Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Copper-Catalyzed Fluoroalkylation of Alkynes, and Alkynyl & Vinyl Carboxylic Acids with Fluoroalkyl halides

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1. General Considerations

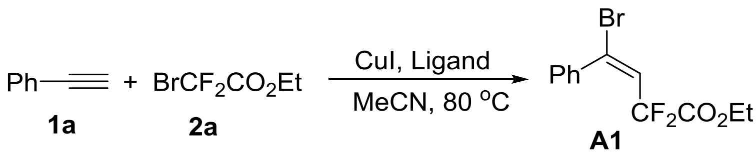
Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used without further purification. ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on a 500 MHz Bruker DRX 500 and tetramethylsilane (TMS) was used as a reference. Chemical shifts were reported in parts per million (ppm), ^{1}H NMR chemical shifts were determined relative to internal $(CH_3)_4Si$ (TMS) at δ 0.0 (sometimes may be two points) or to the signal of a residual protonated solvent: $CDCl_3$ δ 7.26 (due to the quality of $CDCl_3$ the water peak may move to about 1.6 ppm). ^{13}C NMR chemical shifts were determined relative to internal TMS at δ 0.0. Data for ^{1}H, ^{13}C and ^{19}F NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, br = broad). GC-MS were performed on an ISQ Trace 1300 (electrospray ionization: EI). HRMS were recorded on the Waters Micromass GCT Premier (electrospray ionization: EI^+).

2. Screening Results

In a sealed glass vial, phenylacetylene (**1a**, 0.2 mmol), ethyl bromodifluoroacetate (**2a**, 1.5 equiv.), catalyst and ligand were dissolved in dry solvent under argon atmosphere following the condition listed in the table below. The mixture was stirred for 24 h. After cooling to room temperature, the reaction mixture was quenched and trifluoroacetophenone (0.2 mmol, 28 μl) was added as an internal standard. The solution was analyzed by ^{19}F NMR to give the yield.

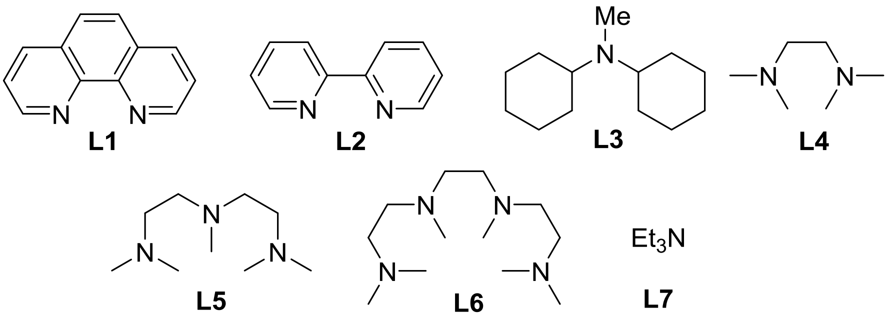
2.1 Screening ligands

Table S1



Entry	Ligand/ (mol%)	Yield
1	L1 (30)	n.r.
2	L2 (30)	47%
3	L3 (30)	trace

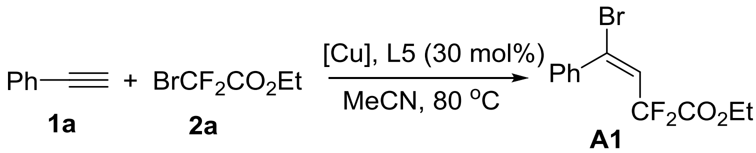
4	L4 (30)	trace
5	L5 (30)	87%
6	L6 (30)	11%
7	L7 (30)	n.r.
8	/	n.r.
9	L5 (10)	30%
10	L5 (15)	42%
11	L5 (20)	59%
12	L5 (40)	84%



Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), CuI (15 mol%), ligand (30 mol%), MeCN (1mL), under argon, 80 °C for 24 h, determined by [19] F NMR using trifluoroacetophenone as the internal standard. n.r. = no reaction.

2.2 Screening copper catalysts

Table S2

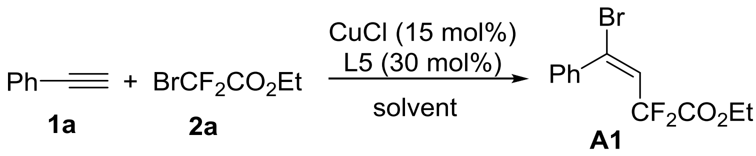


Entry	[Cu] (mol%)	Yield
1	CuCl (15)	94%
2	CuBr (15)	44%
3	CuI (15)	87%
4	$Cu(OTf)_2$ (15)	32%
5	Cu_2O (15)	62%
6	/	n.r.
7	CuCl (5)	39%
8	CuCl (10)	80%
9	CuCl (20)	51%
10	CuCl (25)	69%

Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), L5 (30 mol%), MeCN (1mL), under argon, 80 °C for 24 h, determined by [19] F NMR using trifluoroacetophenone as the internal standard. n.r. = no reaction.

2.3 Screening temperature and solvents

Table S3



Entry	Solvent	Tem. (^{o}C)	Yield
1	MeCN	r.t.	n.r.
2	MeCN	40	21%
3	MeCN	60	41%
4	MeCN	80	94%
5	MeCN	100	45%
6	Toluene	80	11%
7	DMSO	80	12%
8	DMF	80	trace
9	EtOH	80	42%
10	1,4-dioxane	80	trace

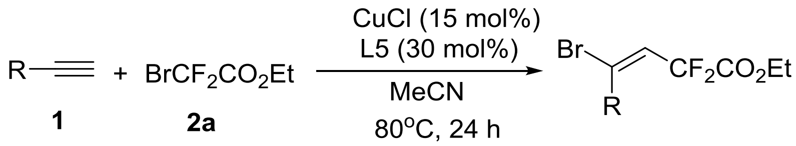
Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), CuCl (15 mol%), L5 (30 mol%), solvent (1mL), under argon for 24 h, determined by ^{19}F NMR using trifluoroacetophenone as the internal standard. n.r. = no reaction.

Initially, we started our investigation by exploring the reaction between phenylacetylene (**1a**) and **2a** (Table S1-S3). After screening, the ligand had a significant influence on the reaction results. bis(2-dimethylaminoethyl) methylamine (L5) was found to be the most suitable choice in the presence of 15 mol% CuI, giving **A1** in 87% yield with > 90% *E*-selectivity (Table S1, entries 1-7). Further study was focused on various copper catalysts and CuCl seemed best (Table S2, entries 1-5). It was worth to mention that no product was detected when the reaction performed in the absence of the catalyst or the ligand, as well as argon. Other solvents such as toluene, DMSO, DMF, EtOH, 1,4-dioxane were also tested (Table S3), with no elevated yield. Allow for the amount of ligand and copper catalyst, as well as temperature, the optimal reaction condition was carried out with CuCl (15 mol%), L5 (30 mol%), MeCN as solvent refluxed at 80 ^{o}C under agron atmosphere for 24 h (Table S3, entry 4).

3. General Procedure for Experiments

Method I:

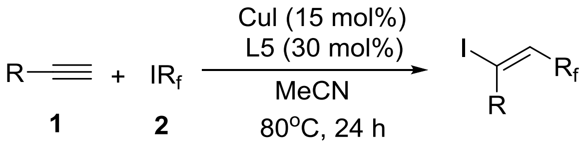
CuCl-catalyzed ATRA reaction:



A reaction tube was charged with CuCl (3.0 mg, 0.03 mmol), L5 (10.4 mg, 0.06 mmol) at room temperature, then phenylacetylene (**1a**) (20.4 mg, 0.2 mmol), ethyl bromodifluoroacetate (60.9 mg, 0.3 mmol) and MeCN (1 mL) were added. The resulting mixture was stirred at 80 ℃ under argon atmosphere for 24 h. After cooling to room temperature, the reaction mixture was quenched and purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc) to afford the desired product **A1** (54.1 mg, 89%).

Method II:

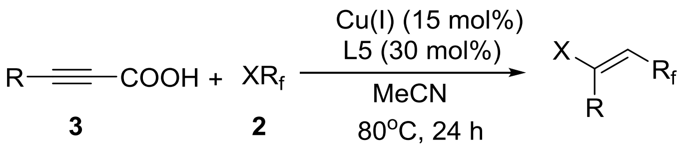
CuI-catalyzed ATRA reaction:



A reaction tube was charged with CuI (5.7 mg, 0.03 mmol), L5 (10.4 mg, 0.06 mmol) at room temperature, then phenylacetylene (**1a**) (20.4 mg, 0.2 mmol), ethyl iododifluoroacetate (**2b**) (75.0 mg, 0.3 mmol) and MeCN (1 mL) were added. The resulting mixture was stirred at 80 ℃ under argon atmosphere for 24 h. After cooling to room temperature, the reaction mixture was quenched and purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc) to afford the desired product **A17** (59.8 mg, 85%).

Method III:

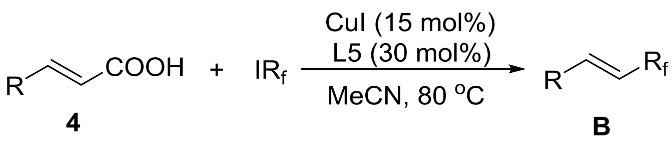
Decarboxylative ATRA of fluoroalkyl halides to alkynyl carboxylic acids:



A reaction tube was charged with CuCl (3.0 mg, 0.03 mmol), L5 (10.4 mg, 0.06 mmol) at room temperature, then phenylpropiolic acid (**3a**) (29.2 mg, 0.2 mmol), ethyl bromodifluoroacetate (**2a**) (60.9 mg, 0.3 mmol) and MeCN (1 mL) were added. The resulting mixture was stirred at 80 ℃ under argon atmosphere for 24 h. After cooling to room temperature, the reaction mixture was quenched and purified by flash silica gel column chromatography (eluent: petroleum ether/EtOAc) to afford the desired product **A1** (47.4 mg, 78%).

Method IV:

Decarboxylative perfluoroalkylation of *α*, *β*-unsaturated carboxylic acids:

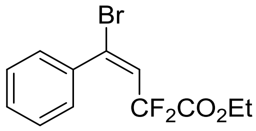


A reaction tube was charged with CuI (5.7 mg, 0.03 mmol), L5 (10.4 mg, 0.06 mmol) at room temperature, then 4-phenylcinnamic acid (**4a**) (44.8 mg, 0.2 mmol), pentafluoroethyl iodide (98.4 mg, 0.4 mmol) and MeCN (1 mL) were added. The resulting mixture was stirred at 80 ℃ under argon atmosphere for 24 h. After cooling to room temperature, the reaction mixture was quenched and purified by flash silica gel column chromatography (eluent: petroleum ether) to afford the desired product **B1** (23.2 mg, 39%).

Hydrolysis-decarboxylative reaction of **A** componds:

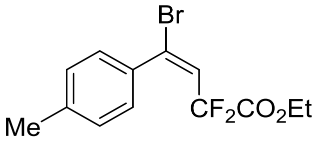
To a methanol (5mL) solution of **A** (0.5 mmol) was added 1 M K_2CO_3 (5 mL) at room temperature. After the reaction was complete (as judged by TLC analysis), the pH value was adjusted to 2~4. Then the mixture was poured into a separatory funnel containing 10 mL H_2O and 10 mL EtOAc. The layers were separated and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried with $MgSO_4$ and concentrated under reduced pressure after filtration. The crude product was followed by decarboxylative step, added 10 equiv KF in 2ml anhydrous DMF, refluxed at 170 ^{o}C under agron atmosphere for 6-10 h, after cooled to the room temperature and purified by flash chromatography on silica gel (eluent: petroleum ether) to afford the desired product **C**.

4. Analytical data of compounds



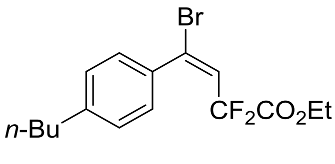
Chemical Formula: $C_{12}H_{11}BrF_2O_2$
Exact Mass: 303.99

Compound **A1**[1]: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A1** (54.1 mg, 89%), yellow liquid (*E*/*Z* = 94:6, the ratio detected by ^{19}F NMR). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (s, 5H), 6.50 (t, *J* = 11.2 Hz, 1H), 3.99 (q, *J* = 7.2 Hz, 2H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.53 (t, *J* = 32.5 Hz), 137.21, 133.59 (t, *J* = 10.2 Hz), 129.98, 128.51 (t, *J* = 2.2 Hz), 128.14, 125.07 (t, *J* = 28.6 Hz), 111.08, 99.99, 63.17, 13.71; ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.72. GC-MS (EI) Calcd. for $C_{12}H_{11}BrF_2O_2$ 303.99, found 304.07.
Z product: ^{19}F NMR (470 MHz, $CDCl_3$) δ -97.61.



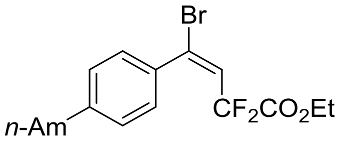
Chemical Formula: $C_{13}H_{13}BrF_2O_2$
Exact Mass: 318.01

Compound **A2**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A2** (51.5 mg, 81%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21-7.16 (m, 2H), 7.08 (d, *J* = 7.7 Hz, 2H), 6.39 (t, *J* = 11.1 Hz, 1H), 3.92 (q, *J* = 7.2 Hz, 2H), 2.28 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.70 (t, *J* = 33.1 Hz), 140.37, 134.49, 134.09, 128.89, 128.60, 124.78 (t, *J* = 28.4 Hz), 111.25 (t, *J* = 248.5 Hz), 63.23, 21.47, 13.78; ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.59. GC-MS (EI) Calcd. for $C_{13}H_{13}BrF_2O_2$ 318.01, found 318.04.



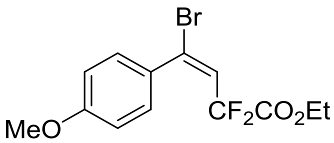
Chemical Formula: $C_{16}H_{19}BrF_2O_2$
Exact Mass: 360.05

Compound **A3**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A3** (56.9 mg, 79%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.46 (t, *J* = 11.0 Hz, 1H), 3.95 (q, *J* = 7.1 Hz, 2H), 2.68-2.54 (m, 2H), 1.65-1.52 (m, 3H), 1.43-1.30 (m, 2H), 1.17 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.65 (t, *J* = 33.4 Hz), 145.37, 134.56, 134.14, 128.64, 128.23, 124.75 (t, *J* = 28.8 Hz), 111.26 (t, *J* = 248.3 Hz), 63.17, 35.56, 33.41, 22.43, 13.89 (d, *J* = 26.6 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.19. GC-MS (EI) Calcd. for $C_{16}H_{19}BrF_2O_2$ 360.05, HRMS (EI^+) found 360.0542.



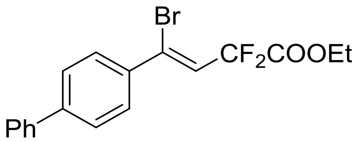
Chemical Formula: $C_{17}H_{21}BrF_2O_2$
Exact Mass: 374.07

Compound **A4**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A4** (56.1 mg, 75%), brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.46 (t, *J* = 11.0 Hz, 1H), 3.95 (q, *J* = 7.2 Hz, 2H), 2.64-2.56 (m, 2H), 1.65-1.56 (m, 2H), 1.31 (qq, *J* = 8.7, 5.5, 3.8 Hz, 4H), 1.17 (t, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.68 (t, *J* = 33.2 Hz), 145.43, 134.56, 134.13 (d, *J* = 9.8 Hz), 128.66, 128.23, 124.77 (t, *J* = 28.8 Hz), 111.27 (t, *J* = 248.7 Hz), 63.20, 35.85, 31.57, 30.95, 22.61, 14.10, 13.78; ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.12. GC-MS (EI) Calcd. for $C_{17}H_{21}BrF_2O_2$ 374.07, HRMS (EI^+) found 374.0698.



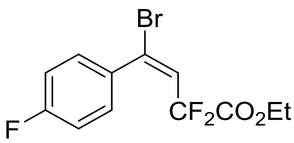
Chemical Formula: $C_{13}H_{13}BrF_2O_3$
Exact Mass: 334.00

Compound **A5**[1]: purified by column chromatography on silica gel (petroleum ether/EtOAc = 12:1) to afford the **A5** (45.4 mg, 68%), brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.44 (t, *J* = 11.0 Hz, 1H), 3.99 (q, *J* = 7.2 Hz, 2H), 3.82 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.59 (t, *J* = 33.4 Hz), 159.79 , 132.94 (t, *J* = 10.1 Hz), 129.30, 128.37, 123.30 (t, *J* = 28.7 Hz), 112.43, 109.19 (d, *J* = 247.8 Hz), 62.13, 54.33, 12.69; ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.21. GC-MS (EI) Calcd. for $C_{13}H_{13}BrF_2O_3$ 334.00, found 334.02.



Chemical Formula: $C_{18}H_{15}BrF_2O_2$
Exact Mass: 380.02

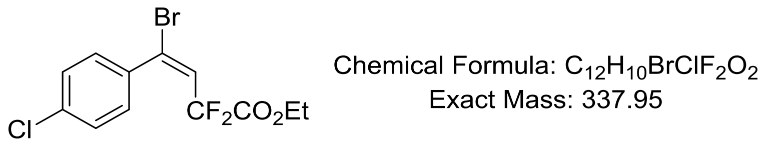
Compound **A6**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 40:1) to afford the **A6** (67.6 mg, 89%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64-7.57 (m, 5H), 7.50-7.43 (m, 4H), 7.43-7.35 (m, 1H), 6.54 (t, *J* = 11.2 Hz, 1H), 4.02 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.71 (t, *J* = 33.2 Hz), 142.94, 140.03, 136.12, 133.58, 129.13 (d, *J* = 18.3 Hz), 128.10, 127.25, 126.89, 125.15 (t, *J* = 28.4 Hz), 111.26 (t, *J* = 248.8 Hz), 63.39, 13.86; ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.60. GC-MS (EI) Calcd. for $C_{18}H_{15}BrF_2O_2$ 380.02, HRMS (EI^+) found 380.0220.



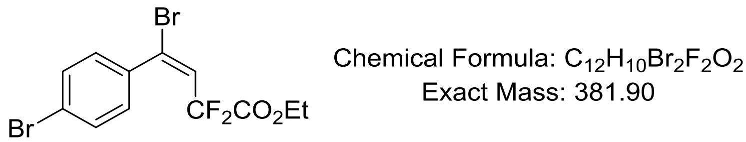
Chemical Formula: $C_{12}H_{10}BrF_3O_2$
Exact Mass: 321.98

Compound **A7**[1]: purified by column chromatography on silica gel (petroleum ether/EtOAc = 40:1) to afford the **A7** (56.0 mg, 87%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.32 (m, 2H), 7.05 (dd, *J* = 9.6, 7.7 Hz, 2H), 6.49 (t, *J* = 11.3 Hz, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.31, 161.31 (t, *J* = 28.7 Hz), 132.33 (d, *J* = 14.5 Hz), 131.95, 131.46

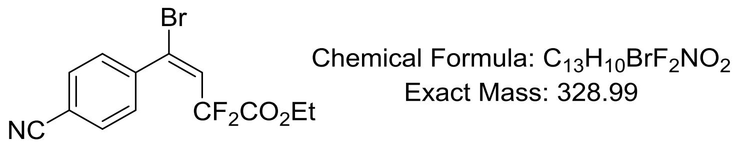
(t, J = 8.8 Hz), 129.64 (d, J = 9.6 Hz), 124.28 (t, J = 28.2 Hz), 114.27 (d, J = 22.2 Hz), 109.96 (t, J = 249.6 Hz), 62.32, 12.72; ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.36, -109.84. GC-MS (EI) Calcd. for $C_{12}H_{10}BrF_3O_2$ 321.98, found 322.02.



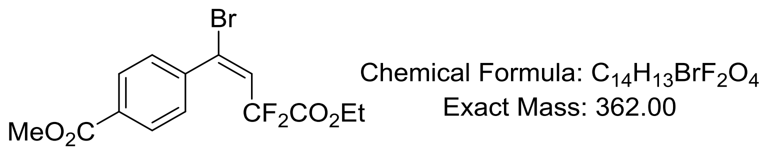
Compound **A8**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A8** (60.2 mg, 89%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.21 (m, 4H), 6.42 (t, J = 11.5 Hz, 1H), 4.02 (q, J = 7.2 Hz, 2H), 1.17 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.48 (t, J = 33.3 Hz), 136.18, 135.81, 132.29, 129.95, 128.53, 125.56 (t, J = 27.9 Hz), 111.06 (t, J = 250.4 Hz), 63.47, 13.85; ^{19}F NMR (470 MHz, $CDCl_3$) δ -91.61. GC-MS (EI) Calcd. for $C_{12}H_{10}BrClF_2O_2$ 337.95, HRMS (EI$^+$) found 337.9523.



Compound **A9**[1]: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A9** (64.2 mg, 84%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 6.49 (t, J = 11.5 Hz, 1H), 4.09 (d, J = 7.1 Hz, 2H), 1.24 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.63 (t, J = 34.0 Hz), 136.29, 132.31, 131.51, 130.14, 125.55 (t, J = 28.0 Hz), 124.47, 111.06 (t, J = 249.5 Hz), 63.50, 13.85; ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.65. GC-MS (EI) Calcd. for $C_{12}H_{10}Br_2F_2O_2$ 381.90, found 381.96.

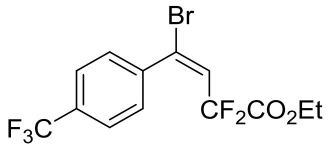


Compound **A10**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A10** (57.2 mg, 87%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69-7.64 (m, 2H), 7.50-7.45 (m, 2H), 6.55 (t, J = 12.0 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.48 (t, J = 33.3 Hz), 141.85, 132.04, 130.84, 129.21, 126.22 (t, J = 26.9 Hz), 118.07, 113.71, 110.88 (t, J = 251.9 Hz), 63.70, 13.93; ^{19}F NMR (470 MHz, $CDCl_3$) δ -95.90. GC-MS (EI) Calcd. for $C_{13}H_{10}BrF_2NO_2$ 328.99, found 328.98.



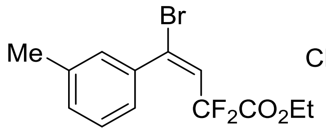
Compound **A11**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 15:1) to afford the **A11** (64.2 mg, 73%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07-7.99 (m, 2H), 7.43 (dd, J = 8.7, 2.1 Hz, 2H), 6.54 (t, J = 11.6 Hz, 1H), 4.08 (q, J = 7.2 Hz, 2H), 3.93 (s, 3H), 1.24 (t, J =

7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.28, 161.33, 141.64, 133.89-131.90 (m), 131.39, 129.69, 129.47, 128.58, 125.80 (t, J = 27.9 Hz), 63.49, 52.47, 13.86; ^{19}F NMR (470 MHz, $CDCl_3$) δ -95.01. GC-MS (EI) Calcd. for $C_{14}H_{13}BrF_2O_4$ 362.00, found 362.01.



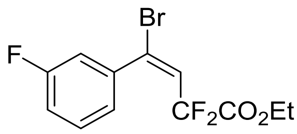
Chemical Formula: $C_{13}H_{10}BrF_5O_2$
Exact Mass: 371.98

Compound **A12**[1]: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A12** (31.2 mg, 42%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 6.55 (t, J = 11.7 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 1.25 (d, J = 7.2 Hz, 3H); ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.97 (d, J = 20.6 Hz), -95.26. GC-MS (EI) Calcd. for $C_{13}H_{10}BrF_5O_2$ 371.98, [M-F] found 353.03.



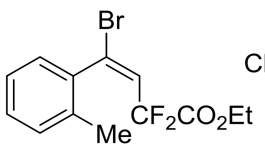
Chemical Formula: $C_{13}H_{13}BrF_2O_2$
Exact Mass: 318.01

Compound **A13**[1]: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A13** (45.8 mg, 72%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.21 (m, 1H), 7.16 (dt, J = 6.1, 3.8 Hz, 3H), 6.47 (t, J = 11.0 Hz, 1H), 3.96 (q, J = 7.2 Hz, 2H), 2.34 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.68 (t, J = 32.8 Hz), 138.04, 137.34 (d, J = 38.4 Hz), 134.12 (d, J = 41.6 Hz), 130.80 (d, J = 15.1 Hz), 129.12, 128.10 (d, J = 13.3 Hz), 125.63 (d, J = 23.2 Hz), 124.97 (t, J = 28.8 Hz), 111.22 (t, J = 248.9 Hz), 63.25, 21.37, 13.76; ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.48. GC-MS (EI) Calcd. for $C_{13}H_{13}BrF_2O_2$ 318.01, found 318.07.



Chemical Formula: $C_{12}H_{10}BrF_3O_2$
Exact Mass: 321.98

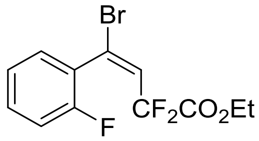
Compound **A14**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 40:1) to afford the **A14** (43.8 mg, 68%), colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (td, J = 7.7, 5.6 Hz, 1H), 7.23-7.17 (m, 1H), 7.13 (t, J = 8.5 Hz, 2H), 6.56 (t, J = 11.5 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.56 (t, J = 35.4 Hz), 159.74, 141.58, 132.57 (t, J = 27.9 Hz), 128.72 (d, J = 8.5 Hz), 122.46, 115.38 (d, J = 21.1 Hz), 113.91 (d, J = 23.3 Hz), 110.79 (d, J = 251.1 Hz), 105.23, 62.30, 12.71; ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.70, -112.15. GC-MS (EI) Calcd. for $C_{12}H_{10}BrF_3O_2$ 321.98, found 322.03.



Chemical Formula: $C_{13}H_{13}BrF_2O_2$
Exact Mass: 318.01

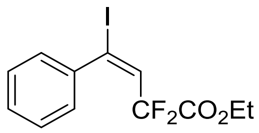
Compound **A15**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 30:1) to afford the **A15** (35.6 mg, 56%), colorless liquid (E/Z = 92:8, the ratio detected by ^{19}F NMR). ^{1}H NMR

(500 MHz, $CDCl_3$) δ 7.27-7.23 (m, 1H), 7.21-7.11 (m, 3H), 6.53 (td, *J* = 10.9, 2.5 Hz, 1H), 3.97 (qd, *J* = 7.2, 2.3 Hz, 2H), 2.33 (d, *J* = 2.5 Hz, 3H), 1.21 (td, *J* = 7.2, 2.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.46 (t, *J* = 33.4 Hz), 135.38, 134.80, 131.93, 129.23, 128.90 (d, *J* = 10.8 Hz), 127.35, 125.19 (t, *J* = 28.5 Hz), 124.52, 109.93 (t, *J* = 249.8 Hz), 62.12, 18.26, 12.67; ^{19}F NMR (470 MHz, $CDCl_3$) δ -95.40 (d, *J* = 272.6 Hz), -97.44 (d, *J* = 272.6 Hz). GC-MS (EI) Calcd. for $C_{13}H_{13}BrF_2O_2$ 318.01, found 318.06.
Z product: ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.87 (d, *J* = 282.0 Hz), -97.12 (d, *J* = 282.0 Hz).



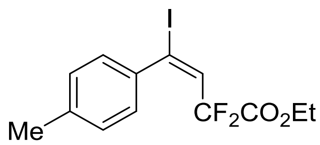
Chemical Formula: $C_{12}H_{10}BrF_3O_2$
Exact Mass: 321.98

Compound **A16**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 40:1) to afford the **A16** (33.5 mg, 52%), yellow liquid (*E*/*Z* = 96:4, the ratio detected by ^{19}F NMR). ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (tdd, *J* = 7.6, 6.3, 1.8 Hz, 1H), 7.28 (td, *J* = 7.5, 1.8 Hz, 1H), 7.14 (td, *J* = 7.6, 1.1 Hz, 1H), 7.07 (ddd, *J* = 9.6, 8.3, 1.1 Hz, 1H), 6.61 (t, *J* = 11.5 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.29 (t, *J* = 33.4 Hz), 157.35 (d, *J* = 251.2 Hz), 130.86 (d, *J* = 8.3 Hz), 129.24, 126.71 (t, *J* = 27.7 Hz), 124.73 (d, *J* = 9.5 Hz), 124.18 (d, *J* = 15.4 Hz), 122.90, 114.73 (d, *J* = 20.9 Hz), 109.84 (t, *J* = 250.5 Hz), 62.31, 12.68; ^{19}F NMR (470 MHz, $CDCl_3$) δ -98.50, -112.60. GC-MS (EI) Calcd. for $C_{12}H_{10}BrF_3O_2$ 321.98, found 322.01.
Z product: ^{19}F NMR (470 MHz, $CDCl_3$) δ -99.02, -113.77.



Chemical Formula: $C_{12}H_{11}F_2IO_2$
Exact Mass: 351.98

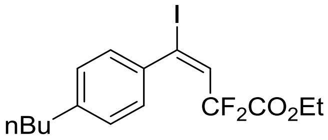
Compound **A17**[2]: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A17** (59.8 mg, 85%), colorless liquid (*E*/*Z* = 94:6, the ratio detected by ^{19}F NMR). ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 2.6 Hz, 5H), 6.72 (t, *J* = 11.0 Hz, 1H), 3.97 (q, *J* = 7.1 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.67 (t, *J* = 33.4 Hz), 140.82, 133.15 (t, *J* = 28.3 Hz), 129.56, 128.17, 127.94, 110.99 (t, *J* = 252.0 Hz), 108.83, 63.26, 13.82; ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.79. GC-MS (EI) Calcd. for $C_{12}H_{11}F_2IO_2$ 351.98, found 352.03.
Z product: ^{19}F NMR (470 MHz, $CDCl_3$) δ -98.04.



Chemical Formula: $C_{13}H_{13}F_2IO_2$
Exact Mass: 365.99

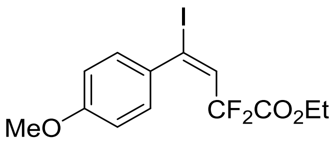
Compound **A18**[2]: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A18** (66.6 mg, 91%), yellow liquid (*E*/*Z* = 94:6, the ratio detected by ^{19}F NMR). ^1H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.70 (t, *J* = 10.9 Hz, 1H), 3.98 (d, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.71 (t, *J* = 33.1 Hz), 139.80, 138.00, 132.84 (t, *J* = 28.4 Hz), 128.83, 127.97, 111.02 (t, *J* = 250.7 Hz), 109.40,

63.24, 21.49, 13.82; ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.67. GC-MS (EI) Calcd. for $C_{13}H_{13}F_2IO_2$ 365.99, HRMS (EI^+) found 365.9931.
Z product: ^{19}F NMR (470 MHz, $CDCl_3$) δ -97.78.



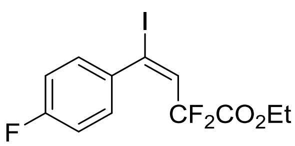
Chemical Formula: $C_{16}H_{19}F_2IO_2$
Exact Mass: 408.04

Compound **A19**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A19** (71.8 mg, 88%), yellow liquid (*E*/*Z* = 97:3, the ratio detected by ^{19}F NMR). ^1H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 6.71 (t, *J* = 10.8 Hz, 1H), 3.95 (q, *J* = 7.1 Hz, 2H), 2.64-2.56 (m, 2H), 1.65-1.55 (m, 2H), 1.41-1.32 (m, 2H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.67 (t, *J* = 33.2 Hz), 144.79, 138.06, 132.82 (t, *J* = 28.6 Hz), 128.15, 128.04,111.00 (t, *J* = 250.7 Hz), 109.53, 63.16, 35.55, 33.42, 22.46, 14.04, 13.80; ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.25. GC-MS (EI) Calcd. for $C_{16}H_{19}F_2IO_2$ 408.04, found 408.17.
Z product: ^{19}F NMR (470 MHz, $CDCl_3$) δ -97.78.



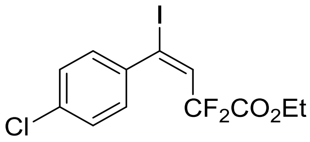
Chemical Formula: $C_{13}H_{13}F_2IO_3$
Exact Mass: 381.99

Compound **A20**[2]: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A20** (56.5 mg, 74%), brown liquid (*E*/*Z* = 93:7, the ratio detected by ^{19}F NMR). ^1H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.4 Hz, 2H), 6.77-6.71 (m, 2H), 6.60 (t, *J* = 10.8 Hz, 1H), 3.92 (q, *J* = 7.2 Hz, 2H), 3.74 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.64 (t, *J* = 32.8 Hz), 159.29, 131.98, 131.49 (t, *J* = 28.6 Hz), 128.67, 112.33, 109.89 (t, *J* = 249.5 Hz), 108.30, 62.08, 54.32, 12.69; ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.32. GC-MS (EI) Calcd. for $C_{13}H_{13}F_2IO_3$ 381.99, found 382.03.
Z product: ^{19}F NMR (470 MHz, $CDCl_3$) δ -97.59.



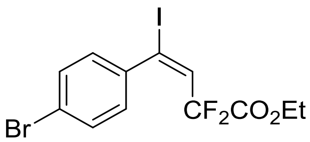
Chemical Formula: $C_{12}H_{10}F_3IO_2$
Exact Mass: 369.97

Compound **A21**[2]: purified by column chromatography on silica gel (petroleum ether/EtOAc = 40:1) to afford the **A21** (63.6 mg, 86%), colorless liquid. ^1H NMR (500 MHz, $CDCl_3$) δ 7.34-7.27 (m, 2H), 7.00 (t, *J* = 8.6 Hz, 2H), 6.71 (t, *J* = 11.2 Hz, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.00 (d, *J* = 126 Hz), 162.64 (t, *J* = 32.8 Hz), 136.97 , 133.52 (t, *J* = 27.8 Hz), 130.04 (d, *J* = 8.7 Hz), 115.28 (d, *J* = 21.9 Hz), 111.96 (d, *J* = 250.9 Hz), 107.44, 63.39, 13.85; ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.34, -110.60. GC-MS (EI) Calcd. for $C_{12}H_{10}F_3IO_2$ 369.97, found 370.01.



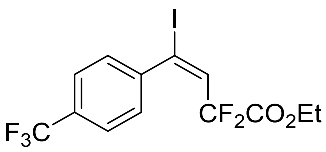
Chemical Formula: $C_{12}H_{10}ClF_2IO_2$
Exact Mass: 385.94

Compound **A22**[2]: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A22** (65.6 mg, 85%), yellow liquid (*E*/*Z* = 96:4, the ratio detected by ^{19}F NMR). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 6.72 (t, *J* = 11.3 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.64 (t, *J* = 32.8 Hz), 139.36, 135.51, 133.55 (t, *J* = 27.9 Hz), 129.24, 128.42, 110.99 (t, *J* = 255.8 Hz), 107.06, 63.45, 13.86; ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.62. GC-MS (EI) Calcd. for $C_{12}H_{10}ClF_2IO_2$ 385.94, found 385.96.
Z product: ^{19}F NMR (470 MHz, $CDCl_3$) δ -98.25.



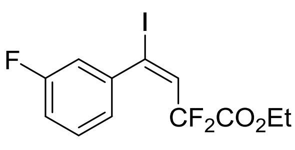
Chemical Formula: $C_{12}H_{10}BrF_2IO_2$
Exact Mass: 429.89

Compound **A23**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A23** (74.4 mg, 88%), yellow liquid (*E*/*Z* = 95:5, the ratio detected by ^{19}F NMR). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.43 (m, 2H), 7.21-7.14 (m, 2H), 6.72 (t, *J* = 11.3 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.62 (t, *J* = 32.8 Hz), 139.84, 133.53 (t, *J* = 27.7 Hz), 131.40, 129.44, 123.77, 110.98 (t, *J* = 251.3 Hz), 107.06, 63.47, 13.88; ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.72. GC-MS (EI) Calcd. for $C_{12}H_{10}BrF_2IO_2$ 429.89, HRMS (EI^+) found 429.8881.
Z product: ^{19}F NMR (470 MHz, $CDCl_3$) δ -97.61.



Chemical Formula: $C_{13}H_{10}F_5IO_2$
Exact Mass: 419.96

Compound **A24**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1) to afford the **A24** (48.7, 58%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 6.76 (t, *J* = 11.5 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.59 (t, *J* = 33.5 Hz), 144.48, 133.91 (t, *J* = 26.8 Hz), 131.18, 128.16, 125.21, 109.99 (t, *J* = 251.7 Hz), 106.08, 63.53, 13.85.^{19}F NMR (470 MHz, $CDCl_3$) δ -62.92, -95.27. GC-MS (EI) Calcd. for $C_{13}H_{10}F_3IO_2$ 419.96, HRMS (EI^+) [M-F] found 400.9668.

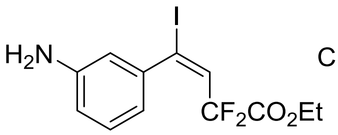


Chemical Formula: $C_{12}H_{10}F_3IO_2$
Exact Mass: 369.97

Compound **A25**[2]: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A25** (54.8 mg, 74%), colorless liquid (*E*/*Z* = 94:6, the ratio detected by ^{19}F NMR). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (ddd, *J* = 13.4, 10.2, 5.7 Hz, 1H), 7.11-7.06 (m, 1H), 7.02 (ddd, *J* = 9.0, 5.2, 2.3 Hz, 2H), 6.73 (t, *J* = 11.2 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126

MHz, $CDCl_3$) δ 161.56 (t, *J* = 35.4 Hz), 159.74, 141.58, 132.57 (t, *J* = 27.9 Hz), 128.72 (d, *J* = 8.5 Hz), 122.46, 115.38 (d, *J* = 21.1 Hz), 113.91 (d, *J* = 23.3 Hz), 110.79 (d, *J* = 251.1 Hz), 105.23, 62.30, 12.71. ^{19}F NMR (470 MHz, $CDCl_3$) δ -94.76, -112.16. GC-MS (EI) Calcd. for $C_{12}H_{10}F_3IO_2$ 369.97, found 369.78.

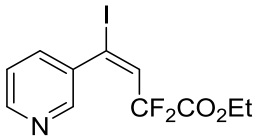
Z product: ^{19}F NMR (470 MHz, $CDCl_3$) δ -98.36, -112.20.



Chemical Formula: $C_{12}H_{12}F_2INO_2$
Exact Mass: 366.99

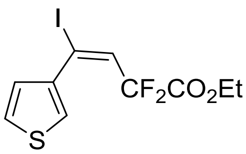
Compound **A26**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A26** (37.4 mg, 51%), green liquid (*E*/*Z* = 96:4, the ratio detected by ^{19}F NMR). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (t, *J* = 7.8 Hz, 1H), 6.71-6.65 (m, 2H), 6.62- 6.54 (m, 2H), 3.96 (q, *J* = 7.2 Hz, 2H), 3.31 (s, 2H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.66 (t, *J* = 17.0 Hz), 144.82, 140.37, 131.73 (t, *J* = 29.1 Hz), 128.00, 115.11 (t, *J* = 255.8 Hz), 109.84, 108.06, 62.10, 12.67; ^{19}F NMR (470 MHz, $CDCl_3$) δ -93.08. GC-MS (EI) Calcd. for $C_{12}H_{12}F_2INO_2$ 366.99, HRMS (EI^+) found 366.9882.

Z Product: ^{19}F NMR (470 MHz, $CDCl_3$) δ, -97.91.



Chemical Formula: $C_{11}H_{10}F_2INO_2$
Exact Mass: 352.97

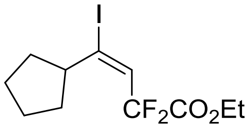
Compound **A27**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A27** (40.9, 58%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37-8.17 (m, 2H), 7.33 (dt, *J* = 8.0, 1.9 Hz, 1H), 7.04-6.91 (m, 1H), 6.53 (t, *J* = 11.6 Hz, 1H), 3.85 (d, *J* = 7.2 Hz, 2H), 0.98 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.54 (t, *J* = 32.8 Hz), 149.07, 146.91, 136.09, 134.07, 133.44 (t, *J* = 27.2 Hz), 121.73, 109.86 (t, *J* = 252.6 Hz), 102.78, 62.49, 12.76; ^{19}F NMR (470 MHz, $CDCl_3$) δ -95.44. GC-MS (EI) Calcd. for $C_{11}H_{10}F_2INO_2$ 352.97, HRMS (EI^+) found 352.9722.



Chemical Formula: $C_{10}H_9F_2IO_2S$
Exact Mass: 357.93

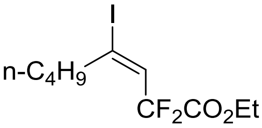
Compound **A28**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A28** (33.7mg, 47%), yellow liquid (*E*/*Z* = 94:6, the ratio detected by ^{19}F NMR). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.28 (dd, *J* = 5.1, 3.0 Hz, 1H), 7.09 (dd, *J* = 5.0, 1.4 Hz, 1H), 6.68 (s, 1H), 4.01 (d, *J* = 7.2 Hz, 2H), 1.19 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.42 (t, *J* = 33.7 Hz), 139.07, 132.26 (t, *J* = 29.0 Hz), 127.44, 124.92, 124.71, 110.01 (t, *J* = 249.2 Hz), 101.16, 62.21, 12.73; ^{19}F NMR (470 MHz, $CDCl_3$) δ -92.47. GC-MS (EI) Calcd. for $C_{10}H_9F_2IO_2S$ 357.93, HRMS (EI^+) found 357.9342.

Z Product: ^{19}F NMR (470 MHz, $CDCl_3$) δ, -97.20.



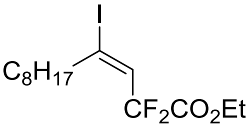
Chemical Formula: $C_{11}H_{15}F_2IO_2$
Exact Mass: 344.01

Compound **A29**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A29** (29.6 mg, 43%), colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.41 (t, *J* = 13.0 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 2.56 (p, *J* = 8.1 Hz, 1H), 1.79-1.68 (m, 4H), 1.67-1.61 (m, 2H), 1.46-1.40 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.50 (t, *J* = 34.0 Hz), 131.24 (t, *J* = 27.8 Hz), 111.81 (t, *J* = 240.7 Hz), 107.56, 63.45, 46.09, 34.96, 25.83, 14.02; ^{19}F NMR (470 MHz, $CDCl_3$) δ -96.78. GC-MS (EI) Calcd. for $C_{11}H_{15}F_2IO_2$ 344.01, found 344.05.



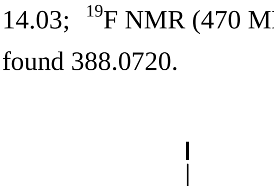
Chemical Formula: $C_{10}H_{15}F_2IO_2$
Exact Mass: 332.01

Compound **A30**[3]: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A30** (15.9 mg, 24%), colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.40 (t, *J* = 13.2 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.54-1.46 (m, 2H), 1.35 (td, *J* = 7.4, 2.9 Hz, 6H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{19}F NMR (470 MHz, $CDCl_3$) δ -97.73. GC-MS (EI) Calcd. for $C_{10}H_{15}F_3IO_2$ 332.01, found 332.05.



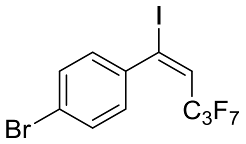
Chemical Formula: $C_{14}H_{23}F_2IO_2$
Exact Mass: 388.07

Compound **A31**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A31** (31.8 mg, 41%), colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.40 (t, *J* = 13.2 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 2.66-2.54 (m, 2H), 1.57-1.49 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.33-1.24 (m, 11H), 0.88 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.37 (t, *J* = 55.4 Hz), 131.31 (t, *J* = 27.7 Hz), 111.69 (t, *J* = 254.0 Hz), 63.46, 40.89, 31.92, 30.04, 29.42, 29.24, 28.51, 22.76, 14.20, 14.03; ^{19}F NMR (470 MHz, $CDCl_3$) δ -97.68. GC-MS (EI) Calcd. for $C_{14}H_{23}F_2IO_2$ 388.07, HRMS (EI^+) found 388.0720.



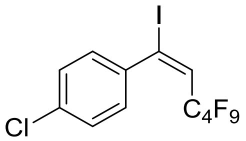
Chemical Formula: $C_{11}H_8F_5IO$
Exact Mass: 377.95

Compound **A32**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 40:1) to afford the **A32** (59.7 mg, 79%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.51 (t, *J* = 13.3 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.24, 132.50, 127.82, 125.23 (t, *J* = 21.9 Hz), 112.55, 112.32, 54.28; ^{19}F NMR (470 MHz, $CDCl_3$) δ -84.95--85.85 (m), -108.45--109.61 (m). GC-MS (EI) Calcd. for $C_{11}H_8F_5IO$ 377.95, HRMS (EI^+) found 377.9545.



Chemical Formula: $C_{11}H_5BrF_7I$
Exact Mass: 475.85

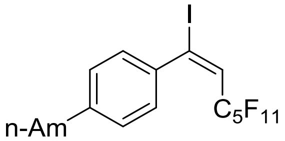
Compound **A33**: purified by column chromatography on silica gel (petroleum ether) to afford the **A33** (50.4 mg, 53%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.65-6.55 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.12, 130.28, 127.40, 126.43 (t, *J* = 22.1 Hz), 122.57, 109.89; ^{19}F NMR (470 MHz, $CDCl_3$) δ -80.22 (t, *J* = 2.52 Hz), -106.12 (d, *J* = 9.4 Hz), -127.14. GC-MS (EI) Calcd. for $C_{11}H_5BrF_7I$ 475.85, HRMS (EI$^+$) found 475.8510.



Chemical Formula: $C_{12}H_5ClF_9I$
Exact Mass: 481.90

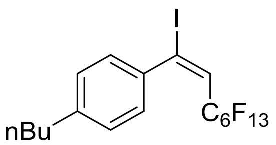
Compound **A34**: purified by column chromatography on silica gel (petroleum ether) to afford the **A34** (70.4 mg, 73%), yellow liquid (*E*/*Z* = 81:19, the ratio detected by ^{1}H NMR). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.6 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 6.61 (t, *J* = 13.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.80, 135.48, 129.47 (d, *J* = 26.1 Hz), 128.90 (d, *J* = 13.4 Hz), 128.47, 128.35, 127.72 (t, *J* = 22.3 Hz), 124.52 (t, *J* = 23.3 Hz), 111.05; ^{19}F NMR (470 MHz, $CDCl_3$) δ -81.02 (t, *J* = 9.7 Hz), -105.42 (t, *J* = 12.3 Hz), -123.57 – -123.96 (m), -125.83 (td, *J* = 12.3, 4.8 Hz). GC-MS (EI) Calcd. for $C_{12}H_5ClF_9I$ 481.90, found 481.90.

Z product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.39 (m, 2H), 7.38-7.34 (m, 2H), 6.51 (t, *J* = 13.1 Hz, 1H).



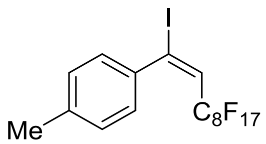
Chemical Formula: $C_{18}H_{16}F_{11}I$
Exact Mass: 568.01

Compound **A35**: purified by column chromatography on silica gel (petroleum ether) to afford the **A35** (73.8 mg, 65%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.57 (t, *J* = 13.5 Hz, 1H), 2.64-2.55 (m, 2H), 1.62 (p, *J* = 7.3 Hz, 2H), 1.33 (dh, *J* = 7.0, 3.9, 3.1 Hz, 4H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.64, 138.67, 128.06, 127.03, 126.72 (t, *J* = 18.9 Hz), 35.86, 31.64, 30.91, 22.63, 14.11; ^{19}F NMR (470 MHz, $CDCl_3$) δ -80.79 (t, *J* = 9.8 Hz), -105.07 (t, *J* = 13.0 Hz), -121.86--122.83 (m), -122.89--123.57 (m), -125.70--126.67 (m). GC-MS (EI) Calcd. for $C_{18}H_{16}F_{11}I$ 568.01, found 568.02.



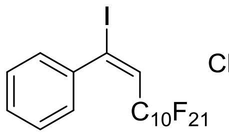
Chemical Formula: $C_{18}H_{14}F_{13}I$
Exact Mass: 603.99

Compound **A36**: purified by column chromatography on silica gel (petroleum ether) to afford the **A36** (73.7 mg, 61%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 6.59 (t, *J* = 13.5 Hz, 1H), 2.66-2.59 (m, 2H), 1.67-1.58 (m, 2H), 1.39 (dt, *J* = 15.0, 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.59, 138.72, 128.49 (d, *J* = 35.1 Hz), 128.05, 127.03, 126.79 (d, *J* = 22.5 Hz), 113.59, 35.56, 33.34, 22.48, 13.95; ^{19}F NMR (470 MHz, $CDCl_3$) δ -80.79 (d, *J* = 8.3 Hz), -104.99 (t, *J* = 13.1 Hz), -121.67 (p, *J* = 13.6 Hz), -122.31 – -123.85 (m), -126.12 (td, *J* = 14.0, 6.3 Hz). GC-MS (EI) Calcd. for $C_{18}H_{14}F_{13}I$ 603.99, HRMS (EI^+) found 603.9938.



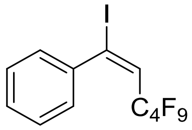
Chemical Formula: $C_{17}H_8F_{17}I$
Exact Mass: 661.94

Compound **A37**: purified by column chromatography on silica gel (petroleum ether) to afford the **A37** (54.3 mg, 41%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 7.9 Hz, 1H), 7.13 (d, *J* = 7.9 Hz, 1H), 6.57 (t, *J* = 13.5 Hz, 0H), 2.35 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.61, 138.63, 128.79 (t, J = 60.5 Hz), 128.76, 126.99, 126.77 (t, *J* = 35.3 Hz), 113.41, 21.42; ^{19}F NMR (470 MHz, $CDCl_3$) δ -80.85 (t, *J* = 9.8 Hz), -105.06 (t, *J* = 13.1 Hz), -121.51 (q, *J* = 14.0, 13.0 Hz), -121.74--122.13 (m), -122.57--123.03 (m), -125.89--126.55 (m). GC-MS (EI) Calcd. for $C_{17}H_8F_{17}I$ 661.94, found 661.74.
Z product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.9 Hz, 1H), 7.16 (s, 0H), 6.49 (t, *J* = 13.3 Hz, 0H), 2.38 (s, 2H).



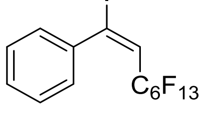
Chemical Formula: $C_{18}H_6F_{21}I$
Exact Mass: 747.92

Compound **A38**: purified by column chromatography on silica gel (petroleum ether) to afford the **A38** (55.4 mg, 37%), white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.27 (m, 5H), 6.59 (t, *J* = 13.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.47, 139.77, 134.71-130.89 (m), 130.21, 129.31, 129.00, 128.64 (d, *J* = 13.4 Hz), 128.04, 127.68, 127.25 (d, *J* = 22.7 Hz), 126.97-126.78 (m), 118.63-118.11 (m), 115.23-115.00 (m), 113.08-12.46 (m), 111.14-110.36 (m), 109.60-107.58 (m); ^{19}F NMR (470 MHz, $CDCl_3$) δ -80.74 (t, *J* = 10.0 Hz), -105.17 (t, *J* = 12.8 Hz), -121.46 , -121.56--122.01 (m), -122.57--122.92 (m), -126.08 (td, *J* = 14.5, 6.8 Hz). GC-MS (EI) Calcd. for $C_{18}H_6F_{21}I$ 747.92, found 746.96.



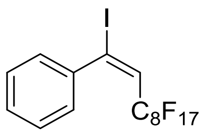
Chemical Formula: $C_{12}H_6F_9I$
Exact Mass: 447.94

Compound **A39**[4]: purified by column chromatography on silica gel (petroleum ether) to afford the **A-39** (48.4 mg, 54%), colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.27 (m, 5H), 6.60 (t, *J* = 13.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.41, 129.39, 128.65, 128.11, 126.94, 112.89; ^{19}F NMR (470 MHz, $CDCl_3$) δ -81.03 (t, *J* = 9.7 Hz), -105.41 (t, *J* = 13.1 Hz), -123.78 (d, *J* = 9.3 Hz), -124.92--127.97 (m). GC-MS (EI) Calcd. for $C_{12}H_6F_9i$ 447.94, found 448.12.



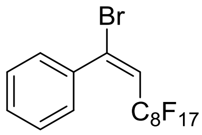
Chemical Formula: $C_{14}H_6F_{13}I$
Exact Mass: 547.93

Compound **A40**[5]: purified by column chromatography on silica gel (petroleum ether) to afford the **A40** (44.9 mg, 41%), colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.20 (m, 5H), 6.52 (t, *J* = 13.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.43, 130.30, 129.38, 128.48 (d, *J* = 40.1 Hz), 128.10, 127.19 (d, *J* = 22.0 Hz), 126.93; ^{19}F NMR (470 MHz, $CDCl_3$) δ -80.82 (d, *J* = 8.1 Hz), -105.19 (t, *J* = 13.1 Hz), -121.71 (t, *J* = 14.6 Hz), -122.84 (d, *J* = 9.0 Hz), -126.15 (ddd, *J* = 19.7, 14.2, 5.9 Hz). GC-MS (EI) Calcd. for $C_{14}H_6F_{13}I$ 547.93, found 548.07.



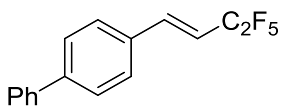
Chemical Formula: $C_{16}H_6F_{17}I$
Exact Mass: 647.92

Compound **A41**[6]: purified by column chromatography on silica gel (petroleum ether) to afford the **A41** (51.8 mg, 40%), colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.27 (m, 5H), 6.60 (t, *J* = 13.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.43, 129.38, 128.10, 127.12, 126.93, 112.79; ^{19}F NMR (470 MHz, $CDCl_3$) δ -80.79 (t, *J* = 10.0 Hz), -105.19 (t, *J* = 13.0 Hz), -120.95--121.64 (m), -121.64--122.18 (m), -122.77 (dddd, *J* = 30.8, 24.1, 15.3, 8.6 Hz), -126.12 (td, *J* = 13.6, 13.0, 7.1 Hz). GC-MS (EI) Calcd. for $C_{16}H_6F_{17}I$ 647.92, found 647.92.



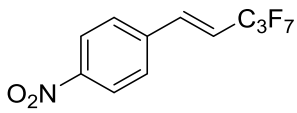
Chemical Formula: $C_{16}H_6BrF_{17}$
Exact Mass: 599.94

Compound **A42**: purified by column chromatography on silica gel (petroleum ether) to afford the **A42** (34.8 mg, 29%), colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 7.0, 3.6 Hz, 5H), 6.39 (t, *J* = 13.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.56 (d, *J* = 32.0 Hz), 129.94, 128.19, 127.87, 126.94, 119.42 (t, *J* = 22.4 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -80.80 (t, *J* = 10.2 Hz), -105.21 (t, *J* = 13.2 Hz), -121.47 (q, *J* = 13.6 Hz), -121.90 (tt, *J* = 23.7, 13.1 Hz), -122.78 (ddd, *J* = 59.7, 21.3, 11.7 Hz), -125.98--126.27 (m). GC-MS (EI) Calcd. for $C_{16}H_6BrF_{17}$ 599.94, found 600.06.



Chemical Formula: $C_{16}H_{11}F_5$
Exact Mass: 298.08

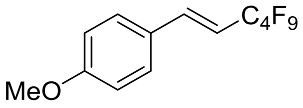
Compound **B1**: purified by column chromatography on silica gel (petroleum ether) to afford the **B1** (23.2 mg, 39%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66-7.58 (m, 4H), 7.58-7.51 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.38 (dd, *J* = 8.4, 6.4 Hz, 1H), 7.20 (d, *J* = 16.7 Hz, 1H), 6.21 (dt, *J* = 16.1, 11.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.10, 140.19, 139.32, 132.55, 129.05, 128.23, 128.01, 127.72, 127.19, 114.02 (t, *J* = 22.9 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -85.00, -114.77 (d, *J* = 2.6 Hz). GC-MS (EI) Calcd. for $C_{16}H_{11}F_5$ 298.08, HRMS (EI^+) found 298.0785.



Chemical Formula: $C_{11}H_6F_7NO_2$
Exact Mass: 317.03

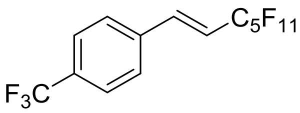
Compound **B2**: purified by column chromatography on silica gel (petroleum ether) to afford the **B2** (19.7 mg, 31%), colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.7 Hz, 2H), 7.65 (d, *J* =

8.7 Hz, 2H), 7.26 (d, *J* = 16.2 Hz, 1H), 6.36 (dt, *J* = 16.2, 11.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.74, 139.53, 137.61, 128.54, 124.39, 118.67 (t, *J* = 23.2 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -80.23 (t, *J* = 9.1 Hz), -112.83 (q, *J* = 9.3 Hz), -127.33. GC-MS (EI) Calcd. for $C_{11}H_6F_7NO_2$ 317.03, HRMS (EI^+) found 317.0284.



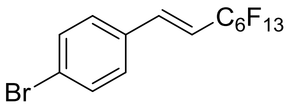
Chemical Formula: $C_{13}H_9F_9O$
Exact Mass: 352.05

Compound **B3**[7]: purified by column chromatography on silica gel (petroleum ether) to afford the **B3** (31.7 mg, 45%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 16.1 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.05 (dt, *J* = 16.2, 12.3 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.31, 139.27, 129.30, 126.36, 114.46, 111.73 (t, *J* = 22.7 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -81.01 (dd, *J* = 11.4, 8.0 Hz), -110.79 (t, *J* = 12.1 Hz), -122.26--125.30 (m), -125.30--126.98 (m). GC-MS (EI) Calcd. for $C_{13}H_9F_9O$ 352.05, found 352.05.



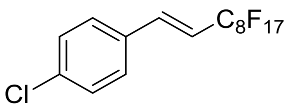
Chemical Formula: $C_{14}H_6F_{14}$
Exact Mass: 440.02

Compound **B4**: purified by column chromatography on silica gel (petroleum ether) to afford the **B4** (25.5 mg, 29%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 16.2 Hz, 1H), 6.30 (dt, *J* = 16.2, 11.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.43, 136.93, 132.19 (t, *J* = 32.8 Hz), 128.02, 126.11, 123.85 (q, *J* = 272.7 Hz), 117.12 (t, *J* = 23.7 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.91 , -80.48--81.18 (m), -111.58 (t, *J* = 12.6 Hz), -122.35 (dtt, *J* = 15.8, 6.0, 3.1 Hz), -122.94--123.73 (m), -126.22 (dtd, *J* = 14.3, 6.9, 3.4 Hz). GC-MS (EI) Calcd. for $C_{14}H_6F_{14}$ 440.02, HRMS (EI^+) found 440.0253.



Chemical Formula: $C_{14}H_6BrF_{13}$
Exact Mass: 499.94

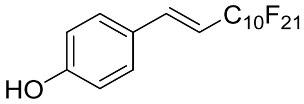
Compound **B5**[7]: purified by column chromatography on silica gel (petroleum ether) to afford the **B5** (46.0 mg, 46%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 16.0 Hz, 1H), 6.20 (dt, *J* = 16.3, 12.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.68, 132.53, 132.34, 129.19, 124.61, 115.19 (t, *J* = 22.7 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -80.75 (t, *J* = 10.2 Hz), -111.24 (dd, *J* = 15.6, 10.8 Hz), -120.67--122.40 (m), -122.60--122.97 (m), -123.15 (td, *J* = 14.8, 6.8 Hz), -126.12 (td, *J* = 14.6, 6.9 Hz). GC-MS (EI) Calcd. for $C_{14}H_6BrF_{13}$ 499.94, found 499.95.



Chemical Formula: $C_{16}H_6ClF_{17}$
Exact Mass: 555.99

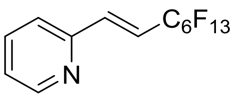
Compound **B6**: purified by column chromatography on silica gel (petroleum ether) to afford the **B6** (42.2 mg, 38%), yellow liquid (*E*/*Z* = 86:14, the ratio detected by ^{1}H NMR). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (q, *J* = 8.7 Hz, 4H), 7.13 (d, *J* = 16.1 Hz, 1H), 6.18 (dt, *J* = 16.2, 12.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.57, 136.32, 132.11, 129.36, 128.95, 115.09 (t, *J* = 23.9 Hz); ^{19}F NMR

(470 MHz, $CDCl_3$) δ -80.56 (t, *J* = 10.0 Hz), -111.03 (t, *J* = 12.8 Hz), -121.21 (q, *J* = 13.1, 11.9 Hz), -121.72 (tt, *J* = 21.5, 12.3 Hz), -122.53 (tq, *J* = 18.8, 8.9, 8.3 Hz), -122.86--123.10 (m), -125.93 (td, *J* = 14.1, 13.6, 6.3 Hz). GC-MS (EI) Calcd. for $C_{14}H_6BrF_{13}$ 555.99, HRMS (EI^+) found 555.9883.
Z Product: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.28 (m, 4H), 7.07 (d, *J* = 12.8 Hz, 1H), 5.77 (q, *J* = 15.2 Hz, 1H).



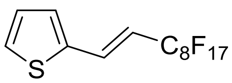
Chemical Formula: $C_{18}H_7F_{21}O$
Exact Mass: 638.02

Compound **B7**: purified by column chromatography on silica gel (petroleum ether) to afford the **B7** (24.2 mg, 19%), yellow solid. ^{1}H NMR (500 MHz, MeOD) δ 7.42-7.31 (m, 2H), 7.07 (dd, *J* = 16.0, 8.9 Hz, 1H), 6.81-6.73 (m, 2H), 6.52 (s, 1H), 6.19-6.03 (m, 1H); ^{13}C NMR (126 MHz, MeOD) δ 158.46, 138.75, 128.10, 123.88, 114.34, 108.70 (t, *J* = 36.5 Hz); ^{19}F NMR (470 MHz, MeOD) δ -82.50 (t, *J* = 10.3 Hz), -111.43 (t, *J* = 13.2 Hz), -122.47, -122.65--123.10 (m), -123.81, -124.19 (d, *J* = 15.5 Hz), -127.39 (dd, *J* = 14.9, 7.2 Hz). GC-MS (EI) Calcd. for $C_{18}H_7F_{21}O$ 638.02, HRMS (EI^+) found 638.0159.



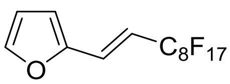
Chemical Formula: $C_{13}H_6F_{13}N$
Exact Mass: 423.03

Compound **B8**: purified by column chromatography on silica gel (petroleum ether) to afford the **B8** (34.7 mg, 41%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (d, *J* = 5.3 Hz, 1H), 7.73 (td, *J* = 7.7, 1.7 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.29 (dd, *J* = 7.6, 4.9 Hz, 1H), 7.20 (d, *J* = 15.7 Hz, 1H), 6.94-6.80 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.68, 149.11, 137.56, 135.88, 123.33, 123.09, 117.73 (t, *J* = 22.9 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -80.78 (t, *J* = 10.2 Hz), -111.66 (q, *J* = 13.3, 12.1 Hz), -121.05--121.88 (m), -122.74--122.96 (m), -123.15 (tt, *J* = 20.3, 9.8 Hz), -126.15 (tt, *J* = 11.2, 5.5 Hz). GC-MS (EI) Calcd. for $C_{13}H_6F_{13}N$ 423.03, HRMS (EI^+) found 423.0297.



Chemical Formula: $C_{14}H_5F_{17}S$
Exact Mass: 527.98

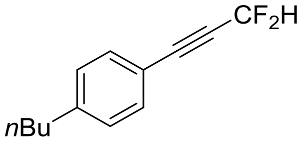
Compound **B9**: purified by column chromatography on silica gel (petroleum ether) to afford the **B9** (33.8 mg, 32%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 5.0 Hz, 1H), 7.27 (dt, *J* = 15.6 Hz, 1H), 7.21 (d, *J* = 3.6 Hz, 1H), 7.05 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.00 (dt, *J* = 15.9, 12.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.39, 132.57, 130.36, 128.16, 128.09, 112.96 (t, *J* = 22.8 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -81.02 (t, *J* = 10.3 Hz), -111.04 (t, *J* = 13.0 Hz), -121.64 (q, *J* = 13.2, 12.0 Hz), -122.15 (tt, *J* = 21.2, 11.5 Hz), -122.96 (dt, *J* = 20.3, 10.1 Hz), -123.32 (q, *J* = 14.3, 10.4 Hz), -126.36 (t, *J* = 13.7 Hz). GC-MS (EI) Calcd. for $C_{14}H_5F_{17}S$ 527.98, found 528.01.



Chemical Formula: $C_{14}H_5F_{17}O$
Exact Mass: 512.01

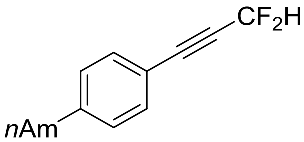
Compound **B10**: purified by column chromatography on silica gel (petroleum ether) to afford the **B10** (36.9 mg, 36%), yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 1.7 Hz, 1H), 6.93 (d, *J* = 15.9 Hz, 1H), 6.58-6.42 (m, 2H), 6.13 (dt, *J* = 16.0, 12.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ

151.41, 148.64, 143.43, 125.62, 112.85, 111.08 (t, J = 39.7 Hz); ^{19}F NMR (470 MHz, $CDCl_3$) δ -80.75 (t, J = 10.4 Hz), -111.11, -120.15--121.71 (m), -121.91 (dt, J = 19.1, 8.4 Hz), -122.42--122.91 (m), -122.91--123.40 (m), -124.95--127.70 (m). GC-MS (EI) Calcd. for $C_{14}H_5F_{17}O$ 512.01, HRMS (EI^+) found 528.0071.



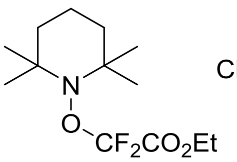
Chemical Formula: $C_{13}H_{14}F_2$
Exact Mass: 208.11

Compound (**C1**): purified by column chromatography on silica gel (petroleum ether) to afford the **C1** (based on 91% ^{19}F NMR yield, the calculated yield is 31%), colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 6.41 (t, J = 55.2 Hz, 1H), 2.67-2.57 (m, 2H), 1.64-1.56 (m, 2H), 1.35 (dt, J = 14.9, 7.4 Hz, 2H), 0.92 (t, J = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.65 , 132.23 , 128.76 , 117.09 , 104.44 (t, J = 231.8 Hz) , 88.94, 79.37, 35.79 , 33.39 , 22.41 , 14.03; ^{19}F NMR (470 MHz, $CDCl_3$) δ -104.85. GC-MS (EI) Calcd. for $C_{13}H_{14}F_2$ 208.11, found 208.13.



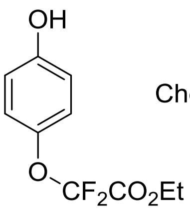
Chemical Formula: $C_{14}H_{16}F_2$
Exact Mass: 222.12

Compound (**C2**): purified by column chromatography on silica gel (petroleum ether) to afford the **C2** (based on 90% ^{19}F NMR yield, the calculated yield is 37%)), colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 7.8 Hz, 2H), 6.41 (t, J = 55.2 Hz, 1H), 2.66-2.56 (m, 2H), 1.61 (dd, J = 10.2, 4.5 Hz, 2H), 1.34-1.29 (m, 4H), 0.89 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.70 , 132.23 , 128.76 , 117.09 , 104.45 (t, J = 231.8 Hz) , 88.94 , 36.08 , 31.54 , 30.96 , 22.64 , 14.14 . ^{19}F NMR (470 MHz, $CDCl_3$) δ -104.85. GC-MS (EI) Calcd. for $C_{14}H_{16}F_2$ 222.12, found 222.16.



Chemical Formula: $C_{13}H_{23}F_2NO_3$
Exact Mass: 279.16

Compound (**5**)[8]: purified by column chromatography on silica gel (petroleum ether/EtOAc = 25:1) to afford the **5**, yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.34 (q, J = 7.1 Hz, 2H), 1.61-1.51 (m, 6H), 1.35 (t, J = 7.1 Hz, 3H), 1.17 (d, J = 13.1 Hz, 12H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 60.36, 39.17, 32.40, 19.73, 15.89; ^{19}F NMR (470 MHz, $CDCl_3$) δ -73.44. GC-MS (EI) Calcd. for $C_{13}H_{23}F_2NO_3$ 279.16, found 279.20.



Chemical Formula: $C_{10}H_{10}F_2O_4$
Exact Mass: 232.05

Compound (**6**): purified by column chromatography on silica gel (petroleum ether/EtOAc = 30:1) to afford the **6**, brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.5 Hz, 2H), 6.87-6.76 (m, 2H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.34, 136.68, 123.41, 116.11, 63.73, 13.98; ^{19}F NMR (470 MHz, $CDCl_3$) δ -75.58. GC-MS (EI) Calcd. for $C_{10}H_{10}F_2O_4$ 232.05, found 232.07.

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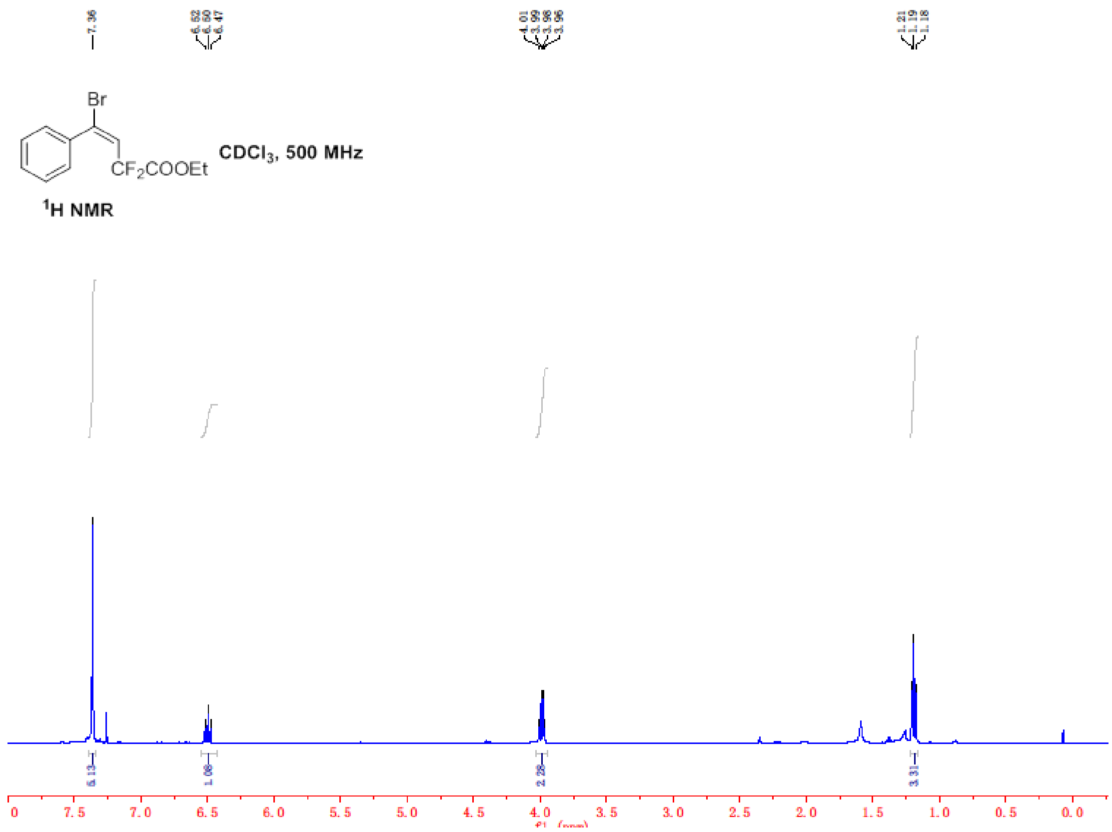
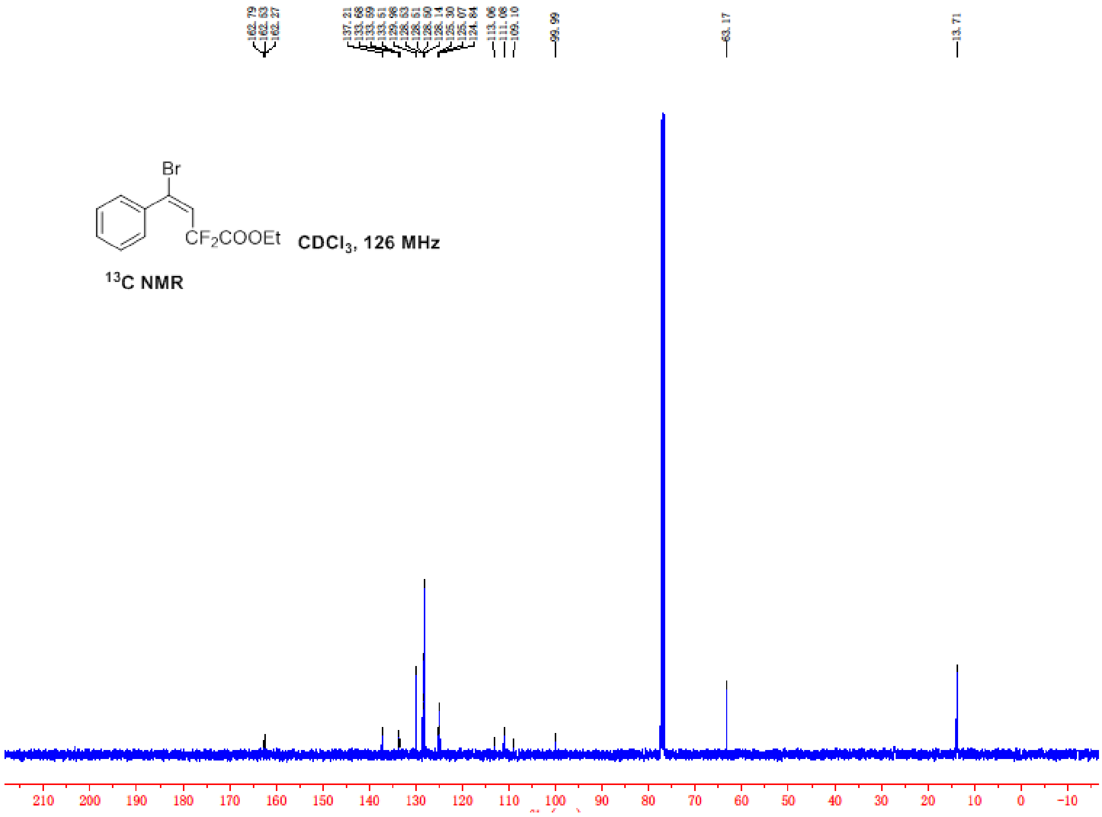
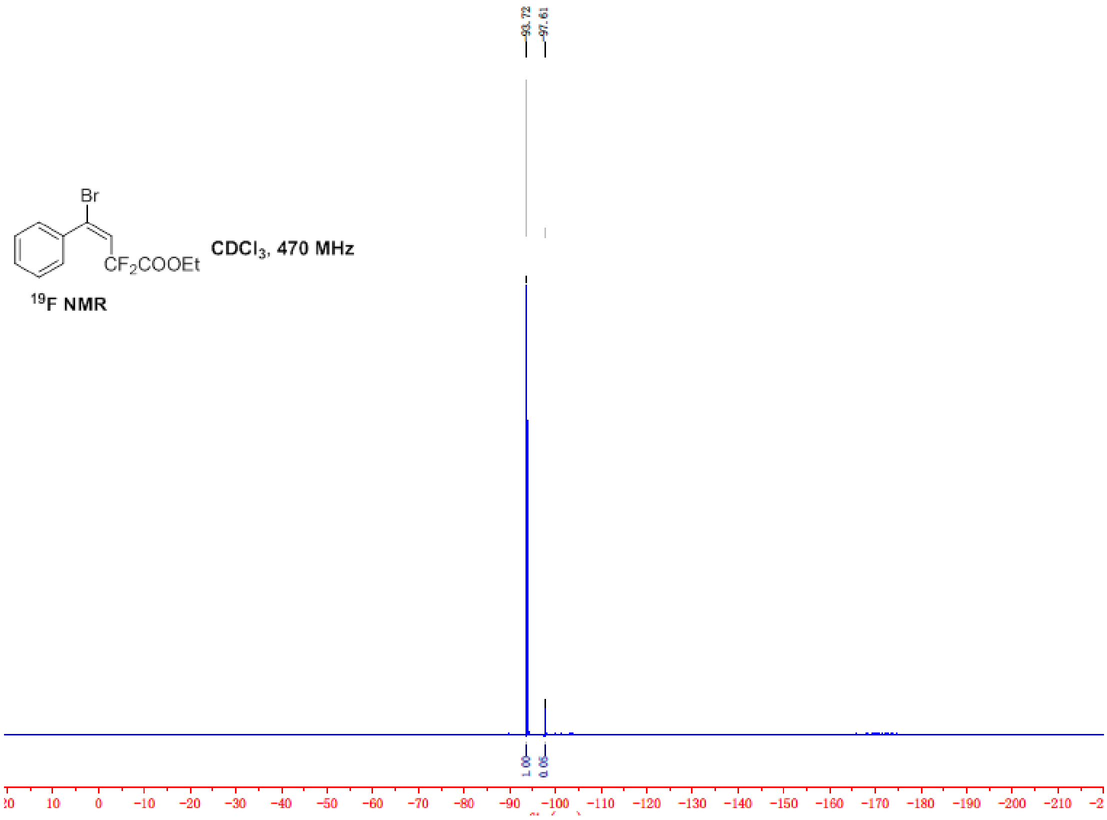
6. NMR Spectra of compounds.





162.79
162.53
162.27
137.21
133.68
133.59
133.51
129.98
128.63
128.51
128.50
128.14
125.30
125.07
124.84
113.06
111.08
109.10
99.99
63.17
13.71
Br
CF2COOEt
CDCl3, 126 MHz
13C NMR



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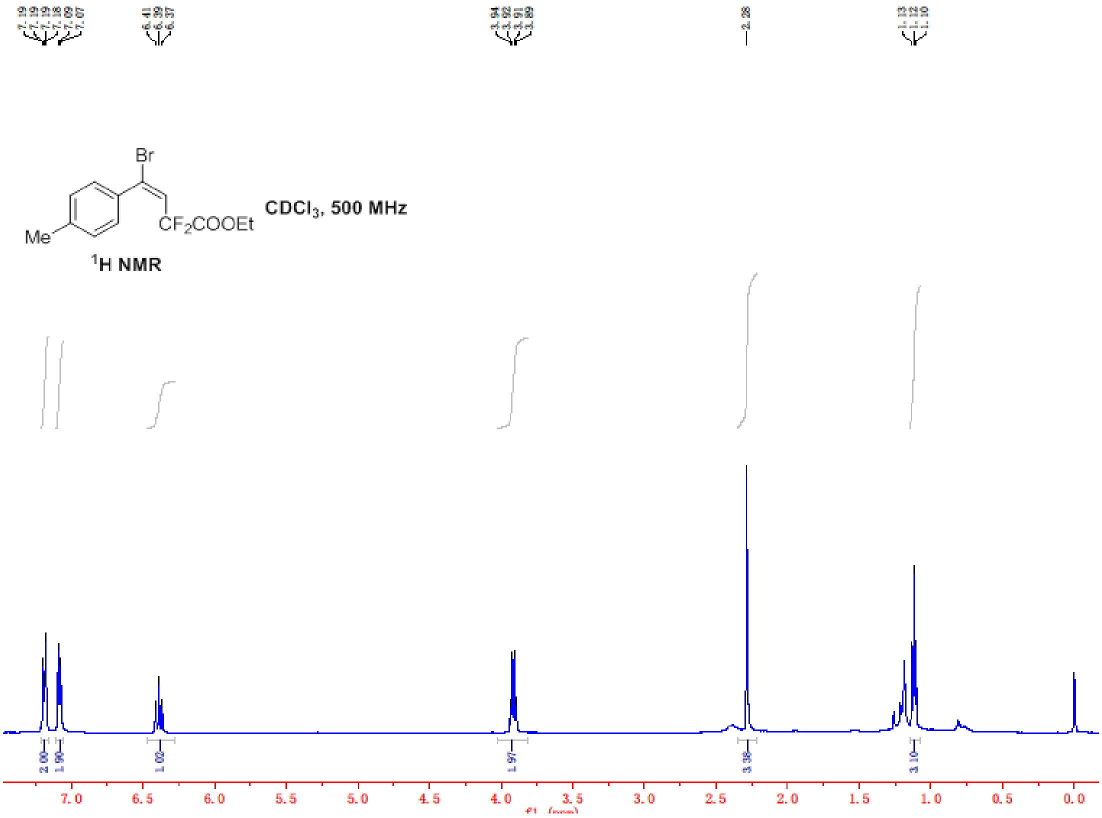
CDCl3, 470 MHz
19F NMR
1.00
0.05



7.19
7.19
7.19
7.18
7.09
7.07
6.41
6.39
6.37
3.94
3.92
3.91
3.89
2.28
1.13
1.12
1.10
Br
Me
CF2COOEt
CDCl3, 500 MHz
1H NMR
2.00
1.90
1.02
1.97
3.38
3.10
7.0
6.5
6.0
5.5
5.0
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3.0
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2.0
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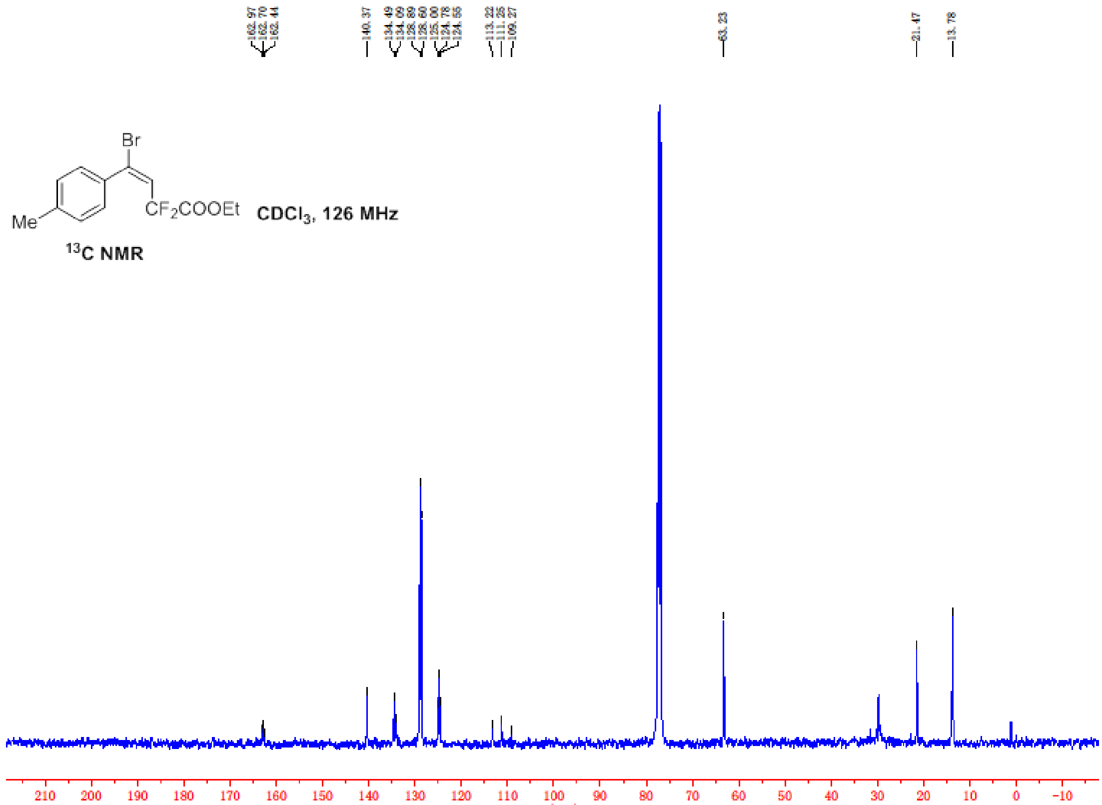

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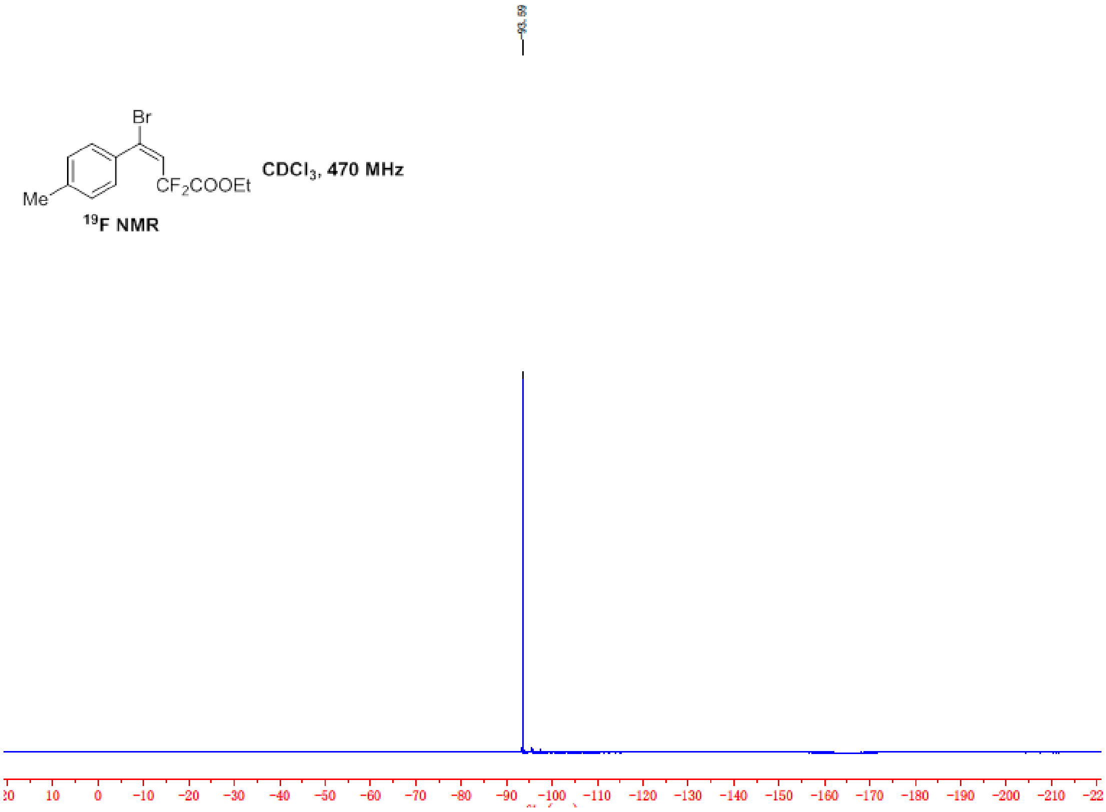
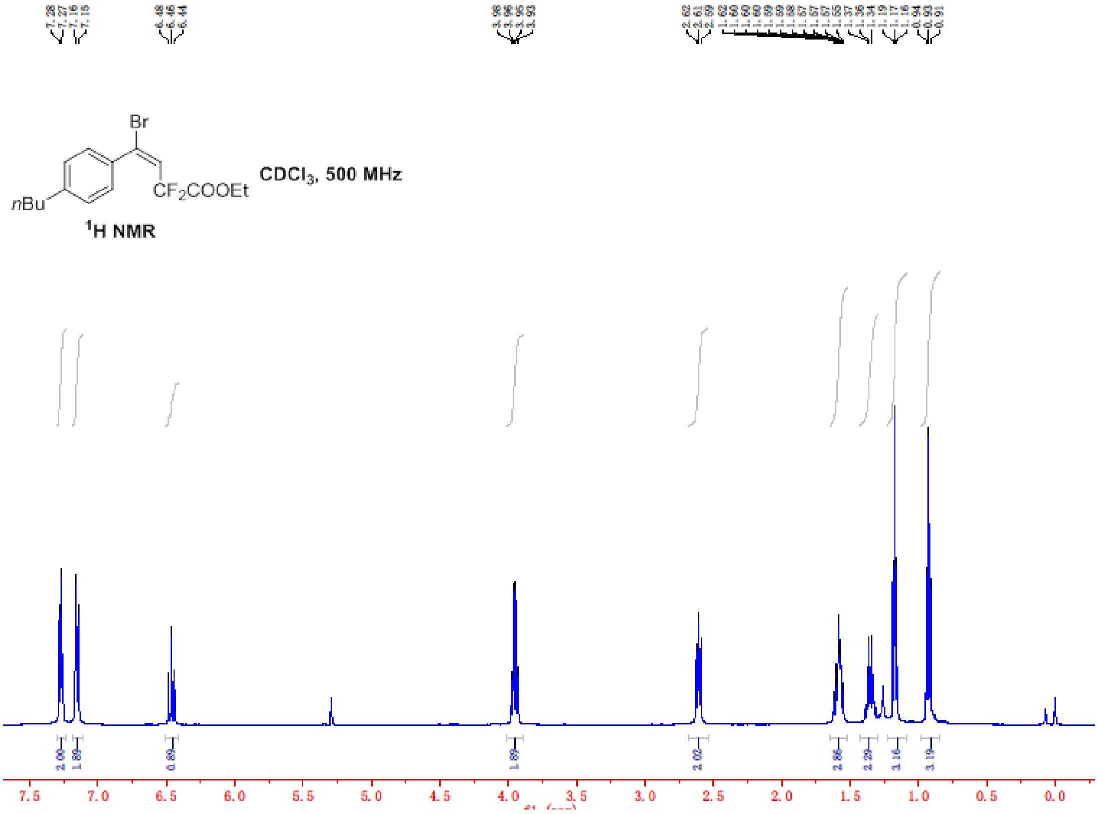
134.49
134.09
128.89
128.60
125.00
124.78
124.55
113.22
111.25
109.27
63.23
21.47
13.78
Br
Me
CF2COOEt
CDCl3, 126 MHz
13C NMR
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10



-93.59
Br
Me
CF2COOEt
CDCl3, 470 MHz
19F NMR



Br
nBu
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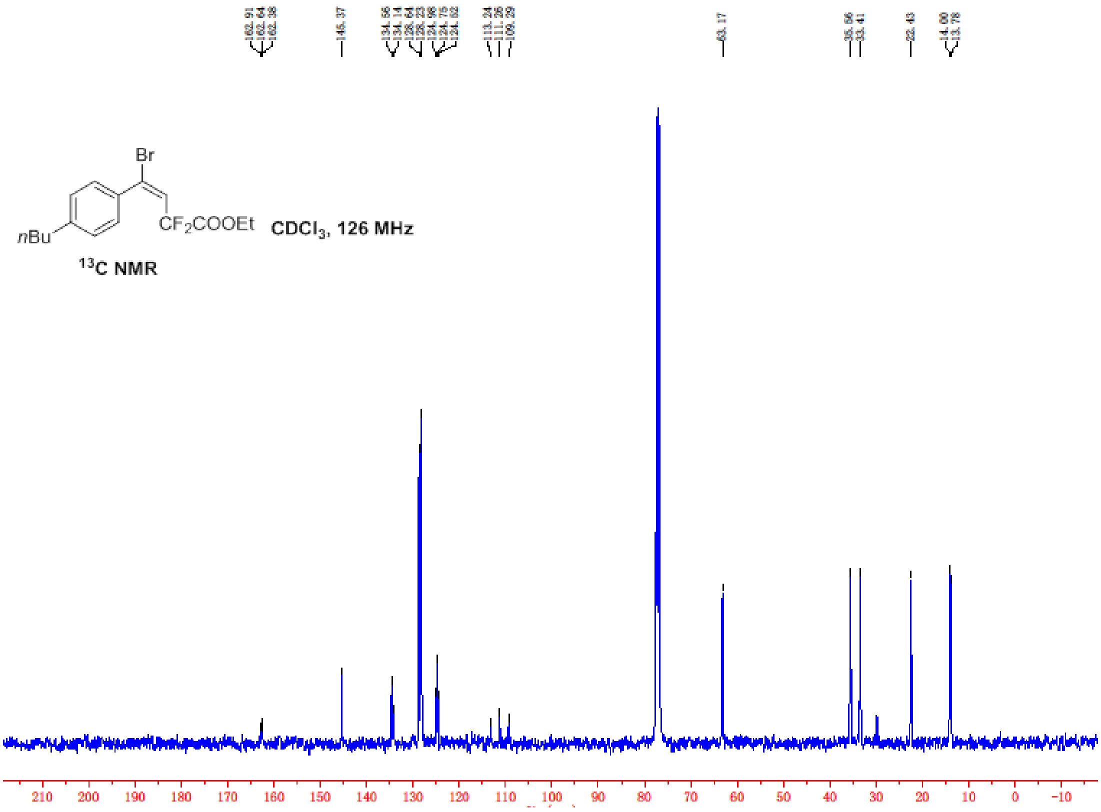
CDCl3, 500 MHz
1H NMR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134.56
134.14
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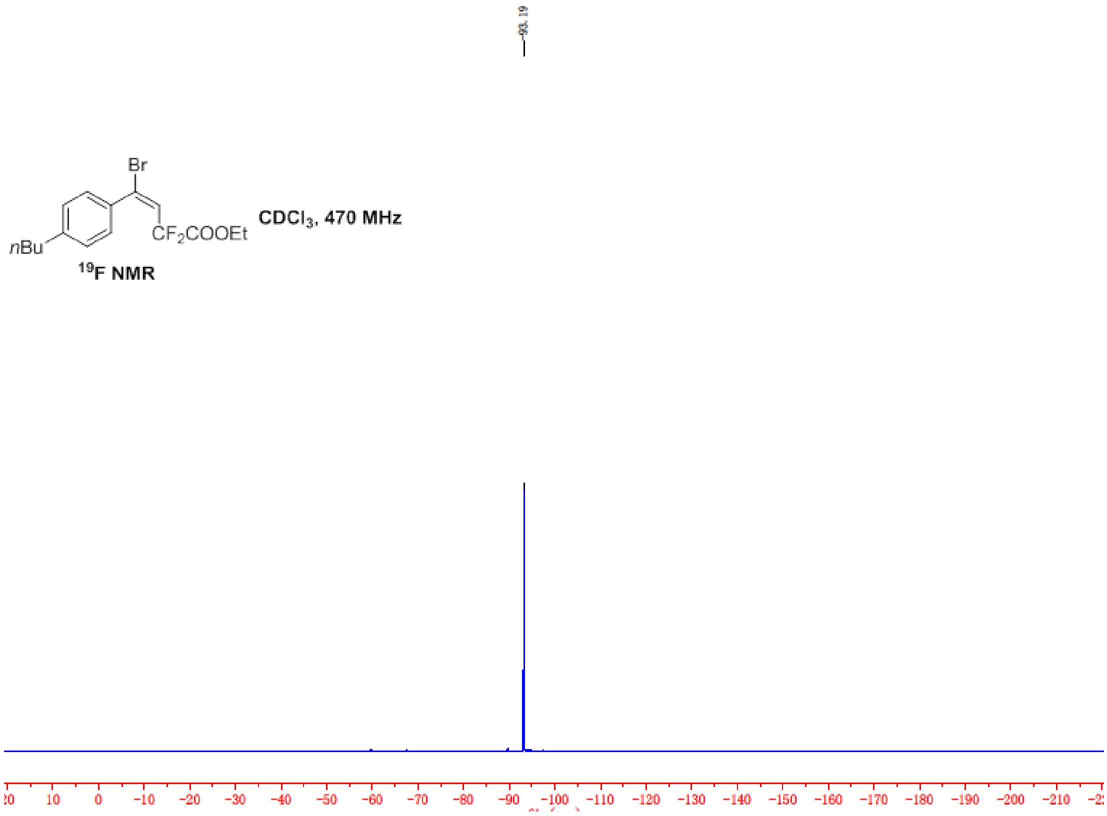
128.23
124.98
124.75
124.52
113.24
111.26
109.29
63.17
35.56
33.41
22.43
14.00
13.78
Br
nBu
CF2COOEt
CDCl3, 126 MHz
13C NMR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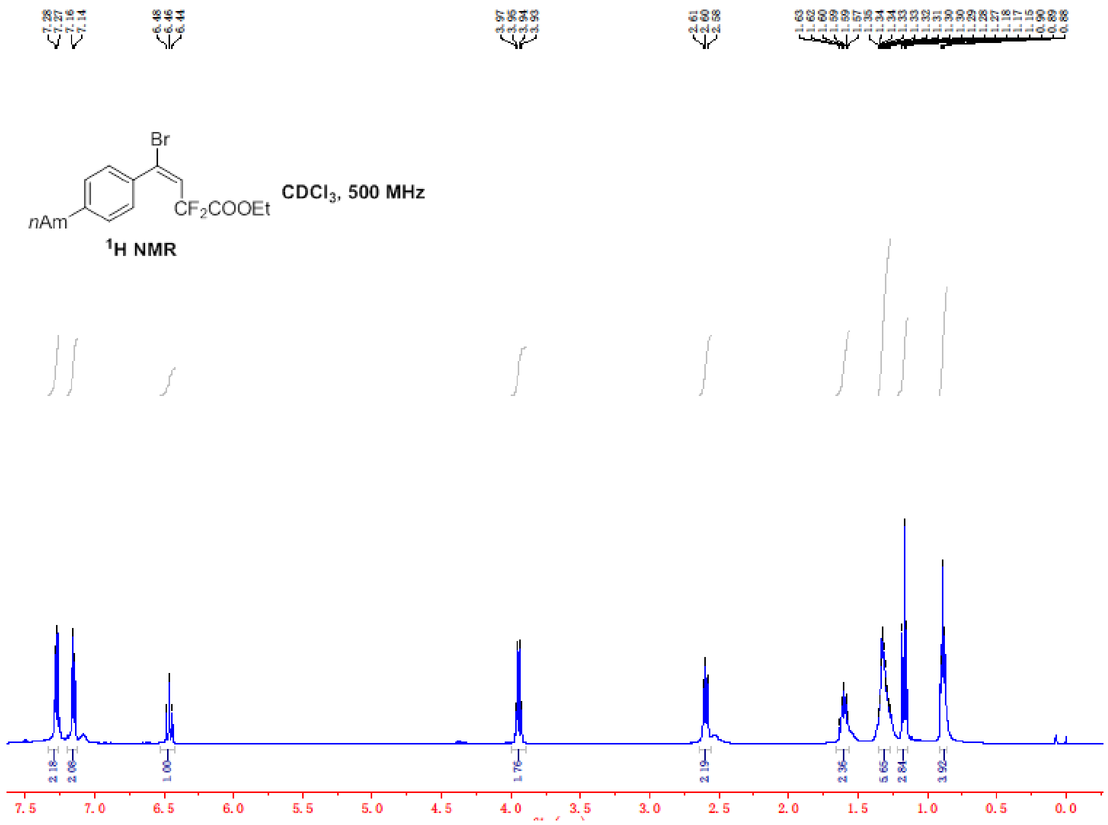
nBu
CF2COOEt
CDCl3, 470 MHz
19F NMR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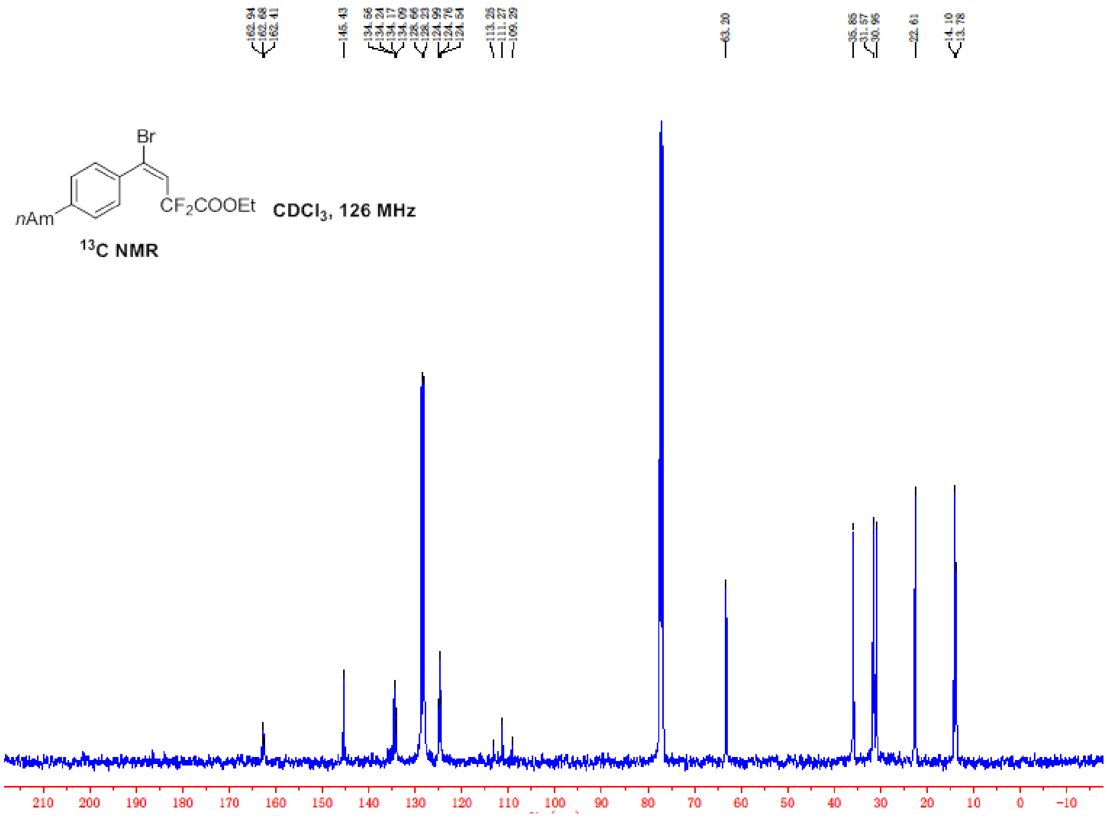
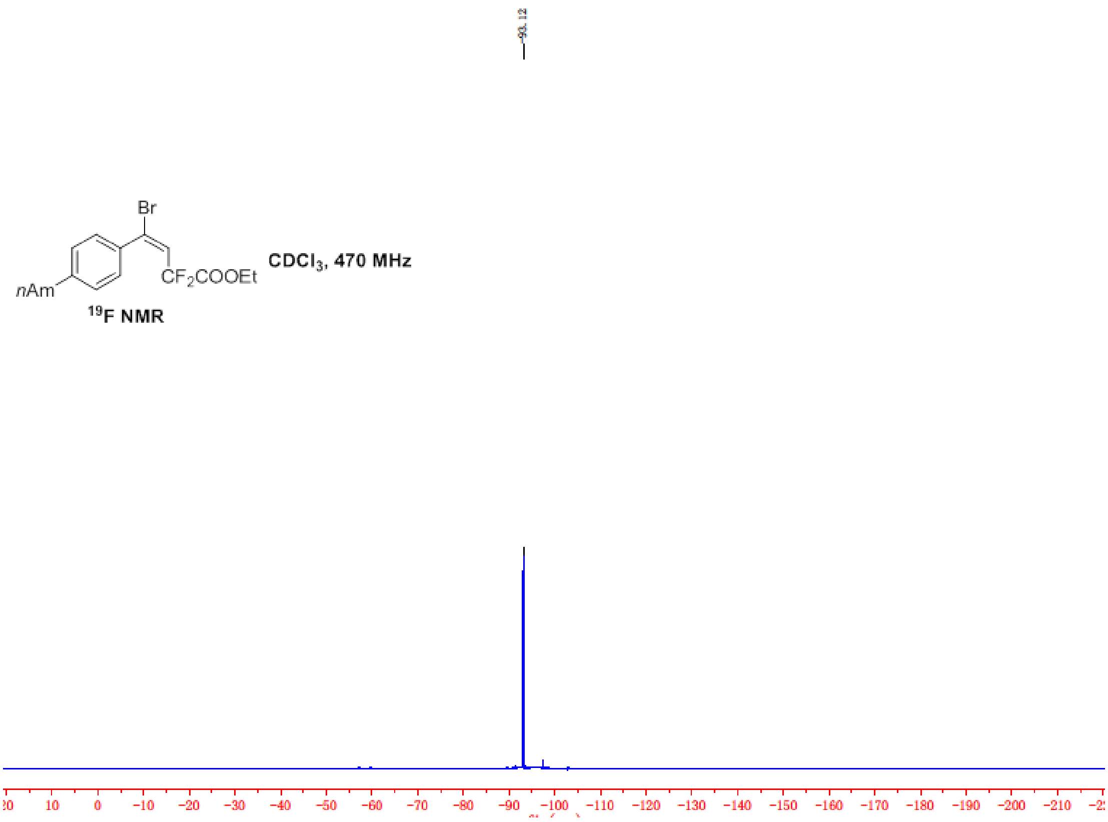
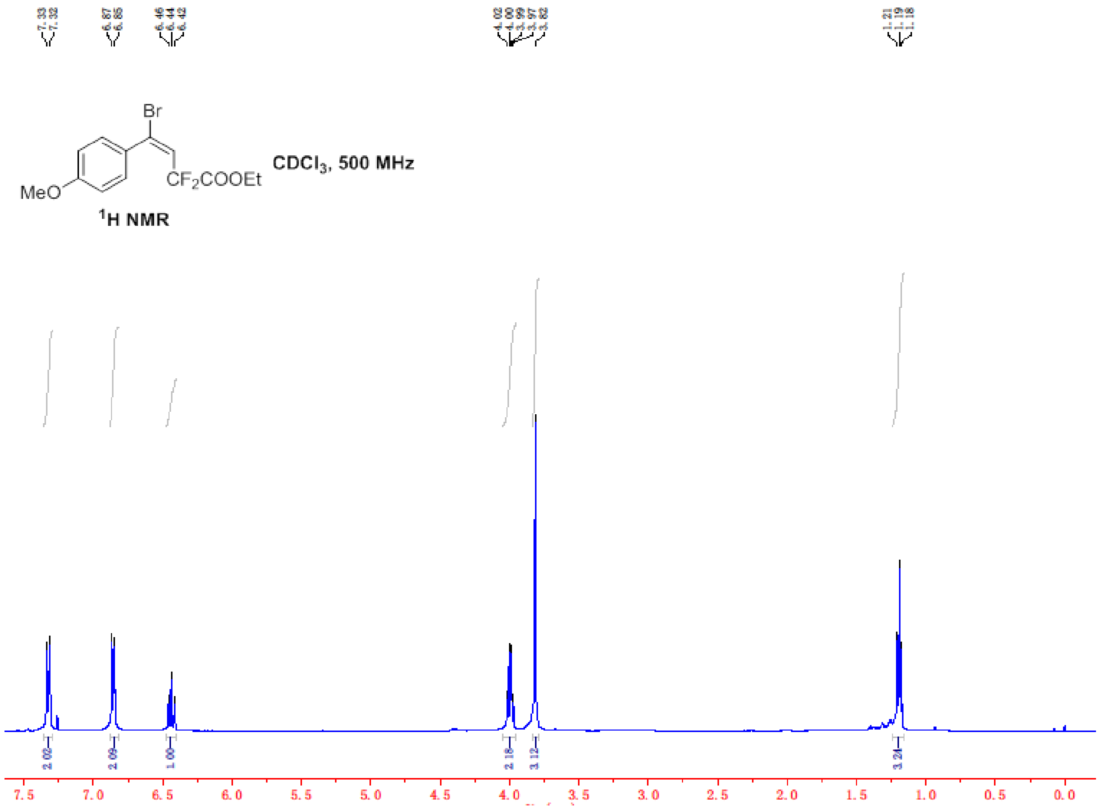
CDCl3, 500 MHz
1H NMR

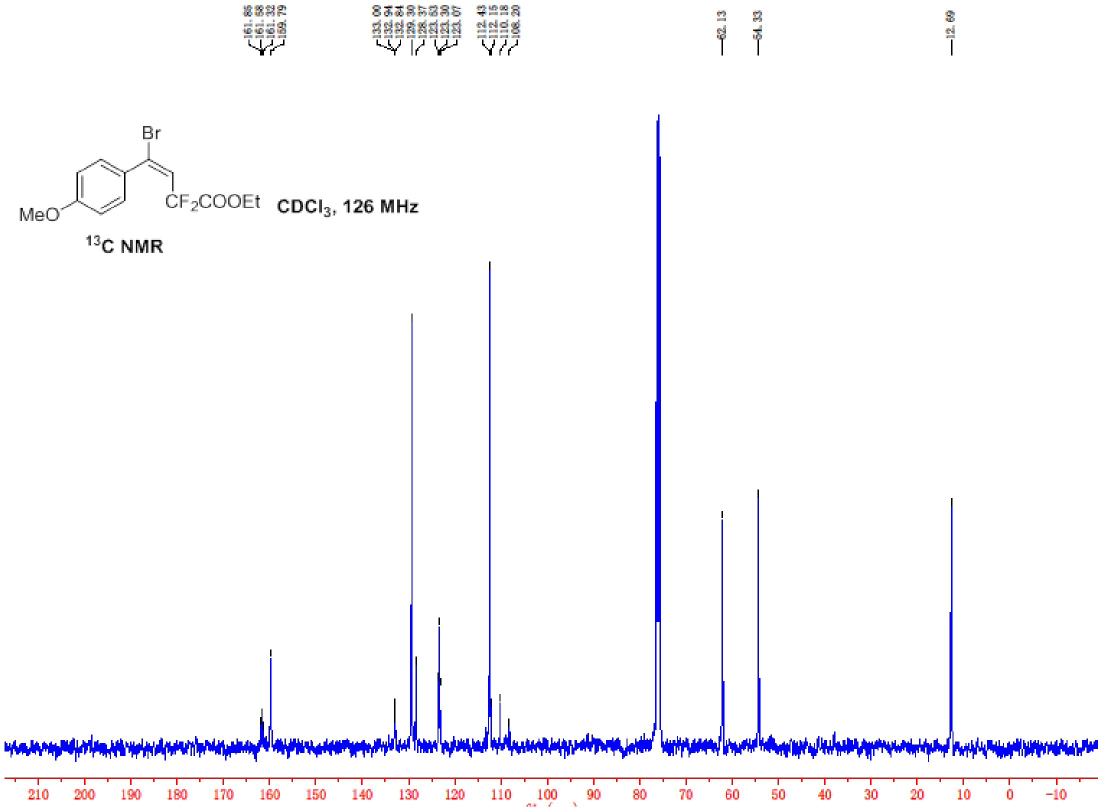

Br
nAm
CF2COOEt
CDCl3, 126 MHz
13C NMR

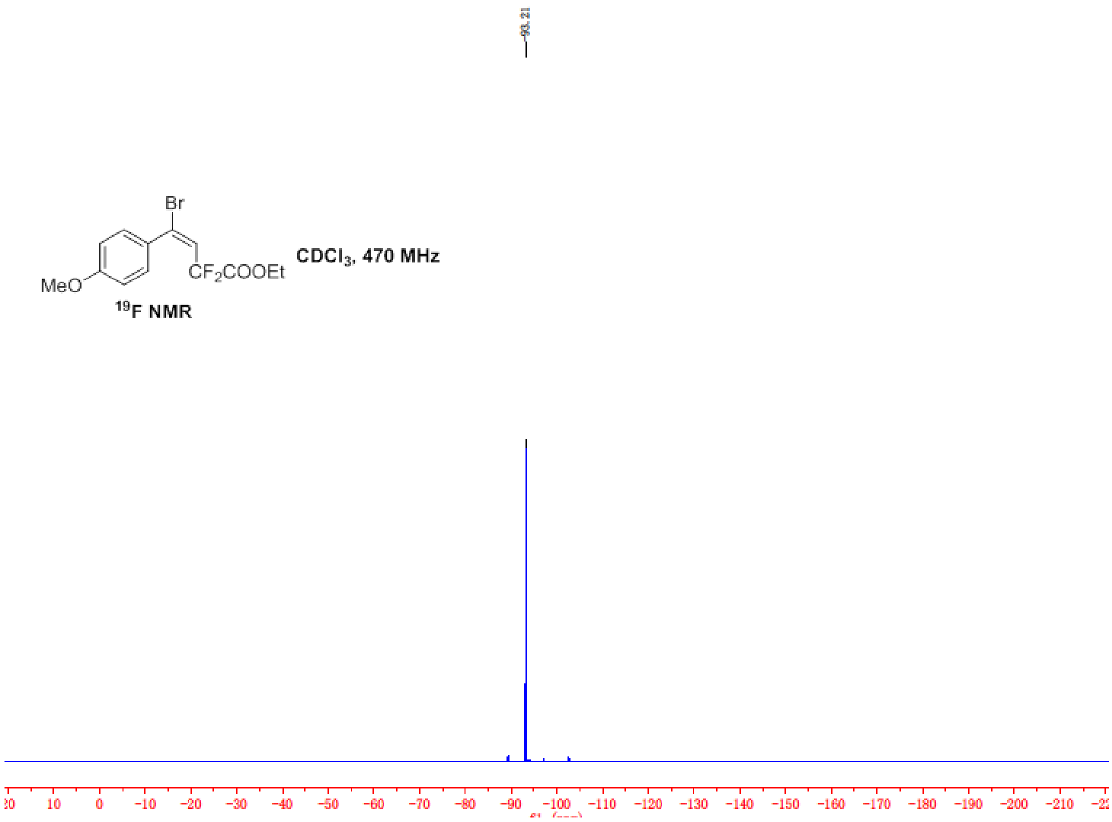


-93.12
Br
nAm
CF2COOEt
CDCl3, 470 MHz
19F NMR



7.33
7.32
6.87
6.85
6.46
6.44
6.42
4.02
4.00
3.99
3.97
3.82
1.21
1.19
1.18
Br
MeO
CF2COOEt
CDCl3, 500 MHz
1H NMR
2.02
2.09
1.00
2.18
3.12
3.24


161.65
161.58
161.32
159.79
133.00
132.94
132.84
129.30
128.37
123.53
123.30
123.07
112.43
112.15
110.18
108.20
62.13
54.33
12.69
Br
MeO
CF2COOEt
CDCl3, 126 MHz
13C NMR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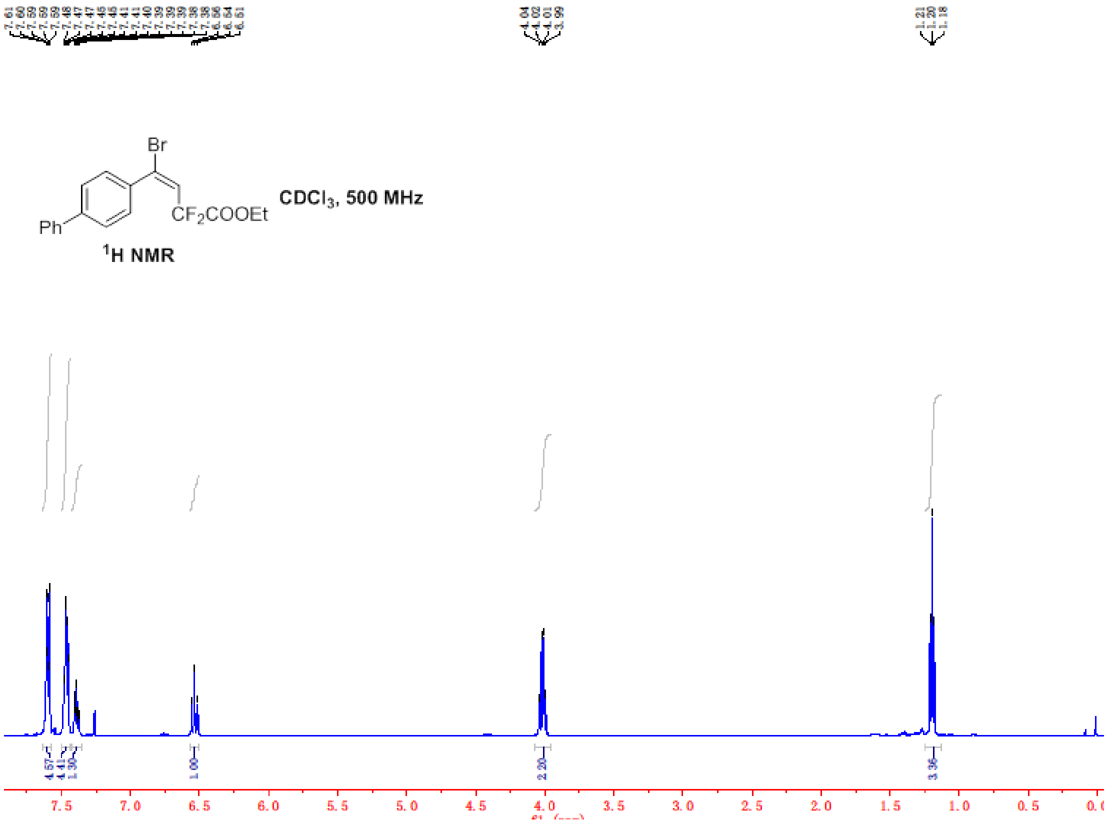
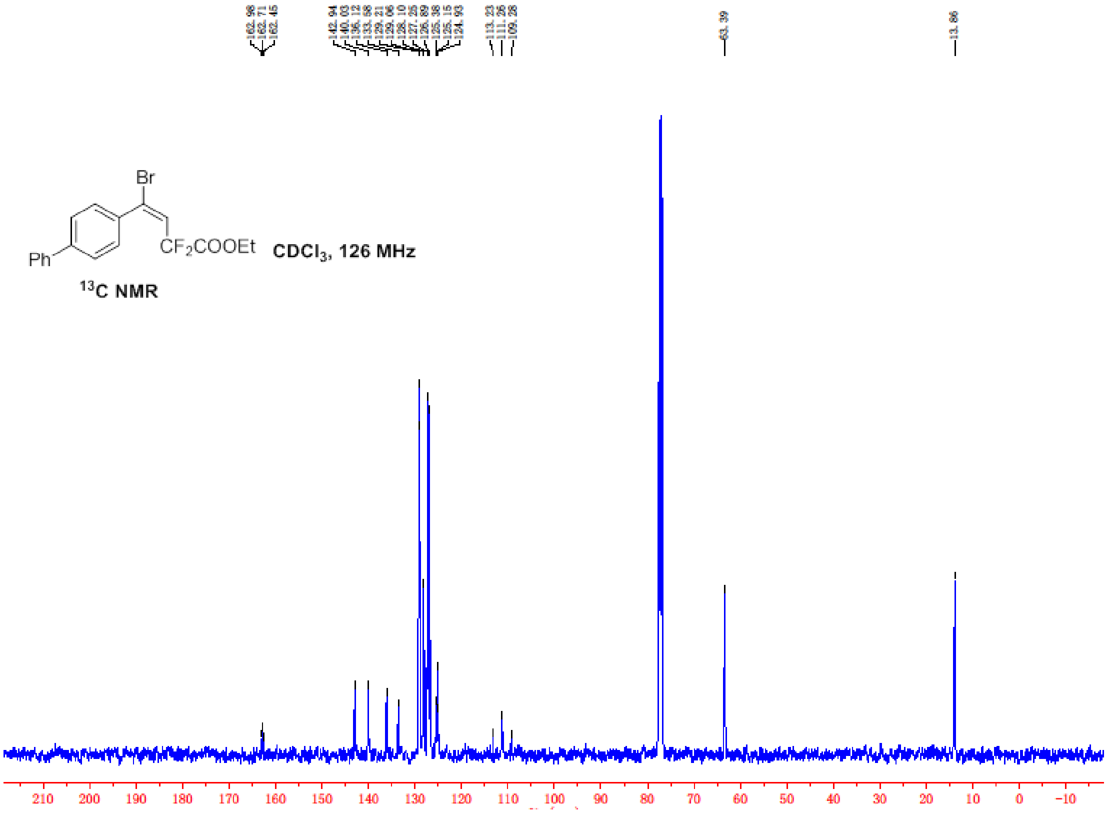
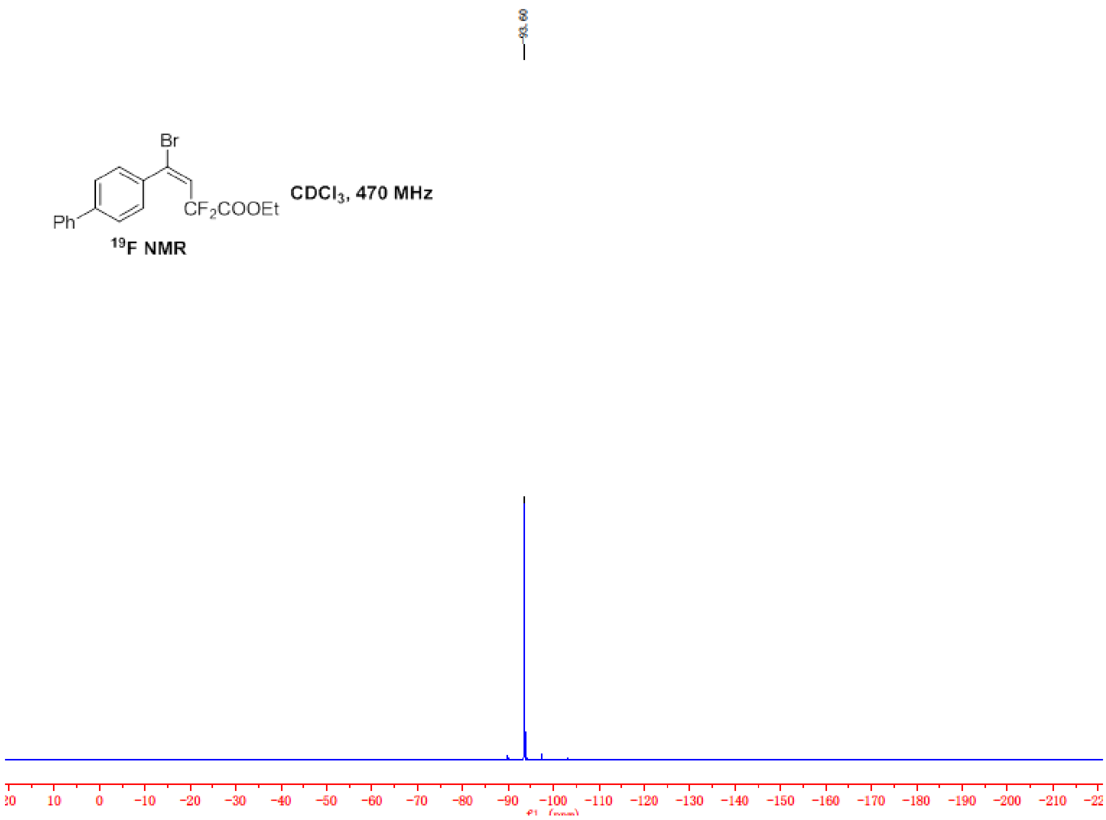
Br
MeO
CF2COOEt
CDCl3, 470 MHz
19F NMR



7.61 7.60 7.59 7.59 7.48 7.47 7.46 7.45 7.41 7.40 7.39 7.39 7.39 7.38 7.38 6.56 6.54 6.51
4.04 4.02 4.01 3.99
1.21 1.20 1.18
Br
Ph
CF2COOEt
CDCl3, 500 MHz
1H NMR
4.57
4.41
1.30
1.00
2.20
3.36
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



162.98 162.71 162.45
142.94 140.03 136.12 133.58 129.21 129.06 128.10 127.25 126.89 125.38 125.15 124.93
113.23 111.26 109.28
63.39
13.86
Br
Ph
CF2COOEt
CDCl3, 126 MHz
13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



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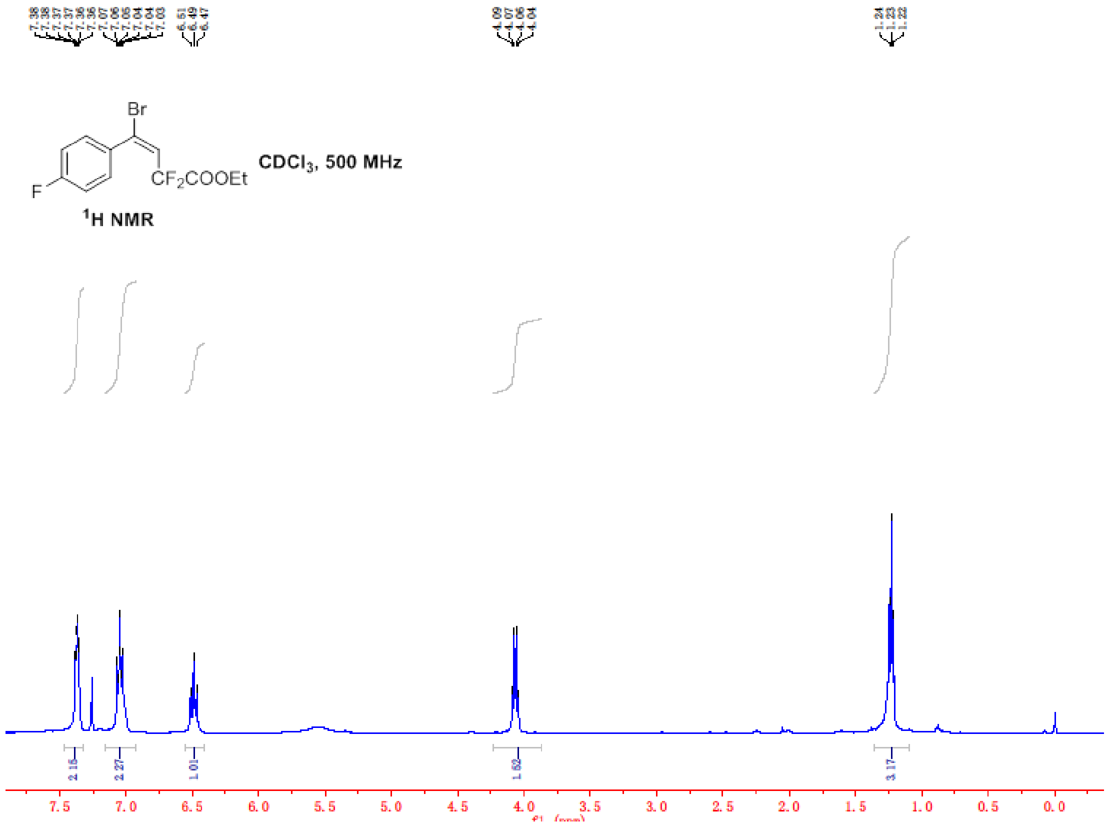
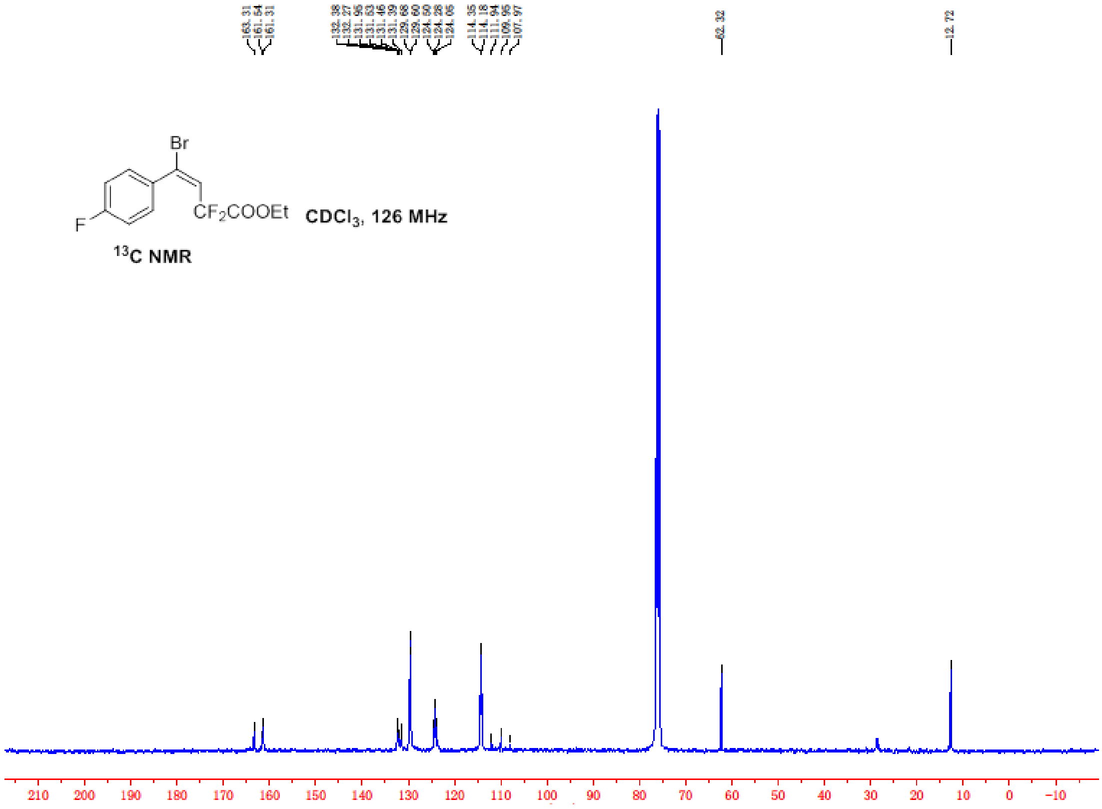
Br
Ph
CF2COOEt
CDCl3, 470 MHz
19F NMR
f1 (ppm)



7.38 7.38 7.37 7.37 7.36 7.07 7.06 7.05 7.04 7.04 7.03 6.51 6.49 6.47
4.09 4.07 4.06 4.04
1.24 1.23 1.22
Br
F
CF2COOEt
CDCl3, 500 MHz
1H NMR
2.15 2.27 1.01 1.52 3.17
f1 (ppm)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161.31
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131.95
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131.46
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129.60
124.50
124.28
124.05
114.35
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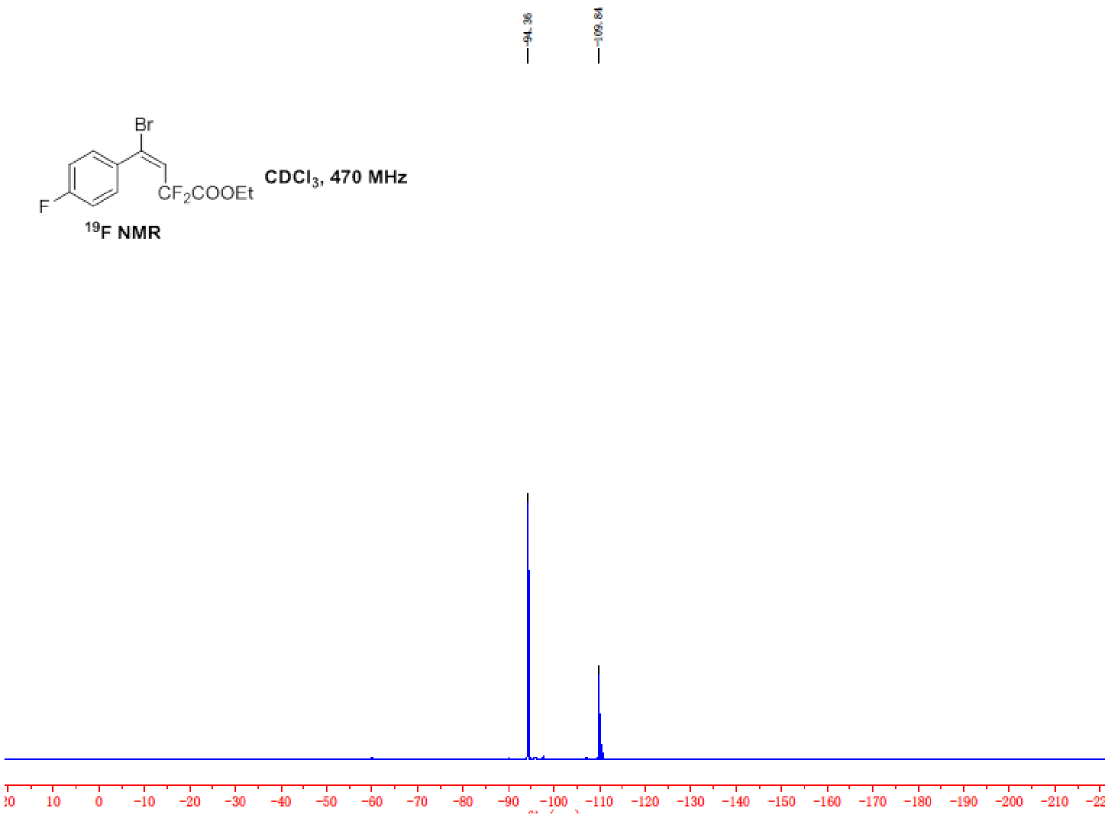
111.94
109.95
107.97
62.32
12.72
Br
F
CF2COOEt
CDCl3, 126 MHz
13C NMR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Br
F
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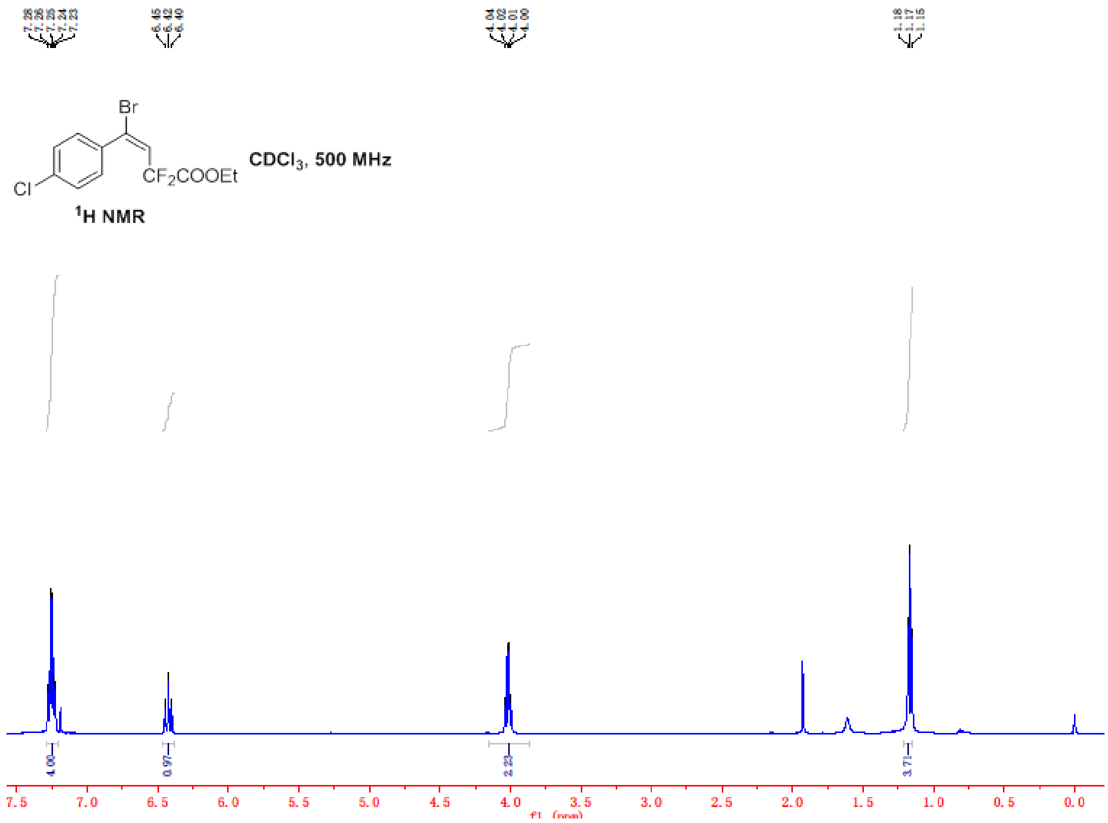
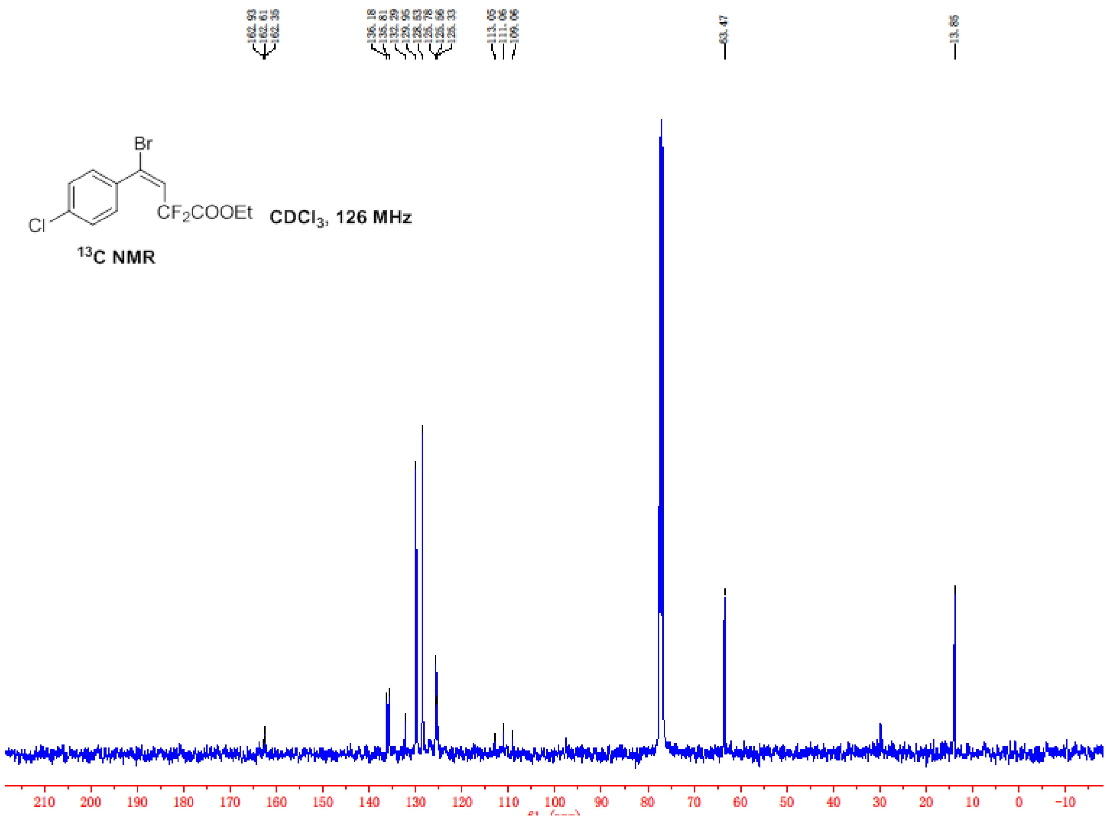
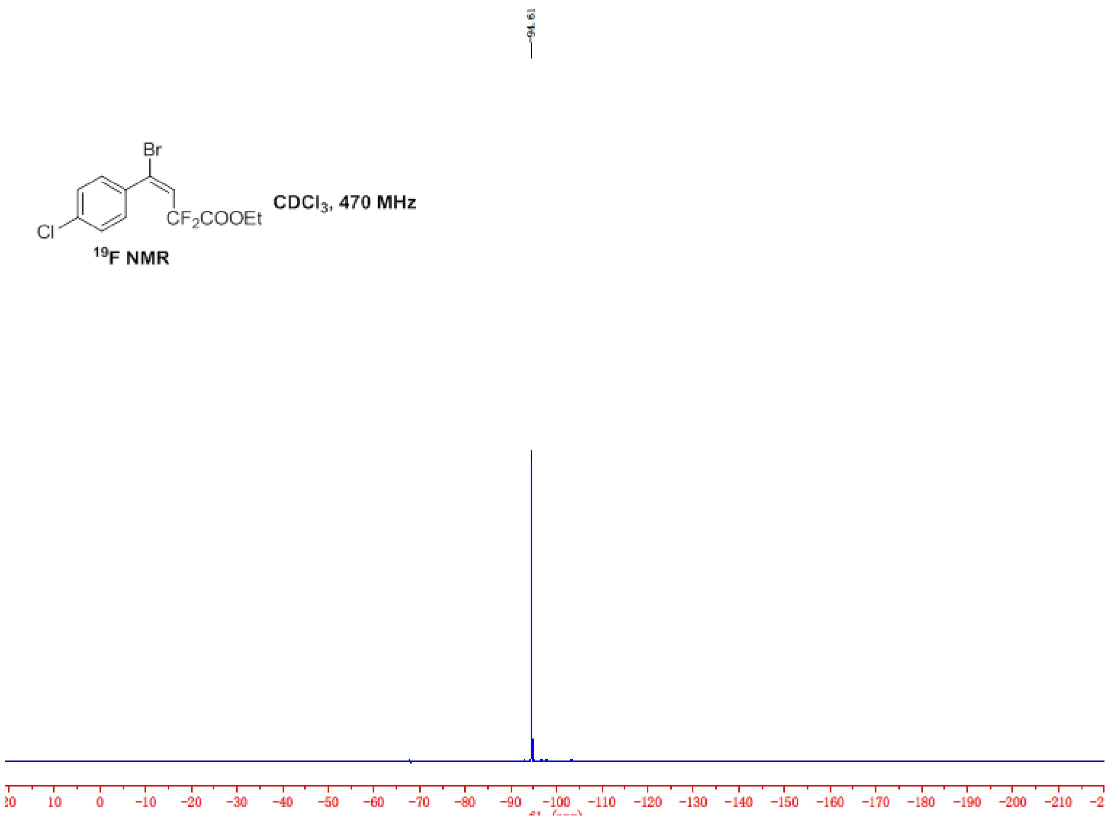
CDCl3, 470 MHz
19F NMR



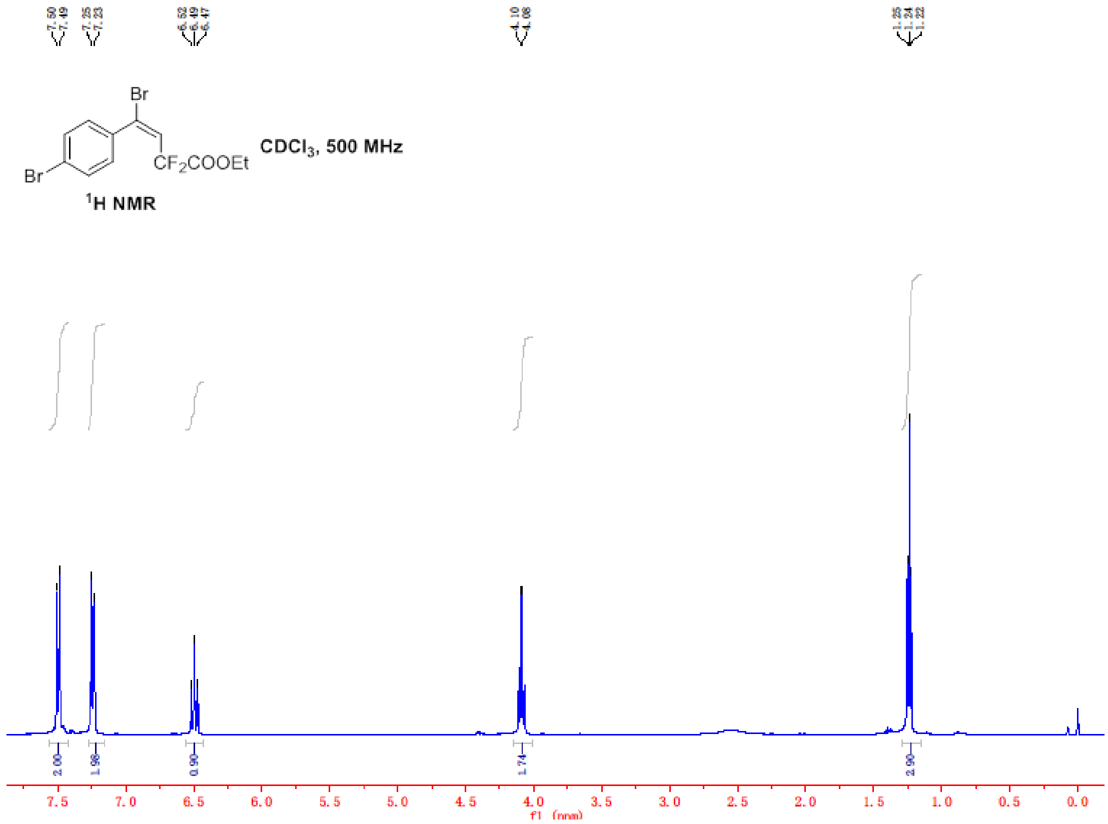
CDCl$_3$, 500 MHz
^{1}H NMR



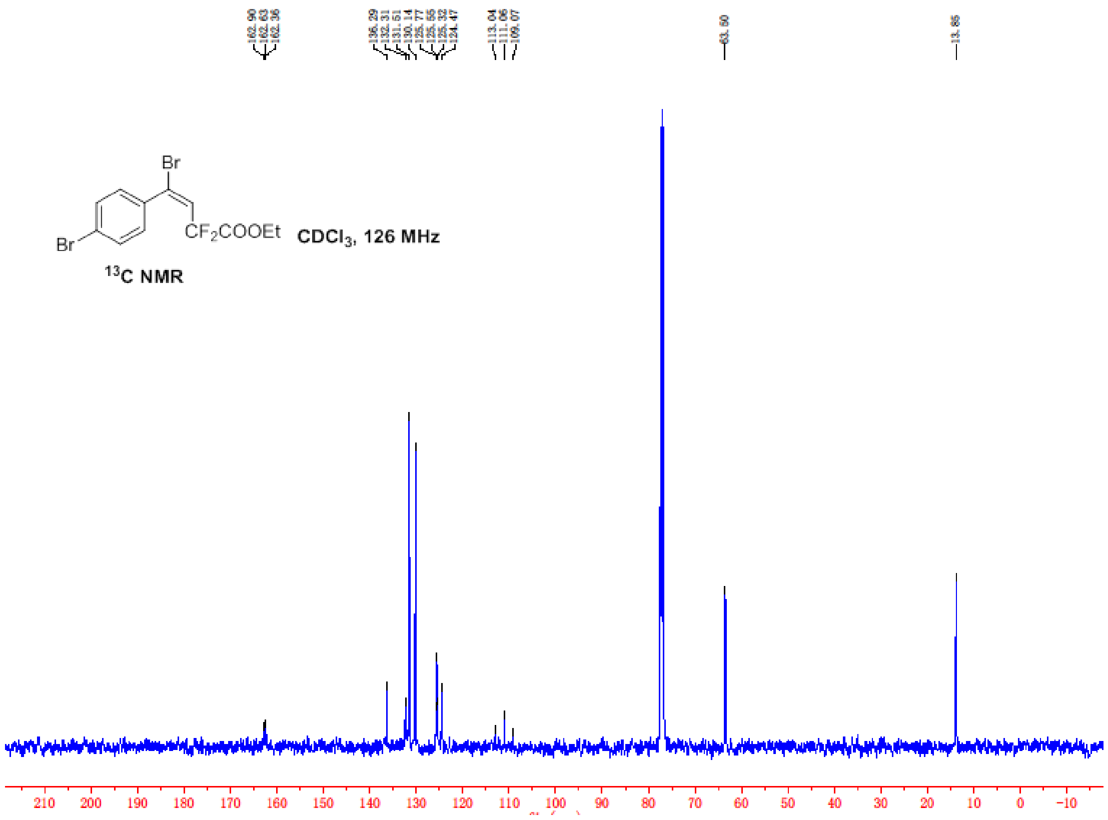
CDCl$_3$, 126 MHz
^{13}C NMR



-94.61
Br
Cl
CF2COOEt
CDCl3, 470 MHz
19F NMR
f1 (ppm)



7.50
7.49
7.25
7.23
6.52
6.49
6.47
4.10
4.08
1.25
1.24
1.22
Br
Br
CF2COOEt
CDCl3, 500 MHz
1H NMR
2.00
1.98
0.90
1.74
2.90
f1 (ppm)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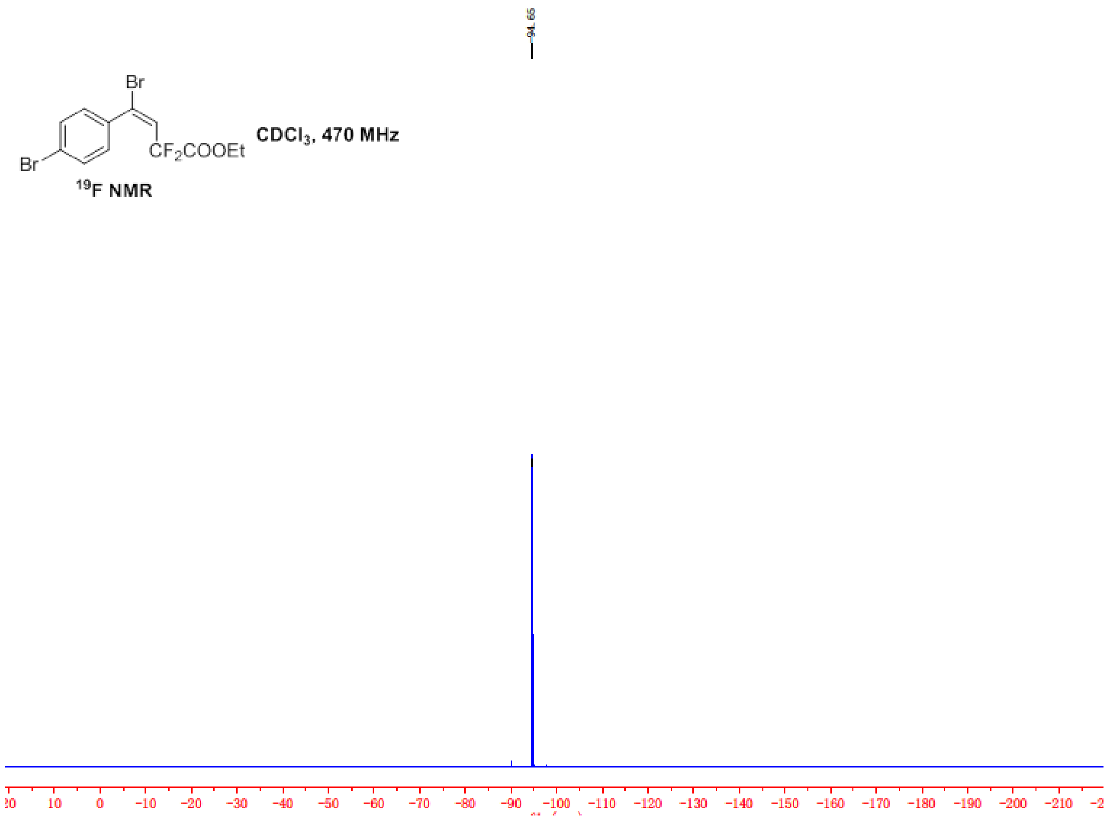
162.36
136.29
132.31
131.51
130.14
125.77
125.55
125.32
124.47
113.04
111.06
109.07
63.60
13.85
Br
Br
CF2COOEt
CDCl3, 126 MHz
13C NMR
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


-94.65
Br
Br
CF2COOEt
CDCl3, 470 MHz
19F NMR
10
0
-10
-20
-30
-40
-50
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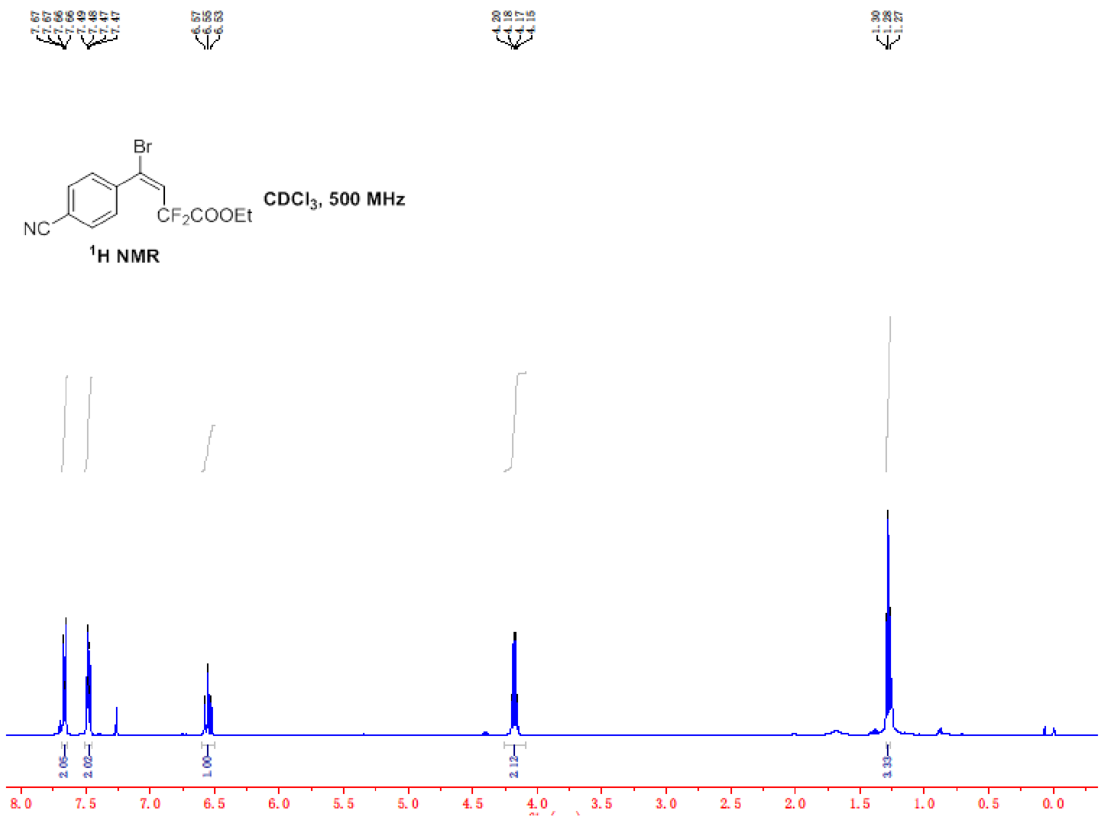
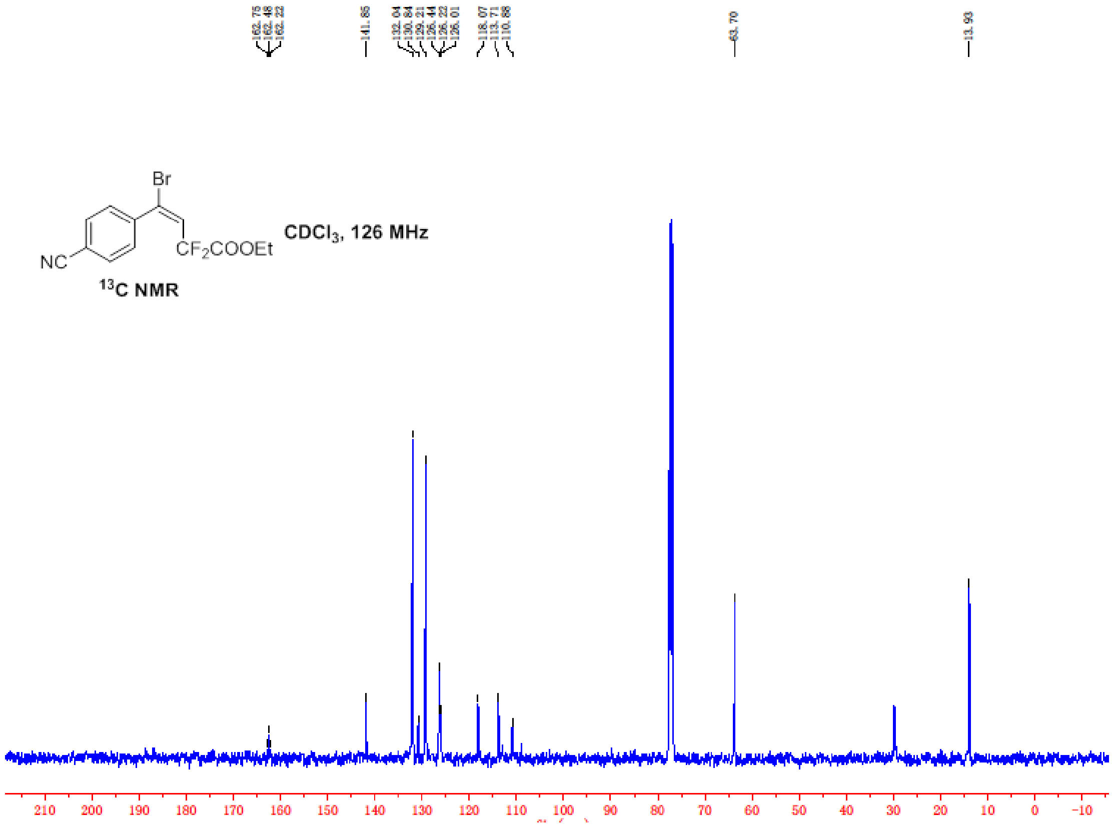
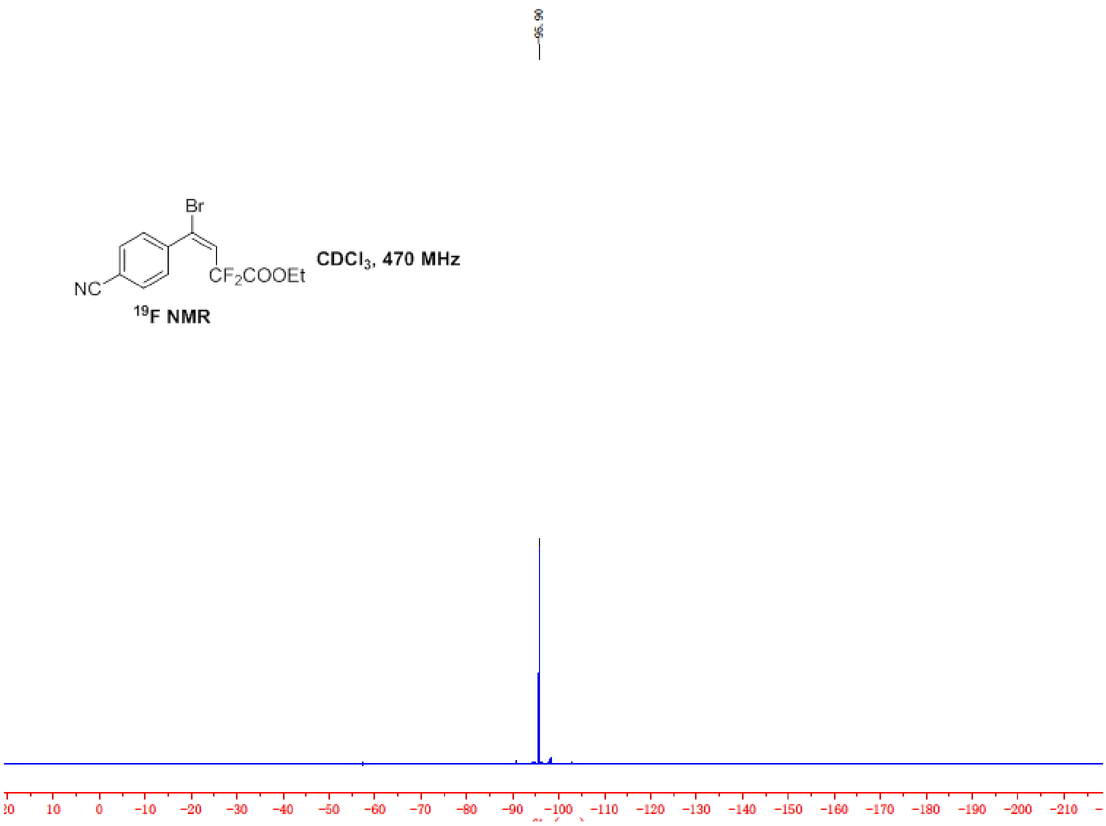
-180
-190
-200
-210


7.67 7.67 7.66 7.49 7.48 7.47 7.47
6.57 6.55 6.53
4.20 4.18 4.17 4.15
1.30 1.28 1.27
Br
NC
CF2COOEt
CDCl3, 500 MHz
1H NMR
2.05 2.02 1.00 2.12 3.33
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


162.75 162.48 162.22
141.85
132.04 130.84 129.21 126.44 126.22 126.01
118.07 113.71 110.88
63.70
13.93
Br
NC
CF2COOEt
CDCl3, 126 MHz
13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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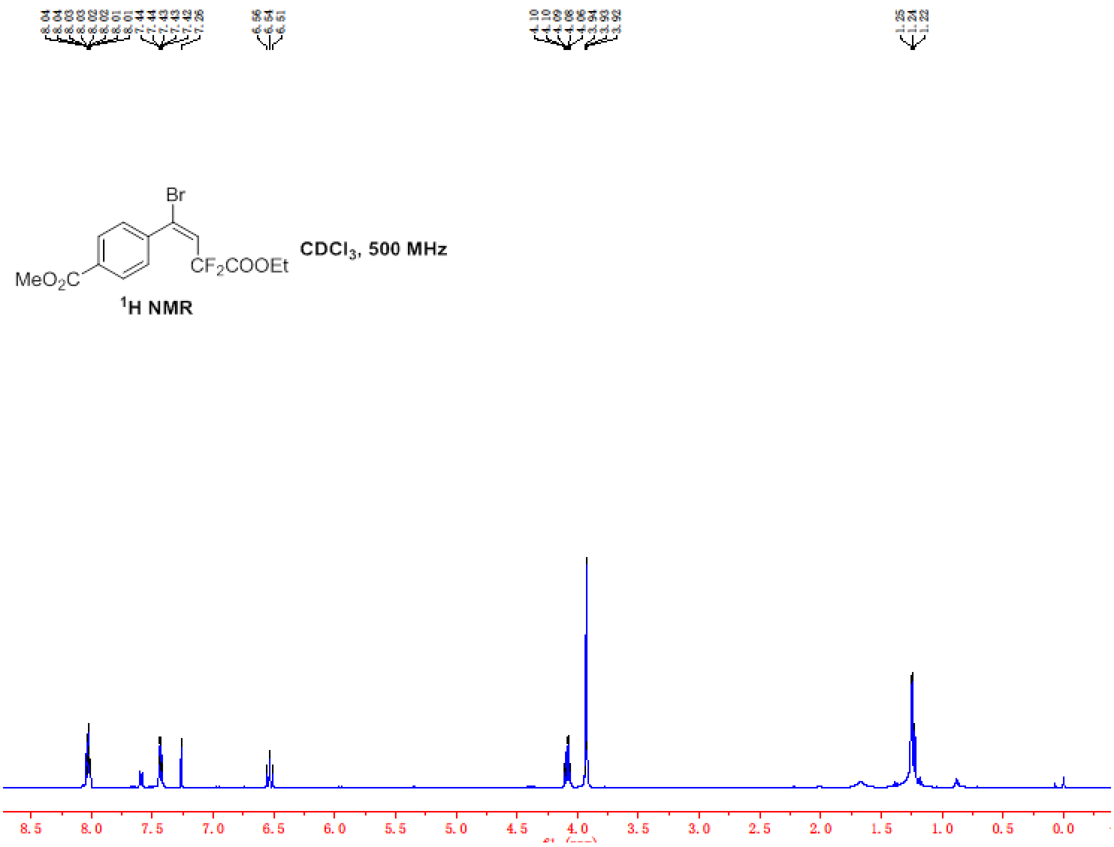
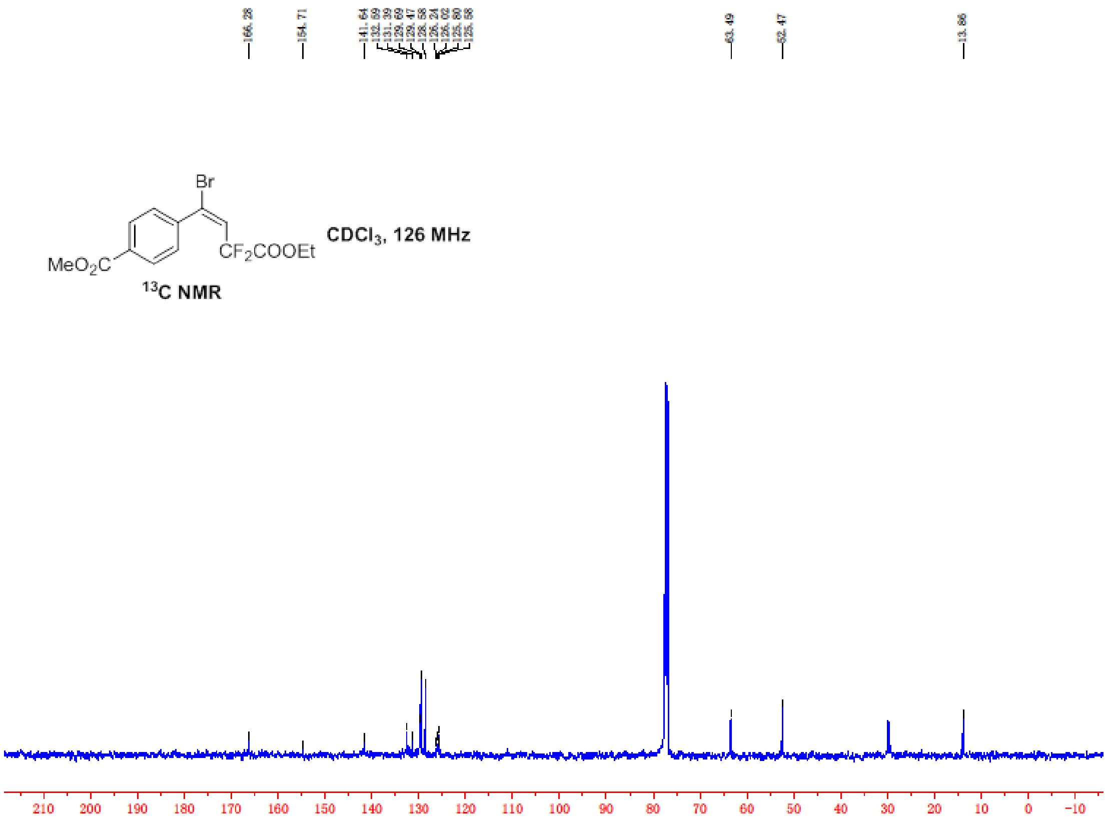
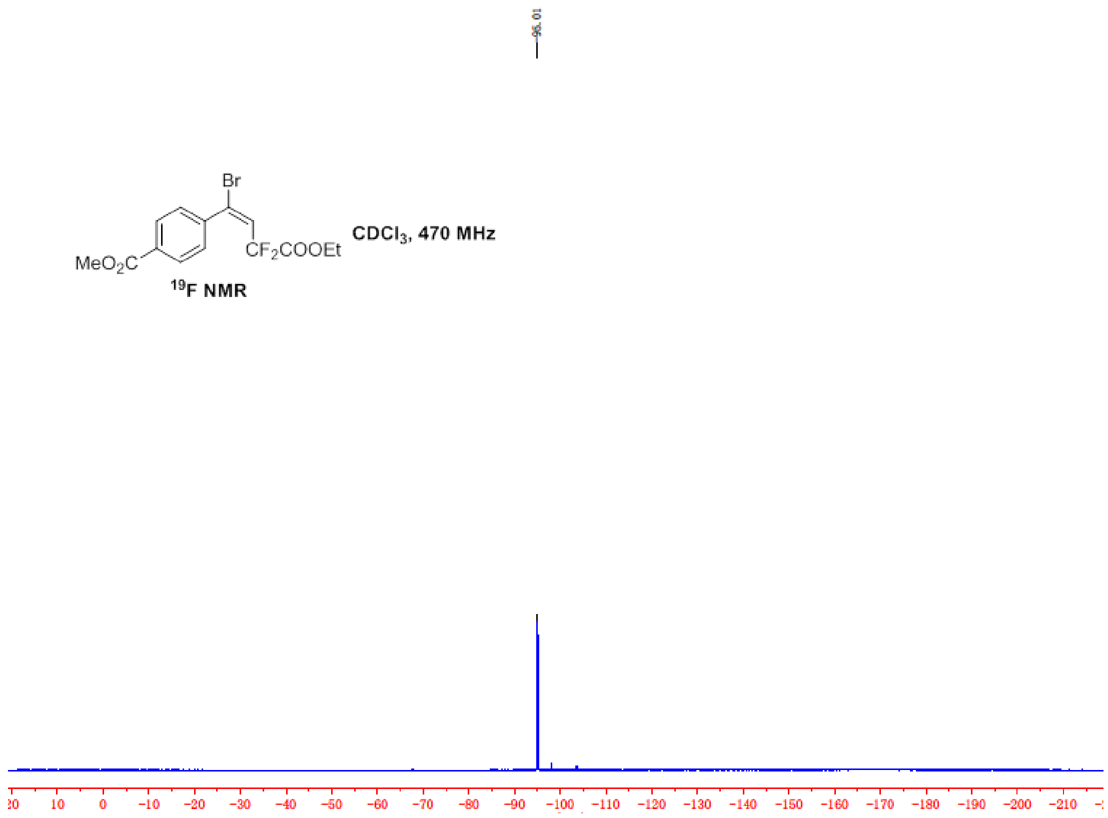
Br
NC
CF2COOEt
CDCl3, 470 MHz
19F NMR


8.04
8.04
8.03
8.03
8.02
8.02
8.01
8.01
7.44
7.44
7.43
7.43
7.42
7.26
6.56
6.54
6.51
4.10
4.10
4.09
4.08
4.06
3.94
3.93
3.92
1.25
1.24
1.22
Br
MeO2C
CF2COOEt
CDCl3, 500 MHz
1H NMR



166.28
154.71
141.64
132.59
131.39
129.69
129.47
128.58
126.24
126.02
125.80
125.58
63.49
52.47
13.86
Br
MeO_2C
CF_2COOEt
$CDCl_3$, 126 MHz
^{13}C NMR



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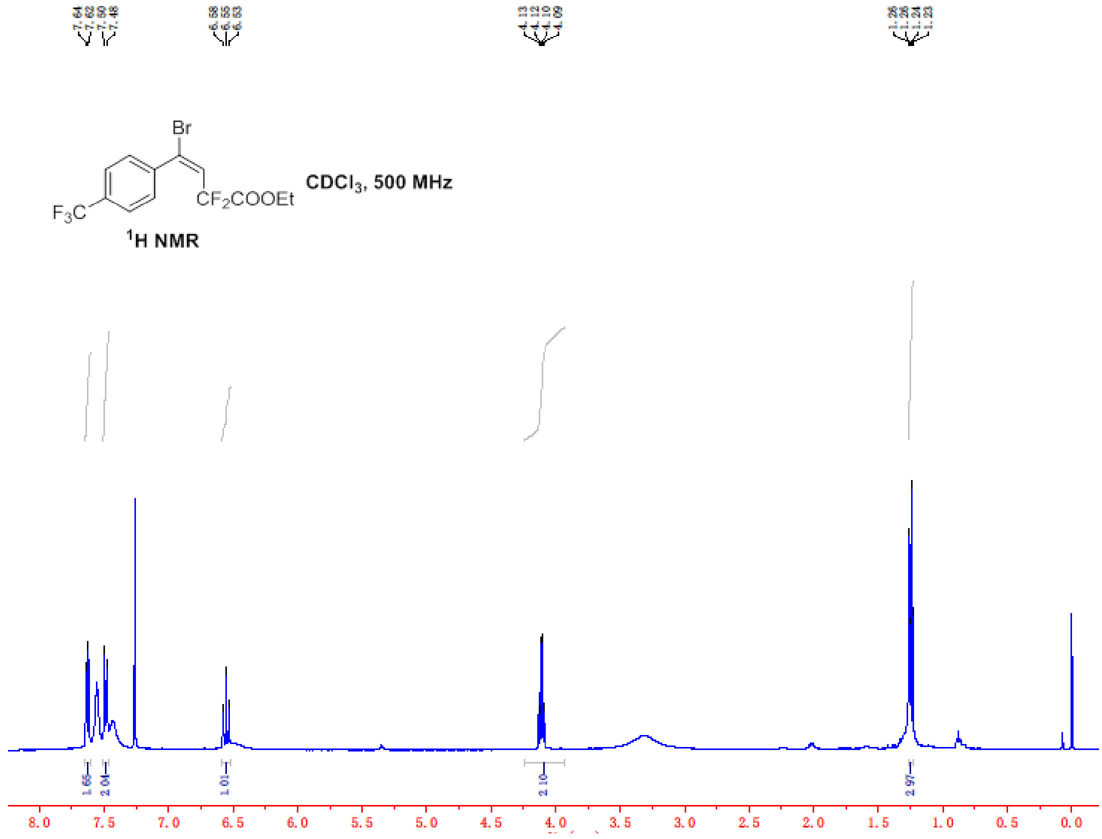
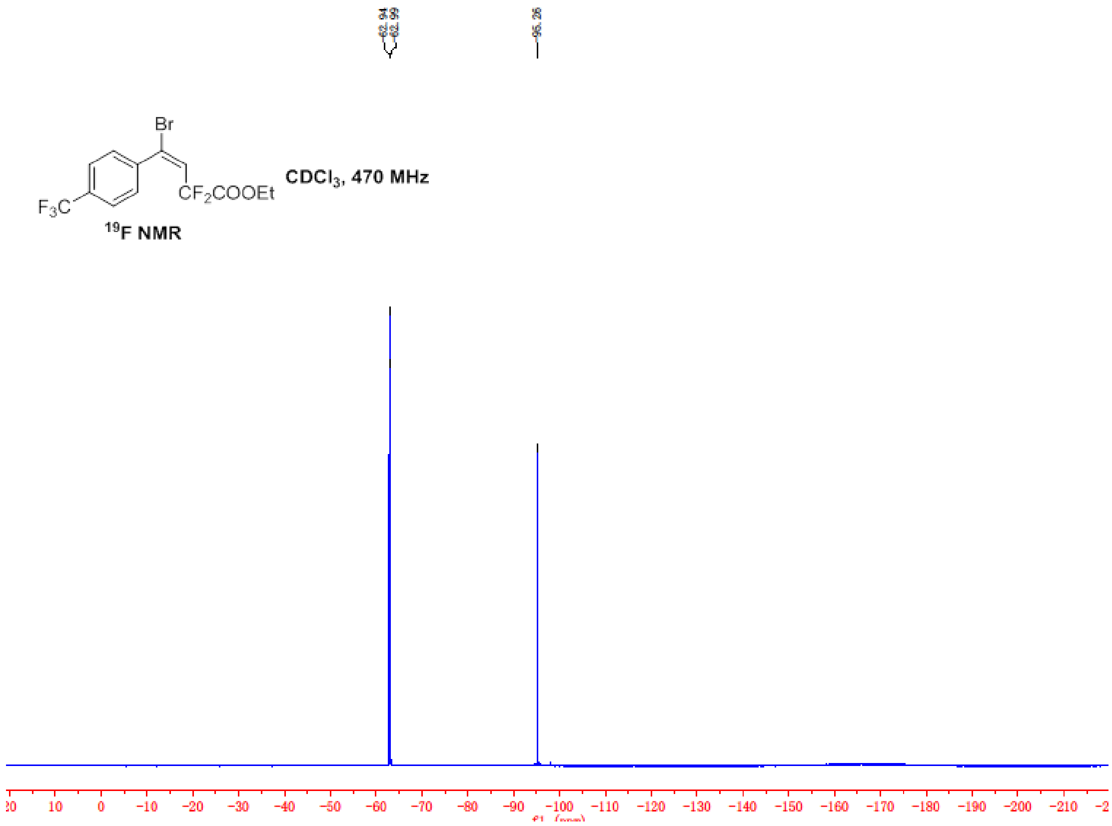
Br
MeO_2C
CF_2COOEt
$CDCl_3$, 470 MHz
^{19}F NMR



7.64
7.62
7.50
7.48
6.58
6.55
6.53
4.13
4.12
4.10
4.09
1.26
1.26
1.24
1.23
Br
F3C
CF2COOEt
CDCl3, 500 MHz
1H NMR
1.65
2.04
1.01
2.10
2.97
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



-62.94
-62.99
-95.26
Br
F3C
CF2COOEt
CDCl3, 470 MHz
19F NMR
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
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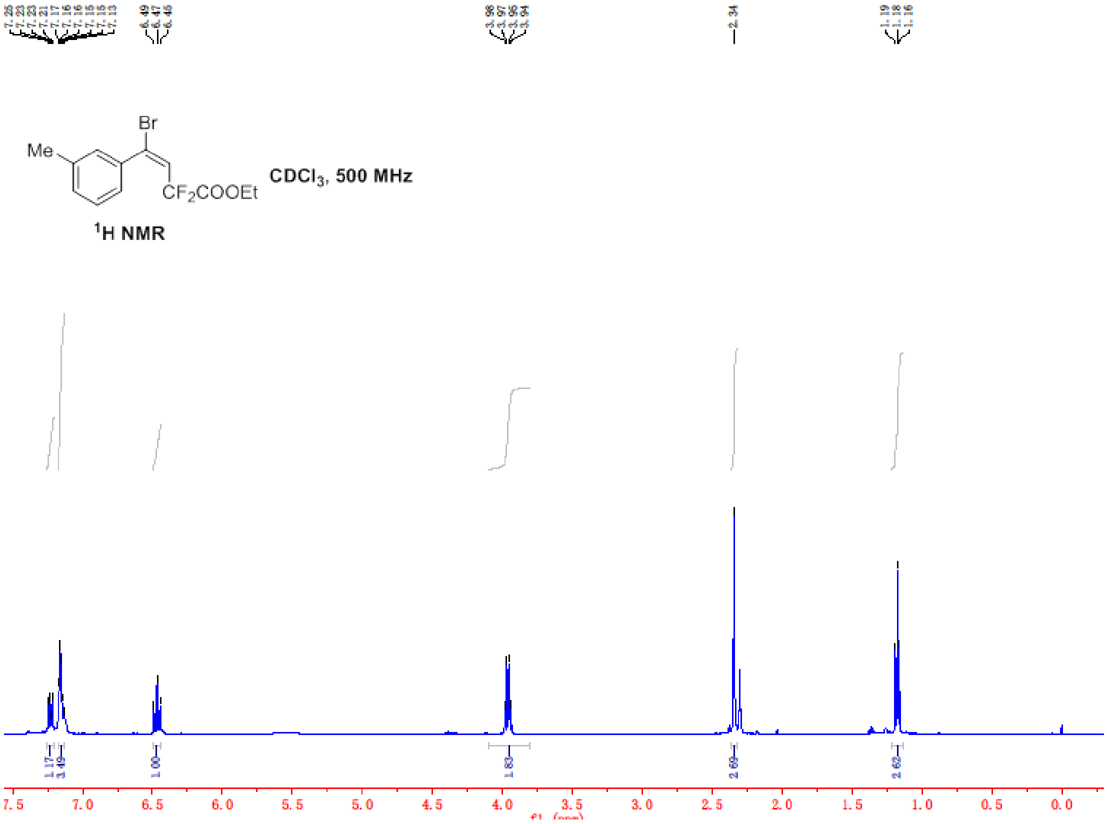
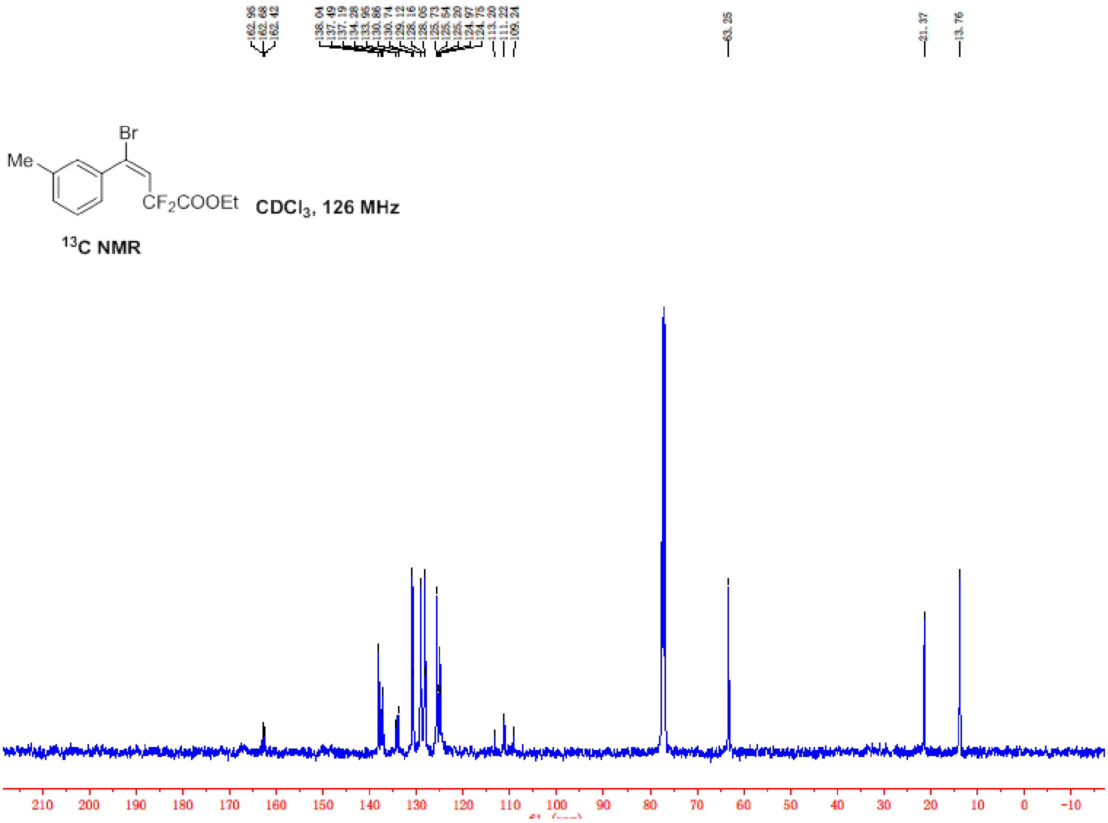
-180
-190
-200
-210


Br
Me
CF2COOEt
CDCl3, 500 MHz
1H NMR
7.25 7.23 7.23 7.21 7.17 7.16 7.16 7.15 7.15 7.13
6.49 6.47 6.45
3.98 3.97 3.95 3.94
2.34
1.19 1.18 1.16
1.17 3.49 1.00 1.83 2.69 2.62
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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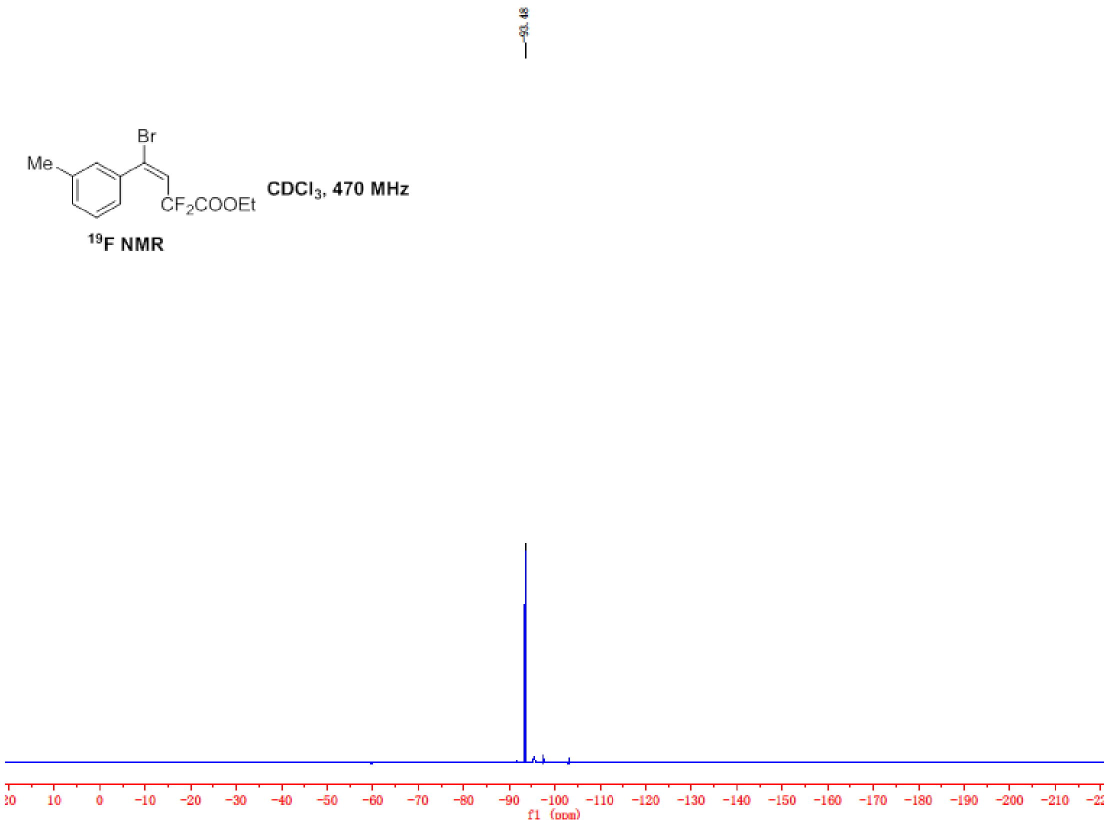
Me
CF2COOEt
CDCl3, 126 MHz
13C NMR
162.95 162.68 162.42
138.04 137.49 137.19 134.28 133.95 130.86 130.74 129.12 128.16 128.05 125.73 125.54 125.20 124.97 124.75 113.20 111.22 109.24
63.25
21.37
13.76
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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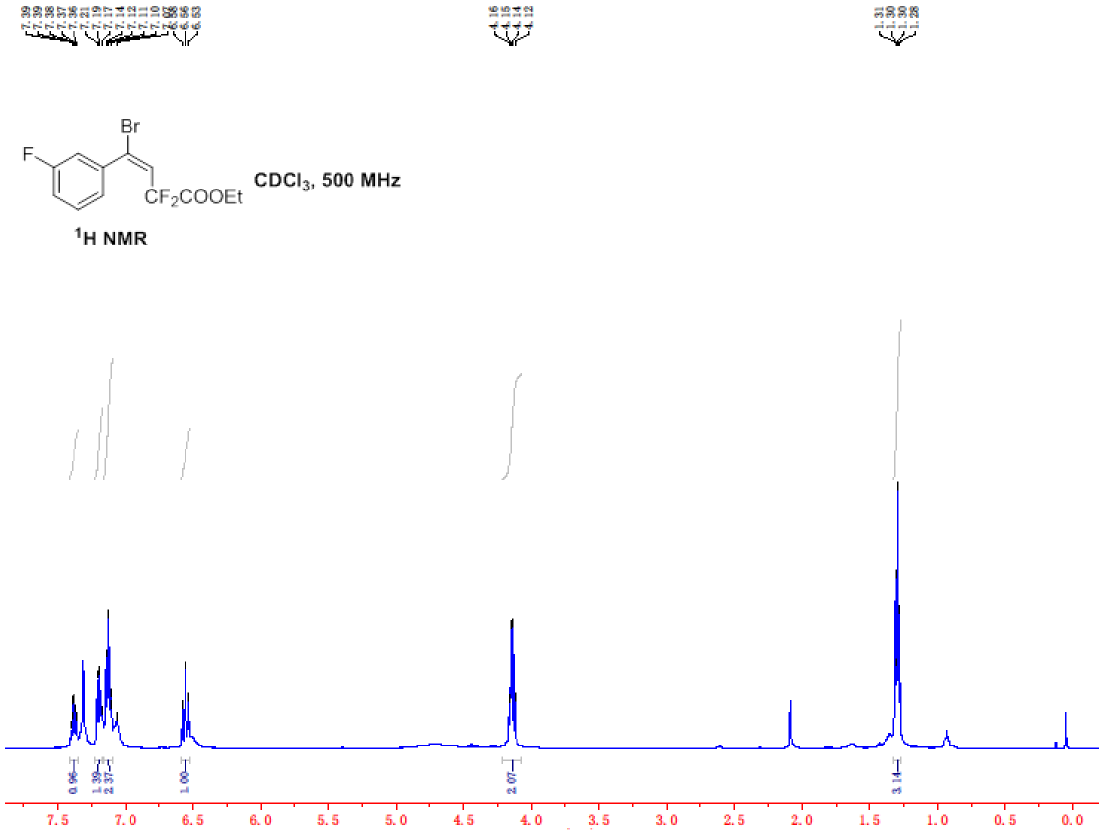
Me
CF2COOEt
CDCl3, 470 MHz
19F NMR
f1 (ppm)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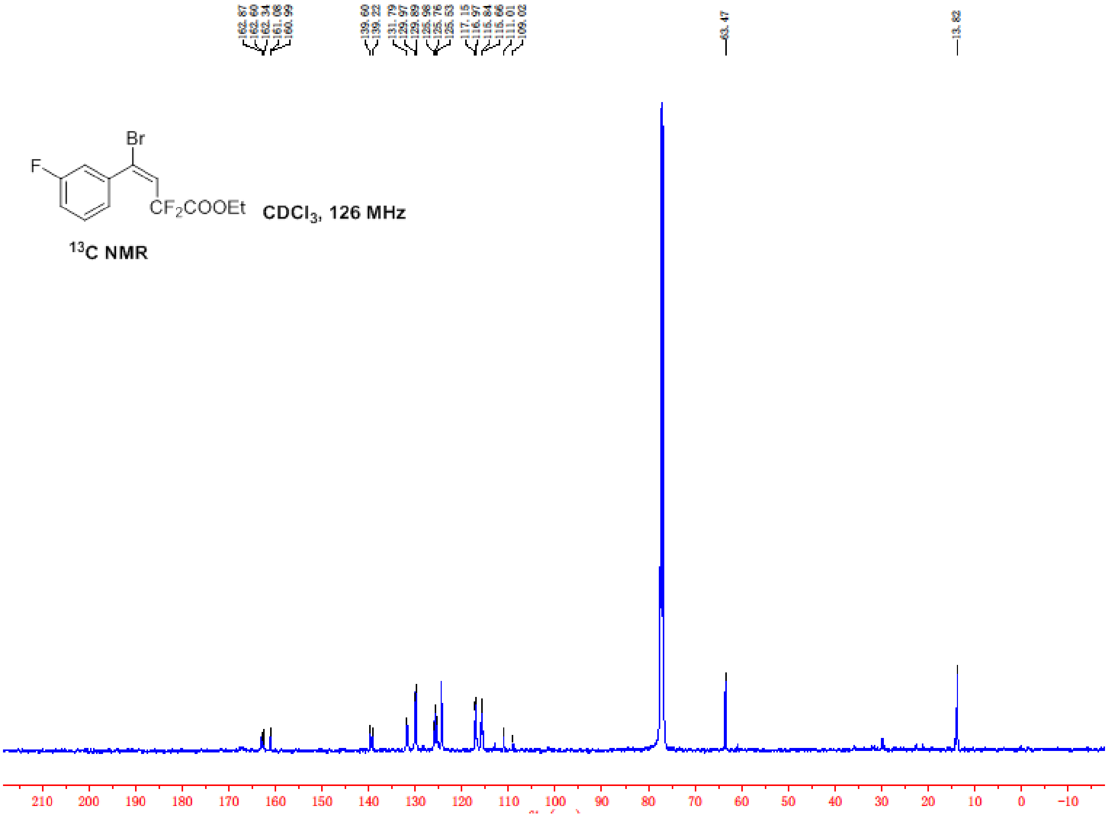
F
CF2COOEt
CDCl3, 500 MHz
1H NMR
0.96
1.39
2.37
1.00
2.07
3.14



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162.60
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161.08
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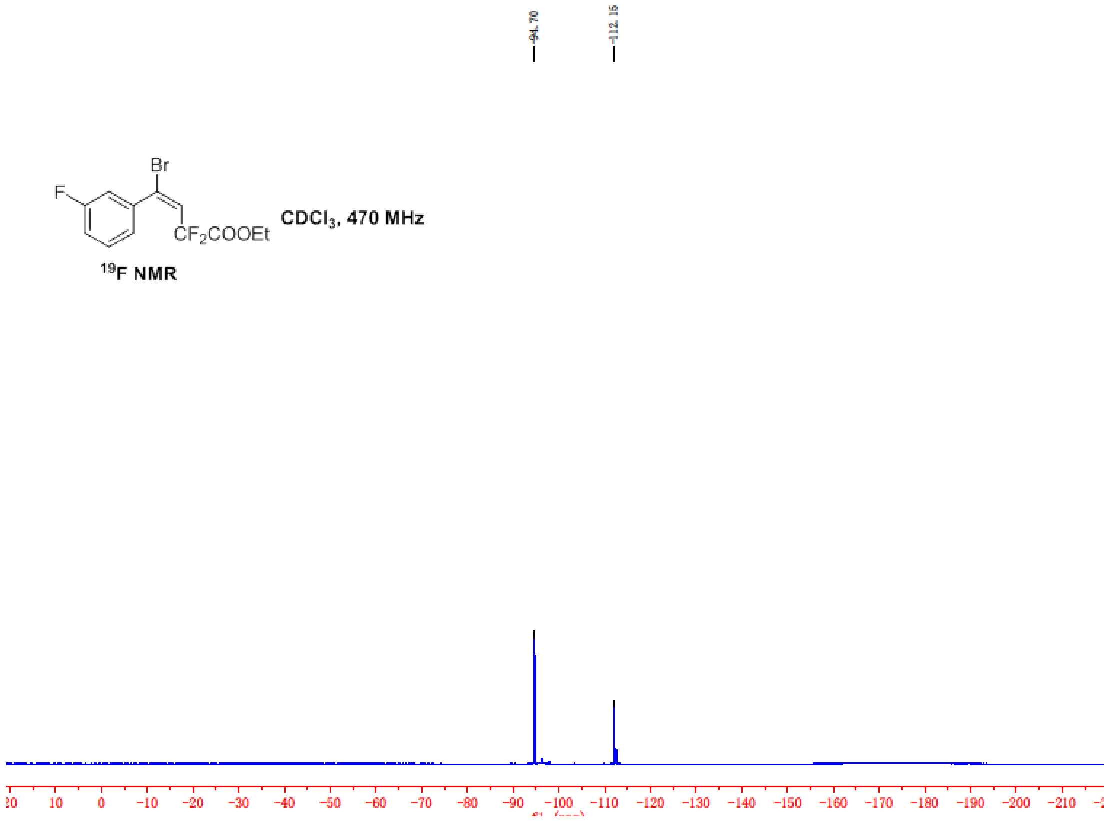
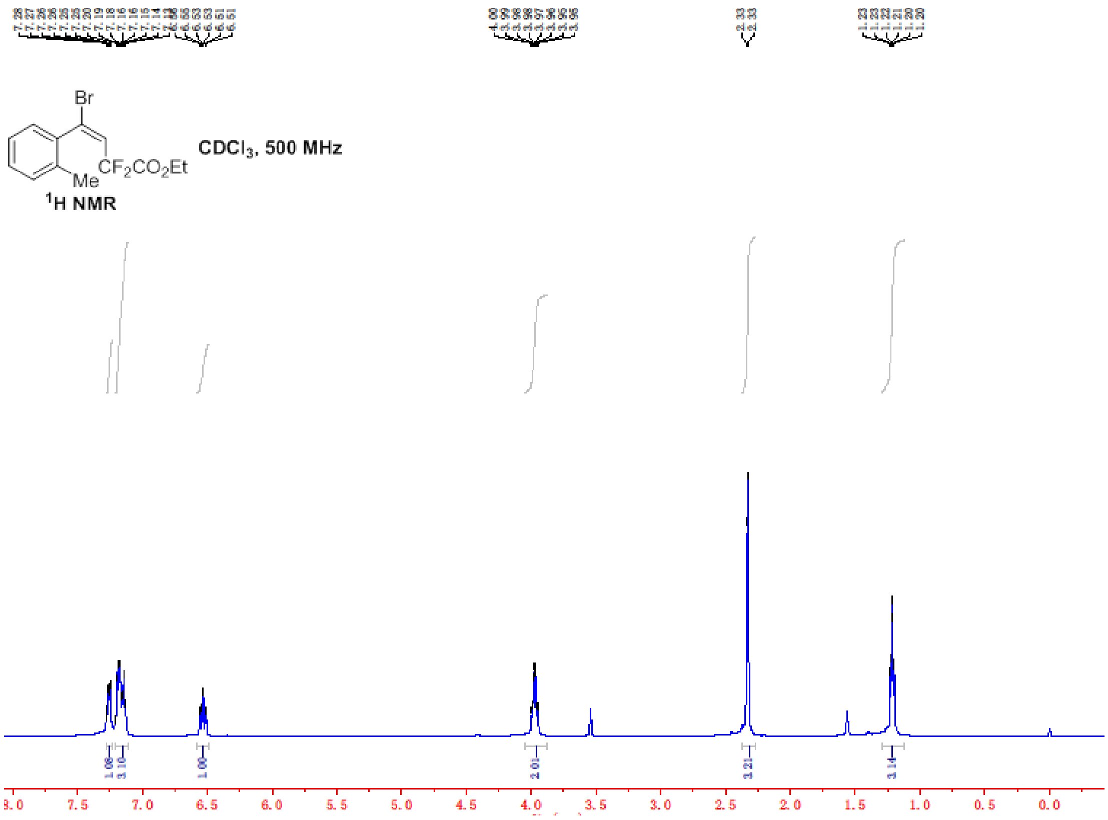
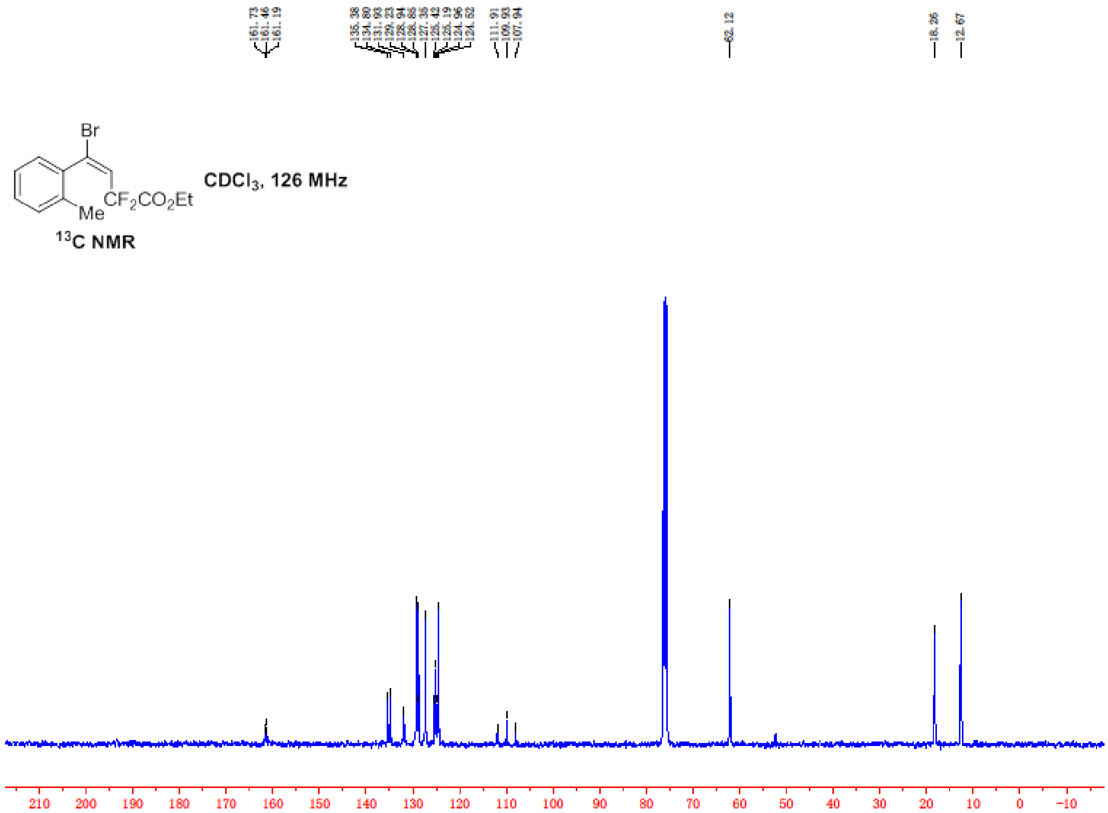
139.60
139.22
131.79
129.97
129.89
125.98
125.76
125.53
117.15
116.97
115.84
115.66
111.01
109.02
63.47
13.82
Br
F
CF2COOEt
CDCl3, 126 MHz
13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



-94.70
-112.15
Br
F
CF2COOEt
CDCl3, 470 MHz
19F NMR
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210


Br
CF2CO2Et
Me
CDCl3, 500 MHz
1H NMR


161.73
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135.38
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129.23
128.94
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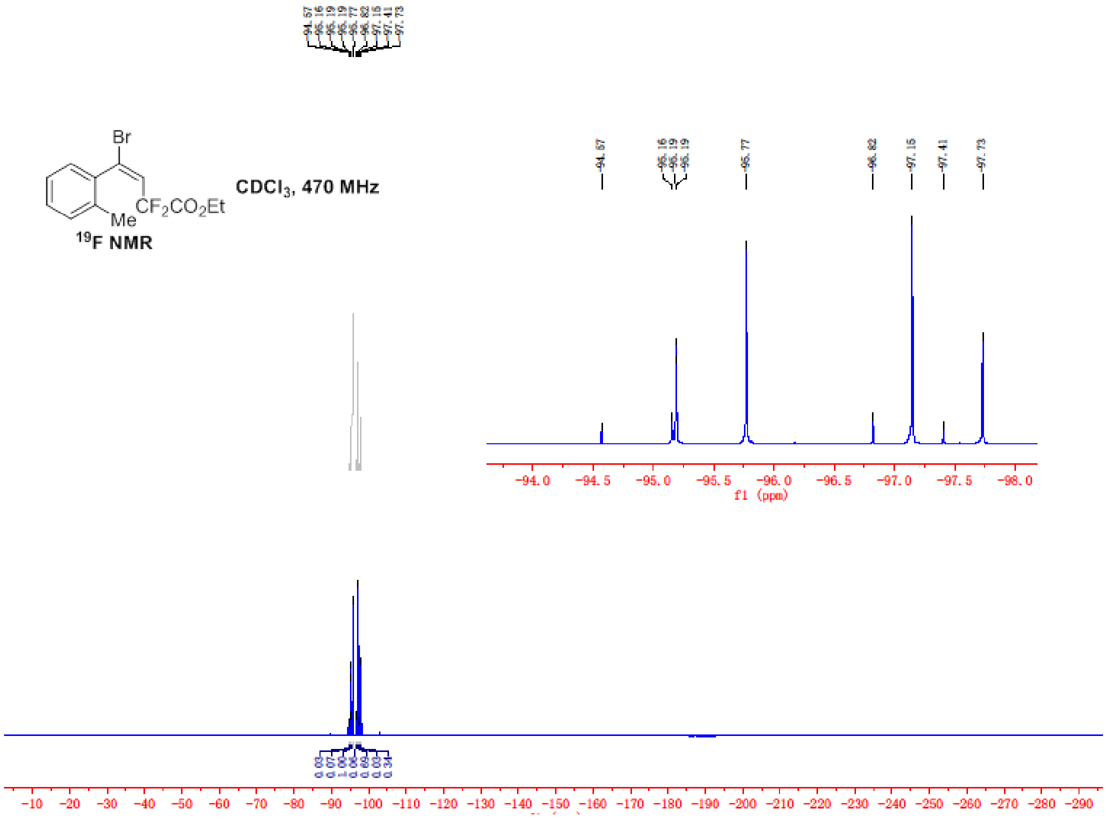
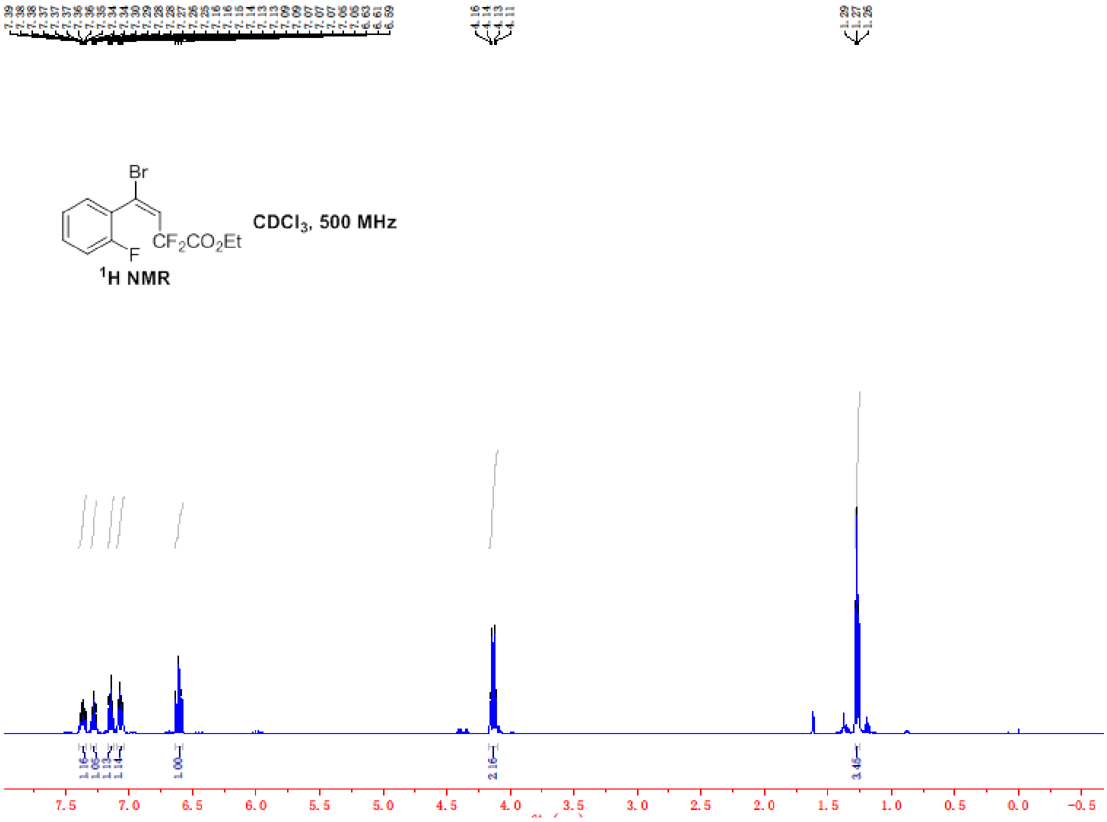
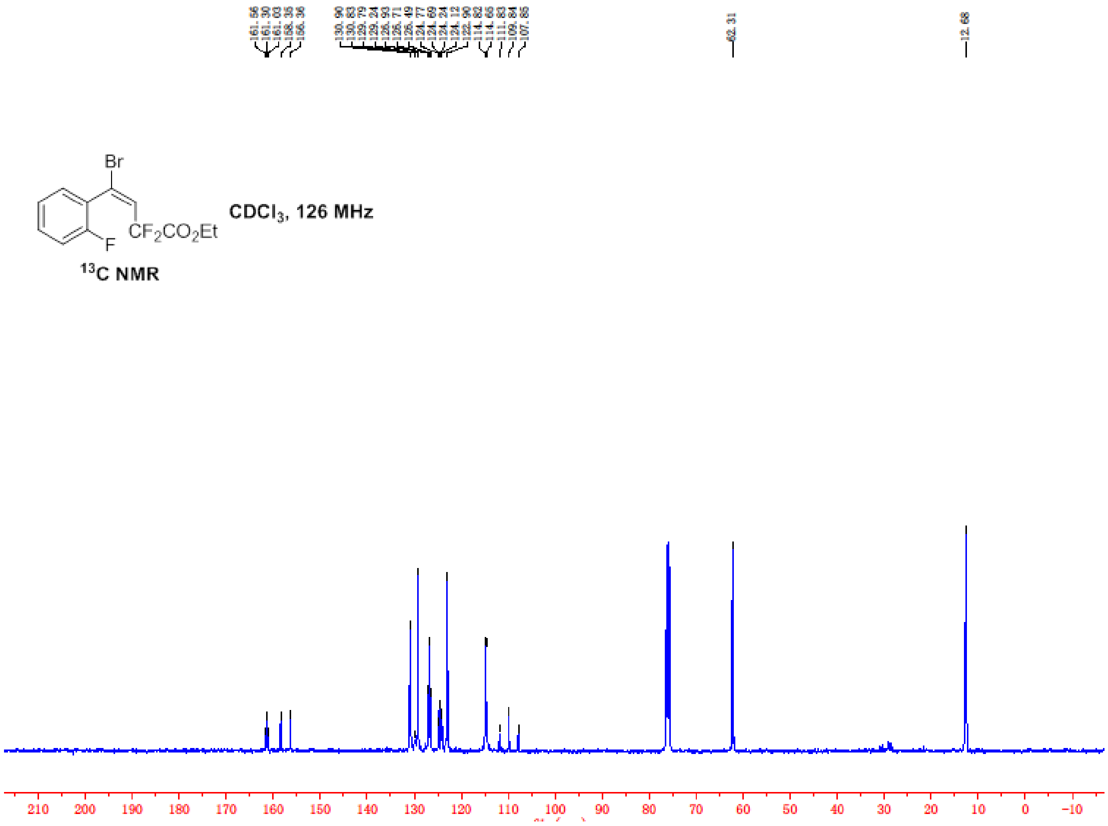
125.42
125.19
124.96
124.52
111.91
109.93
107.94
62.12
18.26
12.67
Br
CF2CO2Et
Me
CDCl3, 126 MHz
13C NMR


Br
Me
CF_2CO_2Et
$CDCl_3$, 470 MHz
^{19}F NMR
-94.57
-95.16
-95.19
-95.19
-95.77
-96.82
-97.15
-97.41
-97.73
f1 (ppm)


Br
F
CF_2CO_2Et
$CDCl_3$, 500 MHz
^{1}H NMR
4.16
4.14
4.13
4.11
1.29
1.27
1.26
1.16
1.05
1.13
1.14
1.00
2.16
3.45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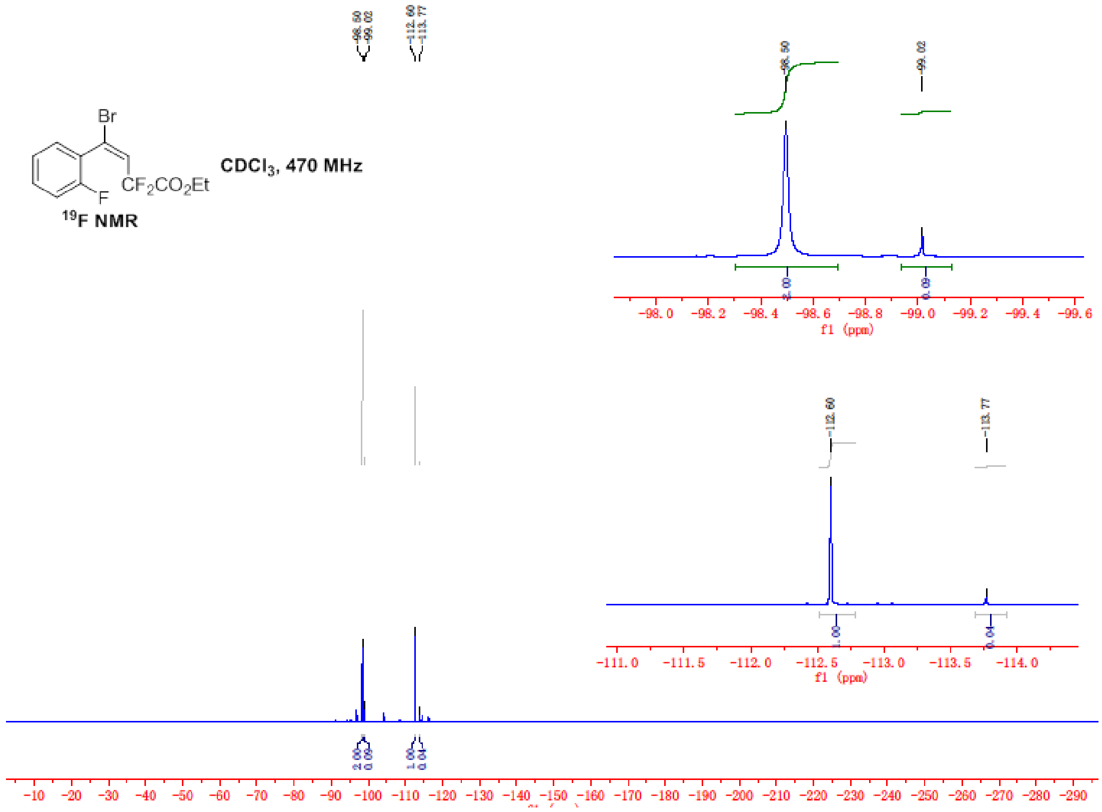
F
CF2CO2Et
13C NMR
CDCl3, 126 MHz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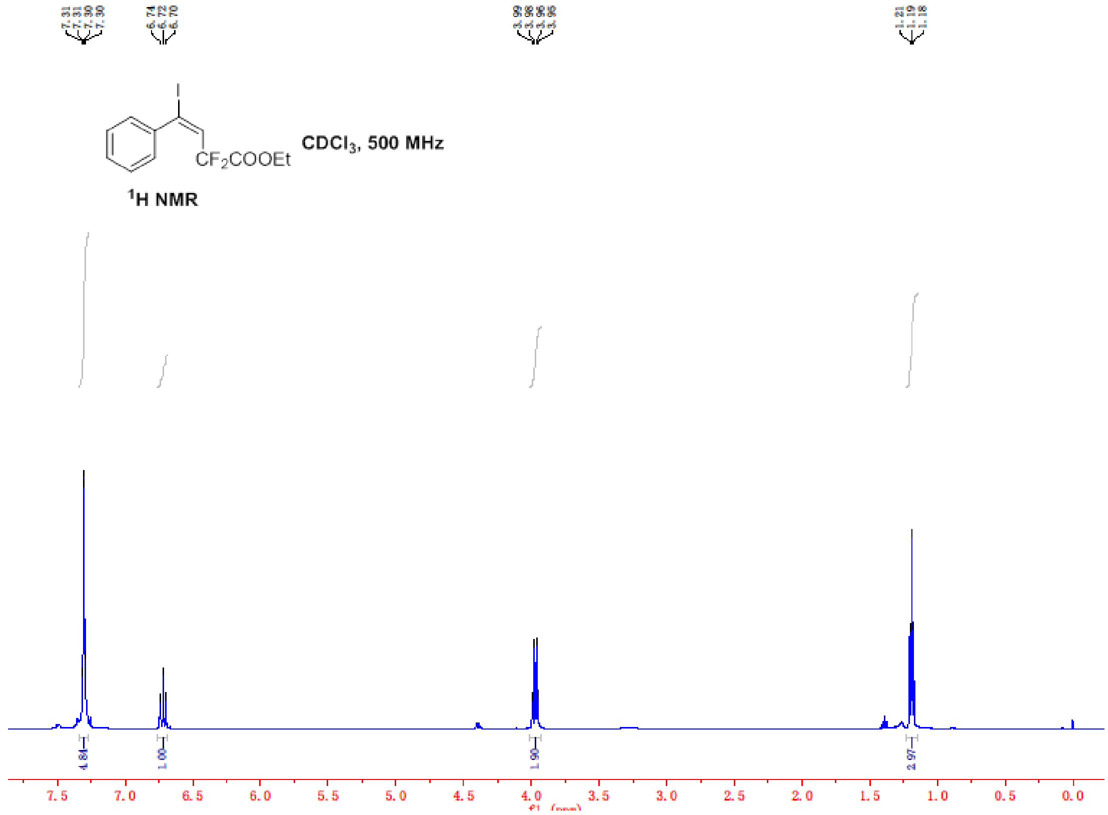
F
CF2CO2Et
19F NMR
CDCl3, 470 MHz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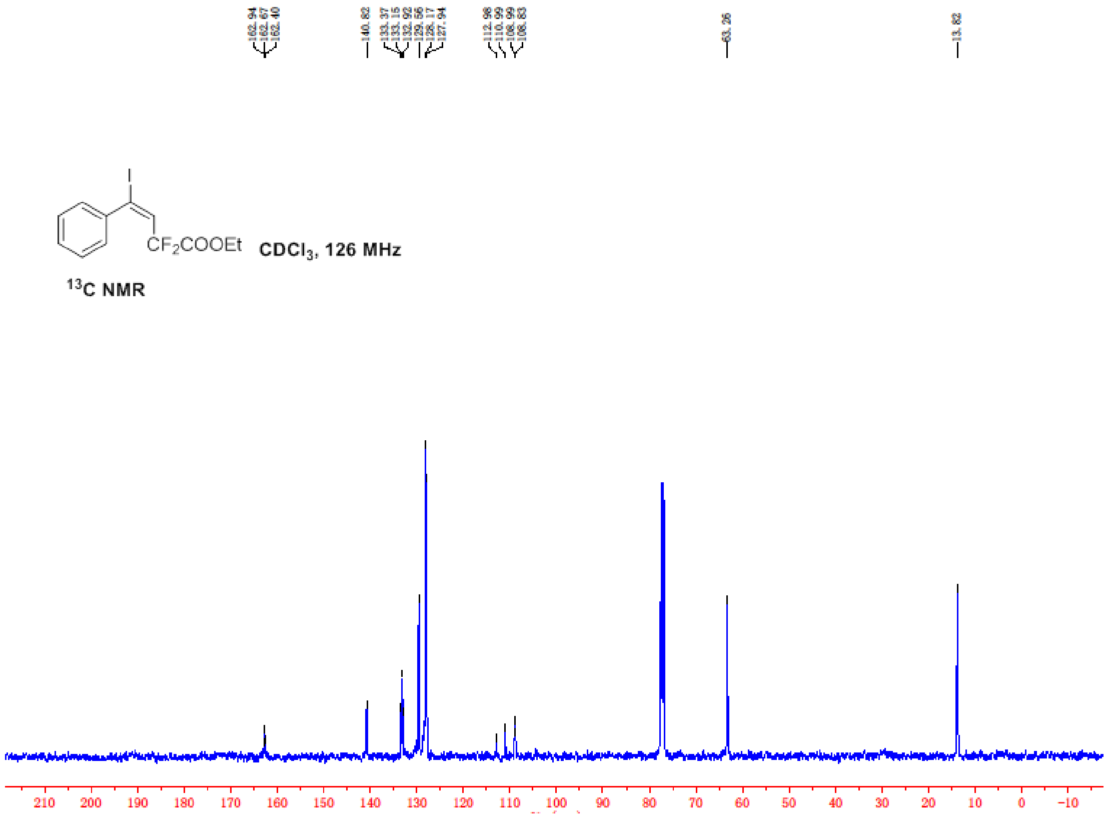
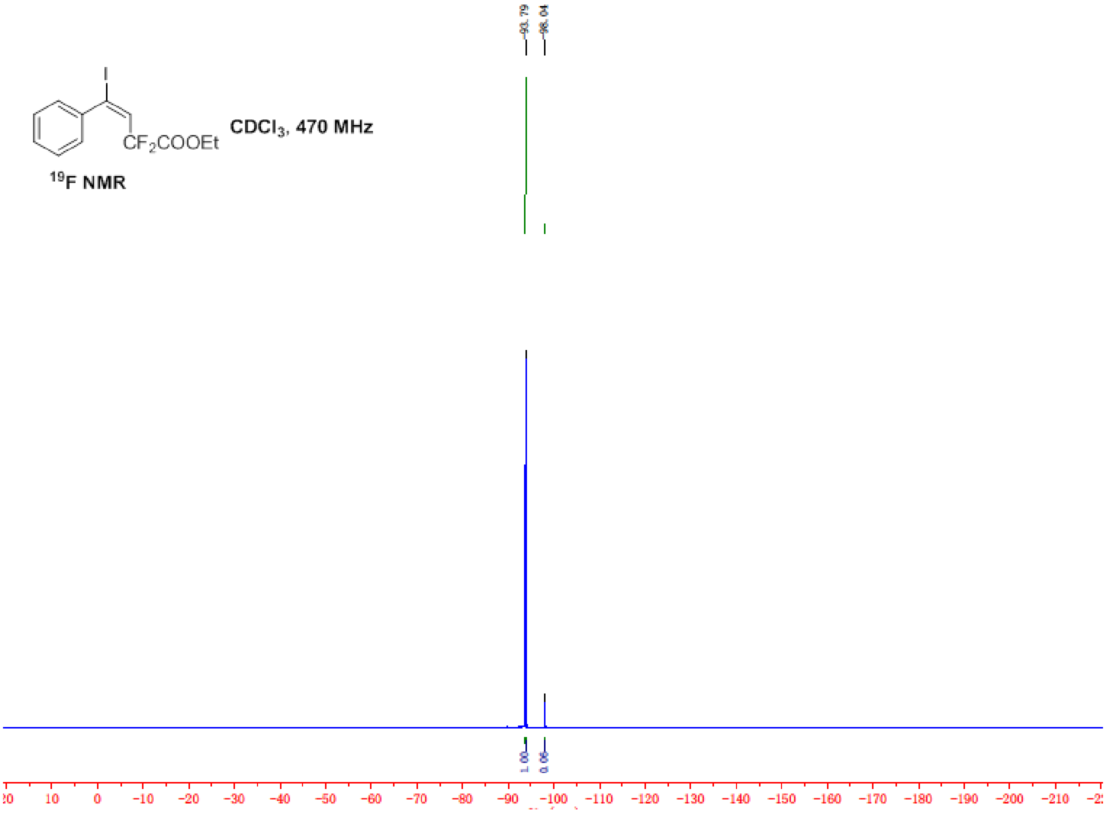
CDCl3, 500 MHz
1H NMR


CF2COOEt
CDCl3, 126 MHz
13C NMR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CDCl3, 470 MHz
19F NMR
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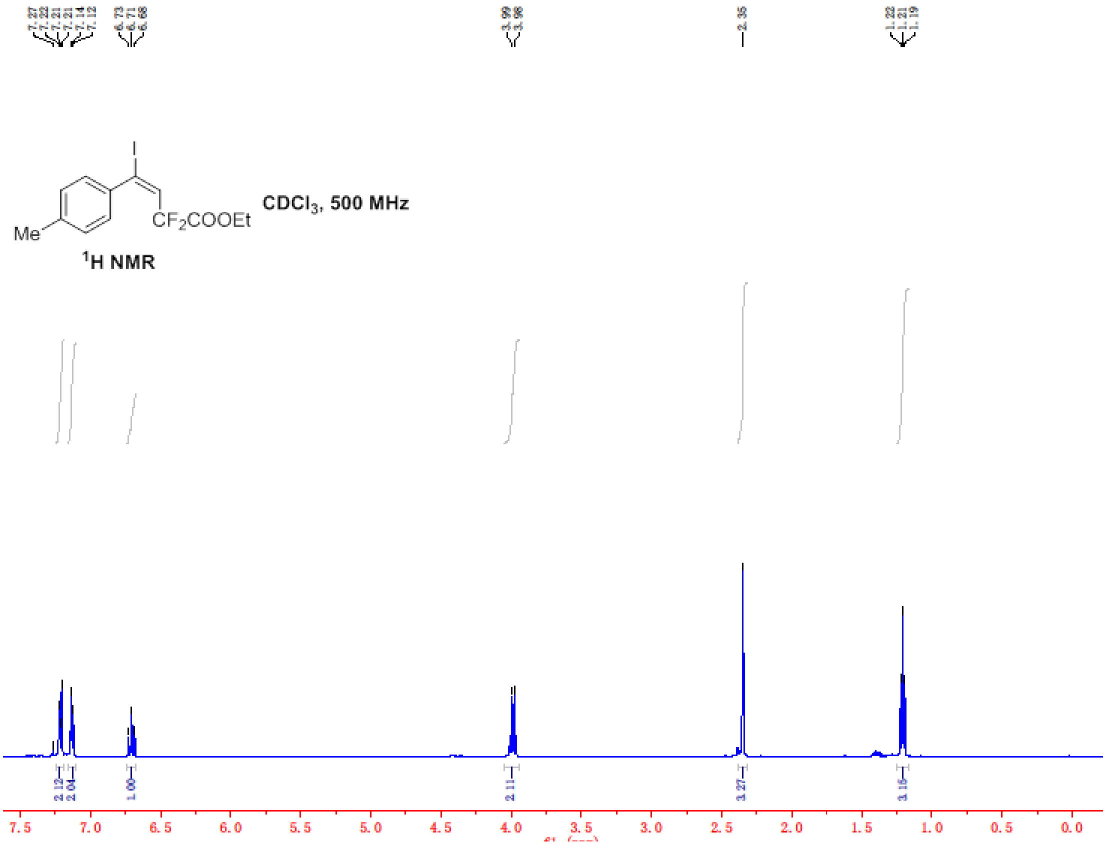
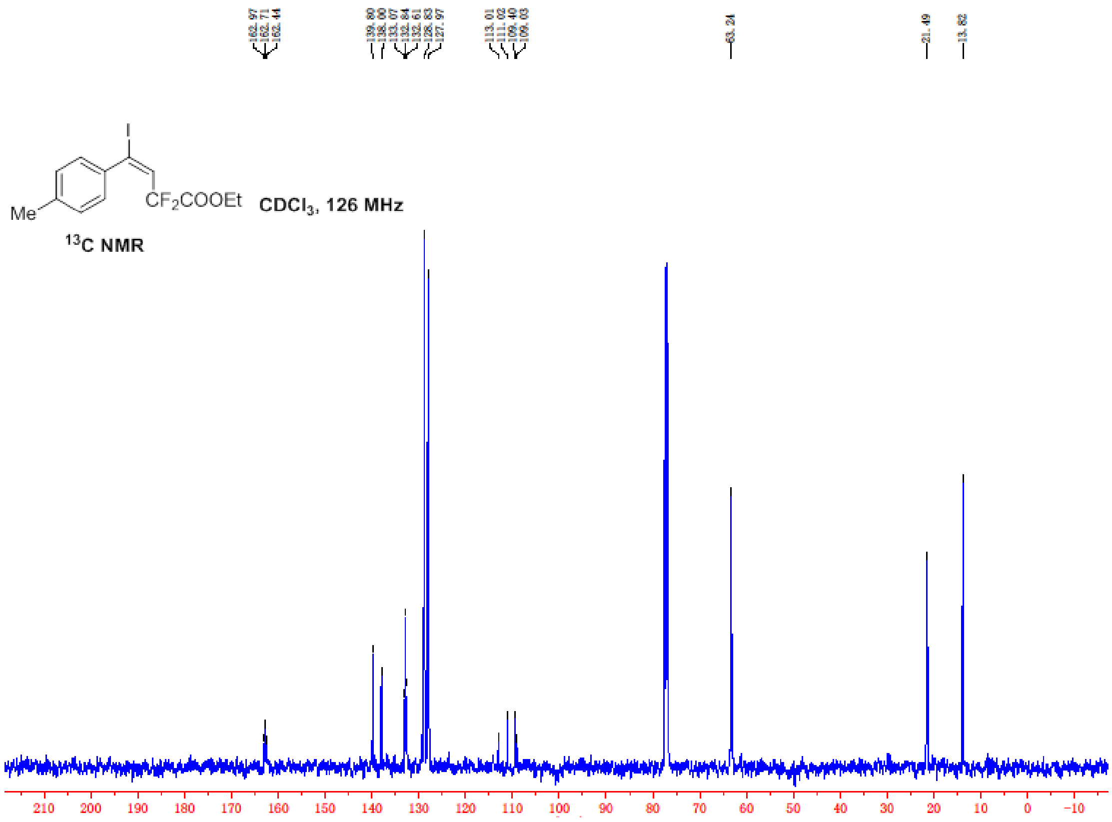
-98.04
1.00
0.06


Me
CF2COOEt
CDCl3, 500 MHz
1H NMR
7.27
7.22
7.21
7.21
7.14
7.12
6.73
6.71
6.68
3.99
3.98
2.35
1.22
1.21
1.19
2.12
2.04
1.00
2.11
3.27
3.16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132.61
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127.97
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111.02
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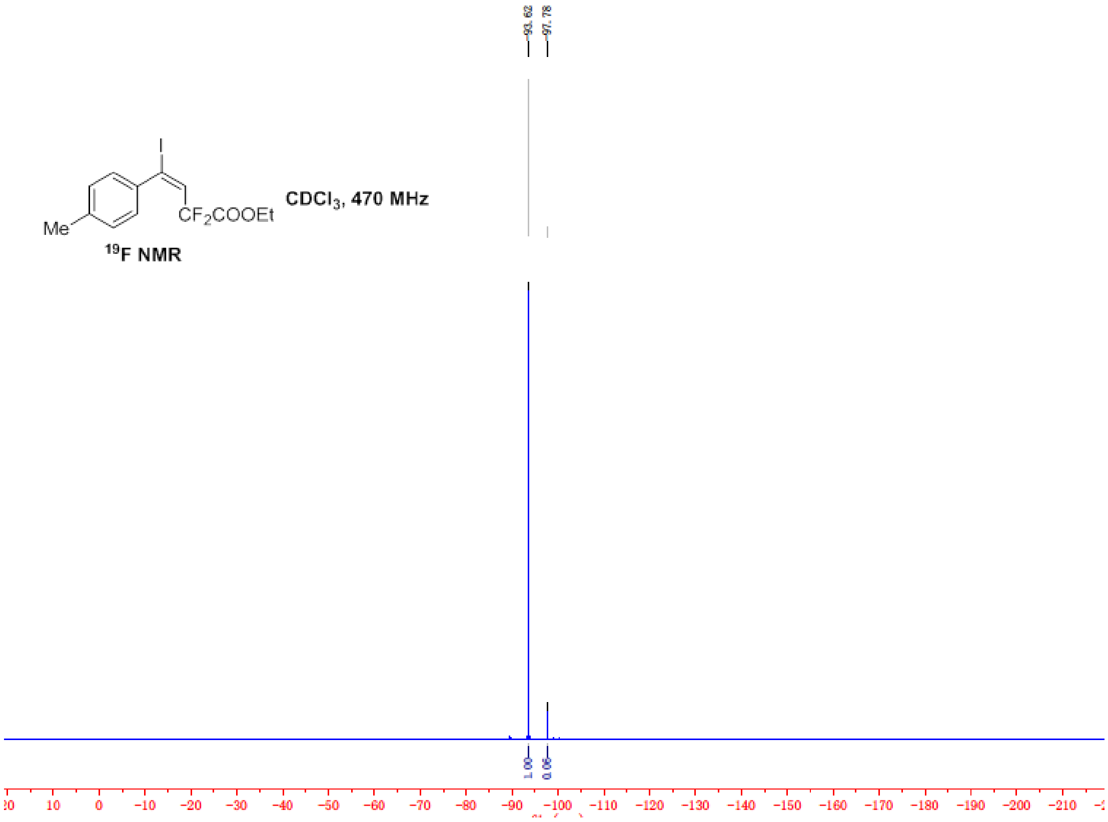
109.03
63.24
21.49
13.82
Me
I
CF2COOEt
CDCl3, 126 MHz
13C NMR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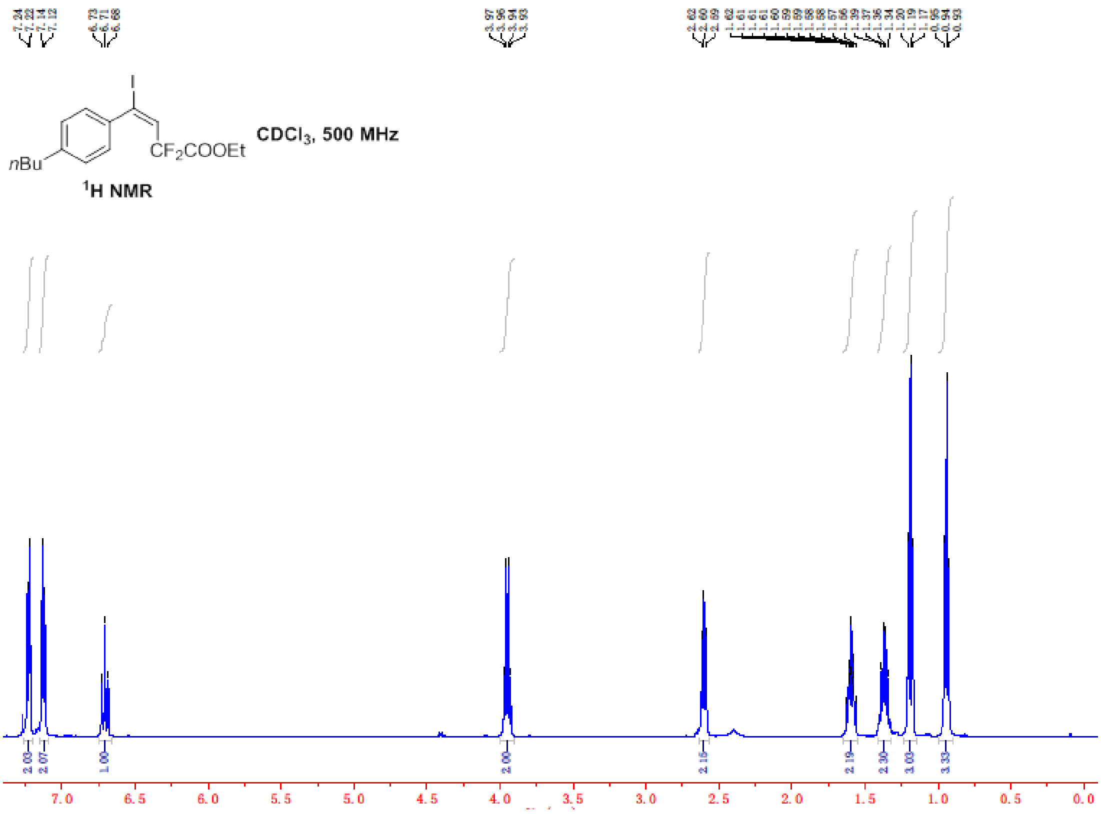
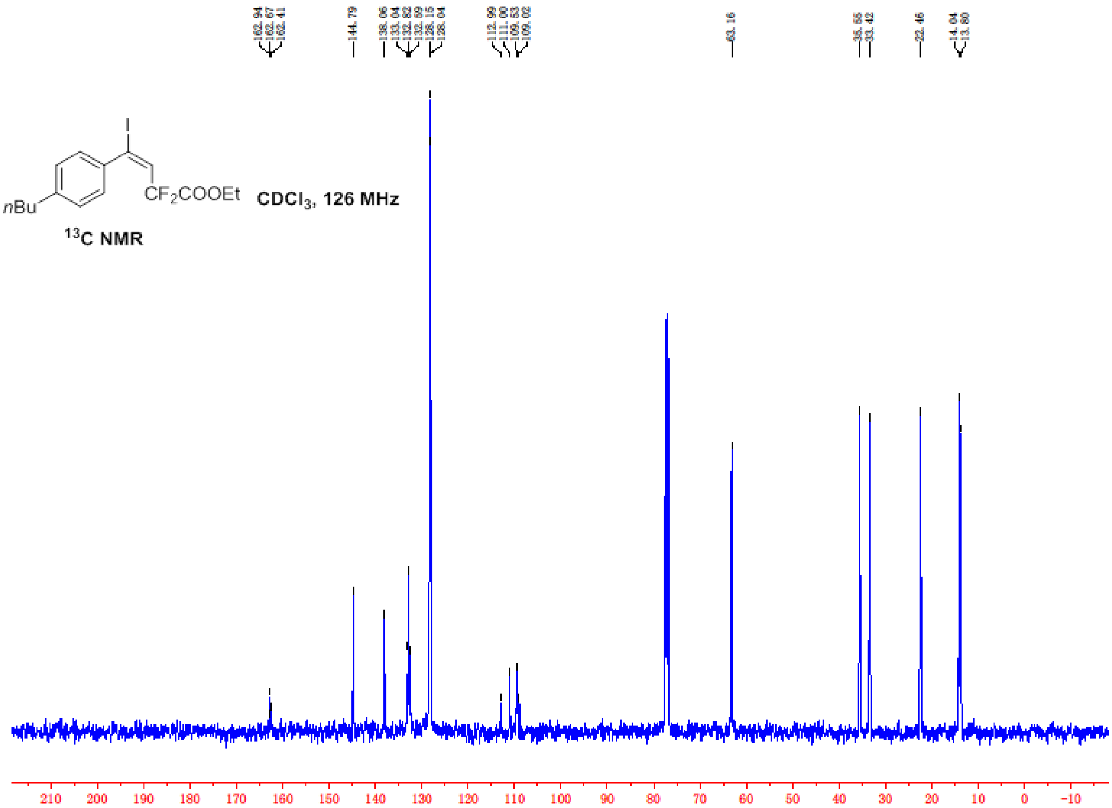
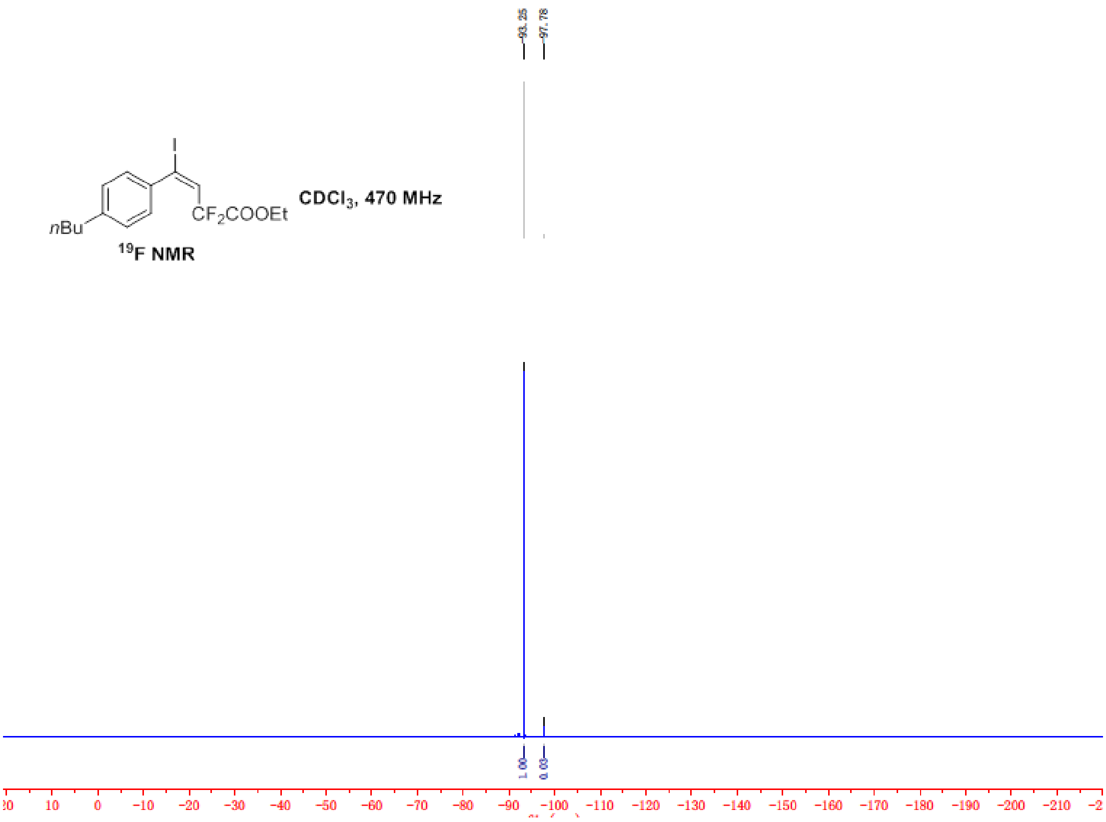
CDCl3, 470 MHz
19F NMR
1.00
0.06

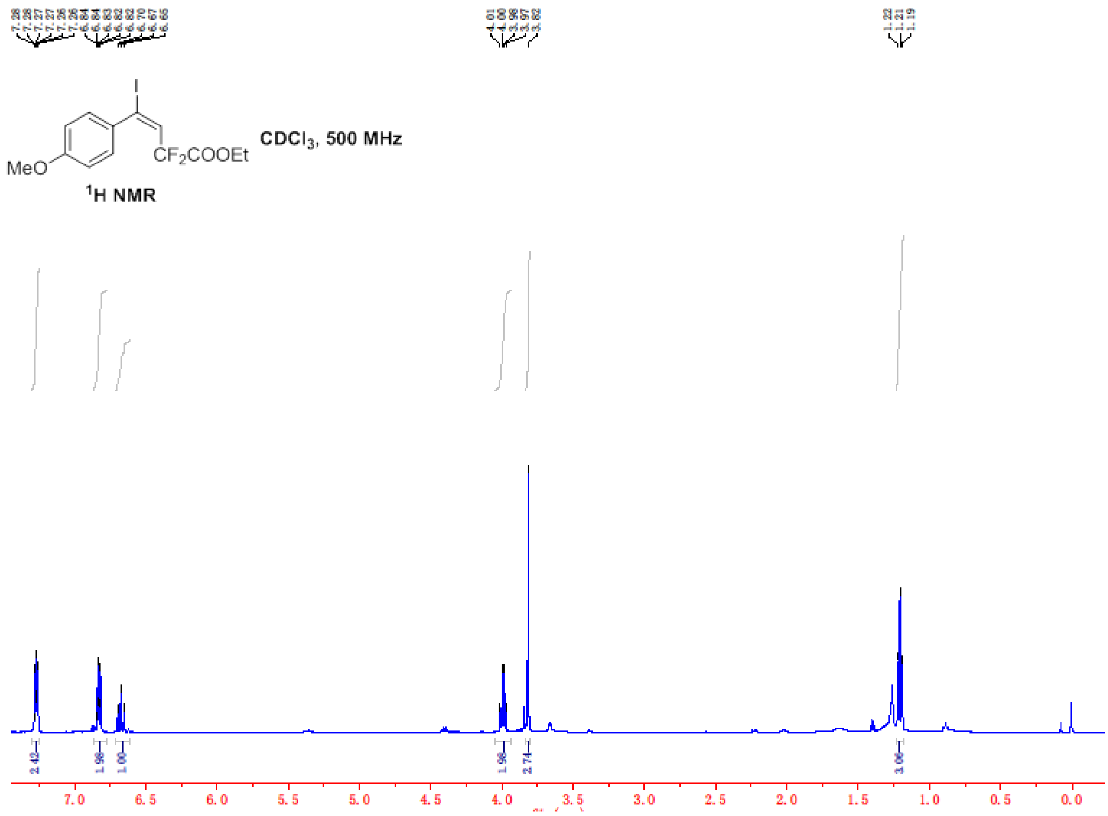


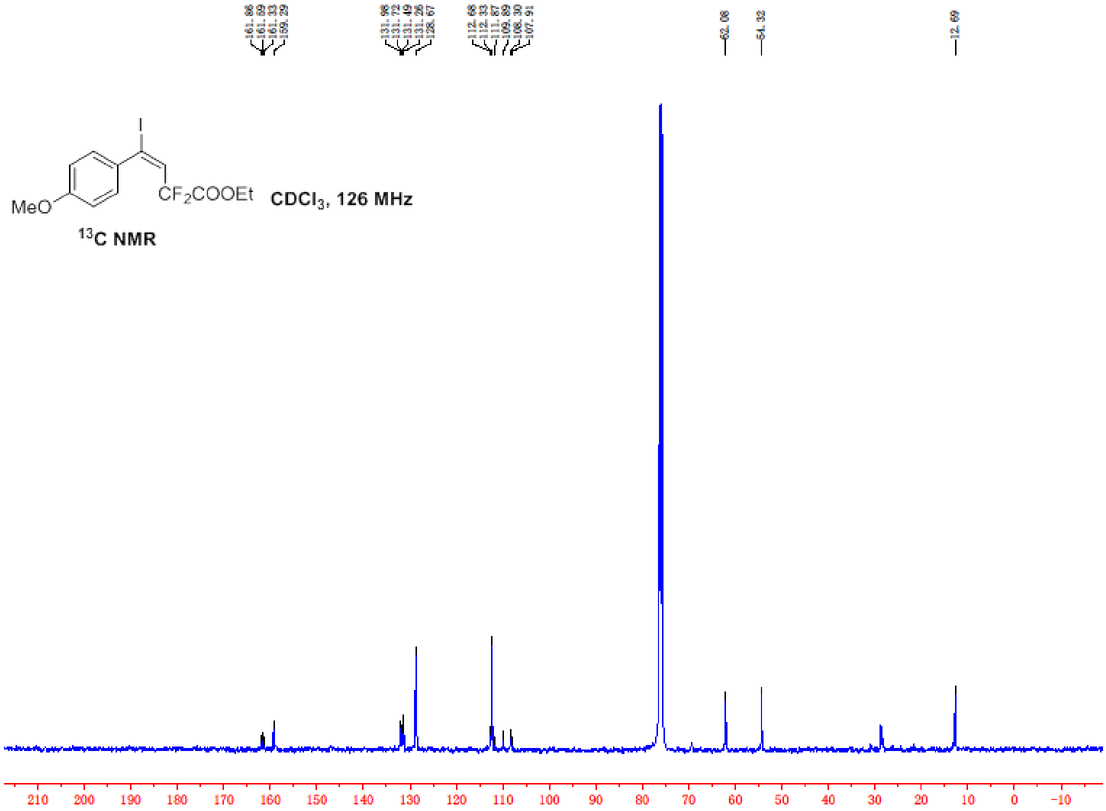
nBu
CF2COOEt
I
CDCl3, 500 MHz
1H NMR

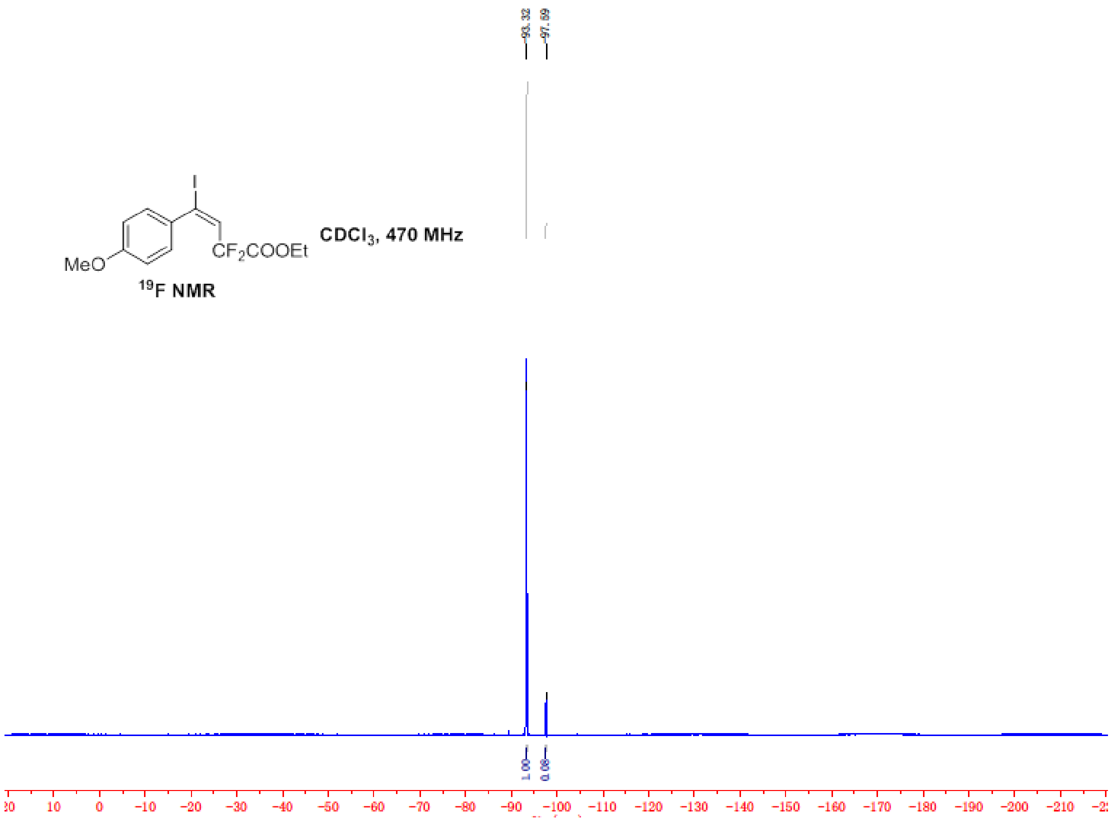


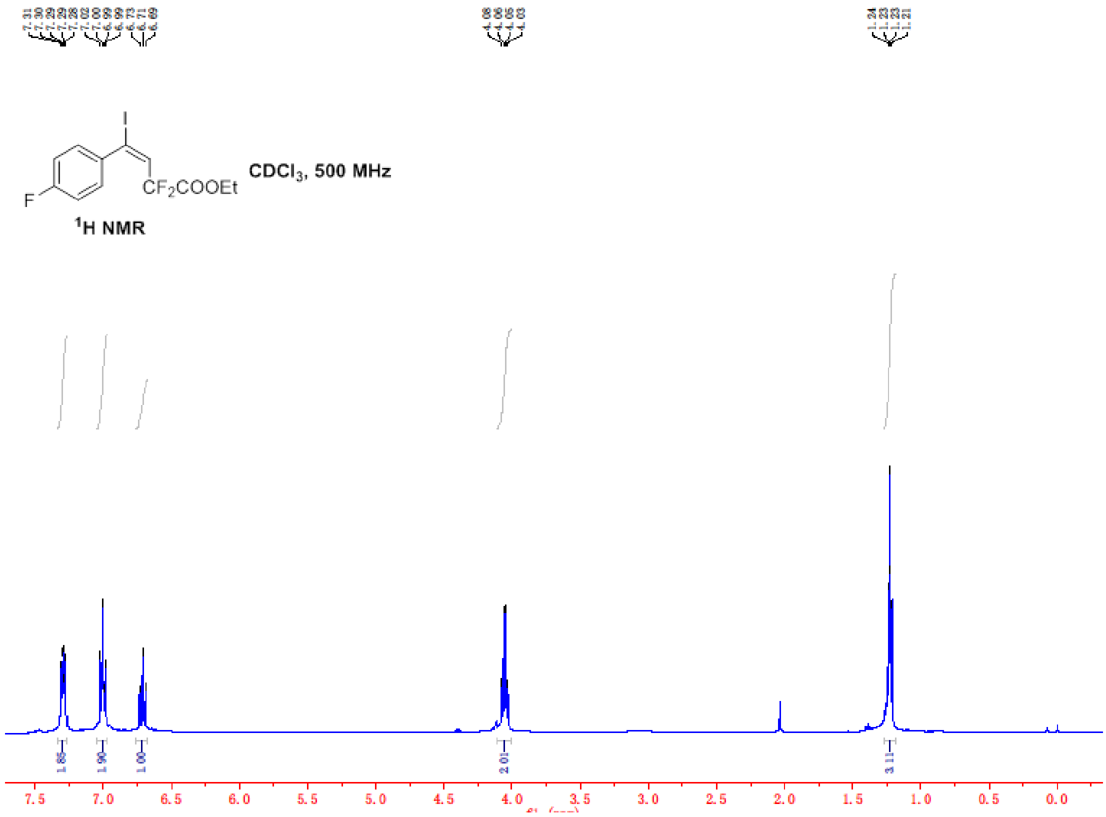
nBu
CF2COOEt
I
CDCl3, 126 MHz
13C NMR

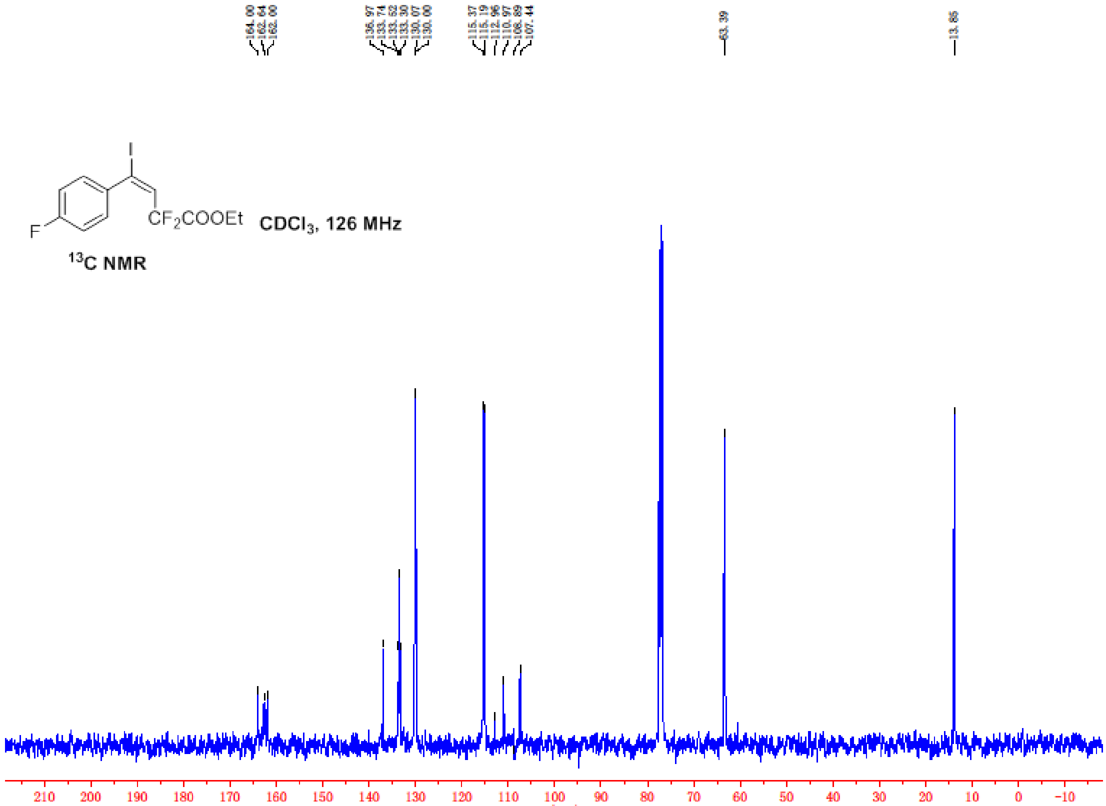

I
nBu
CF2COOEt
CDCl3, 470 MHz
19F NMR
-93.25
-97.78
1.00
0.03

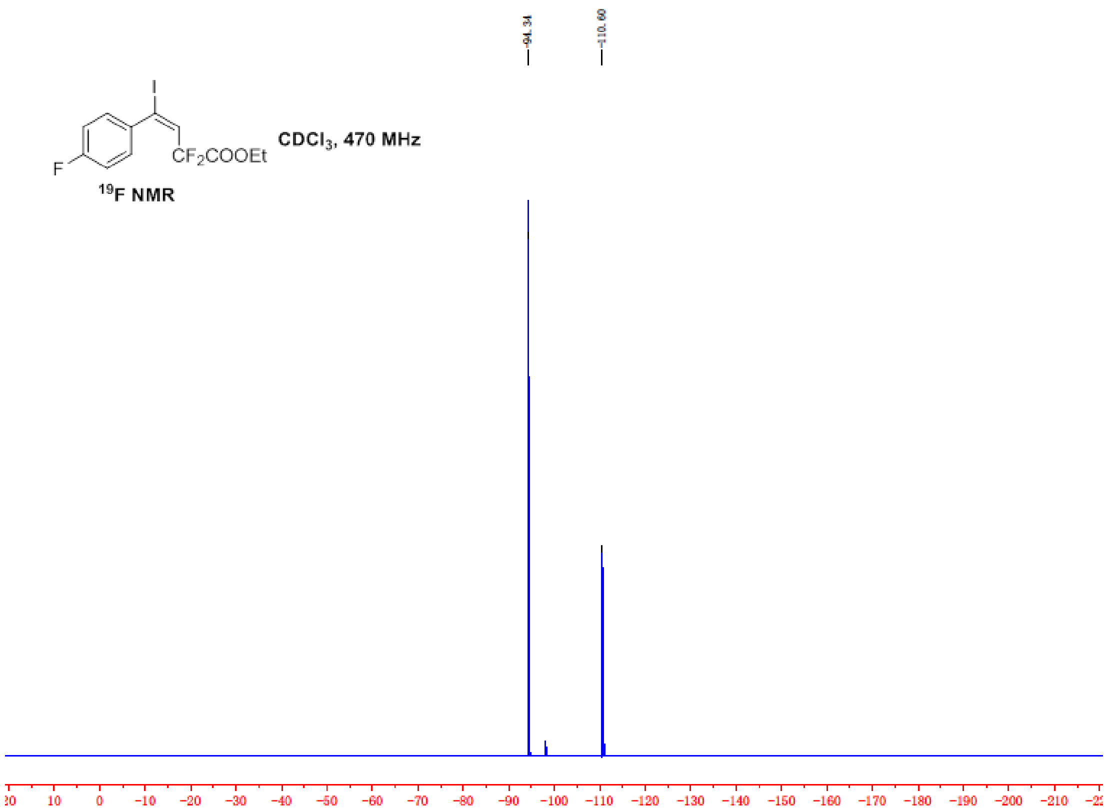

I
MeO
CF2COOEt
CDCl3, 500 MHz
1H NMR
2.42
1.98
1.00
1.98
2.74
3.06


161.86
161.59
161.33
159.29
131.98
131.72
131.49
131.26
128.67
112.68
112.33
111.87
109.89
108.30
107.91
62.08
54.32
12.69
I
MeO
CF2COOEt
CDCl3, 126 MHz
13C NMR

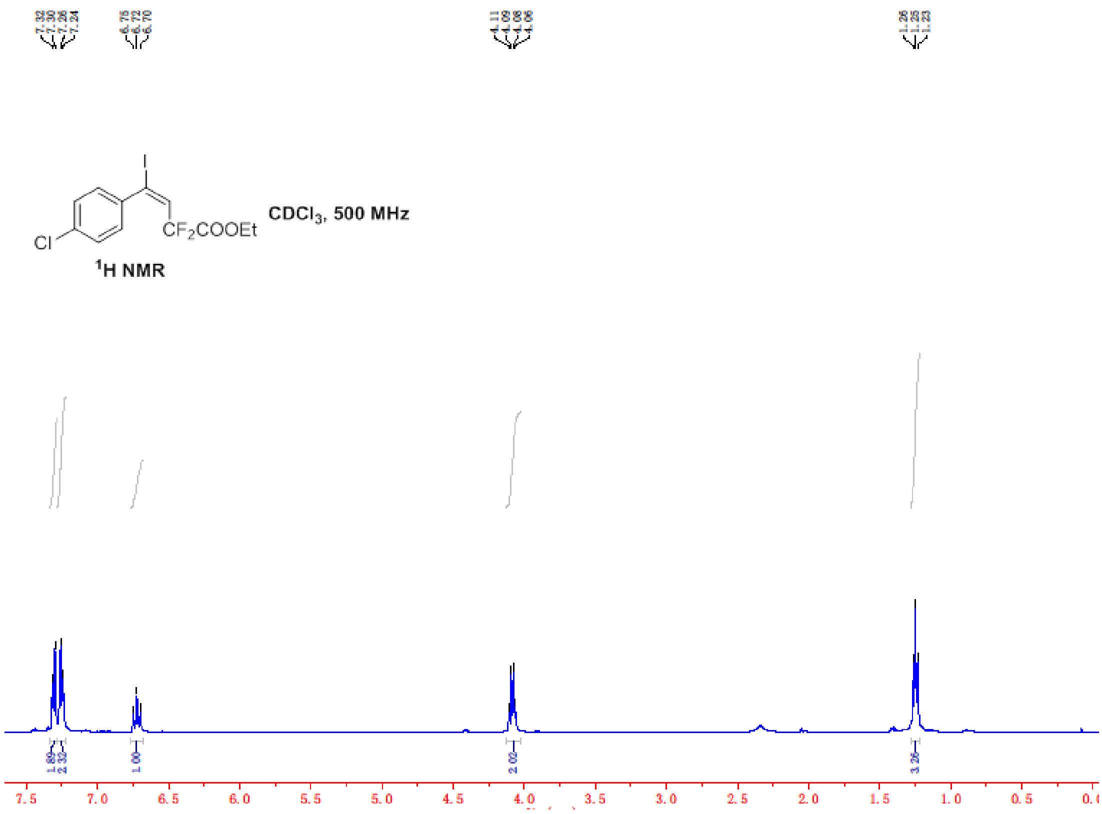

-93.32
-97.59
I
MeO
CF2COOEt
CDCl3, 470 MHz
19F NMR
1.00
0.08



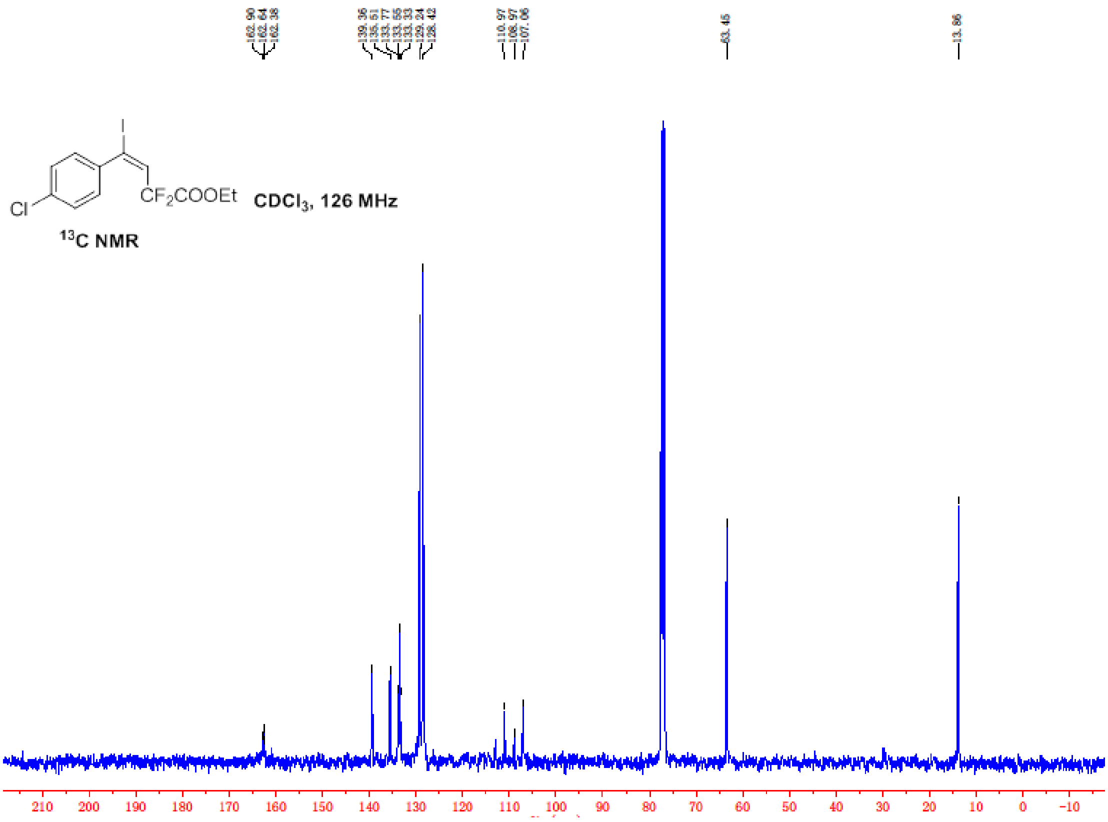


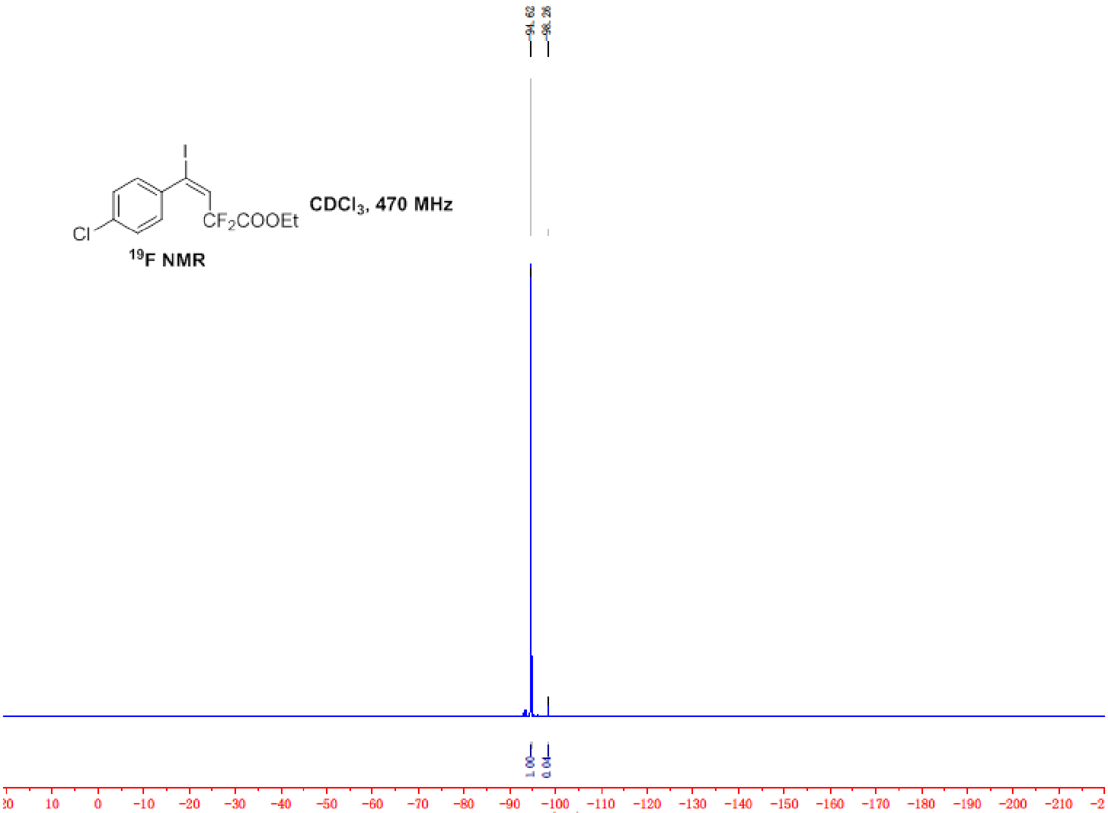


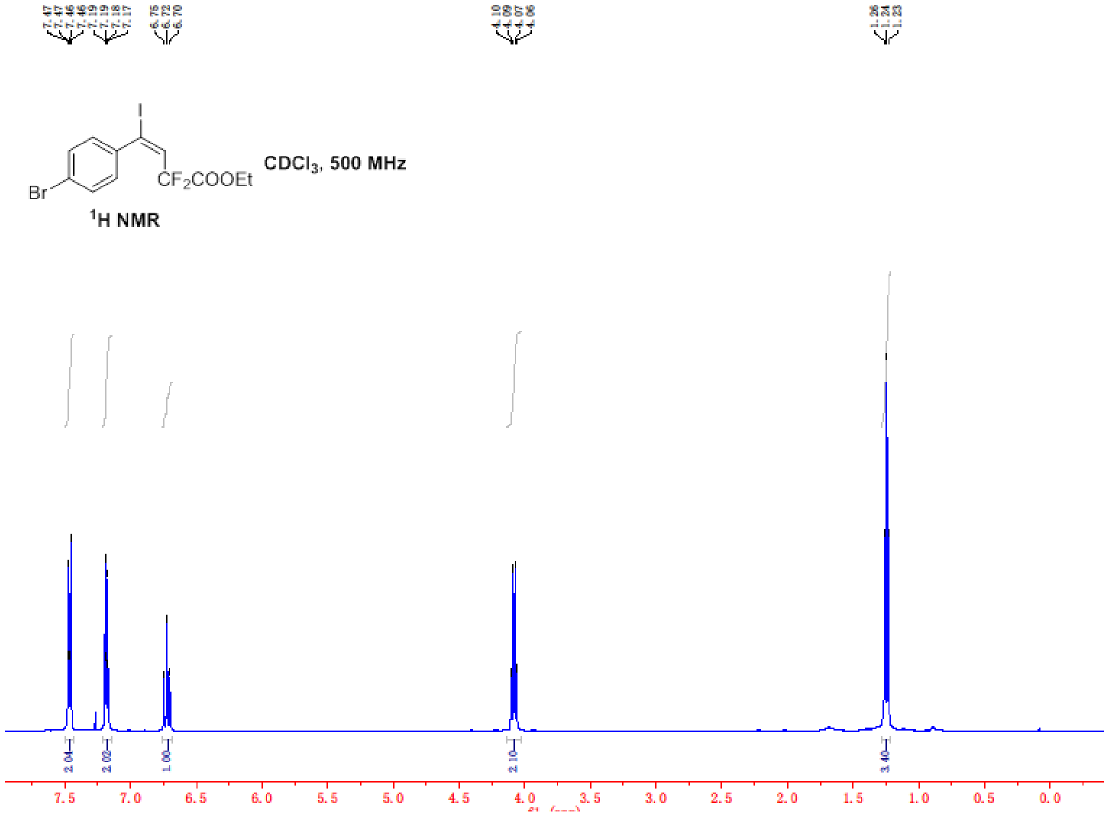
F
I
CF2COOEt
CDCl3, 470 MHz
19F NMR
-94.34
-110.60
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

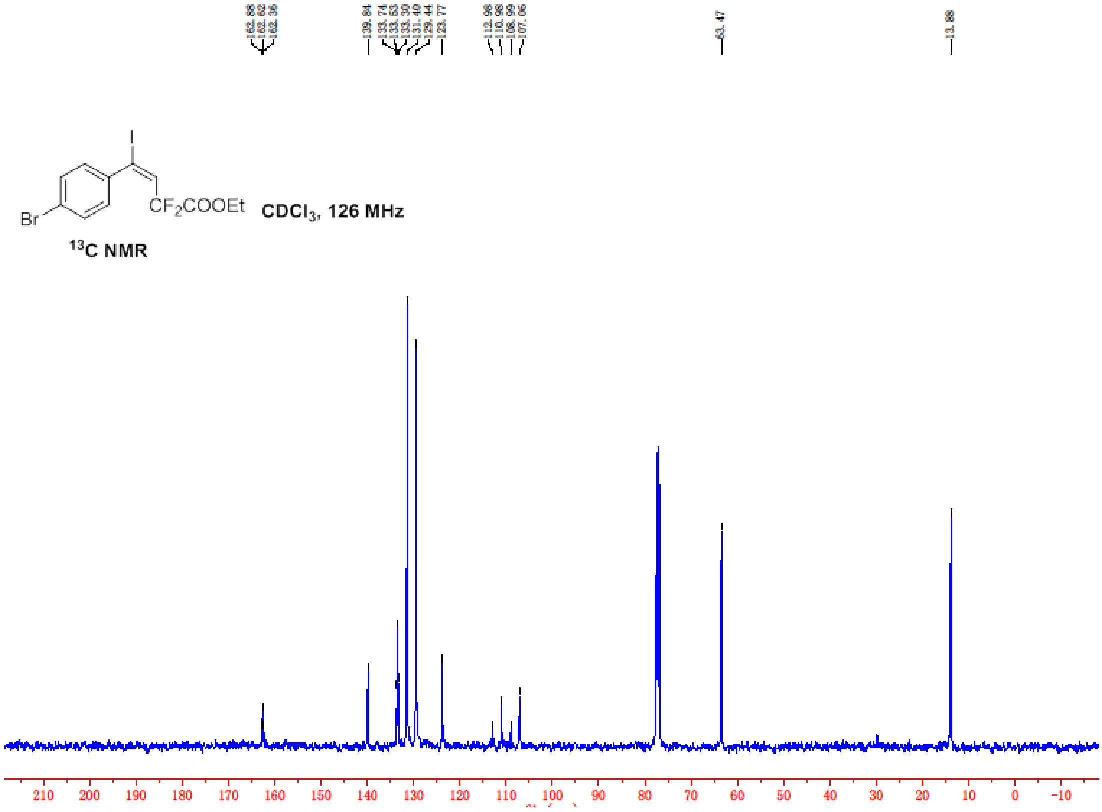


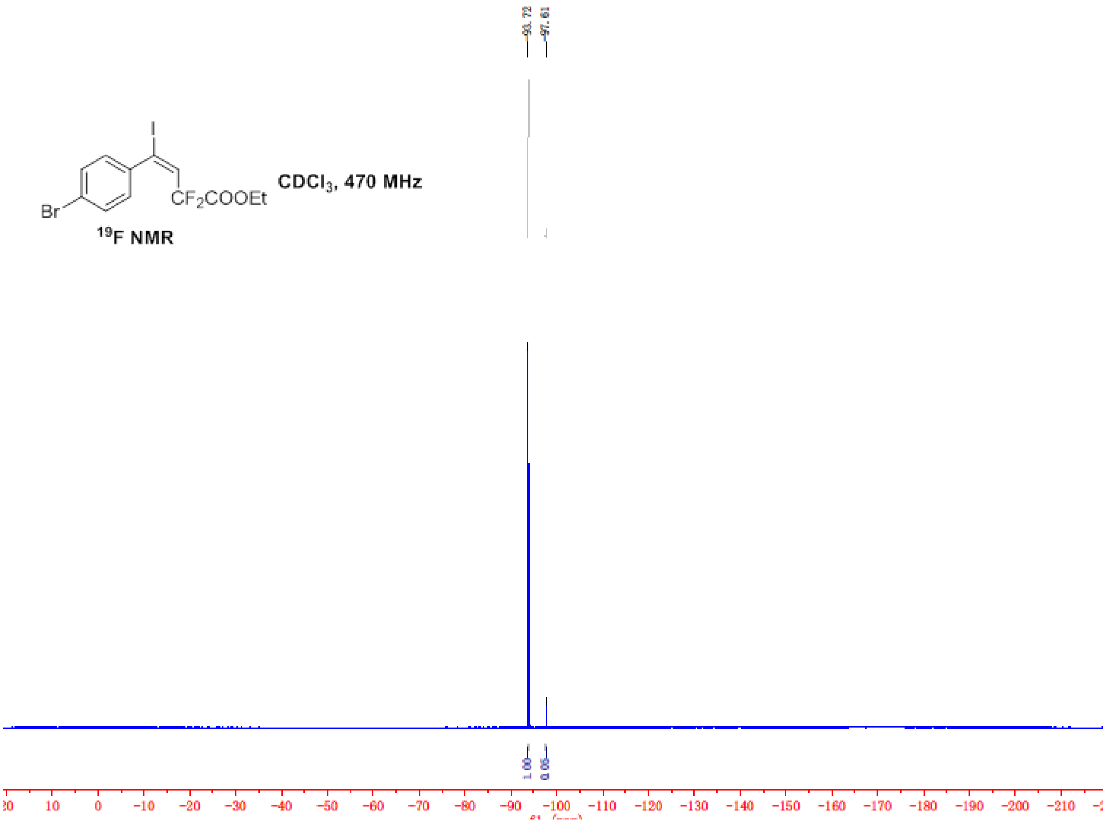
Cl
I
CF2COOEt
CDCl3, 500 MHz
1H NMR
7.32 7.30 7.26 7.24
6.75 6.72 6.70
4.11 4.09 4.08 4.06
1.26 1.25 1.23
1.89 2.32 1.00 2.02 3.26
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5


162.90
162.64
162.38
139.36
135.51
133.77
133.55
133.33
129.24
128.42
110.97
108.97
107.06
63.45
13.86
Cl
I
CF2COOEt
CDCl3, 126 MHz
13C NMR

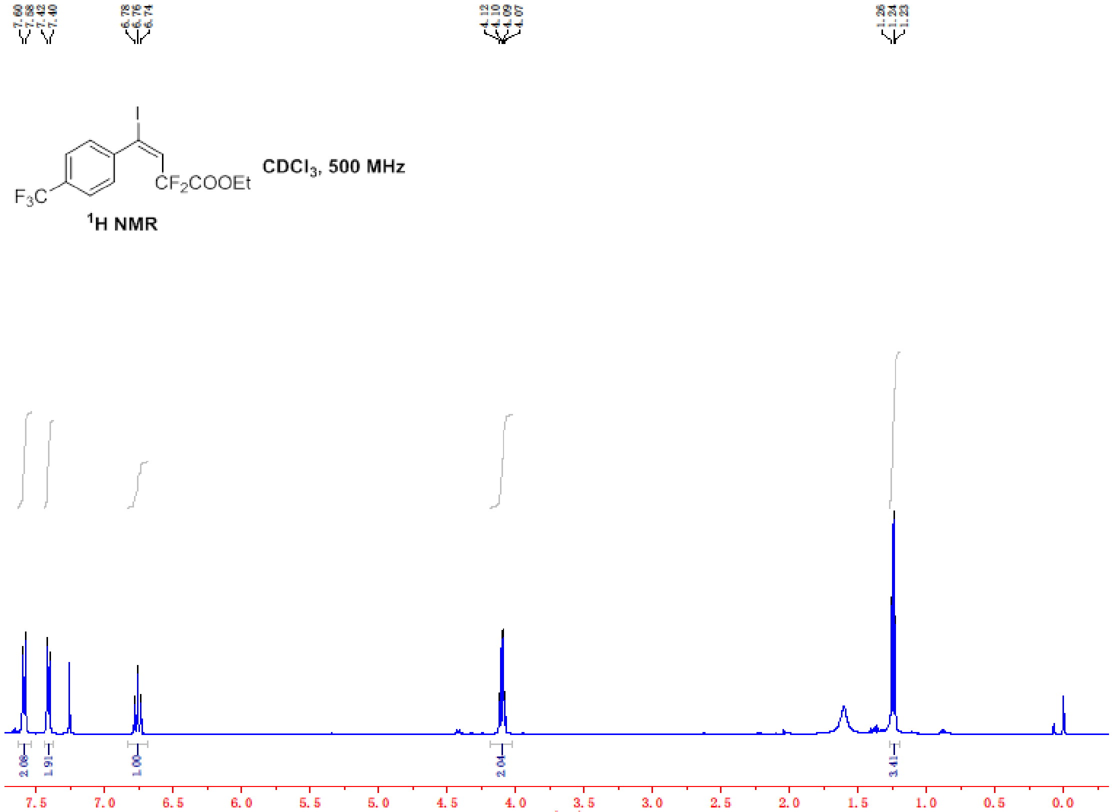

-94.62
-98.26
Cl
I
CF2COOEt
CDCl3, 470 MHz
19F NMR
1.00
0.04


7.47
7.47
7.46
7.46
7.19
7.19
7.18
7.17
6.75
6.72
6.70
4.10
4.09
4.07
4.06
1.26
1.24
1.23
I
Br
CF2COOEt
CDCl3, 500 MHz
1H NMR
2.04
2.02
1.00
2.10
3.40
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

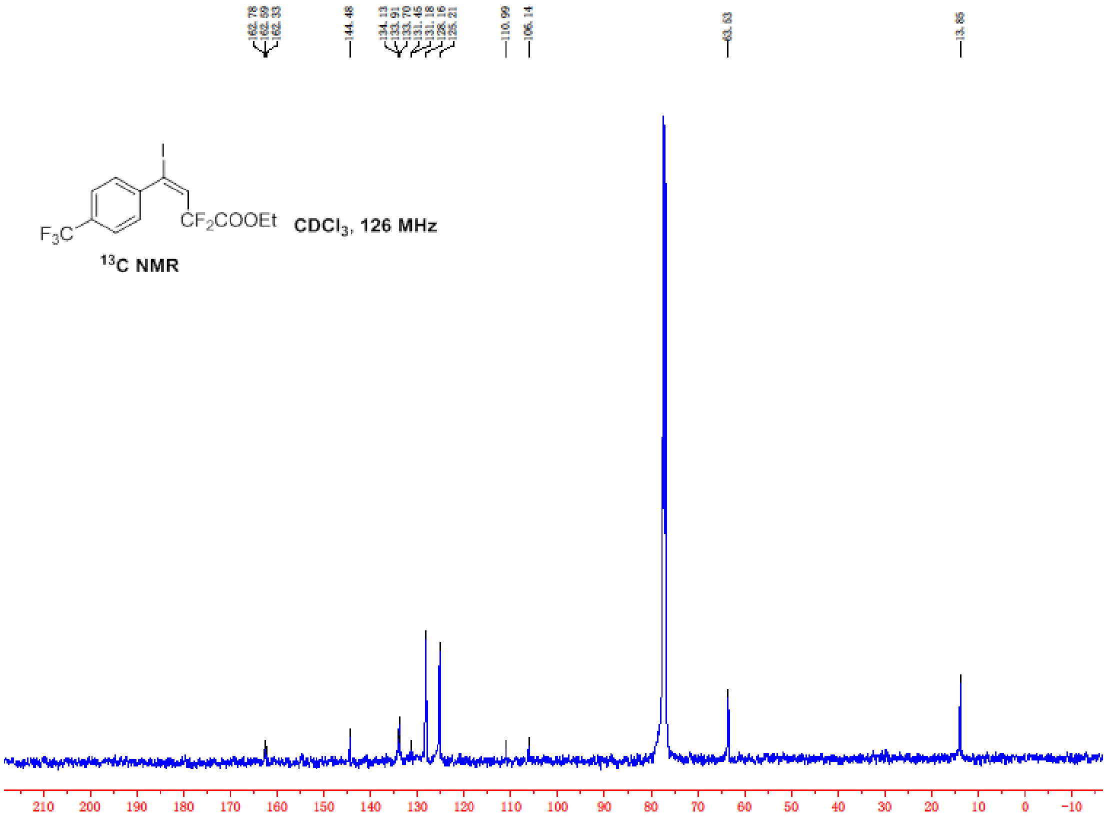

162.88
162.62
162.36
139.84
133.74
133.53
133.30
131.40
129.44
123.77
112.98
110.98
108.99
107.06
63.47
13.88
I
Br
CF2COOEt
CDCl3, 126 MHz
13C NMR
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10



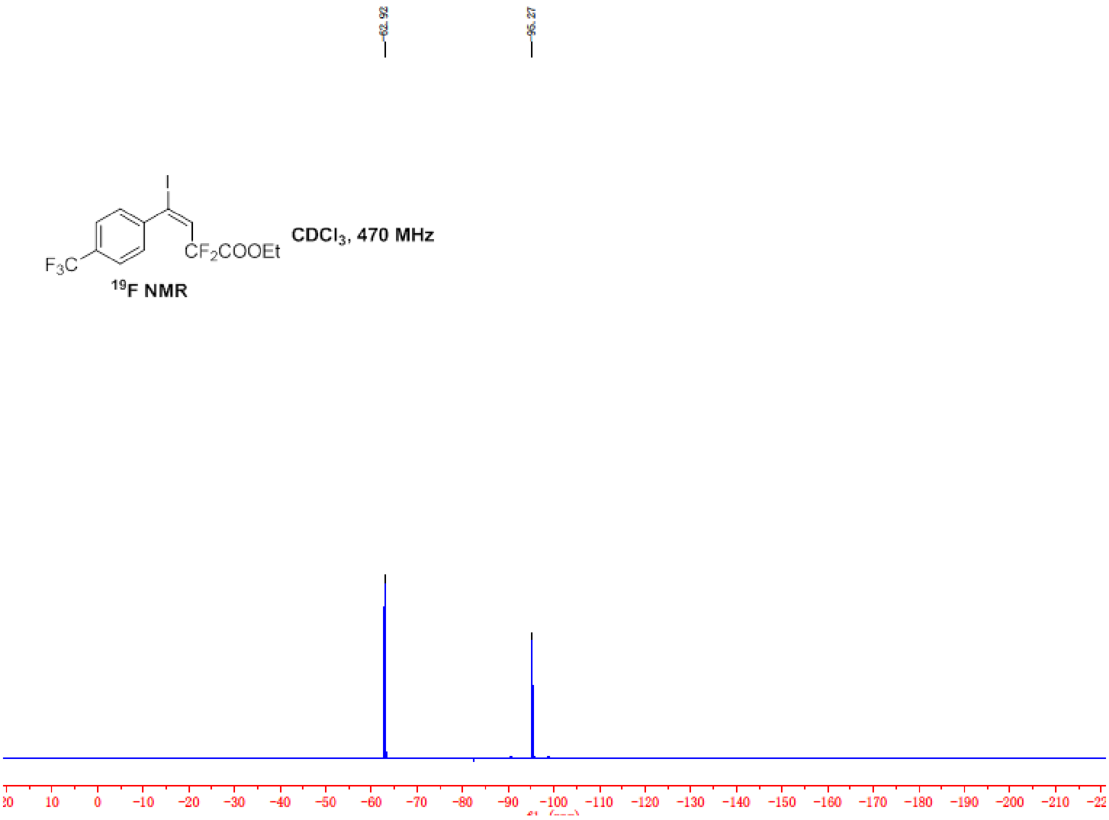
Br
CF2COOEt
CDCl3, 470 MHz
19F NMR
-93.72
-97.61
1.00
0.05



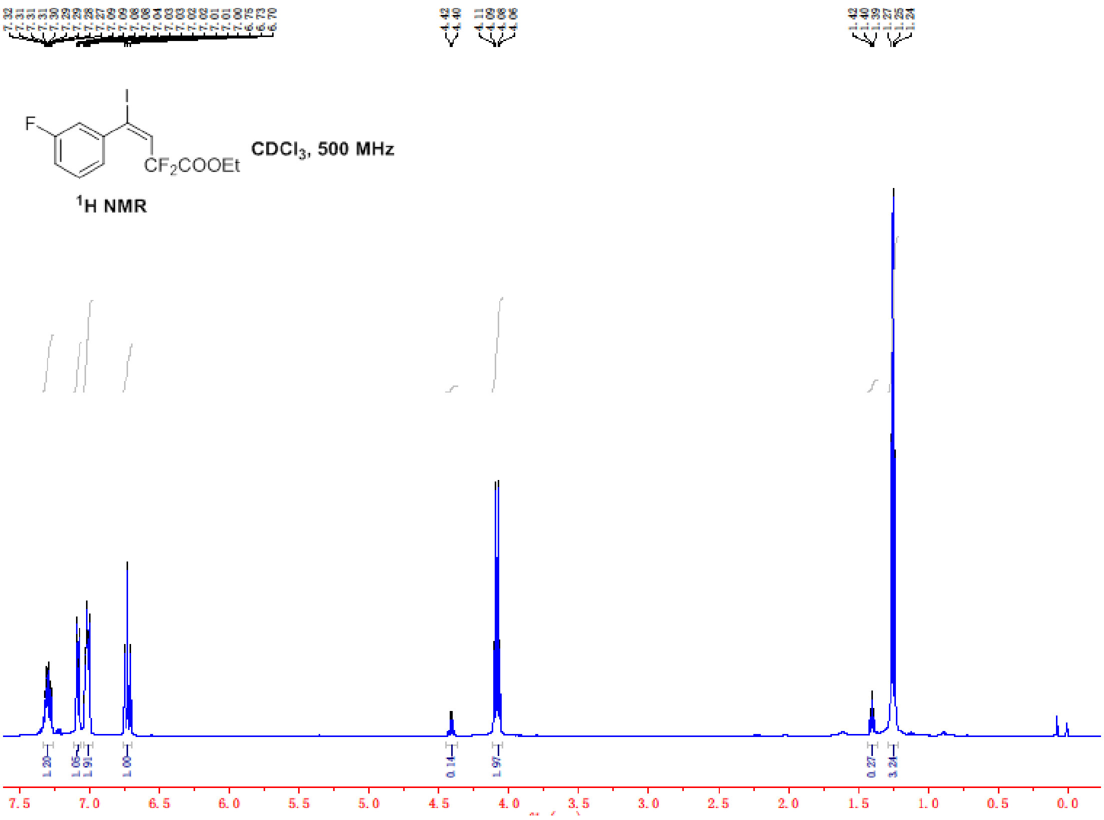
F3C
CF2COOEt
CDCl3, 500 MHz
1H NMR
7.60
7.58
7.42
7.40
6.78
6.76
6.74
4.12
4.10
4.09
4.07
1.26
1.24
1.23
2.08
1.91
1.00
2.04
3.41

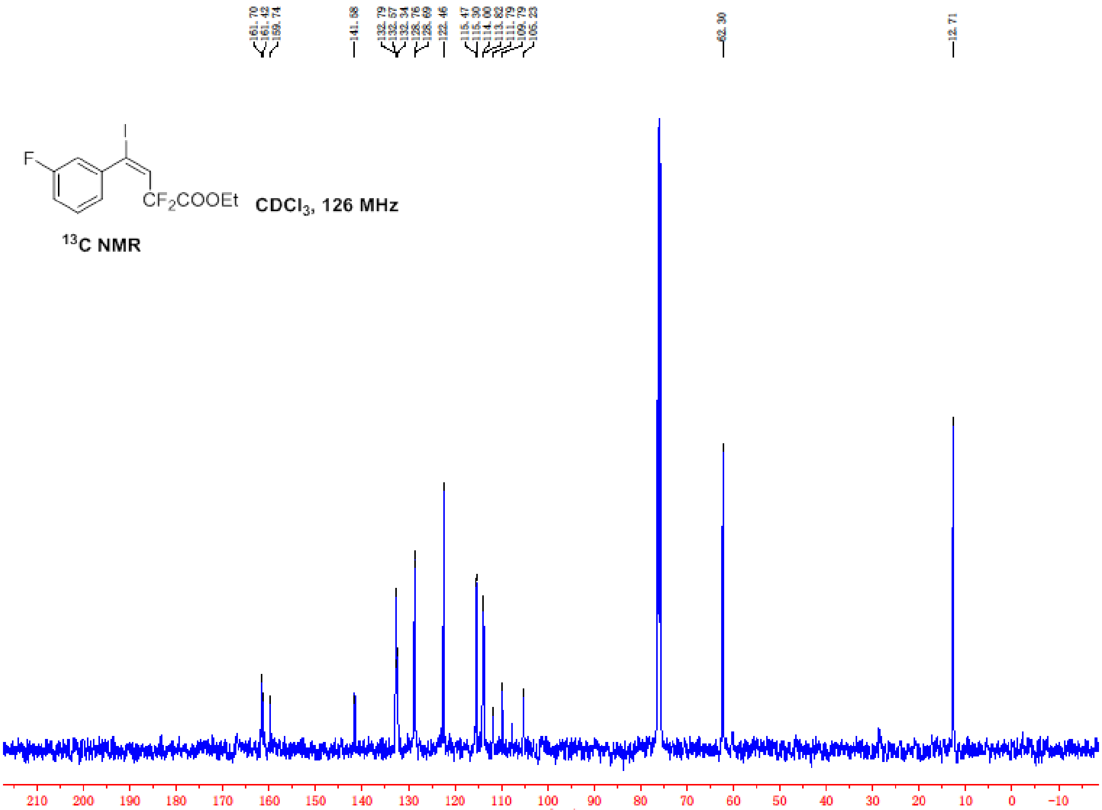


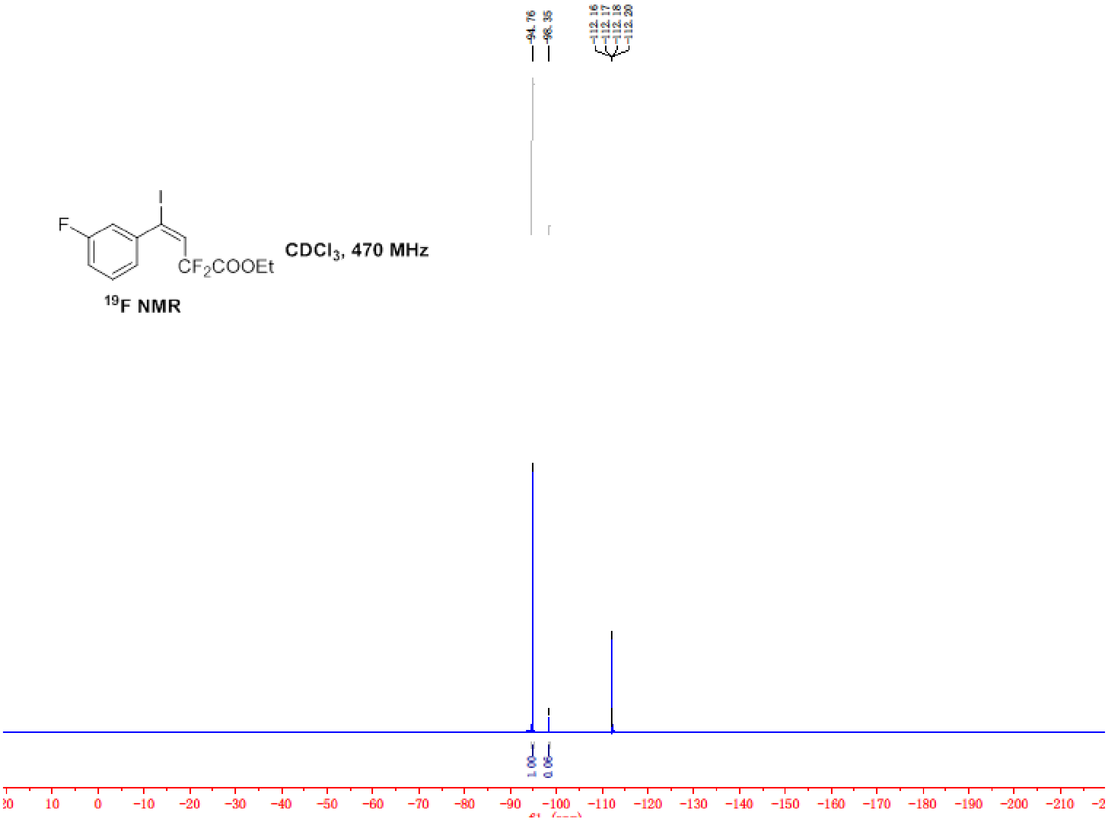
162.78
162.59
162.33
144.48
134.13
133.91
133.70
131.45
131.18
128.16
125.21
110.99
106.14
63.53
13.85
CF2COOEt
F3C
I
CDCl3, 126 MHz
13C NMR
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10



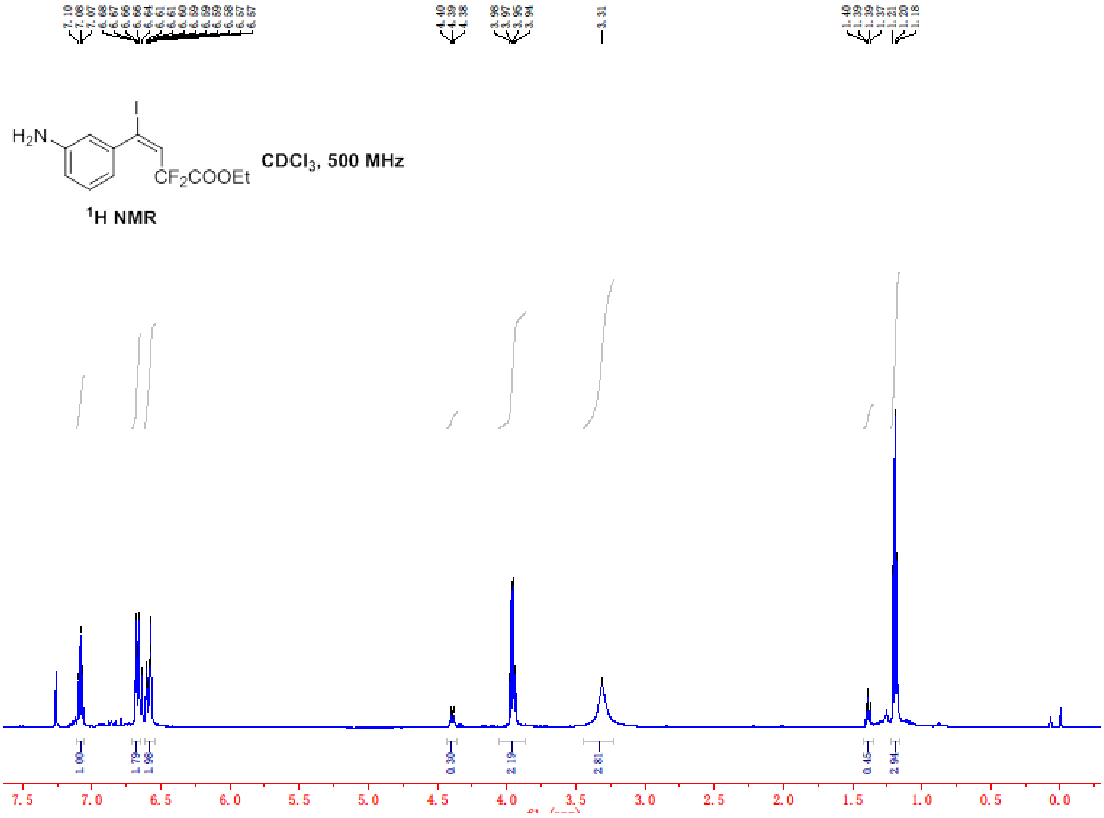
−62.92
−95.27
CF2COOEt
F3C
I
CDCl3, 470 MHz
19F NMR
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210


F
I
CF_2COOEt
$CDCl_3$, 500 MHz
^1H NMR

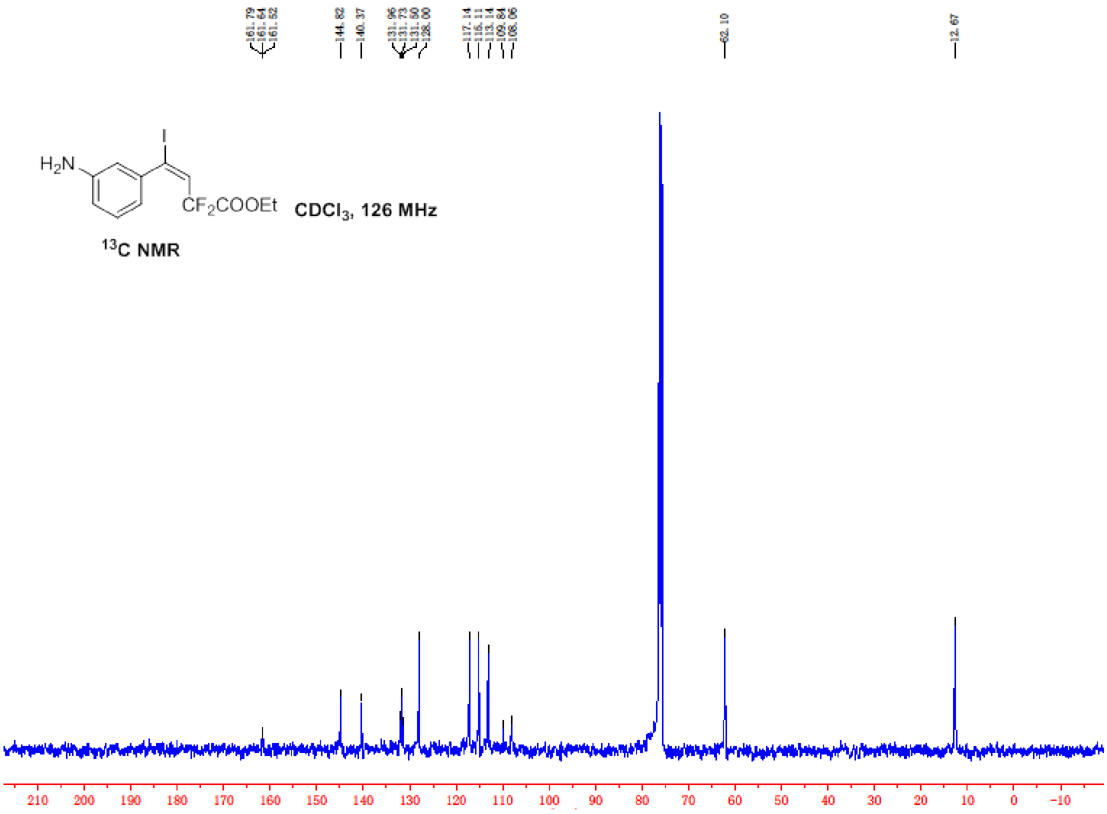

F
I
CF_2COOEt
$CDCl_3$, 126 MHz
^{13}C NMR



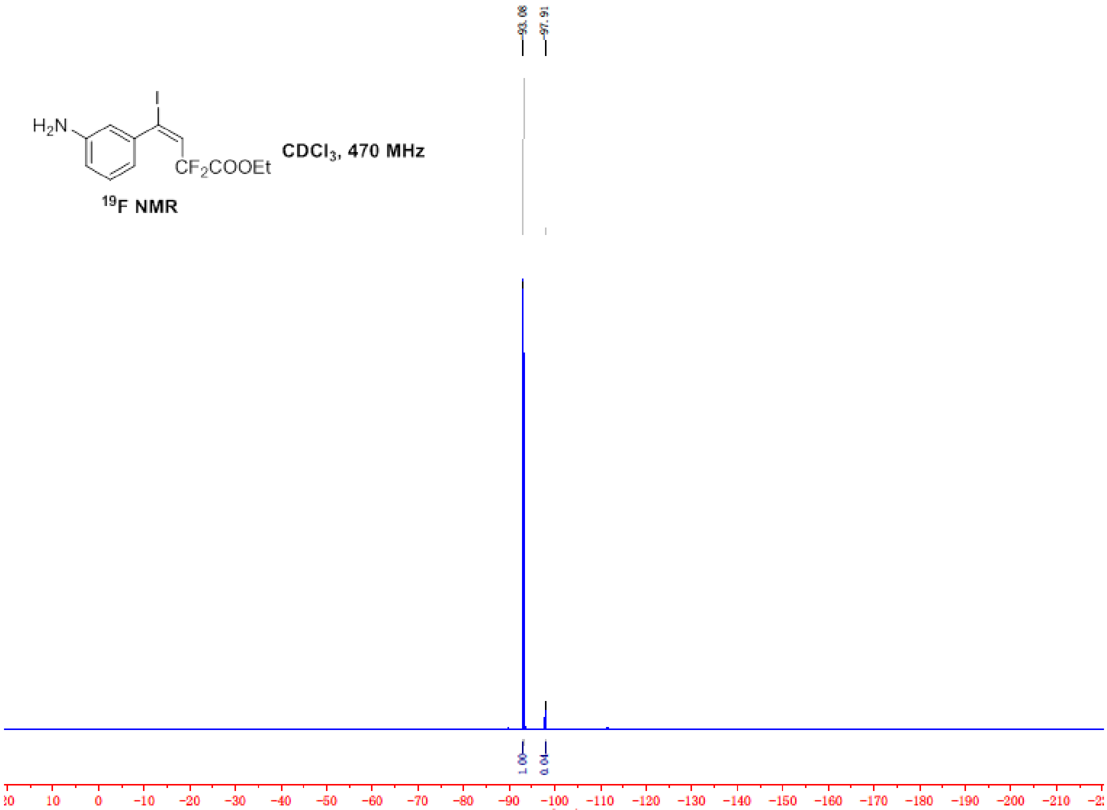
CDCl3, 470 MHz
19F NMR
-94.76
-98.35
-112.16
-112.17
-112.18
-112.20
1.00
0.06



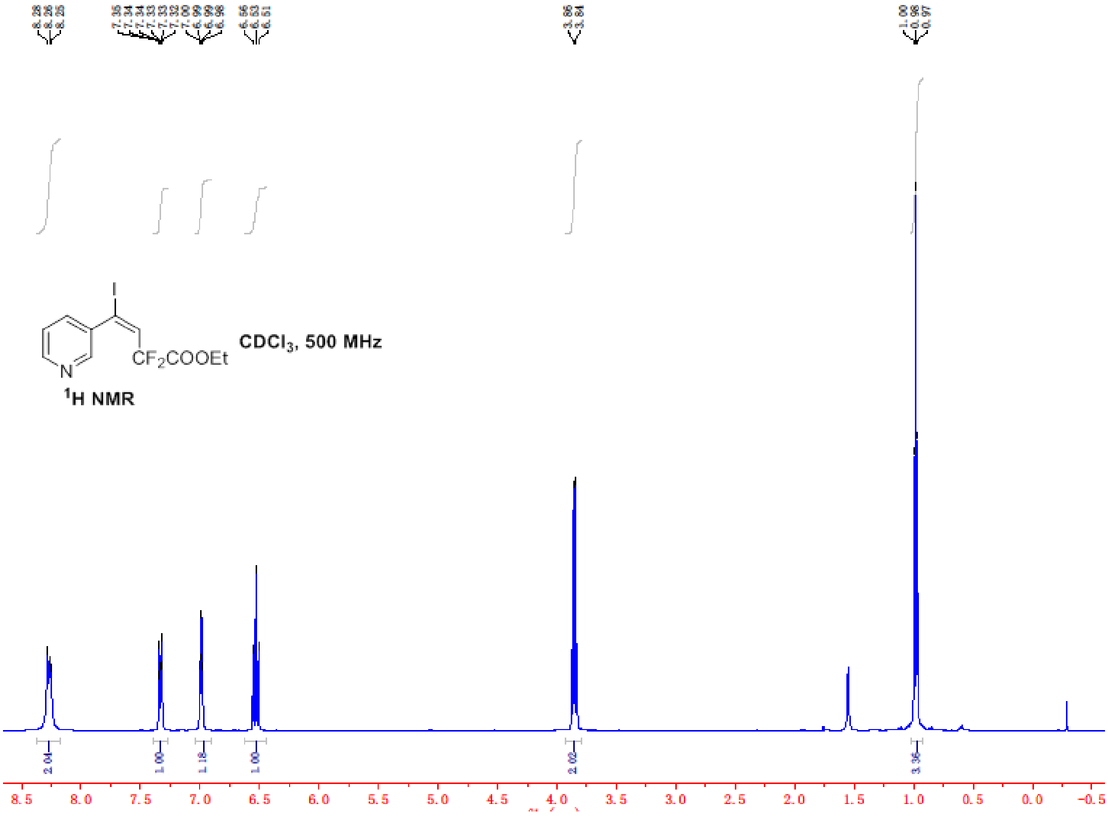
CDCl3, 500 MHz
1H NMR
3.31
1.00
1.79
1.98
0.30
2.19
2.81
0.45
2.94

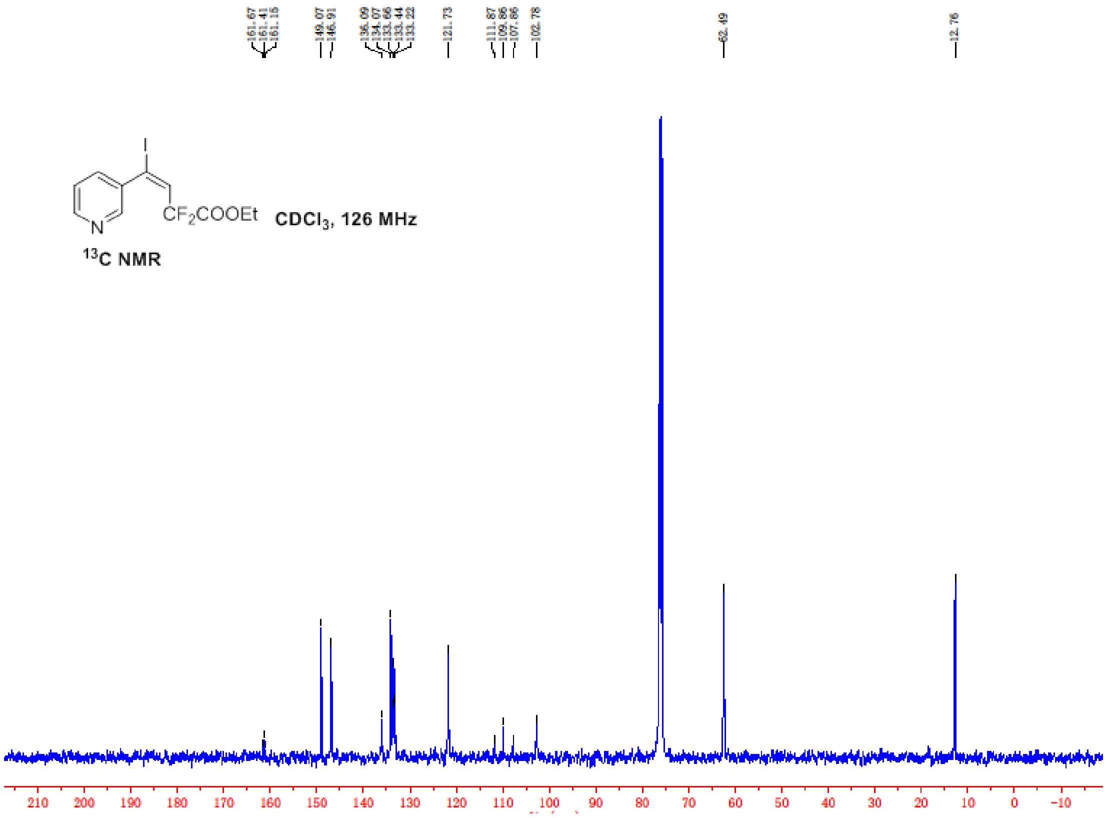


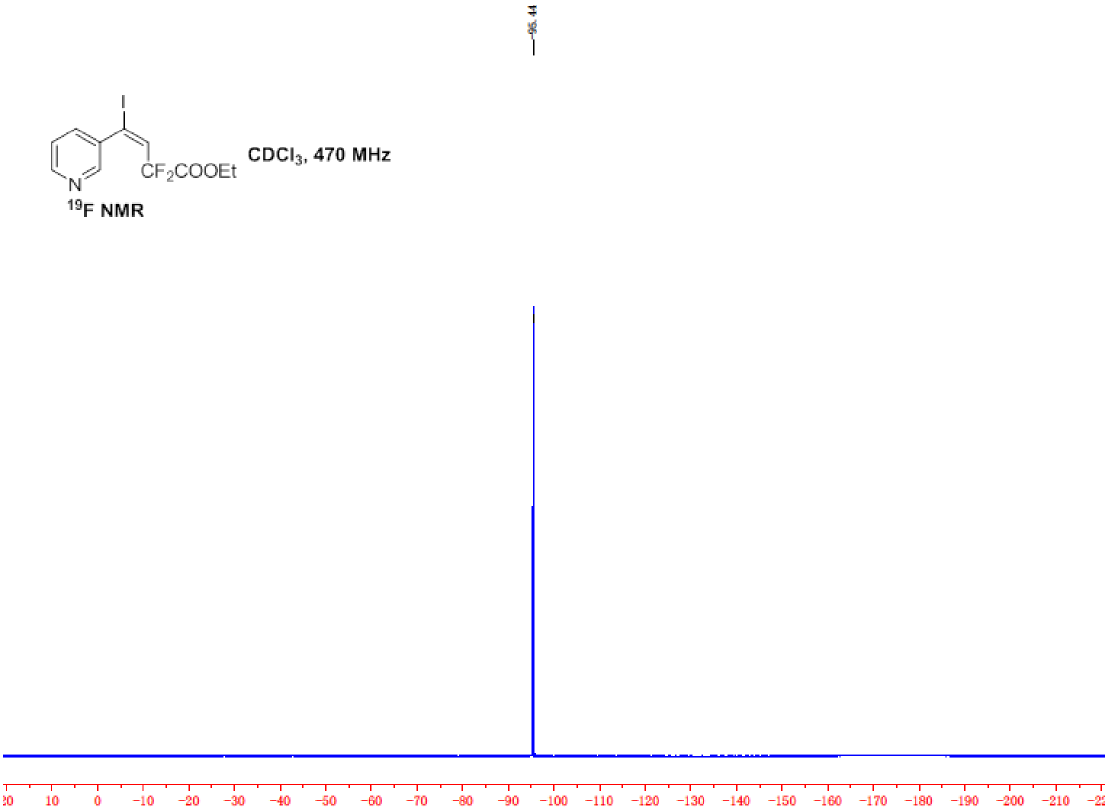
161.79
161.64
161.52
144.82
140.37
131.96
131.73
131.50
128.00
117.14
115.11
113.14
109.84
108.06
62.10
12.67
H2N
I
CF2COOEt
CDCl3, 126 MHz
13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



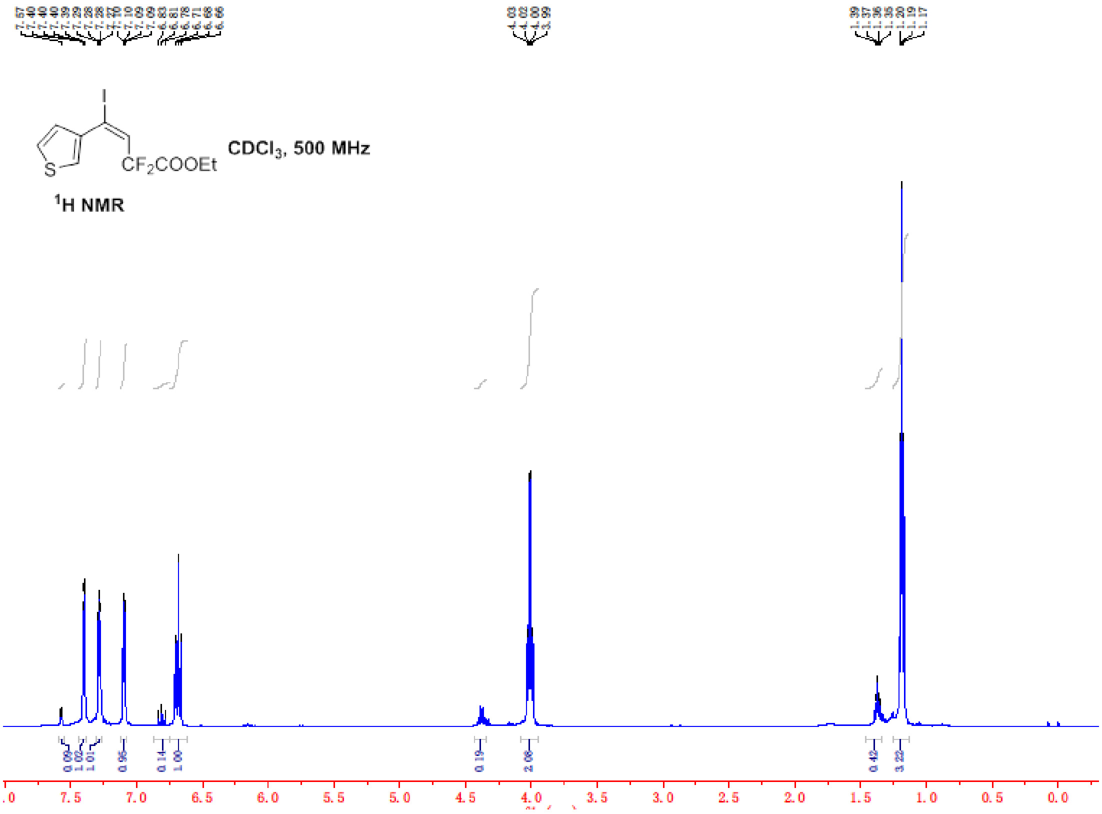
-93.08
-97.91
H2N
I
CF2COOEt
CDCl3, 470 MHz
19F NMR
1.00
0.04
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210


CDCl3, 500 MHz
CF2COOEt
N
I
1H NMR

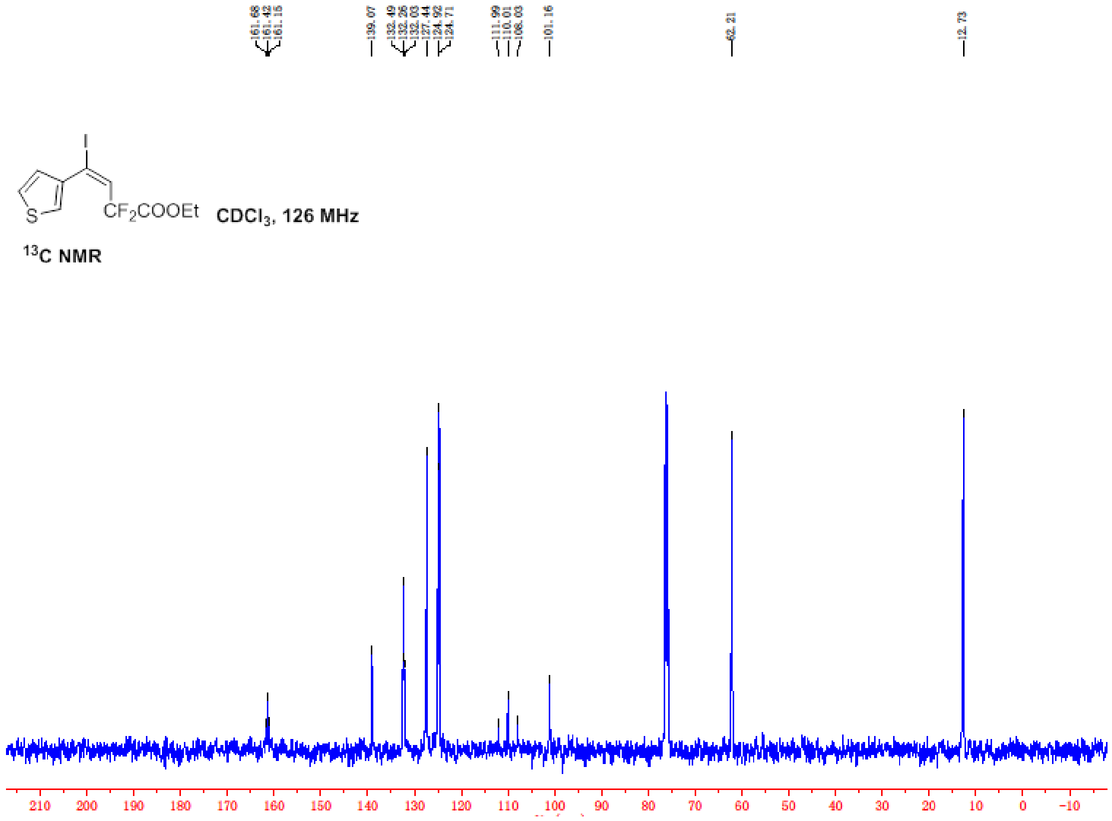

CDCl3, 126 MHz
CF2COOEt
N
I
13C NMR

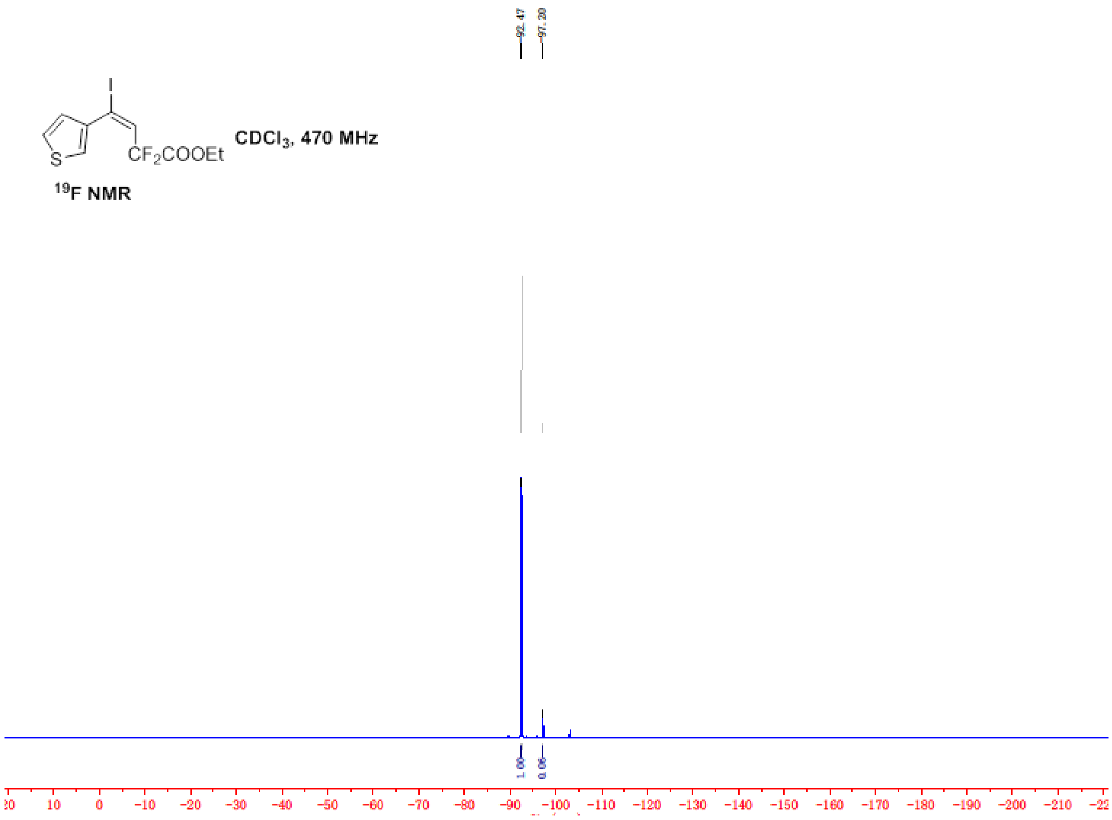


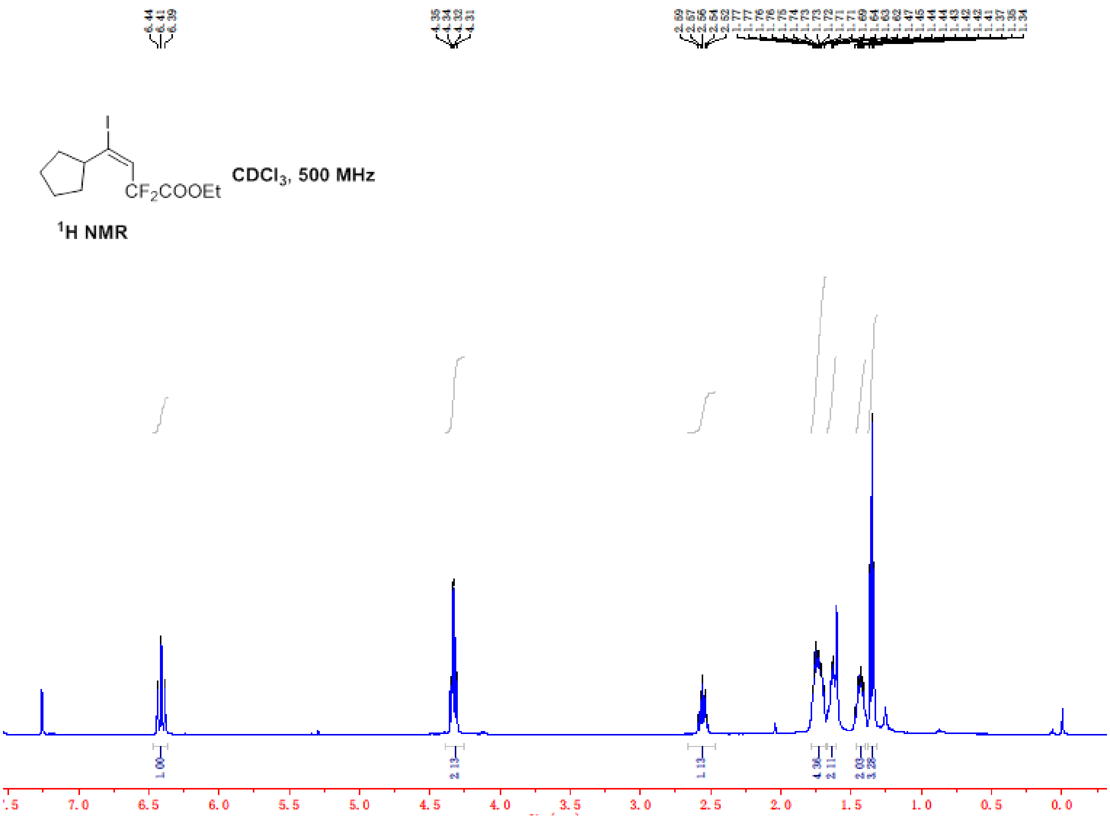
CF2COOEt
CDCl3, 470 MHz
19F NMR
-95.44

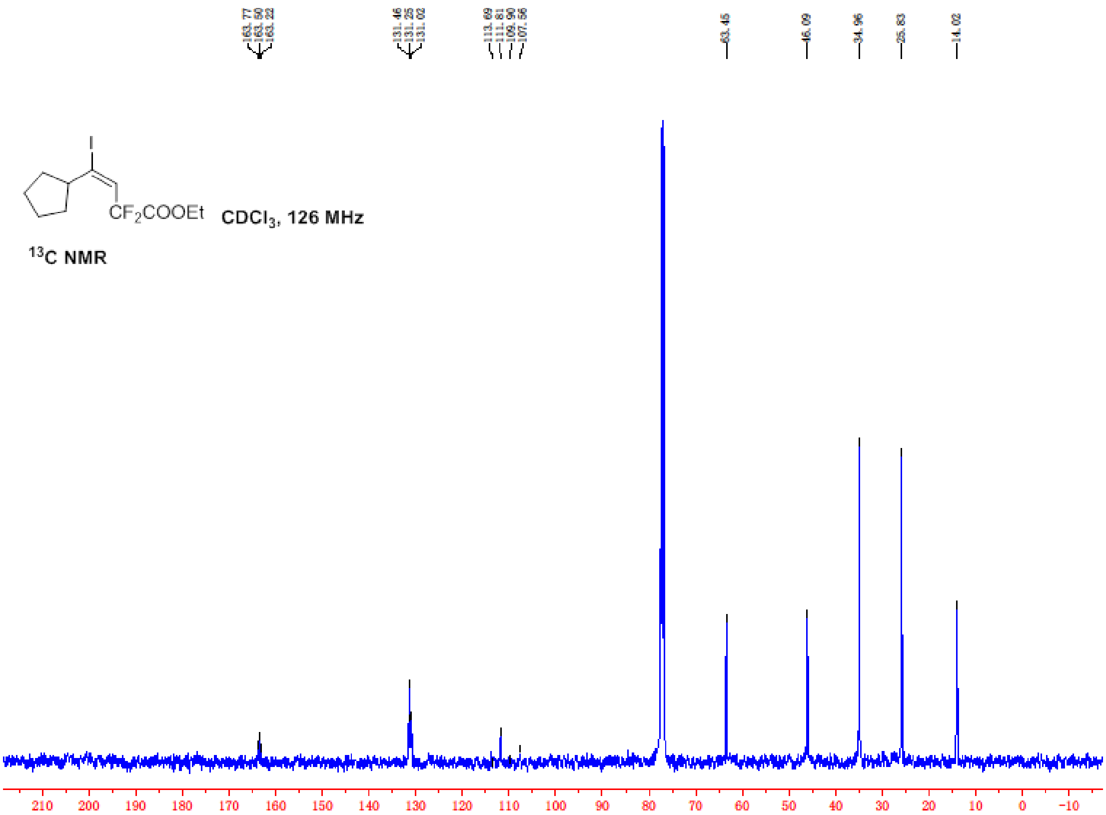


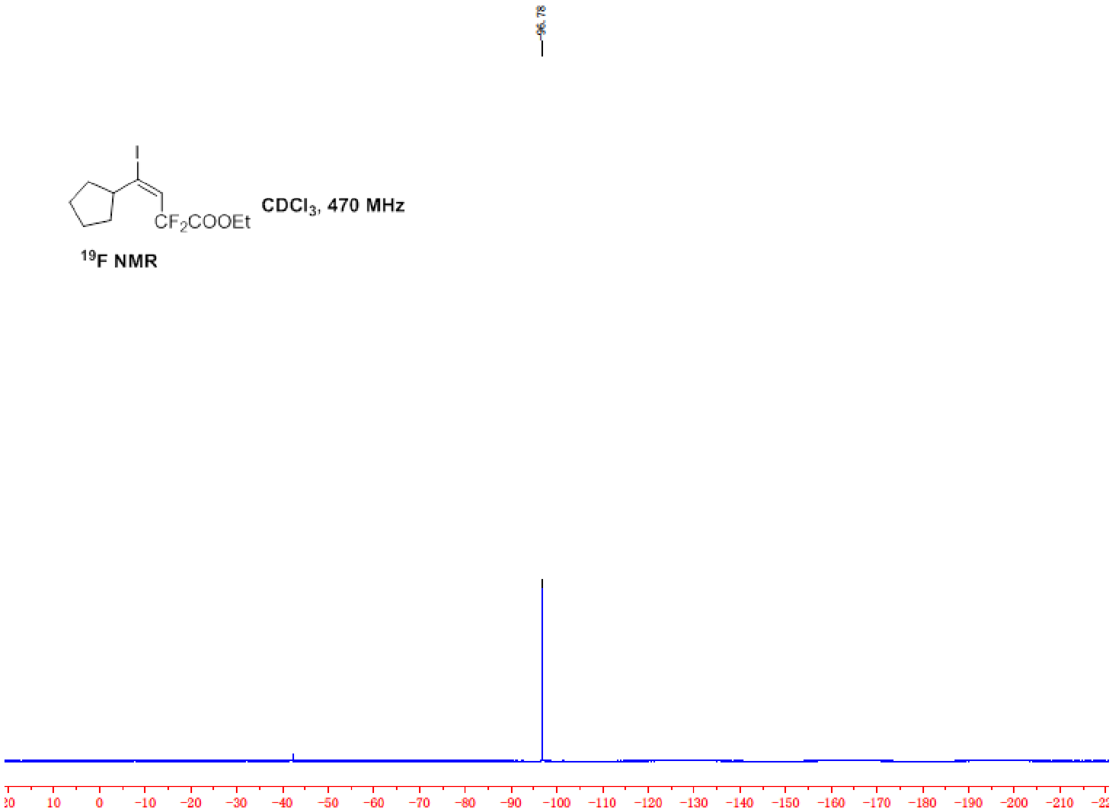
CF2COOEt
CDCl3, 500 MHz
1H NMR


161.68
161.42
161.15
139.07
132.49
132.26
132.03
127.44
124.92
124.71
111.99
110.01
108.03
101.16
62.21
12.73
CF2COOEt
CDCl3, 126 MHz
13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

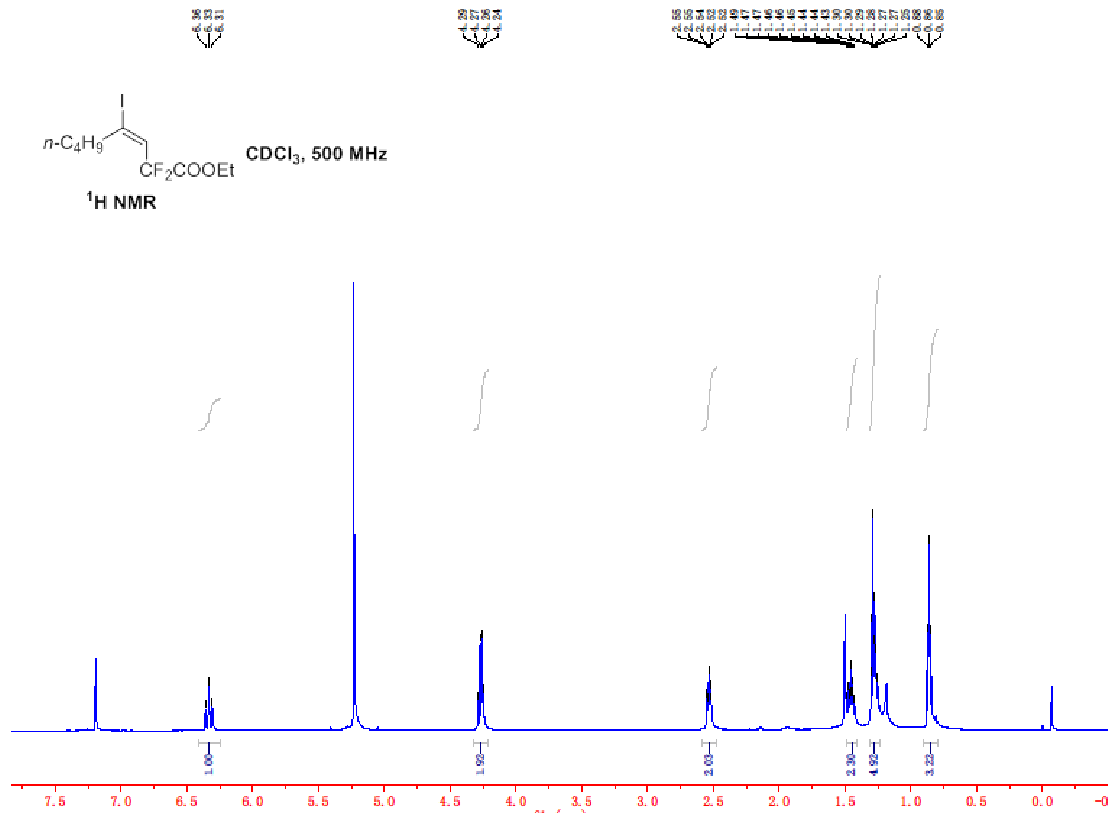

-92.47
-97.20
CF2COOEt
CDCl3, 470 MHz
19F NMR
1.00
0.06
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22


CDCl3, 500 MHz
1H NMR

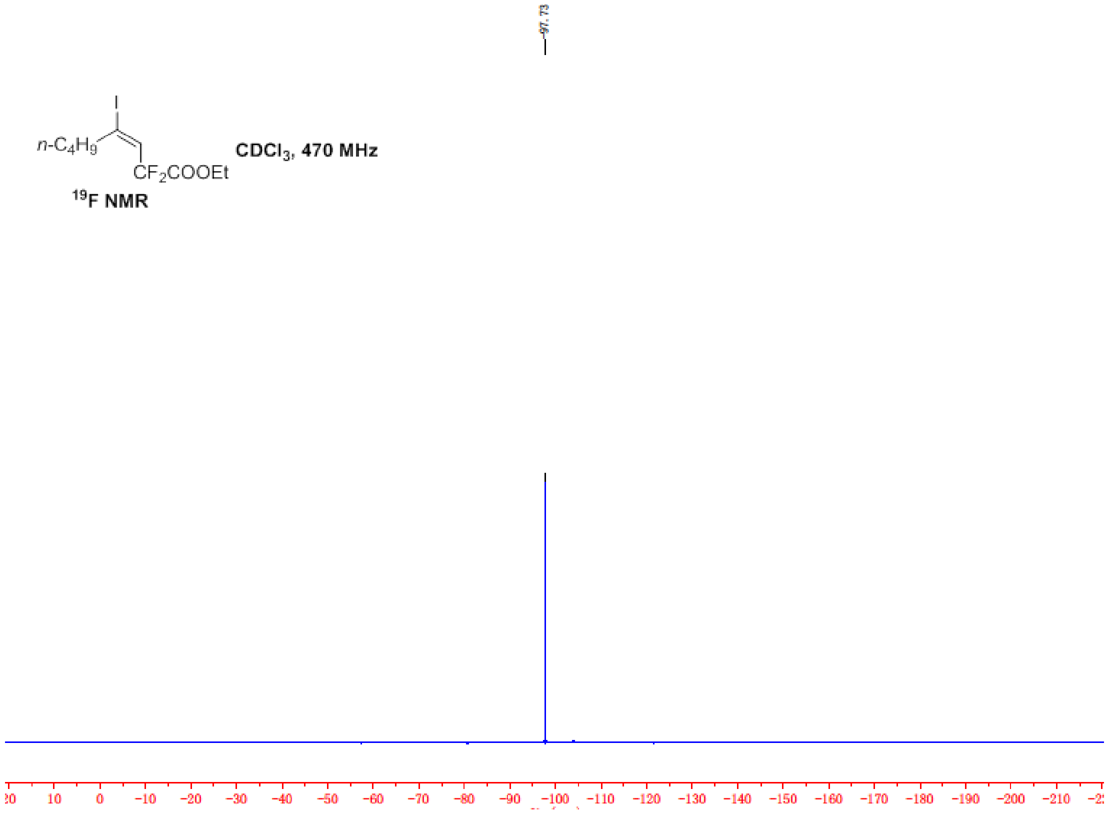

CDCl3, 126 MHz
13C NMR

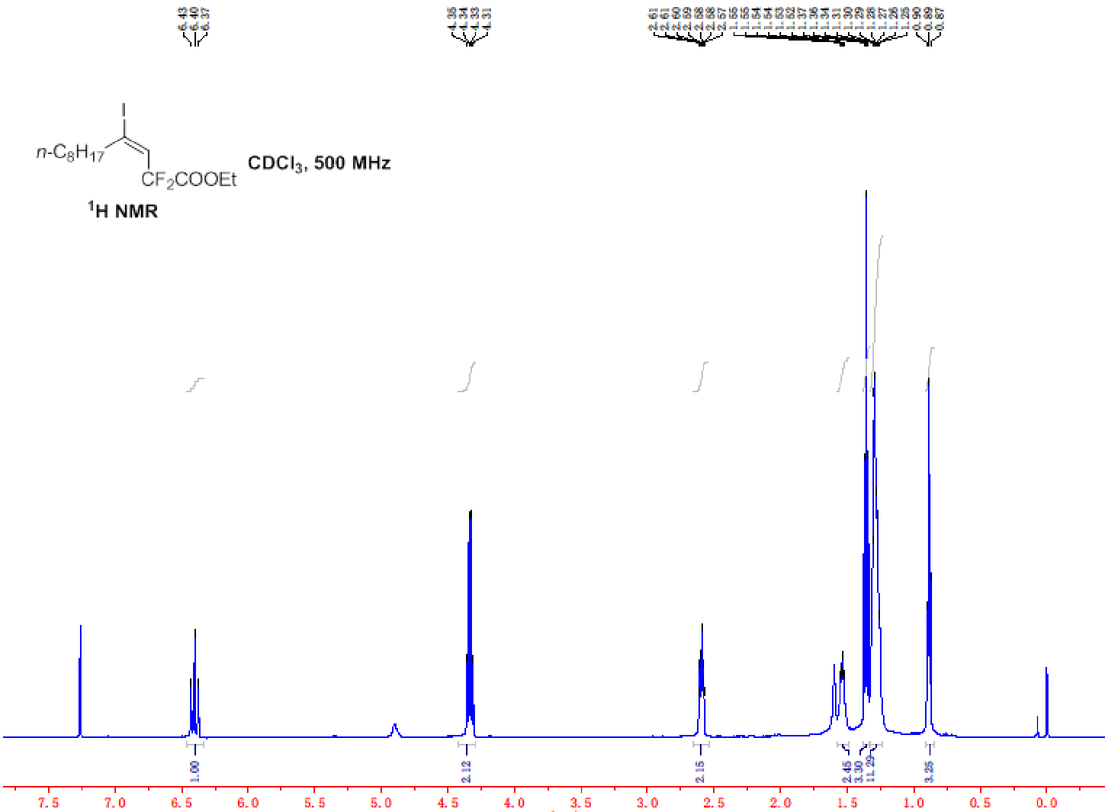


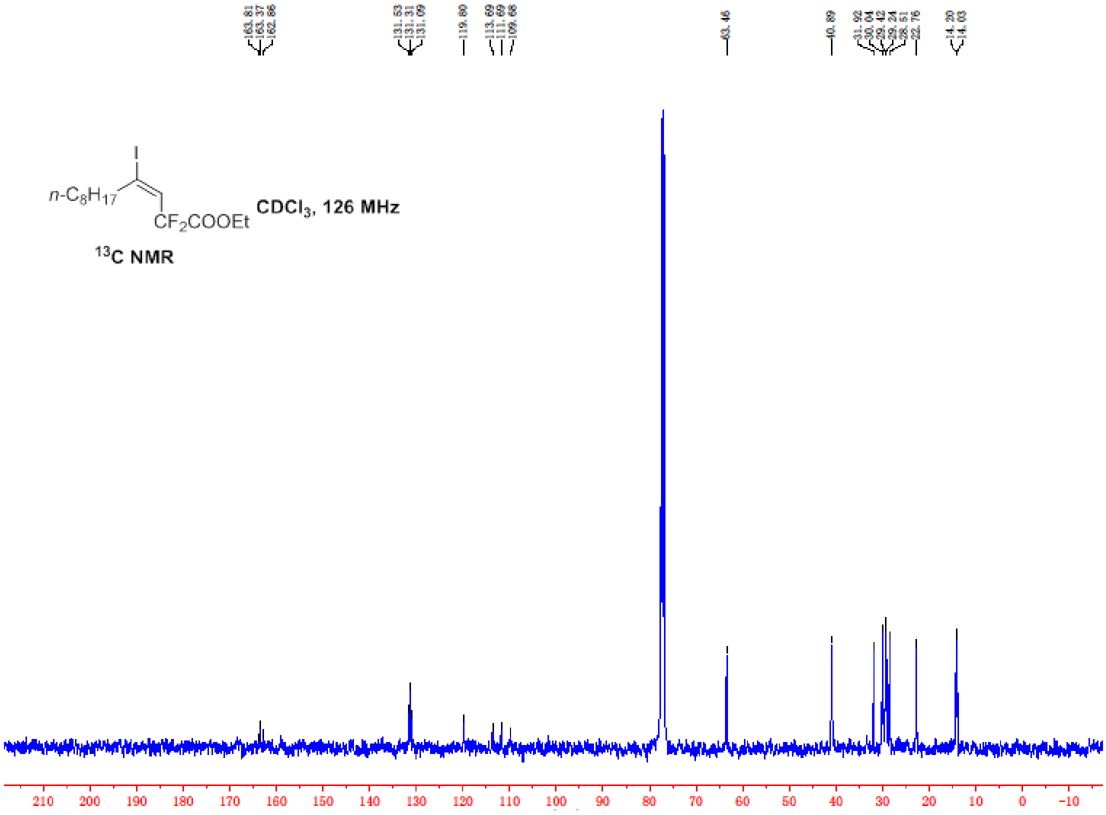
-96.78
I
CF2COOEt
CDCl3, 470 MHz
19F NMR



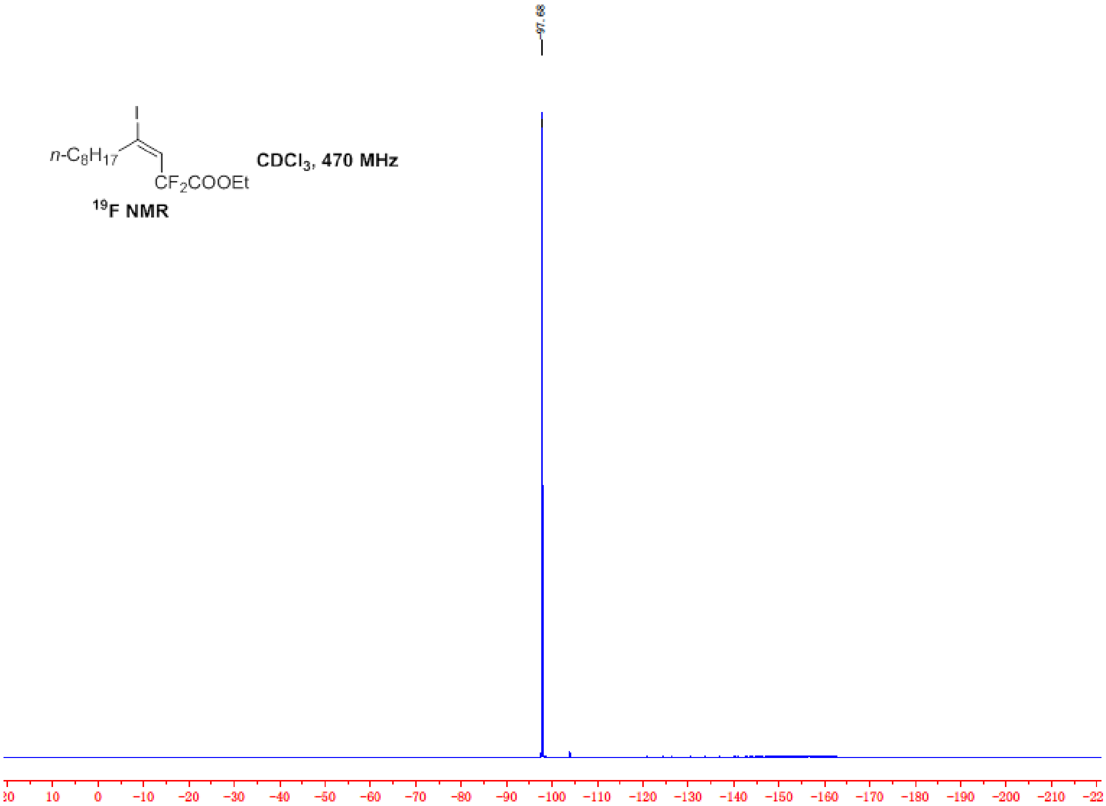
I
n-C4H9
CF2COOEt
CDCl3, 500 MHz
1H NMR
1.00
1.92
2.03
2.30
4.92
3.22


-97.73
n-C4H9
CF2COOEt
CDCl3, 470 MHz
19F NMR

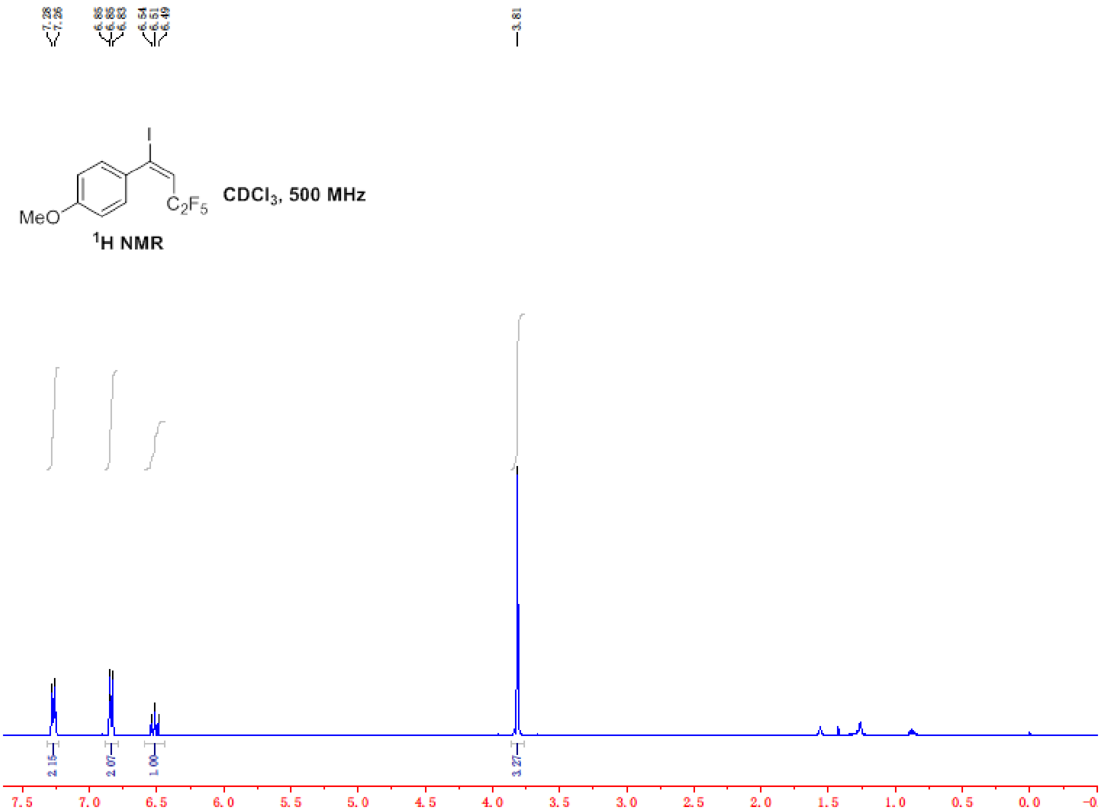

n-C8H17
CF2COOEt
CDCl3, 500 MHz
1H NMR

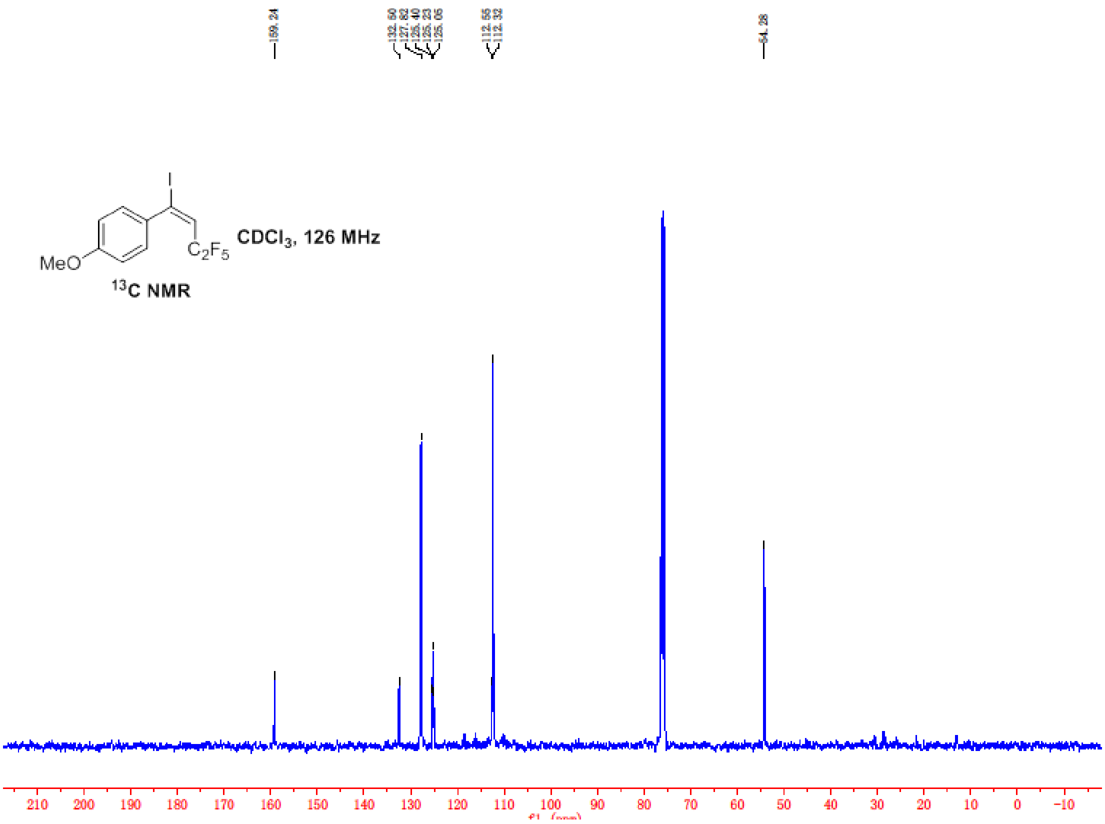


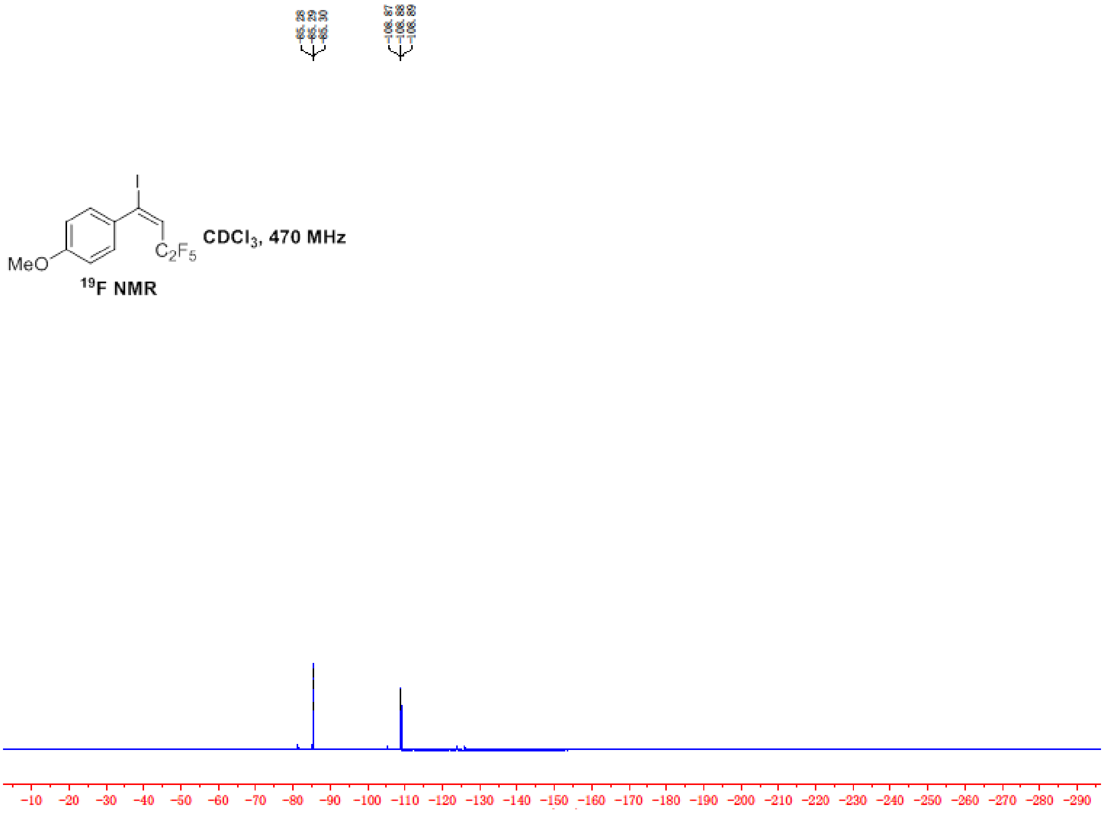
163.81
163.37
162.86
131.53
131.31
131.09
119.80
113.69
111.69
109.68
63.46
40.89
31.92
30.04
29.42
29.24
28.51
22.76
14.20
14.03
n-C8H17
I
CF2COOEt
CDCl3, 126 MHz
13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

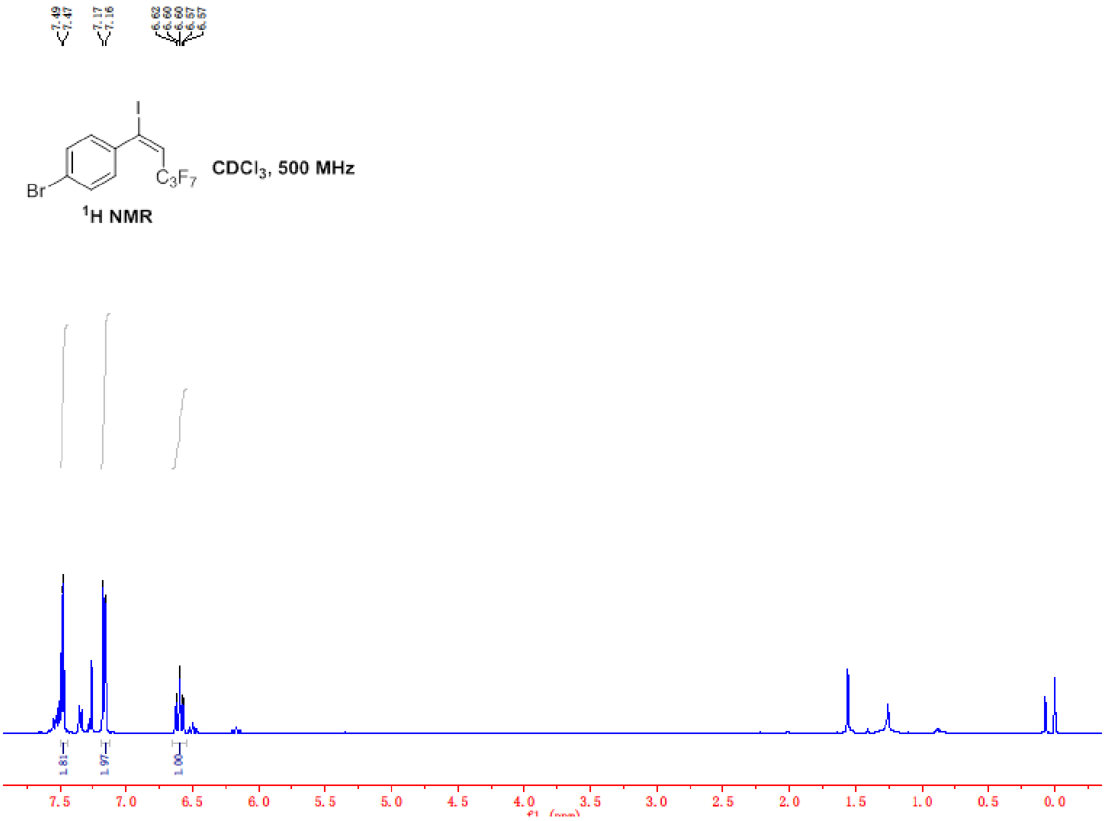


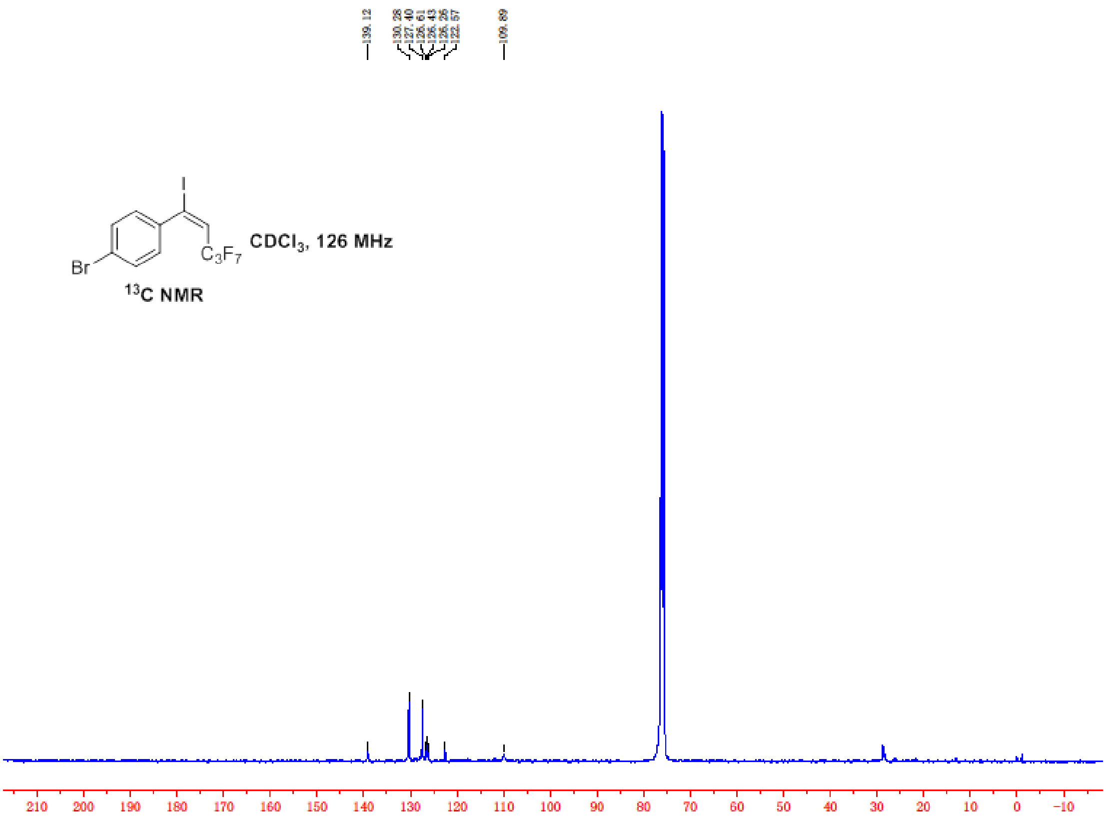
-97.68
n-C8H17
I
CF2COOEt
CDCl3, 470 MHz
19F NMR
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210


7.28
7.26
6.85
6.85
6.83
6.54
6.51
6.49
3.81
I
MeO
C2F5
CDCl3, 500 MHz
1H NMR
2.15
2.07
1.00
3.27
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

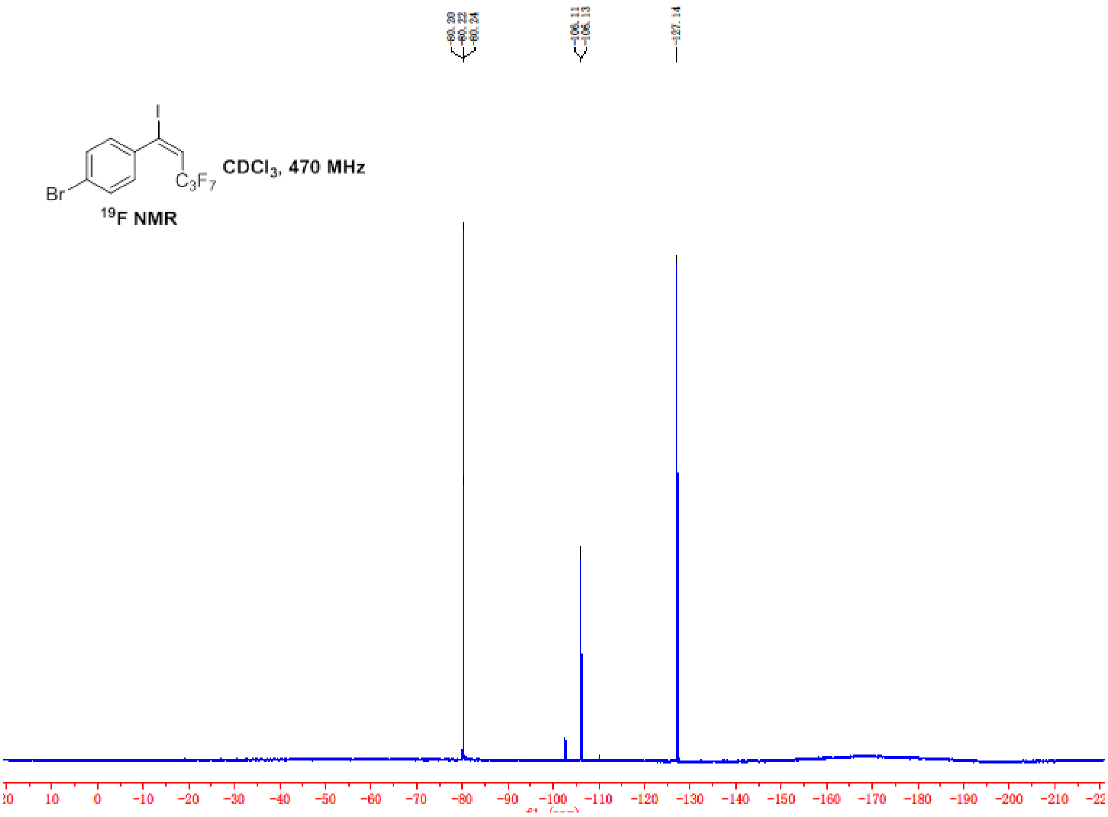

159.24
132.50
127.82
125.40
125.23
125.06
112.55
112.32
54.28
I
MeO
C2F5
CDCl3, 126 MHz
13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-85.28
-85.29
-85.30
-108.87
-108.88
-108.89
MeO
I
C_2F_5
$CDCl_3$, 470 MHz
^{19}F NMR
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240 -250 -260 -270 -280 -290

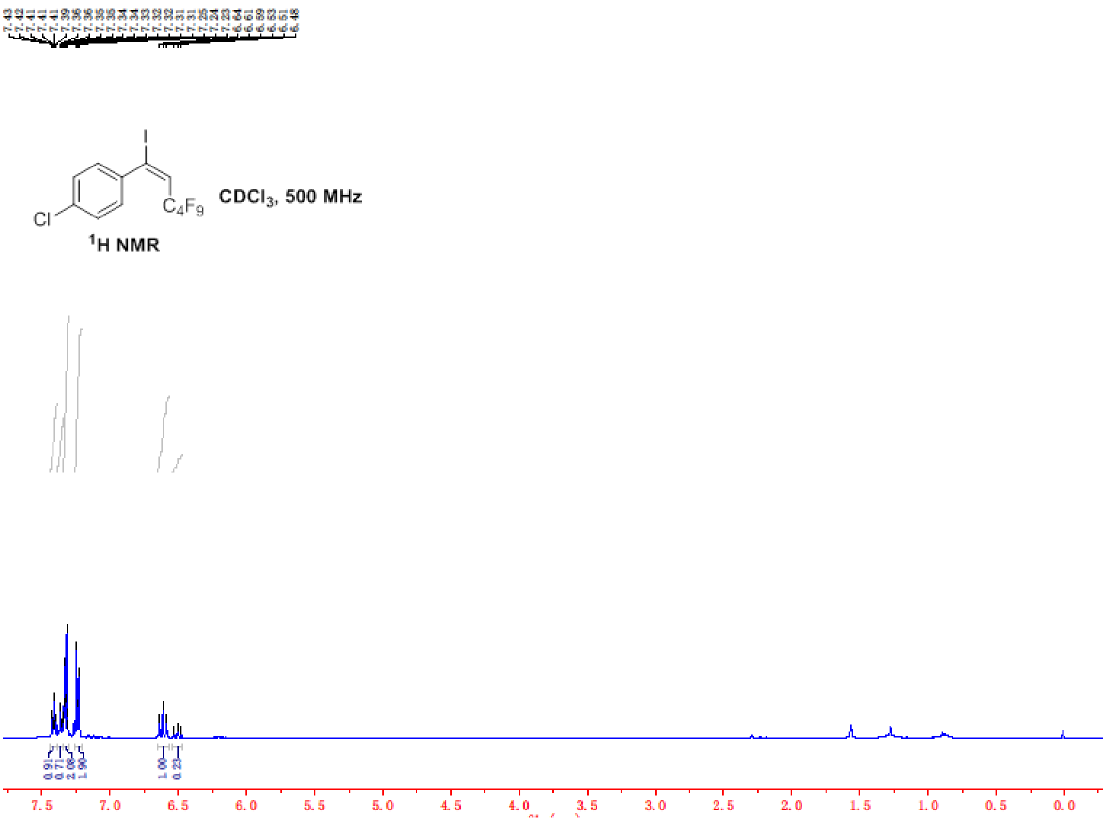

7.49
7.47
7.17
7.16
6.62
6.60
6.60
6.57
6.57
Br
I
C_3F_7
$CDCl_3$, 500 MHz
^{1}H NMR
1.81
1.97
1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

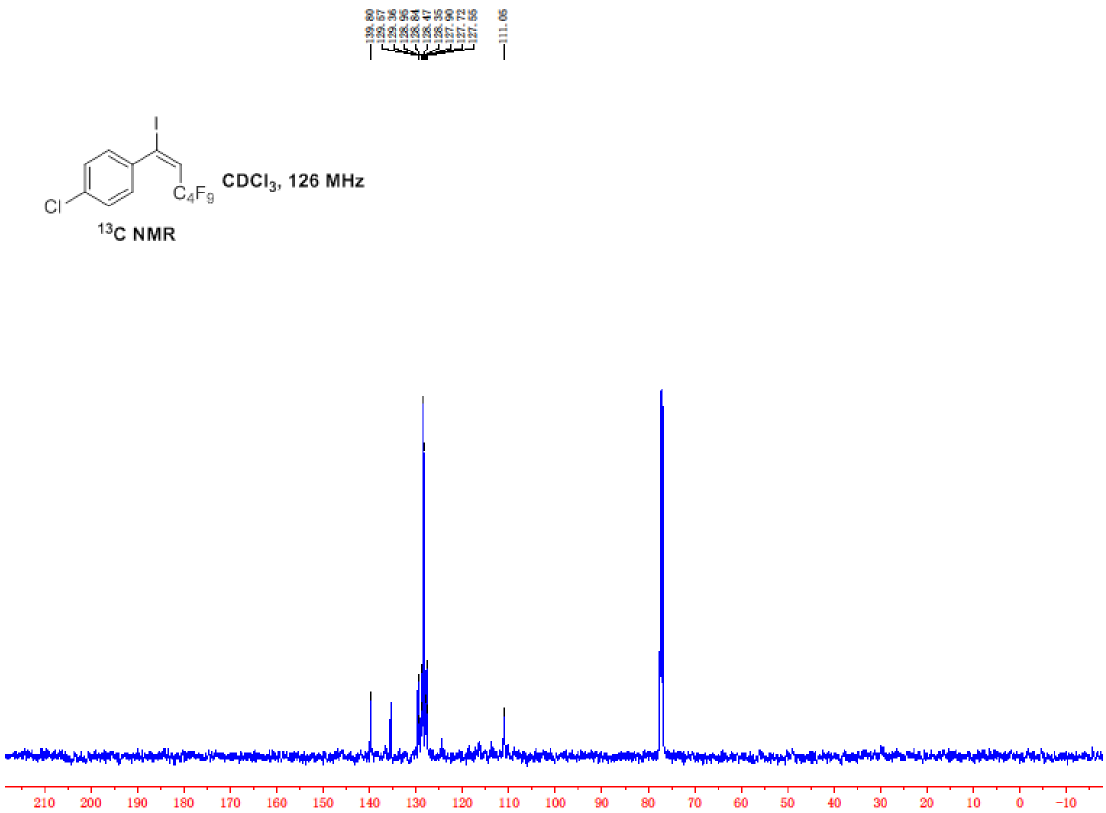


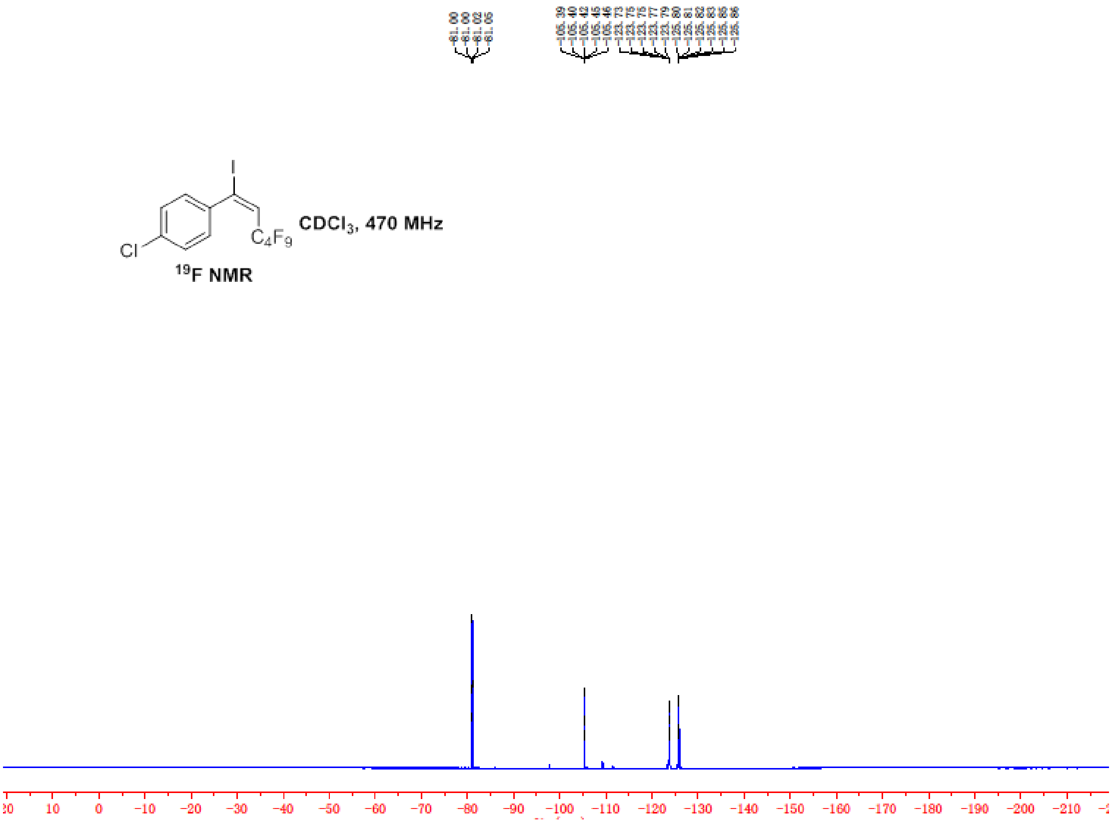
139.12
130.28
127.40
126.61
126.43
126.26
122.57
109.89
CDCl3, 126 MHz
13C NMR
Br
I
C3F7



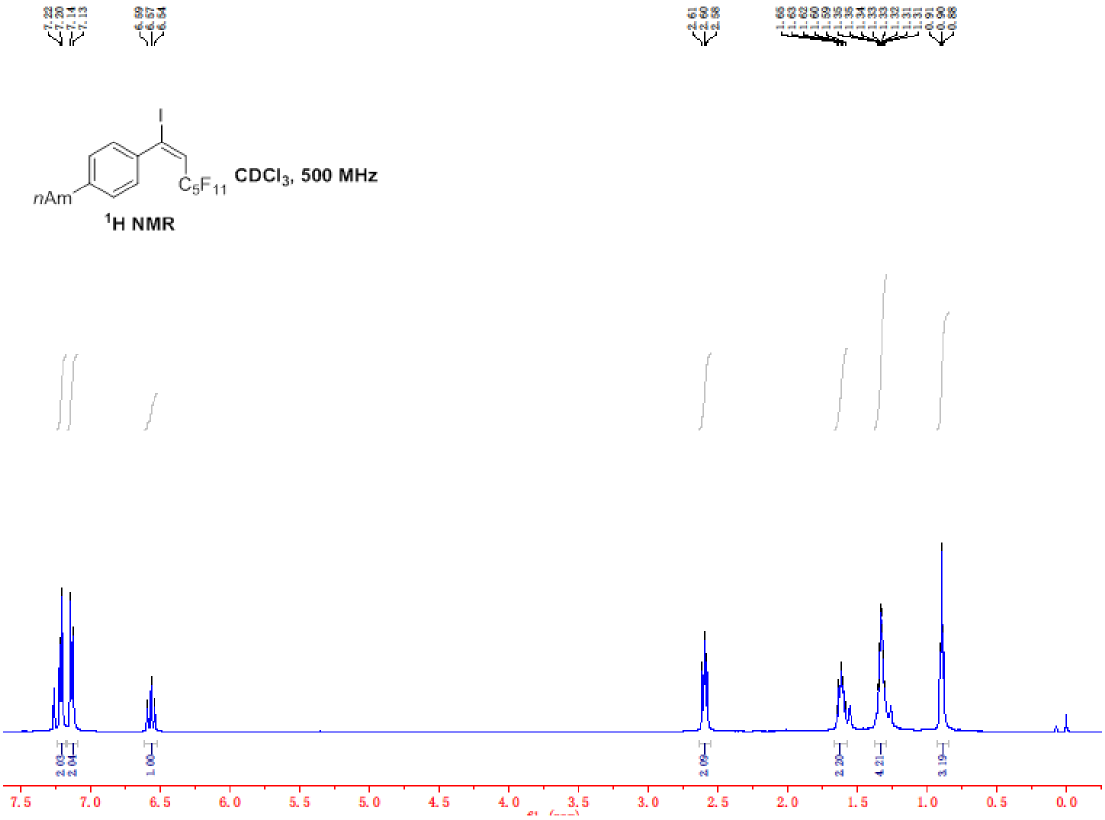
-80.20
-80.22
-80.24
-106.11
-106.13
-127.14
CDCl3, 470 MHz
19F NMR
Br
I
C3F7


7.43
7.42
7.41
7.41
7.39
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.25
7.24
7.23
6.64
6.61
6.59
6.53
6.51
6.48
Cl
I
C4F9
CDCl3, 500 MHz
1H NMR
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

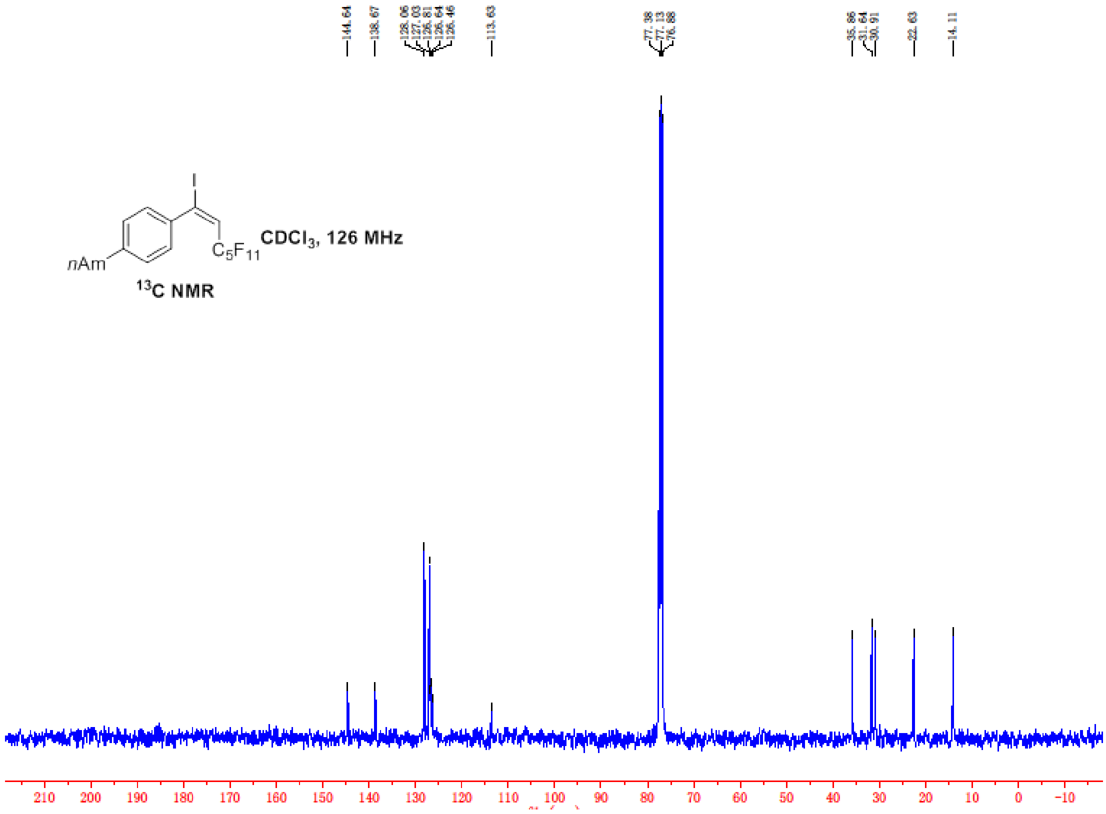

139.80
129.57
129.36
128.95
128.84
128.47
128.35
127.90
127.72
127.55
111.05
Cl
I
C4F9
CDCl3, 126 MHz
13C NMR
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10



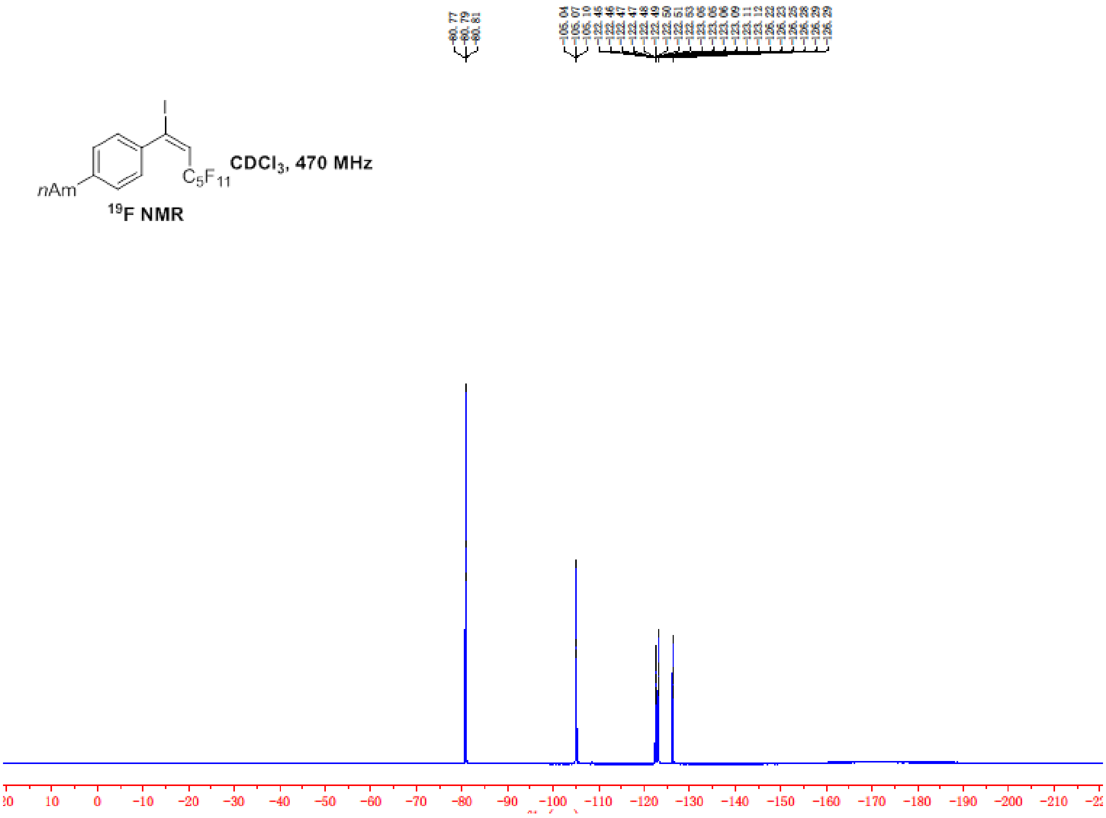
CDCl3, 470 MHz
19F NMR



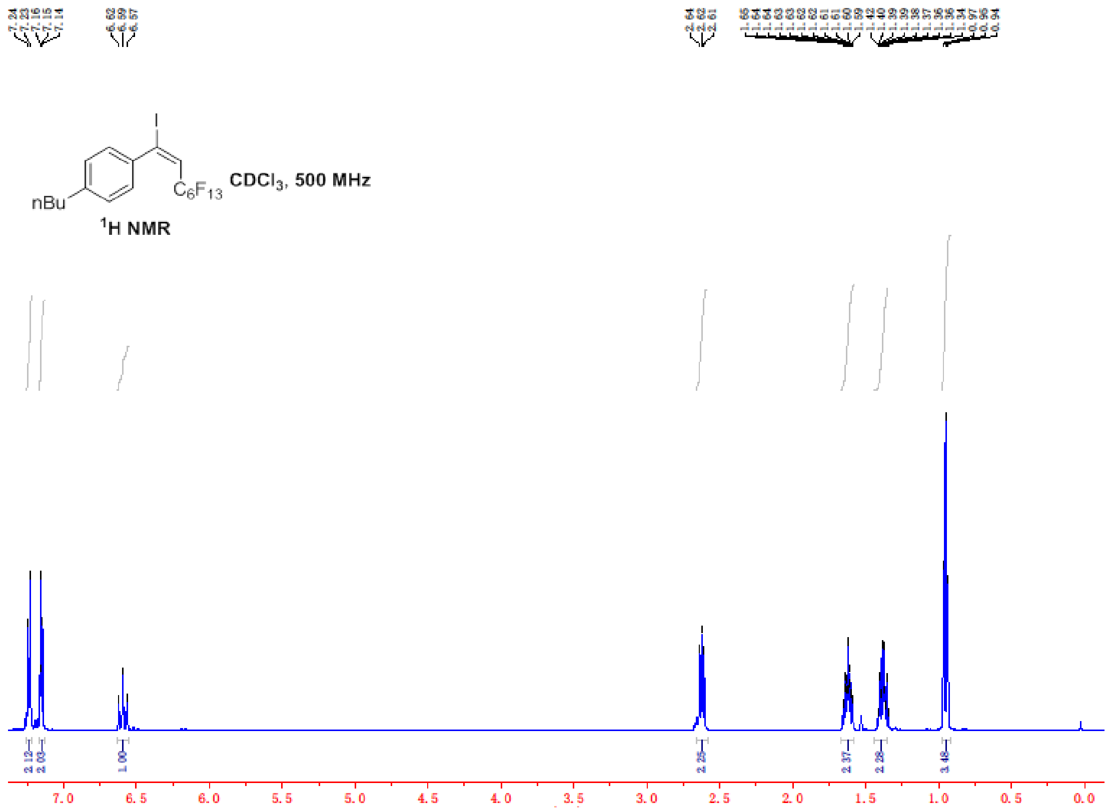
nAm
CDCl3, 500 MHz
1H NMR



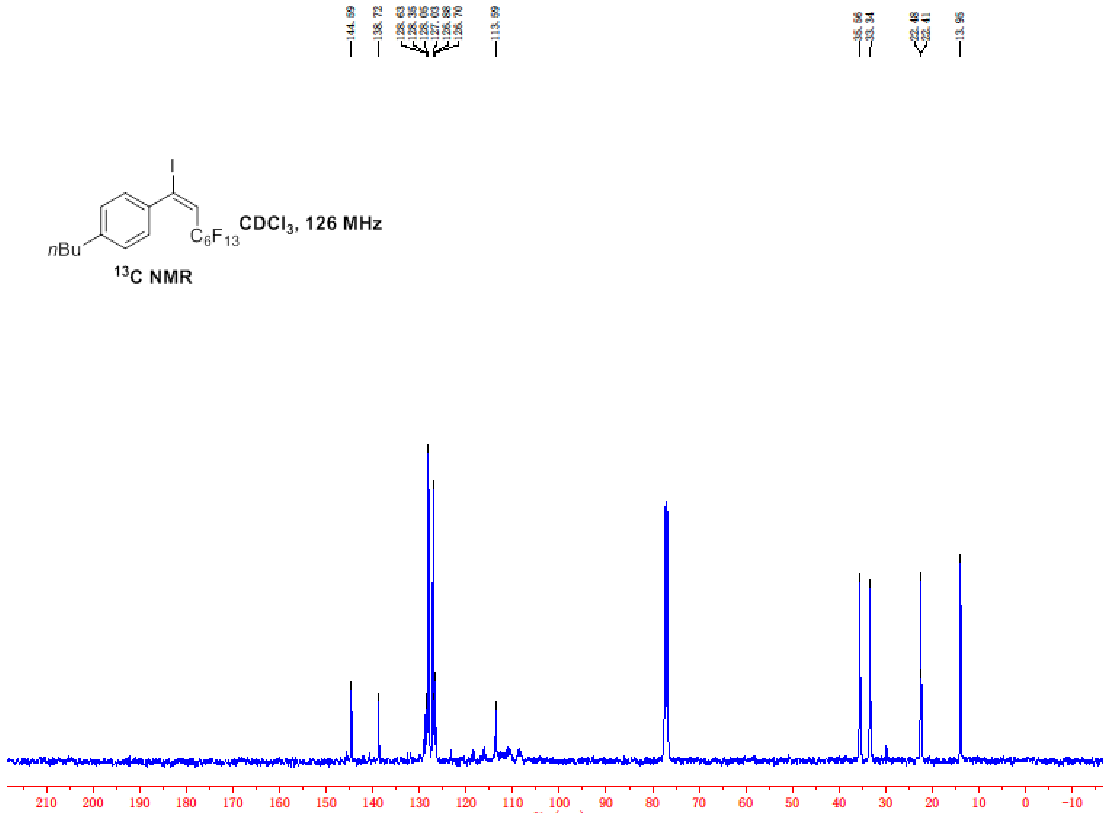
CDCl$_3$, 126 MHz
^{13}C NMR



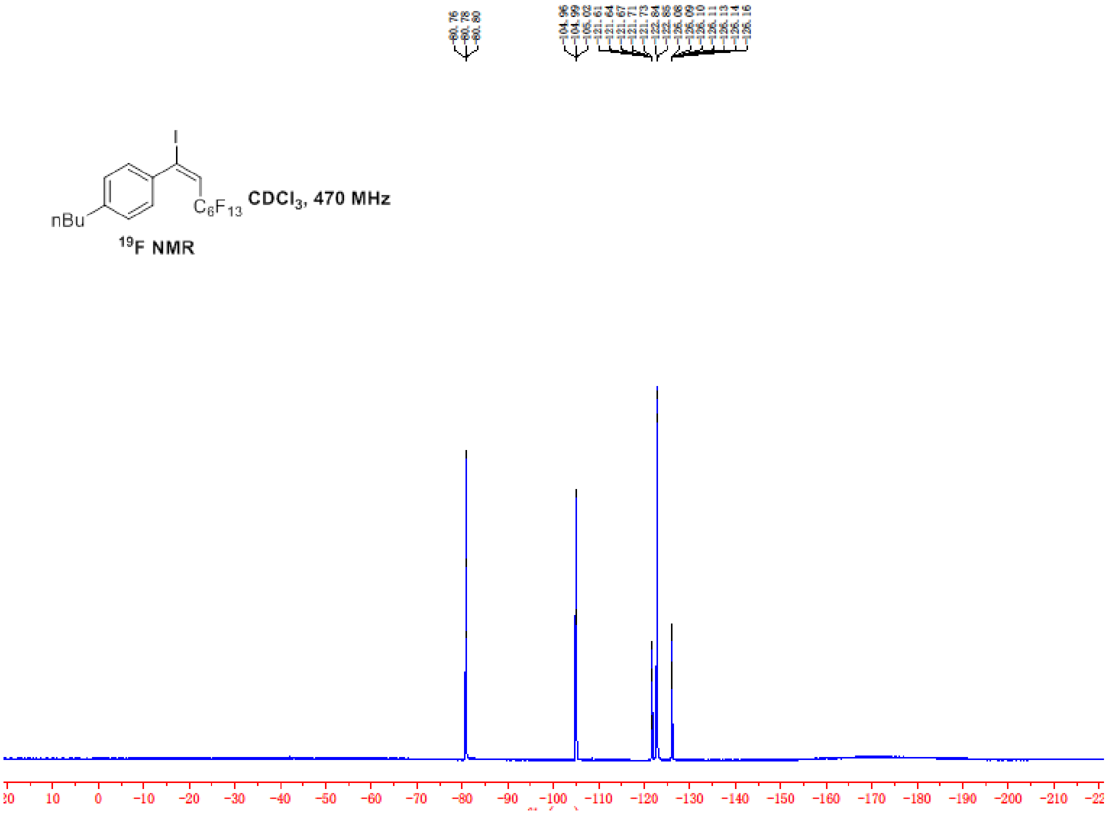
CDCl$_3$, 470 MHz
^{19}F NMR



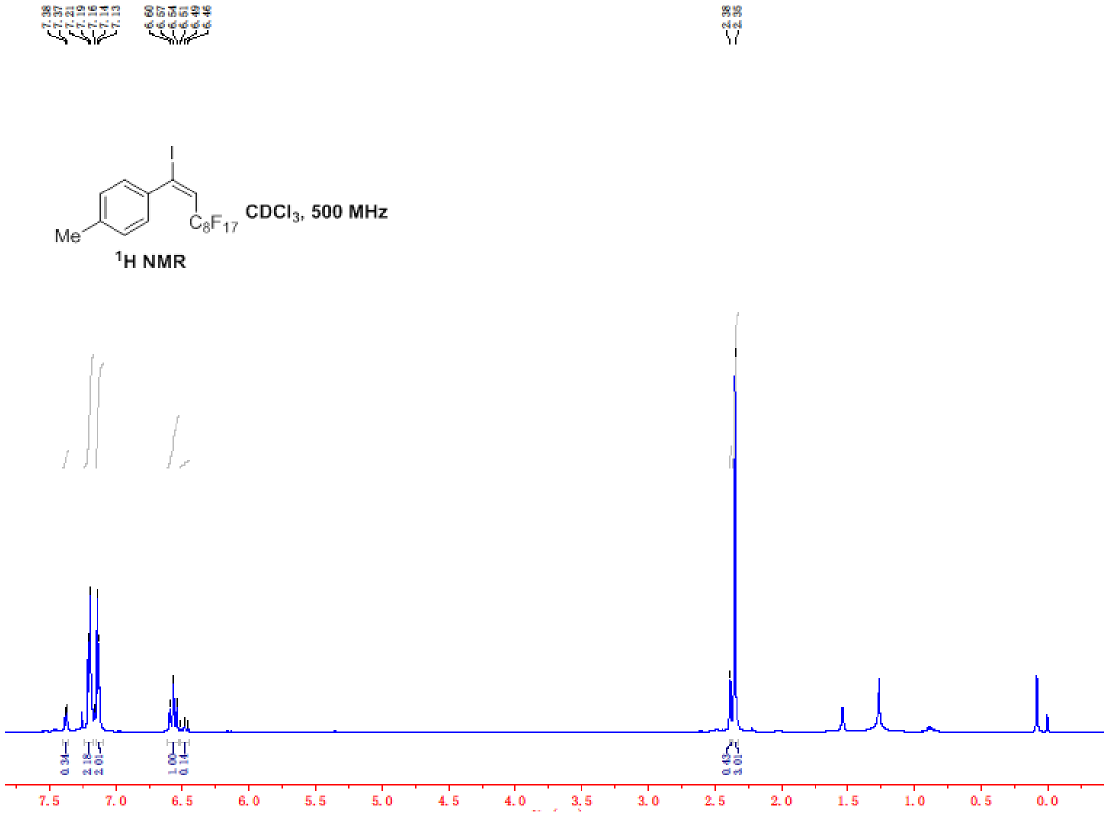
7.24
7.23
7.16
7.15
7.14
6.62
6.59
6.57
2.64
2.62
2.61
1.65
1.64
1.64
1.63
1.63
1.62
1.62
1.61
1.61
1.60
1.59
1.42
1.40
1.39
1.39
1.38
1.37
1.36
1.36
1.34
0.97
0.95
0.94
I
nBu
C6F13
CDCl3, 500 MHz
1H NMR
2.12
2.03
1.00
2.25
2.37
2.28
3.48
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



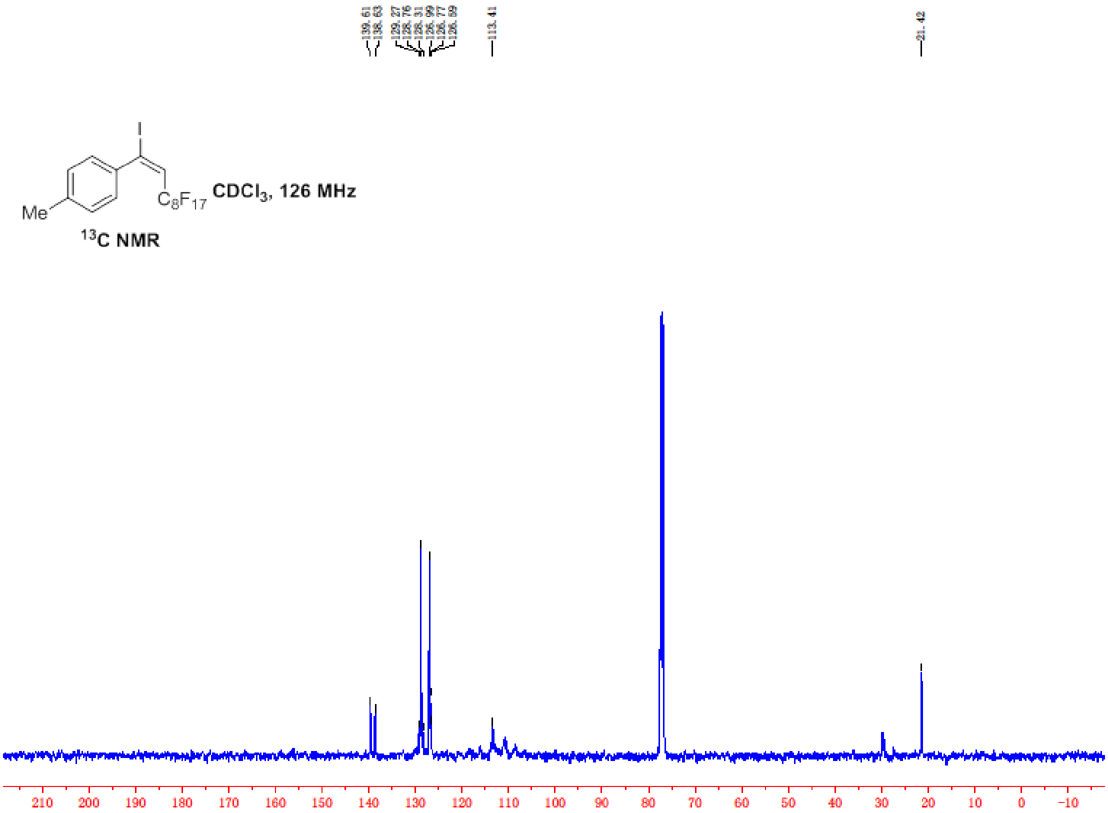
144.69
138.72
128.63
128.35
128.05
127.03
126.88
126.70
113.59
35.56
33.34
22.48
22.41
13.96
I
nBu
C6F13
CDCl3, 126 MHz
13C NMR
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10



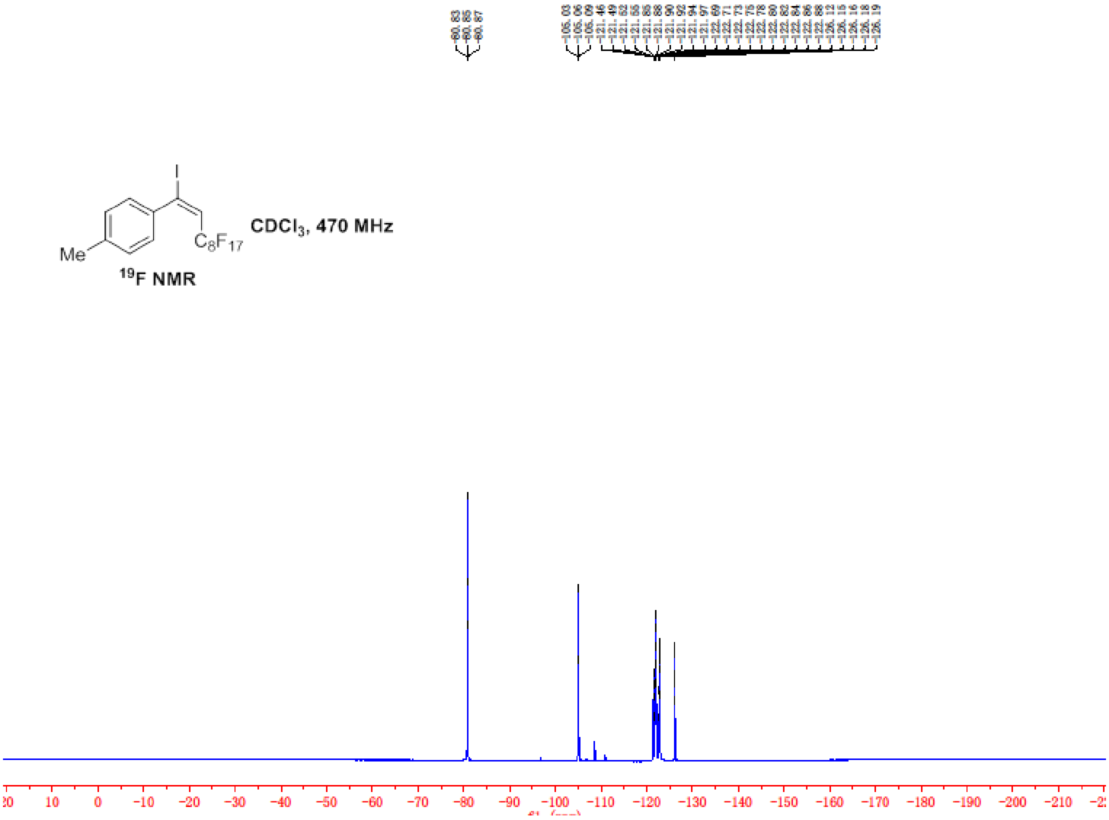
CDCl3, 470 MHz
19F NMR
nBu
C6F13



CDCl3, 500 MHz
1H NMR
Me
C8F17



139.61
138.63
129.27
128.76
128.31
126.99
126.77
126.59
113.41
21.42
I
Me
C8F17
CDCl3, 126 MHz
13C NMR



-80.83
-80.85
-80.87
-105.03
-105.06
-105.09
-121.46
-121.49
-121.52
-121.55
-121.85
-121.88
-121.90
-121.92
-121.94
-121.97
-122.69
-122.71
-122.73
-122.75
-122.78
-122.80
-122.82
-122.84
-122.86
-122.88
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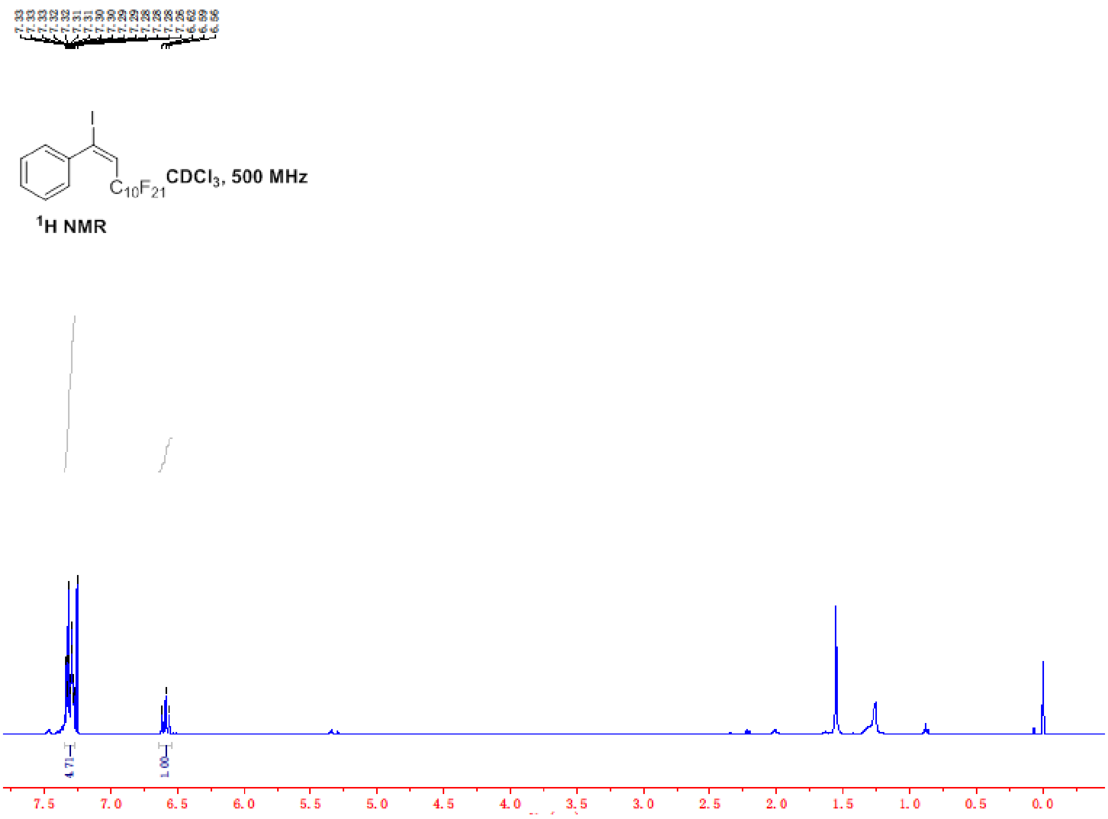
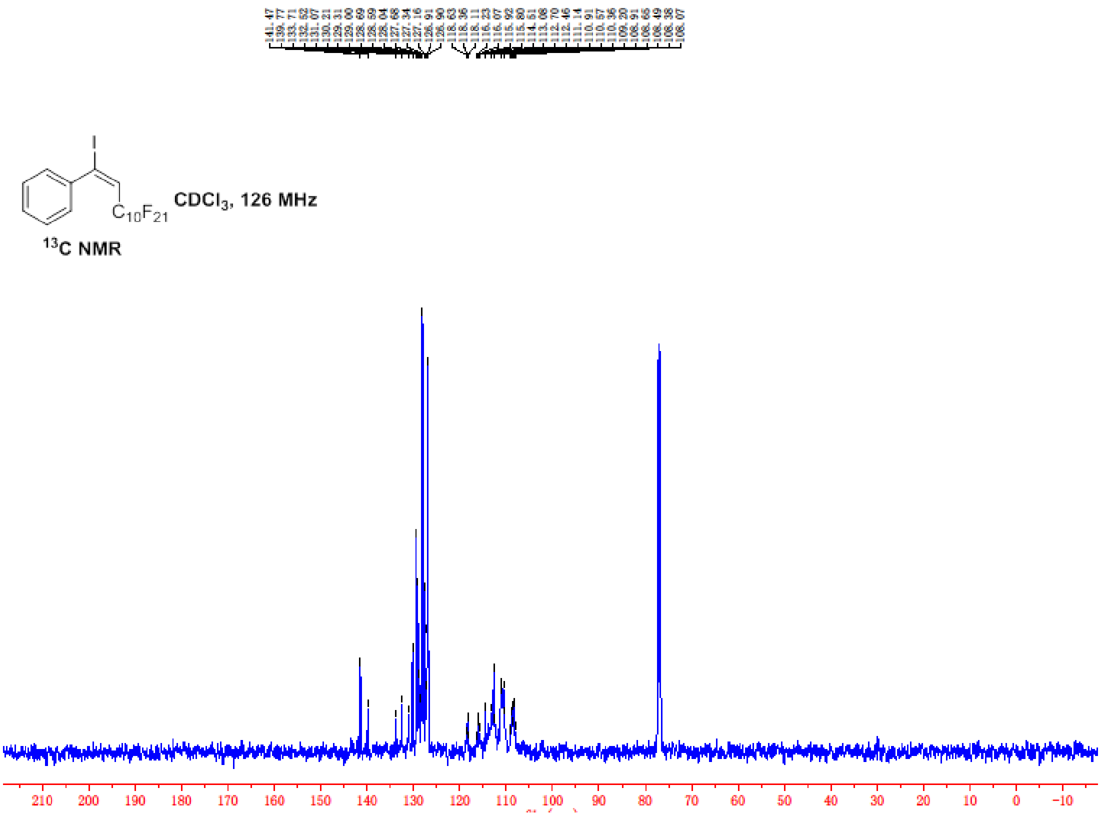
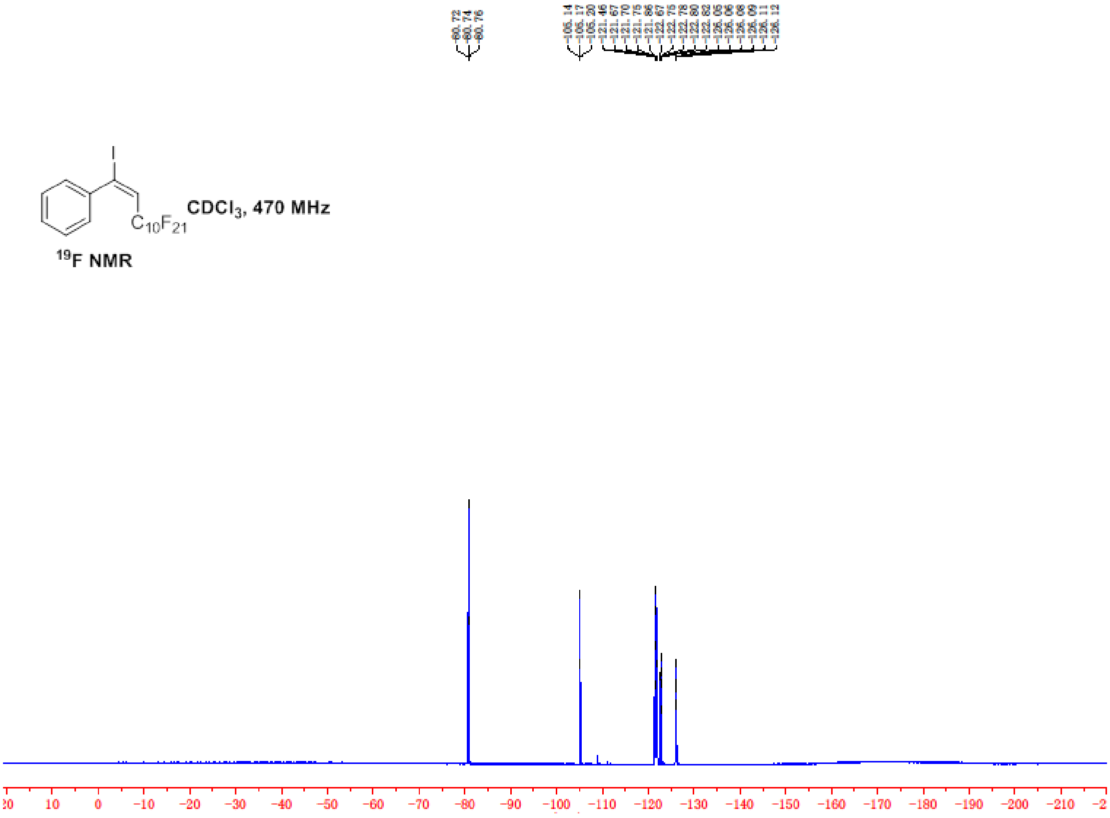
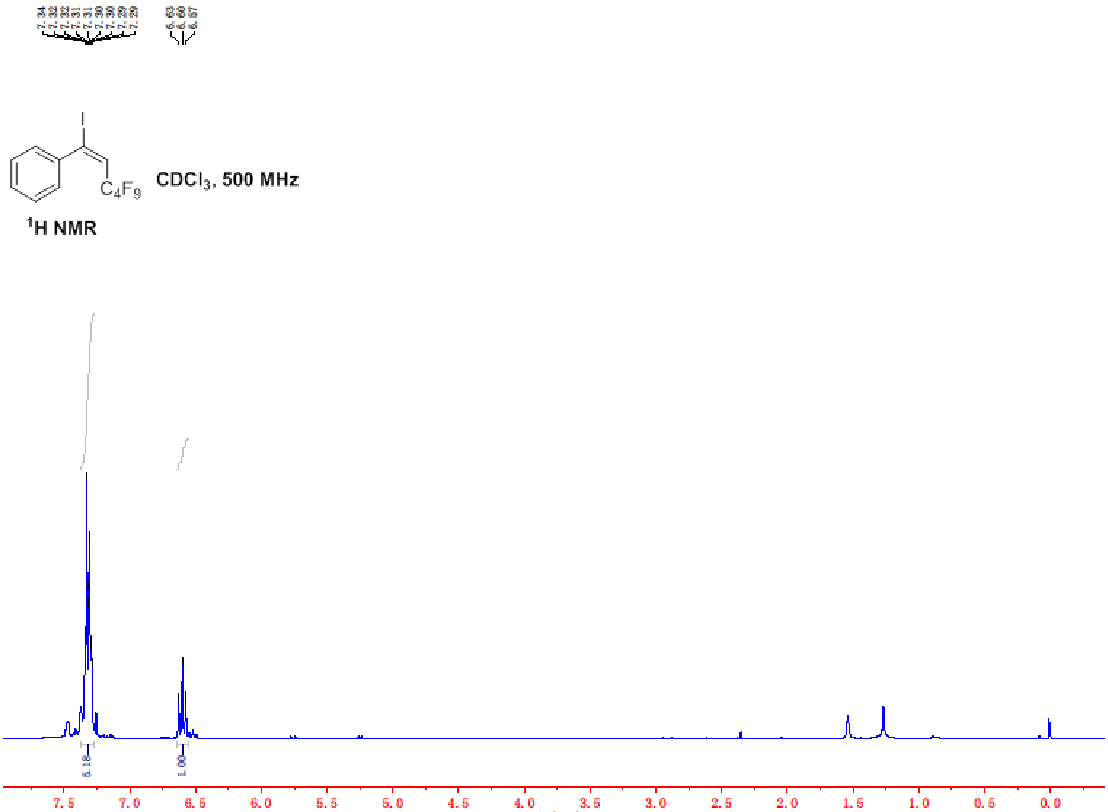
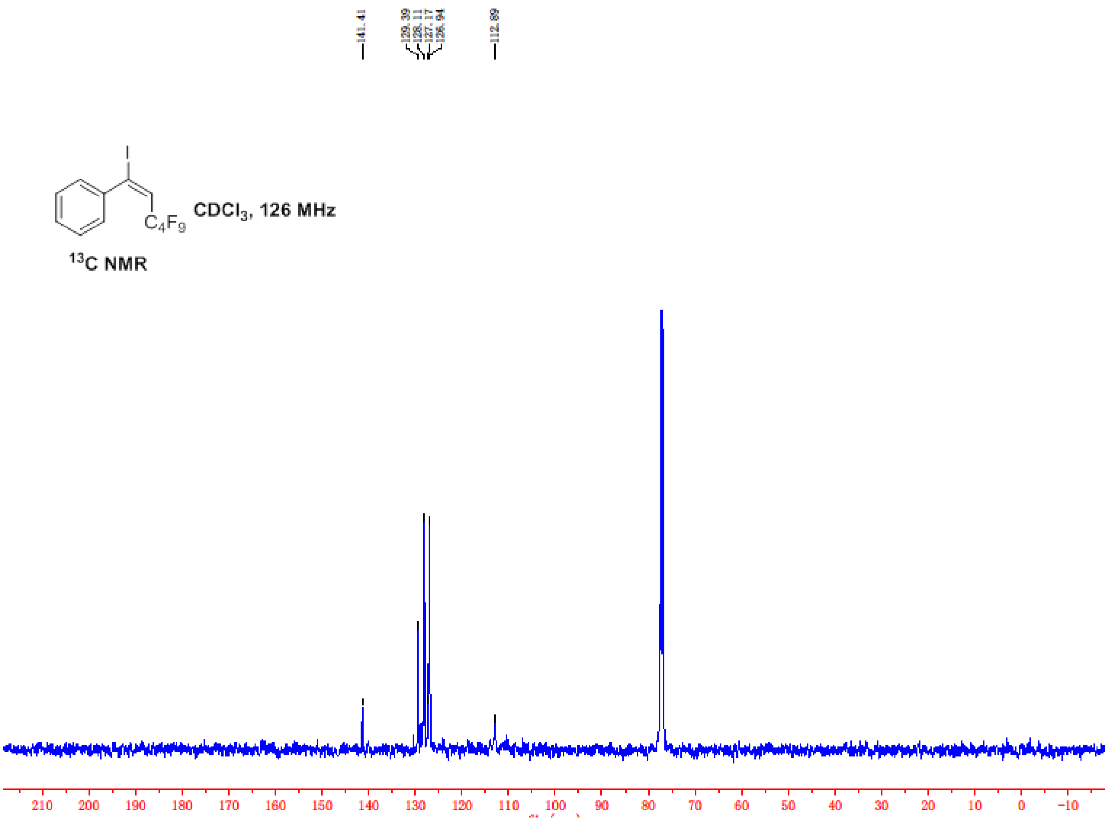
-126.15
-126.16
-126.18
-126.19
I
Me
C8F17
CDCl3, 470 MHz
19F NMR

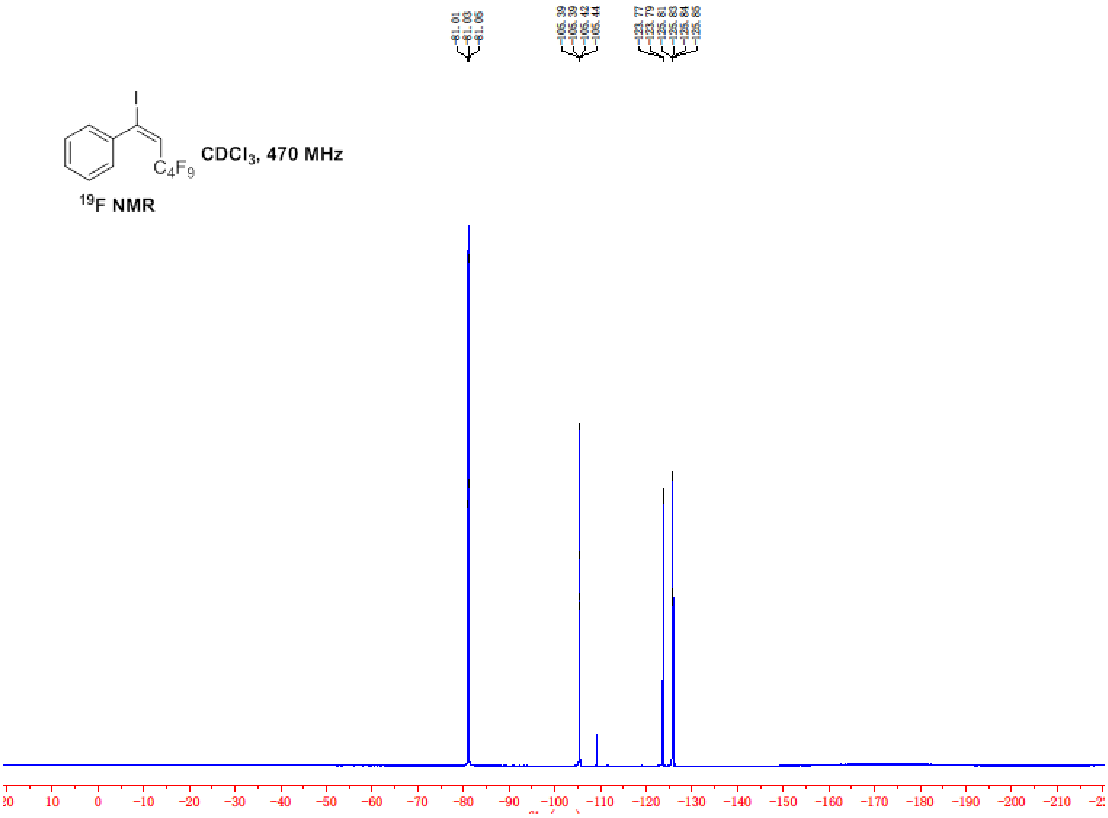

I
C10F21
CDCl3, 500 MHz
1H NMR
4.71
1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

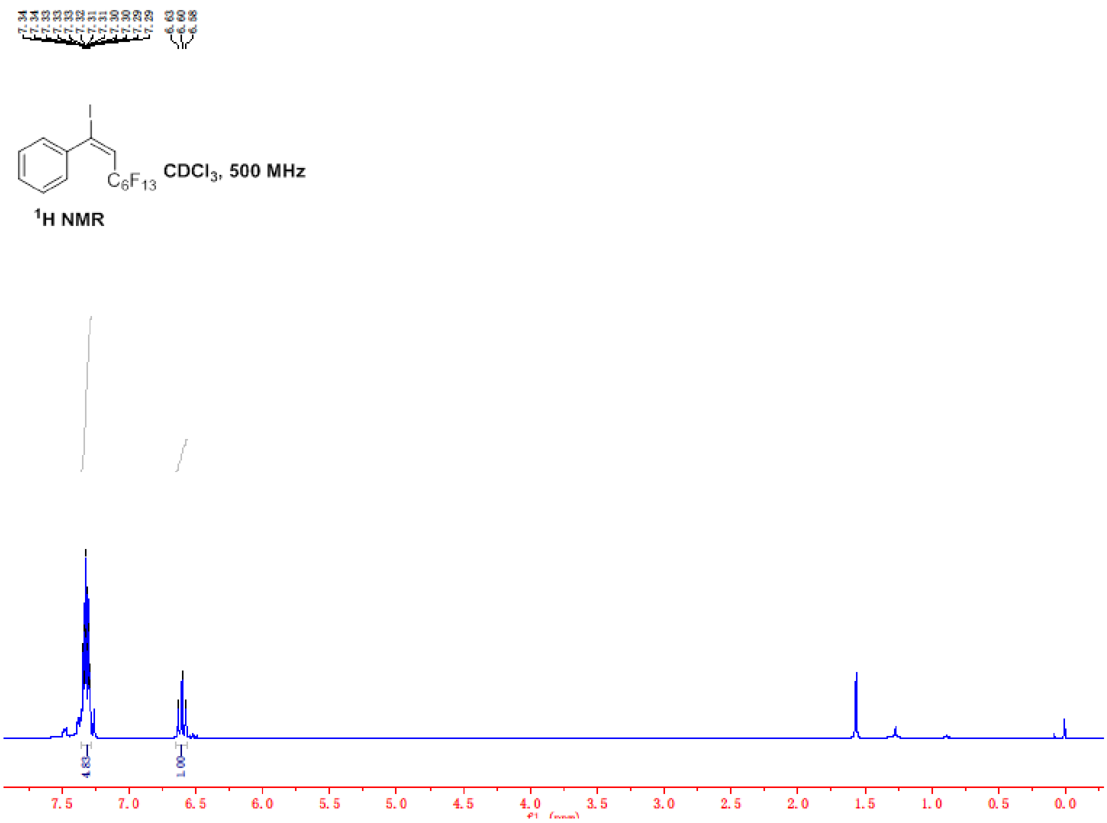

I
C10F21
CDCl3, 126 MHz
13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

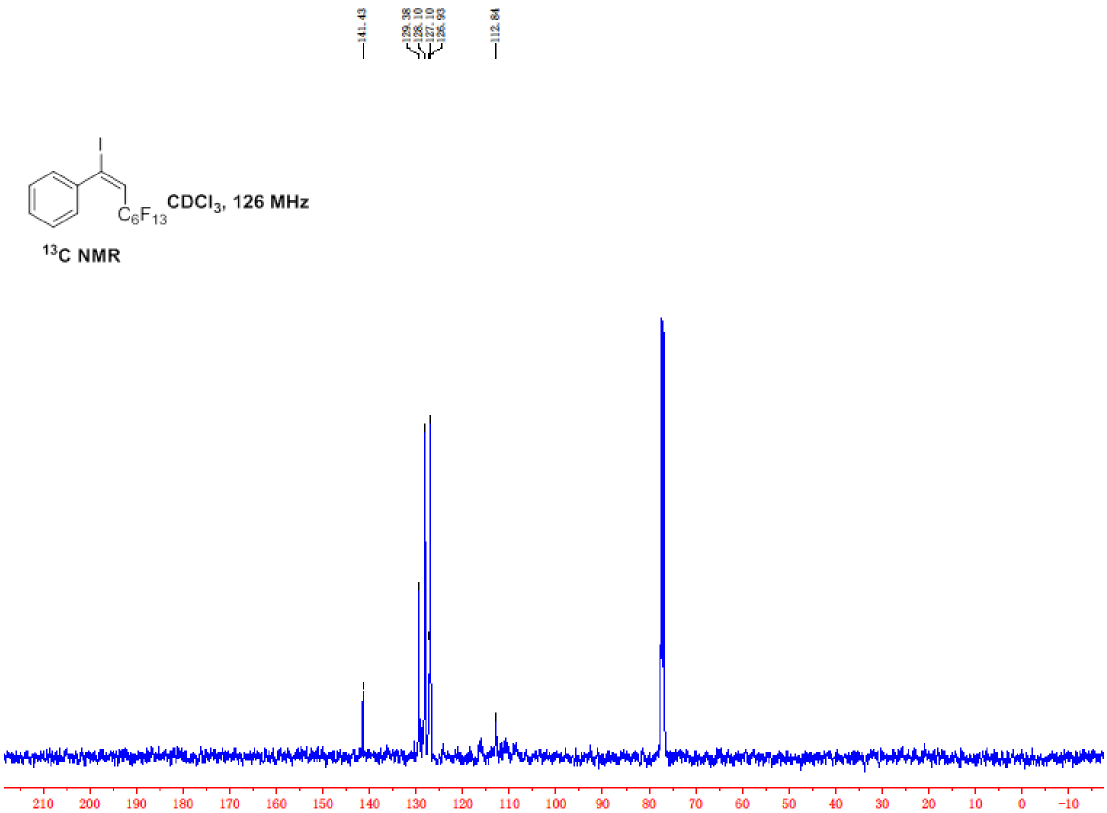

I
C10F21
CDCl3, 470 MHz
19F NMR

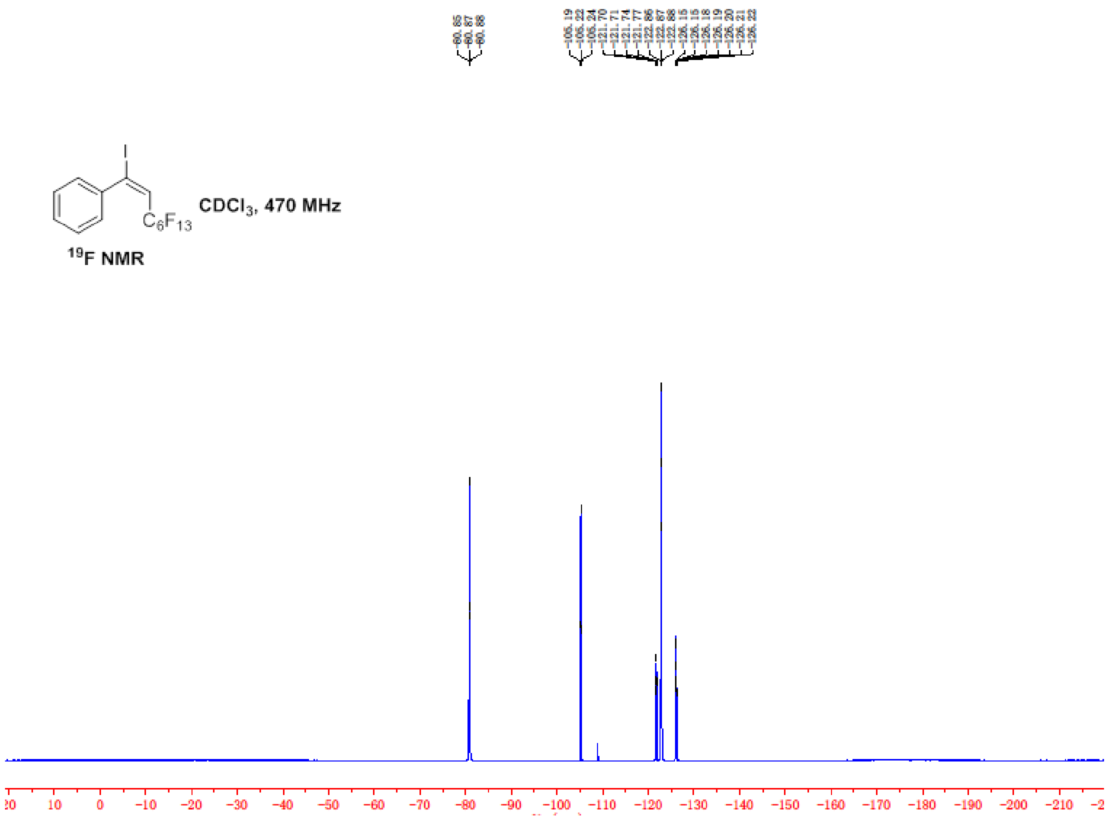

I
C4F9
CDCl3, 500 MHz
1H NMR

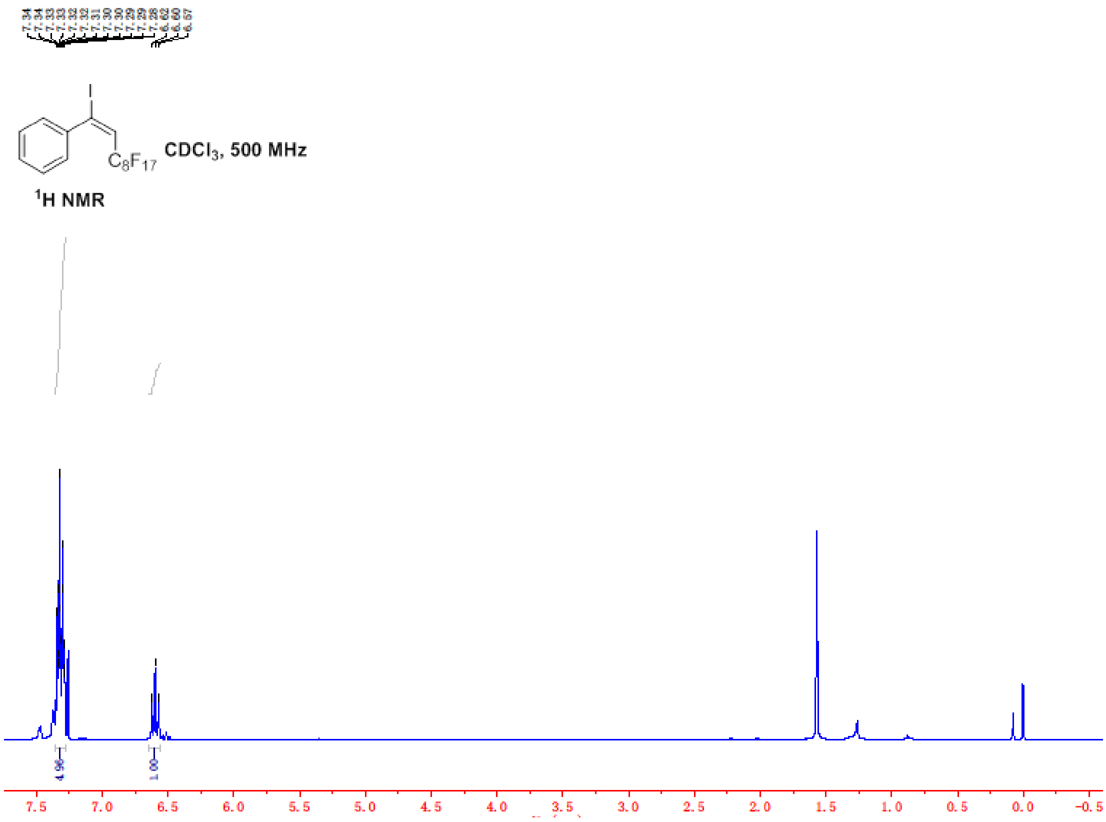

141.41
129.39
128.11
127.17
126.94
112.89
I
C4F9
CDCl3, 126 MHz
13C NMR

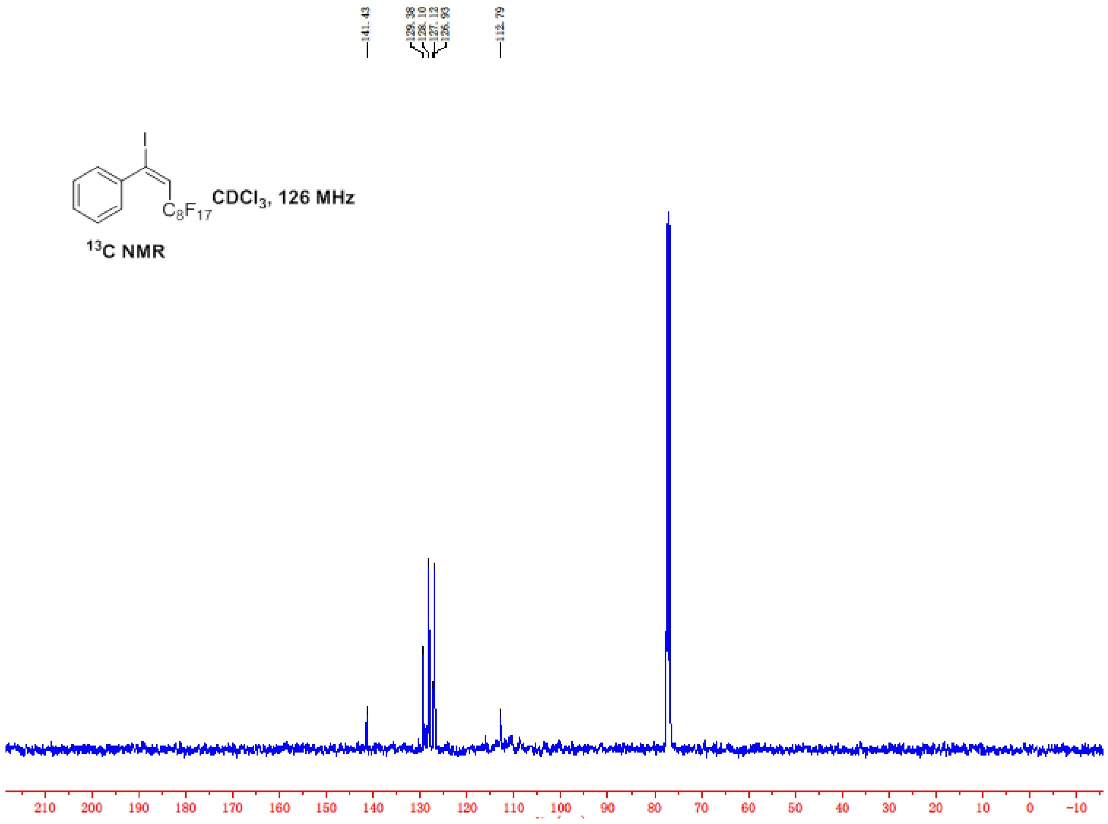

-81.01
-81.03
-81.05
-105.39
-105.39
-105.42
-105.44
-123.77
-123.79
-125.81
-125.83
-125.84
-125.85
I
C4F9
CDCl3, 470 MHz
19F NMR

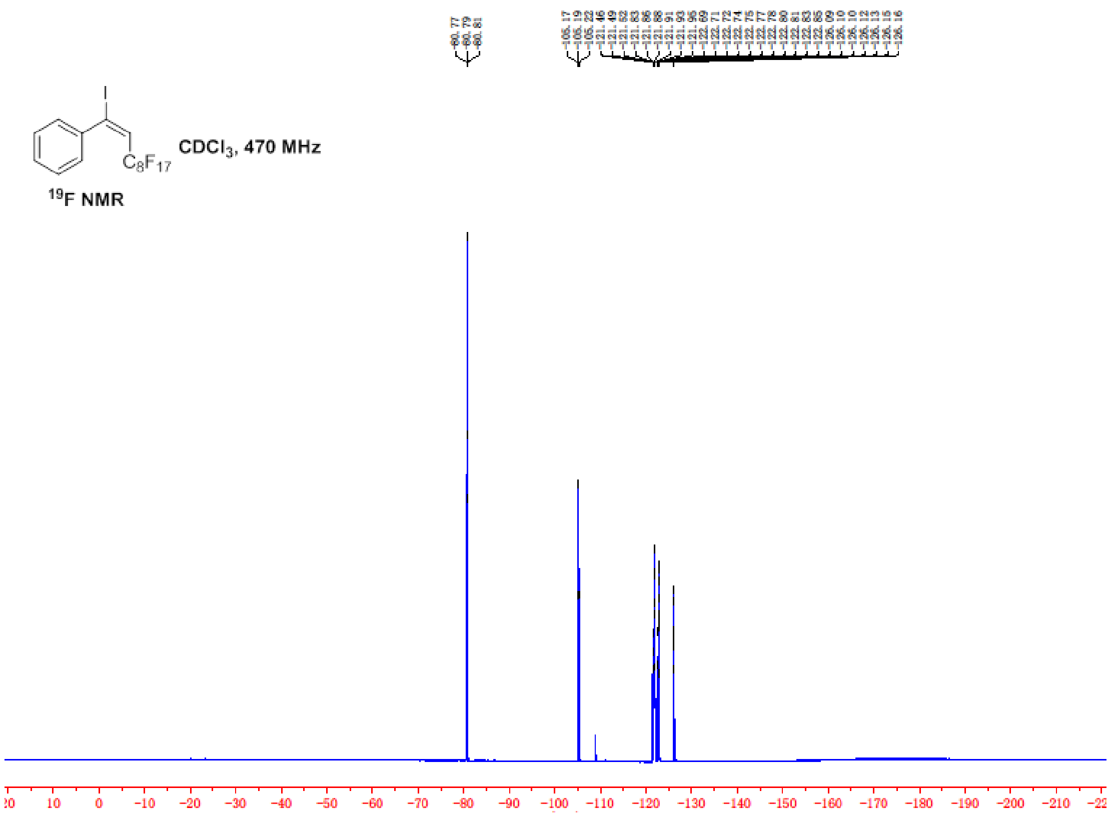

7.34
7.34
7.33
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.29
6.63
6.60
6.58
I
C6F13
CDCl3, 500 MHz
1H NMR
4.83
1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

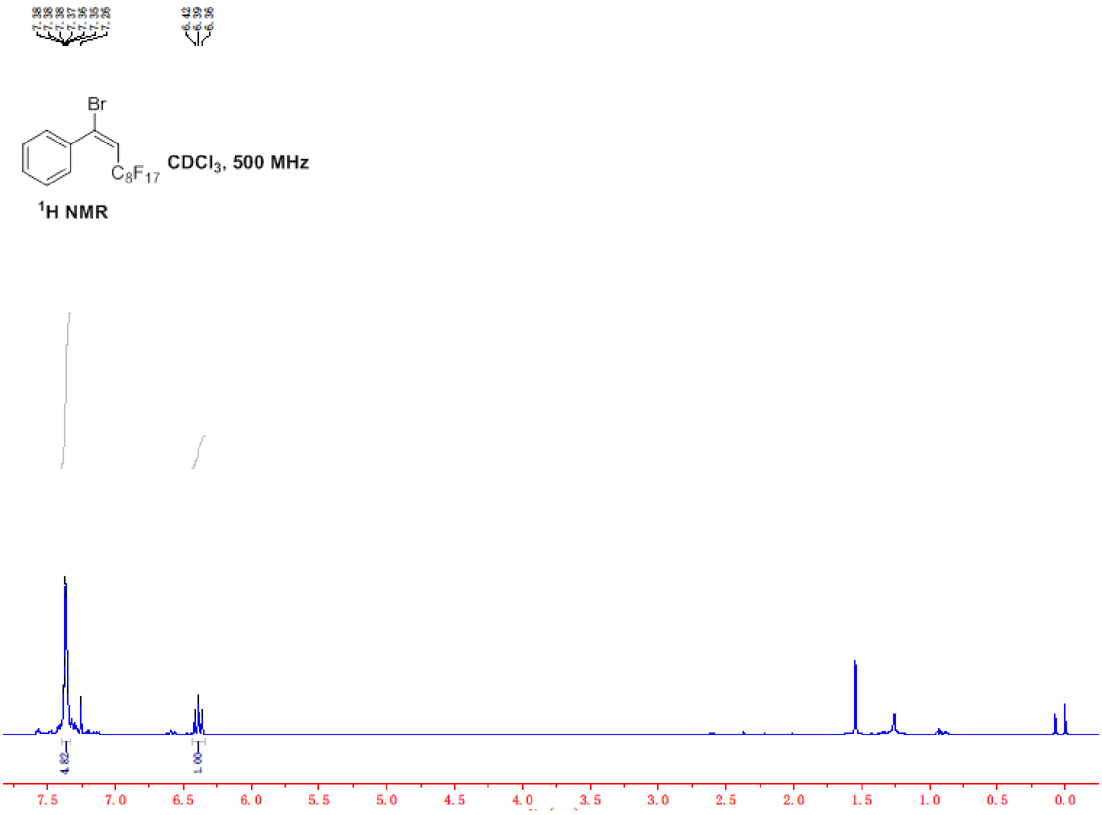

141.43
129.38
128.10
127.10
126.93
112.84
I
C6F13
CDCl3, 126 MHz
13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

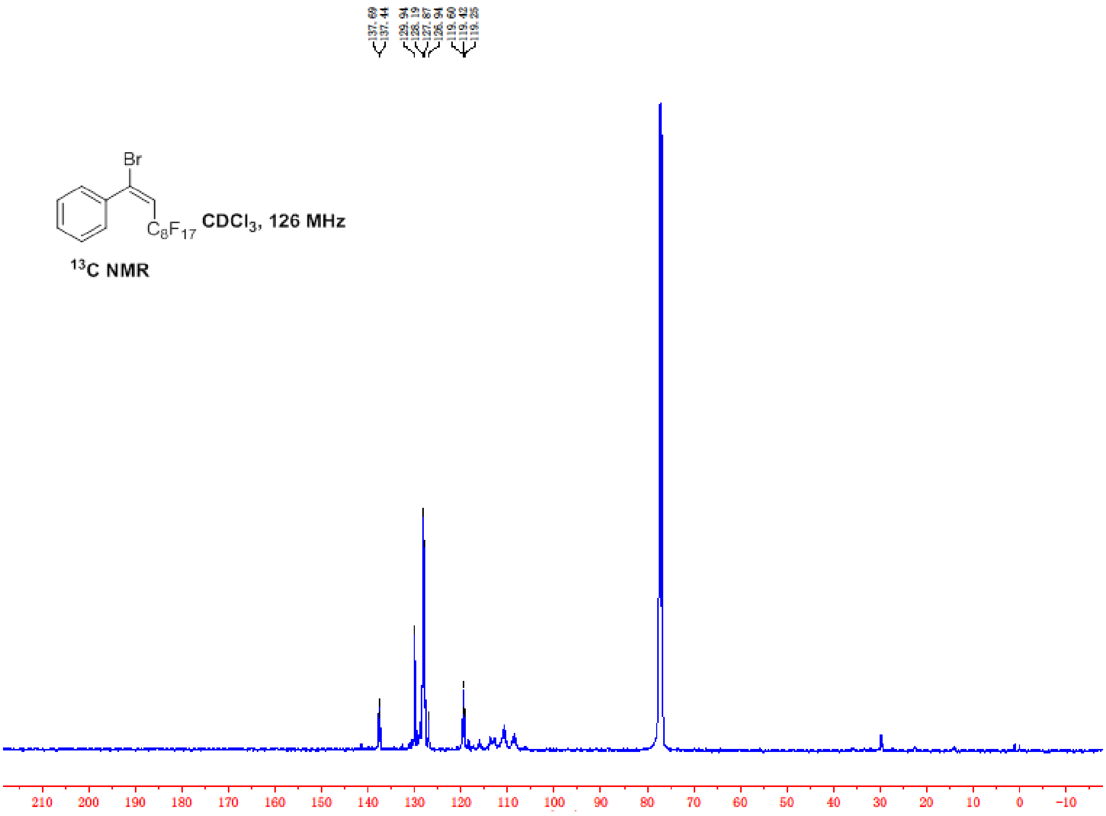

-80.85
-80.87
-80.88
-105.19
-105.22
-105.24
-121.70
-121.71
-121.74
-121.77
-122.85
-122.87
-122.88
-126.15
-126.15
-126.18
-126.19
-126.20
-126.21
-126.22
I
C6F13
CDCl3, 470 MHz
19F NMR
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

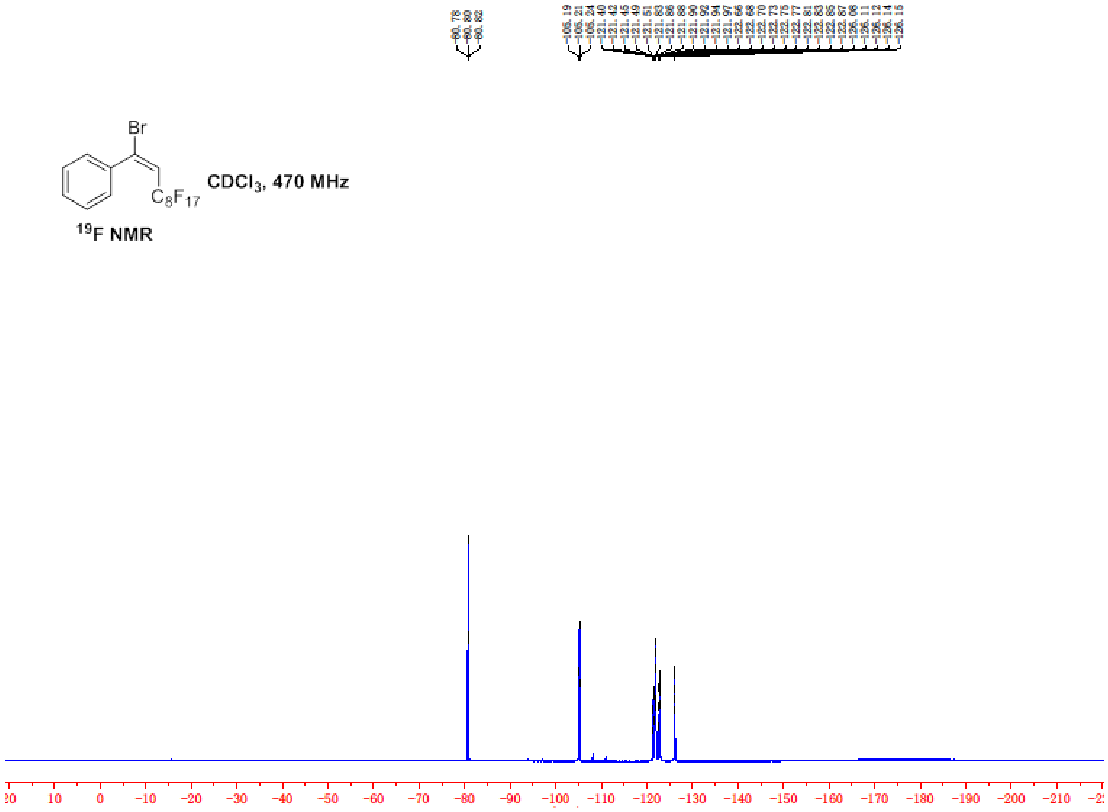

7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.30
7.30
7.29
7.29
7.28
6.62
6.60
6.57
I
C8F17
CDCl3, 500 MHz
1H NMR
4.96
1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


CDCl3, 126 MHz
13C NMR

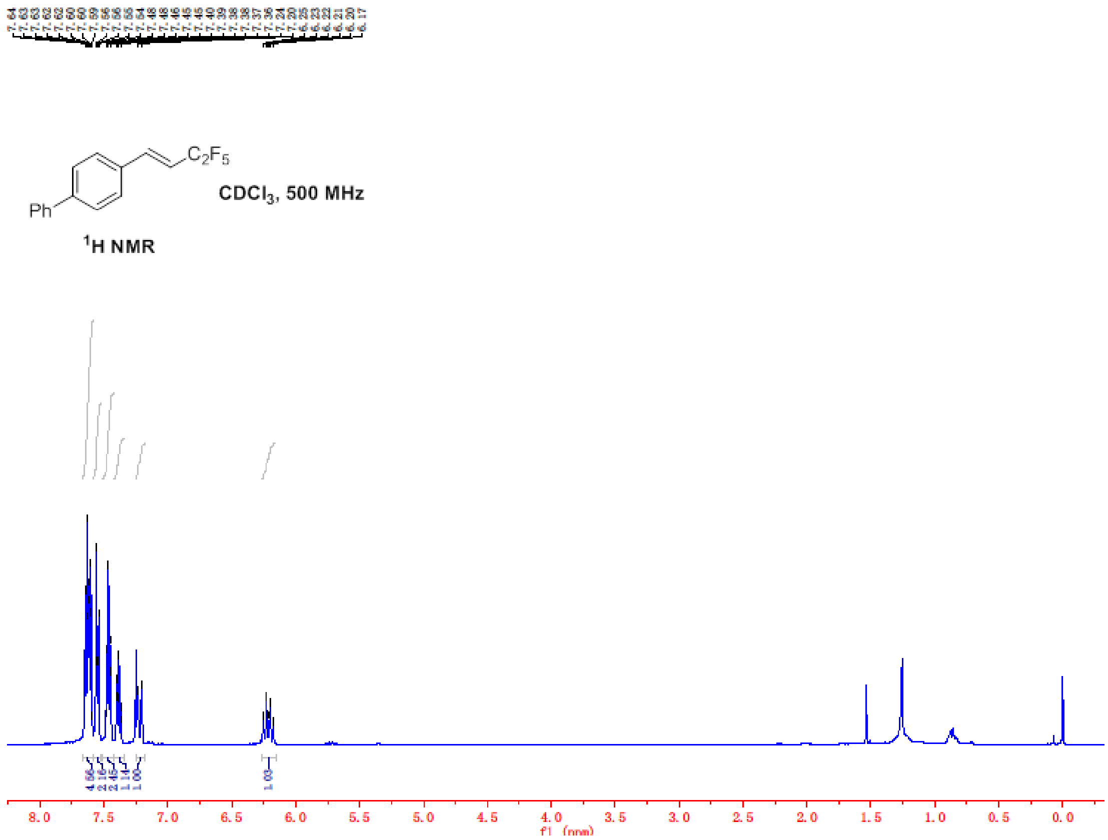

CDCl3, 470 MHz
19F NMR


7.38
7.38
7.38
7.37
7.36
7.35
7.26
6.42
6.39
6.36
Br
C8F17
CDCl3, 500 MHz
1H NMR
4.82
1.00
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

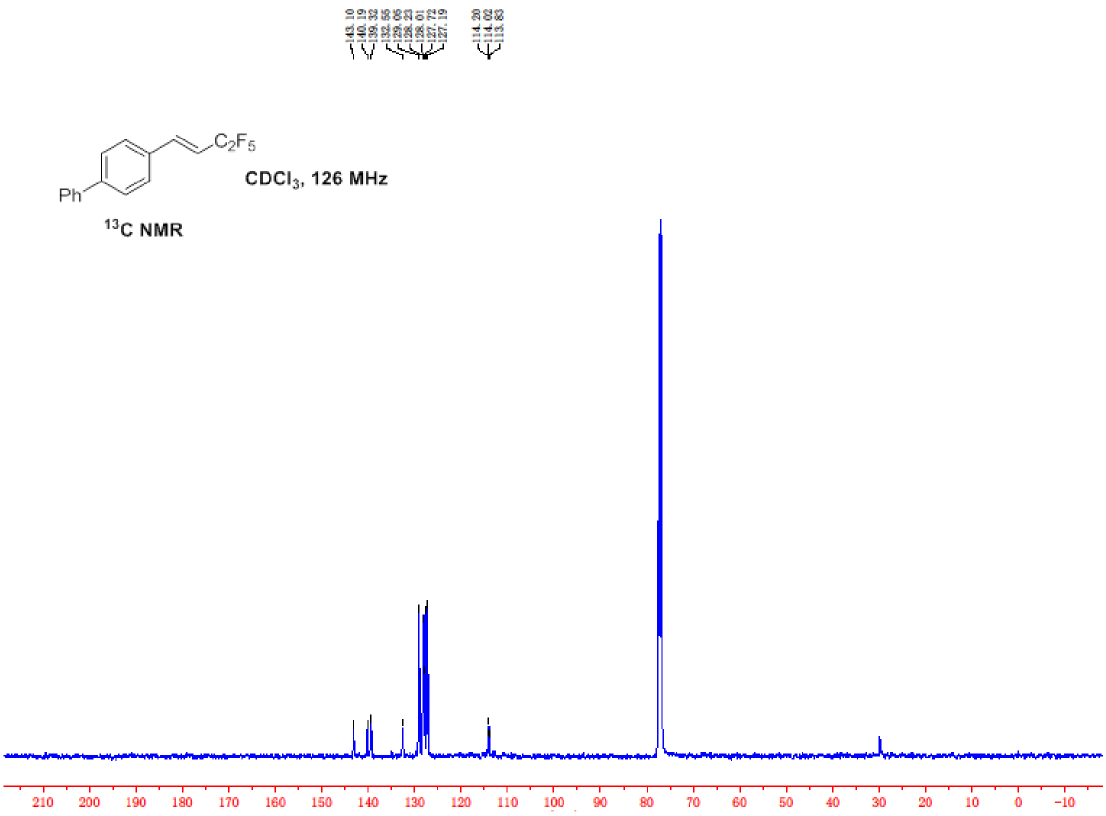

137.69
137.44
129.94
128.19
127.87
126.94
119.60
119.42
119.25
Br
C8F17
CDCl3, 126 MHz
13C NMR
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

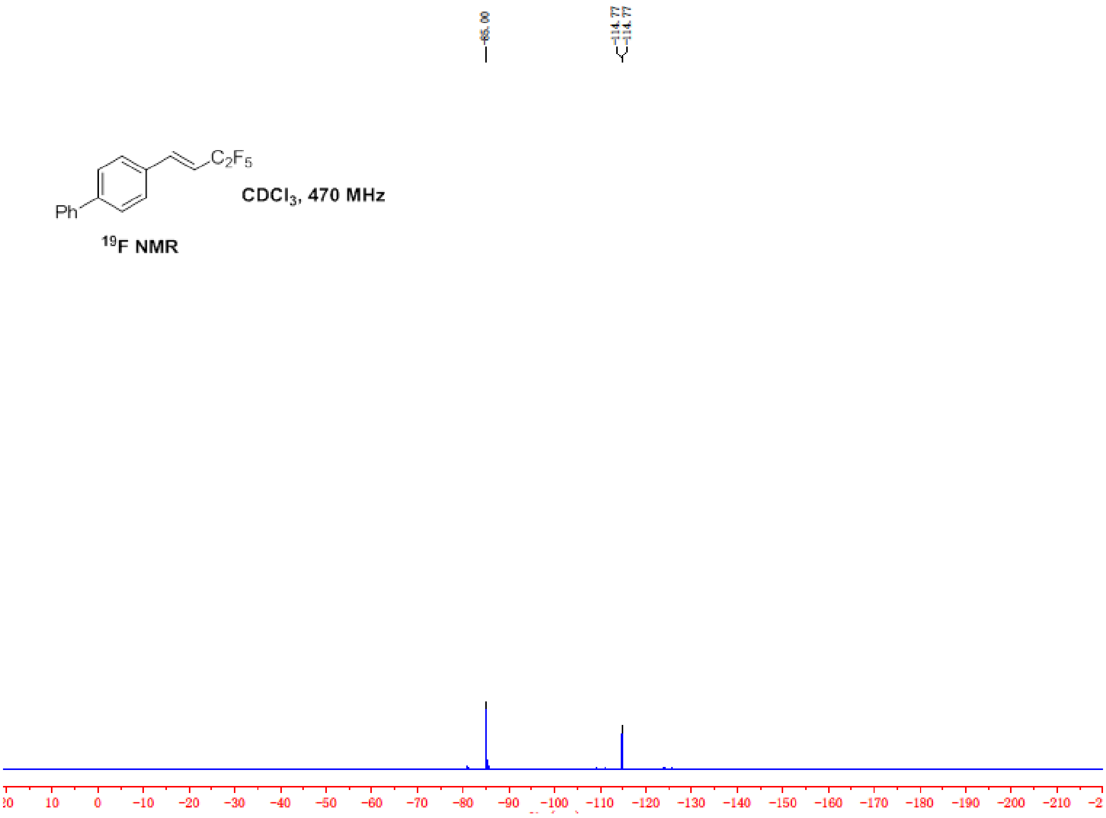


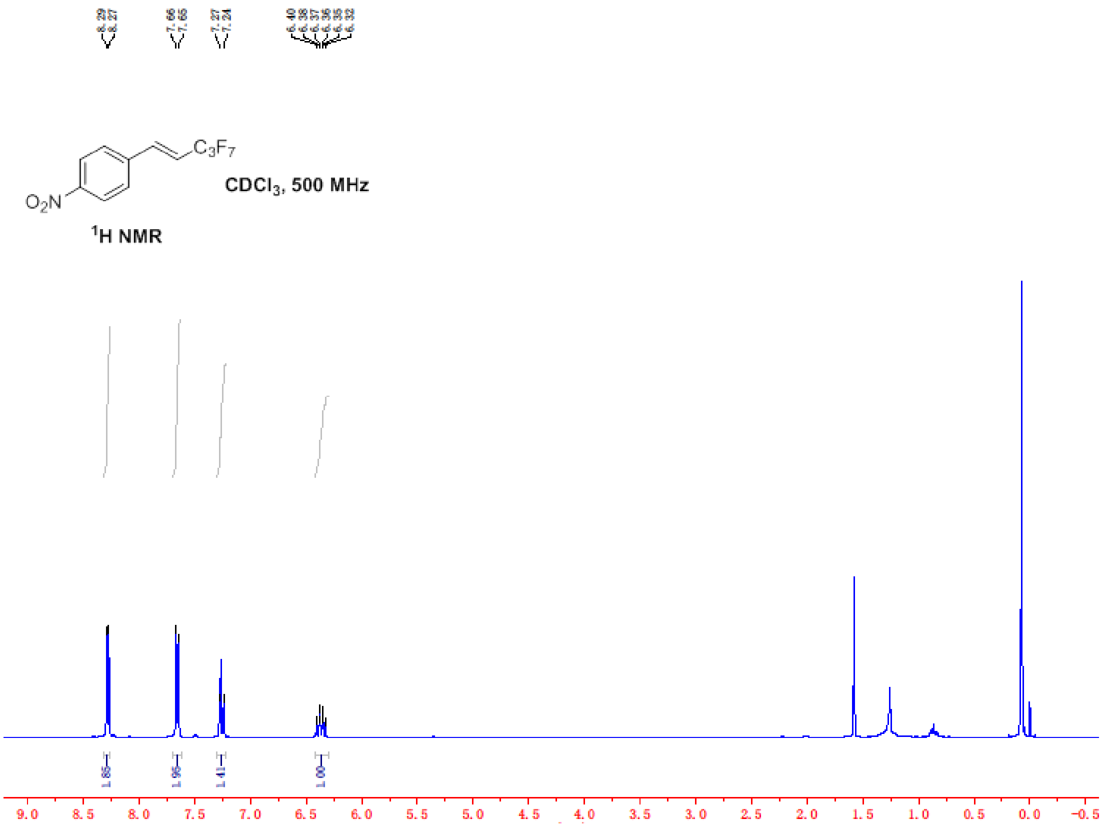
Br
C_8F_{17}
$CDCl_3$, 470 MHz
^{19}F NMR

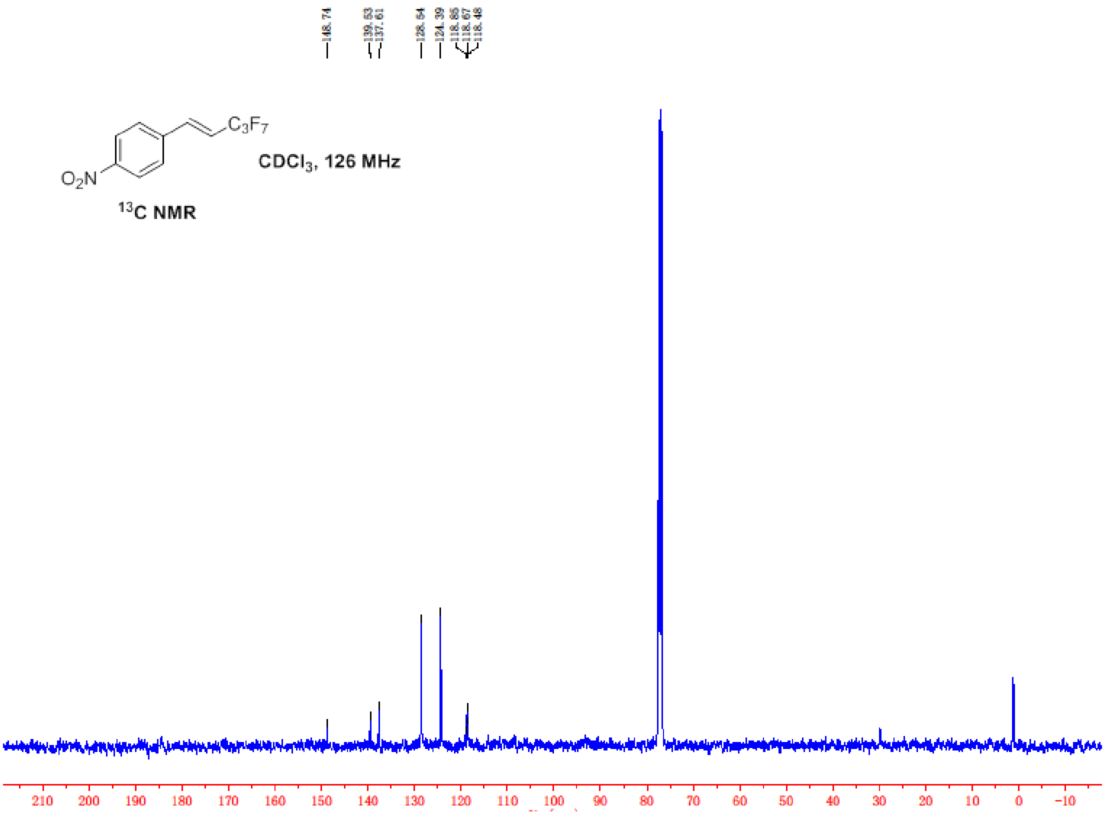


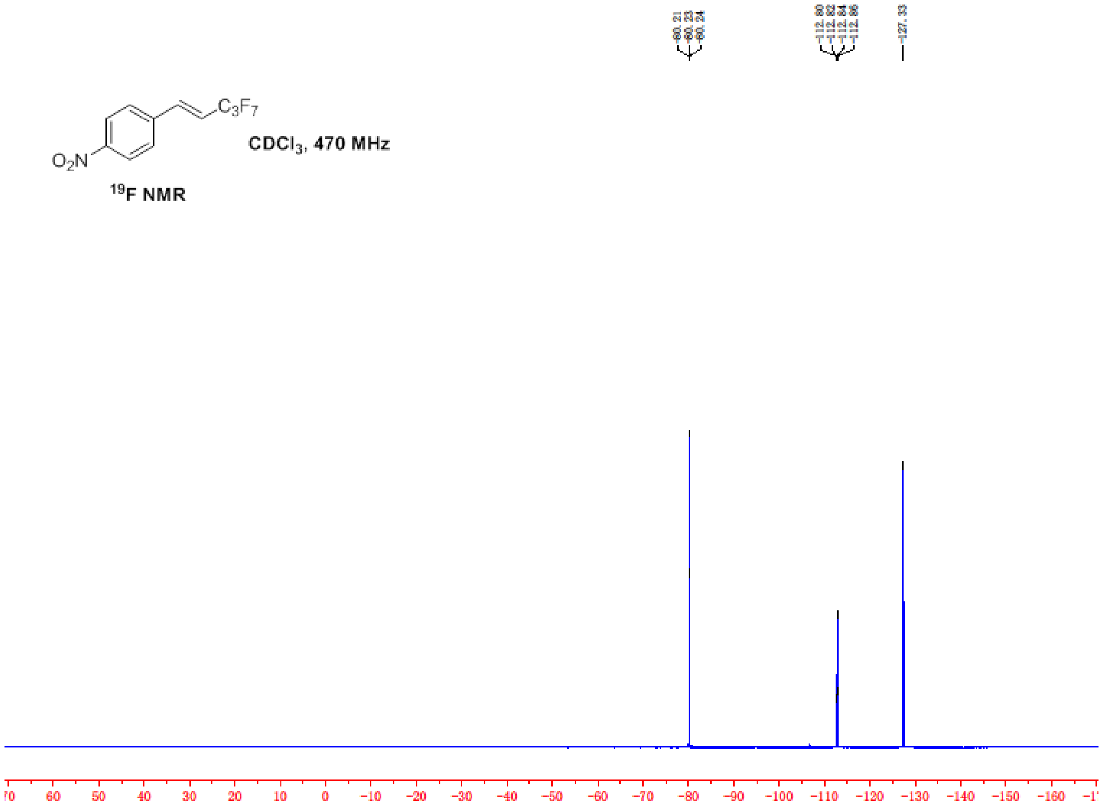
C_2F_5
Ph
$CDCl_3$, 500 MHz
^1H NMR
f1 (ppm)


143.10
140.19
139.32
132.56
129.05
128.23
128.01
127.72
127.19
114.20
114.02
113.83
C2F5
Ph
CDCl3, 126 MHz
13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


-85.00
-114.77
-114.77
C2F5
Ph
CDCl3, 470 MHz
19F NMR
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210


8.29
8.27
7.66
7.65
7.27
7.24
6.40
6.38
6.37
6.36
6.35
6.32
C_3F_7
O_2N
$CDCl_3$, 500 MHz
^{1}H NMR
1.85
1.95
1.41
1.00
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


148.74
139.53
137.61
128.54
124.39
118.85
118.67
118.48
C_3F_7
O_2N
$CDCl_3$, 126 MHz
^{13}C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



-80.21
-80.23
-80.24
-112.80
-112.82
-112.84
-112.86
-127.33
C_3F_7
O_2N
CDCl3, 470 MHz
19F NMR
70
60
50
40
30
20
10
0
-10
-20
-30
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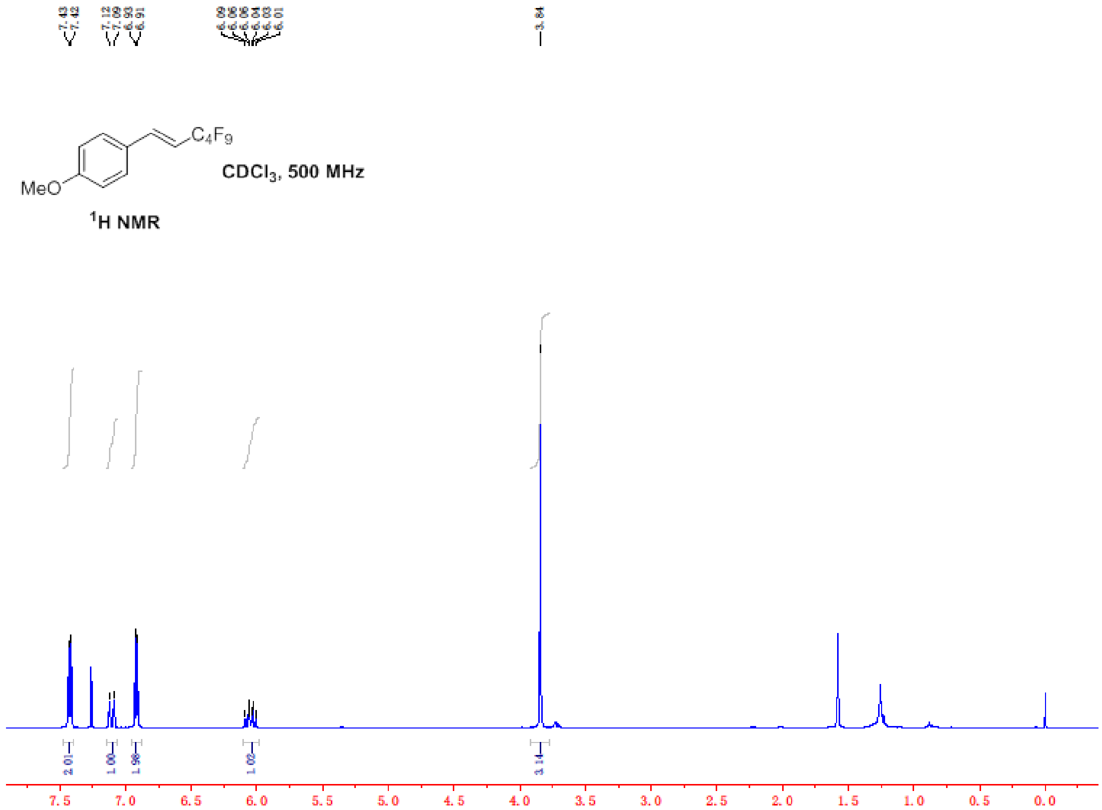
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160



7.43
7.42
7.12
7.09
6.93
6.91
6.09
6.06
6.06
6.04
6.03
6.01
3.84
C_4F_9
MeO
CDCl3, 500 MHz
1H NMR
2.01
1.00
1.98
1.02
3.14
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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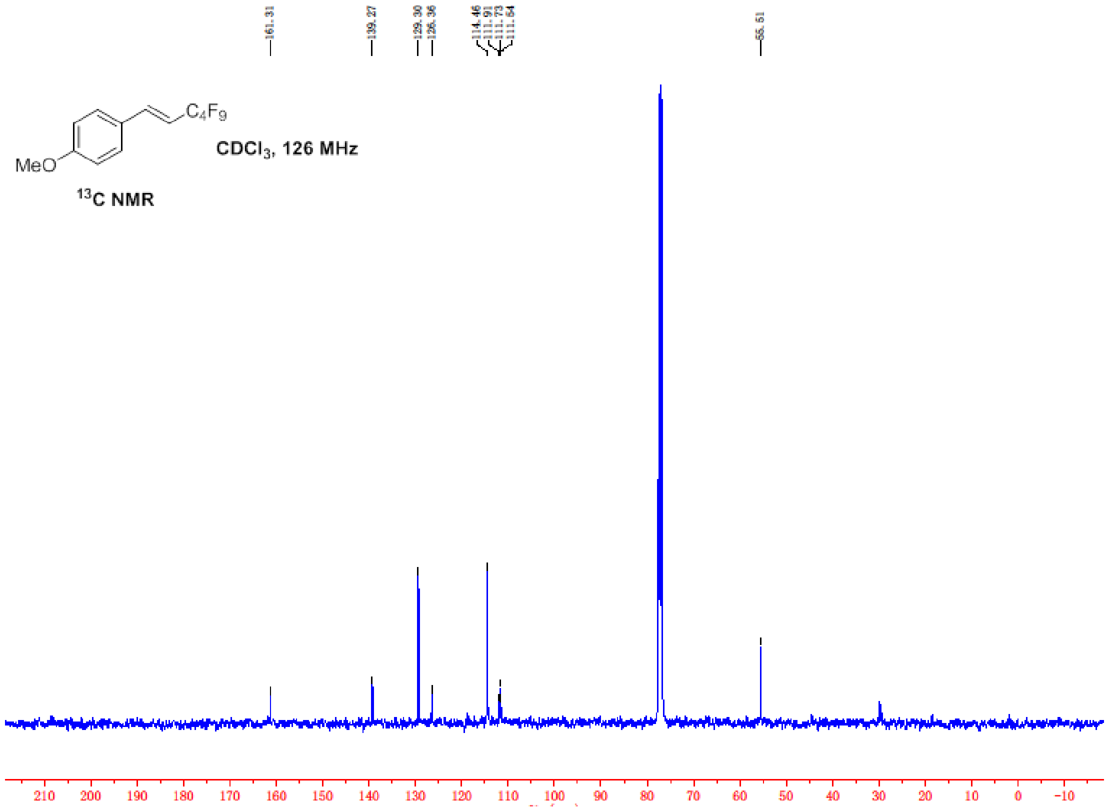
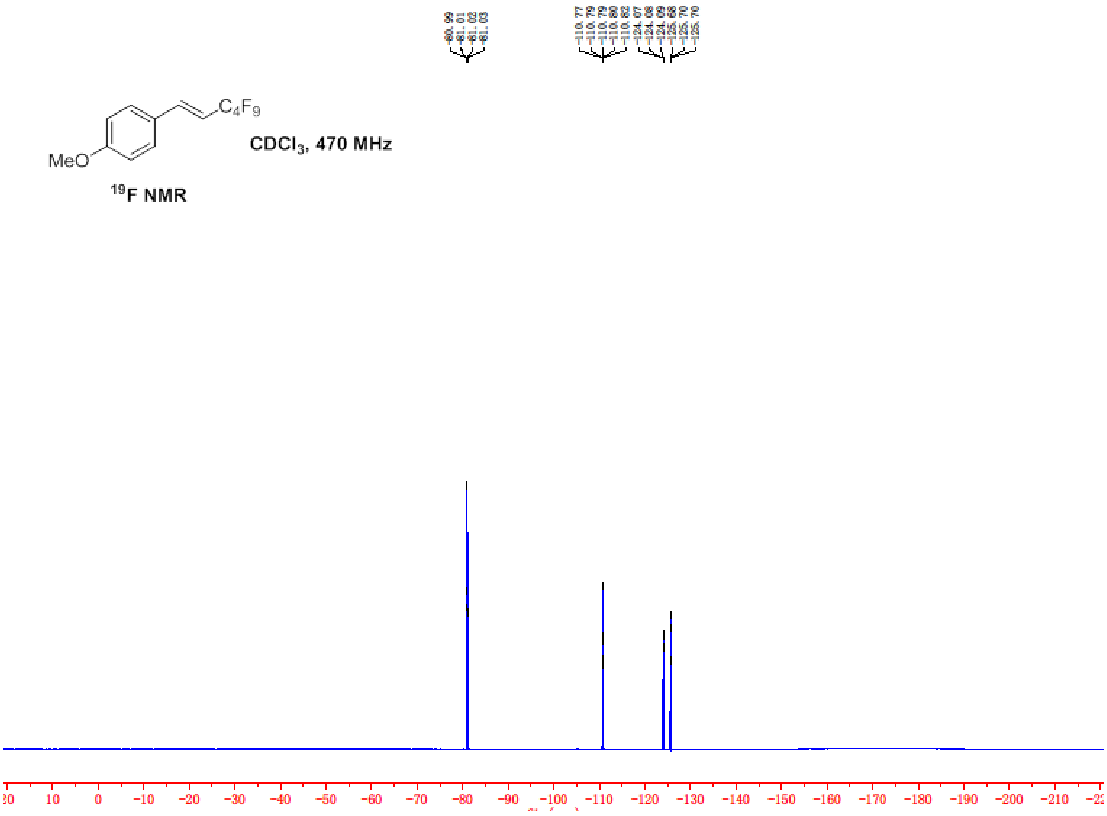
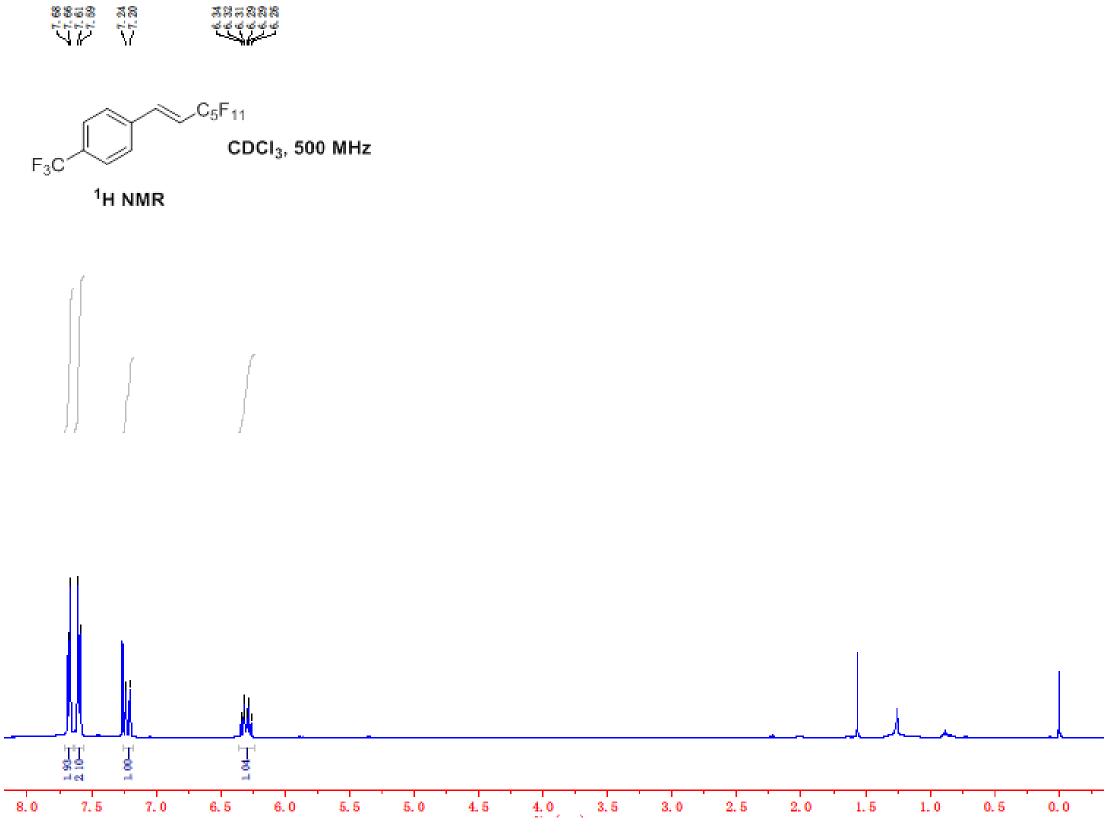
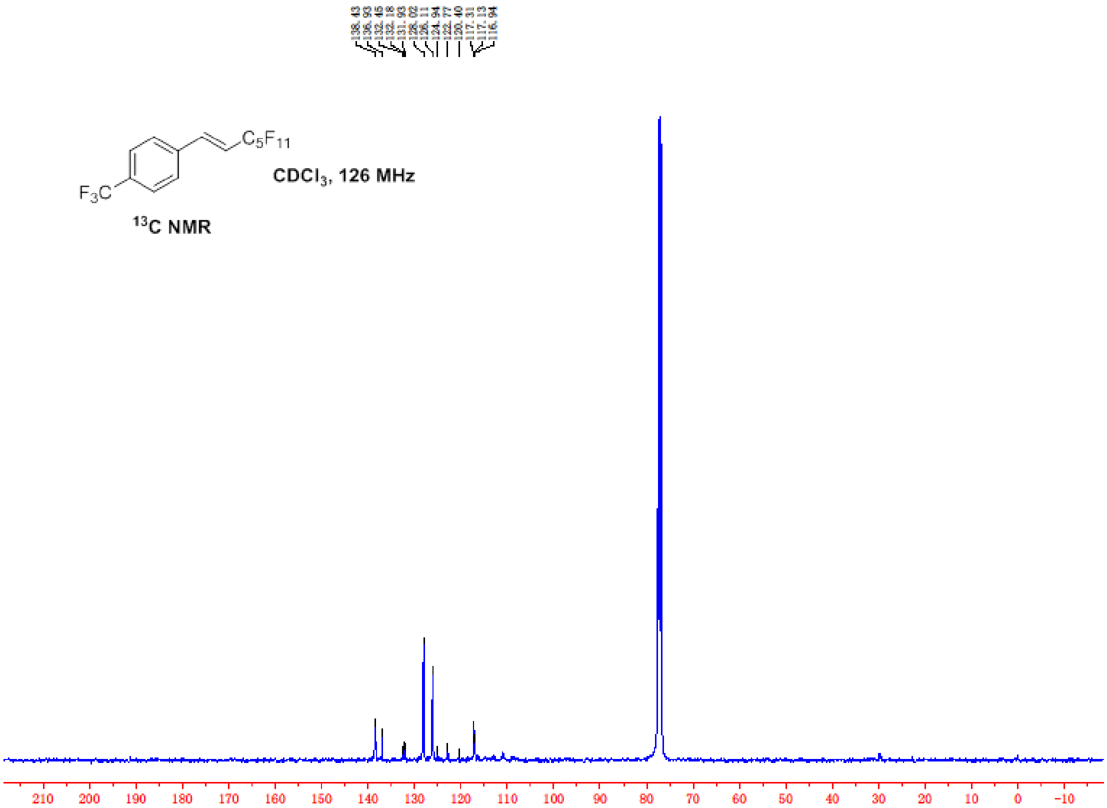


161.31
139.27
129.30
126.36
114.46
111.91
111.73
111.54
55.51
C4F9
MeO
CDCl3, 126 MHz
13C NMR



-80.99
-81.01
-81.02
-81.03
C4F9
MeO
CDCl3, 470 MHz
19F NMR


7.68
7.66
7.61
7.59
7.24
7.20
6.34
6.32
6.31
6.29
6.29
6.26
C5F11
F3C
CDCl3, 500 MHz
1H NMR
1.93
2.10
1.00
1.04
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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136.93
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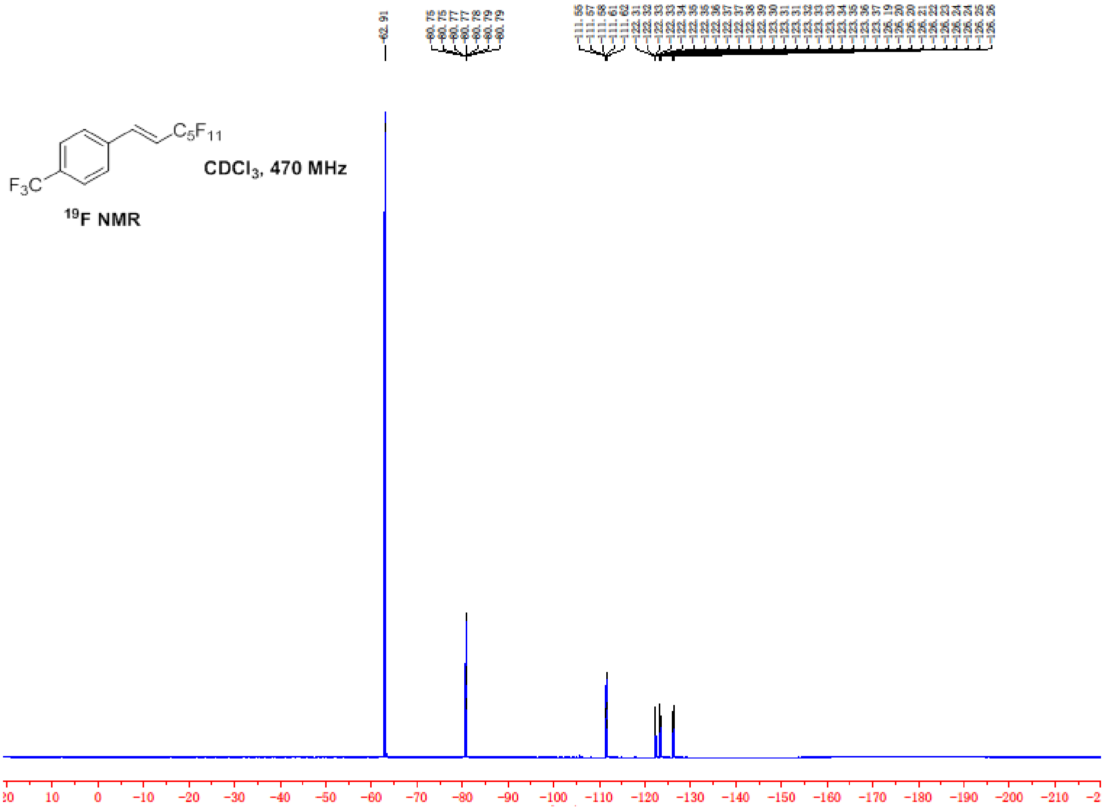
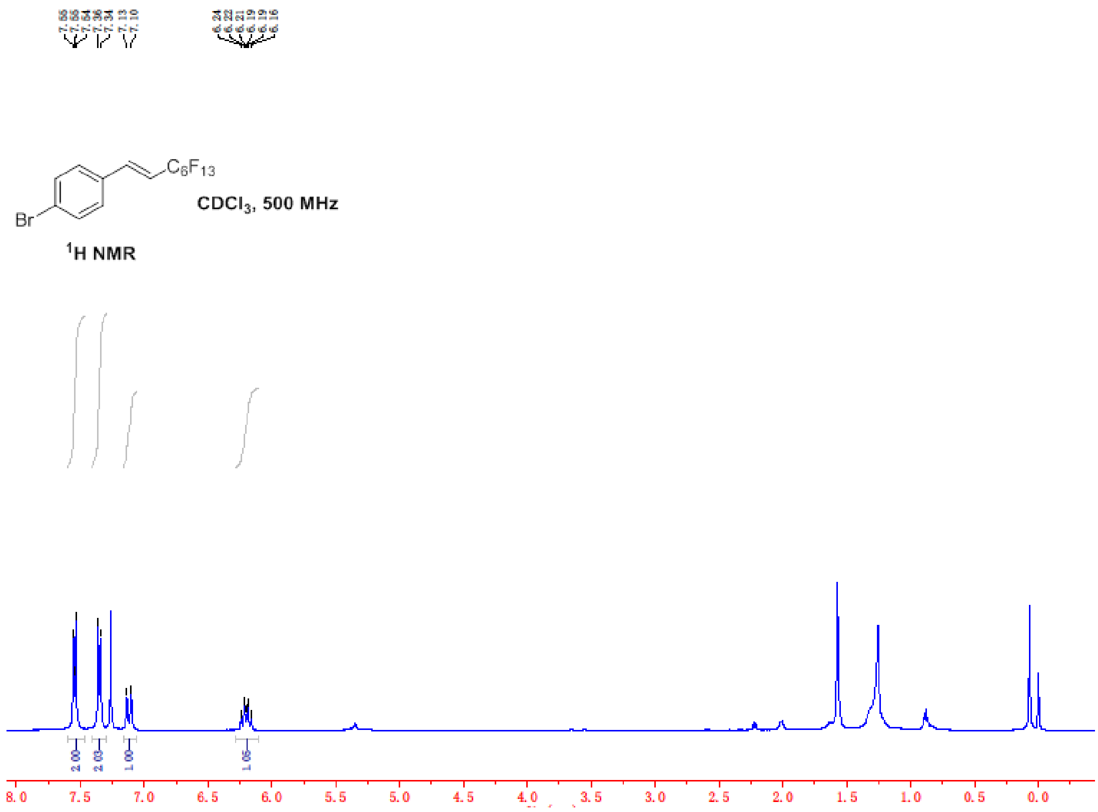
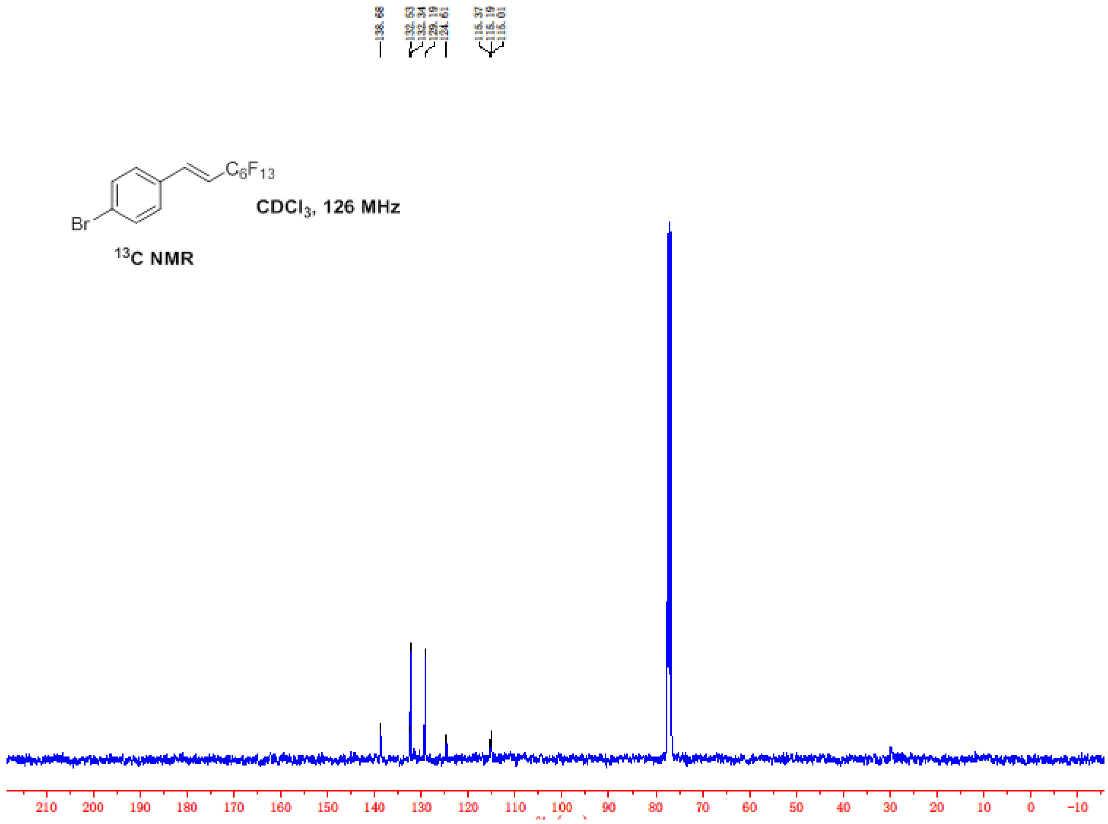
132.18
131.93
128.02
126.11
124.94
122.77
120.40
117.31
117.13
116.94
C5F11
F3C
CDCl3, 126 MHz
13C NMR
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


C5F11
F3C
CDCl3, 470 MHz
19F NMR


C6F13
Br
CDCl3, 500 MHz
1H NMR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132.53
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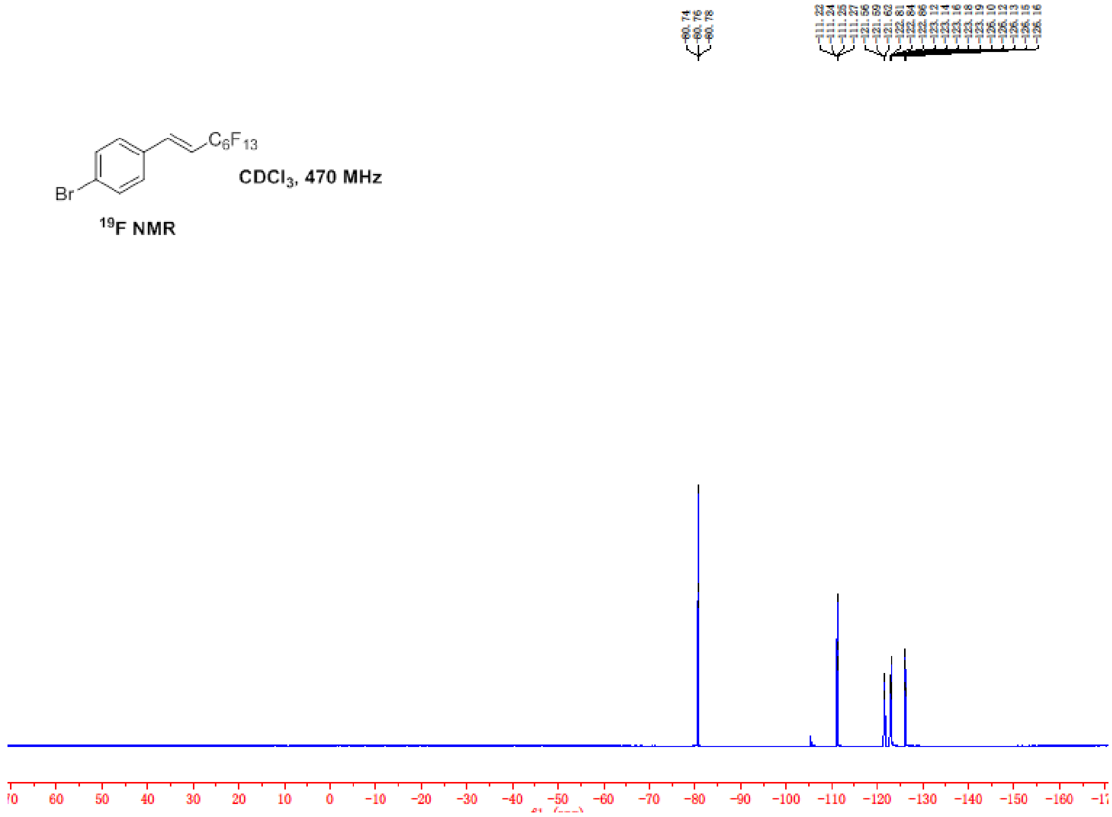
129.19
124.61
115.37
115.19
115.01
Br
C6F13
CDCl3, 126 MHz
13C NMR


-80.74
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-111.22
-111.24
-111.25
-111.27
-121.56
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-122.84
-122.86
-123.12
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-123.16
-123.18
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-126.12
-126.13
-126.15
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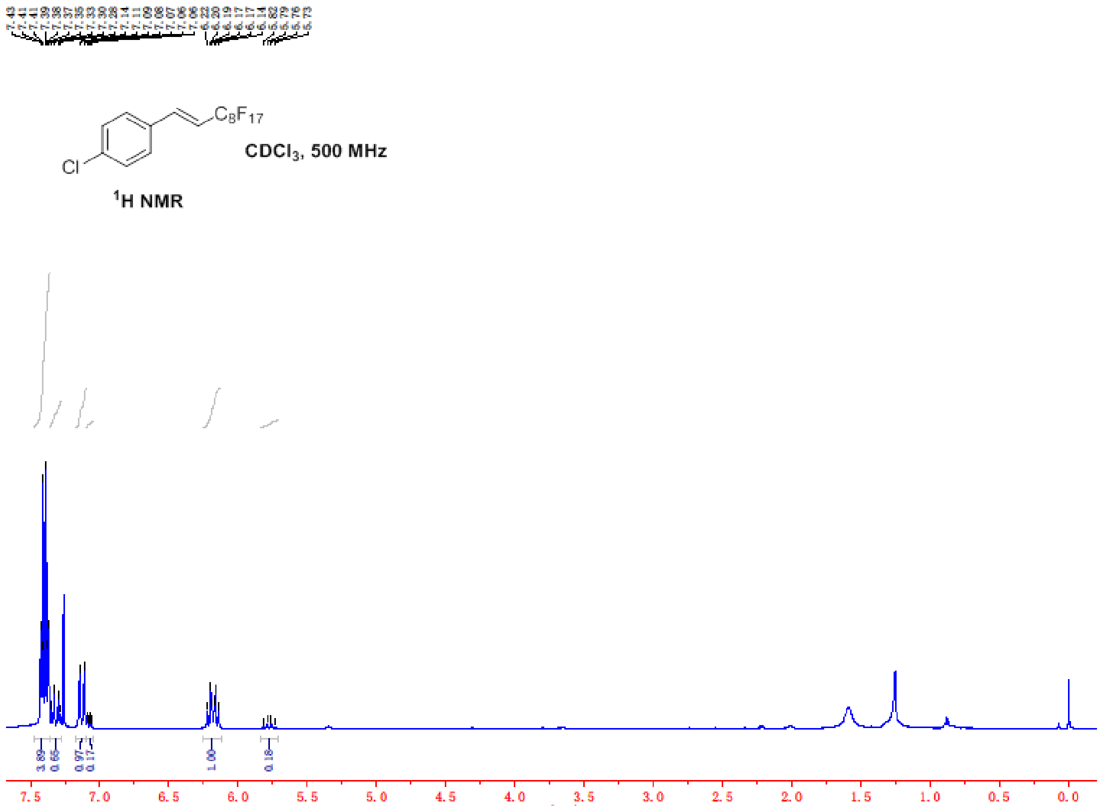
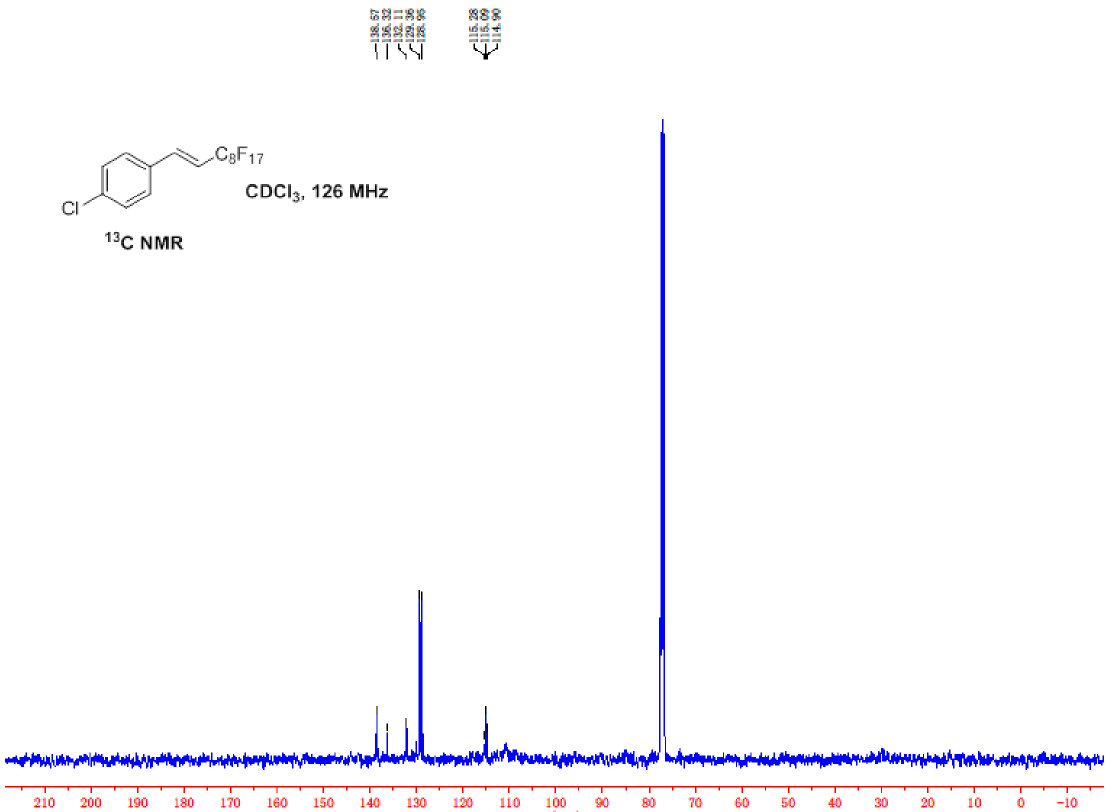
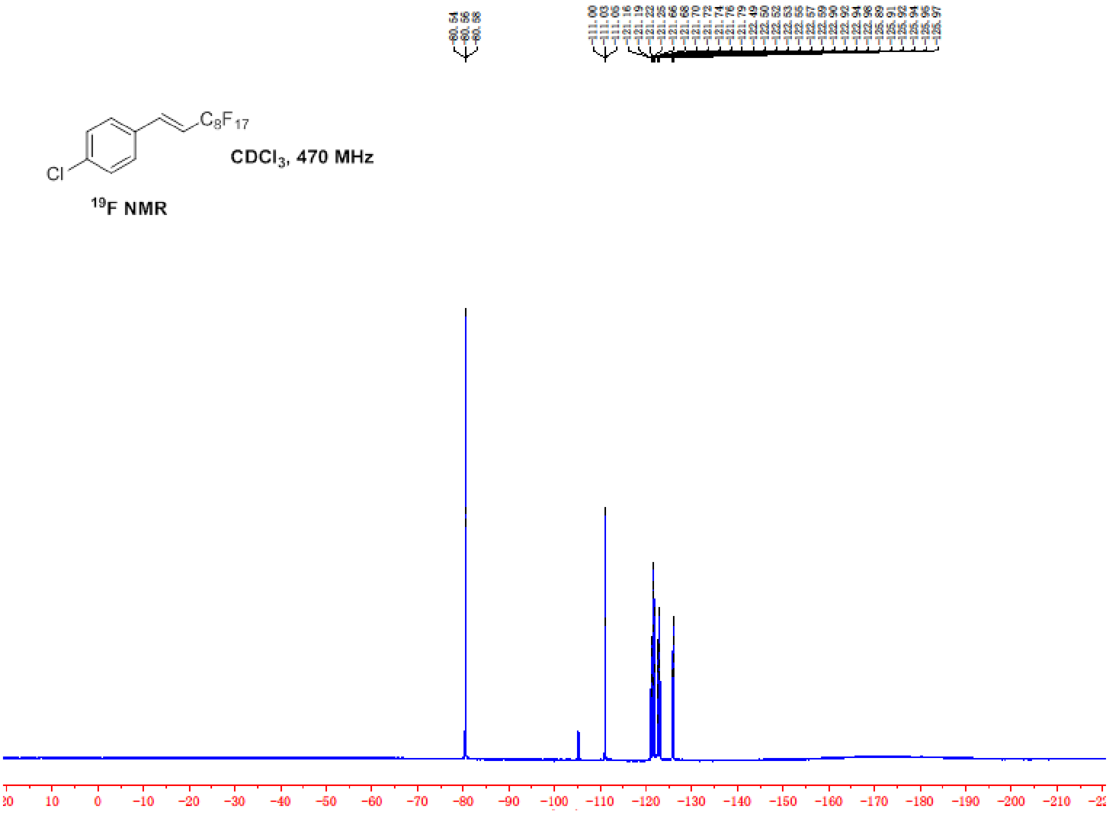
Br
C6F13
CDCl3, 470 MHz
19F NMR



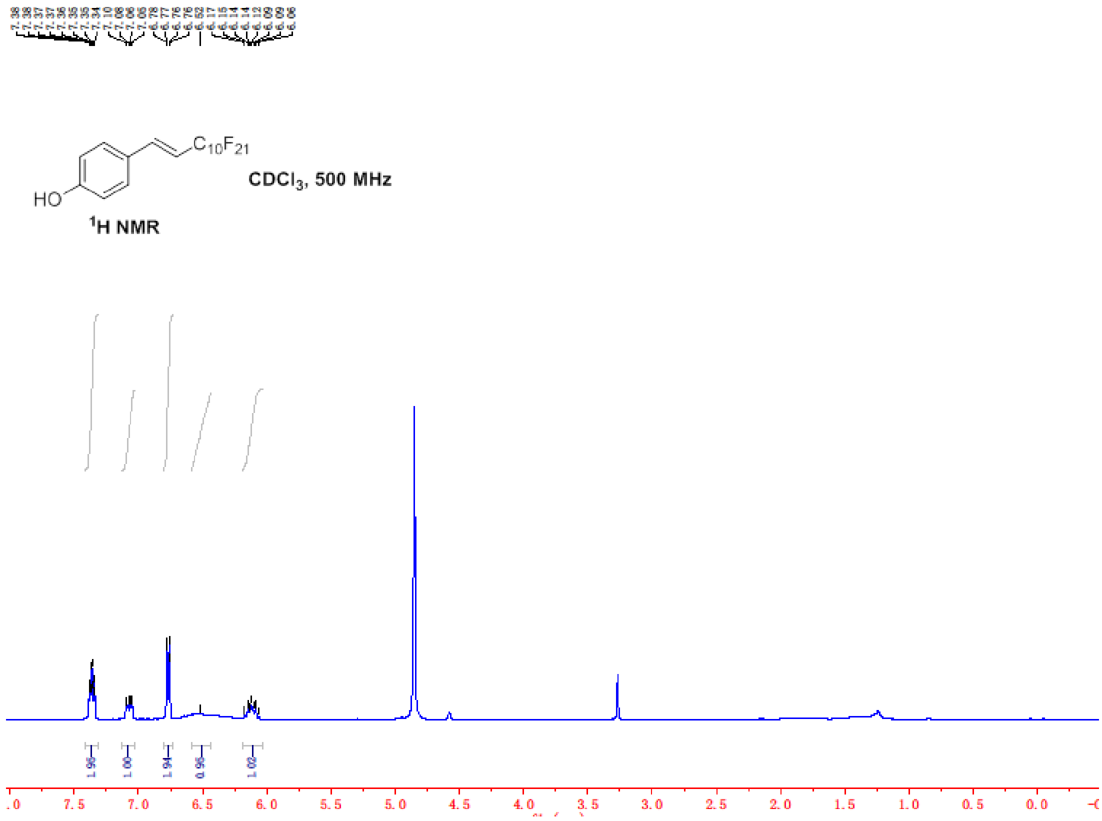
C8F17
Cl
CDCl3, 500 MHz
1H NMR
7.43 7.41 7.39 7.38 7.37 7.35 7.33 7.30 7.28 7.14 7.11 7.09 7.08 7.07 7.06 7.06 6.22 6.20 6.19 6.17 6.17 6.14 5.82 5.79 5.76 5.73
3.89 0.65 0.97 0.17 1.00 0.18
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0



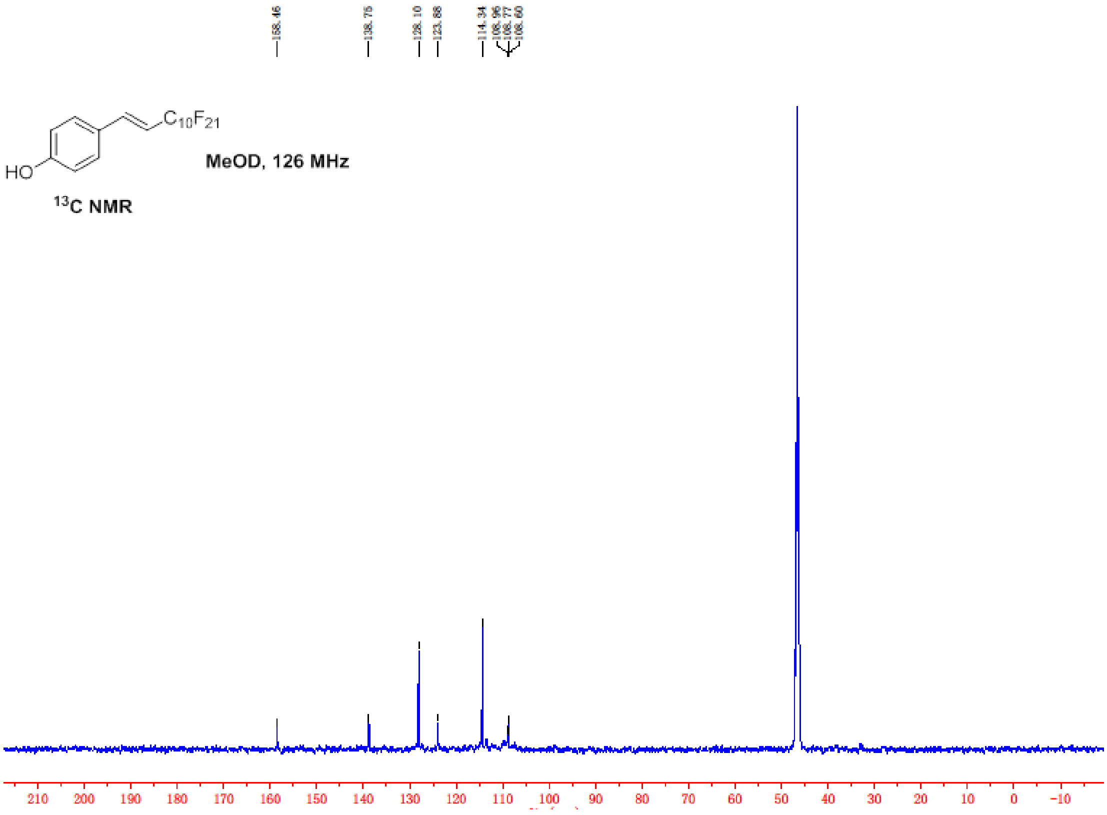
C8F17
Cl
CDCl3, 126 MHz
13C NMR
138.57 136.32 132.11 129.36 128.95
115.28 115.09 114.90
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

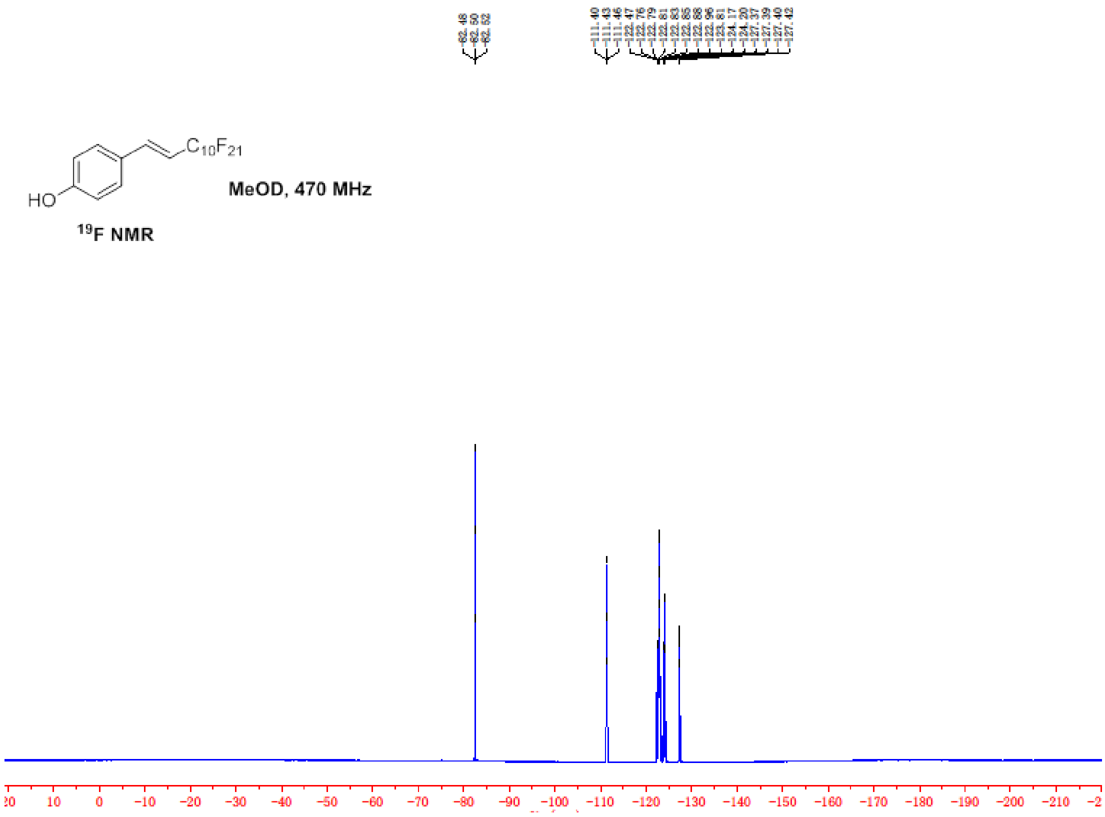


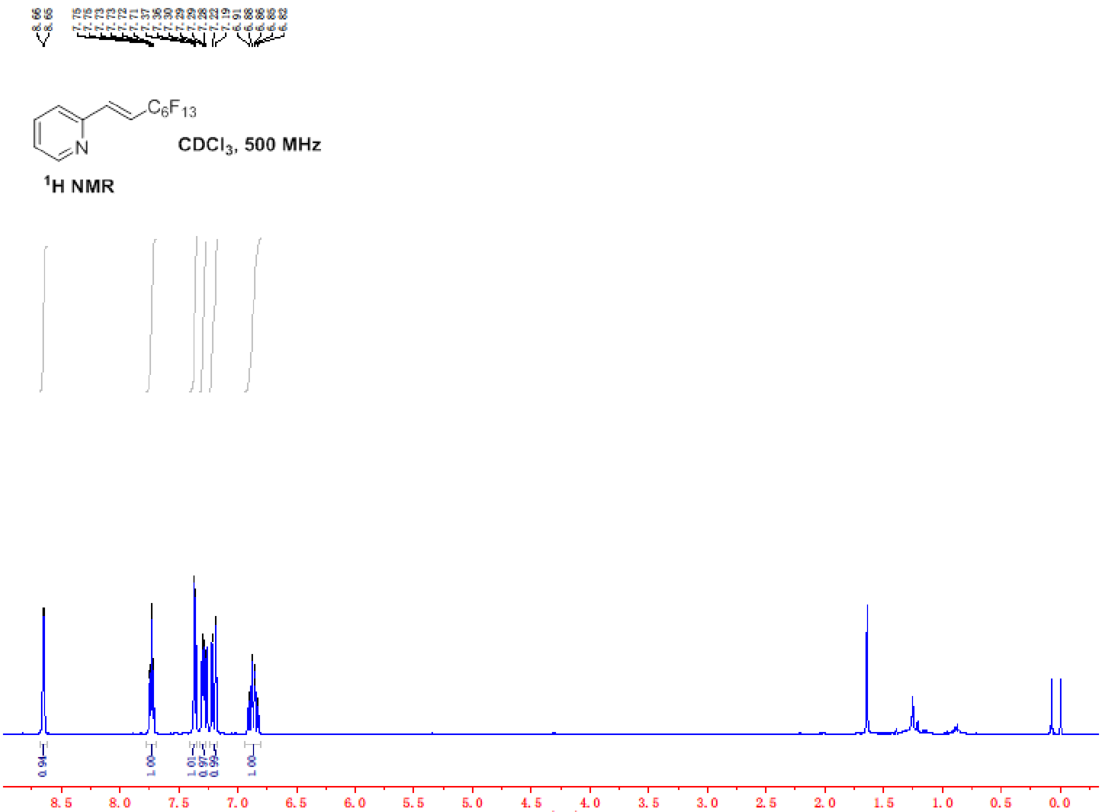
C_8F_{17}
Cl
$CDCl_3$, 470 MHz
^{19}F NMR



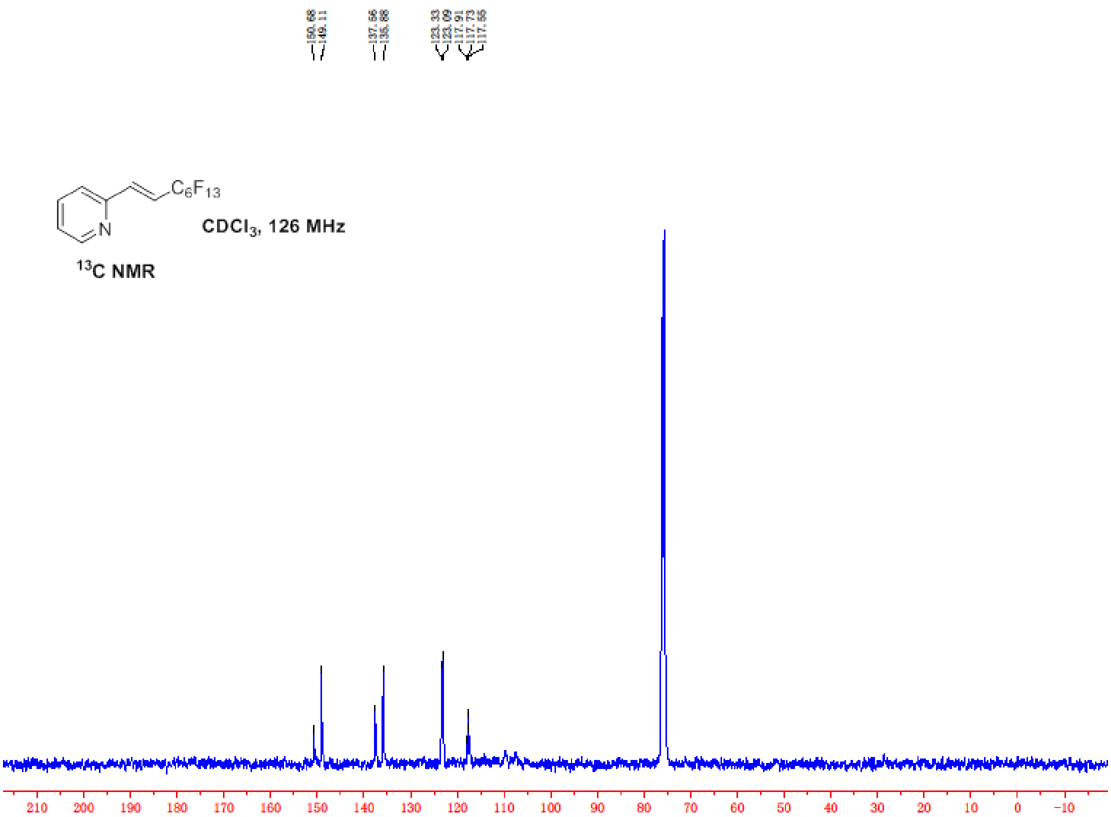
$C_{10}F_{21}$
HO
$CDCl_3$, 500 MHz
^{1}H NMR


158.46
138.75
128.10
123.88
114.34
108.96
108.77
108.60
HO
$C_{10}F_{21}$
MeOD, 126 MHz
^{13}C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

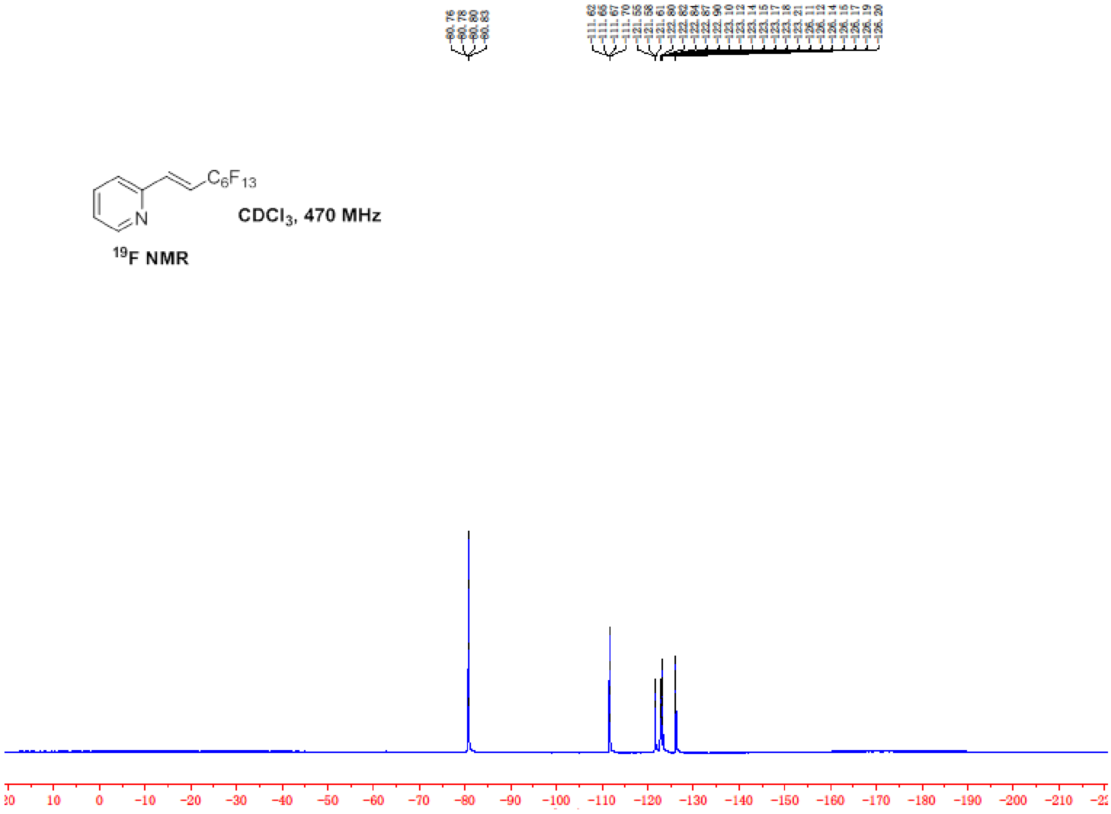

-82.48
-82.50
-82.52
-111.40
-111.43
-111.46
-122.47
-122.76
-122.79
-122.81
-122.83
-122.85
-122.88
-122.96
-123.81
-124.17
-124.20
-127.37
-127.39
-127.40
-127.42
HO
$C_{10}F_{21}$
MeOD, 470 MHz
^{19}F NMR
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210



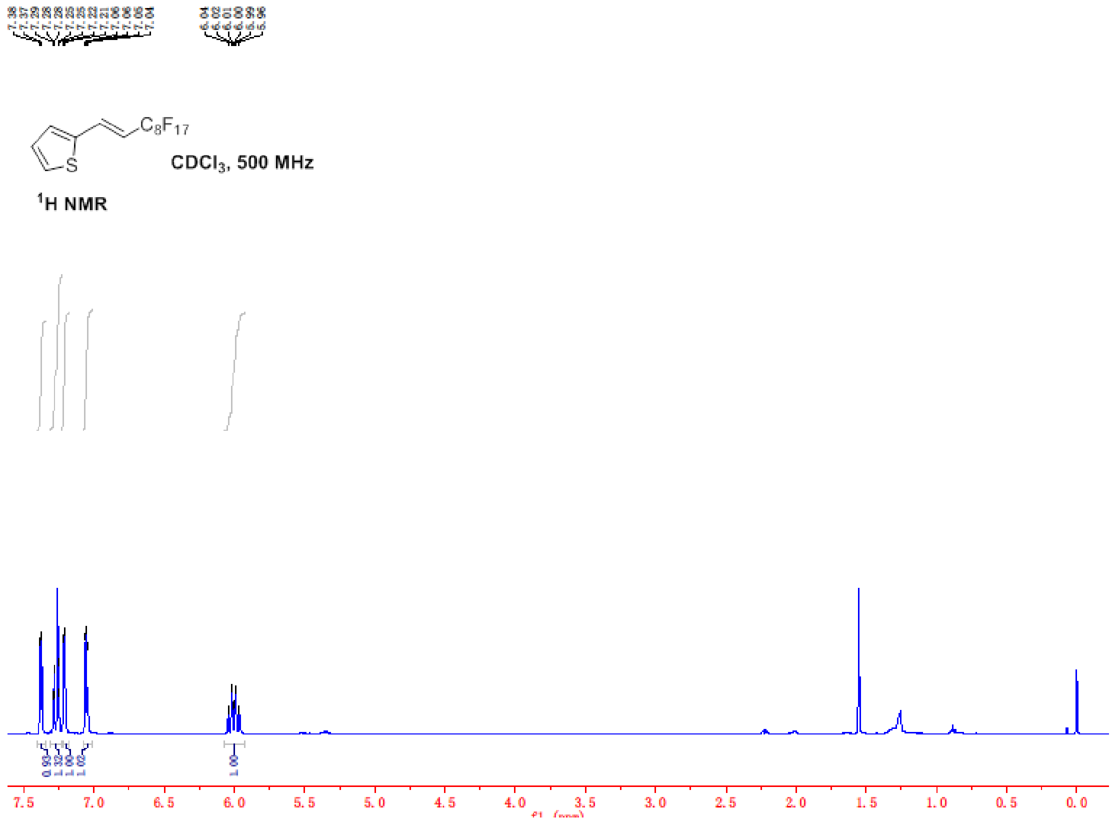
CDCl3, 500 MHz
1H NMR



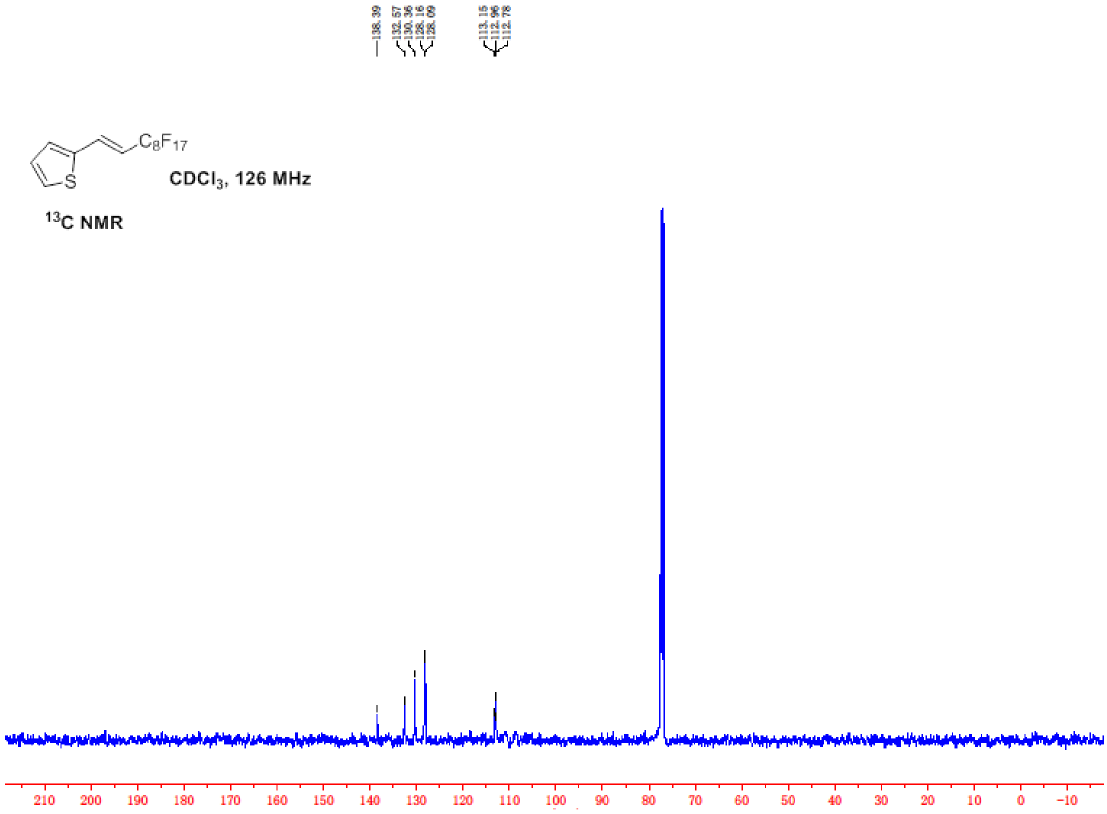
CDCl3, 126 MHz
13C NMR

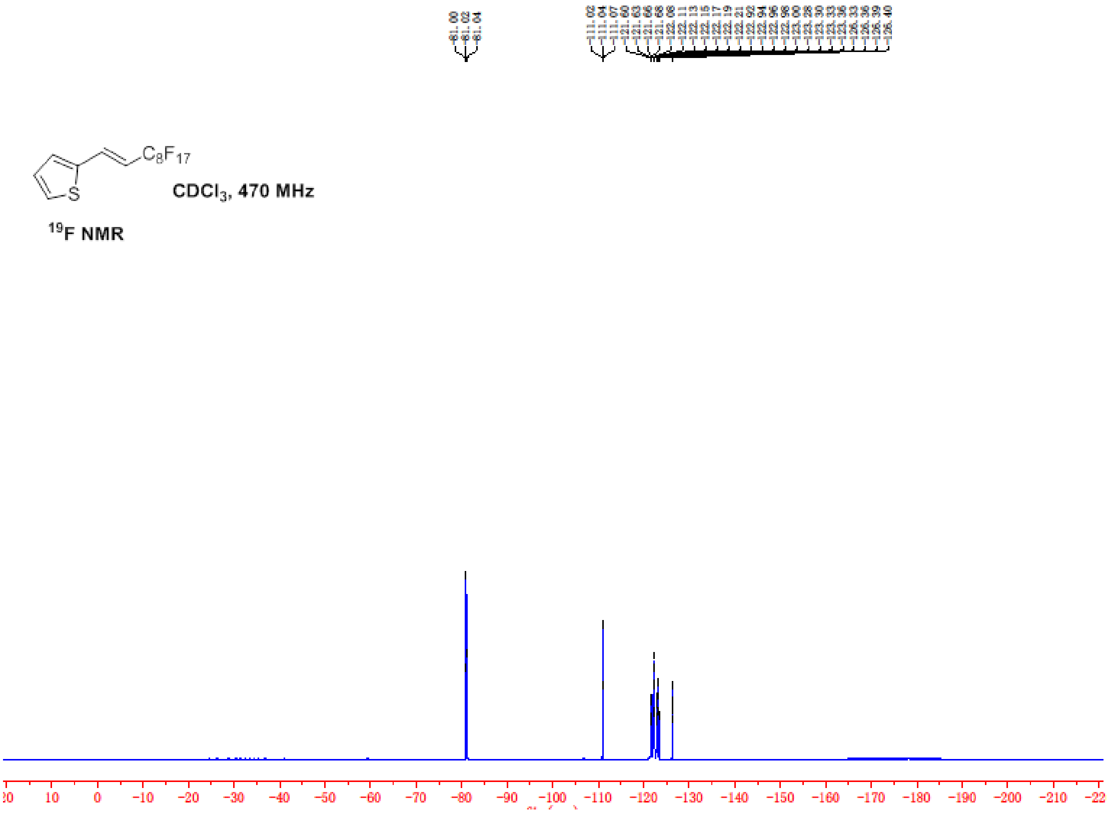


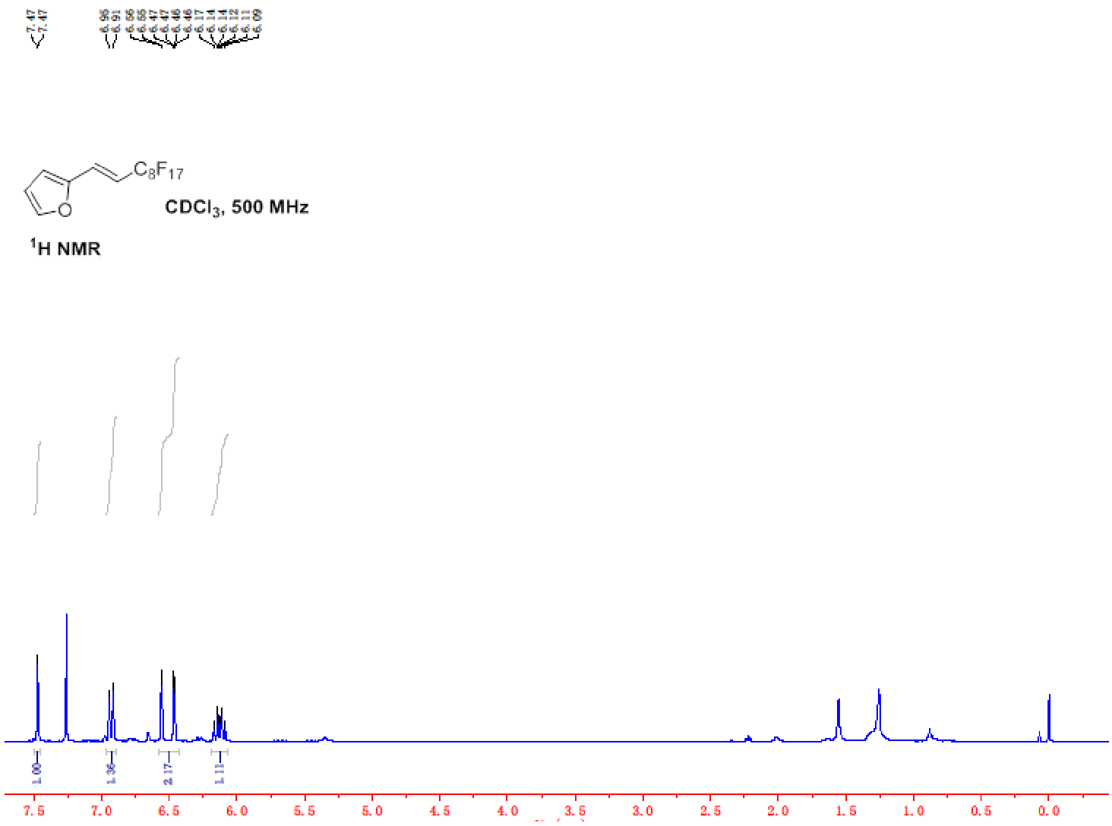
-80.76
-80.78
-80.80
-80.83
-111.62
-111.65
-111.67
-111.70
-121.55
-121.58
-121.61
-122.80
-122.82
-122.84
-122.87
-122.90
-123.10
-123.12
-123.14
-123.15
-123.17
-123.18
-123.21
-126.11
-126.12
-126.14
-126.15
-126.17
-126.19
-126.20
C_6F_{13}
N
CDCl3, 470 MHz
19F NMR

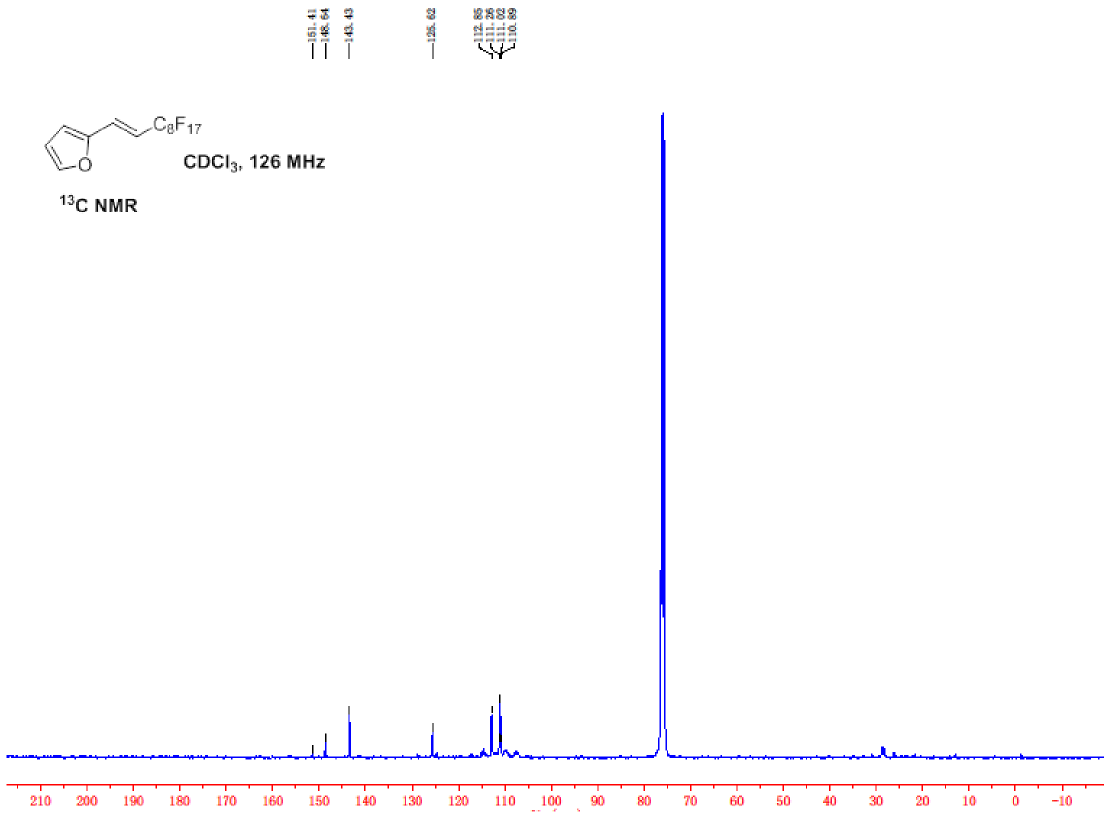


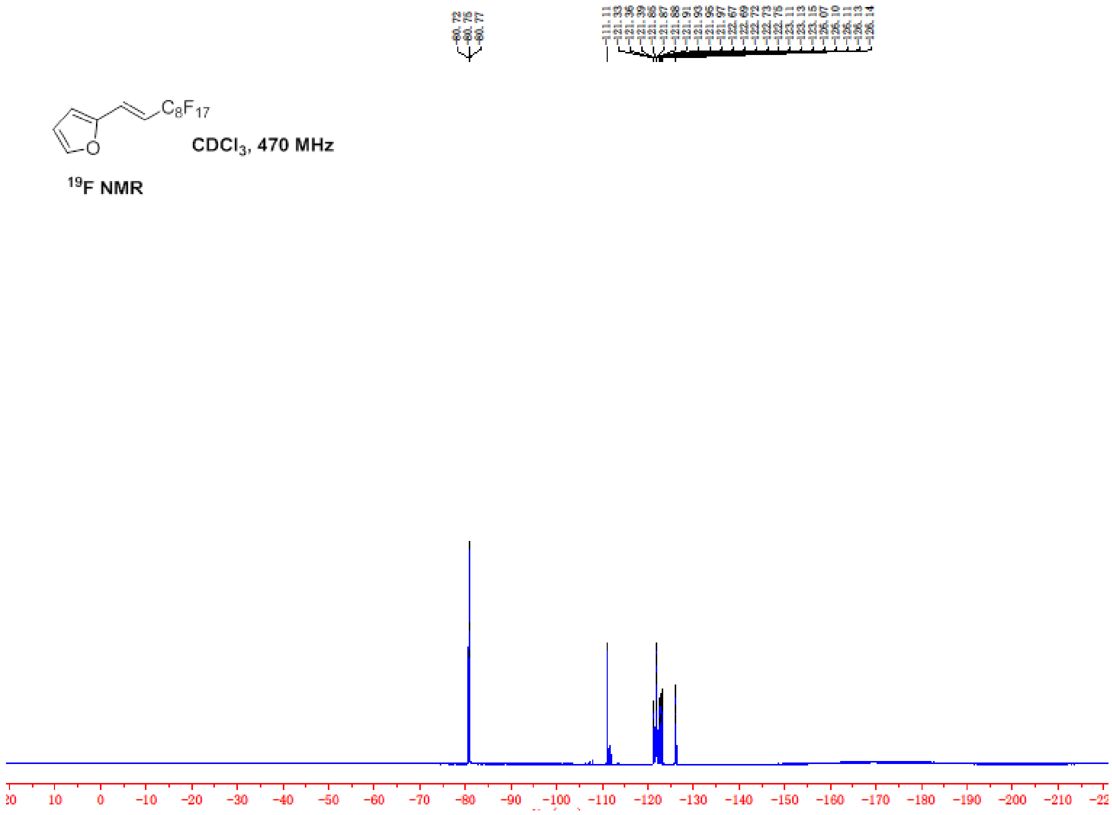
7.38
7.37
7.29
7.28
7.28
7.25
7.22
7.21
7.06
7.06
7.05
7.04
6.04
6.02
6.01
6.00
5.99
5.96
C_8F_{17}
S
CDCl3, 500 MHz
1H NMR

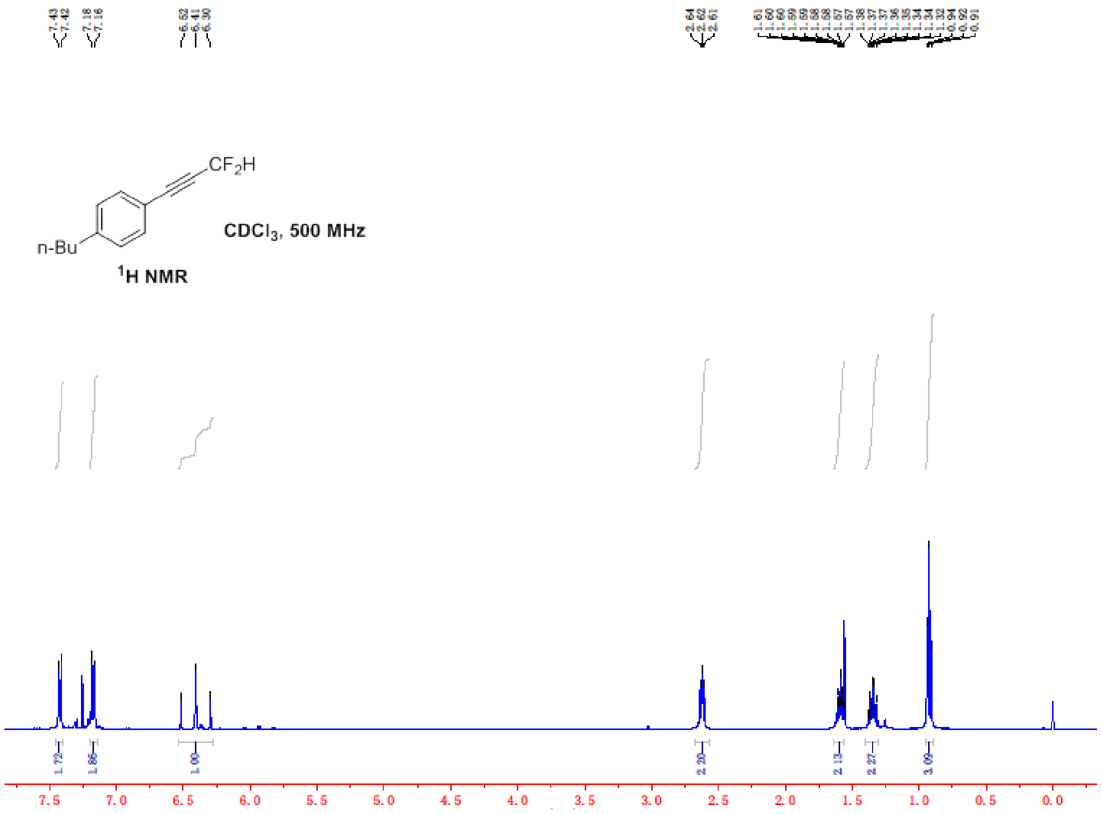

138.39
132.57
130.36
128.16
128.09
113.15
112.96
112.78
C_8F_{17}
S
$CDCl_3$, 126 MHz
^{13}C NMR

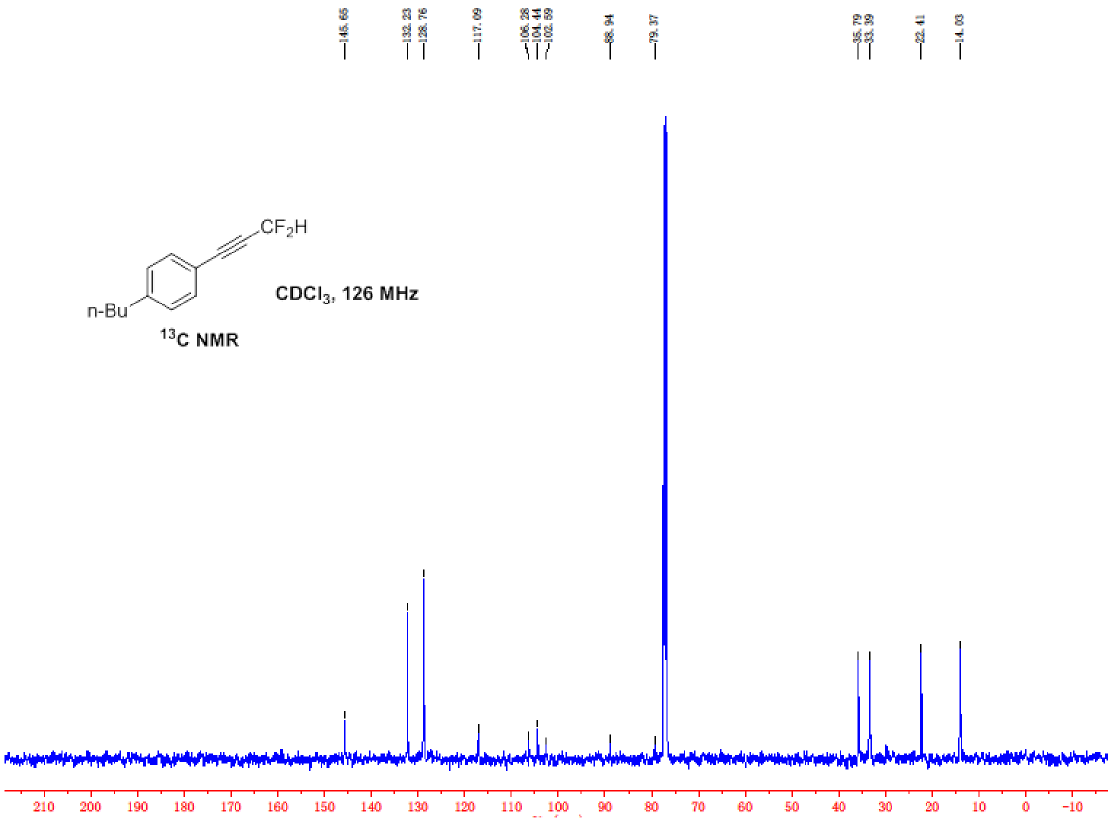

-81.00
-81.02
-81.04
-111.02
-111.04
-111.07
C_8F_{17}
S
$CDCl_3$, 470 MHz
^{19}F NMR

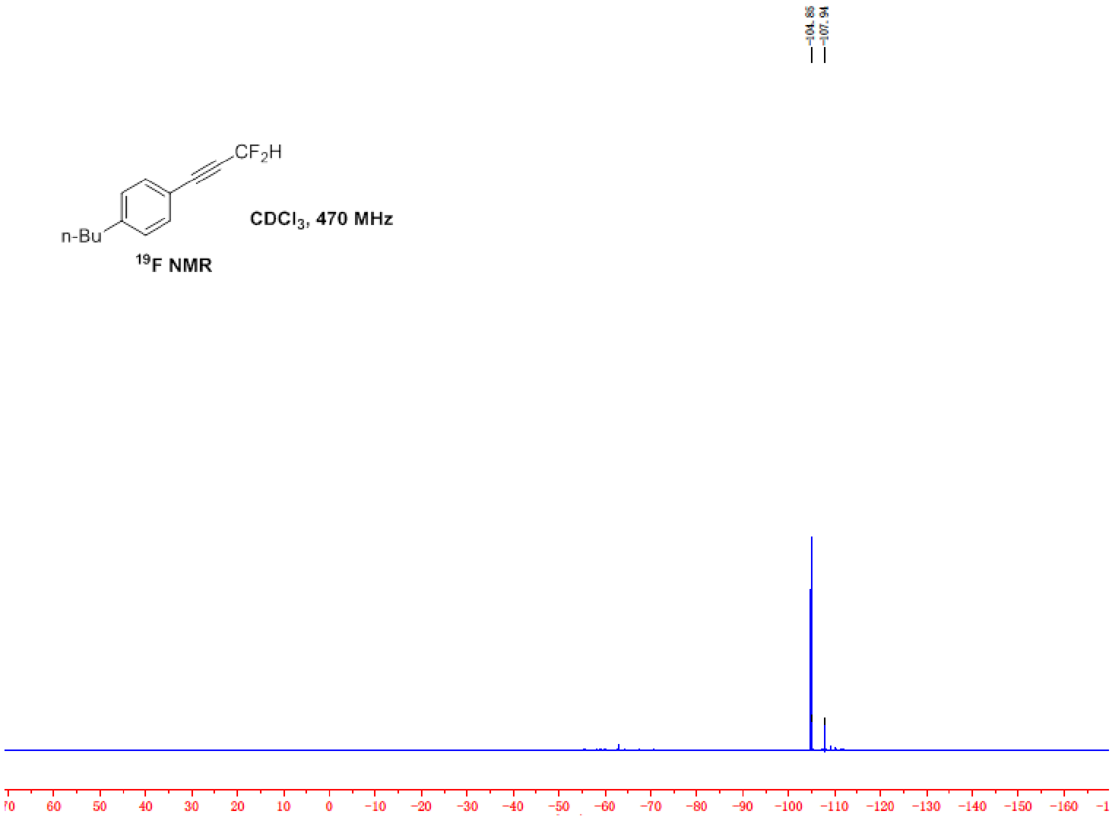

7.47
7.47
6.95
6.91
6.56
6.55
6.47
6.47
6.46
6.46
6.17
6.14
6.14
6.12
6.11
6.09
C8F17
O
CDCl3, 500 MHz
1H NMR
1.00
1.36
2.17
1.11
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

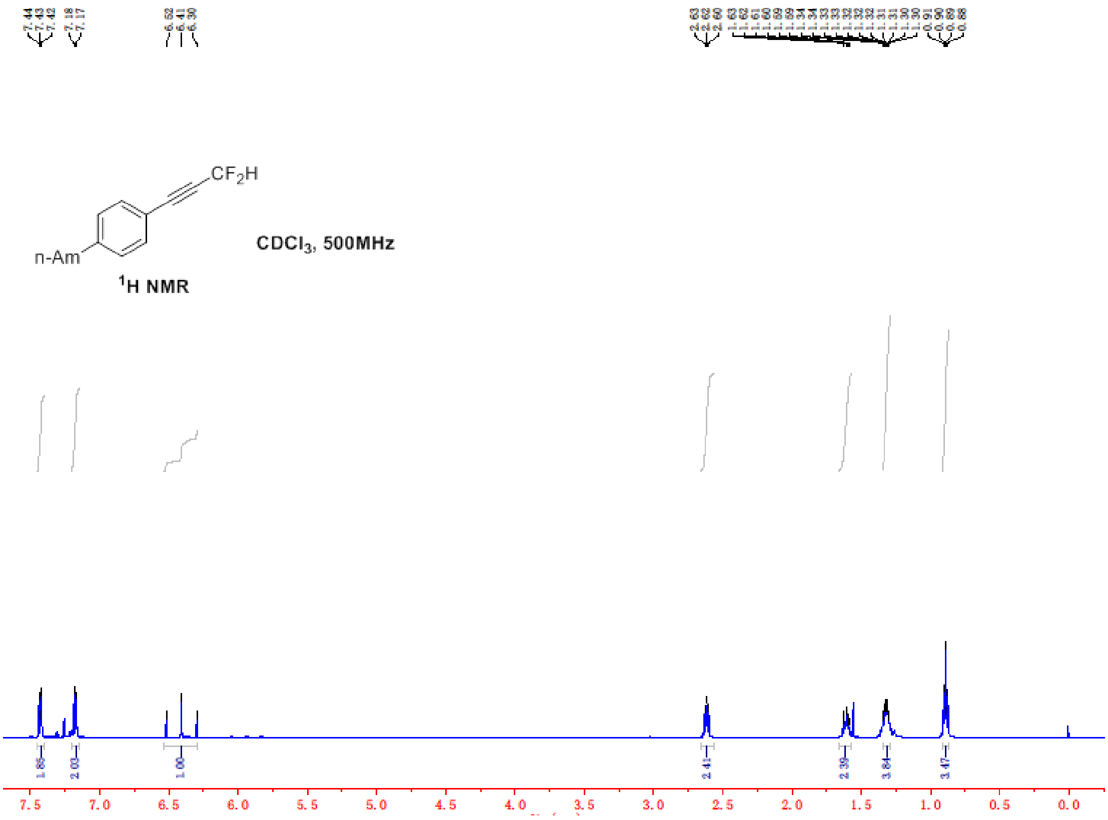

151.41
148.64
143.43
125.62
112.85
111.26
111.02
110.89
C8F17
O
CDCl3, 126 MHz
13C NMR
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


C8F17
CDCl3, 470 MHz
19F NMR

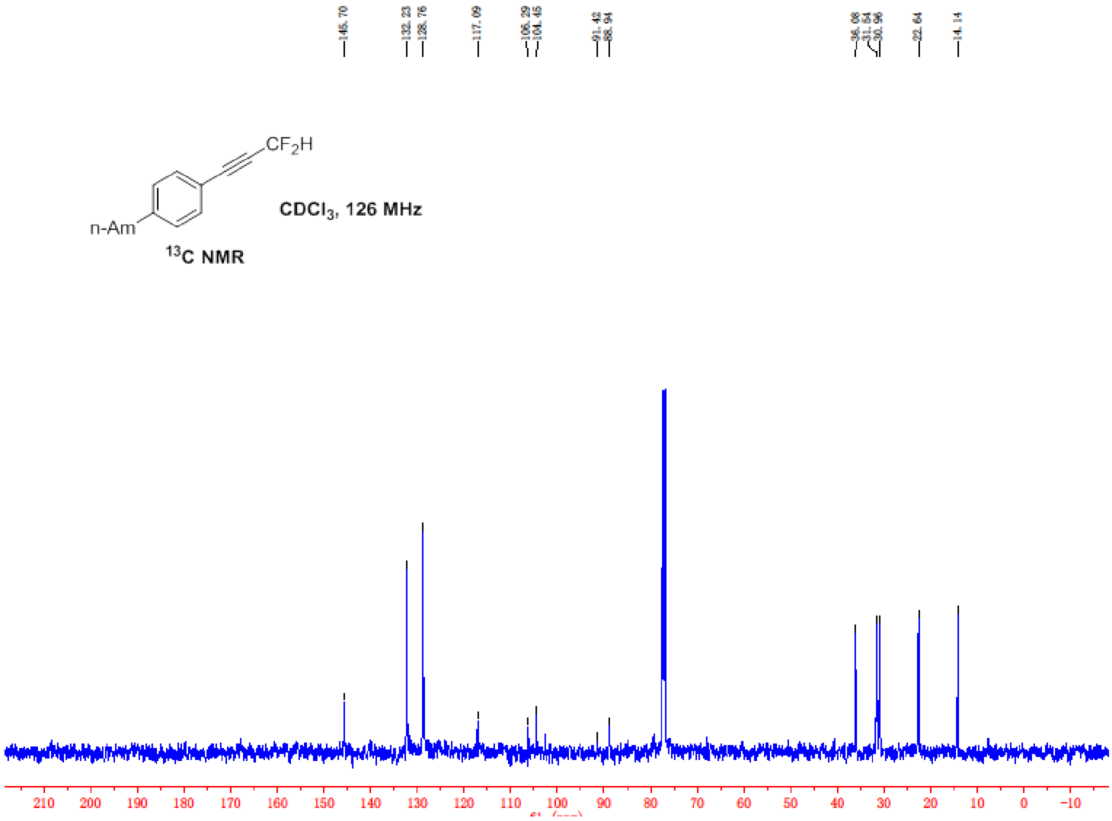

CF2H
n-Bu
CDCl3, 500 MHz
1H NMR


145.65
132.23
128.76
117.09
106.28
104.44
102.59
88.94
79.37
35.79
33.39
22.41
14.03
CF2H
n-Bu
CDCl3, 126 MHz
13C NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

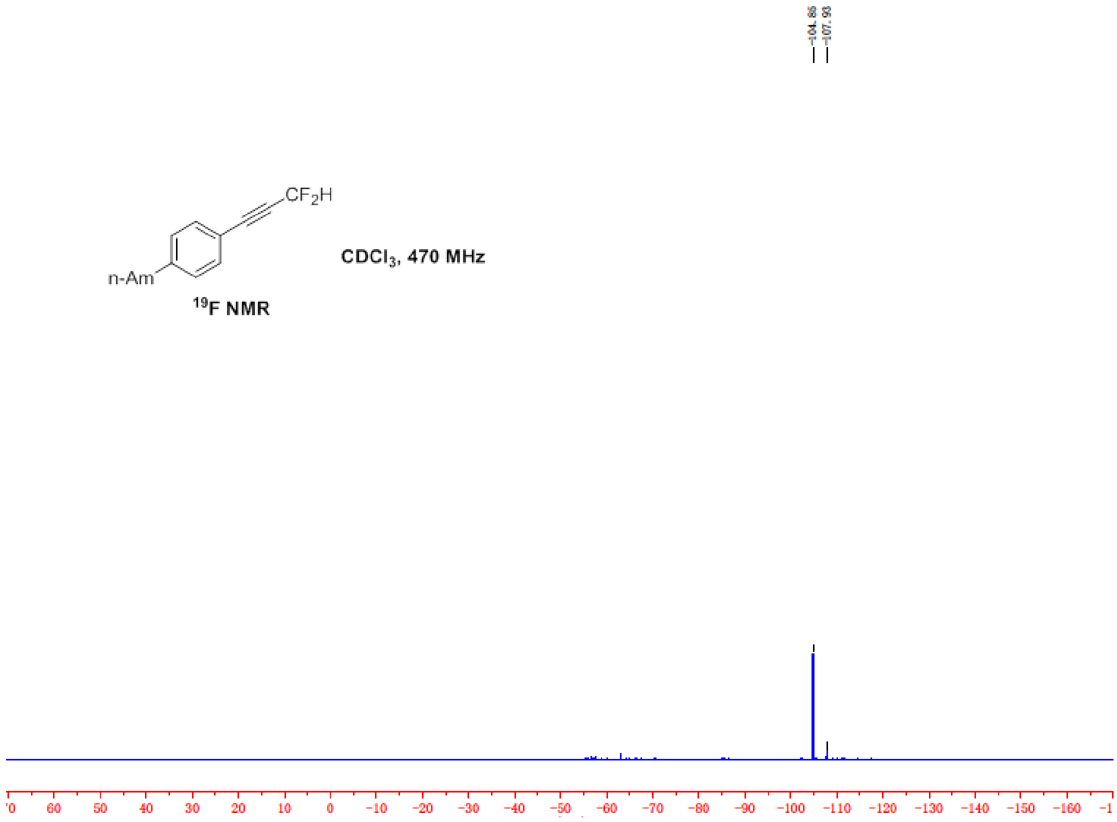

-104.86
-107.94
CF2H
n-Bu
CDCl3, 470 MHz
19F NMR
60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160



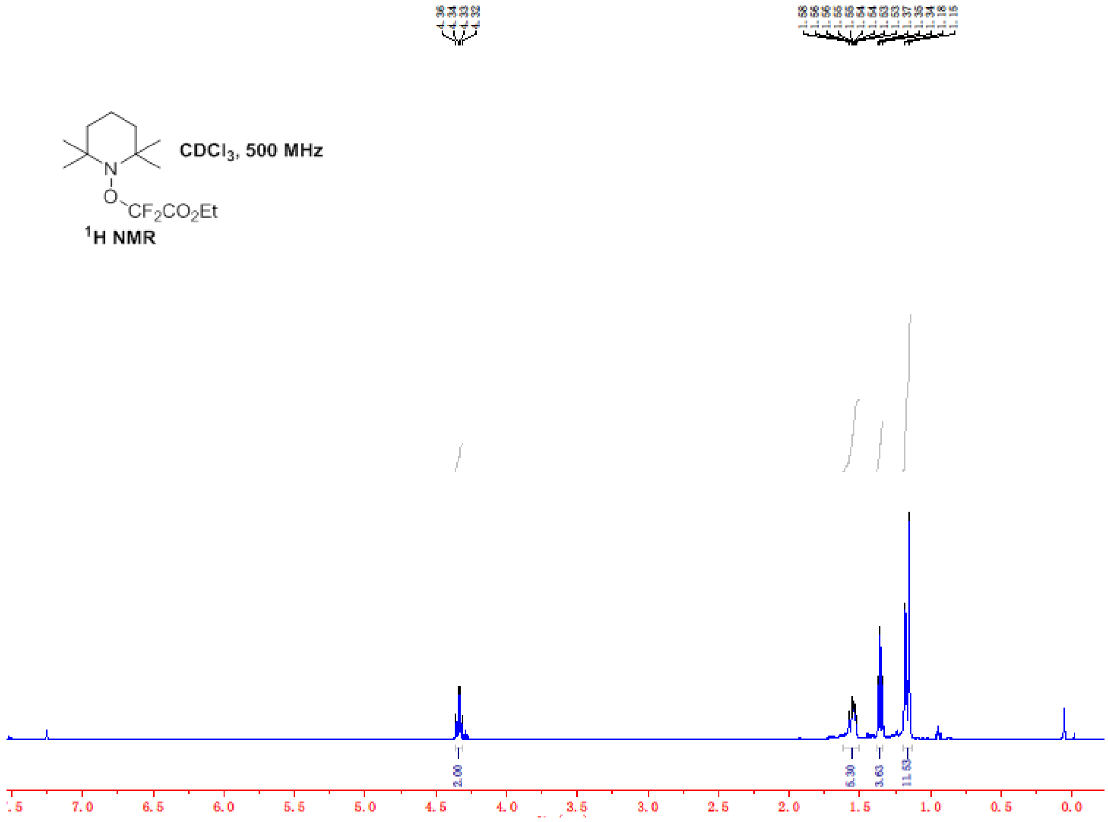
CF2H
n-Am
CDCl3, 500MHz
1H NMR
7.44
7.43
7.42
7.18
7.17
6.52
6.41
6.30
0.91
0.90
0.89
0.88
1.85
2.03
1.00
2.41
2.39
3.84
3.47
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



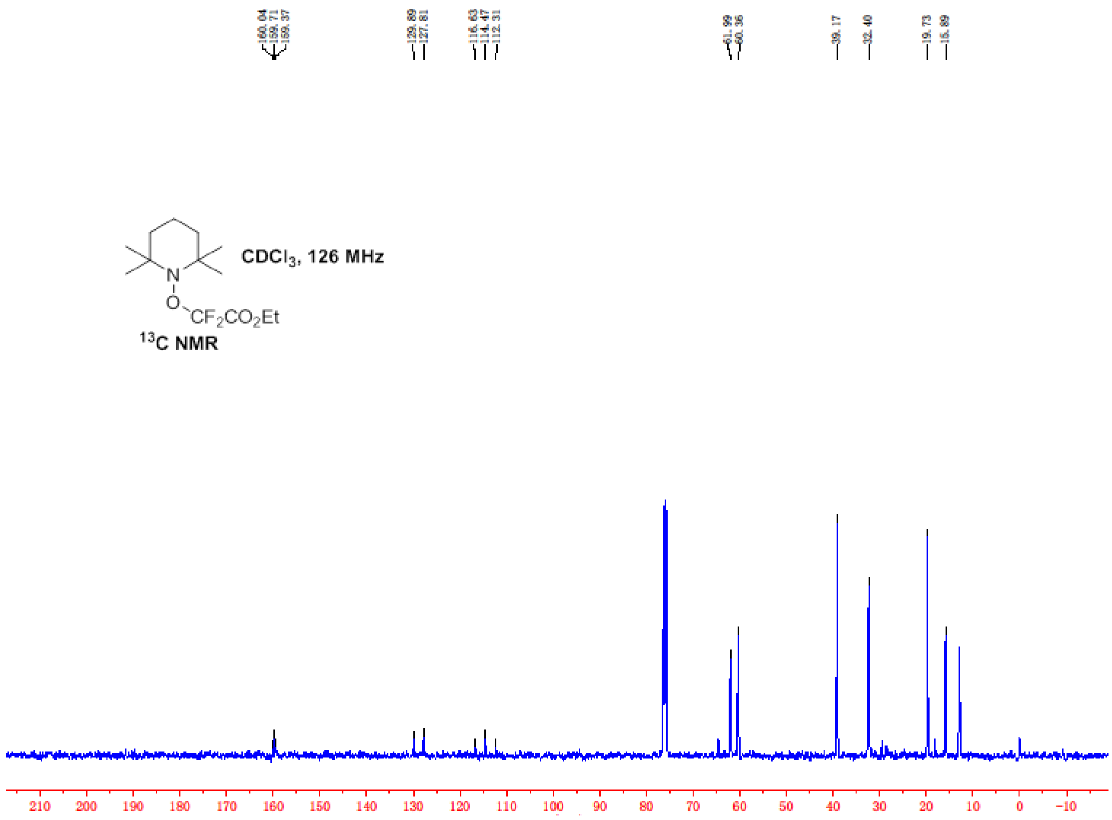
145.70
132.23
128.76
117.09
106.29
104.45
91.42
88.94
36.08
31.54
30.96
22.64
14.14
CF2H
n-Am
CDCl3, 126 MHz
13C NMR
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

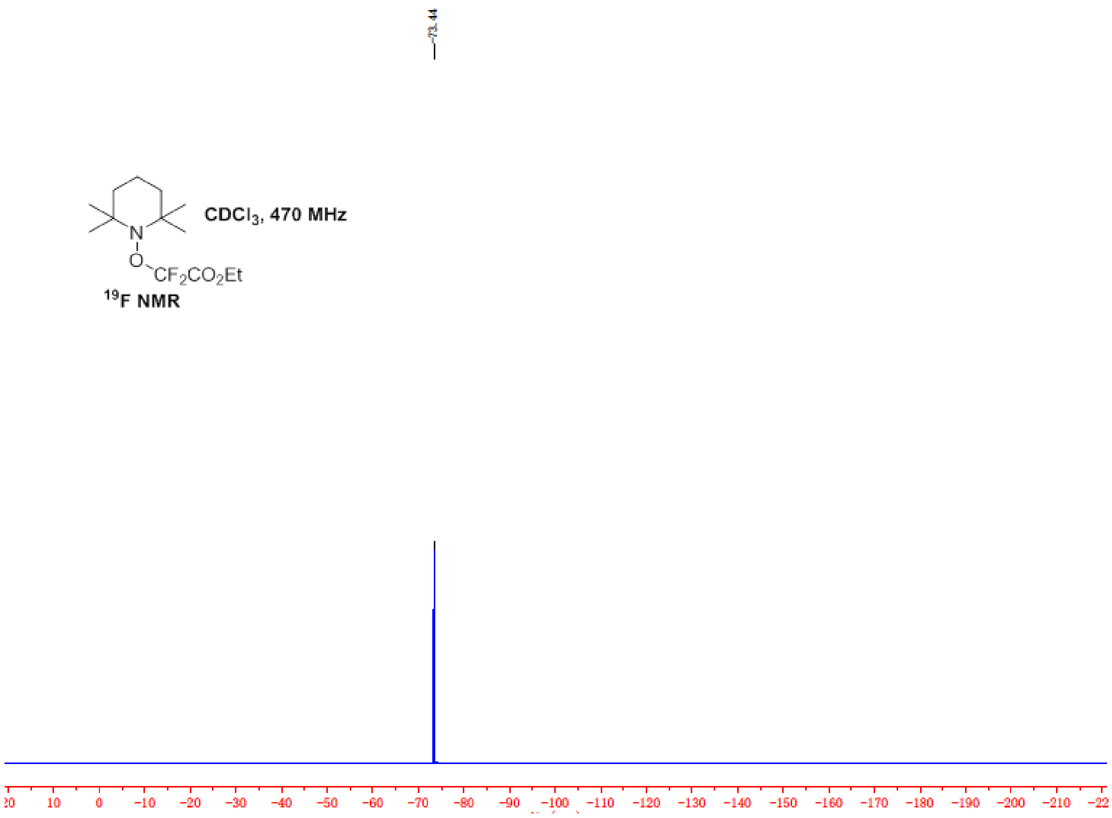


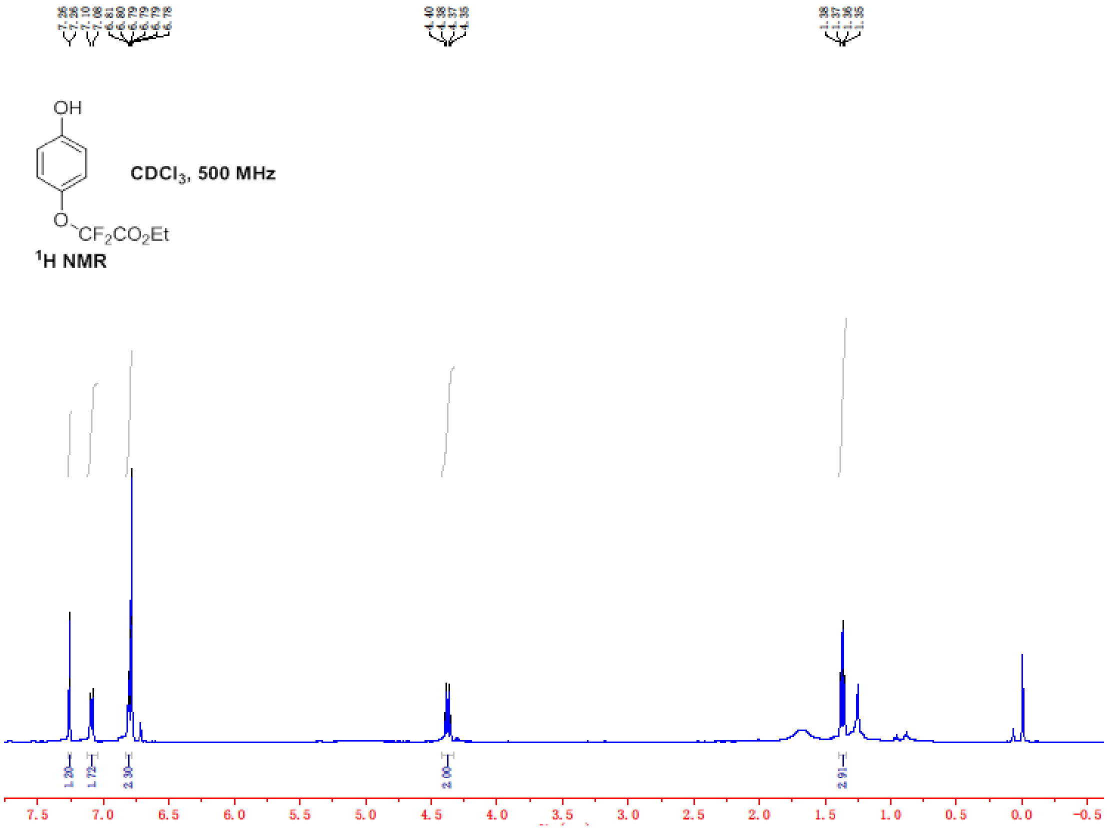
-104.86
-107.93
CF2H
n-Am
CDCl3, 470 MHz
19F NMR



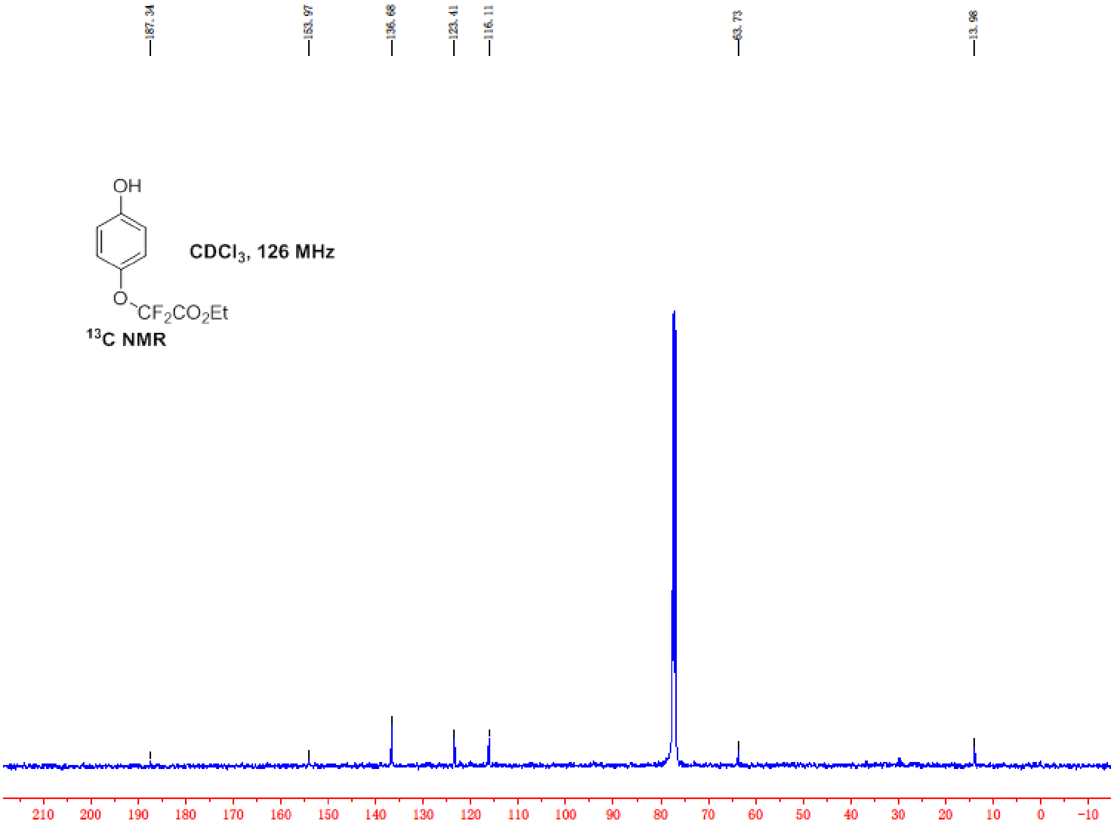
4.36 4.34 4.33 4.32
1.58 1.56 1.56 1.55 1.55 1.54 1.54 1.53 1.53 1.37 1.35 1.34 1.18 1.15
N
O
CF2CO2Et
CDCl3, 500 MHz
1H NMR
2.00
6.30
3.63
11.63


160.04
159.71
159.37
129.89
127.81
116.63
114.47
112.31
61.99
60.36
39.17
32.40
19.73
15.89
CDCl3, 126 MHz
CF2CO2Et
13C NMR

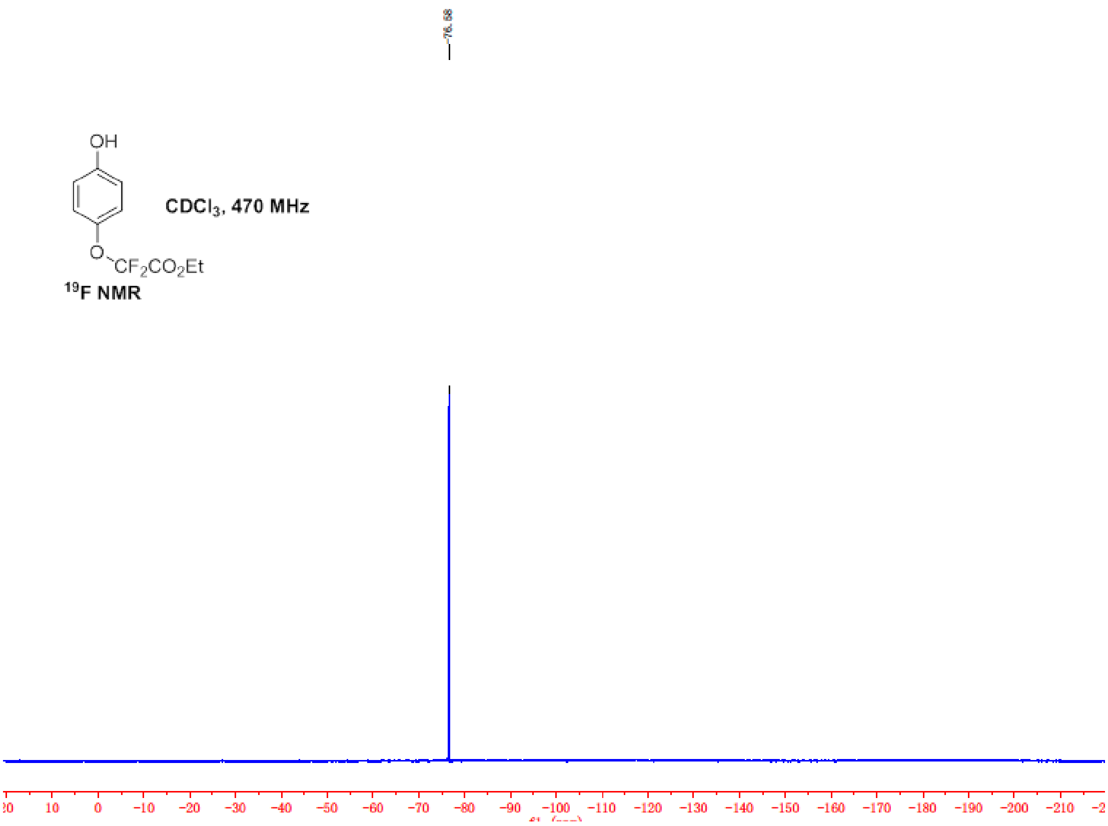

-73.44
CDCl3, 470 MHz
CF2CO2Et
19F NMR



OH
O
CF2CO2Et
CDCl3, 500 MHz
1H NMR



OH
O
CF2CO2Et
CDCl3, 126 MHz
13C NMR



-76.58
OH
O
CF2CO2Et
CDCl3, 470 MHz
19F NMR
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210