Supporting Information

Trifluoromethyl-Substitued Selenium Ylide: A Broadly Applicable Electrophlic Trifluoromethylating Reagent

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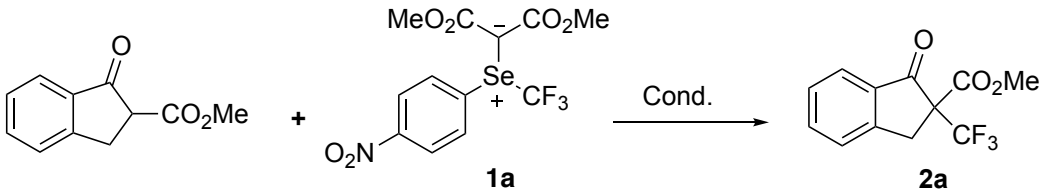
General information. All reactions were maintained under an argon atmosphere unless otherwise stated. All solvents were purified by standard methods. ^{1}H, ^{13}C and ^{19}F NMR spectra were acquired on 400 MHz, 125 MHz, 100 MHz, 375 MHz spectrometer (400 MHz for ^{1}H ; 101 MHz for ^{13}C; 375 MHz for ^{19}F). ^{1}H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 ppm and ^{19}F NMR chemical shifts were determined relative to fluorobenzene as inter standard. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. All reactions were monitored by TLC or ^{19}F NMR. Flash column chromatograph was carried out using 300-400 mesh silica gel at medium pressure.

Materials. All reagents were received from commercial sources. Solvents were freshly dried and degassed according to the purification handbook Purification of Laboratory Chemicals before using.

Table S1. Optimization of the reaction conditions for the β-ketoester with reagent 1a.[a,b]

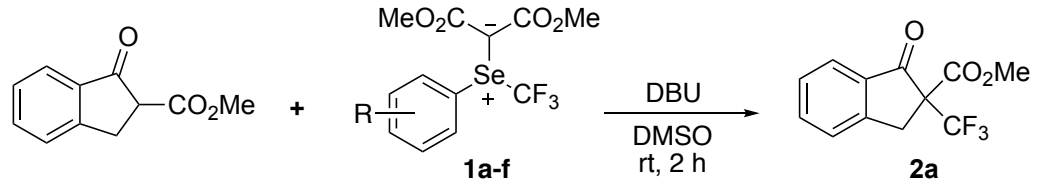


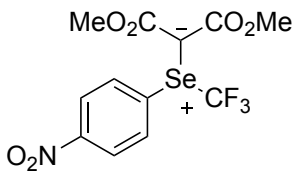
1a **2a**

entry	base	solvemt	yield (%)
1	K_2CO_3	DMF	70
2	K_2CO_3	DMSO	74
3	K_2CO_3	CH_2Cl_2	-
4	K_2CO_3	THF	-
4	K_2CO_3	$ClCH_2CH_2Cl$	-
5	K_2CO_3	CH_3CN	-
6	KO^{t}Bu	DMSO	88
7	NaO^{t}Bu	DMSO	53
8	KOH	DMSO	60
9	NaOH	DMSO	40
10	$KePO_4$	DMSO	82
11	Cs_2CO_3	DMSO	83
12	Na_2CO_3	DMSO	87
13	DBU	DMSO	>99
14	DMAP	DMSO	13
15	DABCO	DMSO	33
16	Et_3N	DMSO	13
17	DBU	DMSO	86 [c]
18	DBU	DMSO	96 [c,d]

[a]Reaction conditions: ketoester (0.05 mmol), reagent **1a** (0.06 mmol), base (0.1 mmol) in 1.0 mL of solvent at 40 °C for 1 h; [b]Yields were determined by ^{19}F NMR analysis of the crude reaction mixture with an internal standard; [c]Reaction with DBU (0.06 mmol) at room temperature; [d]Reaction for 2 h.

Table S2. Reactivity of different trifluoromethyl-substituted selenium ylides with β-ketoester.[a,b]





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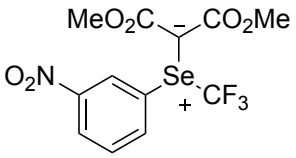

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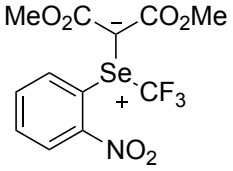

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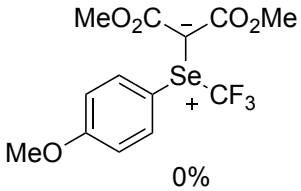

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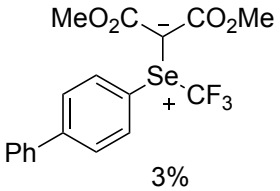

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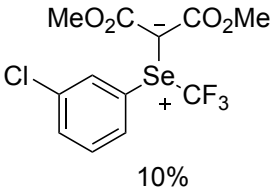
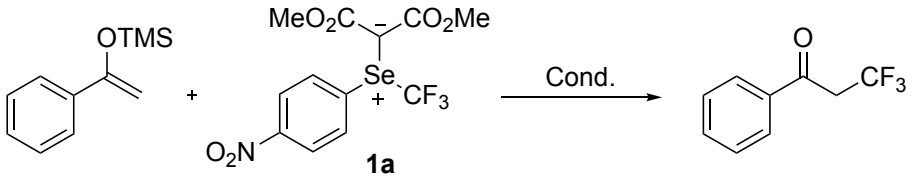


10%

[a]Reaction conditions: ketoester (0.05 mmol), reagent **1a** (0.06 mmol), DBU (0.06 mmol) in DMSO (1.0 mL) at RT for 2 h; [b]Yields were determined by ^{19}F NMR analysis of the crude reaction mixture with an internal standard.

Table S3. Optimization of the reaction conditions for reaction of silyl enol ether with reagent 1a.[a,b]

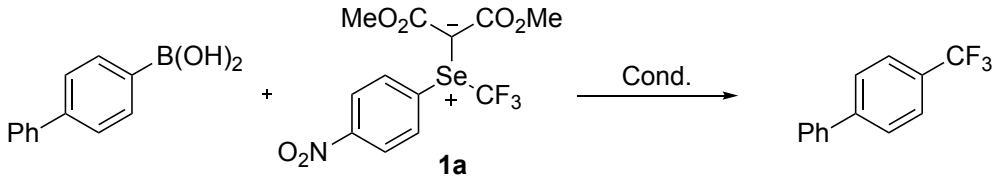


1a

entry	[CuX]	solvent	temp. (°C)	yield (%)
1	CuSCN	DMF	50	34
2	CuSCN	CH_2Cl_2	50	5
3	CuSCN	THF	50	1
4	CuSCN	Dioxane	50	1
5	CuSCN	NMP	50	38
6	CuSCN	DMAc	50	59
7	CuCl	DMAc	50	22
8	CuBr	DMAc	50	29
9	CuI	DMAc	50	59
10	CuTc	DMAc	50	32
11	$Cu(MeCN)_4BF_4$	DMAc	50	20
12	CuSCN	DMAc	40	76
13	CuSCN	DMAc	30	12
14	CuSCN	DMAc	40	61 [c]
15	CuSCN	DMAc	40	8 [d]
16	CuSCN	DMAc	40	36 [e]
17	CuSCN	DMAc	40	40 [f]
18	CuSCN	DMAc	40	68 [g]

[a]Reaction conditions: silyl enol ether (0.05 mmol), reagent **1a** (0.075 mmol), [CuX] (0.005 mmol) in solvent (1.0 mL) at temperature indicated in the Table for 16 h; [b]Yields were determined by ^{19}F NMR analysis of the crude reaction mixture with an internal standard; [c]Reagent **1a** (0.06 mmol) was used; [d]CuSCN (1.0 mol%) was used; [d]CuSCN (2.0 mol%) was used; [d]CuSCN (5.0 mol%) was used; [d]CuSCN (20.0 mol%) was used.

Table S4. Optimization of the reaction conditions for copper-mediated trifluoromethylation of aryl boronic acid with reagent 1a.[a,b]

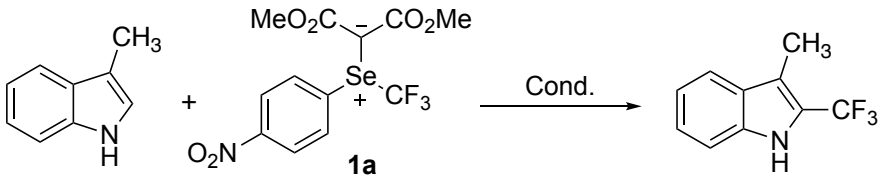


1a

entry	[CuX]	base	solvent	yield (%)
1	Cu	K_2CO_3	DMF	13
2	$CuCl_2$	K_2CO_3	DMF	12
3	CuBr	K_2CO_3	DMF	50
4	CuI	K_2CO_3	DMF	23
5	CuSCN	K_2CO_3	DMF	52
6	CuTc	K_2CO_3	DMF	62
7	CuOTf	K_2CO_3	DMF	41
8	CuOAc	K_2CO_3	DMF	72
9	CuCl	K_2CO_3	DMF	75
10	CuCl	K_2CO_3	DMSO	57
11	CuCl	K_2CO_3	CH_3CN	26
12	CuCl	K_2CO_3	THF	-
13	CuCl	K_2CO_3	NMP	-
14	CuCl	K_2CO_3	DCE	8
15	CuCl	K_2CO_3	DCM	10
16	CuCl	K_2CO_3	Toluene	5
17	CuCl	K_2CO_3	Dioxane	4
18	CuCl	K_2CO_3	Diglyme	-
19	CuCl	NaOH	DMF	70
20	CuCl	KOH	DMF	54
21	CuCl	Na_2CO_3	DMF	64
22	CuCl	Cs_2CO_3	DMF	74
23	CuCl	K_3PO_4	DMF	73
24	CuCl	KO^{t}Bu	DMF	80
25	CuCl	NaO^{t}Bu	DMF	60
26	CuCl	LiOH	DMF	64
27	CuCl	Li_2CO_3	DMF	54
28	CuCl	K_2CO_3	DMF	64
29	CuCl	Cs_2CO_3	DMF	98 [c]
30	CuCl	Cs_2CO_3	DMF	97 [c,d]

[a]Reaction conditions: arylboronic acid (0.05 mmol), reagent **1a** (0.1 mmol), base (0.1 mmol) in solvent (1.0 mL) at 50 °C for 12 h; [b]Yields were determined by ^{19}F NMR analysis of the crude reaction mixture with an internal standard; [c]Reaction was conducted at room temperature; [d]Reagent **1a** (0.075 mmol) and Cs_2CO_3 (0.04 mmol) were used.

Table S5. Optimization of the reaction conditions for visible light promoted trifluoromethylation of indole with reagent 1a.[a,b]

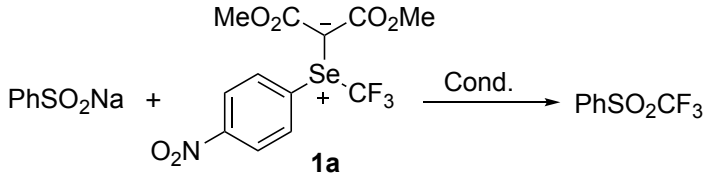


1a

entry	amine	solvent	yield (%)
1	DBU	DMSO	77
2	DBU	NMP	28
3	DBU	H_2O	74
4	DBU	Tol	18
5	DBU	Dioxane	42
6	DBU	Et_2O	47
7	DBU	DMA	37
8	DBU	CH_2Cl_2	85
9	Et_3N	CH_2Cl_2	58
10	DIEA	CH_2Cl_2	16
11	DABCO	CH_2Cl_2	97
12	DMAP	CH_2Cl_2	27
13	*N*-Methylaniline	CH_2Cl_2	33
14	NMM	CH_2Cl_2	63
15	DABCO	CH_2Cl_2	89
16	DABCO	CH_2Cl_2	88[c]
17	-	CH_2Cl_2	40
18	DABCO	CH_2Cl_2	<1 [c,d]

[a]Reaction conditions: 3-methylindole (0.05 mmol), reagent **1a** (0.075 mmol), amine (0.075 mmol) in 1.0 mL of solvent under irradiation of blue LED light at room temperature for 12 h; [b]Yields were determined by ^{19}F NMR analysis of the crude reaction mixture with an internal standard; [c]Reagent **1a** (0.06 mmol) was used; [d]In the absence of blue LED light.

Table S6. Optimisation of the reaction conditions for visible light promoted trifluoromethylation of sodium benzenesulfinate with reagent 1a.[a,b]



1a

entry	solvent	yield (%)
1	CH_2Cl_2	-
2	Et_2O	-
3	THF	-
4	H_2O	-
5	CH_3CN	-
6	DMF	28
7	DMF	95 [c]
8	DMSO	82
9	DMSO	>99[c]

[a]Reaction conditions: sodium arylsulfonate (0.05 mmol), reagent **1a** (0.06 mmol) in 1.0 mL of solvent for 12 h; [b]Yields were determined by ^{19}F NMR analysis of the crude reaction mixture with an internal standard; [c]Under irradiation of blue LED light.

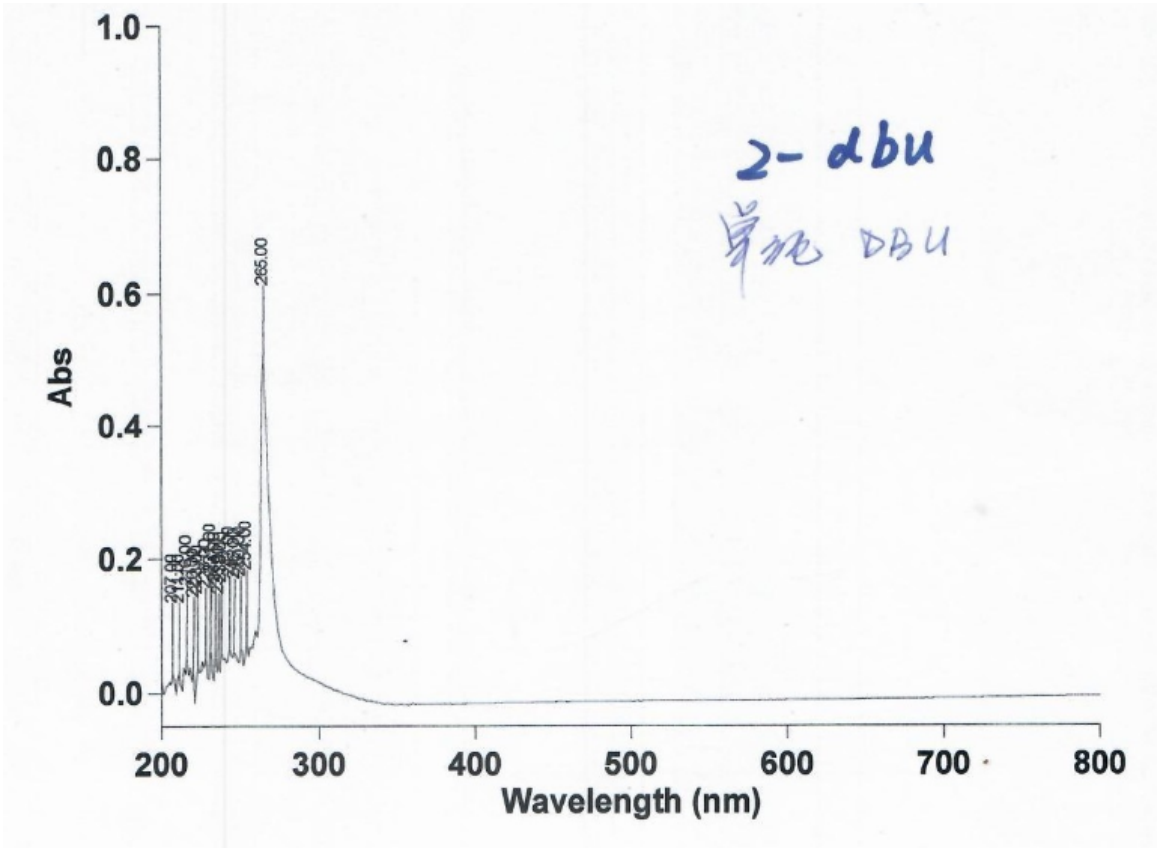


Figure S1. UV-Visible absorption spectrum of DBU in DMF (λ_{max} = 265 nm).

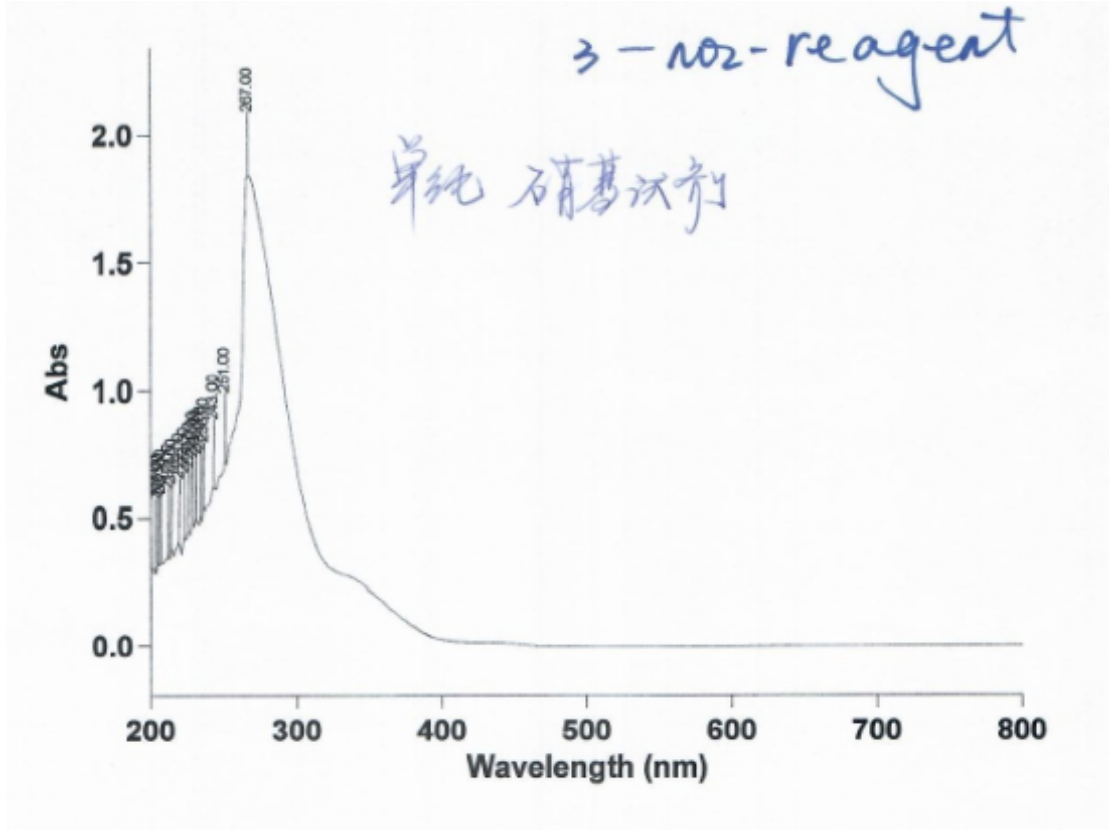


Figure S2. UV-Visible absorption spectrum of reagent 1a in DMF (λ_{max} = 267 nm).

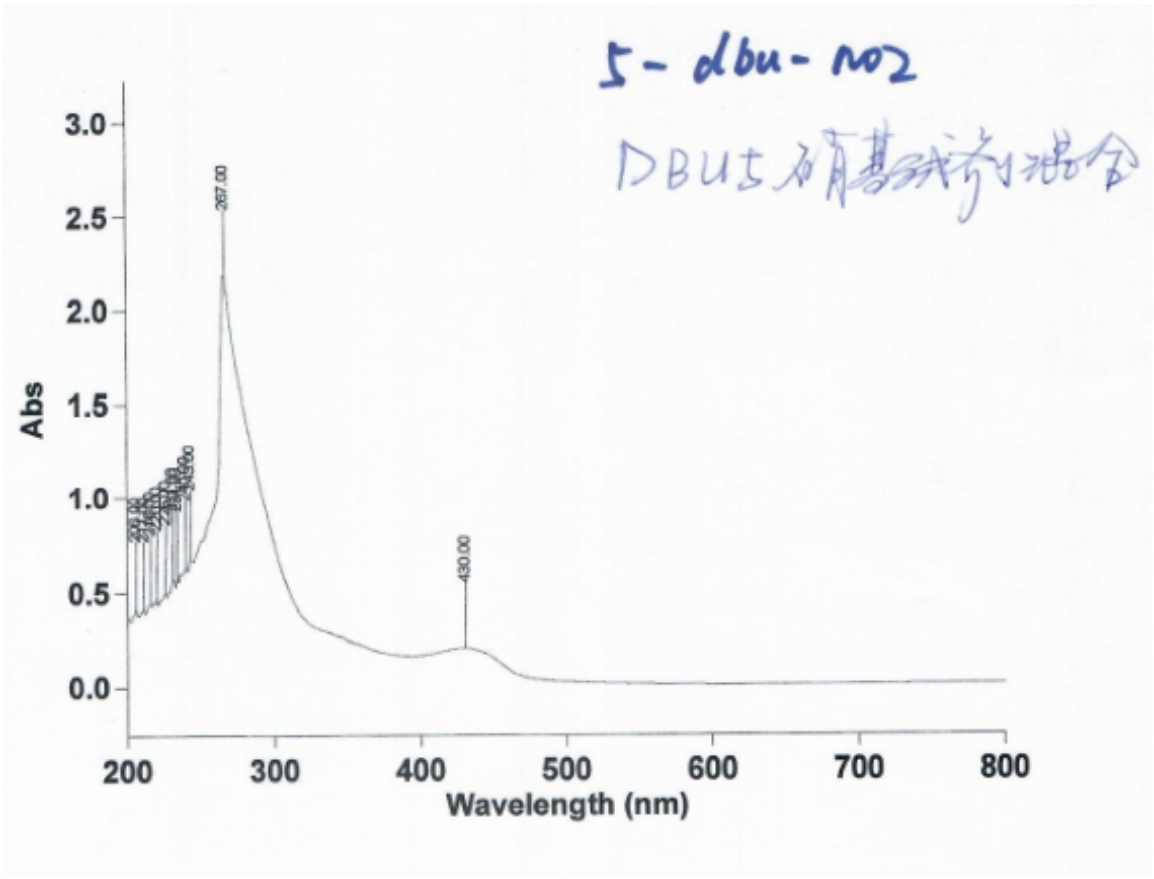


Figure S3. UV-Visible absorption spectrum of reagent 1a with 1.0 equivalent of DBU in DMF (λ_{max} = 267, 430 nm).

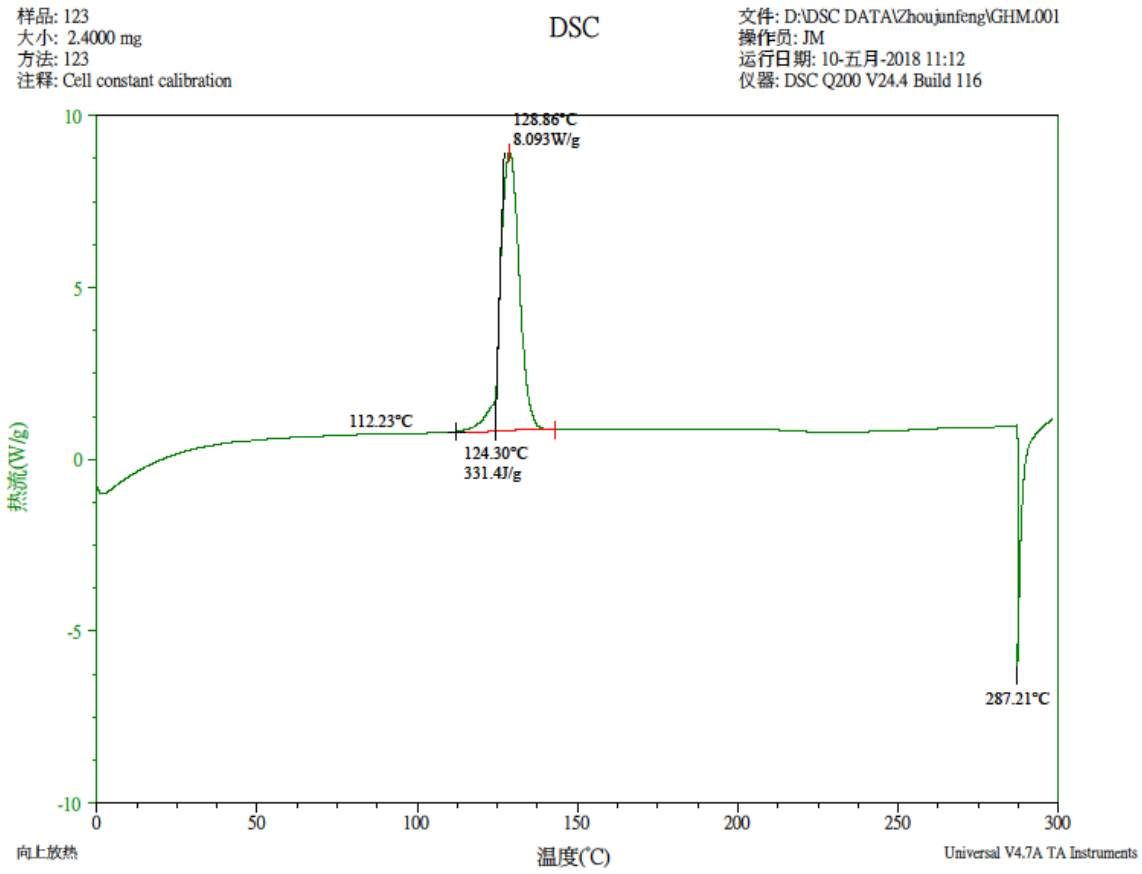


Figure S4. Differential scanning calorimeter spectrum of Reagent 1a

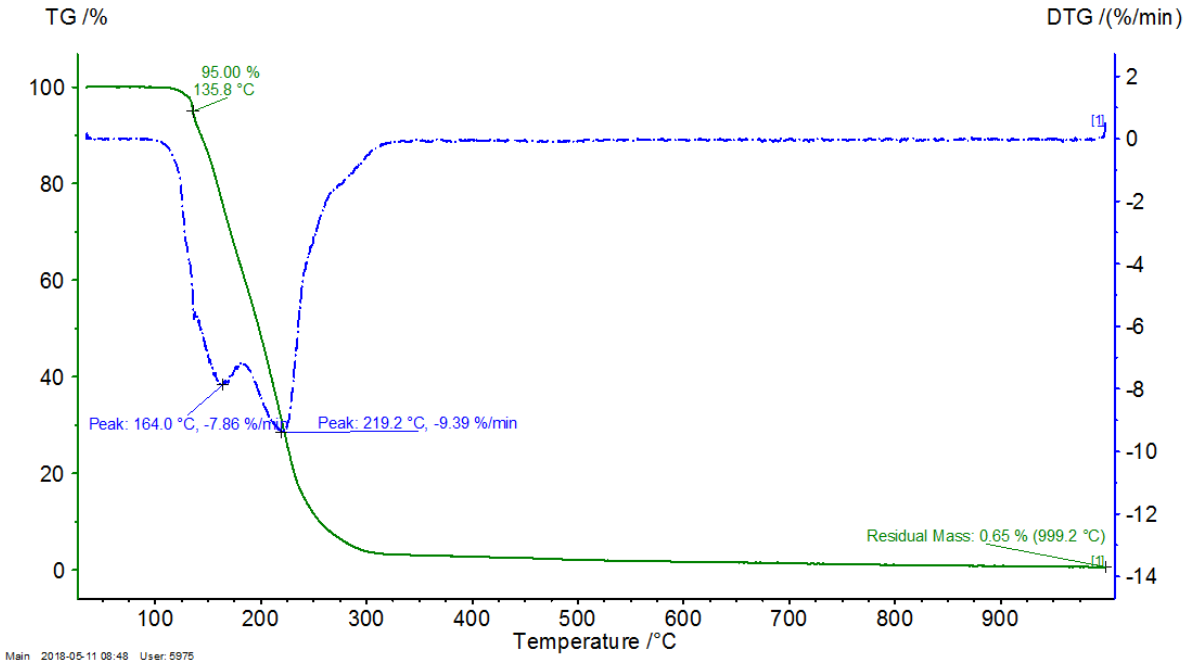
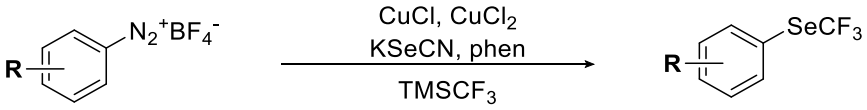


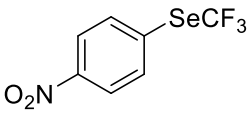
Figure S5. Thermogravimetric Analysis of Reagent 1a.

General procedure for the preparation of aryl trifluoromethylselenoether



An oven-dried reaction tube equipped with a stirring bar and a septum was loaded with dry Cs_2CO_3 (3.56 g, 10.5 mmol, 1.50 equiv.), CuCl (71 mg, 0.70 mmol, 0.10 equiv.), $CuCl_2$ (96 mg, 0.70 mmol, 0.10 equiv.), 1,10-phenanthroline (128 mg, 0.700 mmol, 0.100 equiv.) and KSeCN (1.53 g, 10.5 mmol, 1.50 equiv.) in a glove box. The tube was closed with a septum and removed from the glove box. Anhydrous CH_3CN (30.0 mL) was added via syringe into the reaction tube and the mixture was quickly cooled down to −25 °C, followed by vigorous stirring for 5 min. Subsequently, a solution of aryldiazonium tetrafluoroborate (7.00 mmol, 1.00 equiv.) in CH_3CN (30.0 mL) was dropwise added. After stirring at −25 °C for 10 min and at room temperature for 10 min, 2.0 mL of $TMSCF_3$ (14.0 mmol. 2.00 equiv.) was added by syringe and the reaction mixture was stirred at room temperature for 12 h. The resulting mixture was filtered through a short pad of silica gel and the solvent was removed under vacuum. The residue was purified by flash column chromatography to give the desired product.

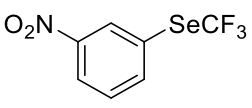
4-Trifluoromethylseleno-nitrobenzene[1]



Yellow solid (1.55 g, 82%).

^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.22 (d, *J* = 5.1 Hz, 2 H), 7.90 (d, *J* = 6.6 Hz, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -34.75 (s, 3 F).

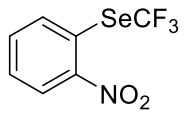
3-Trifluoromethylseleno-nitrobenzene[1]



Yellow oil (1.27 g, 67%).

^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.62 (s, 1 H), 8.35 (d, *J* = 7.5 Hz, 1 H), 8.08 (d, *J* = 7.7 Hz, 1 H), 7.62 (t, *J* = 8.0 Hz, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -35.35 (s, 3 F).

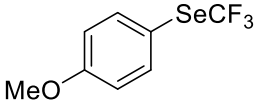
2-Trifluoromethylseleno-nitrobenzene[1]



Yellow oil (248 mg, 13%).

^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.35 (d, J = 8.2 Hz, 1 H), 7.88 (d, J = 8.1 Hz, 1 H), 7.67 (t, J = 7.7 Hz, 1 H), 7.51 (t, J = 7.8 Hz, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -37.02 (s, 3 F).

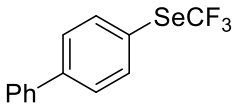
4-Trifluoromethylseleno-anisole[1]



Colorless oil (1.39 g, 78%).

^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.66 (d, J = 8.4 Hz, 2 H), 6.91 (d, J = 8.4 Hz, 2 H), 3.83 (s, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -37.19 (s, 3 F).

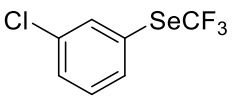
4-Trifluoromethylseleno-biphenyl[1]



White solid (1.52 g, 72%).

^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.81 (d, J = 8.3 Hz, 2 H), 7.64 – 7.56 (m, 4 H), 7.47 (t, J = 7.4 Hz, 2 H), 7.42 - 7.37 (m, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -36.09 (s, 3 F).

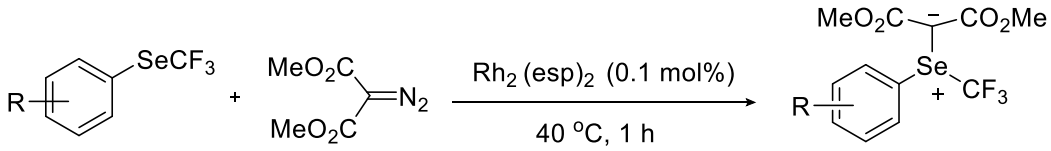
3-Trifluoromethylseleno-chlorobenzene[1]



Colorless oil (1.52 g, 72%).

^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.75 (s, 1 H), 7.63 (d, J = 7.5 Hz, 1 H), 7.46 (d, J = 8.8 Hz, 1 H), 7.34 (t, J = 7.8 Hz, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -36.11 (s, 3 F).

General procedure for the preparation of selenium ylides 1a-f.

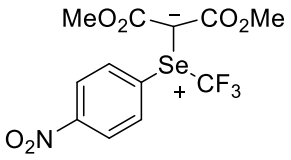


Aryl trifluoromethylselenoether (1.00 equiv.), $Rh_2(esp)_2$ (0.1 mol%) and CH_2Cl_2 were placed into an oven-dried Schlenk tube that was equipped with a stirring bar under Ar. A solution of diazomalonate (1.90 g, 1.20 equiv.) in CH_2Cl_2 (20.0 mL) was added slowly during a period of 30 min. The reaction was stirred at 40 °C for 1 h. The mixture was then cooled to room temperature, then concentrated in *vacuo*.

Method A. The residue was purified by flash chromatography (eluent: petroleum ether: ethyl acetate = 1:1) to afford compounds **1a** and **1d**.

Method B. The residue was purified by recrystallization from layering a solution of the residue in dichloromethane with diethyl ether to afford compounds **1a**, **1b**, **1c**, **1e** and **1f**.

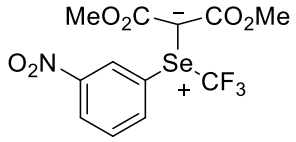
Trifluoromethyl-(4-nitrophenyl)bis(carbomethoxy)methylide 1a



4-Trifluoromethylselenonitrobenzene (2.70 g, 10.0 mmol, 1.00 equiv.), $Rh_2(esp)_2$ (7.6 mg, 0.10 mol%) in CH_2Cl_2 (80.0 mL) were placed into an oven-dried Schlenk tube that was equipped with a stirring bar under argon. A solution of diazomalonate (1.90 g, 12.0 mmol, 1.20 equiv.) in CH_2Cl_2 (20.0 mL) was added slowly during a period of 30 min. The reaction was stirred at 40 °C for 1 h. The mixture was cooled to room temperature, then concentrated in *vacuo*. The residue was purified by flash chromatography to give trifluoromethyl-(4-nitrophenyl)bis(carbomethoxy)methylide **1a** as a yellow solid (3.64 g, 91%). Eluent: ethyl acetate/petroleum ether = 1/2 (R_f = 0.5). Mp: 113-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.42 (d, J = 7.4 Hz, 2 H), 7.85 (d, J = 7.8 Hz, 2 H), 3.72 (s, 6 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -48.32 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 166.08, 150.58, 133.92, 130.30, 125.66, 120.84 (q, J = 358.8 Hz), 65.68, 52.16 ppm. MS (ESI): 402.0 (M^++H); HRMS (ESI): Calcd for

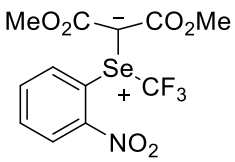
$C_{12}H_{11}O_6NF_3{}^{74}Se$: 395.9757 ($M^+$+H), Found: 395.9758. IR (KBr): ν_{max} = 3105, 1523, 1349, 1239, 1074 cm^{-1}. Anal. Calcd for $C_{12}H_{11}O_6NF_3Se$: C, 36.02; H, 2.52; N, 3.50; Found: C, 36.28; H, 2.68; N, 3.37.

Trifluoromethyl-3-nitrophenyl)bis(carbomethoxy)methylide 1b



3-Trifluoromethylseleno-nitrobenzene (1.27 g, 4.70 mmol, 1.00 equiv.), $Rh_2(esp)_2$ (3.6 mg, 0.10 mol%) and CH_2Cl_2 (40.0 mL) were placed into an oven-dried Schlenk tube that was equipped with a stirring bar under argon. A solution of diazomalonate (891 mg, 5.64 mmol, 1.20 equiv.) in CH_2Cl_2 (10.0 mL) was added slowly for 30 min. The reaction was stirred at 40 °C for 1 h. The mixture was cooled to room temperature, then concentrated in *vacuo*. The product was purified by **Method B** to give trifluoromethyl-3-nitrophenyl)bis(carbomethoxy)methylide **1b** as a grey solid (860 mg, 46%). Eluent: ethyl acetate/petroleum ether = 1/2 (R_f = 0.5). Mp: 127-128 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.48 - 8.45 (m, 2 H), 7.98 (d, *J* = 7.9 Hz, 1 H), 7.81 (t, *J* = 8.0 Hz, 1 H), 3.72 (s, 6 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -43.71 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 166.09, 149.39, 134.70, 131.86, 129.15, 127.50, 124.48, 120.82 (q, *J* = 358.7 Hz), 65.53, 52.15 ppm. MS (ESI): 401.9 (M^++H); HRMS (ESI): Calcd for $C_{12}H_{11}O_6NF_3Se$: 401.9698 (M^++H), Found: 401.9695. IR (KBr): ν_{max} = 3068, 1609, 1297, 1051 cm^{-1}. Anal. Calcd for $C_{12}H_{11}O_6NF_3Se$: C, 36.02; H, 2.52; N, 3.50; Found: C, 36.40; H, 2.76; N, 3.76.

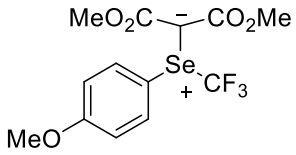
Trifluoromethyl-(2-nitrophenyl) bis(carbomethoxy) methylide 1c



2-Trifluoromethylseleno-nitrobenzene (248 mg, 0.920 mmol, 1.00 equiv.), $Rh_2(esp)_2$ (0.7 mg, 0.1 mol%) and CH_2Cl_2 (7.0 mL) were placed into an oven-dried Schlenk tube that was equipped with a stirring bar under argon. A solution of diazomalonate (174 mg, 1.10 mmol, 1.20 equiv) in CH_2Cl_2 (3.0 mL) was added slowly during a period of 30

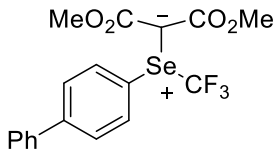
min. The reaction was stirred at 40 °C for 1 h. The mixture was cooled to room temperature, then concentrated in *vacuo*. The product was purified by **Method B** to give trifluoromethyl-(2-nitrophenyl)bis(carbomethoxy)methylide **1c** as a yellow solid (167 mg, 45%). Eluent: ethyl acetate/petroleum ether = 1/2 (R_f = 0.5). Mp: 115-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.52 (dd, *J* = 7.8, 1.6 Hz, 1 H), 7.99 - 7.96 (m, 1 H), 7.94 - 7.84 (m, 2 H), 3.71 (s, 6 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -42.73 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 166.43, 146.58, 135.99, 134.08, 132.64, 126.97, 123.19, 120.72 (q, *J* = 357.4 Hz), 65.49, 51.89 ppm. MS (ESI): 401.9 (M^++H); HRMS (ESI): Calcd for $C_{12}H_{11}O_6NF_3Se$: 401.9698 (M^++H), Found: 401.9697. IR (KBr): ν_{max} = 1685, 1538, 1348, 1183, 1067 cm^{-1}. Anal. Calcd for $C_{12}H_{11}O_6NF_3Se$: C, 36.02; H, 2.52; N, 3.50; Found: C, 36.26; H, 2.68; N, 3.49.

Trifluoromethyl-(4-methoxylphenyl)bis(carbomethoxy)methylide 1d



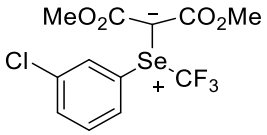
4-Trifluoromethylseleno-anisole (2.55 g, 10.0 mmol, 1.00 equiv.), $Rh_2(esp)_2$ (7.6 mg, 0.10 mol%) and CH_2Cl_2 (80.0 mL) were placed into an oven-dried Schlenk tube that was equipped with a stirring bar under argon. A solution of diazomalonate (1.90 g, 12.0 mmol, 1.20 equiv) in CH_2Cl_2 (30.0 mL) was added slowly during a period of 30 min. The reaction was stirred at 40 °C for 1 h. The mixture was cooled to room temperature, then concentrated in *vacuo*. The product was purified by **Method A** to give trifluoromethyl-(4-methoxylphenyl)bis(carbomethoxy)methylide **1d** as a pale yellow oil (2.36 g, 61%). Eluent: ethyl acetate/petroleum ether = 1/2 (R_f = 0.6). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.59 (d, *J* = 8.8 Hz, 2 H), 7.05 (d, *J* = 8.8 Hz, 2 H), 3.87 (s, 3 H), 3.71 (s, 6 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -45.95 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.37, 163.30, 131.17, 120.69 (q, *J* = 357.2 Hz), 117.28, 116.34, 65.54, 55.90, 51.60 ppm. MS (ESI): 386.9 (M^++H); HRMS (ESI): Calcd for $C_{13}H_{14}O_5F_3{}^{74}Se$: 381.0014 ($M^+$+H), Found: 381.0013. IR (KBr): ν_{max} = 1682, 1626, 1328, 1080, 1061 cm^{-1}. Anal. Calcd for $C_{13}H_{14}O_5F_3Se$: C, 40.54; H, 3.40; Found: C, 40.87; H, 3.74.

Trifluoromethyl-(4-biphenyl)bis(carbomethoxy)methylide 1e



4-Trifluoromethylseleno-biphenyl (1.50 g, 5.00 mmol, 1.00 equiv.), $Rh_2(esp)_2$ (3.8 mg, 0.1 mol%) and CH_2Cl_2 (40.0 mL) were placed into an oven-dried Schlenk tube that was equipped with a stirring bar under argon. A solution of diazomalonate (948 mg, 6.00 mmol, 1.20 equiv) in CH_2Cl_2 (10.0 mL) was added slowly during a period of 30 min. The reaction was stirred at 40 °C for 1 h. The mixture was cooled to room temperature, then concentrated in *vacuo*. The product was purified by **Method B** to give trifluoromethyl-(4-biphenyl)bis(carbomethoxy)methylide **1e** as a white solid (1.56 g, 73%). Eluent: ethyl acetate/petroleum ether = 1/2 (R_f = 0.6). Mp: 106-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.73 (dd, *J* = 28.2, 8.3 Hz, 4 H), 7.59 - 7.57 (m, 2 H), 7.50 – 7.40 (m, 3 H), 3.73 (s, 6 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -44.93 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 166.45, 146.07, 139.19, 129.56, 129.49, 129.45, 129.02, 127.62, 125.69, 120.85 (q, *J* = 357.6 Hz), 65.21, 51.84 ppm. MS (ESI): 433.0 (M^++H); HRMS (ESI): Calcd for $C_{18}H_{16}O_4F_3{}^{74}Se$: 427.0220 ($M^+$+H), Found: 427.0220. IR (KBr): ν_{max} = 1692, 1465, 1326, 1166, 1081, 1039 cm^{-1}. Anal. Calcd for $C_{18}H_{16}O_4F_3Se$: C, 50.13; H, 3.51; Found: C, 49.85; H, 3.79.

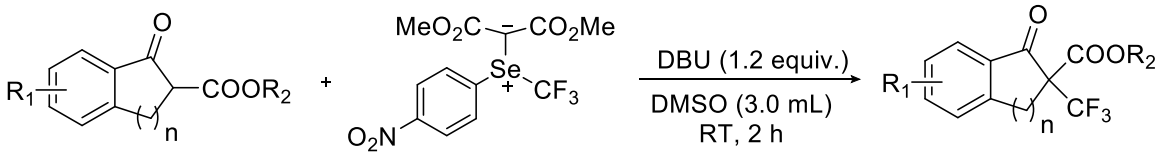
Trifluoromethyl-(3-chlorophenyl)bis(carbomethoxy)methylide 1f



3-Trifluoromethylseleno-chlorobenzene (2.60 g, 10.0 mmol, 1.00 equiv), $Rh_2(esp)_2$ (7.6 mg, 0.10 mol%) and CH_2Cl_2 (80.0 mL) were placed into an oven-dried Schlenk tube that was equipped with a stirring bar under argon. A solution of diazomalonate (1.90 g, 12.0 mmol, 1.20 equiv) in CH_2Cl_2 (20.0 mL) was added slowly during a period of 30 min. The reaction was stirred at 40 °C for 1 h. The mixture was cooled to room temperature, then concentrated in *vacuo*. The product was purified by **Method B** to give trifluoromethyl-(3-chlorophenyl)bis(carbomethoxy)methylide **1f** as a white solid

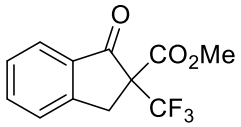
(2.61 g, 67%). Eluent: ethyl acetate/petroleum ether = 1/2 (R_f = 0.6). Mp: 113-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.61 – 7.58 (m, 2 H), 7.51-7.55 (m, 2 H), 3.72 (s, 6 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -44.25 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 166.25, 137.12, 133.17, 131.87, 128.93, 128.62, 127.11, 120.85 (q, J = 357.7 Hz), 65.31, 51.98 ppm. MS (ESI): 390.9 (M^++H); HRMS (ESI): Calcd for $C_{12}H_{11}O_4ClF_3Se$: 390.9458 (M^++H), Found: 390.9455. IR (KBr): ν_{max} = 1698, 1647, 1440, 1323, 1236, 1166, 1077, 1056 cm^{-1}. Anal. Calcd for $C_{12}H_{10}ClO_4F_3Se$: C, 36.99; H, 2.59; Found: C, 37.01; H, 2.82.

General procedure for trifluoromethylation of β-ketoesters 2a-k with reagent 1a



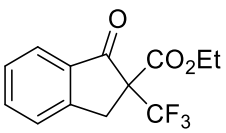
β-ketoester (0.50 mmol, 1.0 equiv.) and reagent **1a** (240 mg, 0.600 mmol, 1.20 equiv.) were placed into an oven-dried Schlenk tube that was equipped with a stirring bar under Ar. The tube was quickly sealed with a rubber stopper and 3.0 mL of freshly distilled DMSO and DBU (91.2 mg, 0.600 mmol, 1.20 equiv.) was added. The reaction was stirred at room temperature for 2 h. Then 20.0 mL of Distilled water and 20.0 mL of Et_2O was added and the organic phase was separated. The aqueous phase was extracted with Et_2O (10.0 mL × 5) and the combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated in vacuo. The product was purified by flash chromatography on silica gel.

Methyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate2a[2]



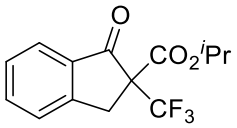
Pale yellow solid (118 mg, 91%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.84 (d, *J* = 7.7 Hz, 1 H), 7.70 (t, *J* = 7.5 Hz, 1 H), 7.53 (d, *J* = 7.7 Hz, 1 H), 7.47 (t, *J* = 7.5 Hz, 1 H), 3.78 (s, 3 H), 3.74 (d, *J* = 17.8 Hz, 1 H), 3.60 (d, *J* = 17.7 Hz, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -69.37 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 193.14, 165.95 (d, *J* = 2.1 Hz), 151.99, 136.62, 134.74, 128.85, 126.65, 125.94, 123.85 (q, *J* = 281.5 Hz), 63.39 (q, *J* = 26.2 Hz), 53.88, 34.52 (d, *J* = 1.8 Hz) ppm. MS (EI): 258 (M^+); HRMS (EI): Calcd for $C_{12}H_9O_3F_3$: 258.0508 (M^+), Found: 258.0504. IR (KBr): ν_{max} = 3436, 1760, 1607, 1436, 1278, 1157, 1046 cm^{-1}.

Ethyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2b[2]



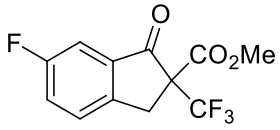
Pale yellow solid (134 mg, 98%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.83 (d, *J* = 7.7 Hz, 1 H), 7.69 (t, *J* = 7.5 Hz, 1 H), 7.53 (d, *J* = 7.7 Hz, 1 H), 7.45 (t, *J* = 7.5 Hz, 1 H), 4.30 - 4.17 (m, 2 H), 3.73 (d, *J* = 17.7 Hz, 1 H), 3.59 (d, *J* = 17.7 Hz, 1 H), 1.23 (t, *J* = 7.1 Hz, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -69.30 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 193.30, 165.46, 152.07, 136.54, 134.77, 128.79, 126.63, 125.84, 123.88 (q, *J* = 281.5 Hz), 63.48 (q, *J* = 26.2 Hz) 63.14, 34.51 (q, *J* = 1.9 Hz), 14.14 ppm. MS (EI): 272 (M^+); HRMS (EI): Calcd for $C_{13}H_{11}O_3F_3$: 272.0670 (M^+), Found: 272.0660. IR (KBr): ν_{max} = 1756, 1727, 1607, 1303, 1186, 1043 cm^{-1}.

Isopropyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2c[2]



Pale yellow solid (139 mg, 97%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.83 (d, *J* = 7.7 Hz, 1 H), 7.68 (t, *J* = 7.4 Hz, 1 H), 7.53 (d, *J* = 7.6 Hz, 1 H), 7.45 (t, *J* = 7.4 Hz, 1 H), 5.10 (hept, *J* = 6.0 Hz, 1 H), 3.71 (d, *J* = 17.6 Hz, 1 H), 3.58 (d, *J* = 17.7 Hz, 1 H), 1.22 (d, *J* = 6.2 Hz, 6 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -69.19 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 193.39, 164.99, 152.03, 136.46, 134.86, 128.75, 126.60, 125.83, 123.91 (q, *J* = 281.5 Hz), 71.21, 63.63 (q, *J* = 26.0 Hz), 34.51 (d, *J* = 1.8 Hz), 21.70, 21.63 ppm. MS (EI): 286 (M^+); HRMS (EI): Calcd for $C_{14}H_{13}O_3F_3$: 286.0819 (M^+), Found: 286.0817. IR (KBr): ν_{max} = 2985, 1751, 1606, 1466, 1279, 1185, 1036 cm^{-1}.

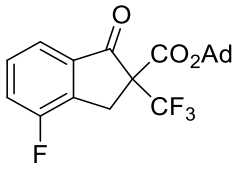
Methyl 6-chloro-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2d



Pale yellow solid (109 mg, 79%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.89 - 7.82 (m, 1 H), 7.23 - 7.13 (m, 2 H), 3.80 (s, 3 H), 3.74 (d, *J* = 18.0 Hz, 1 H), 3.57 (d, *J* = 18.0 Hz, 1 H); ^{19}F NMR (375

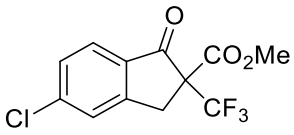
MHz, $CDCl_3$) δ -69.42 (s, 3 F), -99.10 - -99.21 (m, 1 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 191.18, 169.59, 167.01, 165.62, 154.95 (d, *J* = 10.7 Hz), 128.40 (d, *J* = 10.8 Hz), 123.69 (d, *J* = 281.6 Hz), 117.44 (d, *J* = 24.0 Hz), 113.57 (d, *J* = 23.2 Hz), 63.69 (q, *J* = 26.4 Hz), 54.02, 34.29 ppm. MS (EI): 276 (M^+); HRMS (EI): Calcd for $C_{12}H_8O_3F_4$: 276.0411 (M^+), Found: 276.0410. IR (KBr): ν_{max} = 1753, 1615, 1312, 1171, 1048 cm^{-1}.

Adamantyl 4-fluoro-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2e



Pale yellow solid (194 mg, 98%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.6). ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.64 (d, *J* = 7.6 Hz, 1 H), 7.45 (td, *J* = 7.9, 4.6 Hz, 1 H), 7.36 (t, *J* = 8.3 Hz, 1 H), 3.69 (d, *J* = 18.0 Hz, 1 H), 3.55 (d, *J* = 17.9 Hz, 1 H), 2.15 (s, 3 H), 2.06 (s, 6 H), 1.62 (s, 6 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -69.19 (s, 3 F), -118.39 (dd, *J* = 8.6, 4.6 Hz, 1 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 192.60, 163.50 (q, *J* = 2.1 Hz), 161.18, 158.68, 137.95 (d, *J* = 19.5 Hz), 130.76 (d, *J* = 6.2 Hz), 123.72 (d, *J* = 281.3 Hz), 122.44 (d, *J* = 19.7 Hz), 121.46 (d, *J* = 4.1 Hz), 85.09, 64.17 (q, *J* = 25.9 Hz), 41.27, 36.26, 31.24, 30.73 (d, *J* = 2.0 Hz) ppm. MS (EI): 396 (M^+); HRMS (EI): Calcd for $C_{21}H_{20}O_3F_4$: 396.1342 (M^+), Found: 396.1349. IR (KBr): ν_{max} = 2916, 1752, 1482, 1314, 1165, 1036 cm^{-1}.

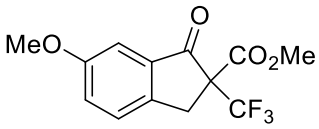
Methyl 5-chloro-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2- carboxylate 2f[3]



Pale yellow solid (136 mg, 93%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.5). ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.78 (d, *J* = 8.2 Hz, 1 H), 7.54 (s, 1 H), 7.45 (d, *J* = 9.0 Hz, 1 H), 3.79 (s, 3 H), 3.73 (d, *J* = 17.9 Hz, 1 H), 3.57 (d, *J* = 17.9 Hz, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -69.38 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$,

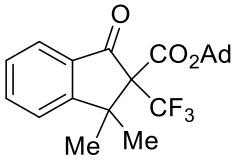
293 K, TMS) δ 191.67, 165.55 (d, *J* = 2.1 Hz), 153.34, 143.48, 133.13 (d, *J* = 1.4 Hz), 129.80, 126.95, 123.64 (q, *J* = 281.6 Hz), 63.54 (q, *J* = 26.3 Hz), 54.06, 34.16 (d, *J* = 1.7 Hz) ppm. MS (EI): 292 (M^+); HRMS (EI): Calcd for $C_{12}H_8O_3ClF_3$: 292.0114 (M^+), Found: 292.0108.

Methyl 6-methoxy-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2g[3]



Pale yellow solid (135 mg, 94%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.44 (d, *J* = 8.3 Hz, 1 H), 7.30 (d, *J* = 8.3 Hz, 1 H), 7.26 (s, 1 H), 3.87 (s, 3 H), 3.80 (s, 3 H), 3.66 (d, *J* = 17.4 Hz, 1 H), 3.54 (d, *J* = 17.4 Hz, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -69.45 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 192.76, 165.65 (d, *J* = 2.1 Hz), 160.11, 144.60, 135.60 (d, *J* = 1.5 Hz), 126.94, 125.90, 123.47 (q, *J* = 281.5 Hz), 106.25, 63.69 (q, *J* = 26.1 Hz), 55.67, 53.48, 33.50 (d, *J* = 1.7 Hz) ppm. MS (EI): 288 (M^+); HRMS (EI): Calculated for $C_{13}H_{11}O_4F_4$: 288.0600 (M^+), Found: 288.0609. IR (KBr): ν_{max} = 1754, 1711, 1323, 1199, 1157, 1074, 1046, 1025 cm^{-1}.

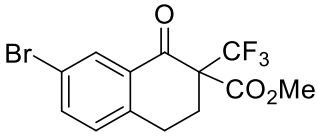
Adamantyl-1,1-dimethyl-3-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2h



Pale yellow solid (199 mg, 98%). Eluent: ethyl acetate/petroleum ether = 1/20 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.77 (d, *J* = 7.6 Hz, 1 H), 7.66 (t, *J* = 7.5 Hz, 1 H), 7.46 (d, *J* = 7.8 Hz, 1 H), 7.41 (t, *J* = 7.4 Hz, 1 H), 2.09 (s, 3 H), 1.95 (s, 6 H), 1.61 (s, 3 H), 1.57 (s, 6 H), 1.49 (s, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -66.65 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 198.67, 168.60, 164.81, 140.36, 138.70, 132.88, 128.95, 128.78 (q, *J* = 281.8 Hz), 127.38, 89.20, 76.64 (q, *J* = 23.6 Hz), 51.12, 45.62, 40.55, 35.46, 34.55 (q, *J* = 3.1 Hz), 29.69 ppm. MS (EI): 406 (M^+); HRMS

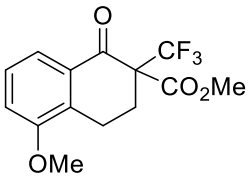
(EI): Calcd for $C_{23}H_{25}O_3F_3$: 406.1756 (M^+), Found: 406.1751. IR (KBr): ν_{max} = 2914, 1728, 1293, 1309, 1252, 1217, 1171, 1146, 1053 cm^{-1}.

Methyl-7-bromo-1-oxo-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalene-2-Carboxylate 2i



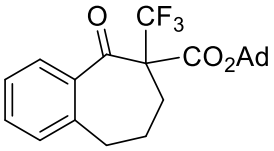
Pale yellow solid (153 mg, 87%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.3). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.22 (d, *J* = 2.1 Hz, 1 H), 7.63 (dd, *J* = 8.2, 2.1 Hz, 1 H), 7.14 (d, *J* = 8.2 Hz, 1 H), 3.77 (s, 3 H), 3.03 - 2.91 (m, 2 H), 2.82 (dt, *J* = 13.7, 4.0 Hz, 1 H), 2.52 - 2.38 (m, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -68.88 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 185.75, 165.41 (q, *J* = 1.8 Hz), 140.70, 137.08, 132.80 (d, *J* = 1.3 Hz), 131.09, 130.47, 123.59 (q, *J* = 284.0 Hz), 121.31, 61.78 (q, *J* = 24.5 Hz), 53.73, 27.45 (q, *J* = 2.2 Hz), 24.66 ppm. MS (EI): 350 (M^+); HRMS (EI): Calcd for $C_{13}H_{10}O_3BrF_3$: 349.9760 (M^+), Found: 349.9765. IR (KBr): ν_{max} = 1732, 1702, 1266, 1176 cm^{-1}.

Methyl-5-methoxy-1-oxo-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate 2j



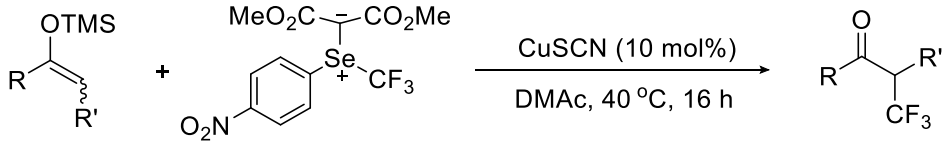
Pale yellow oil (150 mg, 99%). Eluent: ethyl acetate/petroleum ether = 1/20 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.71 (d, *J* = 7.9 Hz, 1 H), 7.32 (t, *J* = 8.0 Hz, 1 H), 7.06 (d, *J* = 8.0 Hz, 1 H), 3.87 (s, 3 H), 3.74 (s, 3 H), 3.23 - 3.10 (m, 1 H), 2.89 - 2.81 (m, 1 H), 2.76 - 2.64 (m, 1 H), 2.38 (td, *J* = 13.2, 5.0 Hz, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -73.77 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 187.57, 165.94, 156.82, 132.67, 131.54, 127.85, 124.18 (q, *J* = 283.9 Hz), 120.10, 115.25, 61.97 (q, *J* = 24.1 Hz), 56.04, 53.91, 27.21 (q, *J* = 1.9 Hz), 19.27 ppm. MS (EI): 302 (M^+); HRMS (EI): Calcd for $C_{13}H_{13}O_4F_3$: 302.0766 (M^+), Found: 302.0763. IR (KBr): ν_{max} = 2958, 1743, 1700, 1586, 1474, 1264, 1180, 1127, 1100, 1067 cm^{-1}.

Adamantyl-5-oxo-6-(trifluoromethyl)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene-6-carboxylate 2k



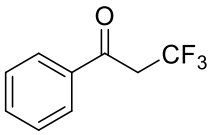
White solid (198 mg, 97%). Eluent: ethyl acetate/petroleum ether = 1/20 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.5 Hz, 1 H), 7.39 (t, *J* = 7.0 Hz, 1 H), 7.29 (t, *J* = 7.5 Hz, 1 H), 7.14 (d, *J* = 7.5 Hz, 1 H), 3.08 - 2.97 (m, 1 H), 2.93 - 2.84 (m, 1 H), 2.66 - 2.54 (m, 1 H), 2.26 - 2.18 (m, 1 H), 2.18 - 2.11 (m, 1 H), 2.08 (s, 3 H), 1.97 - 1.92 (m, 1 H), 1.91 (d, *J* = 11.9 Hz, 3 H), 1.79 (d, *J* = 11.3 Hz, 3 H), 1.57 (s, 6 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -67.99 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 197.06, 164.23, 139.39 (q, *J* = 1.5 Hz), 139.13, 131.88, 130.25, 129.66, 126.76, 124.40 (q, *J* = 285.0 Hz), 84.61, 67.84 (q, *J* = 22.5 Hz), 40.84, 36.23, 32.82, 31.08, 28.23 (q, *J* = 2.0 Hz), 23.66 ppm. MS (EI): 406 (M^+); HRMS (EI): Calcd for $C_{23}H_{25}O_3F_3$: 406.1756 (M^+), Found: 406.1755. IR (KBr): ν_{max} = 2914, 1743, 1701, 1259, 1198, 1158, 1050 cm^{-1}.

General procedure for the trifluoromethylation of silyl enol ethers 3a-k



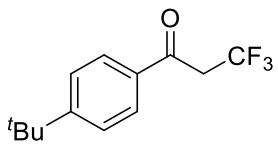
Silyl enol ethers (0.50 mmol, 1.0 equiv.), CuSCN (6.0 mg, 0.050 mmol, 0.10 equiv.), reagent **1a** (300 mg, 0.750 mmol, 1.50 equiv.) were placed into an oven-dried Schlenk tube that was equipped with a stirring bar under argon. Freshly distilled DMAc (10.0 mL) was added and the tube was quickly sealed with a rubber stopper. The mixture was stirred at 40 °C for 16 h. 20.0 mL of water and 40.0 mL of CH_2Cl_2 was added to the mixture. The organic phase was separated and extracted with water (5 × 10.0 mL), dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel.

3,3,3-Trifluoro-1-phenylpropan-1-one 3a[4]



Colorless oil (102 mg, 73%). Eluent: ethyl acetate/petroleum ether = 1/20 (R_f = 0.4). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.94 (d, *J* = 7.3 Hz, 2 H), 7.64 (t, *J* = 7.4 Hz, 1 H), 7.51 (t, *J* = 7.9 Hz, 2 H), 3.80 (q, *J* = 10.0 Hz, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.08 (t, *J* = 9.9 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 189.69, 135.86, 134.20, 128.96, 128.38, 124.02 (q, *J* = 277.1 Hz), 42.13 (q, *J* = 28.2 Hz). MS (EI): 188 (M^+); HRMS (EI): Calcd for $C_9H_7OF_3$: 188.0449 (M^+), Found: 188.0451 (M^+). IR (KBr): ν_{max} = 3359, 3090, 2978, 2947, 1686, 1651, 1597, 1581, 1493, 1474, 1451, 1421, 1373, 1326, 1274, 1228, 1186, 1100, 1001cm^{-1}.

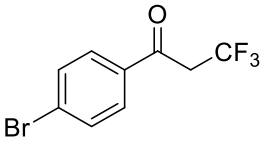
1-(4-*tert*-Butylphenyl)-3,3,3-trifluoropropan-1-one 3b[5]



Colorless oil (101 mg, 83%). Eluent: dichloromethane/petroleum ether = 1/5 (R_f = 0.4). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.86 (d, *J* = 8.5 Hz, 2 H), 7.50 (d, *J* = 8.5 Hz, 2 H), 3.76 (q, *J* = 10.1 Hz, 2 H), 1.33 (s, 9 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -

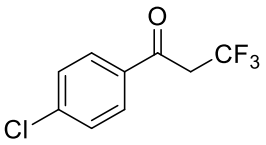
62.03 (t, J = 10.1 Hz, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 189.62, 158.54, 133.69, 128.73, 126.24, 124.44 (q, J = 276.9 Hz), 42.34 (q, J = 28.1 Hz), 35.59, 31.33 ppm. MS (EI): 244 (M^+); HRMS (EI): Calcd for $C_{13}H_{15}OF_3$: 244.1075 (M^+), Found: 244.1076 (M^+). IR (KBr): ν_{max} = 2967, 1698, 1606, 1371, 1235, 1135, 1105 cm^{-1}.

1-(4-Bromophenyl)-3,3,3-trifluoropropan-1-one 3c[5]



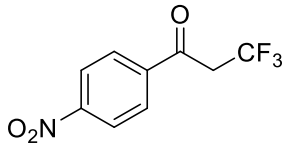
White solid (86 mg, 64%). Eluent: ethyl acetate/petroleum ether = 1/20 (R_f = 0.4). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.79 (d, J = 8.5 Hz, 2 H), 7.65 (d, J = 8.5 Hz, 2 H), 3.76 (q, J = 9.9 Hz, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.03 (t, J = 10.1 Hz, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 189.07, 134.88, 132.67, 132.24, 130.15, 124.15 (q, J = 277.1 Hz), 42.48 (q, J = 28.5 Hz) ppm. MS (EI): 266 (M^+); HRMS (EI): Calcd for $C_9H_6OF_3Br$: 265.9554 (M^+), Found: 265.9555 (M^+). IR (KBr): ν_{max} = 1700, 1587, 1422, 1373, 1267, 1128, 1101, 995, 809, 632 cm^{-1}.

1-(4-Chlorophenyl)-3,3,3-trifluoropropan-1-one 3d[6]



White solid (69 mg, 62%). Eluent: ethyl acetate/petroleum ether = 1/20 (R_f = 0.4). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.88 (d, J = 8.3 Hz, 2 H), 7.49 (d, J = 8.3 Hz, 2 H), 3.77 (q, J = 9.9 Hz, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.04 (t, J = 9.9 Hz, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 188.86, 141.25, 134.48, 130.11, 129.67, 124.17 (q, J = 277.1 Hz), 42.52 (q, J = 28.4 Hz) ppm. MS (EI): 222 (M^+); HRMS (EI): Calcd for $C_9H_6OClF_3$: 222.0059 (M^+), Found: 222.0065 (M^+). IR (KBr): ν_{max} = 1701, 1592, 1424, 1371, 1269, 1226, 1103, 998, 812 cm^{-1}.

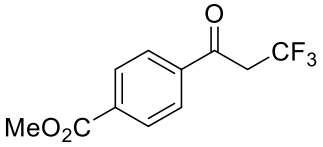
1-(4-Nitrophenyl)-3,3,3-trifluoropropan-1-one 3e[6]



Yellow solid (105 mg, 90%). Eluent: dichloromethane/petroleum ether = 1/1 (R_f = 0.4).

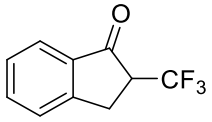
^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.36 (d, *J* = 9.0 Hz, 2 H), 8.11 (d, *J* = 8.9 Hz, 2 H), 3.86 (q, *J* = 9.7 Hz, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -61.99 (t, *J* = 9.7 Hz, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 188.65, 151.30, 140.30, 129.82, 124.53, 123.87 (q, *J* = 277.4 Hz), 43.08 (q, *J* = 29.0 Hz) ppm. MS (EI): 233 (M^+); HRMS (EI): Calcd for $C_9H_6O_3NF_3$: 233.0300 (M^+), Found: 233.0308 (M^+). IR (KBr): ν_{max} = 1698, 1606, 1522, 1351, 1131, 1104, 857 cm^{-1}.

Methyl-4-(3,3,3-trifluoropropanoyl)benzoate 3f[6]



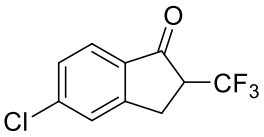
White solid (63 mg, 51%). Eluent: dichloromethane/petroleum ether = 1/1 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.15 (d, *J* = 8.3 Hz, 2 H), 7.98 (d, *J* = 8.6 Hz, 2 H), 3.95 (s, 3 H), 3.83 (q, *J* = 9.9 Hz, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.10 (t, *J* = 9.9 Hz, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 189.60, 166.20, 139.16, 135.23, 130.43, 128.61, 124.14 (q, *J* = 277.1 Hz), 52.92, 42.79 (q, *J* = 28.5 Hz) ppm. MS (EI): 246 (M^+); HRMS (EI): Calcd for $C_{11}H_9O_3F_3$: 246.0504 (M^+), Found: 246.0509 (M^+). IR (KBr): ν_{max} = 1720, 1694, 1419, 1281, 1226, 1105, 1000 cm^{-1}.

2-(Trifluoromethyl)-2,3-dihydro-1H-inden-1-one 3g[4]



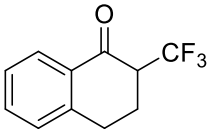
White solid (62 mg, 62%). Eluent: dichloromethane/petroleum ether = 1/5 (R_f = 0.4). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.81 (d, *J* = 7.7 Hz, 1 H), 7.66 (t, *J* = 7.4 Hz, 1 H), 7.52 (d, *J* = 7.7 Hz, 1 H), 7.43 (t, *J* = 7.4 Hz, 1 H), 3.53 - 3.38 (m, 2 H), 3.34 - 3.29 (m, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -67.58 (d, *J* = 8.8 Hz, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 197.14, 152.41, 136.15, 128.52, 126.85, 125.27 (q, *J* = 278.4 Hz), 125.03, 50.11 (q, *J* = 27.4 Hz), 27.93 (q, *J* = 2.2 Hz) ppm. MS (EI): 200 (M^+); HRMS (EI): Calcd for $C_{10}H_7OF_3$: 200.0449 (M^+), Found: 200.0451 (M^+). IR (KBr): ν_{max} = 1723, 1602, 1345, 1250, 1184, 1098 cm^{-1}.

5-Chloro-2-(trifluoromethyl)-2,3-dihydro-1*H*-inden-1-one 3h



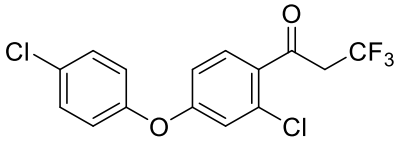
Yellow solid (66 mg, 56%). Eluent: dichloromethane/petroleum ether = 1/5 (R_f = 0.3). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.74 (d, *J* = 8.2 Hz, 1 H), 7.52 (s, 1 H), 7.41 (d, *J* = 8.2 Hz, 1 H), 3.48 - 3.40 (m, 2 H), 3.34 - 3.25 (m, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -73.18 (d, *J* = 9.4 Hz, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 195.62, 153.77, 142.91, 134.62, 129.47, 127.10, 126.16, 125.04 (q, *J* = 278.5 Hz), 50.22 (q, *J* = 27.7 Hz), 27.68 (q, *J* = 2.4 Hz) ppm. MS (EI): 234 (M^+); HRMS (EI): Calcd for $C_{10}H_6OClF_3$: 234.0059 (M^+), Found: 234.0058 (M^+). IR (KBr): ν_{max} = 1732, 1601, 1348, 1289, 1254, 1111, 1070 cm^{-1}.

2-(Trifluoromethyl)-3,4-dihydronaphthalen-1(2H)-one 3i[4]



White solid (68 mg, 63%). Eluent: dichloromethane/petroleum ether = 1/5 (R_f = 0.4). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.06 (d, *J* = 7.8 Hz, 1 H), 7.52 (t, *J* = 7.2 Hz, 1 H), 7.35 (t, *J* = 7.5 Hz, 1 H), 7.27 (d, *J* = 7.8 Hz, 1 H), 3.33 - 3.22 (m, 1 H), 3.16 - 3.02 (m, 2 H), 2.55 - 2.45 (m, 1 H), 2.34 - 2.21 (m, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -67.79 (d, *J* = 9.5 Hz, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 190.54, 143.41, 134.52, 132.29, 129.12, 128.21, 127.45, 125.41 (q, *J* = 279.9 Hz), 51.24 (q, *J* = 25.5 Hz), 27.87, 23.79 (q, *J* = 2.6 Hz) ppm. MS (EI): 214 (M^+); HRMS (EI): Calcd for $C_{11}H_9OF_3$: 214.0605 (M^+), Found: 214.0607 (M^+). IR (KBr): ν_{max} = 1700, 1596, 1382, 1257, 1181, 1097 cm^{-1}.

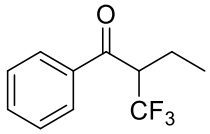
1-(2-Chloro-4-(4-chlorophenoxy)phenyl)-3,3,3-trifluoropropan-1-one 3j



Yellow oil (72 mg, 41%). Eluent: dichloromethane/petroleum ether = 1/5 (R_f = 0.3). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.64 (d, *J* = 8.7 Hz, 1 H), 7.39 (d, *J* = 8.7 Hz, 2 H), 7.02 (d, *J* = 8.8 Hz, 2 H), 6.99 (d, *J* = 2.2 Hz, 1 H), 6.92 (dd, *J* = 8.7, 2.2 Hz, 1

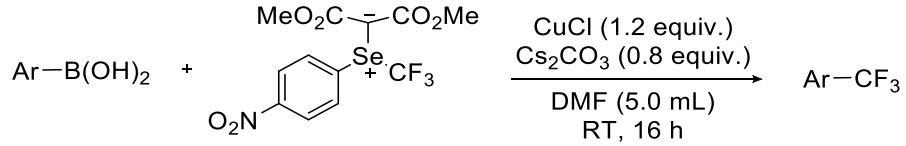
H), 3.86 (q, J = 9.9 Hz, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.22 (t, J = 9.9 Hz, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 161.53, 153.58, 134.01, 132.66, 131.87, 130.96, 130.70, 123.98 (q, J = 277.5 Hz), 122.02, 121.78, 119.70, 116.42, 46.30 (q, J = 28.1 Hz) ppm. MS (EI): 348 (M^+); HRMS (EI): Calcd for $C_{15}H_9O_2Cl_2F_3$: 347.9932 (M^+), Found: 347.9937 (M^+). IR (KBr): ν_{max} = 1702, 1584, 1485, 1370, 1231, 1134, 1102, 1054, 920 cm^{-1}.

1-Phenyl-2-(trifluoromethyl)butan-1-one 3k[4]



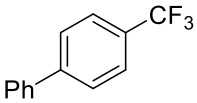
Colorless oil (60 mg, 56%). Eluent: ethyl acetate/petroleum ether = 1/20 (R_f = 0.4). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.97 (d, J = 7.7 Hz, 2 H), 7.63 (t, J = 7.3 Hz, 1 H), 7.52 (t, J = 7.6 Hz, 2 H), 4.21 - 4.03 (m, 1 H), 2.19 - 2.07 (m, 1 H), 2.01 - 1.90 (m, 1 H), 0.96 (t, J = 7.4 Hz, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -66.21 (d, J = 8.2 Hz, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 194.36, 136.81, 133.76, 128.72, 128.34, 124.83 (q, J = 280.8 Hz), 50.60 (q, J = 25.3 Hz), 20.26, 11.38 ppm.

General procedure for trifluoromethylation of arylboronic acids with reagent 1a



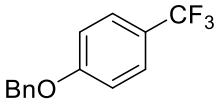
In the glove box, CuCl (60.0 mg, 0.600 mmol, 1.20 equiv.) and Cs_2CO_3 (130 mg, 0.400 mmol, 0.800 equiv.) were placed into an oven-dried Schlenk tube that was equipped with a stirring bar. A solution of aryl boronic acid (0.50 mmol, 1.0 equiv.) and reagent **1a** (300 mg, 0.750 mmol, 1.50 equiv.) in 5.0 mL of freshly distilled DMF was added. The reaction was stirred at room temperature for 16 h. Distilled water (20.0 mL) and CH_2Cl_2 (20.0 mL) were added and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (10.0 mL × 5) and the combined organic extracts were dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The product was purified by flash chromatography on silica gel or further purified by Kugelrohr distillation.

4-(Trifluoromethyl)biphenyl 4a[7]



White solid (99 mg, 89%). Eluent: petroleum ether (R_f = 0.8). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.70 (s, 4 H), 7.64 - 7.58 (m, 2 H), 7.48 (t, *J* = 7.4 Hz, 2 H), 7.44 - 7.38 (m, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.41 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 145.07, 140.10, 129.68 (q, *J* = 32.4 Hz), 129.32, 128.52, 127.75, 127.61, 126.04 (q, *J* = 3.8 Hz), 124.65 (q, *J* = 268.1 Hz) ppm. MS (EI): 222 (M^+); HRMS (EI): Calculated for $C_{13}H_9F_3$: 222.0652 (M^+), Found: 222.0656. IR (KBr): ν_{max} = 1332, 1162, 1114, 1075, 844, 768, 729, 690 cm^{-1}.

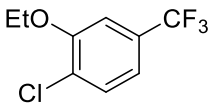
1-(Benzyloxy)-4-(trifluoromethyl)benzene 4b[7]



White solid (107mg, 85%). Eluent: petroleum ether (R_f = 0.8). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.55 (d, *J* = 8.5 Hz, 2 H), 7.46 - 7.32 (m, 5 H), 7.04 (d, *J* = 8.5 Hz, 2 H), 5.11 (s, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -61.52 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 161.50, 136.54, 129.05, 128.59, 127.79, 127.27 (q, *J* =

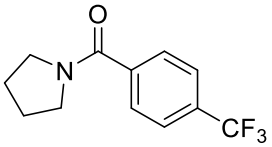
3.7 Hz), 124.75 (d, J = 271.0 Hz), 123.45 (q, J = 32.7 Hz), 115.18, 70.51 ppm. MS (EI): 252 (M^+); HRMS (EI): Calculated for $C_{14}H_{11}OF_3$: 252.0754 (M^+), Found: 252.0762. IR (KBr): ν_{max} = 1614, 1519, 1336, 1247, 1168, 1098, 1064, 1005 cm^{-1}.

1-Chloro-2-ethoxy-4-(trifluoromethyl)-benzene 4c



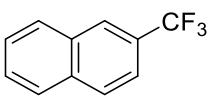
Colorless oil (102 mg, 91%). Eluent: petroleum ether (R_f = 0.8). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.53 (s, 1 H), 7.41 (d, J = 8.6 Hz, 1 H), 7.26 (s, 1 H), 6.91 (d, J = 8.7 Hz, 1 H), 4.09 (q, J = 12.4, 5.8 Hz, 2 H), 1.44 (t, J = 5.8 Hz, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.87 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 155.90, 133.21, 127.50 (q, J = 5.4 Hz), 125.25, 123.20 (q, J = 272.7 Hz), 120.70 (q, J = 31.5 Hz), 114.64, 65.26, 14.80 ppm. MS (EI): 224 (M^+); HRMS (EI): Calcd for $C_9H_8OF_3Cl$: 224.0212 (M^+), Found: 224.0216. IR (KBr): ν_{max} = 2987, 1608, 1495, 1319, 1280, 1138, 1053, 692 cm^{-1}.

1-Pyrrolidinyl[4-(trifluoromethyl)phenyl]-methanone 4d[8]



Yellow oil (98 mg, 81%). Eluent: ethyl acetate/petroleum ether = 1/3 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.66 (d, J = 8.2 Hz, 2 H), 7.61 (d, J = 8.1 Hz, 2 H). 3.65 (t, J = 6.9 Hz, 2 H), 3.38 (t, J = 6.5 Hz, 2 H), 2.05 - 1.83 (m, 4 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.97 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 168.58, 141.03, 132.01 (q, J = 32.5 Hz), 128.99, 128.84, 127.79, 125.71 (q, J = 3.7 Hz), 124.11 (q, J = 272.5 Hz), 49.81, 46.58, 26.70, 24.73 ppm. MS (EI): 243 (M^+); HRMS (EI): Calcd for $C_{12}H_{12}NOF_3$: 243.0867 (M^+), Found: 243.0871. IR (KBr): ν_{max} = 1613, 1448, 1325, 1131, 1110, 1067, 863 cm^{-1}.

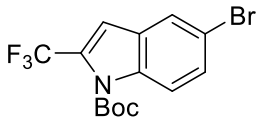
2-(Trifluoromethyl)naphthalene 4e[7]



White solid (70 mg, 71%). Eluent: petroleum ether (R_f = 0.8). ^{1}H NMR (400 MHz,

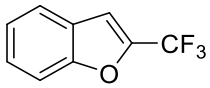
$CDCl_3$, 293 K, TMS) δ 8.16 (s, 1 H), 7.99 - 7.88 (m, 3 H), 7.69 - 7.55 (m, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.28 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 134.90, 132.53, 129.31, 129.15, 128.39, 128.20, 127.91, 127.49, 126.02 (q, *J* = 4.5 Hz), 124.74 (d, *J* = 270.6 Hz), 121.78 (q, *J* = 3.1 Hz) ppm. MS (EI): 196 (M^+); HRMS (EI): Calcd for $C_{11}H_7F_3$: 196.0494 (M^+), Found: 196.0500. IR (KBr): ν_{max} = 1147, 1132, 1111, 826, 753 cm^{-1}.

5-Bromo-N-boc-2-(trifluoromethyl)-1-*H*-indole 4f



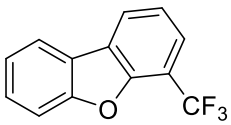
Pale yellow oil (141 mg, 91%). Eluent: petroleum ether (R_f = 0.8). ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.17 (d, *J* = 9.0 Hz, 1 H), 7.74 (d, *J* = 1.9 Hz, 1 H), 7.53 (dd, *J* = 9.0, 2.0 Hz, 1 H), 7.06 (s, 1 H), 1.67 (s, 9 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -58.38 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 148.56, 136.77, 130.28, 128.38, 128.30 (d, *J* = 39.2 Hz), 124.83, 120.74 (q, *J* = 268.0 Hz), 117.98, 117.11, 112.68 (q, *J* = 5.1 Hz), 86.37, 28.15 ppm. MS (EI): 363 (M^+); HRMS (EI): Calcd for $C_{14}H_{13}NO_2BrF_3$: 363.0083 (M^+), Found: 363.0082. IR (KBr): ν_{max} = 1759, 1385, 1347, 1284, 1240, 1145 cm^{-1}.

2-(Trifluoromethyl)benzofurane 4g[7]



Colorless oil (85 mg, 92%). Eluent: petroleum ether (R_f = 0.8). ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.73 - 7.55 (m, 2 H), 7.50 - 7.31 (m, 2 H), 7.17 (s, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -64.88 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 143.64, 127.28, 126.36, 125.87, 124.33, 122.84, 119.68 (q, *J* = 267.9 Hz), 112.47, 108.47 (q, *J* = 3.0 Hz) ppm.

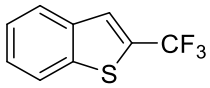
4-(Trifluoromethyl)-dibenzofuran 4h



White solid (97 mg, 82%). Eluent: pentane (R_f = 0.8). ^1H NMR (400 MHz, $CDCl_3$, 293

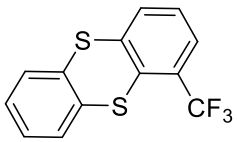
K, TMS) δ 8.09 (d, *J* = 7.7 Hz, 1 H), 7.95 (d, *J* = 7.6 Hz, 1 H), 7.73 - 7.62 (m, 2 H), 7.52 (t, *J* = 7.7 Hz, 1 H), 7.43 - 7.36 (m, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -61.05 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 138.76, 135.97, 135.61, 134.11, 132.21, 129.35, 128.64, 128.34, 128.09, 127.03, 127.65, 125.50 (q, *J* = 5.5 Hz), 123.37 (d, *J* = 274.1 Hz) ppm. MS (EI): 236 (M^+); HRMS (EI): Calcd for $C_{13}H_7OF_3$: 236.0453 (M^+), Found: 236.0449. IR (KBr): ν_{max} = 1453, 1429, 1326, 1197, 1121, 1034, 746 cm^{-1}.

2-(Trifluoromethyl)benzo[b]thiophene 4i[7]



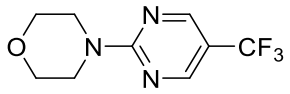
White solid (85 mg, 83%). Eluent: petroleum ether (R_f = 0.8). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.88 (t, *J* = 5.9 Hz, 2 H), 7.70 (s, 1 H), 7.52 - 7.42 (m, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -56.33 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 140.50, 138.12, 130.35 (q, *J* = 36.6 Hz), 126.91, 125.98 (q, *J* = 4.2 Hz), 125.57, 125.46, 122.98, 122.84 (d, *J* = 275.7 Hz) ppm. MS (EI): 202 (M^+); HRMS (EI): Calcd for $C_9H_5F_3S$: 202.0059 (M^+), Found: 202.0064. IR (KBr): ν_{max} = 2961, 1261, 1093, 1020, 800 cm^{-1}.

1-(Trifluoromethyl)-thianthrene 4j



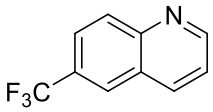
White solid (97 mg, 82%). Eluent: pentane (R_f = 0.8). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.68 (d, *J* = 7.8 Hz, 1 H), 7.62 (d, *J* = 7.8 Hz, 1 H), 7.60 – 7.57 (m, 1 H), 7.53 - 7.50 (m, 1 H), 7.36 - 7.27 (m, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -60.83 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 139.13, 136.34, 136.00, 134.51, 132.58, 130.13 (d, *J* = 30.7 Hz), 129.73, 129.01, 128.70, 128.46, 127.39, 125.87 (q, *J* = 5.5 Hz), 123.71 (d, *J* = 274.1 Hz) ppm. MS (EI): 284 (M^+); HRMS (EI): Calcd for $C_{13}H_7S_2F_3$: 283.9944 (M^+), Found: 283.9941. IR (KBr): ν_{max} = 1408, 1313, 1121, 788, 746, 721 cm^{-1}.

4-[5-(Trifluoromethyl)-2-pyrimidinyl]-morpholine 4k



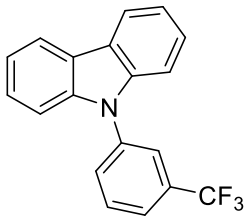
Pale yellow oil (112 mg, 96%). Eluent: ethyl acetate/petroleum ether = 1/40 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.49 (s, 2 H), 3.91 - 3.85 (m, 4 H), 3.78 - 3.73 (m, 4 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -61.18 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 162.60, 155.74 (q, *J* = 3.5 Hz), 124.43 (q, *J* = 270.0 Hz), 113.62 (q, *J* = 33.9 Hz), 67.02, 44.56 ppm. MS (EI): 233 (M^+); HRMS (EI): Calcd for $C_9H_{10}N_3OF_3$: 233.0780 (M^+), Found: 233.0776. IR (KBr): ν_{max} = 1616, 1550, 1326, 1254, 1101, 959 cm^{-1}.

6-(Trifluoromethyl)quinolone 4l[9]



White solid (54mg, 55%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 9.03 (s, 1 H), 8.23 (t, *J* = 9.3 Hz, 2 H), 8.13 (s, 1 H), 7.88 (d, *J* = 8.8 Hz, 1 H), 7.54 - 7.44 (m, 1 H);^{19}F NMR (375 MHz, $CDCl_3$) δ -62.41 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 152.31, 148.95, 136.66, 130.55, 128.24 (q, *J* = 32.6 Hz), 127.01, 125.63 (q, *J* = 4.4 Hz), 124.93 (q, *J* = 3.0 Hz), 123.84 (q, *J* = 272.3 Hz), 122.10 ppm.

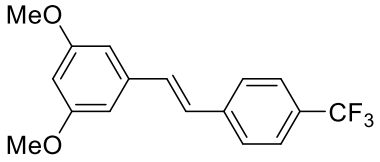
9-[3-(Trifluoromethyl)phenyl]-9*H*-carbazole 4m



White solid (114 mg, 73%). Eluent: petroleum ether (R_f = 0.7). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.16 (d, *J* = 7.7 Hz, 2 H), 7.88 (s, 1 H), 7.82 - 7.70 (m, 3 H), 7.49 - 7.29 (m, 6 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.69 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 140.84, 138.82, 132.91 (q, *J* = 35.2 Hz), 130.92, 130.69, 126.57, 124.41 (q, *J* = 3.6 Hz), 124.30 (q, *J* = 3.7 Hz), 124.02 (q, *J* = 272.4 Hz), 123.98, 120.84, 120.83, 109.76 ppm. MS (EI): 311 (M^+); HRMS (EI): Calculated for $C_{19}H_{12}NF_3$: 311.0931 (M^+), Found: 311.0922. IR (KBr): ν_{max} = 1593, 1499, 1451, 1323, 1230, 1129,

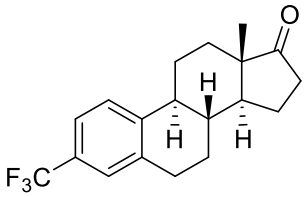
749 cm^{-1}.

1,3-Dimethoxy-5-[(1*E*)-2-[4-(trifluoromethyl)phenyl]ethenyl]-benzene 4n[10]



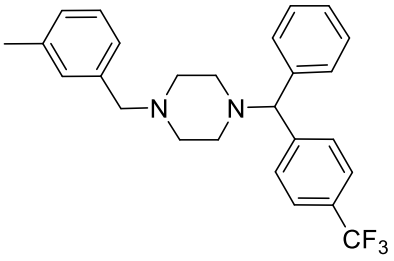
Pale yellow oil (133 mg, 86%). Eluent: ethyl acetate/petroleum ether = 1/20 (R_f = 0.7). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.73 - 7.50 (m, 4 H), 7.10 (s, 2 H), 6.70 (s, 2 H), 6.46 (s, 1 H), 3.84 (s, 6 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.77 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 161.34, 140.90, 138.90, 131.44, 129.53 (q, *J* = 32.4 Hz), 127.84, 126.92, 125.86 (q, *J* = 3.8 Hz), 124.56 (d, *J* = 272.2 Hz), 105.16, 100.79, 55.59 ppm. MS (EI): 308 (M^+); HRMS (EI): Calcd for $C_{17}H_{15}O_2F_3$: 308.1026 (M^+), Found: 308.1024. IR (KBr): ν_{max} = 1614, 1589, 1458, 1326, 1208, 1111, 1068, 841 cm^{-1}.

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(trifluoromethyl)-7,8,9,11,12,13,15,16-octahydro-6*H*-cyclopenta[*a*]phenanthren-17(14*H*)-one 4o[11]



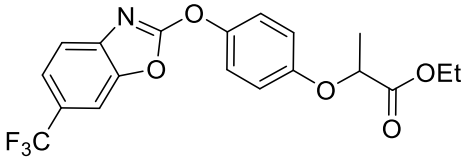
White solid (114 mg, 71%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.7). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.43 - 7.32 (m, 2 H), 7.22 - 7.06 (m, 1 H), 3.10 - 2.83 (m, 2 H), 2.60 - 2.50 (m, 1 H), 2.48 - 2.41 (m, 1 H), 2.39 - 2.31 (m, 1 H), 2.23 - 1.97 (m, 4 H), 1.70 - 1.40 (m, 6 H), 0.92 (s, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.82 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 219.37, 142.72, 136.24, 127.09 (q, *J* = 32.2 Hz), 124.75, 124.70 (q, *J* = 3.8 Hz), 121.43 (q, *J* = 3.8 Hz), 120.63 (q, *J* = 271.8 Hz), 49.49, 46.86, 43.43, 36.81, 34.78, 30.52, 28.26, 25.18, 24.60, 20.56, 12.78 ppm. MS (EI): 322 (M^+). HRMS (EI): Calcd for $C_{19}H_{21}OF_3$: 322.1555 (M^+), Found: 322.1545; IR (KBr): ν_{max} = 2937, 1732, 1507, 1326, 1138, 1006, 844 cm^{-1}.

1-[(3-Methylphenyl)methyl]-4-[phenyl[4-(trifluoromethyl)phenyl]methyl]-piperazine 4p[12]



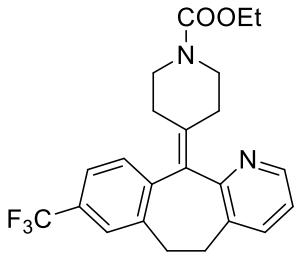
Pale yellow oil (188 mg, 89%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.6). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.57 (s, 4 H), 7.42 (d, *J* = 7.1 Hz, 2 H), 7.31 (t, *J* = 7.2 Hz, 2 H), 7.27 - 7.20 (m, 2 H), 7.18 - 7.07 (m, 3 H), 4.34 (s, 1 H), 3.54 (s, 2 H), 2.76 - 2.42 (m, 8 H), 2.37 (s, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.70 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 147.34, 142.01, 138.05, 137.98, 130.33, 129.36 (q, *J* = 31.8 Hz), 128.93, 128.43, 128.36, 128.25, 128.12, 127.59, 126.71, 125.73 (q, *J* = 3.7 Hz), 124.49 (q, *J* = 271.8 Hz), 76.08, 63.33, 53.55, 52.07, 21.67 ppm. MS (EI): 424 (M^+); HRMS (EI): Calcd for $C_{26}H_{27}N_2F_3$: 424.2119 (M^+), Found: 424.2126. IR (KBr): ν_{max} = 2925, 1324, 1162, 1125, 1066 cm^{-1}.

Ethyl-2-[4-(5-trifluoromethylbenzoxazol-2-yloxy)phenoxy]propionate 4q



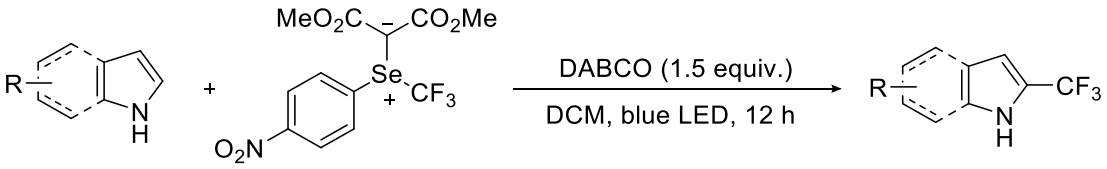
Pale yellow solid (160 mg, 86%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.3). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.69 (s, 1 H), 7.56 (s, 2 H), 7.32 (d, *J* = 9.1 Hz, 2 H), 6.96 (d, *J* = 9.0 Hz, 2 H), 4.74 (q, *J* = 6.6 Hz, 1 H), 4.24 (q, *J* = 7.1 Hz, 2 H), 1.64 (d, *J* = 6.8 Hz, 3 H), 1.28 (t, *J* = 7.1 Hz, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -61.45 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 172.17, 164.37, 156.31, 148.18, 146.99, 144.18, 126.15 (q, *J* = 33.0 Hz), 124.43 (q, *J* = 271.8 Hz), 122.31 (q, *J* = 3.8 Hz), 121.56, 119.17, 116.66, 107.92 (q, *J* = 4.1 Hz), 73.58, 61.79, 18.90, 14.48 ppm. MS (EI): 395 (M^+); HRMS (EI): Calcd for $C_{19}H_{16}NO_5F_3$: 395.0978 (M^+), Found: 395.0981. IR (KBr): ν_{max} = 1739, 1630, 1574, 1325, 1191, 1118 cm^{-1}.

Ethyl-4-[8-(trifluoromethyl)-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*] pyridin-11-ylidene]-1-piperidinecarboxylate 4r



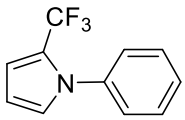
Pale yellow solid (160 mg, 77%). Eluent: ethyl acetate/petroleum ether = 1/1 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.41 (d, *J* = 3.9 Hz, 1 H), 7.43 (t, *J* = 8.8 Hz, 2 H), 7.30 (d, *J* = 7.8 Hz, 1 H), 7.26 (s, 1 H), 7.15 - 7.07 (m, 1 H), 4.13 (q, *J* = 7.1 Hz, 2 H), 3.87 - 3.70 (m, 2 H), 3.55 - 3.30 (m, 2 H), 3.23 - 3.08 (m, 2 H), 2.96 - 2.77 (m, 2 H), 2.57 - 2.45 (m, 1 H), 2.41 - 2.25 (m, 3 H), 1.24 (t, *J* = 7.1 Hz, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -67.28 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 156.83, 155.81, 147.15, 143.38, 138.87, 138.40, 138.01, 134.56, 133.63, 129.92, 126.18 (q, *J* = 3.7 Hz), 124.45 (d, *J* = 272.1 Hz), 123.29 (q, *J* = 3.9 Hz), 122.76, 61.69, 45.12, 45.10, 32.07, 31.86, 31.12, 30.87, 15.02 ppm. MS (EI): 416 (M^+); HRMS (EI): Calcd for $C_{23}H_{23}N_2O_2F_3$: 416.1723 (M^+), Found: 416.1712. IR (KBr): ν_{max} = 1698, 1437, 1327, 1231, 1161, 1120 cm^{-1}.

General procedure for the trifluoromethylation of electron-rich arene with reagent 1a



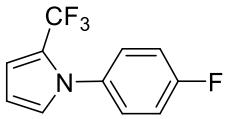
Heteroarene (0.50 mmol, 1.0 equiv.), DABCO (84 mg, 0.75 mmol, 1.5 equiv.), reagent **1a** (240 mg, 0.600 mmol, 1.20 equiv.) were placed into an oven-dried Schlenk tube that was equipped with a stirring bar under Ar. Freshly distilled CH_2Cl_2 (10.0 mL) was added and the tube was quickly sealed with a rubber stopper. The mixture was stirred under blue LED for 12 h. The mixture was concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel or further purified by Kugelrohr distillation.

1-Phenyl-2-(trifluoromethyl)-1*H*-Pyrrole 5a[13]



Colorless liquid (105 mg, 99%). Eluent: petroleum ether (R_f = 0.8). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.48 - 7.44 (m, 3 H), 7.42 - 7.38 (m, 2 H), 6.90 (t, 1 H), 6.77 - 6.74 (m, 1 H), 6.29 (t, *J* = 3.2 Hz, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -55.95 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 139.51, 129.33, 128.84, 127.62, 126.89, 122.63 (q, *J* = 38.2 Hz), 121.57 (q, *J* = 266.9 Hz), 113.09 (q, *J* = 3.4 Hz), 108.59 ppm. MS (EI): 211 (M^+); HRMS (EI): Calcd for $C_{11}H_8F_3N$: 211.0609 (M^+), Found: 211.0611. IR (KBr): ν_{max} = 1552, 1501, 1285, 1151, 1108, 733, 696 cm^{-1}.

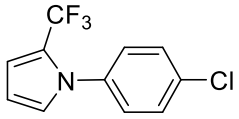
1-(4-Fluorophenyl)-2-(trifluoromethyl)-1*H*-pyrrole 5b



Colorless liquid (102 mg, 89%). Eluent: petroleum ether (R_f = 0.8). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.41 - 7.30 (m, 2 H), 7.13 (t, *J* = 8.5 Hz, 2 H), 6.85 (s, 1 H), 6.75 - 6.69 (m, 1 H), 6.27 (t, *J* = 3.1 Hz, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -56.14 (s, 3 F), -112.63 - -112.79 (m, 1 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 162.71

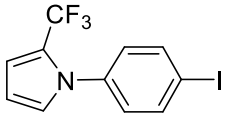
(d, J = 248.4 Hz), 135.00 (d, J = 3.4 Hz), 128.38 (d, J = 8.7 Hz), 127.31 (d, J = 1.9 Hz), 121.04 (q, J = 266.8 Hz), 115.87 (d, J = 22.9 Hz), 112.70 (q, J = 3.4 Hz), 108.31 ppm. MS (EI): 229 (M^+); HRMS (EI): Calcd for $C_{11}H_7F_4N$: 229.0515 (M^+), Found: 229.0518. IR (KBr): ν_{max} = 2954, 2920, 2850, 1733, 1457, 1377, 1260, 1026 cm^{-1}.

1-(4-Chlorophenyl)-2-(trifluoromethyl)-1*H*-pyrrole 5c



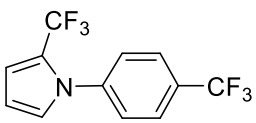
Colorless solid (114 mg, 93%). Eluent: petroleum ether (R_f = 0.8). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.43 (d, J = 8.7 Hz, 2 H), 7.33 (d, J = 8.7 Hz, 2 H), 6.88 - 6.83 (m, 1 H), 6.76 - 6.75 (m, 1 H), 6.33 - 6.26 (m, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -56.87 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 137.95, 134.87, 129.59, 128.15, 127.51 (q, J = 1.9 Hz), 122.67 (q, J = 38.3 Hz), 121.43 (q, J = 266.8 Hz), 113.43 (q, J = 3.4 Hz), 108.97 ppm. MS (EI): 245 (M^+); HRMS (EI): Calcd for $C_{11}H_7F_3NCl$: 245.0219 (M^+), Found: 245.0226. IR (KBr): ν_{max} = 3130, 2924, 1900, 1684, 1598, 1553, 1500, 1466, 1438, 1367, 1320, 1286, 1214, 1153, 1108, 1076, 1038, 1017 cm^{-1}.

1-(4-Iodophenyl)-2-(trifluoromethyl)-1*H*-pyrrole 5d[14]



Colorless solid (152 mg, 90%). Eluent: petroleum ether (R_f = 0.8). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.79 (d, J = 8.2 Hz, 2 H), 7.14 (d, J = 8.2 Hz, 2 H), 6.86 (s, 1 H), 6.75-6.77 (m, 1 H), 6.29-6.31 (m, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -55.80 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 139.11, 138.57, 128.57, 127.36, 122.47 (q, J = 38.4 Hz), 121.37 (q, J = 266.9 Hz), 113.52 (q, J = 3.4 Hz), 109.02, 94.22 ppm. MS (EI): 337 (M^+); HRMS (EI): Calcd for $C_{11}H_7F_3NI$: 336.9575 (M^+), Found: 336.9580. IR (KBr): ν_{max} = 1552, 1493, 1283, 1103, 829, 729, 536 cm^{-1}.

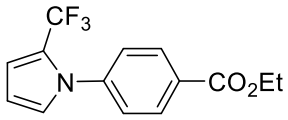
1-(4-Trifluoromethylphenyl)-2-(trifluoromethyl)-1*H*-pyrrole 5e



Colorless liquid (95 mg, 91%). Eluent: petroleum ether (R_f = 0.8). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.74 (d, J = 8.3 Hz, 2 H), 7.53 (d, J = 8.2 Hz, 2 H), 6.90-6.93

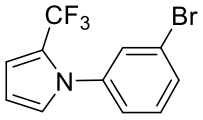
(m, 1 H), 6.79 (s, 1 H), 6.33 (t, *J* = 3.0 Hz, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -55.76 (s, 3 F), -62.69 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 142.43, 131.04 (q, *J* = 33.0 Hz), 127.41 (d, *J* = 1.8 Hz), 127.10 (d, *J* = 0.6 Hz), 126.70 (q, *J* = 3.7 Hz), 124.05 (q, *J* = 267.2 Hz), 122.66 (q, *J* = 38.4 Hz), 121.39 (q, *J* = 267.1 Hz), 114.02 (q, *J* = 3.4 Hz), 109.44 ppm. MS (EI): 279 (M^+); HRMS (EI): Calcd for $C_{12}H_7F_6N$: 279.0483 (M^+), Found: 279.0490. IR (KBr): ν_{max} = 1468, 1440, 1327, 1284, 1105, 1066, 851, 735 cm^{-1}.

Ethyl-4-(2-(trifluoromethyl)-1*H*-pyrrol-1-yl)benzoate 5f



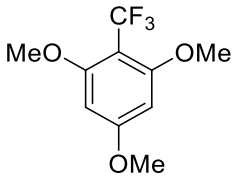
Colorless liquid (121 mg, 85%). Eluent: ethyl acetate/petroleum ether = 1/40 (R_f = 0.5). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.14 (d, *J* = 8.4 Hz, 2 H), 7.46 (d, *J* = 8.4 Hz, 2 H), 6.91 (t, *J* = 3.3 Hz, 1 H), 6.79 - 6.73 (m, 1 H), 6.31 (t, *J* = 3.3 Hz, 1 H), 4.41 (q, *J* = 7.1 Hz, 2 H), 1.42 (t, *J* = 7.1 Hz, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -55.69 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 165.96, 143.10, 130.83, 130.79, 127.32, 126.43, 122.48 (q, *J* = 38.3 Hz), 121.37 (q, *J* = 266.9 Hz), 113.90 (q, *J* = 3.2 Hz), 109.25, 61.66, 14.63 ppm. MS (ESI): 284 ($M+H^+$); HRMS (ESI): Calcd for $C_{14}H_{13}F_3NO_2$: 284.0893 ($M+H^+$), Found: 284.0893. IR (KBr): ν_{max} = 1721, 1610, 1553, 1367, 1283, 1153, 1113, 1078 cm^{-1}.

1-(3-Bromophenyl)-2-(trifluoromethyl)-1*H*-pyrrole 5g



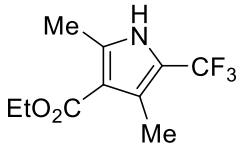
Colorless liquid (130 mg, 90%). Eluent: petroleum ether (R_f = 0.6). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.62 - 7.54 (m, 2 H), 7.38 - 7.30 (m, 2 H), 6.87 (s, 1 H), 6.75 (s, 1 H), 6.30 (s, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -55.87 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 140.52, 132.03, 130.57, 130.02, 127.46 (d, *J* = 1.8 Hz), 125.55, 122.68, 122.58 (q, *J* = 38.4 Hz), 121.36 (q, *J* = 265.8 Hz), 113.56 (q, *J* = 6.9, 3.4 Hz), 109.06 ppm. MS (EI): 289 (M^+); HRMS (EI): Calcd for $C_{11}H_7F_3NBr$: 288.9714 (M^+), Found: 288.9722. IR (KBr): ν_{max} = 1593, 1486, 1365, 1285, 1153, 1112, 729 cm^{-1}.

1,3,5-Trimethoxy-4-(trifluoromethyl)benzene 5h[15]



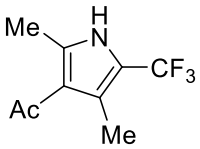
White solid (95 mg, 80%). Eluent: CH_2Cl_2/petroleum ether = 1：10 (R_f = 0.4). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 6.13 (s, 2 H), 3.83 (s, 9 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -54.14 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 163.86, 160.78 (q, *J* = 1.2 Hz), 124.68 (q, *J* = 273.3 Hz), 100.81 (q, *J* = 30.2 Hz), 91.64, 56.60, 55.71 ppm. MS (EI): 236 (M^+); HRMS (EI): Calcd for $C_7H_{12}F_4O_4$: 236.0672 (M^+), Found: 236.0677. IR (KBr): ν_{max} = 1592, 1474, 1290, 1166, 1115, 1024, 817 cm^{-1}.

Ethyl-2,4-dimethyl-5-(trifluoromethyl)-1*H*-pyrrole-3-carboxylate 5i[15]



Yellow solid (109 mg, 93%). Eluent: ethyl acetate/petroleum ether = 1/8 (R_f = 0.7). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.63 (s, 1 H), 4.28 (q, *J* = 7.1 Hz, 2 H), 2.50 (s, 3 H), 2.34 (s, 3 H), 1.35 (t, *J* = 7.1 Hz, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -57.92 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 165.47, 136.83, 123.89 (q, *J* = 2.8 Hz), 121.68 (q, *J* = 267.2 Hz), 115.34 (q, *J* = 37.4 Hz), 112.73, 59.62, 14.38, 13.95, 10.57 ppm. MS (EI): 235 (M^+); HRMS (EI): Calcd for $C_{10}H_{12}F_3NO_2$: 235.0820 (M^+), Found: 235.0813. IR (KBr): ν_{max} = 3275, 1674, 1491, 1441, 1302, 1209, 1104, 1038 cm^{-1}.

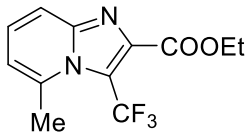
1-(2,4-Dimethyl-5-(trifluoromethyl)-1*H*-pyrrol-3-yl)ethanone 5j[16]



Yellow solid (102 mg, 99%). Eluent: ethyl acetate/petroleum ether = 1/4 (R_f = 0.4). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.63 (s, 1 H), 2.52 (s, 3 H), 2.44 (s, 3 H), 2.36 (s, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -58.11 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 195.63, 136.26, 123.02 (q, *J* = 2.6 Hz), 122.95, 121.96 (q, *J* = 267.4

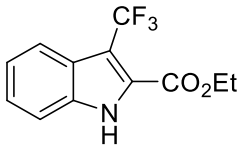
Hz), 115.97 (q, J = 37.0 Hz), 31.51, 15.35, 11.77 ppm. MS (EI): 205 (M^+); HRMS (EI): Calcd for $C_9H_{10}F_3NO$: 205.0714 (M^+), Found: 205.0711. IR (KBr): ν_{max} = 3239, 1633, 1437, 1304, 1204, 1161, 1110, 1035 cm^{-1}.

Ethyl-5-methyl-3-(trifluoromethyl)imidazo[1.2-a]pyridine-2-carboxylate 5k



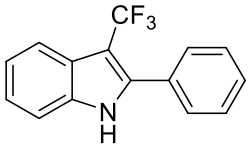
Yellow solid (54 mg, 40%). Eluent: ethyl acetate/petroleum ether = 1/3 (R_f = 0.4). ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.67 (d, J = 8.9 Hz, 1 H), 7.38 (dd, J = 9.0, 7.1 Hz, 1 H), 6.87 (d, J = 7.1 Hz, 1 H), 4.48 (q, J = 7.2 Hz, 2 H), 2.79 (s, 3 H), 1.43 (t, J = 7.1 Hz, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -48.44 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 163.82, 148.40, 141.98, 137.86, 128.61, 121.31 (d, J = 267.2 Hz), 117.24, 117.16, 106.79, 62.69, 20.73 (dd, J = 13.4, 6.7 Hz), 14.41 ppm. MS (EI): 272 (M^+); HRMS (EI): Calcd for $C_{12}H_{11}F_3N_2O_2$: 272.0773 (M^+), Found: 205.0775. IR (KBr): ν_{max} = 1742, 1542, 1513, 1346, 1227, 1112 cm^{-1}.

Ethyl 3-(trifluoromethyl)-1*H*-indole-2-carboxylate 5l[16]



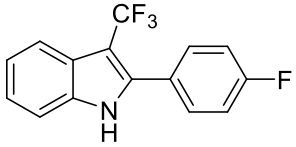
Yellow solid (78 mg, 61%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.6). ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 9.47 (s, 1 H), 7.92 (d, J = 8.2 Hz, 1 H), 7.47 (d, J = 8.3 Hz, 1 H), 7.39 (t, J = 7.5 Hz, 1 H), 7.30 - 7.24 (m, 1 H), 4.48 (q, J = 7.1 Hz, 2 H), 1.45 (t, J = 7.1 Hz, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -53.77 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 160.34, 134.50, 126.11, 125.91 (q, J = 4.0 Hz), 124.99 (q, J = 1.5 Hz), 123.83 (q, J = 268.2 Hz), 122.67, 121.96 (q, J = 3.1 Hz), 112.07, 109.97 (q, J = 37.9 Hz), 62.18, 14.00 ppm. MS (EI): 257 (M^+); HRMS (EI): Calcd for $C_{12}H_{10}F_3NO_2$: 257.0664 (M^+), Found: 257.0674. IR (KBr): ν_{max} = 3310, 1690, 1544, 1266, 1134, 1016, 754 cm^{-1}.

2-(4-Phenyl)-3-(trifluoromethyl)-1*H*-indole 5m[17]



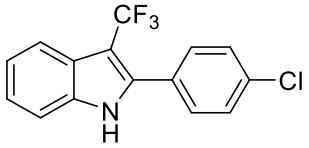
Yellow solid (126 mg, 94%). Eluent: ethyl acetate/petroleum ether = 1/20 (R_f = 0.3). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.36 (s, 1 H), 7.84 (d, *J* = 7.9 Hz, 1 H), 7.63 - 7.58 (m, 2 H), 7.53 - 7.46 (m, 3 H), 7.42 (d, *J* = 8.0 Hz, 1 H), 7.34 - 7.24 (m, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -52.92 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 138.87 (q, *J* = 3.9 Hz), 135.22, 131.42, 129.71, 129.36, 129.00, 125.93, 125.07 (q, *J* = 267.1 Hz), 123.79, 122.05, 120.38, 111.42, 103.90 (q, *J* = 35.8 Hz) ppm. MS (EI): 261 (M^+); HRMS (EI): Calcd for $C_{15}H_{10}F_3N$: 261.0765 (M^+), Found: 261.0762. IR (KBr): ν_{max} = 3408, 1493, 1452, 1168, 1000, 987, 747, 698 cm^{-1}.

2-(4-Fluorophenyl)-3-(trifluoromethyl)-1*H*-indole 5n



Yellow solid (127 mg, 91%). Eluent: ethyl acetate/petroleum ether = 1/15 (R_f = 0.3). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.28 (s, 1 H), 7.84 (d, *J* = 7.5 Hz, 1 H), 7.57 (dd, *J* = 8.1, 5.5 Hz, 2 H), 7.41 (d, *J* = 7.7 Hz, 1 H), 7.35 – 7.25 (m, 2 H), 7.19 (t, *J* = 8.6 Hz, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -52.97 (s, 3 F), -111.23 – -111.33 (m, 1 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 163.73 (d, *J* = 250.0 Hz), 137.78 (q, *J* = 3.9 Hz), 135.21, 131.28 (dd, *J* = 8.4, 1.3 Hz), 127.48 (d, *J* = 3.5 Hz), 125.83 (d, *J* = 1.6 Hz), 125.01 (q, *J* = 267.4 Hz), 123.95, 122.18, 120.37 (d, *J* = 1.5 Hz), 116.16 (d, *J* = 21.8 Hz), 111.44, 104.15 (q, *J* = 35.7 Hz) ppm. MS (EI): 279 (M^+); HRMS (EI): Calcd for $C_{15}H_9F_4N$: 279.0671 (M^+), Found: 279.0668. IR (KBr): ν_{max} = 3400, 1506, 1446, 1172, 1110, 987, 751 cm^{-1}.

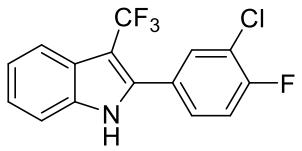
2-(4-Clorophenyl)-3-(trifluoromethyl)-1*H*-indole 5o[18]



Yellow solid (134 mg, 91%). Eluent: ethyl acetate/petroleum ether = 1/10 (R_f = 0.3). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.34 (s, 1 H), 7.82 (d, *J* = 7.8 Hz, 1 H),

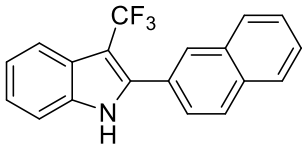
7.51 (d, *J* = 8.5 Hz, 2 H), 7.45 (d, *J* = 8.4 Hz, 2 H), 7.40 (d, *J* = 8.0 Hz, 1 H), 7.33 - 7.23 (m, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -52.88 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 137.46 (q, *J* = 4.0 Hz), 135.94, 135.27, 130.61, 129.28, 125.81 (q, *J* = 1.8 Hz), 124.94 (q, *J* = 267.4 Hz), 124.59, 124.05, 122.22, 120.40 (d, *J* = 1.5 Hz), 111.49, 104.26 (q, *J* = 35.8 Hz) ppm. MS (EI): 295 (M^+); HRMS (EI): Calcd for $C_{15}H_9F_3NCl$: 295.0376 (M^+), Found: 295.0373. IR (KBr): ν_{max} = 3404, 1490, 1443, 1167, 1089, 987, 834, 747 cm^{-1}.

2-(3-Chloro-4-fluorophenyl)-3-(trifluoromethyl)-1*H*-indole 5p



Yellow solid (147 mg, 94%). Eluent: ethyl acetate/petroleum ether = 1/20 (R_f = 0.3). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.37 (s, 1 H), 7.85 (d, *J* = 7.7 Hz, 1 H), 7.66 (dd, *J* = 6.8, 1.8 Hz, 1 H), 7.53 - 7.48 (m, 1 H), 7.44 (d, *J* = 7.9 Hz, 1 H), 7.35 (t, *J* = 7.1 Hz, 1 H), 7.33 - 7.27 (m, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -53.24 (s, 3 F), -113.79 (ddd, *J* = 8.5, 7.1, 4.7 Hz, 1 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 160.33, 157.82, 136.18 (q, *J* = 4.0 Hz), 135.30, 131.56, 129.53 (dq, *J* = 7.5, 1.6 Hz), 128.55 (d, *J* = 4.1 Hz), 125.67 (q, *J* = 1.6 Hz), 124.82 (q, *J* = 267.5 Hz), 124.29, 122.37, 120.48 (q, *J* = 1.5 Hz), 117.30 (d, *J* = 21.5 Hz), 111.53, 104.72 (q, *J* = 36.0 Hz) ppm. MS (EI): 313 (M^+); HRMS (EI): Calcd for $C_{15}H_8F_4NCl$: 313.0281 (M^+), Found: 313.0283. IR (KBr): ν_{max} = 3478, 1496, 1442, 1085, 988, 741, 532 cm^{-1}.

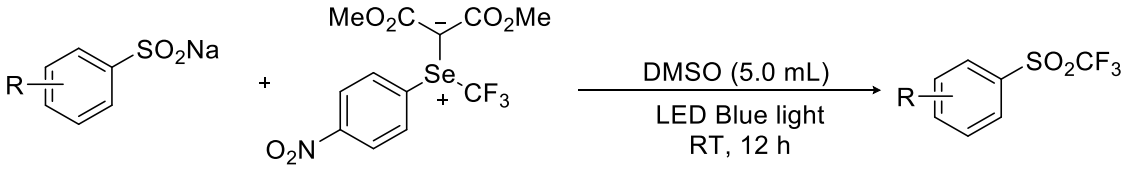
2-(Naphthalen-2-yl)-3-(trifluoromethyl)-1*H*-indole 5q



Yellow solid (93 mg, 60%). Eluent: ethyl acetate/petroleum ether = 1：15 (R_f = 0.3). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.43 (s, 1 H), 8.07 (s, 1 H), 7.97 - 7.86 (m, 4 H), 7.70 (d, *J* = 8.3 Hz, 1 H), 7.61 - 7.54 (m, 2 H), 7.43 (d, *J* = 7.2 Hz, 1 H), 7.36 - 7.27 (m, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -52.70 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 138.82 (q, *J* = 4.0 Hz), 135.33, 133.71, 133.27, 128.81 (d, *J* =

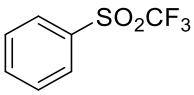
1.1 Hz), 128.75, 128.72, 128.67, 128.15, 127.43, 127.18, 126.62 (d, J = 1.6 Hz), 126.02 (d, J = 1.8 Hz), 125.16 (q, J = 264.9 Hz), 123.84, 122.09, 120.39 (d, J = 1.6 Hz), 111.46, 104.10 (q, J = 35.8 Hz) ppm. MS (EI): 311 (M^+); HRMS (EI): Calcd for $C_{19}H_{12}F_3N$: 311.0922 (M^+), Found: 311.0927. IR (KBr): ν_{max} = 3409, 1455, 1280, 1093, 998, 749 cm^{-1}.

General procedure for the trifluoromethylation of sodium arylsulfinate with reagent 1a



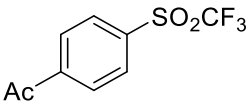
Sodium arylsulfinate (0.50 mmol, 1.0 equiv.), reagent **1a** (240 mg, 0.60 mmol, 1.20 equiv.) were placed into an oven-dried Schlenk tube that was equipped with a stirring bar under Ar and 5.0 mL of freshly distilled DMSO was added. The tube was quickly sealed with a rubber stopper. The mixture was stirred at room temperature under irradiation of blue LED light for 12 h. 20.0 mL of Water and 40.0 mL of ether was added to the mixture and the organic phase was separated and extracted with water (10.0 mL × 5), dried over anhydrous Na_2SO_4, and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel or further purified by Kugelrohr distillation.

[(Trifluoromethyl)sulfonyl]-benzene 6a[19]



Yellow liquid (100 mg, 95%). Eluent: ethyl acetate / petroleum ether = 1/100 (R_f = 0.8). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.06 (d, *J* = 7.9 Hz, 2 H), 7.85 (t, *J* = 7.5 Hz, 1 H), 7.69 (t, *J* = 7.9 Hz, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -78.47 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 136.87, 131.73, 131.13, 130.21, 120.12 (q, *J* = 325.8 Hz) ppm. MS (EI): 210 (M^+); HRMS (EI): Calcd for $C_7H_5F_3O_2S$: 209.9962 (M^+), Found: 209.9971. IR (KBr): ν = 2962, 1261, 1095, 800 cm^{-1}.

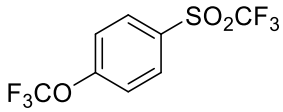
1-[4-[(Trifluoromethyl)sulfonyl]phenyl]-ethanone 6b[20]



Yellow solid (100 mg, 79%). Eluent: ethyl acetate / petroleum ether = 1/100 (R_f = 0.7). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.20 (d, *J* = 8.7 Hz, 2 H), 8.15 (d, *J* = 8.5 Hz, 2 H), 2.69 (s, 3 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -80.64 (s, 3 F); ^{13}C NMR (101

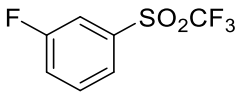
MHz, $CDCl_3$, 293 K, TMS) δ 196.51, 143.31, 135.36, 131.57, 129.67, 120.01 (q, *J* = 325.9 Hz), 27.30 ppm. MS (EI): 252 (M^+); HRMS (EI): Calcd for $C_9H_7F_3O_3S$: 252.0068 (M^+), Found: 252.0075. IR (KBr): ν = 1686, 1368, 1220, 1197, 1139, 1081, 780, 641, 604 cm^{-1}.

1-(Trifluoromethoxy)-4-[(trifluoromethyl)sulfonyl]-benzene 6c



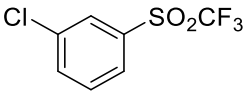
Yellow solid (145 mg, 96%). Eluent: ethyl acetate / petroleum ether = 1/80 (R_f = 0.8). ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.11 (d, *J* = 8.9 Hz, 2 H), 7.49 (d, *J* = 8.2 Hz, 2 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -57.69 (s, 3 F), -78.27 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 155.62, 133.63, 129.53, 121.48, 120.45 (q, *J* = 261.2 Hz), 120.02 (q, *J* = 325.6 Hz) ppm. MS (EI): 294 (M^+); HRMS (EI): Calcd for $C_8H_4F_6O_3S$: 293.9785 (M^+), Found: 293.9784. IR (KBr): ν = 1589, 1494, 1374, 1261, 1076, 1017, 809, 613 cm^{-1}.

1-Fluoro-3-[(trifluoromethyl)sulfonyl]-benzene 6d



Colorless liquid (110 mg, 96%). Eluent: ethyl acetate / petroleum ether = 1/100 (R_f = 0.8). ^1H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 7.87 (d, *J* = 7.8 Hz, 1 H), 7.75 (d, *J* = 7.3 Hz, 1 H), 7.70 (td, *J* = 8.1, 5.1 Hz, 1 H), 7.56 (td, *J* = 8.2, 1.7 Hz, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -78.09 (s, 3 F), -107.47 (td, *J* = 7.7, 5.3 Hz, 1 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 162.93 (d, *J* = 254.6 Hz), 133.69 (d, *J* = 7.2 Hz), 132.17 (d, *J* = 7.7 Hz), 127.06 (d, *J* = 3.5 Hz), 124.40 (d, *J* = 21.2 Hz), 120.00 (d, *J* = 322.4 Hz), 118.30 (d, *J* = 25.0 Hz) ppm. MS (EI): 228 (M^+); HRMS (EI): Calcd for $C_7H_4F_4O_2S$: 227.9868 (M^+), Found: 227.9874. IR (KBr): ν = 2961, 1261, 1094, 1020, 800 cm^{-1}.

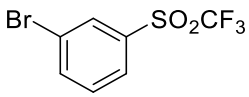
1-Chloro-3-[(trifluoromethyl)sulfonyl]-benzene 6e



Colorless liquid (116 mg, 95%). Eluent: ethyl acetate / petroleum ether = 1/100 (R_f =

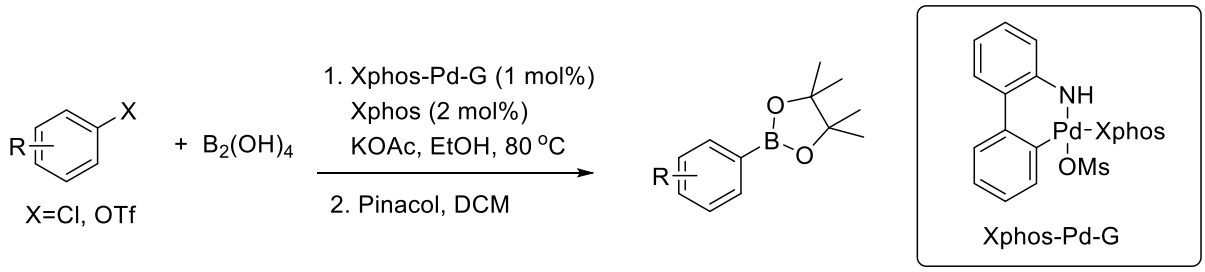
0.8). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.03 (s, 1 H), 7.95 (d, *J* = 7.9 Hz, 1 H), 7.82 (d, *J* = 8.0 Hz, 1 H), 7.64 (t, *J* = 8.0 Hz, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -78.03 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 137.09, 136.71, 131.48, 130.92, 129.20, 124.73, 119.98 (q, *J* = 325.9 Hz) ppm. MS (EI): 244 (M^+); HRMS (EI): Calcd for $C_7H_4F_3O_2SCl$: 243.9573 (M^+), Found: 243.9579. IR (KBr): ν = 2962, 1261, 1020, 800 cm^{-1}.

1-Bromo-3-[(trifluoromethyl)sulfonyl]-benzene 6f

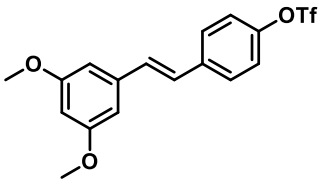


Colorless liquid (140 mg, 97%). Eluent: ethyl acetate / petroleum ether = 1/100 (R_f = 0.8). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K, TMS) δ 8.18 (s, 1 H), 7.98 (t, *J* = 7.6 Hz, 2 H), 7.57 (t, *J* = 8.0 Hz, 1 H); ^{19}F NMR (375 MHz, $CDCl_3$) δ -78.02 (s, 3 F); ^{13}C NMR (101 MHz, $CDCl_3$, 293 K, TMS) δ 140.00, 133.72, 133.61, 131.64, 129.63, 124.24, 119.96 (q, *J* = 325.9 Hz) ppm. MS (EI): 287.9 (M^+); HRMS (EI): Calcd for $C_7H_4F_3O_2SBr$: 287.9067 (M^+), Found: 287.9063. IR (KBr): ν = 2962, 2920, 1739, 1457, 1261, 1096, 800 cm^{-1}.

Procedure for the preparation of S-4n, S-4p and S-4q[21]

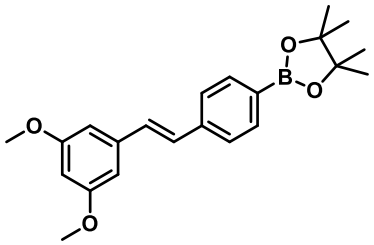


(*E*)-4-(3,5-Dimethoxystyryl)phenyl trifluoromethanesulfonate (S1-4n)



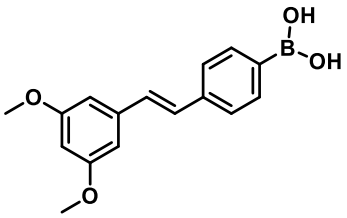
To a dried flask equipped with a stir bar and an argon balloon were added Pterostilbene (5.20 g, 20.0 mmol, 1.00 equiv.), pyridine (3.20 g, 40.0 mmol, 2.00 equiv.), and CH_2Cl_2 (60.0 mL), then trifluoromethanesulfonic anhydride (6.30 g, 30.0 mmol, 1.50 equiv.) was added dropwise at 0 °C. The solution was stirred for 2 h at 0 °C, and then 20.0 mL of water and 30.0 mL of CH_2Cl_2 were added. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified with silica gel chromatography (Eluent: ethyl acetate/petroleum ether: 1/5, R_f = 0.8) to give the product (7.4 g, 94%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.8 Hz, 2 H), 7.24 (d, *J* = 8.8 Hz, 2 H), 7.02 (d, *J* = 1.0 Hz, 2 H), 6.65-6.66 (m, 2 H), 6.42 (t, *J* = 2.2 Hz, 1 H), 3.82 (s, 6 H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.85 (s); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.02, 148.62, 138.56, 137.58, 130.74, 128.00, 126.96, 121.55, 118.73 (q, *J* = 320.9 Hz), 104.77, 100.39, 55.33 ppm. MS (ESI): 389.0 ($M+H^+$); HRMS (ESI) Calcd for $C_{17}H_{16}O_5F_3S$: 389.0665($M+H^+$). Found: 389.0658. IR (KBr): ν = 3004, 1593, 1501, 1424, 1205, 1139, 1067, 962 cm^{-1}.

(*E*)-2-(4-(3,5-Dimethoxystyryl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(S2-4n)



To a 100 mL of Schlenk tube were added anhydrous KOAc (2.94 g, 30.0 mmol, 3.00 equiv), XPhos-Pd-G (84 mg, 1.0 mol%), Xphos (95 mg, 2.0 mol%), $B_2(OH)_4$ (1.80 g, 20.0 mmol, 2.00 equiv), (*E*)-4-(3,5-dimethoxystyryl)phenyl trifluoromethanesulfonate (3.90 g, 10.0 mmol, 1.00 equiv.) under argon, followed by fresh distilled EtOH (40.0 mL). The resulting mixture was then stirred at 80 °C for 4 h. The reaction was cooled to room temperature and concentrated. The residue was dissolved in dichloromethane, and pinacol (2.36 g, 20.00 mmol, 2.00 equiv.) was added. After the resulting mixture was stirred at room temperature for 8 h, the reaction mixture was then concentrated. he residue was purified with silica gel chromatography (Eluent: ethyl acetate/petroleum ether: 1/5, R_f = 0.7) to give (*E*)-2-(4-(3,5-dimethoxystyryl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.0 g, 82%) as a white solid (Mp: 65 - 67 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.8 Hz, 2 H), 7.51 (d, *J* = 7.9 Hz, 2 H), 7.10 (s, 2 H), 6.68-6.69 (m, 2 H), 6.41 (s, 1 H), 3.83 (s, 6 H), 1.36 (s, 12 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.96, 139.78, 139.18, 135.14, 129.60, 129.12, 125.84, 104.63, 100.26, 83.79, 55.37, 24.87 ppm. MS (ESI): 367.2 ($M+H^+$). HRMS (ESI) Calcd for $C_{22}H_{28}O_4{}^{10}B$: 366.2111 ($M+H^+$). Found: 366.2112. IR (KBr): ν_{max} = 2993, 1605, 1515, 1359, 1204, 1146, 1088, 964 cm^{-1}.

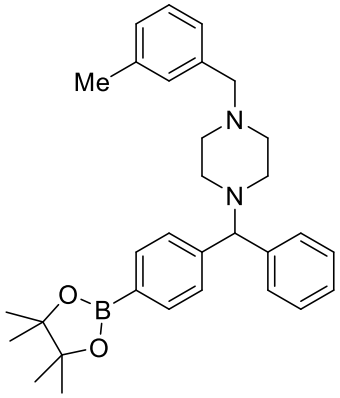
(*E*)-(4-(3,5-Dimethoxystyryl)phenyl)boronic acid (S-4n)



To a 250 mL round-bottom flask were added (*E*)-2-(4-(3,5-dimethoxystyryl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.20 g, 3.30 mmol), $NaIO_4$ (4.20 g, 20.0 mmol), NH_4OAc (1.50 g, 20.0 mmol), acetone (80.0 mL), and H_2O (40.0 mL). After stirring at room temperature for 48 h, the reaction mixture was filtered with a pad of

Celite. The filtrate was concentrated. The residue was diluted with ethyl acetate (200.0 mL) and washed with saturated brine. The organic layer was filtered through a pad of $MgSO_4$ and concentrated. The residue was purified with flash column chromatography through a short silica gel column to afford the corresponding boronic acid as a pale yellow solid. The product was used in the next step without purification.

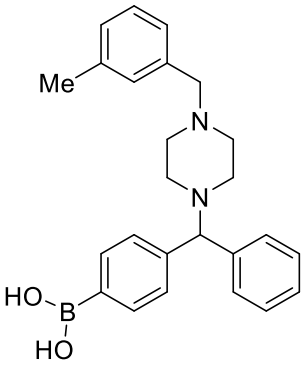
1-(3-Methylbenzyl)-4-(phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-phenyl)methyl)piperazine (S1-4p)



To a 100 mL of Schlenk tube were added anhydrous KOAc (2.94 g, 30.0 mmol, 3.00 equiv), XPhos-Pd-G (84 mg, 1.0 mol%), Xphos (95 mg, 2.0 mol%), $B_2(OH)_4$ (1.80 g, 20.0 mmol, 2.00 equiv.), 1-((4-chlorophenyl)(phenyl)methyl)-4-(3-methylbenzyl)piperazine (3.90 g, 10.0 mmol, 1.00 equiv.) under argon, followed by fresh distilled EtOH (40.0 mL). The resulting mixture was then stirred at 80 °C for 4 h. The reaction was cooled to room temperature and concentrated. The residue was dissolved in dichloromethane, and pinacol (2.36 g, 20.0 mmol, 2.00 equiv.) was added. After the resulting mixture was stirred at room temperature for 8 h, the reaction mixture was then concentrated. The residue was purified with silica gel chromatography (Eluent: ethyl acetate/petroleum ether: 1/3, R_f = 0.7) to give 1-(3-methylbenzyl)-4-(phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl)methyl)piperazine (3.6 g, 75% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 2 H), 7.43-7.37 (m, 4 H), 7.24-7.02 (m, 7 H), 4.23 (s, 1 H), 3.46 (s, 2 H), 2.46-2.31 (m, 12 H), 1.29 (s, 12 H); ^{13}C NMR (101 MHz, $cdcl_3$) δ 146.09, 142.42, 137.82, 137.65, 134.93, 129.93, 128.37, 127.96, 127.90, 127.67, 127.27, 126.84, 126.31, 83.59, 76.31, 63.02, 53.28, 51.82, 24.79, 21.33 ppm. MS (ESI): 483.3 ($M+H^+$). HRMS (ESI) Calcd for

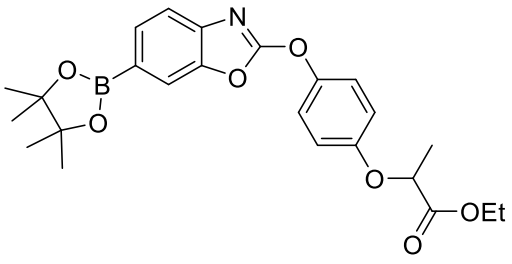
$C_{31}H_{40}O_2N_2{}^{10}B$: 482.3214($M+H^+$). Found: 482.3213. IR (KBr): ν_{max} = 2976, 1663, 1610, 1452 cm^{-1}.

1-(3-Methylbenzyl)-4-(phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methyl)piperazine (S-4p)



To a 100 mL of Schlenk tube were added anhydrous KOAc (2.94 g, 30.0 mmol, 3.00 equiv), XPhos-Pd-G (84 mg, 1.0 mol%), Xphos (95 mg, 2.0 mol%), $B_2(OH)_4$ (1.80 g, 20.0 mmol, 2.00 equiv), 1-((4-chlorophenyl)(phenyl)methyl)-4-(3-methylbenzyl)piperazine (3.90 g, 10.0 mmol) under argon, followed by fresh distilled EtOH (40.0 mL). The resulting mixture was then stirred at 80 °C for 4 h. The reaction was cooled to room temperature and concentrated. The residue was diluted with ethyl acetate and washed with saturated brine. The organic layer was filtered through a pad of $MgSO_4$ and concentrated. Use EA to dissolve the oil and add petroleum ether to get yellow precipitation. The product was used in the next step without purification.

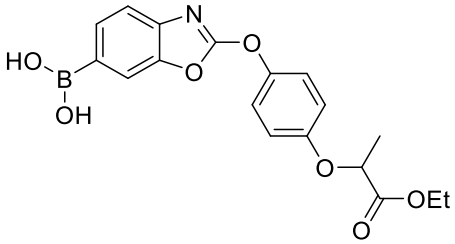
Ethyl-2-(4-((6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*d*]oxazol-2-yl)oxy)phenoxy)propanoate (S1-4q)



To a 100 mL of Schlenk tube were added anhydrous KOAc (0.75 g, 7.5 mmol, 3.0 equiv), XPhos-Pd-G (21 mg, 1.0 mol%), Xphos (24 mg, 2.0 mol%), $B_2(OH)_4$ (0.45 g, 5.0 mmol, 2.00 equiv), ethyl-2-(4-((5-chlorobenzo[*d*]oxazol-2-yl)oxy)phenoxy)propanoate (0.90 g, 2.5 mmol, 1.0 equiv.) under argon, followed by

fresh distilled EtOH (10.0 mL). The resulting mixture was then stirred at 80 °C for 4 h. The reaction was cooled to room temperature and concentrated. The residue was dissolved in dichloromethane, and pinacol (0.59 g, 5.0 mmol, 2.0 equiv) was added. After the resulting mixture was stirred at room temperature for 8 h, the reaction mixture was then concentrated. The residue was purified with silica gel chromatography (Eluent: ethyl acetate/petroleum ether: 1/3, R_f = 0.7) to give 1-(3-methylbenzyl)-4-(phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl)methyl)piperazine (0.68 g, 60% yield) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1 H), 7.72 (d, *J* = 7.8 Hz, 1 H), 7.48 (d, *J* = 7.8 Hz, 1 H), 7.33 (d, *J* = 9.0 Hz, 2 H), 6.95 (d, *J* = 9.0 Hz, 2 H), 4.73 (q, *J* = 6.7 Hz, 1 H), 4.24 (q, *J* = 7.1 Hz, 2 H), 1.63 (d, *J* = 6.7 Hz, 3 H), 1.36 (s, 12 H), 1.27 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.24, 163.61, 156.06, 148.65, 147.19, 143.87, 131.52, 121.60, 118.38, 116.60, 116.38, 116.01, 84.30, 73.57, 61.75, 25.20, 18.88, 14.47 ppm. MS (ESI): 454.0 ($M+H^+$). HRMS (ESI) Calcd for $C_{24}H_{29}O_7N^{10}B$: 453.2068 ($M+H^+$); Found: 453.2067. IR (KBr): ν_{max}= 2980, 1752, 1618, 1502, 1297, 1167, 718 cm^{-1}.

2-(4-((1-Ethoxy-1-oxopropan-2-yl)oxy)pbenoxy)benzo[*d*]oxazol-6-yl)boronic acid (S-4q)



To a 100 mL of Schlenk tube were added anhydrous KOAc (0.75 g, 7.5 mmol, 3.0 equiv), XPhos-Pd-G (21 mg, 1.0 mol%), Xphos (24 mg, 2.0 mol%), $B_2(OH)_4$ (0.45 g, 5.0 mmol, 2.00 equiv), ethyl-2-(4-((6-chlorobenzo[*d*]oxazol-2-yl)oxy)phenoxy)propanoate (0.90 g, 2.5 mmol, 1.0 equiv.) under argon, followed by fresh distilled EtOH (10.0 mL). The resulting mixture was then stirred at 80 °C for 4 h. The reaction was cooled to room temperature and concentrated. The residue was purified with silica gel chromatography (Eluent: ethyl acetate/petroleum ether: 1/10 to ethyl acetate) to give brown oil. The product was used in the next step without purification.

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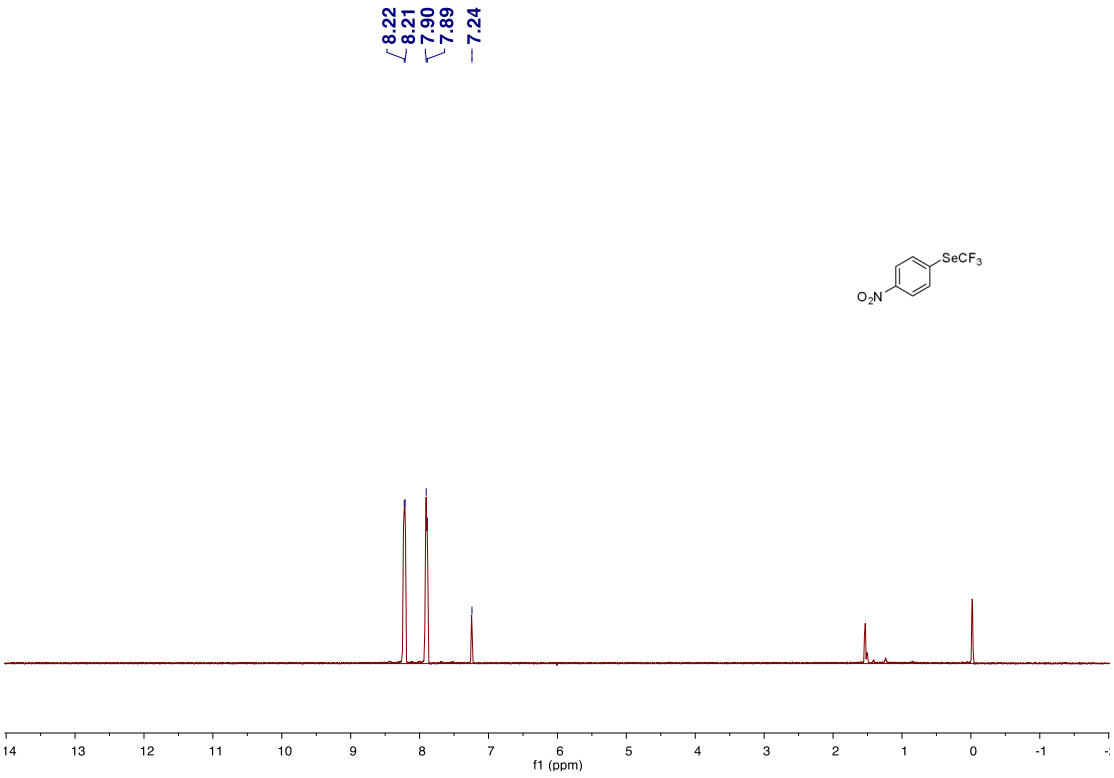
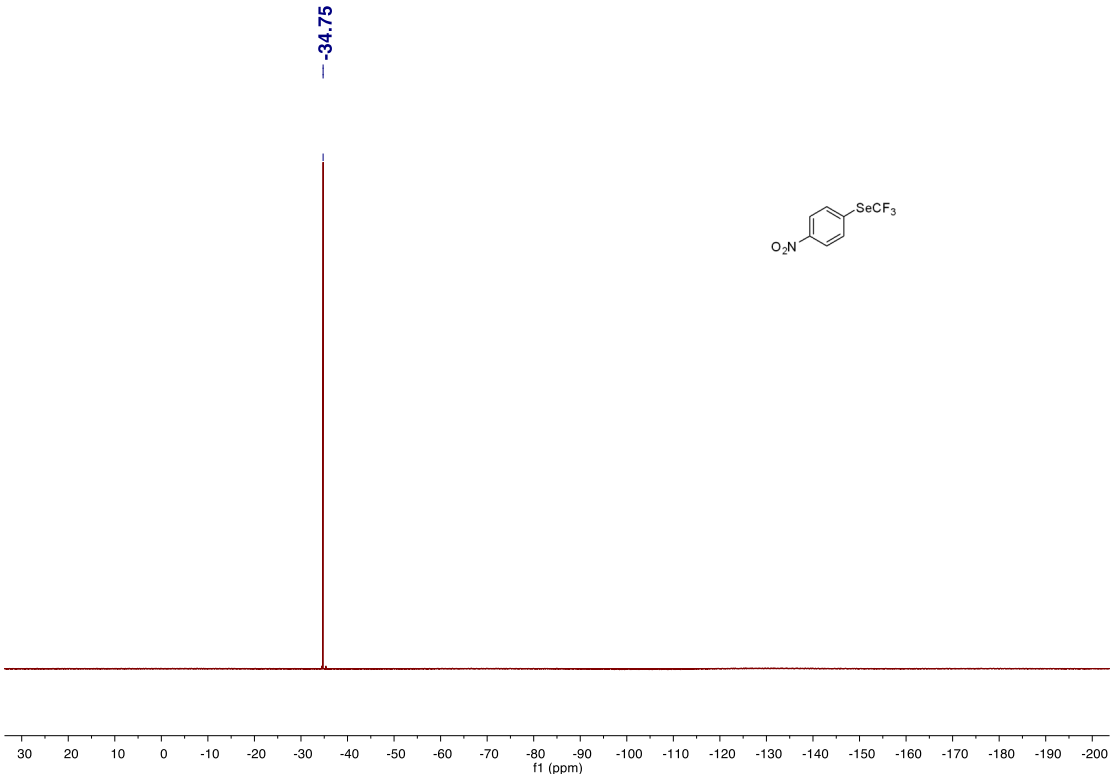
^{1}H NMR spectrum of 4-trifluoromethylseleno-nitrobenzene



^{19}F NMR spectrum of 4-trifluoromethylseleno-nitrobenzene



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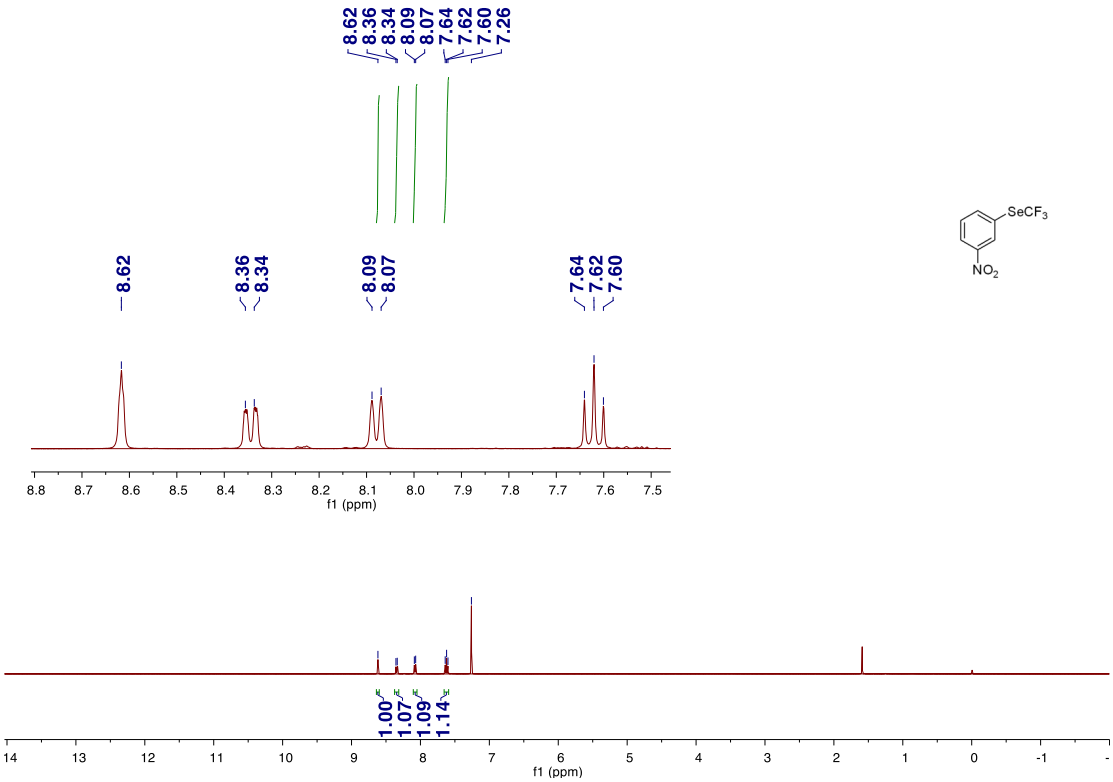

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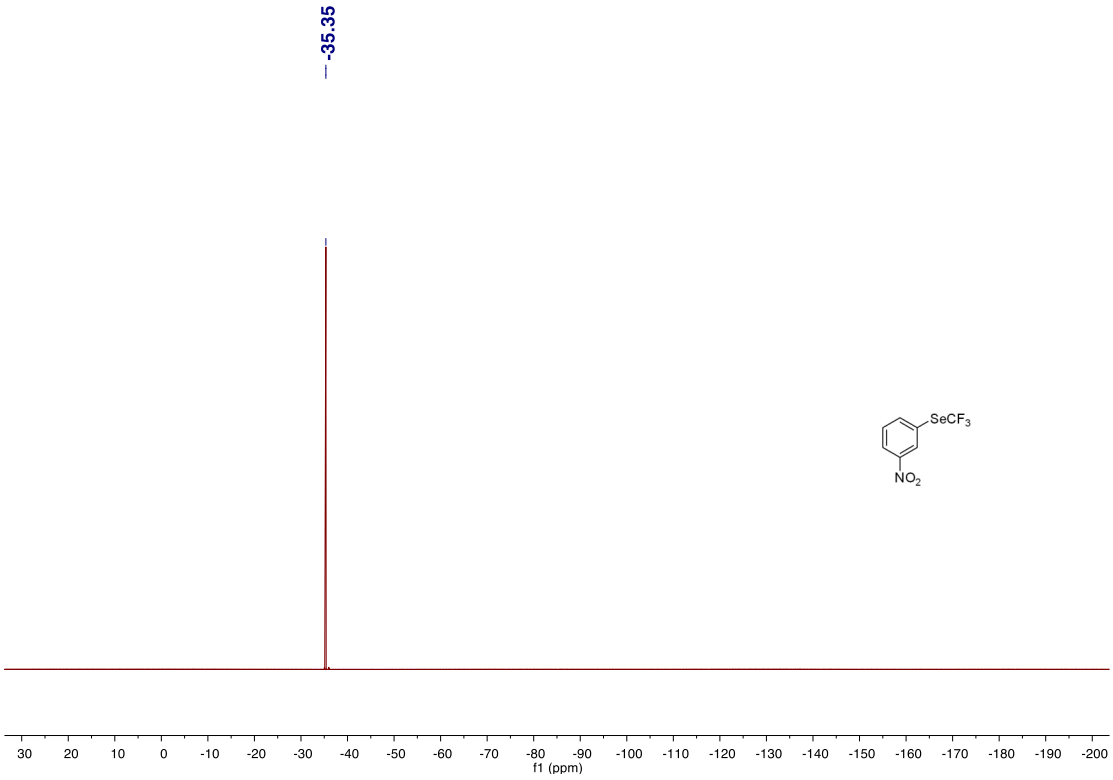

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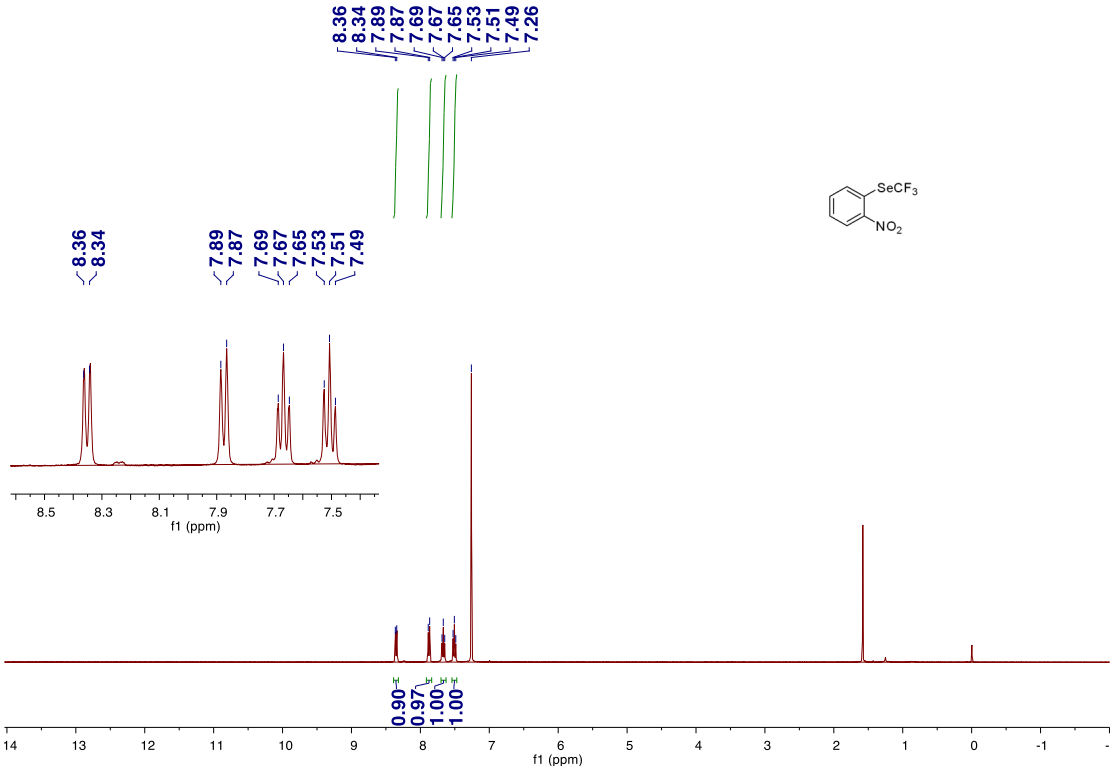

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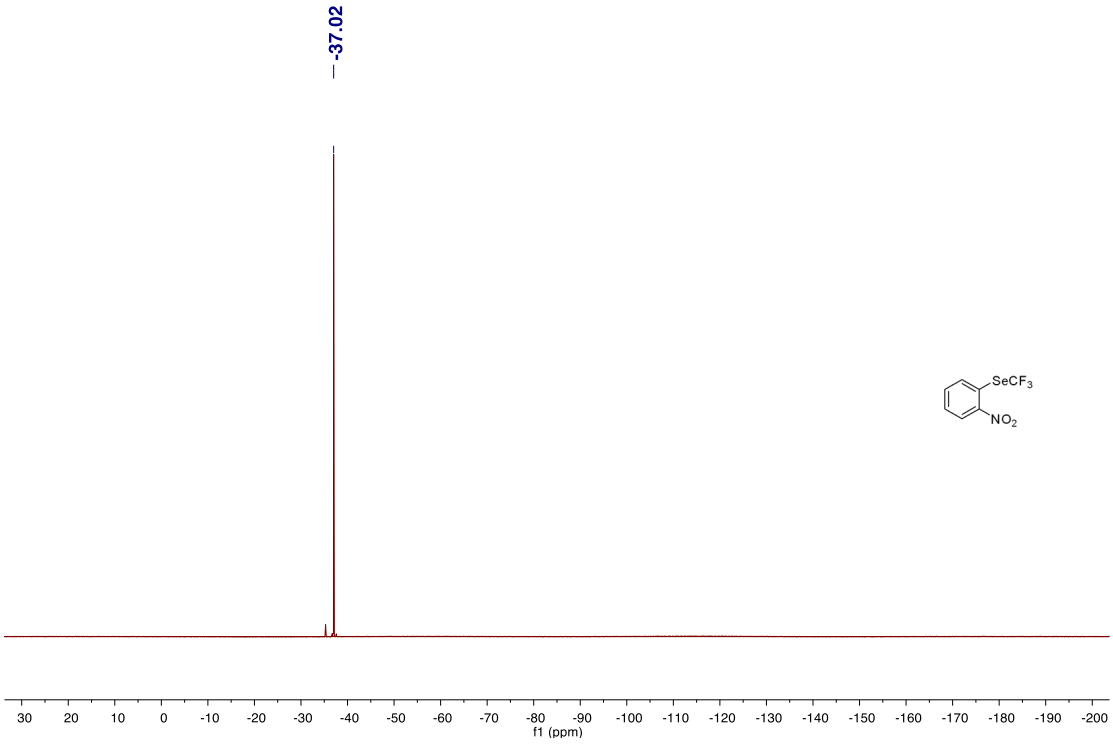

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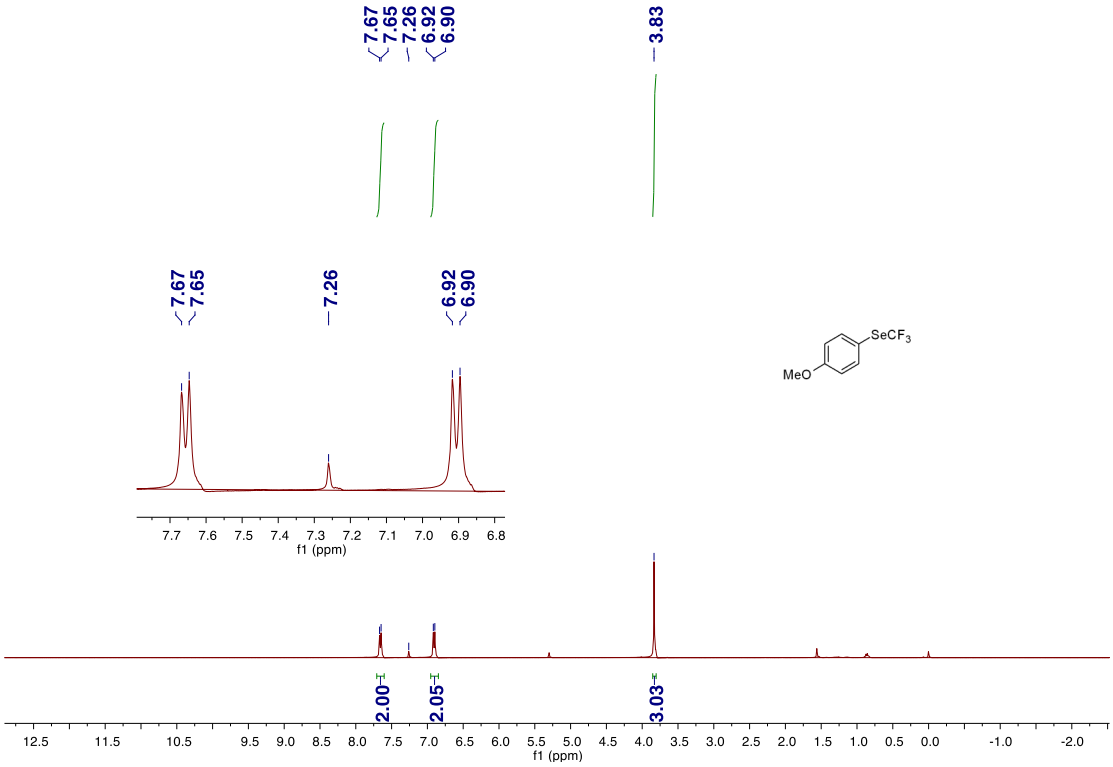

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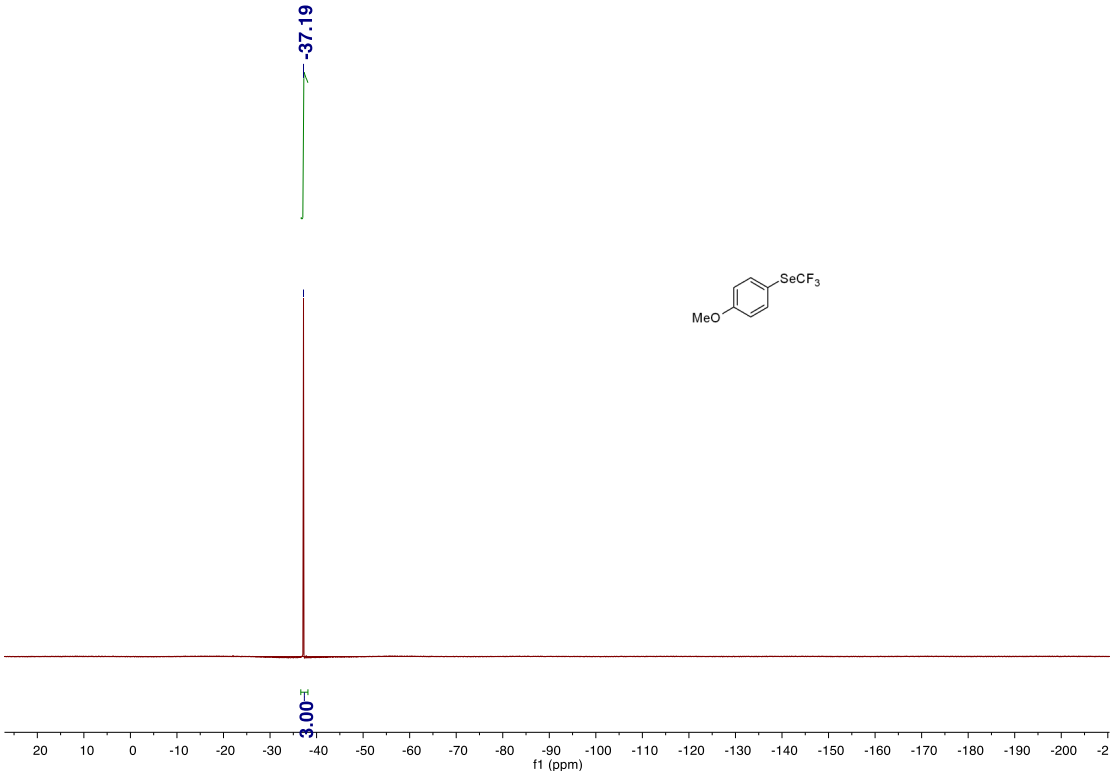

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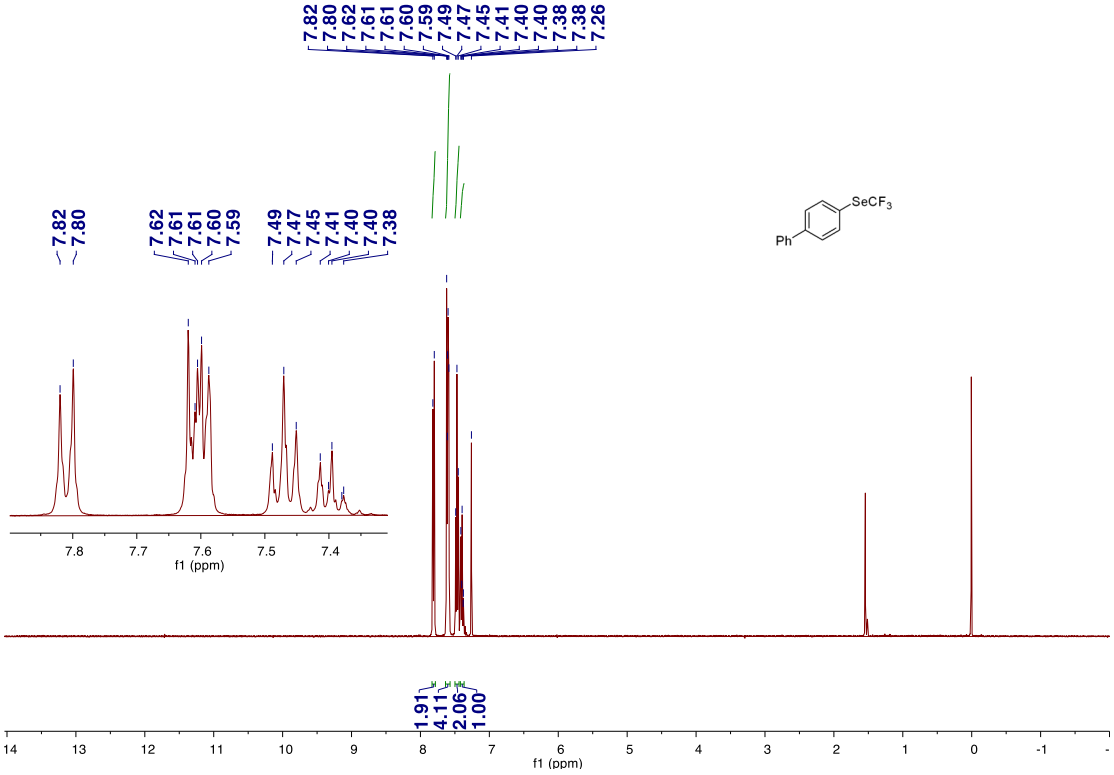

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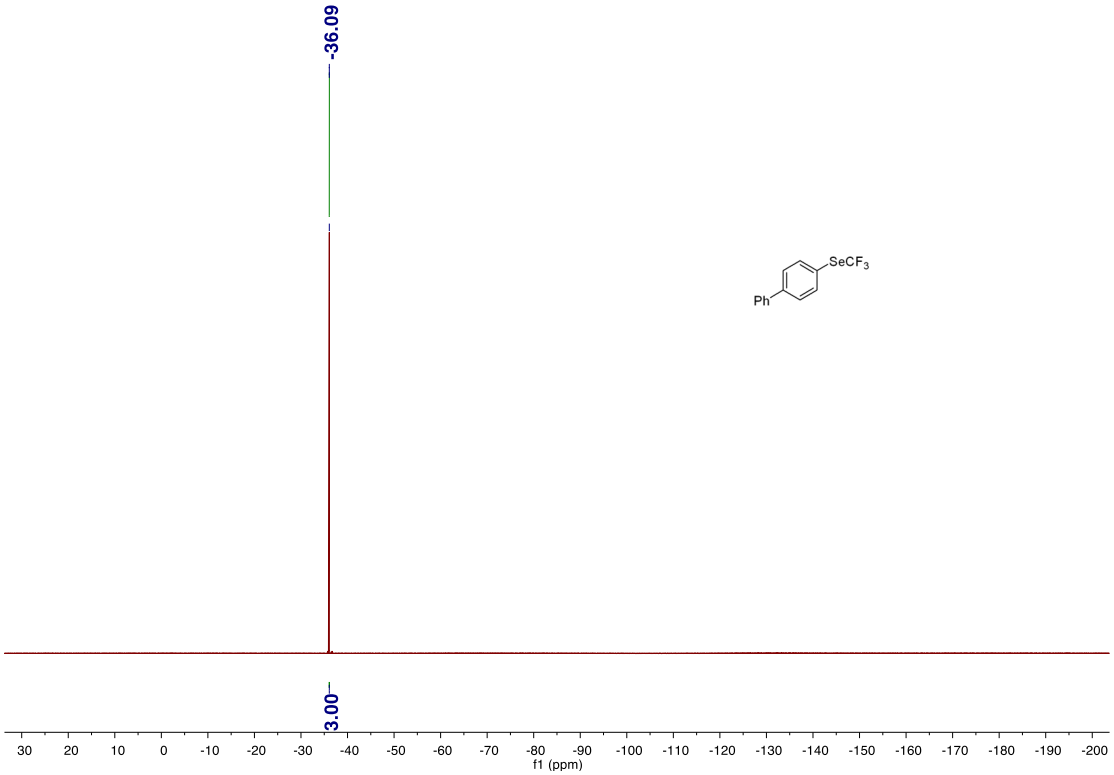

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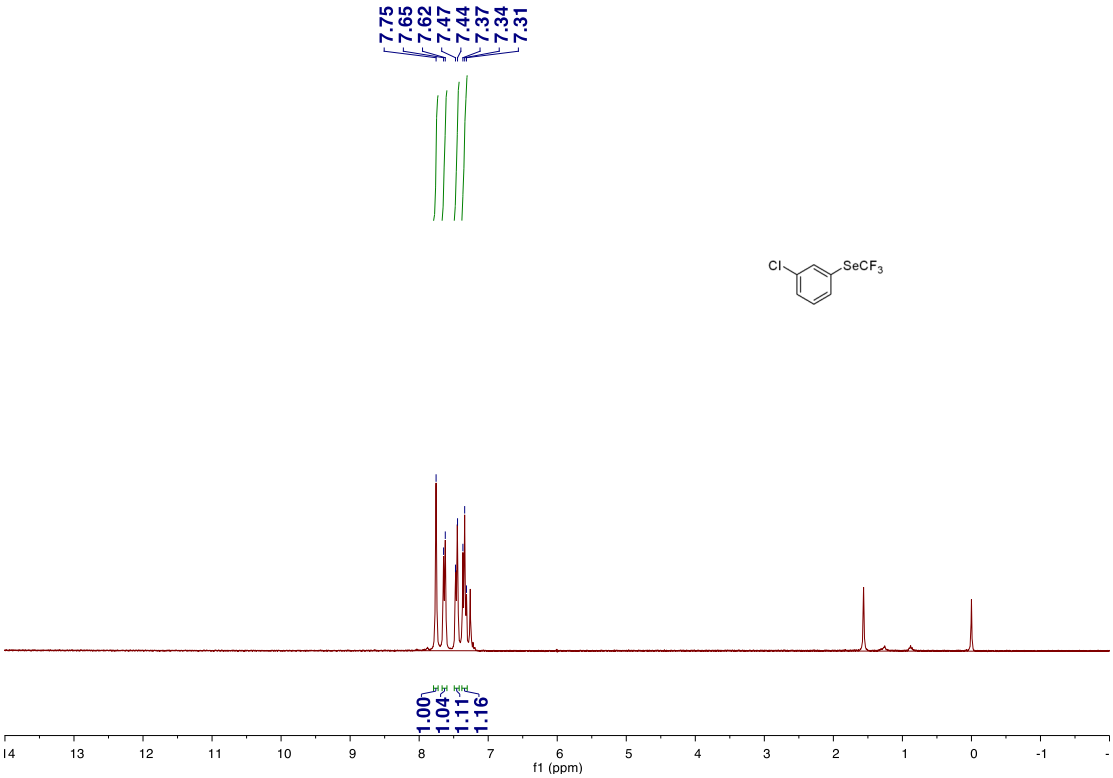

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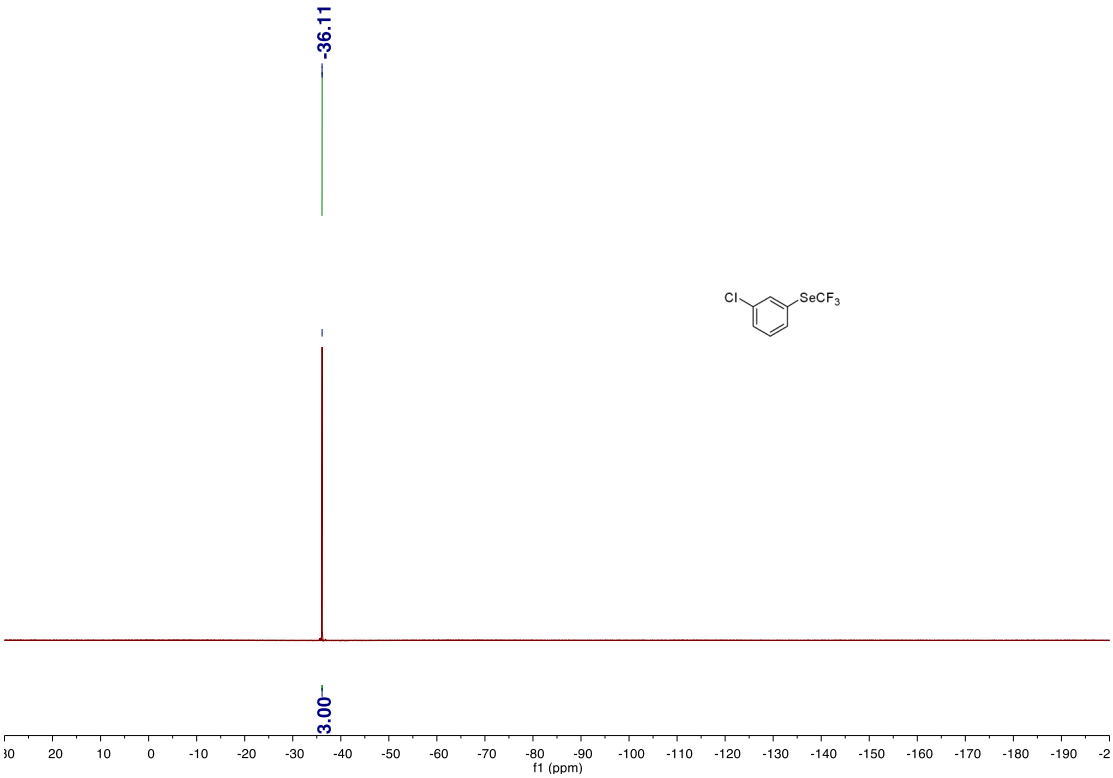

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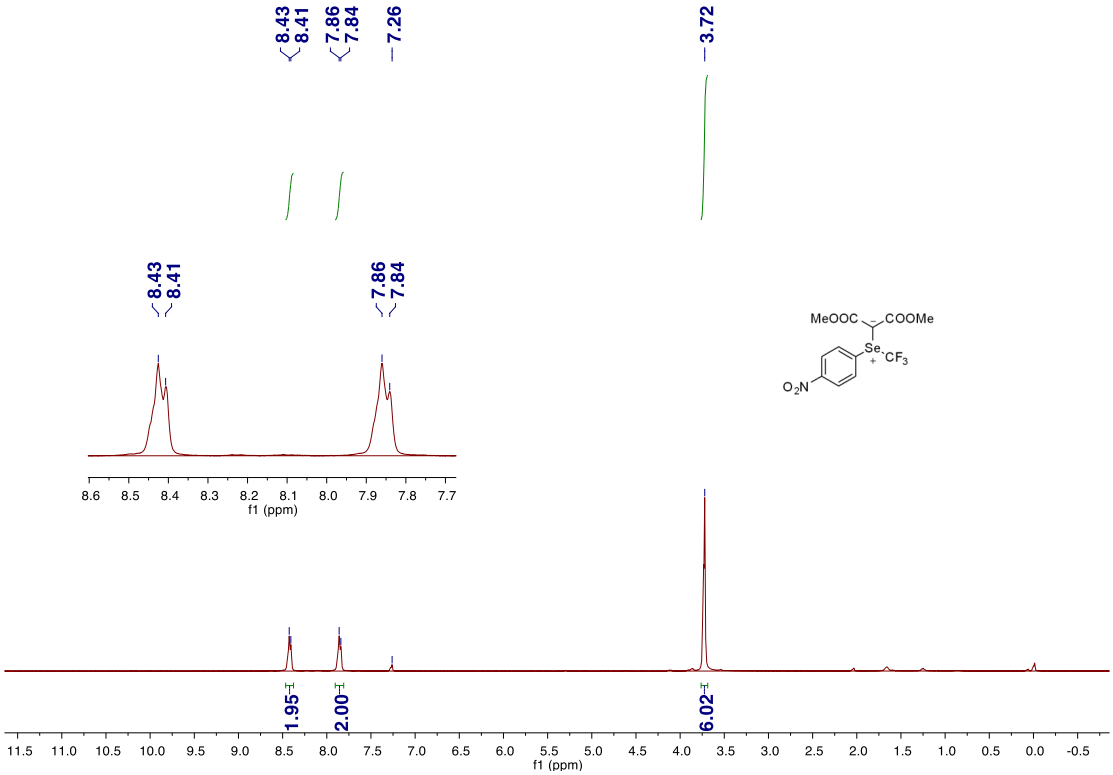

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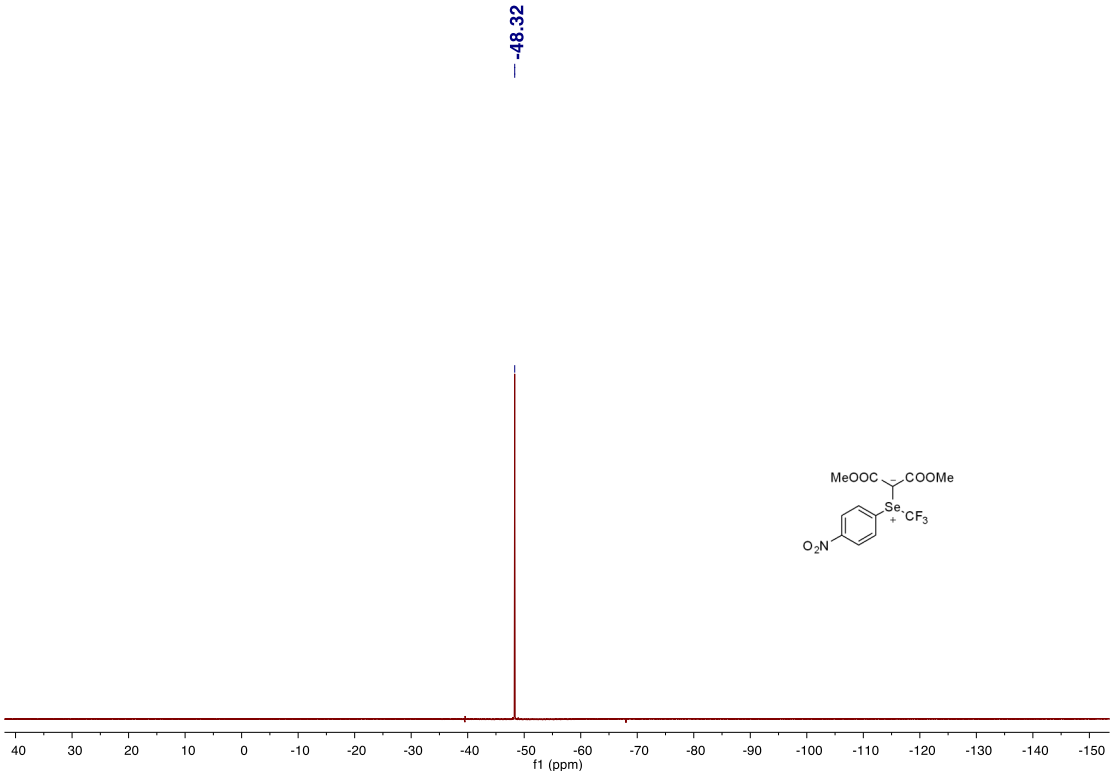

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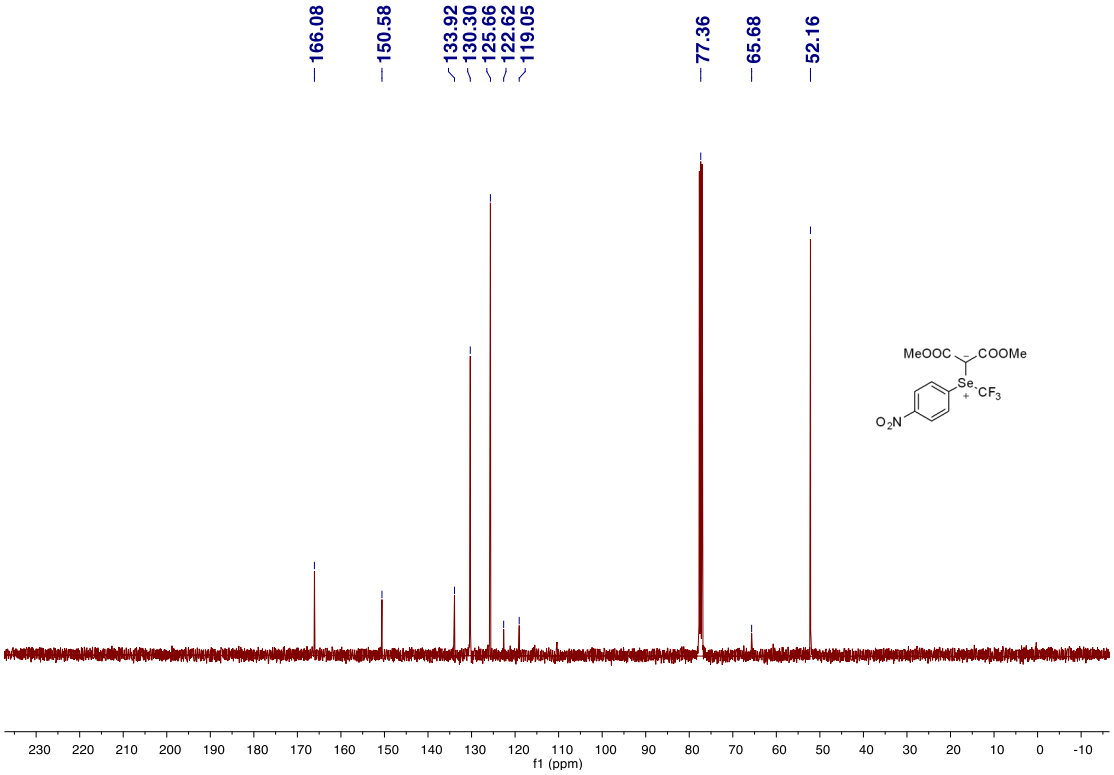

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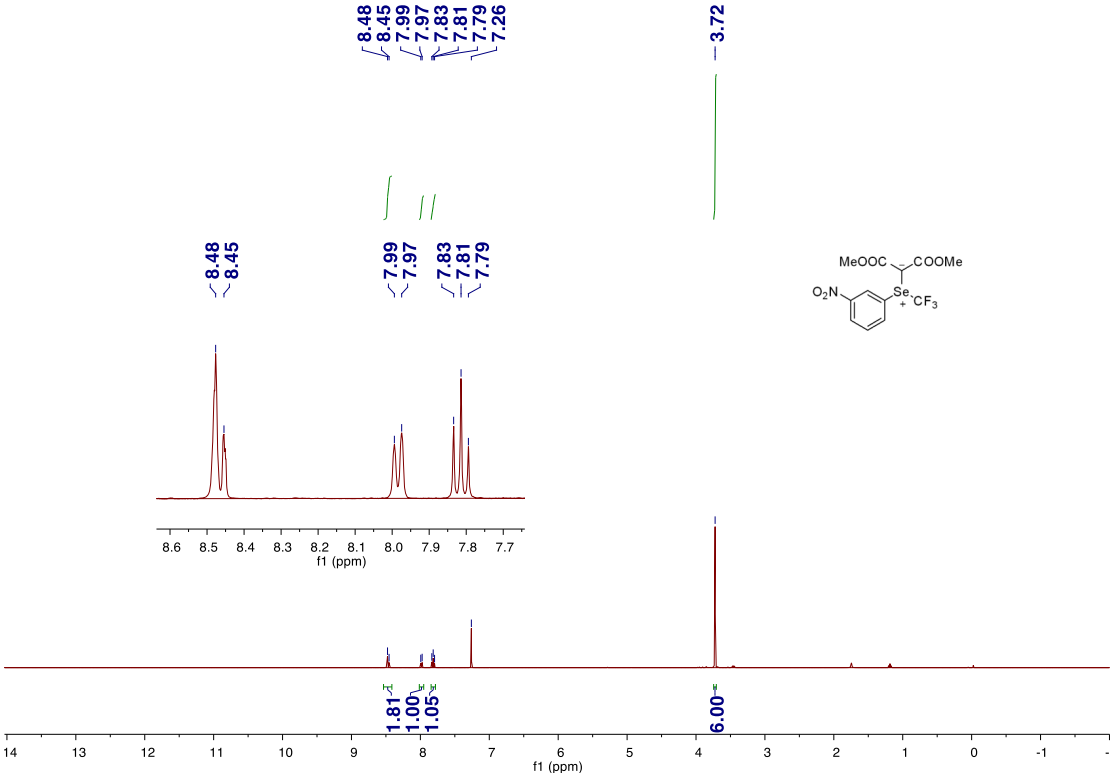

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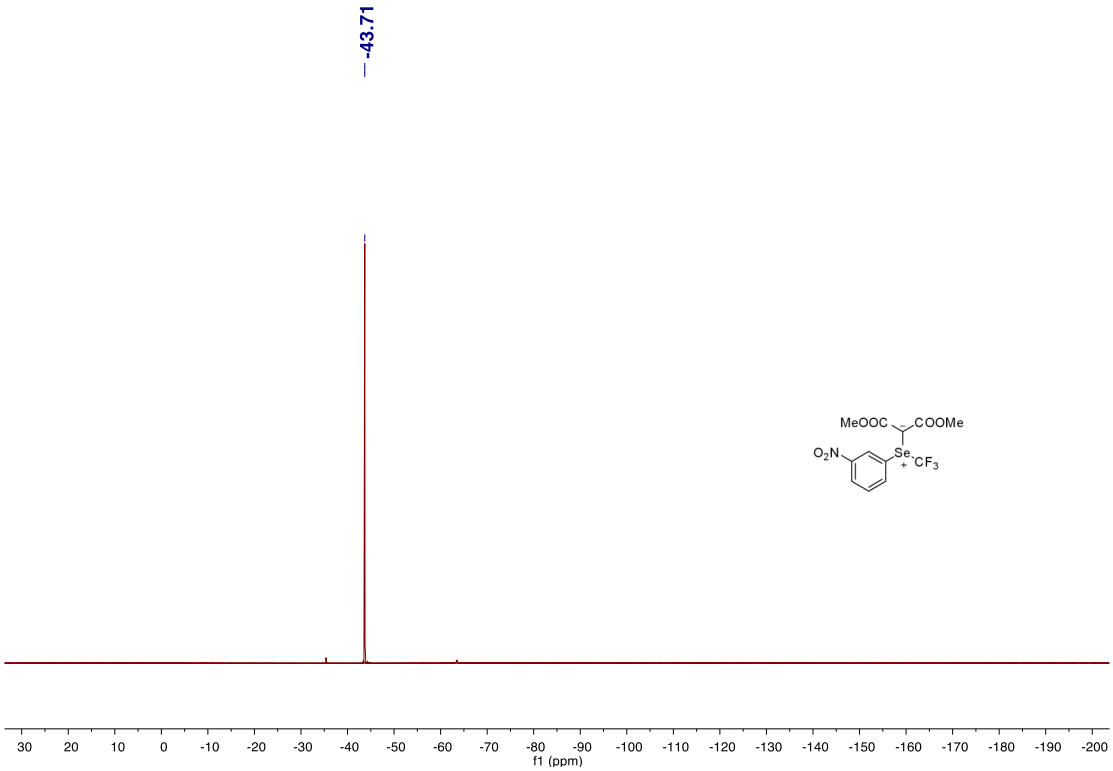

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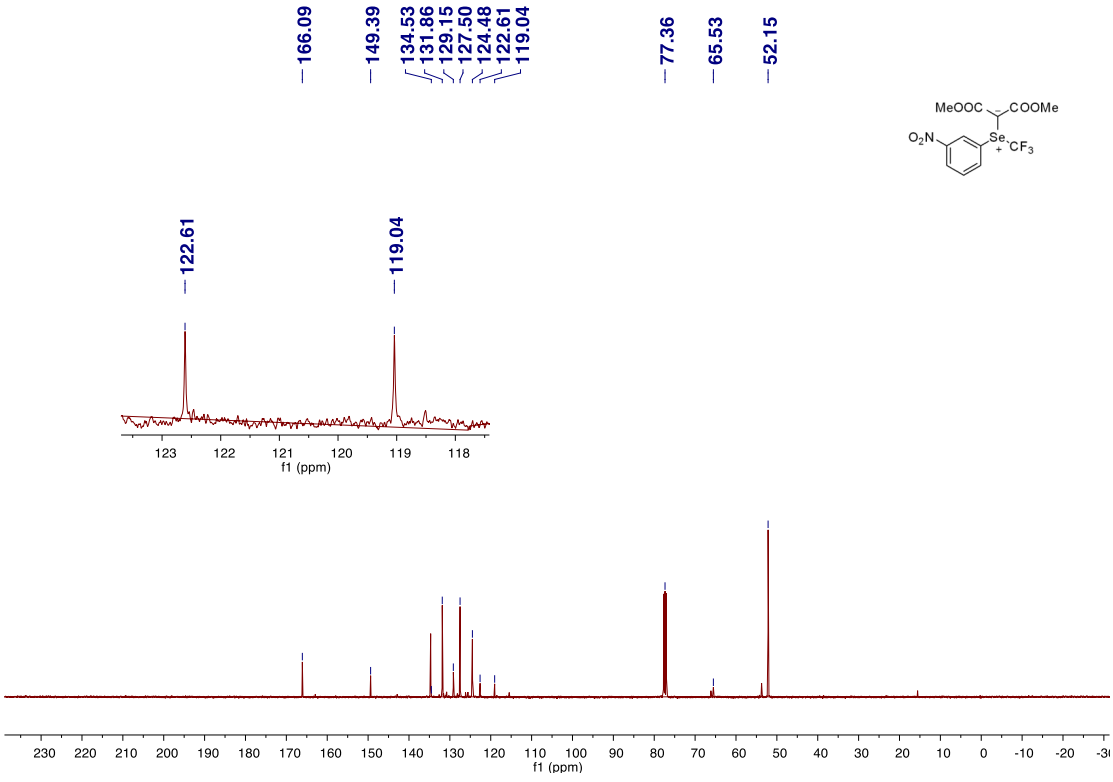

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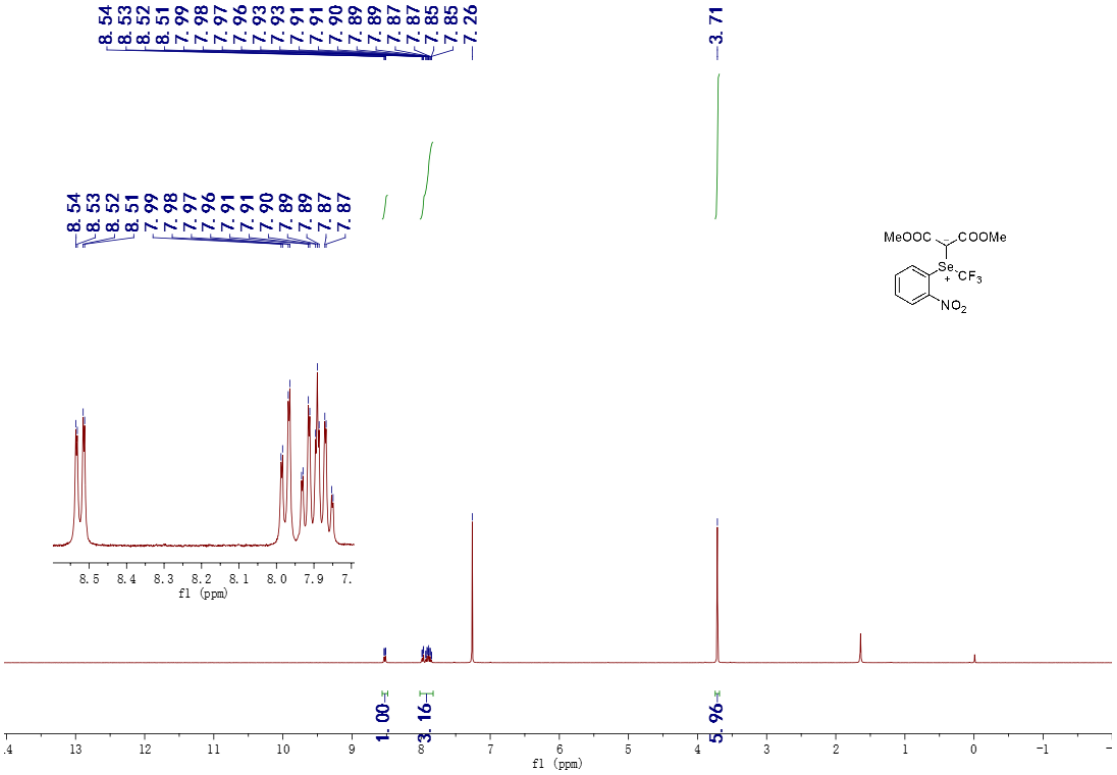

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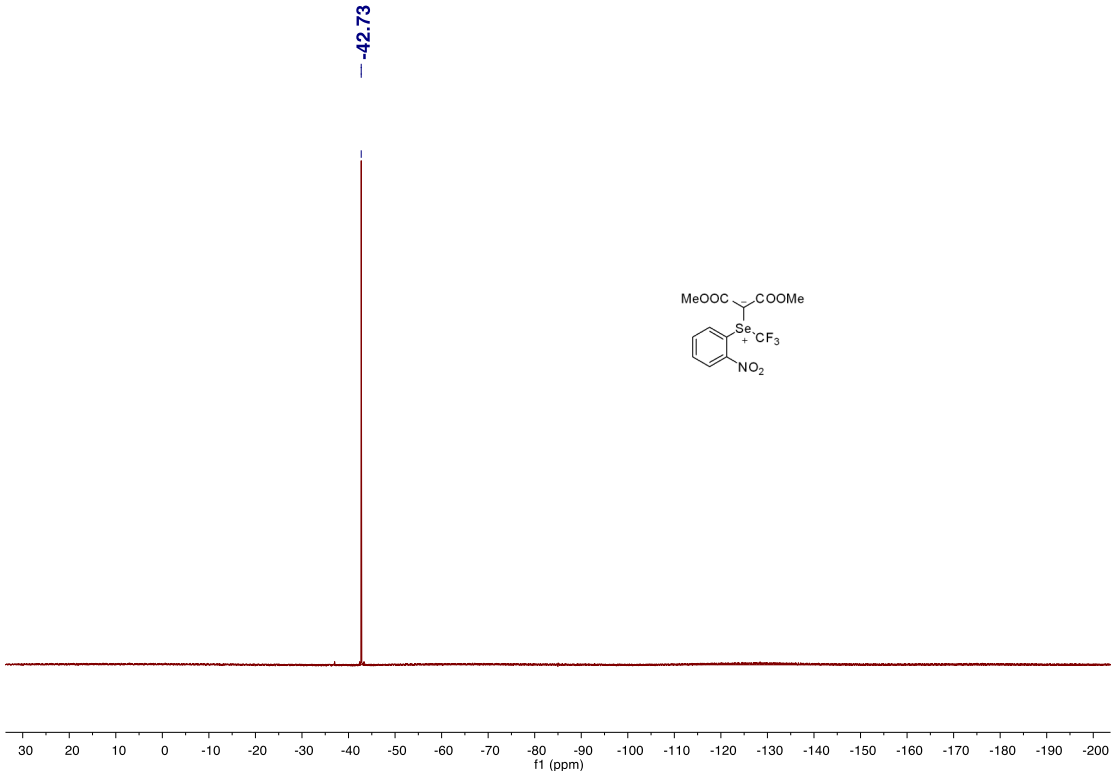

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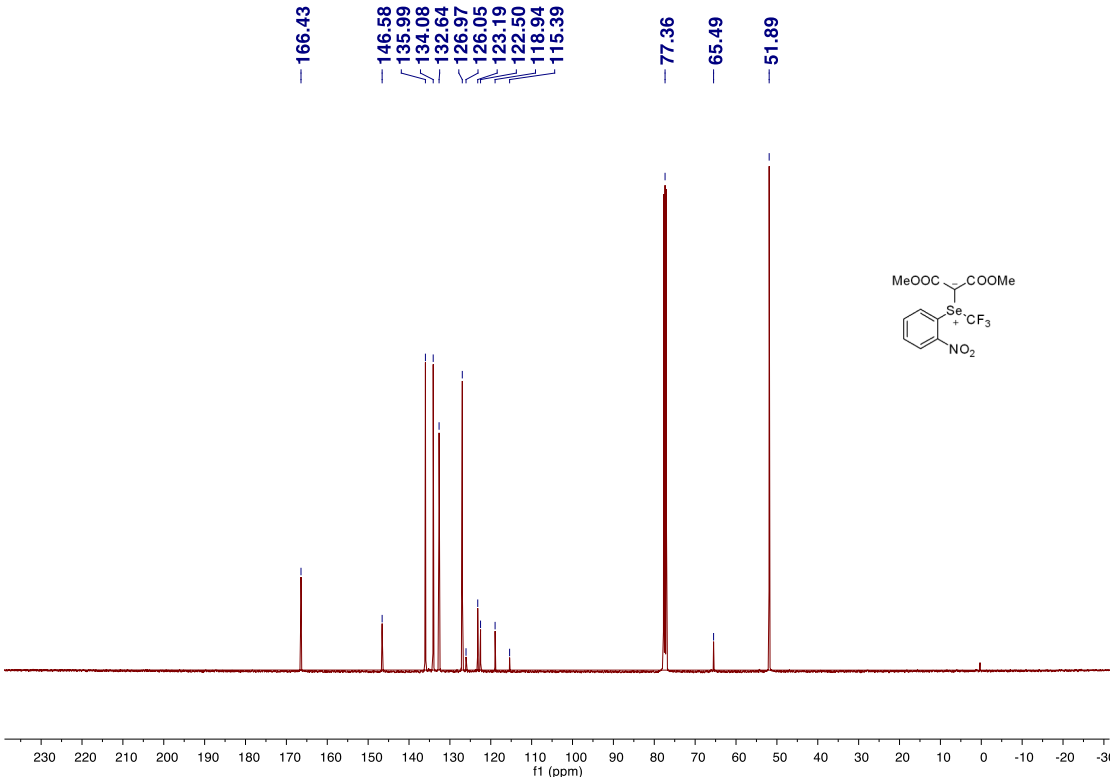

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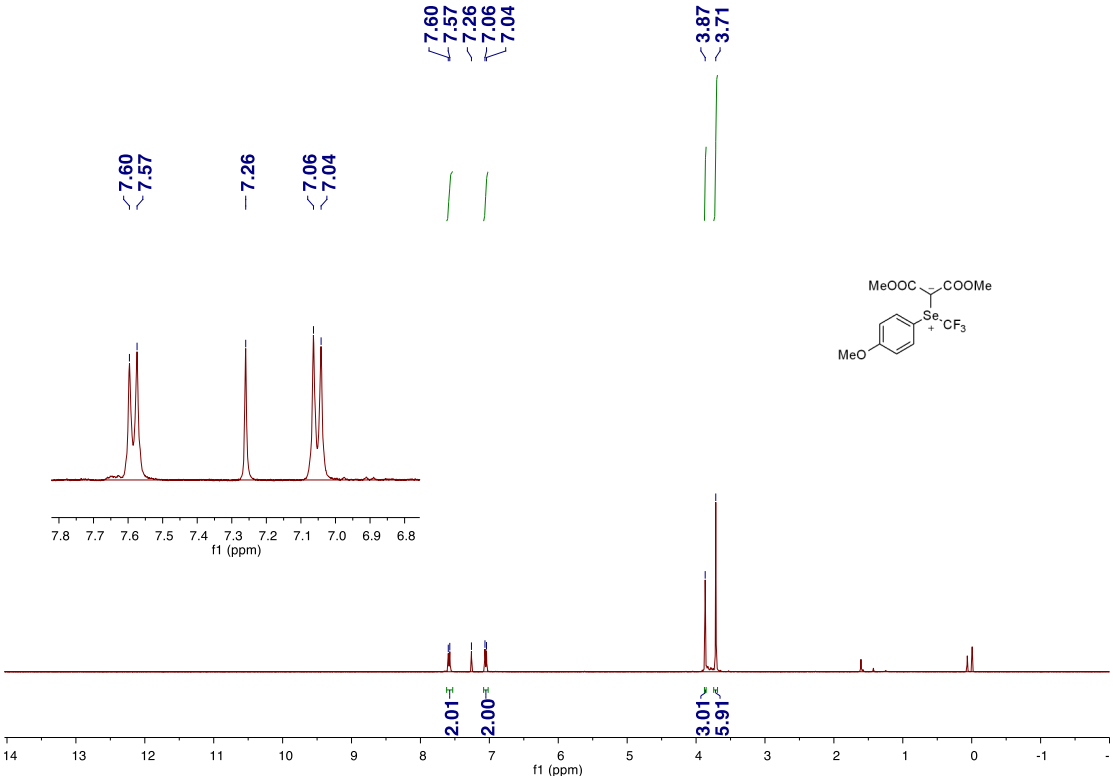

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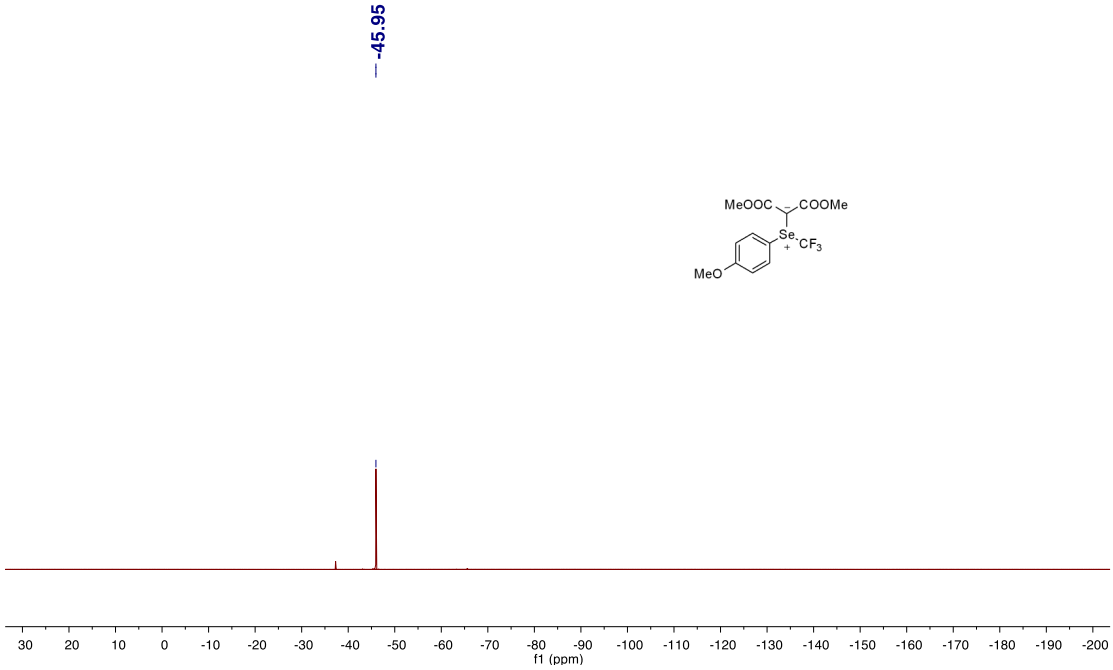
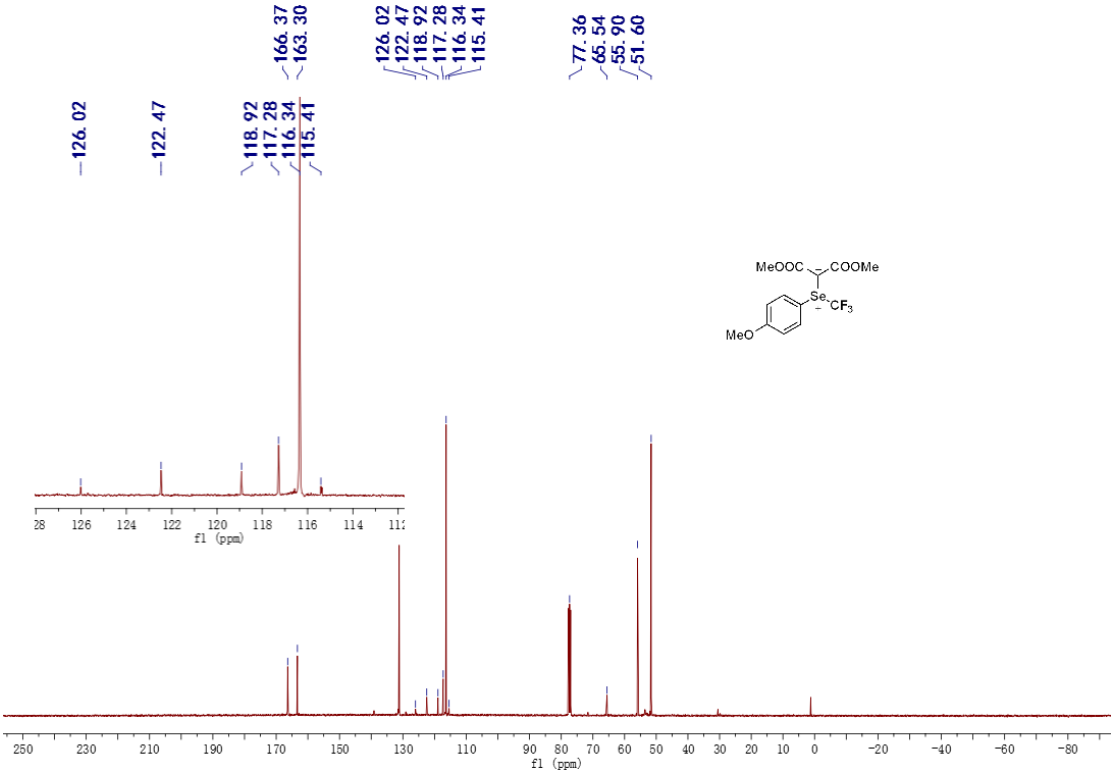
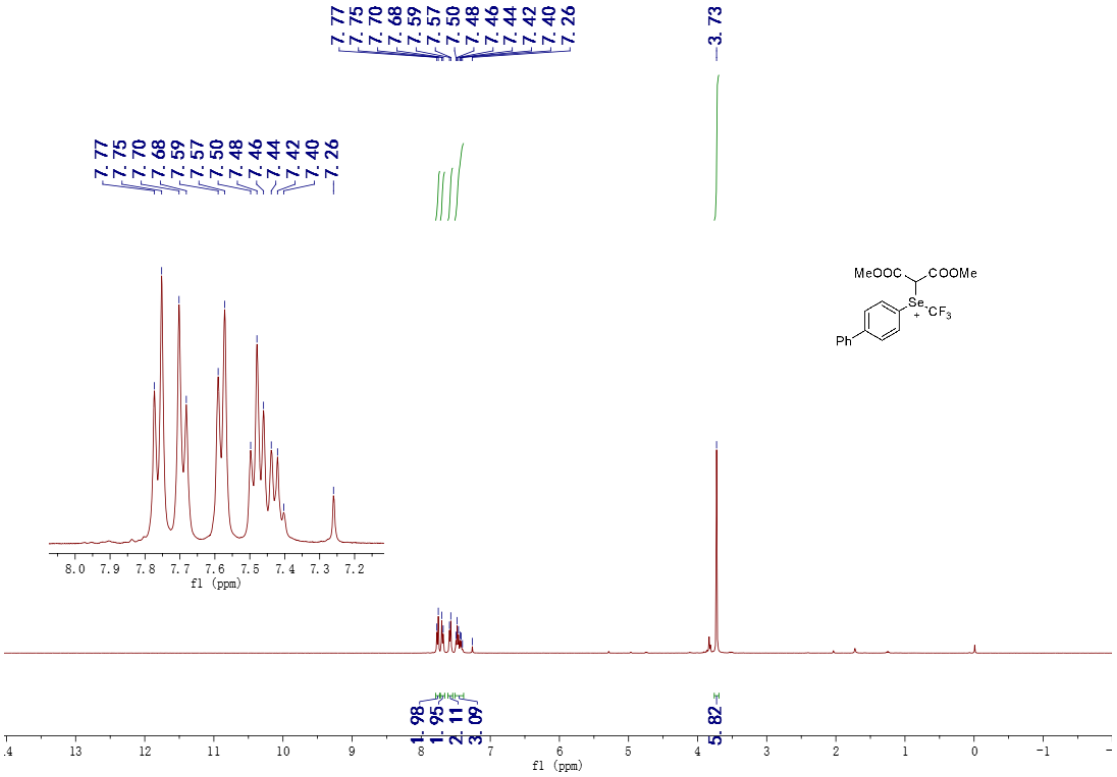


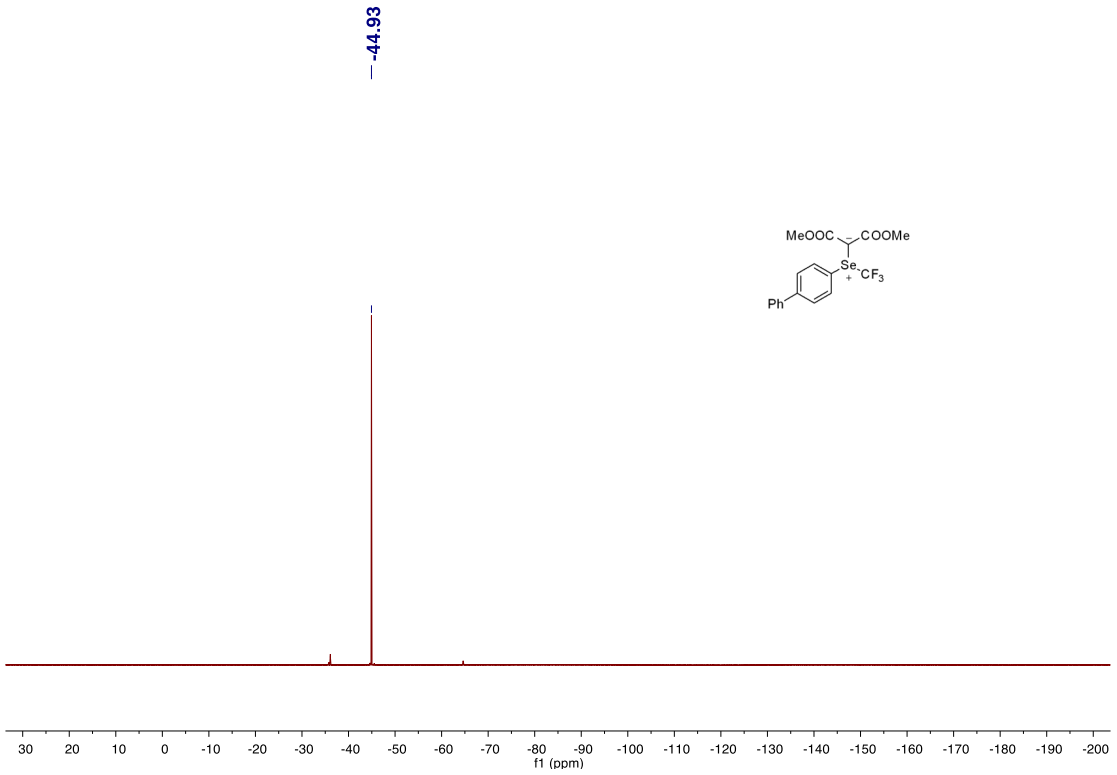
^{13}C NMR spectrum of trifluoromethyl-(4-methoxylphenyl) bis(carbomethoxy) methylide 1d



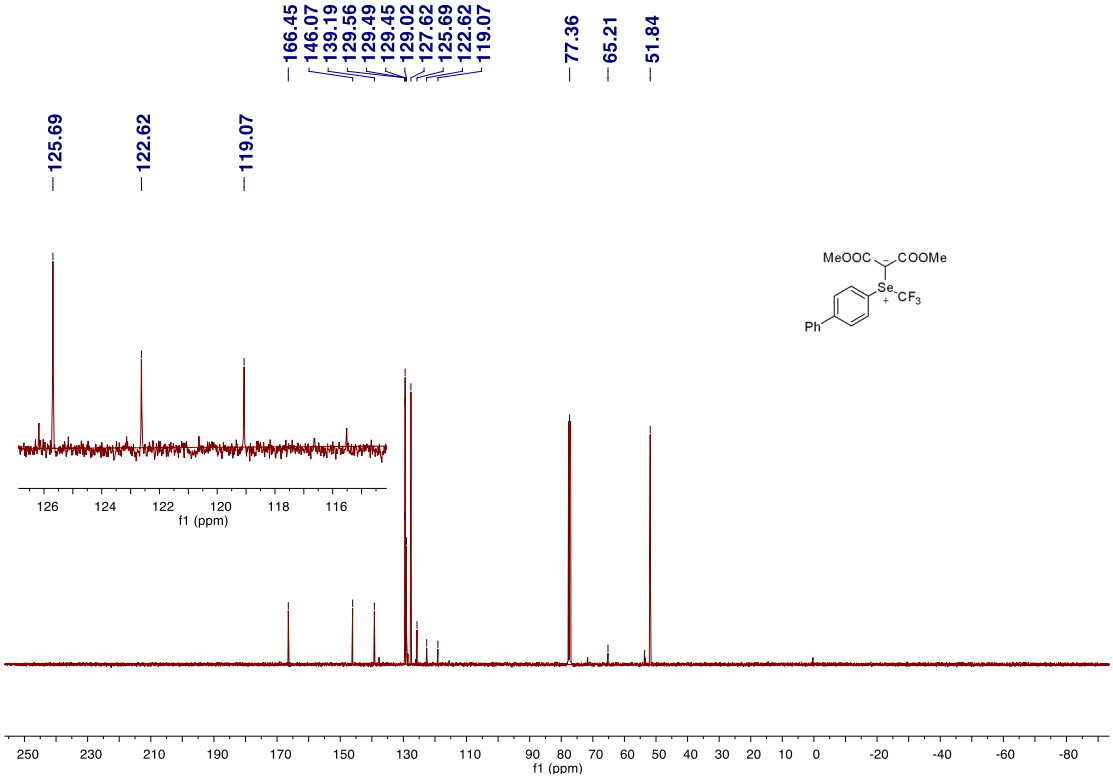
^{1}H NMR spectrum of trifluoromethyl-(4-biphenyl) bis(carbomethoxy) methylide 1e



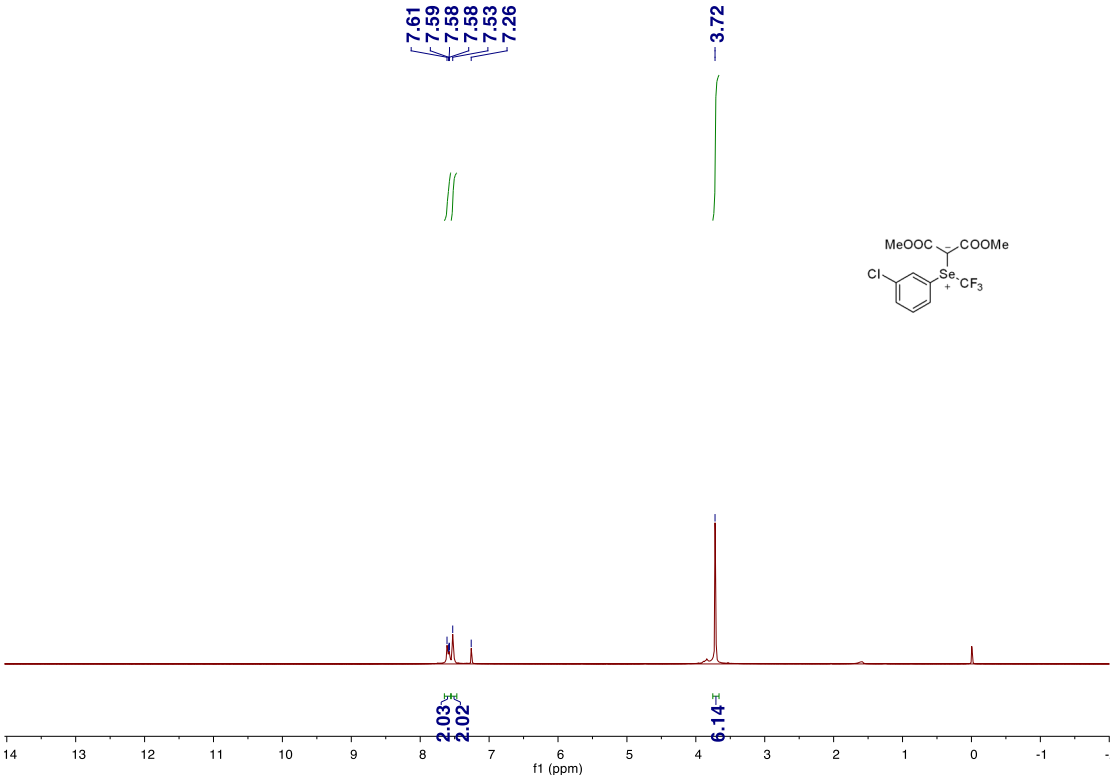
^{19}F NMR spectrum of trifluoromethyl-(4-biphenyl) bis(carbomethoxy) methylide 1e



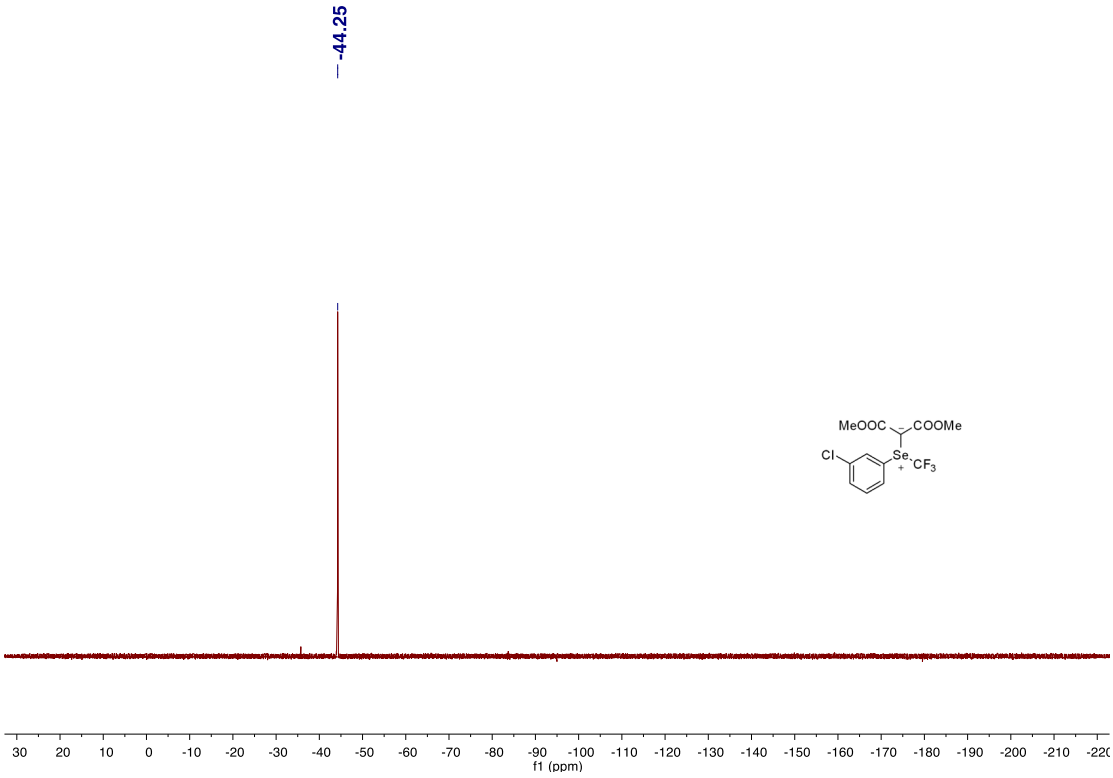
^{13}C NMR spectrum of trifluoromethyl-(4-biphenyl) bis(carbomethoxy) methylide 1e



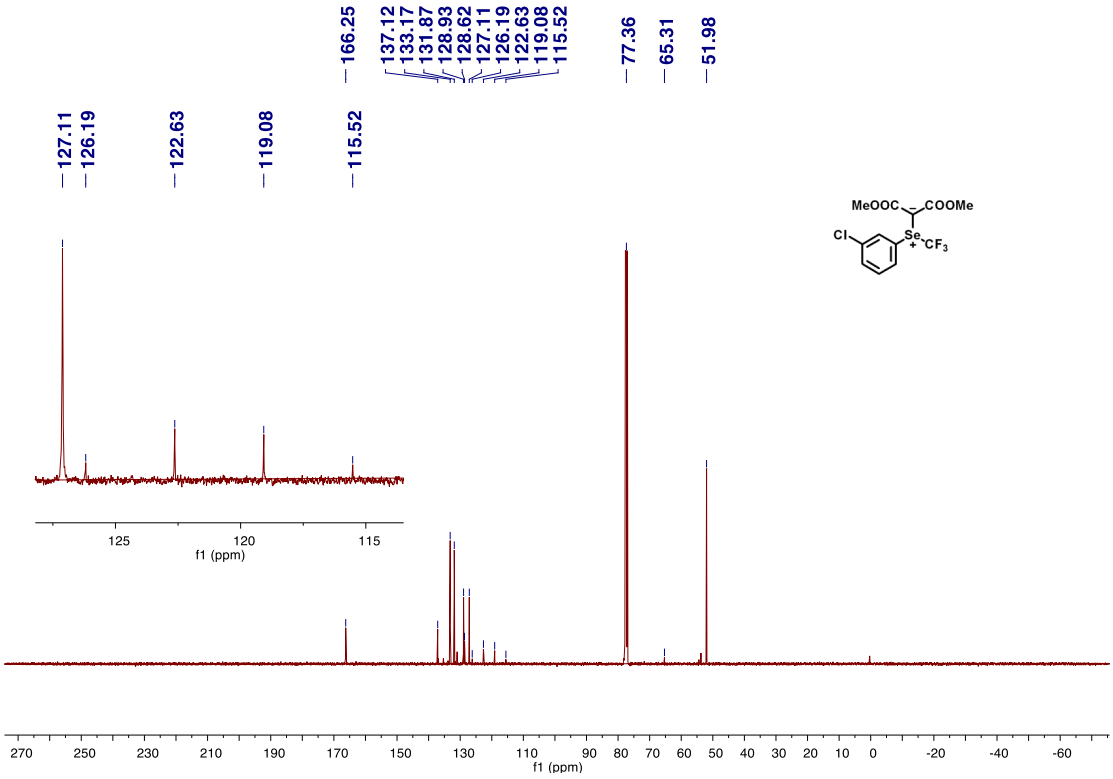
^{1}H NMR spectrum of trifluoromethyl-(3-chlorophenyl) bis(carbomethoxy) methylide 1f



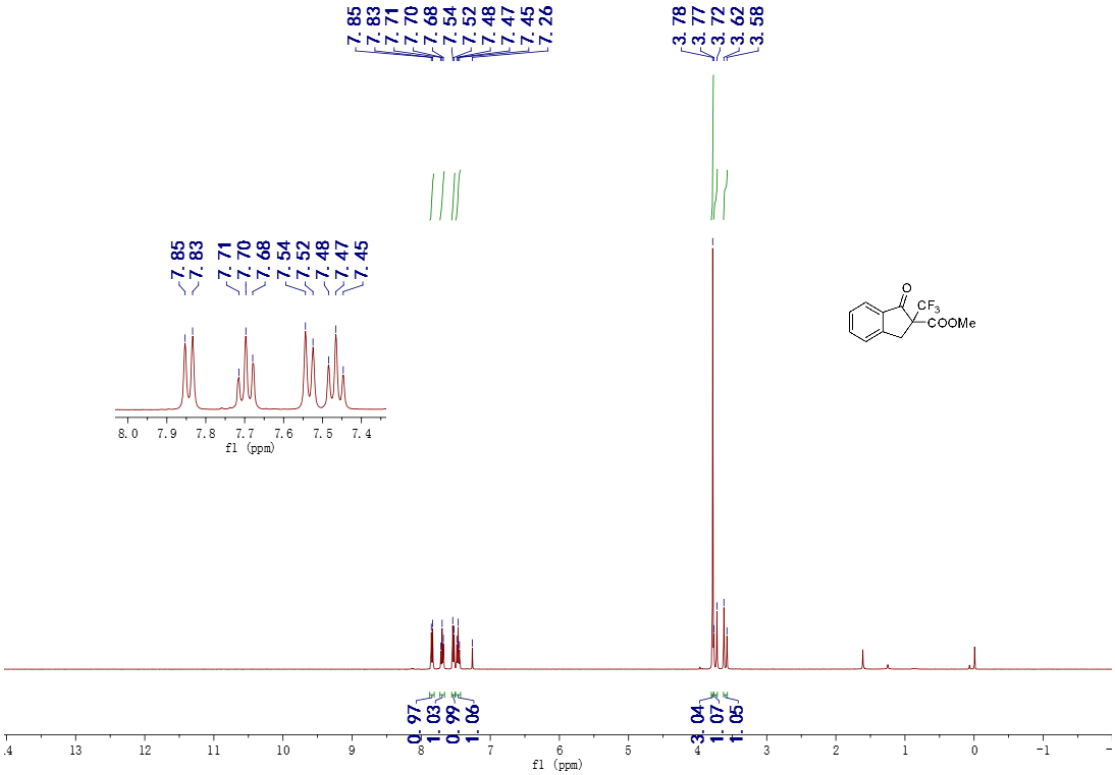
^{19}F NMR spectrum of trifluoromethyl-(3-chlorophenyl) bis(carbomethoxy) methylide 1f



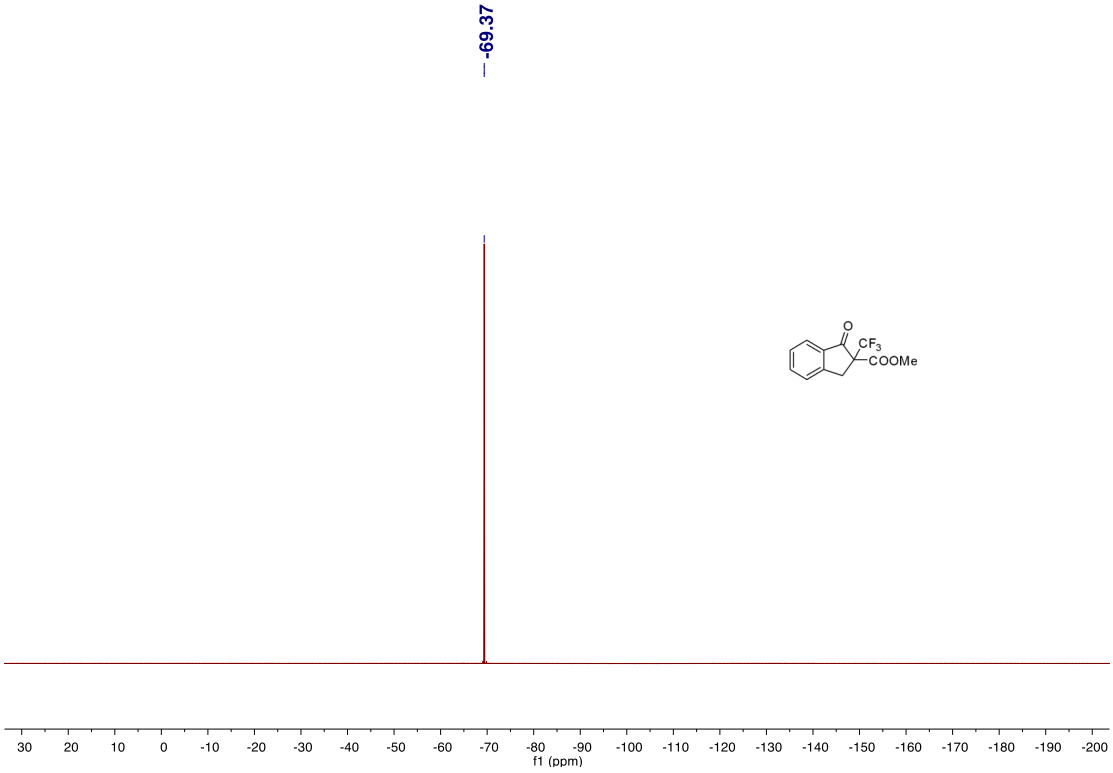
^{13}C NMR spectrum of trifluoromethyl-(3-chlorophenyl) bis(carbomethoxy) methylide 1f



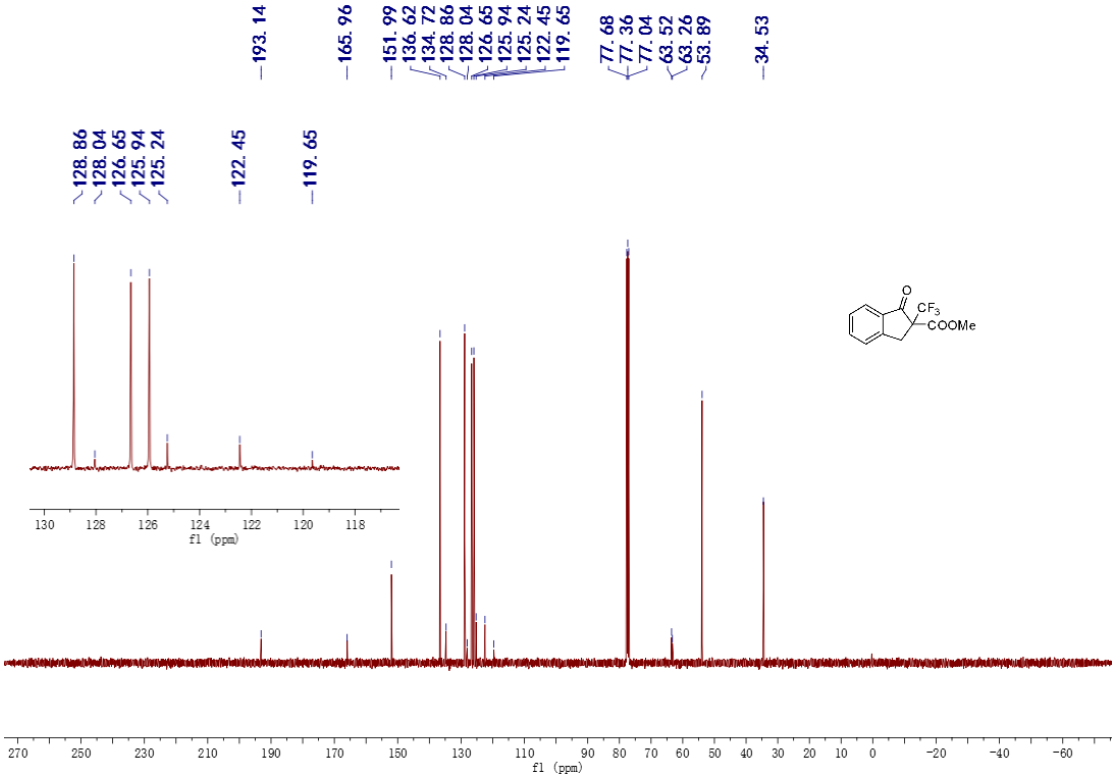
^{1}H NMR spectrum of methyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2a



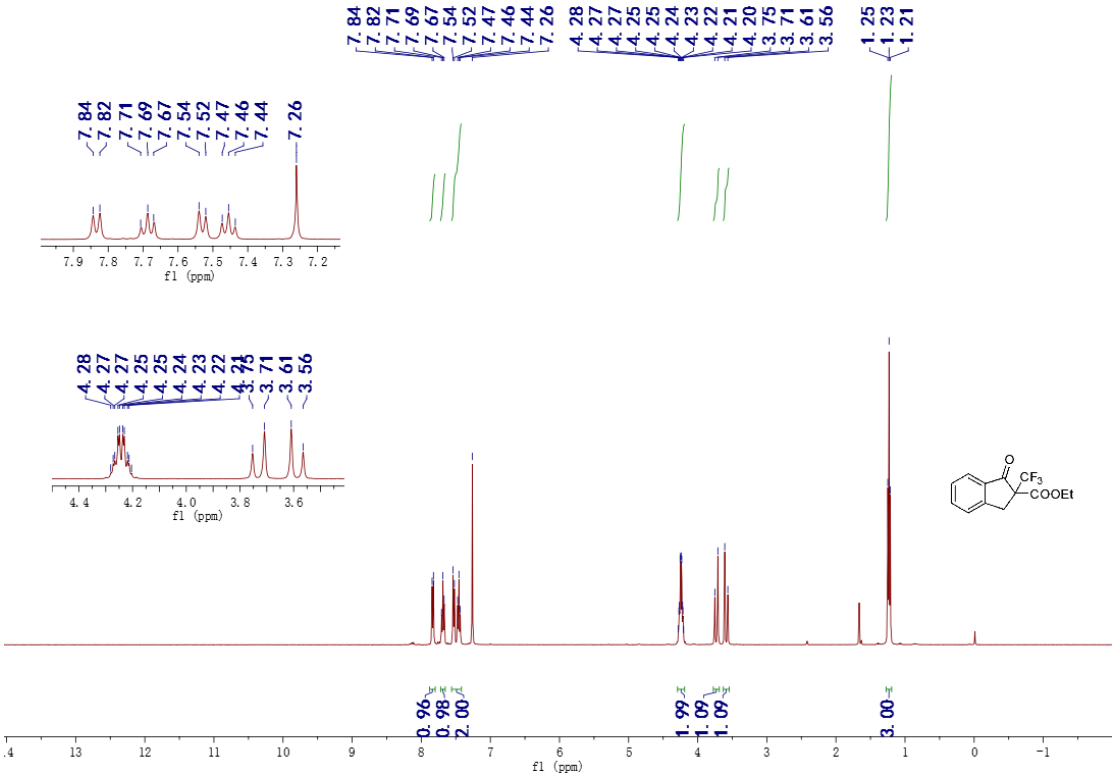
^{19}F NMR spectrum of methyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2a



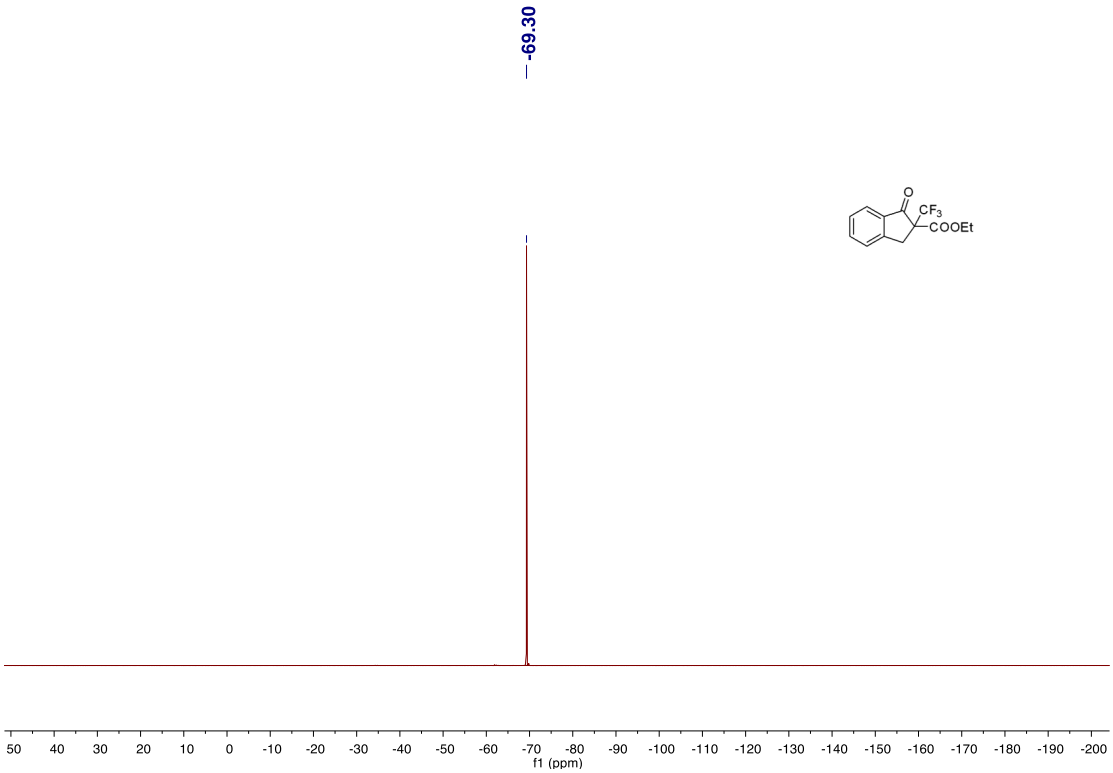
^{13}C NMR spectrum of methyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2a



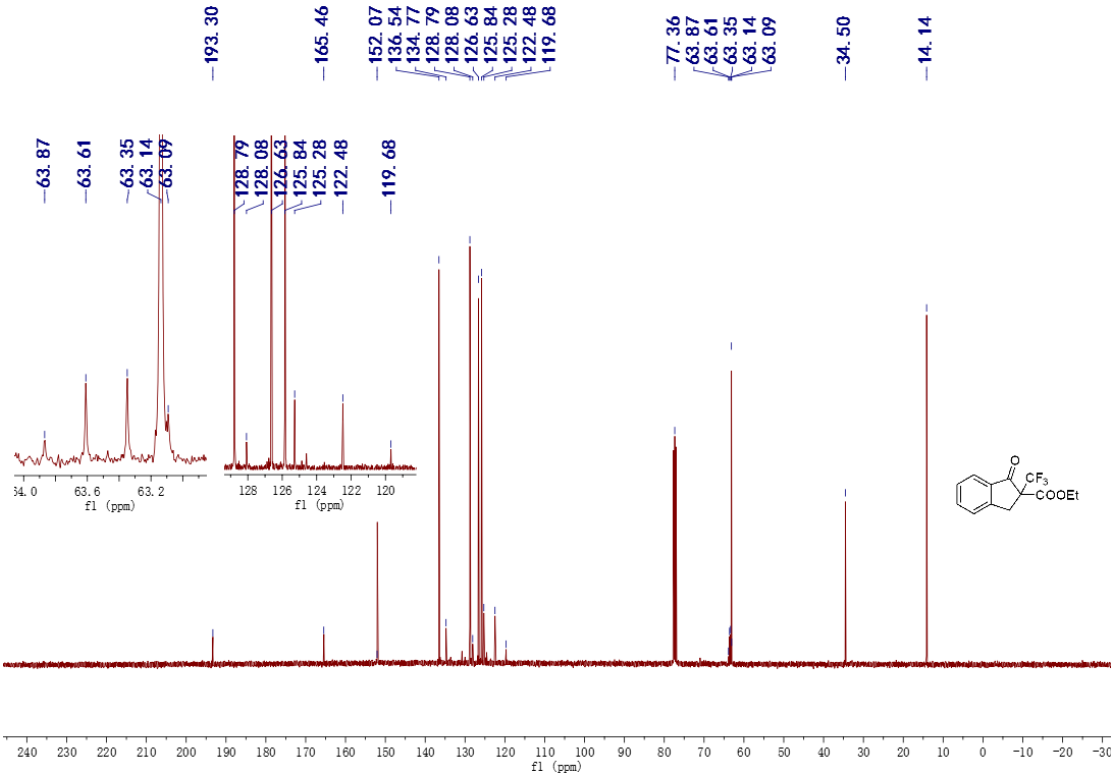
^{1}H NMR spectrum of Ethyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2b



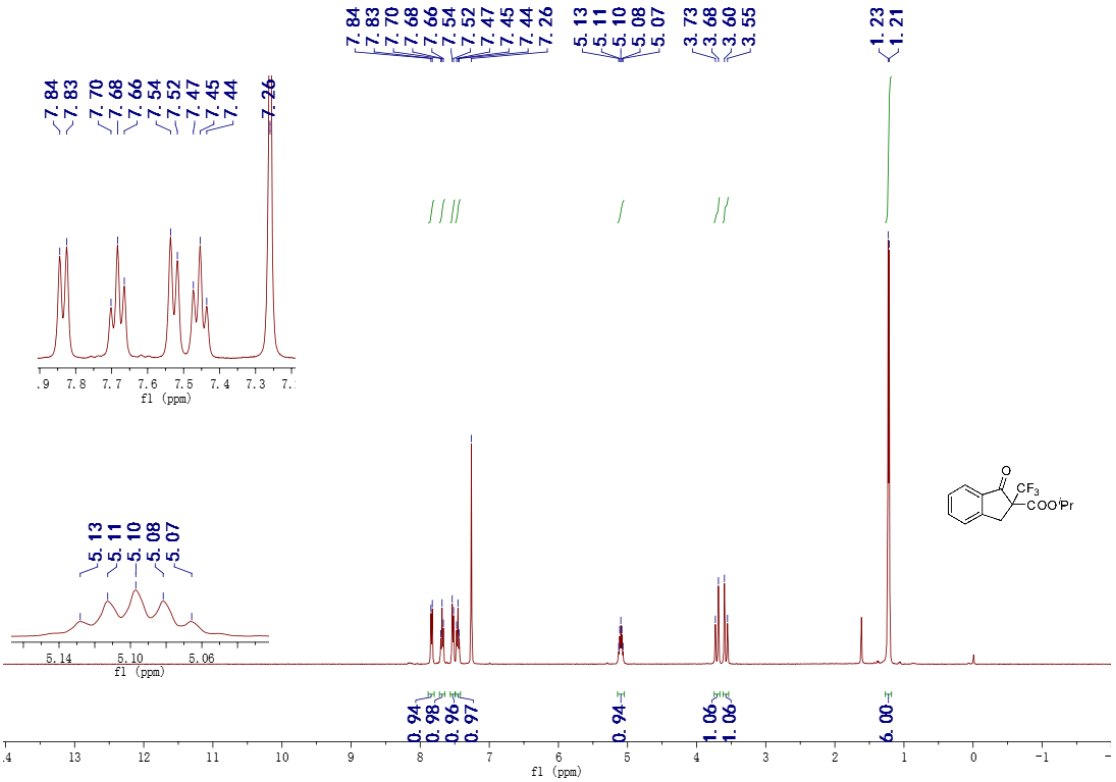
^{19}F NMR spectrum of Ethyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2b



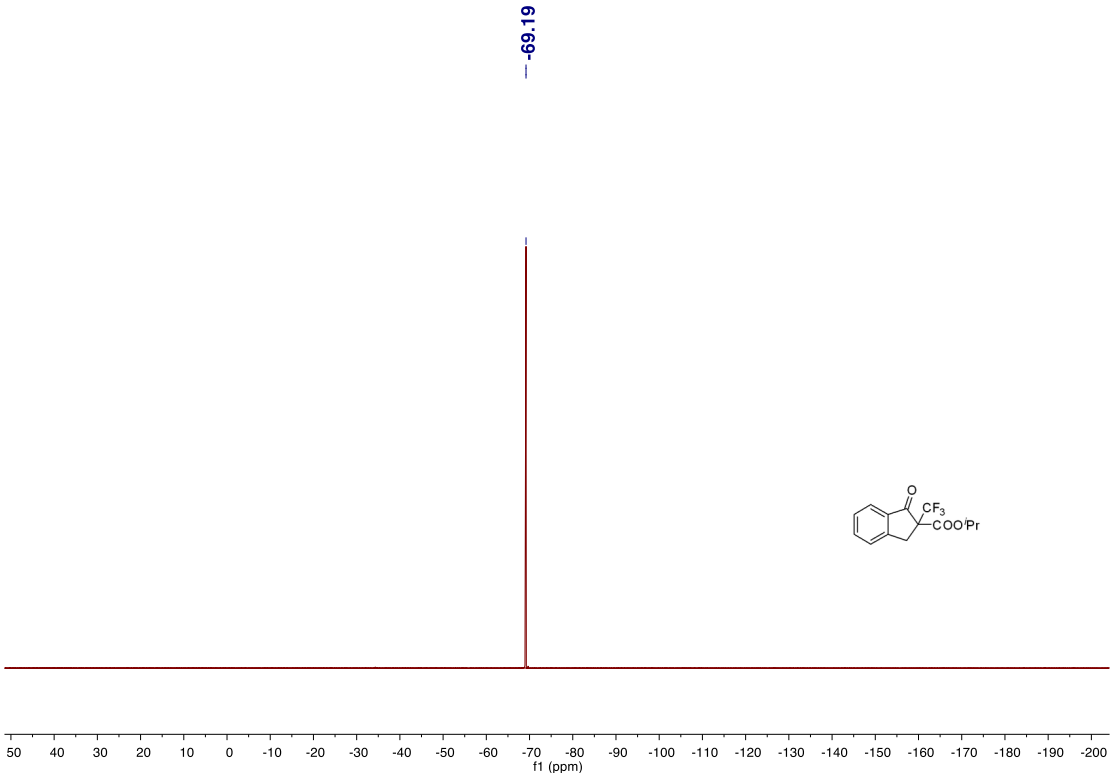
^{13}C NMR spectrum of Ethyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2b



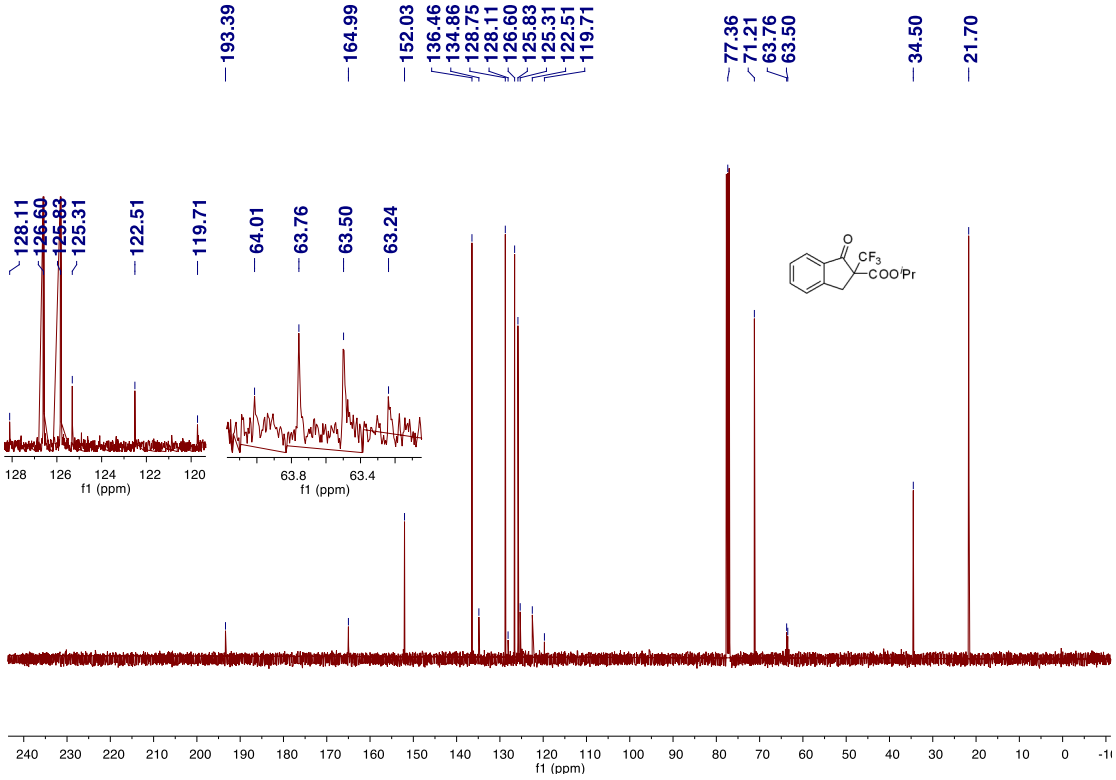
^{1}H NMR spectrum of Isopropyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2c



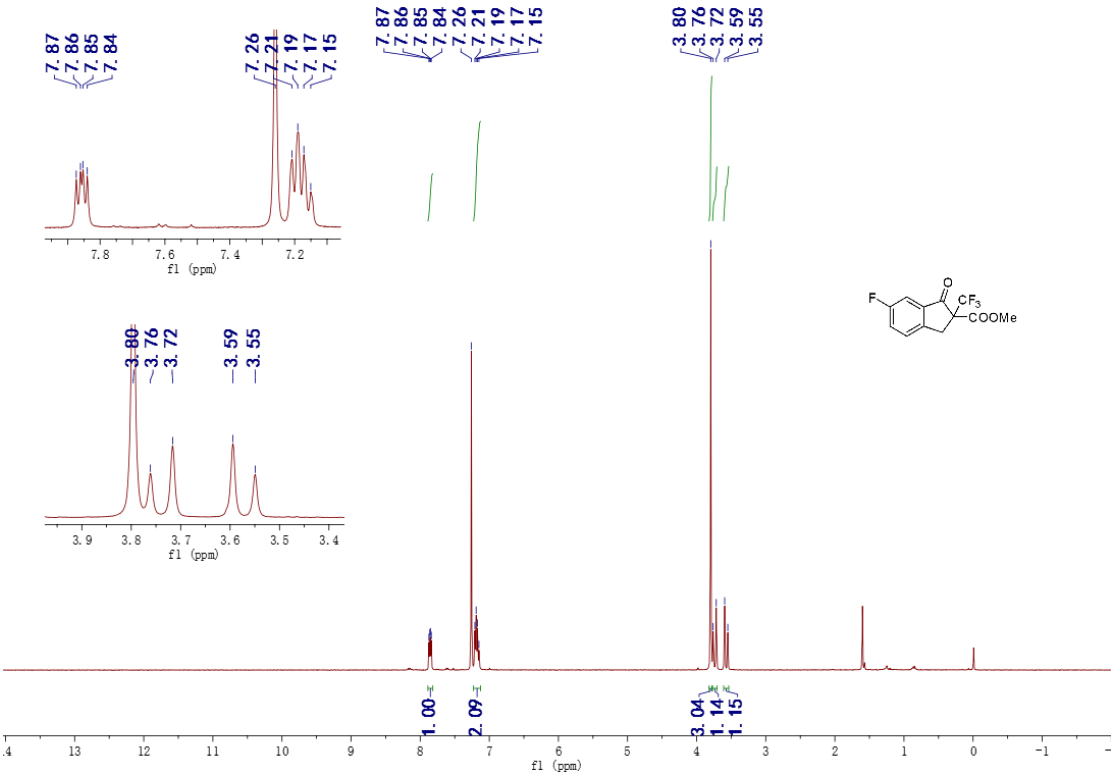
^{19}F NMR spectrum of Isopropyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2c



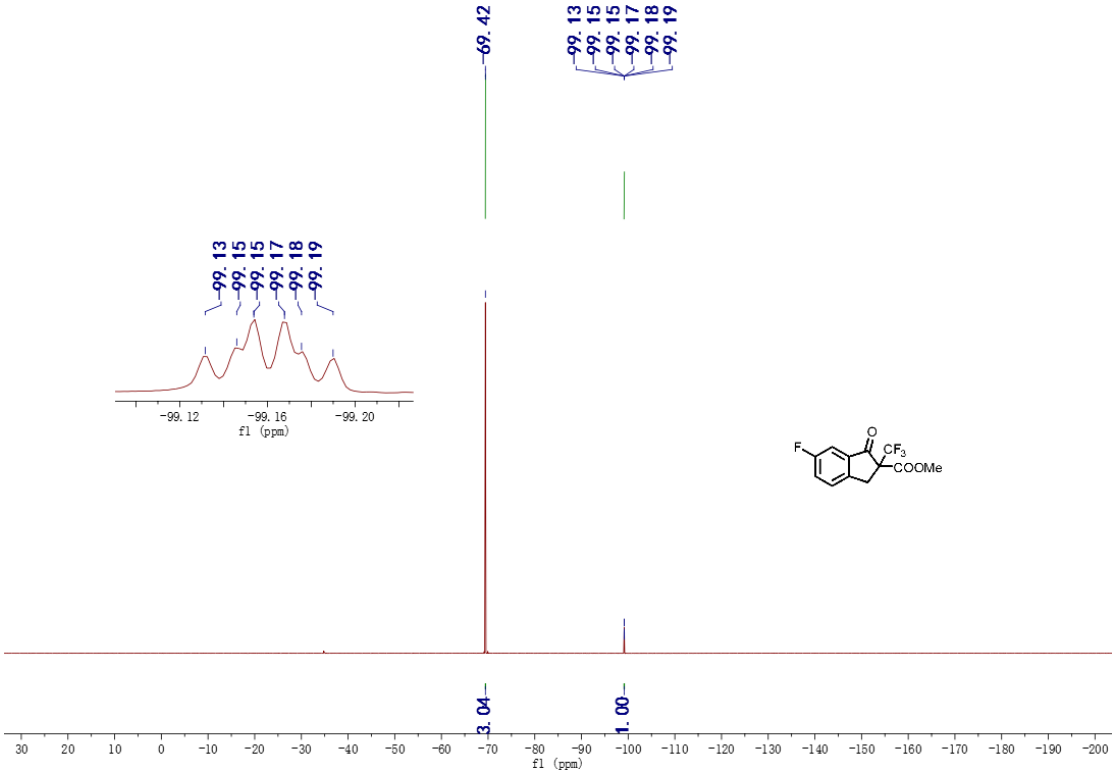
^{13}C NMR spectrum of Isopropyl 1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2c



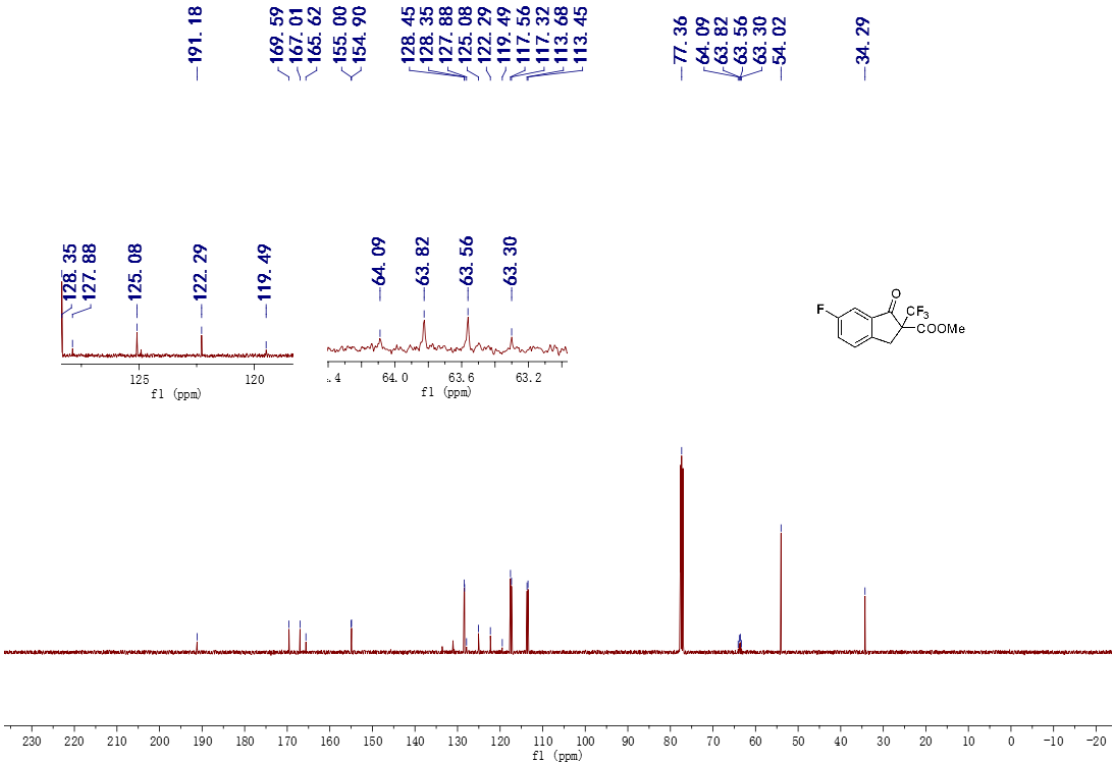
^{1}H NMR spectrum of Methyl 6-chloro-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2d



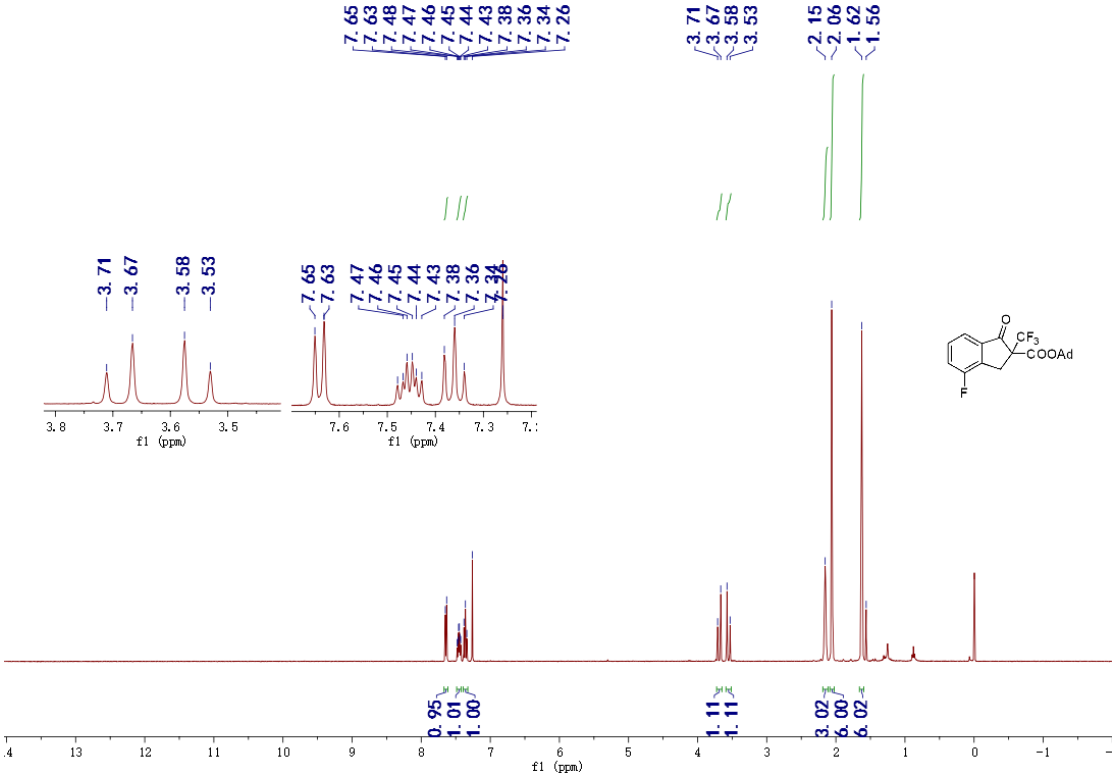
^{19}F NMR spectrum of Methyl 6-chloro-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2d



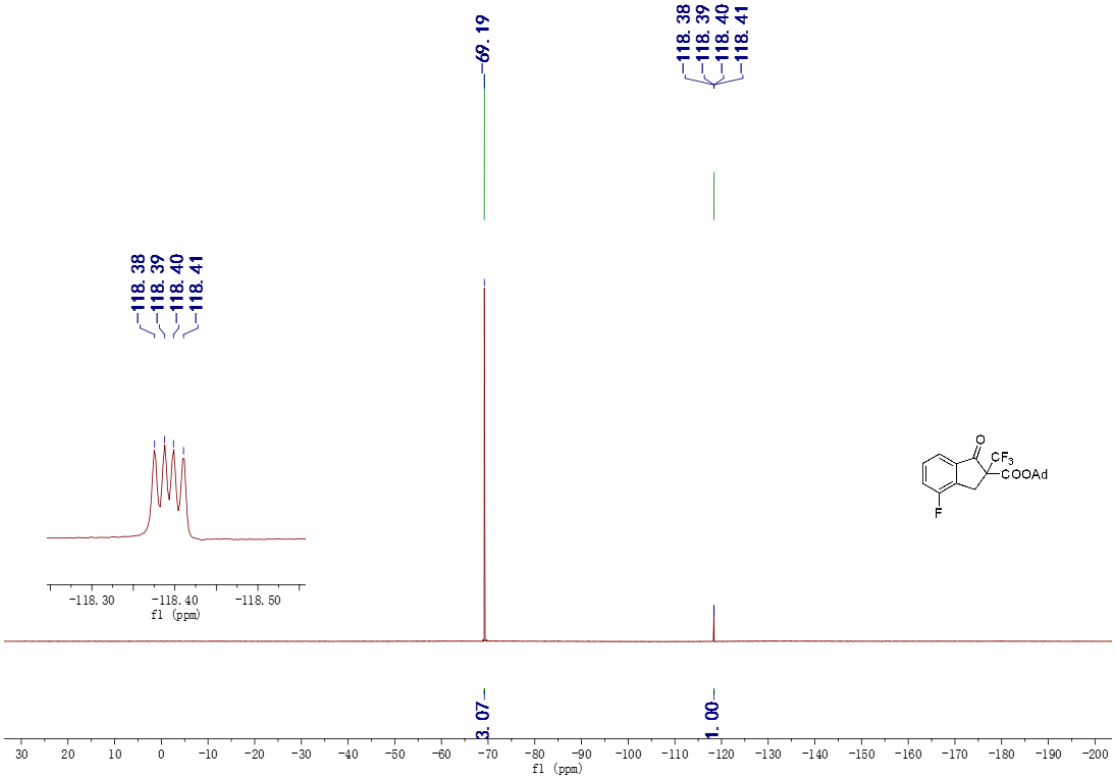
^{13}C NMR spectrum of Methyl 6-chloro-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2d



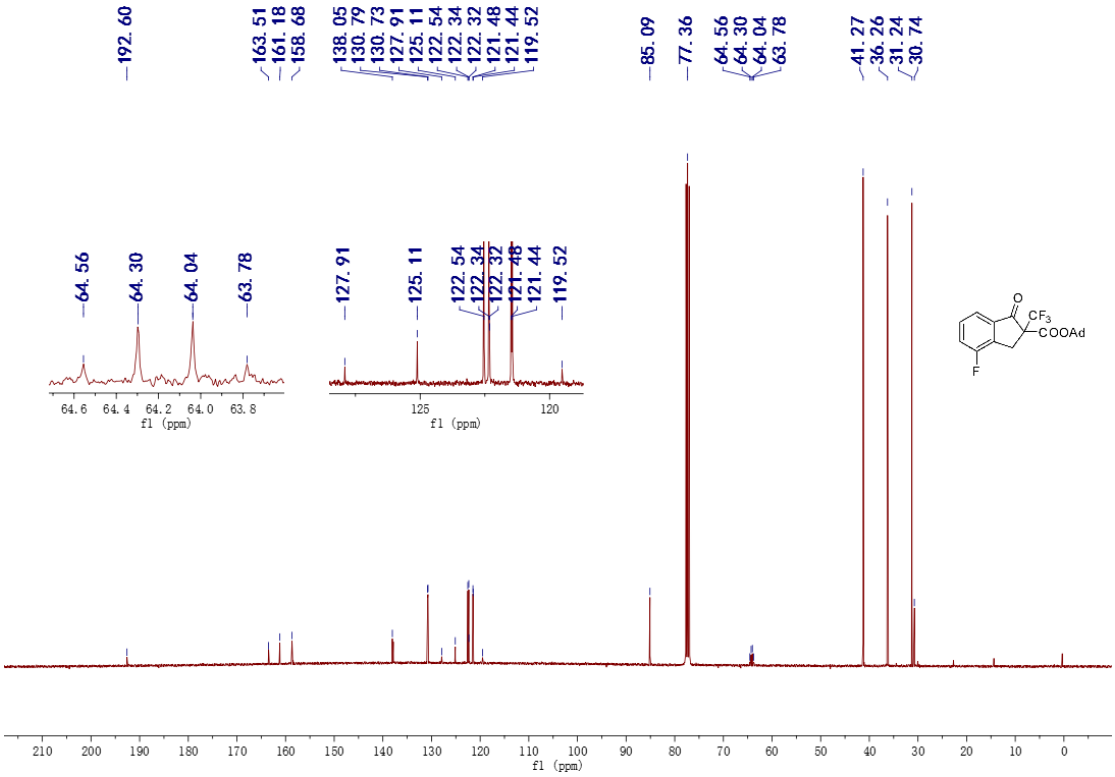
^{1}H NMR spectrum of Adamantyl 4-fluoro-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-indene-2-carboxylate 2e



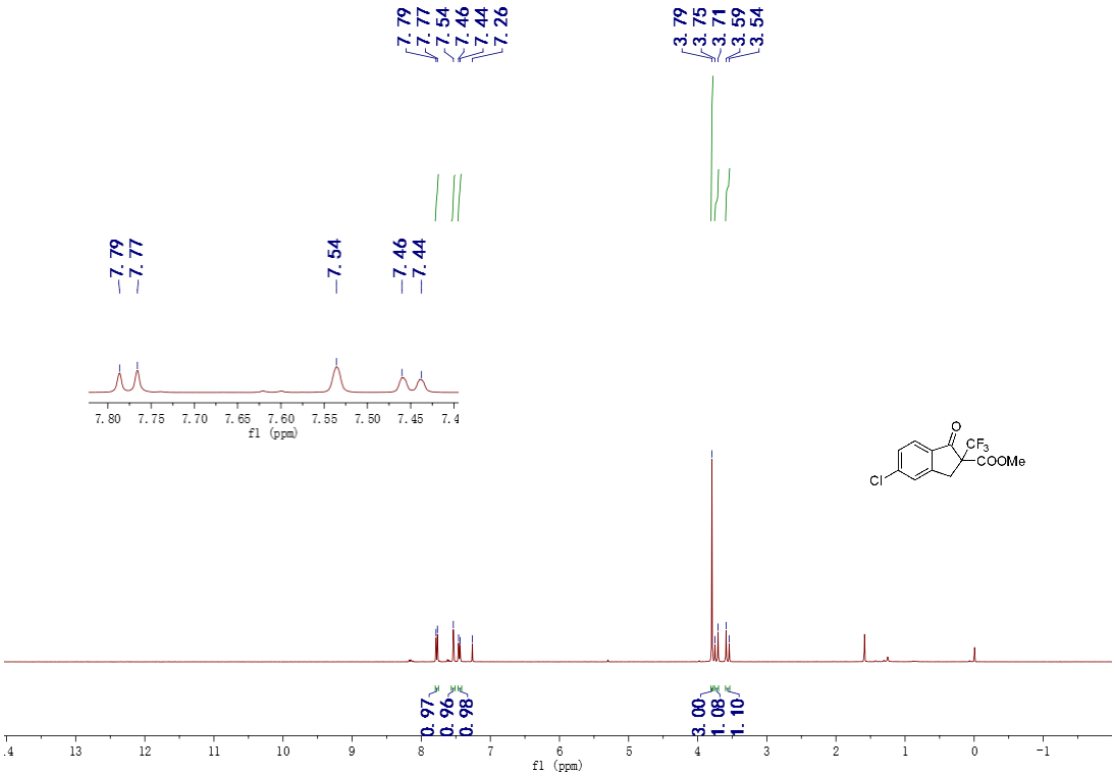
^{19}F NMR spectrum of Adamantyl 4-fluoro-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-indene-2-carboxylate 2e



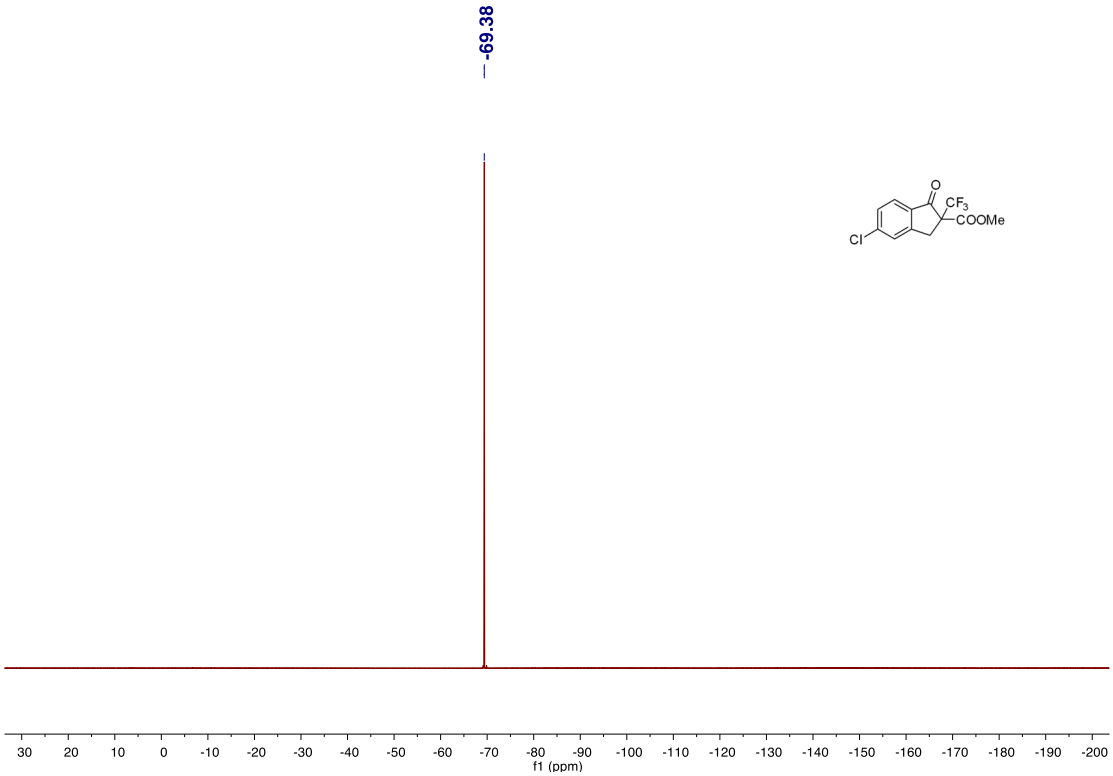
^{13}C NMR spectrum of Adamantyl 4-fluoro-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-indene-2-carboxylate 2e



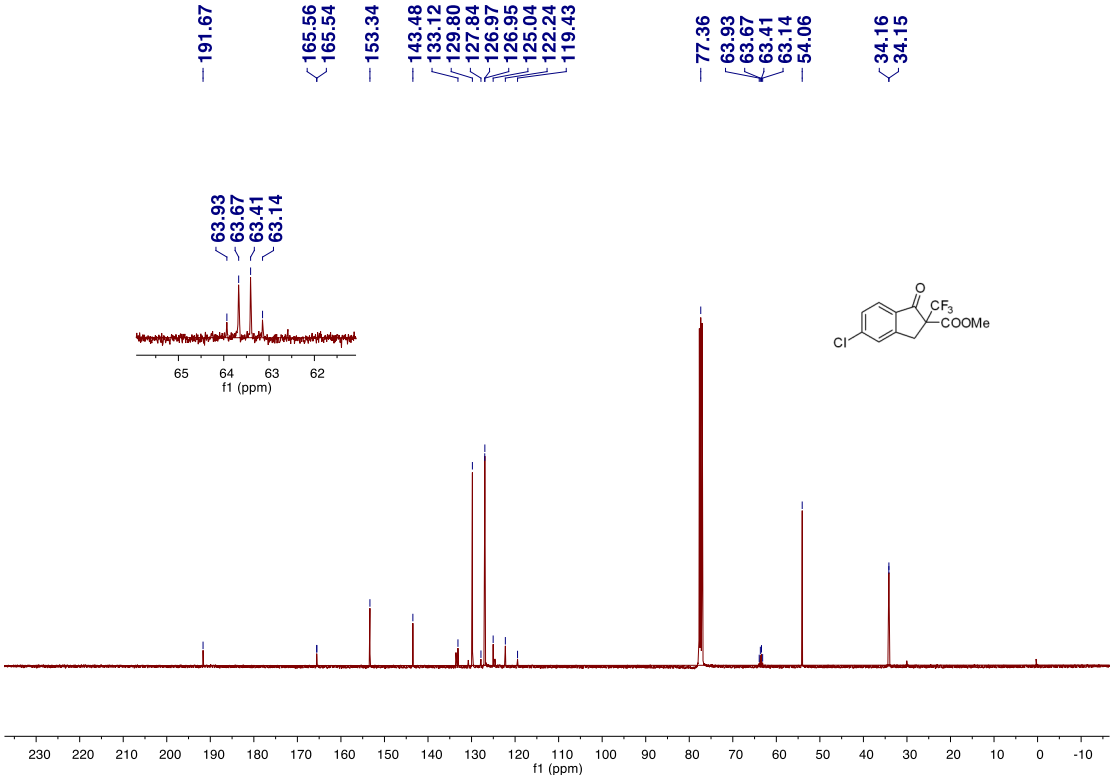
^{1}H NMR spectrum of Methyl 5-chloro-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-indene-2-carboxylate 2f



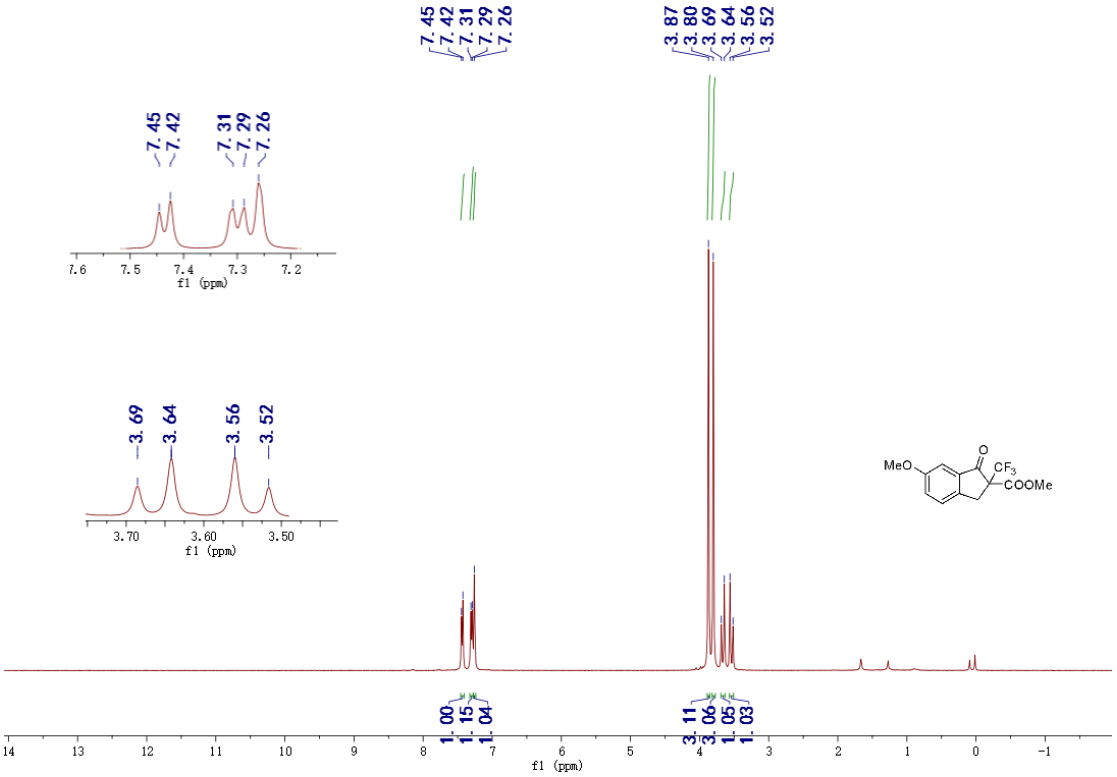
^{19}F NMR spectrum of Methyl 5-chloro-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-indene-2-carboxylate 2f



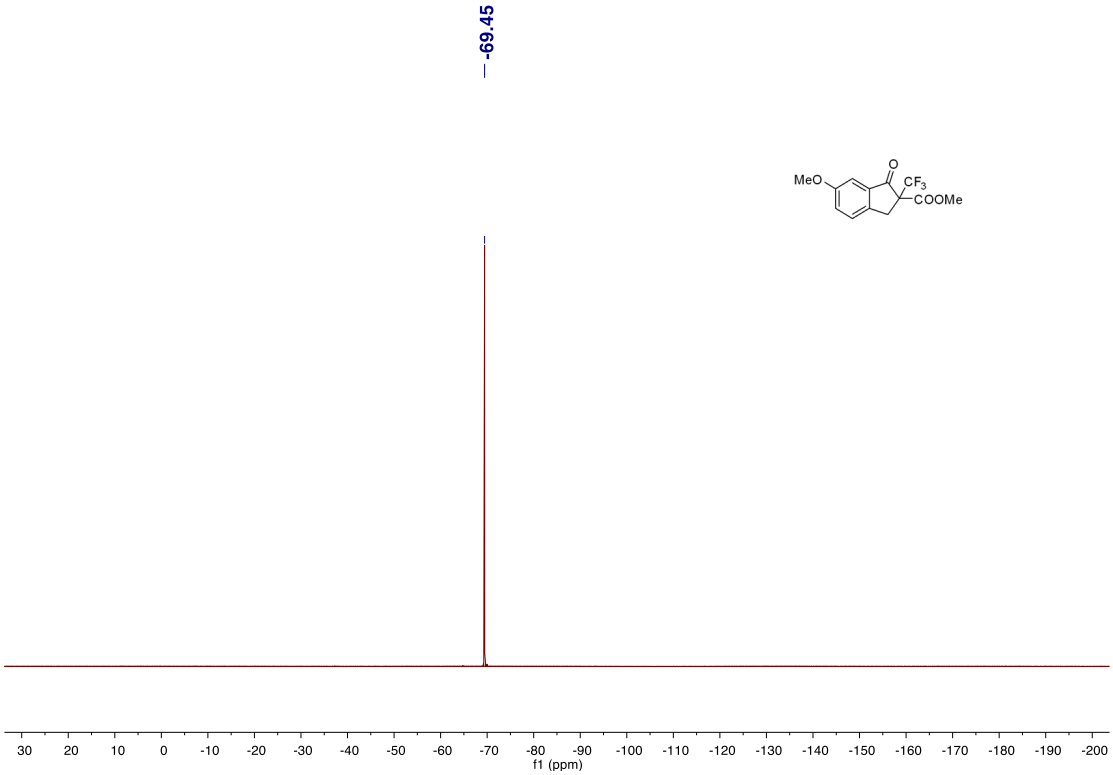
^{13}C NMR spectrum of Methyl 5-chloro-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-indene-2-carboxylate 2f



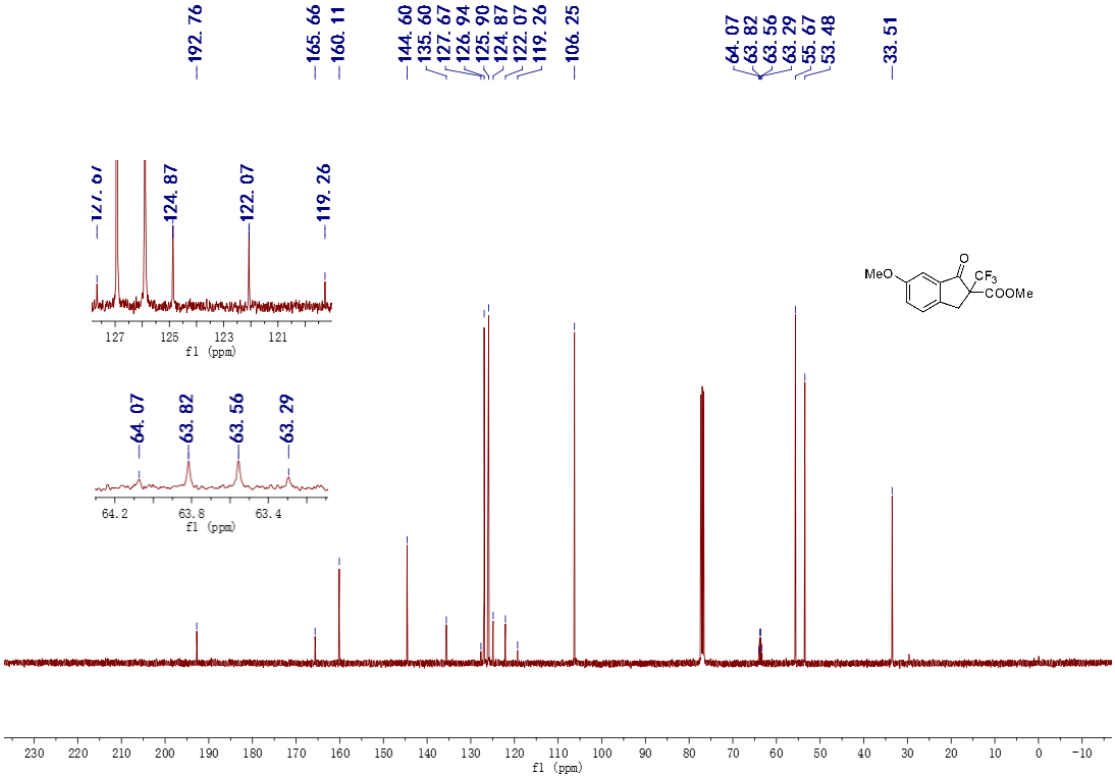
^{1}H NMR spectrum of Methyl 6-methoxy-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-indene-2-carboxylate 2g



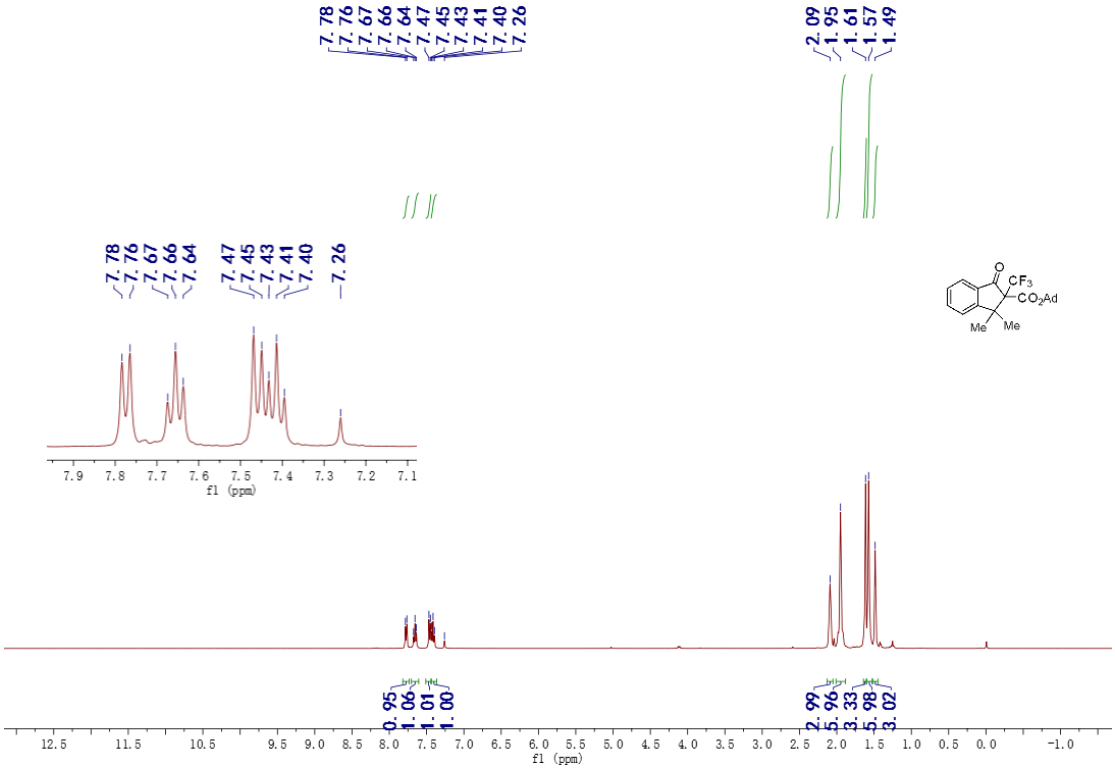
^{19}F NMR spectrum of Methyl 6-methoxy-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-indene-2-carboxylate 2g



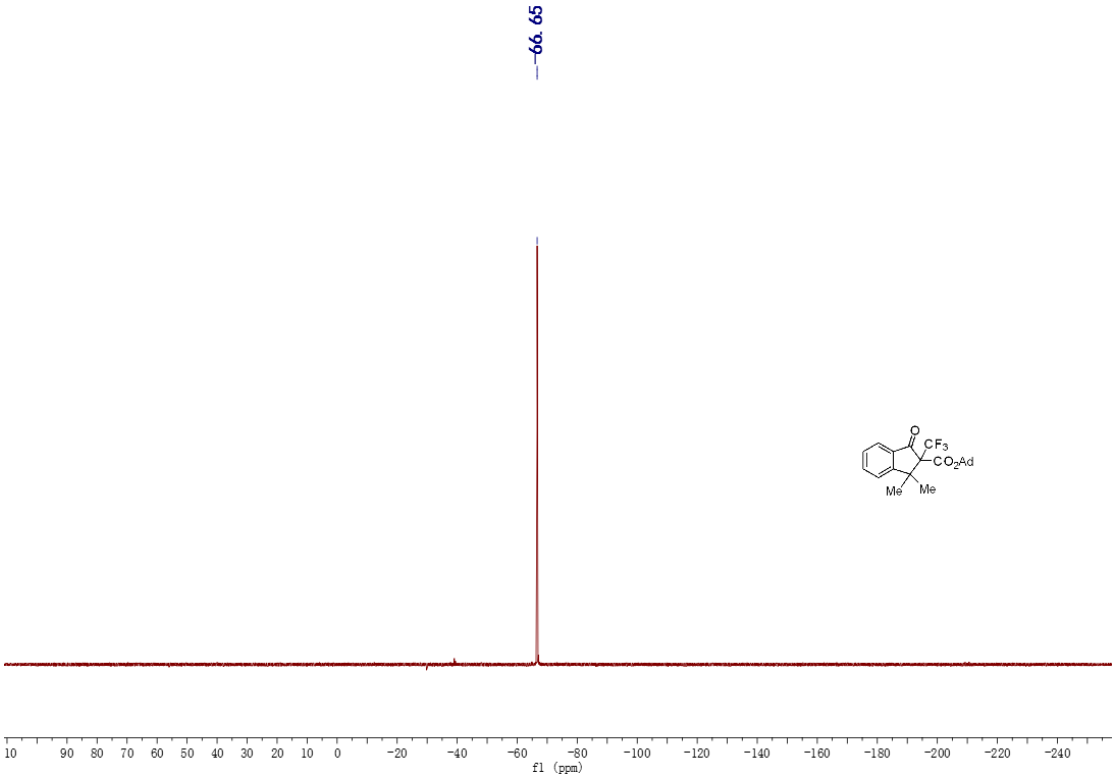
^{13}C NMR spectrum of Methyl 6-methoxy-1-oxo-2-(trifluoromethyl)-2,3-dihydro-1H-indene-2-carboxylate 2g



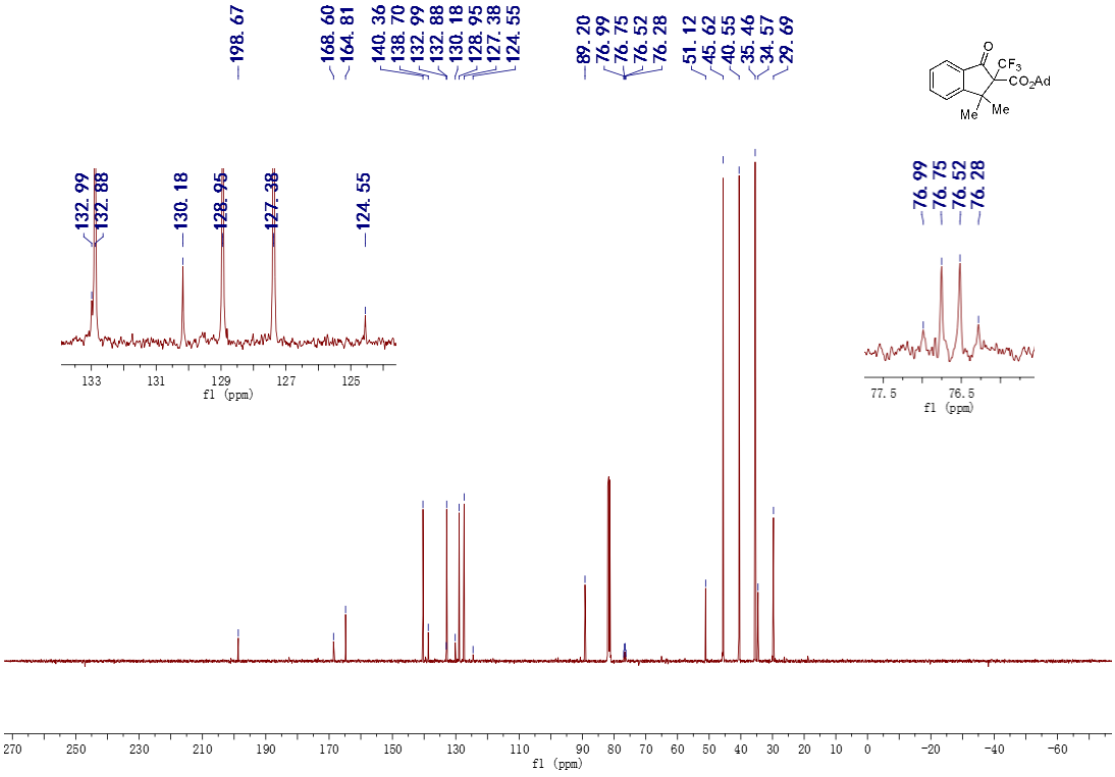
^{1}H NMR spectrum of Adamantyl-1,1-dimethyl-3-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2h



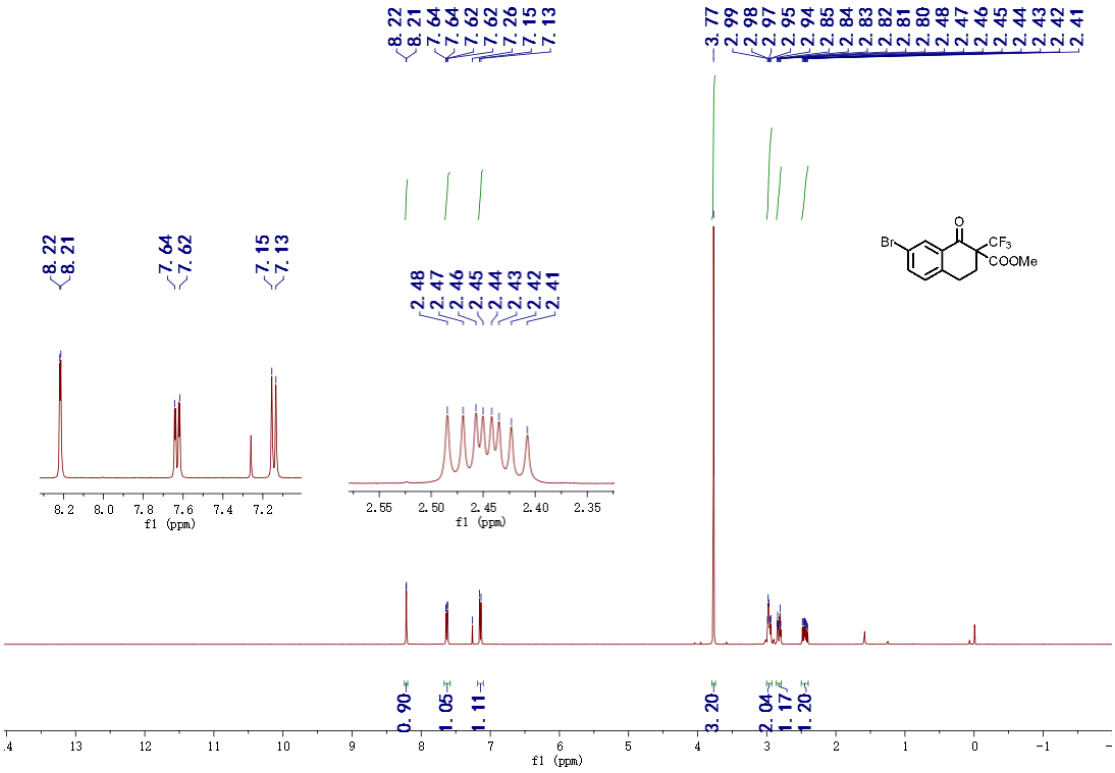
^{19}F NMR spectrum of Adamantyl-1,1-dimethyl-3-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2h



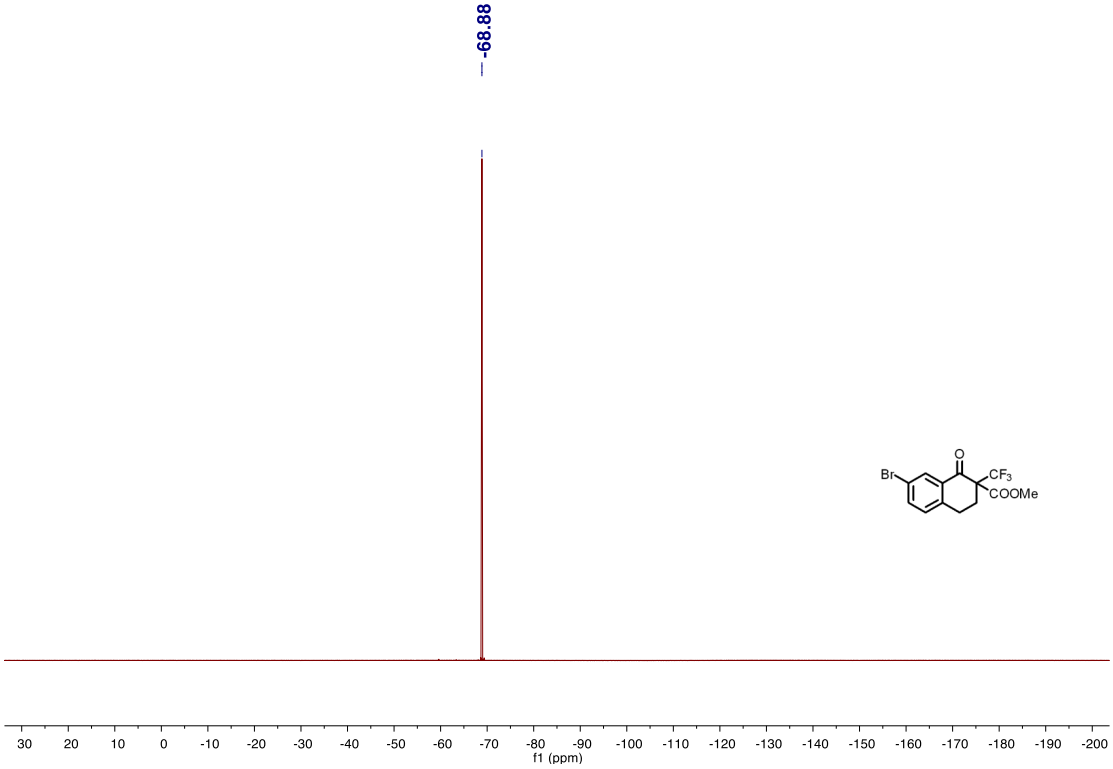
^{13}C NMR spectrum of Adamantyl-1,1-dimethyl-3-oxo-2-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate 2h



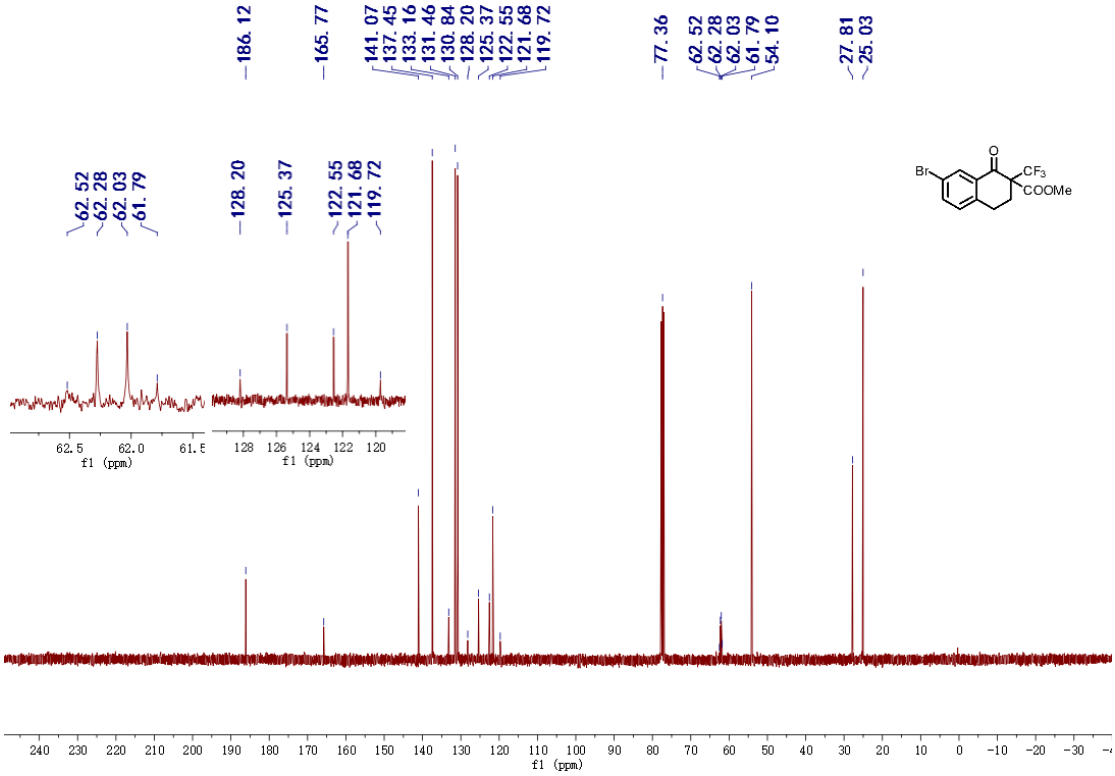
^{1}H NMR spectrum of Methyl-7-bromo-1-oxo-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate 2i



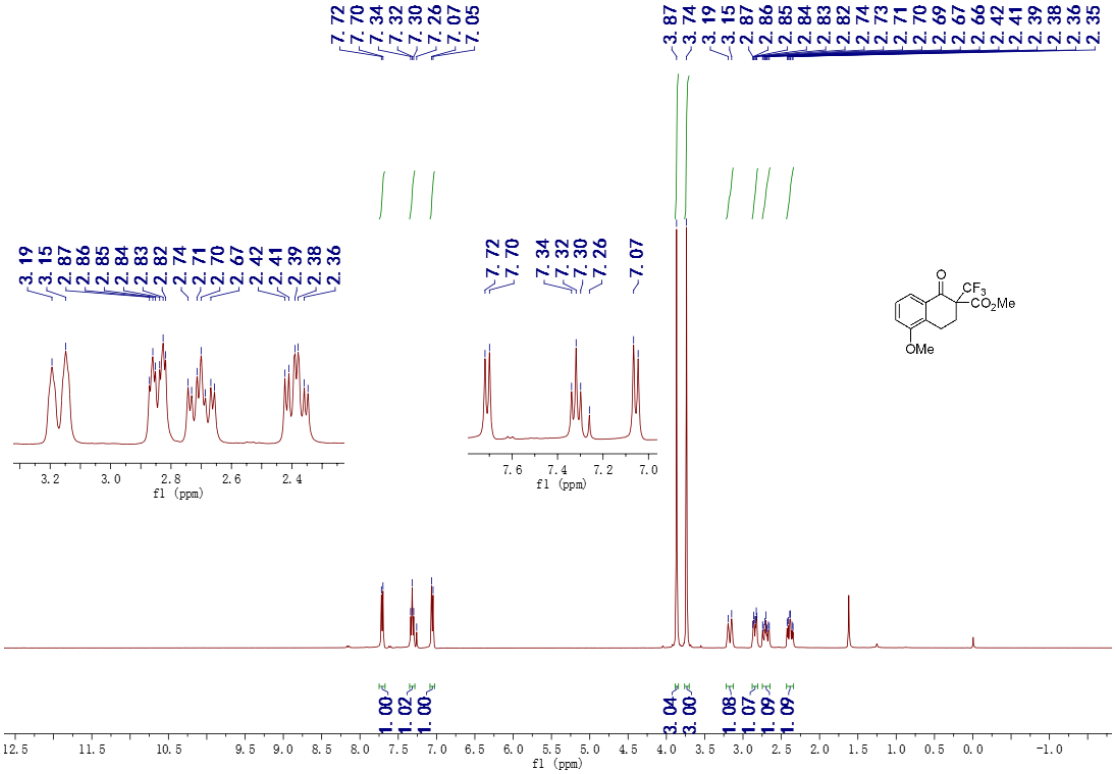
^{19}F NMR spectrum of Methyl-7-bromo-1-oxo-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate 2i



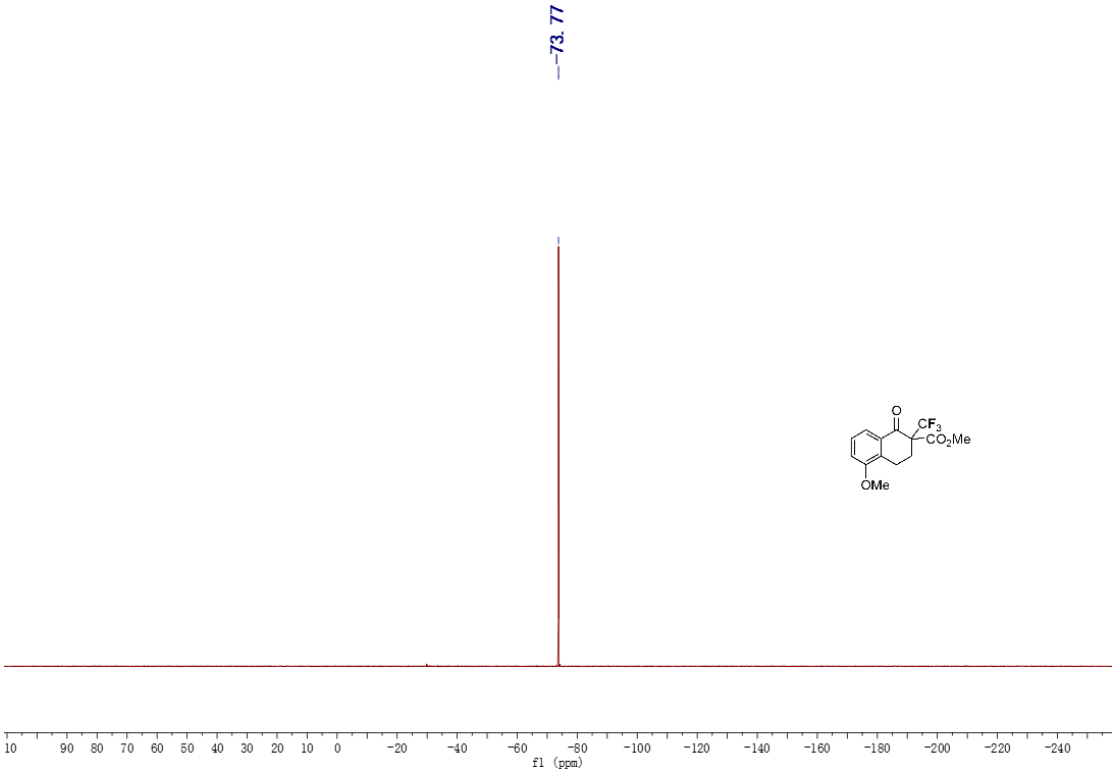
^{13}C NMR spectrum of Methyl-7-bromo-1-oxo-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate 2i



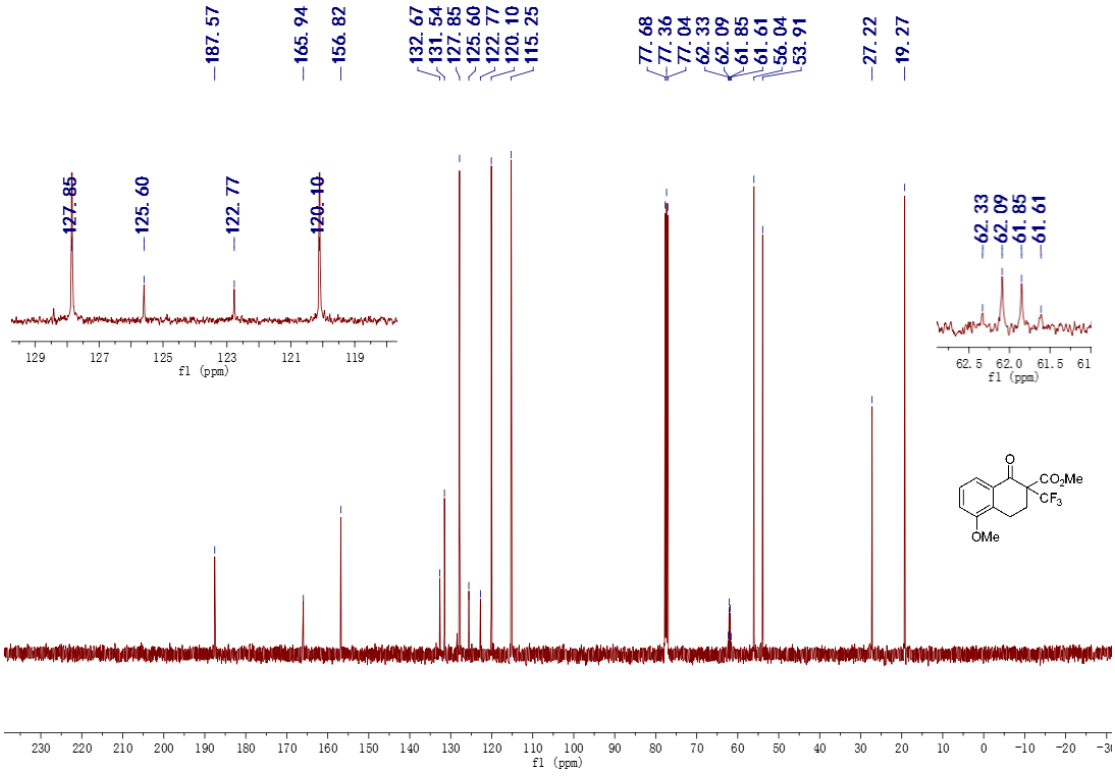
^{1}H NMR spectrum of Methyl-5-methoxy-1-oxo-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate 2j



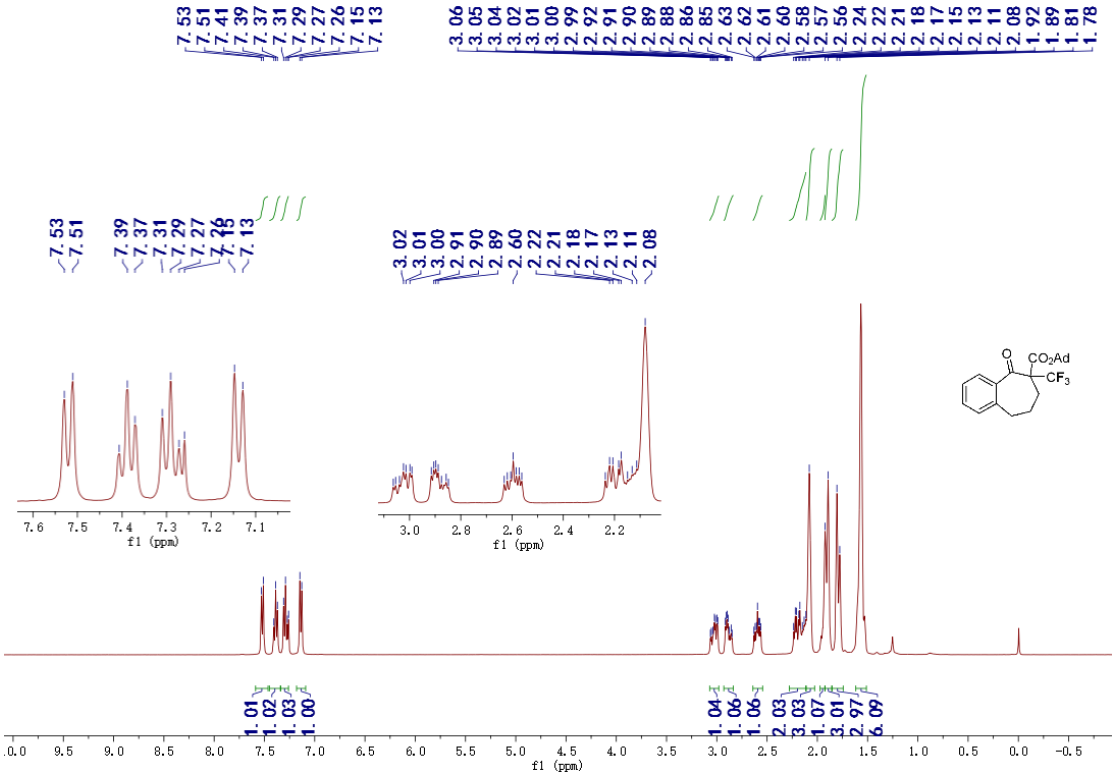
^{19}F NMR spectrum of Methyl-5-methoxy-1-oxo-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate 2j



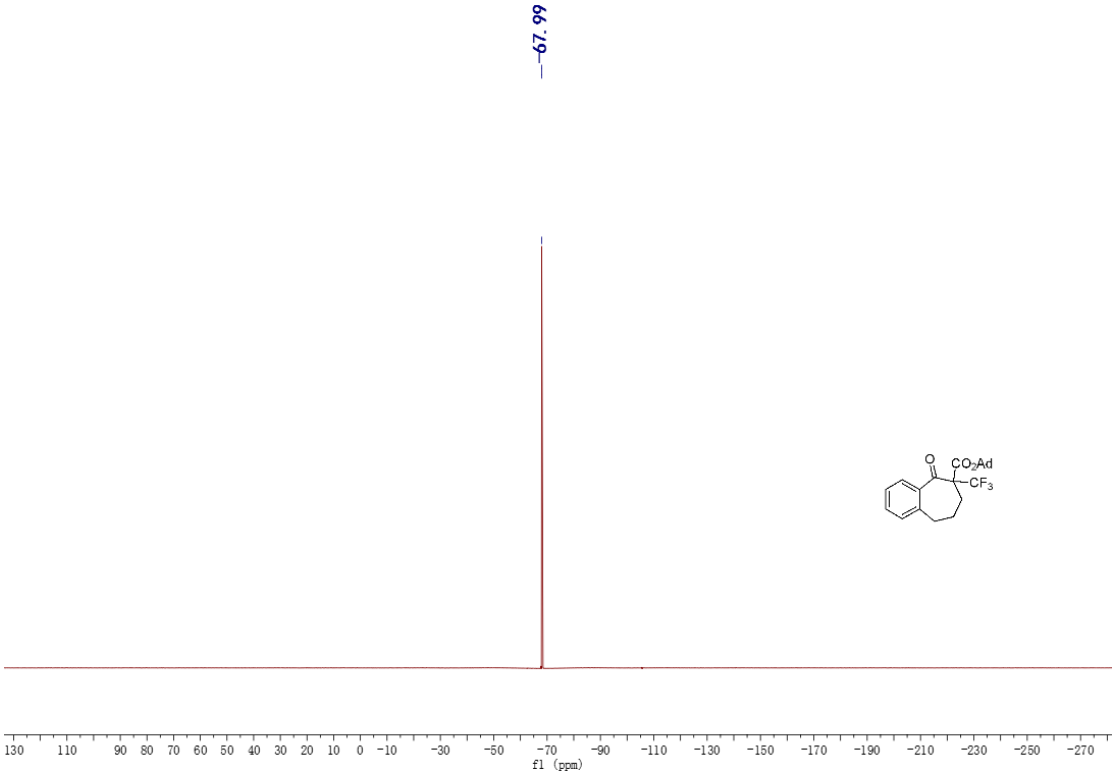
^{13}C NMR spectrum of Methyl-5-methoxy-1-oxo-2-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate 2j



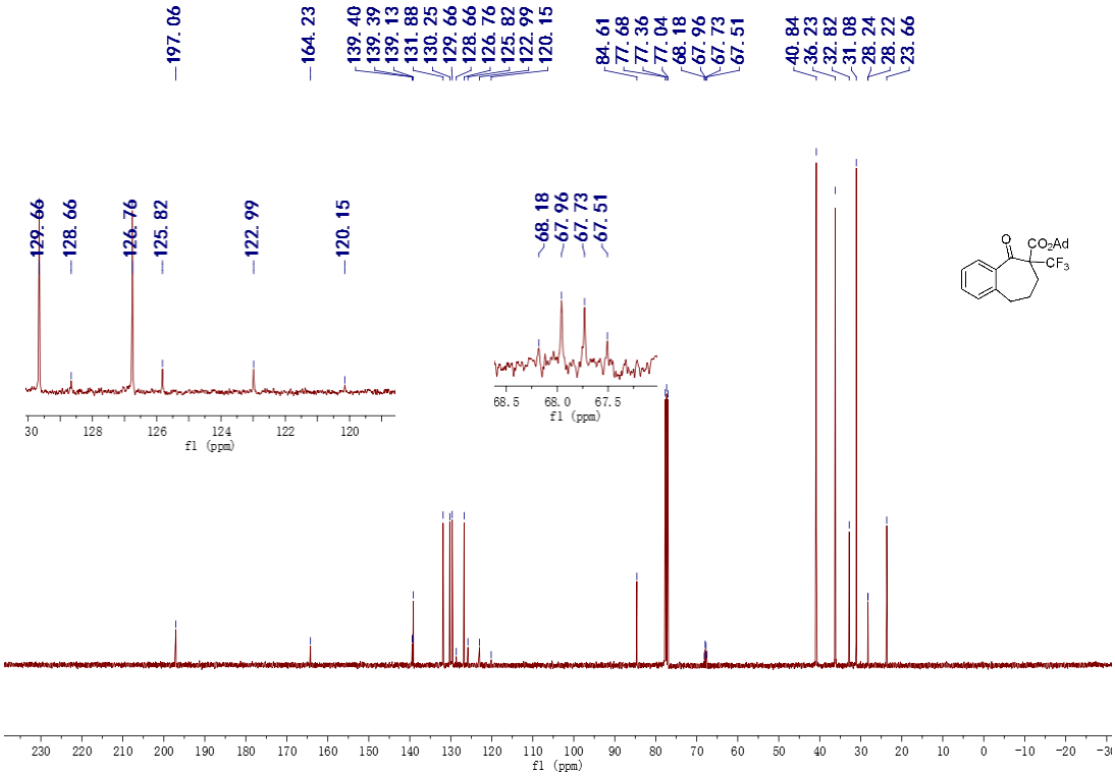
^{1}H NMR spectrum of Adamantyl-5-oxo-6-(trifluoromethyl)-6,7,8,9-tetrahydro-5H-benzo[7]annulene-6-carboxylate 2k



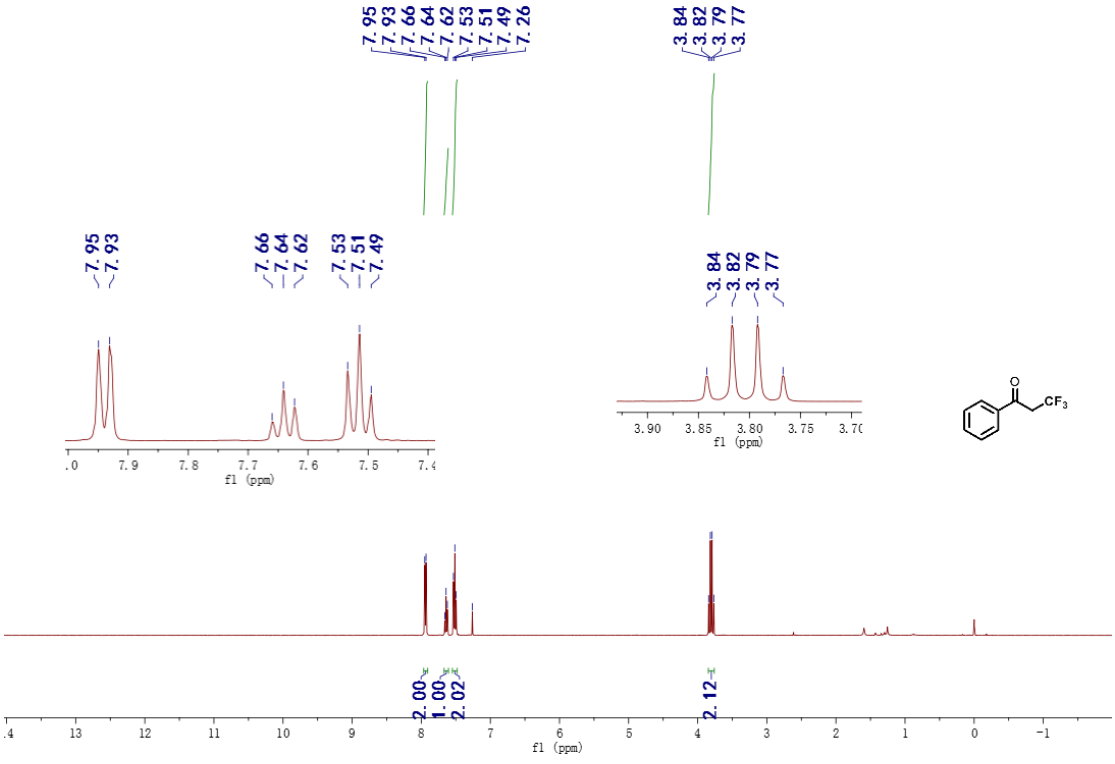
^{19}F NMR spectrum of Adamantyl-5-oxo-6-(trifluoromethyl)-6,7,8,9-tetrahydro-5H-benzo[7]annulene-6-carboxylate 2k



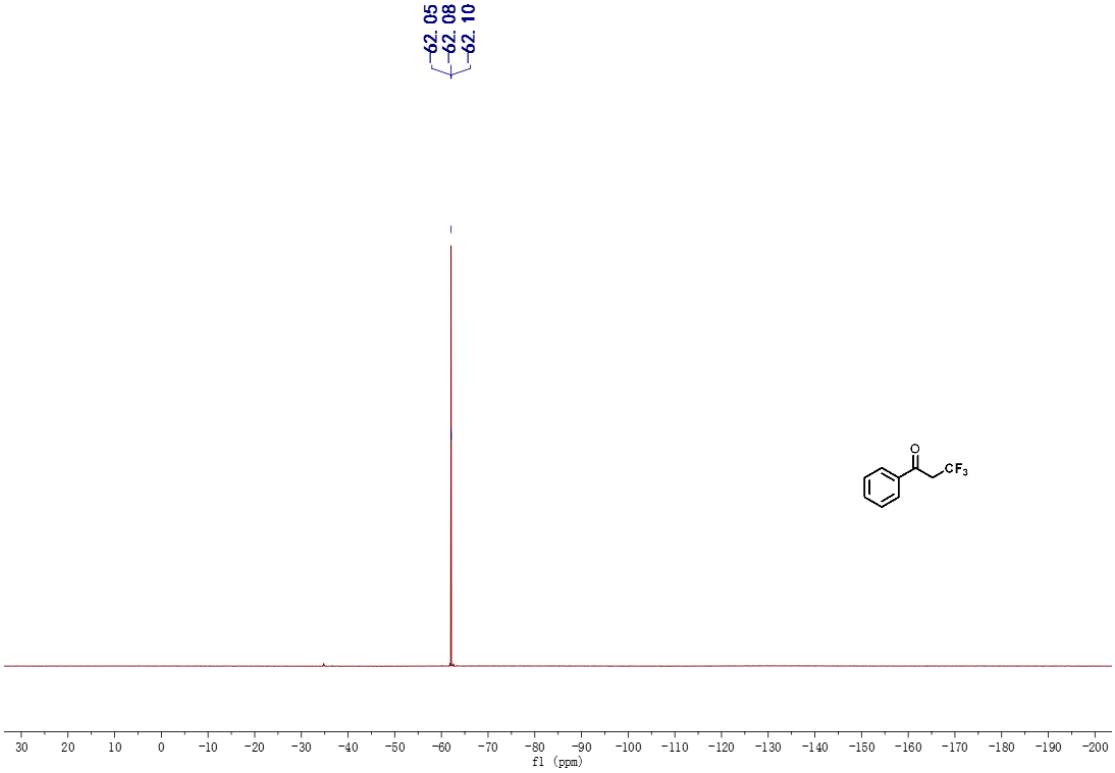
^{13}C NMR spectrum of Adamantyl-5-oxo-6-(trifluoromethyl)-6,7,8,9-tetrahydro-5H-benzo[7]annulene-6-carboxylate 2k



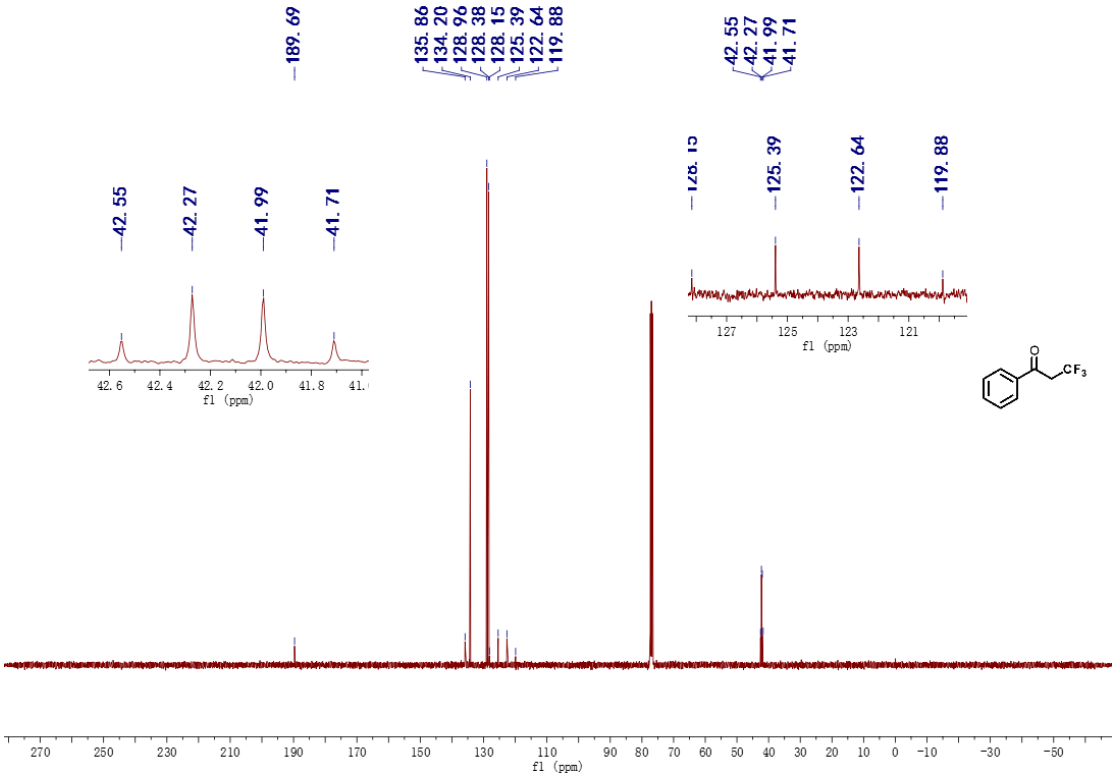
^{1}H NMR spectrum of 3,3,3-trifluoro-1-phenylpropan-1-one 3a



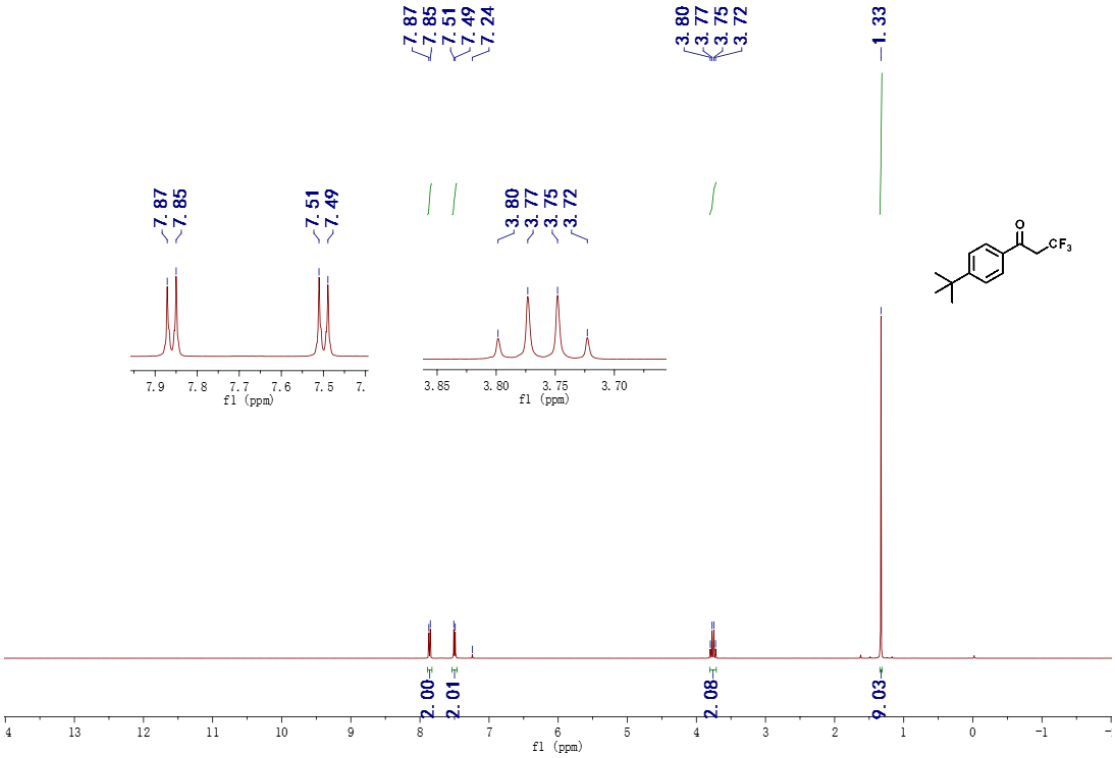
^{19}F NMR spectrum of 3,3,3-trifluoro-1-phenylpropan-1-one 3a



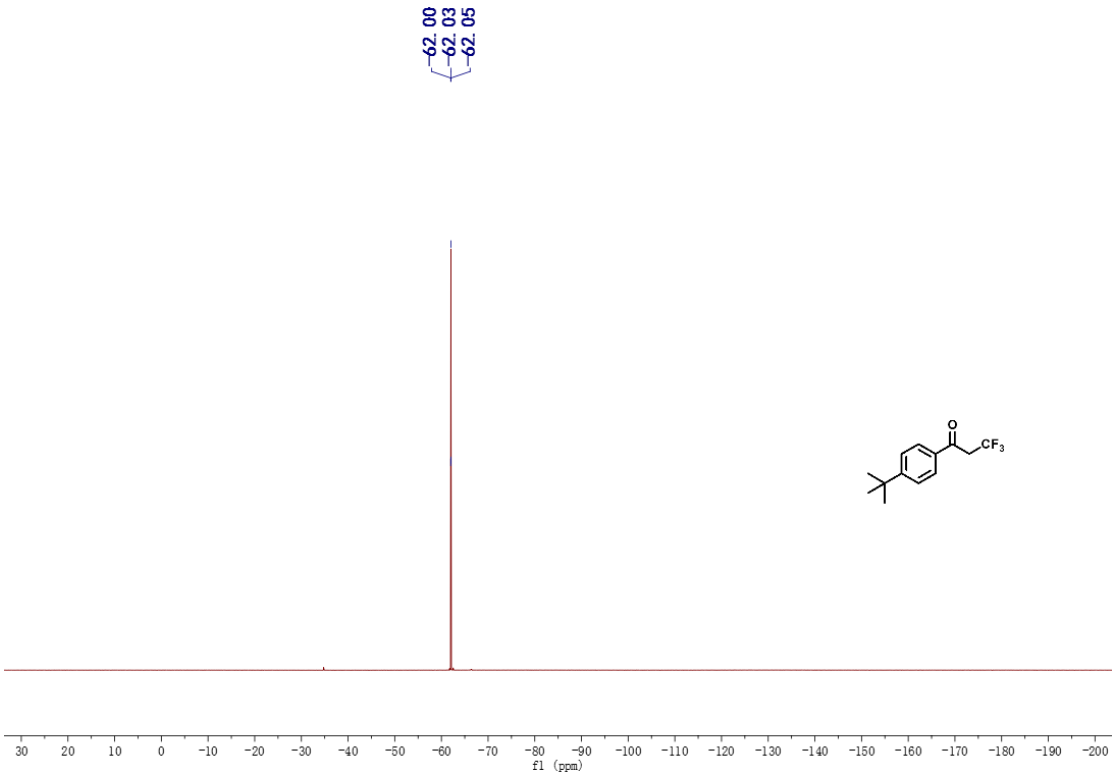
^{13}C NMR spectrum of 3,3,3-trifluoro-1-phenylpropan-1-one 3a



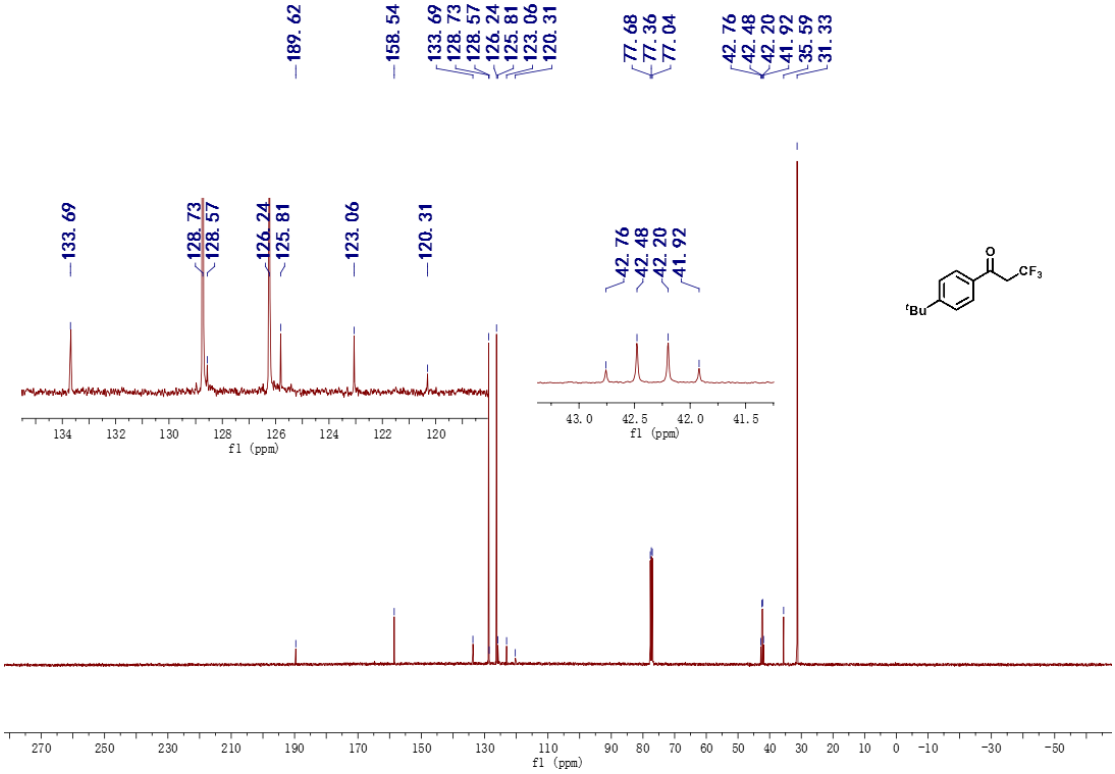
^{1}H NMR spectrum of 1-(4-*tert*-butylphenyl)-3,3,3-trifluoropropan-1-one 3b



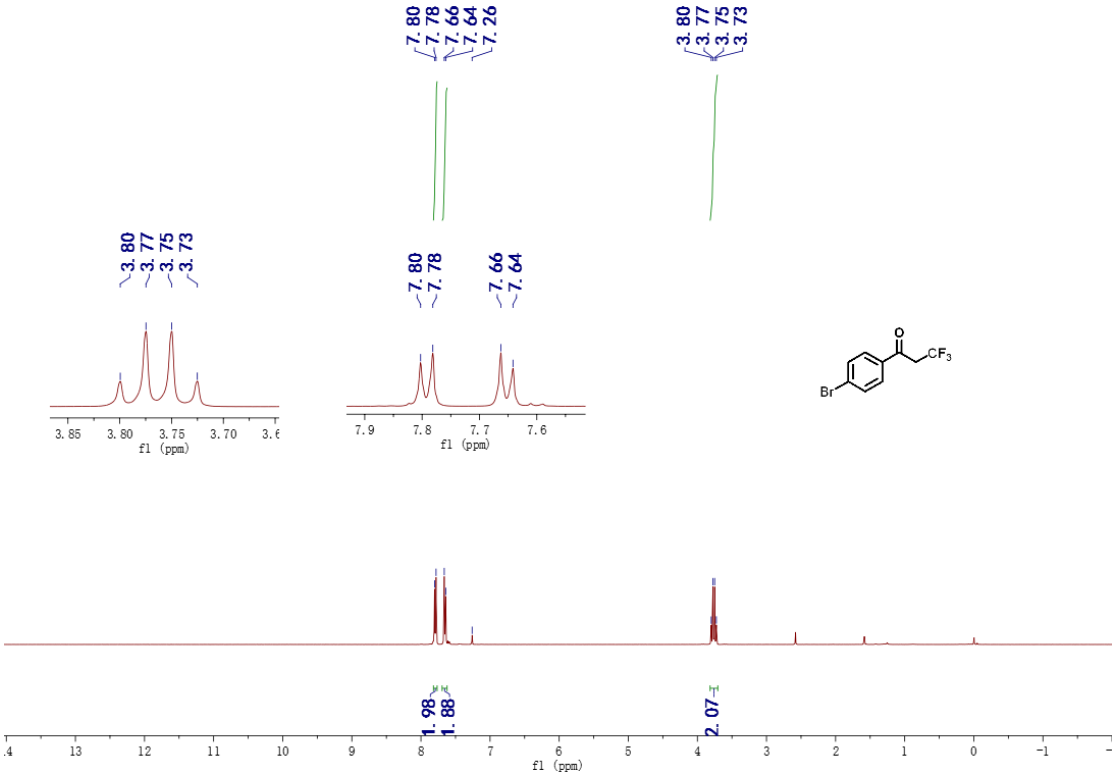
^{19}F NMR spectrum of 1-(4- *tert*-butylphenyl)-3,3,3-trifluoropropan-1-one 3b



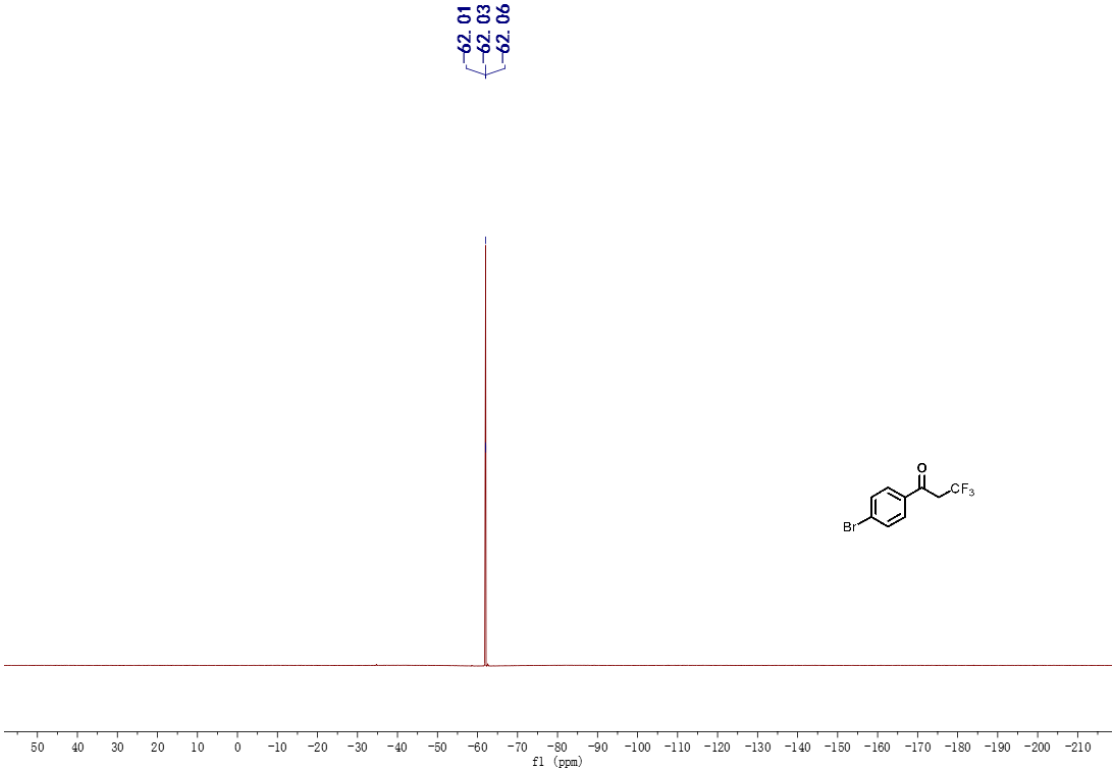
^{13}C NMR spectrum of 1-(4- *tert*-butylphenyl)-3,3,3-trifluoropropan-1-one 3b



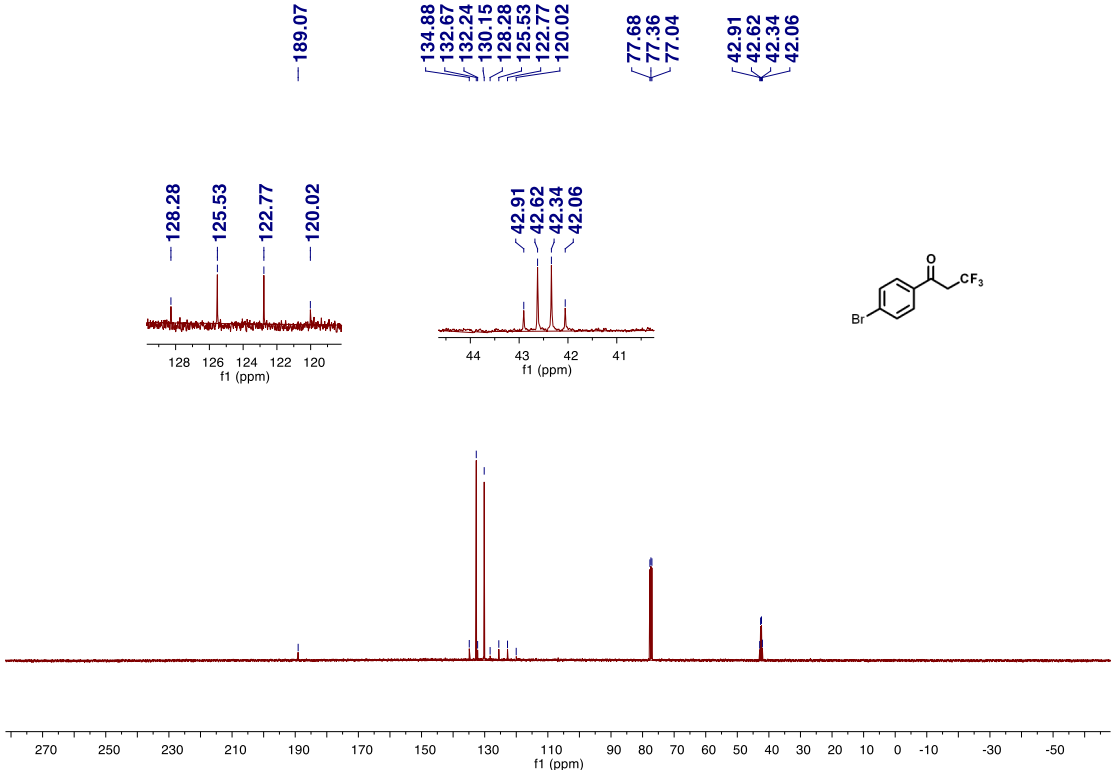
^{1}H NMR spectrum of 1-(4-bromophenyl)-3,3,3-trifluoropropan-1-one 3c



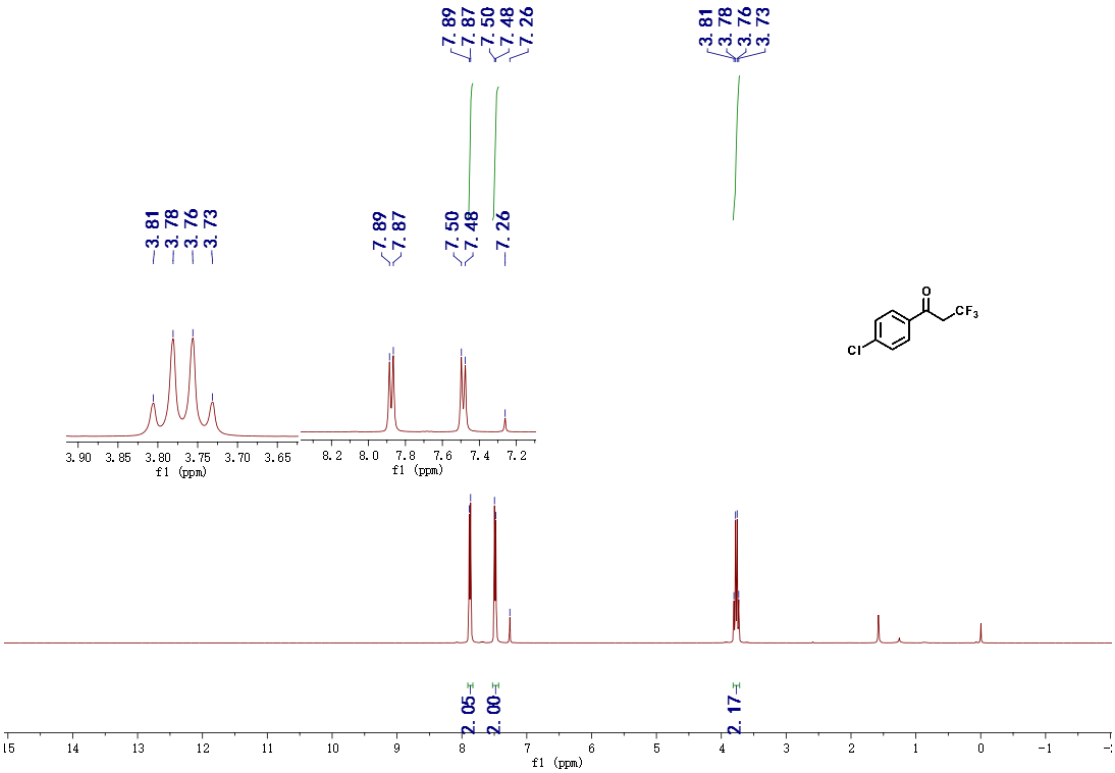
^{19}F NMR spectrum of 1-(4-bromophenyl)-3,3,3-trifluoropropan-1-one 3c



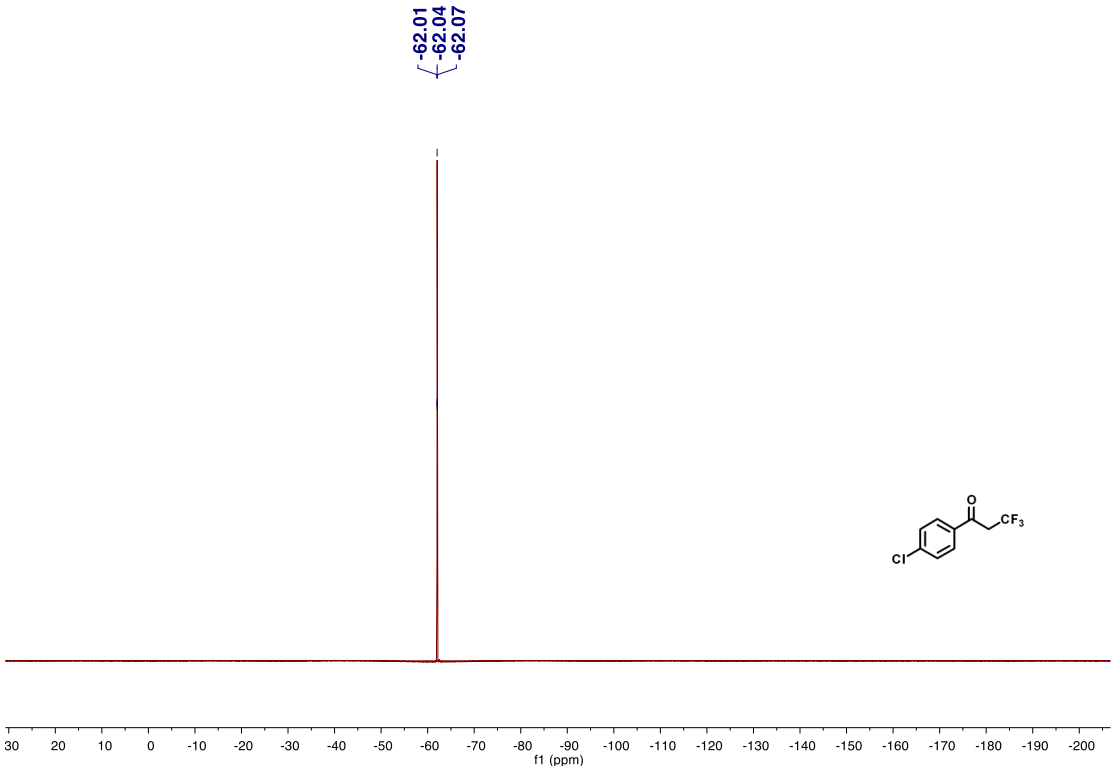
^{13}C NMR spectrum of 1-(4-bromophenyl)-3,3,3-trifluoropropan-1-one 3c



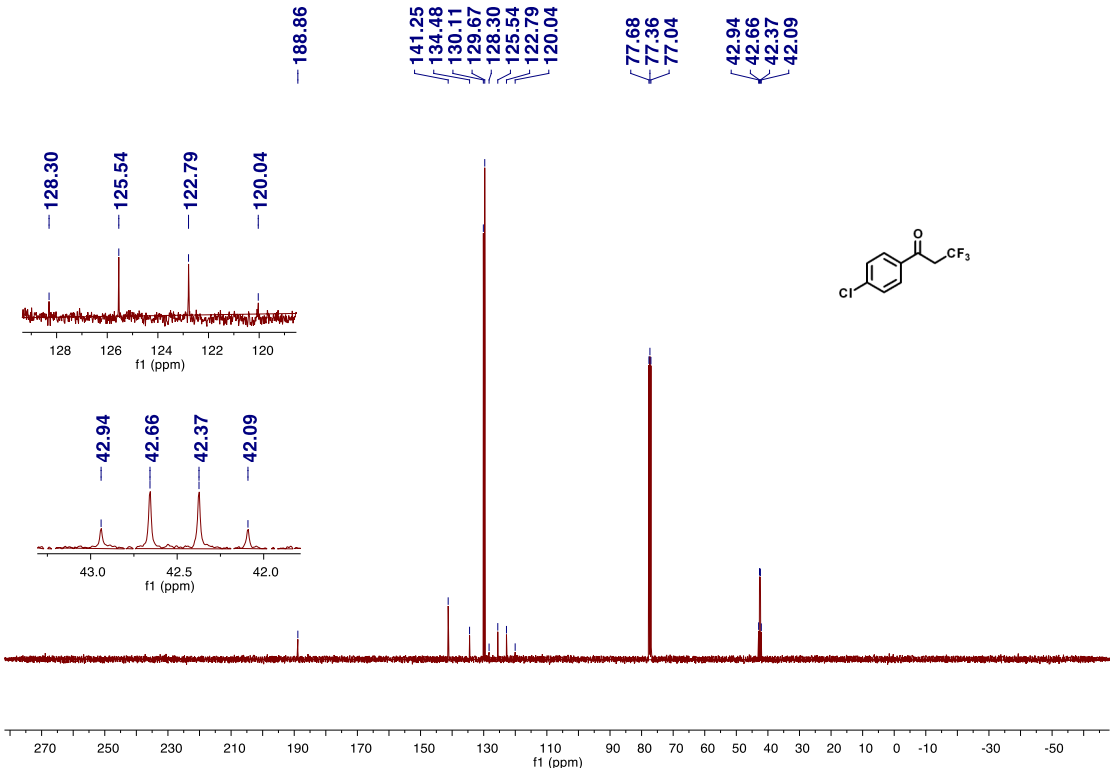
^{1}H NMR spectrum of 1-(4-chlorophenyl)-3,3,3-trifluoropropan-1-one 3d



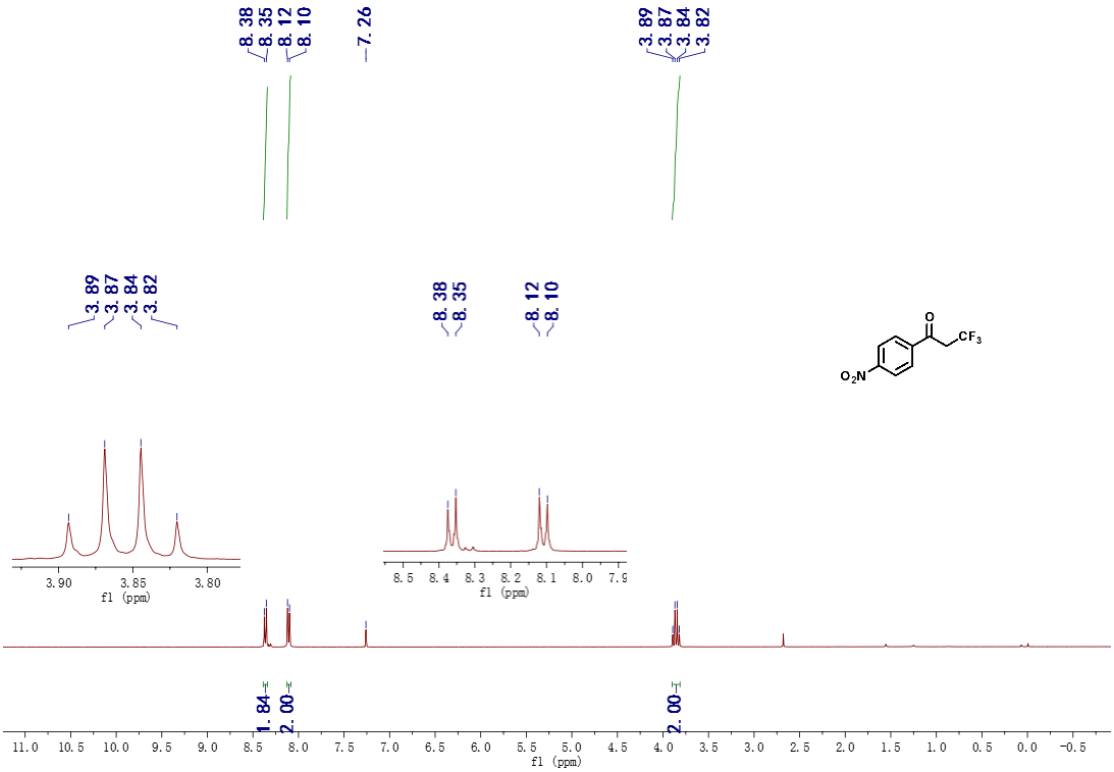
^{19}F NMR spectrum of 1-(4-chlorophenyl)-3,3,3-trifluoropropan-1-one 3d



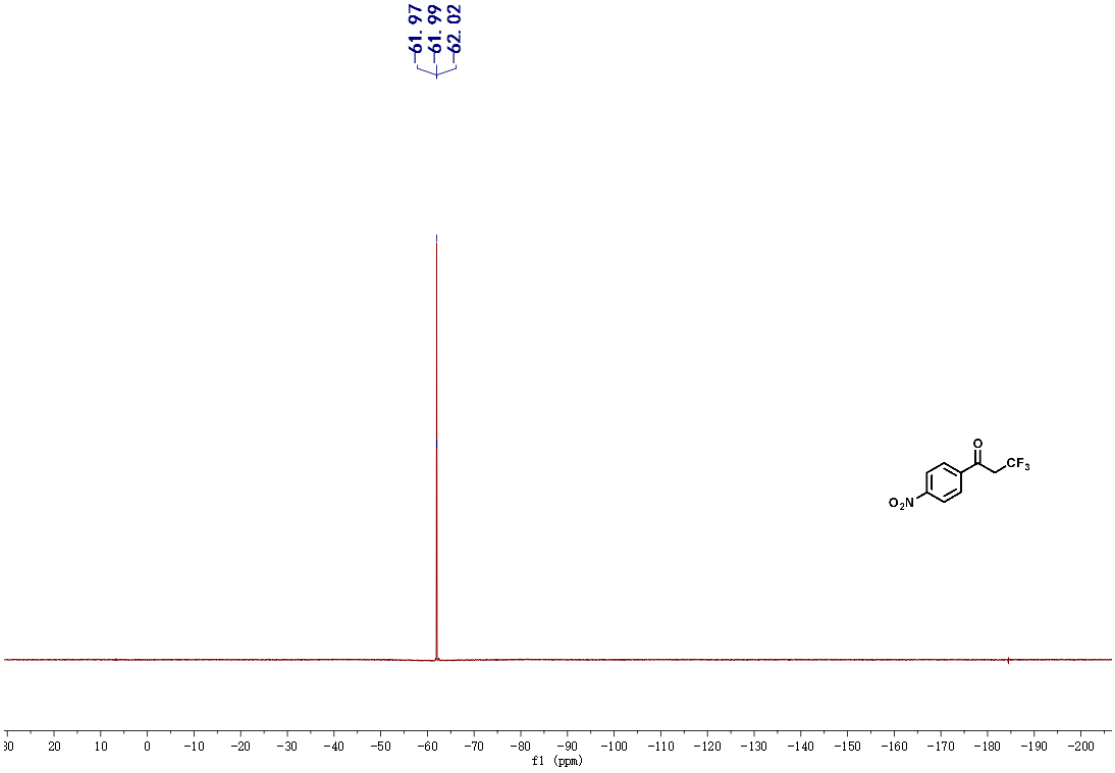
^{13}C NMR spectrum of 1-(4-chlorophenyl)-3,3,3-trifluoropropan-1-one 3d



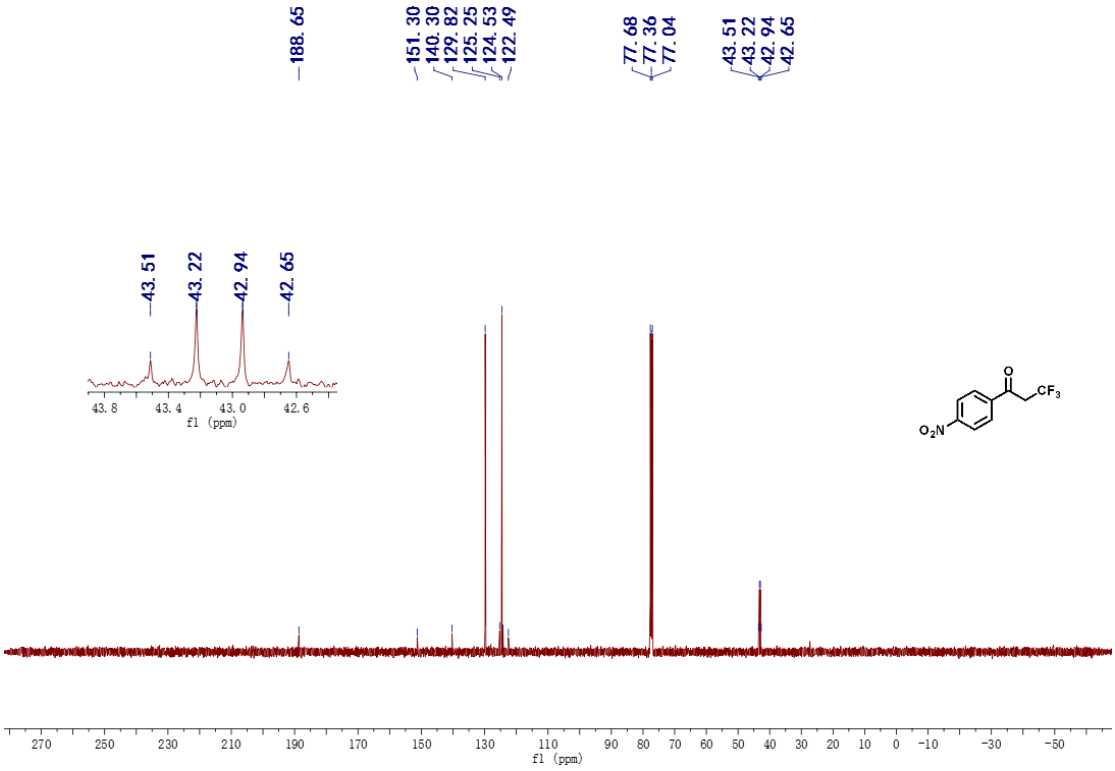
^{1}H NMR spectrum of 1-(4-nitrophenyl)-3,3,3-trifluoropropan-1-one 3e



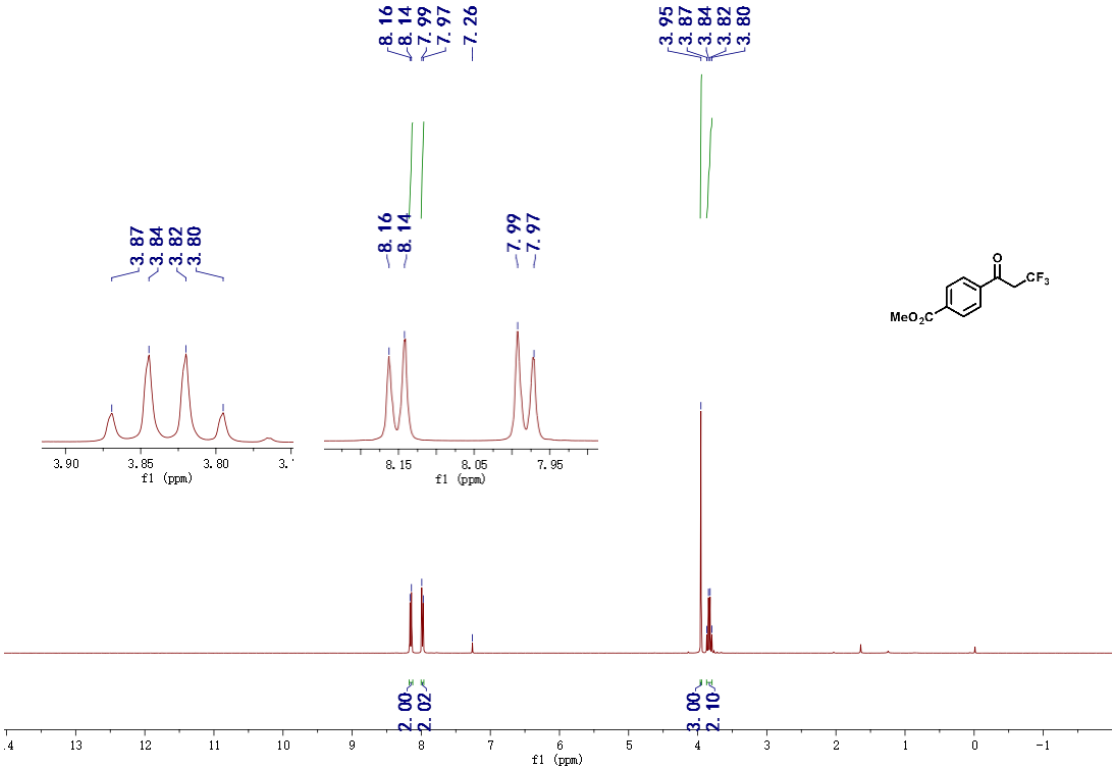
^{19}F NMR spectrum of 1-(4-nitrophenyl)-3,3,3-trifluoropropan-1-one 3e



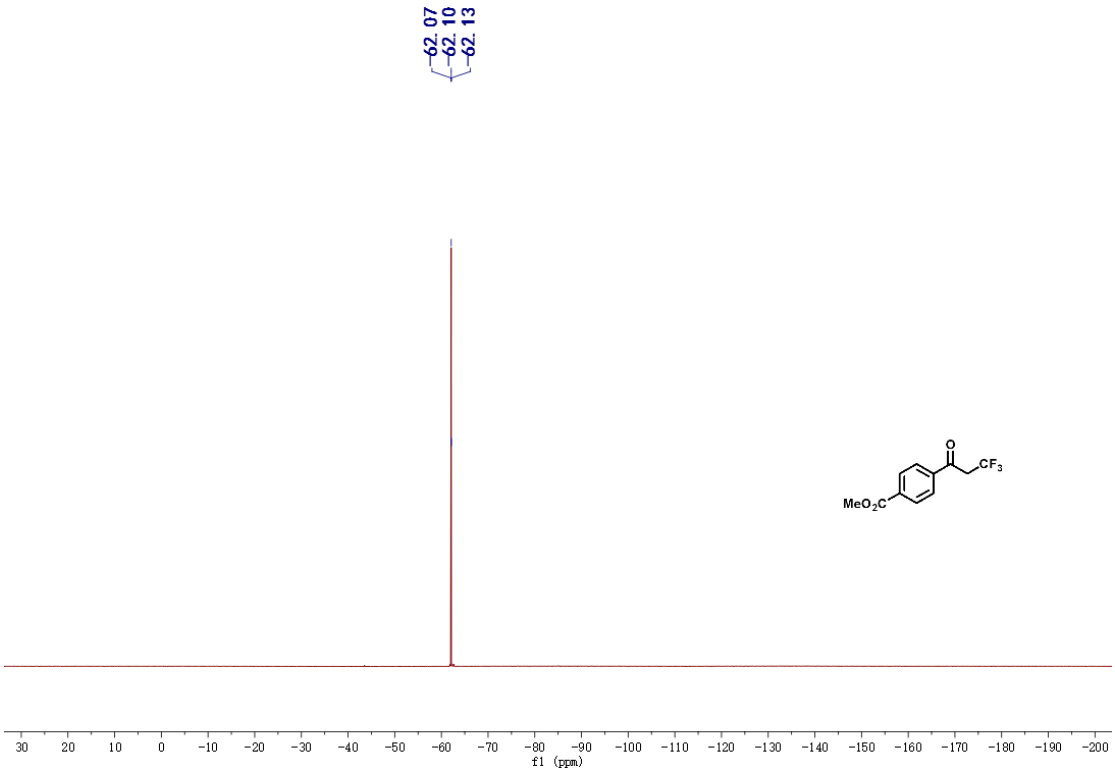
^{13}C NMR spectrum of 1-(4-nitrophenyl)-3,3,3-trifluoropropan-1-one 3e



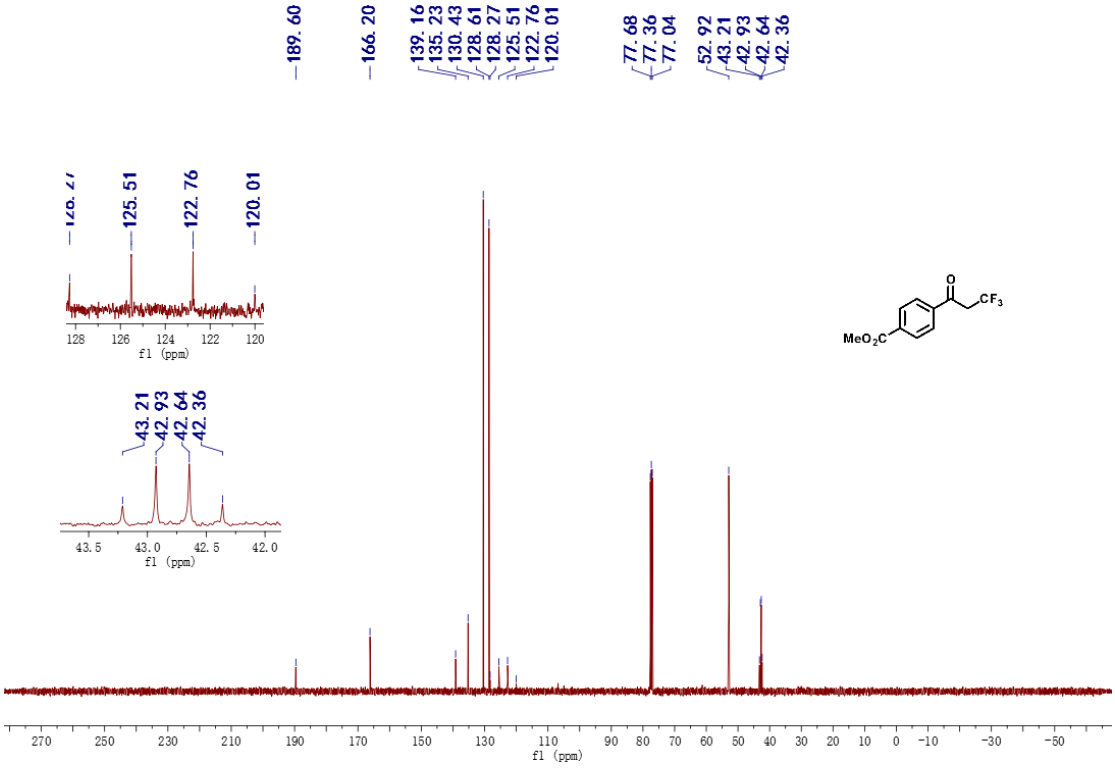
^{1}H NMR spectrum methyl-4-(3,3,3-trifluoropropanoyl)benzoate of 3f



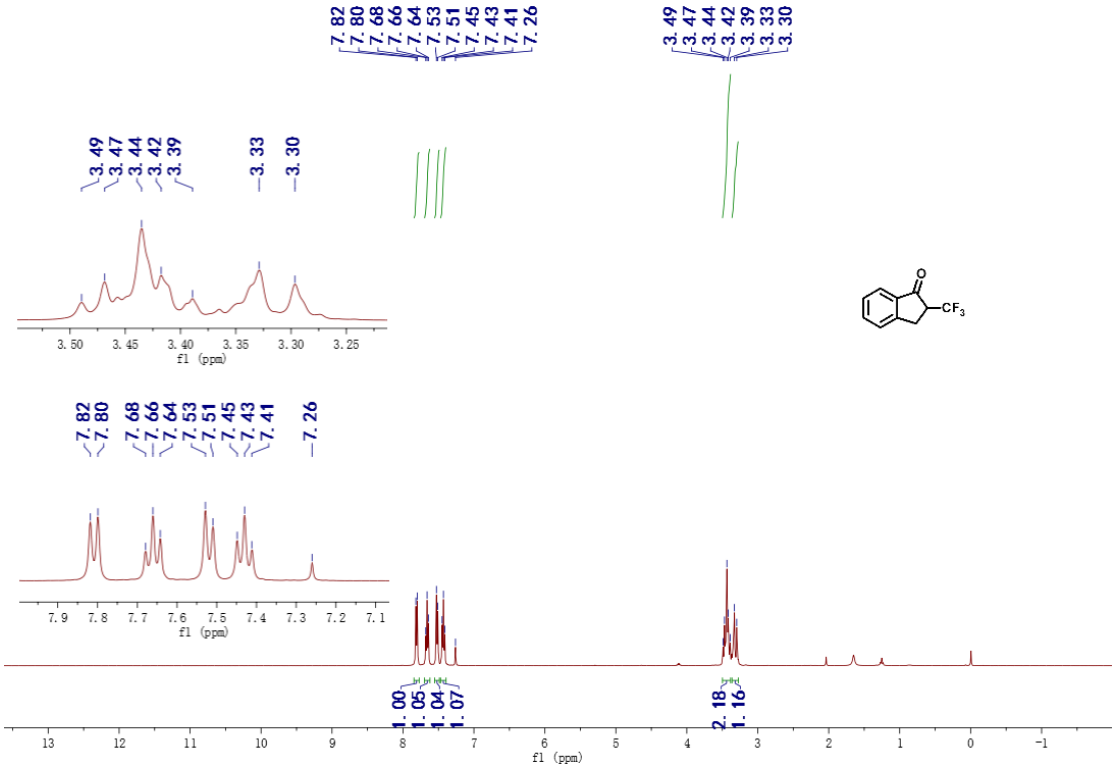
^{19}F NMR spectrum methyl-4-(3,3,3-trifluoropropanoyl)benzoate of 3f



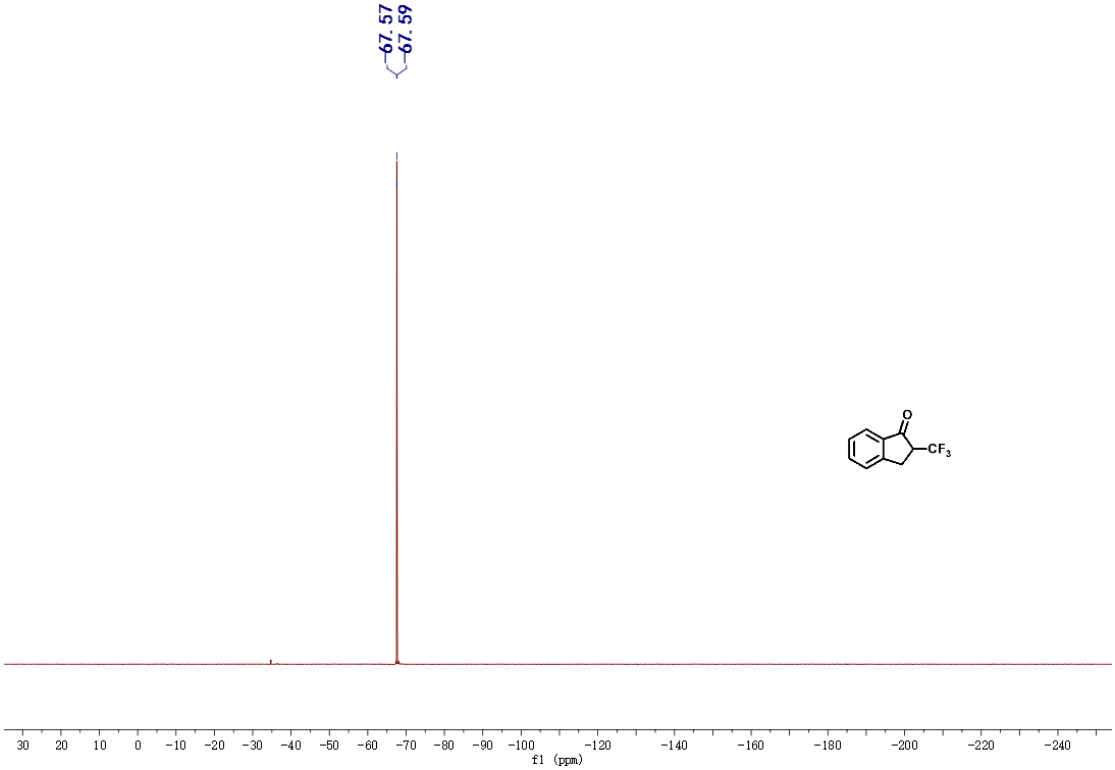
^{13}C NMR spectrum methyl-4-(3,3,3-trifluoropropanoyl)benzoate of 3f



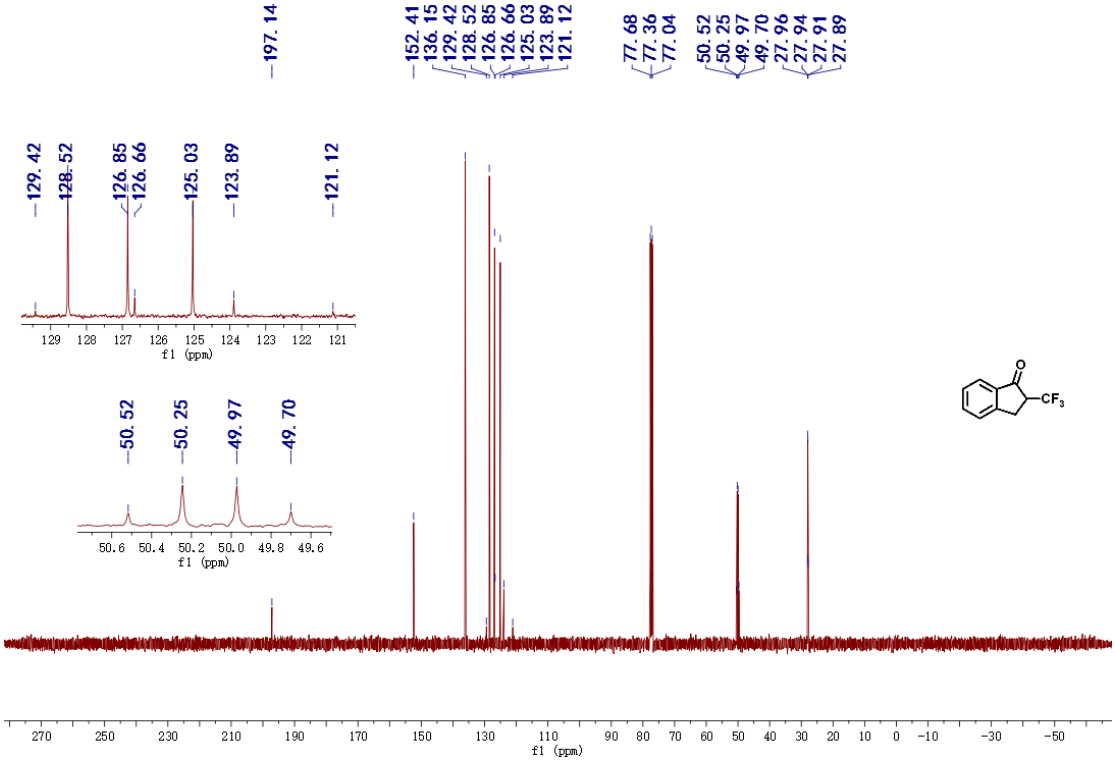
^{1}H NMR spectrum of 2-(trifluoromethyl)-2,3-dihydro-1H-inden-1-one 3g



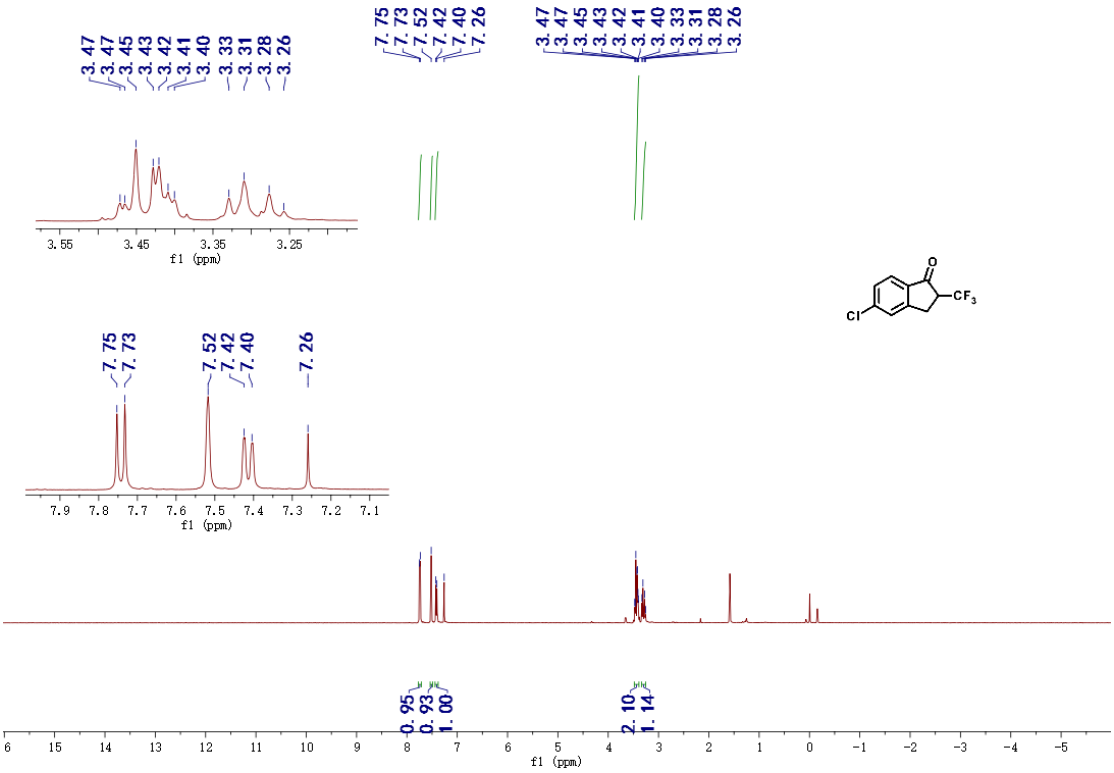
^{19}F NMR spectrum of 2-(trifluoromethyl)-2,3-dihydro-1H-inden-1-one 3g



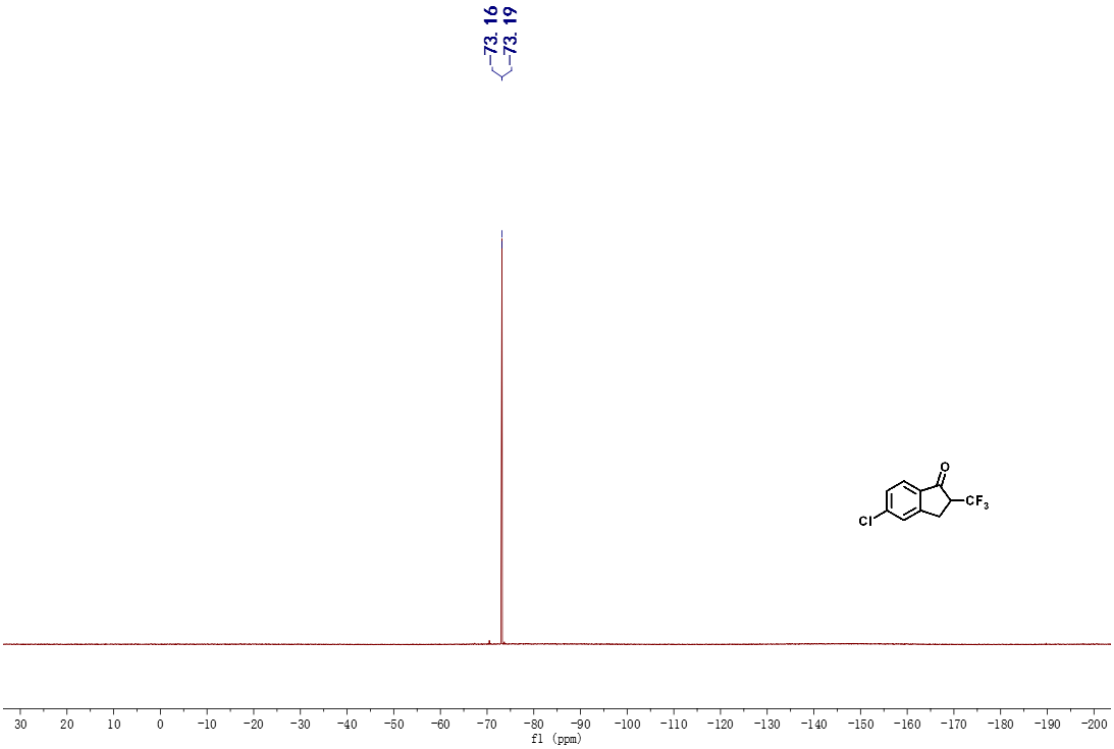
^{13}C NMR spectrum of 2-(trifluoromethyl)-2,3-dihydro-1H-inden-1-one 3g



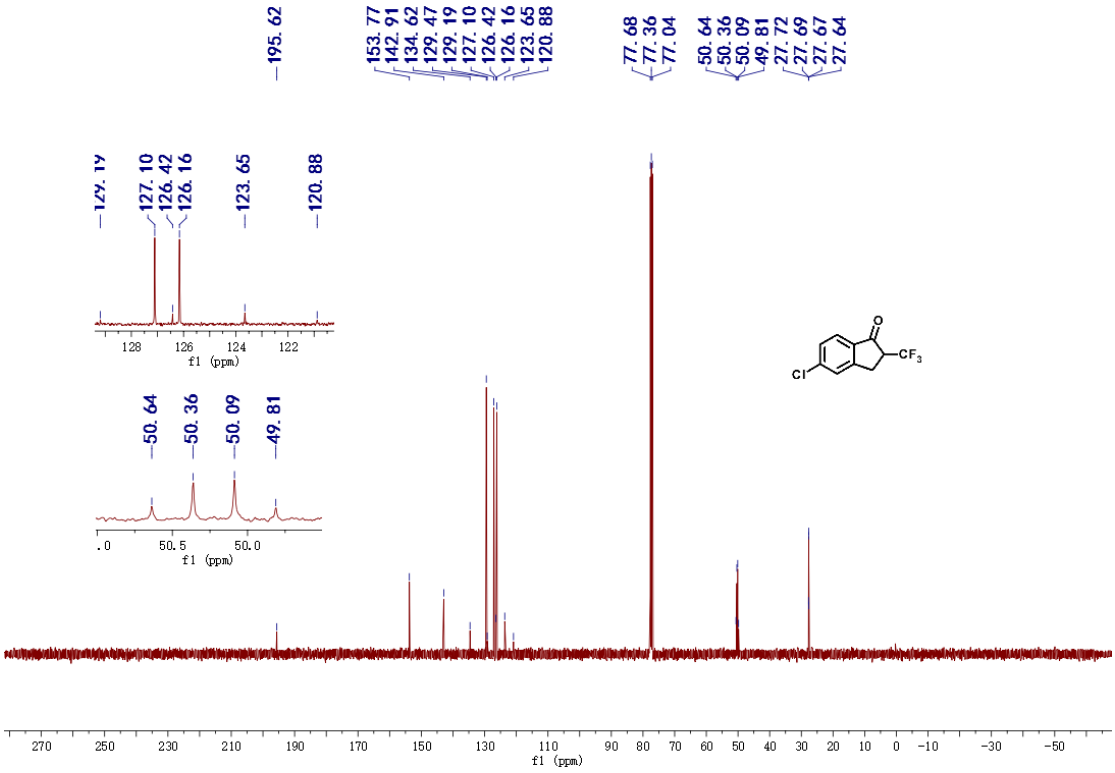
^{1}H NMR spectrum of 5-chloro-2-(trifluoromethyl)-2,3-dihydro-1*H*-inden-1-one 3h



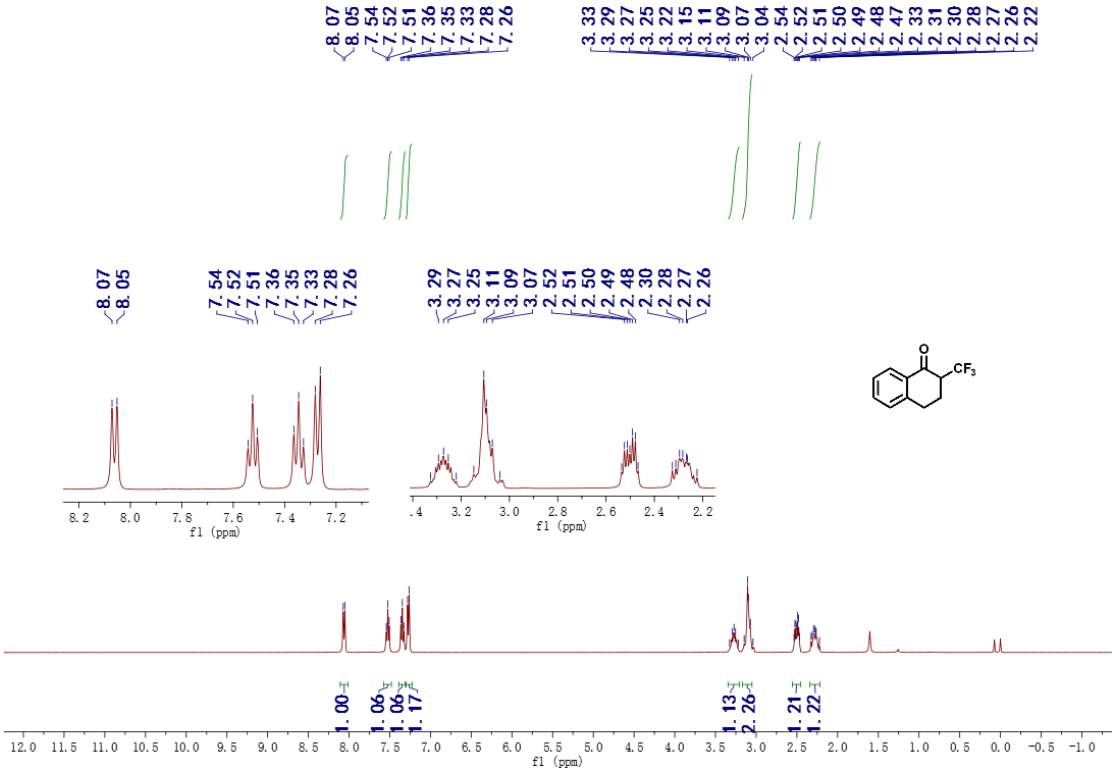
^{19}F NMR spectrum of 5-Chloro-2-(trifluoromethyl)-2,3-dihydro-1*H*-inden-1-one 3h



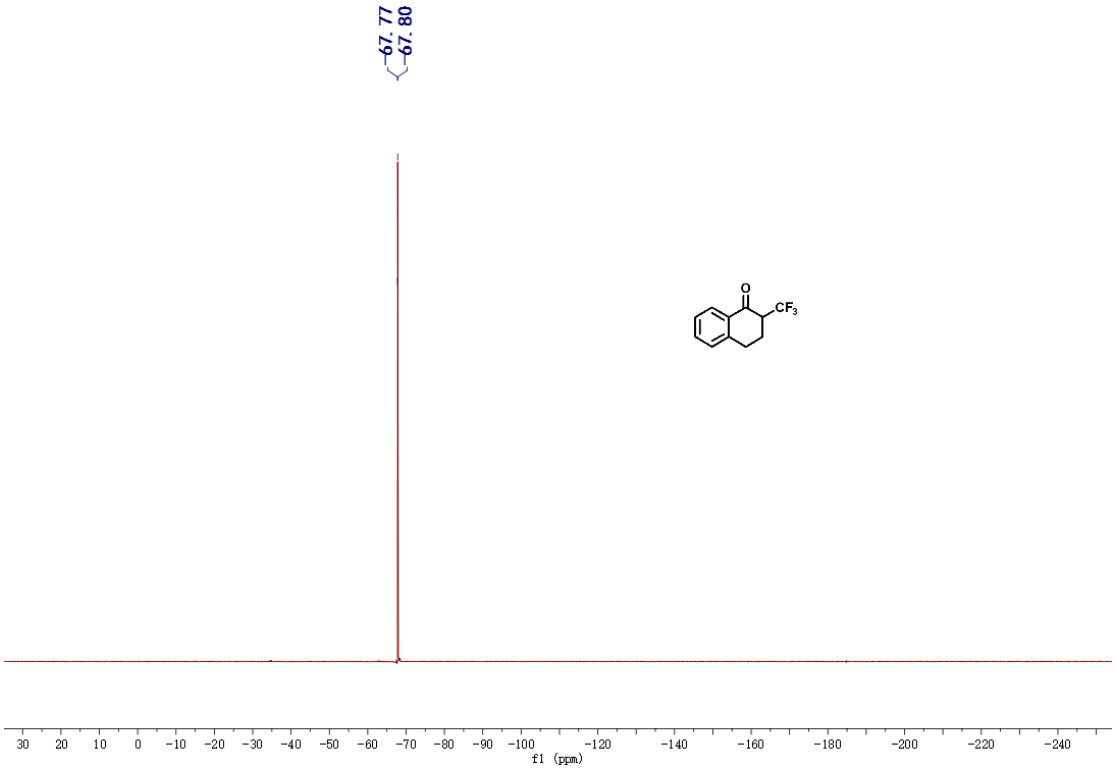
^{13}C NMR spectrum of 5-Chloro-2-(trifluoromethyl)-2,3-dihydro-1*H*-inden-1-one 3h



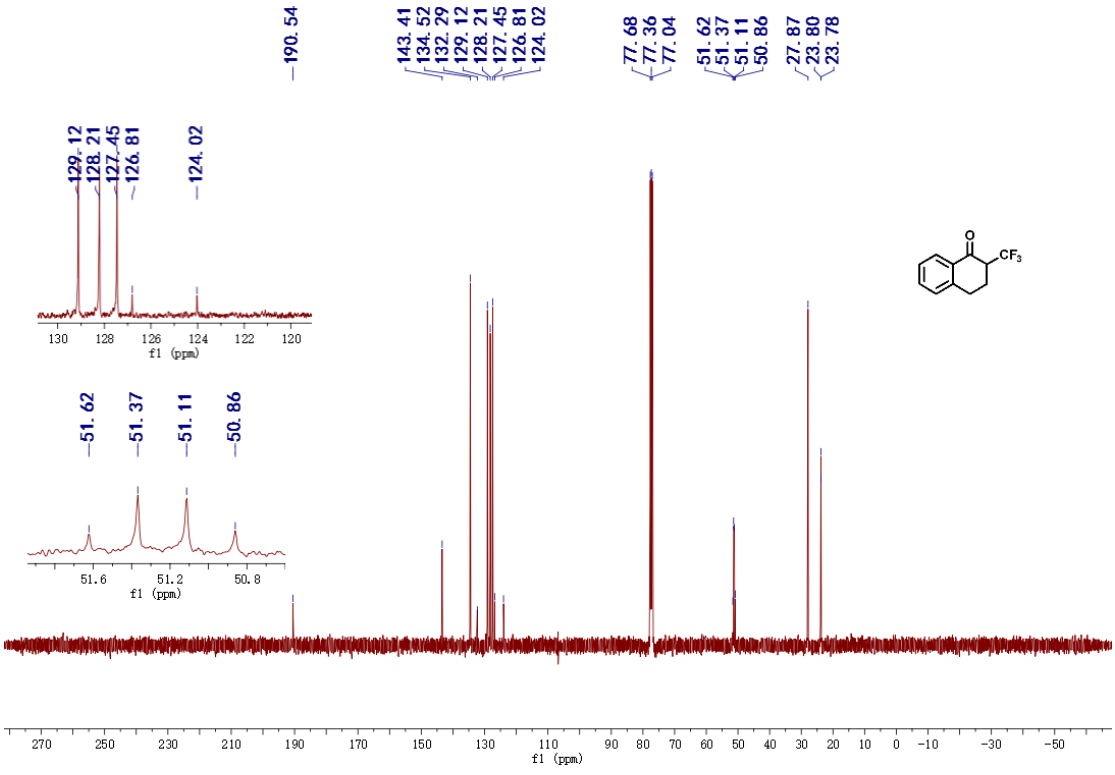
^{1}H NMR spectrum of 2-(trifluoromethyl)-3,4-dihydronaphthalen-1(2H)-one 3i



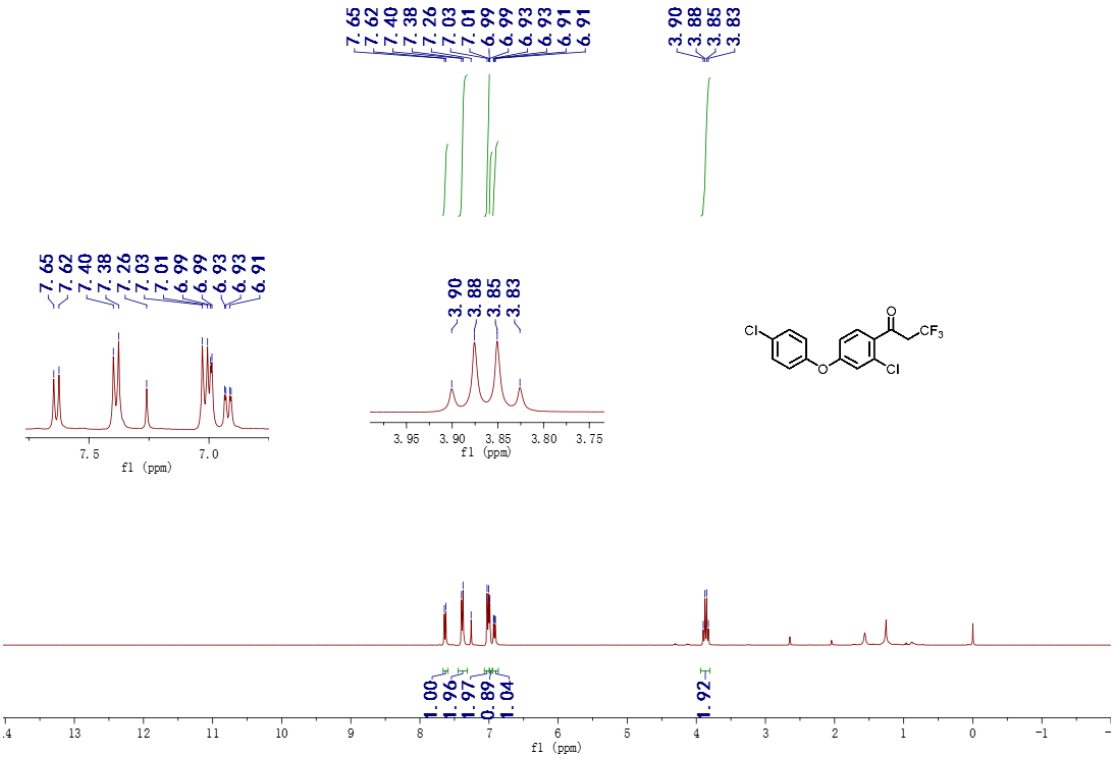
^{19}F NMR spectrum of 2-(trifluoromethyl)-3,4-dihydronaphthalen-1(2H)-one 3i



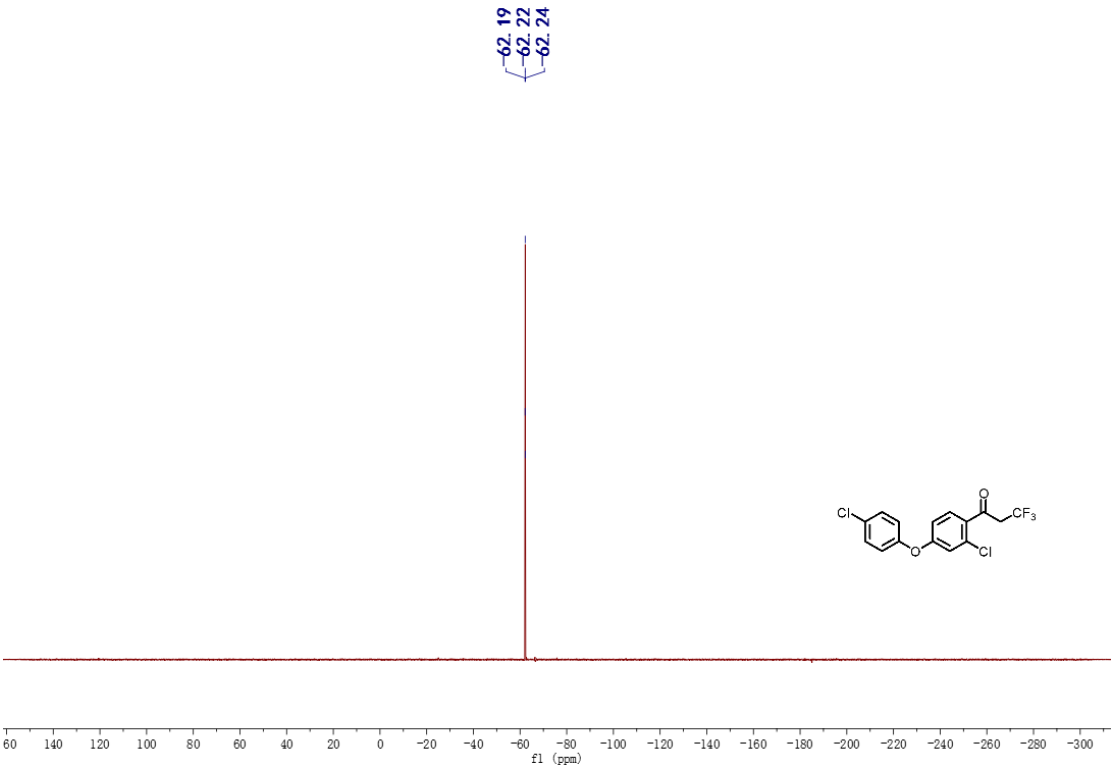
^{13}C NMR spectrum of 2-(trifluoromethyl)-3,4-dihydronaphthalen-1(2H)-one 3i



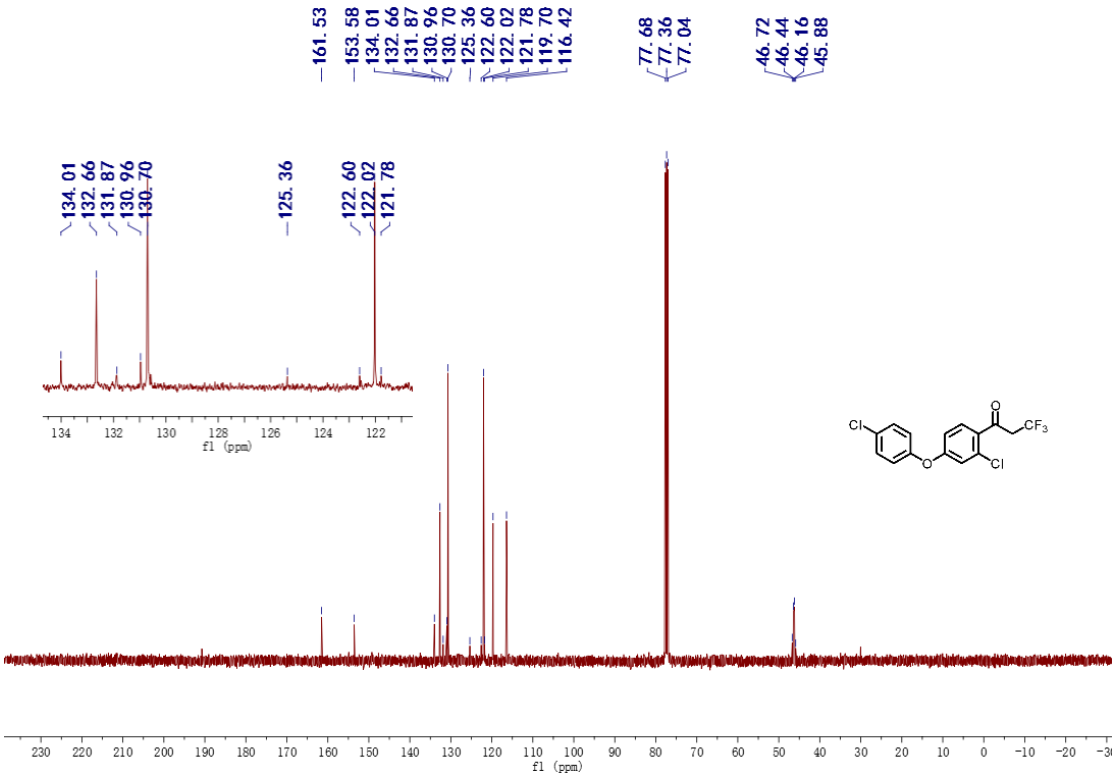
^{1}H NMR spectrum of 1-(2-chloro-4-(4-chlorophenoxy)phenyl)-3,3,3-trifluoropropan-1-one 3j



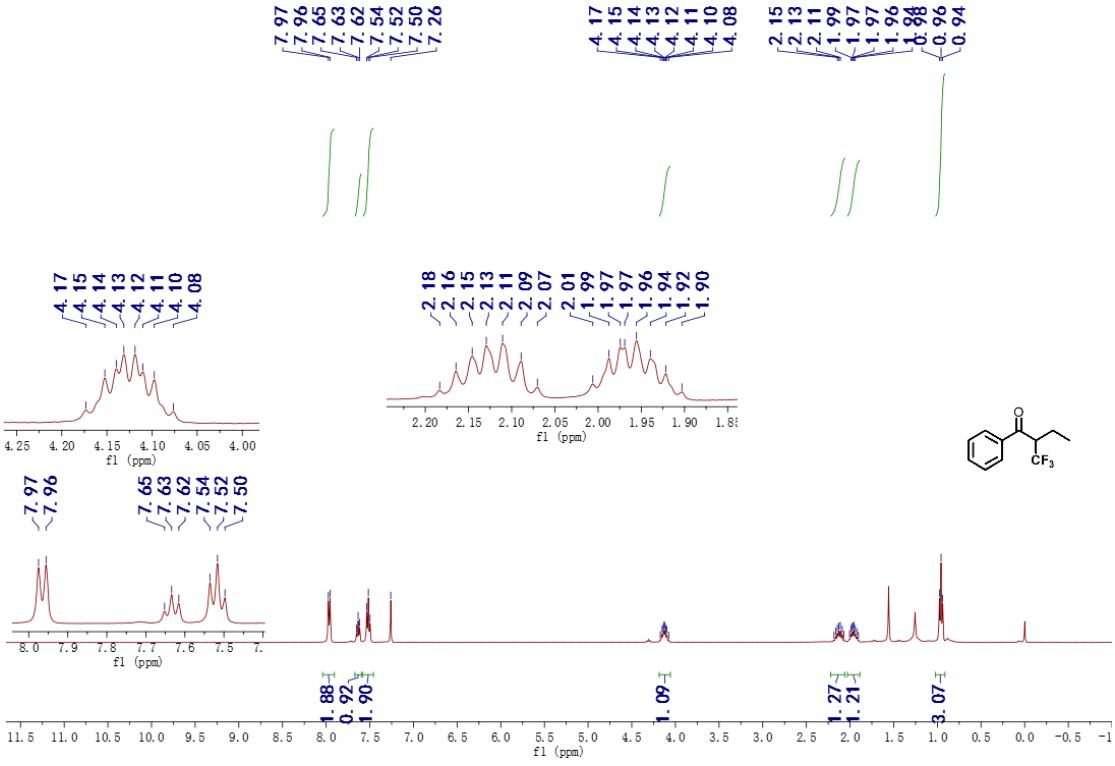
^{19}F NMR spectrum of 1-(2-chloro-4-(4-chlorophenoxy)phenyl)-3,3,3-trifluoropropan-1-one 3j



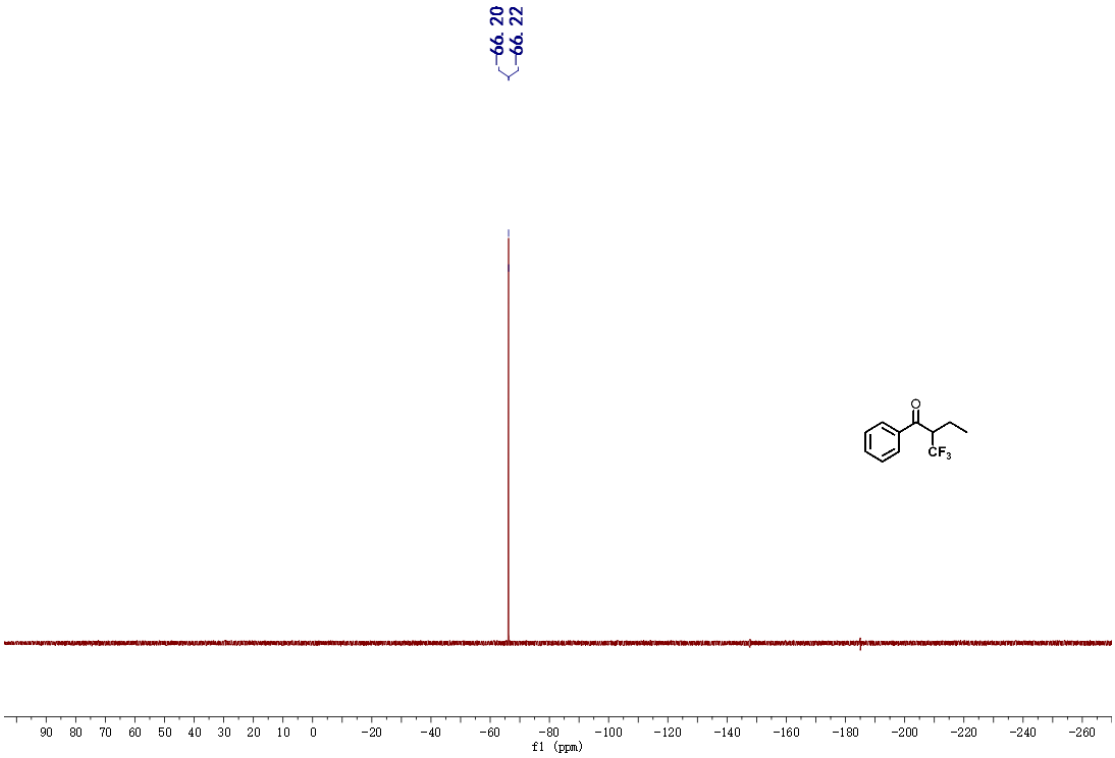
^{13}C NMR spectrum of 1-(2-chloro-4-(4-chlorophenoxy)phenyl)-3,3,3-trifluoropropan-1-one 3j



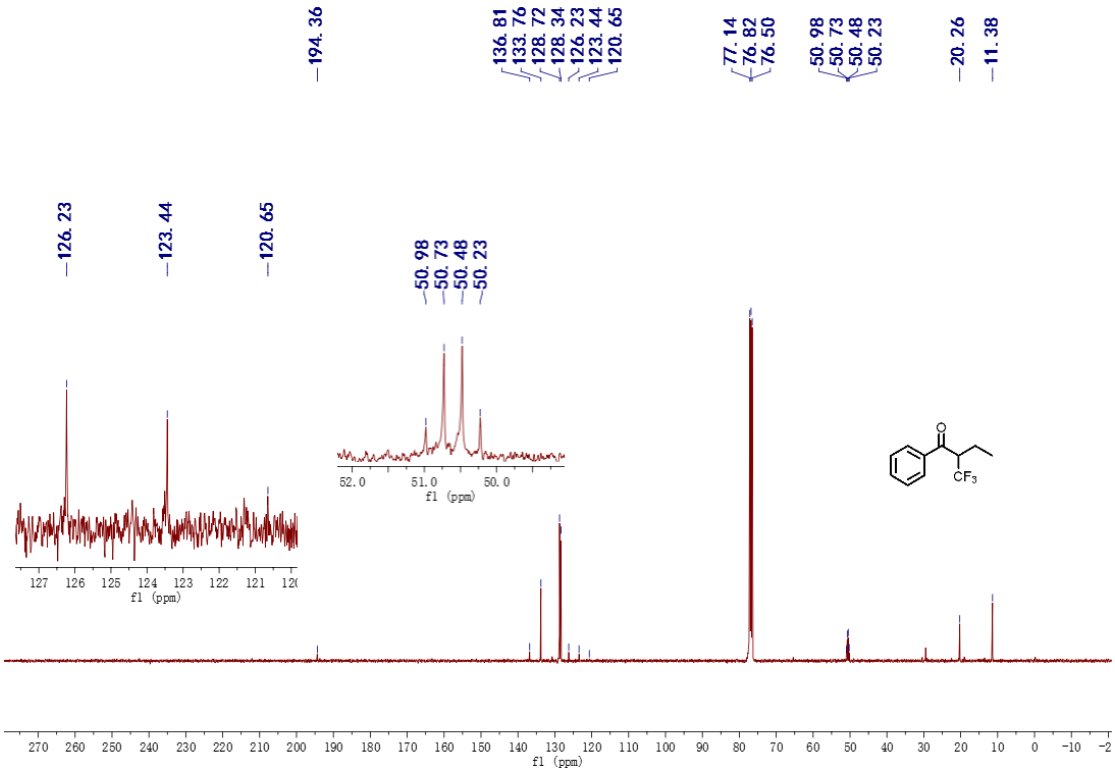
^{1}H NMR spectrum of 1-Phenyl-2-(trifluoromethyl)butan-1-one 3k



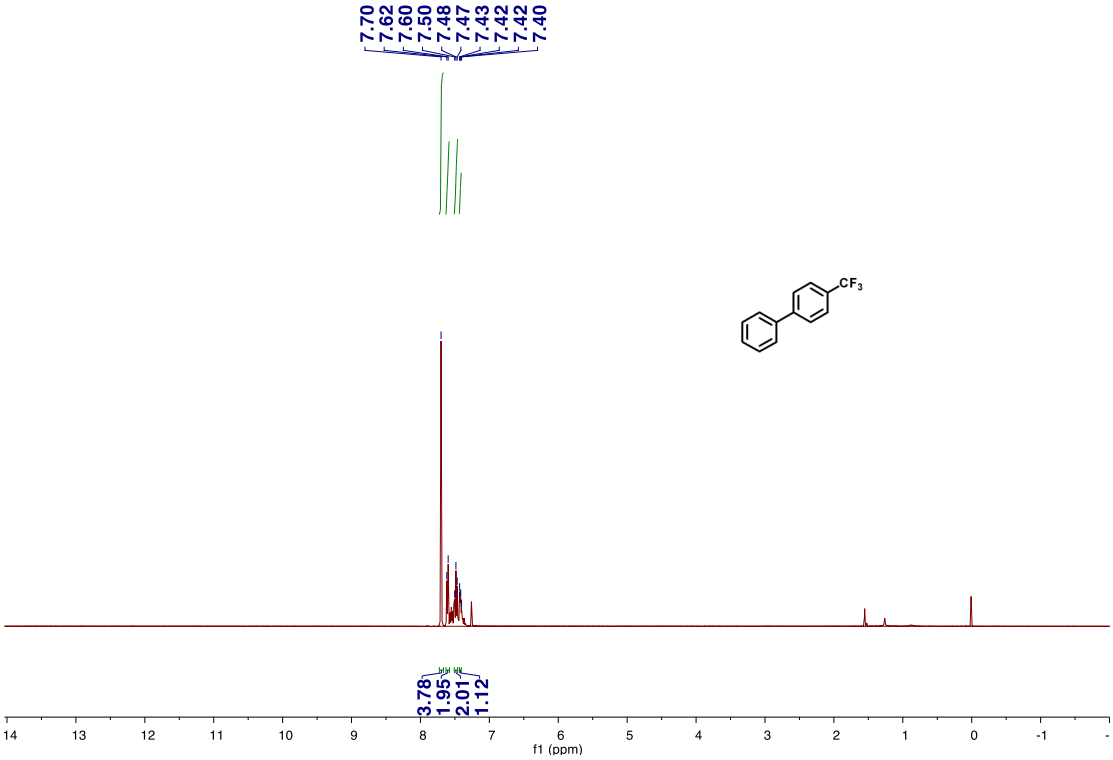
^{19}F NMR spectrum of 1-phenyl-2-(trifluoromethyl)butan-1-one 3k



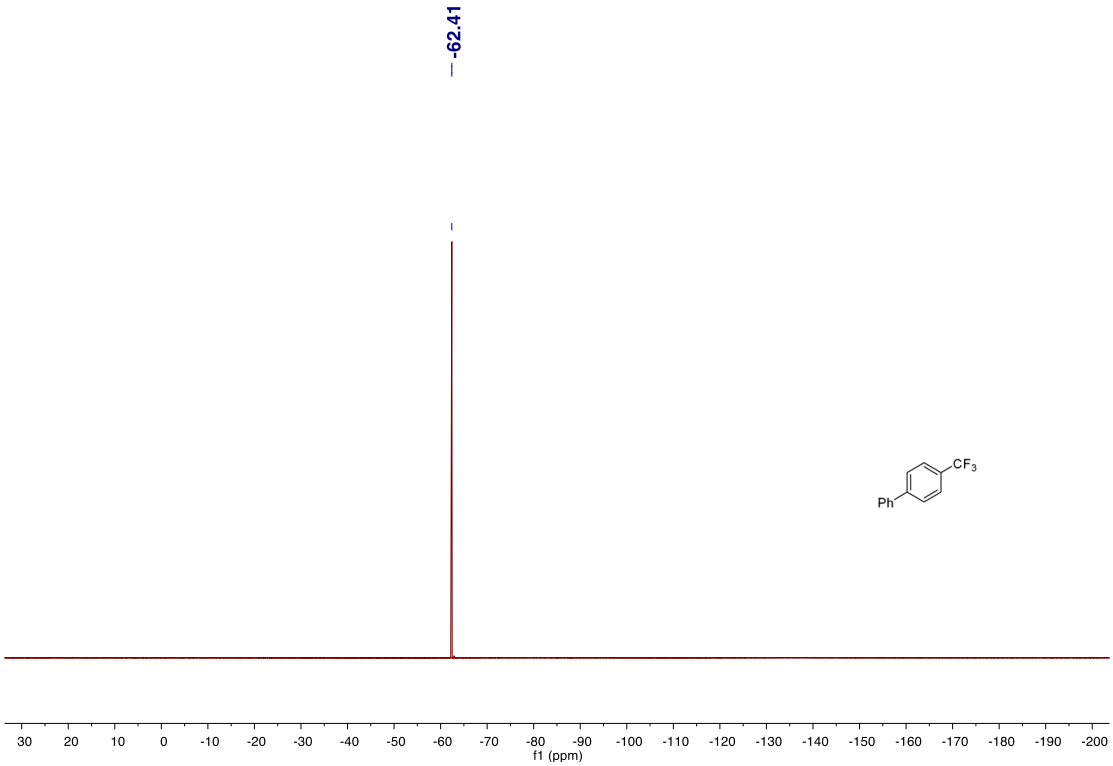
^{13}C NMR spectrum of 1-phenyl-2-(trifluoromethyl)butan-1-one 3k



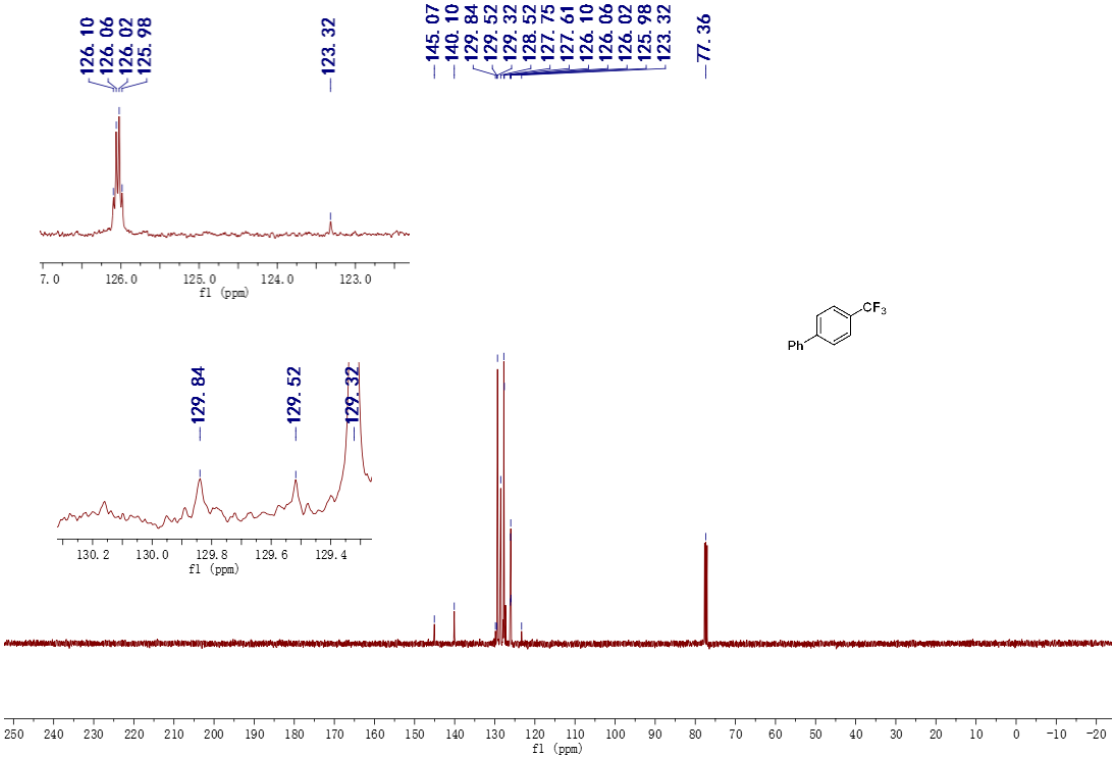
^{1}H NMR spectrum of 4-(trifluoromethyl)biphenyl 4a



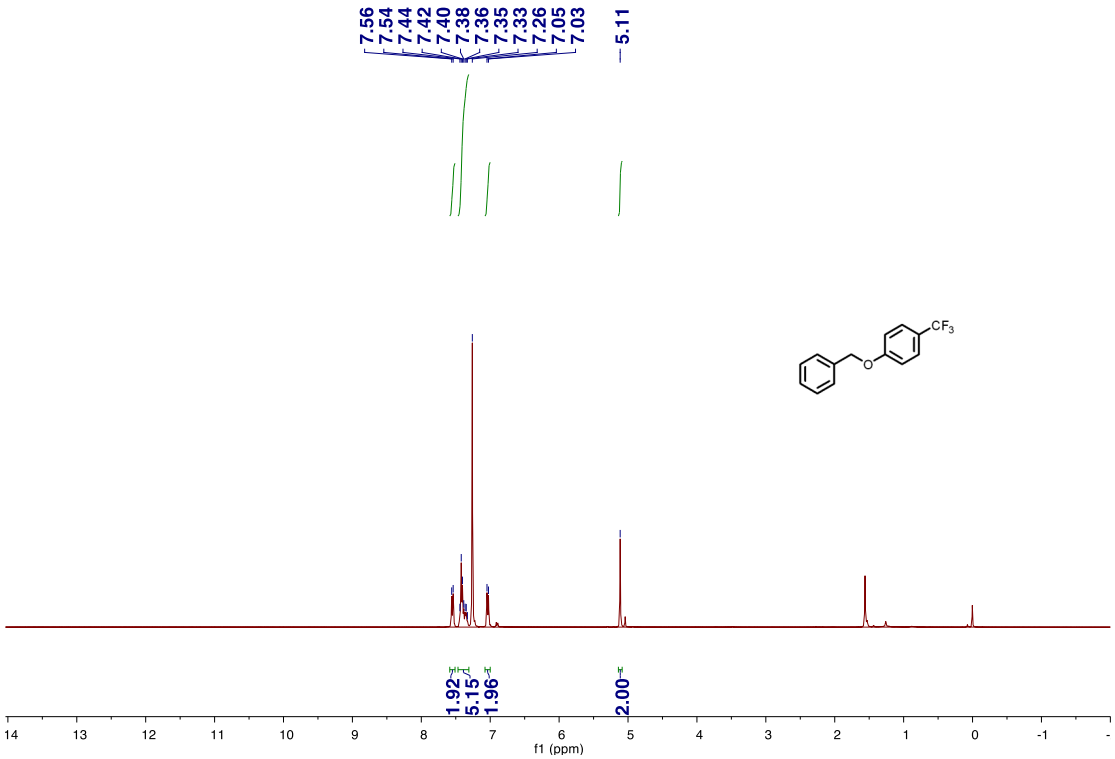
^{19}F NMR spectrum of 4-(trifluoromethyl)biphenyl 4a



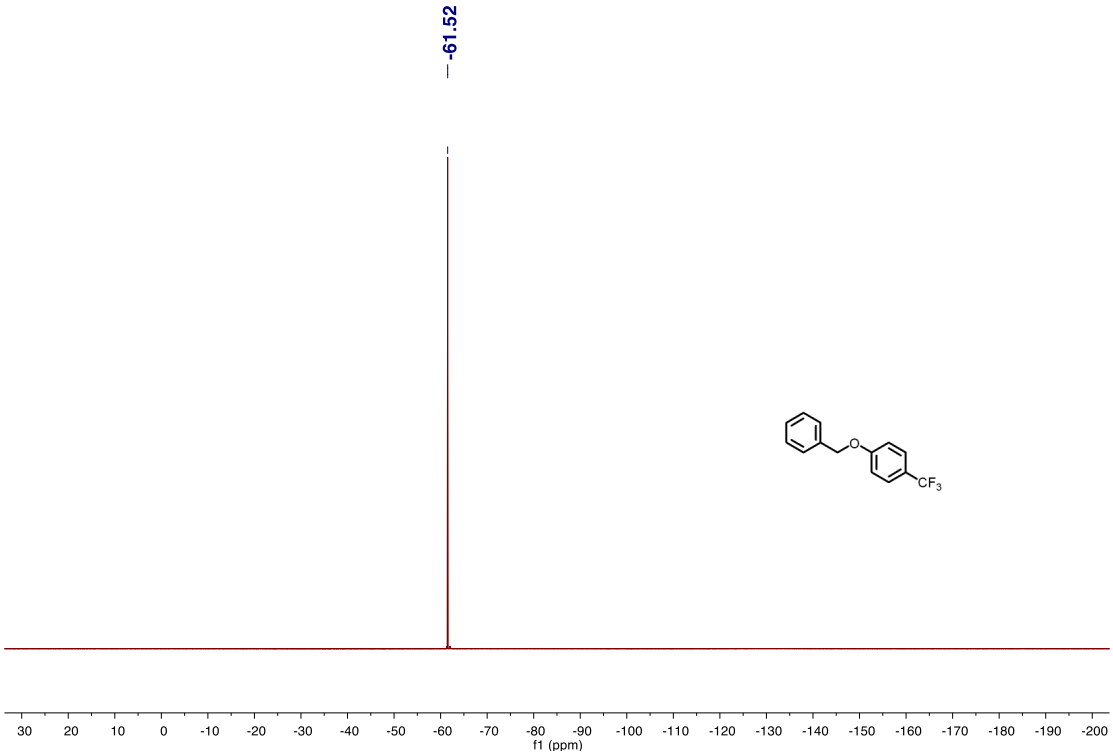
^{13}C NMR spectrum of 4-(trifluoromethyl)biphenyl 4a



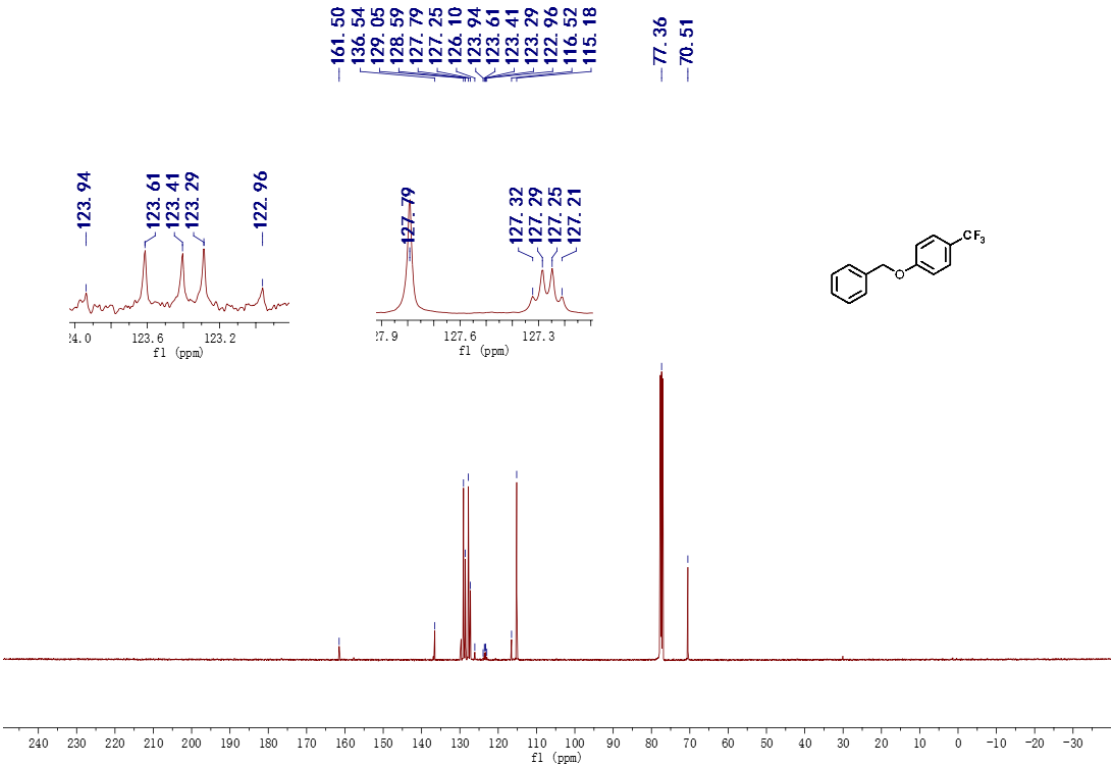
^{1}H NMR spectrum of 1-(benzyloxy)-4-(trifluoromethyl)benzene 4b



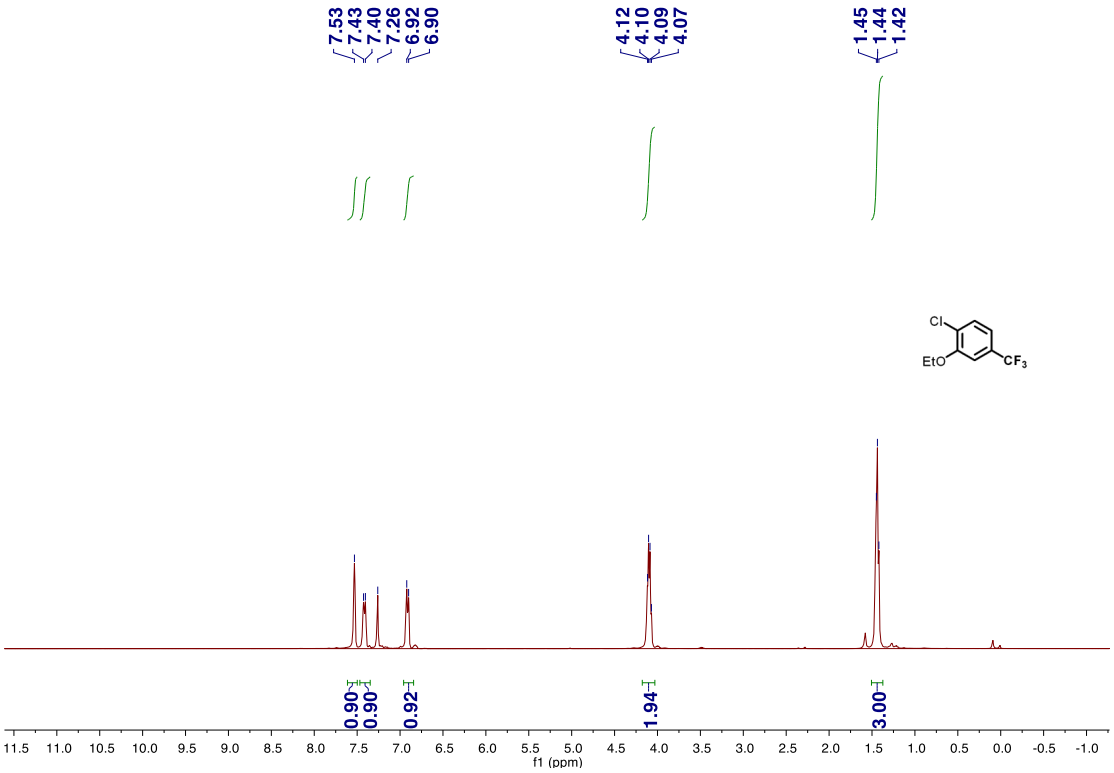
^{19}F NMR spectrum of 1-(benzyloxy)-4-(trifluoromethyl)benzene 4b



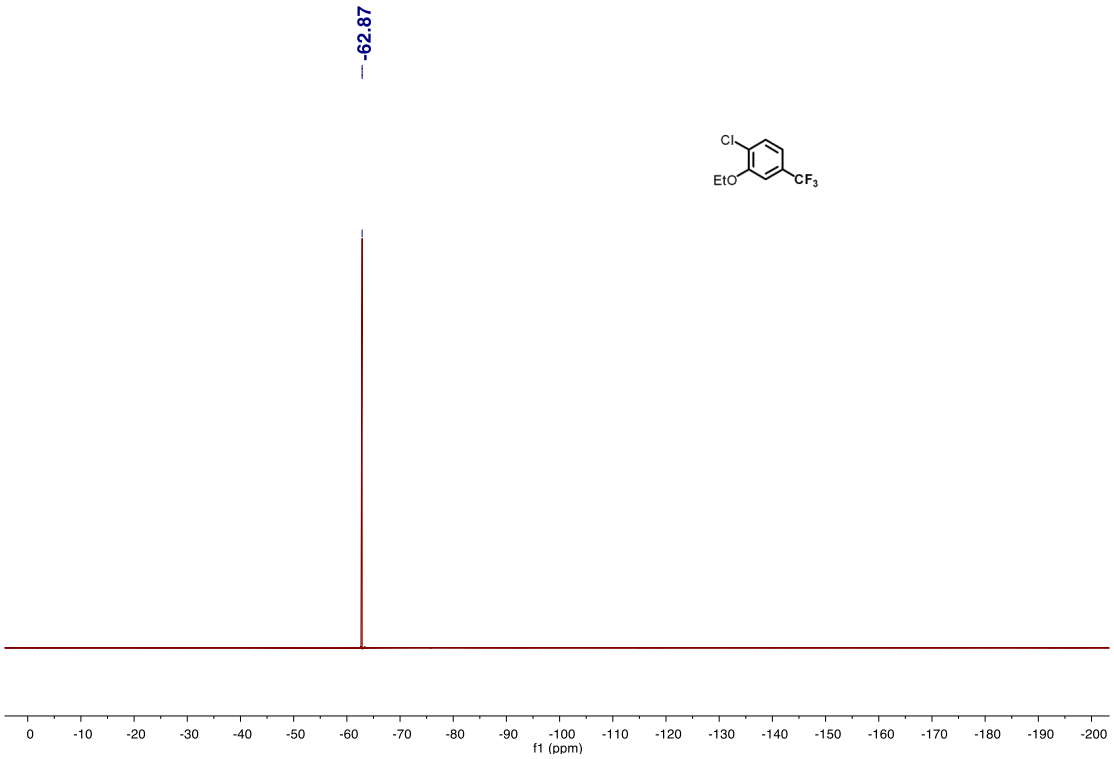
^{13}C NMR spectrum of 1-(benzyloxy)-4-(trifluoromethyl)benzene 4b



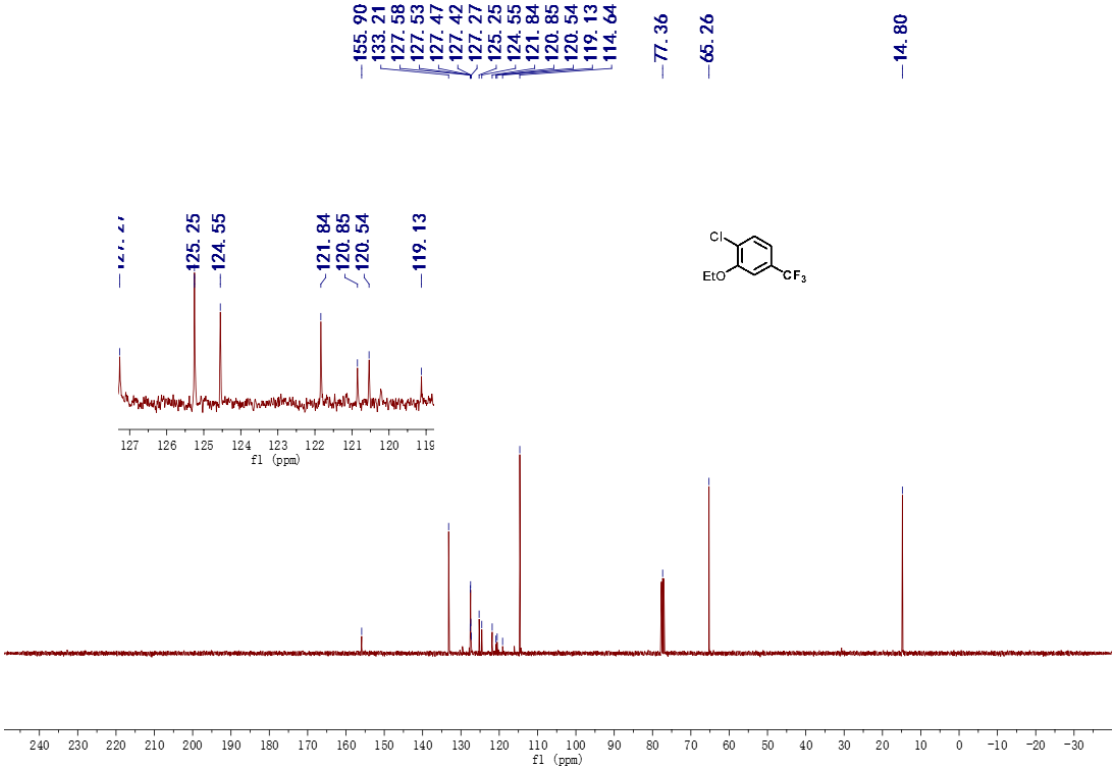
^{1}H NMR spectrum of 1-chloro-2-ethoxy-4-(trifluoromethyl)-benzene 4c



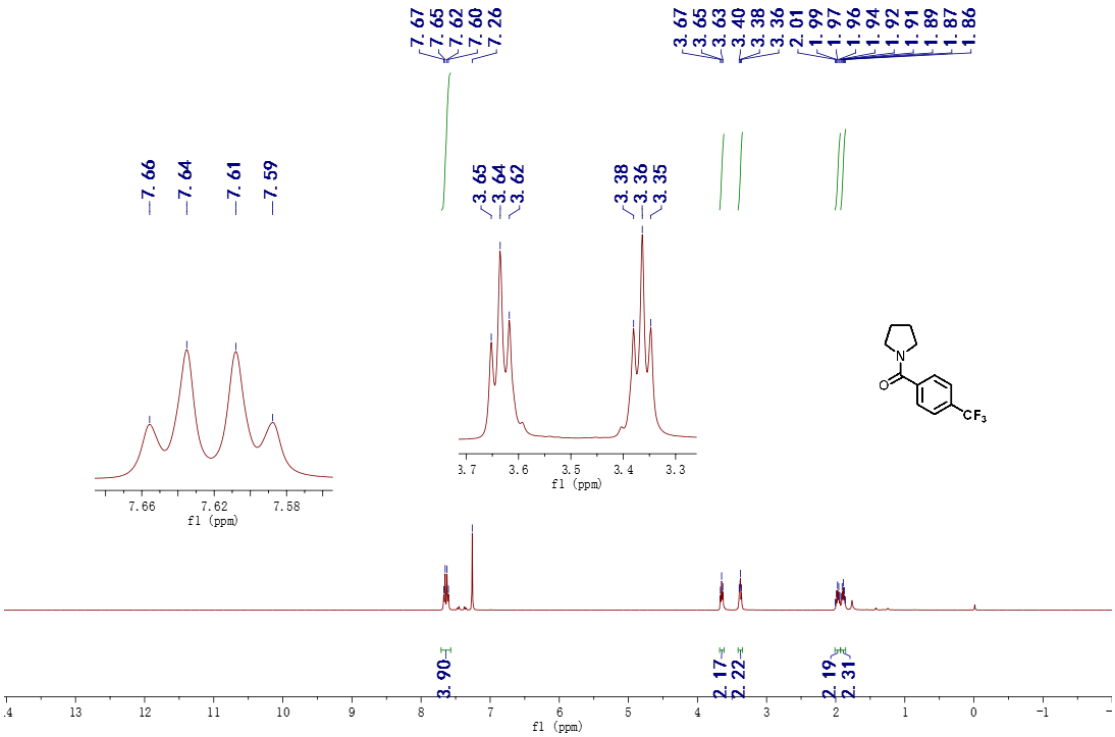
^{19}F NMR spectrum of 1-chloro-2-ethoxy-4-(trifluoromethyl)-benzene 4c



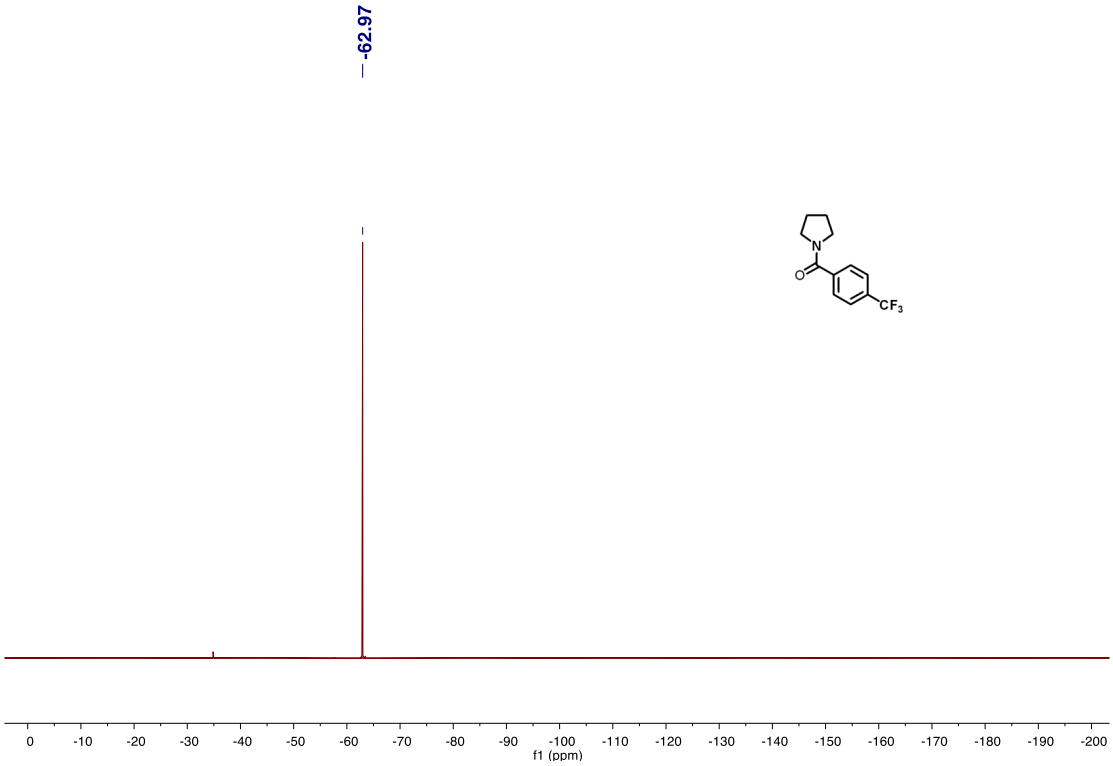
^{13}C NMR spectrum of 1-chloro-2-ethoxy-4-(trifluoromethyl)-benzene 4c



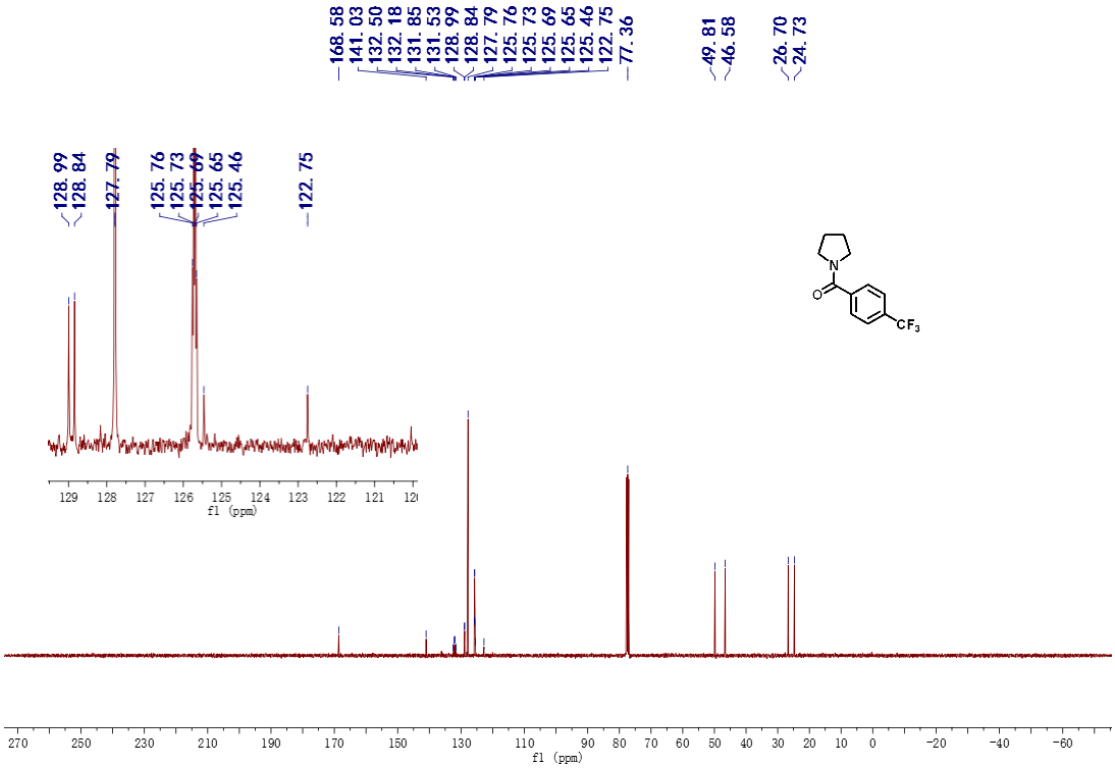
^{1}H NMR spectrum of 1-pyrrolidinyl[4-(trifluoromethyl)phenyl]-methanone 4d



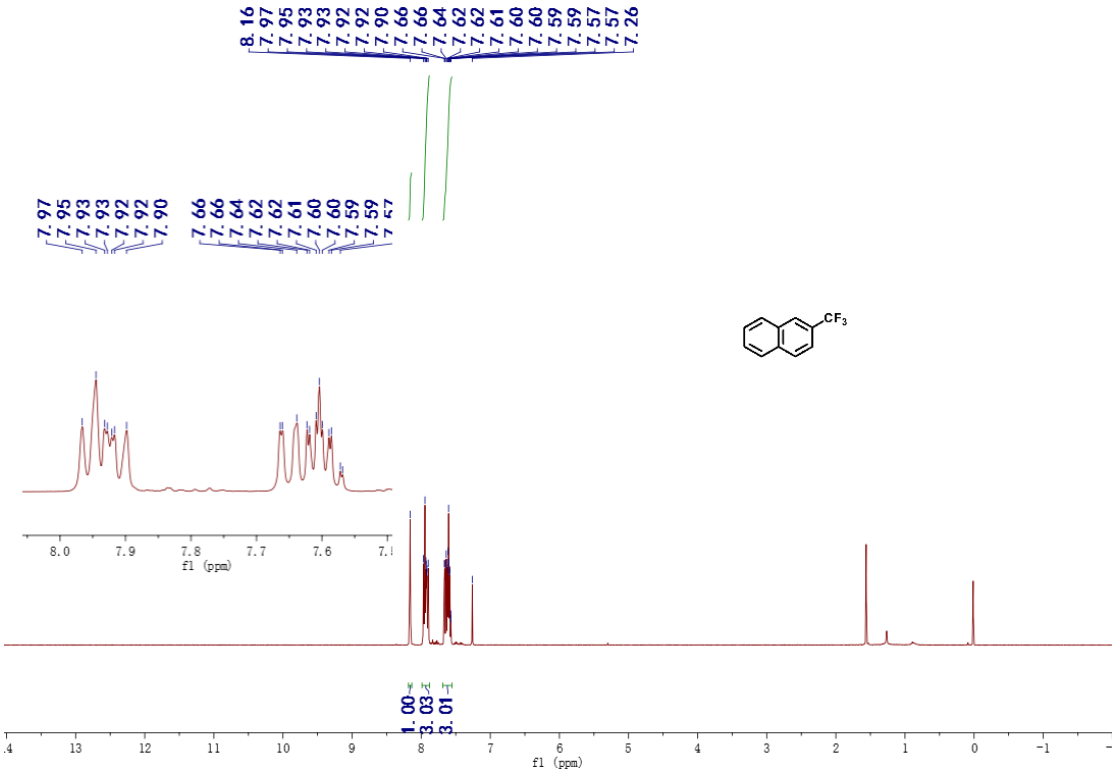
^{19}F NMR spectrum of 1-pyrrolidinyl[4-(trifluoromethyl)phenyl]-methanone 4d



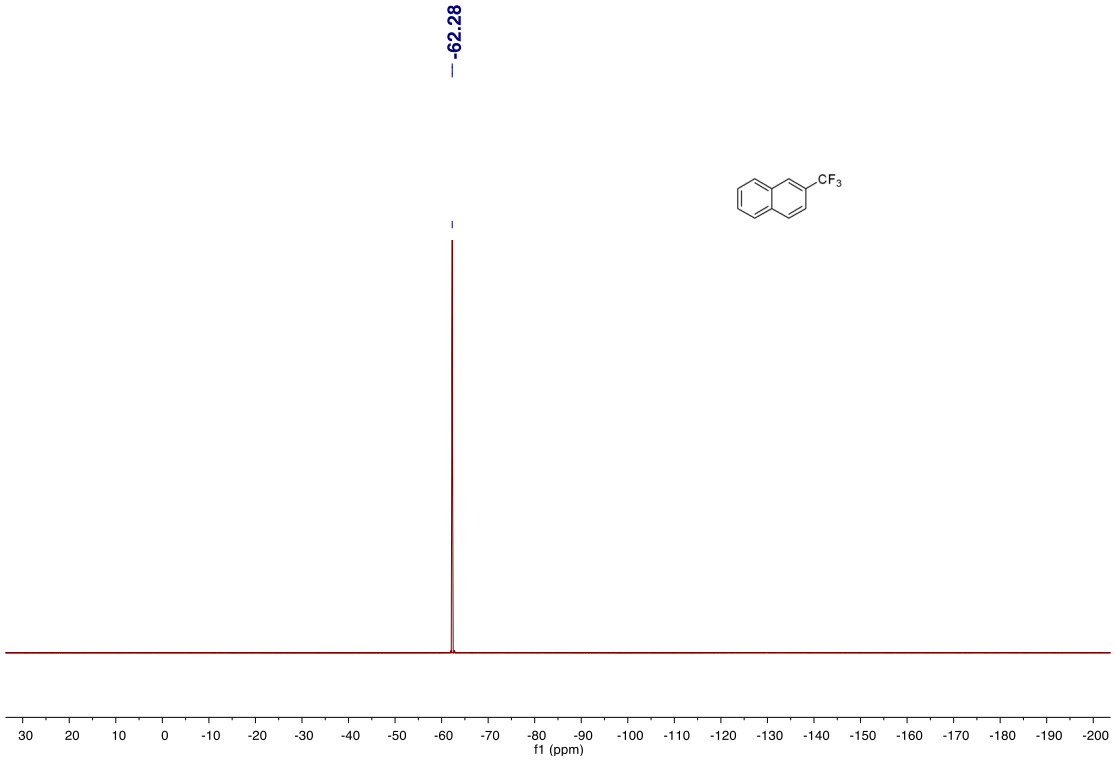
^{13}C NMR spectrum of 1-pyrrolidinyl[4-(trifluoromethyl)phenyl]-methanone 4d



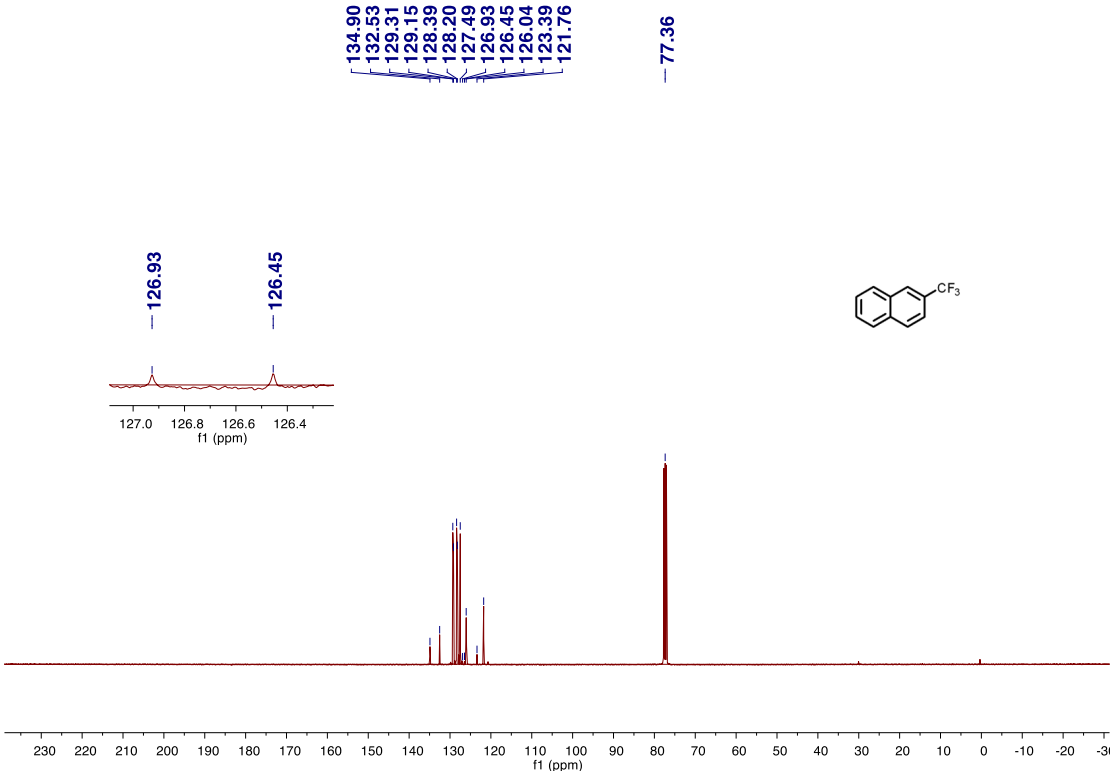
^{1}H NMR spectrum of 2-(trifluoromethyl)naphthalene 4e



^{19}F NMR spectrum of 2-(trifluoromethyl)naphthalene 4e



^{13}C NMR spectrum of 2-(trifluoromethyl)naphthalene 4e



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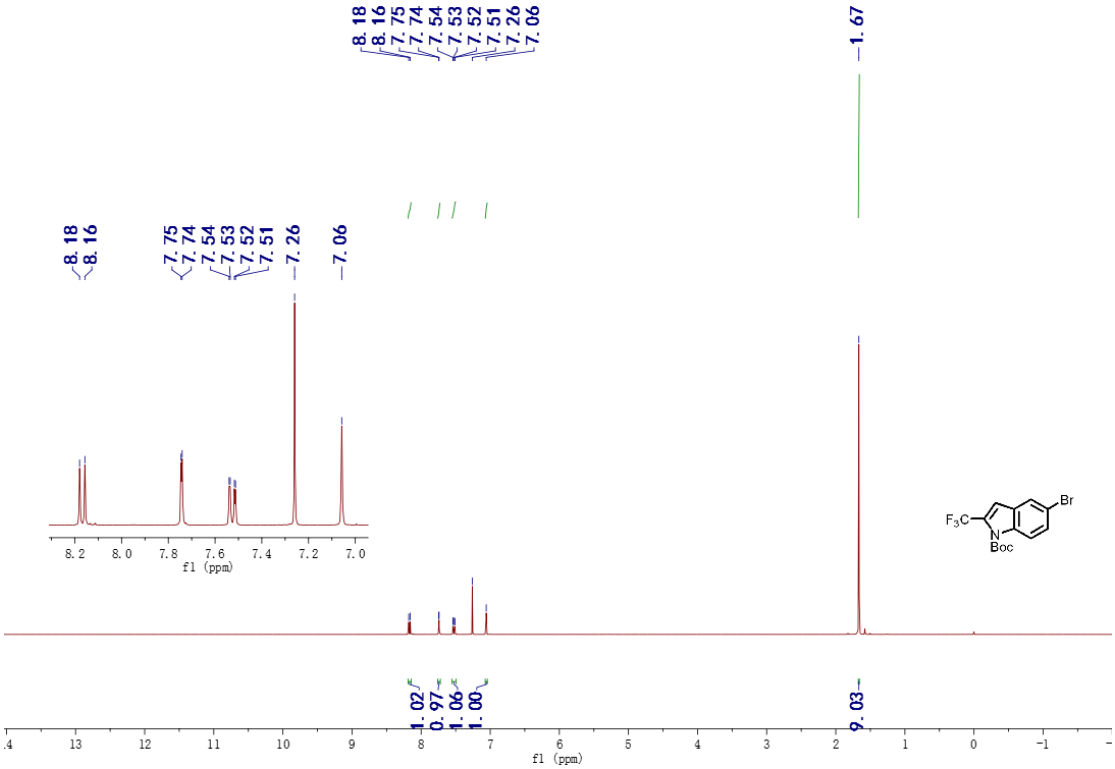
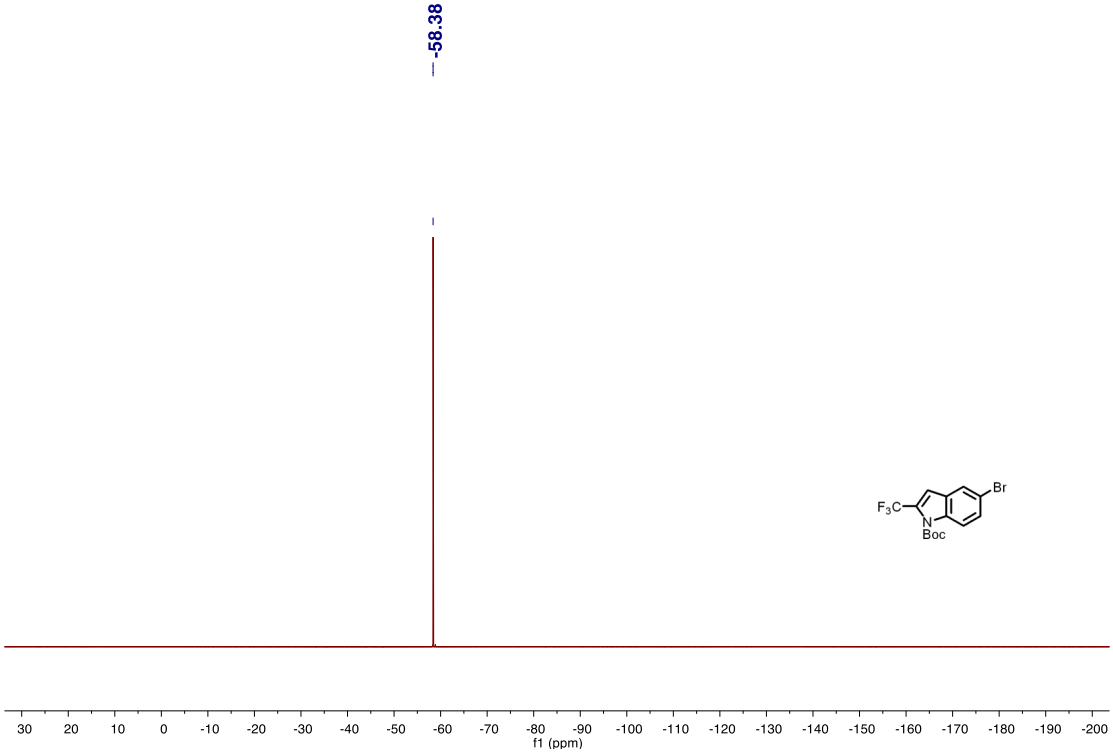
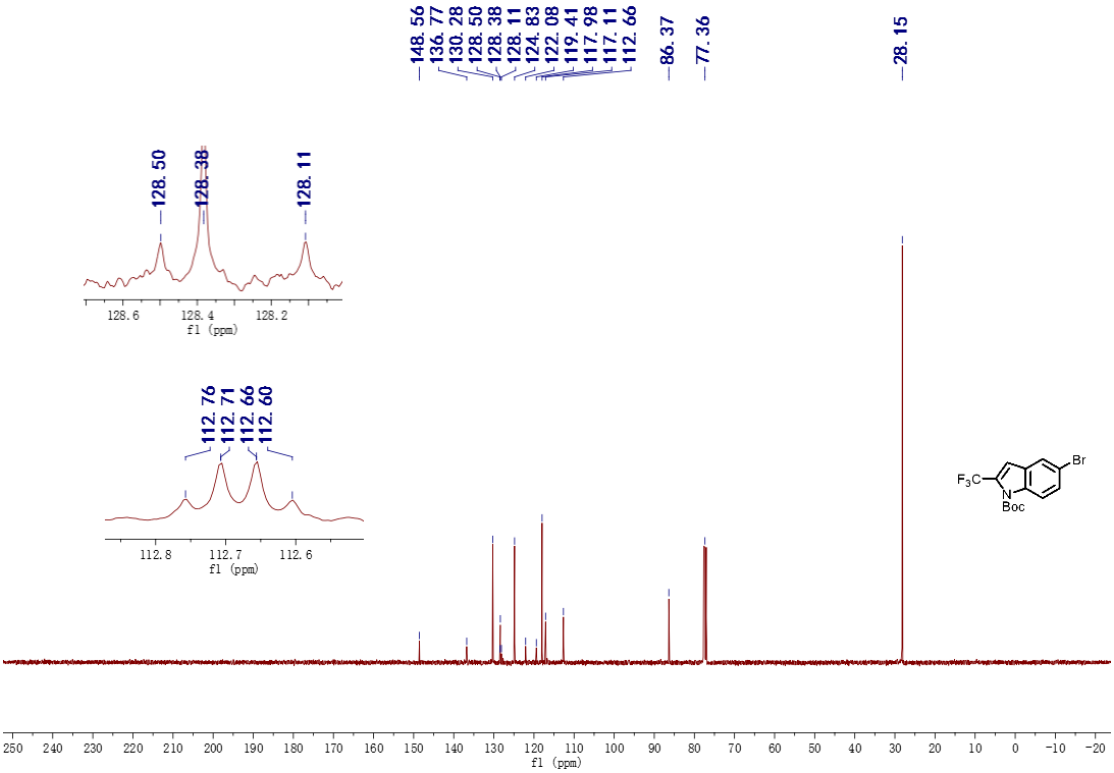
H NMR spectrum of 5-bromo-N-boc-2-(trifluoromethyl)-1-H-Indole 4f



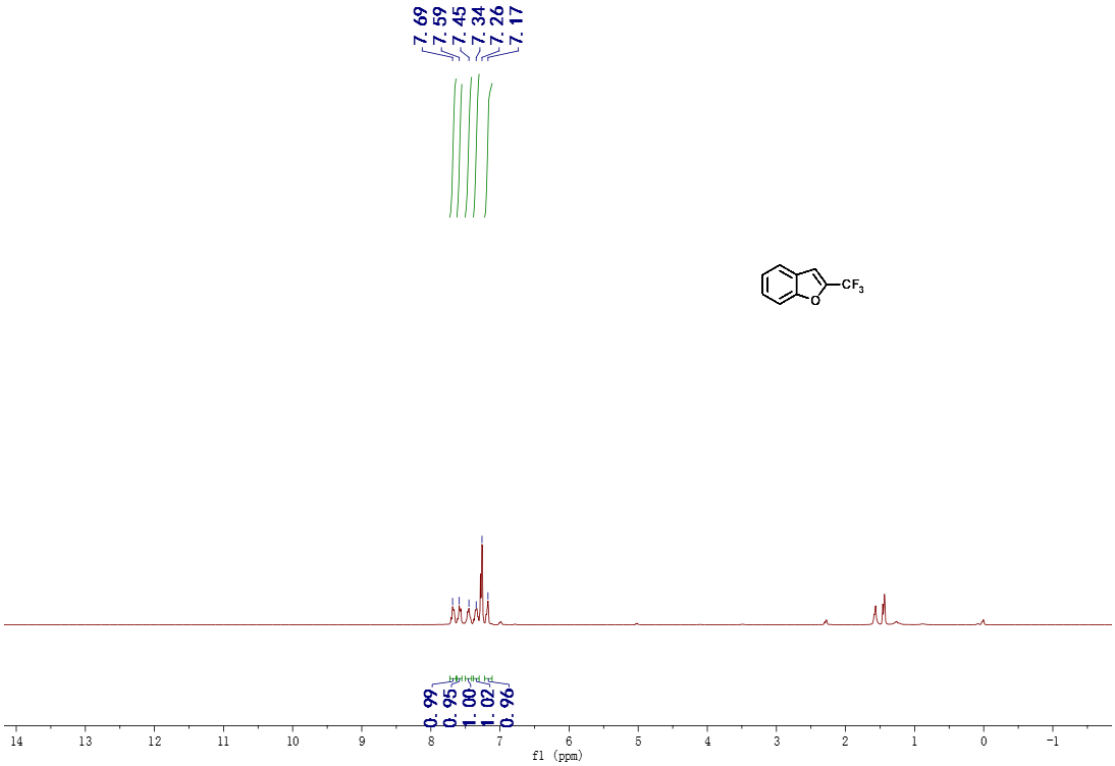
^{19}F NMR spectrum of 5-bromo-N-boc-2-(trifluoromethyl)-1-H-Indole 4f



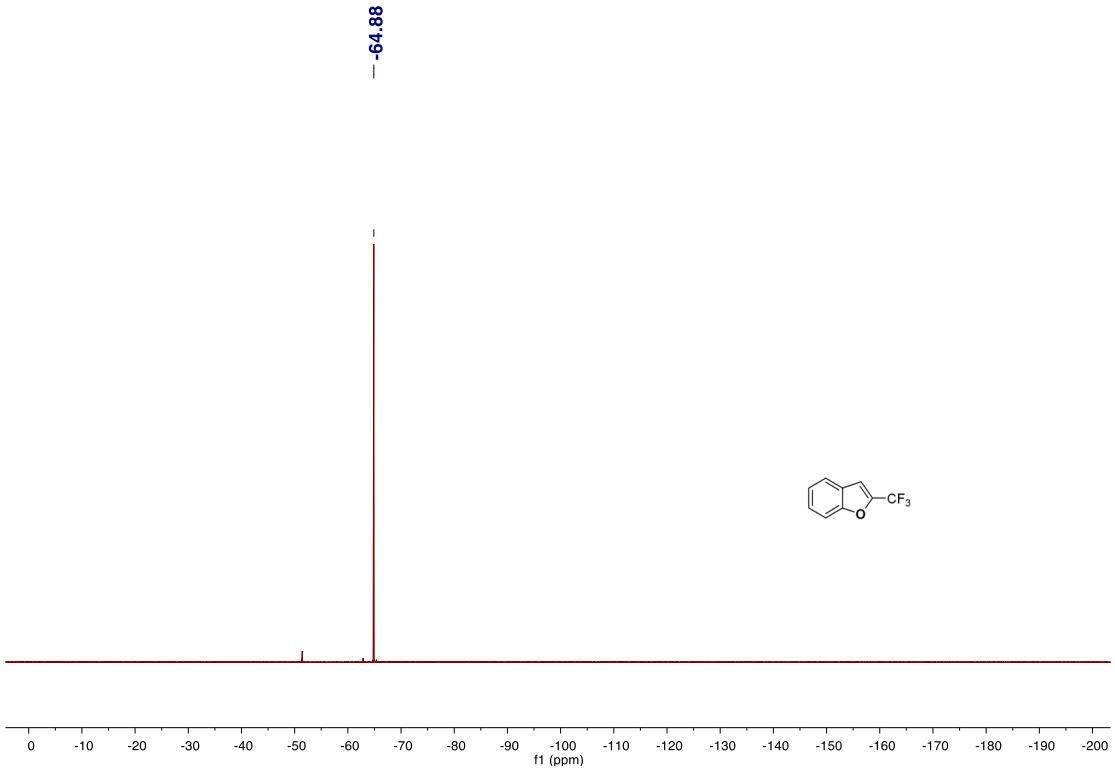
^{13}C NMR spectrum of 5-bromo-N-boc-2-(trifluoromethyl)-1-H-Indole 4f



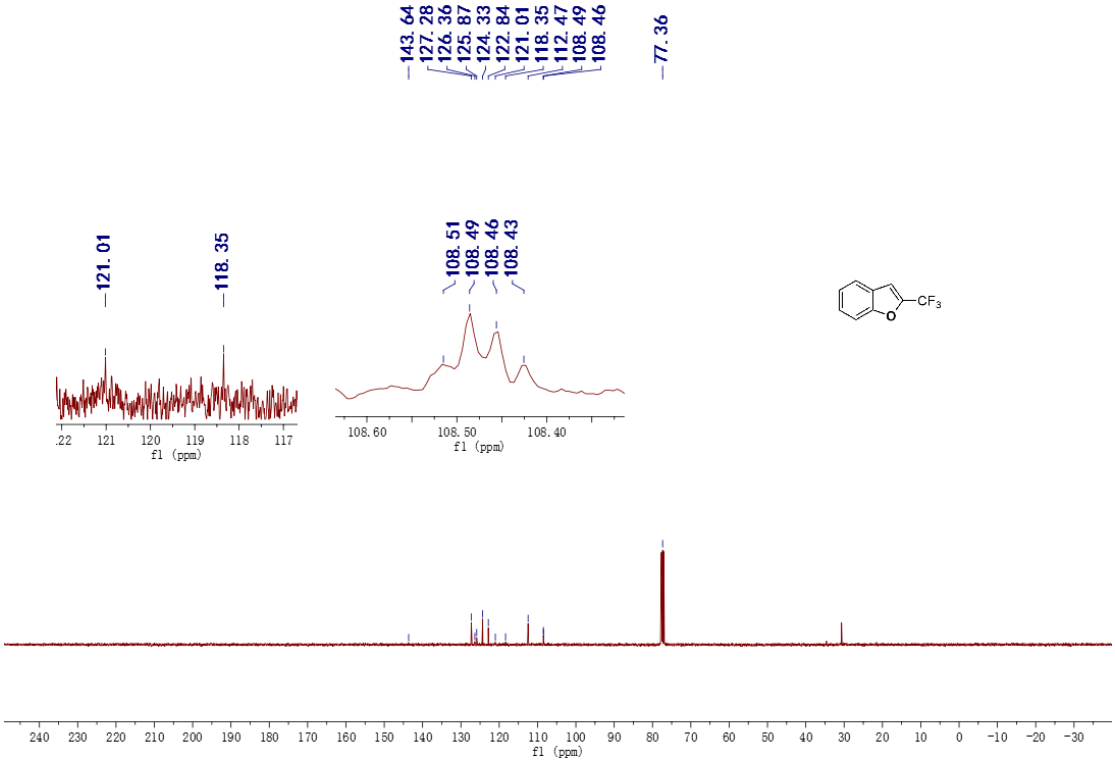
^{1}H NMR spectrum of 2-(trifluoromethyl)benzofurane 4g



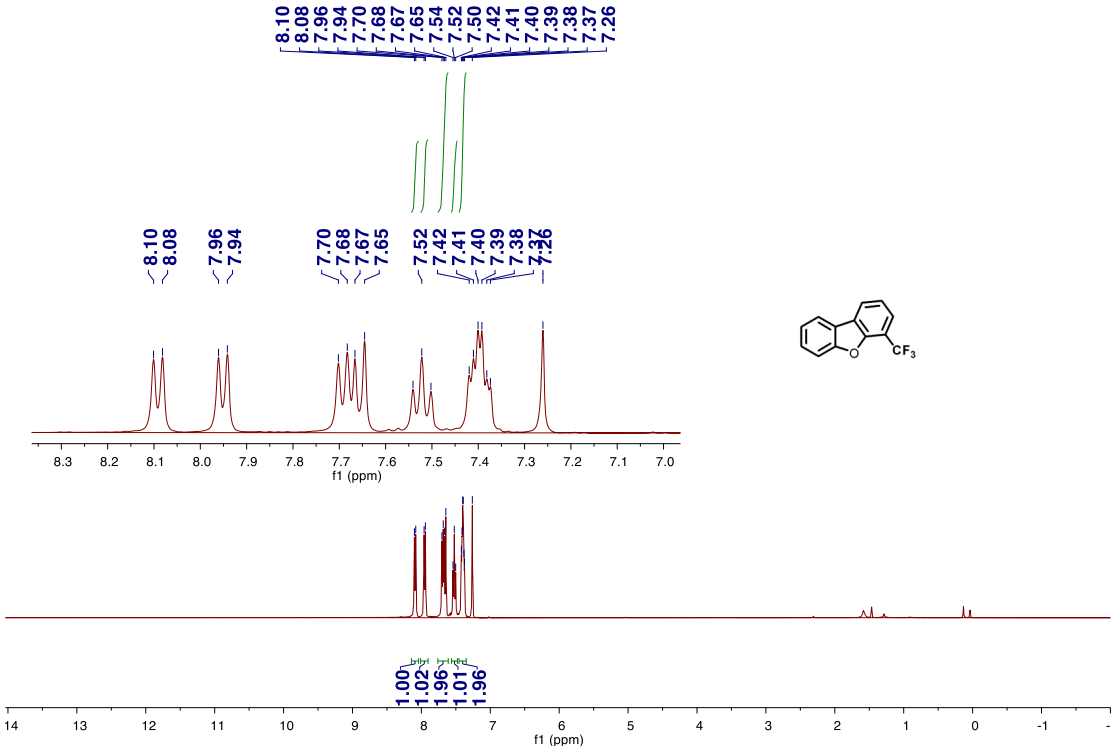
^{19}F NMR spectrum of 2-(trifluoromethyl)benzofurane 4g



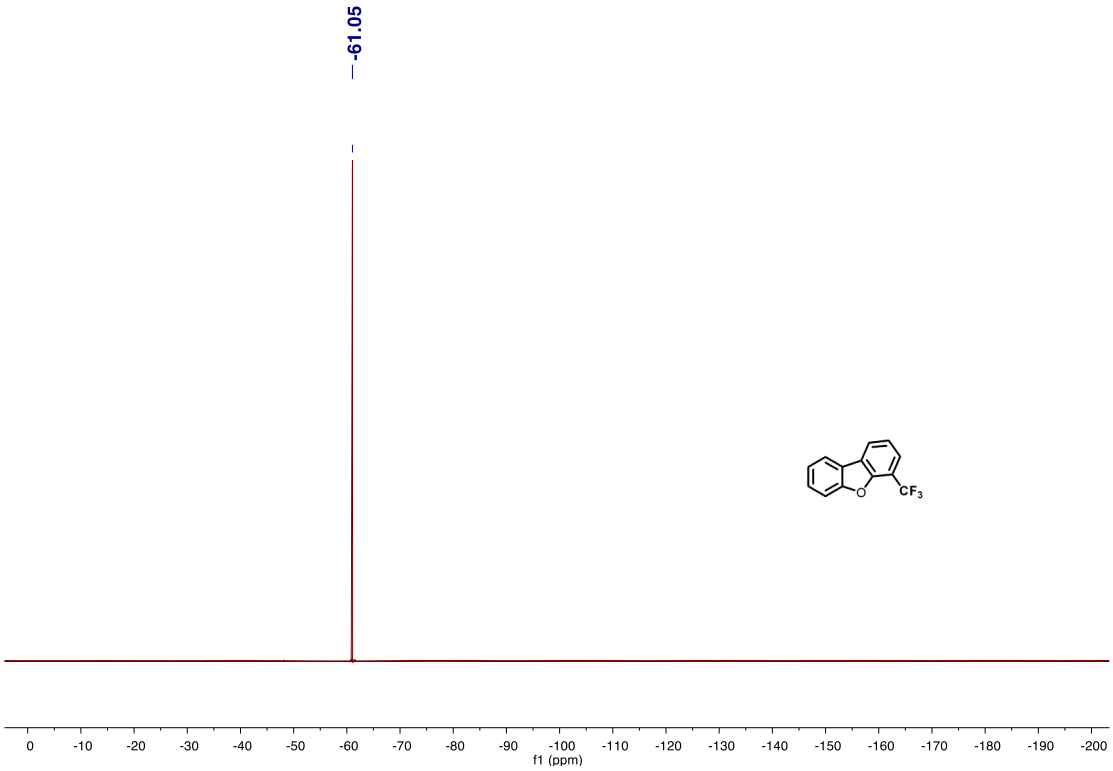
^{13}C NMR spectrum of 2-(trifluoromethyl)benzofurane 4g



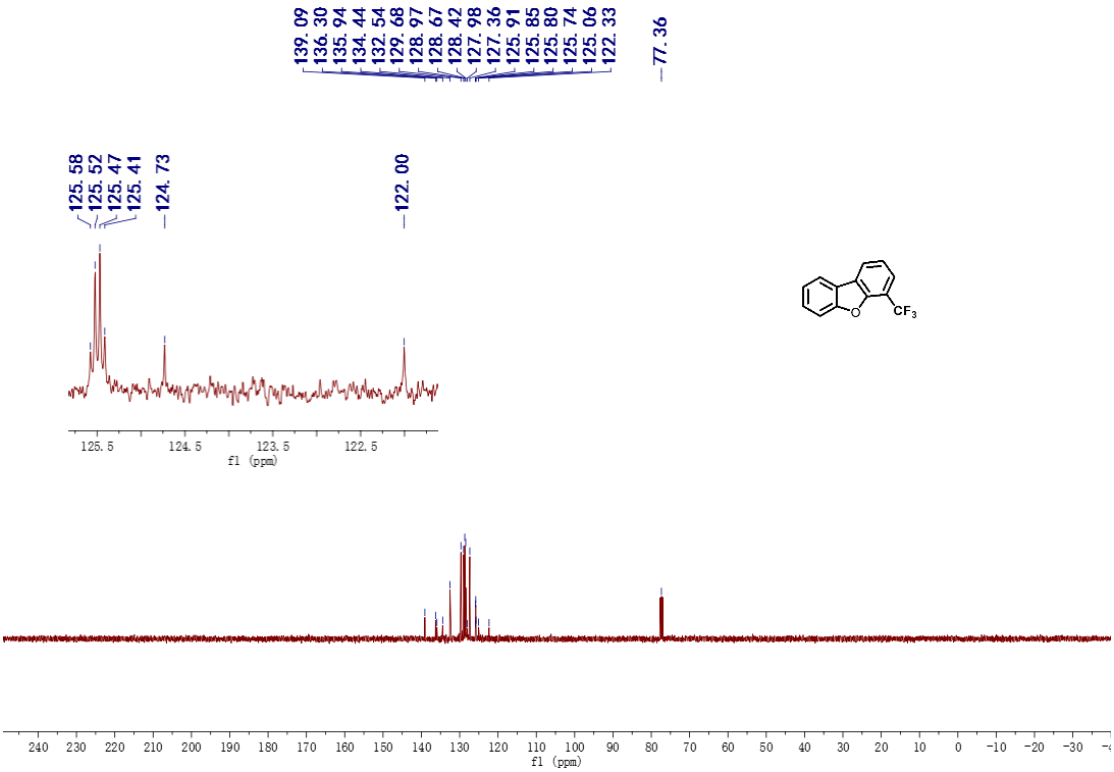
^{1}H NMR spectrum of 4-(trifluoromethyl)-dibenzofuran 4h



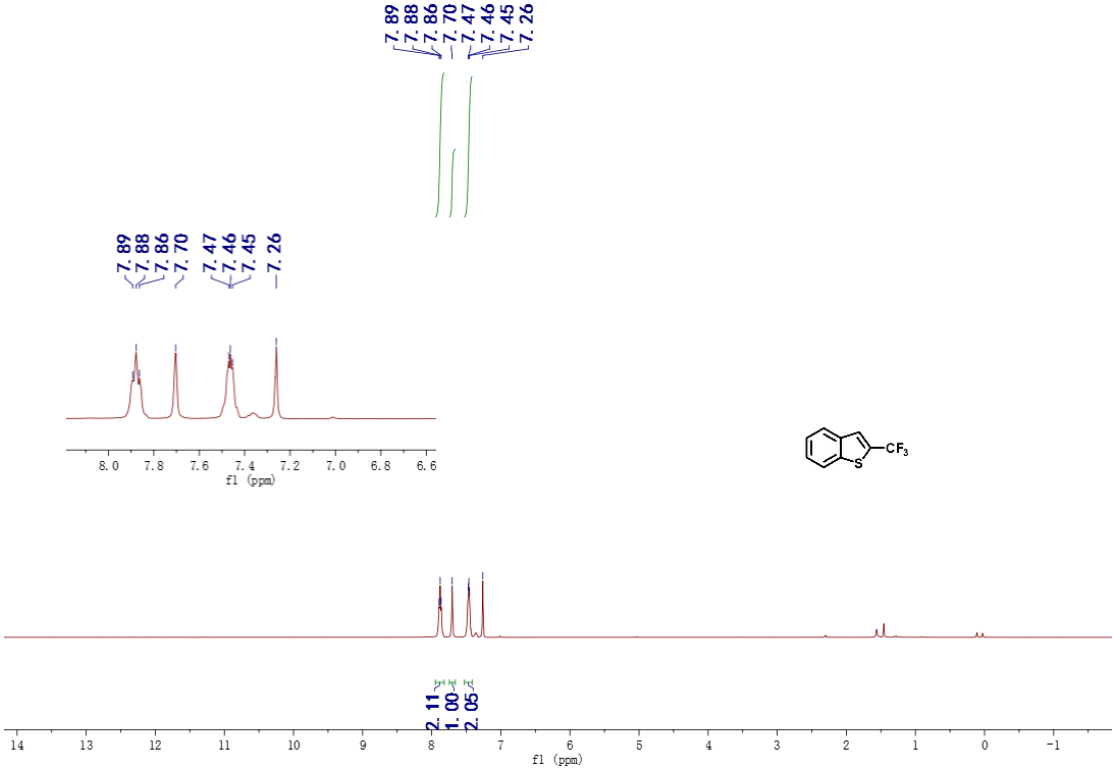
^{19}F NMR spectrum of 4-(trifluoromethyl)-dibenzofuran 4h



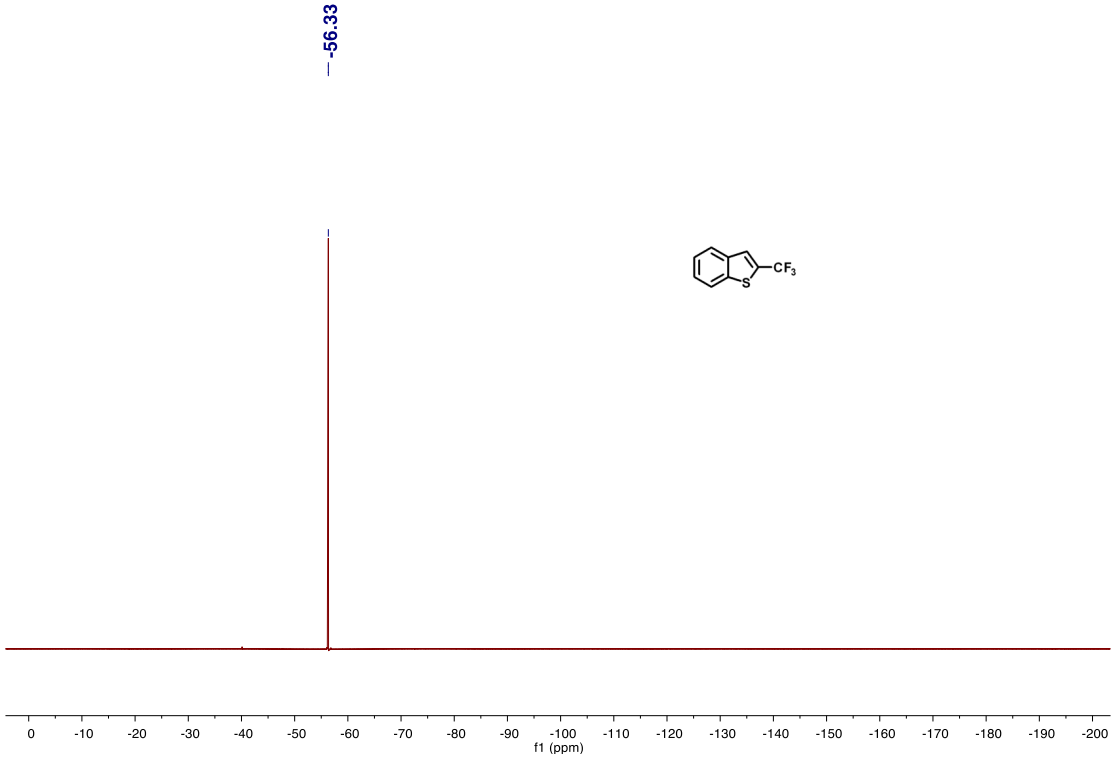
^{13}C NMR spectrum of 4-(trifluoromethyl)-dibenzofuran 4h



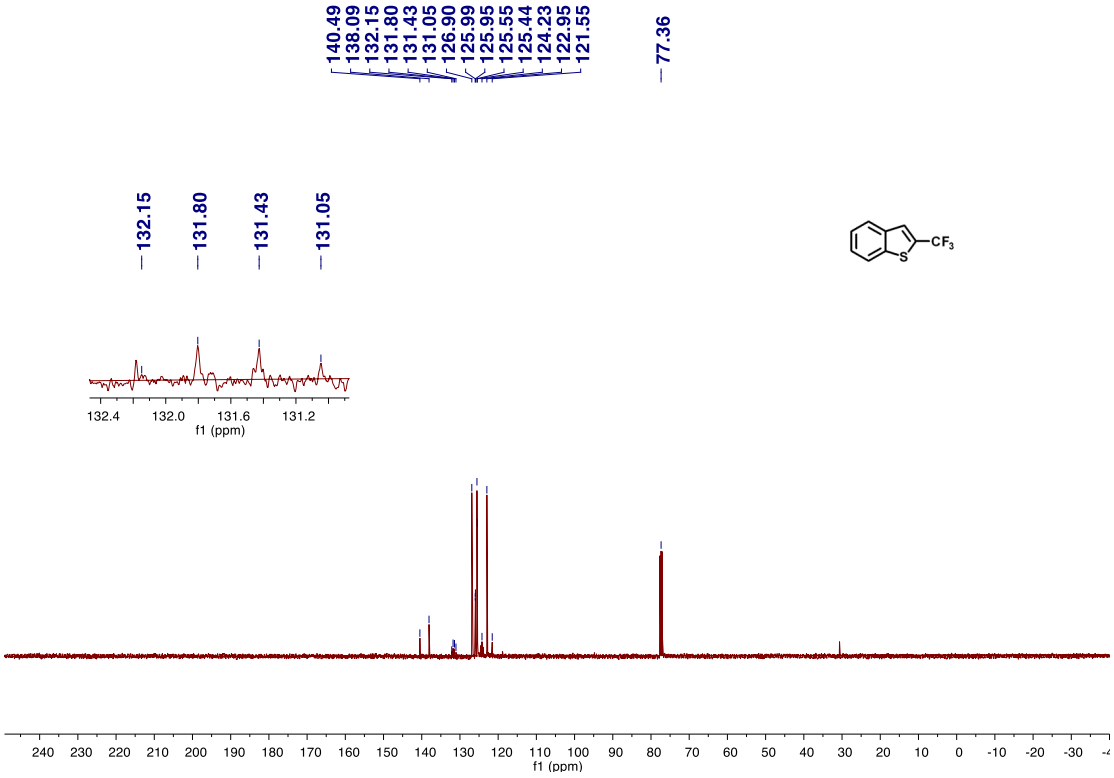
^{1}H NMR spectrum of 2-(trifluoromethyl)benzo[b]thiophene 4i



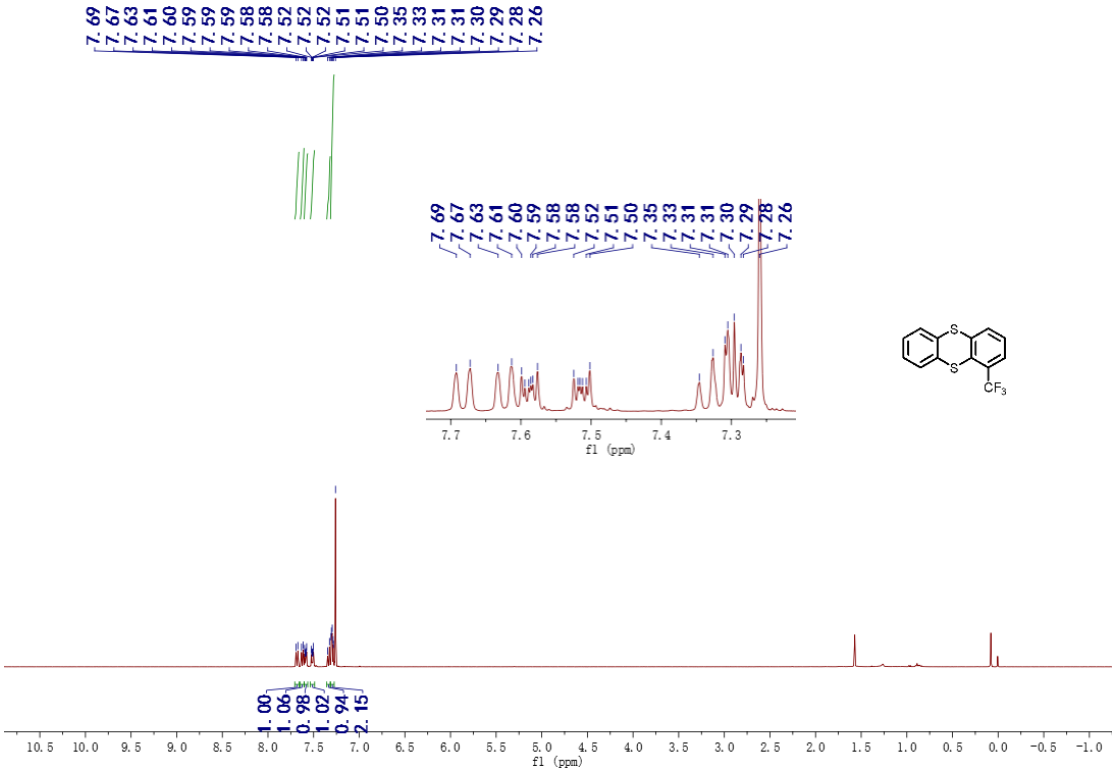
^{19}F NMR spectrum of 2-(trifluoromethyl)benzo[b]thiophene 4i



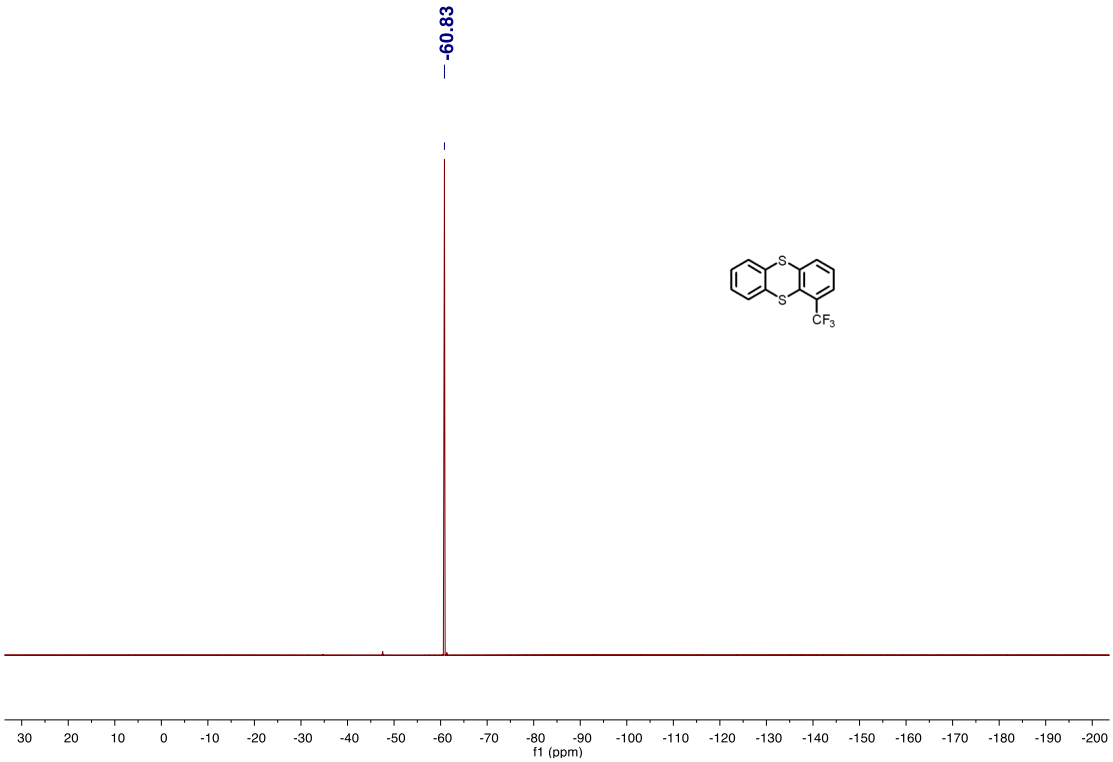
^{13}C NMR spectrum of 2-(trifluoromethyl)benzo[b]thiophene 4i



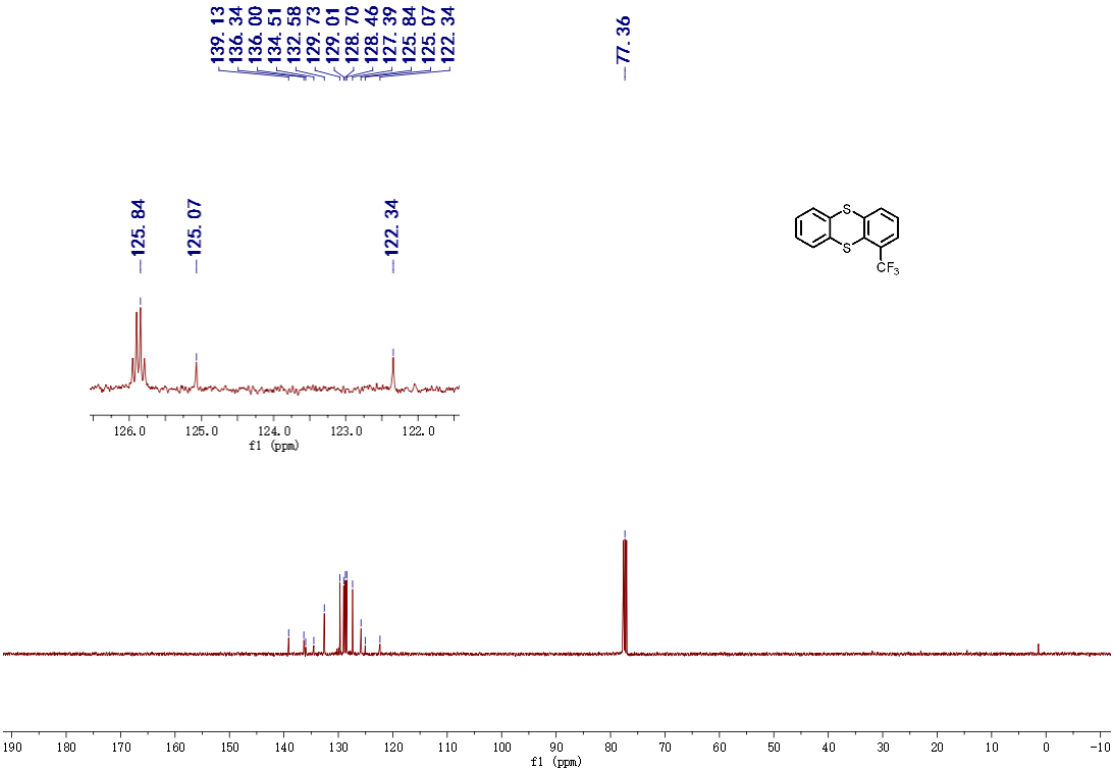
^{1}H NMR spectrum of 1-(trifluoromethyl)-thianthrene 4j



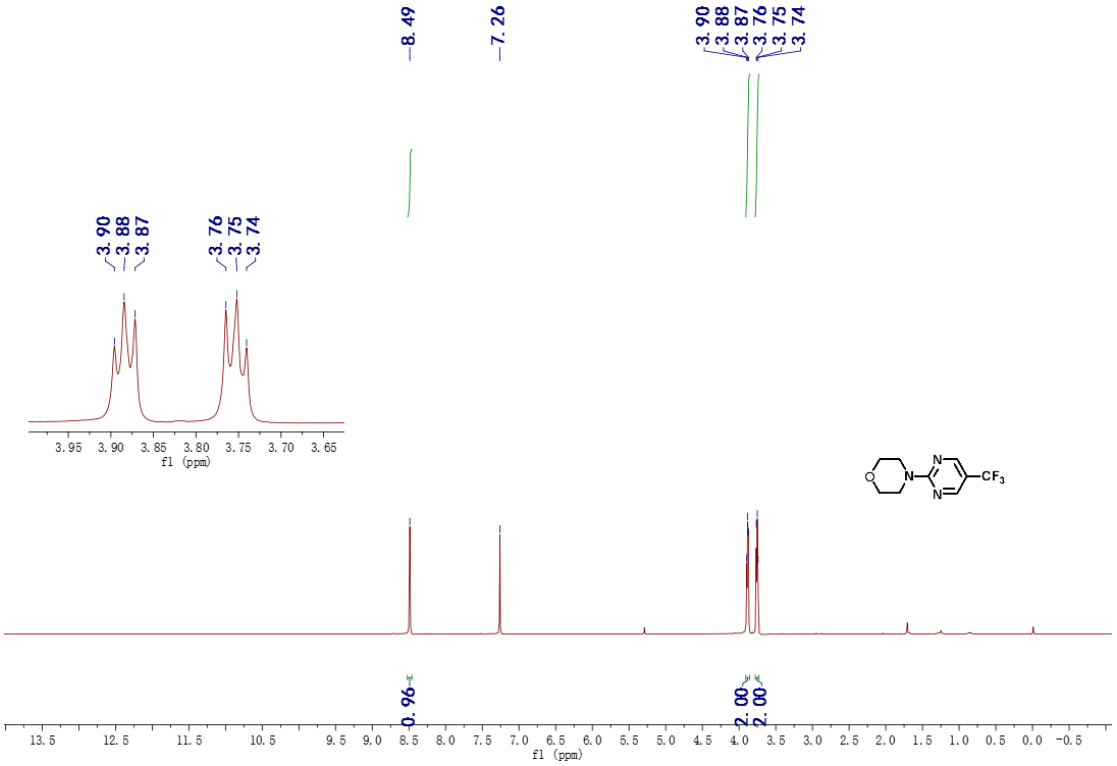
^{19}F NMR spectrum of 1-(trifluoromethyl)-thianthrene 4j



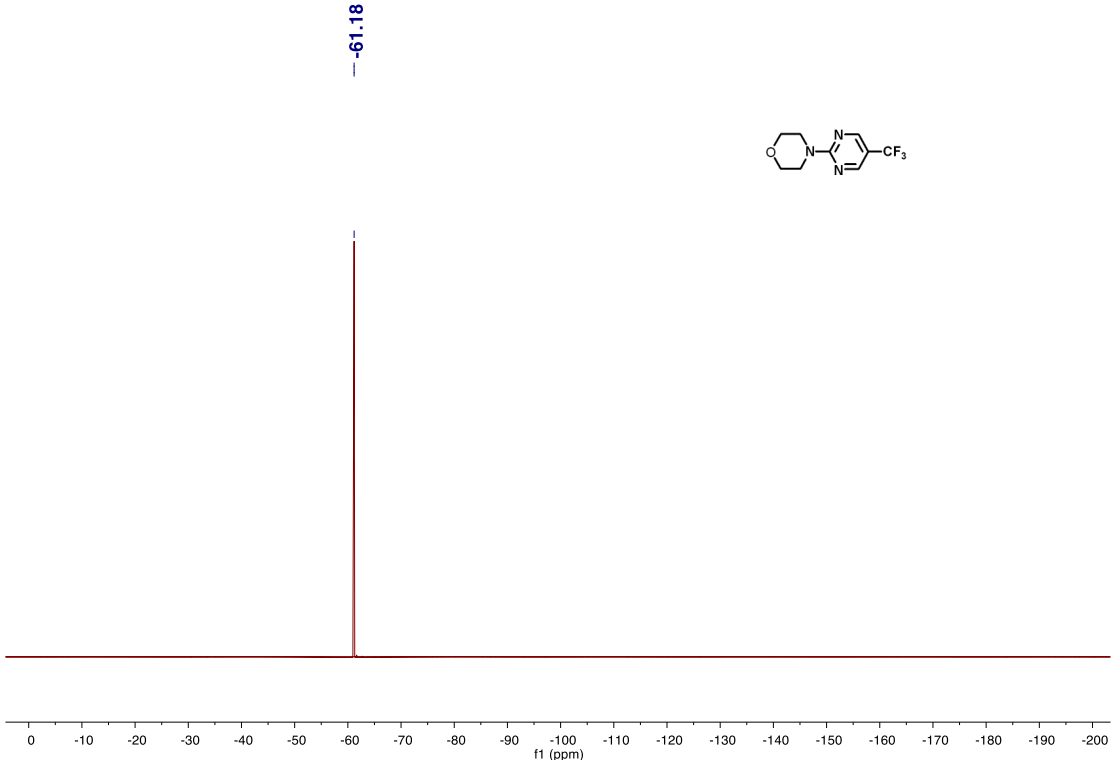
^{13}C NMR spectrum of 1-(trifluoromethyl)-thianthrene 4j



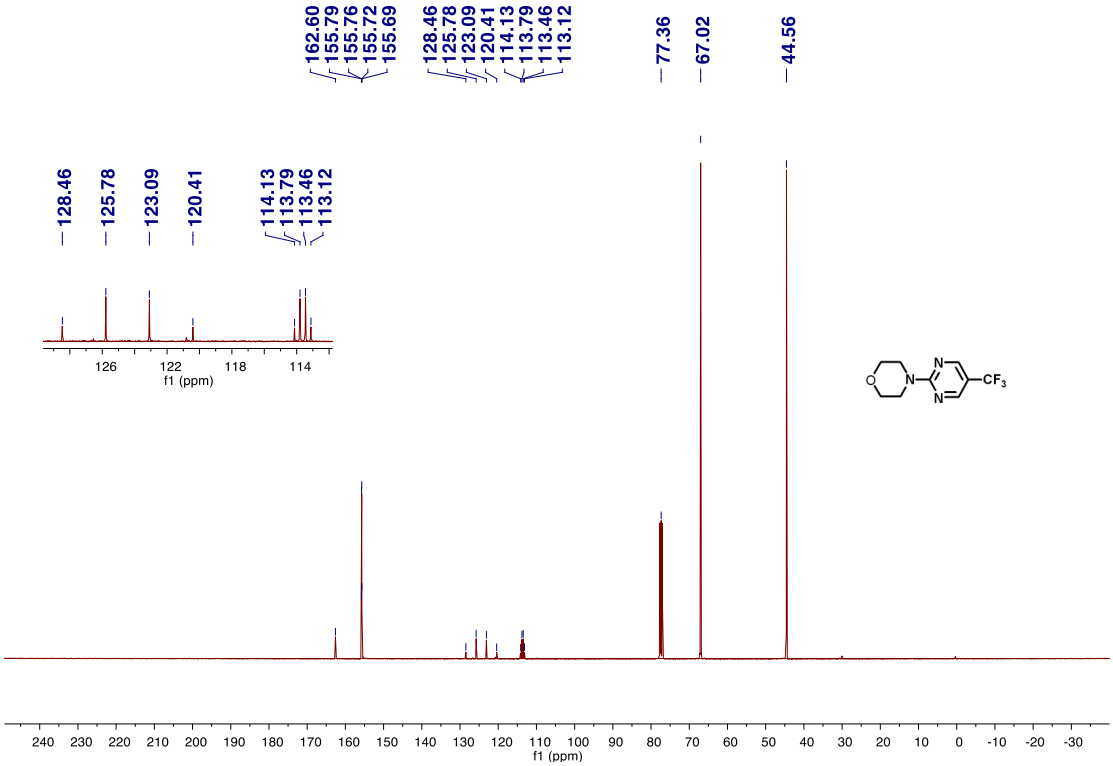
^{1}H NMR spectrum of 4-[5-(trifluoromethyl)-2-pyrimidinyl]-morpholine 4k



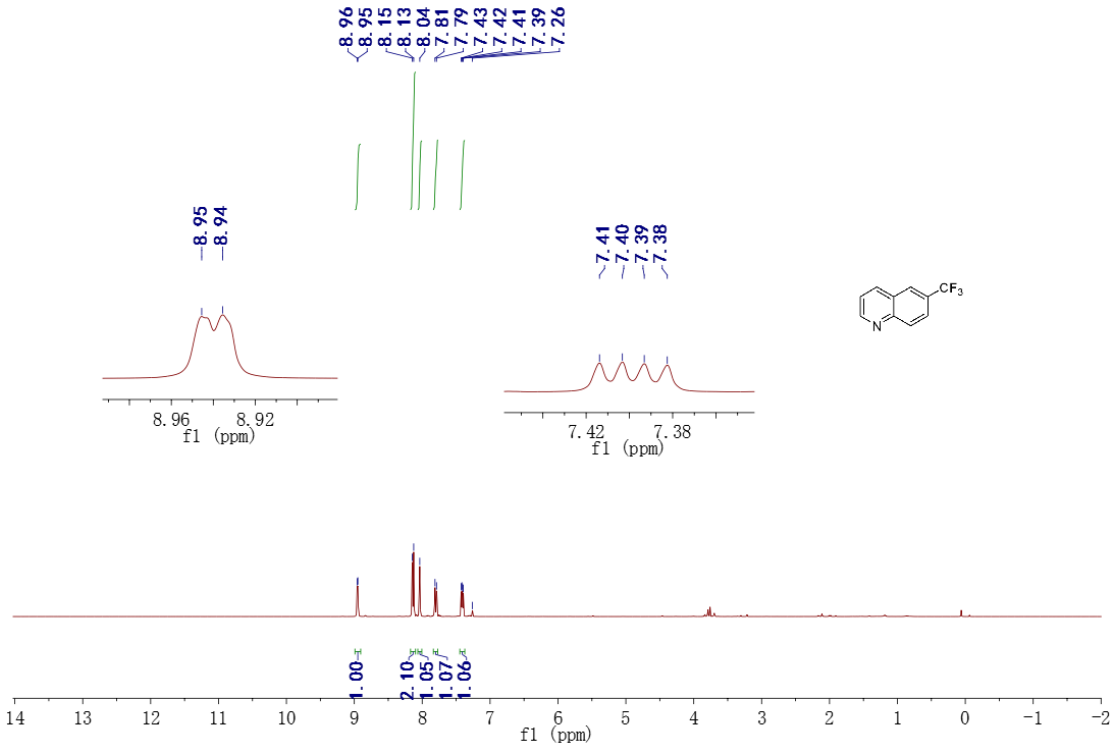
^{19}F NMR spectrum of 4-[5-(trifluoromethyl)-2-pyrimidinyl]-morpholine 4k



^{13}C NMR spectrum of 4-[5-(trifluoromethyl)-2-pyrimidinyl]-morpholine 4k



^{1}H NMR spectrum of 6-(trifluoromethyl)quinolone 4l



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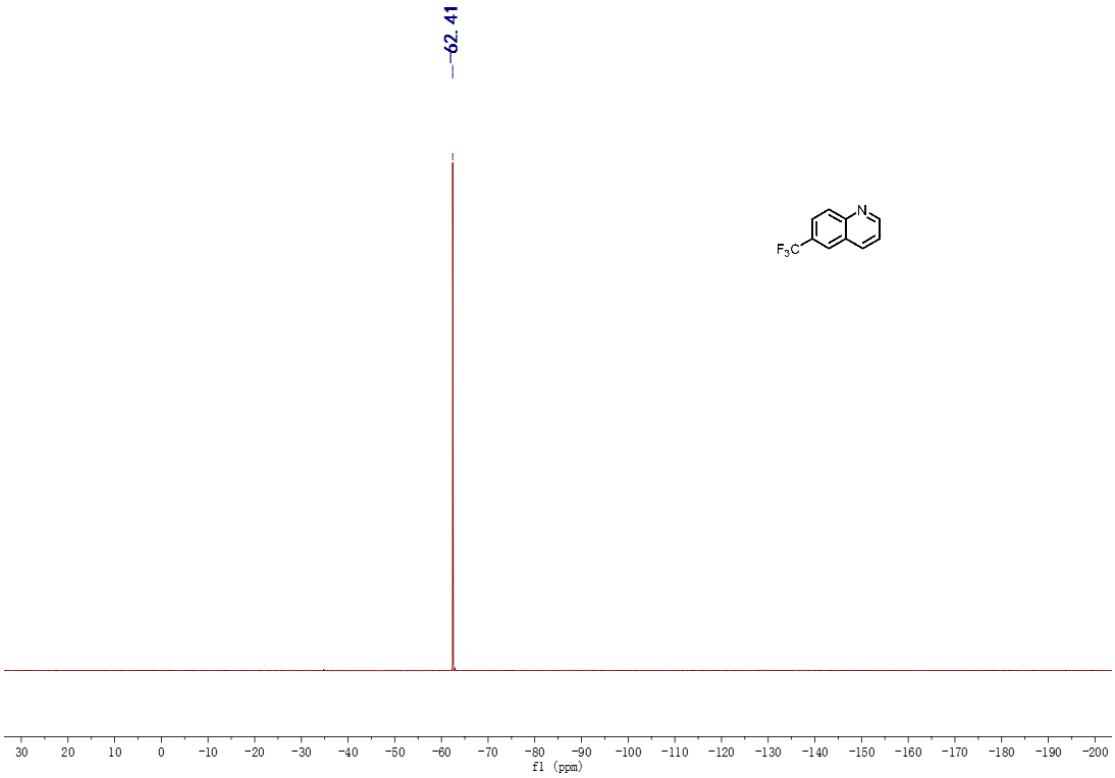
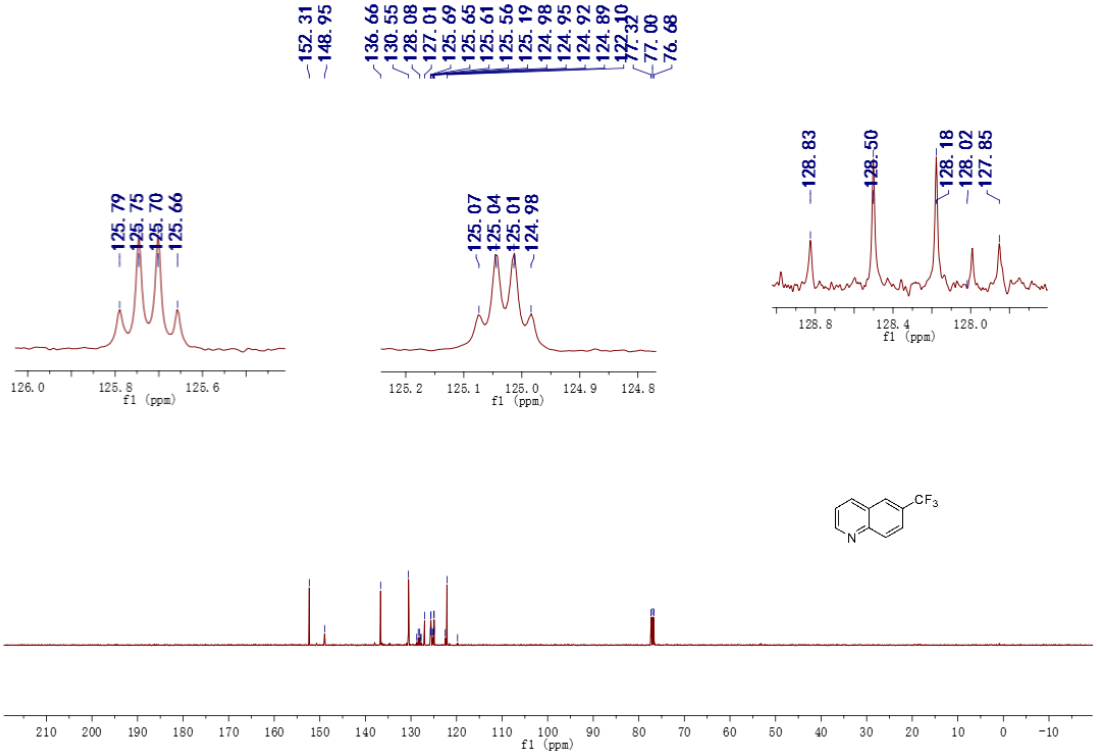
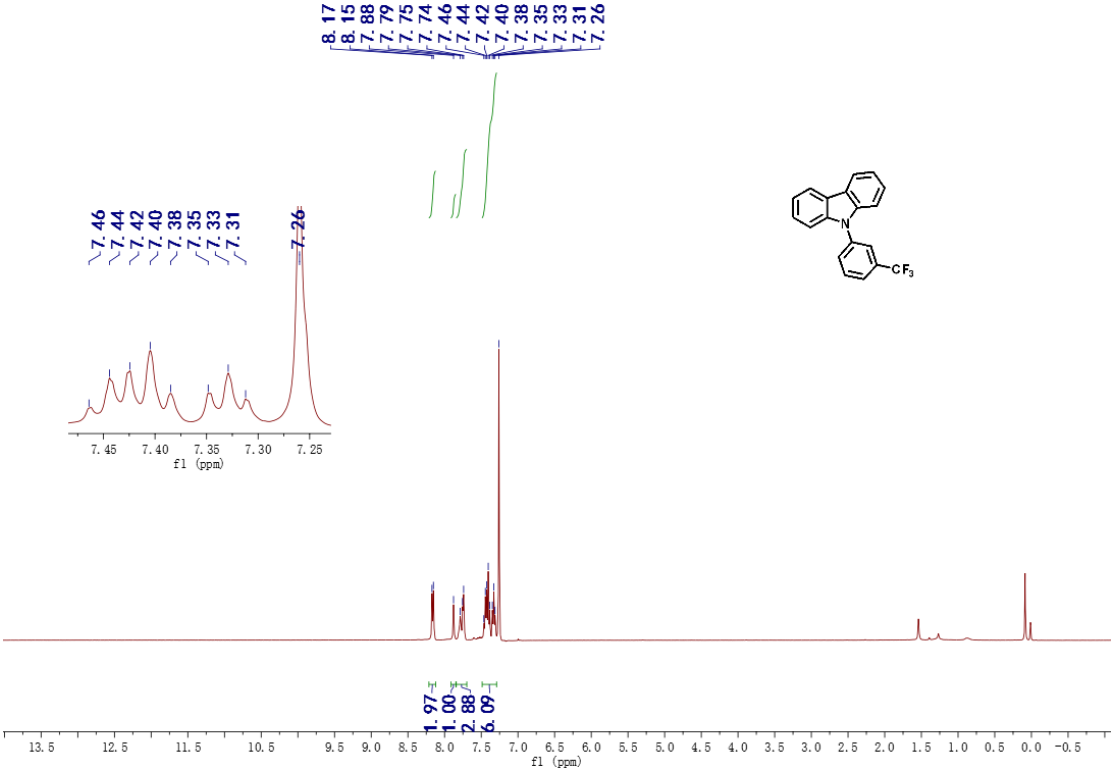


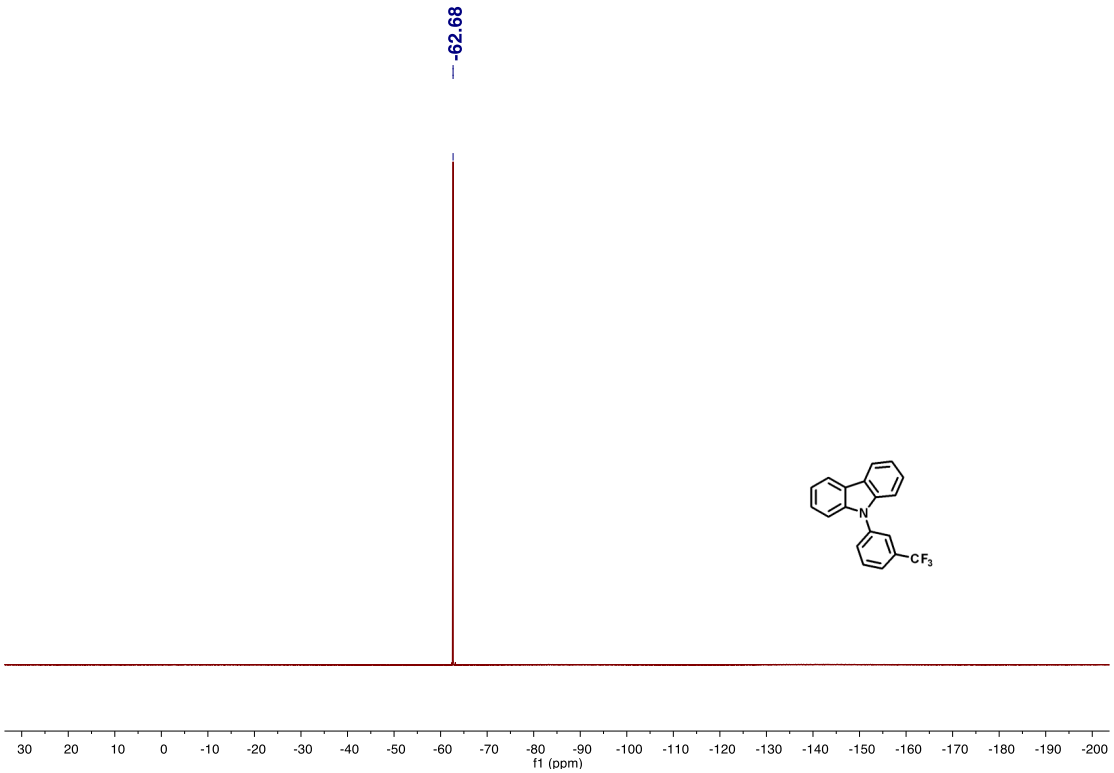
^{13}C NMR spectrum of 6-(trifluoromethyl)quinolone 4l



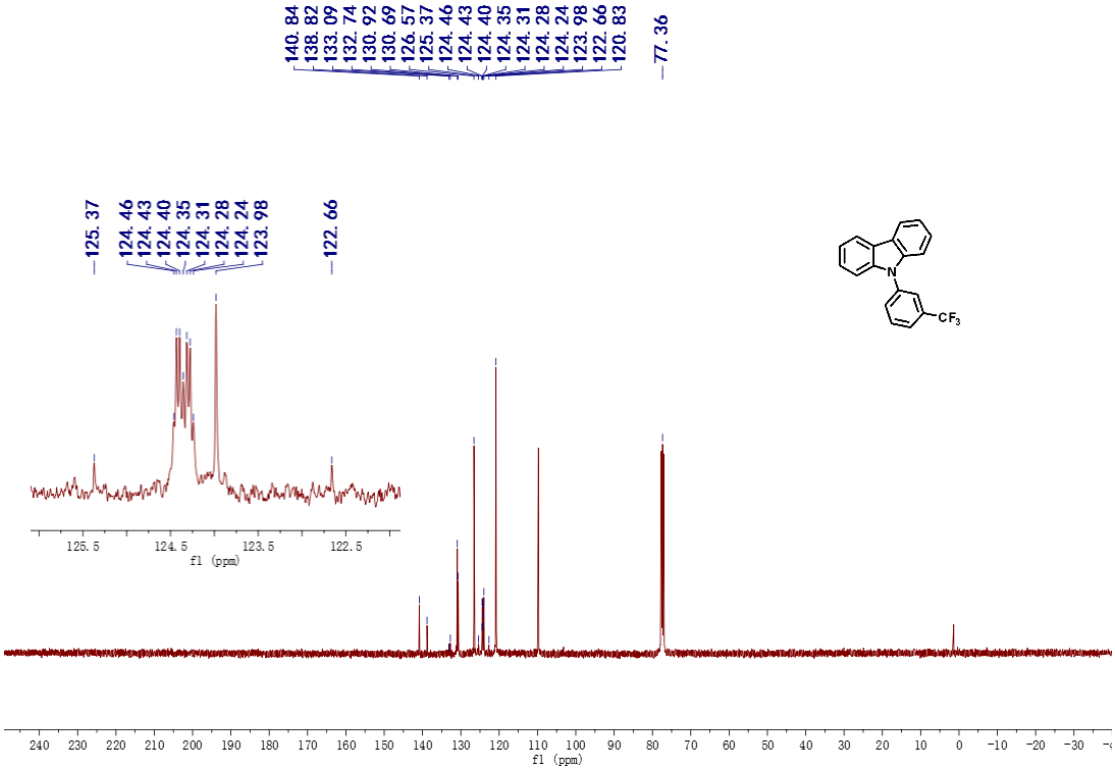
^{1}H NMR spectrum of 9-[3-(trifluoromethyl)phenyl]-9*H*-carbazole 4m



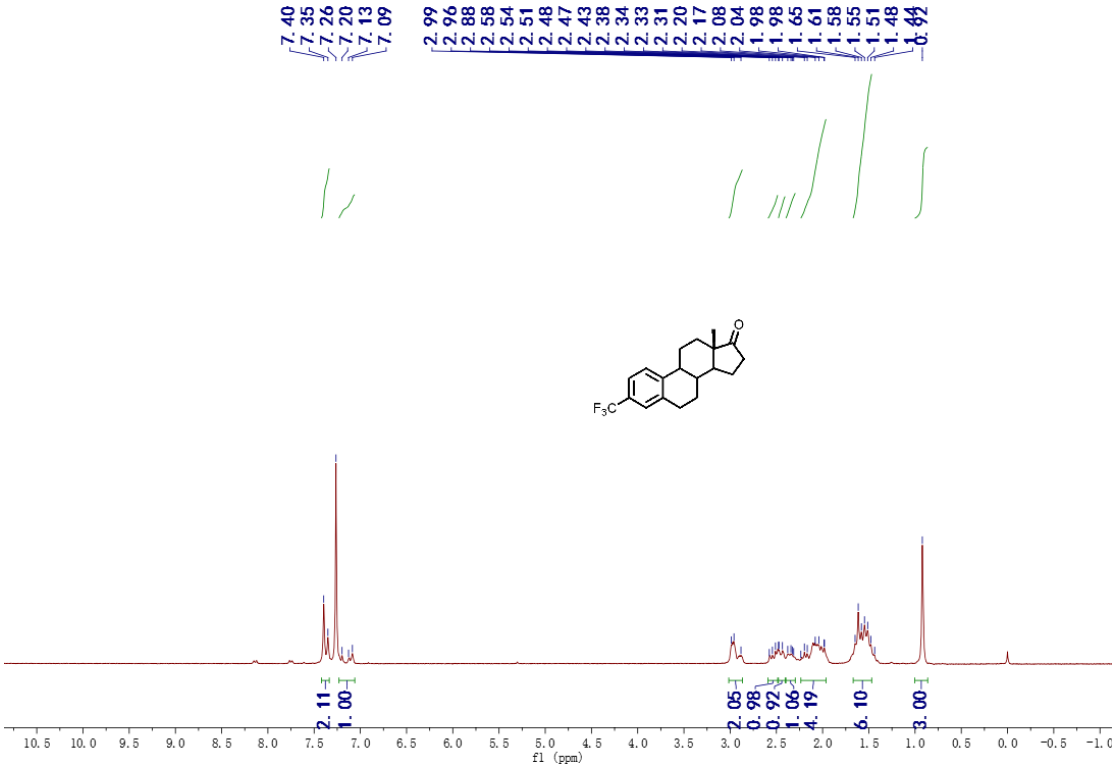
^{19}F NMR spectrum of 9-[3-(trifluoromethyl)phenyl]-9*H*-carbazole 4m



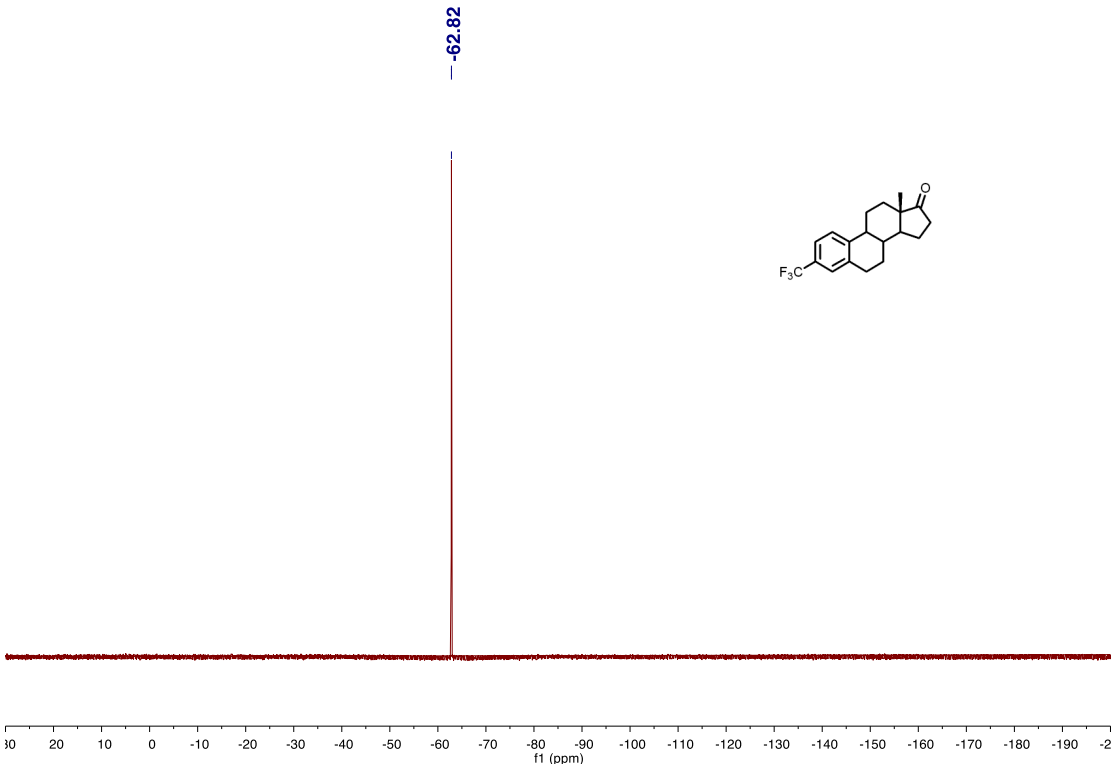
^{13}C NMR spectrum of 9-[3-(trifluoromethyl)phenyl]-9*H*-carbazole 4m



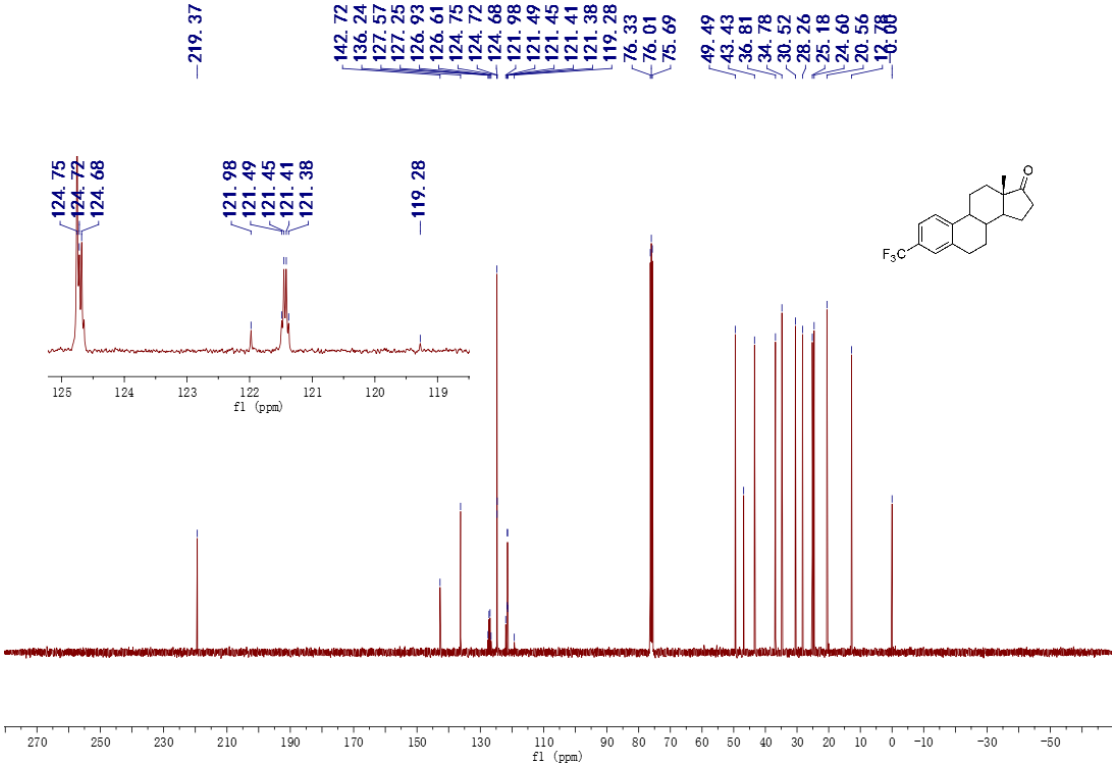
^{1}H NMR spectrum of (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(trifluoromethyl)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[*a*]phenanthren-17(14*H*)-one 4o



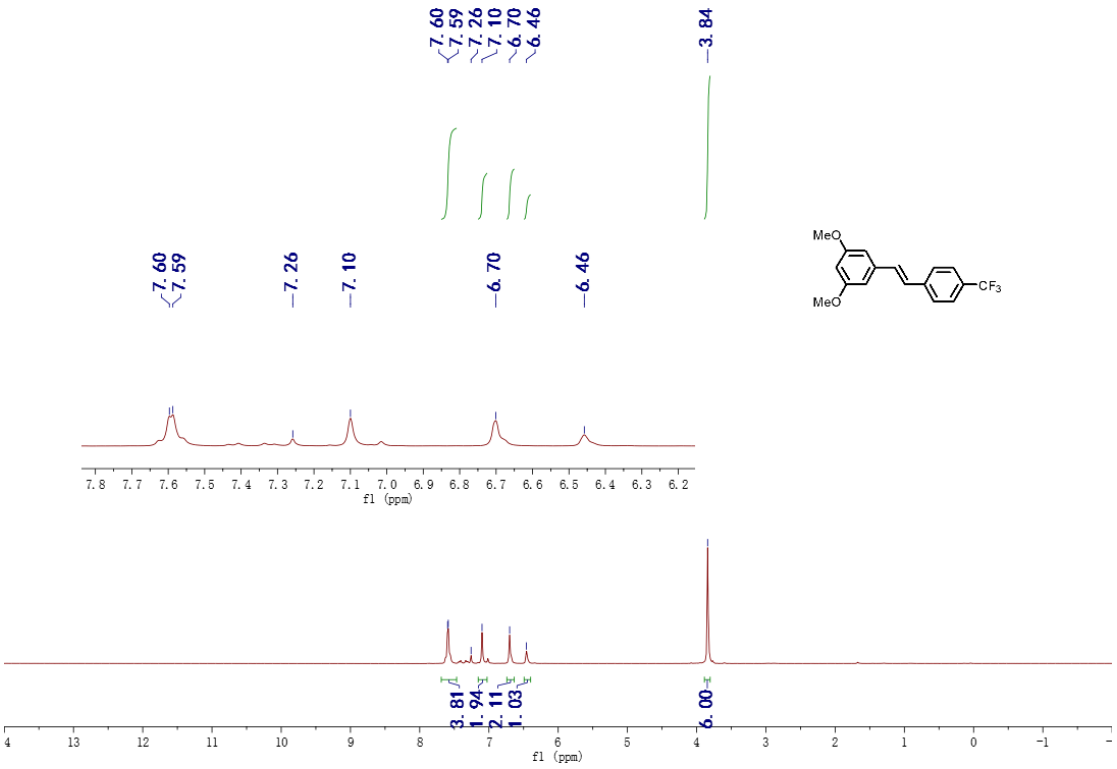
^{19}F NMR spectrum of (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(trifluoromethyl)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[*a*]phenanthren-17(14*H*)-one 4o



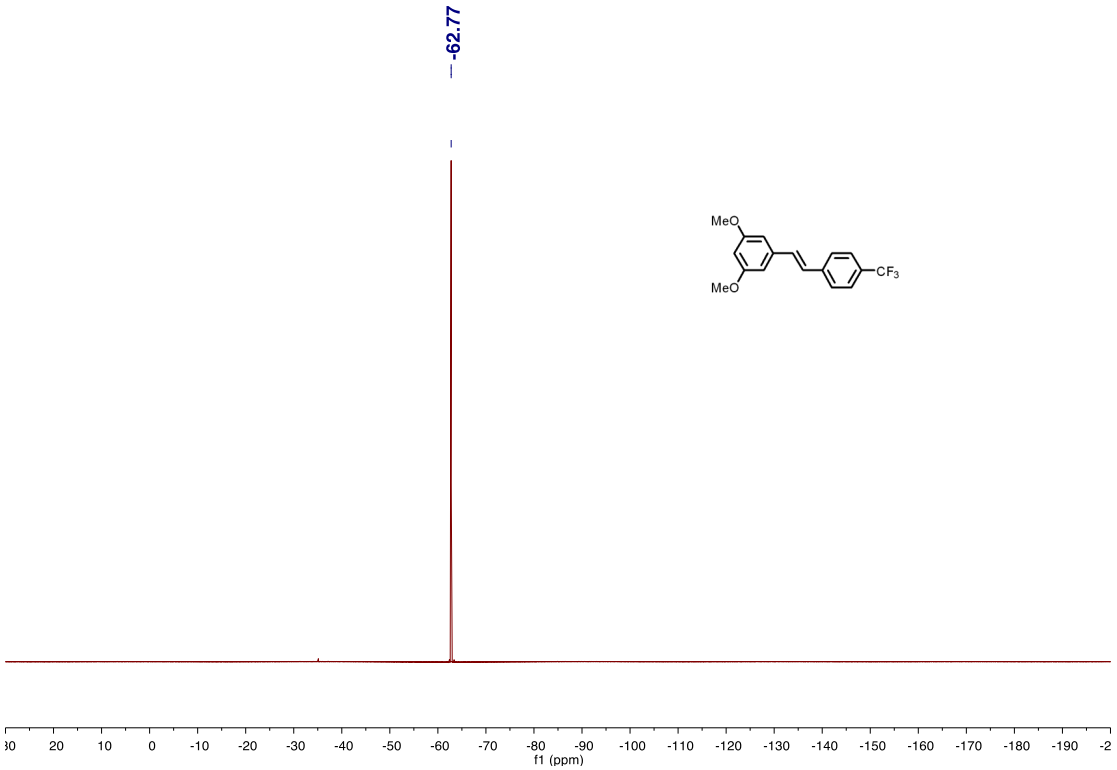
^{13}C NMR spectrum of (name) (8*R*,9*S*,13*S*,14*S*)-13-methyl-3-(trifluoromethyl)-7,8,9,11,12,13,15,16-octahydro-6H-cyclopenta[*a*]phenanthren-17(14*H*)-one 4o



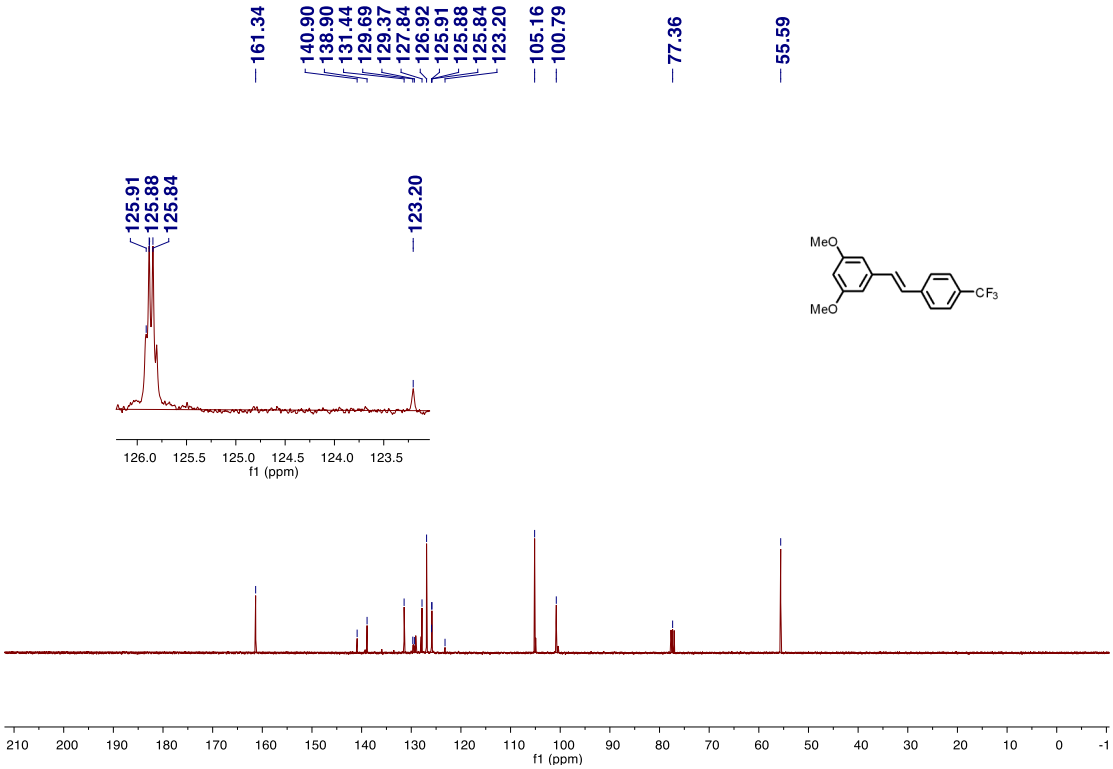
^{1}H NMR spectrum of 1,3-dimethoxy-5-[(1*E*)-2-[4-(trifluoromethyl)phenyl] ethenyl]-benzene 4n



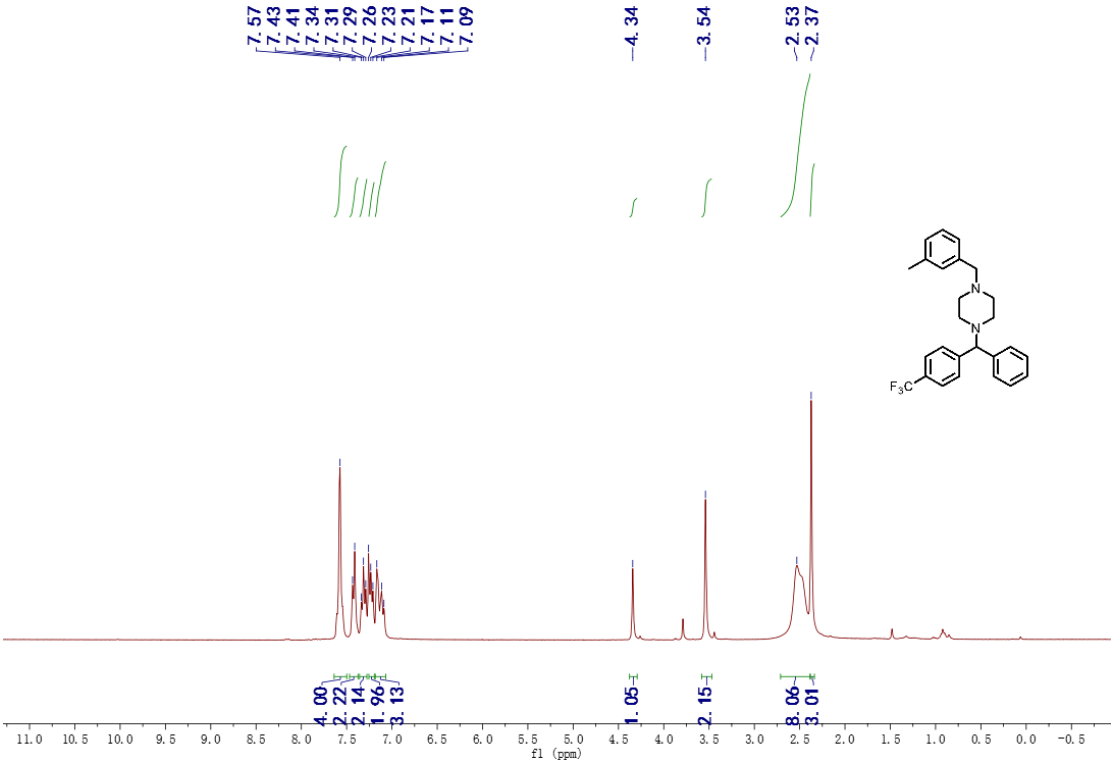
^{19}F NMR spectrum of 1,3-dimethoxy-5-[(1*E*)-2-[4-(trifluoromethyl)phenyl] ethenyl]-benzene 4n



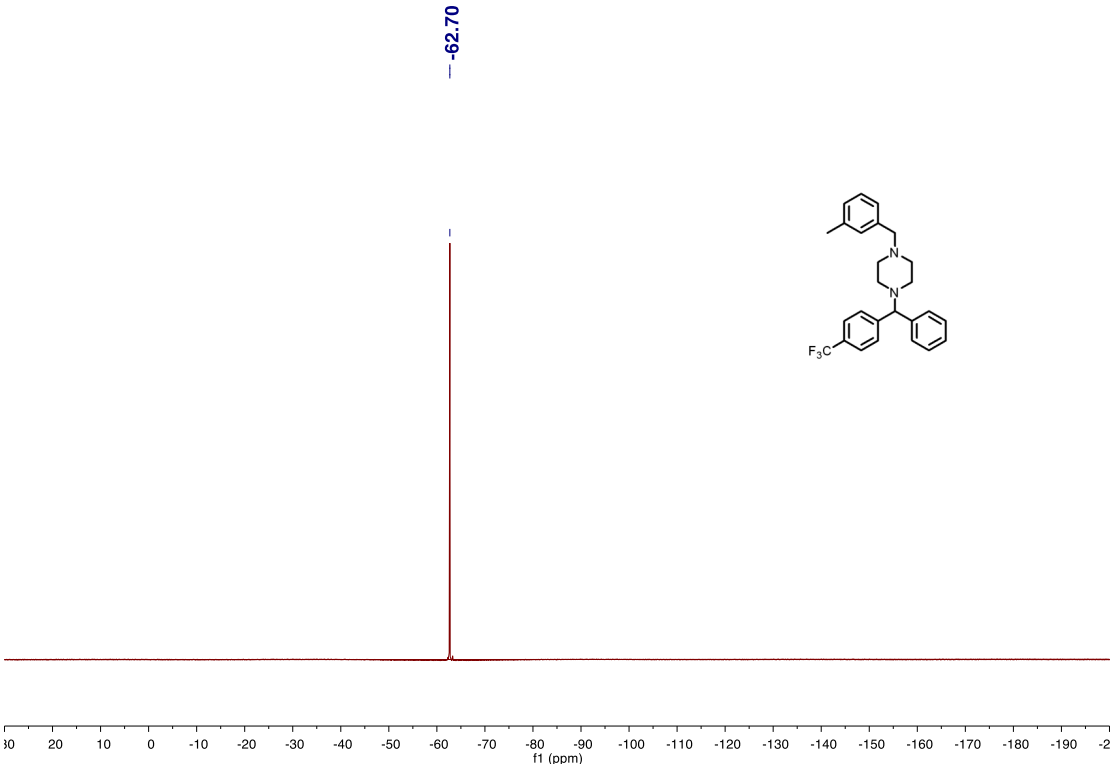
^{13}C NMR spectrum of 1,3-dimethoxy-5-[(1*E*)-2-[4-(trifluoromethyl)phenyl] ethenyl]-benzene 4n



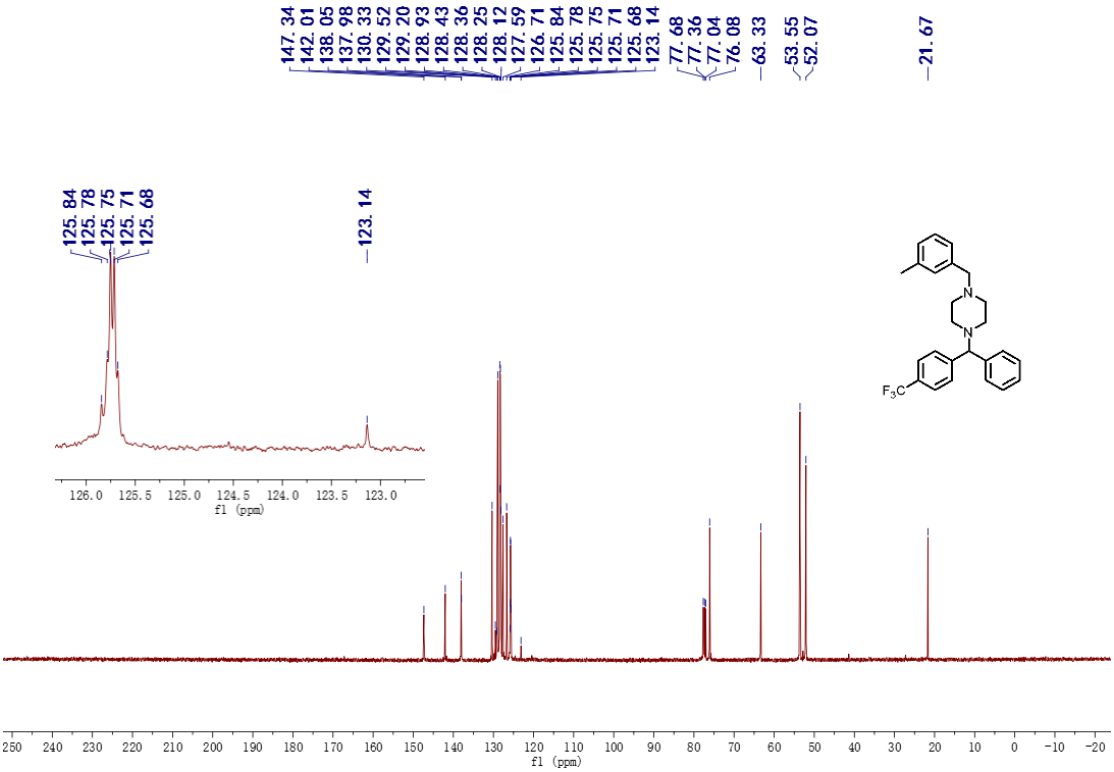
^{1}H NMR spectrum of 1-[(3-methylphenyl)methyl]-4-[phenyl[4-(trifluoromethyl) phenyl]methyl]-piperazine 4p



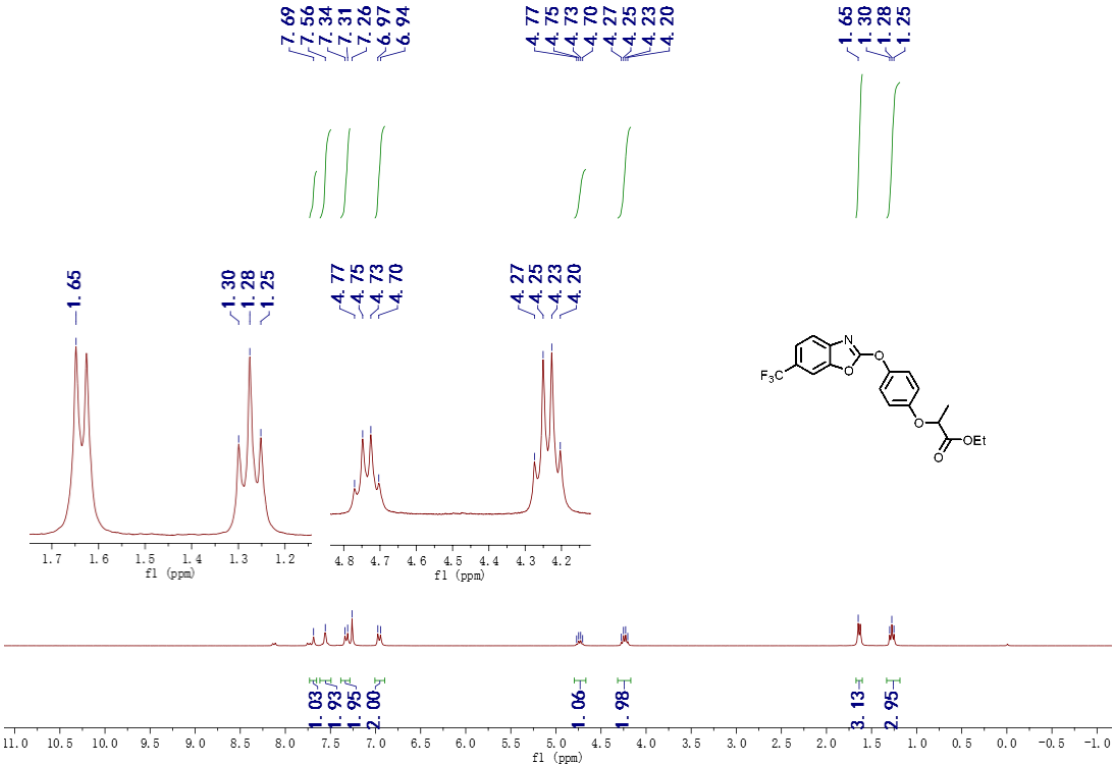
^{19}F NMR spectrum of 1-[(3-methylphenyl)methyl]-4-[phenyl[4-(trifluoromethyl) phenyl]methyl]-piperazine 4p



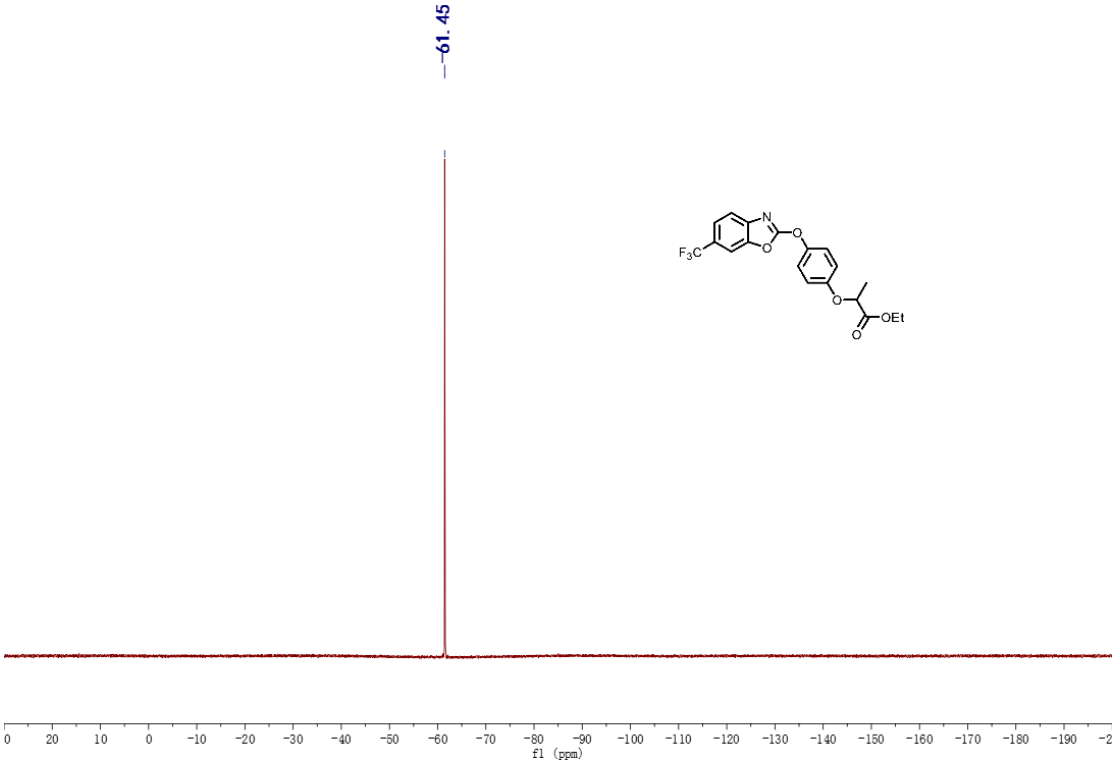
^{13}C NMR spectrum of 1-[(3-methylphenyl)methyl]-4-[phenyl[4-(trifluoromethyl) phenyl]methyl]-piperazine 4p



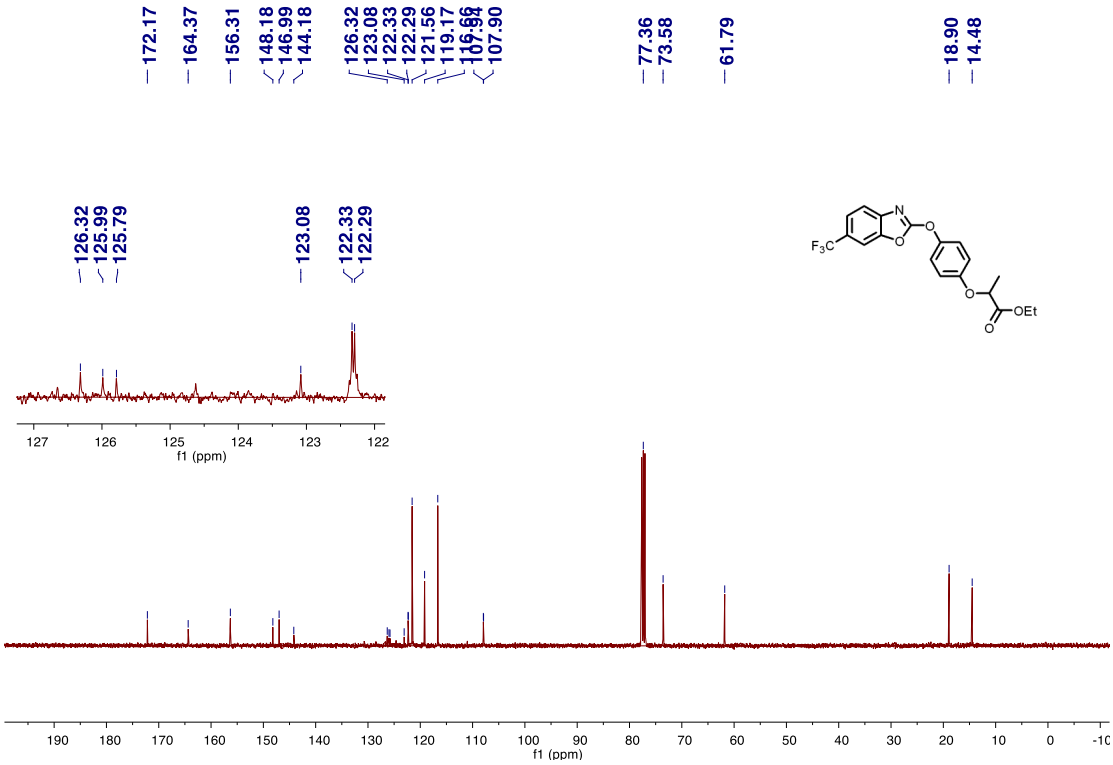
^{1}H NMR spectrum of ethyl-2-[4-(5-trifluoromethylbenzoxazol-2-yloxy)phenoxy]propionate 4q



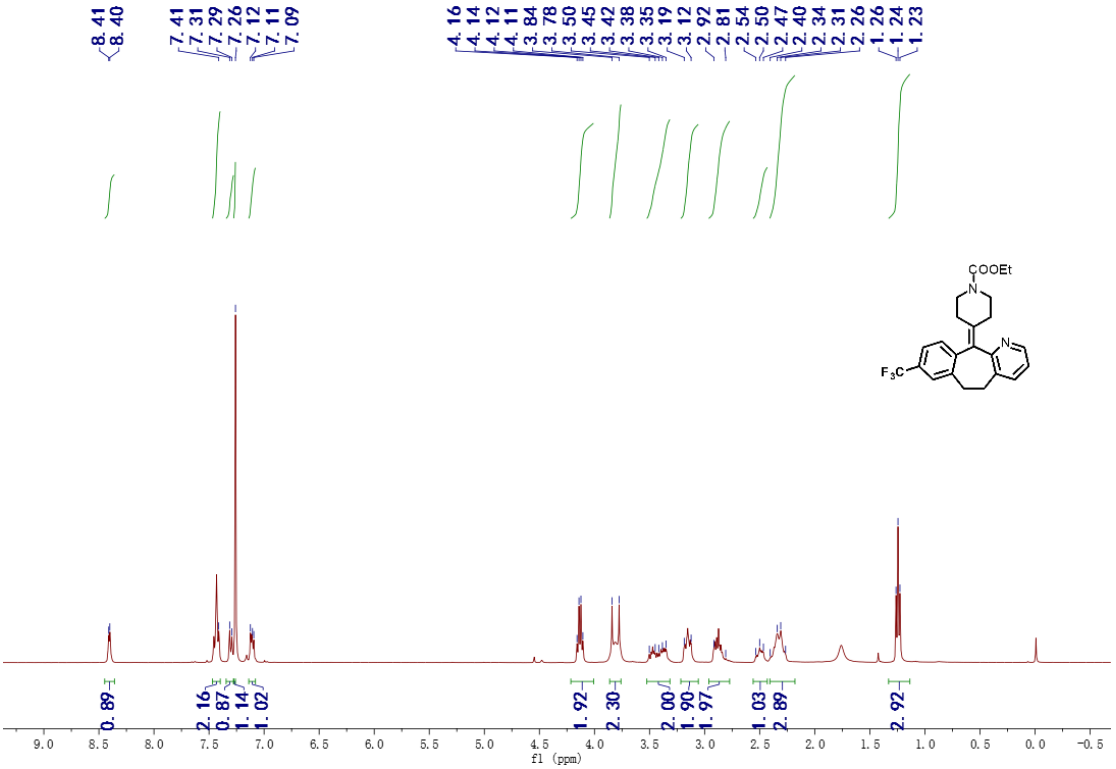
^{19}F NMR spectrum of ethyl-2-[4-(5-trifluoromethylbenzoxazol-2-yloxy)phenoxy]propionate 4q



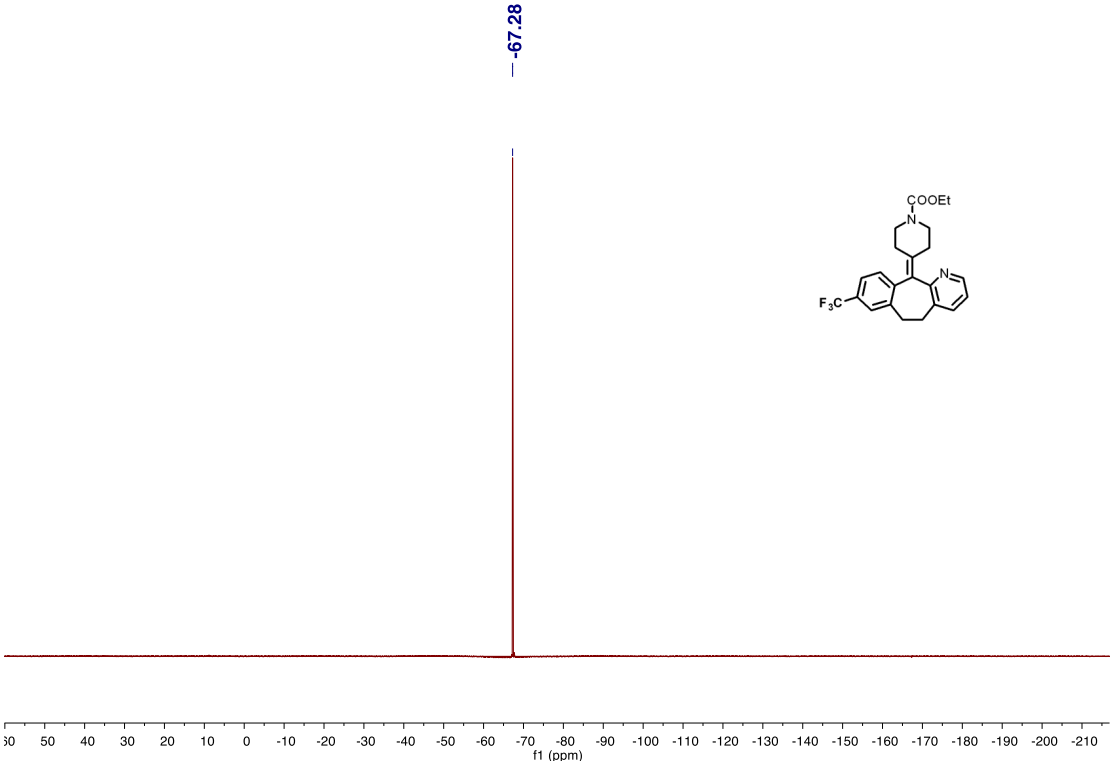
^{13}C NMR spectrum of ethyl-2-[4-(5-trifluoromethylbenzoxazol-2-yloxy)phenoxy]propionate 4q



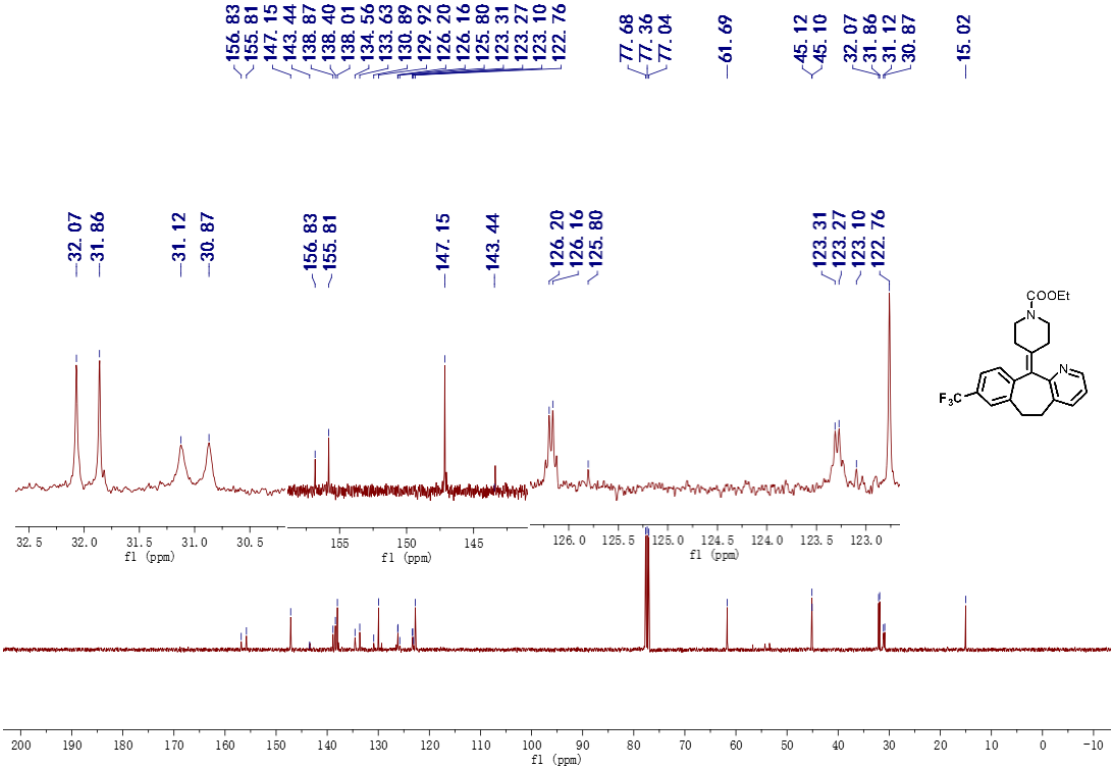
^{1}H NMR spectrum of ethyl-4-[8-(trifluoromethyl)-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene]-1-piperidinecarboxylate 3r



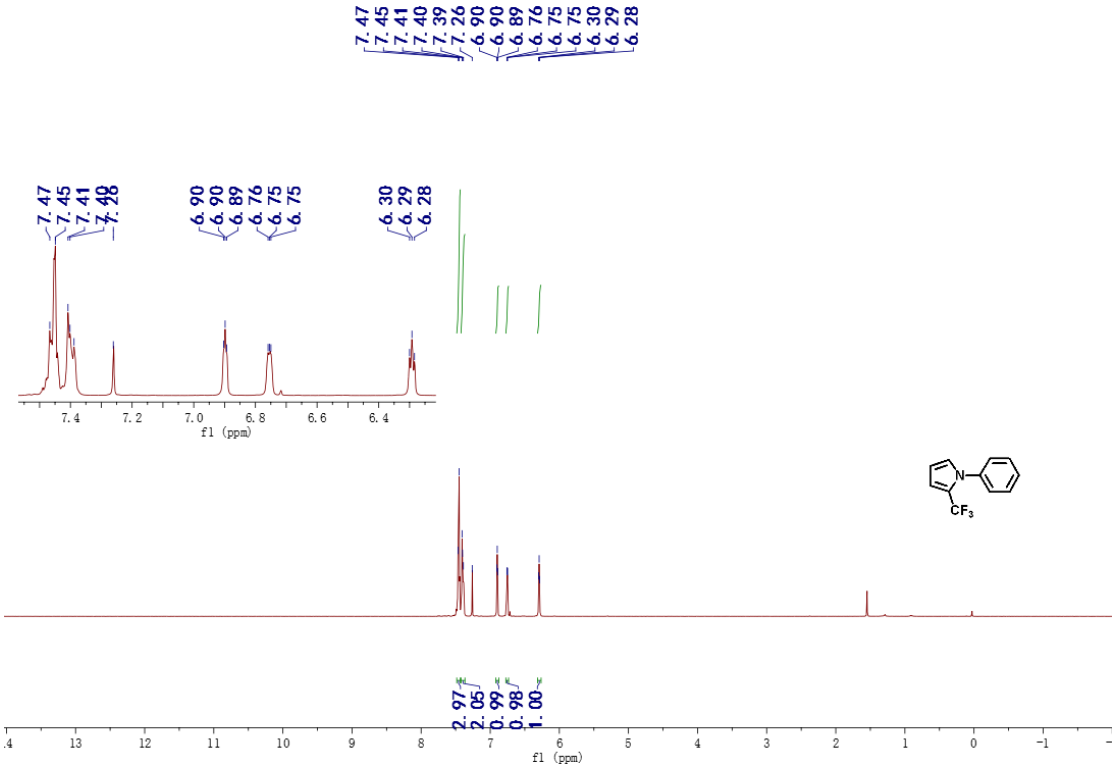
^{19}F NMR spectrum of Ethyl-4-[8-(trifluoromethyl)-5,6-dihydro-11*H*-benzo[5,6] cyclohepta[1,2-*b*]pyridin-11-ylidene]-1-piperidinecarboxylate 3r



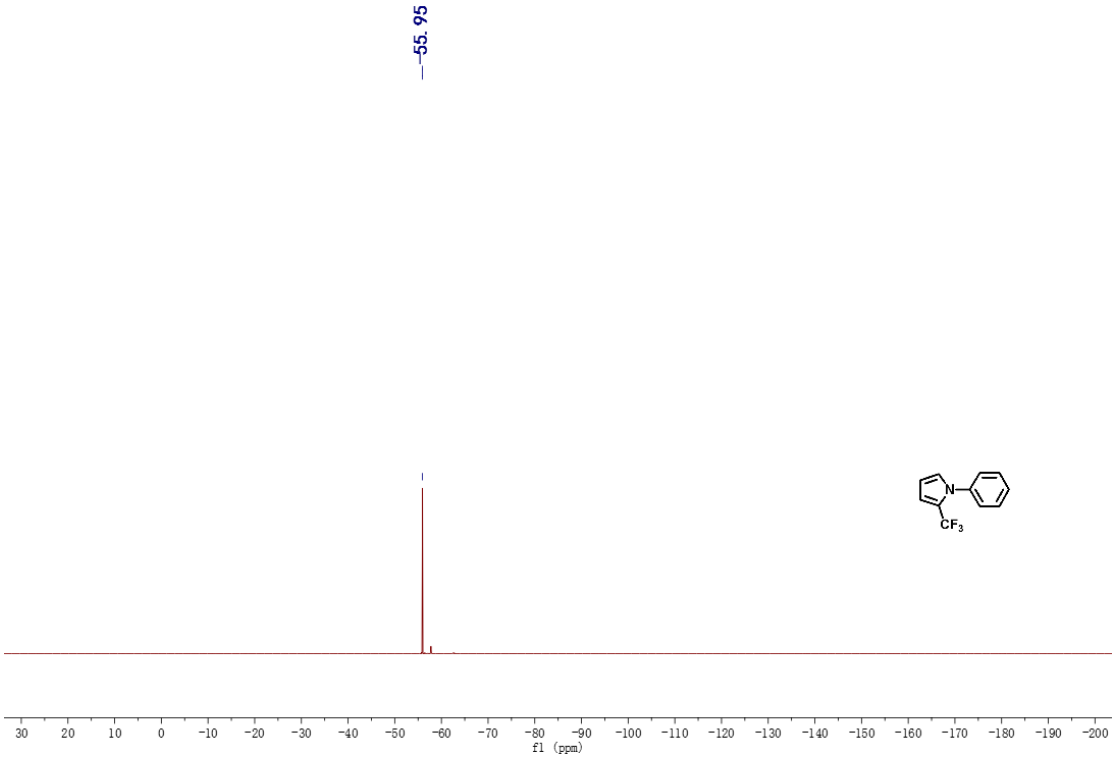
^{13}C NMR spectrum of Ethyl-4-[8-(trifluoromethyl)-5,6-dihydro-11*H*-benzo[5,6] cyclohepta[1,2-*b*]pyridin-11-ylidene]-1-piperidinecarboxylate 3r



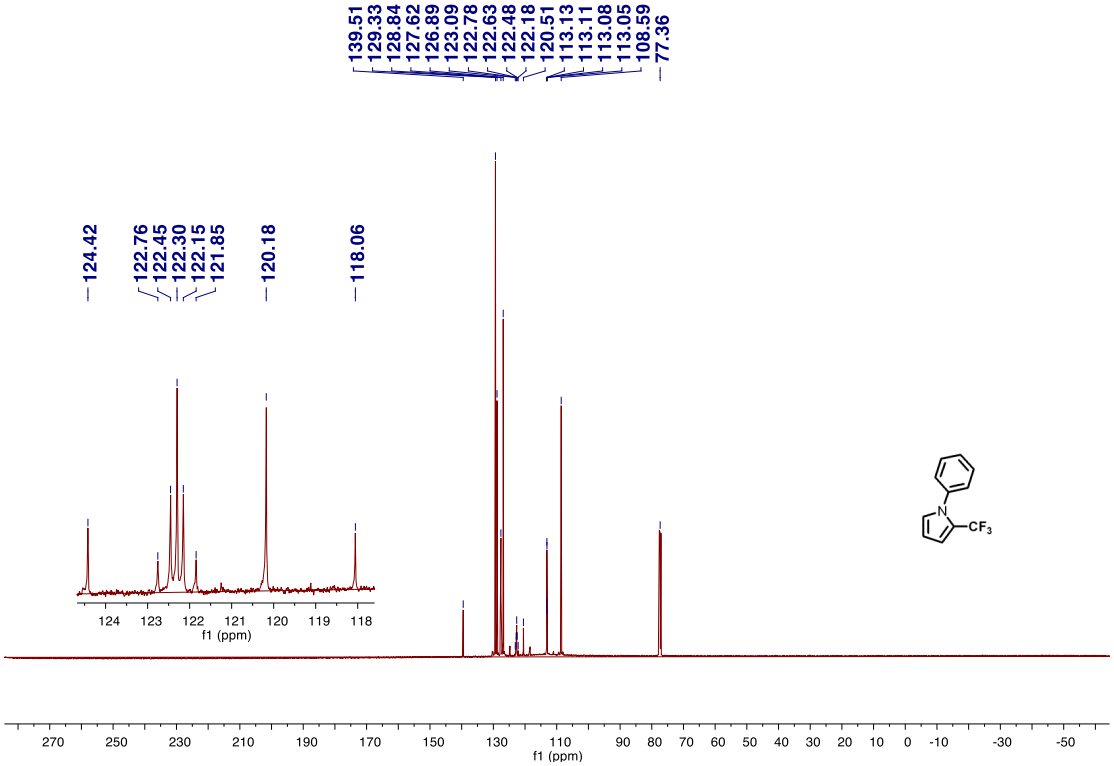
^{1}H NMR spectrum of 1-phenyl-2-(trifluoromethyl)-1*H*-pyrrole 5a



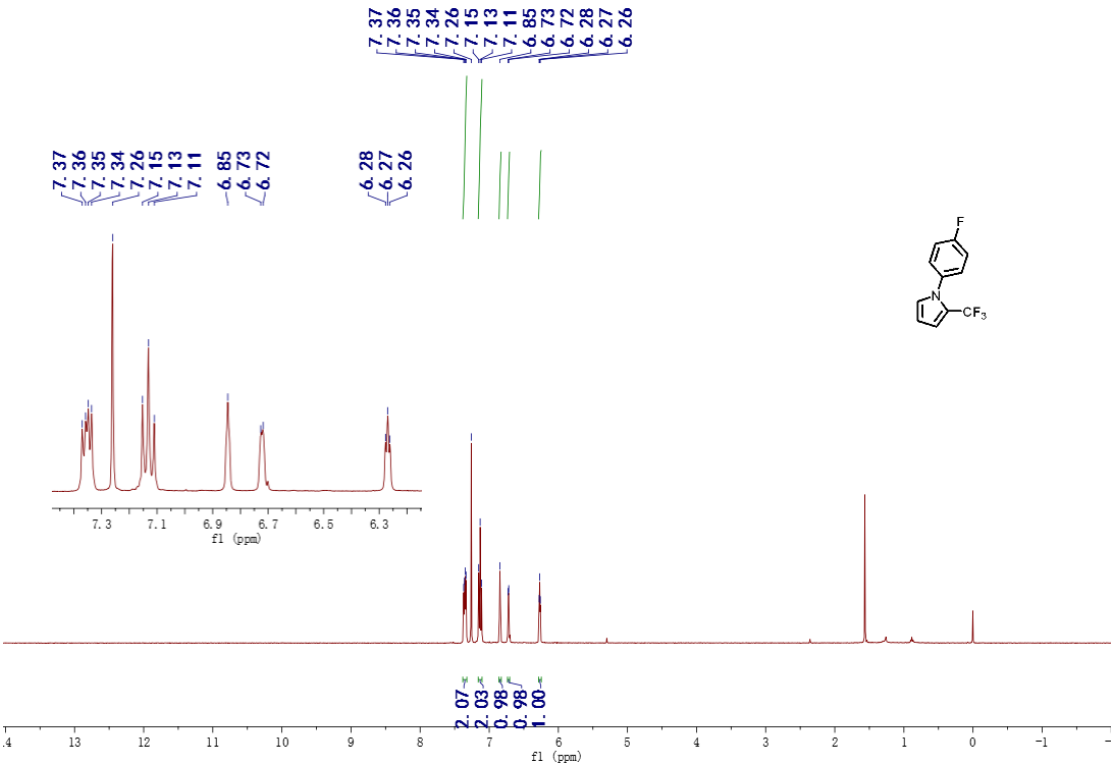
^{19}F NMR spectrum of 1-phenyl-2-(trifluoromethyl)-1*H*-pyrrole 5a



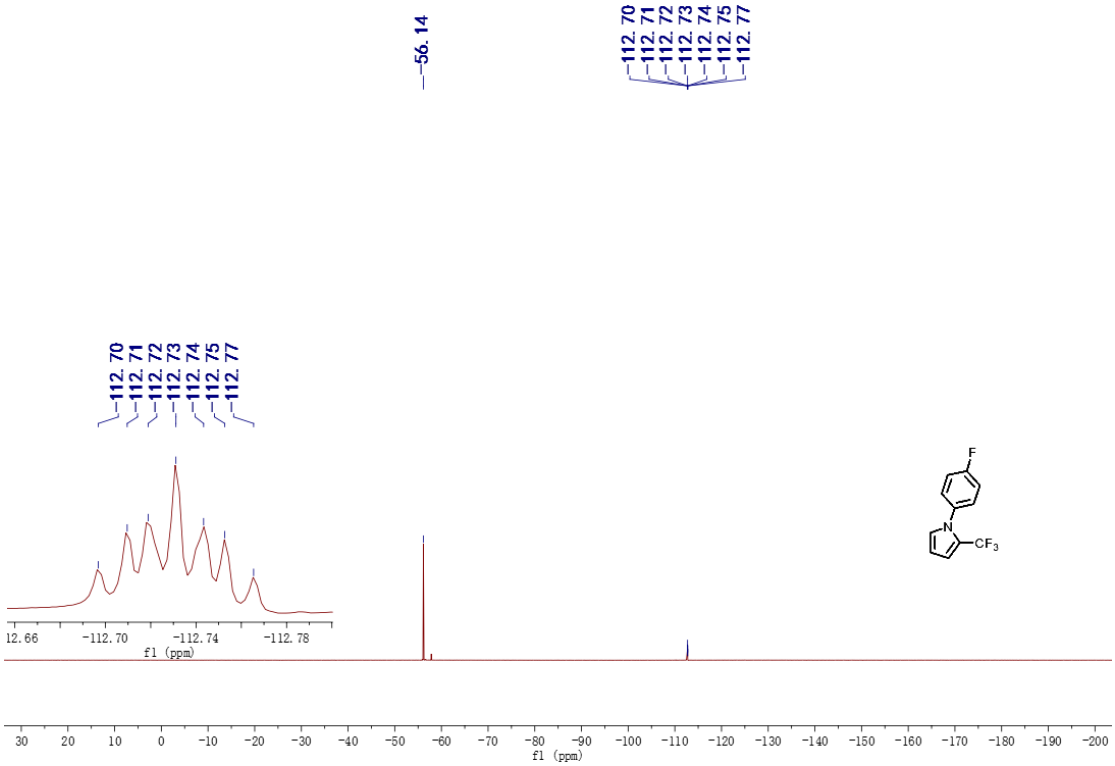
^{13}C NMR spectrum of 1-phenyl-2-(trifluoromethyl)-1*H*-pyrrole 5a



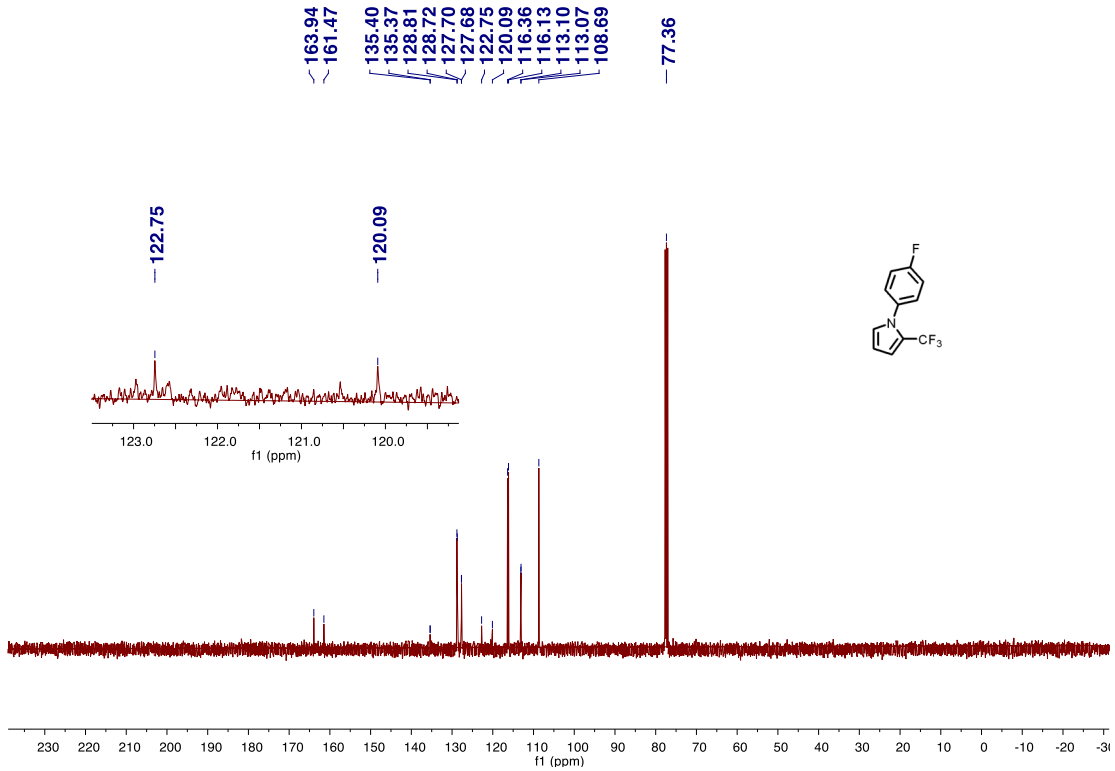
^{1}H NMR spectrum of 1-(4-fluorophenyl)-2-(trifluoromethyl)-1*H*-pyrrole 5b



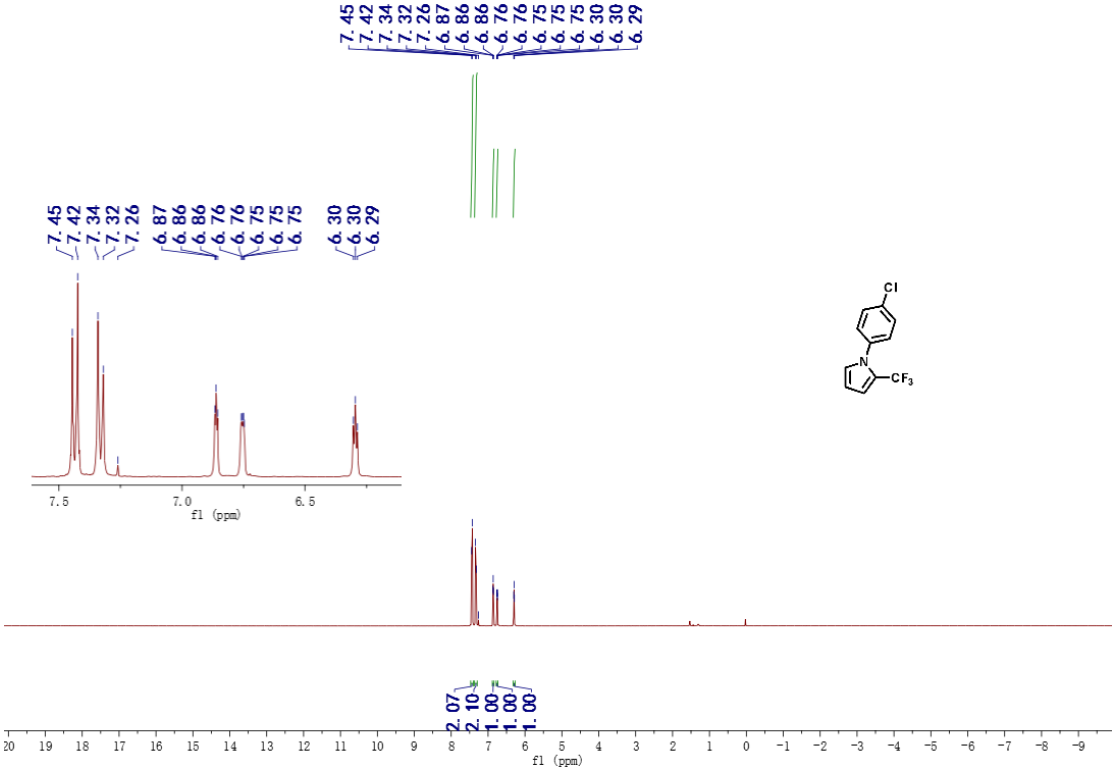
^{19}F NMR spectrum of 1-(4-fluorophenyl)-2-(trifluoromethyl)-1*H*-pyrrole 5b



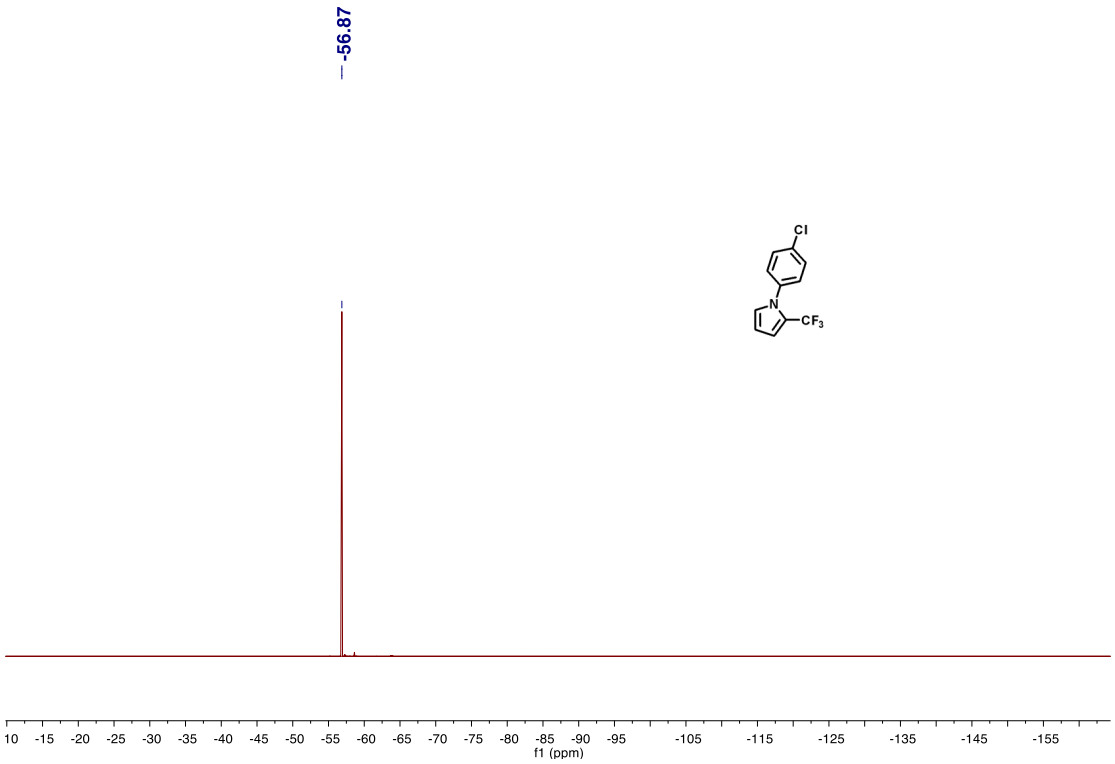
^{13}C NMR spectrum of 1-(4-fluorophenyl)-2-(trifluoromethyl)-1*H*-pyrrole 5b



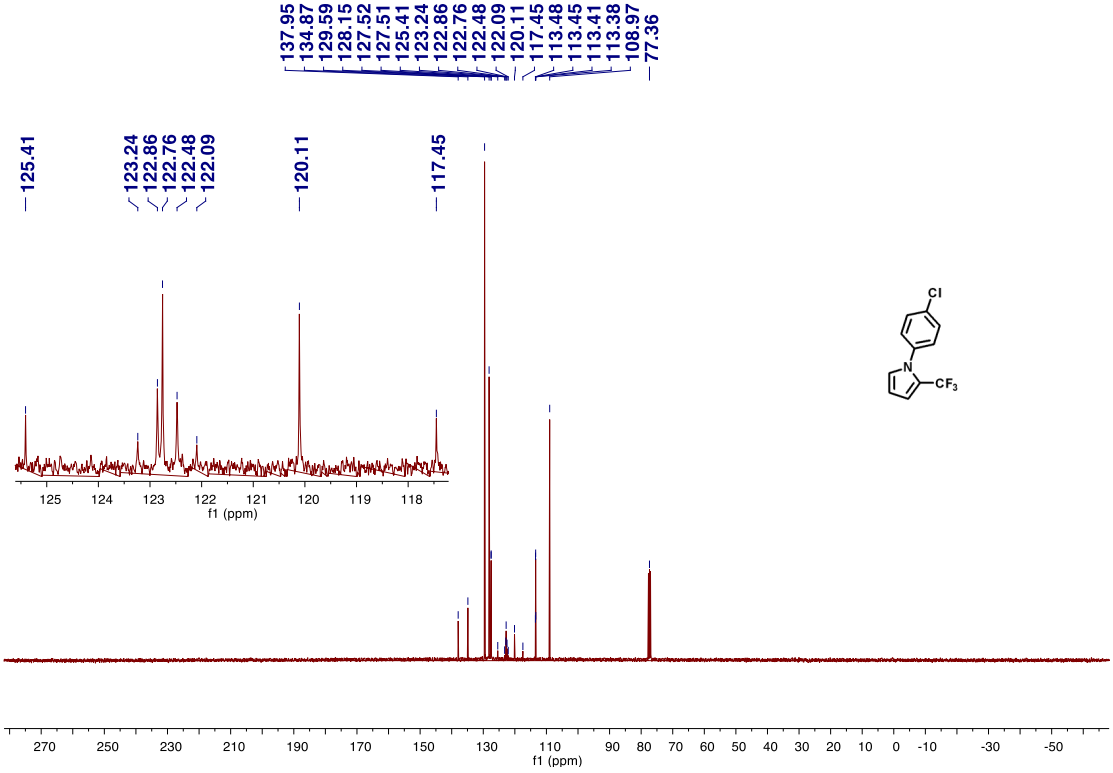
^{1}H NMR spectrum of 2-(4-clorophenyl)-3-(trifluoromethyl)-1*H*-indole 5c



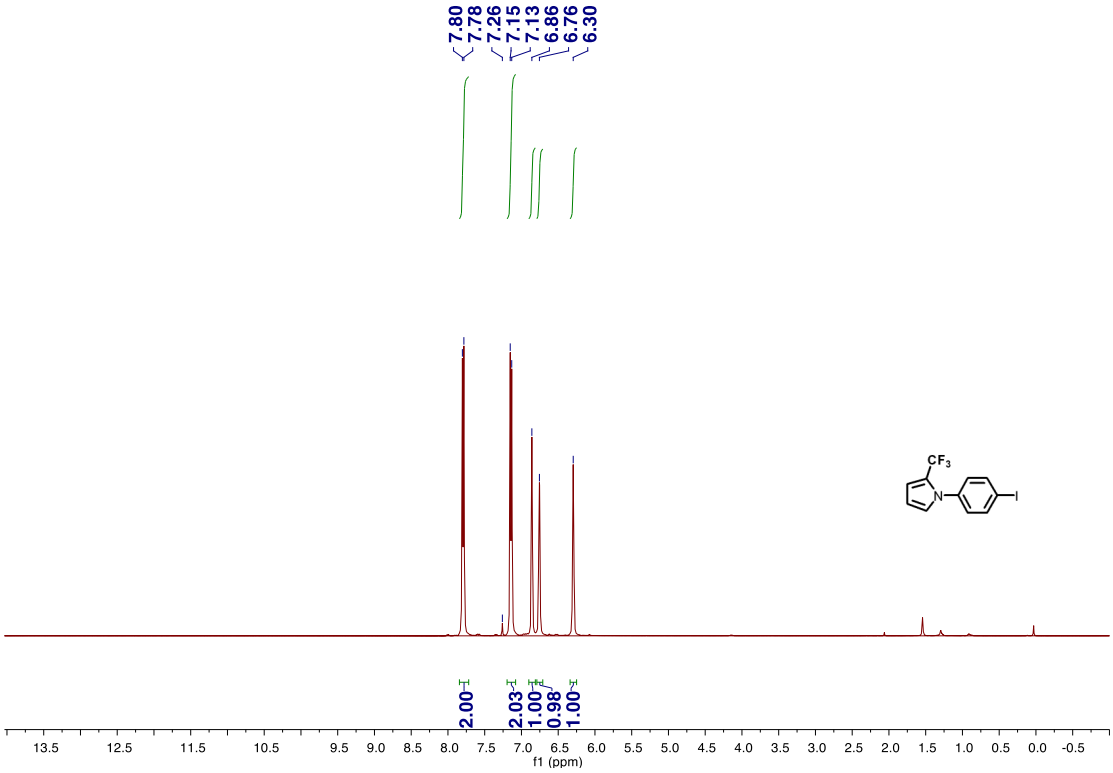
^{19}F NMR spectrum of 2-(4-clorophenyl)-3-(trifluoromethyl)-1H-indole 5c



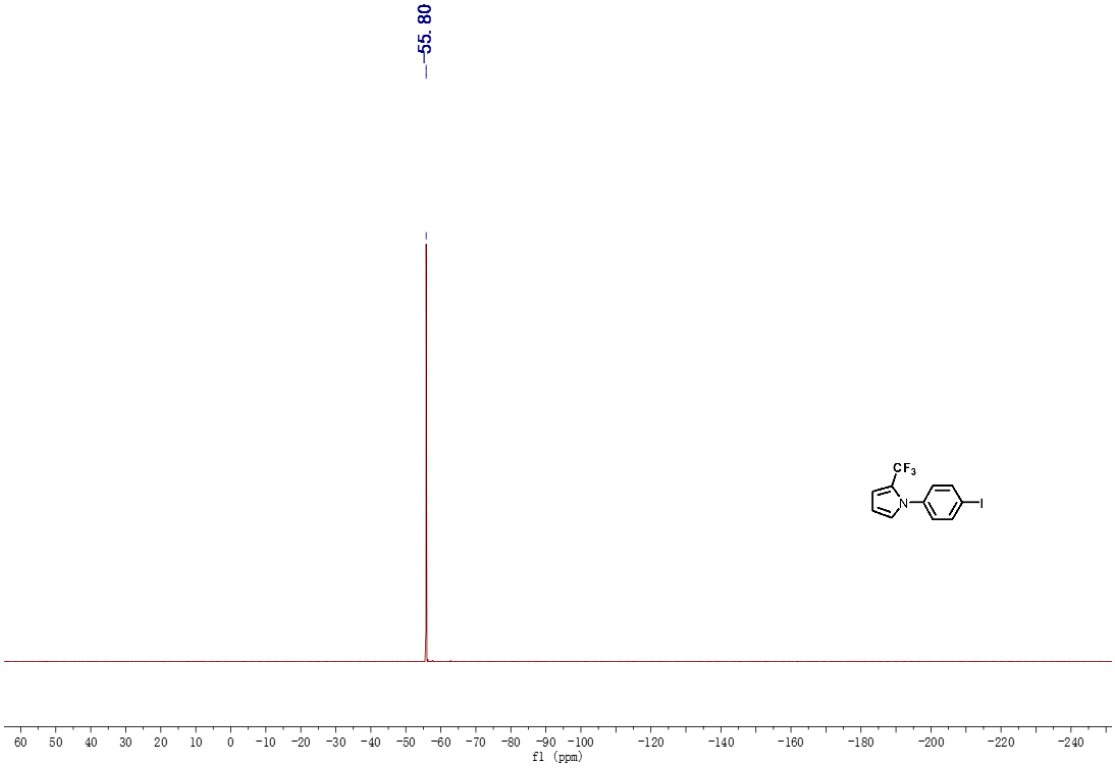
^{13}C NMR spectrum of 2-(4-clorophenyl)-3-(trifluoromethyl)-1*H*-indole 5c



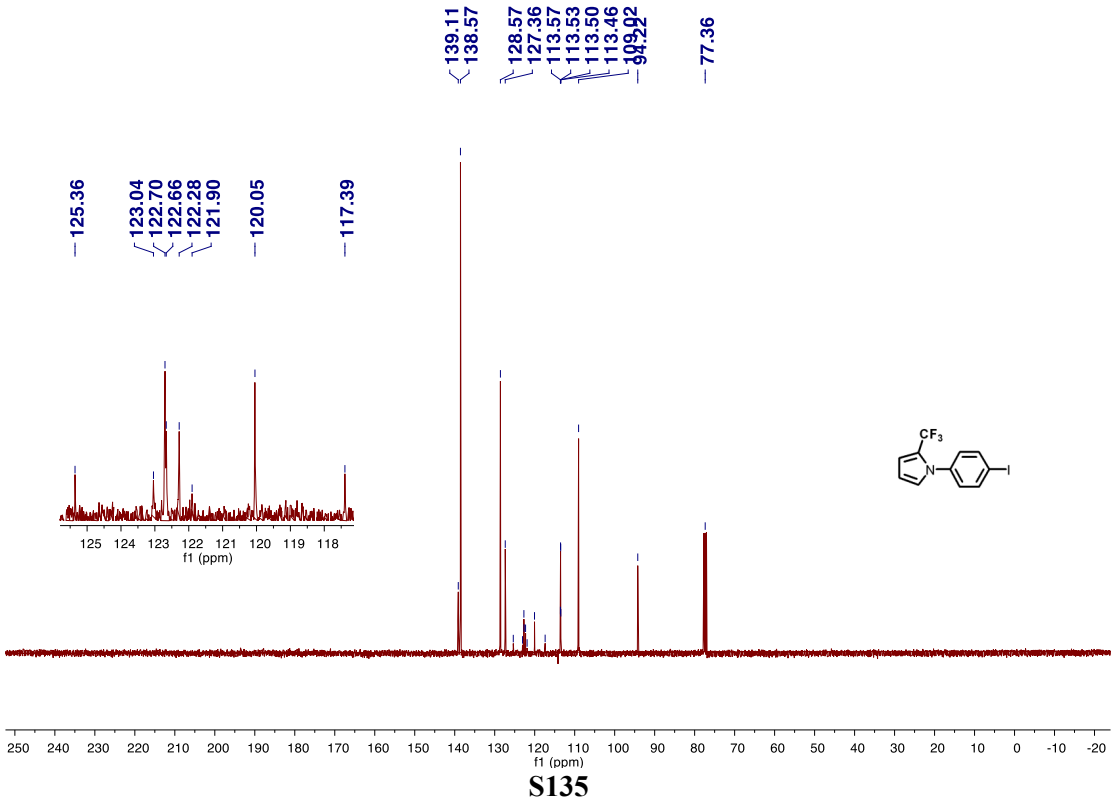
^{1}H NMR spectrum of 1-(4-iodophenyl)-2-(trifluoromethyl)-1*H*-pyrrole 5d



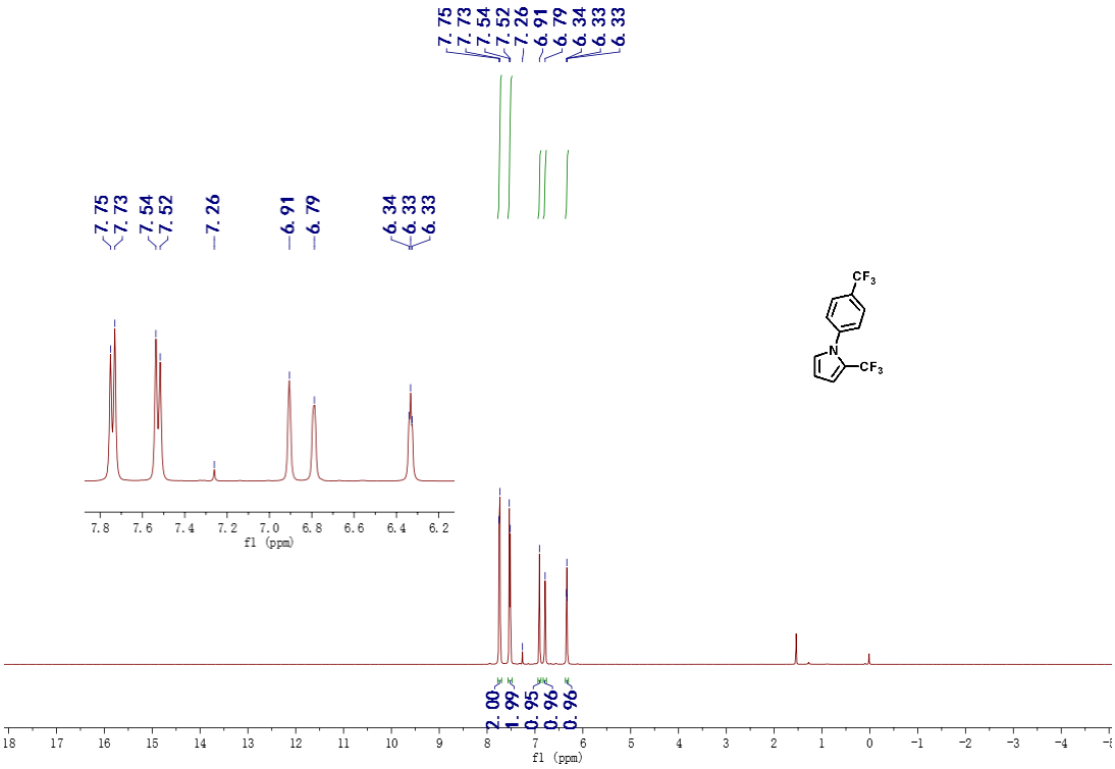
^{19}F NMR spectrum of 1-(4-iodophenyl)-2-(trifluoromethyl)-1*H*-pyrrole 5d



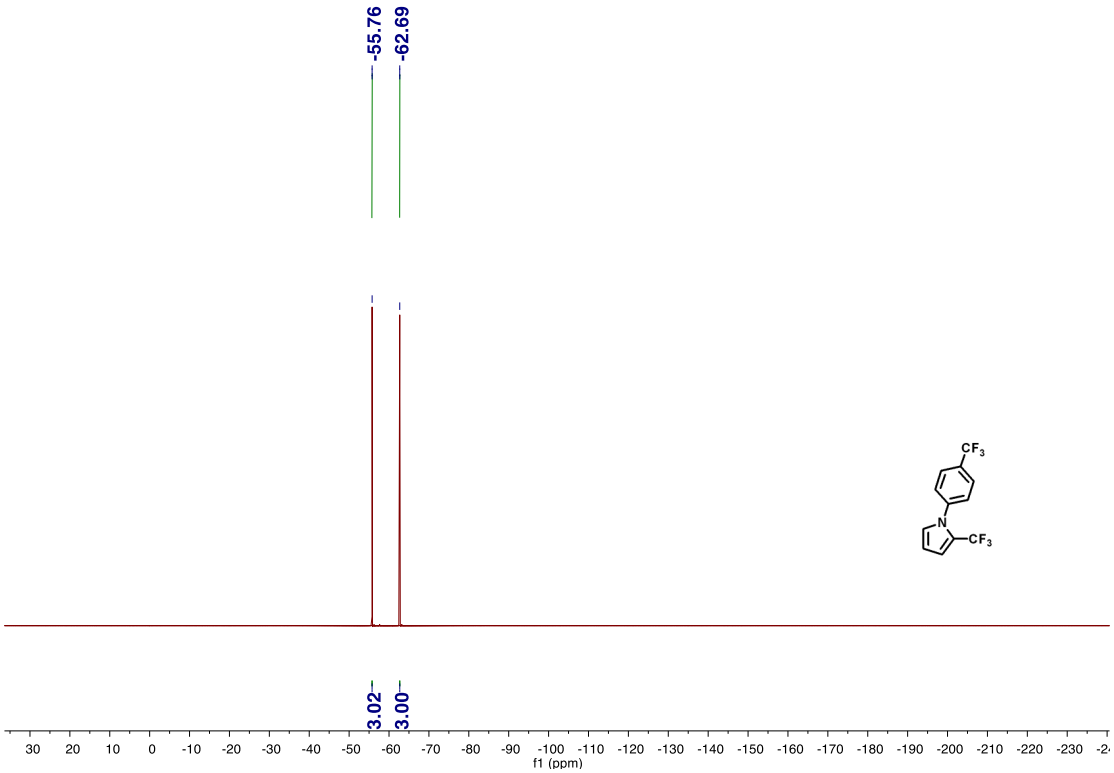
^{13}C NMR spectrum of 1-(4-iodophenyl)-2-(trifluoromethyl)-1*H*-pyrrole 5d



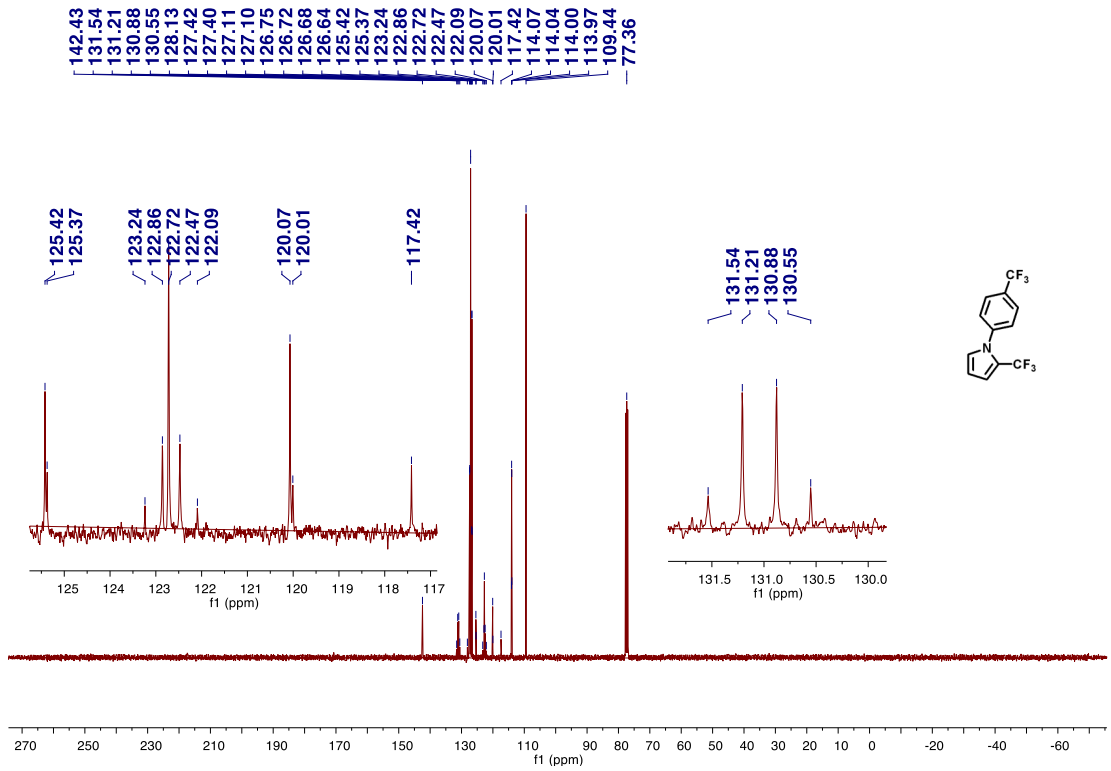
^{1}H NMR spectrum of 1-(4-trifluoromethylphenyl) -2-(trifluoromethyl)-1*H*-pyrrole 5e



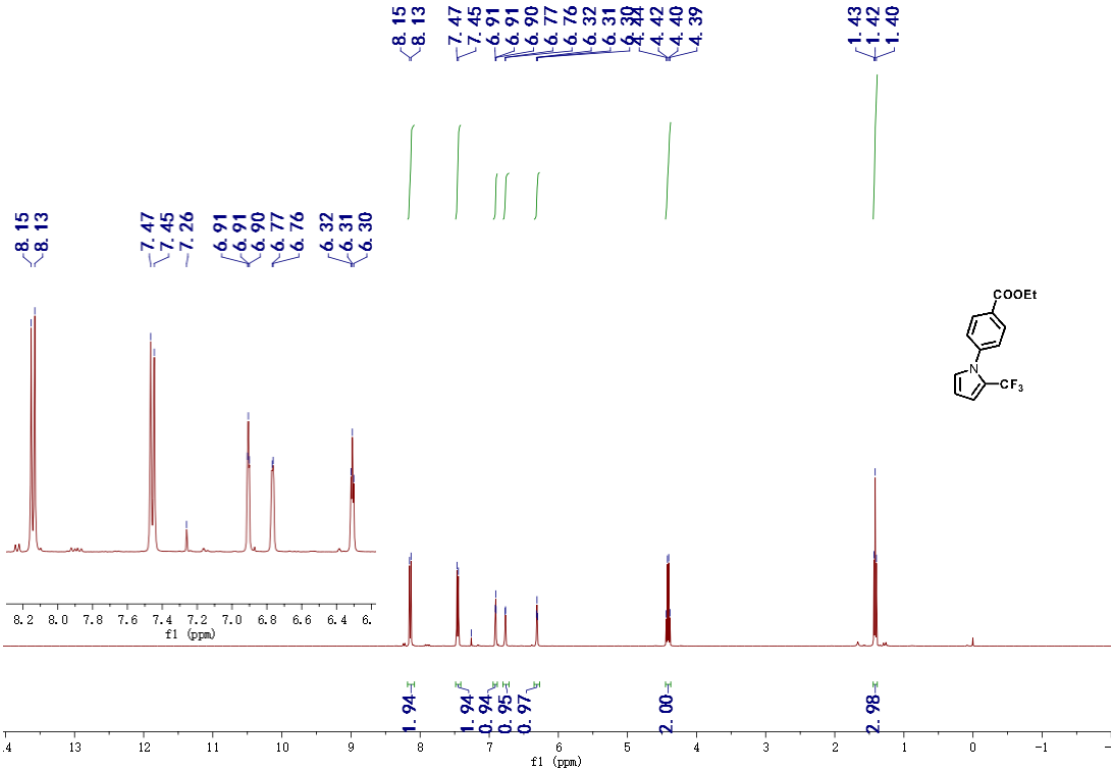
^{19}F NMR spectrum of 1-(4-trifluoromethylphenyl) -2-(trifluoromethyl)-1*H*-pyrrole 5e



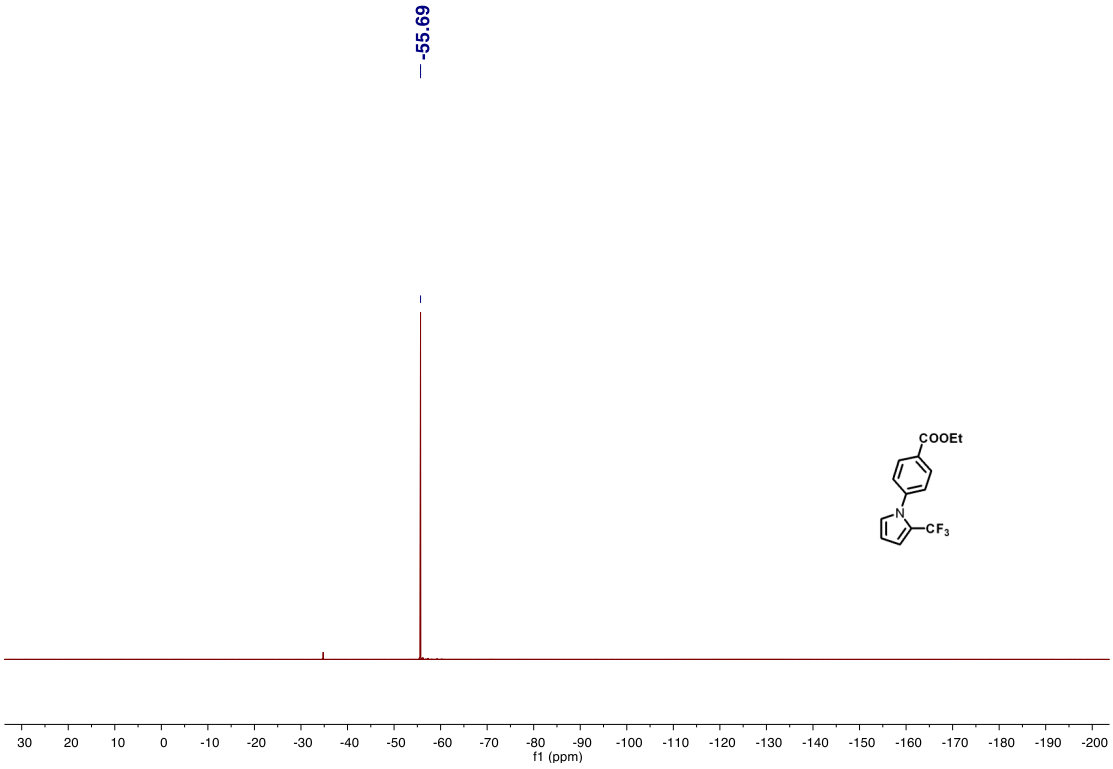
^{13}C NMR spectrum of 1-(4-trifluoromethylphenyl) -2-(trifluoromethyl)-1*H*-pyrrole 5e



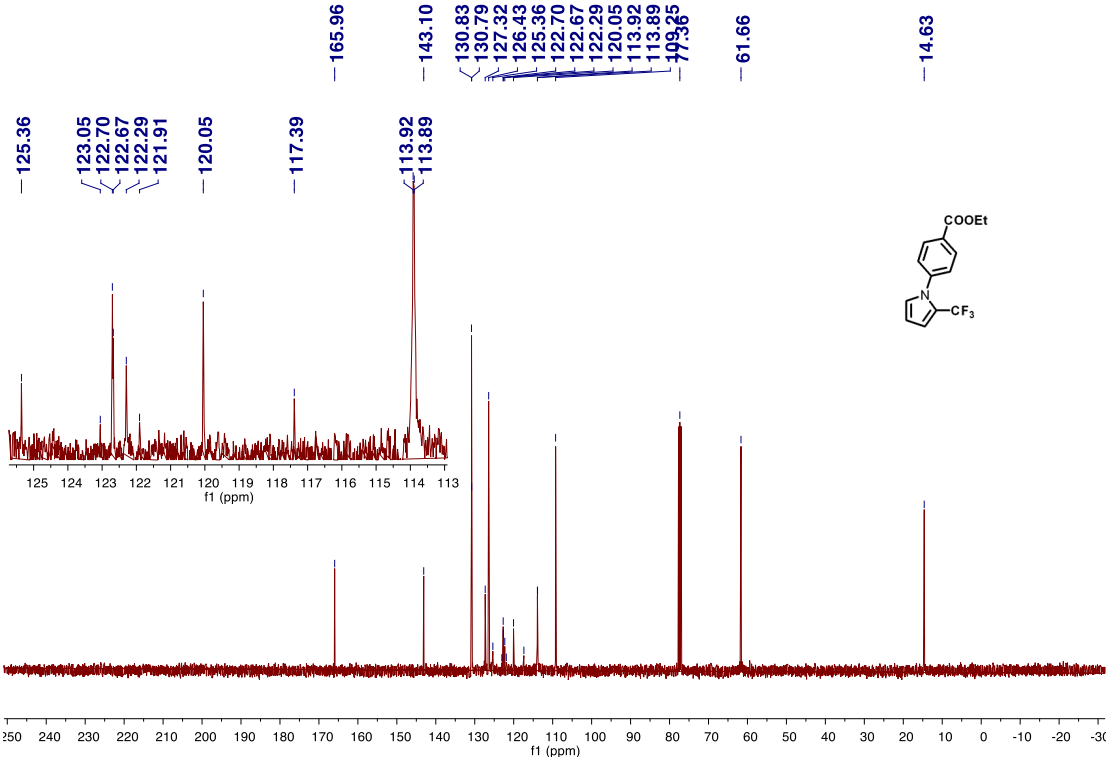
^{1}H NMR spectrum of methyl 4-(2-(trifluoromethyl)-1*H*-pyrrol-1-yl)benzoate 5f



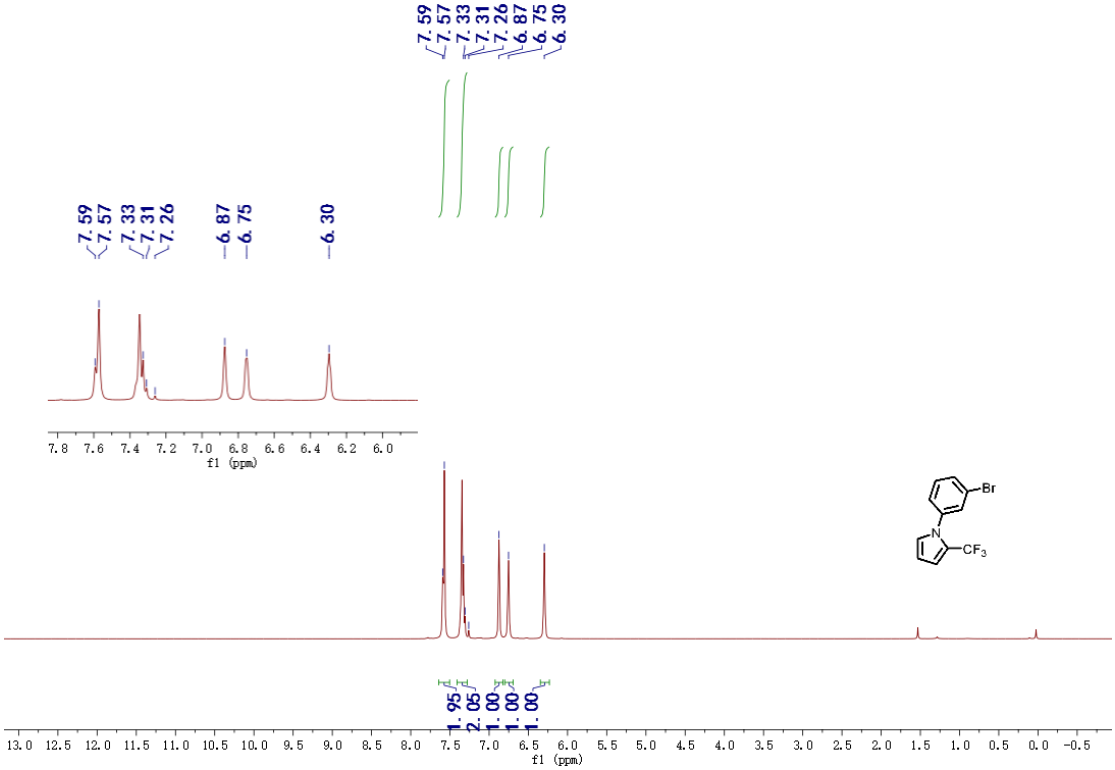
^{19}F NMR spectrum of Methyl 4-(2-(trifluoromethyl)-1*H*-pyrrol-1-yl)benzoate 5f



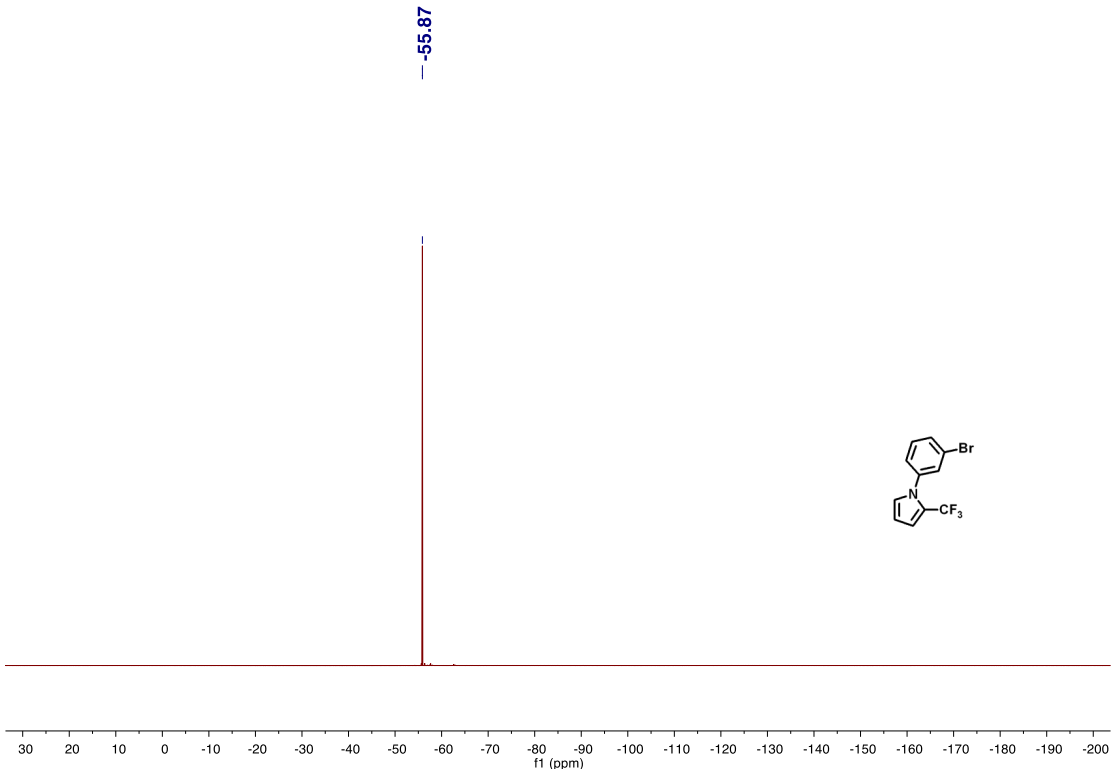
^{13}C NMR spectrum of Methyl 4-(2-(trifluoromethyl)-1*H*-pyrrol-1-yl)benzoate 5f



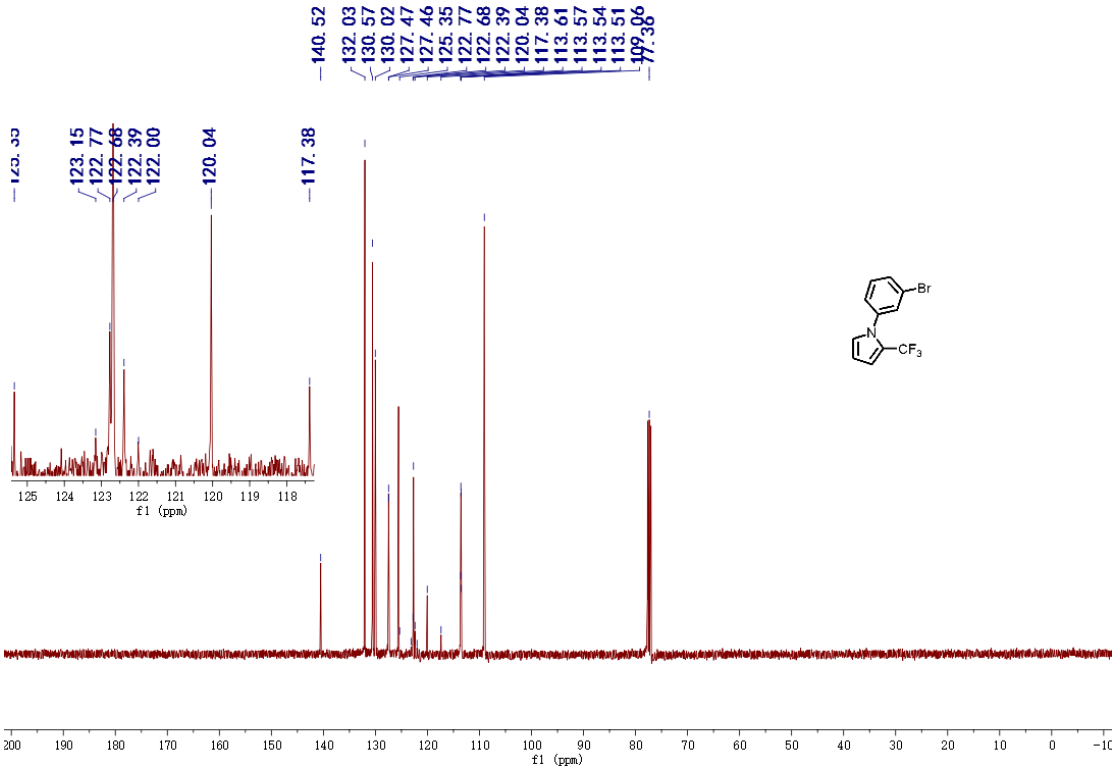
^{1}H NMR spectrum of 1-(3-bromophenyl)-2-(trifluoromethyl)-1*H*-pyrrole 5g



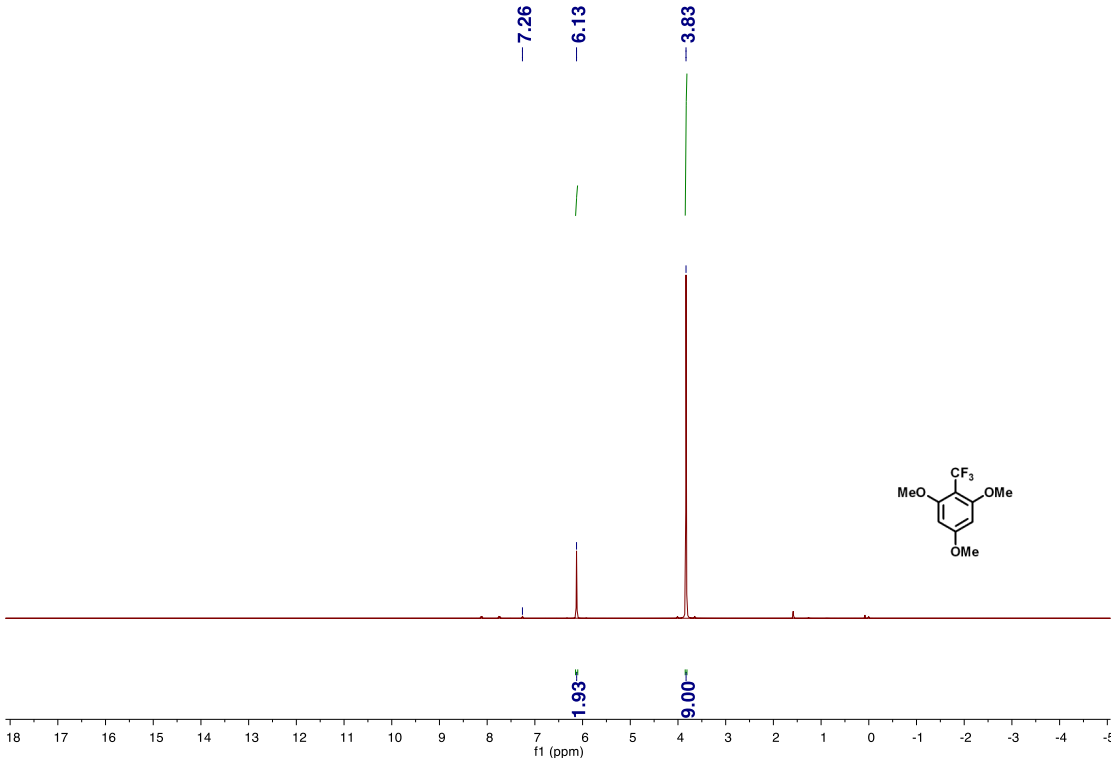
^{19}F NMR spectrum of 1-(3-bromophenyl)-2-(trifluoromethyl)-1*H*-pyrrole 5g



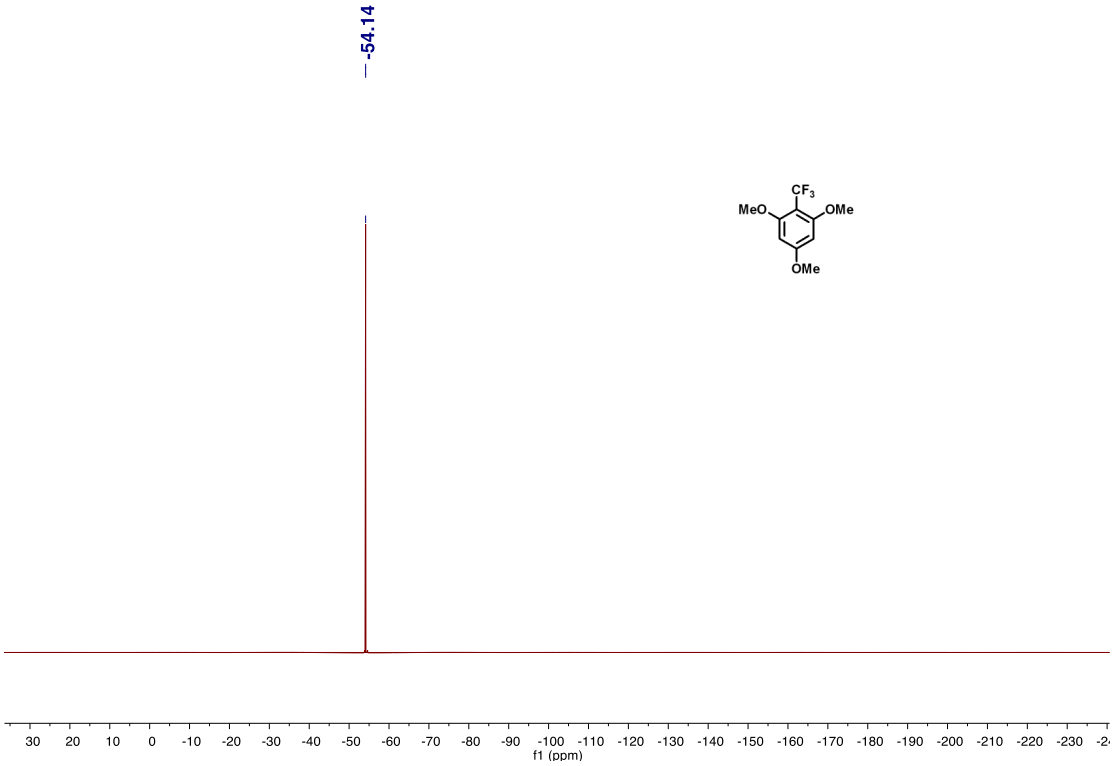
^{13}C NMR spectrum of 1-(3-bromophenyl)-2-(trifluoromethyl)-1*H*-pyrrole 5g



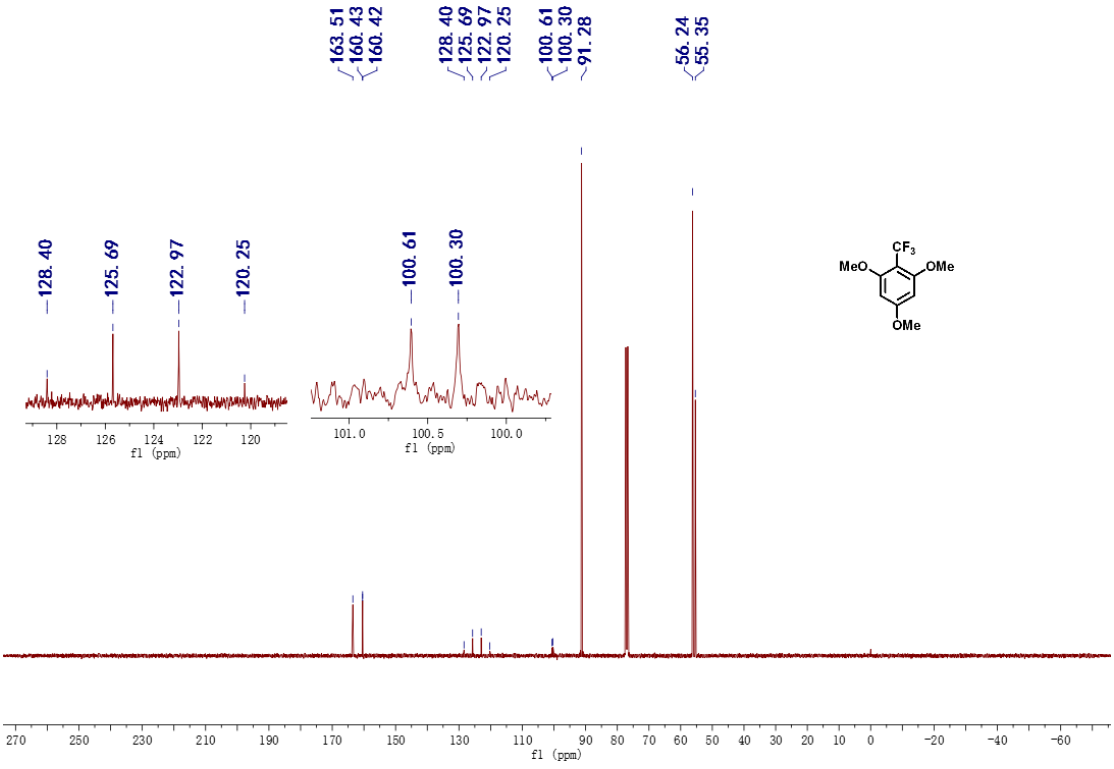
^{1}H NMR spectrum of 1,3,5-trimethoxy-4-(trifluoromethyl)benzene 5h



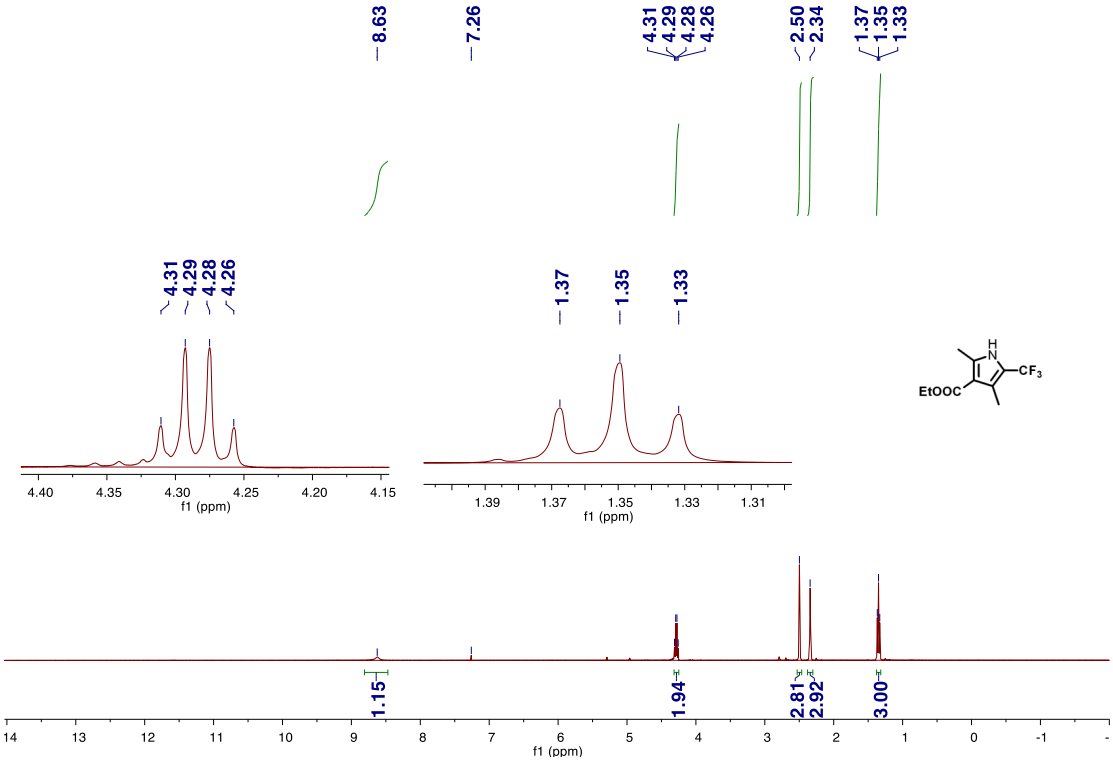
^{19}F NMR spectrum of 1,3,5-trimethoxy-4-(trifluoromethyl)benzene 5h



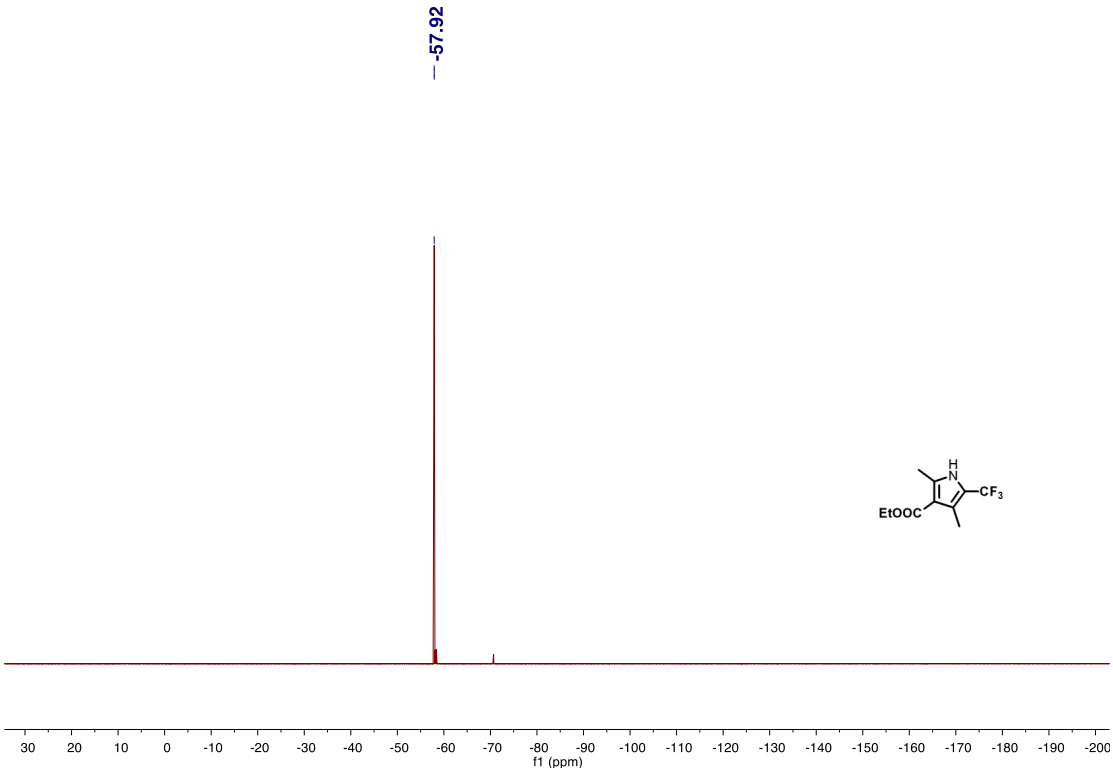
^{13}C NMR spectrum of 1,3,5-trimethoxy-4-(trifluoromethyl)benzene 5h



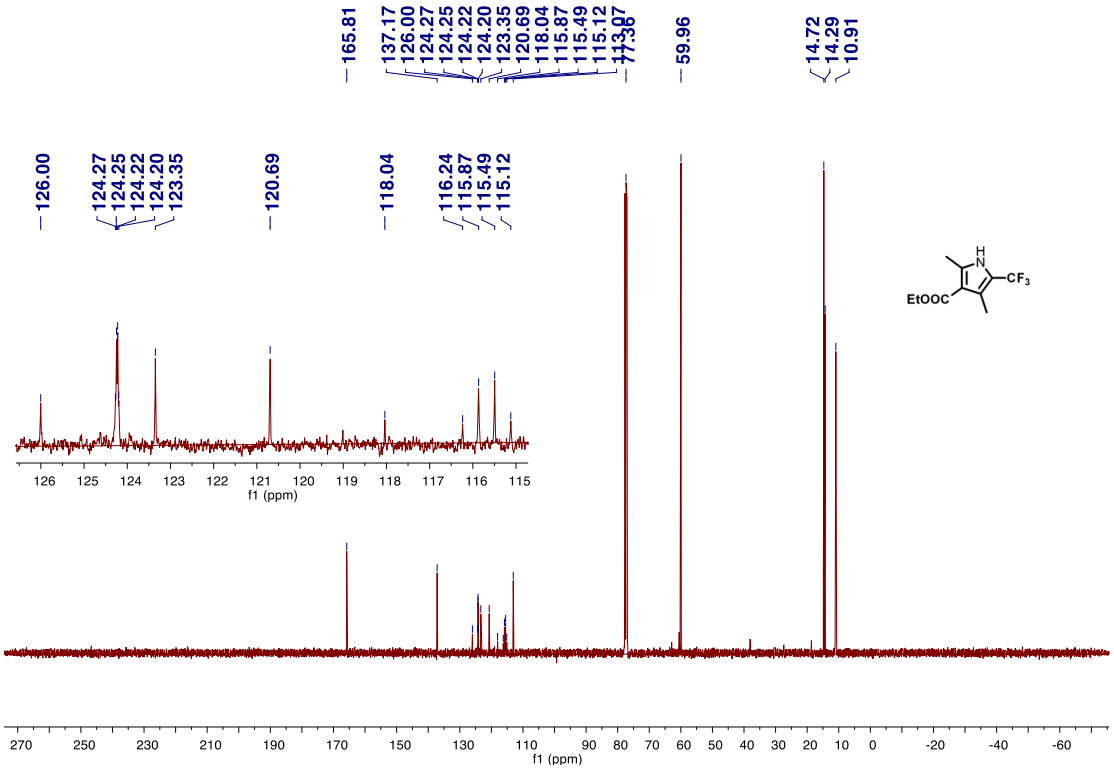
^{1}H NMR spectrum of ethyl 2,4-dimethyl-5-(trifluoromethyl)-1*H*-pyrrole-3-carboxylate 5i



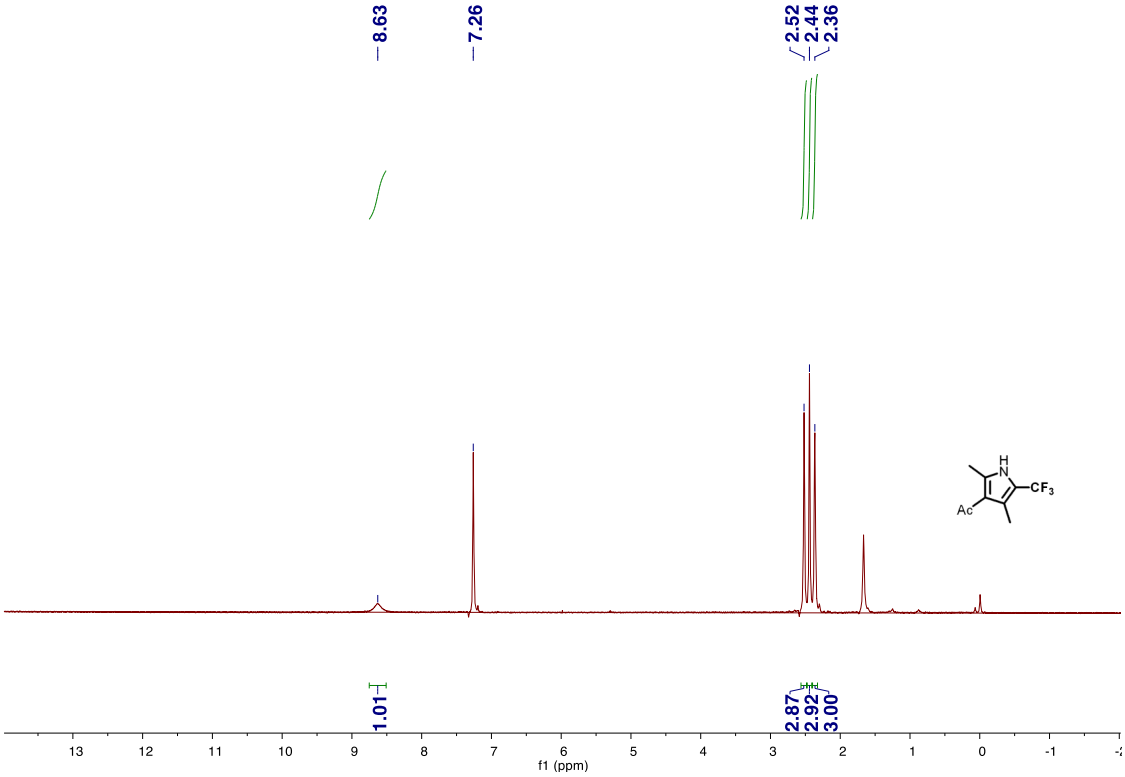
^{19}F NMR spectrum of ethyl 2,4-dimethyl-5-(trifluoromethyl)-1*H*-pyrrole-3-carboxylate 5i



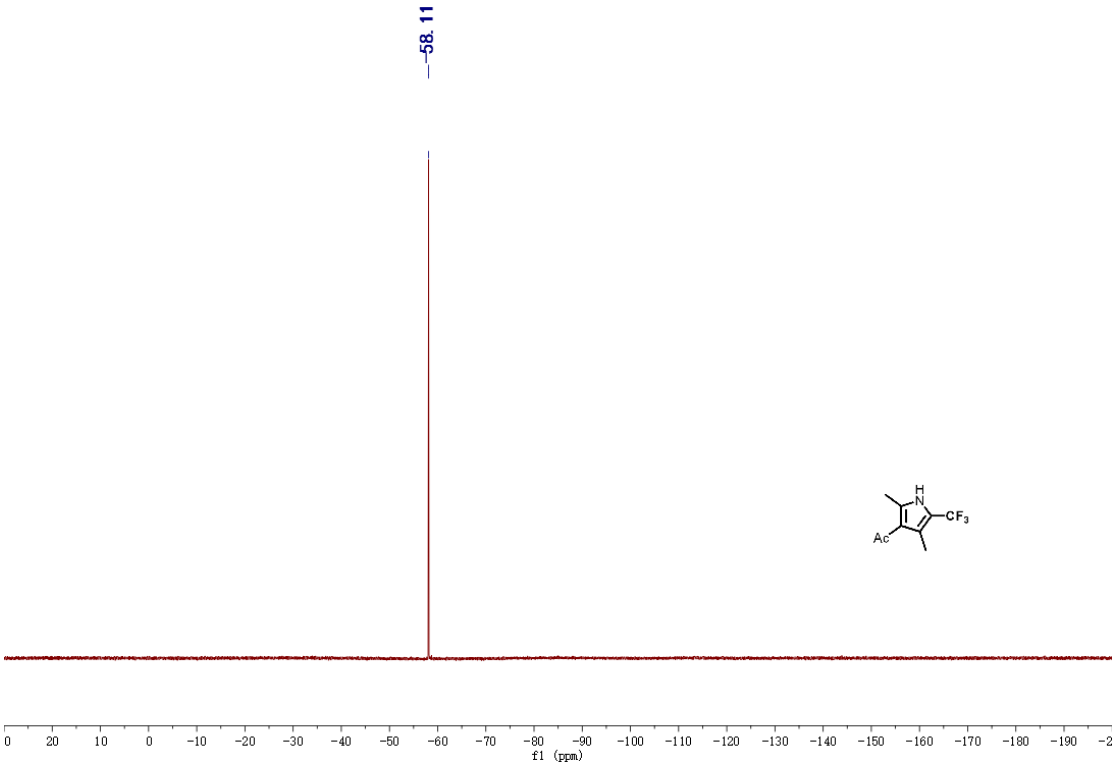
^{13}C NMR spectrum of ethyl 2,4-dimethyl-5-(trifluoromethyl)-1*H*-pyrrole-3-carboxylate 5i



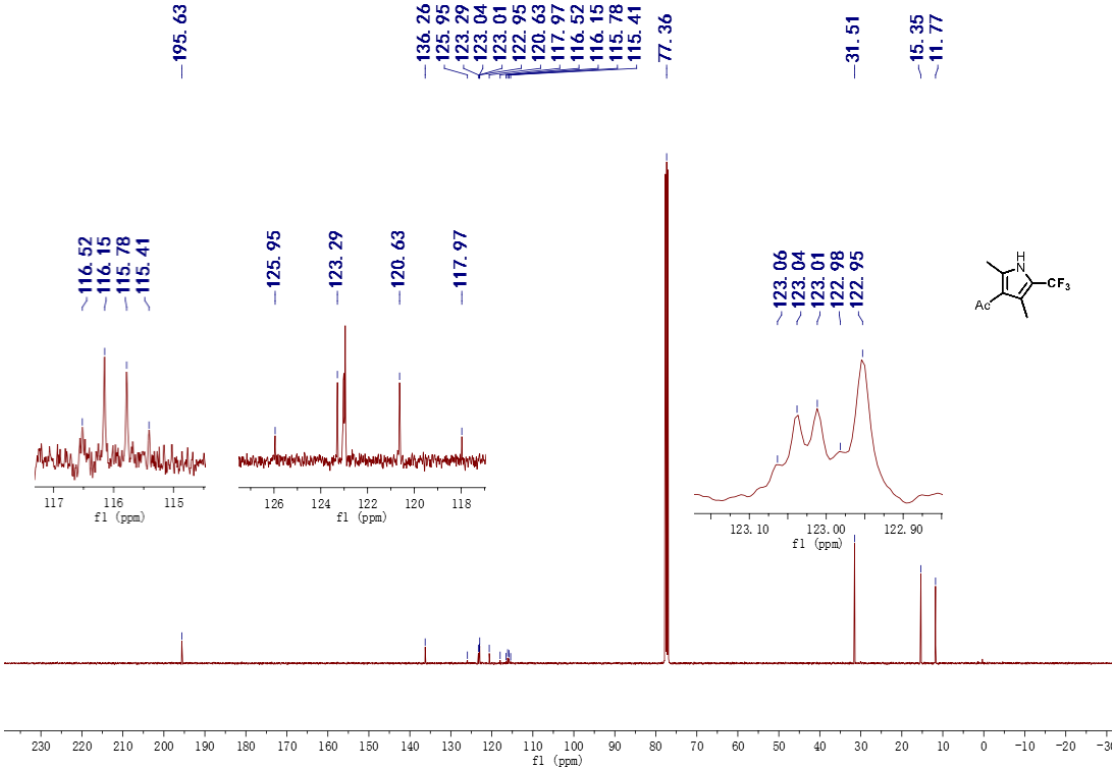
^{1}H NMR spectrum of 1-(2,4-Dimethyl-5-(trifluoromethyl)-1*H*-pyrrol-3-yl)ethanone 5j



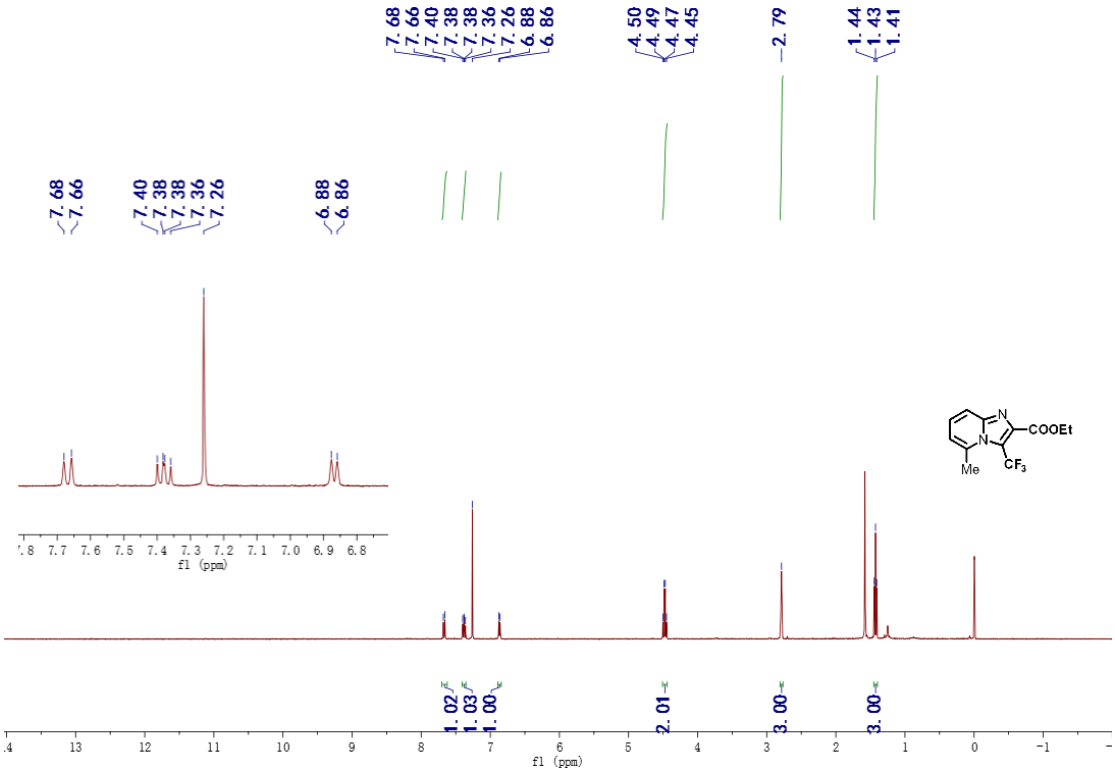
^{19}F NMR spectrum of 1-(2,4-Dimethyl-5-(trifluoromethyl)-1*H*-pyrrol-3-yl)ethanone 5j



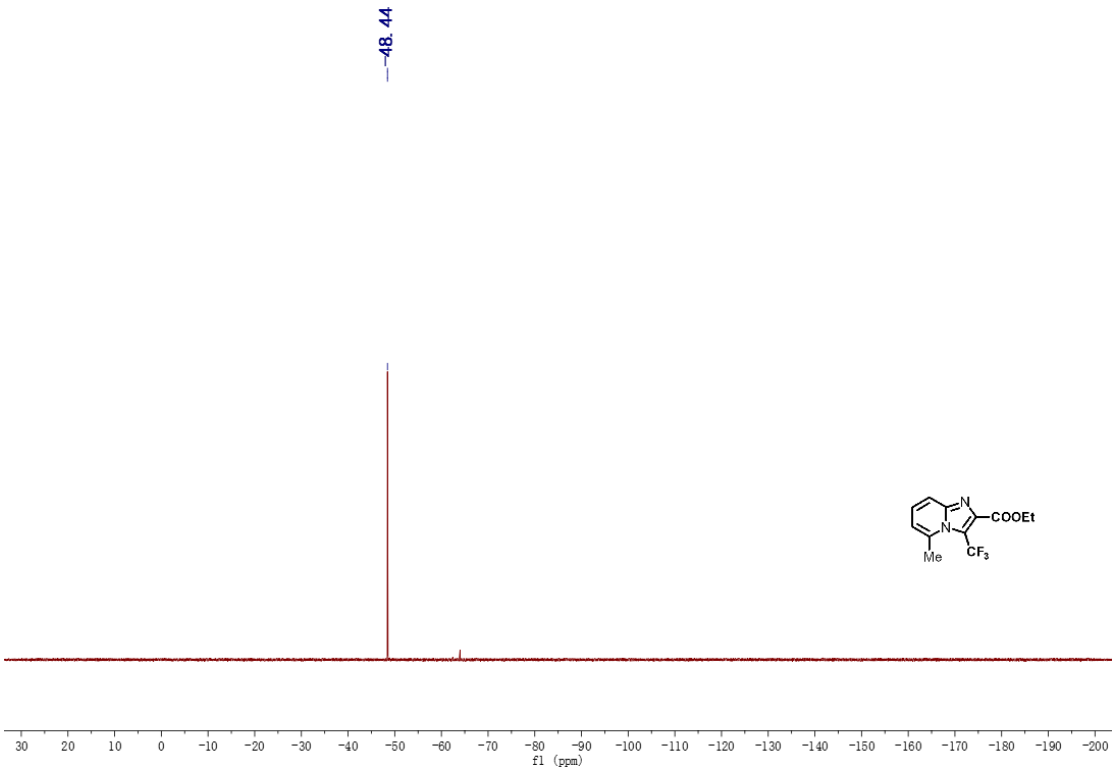
^{13}C NMR spectrum of 1-(2,4-Dimethyl-5-(trifluoromethyl)-1*H*-pyrrol-3-yl)ethanone 5j



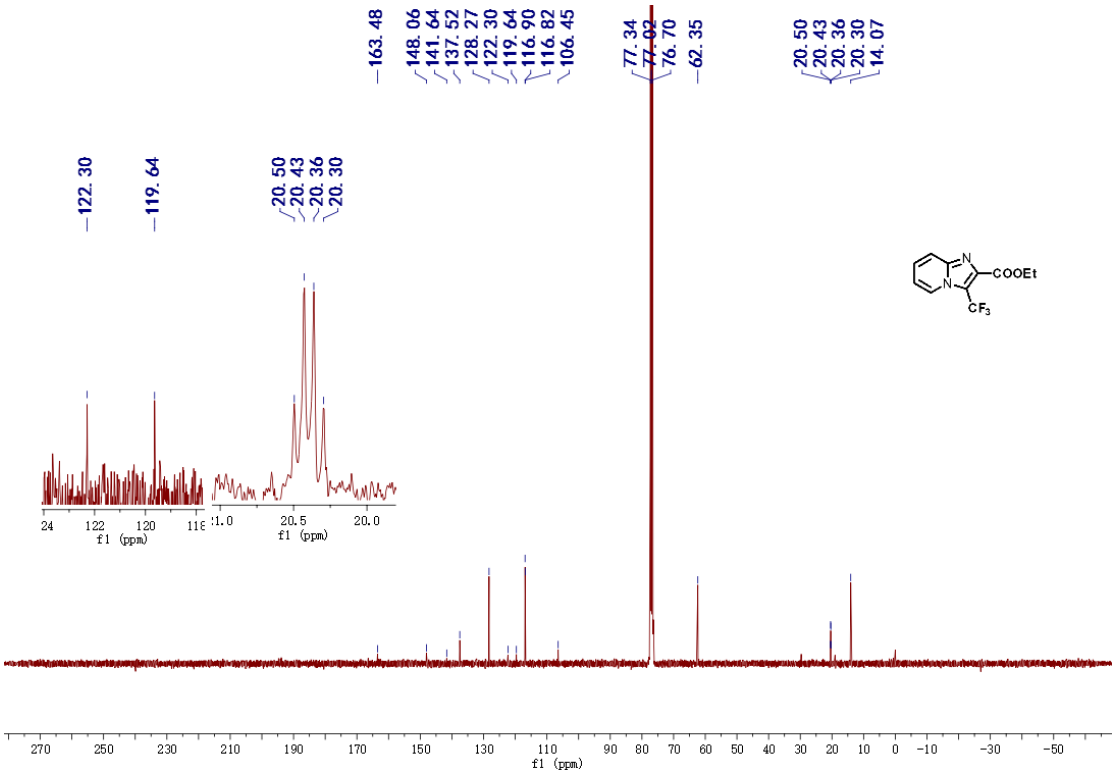
^{1}H NMR spectrum of ethyl-5-methyl-3-(trifluoromethyl)imidazo[1.2-a]pyridine-2-carboxylate 5k



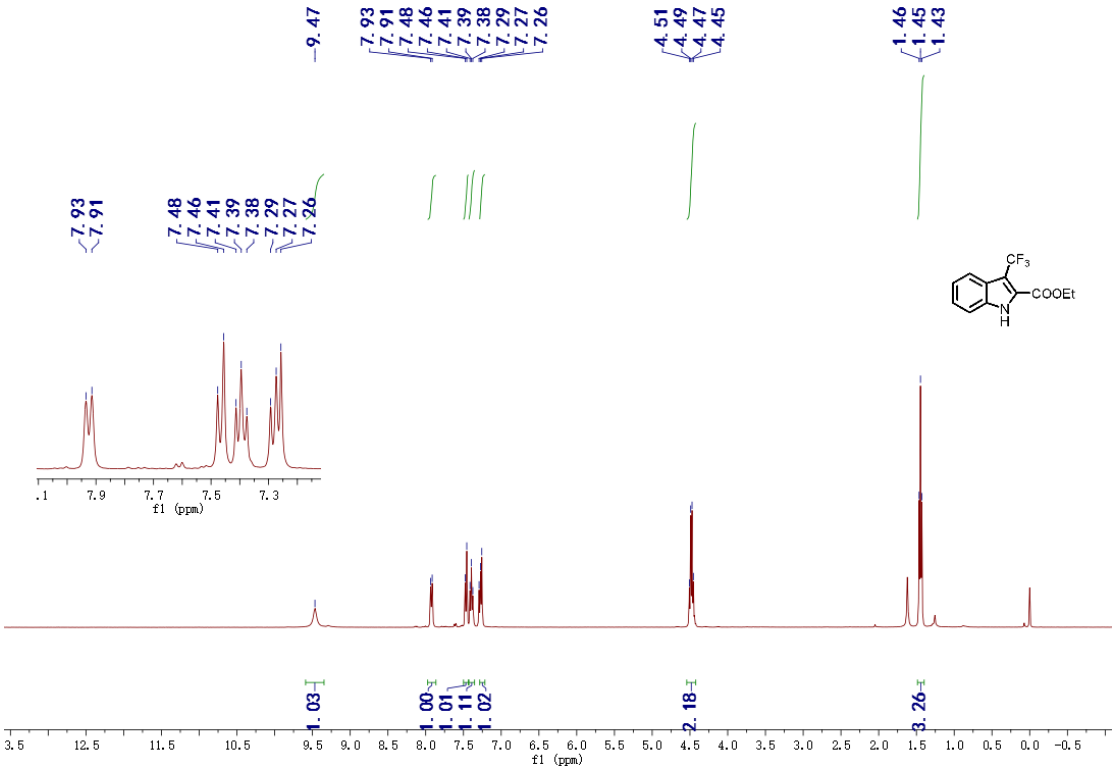
^{19}F NMR spectrum of ethyl-5-methyl-3-(trifluoromethyl)imidazo[1.2-a]pyridine-2-carboxylate 5k



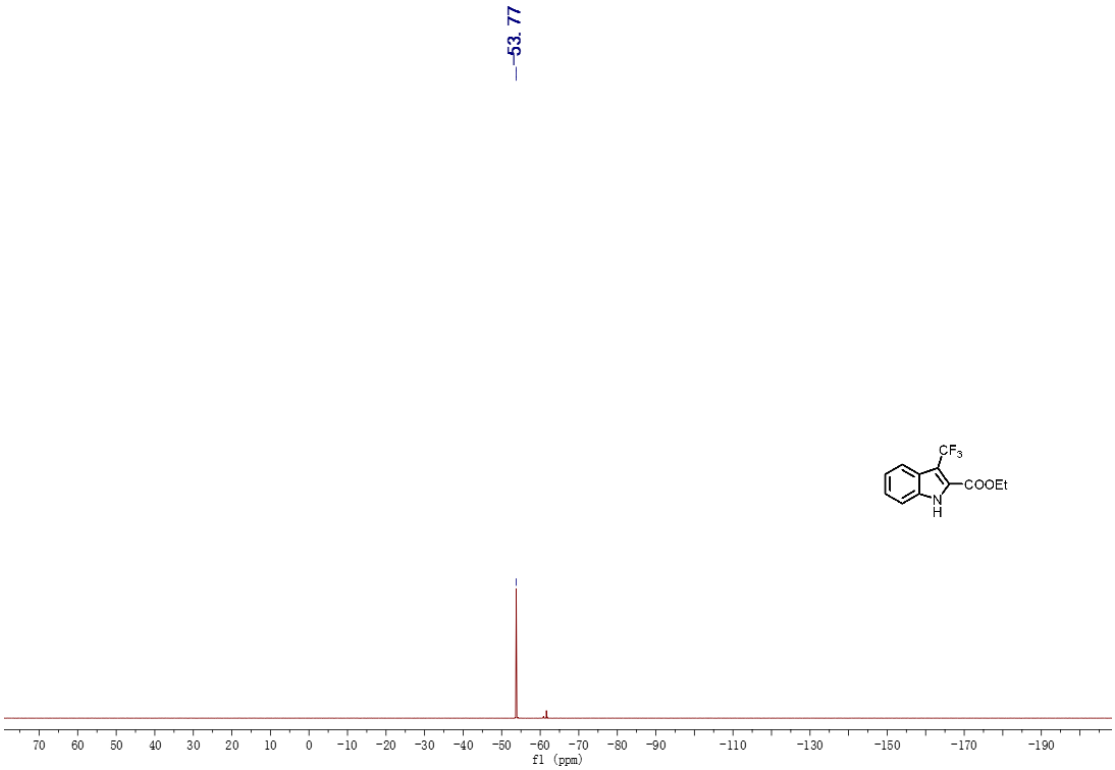
^{13}C NMR spectrum of ethyl-5-methyl-3-(trifluoromethyl)imidazo[1.2-a]pyridine-2-carboxylate 5k



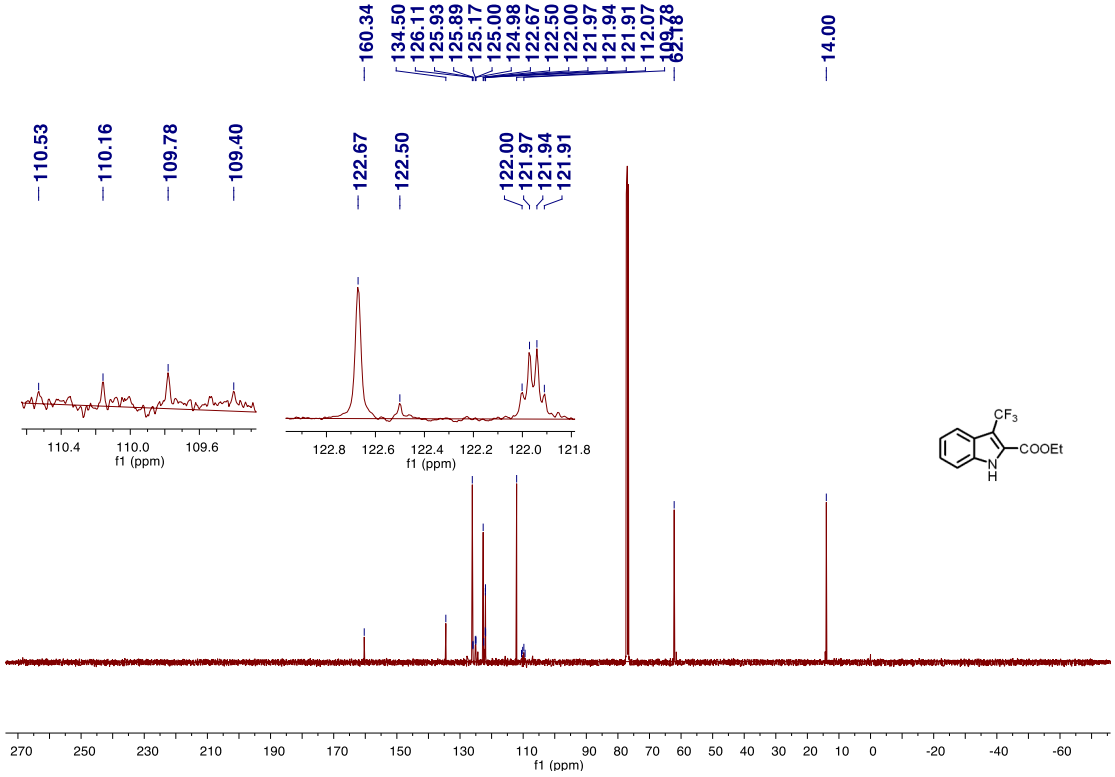
^{1}H NMR spectrum of ethyl 3-(trifluoromethyl)-1*H*-indole-2-carboxylate 5l



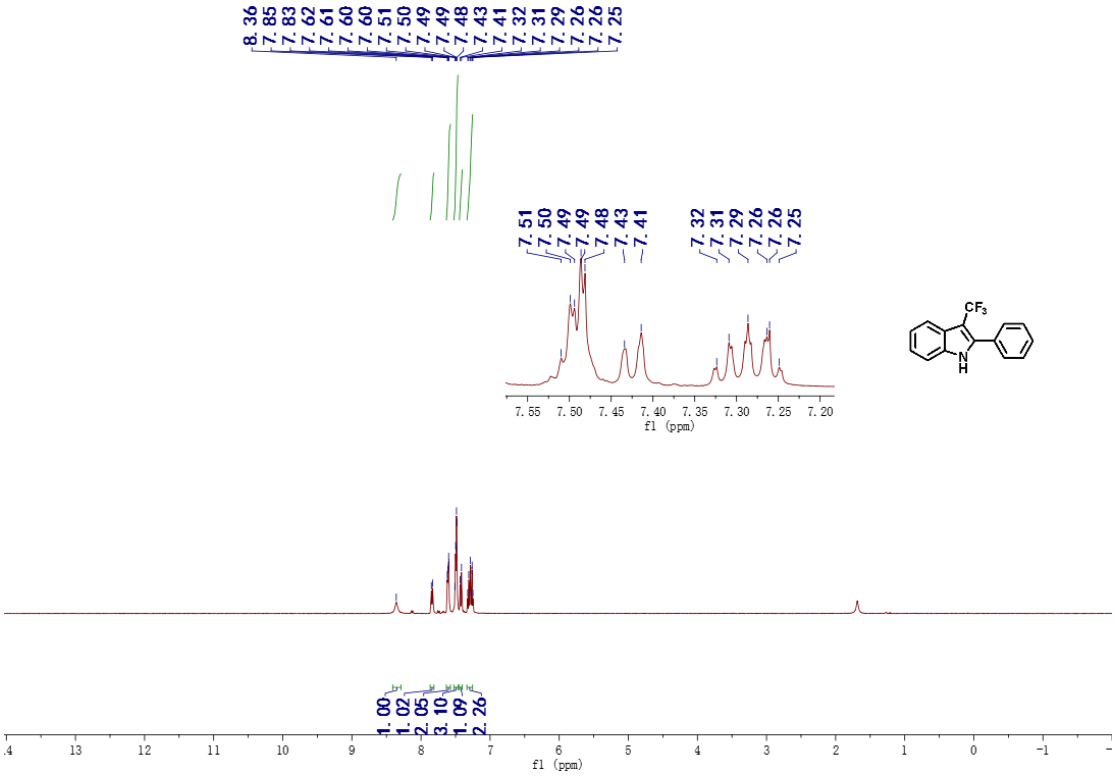
^{19}F NMR spectrum of ethyl 3-(trifluoromethyl)-1*H*-indole-2-carboxylate 5l



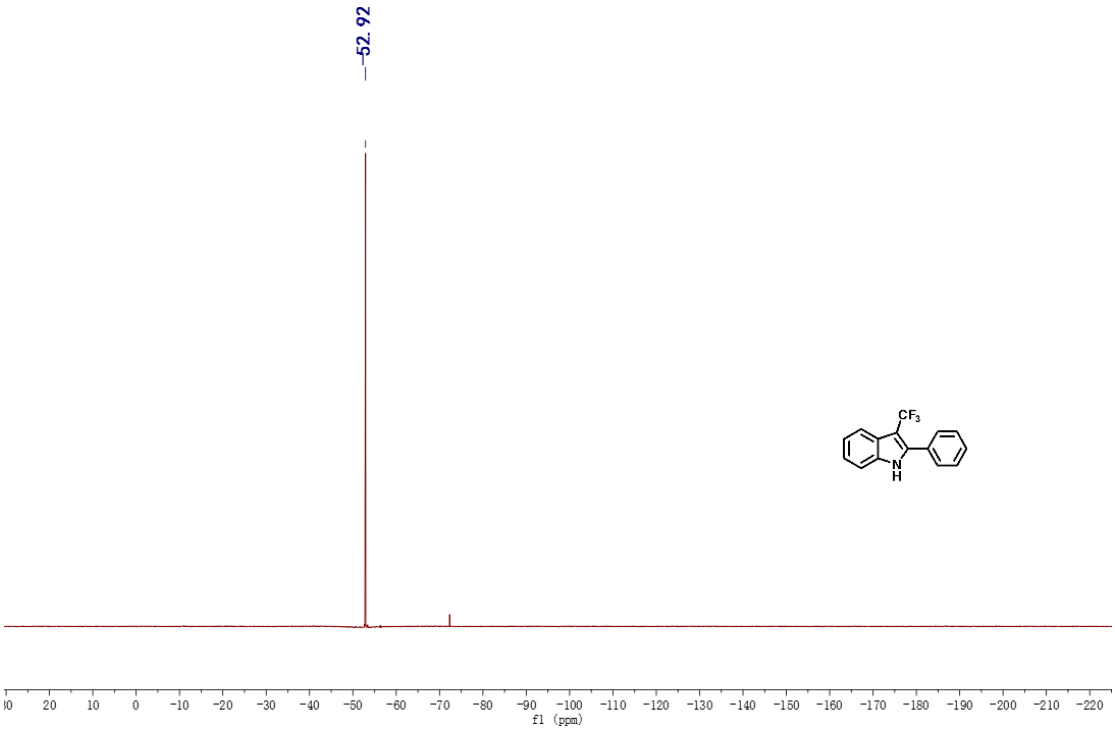
^{13}C NMR spectrum of ethyl 3-(trifluoromethyl)-1*H*-indole-2-carboxylate 5l



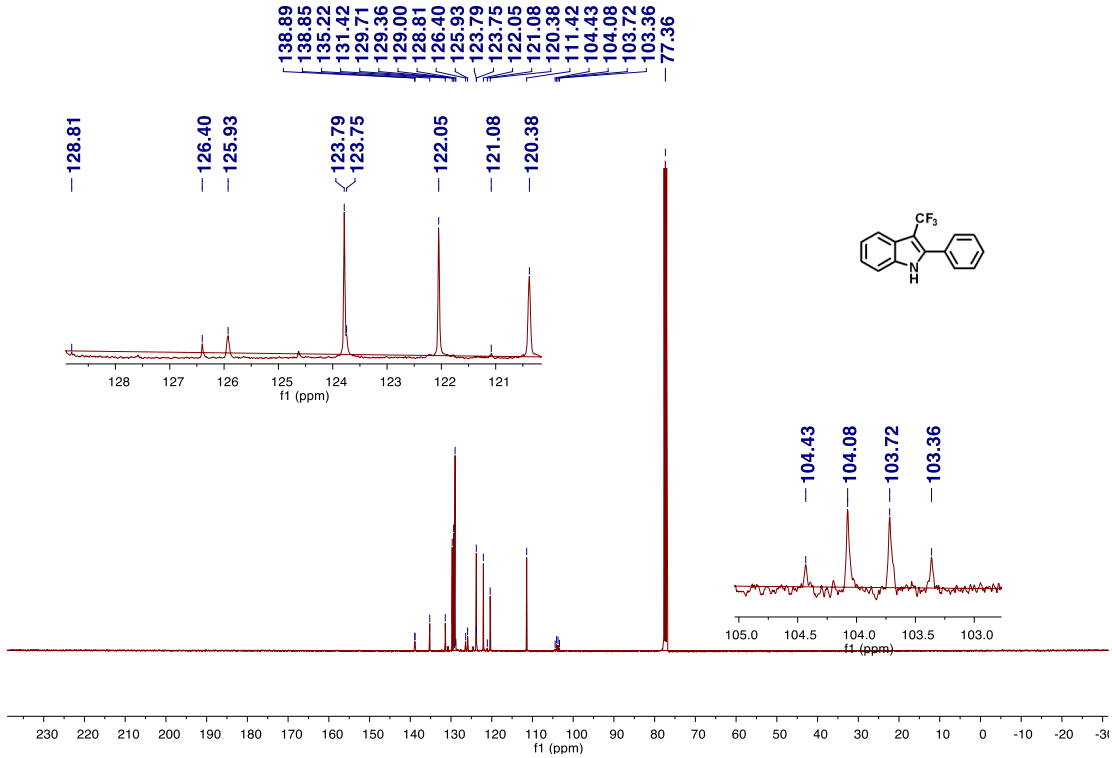
^{1}H NMR spectrum of 2-(4-phenyl)-3-(trifluoromethyl)-1*H*-indole 5m



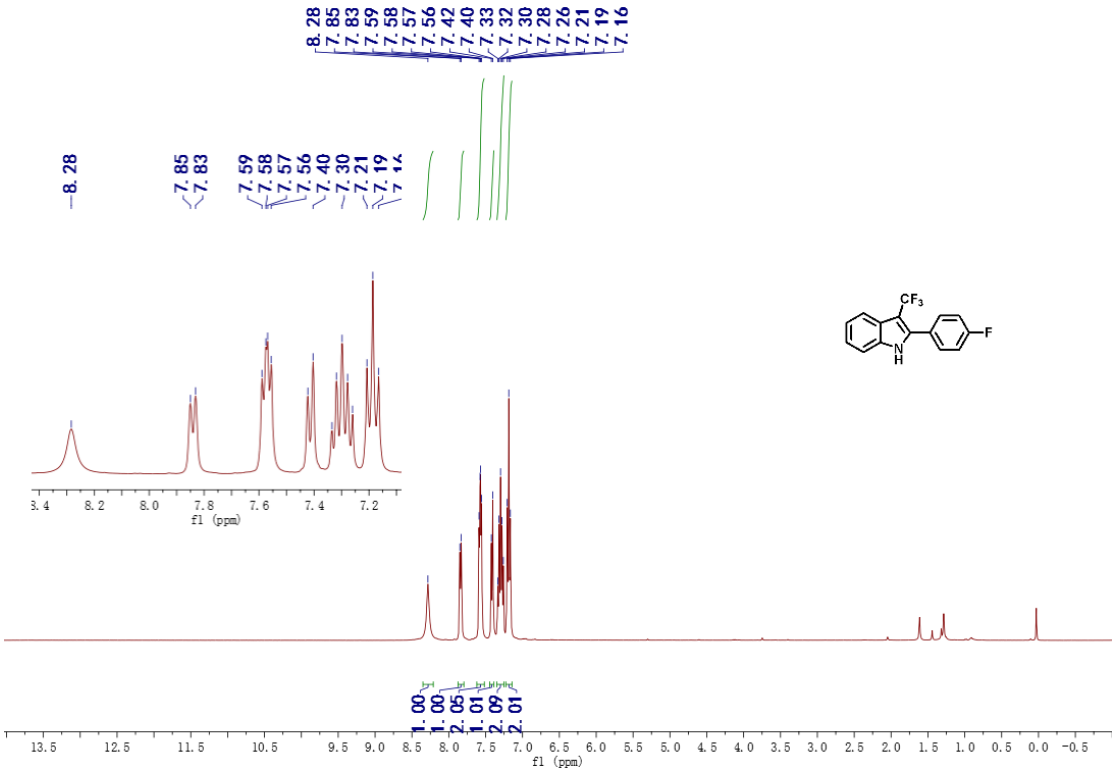
^{19}F NMR spectrum of 2-(4-phenyl)-3-(trifluoromethyl)-1*H*-indole 5m



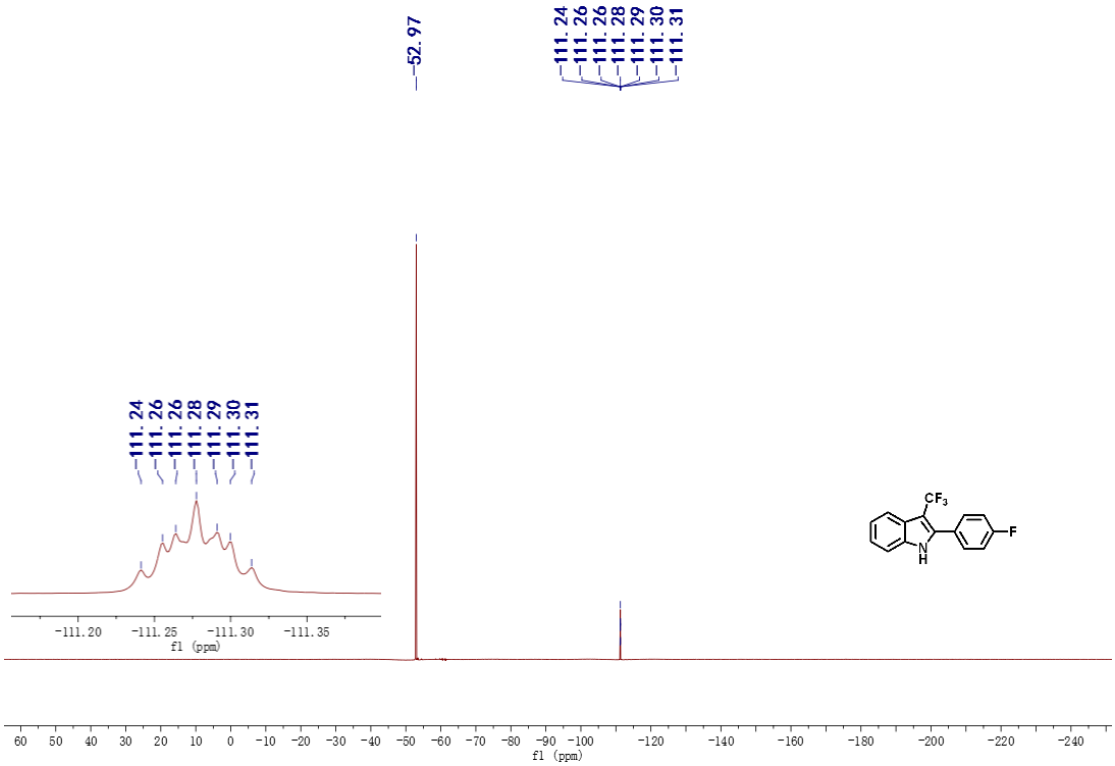
^{13}C NMR spectrum of 2-(4-phenyl)-3-(trifluoromethyl)-1*H*-indole 5m



^{1}H NMR spectrum of 2-(4-fluorophenyl)-3-(trifluoromethyl)-1*H*-indole 5n



^{19}F NMR spectrum of 2-(4-fluorophenyl)-3-(trifluoromethyl)-1*H*-indole 5n



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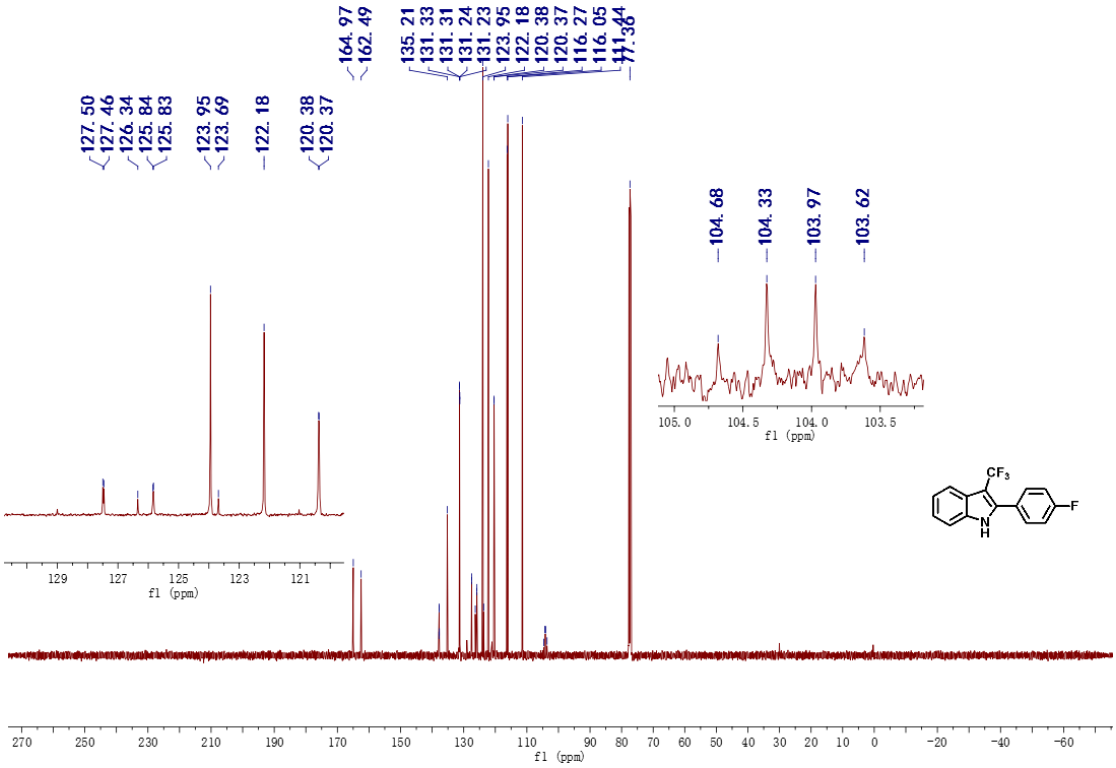
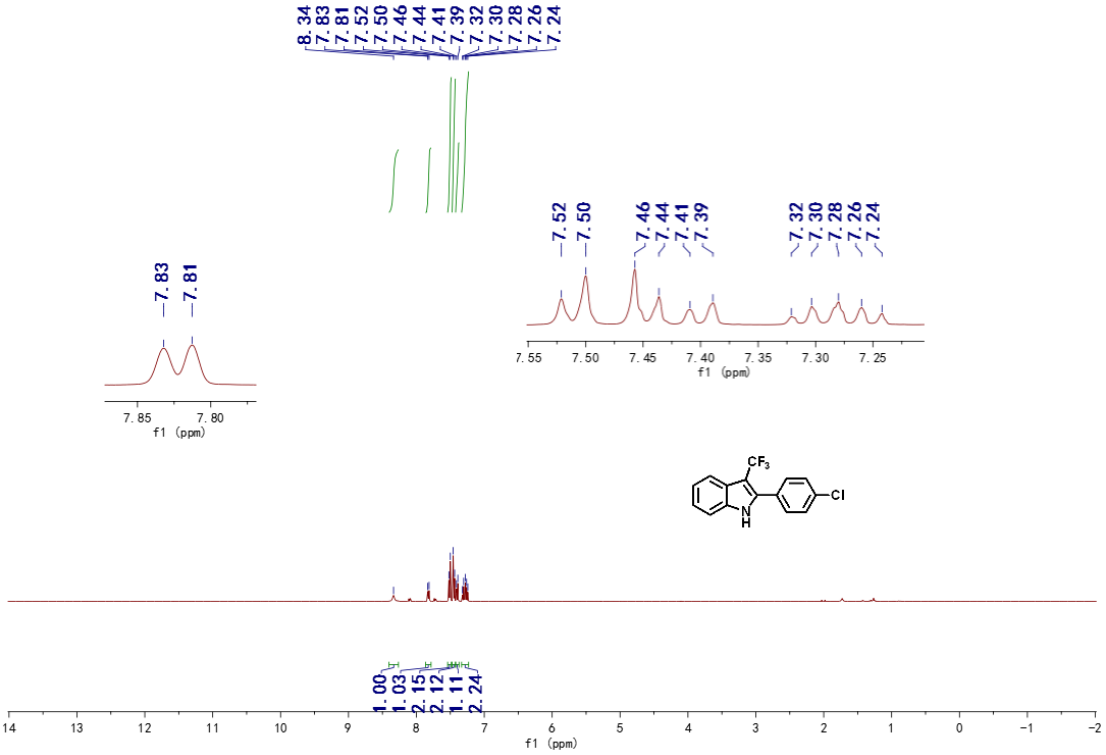
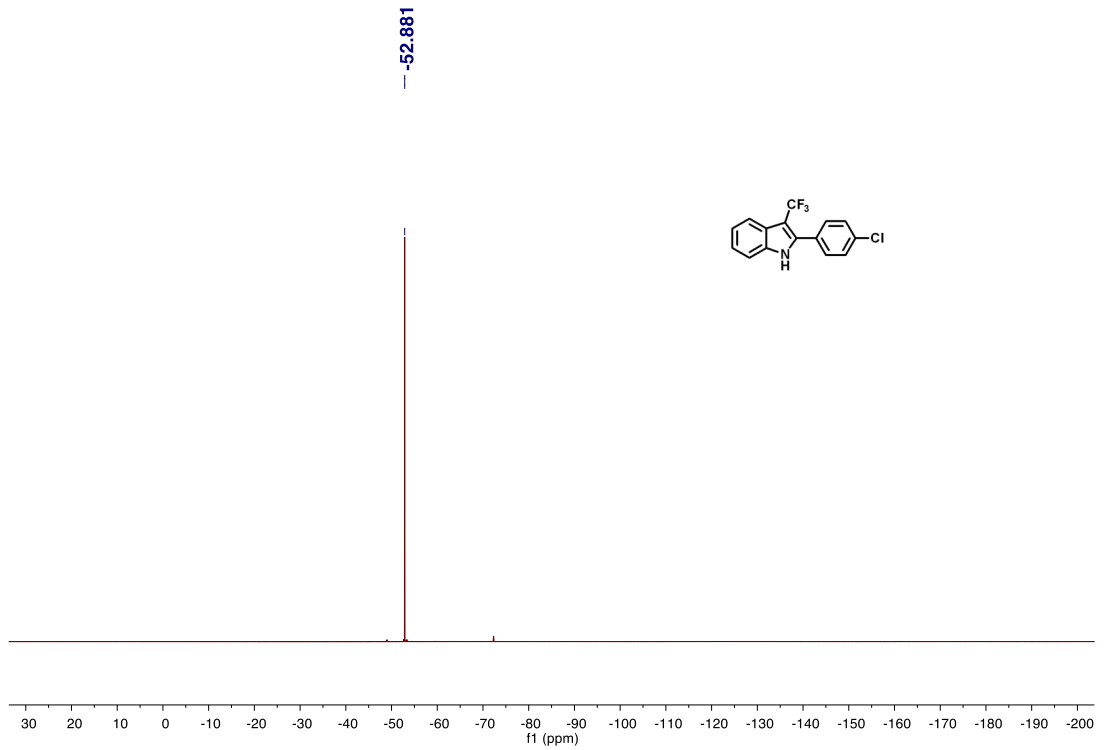


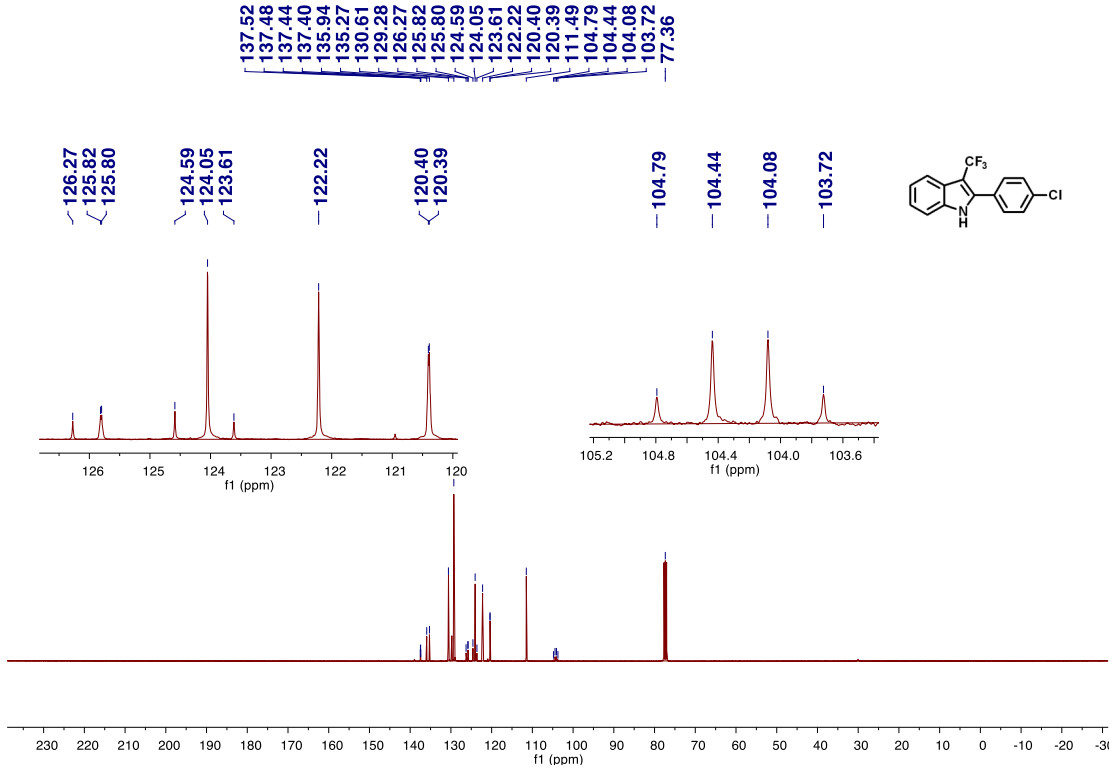
^{1}H NMR spectrum of 2-(4-clorophenyl)-3-(trifluoromethyl)-1*H*-indole 5o



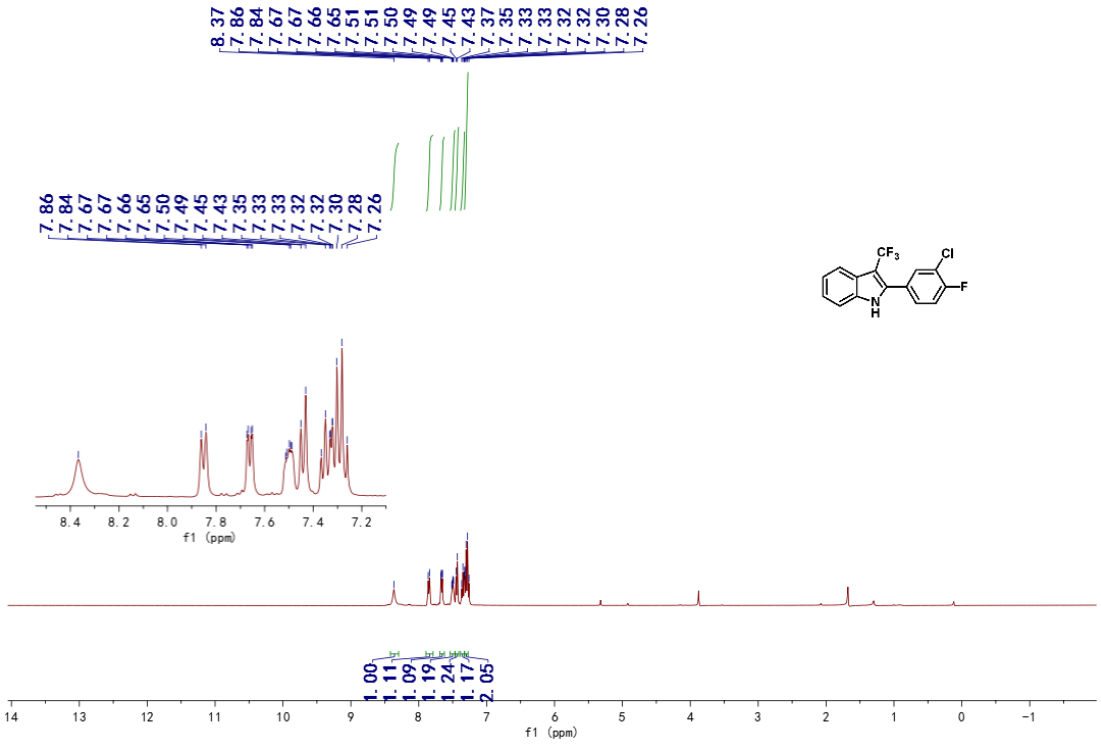
^{19}F NMR spectrum of 2-(4-clorophenyl)-3-(trifluoromethyl)-1*H*-indole 5o



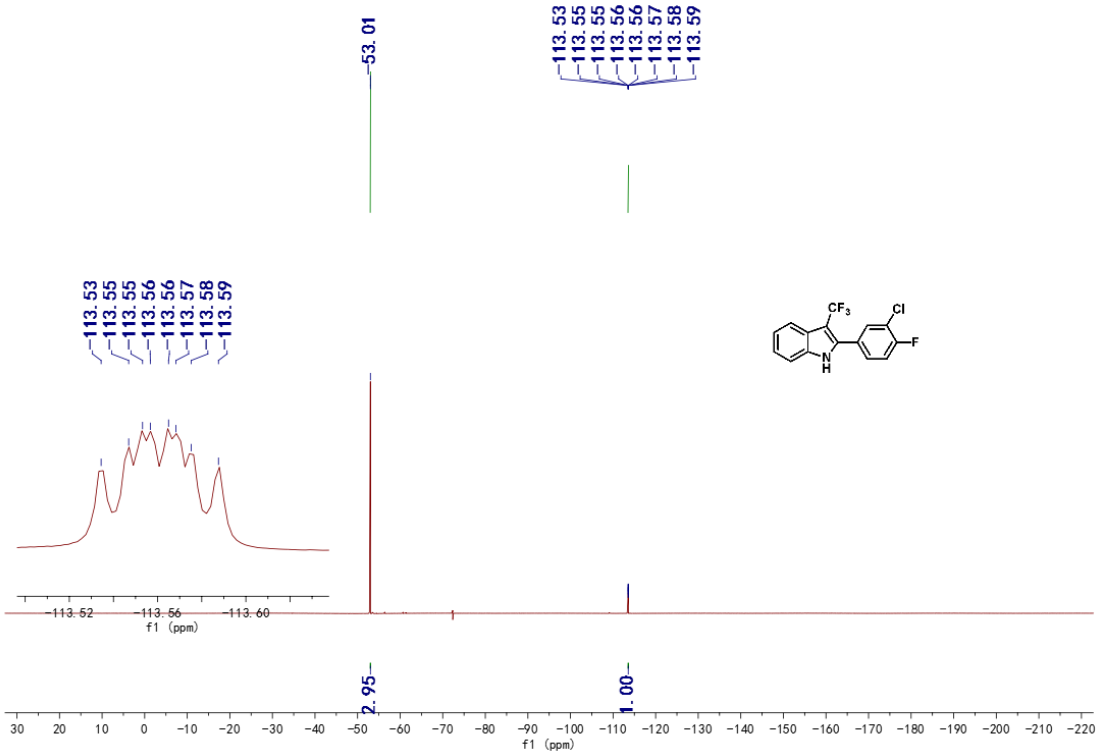
^{13}C NMR spectrum of 2-(4-clorophenyl)-3-(trifluoromethyl)-1*H*-indole 5o



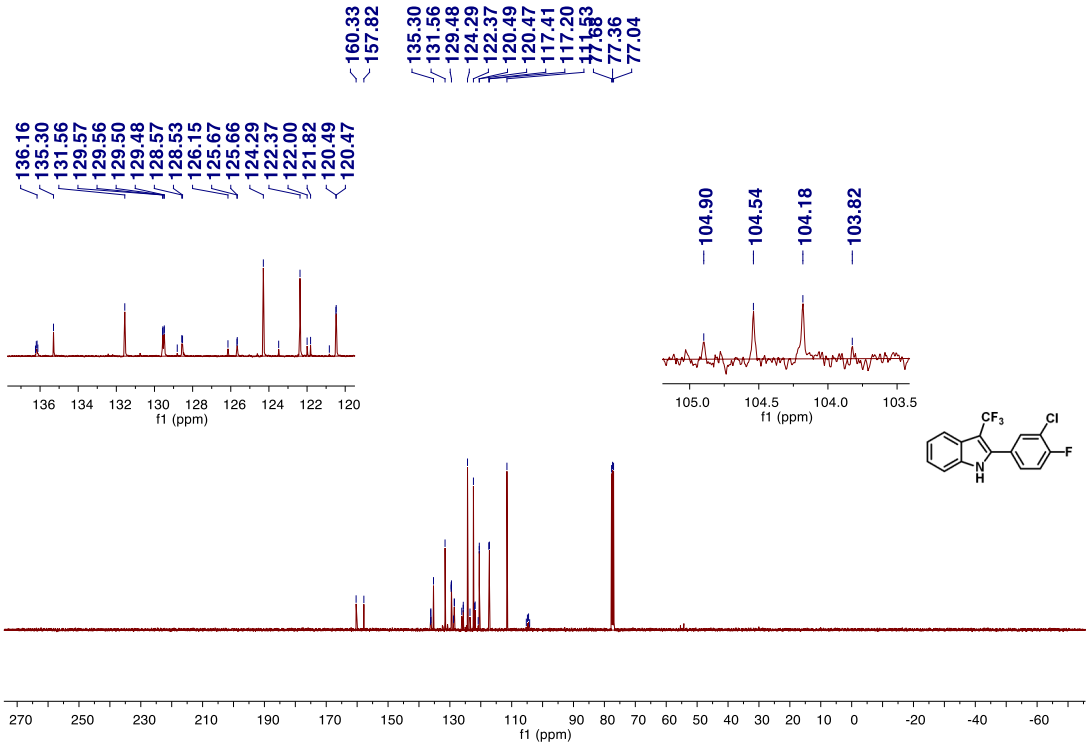
^{1}H NMR spectrum of 2-(3-chloro-4-fluorophenyl) -3-(trifluoromethyl)-1*H*-indole 5p



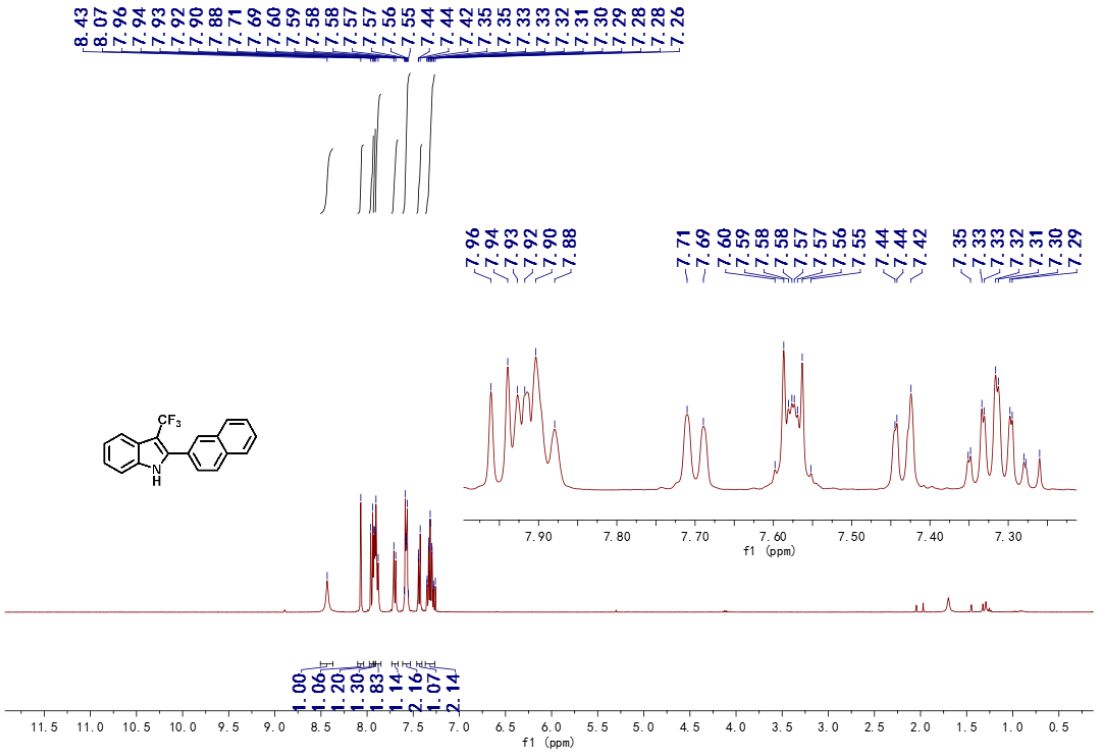
^{19}F NMR spectrum of 2-(3-chloro-4-fluorophenyl) -3-(trifluoromethyl)-1*H*-indole 5p



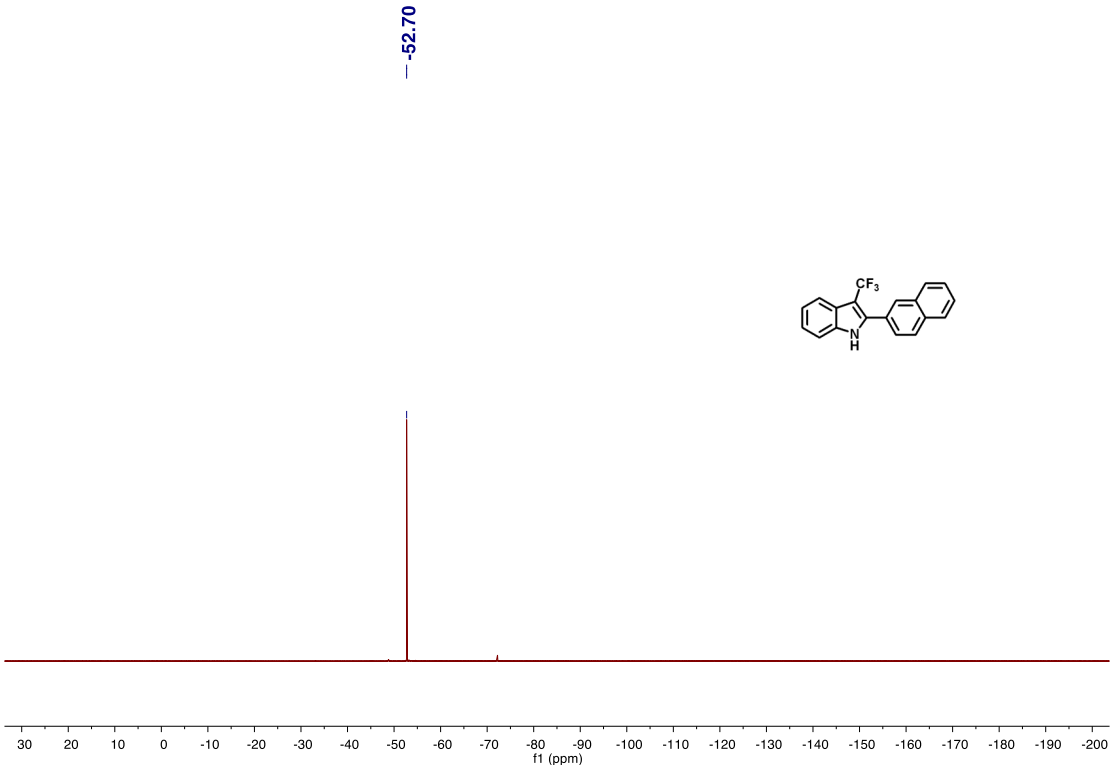
^{13}C NMR spectrum of 2-(3-chloro-4-fluorophenyl) -3-(trifluoromethyl)-1*H*-indole 5p



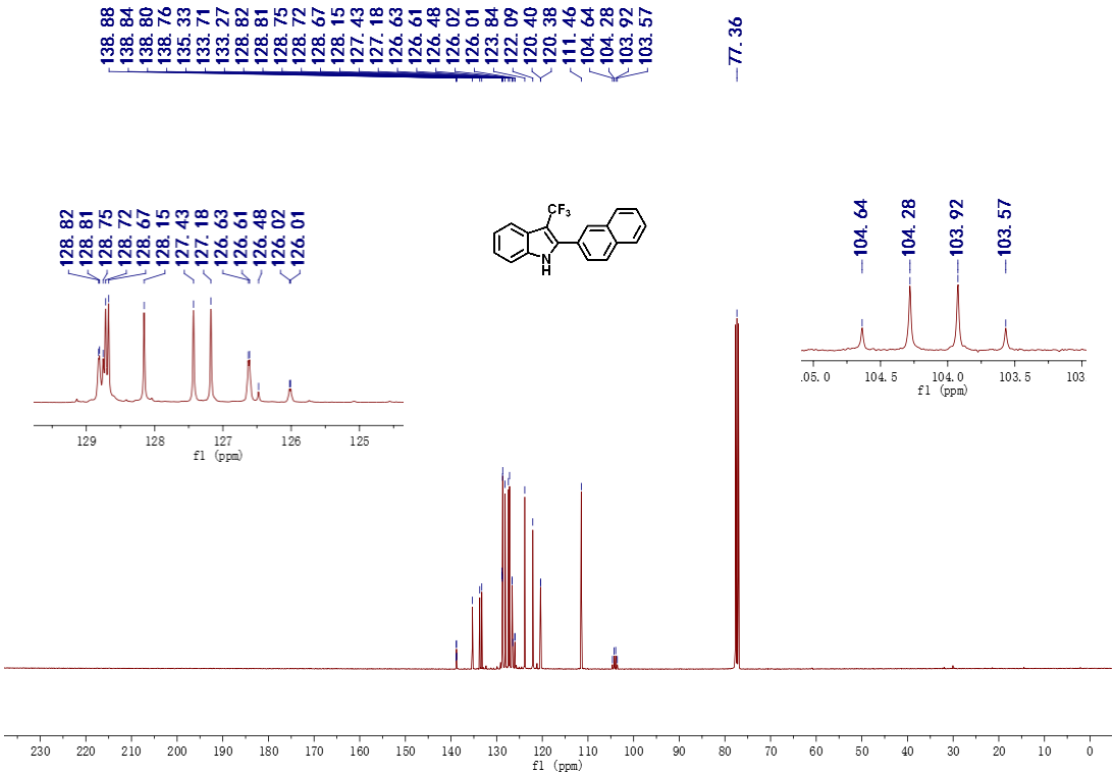
^{1}H NMR spectrum of 2-(naphthalen-2-yl)-3-(trifluoromethyl)-1*H*-indole 5q



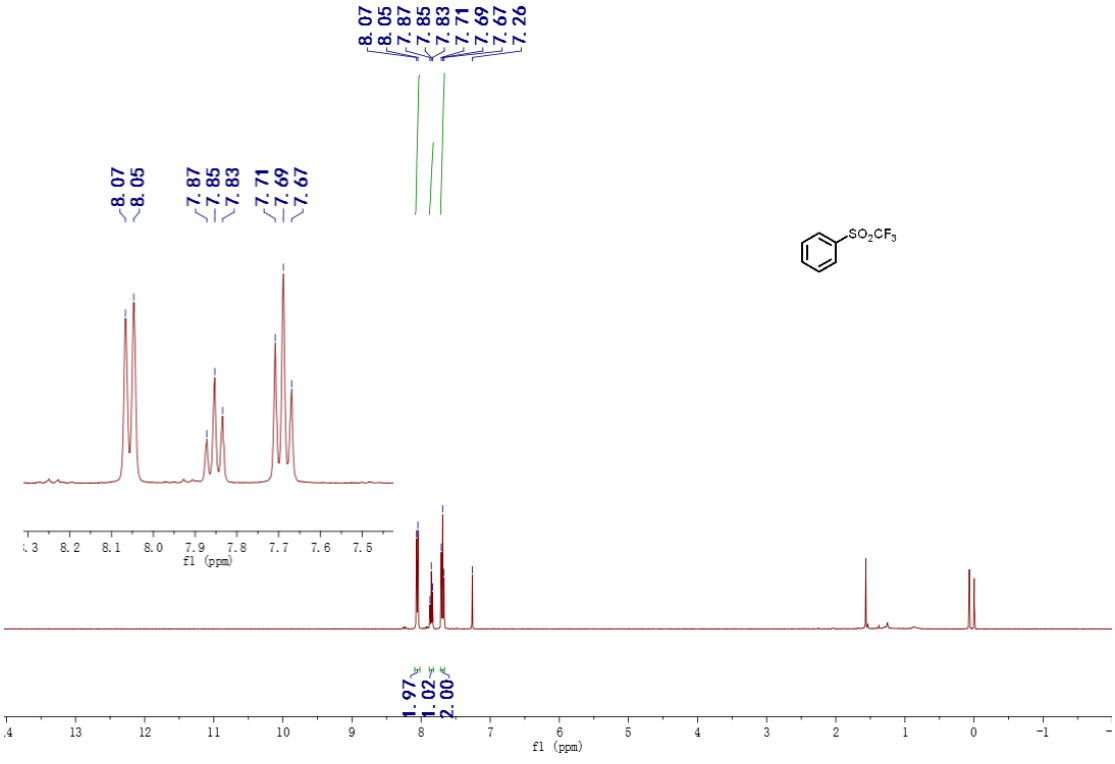
^{19}F NMR spectrum of 2-(naphthalen-2-yl)-3-(trifluoromethyl)-1*H*-indole 5q



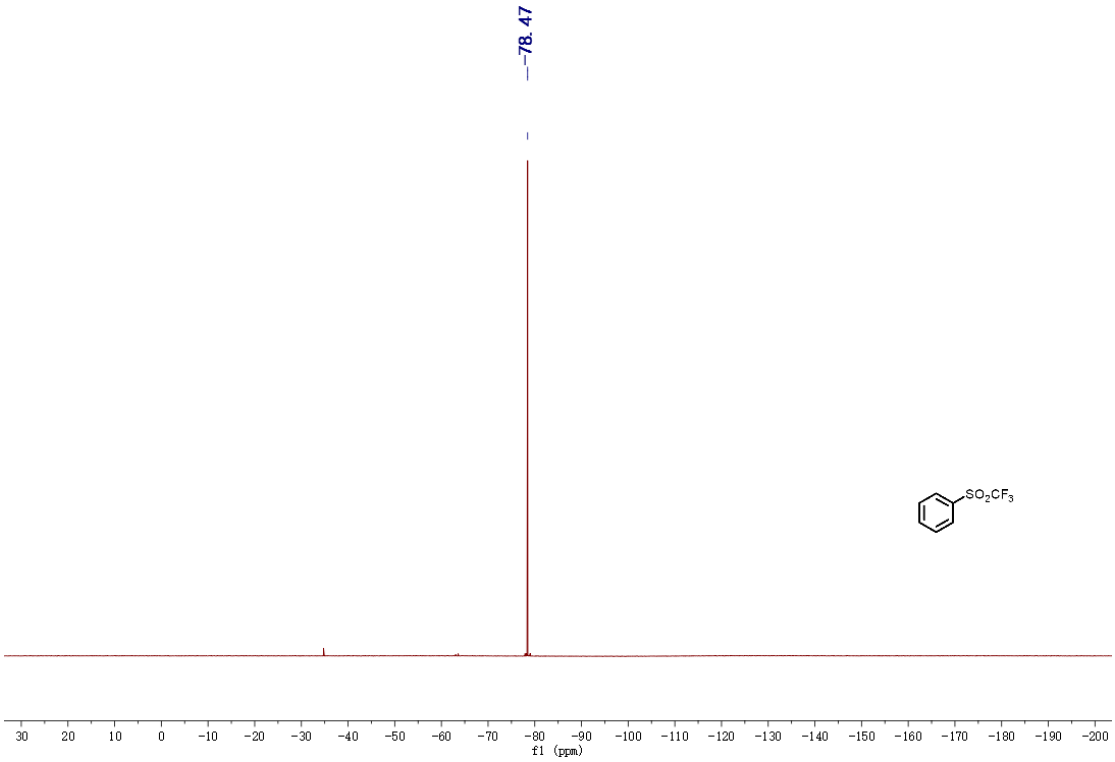
^{13}C NMR spectrum of 2-(naphthalen-2-yl)-3-(trifluoromethyl)-1*H*-indole 5q



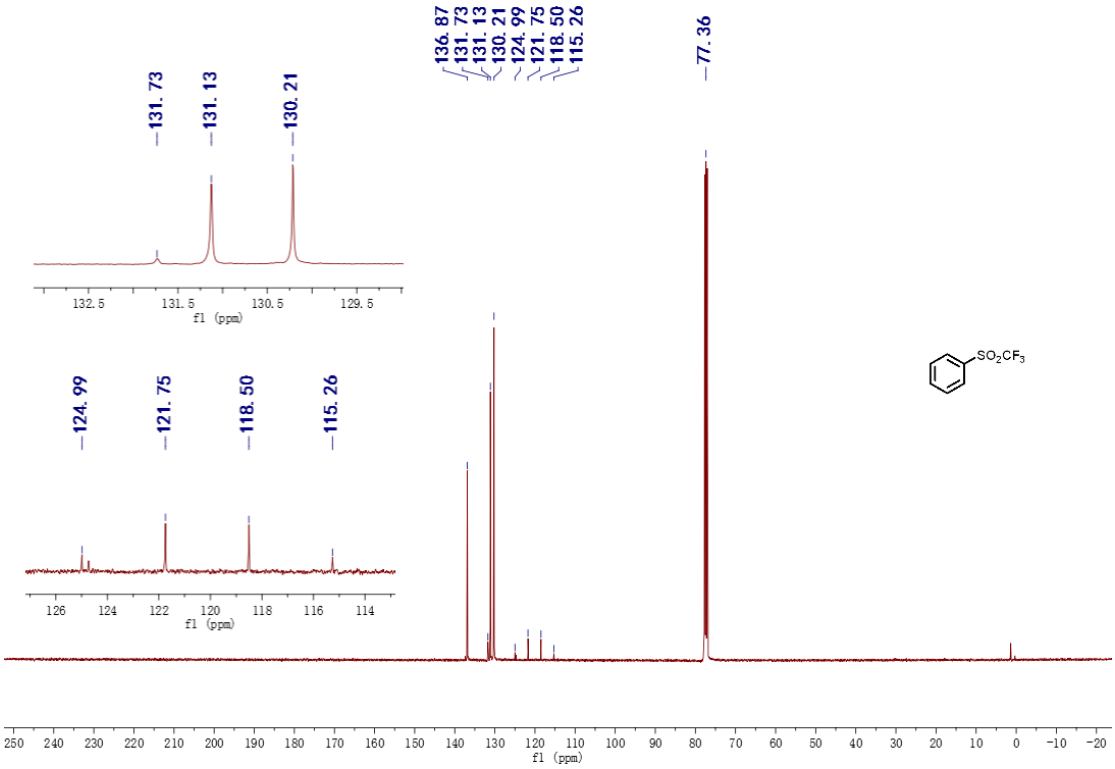
^{1}H NMR spectrum of [(trifluoromethyl)sulfonyl]-benzene 6a



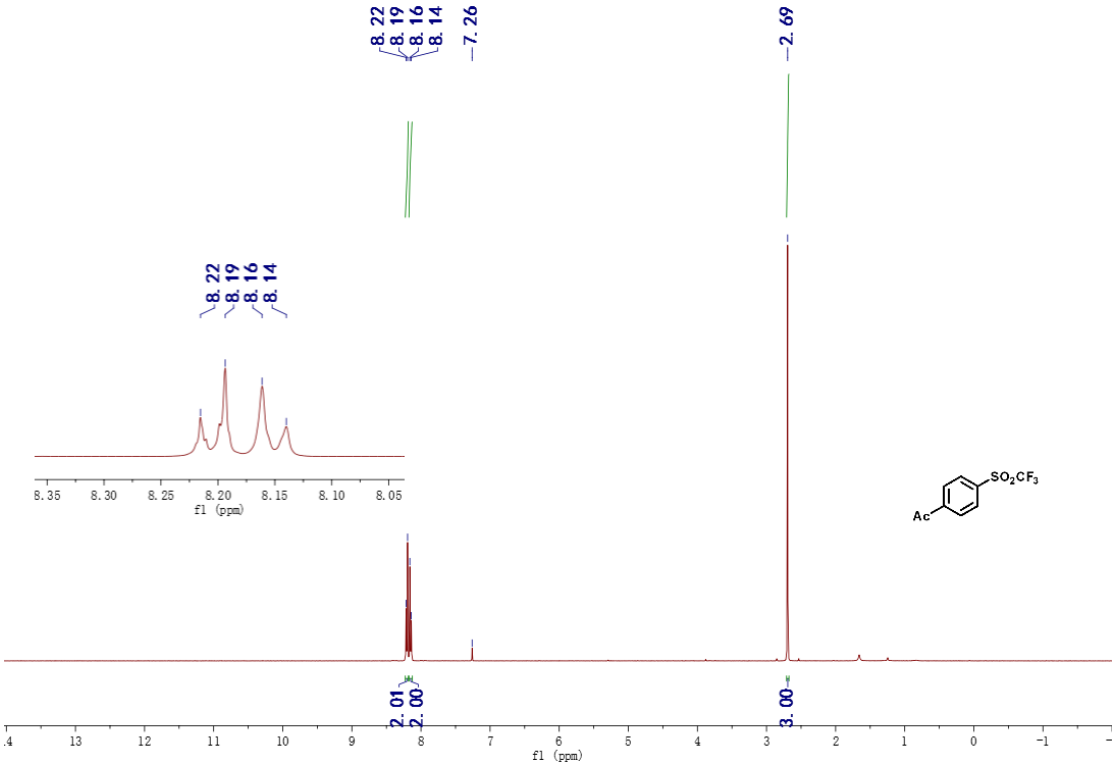
^{19}F NMR spectrum of [(trifluoromethyl)sulfonyl]-benzene 6a



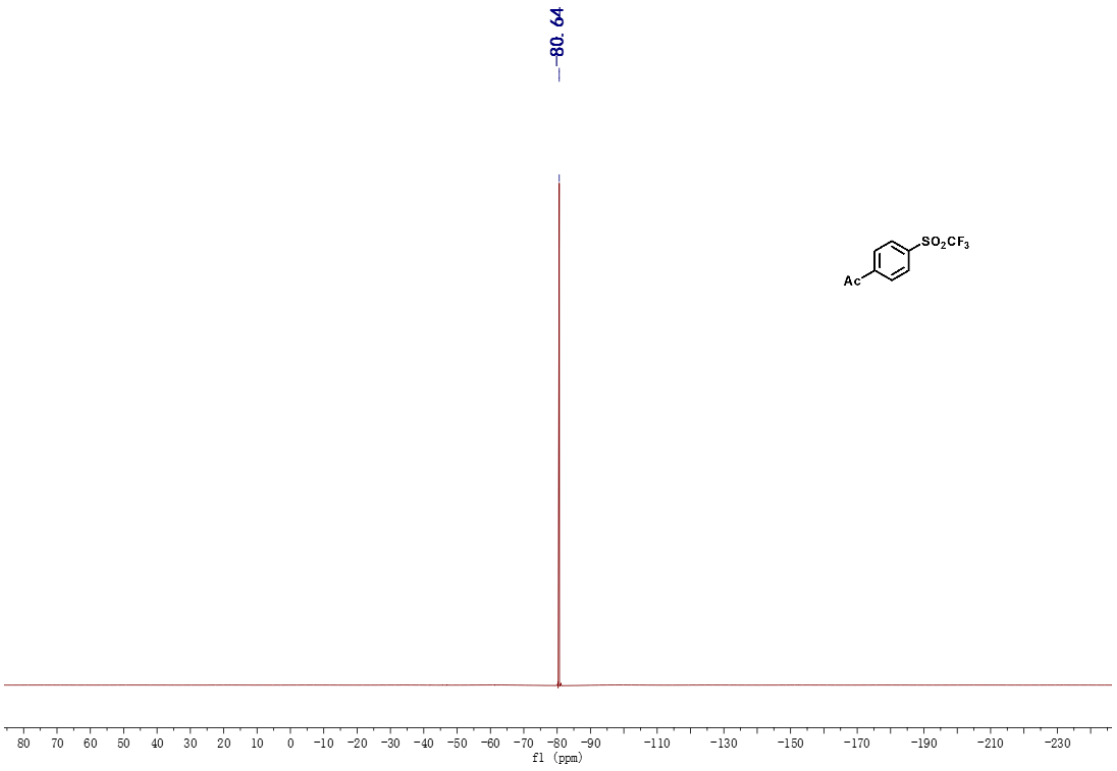
^{13}C NMR spectrum of [(trifluoromethyl)sulfonyl]-benzene 6a



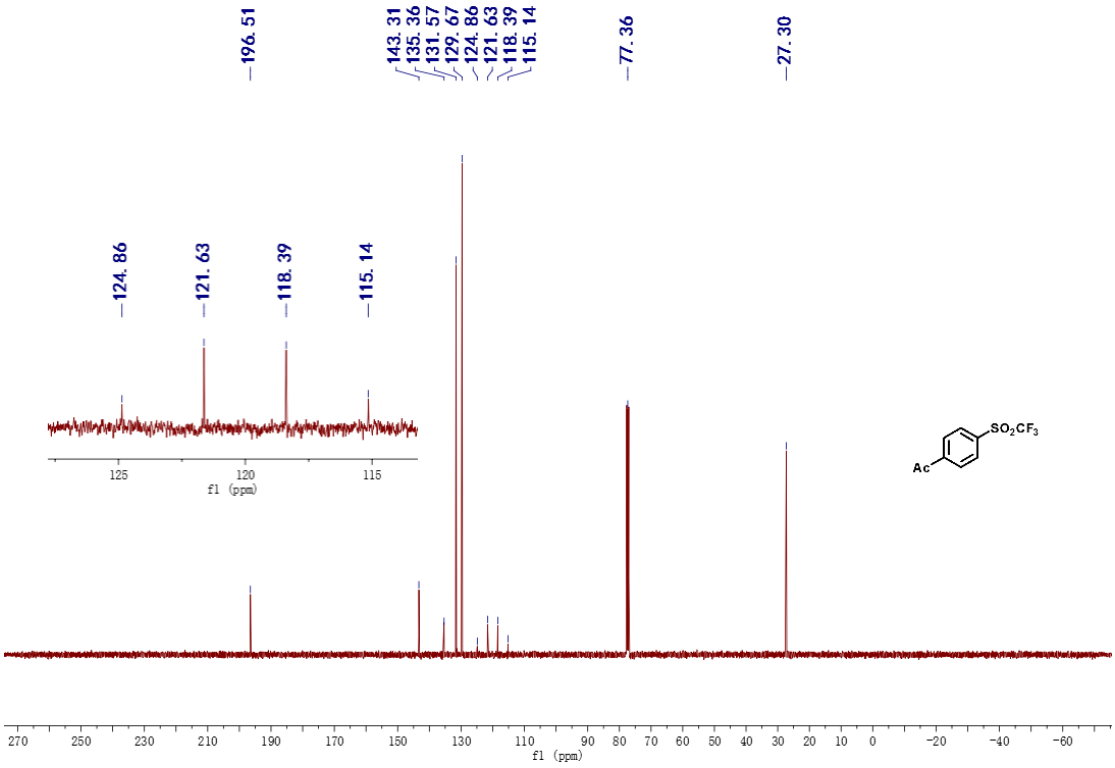
^{1}H NMR spectrum of 1-[4-[(trifluoromethyl)sulfonyl]phenyl]-ethanone 6b



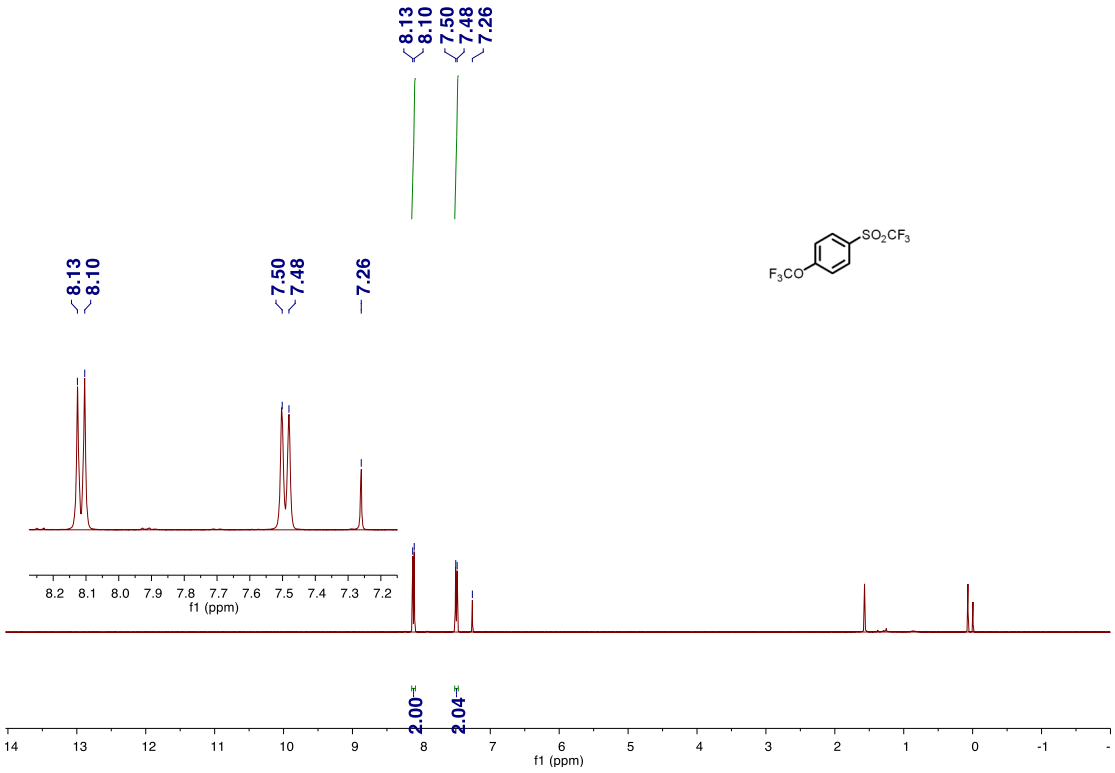
^{19}F NMR spectrum of 1-[4-[(trifluoromethyl)sulfonyl]phenyl]-ethanone 6b



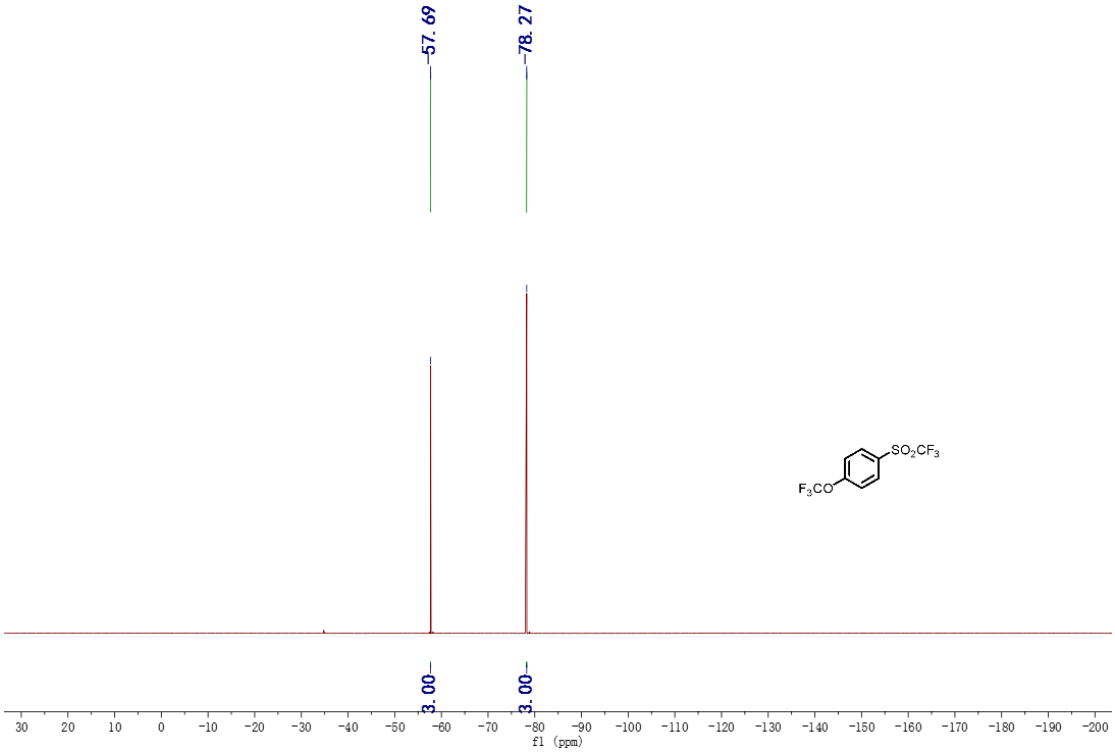
^{13}C NMR spectrum of 1-[4-[(trifluoromethyl)sulfonyl]phenyl]-ethanone 6b



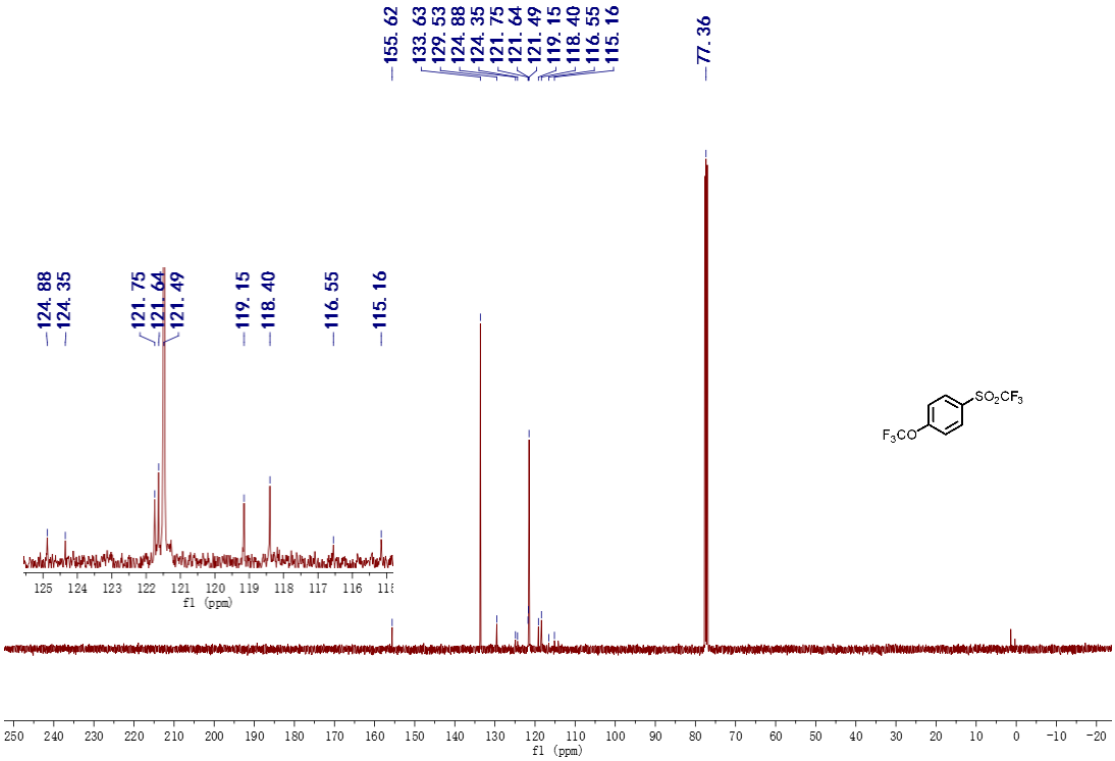
^{1}H NMR spectrum of 1-(trifluoromethoxy)-4-[(trifluoromethyl) sulfonyl]-benzene 6c



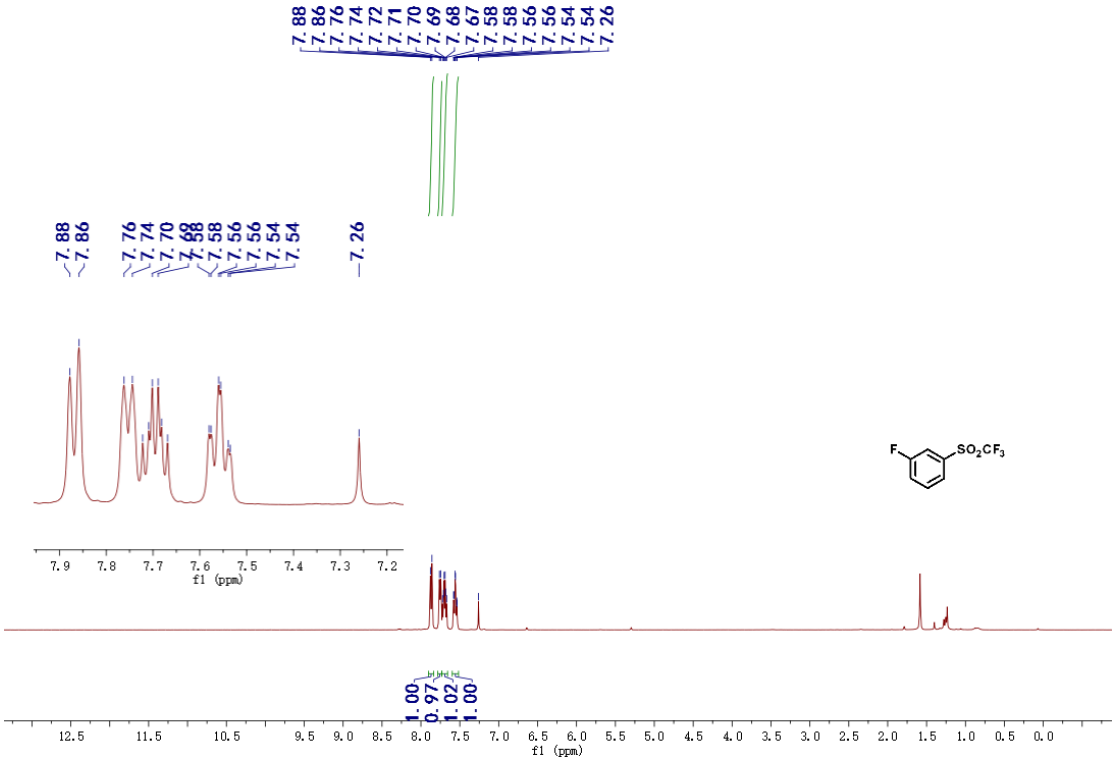
^{19}F NMR spectrum of 1-(trifluoromethoxy)-4-[(trifluoromethyl)sulfonyl] -benzene 6c



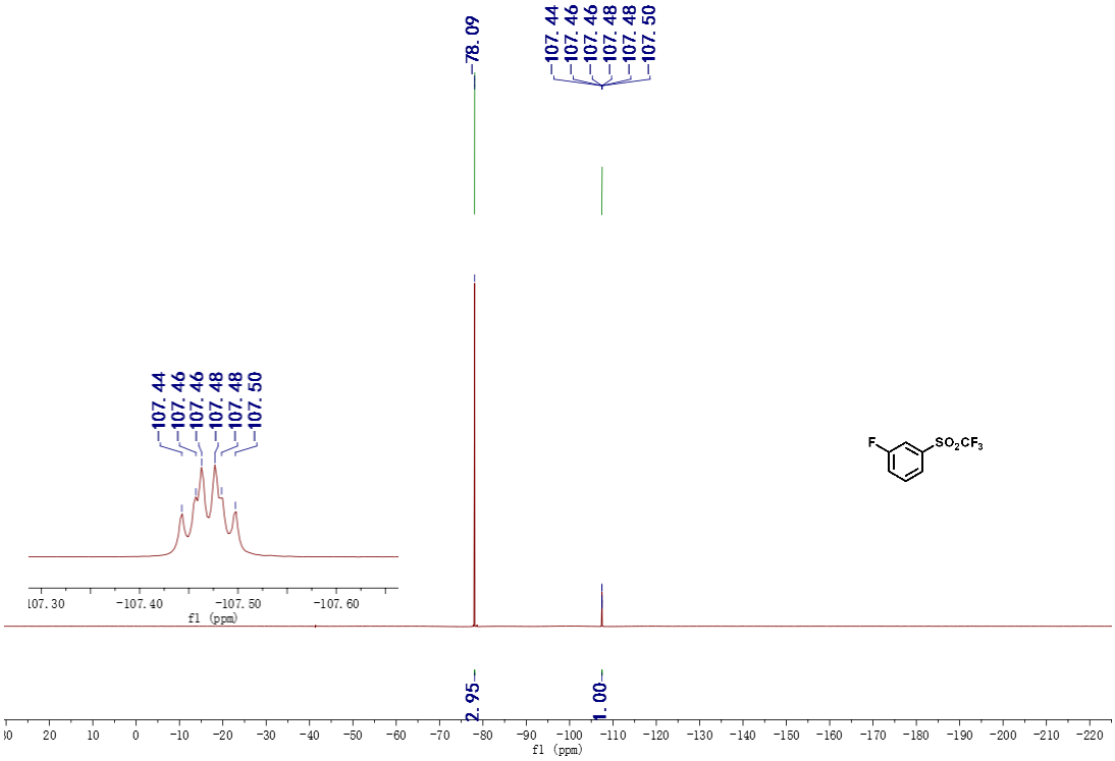
^{13}C NMR spectrum of 1-(Trifluoromethoxy)-4-[(trifluoromethyl)sulfonyl]- benzene 6c



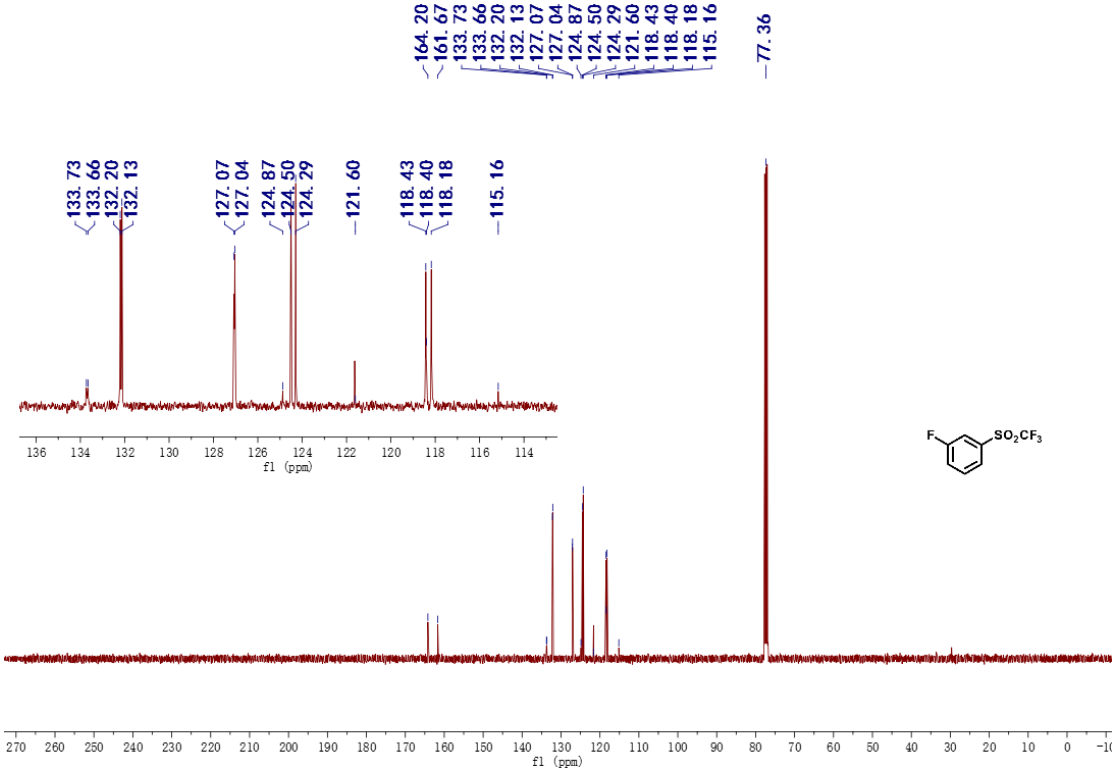
^{1}H NMR spectrum of 1-fluoro-3-[(trifluoromethyl)sulfonyl]-benzene 6d



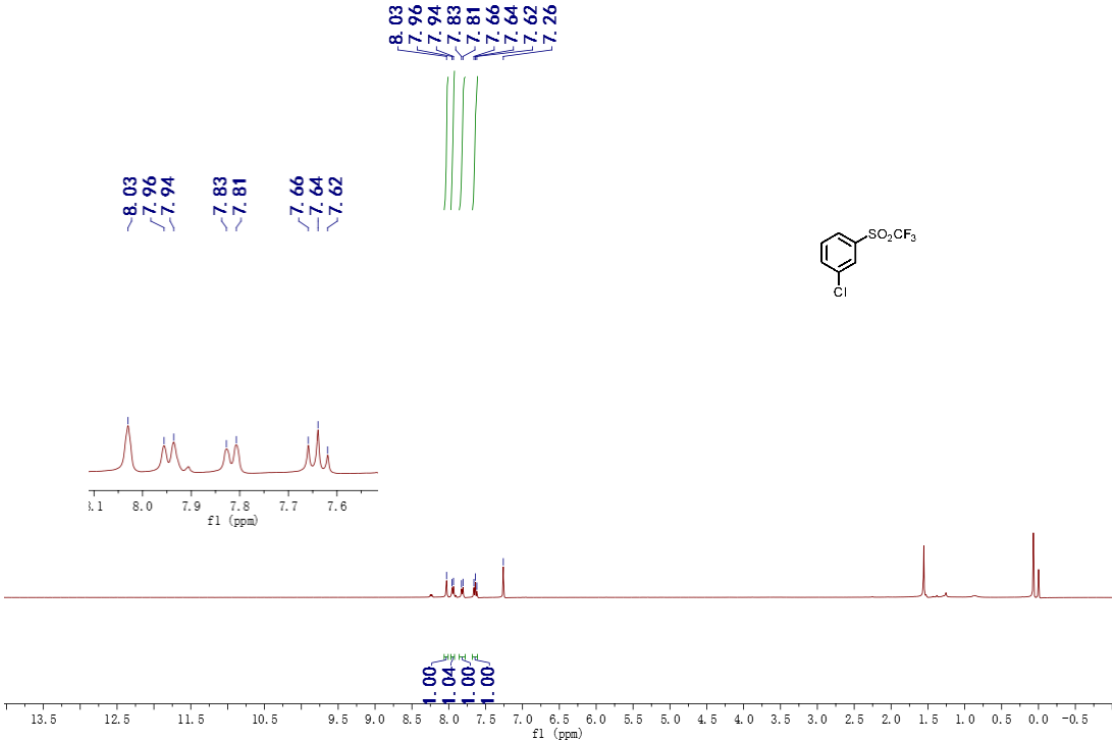
^{19}F NMR spectrum of 1-fluoro-3-[(trifluoromethyl)sulfonyl]-benzene 6d



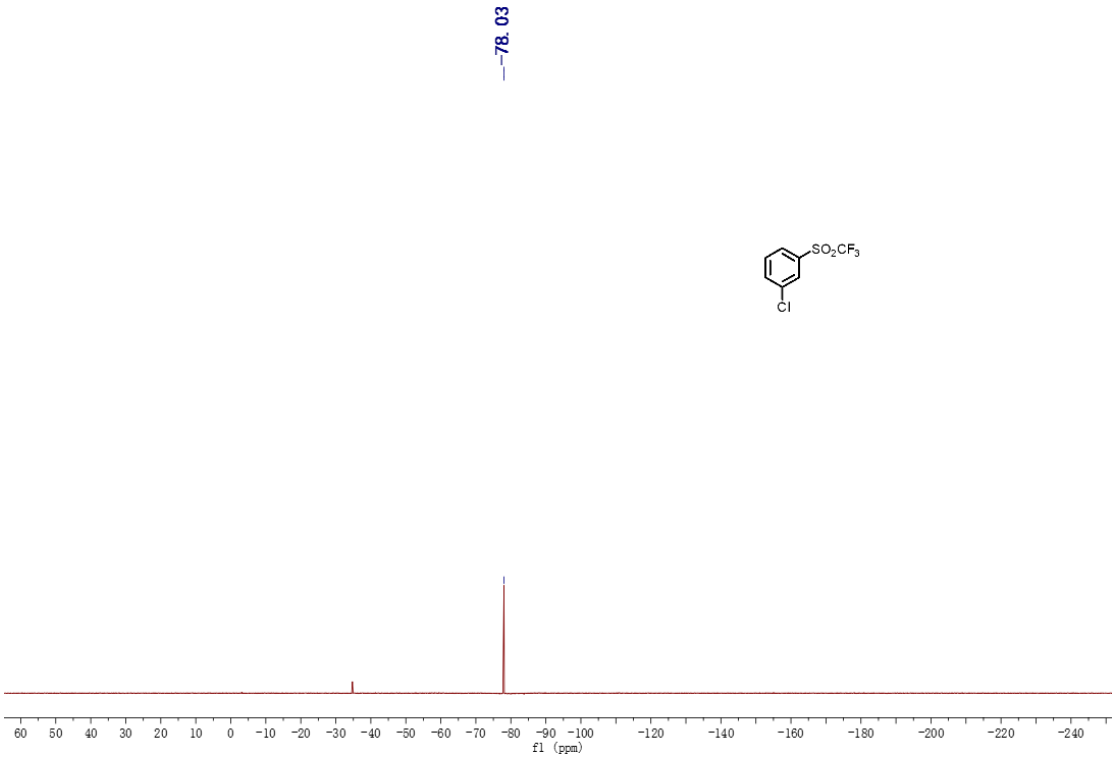
^{13}C NMR spectrum of 1-fluoro-3-[(trifluoromethyl)sulfonyl]-benzene 6d



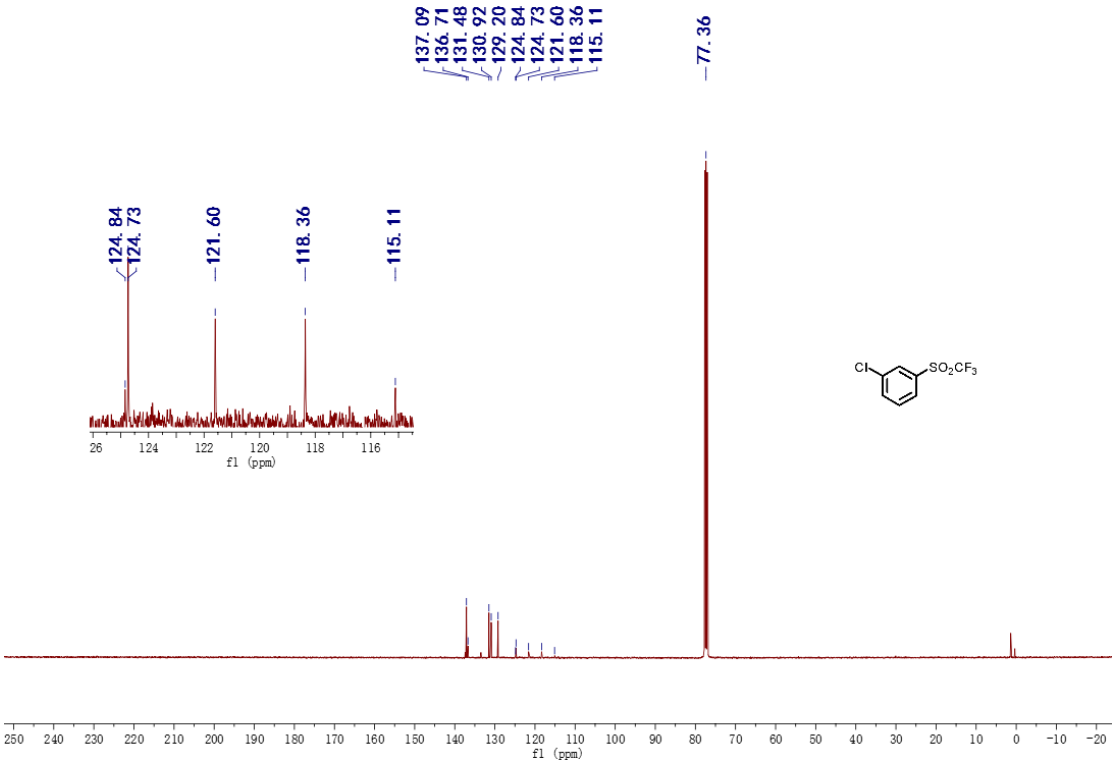
^{1}H NMR spectrum of 1-chloro-3-[(trifluoromethyl)sulfonyl]-benzene 6e



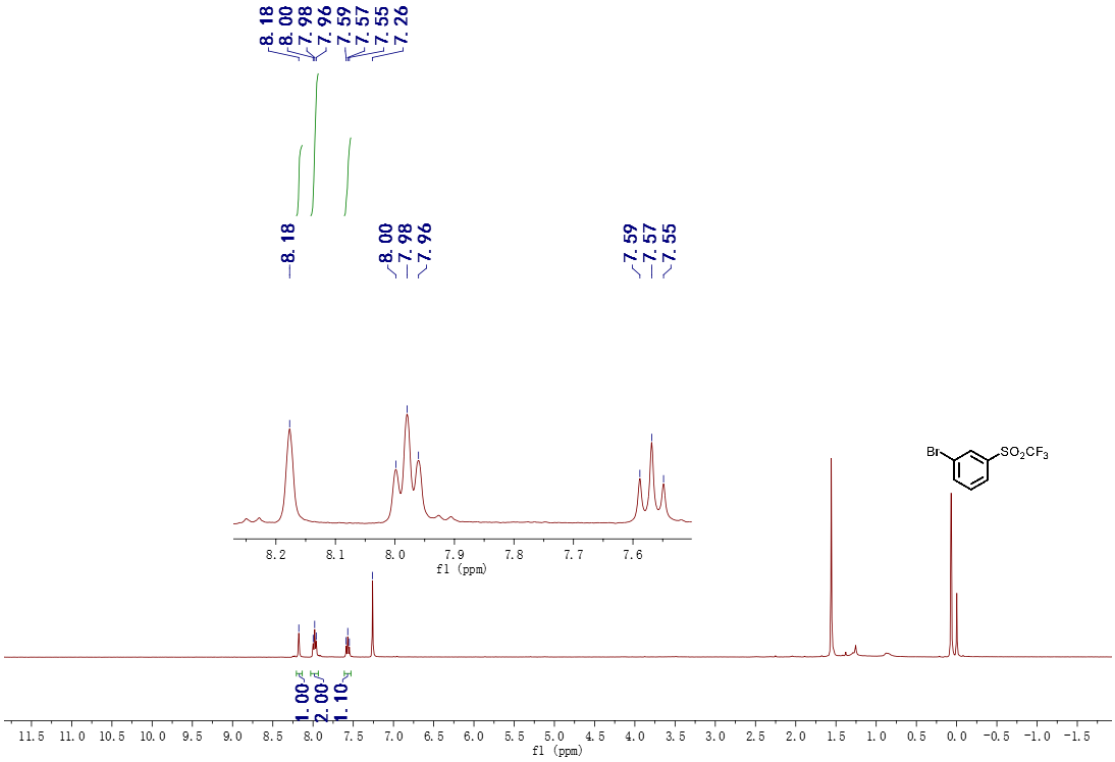
^{19}F NMR spectrum of 1-chloro-3-[(trifluoromethyl)sulfonyl]-benzene 6e



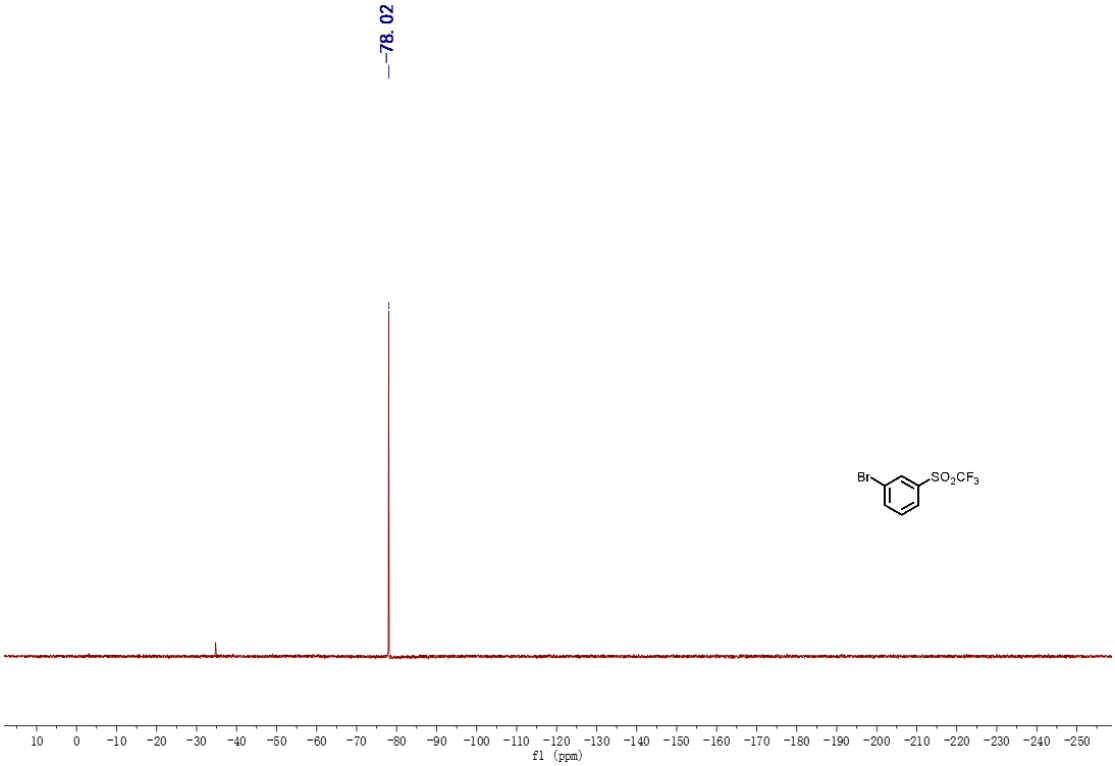
^{13}C NMR spectrum of 1-chloro-3-[(trifluoromethyl)sulfonyl]-benzene 6e



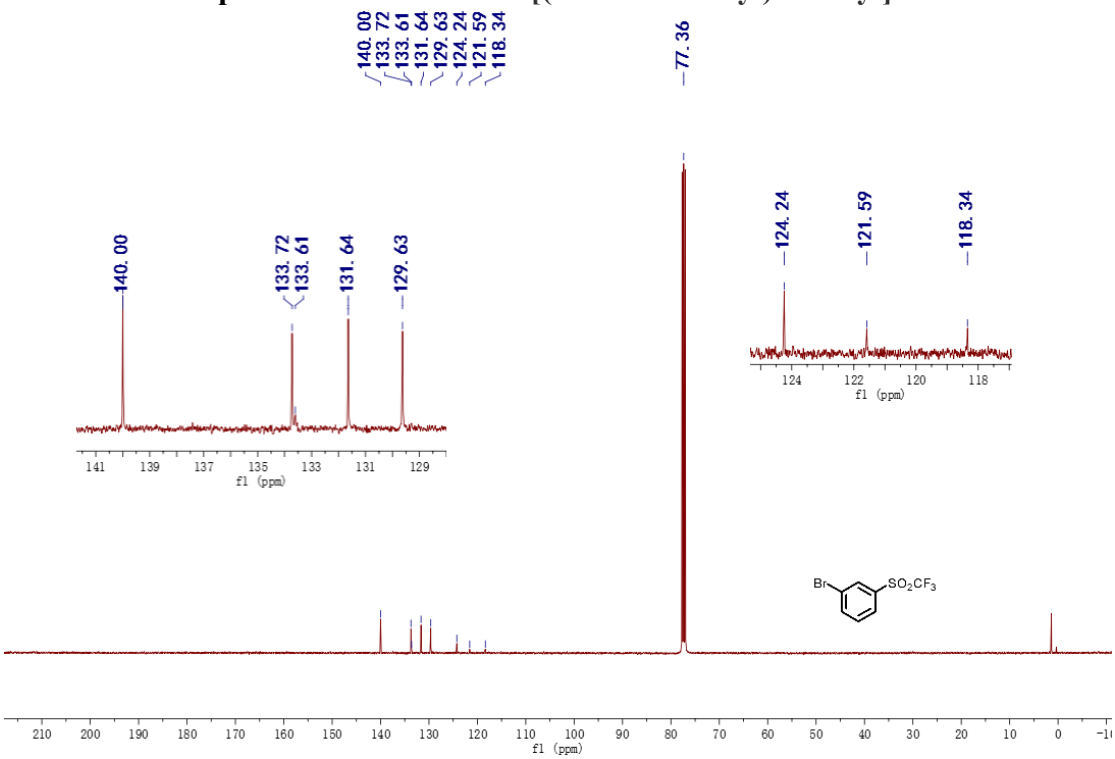
^{1}H NMR spectrum of 1-bromo-3-[(trifluoromethyl)sulfonyl]-benzene 6f



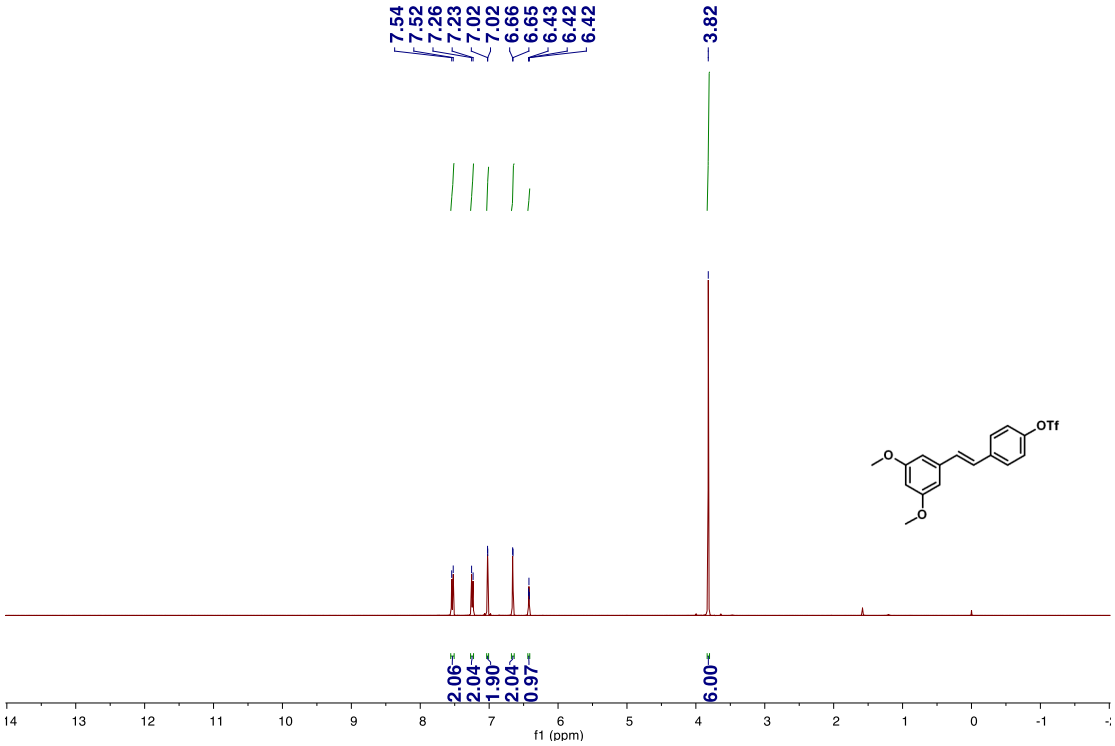
^{19}F NMR spectrum of 1-bromo-3-[(trifluoromethyl)sulfonyl]-benzene 6f



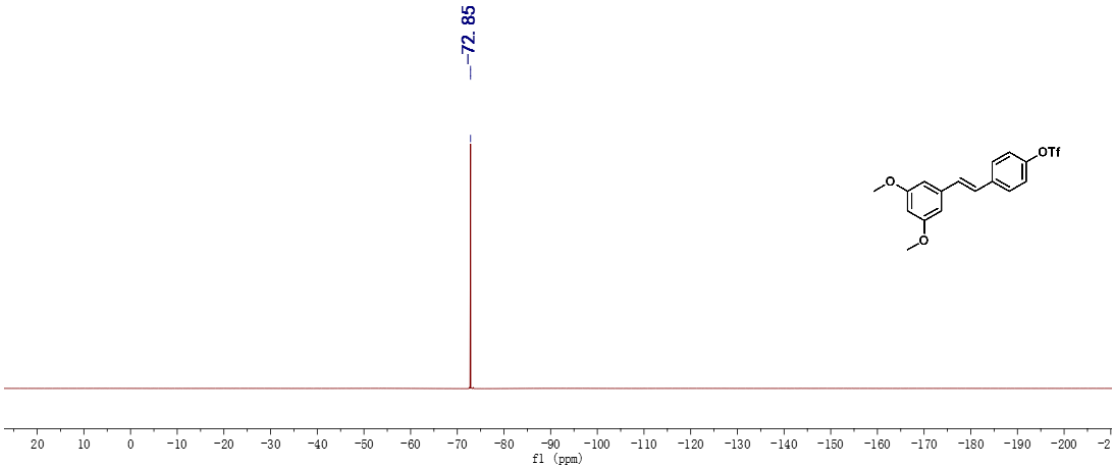
^{13}C NMR spectrum of 1-bromo-3-[(trifluoromethyl)sulfonyl]-benzene 6f



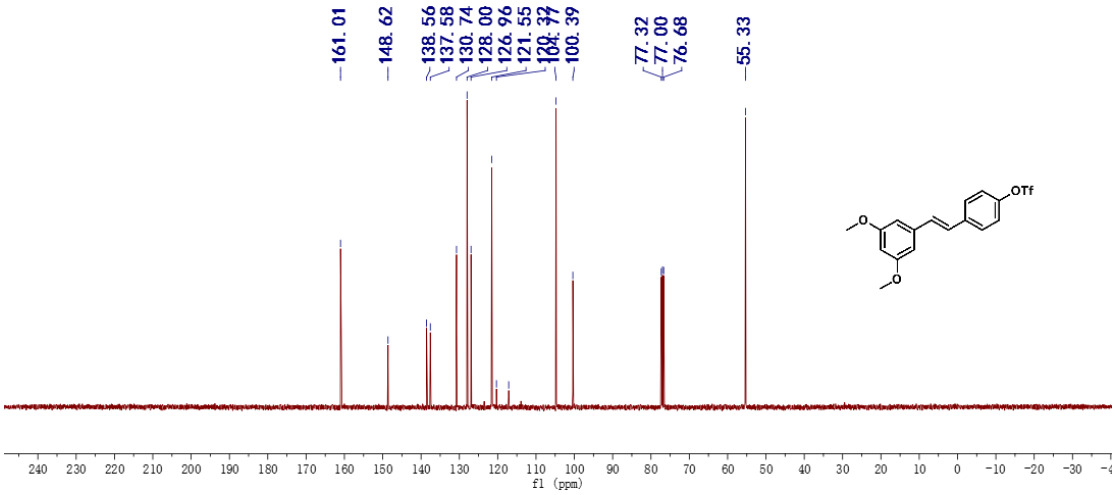
^{1}H NMR spectrum of (*E*)-4-(3,5-dimethoxystyryl)phenyltrifluoromethanesulfonate (S1-4n)



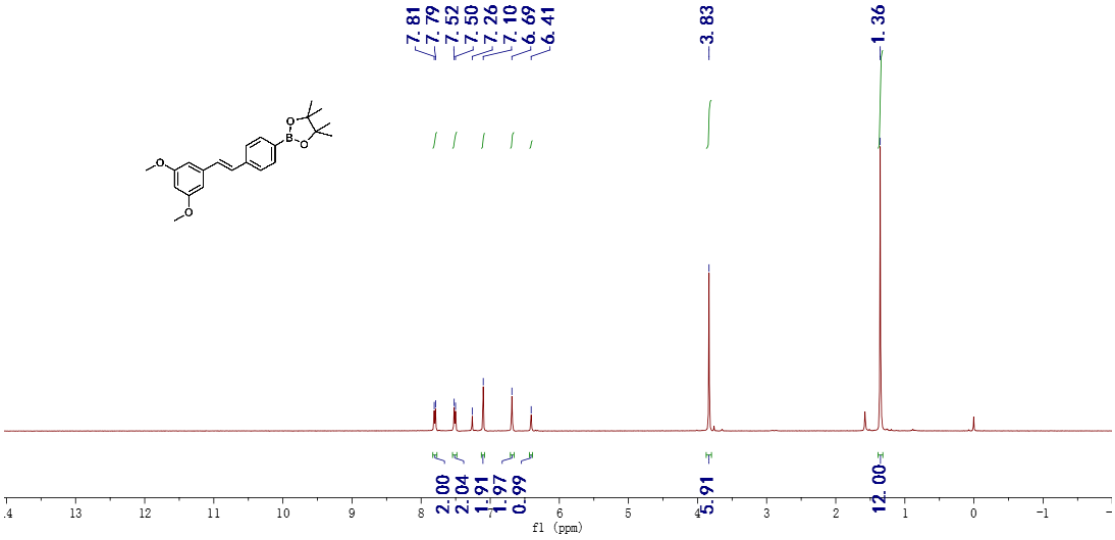
^{19}F NMR spectrum of (*E*)-4-(3,5-dimethoxystyryl)phenyltrifluoromethanesulfonate (S1-4n)



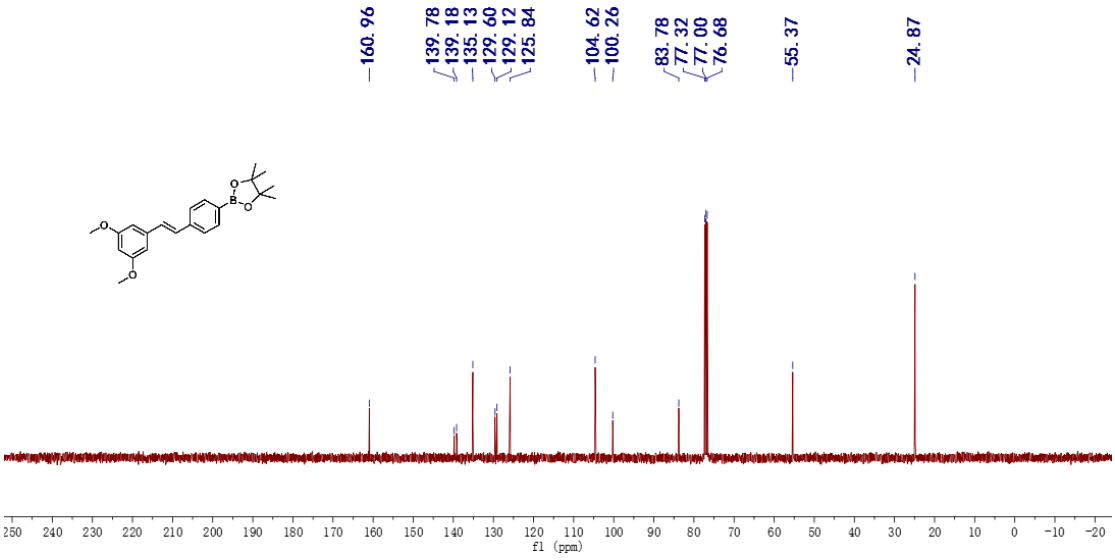
^{13}C NMR spectrum of (*E*)-4-(3,5-dimethoxystyryl)phenyltrifluoromethanesulfonate (S1-4n)



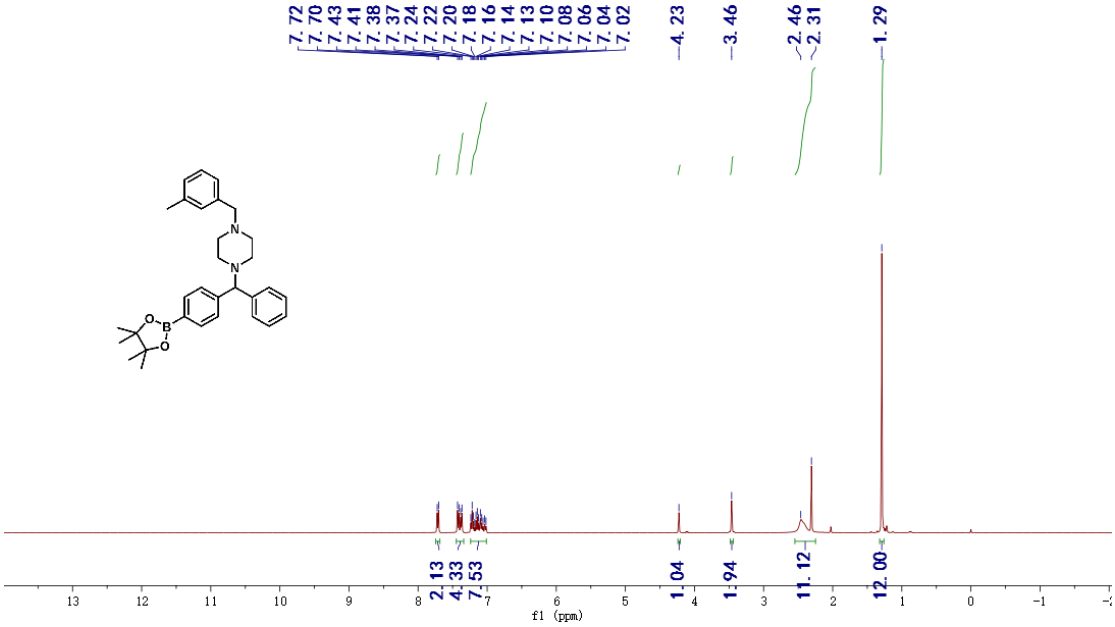
^{1}H NMR spectrum of (*E*)-2-(4-(3,5-dimethoxystyryl)phenyl)-4,4,5,5 -tetramethyl-1,3,2-dioxaborolane(S2-4n)



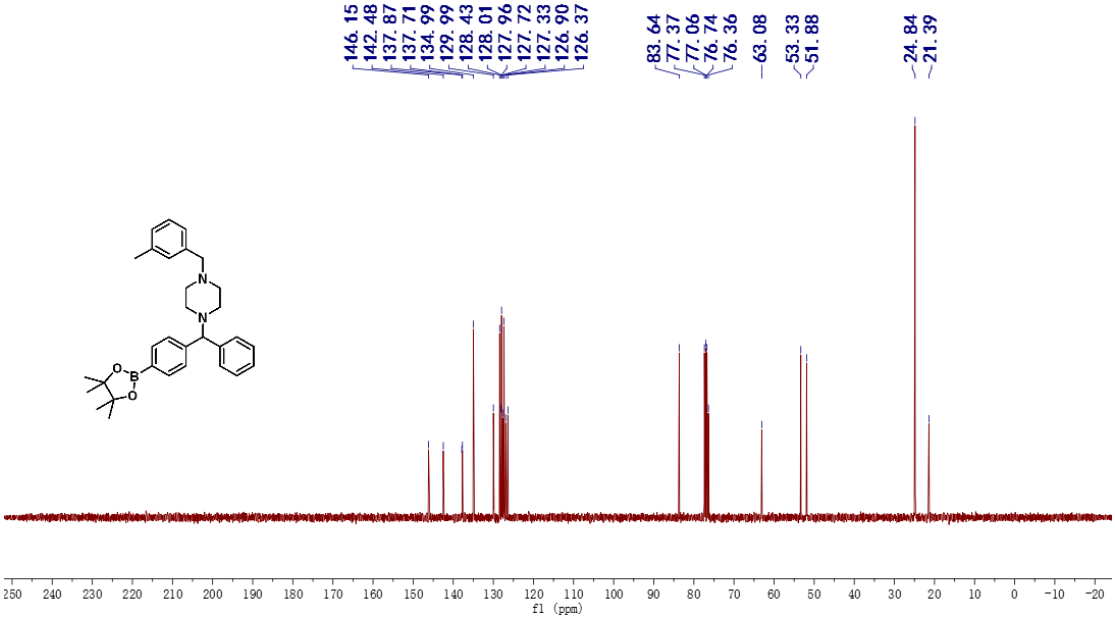
^{13}C NMR spectrum of (*E*)-2-(4-(3,5-dimethoxystyryl)phenyl)-4,4,5,5-tetramethyl -1,3,2-dioxaborolane(S2-4n)



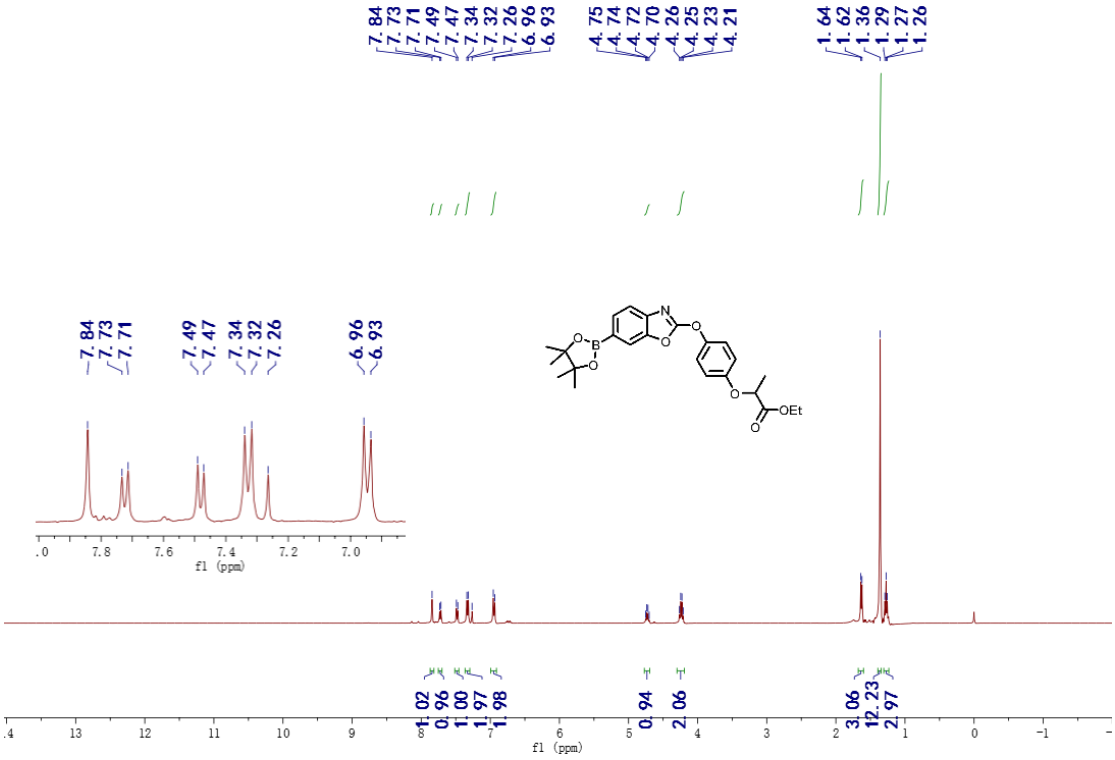
^{1}H NMR spectrum of 1-(3-methylbenzyl)-4-(phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)- phenyl)methyl)piperazine (S1-4p)



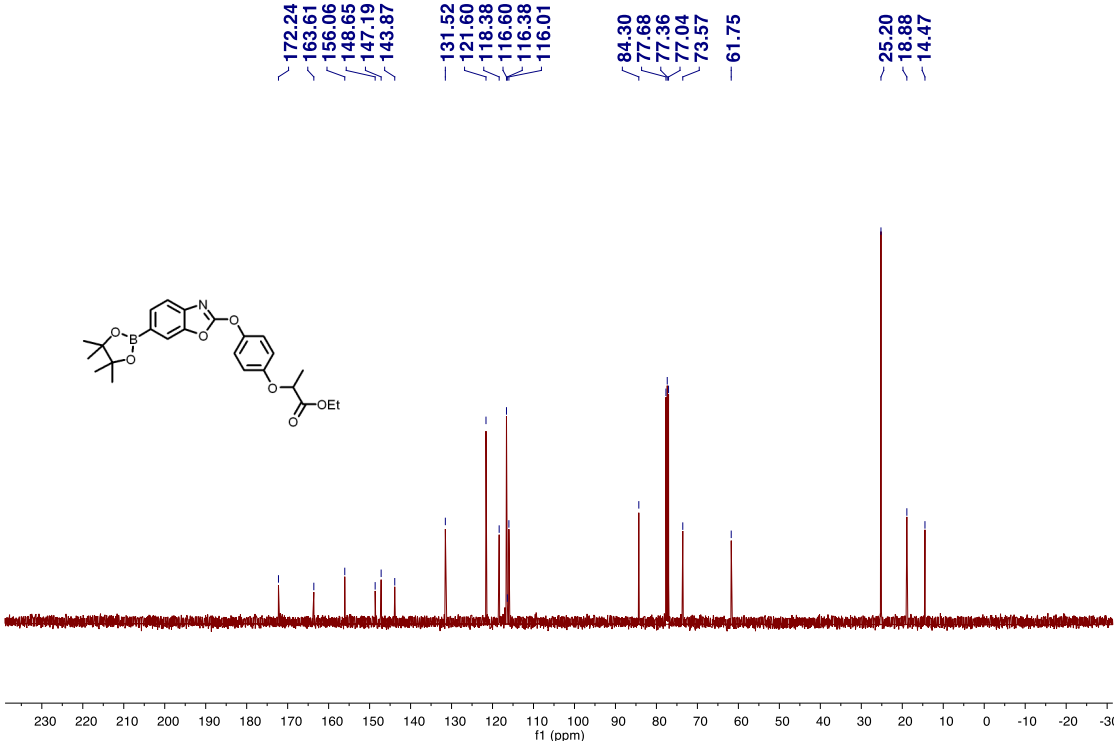
^{13}C NMR spectrum of 1-(3-methylbenzyl)-4-(phenyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)- phenyl)methyl)piperazine (S1-4p)



^{1}H NMR spectrum of ethyl-2-(4-((6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[d]oxazol-2-yl)oxy)phenoxy)propanoate (S1-4q)



^{13}C NMR spectrum of ethyl-2-(4-((6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[d]oxazol-2-yl)oxy)phenoxy)propanoate (S1-4q)



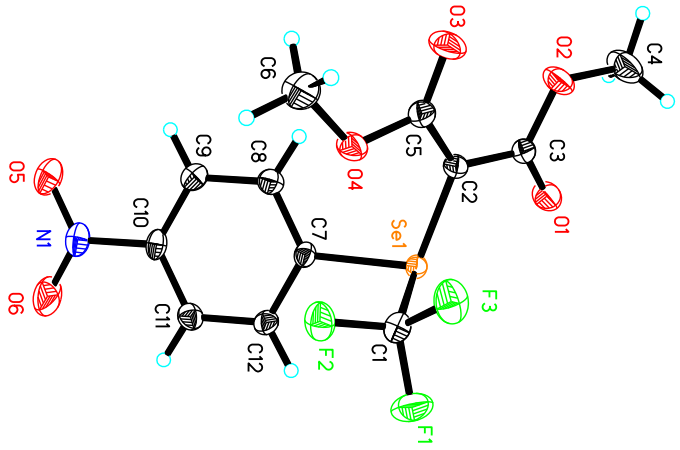


Figure S1. X-ray structure of reagent 1a.

Table S1. Crystal data and structure refinement for cd16760.

Identification code	cd16760	
Empirical formula	C12 H10 F3 N O6 Se	
Formula weight	400.17	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.809(8) Å	α= 66.084(14)°.
	b = 9.877(8) Å	β= 65.463(14)°.
	c = 9.925(8) Å	γ = 64.347(15)°.
Volume	758.0(10) $Å^3$	
Z	2	
Density (calculated)	1.753 Mg/m^3	
Absorption coefficient	2.539 mm^{-1}	
F(000)	396	
Crystal size	0.200 x 0.160 x 0.100 mm^3	
Theta range for data collection	2.346 to 25.497°.	
Index ranges	-11<=h<=8, -11<=k<=8, -12<=l<=11	
Reflections collected	4158	
Independent reflections	2778 [R(int) = 0.0283]	
Completeness to theta = 25.242°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.4196	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2778 / 0 / 210	
Goodness-of-fit on F^2	1.001	
Final R indices [I>2sigma(I)]	R1 = 0.0435, wR2 = 0.0930	
R indices (all data)	R1 = 0.0583, wR2 = 0.0982	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.051 and -0.447 $e.Å^{-3}$	

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for cd16760. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Se(1)	8580(1)	9123(1)	6836(1)	28(1)
F(1)	5884(4)	11341(3)	6137(3)	66(1)
F(2)	5331(3)	10033(3)	8487(3)	51(1)
F(3)	5835(3)	9016(4)	6728(3)	60(1)
N(1)	7901(5)	10515(5)	12623(4)	45(1)
O(1)	11232(4)	7382(4)	4920(3)	50(1)
O(2)	11056(4)	4969(3)	6097(4)	55(1)
O(3)	8583(4)	4625(3)	8705(4)	59(1)
O(4)	7054(4)	6828(3)	9400(3)	44(1)
O(5)	8217(5)	9412(5)	13721(4)	73(1)
O(6)	7496(6)	11858(5)	12595(4)	83(1)
C(1)	6221(6)	9922(5)	7096(5)	39(1)
C(2)	9160(5)	6978(4)	7193(4)	32(1)
C(3)	10546(6)	6496(5)	5976(5)	36(1)
C(4)	12437(8)	4464(6)	4873(6)	73(2)
C(5)	8289(5)	6017(5)	8447(5)	37(1)
C(6)	6253(7)	5935(6)	10822(6)	66(2)
C(7)	8344(5)	9497(4)	8722(4)	29(1)
C(8)	8789(5)	8279(5)	9945(5)	33(1)
C(9)	8650(5)	8609(5)	11243(5)	36(1)
C(10)	8058(5)	10146(5)	11248(4)	31(1)
C(11)	7677(5)	11384(5)	9999(5)	35(1)
C(12)	7823(5)	11050(5)	8708(4)	33(1)

Table S3. Bond lengths [Å] and angles [°] for cd16760.

Se(1)-C(2)	1.858(4)
Se(1)-C(7)	1.954(4)
Se(1)-C(1)	2.033(5)
F(1)-C(1)	1.326(5)
F(2)-C(1)	1.311(5)
F(3)-C(1)	1.324(5)
N(1)-O(6)	1.201(5)
N(1)-O(5)	1.223(5)
N(1)-C(10)	1.483(5)
O(1)-C(3)	1.223(5)
O(2)-C(3)	1.338(5)
O(2)-C(4)	1.449(6)
O(3)-C(5)	1.213(5)
O(4)-C(5)	1.352(5)
O(4)-C(6)	1.434(5)
C(2)-C(5)	1.429(6)
C(2)-C(3)	1.440(6)
C(4)-H(4A)	0.9600
C(4)-H(4B)	0.9600
C(4)-H(4C)	0.9600
C(6)-H(6A)	0.9600
C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600
C(7)-C(8)	1.382(6)
C(7)-C(12)	1.387(5)
C(8)-C(9)	1.393(6)
C(8)-H(8)	0.9300
C(9)-C(10)	1.372(6)
C(9)-H(9)	0.9300
C(10)-C(11)	1.390(6)
C(11)-C(12)	1.386(5)
C(11)-H(11)	0.9300
C(12)-H(12)	0.9300
C(2)-Se(1)-C(7)	107.55(17)
C(2)-Se(1)-C(1)	104.85(19)

C(7)-Se(1)-C(1)	94.69(17)
O(6)-N(1)-O(5)	123.8(4)
O(6)-N(1)-C(10)	118.9(4)
O(5)-N(1)-C(10)	117.2(4)
C(3)-O(2)-C(4)	115.2(4)
C(5)-O(4)-C(6)	116.7(3)
F(2)-C(1)-F(3)	108.6(4)
F(2)-C(1)-F(1)	107.4(4)
F(3)-C(1)-F(1)	108.1(4)
F(2)-C(1)-Se(1)	114.1(3)
F(3)-C(1)-Se(1)	110.5(3)
F(1)-C(1)-Se(1)	107.9(3)
C(5)-C(2)-C(3)	127.0(4)
C(5)-C(2)-Se(1)	123.8(3)
C(3)-C(2)-Se(1)	109.1(3)
O(1)-C(3)-O(2)	121.7(4)
O(1)-C(3)-C(2)	124.0(4)
O(2)-C(3)-C(2)	114.4(4)
O(2)-C(4)-H(4A)	109.5
O(2)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
O(2)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
O(3)-C(5)-O(4)	121.1(4)
O(3)-C(5)-C(2)	126.6(4)
O(4)-C(5)-C(2)	112.3(3)
O(4)-C(6)-H(6A)	109.5
O(4)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
O(4)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(8)-C(7)-C(12)	122.4(4)
C(8)-C(7)-Se(1)	121.4(3)
C(12)-C(7)-Se(1)	116.0(3)
C(7)-C(8)-C(9)	119.2(4)
C(7)-C(8)-H(8)	120.4

C(9)-C(8)-H(8)	120.4
C(10)-C(9)-C(8)	117.8(4)
C(10)-C(9)-H(9)	121.1
C(8)-C(9)-H(9)	121.1
C(9)-C(10)-C(11)	123.5(3)
C(9)-C(10)-N(1)	118.4(4)
C(11)-C(10)-N(1)	118.0(4)
C(12)-C(11)-C(10)	118.4(4)
C(12)-C(11)-H(11)	120.8
C(10)-C(11)-H(11)	120.8
C(11)-C(12)-C(7)	118.5(4)
C(11)-C(12)-H(12)	120.8
C(7)-C(12)-H(12)	120.8

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for cd16760. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Se(1)	36(1)	26(1)	23(1)	-7(1)	-7(1)	-12(1)
F(1)	61(2)	51(2)	62(2)	2(2)	-31(2)	-3(2)
F(2)	35(2)	70(2)	47(2)	-27(1)	-4(1)	-13(1)
F(3)	52(2)	83(2)	70(2)	-37(2)	-23(2)	-22(2)
N(1)	50(3)	61(3)	35(2)	-18(2)	-6(2)	-27(2)
O(1)	57(2)	39(2)	42(2)	-12(2)	2(2)	-20(2)
O(2)	62(2)	32(2)	48(2)	-17(1)	6(2)	-10(2)
O(3)	70(3)	29(2)	58(2)	-10(2)	0(2)	-19(2)
O(4)	48(2)	32(2)	41(2)	-9(1)	0(2)	-16(1)
O(5)	97(3)	82(3)	43(2)	-21(2)	-34(2)	-14(2)
O(6)	151(4)	69(3)	48(2)	-23(2)	-23(2)	-51(3)
C(1)	45(3)	43(3)	32(2)	-10(2)	-12(2)	-16(2)
C(2)	41(3)	26(2)	28(2)	-7(2)	-7(2)	-13(2)
C(3)	51(3)	29(2)	30(2)	-8(2)	-15(2)	-11(2)
C(4)	79(5)	45(3)	65(4)	-27(3)	13(3)	-14(3)
C(5)	45(3)	33(2)	33(2)	-7(2)	-11(2)	-14(2)
C(6)	63(4)	58(3)	48(3)	-9(3)	18(3)	-31(3)
C(7)	34(3)	32(2)	22(2)	-7(2)	-4(2)	-16(2)
C(8)	34(3)	32(2)	37(2)	-10(2)	-13(2)	-9(2)
C(9)	37(3)	40(2)	33(2)	-6(2)	-11(2)	-18(2)
C(10)	30(3)	48(3)	26(2)	-15(2)	-3(2)	-20(2)
C(11)	39(3)	33(2)	37(2)	-12(2)	-7(2)	-15(2)
C(12)	41(3)	29(2)	27(2)	-4(2)	-9(2)	-15(2)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for cd16760.

	x	y	z	U(eq)
H(4A)	12180	4930	3917	110
H(4B)	12775	3347	5101	110
H(4C)	13273	4780	4792	110
H(6A)	5689	5488	10615	99
H(6B)	5521	6604	11475	99
H(6C)	7012	5114	11328	99
H(8)	9177	7251	9901	40
H(9)	8948	7814	12079	43
H(11)	7333	12412	10029	42
H(12)	7577	11849	7852	39

Table S6. Torsion angles [°] for cd16760.

C(7)-Se(1)-C(2)-C(5)	54.4(4)
C(1)-Se(1)-C(2)-C(5)	-45.5(4)
C(7)-Se(1)-C(2)-C(3)	-128.5(3)
C(1)-Se(1)-C(2)-C(3)	131.6(3)
C(4)-O(2)-C(3)-O(1)	-1.6(7)
C(4)-O(2)-C(3)-C(2)	179.3(5)
C(5)-C(2)-C(3)-O(1)	179.1(5)
Se(1)-C(2)-C(3)-O(1)	2.1(6)
C(5)-C(2)-C(3)-O(2)	-1.8(7)
Se(1)-C(2)-C(3)-O(2)	-178.8(3)
C(6)-O(4)-C(5)-O(3)	8.2(7)
C(6)-O(4)-C(5)-C(2)	-170.4(4)
C(3)-C(2)-C(5)-O(3)	0.9(8)
Se(1)-C(2)-C(5)-O(3)	177.4(4)
C(3)-C(2)-C(5)-O(4)	179.4(4)
Se(1)-C(2)-C(5)-O(4)	-4.0(6)
C(12)-C(7)-C(8)-C(9)	2.8(6)
Se(1)-C(7)-C(8)-C(9)	177.8(3)
C(7)-C(8)-C(9)-C(10)	0.5(6)
C(8)-C(9)-C(10)-C(11)	-3.7(6)
C(8)-C(9)-C(10)-N(1)	179.9(4)
O(6)-N(1)-C(10)-C(9)	174.5(4)
O(5)-N(1)-C(10)-C(9)	-4.5(6)
O(6)-N(1)-C(10)-C(11)	-2.1(6)
O(5)-N(1)-C(10)-C(11)	178.9(4)
C(9)-C(10)-C(11)-C(12)	3.5(7)
N(1)-C(10)-C(11)-C(12)	179.9(4)
C(10)-C(11)-C(12)-C(7)	-0.1(6)
C(8)-C(7)-C(12)-C(11)	-3.0(6)
Se(1)-C(7)-C(12)-C(11)	-178.2(3)

Symmetry transformations used to generate equivalent atoms:

Table S7. Hydrogen bonds for cd16760 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(9)-H(9)...O(2)#1	0.93	2.61	3.425(6)	146.9
C(11)-H(11)...O(3)#2	0.93	2.58	3.297(6)	134.1
C(12)-H(12)...O(1)#3	0.93	2.43	3.190(5)	138.6

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+1,-z+2 #2 x,y+1,z #3 -x+2,-y+2,-z+1