Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

The Stability and reactivity of Tri-, Di- and Monofluoromethyl/Methoxy/Methylthio Groups on Arenes under Acidic or Basic Conditions

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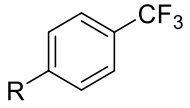
1. Detailed Data of Experiments Results

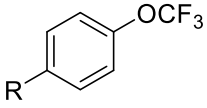
Table S1: The results of CF_3-containing substrates under acidic or basic conditions.



entry	R	Acid/ Base	*T*(°C)	*t* (h)	Solvent	Yield (%)	Recovery (%)[b]
1	H	TfOH	r.t.	24	PhMe	**2a**, 51%; **3a**, 32%	
2	H	TfOH	r.t.	24	HAc	-	88
3	H	TFA	r.t.	10	PhMe	-	100
4	H	TFA	60	10	PhMe	-	100
5	H	KHMDS	r.t.	10	THF	-	100
6	OCH_3	TfOH	r.t.	24	PhMe	**2b**, 41%; **3b**, 26%	
7	OCH_3	TFA	r.t.	10	PhMe	-	97
8	OCH_3	TFA	60	10	PhMe	-	97
9	OCH_3	KHMDS	r.t.	10	THF	-	100
10	$PhSO_2$	TfOH	r.t.	10	PhMe		100
11	$PhSO_2$	TfOH	80	10	PhMe	-	93
12	$PhSO_2$	TfOH	r.t.	10	HAc	-	100
13	$PhSO_2$	TfOH	80	10	HAc	-	100
14	$PhSO_2$	KHMDS	r.t.	10	THF	-	76
15	$PhSO_2$	^{t}BuOK	r.t.	10	THF	-	93
16	$PhSO_2$	MeONa	r.t.	10	THF	-	100

Unless otherwise noted, all reactions were performed by mixing the substrates (0.2 mmol) and the acid (10.0 equiv) or the base (5.0 equiv) in 3.0 mL solvent and yields are of isolated products. a) The yield was determined by GC-MS. b) All the recovered rates were determined by ^{19}F NMR spectroscopy.

Table S2: The results of OCF_3-containing substrates under acidic or basic conditions.

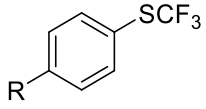


entry	R	acid/ base	*T* (°C)	*t* (h)	solvent	Yield (%)	Recovery (%)[b]
1	H	TfOH	r.t.	10	PhMe		100
2	H	TfOH	80	10	PhMe		98
3	H	TfOH	r.t.	10	HAc		87
4	H	TfOH	80	10	HAc		83
5	H	KHMDS	r.t.	10	THF		100
6	H	TfOH	r.t.	10	PhMe		100

7	OCH_3	TfOH	r.t.	10	HAc	100
8	OCH_3	TfOH	80	10	HAc	100
9	OCH_3	KHMDS	50	10	THF	98
10	$PhSO_2$	TfOH	r.t.	10	PhMe	100
11	$PhSO_2$	TfOH	80	10	PhMe	97
12	$PhSO_2$	TfOH	r.t.	10	HAc	100
13	$PhSO_2$	TfOH	80	10	HAc	100
14	$PhSO_2$	KHMDS	r.t.	10	THF	98

Unless otherwise noted, all reactions were performed by mixing the substrates (0.2 mmol) and the acid (10.0 equiv) or the base (5.0 equiv) in 3.0 mL solvent and yields are of isolated products. a) The yield was determined by GC-MS. b) All the recovered rates were determined by ^{19}F NMR spectroscopy.

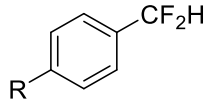
Table S3: The results of SCF_3-containing substrates under acidic or basic conditions.



entry	R	acid/ base	*T* (°C)	*t* (h)	solvent	Yield (%)	Recovery (%)[b]
1	H	TfOH	r.t.	10	PhMe		91
2	H	TfOH	80	10	PhMe	**6a**, 22%[a] **7**, 31%[a]	63
3	H	TfOH	r.t.	10	HAc		94
4	H	TfOH	80	10	HAc		94
5	H	KHMDS	r.t.	10	THF		100
6	H	^{t}BuOK	r.t.	10	THF		93
7	H	^{t}BuOK	50	10	THF		93
8	OCH_3	TfOH	r.t.	10	PhMe		100
9	OCH_3	TfOH	80	10	PhMe	**6b**, 52%[a] **7**, 40%[a]	35
10	OCH_3	TfOH	r.t.	10	HAc		100
11	OCH_3	TfOH	80	10	HAc		100
12	OCH_3	KHMDS	r.t.	10	THF	**8b**, 8%[a]	88
13	OCH_3	^{t}BuOK	r.t.	10	THF		65
14	OCH_3	^{t}BuOK	50	10	THF		45
15	OCH_3	MeONa	r.t.	10	THF		95
16	OCH_3	MeONa	60	10	THF		94
17	$PhSO_2$	TfOH	r.t.	10	PhMe		100
18	$PhSO_2$	TfOH	80	10	PhMe		97
19	$PhSO_2$	KHMDS	r.t.	10min	THF		0
20	$PhSO_2$	^{t}BuOK	r.t.	10min	THF		0
21	$PhSO_2$	MeONa	r.t.	10	THF		93

Unless otherwise noted, all reactions were performed by mixing the substrates (0.2 mmol) and the acid (10.0 equiv) or the base (5.0 equiv) in 3.0 mL solvent and yields are of isolated products. a) The yield was determined by GC-MS. b) All the recovered rates were determined by ^{19}F NMR spectroscopy.

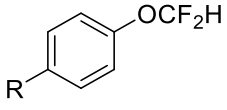
Table S4: The results of CF_2H-containing substrates under acidic or basic conditions.



entry	R	acid/ base	*T* (°C)	*t*(h)	solvent	Yield (%)	Recovery (%)[b]
1	H	TfOH	r.t.	10min	PhMe		0
2	H	TFA	r.t.	10	PhMe	**10a**, 12%[a]	92
3	H	TFA	60	10	PhMe		92
4	H	KHMDS	r.t.	10	THF		98
5	OCH_3	TfOH	r.t.	10min	PhMe		0
6	OCH_3	TFA	r.t.	5	*p*-Xylene	**10b**, 61%	0
7	OCH_3	HAc	r.t.	10	PhMe		94
8	OCH_3	HAc	50	10	PhMe		91
9	OCH_3	KHMDS	r.t.	10	THF		100
10	$PhSO_2$	TfOH	70	10	PhMe	**11**, 89%	0
11	$PhSO_2$	TFA	r.t	10	PhMe		93
12	$PhSO_2$	TFA	60	10	PhMe		93
13	$PhSO_2$	KHMDS	r.t.	10min	THF		0
14	$PhSO_2$	^{t}BuOK	r.t.	10	THF		100
15	$PhSO_2$	^{t}BuOK	r.t.	10	THF		100

Unless otherwise noted, all reactions were performed by mixing the substrates (0.2 mmol) and the acid (10.0 equiv) or the base (5.0 equiv) in 3.0 mL solvent and yields are of isolated products. a) The yield was determined by GC-MS. b) All the recovered rates were determined by ^{19}F NMR spectroscopy.

Table S5: The results of OCF_2H-containing substrates under acidic or basic conditions.

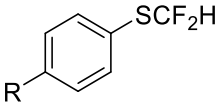


entry	R	acid/ base	*T* (°C)	*t*(h)	solvent	Yield (%)	Recovery (%)[b]
1	H	TfOH	r.t.	1	*p*-Xylene	**13a**, 19%[a] **14**, 41%	0
2	H	TFA	r.t.	10	PhMe		100
3	H	TFA	60	10	PhMe		100
4	H	KHMDS	r.t.	1	THF		0
5	H	^{t}BuOK	r.t.	1	THF	**13a**, 32%	0

6	H	MeONa	r.t	10	THF		93
7	OCH_3	TfOH	r.t.	1	*p*-Xylene	**13b**, 35%	0
						14, 29%	
8	OCH_3	TFA	r.t.	10	PhMe		100
9	OCH_3	TFA	60	10	PhMe		100
10	OCH_3	KHMDS	r.t.	10	THF		0
11	OCH_3	^{t}BuOK	r.t.	1	THF	**13b**, 60%	0
12	OCH_3	MeONa	r.t.	10	THF		76
13	$PhSO_2$	TfOH	r.t.	1	*p*-Xylene	**13c**, 87%	0
						14,74%	
14	$PhSO_2$	TFA	r.t.	10	PhMe		100
15	$PhSO_2$	TFA	60	10	PhMe		100
16	$PhSO_2$	KHMDS	r.t.	10	THF		0
17	$PhSO_2$	^{t}BuOK	r.t.	1	THF	**13c**, 89%	0
18	$PhSO_2$	MeONa	r.t.	10	THF		43

Unless otherwise noted, all reactions were performed by mixing the substrates (0.2 mmol) and the acid (10.0 equiv) or the base (5.0 equiv) in 3.0 mL solvent and yields are of isolated products. a) The yield was determined by GC-MS. b) All the recovered rates were determined by ^{19}F NMR spectroscopy.

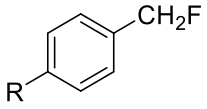
Table S6: The results of SCF_2H-containing substrates under acidic or basic conditions.



entry	R	acid/ base	*T*(°C)	*t*(h)	solvent	Yield (%)	Recovery (%)[b]
1	H	TfOH	r.t.	1	*p*-Xylene	**6a**,12%[a]	0
						14, 38%[c]	
2	H	TFA	r.t.	10	PhMe		90
3	H	TFA	60	10	PhMe		90
4	H	KHMDS	r.t.	10min	THF		0
5	H	^{t}BuOK	r.t.	1	THF	**8a**, 12%[a]	0
6	H	MeONa	r.t.	10	THF	**8a**, 9%[a]	82
7	OCH_3	TfOH	r.t.	1	*p*-Xylene	**6a**, trace[a]	0
						14, 30%[c]	
8	OCH_3	TFA	r.t.	10	PhMe		100
9	OCH_3	TFA	60	10	PhMe		100
10	OCH_3	KHMDS	r.t.	10	THF		0
11	OCH_3	^{t}BuOK	r.t.	1	THF	**8b**, 36%	0
12	OCH_3	MeONa	r.t.	10	THF		100
13	OCH_3	MeONa	50	10	THF		100

Unless otherwise noted, all reactions were performed by mixing the substrates (0.2 mmol) and the acid (10.0 equiv) or the base (5.0 equiv) in 3.0 mL solvent and yields are of isolated products. a) The yield was determined by GC-MS. b) All the recovered rates were determined by ^{19}F NMR spectroscopy.

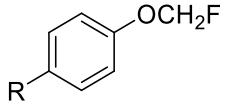
Table S7: The results of CH_2F-containing substrates under acidic or basic conditions.



entry	R	acid/ base	*T* (°C)	t(h)	solvent	Yield (%)	Recover (%)[b]
1	$PhSO_2$	TfOH	70	10	*p*-Xylene	**17**, 69%	0
2	$PhSO_2$	TFA	r.t.	10	Toluene		100
3	$PhSO_2$	TFA	60	10	Toluene		94
4	$PhSO_2$	KHMDS	r.t.	10min	THF		0
5	$PhSO_2$	^{t}BuOK	r.t.	10min	THF		48
6	$PhSO_2$	MeONa	r.t.	10	THF		100
7	$PhSO_2$	MeONa	50	10	THF		91
8	$PhSO_2$	morpholine	70	10	H_2O/*i*-PrOH	**18**, 38%	40

Unless otherwise noted, all reactions were performed by mixing the substrates (0.2 mmol) and the acid (10.0 equiv) or the base (5.0 equiv) in 3.0 mL solvent and yields are of isolated products. a) The yield was determined by GC-MS. b) All the recovered rates were determined by ^{19}F NMR spectroscopy.

Table S8: The results of OCH_2F-containing substrates under acidic or basic conditions.

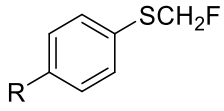


entry	R	acid/ base	*T* (°C)	t(h)	solvent	Yield (%)	Recovery (%)[b]
1	H	TFA	r.t.	1	*p*-Xylene	**20a,** 13%	0
						13a, trace[a]	
2	H	HAc	r.t.	10	Toluene		100
3	H	HAc	50	10	Toluene		100
4	H	KHMDS	r.t	10	THF		93
5	H	^{t}BuOK	r.t	10	THF		88
6	H	^{t}BuOK	50	10	THF		88
7	H	morpholine	70	10	H_2O/*i*-PrOH	**13a**, trace[a]	85
8	OCH_3	TFA	r.t.	1	*p*-Xylene	**20b,** 11%	0
						13b, 12%[a]	
9	OCH_3	HAc	r.t.	10	Toluene		100
10	OCH_3	HAc	50	10	Toluene		100
11	OCH_3	KHMDS	r.t	10	THF		100

12	OCH_3	KHMDS	50	10	THF		100
13	OCH_3	morpholine	70	10	H_2O/*i*-PrOH	**13b**, trace[a]	81
14	$PhSO_2$	TfOH	r.t.	1	*p*-Xylene	**13c,** 85%	0
						21, 53%	
15	$PhSO_2$	TFA	r.t.	10	Toluene		93
16	$PhSO_2$	TFA	60	10	Toluene		93
17	$PhSO_2$	KHMDS	r.t	10	THF		100
18	$PhSO_2$	KHMDS	50	10	THF		100
19	$PhSO_2$	morpholine	70	10	H_2O/*i*-PrOH	**13c,** 40%	42

Unless otherwise noted, all reactions were performed by mixing the substrates (0.2 mmol) and the acid (10.0 equiv) or the base (5.0 equiv) in 3.0 mL solvent and yields are of isolated products. a) The yield was determined by GC-MS. b) All the recovered rates were determined by ^{19}F NMR spectroscopy.

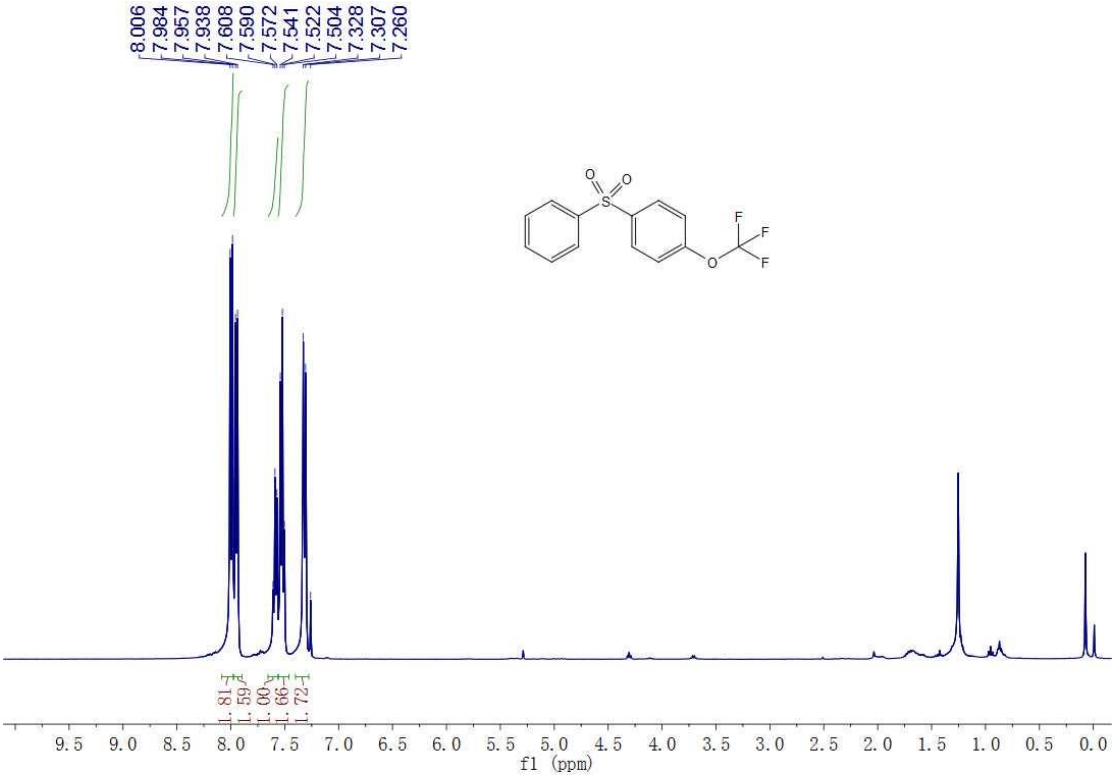
Table S9: The results of OCH_2F-containing substrates under acidic or basic conditions.



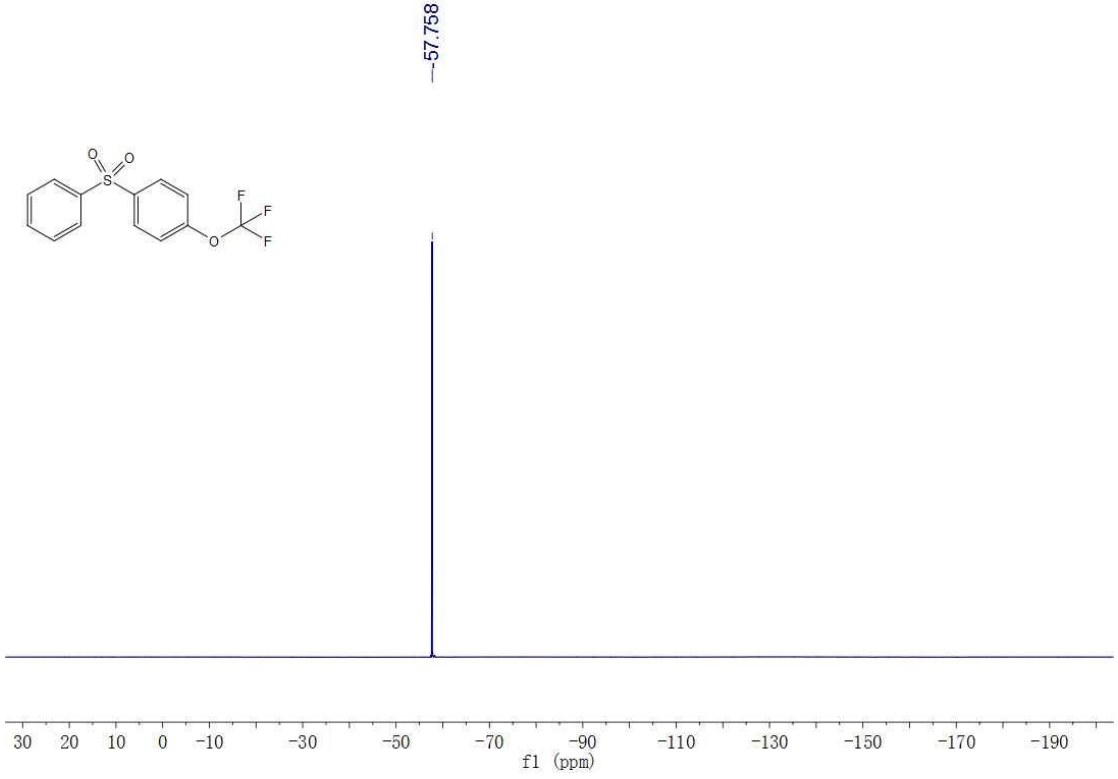
entry	R	acid/ base	*T* (°C)	t(h)	solvent	Yield (%)	Recovery (%)[b]
1	$PhSO_2$	TFA	r.t.	1	*p*-Xylene	**23**, 73%	0
2	$PhSO_2$	HAc	r.t.	10	Toluene		100
3	$PhSO_2$	HAc	50	10	Toluene		100
4	$PhSO_2$	KHMDS	r.t.	10min	THF		0
5	$PhSO_2$	^{t}BuOK	r.t.	1	THF	**24**, 71%	0
6	$PhSO_2$	MeONa	r.t.	10	THF		100
7	$PhSO_2$	MeONa	50	10	THF		91
8	$PhSO_2$	morpholine	70	10	H_2O/*i*-PrOH		87

Unless otherwise noted, all reactions were performed by mixing the substrates (0.2 mmol) and the acid (10.0 equiv) or the base (5.0 equiv) in 3.0 mL solvent and yields are of isolated products. a) The yield was determined by GC-MS. b) All the recovered rates were determined by ^{19}F NMR spectroscopy.

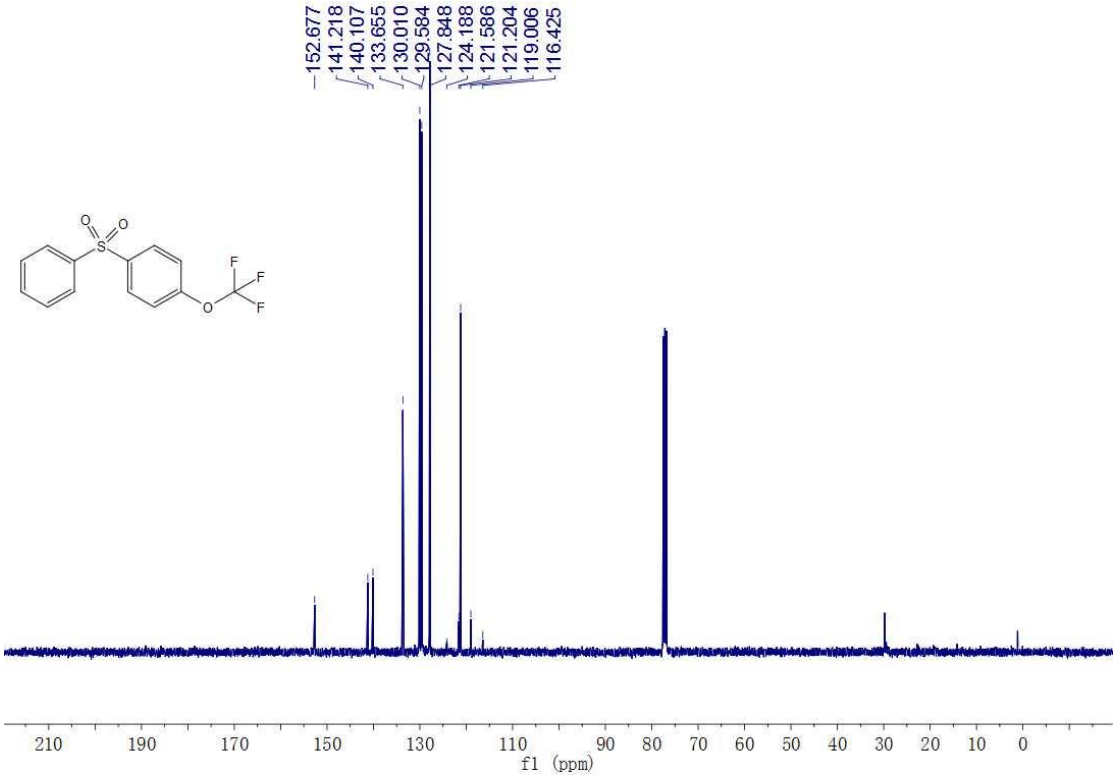
2. ^{1}H, ^{19}F and ^{13}C NMR spectra of new compounds.



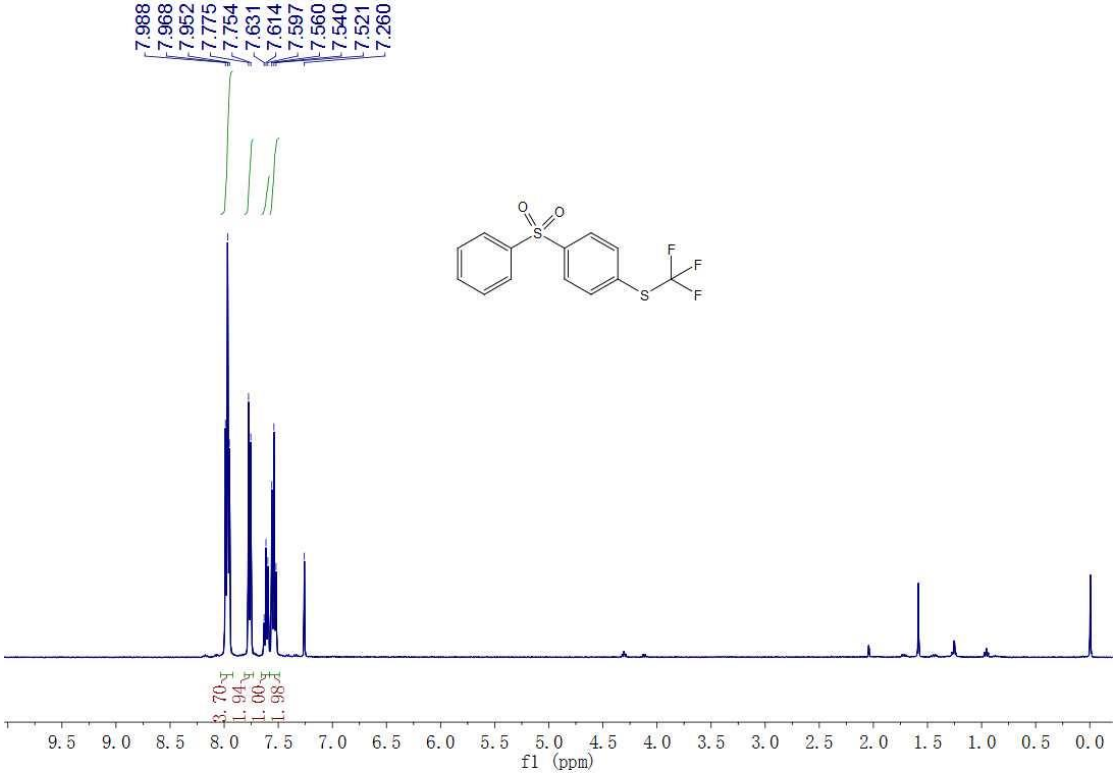
^{1}H NMR spectra of **4c** (400 MHz, $CDCl_3$)



^{19}F NMR spectra of **4c** (400 MHz, $CDCl_3$)

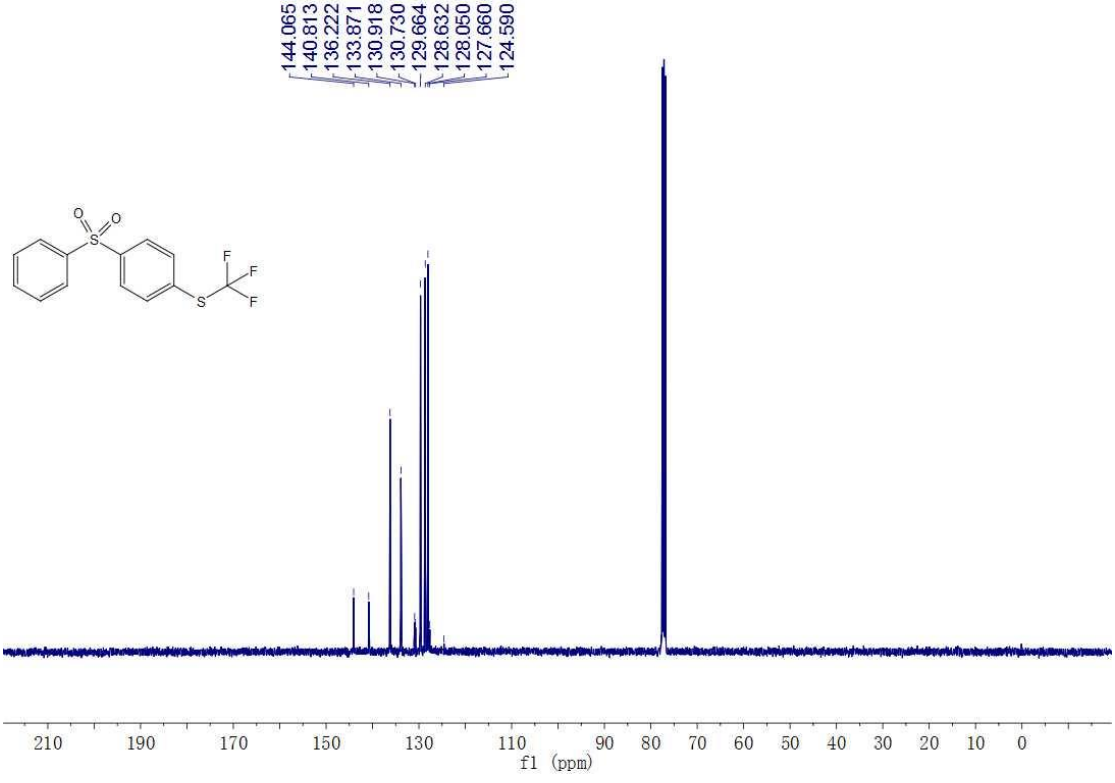


^{13}C NMR spectra of **4c** (400 MHz, $CDCl_3$)

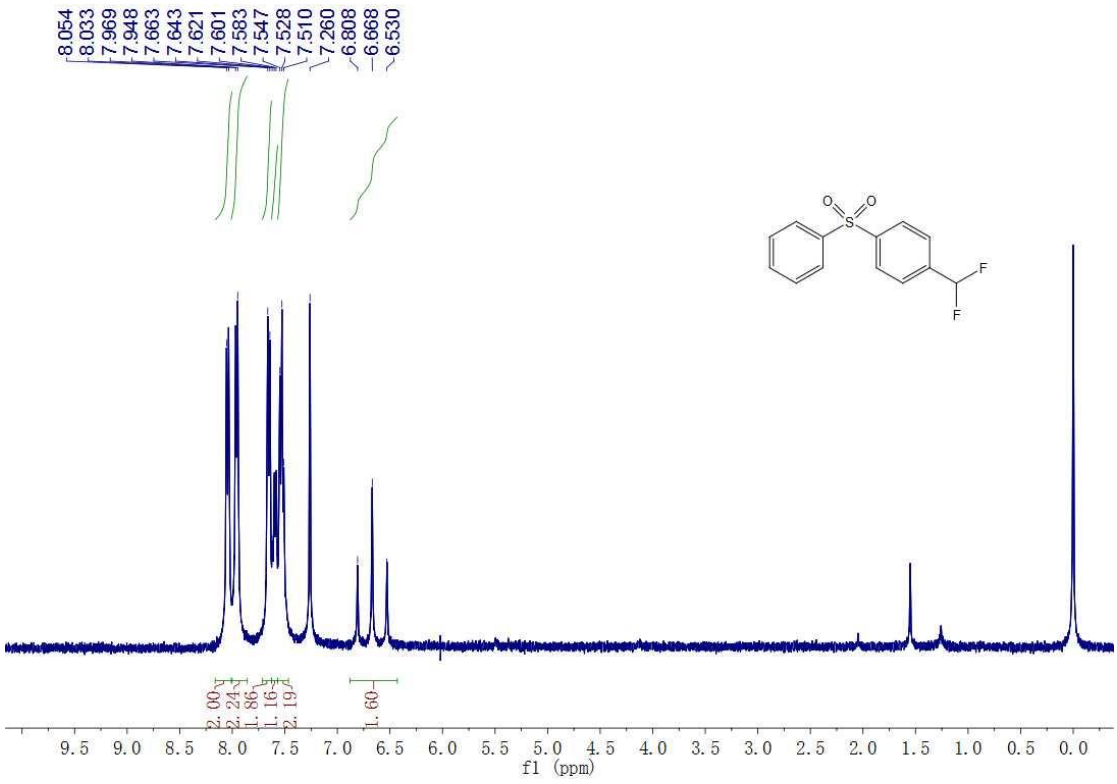


^{1}H NMR spectra of **5c** (400 MHz, $CDCl_3$)

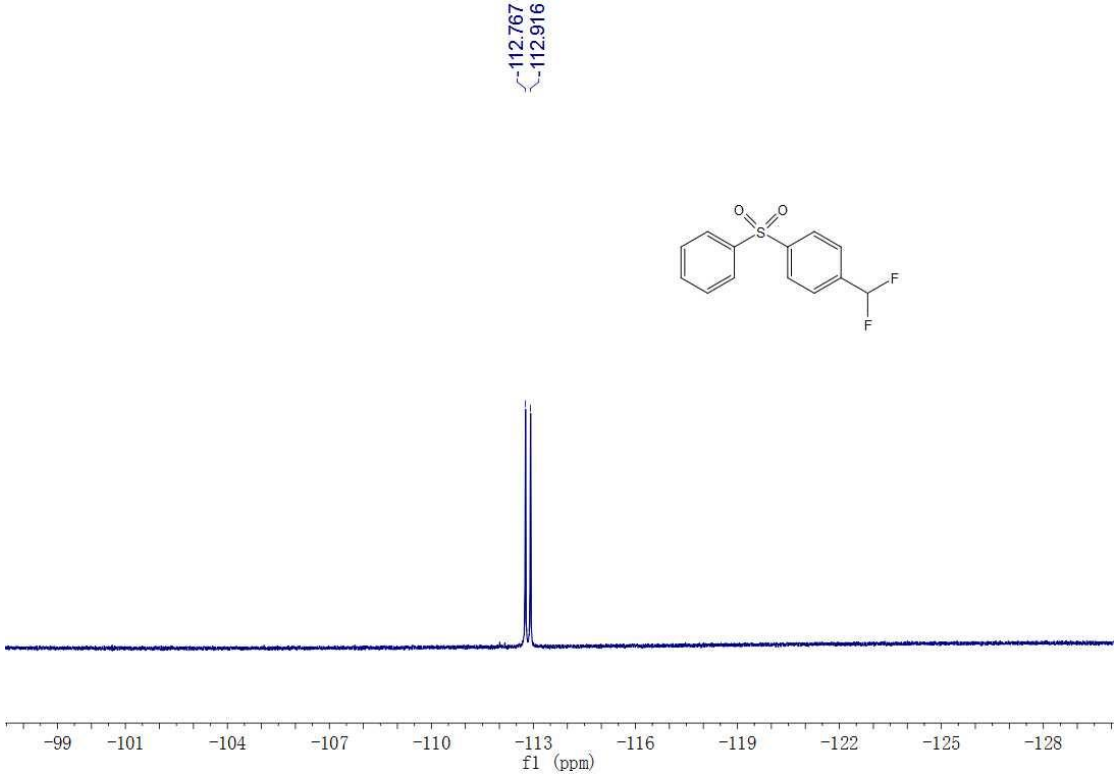
^{19}F NMR spectra of **5c** (400 MHz, $CDCl_3$)



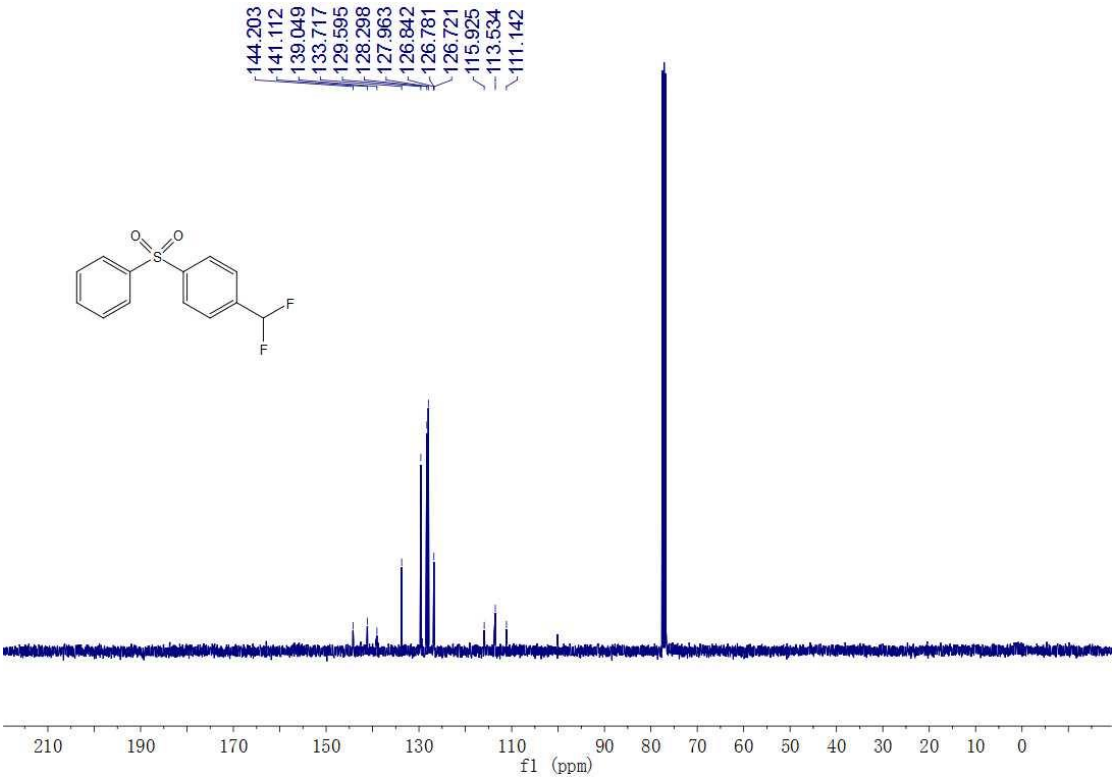
^{13}C NMR spectra of **5c** (400 MHz, $CDCl_3$)



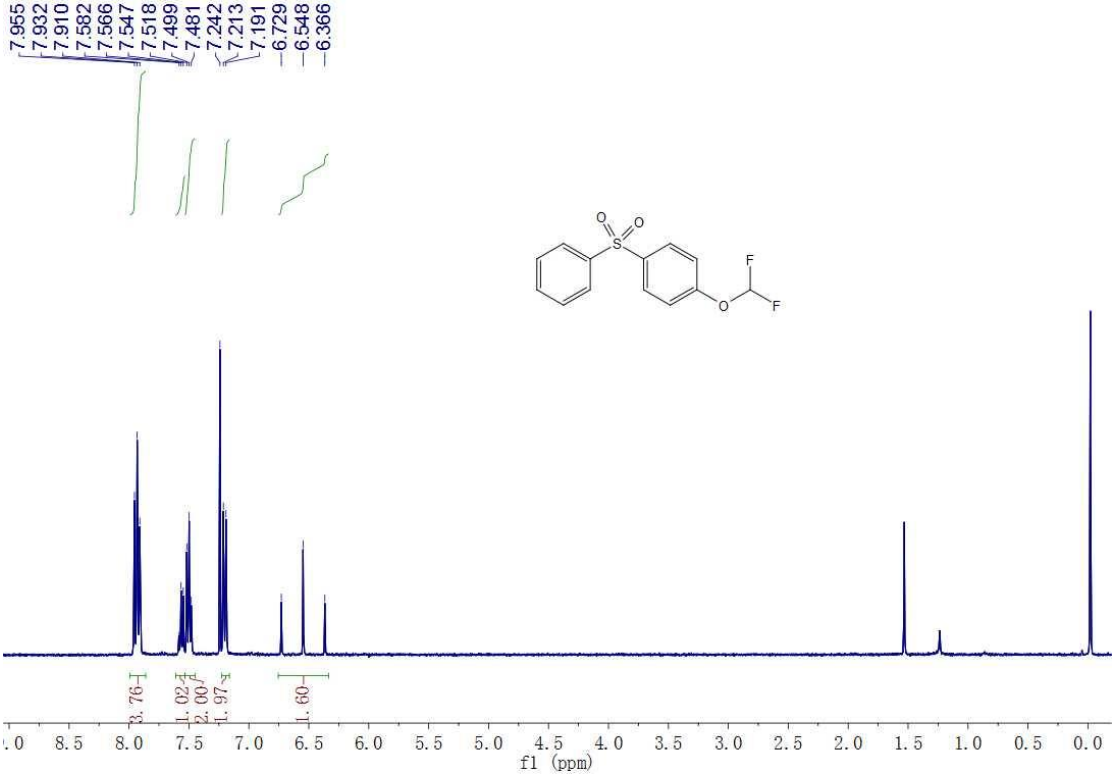
^{1}H NMR spectra of **9c** (400 MHz, $CDCl_3$)



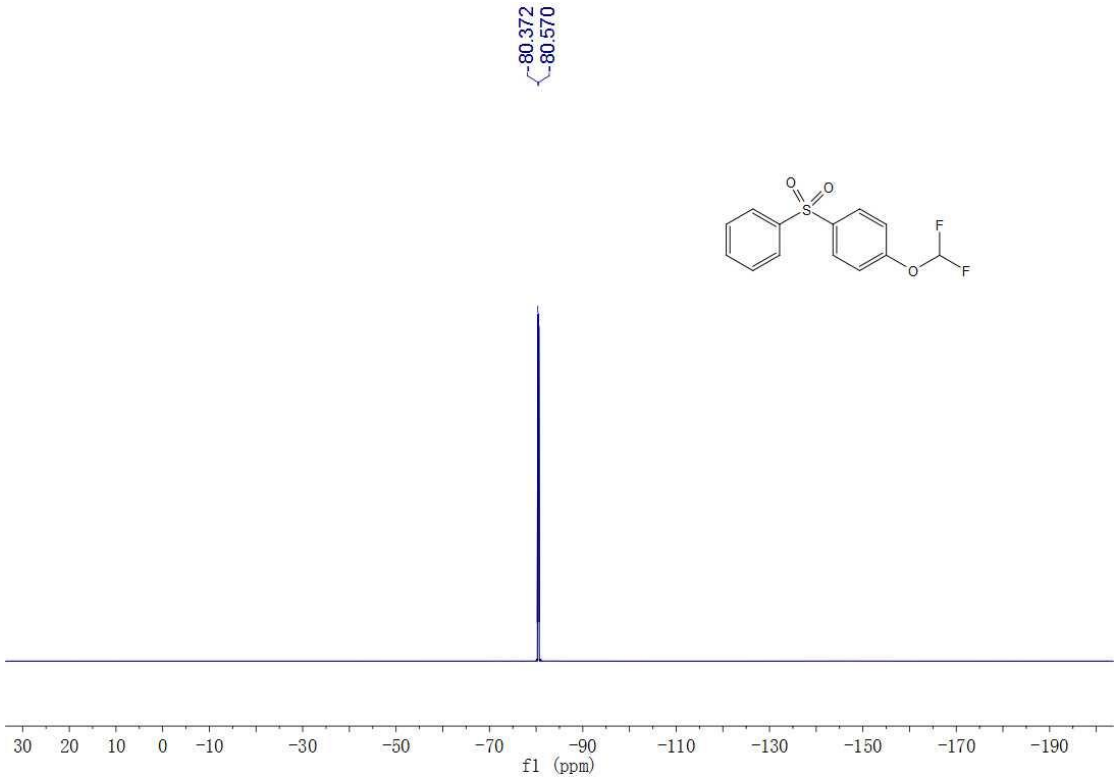
^{19}F NMR spectra of **9c** (400 MHz, $CDCl_3$)



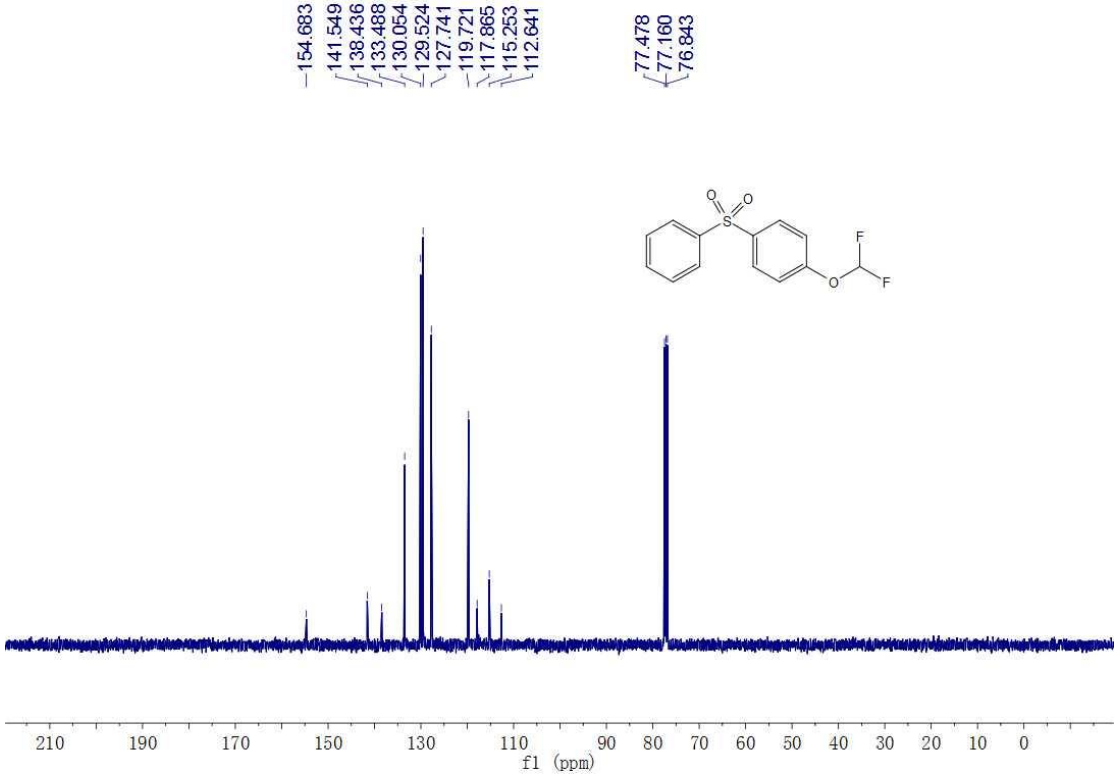
^{13}C NMR spectra of **9c** (400 MHz, $CDCl_3$)



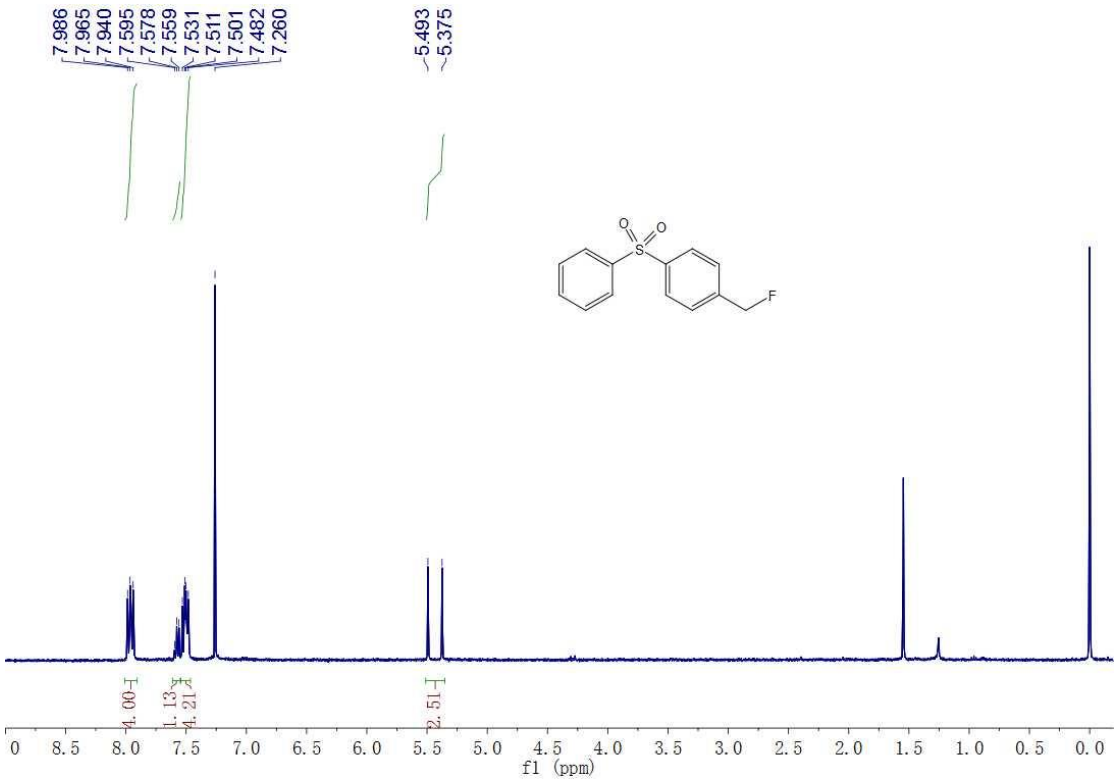
^{1}H NMR spectra of **12c** (400 MHz, $CDCl_3$)



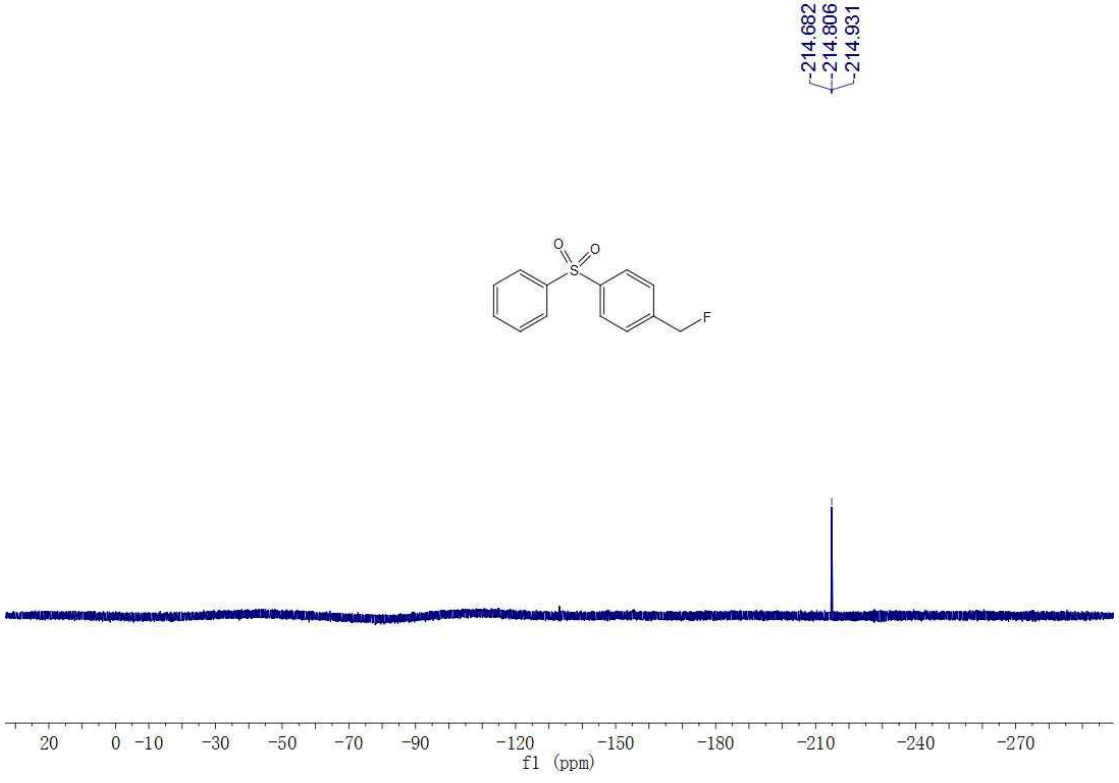
^{19}F NMR spectra of **12c** (400 MHz, $CDCl_3$)



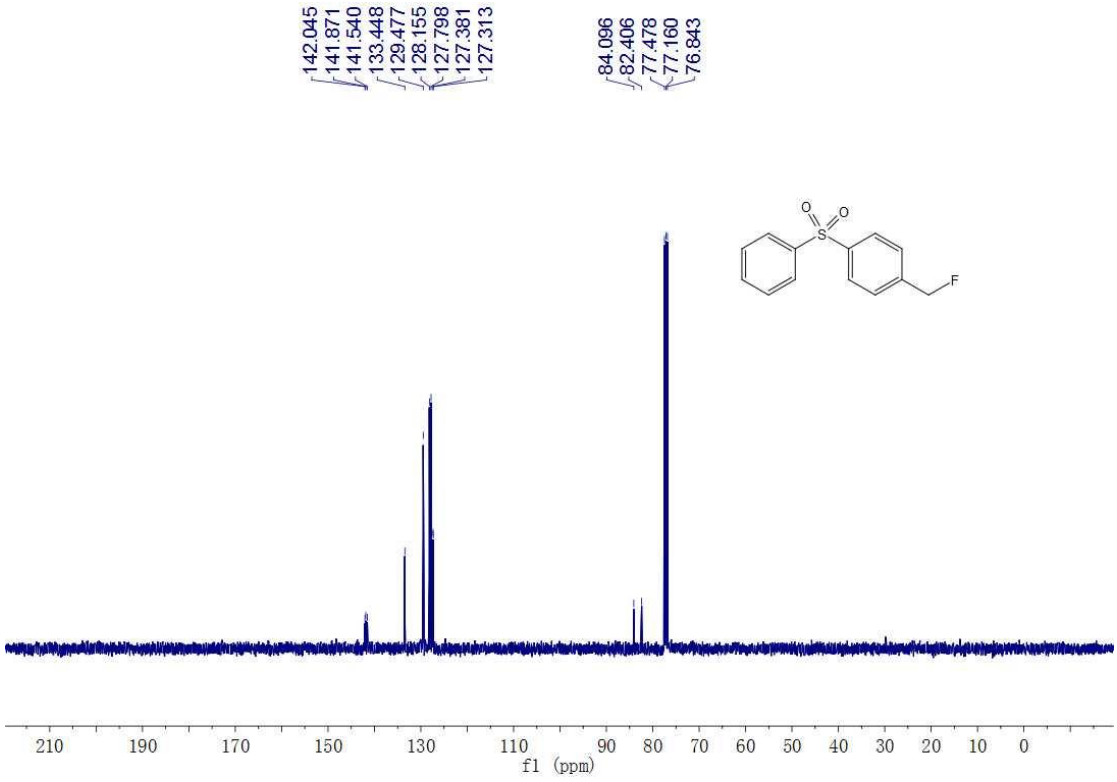
^{13}C NMR spectra of **12c** (400 MHz, $CDCl_3$)



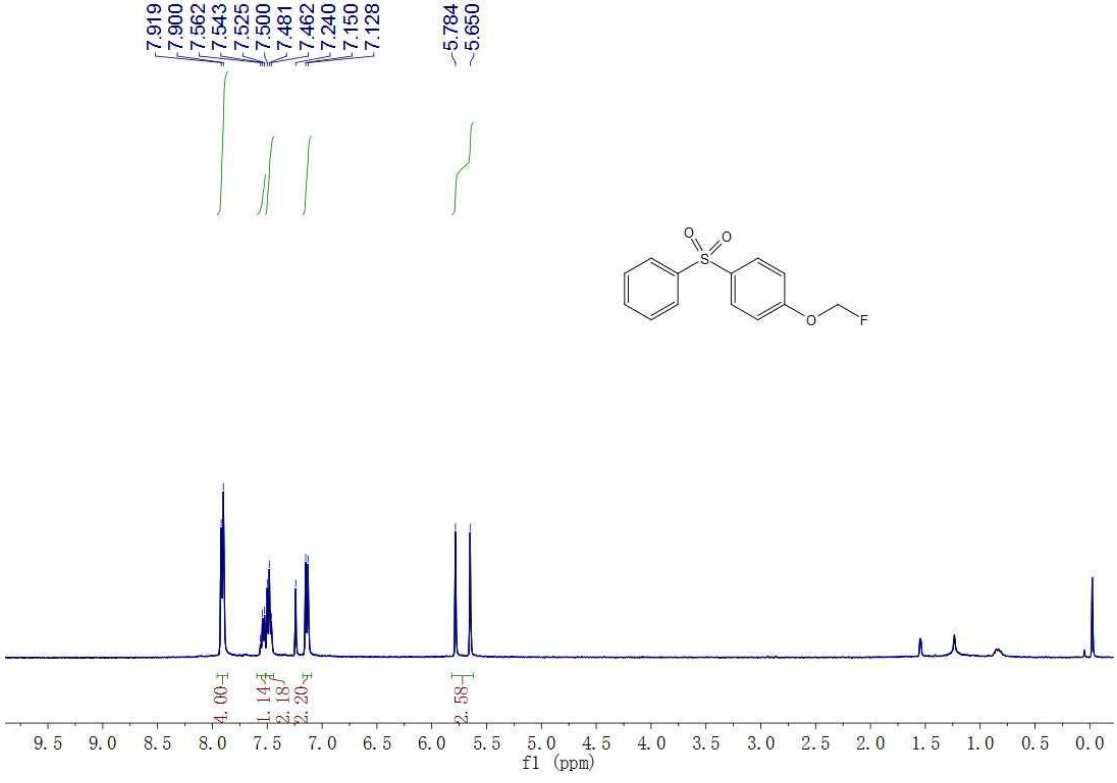
^{1}H NMR spectra of **16** (400 MHz, $CDCl_3$)



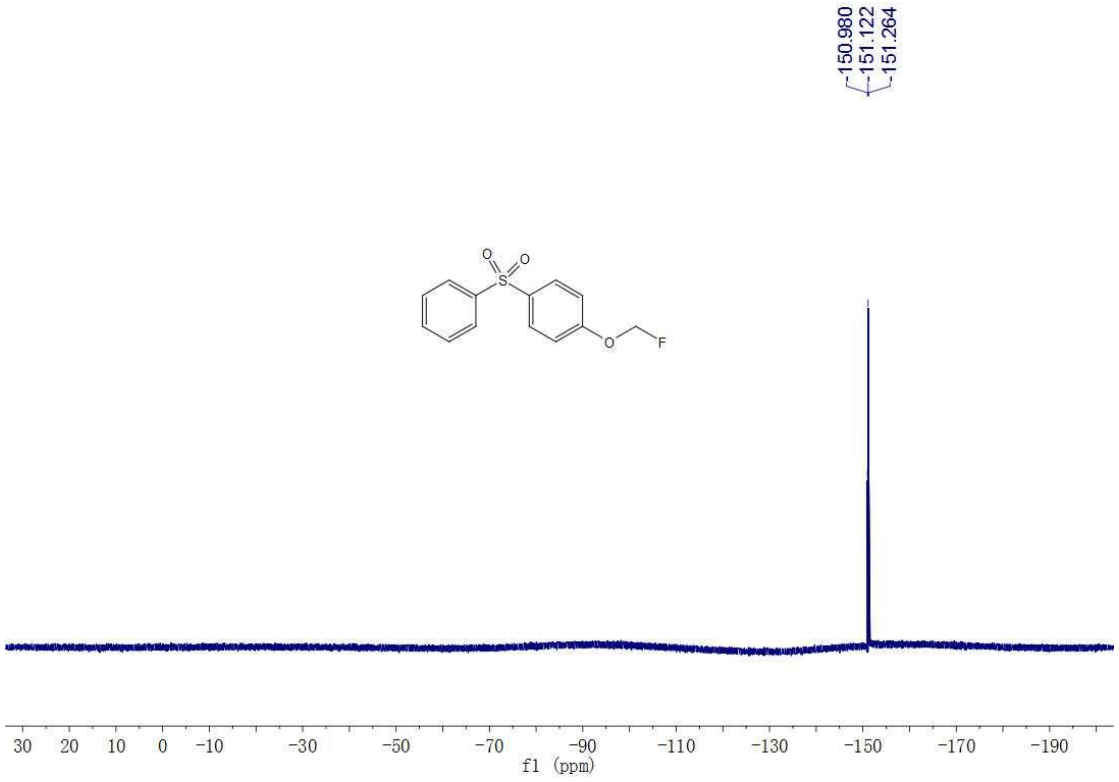
^{19}F NMR spectra of **16** (400 MHz, $CDCl_3$)



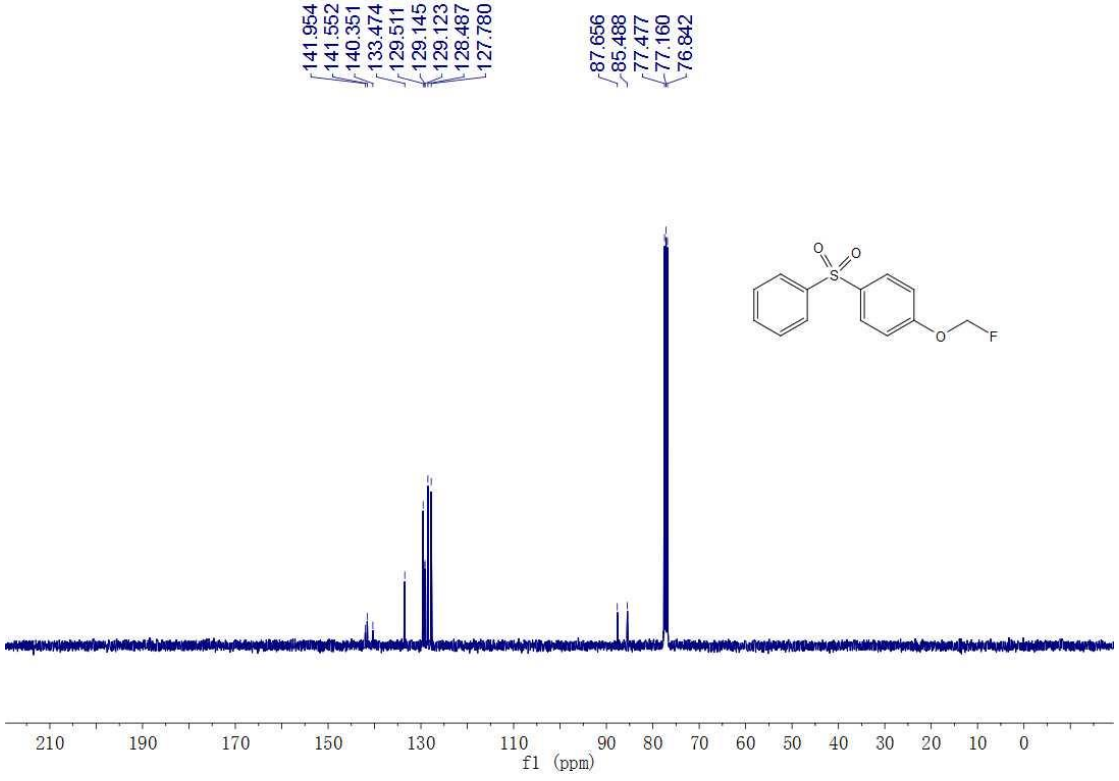
^{13}C NMR spectra of **16** (400 MHz, $CDCl_3$)



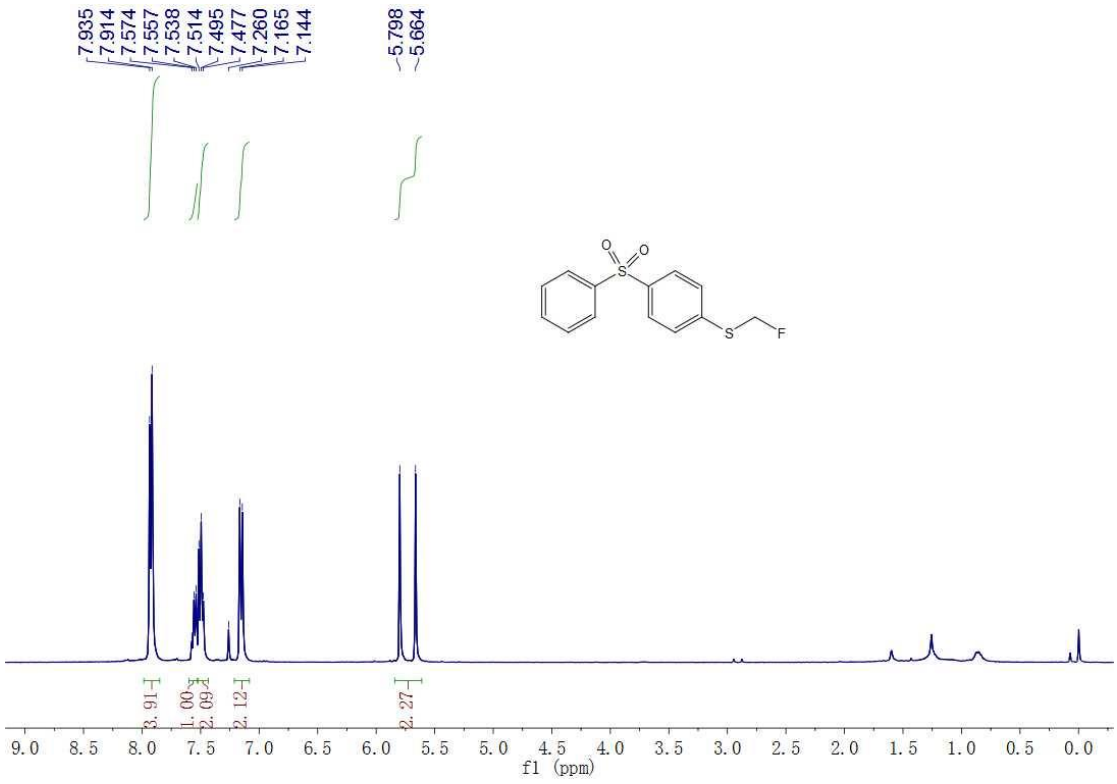
^{1}H NMR spectra of **19c** (400 MHz, $CDCl_3$)



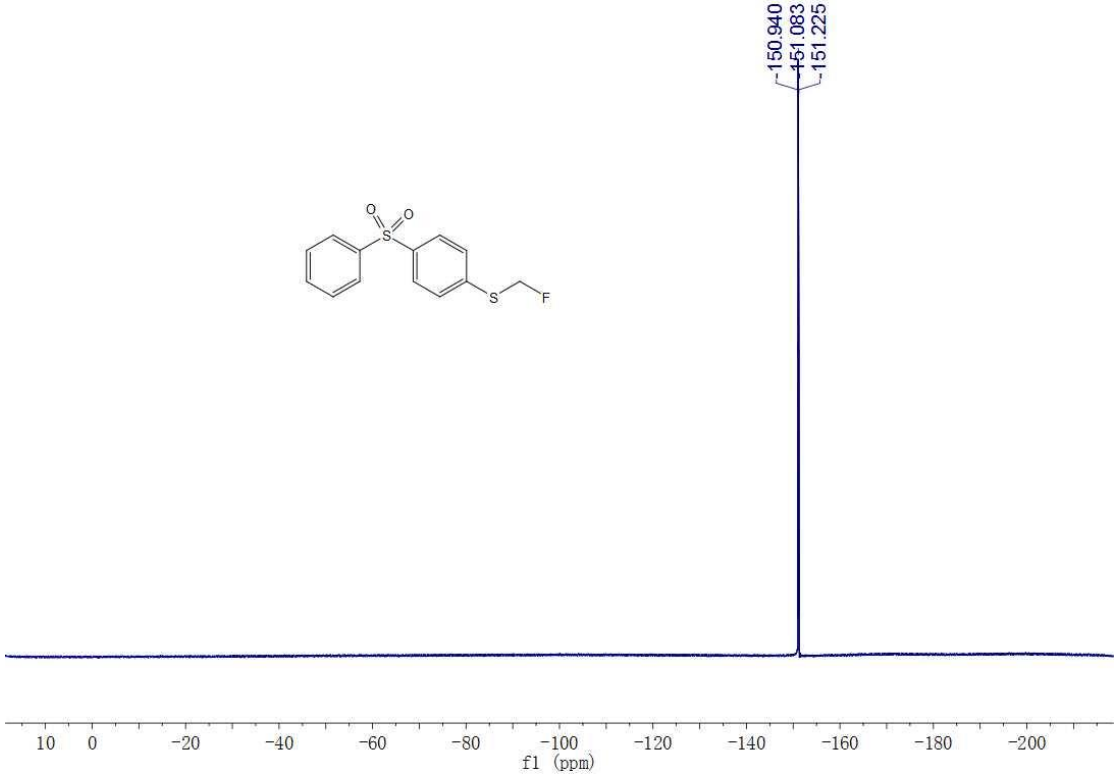
^{19}F NMR spectra of **19c** (400 MHz, $CDCl_3$)



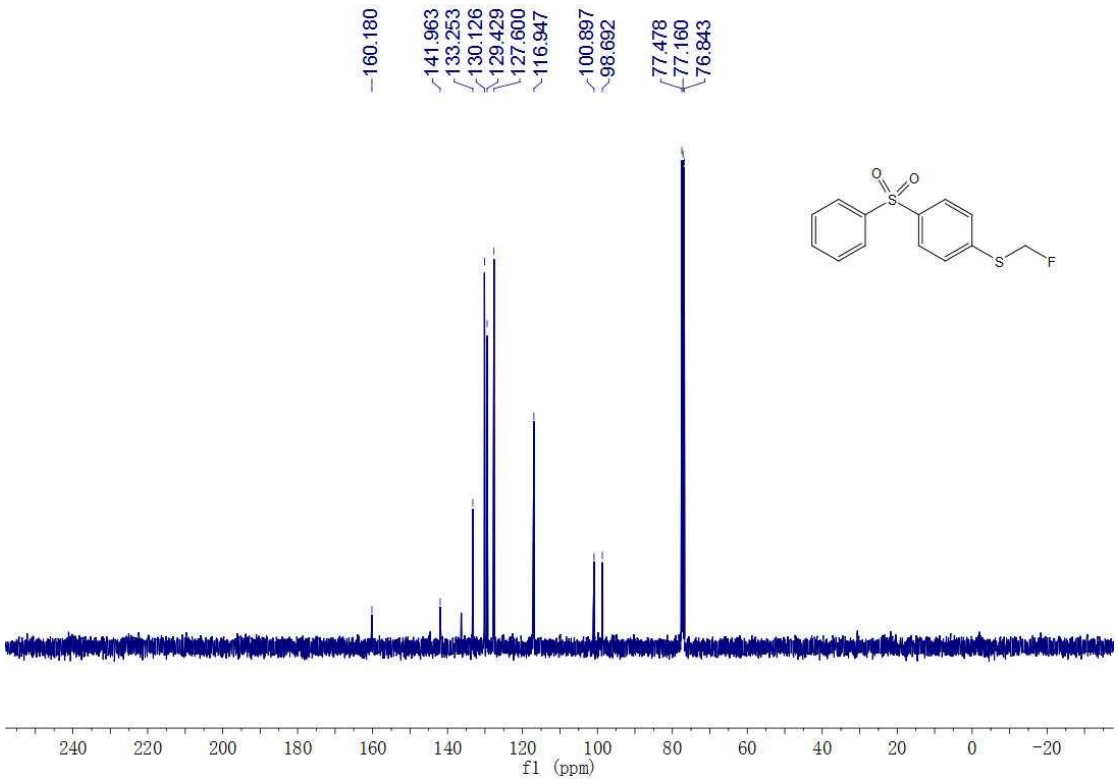
^{13}C NMR spectra of **19c** (400 MHz, $CDCl_3$)



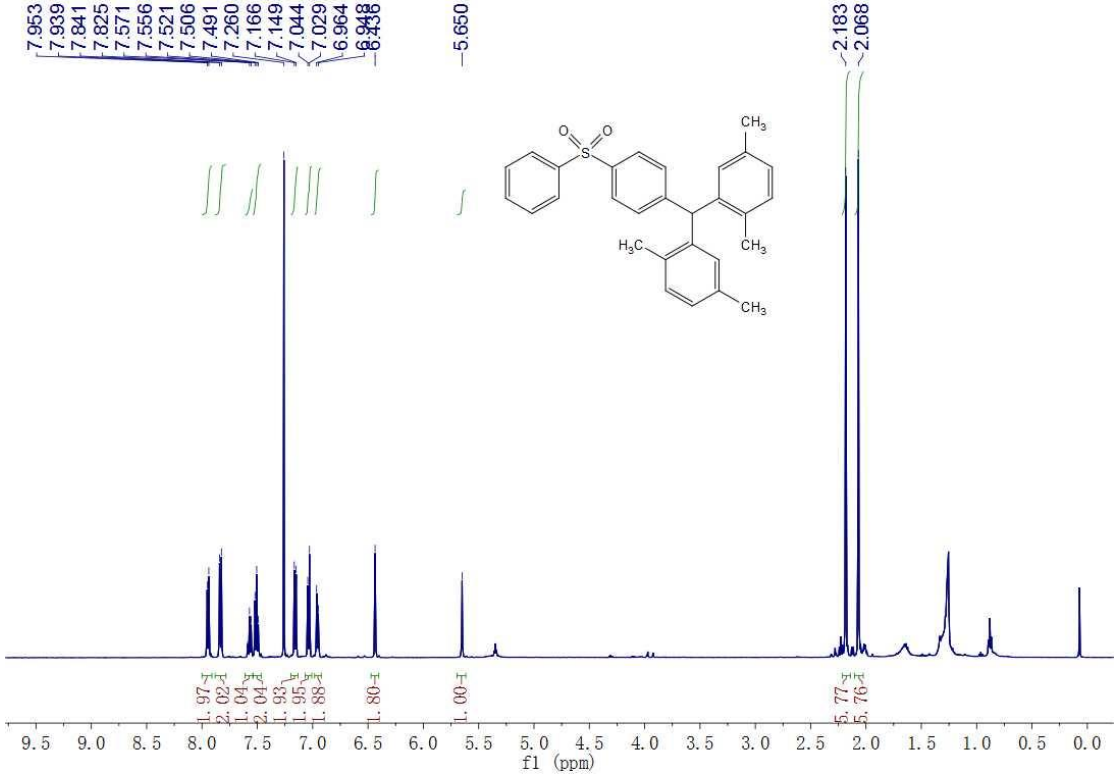
^{1}H NMR spectra of **22** (400 MHz, $CDCl_3$)



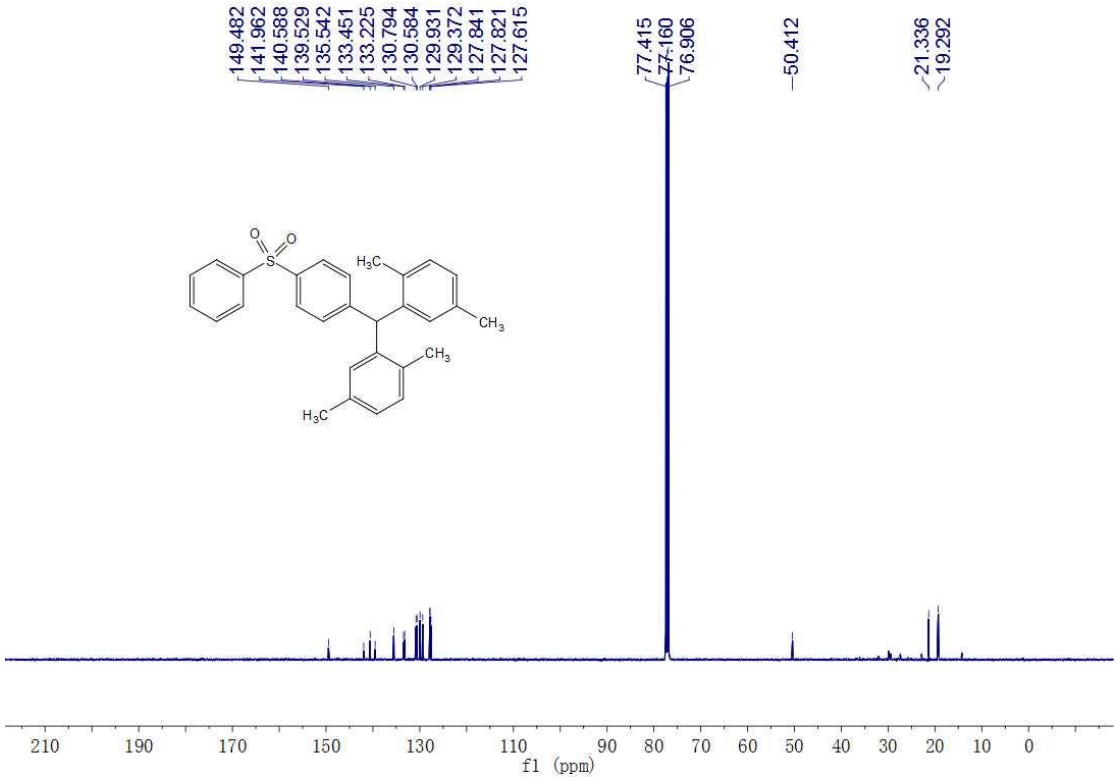
^{19}F NMR spectra of **22** (400 MHz, $CDCl_3$)



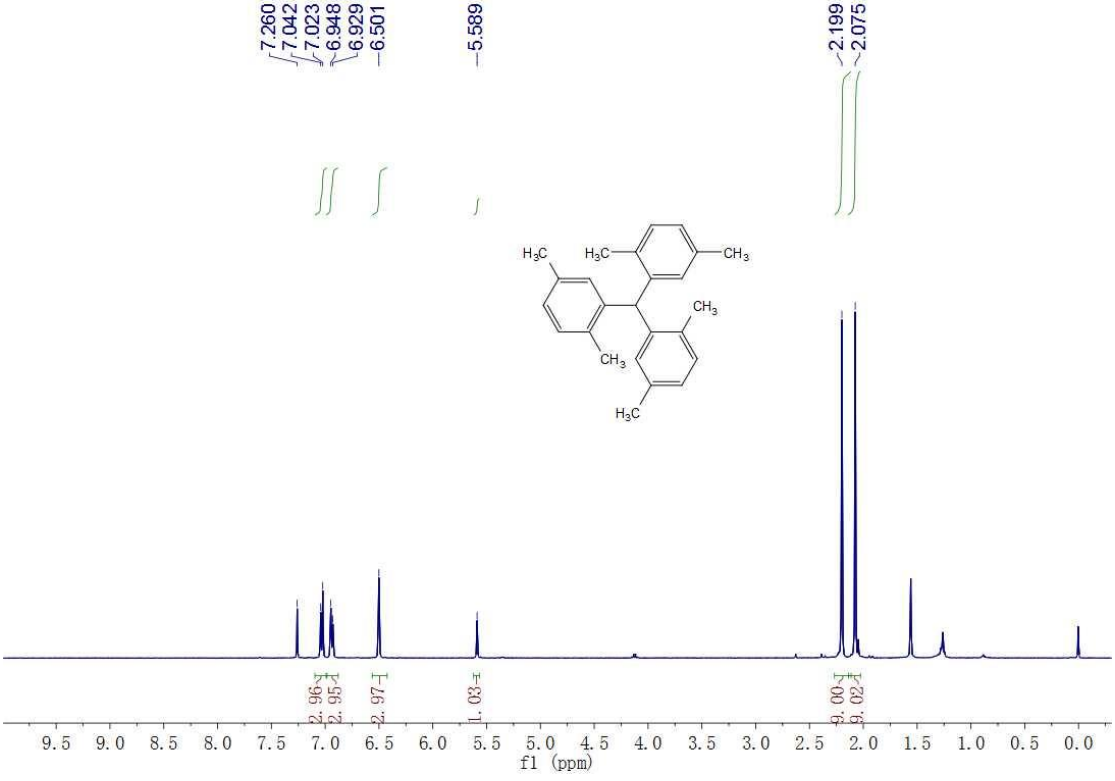
^{13}C NMR spectra of **22** (400 MHz, $CDCl_3$)



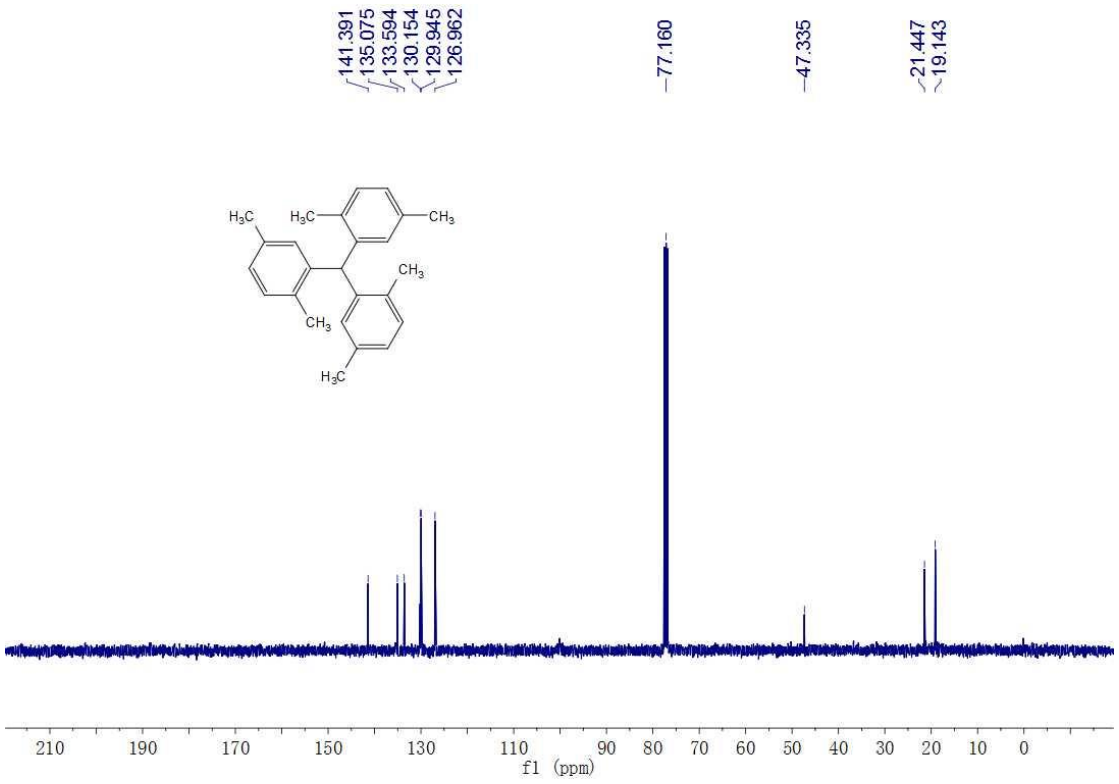
^{1}H NMR spectra of **11** (500 MHz, $CDCl_3$)



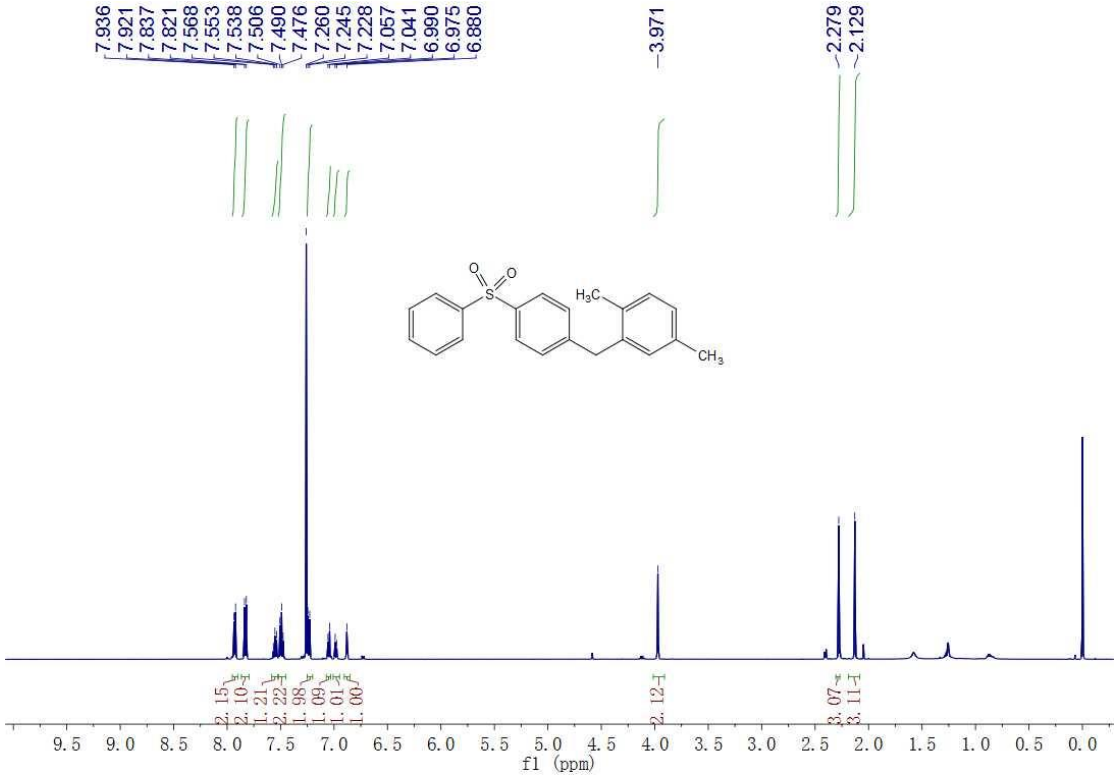
^{13}C NMR spectra of **11** (500 MHz, $CDCl_3$)



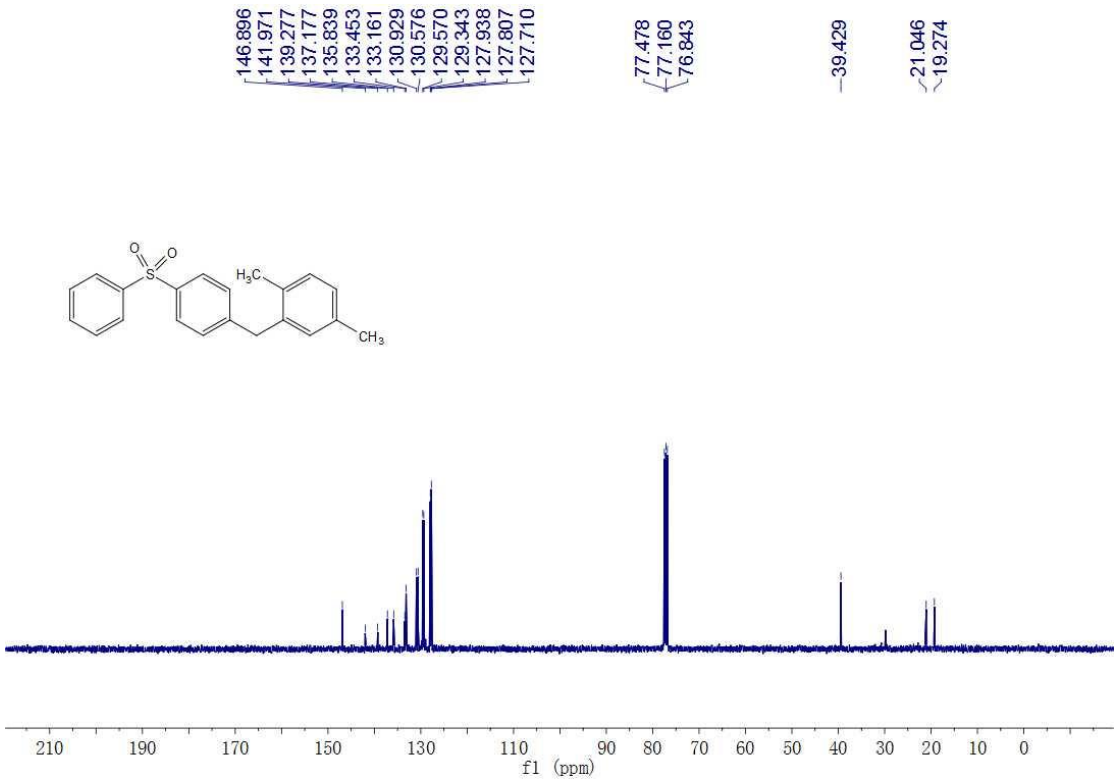
^{1}H NMR spectra of **14** (400 MHz, $CDCl_3$)



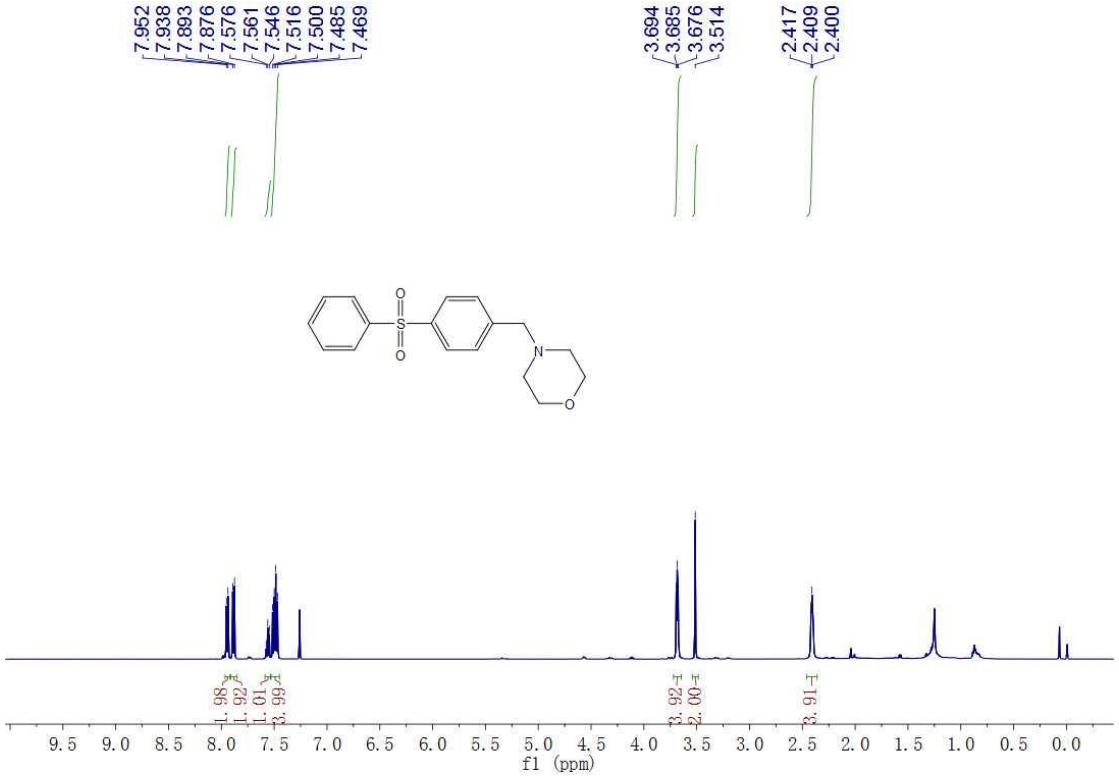
^{13}C NMR spectra of **14** (400 MHz, $CDCl_3$)



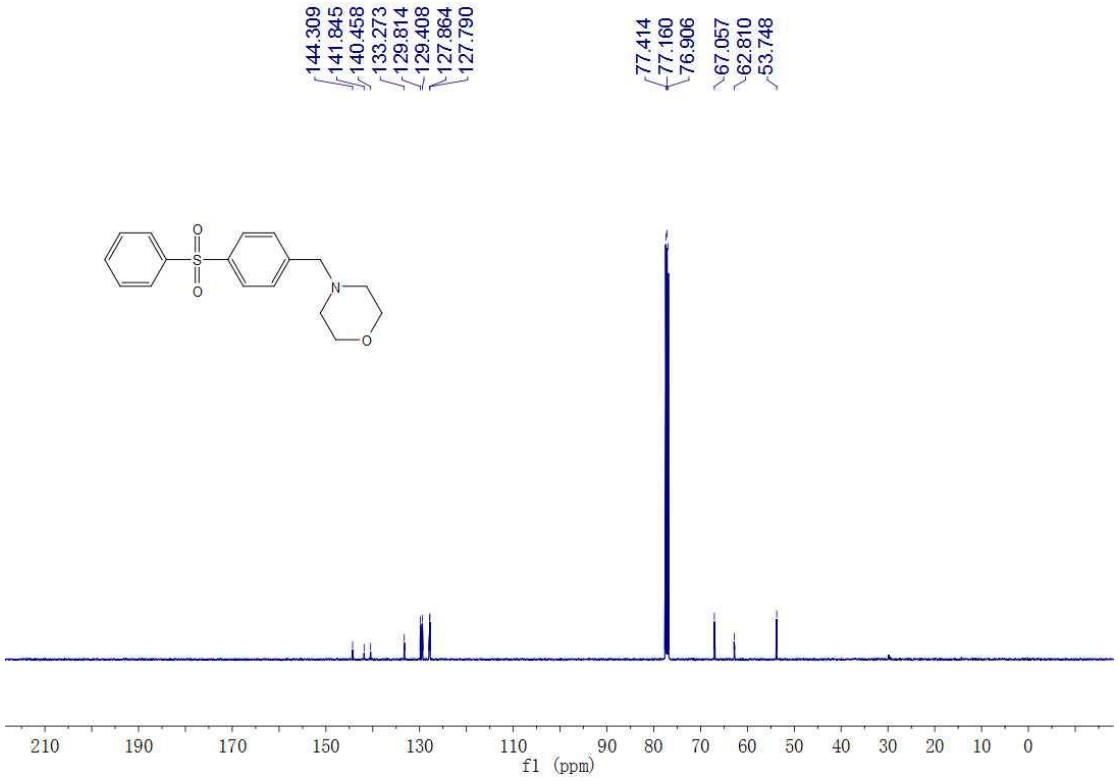
^{1}H NMR spectra of **17** (400 MHz, $CDCl_3$)



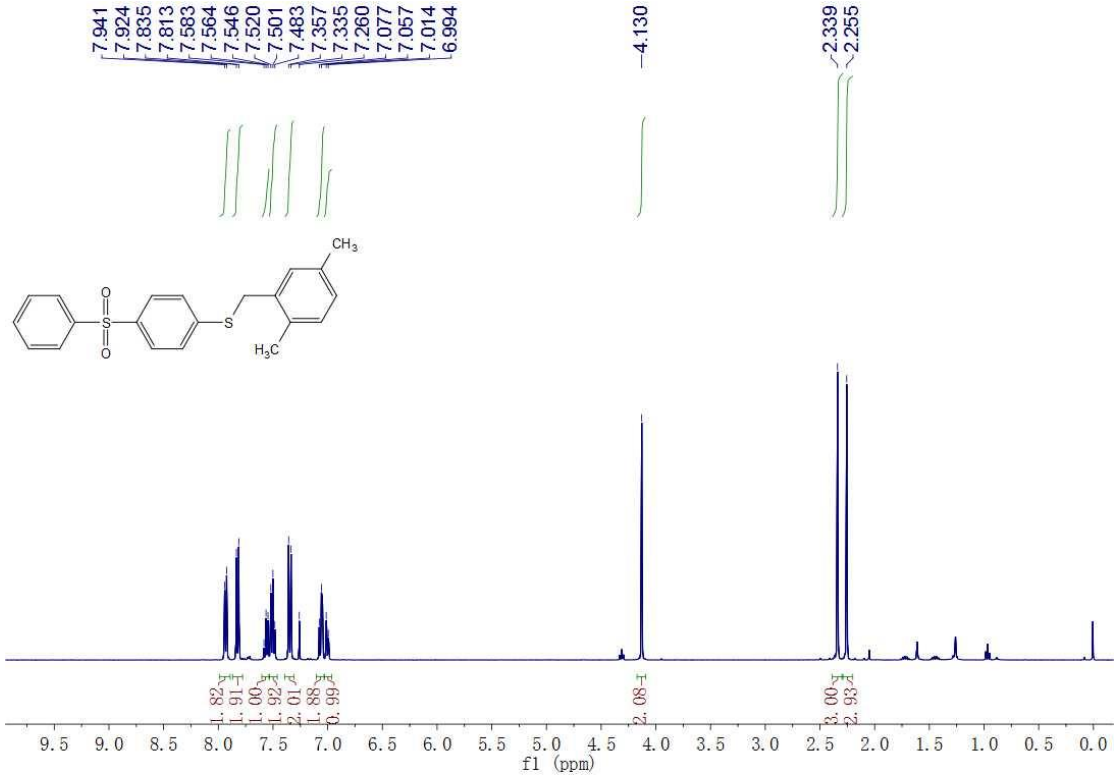
^{13}C NMR spectra of **17** (400 MHz, $CDCl_3$)



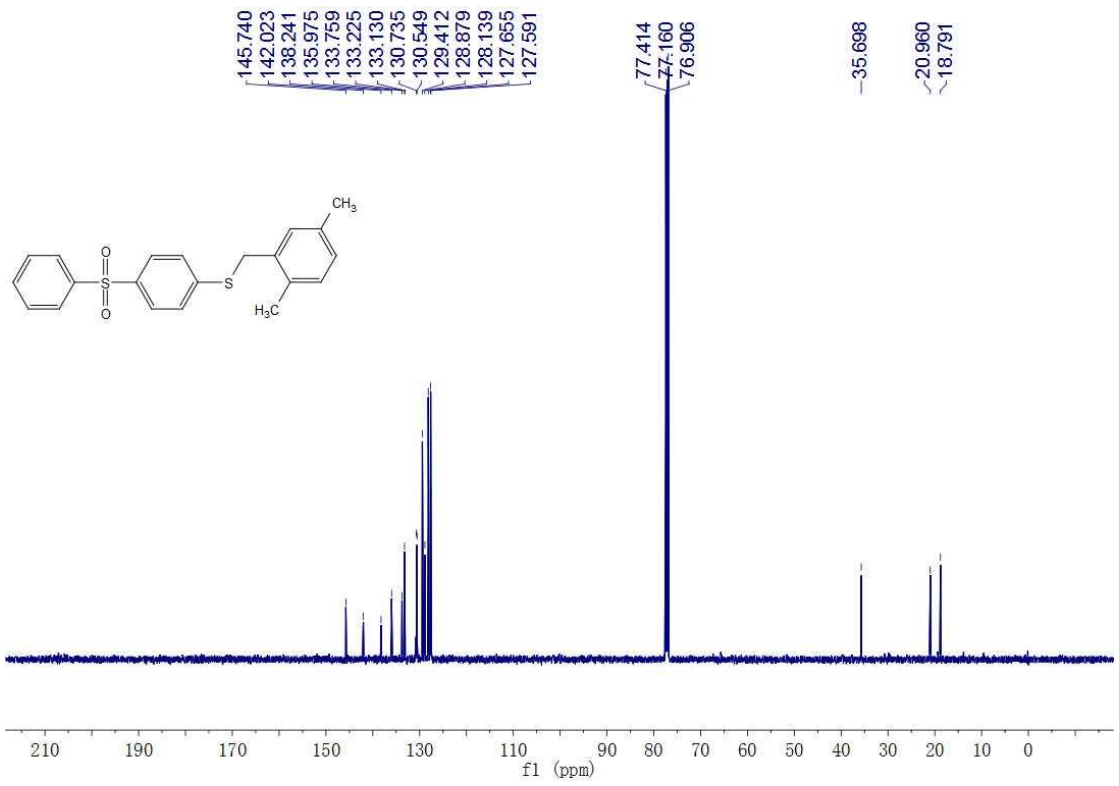
^{1}H NMR spectra of **18** (500 MHz, $CDCl_3$)



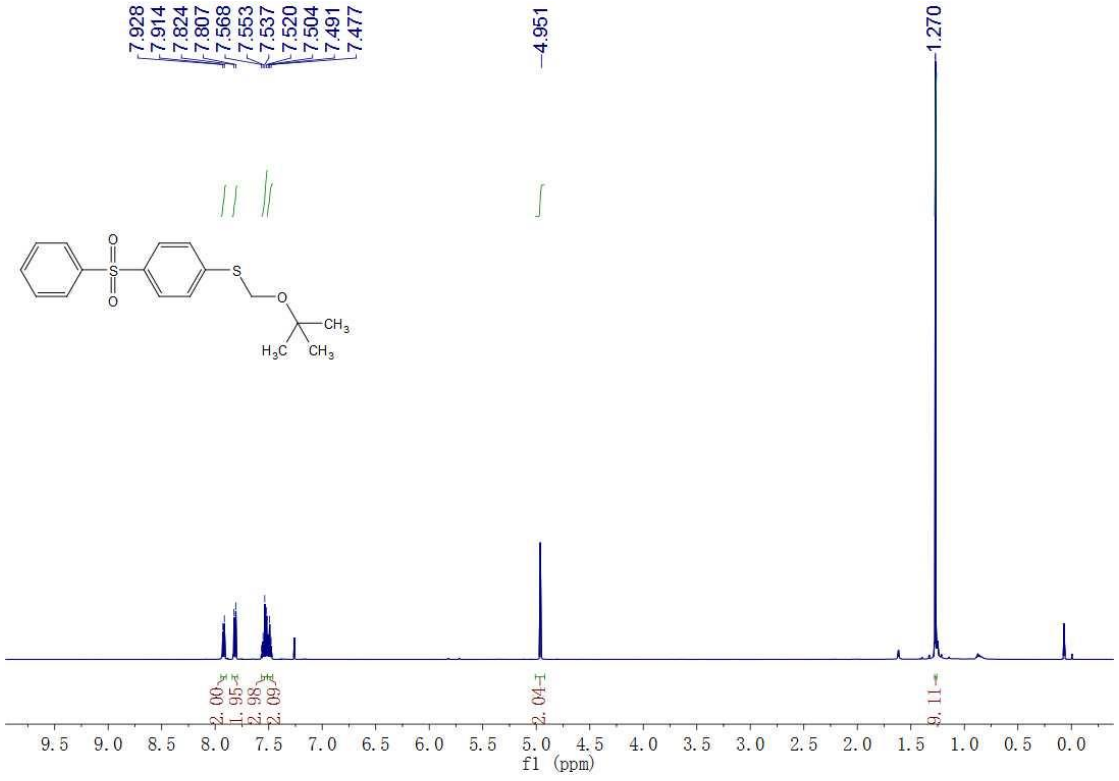
^{13}C NMR spectra of **18** (500 MHz, $CDCl_3$)



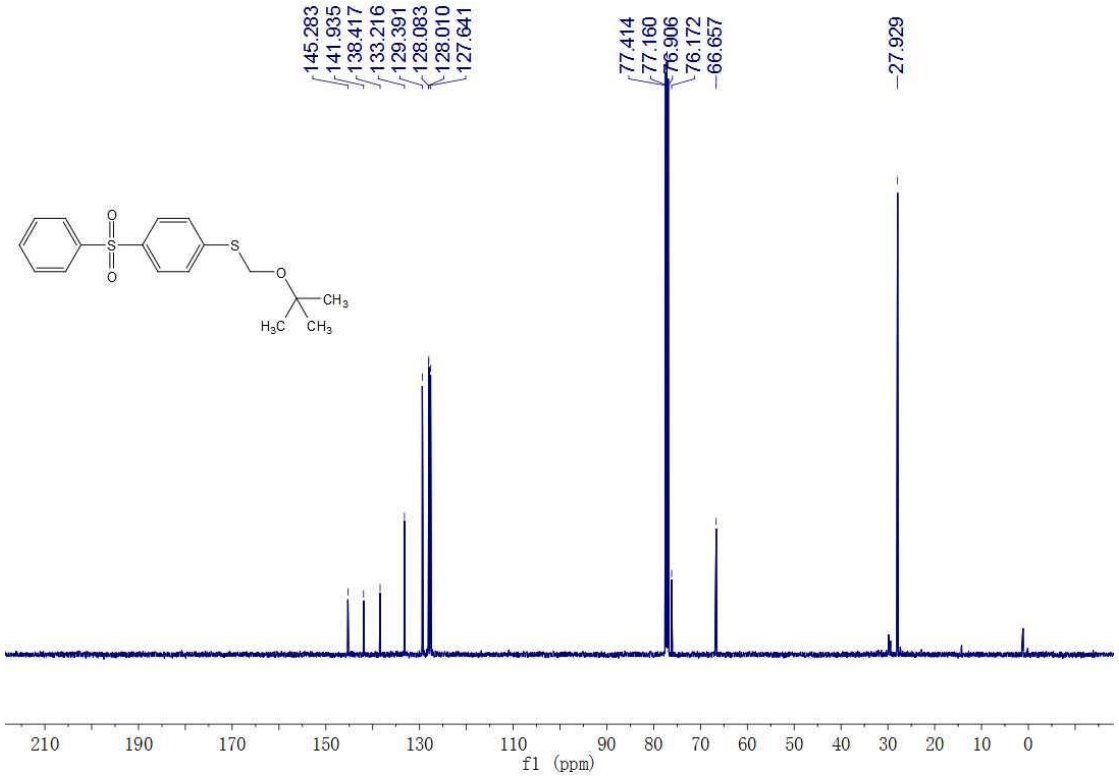
^{1}H NMR spectra of **23** (400 MHz, $CDCl_3$)



^{13}C NMR spectra of **23** (400 MHz, $CDCl_3$)



^{1}H NMR spectra of **24** (500 MHz, $CDCl_3$)



^{13}C NMR spectra of **24** (500 MHz, $CDCl_3$)