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Supporting Information

Highly regio- and diastereoselective Cu-catalyzed hydroborylation and hydrosilylation of difluorocyclopropenes with B_2pin_2 and Me_2PhSi-Bpin

Xianghu Zhao, Sixue Xu, Jingjing He, Yao Zhou and Song Cao*

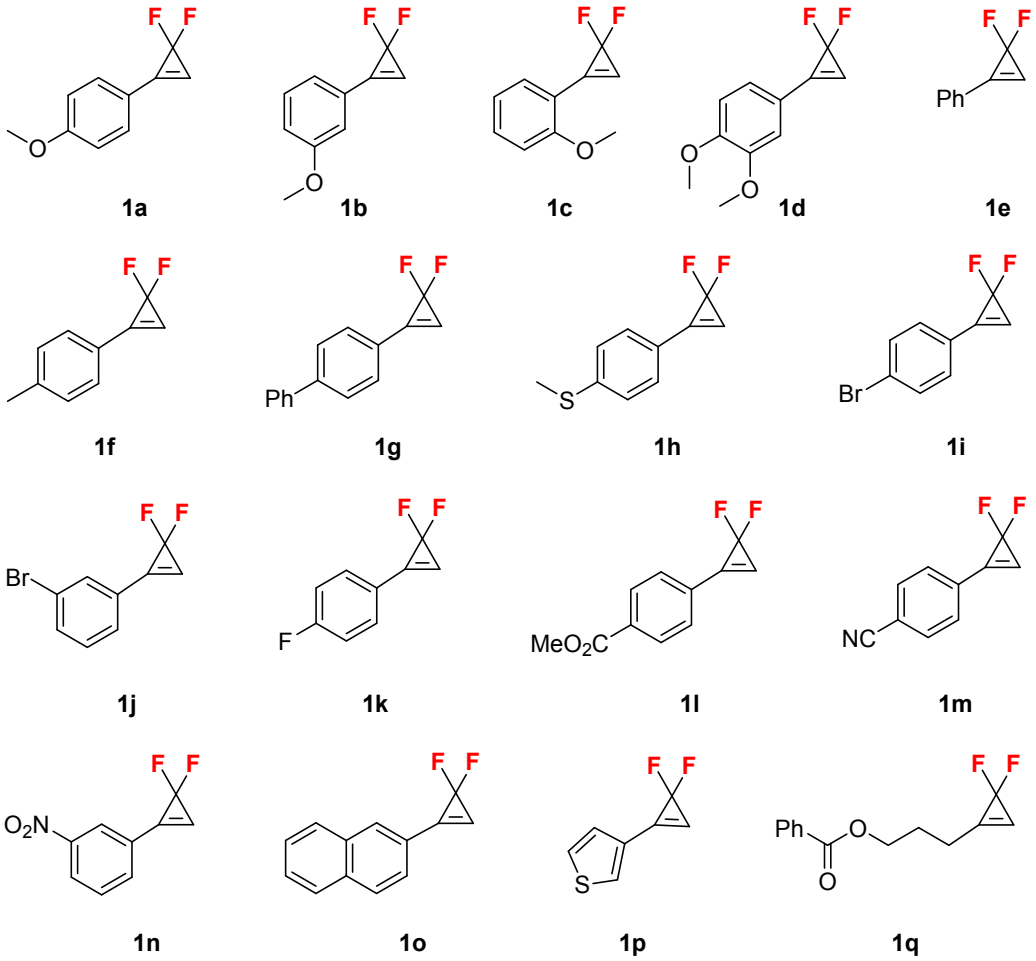
Shanghai Key Laboratory of Chemical Biology, School of Pharmacy, East China University of Science and Technology (*ECUST)*, Shanghai 200237, China

Table of contents

1. General information

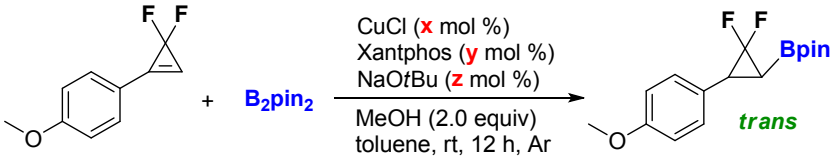
All reagents were of analytical grade, and obtained from commercial suppliers and used without further purification. All *gem*-difluorocyclopropenes were prepared according to previously reported procedures. Toluene and other solvents were dried by standard method prior to use. Melting points were measured in an open capillary using Büchi melting point B-540 apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C, respectively) using TMS as internal standard. The ^{19}F NMR spectra were obtained using a 400 spectrometer (376 MHz). $CDCl_3$ was used as the NMR solvents. High resolution mass spectra (HRMS) were acquired in the electron impact mode (EI) using a TOF mass analyzer. High-resolution mass spectra (ESI) were recorded with a MicroMass LCTTM spectrometer. Silica gel (300–400 mesh size) was used for column chromatography. TLC analysis of reaction mixtures was performed using silica gel plates.

2. The substrates 1a–q used in this reaction



The *gem*-difluorocyclopropenes **1a**–**q** were prepared according to the reported procedure.[1]

3. Table S1 The influence of the amounts of B_2pin_2, CuCl, Xantphos and NaOtBu on the yield of the reaction[a]



1a 2a 3aa

entry	**2a** (equiv)	x	y	z	yield (%)[b]
1	1.5	10	15	12	83
2	2.0	10	15	12	99
3	2.5	10	15	12	99
4	2.0	5	15	12	32
5	2.0	15	15	12	99
6	2.0	10	10	12	89
7	2.0	10	20	12	99
8	2.0	10	15	10	89
9	2.0	10	15	8	60
10	2.0	10	15	20	99

[a]Reaction conditions: **1a** (0.2 mmol), MeOH (2.0 equiv), toluene (2 mL), rt, 12 h, Ar. [b]Yields are determined by GC analysis based on **1a**.

4. General procedures for the synthesis of target compounds

4.1 Cu-catalyzed hydroborylation of various difluorocyclopropenes

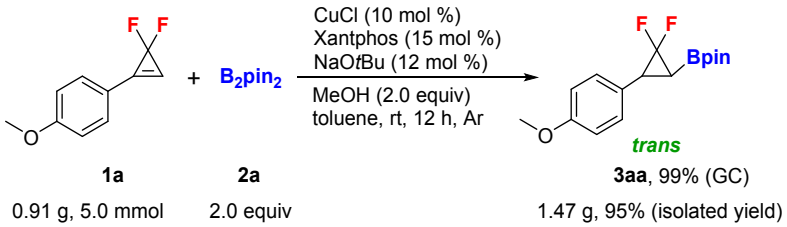
An oven dried Schlenk tube containing a stirring bar was charged with CuCl (2.0 mg, 0.02 mmol, 10 mol%), Xantphos (17.3 mg, 0.03 mmol, 15 mol%), B_2pin_2 **2a** (101.6 mg, 0.4 mmol, 2.0 equiv), NaO*t*Bu (2.3 mg, 0.024 mmol, 12 mol%) and toluene (1.0 mL) under an argon atmosphere. After the mixture was stirred at room temperature for 30 minutes, a solution of *gem*-difluorocyclopropenes **1a**–**q** (0.2 mmol) in toluene (0.5 mL) was added, followed by addition of MeOH (12.8 mg, 0.40 mmol, 2.0 equiv) in toluene (0.5 mL). The resulting mixture was stirred at room temperature for 12 h. After the completion of reaction, the reaction mixture was quenched with H_2O (20 mL) and extracted with ethyl acetate (10 mL×3). The organic layer was separated and dried over Na_2SO_4, filtered and evaporated under vacuum. The crude product was purified by column chromatography on silica gel using *n*-hexane/ethyl acetate as eluent to afford the pure target compounds **3aa**–**qa**.

4.2 Cu-catalyzed hydrosilylation of various difluorocyclopropenes

An oven dried Schlenk tube containing a stirring bar was charged with CuCl (2.0 mg, 0.02 mmol, 10 mol%), Xantphos (17.3 mg, 0.03 mmol, 15 mol%), $PhMe_2Si$–Bpin **2b** (78.6 mg, 0.3 mmol, 1.5 equiv), NaO*t*Bu (2.3 mg, 0.024 mmol, 12 mol%) and toluene (1.0 mL) under an argon atmosphere. After the mixture was stirred at room temperature for 30 minutes, a solution of *gem*-difluorocyclopropenes **1a**–**d**, **1f**–**h**, **1k**–**o**, **1q** (0.2 mmol) in toluene

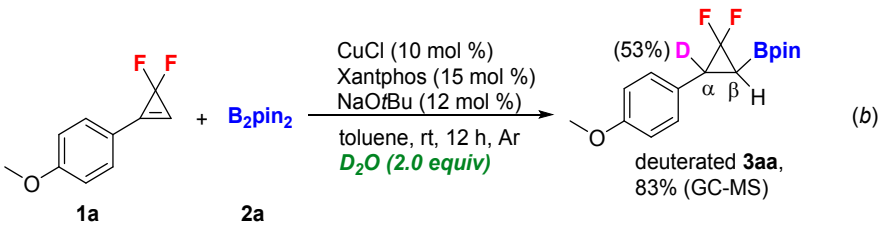
(0.5 mL) was added, followed by addition of MeOH (12.8 mg, 0.40 mmol, 2.0 equiv) in toluene (0.5 mL). The resulting mixture was stirred at room temperature for 12 h. After the completion of reaction, the reaction mixture was quenched with H_2O (20 mL) and extracted with ethyl acetate (10 mL×3). The organic layer was separated and dried over Na_2SO_4, filtered and evaporated under vacuum. The crude product was purified by column chromatography on silica gel using *n*-hexane/ethyl acetate as eluent to afford the pure target compounds **3ab**–**db**, **3fb**–**hb**, **3kb**–**ob**, **3qb**.

5. Hydroborylation of 1a on a 5.0 mmol scale



An oven dried 100 mL reaction vial containing a stirring bar was charged with CuCl (49.5 mg, 0.5 mmol, 10 mol%), Xantphos (433.5 mg, 0.75 mmol, 15 mol%), B_2pin_2 **2a** (2.54 g, 10.0 mmol, 2.0 equiv), NaO*t*Bu (57.6 mg, 0.6 mmol, 12 mol%) and toluene (40 mL) under an argon atmosphere. After the mixture was stirred at room temperature for 30 minutes, a solution of *gem*-difluorocyclopropenes **1a** (910 mg, 5.0 mmol, 1.0 equiv) in toluene (5 mL) was added, followed by addition of MeOH (320 mg, 10.0 mmol, 2.0 equiv) in toluene (5 mL). The resulting mixture was stirred at room temperature for 12 h. After the completion of reaction, the reaction mixture was quenched with H_2O (30 mL) and extracted with ethyl acetate (20 mL×3). The organic layer was separated and dried over Na_2SO_4, filtered and evaporated under vacuum. The crude product was purified by column chromatography on silica gel using *n*-hexane/ethyl acetate as eluent to afford the pure target compounds **3aa**.

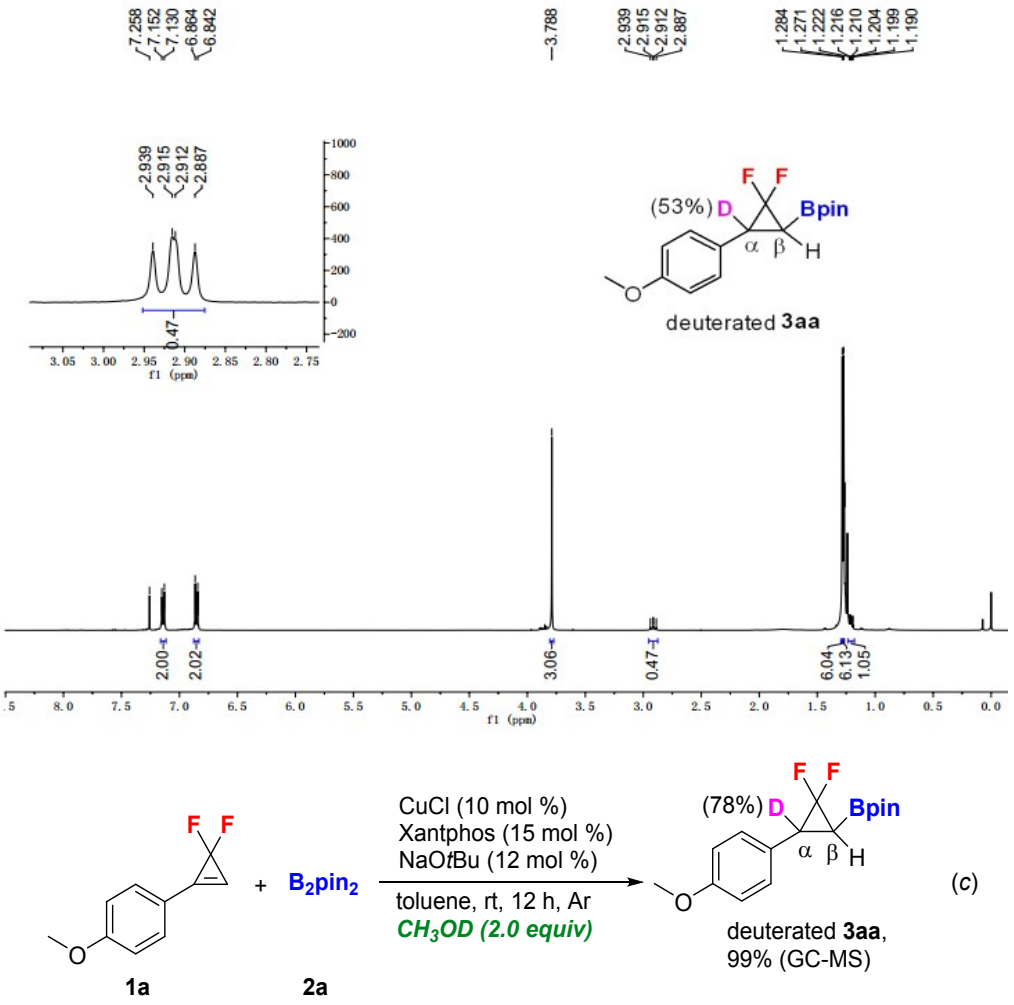
6. Deuterated experiments (*b* and *c*)



An oven dried Schlenk tube containing a stirring bar was charged with CuCl (2.0 mg, 0.02 mmol, 10 mol%), Xantphos (17.3 mg, 0.03 mmol, 15 mol%), B_2pin_2 **2a** (101.6 mg, 0.4 mmol, 2.0 equiv), NaO*t*Bu (2.3 mg, 0.024 mmol, 12 mol%) and toluene (1.0 mL) under an argon atmosphere. After the mixture was stirred at room temperature for 30 minutes, a solution of *gem*-difluorocyclopropenes **1a** (36.4 mg, 0.2 mmol, 1.0 equiv) in toluene (0.5 mL) was added, followed by addition of D_2O (8.0 mg, 0.40 mmol, 2.0 equiv) in toluene (0.5 mL). The resulting mixture was stirred at room temperature for 12 h. After the completion of reaction, the reaction mixture was quenched with H_2O

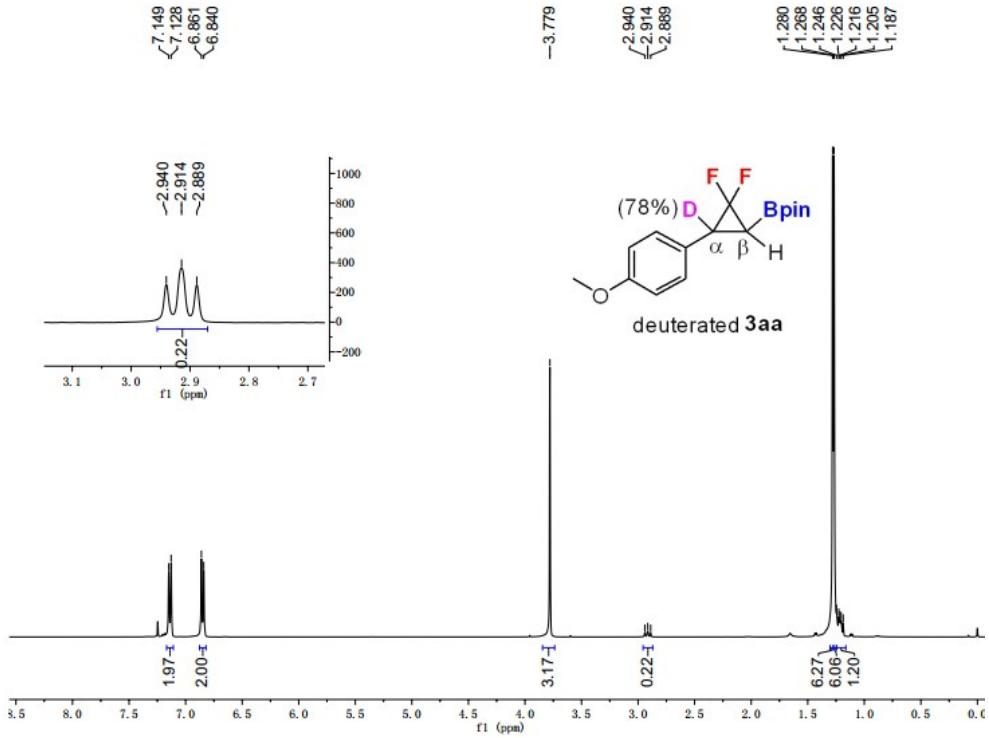
(20 mL) and extracted with ethyl acetate (10 mL×3). The organic layer was separated and dried over Na_2SO_4, filtered and evaporated under vacuum. The crude product was purified by column chromatography on silica gel using *n*-hexane/ethyl acetate as eluent to afford the deuterated **3aa** with 53% deuterium content (determined by ^{1}H NMR).

^{1}H NMR spectrum of deuterated 3aa

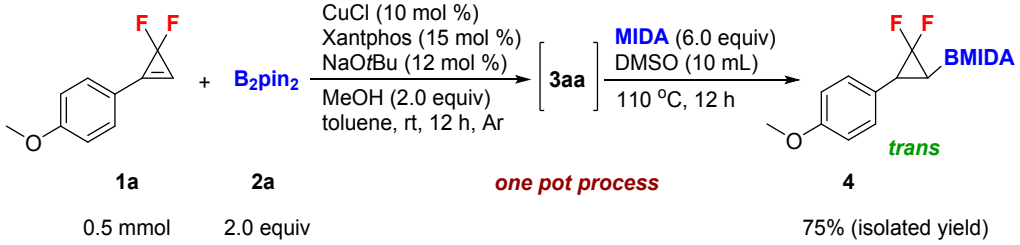


An oven dried Schlenk tube containing a stirring bar was charged with CuCl (2.0 mg, 0.02 mmol, 10 mol%), Xantphos (17.3 mg, 0.03 mmol, 15 mol%), B_2pin_2 **2a** (101.6 mg, 0.4 mmol, 2.0 equiv), NaO*t*Bu (2.3 mg, 0.024 mmol, 12 mol%) and toluene (1.0 mL) under an argon atmosphere. After the mixture was stirred at room temperature for 30 minutes, a solution of *gem*-difluorocyclopropenes **1a** (36.4 mg, 0.2 mmol, 1.0 equiv) in toluene (0.5 mL) was added, followed by addition of MeOD (13.2 mg, 0.40 mmol, 2.0 equiv) in toluene (0.5 mL). The resulting mixture was stirred at room temperature for 12 h. After the completion of reaction, the reaction mixture was quenched with H_2O (20 mL) and extracted with ethyl acetate (10 mL×3). The organic layer was separated and dried over Na_2SO_4, filtered and evaporated under vacuum. The crude product was purified by column chromatography on silica gel using *n*-hexane/ethyl acetate as eluent to afford the deuterated **3aa** with 78% deuterium content (determined by ^{1}H NMR).

^{1}H NMR spectrum of deuterated 3aa



7. One-pot synthesis of *trans*-difluorocyclopropyl MIDA boronate 4

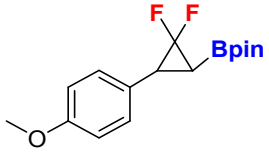


An oven dried 25 mL reaction vial containing a stirring bar was charged with CuCl (5.0 mg, 0.05 mmol, 10 mol%), Xantphos (43.4 mg, 0.075 mmol, 15 mol%), B_2pin_2 **2a** (254.0 mg, 1.0 mmol, 2.0 equiv), NaO*t*Bu (5.8 mg, 0.06 mmol, 12 mol%) and toluene (4.0 mL) under an argon atmosphere. After the mixture was stirred at room temperature for 30 minutes, a solution of *gem*-difluorocyclopropenes **1a** (91.0 mg, 0.5 mmol, 1.0 equiv) in toluene (0.5 mL) was added, followed by addition of MeOH (32.0 mg, 1.0 mmol, 2.0 equiv) in toluene (0.5 mL). The resulting mixture was stirred at room temperature for 12 h. After the completion of reaction, the reaction mixture was filtered and evaporated under vacuum.

The solution of MIDA (441 mg, 3.0 mmol, 6.0 equiv) in DMSO (10 mL) was added to the mixture and was stirred at 110 °C for 12 h under an argon atmosphere. After the completion of reaction, the reaction mixture was quenched with H_2O (20 mL) and extracted with ethyl acetate (10 mL×3). The organic layer was separated and dried over

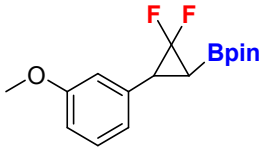
Na_2SO_4, filtered and evaporated under vacuum. Recrystallization with Et_2O to afford the pure product **4**.

8. Analytical data of compounds



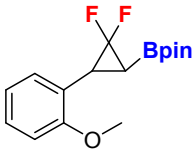
3aa

***trans*-2-(2,2-Difluoro-3-(4-methoxyphenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3aa)**. Yield 97% (60.1 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, J = 8.8 Hz, 2H), 6.77 (d, J = 8.8 Hz, 2H), 3.70 (s, 3H), 2.84 (dd, J = 11.2, 9.6 Hz, 1H), 1.20 (s, 6H), 1.19 (s, 6H), 1.16–1.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 127.9, 124.8, 113.6 (dd, $^1J_{CF}$ = 286.9, 281.4 Hz), 112.8, 83.1, 54.2, 29.8 (dd, $^2J_{CF}$ = 11.0, 10.5 Hz), 23.8, 23.5 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; ^{19}F NMR (376 MHz, $CDCl_3$): δ –125.2 (ddd, J_{FF} = 146.4 Hz, $^3J_{HF}$ = 11.2, 4.5 Hz, 1F), –135.4 (dd, J_{FF} = 145.9 Hz, $^3J_{HF}$ = 16.2 Hz, 1F); HRMS (EI): calcd for $C_{16}H_{21}BF_2O_3$ $[M]^+$: 310.1552, found: 310.1553.



3ba

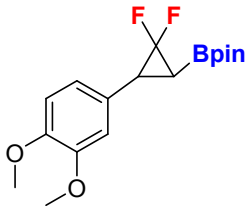
***trans*-2-(2,2-Difluoro-3-(3-methoxyphenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ba)**. Yield 99% (61.4 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.20 (m, 1H), δ 6.82–6.78 (m, 2H), 6.76 (s, 1H), 3.78 (s, 3H), 2.94 (t, J = 9.6 Hz, 1H), 1.35–1.31 (m, 1H), 1.28 (s, 6H), 1.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 135.4, 129.4, 120.2, 114.5 (dd, $^1J_{CF}$ = 286.7, 282.0 Hz), 113.7, 112.6, 84.2, 55.2, 31.5 (dd, $^2J_{CF}$ = 11.2, 10.4 Hz), 24.8, 24.5 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; ^{19}F NMR (376 MHz, $CDCl_3$): δ –124.7 (ddd, J_{FF} = 146.3 Hz, $^3J_{HF}$ = 11.6, 4.9 Hz, 1F), –135.4 (dd, J_{FF} = 146.3 Hz, $^3J_{HF}$ = 15.8 Hz, 1F); HRMS (EI): calcd for $C_{16}H_{21}BF_2O_3$ $[M]^+$: 310.1552, found: 310.1551.



3ca

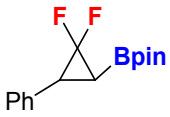
***trans*-2-(2,2-Difluoro-3-(2-methoxyphenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ca)**. Yield 78% (48.4 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.22 (m, 1H), 7.09 (d, J = 7.2 Hz, 1H), 6.92–6.87 (m, 1H), 6.87 (d, J = 8.4 Hz, 1H), 3.84 (s, 3H), 3.09 (t, J = 10.8 Hz, 1H), 1.28 (s, 12 H), 1.24–1.19 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 128.4, 127.7, 122.4, 120.3, 115.2 (dd, $^1J_{CF}$ = 286.5, 280.7 Hz), 110.3, 84.0, 55.5, 26.8

(dd, $^{2}J_{CF}$ = 11.9, 10.1 Hz), 24.8, 24.6 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; ^{19}F NMR (376 MHz, $CDCl_3$): δ –125.7 (ddd, J_{FF} = 144.4 Hz, $^{3}J_{HF}$ = 11.6, 4.1 Hz, 1F), –135.4 (dd, J_{FF} = 144.4 Hz, $^{3}J_{HF}$ = 15.9 Hz, 1F); HRMS (EI): calcd for $C_{16}H_{21}BF_2O_3$ $[M]^+$: 310.1552, found: 310.1550.



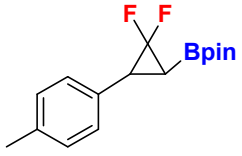
3da

***trans*-2-(3-(3,4-Dimethoxyphenyl)-2,2-difluorocyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane** (**3da**). Yield 70% (47.6 mg), yellow solid, m.p.: 98.6–100.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (d, J = 8.0 Hz, 1H), 6.78–6.76 (m, 1H), 6.73 (s, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 2.92 (dd, J = 11.2, 9.2 Hz, 1H), 1.29 (s, 6H), 1.28 (s, 6H), 1.24–1.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 148.3, 126.3, 120.0, 114.6 (dd, $^{1}J_{CF}$ = 287.0, 281.6 Hz), 111.2, 111.1, 84.2, 55.9, 55.9, 31.1 (t, $^{2}J_{CF}$ = 10.9 Hz), 24.9, 24.6 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; ^{19}F NMR (376 MHz, $CDCl_3$) δ –124.9 – –125.3 (m, 1F), –135.3 (dd, J_{FF} = 145.5 Hz, $^{3}J_{HF}$ = 15.8 Hz, 1F); HRMS (EI): calcd for $C_{17}H_{23}BF_2O_4$ $[M]^+$: 340.1657, found: 340.1658.



3ea

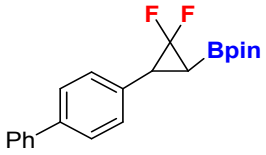
***trans*-2-(2,2-Difluoro-3-phenylcyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane** (**3ea**, CAS: 1010689-67-4).[2] Yield 87% (48.7 mg), colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.27 (m, 3H), 7.21 (d, J = 7.2 Hz, 2H), 2.96 (t, J = 10.4 Hz, 1H), 1.36–1.33 (m, 1H), 1.28 (s, 6H), 1.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.0, 128.4, 127.8, 127.2, 114.5 (dd, $^{1}J_{CF}$ = 286.8, 281.8 Hz), 84.2, 31.5 (t, $^{2}J_{CF}$ = 10.5 Hz), 24.9, 24.6 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; ^{19}F NMR (376 MHz, $CDCl_3$) δ –124.8 (ddd, J_{FF} = 146.3 Hz, $^{3}J_{HF}$ = 11.6, 4.5 Hz, 1F), –135.5 (dd, J_{FF} = 146.3 Hz, $^{3}J_{HF}$ = 15.8 Hz, 1F).



3fa

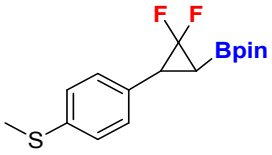
***trans*-2-(2,2-Difluoro-3-(p-tolyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane** (**3fa**). Yield 82% (48.2 mg), colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06–7.01 (m, 4H), 2.85 (dd, J = 10.8, 9.6 Hz, 1H), 2.25 (s, 3H), 1.24–1.23 (m, 1H), 1.21 (s, 6H), 1.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 129.8, 128.1, 126.7, 113.5 (dd,

$^{1}J_{CF}$ = 286.8, 281.7 Hz), 83.1, 30.2 (t, $^{2}J_{CF}$ = 11.2 Hz), 23.8, 23.5, 20.0 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; ^{19}F NMR (376 MHz, $CDCl_3$): δ –125.0 (ddd, J_{FF} = 146.1 Hz, $^{3}J_{HF}$ = 11.6, 4.5 Hz, 1F), –135.4 (dd, J_{FF} = 146.0 Hz, $^{3}J_{HF}$ = 15.9 Hz, 1F); HRMS (EI): calcd for $C_{16}H_{21}BF_2O_2$ $[M]^+$: 294.1603, found: 294.1604.



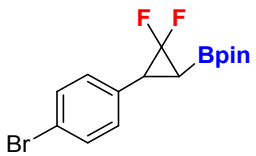
3ga

***trans*-2-(3-([1,1'-Biphenyl]-4-yl)-2,2-difluorocyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane** (**3ga**). Yield 95% (67.6 mg), white solid, m.p.: 115.6–117.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.53 (m, 4H), 7.44–7.40 (m, 2H), 7.35–7.33 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.03 (dd, *J* = 11.2, 9.6 Hz, 1H), 1.36 (ddd, *J* = 15.6, 9.2, 4.4 Hz, 1H), 1.29 (s, 6H), 1.28(s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 140.2, 133.1, 128.8, 128.3, 127.4, 127.2, 127.1, 114.5 (dd, $^{1}J_{CF}$ = 287.1, 281.8 Hz), 84.3, 31.3 (t, $^{2}J_{CF}$ = 10.9 Hz), 24.9, 24.6 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; ^{19}F NMR (376 MHz, $CDCl_3$): δ –124.7 (ddd, J_{FF} = 146.4 Hz, $^{3}J_{HF}$ = 11.4, 4.4 Hz, 1F), –135.4 (dd, J_{FF} = 146.4 Hz, $^{3}J_{HF}$ = 15.8 Hz, 1F); HRMS (EI): calcd for $C_{21}H_{23}BF_2O_2$ $[M]^+$: 356.1759, found: 356.1758.



3ha

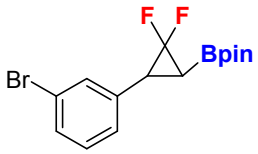
***trans*-2-(2,2-Difluoro-3-(4-(methylthio)phenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane** (**3ha**). Yield 63% (41.0 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 2.84 (t, *J* = 10.0 Hz, 1H), 2.38 (s, 3H), 1.21 (s, 6H), 1.19 (s, 6H), 1.17–1.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 129.7, 127.3, 125.7, 113.4 (dd, $^{1}J_{CF}$ = 287.2, 281.7 Hz), 83.2, 29.9 (dd, $^{2}J_{CF}$ = 11.4, 10.4 Hz), 23.8, 23.5, 14.9 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; ^{19}F NMR (376 MHz, $CDCl_3$) δ –124.9 (ddd, J_{FF} = 146.3 Hz, $^{3}J_{HF}$ = 11.3, 4.5 Hz, 1F), –135.3 (dd, J_{FF} = 146.3 Hz, $^{3}J_{HF}$ = 16.2 Hz, 1F); HRMS (EI): calcd for $C_{16}H_{21}BF_2O_2S$ $[M]^+$: 326.1323, found: 326.1324.



3ia

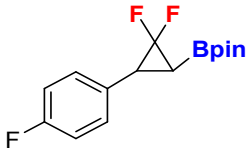
***trans*-2-(3-(4-Bromophenyl)-2,2-difluorocyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane** (**3ia**). Yield 92% (65.9 mg), white solid, m.p.: 77.3–78.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 2.90 (dd, *J* = 11.2, 9.6 Hz, 1H), 1.28 (s, 6H), 1.27 (s, 6H), 1.26–1.23 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$)

δ 133.0, 131.5, 129.6, 121.1, 114.1 (dd, $^{1}J_{CF}$ = 288.2, 281.7 Hz), 84.3,30.8 (dd, $^{2}J_{CF}$ = 11.6, 10.2 Hz), 24.9, 24.5 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; ^{19}F NMR (376 MHz, $CDCl_3$) δ –125.0 (ddd, J_{FF} = 146.6 Hz, $^{3}J_{HF}$ = 11.3, 3.8 Hz, 1F), –135.3 (dd, J_{FF} = 146.6 Hz, $^{3}J_{HF}$ = 15.8 Hz, 1F); HRMS (EI): calcd for $C_{15}H_{18}BBrF_2O_2$ $[M]^+$: 358.0551, found: 358.0552.



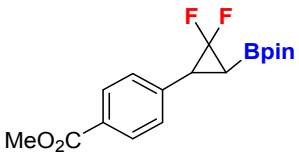
3ja

***trans*-2-(3-(3-Bromophenyl)-2,2-difluorocyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ja)**. Yield 62% (44.0 mg), colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 8.0 Hz, 1H), 7.37 (s, 1H), 7.20–7.16 (m, 1H), 7.14 (d, J = 7.6 Hz, 1H), 2.91 (t, J = 10.4 Hz, 1H), 1.33–1.31 (m, 1H), 1.29 (s, 6H), 1.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 131.0, 130.3, 129.9, 126.5, 122.5, 114.1 (dd, $^{1}J_{CF}$ = 287.1, 281.9 Hz), 84.4, 30.8 (dd, $^{2}J_{CF}$ = 11.7, 10.2 Hz), 24.9, 24.5 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; ^{19}F NMR (376 MHz, $CDCl_3$) δ –124.9 (ddd, J_{FF} = 147.0 Hz, $^{3}J_{HF}$ = 11.3, 4.5 Hz, 1F), –135.1 (dd, J_{FF} = 147.0 Hz, $^{3}J_{HF}$ = 16.2 Hz, 1F); HRMS (EI): calcd for $C_{15}H_{18}BBrF2O_2$ $[M]^+$: 358.0551, found: 358.0555.



3ka

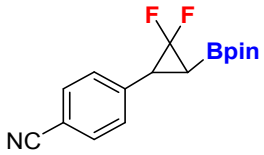
***trans*-2-(2,2-Difluoro-3-(4-fluorophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3ka)**. Yield 80% (47.6 mg), colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11–7.08 (m, 2H), 6.93–6.89 (m, 2H), 2.85 (t, J = 10.4 Hz, 1H), 1.16–1.13 (m, 1H), 1.20 (s, 6H), 1.18 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0 (d, $^{1}J_{CF}$ = 245.8 Hz), 128.6 (d, $^{4}J_{CF}$ = 2.6 Hz), 128.4 (d, $^{3}J_{CF}$ = 8.1 Hz), 124.3 (d, $^{2}J_{CF}$ = 21.6 Hz), 113.2 (dd, $^{1}J_{CF}$ = 286.8, 281.3 Hz), 83.2, 29.6 (t, $^{2}J_{CF}$ = 11.3 Hz), 23.8, 23.5 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; ^{19}F NMR (376 MHz, $CDCl_3$): δ –115.2 – –115.3 (m, 1F), –125.3 (ddd, J_{FF} = 146.7 Hz, $^{3}J_{HF}$ = 11.4, 4.4 Hz, 1F), –135.4 (dd, J_{FF} = 146.7 Hz, $^{3}J_{HF}$ = 16.0 Hz, 1F); HRMS (EI): calcd for $C_{15}H_{18}BF_3O_2$ $[M]^+$: 298.1352, found: 298.1351.



3la

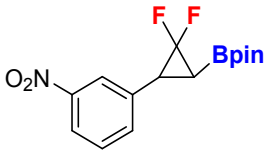
***trans*-Methyl-4-(2,2-difluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)benzoate (3la)**. Yield 75% (50.7 mg), colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 3.91 (s, 3H), 2.99 (t, J = 10.0 Hz, 1H), 1.38 (ddd, J = 16.0, 9.6, 4.8 Hz, 1H), 1.29 (s, 6H), 1.28 (s, 6H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 166.8, 139.3, 129.6, 129.0, 127.8, 114.1 (dd, $^1J_{CF}$ = 287.5, 282.0 Hz), 84.4, 52.1, 31.3 (t, $^2J_{CF}$ = 10.5 Hz), 24.8, 24.5 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; ^{19}F NMR (376 MHz, $CDCl_3$) δ –124.6 (ddd, J_{FF} = 146.6 Hz, $^3J_{HF}$ = 11.3, 4.5 Hz, 1F), –135.3 (dd, J_{FF} = 146.6 Hz, $^3J_{HF}$ = 15.8 Hz, 1F); HRMS (EI): calcd for $C_{17}H_{21}BF_2O_4$ $[M]^+$: 338.1501, found: 338.1502.



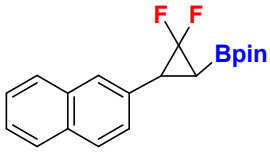
3ma

***trans*-4-(2,2-Difluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)benzonitrile (3ma)**. Yield 68% (41.5 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 2.98 (t, J = 10.0 Hz, 1H), 1.40–1.32 (m, 1H), 1.29 (s, 6H), 1.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 132.2, 128.5, 118.6, 113.8 (dd, $^1J_{CF}$ = 288.2, 282.1 Hz), 111.0, 84.5, 31.2 (dd, $^2J_{CF}$ = 11.9, 9.9 Hz), 24.9, 24.5 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; ^{19}F NMR (376 MHz, $CDCl_3$): δ –124.6 (ddd, J_{FF} = 147.7 Hz, $^3J_{HF}$ = 11.0, 4.6 Hz, 1F), –135.2 (dd, J_{FF} = 147.7 Hz, $^3J_{HF}$ = 15.9 Hz, 1F); HRMS (EI): calcd for $C_{16}H_{18}BF_2NO_2$ $[M]^+$: 305.1399, found: 305.1401.



3na

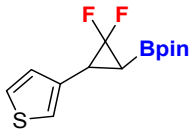
***trans*-2-(2,2-Difluoro-3-(3-nitrophenyl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3na)**. Yield 74% (48.1 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.0 Hz, 1H), 8.09 (s, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.52–7.48 (m, 1H), 3.05 (t, J = 10.0 Hz, 1H), 1.40 (ddd, J = 16.0, 9.2, 4.4 Hz, 1H), 1.30 (s, 6H), 1.29 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 136.2, 134.0, 129.4, 122.9, 122.2, 113.7 (dd, $^1J_{CF}$ = 287.8, 281.7 Hz), 84.5, 30.6 (dd, $^2J_{CF}$ = 12.0, 10.0 Hz), 24.9, 24.5 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; ^{19}F NMR (376 MHz, $CDCl_3$): δ –125.1 (ddd, J_{FF} = 147.8 Hz, $^3J_{HF}$ = 10.9, 3.8 Hz, 1F), –135.1 (dd, J_{FF} = 147.8 Hz, $^3J_{HF}$ = 15.8 Hz, 1F); HRMS (EI): calcd for $C_{14}H_{15}BF_2NO_4$ $[M\text{-}CH_3]^+$: 310.1062, found: 310.1062.



3oa

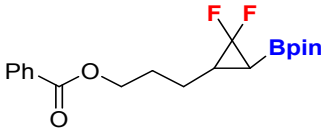
***trans*-2-(2,2-Difluoro-3-(naphthalen-2-yl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3oa)**. Yield 91% (60.0 mg), white solid, m.p.: 60.2–61.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.69 (m, 3H), 7.59 (s, 1H), 7.39–7.33 (m, 2H), 7.25 (d, J = 8.4 Hz, 1H), 3.05 (t, J = 10.4 Hz, 1H), 1.41–1.34 (m, 1H), 1.21 (s, 6H), 1.20 (s, 6H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 132.2, 131.5, 130.3, 127.0, 126.6, 125.6, 125.6, 125.2, 124.9, 124.8, 113.6 (dd, $^1J_{CF}$ = 287.0, 282.0 Hz), 83.2, 30.6 (t, $^2J_{CF}$ = 10.5 Hz), 23.8, 23.5 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; ^{19}F NMR (376 MHz, $CDCl_3$) δ –124.6 (ddd, J_{FF} = 146.2 Hz, $^3J_{HF}$ = 11.6, 4.5 Hz, 1F), –135.0 (dd, J_{FF} = 146.2 Hz, $^3J_{HF}$ = 15.8 Hz, 1F); HRMS (EI): calcd for $C_{19}H_{21}BF_2O_2$ $[M]^+$: 330.1603, found: 330.1604.



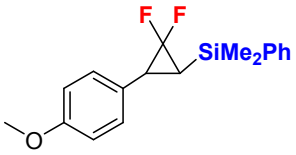
3pa

***trans*-2-(2,2-Difluoro-3-(thiophen-3-yl)cyclopropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3pa)**. Yield 63% (36.0 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.26 (m, 1H), 7.09 (d, *J* = 2.4 Hz, 1H), 6.95 (d, *J* = 4.8 Hz, 1H), 2.96 (t, *J* = 10.8 Hz, 1H), 1.20 (ddd, *J* = 16.0, 9.2, 4.4 Hz, 1H), 1.28 (s, 6H), 1.27 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.9, 127.1, 125.7, 121.8, 114.6 (dd, $^1J_{CF}$ = 286.9, 282.3 Hz), 84.2, 27.3 (dd, $^2J_{CF}$ = 12.3, 10.5 Hz), 24.9, 24.5 [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; ^{19}F NMR (376 MHz, $CDCl_3$): δ –126.2 (ddd, J_{FF} = 146.6 Hz, $^3J_{HF}$ = 11.3, 4.8 Hz, 1F), –134.4 (dd, J_{FF} = 146.3 Hz, $^3J_{HF}$ = 16.1 Hz, 1F); HRMS (EI): calcd for $C_{13}H_{17}BF_2O_2S$ $[M]^+$: 286.1010, found: 286.1011.



3qa

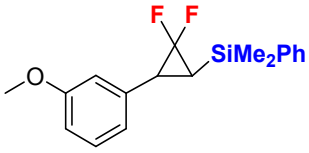
***trans*-3-(2,2-Difluoro-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl)propyl benzoate (3qa)**. Yield 42% (30.7 mg), colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.57–7.54 (m, 1H), 7.46–7.42 (m, 2H), 4.32 (t, *J* = 6.4 Hz, 2H), 1.93–1.86 (m, 2H), 1.84–1.78 (m, 1H), 1.69–1.63 (m, 1H), 1.56–1.49 (m, 1H), 1.24 (s, 6H), 1.22 (s, 6H), 1.03 (ddd, *J* = 11.9, 6.5, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 132.8, 130.4, 129.6, 128.3, 116.5 (t, $^1J_{CF}$ = 282.4 Hz), 84.1, 64.6, 27.7 (d, *J* = 2.3 Hz), 25.8 (d, *J* = 6.2 Hz), 24.8, 24.3, 20.1 (t, $^2J_{CF}$ = 10.1 Hz) [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; ^{19}F NMR (376 MHz, $CDCl_3$) δ –126.4 (dd, J_{FF} = 150.0 Hz, $^3J_{HF}$ = 10.9 Hz, 1F), –138.3 (ddd, J_{FF} = 150.0 Hz, $^3J_{HF}$ = 11.6, 3.0 Hz, 1F); HRMS (EI): calcd for $C_{19}H_{25}BF_2O_4$ $[M]^+$: 366.1814, found: 366.1807.



3ab

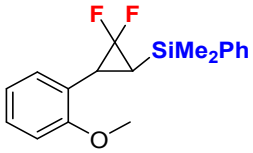
***trans*-(2,2-Difluoro-3-(4-methoxyphenyl)cyclopropyl)dimethyl(phenyl)silane (3ab)**. Yield 97% (61.7 mg), colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.58–7.55 (m, 2H), 7.39–7.37 (m, 3H), 7.15 (d, *J* = 8.8 Hz, 2H), 6.84

(d, J = 8.8 Hz, 2H), 3.77 (s, 3H), 2.59 (t, J = 10.4 Hz, 1H), 1.17 (ddd, J_{HF} = 17.6 Hz, J_{HH} = 10.0, 8.0 Hz, 1H), 0.42 (s, 3H), 0.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 136.9, 133.8, 129.6, 129.1, 128.1, 126.7 (d, J = 1.7 Hz), 115.6 (t, $^1J_{CF}$ = 283.6 Hz), 113.9, 55.3, 30.1 (t, $^2J_{CF}$ = 11.2 Hz), 19.0 (dd, $^2J_{CF}$ = 18.2, 4.3 Hz), –2.8, –3.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ –123.2 (ddd, J_{FF} = 146.3 Hz, $^3J_{HF}$ = 10.1, 8.3 Hz, 1F), –132.3 (dd, J_{FF} = 146.7 Hz, $^3J_{HF}$ = 17.2 Hz, 1F); HRMS (EI): calcd for $C_{18}H_{20}F_2OSi$ $[M]^+$: 318.1251, found: 318.1253.



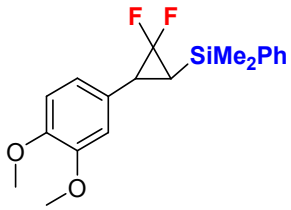
3bb

***trans*-(2,2-Difluoro-3-(3-methoxyphenyl)cyclopropyl)dimethyl(phenyl)silane** (**3bb**). Yield 99% (62.9 mg), colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.47 (m, 2H), 7.30–7.29 (m, 3H), 7.14–7.10 (m, 1H), 6.70 (d, J = 8.0 Hz, 2H), 6.64 (s, 1H), 3.67 (s, 3H), 2.52 (t, J = 10.0 Hz, 1H), 1.15 (ddd, J = 17.6, 9.6, 8.0 Hz, 1H), 0.34 (s, 3H), 0.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 135.7, 135.2 (d, J = 1.6 Hz), 132.7, 128.5, 128.4, 127.0, 119.2, 114.3 (t, $^1J_{CF}$ = 284.0 Hz), 112.7, 111.4, 54.1, 29.8 (t, $^2J_{CF}$ = 11.2 Hz), 18.1 (dd, $^2J_{CF}$ = 18.3, 4.2 Hz), –4.0, –4.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ –122.7 (ddd, J_{FF} = 147.0 Hz, $^3J_{HF}$ = 9.4, 9.0 Hz, 1F), –132.3 (dd, J_{FF} = 146.6 Hz, $^3J_{HF}$ = 17.3 Hz, 1F); HRMS (EI): calcd for $C_{18}H_{20}F_2OSi$ $[M]^+$: 318.1251, found: 318.1253.



3cb

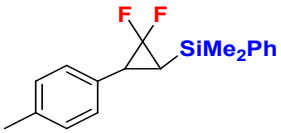
***trans*-(2,2-Difluoro-3-(2-methoxyphenyl)cyclopropyl)dimethyl(phenyl)silane** (**3cb**). Yield 87% (55.3 mg), colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.58 (m, 2H), 7.38–7.37 (m, 3H), 7.25–7.21 (m, 1H), 7.09 (d, J = 7.6 Hz, 1H), 6.90–6.87 (m, 1H), 6.85 (d, J = 8.4 Hz, 1H), 3.81 (s, 3H), 2.76 (t, J = 10.4 Hz, 1H), 1.15 (ddd, J = 18.0, 10.4, 8.0 Hz, 1H), 0.43 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 137.2, 133.8, 129.5, 128.4, 128.1 (t, $^3J_{CF}$ = 2.6 Hz), 128.0, 123.4, 120.3, 116.1 (t, $^1J_{CF}$ = 282.6 Hz), 110.2, 55.4, 25.9 (t, $^2J_{CF}$ = 11.1 Hz), 18.0 (dd, $^2J_{CF}$ = 18.0, 4.4 Hz), –2.8, –3.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ –123.7 (dd, J_{FF} = 145.5 Hz, $^3J_{HF}$ = 9.8 Hz, 1F), –131.5 (dd, J_{FF} = 145.1 Hz, $^3J_{HF}$ = 17.3 Hz, 1F); HRMS (EI): calcd for $C_{18}H_{20}F_2OSi$ $[M]^+$: 318.1251, found: 318.1250.



3db

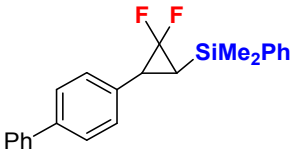
***trans*-(3-(3,4-Dimethoxyphenyl)-2,2-difluorocyclopropyl)dimethyl(phenyl)silane** (**3db**). Yield 77% (53.6 mg),

colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.57 (m, 2H), 7.39–7.37 (m, 3H), 6.80 (d, J = 8.0 Hz, 1H), 6.73 (d, J = 8.4 Hz, 1H), 6.68 (s, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 2.60 (t, J = 10.4 Hz, 1H), 1.17 (ddd, J = 17.6, 10.0, 8.0 Hz, 1H), 0.43 (s, 3H), 0.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 148.2, 136.9, 133.7, 129.6, 128.1, 127.2, 120.0, 115.5 (t, $^1J_{CF}$ = 283.9 Hz), 111.4, 111.1, 55.9, 55.8, 30.4 (t, $^2J_{CF}$ = 11.2 Hz), 19.1 (dd, $^2J_{CF}$ = 18.3, 4.3 Hz), –2.9, –3.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ –123.1 (ddd, J_{FF} = 146.3 Hz, $^3J_{HF}$ = 9.0, 9.0 Hz, 1F), –132.0 (dd, J_{FF} = 146.3 Hz, $^3J_{HF}$ = 17.3 Hz, 1F); HRMS (EI): calcd for $C_{19}H_{22}F_2O_2Si$ [M]$^+$: 348.1357, found: 348.1355.



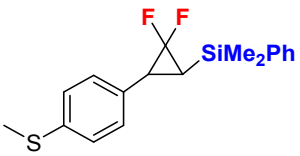
3fb

***trans*-(2,2-Difluoro-3-(p-tolyl)cyclopropyl)dimethyl(phenyl)silane (3fb)**. Yield 87% (52.5 mg), colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.48 (m, 2H), 7.31–7.29 (m, 3H), 7.03 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 2.52 (t, J = 10.4 Hz, 1H), 2.24 (s, 3H), 1.18–1.09 (m, 1H), 0.34 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 135.7, 132.7, 130.6 (d, $^3J_{CF}$ = 1.7 Hz), 128.5, 128.1, 126.9, 126.7, 114.4 (t, $^1J_{CF}$ = 283.7 Hz), 29.5 (t, $^2J_{CF}$ = 11.2 Hz), 20.0, 17.8 (dd, $^2J_{CF}$ = 18.3, 4.3 Hz), –3.9, –4.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ –123.0 (ddd, J_{FF} = 146.6 Hz, $^3J_{HF}$ = 9.4, 9.0 Hz, 1F), –132.3 (dd, J_{FF} = 146.6 Hz, $^3J_{HF}$ = 17.3 Hz, 1F).



3gb

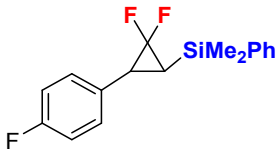
***trans*-(3-([1,1'-Biphenyl]-4-yl)-2,2-difluorocyclopropyl)dimethyl(phenyl)silane (3gb)**. Yield 85% (61.9 mg), colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.47 (m, 3H), 7.45–7.42 (m, 3H), 7.33–7.28 (m, 5H), 7.24–7.20 (m, 1H), 7.16 (d, J = 8.0 Hz, 2H), 2.57 (t, J = 10.4 Hz, 1H), 1.19 (ddd, J = 17.6, 10.0, 8.0 Hz, 1H), 0.35 (s, 3H), 0.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 140.1, 136.8, 133.9 (d, J = 1.3 Hz), 133.8, 129.7, 128.9, 128.4, 128.2, 127.4, 127.2, 127.1, 115.5 (t, $^1J_{CF}$ = 283.9 Hz), 30.7 (t, $^2J_{CF}$ = 11.3 Hz), 19.4 (dd, $^2J_{CF}$ = 18.2, 3.8 Hz), –2.8, –3.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ –122.7 (dt, J_{FF} = 147.4 Hz, $^3J_{HF}$ = 9.4 Hz, 1F), –132.1 (dd, J_{FF} = 147.4 Hz, $^3J_{HF}$ = 17.3 Hz, 1F); HRMS (EI): calcd for $C_{23}H_{22}F_2Si$ [M]$^+$: 364.1459, found: 364.1461.



3hb

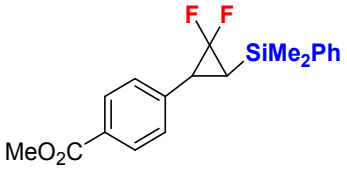
***trans*-(2,2-Difluoro-3-(4-(methylthio)phenyl)cyclopropyl)dimethyl(phenyl)silane (3hb)**. Yield 75% (50.1 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.55 (m, 2H), 7.39–7.36 (m, 3H), 7.19 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 2.58 (t, J = 10.4 Hz, 1H), 2.45 (s, 3H), 1.20 (ddd, J = 17.6, 9.6, 8.4 Hz, 1H), 0.42 (s, 3H), 0.41 (s,

3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 136.7, 133.7, 131.6, 129.6, 128.4, 128.1, 126.7, 115.3 (t, $^1J_{CF}$ = 283.9 Hz), 30.4 (t, $^2J_{CF}$ = 11.3 Hz), 19.2 (dd, $^2J_{CF}$ = 18.2, 4.1 Hz), 15.9, –2.9, –3.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ –123.0 (ddd, J_{FF} = 147.0 Hz, $^3J_{HF}$ = 9.4, 9.0 Hz, 1F), –132.2 (dd, J_{FF} = 147.0 Hz, $^3J_{HF}$ = 17.3 Hz, 1F); HRMS (EI): calcd for $C_{18}H_{20}F_2SSi$ [M]$^+$: 334.1023, found: 334.1022.



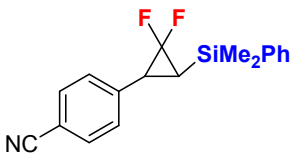
3kb

***trans*-(2,2-Difluoro-3-(4-fluorophenyl)cyclopropyl)dimethyl(phenyl)silane (3kb)**. Yield 82% (50.2 mg), colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.55 (m, 2H), 7.41–7.36 (m, 3H), 7.14 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.00–6.96 (m, 2H), 2.59 (t, *J* = 10.4 Hz, 1H), 1.18 (ddd, *J* = 17.6, 10.0, 8.0 Hz, 1H), 0.43 (s, 3H), 0.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0 (d, $^1J_{CF}$ = 244.2 Hz), 136.7, 133.7, 130.5 (d, *J* = 2.9 Hz), 129.7, 129.5 (d, *J* = 8.0 Hz), 128.1, 115.4 (d, $^2J_{CF}$ = 21.5 Hz), 115.2 (t, $^1J_{CF}$ = 283.3 Hz), 30.0 (t, $^2J_{CF}$ = 11.3 Hz), 19.4 (dd, $^2J_{CF}$ = 18.4, 4.2 Hz), –2.9, –3.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ –115.3 – –115.4 (m, 1F), –123.4 (ddd, J_{FF} = 147.4 Hz, $^3J_{HF}$ = 9.8, 9.8 Hz, 1F), –132.2 (dd, J_{FF} = 147.4 Hz, $^3J_{HF}$ = 17.7 Hz, 1F); HRMS (EI): calcd for $C_{17}H_{16}F_2Si$ [M-HF]$^+$: 286.0989, found: 286.0998.



3lb

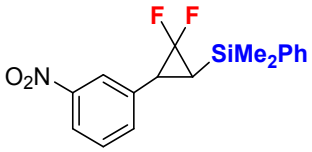
***trans*-Methyl-4-(3-(dimethyl(phenyl)silyl)-2,2-difluorocyclopropyl)benzoate (3lb)**. Yield 83% (57.4 mg), colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.56–7.54 (m, 2H), 7.40–7.37 (m, 3H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H), 2.64 (t, *J* = 10.0 Hz, 1H), 1.30 (ddd, *J* = 17.6, 10.0, 8.4 Hz, 1H), 0.44 (s, 3H), 0.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 140.2 (d, *J* = 1.7 Hz), 136.4, 133.7, 129.7, 129.7, 128.9, 128.1, 127.8, 115.1 (t, $^1J_{CF}$ = 284.1 Hz), 52.1, 30.9 (t, $^2J_{CF}$ = 11.3 Hz), 20.0 (dd, $^2J_{CF}$ = 18.2, 3.9 Hz), –2.9, –3.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ –122.5 (dt, J_{FF} = 147.8 Hz, $^3J_{HF}$ = 9.0 Hz, 1F), –132.1 (dd, J_{FF} = 147.8 Hz, $^3J_{HF}$ = 17.3 Hz, 1F); HRMS (EI): calcd for $C_{19}H_{20}F_2O_2Si$ [M]$^+$: 346.1201, found: 346.1200.



3mb

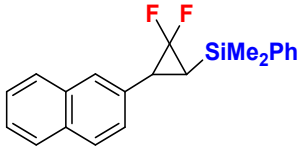
***trans*-4-(3-(Dimethyl(phenyl)silyl)-2,2-difluorocyclopropyl)benzonitrile (3mb)**. Yield 53% (33.2 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.55–7.53 (m, 2H), 7.42–7.36 (m, 3H), 7.27 (d, *J* = 8.0 Hz,

2H), 2.62 (t, J = 10.0 Hz, 1H), 1.28 (ddd, J = 17.6, 9.6, 8.0 Hz, 1H), 0.44 (s, 3H), 0.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 136.1, 133.7, 132.2, 129.8, 128.5, 128.2, 118.7, 114.8 (t, $^1J_{CF}$ = 284.3 Hz), 110.9, 30.8 (t, $^2J_{CF}$ = 12.3 Hz), 20.4 (dd, $^2J_{CF}$ = 18.5, 3.9 Hz), –3.0, –3.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ –122.6 (d, J_{FF} = 148.5 Hz, 1F), –131.97 (dd, J_{FF} = 148.9 Hz, $^3J_{HF}$ = 17.7 Hz, 1F); HRMS (EI): calcd for $C_{18}H_{17}F_2NSi$ $[M]^+$: 313.1098, found: 313.1096.



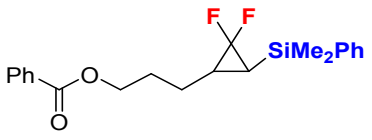
3nb

***trans*-(2,2-Difluoro-3-(3-nitrophenyl)cyclopropyl)dimethyl(phenyl)silane (3nb)**. Yield 82% (54.6 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 7.6 Hz, 1H), 8.04 (s, 1H), 7.57–7.55 (m, 2H), 7.52–7.45 (m, 2H), 7.41–7.39 (m, 3H), 2.68 (t, J = 9.6 Hz, 1H), 1.37–1.28 (m, 1H), 0.46 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 137.1 (d, J = 1.7 Hz), 136.1, 133.9, 133.7, 129.9, 129.4, 128.2, 122.8, 122.1, 114.6 (t, $^1J_{CF}$ = 284.2 Hz), 30.2 (t, $^2J_{CF}$ = 11.3 Hz), 20.1 (dd, $^2J_{CF}$ = 18.5, 3.9 Hz), –3.0, –3.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ –123.2 (dt, J_{FF} = 148.9 Hz, $^3J_{HF}$ = 8.3 Hz, 1F), –132.10 (dd, J_{FF} = 148.9 Hz, $^3J_{HF}$ = 17.7 Hz, 1F); HRMS (EI): calcd for $C_{17}H_{17}F_2NO_2Si$ $[M]^+$: 333.0997, found: 333.0996.



3ob

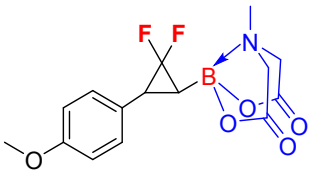
***trans*-(2,2-Difluoro-3-(naphthalen-2-yl)cyclopropyl)dimethyl(phenyl)silane (3ob)**. Yield 98% (66.2 mg), yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.74 (m, 3H), 7.63 (s, 1H), 7.59–7.58 (m, 2H), 7.44–7.43 (m, 2H), 7.39–7.37 (m, 3H), 7.30 (d, J = 8.4 Hz, 1H), 2.79 (t, J = 10.0 Hz, 1H), 1.37 (ddd, J = 17.6, 9.6, 8.4 Hz, 1H), 0.46 (s, 3H), 0.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 133.8, 133.4, 132.6, 132.3 (d, J = 1.7 Hz), 129.7, 128.2, 128.2, 127.7, 127.7, 126.7, 126.4, 126.1, 125.9, 115.6 (t, $^1J_{CF}$ = 284.0 Hz), 31.1 (t, $^2J_{CF}$ = 11.2 Hz), 19.4 (dd, $^2J_{CF}$ = 18.2, 4.2 Hz), –2.8, –3.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ –122.5 (dt, J_{FF} = 147.0 Hz, $^3J_{HF}$ = 9.0 Hz, 1F), –131.9 (dd, J_{FF} = 147.0 Hz, $^3J_{HF}$ = 17.3 Hz, 1F); HRMS (EI): calcd for $C_{21}H_{20}F_2Si$ $[M]^+$: 338.1302, found: 338.1301.



3qb

***trans*-3-(3-(Dimethyl(phenyl)silyl)-2,2-difluorocyclopropyl)propyl benzoate (3qb)**. Yield 74% (55.3 mg), colourless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.95–7.93 (m, 2H), 7.46–7.43 (m, 3H), 7.36–7.32 (m, 2H), 7.28–7.27 (m, 3H), 4.22 (t, J = 6.4 Hz, 2H), 1.76–1.70 (m, 2H), 1.69–1.60 (m, 1H), 1.56–1.47 (m, 1H), 1.42–1.34 (m, 1H), 0.45 (ddd, J = 17.2, 9.6, 7.6 Hz, 1H), 0.26 (s, 3H), 0.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 137.1, 133.6, 132.9,

130.3, 129.5, 129.4, 128.4, 128.0, 117.3 (dd, $^{1}J_{CF}$ = 283.3, 281.2 Hz), 64.1, 28.2 (d, J = 2.0 Hz), 25.8 (dd, $^{2}J_{CF}$ = 11.2, 9.9 Hz), 25.0 (d, J = 1.9 Hz), 18.1 (dd, $^{2}J_{CF}$ = 18.6, 4.9 Hz), –2.9, –3.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ –125.4 (d, J_{FF} = 148.5 Hz, 1F), –134.25 (dd, J_{FF} = 148.9 Hz, $^{3}J_{HF}$ = 17.3 Hz, 1F); HRMS (EI): calcd for $C_{21}H_{24}F_2O_2Si$ $[M]^+$: 374.1514, found: 374.1513.



4

***trans*-2-(2,2-Difluoro-3-(4-methoxyphenyl)cyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione** (**4**). Yield 75% (127.1 mg), white solid; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.21 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 4.31 (dd, J = 32.0, 17.2 Hz, 2H), 4.08 (dd, J = 16.8, 11.6 Hz, 2H), 3.74 (s, 3H), 2.95 (s, 3H), 2.70 (t, J = 10.4 Hz, 1H), 1.51 (ddd, J = 17.2, 9.6, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.1, 168.3, 158.1, 128.7, 125.9, 115.8 (dd, $^{1}J_{CF}$ = 287.7, 279.5 Hz), 113.7, 61.9, 61.8, 55.0, 46.6, 28.5 (t, $^{2}J_{CF}$ = 10.6 Hz) [Note: the carbon attached to boron was not observed due to quadrupole broadening caused by the ^{11}B nucleus]; ^{19}F NMR (376 MHz, DMSO-d_6) δ –127.0 (ddd, J_{FF} = 145.8 Hz, $^{3}J_{HF}$ = 11.3, 4.9 Hz, 1F), –134.1 (dd, J_{FF} = 145.8 Hz, $^{3}J_{HF}$ = 17.6, 4.1 Hz, 1F); HRMS (ESI): calcd for $C_{15}H_{15}BF_2NO_5$ $[M–H]^+$: 338.1011, found: 338.1010.

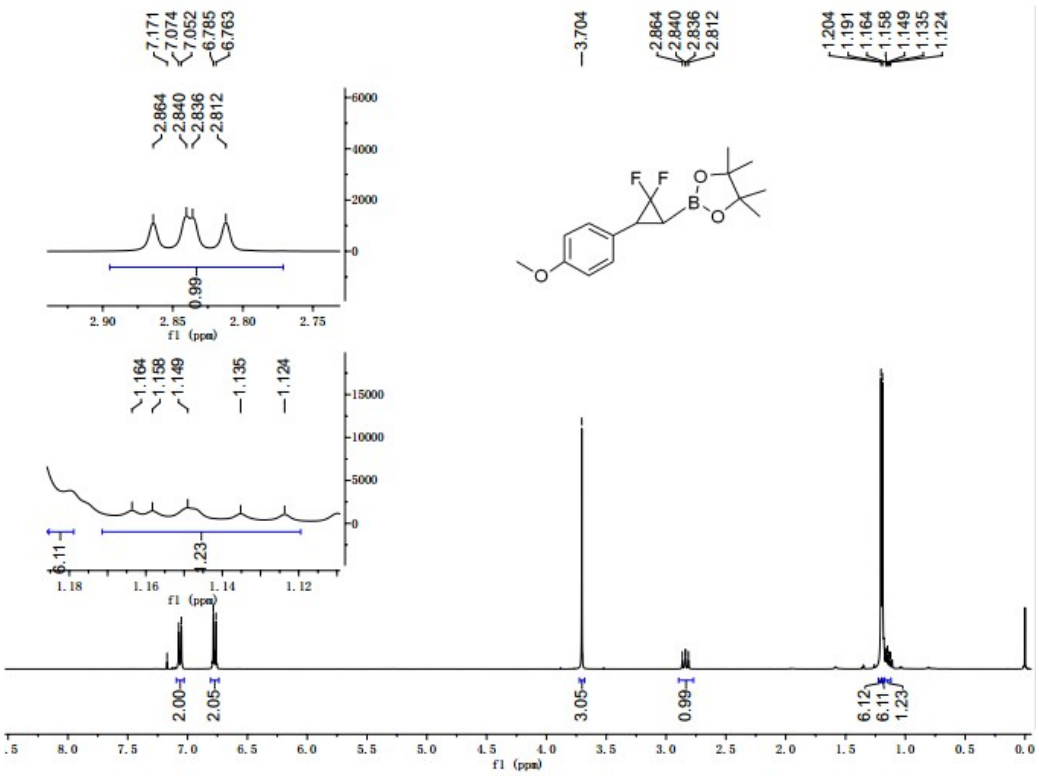
9. References

1. Wang, F.; Hu, J.; Prakash, G. K. S.; Olah, G. A. *Angew. Chem. Int. Ed.* **2011**, *50*, 7153.

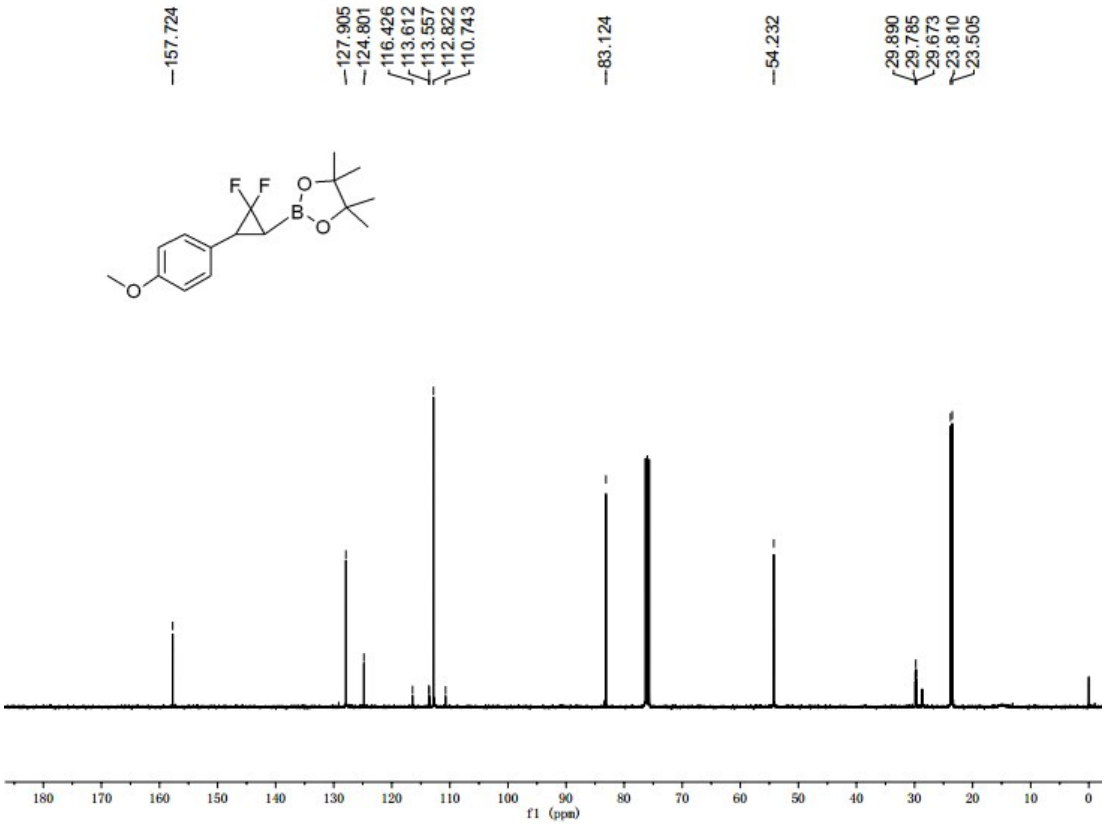
2. Fujioka, Y.; Amii, H. *Org. Lett.* **2008**, *10*, 769.

10. ^{1}H, ^{13}C, ^{19}F NMR and HRMS (EI) spectra of target compounds

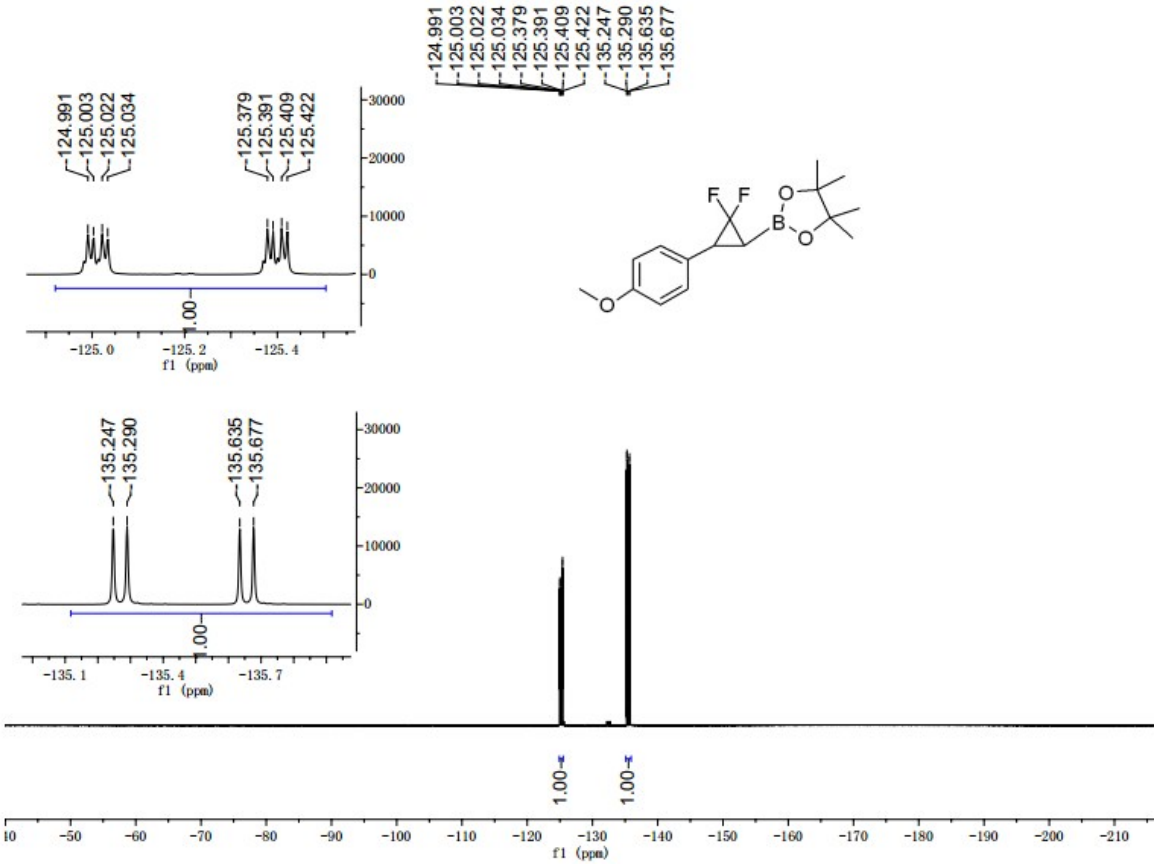
^{1}H NMR spectrum of 3aa



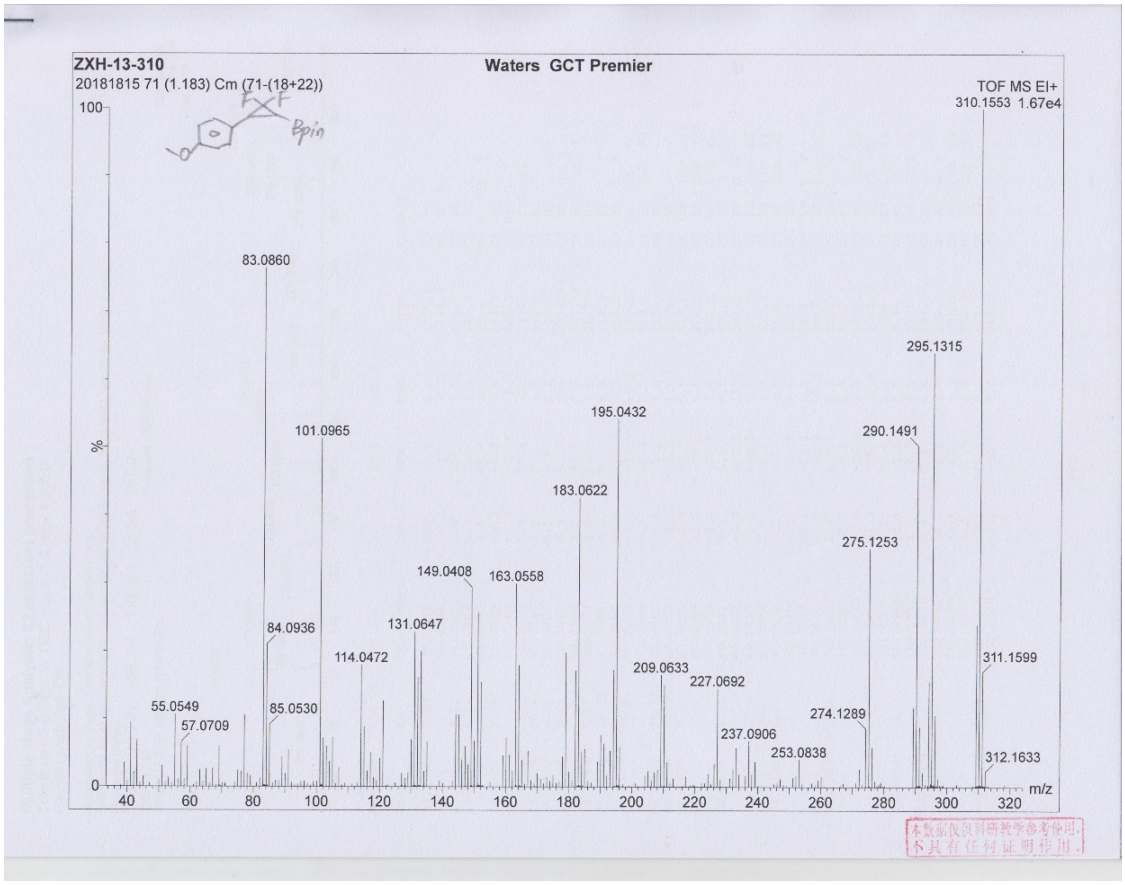
^{13}C NMR spectrum of 3aa



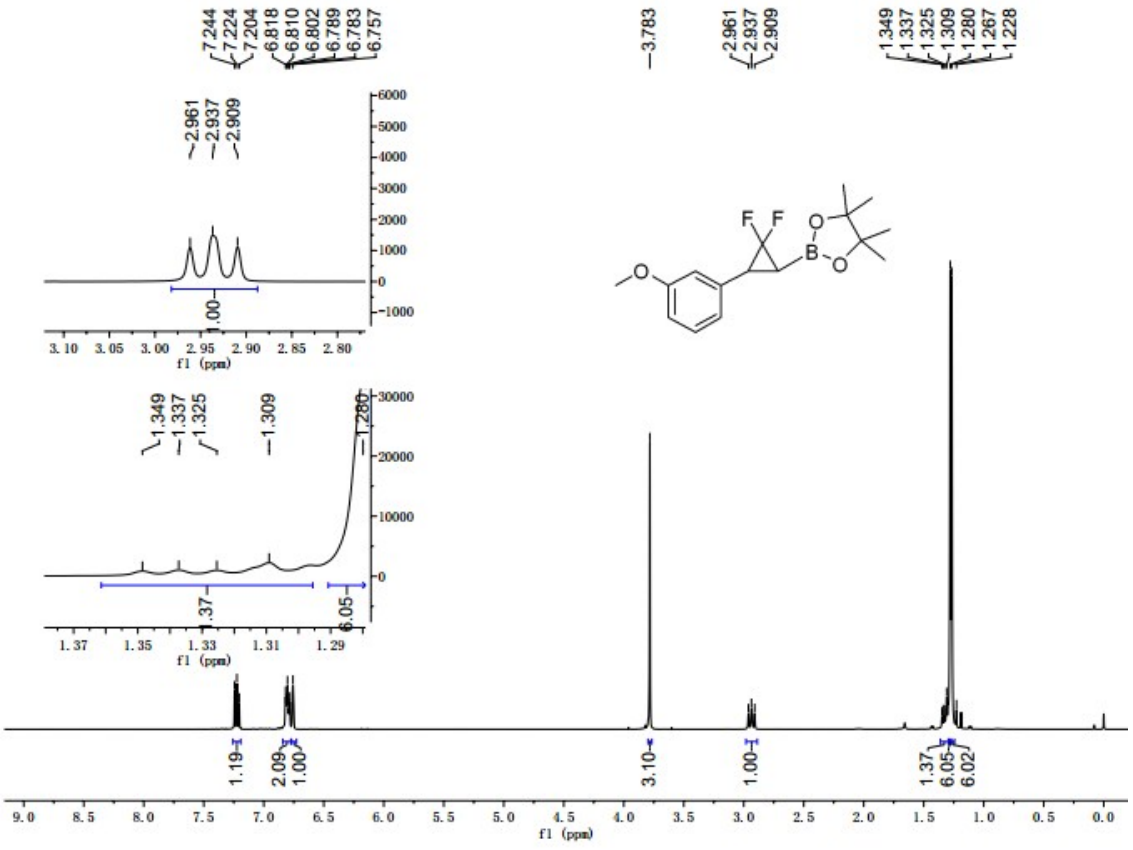
^{19}F NMR spectrum of 3aa



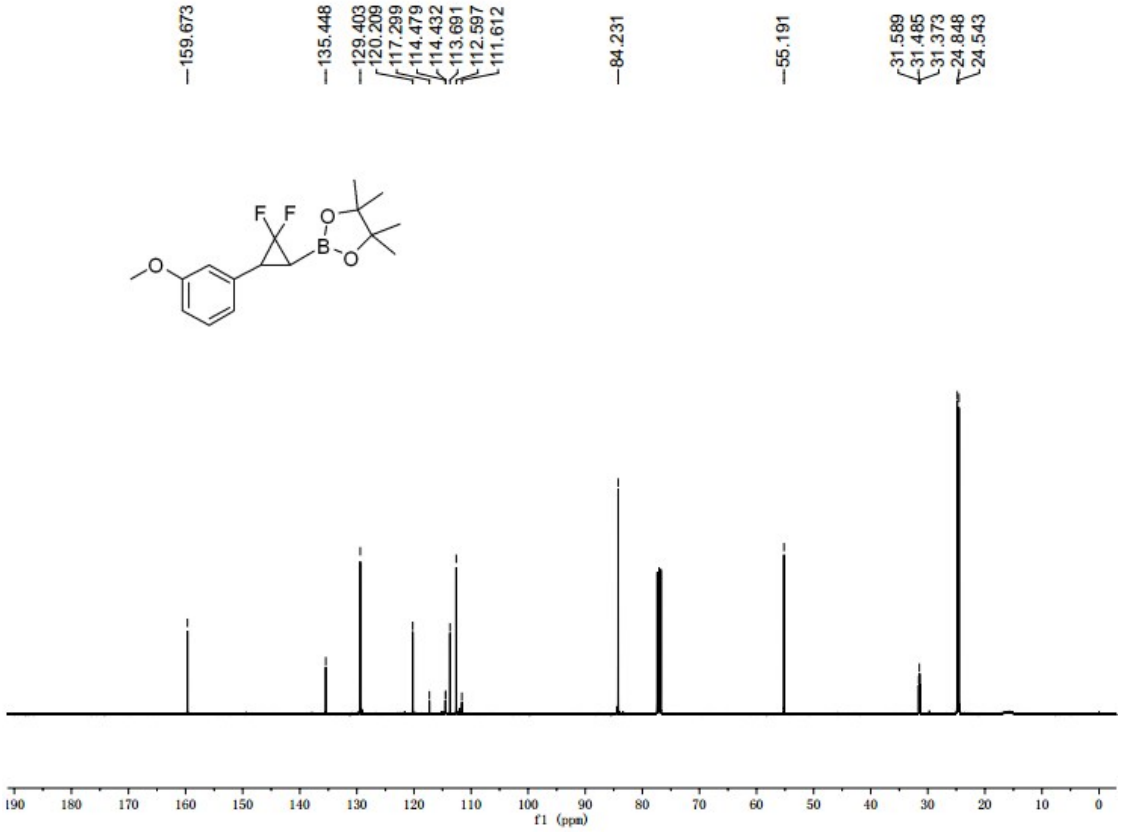
HRMS (EI) of 3aa



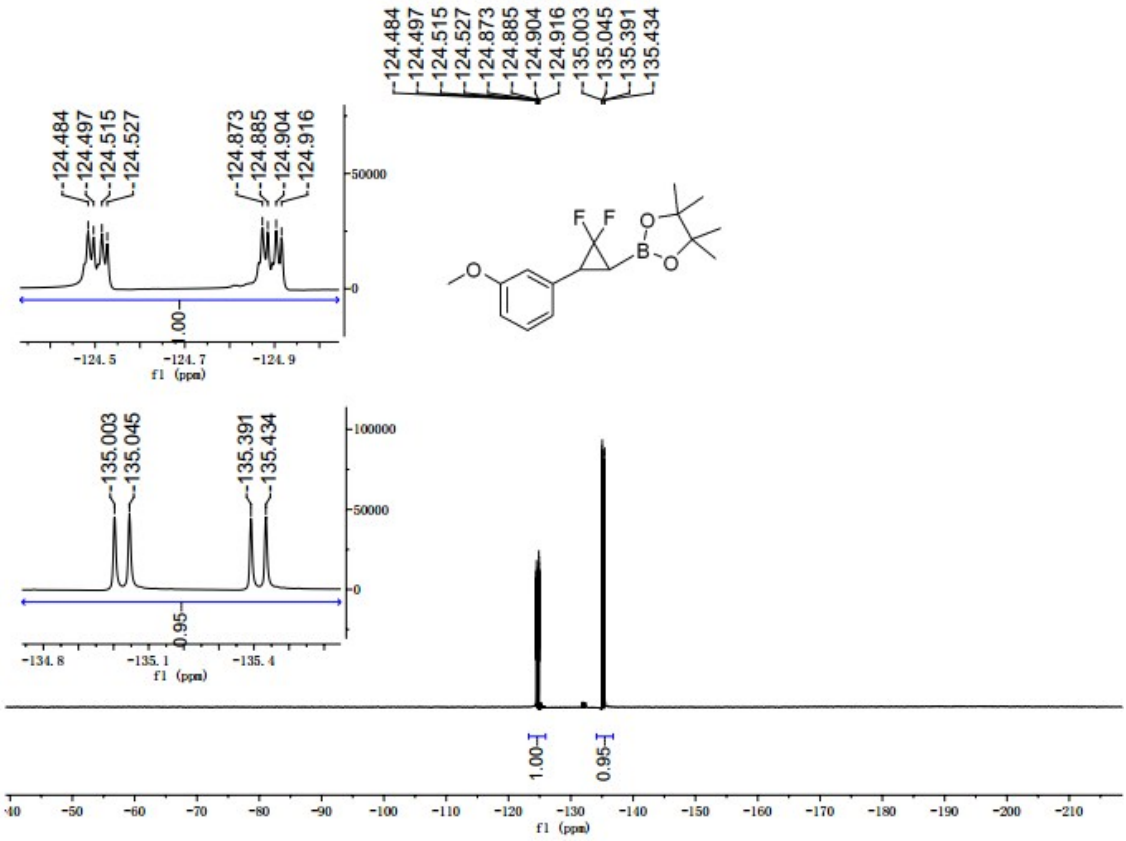
[1]H NMR spectrum of 3ba



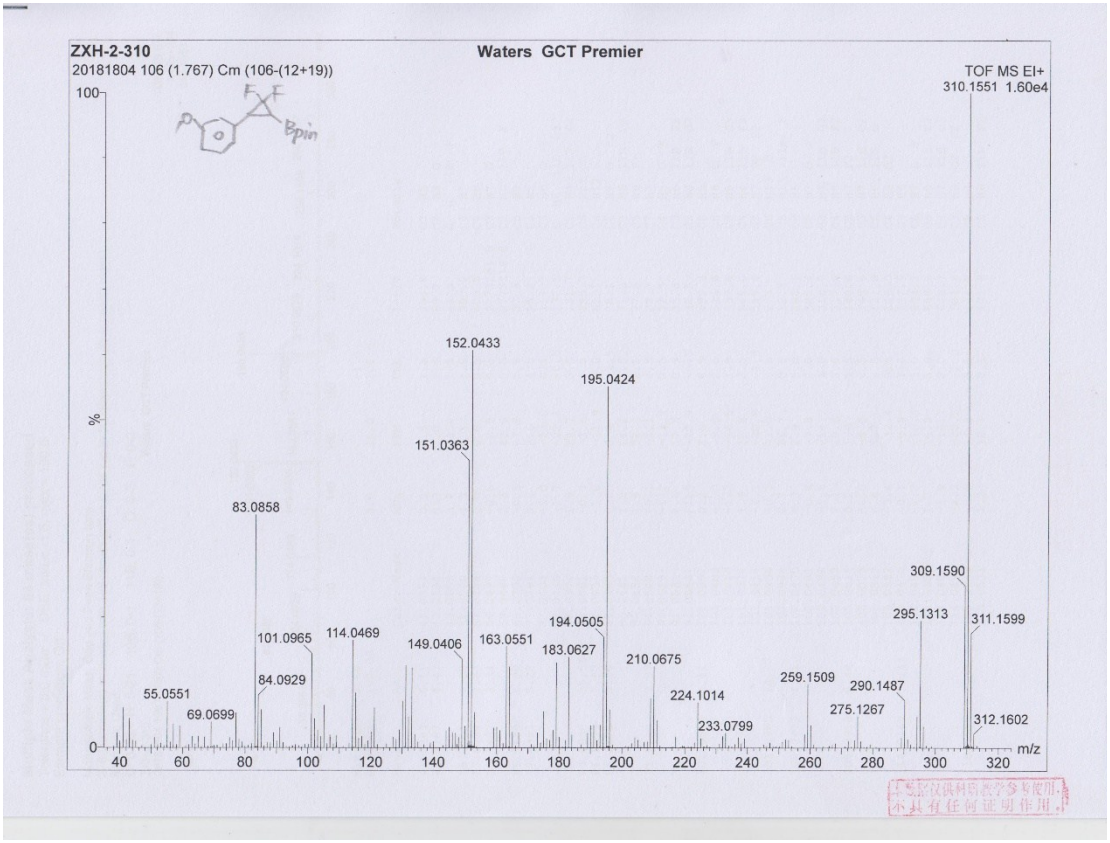
^{13}C NMR spectrum of 3ba



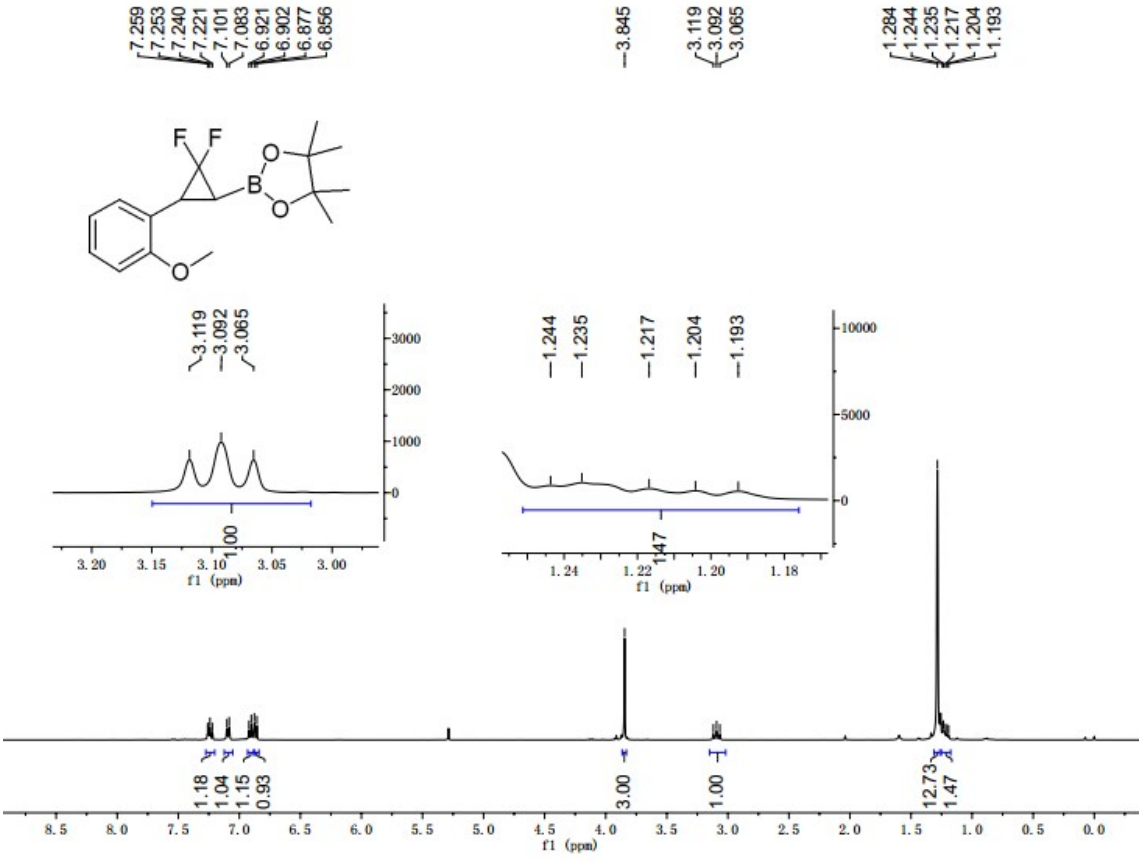
^{19}F NMR spectrum of 3ba



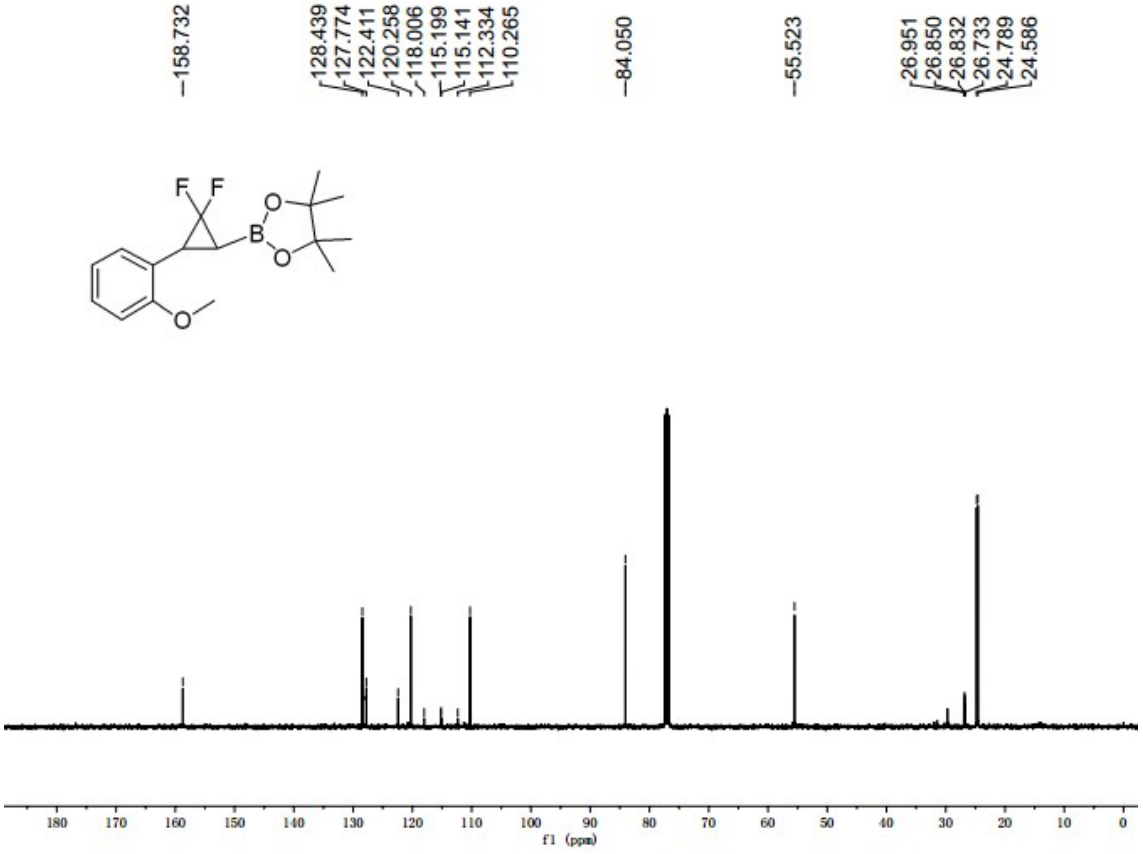
HRMS (EI) of 3ba



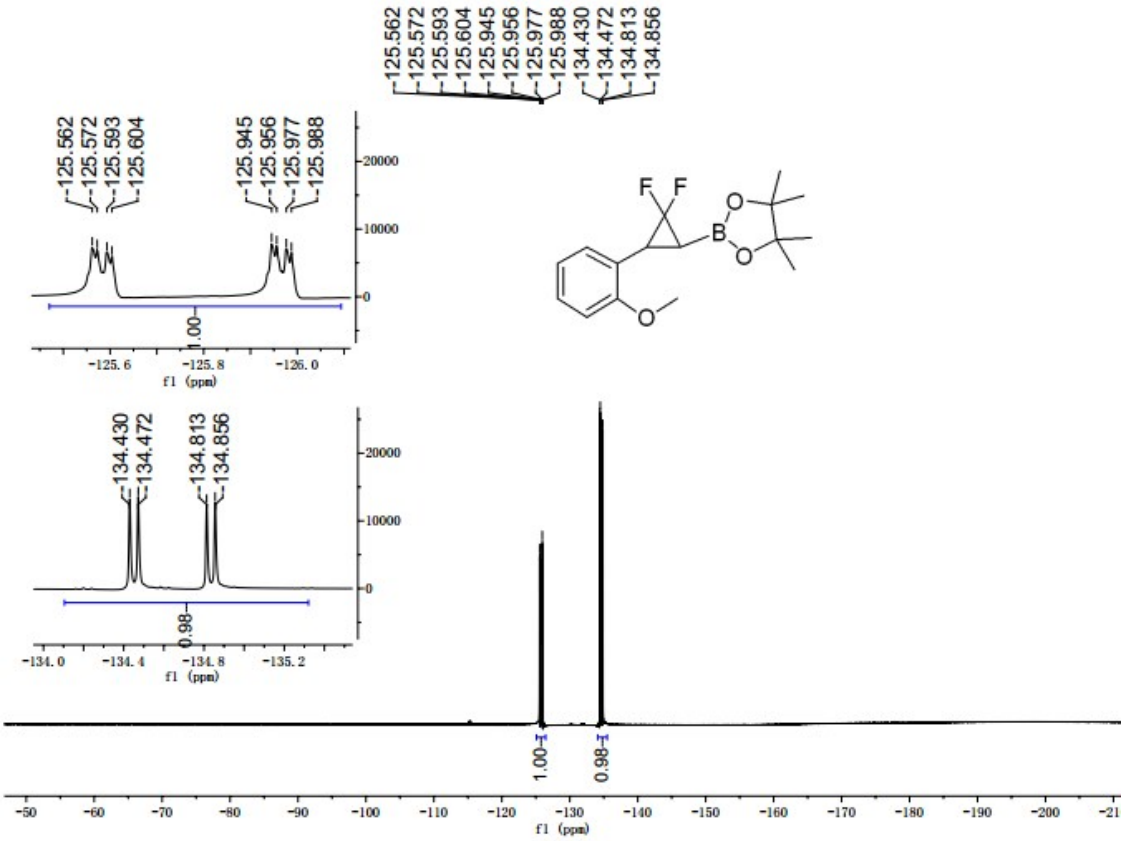
^{1}H NMR spectrum of 3ca



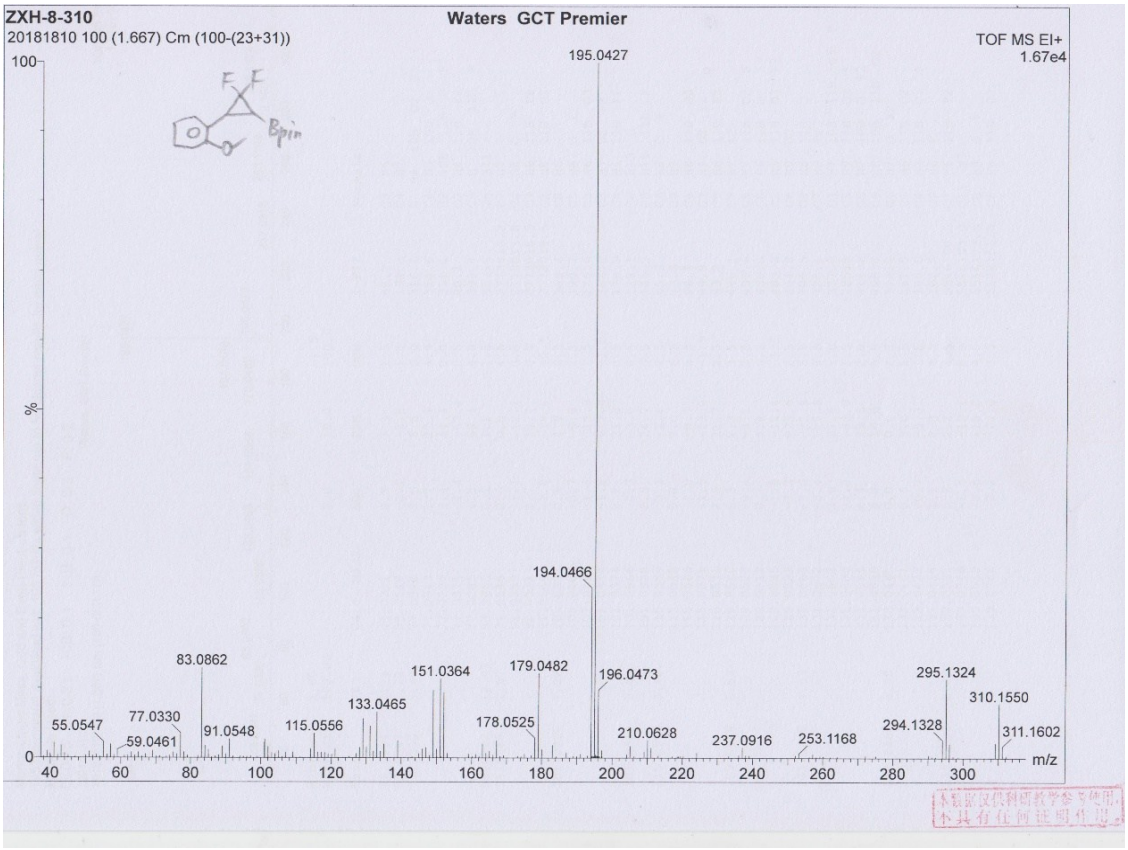
^{13}C NMR spectrum of 3ca



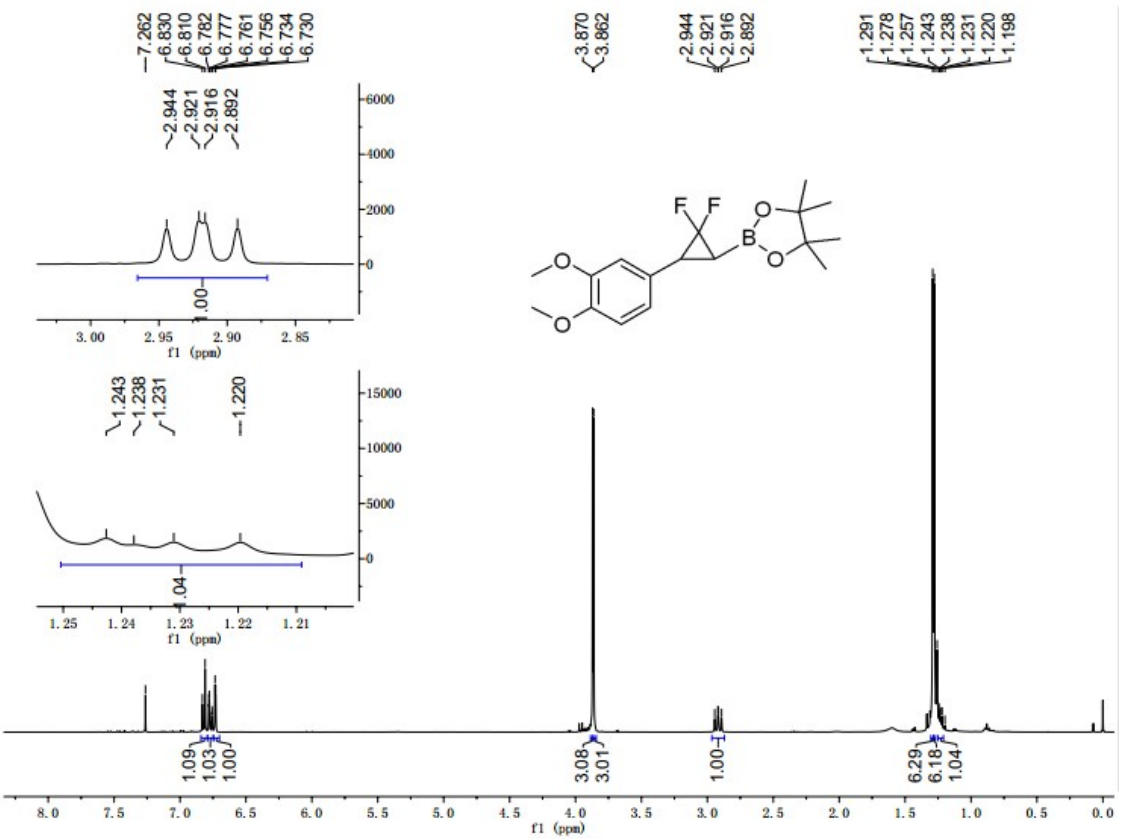
^{19}F NMR spectrum of 3ca



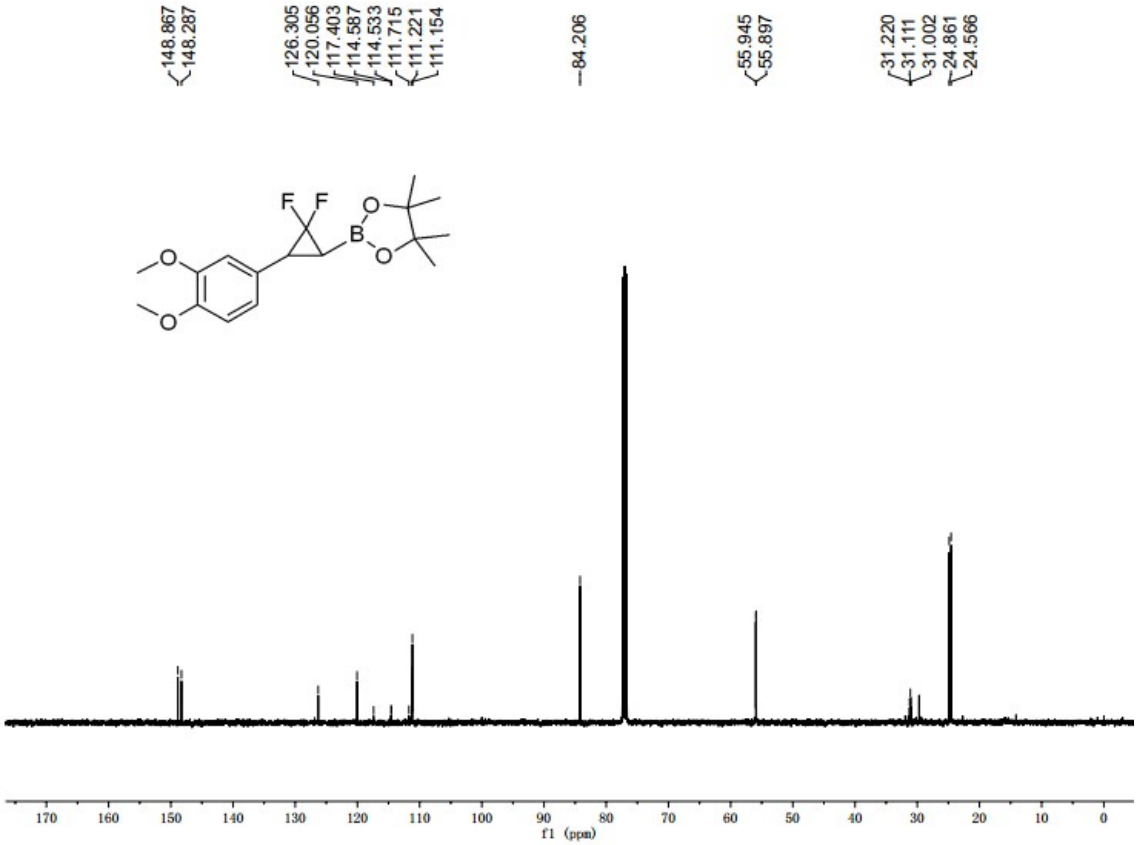
HRMS (EI) of 3ca



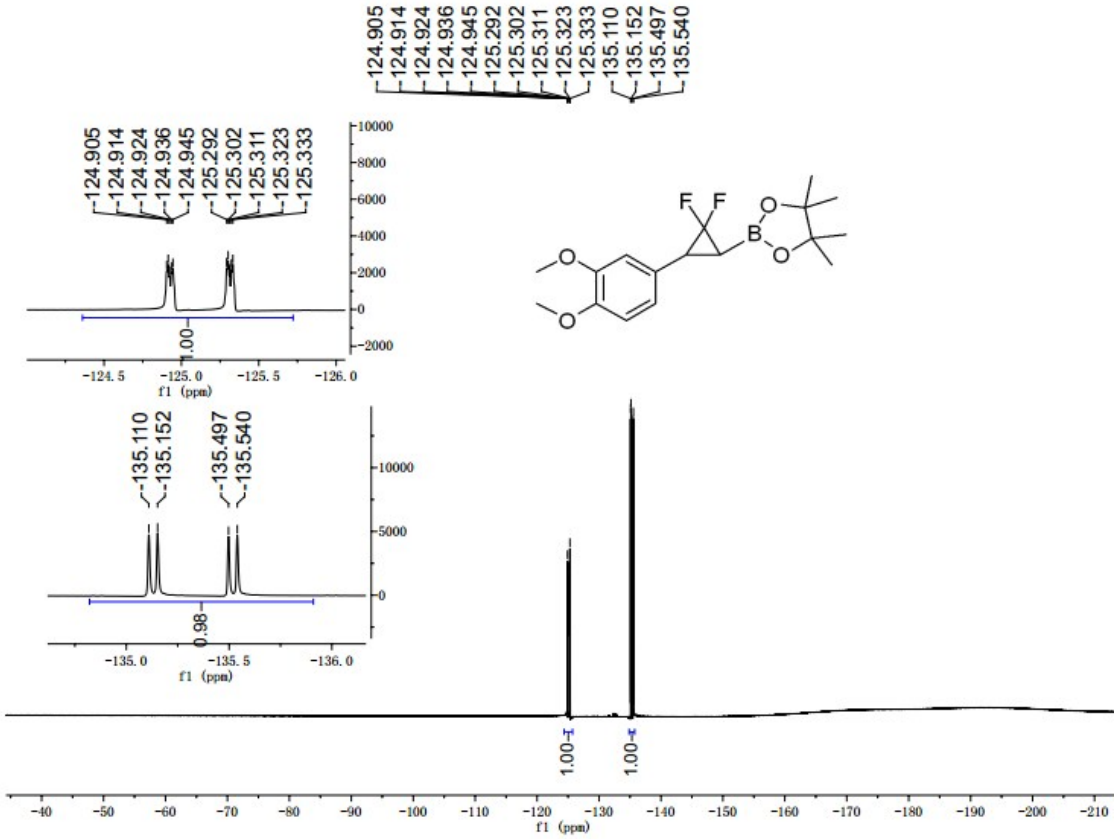
^{1}H NMR spectrum of 3da



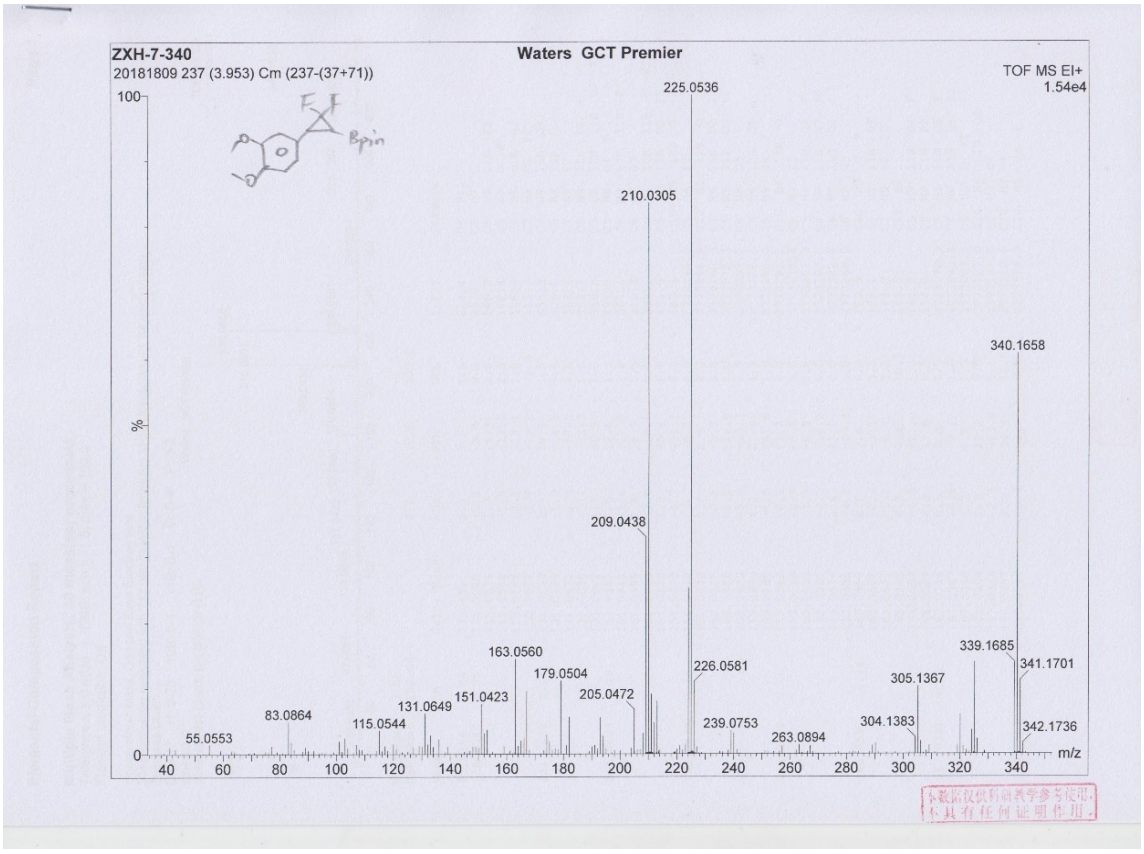
^{13}C NMR spectrum of 3da



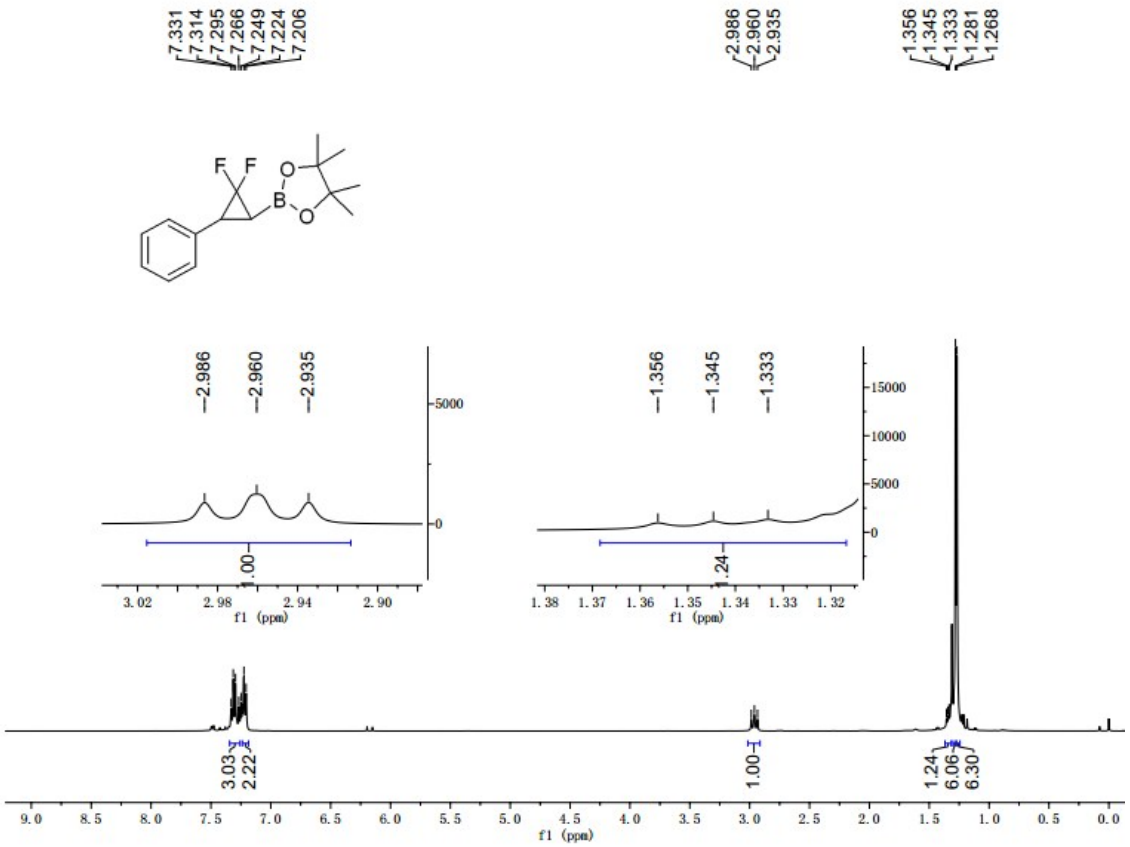
^{19}F NMR spectrum of 3da



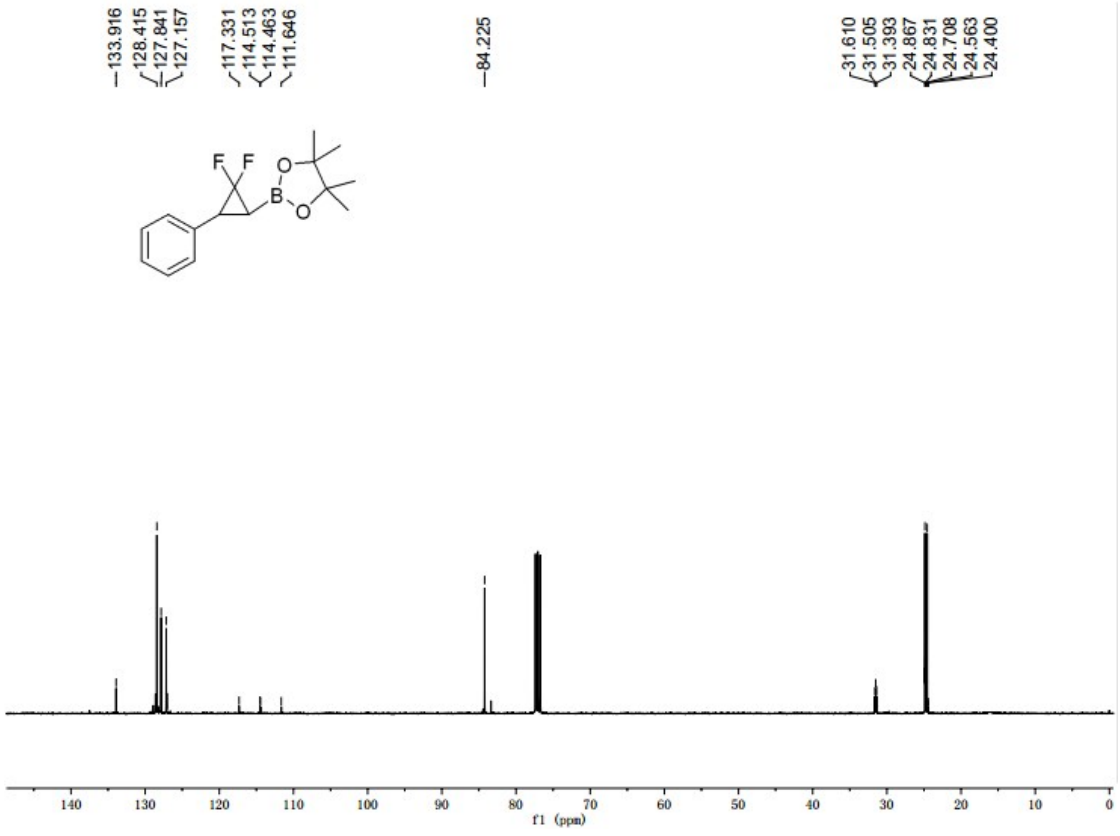
HRMS (EI) of 3da



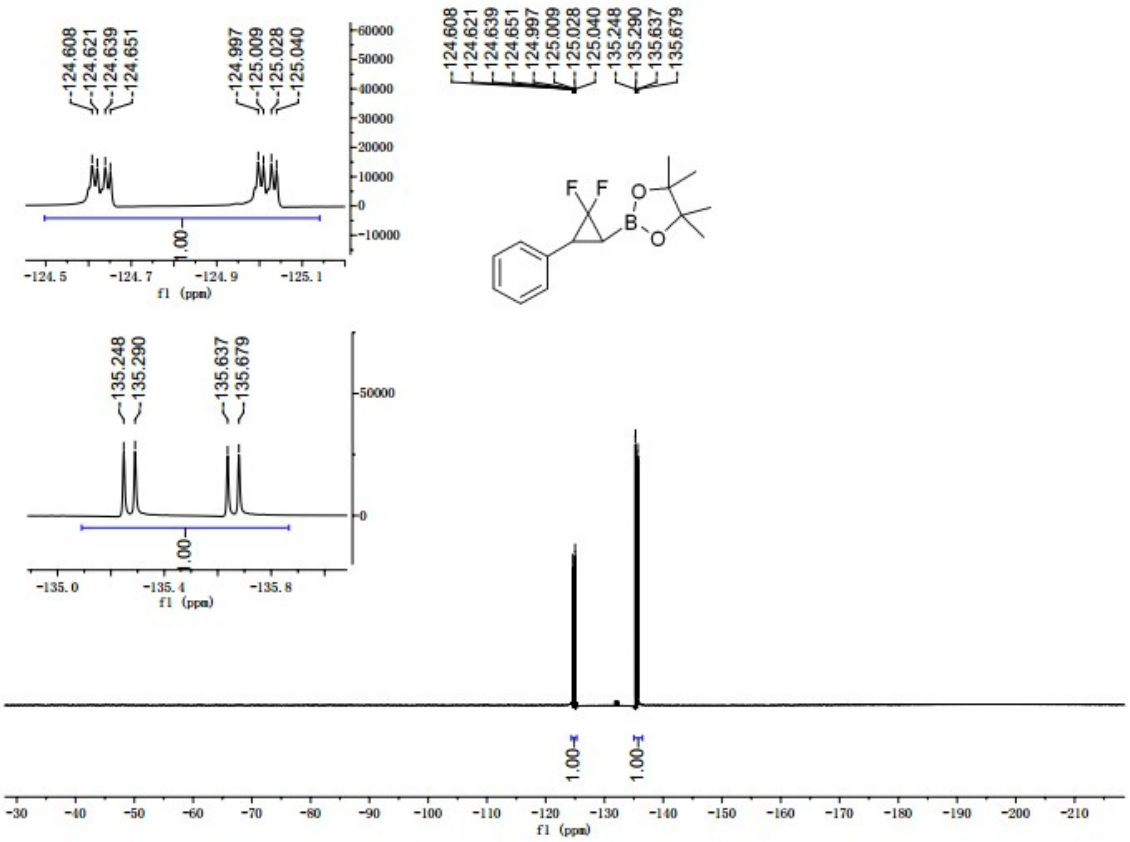
^{1}H NMR spectrum of 3ea



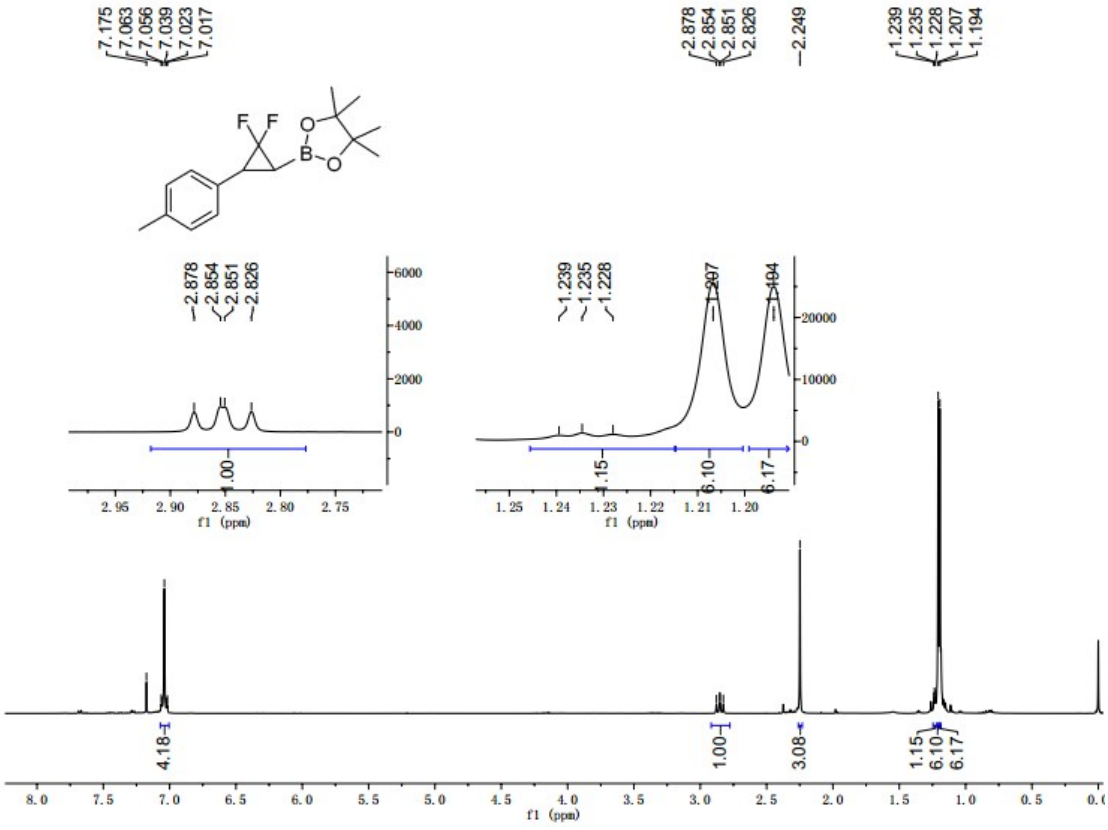
^{13}C NMR spectrum of 3ea



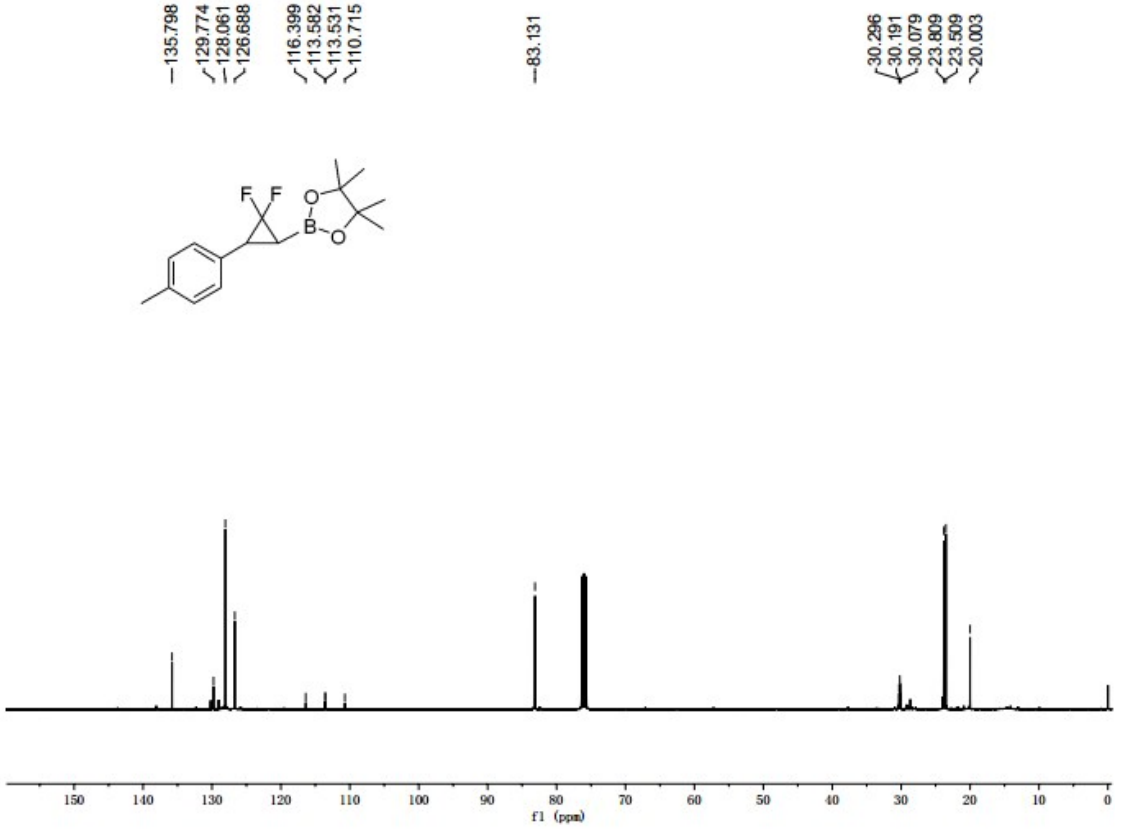
^{19}F NMR spectrum of 3ea



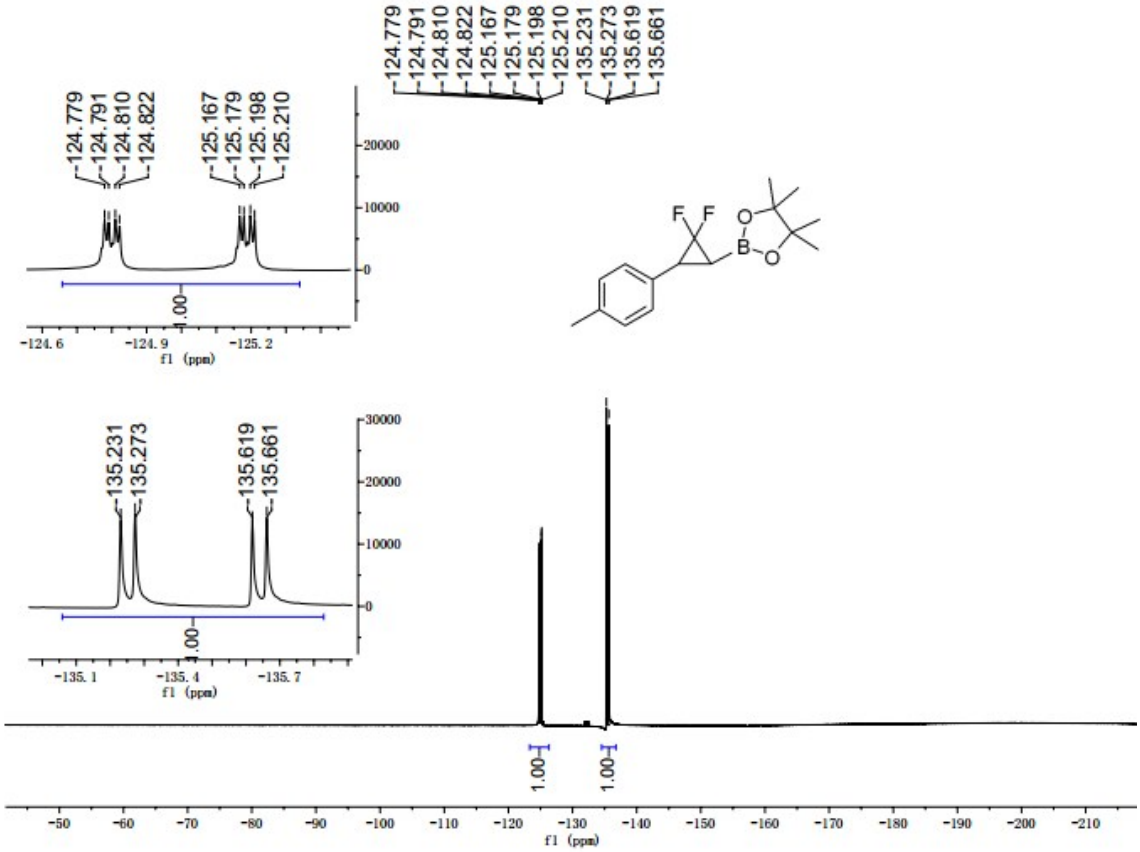
^{1}H NMR spectrum of 3fa



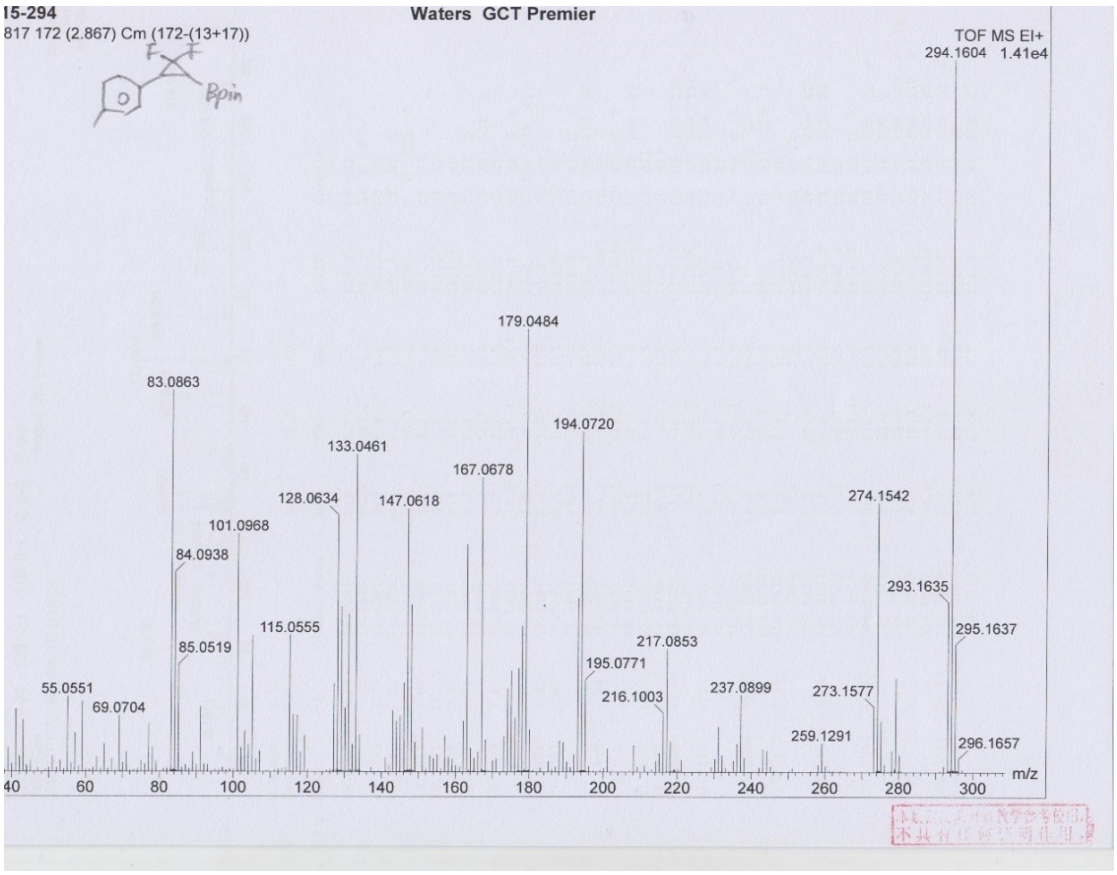
^{13}C NMR spectrum of 3fa



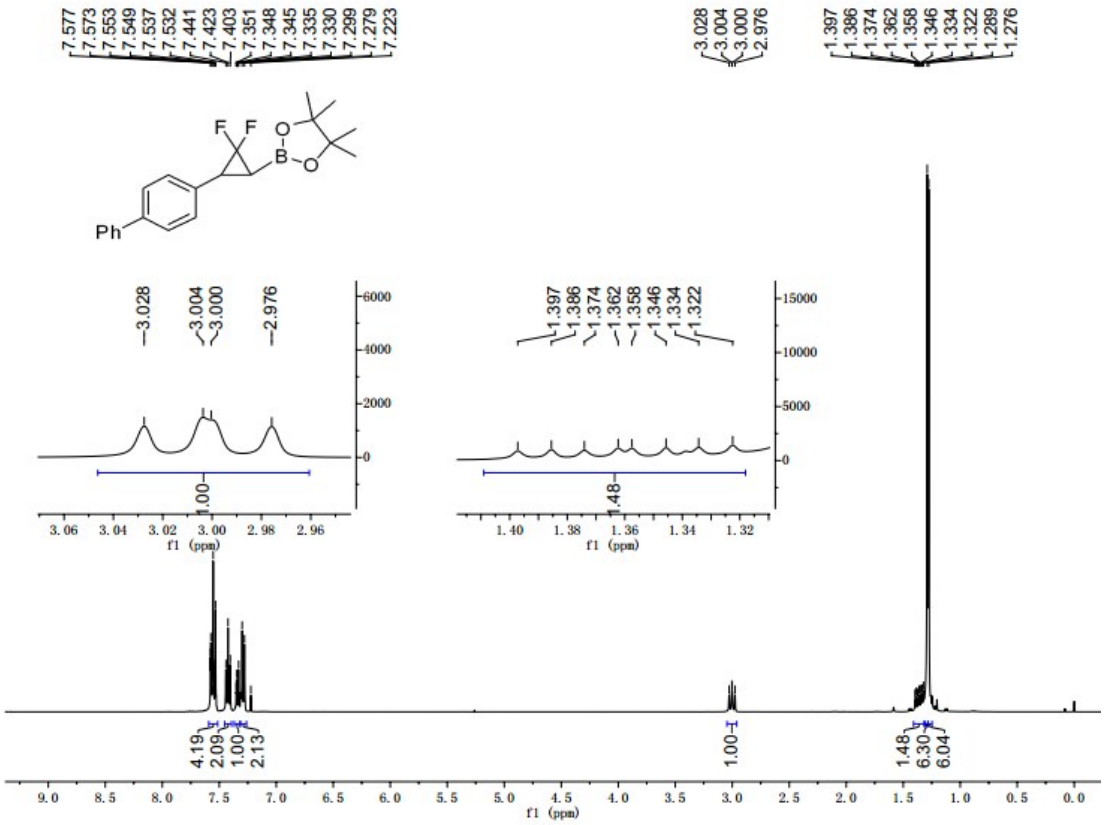
^{19}F NMR spectrum of 3fa



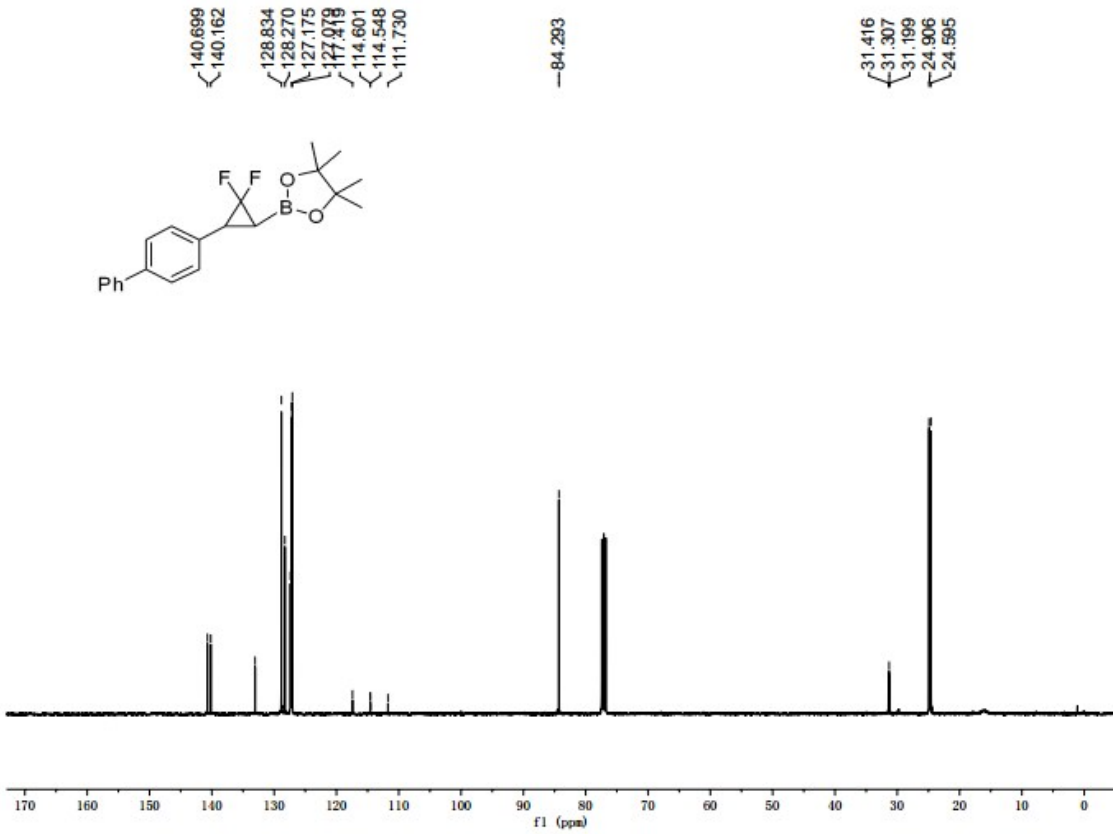
HRMS (EI) of 3fa



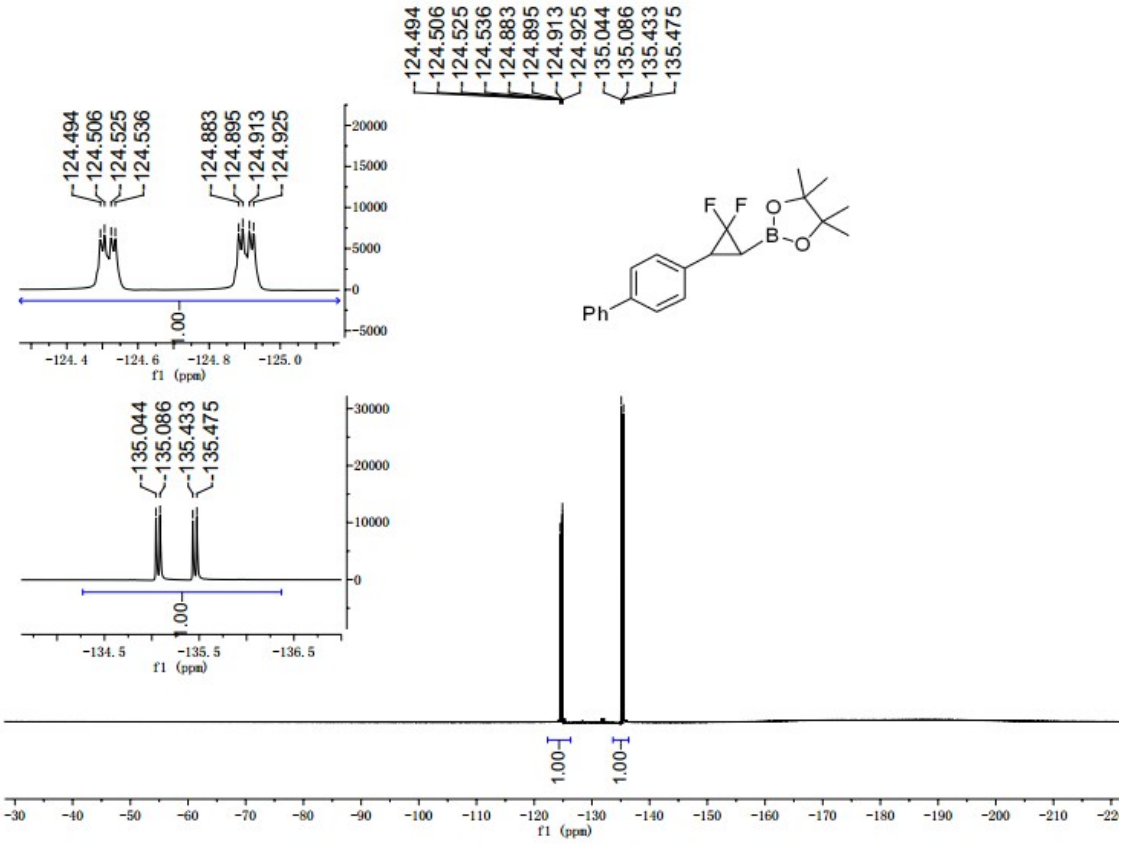
[1]H NMR spectrum of 3ga



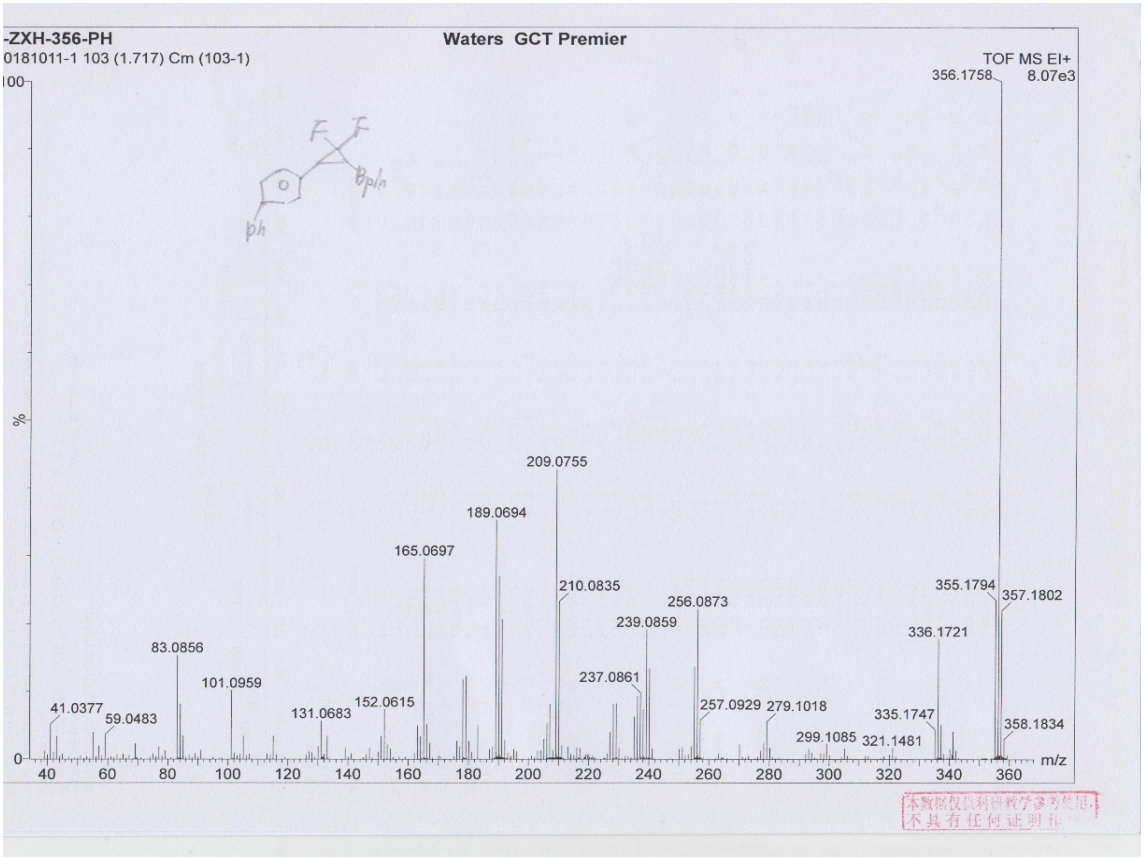
[13]C NMR spectrum of 3ga



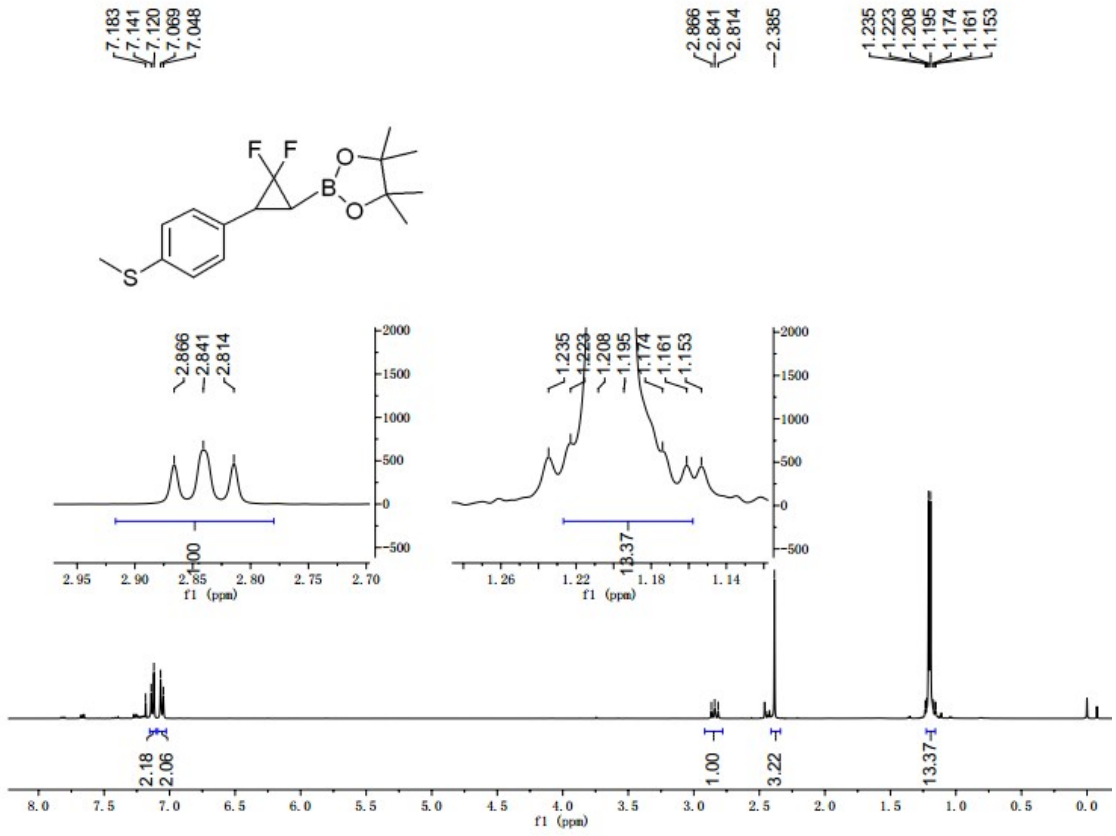
^{19}F NMR spectrum of 3ga



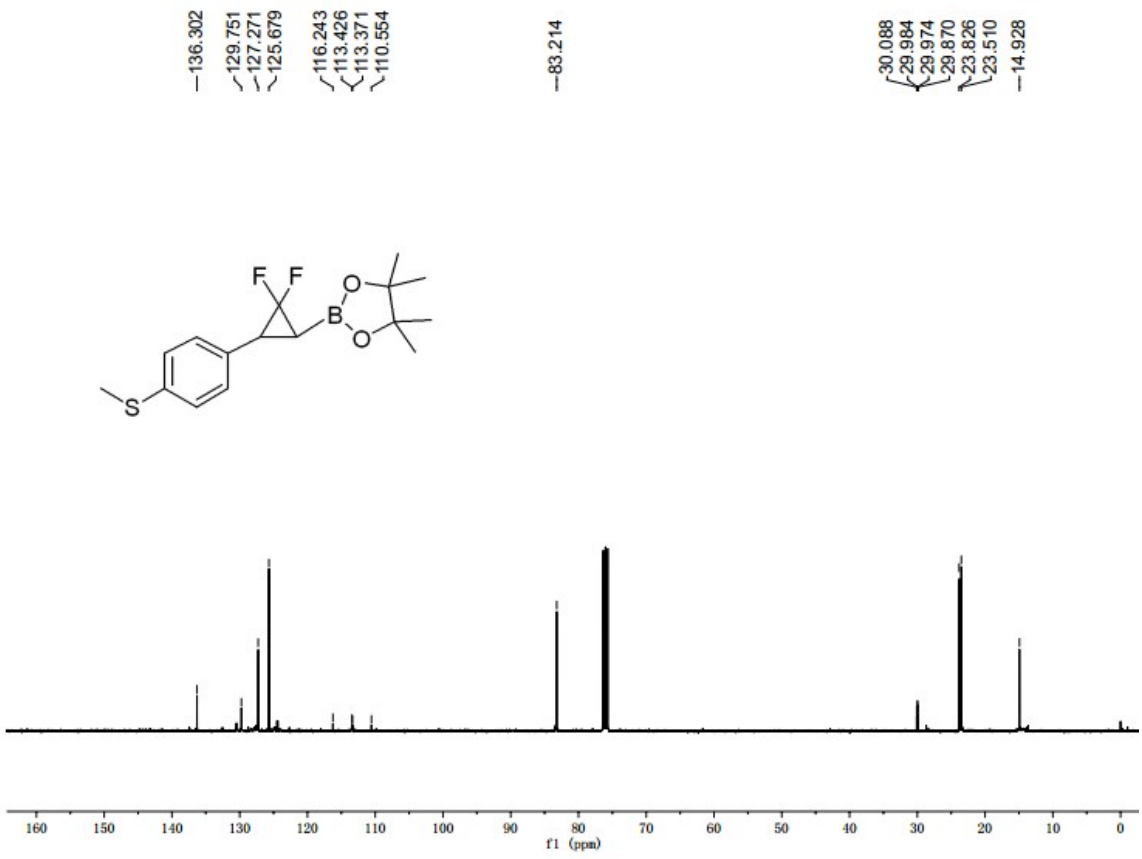
HRMS (EI) of 3ga



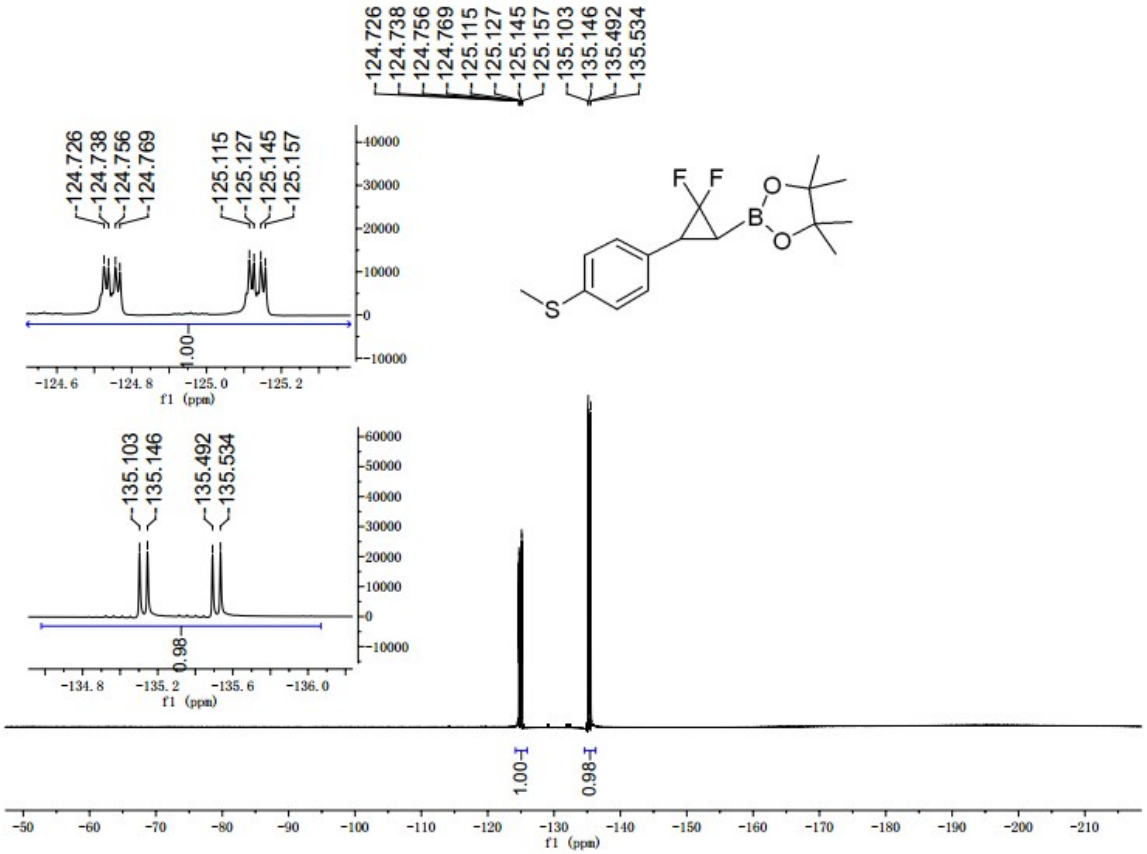
[1]H NMR spectrum of 3ha



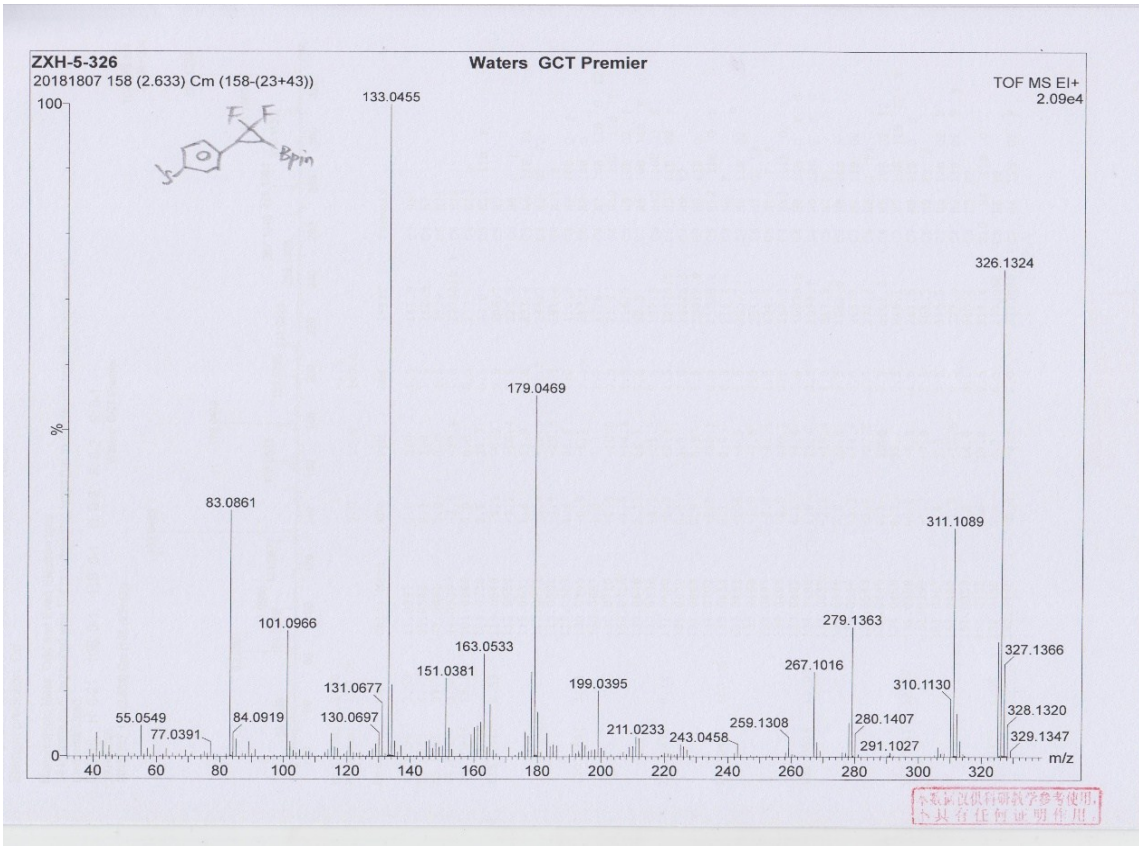
[13]C NMR spectrum of 3ha



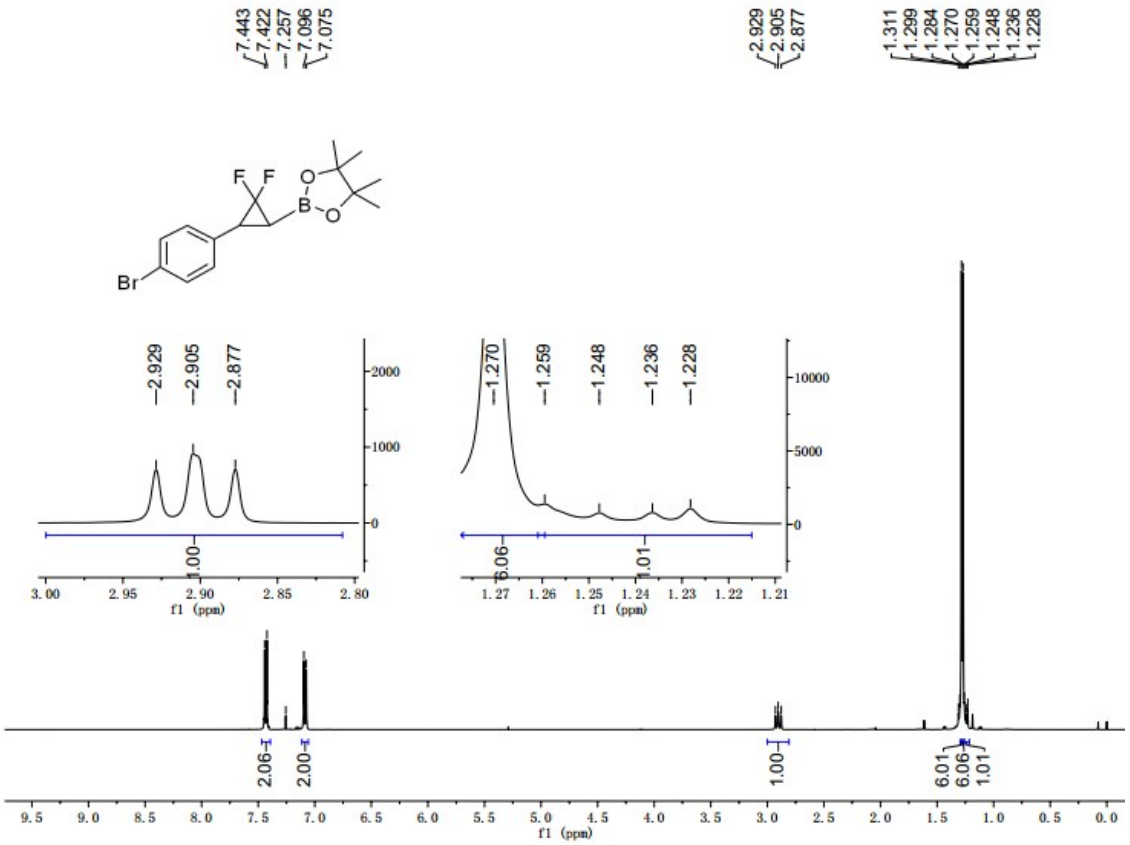
^{19}F NMR spectrum of 3ha



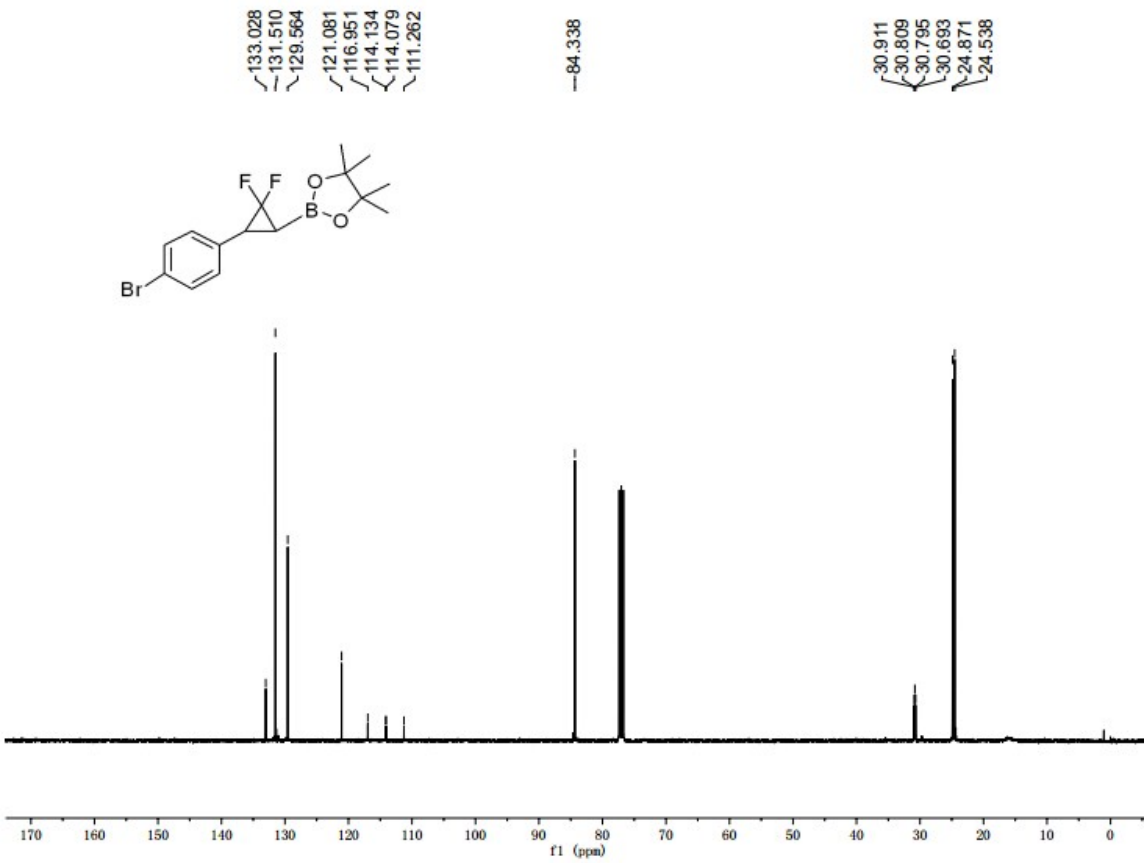
HRMS (EI) of 3ha



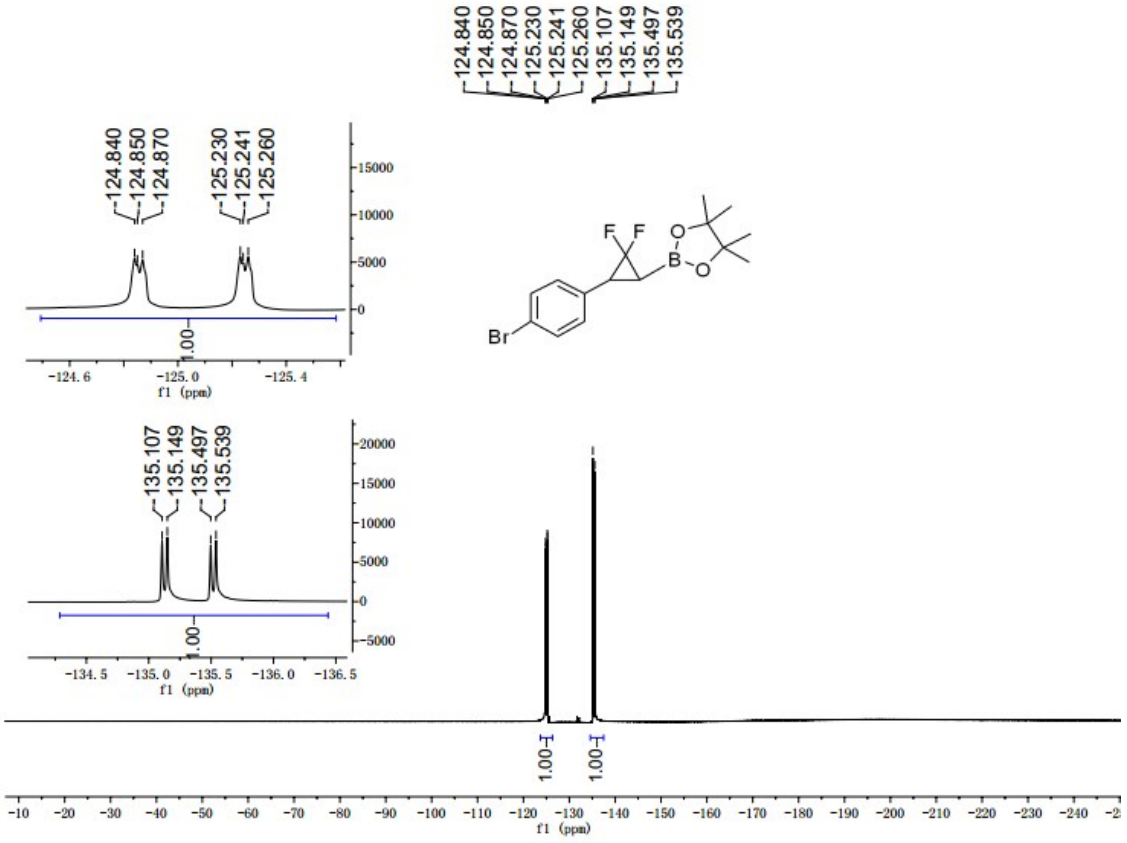
^{1}H NMR spectrum of 3ia



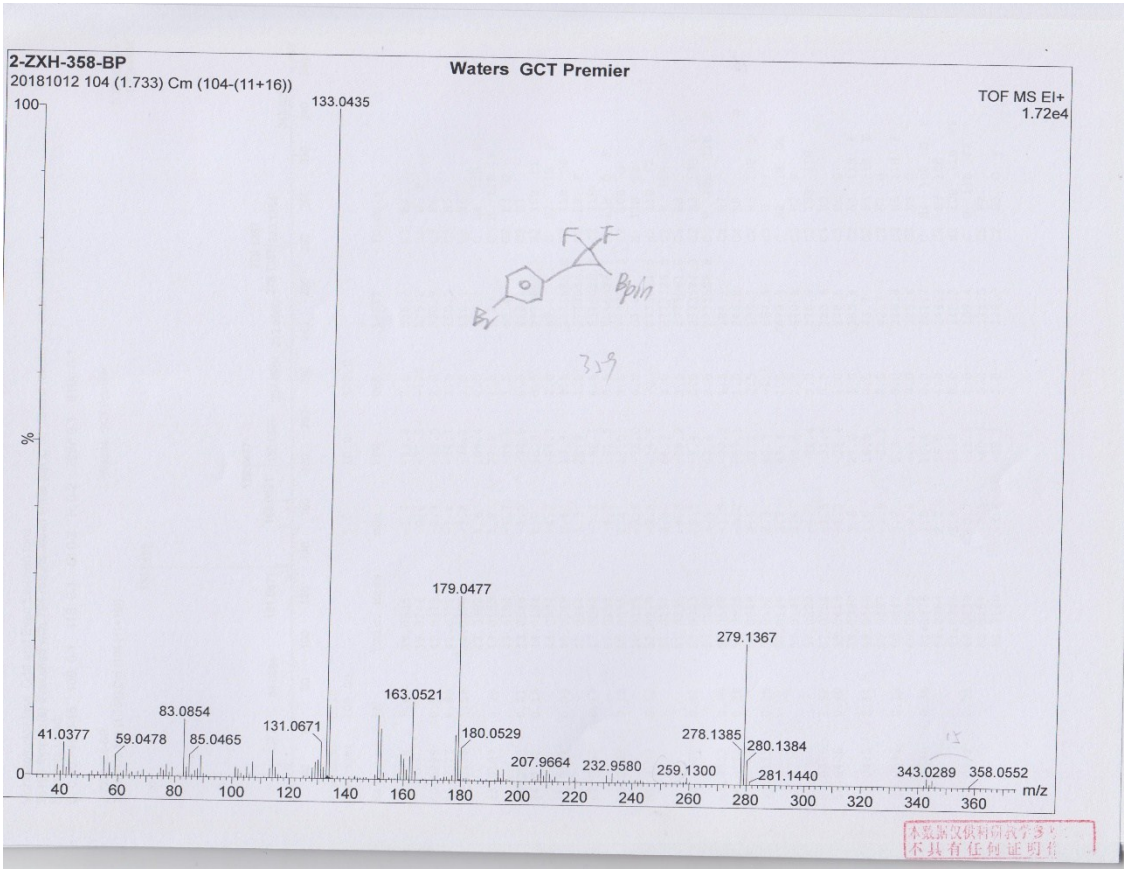
^{13}C NMR spectrum of 3ia



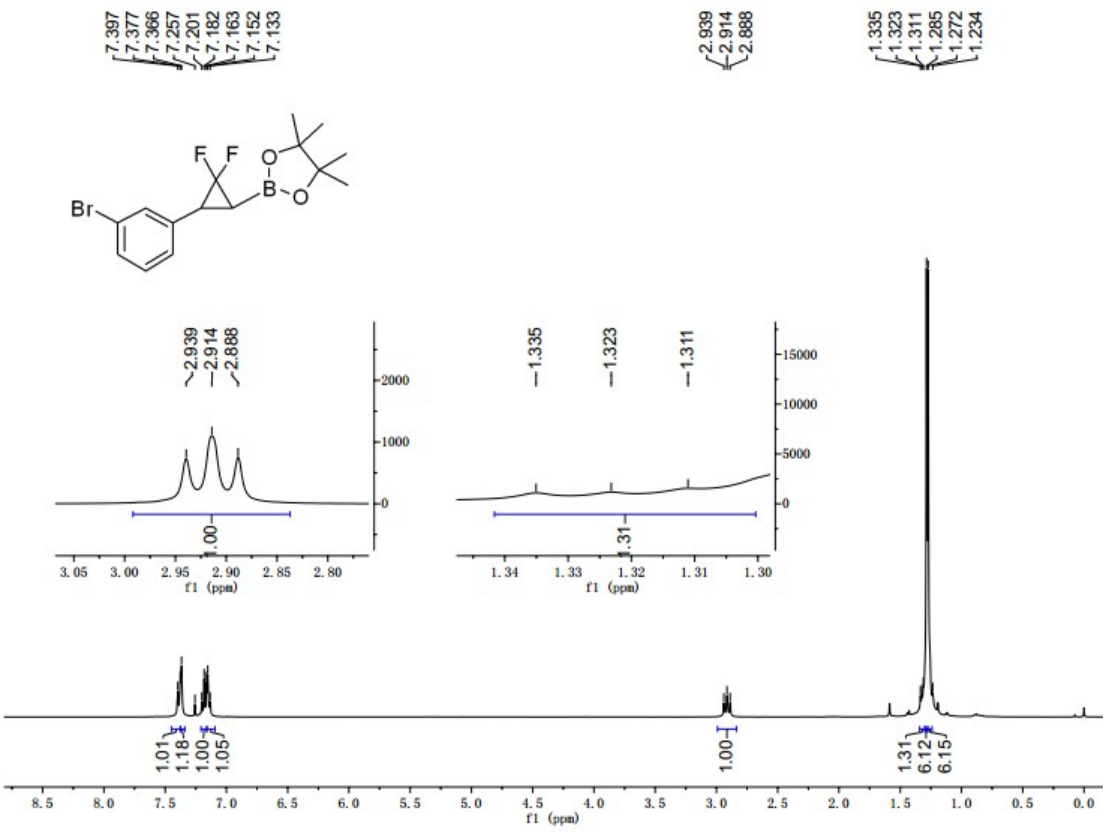
^{19}F NMR spectrum of 3ia



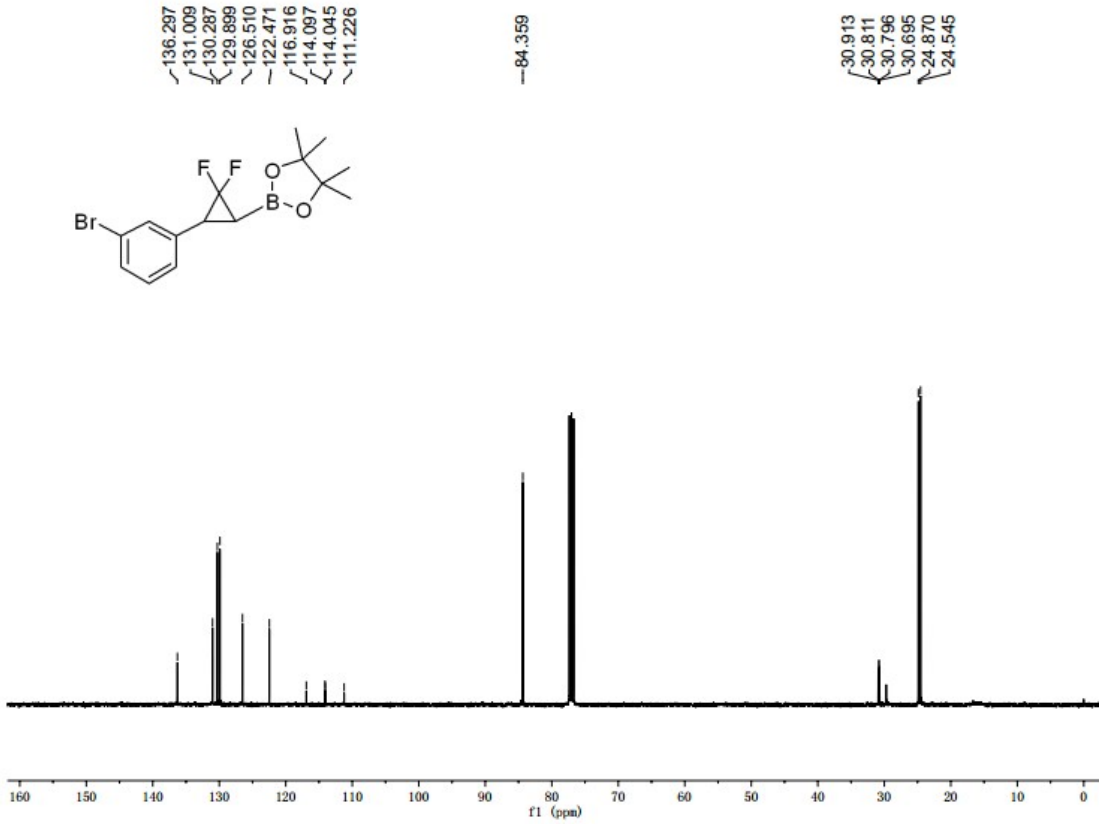
HRMS (EI) of 3ia



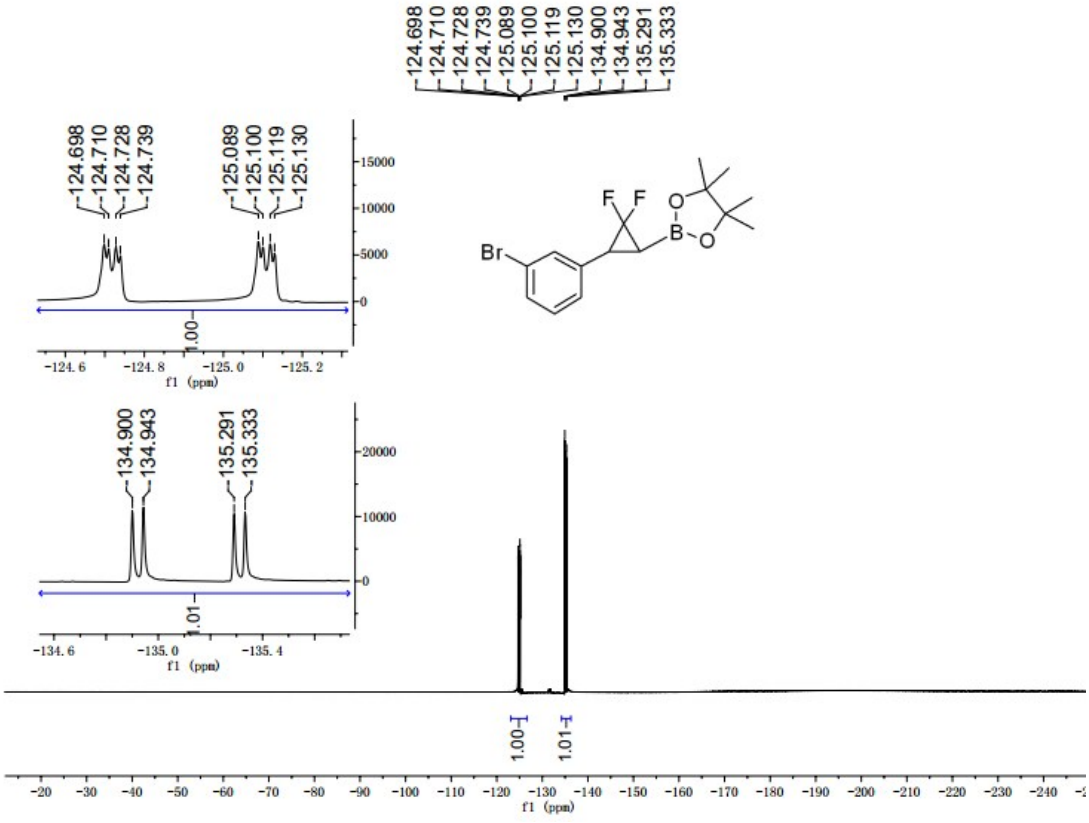
^{1}H NMR spectrum of 3ja



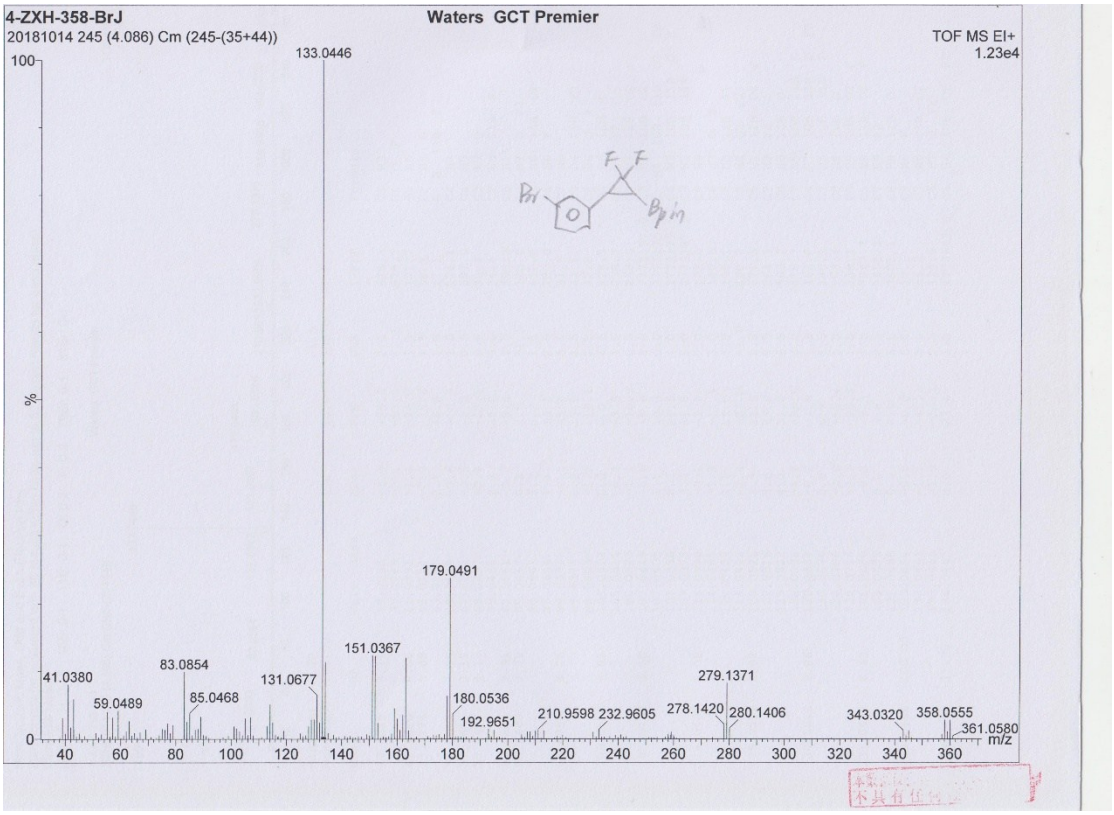
^{13}C NMR spectrum of 3ja



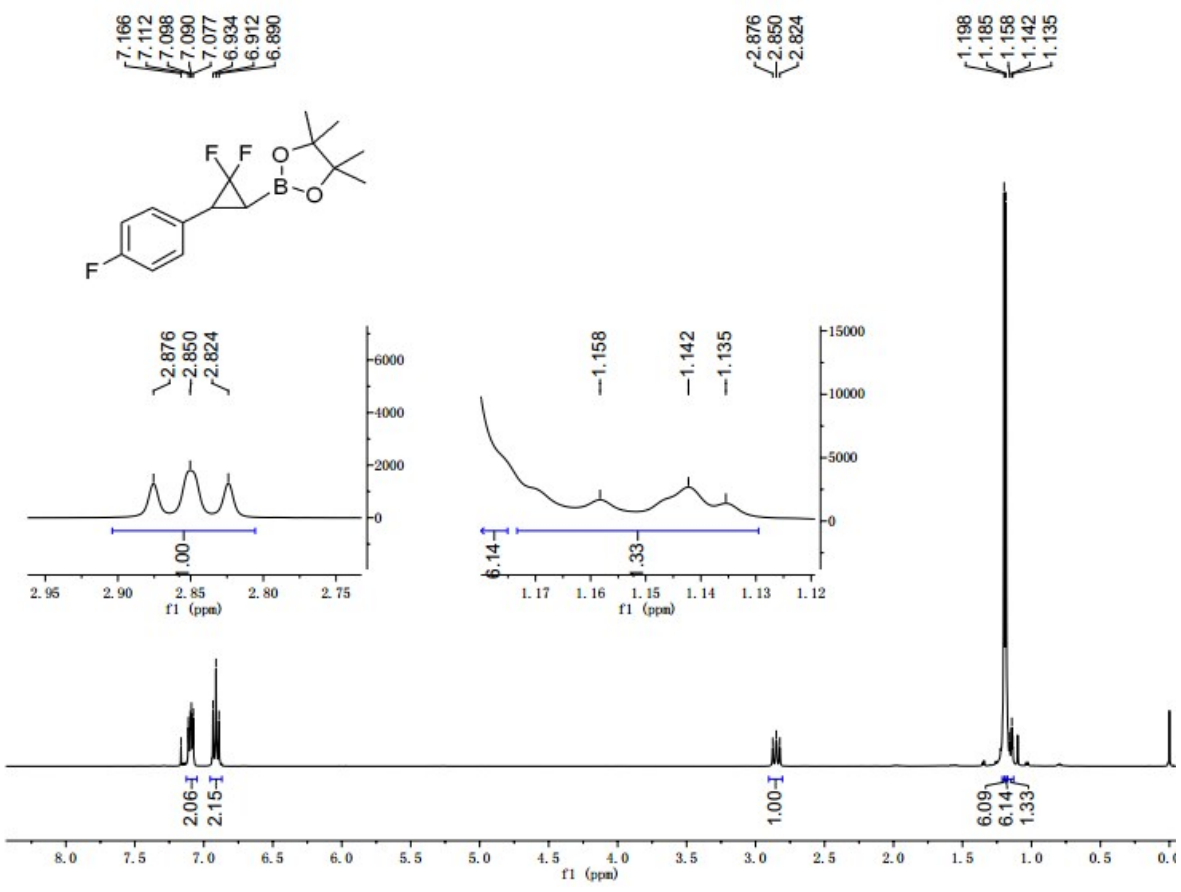
^{19}F NMR spectrum of 3ja



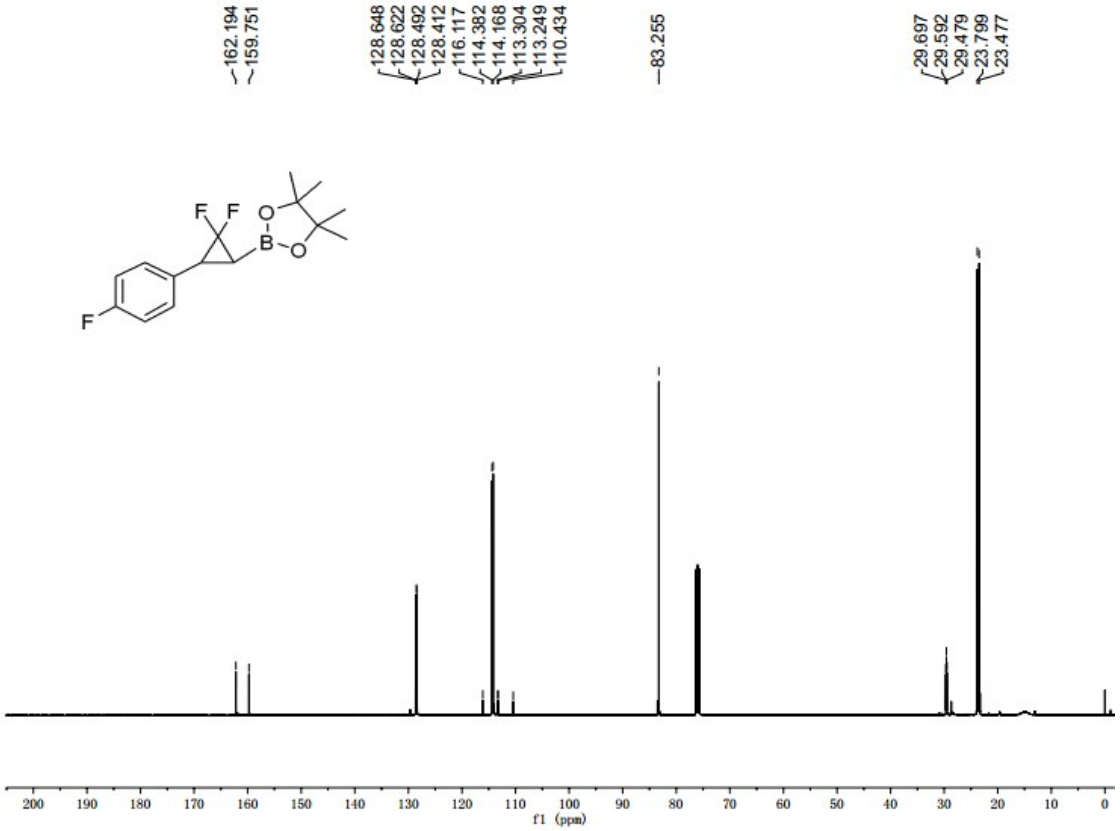
HRMS (EI) of 3ja



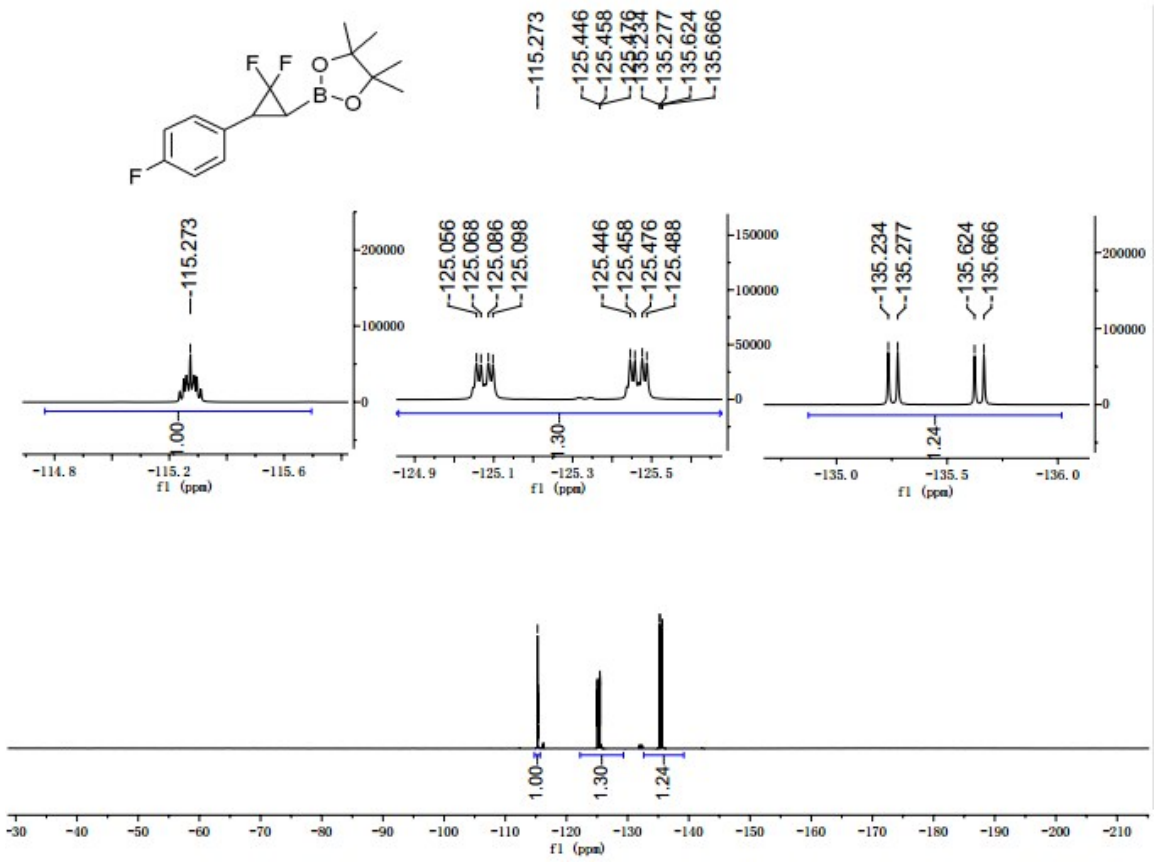
[1]H NMR spectrum of 3ka



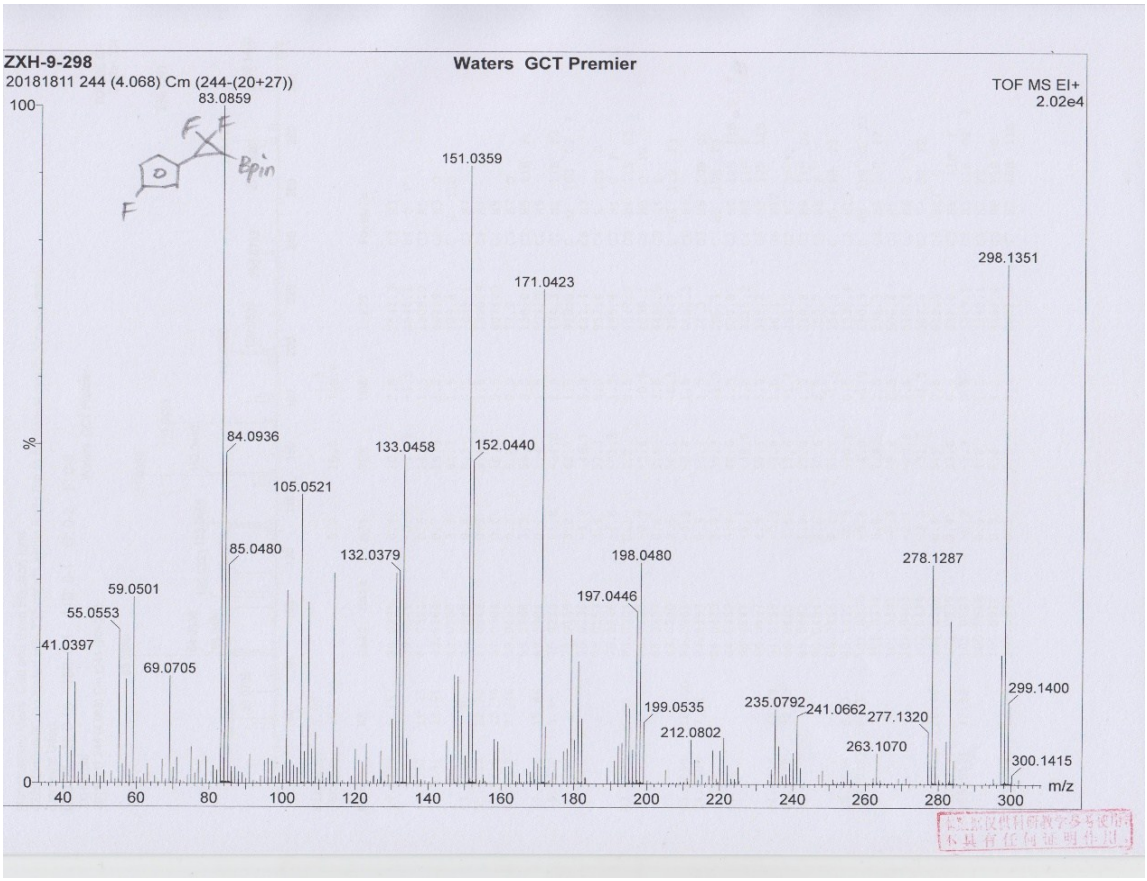
[13]C NMR spectrum of 3ka



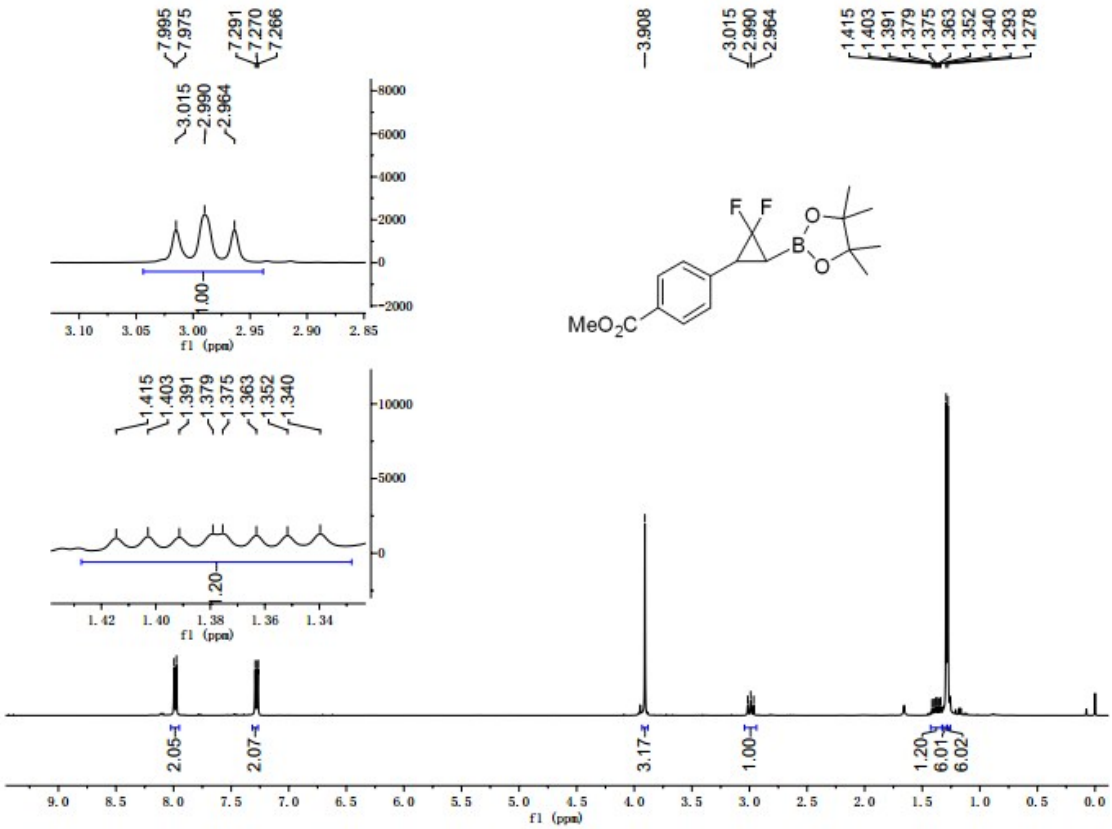
^{19}F NMR spectrum of 3ka



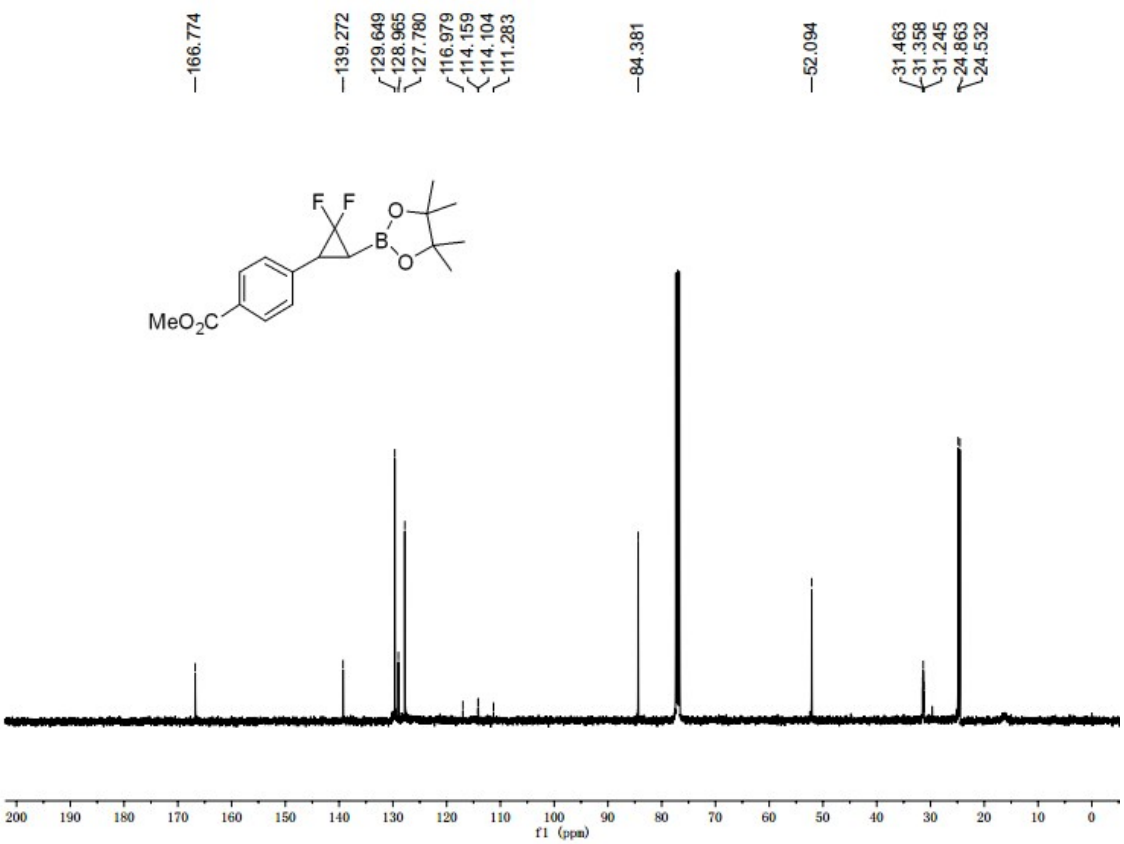
HRMS (EI) of 3ka



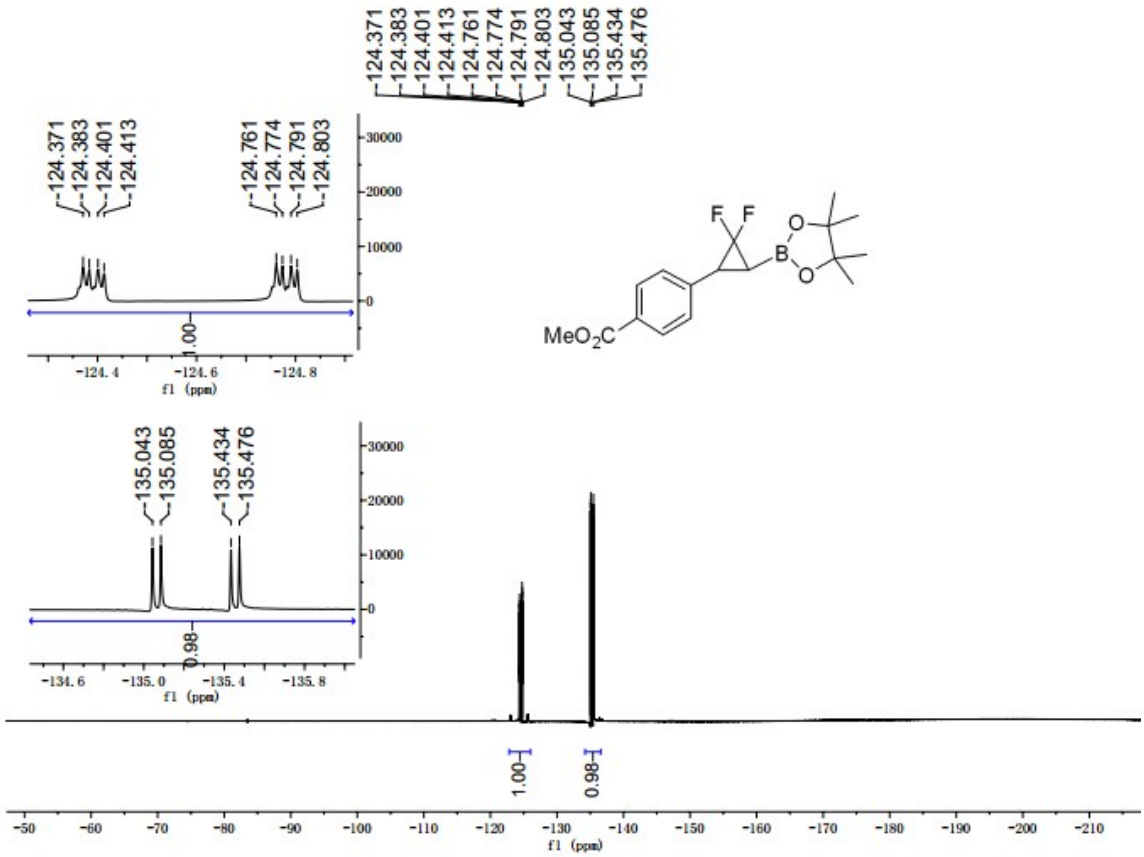
[1]H NMR spectrum of 3la



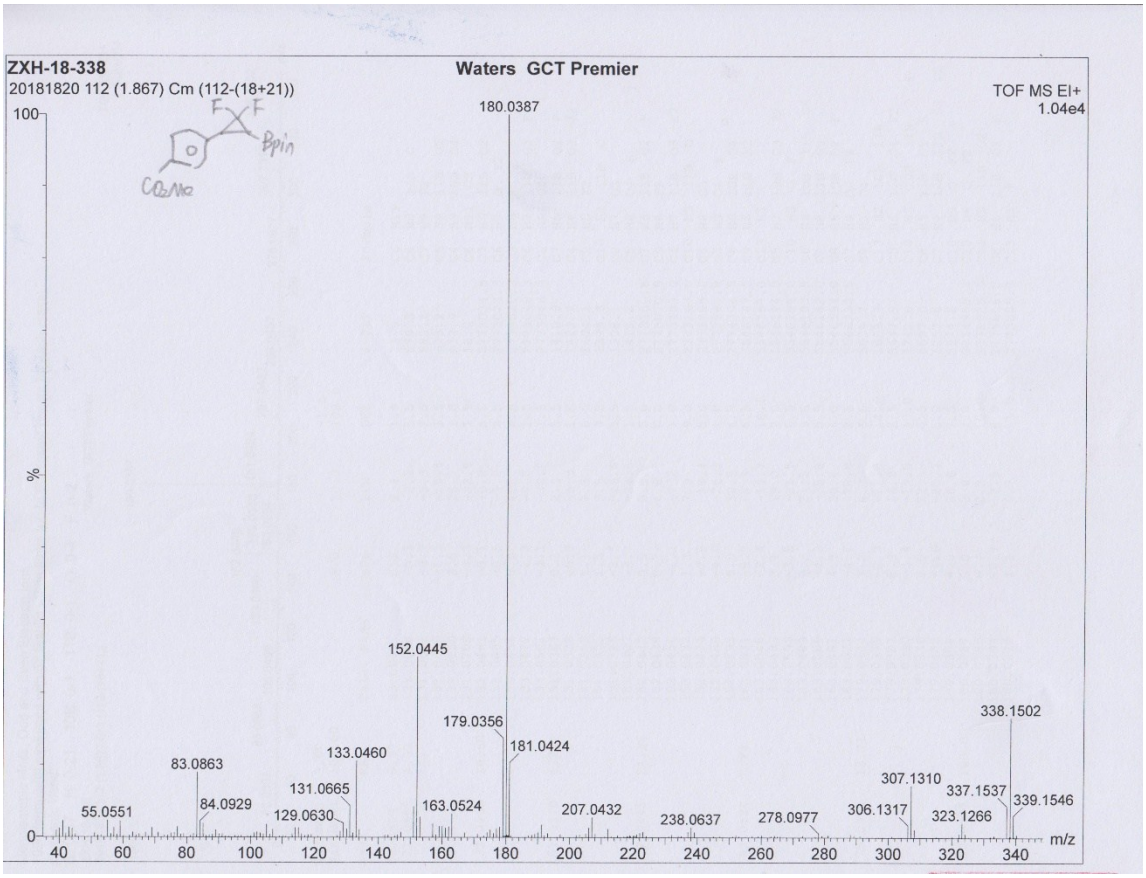
[13]C NMR spectrum of 3la



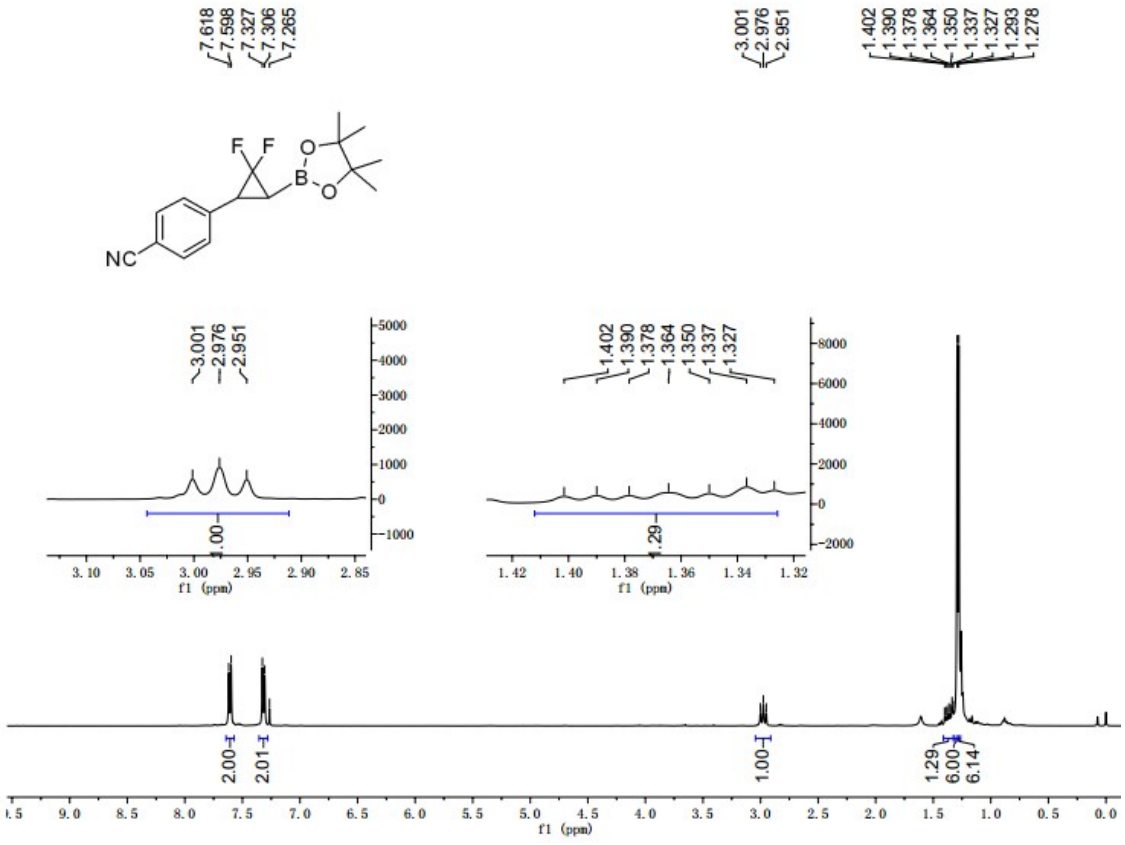
^{19}F NMR spectrum of 3la



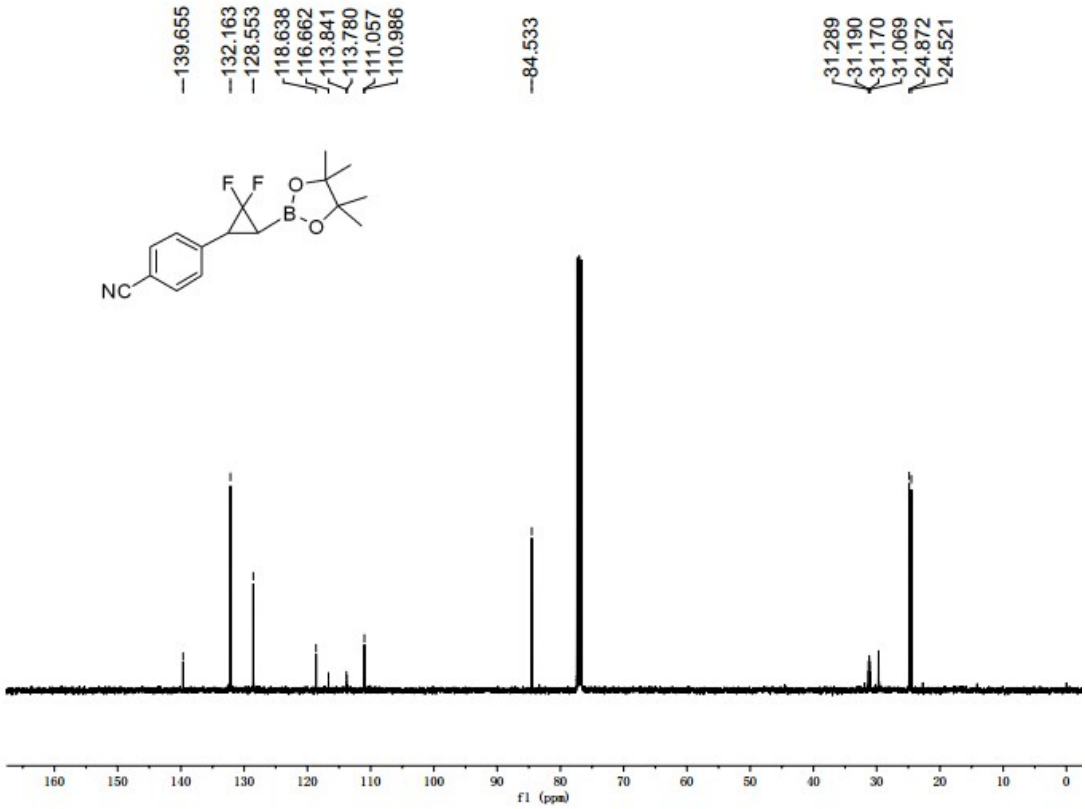
HRMS (EI) of 3la



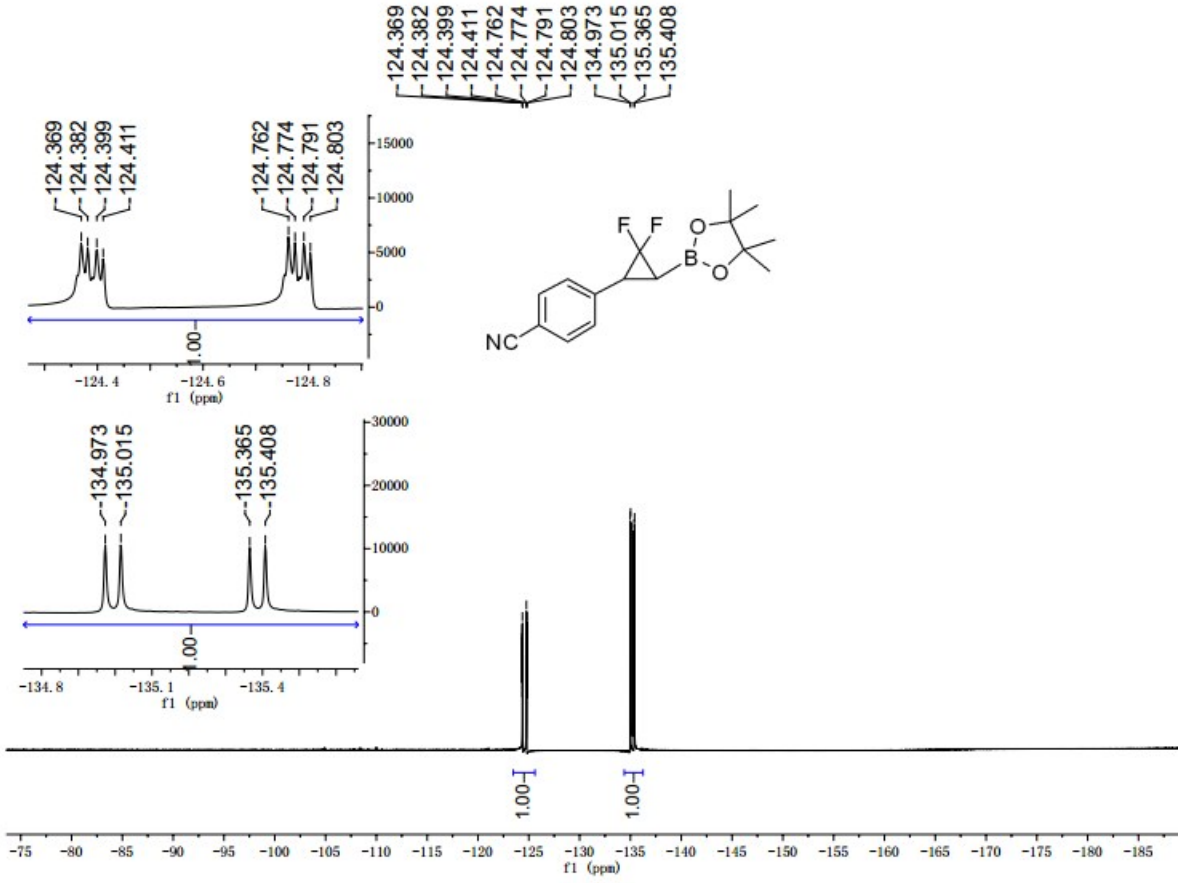
[1]H NMR spectrum of 3ma



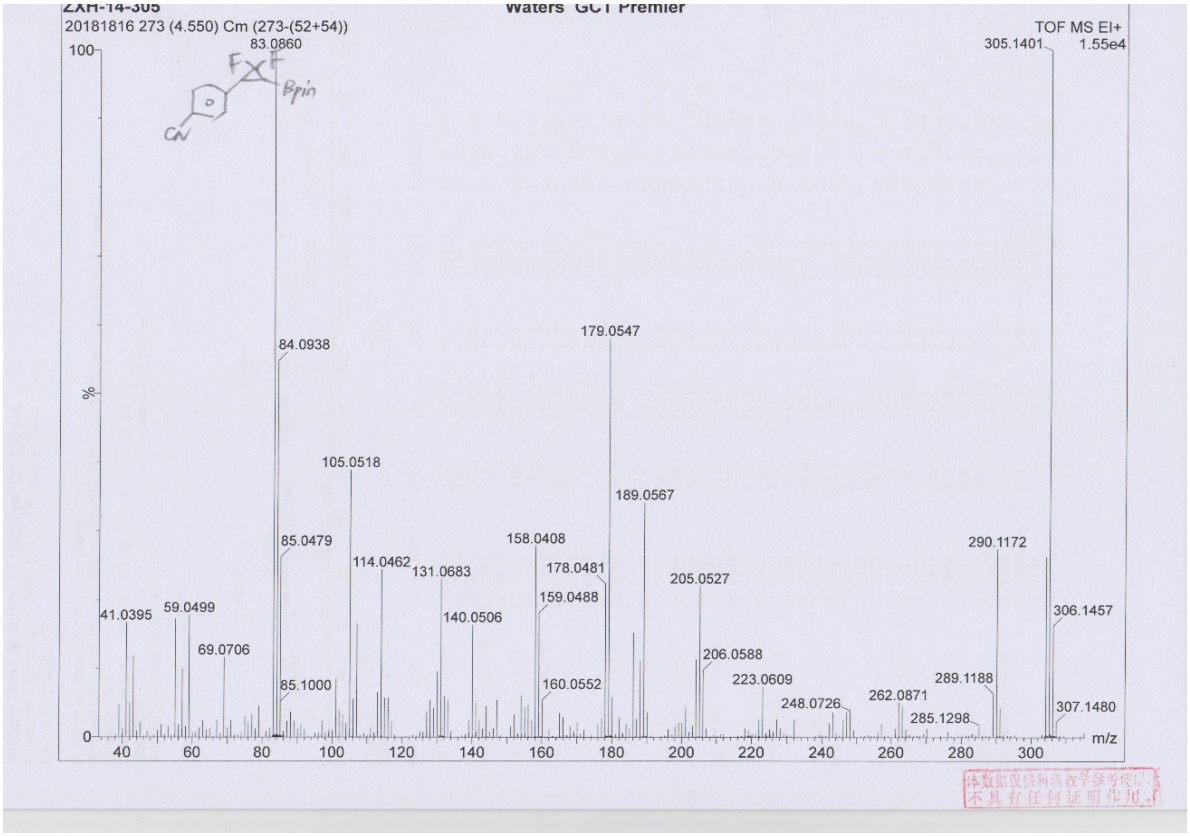
[13]C NMR spectrum of 3ma



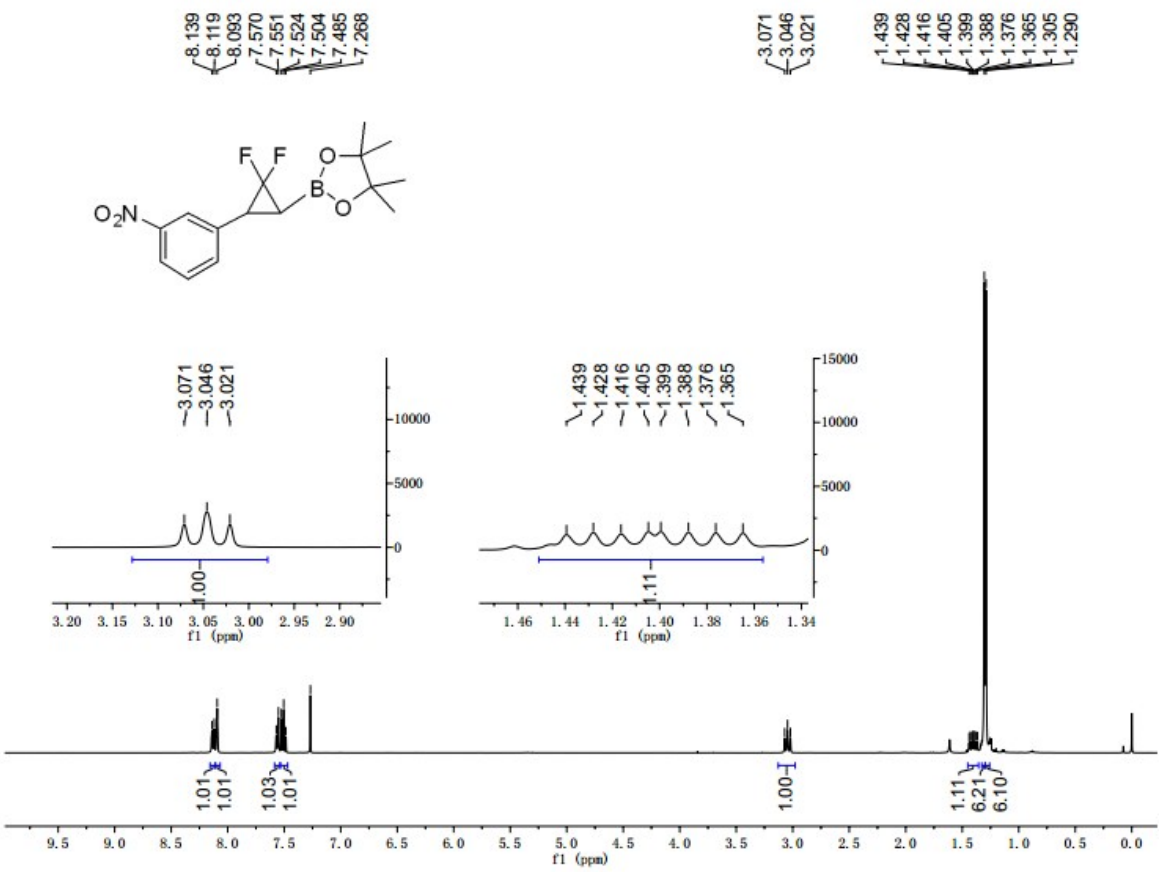
^{19}F NMR spectrum of 3ma



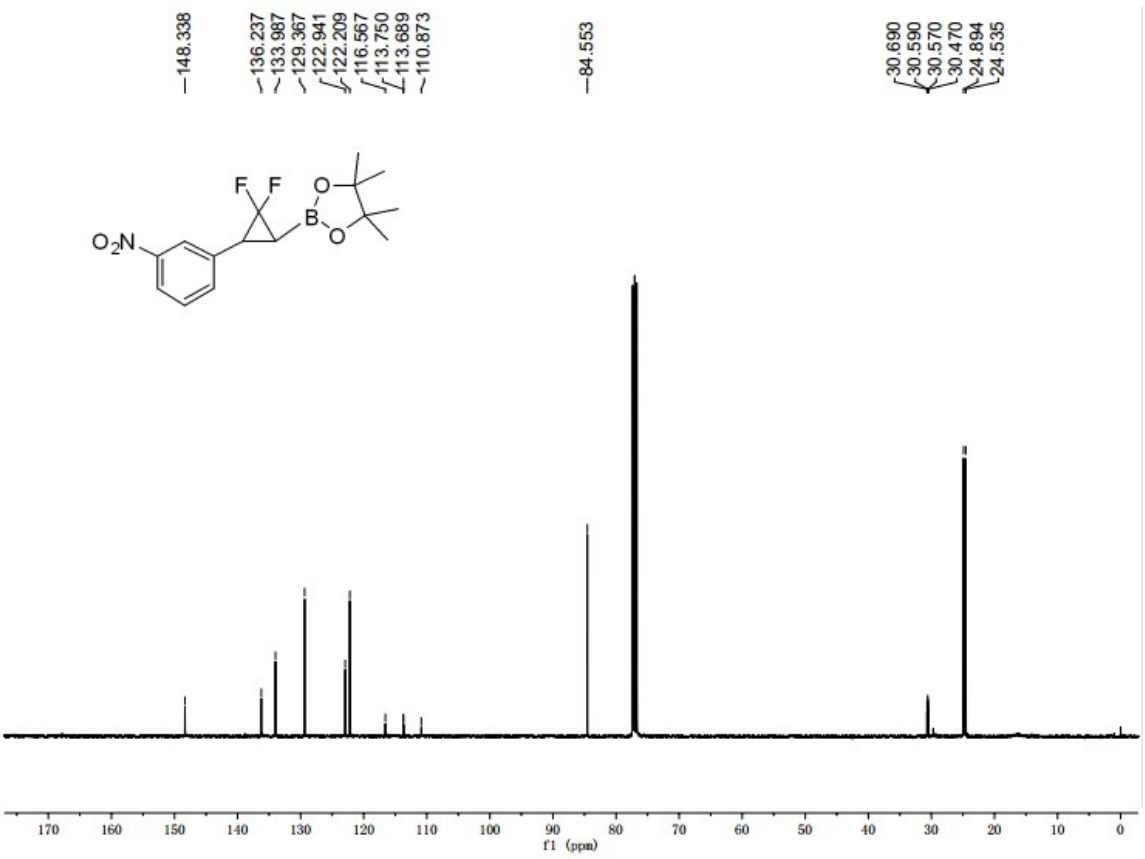
HRMS (EI) of 3ma



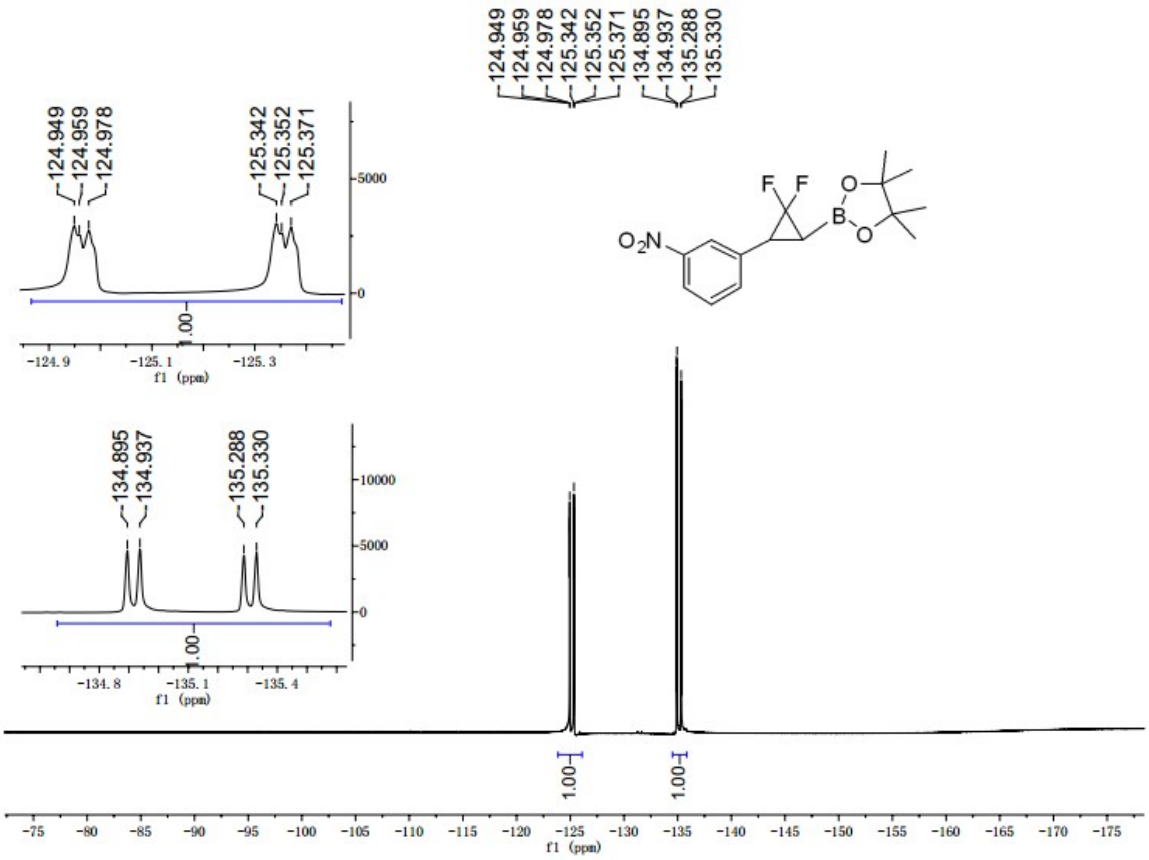
[1]H NMR spectrum of 3na



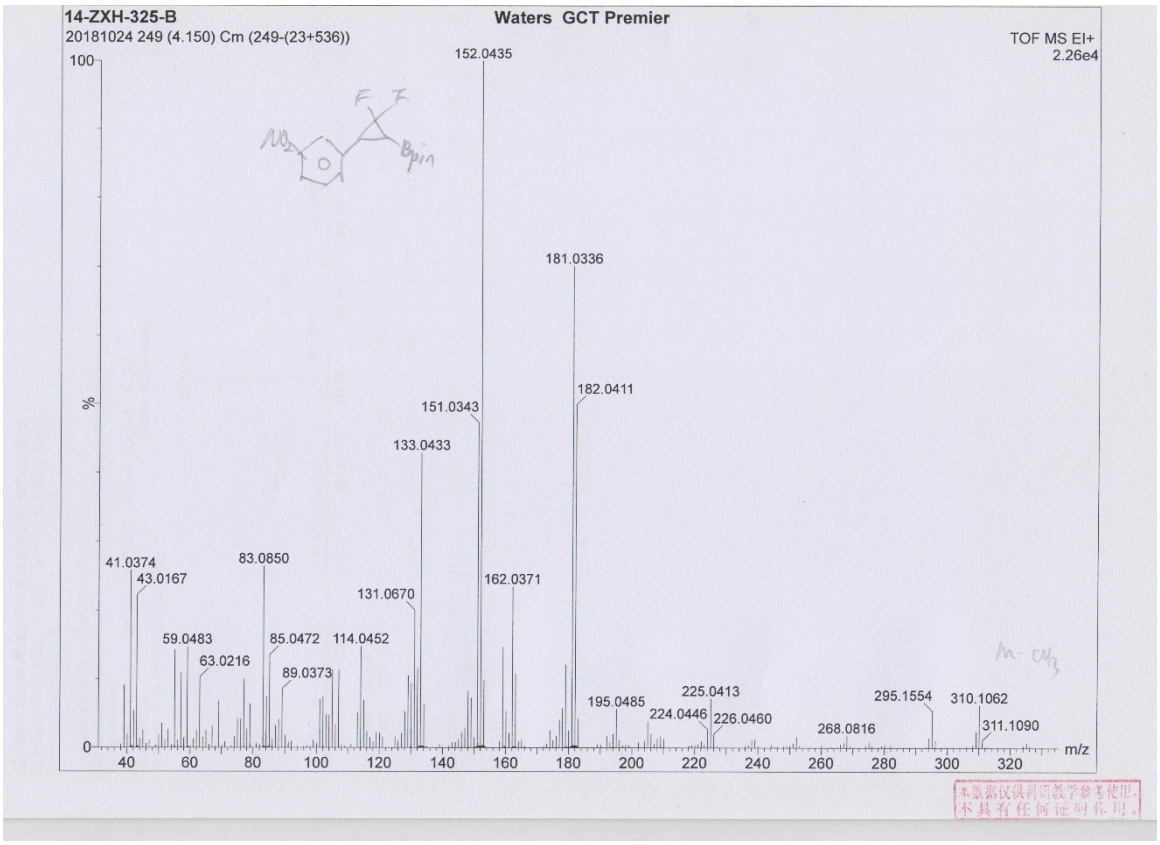
[13]C NMR spectrum of 3na



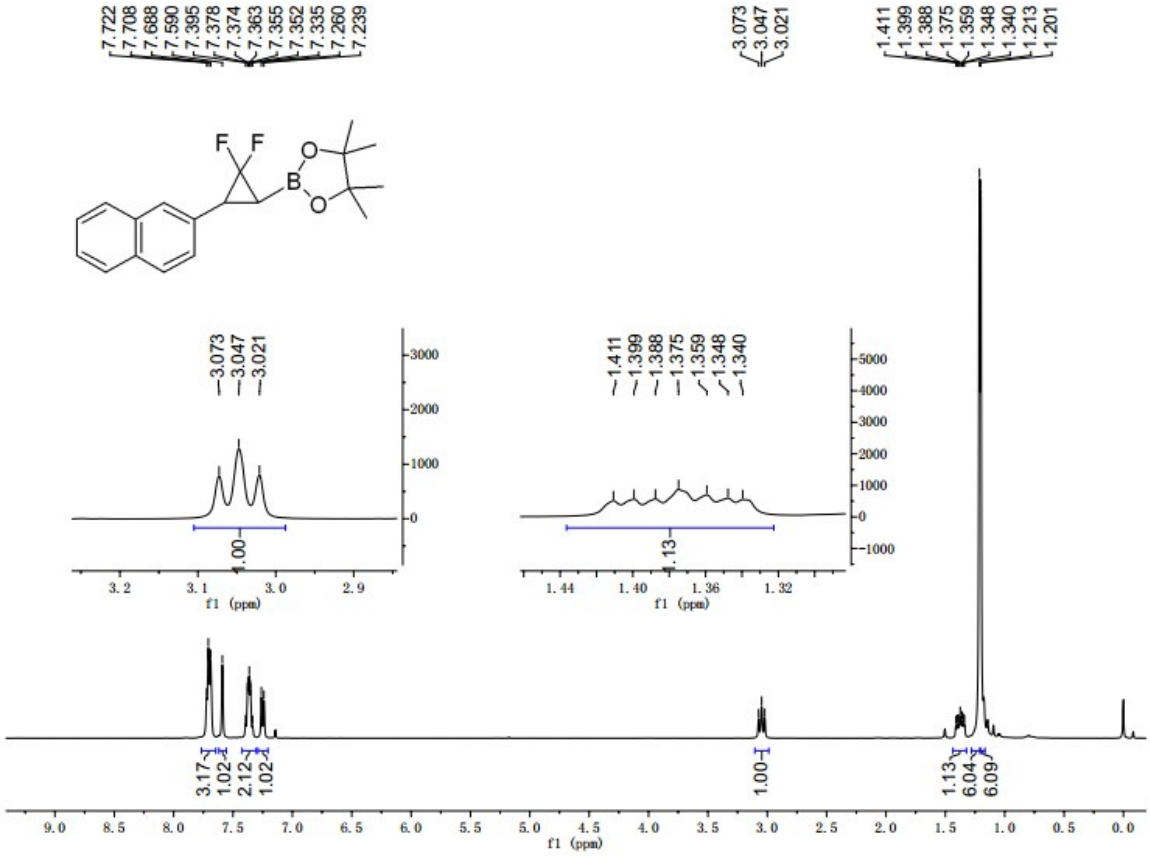
^{19}F NMR spectrum of 3na



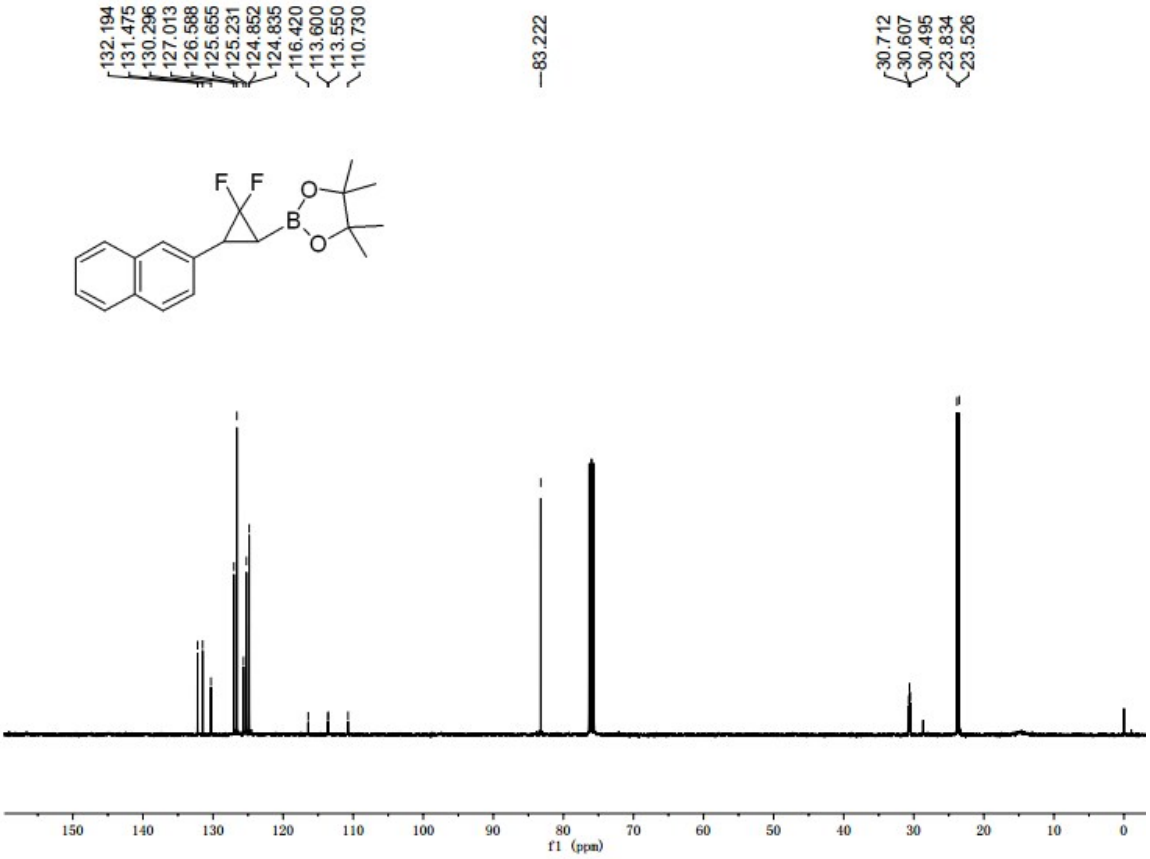
HRMS (EI) of 3na



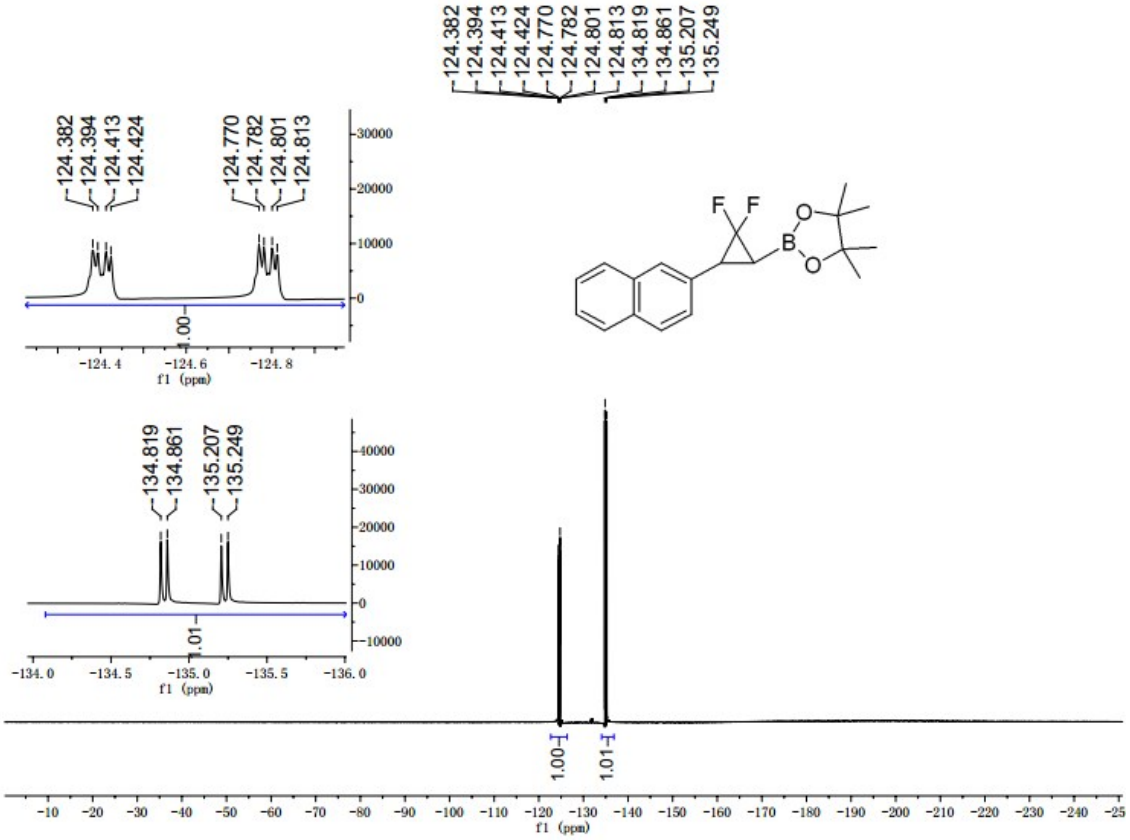
[1]H NMR spectrum of 3oa



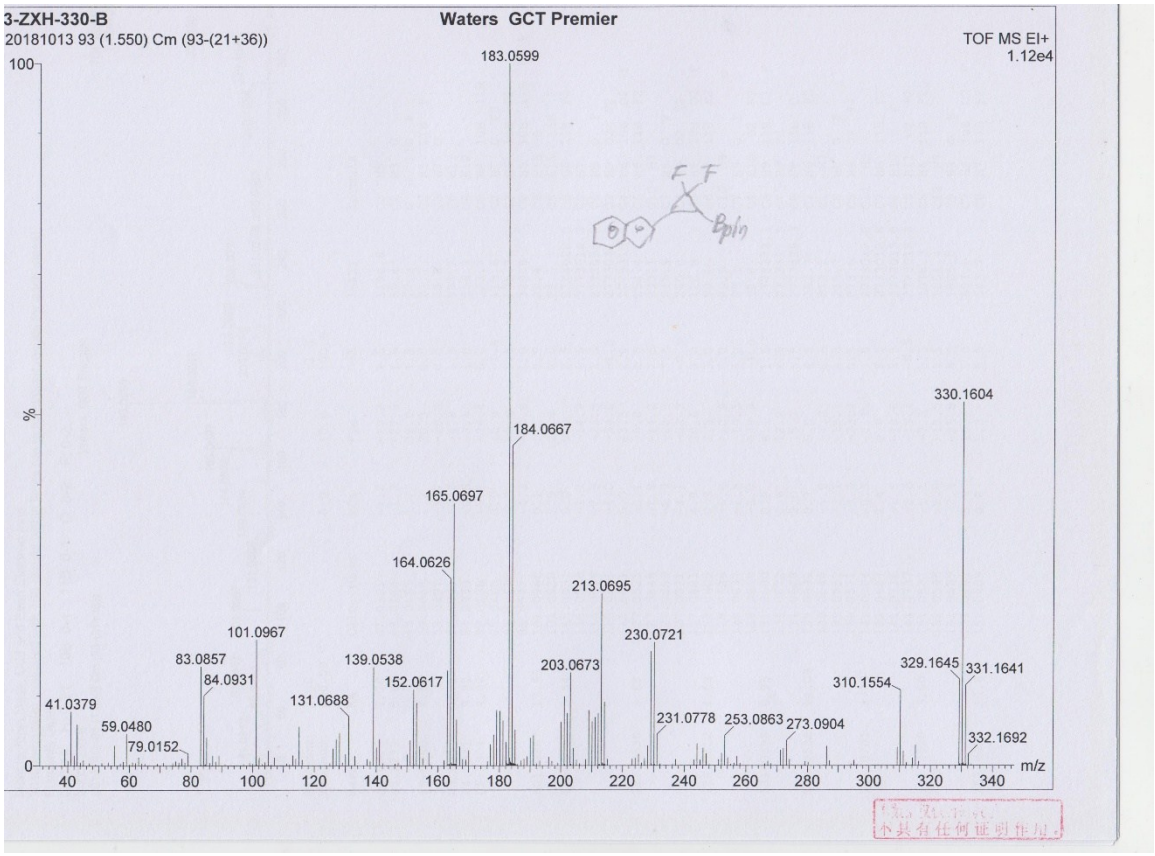
[13]C NMR spectrum of 3oa



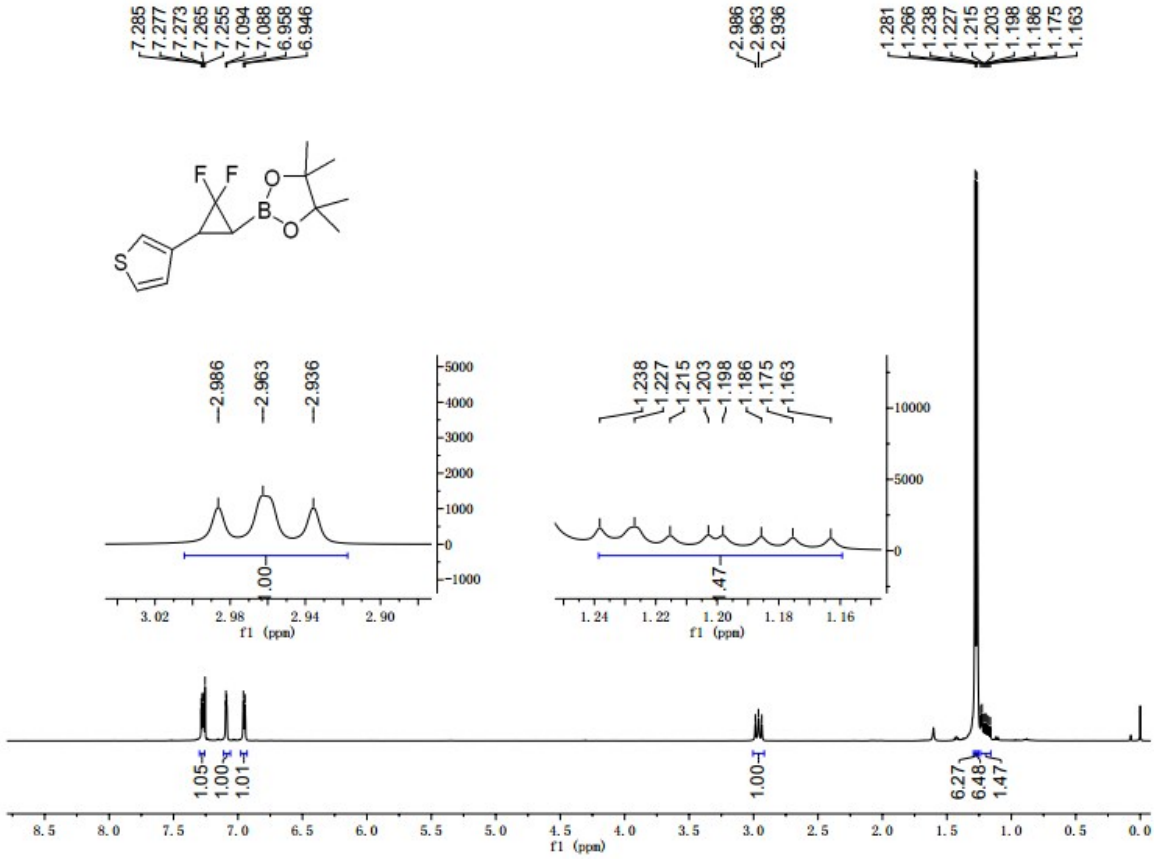
^{19}F NMR spectrum of 3oa



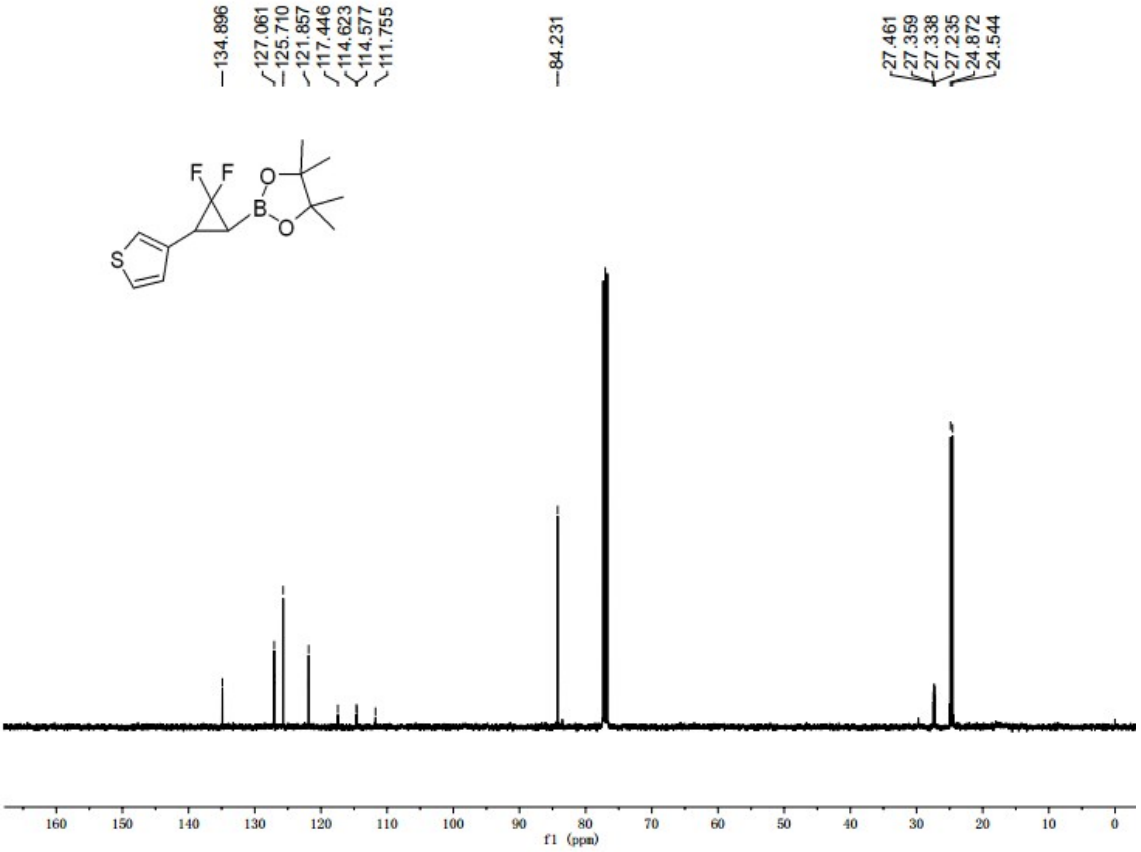
HRMS (EI) of 3oa



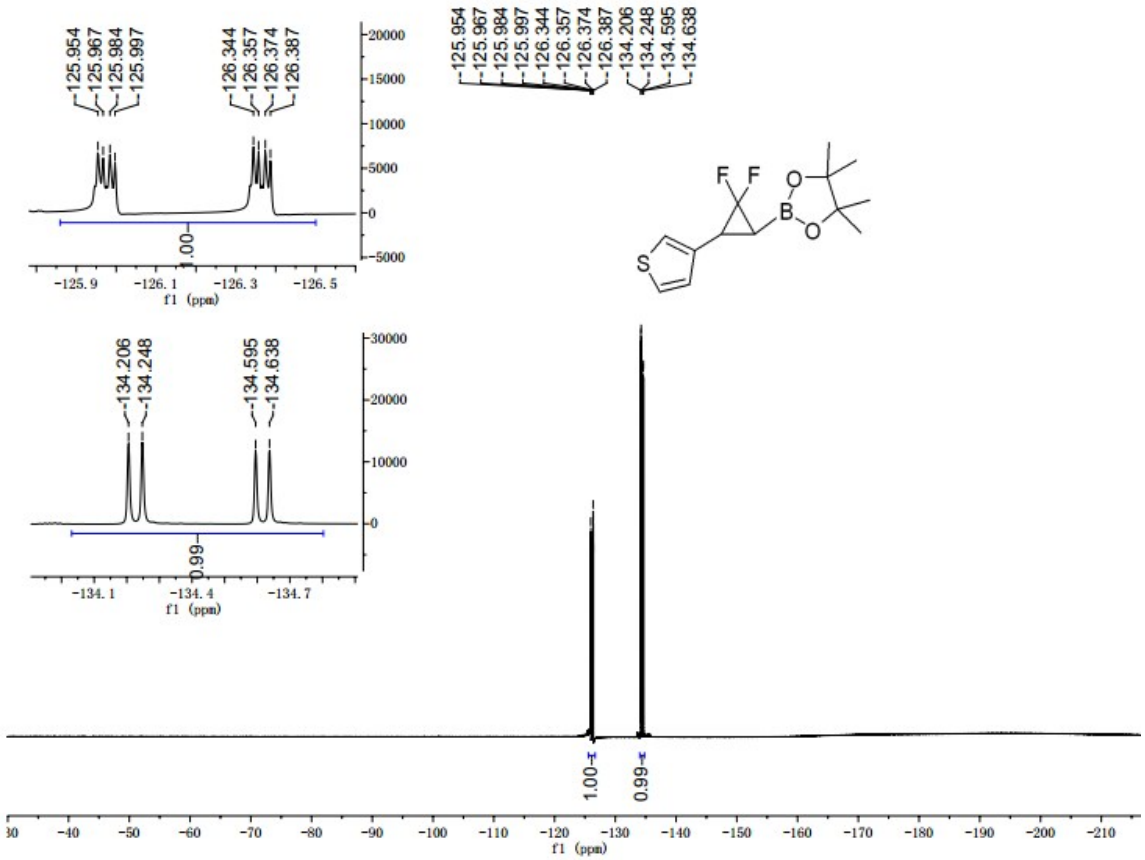
^{1}H NMR spectrum of 3pa



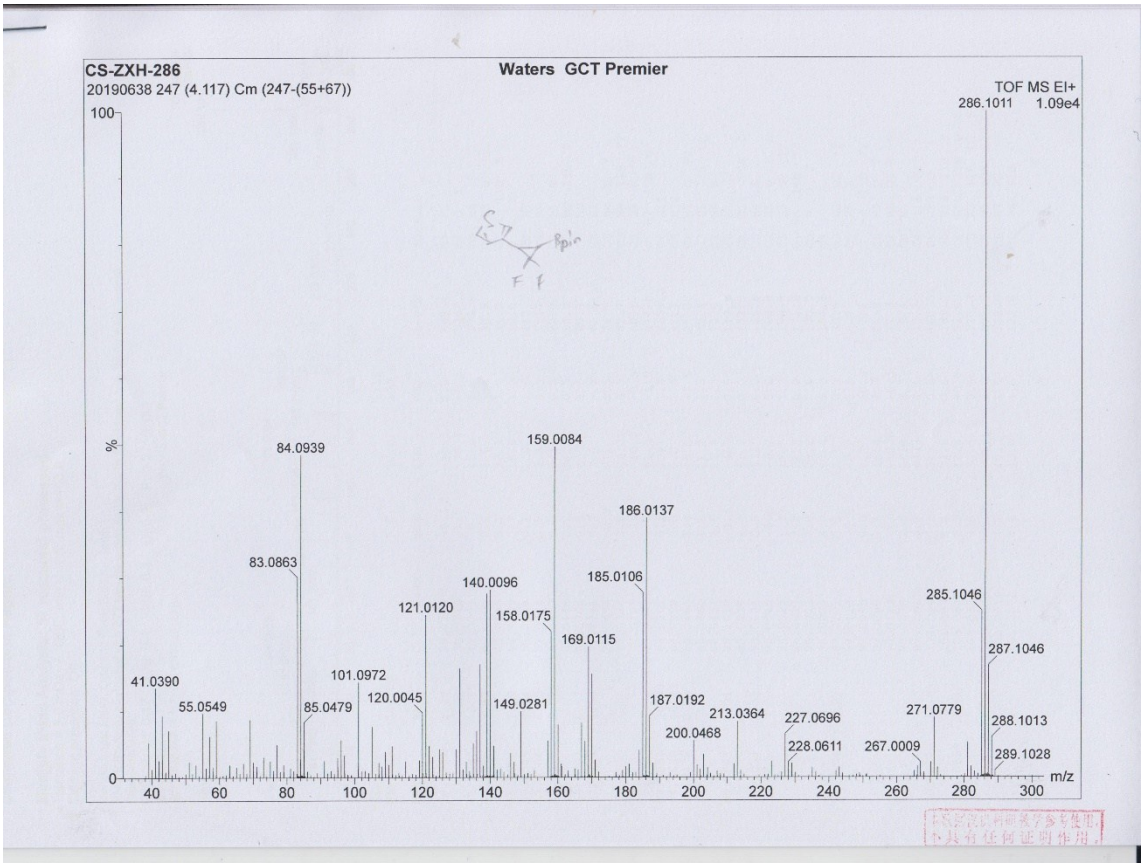
^{13}C NMR spectrum of 3pa



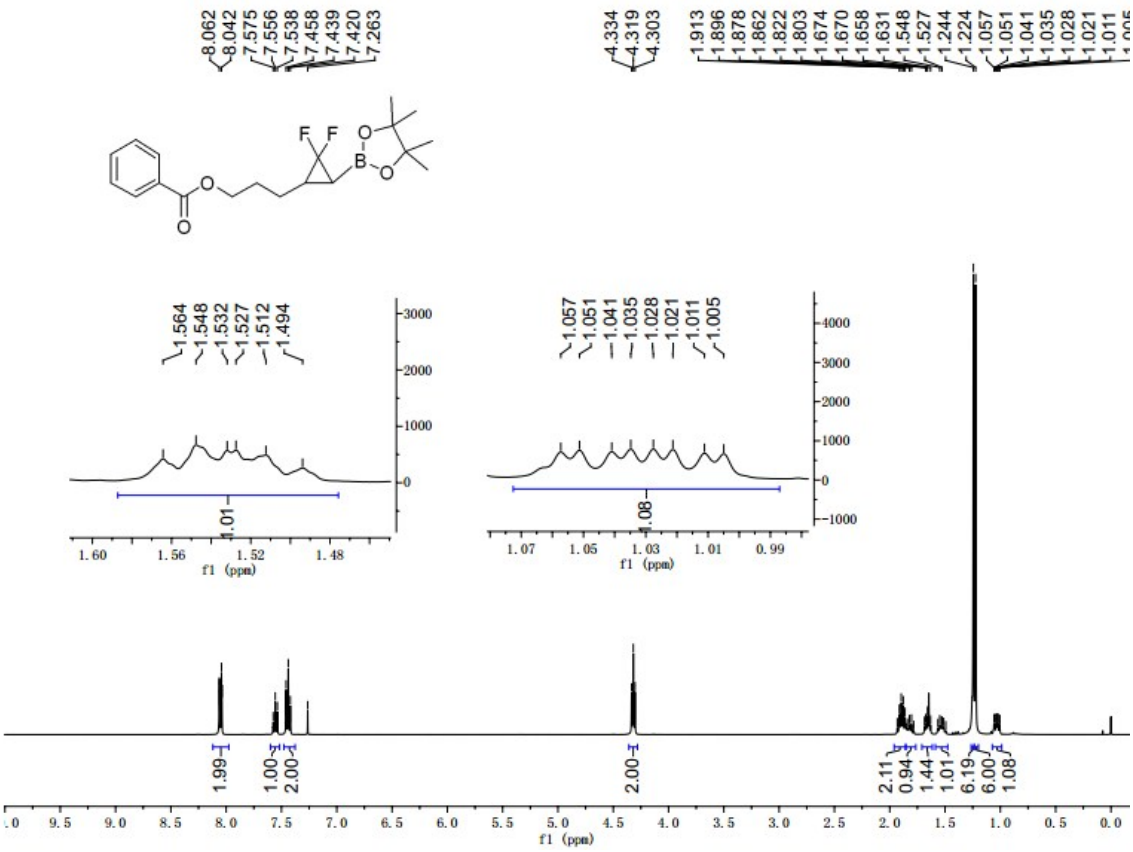
^{19}F NMR spectrum of 3pa



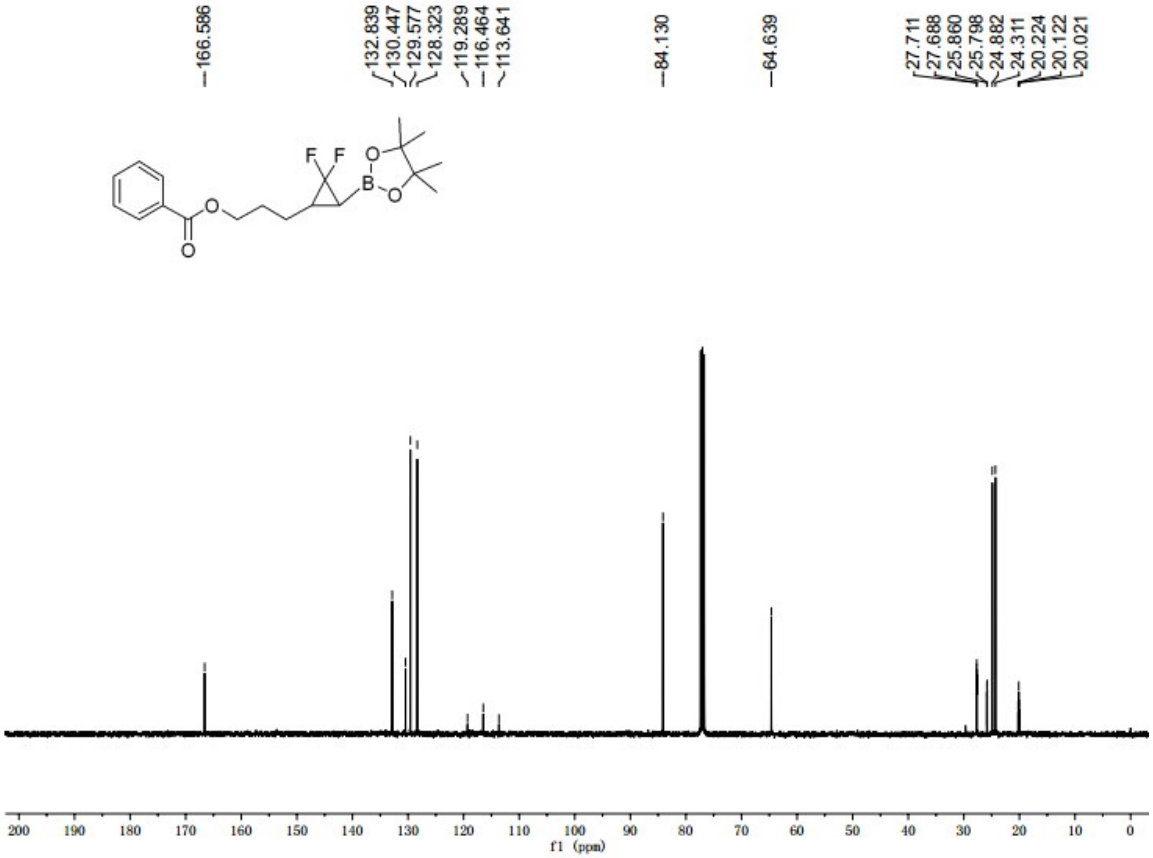
HRMS (EI) of 3pa



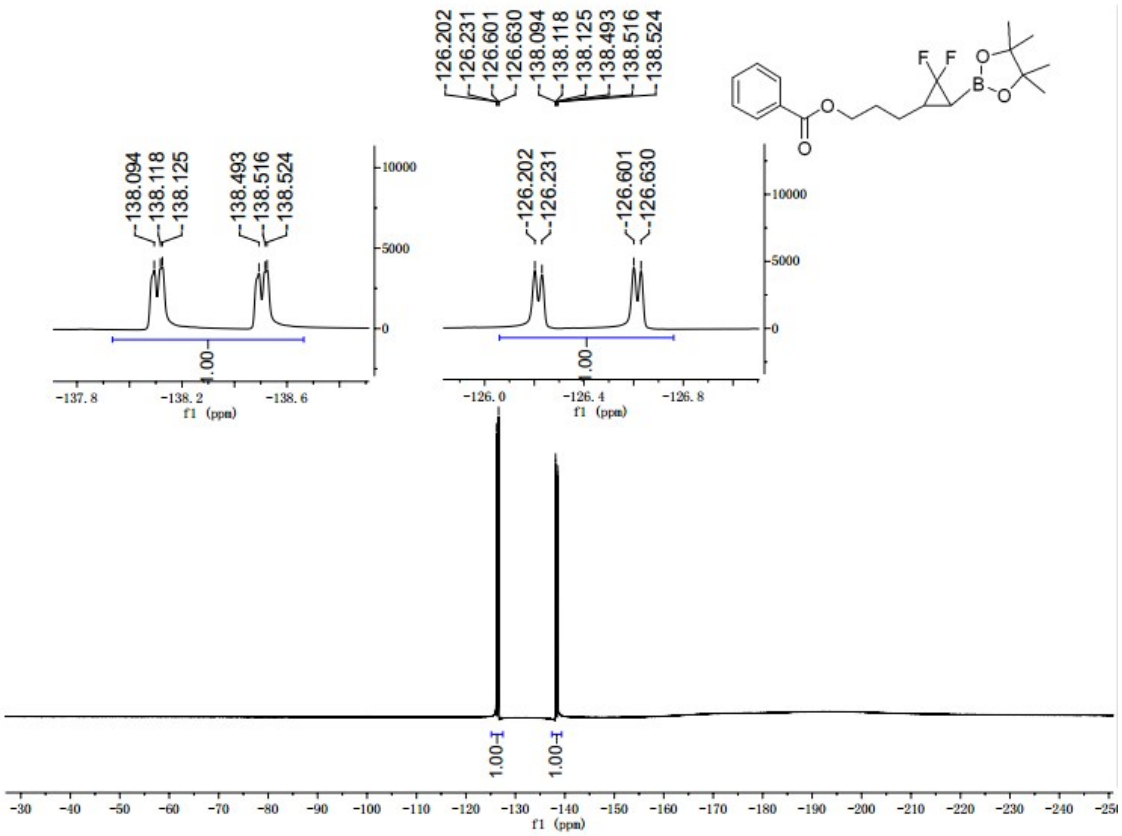
^{1}H NMR spectrum of 3qa



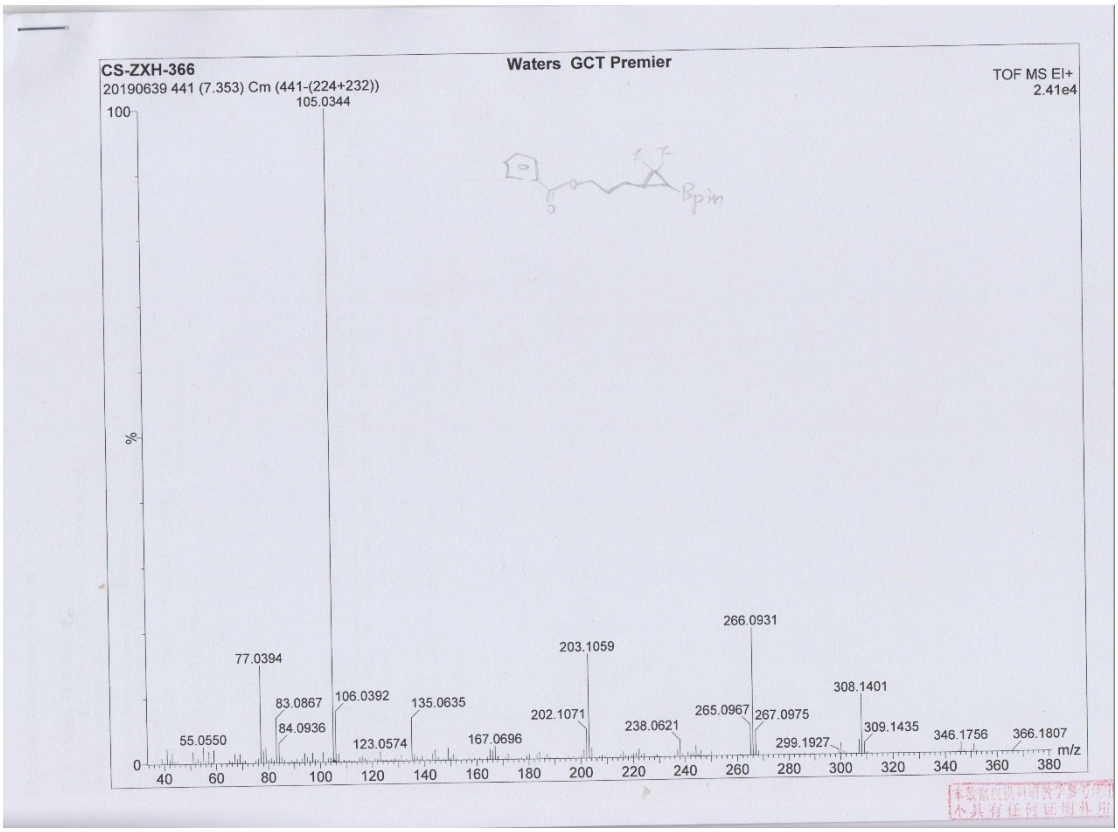
^{13}C NMR spectrum of 3qa



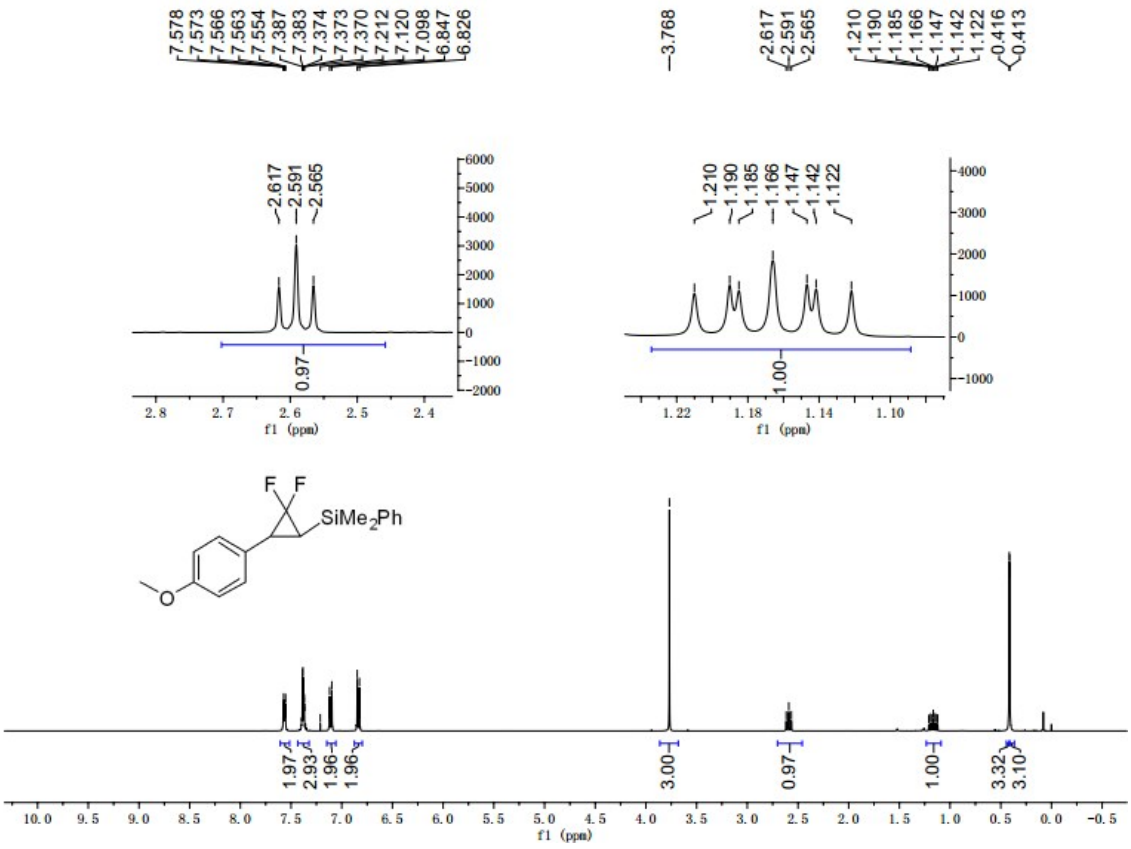
^{19}F NMR spectrum of 3qa



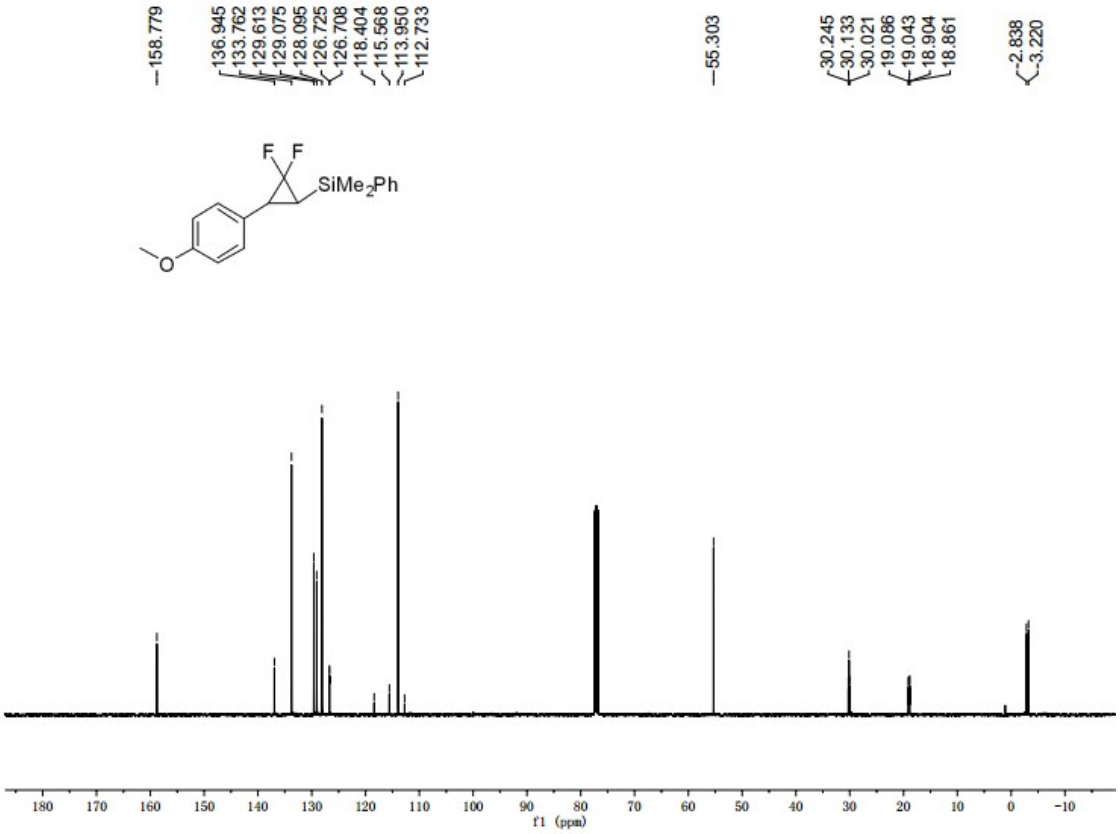
HRMS (EI) of 3qa



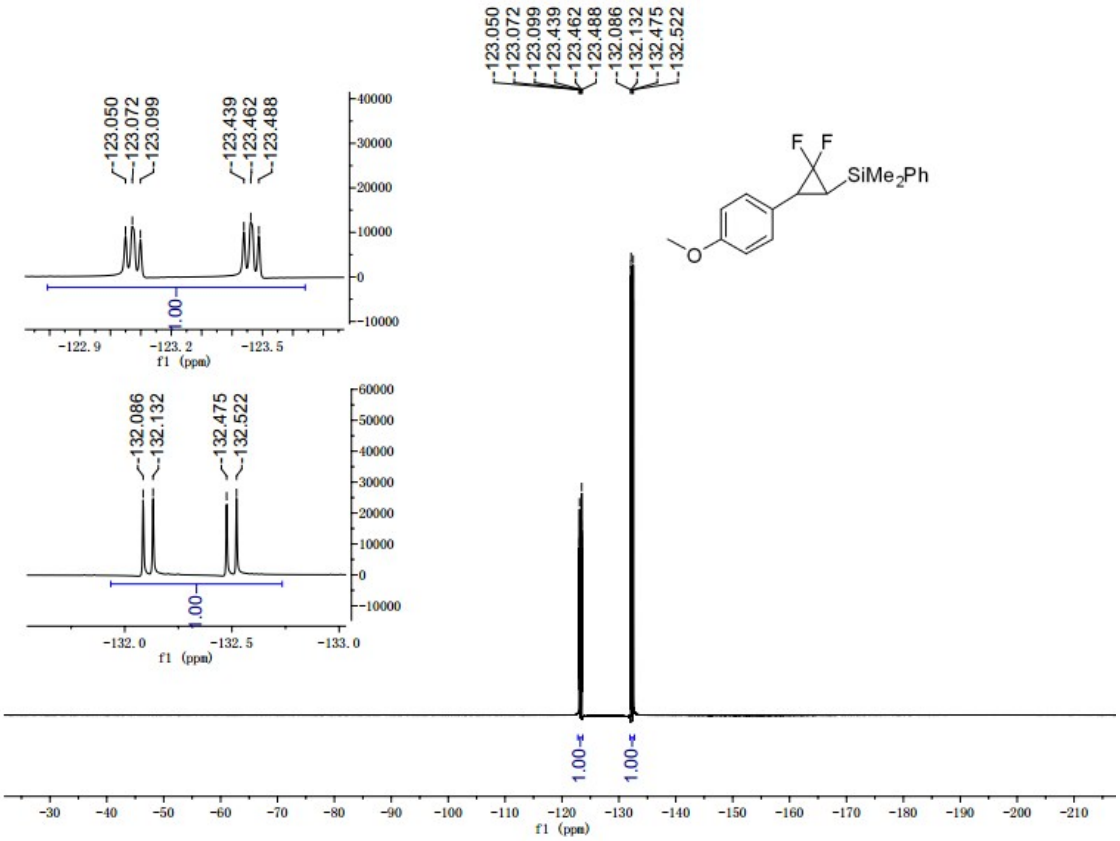
^{1}H NMR spectrum of 3ab



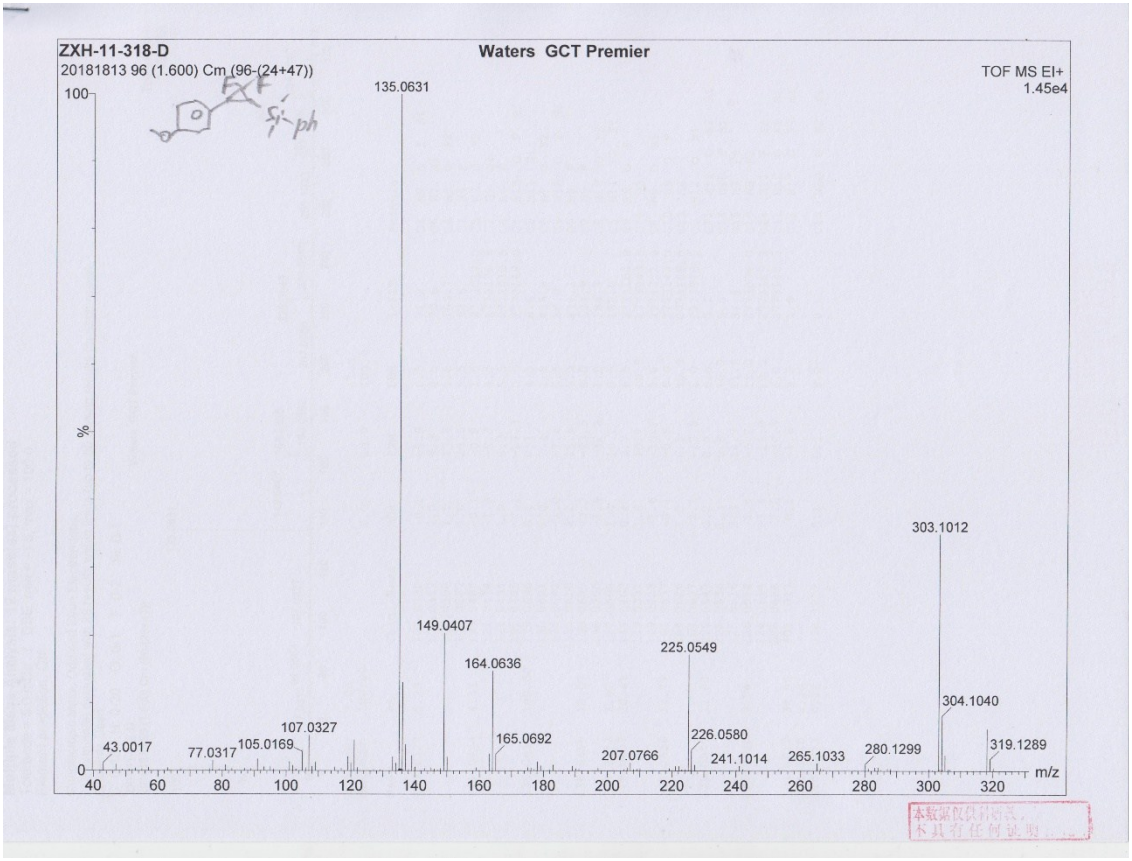
^{13}C NMR spectrum of 3ab



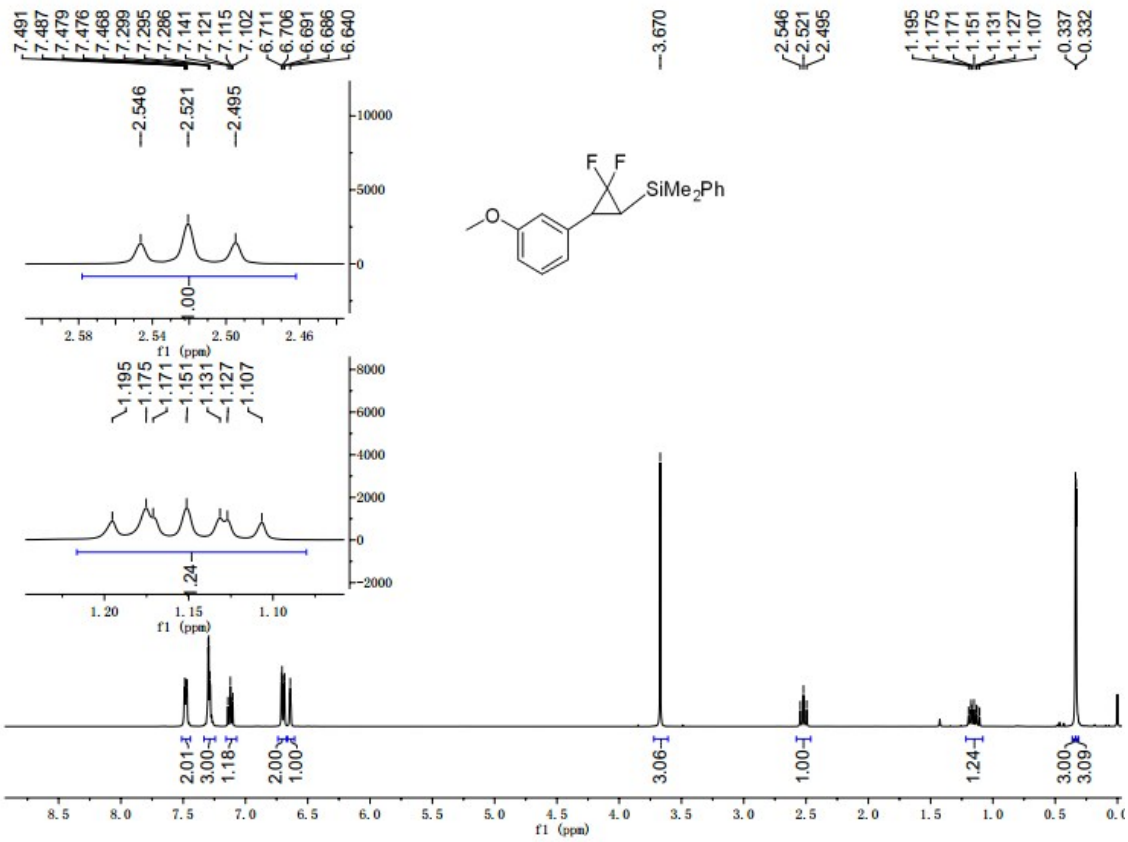
^{19}F NMR spectrum of 3ab



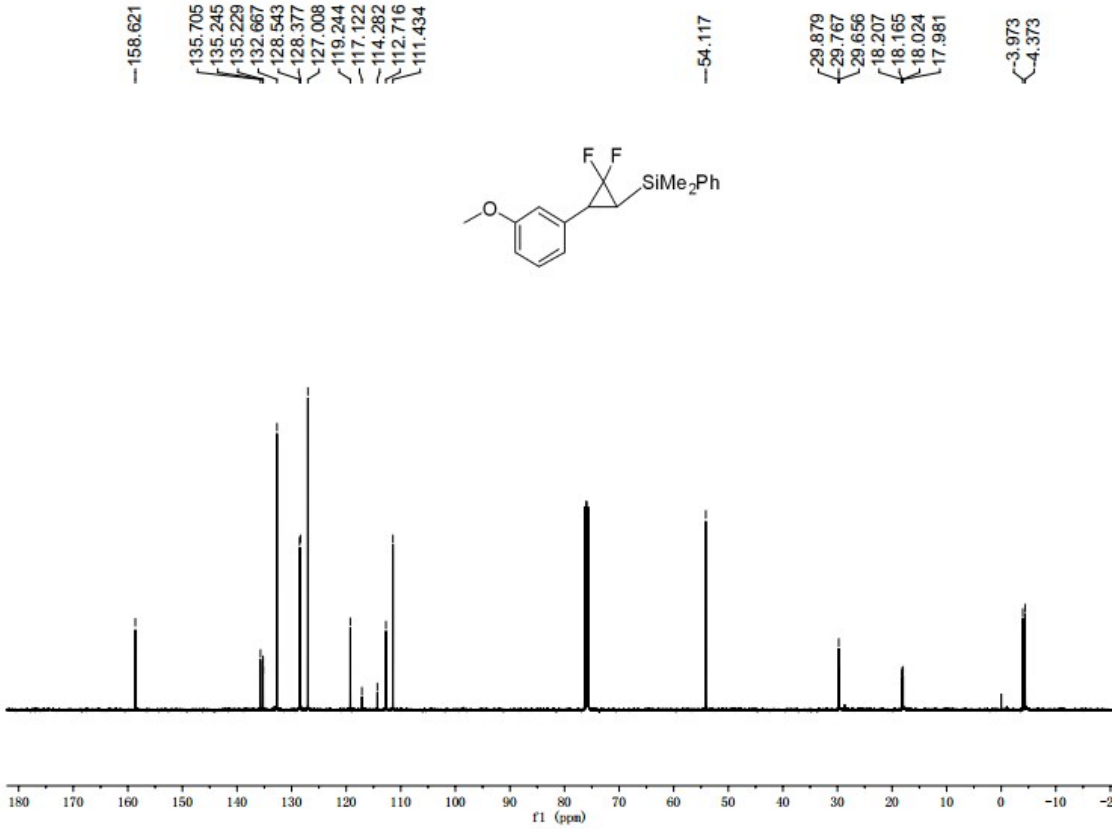
HRMS (EI) of 3ab



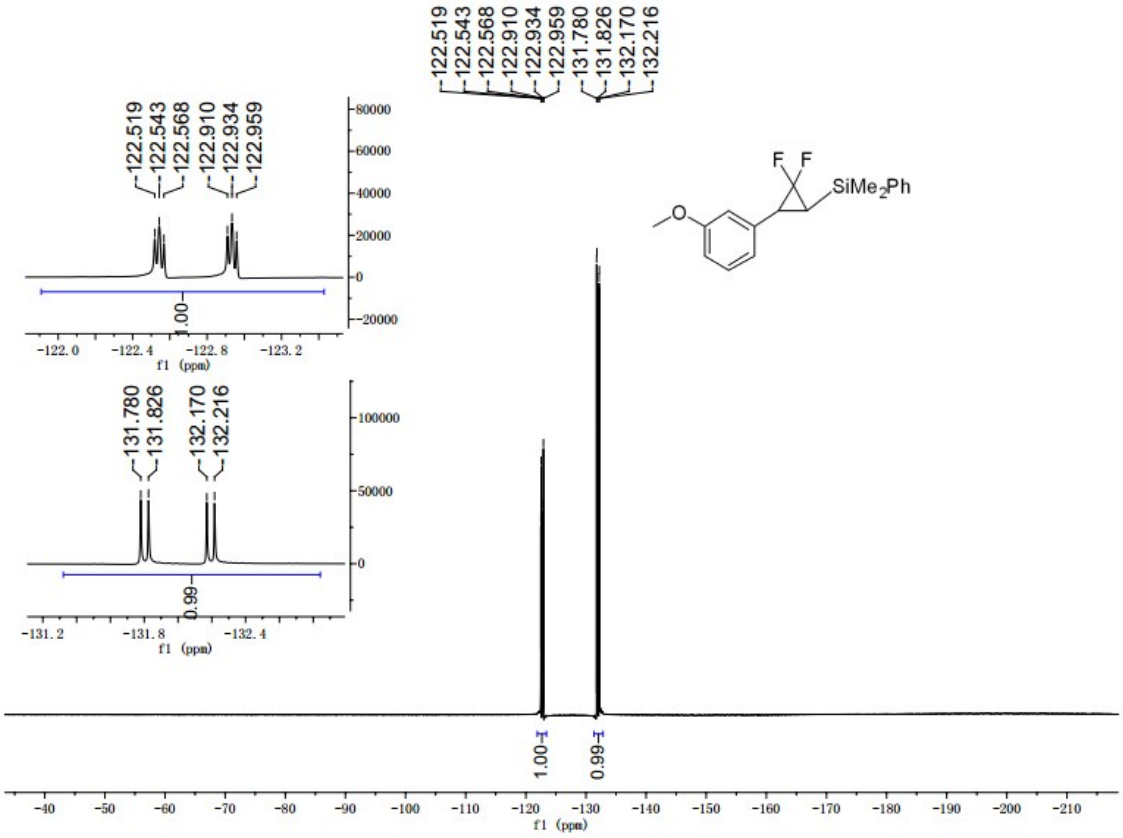
^{1}H NMR spectrum of 3bb



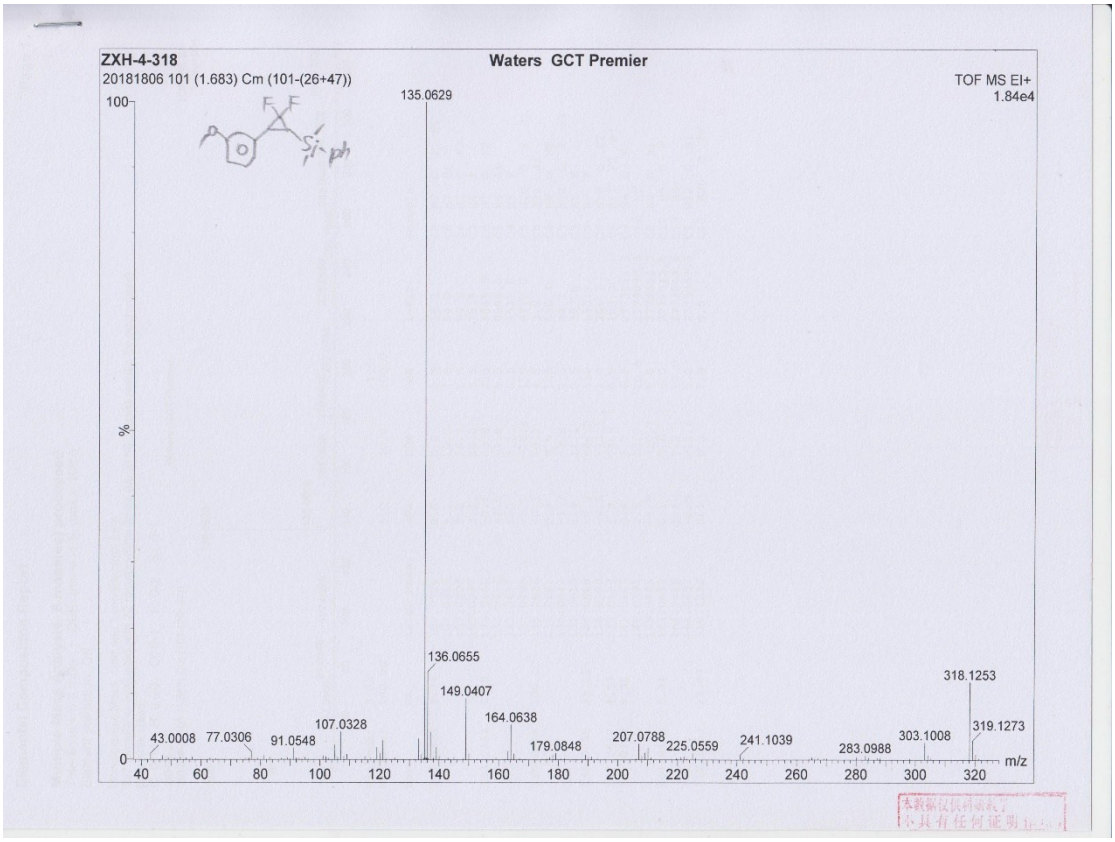
^{13}C NMR spectrum of 3bb



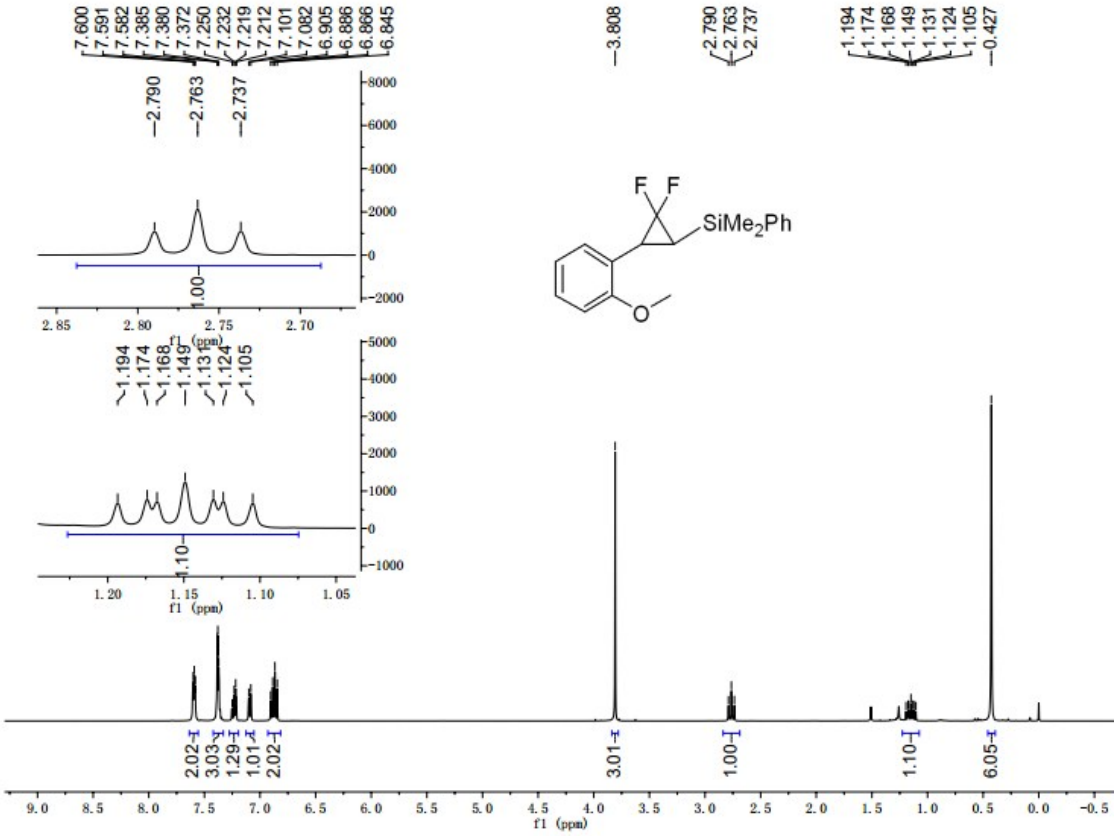
^{19}F NMR spectrum of 3bb



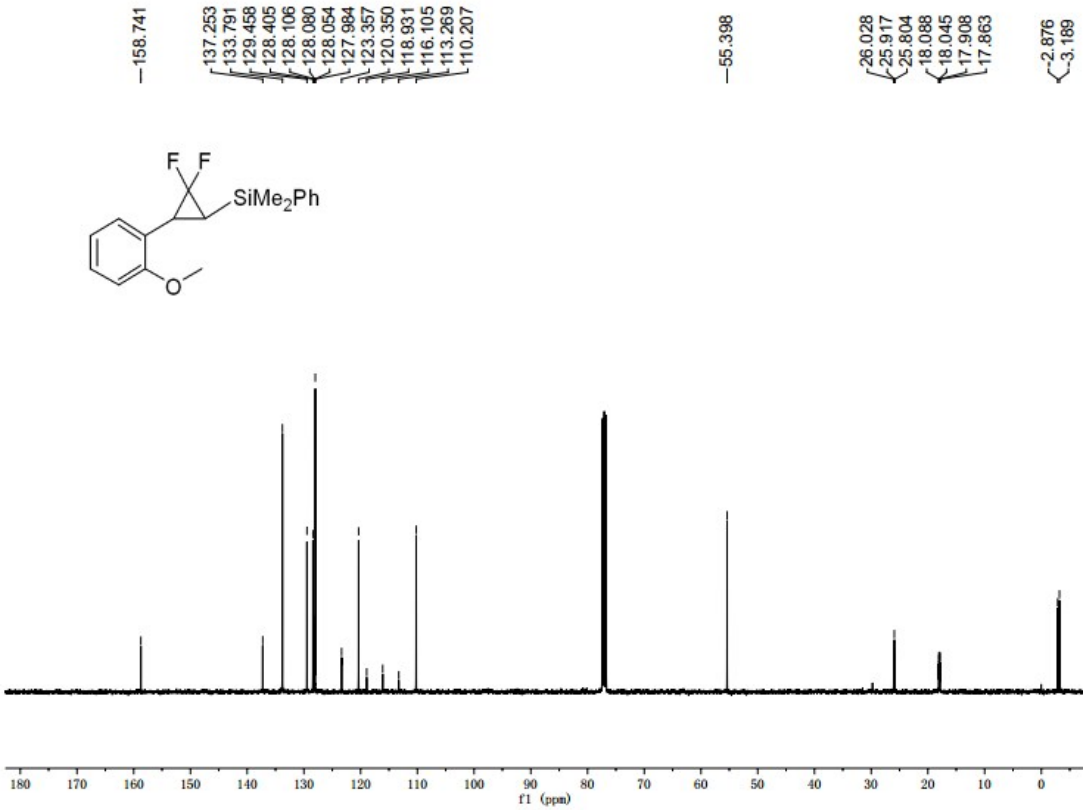
HRMS (EI) of 3bb



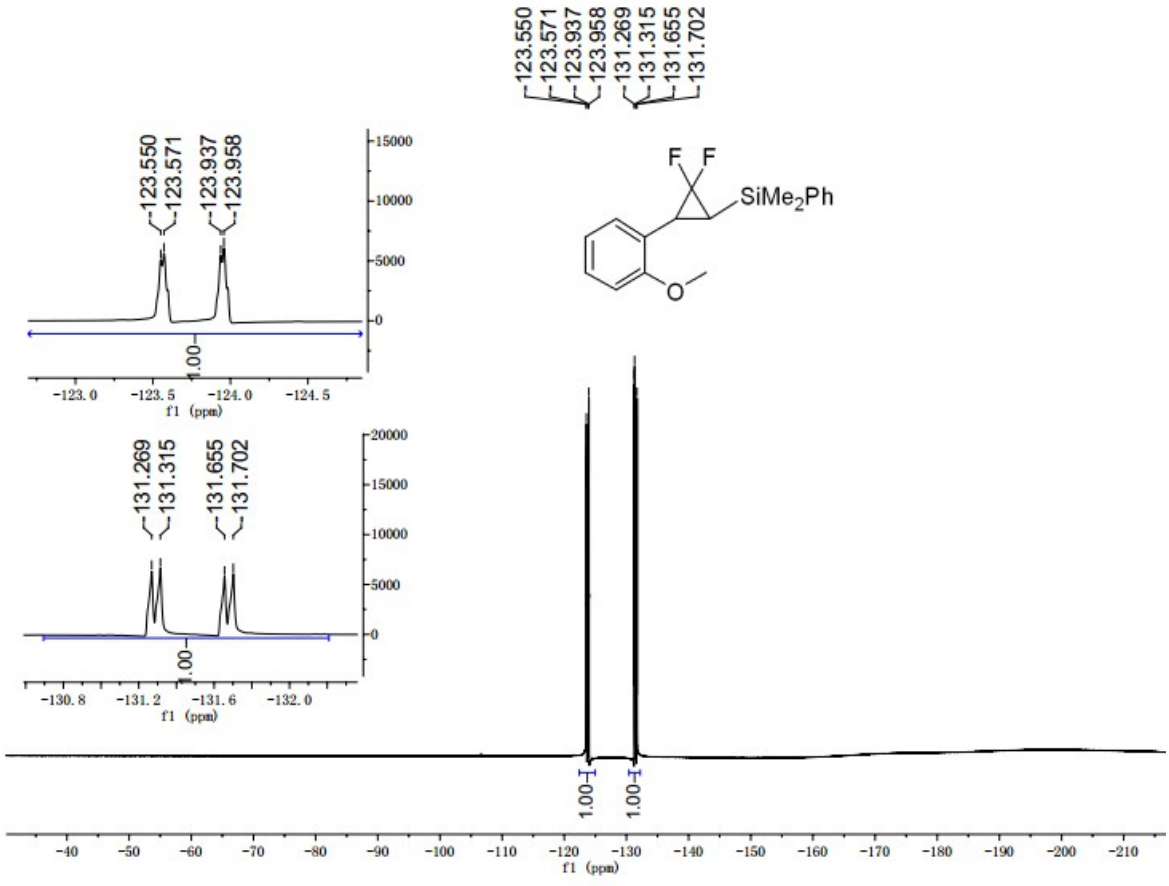
^{1}H NMR spectrum of 3cb



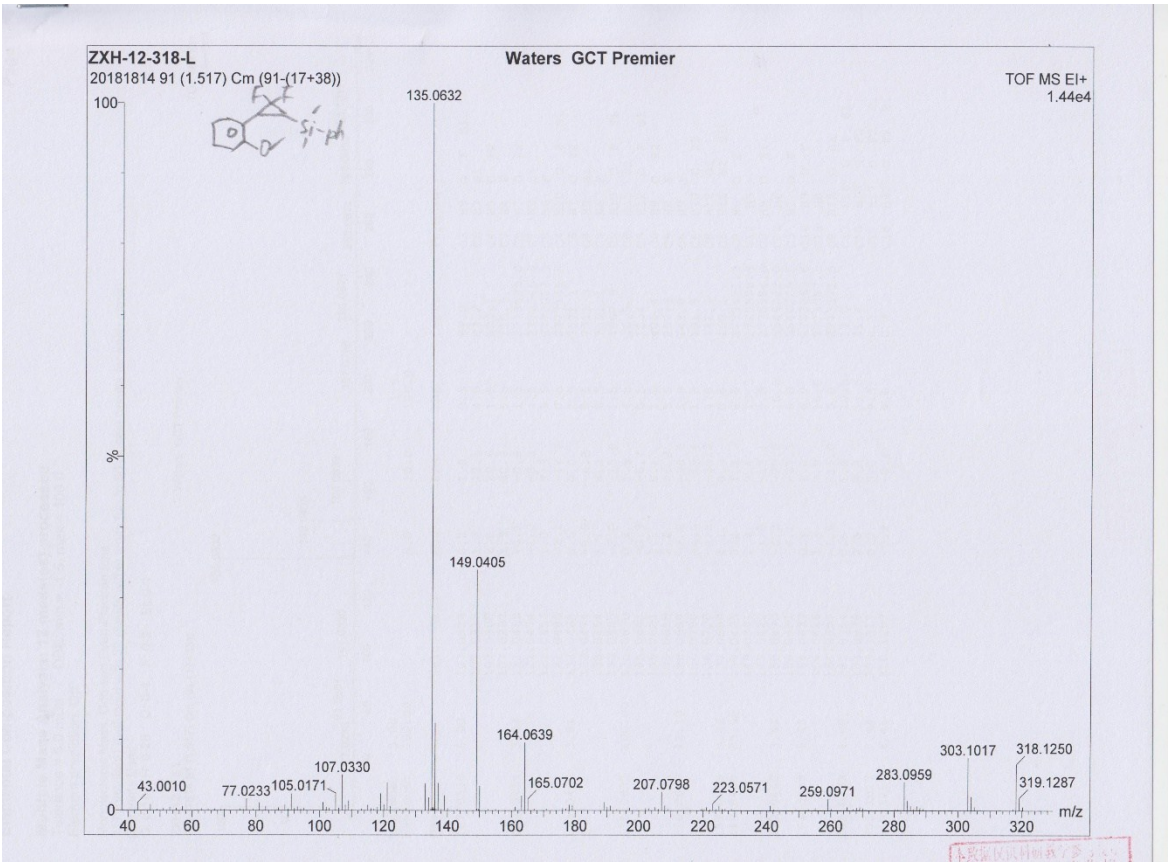
^{13}C NMR spectrum of 3cb



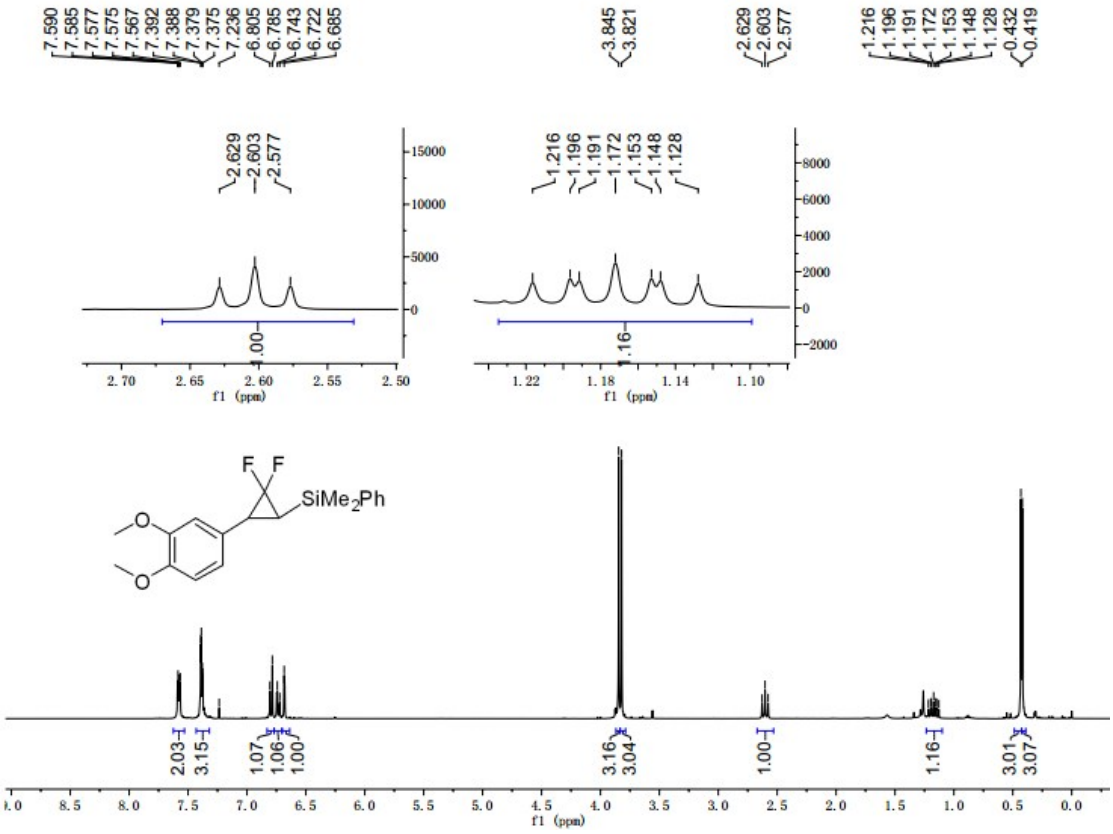
^{19}F NMR spectrum of 3cb



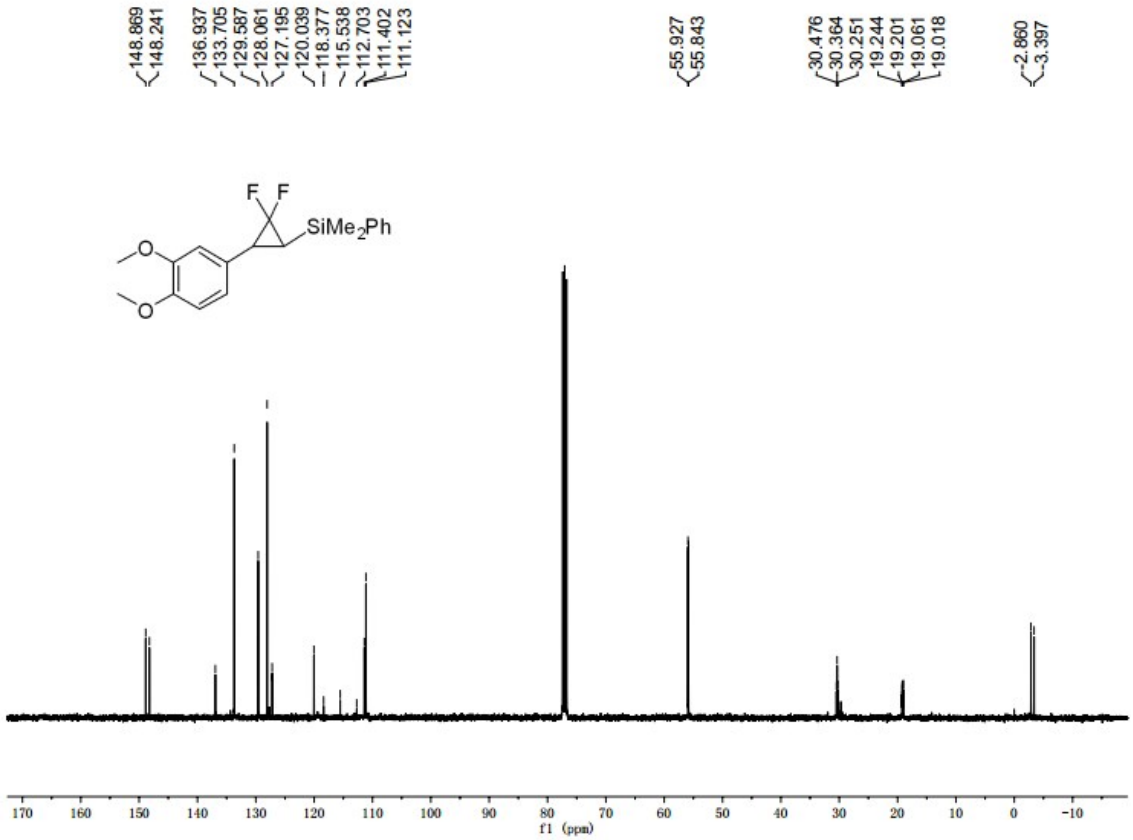
HRMS (EI) of 3cb



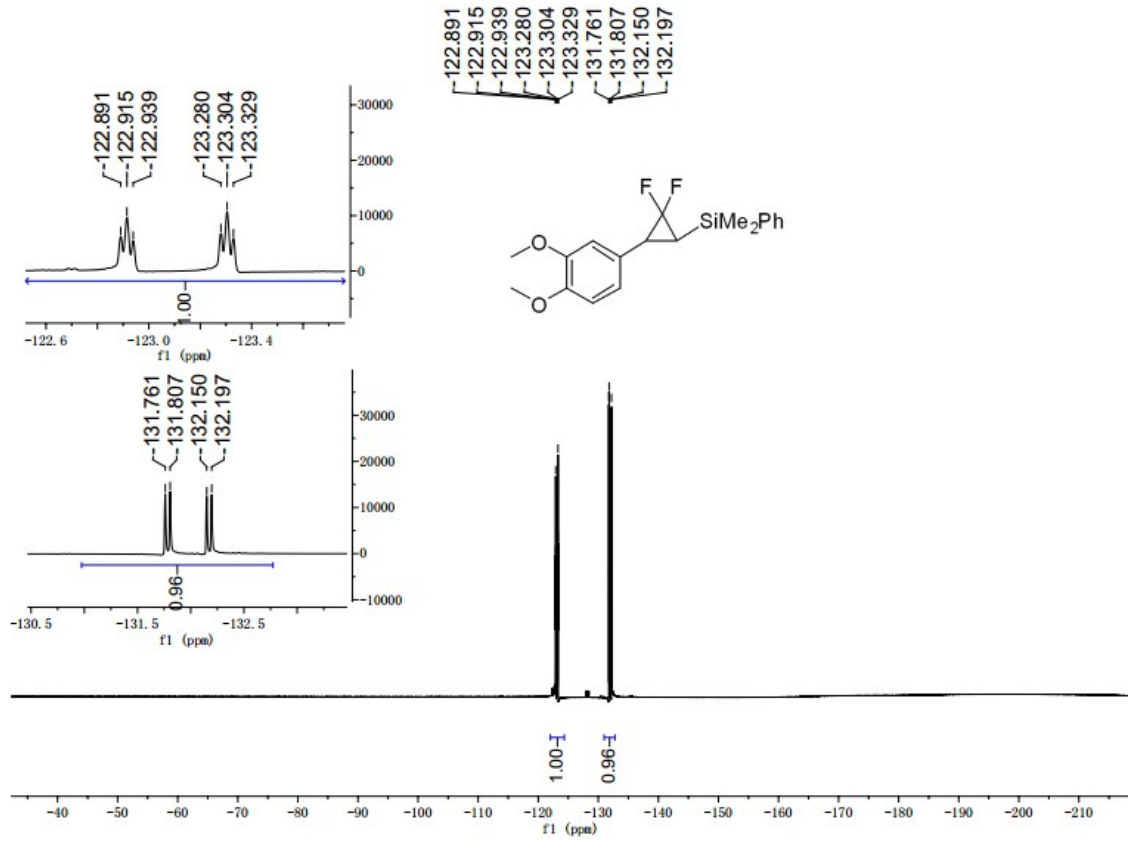
[1]H NMR spectrum of 3db



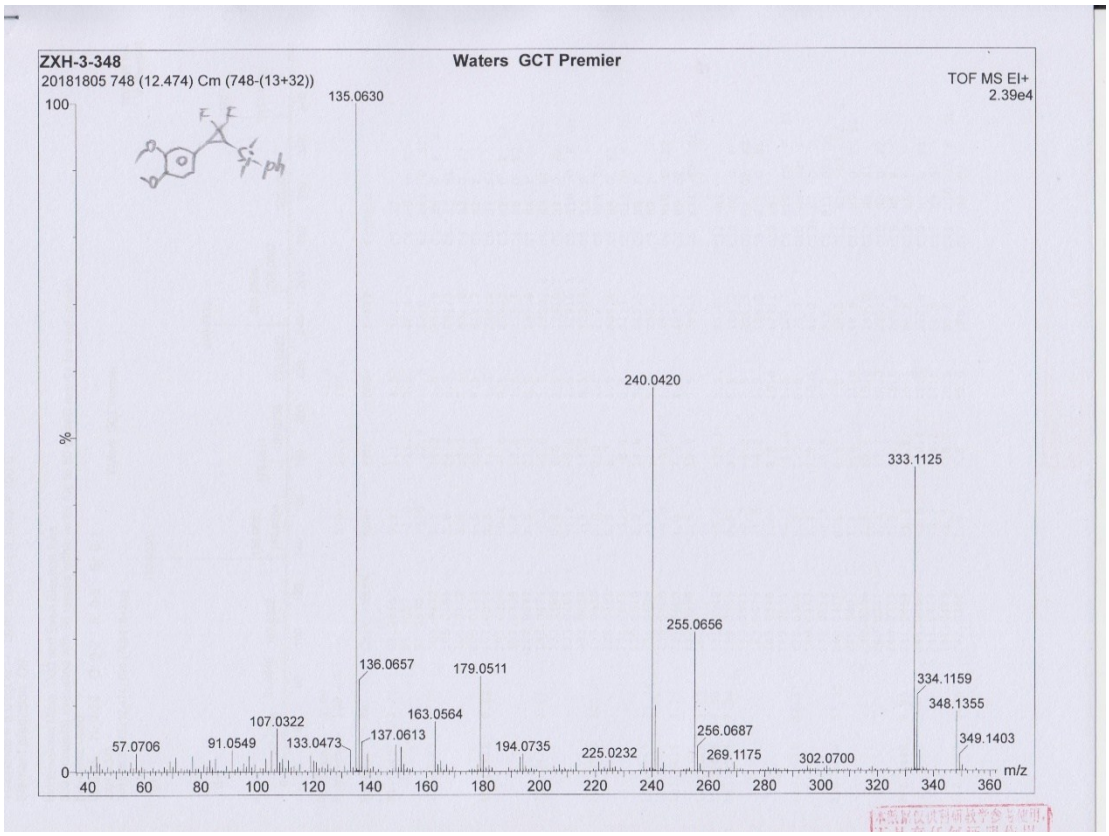
[13]C NMR spectrum of 3db



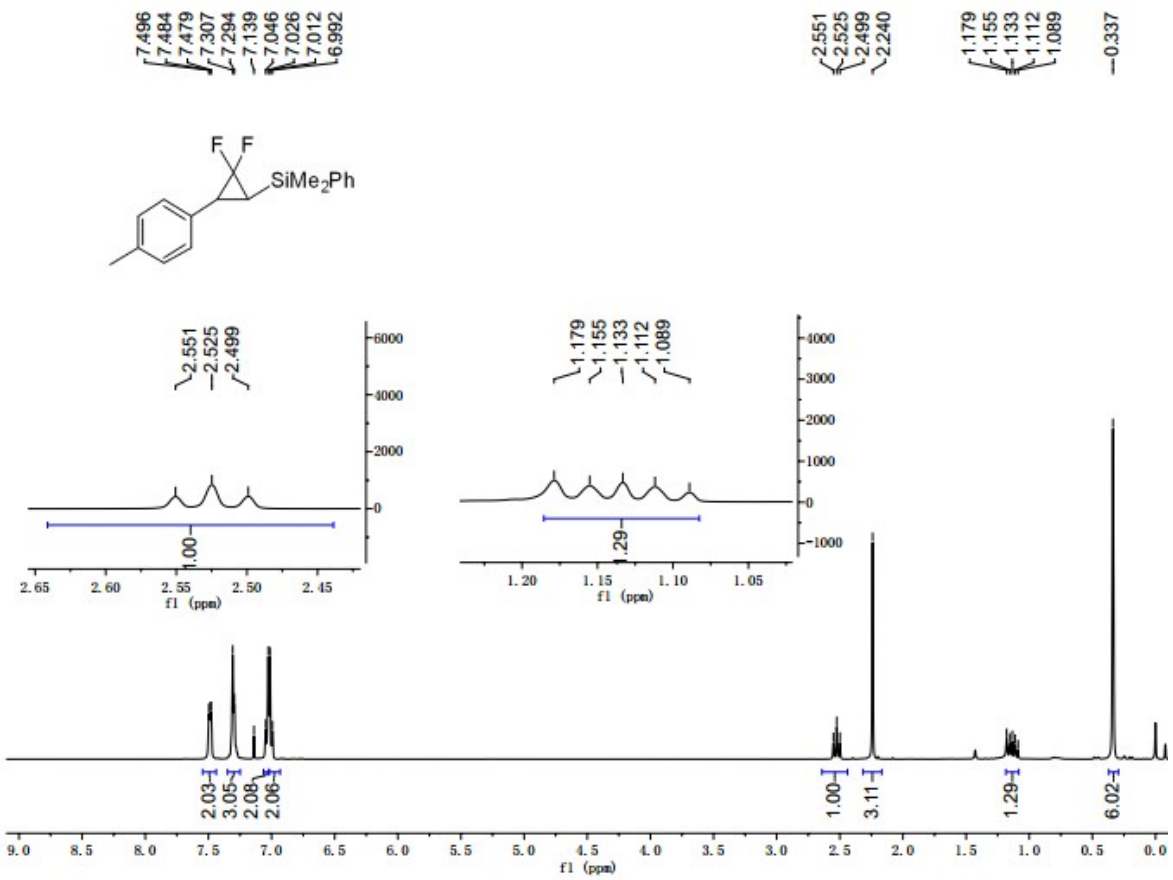
^{19}F NMR spectrum of 3db



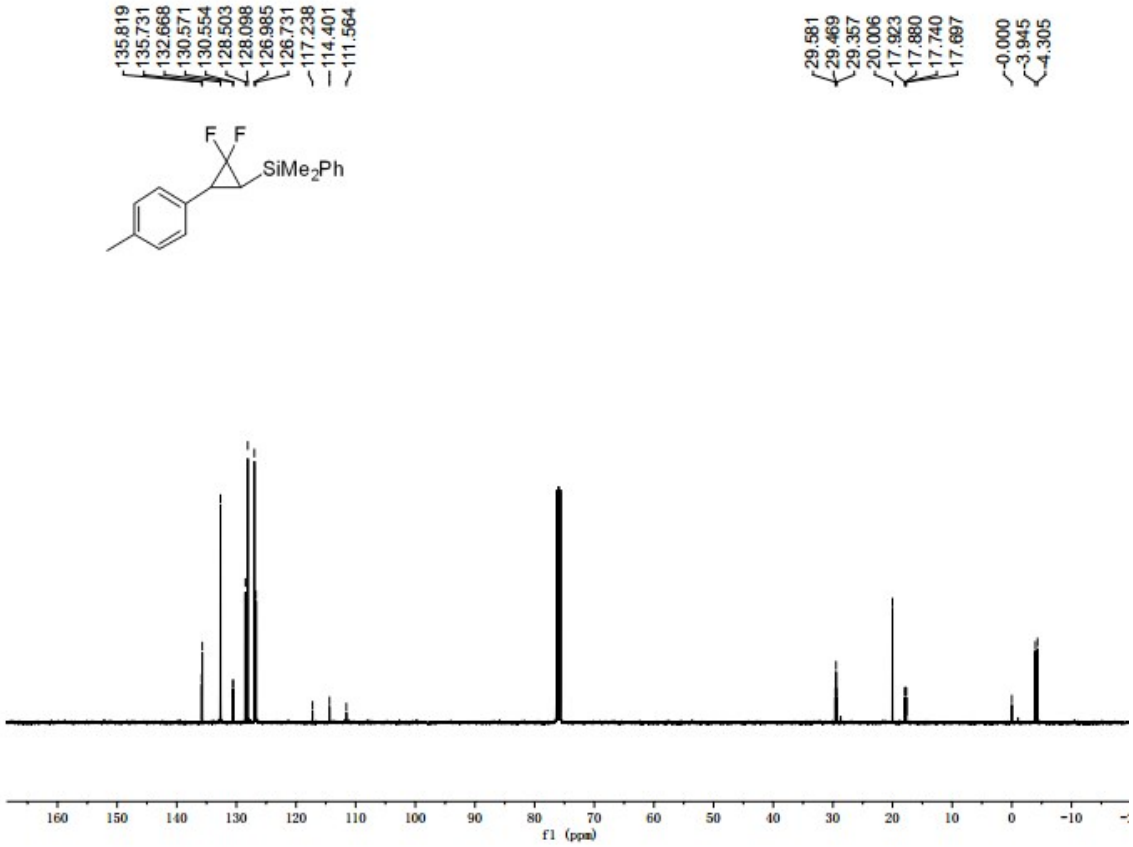
HRMS (EI) of 3db



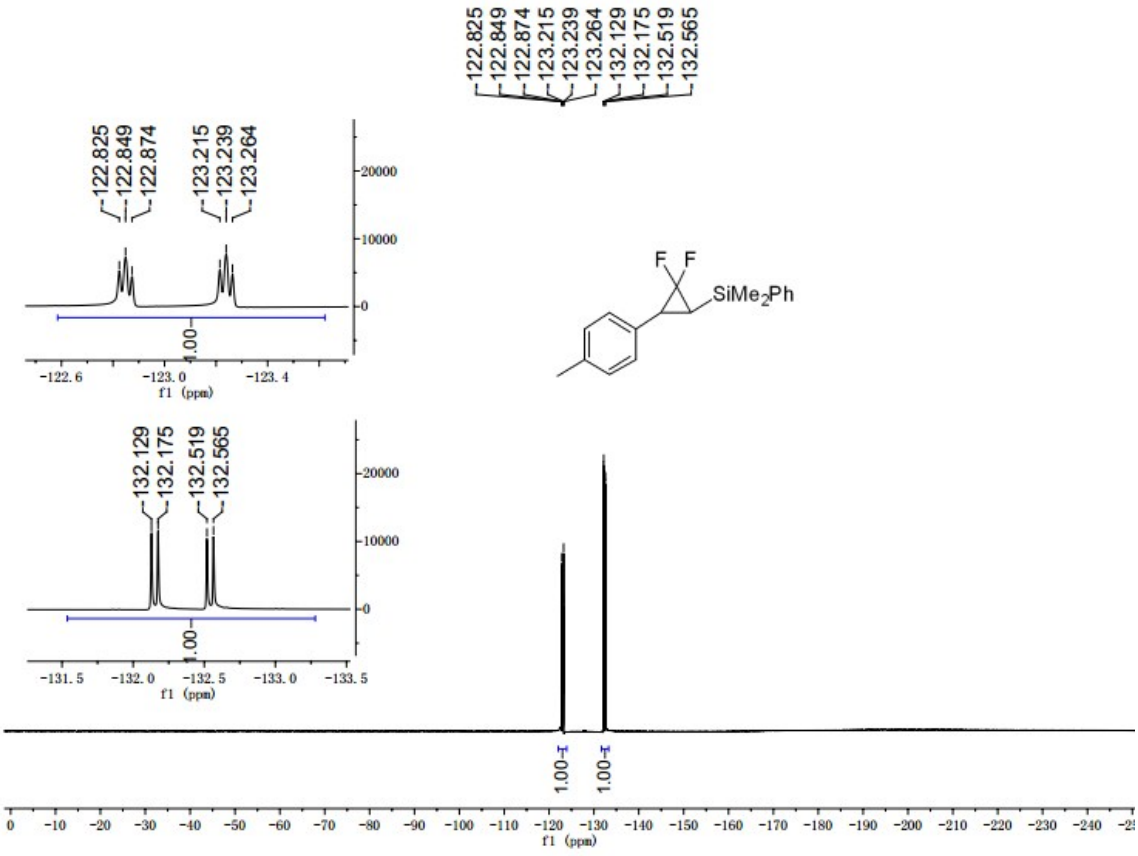
[1]H NMR spectrum of 3fb



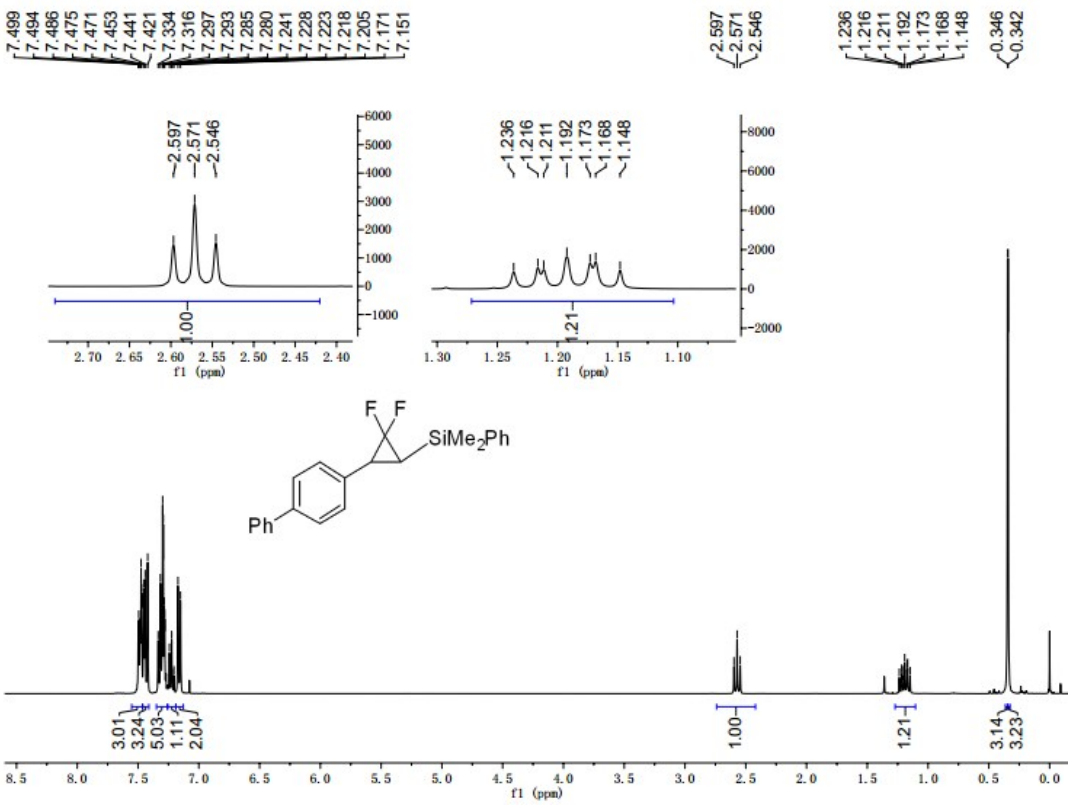
[13]C NMR spectrum of 3fb



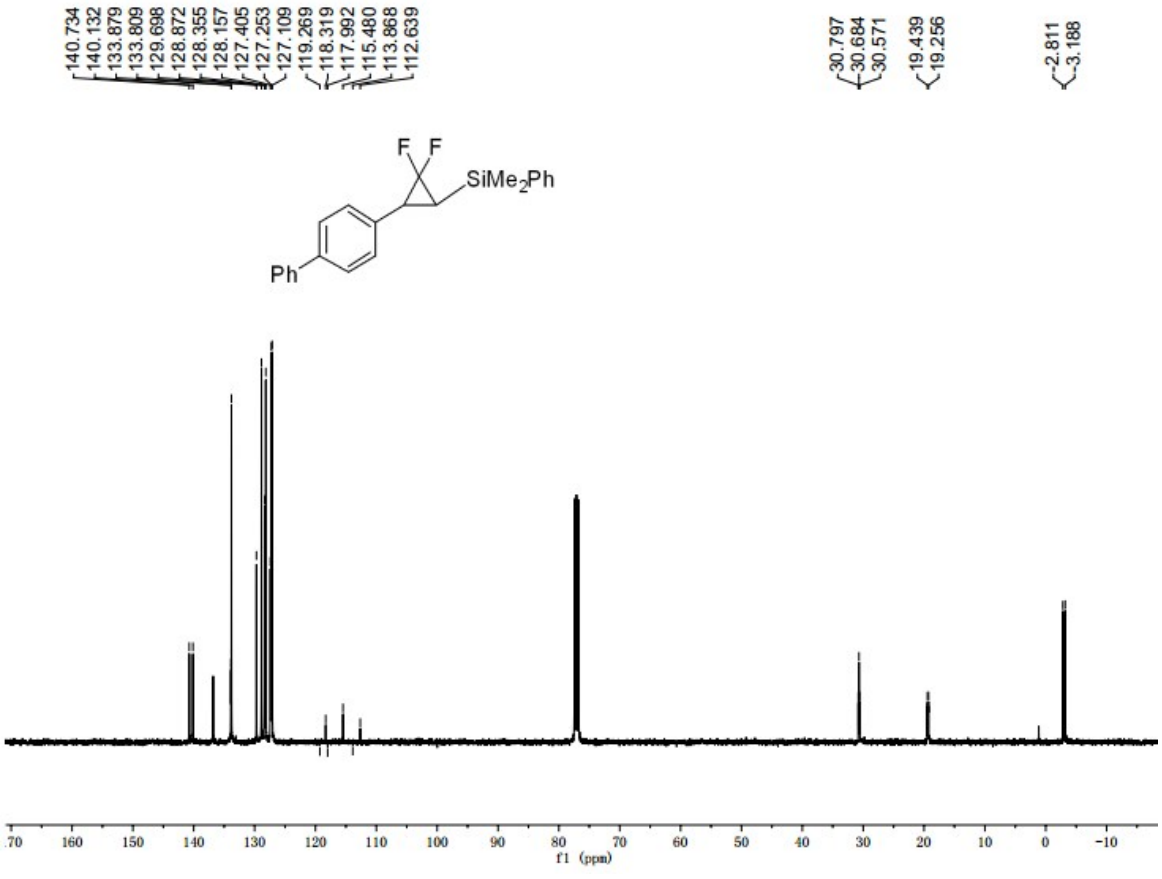
^{19}F NMR spectrum of 3fb



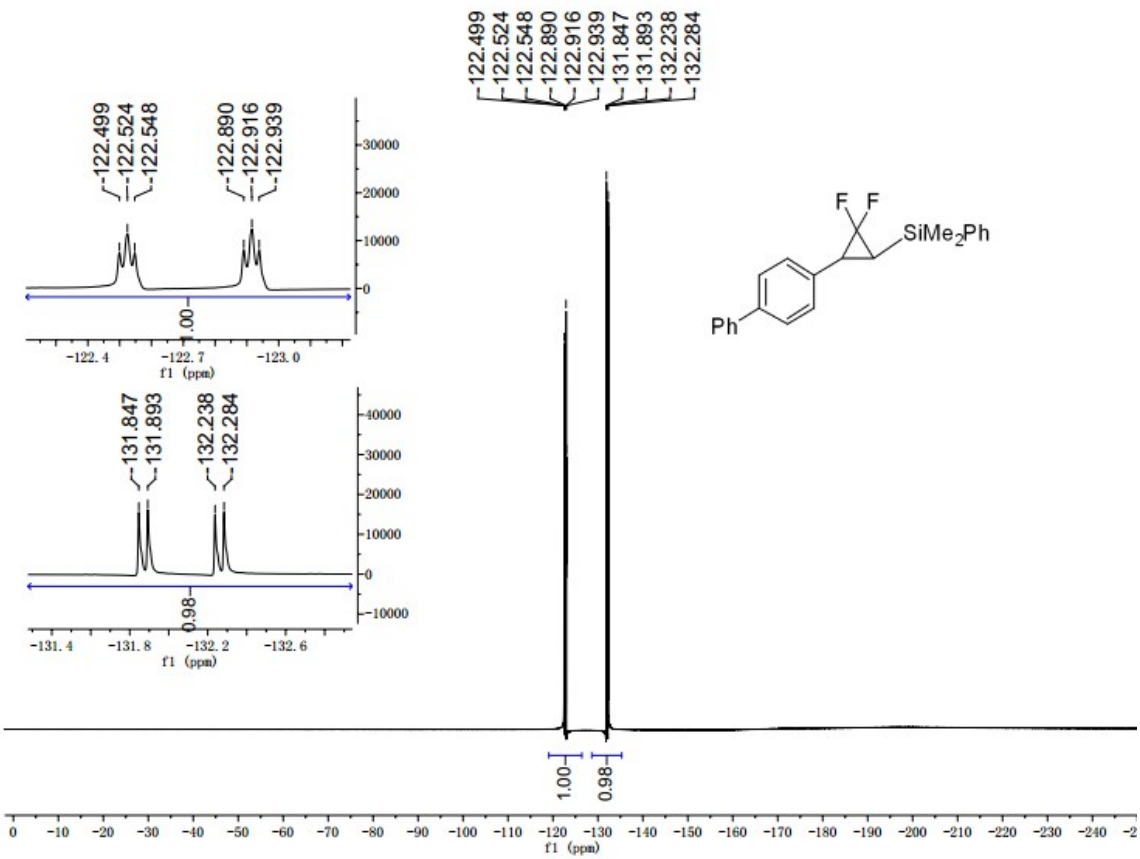
^{1}H NMR spectrum of 3gb



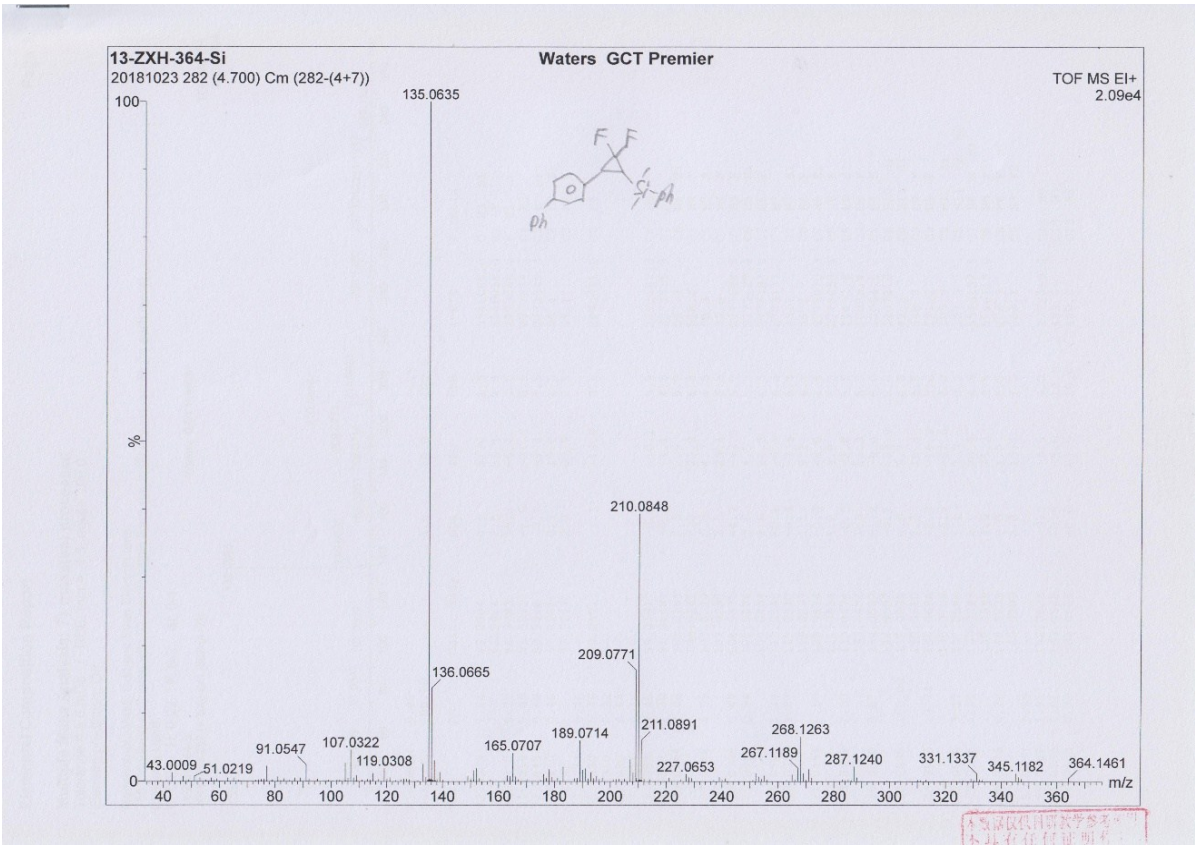
^{13}C NMR spectrum of 3gb



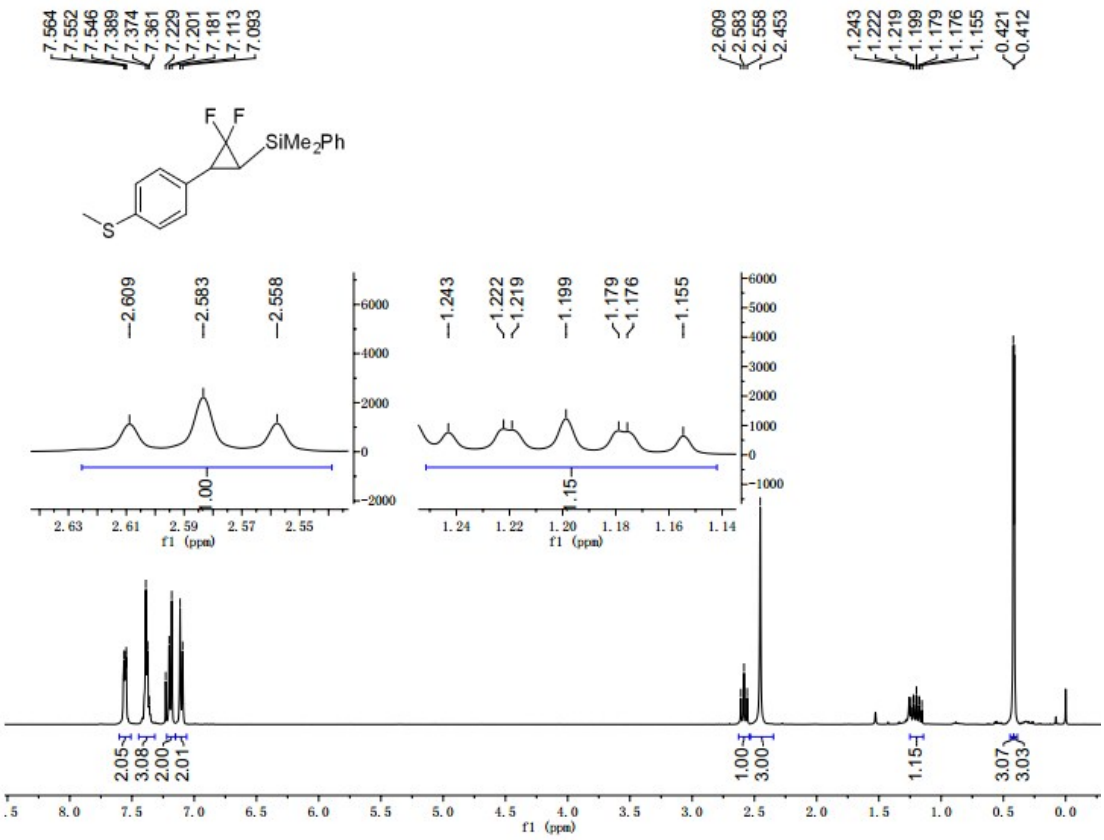
^{19}F NMR spectrum of 3gb



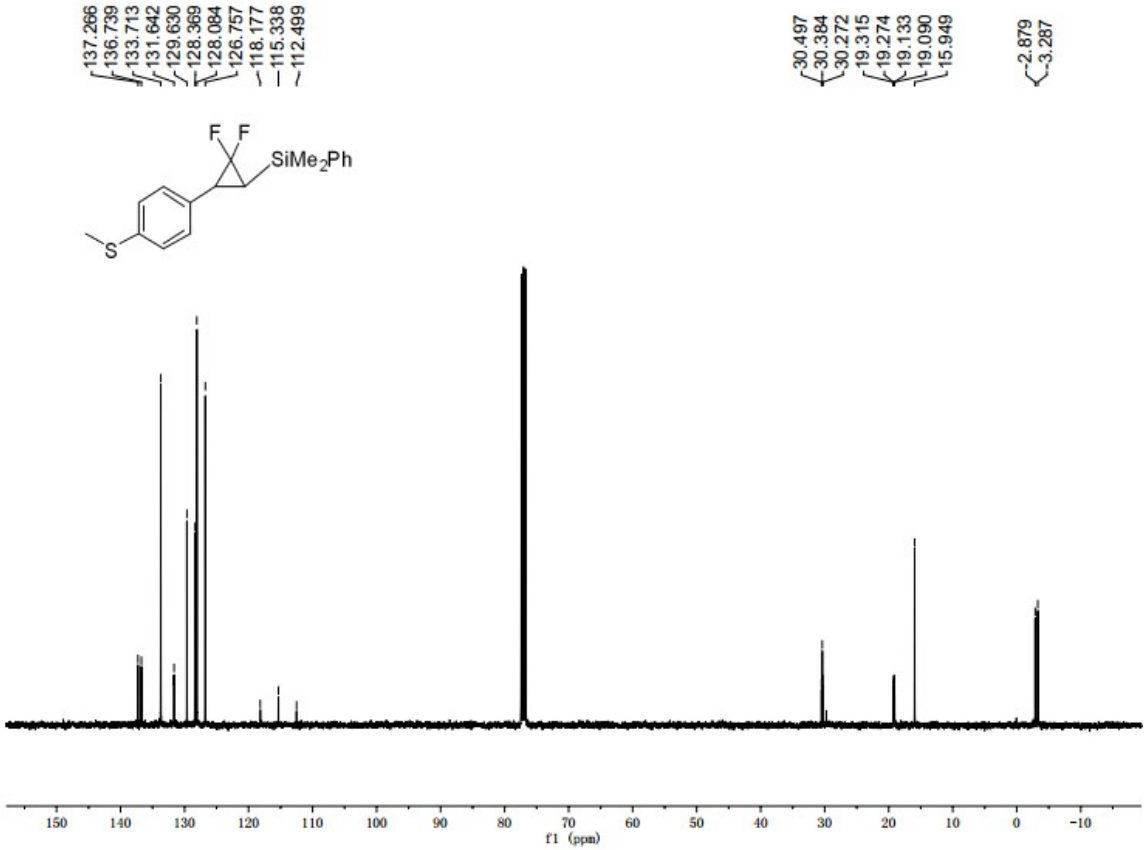
HRMS (EI) of 3gb



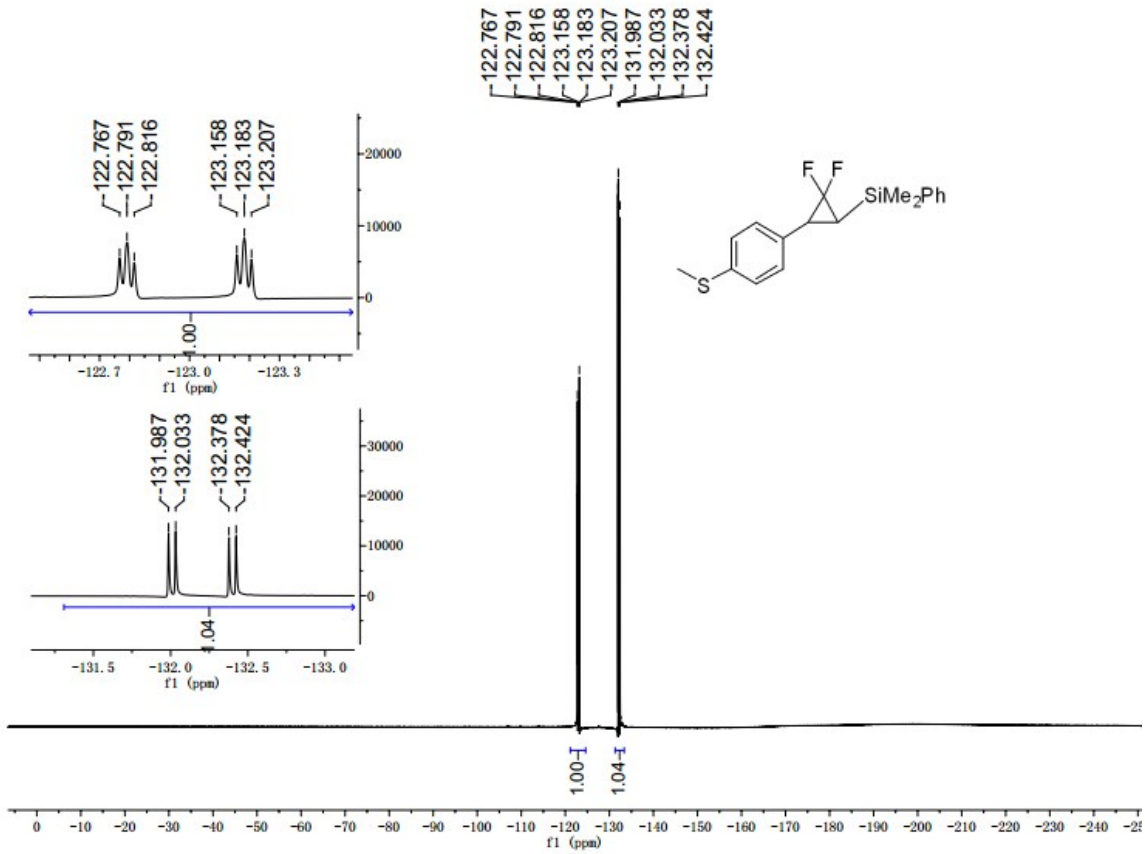
^{1}H NMR spectrum of 3hb



^{13}C NMR spectrum of 3hb



^{19}F NMR spectrum of 3hb



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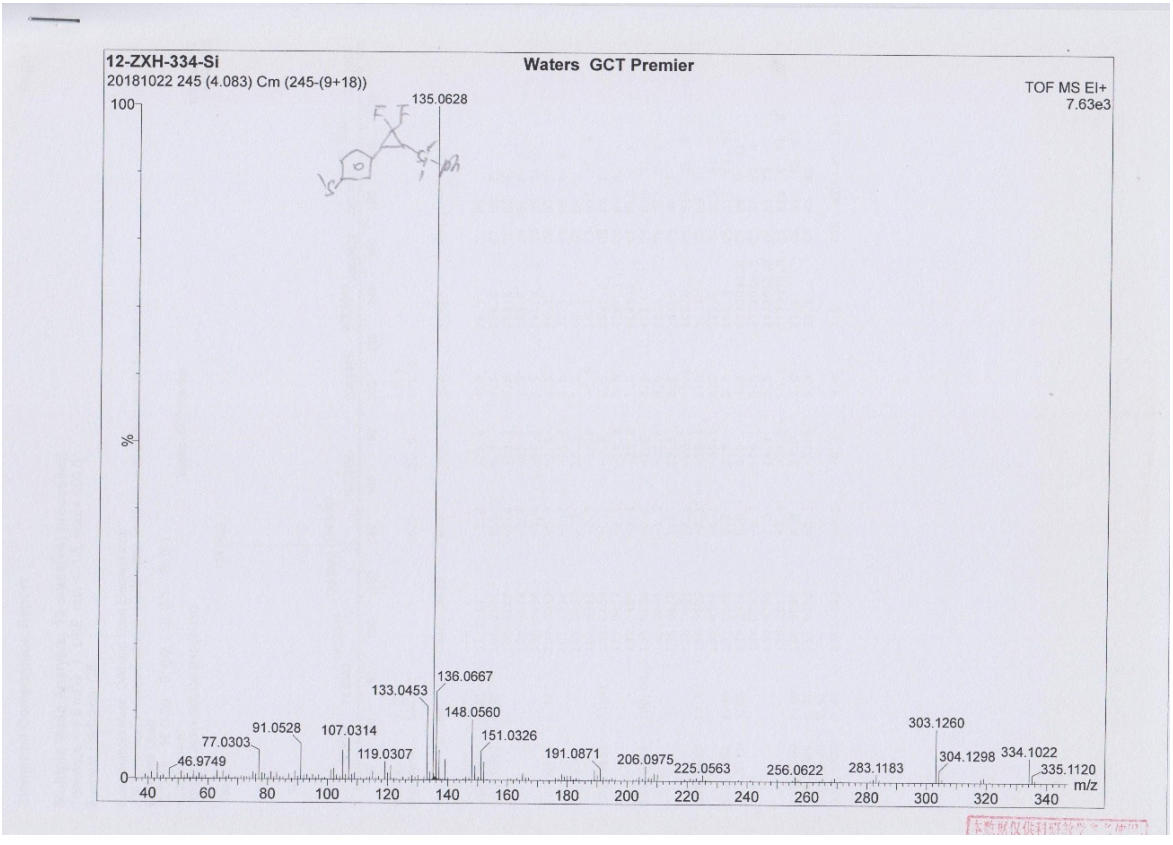
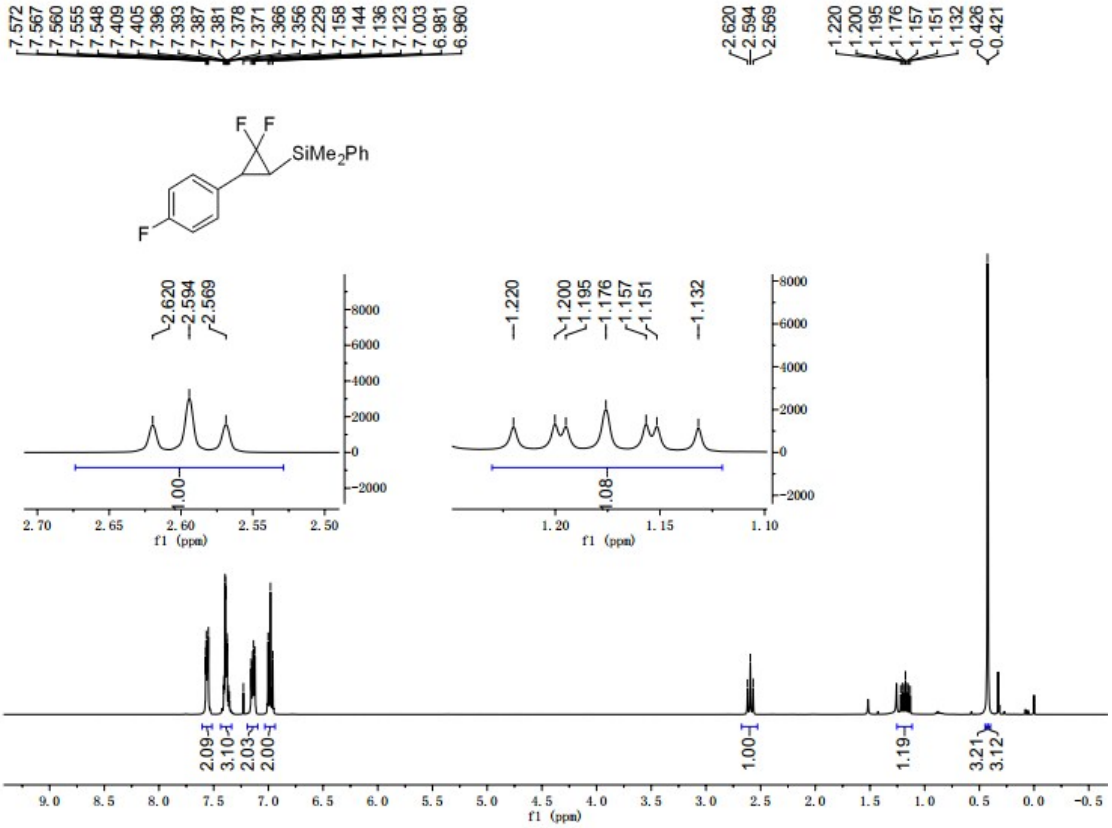
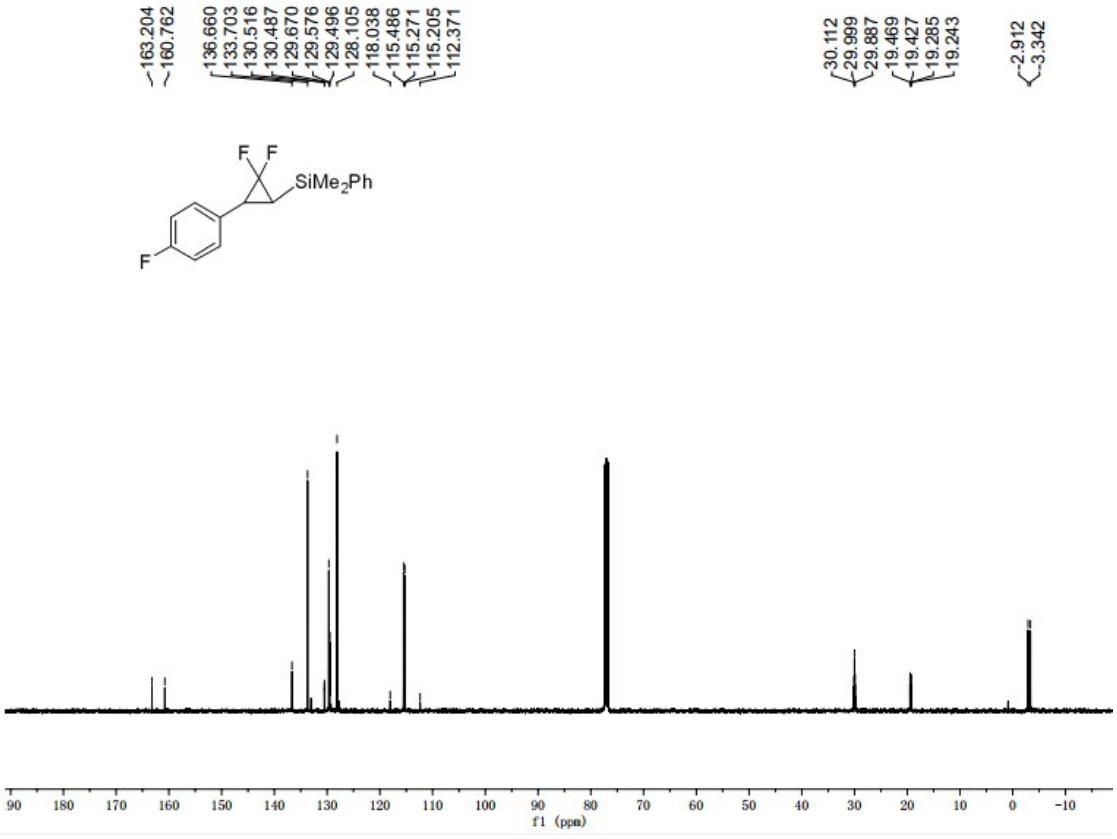


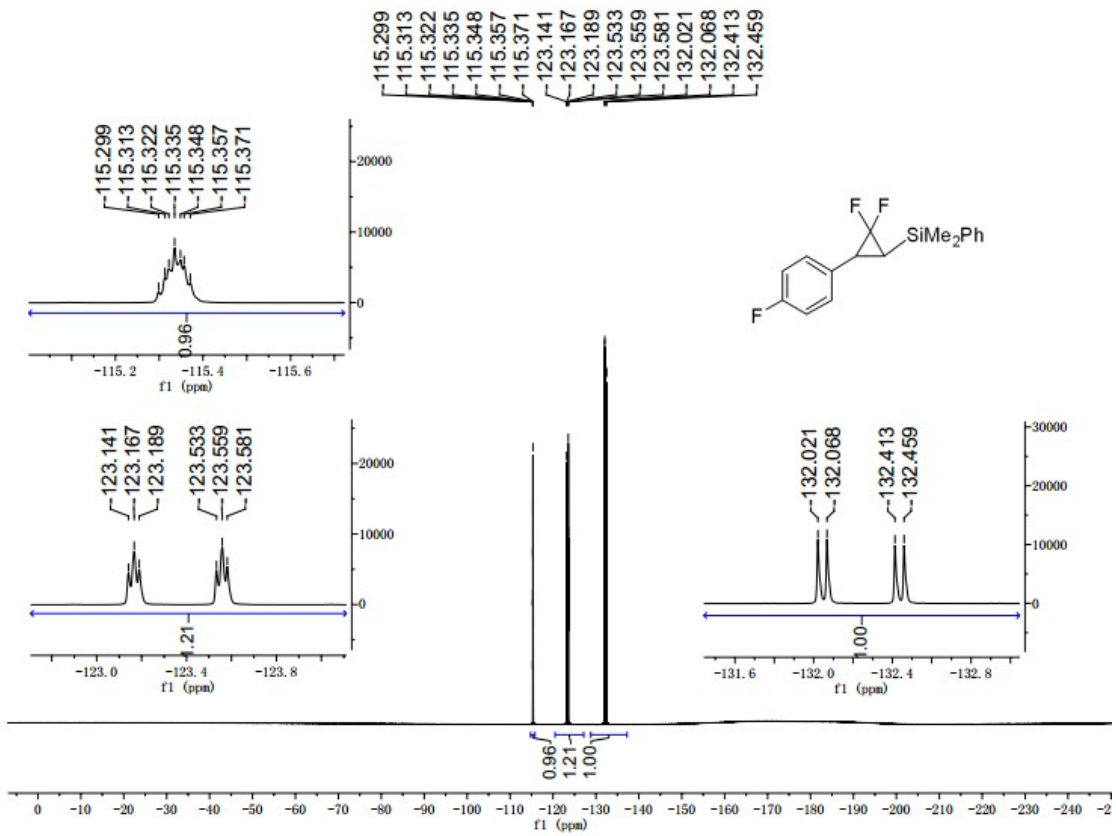
^{1}H NMR spectrum of 3kb



^{13}C NMR spectrum of 3kb



^{19}F NMR spectrum of 3kb



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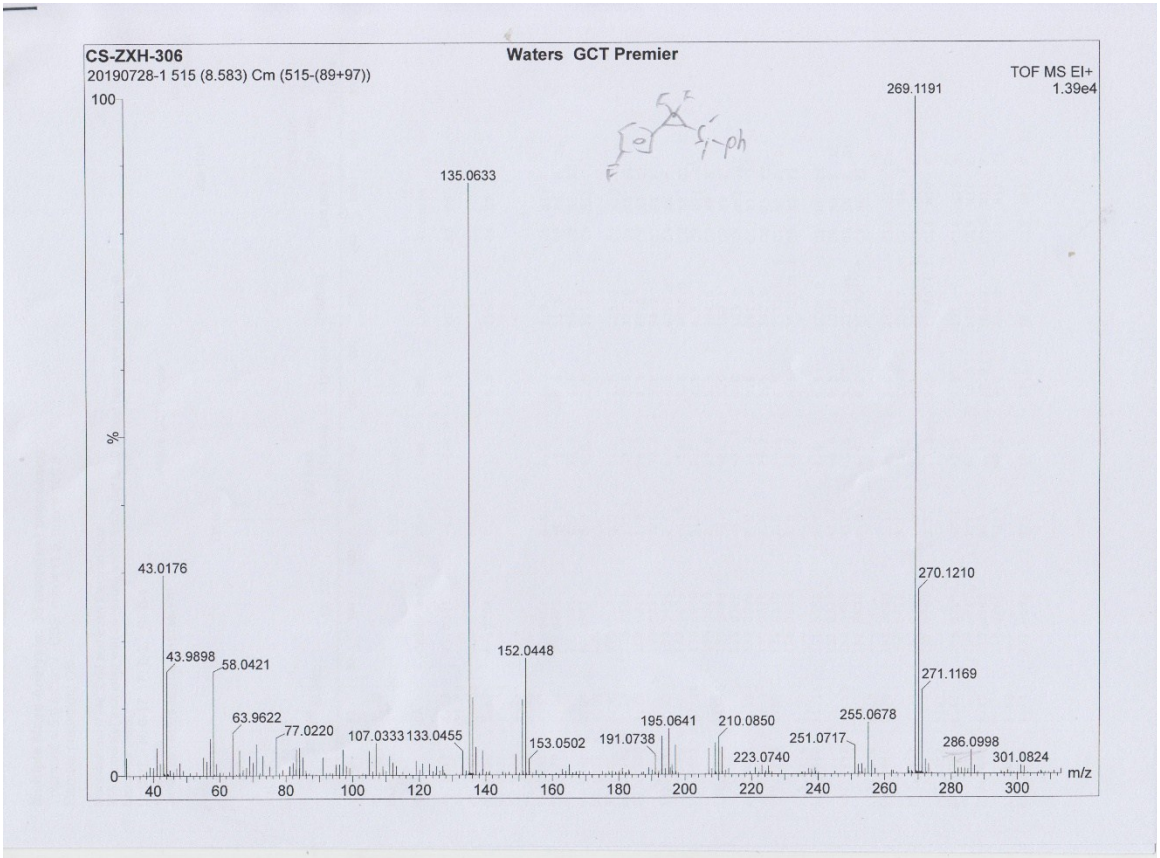
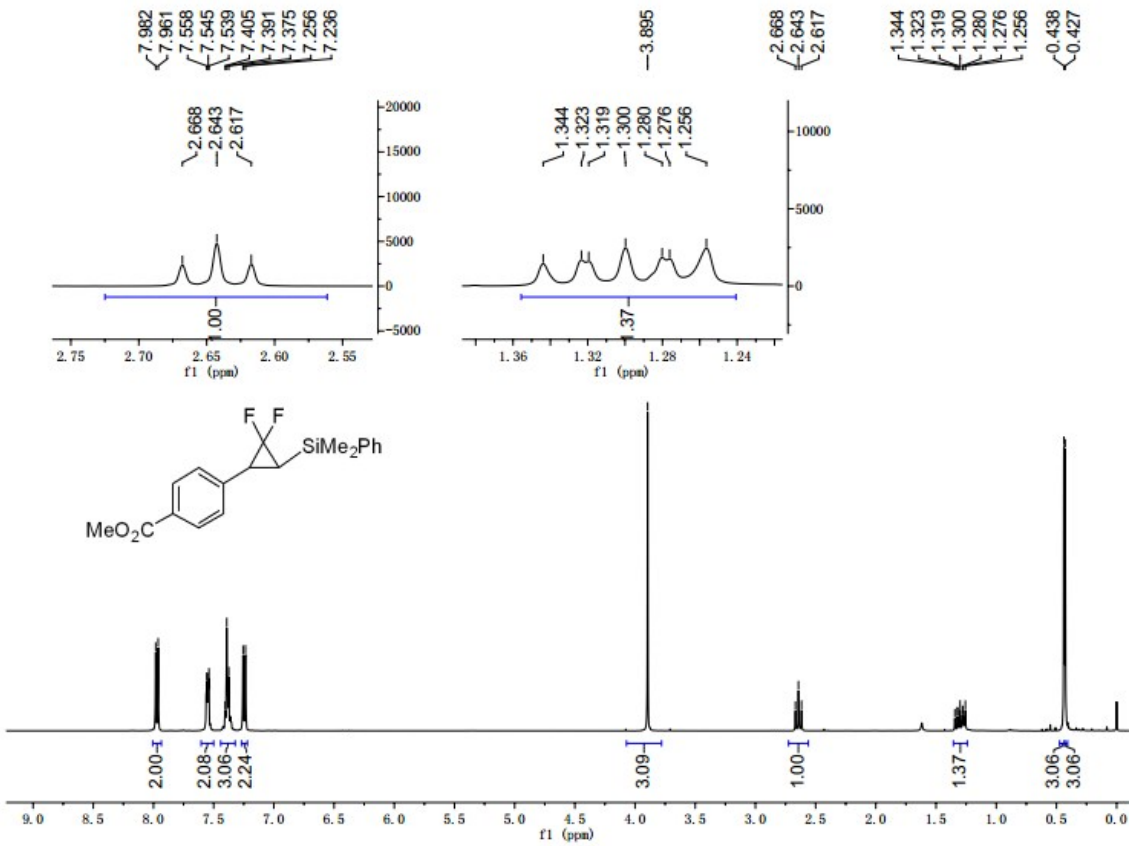
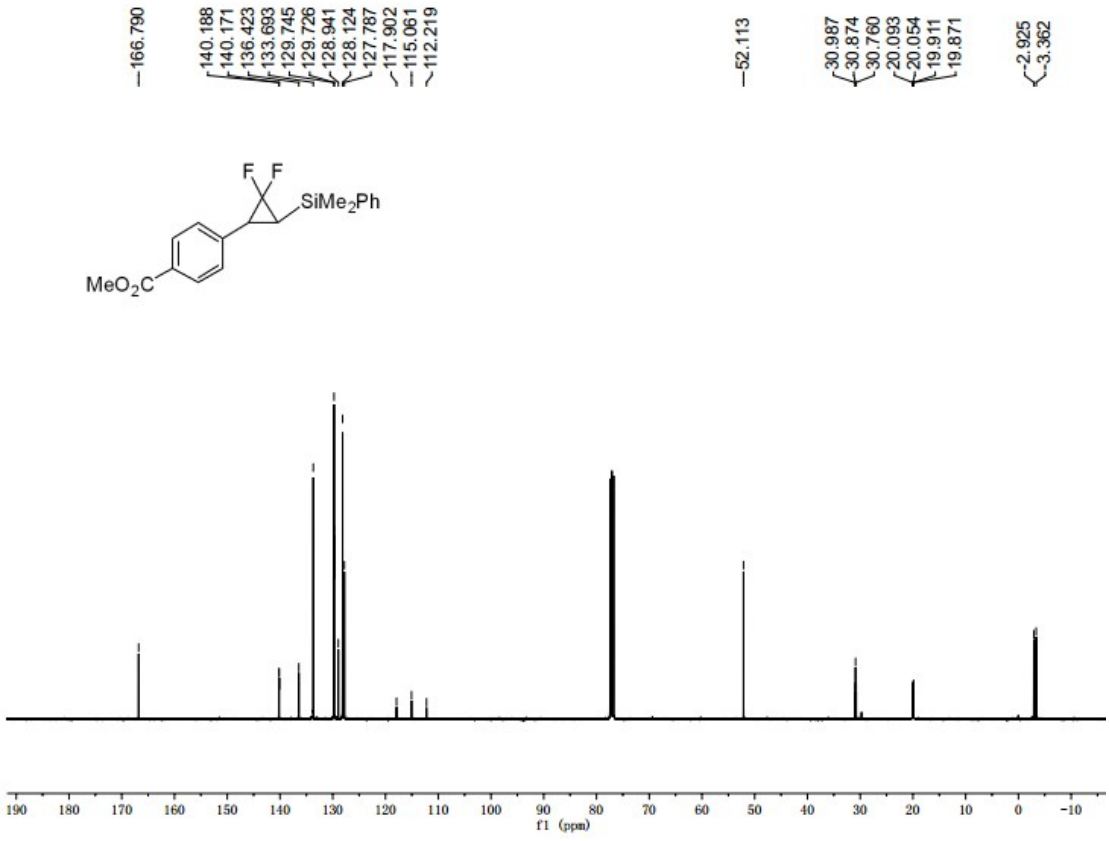


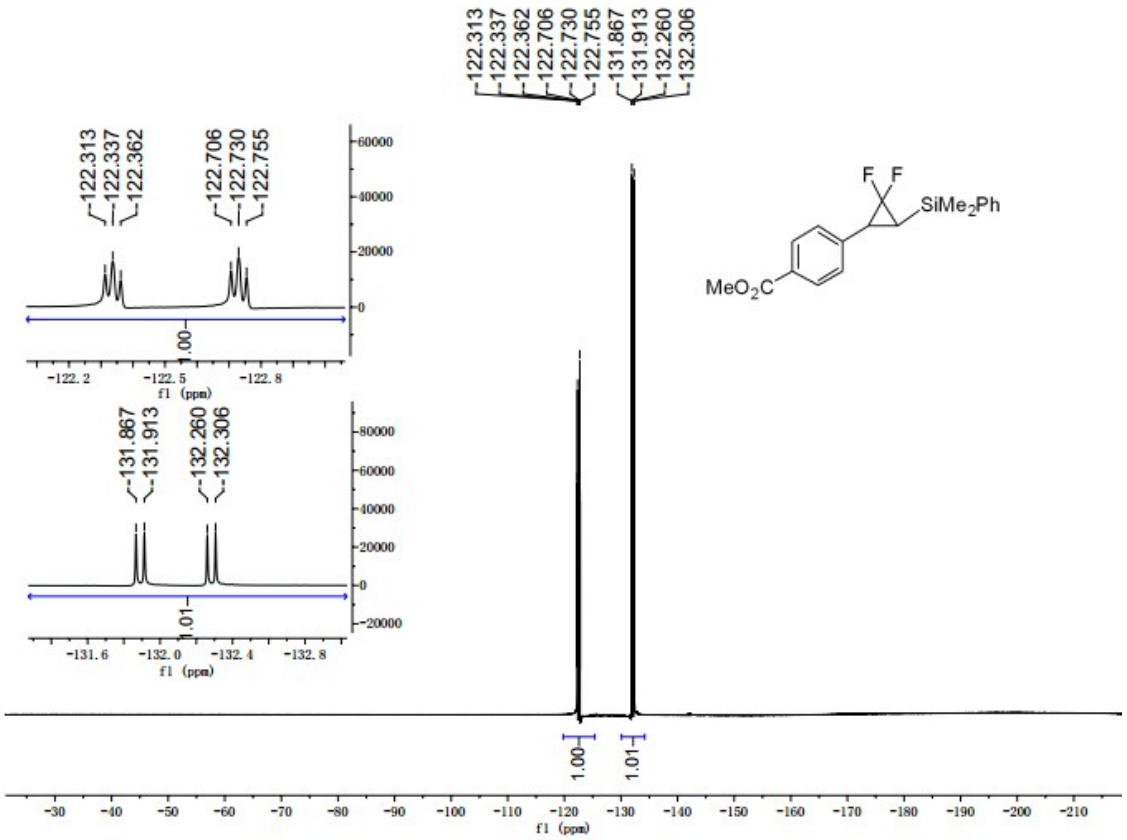
[1]H NMR spectrum of 3lb



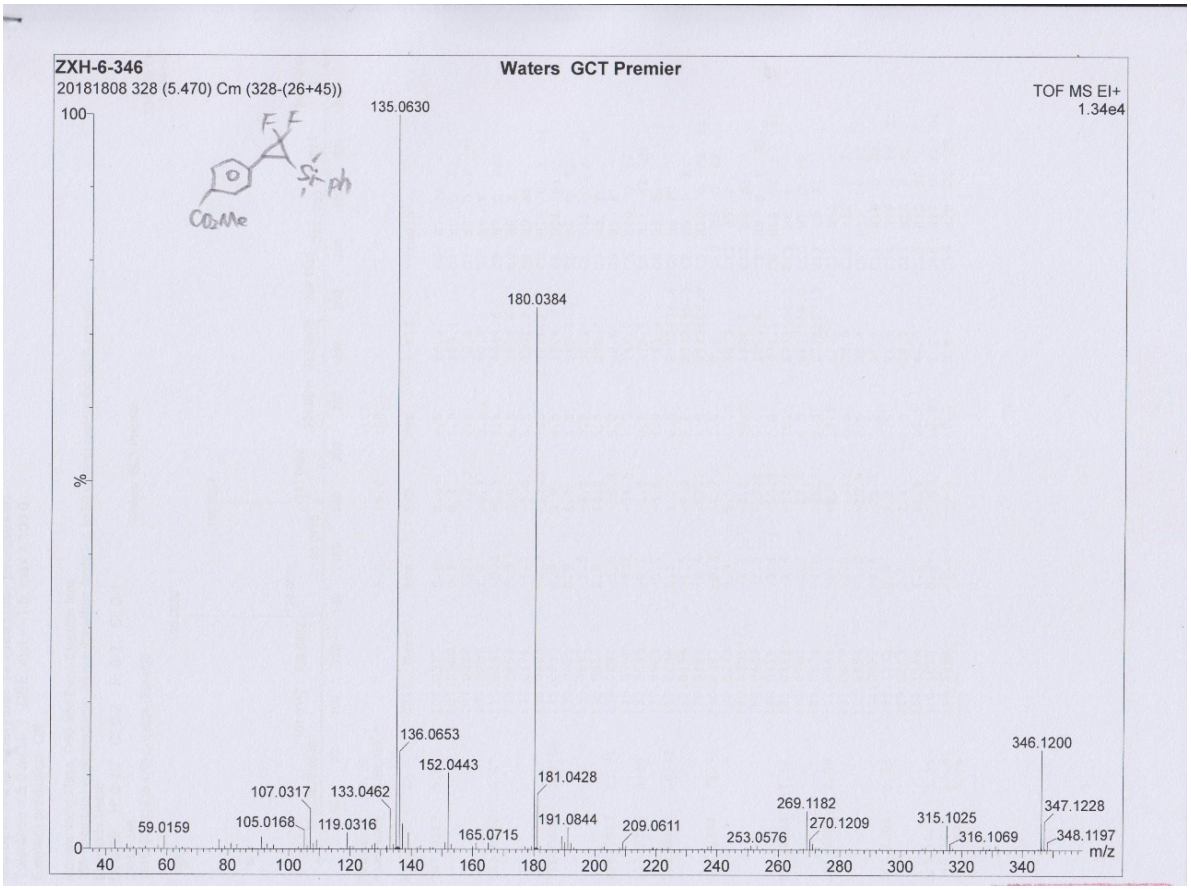
^{13}C NMR spectrum of 3lb



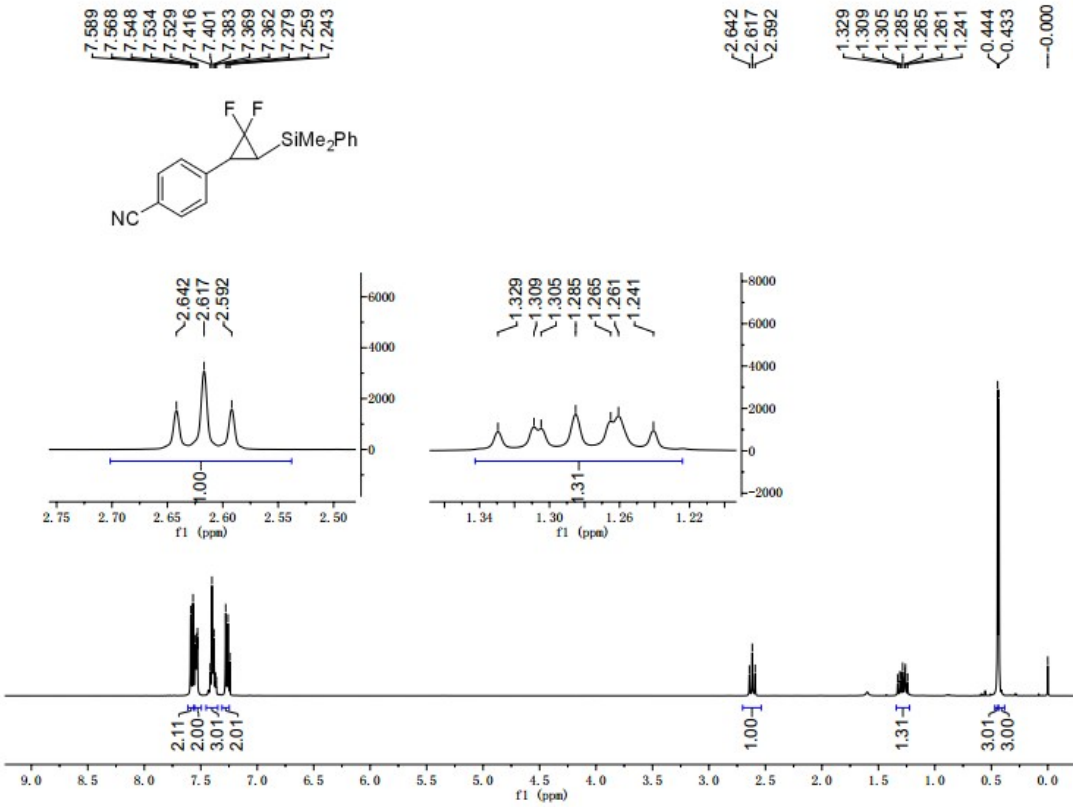
^{19}F NMR spectrum of 3lb



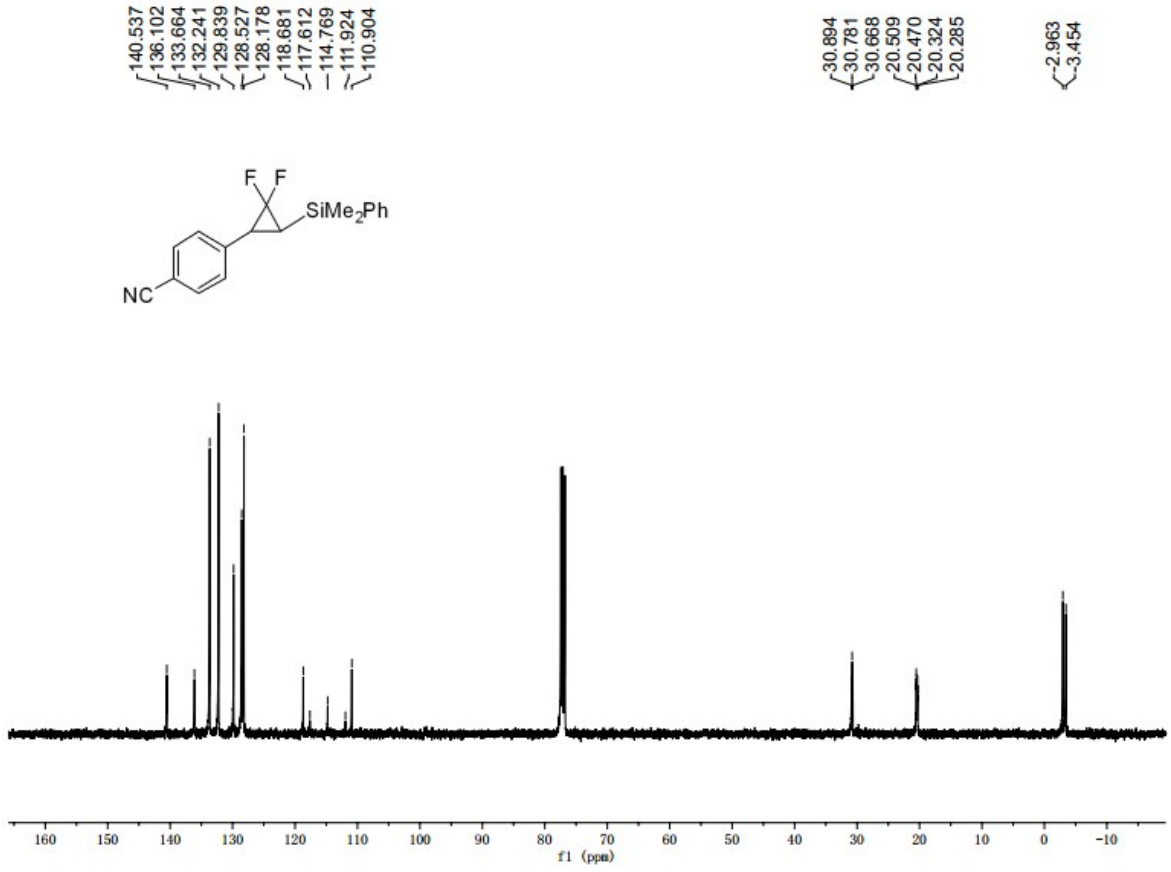
HRMS (EI) of 3lb



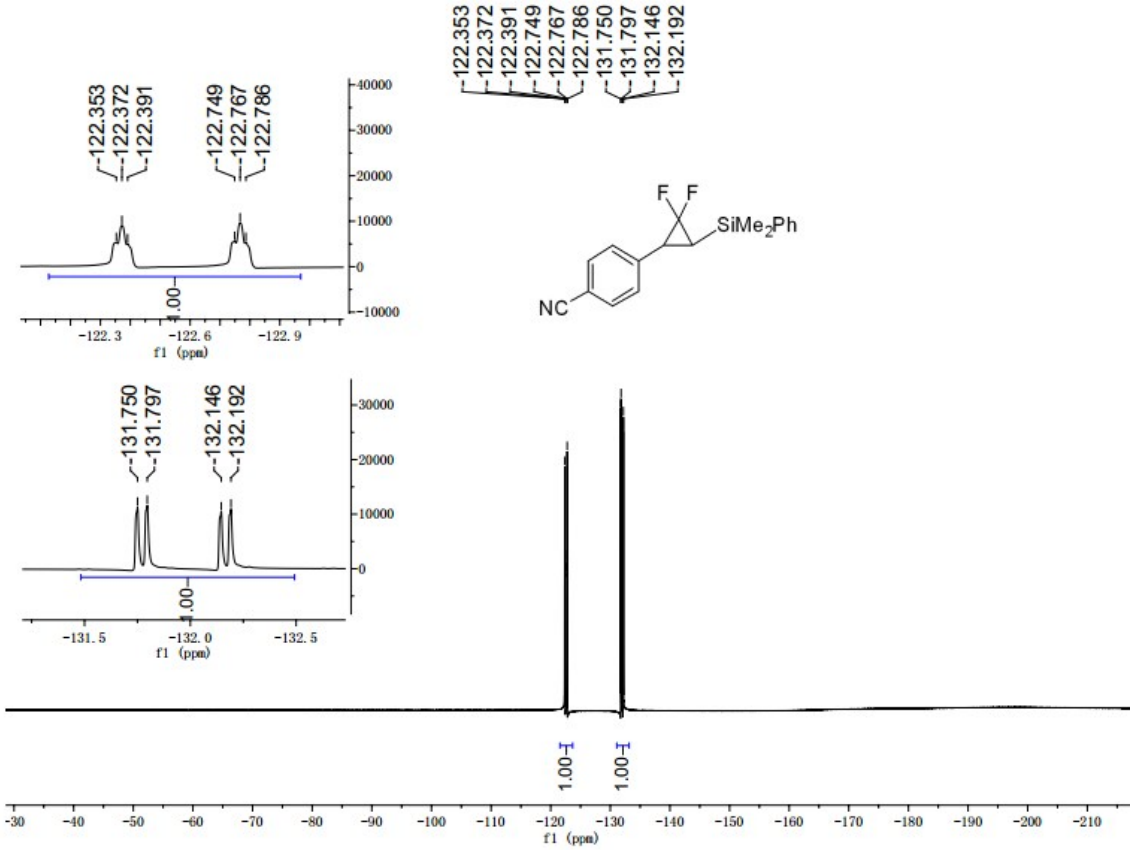
^{1}H NMR spectrum of 3mb



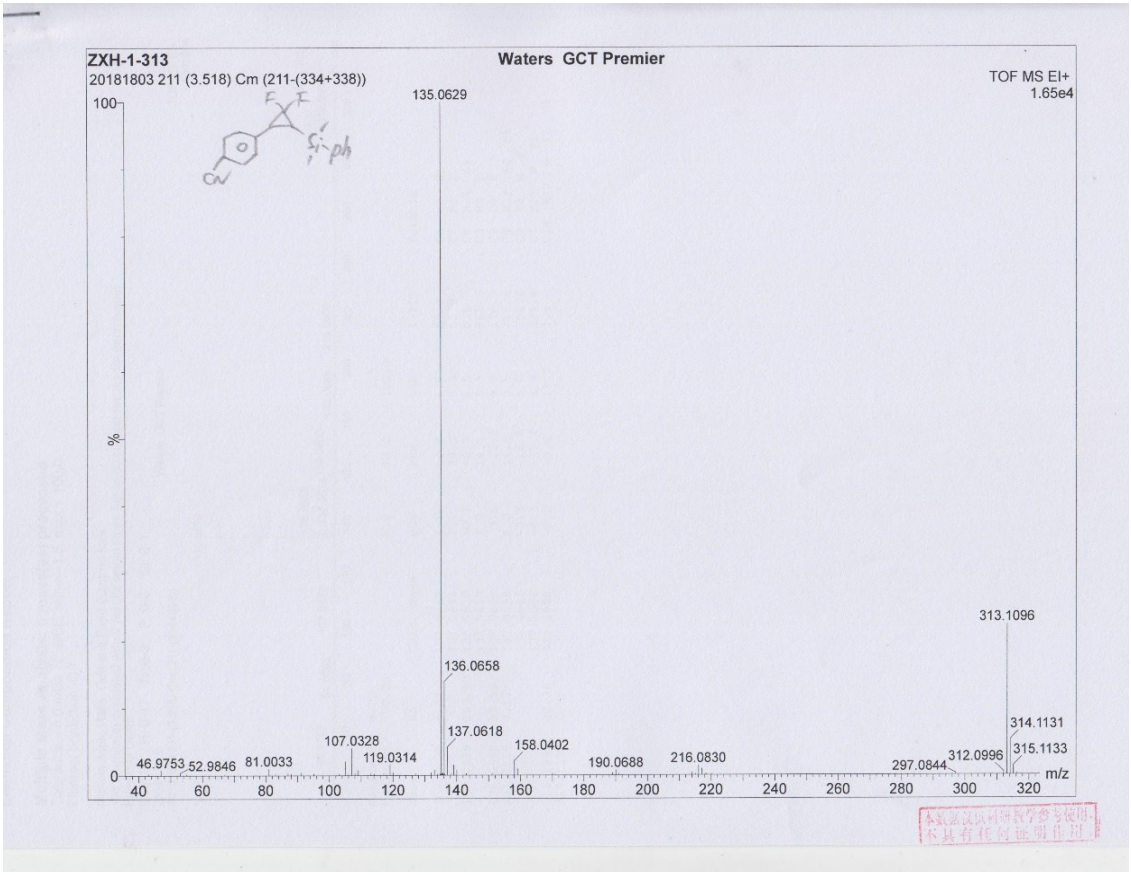
^{13}C NMR spectrum of 3mb



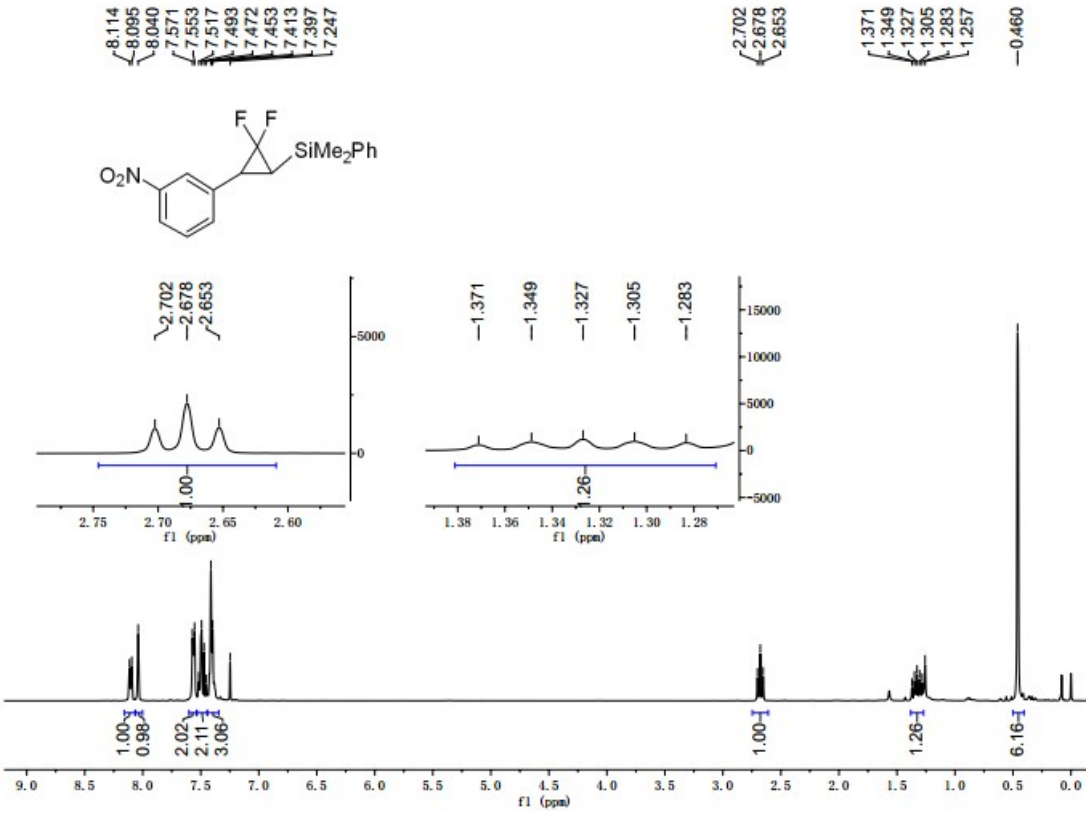
^{19}F NMR spectrum of 3mb



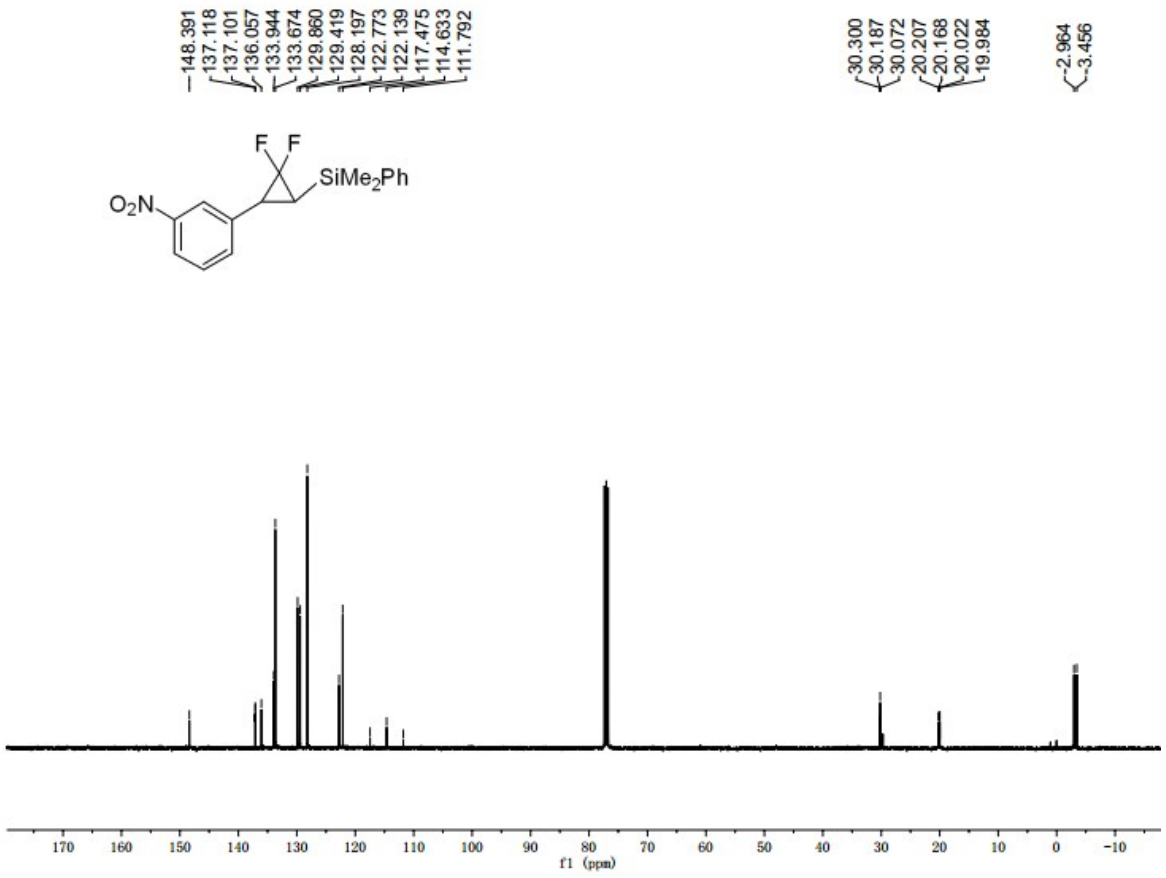
HRMS (EI) of 3mb



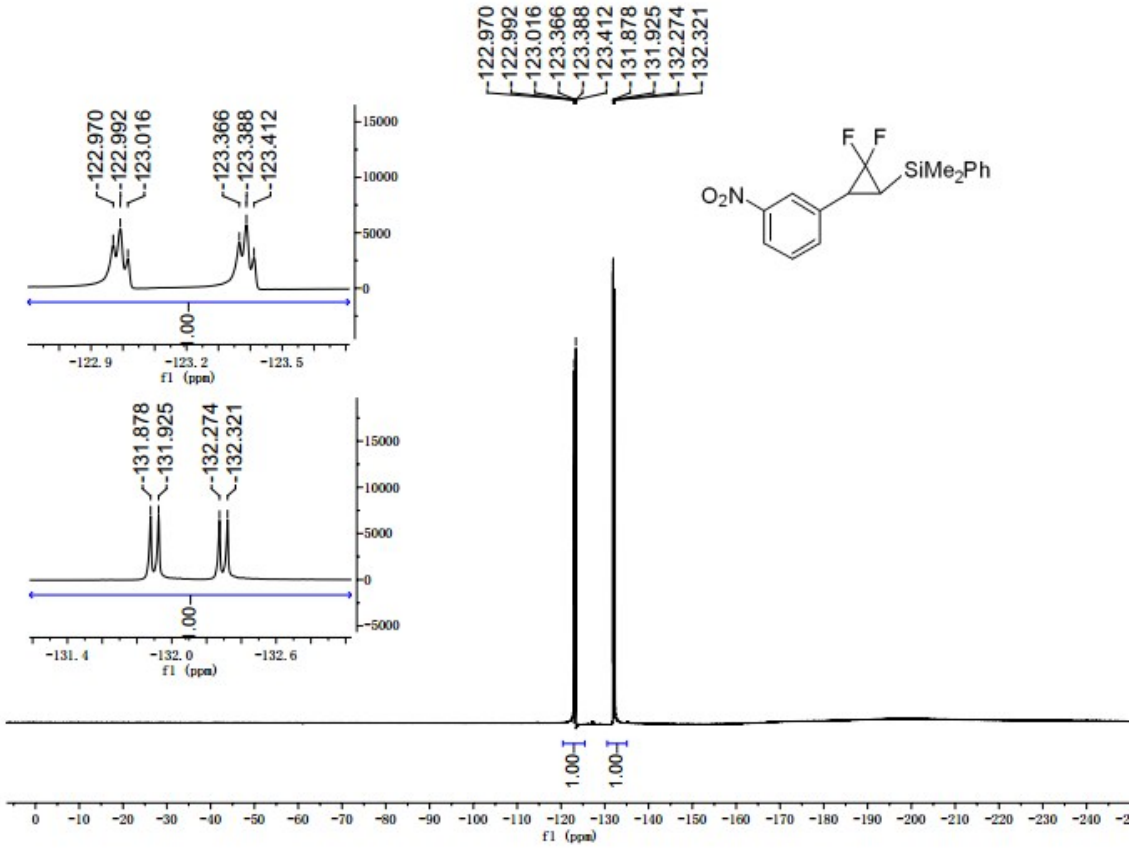
^{1}H NMR spectrum of 3nb



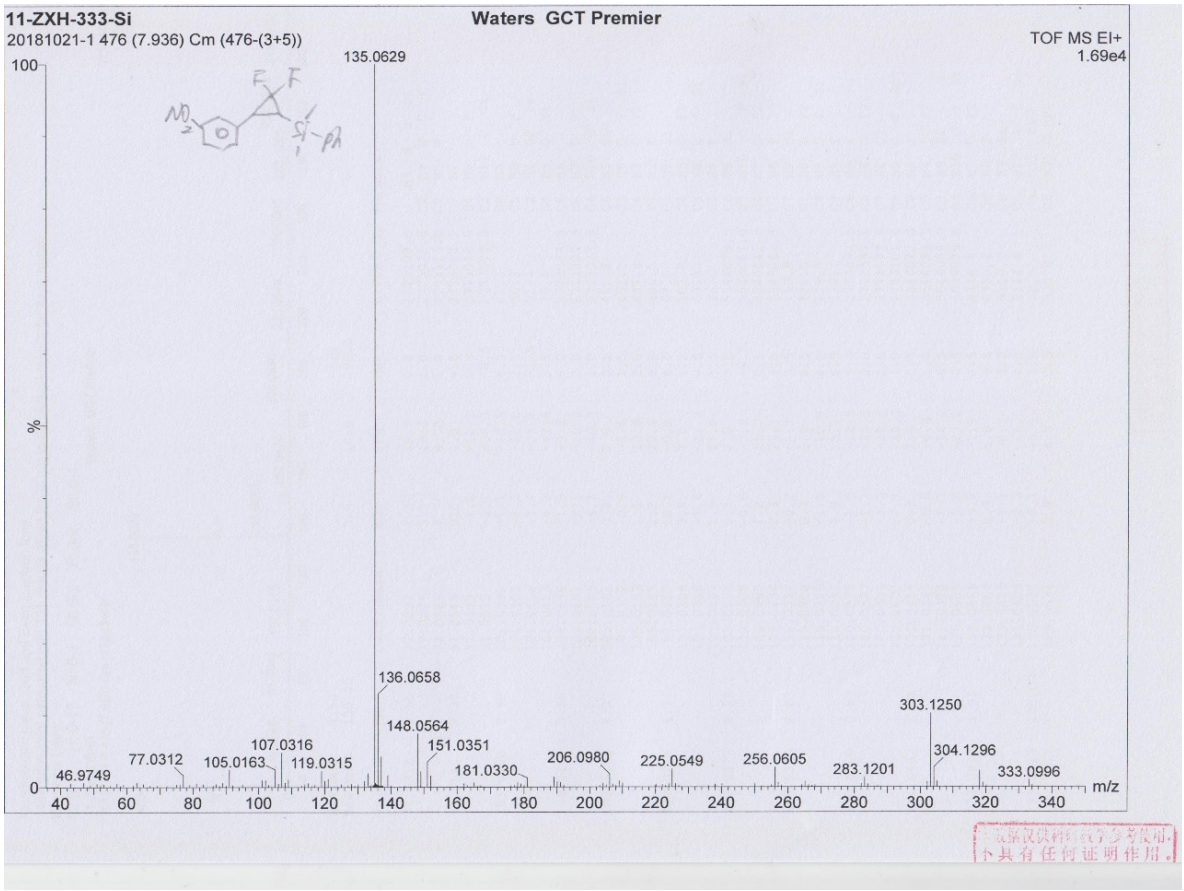
^{13}C NMR spectrum of 3nb



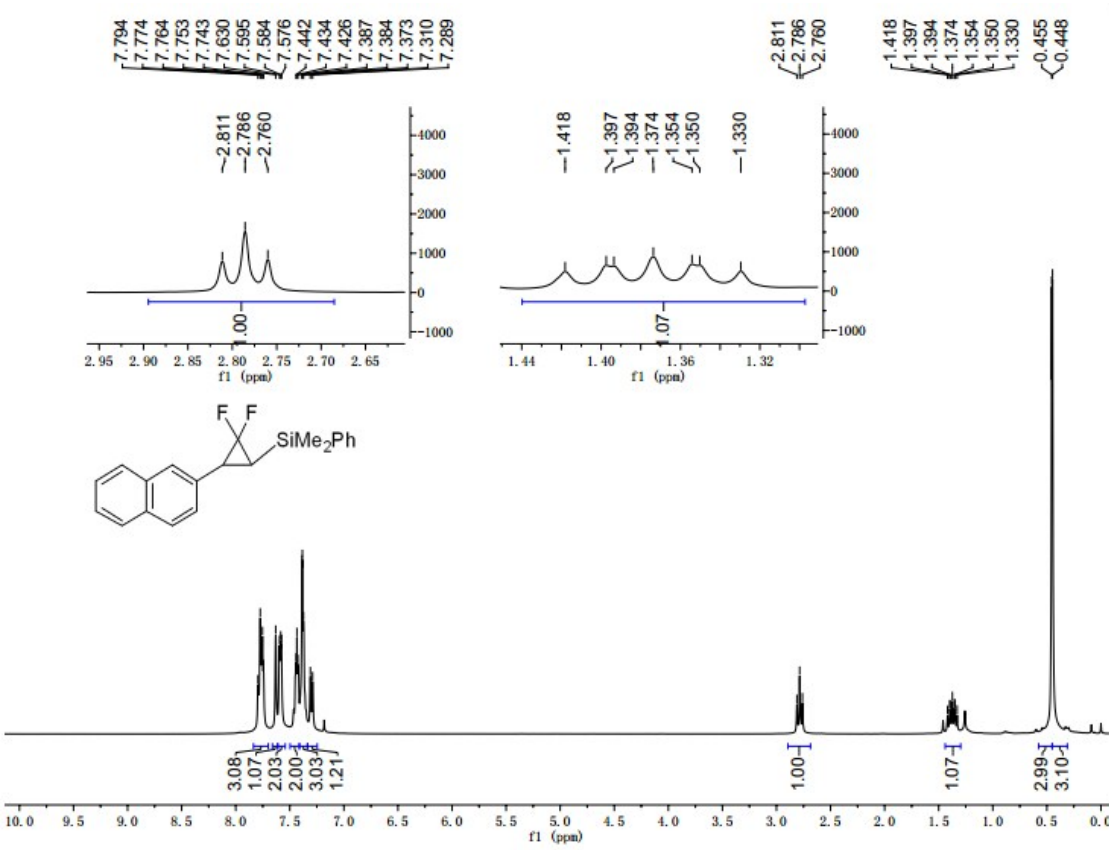
^{19}F NMR spectrum of 3nb



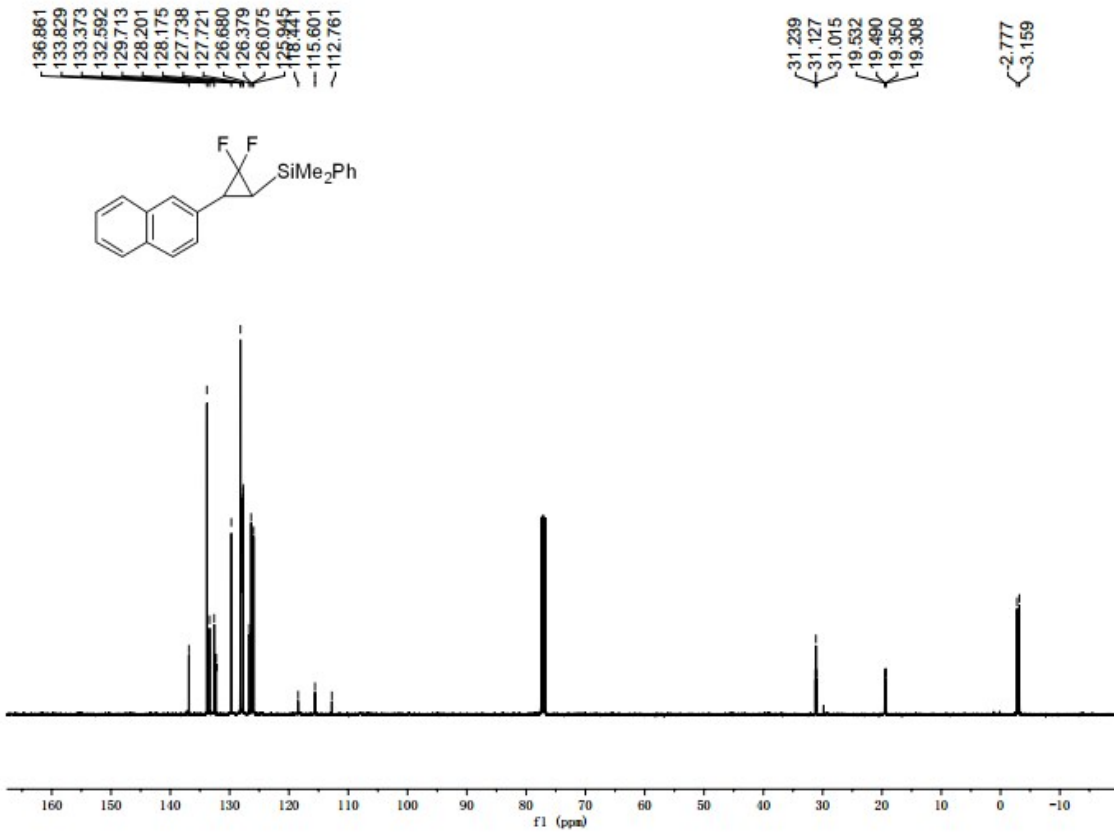
HRMS (EI) of 3nb



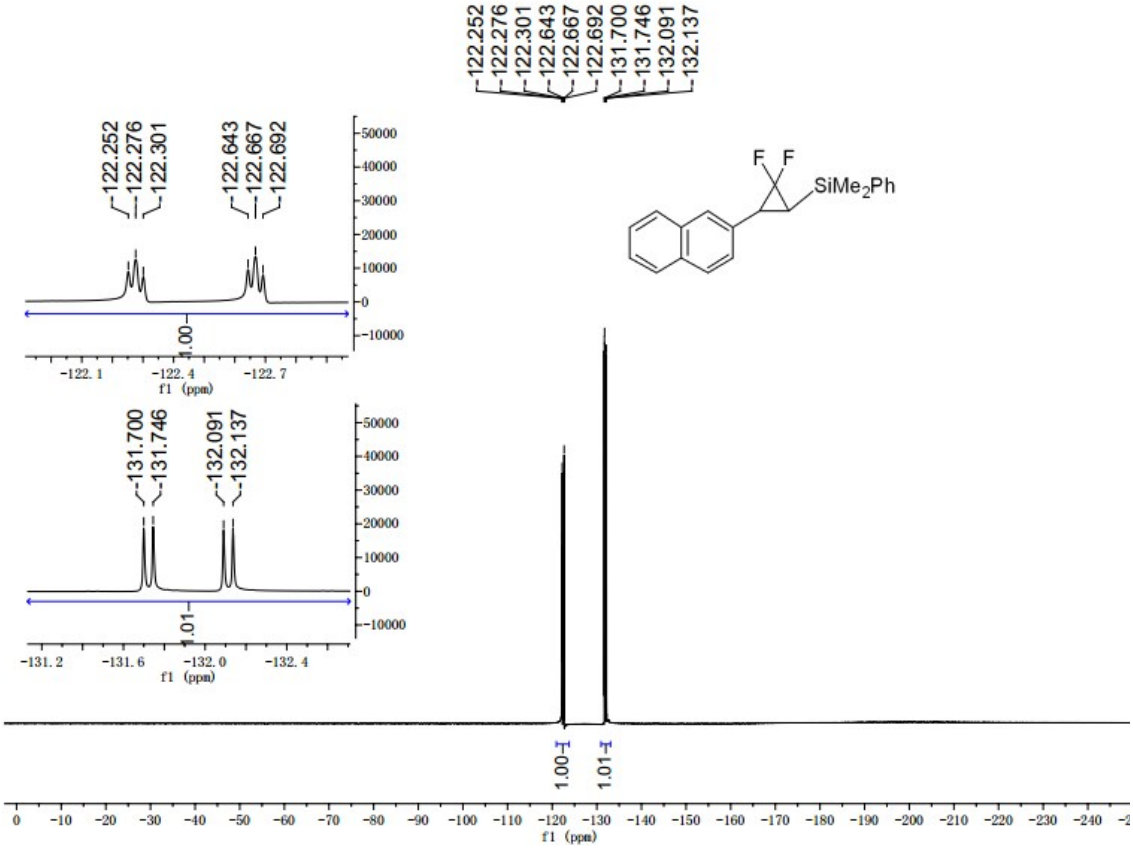
^{1}H NMR spectrum of 3ob



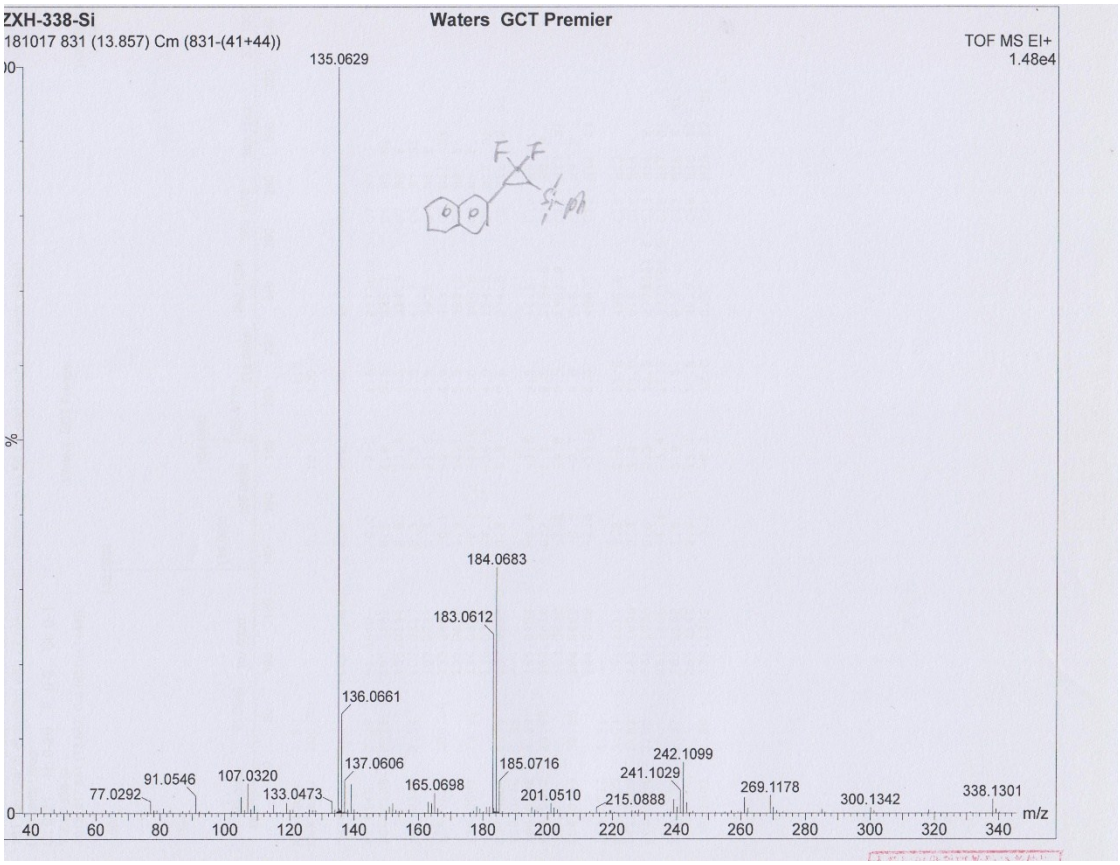
^{13}C NMR spectrum of 3ob



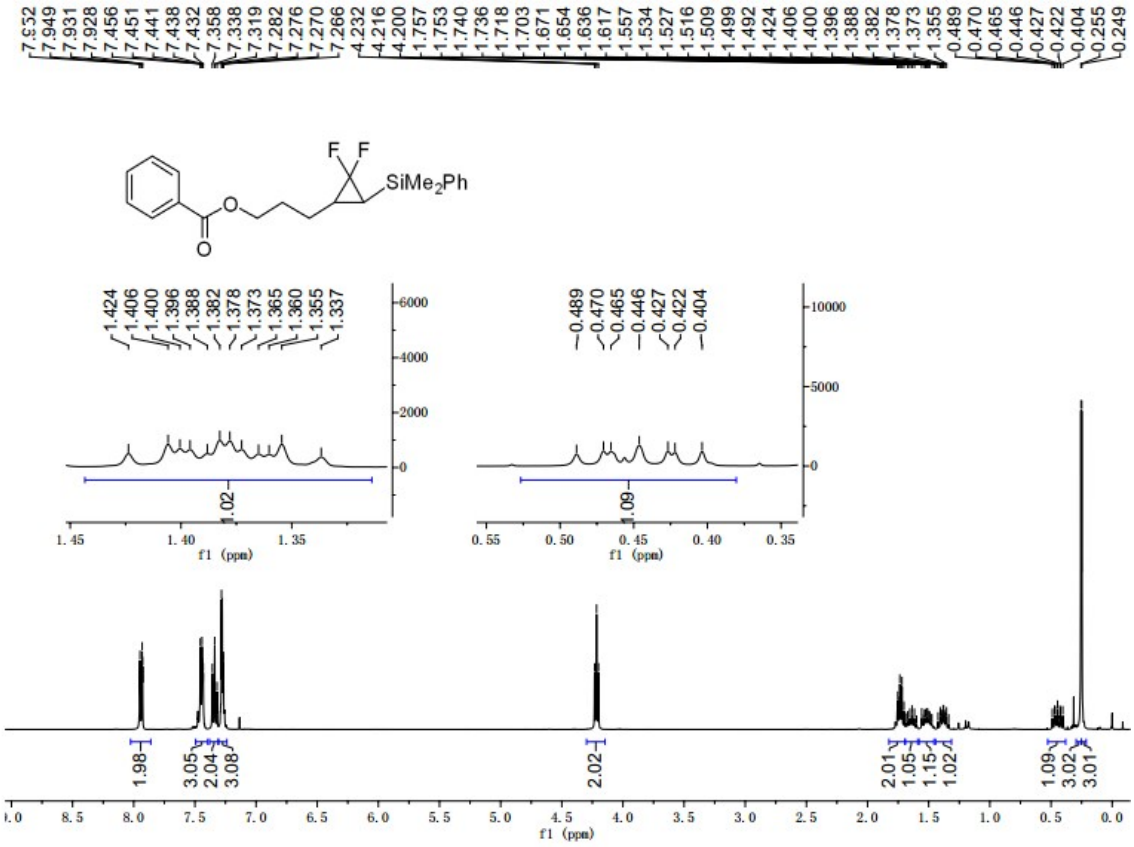
^{19}F NMR spectrum of 3ob



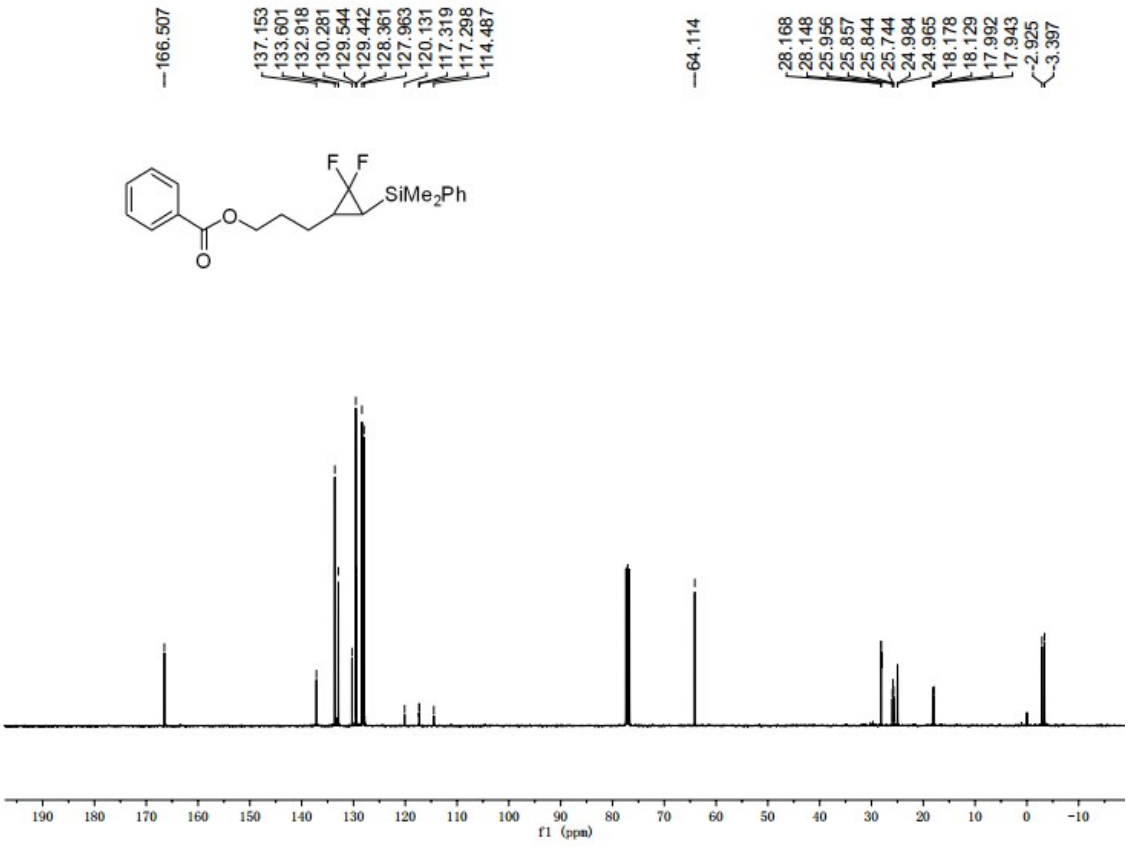
HRMS (EI) of 3ob



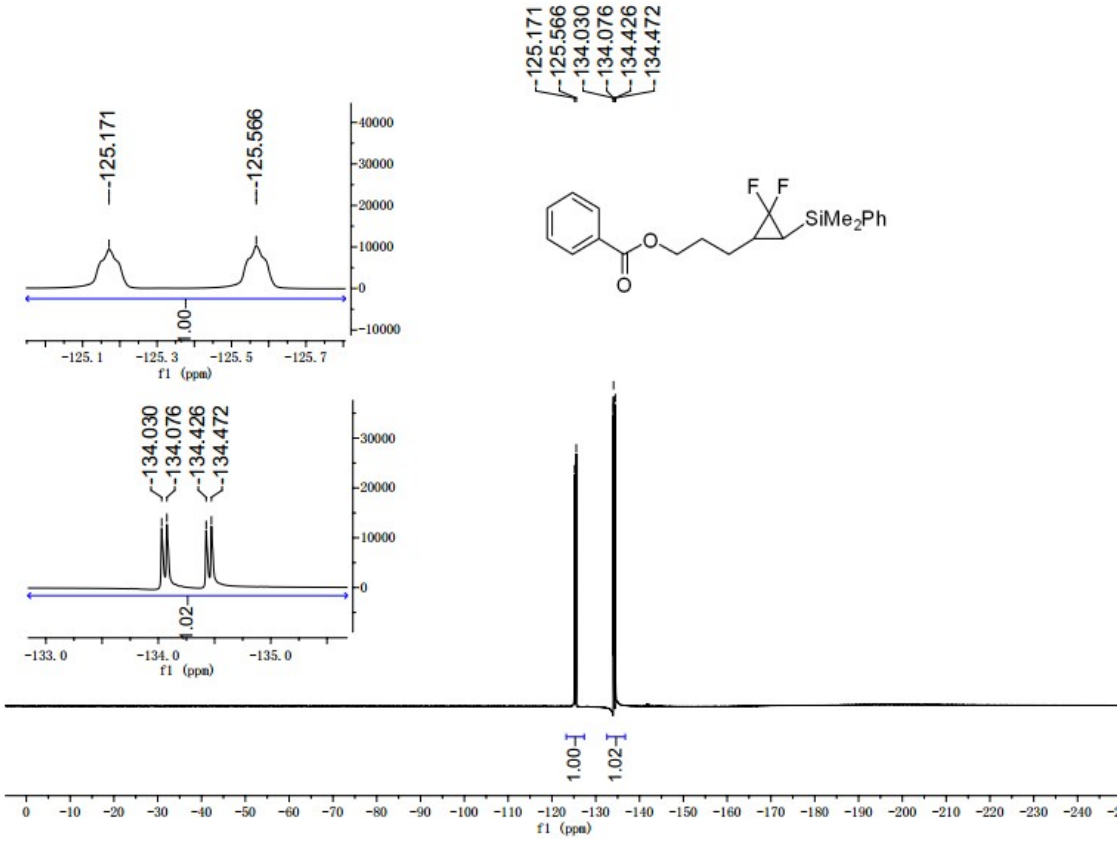
^{1}H NMR spectrum of 3qb



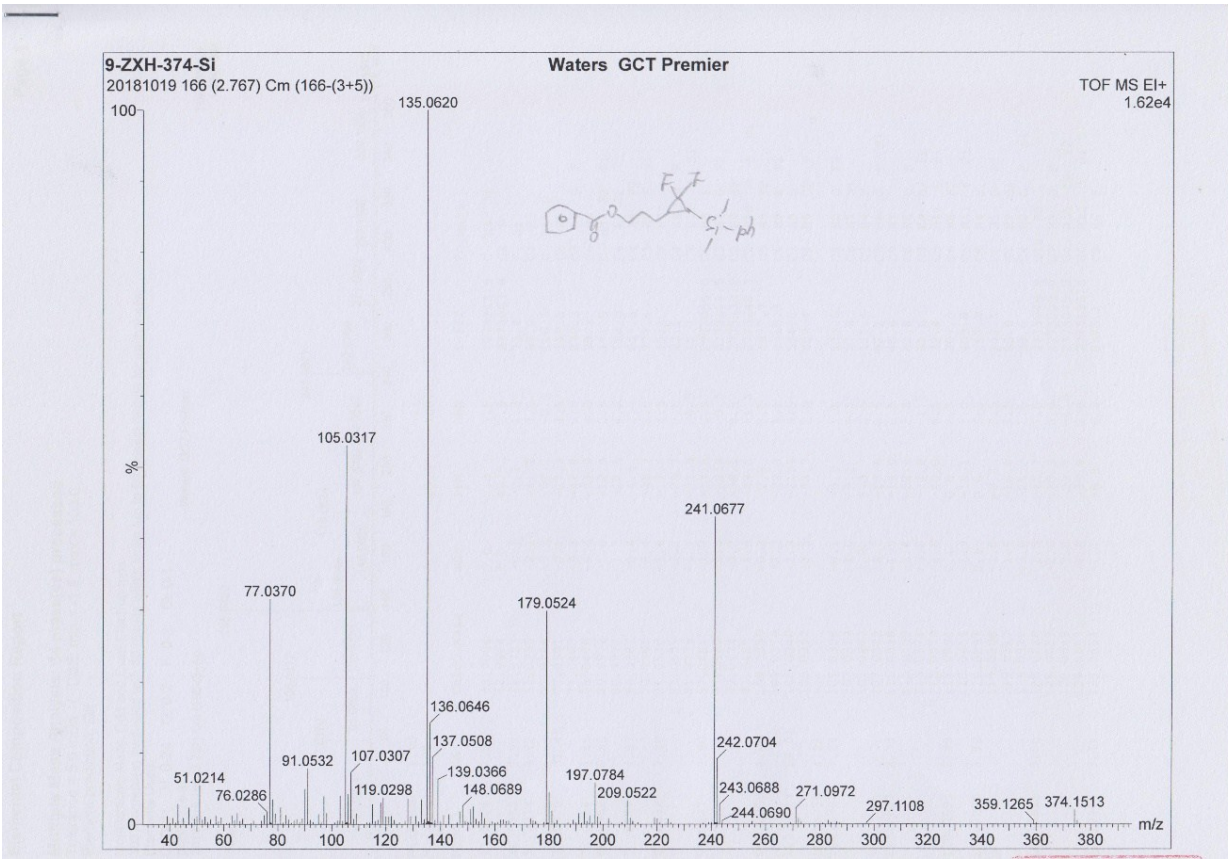
^{13}C NMR spectrum of 3qb



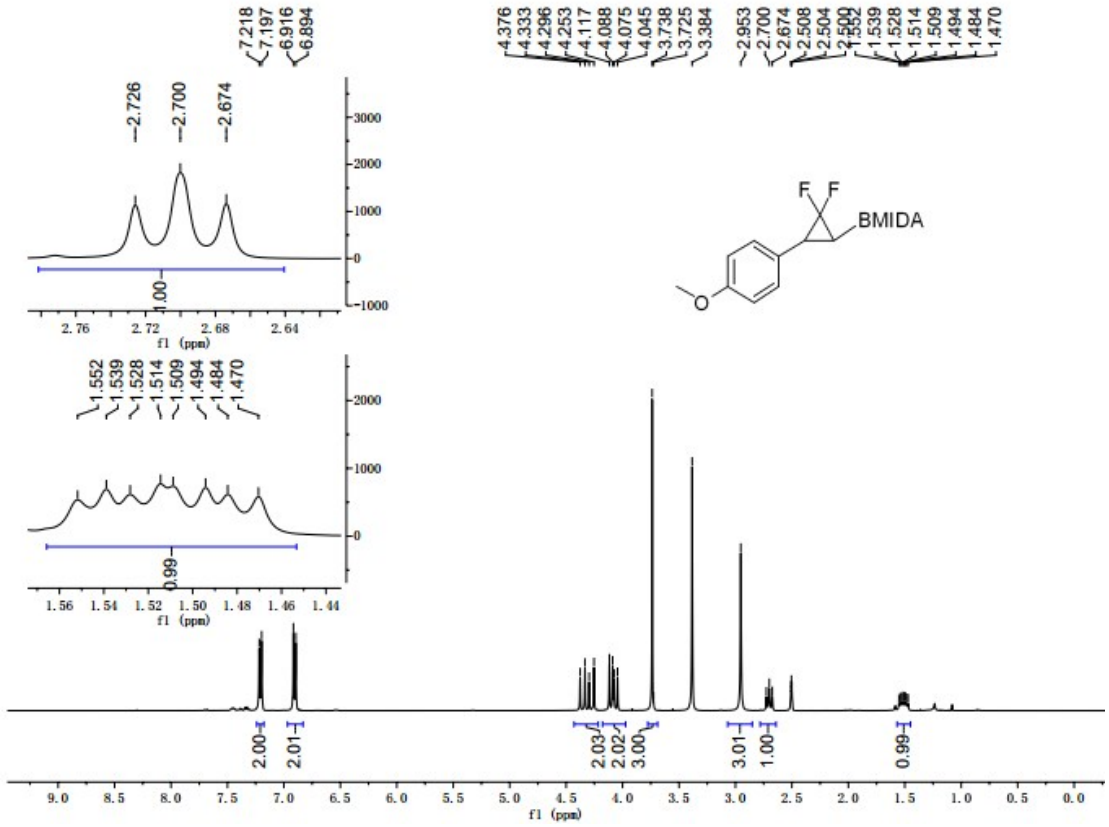
^{19}F NMR spectrum of 3qb



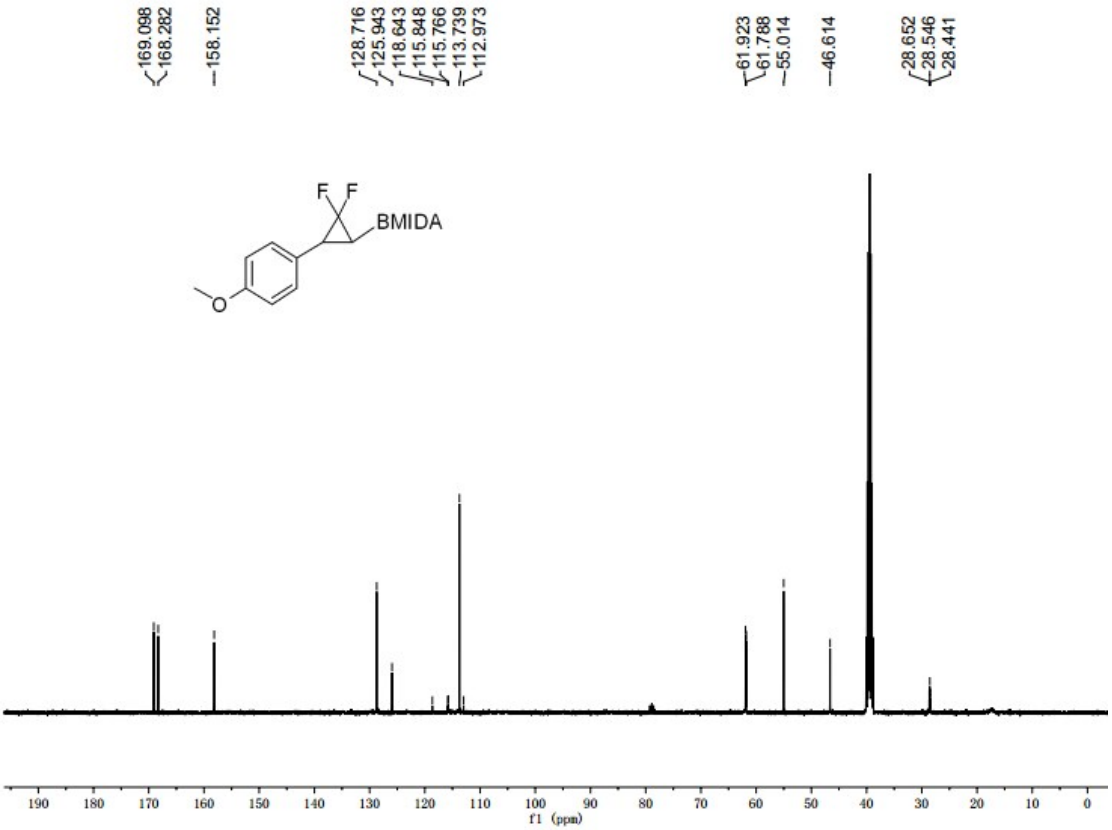
HRMS (EI) of 3qb



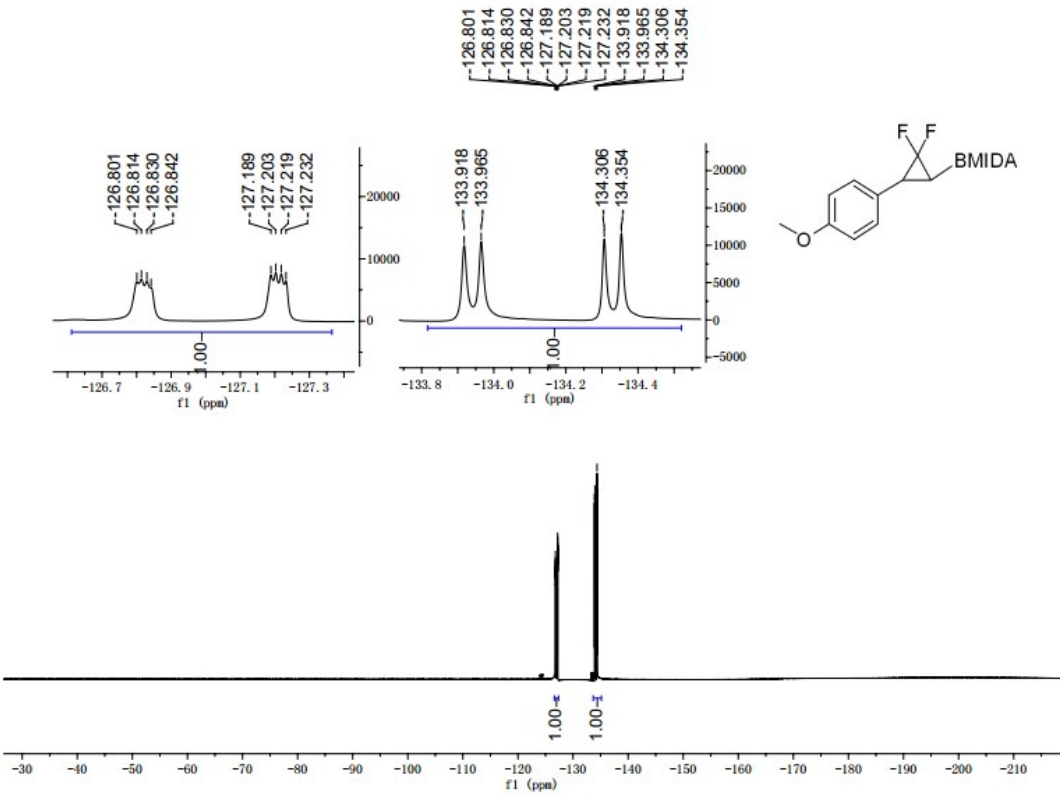
^{1}H NMR spectrum of 4 (DMSO-d_6)



^{13}C NMR spectrum of 4 (DMSO-d_6)



^{19}F NMR spectrum of 4 (DMSO-d_6)



HRMS (ESI) of 3qb