

Supporting Information

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

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1. General Considerations

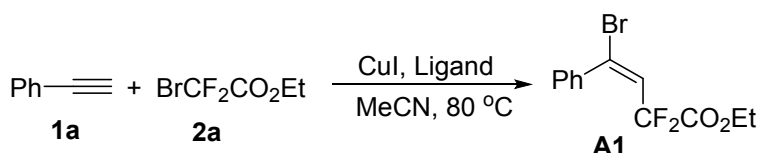
Unless otherwise mentioned, solvents and reagents were purchased from commercial sources and used without further purification. ^1H , ^{19}F and ^{13}C NMR spectra were recorded on a 500 MHz Bruker DRX 500 and tetramethylsilane (TMS) was used as a reference. Chemical shifts were reported in parts per million (ppm), ^1H NMR chemical shifts were determined relative to internal $(\text{CH}_3)_4\text{Si}$ (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 ^1H , ^{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

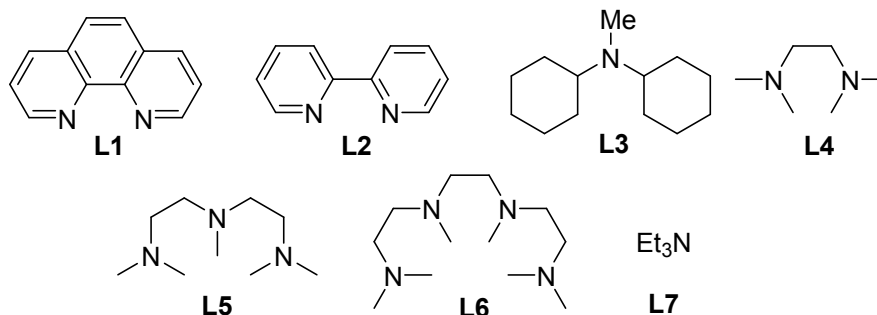
In a sealed glass vial, phenylacetylene (**1a**, 0.2 mmol), ethyl bromodifluoroacetate (**2a**, 1.5 equiv.), catalyst and ligand were dissolved in dry solvent under argon atmosphere following the condition listed in the table below. The mixture was stirred for 24 h. After cooling to room temperature, 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

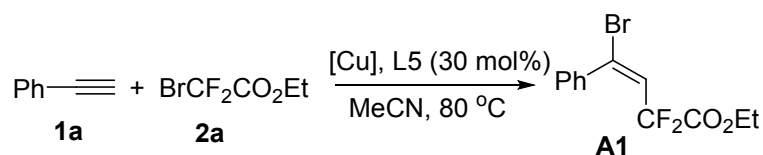
4	L4 (30)	trace
5	L5 (30)	87%
6	L6 (30)	11%
7	L7 (30)	n.r.
8	/	n.r.
9	L5 (10)	30%
10	L5 (15)	42%
11	L5 (20)	59%
12	L5 (40)	84%



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 ¹⁹F NMR using trifluoroacetophenone as the internal standard. n.r. = no reaction.

2.2 Screening copper catalysts

Table S2

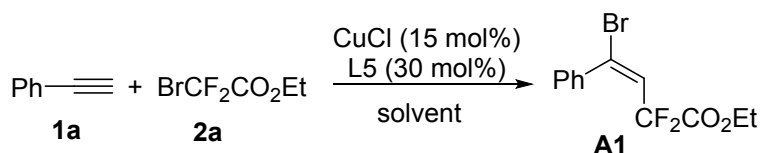


Entry	[Cu] (mol%)	Yield
1	CuCl (15)	94%
2	CuBr (15)	44%
3	CuI (15)	87%
4	Cu(OTf) ₂ (15)	32%
5	Cu ₂ O (15)	62%
6	/	n.r.
7	CuCl (5)	39%
8	CuCl (10)	80%
9	CuCl (20)	51%
10	CuCl (25)	69%

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

2.3 Screening temperature and solvents

Table S3



Entry	Solvent	Tem. (°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 (1 mL), under argon for 24 h, determined by

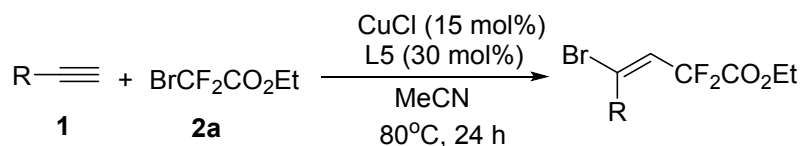
¹⁹F NMR using trifluoroacetophenone as the internal standard. n.r. = no reaction.

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 °C under argon atmosphere for 24 h (Table S3, entry 4).

3. General Procedure for Experiments

Method I:

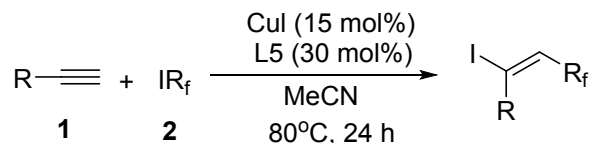
CuCl-catalyzed ATRA reaction:



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 °C 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:

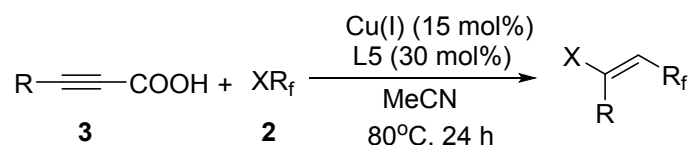
CuI-catalyzed ATRA reaction:



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 °C 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:

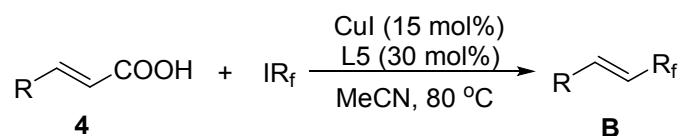
Decarboxylative ATRA of fluoroalkyl halides to alkynyl carboxylic acids:



A reaction tube was charged with CuCl (3.0 mg, 0.03 mmol), L5 (10.4 mg, 0.06 mmol) at room temperature, then phenylpropionic 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 °C 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:



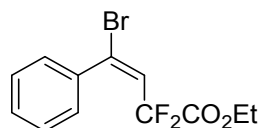
A reaction tube was charged with CuI (5.7 mg, 0.03 mmol), L5 (10.4 mg, 0.06 mmol) at room temperature, then 4-phenylcinnamic acid (**4a**) (44.8 mg, 0.2 mmol), pentafluoroethyl iodide (98.4 mg, 0.4 mmol) and MeCN (1 mL) were added. The resulting mixture was stirred at 80 °C under argon atmosphere for 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** compounds:

To a methanol (5mL) solution of **A** (0.5 mmol) was added 1 M K₂CO₃ (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 H₂O 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°C under argon 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.

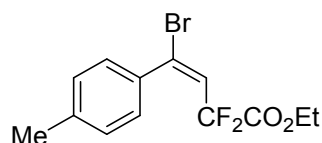
4. Analytical data of compounds



Chemical Formula: $\text{C}_{12}\text{H}_{11}\text{BrF}_2\text{O}_2$
Exact Mass: 303.99

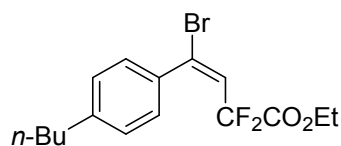
Compound **A1**¹: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A1** (54.1 mg, 89%), yellow liquid (*E/Z* = 94:6, the ratio detected by ^{19}F NMR). ^1H NMR (500 MHz, CDCl_3) δ 7.36 (s, 5H), 6.50 (t, J = 11.2 Hz, 1H), 3.99 (q, J = 7.2 Hz, 2H), 1.19 (t, 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 $\text{C}_{12}\text{H}_{11}\text{BrF}_2\text{O}_2$ 303.99, found 304.07.

Z product: ^{19}F NMR (470 MHz, CDCl_3) δ -97.61.



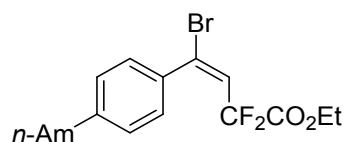
Chemical Formula: $\text{C}_{13}\text{H}_{13}\text{BrF}_2\text{O}_2$
Exact Mass: 318.01

Compound **A2**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A2** (51.5 mg, 81%), yellow liquid. ^1H 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 $\text{C}_{13}\text{H}_{13}\text{BrF}_2\text{O}_2$ 318.01, found 318.04.



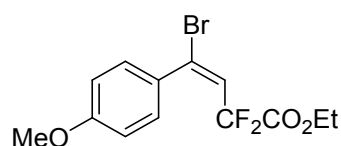
Chemical Formula: $\text{C}_{16}\text{H}_{19}\text{BrF}_2\text{O}_2$
Exact Mass: 360.05

Compound **A3**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A3** (56.9 mg, 79%), yellow liquid. ^1H 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 $\text{C}_{16}\text{H}_{19}\text{BrF}_2\text{O}_2$ 360.05, HRMS (EI⁺) found 360.0542.



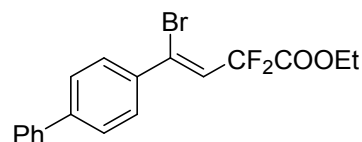
Chemical Formula: $C_{17}H_{21}BrF_2O_2$
Exact Mass: 374.07

Compound **A4**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A4** (56.1 mg, 75%), brown liquid. 1H 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.



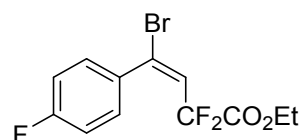
Chemical Formula: $C_{13}H_{13}BrF_2O_3$
Exact Mass: 334.00

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. 1H 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

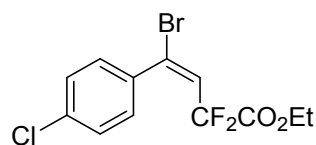
Compound **A6**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 40:1) to afford the **A6** (67.6 mg, 89%), yellow liquid. 1H NMR (500 MHz, $CDCl_3$) δ 7.64-7.57 (m, 5H), 7.50-7.43 (m, 4H), 7.43-7.35 (m, 1H), 6.54 (t, J = 11.2 Hz, 1H), 4.02 (q, J = 7.2 Hz, 2H), 1.20 (t, J = 7.1 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

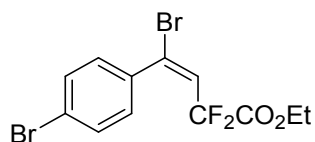
Compound **A7**¹: purified by column chromatography on silica gel (petroleum ether/EtOAc = 40:1) to afford the **A7** (56.0 mg, 87%), yellow liquid. 1H NMR (500 MHz, $CDCl_3$) δ 7.47-7.32 (m, 2H), 7.05 (dd, J = 9.6, 7.7 Hz, 2H), 6.49 (t, J = 11.3 Hz, 1H), 4.07 (q, J = 7.2 Hz, 2H), 1.23 (t, J = 7.1 Hz, 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 $\text{C}_{12}\text{H}_{10}\text{BrF}_3\text{O}_2$ 321.98, found 322.02.



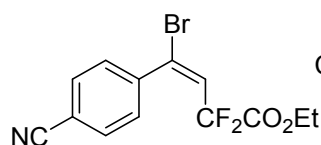
Chemical Formula: $\text{C}_{12}\text{H}_{10}\text{BrClF}_2\text{O}_2$
Exact Mass: 337.95

Compound **A8**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A8** (60.2 mg, 89%), yellow liquid. ^1H 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 $\text{C}_{12}\text{H}_{10}\text{BrClF}_2\text{O}_2$ 337.95, HRMS (EI^+) found 337.9523.



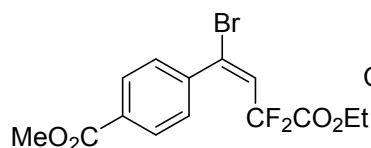
Chemical Formula: $\text{C}_{12}\text{H}_{10}\text{Br}_2\text{F}_2\text{O}_2$
Exact Mass: 381.90

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. ^1H 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 $\text{C}_{12}\text{H}_{10}\text{Br}_2\text{F}_2\text{O}_2$ 381.90, found 381.96.



Chemical Formula: $\text{C}_{13}\text{H}_{10}\text{BrF}_2\text{NO}_2$
Exact Mass: 328.99

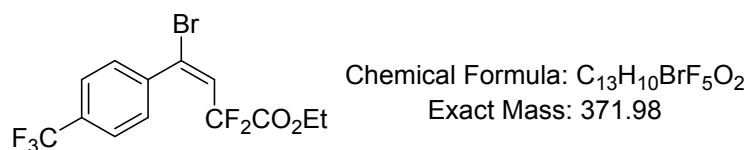
Compound **A10**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A10** (57.2 mg, 87%), yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 7.69-7.64 (m, 2H), 7.50-7.45 (m, 2H), 6.55 (t, $J = 12.0$ Hz, 1H), 4.18 (q, $J = 7.2$ Hz, 2H), 1.28 (t, $J = 7.1$ Hz, 3H); ^{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 $\text{C}_{13}\text{H}_{10}\text{BrF}_2\text{NO}_2$ 328.99, found 328.98.



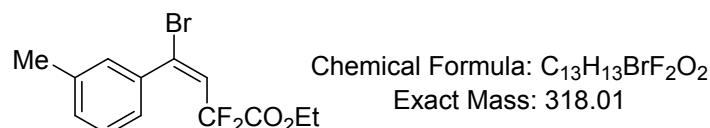
Chemical Formula: $\text{C}_{14}\text{H}_{13}\text{BrF}_2\text{O}_4$
Exact Mass: 362.00

Compound **A11**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 15:1) to afford the **A11** (64.2 mg, 73%), yellow liquid. ^1H 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, $J =$

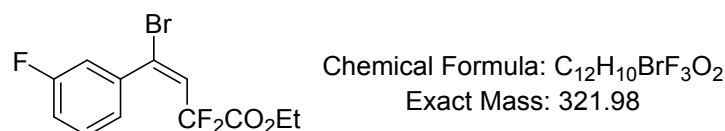
7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.28, 161.33, 141.64, 133.89-131.90 (m), 131.39, 129.69, 129.47, 128.58, 125.80 (t, $J = 27.9$ Hz), 63.49, 52.47, 13.86; ^{19}F NMR (470 MHz, CDCl_3) δ -95.01. GC-MS (EI) Calcd. for $\text{C}_{14}\text{H}_{13}\text{BrF}_2\text{O}_4$ 362.00, found 362.01.



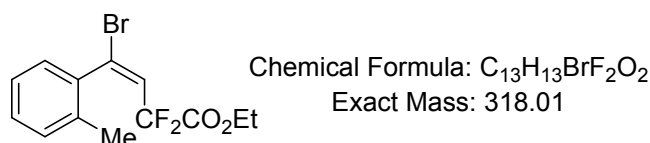
Compound **A12**¹: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A12** (31.2 mg, 42%), yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 7.63 (d, $J = 8.1$ Hz, 2H), 7.49 (d, $J = 8.0$ Hz, 2H), 6.55 (t, $J = 11.7$ Hz, 1H), 4.11 (q, $J = 7.1$ Hz, 2H), 1.25 (d, $J = 7.2$ Hz, 3H); ^{19}F NMR (470 MHz, CDCl_3) δ -62.97 (d, $J = 20.6$ Hz), -95.26. GC-MS (EI) Calcd. for $\text{C}_{13}\text{H}_{10}\text{BrF}_5\text{O}_2$ 371.98, [M-F] found 353.03.



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. ^1H 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 $\text{C}_{13}\text{H}_{13}\text{BrF}_2\text{O}_2$ 318.01, found 318.07.



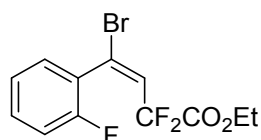
Compound **A14**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 40:1) to afford the **A14** (43.8 mg, 68%), colorless liquid. ^1H NMR (500 MHz, CDCl_3) δ 7.38 (td, $J = 7.7, 5.6$ Hz, 1H), 7.23-7.17 (m, 1H), 7.13 (t, $J = 8.5$ Hz, 2H), 6.56 (t, $J = 11.5$ Hz, 1H), 4.14 (q, $J = 7.1$ 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 $\text{C}_{12}\text{H}_{10}\text{BrF}_3\text{O}_2$ 321.98, found 322.03.



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). ^1H NMR

(500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; ¹⁹F NMR (470 MHz, CDCl₃) δ -95.40 (d, J = 272.6 Hz), -97.44 (d, J = 272.6 Hz). GC-MS (EI) Calcd. for C₁₃H₁₃BrF₂O₂ 318.01, found 318.06.

Z product: ¹⁹F NMR (470 MHz, CDCl₃) δ -94.87 (d, J = 282.0 Hz), -97.12 (d, J = 282.0 Hz).

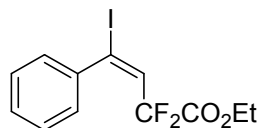


Chemical Formula: C₁₂H₁₀BrF₃O₂

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 ¹⁹F NMR). ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; ¹⁹F NMR (470 MHz, CDCl₃) δ -98.50, -112.60. GC-MS (EI) Calcd. for C₁₂H₁₀BrF₃O₂ 321.98, found 322.01.

Z product: ¹⁹F NMR (470 MHz, CDCl₃) δ -99.02, -113.77.

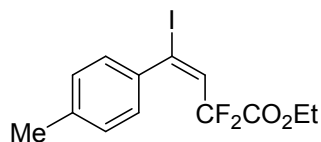


Chemical Formula: C₁₂H₁₁F₂IO₂

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 ¹⁹F NMR). ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; ¹⁹F NMR (470 MHz, CDCl₃) δ -93.79. GC-MS (EI) Calcd. for C₁₂H₁₁F₂IO₂ 351.98, found 352.03.

Z product: ¹⁹F NMR (470 MHz, CDCl₃) δ -98.04.



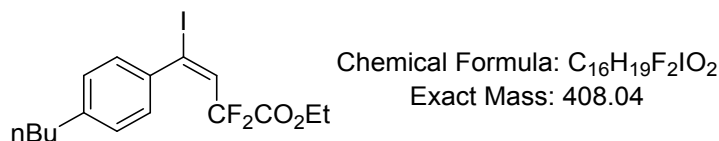
Chemical Formula: C₁₃H₁₃F₂IO₂

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 ¹⁹F NMR). ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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,

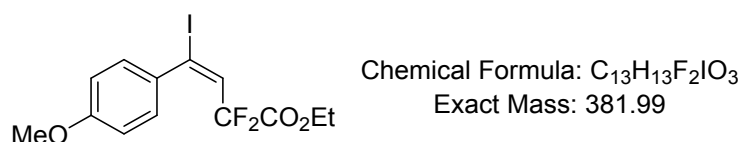
63.24, 21.49, 13.82; ^{19}F NMR (470 MHz, CDCl_3) δ -93.67. GC-MS (EI) Calcd. for $\text{C}_{13}\text{H}_{13}\text{F}_2\text{IO}_2$ 365.99, HRMS (EI $^+$) found 365.9931.

Z product: ^{19}F NMR (470 MHz, CDCl_3) δ -97.78.



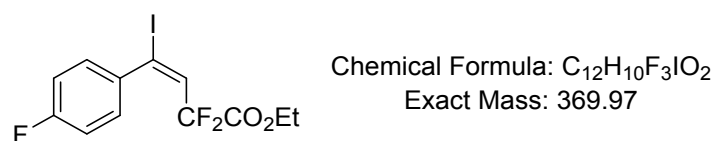
Compound **A19**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A19** (71.8 mg, 88%), yellow liquid (E/Z = 97:3, the ratio detected by ^{19}F NMR). ^1H NMR (500 MHz, CDCl_3) δ 7.23 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 6.71 (t, J = 10.8 Hz, 1H), 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 $\text{C}_{16}\text{H}_{19}\text{F}_2\text{IO}_2$ 408.04, found 408.17.

Z product: ^{19}F NMR (470 MHz, CDCl_3) δ -97.78.

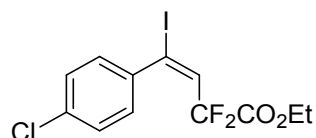


Compound **A20**²: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A20** (56.5 mg, 74%), brown liquid (E/Z = 93:7, the ratio detected by ^{19}F NMR). ^1H NMR (500 MHz, CDCl_3) δ 7.19 (d, J = 8.4 Hz, 2H), 6.77-6.71 (m, 2H), 6.60 (t, J = 10.8 Hz, 1H), 3.92 (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 $\text{C}_{13}\text{H}_{13}\text{F}_2\text{IO}_3$ 381.99, found 382.03.

Z product: ^{19}F NMR (470 MHz, CDCl_3) δ -97.59.



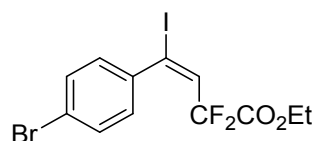
Compound **A21**²: purified by column chromatography on silica gel (petroleum ether/EtOAc = 40:1) to afford the **A21** (63.6 mg, 86%), colorless liquid. ^1H NMR (500 MHz, CDCl_3) δ 7.34-7.27 (m, 2H), 7.00 (t, J = 8.6 Hz, 2H), 6.71 (t, J = 11.2 Hz, 1H), 4.05 (q, J = 7.1 Hz, 2H), 1.23 (t, J = 7.1 Hz, 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 $\text{C}_{12}\text{H}_{10}\text{F}_3\text{IO}_2$ 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). 1H 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.

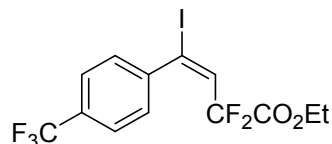
Z product: ^{19}F NMR (470 MHz, $CDCl_3$) δ -98.25.



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

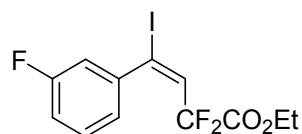
Compound **A23**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A23** (74.4 mg, 88%), yellow liquid (*E/Z* = 95:5, the ratio detected by ^{19}F NMR). 1H NMR (500 MHz, $CDCl_3$) δ 7.50-7.43 (m, 2H), 7.21-7.14 (m, 2H), 6.72 (t, *J* = 11.3 Hz, 1H), 4.08 (q, *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. 1H 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.

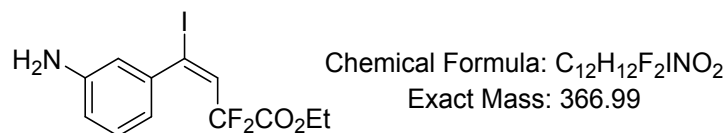


Chemical Formula: $C_{12}H_{10}F_3IO_2$
Exact Mass: 369.97

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). 1H 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

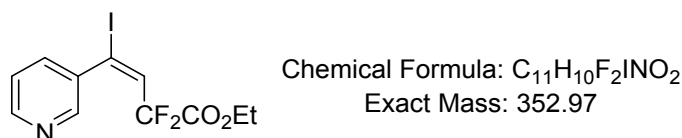
MHz, CDCl₃) δ 161.56 (t, J = 35.4 Hz), 159.74, 141.58, 132.57 (t, J = 27.9 Hz), 128.72 (d, J = 8.5 Hz), 122.46, 115.38 (d, J = 21.1 Hz), 113.91 (d, J = 23.3 Hz), 110.79 (d, J = 251.1 Hz), 105.23, 62.30, 12.71. ¹⁹F NMR (470 MHz, CDCl₃) δ -94.76, -112.16. GC-MS (EI) Calcd. for C₁₂H₁₀F₃IO₂ 369.97, found 369.78.

Z product: ¹⁹F NMR (470 MHz, CDCl₃) δ -98.36, -112.20.

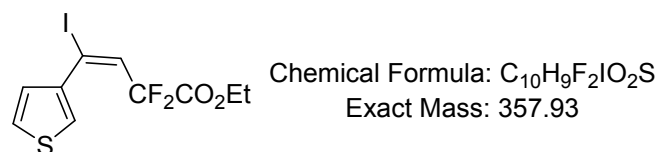


Compound **A26**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A26** (37.4 mg, 51%), green liquid (E/Z = 96:4, the ratio detected by ¹⁹F NMR). ¹H NMR (500 MHz, CDCl₃) δ 7.08 (t, J = 7.8 Hz, 1H), 6.71-6.65 (m, 2H), 6.62- 6.54 (m, 2H), 3.96 (q, J = 7.2 Hz, 2H), 3.31 (s, 2H), 1.20 (t, J = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) 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; ¹⁹F NMR (470 MHz, CDCl₃) δ -93.08. GC-MS (EI) Calcd. for C₁₂H₁₂F₂INO₂ 366.99, HRMS (EI⁺) found 366.9882.

Z Product: ¹⁹F NMR (470 MHz, CDCl₃) δ , -97.91.

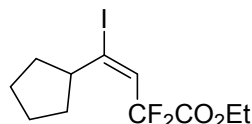


Compound **A27**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A27** (40.9, 58%), yellow liquid. ¹H NMR (500 MHz, CDCl₃) δ 8.37-8.17 (m, 2H), 7.33 (dt, J = 8.0, 1.9 Hz, 1H), 7.04-6.91 (m, 1H), 6.53 (t, J = 11.6 Hz, 1H), 3.85 (d, J = 7.2 Hz, 2H), 0.98 (t, J = 7.2 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) 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; ¹⁹F NMR (470 MHz, CDCl₃) δ -95.44. GC-MS (EI) Calcd. for C₁₁H₁₀F₂INO₂ 352.97, HRMS (EI⁺) found 352.9722.



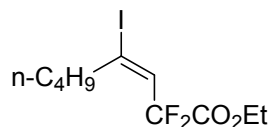
Compound **A28**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A28** (33.7mg, 47%), yellow liquid (E/Z = 94:6, the ratio detected by ¹⁹F NMR). ¹H NMR (500 MHz, CDCl₃) δ 7.40 (dd, J = 3.0, 1.3 Hz, 1H), 7.28 (dd, J = 5.1, 3.0 Hz, 1H), 7.09 (dd, J = 5.0, 1.4 Hz, 1H), 6.68 (s, 1H), 4.01 (d, J = 7.2 Hz, 2H), 1.19 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) 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; ¹⁹F NMR (470 MHz, CDCl₃) δ -92.47. GC-MS (EI) Calcd. for C₁₀H₉F₂IO₂S 357.93, HRMS (EI⁺) found 357.9342.

Z Product: ¹⁹F NMR (470 MHz, CDCl₃) δ , -97.20.



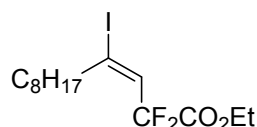
Chemical Formula: $C_{11}H_{15}F_2IO_2$
Exact Mass: 344.01

Compound **A29**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A29** (29.6 mg, 43%), colorless liquid. 1H 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.



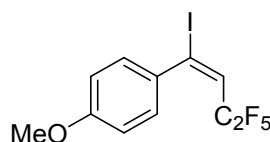
Chemical Formula: $C_{10}H_{15}F_2IO_2$
Exact Mass: 332.01

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. 1H 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 $C_{10}H_{15}F_2IO_2$ 332.01, found 332.05.



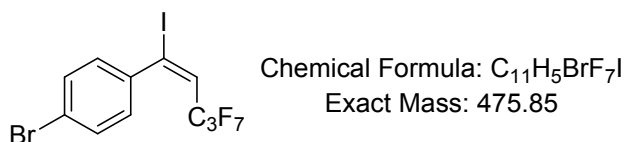
Chemical Formula: $C_{14}H_{23}F_2IO_2$
Exact Mass: 388.07

Compound **A31**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford the **A31** (31.8 mg, 41%), colorless liquid. 1H 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.

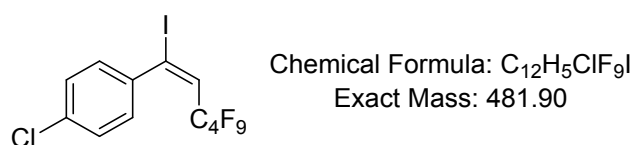


Chemical Formula: $C_{11}H_8F_5IO$
Exact Mass: 377.95

Compound **A32**: purified by column chromatography on silica gel (petroleum ether/EtOAc = 40:1) to afford the **A32** (59.7 mg, 79%), yellow liquid. 1H 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.

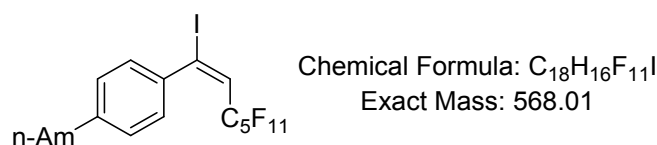


Compound **A33**: purified by column chromatography on silica gel (petroleum ether) to afford the **A33** (50.4 mg, 53%), yellow liquid. 1H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.2 Hz, 2H), 6.65-6.55 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.12, 130.28, 127.40, 126.43 (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.

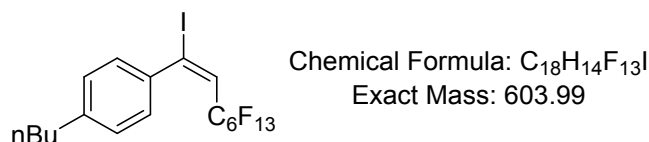


Compound **A34**: purified by column chromatography on silica gel (petroleum ether) to afford the **A34** (70.4 mg, 73%), yellow liquid (E/Z = 81:19, the ratio detected by 1H NMR). 1H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 8.6 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 6.61 (t, J = 13.4 Hz, 1H); ^{13}C NMR (126 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: 1H 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).

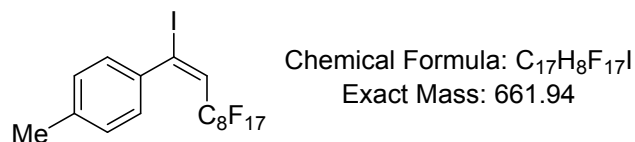


Compound **A35**: purified by column chromatography on silica gel (petroleum ether) to afford the **A35** (73.8 mg, 65%), yellow liquid. 1H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, J = 7.8 Hz, 2H), 7.13 (d, J = 7.9 Hz, 2H), 6.57 (t, J = 13.5 Hz, 1H), 2.64-2.55 (m, 2H), 1.62 (p, J = 7.3 Hz, 2H), 1.33 (dh, J = 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.



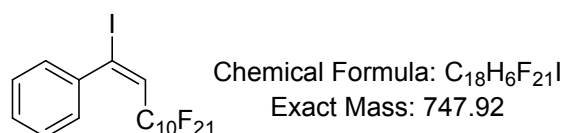
Compound **A36**: purified by column chromatography on silica gel (petroleum ether) to afford the **A36** (73.7 mg, 61%), yellow liquid. 1H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, J = 8.2 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 6.59 (t, J = 13.5 Hz, 1H), 2.66-2.59 (m, 2H), 1.67-1.58 (m, 2H), 1.39 (dt, J = 15.0, 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 $\text{C}_{18}\text{H}_{14}\text{F}_{13}\text{I}$ 603.99, HRMS (EI^+) found 603.9938.

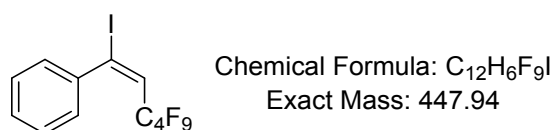


Compound **A37**: purified by column chromatography on silica gel (petroleum ether) to afford the **A37** (54.3 mg, 41%), yellow liquid. ^1H NMR (500 MHz, CDCl_3) δ 7.20 (d, $J = 7.9$ Hz, 1H), 7.13 (d, $J = 7.9$ Hz, 1H), 6.57 (t, $J = 13.5$ Hz, 0H), 2.35 (s, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 139.61, 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 $\text{C}_{17}\text{H}_8\text{F}_{17}\text{I}$ 661.94, found 661.74.

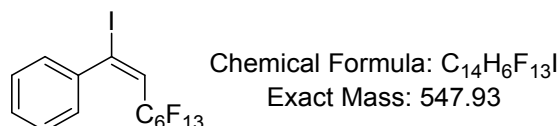
Z product: ^1H NMR (500 MHz, CDCl_3) δ 7.38 (d, $J = 7.9$ Hz, 1H), 7.16 (s, 0H), 6.49 (t, $J = 13.3$ Hz, 0H), 2.38 (s, 2H).



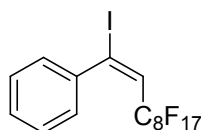
Compound **A38**: purified by column chromatography on silica gel (petroleum ether) to afford the **A38** (55.4 mg, 37%), white solid. ^1H NMR (500 MHz, CDCl_3) δ 7.35-7.27 (m, 5H), 6.59 (t, $J = 13.5$ Hz, 1H); ^{13}C NMR (126 MHz, CDCl_3) δ 141.47, 139.77, 134.71-130.89 (m), 130.21, 129.31, 129.00, 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 $\text{C}_{18}\text{H}_6\text{F}_{21}\text{I}$ 747.92, found 746.96.



Compound **A39**⁴: purified by column chromatography on silica gel (petroleum ether) to afford the **A-39** (48.4 mg, 54%), colorless liquid. ^1H 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 $\text{C}_{12}\text{H}_6\text{F}_9\text{I}$ 447.94, found 448.12.

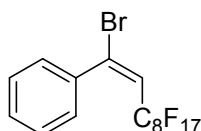


Compound **A40**⁵: purified by column chromatography on silica gel (petroleum ether) to afford the **A40** (44.9 mg, 41%), colorless liquid. ¹H NMR (500 MHz, CDCl₃) δ 7.28-7.20 (m, 5H), 6.52 (t, *J* = 13.5 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 141.43, 130.30, 129.38, 128.48 (d, *J* = 40.1 Hz), 128.10, 127.19 (d, *J* = 22.0 Hz), 126.93; ¹⁹F NMR (470 MHz, CDCl₃) 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 C₁₄H₆F₁₃I 547.93, found 548.07.



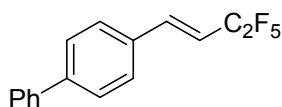
Chemical Formula: C₁₆H₆F₁₇I
Exact Mass: 647.92

Compound **A41**⁶: purified by column chromatography on silica gel (petroleum ether) to afford the **A41** (51.8 mg, 40%), colorless liquid. ¹H NMR (500 MHz, CDCl₃) δ 7.36-7.27 (m, 5H), 6.60 (t, *J* = 13.5 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 141.43, 129.38, 128.10, 127.12, 126.93, 112.79; ¹⁹F NMR (470 MHz, CDCl₃) 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 C₁₆H₆F₁₇I 647.92, found 647.92.



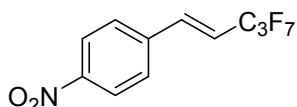
Chemical Formula: C₁₆H₆BrF₁₇
Exact Mass: 599.94

Compound **A42**: purified by column chromatography on silica gel (petroleum ether) to afford the **A42** (34.8 mg, 29%), colorless liquid. ¹H NMR (500 MHz, CDCl₃) δ 7.37 (dd, *J* = 7.0, 3.6 Hz, 5H), 6.39 (t, *J* = 13.5 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 137.56 (d, *J* = 32.0 Hz), 129.94, 128.19, 127.87, 126.94, 119.42 (t, *J* = 22.4 Hz); ¹⁹F NMR (470 MHz, CDCl₃) 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 C₁₆H₆BrF₁₇ 599.94, found 600.06.



Chemical Formula: C₁₆H₁₁F₅
Exact Mass: 298.08

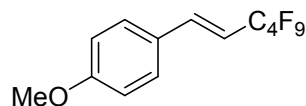
Compound **B1**: purified by column chromatography on silica gel (petroleum ether) to afford the **B1** (23.2 mg, 39%), yellow liquid. ¹H NMR (500 MHz, CDCl₃) δ 7.66-7.58 (m, 4H), 7.58-7.51 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.38 (dd, *J* = 8.4, 6.4 Hz, 1H), 7.20 (d, *J* = 16.7 Hz, 1H), 6.21 (dt, *J* = 16.1, 11.8 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) 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); ¹⁹F NMR (470 MHz, CDCl₃) δ -85.00, -114.77 (d, *J* = 2.6 Hz). GC-MS (EI) Calcd. for C₁₆H₁₁F₅ 298.08, HRMS (EI⁺) found 298.0785.



Chemical Formula: C₁₁H₆F₇NO₂
Exact Mass: 317.03

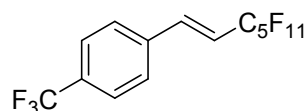
Compound **B2**: purified by column chromatography on silica gel (petroleum ether) to afford the **B2** (19.7 mg, 31%), colorless liquid. ¹H NMR (500 MHz, CDCl₃) δ 8.28 (d, *J* = 8.7 Hz, 2H), 7.65 (d, *J* =

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 $\text{C}_{11}\text{H}_6\text{F}_7\text{NO}_2$ 317.03, HRMS (EI^+) found 317.0284.



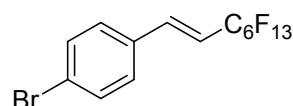
Chemical Formula: $\text{C}_{13}\text{H}_9\text{F}_9\text{O}$
Exact Mass: 352.05

Compound **B3**⁷: purified by column chromatography on silica gel (petroleum ether) to afford the **B3** (31.7 mg, 45%), yellow liquid. ^1H 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 $\text{C}_{13}\text{H}_9\text{F}_9\text{O}$ 352.05, found 352.05.



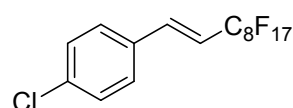
Chemical Formula: $\text{C}_{14}\text{H}_6\text{F}_{14}$
Exact Mass: 440.02

Compound **B4**: purified by column chromatography on silica gel (petroleum ether) to afford the **B4** (25.5 mg, 29%), yellow liquid. ^1H 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 $\text{C}_{14}\text{H}_6\text{F}_{14}$ 440.02, HRMS (EI^+) found 440.0253.



Chemical Formula: $\text{C}_{14}\text{H}_6\text{BrF}_{13}$
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. ^1H 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 $\text{C}_{14}\text{H}_6\text{BrF}_{13}$ 499.94, found 499.95.

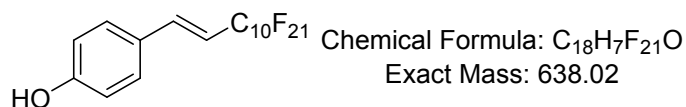


Chemical Formula: $\text{C}_{16}\text{H}_6\text{ClF}_{17}$
Exact Mass: 555.99

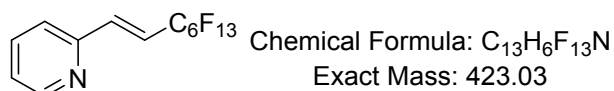
Compound **B6**: purified by column chromatography on silica gel (petroleum ether) to afford the **B6** (42.2 mg, 38%), yellow liquid ($E/Z = 86:14$, the ratio detected by ^1H NMR). ^1H NMR (500 MHz, CDCl_3) δ 7.40 (q, $J = 8.7$ Hz, 4H), 7.13 (d, $J = 16.1$ Hz, 1H), 6.18 (dt, $J = 16.2, 12.0$ Hz, 1H); ^{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, CDCl₃) 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 C₁₄H₆BrF₁₃ 555.99, HRMS (EI⁺) found 555.9883.

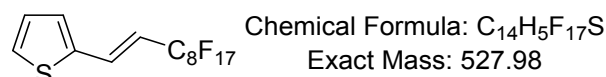
Z Product: ¹H NMR (500 MHz, CDCl₃) δ 7.35-7.28 (m, 4H), 7.07 (d, J = 12.8 Hz, 1H), 5.77 (q, J = 15.2 Hz, 1H).



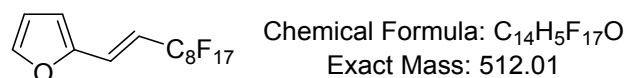
Compound **B7**: purified by column chromatography on silica gel (petroleum ether) to afford the **B7** (24.2 mg, 19%), yellow solid. ¹H NMR (500 MHz, MeOD) δ 7.42-7.31 (m, 2H), 7.07 (dd, J = 16.0, 8.9 Hz, 1H), 6.81-6.73 (m, 2H), 6.52 (s, 1H), 6.19-6.03 (m, 1H); ¹³C NMR (126 MHz, MeOD) δ 158.46, 138.75, 128.10, 123.88, 114.34, 108.70 (t, J = 36.5 Hz); ¹⁹F 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 C₁₈H₇F₂₁O 638.02, HRMS (EI⁺) found 638.0159.



Compound **B8**: purified by column chromatography on silica gel (petroleum ether) to afford the **B8** (34.7 mg, 41%), yellow liquid. ¹H NMR (500 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) δ 150.68, 149.11, 137.56, 135.88, 123.33, 123.09, 117.73 (t, J = 22.9 Hz); ¹⁹F NMR (470 MHz, CDCl₃) 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 C₁₃H₆F₁₃N 423.03, HRMS (EI⁺) found 423.0297.

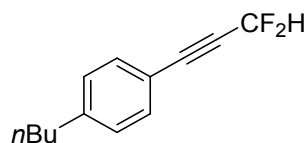


Compound **B9**: purified by column chromatography on silica gel (petroleum ether) to afford the **B9** (33.8 mg, 32%), yellow liquid. ¹H NMR (500 MHz, CDCl₃) δ 7.38 (d, J = 5.0 Hz, 1H), 7.27 (dt, J = 15.6 Hz, 1H), 7.21 (d, J = 3.6 Hz, 1H), 7.05 (dd, J = 5.1, 3.6 Hz, 1H), 6.00 (dt, J = 15.9, 12.3 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 138.39, 132.57, 130.36, 128.16, 128.09, 112.96 (t, J = 22.8 Hz); ¹⁹F NMR (470 MHz, CDCl₃) 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 C₁₄H₅F₁₇S 527.98, found 528.01.



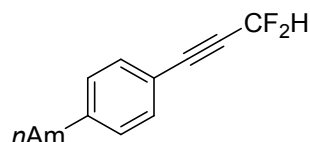
Compound **B10**: purified by column chromatography on silica gel (petroleum ether) to afford the **B10** (36.9 mg, 36%), yellow liquid. ¹H NMR (500 MHz, CDCl₃) δ 7.47 (d, J = 1.7 Hz, 1H), 6.93 (d, J = 15.9 Hz, 1H), 6.58-6.42 (m, 2H), 6.13 (dt, J = 16.0, 12.9 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 151.41, 148.64, 143.43, 125.62, 112.85, 111.08 (t, J = 39.7 Hz); ¹⁹F NMR (470 MHz, CDCl₃) 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.



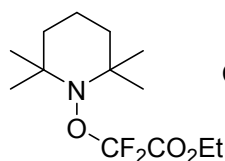
Chemical Formula: $C_{13}H_{14}F_2$
Exact Mass: 208.11

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. 1H 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.



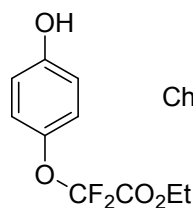
Chemical Formula: $C_{14}H_{16}F_2$
Exact Mass: 222.12

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. 1H 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. 1H 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.



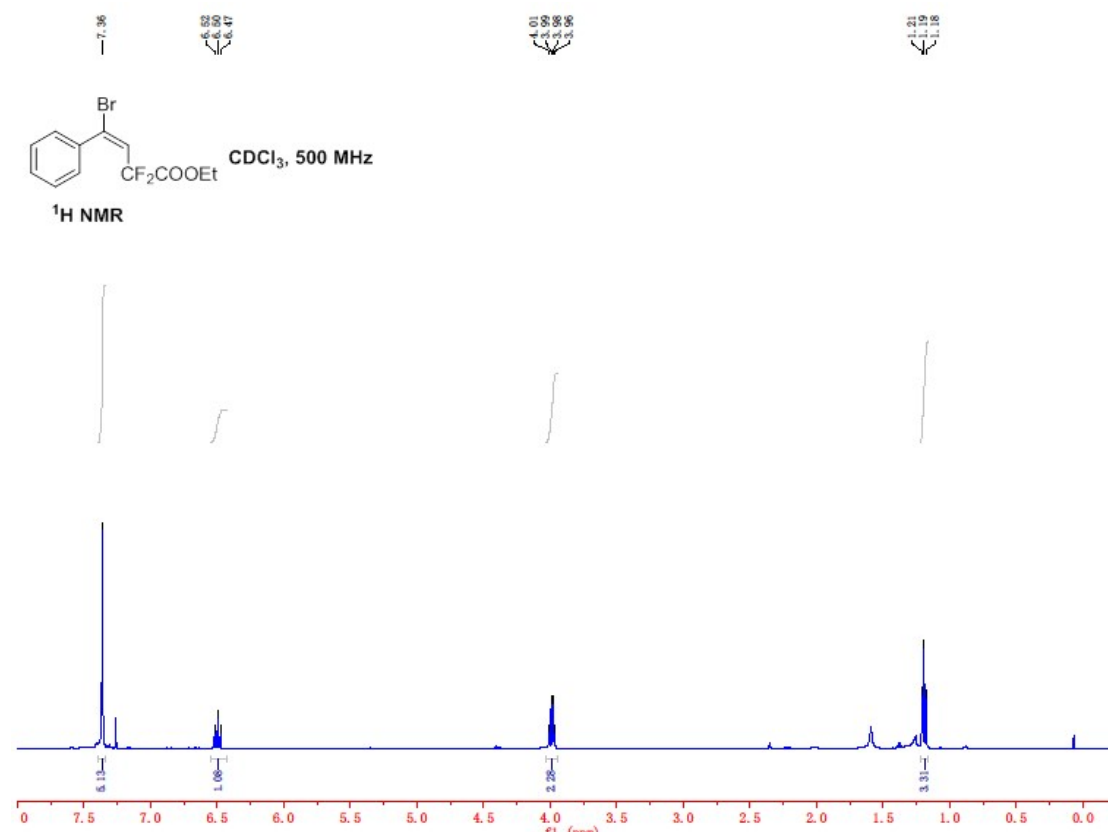
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Exact Mass: 232.05

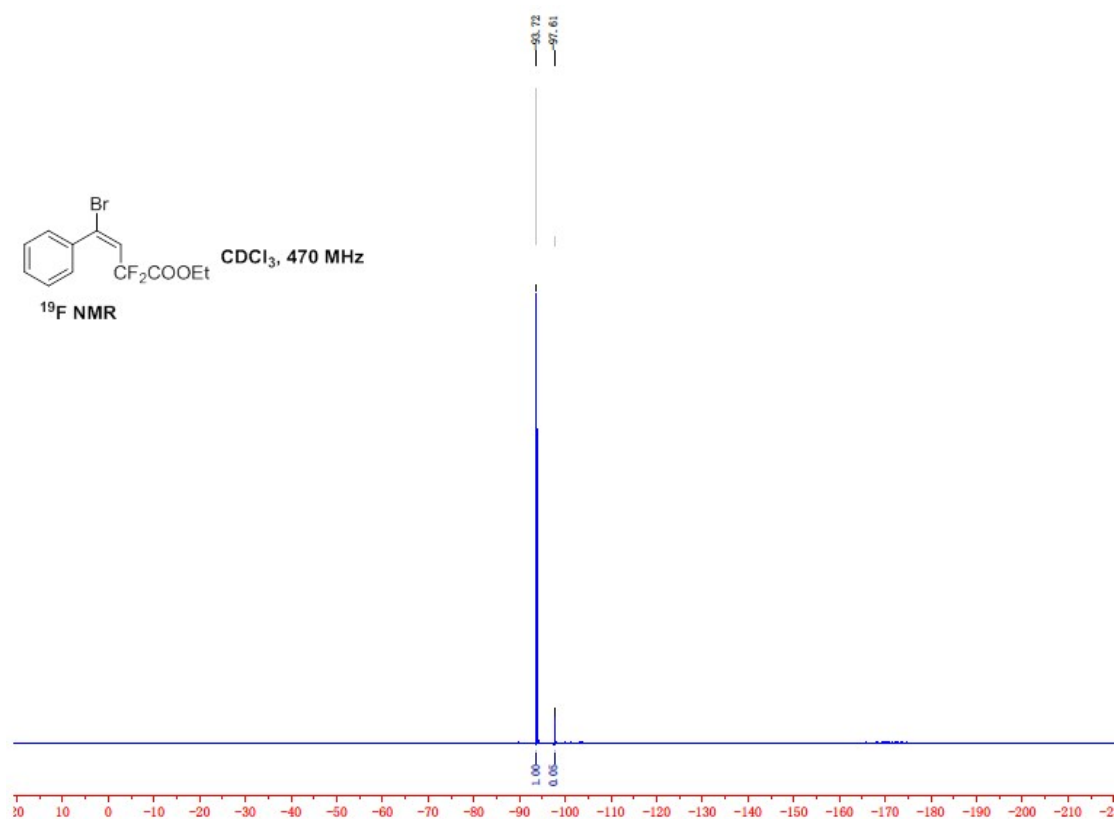
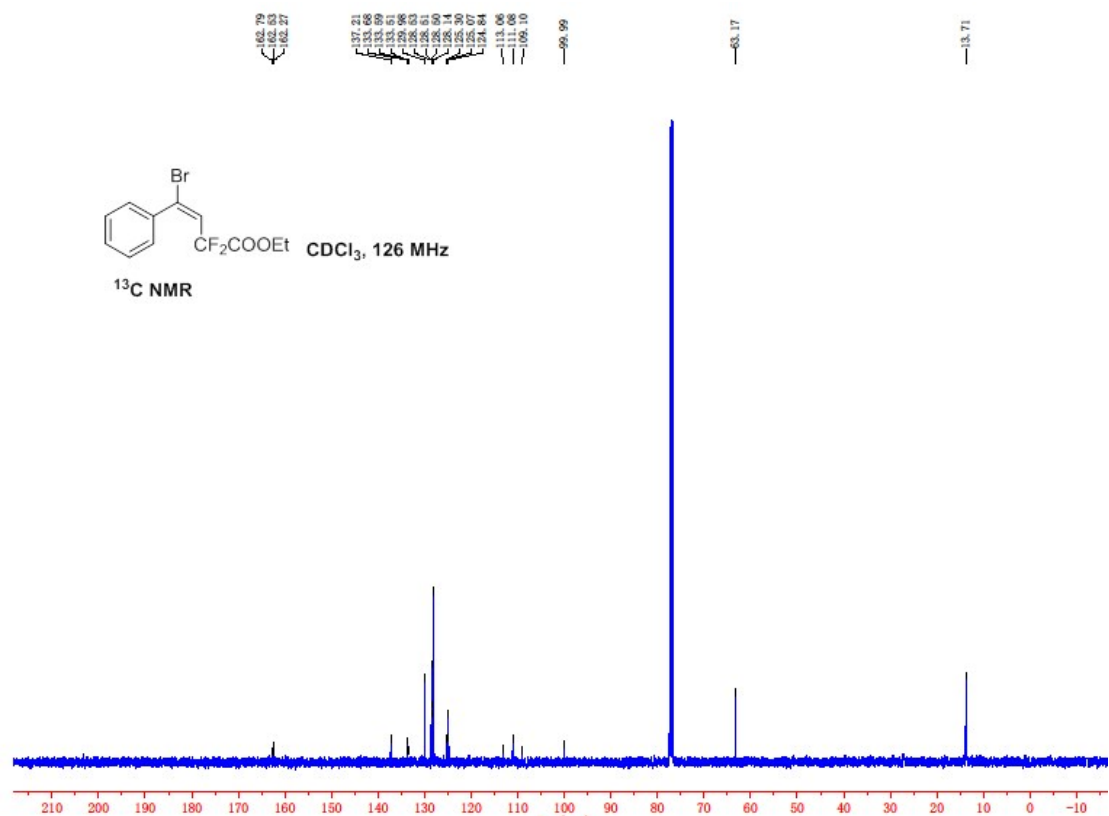
Compound (**6**): purified by column chromatography on silica gel (petroleum ether/EtOAc = 30:1) to afford the **6**, brown liquid. ^1H NMR (500 MHz, CDCl_3) δ 7.09 (d, J = 8.5 Hz, 2H), 6.87-6.76 (m, 2H), 4.38 (q, J = 7.2 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 187.34, 136.68, 123.41, 116.11, 63.73, 13.98; ^{19}F NMR (470 MHz, CDCl_3) δ -75.58. GC-MS (EI) Calcd. for $\text{C}_{10}\text{H}_{10}\text{F}_2\text{O}_4$ 232.05, found 232.07.

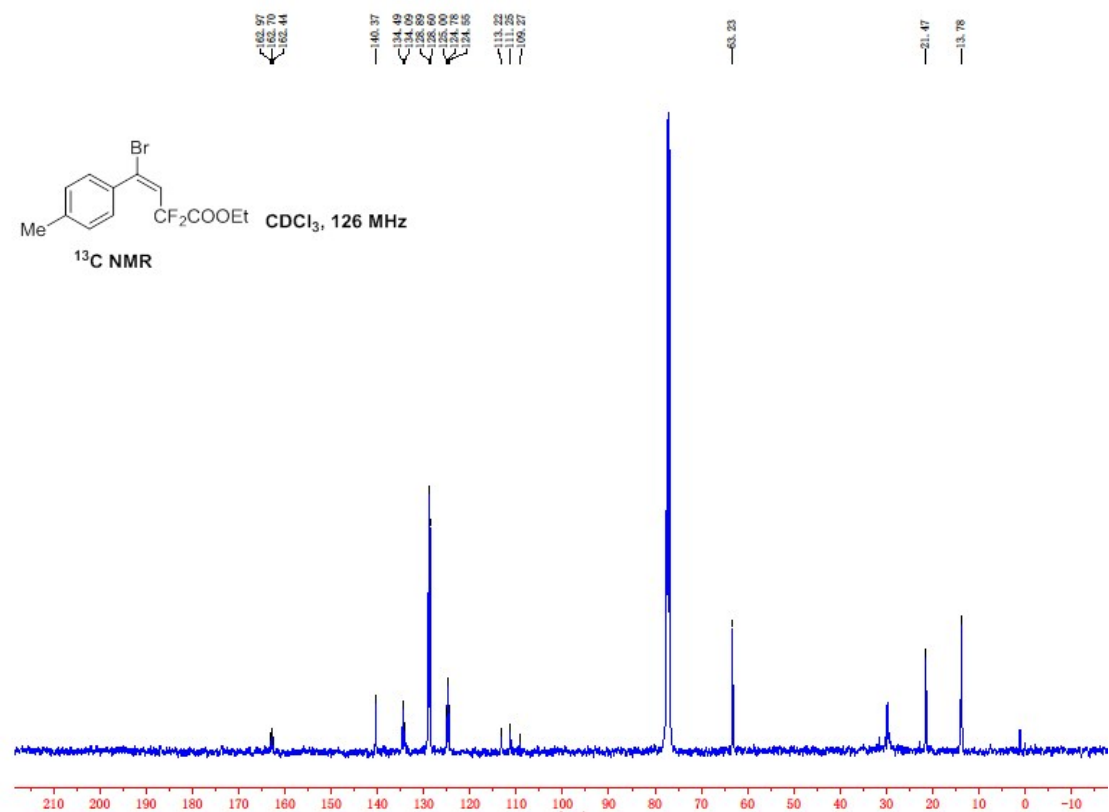
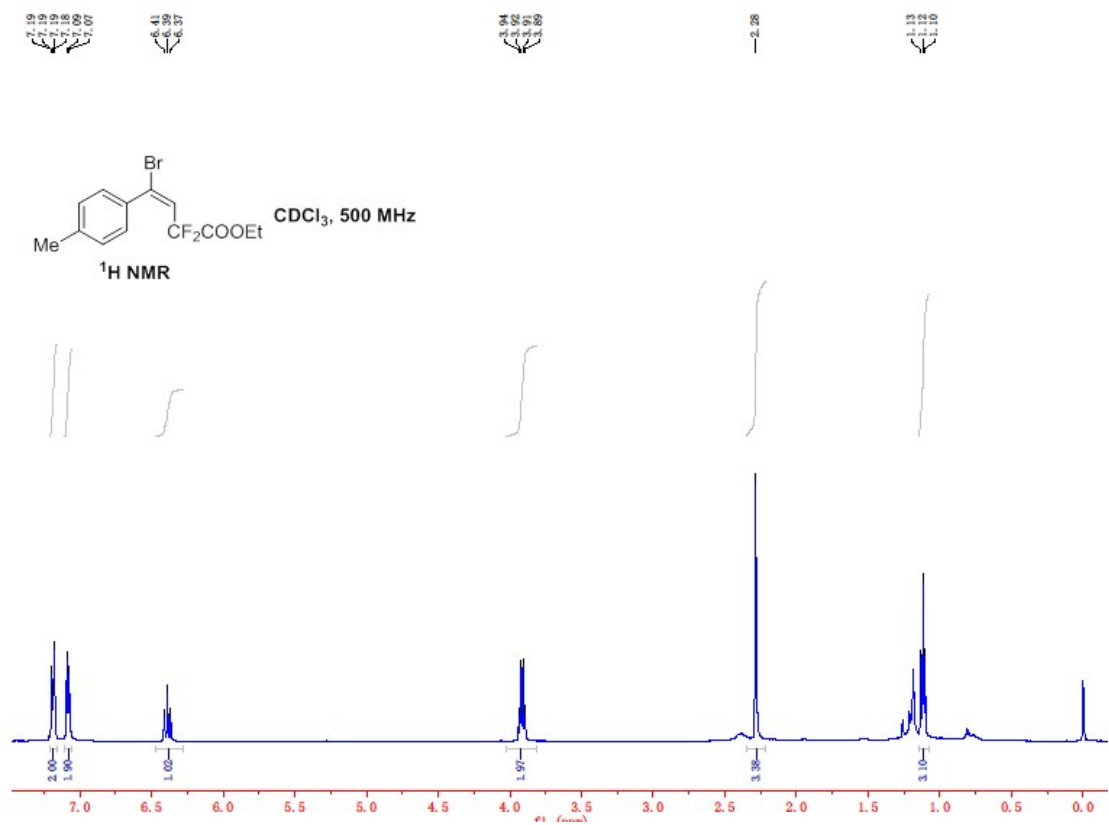
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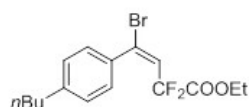
- [1] M.-C. Belhomme, D. Dru, H.-Y. Xiong, D. Cahard, T. Besset, T. Poisson and X. Pannecoucke, *Synthesis*, 2014, **46**, 1859-1870.
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- [4] M. P. Jennings, E. A. Cork and P. V. Ramachandran, *J. Org. Chem.* 2000, **65**, 8763-8766
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6. NMR Spectra of compounds.

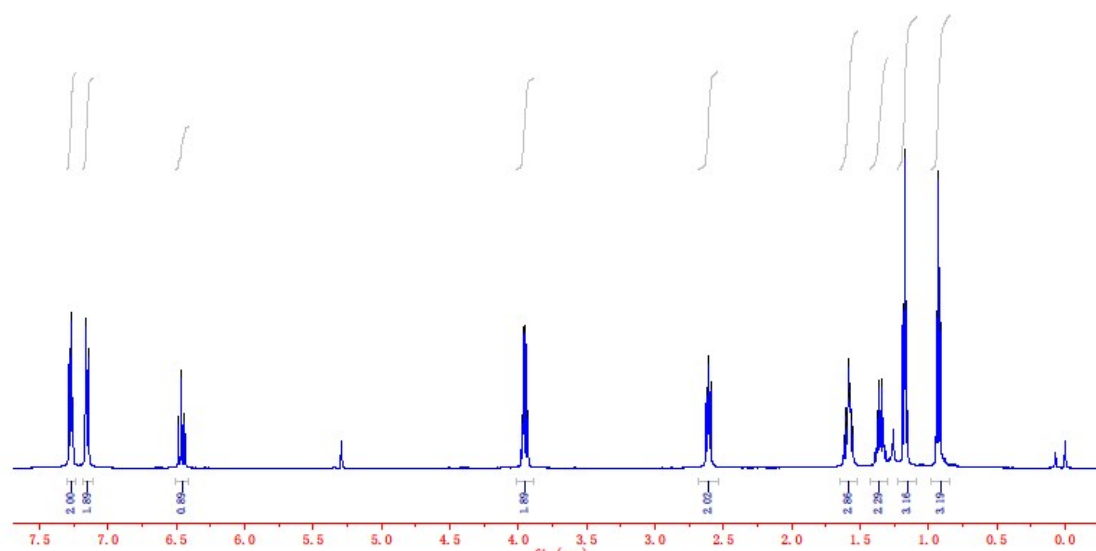


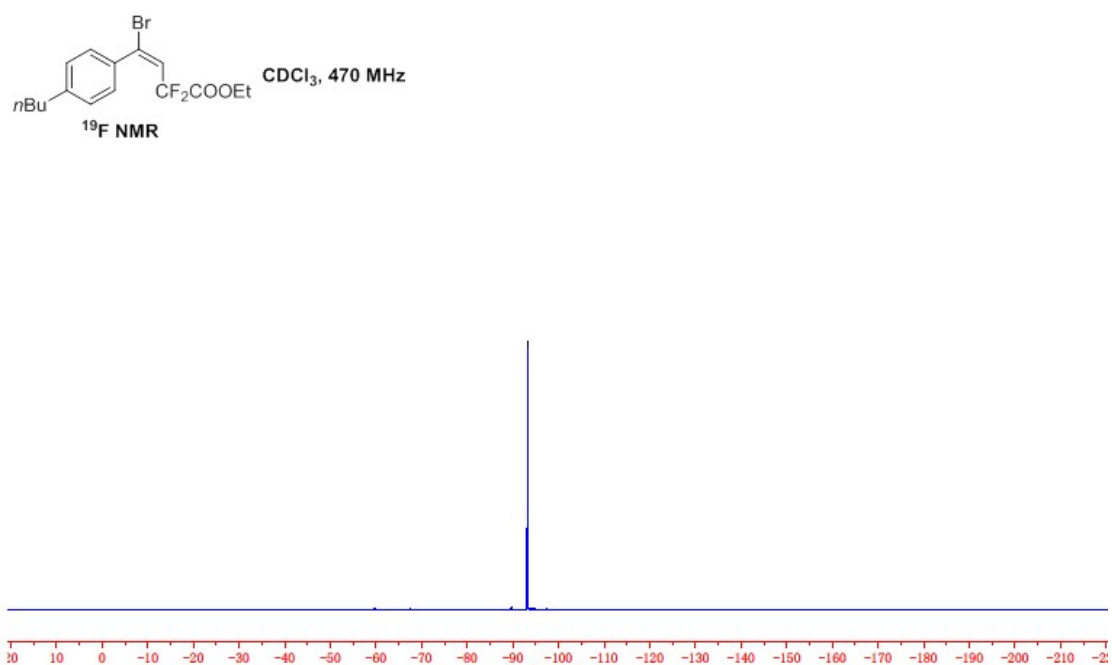
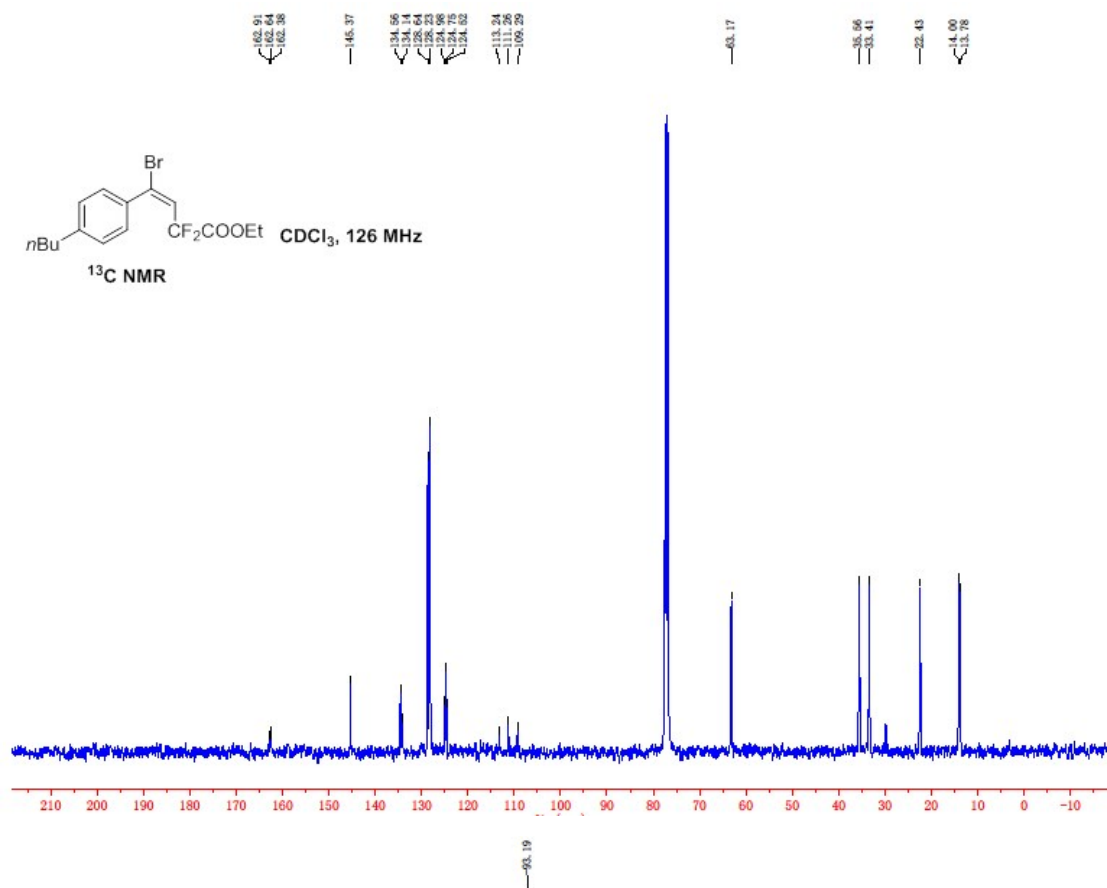


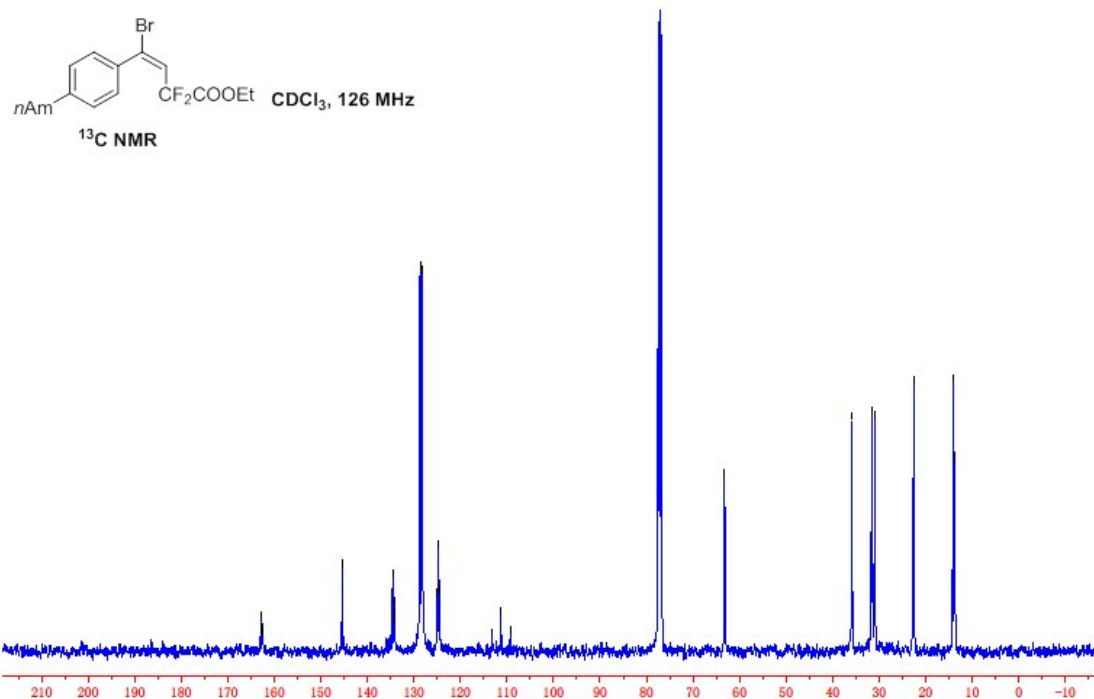
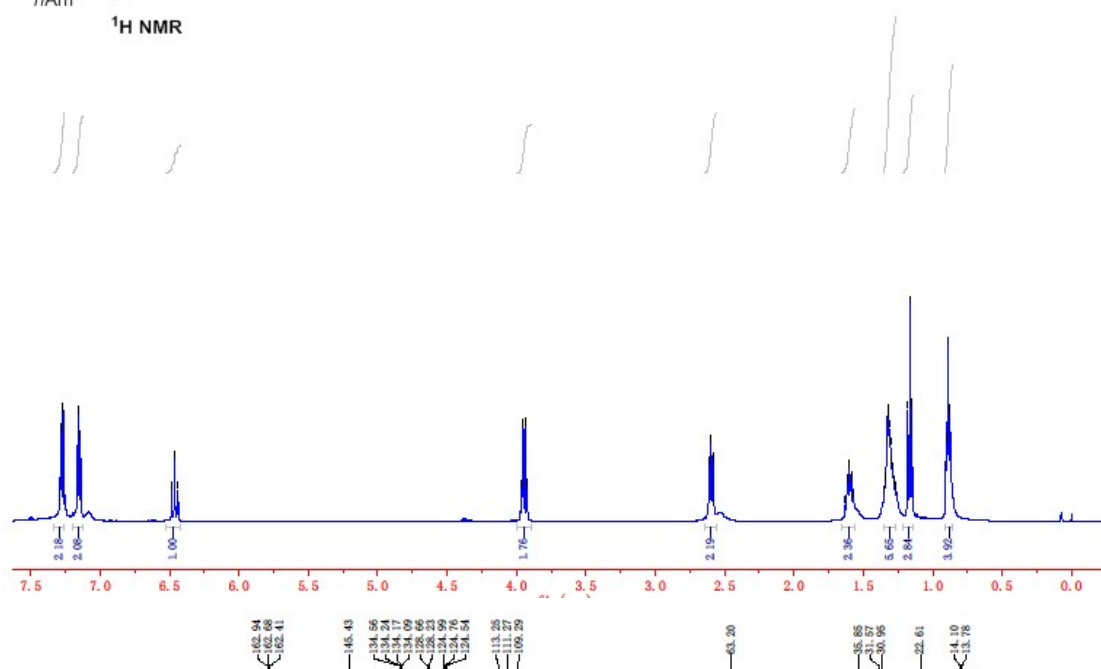


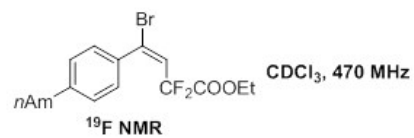
¹⁹F NMR

CDCl₃, 500 MHz

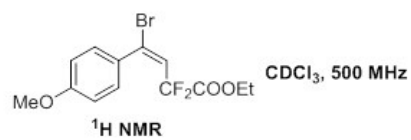
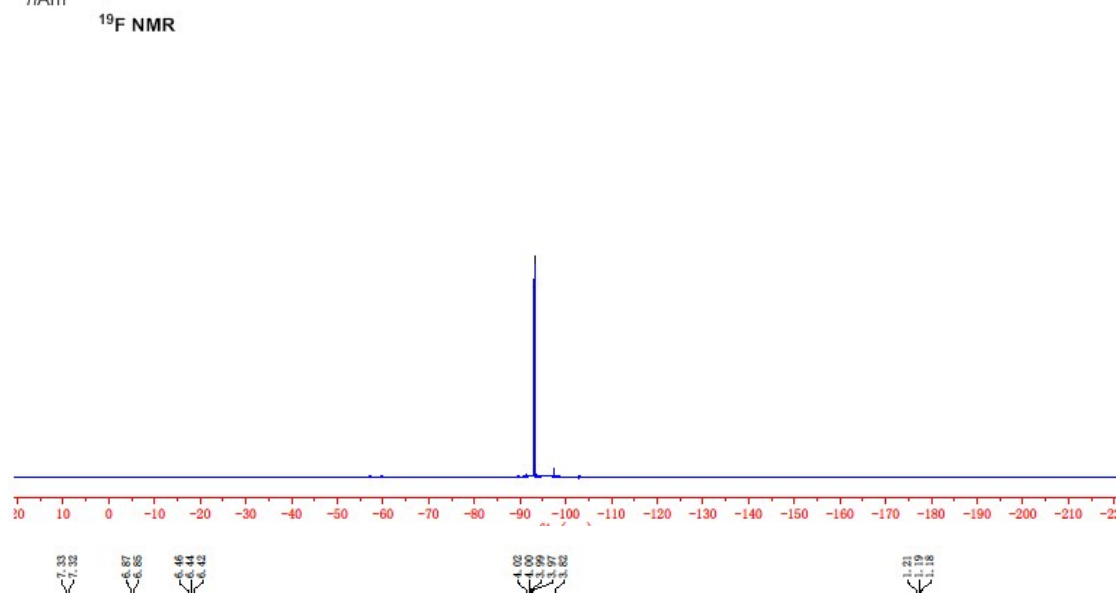
¹H NMR



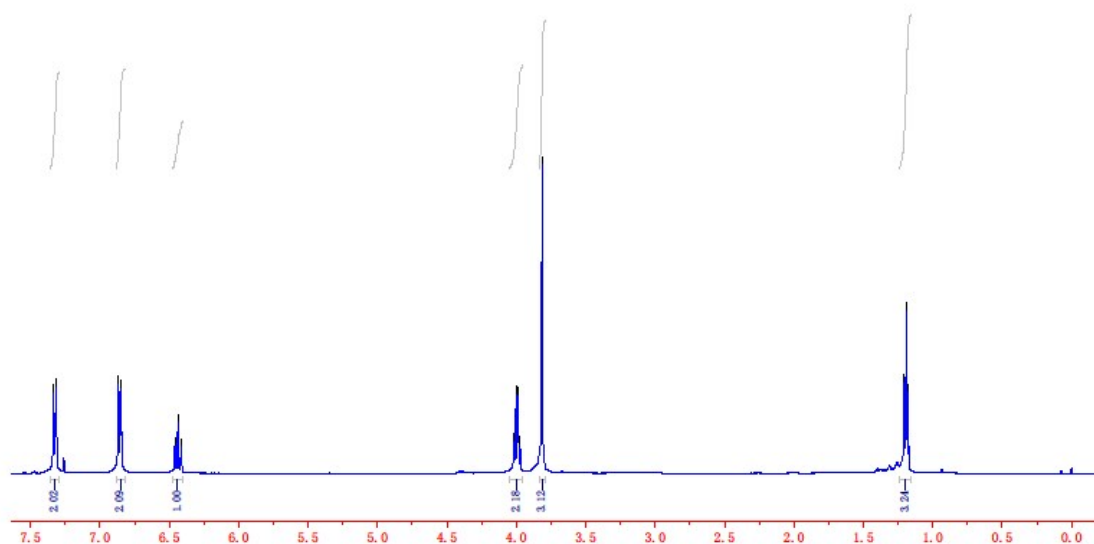


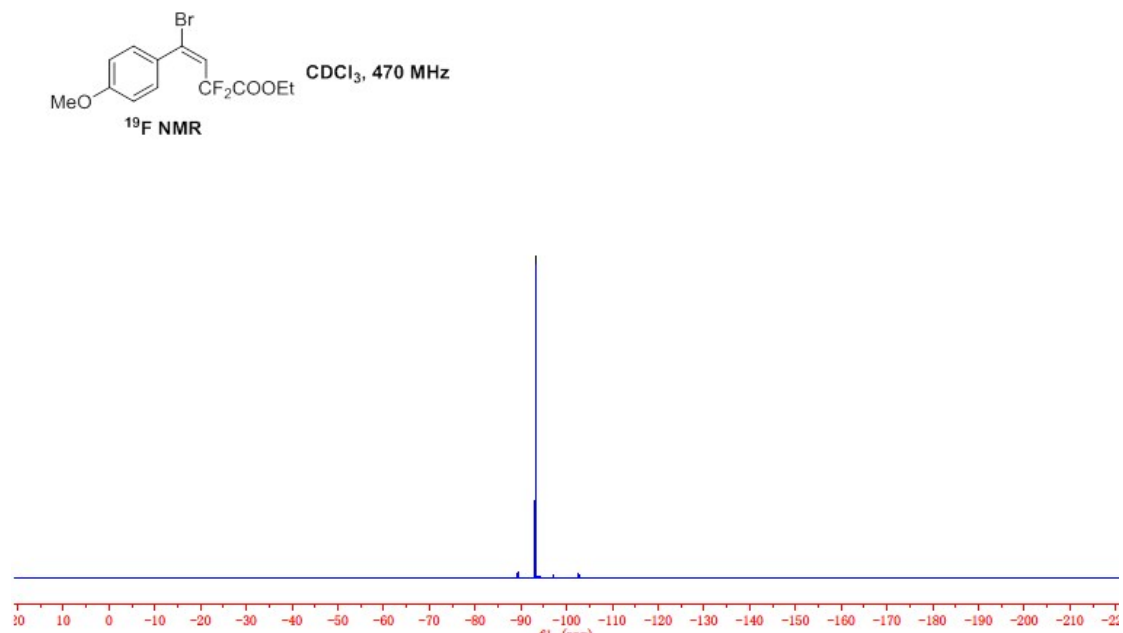
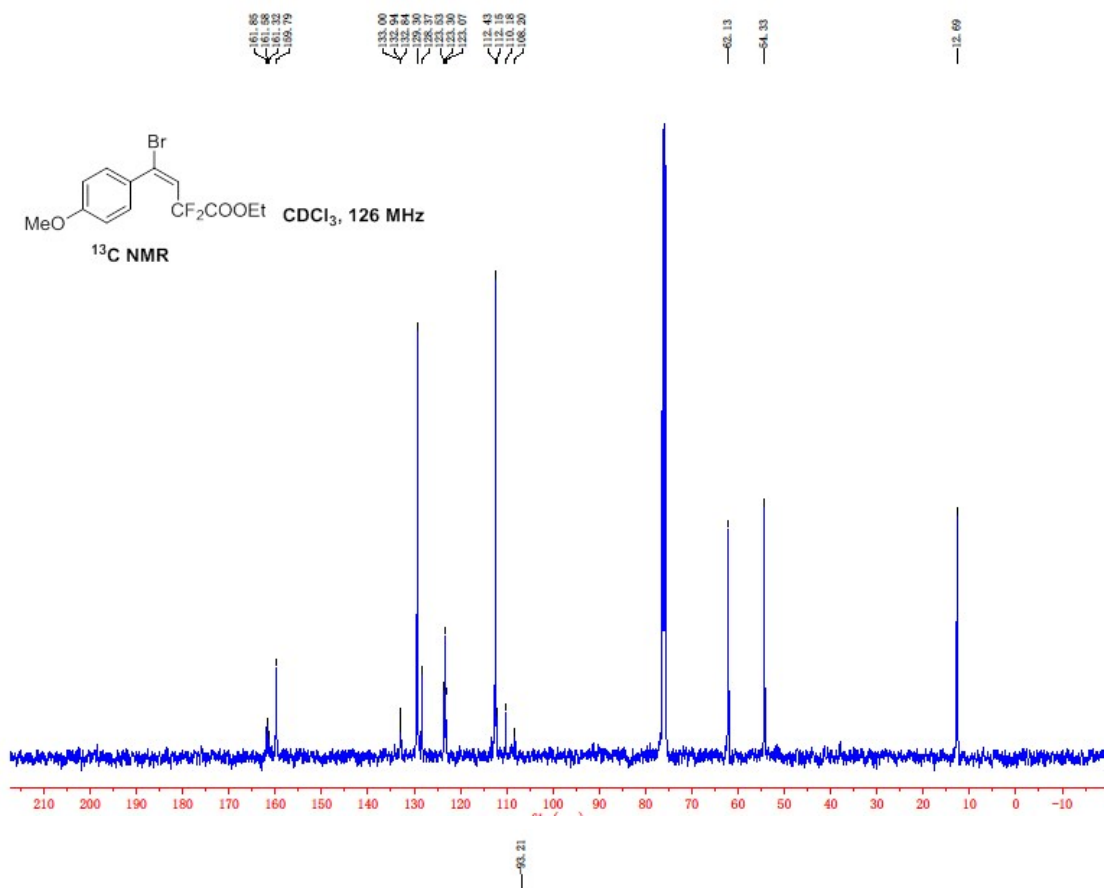


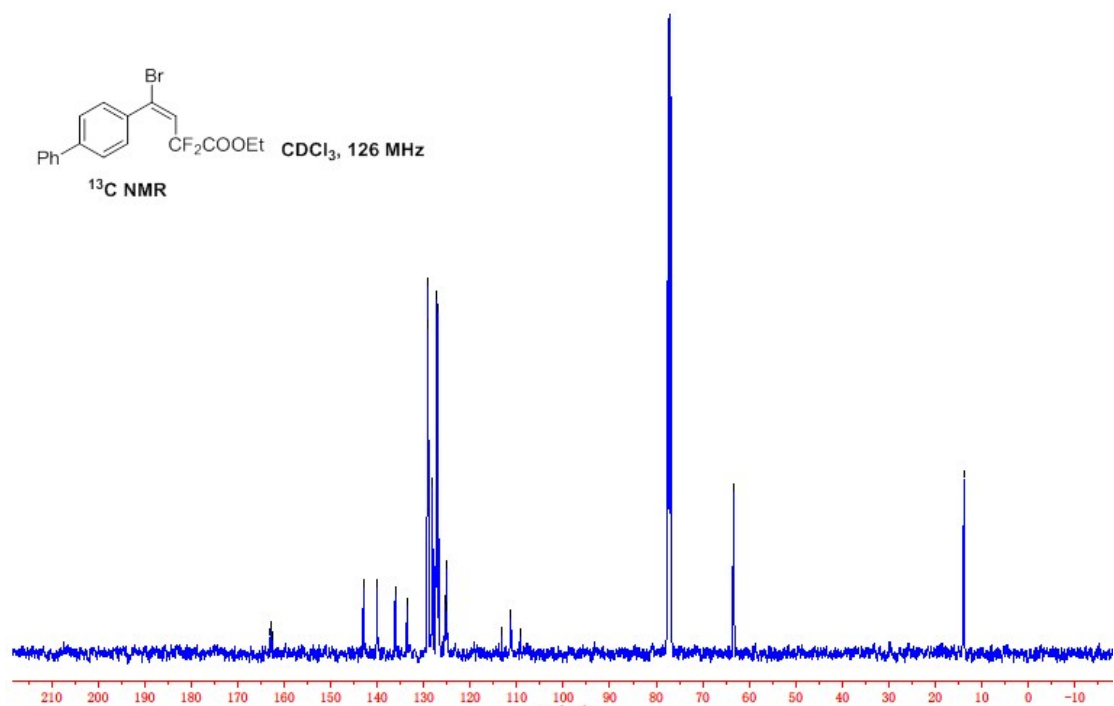
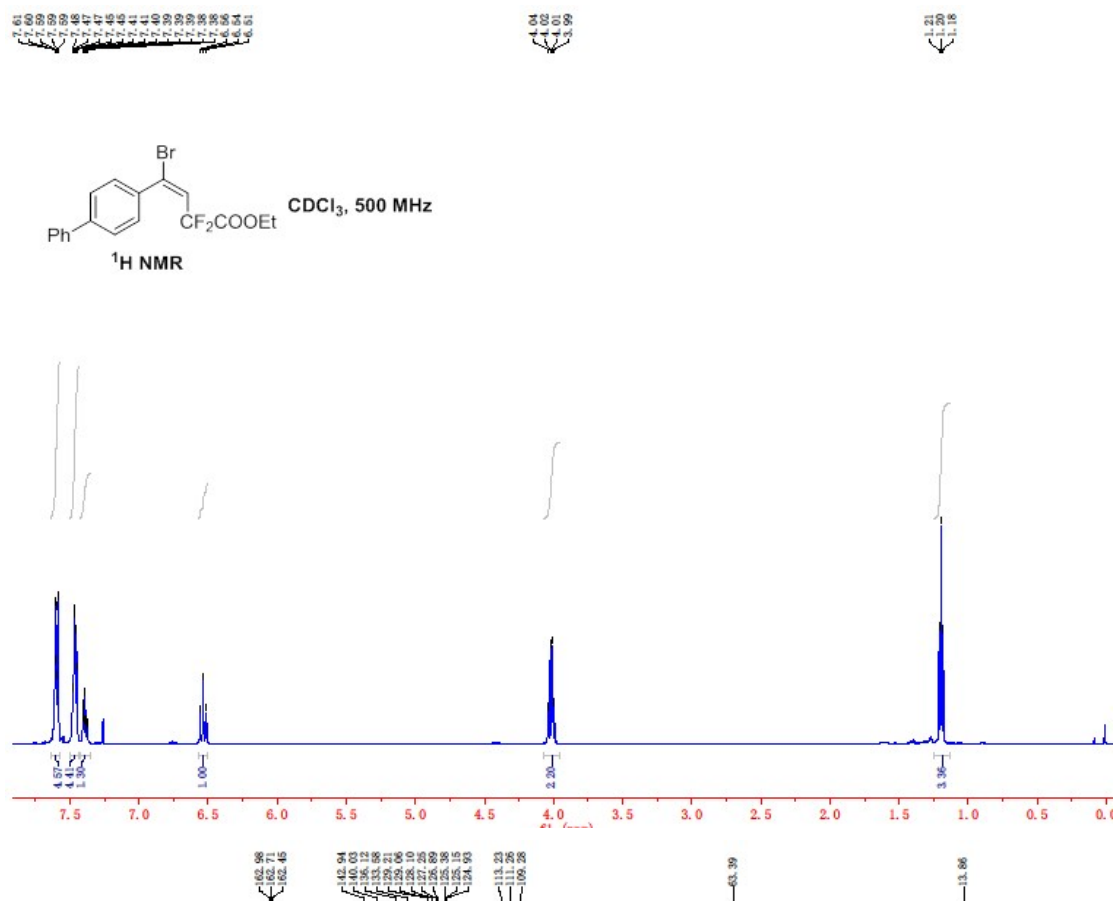
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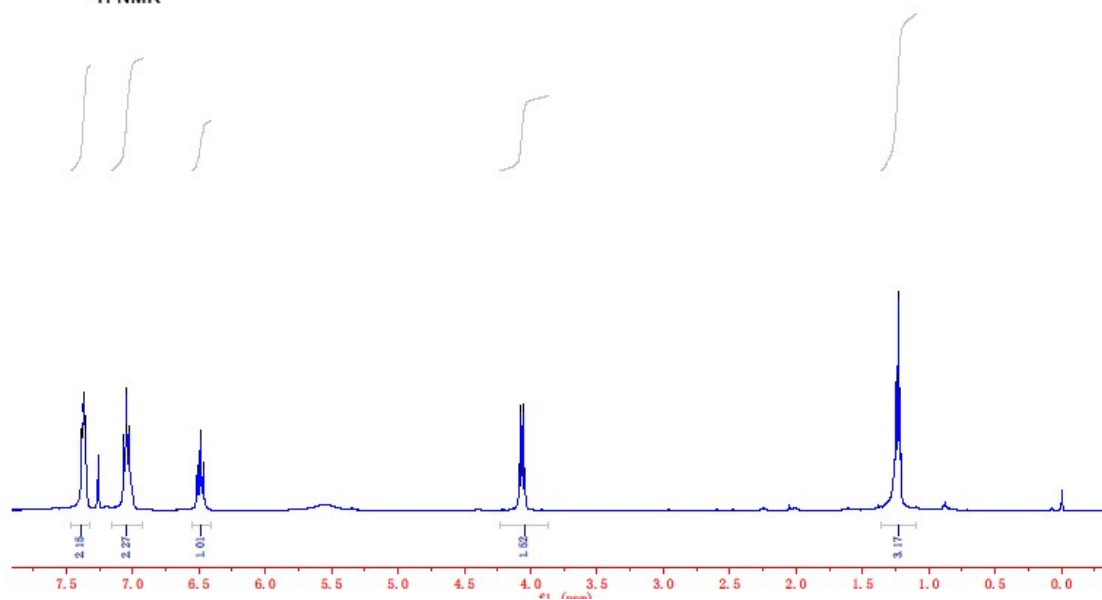
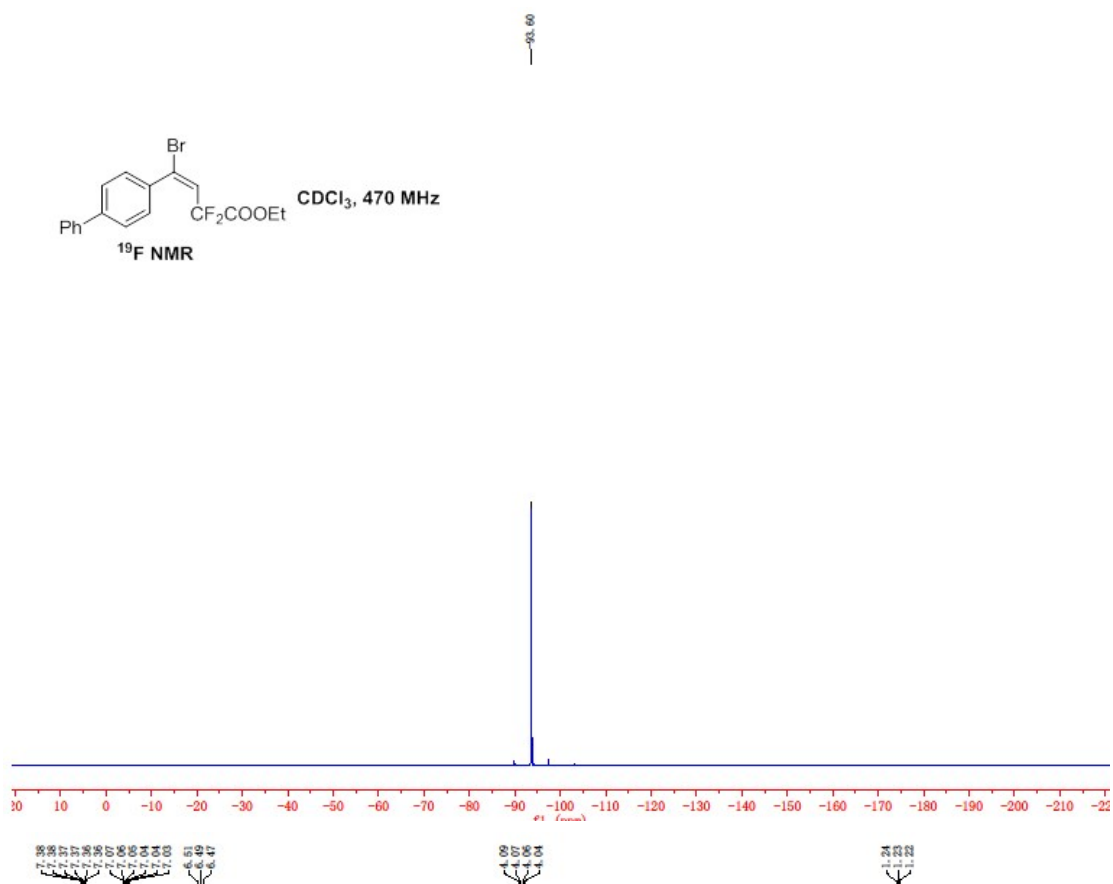


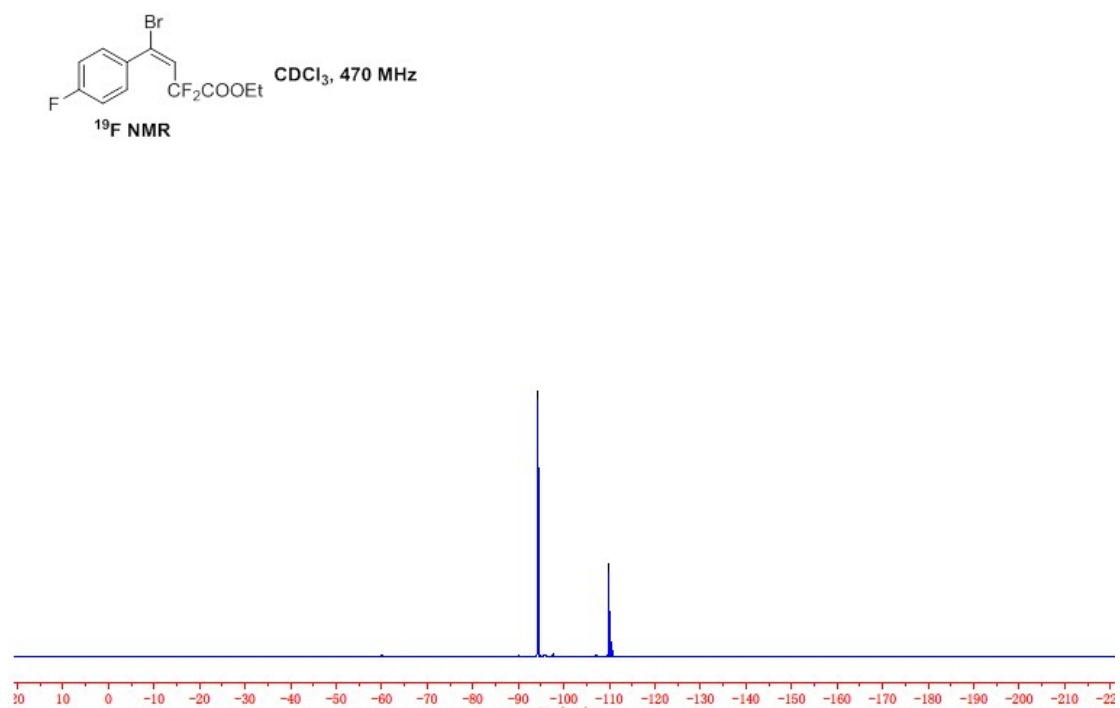
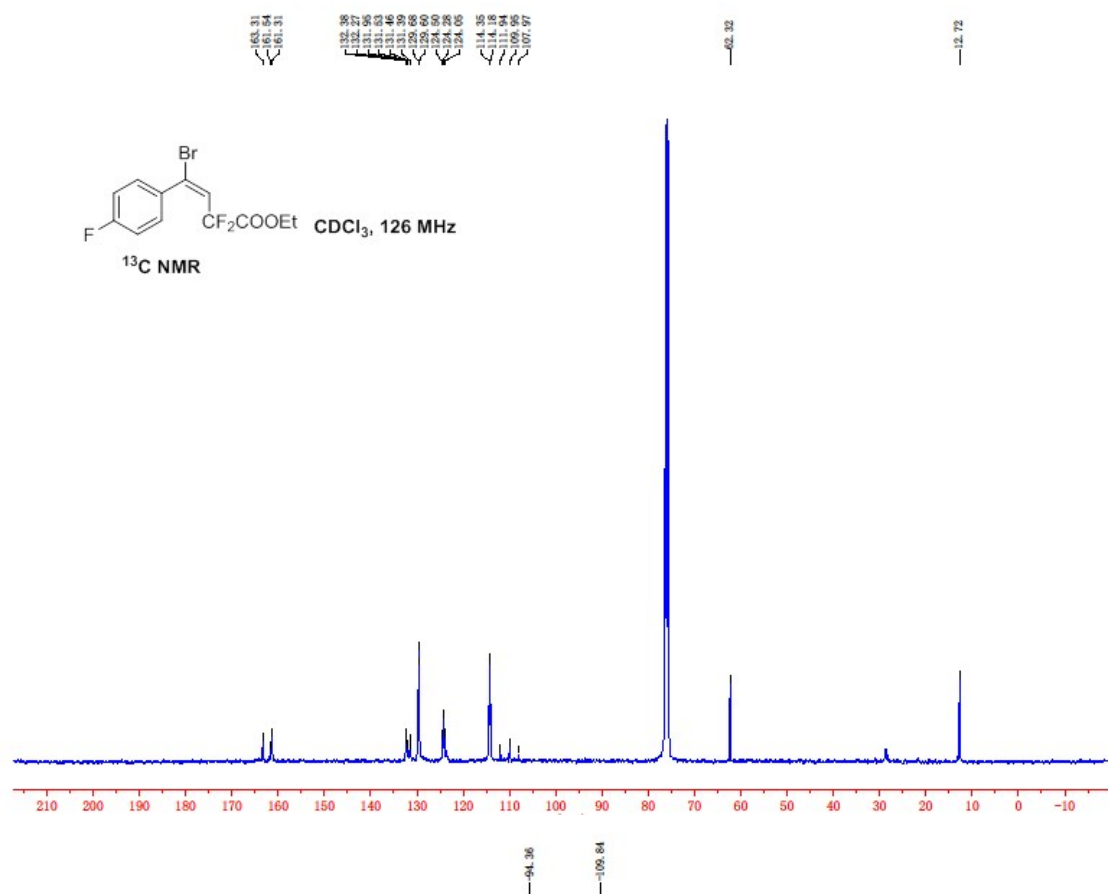
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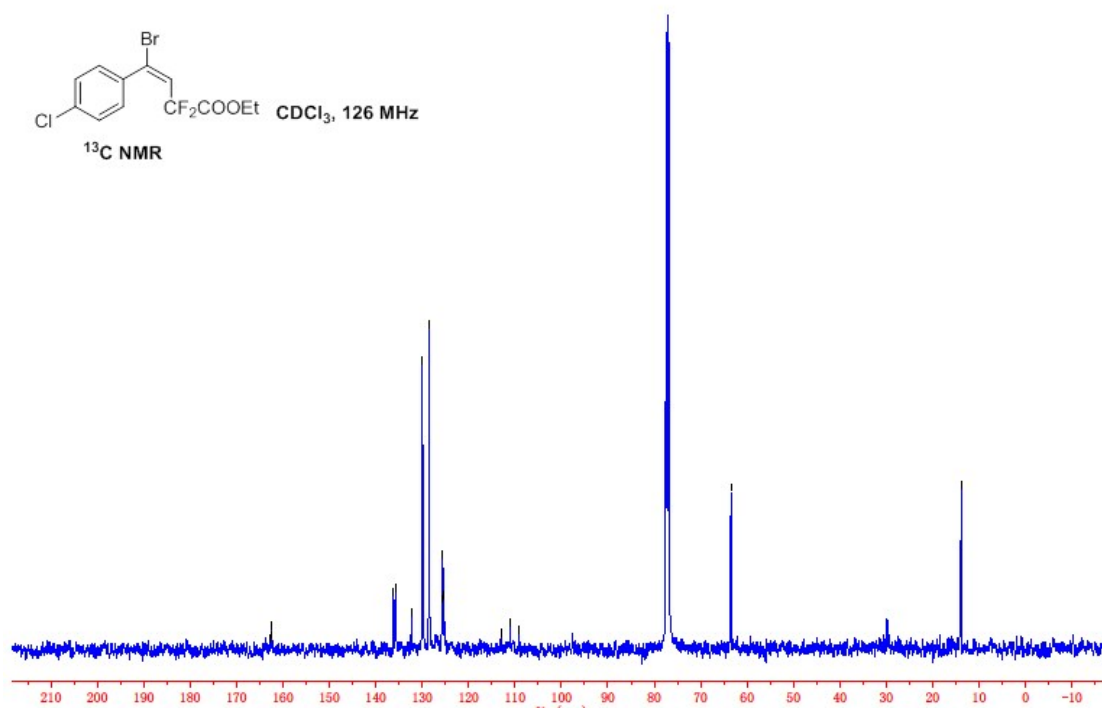
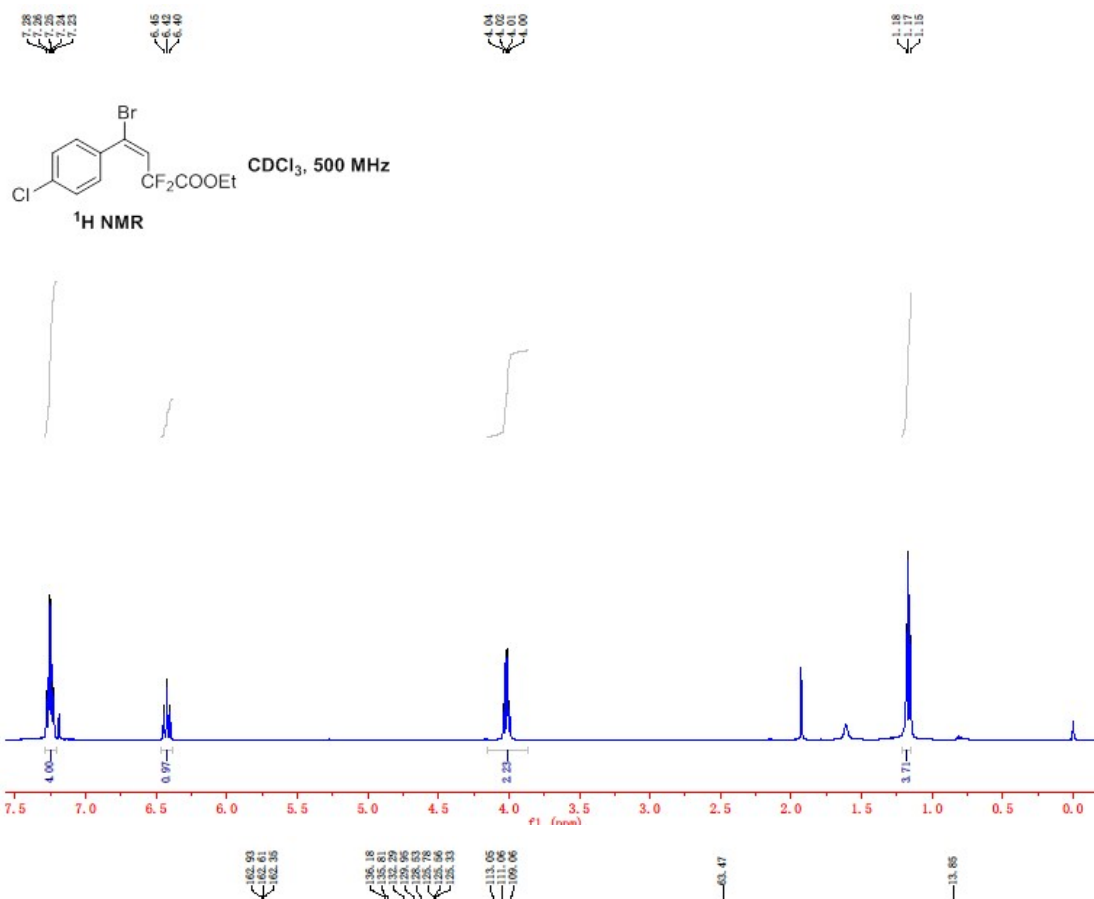


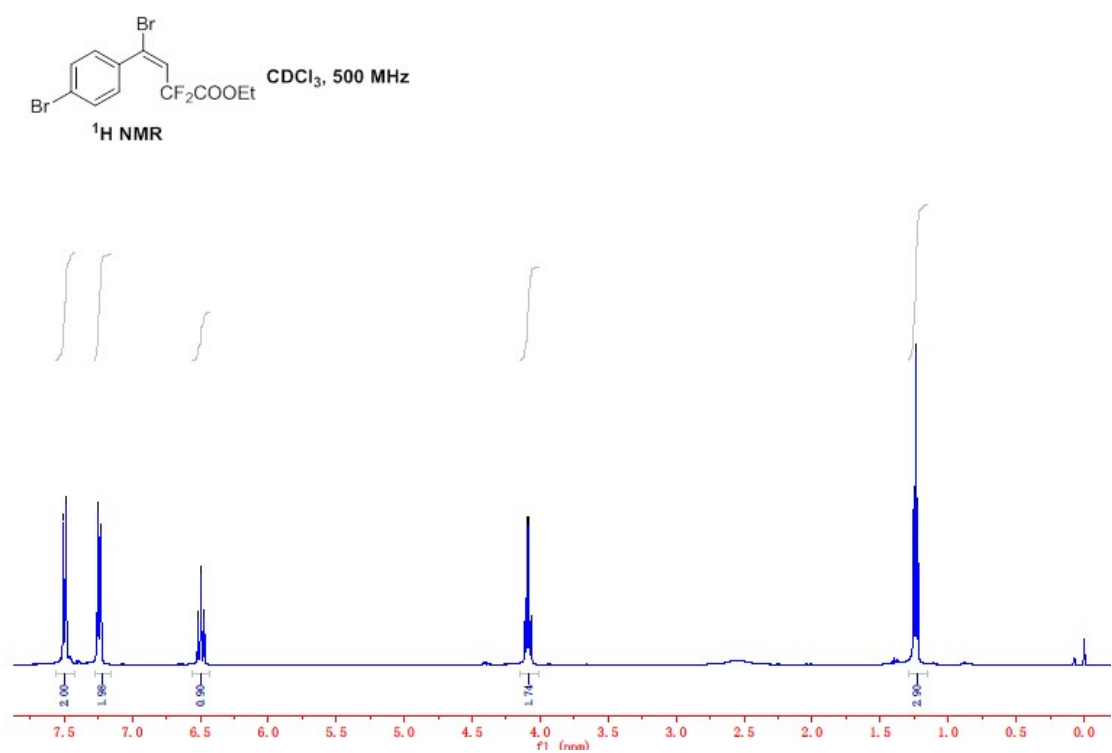
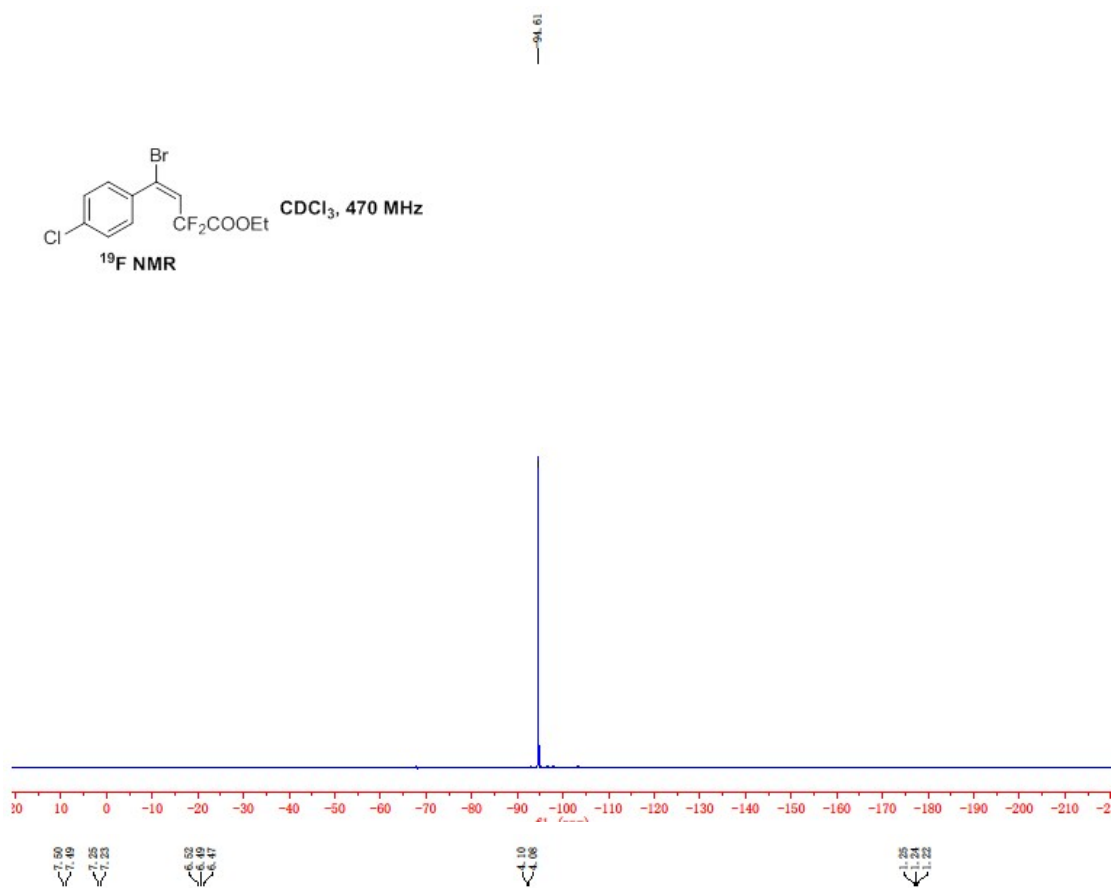


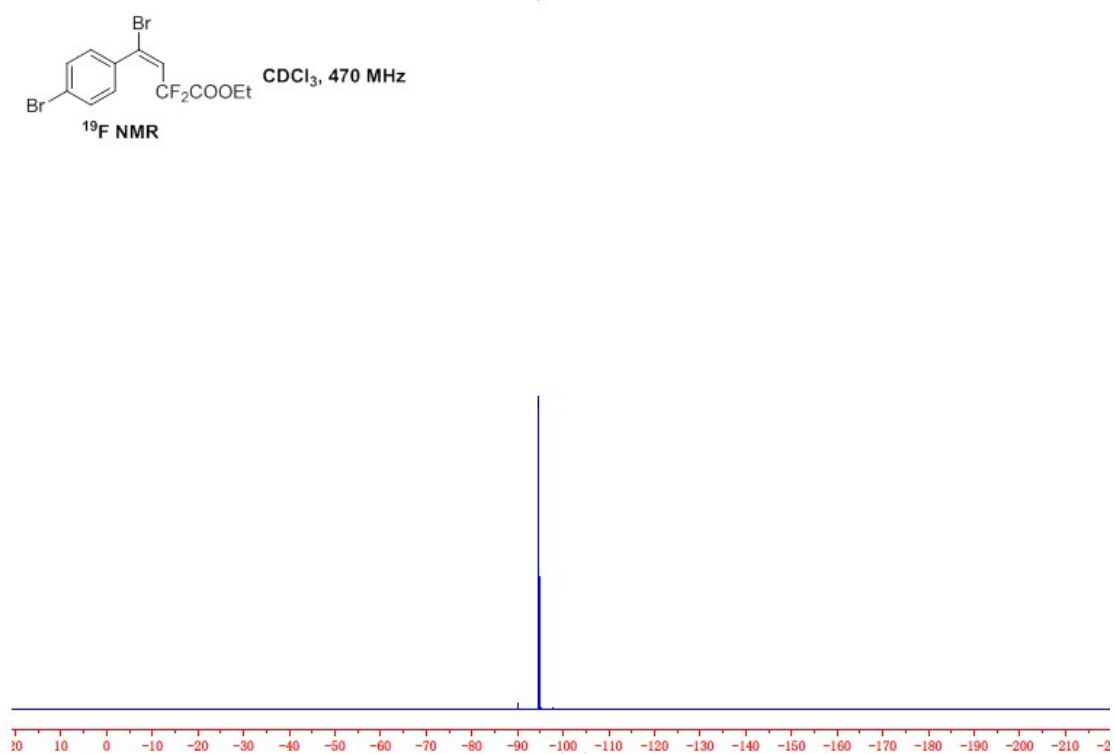
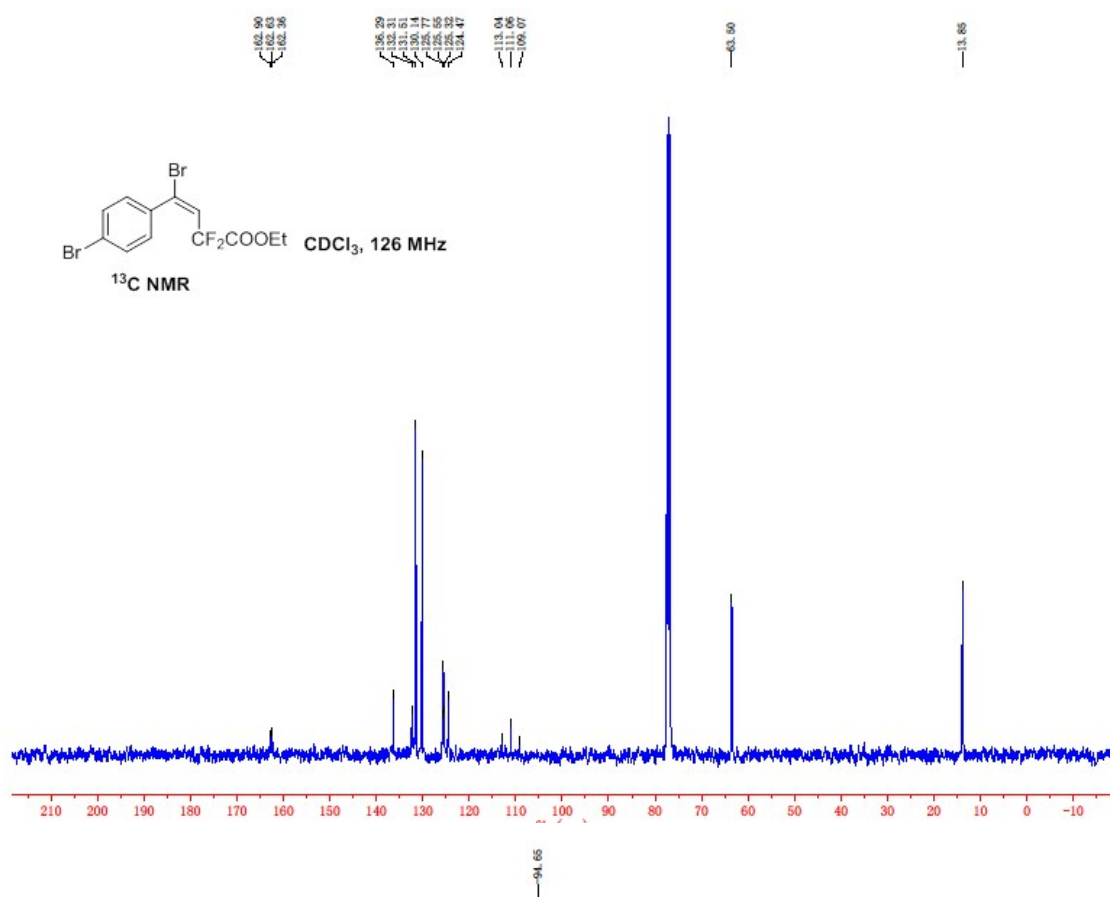


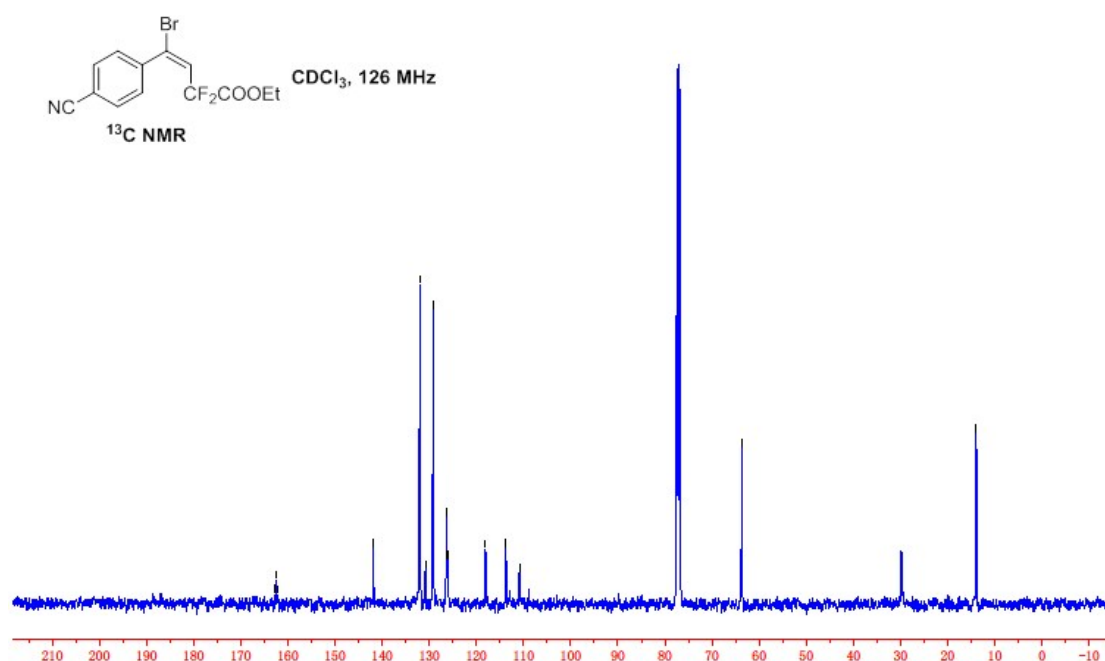
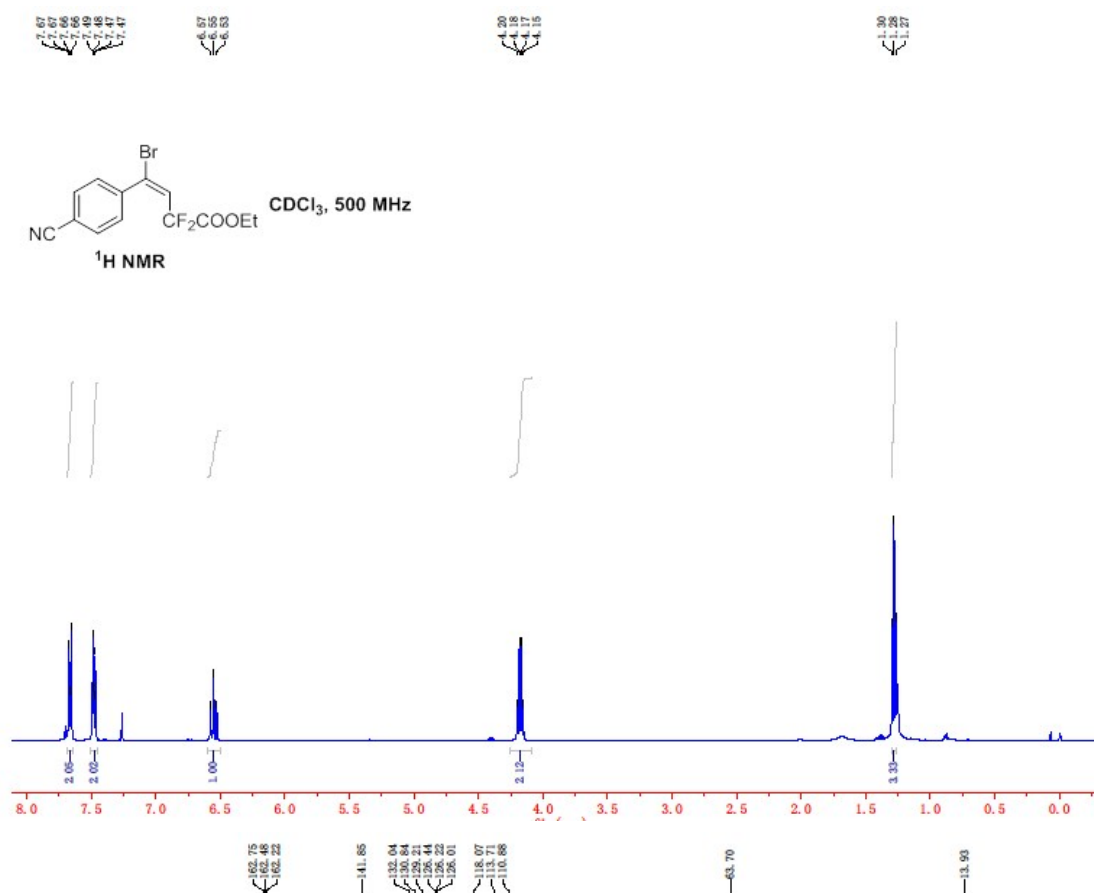


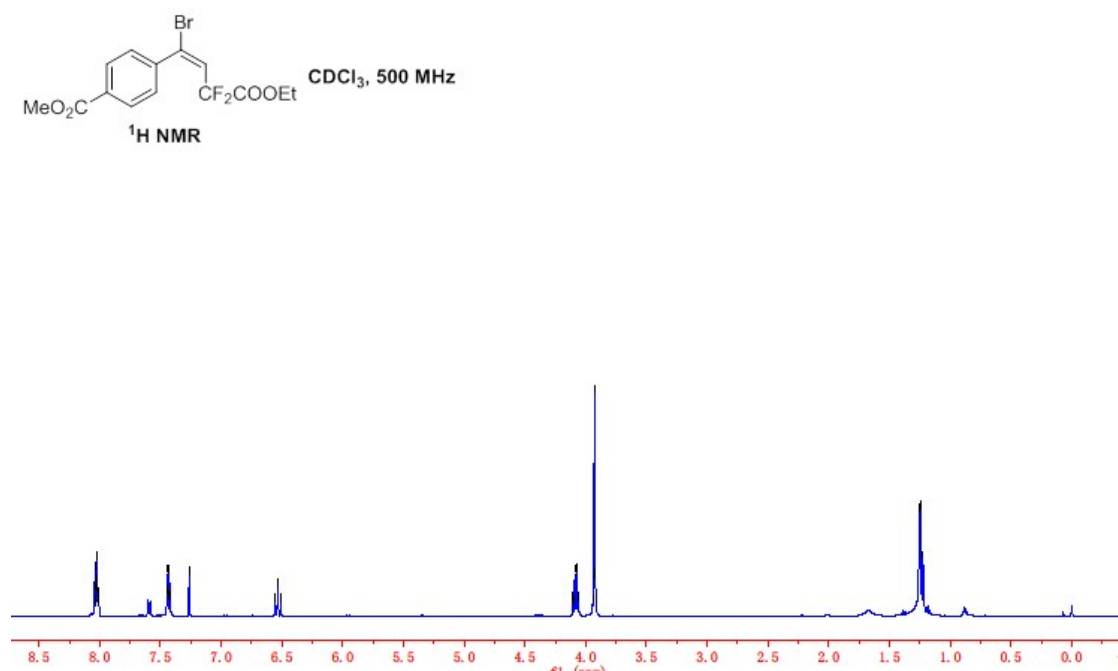
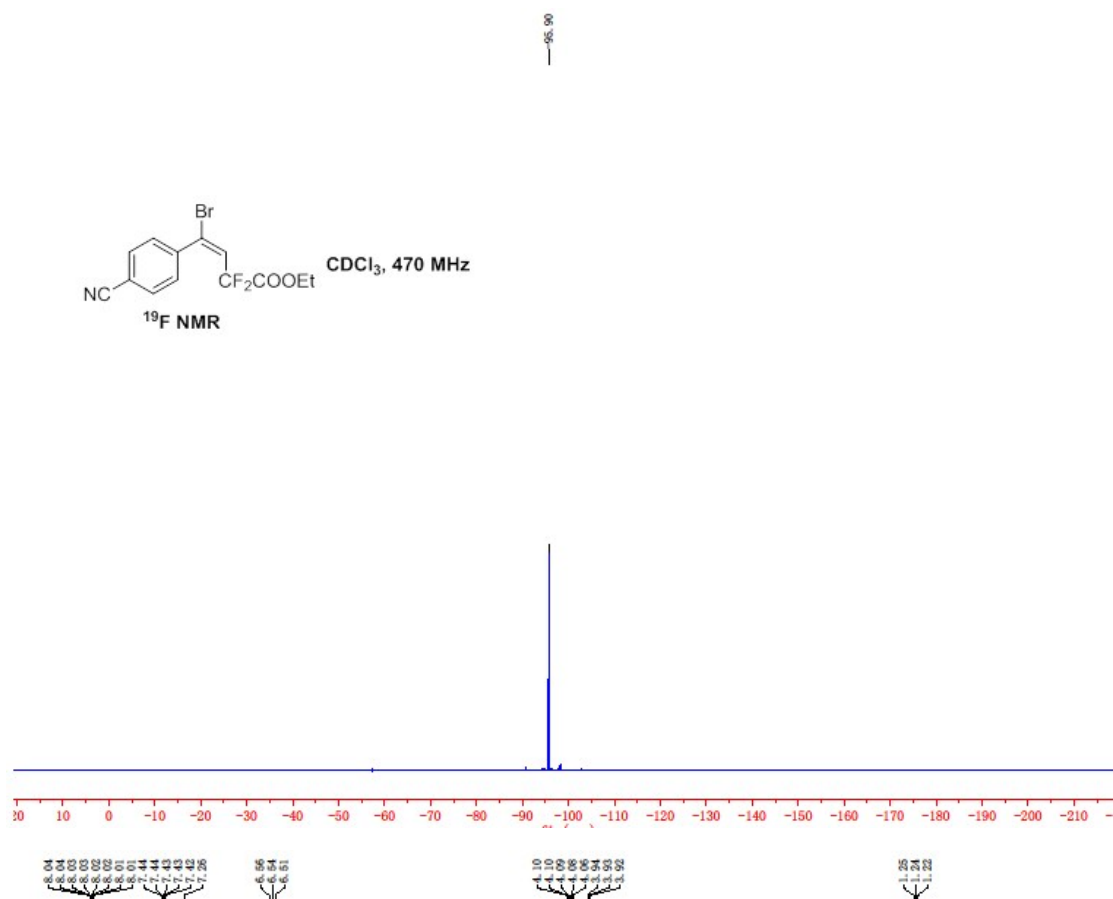


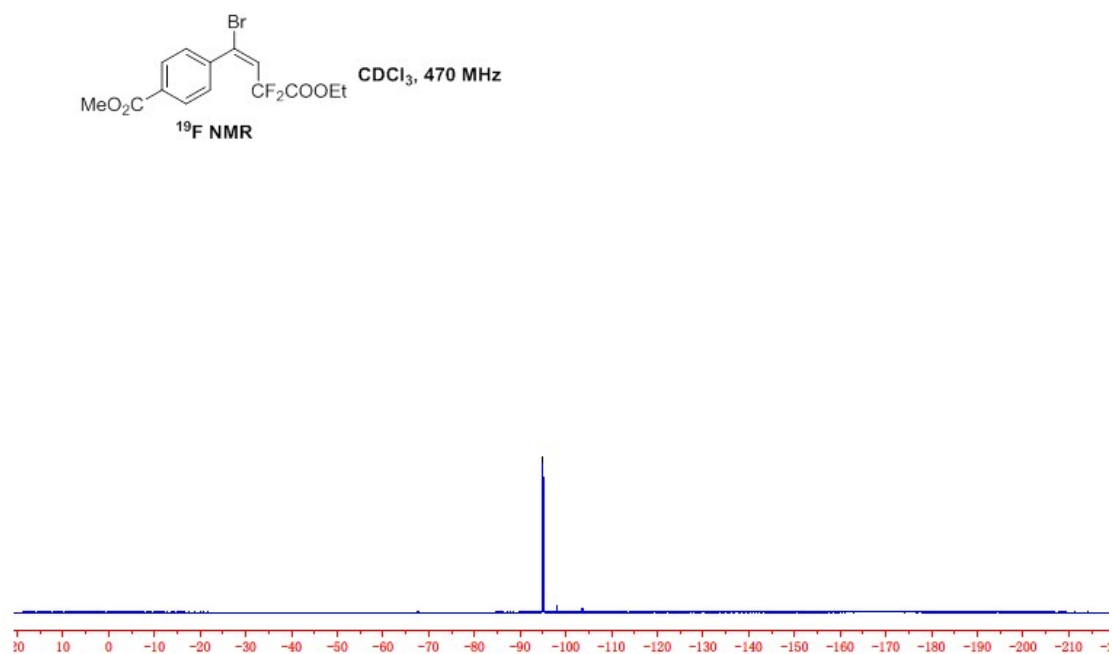
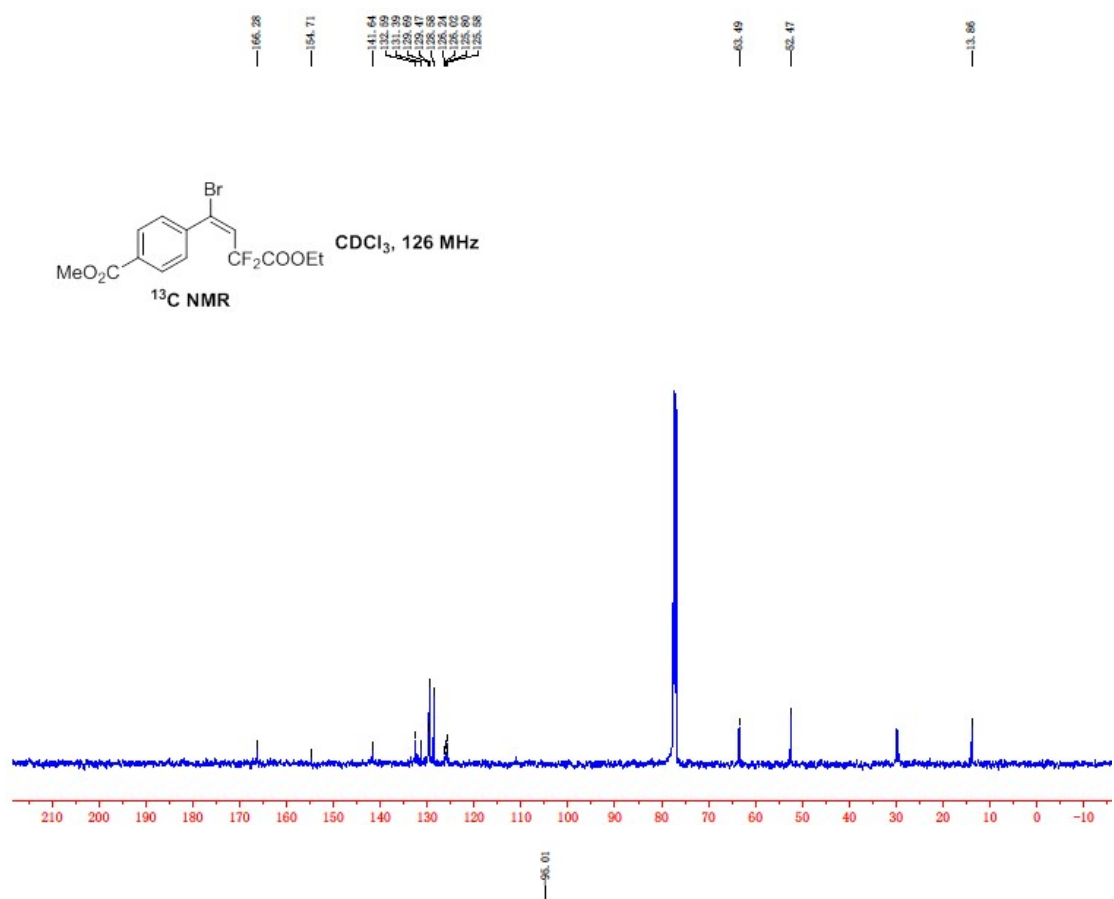


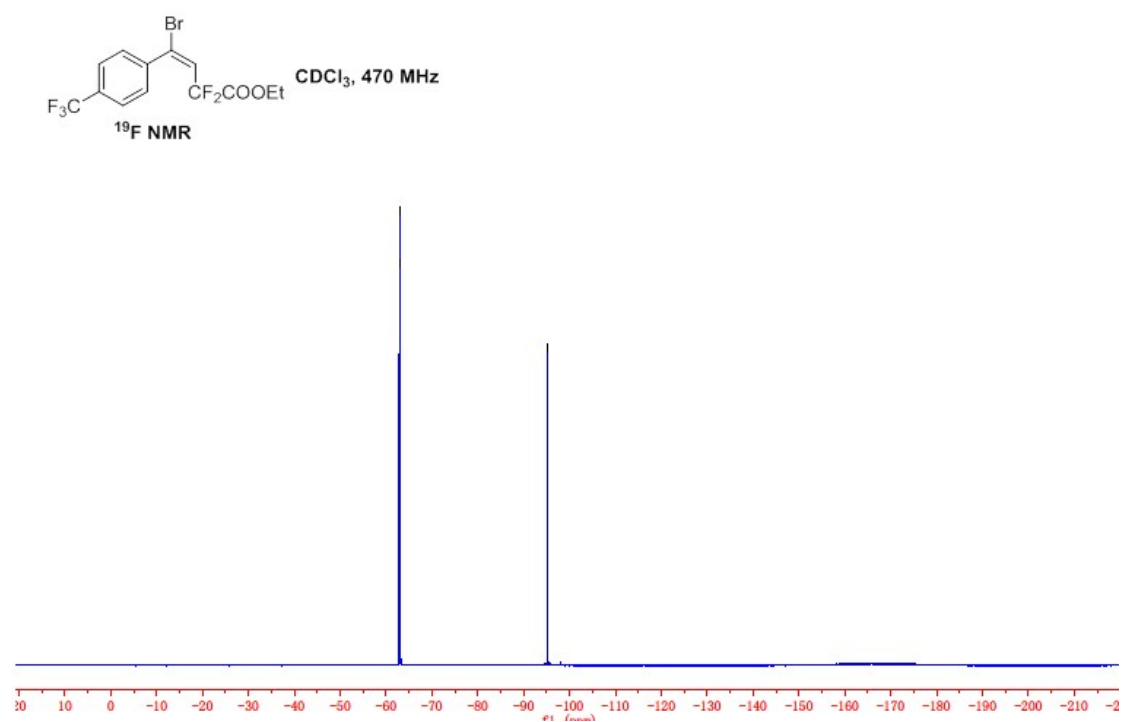
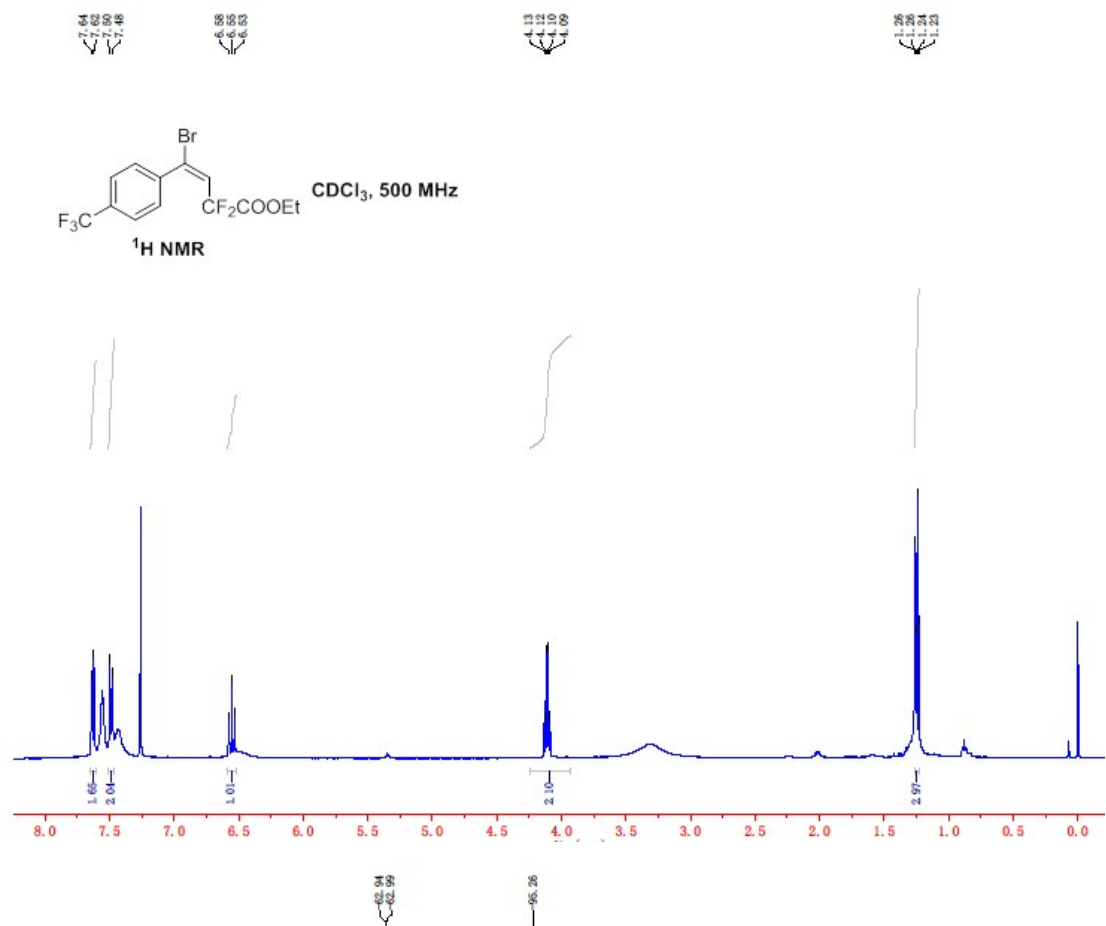


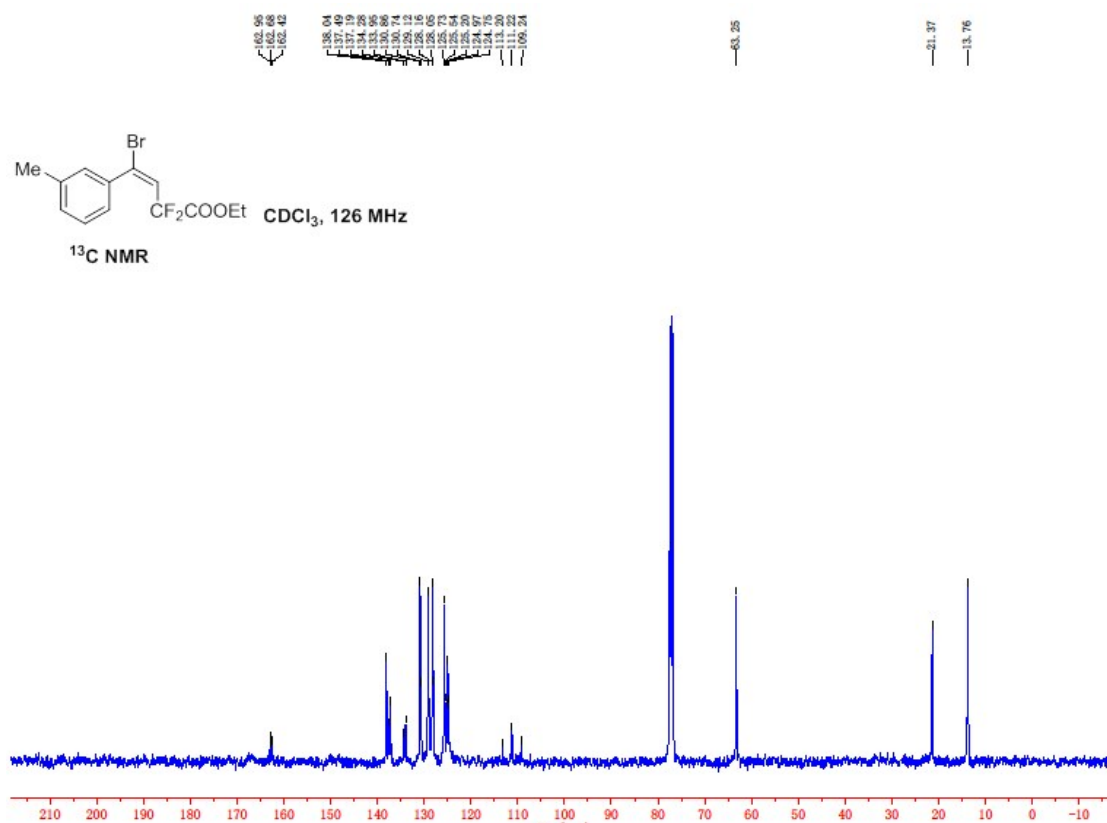
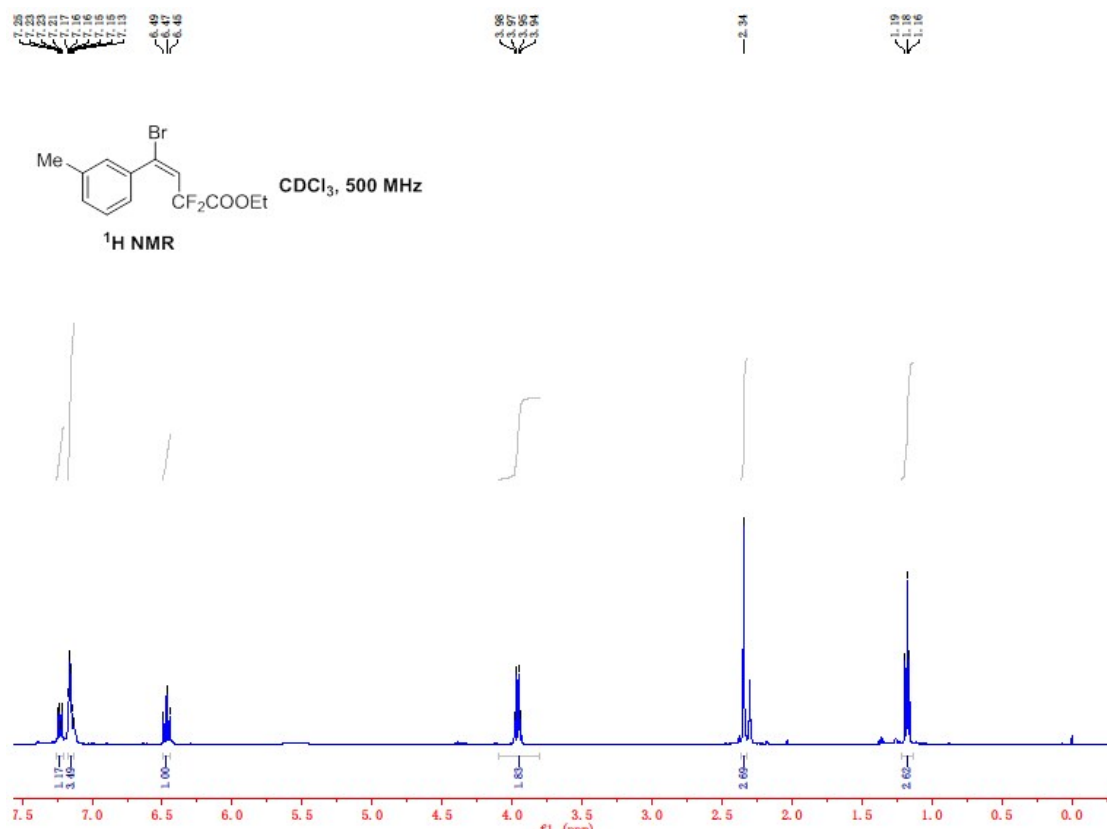


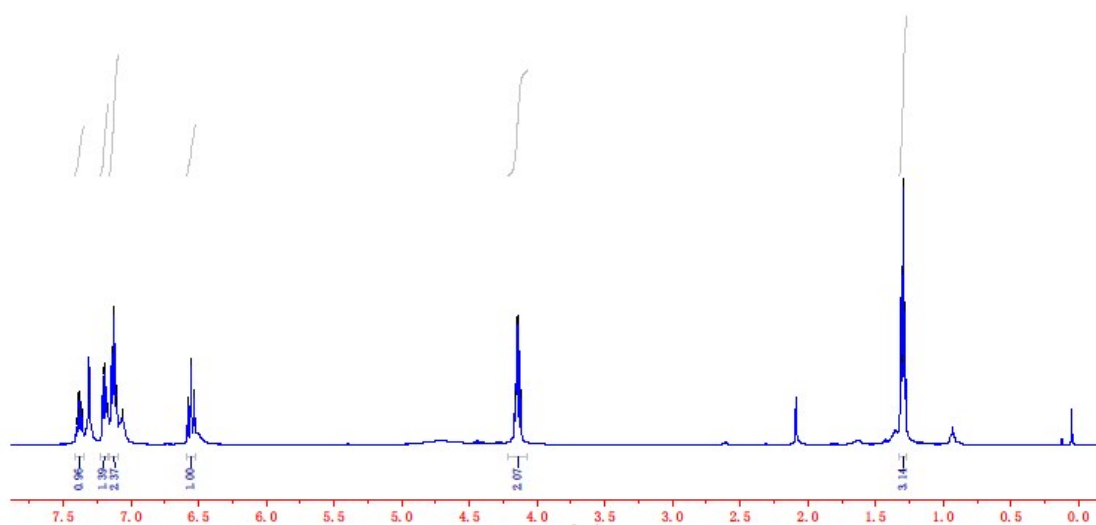
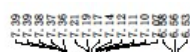


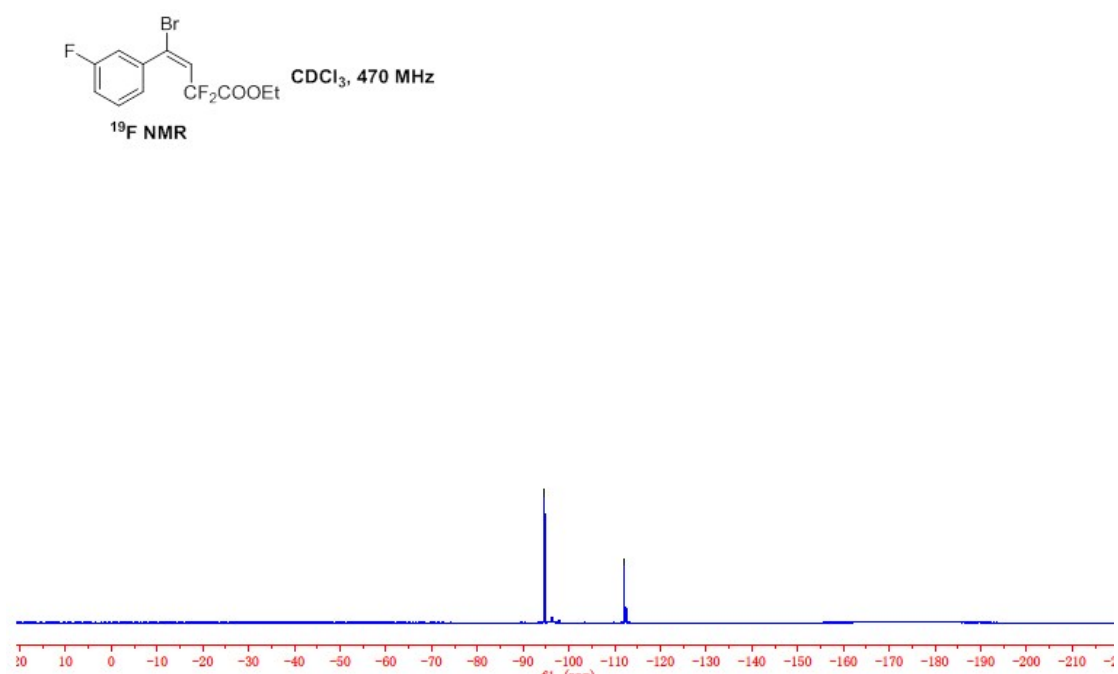
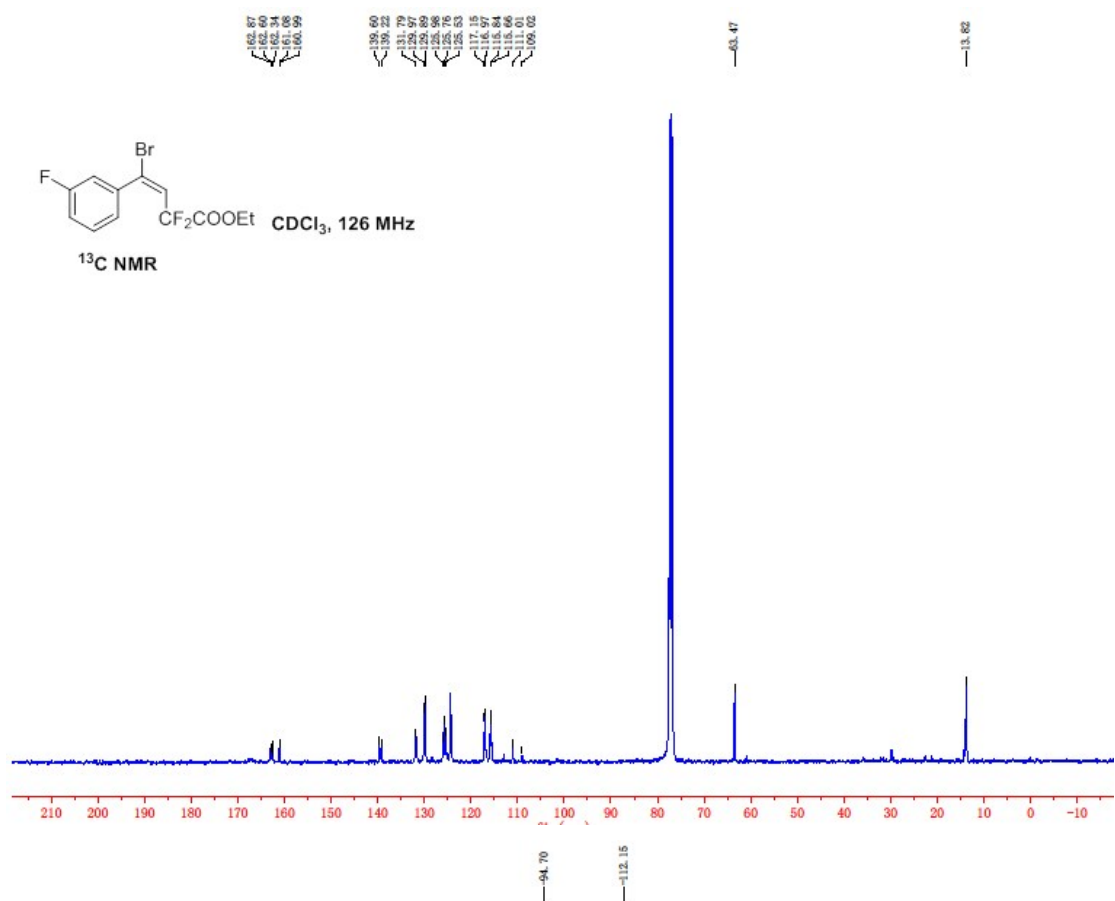


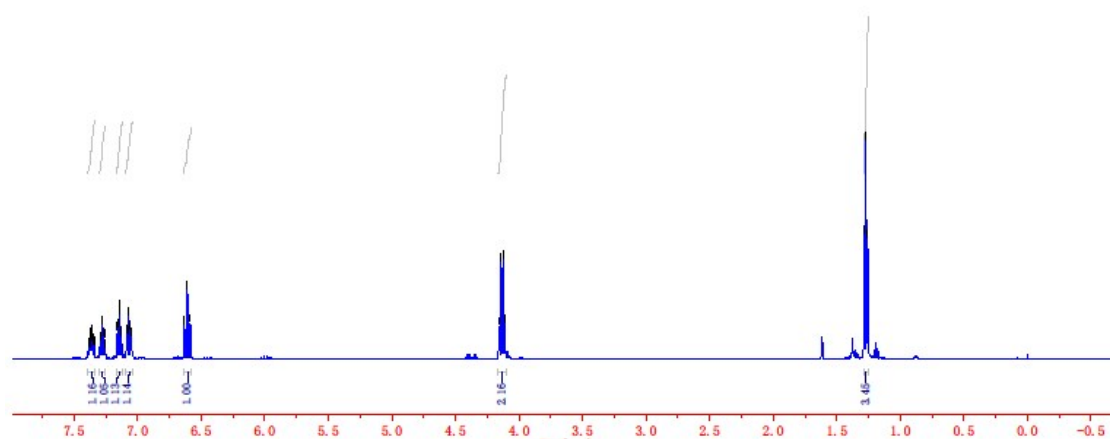
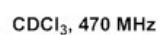


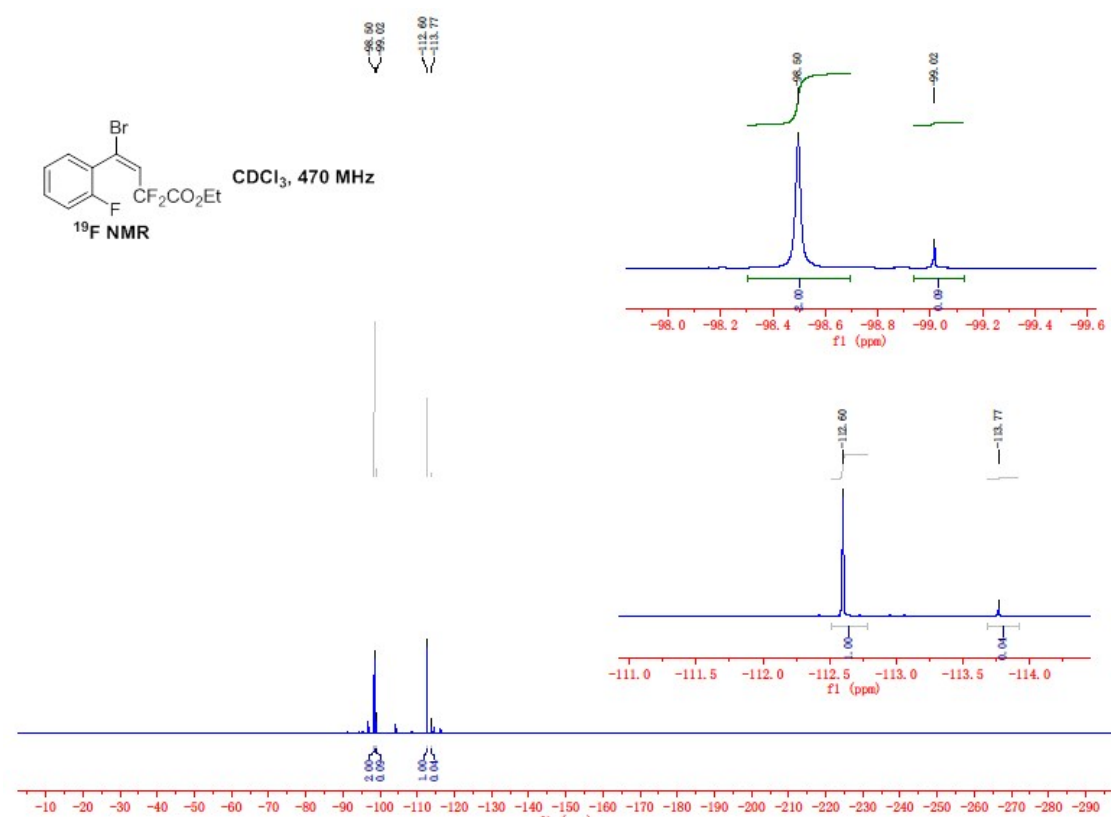
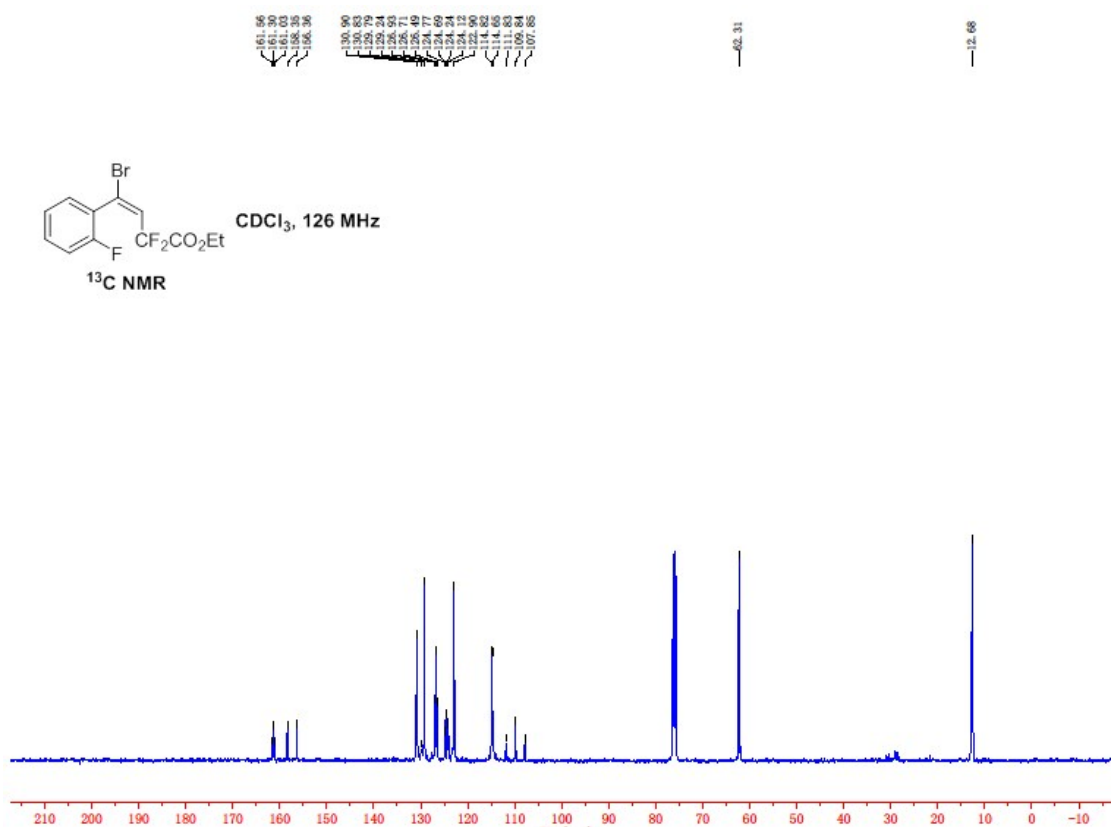


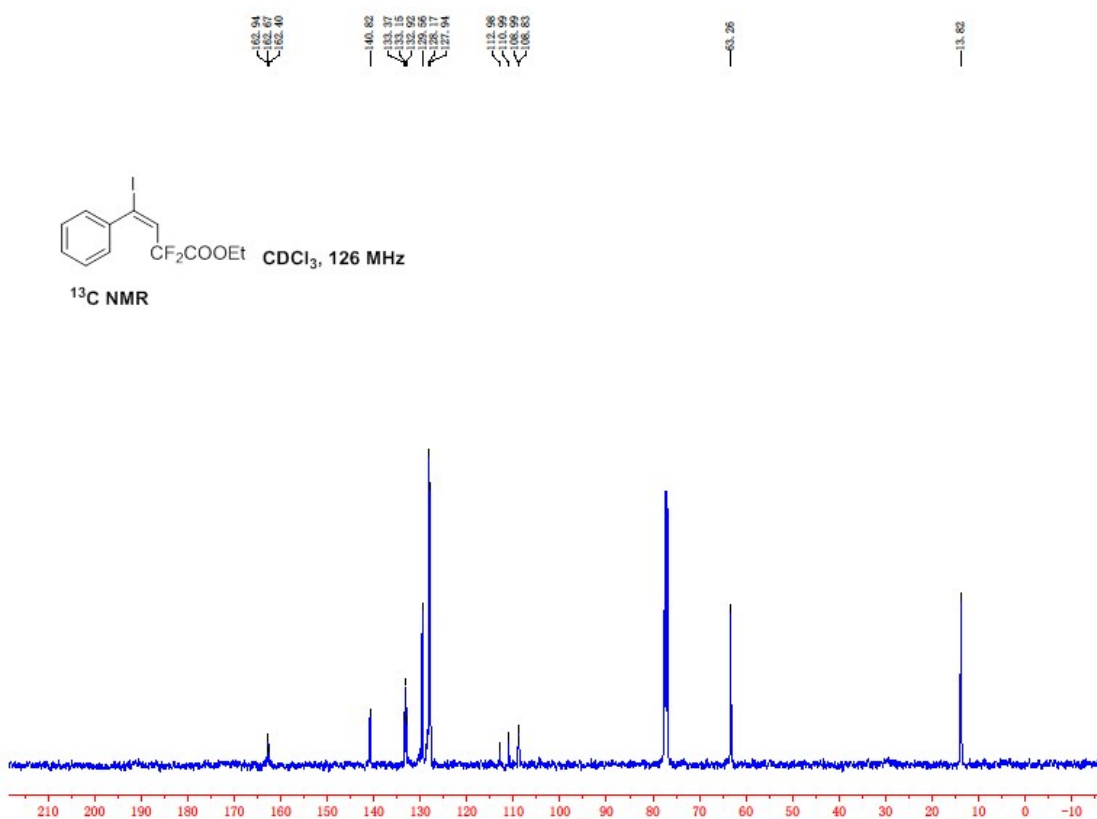
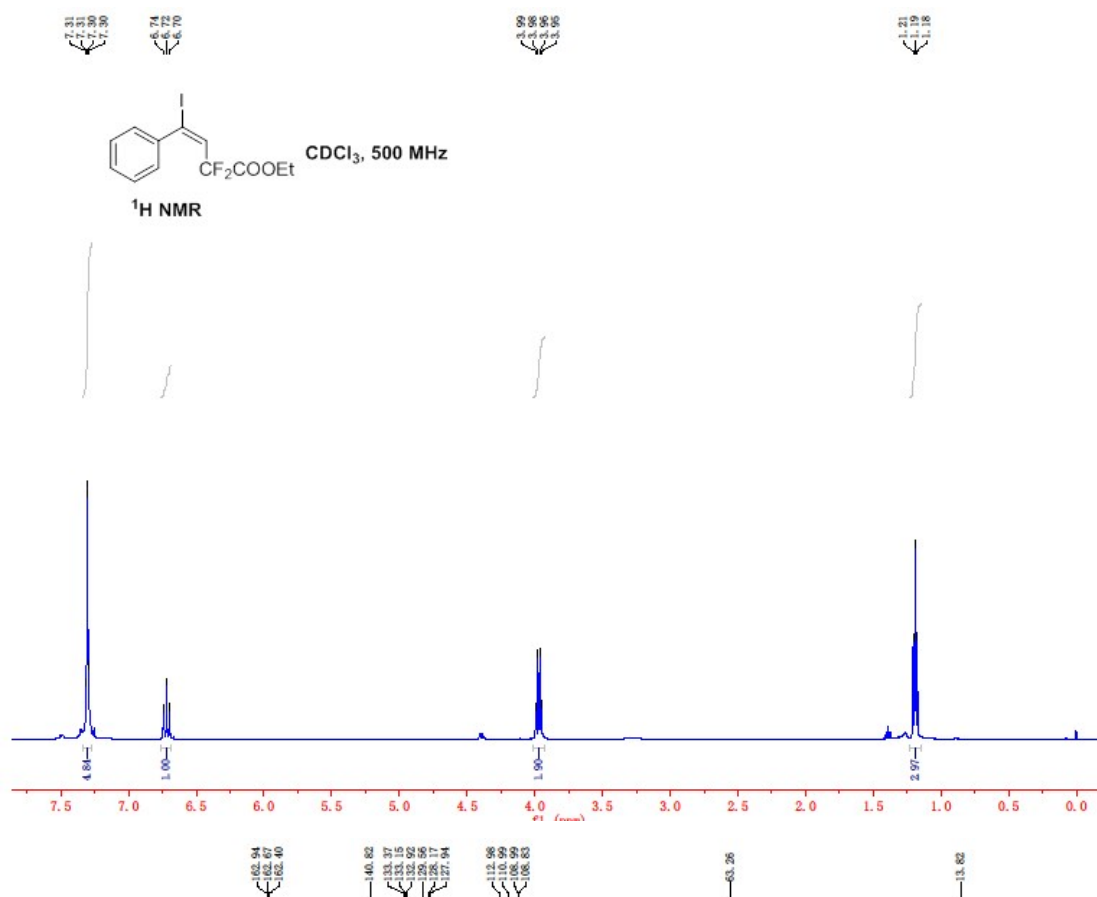


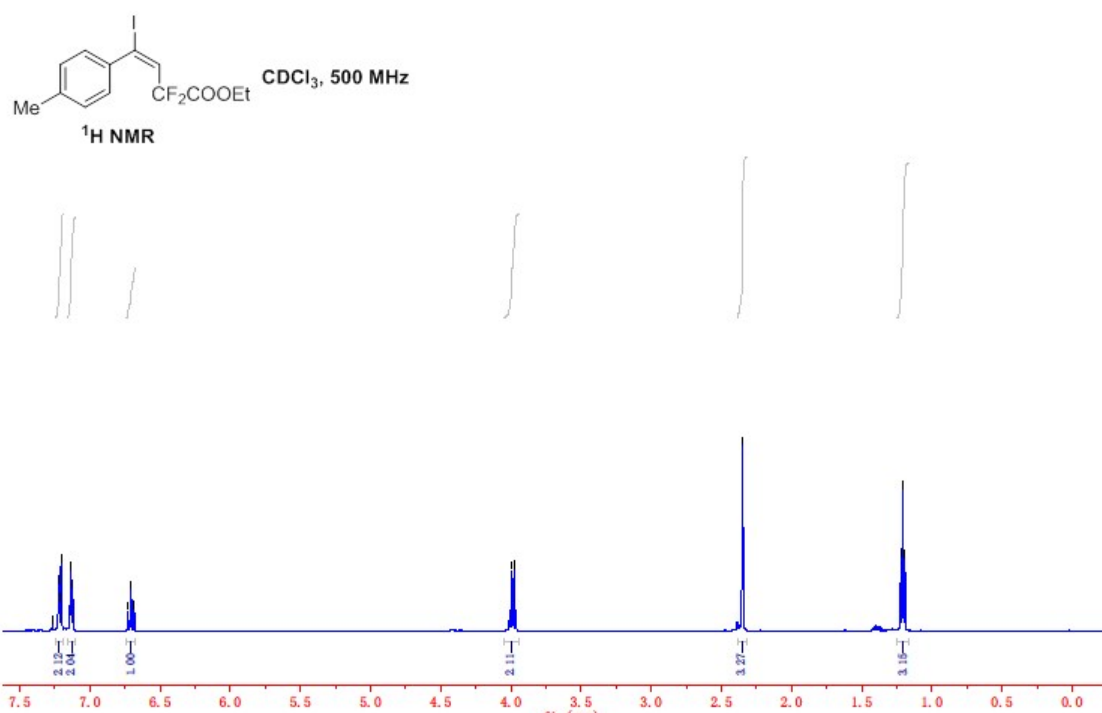
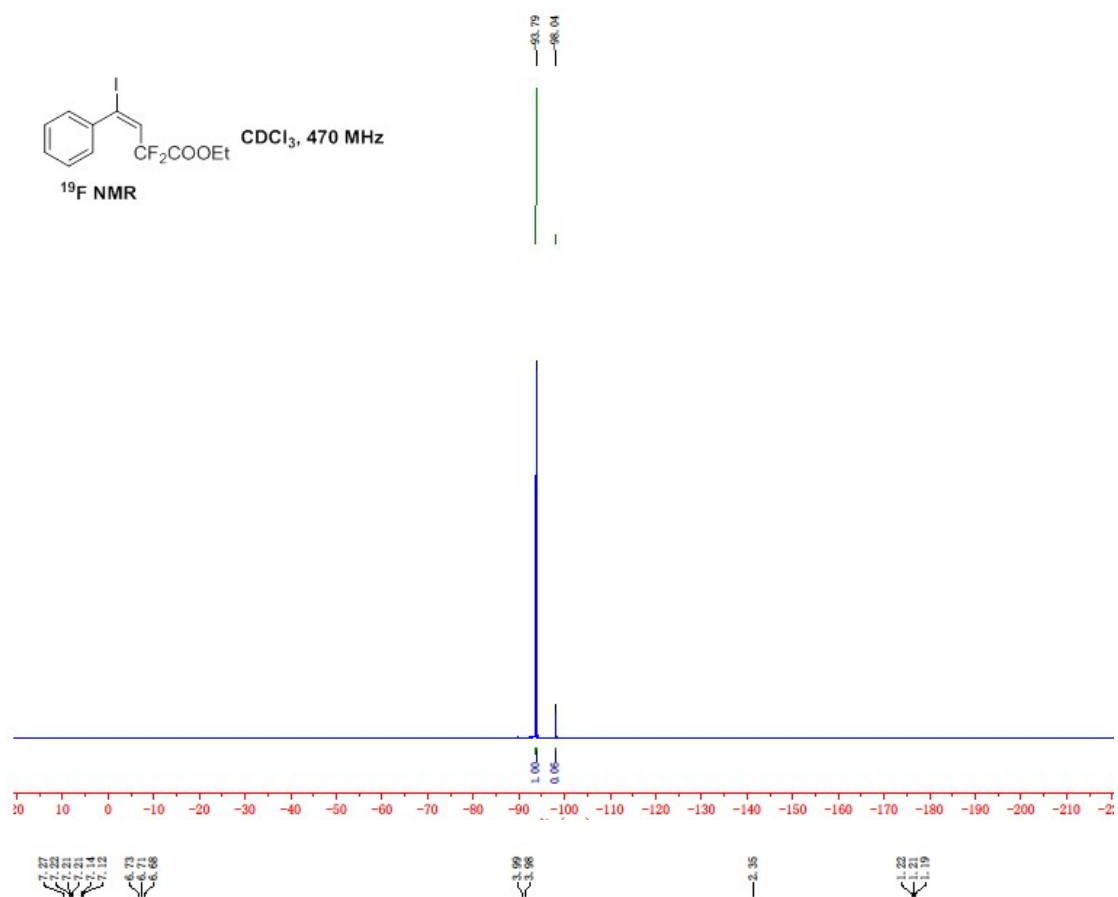


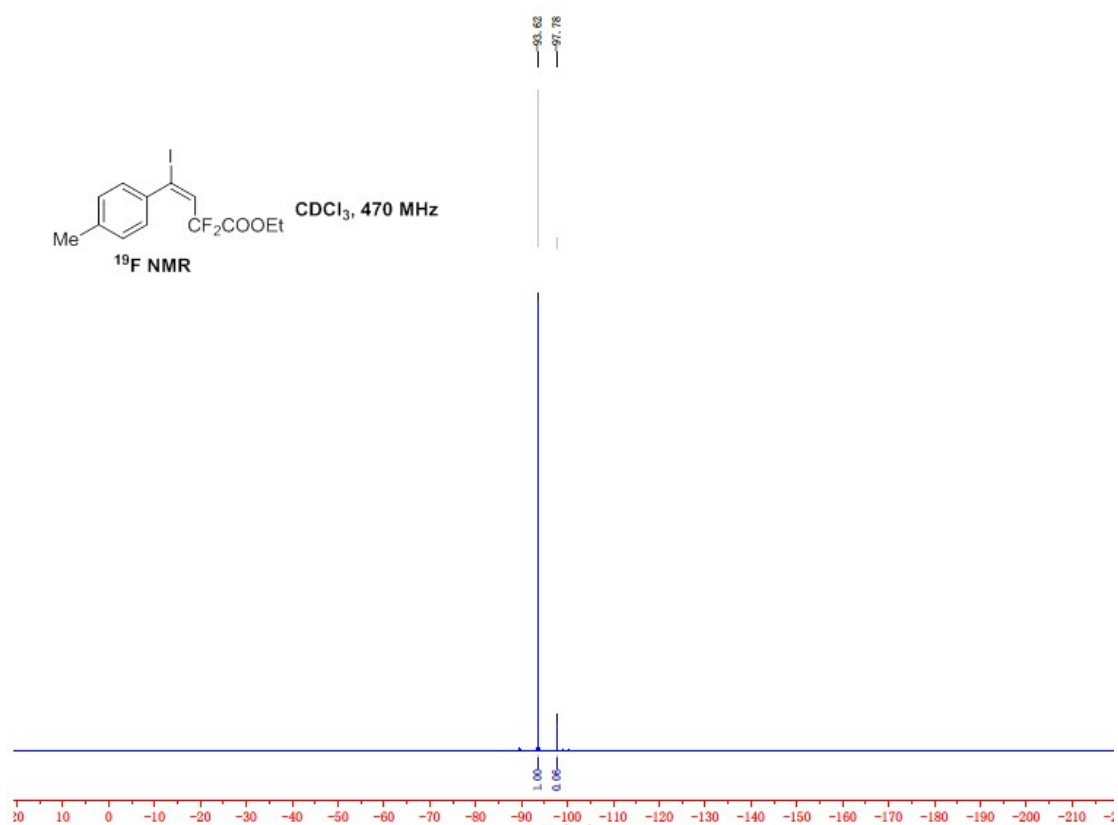
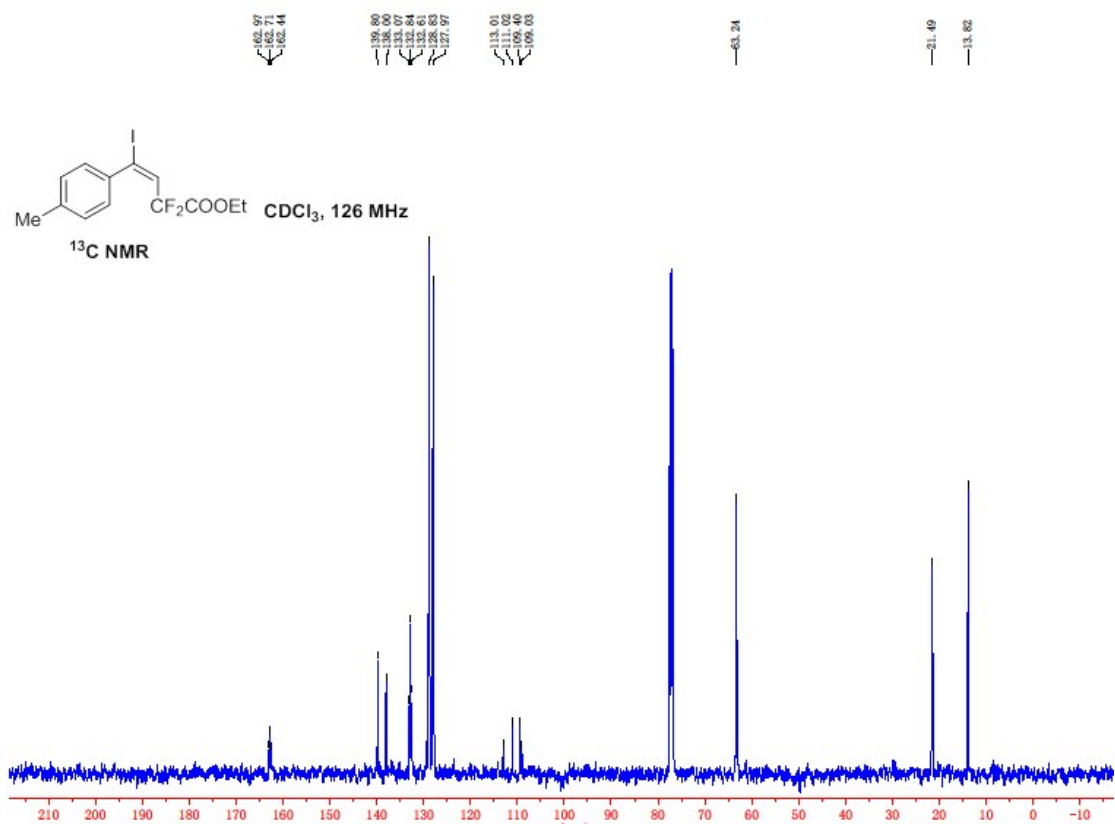


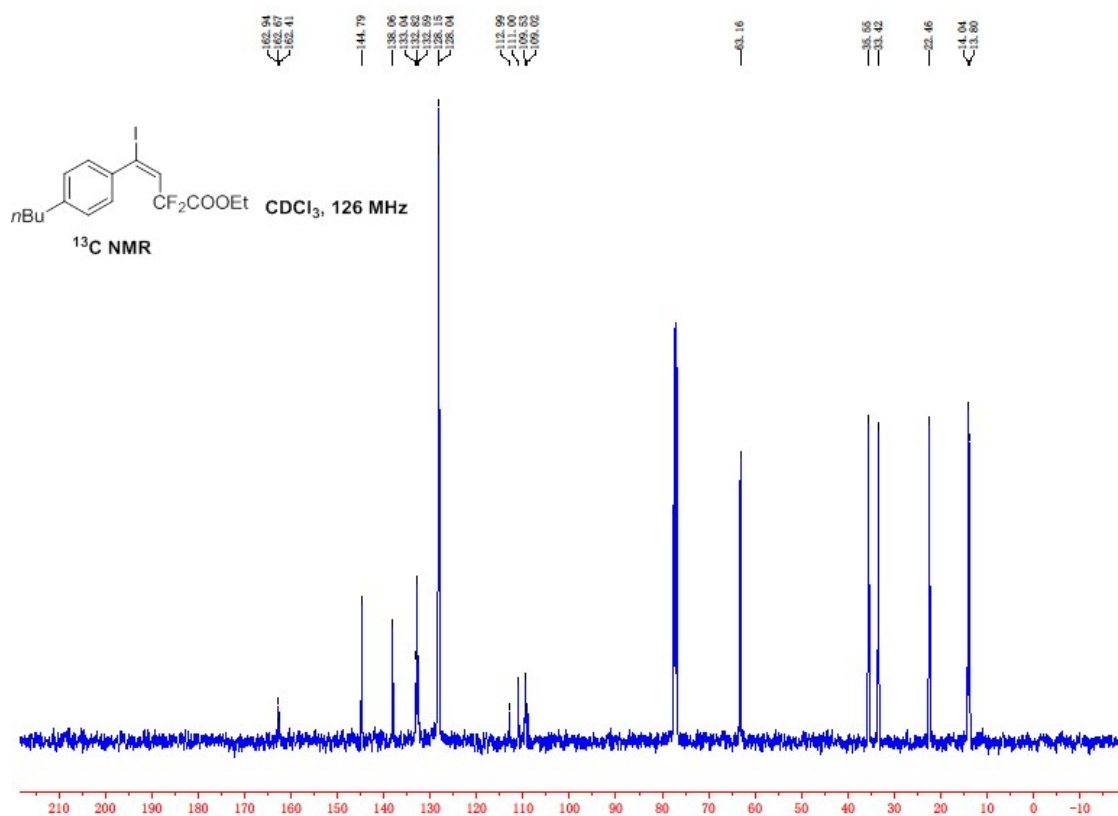
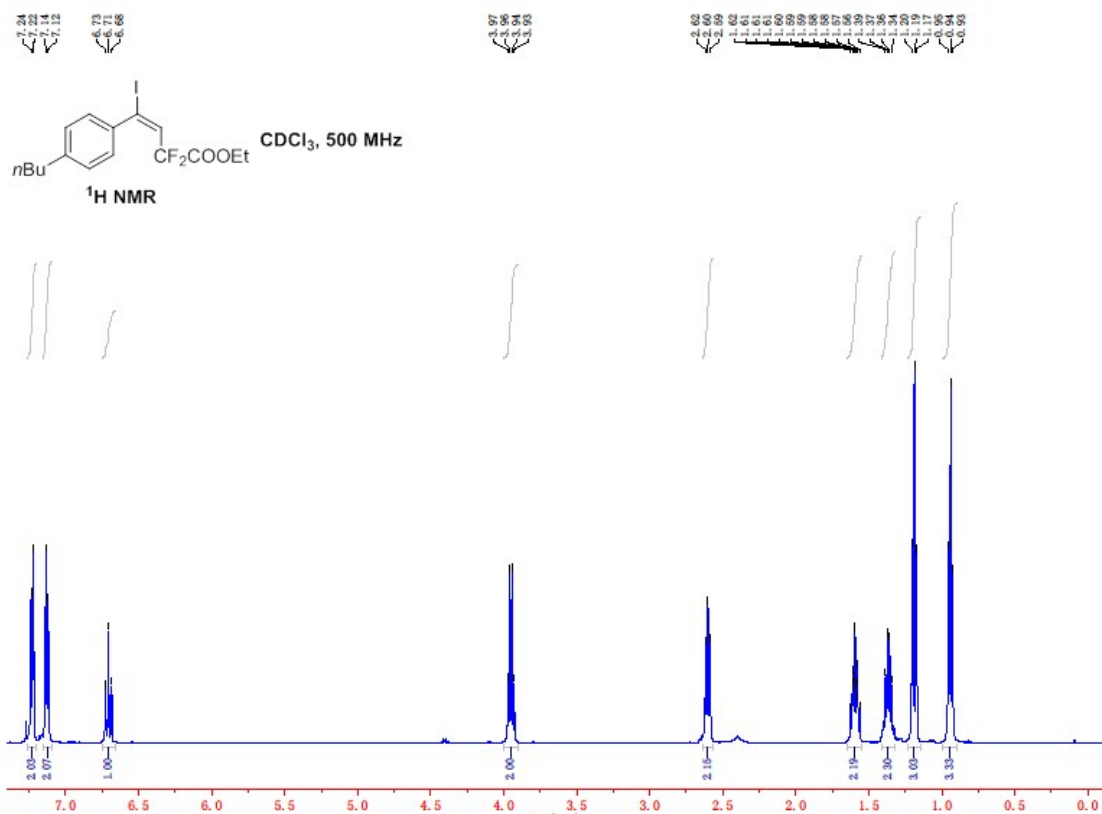


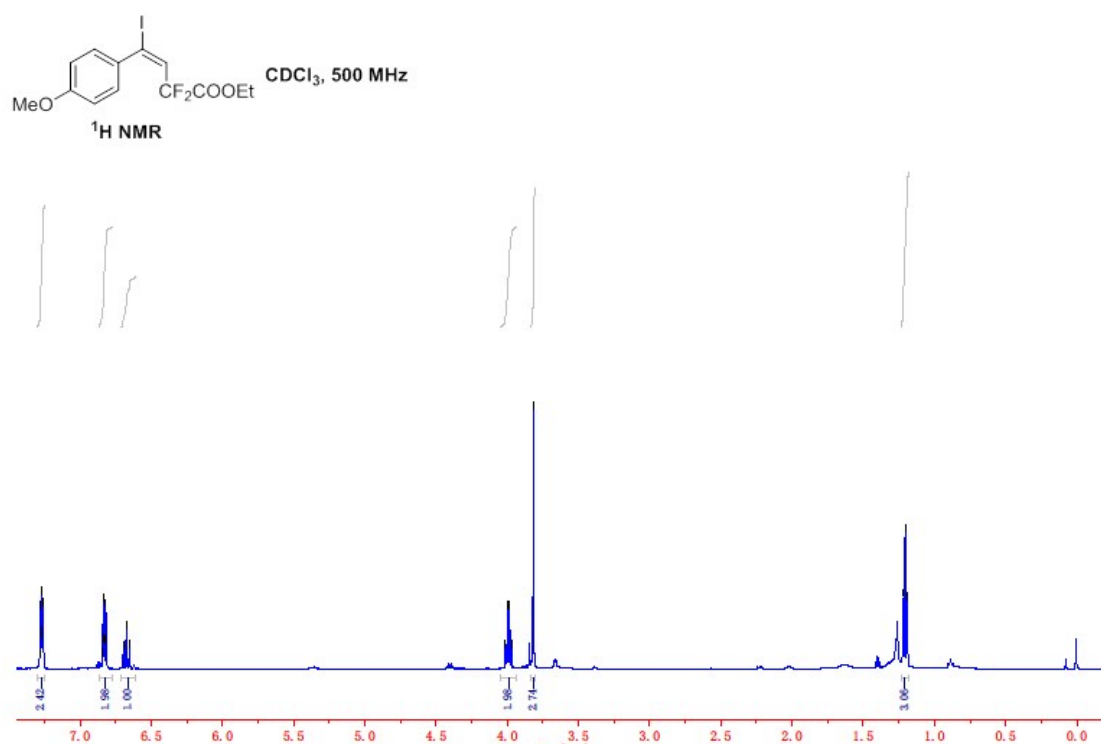
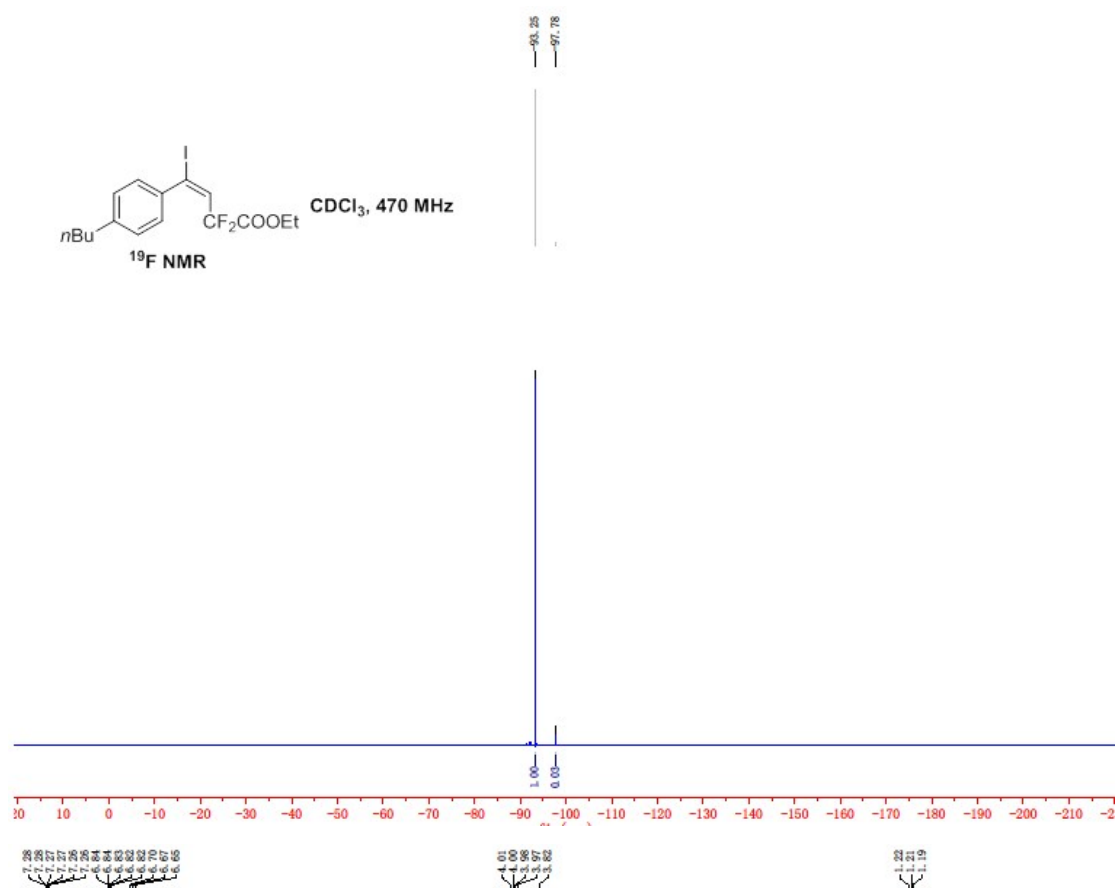


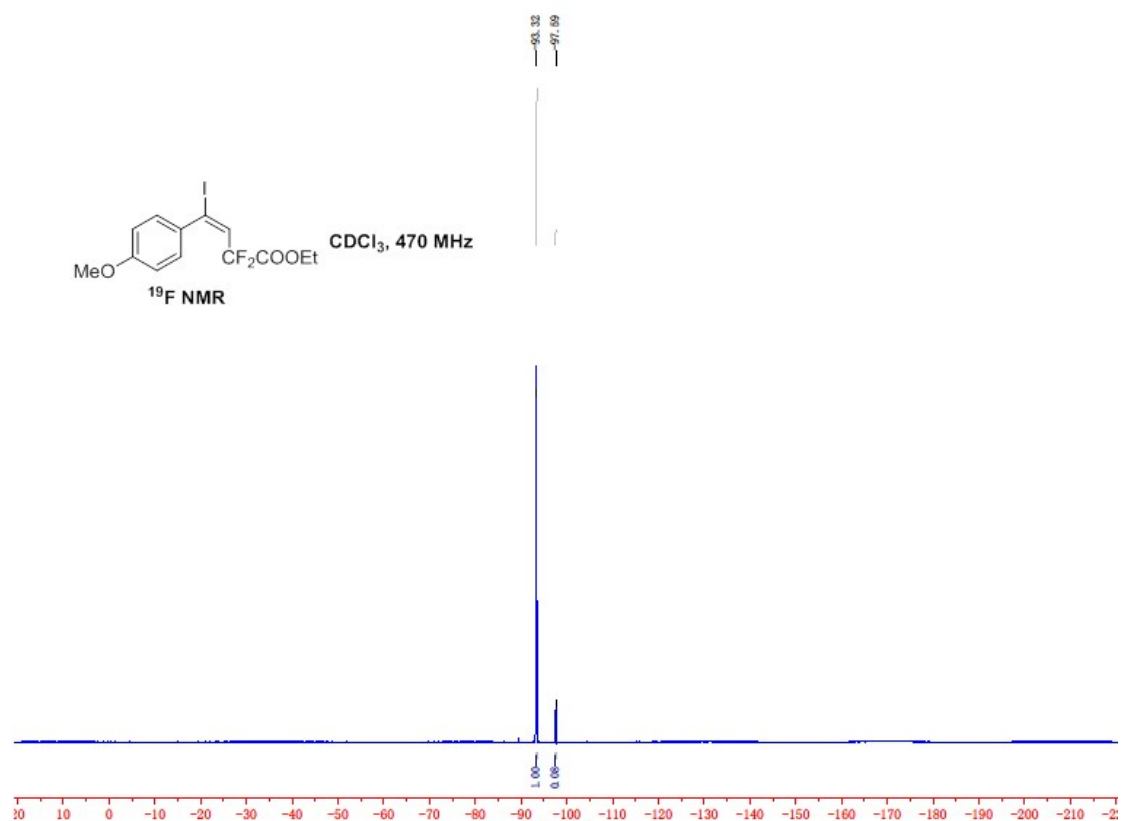
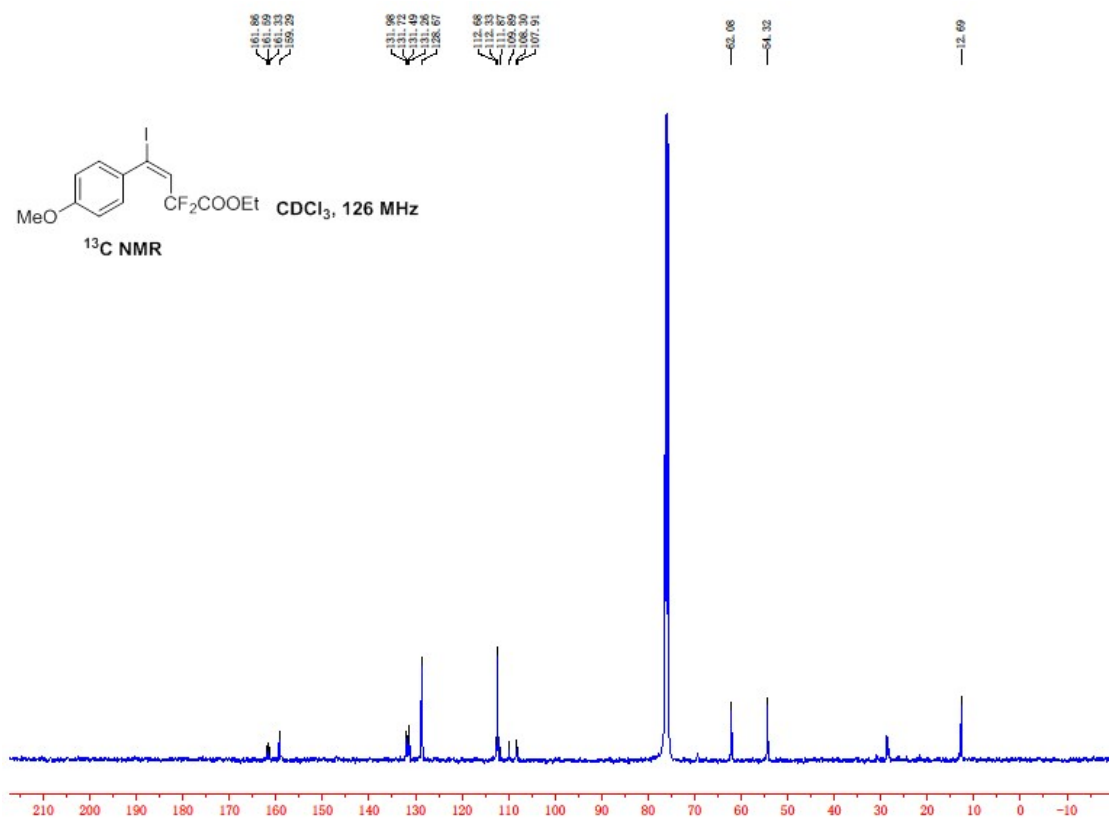








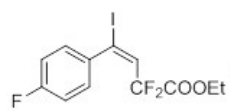




7.30, 7.29, 7.28, 7.03, 7.00, 6.99, 6.73, 6.71, 6.69

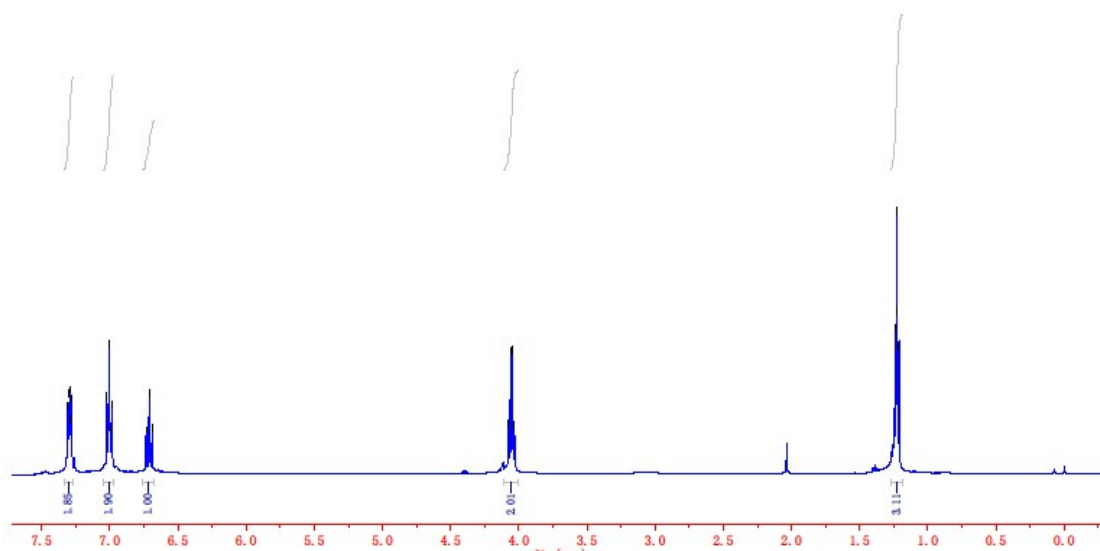
4.00, 3.99, 3.98

1.24, 1.23, 1.22



CDCl₃, 500 MHz

¹H NMR



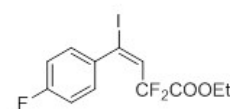
164.00, 162.04, 162.00

136.97, 133.74, 133.62, 133.30, 130.07, 130.00

115.37, 115.19, 112.96, 110.87, 108.69, 107.44

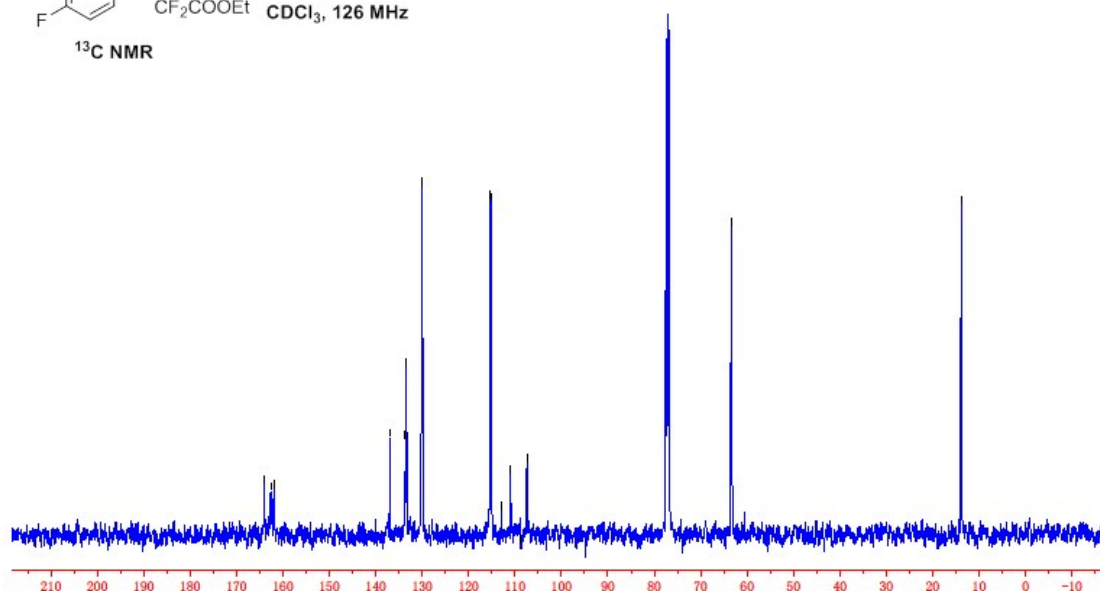
-63.99

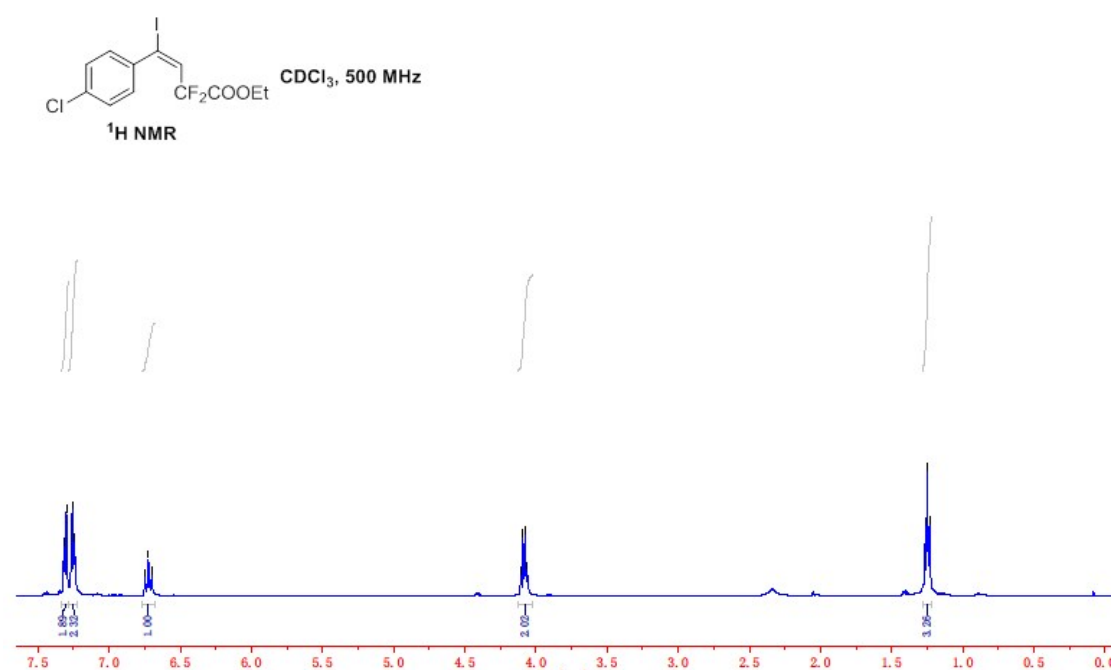
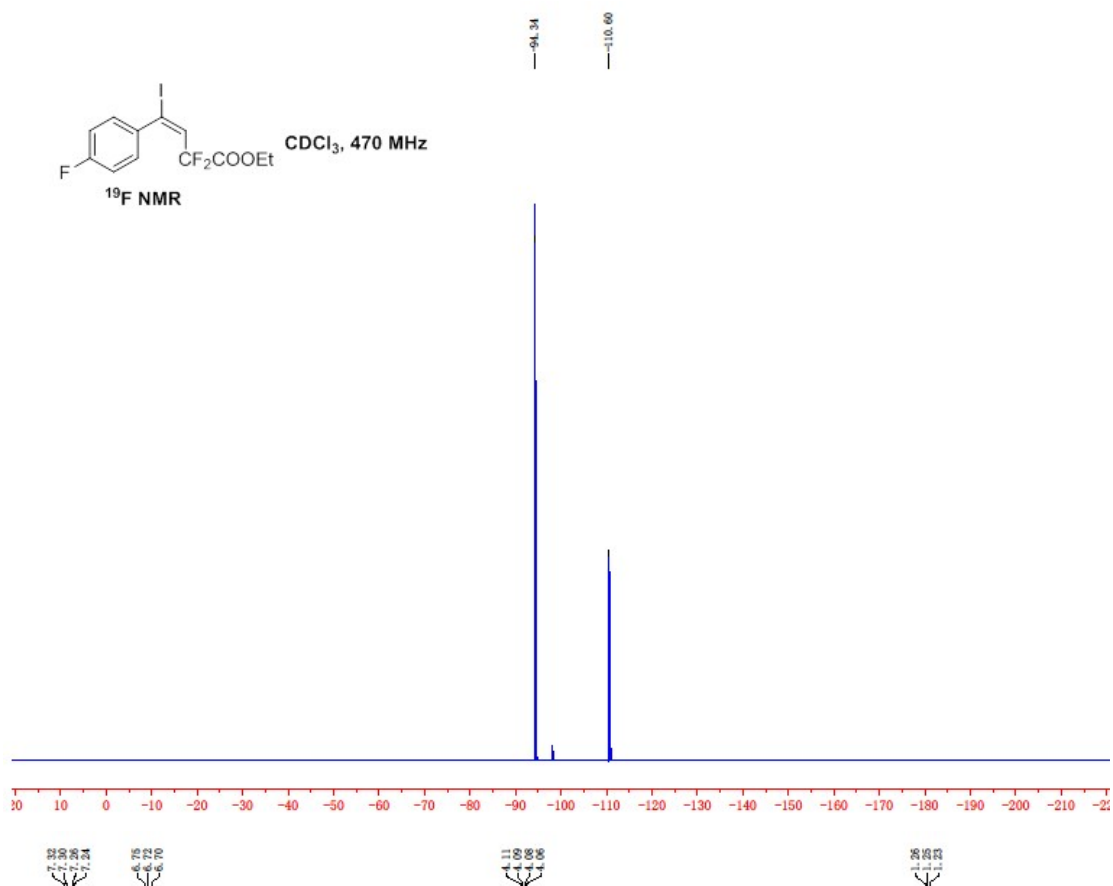
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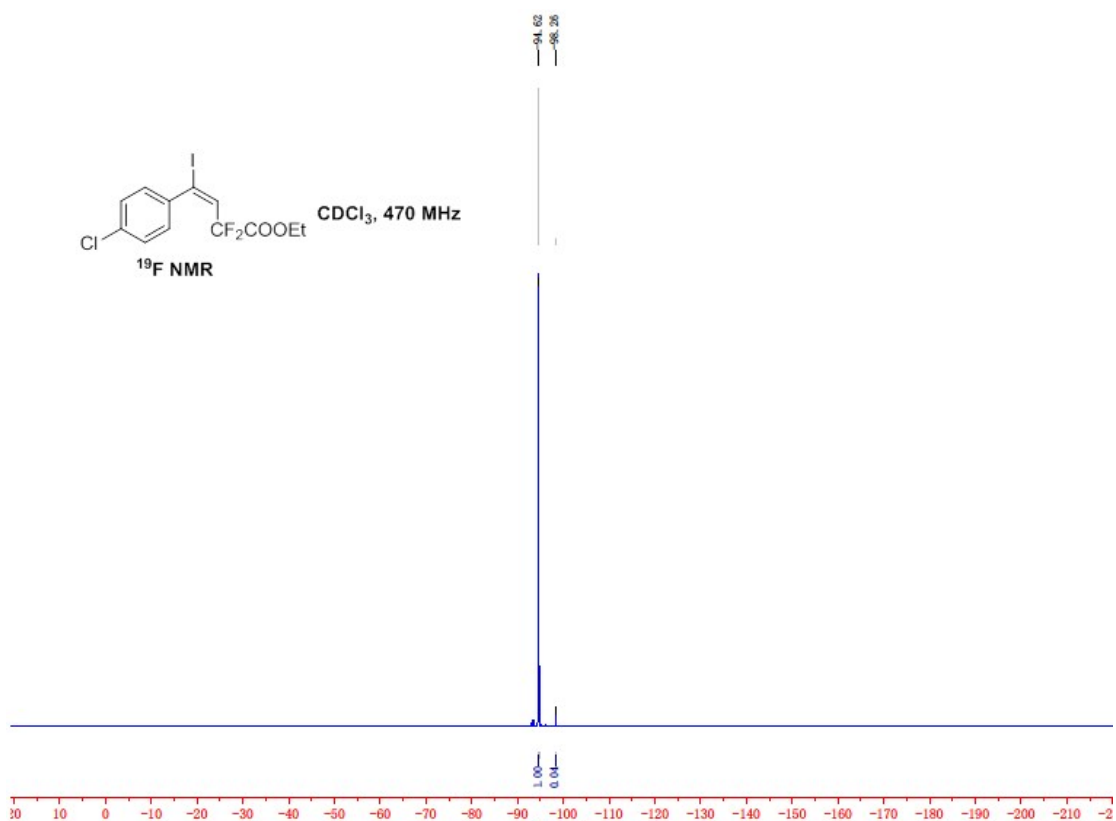
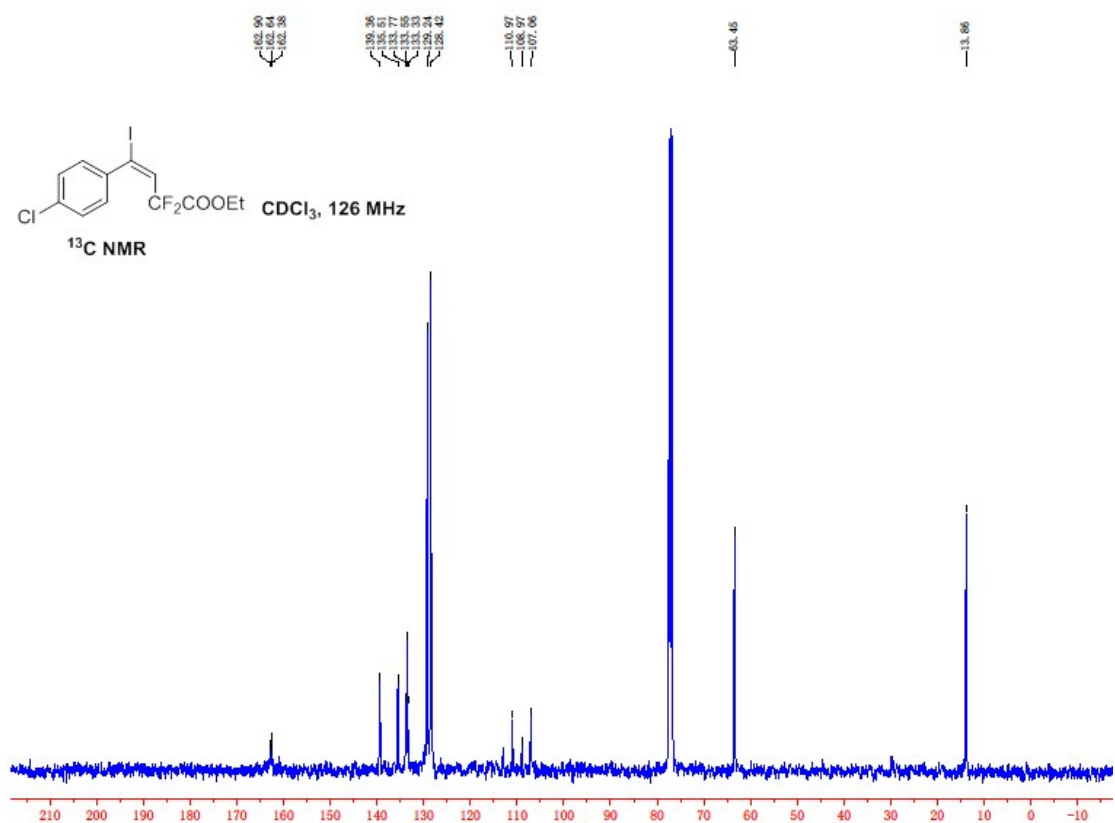


CDCl₃, 126 MHz

¹³C NMR



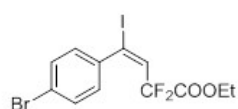




7.47
7.46
7.46
7.46
7.19
7.18
7.17
6.75
6.72
6.70

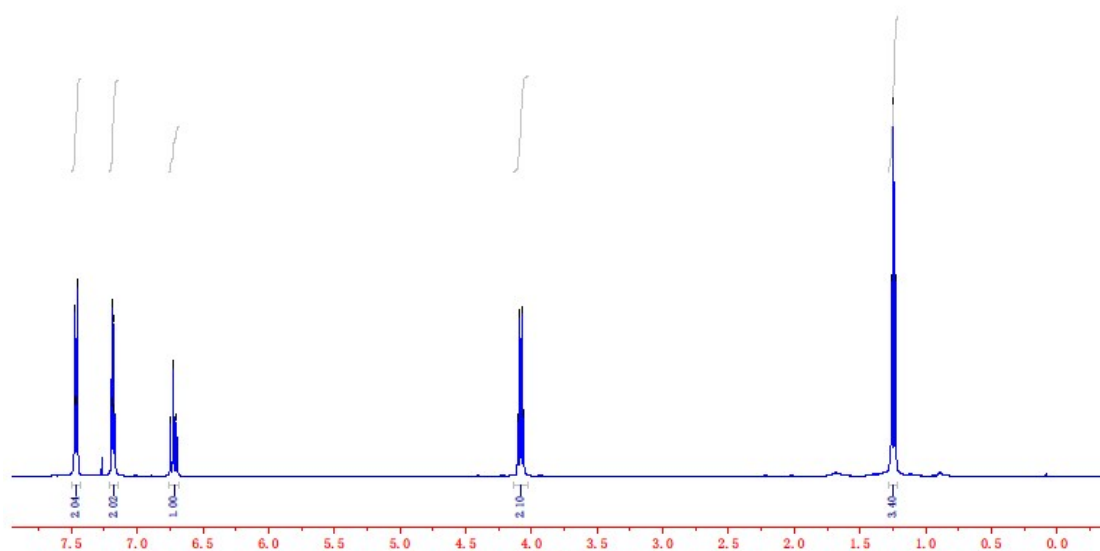
4.10
4.09
4.08

2.28
2.24
2.23



CDCl₃, 500 MHz

¹H NMR



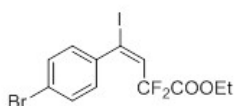
162.88
162.82
162.96

139.84
133.74
133.53
133.50
131.40
129.44
123.77

112.98
108.98
108.98
107.06

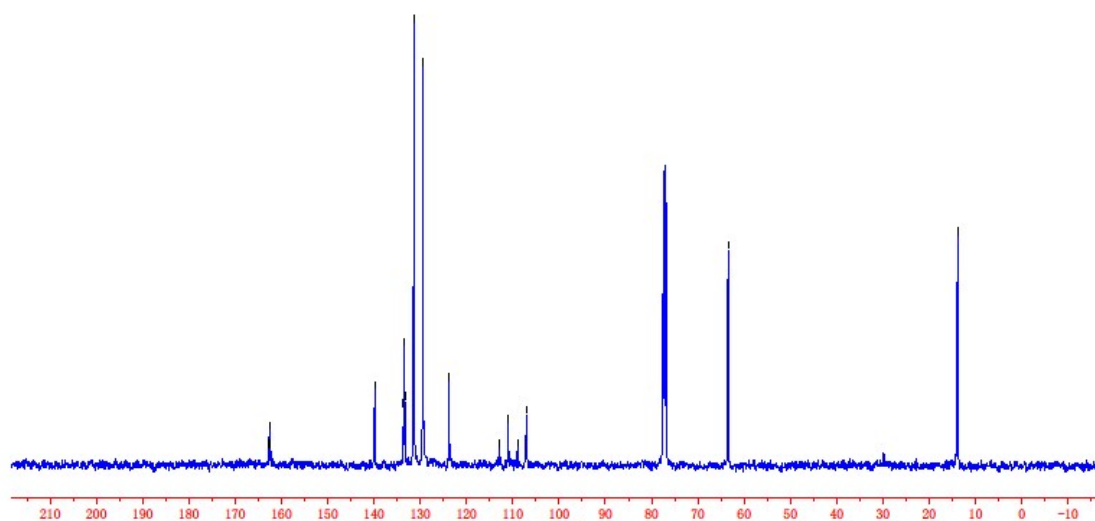
63.47

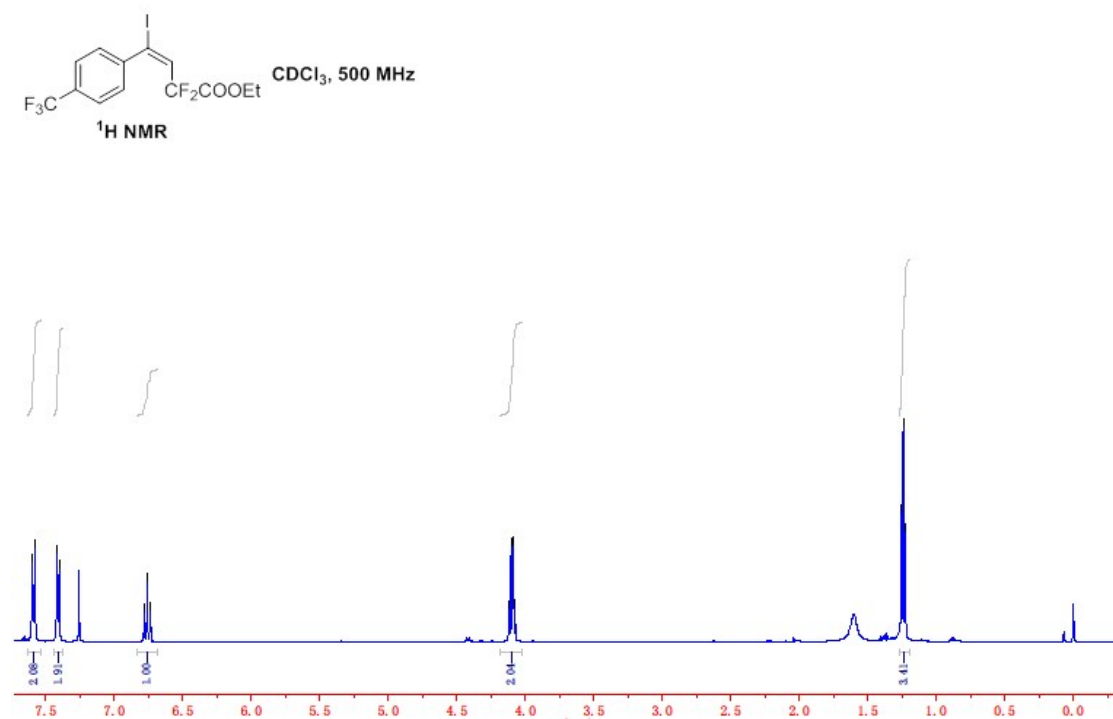
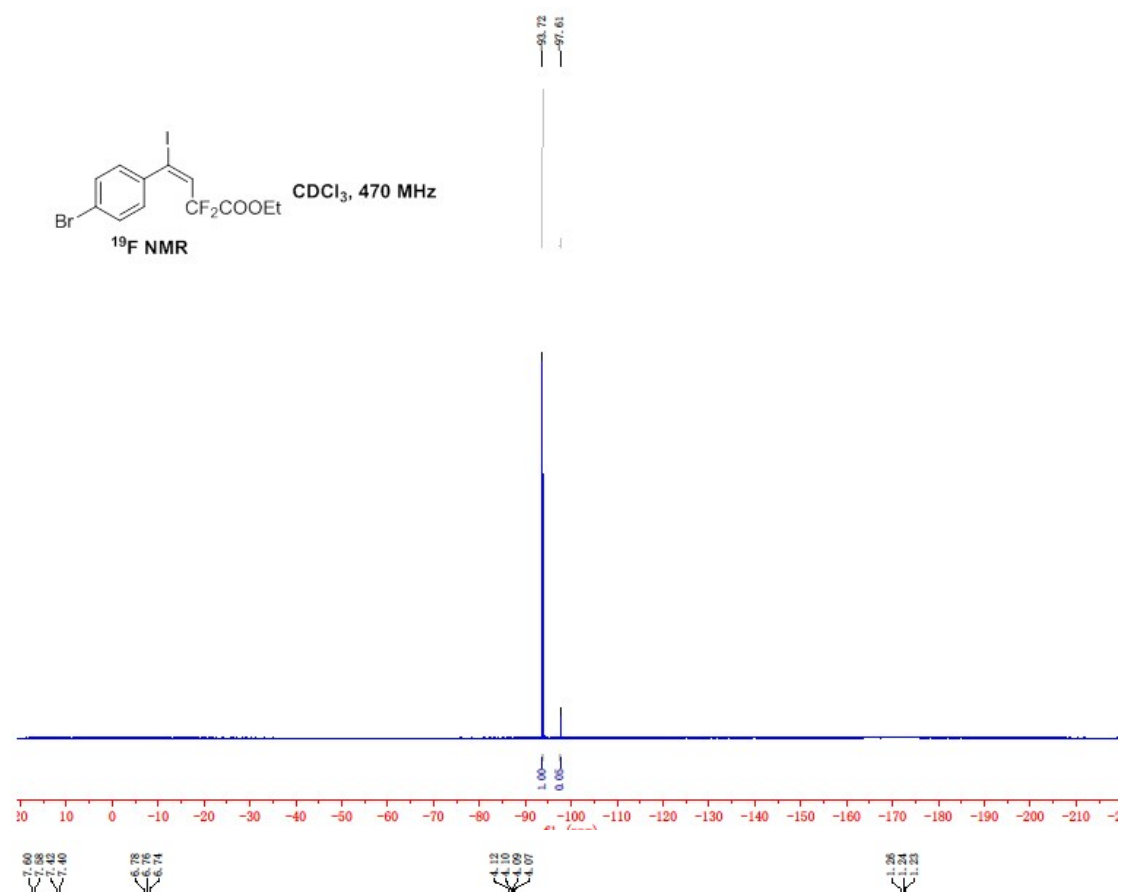
13.88

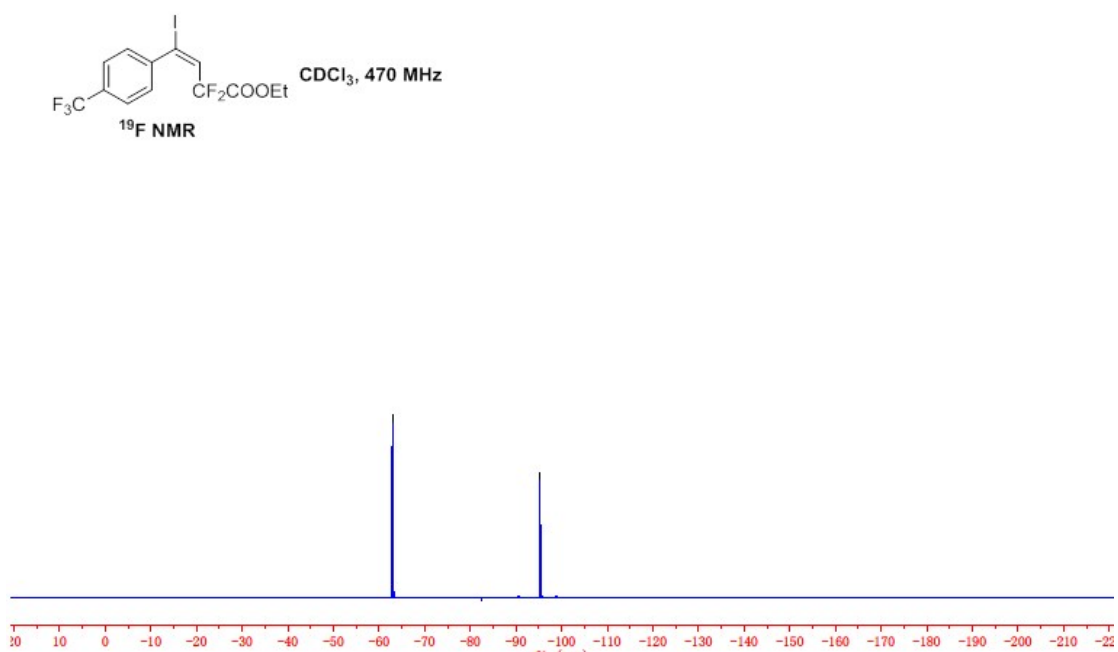
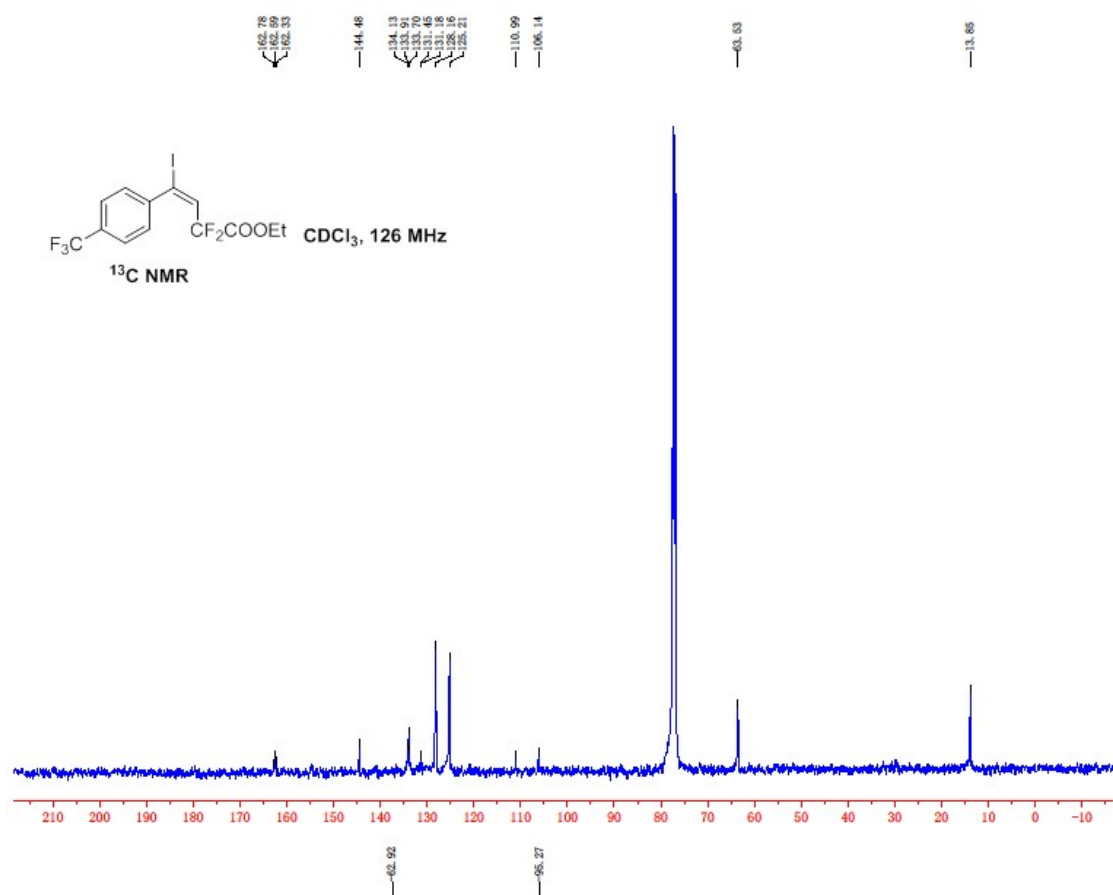


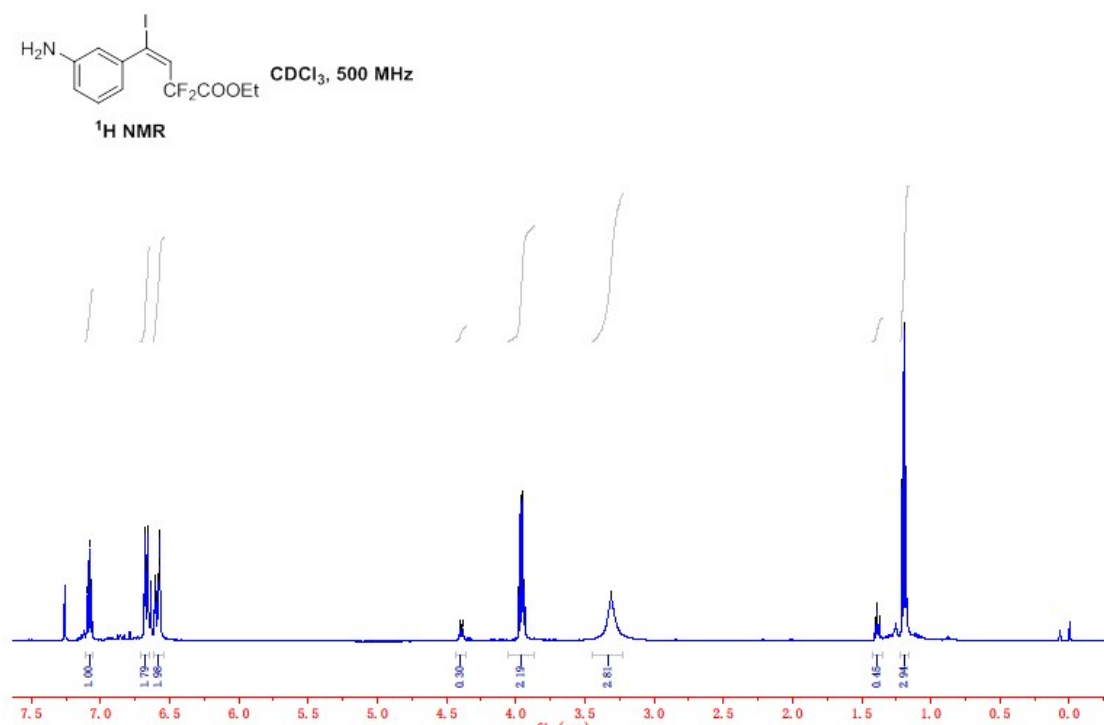
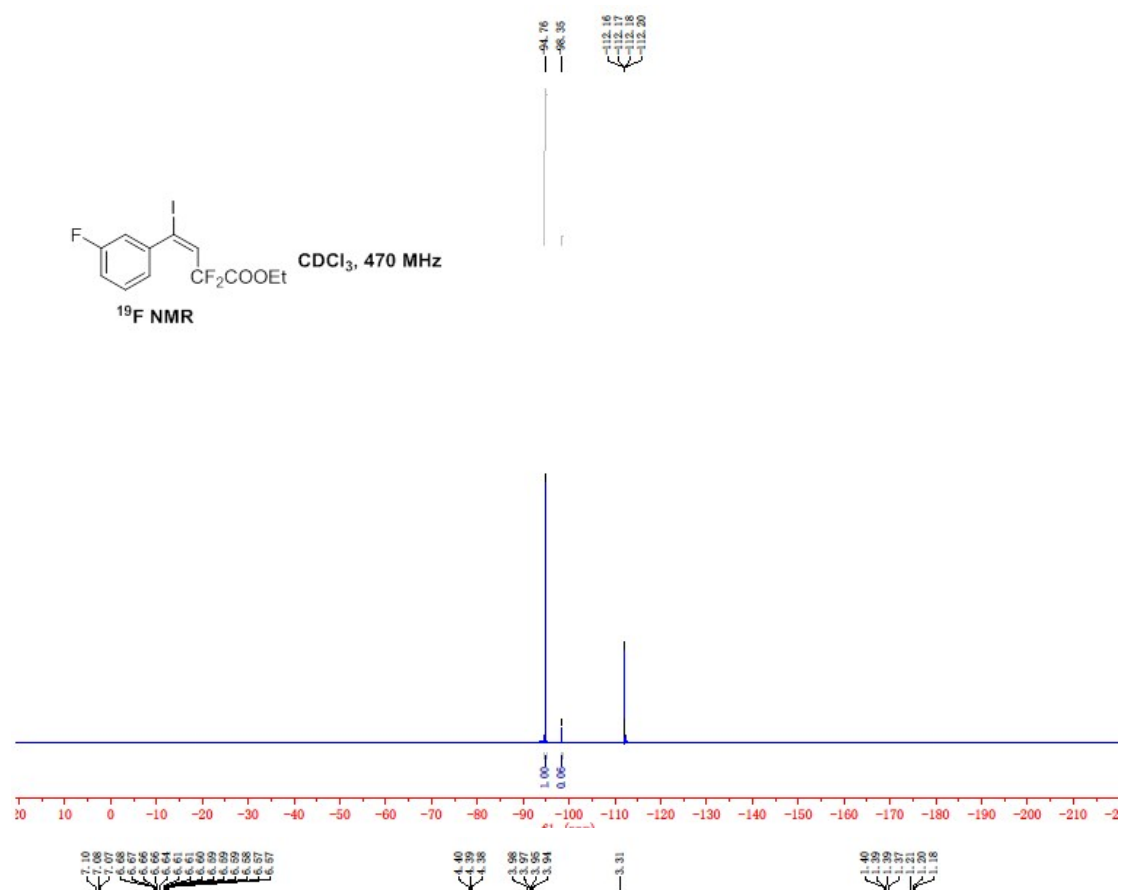
CDCl₃, 126 MHz

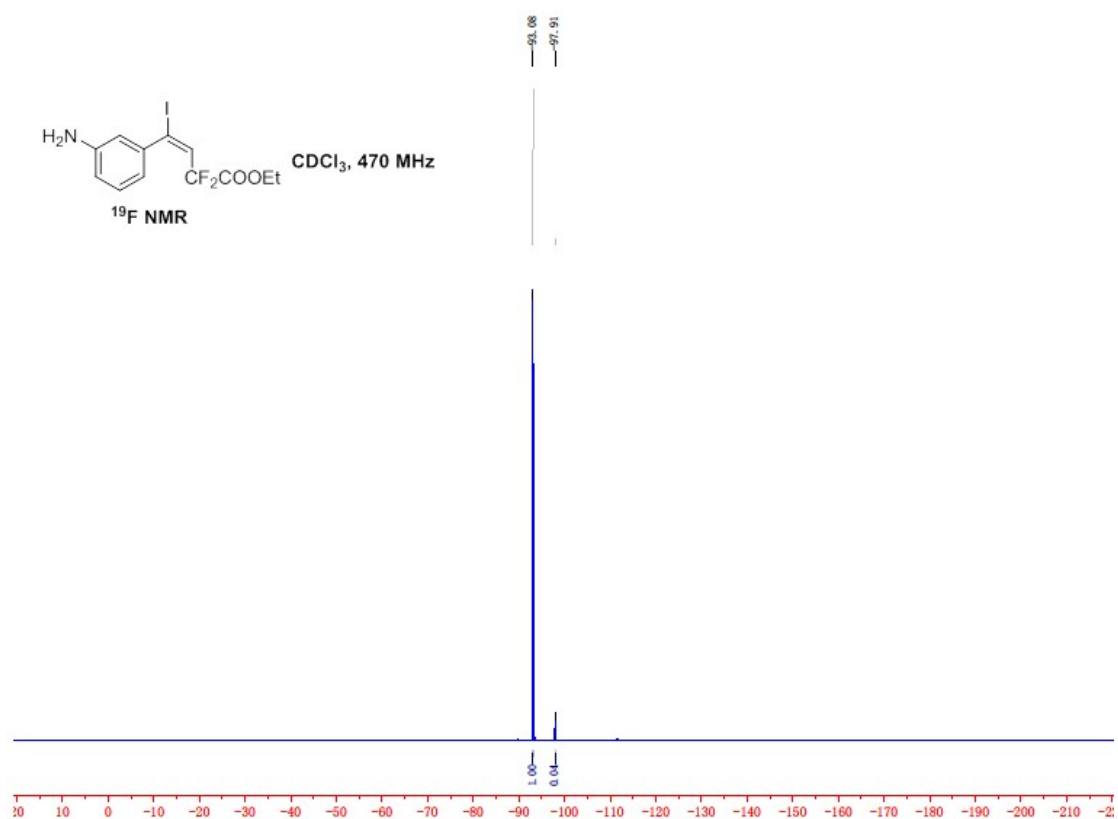
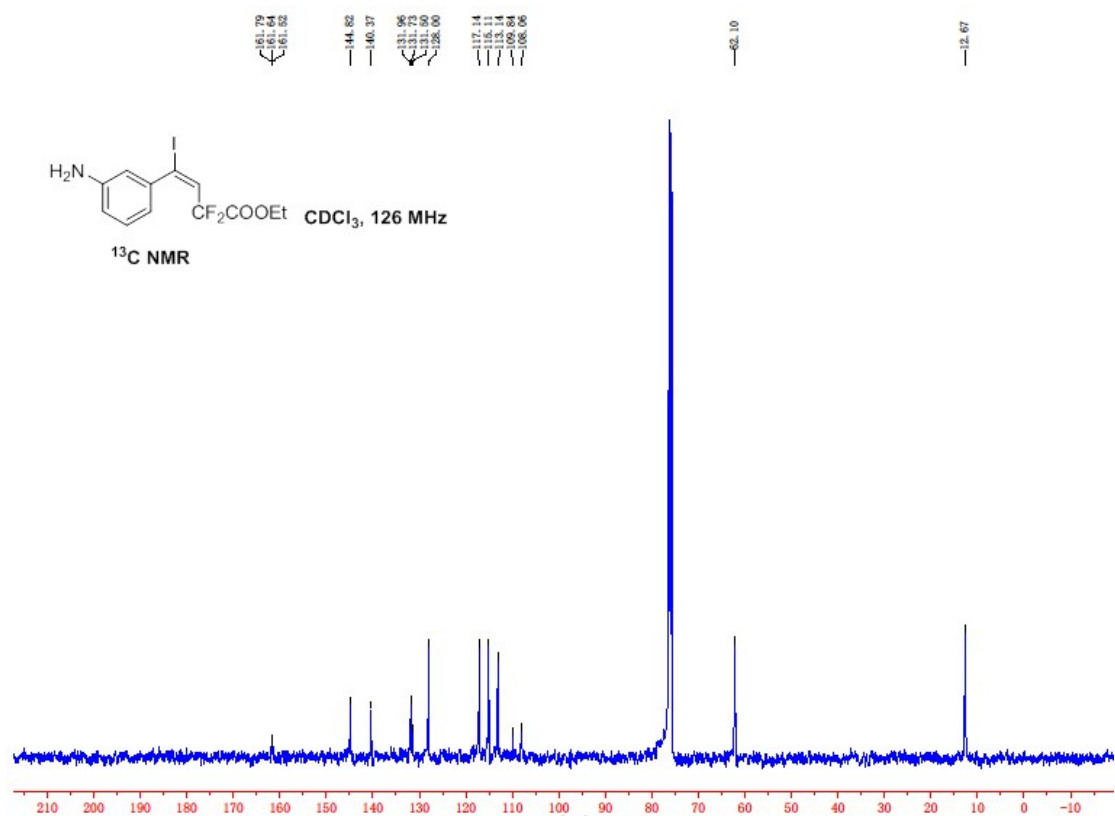
¹³C NMR

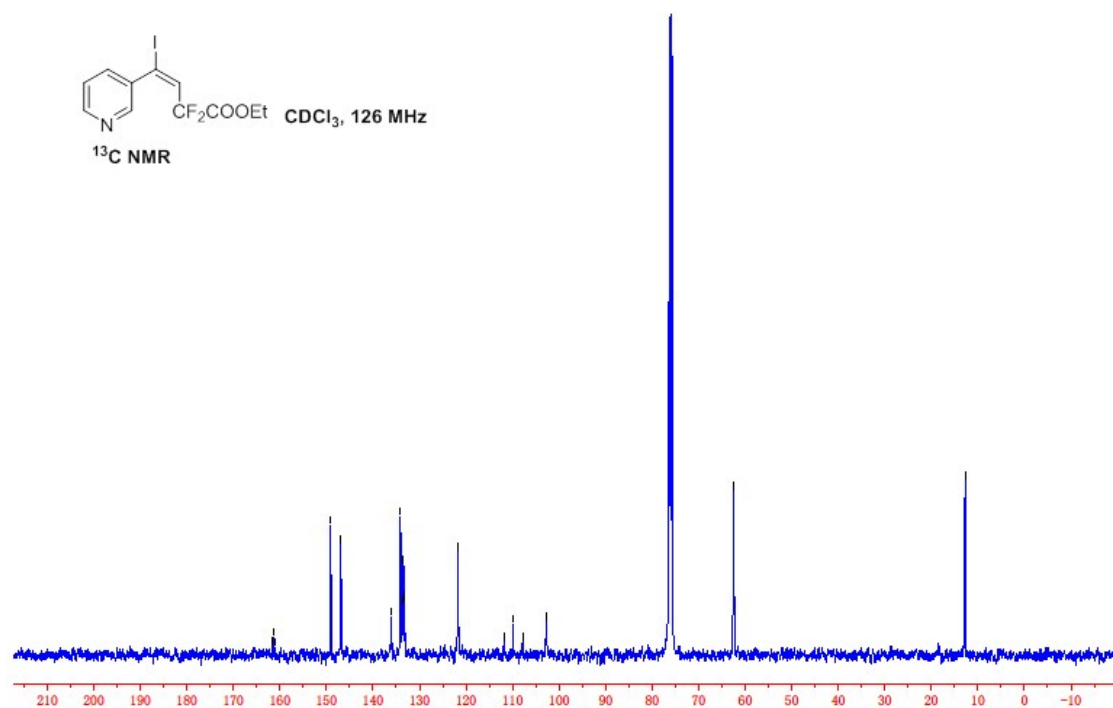
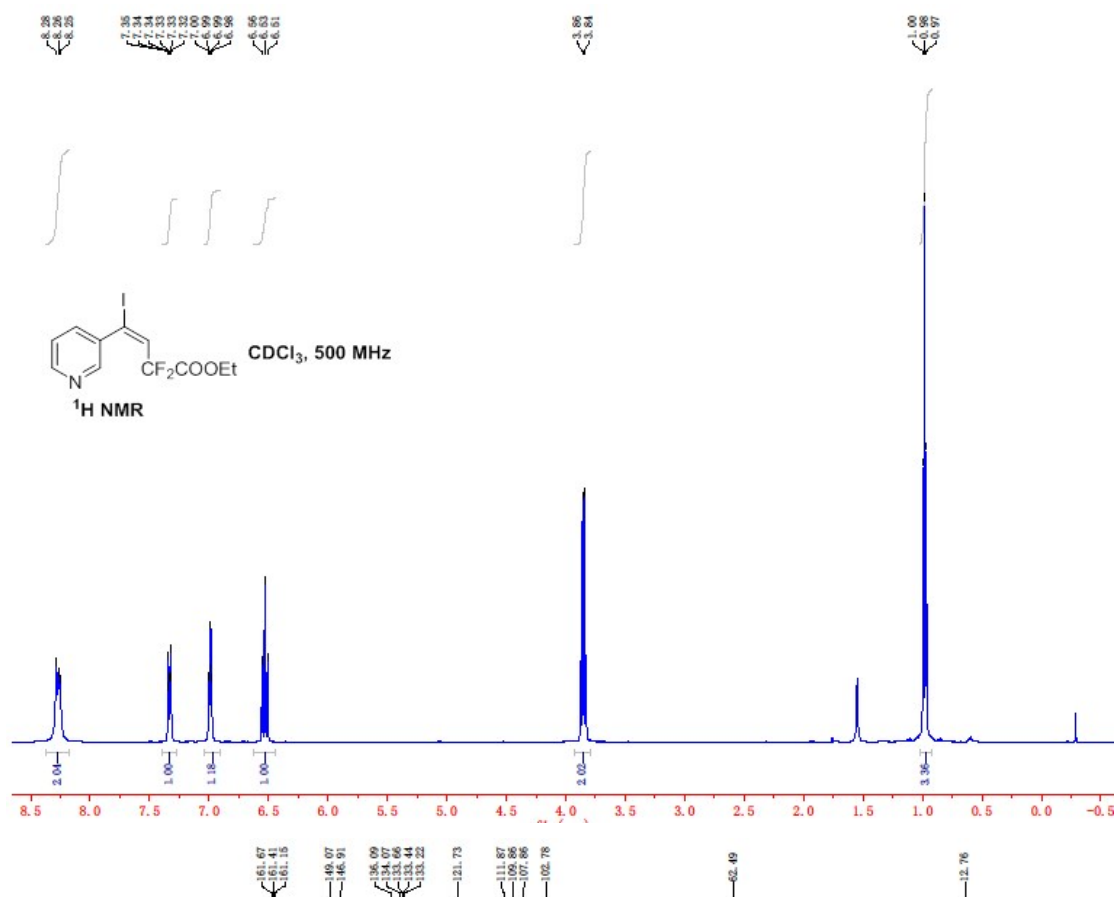


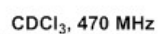
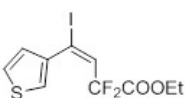




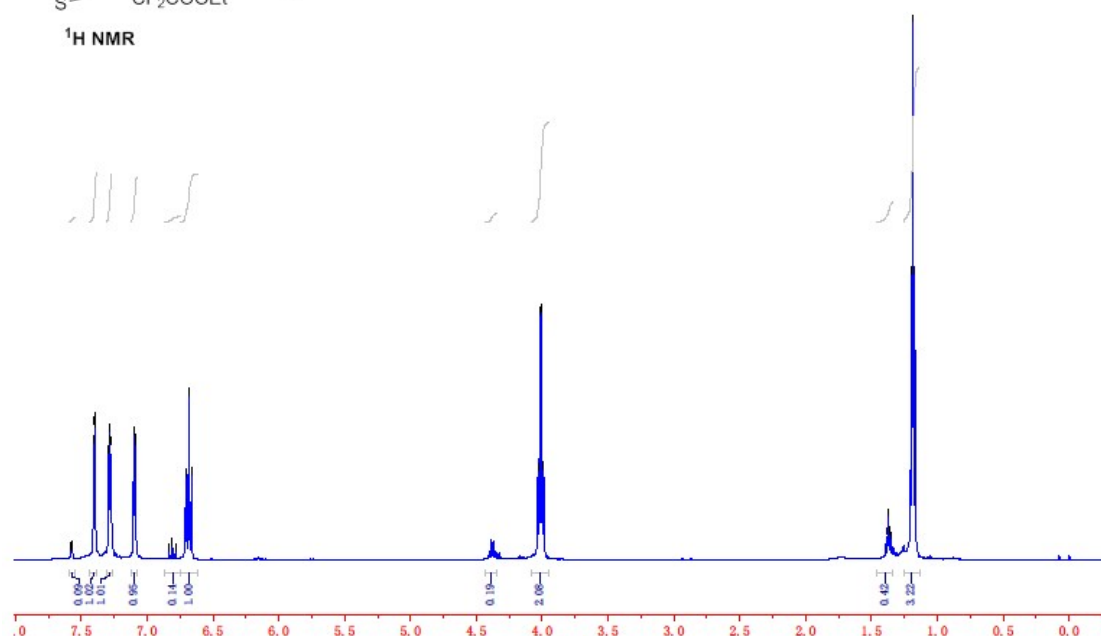


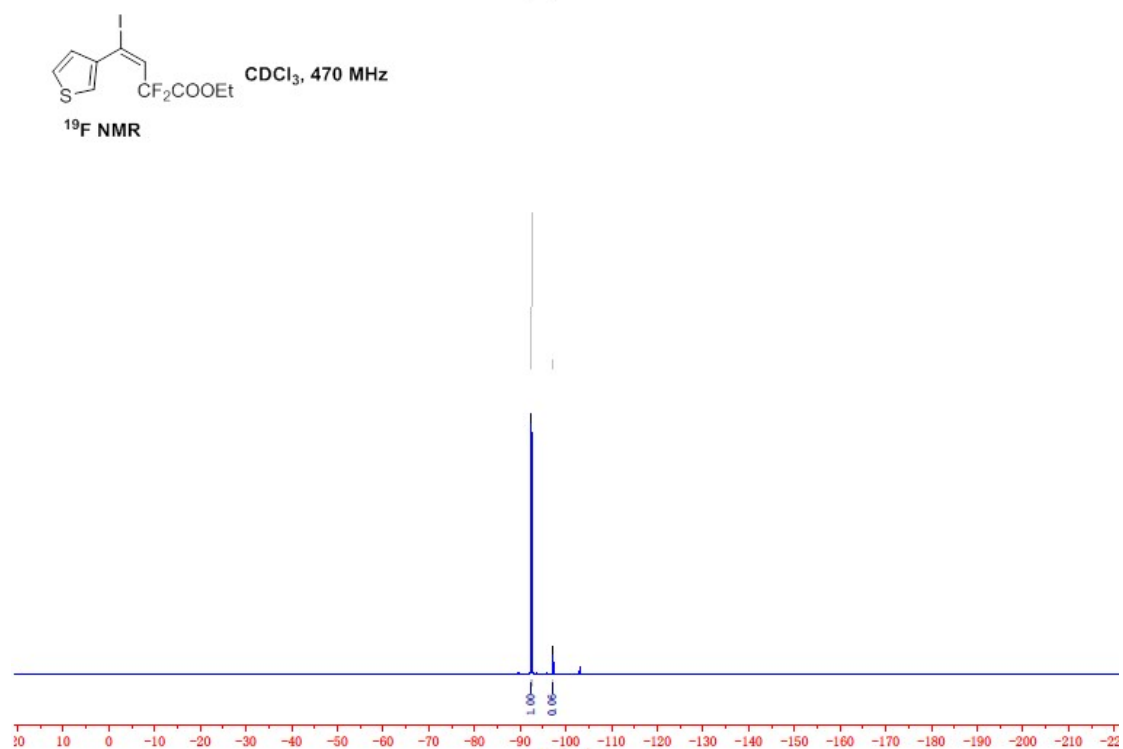
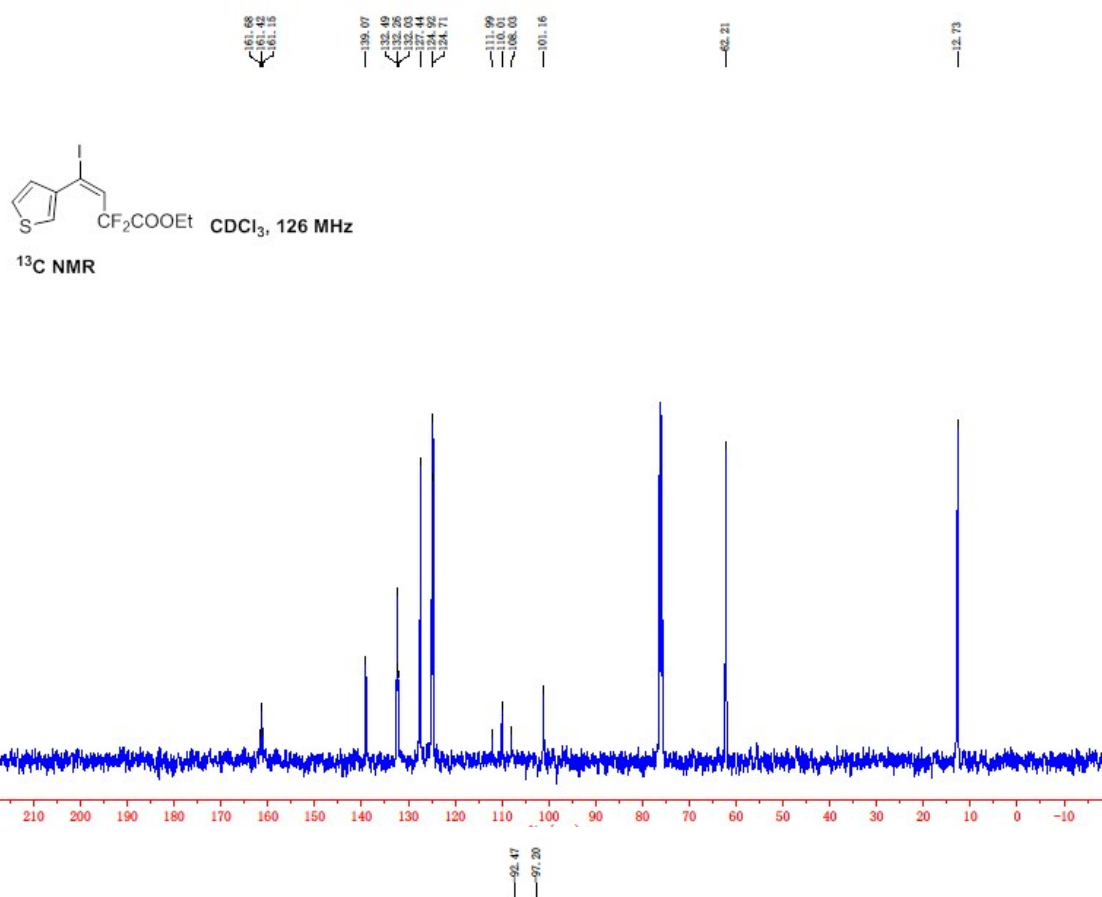


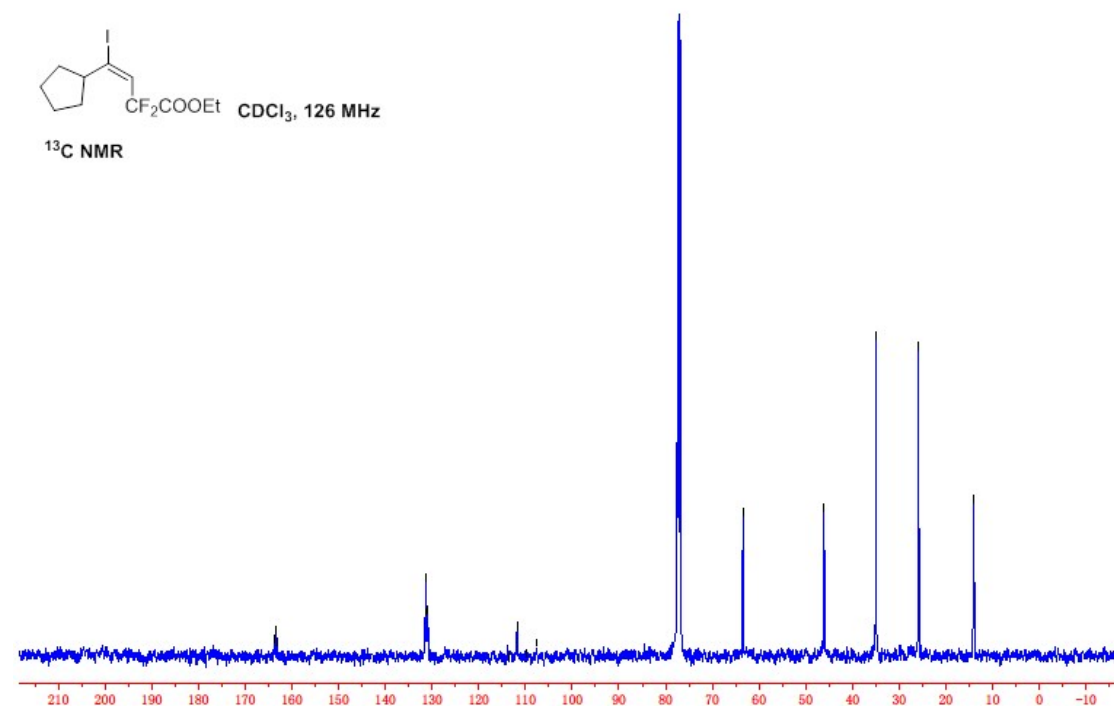
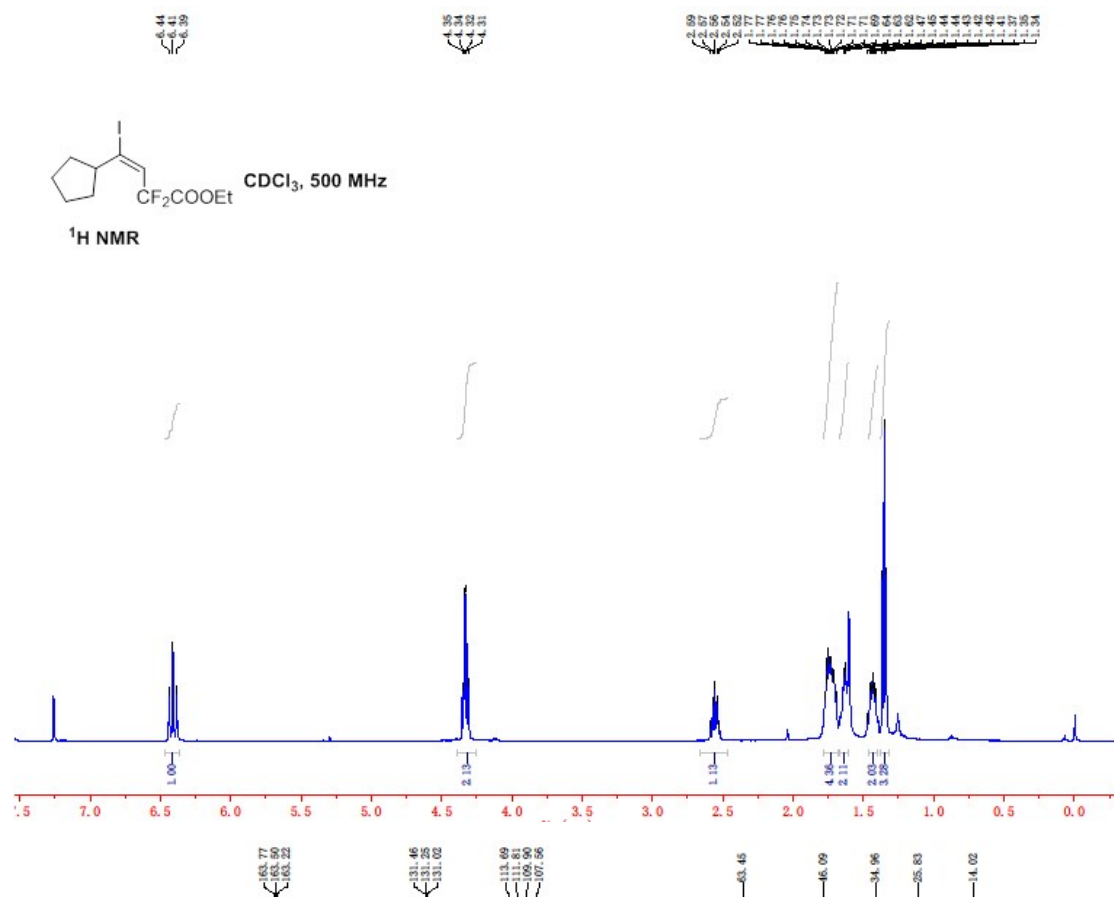


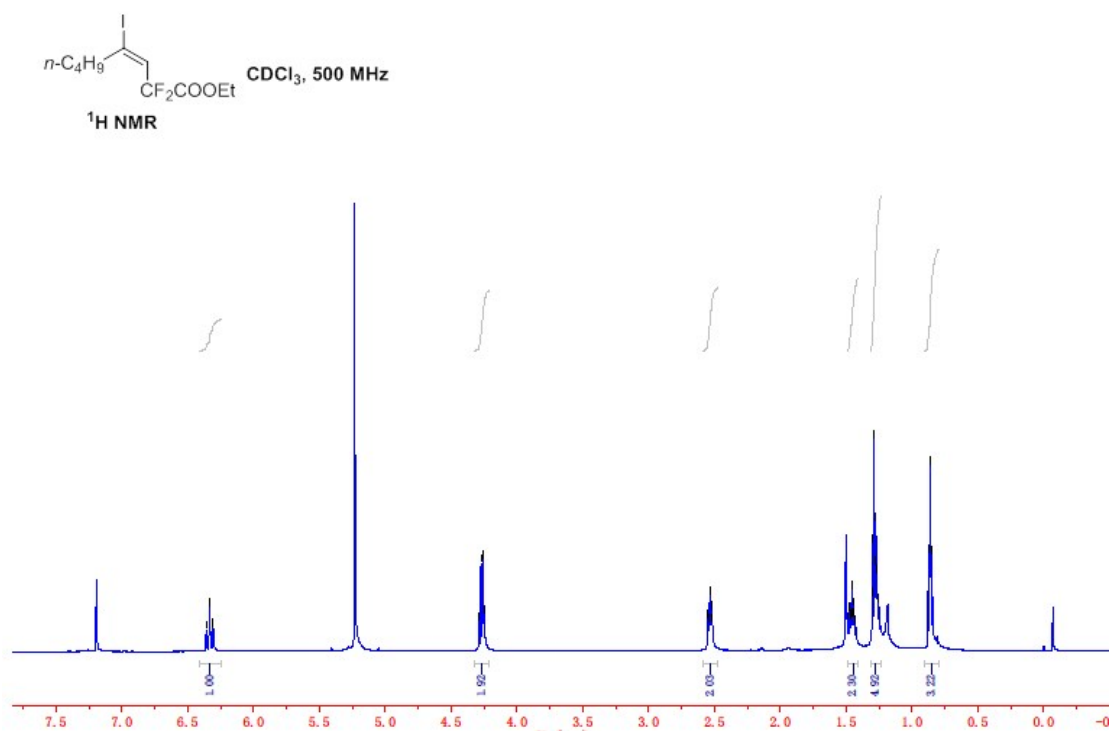
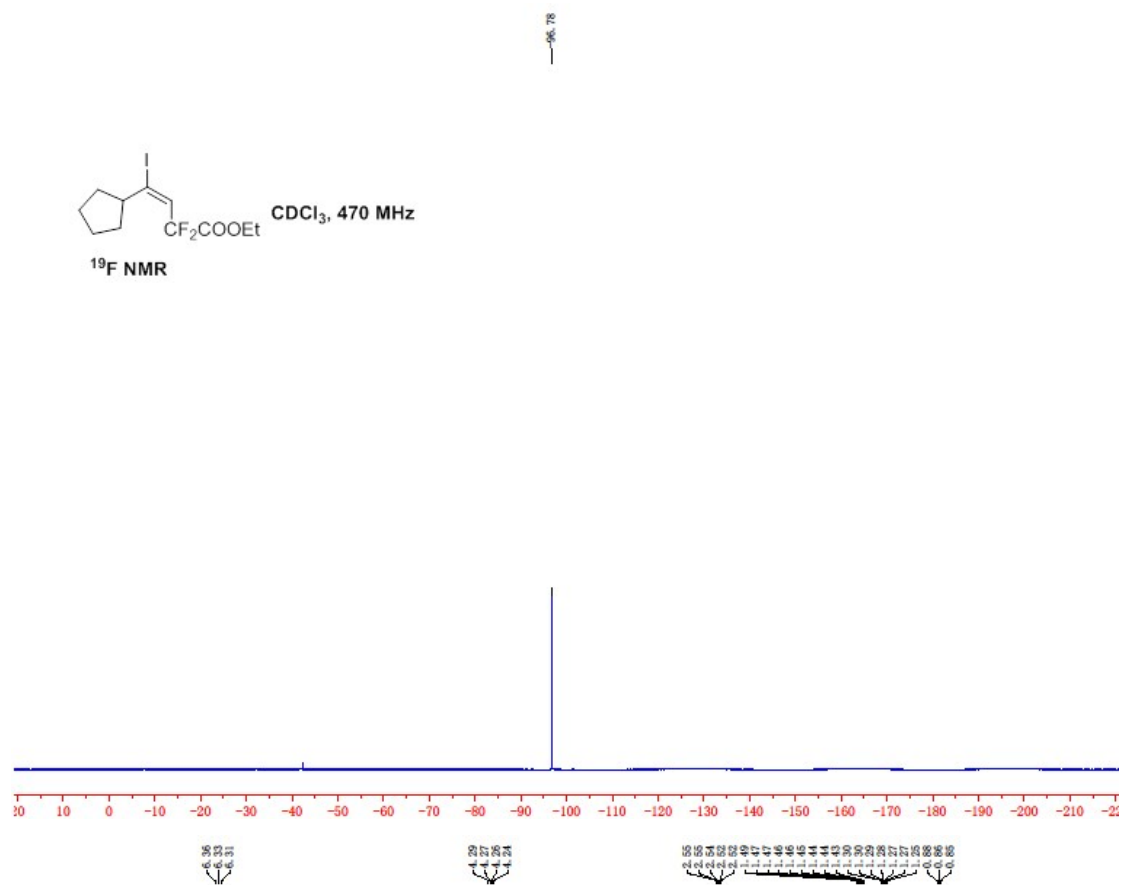
¹⁹F NMR

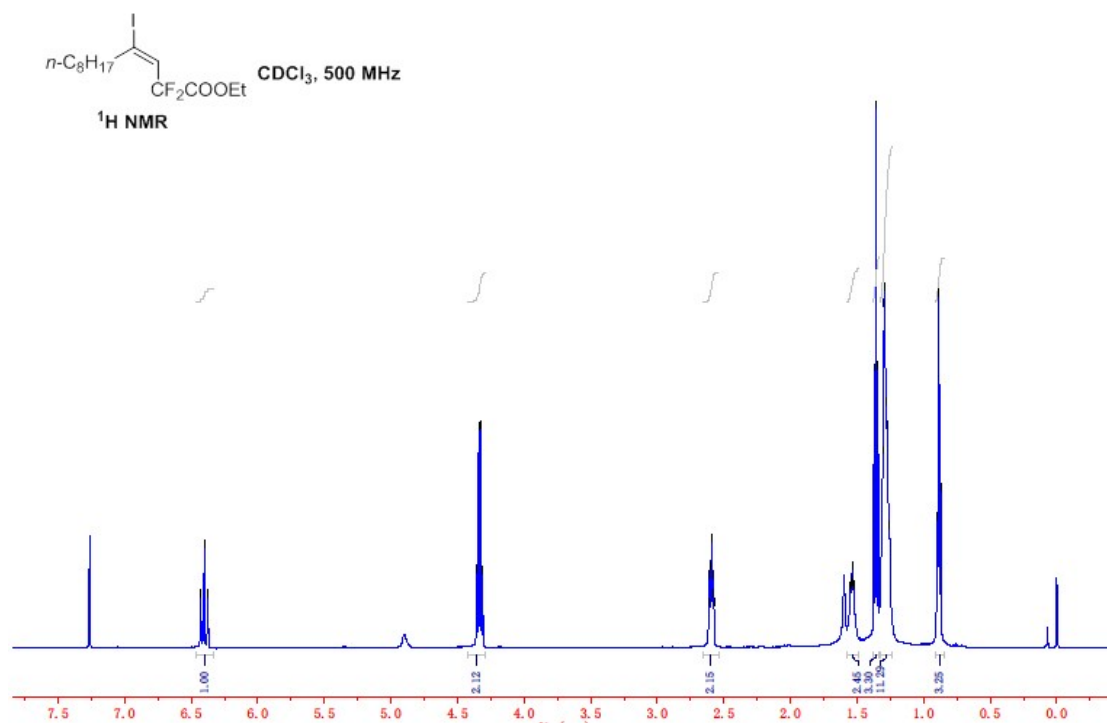
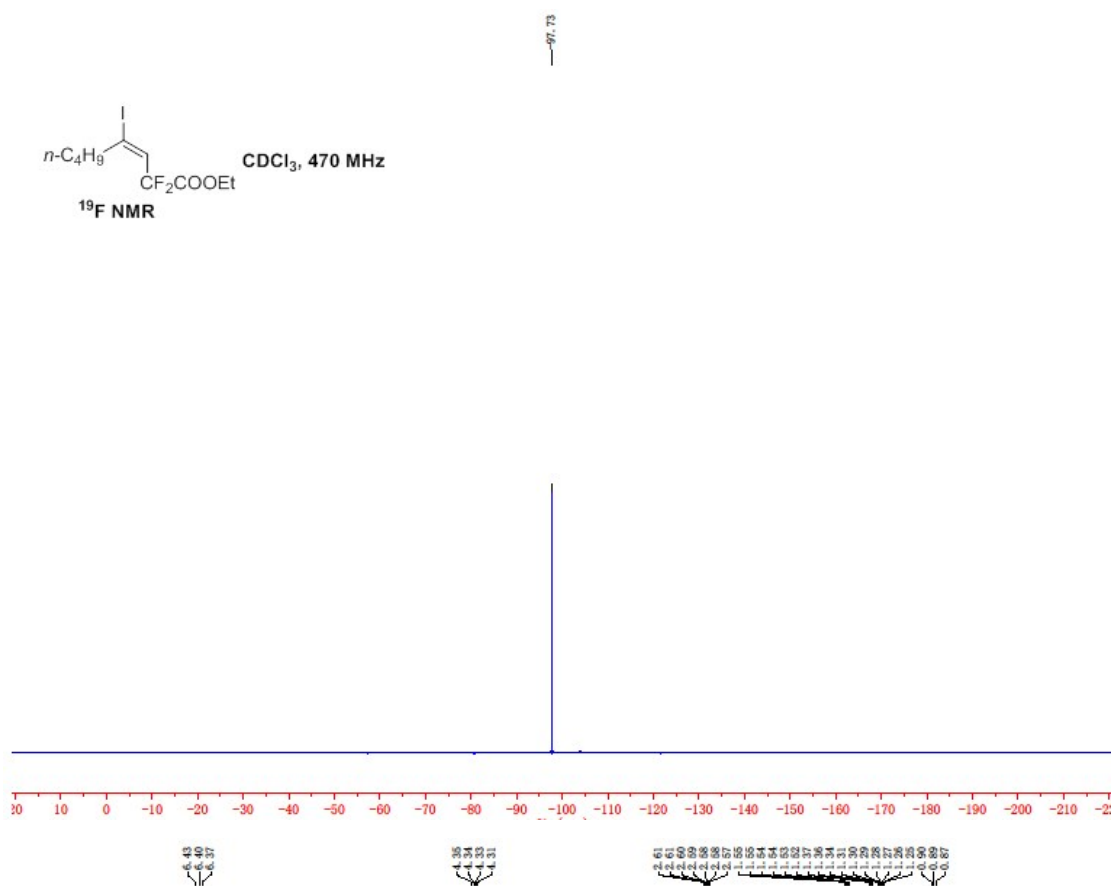
CDCl₃, 500 MHz

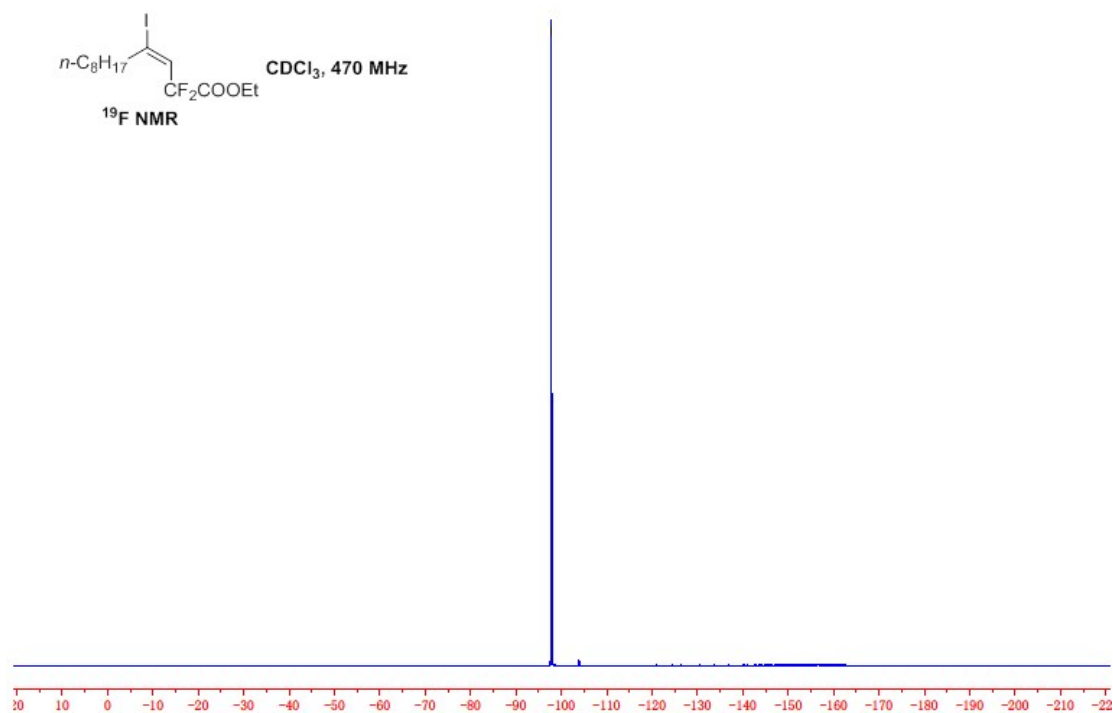
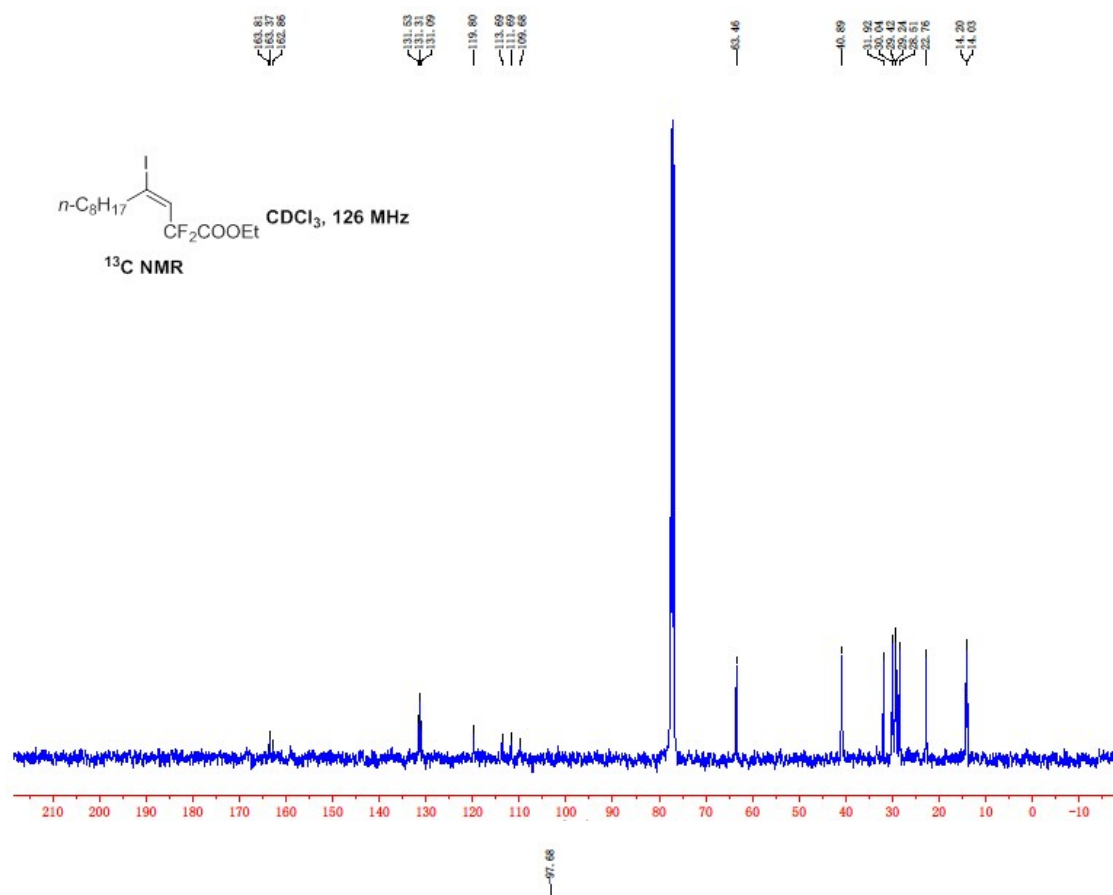
¹H NMR

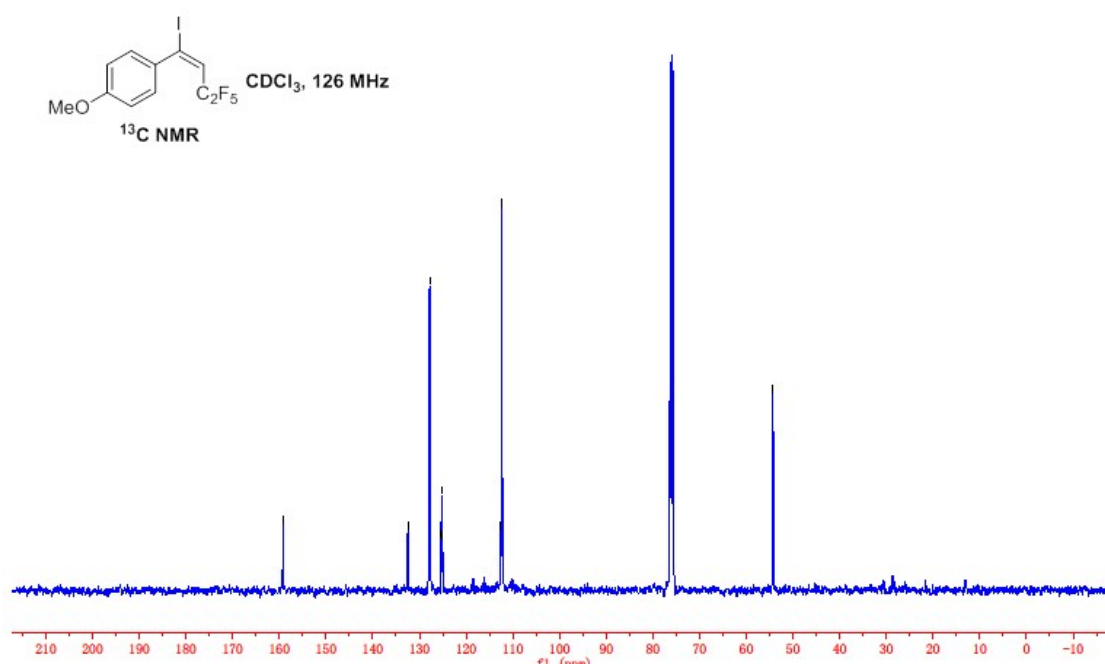
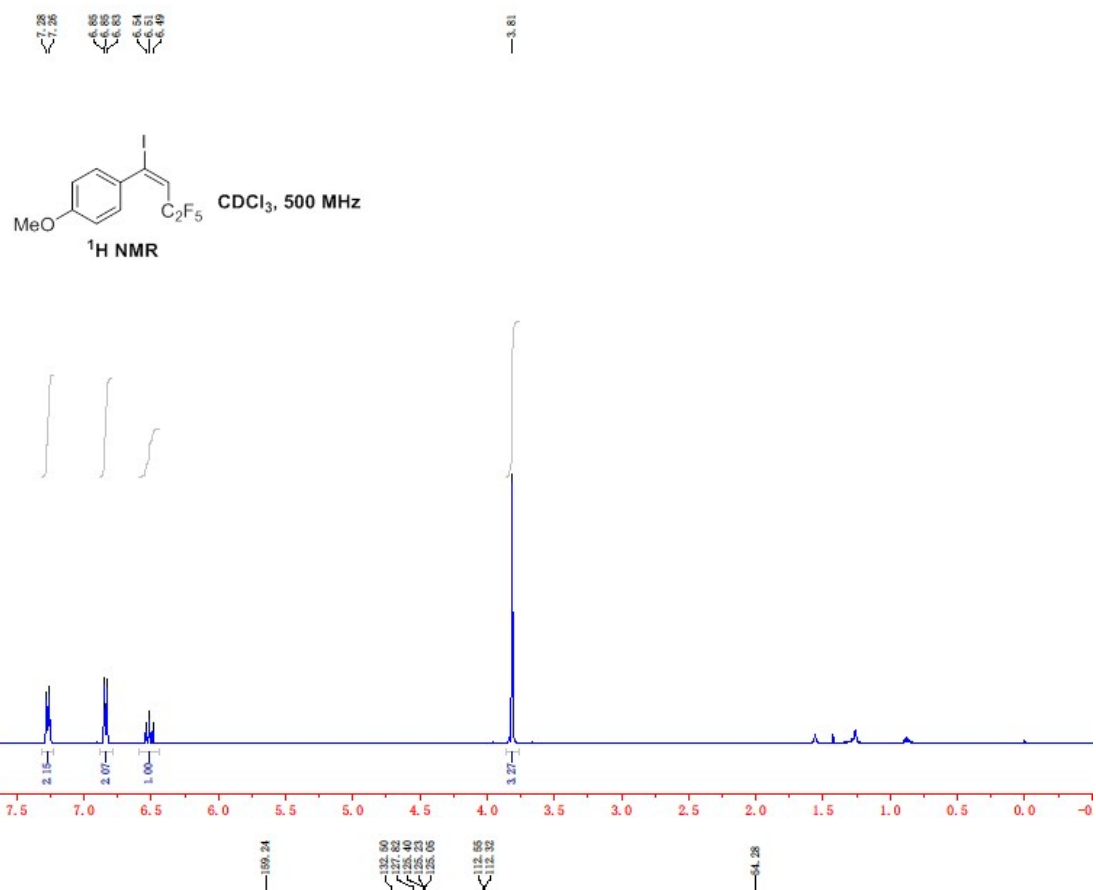


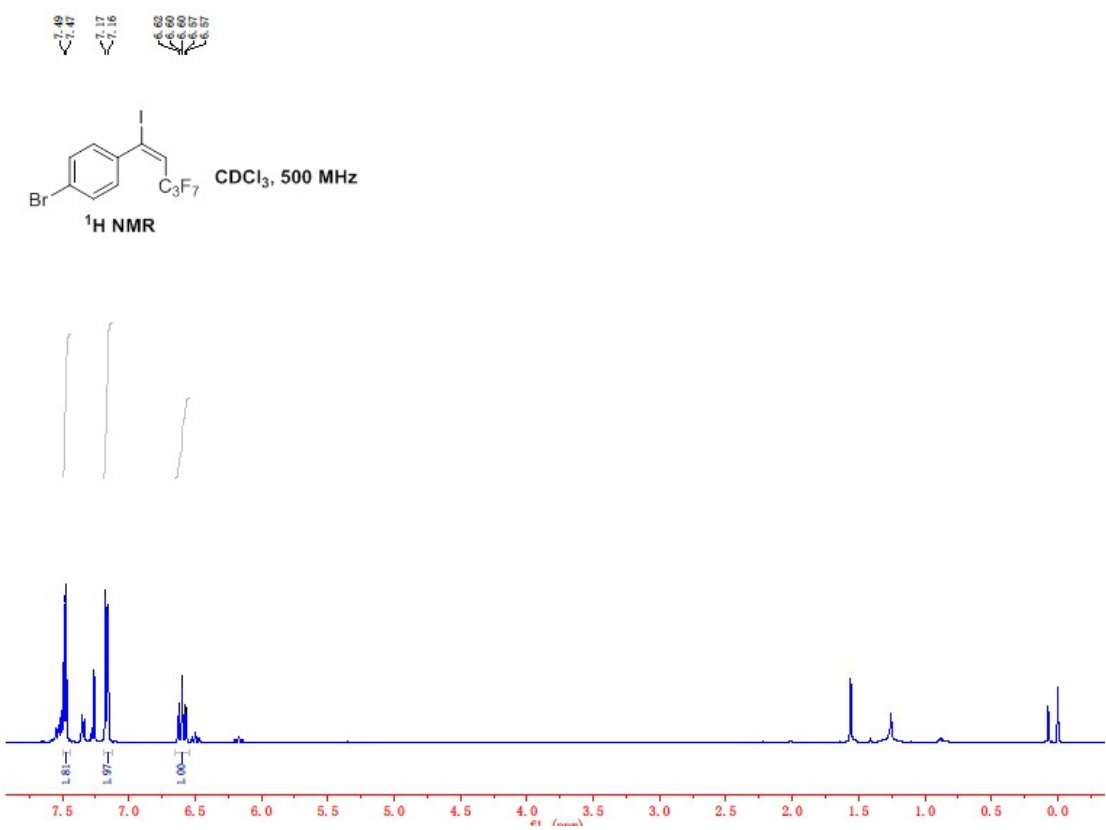
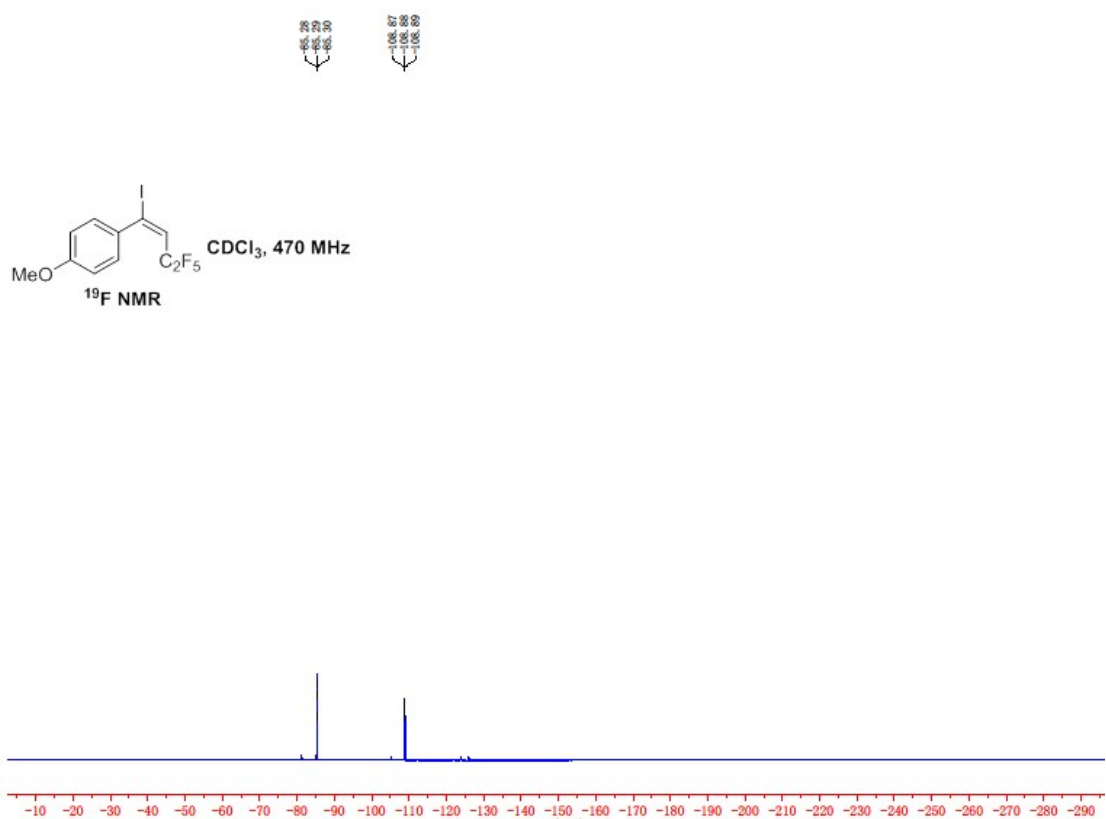


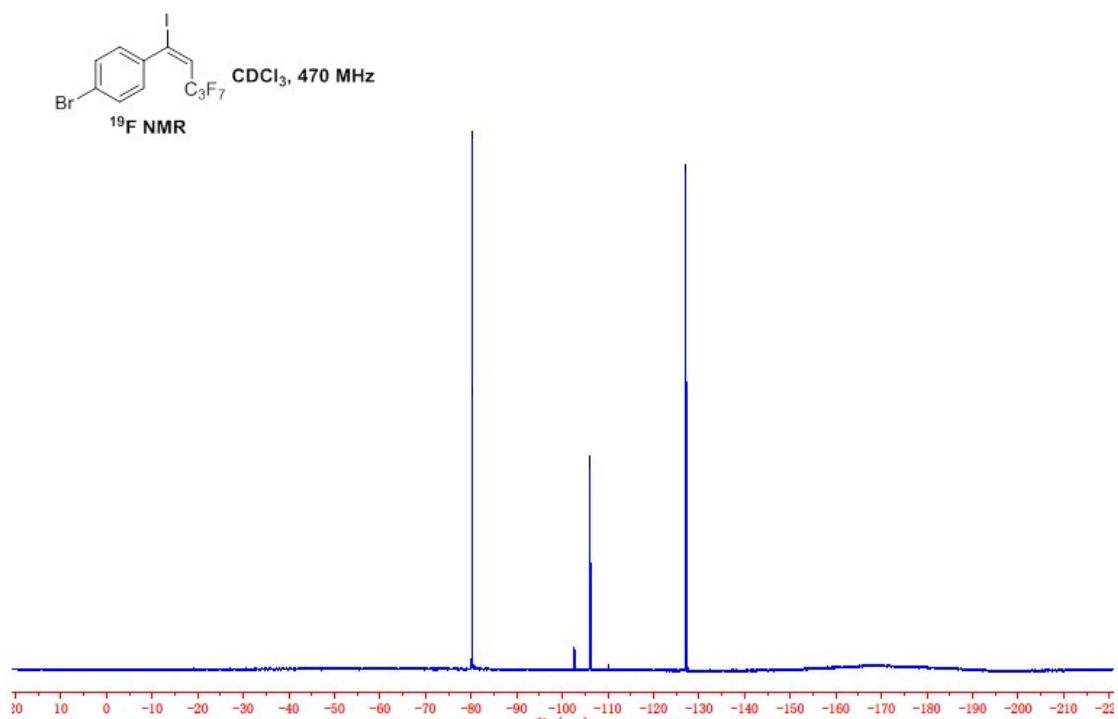
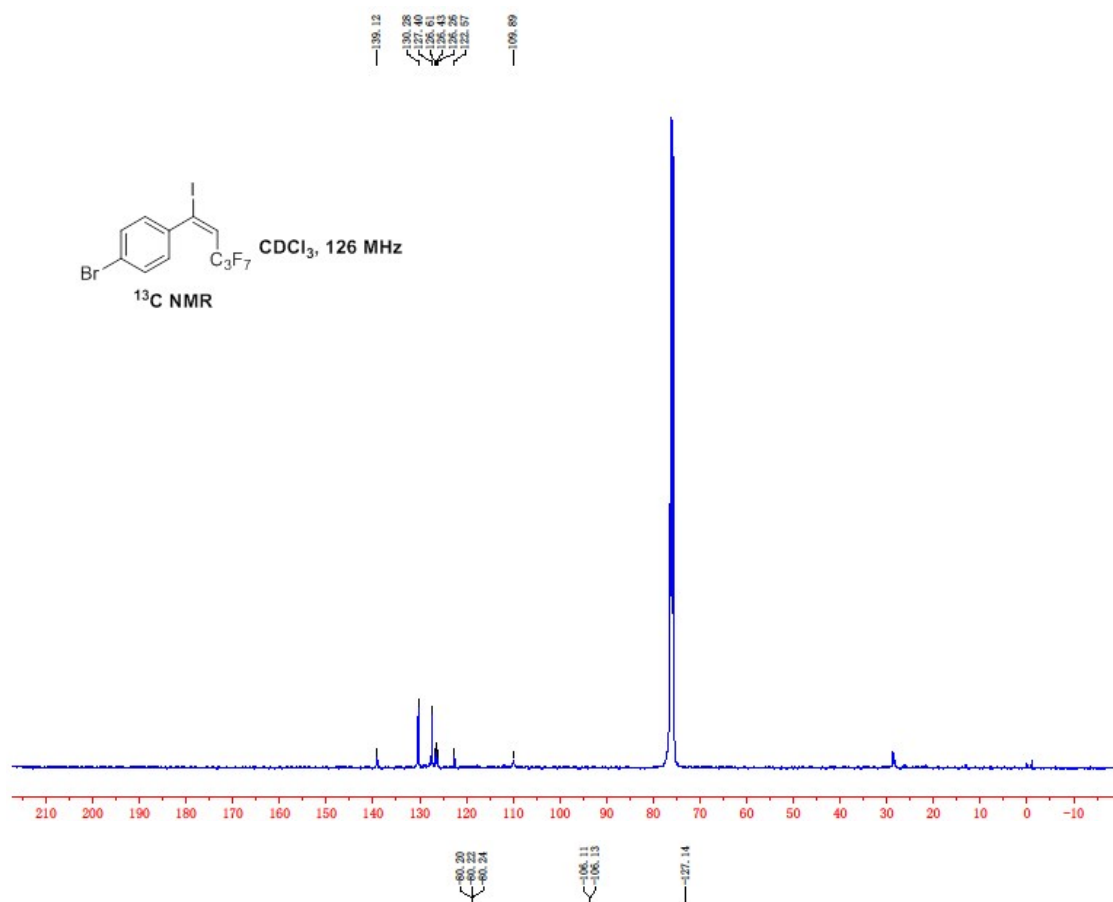


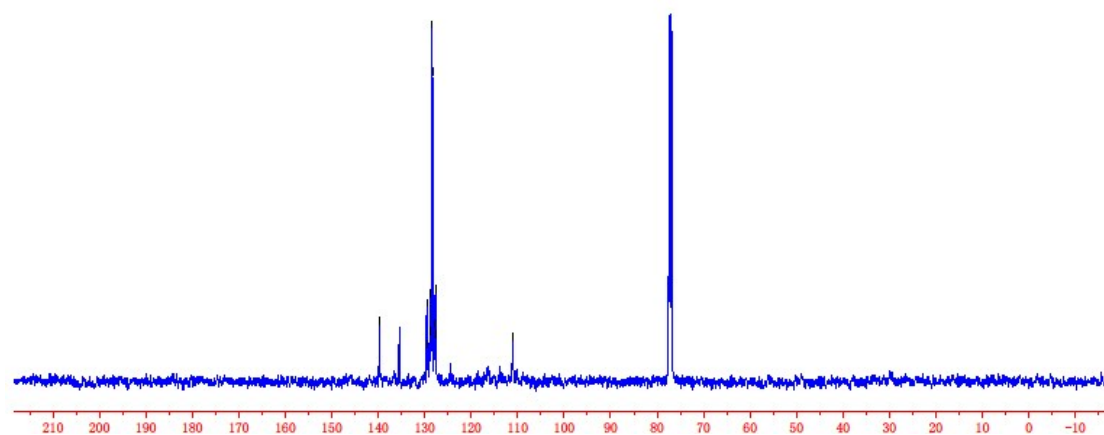
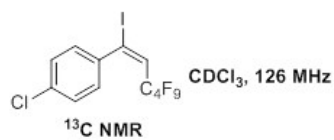
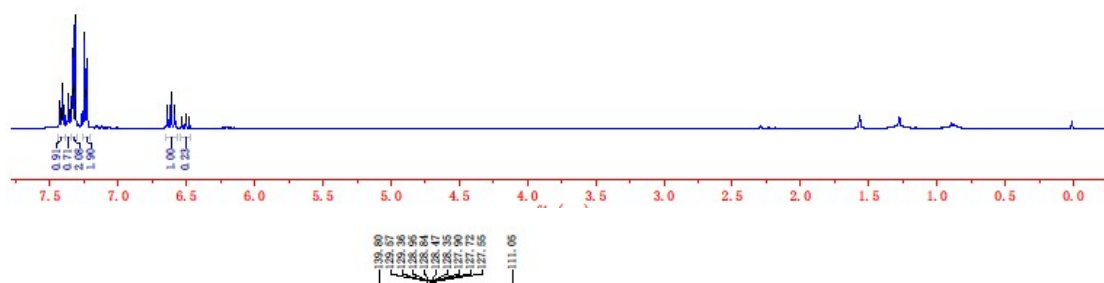
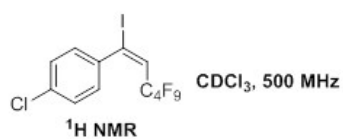
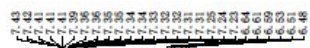


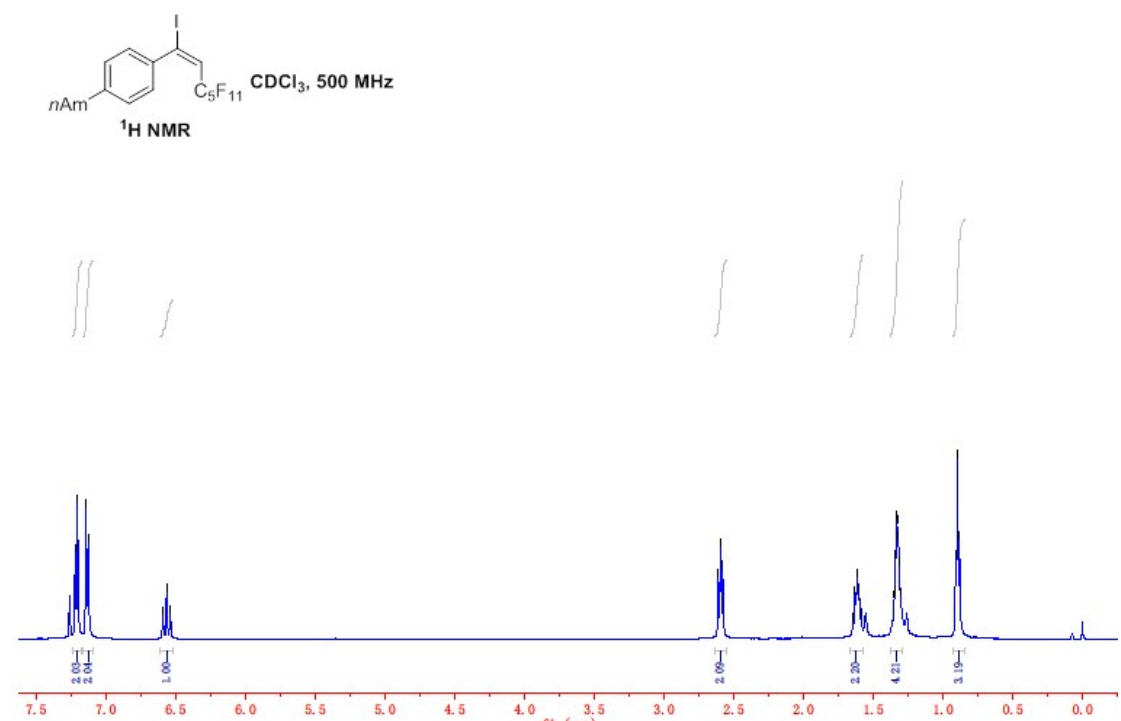
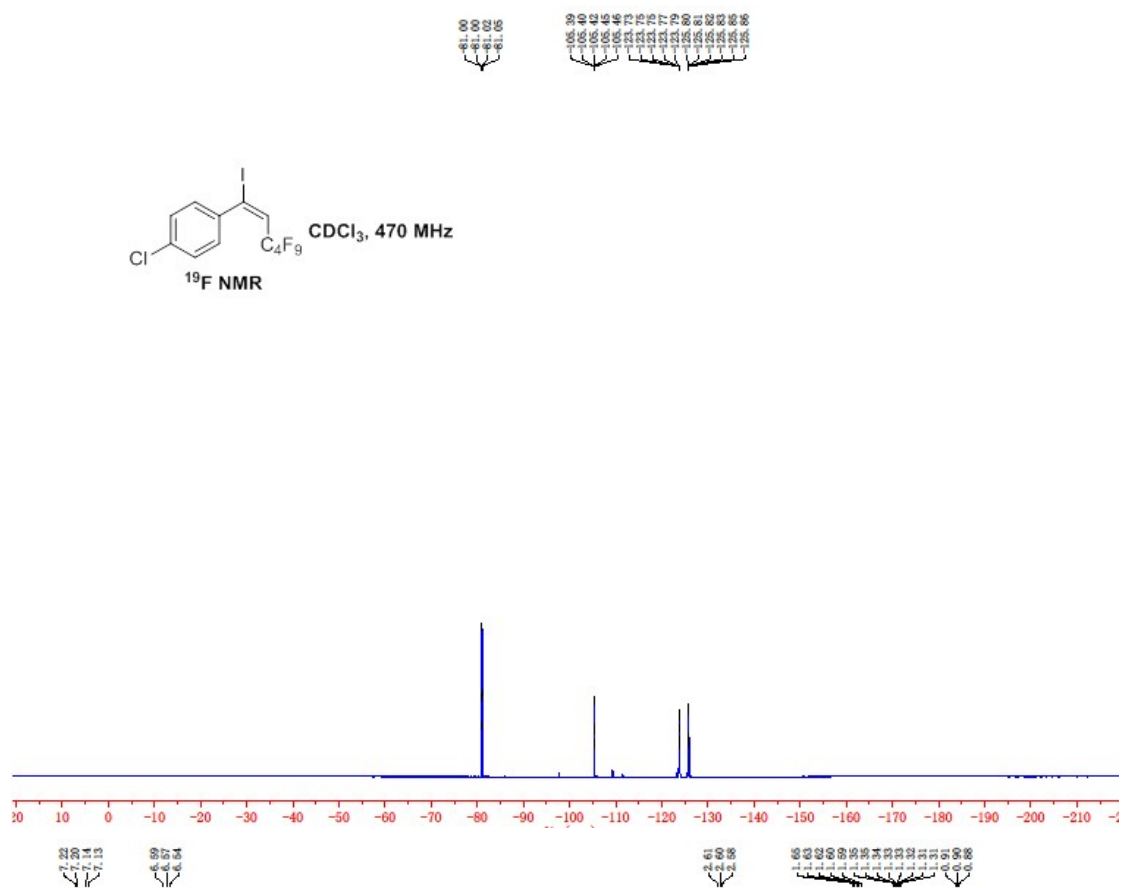


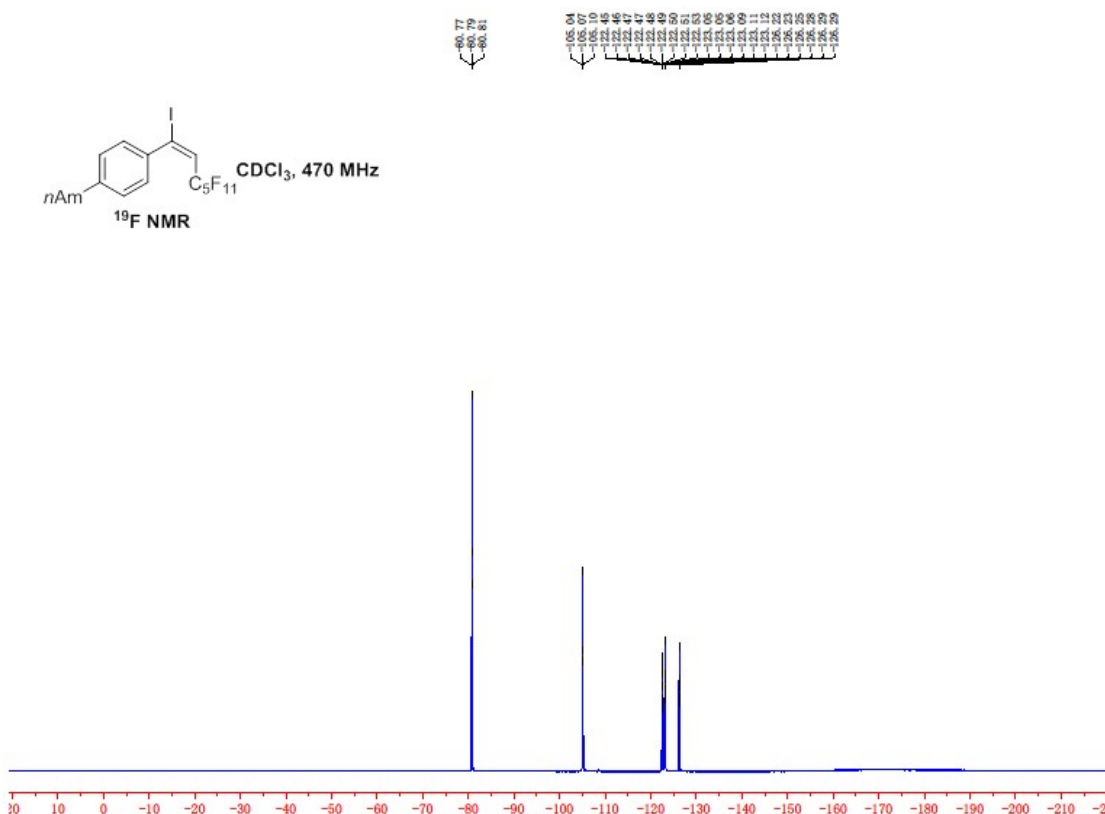


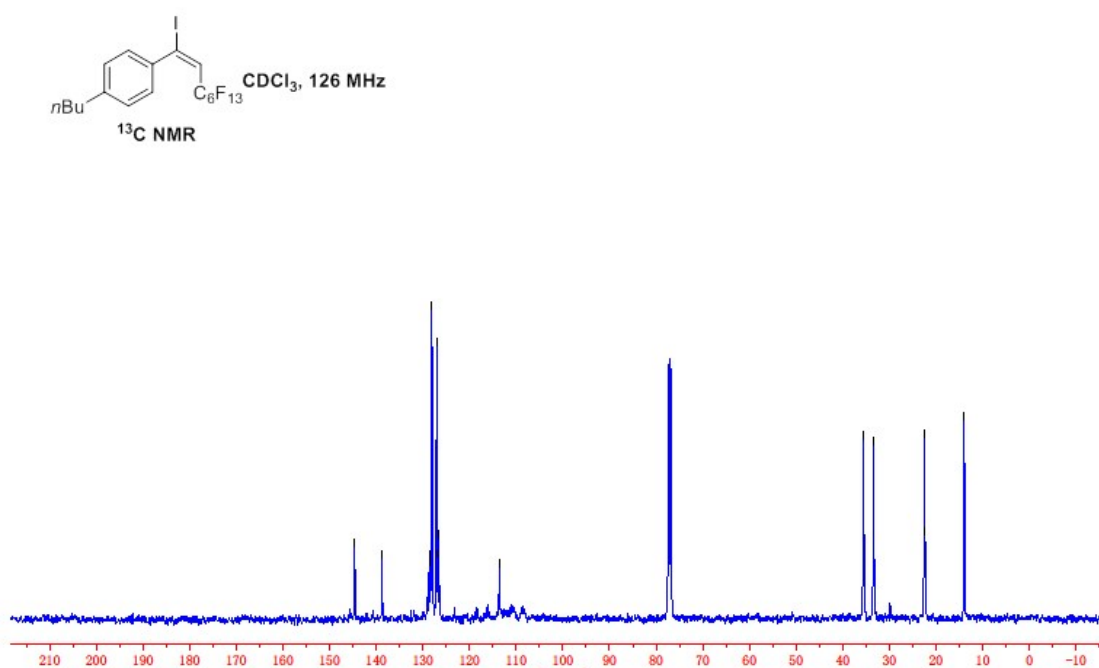
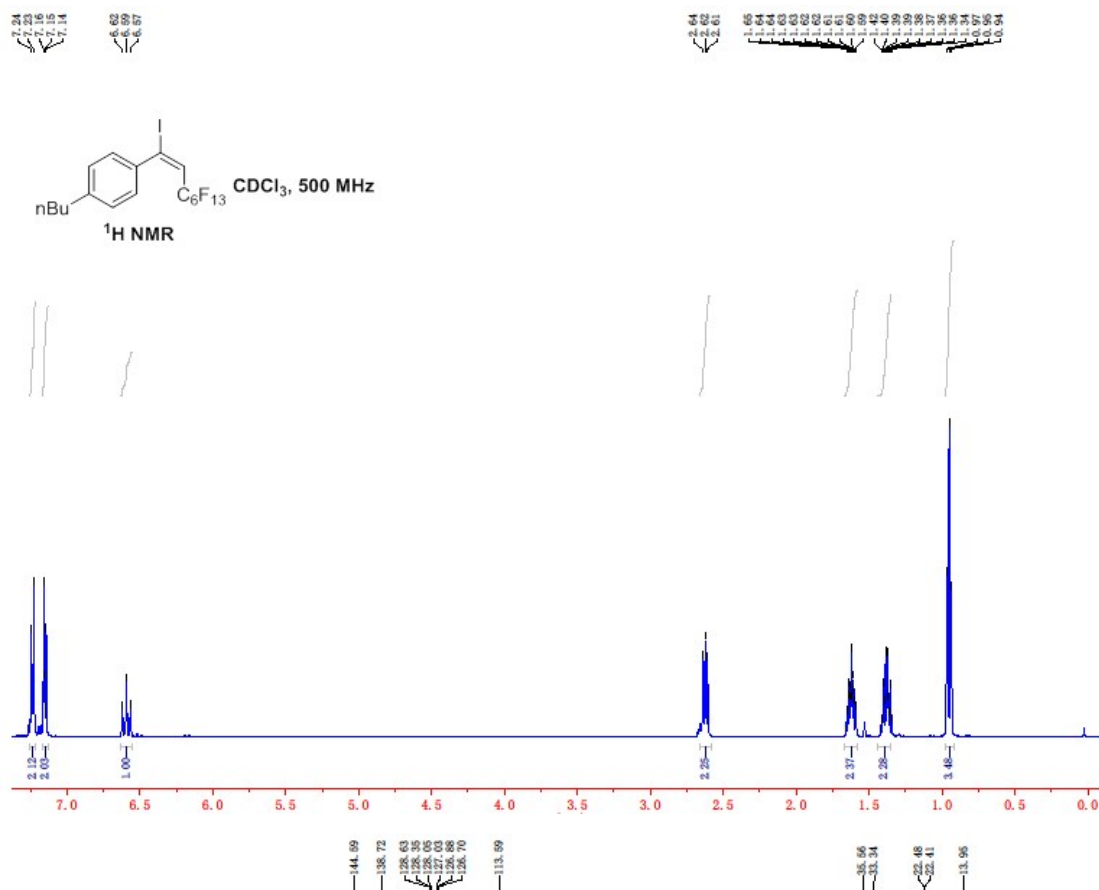


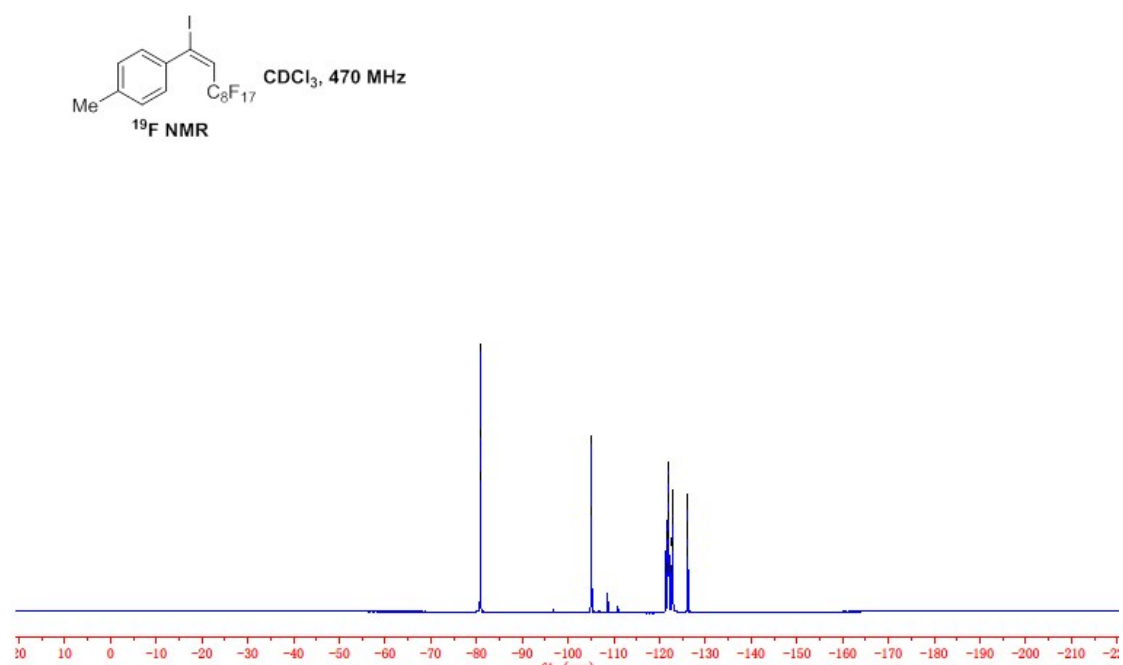
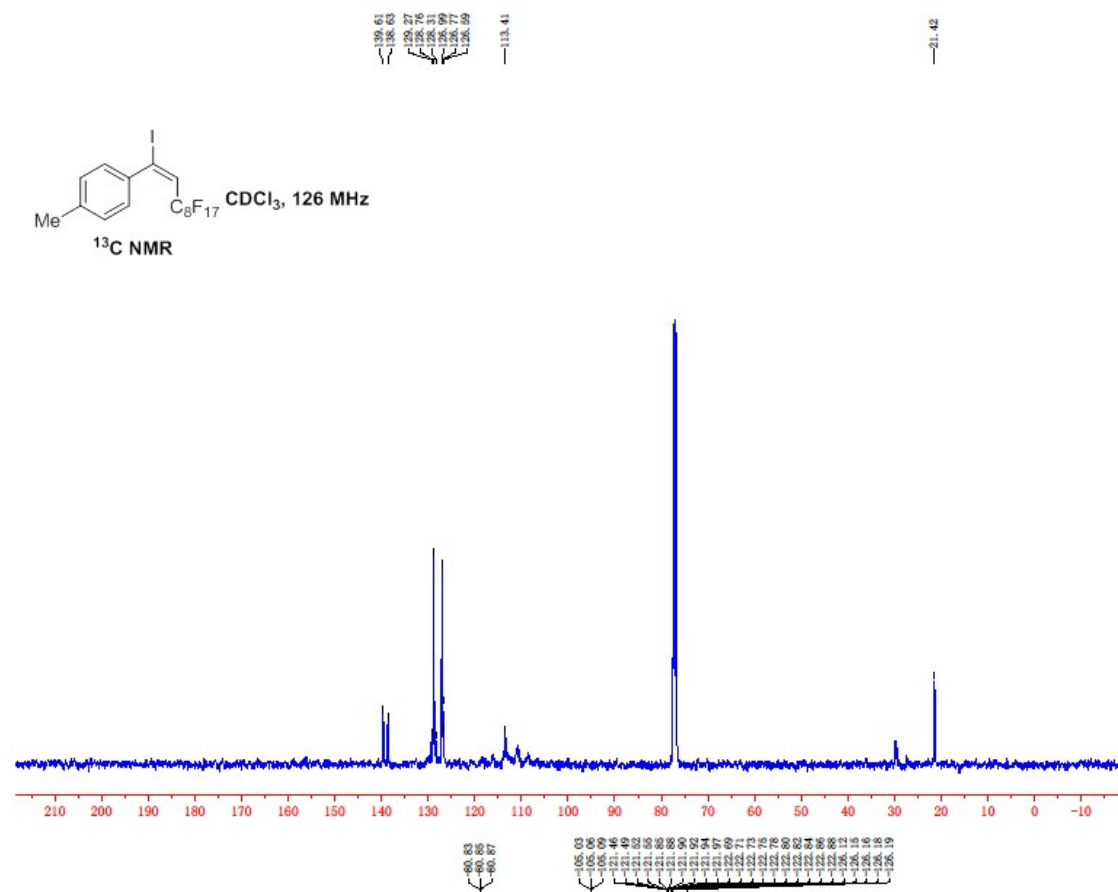


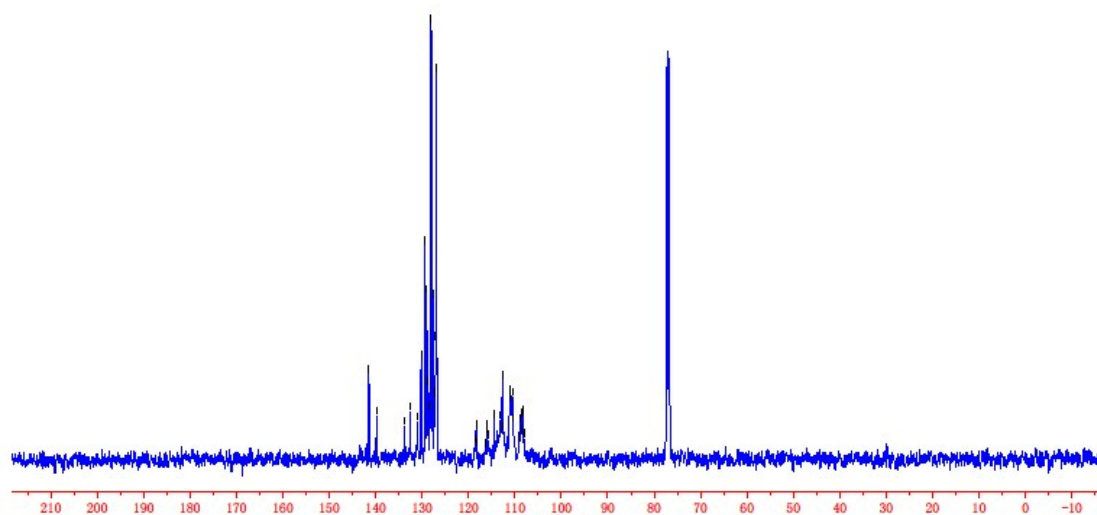
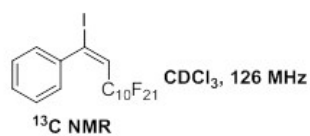
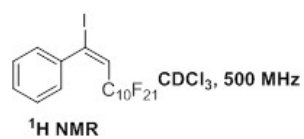


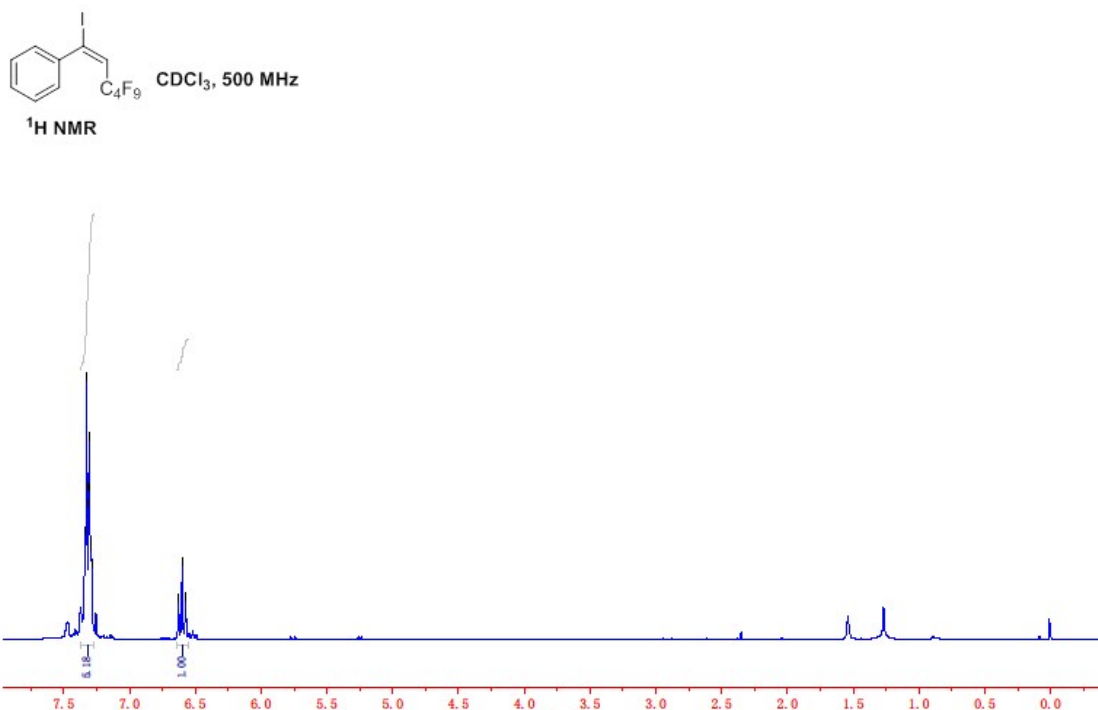


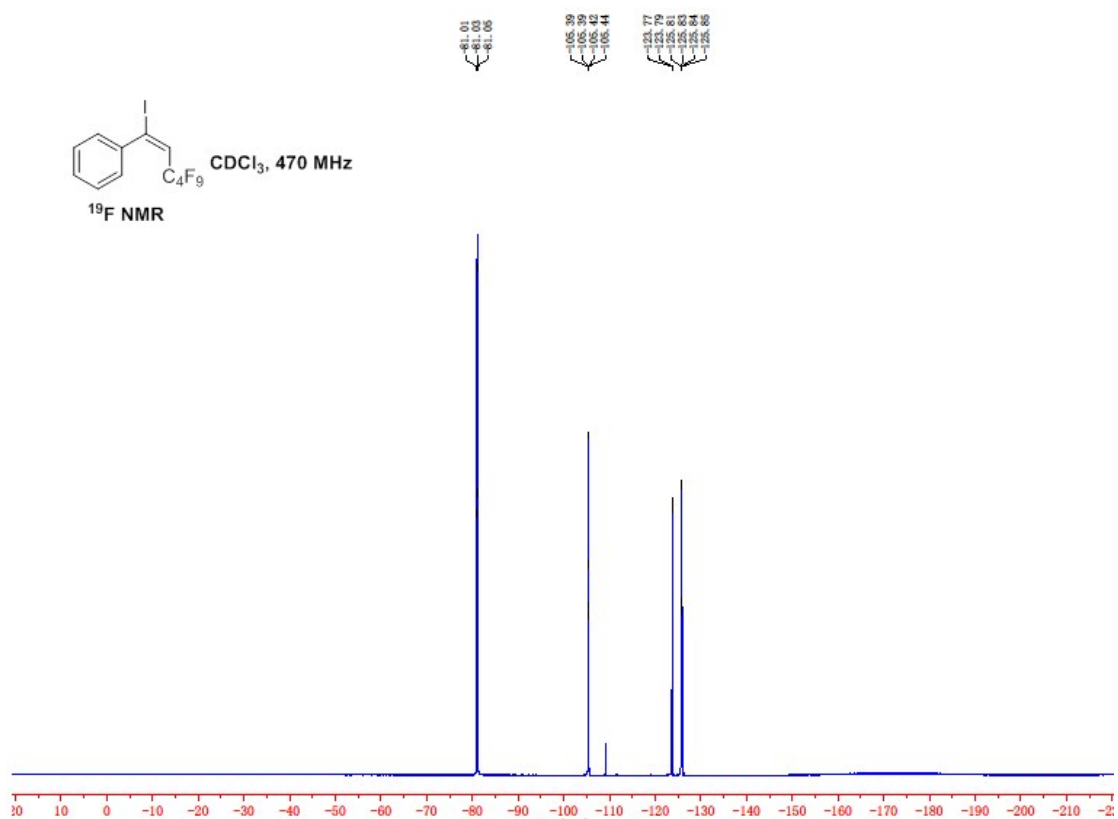
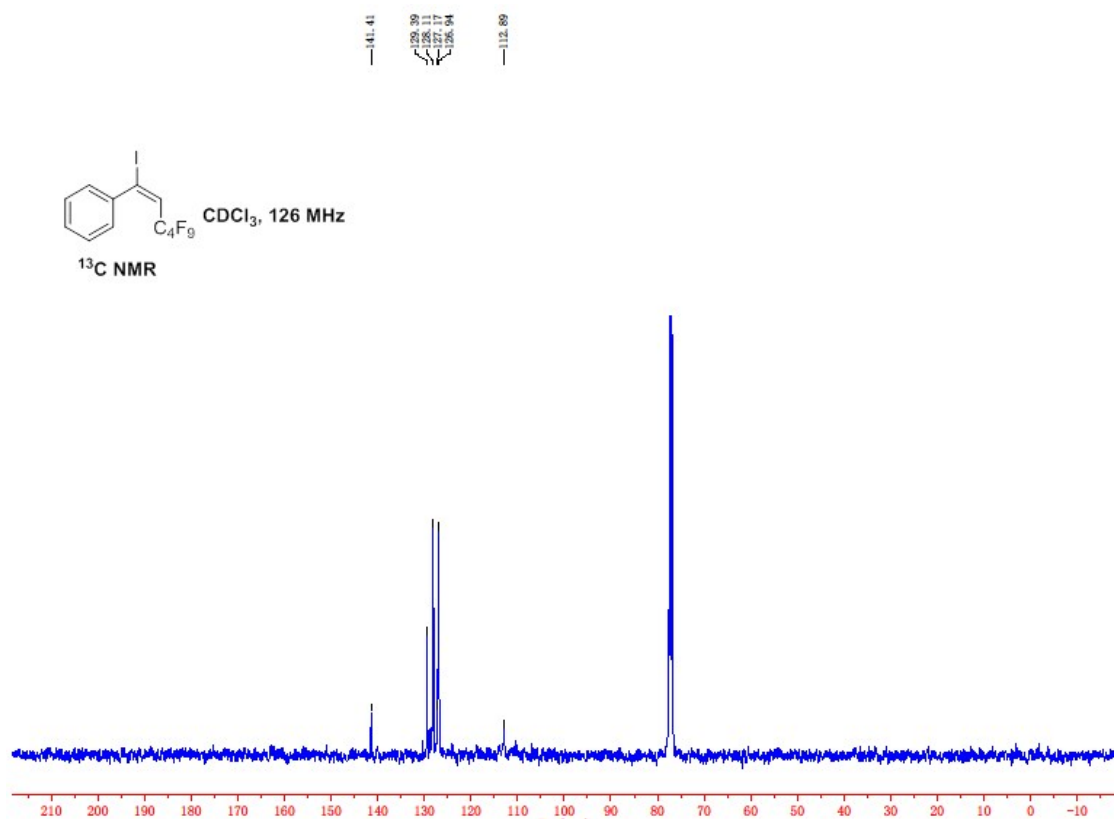


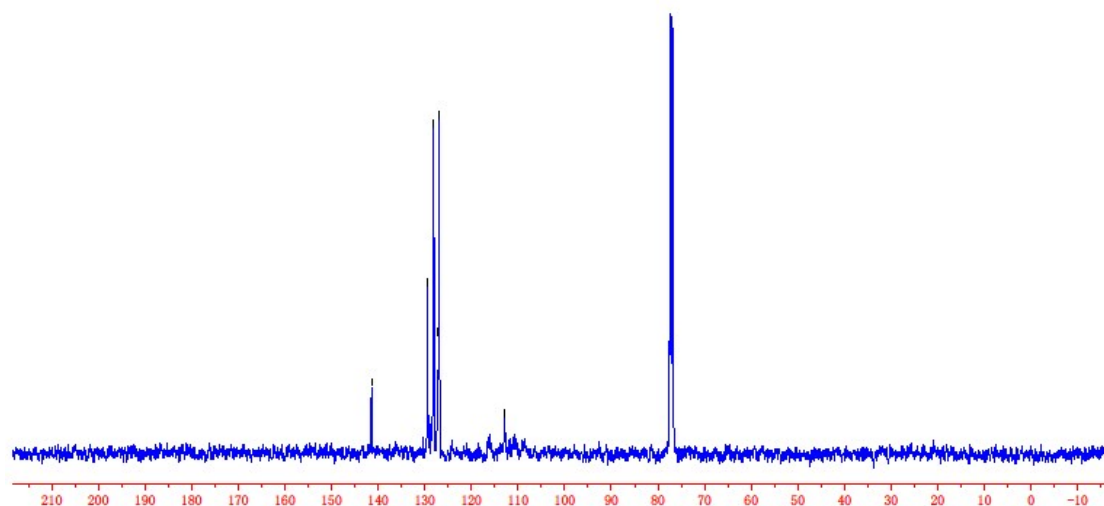
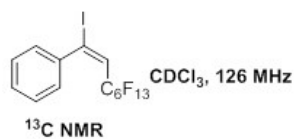
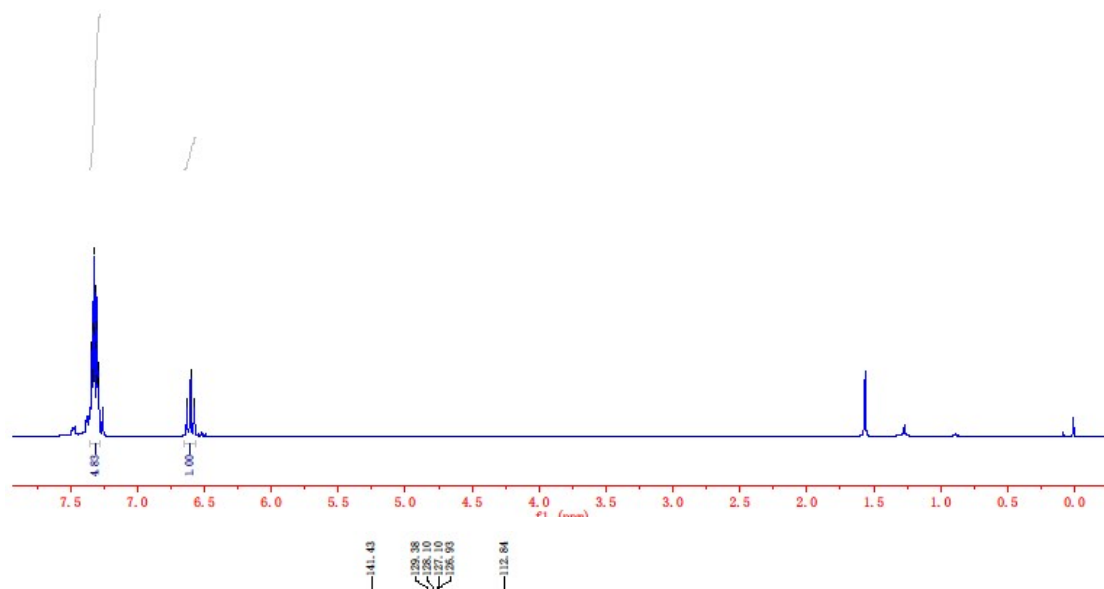
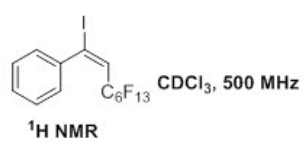
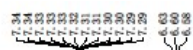


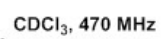
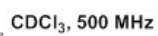
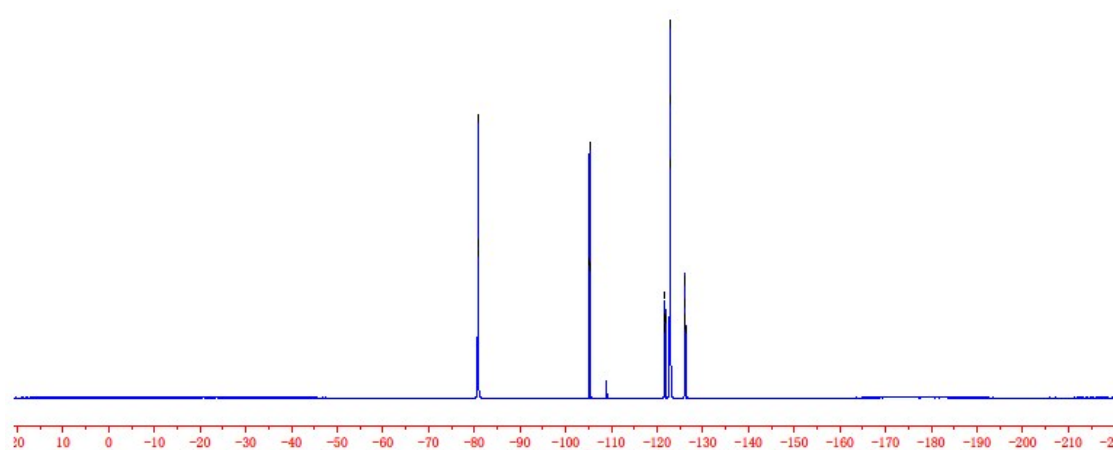
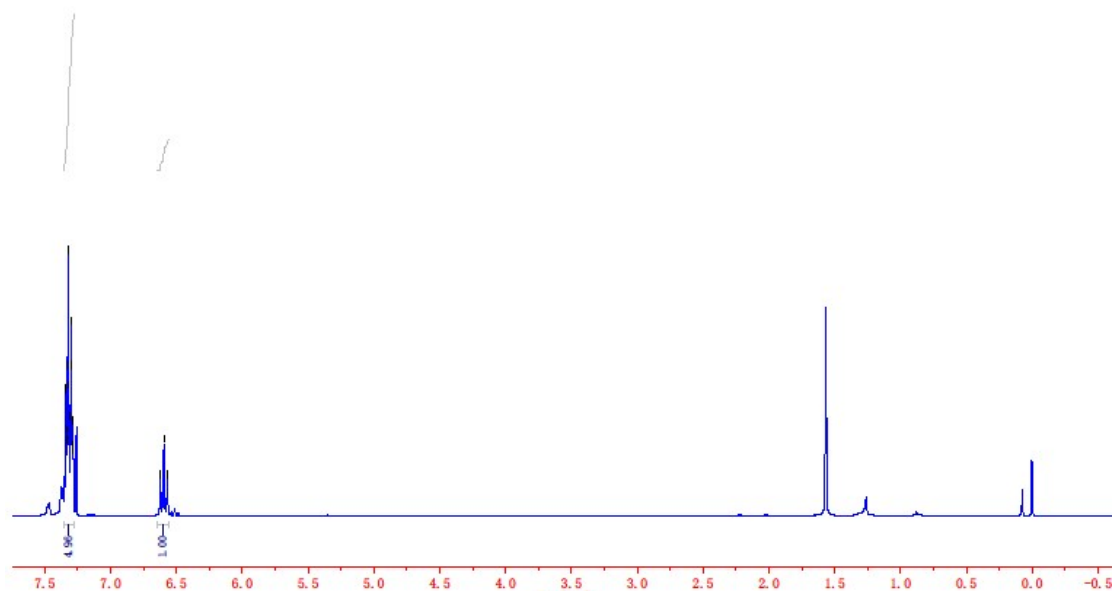


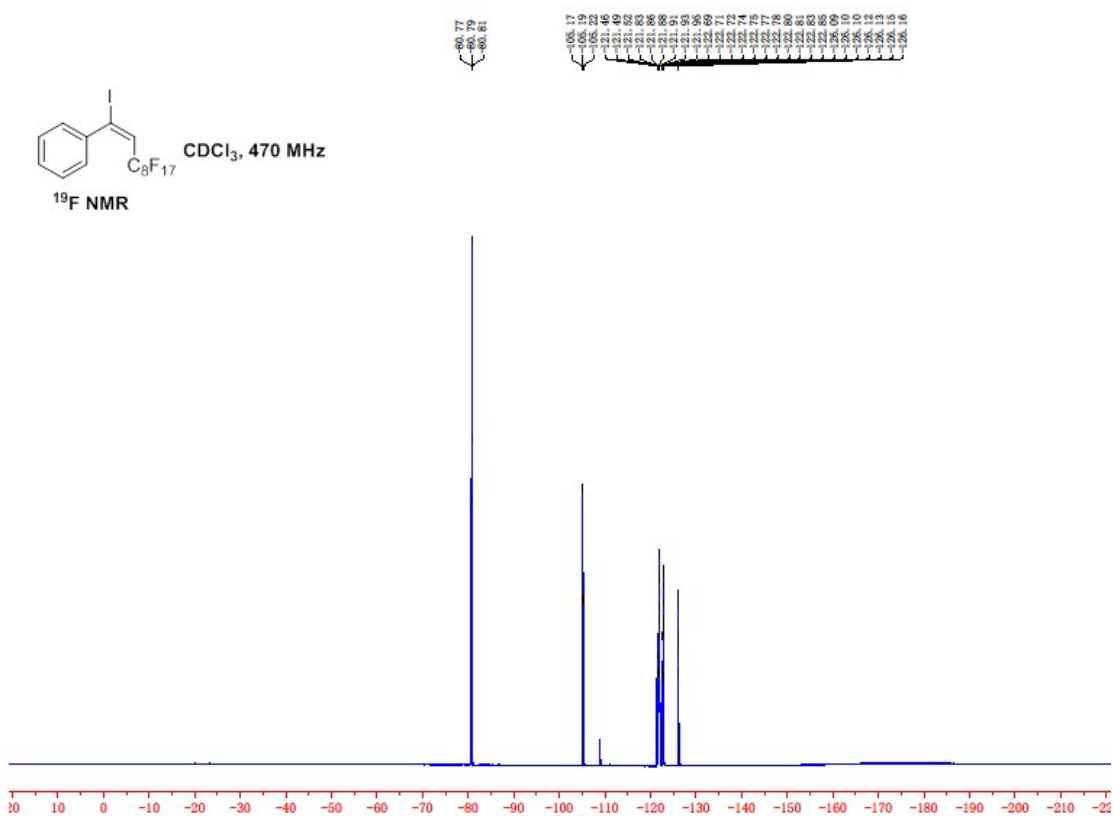


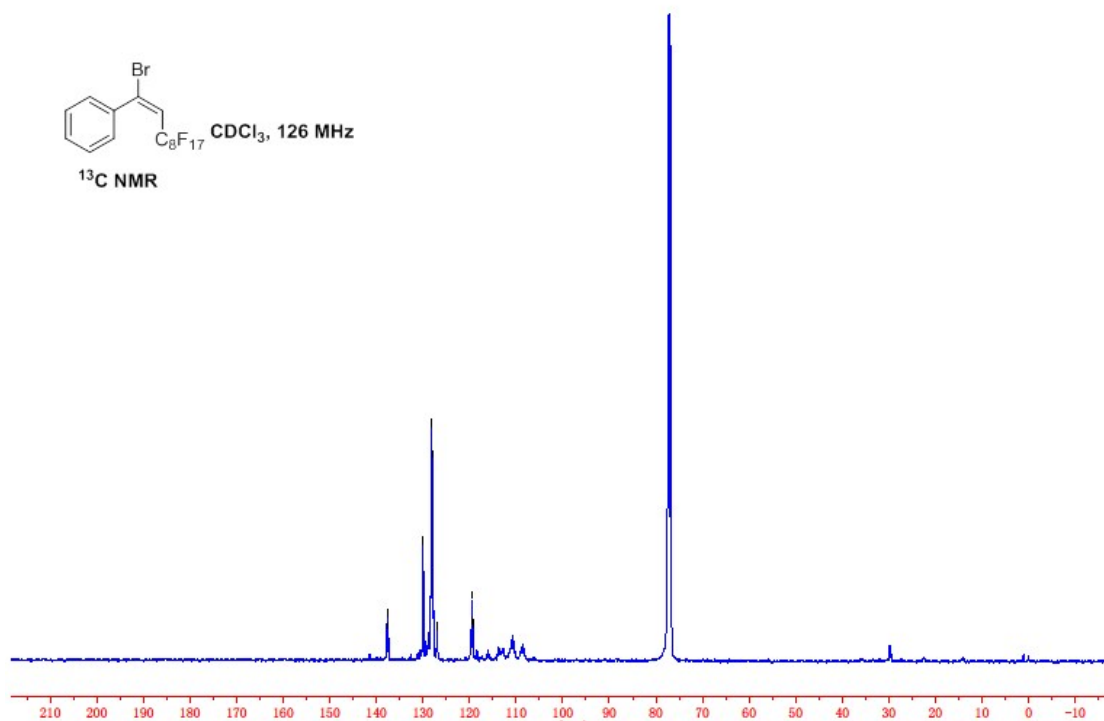
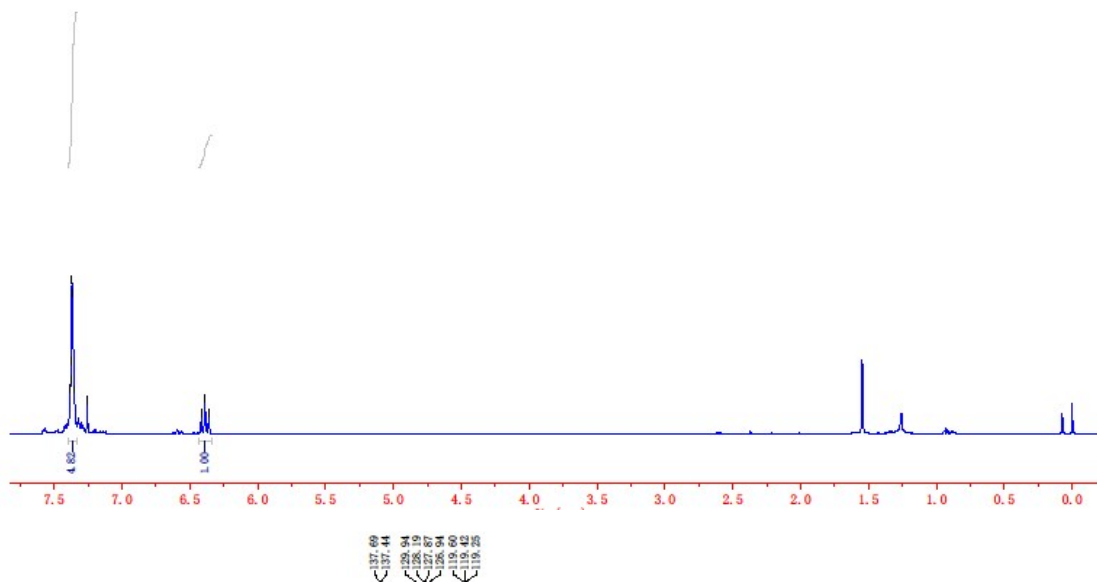
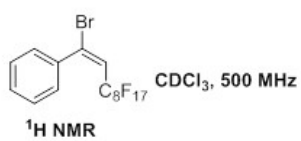






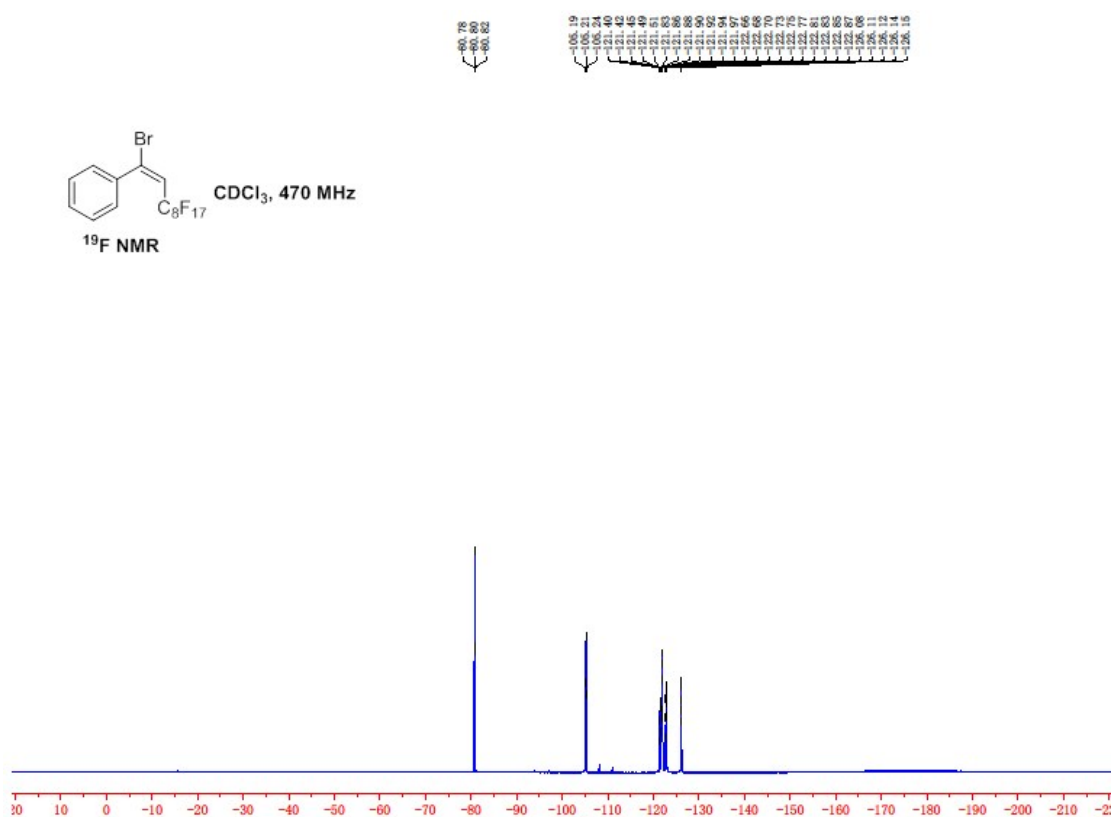
¹⁹F NMR¹H NMR



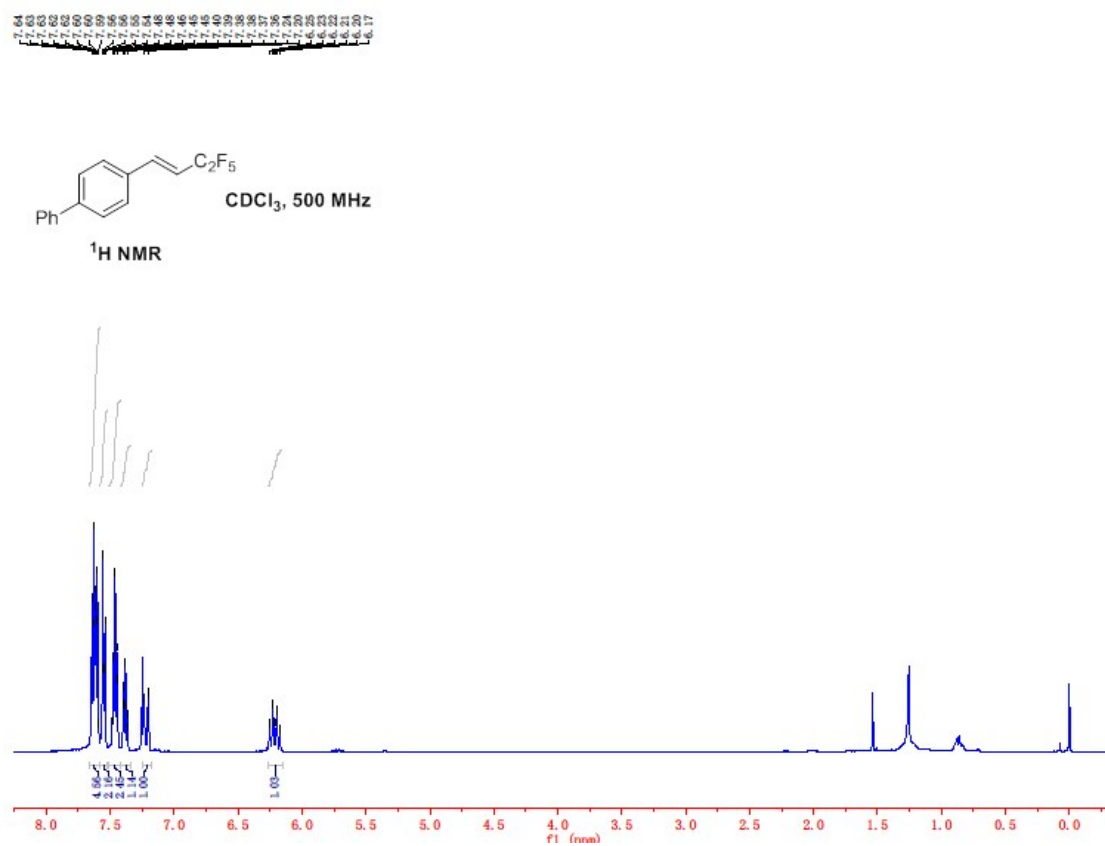


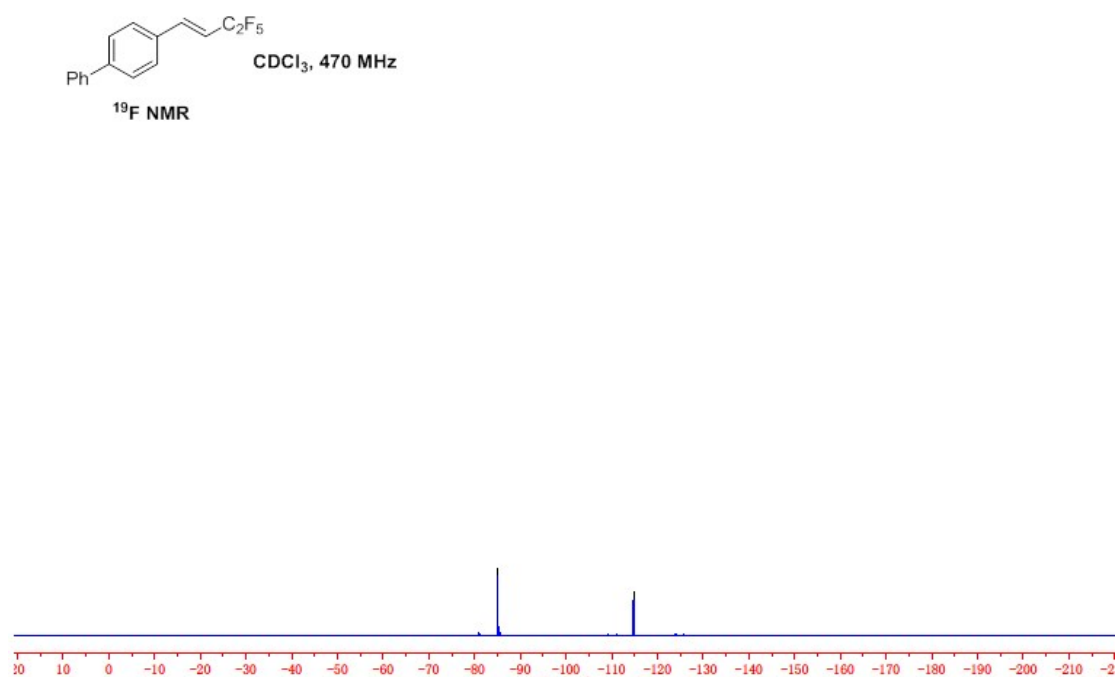
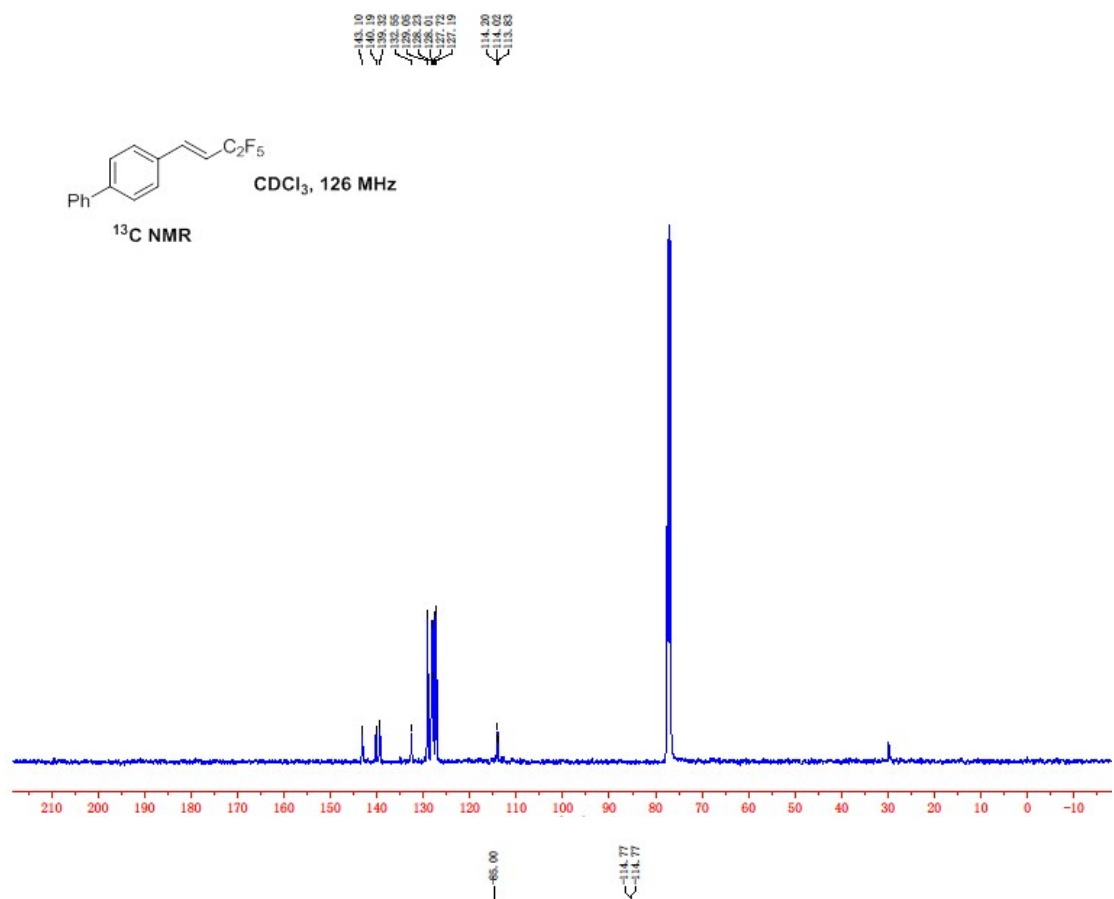


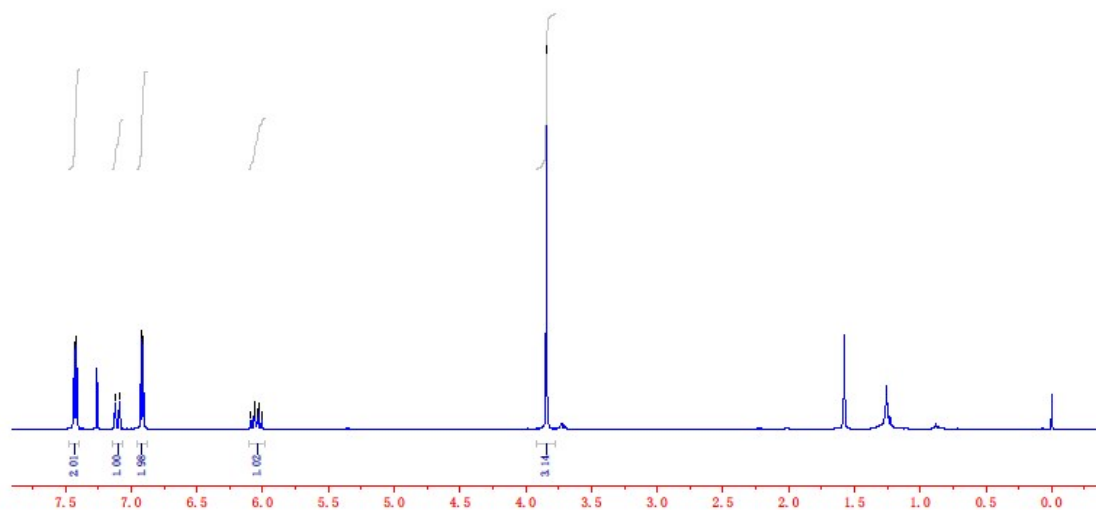
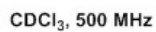
CDCl₃, 470 MHz

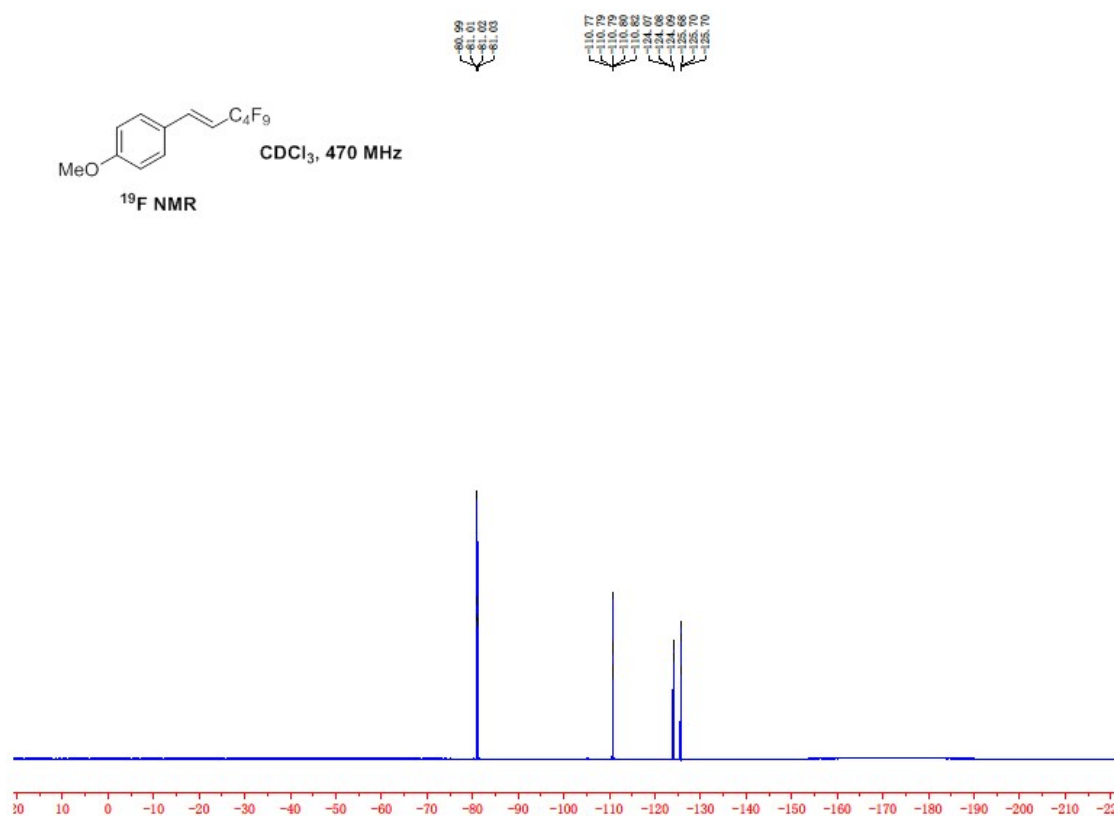
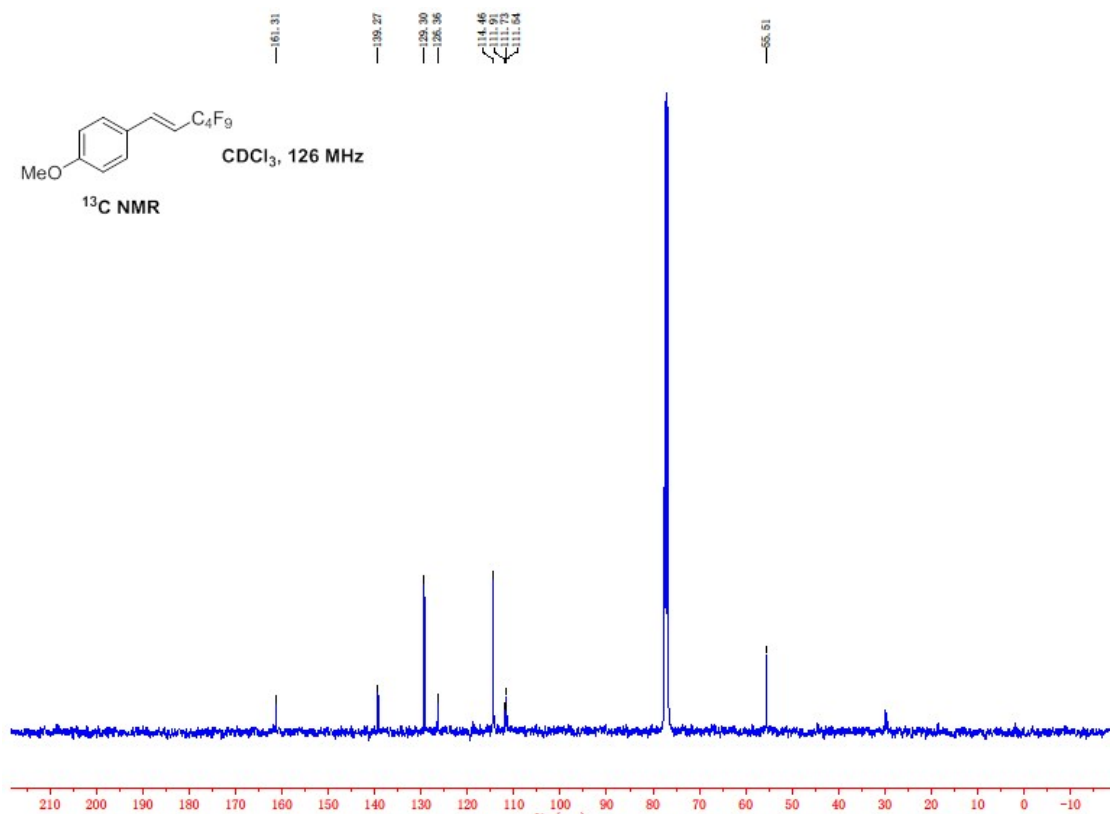


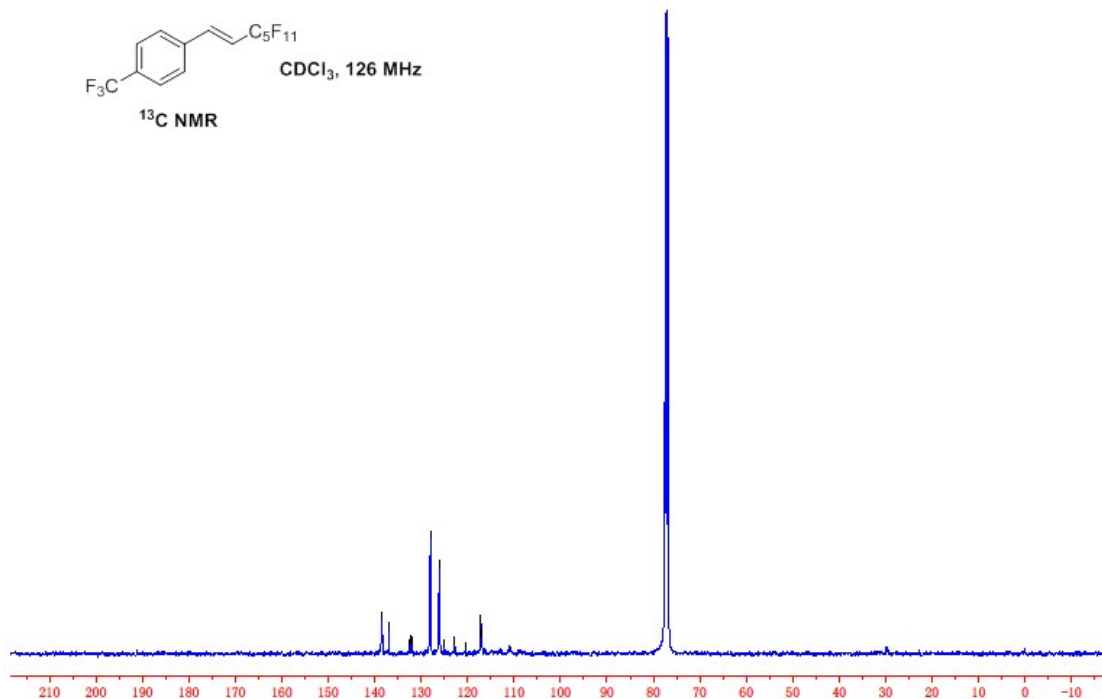
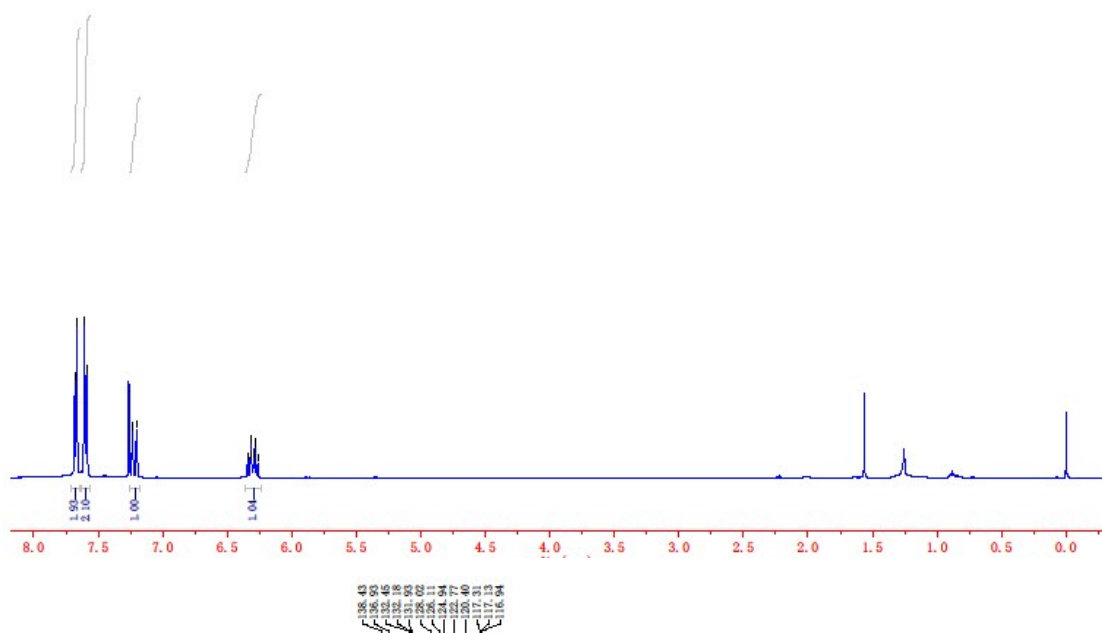
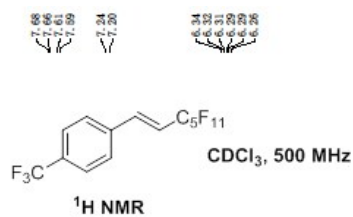
CDCl₃, 500 MHz

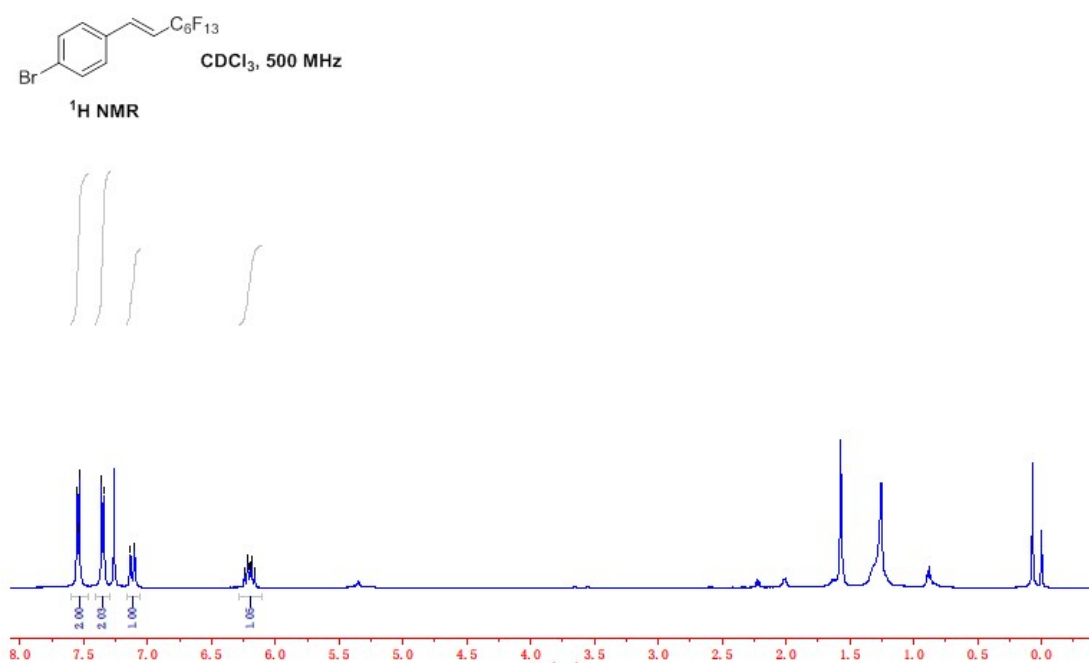
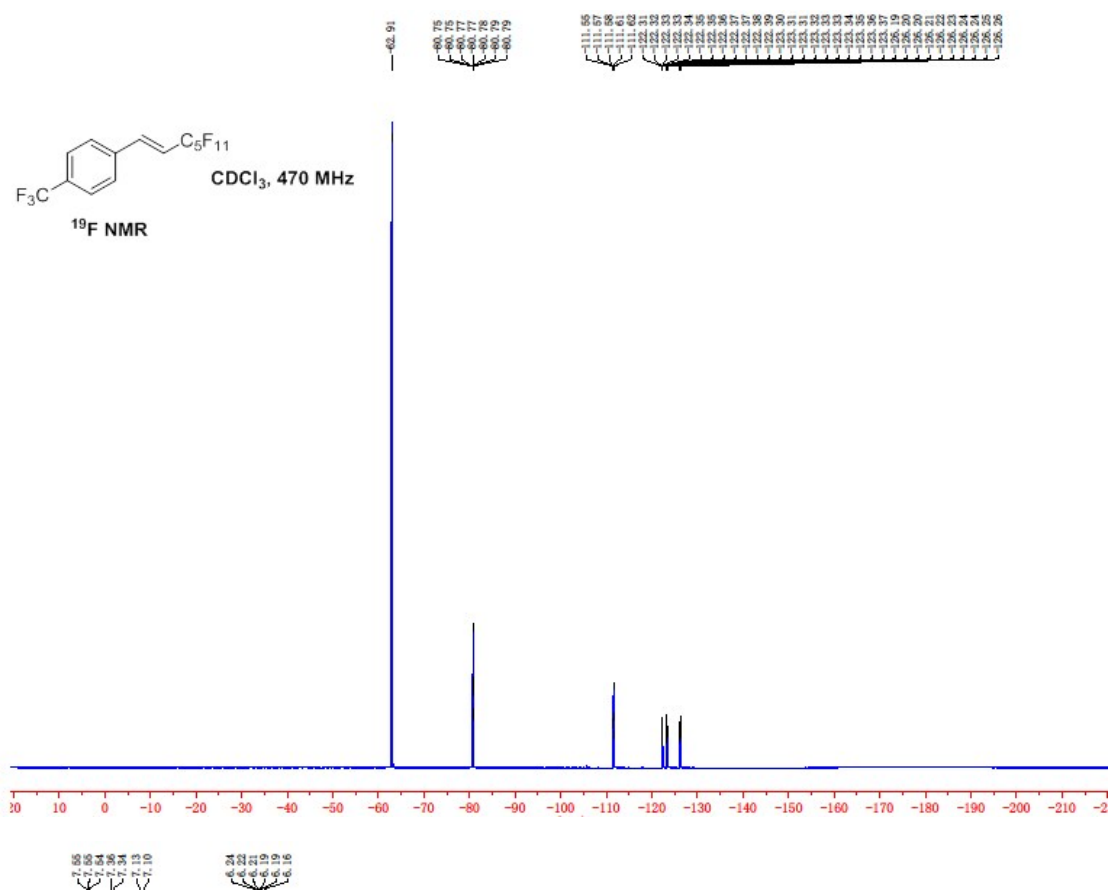


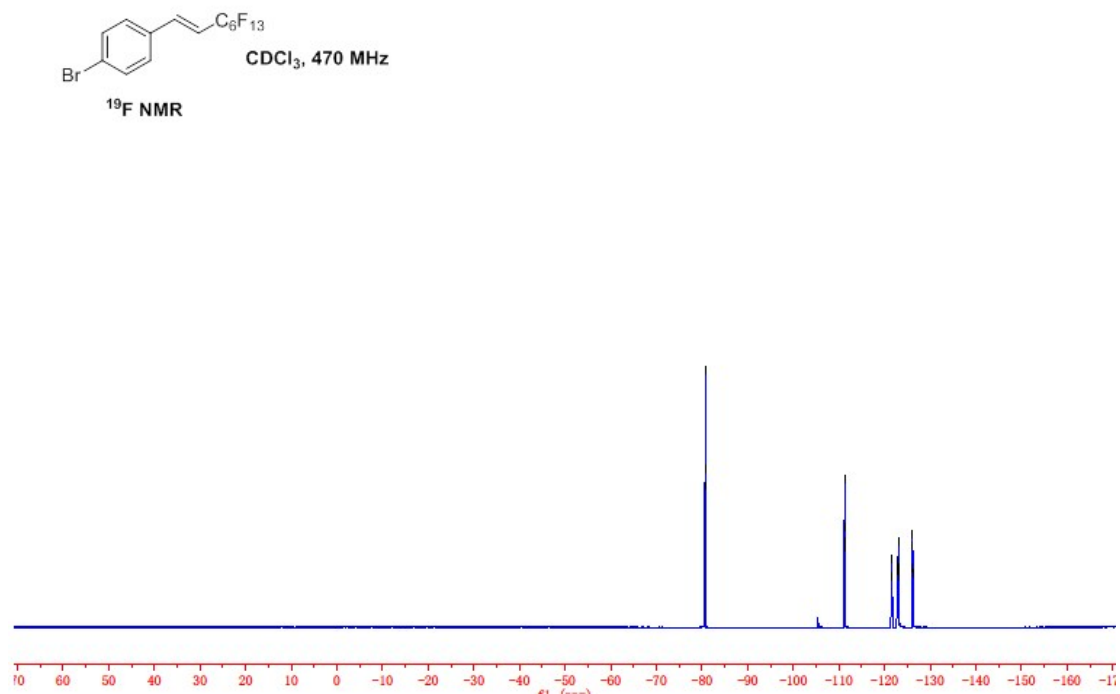
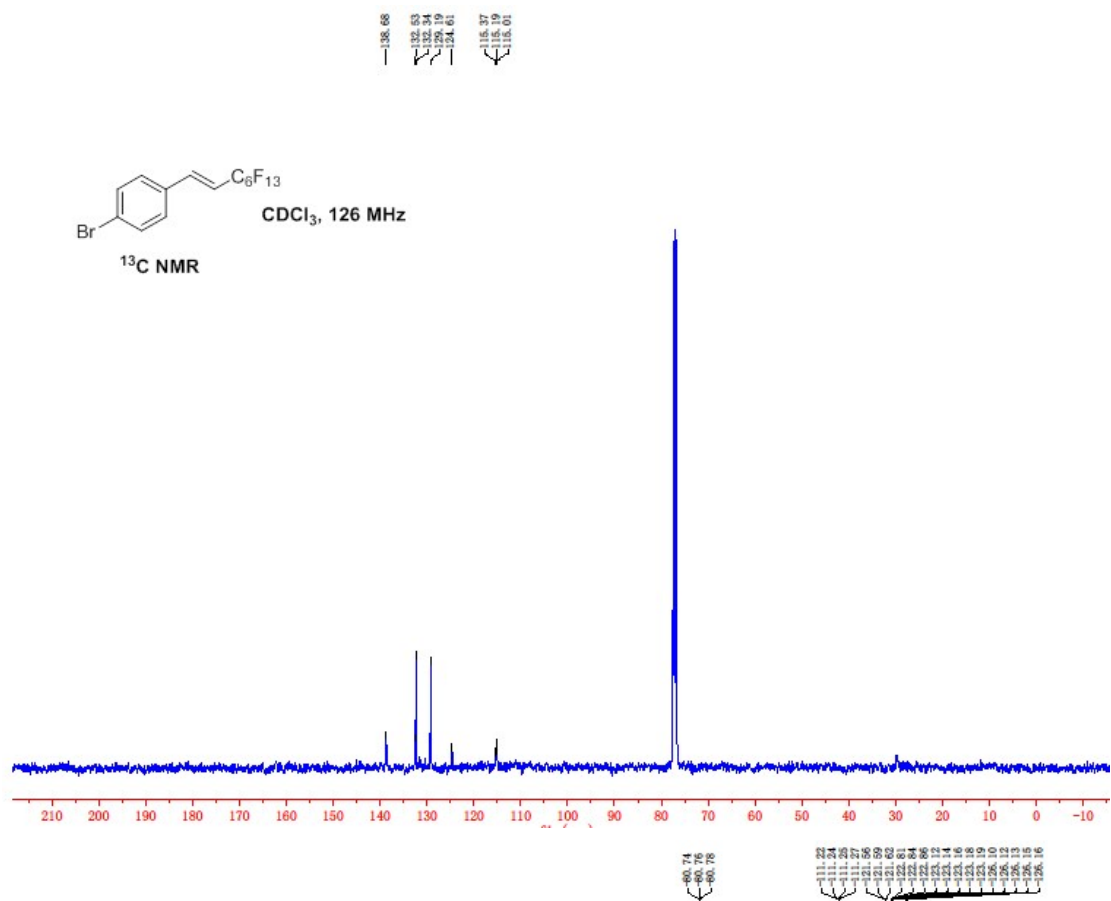


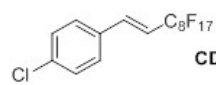
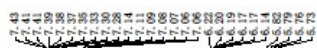






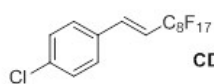
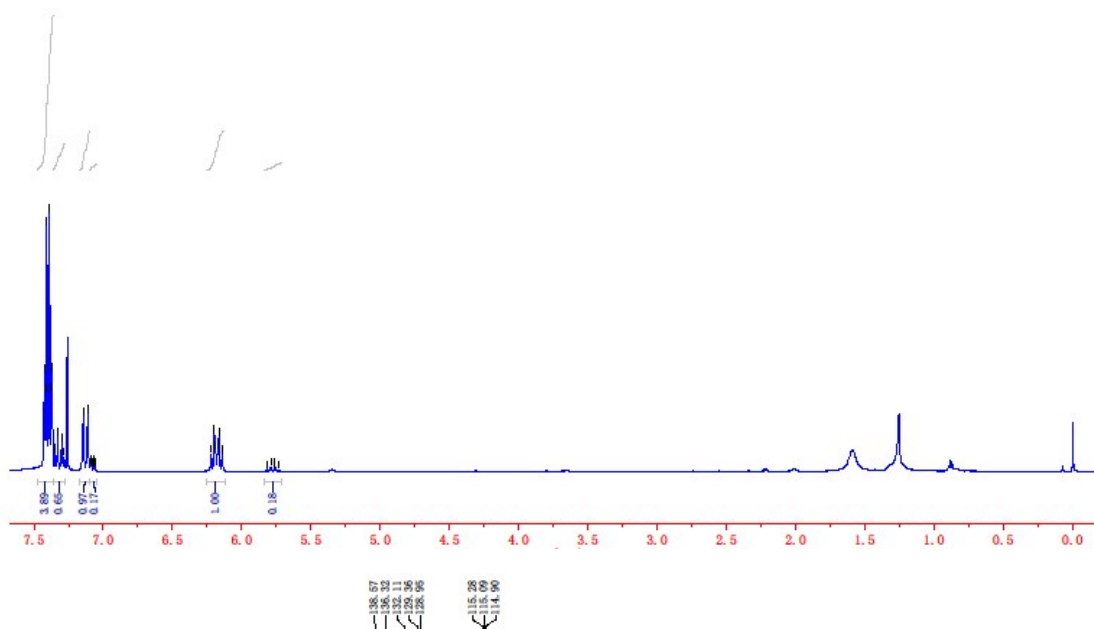






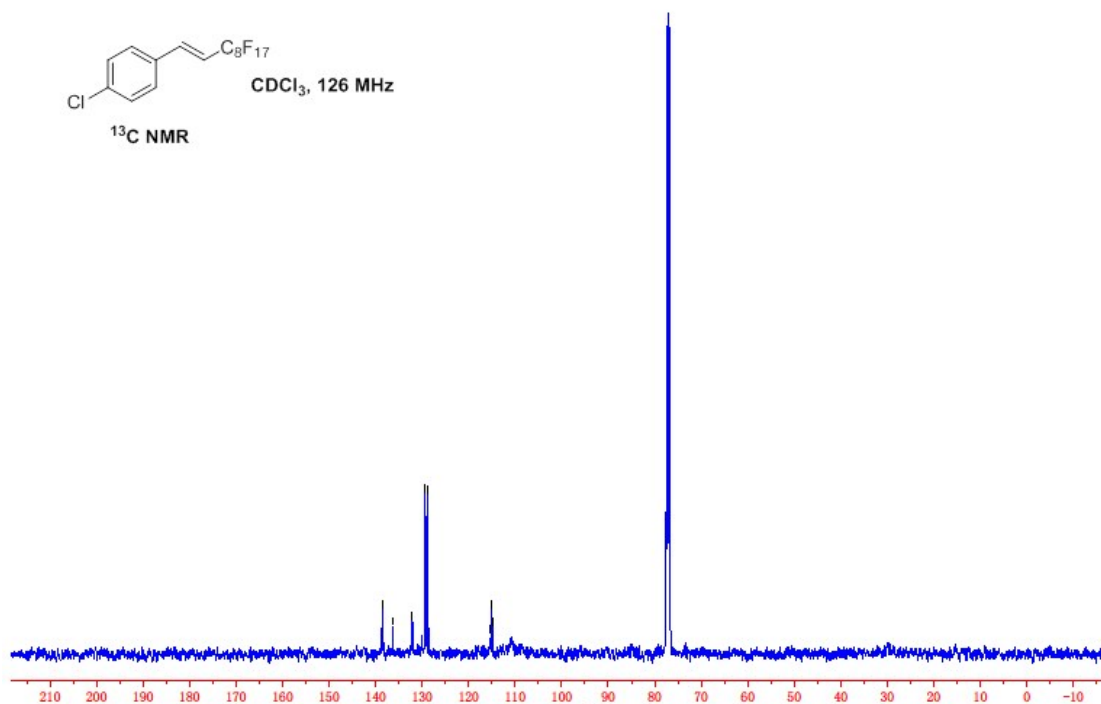
CDCl₃, 500 MHz

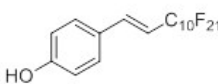
¹H NMR



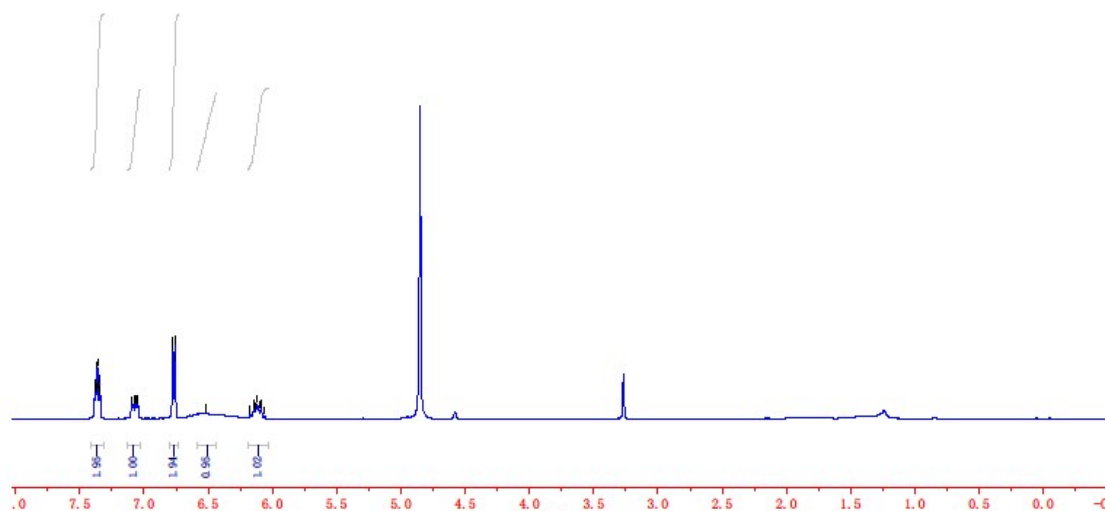
CDCl₃, 126 MHz

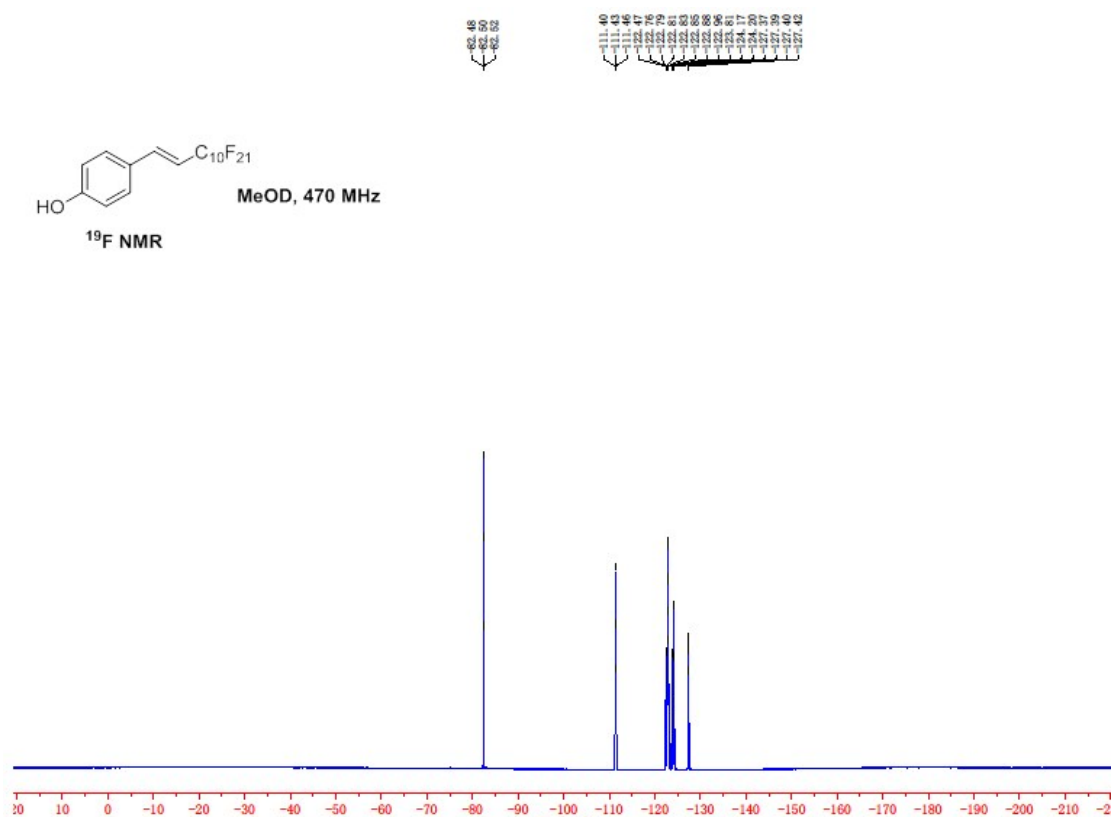
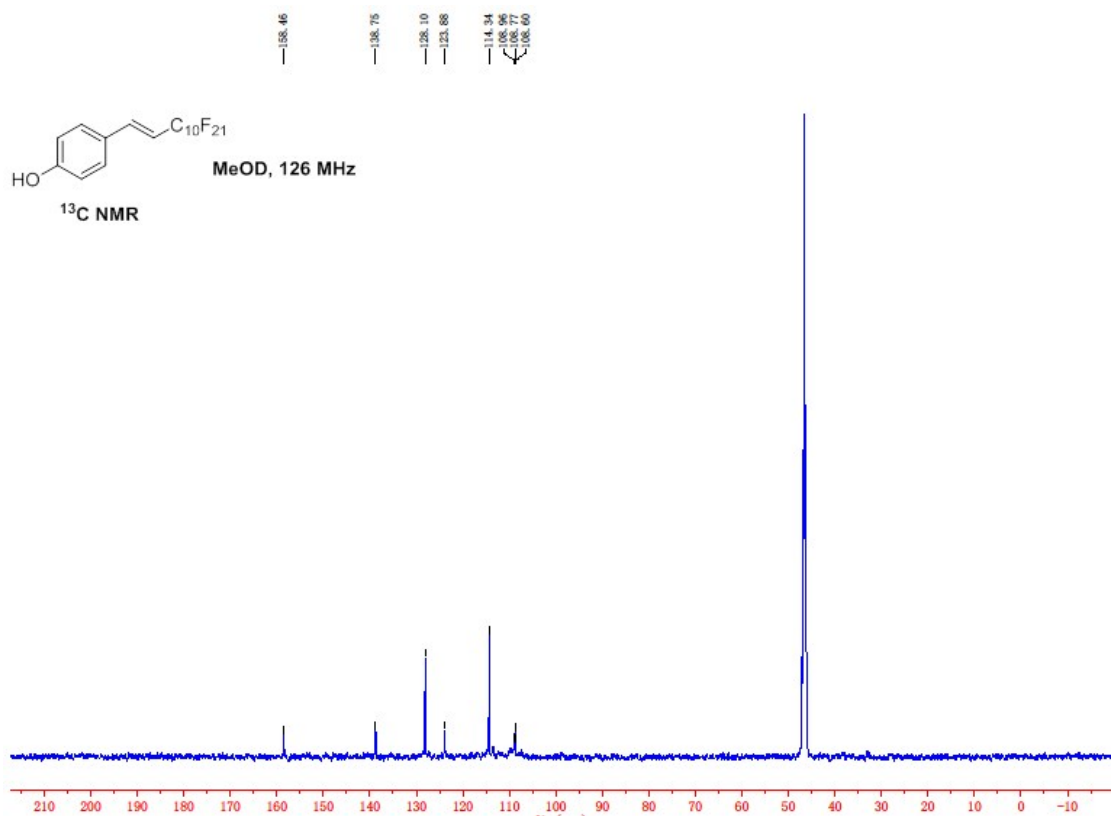
¹³C NMR

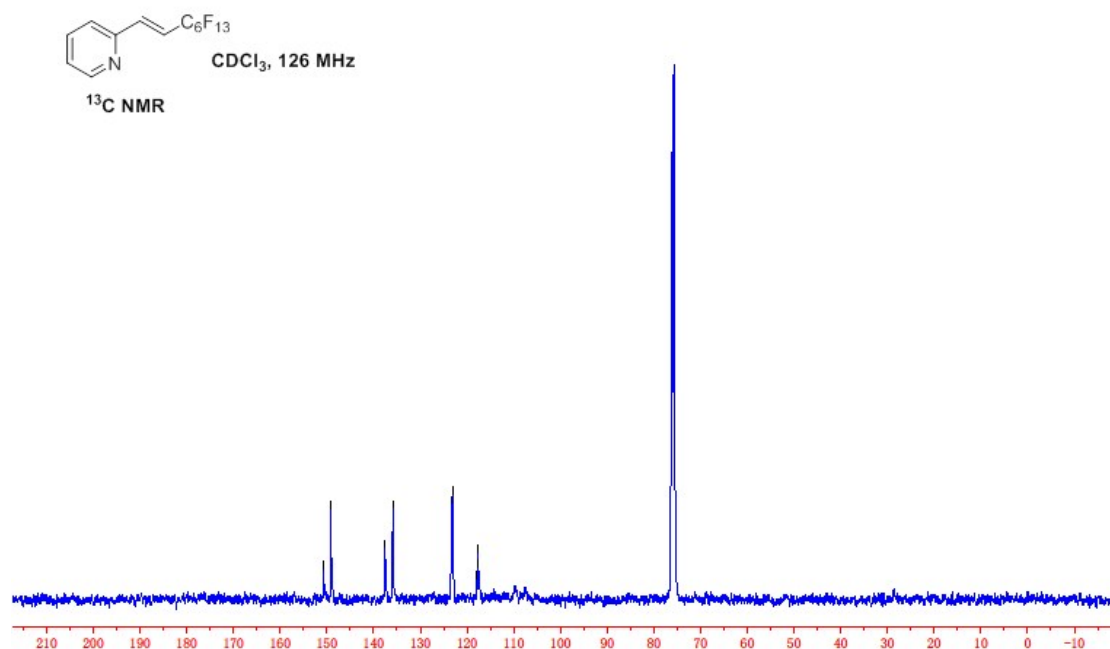
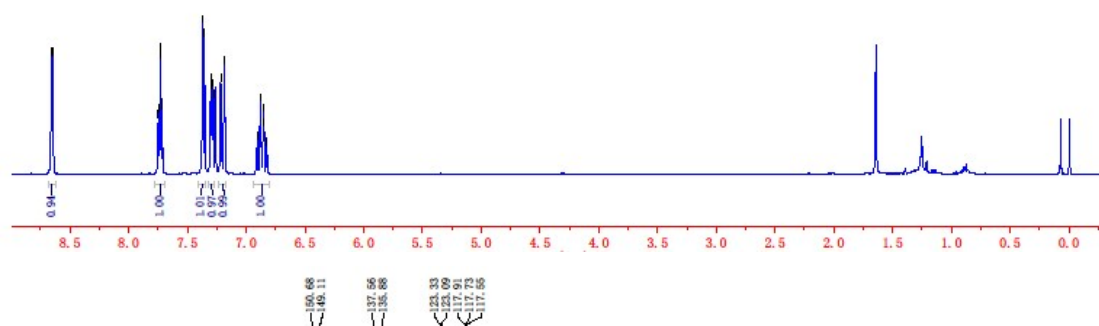
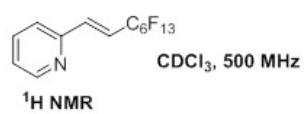


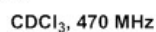
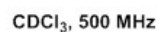
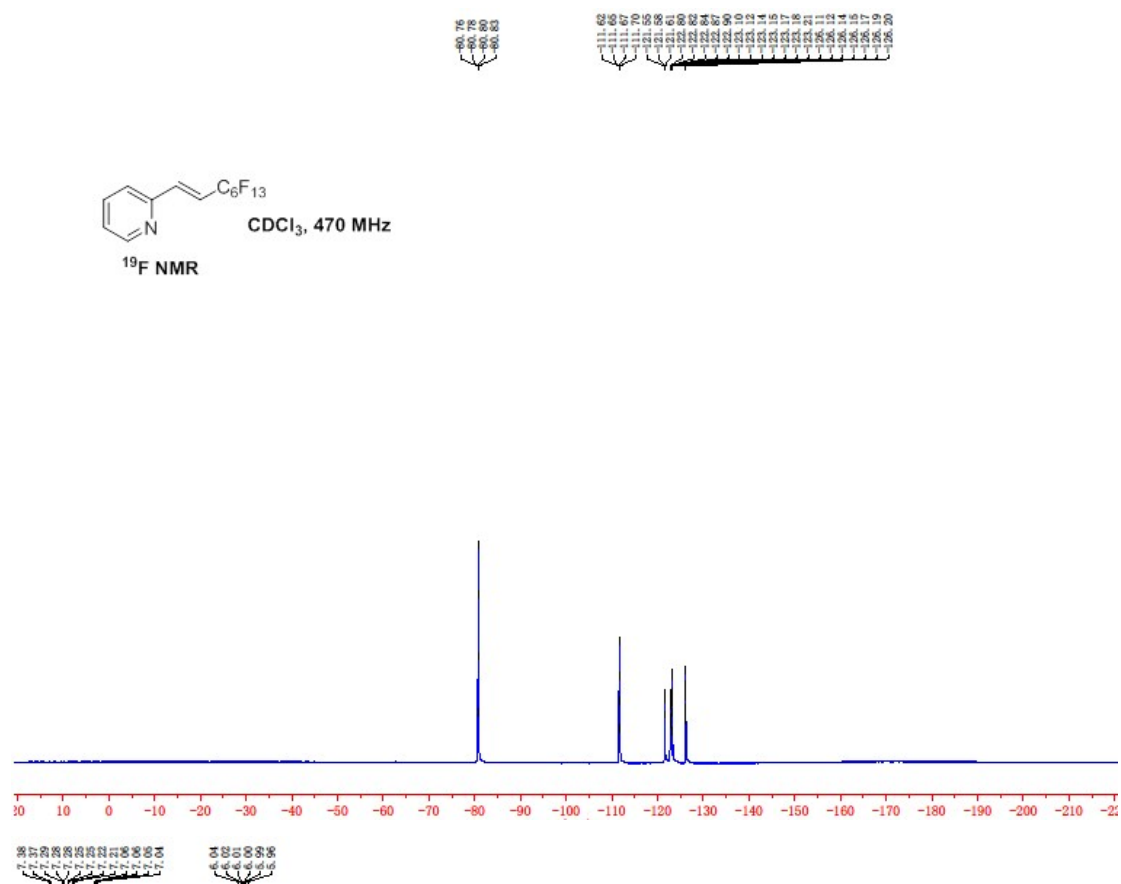
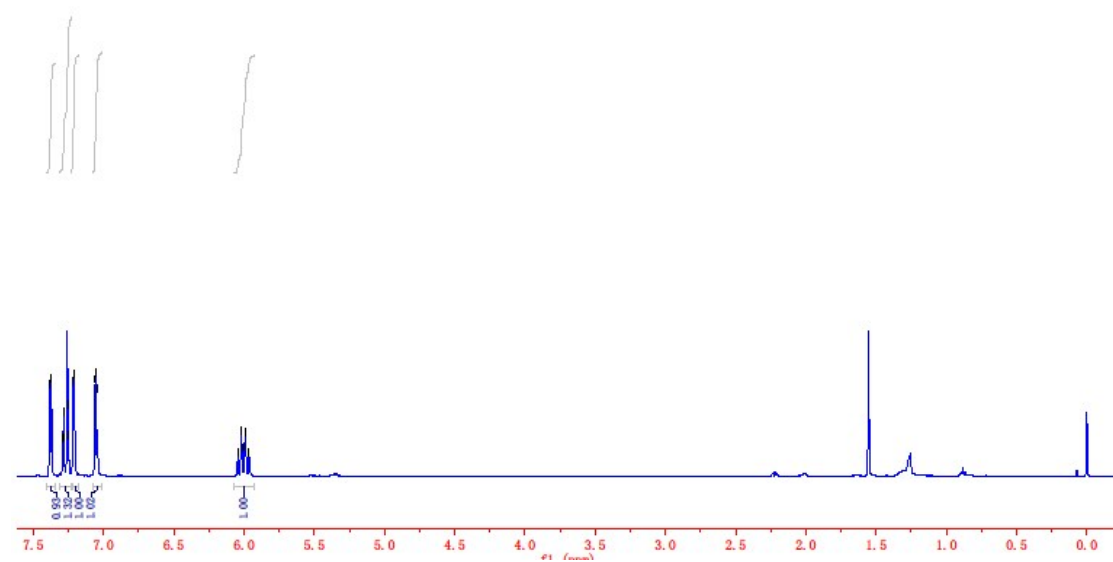
¹⁹F NMR

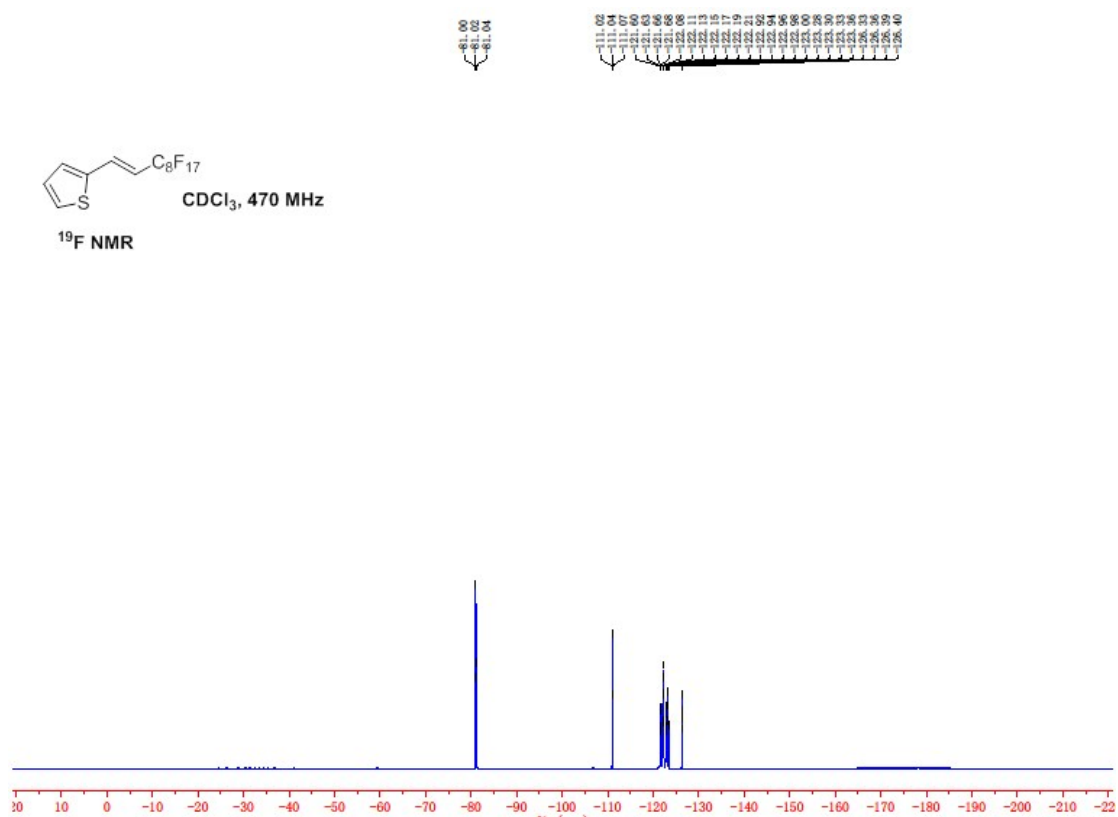
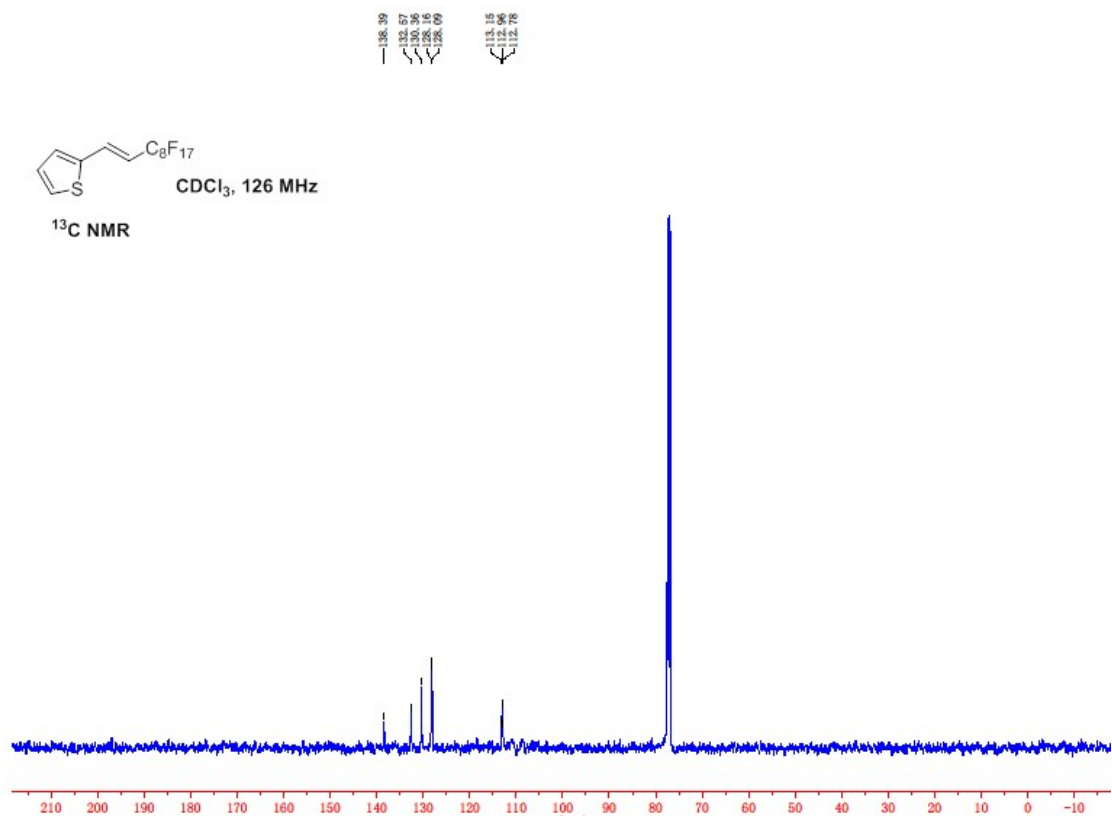
CDCl₃, 500 MHz

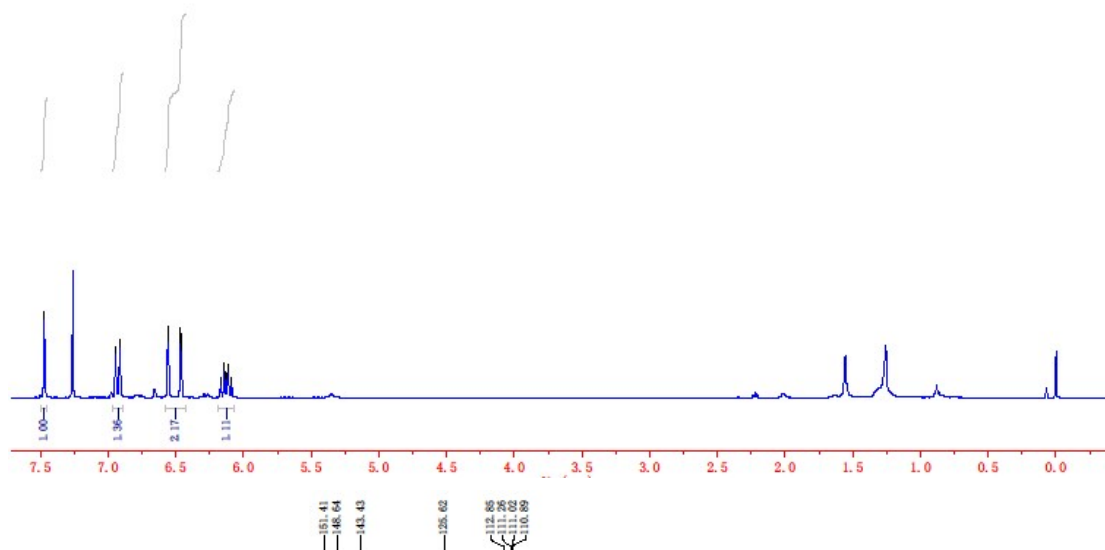
¹H NMR



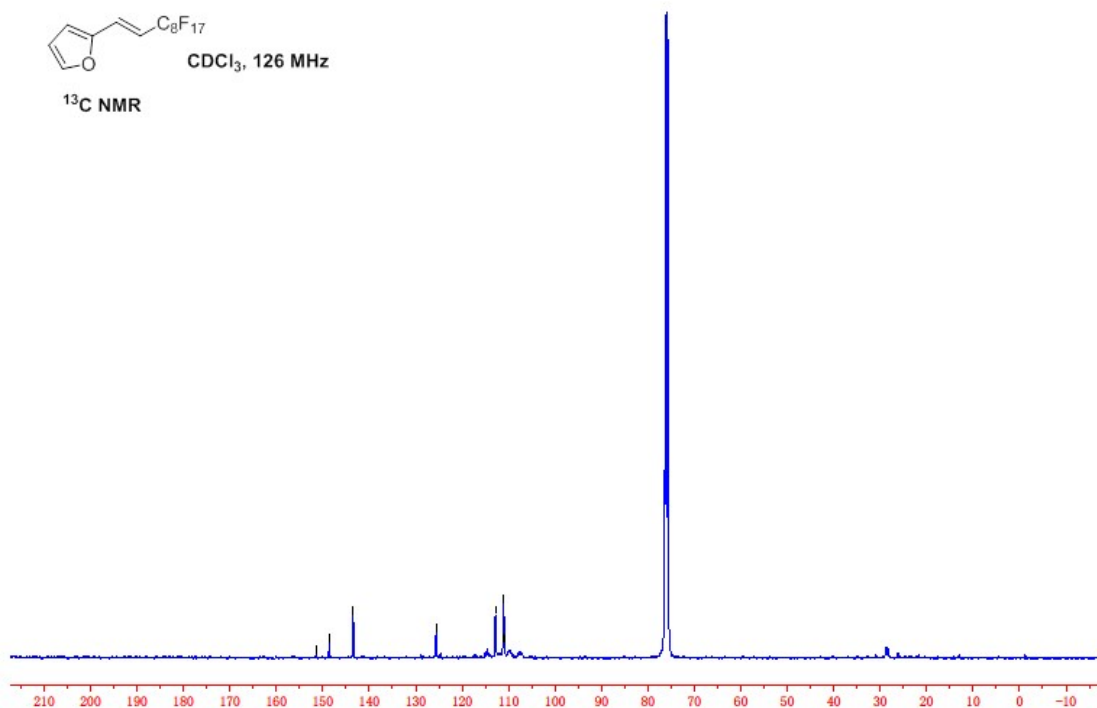


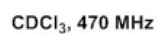
¹⁹F NMR¹H NMR



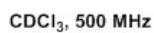
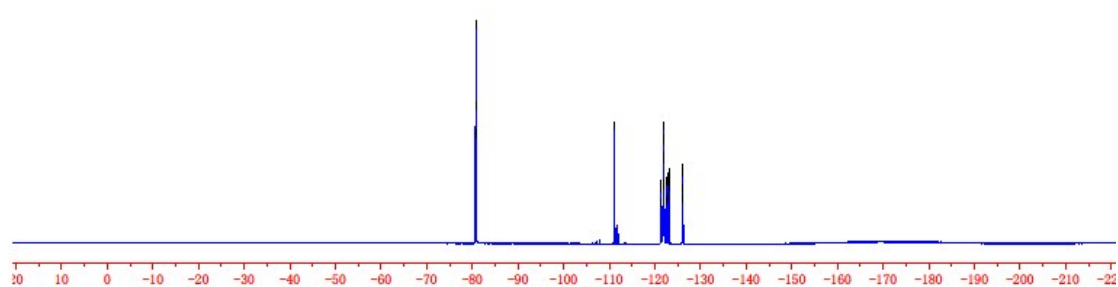
¹H NMR

CDCl₃, 126 MHz

¹³C NMR



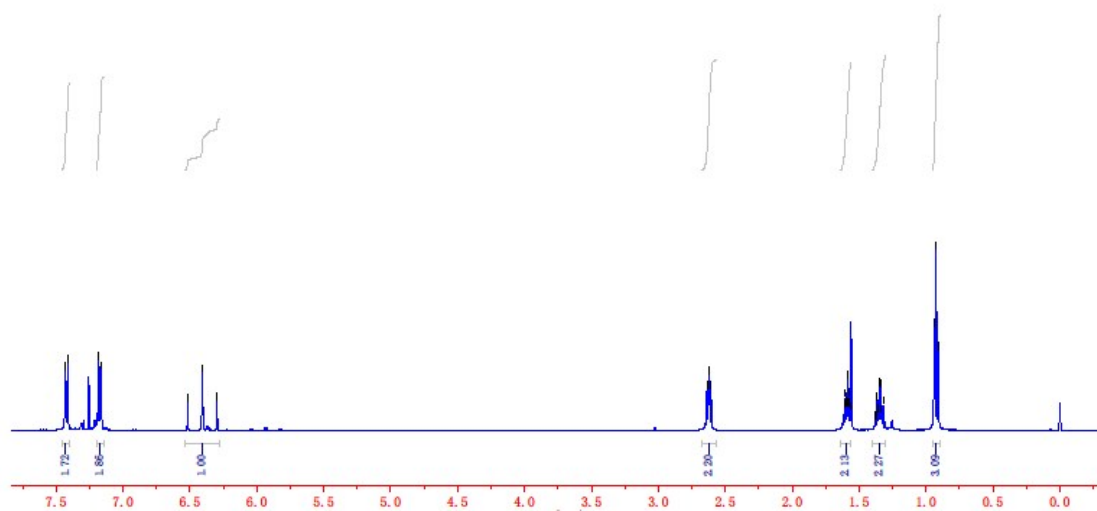
Month	Number of cases
Jan	11
Feb	11
Mar	11
Apr	11
May	11
Jun	11
Jul	11
Aug	11
Sep	11
Oct	11
Nov	11
Dec	11

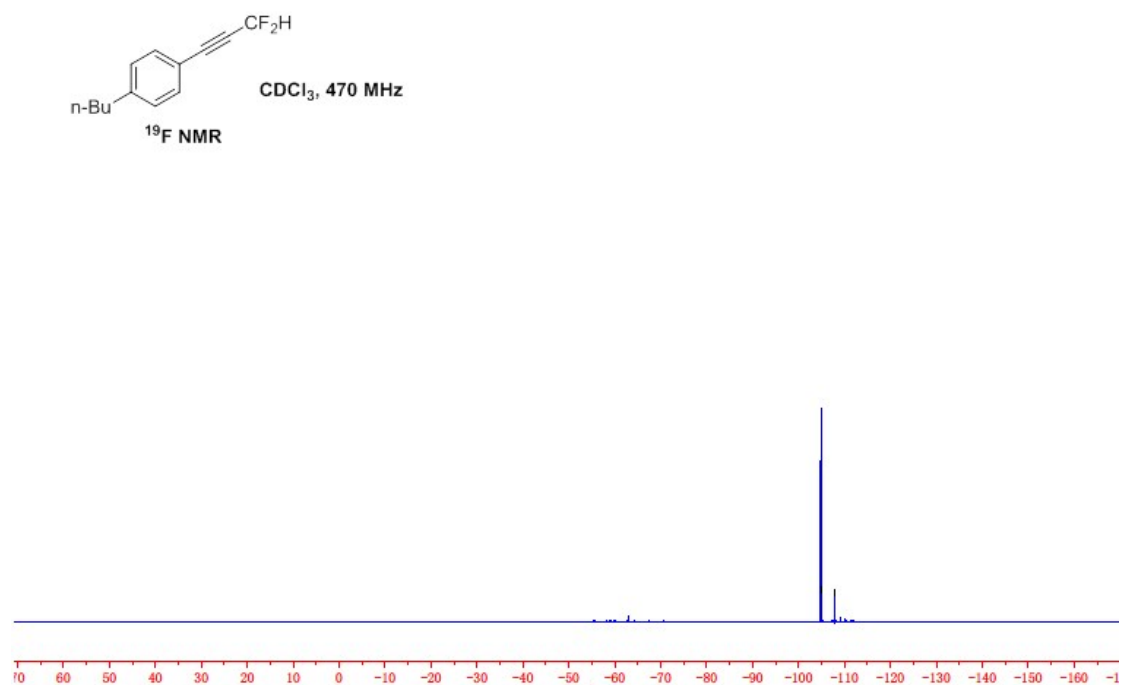
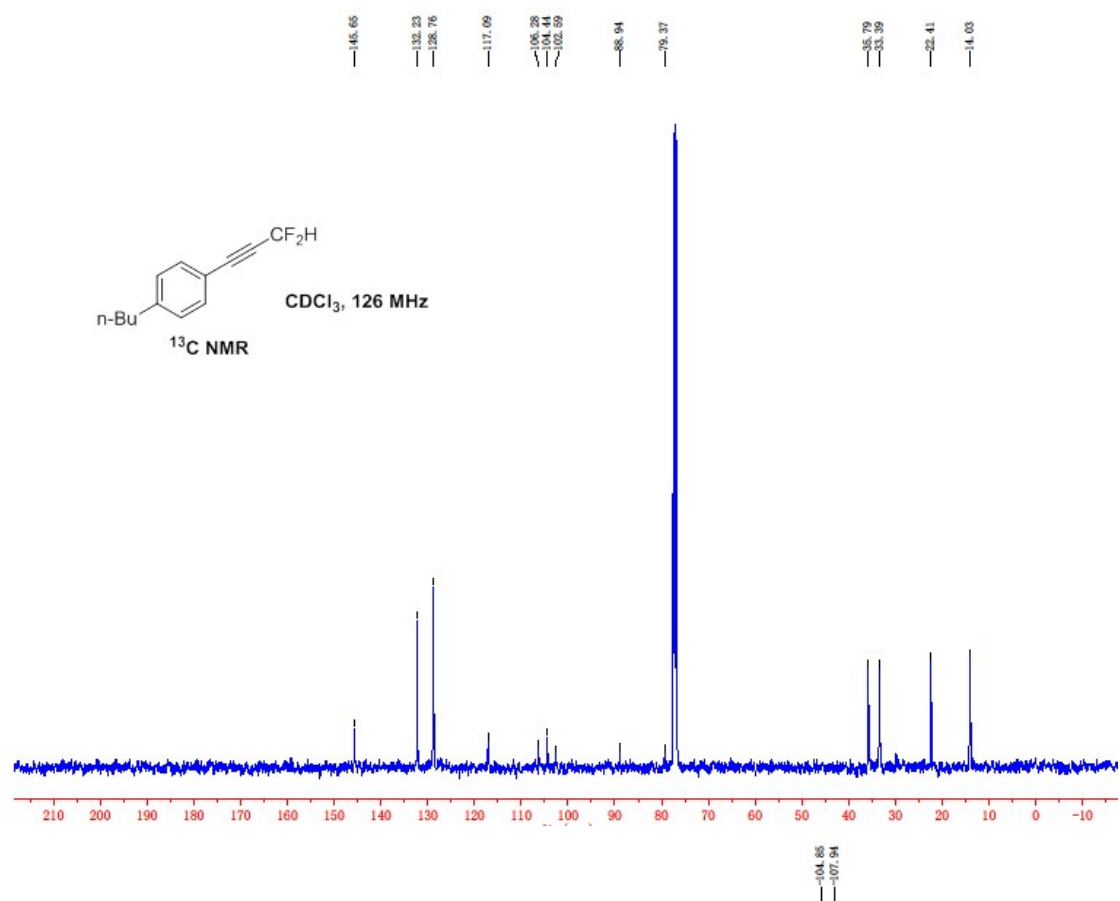

$$\begin{array}{r} 7.43 \\ - 7.42 \\ \hline \end{array} \qquad \begin{array}{r} 7.18 \\ - 7.16 \\ \hline \end{array}$$

6.52
6.41
6.39

2.64
2.62
2.61

1.61 1.60 1.60 1.59 1.59 1.58 1.57 1.57 1.38 1.37 1.37 1.36 1.35 1.34 1.34 1.32 0.94 0.92 0.91

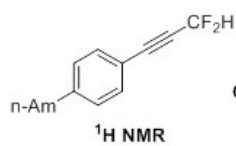




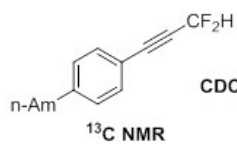
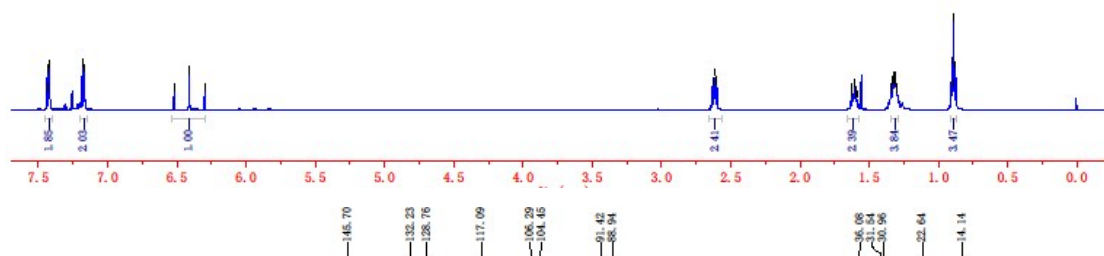
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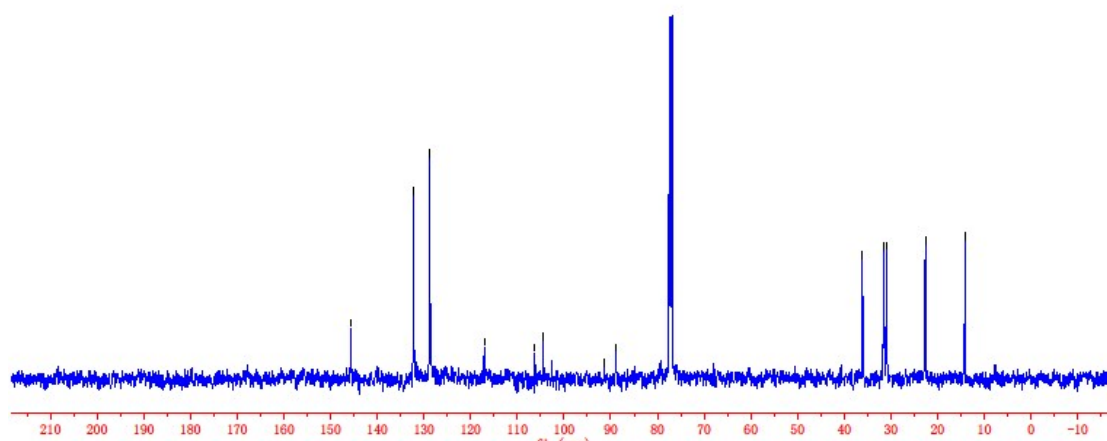
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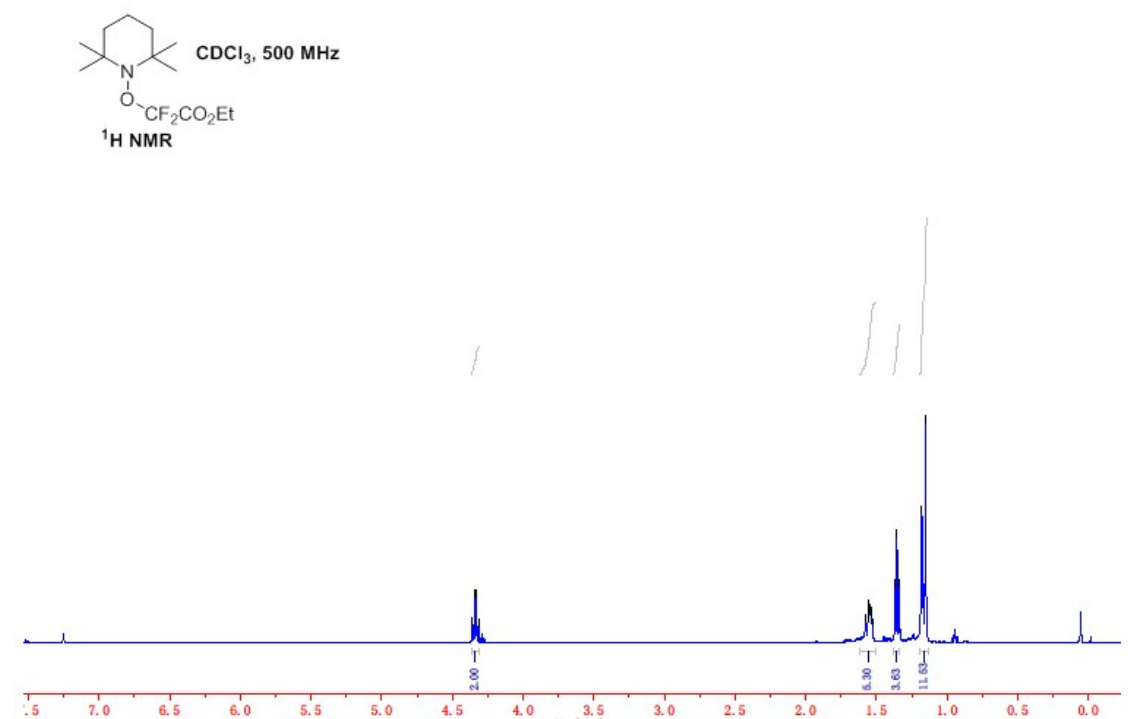
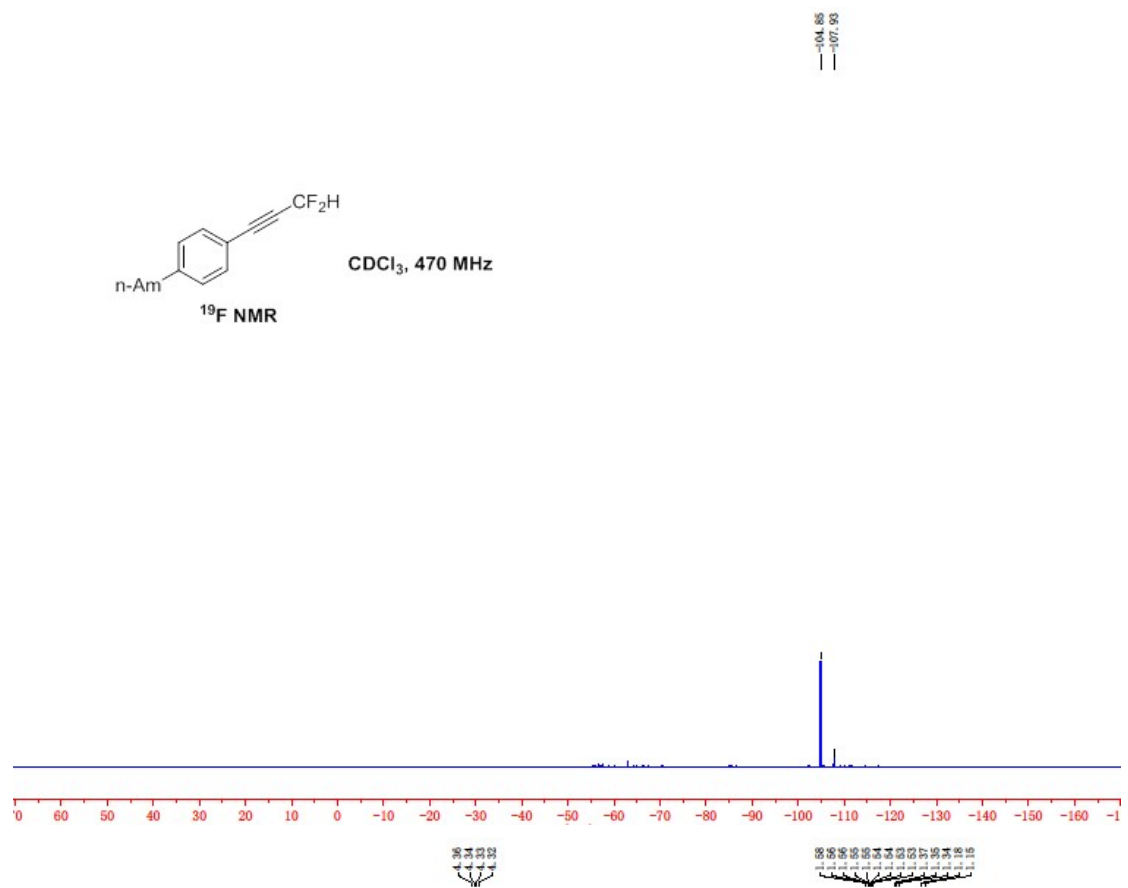


CDCl₃, 500MHz



CDCl₃, 126 MHz





160.04
159.71
156.37

129.89
127.81

116.63
114.47
112.31

61.99
60.36

39.17
32.40

19.73
15.89

