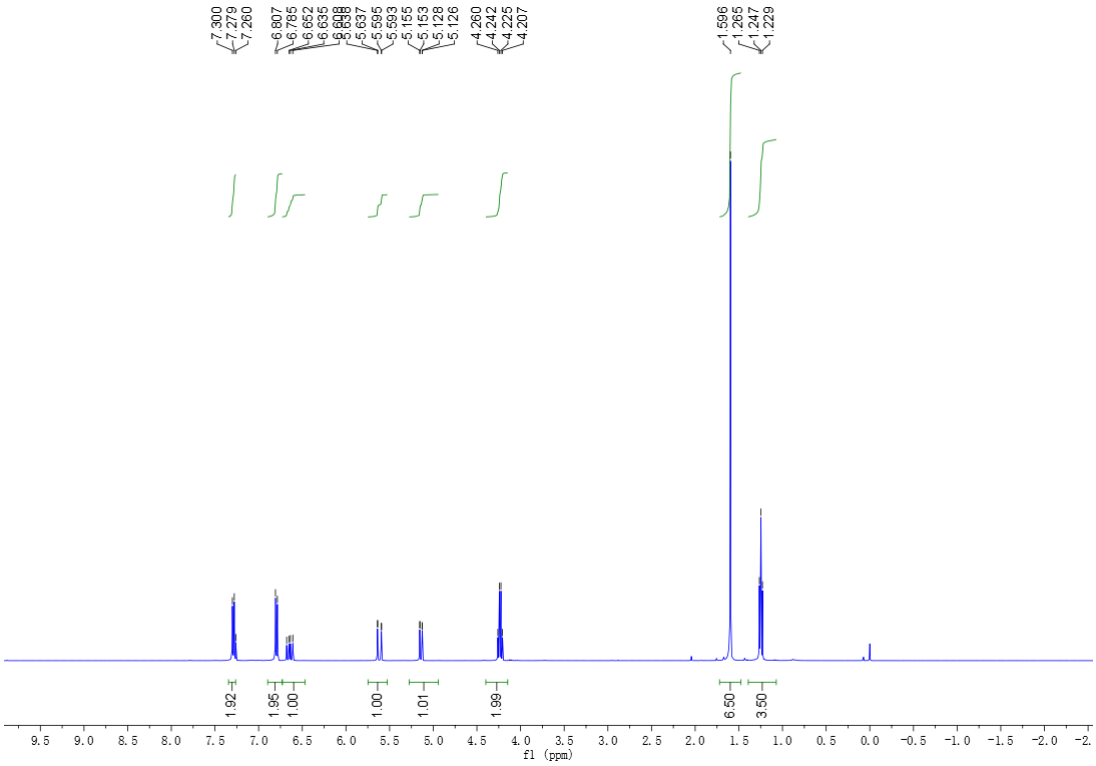

13C NMR
Br
F
4


155.81
153.20
132.38
129.05
128.98
128.66
128.21
110.57
110.49
29.84
29.53
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
f1 (ppm)

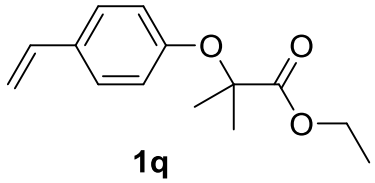
^{1}H NMR



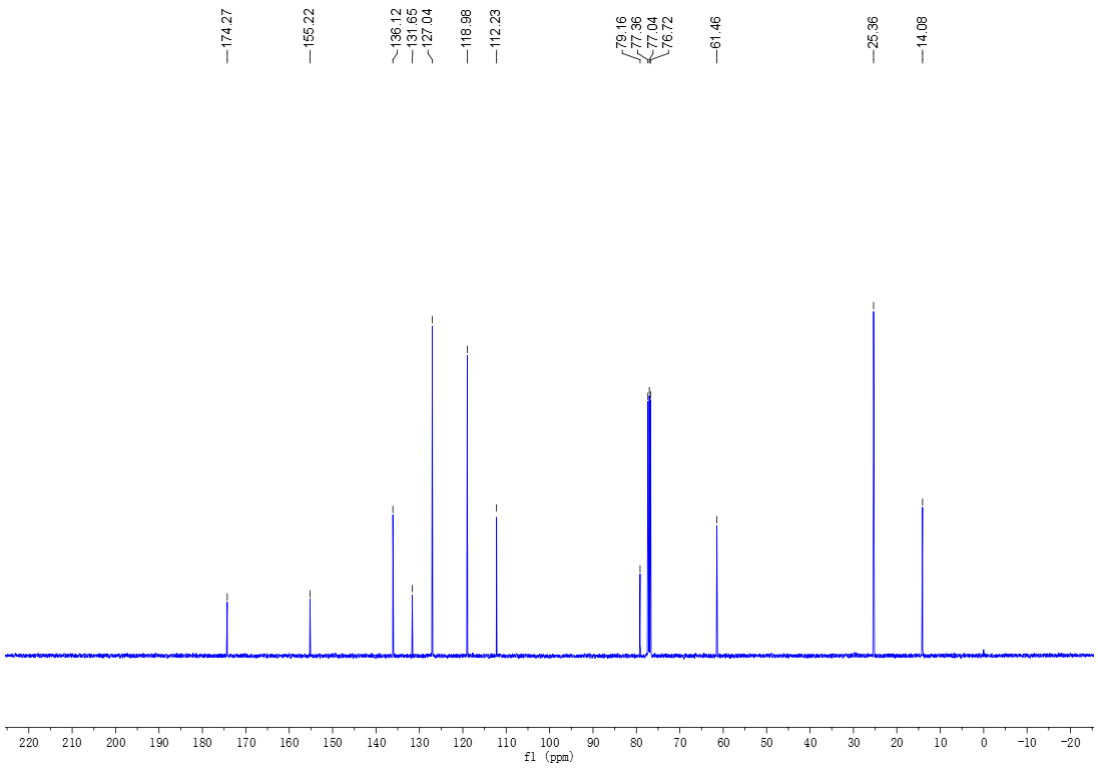
1q

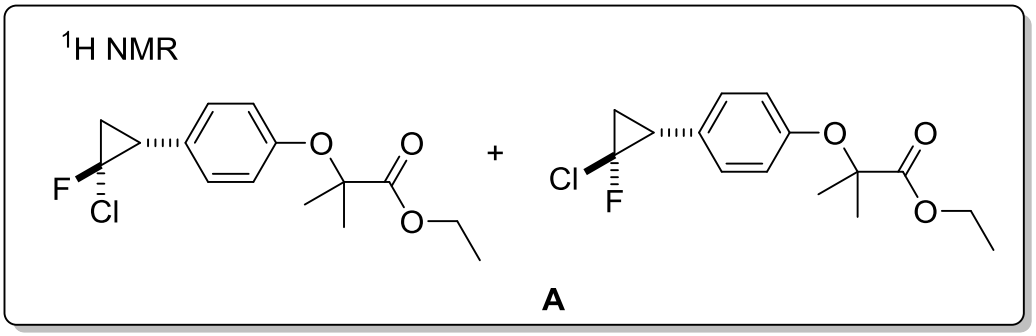

7.300
7.279
7.260
6.907
6.785
6.652
6.635
5.637
5.595
5.593
5.155
5.153
5.128
5.126
4.260
4.242
4.225
4.207
1.596
1.265
1.247
1.229
1.92
1.95
1.00
1.00
1.01
1.99
6.50
3.50
f1 (ppm)

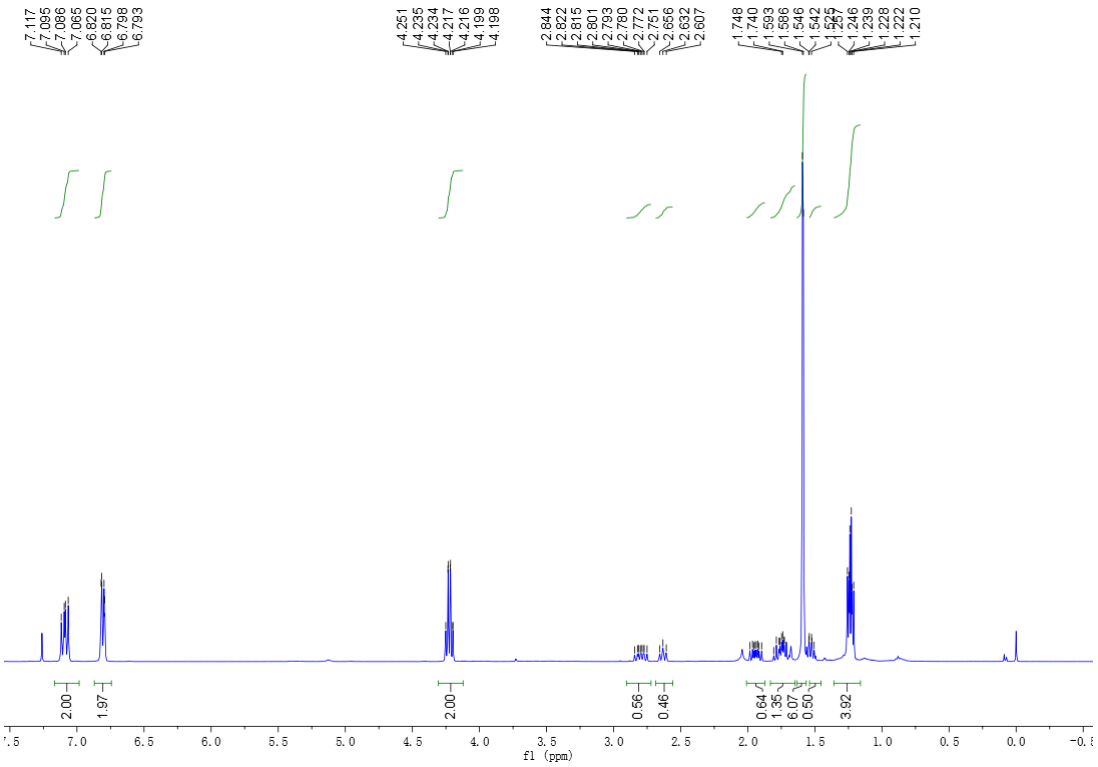
^{13}C NMR



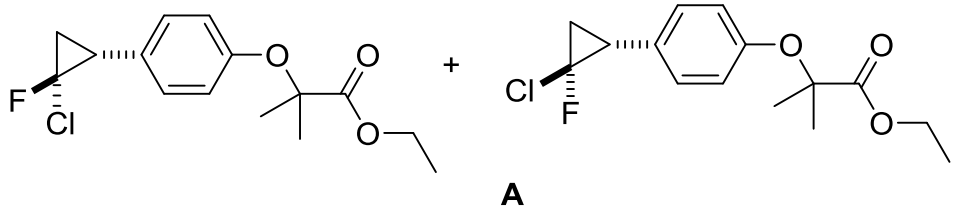
1q


174.27
155.22
136.12
131.65
127.04
118.98
112.23
79.16
77.36
77.04
76.72
61.46
25.36
14.08
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
f1 (ppm)

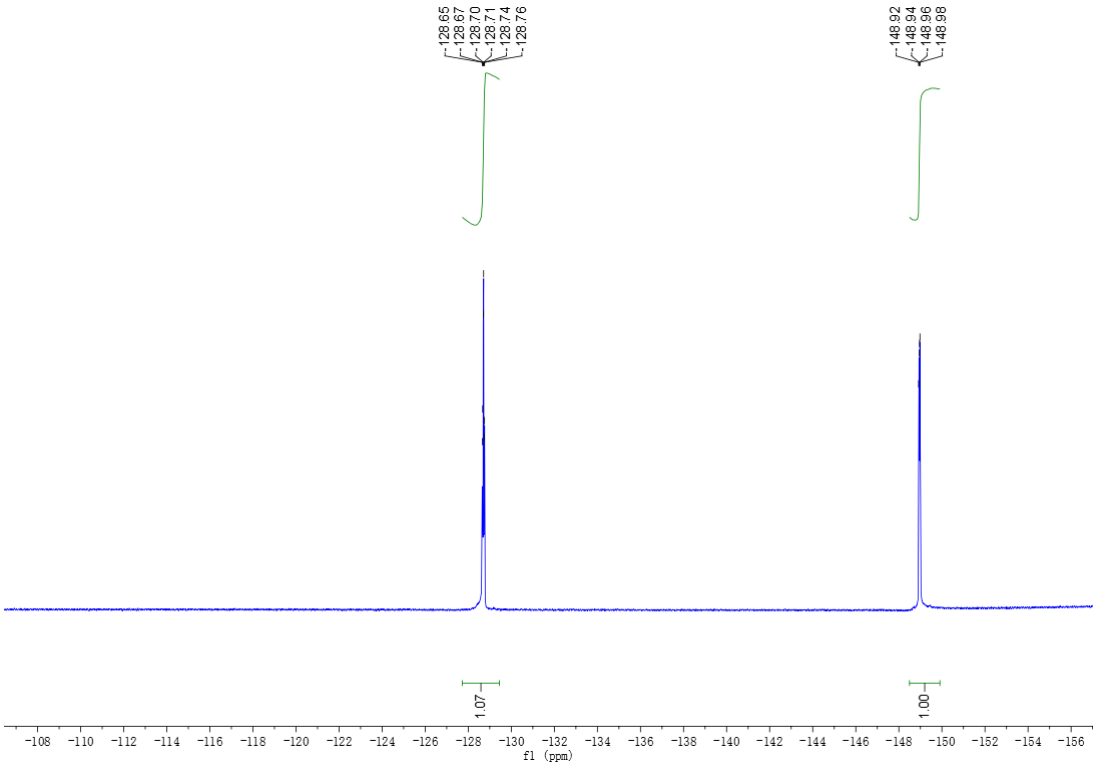

1H NMR
F
Cl
O
O
O
+
Cl
F
O
O
O
A


7.117
7.095
7.086
7.065
6.820
6.815
6.798
6.793
4.251
4.235
4.234
4.217
4.216
4.199
4.198
2.844
2.822
2.615
2.801
2.793
2.780
2.772
2.751
2.656
2.632
2.607
1.748
1.740
1.593
1.586
1.546
1.542
1.246
1.239
1.228
1.222
1.210
2.00
1.97
2.00
0.56
0.46
0.64
1.35
6.07
0.50
3.92
f1 (ppm)

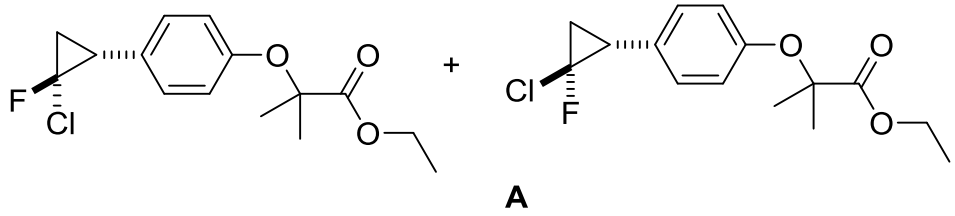
^{19}F NMR


F
Cl
O
O
O
+
Cl
F
O
O
O

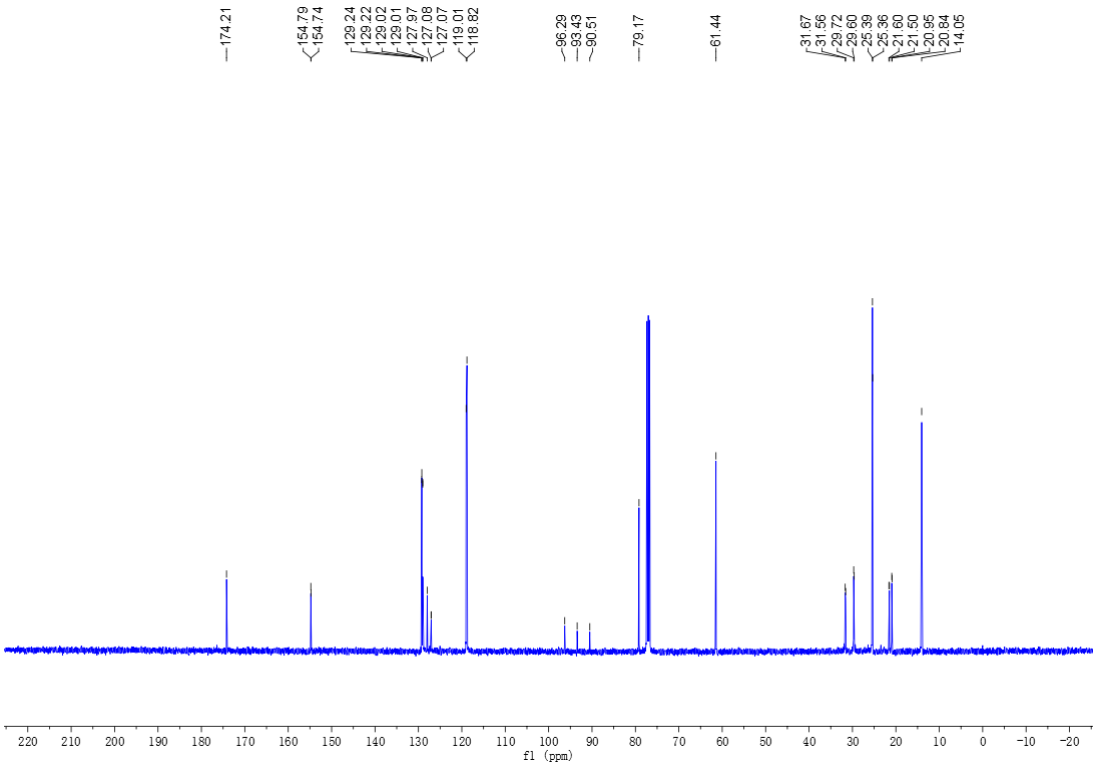
A


128.65
128.67
128.70
128.71
128.74
128.76
148.92
148.94
148.96
148.98
1.07
1.00
-108 -110 -112 -114 -116 -118 -120 -122 -124 -126 -128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150 -152 -154 -156
f1 (ppm)

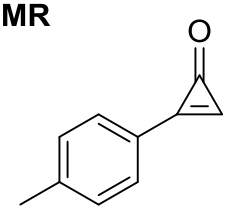
^{13}C NMR

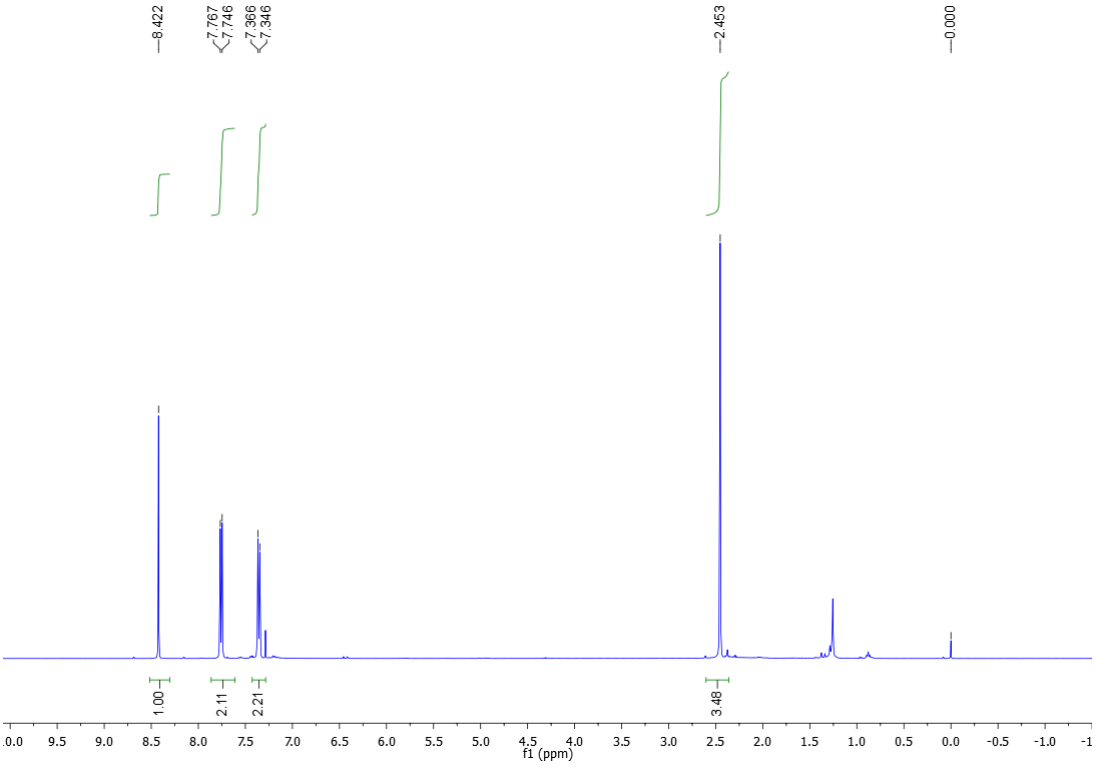


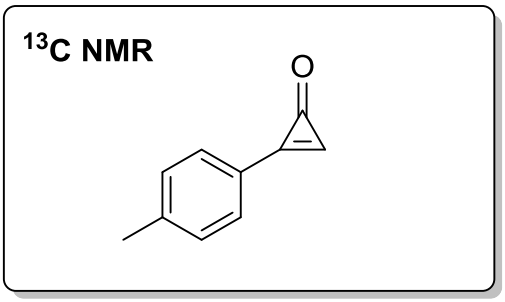
A

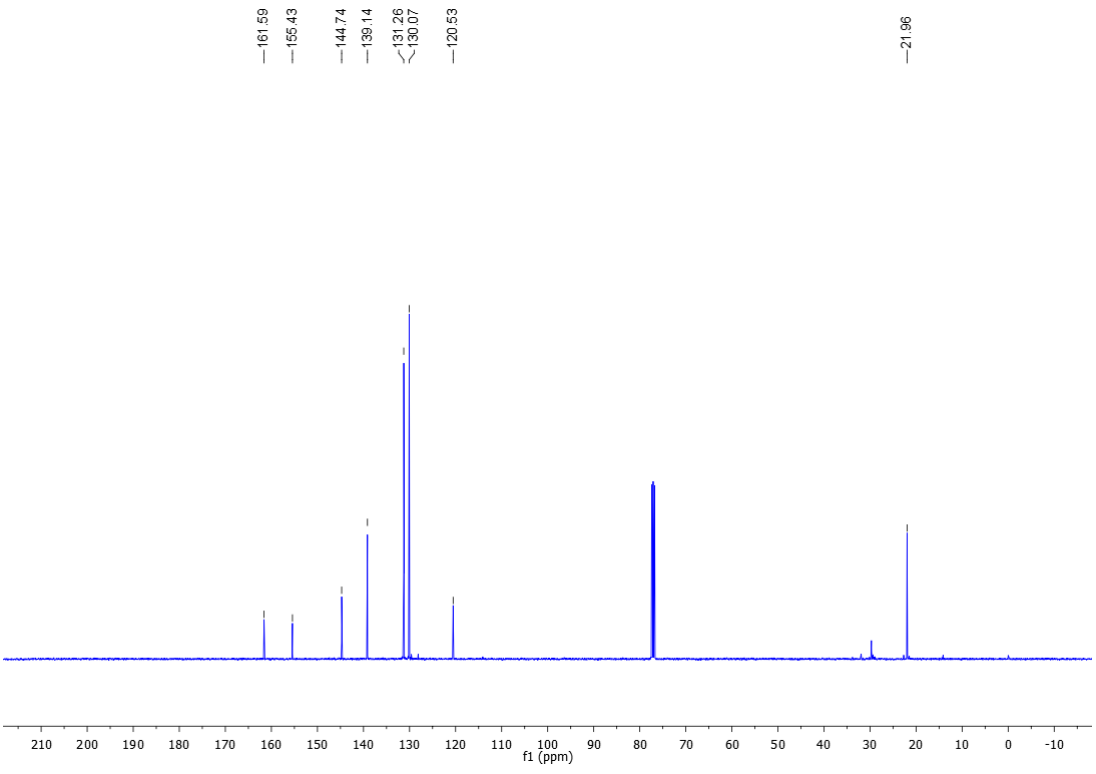

174.21
154.79
154.74
129.24
129.22
129.02
129.01
127.97
127.08
127.07
119.01
118.82
96.29
93.43
90.51
79.17
61.44
31.67
31.56
29.72
29.60
25.39
25.36
21.60
21.50
20.95
20.84
14.05
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

^{1}H NMR






13C NMR
O


161.59
155.43
144.74
139.14
131.26
130.07
120.53
21.96
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)