

Supporting Information for

Silver-Catalyzed C–H Trifluoromethylation of Arenes Using Trifluoroacetic Acid as the Trifluoromethylating Reagent

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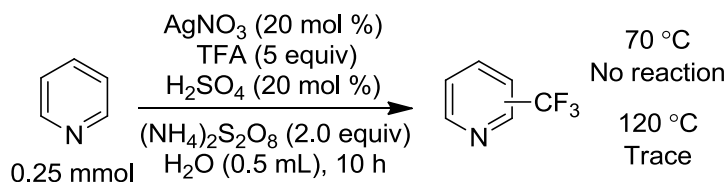
General Information: All of the solvents were purified by distillation prior to use. Unless otherwise noted, the other commercial materials were used without further purification. ^1H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded with Bruker ARX400. GC-MS data were tested with ThermoFisher Trace1300-ISQ (EI). High resolution mass spectra were measured on Bruker MicroTOF II ESI-TOF mass spectrometer. ^1H NMR spectra were recorded in CDCl_3 and referenced to residual CHCl_3 at 7.26 ppm, ^{19}F NMR were referenced to $\text{CF}_3\text{CH}_2\text{OH}$ at -77.56 ppm in CDCl_3 , and ^{13}C NMR spectra were referenced to the central peak of CDCl_3 at 77.0 ppm. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

Some of the trifluoromethylated products were isolated. For the inseparable isomers, the authentic samples were purchased or synthesized. The products were identified by comparing the ^{19}F NMR and ^1H NMR spectroscopic data of the products with those of authentic samples and confirmed by GC-MS analysis.

I. Attempts towards Trifluoromethylation of Pyridine with TFA under Minisci Reaction Conditions:

General procedure for trifluoromethylation of pyridine with TFA under Minisci reaction conditions: A 50 mL Schlenk-type tube (with a Teflon high pressure valve) equipped with a magnetic stir bar was charged with pyridine (0.25 mmol, 20.1 μL), AgNO_3 (20 mol %, 8.5 mg), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (2.0 equiv, 114.1 mg), followed by TFA (5.0 equiv, 92.8 μL), concd H_2SO_4 (20 mol %, 6.8 μL), and H_2O (0.5 mL) as the solvent. After the reaction mixture was stirred at 70 $^\circ\text{C}$ or 120 $^\circ\text{C}$ for 10 h (500 rpm), it was allowed to cool to ambient temperature. The reaction mixture was diluted with ethyl acetate (10 mL) and washed with saturated aqueous NaHCO_3 (3 mL) and brine (3 mL, twice). The organic phase was dried with Na_2SO_4 and analyzed by GC-MS. No or only a trace amount of desired product was detected for the reaction at 70 $^\circ\text{C}$ or 120 $^\circ\text{C}$ respectively.

Scheme S1. Attempts towards Trifluoromethylation of Pyridine with TFA under Minisci Reaction Conditions

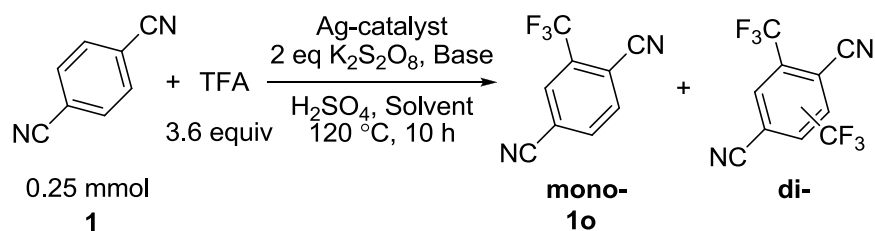


II. General Procedure for the Screening of Reaction Conditions:

Conditions A: A 50 mL Schlenk-type tube (with a Teflon high pressure valve and side arm) equipped with a magnetic stir bar was charged with terephthalonitrile (0.25 mmol, 32.0 mg), Ag-catalyst, $\text{K}_2\text{S}_2\text{O}_8$ (2.0 equiv, 135.2 mg), base, followed by TFA, concd H_2SO_4 , and MeCN as the solvent. The reaction tube closed with a tiny opening. After the reaction mixture was stirred at 120 °C for 10 h, it was allowed to cool to ambient temperature. The reaction mixture was diluted with ethyl acetate (10 mL) and washed with saturated aqueous NaHCO_3 (3 mL) and brine (3 mL, twice). The organic phase was dried with Na_2SO_4 , filtered, and concentrated *in vacuo*. The yield was determined by ^{19}F NMR and ^1H NMR analysis of crude product using $\text{CF}_3\text{CH}_2\text{OH}$ and CH_2Br_2 as the internal standard respectively.

Conditions B: A 50 mL Schlenk-type tube (with a Teflon high pressure valve and side arm) equipped with a magnetic stir bar was charged with terephthalonitrile (0.25 mmol, 32.0 mg), Ag-catalyst, $\text{K}_2\text{S}_2\text{O}_8$ (2.0 equiv, 135.2 mg), base, followed by TFA, concd H_2SO_4 , and DCM as the solvent. After the reaction mixture was stirred at 120 °C for 10 h, it was allowed to cool to ambient temperature. The reaction mixture was diluted with ethyl acetate (10 mL) and washed with saturated aqueous NaHCO_3 (3 mL) and brine (3 mL, twice). The organic phase was dried with Na_2SO_4 , filtered, and concentrated *in vacuo*. The yield was determined by ^{19}F NMR and ^1H NMR analysis of crude product using $\text{CF}_3\text{CH}_2\text{OH}$ and CH_2Br_2 as the internal standard respectively.

Table S1. Condition Optimization of C–H Trifluoromethylation of Terephthalonitrile Using TFA as the Trifluoromethylating Reagent



entry	Ag-catalyst (mol %)	base (equiv)	H ₂ SO ₄ (eq)	solvent (mL)	yield (%) ^a
1 ^b	Ag ₂ CO ₃ (40)	-	-	MeCN (0.4)	trace
2 ^b	Ag ₂ CO ₃ (40)	-	0.2	MeCN (0.4)	trace
3 ^b	Ag ₂ CO ₃ (40)	Na ₂ CO ₃ (1.5)	-	MeCN (0.4)	17
4	Ag ₂ CO ₃ (40)	Na ₂ CO ₃ (1.5)	-	MeCN (0.4)	55 (di-:17)
5	Ag ₂ CO ₃ (40)	Na ₂ CO ₃ (1.5)	0.5	MeCN (0.4)	56 (di-:8)
6	Ag ₂ CO ₃ (40)	Na ₂ CO ₃ (1.5)	-	MeCN (0.9)	57 (di-:14)
7	Ag₂CO₃ (40)	Na₂CO₃ (1.5)	0.5	MeCN (0.9)	81 (di-:21)
8 ^b	Ag ₂ CO ₃ (40)	Na ₂ CO ₃ (1.5)	0.5	MeCN (0.2)	27 (di-:5)
9 ^b	Ag ₂ CO ₃ (40)	Na ₂ CO ₃ (1.5)	0.5	MeCN (0.4)	20
10 ^b	Ag ₂ CO ₃ (40)	Na ₂ CO ₃ (1.5)	0.5	MeCN (0.9)	11
11 ^c	Ag ₂ CO ₃ (40)	Na ₂ CO ₃ (1.5)	0.5	MeCN (0.9)	-
12 ^d	Ag ₂ CO ₃ (40)	Na ₂ CO ₃ (1.5)	0.5	MeCN (0.9)	-
13	Ag ₂ O (40)	Na ₂ CO ₃ (1.5)	0.5	MeCN (0.9)	10
14	AgNO ₃ (80)	Na ₂ CO ₃ (1.5)	0.5	MeCN (0.9)	6
15	Ag ₂ CO ₃ (40)	NaHCO ₃ (3.0)	0.5	MeCN (0.9)	22
16	Ag ₂ CO ₃ (40)	K ₂ CO ₃ (1.5)	0.5	MeCN (0.9)	24
17	Ag ₂ CO ₃ (40)	KF (3.0)	0.5	MeCN (0.9)	5
18	Ag ₂ CO ₃ (40)	K ₃ PO ₄ (1.0)	0.5	MeCN (0.9)	27
19	Ag ₂ CO ₃ (40)	Na ₂ CO ₃ (1.5)	0.5	H ₂ O (0.9)	-
20	Ag ₂ CO ₃ (40)	Na ₂ CO ₃ (1.5)	0.5	Acetone (0.9)	-
21	Ag ₂ CO ₃ (40)	Na ₂ CO ₃ (1.5)	0.5	DMF (0.9)	-
22	Ag ₂ CO ₃ (40)	Na ₂ CO ₃ (1.5)	0.5	Hexane (0.9)	-
23	Ag ₂ CO ₃ (40)	Na ₂ CO ₃ (1.5)	0.5	DCM (0.9)	20
24 ^b	Ag ₂ CO ₃ (40)	Na ₂ CO ₃ (1.5)	0.5	DCM (0.9)	40 (di-:5)
25 ^b	Ag ₂ CO ₃ (40)	Na ₂ CO ₃ (1.5)	0.5	DCM (0.7)	57 (di-:6)
26^{b,e}	Ag₂CO₃ (40)	Na₂CO₃ (2.5)	0.2	DCM (0.7)	77 (di-:19)
27 ^{b,e}	Ag ₂ CO ₃ (40)	Na ₂ CO ₃ (2.5)	0.2	DCM (0.4)	25
28 ^{b,e}	Ag ₂ CO ₃ (20)	Na ₂ CO ₃ (2.5)	0.2	DCM (0.7)	64 (di-:10)
29 ^{b,e}	Ag ₂ CO ₃ (5)	Na ₂ CO ₃ (2.5)	0.2	DCM (0.7)	27
30 ^{b,e}	-	Na ₂ CO ₃ (2.5)	0.2	DCM (0.7)	trace
31	Ag ₂ CO ₃ (10)	Na ₂ CO ₃ (1.5)	0.5	MeCN (0.9)	31
32	-	Na ₂ CO ₃ (1.5)	0.5	MeCN (0.9)	trace

Note: ^a The yields were determined by ¹⁹F NMR analysis of crude products using CF₃CH₂OH as the internal standard. ^b The reaction flask was well-sealed. ^c no K₂S₂O₈. ^d DTBP instead of K₂S₂O₈. ^e 6.1 equiv TFA.

III. General Procedure for Silver-Catalyzed Trifluoromethylation with TFA:

Conditions A: A 50 mL Schlenk-type tube (with a Teflon high pressure valve and side arm) equipped with a magnetic stir bar was charged with substrate (0.25 mmol), Ag₂CO₃ (40 mol %, 27.6 mg), K₂S₂O₈ (2.0 equiv, 135.2 mg), Na₂CO₃ (1.5 equiv, 39.8 mg), followed by TFA (3.6 equiv, 66.8 uL), concd H₂SO₄ (50 mol %, 6.8 uL), and MeCN (0.9 mL) as the solvent. The reaction tube was closed with a tiny opening. After the reaction mixture was stirred at 120 °C for 10 h, it was allowed to cool to ambient temperature. The reaction mixture was diluted with ethyl acetate (10 mL) and washed with saturated aqueous NaHCO₃ (3 mL) and brine (3 mL, twice). The organic phase was dried with Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatograph (*n*-hexane/ethyl acetate mixtures) to give inseparable products. The products were analyzed by ¹⁹F NMR and ¹H NMR spectroscopy and GC-MS. The NMR spectroscopic data matched those obtained for an authentic sample. The yield was determined by ¹⁹F NMR and ¹H NMR analysis of crude product using CF₃CH₂OH and CH₂Br₂ as the internal standard respectively. For volatile products, the reaction mixture was analyzed by ¹⁹F NMR spectroscopy and GC-MS without workup.

Conditions B: A 50 mL Schlenk-type tube (with a Teflon high pressure valve) equipped with a magnetic stir bar was charged with substrate (0.25 mmol), Ag₂CO₃ (40 mol %, 27.6 mg), K₂S₂O₈ (2.0 equiv, 135.2 mg), Na₂CO₃ (2.5 equiv, 66.3 mg), followed by TFA (6.1 equiv, 113.2 uL), concd H₂SO₄ (20 mol %, 2.7 uL), and DCM (0.7 mL) as the solvent. After the reaction mixture was stirred at 120 °C for 10 h, it was allowed to cool to ambient temperature. The reaction mixture was diluted with ethyl acetate (10 mL) and washed with saturated aqueous NaHCO₃ (3 mL) and brine (3 mL, twice). The organic phase was dried with Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by silica gel column chromatograph (*n*-hexane/ethyl acetate mixtures) to give inseparable products. The products were analyzed by ¹⁹F NMR and ¹H NMR spectroscopy and GC-MS. The NMR spectroscopic data matched those obtained for an authentic sample. The yield was determined by ¹⁹F NMR and ¹H NMR analysis of crude product using CF₃CH₂OH and CH₂Br₂ as the internal standard

respectively. For volatile products, the reaction mixture was analyzed by ^{19}F NMR spectroscopy and GC-MS without workup.

Table S2. Silver-catalyzed C-H Trifluoromethylation of Arenes using TFA as the Trifluoromethylating Reagent

0.25 mmol
2-21

conditions **A** or **B**

mono-2-21o-p **di-2-21o-p**

entry	substrates	products	conditions	yield and ^e isomer ratio	entry	substrates	products	conditions	yield and ^e isomer ratio
1			B	69% (di:10%)	12			B	57% (o:m:di = 21:27:9)
2			B	88% (o:m:p:di = 28:11:29:20)	13			A^{b, c}	83% (m:p:di = 44:29:10)
3			B	74% (o:m:p:di = 35:11:19:9)	14			B^a	44% (o:m = 26:18)
4			B^a	81% (isomer ratio 46:29:6)	15			B	60% (o:m:di = 29:25:6)
5			A^{b, c}	81% (o:m:p:di = 25:22:19:15)	16			B	53% (o:m = 29:24)
6			B^{a, b}	63% (o:m:di = 33:21:9)	17			B	76% (o:m:di = 35:26:15)
7			B	73% (o:m:di = 42:15:16)	18			B	75% (di:15%)
8			B^a	48% (o:m = 27:21)	19			A^{b, c}	56% (o:m:di = 23:27:6)
9			B	78% (o:m:di = 36:24:18)	20			A	54% (di:8) (isomer ratio 26:20)
10			B^{a, b}	76% (o:m:di = 40:24:12)					
11			A^{b, c}	64% (o:m:di = 41:7:16)					

Note: ^a 3.6 equiv TFA. 1.5 equiv Na_2CO_3 . ^b no concd H_2SO_4 . ^c 0.4 mL MeCN. ^d 5 mol % Ag_2CO_3 . ^e The yield and isomer ratio were determined by ^{19}F NMR and ^1H NMR using $\text{CF}_3\text{CH}_2\text{OH}$ and CH_2Br_2 as the internal standard respectively.

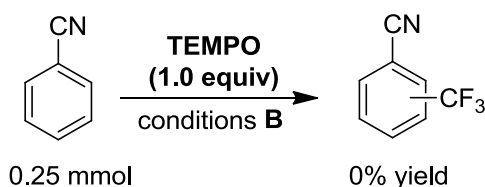
Condition **A**: Ag_2CO_3 (40 mol %), $\text{K}_2\text{S}_2\text{O}_8$ (2.0 equiv), TFA (3.6 equiv), Na_2CO_3 (1.5 equiv), H_2SO_4 (0.5 equiv), MeCN (0.9 mL), 120°C , 10 h, not well-sealed.

Condition **B**: Ag_2CO_3 (40 mol %), $\text{K}_2\text{S}_2\text{O}_8$ (2.0 equiv), TFA (6.1 equiv), Na_2CO_3 (2.5 equiv), H_2SO_4 (0.2 equiv), DCM (0.7 mL), 120 °C, 10 h.

IV. Preliminary Mechanistic Studies:

1. Inhibition of the trifluoromethylation reaction with TEMPO: A 50 mL Schlenk-type tube (with a Teflon high pressure valve) equipped with a magnetic stir bar was charged with benzonitrile (0.25 mmol, 25.5 uL), Ag_2CO_3 (40 mol %, 27.6 mg), $\text{K}_2\text{S}_2\text{O}_8$ (2.0 equiv, 135.2 mg), Na_2CO_3 (1.5 equiv, 39.8 mg), followed by TFA (3.6 equiv, 66.8 uL), concd H_2SO_4 (20 mol %, 2.7 uL), TEMPO (1.0 equiv, 39.1 mg) and DCM (0.7 mL) as the solvent. After the reaction mixture was stirred at 120 °C for 10, it was allowed to cool to ambient temperature. The reaction mixture was diluted with ethyl acetate (10 mL) and washed with saturated aqueous NaHCO_3 (3 mL) and brine (3 mL, twice). The organic phase was dried with Na_2SO_4 , filtered, and concentrated *in vacuo*. No desired product was detected by ^1H NMR, ^{19}F NMR and GC-MS.

Scheme S2. Inhibition of the Trifluoromethylation Reaction with TEMPO

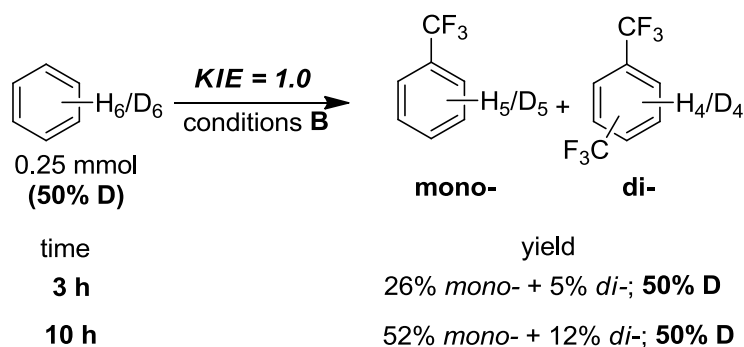


Condition **B**: Ag_2CO_3 (40 mol %), $\text{K}_2\text{S}_2\text{O}_8$ (2.0 equiv), TFA (6.1 equiv), Na_2CO_3 (2.5 equiv), H_2SO_4 (0.2 equiv), DCM (0.7 mL), 120 °C, 10 h.

2. Kinetic isotope effect experiment: A 50 mL Schlenk-type tube (with a Teflon high pressure valve) equipped with a magnetic stir bar was charged with benzene (0.125 mmol, 11.14 uL) and d_6 -benzene (0.125 mmol, 11.07 uL), Ag_2CO_3 (40 mol %, 27.6 mg), $\text{K}_2\text{S}_2\text{O}_8$ (2.0 equiv, 135.2 mg), Na_2CO_3 (2.5 equiv, 66.3 mg), followed by TFA (6.1 equiv, 113.2 uL), concd H_2SO_4 (20 mol %, 2.7 uL), and DCM (0.7 mL) as the solvent. After the reaction mixture was stirred at 120 °C for 3 h or 10 h, it was allowed to cool to ambient temperature. The reaction mixture was diluted with CDCl_3

(3 mL) and washed with saturated aqueous NaHCO₃ (2 mL). The ratios of trifluorotoluene to *d*₅-trifluorotoluene were determined by ¹H NMR and ¹⁹F NMR analysis of crude products using CH₂Br₂ and CF₃CO₂CH₃ as the internal standard respectively.

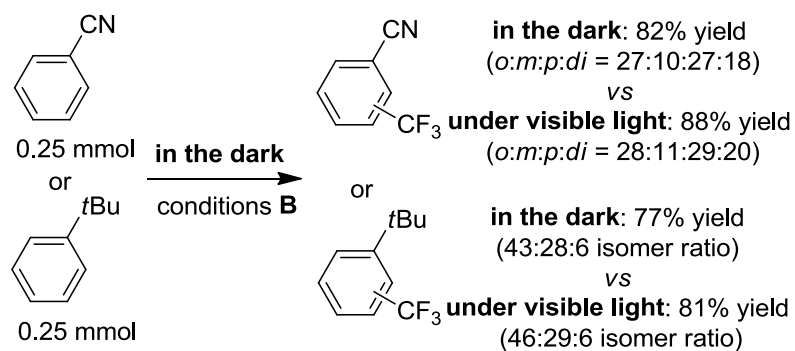
Scheme S3. Kinetic Isotope Effect Experiments



Condition **B**: Ag₂CO₃ (40 mol %), K₂S₂O₈ (2.0 equiv), TFA (6.1 equiv), Na₂CO₃ (2.5 equiv), H₂SO₄ (0.2 equiv), DCM (0.7 mL), 120 °C, 10 h.

3. Reactions in the dark: A 50 mL Schlenk-type tubes wrapped with aluminum foil (with a Teflon high pressure valve) equipped with a magnetic stir bar were charged with benzonitrile (0.25 mmol, 25.5 uL) or *tert*-butylbenzene (0.25 mmol, 38.5 uL), followed by Ag₂CO₃ (40 mol %, 27.6 mg), K₂S₂O₈ (2.0 equiv, 135.2 mg), TFA (3.6 equiv, 66.8 uL), Na₂CO₃ (1.5 equiv, 39.8 mg), concd H₂SO₄ (20 mol %, 2.7 uL), and DCM (0.7 mL) as the solvent. After the reaction mixture was stirred at 120 °C in the dark for 10 h, it was allowed to cool to ambient temperature. The reaction mixture was diluted with ethyl acetate (10 mL) and washed with saturated aqueous NaHCO₃ (3 mL) and brine (3 mL, twice). The organic phase was dried with Na₂SO₄ and filtered. The reactions were analyzed by ¹⁹F NMR using CF₃CH₂OH as the internal standard, which showed similar results to those under visible light.

Scheme S4. Investigation of the Influence of Light Radiation on the C-H Trifluoromethylation Reaction

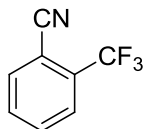


Condition **B**: Ag_2CO_3 (40 mol %), $\text{K}_2\text{S}_2\text{O}_8$ (2.0 equiv), TFA (6.1 equiv), Na_2CO_3 (2.5 equiv), H_2SO_4 (0.2 equiv), DCM (0.7 mL), 120 °C, 10 h.

V. Characterization of the Authentic Samples

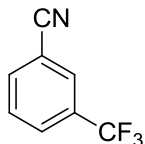
1. Commercially available authentic samples:

2-(Trifluoromethyl)benzonitrile (3o):



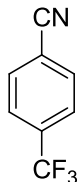
^1H NMR (400 MHz, CDCl_3): δ = 7.86 (d, J = 7.5 Hz, 1H), 7.81 (d, J = 7.4 Hz, 1H), 7.75 (m, 1H), 7.70 (m, 1H). ^{19}F NMR (376 MHz, CDCl_3): δ = -62.38 (s, 3F).

3-(Trifluoromethyl)benzonitrile (3m):



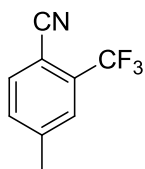
^1H NMR (400 MHz, CDCl_3): δ = 7.93 (s, 1H), 7.87 (m, 2H), 7.66 (t, J = 7.9 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3): δ = -63.61 (s, 3F).

4-(Trifluoromethyl)benzonitrile (3p):



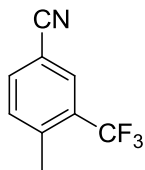
^1H NMR (400 MHz, CDCl_3): δ = 7.82 (d, J = 8.3 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H). ^{19}F NMR (376 MHz, CDCl_3): δ = -63.93 (s, 3F).

4-Methyl-2-(trifluoromethyl)benzonitrile (7o):



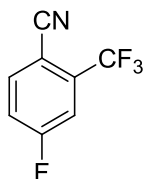
^1H NMR (400 MHz, CDCl_3): δ = 7.72 (d, J = 7.9 Hz, 1H), 7.60 (s, 1H), 7.48 (d, J = 7.9 Hz, 1H), 2.50 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3): δ = -62.38 (s, 3F).

4-Methyl-3-(trifluoromethyl)benzonitrile (7m):



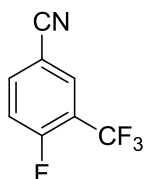
^1H NMR (400 MHz, CDCl_3): δ = 7.89 (s, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.43 (d, J = 7.9 Hz, 1H), 2.56 (d, J = 1.1 Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3): δ = -62.89 (s, 3F).

4-Fluoro-2-(trifluoromethyl)benzonitrile (8o):



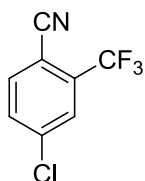
^1H NMR (400 MHz, CDCl_3): δ = 7.88 (m, 1H), 7.52 (dd, J = 8.2, 2.3 Hz, 1H), 7.43 (m, 1H). ^{19}F NMR (376 MHz, CDCl_3): δ = -62.81 (s, 3F), -100.22 (s, 1F).

4-Fluoro-3-(trifluoromethyl)benzonitrile (8m):



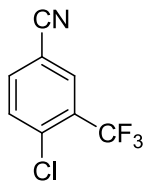
^1H NMR (400 MHz, CDCl_3): δ = 7.96 (dd, J = 6.4, 1.6 Hz, 1H), 7.89 (m, 1H), 7.37 (t, J = 9.1 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3): δ = -62.40 (d, J = 12.7 Hz, 3F), -104.30 (q, J = 12.7 Hz, 1F).

4-Chloro-2-(trifluoromethyl)benzonitrile (9o):



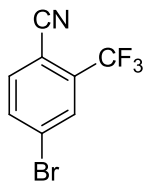
^1H NMR (400 MHz, CDCl_3): δ = 7.80 (m, 2H), 7.68 (dd, J = 8.2, 1.9 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3): δ = -62.73 (s, 3F).

4-Chloro-3-(trifluoromethyl)benzonitrile (9m):



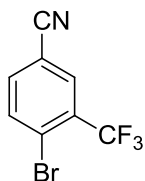
^1H NMR (400 MHz, CDCl_3): δ = 7.99 (d, J = 1.6 Hz, 1H), 7.78 (dd, J = 8.3, 1.7 Hz, 1H), 7.67 (d, J = 8.3 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3): δ = -63.73 (s, 3F).

4-Bromo-2-(trifluoromethyl)benzonitrile (10o):



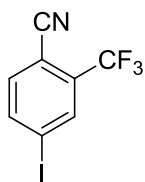
^1H NMR (400 MHz, CDCl_3): δ = 7.95 (s, 1H), 7.85 (dd, J = 8.2, 1.4 Hz, 1H), 7.71 (d, J = 8.2 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3): δ = -62.61 (s, 3F).

4-Bromo-3-(trifluoromethyl)benzonitrile (10m):



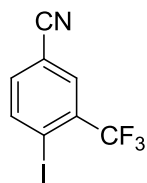
^1H NMR (400 MHz, CDCl_3): δ = 7.96 (d, J = 1.4 Hz, 1H), 7.88 (d, J = 8.3 Hz, 1H), 7.67 (dd, J = 8.3, 1.7 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3): δ = -63.81 (s, 3F).

4-Iodo-2-(trifluoromethyl)benzonitrile (11o):



^1H NMR (400 MHz, CDCl_3): δ = 8.14 (s, 1H), 8.06 (d, J = 8.1 Hz, 1H), 7.54 (d, J = 8.1 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3): δ = -62.56 (s, 3F).

4-Iodo-3-(trifluoromethyl)benzonitrile (11m):



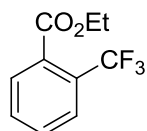
^1H NMR (400 MHz, CDCl_3): δ = 8.19 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 1.6 Hz, 1H), 7.46 (dd, J = 8.2, 1.7 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3): δ = -64.02 (s, 3F).

2. Synthetic samples:

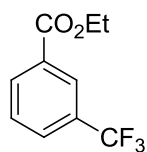
General Procedure for the Preparation of Ethyl Benzoates from the Corresponding Benzonitriles:

The ethyl benzoates were synthesized following a literature procedure.^[1] To a solution of NaOH (1.25 mmol, 50.0 mg) in water (1.0 mL) and ethanol (0.1 mL) was added benzonitrile (0.25 mmol). The reaction mixture was stirred at reflux for 6 h. The mixture was cooled to room temperature and diluted with 5 mL H_2O , and then washed with DCM (5 mL \times 2). The aqueous phase was acidified by 1N HCl and extracted with 10 mL ethyl acetate. The organic layer was washed with brine and dried over Na_2SO_4 , filtered and concentrated in vacuum. The crude benzoic acid was added to a solution of H_2SO_4 (0.5 mL) in ethanol (2 mL), and refluxed for 10 h. The reaction solution was diluted with 10 mL ethyl acetate and washed with H_2O (5 mL), saturated NaHCO_3 solution (3 mL \times 3) and brine (3 mL \times 1), and then dried over Na_2SO_4 , filtered and concentrated in vacuum. The crude product was purified by silica gel column chromatography.

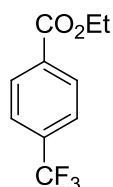
Ethyl 2-(trifluoromethyl)benzoate (4o):



The general procedure was followed with 2-(trifluoromethyl)benzonitrile (0.25 mmol, 42.75 mg) as the substrate to give a colorless liquid (38.8 mg. Yield: 65%). ^1H NMR (400 MHz, CDCl_3): δ = 7.77 (m, 1H), 7.73 (m, 1H), 7.59 (m, 2H), 4.39 (q, J = 7.2 Hz, 2H), 1.38 (t, J = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3): δ = -59.75 (s, 3F). HRMS (ESI-TOF) m/z : calcd for $\text{C}_{10}\text{H}_9\text{F}_3\text{NaO}_2$ ($\text{M}+\text{Na}$) $^+$: 241.0447; found: 241.0461. The ^1H NMR data matched that in literature.^[2]

Ethyl 3-(trifluoromethyl)benzoate (4m):

The general procedure was followed with 3-(trifluoromethyl)benzonitrile (0.25 mmol, 42.75 mg) as the substrate to give a colorless liquid (41.8 mg. Yield: 70%). ^1H NMR (400 MHz, CDCl_3): δ = 8.28 (s, 1H), 8.21 (d, J = 7.8 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H), 4.40 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3): δ = -63.29 (s, 3F). HRMS (ESI-TOF) m/z : calcd for $\text{C}_{10}\text{H}_9\text{F}_3\text{NaO}_2$ ($\text{M}+\text{Na}$) $^+$: 241.0447; found: 241.0462. The ^1H NMR data matched that in literature.^[3]

Ethyl 4-(trifluoromethyl)benzoate (4p):

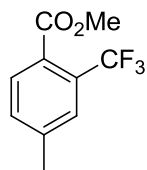
The general procedure was followed with 4-(trifluoromethyl)benzonitrile (0.25 mmol, 42.75 mg) as the substrate to give a colorless liquid (34.7mg. Yield: 58%). ^1H NMR (400 MHz, CDCl_3): δ = 8.15 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H), 4.40 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, CDCl_3): δ = -63.53 (s, 3F). HRMS (ESI-TOF) m/z : calcd for $\text{C}_{10}\text{H}_9\text{F}_3\text{NaO}_2$ ($\text{M}+\text{Na}$) $^+$: 241.0447; found: 241.0421. The ^1H NMR data matched that in literature.^[3]

General Procedure for the Preparation of Methyl Benzoates from the Corresponding Benzonitriles:

The benzoic acids were synthesized following a literature procedure.^[1] To a solution of NaOH (1.25 mmol, 50.0 mg) in water (1.0 mL) and ethanol (0.1 mL) was added benzonitrile (0.25 mmol). The reaction mixture was stirred at reflux for 6 h. The mixture was cooled to room temperature and diluted with 5 mL H_2O , and then washed with DCM (5 mL \times 2). The aqueous phase was acidified by 1N HCl and extracted with 10 mL ethyl acetate. The organic layer was washed with brine and dried over Na_2SO_4 , filtered and concentrated in vacuum. The crude benzoic acid was methylated with fresh CH_2N_2 in ether. The reaction solution was diluted with 5 mL ether and washed with saturated NaHCO_3 solution (3 mL \times 3) and brine (3 mL \times 1), and then dried over Na_2SO_4 , filtered and concentrated in vacuum. The crude product was

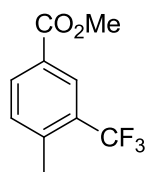
purified by silica gel column chromatography.

Methyl 4-methyl-2-(trifluoromethyl)benzoate (15o):



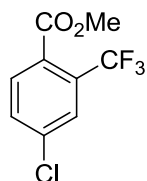
The general procedure was followed with 4-methyl-2-(trifluoromethyl)benzonitrile (0.25 mmol, 46.25 mg) as the substrate to give a colorless liquid (21.3 mg. Yield: 37%). ^1H NMR (400 MHz, CDCl_3): δ = 7.70 (d, J = 7.9 Hz, 1H), 7.54 (s, 1H), 7.39 (d, J = 7.8 Hz, 1H), 3.91 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 167.21, 142.02, 132.12, 130.50, 128.84 (q, J = 32.0 Hz), 128.06, 127.36 (q, J = 5.4 Hz), 123.38 (q, J = 271.6 Hz), 52.63, 21.37. ^{19}F NMR (376 MHz, CDCl_3): δ = -60.07 (s, 3F). HRMS (ESI-TOF) m/z : calcd for $\text{C}_{10}\text{H}_9\text{F}_3\text{NaO}_2$ ($\text{M}+\text{Na}$) $^+$: 241.0447; found: 241.0454.

Methyl 4-methyl-3-(trifluoromethyl)benzoate (15m):



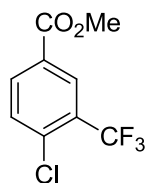
The general procedure was followed with 4-methyl-3-(trifluoromethyl)benzonitrile (0.25 mmol, 46.25 mg) as the substrate to give a colorless liquid (47.1 mg. Yield: 82%). ^1H NMR (400 MHz, CDCl_3): δ = 8.27 (s, 1H), 8.07 (d, J = 7.9 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 3.93 (s, 3H), 2.54 (d, J = 1.0 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 165.95, 142.04 (m), 132.57, 131.13, 129.22 (q, J = 30.4 Hz), 128.09, 127.11 (q, J = 5.7 Hz), 124.02 (q, J = 272.1 Hz), 52.30, 19.52 (m). ^{19}F NMR (376 MHz, CDCl_3): δ = -62.44 (s, 3F). HRMS (ESI-TOF) m/z : calcd for $\text{C}_{10}\text{H}_9\text{F}_3\text{NaO}_2$ ($\text{M}+\text{Na}$) $^+$: 241.0447; found: 241.0463.

Methyl 4-chloro-2-(trifluoromethyl)benzoate (16o):



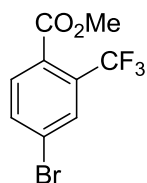
The general procedure was followed with 4-chloro-2-(trifluoromethyl)benzonitrile (0.25 mmol, 51.4 mg) as the substrate to give a colorless solid (29.4 mg. Yield: 47%). ¹H NMR (400 MHz, CDCl₃): δ = 7.79 (d, *J* = 8.3 Hz, 1H), 7.75 (s, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 3.95 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 166.14, 137.73, 131.94, 131.81, 130.57 (q, *J* = 33.1 Hz), 129.25, 127.22 (q, *J* = 5.7 Hz), 122.47 (q, *J* = 272.2 Hz), 52.94. ¹⁹F NMR (376 MHz, CDCl₃): δ = -60.43 (s, 3F). HRMS (ESI-TOF) *m/z*: calcd for C₉H₆ClF₃NaO₂ (M+Na)⁺: 260.9901; found: 260.9909.

Methyl 4-chloro-3-(trifluoromethyl)benzoate (16m):



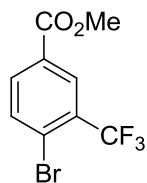
The general procedure was followed with 4-chloro-3-(trifluoromethyl)benzonitrile (0.25 mmol, 51.4 mg) as the substrate to give a colorless solid (53.3 mg. Yield: 85%). ¹H NMR (400 MHz, CDCl₃): δ = 8.34 (s, 1H), 8.12 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 3.94 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 165.01, 137.22 (m), 133.67, 131.73, 129.00, 128.77 (q, *J* = 31.9 Hz), 128.79 (q, *J* = 5.3 Hz), 122.37 (q, *J* = 271.7 Hz), 52.62. ¹⁹F NMR (376 MHz, CDCl₃): δ = -63.39 (s, 3F). HRMS (ESI-TOF) *m/z*: calcd for C₉H₆ClF₃NaO₂ (M+Na)⁺: 260.9901; found: 260.9878.

Methyl 4-bromo-2-(trifluoromethyl)benzoate (17o):



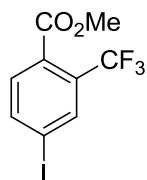
The general procedure was followed with 4-bromo-2-(trifluoromethyl)benzonitrile (0.25 mmol, 62.5 mg) as the substrate to give a colorless solid (40.6 mg. Yield: 55%). ¹H NMR (400 MHz, CDCl₃): δ = 7.89 (d, *J* = 1.5 Hz, 1H), 7.75 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 3.93 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃): δ = -60.35 (s, 3F). HRMS (ESI-TOF) *m/z*: calcd for C₉H₇BrF₃O₂ (M+H)⁺: 282.9576; found: 282.9532.

Methyl 4-bromo-3-(trifluoromethyl)benzoate (17m):



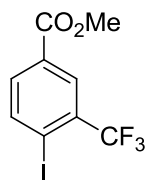
The general procedure was followed with 4-bromo-3-(trifluoromethyl)benzonitrile (0.25 mmol, 62.5 mg) as the substrate to give a colorless solid (64.2 mg. Yield: 87%). ^1H NMR (400 MHz, CDCl_3): δ = 8.33 (d, J = 1.7 Hz, 1H), 8.02 (dd, J = 8.3, 1.9 Hz, 1H), 7.79 (d, J = 8.3 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 165.17, 135.31, 133.59, 130.62 (q, J = 31.8 Hz), 129.56, 128.90 (q, J = 5.5 Hz), 125.43 (m), 122.48 (q, J = 271.9 Hz), 52.67. ^{19}F NMR (376 MHz, CDCl_3): δ = -63.36 (s, 3F). HRMS (ESI-TOF) m/z : calcd for $\text{C}_9\text{H}_6\text{BrF}_3\text{NaO}_2$ ($\text{M}+\text{Na}$) $^+$: 304.9395; found: 304.9358.

Methyl 4-iodo-2-(trifluoromethyl)benzoate (18o):



The general procedure was followed with 4-iodo-2-(trifluoromethyl)benzonitrile (0.25 mmol, 82.5 mg) as the substrate to give a colorless solid (30.1 mg. Yield: 32%). ^1H NMR (400 MHz, CDCl_3): δ = 8.07 (s, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.1 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 166.48, 140.90, 135.73 (q, J = 5.6 Hz), 131.65, 131.14, 130.34, 130.20 (q, J = 32.8 Hz), 130.13, 122.14 (q, J = 272.5 Hz), 52.96. ^{19}F NMR (376 MHz, CDCl_3): δ = -60.32 (s, 3F). HRMS (ESI-TOF) m/z : calcd for $\text{C}_9\text{H}_6\text{IF}_3\text{NaO}_2$ ($\text{M}+\text{Na}$) $^+$: 352.9257; found: 352.9276.

Methyl 4-iodo-3-(trifluoromethyl)benzoate (18m):

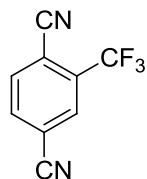


The general procedure was followed with 4-iodo-3-(trifluoromethyl)benzonitrile (0.25 mmol, 82.5 mg) as the substrate to give a colorless solid (71.3 mg. Yield: 76%). ^1H NMR (400 MHz, CDCl_3): δ = 8.25 (d, J = 1.8 Hz, 1H), 8.11 (d, J = 8.2 Hz, 1H), 7.80 (dd, J = 8.2, 1.7 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 165.36,

142.49, 134.11 (q, $J = 31.4$ Hz), 133.24, 130.24, 129.02, 128.38 (q, $J = 5.6$ Hz), 122.38 (q, $J = 272.4$ Hz), 52.62. ^{19}F NMR (376 MHz, CDCl_3): $\delta = -63.46$ (s, 3F). HRMS (ESI-TOF) m/z : calcd for $\text{C}_9\text{H}_6\text{IF}_3\text{NaO}_2 (\text{M}+\text{Na})^+$: 352.9257; found: 352.9274.

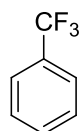
VI. Characterization of the Products

2-(Trifluoromethyl)terephthalonitrile (1o):



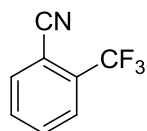
The product was isolated by preparative HPLC as a colorless solid. ^1H NMR (400 MHz, CDCl_3): $\delta = 8.09$ (s, 1H), 8.01 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 135.66$, 135.46, 134.18 (q, $J = 33.8$ Hz), 130.16 (q, $J = 4.7$ Hz), 121.25 (q, $J = 272.9$ Hz), 117.20, 115.74, 114.29, 113.76. ^{19}F NMR (376 MHz, CDCl_3): $\delta = -62.83$ (s, 3F). HRMS (ESI-TOF) m/z : calcd for $\text{C}_9\text{H}_3\text{F}_2\text{N}_2 (\text{M}-\text{F})^+$: 177.0259; found: 177.0259.

Trifluorotoluene (2o):



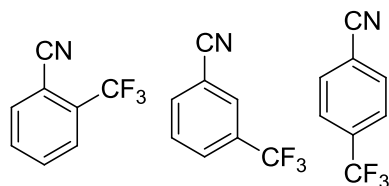
The ^{19}F NMR spectroscopic data of the crude product showed a single peak of -63.14 ppm in CDCl_3 (lit. s, -63.3 ppm in CDCl_3).^[4] The identity of the product was confirmed by GC-MS.

2-(Trifluoromethyl)benzonitrile (3o):



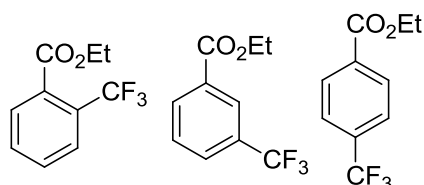
The product was isolated by silica gel preparative TLC as a colorless liquid. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.86$ (d, $J = 7.4$ Hz, 1H), 7.81 (d, $J = 7.6$ Hz, 1H), 7.75 (t, $J = 7.5$ Hz, 1H), 7.70 (t, $J = 7.4$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3): $\delta = -62.61$ (s, 3F). The NMR spectroscopic data matched that of the authentic samples.

2-(Trifluoromethyl)benzonitrile (3o), 3-(trifluoromethyl)benzonitrile (3m) and 4-(trifluoromethyl)benzonitrile (3p):



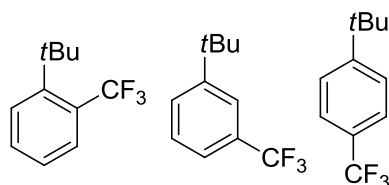
The yield and the isomer ratio were determined by ¹⁹F NMR using CF₃CH₂OH as the internal standard by comparing ¹⁹F NMR with those of authentic samples. The isomer ratio was *o*:*m*:*p* = 28:11:29. ¹⁹F NMR (376 MHz, CDCl₃): δ = -62.38 (*o*-isomer), -63.53 (*m*-isomer), -63.91 (*p*-isomer). The ¹⁹F NMR spectroscopic data matched that of the authentic samples and the identity of the products was confirmed by GC-MS.

Ethyl 2-(trifluoromethyl)benzoate (4o), ethyl 3-(trifluoromethyl)benzoate (4m) and ethyl 4-(trifluoromethyl)benzoate (4p):



The yield and the isomer ratio were determined by ¹⁹F NMR using CF₃CH₂OH as the internal standard by comparing ¹⁹F NMR with those of authentic samples. The isomer ratio was *o*:*m*:*p* = 35:11:19. ¹⁹F NMR (376 MHz, CDCl₃): δ = -59.72 (*o*-isomer), -63.23 (*m*-isomer), -63.51 (*p*-isomer). The ¹⁹F NMR spectroscopic data matched that of the authentic samples synthesized above and the identity of the products was confirmed by GC-MS.

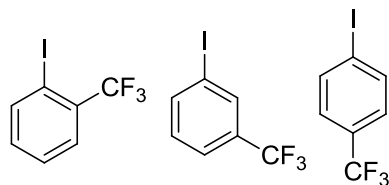
1-(*tert*-Butyl)-2-(trifluoromethyl)benzene (5o), 1-(*tert*-butyl)-3-(trifluoromethyl)benzene (5m) and 1-(*tert*-butyl)-4-(trifluoromethyl)benzene (5p):



The yield and the isomer ratio were determined by ¹⁹F NMR using CF₃CH₂OH as the internal standard. The isomer ratio was 46:29:6. ¹⁹F NMR (376 MHz, CDCl₃): δ = -53.18 (s, 3F), -62.75 (s, 3F), -62.87 (s, 3F). The identity of the products was

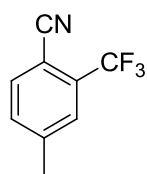
confirmed by GC-MS.

1-Iodo-2-(trifluoromethyl)benzene (6o), 1-iodo-3-(trifluoromethyl)benzene (6m) and 1-iodo-4-(trifluoromethyl)benzene (6p):



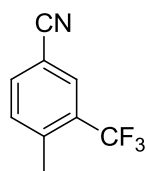
The yield and the isomer ratio were determined by ¹⁹F NMR using CF₃CH₂OH as the internal standard by comparing ¹⁹F NMR with the reported ones. The isomer ratio was *o*:*m*:*p* = 25:22:19. ¹⁹F NMR (376 MHz, CDCl₃): δ = -63.13 (*o*-isomer, lit. -62.7 ppm in CDCl₃)^[4], -63.33 (*m*-isomer, lit. -62.9 ppm in CDCl₃)^[4], -63.41 (*p*-isomer, lit. -63.0 ppm in CDCl₃)^[4]. The identity of the products was confirmed by GC-MS.

4-Methyl-2-(trifluoromethyl)benzonitrile (7o):



The product was isolated by silica gel preparative TLC as a colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ = 7.73 (d, *J* = 7.9 Hz, 1H), 7.60 (s, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 2.50 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 144.27, 134.62, 132.71, 127.44 (q, *J* = 4.5 Hz), 122.44 (q, *J* = 272.0 Hz), 115.68, 107.18, 21.79. ¹⁹F NMR (376 MHz, CDCl₃): δ = -62.34 (s, 3F). HRMS (ESI-TOF) *m/z*: calcd for C₉H₆F₃NaN₂ (M+Na)⁺: 208.0345; found: 208.0349. The NMR spectroscopic data matched that of the authentic sample.

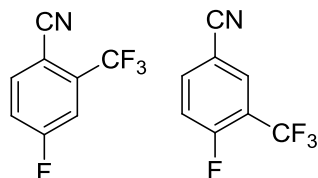
4-Methyl-3-(trifluoromethyl)benzonitrile (7m):



The product was isolated by silica gel preparative TLC as a colorless solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.90 (s, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 2.57 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃): δ = -62.88 (s, 3F). The identity of the

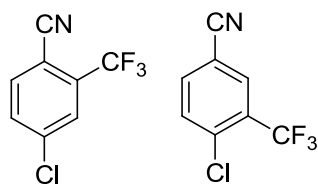
product was confirmed by GC-MS. The NMR spectroscopic data matched that of the authentic sample.

**4-Fluoro-2-(trifluoromethyl)benzonitrile (8o) and
4-fluoro-3-(trifluoromethyl)benzonitrile (8m):**



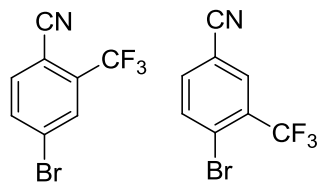
The yield and the isomer ratio were determined by ¹⁹F NMR using CF₃CH₂OH as the internal standard by comparing ¹⁹F NMR with those of authentic samples. The isomer ratio was *o*:*m* = 42:15. **4-Fluoro-2-(trifluoromethyl)benzonitrile (8o):** ¹H NMR (400 MHz, CDCl₃): δ = 7.89 (m, 1H), 7.52 (dd, *J* = 8.2, 2.4 Hz, 1H), 7.40 (m, 1H). ¹⁹F NMR (376 MHz, CDCl₃): δ = -62.79 (s, 3F), -100.23 (s, 1F). **4-Fluoro-3-(trifluoromethyl)benzonitrile (8m):** ¹H NMR (400 MHz, CDCl₃): δ = 7.95 (d, *J* = 7.4 Hz, 1H), 7.89 (m, 1H), 7.37 (m, 1H). ¹⁹F NMR (376 MHz, CDCl₃): δ = -62.40 (d, *J* = 12.4 Hz, 3F), -104.27 (q, *J* = 12.5 Hz, 1F). The NMR spectroscopic data matched that of the authentic samples and the identity of the products was confirmed by GC-MS.

**4-Chloro-2-(trifluoromethyl)benzonitrile (9o) and
4-chloro-3-(trifluoromethyl)benzonitrile (9m):**



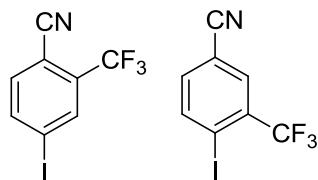
The yield and the isomer ratio were determined by ¹⁹F NMR using CF₃CH₂OH as the internal standard by comparing ¹⁹F NMR with those of authentic samples. The isomer ratio was *o*:*m* = 27:21. **4-Chloro-2-(trifluoromethyl)benzonitrile (9o):** ¹H NMR (400 MHz, CDCl₃): δ = 7.79 (m, 2H), 7.67 (m, 1H). ¹⁹F NMR (376 MHz, CDCl₃): δ = -62.70 (s, 3F). **4-Chloro-3-(trifluoromethyl)benzonitrile (9m):** ¹H NMR (400 MHz, CDCl₃): δ = 7.99 (s, 1H), 7.79 (m, 1H), 7.67 (m, 1H). ¹⁹F NMR (376 MHz, CDCl₃): δ = -63.77 (s, 3F). The NMR spectroscopic data matched that of the authentic samples and the identity of the products was confirmed by GC-MS.

**4-Bromo-2-(trifluoromethyl)benzonitrile (10o) and
4-bromo-3-(trifluoromethyl)benzonitrile (10m):**



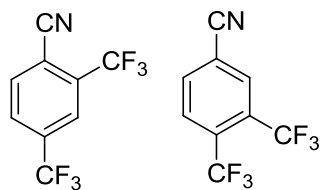
The yield and the isomer ratio were determined by ^{19}F NMR using $\text{CF}_3\text{CH}_2\text{OH}$ as the internal standard by comparing ^{19}F NMR with those of authentic samples. The isomer ratio was $o:m = 36:24$. **4-Bromo-2-(trifluoromethyl)benzonitrile (10o):** ^1H NMR (400 MHz, CDCl_3): $\delta = 7.95$ (s, 1H), 7.85 (d, $J = 8.3$ Hz, 1H), 7.71 (d, $J = 8.2$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3): $\delta = -62.59$ (s, 3F). **4-Bromo-3-(trifluoromethyl)benzonitrile (10m):** ^1H NMR (400 MHz, CDCl_3): $\delta = 7.96$ (s, 1H), 7.88 (d, $J = 8.3$ Hz, 1H), 7.68 (d, $J = 8.3$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3): $\delta = -63.80$ (s, 3F). The NMR spectroscopic data matched that of the authentic samples and the identity of the products was confirmed by GC-MS.

**4-Iodo-2-(trifluoromethyl)benzonitrile (11o) and
4-iodo-3-(trifluoromethyl)benzonitrile (11m):**



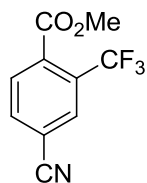
The yield and the isomer ratio were determined by ^{19}F NMR using $\text{CF}_3\text{CH}_2\text{OH}$ as the internal standard by comparing ^{19}F NMR with those of authentic samples. The isomer ratio was $o:m = 40:24$. **4-Iodo-2-(trifluoromethyl)benzonitrile (11o):** ^1H NMR (400 MHz, CDCl_3): $\delta = 8.14$ (s, 1H), 8.06 (d, $J = 7.9$ Hz, 1H), 7.54 (d, $J = 8.1$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3): $\delta = -62.57$ (s, 3F). **4-Iodo-3-(trifluoromethyl)benzonitrile (11m):** ^1H NMR (400 MHz, CDCl_3): $\delta = 8.20$ (d, $J = 8.2$ Hz, 1H), 7.90 (s, 1H), 7.46 (d, $J = 8.1$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3): $\delta = -64.04$ (s, 3F). The NMR spectroscopic data matched that of the authentic samples and the identity of the products was confirmed by GC-MS.

**2,4-Bis(trifluoromethyl)benzonitrile (12o) and
3,4-bis(trifluoromethyl)benzonitrile (12m):**



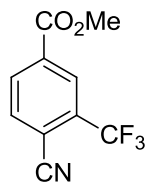
The yield was determined by ^{19}F NMR using $\text{CF}_3\text{CH}_2\text{OH}$ as the internal standard. The isomer ratio was $o:m = 41:7$. **2,4-Bis(trifluoromethyl)benzonitrile (12o):** ^1H NMR (400 MHz, CDCl_3): $\delta = 8.06$ (s, 1H), 8.03 (m, 1H), 7.98 (d, $J = 8.2$ Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3): $\delta = -62.37$ (s, 3F), -63.75 (s, 3F). **3,4-Bis(trifluoromethyl)benzonitrile (12m):** ^1H NMR (400 MHz, CDCl_3): $\delta = 8.15$ (s, 1H), 8.02 (m, 2H). ^{19}F NMR (376 MHz, CDCl_3): $\delta = -59.98$ (m, 3F), -60.10 (m, 3F). The identity of products was further confirmed by GC-MS.

Methyl 4-cyano-2-(trifluoromethyl)benzoate (13o):



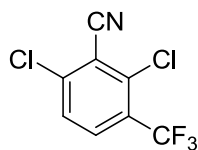
The product was isolated by preparative HPLC as a colorless solid. ^1H NMR (400 MHz, CDCl_3): $\delta = 8.03$ (s, 1H), 7.91 (m, 2H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 165.55$, 135.25, 134.97, 131.05, 130.41 (q, $J = 5.4$ Hz), 130.14 (q, $J = 33.7$ Hz), 122.14 (q, $J = 272.4$ Hz), 116.55, 115.48, 53.37. ^{19}F NMR (376 MHz, CDCl_3): $\delta = -60.65$ (s, 3F). HRMS (ESI-TOF) m/z : calcd for $\text{C}_{10}\text{H}_6\text{F}_2\text{NO}_2$ (M-F) $^+$: 210.0361; found: 210.0381.

Methyl 4-cyano-3-(trifluoromethyl)benzoate (13m):



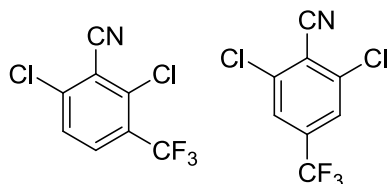
The product was isolated by preparative HPLC as a colorless solid. ^1H NMR (400 MHz, CDCl_3): $\delta = 8.45$ (s, 1H), 8.34 (d, $J = 8.0$ Hz, 1H), 7.95 (d, $J = 8.0$ Hz, 1H), 4.00 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 164.16$, 135.00, 134.32, 133.33 (q, $J = 33.2$ Hz), 132.97, 127.66 (q, $J = 4.7$ Hz), 121.95 (q, $J = 272.5$ Hz), 114.68, 113.90, 53.15. ^{19}F NMR (376 MHz, CDCl_3): $\delta = -62.44$ (s, 3F). HRMS (ESI-TOF) m/z : calcd for $\text{C}_{10}\text{H}_6\text{F}_2\text{NO}_2$ (M-F) $^+$: 210.0361; found: 210.0361.

2,6-Dichloro-3-(trifluoromethyl)benzonitrile (14m):



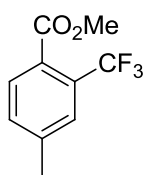
The product was isolated by preparative HPLC as a colorless solid. ^1H NMR (400 MHz, CDCl_3): δ = 7.85 (d, J = 8.6 Hz, 1H), 7.58 (d, J = 8.5 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ = 142.17, 137.32, 131.40, 128.27, 121.72 (J = 272.4 Hz), 117.41, 112.32. ^{19}F NMR (376 MHz, CDCl_3): δ = -63.37 (s, 3F). HRMS (ESI-TOF) m/z : calcd for $\text{C}_8\text{H}_2\text{Cl}_2\text{F}_2\text{N}$ (M-F) $^+$: 219.9527; found: 219.9512.

**2,6-Dichloro-3-(trifluoromethyl)benzonitrile (14m) and
2,6-dichloro-4-(trifluoromethyl)benzonitrile (14p):**



The yield was determined by ^{19}F NMR using $\text{CF}_3\text{CH}_2\text{OH}$ as the internal standard. The isomer ratio was $m:p$ = 44:29. **2,6-Dichloro-4-(trifluoromethyl)benzonitrile (14p):** ^1H NMR (400 MHz, CDCl_3): δ = 7.70 (s, 2H). ^{19}F NMR (376 MHz, CDCl_3): δ = -64.07 (s, 3F). The identity of products was further confirmed by GC-MS.

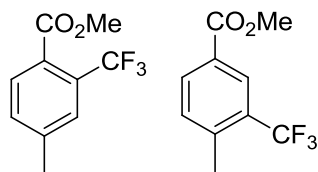
Methyl 4-methyl-2-(trifluoromethyl)benzoate (15o):



The product was isolated by silica gel preparative TLC as a colorless solid. ^1H NMR (400 MHz, CDCl_3): δ = 7.72 (d, J = 7.8 Hz, 1H), 7.55 (s, 1H), 7.40 (d, J = 7.8 Hz, 1H), 3.92 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 167.21, 142.02, 132.12, 130.51, 128.86 (q, J = 32.0 Hz), 128.09, 127.37 (q, J = 5.4 Hz), 123.38 (q, J = 271.7 Hz), 52.65, 21.40. ^{19}F NMR (376 MHz, CDCl_3): δ = -60.06 (s, 3F). HRMS (ESI-TOF) m/z : calcd for $\text{C}_{10}\text{H}_9\text{F}_3\text{NaO}_2$ (M+Na) $^+$: 241.0447; found: 241.0443. The NMR spectroscopic data matched that of the authentic sample synthesized above.

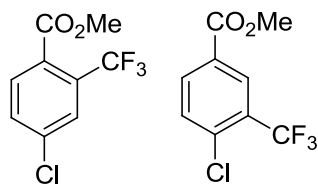
Methyl 4-methyl-2-(trifluoromethyl)benzoate (15o) and methyl

4-methyl-3-(trifluoromethyl)benzoate (15m):



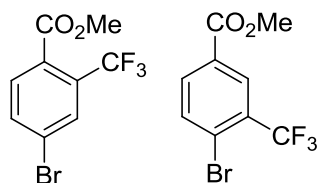
The yield and the isomer ratio were determined by ¹⁹F NMR using CF₃CH₂OH as the internal standard by comparing ¹⁹F NMR with those of authentic samples. The isomer ratio was *o*:*m* = 26:18. **Methyl 4-methyl-3-(trifluoromethyl)benzoate (15m):** ¹H NMR (400 MHz, CDCl₃): δ = 8.28 (s, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 3.93 (s, 3H), 2.54 (d, *J* = 1.0 Hz, 3H). ¹⁹F NMR (376 MHz, CDCl₃): δ = -62.40 (s, 3F). The NMR spectroscopic data matched that of the authentic samples synthesized above, and the products were further confirmed by GC-MS.

Methyl 4-chloro-2-(trifluoromethyl)benzoate (16o) and methyl 4-chloro-3-(trifluoromethyl)benzoate (16m):



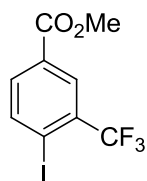
The yield and the isomer ratio were determined by ¹⁹F NMR using CF₃CH₂OH as the internal standard by comparing ¹⁹F NMR with those of authentic samples. The isomer ratio was *o*:*m* = 29:25. **Methyl 4-chloro-2-(trifluoromethyl)benzoate (16o):** ¹H NMR (400 MHz, CDCl₃): δ = 7.77 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 1.9 Hz, 1H), 7.59 (m, 1H), 3.93 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃): δ = -60.42 (s, 3F). **Methyl 4-chloro-3-(trifluoromethyl)benzoate (16m):** ¹H NMR (400 MHz, CDCl₃): δ = 8.35 (d, *J* = 1.8 Hz, 1H), 8.13 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.58 (m, 1H), 3.95 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃): δ = -63.32 (s, 3F). The NMR spectroscopic data matched that of the authentic samples synthesized above, and the products were further confirmed by GC-MS.

Methyl 4-bromo-2-(trifluoromethyl)benzoate (17o) and methyl 4-bromo-3-(trifluoromethyl)benzoate (17m):



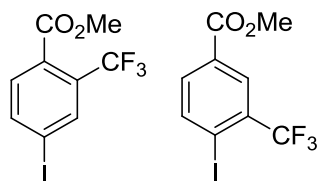
The yield and the isomer ratio were determined by ¹⁹F NMR using CF₃CH₂OH as the internal standard by comparing ¹⁹F NMR with those of authentic samples. The isomer ratio was *o*:*m* = 29:24. **Methyl 4-bromo-2-(trifluoromethyl)benzoate (17o):** ¹H NMR (400 MHz, CDCl₃): δ = 7.89 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 3.93 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃): δ = -60.36 (s, 3F). **Methyl 4-bromo-3-(trifluoromethyl)benzoate (17m):** ¹H NMR (400 MHz, CDCl₃): δ = 8.35 (s, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 3.95 (s, 3H). ¹⁹F NMR (376 MHz, CDCl₃): δ = -63.33 (s, 3F). The NMR spectroscopic data matched that of the authentic samples synthesized above, and the products were further confirmed by GC-MS.

Methyl 4-iodo-3-(trifluoromethyl)benzoate (18m):



The product was isolated by preparative HPLC as a colorless solid. ¹H NMR (400 MHz, CDCl₃): δ = 8.28 (s, 1H), 8.13 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 3.95 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ = 165.39, 142.53, 133.26, 130.30, 128.45, 97.21, 52.63. ¹⁹F NMR (376 MHz, CDCl₃): δ = -63.44 (s, 3F). HRMS (ESI-TOF) *m/z*: calcd for C₉H₆IF₃NaO₂ (M+Na)⁺: 352.9257; found: 352.9254. The NMR spectroscopic data matched that of the authentic samples synthesized above.

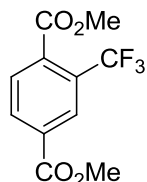
Methyl 4-iodo-2-(trifluoromethyl)benzoate (18o) and methyl 4-iodo-3-(trifluoromethyl)benzoate (18m):



The yield and the isomer ratio were determined by ¹⁹F NMR using CF₃CH₂OH as the internal standard by comparing ¹⁹F NMR with those of authentic samples. The isomer

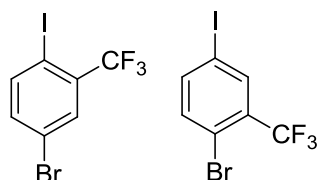
ratio was *o*:*m* = 35:26. **Methyl 4-iodo-2-(trifluoromethyl)benzoate (18o)**: ^1H NMR (400 MHz, CDCl_3): δ = 8.08 (s, 1H), 7.96 (d, J = 8.1 Hz, 1H), 7.51 (d, J = 8.1 Hz, 1H), 3.93 (s, 3H). ^{19}F NMR (376 MHz, CDCl_3): δ = -60.31 (s, 3F). The NMR spectroscopic data matched that of the authentic samples synthesized above, and the products were further confirmed by GC-MS.

Dimethyl 2-(trifluoromethyl)terephthalate (19o):



The product was isolated by preparative HPLC as a colorless solid. ^1H NMR (400 MHz, CDCl_3): δ = 8.39 (s, 1H), 8.25 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 3.96 (s, 3H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 166.47, 164.88, 134.80, 132.70, 132.61, 130.27, 129.06 (q, J = 32.9 Hz), 127.82 (q, J = 5.3 Hz), 122.83 (q, J = 272.0 Hz), 52.99, 52.66. ^{19}F NMR (376 MHz, CDCl_3): δ = -60.31 (s, 3F). HRMS (ESI-TOF) m/z : calcd for $\text{C}_{11}\text{H}_9\text{F}_3\text{NaO}_4$ ($\text{M}+\text{Na}$) $^+$: 285.0345; found: 285.0351.

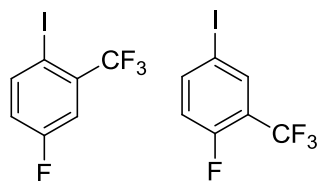
4-Bromo-1-iodo-2-(trifluoromethyl)benzene (20o) and 4-bromo-1-iodo-3-(trifluoromethyl)benzene (20m):



The yield and the isomer ratio were determined by ^{19}F NMR using $\text{CF}_3\text{CH}_2\text{OH}$ as the internal standard by comparing ^{19}F NMR with the reported ones. The isomer ratio was *o*:*m* = 23:27. **4-Bromo-1-iodo-2-(trifluoromethyl)benzene (20o)**: ^1H NMR (400 MHz, CDCl_3): δ = 7.87 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 1.9 Hz, 1H), 7.33 (dd, J = 8.3, 1.9 Hz, 1H). The ^1H NMR data matched that in literature^[5]. ^{19}F NMR (376 MHz, CDCl_3): δ = -63.68 (s, 3F). **4-Bromo-1-iodo-3-(trifluoromethyl)benzene (20m)**: ^1H NMR (400 MHz, CDCl_3): δ = 7.98 (s, 1H), 7.70 (d, J = 8.4 Hz, 1H), 7.42 (d, J = 8.4 Hz, 1H). ^{19}F NMR (376 MHz, CDCl_3): δ = -63.45 (s, 3F). The identity of products was further confirmed by GC-MS.

4-Fluoro-1-iodo-2-(trifluoromethyl)benzene (21o) and

4-fluoro-1-iodo-3-(trifluoromethyl)benzene (21m):



The yield was determined by ^{19}F NMR using $\text{CF}_3\text{CH}_2\text{OH}$ as the internal standard. The isomer ratio was $o:m = 26:20$. ^{19}F NMR: *m*-isomer: -63.83 (s), -112.45 (s); *o*-isomer: -62.12 (d, $J = 12.4$ Hz, 3F), -115.96 (q, $J = 12.6$ Hz, F). The identity of products was further confirmed by GC-MS.

Reference:

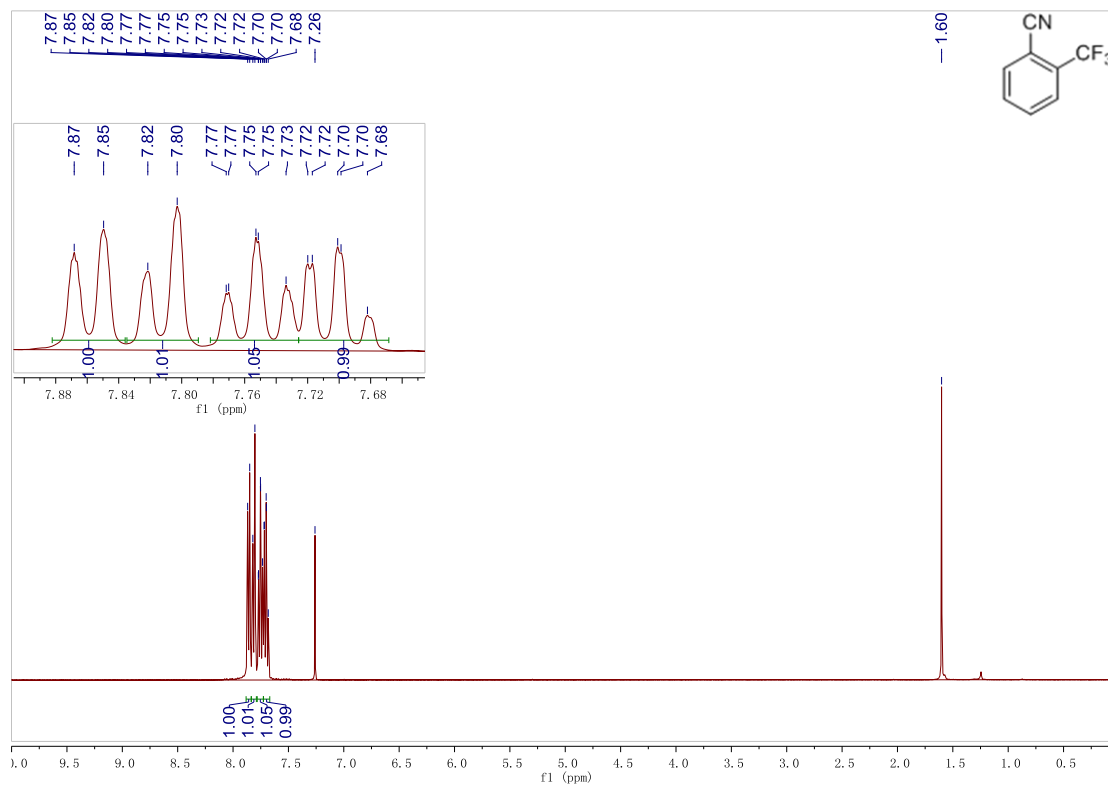
- [1] Liu, C.-Y.;* Wang, X.; Furuyama, T.; Yasuike, S.; Muranaka, A.; Morokuma, K.;* Uchiyama, M.* *Chem. Eur. J.* **2010**, *16*, 1780.
- [2] Popov, I.; Lindeman, S.; Daugulis, O.* *J. Am. Chem. Soc.* **2011**, *133*, 9286.
- [3] R. Shang, Y. Fu,* J.-B. Li, S.-L. Zhang, Q.-X. Guo, L. Liu,* *J. Am. Chem. Soc.*, **2009**, *131*, 5738.
- [4] Ye, Y.-D.; Lee, S. H.; Sanford, M. S.;* *Org. Lett.*, **2011**, *13*, 5464.
- [5] Hattori, Y.; Yamamoto, H.; Ando, H.; Kondoh, H.; Asano, T.; Kirihata, M.; Yamaguchia, Y.; Wakamiyaa, T.* *Bioorgan. Med. Chem.* **2007**, *15*, 2198.

VII. Spectra

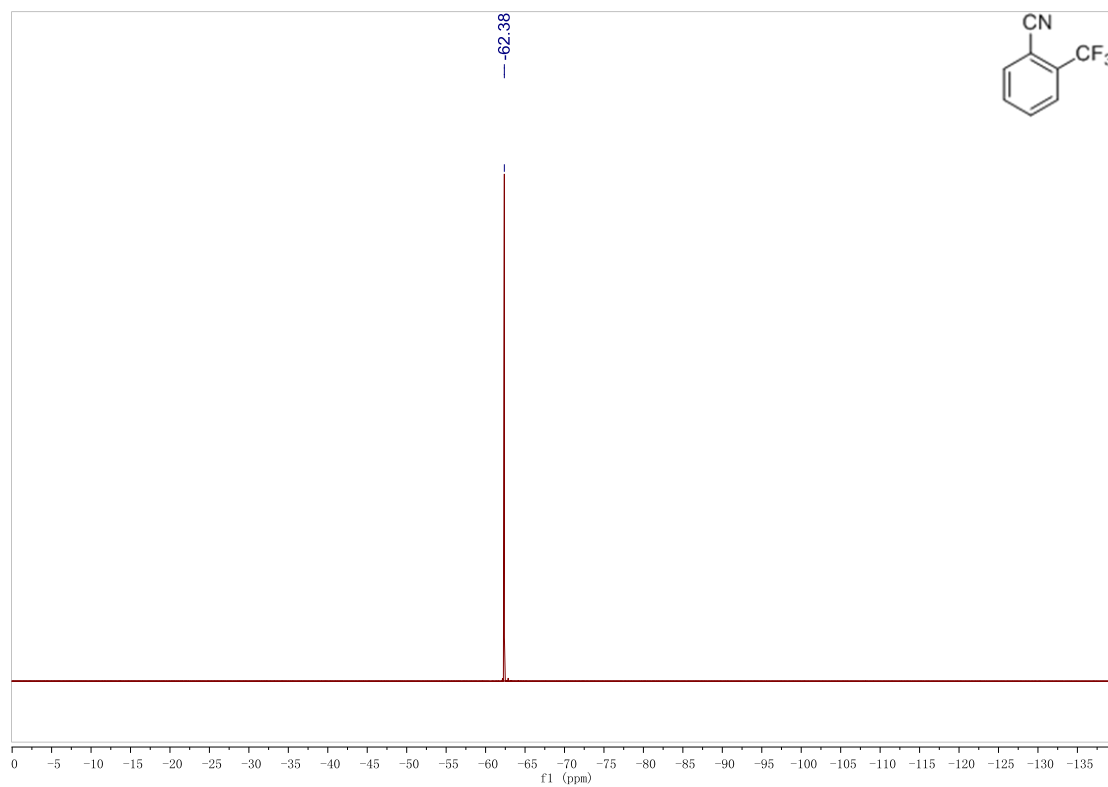
Spectra of authentic samples:

2-(Trifluoromethyl)benzonitrile:

^1H NMR

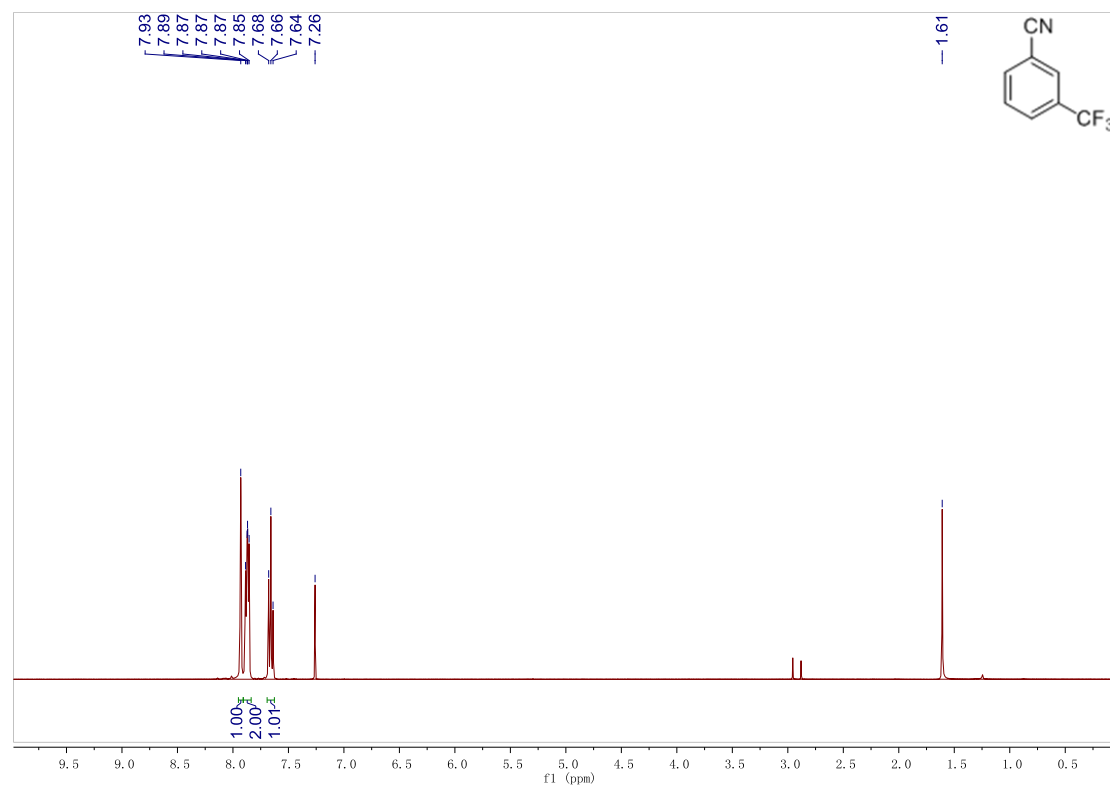


^{19}F NMR

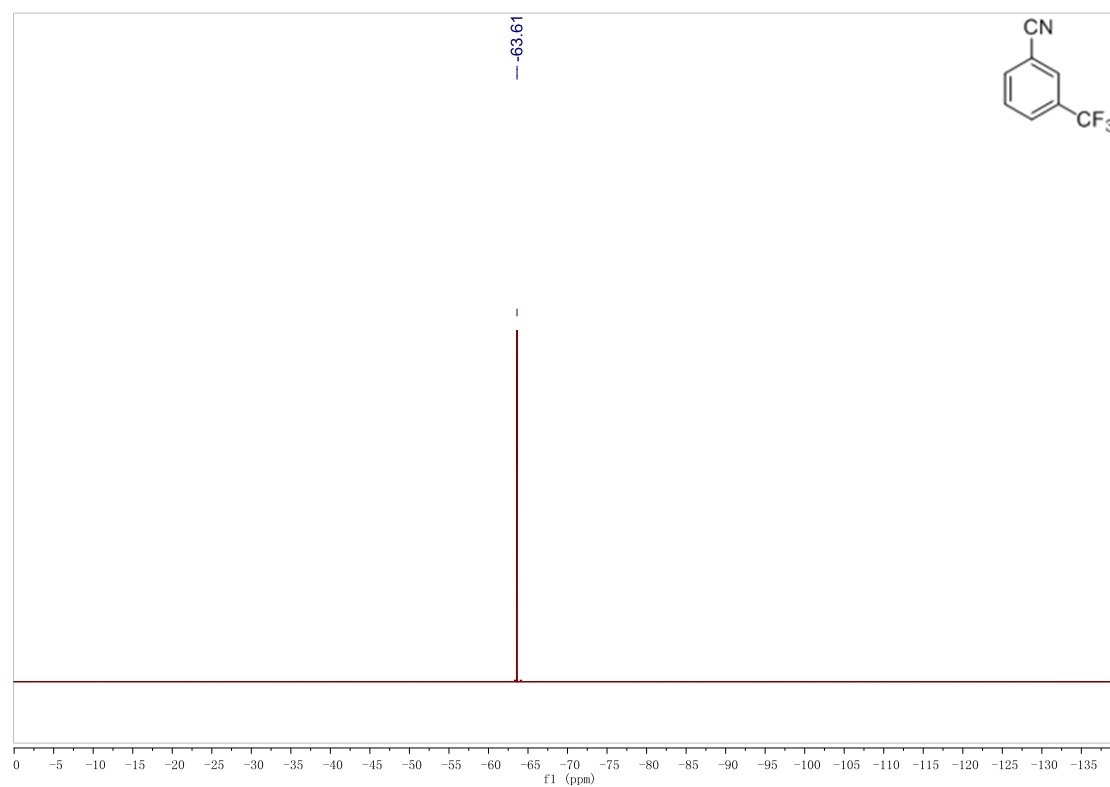


3-(Trifluoromethyl)benzonitrile:

^1H NMR

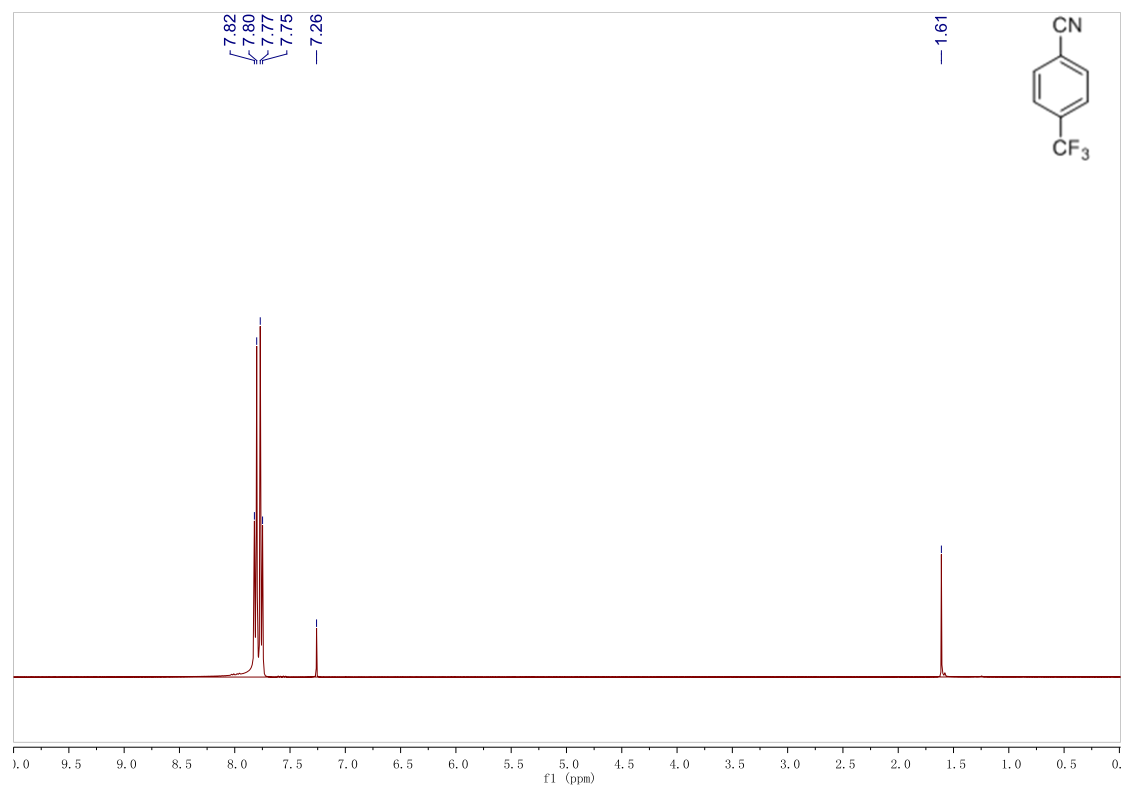


^{19}F NMR

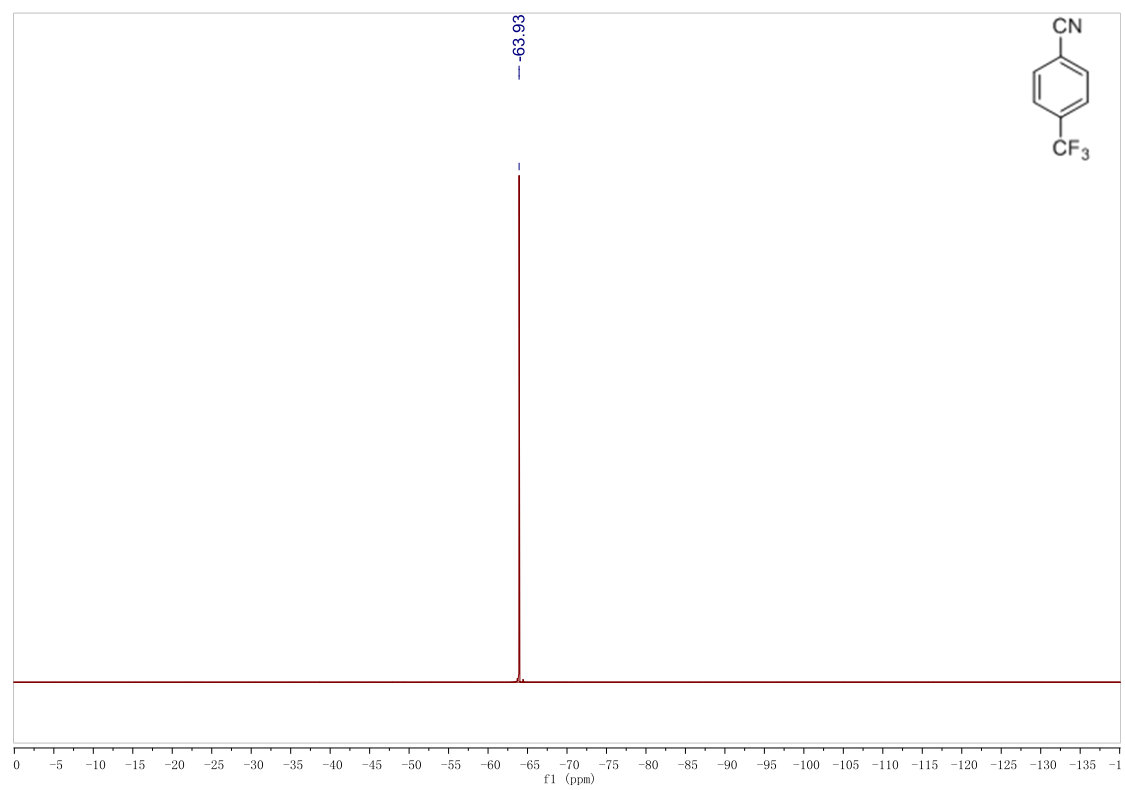


4-(Trifluoromethyl)benzonitrile:

¹H NMR

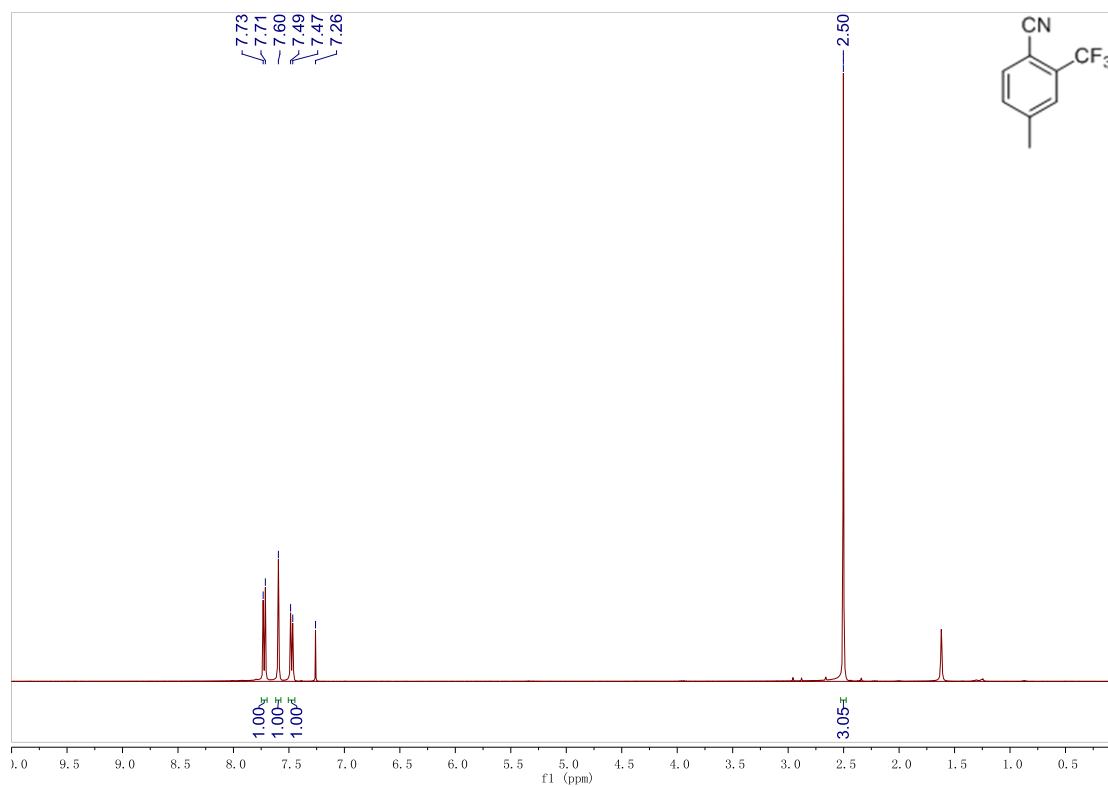


¹⁹F NMR

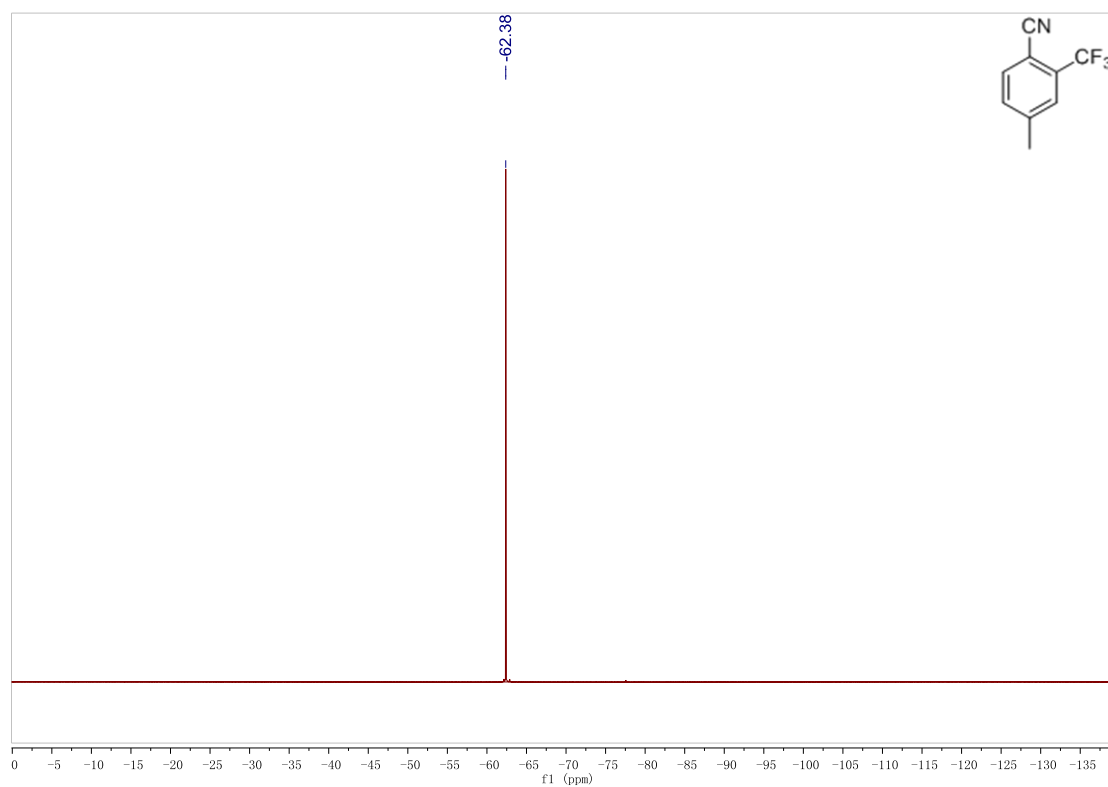


4-Methyl-2-(trifluoromethyl)benzonitrile:

¹H NMR

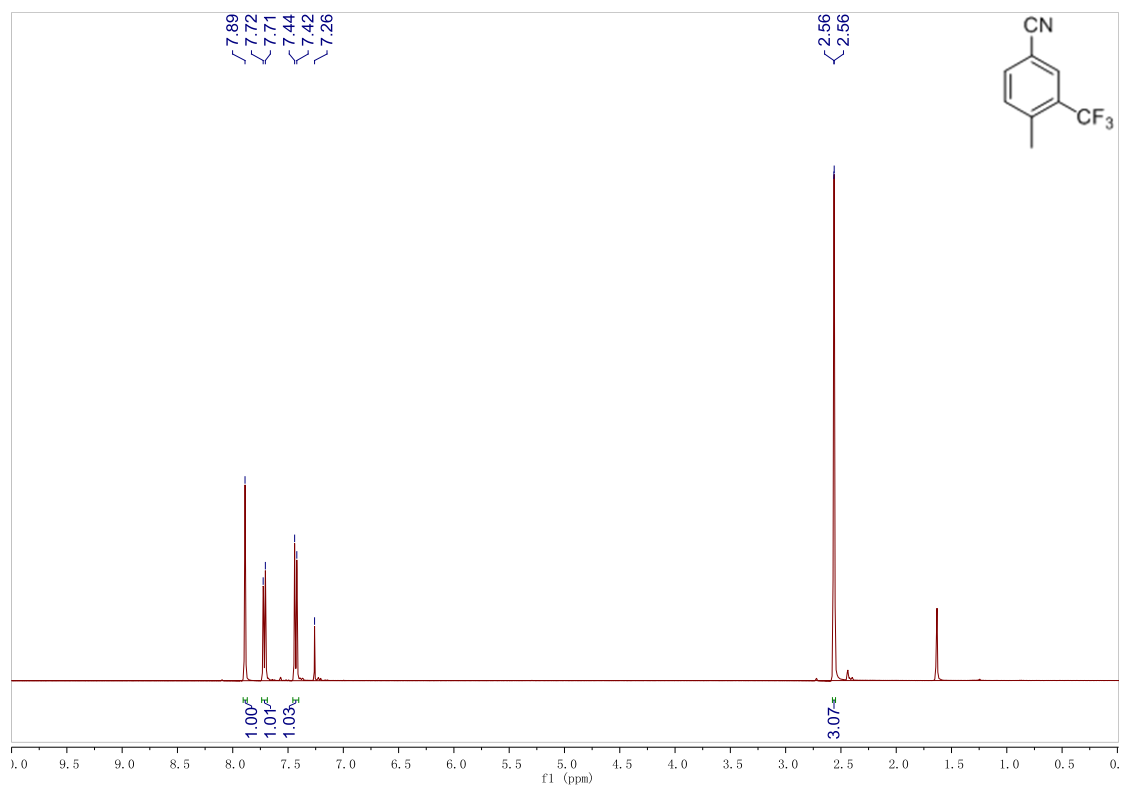


¹⁹F NMR

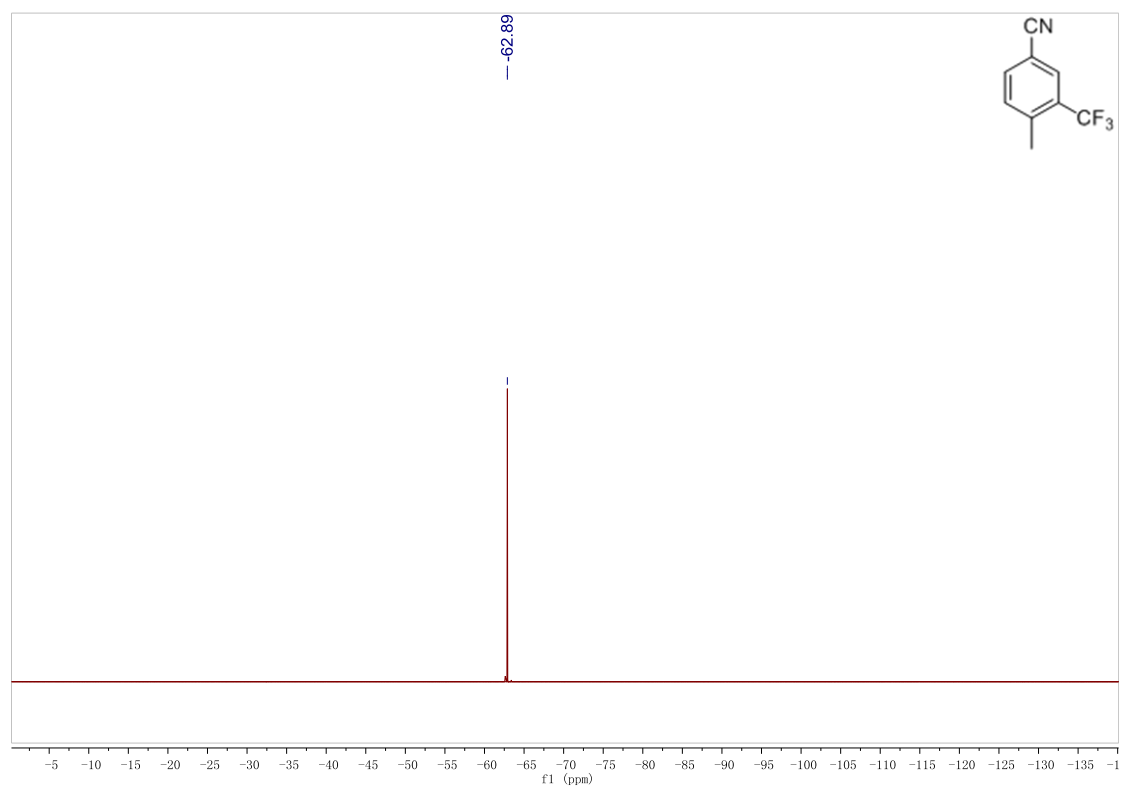


4-Methyl-3-(trifluoromethyl)benzonitrile:

¹H NMR

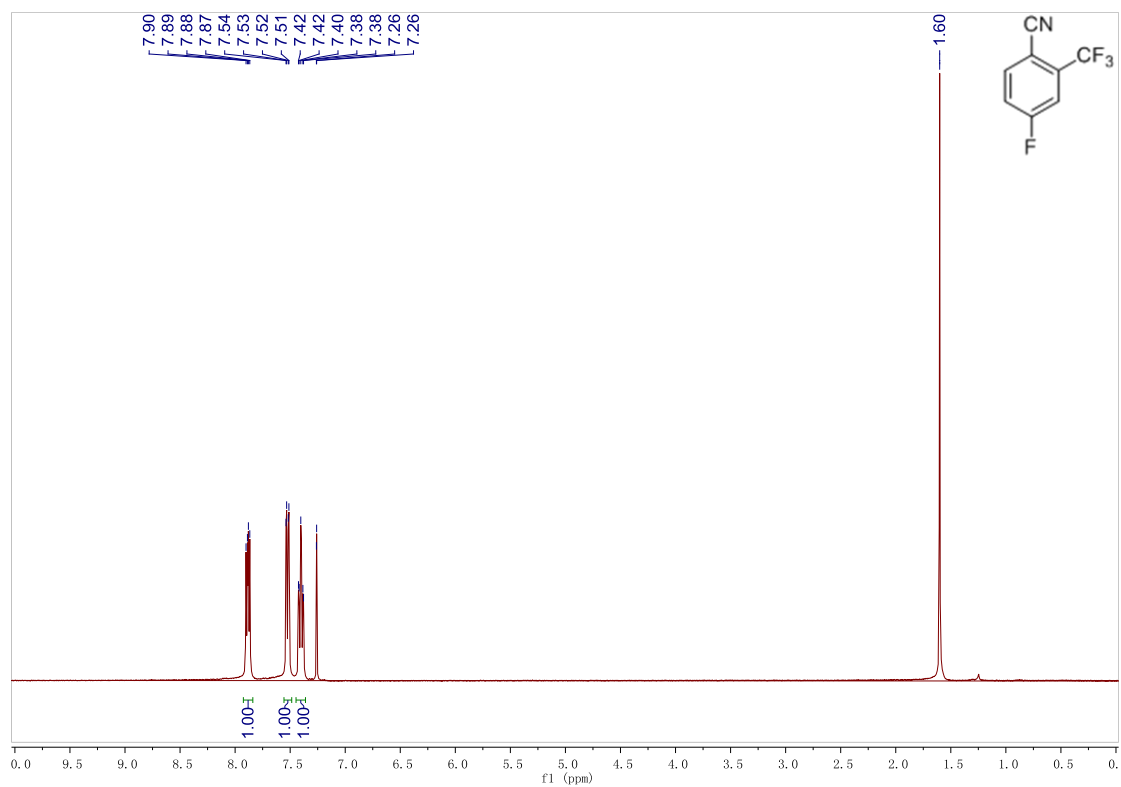


¹⁹F NMR

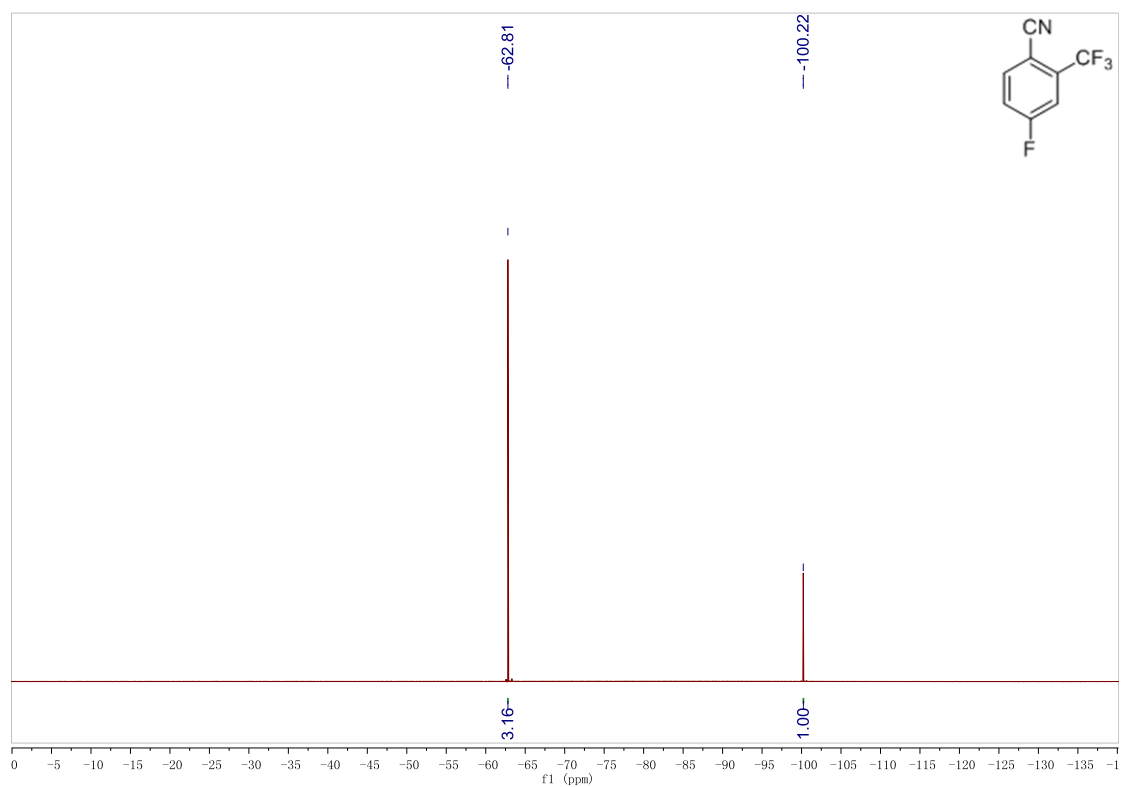


4-Fluoro-2-(trifluoromethyl)benzonitrile:

^1H NMR

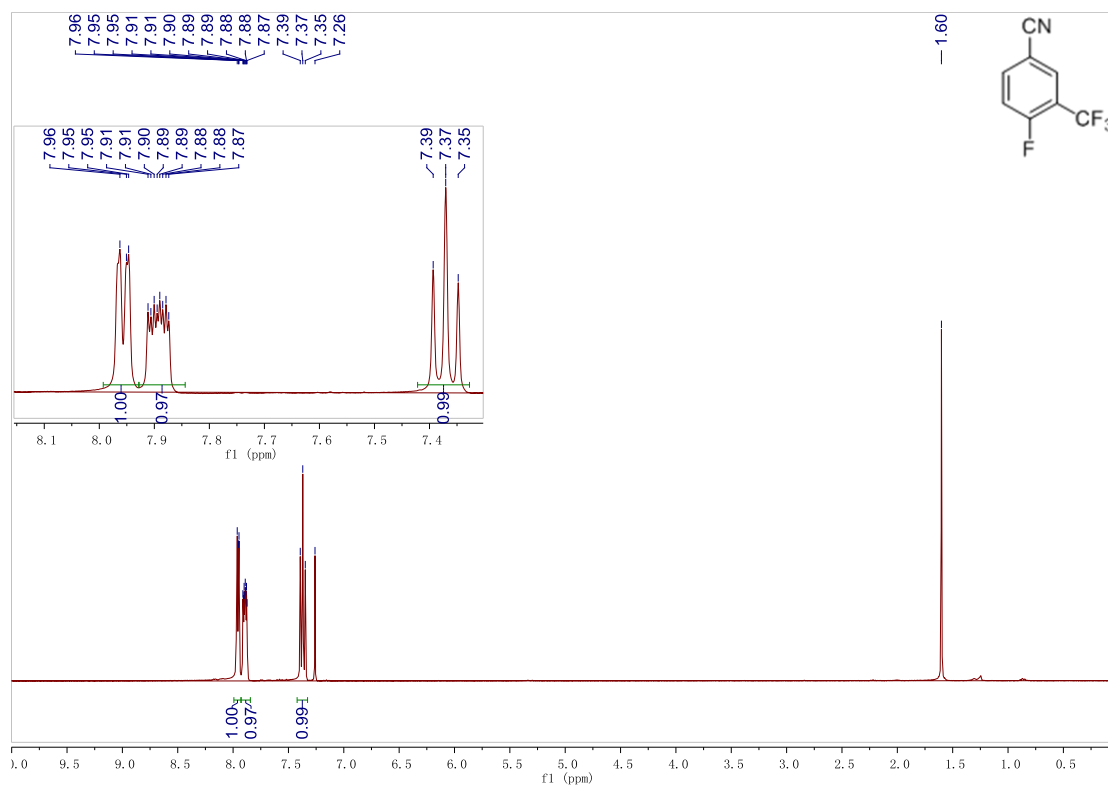


^{19}F NMR

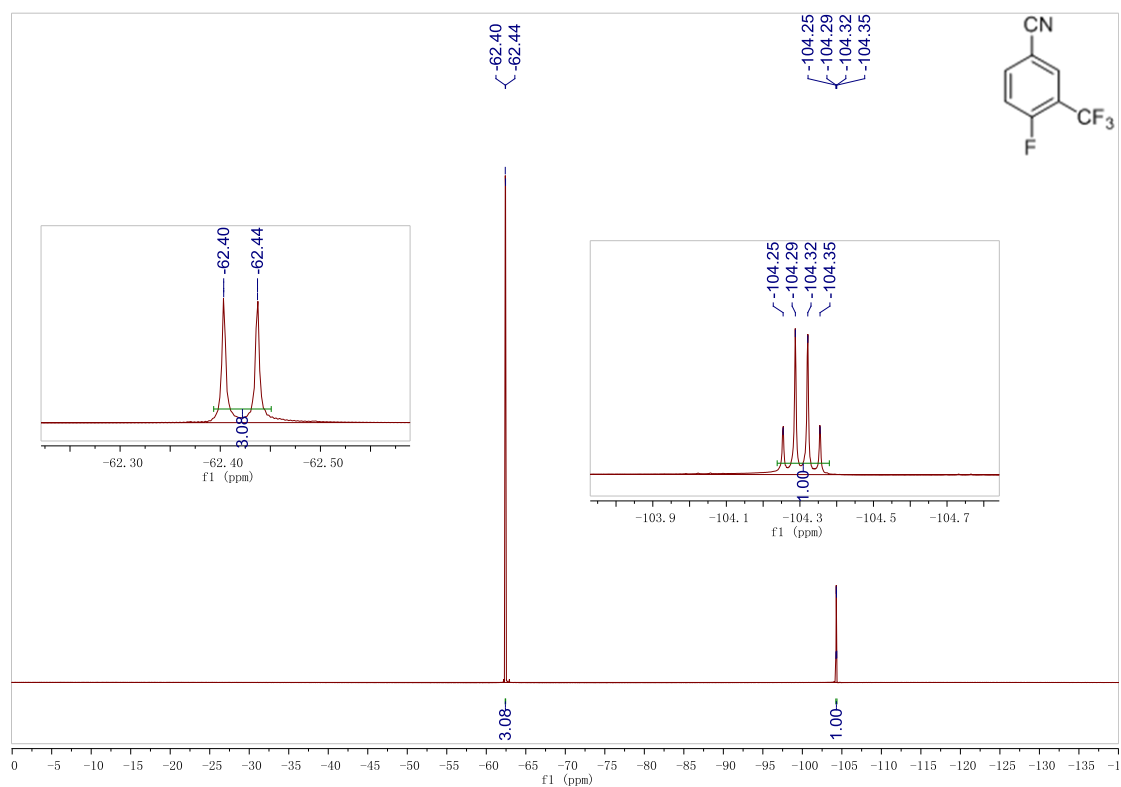


4-Fluoro-3-(trifluoromethyl)benzonitrile:

¹H NMR

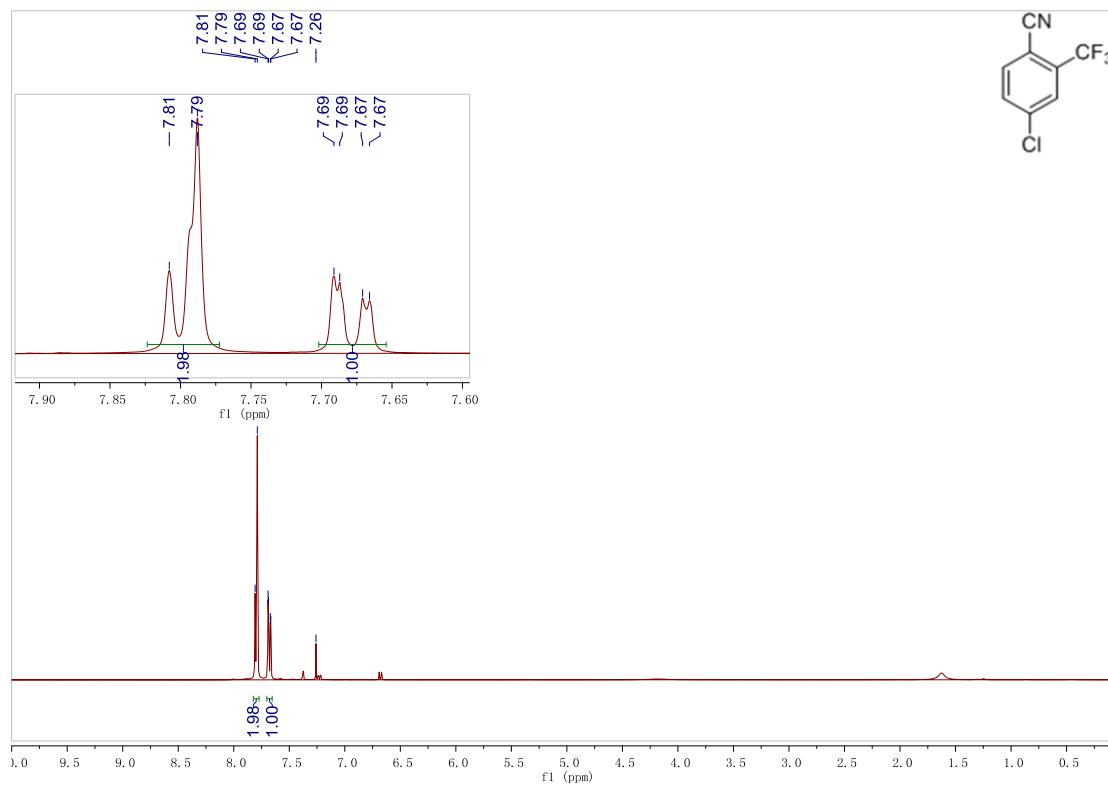


¹⁹F NMR



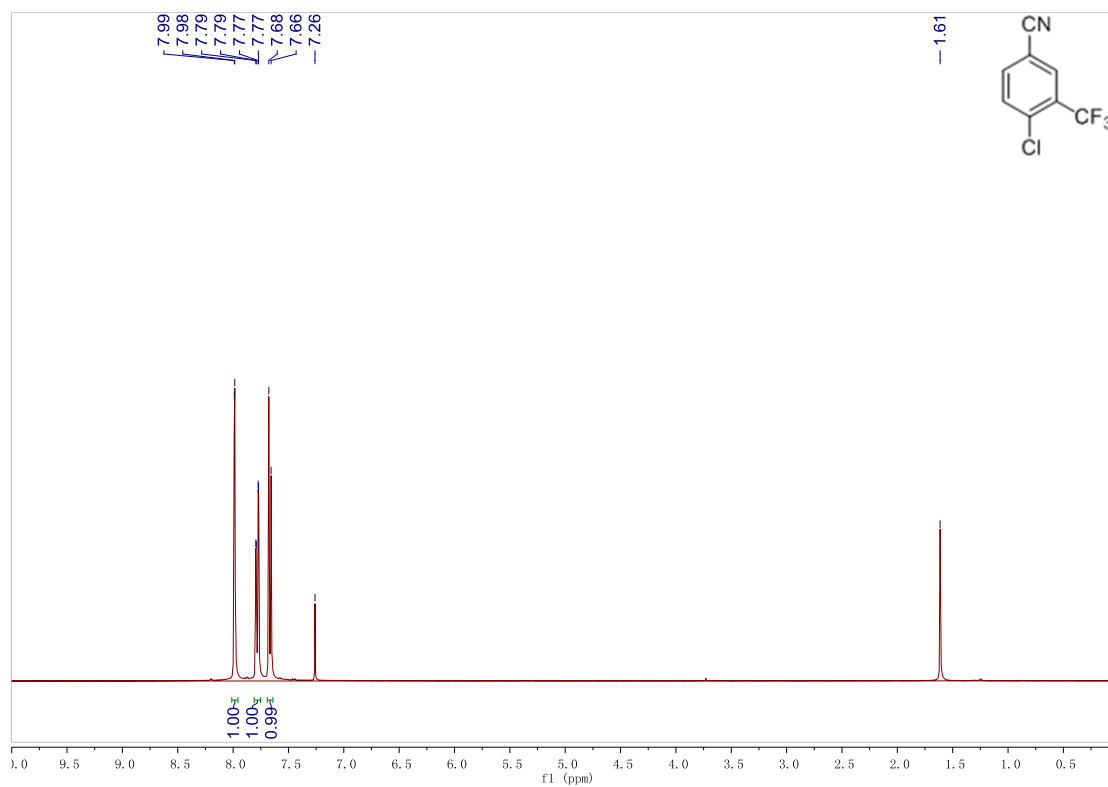
4-Chloro-2-(trifluoromethyl)benzonitrile:

^1H NMR

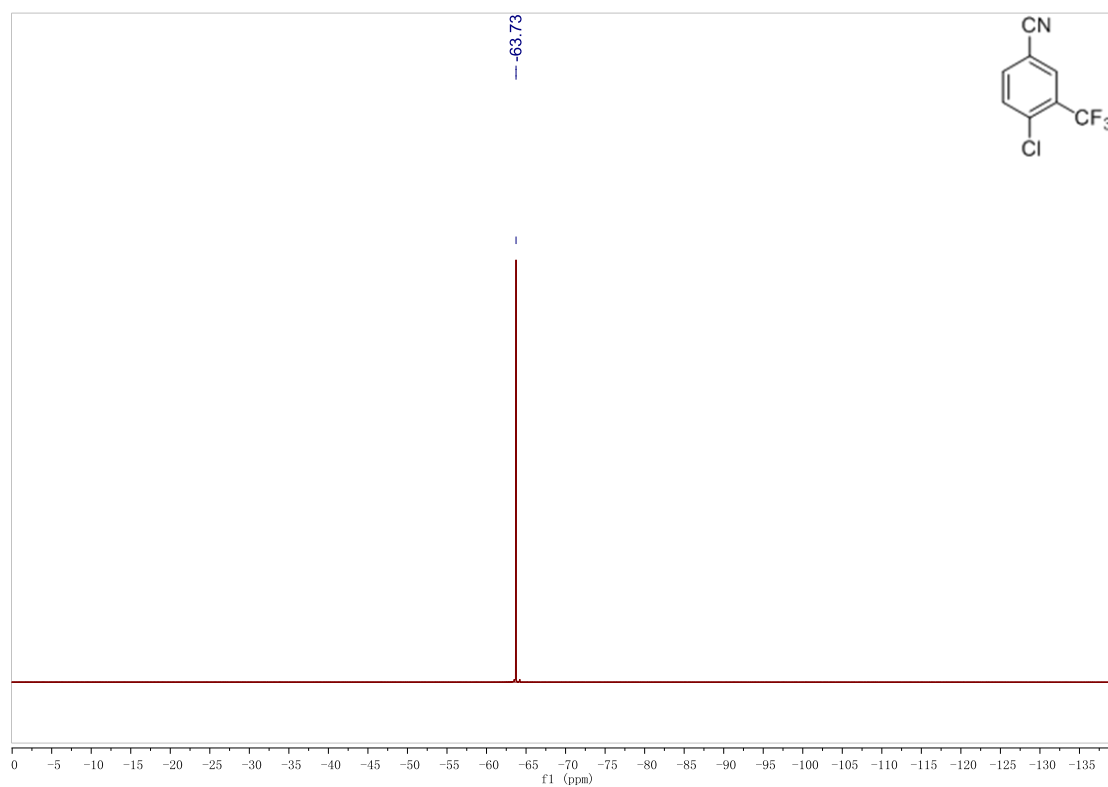


4-Chloro-3-(trifluoromethyl)benzonitrile:

¹H NMR

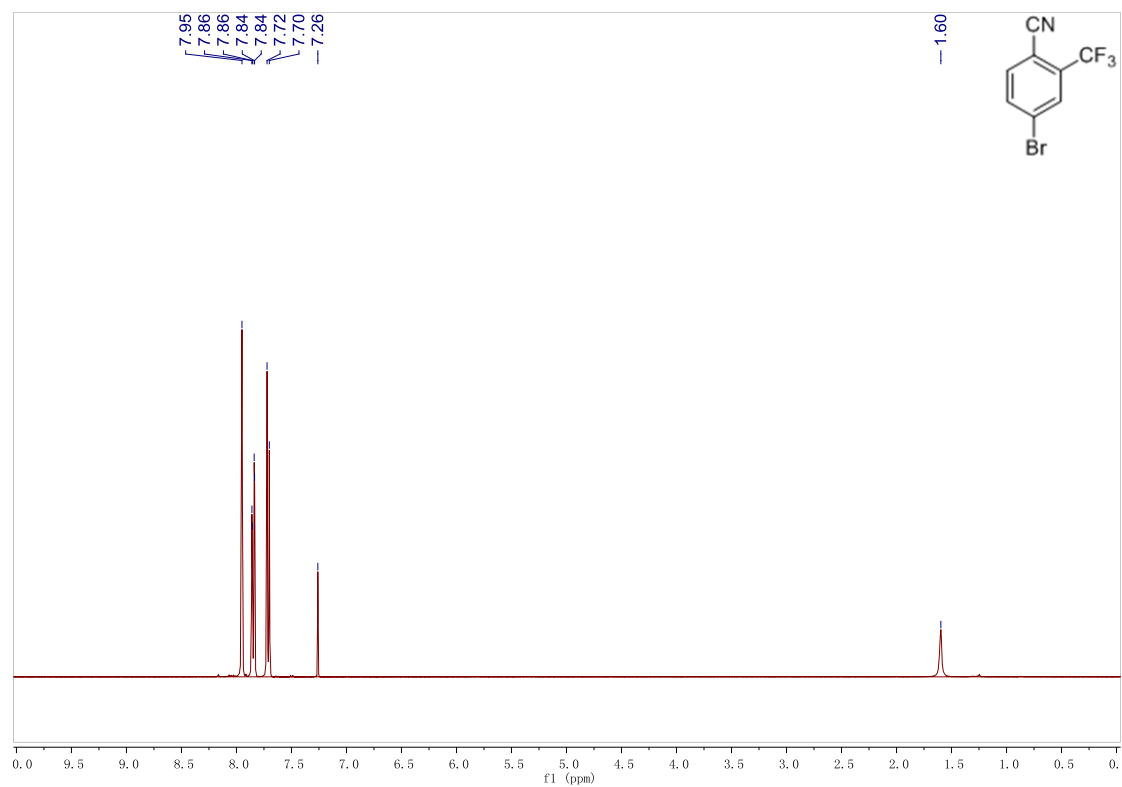


¹⁹F NMR

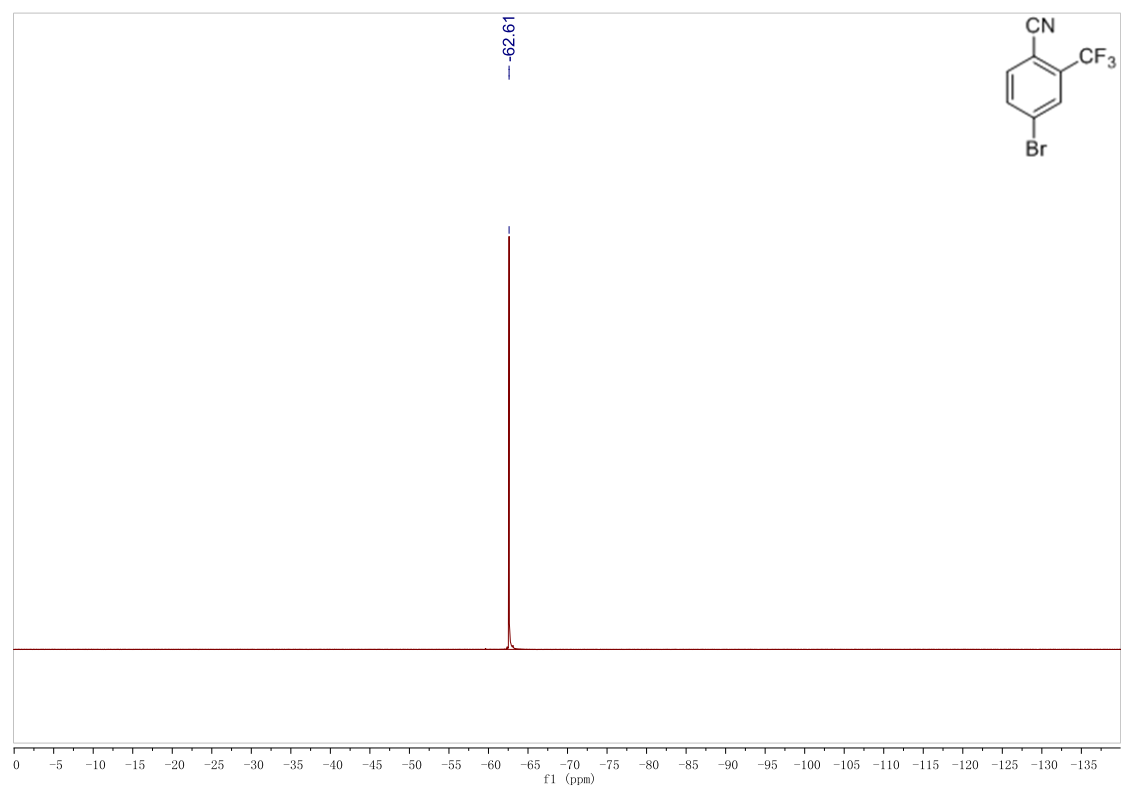


4-Bromo-2-(trifluoromethyl)benzonitrile:

^1H NMR

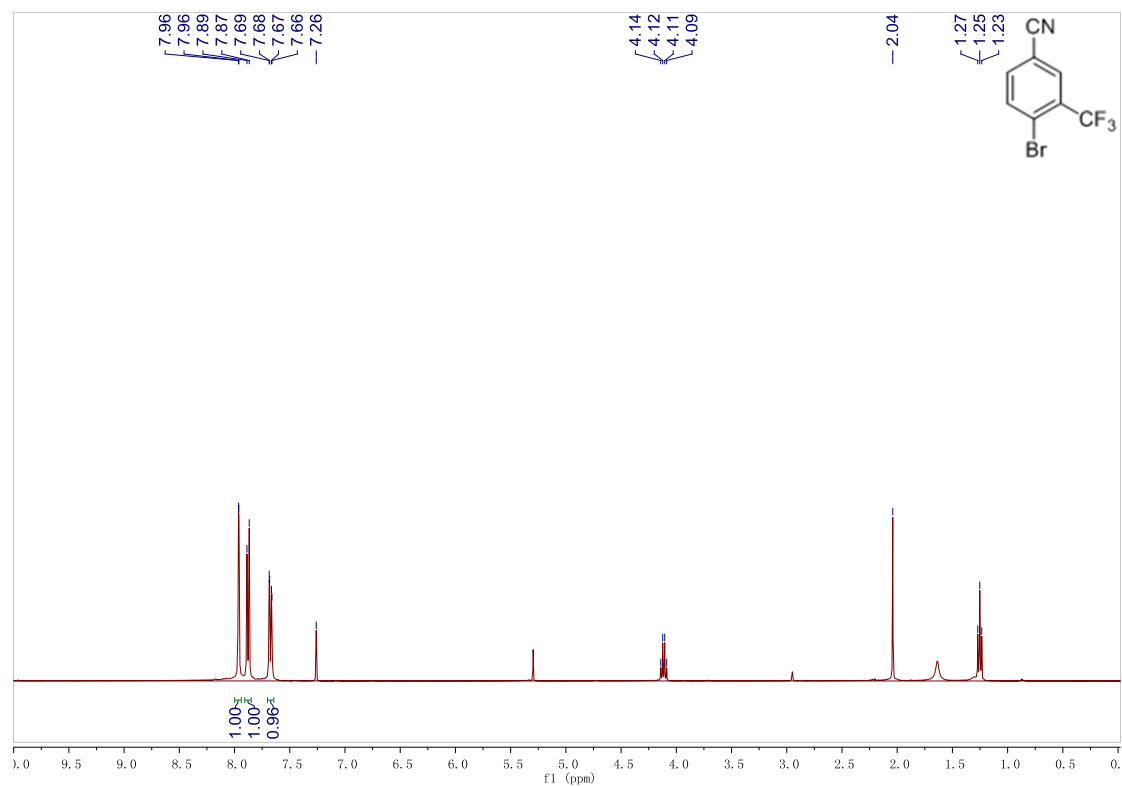


^{19}F NMR

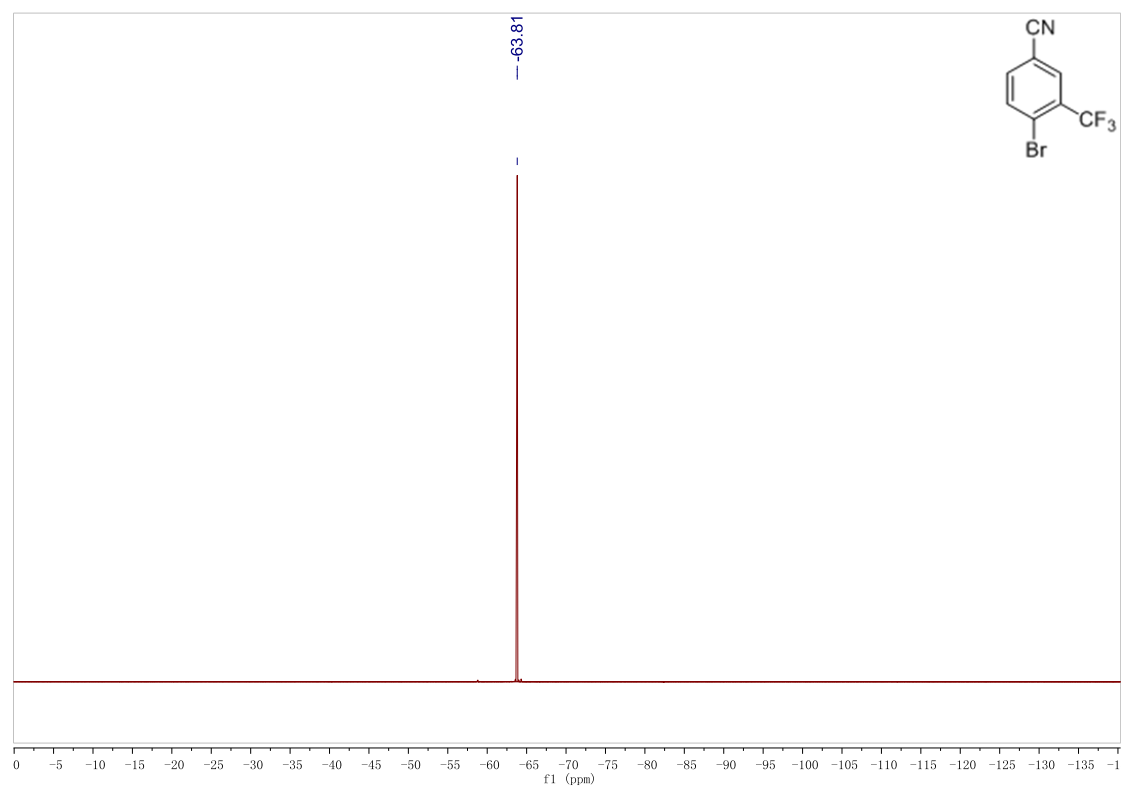


4-Bromo-3-(trifluoromethyl)benzonitrile:

^1H NMR

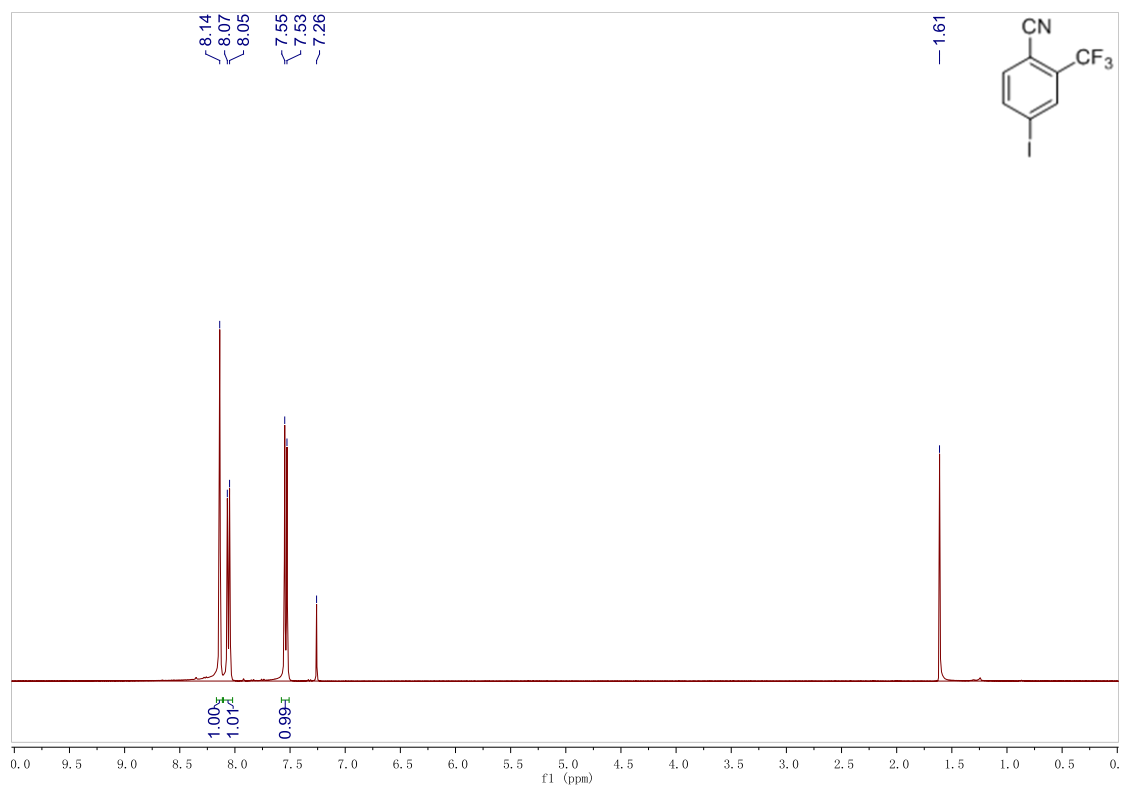


^{19}F NMR

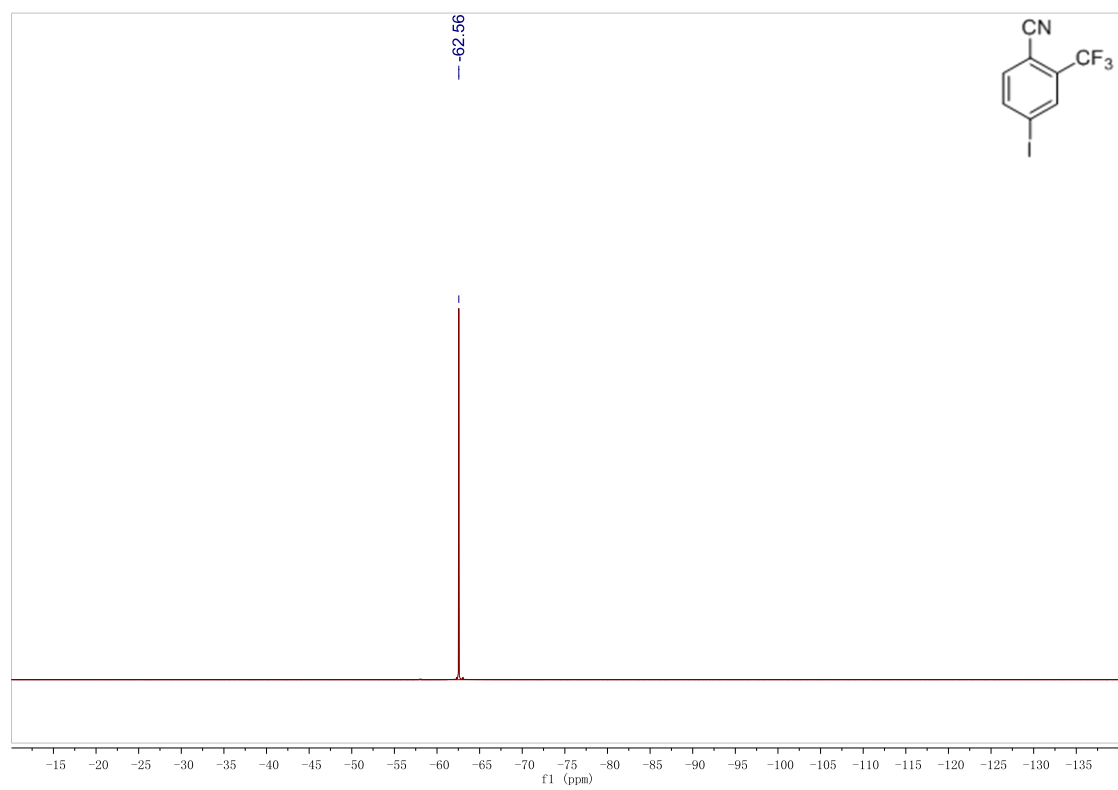


4-Iodo-2-(trifluoromethyl)benzonitrile:

^1H NMR

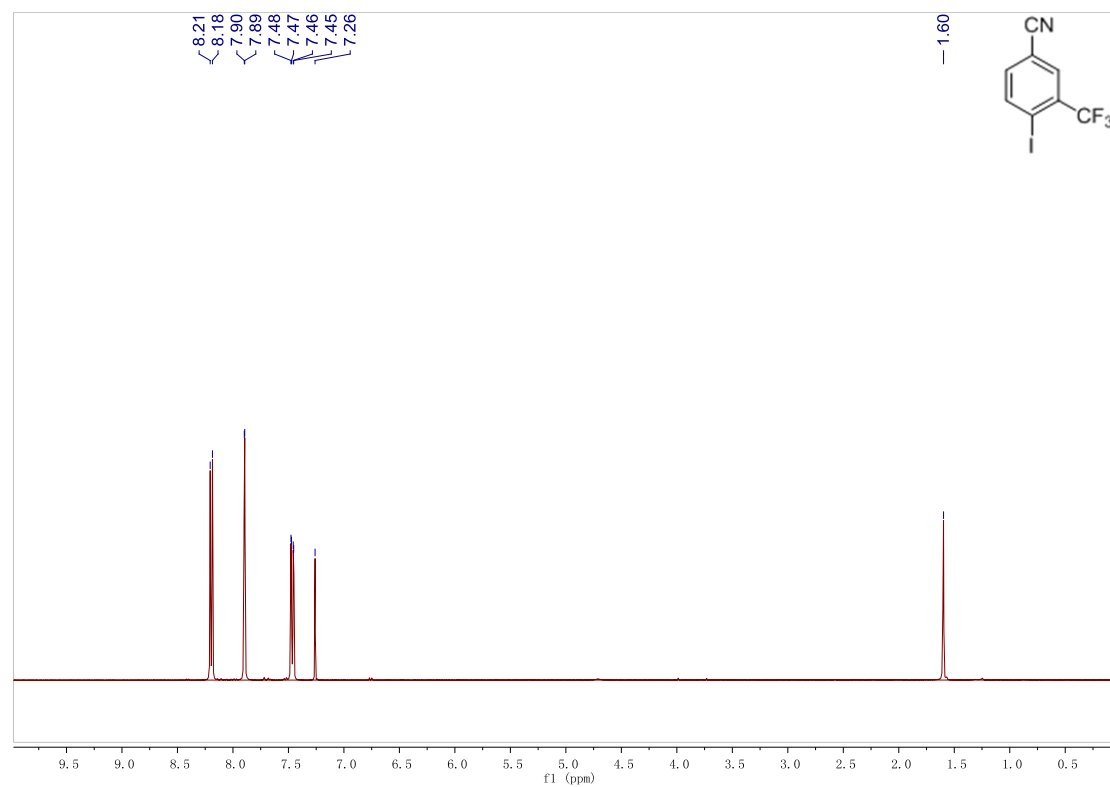


^{19}F NMR

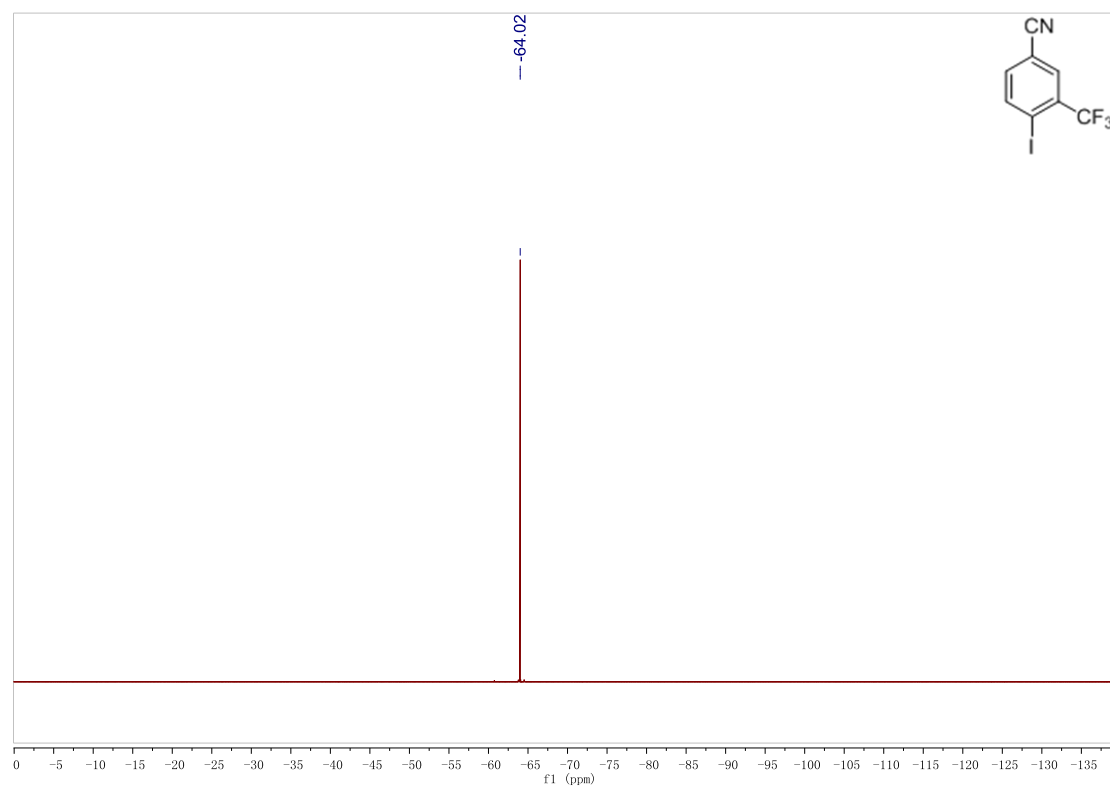


4-Iodo-3-(trifluoromethyl)benzonitrile:

^1H NMR

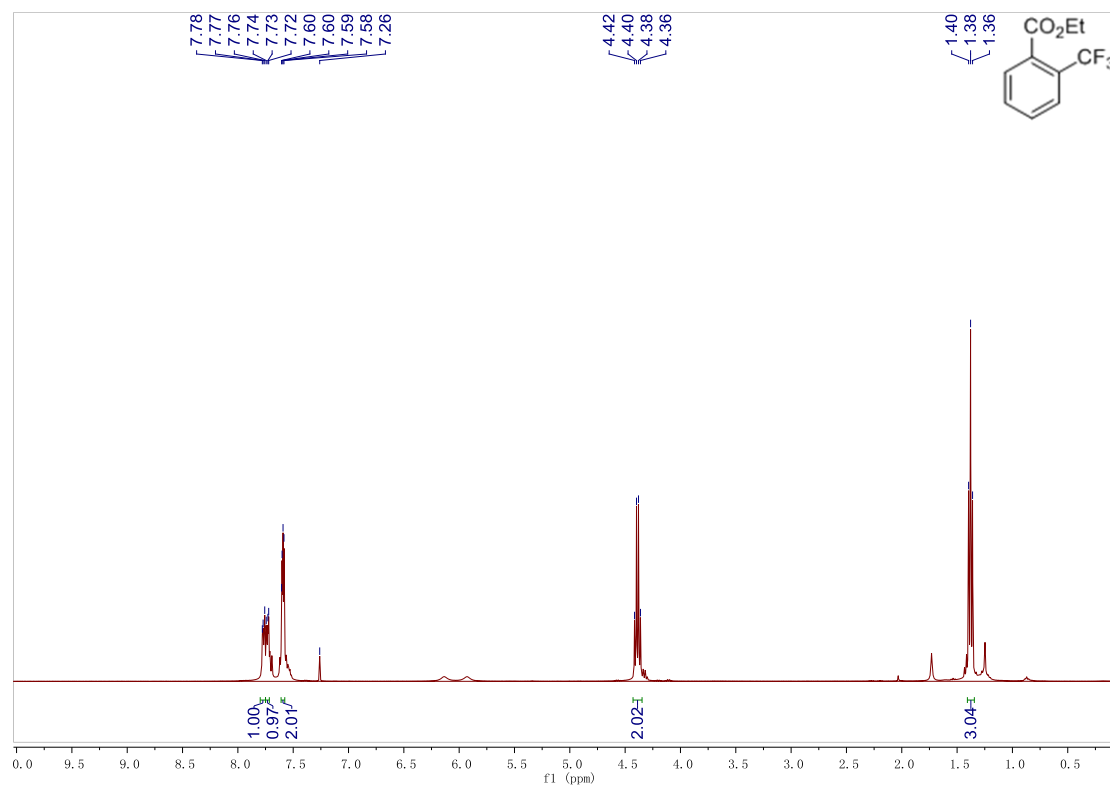


^{19}F NMR

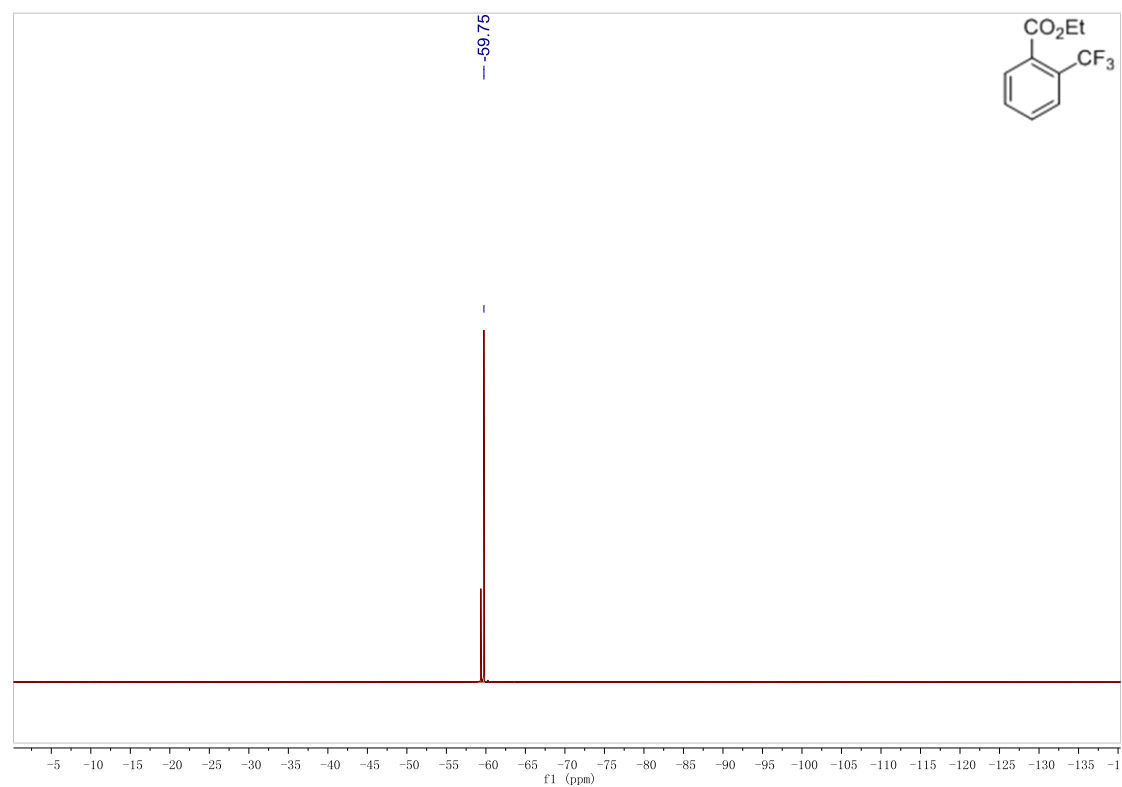


Ethyl 2-(trifluoromethyl)benzoate:

^1H NMR

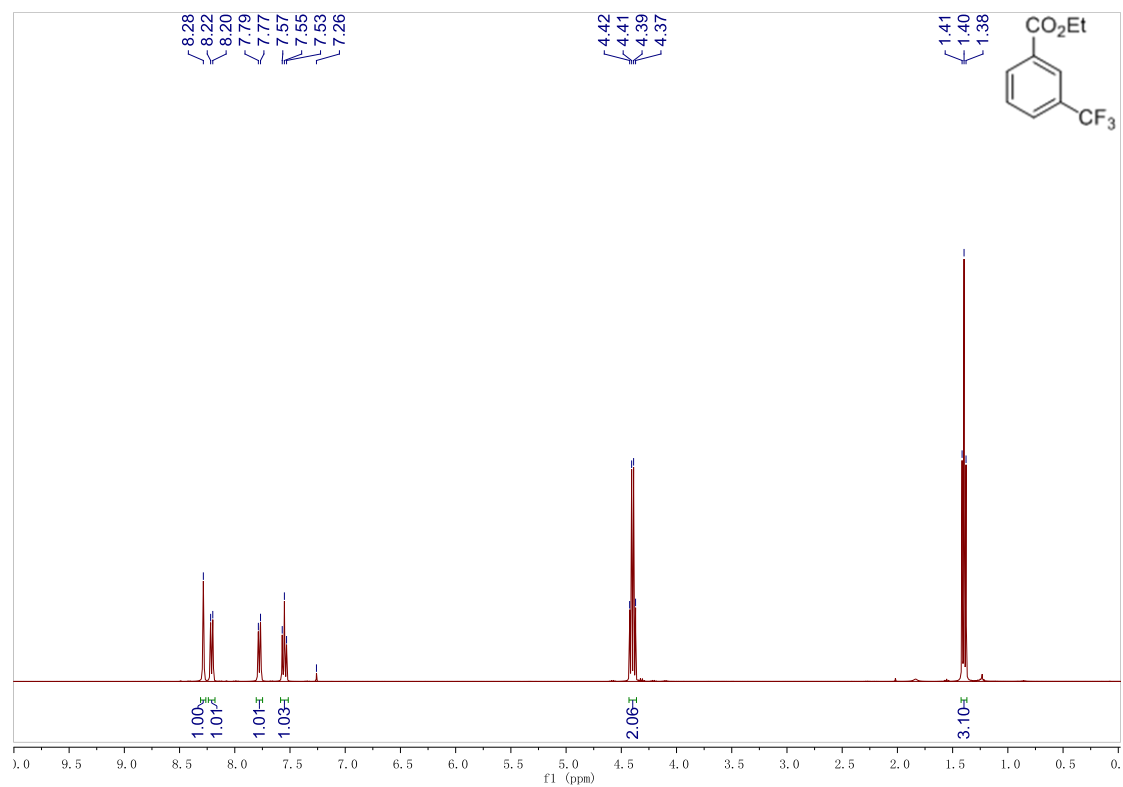


^{19}F NMR

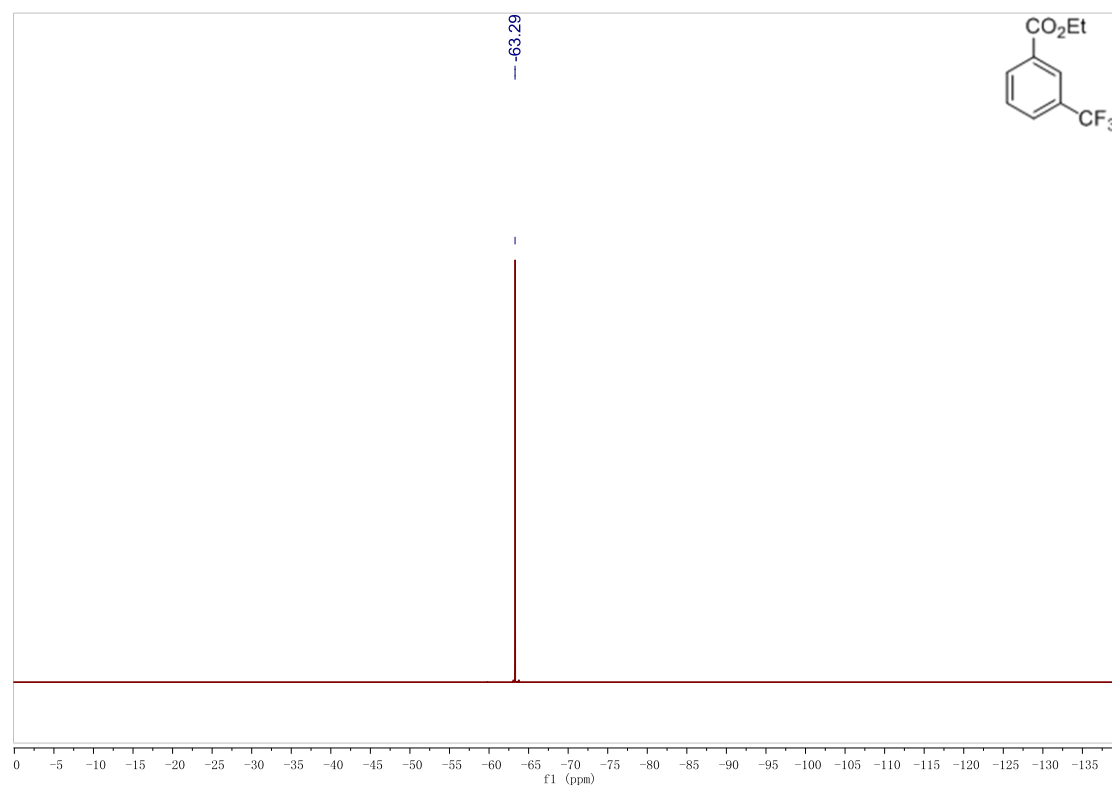


Ethyl 3-(trifluoromethyl)benzoate:

^1H NMR

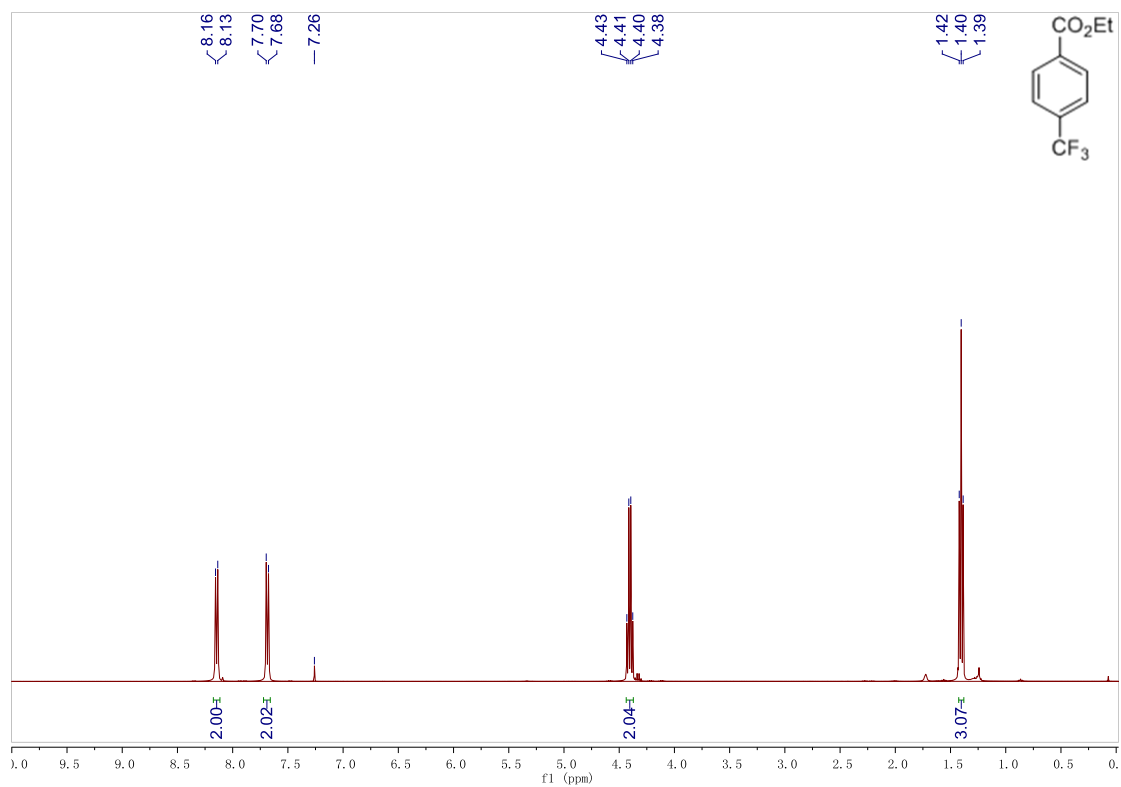


^{19}F NMR

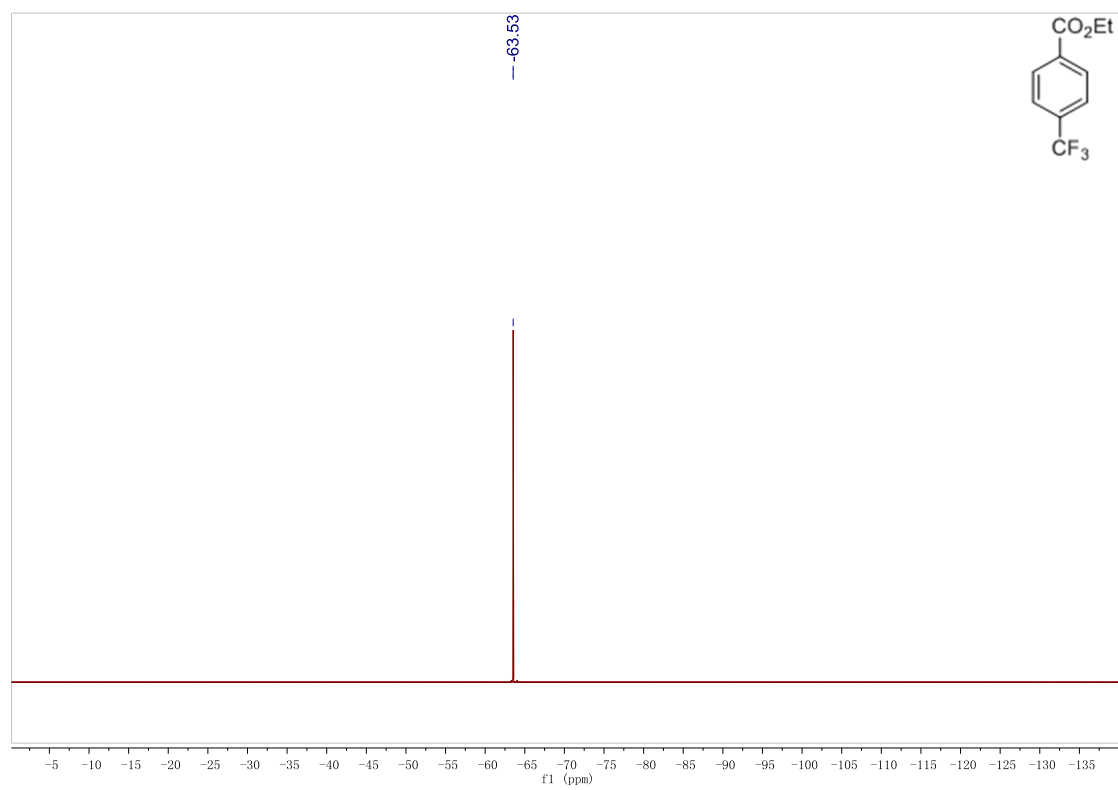


Ethyl 4-(trifluoromethyl)benzoate:

^1H NMR

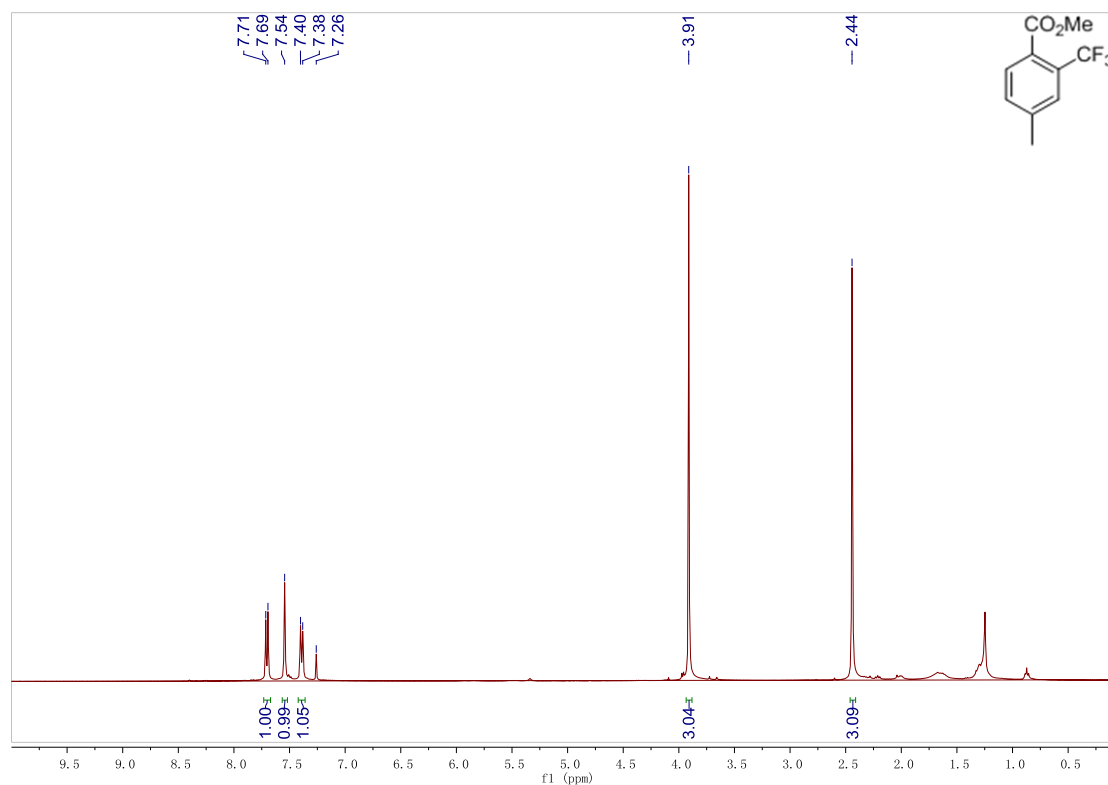


^{19}F NMR

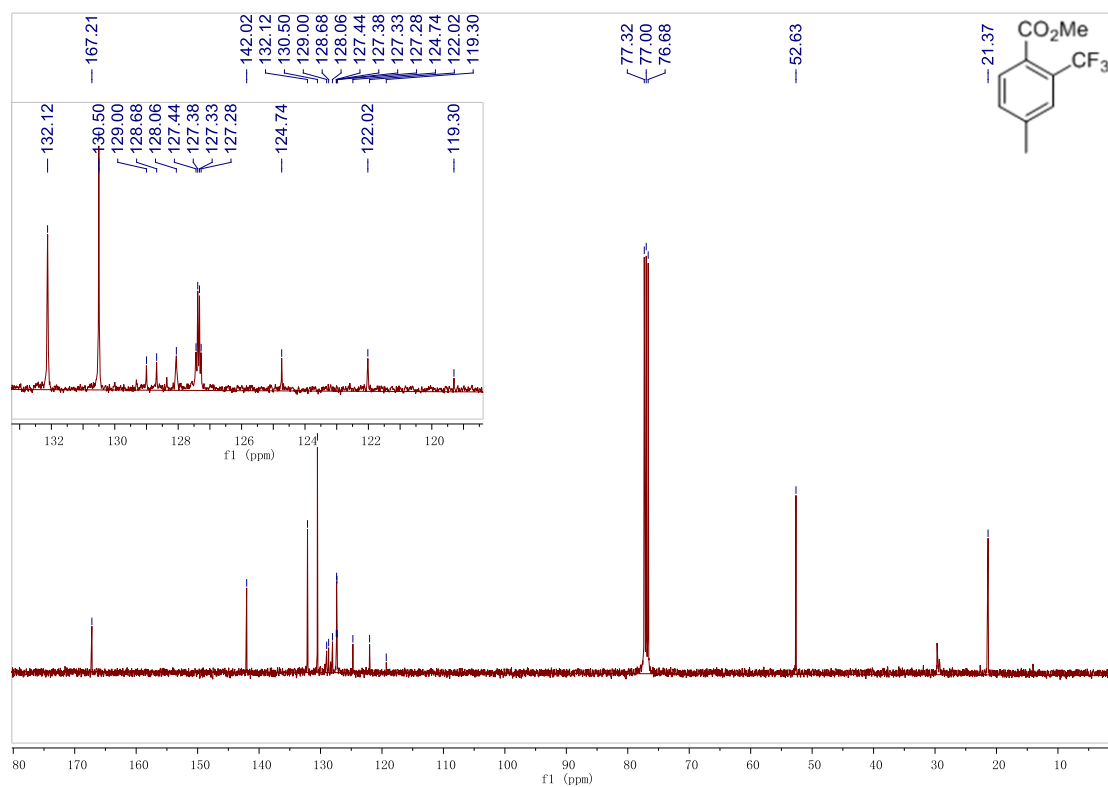


Methyl 4-methyl-2-(trifluoromethyl)benzoate:

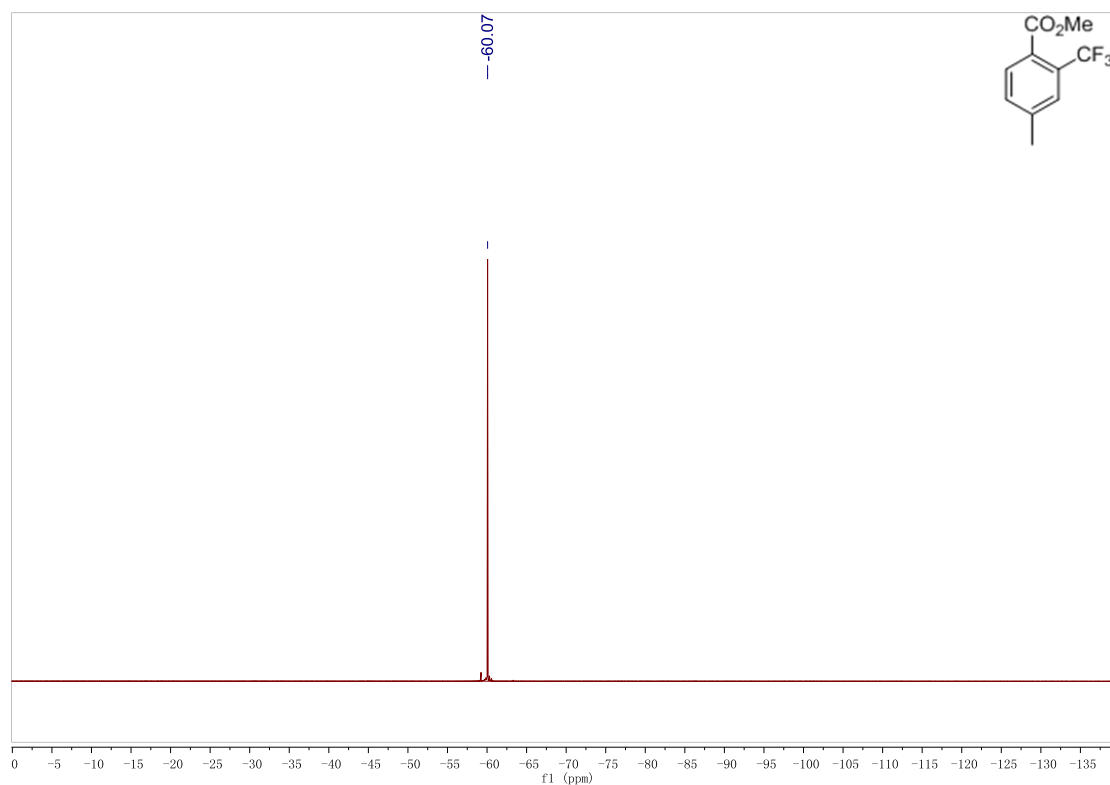
¹H NMR



¹³C NMR

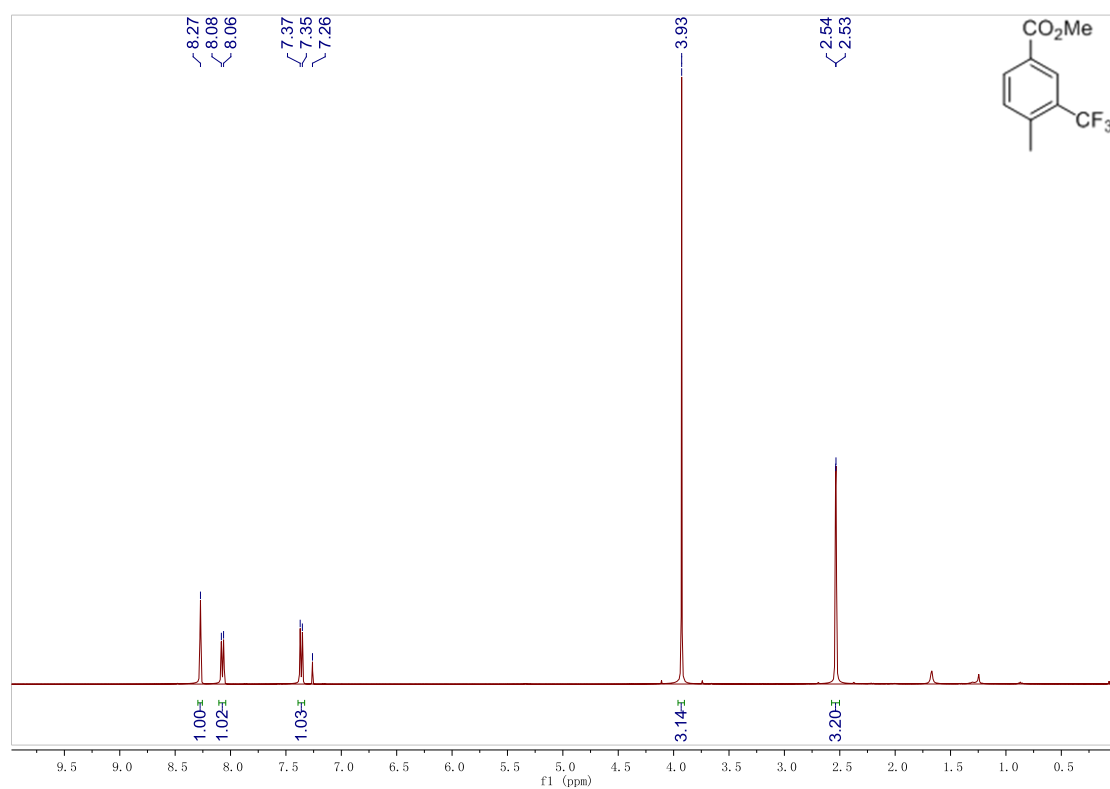


^{19}F NMR

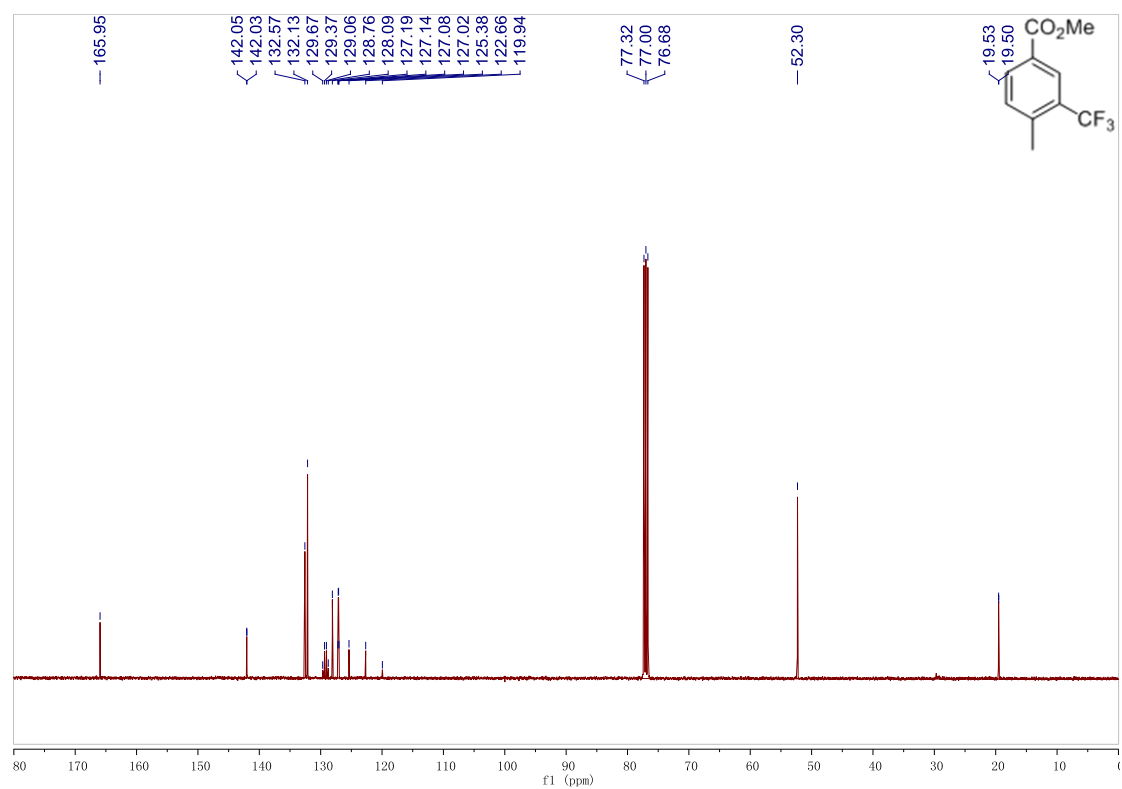


Methyl 4-methyl-3-(trifluoromethyl)benzoate:

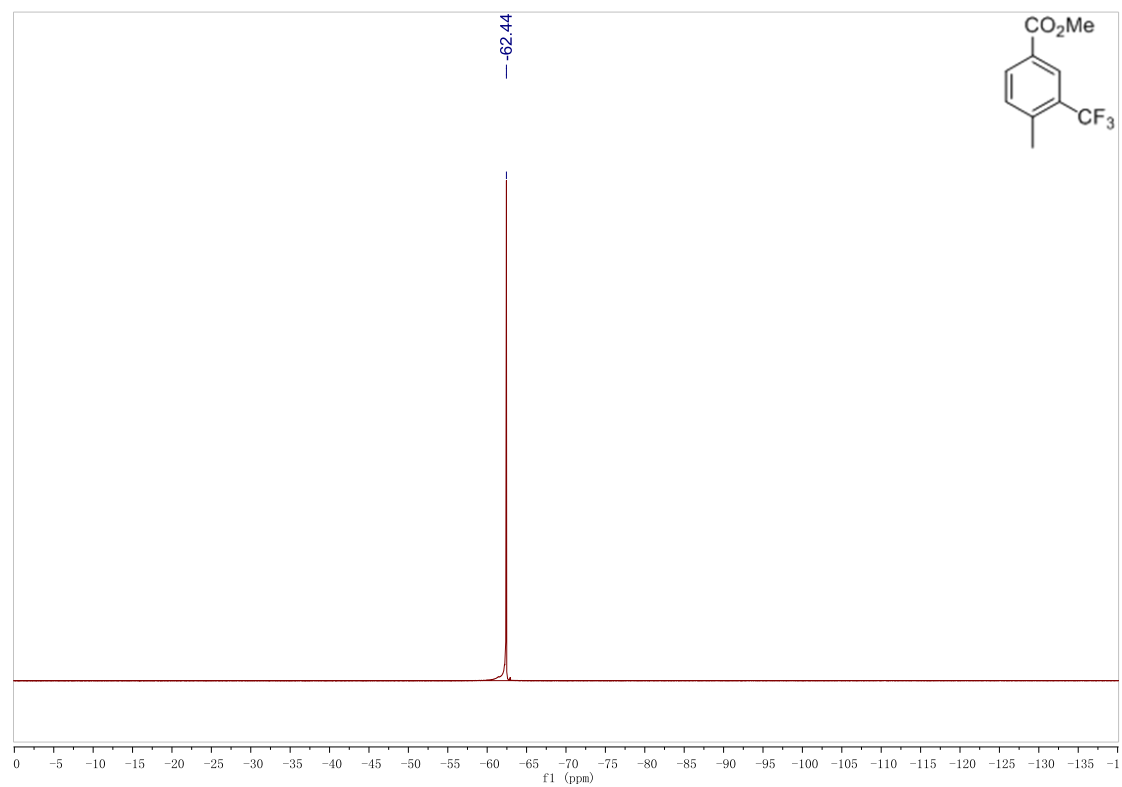
^1H NMR



¹³C NMR

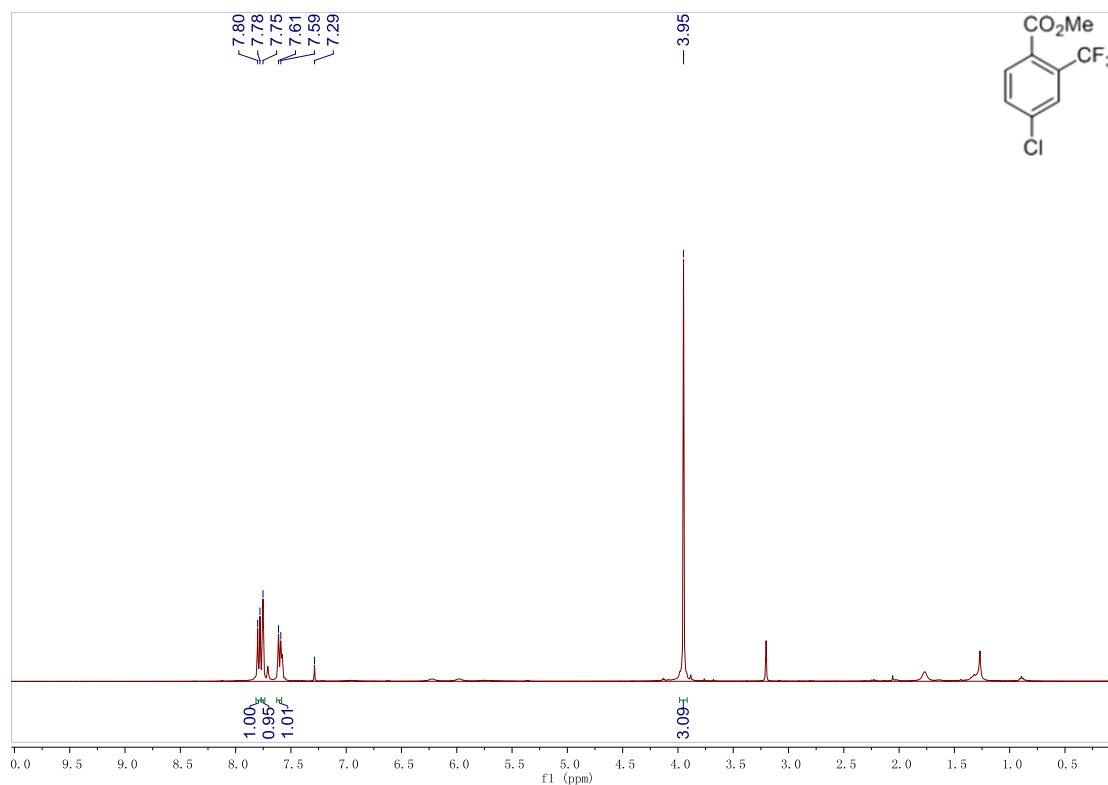


¹⁹F NMR

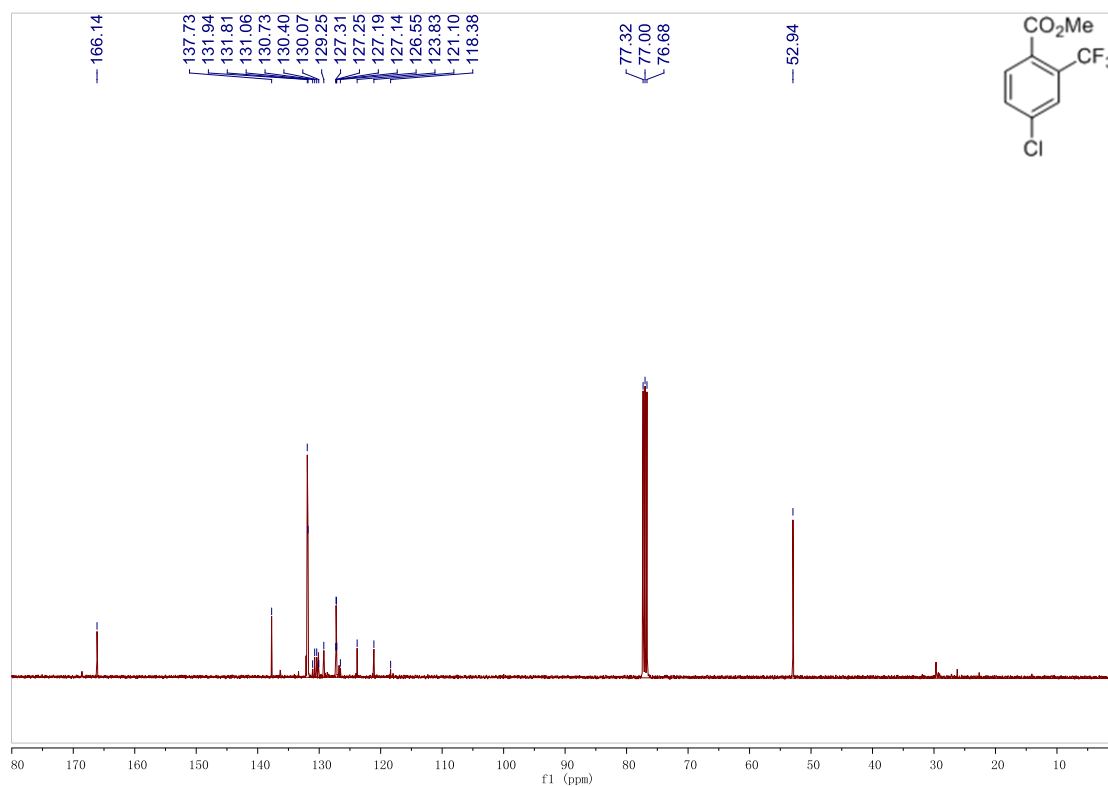


Methyl 4-chloro-2-(trifluoromethyl)benzoate:

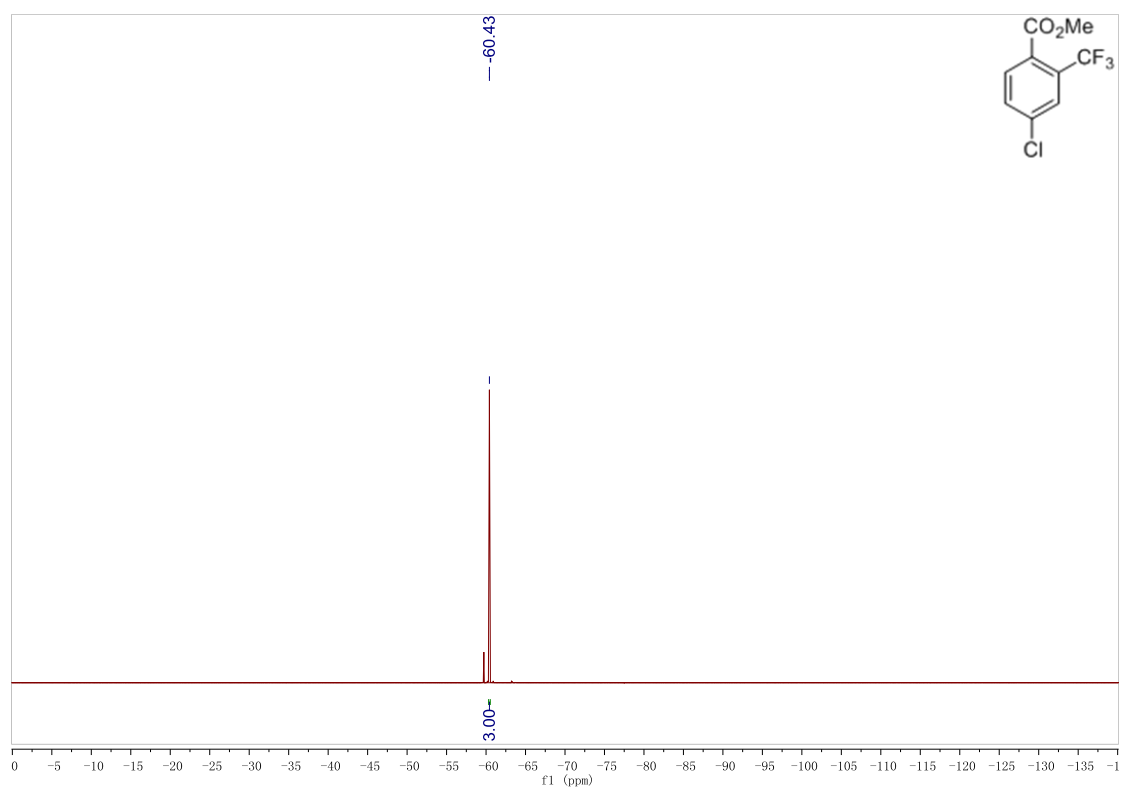
¹H NMR



¹³C NMR

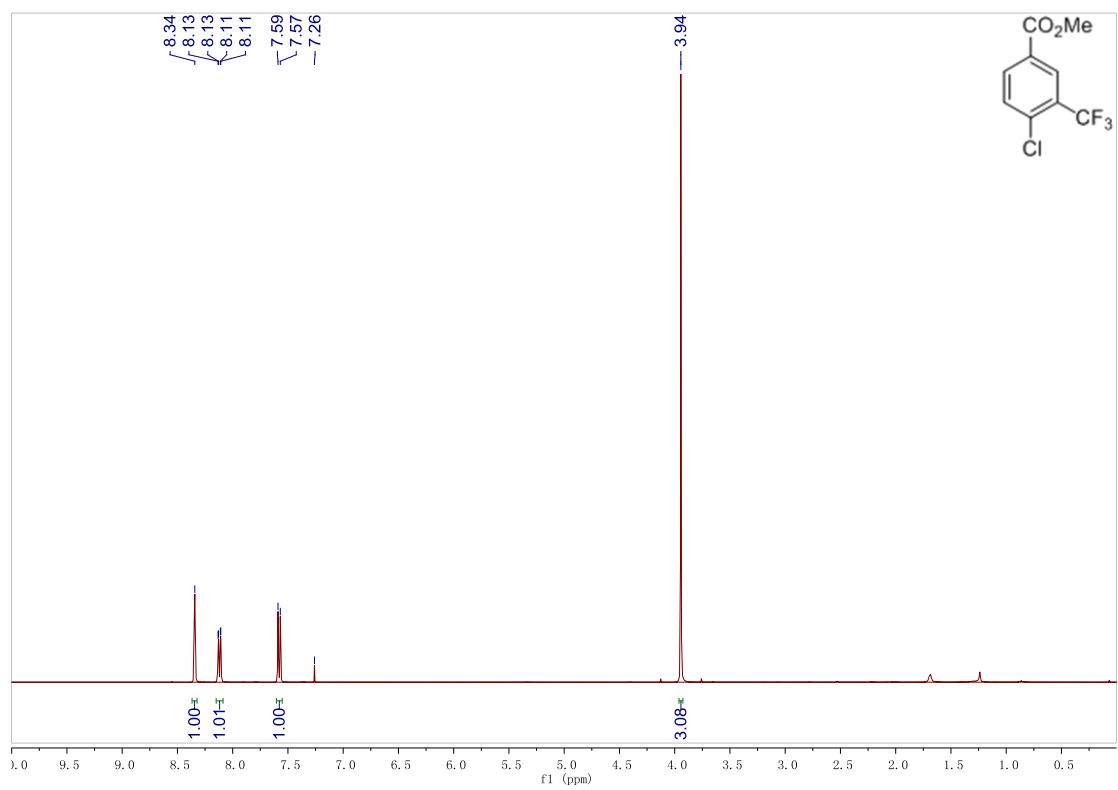


^{19}F NMR

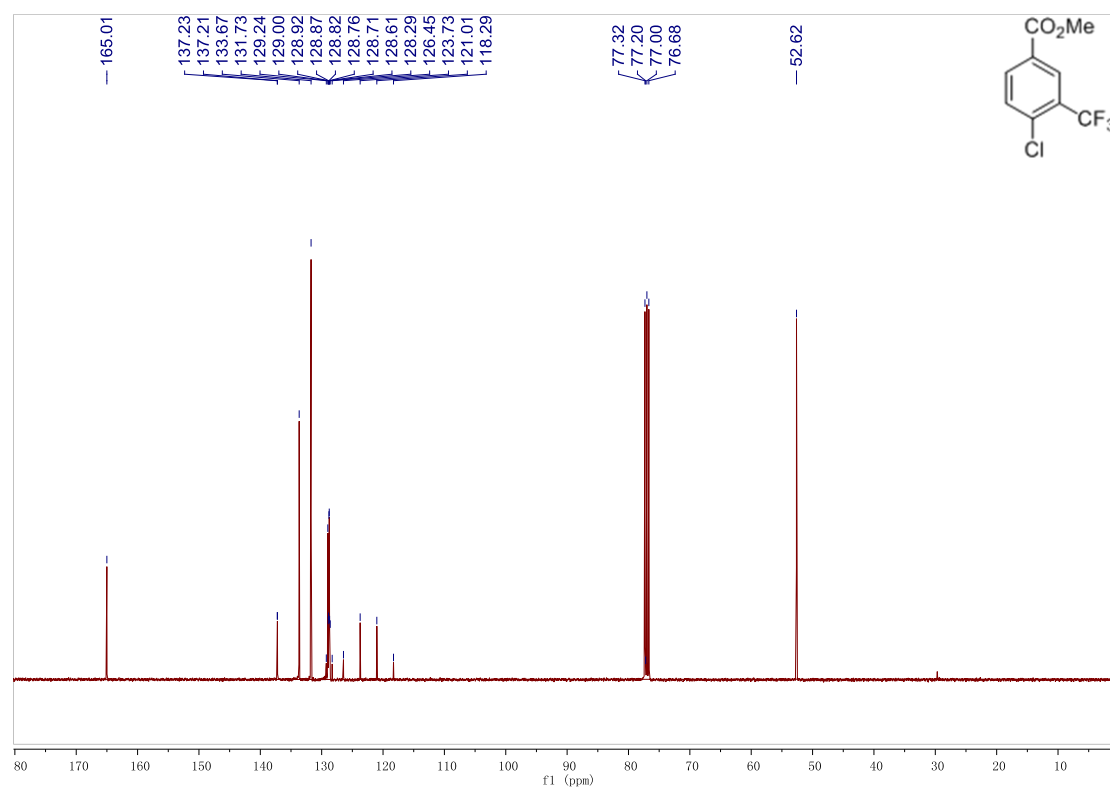


Methyl 4-chloro-3-(trifluoromethyl)benzoate:

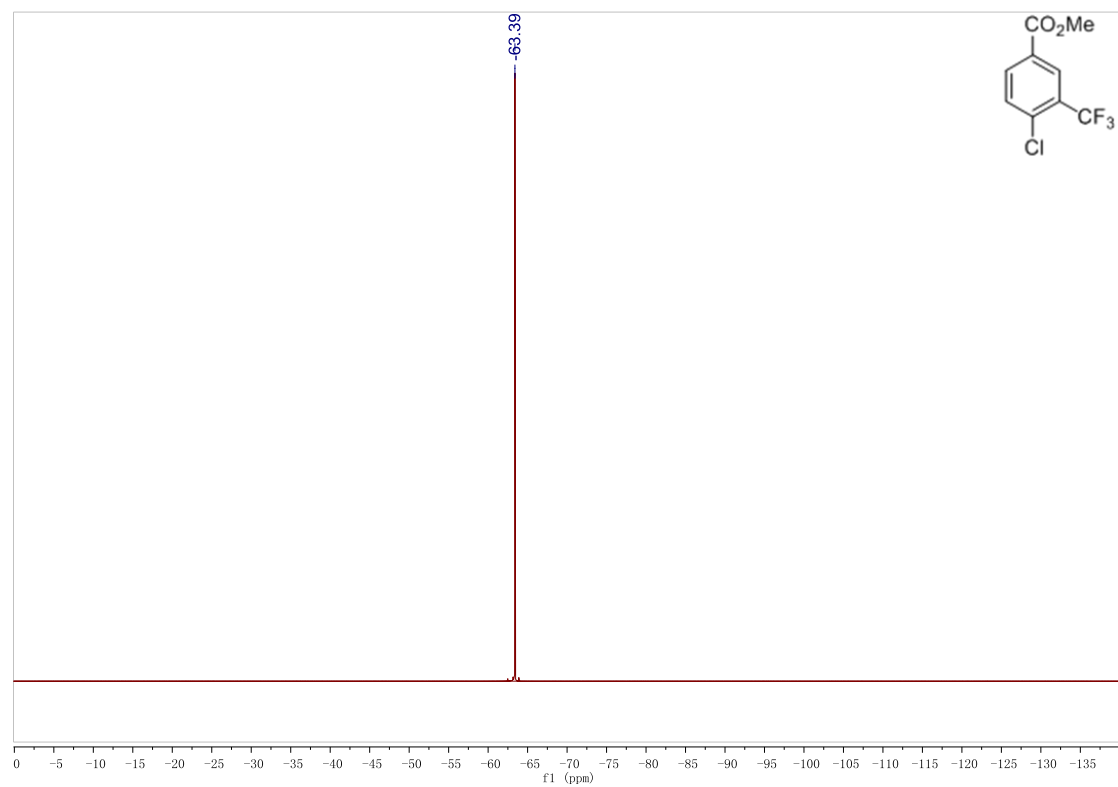
^1H NMR



¹³C NMR

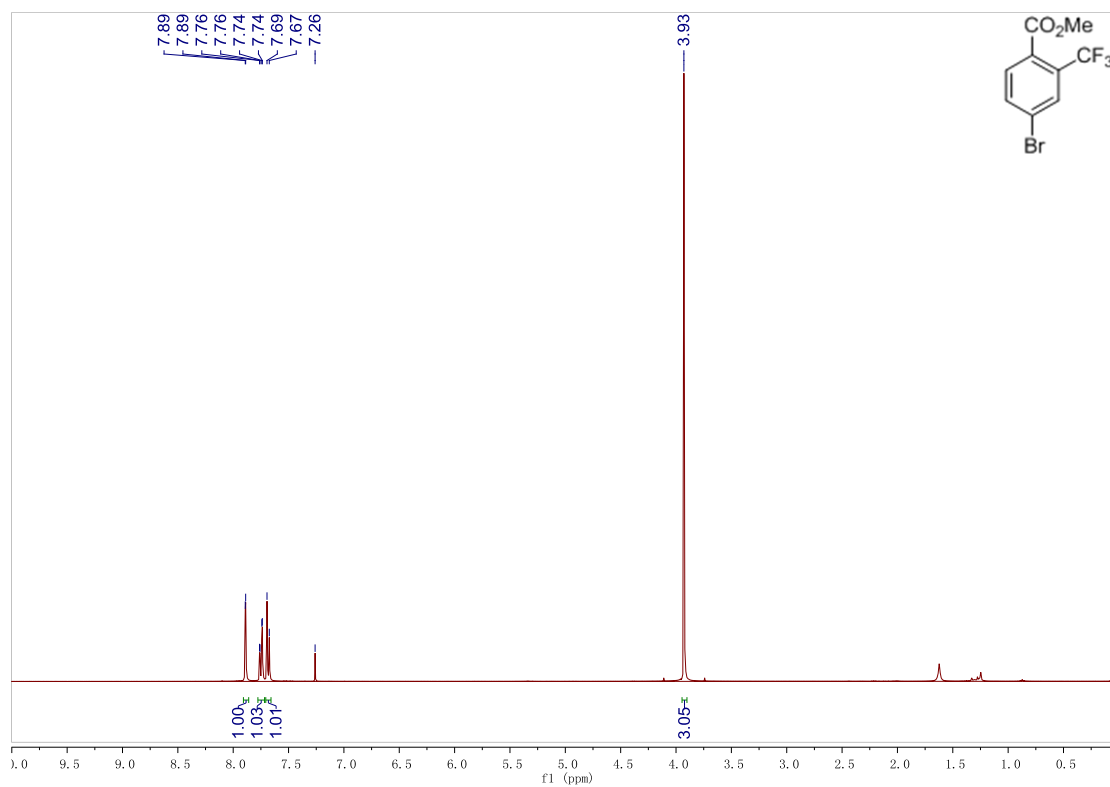


¹⁹F NMR

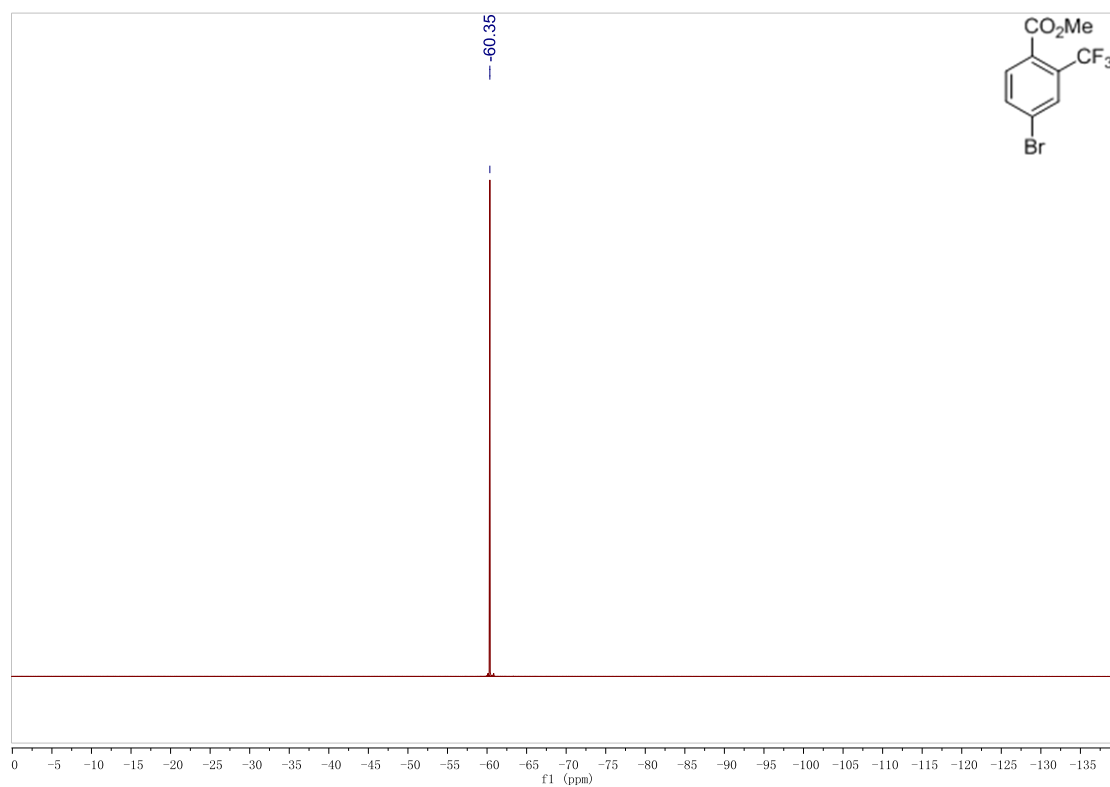


Methyl 4-bromo-2-(trifluoromethyl)benzoate:

¹H NMR

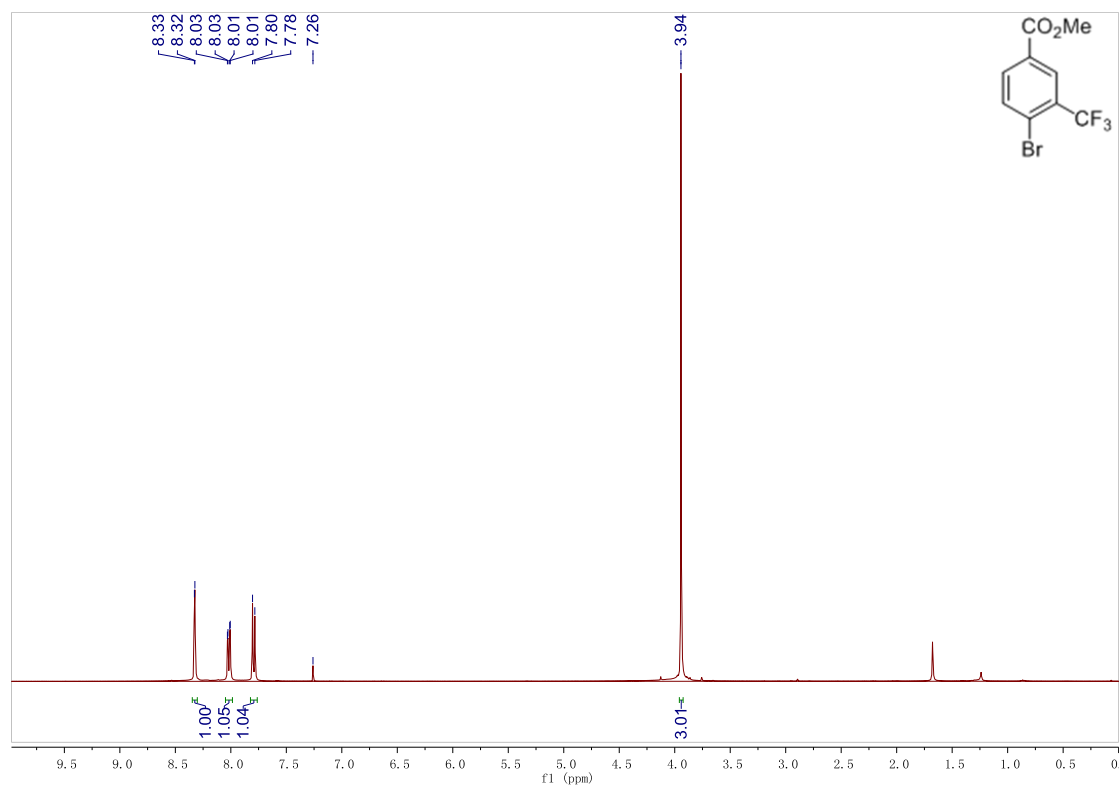


¹⁹F NMR

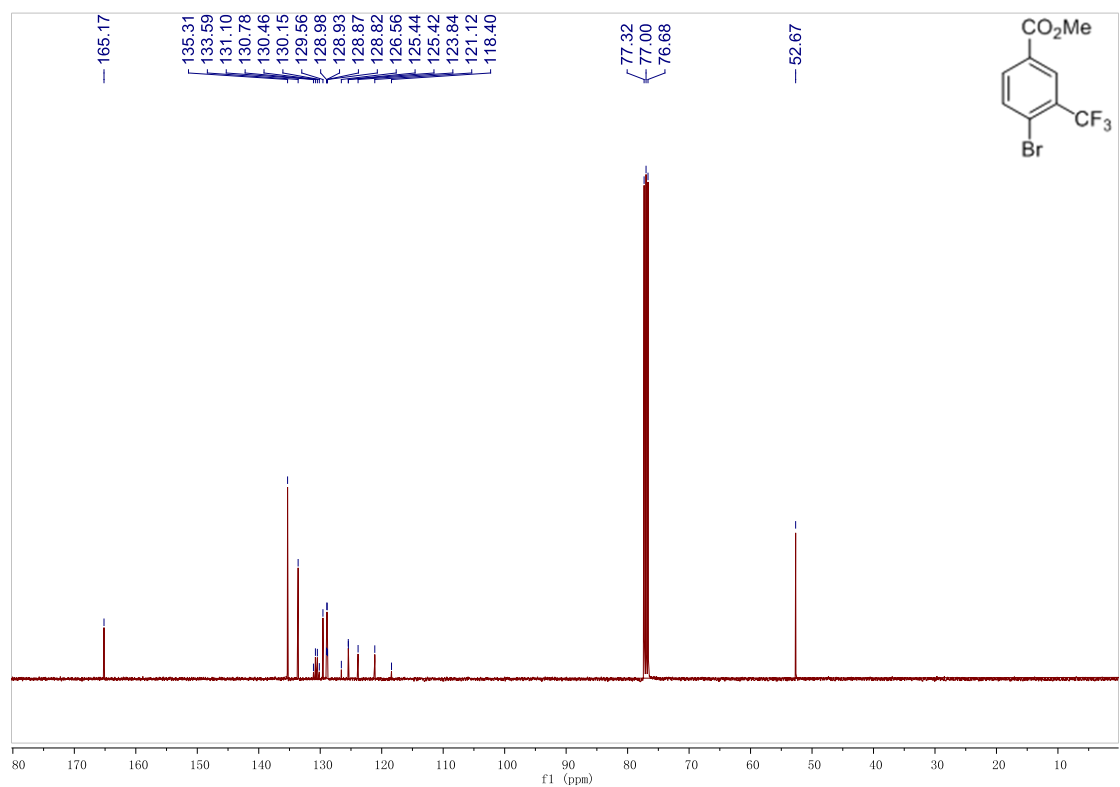


Methyl 4-bromo-3-(trifluoromethyl)benzoate:

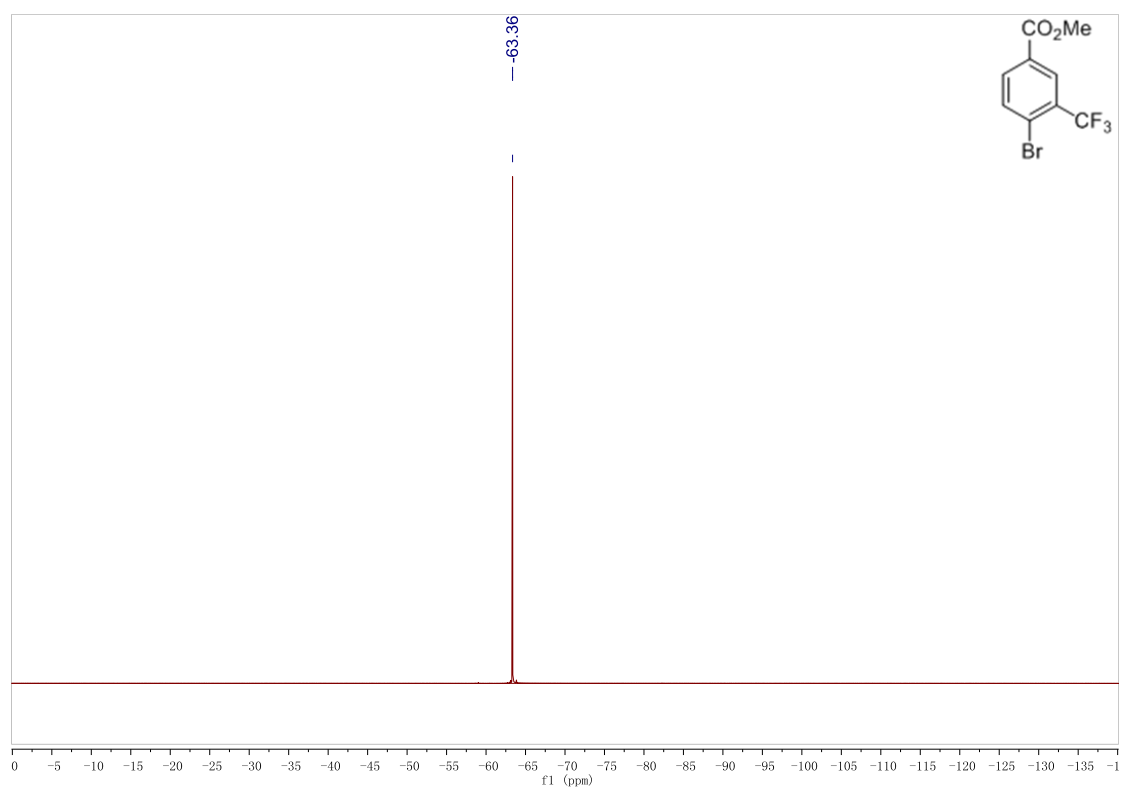
^1H NMR



^{13}C NMR

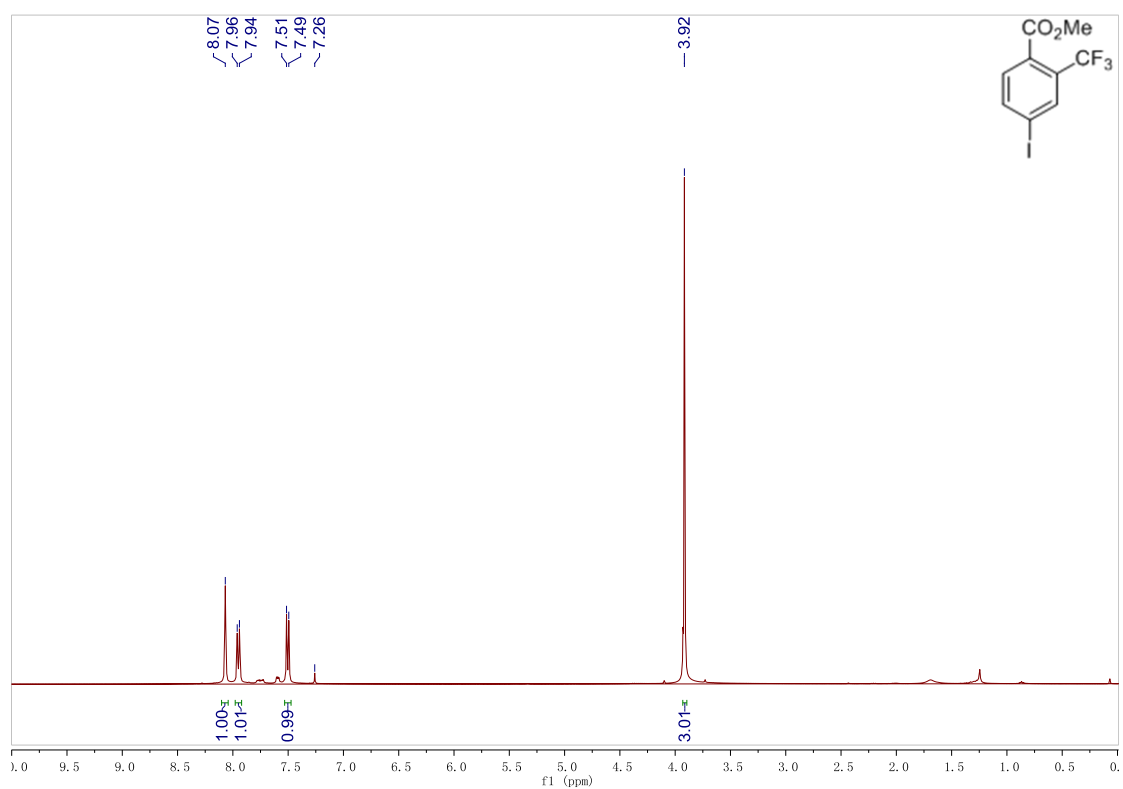


^{19}F NMR

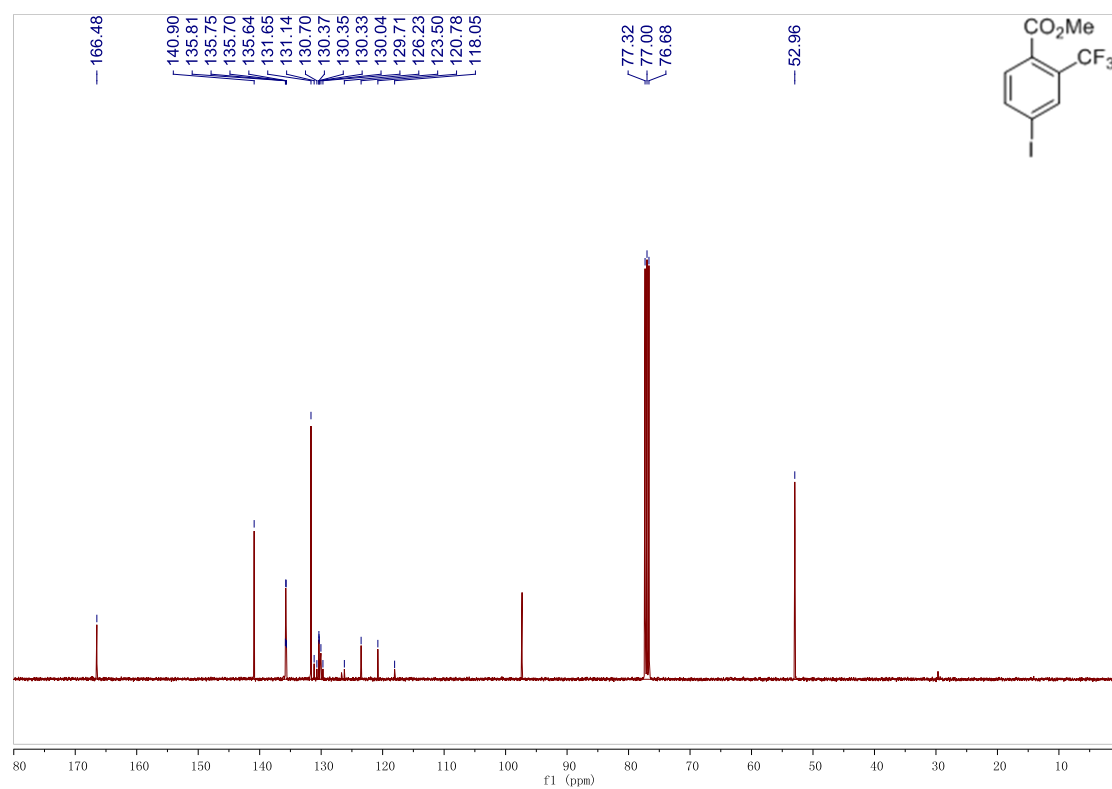


Methyl 4-iodo-2-(trifluoromethyl)benzoate:

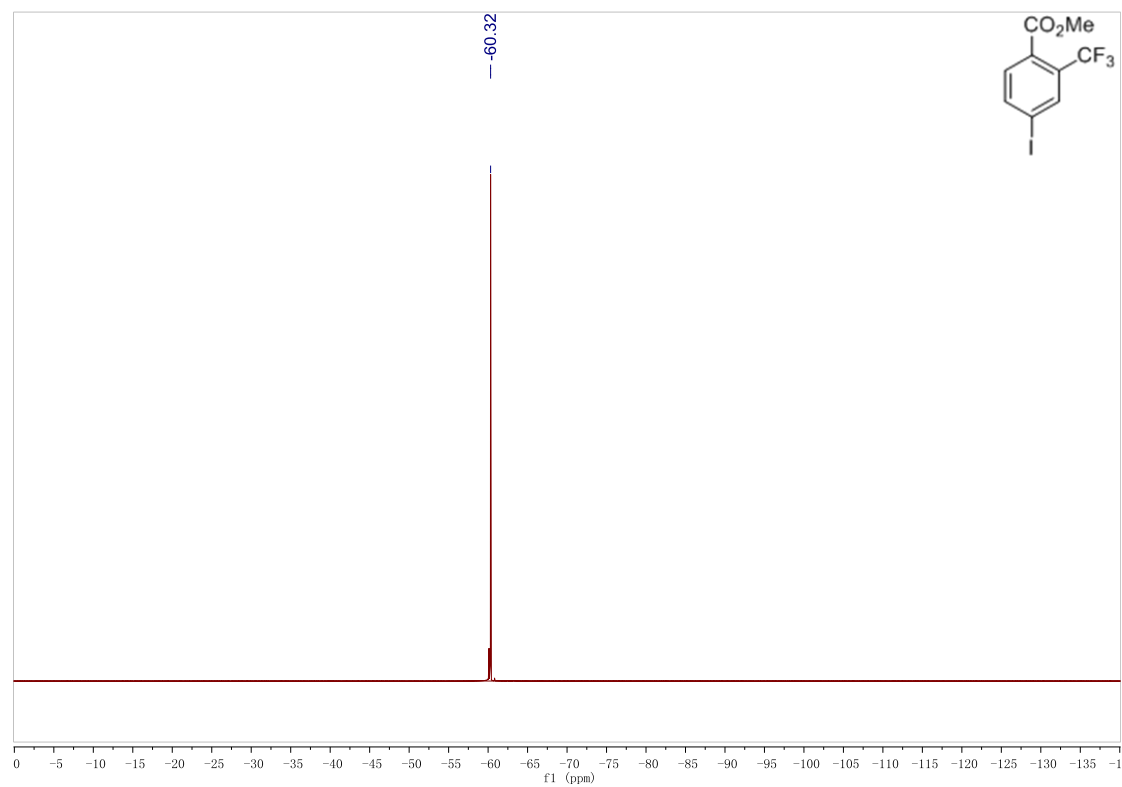
^1H NMR



¹³C NMR

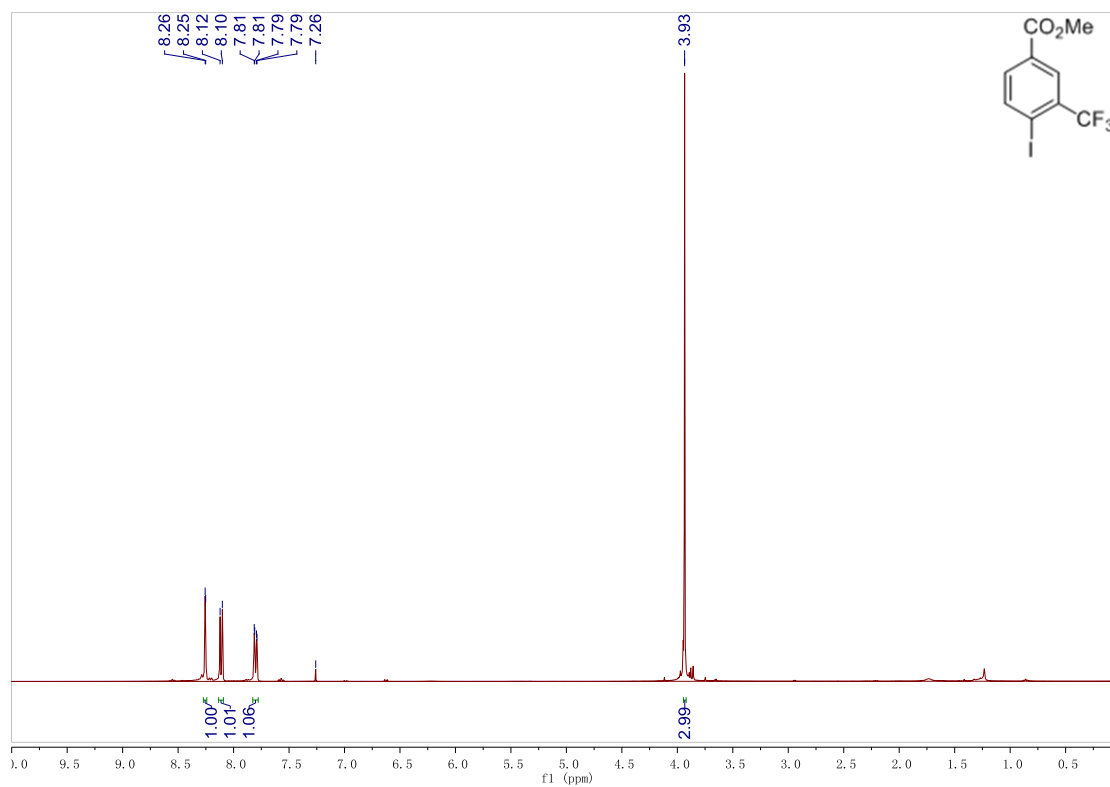


¹⁹F NMR

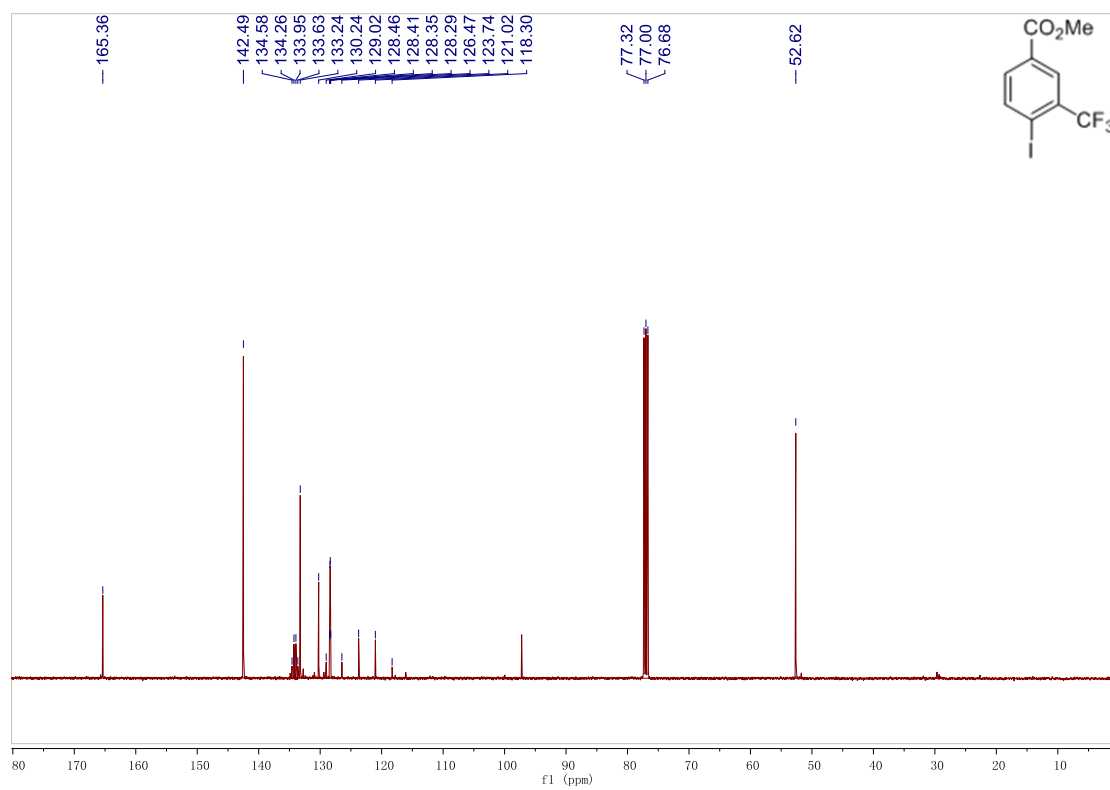


Methyl 4-iodo-3-(trifluoromethyl)benzoate:

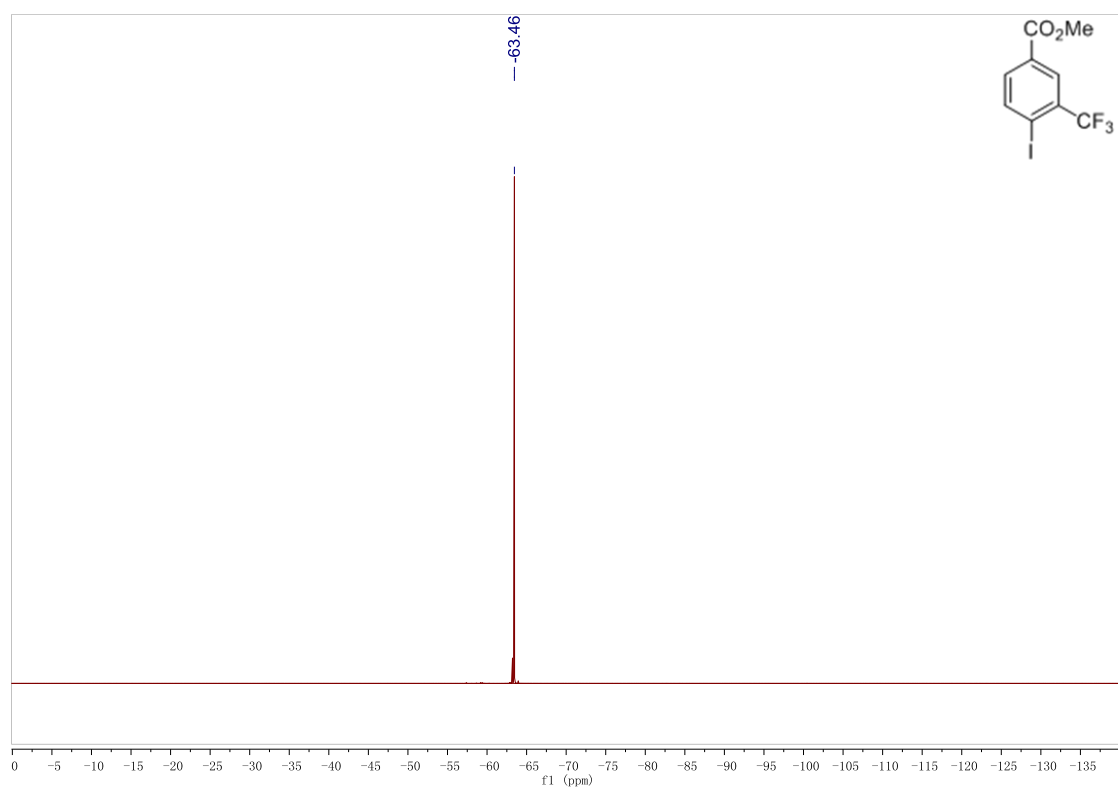
^1H NMR



^{13}C NMR



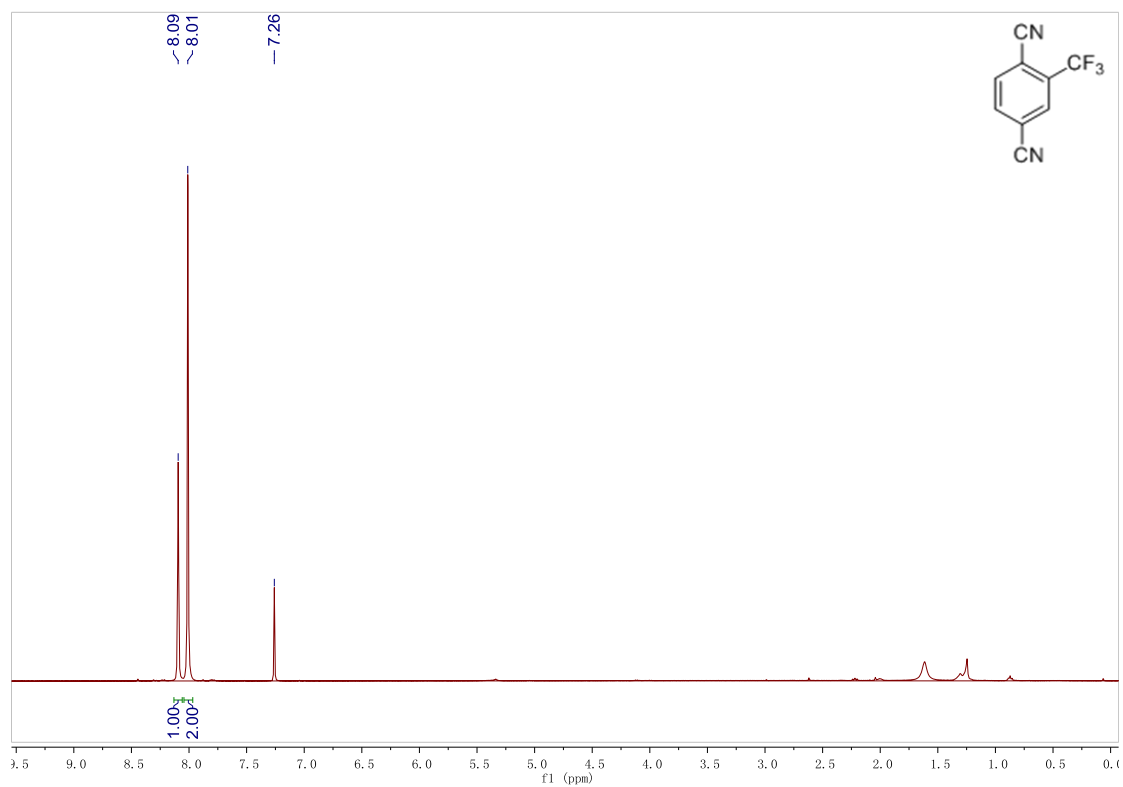
^{19}F NMR



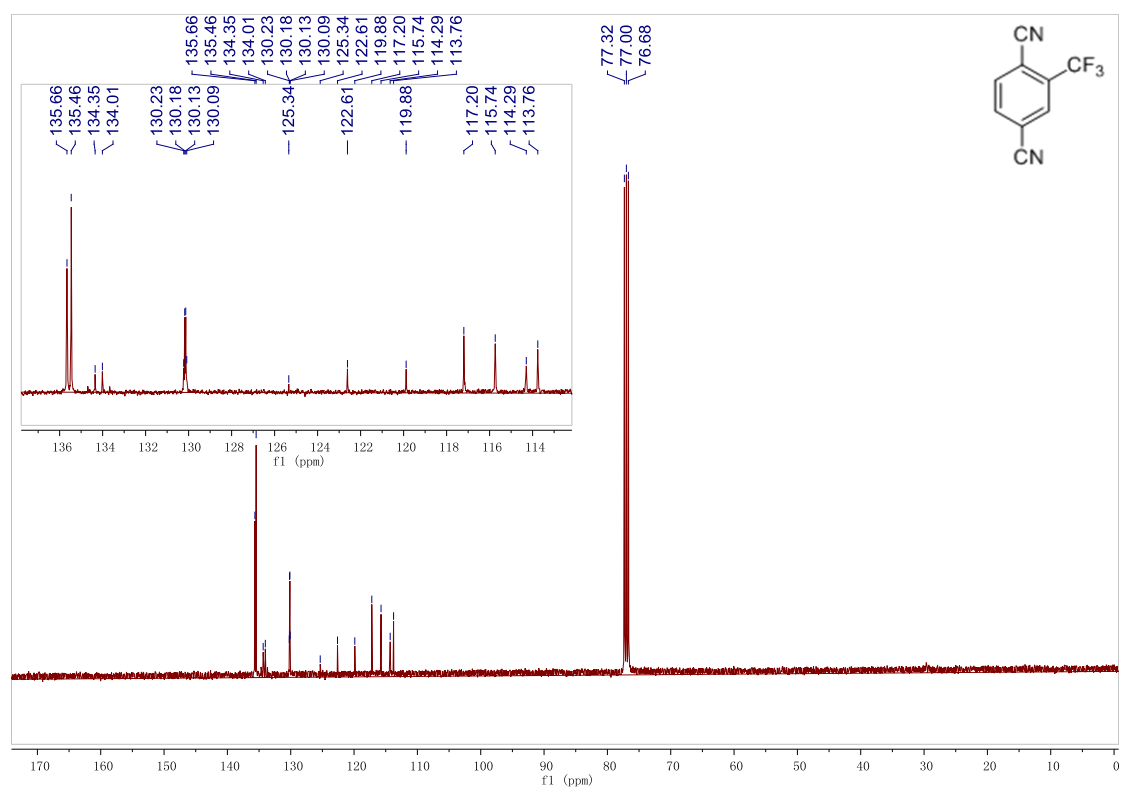
Spectra of products:

Compound 1o:

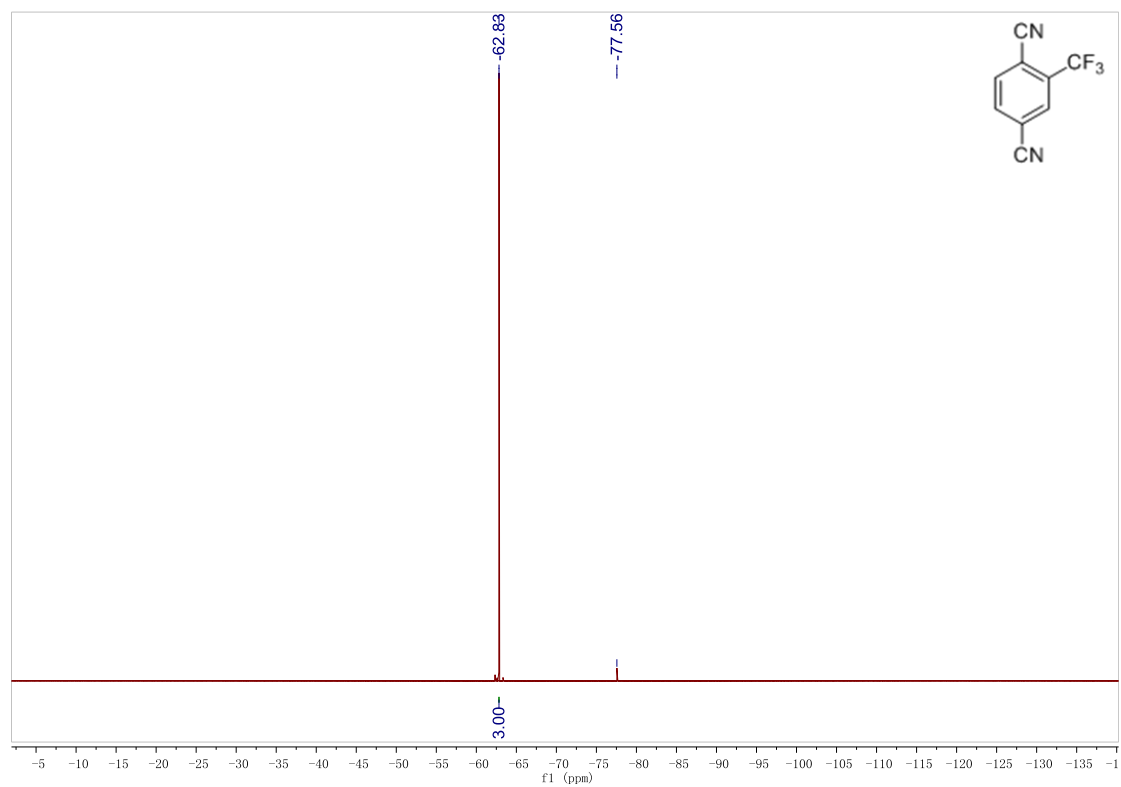
^1H NMR



¹³C NMR

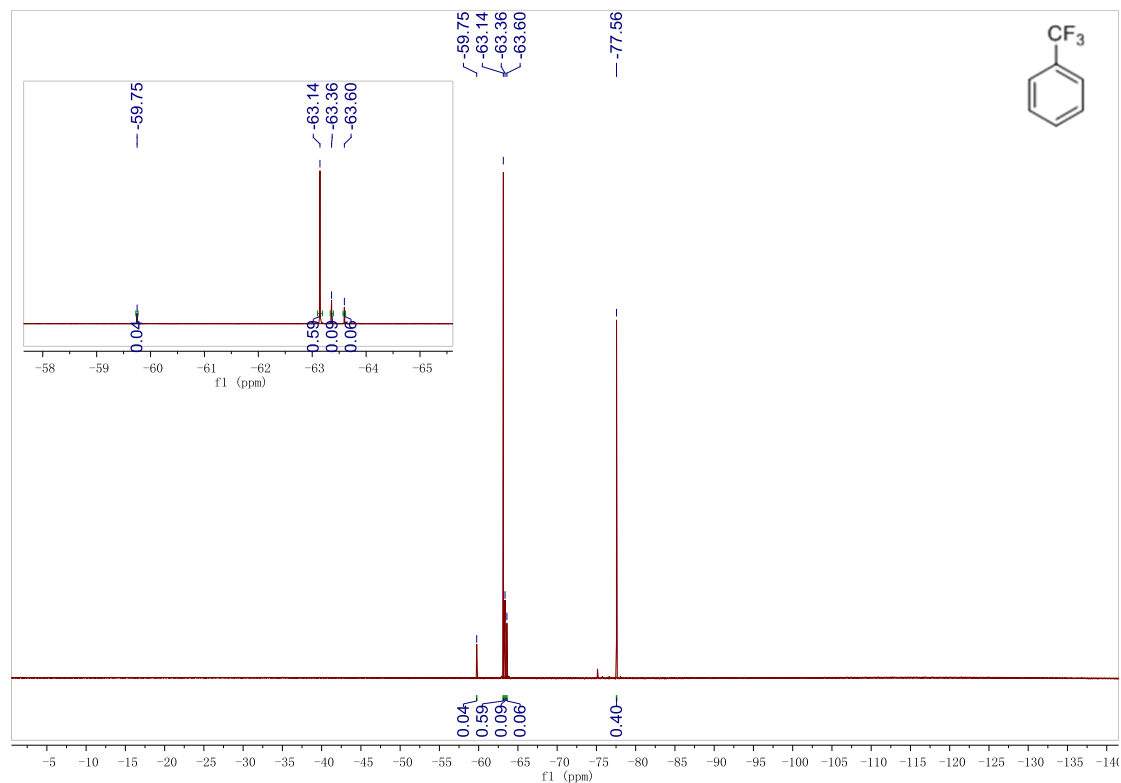


¹⁹F NMR



Compound 2o:

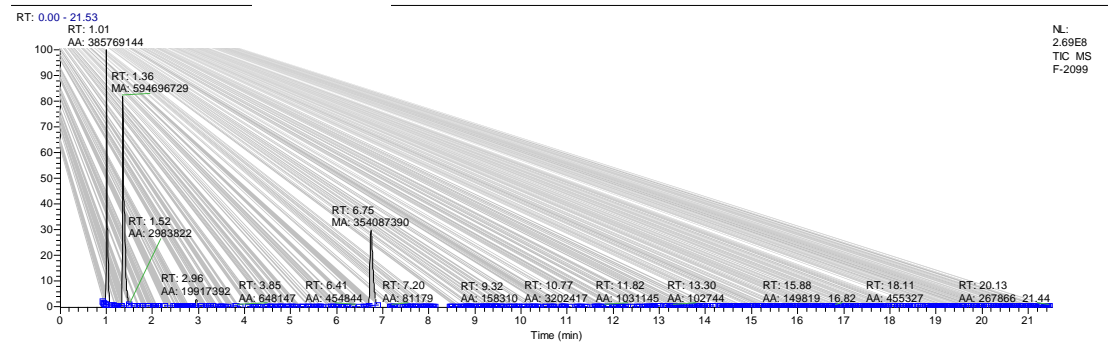
^{19}F NMR



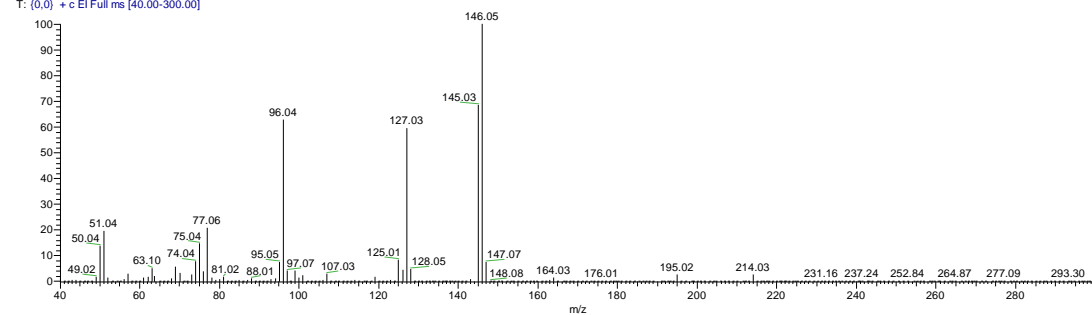
GC-MS

F:\DATA\...CF3 of p-nitrofluorobenzene\F-2099

7/24/2014 5:26:12 PM

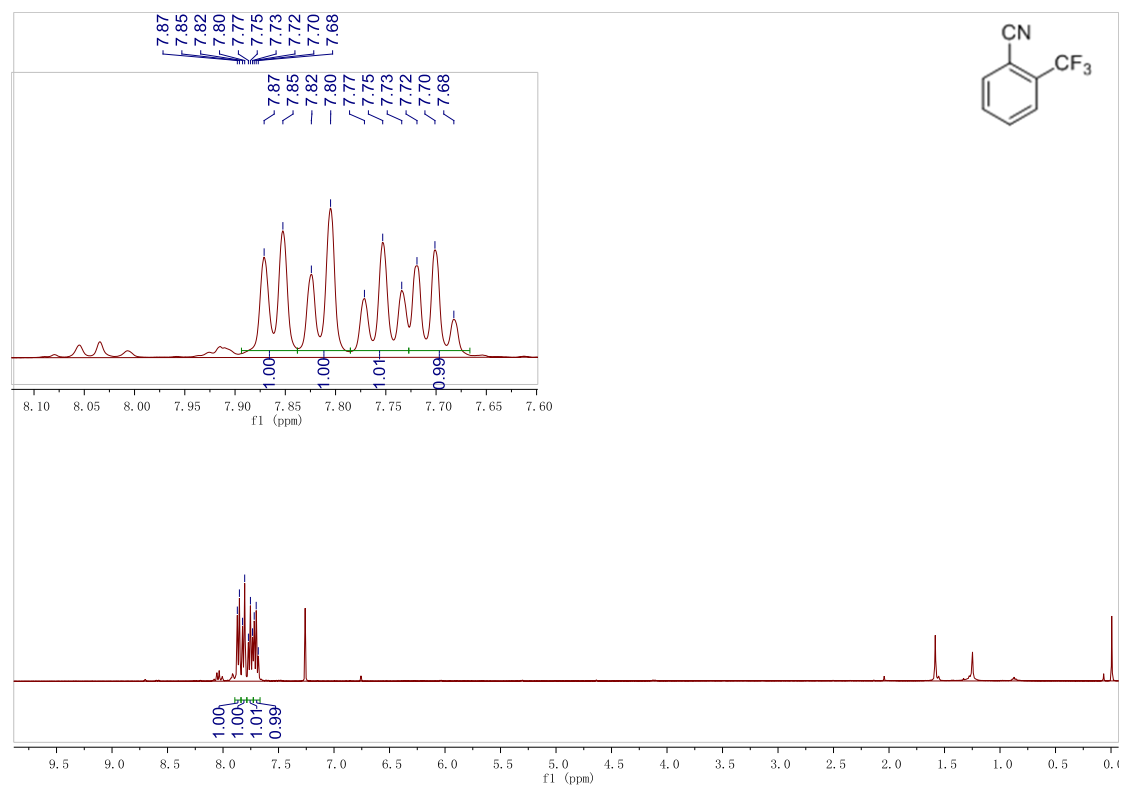


F-2099 #129 RT: 1.36 AV: 1 NL: 3.93E7
T: (0.0) + c El Full ms [40.00-300.00]

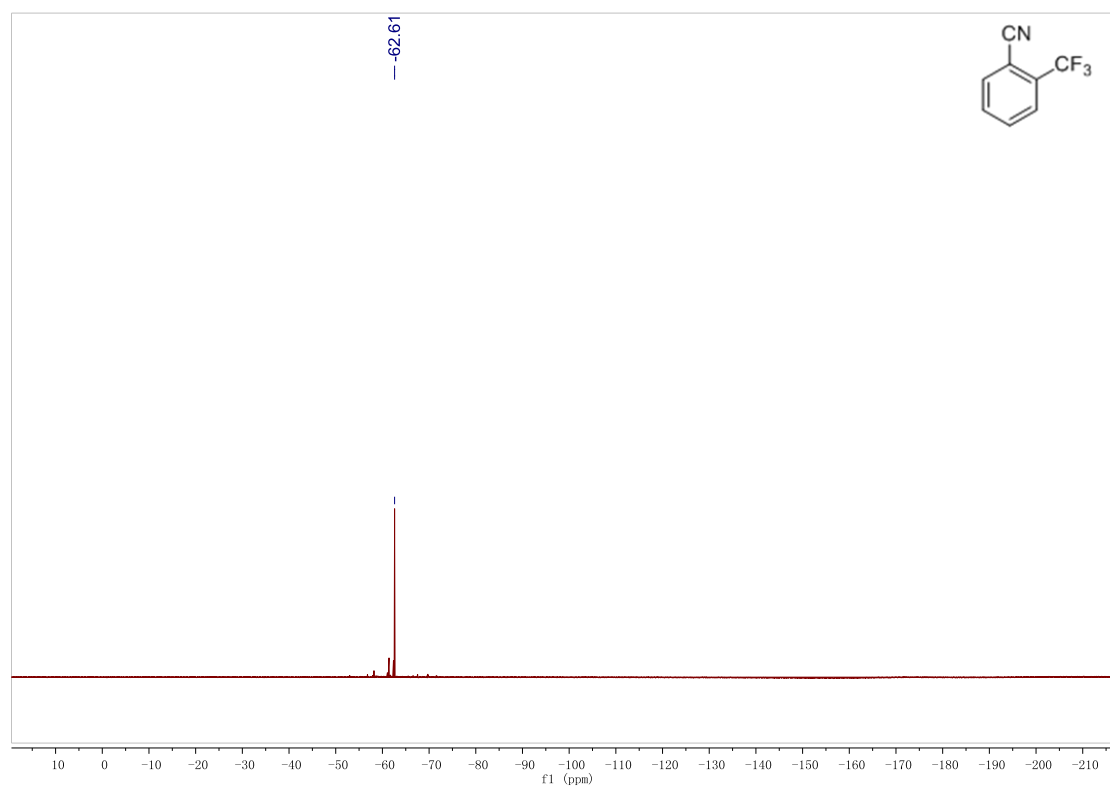


Compound 3o:

^1H NMR

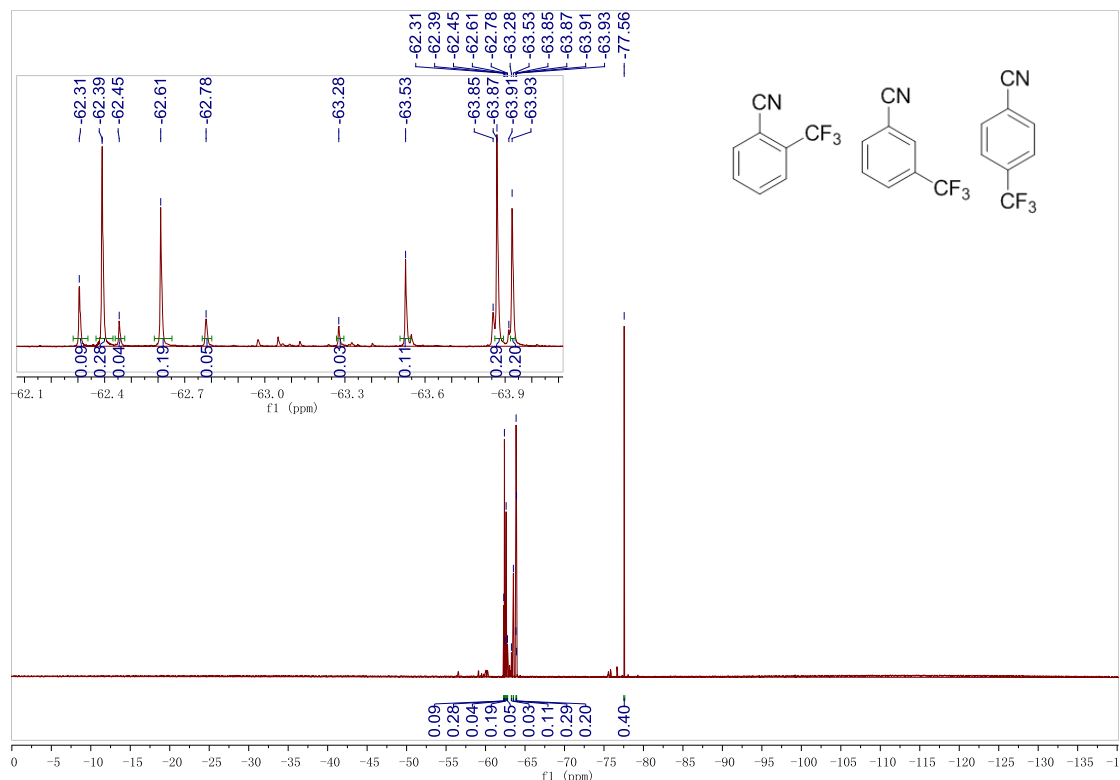


^{19}F NMR



Compound 3o-p:

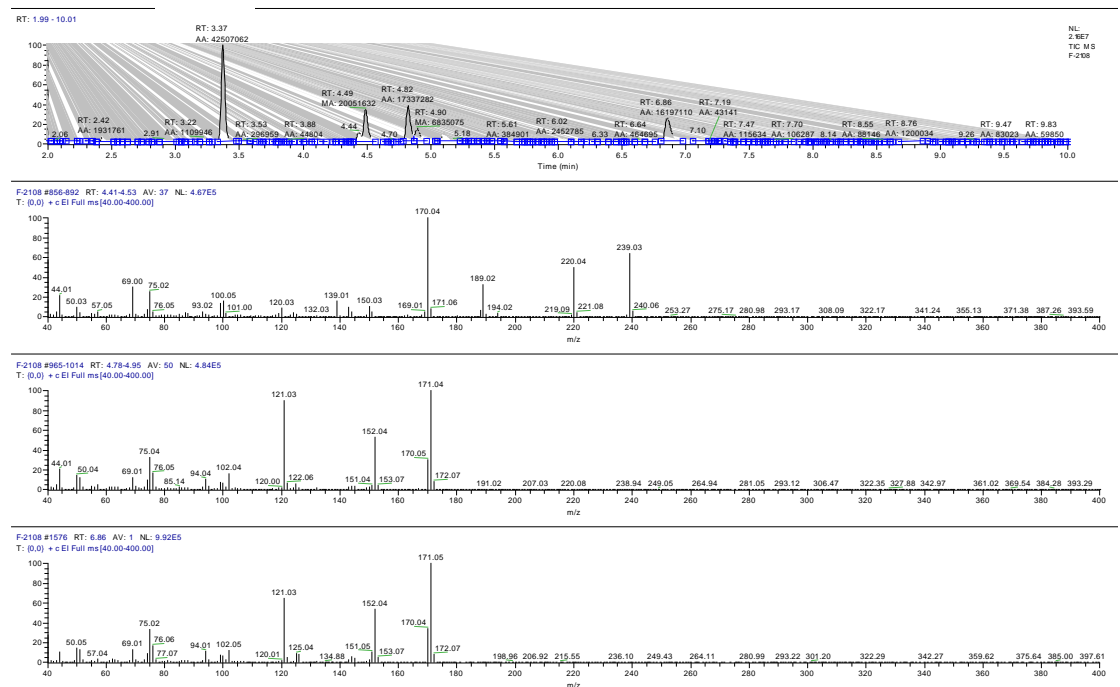
¹⁹F NMR

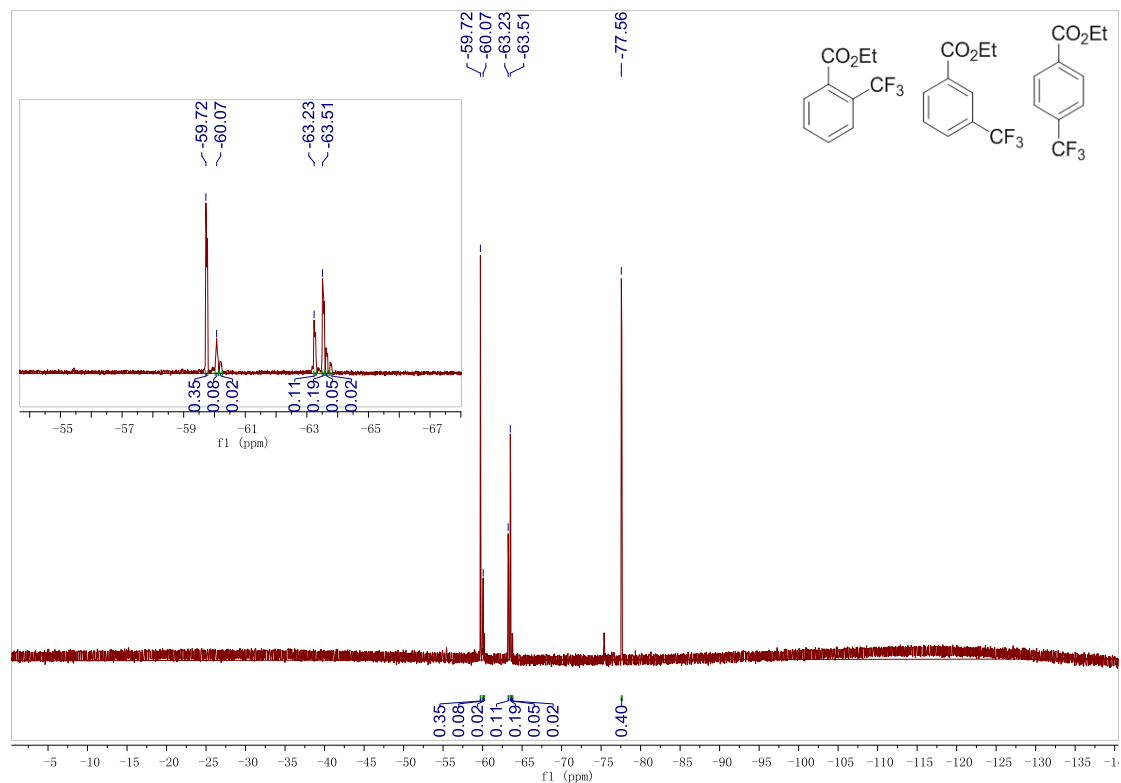


GC-MS

F:\DATA\...CF3 of p-nitro

6/25/2014 12:47:48 PM

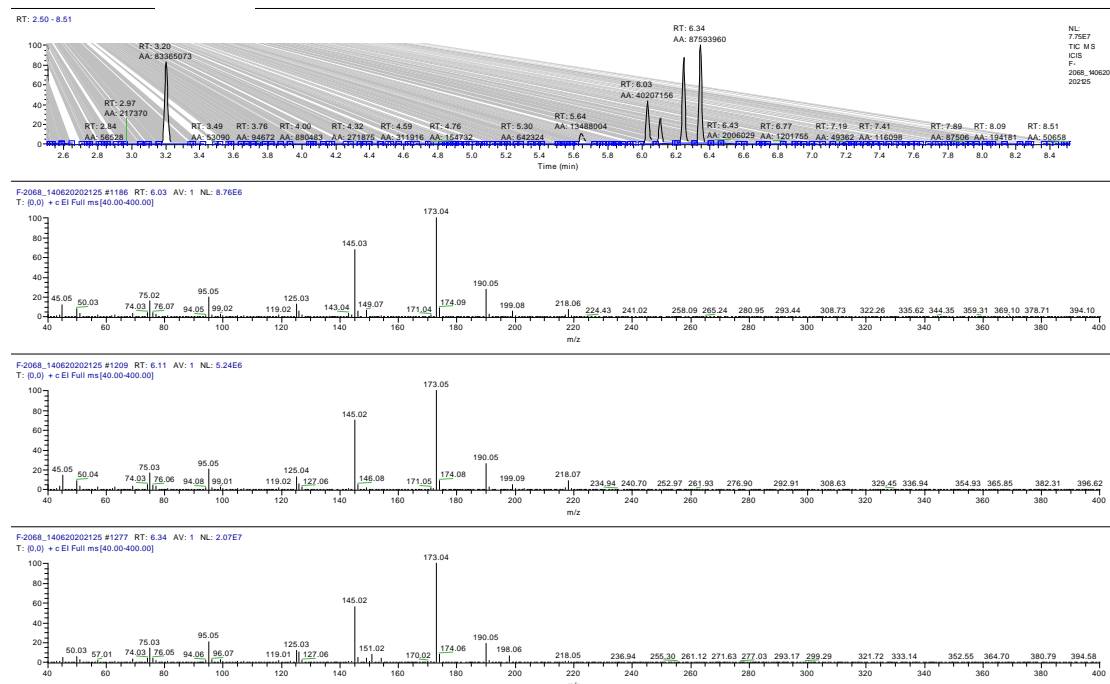


¹⁹F NMR

GC-MS

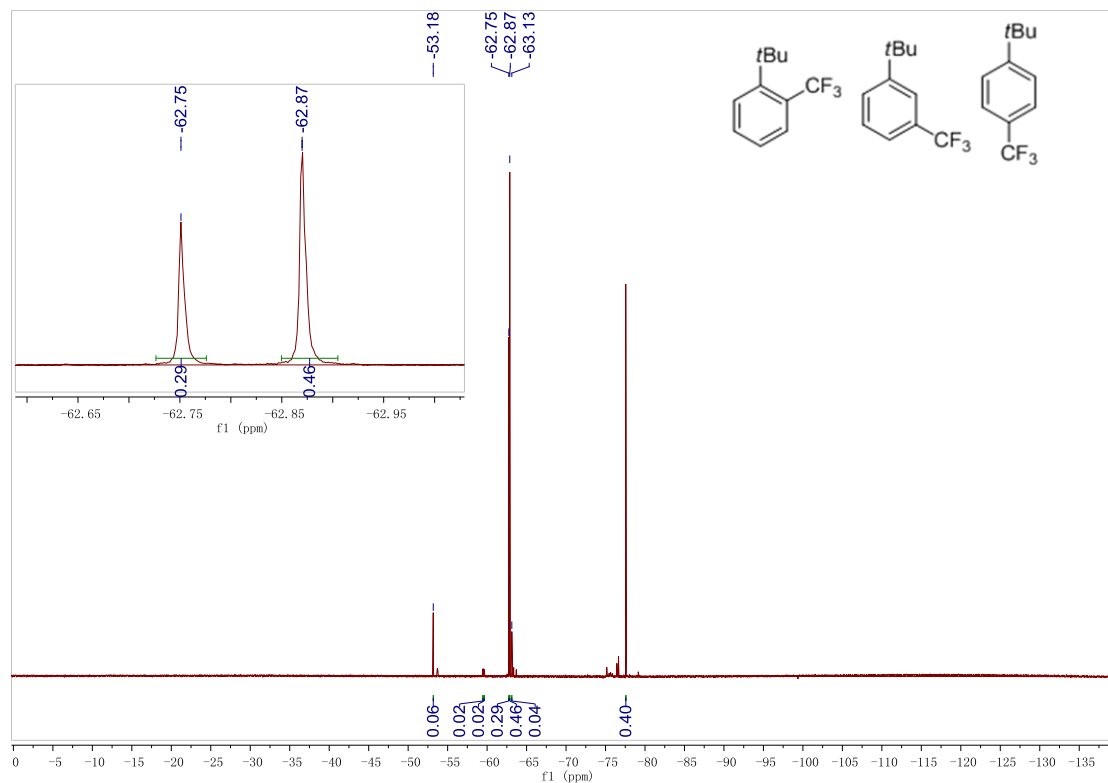
F:\DATA\...F-2068_14062

6/20/2014 8:21:25 PM



Compound 5o-p:

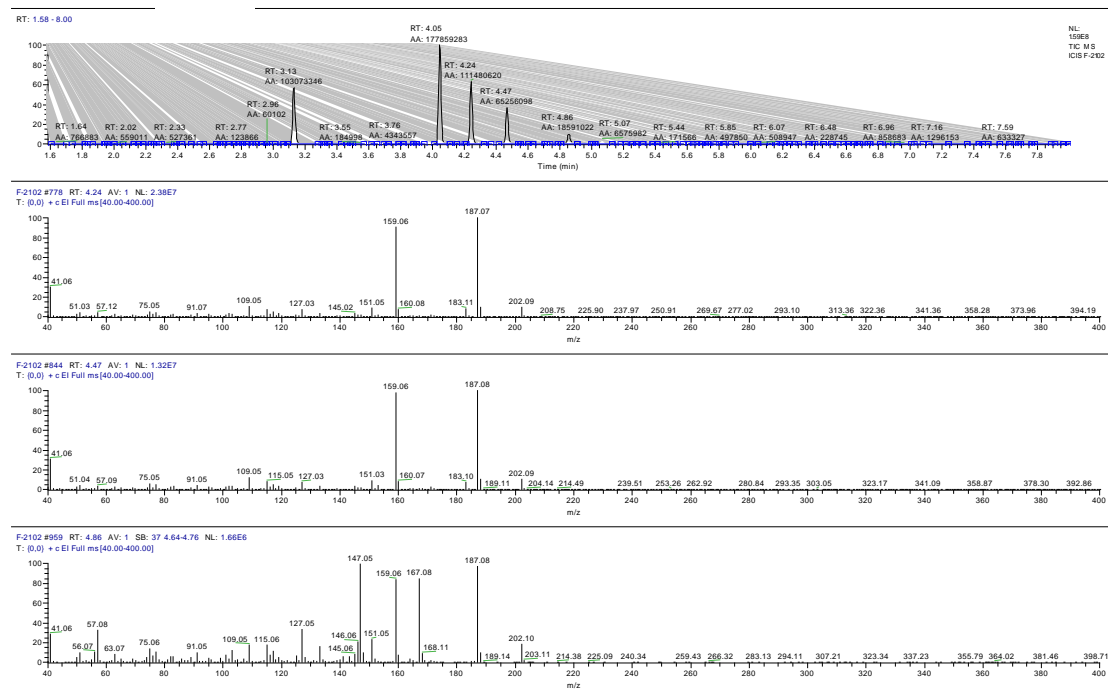
¹⁹F NMR



GC-MS

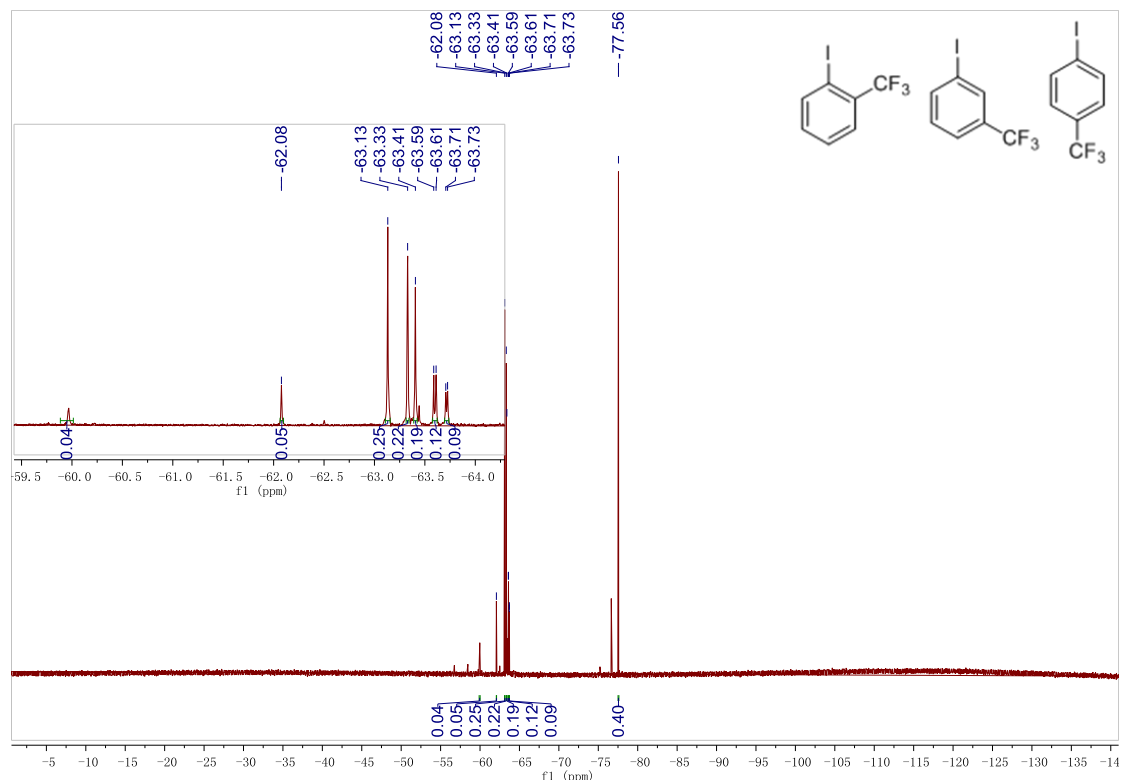
F:\DATA\CF3 of p-nitro

6/24/2014 7:17:38 PM



Compound 60-p:

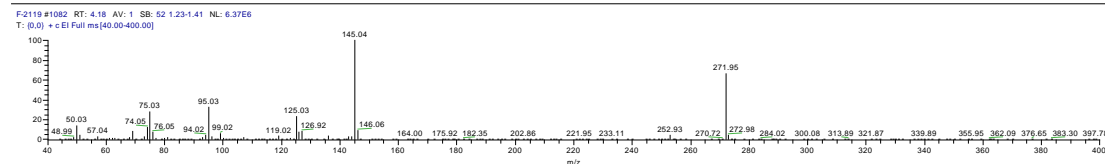
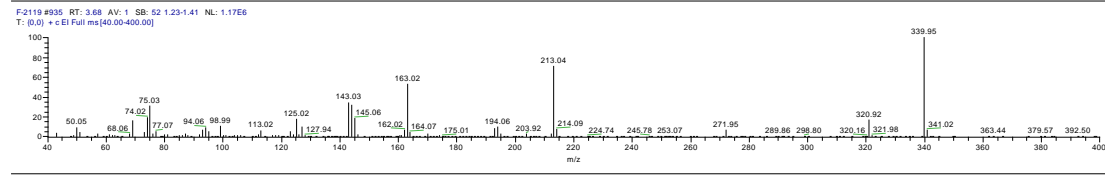
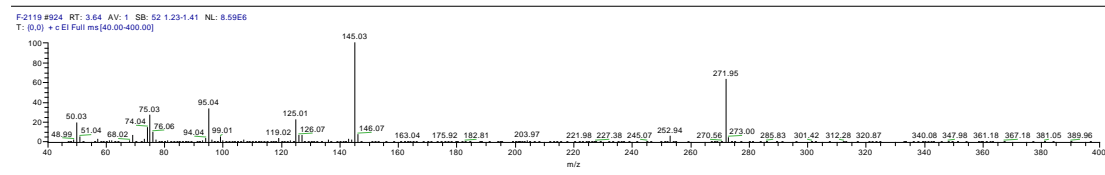
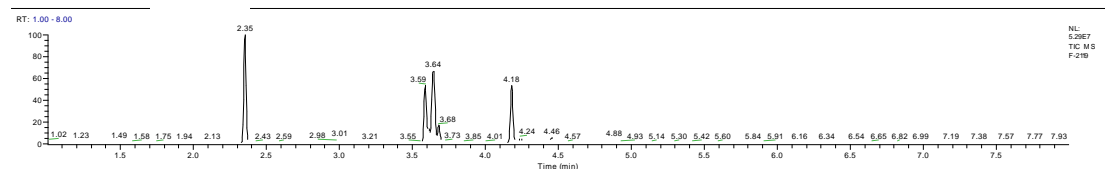
¹⁹F NMR



GC-MS

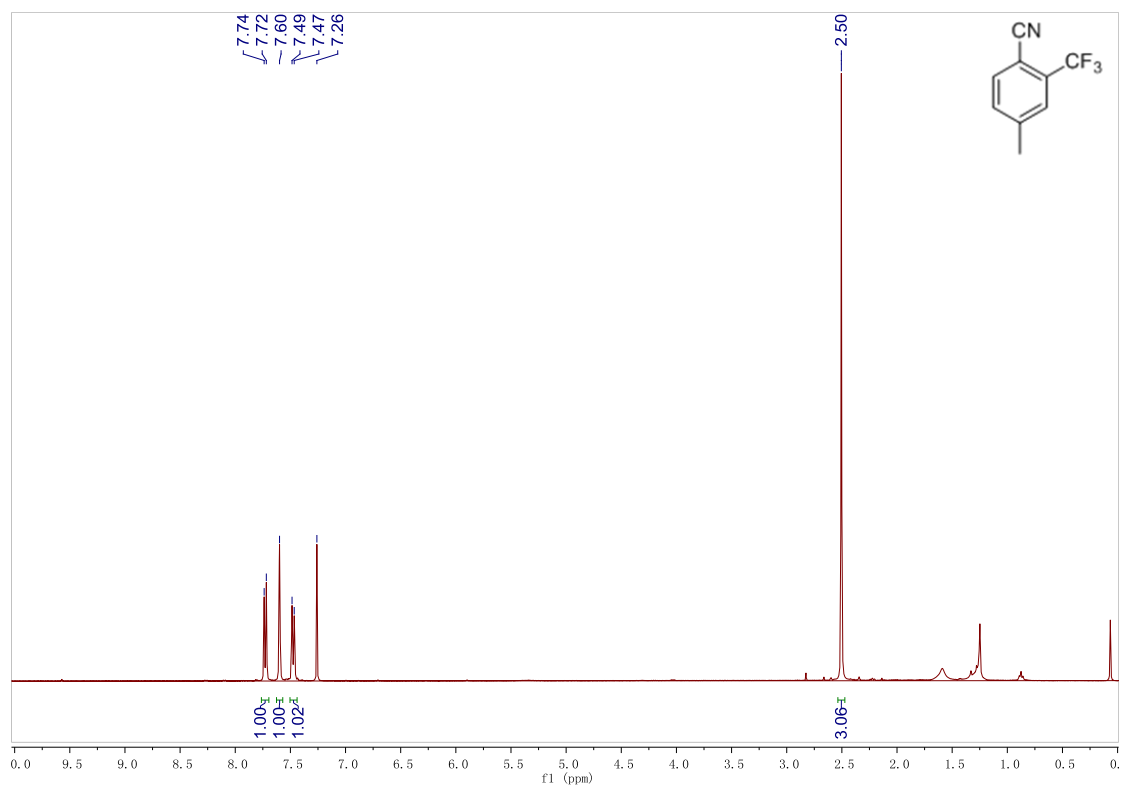
F:\DATA\...CF3 of p-nitro

6/27/2014 12:52:16 PM

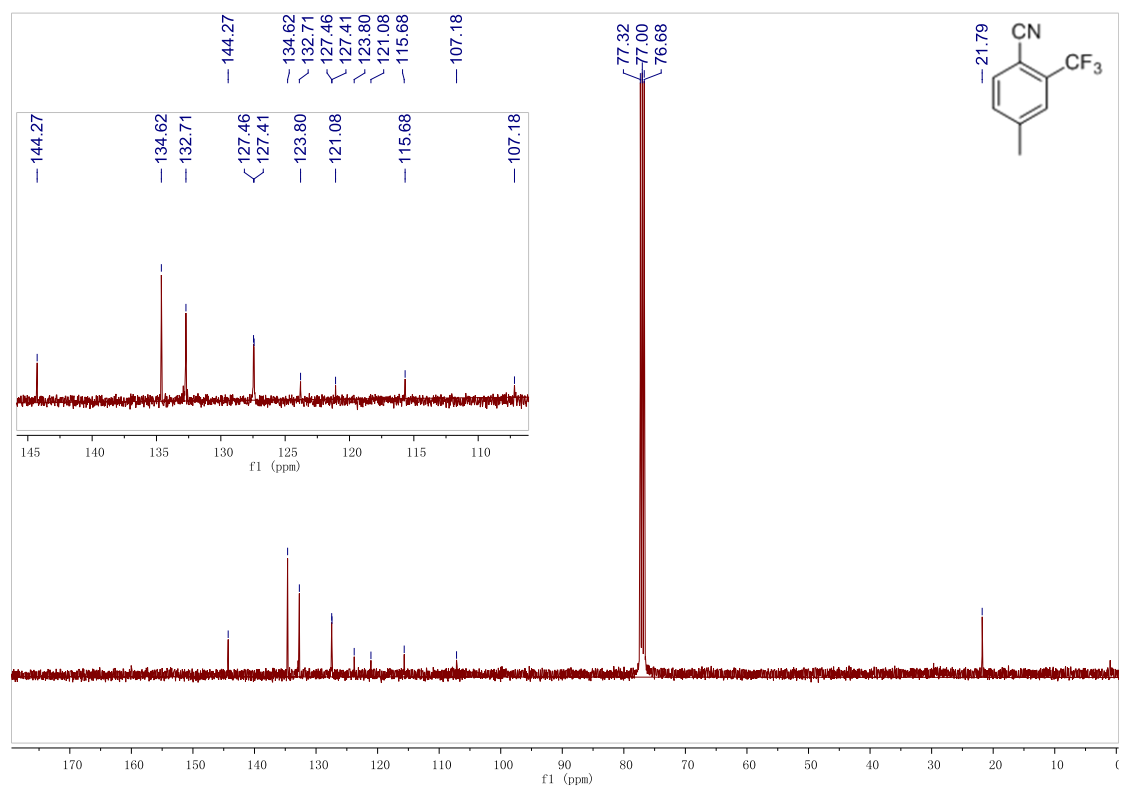


Compound 7o:

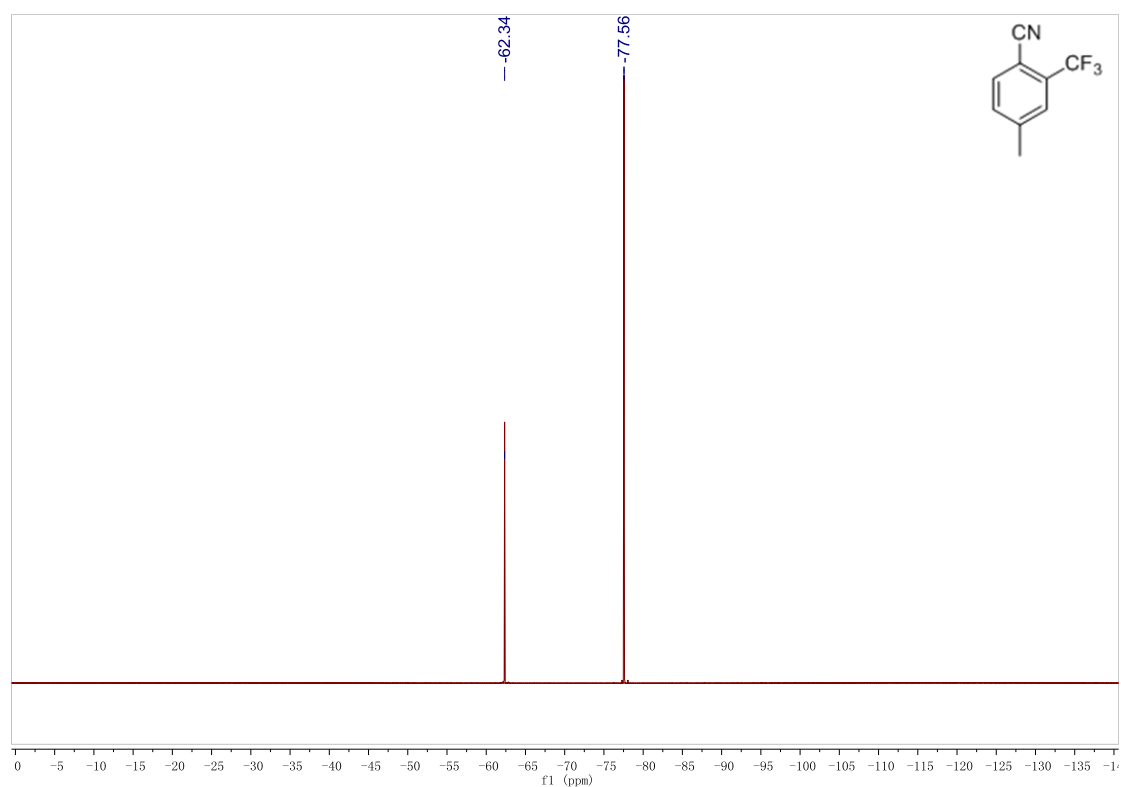
^1H NMR



^{13}C NMR

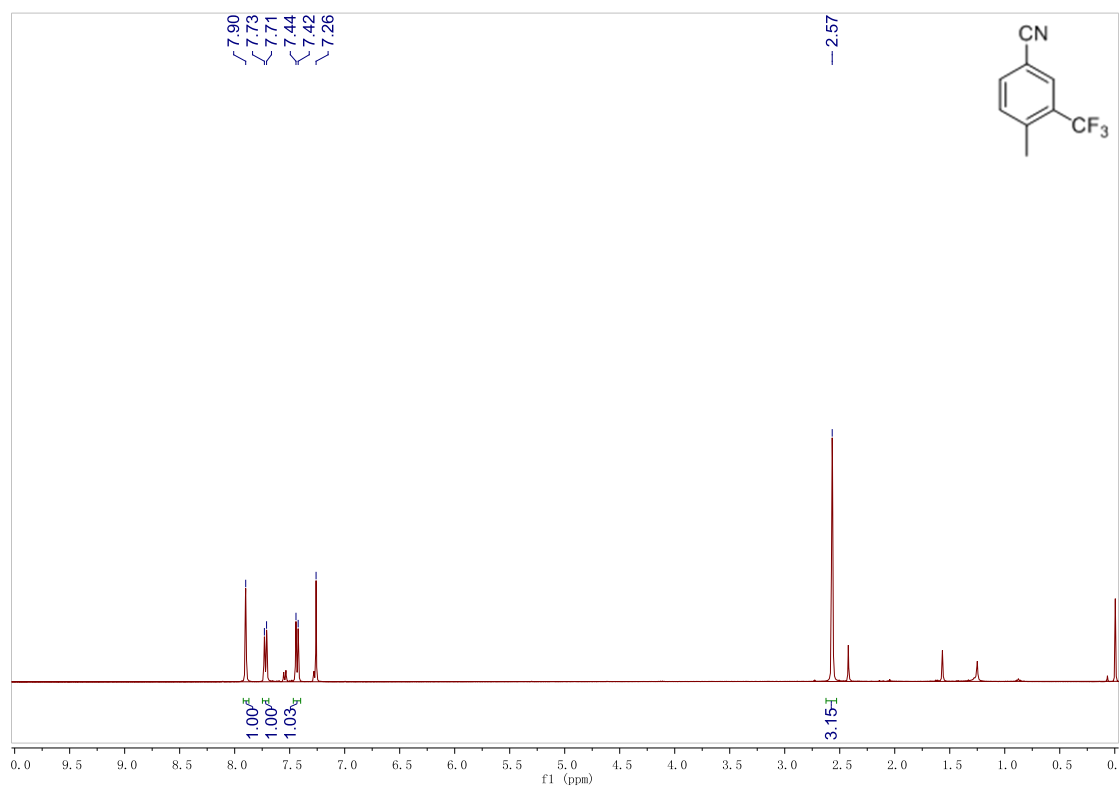


¹⁹F NMR

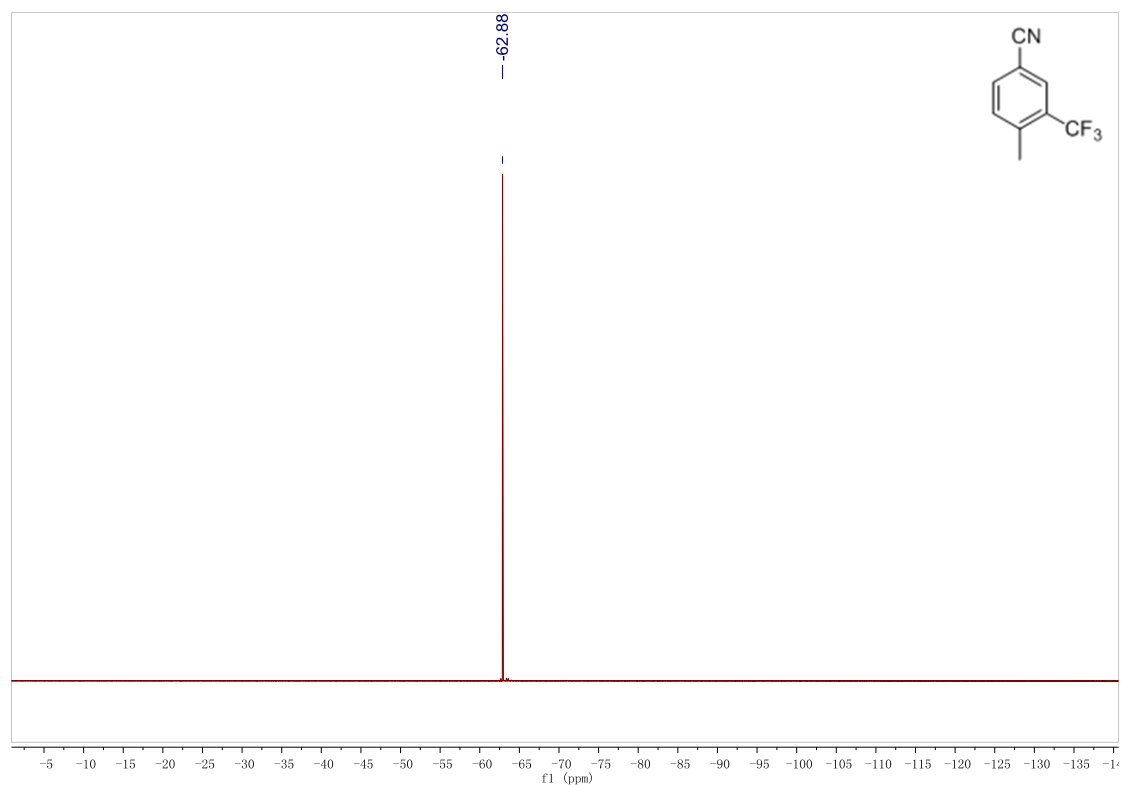


Compound 7m:

¹H NMR

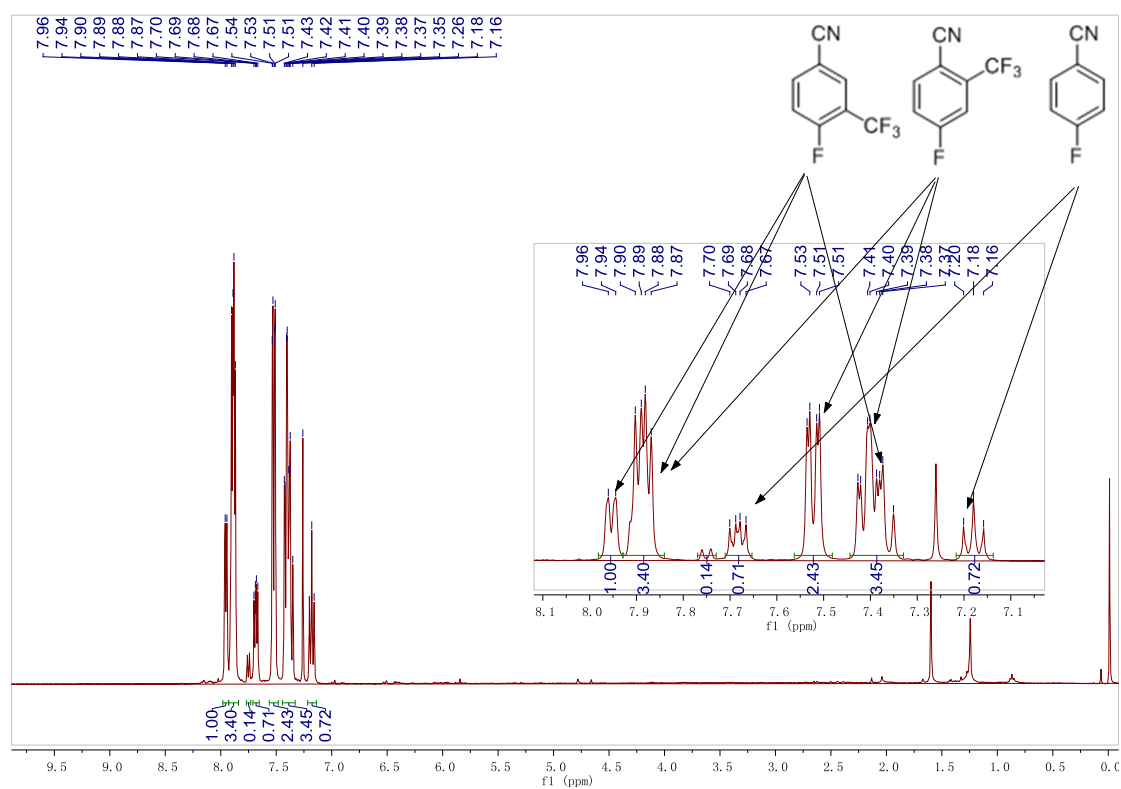


¹⁹F NMR

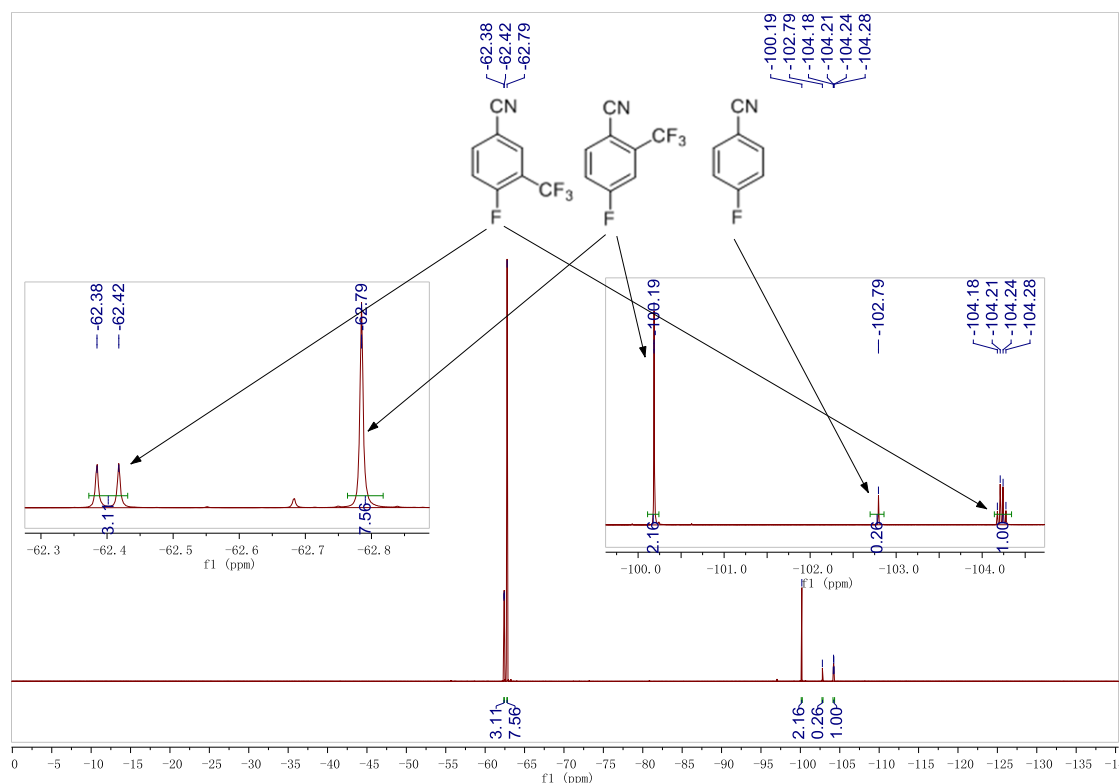


Compound 80-m:

¹H NMR



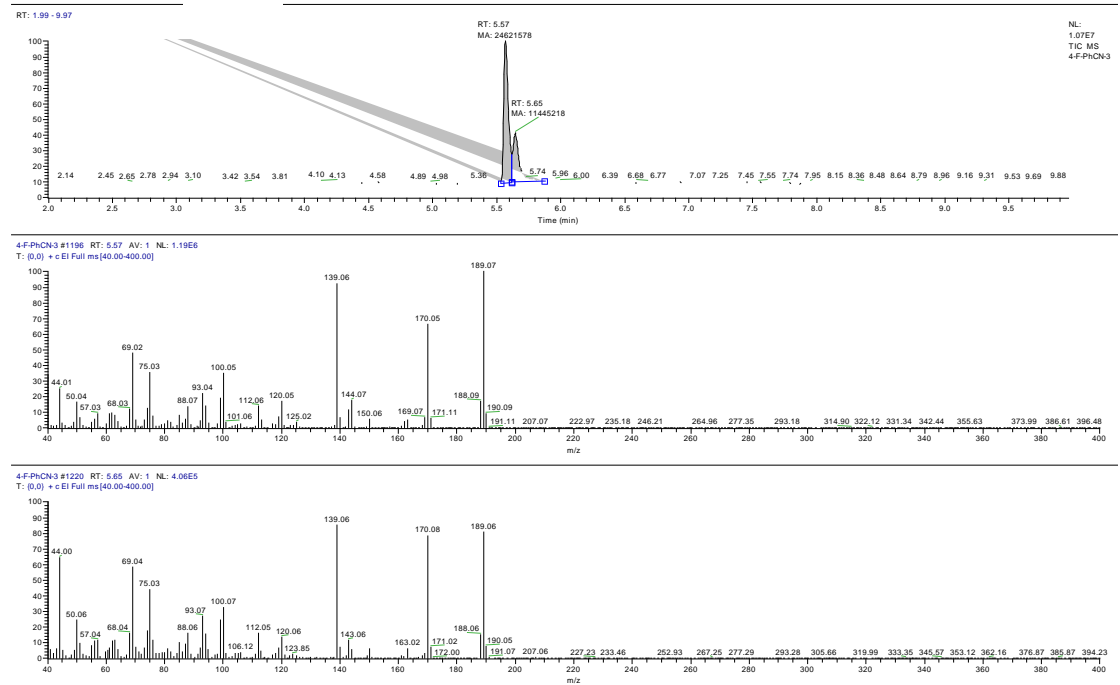
¹⁹F NMR



GC-MS

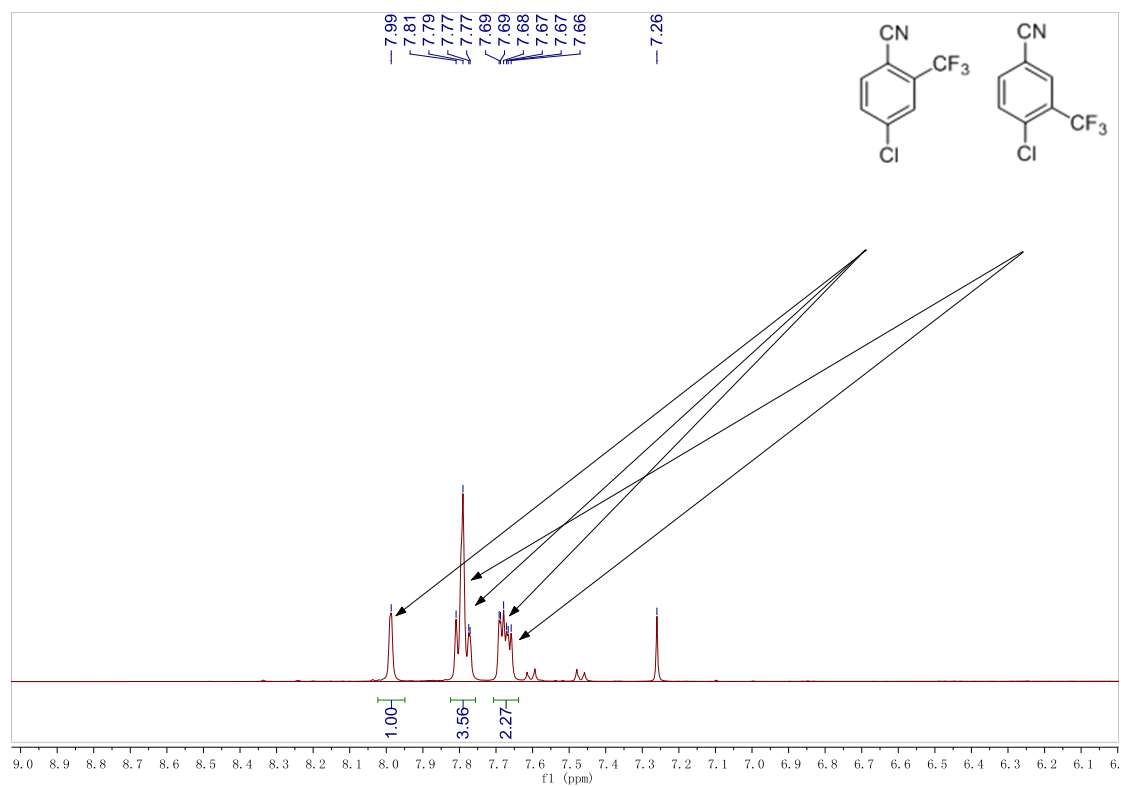
F:\DATA\...4-F-PhCN-3

6/9/2014 10:50:28 AM

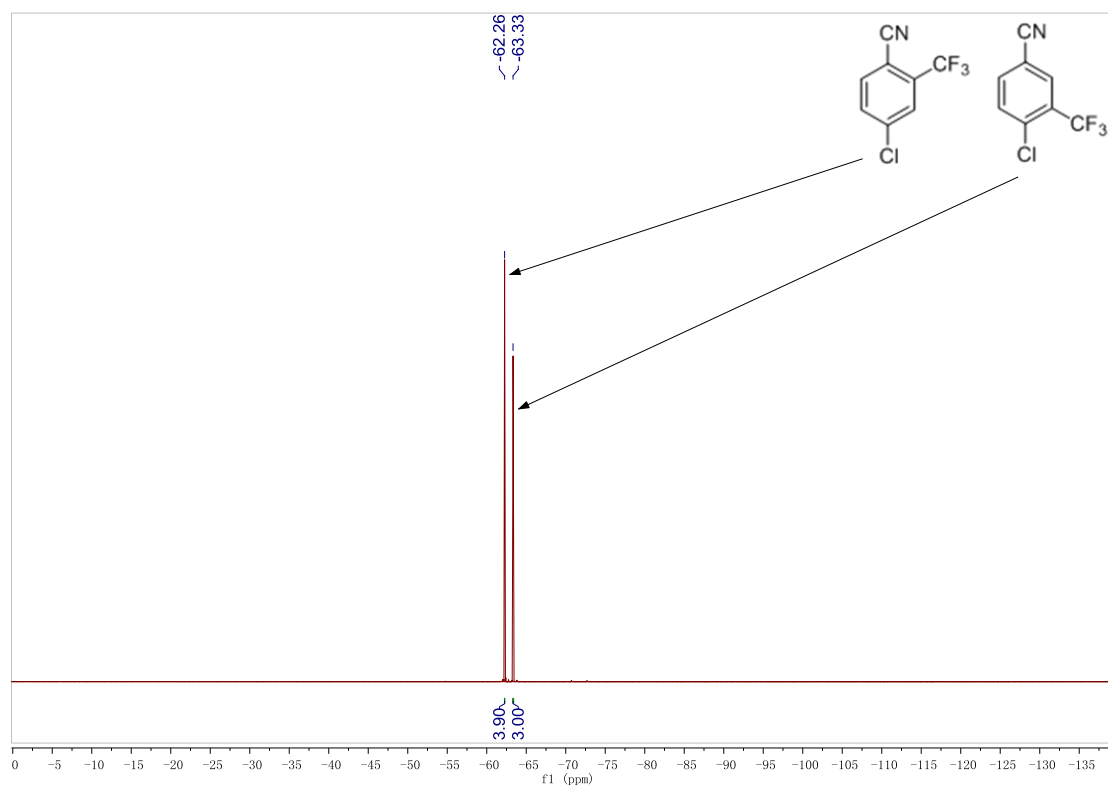


Compound 9o-m:

^1H NMR



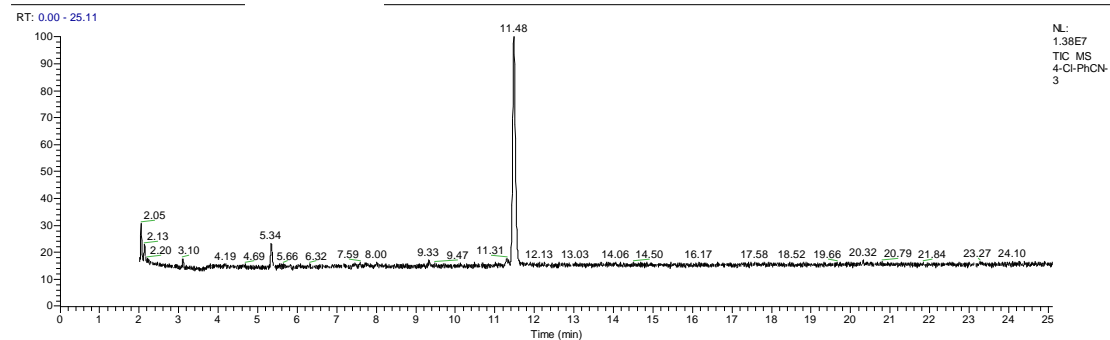
^{19}F NMR



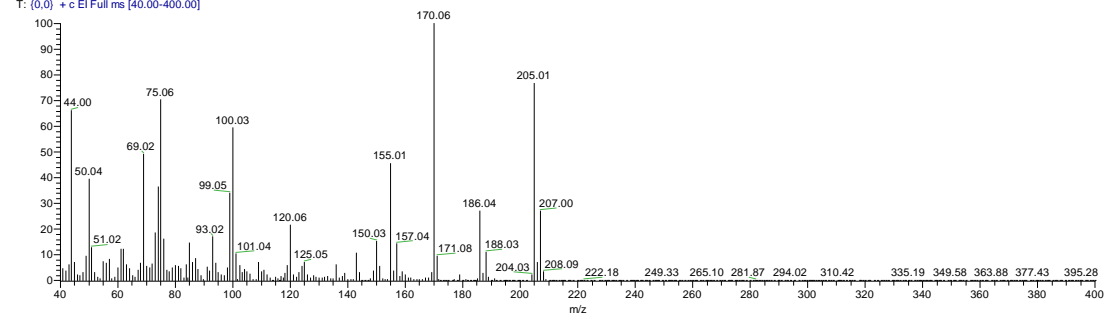
GC-MS

F:\DATA\14-Cl-PhCN-3

1/11/2014 6:58:12 PM

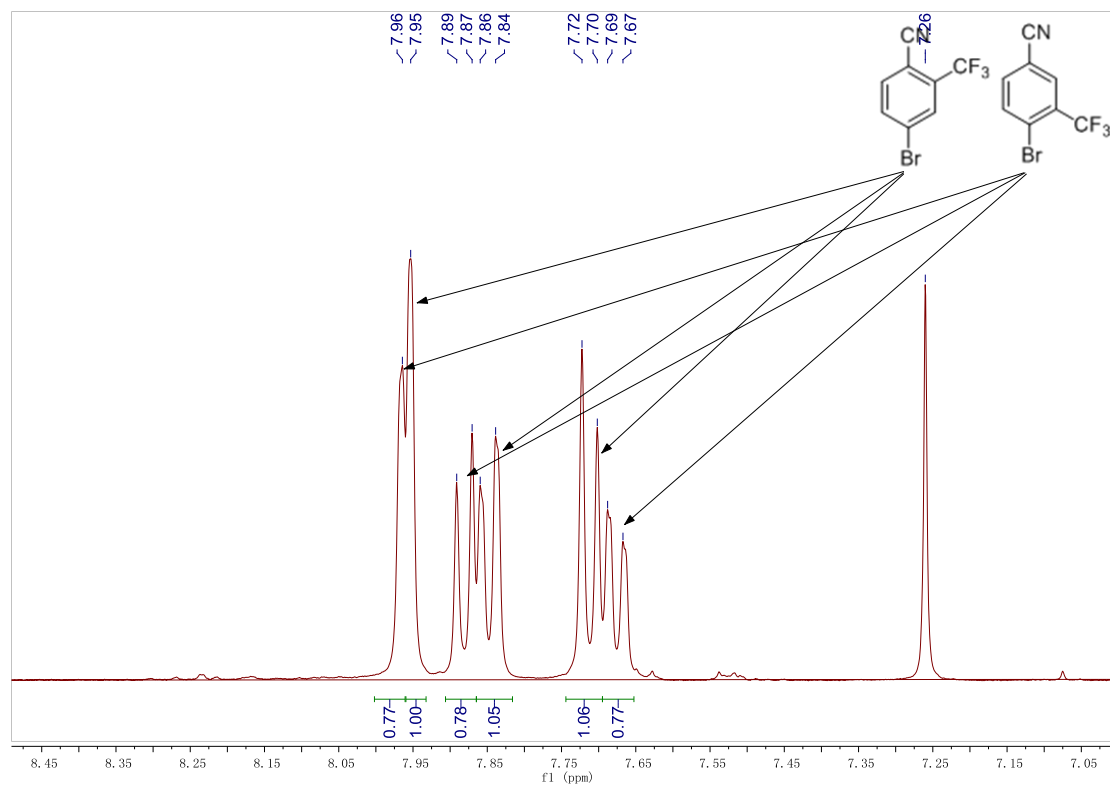


4-Cl-PhCN-3 #2788 RT: 11.48 AV: 1 NL: 1.14E6
T: (0.0) + c EI Full ms [40.00-400.00]

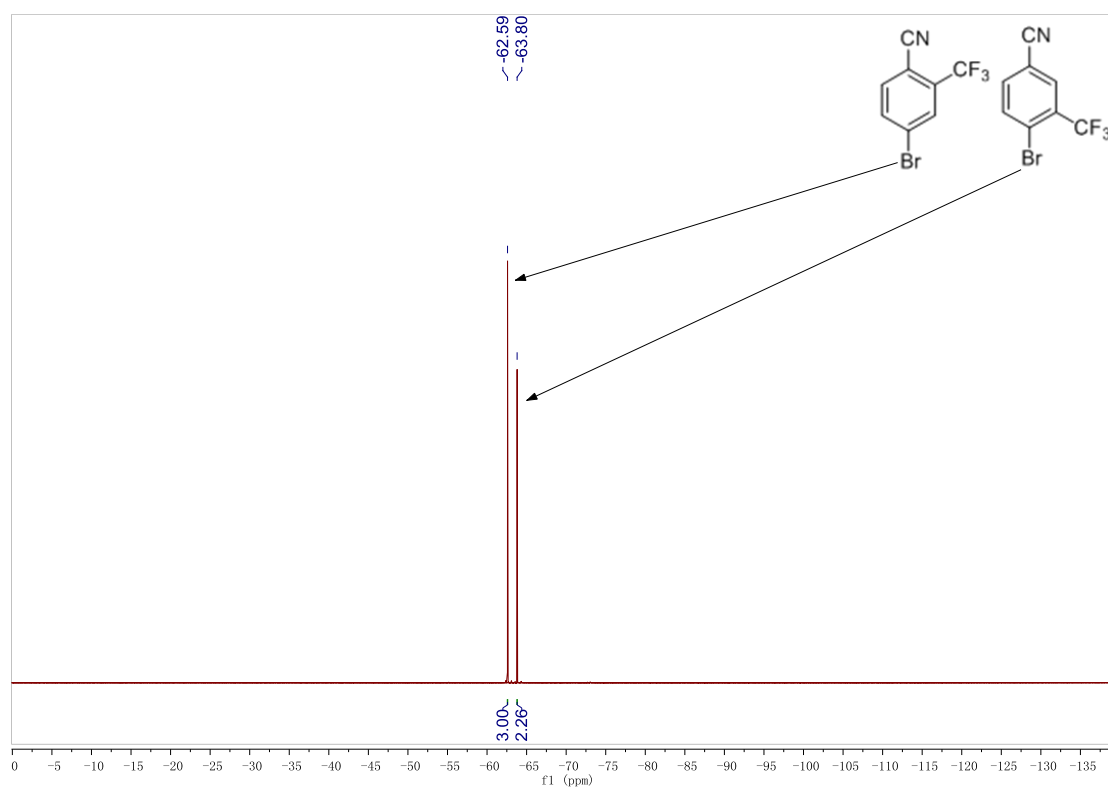


Compound 10o-m:

¹H NMR

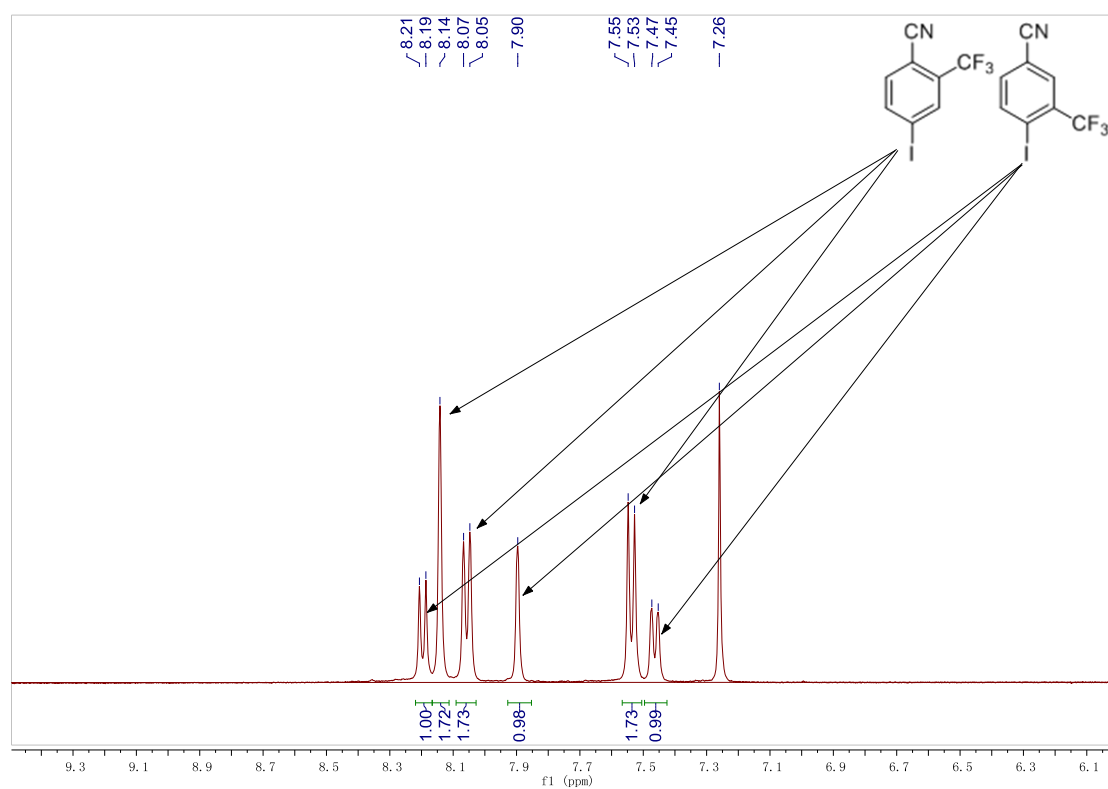


¹⁹F NMR

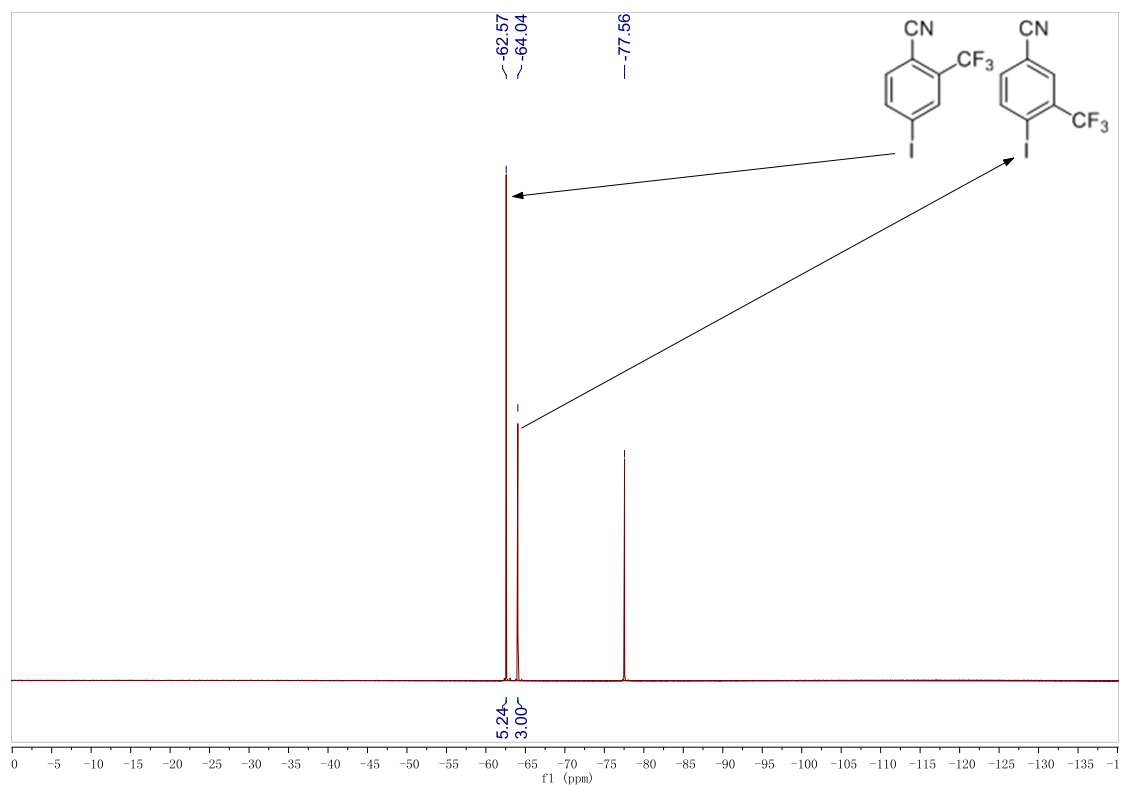


Compound 11o-m:

¹H NMR



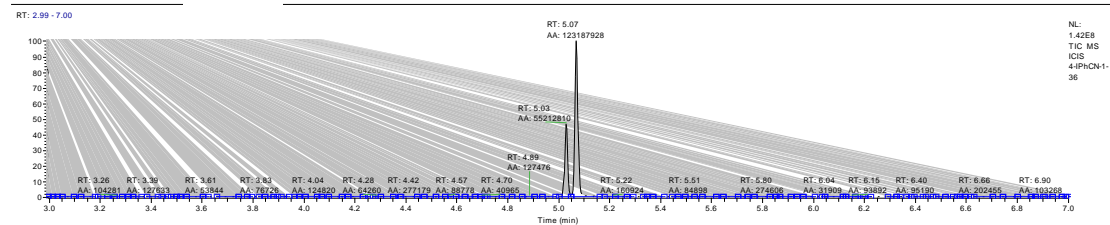
¹⁹F NMR



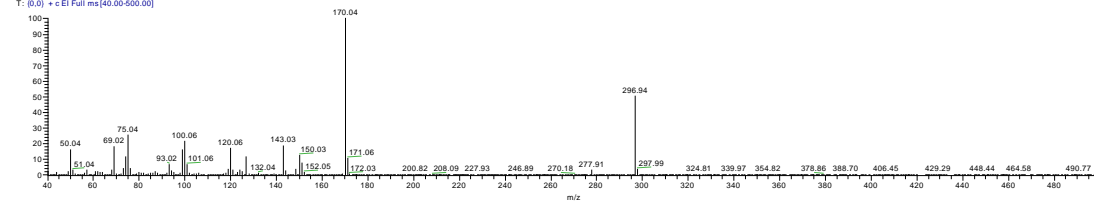
GC-MS

F:\DATA\14-PhCN-1-36

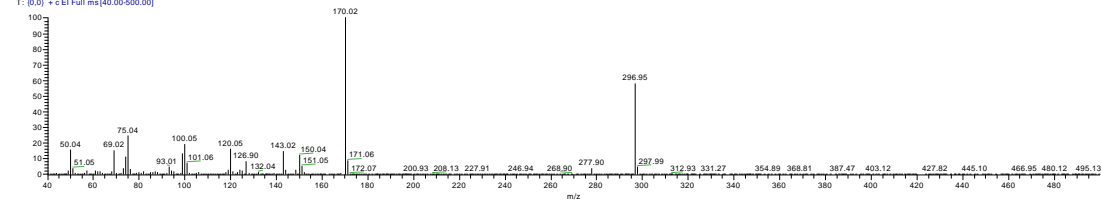
5/27/2014 4:17:03 PM



4-PhCN-1-36 #890 RT: 5.03 AV: 1 NL: 1.35E7
T: (0.0) + c EI Full ms[40.00-500.00]

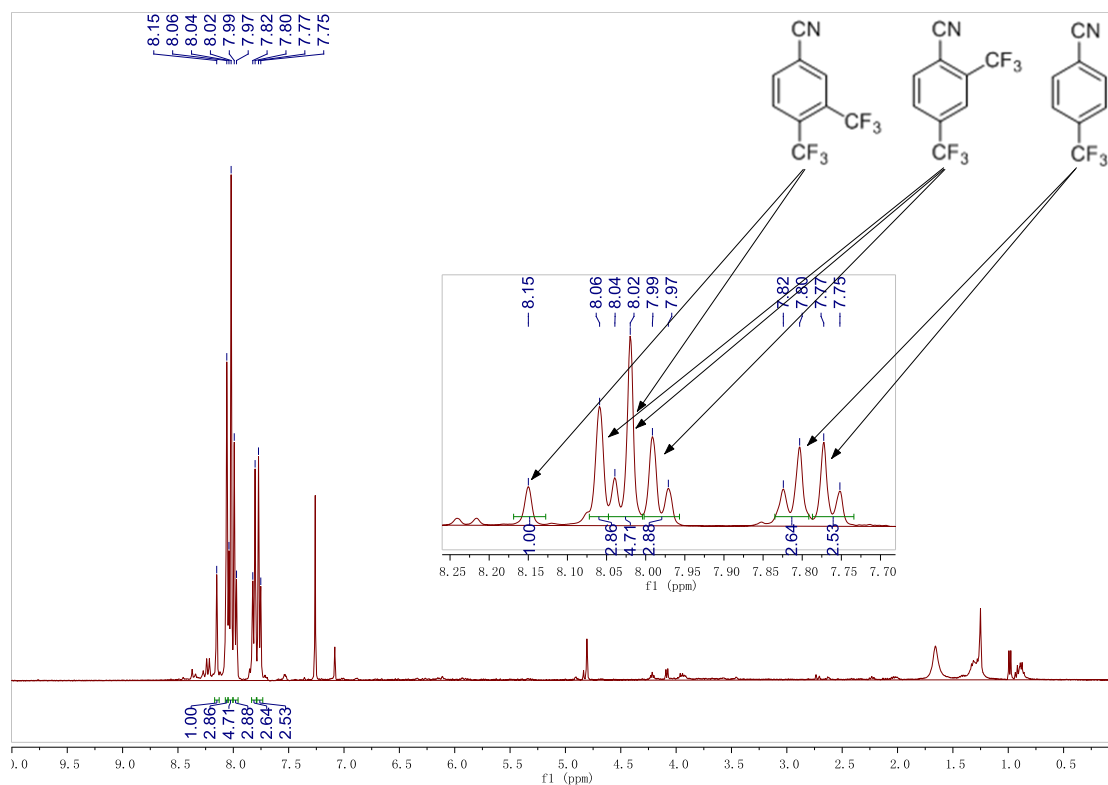


4-PhCN-1-36 #901 RT: 5.07 AV: 1 NL: 3.40E7
T: (0.0) + c EI Full ms[40.00-500.00]

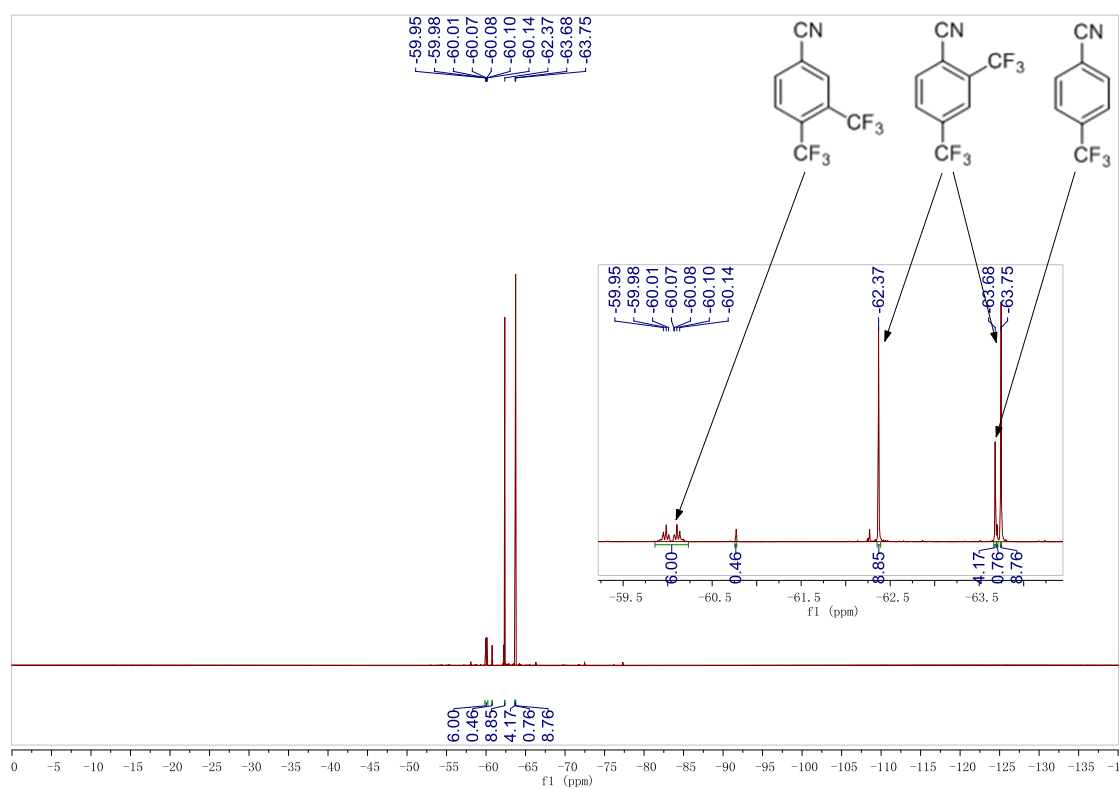


Compound 12o-m:

¹H NMR



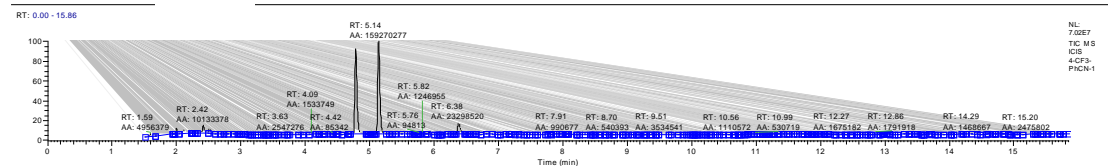
¹⁹F NMR



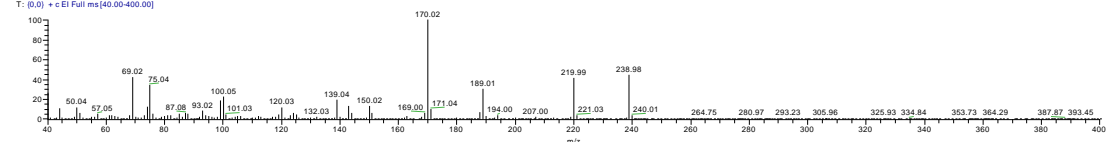
GC-MS

F:\DATA\...4-CF3-PhCN-1

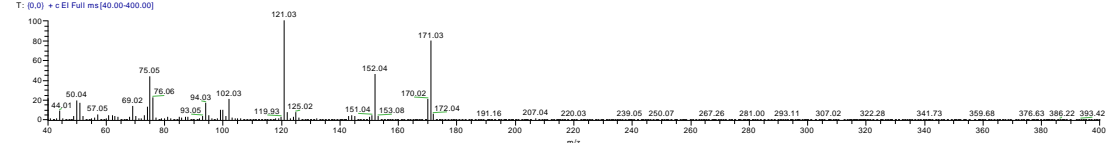
3/19/2014 9:58:21 PM



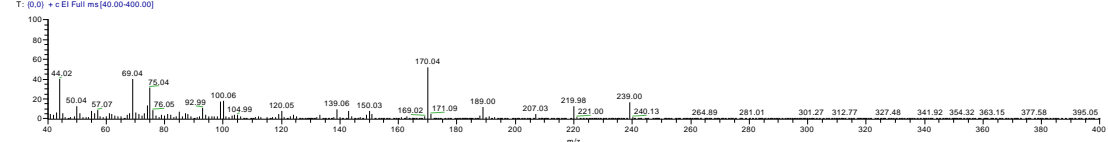
4-CF3-PhCN-1 #966 RT: 4.78 AV: 1 NL: 9.38E6
T: (0.0) + c EI Full ms[40.00-400.00]



4-CF3-PhCN-1 #1071 RT: 5.14 AV: 1 NL: 1.13E7
T: (0.0) + c EI Full ms[40.00-400.00]

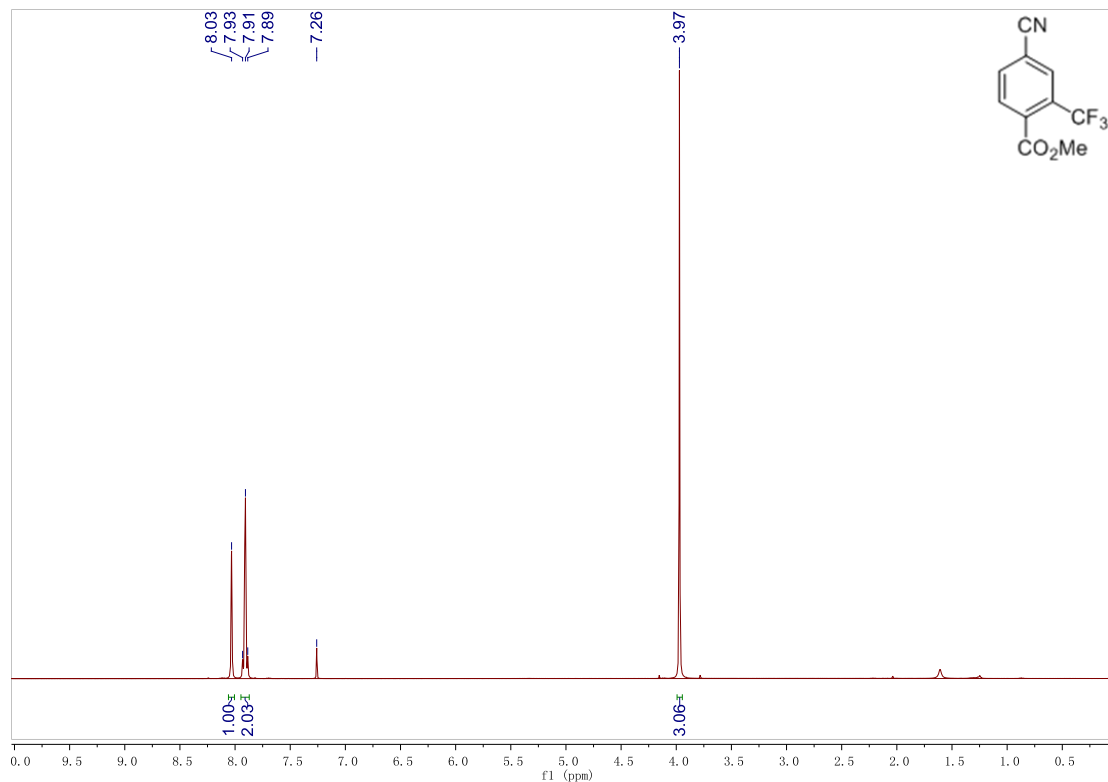


4-CF3-PhCN-1 #1436 RT: 6.38 AV: 1 NL: 1.90E6
T: (0.0) + c EI Full ms[40.00-400.00]



Compound 13o:

¹H NMR



Chemical Structure: COC(=O)c1cc(C#N)c(C(F)(F)F)cc1

¹³C NMR Peaks (ppm):

- 135.25, 134.98, 134.97
- 131.05, 130.55, 130.49, 130.44, 130.39, 130.33, 130.31, 129.93, 129.92, 129.64, 126.23, 123.50, 120.78, 120.05, 118.05, 116.55, 115.48
- 77.32, 77.00, 76.68 (CDCl₃ solvent triplet)
- 53.37 (methoxy group)

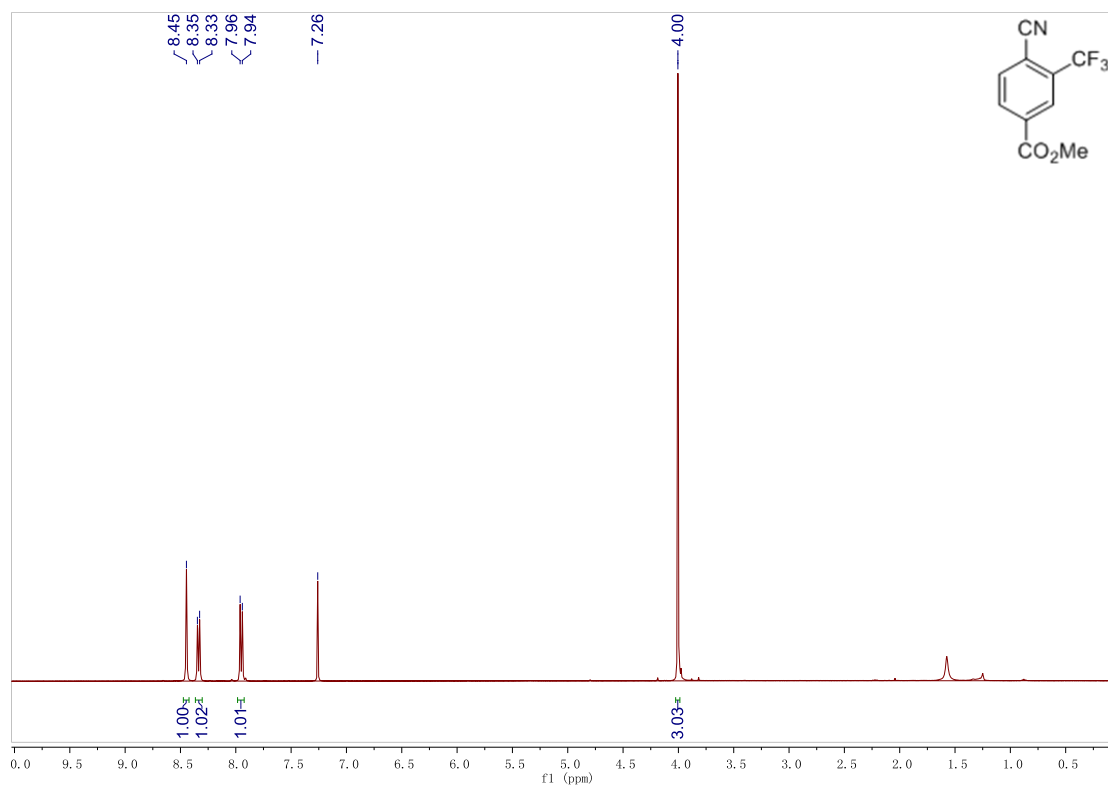
Chemical structure: COC(=O)c1cc(C#N)c(C(F)(F)F)cc1

¹³C NMR spectrum (ppm):

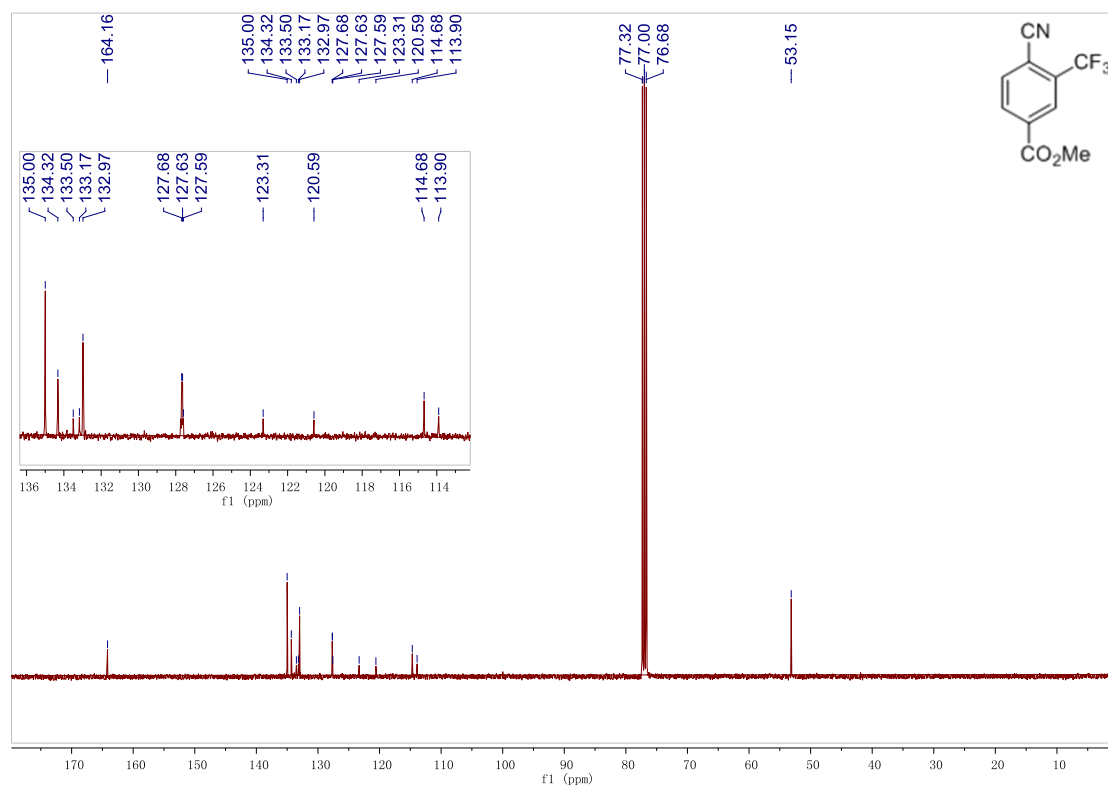
- 60.65
- 77.56

Compound 13m:

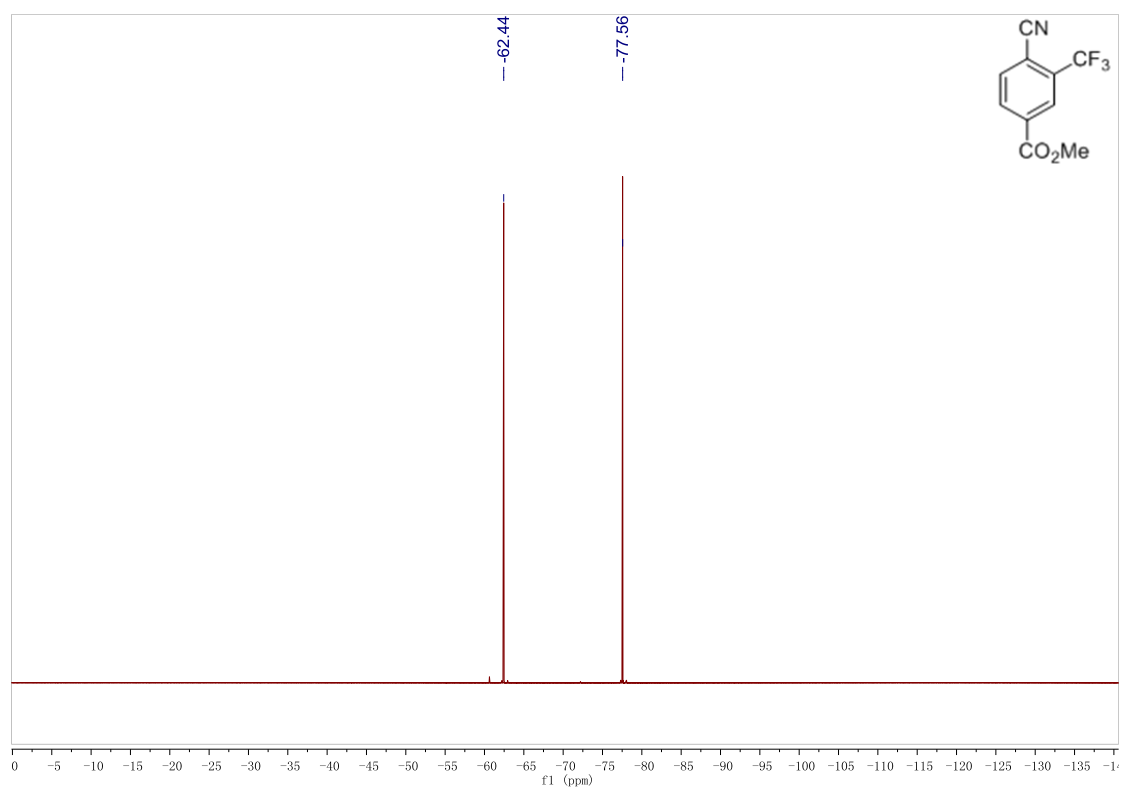
^1H NMR



^{13}C NMR

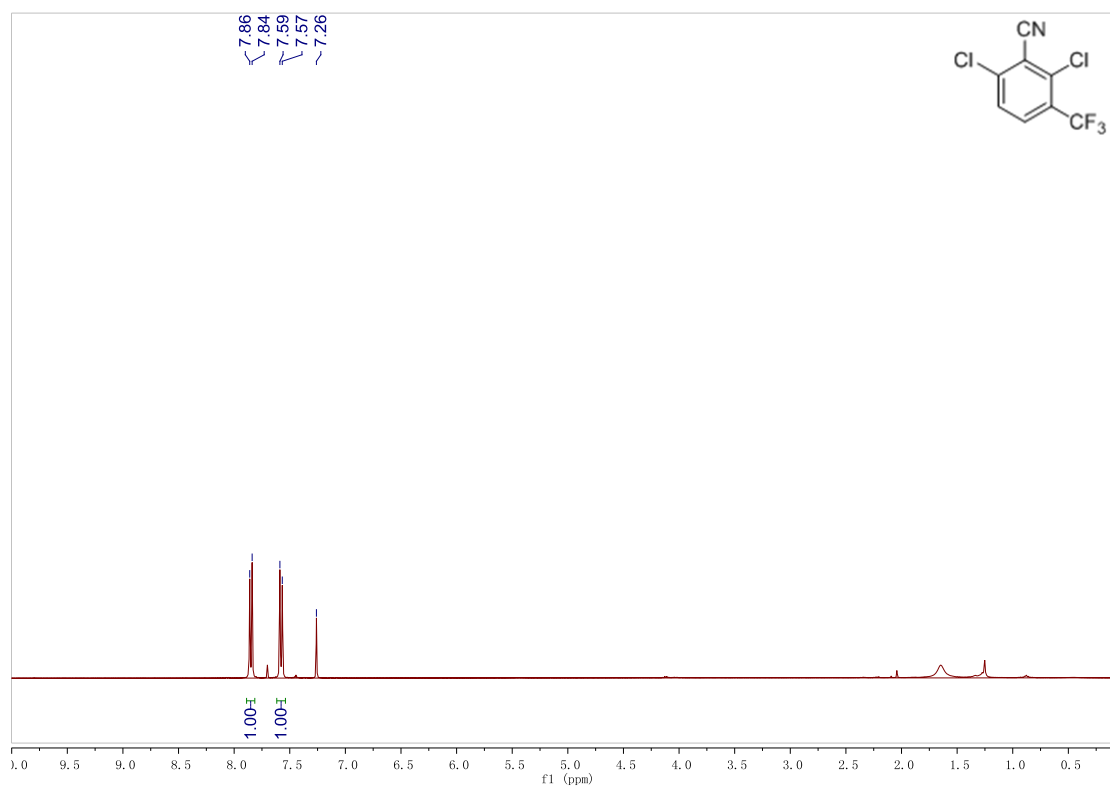


¹⁹F NMR

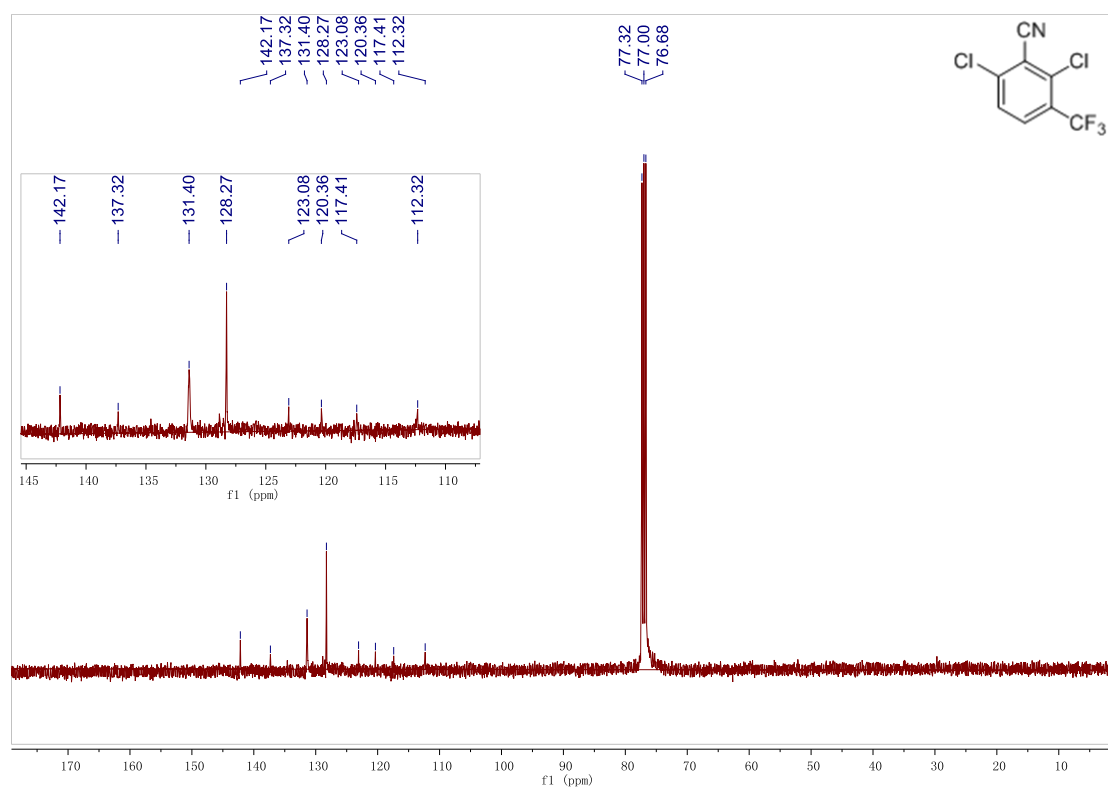


Compound 14m:

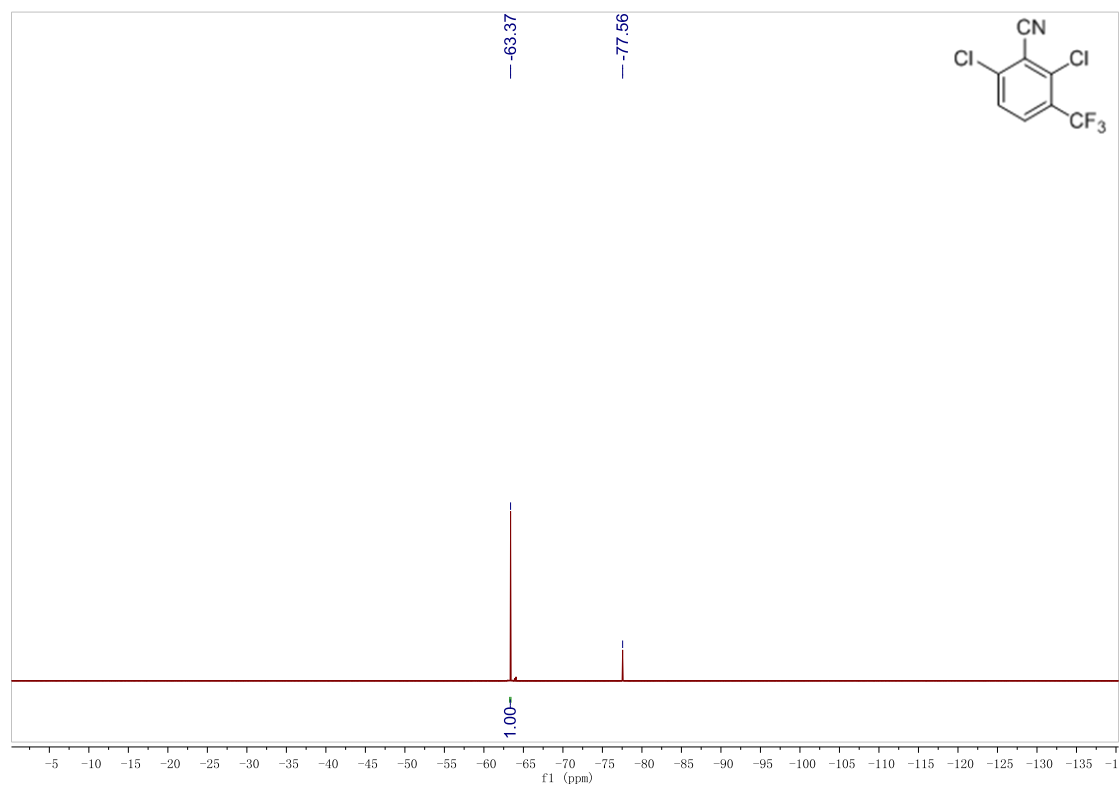
¹H NMR



¹³C NMR

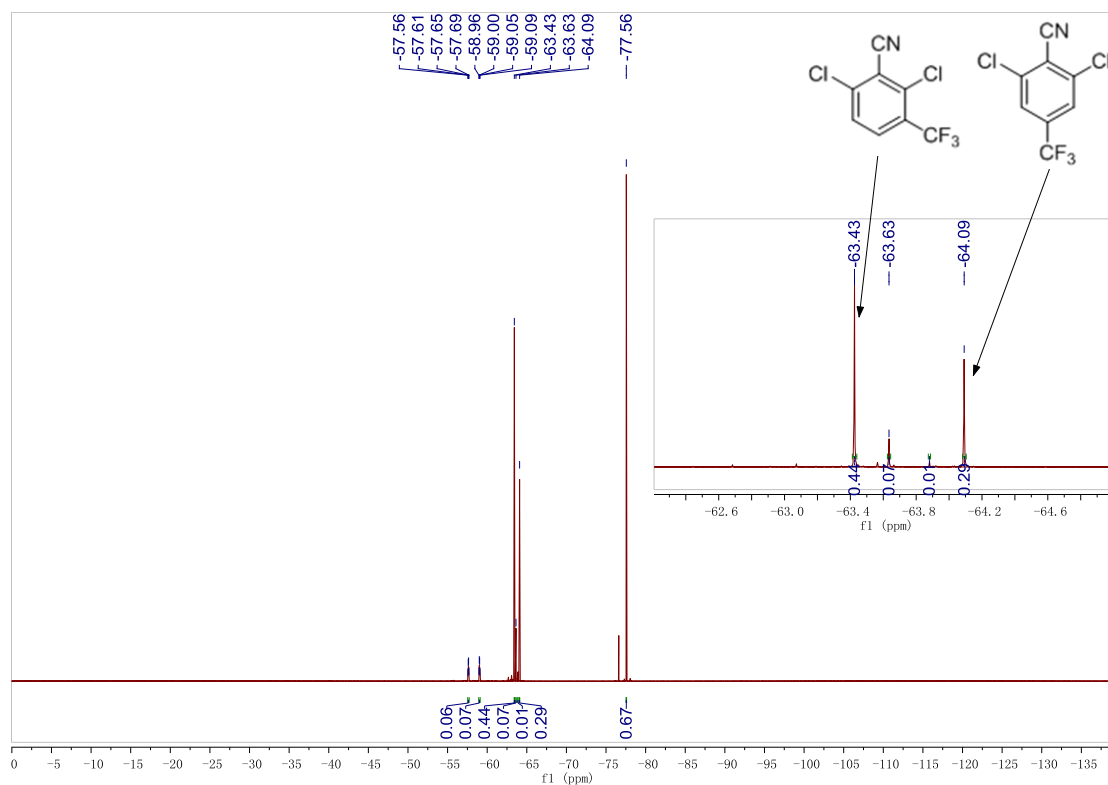


¹⁹F NMR



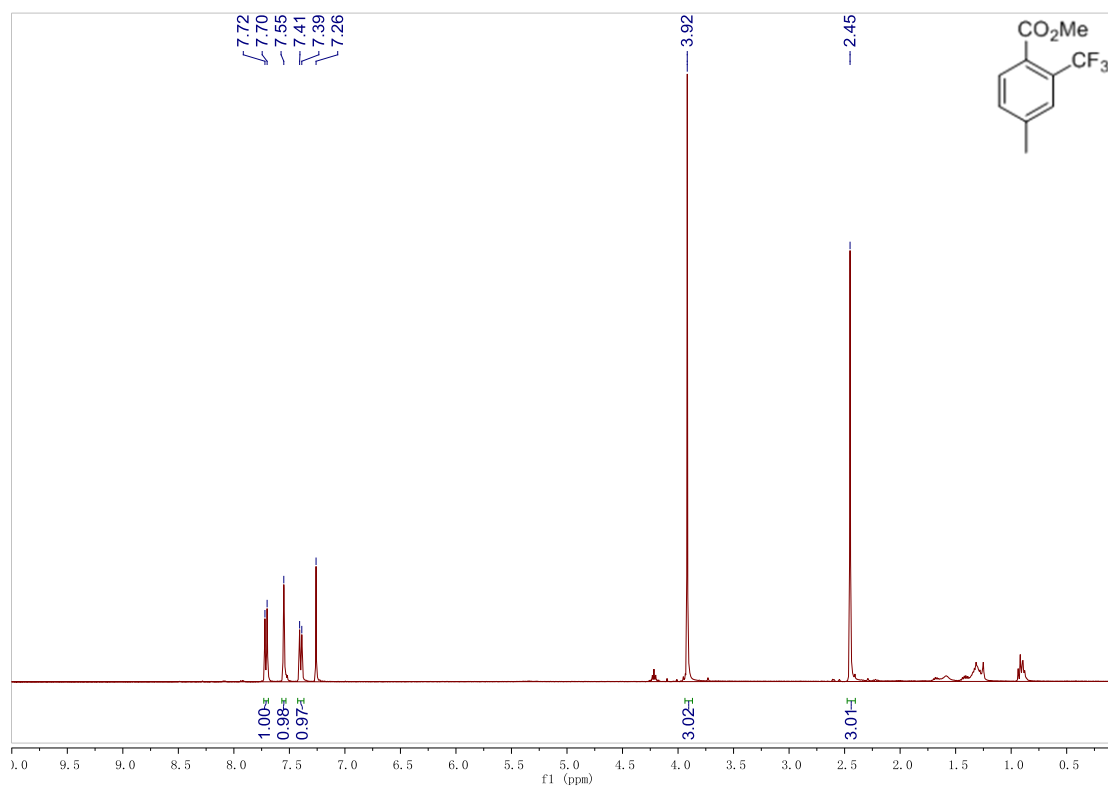
Compound 14m-p:

¹⁹F NMR

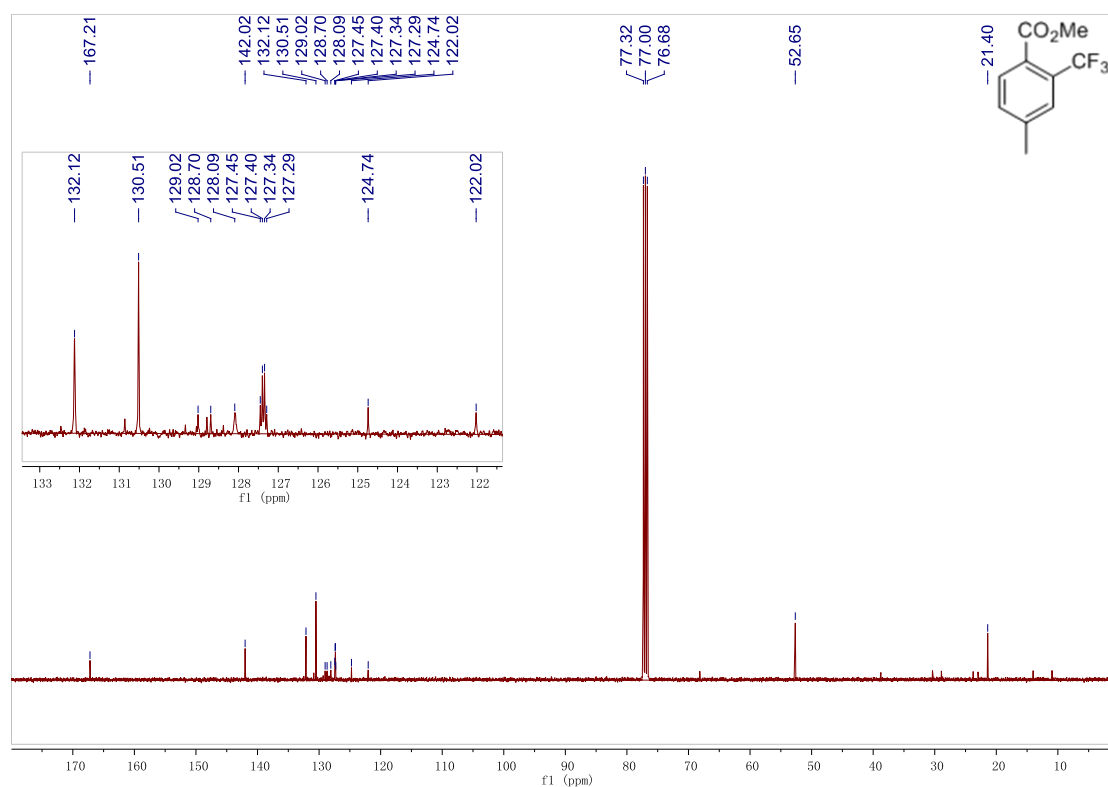


Compound 15o:

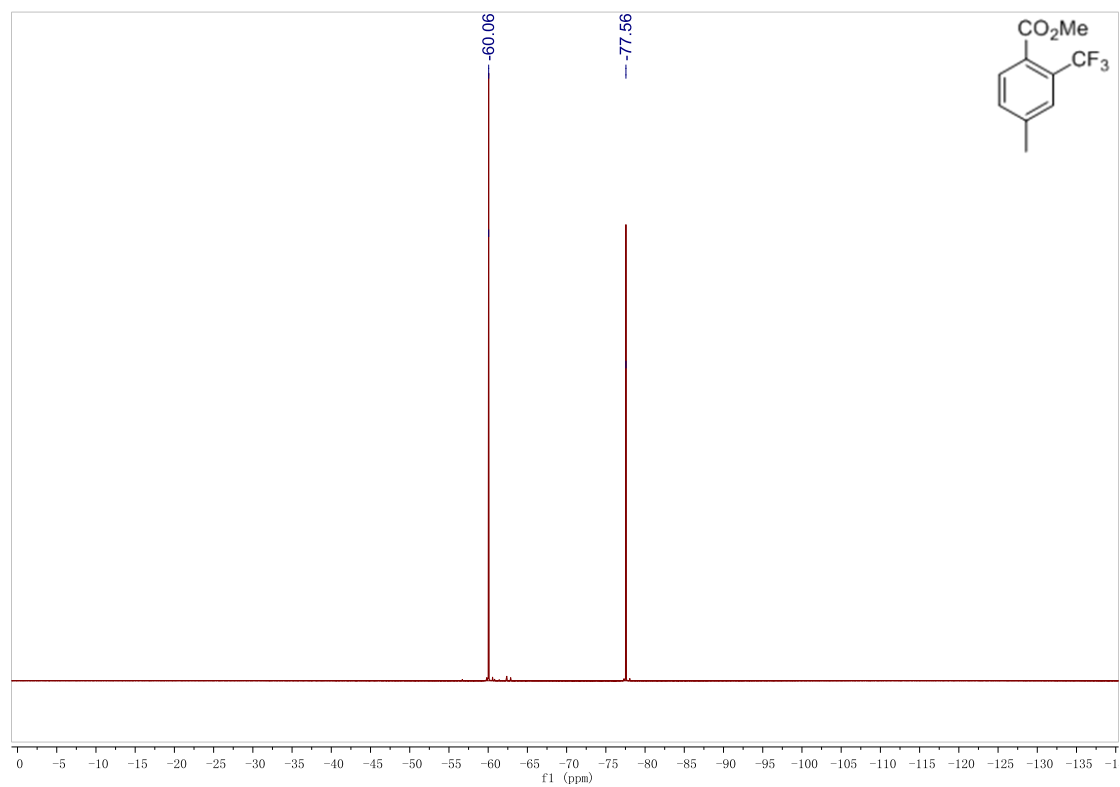
¹H NMR



¹³C NMR

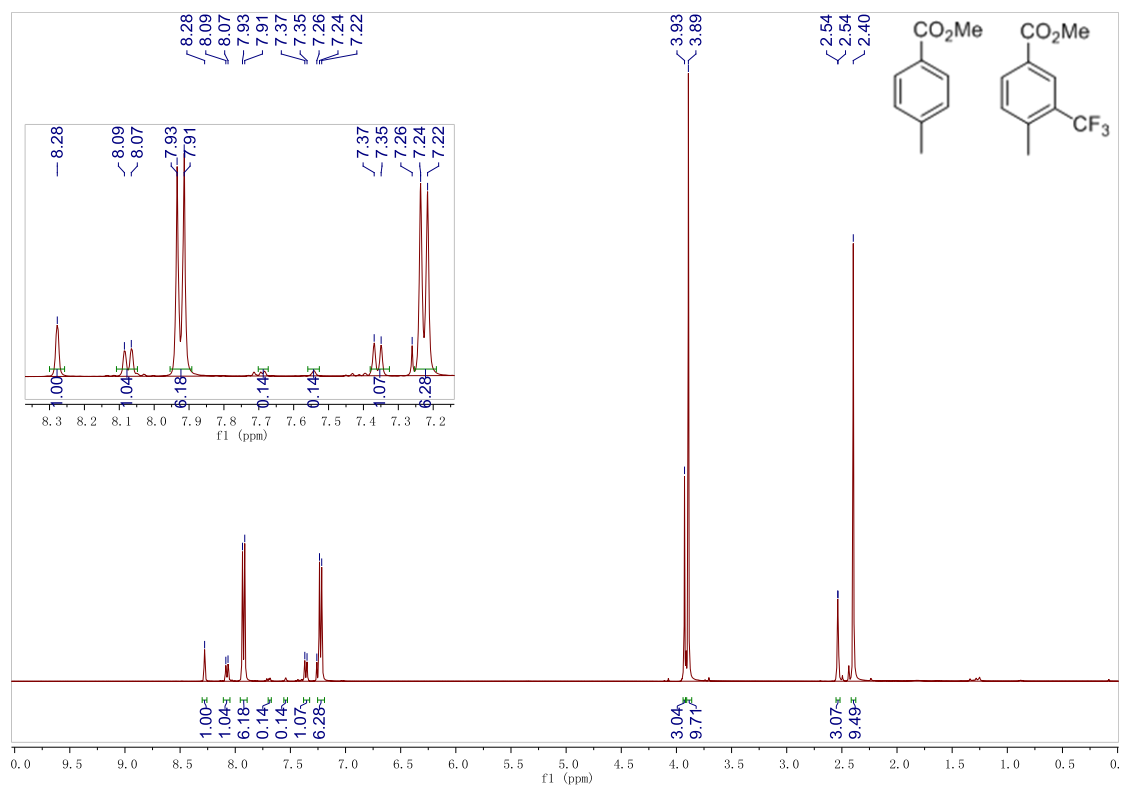


¹⁹F NMR

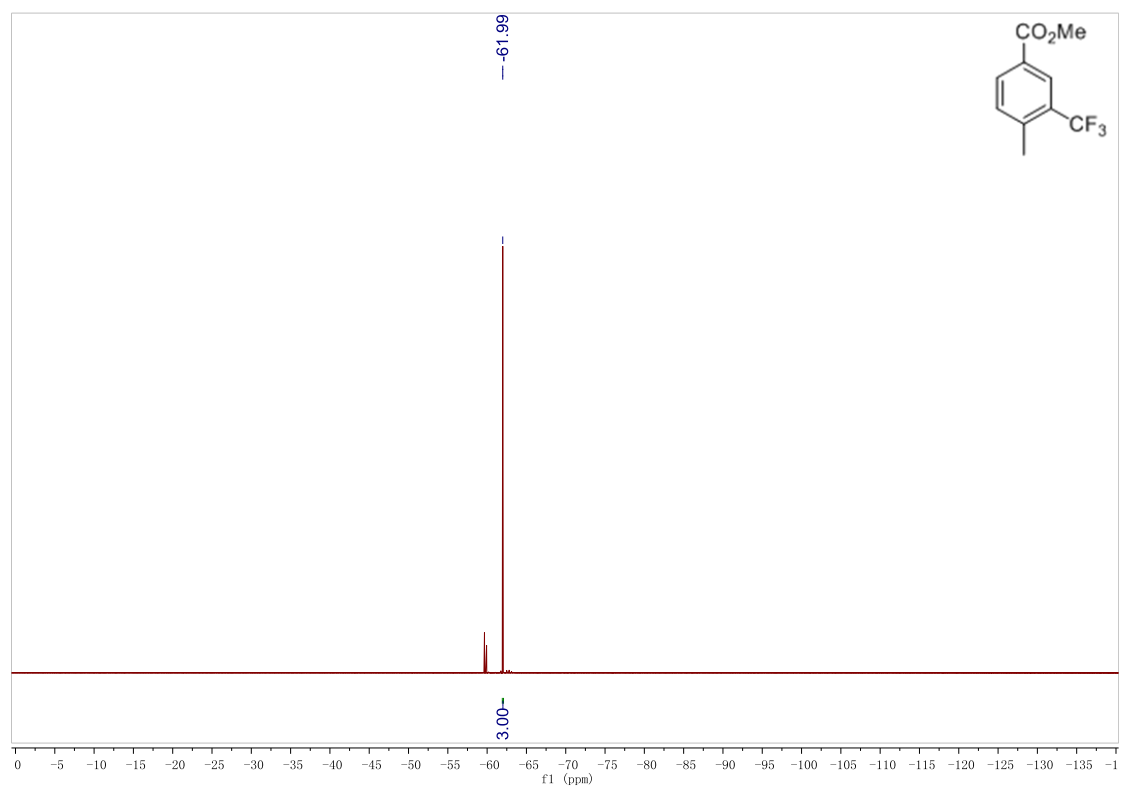


Compound 15m:

¹H NMR



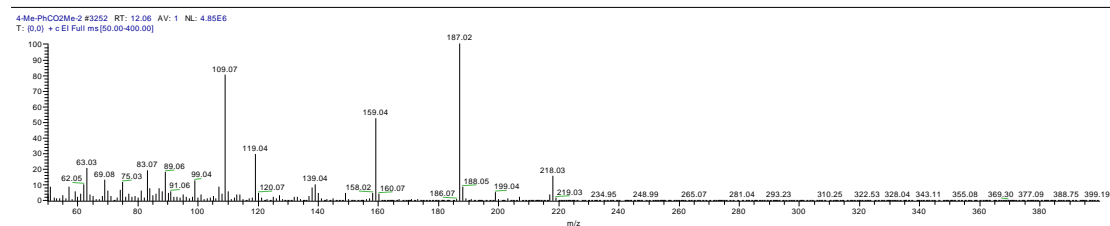
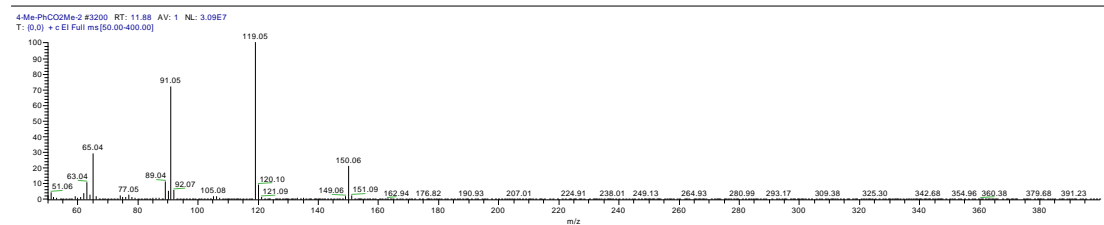
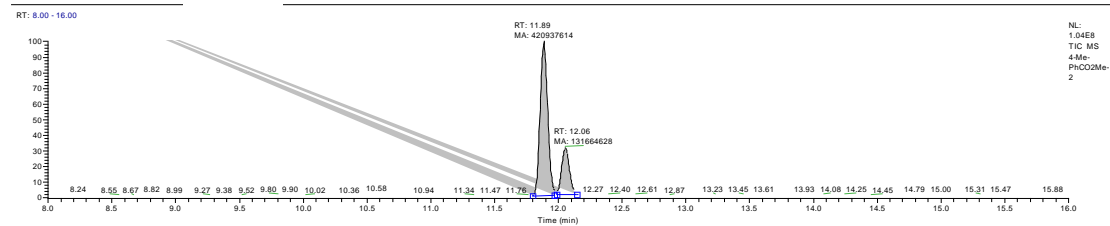
¹⁹F NMR



GC-MS

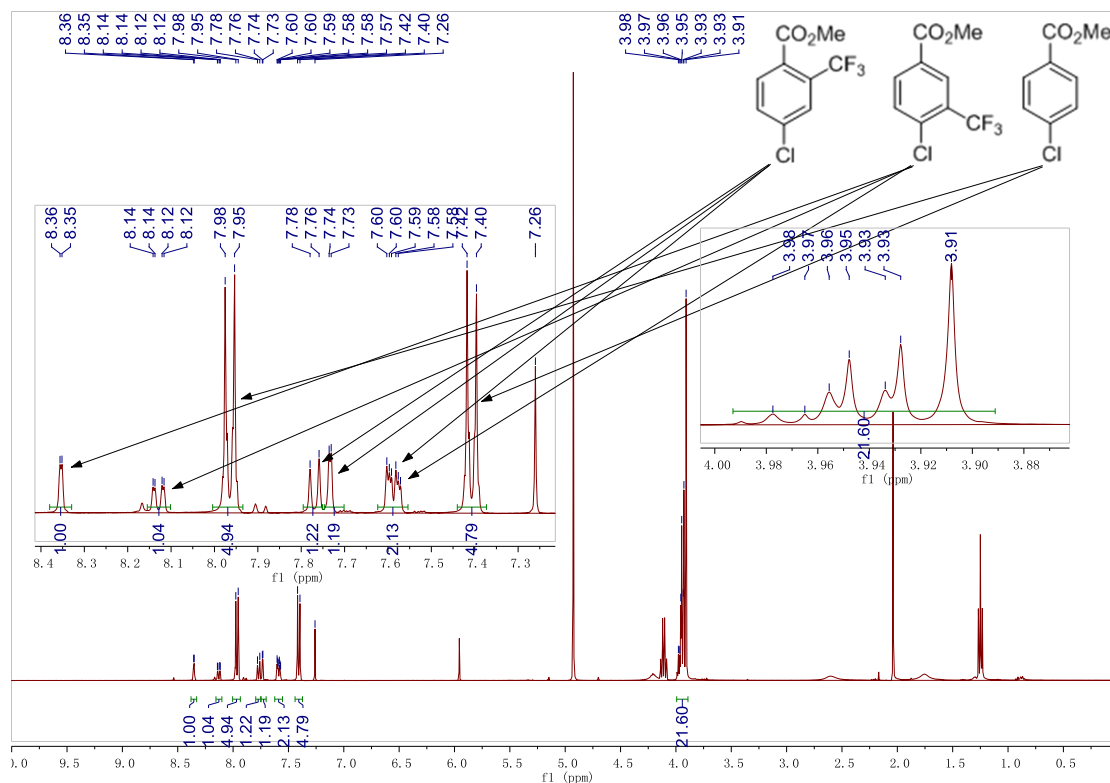
F:\DATA\...4-Me-PhCO2Me-2

3/20/2014 4:45:57 PM

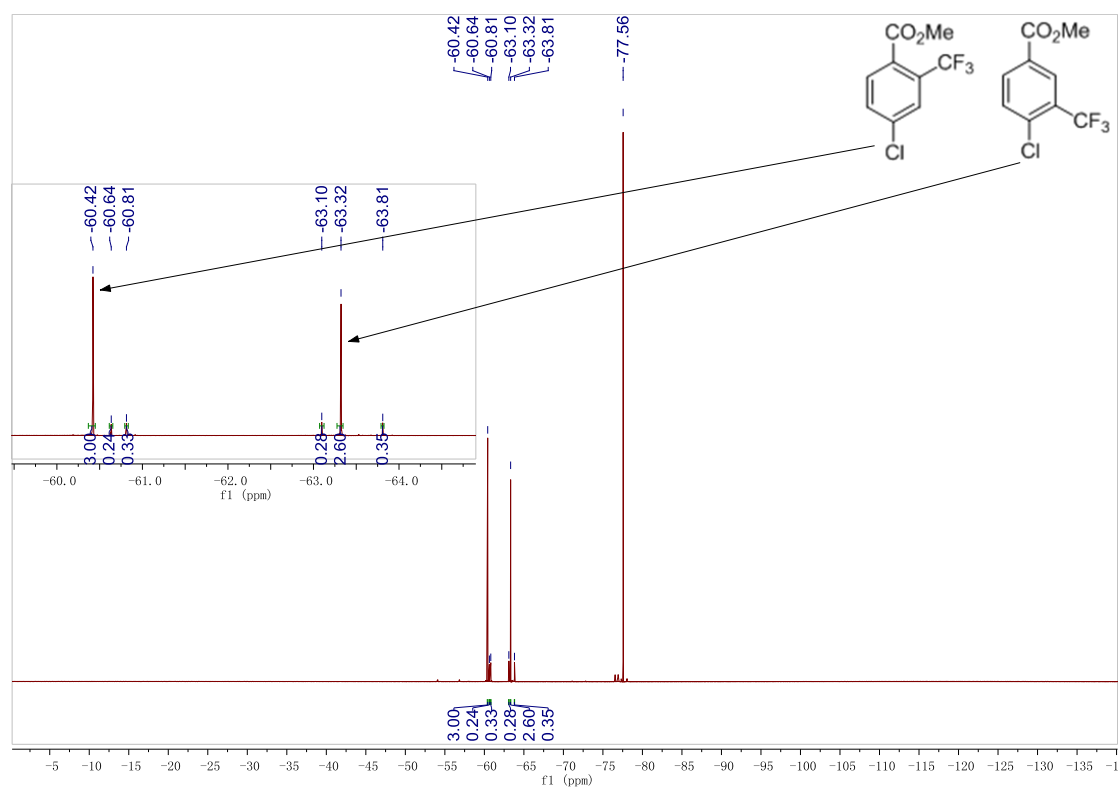


Compound 160-m:

¹H NMR



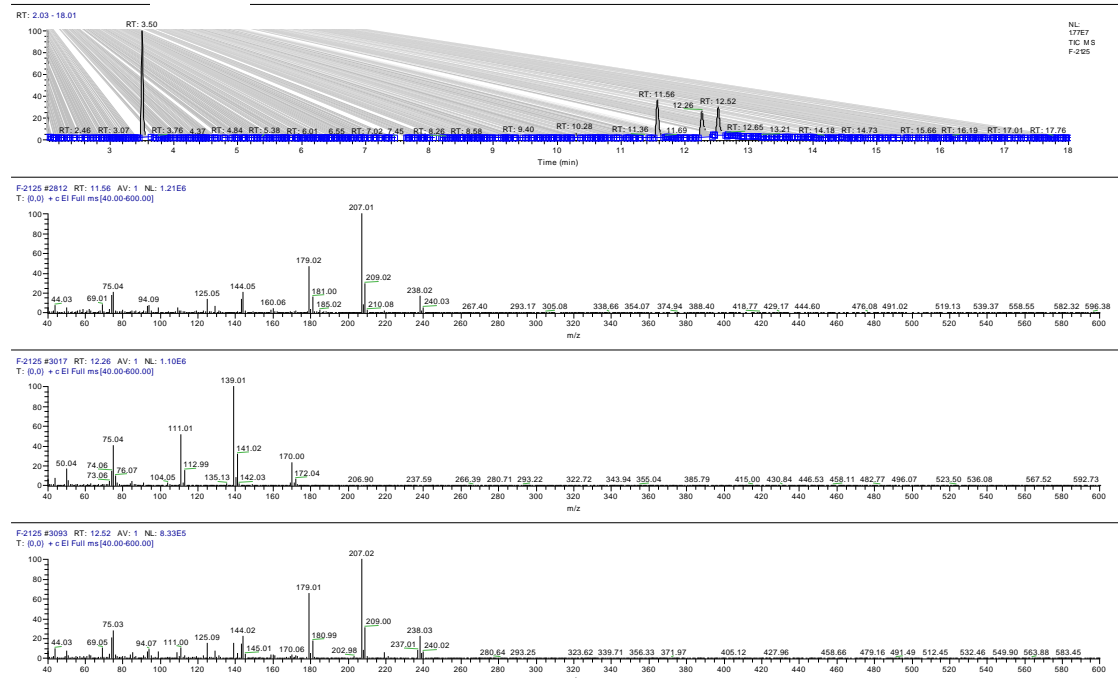
¹⁹F NMR



GC-MS

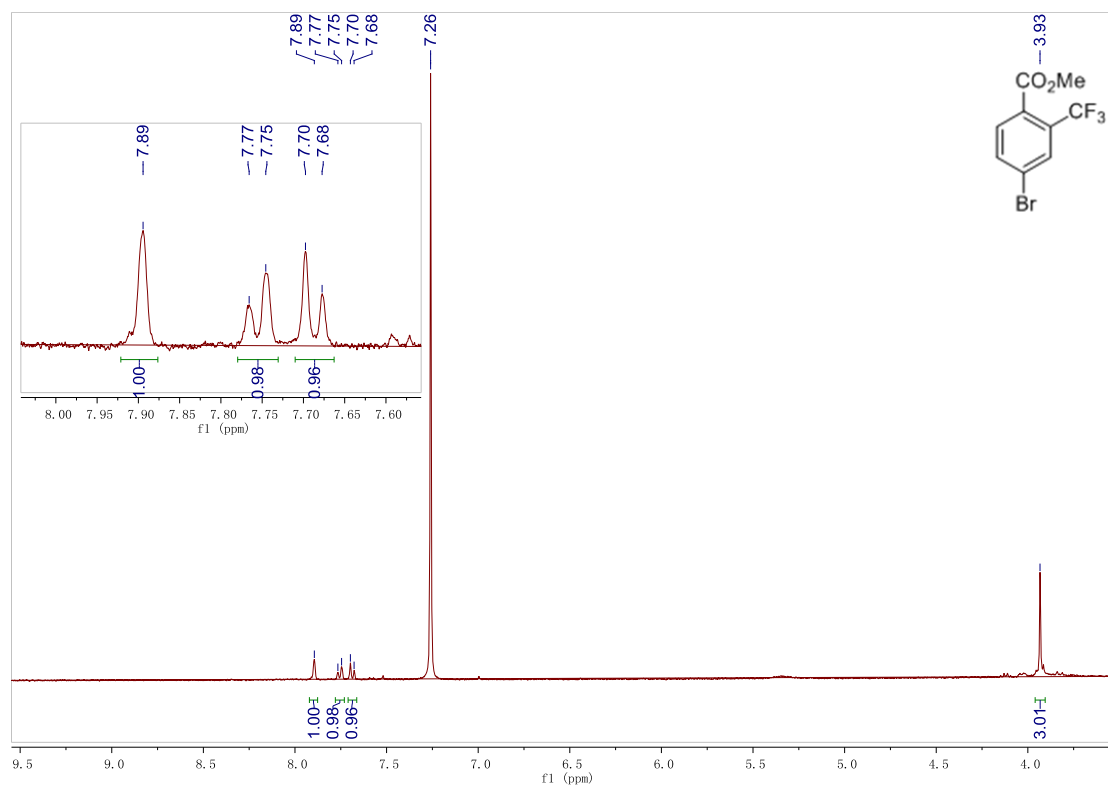
F:\DATA\...CF3 of p-nitro

7/4/2014 10:46:10 PM

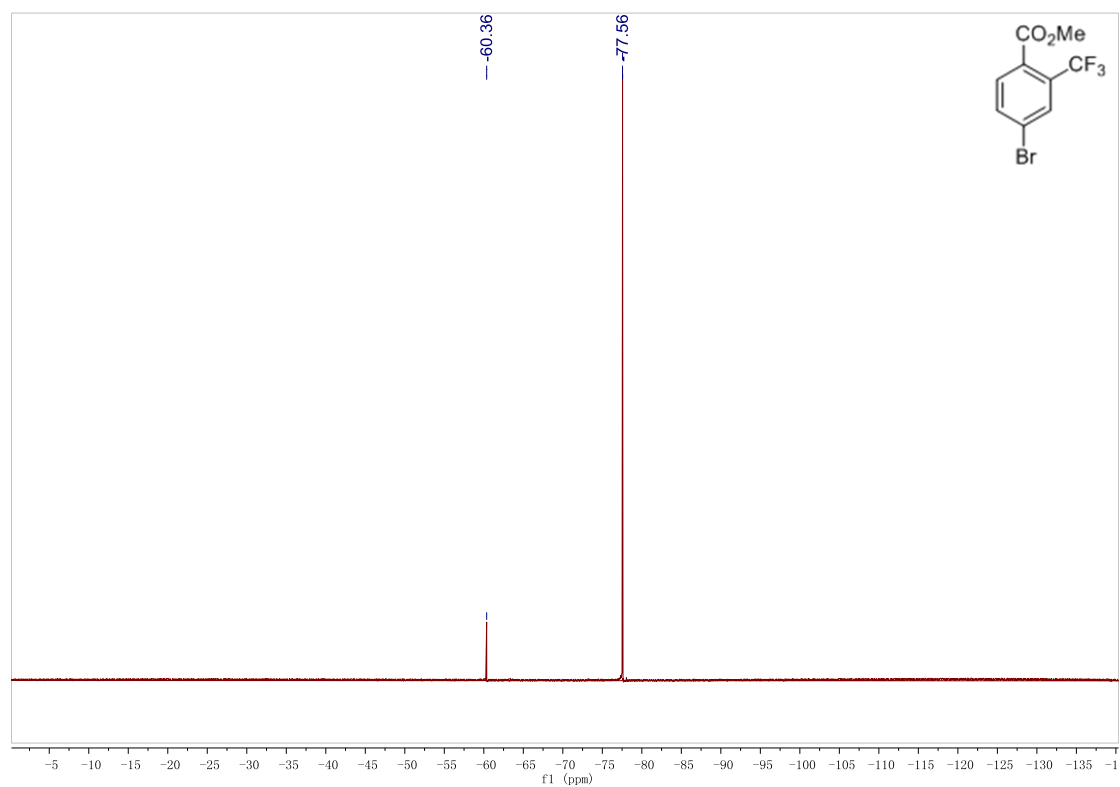


Compound 17o:

^1H NMR

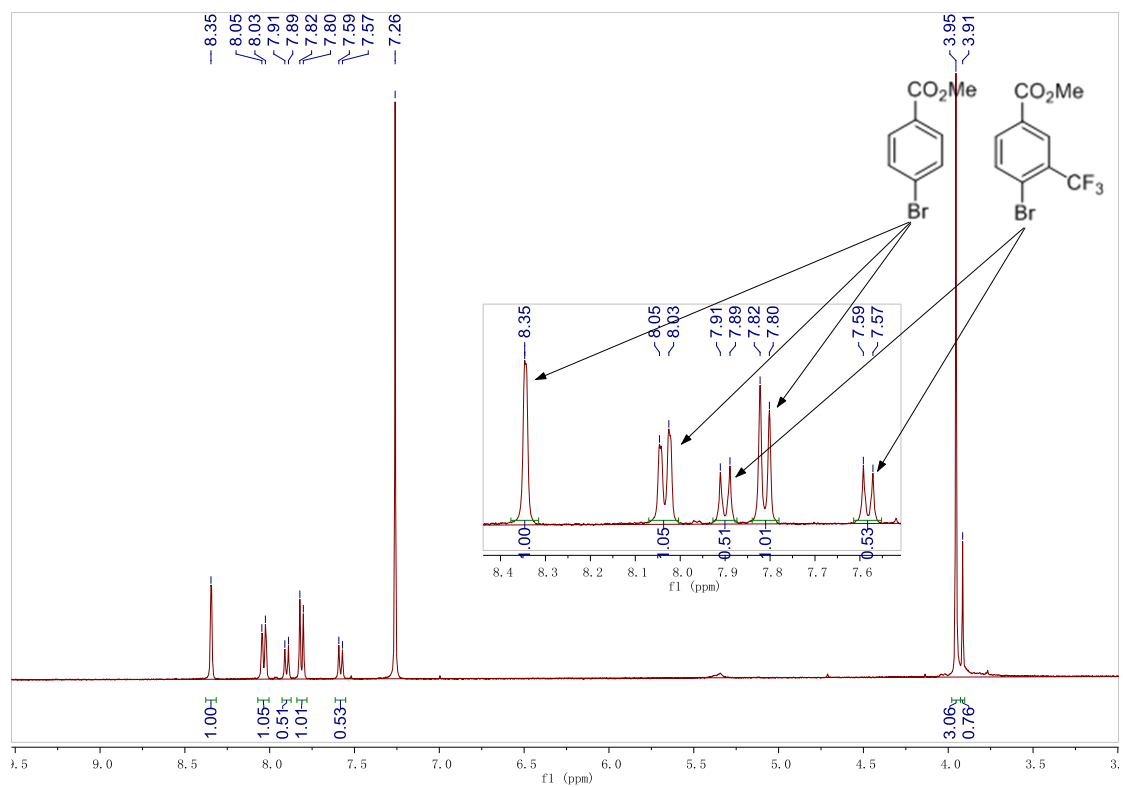


^{19}F NMR

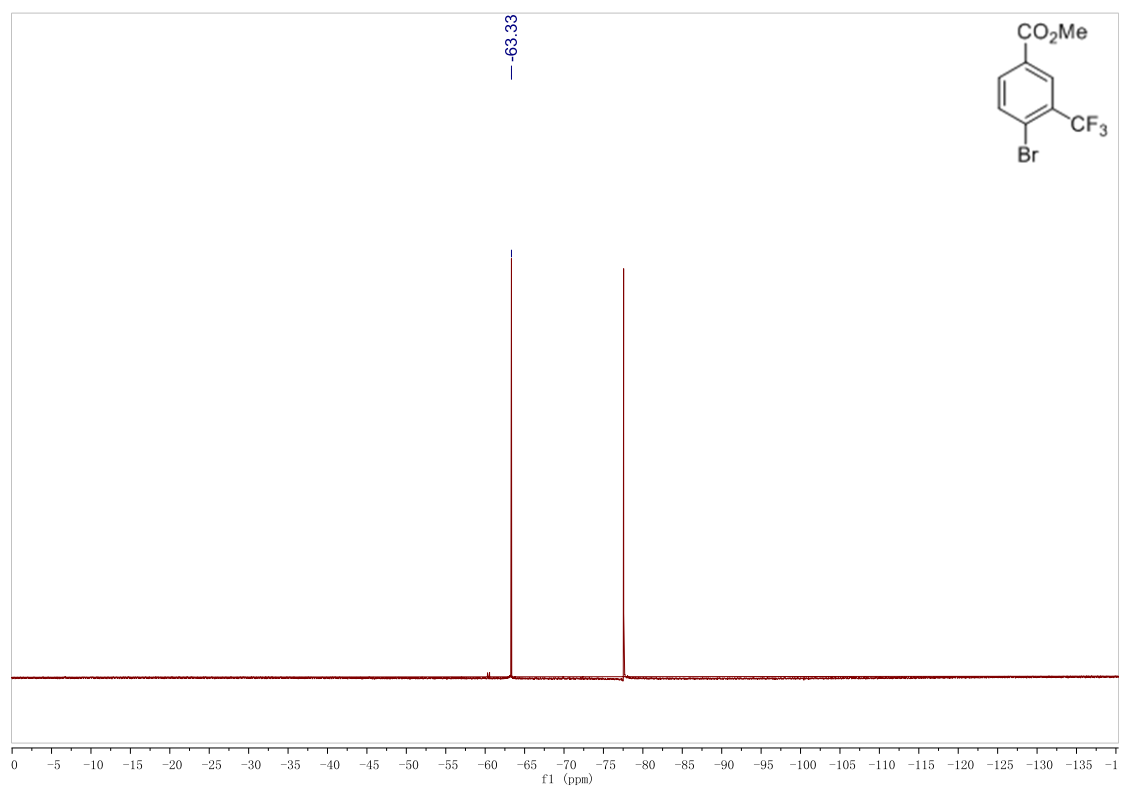


Compound 17m:

^1H NMR

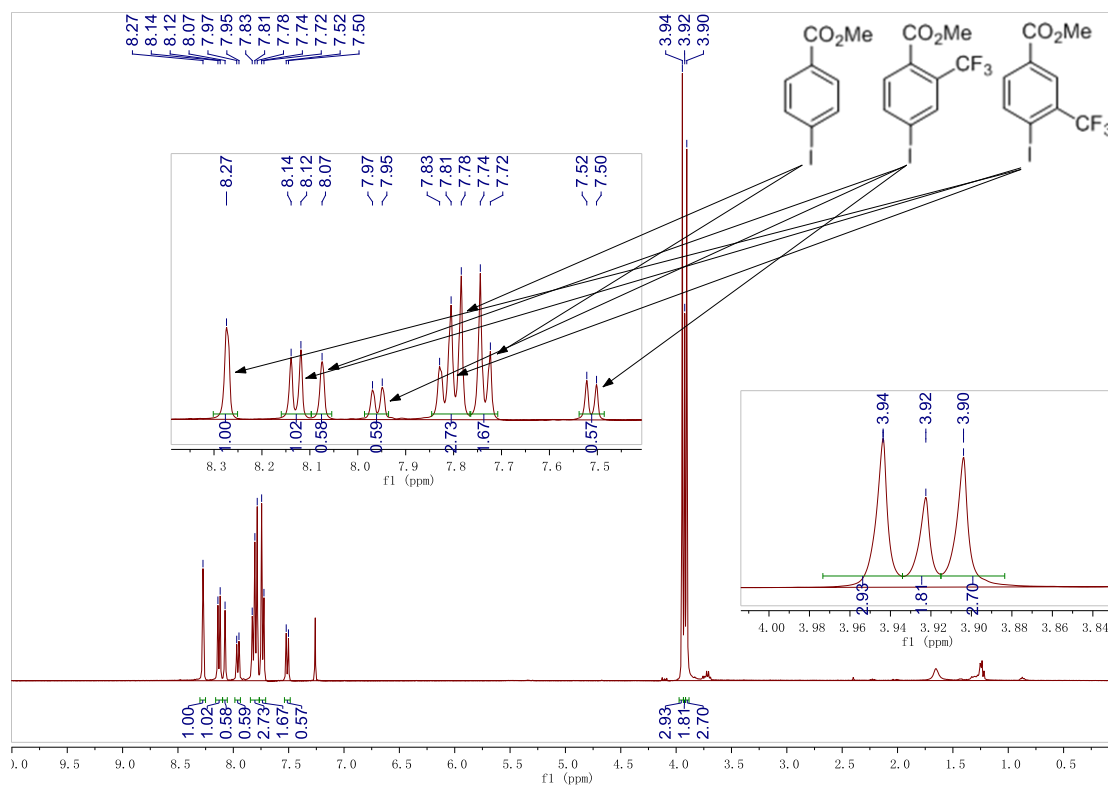


^{19}F NMR

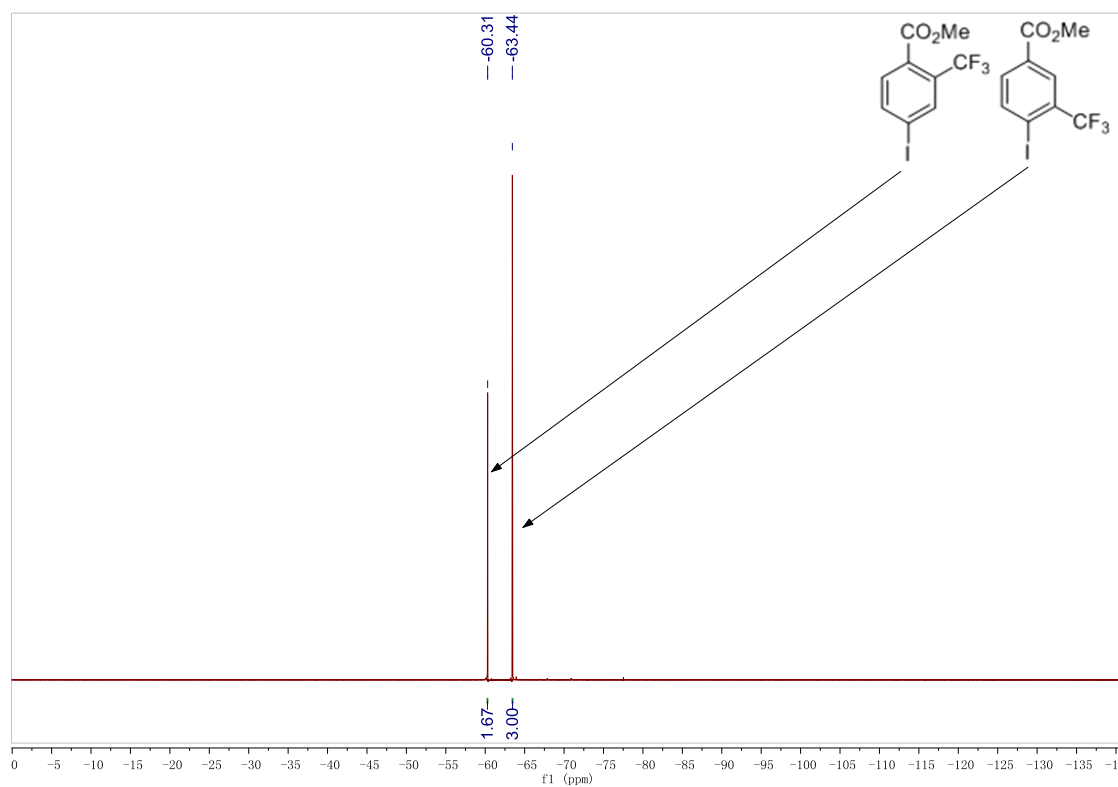


Compound 18o-m:

¹H NMR



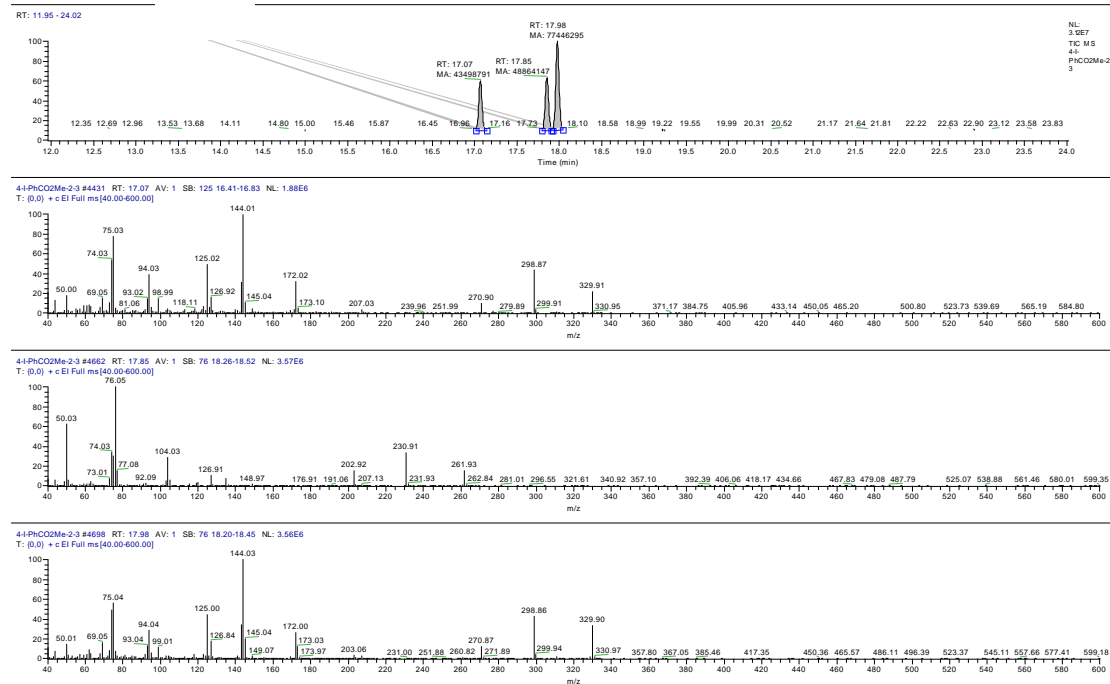
¹⁹F NMR



GC-MS

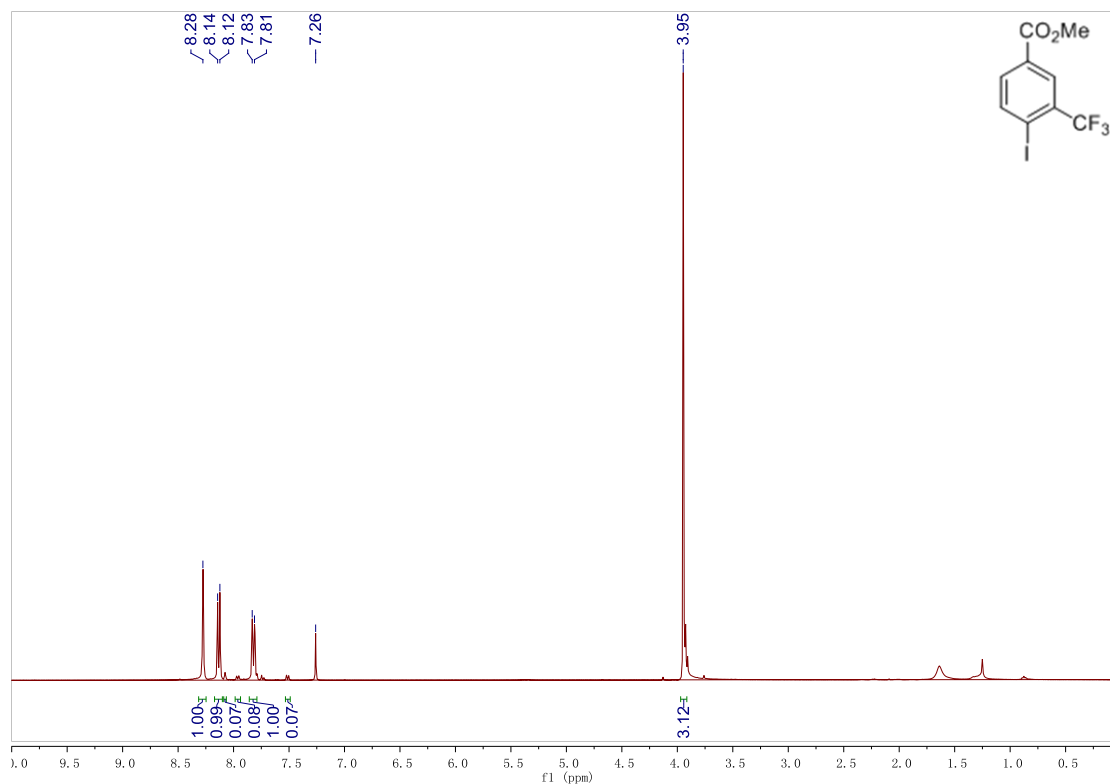
F:\DATA\L\4-IPhCO2Me-

3/23/2014 4:41:08 PM

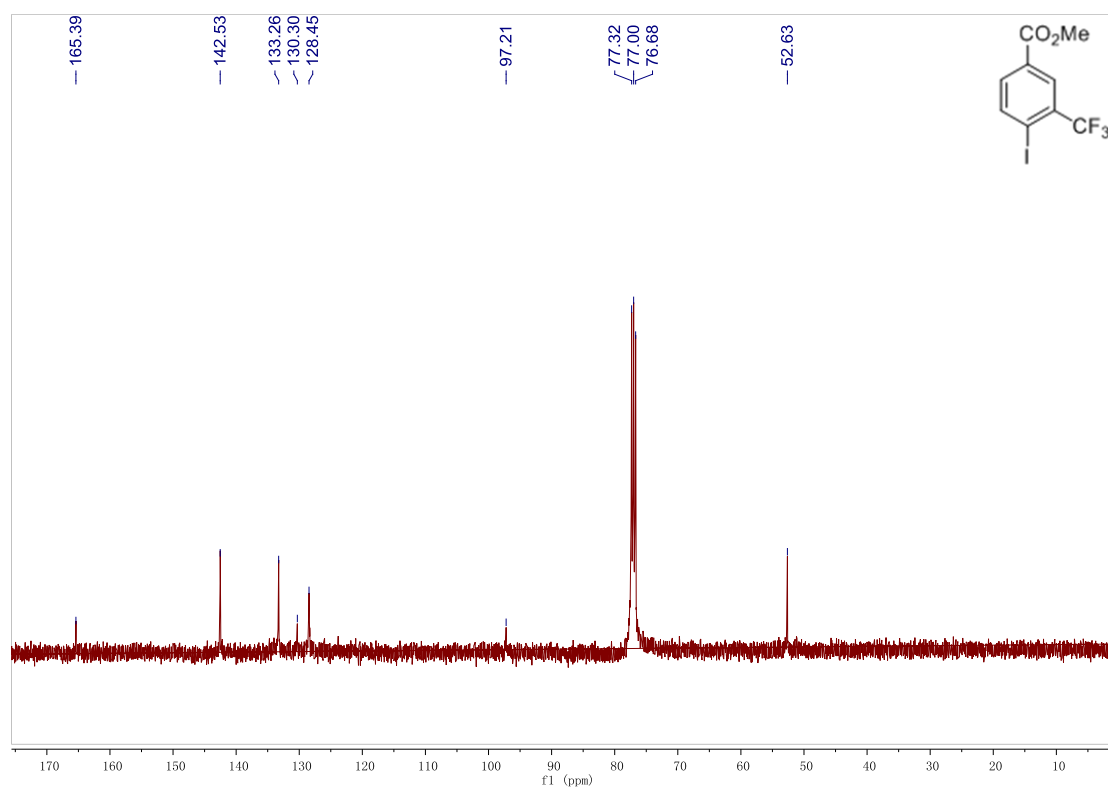


Compound 18m:

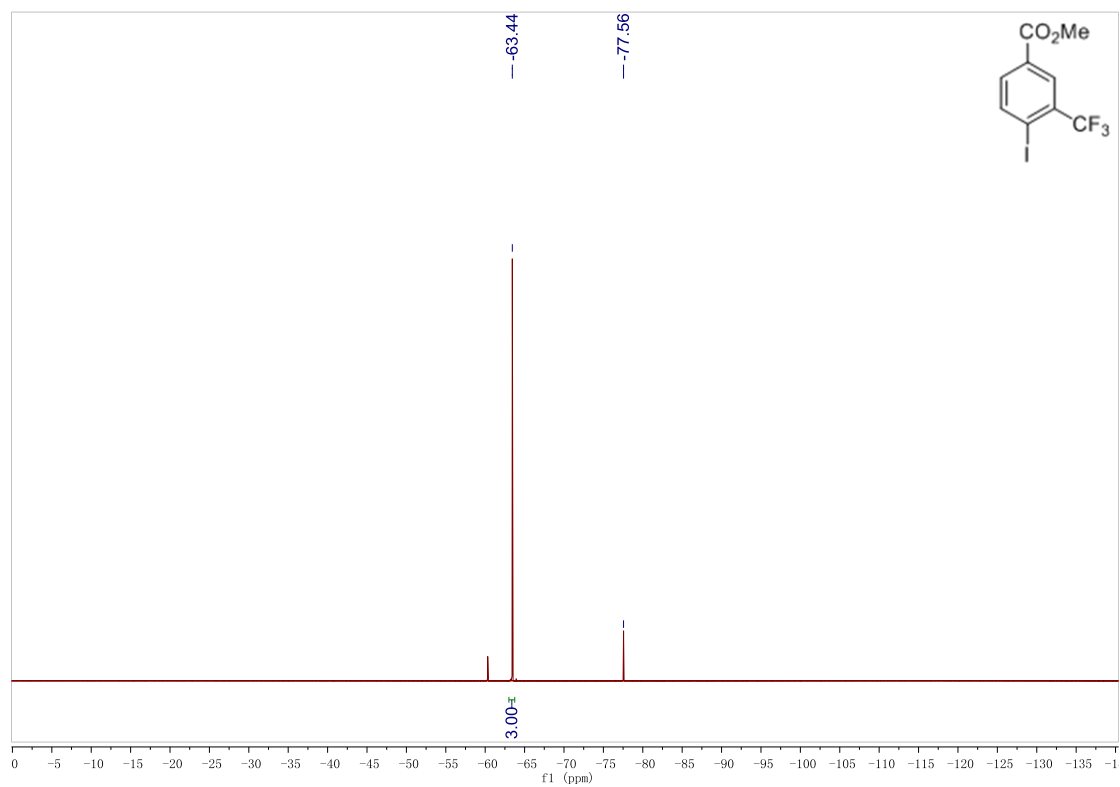
¹H NMR



¹³C NMR

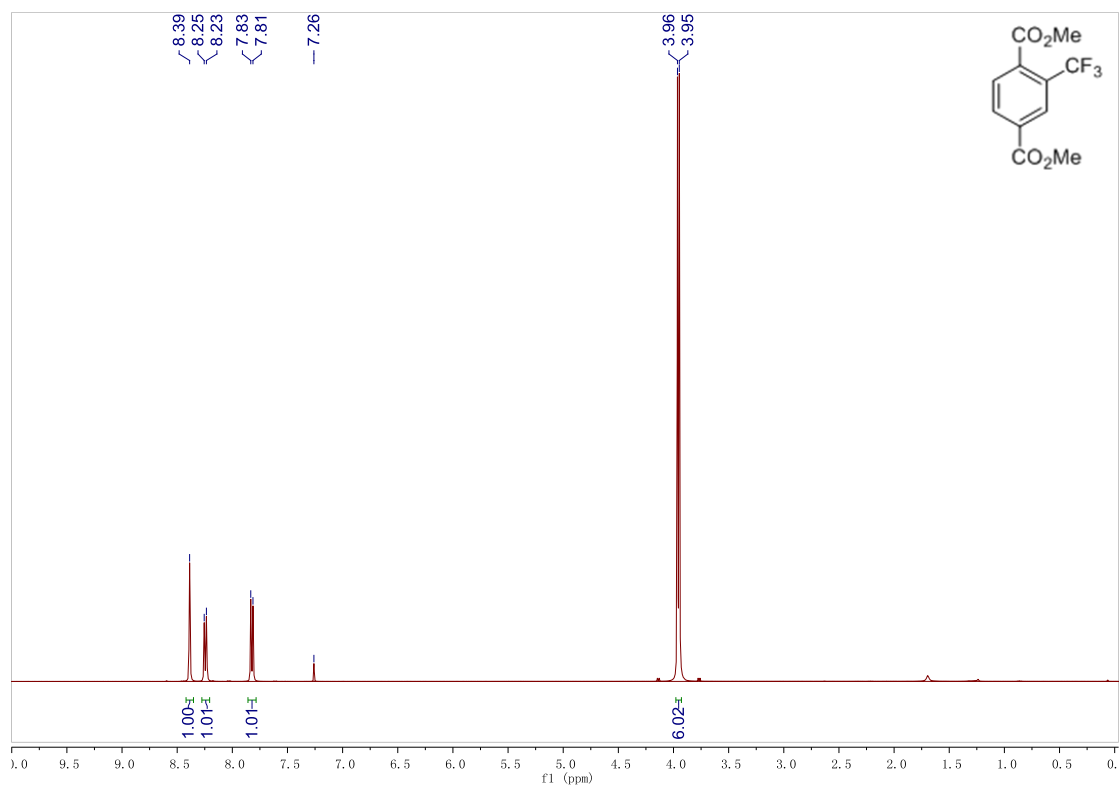


¹⁹F NMR

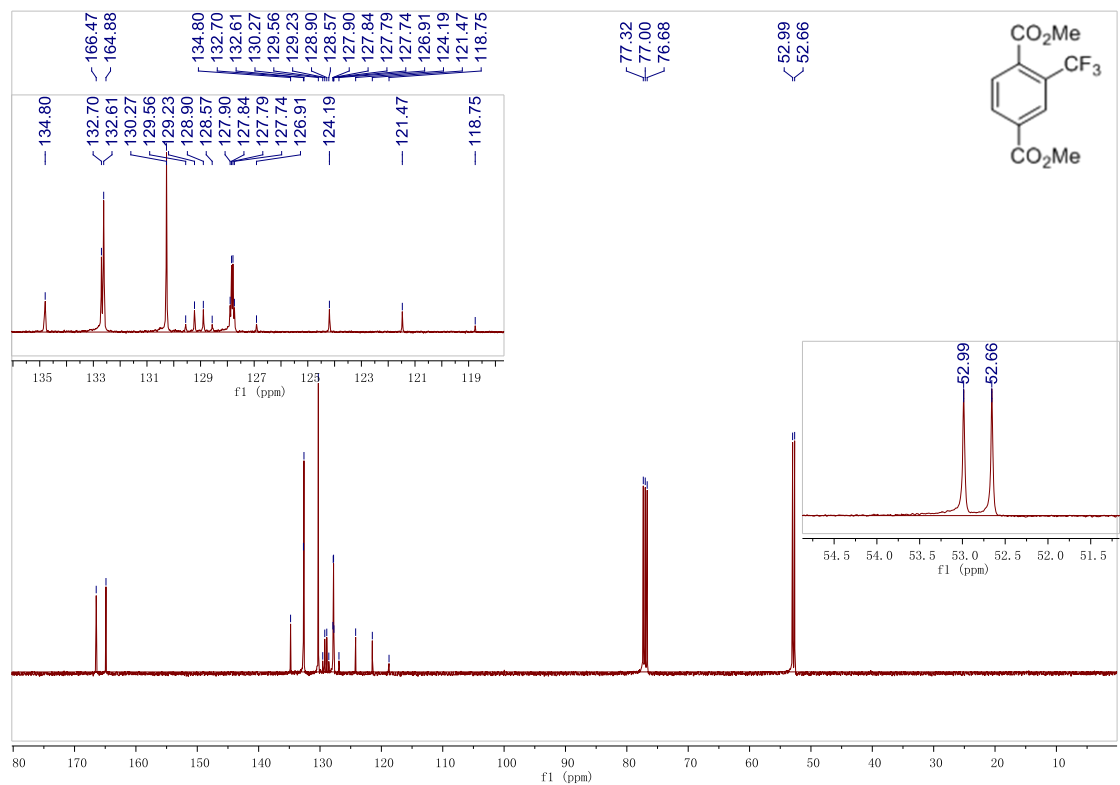


Compound 19o:

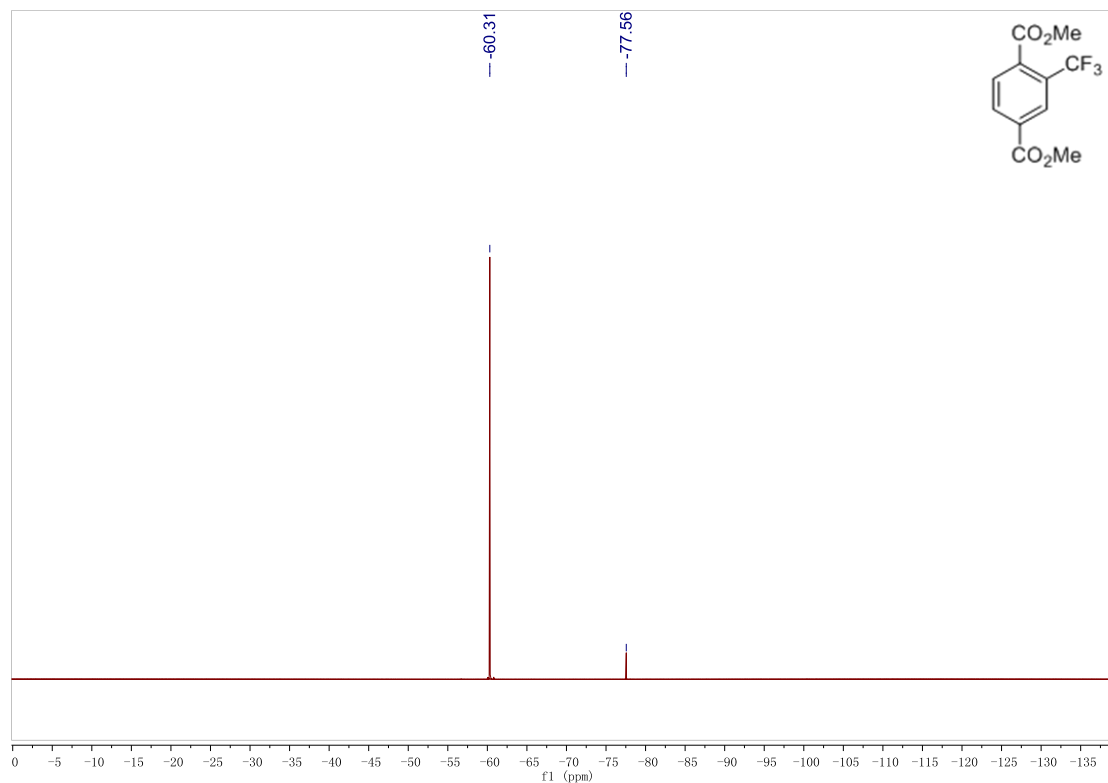
¹H NMR



¹³C NMR

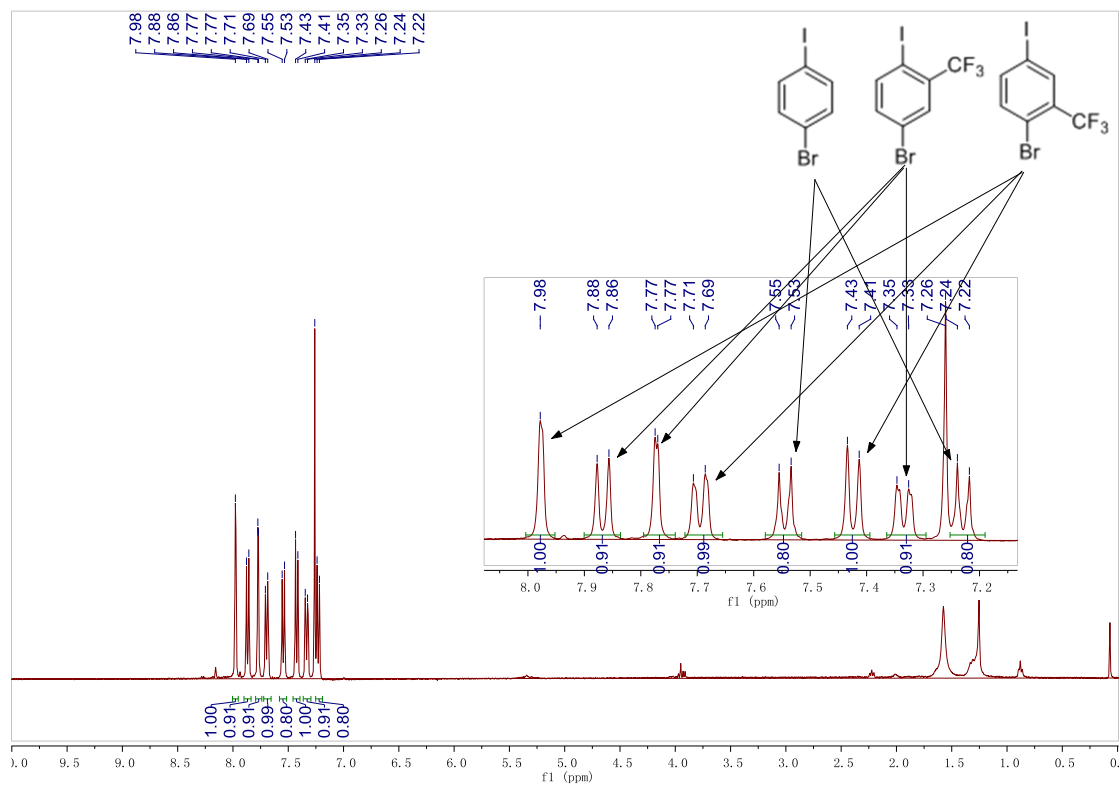


^{19}F NMR

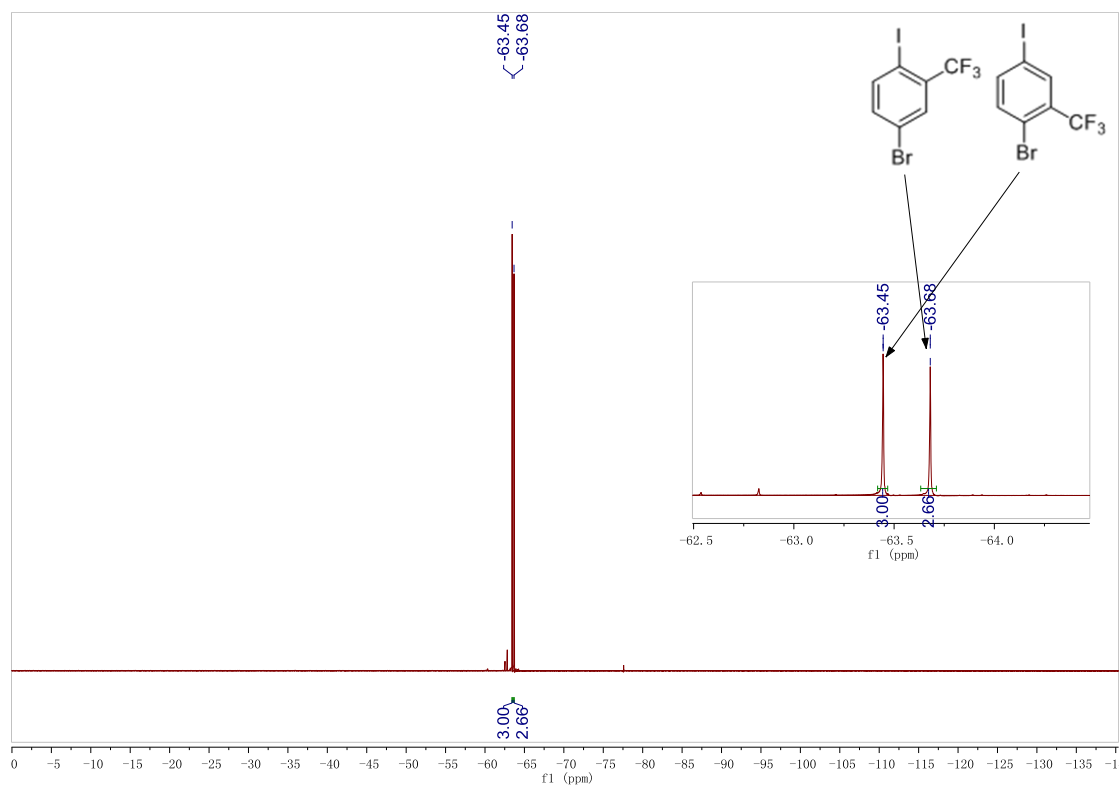


Compound 20o-m:

^1H NMR



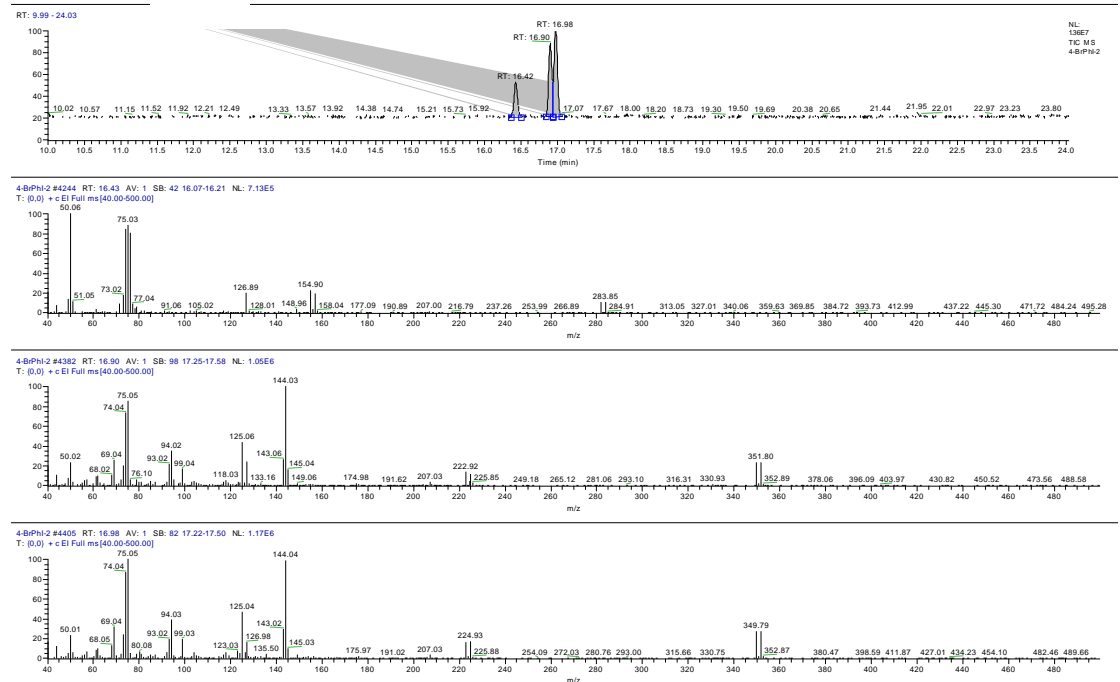
¹⁹F NMR



GC-MS

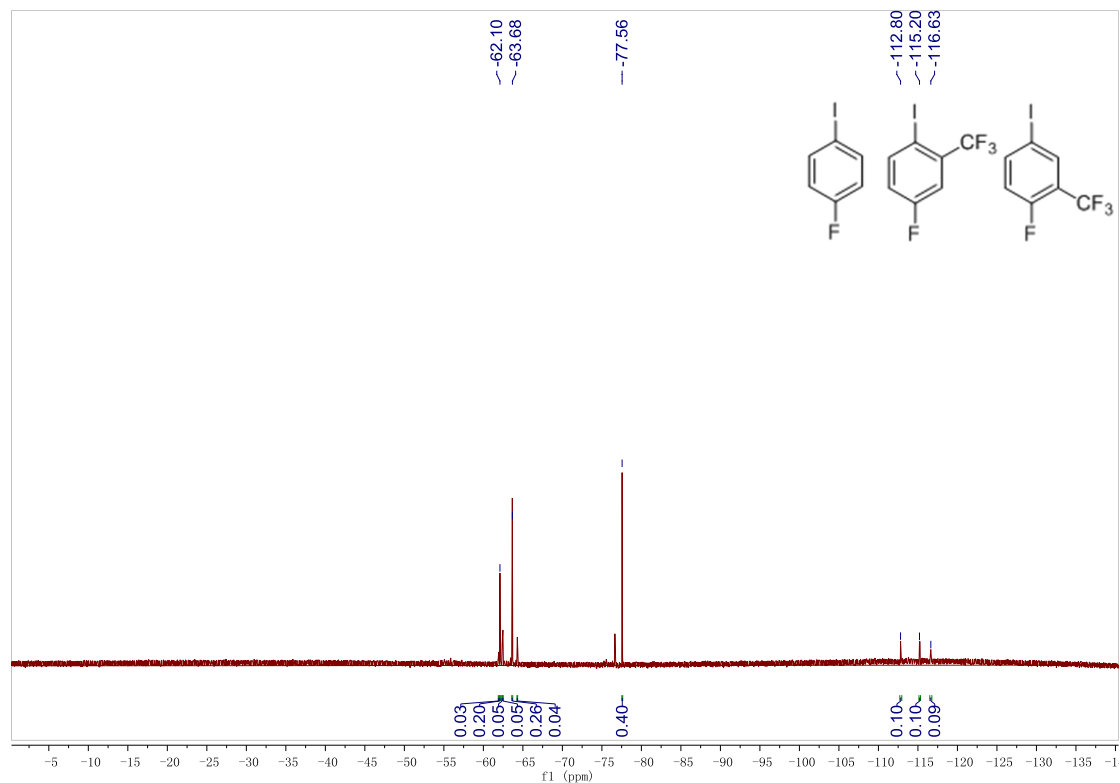
F:\DATA\14-BrPhI-2

3/23/2014 5:48:45 PM



Compound 21o-m:

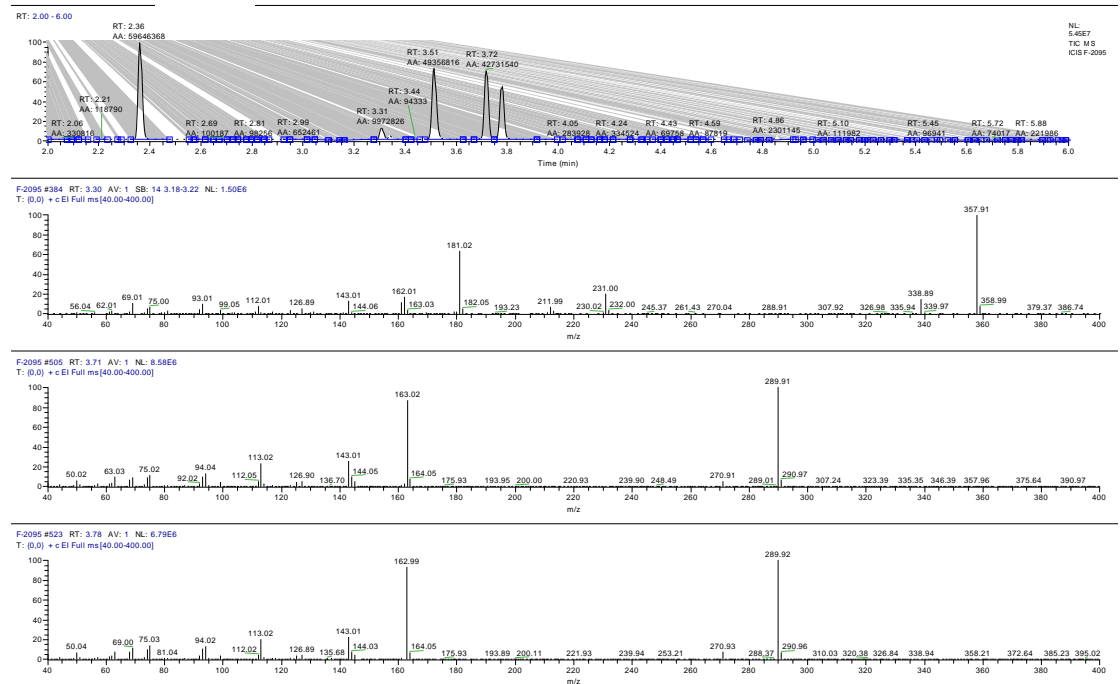
¹⁹F NMR



GC-MS

F:\DATA\...CF3 of p-nitro

6/23/2014 4:43:46 PM

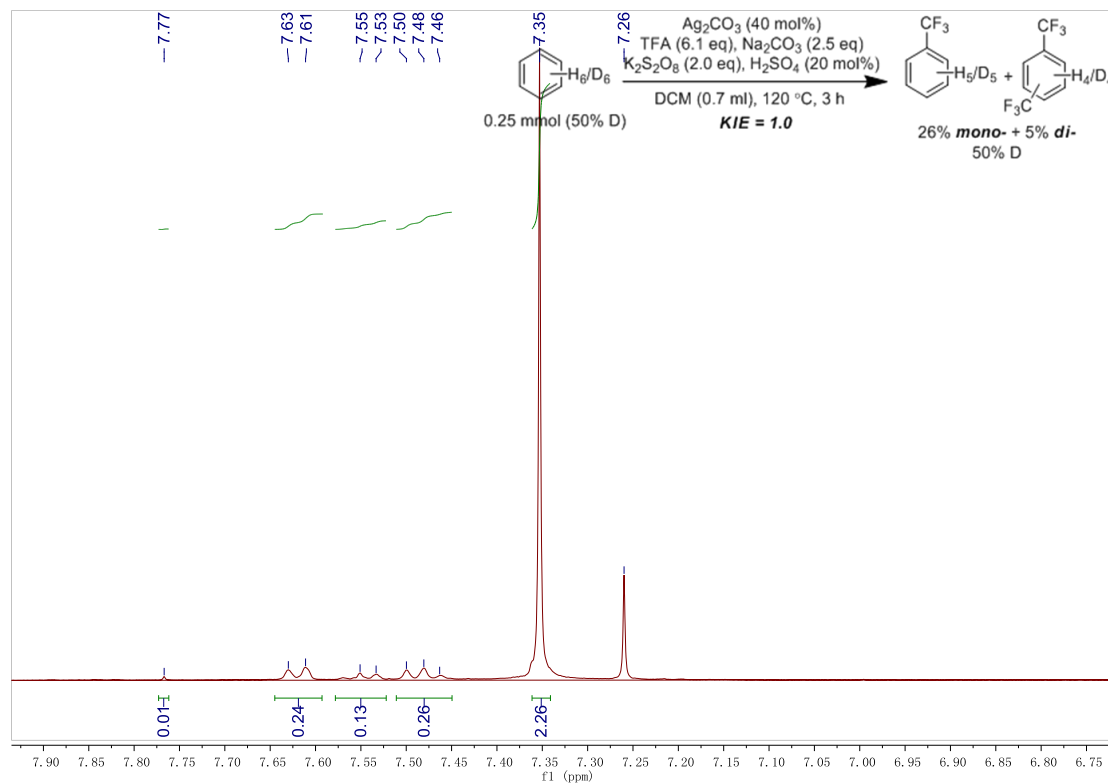


NMR Spectra for Preliminary Mechanistic Studies:

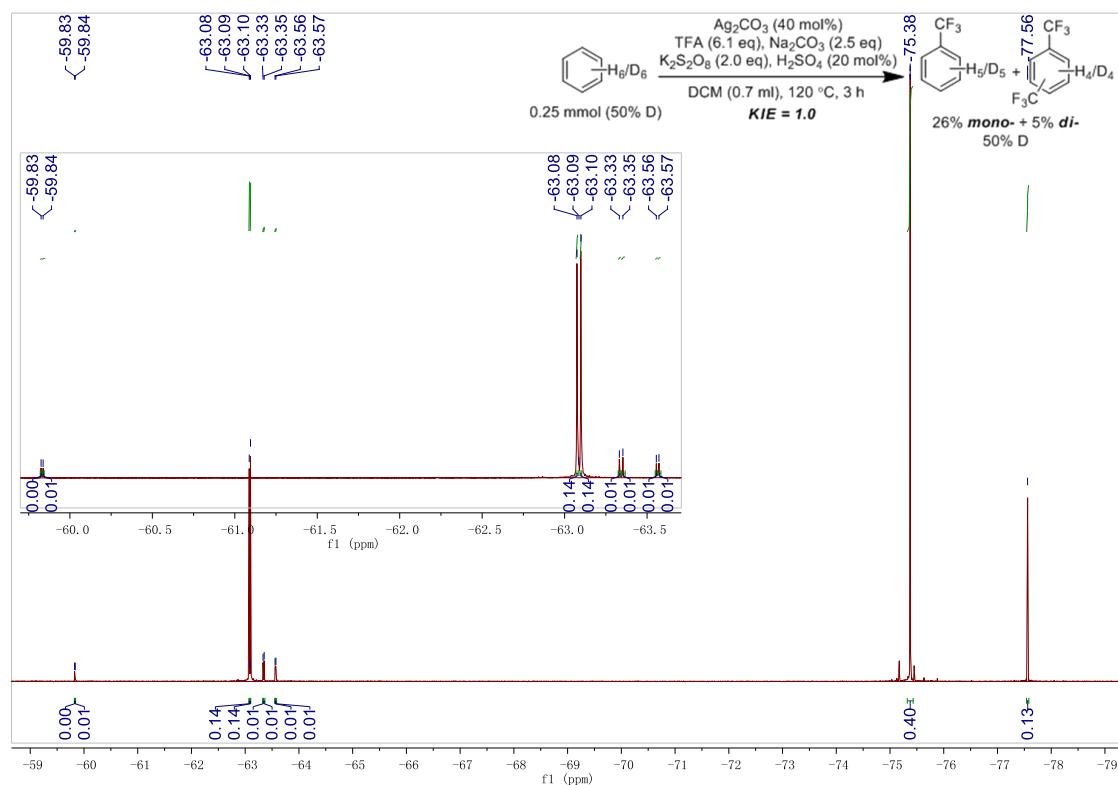
1. Kinetic Isotope Effect experiments with benzene and *d*₆-benzene:

time = 3 h:

¹H NMR

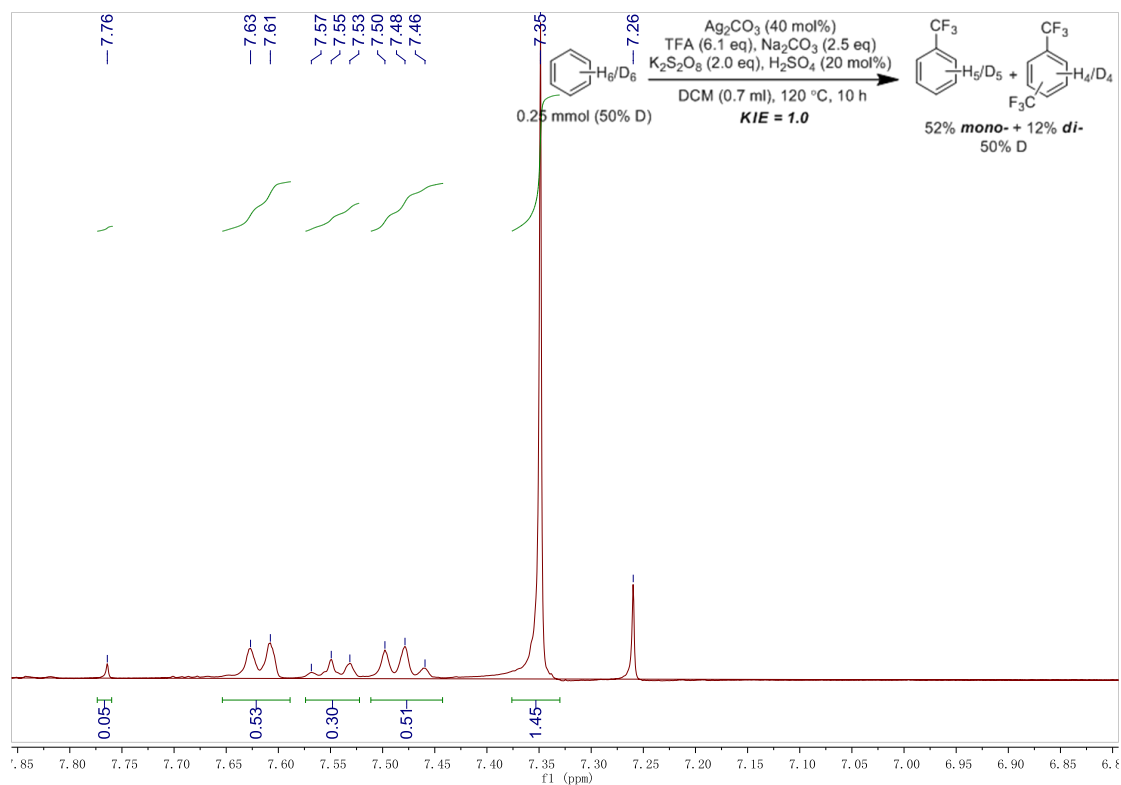


¹⁹F NMR



time = 10 h:

^1H NMR



^{19}F NMR

