

Supporting Information

Photocatalytic hydro-fluorosulfonylation of alkenes with N-fluorosulfonyl aldimines

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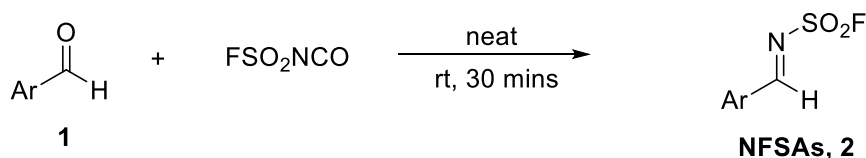
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1. General information

NMR spectra were recorded with Bruker Avance III HD500 and Bruker Avance III HD400 spectrometer at 500 MHz or 400 MHz. All ^1H , ^{19}F and ^{13}C NMR spectra were recorded using CDCl_3 or $\text{DMSO}-d_6$ as solvent. Tetramethylsilane (TMS) signals or residual solvent signals were used [TMS $\delta = 0.00$ (^1H NMR), Chloroform-*d* $\delta = 77.16$ (^{13}C NMR), $\text{DMSO}-d_6$ $\delta = 2.50$ (^1H NMR), 39.52 (^{13}C NMR)] as internal standards. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectrometry (HRMS) was performed via electron ionization (EI) or electrospray ionization (ESI) sources or atmospheric pressure chemical ionization (APCI) source. The m/z ratios are reported in Daltons; high-resolution values are calculated to four decimal places from the molecular formula. All the reactions were monitored by thin layer chromatography (TLC), carried out on 0.25 mm silica gel plates using UV light as visualizing agent. Column chromatography was carried out on silica gel (230-400 mesh). The alkenes were synthesized according to procedures described in the literature.^[1,2,3,4]

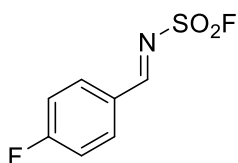
2. Experimental procedures and characterization data

2.1 General procedure for the preparation of imidosulfonyl fluoride



Following a modified literature procedure,^[5] aldehyde **1** (12.5 mmol, 1.0 eq) was added to a 10 mL Schlenk tube equipped with a magnetic stir bar under nitrogen atmosphere. FSO_2NCO (FSI, 12.5 mmol, 1.0 eq) was then slowly added while stirring, and the mixture was stirred at room temperature for an additional 30 minutes. The solid product obtained can be used directly or recrystallized from hexane.

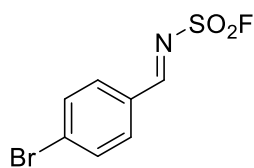
2.2 Characterization data of compounds **2a-2j**



(E)-(4-fluorobenzylidene)sulfamoyl fluoride (**2a**)

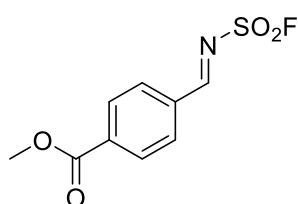
Following the **General procedure for the preparation of imidosulfonyl fluoride**, recrystallization using n-hexane yielded **2a** as light yellow solid (94% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.08 (s, 1H), 8.23 - 7.94 (m, 2H), 7.29 (t, $J = 8.5$ Hz, 2H), ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.00 (d, $J = 3.8$ Hz), 169.48, 166.88, 135.15 (d, $J =$

10.3 Hz), 127.62, 117.46, 117.24, ^{19}F NMR (376 MHz, Chloroform-*d*) δ 43.81, -95.07 - -100.30 (m), HRMS (ESI): m/z calculated for $[\text{C}_7\text{H}_4\text{F}_2\text{NO}_2\text{S}]$ $[\text{M}-\text{H}]^-$: 203.9936, found: 203.9938.



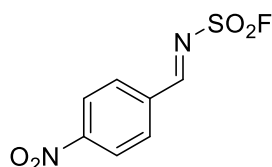
(*E*)-(4-bromobenzylidene)sulfamoyl fluoride (**2b**)

Following the **General procedure for the preparation of imidosulfonyl fluoride**, recrystallization using n-hexane yielded **2b** as yellow solid (95% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.06 (s, 1H), 7.88 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.49 (d, J = 3.8 Hz), 133.31, 133.20, 132.98, 132.50, 131.08, 129.93. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 43.78, HRMS (ESI): m/z calculated for $[\text{C}_7\text{H}_4\text{ClFNO}_2\text{S}]$ $[\text{M}-\text{H}]^-$: 263.9136, found: 263.9138.



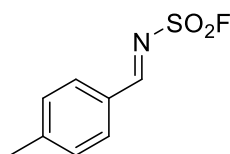
methyl (*E*)-4-((fluorosulfonyl)imino)methylbenzoate (**2c**)

Following the **General procedure for the preparation of imidosulfonyl fluoride**, recrystallization using n-hexane yielded **2c** as yellow solid (96% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.15 (s, 1H), 8.38 - 8.19 (m, 2H), 8.10 (d, J = 8.4 Hz, 2H), 3.98 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.62 (d, J = 4.0 Hz), 165.58, 137.05, 134.42, 132.02, 130.48, 130.20, 129.55, 52.86. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 43.48, HRMS (ESI): m/z calculated for $[\text{C}_9\text{H}_7\text{FNO}_4\text{S}]$ $[\text{M}-\text{H}]^-$: 244.0085, found: 244.0088.



(*E*)-(4-nitrobenzylidene)sulfamoyl fluoride (**2d**)

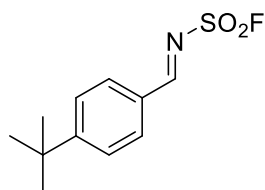
Following the **General procedure for the preparation of imidosulfonyl fluoride**, recrystallization using n-hexane yielded **2d** as brown solid (96% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 10.17 (s, 1H), 8.44 - 8.35 (m, 2H), 8.14 - 8.00 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.35 (d, J = 2.5 Hz), 151.15, 140.07, 130.50, 124.31. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 44.73, HRMS (ESI): m/z calculated for $[\text{C}_7\text{H}_4\text{FN}_2\text{O}_4\text{S}]$ $[\text{M}-\text{H}]^-$: 230.9881, found: 230.9885.



(*E*)-(4-methylbenzylidene)sulfamoyl fluoride (**2e**)

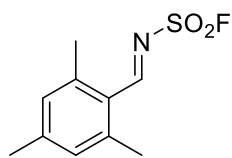
Following the **General procedure for the preparation of imidosulfonyl fluoride**, recrystallization using n-hexane yielded **2e** as light yellow solid (95% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.04 (s, 1H), 7.91 (d, J = 8.2 Hz,

2H), 7.39 (d, $J = 8.1$ Hz, 2H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 177.33 (d, $J = 3.3$ Hz), 149.29, 132.56, 130.48, 128.66, 22.29. ^{19}F NMR (376 MHz, Chloroform- d) δ 43.92, HRMS (ESI): m/z calculated for $[\text{C}_8\text{H}_7\text{FNO}_2\text{S}]$ $[\text{M}-\text{H}]^-$: 200.0187, found: 200.0190.



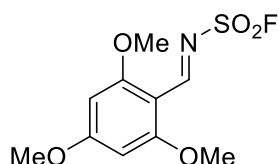
(*E*)-(4-(*tert*-butyl)benzylidene)sulfamoyl fluoride (**2f**)

Following the **General procedure for the preparation of imidosulfonyl fluoride**, recrystallization using *n*-hexane yielded **2f** as light yellow solid (96% yield). ^1H NMR (400 MHz, Chloroform- d) δ 9.07 (s, 1H), 7.96 (d, $J = 8.5$ Hz, 2H), 7.61 (d, $J = 8.5$ Hz, 2H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, Chloroform- d) δ 177.28 (d, $J = 3.6$ Hz), 162.04, 132.47, 128.59, 126.78, 35.79, 30.87. ^{19}F NMR (376 MHz, Chloroform- d) δ 43.97, HRMS (ESI): m/z calculated for $[\text{C}_{11}\text{H}_{13}\text{FNO}_2\text{S}]$ $[\text{M}-\text{H}]^-$: 242.0657, found: 242.0660.



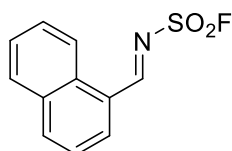
(*E*)-(2,4,6-trimethylbenzylidene)sulfamoyl fluoride (**2g**)

Following the **General procedure for the preparation of imidosulfonyl fluoride**, recrystallization using *n*-hexane yielded **2g** as light yellow solid (96% yield). ^1H NMR (400 MHz, Chloroform- d) δ 9.51 (s, 1H), 7.02 (s, 2H), 2.62 (s, 6H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 175.73 (d, $J = 3.4$ Hz), 147.80, 145.17, 131.26, 125.10, 22.08, 21.86. ^{19}F NMR (376 MHz, Chloroform- d) δ 44.23, HRMS (ESI): m/z calculated for $[\text{C}_{10}\text{H}_{11}\text{FNO}_2\text{S}]$ $[\text{M}-\text{H}]^-$: 228.0500, found: 228.0505.



(*E*)-(2,4,6-trimethoxybenzylidene)sulfamoyl fluoride (**2h**)

Following the **General procedure for the preparation of imidosulfonyl fluoride**, recrystallization using *n*-hexane yielded **2h** as light yellow solid (96% yield). ^1H NMR (400 MHz, Chloroform- d) δ 9.43 (s, 1H), 6.08 (s, 2H), 3.93 (s, 9H). ^{13}C NMR (101 MHz, Chloroform- d) δ 170.14, 169.87, 165.70, 103.91, 90.62, 56.39, 55.95. ^{19}F NMR (376 MHz, Chloroform- d) δ 44.92, HRMS (ESI): m/z calculated for $[\text{C}_{10}\text{H}_{11}\text{FNO}_5\text{S}]$ $[\text{M}-\text{H}]^-$: 276.0347, found: 276.0350.



(*E*)-(naphthalen-1-ylmethylene)sulfamoyl fluoride (**2i**)

Following the **General procedure for the preparation of imidosulfonyl fluoride**, recrystallization using *n*-hexane yielded **2i** as light yellow solid (96% yield). ^1H NMR (400 MHz, Chloroform- d) δ 9.22 (s, 1H), 8.43 (s, 1H), 8.14 - 7.86 (m, 4H), 7.79 - 7.58 (m, 2H). ^{13}C NMR (101 MHz, Chloroform- d) δ 177.32 (d, $J = 3.7$ Hz), 138.64, 137.46, 132.52,

130.77, 130.01, 129.85, 128.88, 128.29, 127.80, 123.77. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ 44.01, HRMS (ESI): *m/z* calculated for [C₁₁H₇FNO₂S] [M-H]⁻: 236.0187, found: 236.0190.



(*E*)-([1,1'-biphenyl]-2-ylmethylene)sulfamoyl fluoride (**2j**)

Following the **General procedure for the preparation of imidosulfonyl fluoride**, recrystallization using *n*-hexane yielded **2j** as light yellow solid (91% yield). ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.08 (s, 1H), 8.30 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.97 – 7.87 (m, 1H), 7.72 – 7.61 (m, 2H), 7.60 – 7.51 (m, 3H), 7.49 (dd, *J* = 7.6, 1.9 Hz, 2H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 179.18 (d, *J* = 3.6 Hz), 148.76, 137.64, 137.23, 131.69, 130.70, 129.57, 129.17, 128.99, 128.65. ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ 45.22, HRMS (ESI): *m/z* calculated for [C₁₃H₉FNO₂S] [M-H]⁻: 262.0344, found: 262.0349.

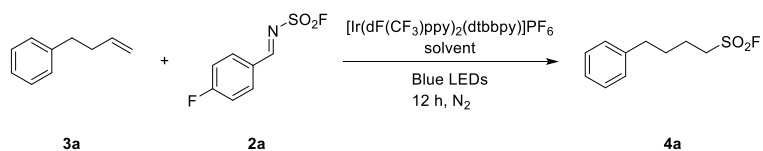
2.3 Optimization of reaction conditions and general procedure

Table S1 Investigating the effect of NFSAs

Entry ^a	NFSAs	Yield(%) ^b
1	2a	23(20)^c
2	2b	20
3	2c	16
4	2d	15
5	2e	14
6	2f	15
7	2g	18
8	2h	14
9	2i	20
10	2j	17

^aGeneral conditions: **3a** (1.0 equiv), **2** (3.0 equiv), [Ir(dF(CF₃)ppy)₂(dtbbpy)]PF₆ (1 mol %), CHCl₃ (3 mL), and nitrogen atmosphere, 30 W blue LEDs, 12 h. ^bDetermined by ¹⁹F NMR analysis using PhCF₃ as the internal standard. ^cIsolated yield.

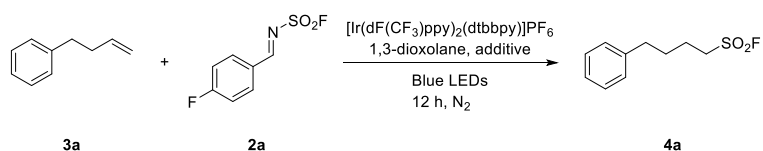
Table S2 Investigating the effect of solvents



Entry ^a	solvents	Yield(%) ^b
1	CHCl ₃	23(20) ^c
2	DCM	10
3	MeCN	N.D.
4	DMF	N.D.
5	DMSO	N.D.
6	MeOH	N.D.
7	DCE	10
8	CCl ₄	trace
9	Et ₂ O	N.D.
10	1,3-dioxolane	40
11	Acetone	12
12	THF	20
13	EA	trace

^aGeneral conditions: **3a** (1.0 equiv), **2a** (3.0 equiv), [Ir(dF(CF₃)ppy)₂(dtbbpy)]PF₆ (1 mol %), solvent (3 mL), and nitrogen atmosphere, 30 W blue LEDs, 12 h. ^bDetermined by ¹⁹F NMR analysis using PhCF₃ as the internal standard. ^cIsolated yield.

Table S3 Investigating the effect of additives

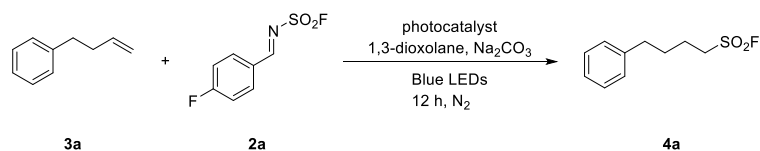


Entry ^a	additives	Yield(%) ^d
1	MgSO ₄	15
2 ^b	5 Å MS	18
3	BnSH	19
4	Ph ₃ SiH	39
5	Et ₃ SiH	38
6	(TMS) ₃ SiH	32
7 ^c	Ph ₃ SiH	27
8 ^c	Ph(Me) ₂ SiH	28
9 ^c	(i-Pr) ₃ SiH	35
10 ^c	(MeO) ₃ SiH	38

11 ^c	CH ₃ Cl ₂ SiH	19
12	Na ₂ CO ₃	60(58)^e
13	NaHCO ₃	50
14	CH ₃ COONa	50
15	K ₂ CO ₃	40
16	K ₃ PO ₄	13
17	CS ₂ CO ₃	25
18	NaOH	13
19	^t BuOK	N.D.
20	TMG	15
21	DBU	N.D.
22	Pyridine	N.D.
23	Et ₃ N	8
24	DMAP	5

^aGeneral conditions: **3a** (1.0 equiv), **2a** (3.0 equiv), additive (1.0 equiv), [Ir(dF(CF₃)ppy)₂(dtbbpy)]PF₆ (1 mol %), 1,3-dioxolane (3 mL), and nitrogen atmosphere, 30 W blue LEDs, 12 h. ^b100 mg 5 Å MS was used. ^c1.0 equiv. additive was used. ^dDetermined by ¹⁹F NMR analysis using PhCF₃ as the internal standard. ^eIsolated yield.

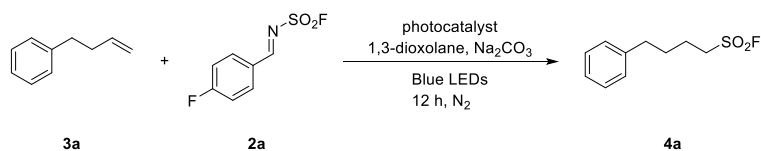
Table S4 Investigating the effect of NFSA loading



Entry ^a	2a loading	Yield (%) ^b
1	3.0 e.q.	60(58)^c
2	2.5 e.q.	52
3	2.0 e.q.	50
4	1.5 e.q.	44
5	1.0 e.q.	34

^aGeneral conditions: **3a** (1.0 equiv), **2a**, Na₂CO₃ (1.0 equiv), [Ir(dF(CF₃)ppy)₂(dtbbpy)]PF₆ (1 mol %), 1,3-dioxolane (3 mL), and nitrogen atmosphere, 30 W blue LEDs, 12 h. ^bDetermined by ¹⁹F NMR analysis using PhCF₃ as the internal standard. ^cIsolated yield.

Table S5 Investigating the effect of photocatalyst

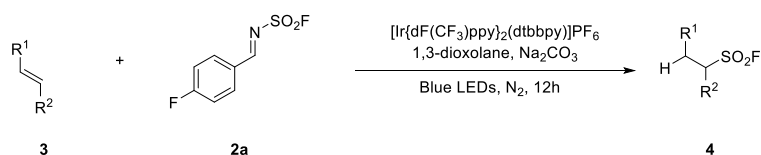


Entry ^a	Photocatalyst	Photocatalyst loading	Yield(%) ^b
1	[Ir{dF(CF₃)ppy}₂(dtbbpy)]PF₆	1%	60(58)^c
2	[Ir{dF(CF ₃)ppy} ₂ (bpy)]PF ₆	1%	44
3	[Ir(ppy) ₂ (dtbbpy)]PF ₆	1%	10
4	[Ir{dF(CF ₃)ppy} ₂ (OMe) ₂]PF ₆	1%	36
5	[Ir{dF(CF ₃)ppy} ₂ (Me) ₂]PF ₆	1%	50
6	[Ir{dF(ppy) ₂ (dtbbpy)]PF ₆	1%	24
7	4CzIPN	5 mol%	39
8	Mes-Acr ⁺ BF ₄ ⁻	5 mol%	Trace
9	Thioxanthone	5 mol%	44
10	Eosin B	5 mol%	Trace
11	Eosin Y	5 mol%	Trace
12	Ru(bpy) ₃ Cl ₂	1 mol%	44
13	[Ir{dF(CF ₃)ppy} ₂ (dtbbpy)]PF ₆	0.5%	55
14	[Ir{dF(CF ₃)ppy} ₂ (dtbbpy)]PF ₆	2.5%	48
15	[Ir{dF(CF ₃)ppy} ₂ (dtbbpy)]PF ₆	5%	40

^aGeneral conditions: **3a** (1.0 equiv), **2a** (3.0 equiv), photocatalyst, 1,3-dioxolane (3 mL), and nitrogen atmosphere, 30 W blue LEDs, 12 h. ^bDetermined by ¹⁹F NMR analysis using PhCF₃ as the internal standard.

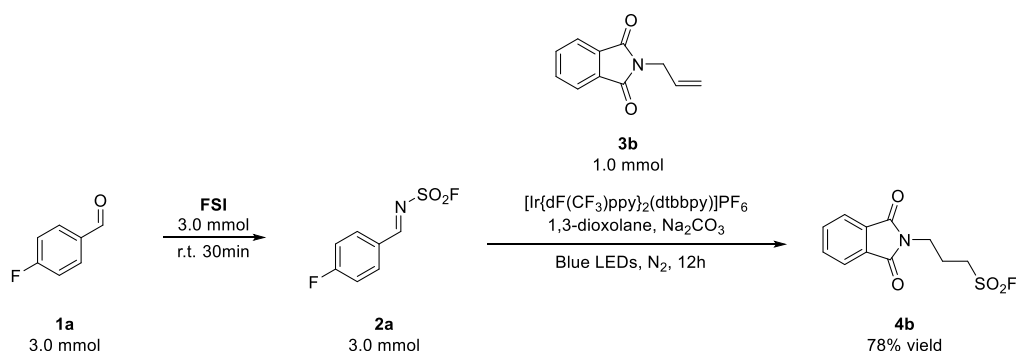
^cIsolated yield.

General procedure for hydro-fluorosulfonylation of alkenes



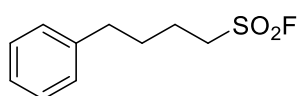
To a 10 mL Schenk tube equipped with a magnetic stirring bar, Na₂CO₃ (0.1 mmol, 1.0 equiv.), [Ir{dF(CF₃)ppy}₂(dtbbpy)]PF₆ (1.1 mg, 0.001 mmol, 1 mol%), alkenes (0.10 mmol, 1.0 equiv.), (*E*)-(4-fluorobenzylidene)sulfamoyl fluoride (**2a**) (0.3 mmol, 3.0 equiv.) and 1,3-dioxolane (3 mL) were added, and the tube was backfilled with nitrogen. The Schlenk tube was stirred at room temperature under irradiation of 30 W blue LEDs for 12 h. The solvent was removed under reduced pressure, and then the residue was purified by flash column chromatography (PE/EA= 15:1-5:1) to afford the desired product **4**.

2.4 Experimental procedure for scale-up reactions



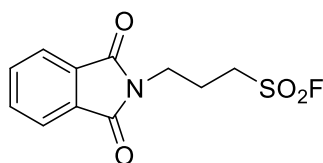
The scale-up reaction was prepared by one-pot method. To a flame-dried round-bottom-flask equipped with a magnetic stirring bar, **1a** (3.0 mmol, 3.0 equiv.) and **FSI** (3.0 mmol, 3.0 equiv.) were added into the reaction bottle. The reaction bottle was backfilled with nitrogen and reacted for 30 min at room temperature (pay attention to exhaust during the reaction). After the end of the reaction, added **3b** (1.0 mmol, 1.0 equiv.), $[\text{Ir}\{\text{dF}(\text{CF}_3)\text{ppy}\}_2(\text{dtbbpy})]\text{PF}_6$ (11.2 mg, 0.01 mmol, 1 mol%), Na_2CO_3 (1 mmol, 1.0 equiv.) and 1,3-dioxolane (30 mL). to the reaction bottle and backfill nitrogen again. The reaction mixture was then irradiated with 30 W blue LEDs for 12 h. After the reaction, the solution was purified by flash column chromatography or on silica gel to give the product **4b** in 80% yield.

2.5 Characterization data of compounds **4a-4al**



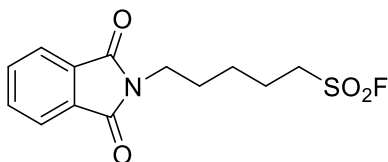
4-phenylbutane-1-sulfonyl fluoride (**4a**)^[6]

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4a** as colorless oil (58% yield). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.30 (t, $J = 7.4$ Hz, 2H), 7.21 (t, $J = 7.3$ Hz, 1H), 7.16 (d, $J = 7.1$ Hz, 2H), 3.42 - 3.30 (m, 2H), 2.68 (t, $J = 7.5$ Hz, 2H), 2.03 - 1.92 (m, 2H), 1.87 - 1.77 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 140.71, 128.60, 128.34, 126.30, 50.76 (d, $J = 16.3$ Hz), 35.06, 29.50, 22.96. $^{19}\text{F NMR}$ (376 MHz, Chloroform-*d*) δ 53.57. **HRMS (ESI)**: m/z calculated for $[\text{C}_{10}\text{H}_{12}\text{FO}_2\text{S}]$ $[\text{M}-\text{H}]^-$: 215.0548, found: 215.0551.



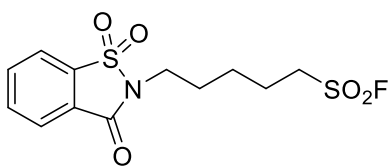
3-(1,3-dioxoisindolin-2-yl)propane-1-sulfonyl fluoride (**4b**)

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4b** as yellow solid (74% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.87 (s, 2H), 7.77 (d, $J = 3.0$ Hz, 2H), 3.88 (t, $J = 6.3$ Hz, 2H), 3.47 (s, 2H), 2.35 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.17, 134.42, 131.75, 123.61, 48.72 (d, $J = 18.2$ Hz), 35.78, 23.27. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ 53.34 (t, $J = 4.4$ Hz). **HRMS (ESI)**: m/z calculated for $[\text{C}_{11}\text{H}_9\text{FNO}_4\text{S}]$ $[\text{M}-\text{H}]^-$: 270.0242, found: 270.0246.



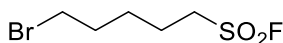
5-(1,3-dioxisoindolin-2-yl)pentane-1-sulfonyl fluoride (4c) ^[6]

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4c** as brown solid (68% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 5.3, 3.1 Hz, 2H), 7.73 (dd, *J* = 5.4, 3.1 Hz, 2H), 3.72 (t, *J* = 7.0 Hz, 2H), 3.51 - 3.27 (m, 2H), 2.11 - 1.97 (m, 2H), 1.83 - 1.72 (m, 2H), 1.56 (q, *J* = 8.0 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 168.41, 134.08, 132.00, 123.31, 50.63 (d, *J* = 16.5 Hz), 37.21, 27.88, 25.11, 22.99. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ 53.43. HRMS (ESI): *m/z* calculated for [C₁₃H₁₄FNO₄SNa⁺] [M+Na⁺]: 322.0520, found: 322.0518.



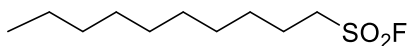
5-(1,1-dioxido-3-oxobenzodisothiazol-2(3H)-yl)pentane-1-sulfonyl fluoride (4d) ^[6]

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4d** as brown solid (61% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.20 - 7.77 (m, 4H), 3.81 (t, *J* = 7.1 Hz, 2H), 3.48 - 3.29 (m, 2H), 2.15 - 1.87 (m, 4H), 1.63 (p, *J* = 7.8 Hz, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 159.06, 137.62, 134.89, 134.45, 127.26, 125.23, 120.99, 50.58 (d, *J* = 16.5 Hz), 38.62, 27.60, 24.98, 22.92. ¹⁹F NMR (377 MHz, Chloroform-*d*) δ 53.51. HRMS (ESI): *m/z* calculated for [C₁₂H₁₄FNO₅S₂Na⁺] [M+Na⁺]: 358.0190, found: 358.0188.



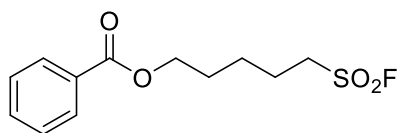
5-bromopentane-1-sulfonyl fluoride (4e) ^[6]

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4e** as yellow oil (60% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 3.46 - 3.31 (m, 4H), 2.06 - 1.87 (m, 4H), 1.73 - 1.62 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 50.66 (d, *J* = 16.7 Hz), 32.55, 31.76, 26.43, 22.74. ¹⁹F NMR (377 MHz, Chloroform-*d*) δ 53.66. HRMS (ESI): *m/z* calculated for [C₅H₉BrFO₂S] [M-H]⁻: 230.9496, found: 230.9500.



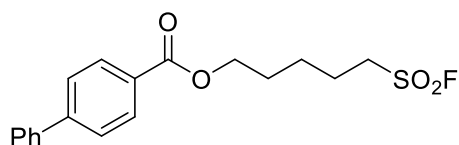
decane-1-sulfonyl fluoride (4f) ^[6]

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4f** as yellow oil (57% yield). ¹H NMR (500 MHz, Chloroform-*d*) δ 3.41 - 3.19 (m, 2H), 2.00 - 1.80 (m, 2H), 1.62 - 1.43 (m, 2H), 1.47 - 1.37 (m, 2H), 1.33 - 1.10 (m, 10H), 1.00 - 0.65 (m, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 49.90 (d, *J* = 16.8 Hz), 30.81, 28.69, 28.37, 28.16 (d, *J* = 4.8 Hz), 27.79, 26.85, 22.37, 21.63, 13.07. ¹⁹F NMR (377 MHz, Chloroform-*d*) δ 53.26. HRMS (ESI): *m/z* calculated for [C₁₀H₂₁FO₂SNa⁺] [M+Na⁺]: 247.1138, found: 247.1125.



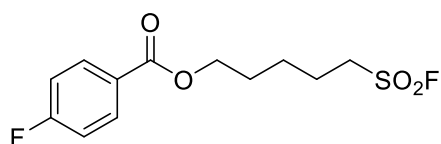
5-(fluorosulfonyl)pentyl benzoate (**4g**)^[6]

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4g** as brown oil (68% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 - 8.00 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 4.35 (t, *J* = 6.3 Hz, 2H), 3.53 - 3.28 (m, 2H), 2.14 - 1.99 (m, 2H), 1.90 - 1.80 (m, 2H), 1.74-1.63 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 166.56, 133.06, 130.14, 129.54, 128.43, 64.13, 50.72 (d, *J* = 16.6 Hz), 28.11, 24.62, 23.23. ¹⁹F NMR (377 MHz, Chloroform-*d*) δ 53.66. HRMS (ESI): *m/z* calculated for [C₁₂H₁₄FO₄S] [M-H]⁻: 273.0602, found: 273.0606.



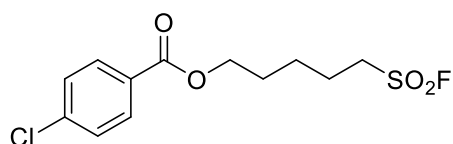
5-(fluorosulfonyl)pentyl [1,1'-biphenyl]-4-carboxylate (**4h**)^[6]

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4h** as brown oil (60% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.14 - 8.02 (m, 2H), 7.72 - 7.65 (m, 2H), 7.65 - 7.59 (m, 2H), 7.52 - 7.44 (m, 2H), 7.43 - 7.34 (m, 1H), 4.37 (t, *J* = 6.3 Hz, 2H), 3.45 - 3.31 (m, 2H), 2.11 - 2.01 (m, 2H), 1.94 - 1.80 (m, 2H), 1.75 - 1.58 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 166.45, 145.82, 139.96, 130.09, 128.97, 128.86, 128.22, 127.29, 127.12, 64.15, 50.74 (d, *J* = 16.5 Hz), 28.16, 24.65, 23.26. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ 53.68. HRMS (ESI): *m/z* calculated for [C₁₈H₁₉FO₄SNa⁺] [M+Na⁺]: 373.0880, found: 373.0882.



5-(fluorosulfonyl)pentyl 4-fluorobenzoate (**4i**)^[6]

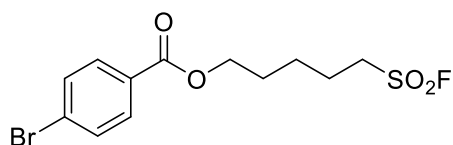
Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4i** as brown oil (65% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.19 - 8.00 (m, 2H), 7.23 - 7.04 (m, 2H), 4.34 (t, *J* = 6.4 Hz, 2H), 3.47 - 3.32 (m, 2H), 2.10 - 1.99 (m, 2H), 1.89 - 1.80 (m, 2H), 1.71 - 1.64 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 165.83 (d, *J* = 254.1 Hz), 165.59, 132.10 (d, *J* = 9.3 Hz), 126.35 (d, *J* = 2.8 Hz), 115.60 (d, *J* = 22.0 Hz), 64.27, 50.62, 28.10, 24.60, 23.23. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ 53.72, -105.51. HRMS (ESI): *m/z* calculated for [C₁₂H₁₄O₄F₂SNa⁺] [M+Na⁺]: 315.0473, found: 315.0472.



5-(fluorosulfonyl)pentyl 4-chlorobenzoate (**4j**)

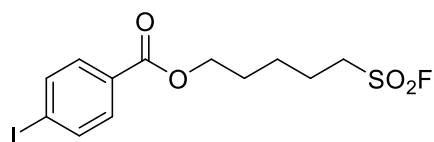
Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4j** as light yellow oil (79% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 4.27 (t, *J* = 6.4 Hz, 2H), 3.52 - 3.27 (m, 2H), 2.11 - 1.88 (m, 2H), 1.85 - 1.74 (m, 2H), 1.68 - 1.56 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 165.67, 139.51, 130.95, 128.78, 128.59, 64.37, 50.69 (d, *J* = 16.6 Hz), 28.06, 24.56, 23.21. ¹⁹F

NMR (376 MHz, Chloroform-*d*) δ 53.80. **HRMS (ESI):** *m/z* calculated for [C₁₂H₁₄O₄ClFSNa⁺] [M+Na⁺]: 331.0178, found: 331.0180.



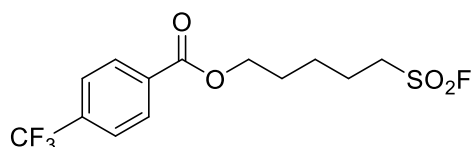
5-(fluorosulfonyl)pentyl 4-bromobenzoate (4k)

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4k** as yellow soild (73% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.92 - 7.68 (m, 2H), 7.62 - 7.45 (m, 2H), 4.27 (t, *J* = 6.4 Hz, 2H), 3.56 - 3.03 (m, 2H), 2.15 - 1.92 (m, 2H), 1.92 - 1.71 (m, 2H), 1.70 - 1.53 (m, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 165.81, 131.79, 131.08, 129.03, 128.18, 64.40, 50.70 (d, *J* = 16.6 Hz), 28.06, 24.57, 23.21. **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ 53.78. **HRMS (ESI):** *m/z* calculated for [C₁₂H₁₄O₄BrFSNa⁺] [M+Na⁺]: 374.9672, found: 374.9675.



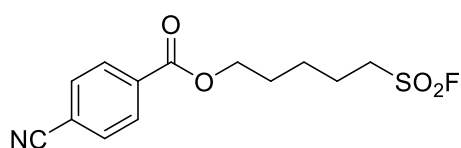
5-(fluorosulfonyl)pentyl 4-iodobenzoate (4l)

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4l** as yellow soild (92% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.77 - 7.69 (m, 2H), 7.68 - 7.61 (m, 2H), 4.25 (t, *J* = 6.3 Hz, 2H), 3.65 - 3.00 (m, 2H), 2.01 - 1.89 (m, 2H), 1.81 - 1.70 (m, 2H), 1.63 - 1.53 (m, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 166.02, 137.79, 130.99, 129.62, 100.85, 64.41, 50.68 (d, *J* = 16.5 Hz), 28.04, 24.55, 23.21. **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ 53.77. **HRMS (ESI):** *m/z* calculated for [C₁₂H₁₄O₄IFSNa⁺] [M+Na⁺]: 422.9534, found: 422.9538.



5-(fluorosulfonyl)pentyl 4-(trifluoromethyl)benzoate (4m) [6]

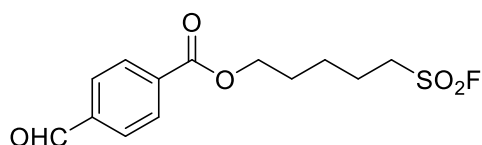
Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4m** as yellow oil (62% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.32 - 8.09 (m, 2H), 7.93 - 7.57 (m, 2H), 4.39 (t, *J* = 6.4 Hz, 2H), 3.89 - 3.28 (m, 2H), 2.45 - 1.95 (m, 2H), 1.93 - 1.81 (m, 2H), 1.77 - 1.62 (m, 2H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 165.3, 134.6 (q, *J* = 32.7 Hz), 133.3, 130.0, 125.5 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 272.9 Hz), 64.7, 50.7 (d, *J* = 16.5 Hz), 28.0, 24.6, 23.2. **¹⁹F NMR (376 MHz, Chloroform-*d*)** δ 53.84, -63.14. **HRMS (ESI):** *m/z* calculated for [C₁₃H₁₄F₄O₄SNa⁺] [M+Na⁺]: 365.0441, found: 365.0442.



5-(fluorosulfonyl)pentyl 4-cyanobenzoate (4n) [6]

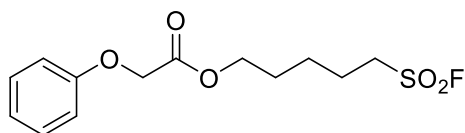
Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4n** as yellow oil (45% yield). **¹H NMR (400 MHz, Chloroform-*d*)** δ 8.31 - 8.07 (m, 2H), 7.93 - 7.69 (m, 2H), 4.39 (t, *J* = 6.4 Hz,

2H), 3.60 - 3.31 (m, 2H), 2.18 - 1.98 (m, 2H), 1.95 - 1.80 (m, 2H), 1.77 - 1.57 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.91, 133.91, 132.30, 130.08, 117.95, 116.53, 64.96, 50.66 (d, $J = 16.5$ Hz), 28.01, 24.52, 23.20. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 53.90. HRMS (ESI): m/z calculated for $[\text{C}_{13}\text{H}_{14}\text{FO}_4\text{NSNa}^+]$ $[\text{M}+\text{Na}^+]$: 322.0520, found: 322.0519.



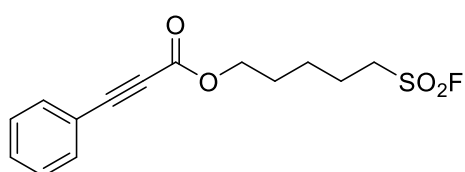
5-(fluorosulfonyl)pentyl 4-formylbenzoate (4o) ^[6]

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4o** as yellow oil (64% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 10.11 (s, 1H), 8.19 (d, $J = 8.2$ Hz, 2H), 7.96 (d, $J = 8.4$ Hz, 2H), 4.40 (t, $J = 6.4$ Hz, 2H), 3.54 - 3.31 (m, 2H), 2.15 - 1.98 (m, 2H), 1.92-1.83 (m, 2H), 1.73 - 1.65 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.57, 165.51, 139.26, 135.06, 130.16, 129.55, 64.74, 50.69 (d, $J = 16.5$ Hz), 28.04, 24.56, 23.21. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 53.85. HRMS (ESI): m/z calculated for $[\text{C}_{13}\text{H}_{15}\text{FO}_5\text{SNa}^+]$ $[\text{M}+\text{Na}^+]$: 325.0516, found: 325.0511.



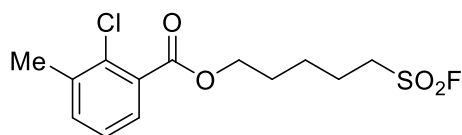
5-(fluorosulfonyl)pentyl 2-phenoxyacetate (4p) ^[6]

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4p** as yellow oil (67% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.35 - 7.27 (m, 2H), 7.08 - 6.98 (m, 1H), 6.97 - 6.87 (m, 2H), 4.64 (d, $J = 1.7$ Hz, 2H), 4.22 (t, $J = 6.3$ Hz, 2H), 3.34 - 3.21 (m, 2H), 1.97 - 1.85 (m, 2H), 1.79 - 1.66 (m, 2H), 1.56 - 1.39 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.06, 157.81, 129.62, 121.81, 114.59, 65.31, 64.40, 50.59 (d, $J = 16.6$ Hz), 27.81, 24.29, 23.02. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 53.70. HRMS (ESI): m/z calculated for $[\text{C}_{13}\text{H}_{17}\text{FO}_5\text{SNa}^+]$ $[\text{M}+\text{Na}^+]$: 327.0673, found: 327.0667.



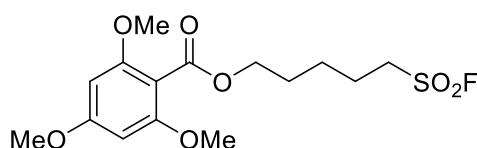
5-(fluorosulfonyl)pentyl 3-phenylpropiolate (4q)

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4q** as brown oil (31% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.58 - 7.48 (m, 2H), 7.43 - 7.35 (m, 1H), 7.34 - 7.27 (m, 2H), 4.18 (t, $J = 6.3$ Hz, 2H), 3.59 - 2.99 (m, 2H), 1.97 - 1.88 (m, 2H), 1.79 - 1.66 (m, 2H), 1.61 - 1.47 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.00, 133.01, 130.77, 128.63, 119.49, 86.63, 80.44, 65.17, 50.68 (d, $J = 16.6$ Hz), 27.81, 24.45, 23.15. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 53.62. HRMS (ESI): m/z calculated for $[\text{C}_{14}\text{H}_{15}\text{O}_4\text{FSNa}^+]$ $[\text{M}+\text{Na}^+]$: 321.0567, found: 321.0577.



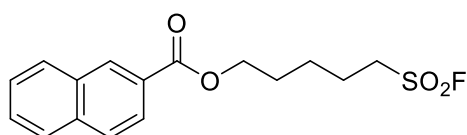
5-(fluorosulfonyl)pentyl 2-chloro-3-methylbenzoate (4r) ^[6]

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4r** as brown oil (64% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.56 - 7.51 (m, 1H), 7.39 - 7.35 (m, 1H), 7.29 - 7.17 (m, 1H), 4.36 (t, *J* = 6.3 Hz, 2H), 3.52 - 3.35 (m, 2H), 2.43 (s, 3H), 2.09 - 1.97 (m, 2H), 1.88 - 1.80 (m, 2H), 1.71 - 1.63 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 166.62, 137.96, 133.68, 132.77, 131.34, 128.26, 126.21, 64.69, 50.71 (d, *J* = 16.5 Hz), 27.97, 24.61, 23.18, 20.66. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ 53.61. HRMS (ESI): *m/z* calculated for [C₁₃H₁₆FCIO₄SNa⁺] [M+Na⁺]: 345.0334, found: 345.0334.



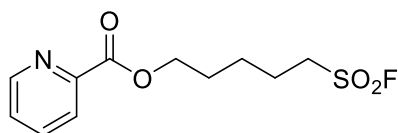
5-(fluorosulfonyl)pentyl 2,4,6-trimethoxybenzoate (4s)

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4s** as brown oil (48% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.51 (d, *J* = 8.9 Hz, 1H), 6.63 (d, *J* = 8.9 Hz, 1H), 4.24 (t, *J* = 6.3 Hz, 2H), 3.86 (s, 3H), 3.84 (s, 3H), 3.80 (s, 3H), 3.36 - 3.28 (m, 2H), 2.09 - 1.89 (m, 2H), 1.84 - 1.68 (m, 2H), 1.68 - 1.50 (m, 2H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 164.56, 156.25, 153.66, 141.98, 125.83, 116.83, 105.93, 62.89, 60.74, 59.99, 55.08, 49.71 (d, *J* = 16.5 Hz), 27.08, 23.61, 22.19. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ 53.70. HRMS (ESI): *m/z* calculated for [C₁₅H₂₁FO₇SNa⁺] [M+Na⁺]: 387.0884, found: 387.0884.



5-(fluorosulfonyl)pentyl 2-naphthoate (4t) ^[6]

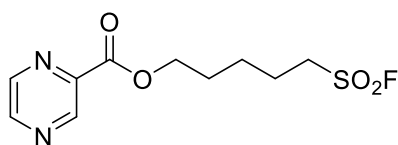
Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4t** as yellow soild (62% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.59 (d, *J* = 1.7 Hz, 1H), 8.05 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.96 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.89 (dd, *J* = 8.6, 1.9 Hz, 2H), 7.65 - 7.50 (m, 2H), 4.42 (t, *J* = 6.4 Hz, 2H), 3.65 - 3.20 (m, 2H), 2.14 - 2.00 (m, 2H), 1.97 - 1.84 (m, 2H), 1.77 - 1.66 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 166.73, 135.59, 132.51, 131.06, 129.37, 128.35, 128.25, 127.79, 127.36, 126.74, 125.14, 64.29, 50.75 (d, *J* = 16.6 Hz), 28.18, 24.69, 23.28. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ 53.72. HRMS (ESI): *m/z* calculated for [C₁₆H₁₈FO₄S⁺] [M+H⁺]: 325.0904, found: 325.0908



5-(fluorosulfonyl)pentyl picolinate (4u) ^[6]

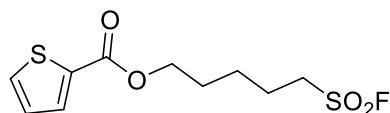
Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4u** as colorless oil (62% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.77 (d, *J* = 4.3 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 8.05 - 7.79 (m, 1H), 7.50 (dd, *J* = 6.7, 4.9 Hz, 1H), 4.45 (t, *J* = 6.5 Hz, 2H), 3.54 - 3.30 (m, 2H), 2.09 - 2.01 (m, 2H), 1.97 -

1.86 (m, 2H), 1.70 - 1.65 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.24, 149.94, 147.95, 137.09, 127.03, 125.20, 65.08, 50.67 (d, $J = 16.5$ Hz), 27.99, 24.56, 23.19. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 53.54. HRMS (ESI): m/z calculated for $[\text{C}_{11}\text{H}_{14}\text{FNO}_4\text{SNa}^+]$ $[\text{M}+\text{Na}^+]$: 298.0520, found: 298.0506.



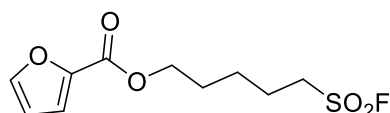
5-(fluorosulfonyl)pentyl pyrazine-2-carboxylate (**4v**)^[6]

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4v** as brown oil (63% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.31 (s, 1H), 8.92 - 8.66 (m, 2H), 4.48 (t, $J = 6.5$ Hz, 2H), 3.49 - 3.36 (m, 2H), 2.11 - 2.00 (m, 2H), 1.99 - 1.87 (m, 2H), 1.74 - 1.64 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.95, 147.78, 146.27, 144.47, 143.33, 65.47, 50.63 (d, $J = 16.8$ Hz), 27.91, 24.50, 23.15. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 53.67. HRMS (ESI): m/z calculated for $[\text{C}_{10}\text{H}_{14}\text{FN}_2\text{O}_4\text{S}^+]$ $[\text{M}+\text{H}^+]$: 277.0653, found: 277.0655.



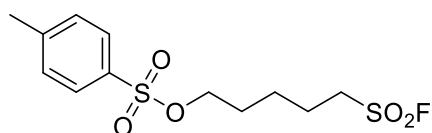
5-(fluorosulfonyl)pentyl thiophene-2-carboxylate (**4w**)^[6]

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4w** as brown oil (68% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.80 (dd, $J = 3.7, 1.3$ Hz, 1H), 7.57 (dd, $J = 5.0, 1.3$ Hz, 1H), 7.11 (dd, $J = 5.0, 3.7$ Hz, 1H), 4.33 (t, $J = 6.3$ Hz, 2H), 3.45 - 3.31 (m, 2H), 2.16 - 1.98 (m, 2H), 1.93 - 1.78 (m, 2H), 1.73 - 1.58 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.18, 133.59, 133.53, 132.50, 127.83, 64.29, 50.72 (d, $J = 16.5$ Hz), 28.07, 24.58, 23.20. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 53.67. HRMS (ESI): m/z calculated for $[\text{C}_{10}\text{H}_{13}\text{FO}_4\text{S}_2\text{Na}^+]$ $[\text{M}+\text{Na}^+]$: 303.0131, found: 303.0141.



5-(fluorosulfonyl)pentyl furan-2-carboxylate (**4x**)^[6]

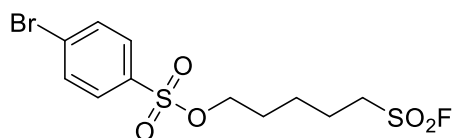
Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4x** as brown oil (64% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, $J = 1.7$ Hz, 1H), 7.19 (d, $J = 3.5$ Hz, 1H), 6.52 (dd, $J = 3.6, 1.8$ Hz, 1H), 4.34 (t, $J = 6.3$ Hz, 2H), 3.43 - 3.32 (m, 2H), 2.12 - 1.97 (m, 2H), 1.93 - 1.80 (m, 2H), 1.76 - 1.58 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.67, 146.42, 144.55, 118.08, 111.91, 64.10, 50.69 (d, $J = 16.5$ Hz), 28.01, 24.55, 23.17. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 53.62. HRMS (ESI): m/z calculated for $[\text{C}_{10}\text{H}_{13}\text{FO}_5\text{SNa}^+]$ $[\text{M}+\text{Na}^+]$: 287.0360, found: 287.0351.



5-(fluorosulfonyl)pentyl 4-methylbenzenesulfonate (**4y**)^[6]

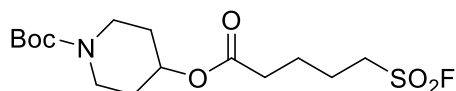
Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4y** as brown oil (62% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, $J = 8.3$ Hz, 2H), 7.36 (d, $J = 8.2$ Hz, 2H), 4.05 (t, $J = 6.1$ Hz, 2H), 3.43 - 3.24 (m, 2H), 2.46 (s, 3H), 1.97 - 1.86 (m, 2H), 1.77 - 1.68 (m, 2H), 1.55 (q, $J = 8.3$ Hz, 2H). ^{13}C

NMR (101 MHz, Chloroform-*d*) δ 145.03, 132.90, 129.96, 127.87, 69.47, 50.55 (d, $J = 16.7$ Hz), 28.18, 23.93, 22.88, 21.65. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ 53.69. **HRMS (ESI):** m/z calculated for $[\text{C}_{12}\text{H}_{17}\text{FO}_5\text{S}_2\text{Na}^+]$ $[\text{M}+\text{Na}^+]$: 347.0394, found: 347.0385.



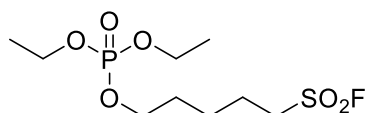
5-(fluorosulfonyl)pentyl 4-bromobenzenesulfonate (4z) ^[6]

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4z** as brown solid (65% yield). **^1H NMR (400 MHz, Chloroform-*d*)** δ 8.04 - 7.57 (m, 4H), 4.09 (t, $J = 6.1$ Hz, 2H), 3.53 - 3.04 (m, 2H), 2.04 - 1.88 (m, 2H), 1.84 - 1.71 (m, 2H), 1.65 - 1.48 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 134.93, 132.72, 129.33, 129.21, 70.01, 50.54 (d, $J = 16.7$ Hz), 28.25, 23.95, 22.94. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ 53.90. **HRMS (ESI):** m/z calculated for $[\text{C}_{11}\text{H}_{13}\text{BrFO}_5\text{S}_2]$ $[\text{M}-\text{H}]^-$: 386.9377, found: 386.9383.



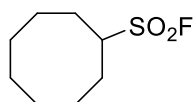
tert-butyl 4-((5-(fluorosulfonyl)pentanoyl)oxy)piperidine-1-carboxylate (4aa) ^[6]

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4aa** as brown oil (68% yield). **^1H NMR (400 MHz, Chloroform-*d*)** δ 4.99 - 4.88 (m, 1H), 3.73 (d, $J = 12.7$ Hz, 2H), 3.47 - 3.35 (m, 2H), 3.25 - 3.15 (m, 2H), 2.40 (t, $J = 7.1$ Hz, 2H), 2.09 - 1.96 (m, 2H), 1.94 - 1.83 (m, $J = 7.5$ Hz, 4H), 1.64 - 1.55 (m, 2H), 1.46 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.78, 154.72, 79.78, 70.28, 50.52 (d, $J = 16.7$ Hz), 33.47, 30.60, 29.70, 28.41, 23.10, 22.91. **^{19}F NMR (377 MHz, Chloroform-*d*)** δ 53.75. **HRMS (ESI):** m/z calculated for $[\text{C}_{15}\text{H}_{26}\text{FNO}_6\text{SNa}^+]$ $[\text{M}+\text{Na}^+]$: 390.1357, found: 390.1356.



diethyl (5-(fluorosulfonyl)pentyl) phosphate (4ab) ^[6]

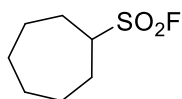
Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4ab** as brown oil (62% yield). **^1H NMR (400 MHz, Chloroform-*d*)** δ 4.24 - 3.94 (m, 6H), 3.44 - 3.32 (m, 2H), 2.07 - 1.93 (m, 2H), 1.85 - 1.70 (m, 2H), 1.69 - 1.56 (m, 2H), 1.40 - 1.31 (m, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 66.63 (d, $J = 5.9$ Hz), 63.84 (d, $J = 5.9$ Hz), 50.71 (d, $J = 16.5$ Hz), 29.51 (d, $J = 6.9$ Hz), 24.07, 23.06, 16.16 (d, $J = 6.6$ Hz). **^{19}F NMR (376 MHz, Chloroform-*d*)** δ 53.67. **^{31}P NMR (162 MHz, Chloroform-*d*)** δ -0.92. **HRMS (ESI):** m/z calculated for $[\text{C}_9\text{H}_{21}\text{FO}_6\text{PS}^+]$ $[\text{M}+\text{H}^+]$: 307.0775, found: 307.0774.



cyclooctanesulfonyl fluoride (4ac) ^[6]

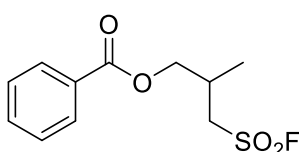
Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4ac** as brown oil (68% yield). **^1H NMR (400 MHz, Chloroform-*d*)** δ 3.61 - 3.38 (m, 1H), 2.39 - 2.22 (m, 2H), 2.05 - 1.77 (m, 4H),

1.72 - 1.52 (m, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 62.23 (d, $J = 10.3$ Hz), 29.71, 26.61, 25.98, 24.66. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 41.08. HRMS (ESI): m/z calculated for $[\text{C}_8\text{H}_{14}\text{FO}_2\text{S}]$ $[\text{M}-\text{H}]^-$: 193.0704, found: 193.0707.



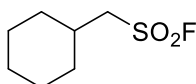
cycloheptanesulfonyl fluoride (**4ad**)^[7]

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4ad** as colorless oil (57% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 3.44 – 3.28 (m, 1H), 2.33 – 2.22 (m, 2H), 1.96 – 1.74 (m, 4H), 1.60 – 1.41 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 61.80 (d, $J = 10.2$ Hz), 27.12, 27.04, 24.31. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 41.47. HRMS (ESI): m/z calculated for $[\text{C}_7\text{H}_{12}\text{FO}_2\text{S}]$ $[\text{M}-\text{H}]^-$: 179.0548, found: 179.0549.



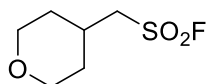
3-(fluorosulfonyl)-2-methylpropyl benzoate (**4ae**)^[6]

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4ae** as yellow oil (63% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, $J = 7.7$ Hz, 2H), 7.60 (t, $J = 7.4$ Hz, 1H), 7.47 (t, $J = 7.6$ Hz, 2H), 4.43 – 4.22 (m, 2H), 3.73 – 3.57 (m, 1H), 3.47 – 3.25 (m, 1H), 2.85 – 2.63 (m, 1H), 1.32 (d, $J = 6.9$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.1, 133.5, 129.6, 129.5, 128.6, 66.9, 54.2 (d, $J = 15.8$ Hz), 29.9, 16.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 59.02. HRMS (ESI): m/z calculated for $[\text{C}_{11}\text{H}_{13}\text{O}_4\text{FSNa}^+]$ $[\text{M}+\text{Na}^+]$: 283.0411, found: 283.0413.



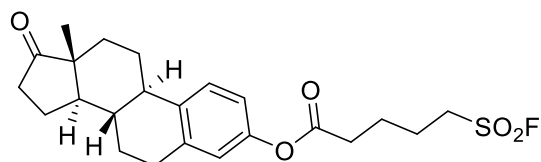
cyclohexylmethanesulfonyl fluoride (**4af**)

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4af** as colorless oil (47% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 3.47 – 3.42 (m, 2H), 1.80 – 1.66 (m, 4H), 1.54 – 1.43 (m, 1H), 1.33 – 1.12 (m, 4H), 1.02 – 0.87 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 68.82, 40.51, 29.57, 26.60, 25.85. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 53.45. HRMS (ESI): m/z calculated for $[\text{C}_7\text{H}_{12}\text{FO}_2\text{S}]$ $[\text{M}-\text{H}]^-$: 179.0548, found: 179.0543.



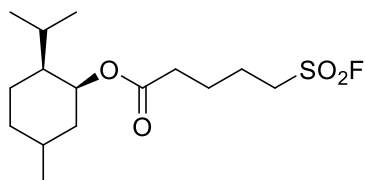
(tetrahydro-2H-pyran-4-yl)methanesulfonyl fluoride (**4ag**)

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4ag** as colorless oil (59% yield). ^1H NMR (400 MHz, Chloroform-*d*) δ 3.98 (m, 2H), 3.43 (m, 2H), 2.29 (d, $J = 7.1$ Hz, 2H), 2.03 (m, 1H), 1.69 (m, 2H), 1.38 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 67.64, 41.08, 32.53, 31.78. ^{19}F NMR (376 MHz, Chloroform-*d*) δ 53.56. HRMS (ESI): m/z calculated for $[\text{C}_6\text{H}_{10}\text{FO}_3\text{S}]$ $[\text{M}-\text{H}]^-$: 181.0340, found: 181.0343.



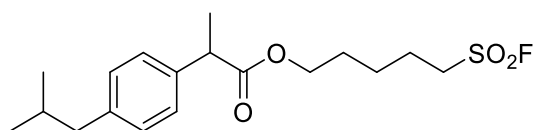
(8*S*,9*R*,13*R*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 5-(fluorosulfonyl)pentanoate (**4ah**)^[6]

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4ad** as yellow solid (52% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.30 - 7.27 (m, 1H), 6.87 - 6.83 (m, 1H), 6.80 (d, *J* = 2.5 Hz, 1H), 3.58 - 3.22 (m, 2H), 2.91 (dd, *J* = 8.6, 3.9 Hz, 2H), 2.64 (t, *J* = 7.1 Hz, 2H), 2.58 - 2.51 (m, 1H), 2.45 - 2.36 (m, 1H), 2.33 - 2.25 (m, 1H), 2.22 - 2.02 (m, 4H), 2.01 - 1.85 (m, 4H), 1.74 - 1.38 (m, 7H), 0.91 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 171.31, 148.35, 138.15, 137.63, 126.49, 121.44, 118.60, 50.63, 50.47, 50.44, 47.95, 44.16, 38.00, 35.86, 33.33, 31.56, 29.41, 26.32, 25.76, 23.07, 22.93, 21.60, 13.84. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ 53.82. HRMS (ESI): *m/z* calculated for [C₂₃H₂₉FO₅SNa⁺] [M+Na⁺]: 459.1612, found: 459.1611.



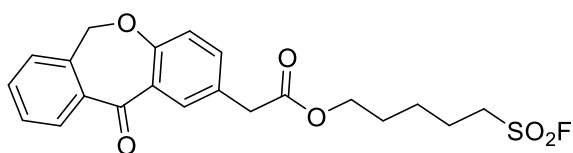
(1*S*,2*S*)-2-isopropyl-5-methylcyclohexyl 5-(fluorosulfonyl)pentanoate (**4ai**)^[6]

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4ae** as brown oil (61% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 4.76 - 4.58 (m, 1H), 3.45 - 3.32 (m, 2H), 2.37 (t, *J* = 7.1 Hz, 2H), 2.09 - 1.90 (m, 3H), 1.90 - 1.77 (m, 3H), 1.74 - 1.62 (m, 3H), 1.56 - 1.45 (m, 1H), 1.43 - 1.31 (m, 1H), 1.15 - 0.95 (m, 2H), 0.93 - 0.78 (m, 6H), 0.76 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 172.05, 74.61, 50.56 (d, *J* = 16.8 Hz), 47.00, 40.94, 34.20, 33.60, 31.39, 26.38, 23.41, 23.24, 22.93, 22.00, 20.74, 16.28. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ 53.56. HRMS (ESI): *m/z* calculated for [C₁₅H₂₇FO₄SNa⁺] [M+Na⁺]: 345.1506, found: 345.1499.



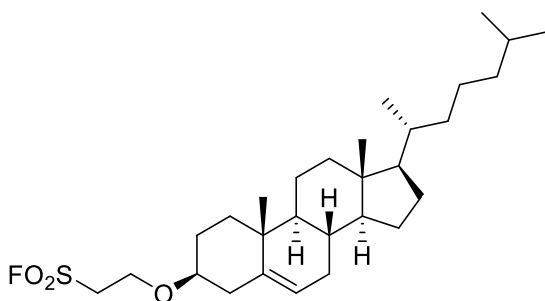
5-(fluorosulfonyl)pentyl 2-(4-isobutylphenyl)propanoate (**4aj**)^[6]

Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4af** as brown oil (50% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.19 (dd, *J* = 8.1, 2.2 Hz, 2H), 7.14 - 7.06 (m, 2H), 4.17 - 3.95 (m, 2H), 3.68 (q, *J* = 7.0 Hz, 1H), 3.30 - 3.18 (m, 2H), 2.45 (dd, *J* = 7.2, 2.1 Hz, 2H), 1.93 - 1.76 (m, 3H), 1.72 - 1.55 (m, 2H), 1.52 - 1.46 (m, 3H), 1.45 - 1.35 (m, 2H), 0.90 (dd, *J* = 6.7, 2.1 Hz, 6H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.71, 140.66, 137.77, 129.35, 127.15, 63.69, 50.61 (d, *J* = 16.5 Hz), 45.16, 44.98, 30.21, 27.78, 24.28, 22.98, 22.37, 18.29. ¹⁹F NMR (377 MHz, Chloroform-*d*) δ 53.50. HRMS (ESI): *m/z* calculated for [C₁₈H₂₇FO₄SNa⁺] [M+Na⁺]: 381.1506, found: 381.1506.



4-(fluorosulfonyl)butyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (**4ak**)^[6]

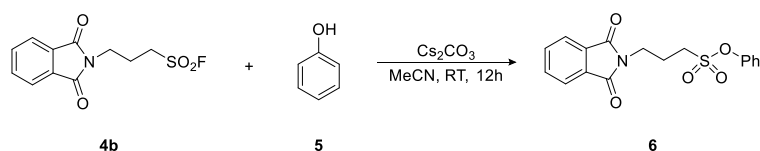
Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4ag** as brown oil (64% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 8.12 (d, *J* = 2.4 Hz, 1H), 7.89 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.60 - 7.52 (m, 1H), 7.51 - 7.45 (m, 1H), 7.41 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.36 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 1H), 5.19 (s, 2H), 4.13 (t, *J* = 6.3 Hz, 2H), 3.64 (s, 2H), 3.47 - 3.33 (m, 2H), 2.16 - 1.87 (m, 2H), 1.76 - 1.64 (m, 2H), 1.60 - 1.48 (m, 2H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 189.82, 170.32, 159.49, 139.35, 135.29, 134.55, 131.84, 131.34, 128.45, 128.29, 126.84, 126.73, 124.18, 120.10, 72.63, 63.11, 49.63 (d, *J* = 16.5 Hz), 39.27, 28.68, 26.88, 23.43, 22.11. ¹⁹F NMR (377 MHz, Chloroform-*d*) δ 53.64. HRMS (APCI): *m/z* calculated for [C₂₁H₂₂FO₆S⁺] [M+H⁺]: 421.1116, found: 421.1115.



2-(((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)ethane-1-sulfonyl fluoride (**4al**)^[6]

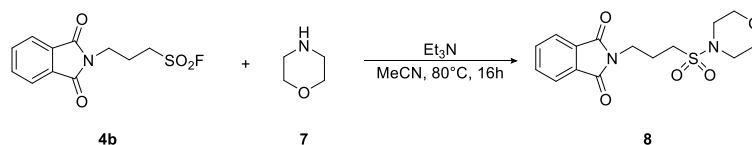
Following the **General procedure for hydro-fluorosulfonylation of alkenes** to afford the desired product **4ah** as white solid (54% yield). ¹H NMR (400 MHz, Chloroform-*d*) δ 5.42 - 5.32 (m, 1H), 4.02 - 3.87 (m, 2H), 3.74 - 3.51 (m, 2H), 3.35 - 3.14 (m, 1H), 2.39 - 2.31 (m, 1H), 2.29 - 2.17 (m, 1H), 2.12 - 1.94 (m, 2H), 1.93 - 1.75 (m, 3H), 1.65 - 1.42 (m, 7H), 1.41 - 1.30 (m, 4H), 1.22 - 1.08 (m, 7H), 1.07 - 0.96 (m, 6H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.86 (dd, *J* = 6.6, 1.9 Hz, 6H), 0.68 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 140.21, 122.19, 80.14, 60.91, 56.75, 56.16, 51.65 (d, *J* = 15.4 Hz), 50.15, 42.33, 39.76, 39.53, 38.73, 37.04, 36.82, 36.20, 35.80, 31.90 (d, *J* = 6.5 Hz), 29.72, 28.24, 28.07 (d, *J* = 7.1 Hz), 24.30, 23.84, 22.84, 22.58, 21.08, 19.36, 18.73, 11.87. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ 58.96. HRMS (APCI): *m/z* calculated for [C₂₉H₅₀FO₃S⁺] [M+H⁺]: 497.3459, found: 497.3456.

2.6 Experimental procedure for synthetic applications

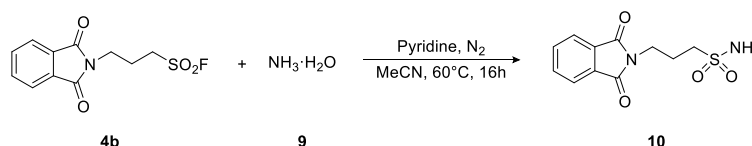


To a 10 mL round-bottomed flask equipped with a magnetic stir bar, **4b** (27.1 mg, 0.10 mmol, 1.0 eq.), phenol **5** (10.4 mg, 0.11 mmol, 1.1 eq) and Cs₂CO₃ (65.2 mg, 0.20 mmol, 2.0 eq.) in MeCN (1 mL) were added. Stir the reaction mixture for 12 hours at 25 °C under nitrogen. After completion of the reaction, purify the residue by silica gel column chromatography (PE/EA = 5:1) and product **6** was obtained in 76% yield (26.2 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.91 - 7.81 (m, 2H), 7.79 - 7.70 (m, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.32 - 7.21 (m, 3H), 3.87 (t, *J* = 6.7 Hz, 2H), 3.57 - 3.06 (m,

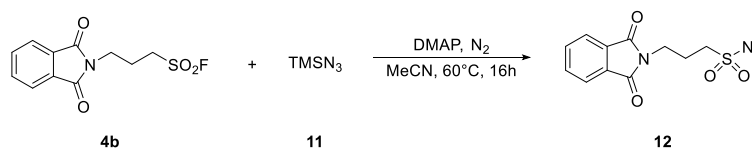
2H), 2.41 - 2.34 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.18, 148.95, 134.30, 131.84, 130.01, 127.31, 123.51, 122.00, 48.13, 36.11, 23.33. HRMS (ESI): m/z calculated for $[\text{C}_{17}\text{H}_{14}\text{NO}_5\text{S}]$ $[\text{M}-\text{H}]^-$: 344.0598, found: 344.0560.



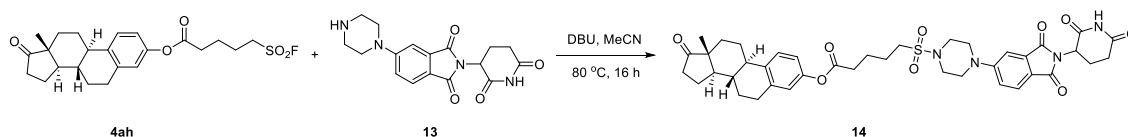
To a 10 mL round-bottomed flask equipped with a magnetic stir bar, **4b** (27.1 mg, 0.10 mmol, 1.0 eq.), morpholine **7** (17.4 mg, 0.2 mmol, 2.0 eq.), triethylamine (28 μL , 0.2 mmol, 2.0 eq.), and MeCN (0.5 mL) were added. Stir the reaction mixture for 16 hours at 80°C under nitrogen. After completion of the reaction, purify the residue by silica gel column chromatography (PE/EA = 3:1) and the product **8** was obtained in 82% yield (27.7 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.89 - 7.81 (m, 2H), 7.78 - 7.70 (m, 2H), 3.83 (t, J = 6.7 Hz, 2H), 3.78 - 3.69 (m, 4H), 3.31 - 3.21 (m, 4H), 3.12 - 2.92 (m, 2H), 2.25 - 2.17 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.27, 134.26, 131.89, 123.47, 66.59, 46.71, 45.83, 36.50, 22.82. HRMS (ESI): m/z calculated for $[\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}_5\text{S}]$ $[\text{M}-\text{H}]^-$: 337.0864, found: 337.0868.



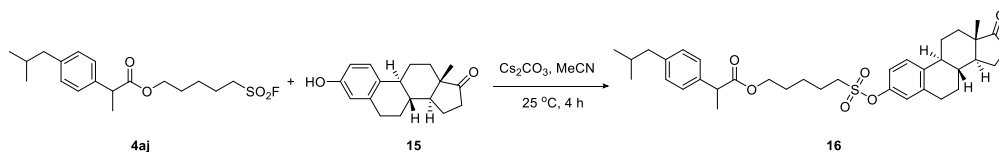
To a 10 mL round-bottomed flask equipped with a magnetic stir bar, **4b** (27.1 mg, 0.10 mmol, 1.0 eq.), $\text{NH}_3\cdot\text{H}_2\text{O}$ **9** (143 μL , 2.0 mmol, 20.0 eq.), pyridine (31.7 mg, 0.4 mmol, 2.0 eq.), and MeCN (2 mL) were added. Stir the reaction mixture for 16 hours at 60°C under nitrogen. After completion of the reaction, purify the residue by silica gel column chromatography and the product **10** was obtained in 72% yield (19.3 mg). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 8.22 - 7.62 (m, 4H), 6.76 (s, 2H), 3.69 (t, J = 6.4 Hz, 2H), 3.10 - 2.94 (m, 2H), 2.13 - 1.90 (m, 2H). ^{13}C NMR (101 MHz, $\text{DMSO } d_6$) δ 168.46, 134.86, 132.14, 123.51, 52.59, 36.63, 23.60. HRMS (ESI): m/z calculated for $[\text{C}_{11}\text{H}_{11}\text{N}_2\text{O}_4\text{S}]$ $[\text{M}-\text{H}]^-$: 267.0445, found: 267.0449.



Under nitrogen atmosphere, add **4b** (27.1 mg, 0.10 mmol, 1.0 eq.), DMAP (36.7 mg, 0.3 mmol, 1.5 eq.), TMSN_3 **11** (20 μL , 0.15 mmol, 1.5 eq.), and 2 mL MeCN to a 5 mL reaction tube equipped with a magnetic stir bar. After 15 minutes of reaction, add TMSN_3 (20 μL , 0.15 mmol, 1.5 eq.) to the mixture. Repeat this addition of TMSN_3 in the same amount after another 15 minutes. Continue the reaction for another 15 minutes and then add an equal amount of TMSN_3 again. Let the reaction proceed at room temperature for an additional 16 hours. Upon completion, remove the solvent under reduced pressure. Purify the product by column chromatography to obtain the **12** in 80% yield (23.5 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.85 (dd, J = 5.3, 3.1 Hz, 2H), 7.74 (dd, J = 5.4, 3.1 Hz, 2H), 3.86 (t, J = 6.6 Hz, 2H), 3.40 (dd, J = 9.0, 6.7 Hz, 2H), 2.47 - 2.03 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.20, 134.37, 131.79, 123.56, 53.58, 35.88, 23.20. HRMS (ESI): m/z calculated for $[\text{C}_{11}\text{H}_9\text{N}_4\text{O}_4\text{S}]$ $[\text{M}-\text{H}]^-$: 293.0350, found: 293.0351.



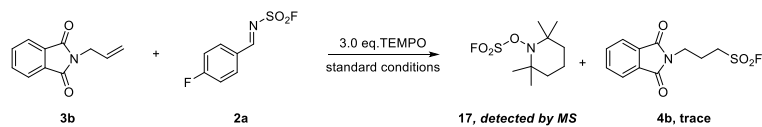
To a round-bottomed flask equipped with a magnetic stir bar, **4ah** (0.1 mmol), pomalidomide derivative **13** and DBU (0.2 mmol) and MeCN (1 mL) were added. Stir the reaction mixture for 16 hours at 80°C under nitrogen. After completion of the reaction, purify the residue by silica gel column chromatography (PE/EA = 1:1) and the product **14** was obtained in 46% yield (34.8 mg). **¹H NMR (400 MHz, DMSO-*d*₆)** δ 11.08 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.40 (s, 1H), 7.29 (t, *J* = 8.9 Hz, 2H), 6.89 - 6.74 (m, 2H), 5.08 (dd, *J* = 12.9, 5.4 Hz, 1H), 3.56 (t, *J* = 4.8 Hz, 4H), 3.16 (d, *J* = 7.5 Hz, 2H), 2.88 (t, *J* = 8.6 Hz, 1H), 2.82 (d, *J* = 5.2 Hz, 2H), 2.62 (t, *J* = 6.5 Hz, 2H), 2.56 (q, *J* = 4.6 Hz, 1H), 2.47 - 2.30 (m, 2H), 2.28 - 2.14 (m, 1H), 2.05 (dd, *J* = 19.3, 9.3 Hz, 2H), 1.91 (s, 2H), 1.69 - 1.17 (m, 16H), 0.83 (s, 3H). **¹³C NMR (101 MHz, DMSO-*d*₆)** δ 220.0, 173.3, 172.2, 170.5, 167.9, 167.4, 155.3, 148.7, 138.2, 137.6, 134.3, 126.8, 125.4, 121.9, 119.5, 119.3, 118.9, 109.0, 60.2, 50.0, 49.3, 47.9, 47.5, 45.2, 44.0, 37.9, 35.8, 33.3, 31.8, 31.5, 29.3, 26.3, 25.8, 23.6, 22.5, 21.6, 21.2, 13.9. **HRMS (ESI):** *m/z* calculated for [C₄₀H₄₅N₄O₉S] [M-H]⁻: 757.2913, found: 757.2919.



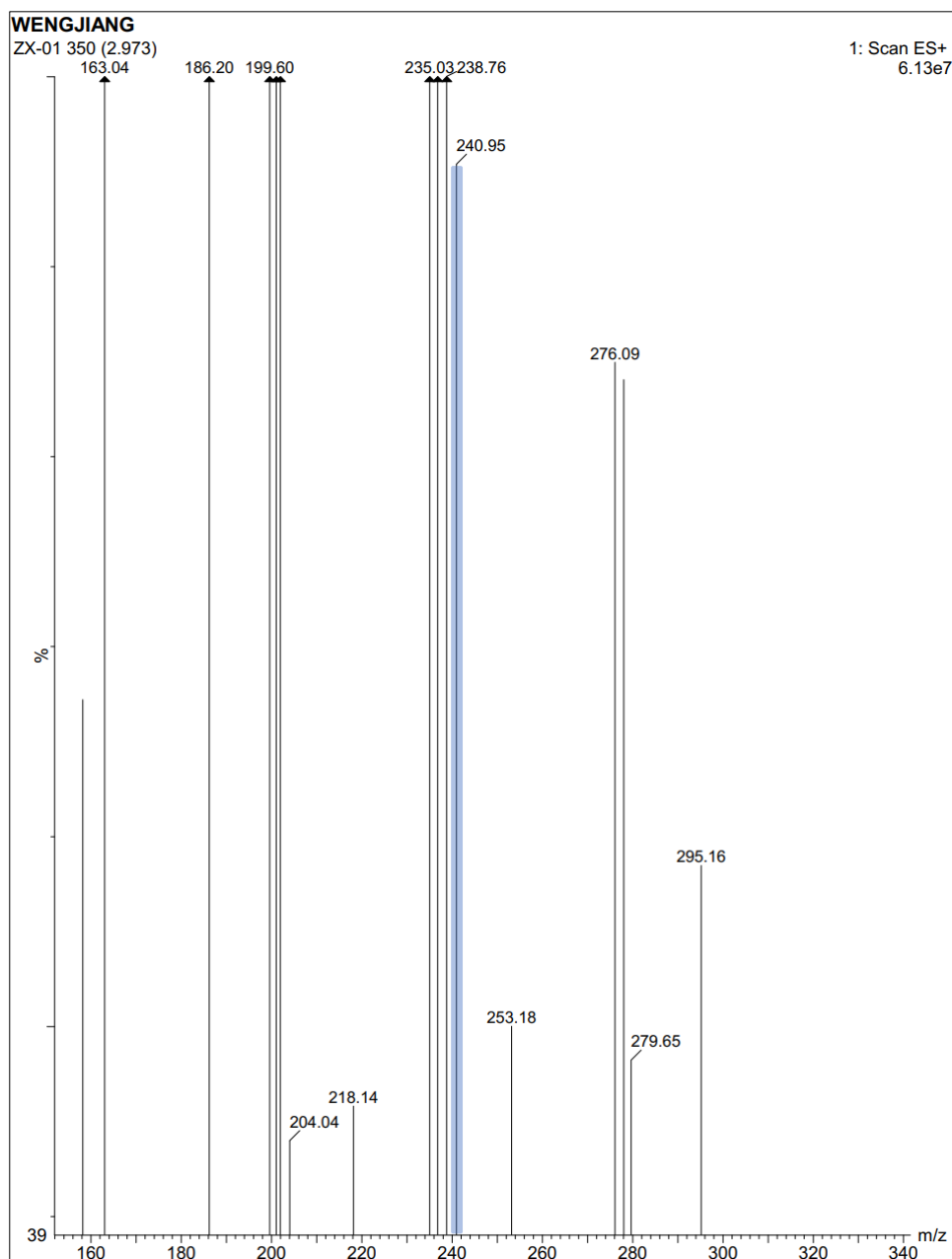
To a 10 mL round-bottomed flask equipped with a magnetic stir bar, **4aj** (0.1 mmol), estrone **15** (0.15 mmol) and Cs₂CO₃ (0.15 mmol) in MeCN (2 mL) were added. Stir the reaction mixture for 4 hours at 25°C under nitrogen. After completion of the reaction, purify the residue by silica gel column chromatography (PE/EA = 2:1) and product **16** was obtained in 85% yield (51.8 mg). **¹H NMR (400 MHz, Chloroform-*d*)** δ 7.30 (d, *J* = 8.4 Hz, 1H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 7.7 Hz, 2H), 7.01 (d, *J* = 11.0 Hz, 2H), 4.06 (dd, *J* = 12.9, 6.2 Hz, 2H), 3.68 (q, *J* = 7.2 Hz, 1H), 3.15 (t, *J* = 7.9 Hz, 2H), 2.93 (dd, *J* = 9.2, 4.2 Hz, 2H), 2.51 (dd, *J* = 18.8, 8.7 Hz, 1H), 2.44 (d, *J* = 7.3 Hz, 2H), 1.97 - 1.79 (m, 4H), 1.69 - 1.36 (m, 14H), 1.27 (s, 1H), 1.25 (d, *J* = 7.4 Hz, 3H), 0.91 (s, 3H), 0.89 (s, 3H), 0.88 (s, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 219.5, 173.7, 145.9, 139.5, 137.9, 137.8, 136.8, 128.3, 126.1, 125.9, 121.0, 118.0, 62.9, 49.4, 49.1, 46.9, 44.1, 44.0, 43.1, 36.9, 34.8, 30.5, 29.1, 28.4, 27.0, 25.2, 24.7, 23.5, 22.1, 21.4, 20.6, 17.3, 12.8. **HRMS (ESI):** *m/z* calculated for [C₃₆H₄₉O₆S]⁺[M+H]⁺: 609.3244, found: 609.3247.

3. Mechanism studies

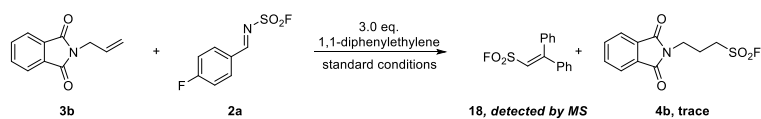
3.1 Radical trapping experiments with TEMPO



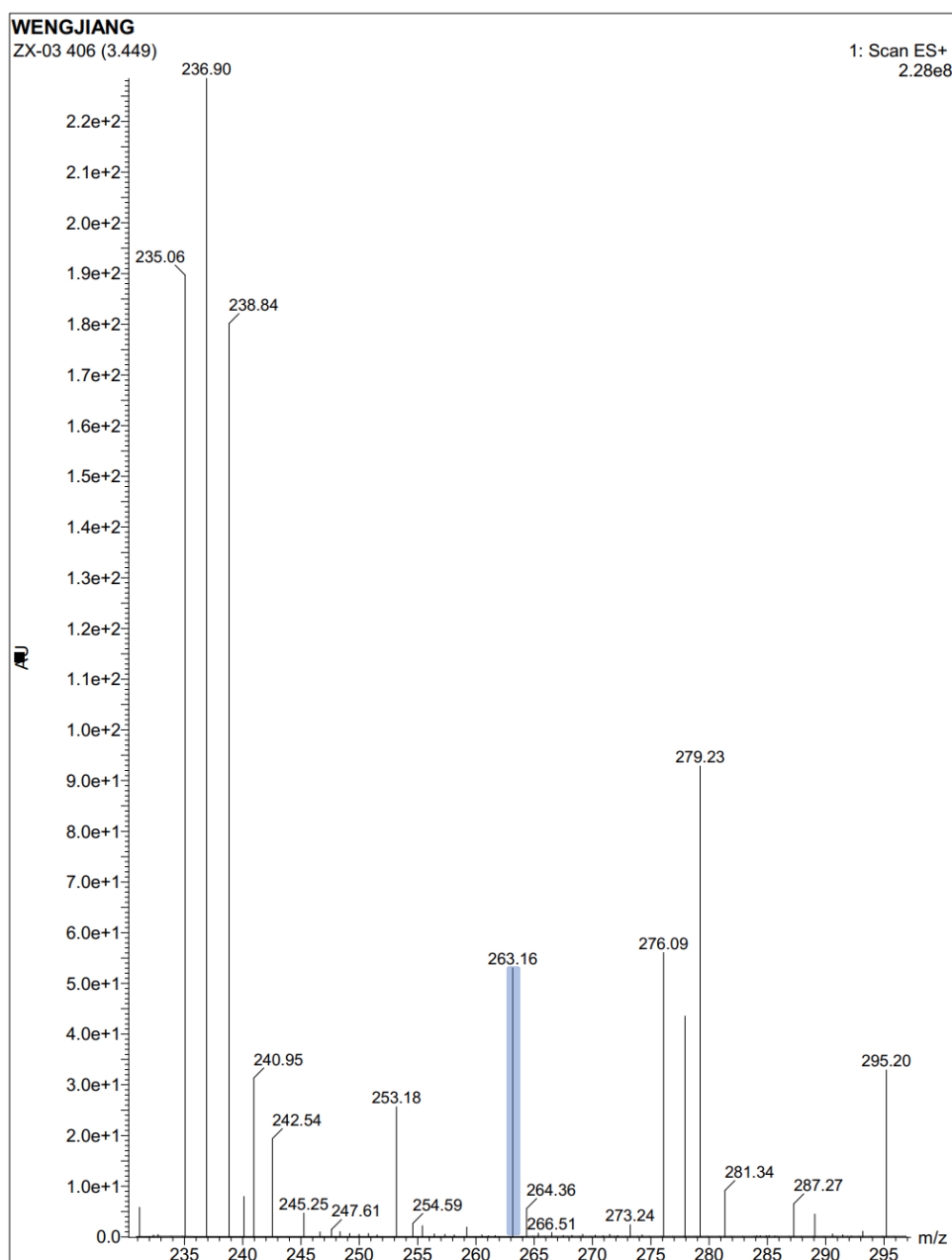
3b (0.1 mmol), **2a** (0.3 mmol), [Ir[dF(CF₃)ppy]₂(dtbbpy)]PF₆ (1 mmol%), Na₂CO₃ (0.1 mmol), TEMPO (0.3 mmol) and 1,3-dioxane (3 mL) were added to a 10 mL Schlenk tube equipped with a magnetic stirring bar. The tube was evacuated and backfilled with nitrogen. The reaction mixture was then irradiated with 30 W blue LEDs for 12 h. TLC and LC-MS analysis demonstrated that **17** is found. **MS (ESI)**: m/z calculated for [C₉H₁₉FNO₃S⁺] [M+H⁺]: 240.11, found: 240.95.



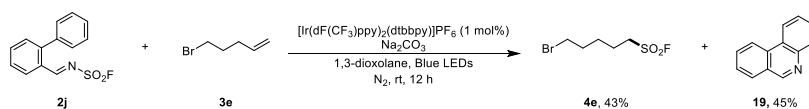
3.2 Radical trapping experiments with 1,1-diphenylethylene



3b (0.1 mmol), **2a** (0.3 mmol), $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (1 mmol%), Na_2CO_3 (0.1 mmol), 1,1-diphenylethylene (0.3 mmol) and 1,3-dioxane (3 mL) were added to a 10 mL Schlenk tube equipped with a magnetic stirring bar. The tube was evacuated and backfilled with nitrogen. The reaction mixture was then irradiated with 30 W blue LEDs for 12 h. TLC and LC-MS analysis demonstrated that **18** is found. **MS (ESI):** m/z calculated for $[\text{C}_{14}\text{H}_{12}\text{FO}_2\text{S}^+]$ $[\text{M}+\text{H}^+]$: 263.05, found: 263.16.



3.3 Iminyl radical trapping experiment



3e (0.1 mmol), **2j** (0.3 mmol), $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ (1 mmol%), Na_2CO_3 (0.1 mmol) and 1,3-dioxane (3 mL) were added to a 10 mL Schlenk tube equipped with a magnetic stirring bar. The flask was backfilled with nitrogen. The reaction mixture was then irradiated with 30 W blue LEDs for 12 h. After the reaction, the solution was purified by flash column chromatography or on silica gel to give the product **4e** in 43% yield and **19**^[8] in 45% yield. Compound **19**: **¹H NMR (400 MHz, Chloroform-*d*)** δ 9.30 (s, 1H), 8.65 – 8.56 (m, 2H), 8.20 (dd, $J = 8.1, 1.4$ Hz, 1H), 8.06 (dd, $J = 8.0, 1.4$ Hz, 1H), 7.91 – 7.84 (m, 1H), 7.80 – 7.66 (m, 3H). **¹³C NMR (101 MHz, Chloroform-*d*)** δ 153.60, 144.49, 132.59, 131.04, 130.17, 128.80, 128.72, 127.52, 127.12, 126.42, 124.13, 122.24, 121.90. **HRMS (ESI):** m/z calculated for $[\text{C}_{13}\text{H}_{10}\text{N}^+][\text{M}+\text{H}^+]$: 180.0808, found: 180.0813.

3.4 Stern-Volmer quenching studies

Stern-Volmer luminescence quenching studies were performed using a Jasco FP-8300 spectrofluorometer using Starna® fluorescence quartz cuvettes (type: 29-F, chamber volume = 1.400 mL, $H \times W \times D = 48 \text{ mm} \times 12.5 \text{ mm} \times 12.5 \text{ mm}$, path length = 10 mm). The following parameters were set: data interval = 0.5 nm, scan-speed = 500 nm/min, excitation wavelength $\lambda_{\text{ex}} = 405 \text{ nm}$, measured luminescence wavelength $\lambda = 471 \text{ nm}$. All samples used in the luminescence quenching-based screening studies were prepared in an argon-filled glovebox with degassed and dry MeCN. Stock solutions of potential quenchers and the photocatalyst $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ ($5 \times 10^{-5} \text{ M}$) were initially prepared. Stern-Volmer luminescence quenching studies were performed using a stock solution of the photocatalyst and variable concentrations of the potential quenchers at rt under an argon atmosphere. The samples were prepared by dilution in the 1.4 mL quartz cuvettes inside the argon-filled glovebox. The solutions were irradiated at 405 nm and the luminescence was measured at 471 nm. The ratio of I_0/I was plotted as a function of the quencher concentration [Quencher] (I_0 = emission intensity of the photocatalyst in isolation at the specified wavelength 471 nm; I = observed emission intensity of the photocatalyst with added quencher).

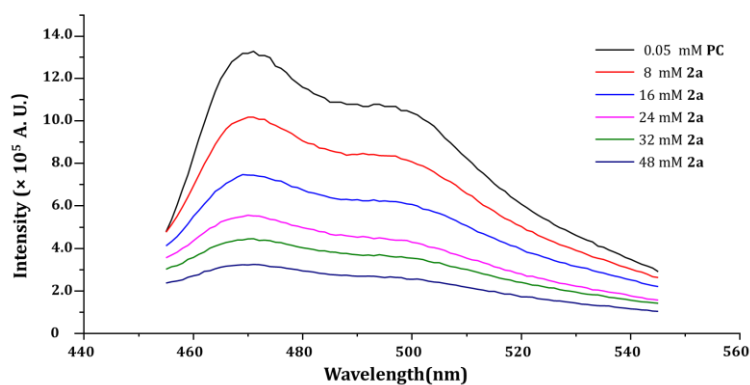


Figure S1. Emission spectra of $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})]\text{PF}_6$ ($5 \times 10^{-5} \text{ M}$) at different concentrations of **2a**

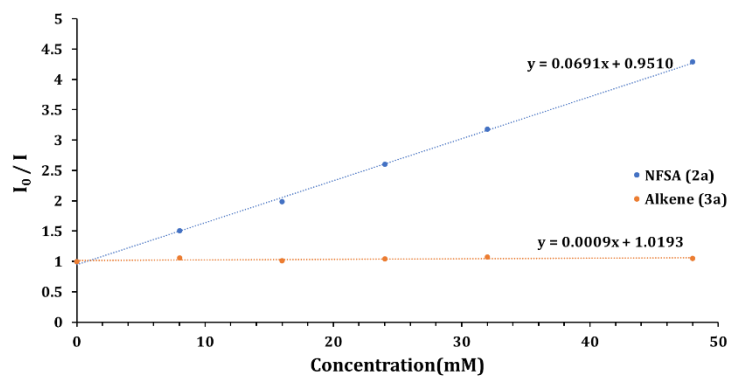


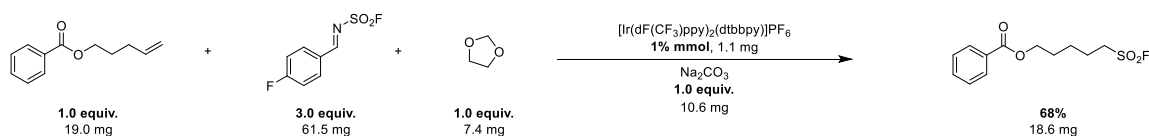
Figure S2. Stern-Volmer plot of $(\text{Ir}[\text{dF}(\text{CF}_3)\text{ppy}]_2(\text{dtbbpy}))\text{PF}_6$ (5×10^{-5} M) at different concentrations of **2a** and **3a**

4. Green metrics^[9]

To give a clear calculation, compound **4g** has been chosen as a representative example.

entry	Work of different groups	<i>E</i> -Factor	AE	RME	PMI
1	This work	4.35	58.4%	21.2%	5.35
2	Wang ^[9]	6.24	35.2%	14.0%	7.24
3	Liao ^[10]	6.94	35.2%	12.6%	7.94
4	Glorius ^[11]	4.48	39.3%	18.5%	5.47
5	Weng ^[6]	4.82	50.5%	17.4%	5.82

Our method



Total amounts of reactants = 99.6 mg

Amount of final product = 18.6 mg

Amount of waste: 99.6 mg – 18.6 mg = 81.0 mg

***E*-Factor** = Amount of waste/Amount of final product = 4.35

Molecular weight of product = 274.1

Sum of molecular weight of reagent = 469.1

AE = Molecular weight of product/Sum of molecular weight of reagent = 58.4%

Mass of product = 18.6 mg

Total mass of reagent = 87.9 mg

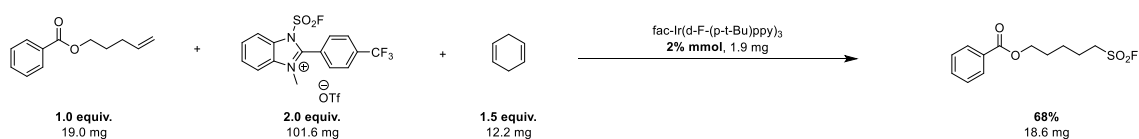
RME = Mass of product/Total mass of reagent = 21.2%

Total mass in process = 99.6 mg

Mass of product = 18.6 mg

PMI = Total mass in process/Mass of product = 5.35

Wang's work^[10]



Total amounts of reactants = 134.7 mg

Amount of final product = 18.6 mg

Amount of waste: 134.7 mg – 18.6 mg = 116.1 mg

E-Factor = Amount of waste/Amount of final product = 6.24

Molecular weight of product = 274.1

Sum of molecular weight of reagent = 778.2

AE = Molecular weight of product/Sum of molecular weight of reagent = 35.2%

Mass of product = 18.6 mg

Total mass of reagent = 132.8 mg

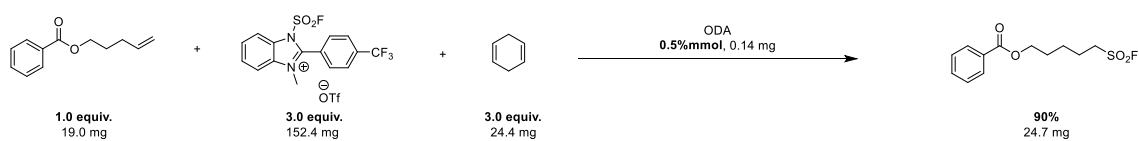
RME = Mass of product/Total mass of reagent = 14.0 %

Total mass in process = 134.7 mg

Mass of product = 18.6 mg

PMI = Total mass in process/Mass of product = 7.24

Liao's work^[11]



Total amounts of reactants = 195.9 mg

Amount of final product = 24.7 mg

Amount of waste: 195.9 mg – 24.7 mg = 171.2 mg

E-Factor = Amount of waste/Amount of final product = 6.94

Molecular weight of product = 274.1

Sum of molecular weight of reagent = 778.2

AE = Molecular weight of product/Sum of molecular weight of reagent = 35.2%

Mass of product = 24.7 mg

Total mass of reagent = 195.8 mg

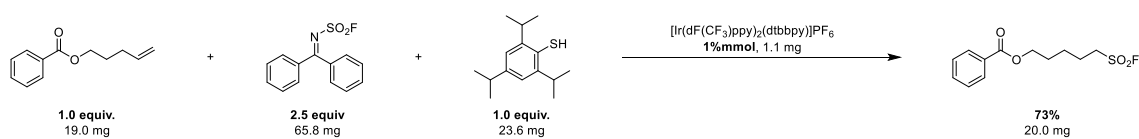
RME = Mass of product/Total mass of reagent = 12.6 %

Total mass in process = 195.9 mg

Mass of product = 24.7 mg

PMI = Total mass in process/Mass of product = 7.94

Glorius's work^[12]



Total amounts of reactants = 109.5 mg

Amount of final product = 20.0 mg

Amount of waste: 109.5 mg – 20.0 mg = 89.5 mg

E-Factor = Amount of waste/Amount of final product = 4.48

Molecular weight of product = 274.1

Sum of molecular weight of reagent = 689.6

AE = Molecular weight of product/Sum of molecular weight of reagent = 39.3%

Mass of product = 20.0 mg

Total mass of reagent = 108.4 mg

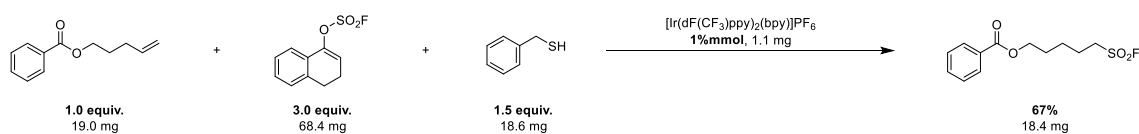
RME = Mass of product/Total mass of reagent = 18.5 %

Total mass in process = 109.5 mg

Mass of product = 20.0 mg

PMI = Total mass in process/Mass of product = 5.47

Weng's work^[6]



Total amounts of reactants = 107.1 mg

Amount of final product = 18.4 mg

Amount of waste: 107.1 mg – 18.4 mg = 88.7 mg

E-Factor = Amount of waste/Amount of final product = 4.82

Molecular weight of product = 274.1

Sum of molecular weight of reagent = 542.3

AE = Molecular weight of product/Sum of molecular weight of reagent = 50.5%

Mass of product = 18.4 mg

Total mass of reagent = 106.0 mg

RME = Mass of product/Total mass of reagent = 17.4 %

Total mass in process = 107.1 mg

Mass of product = 18.4 mg

PMI = Total mass in process/Mass of product = 5.82

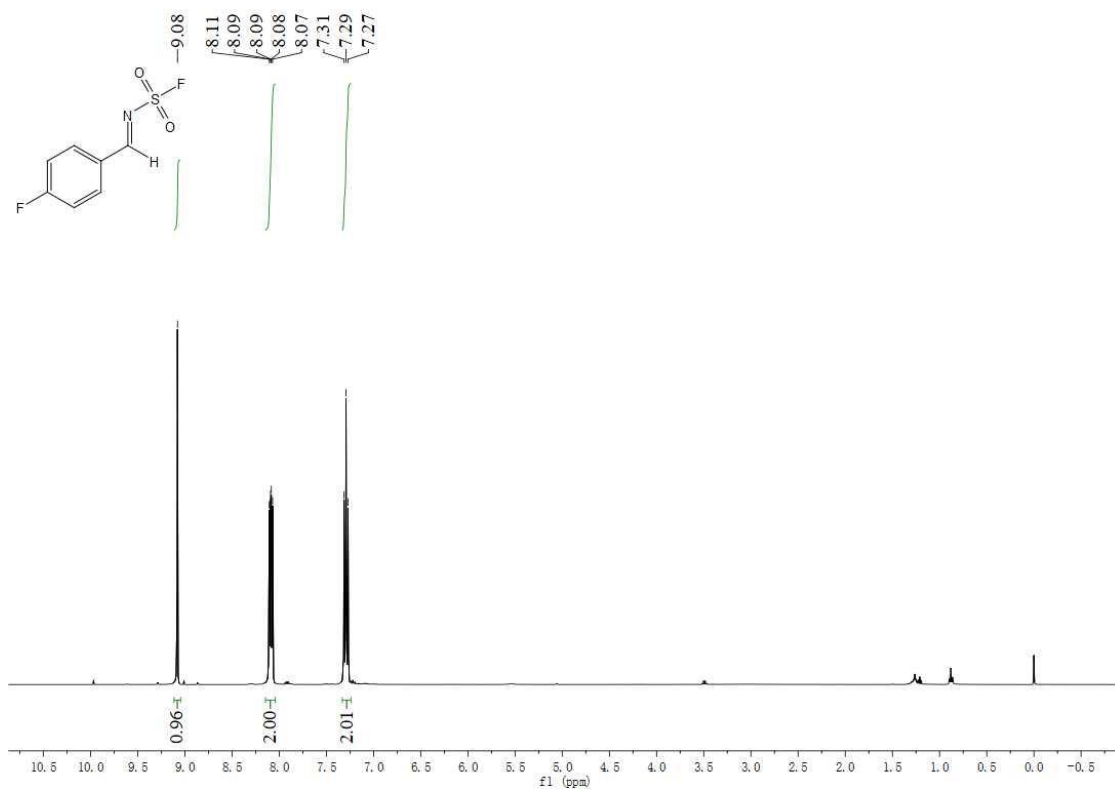
5. Reference

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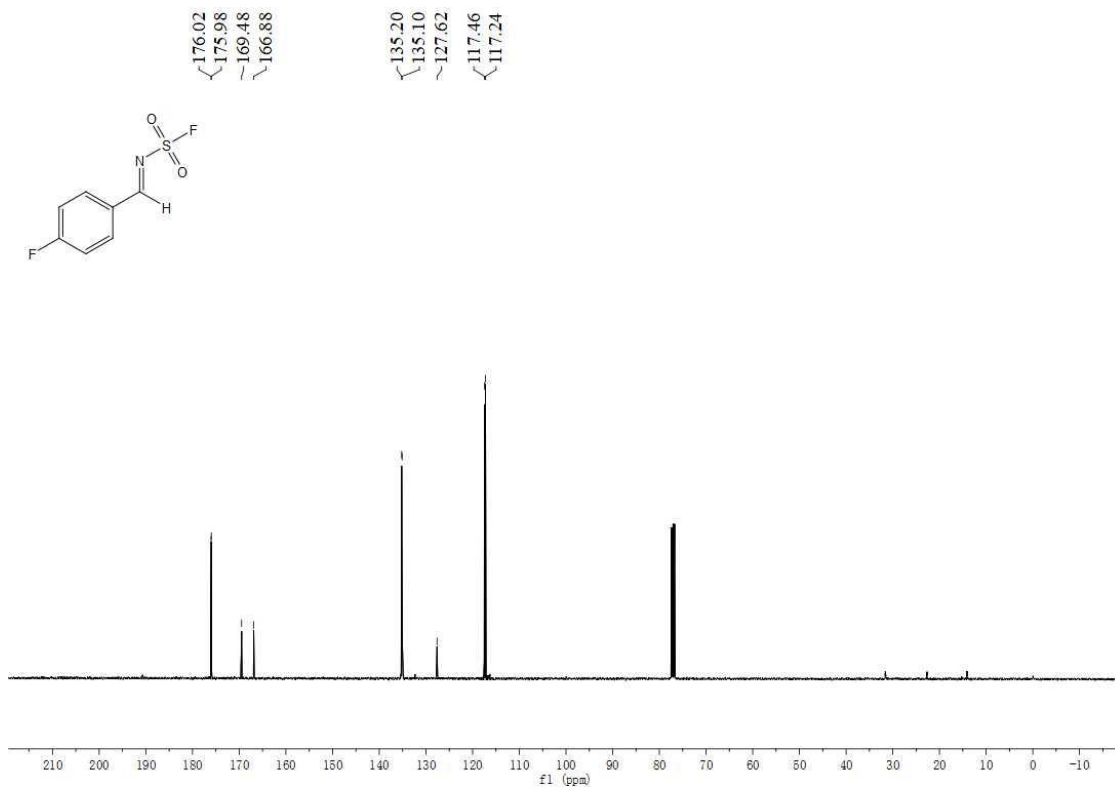
6. ^1H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR spectra for compounds

(*E*)-(4-fluorobenzylidene)sulfamoyl fluoride (**2a**)

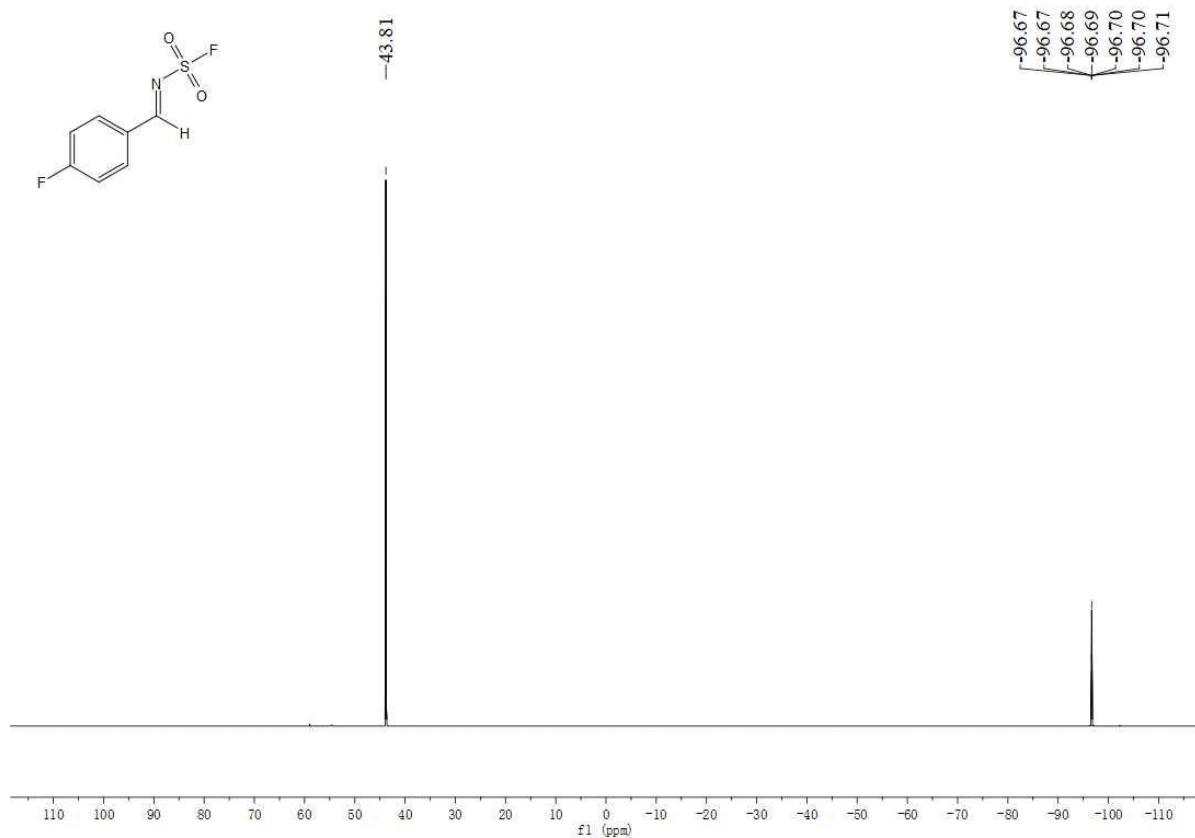
^1H NMR



^{13}C NMR

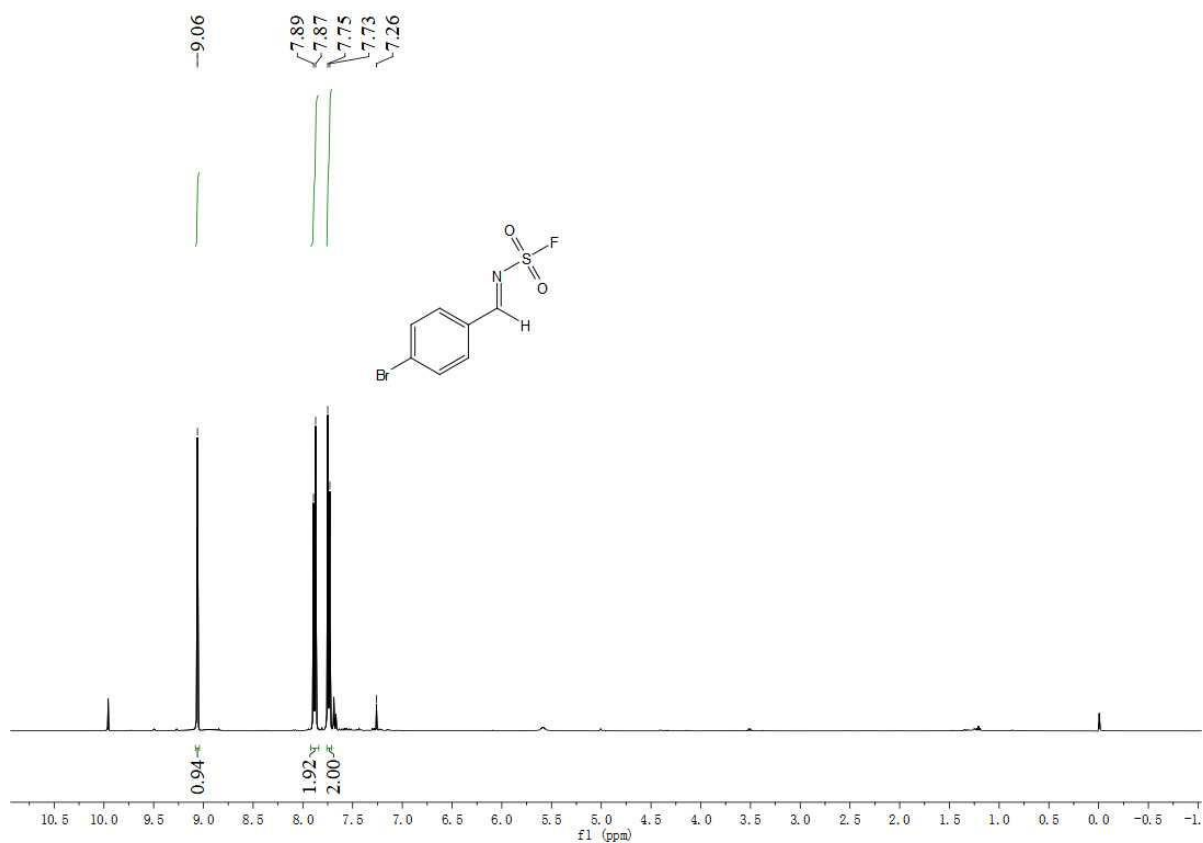


¹⁹F NMR

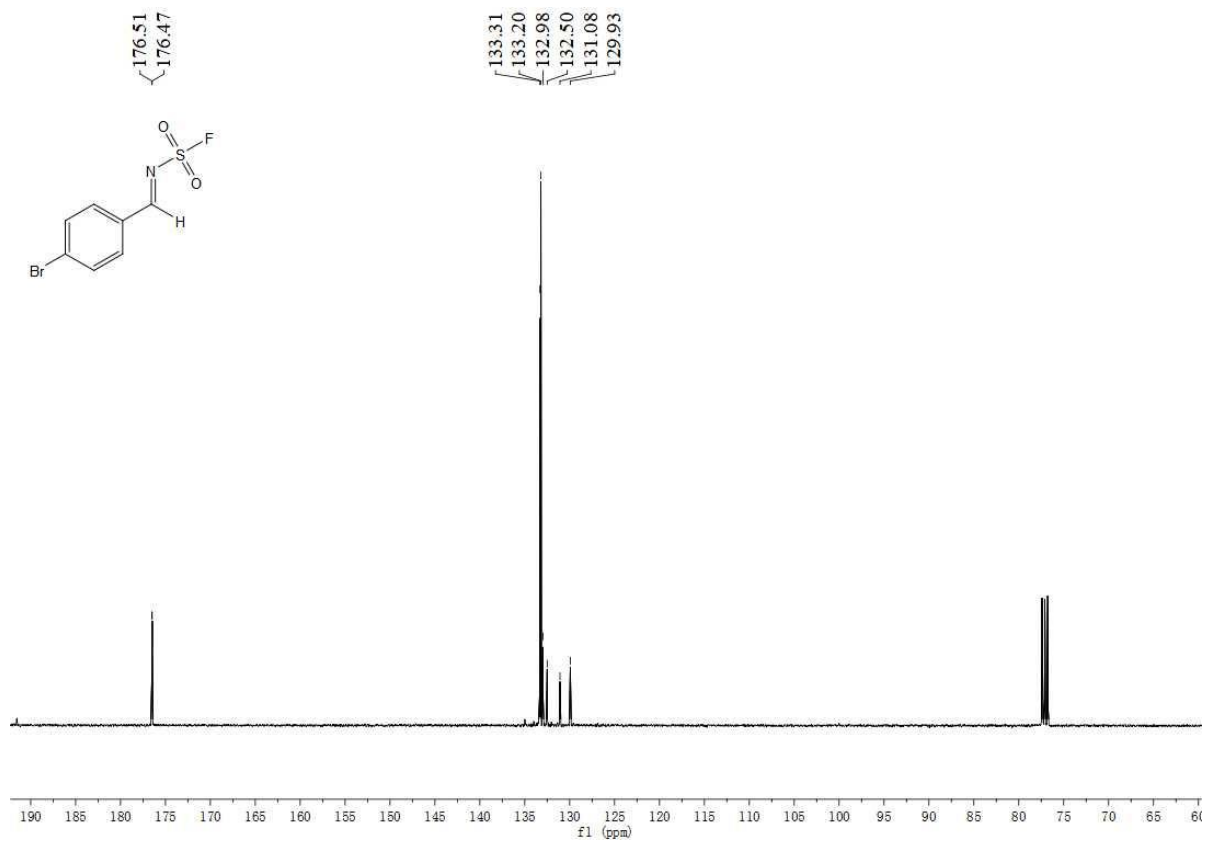


(E)-4-(4-bromobenzylidene)sulfamoyl fluoride (2b)

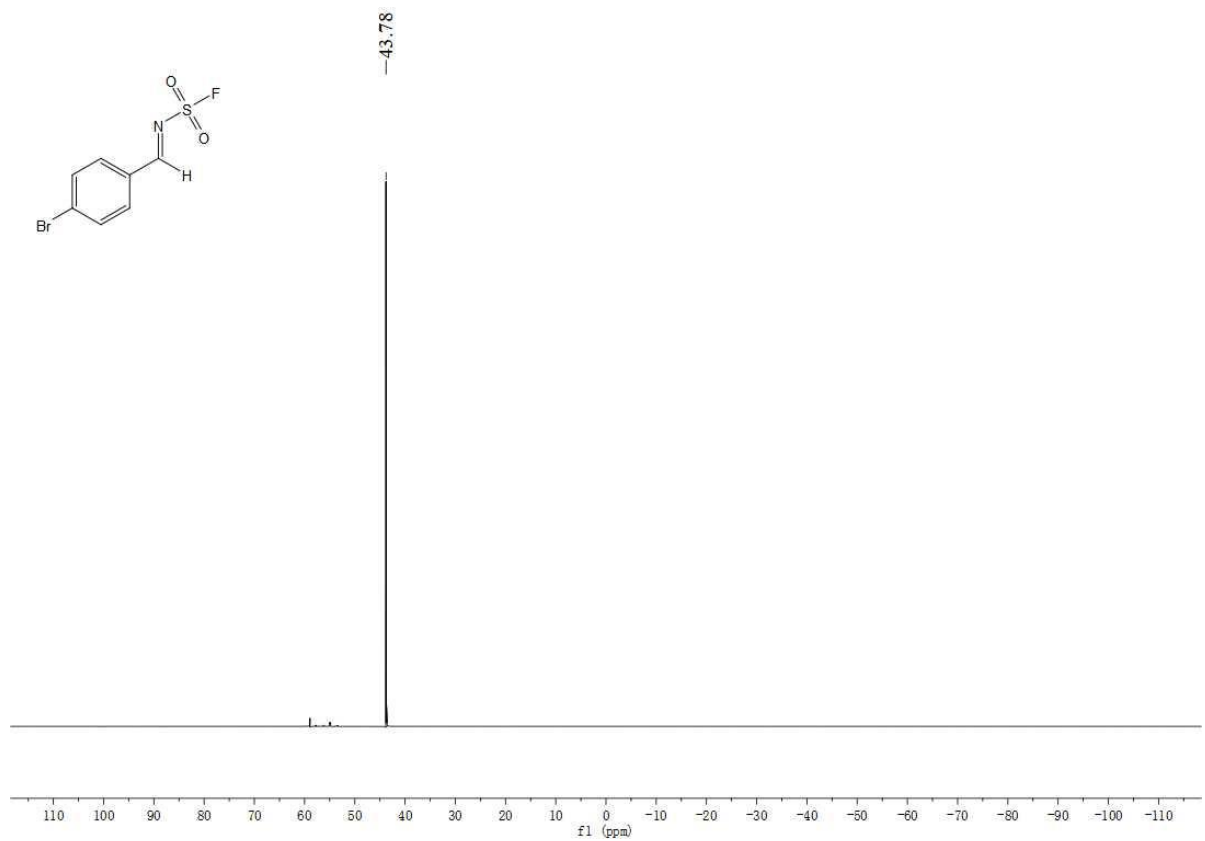
¹H NMR



¹³C NMR

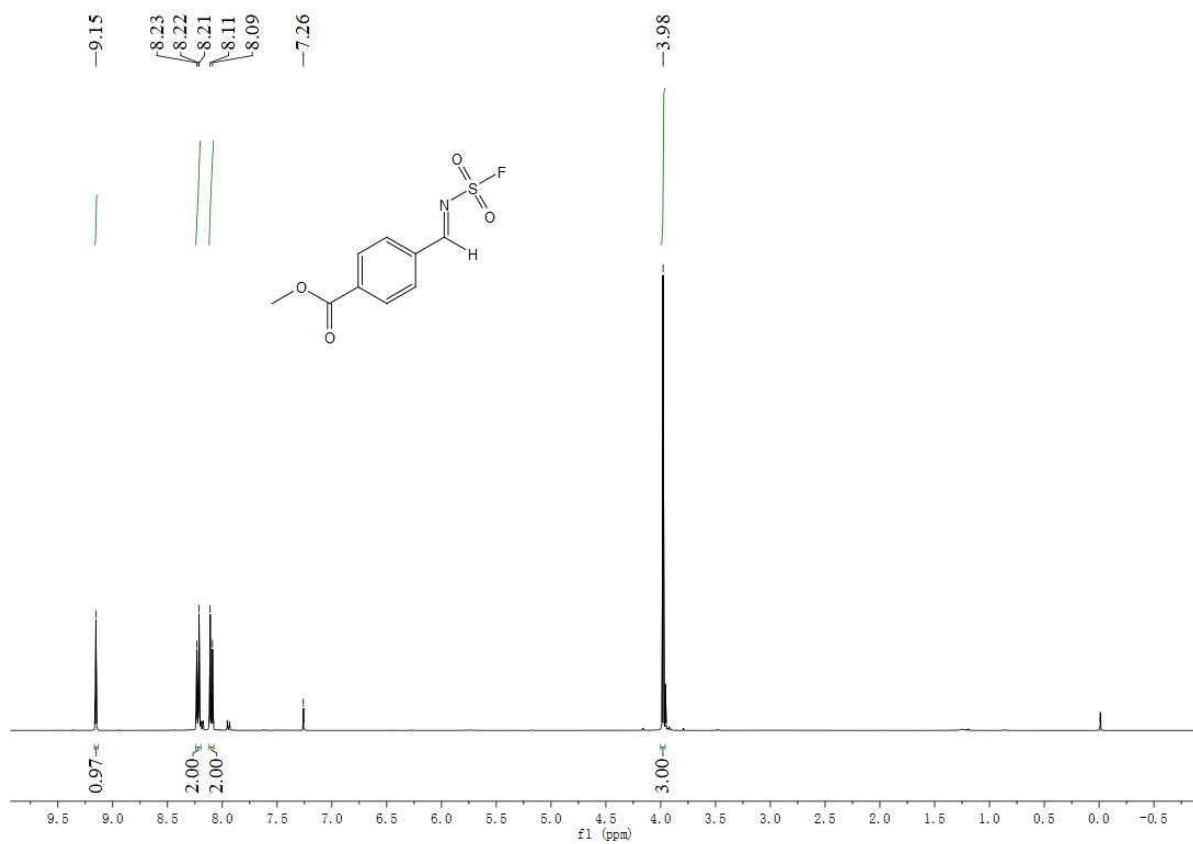


¹⁹F NMR

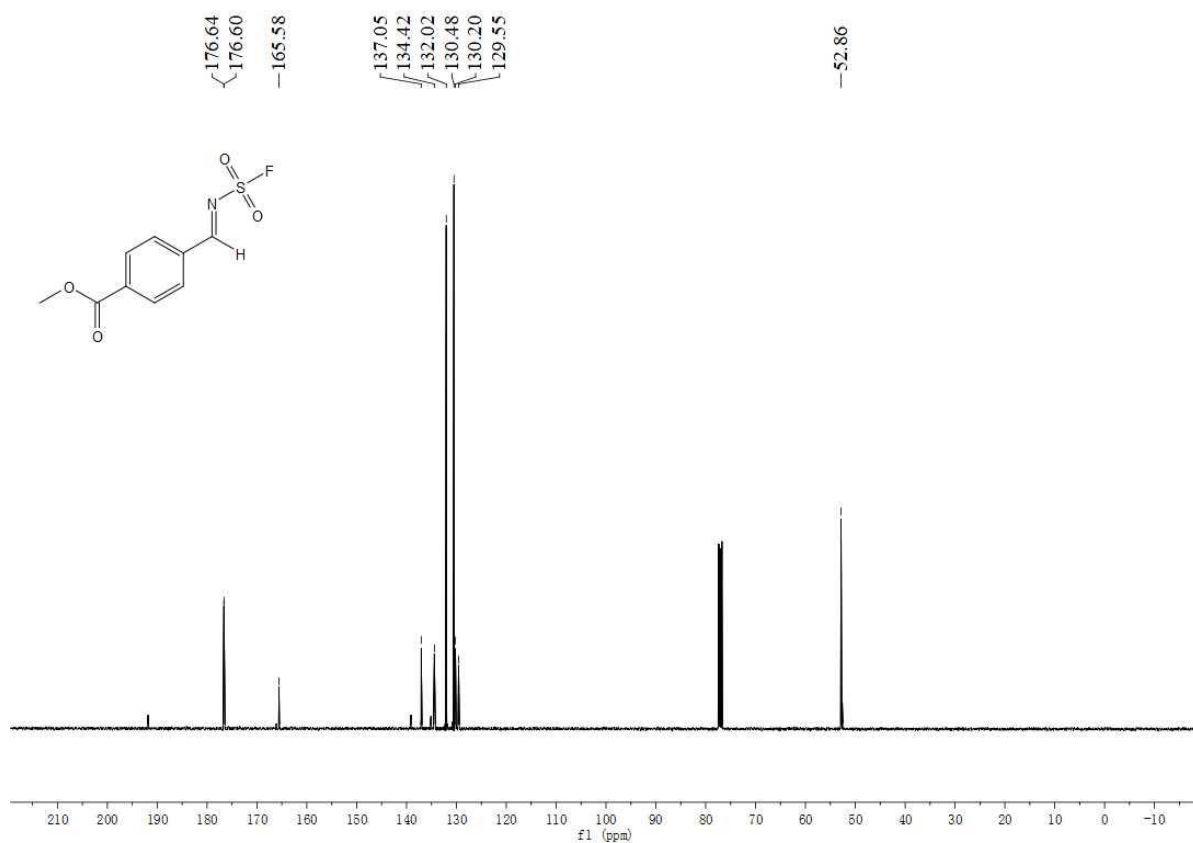


methyl (E)-4-(((fluorosulfonyl)imino)methyl)benzoate (2c)

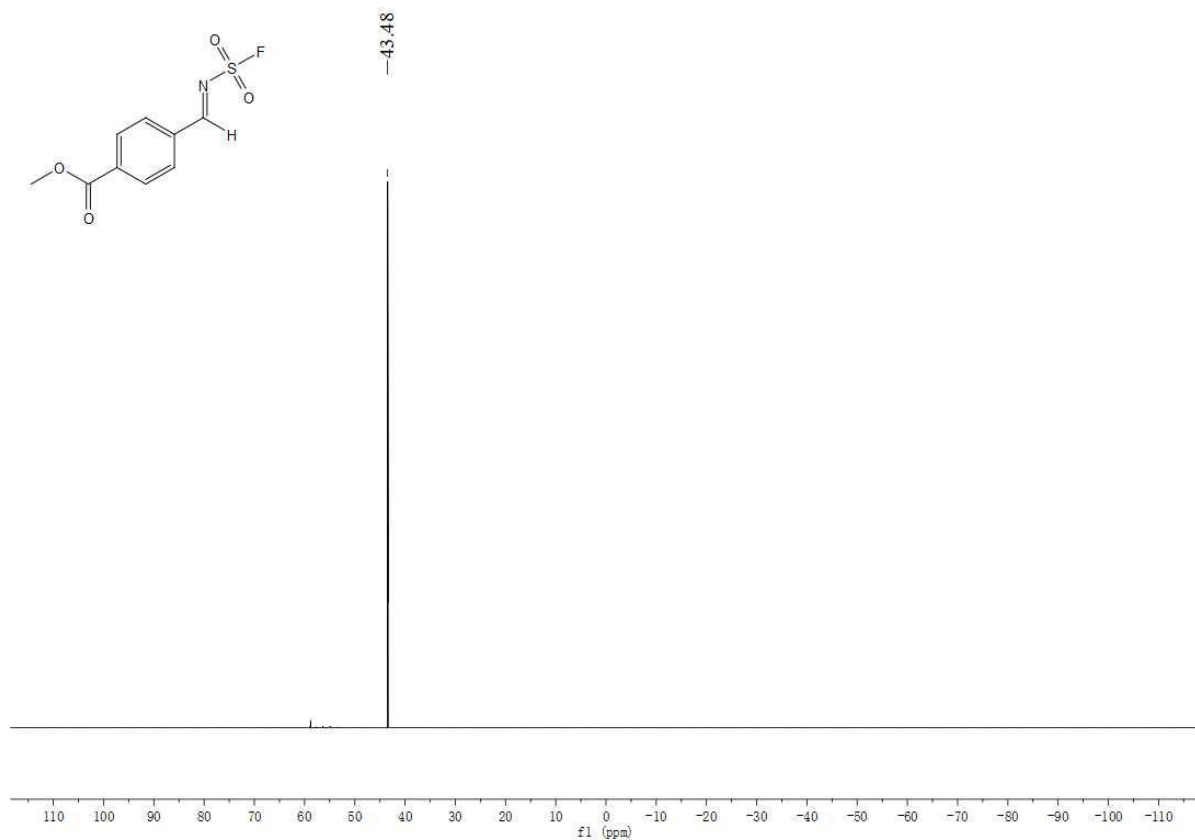
¹H NMR



¹³C NMR

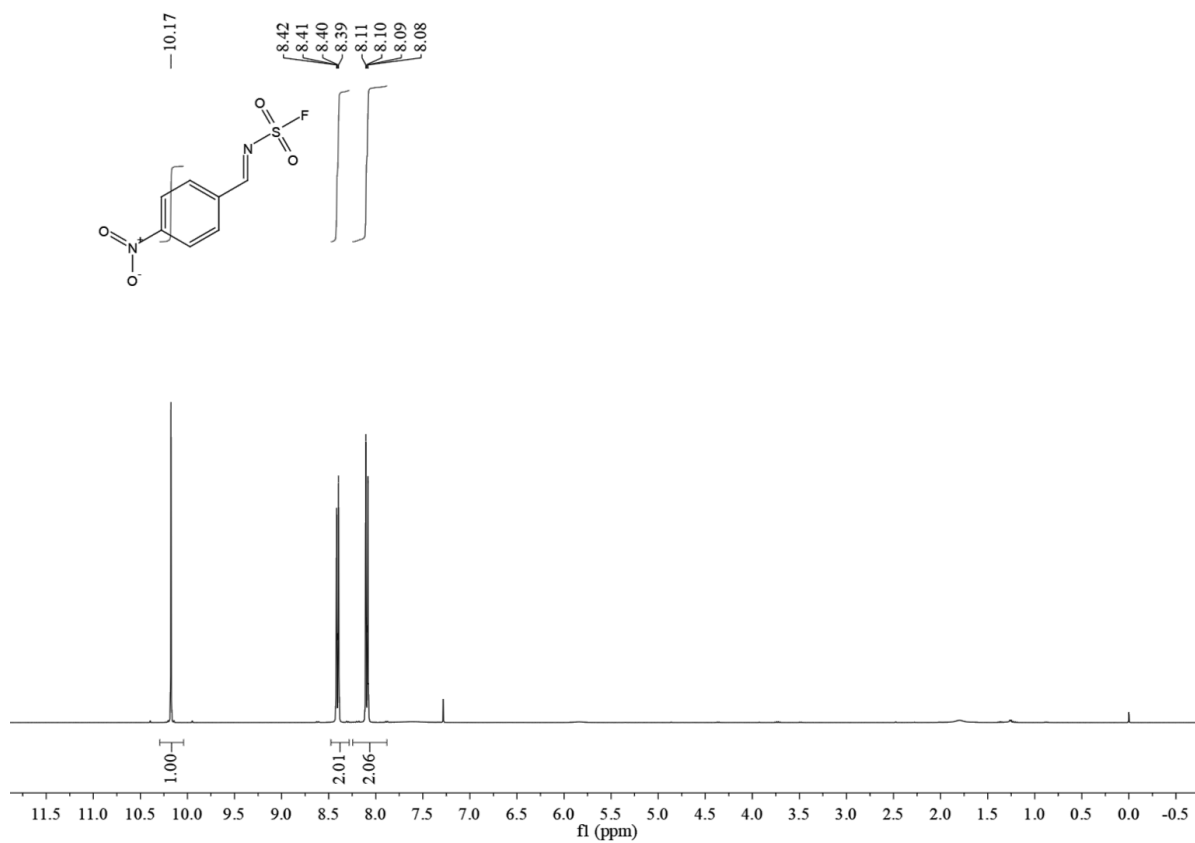


¹⁹F NMR

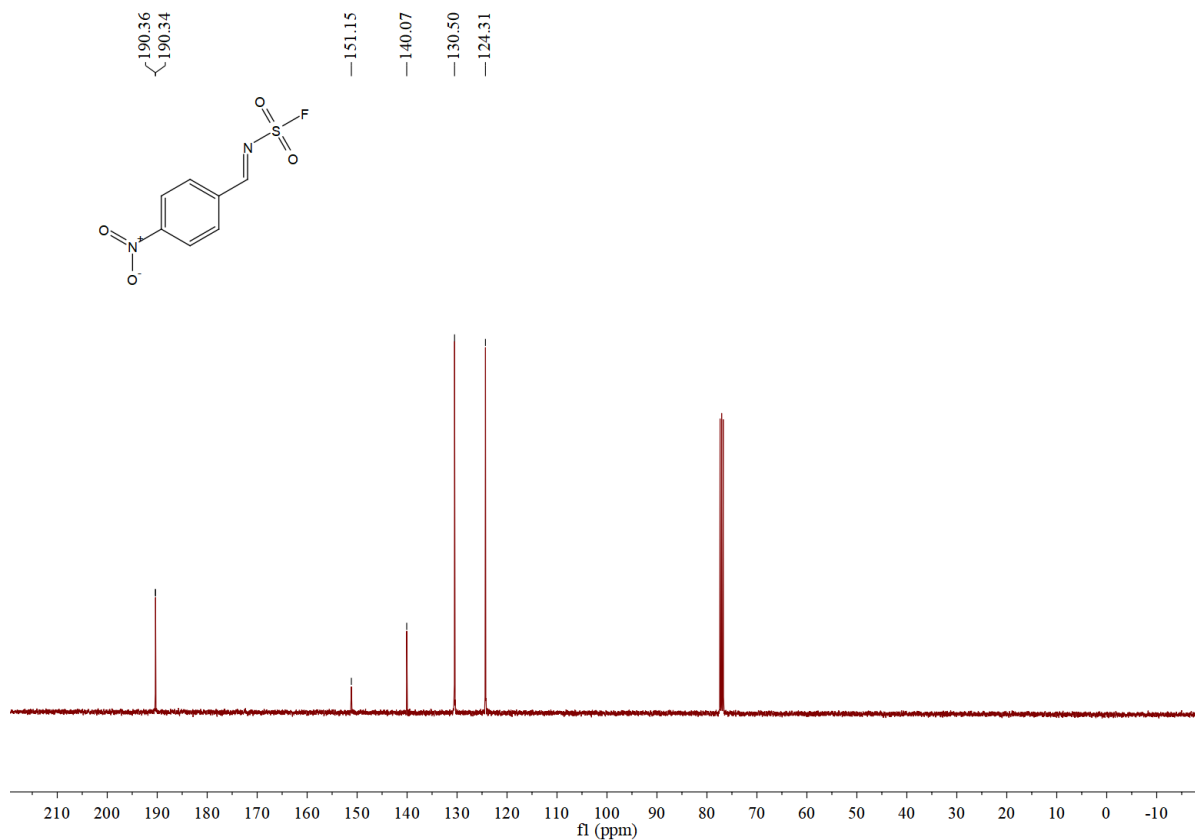


(E)-4-(4-nitrobenzylidene)sulfamoyl fluoride (2d)

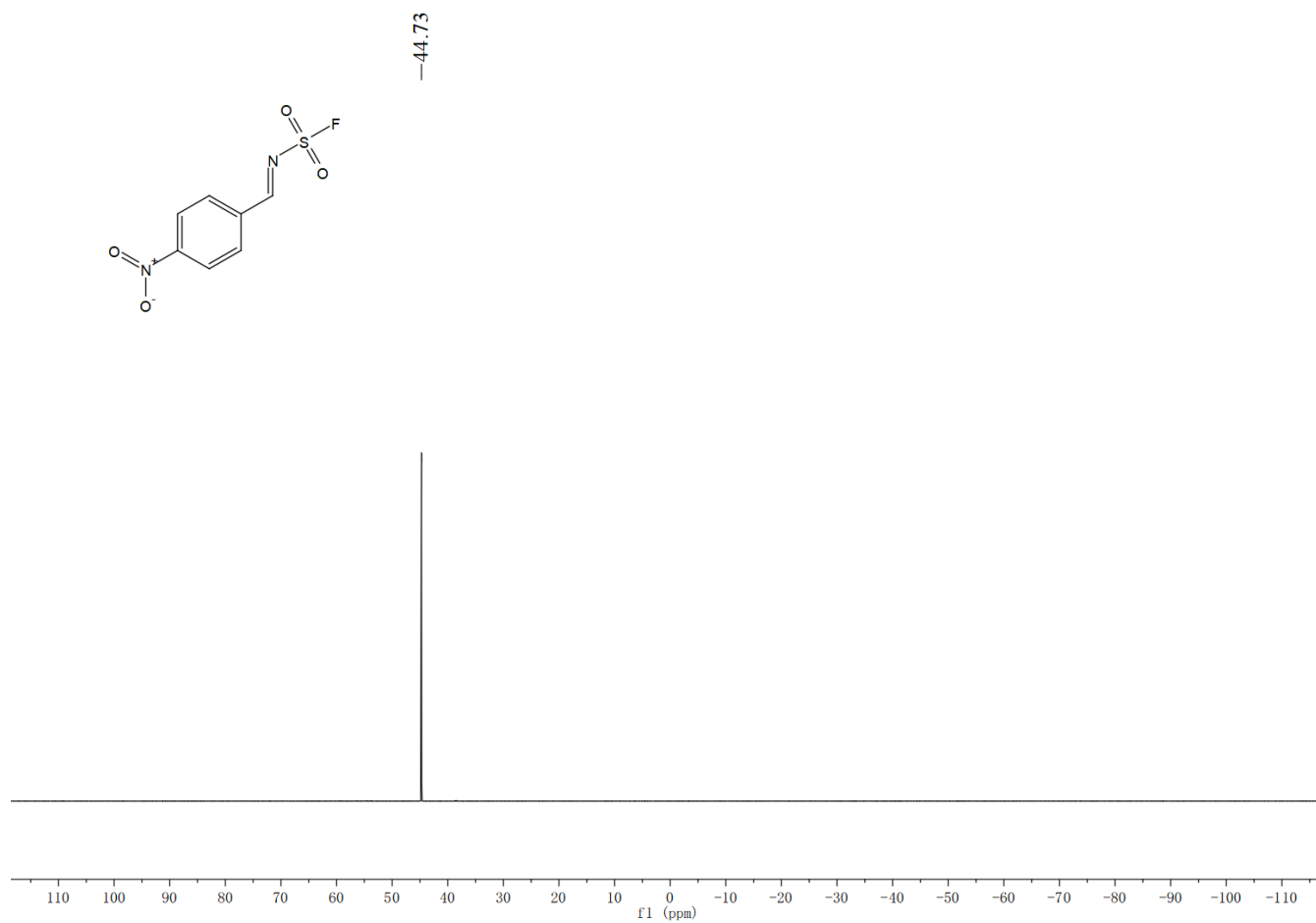
¹H NMR



¹³C NMR

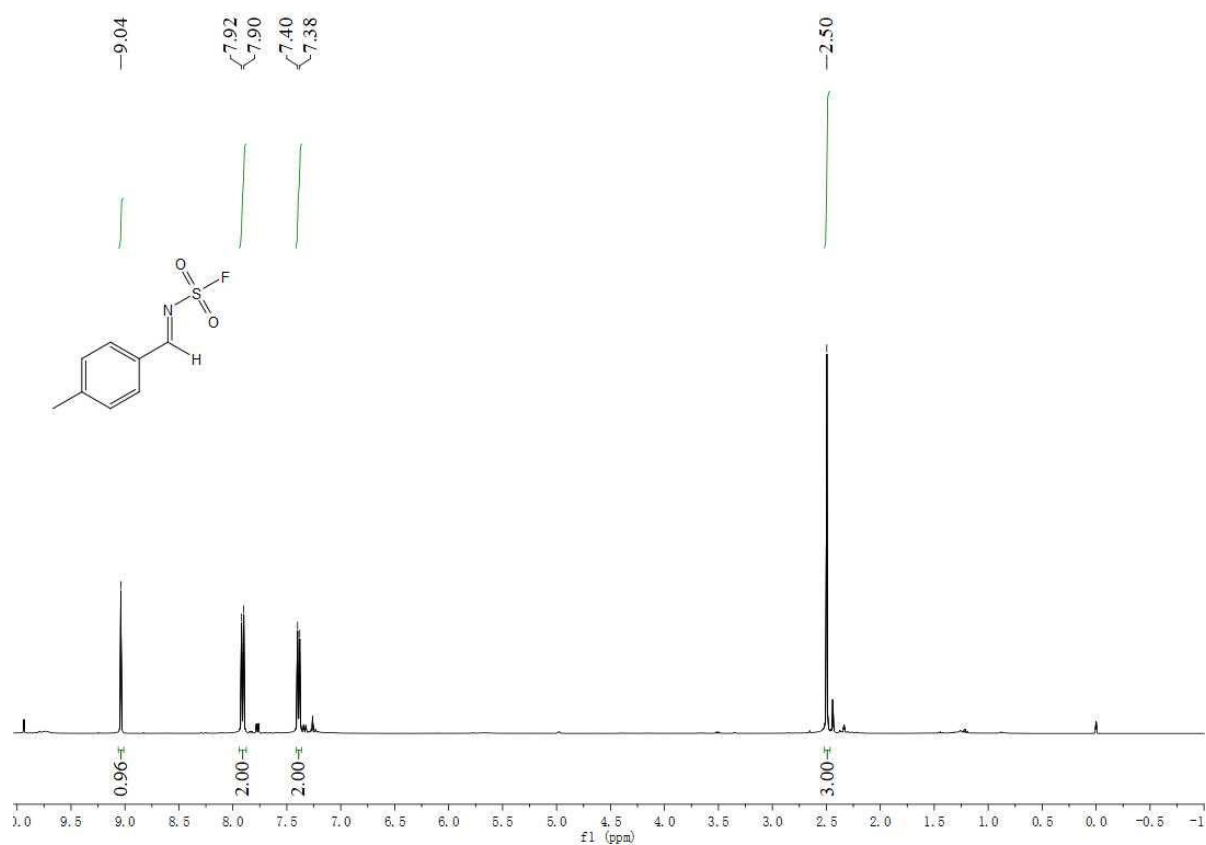


¹⁹F NMR

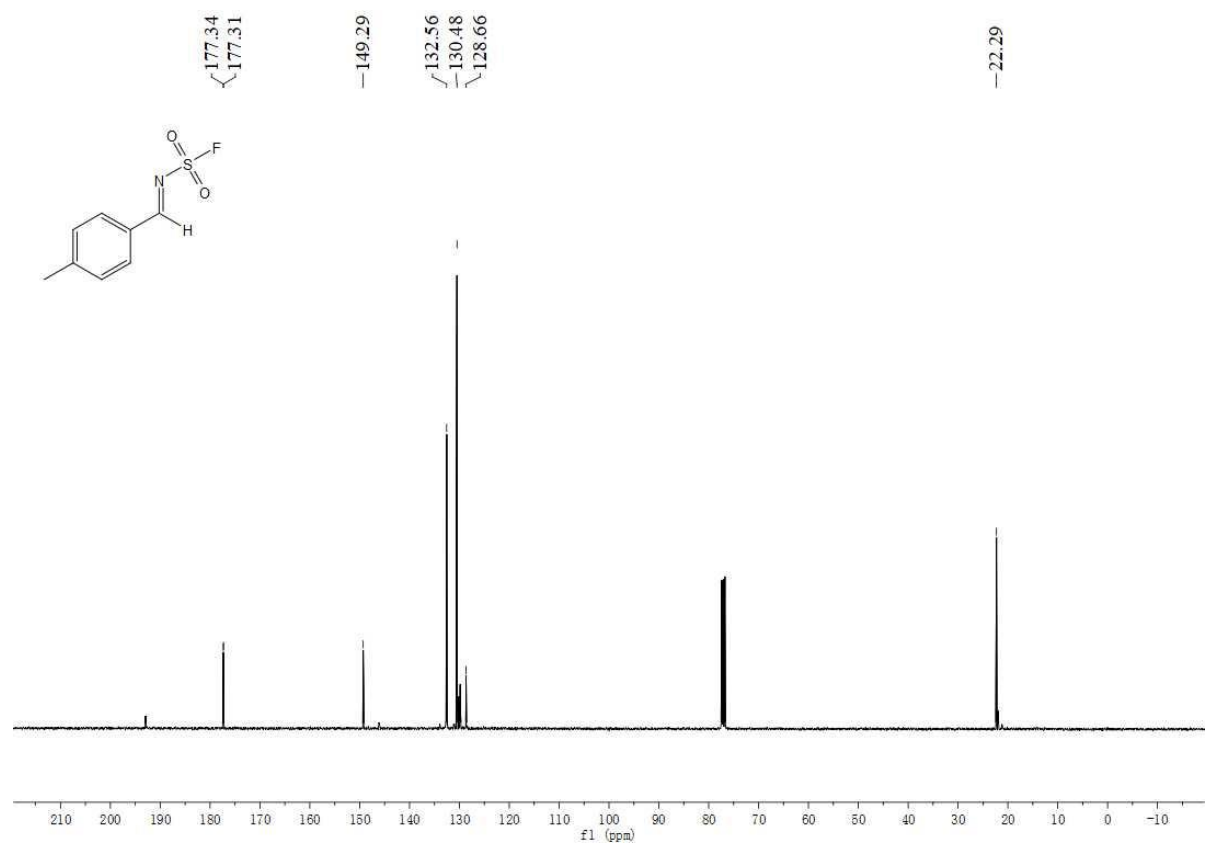


(E)-(4-methylbenzylidene)sulfamoyl fluoride (2e)

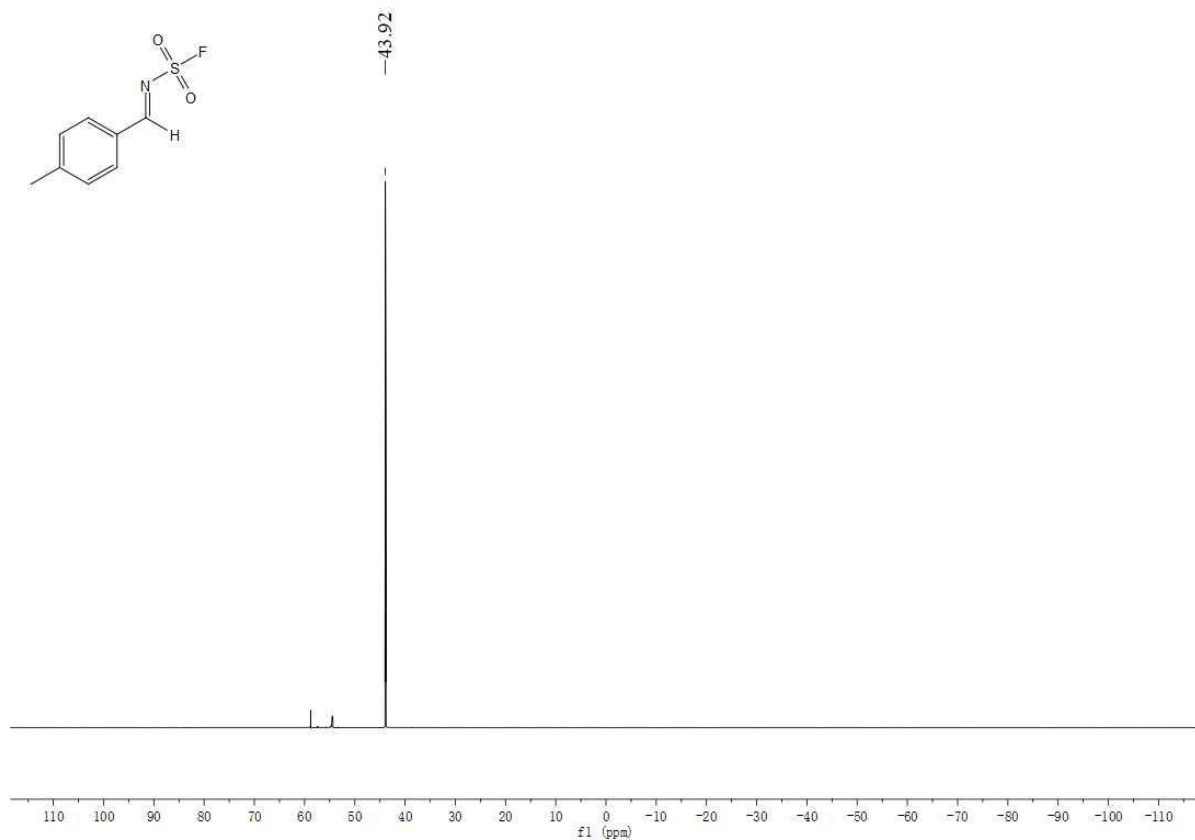
¹H NMR



¹³C NMR

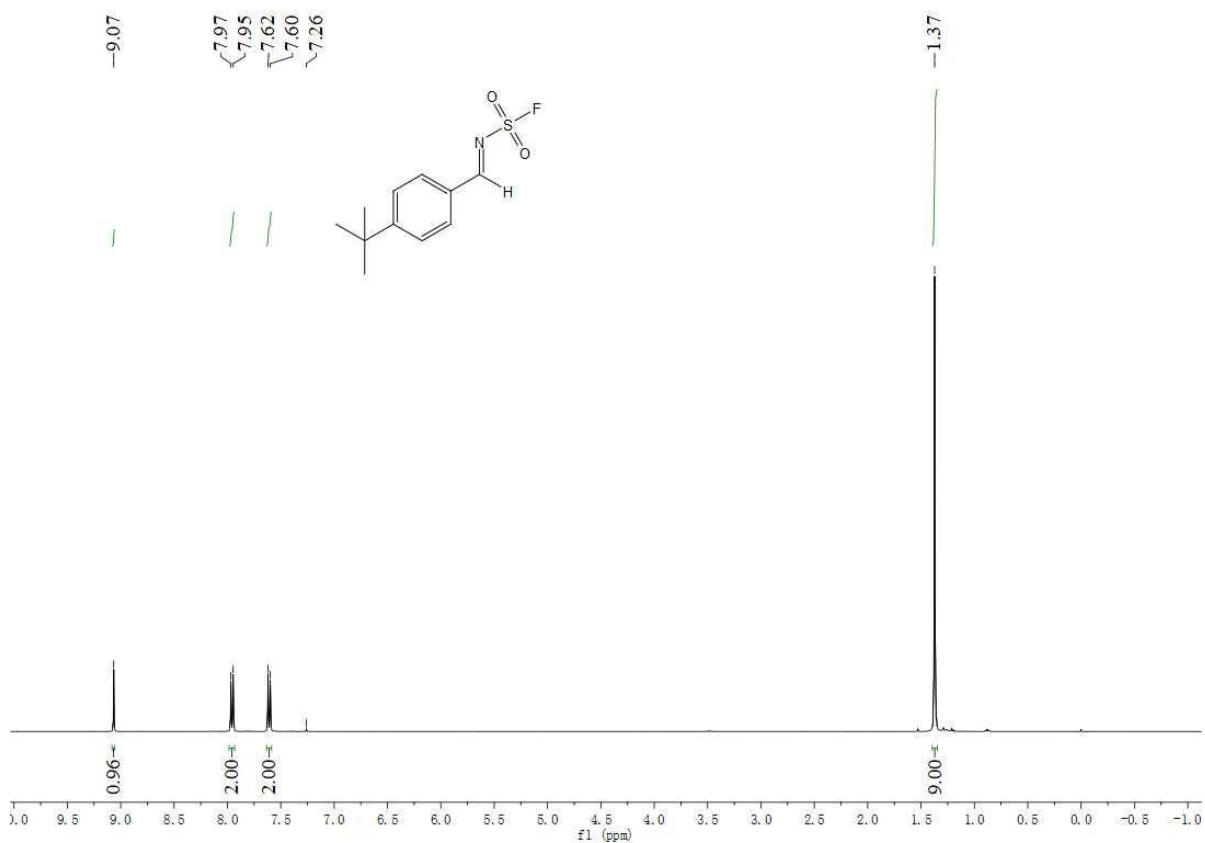


¹⁹F NMR

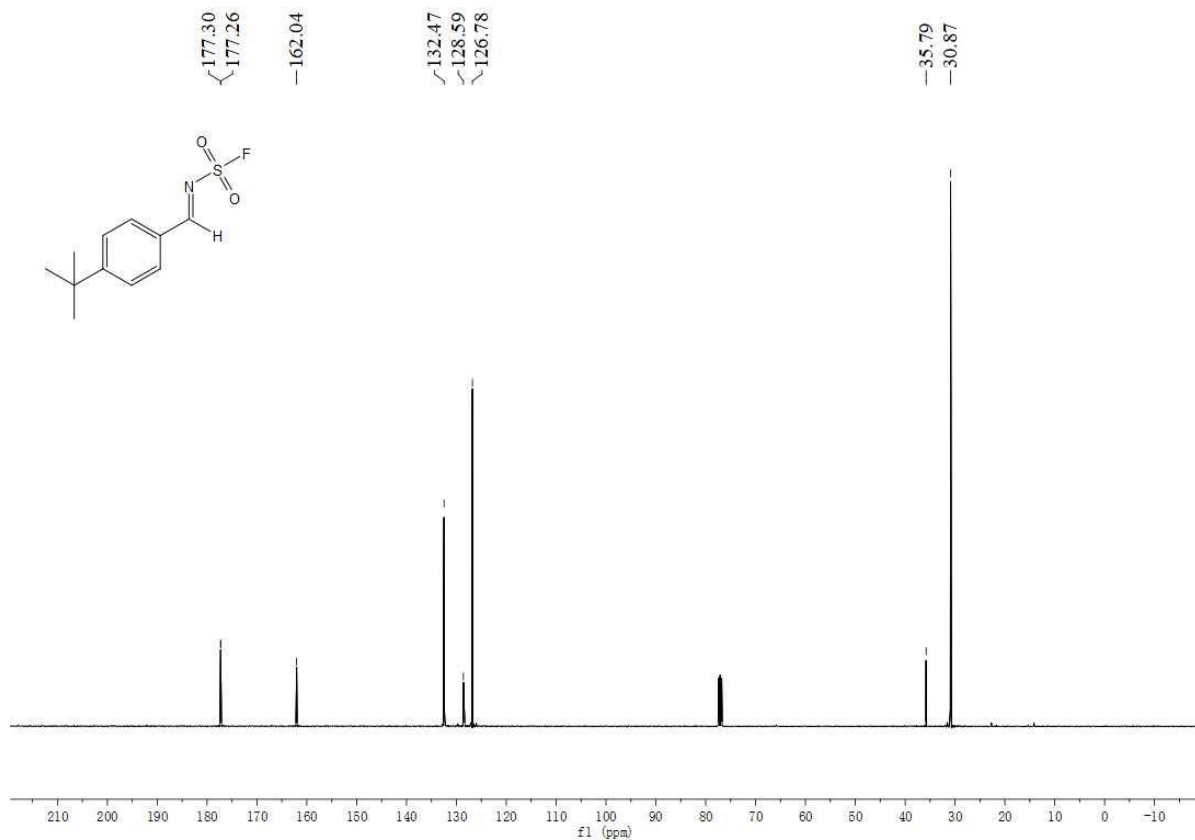


(E)-4-(4-*tert*-butyl)benzylidene)sulfamoyl fluoride (2f)

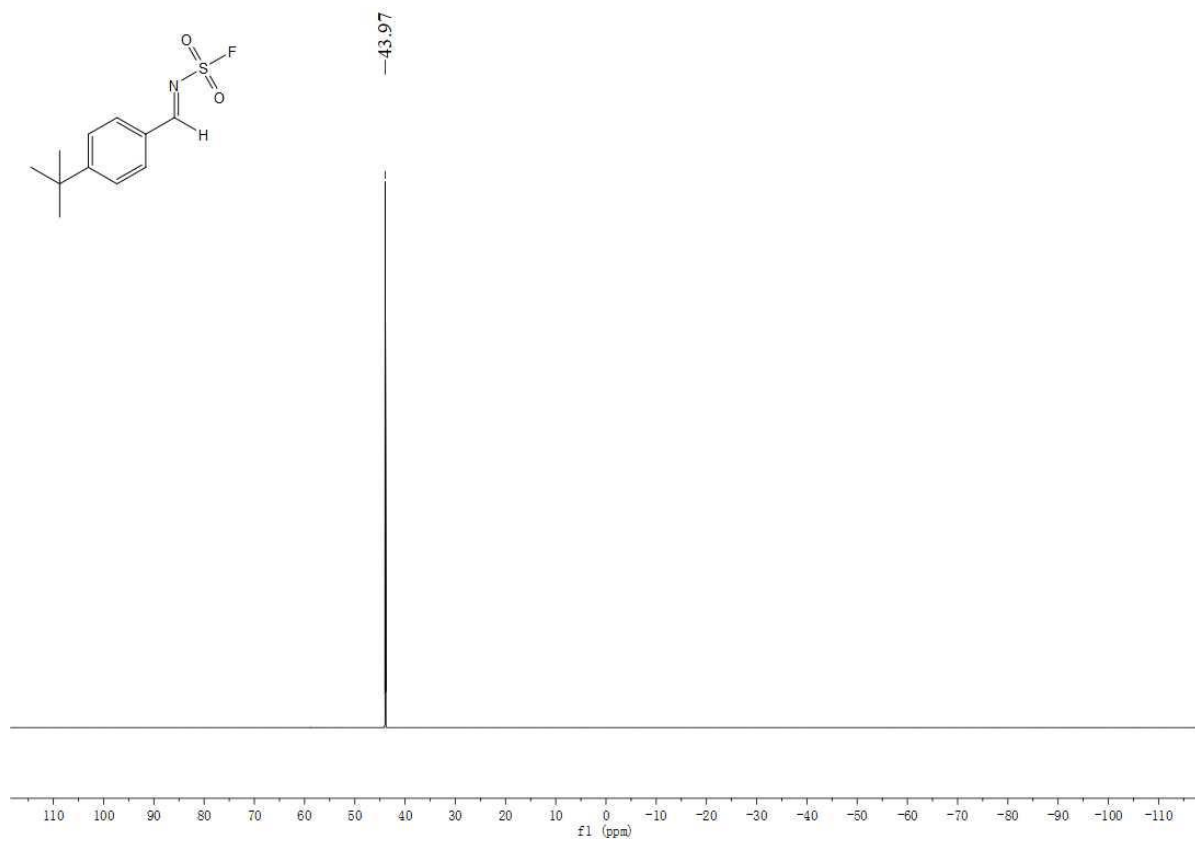
¹H NMR



¹³C NMR

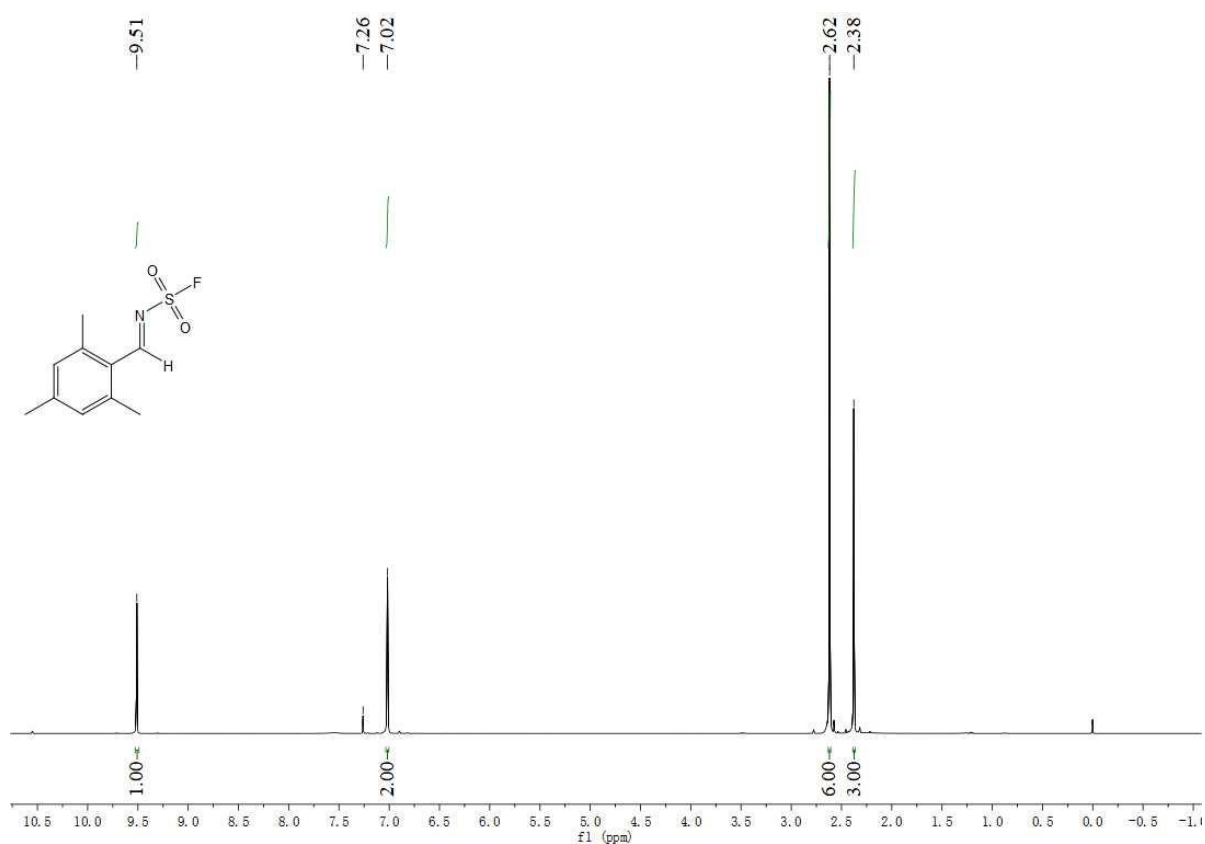


¹⁹F NMR

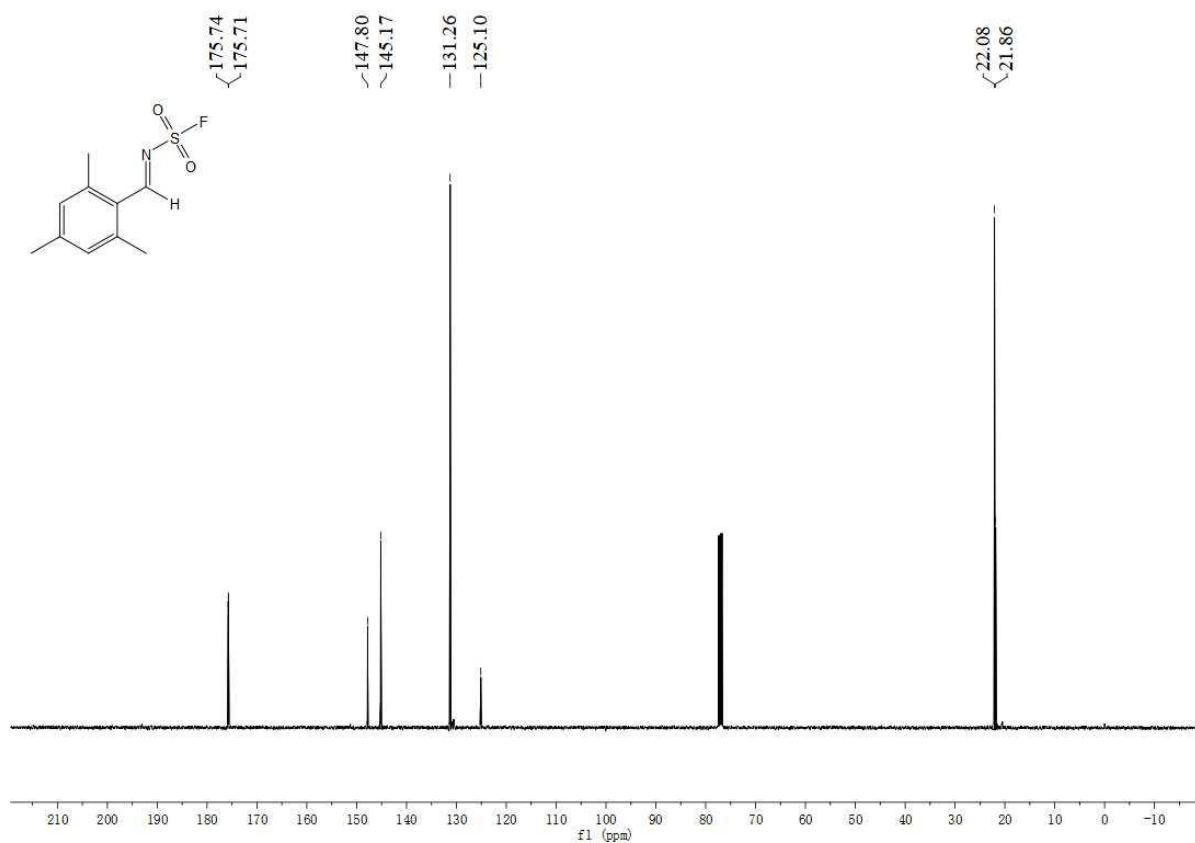


(E)-(2,4,6-trimethylbenzylidene)sulfamoyl fluoride (2g)

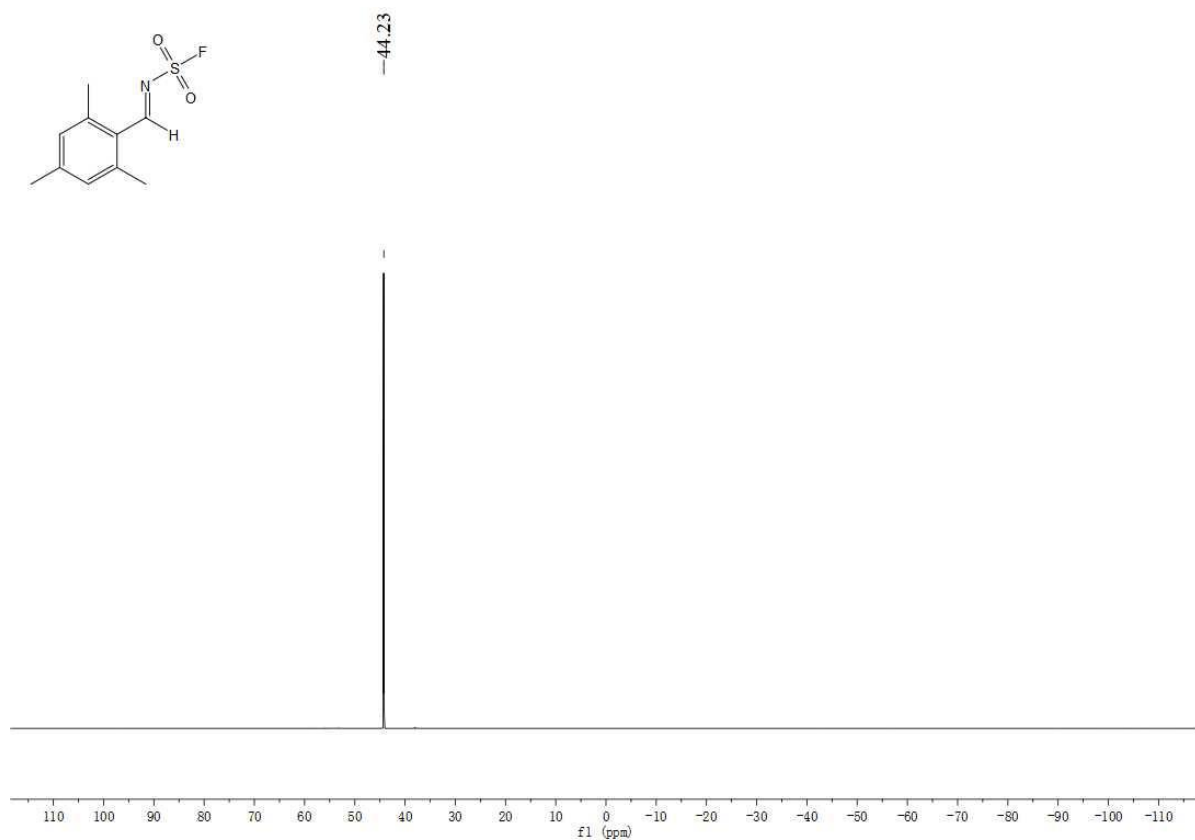
¹H NMR



¹³C NMR

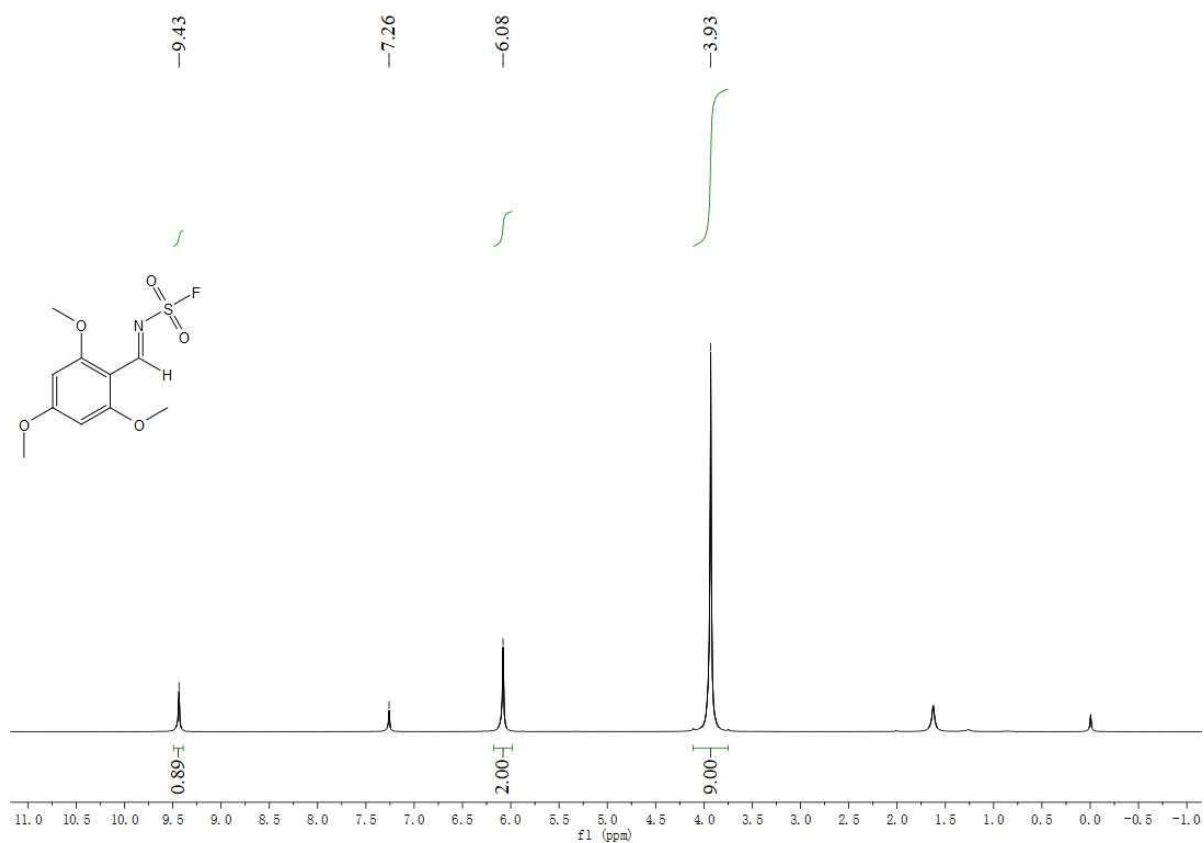


¹⁹F NMR

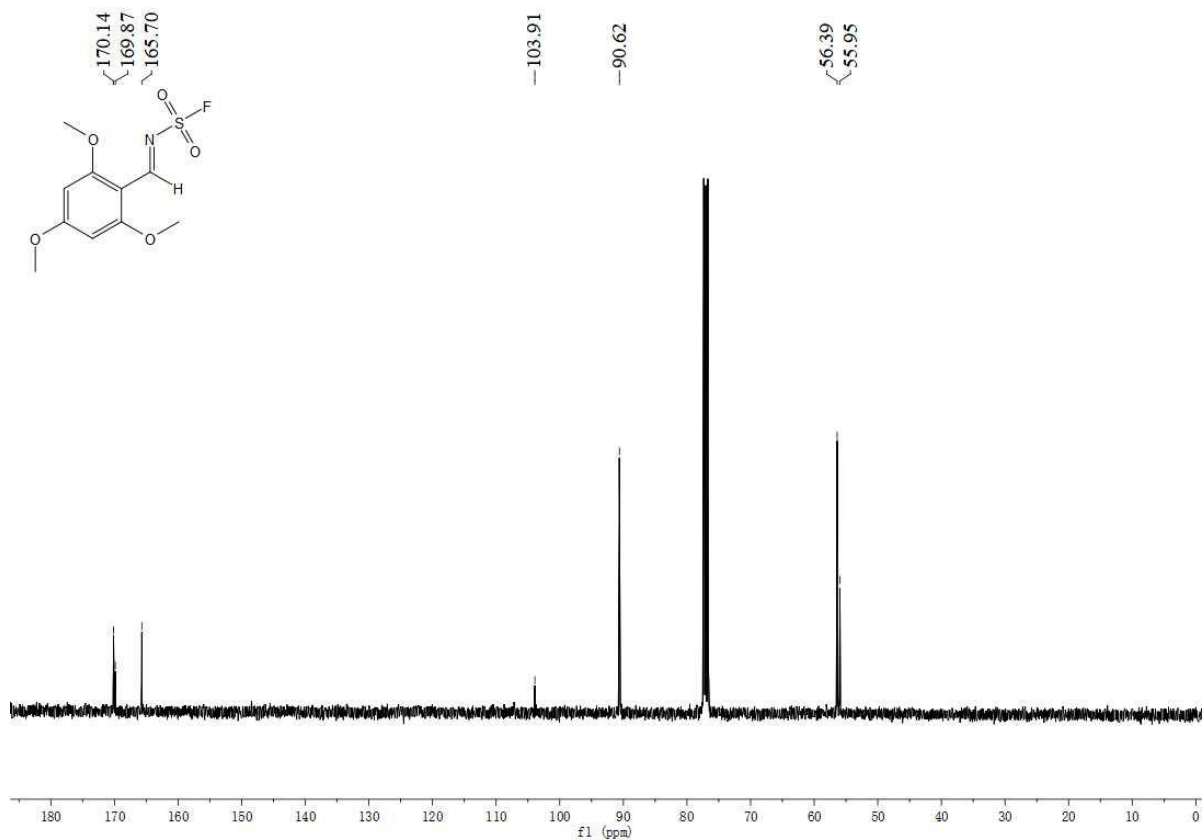


(E)-(2,4,6-trimethoxybenzylidene)sulfamoyl fluoride (2h)

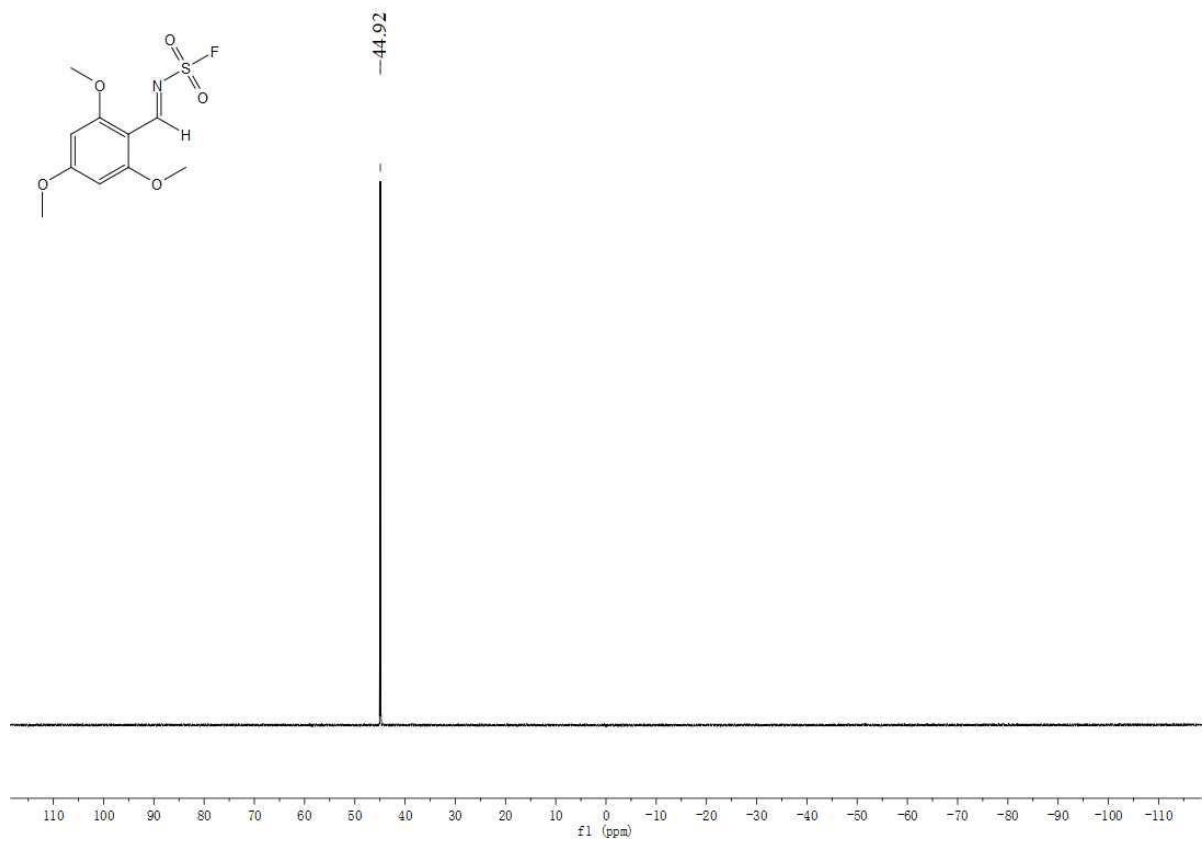
¹H NMR



¹³C NMR

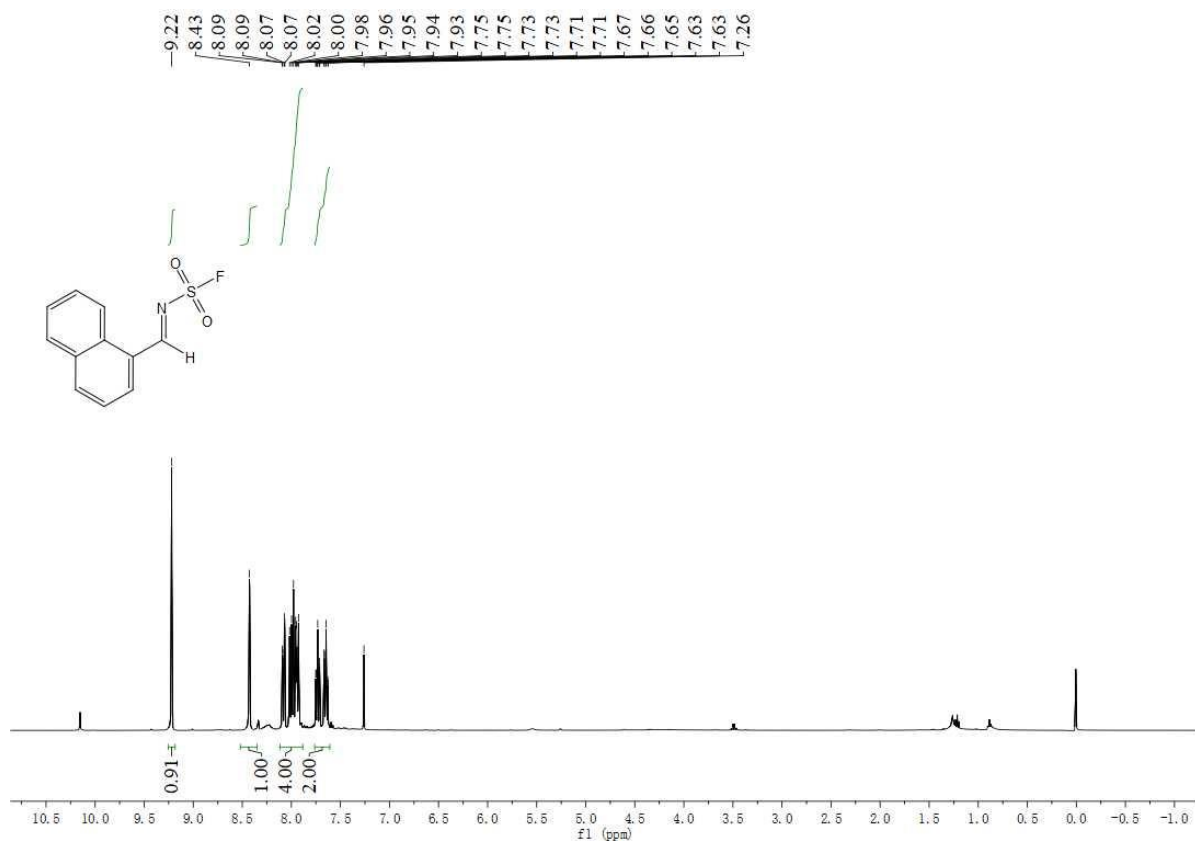


¹⁹F NMR

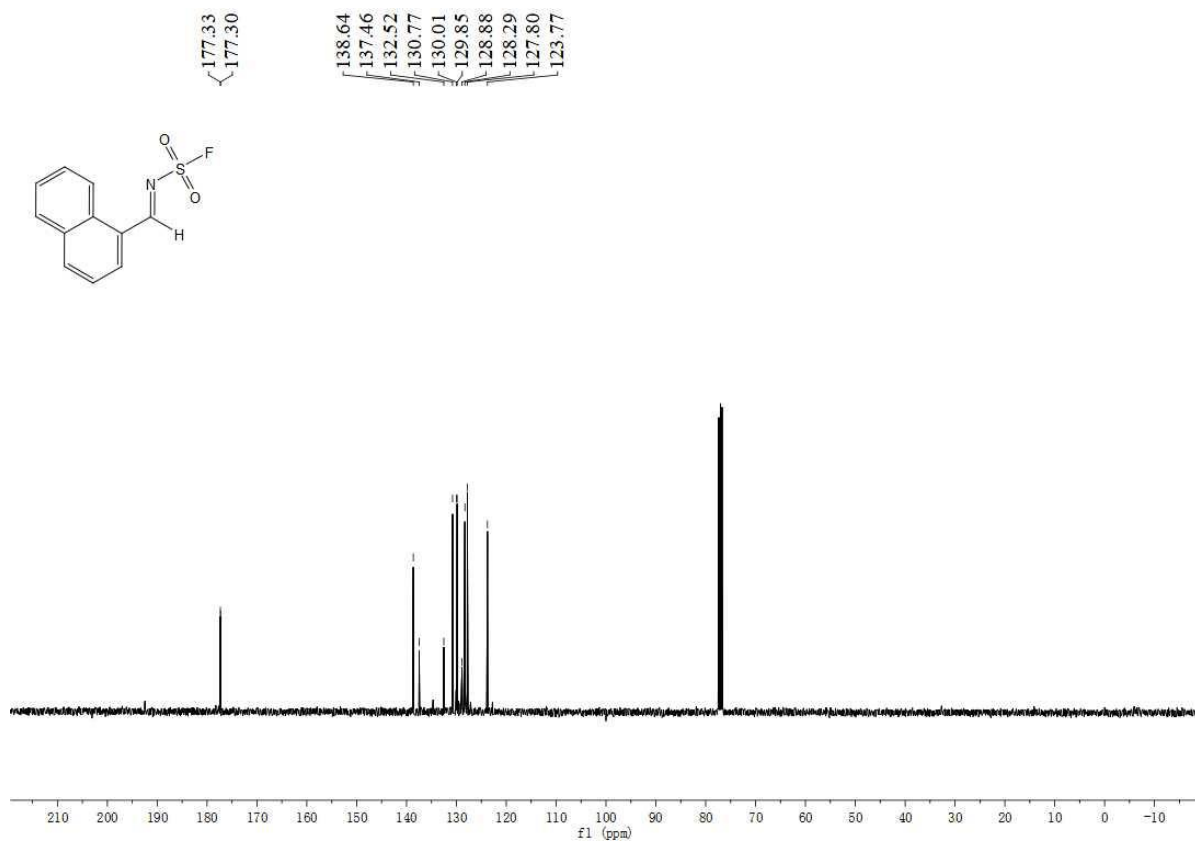


(E)-(naphthalen-1-ylmethylene)sulfamoyl fluoride (2i)

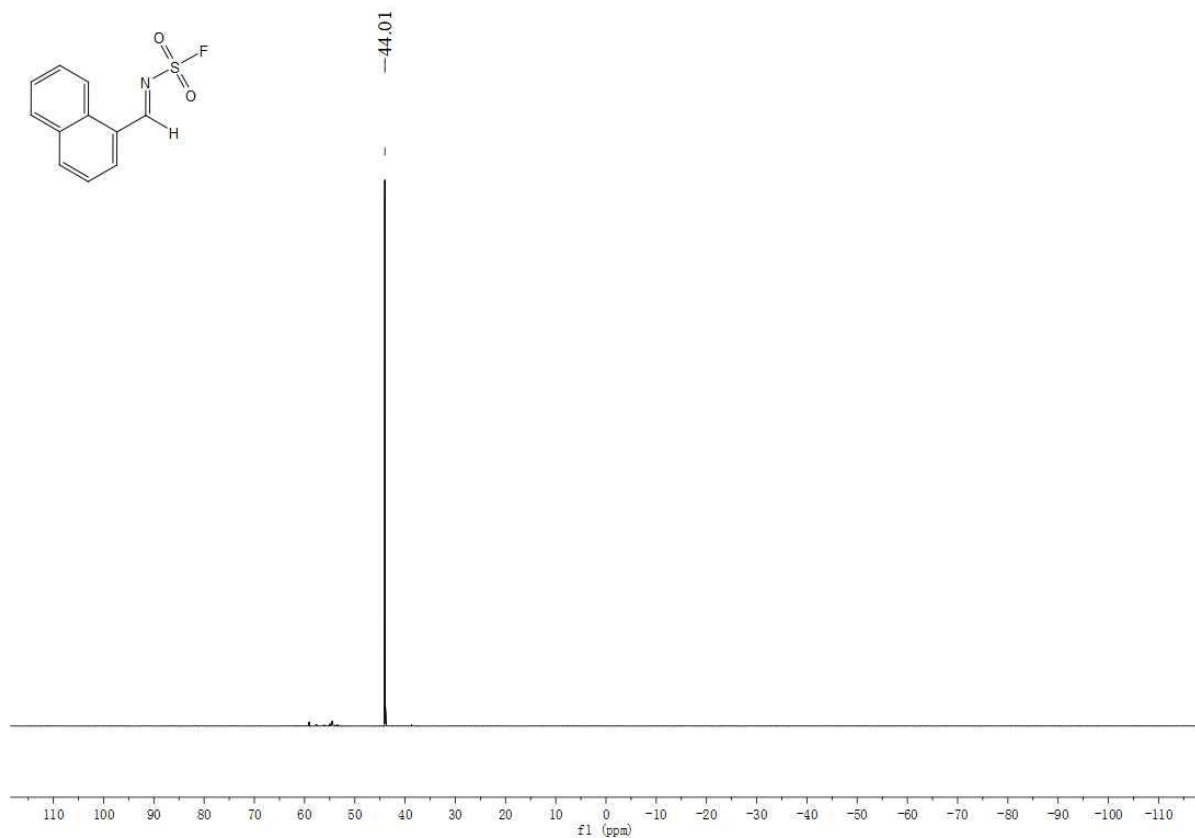
¹H NMR



¹³C NMR

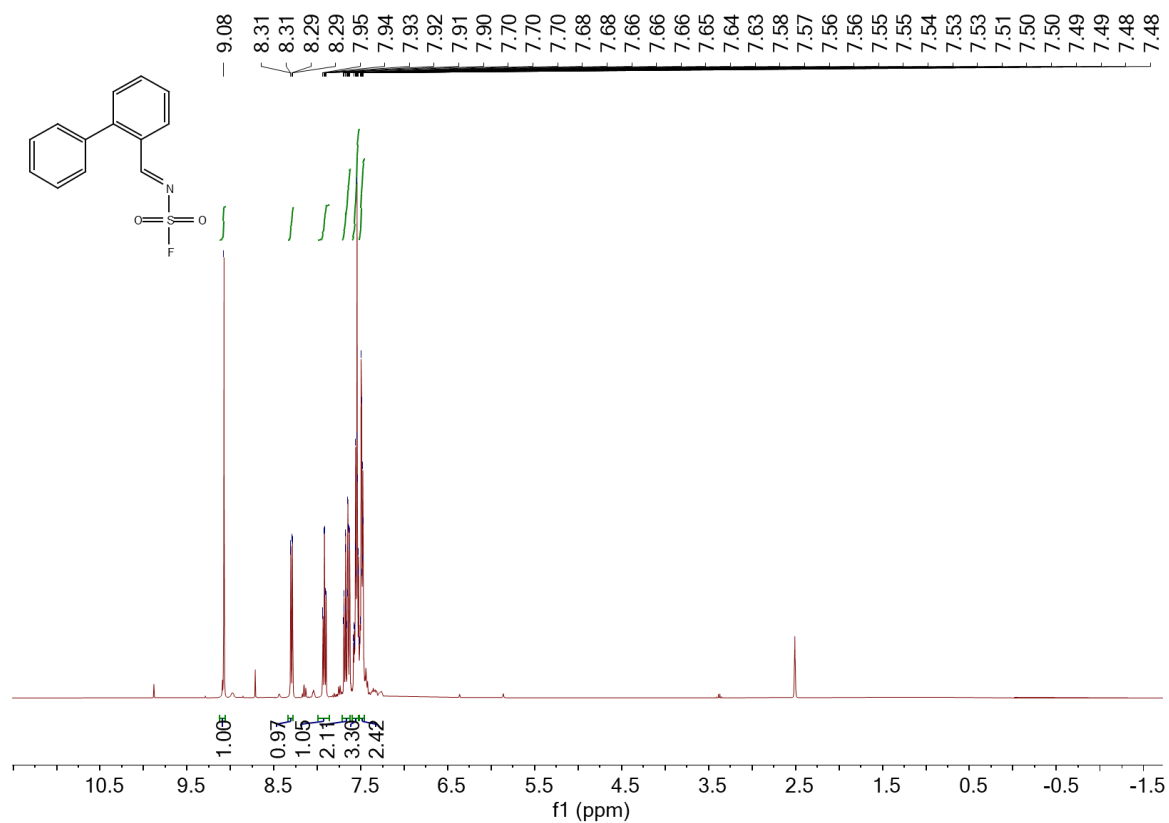


¹⁹F NMR

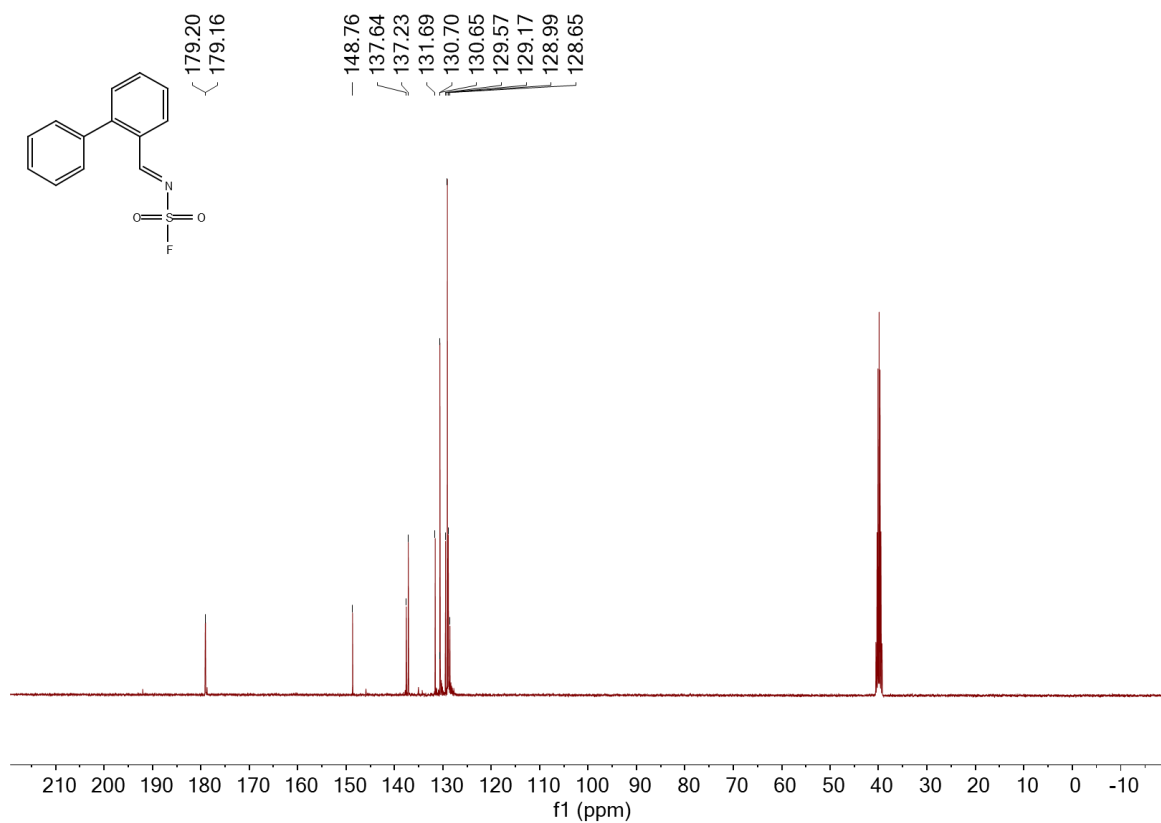


(E)-[1,1'-biphenyl]-2-yl((fluorosulfonyl)imino)methanide (2j)

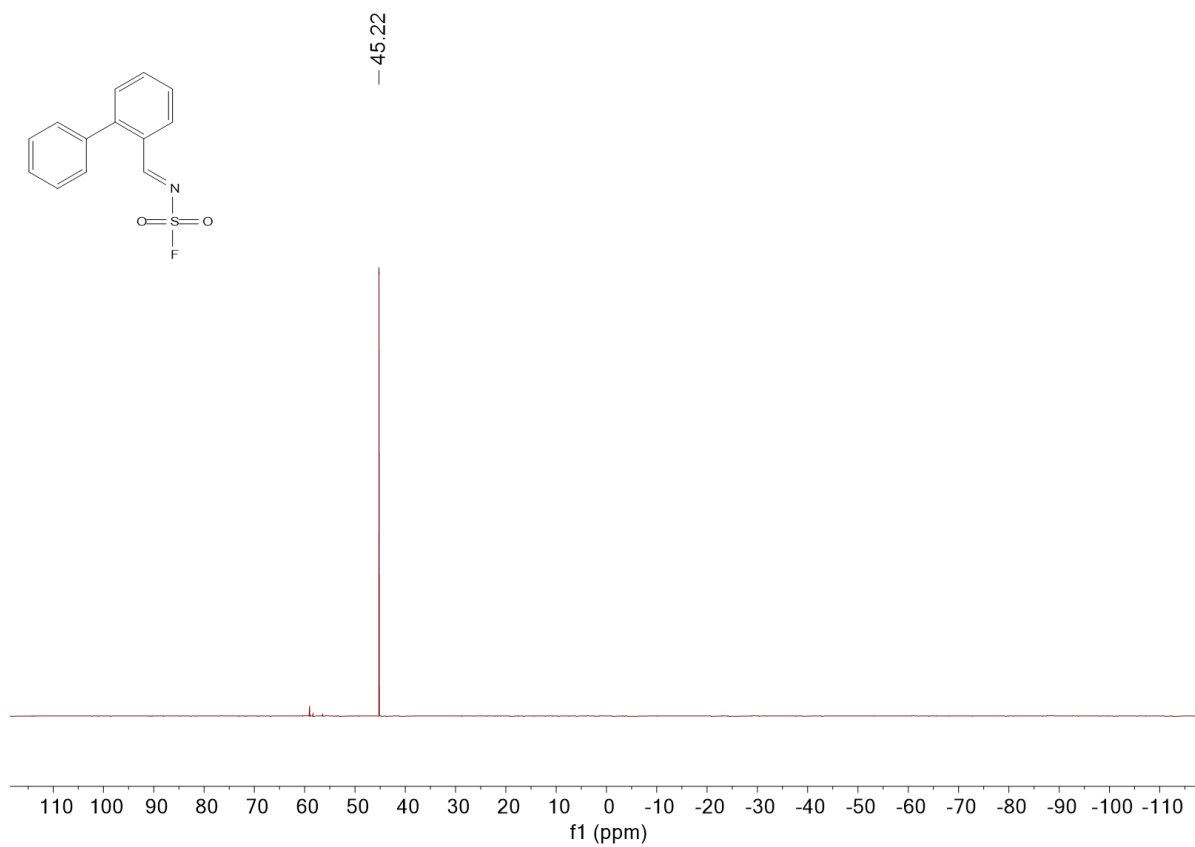
¹H NMR



¹³C NMR

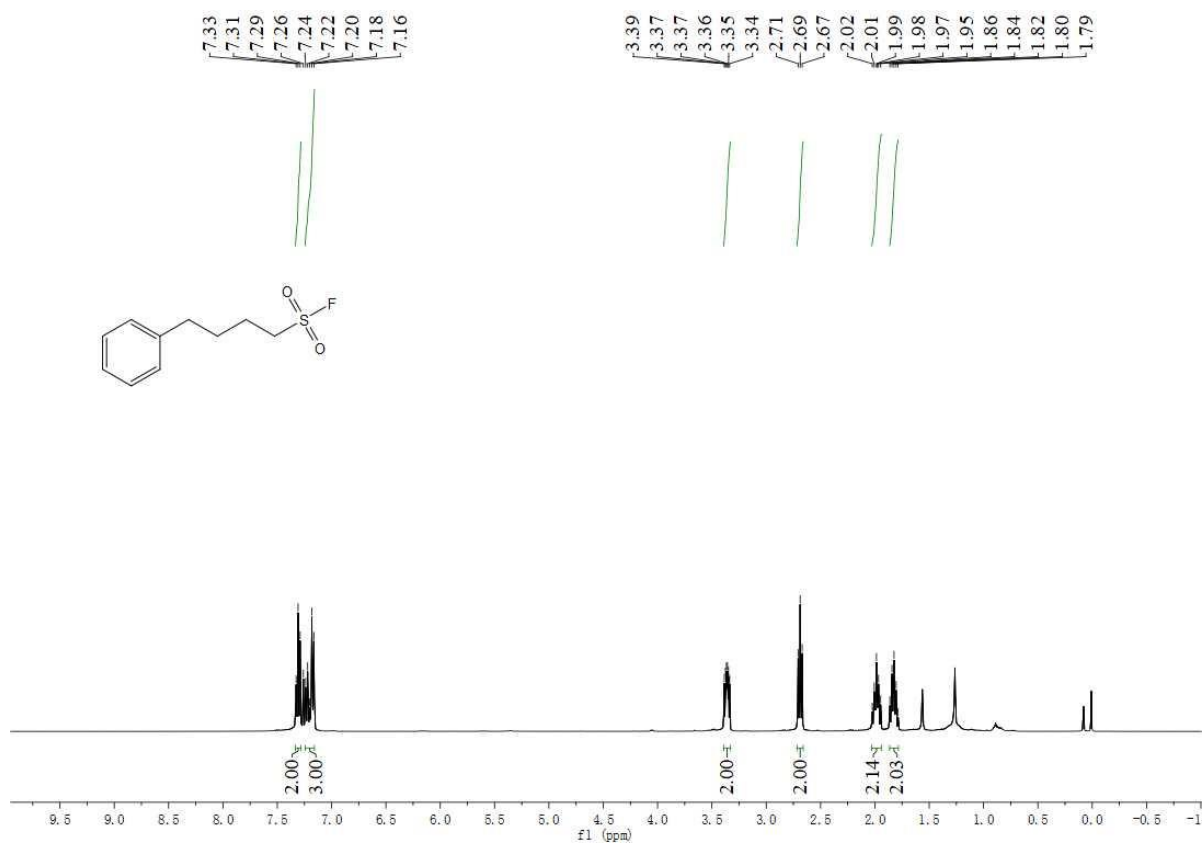


¹⁹F NMR

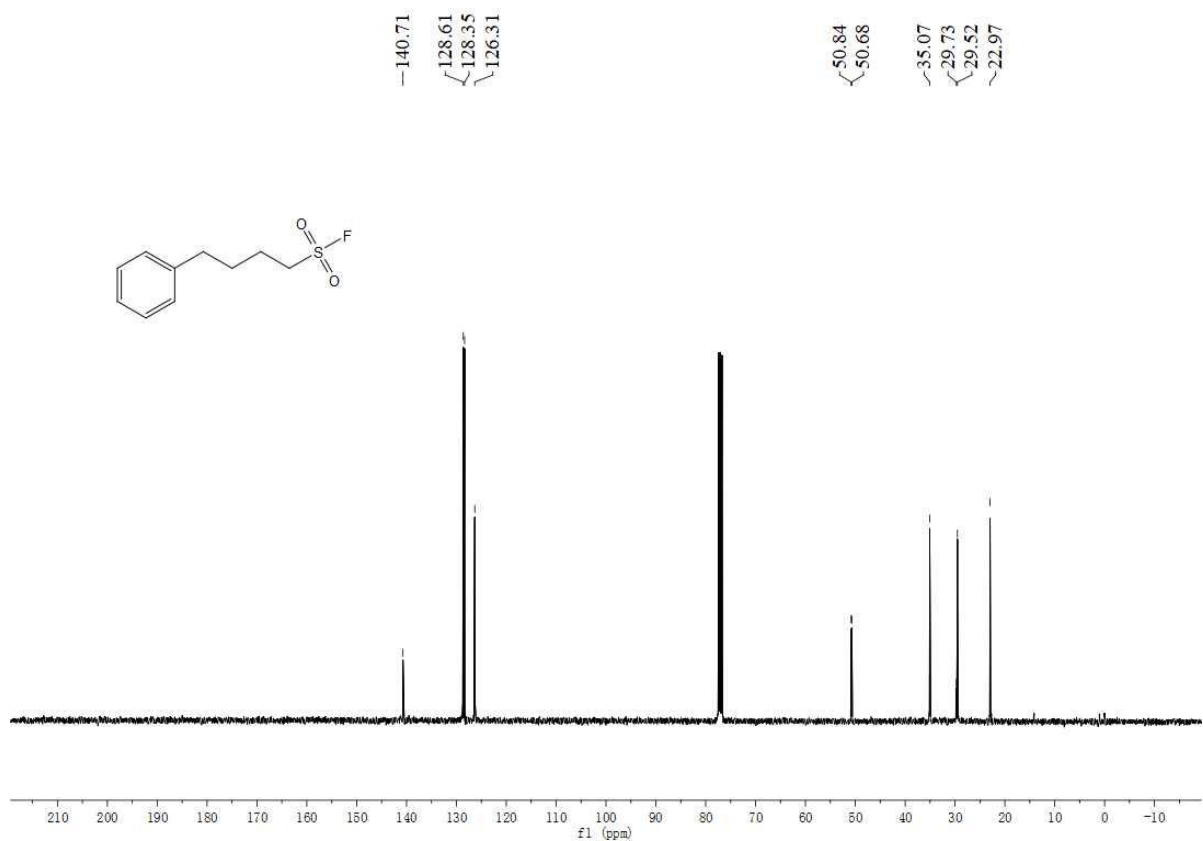


4-phenylbutane-1-sulfonyl fluoride (4a)

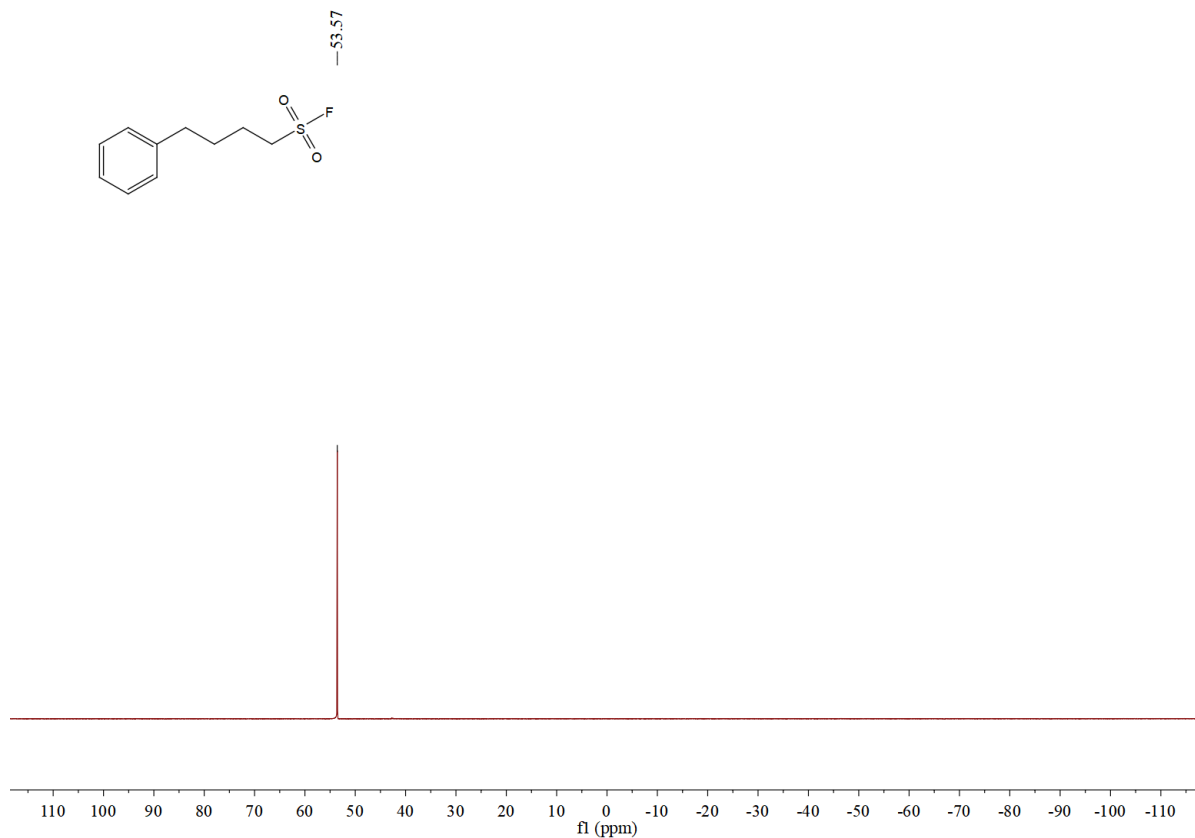
¹H NMR



¹³C NMR

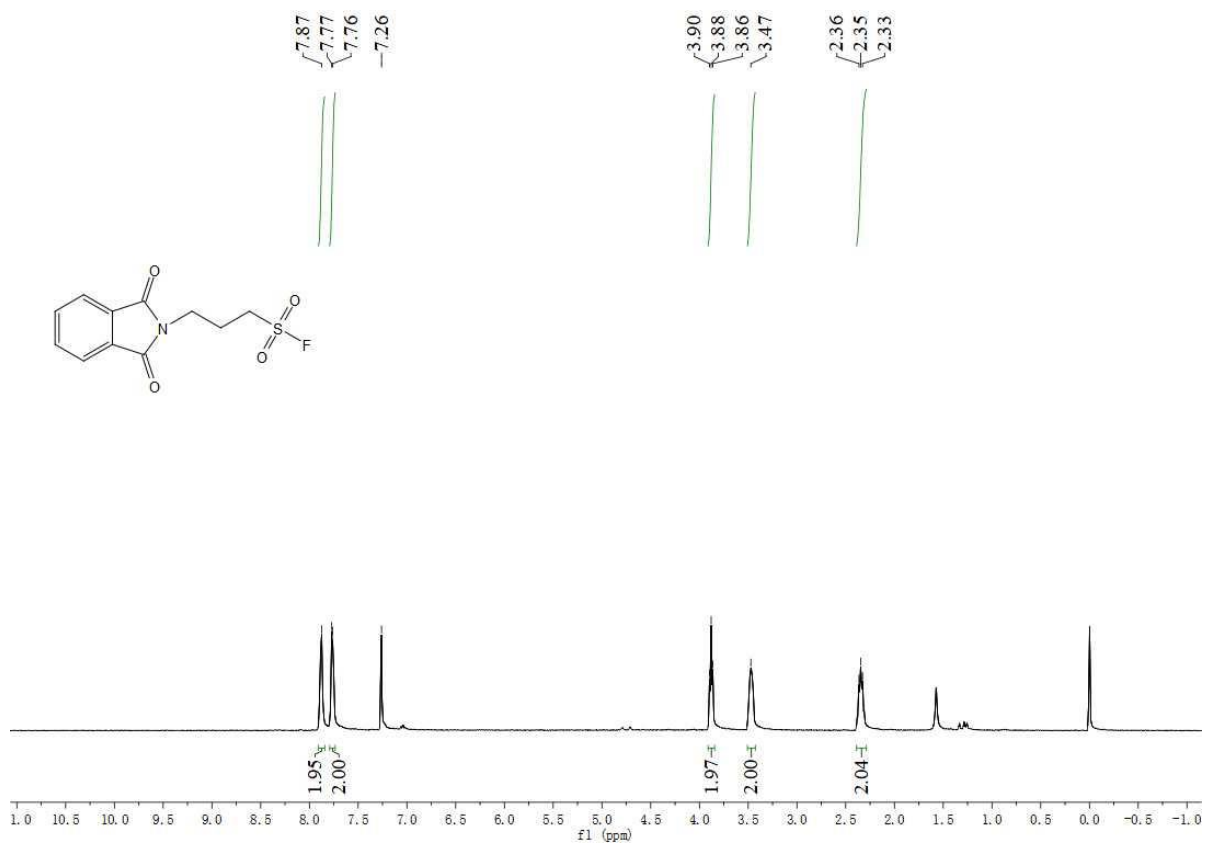


¹⁹F NMR

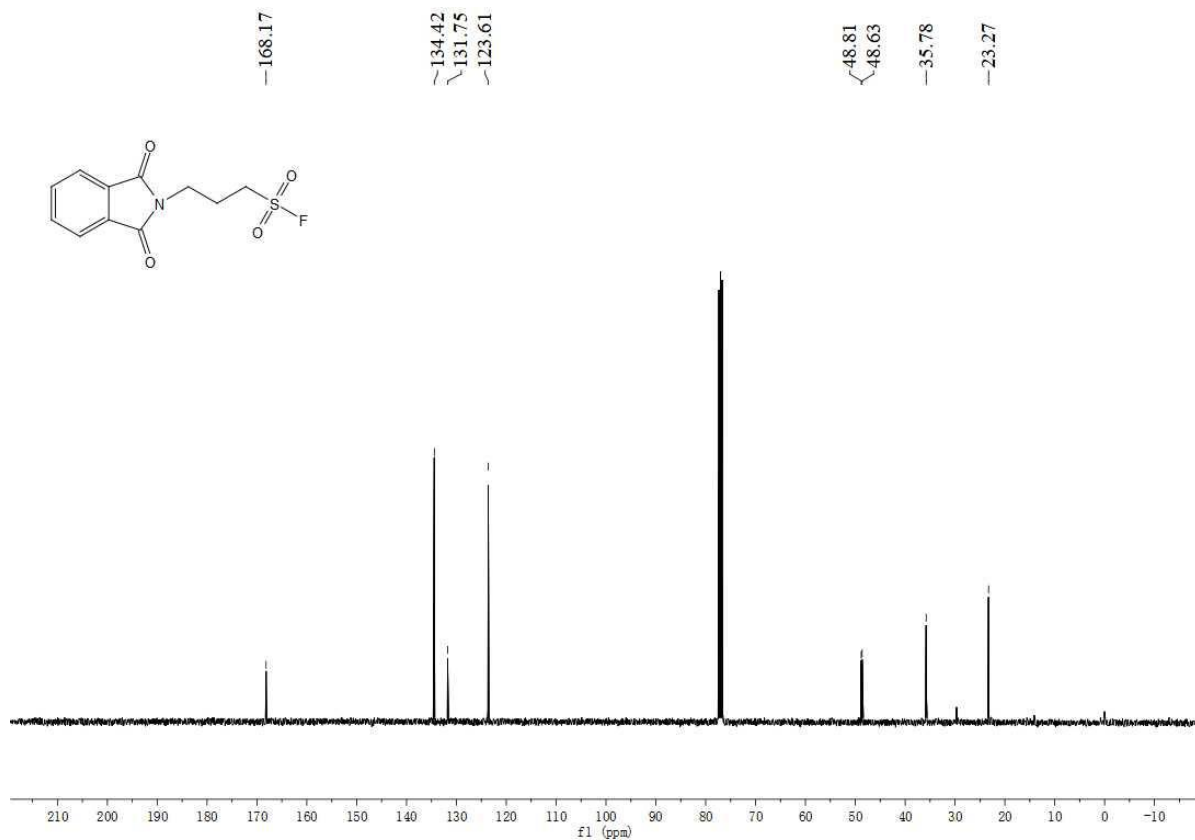


3-(1,3-dioxisoindolin-2-yl)propane-1-sulfonyl fluoride (4b)

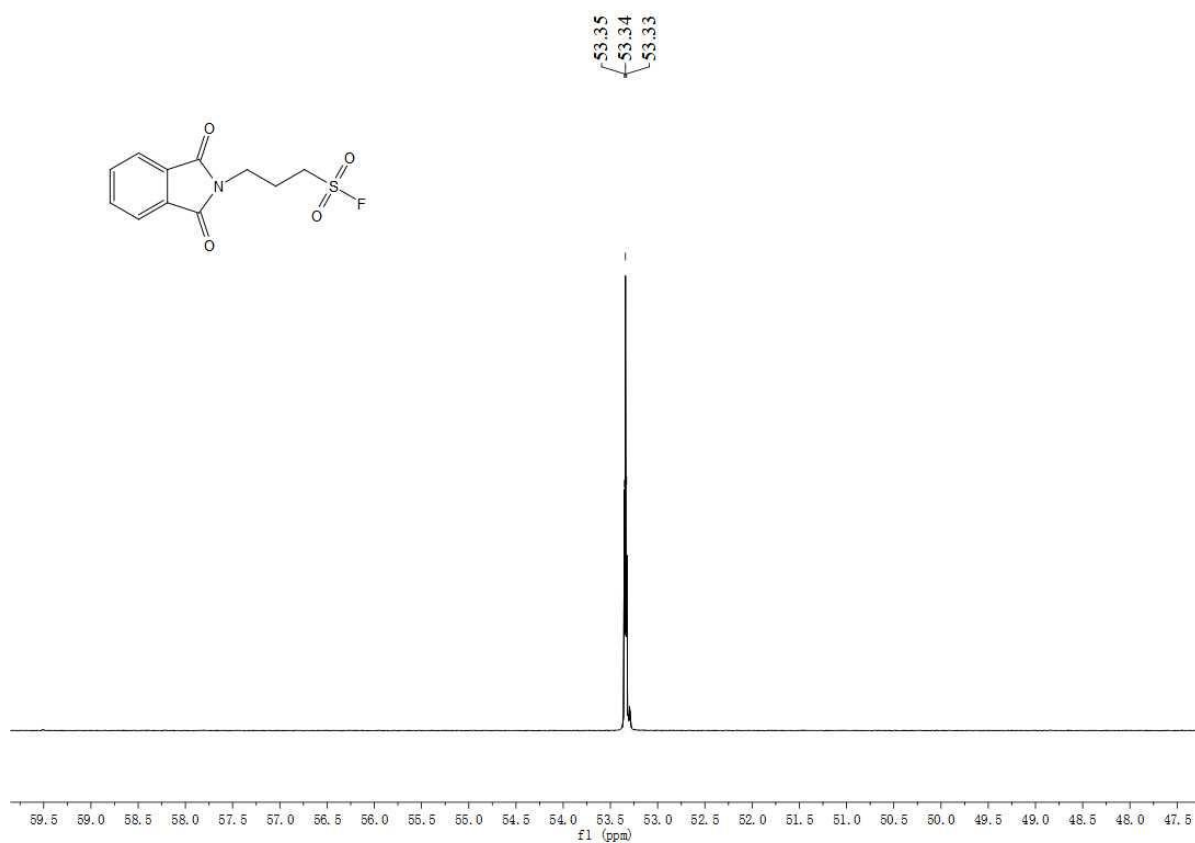
¹H NMR



¹³C NMR

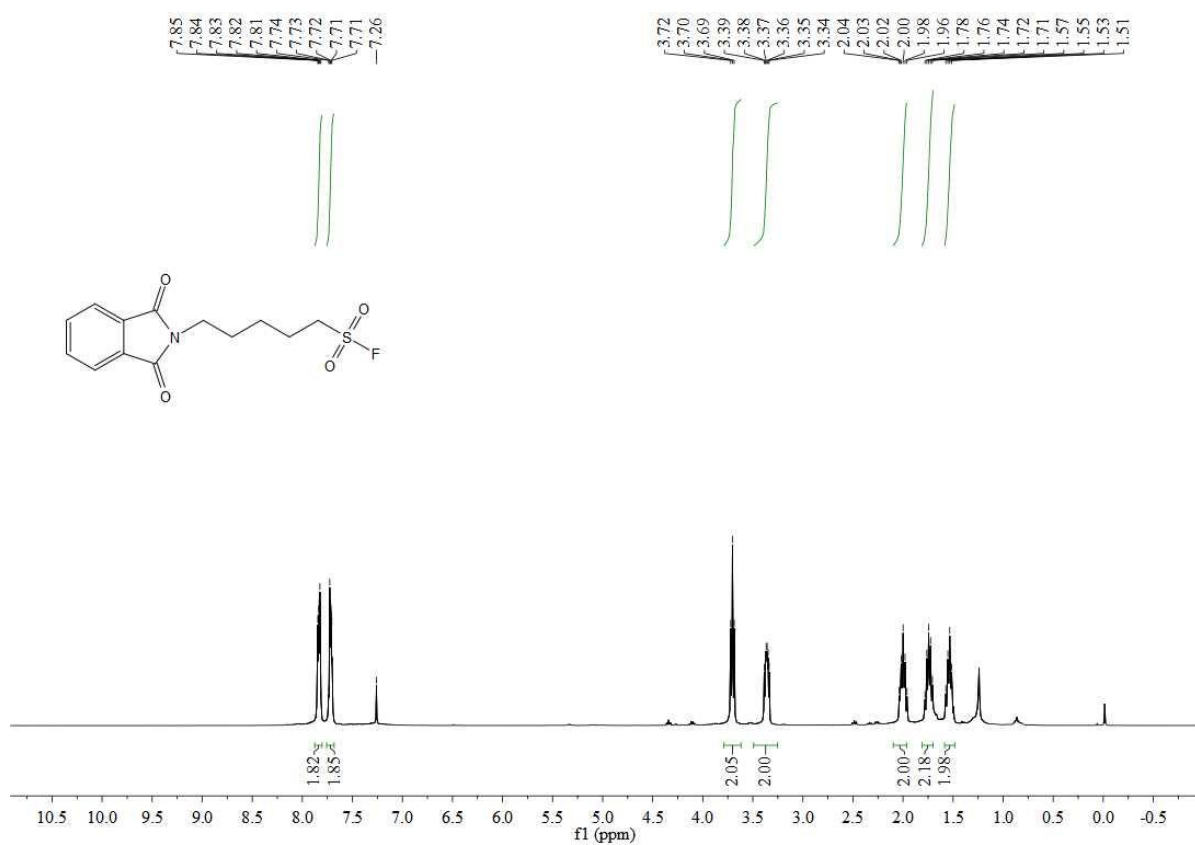


¹⁹F NMR

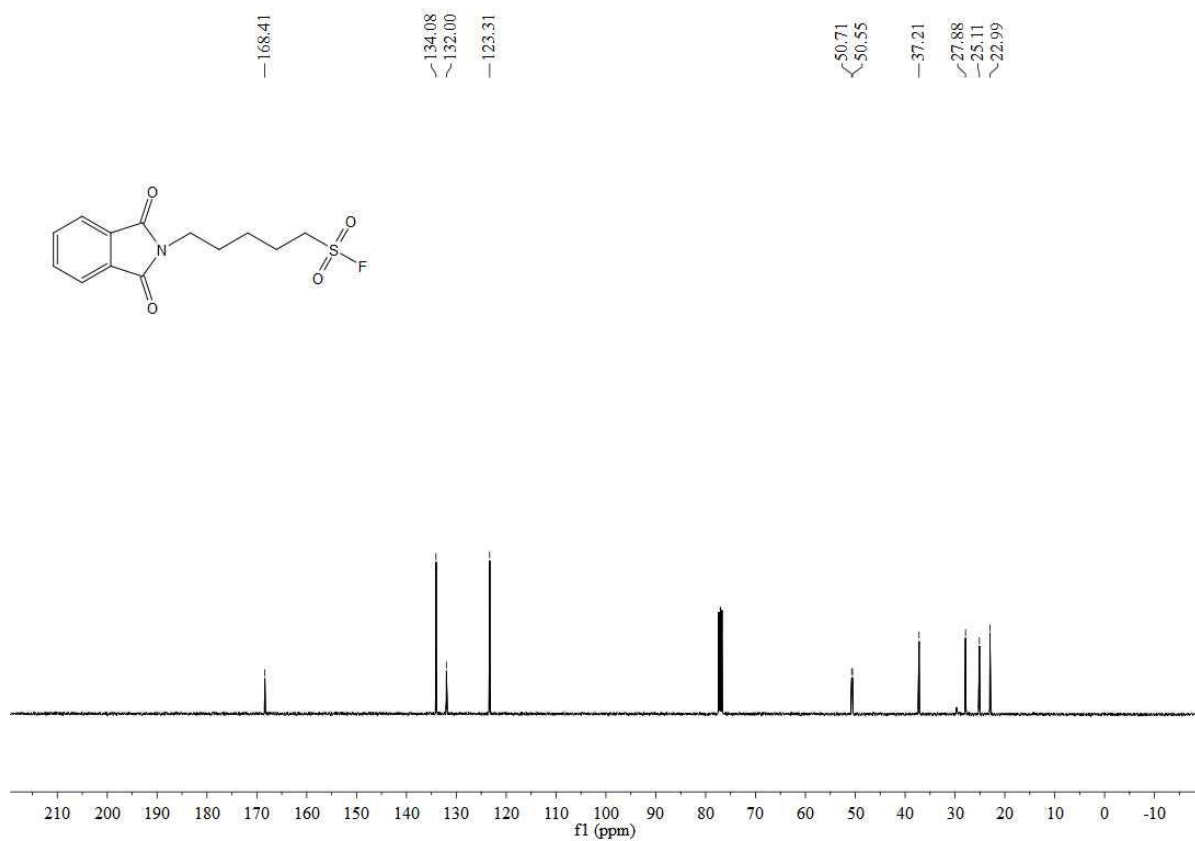


5-(1,3-dioxisoindolin-2-yl)pentane-1-sulfonyl fluoride (**4c**)

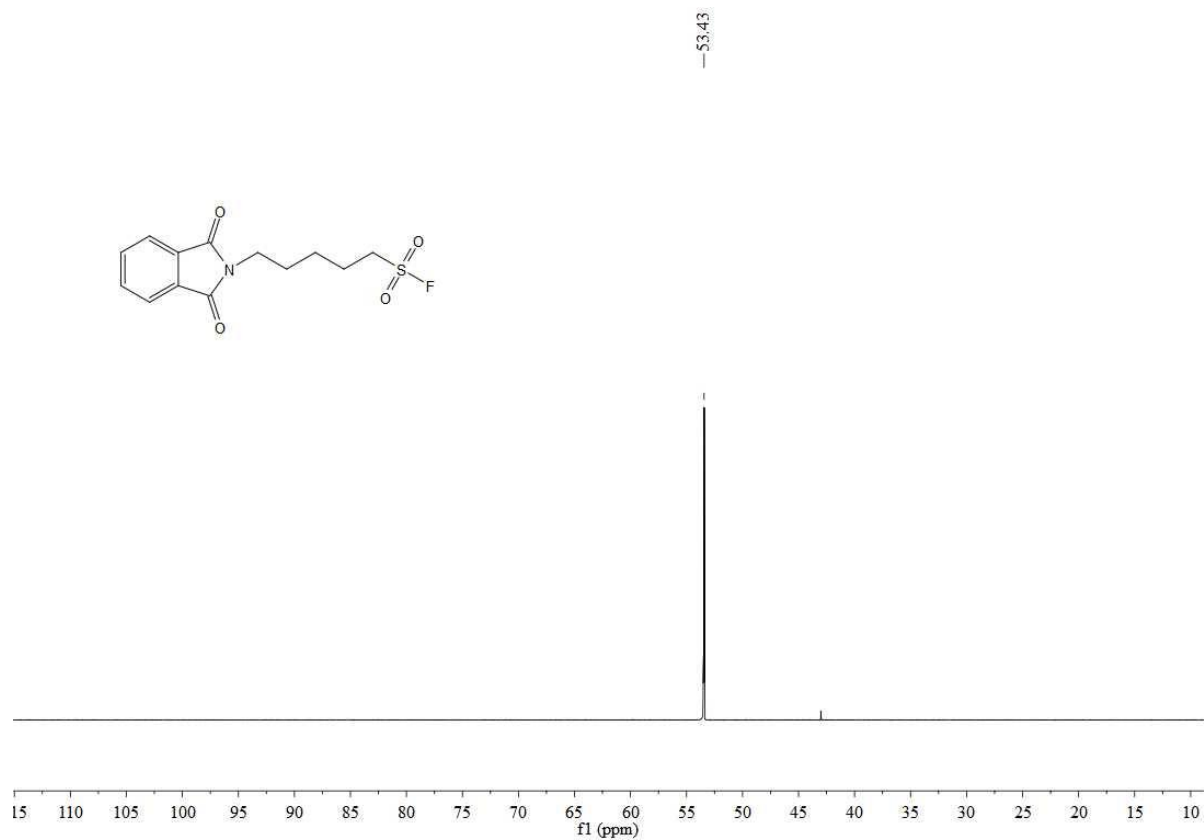
¹H NMR



¹³C NMR

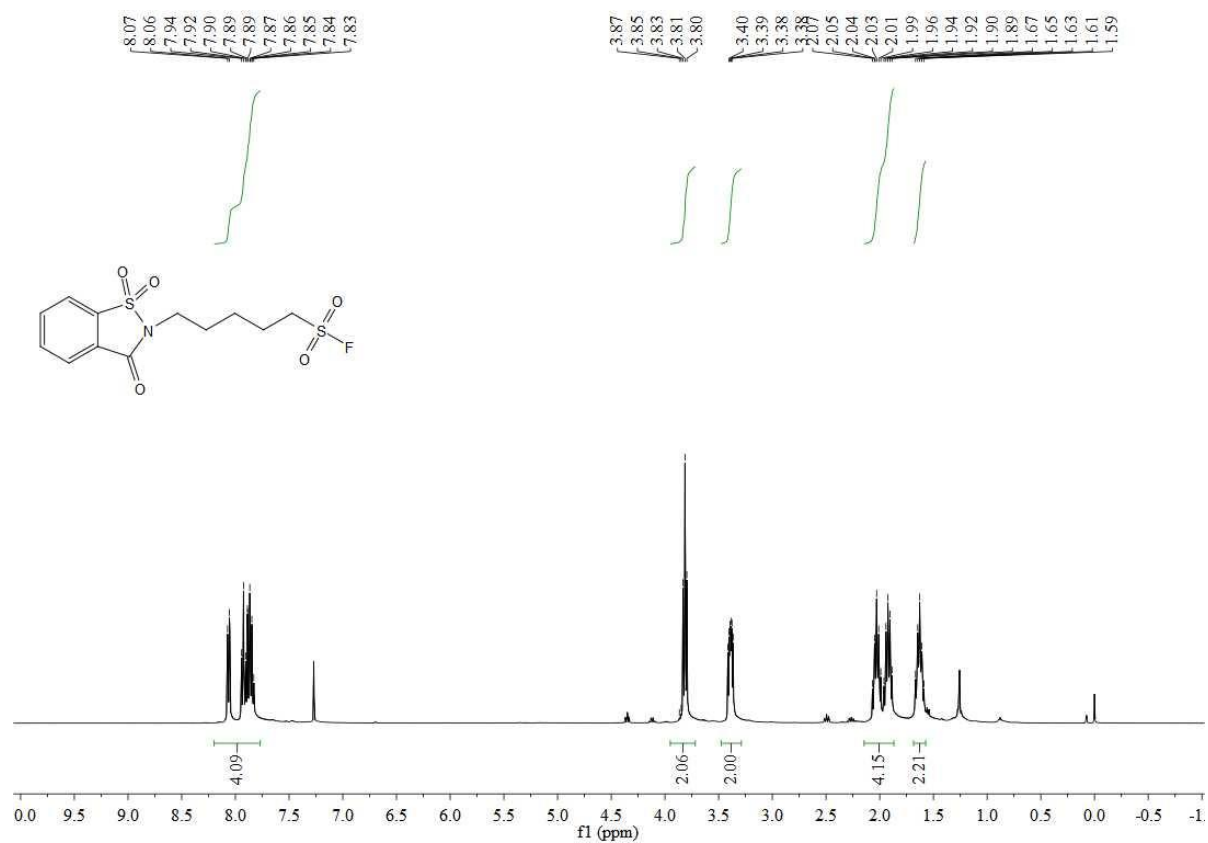


¹⁹F NMR

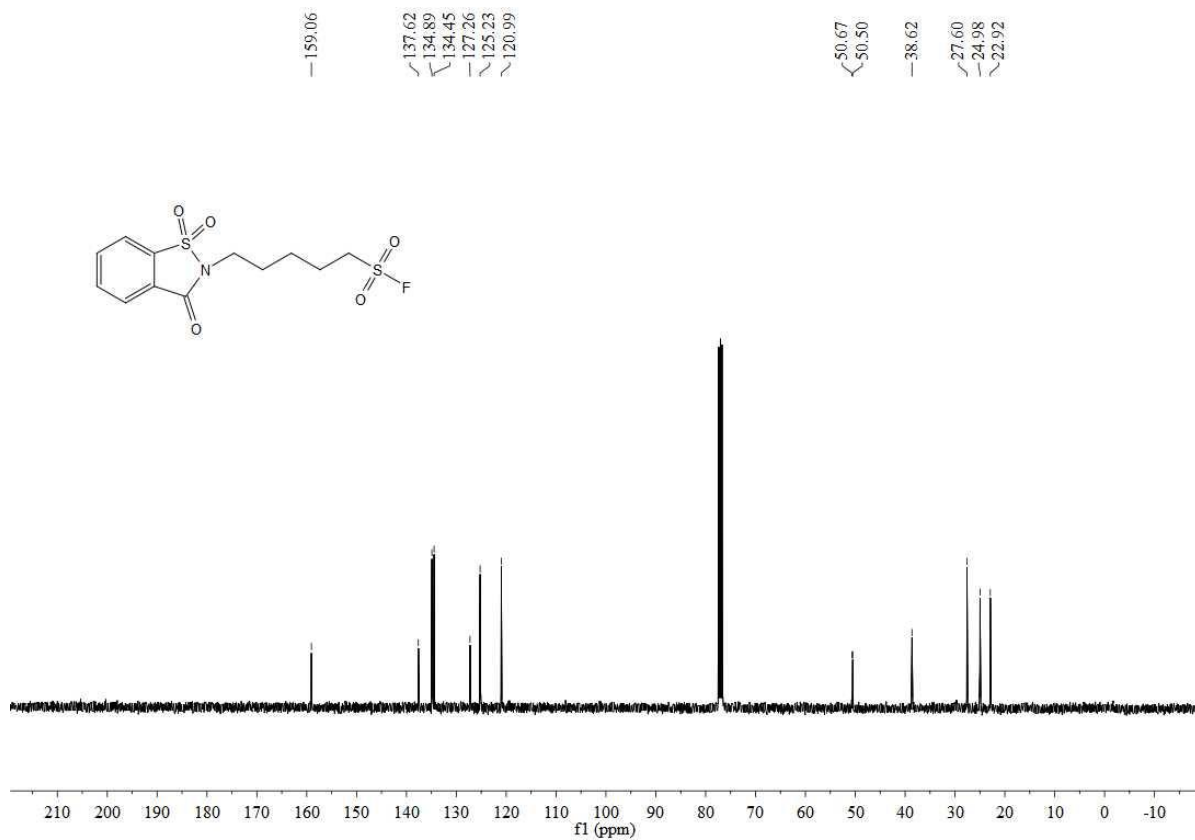


5-(1,1-dioxido-3-oxobenzodisothiazol-2(3H)-yl)pentane-1-sulfonyl fluoride (4d)

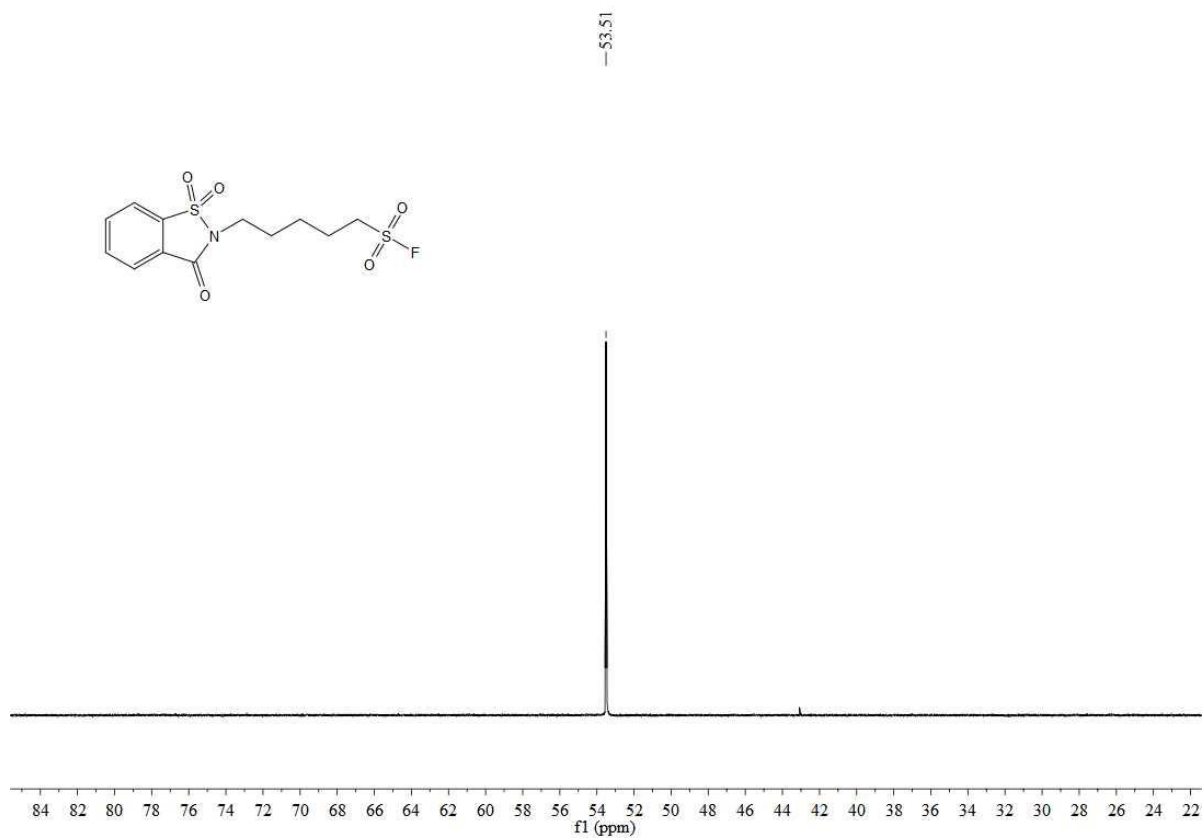
¹H NMR



¹³C NMR

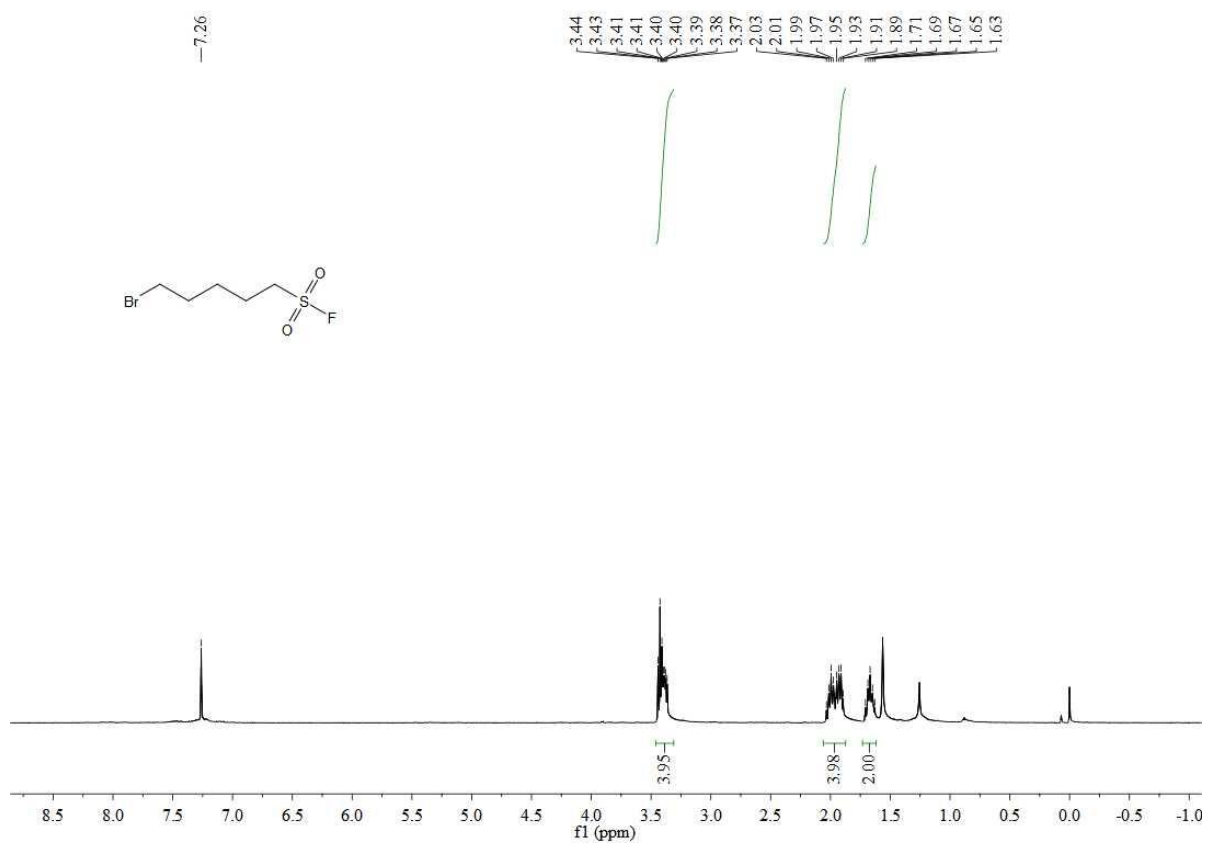


¹⁹F NMR

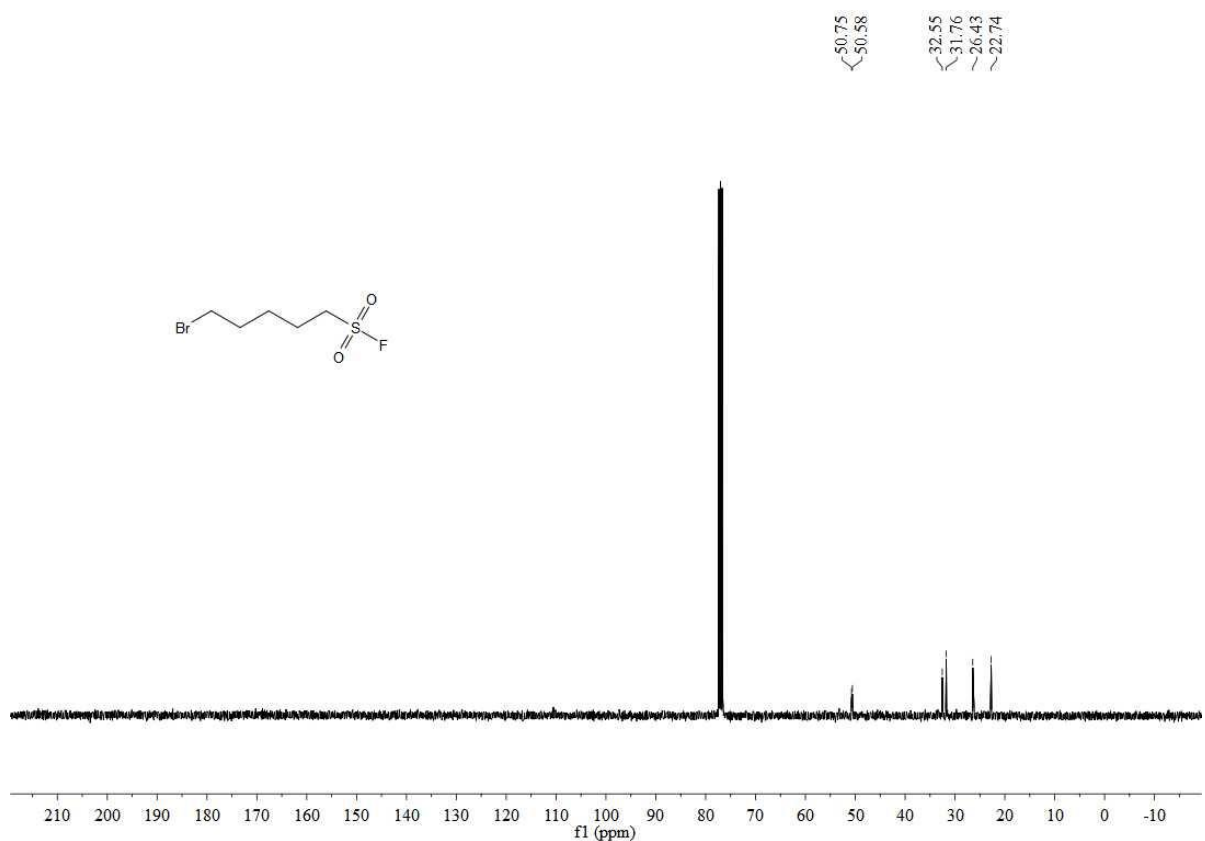


5-bromopentane-1-sulfonyl fluoride (4e)

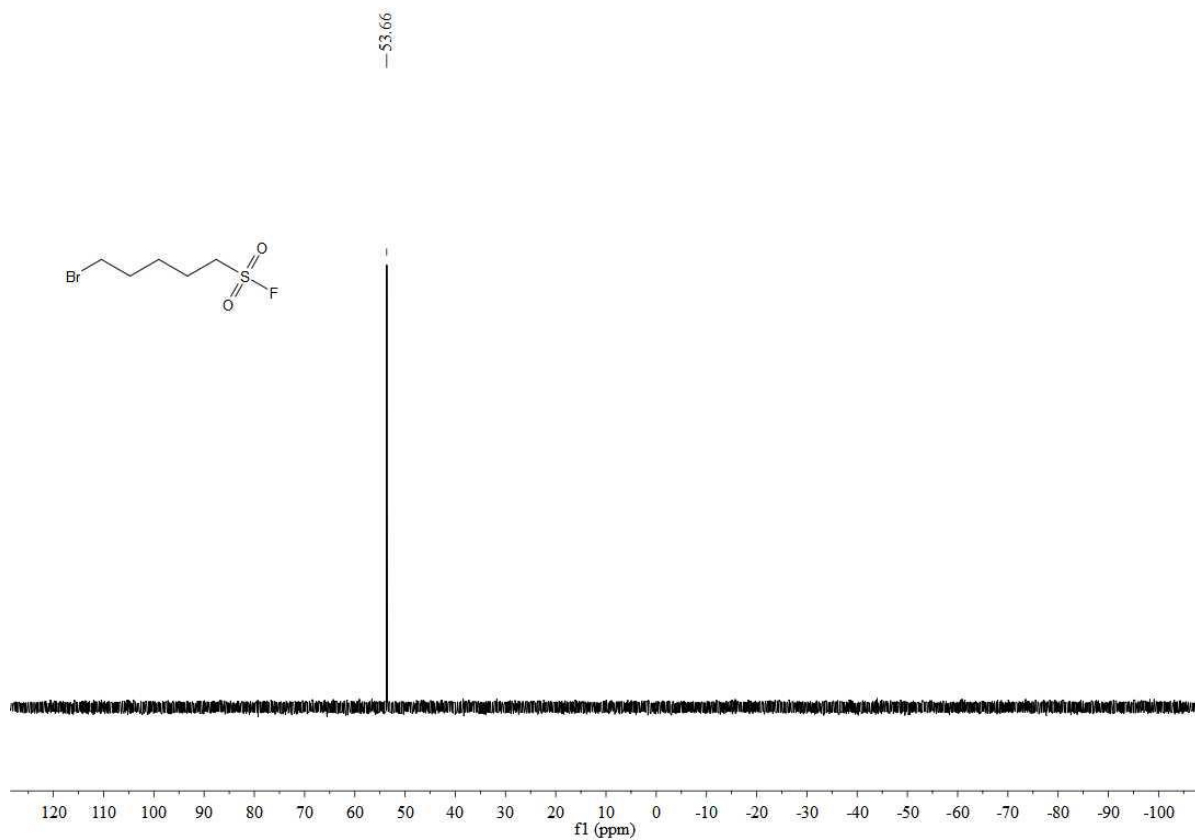
¹H NMR



¹³C NMR

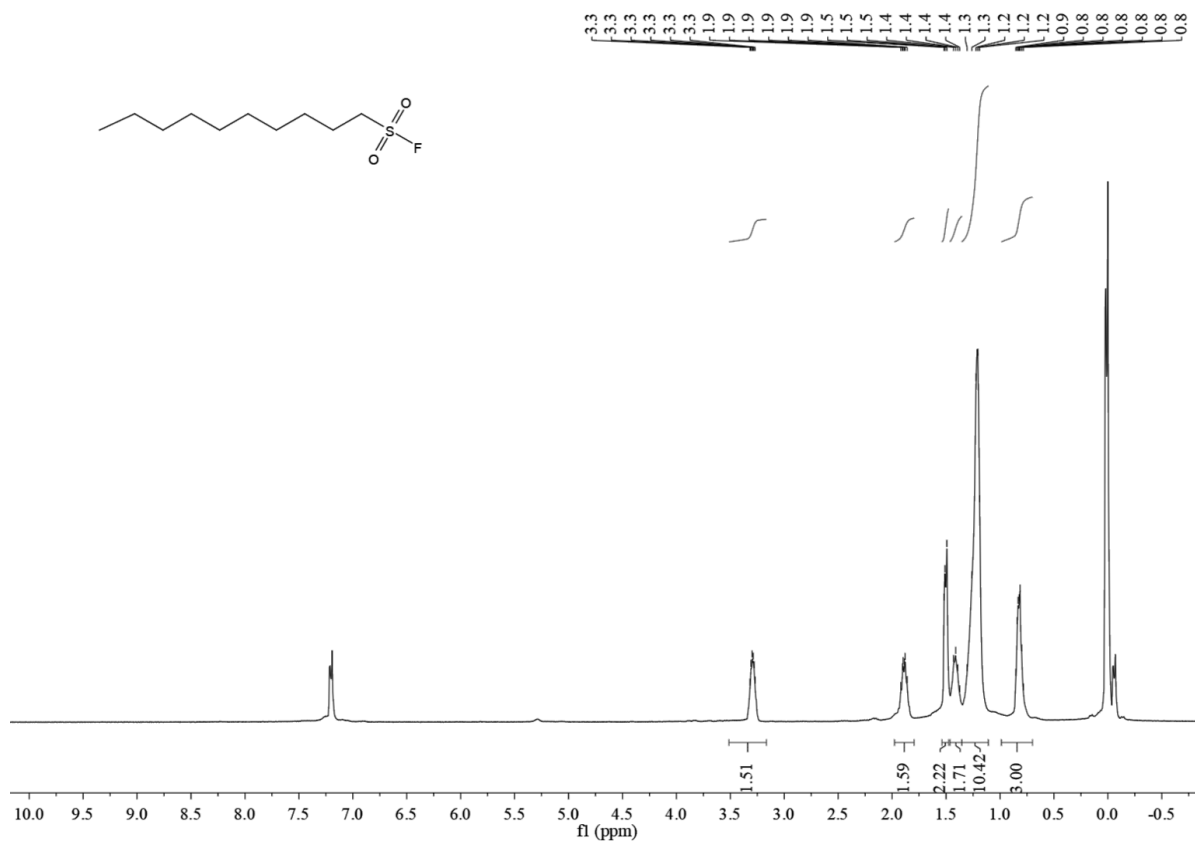


¹⁹F NMR

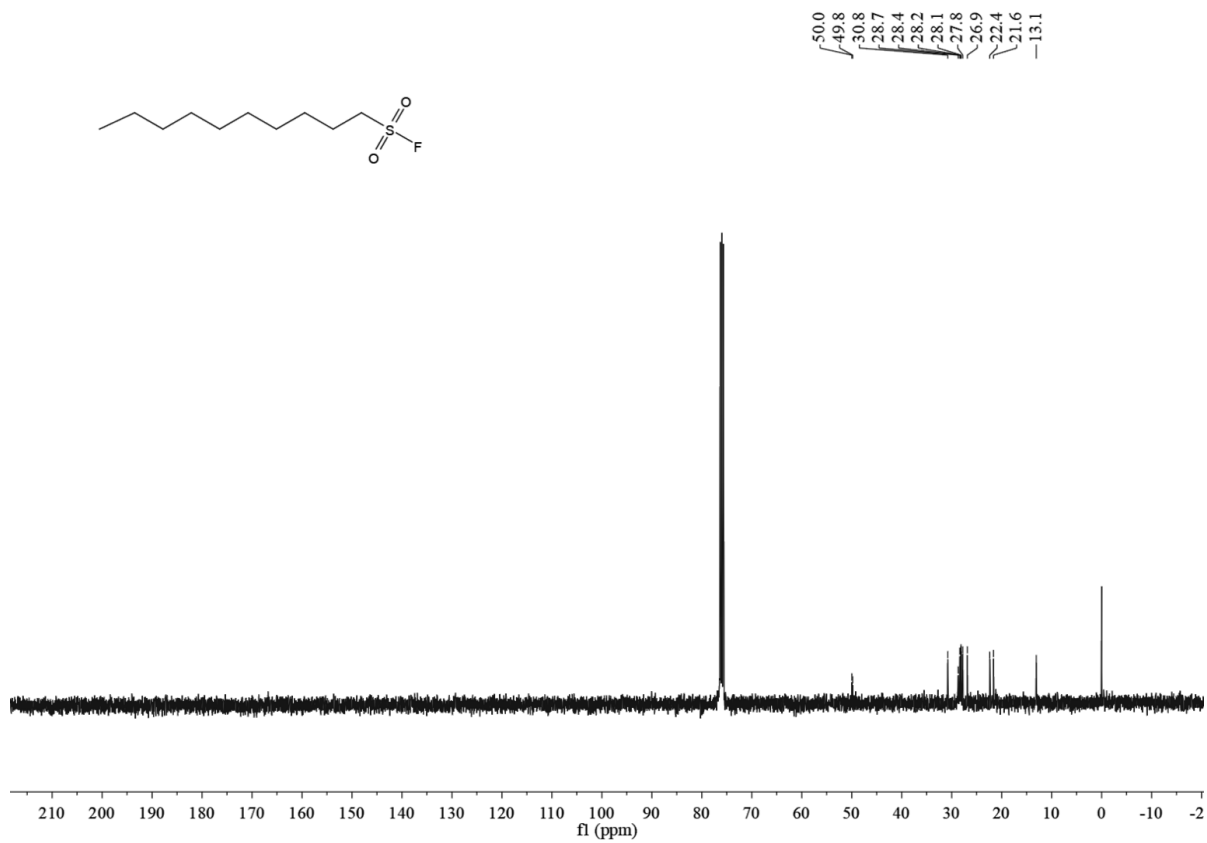


decane-1-sulfonyl fluoride (4f)

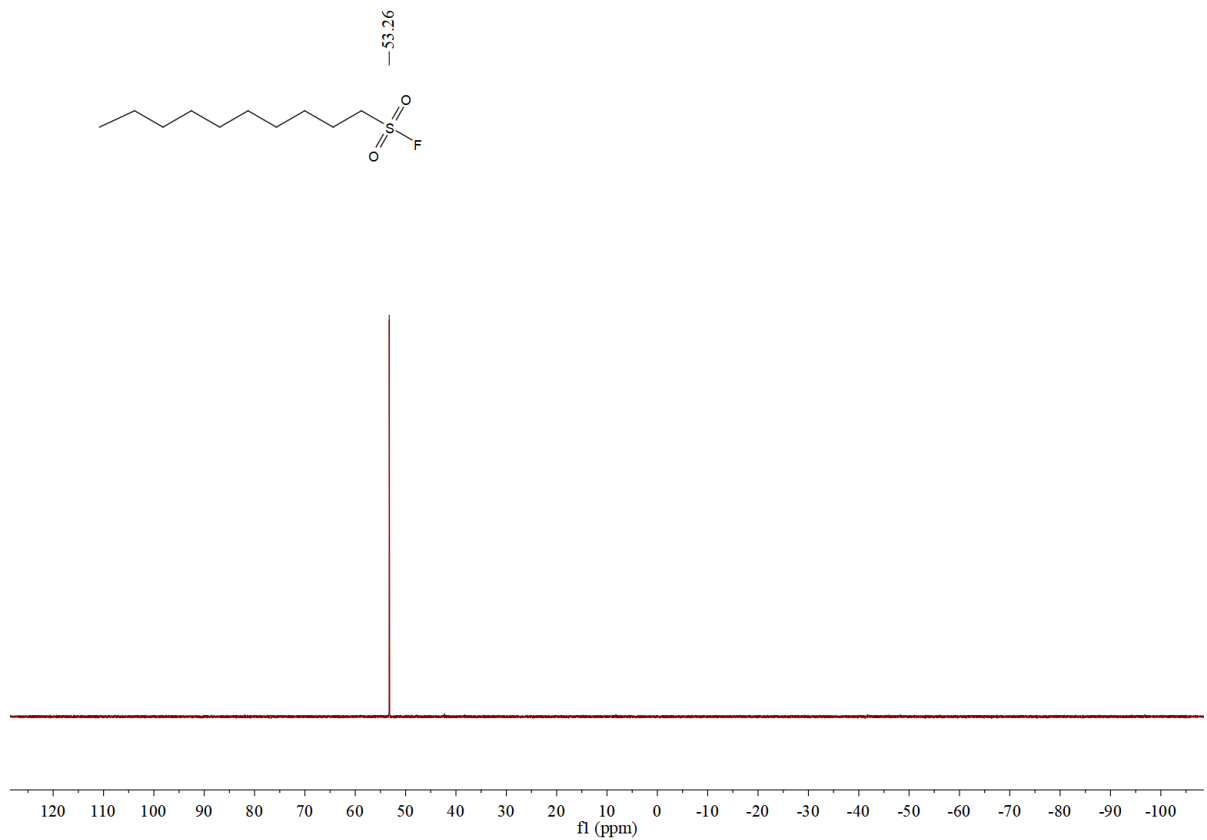
¹H NMR



¹³C NMR

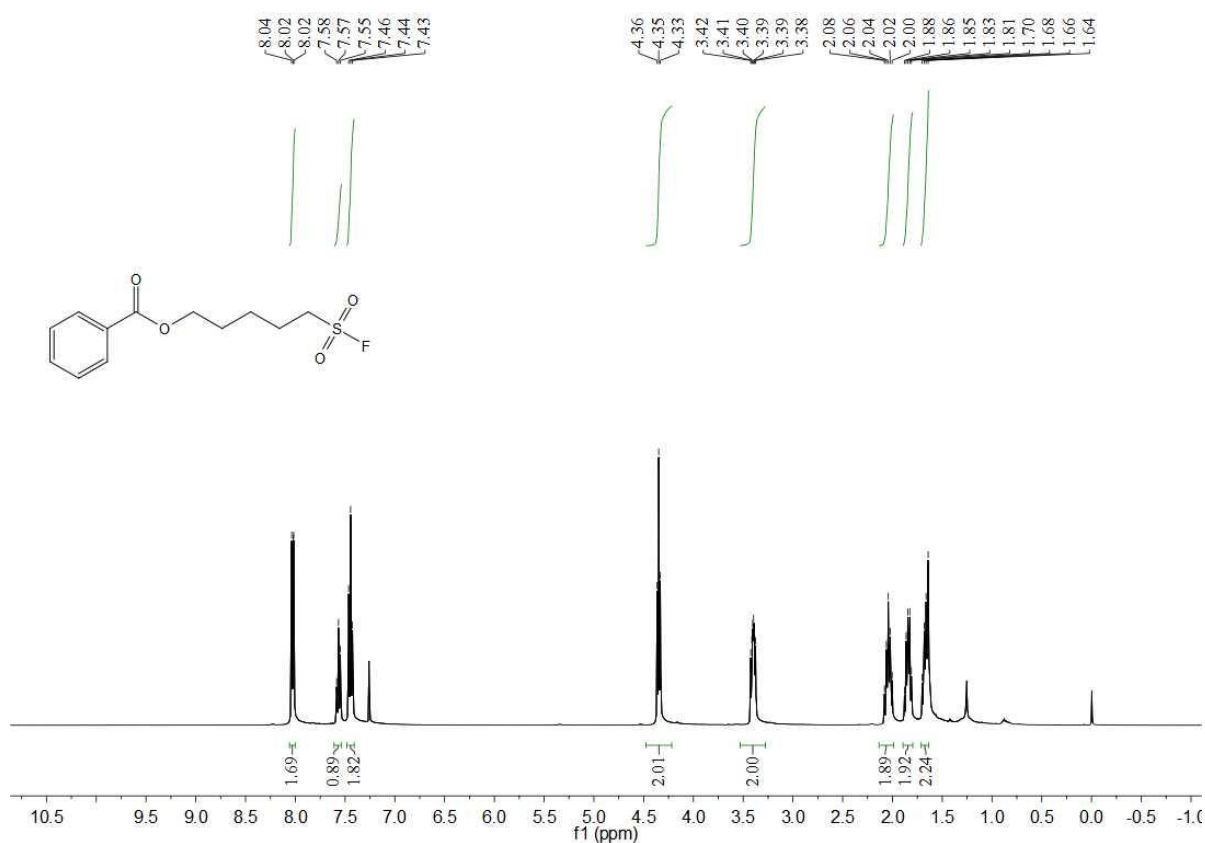


¹⁹F NMR

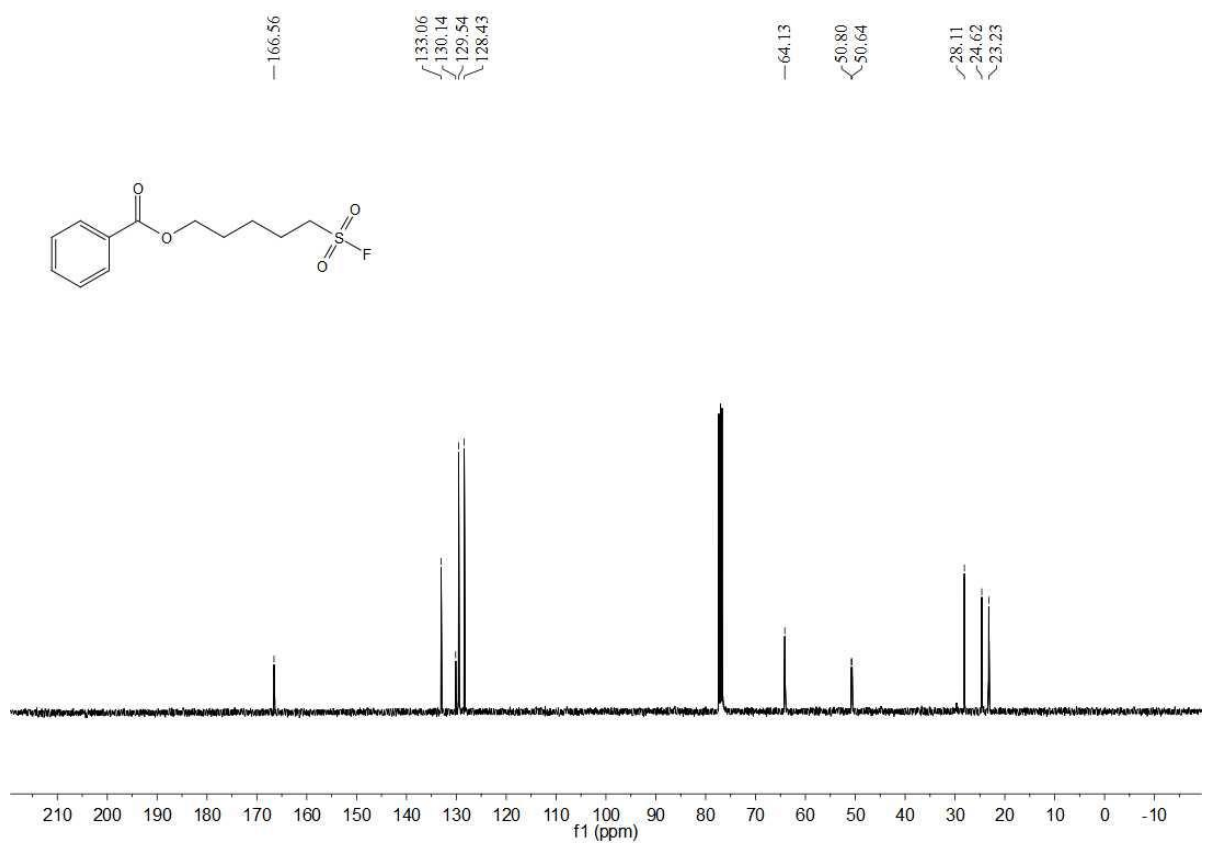


5-(fluorosulfonyl)pentyl benzoate (4g)

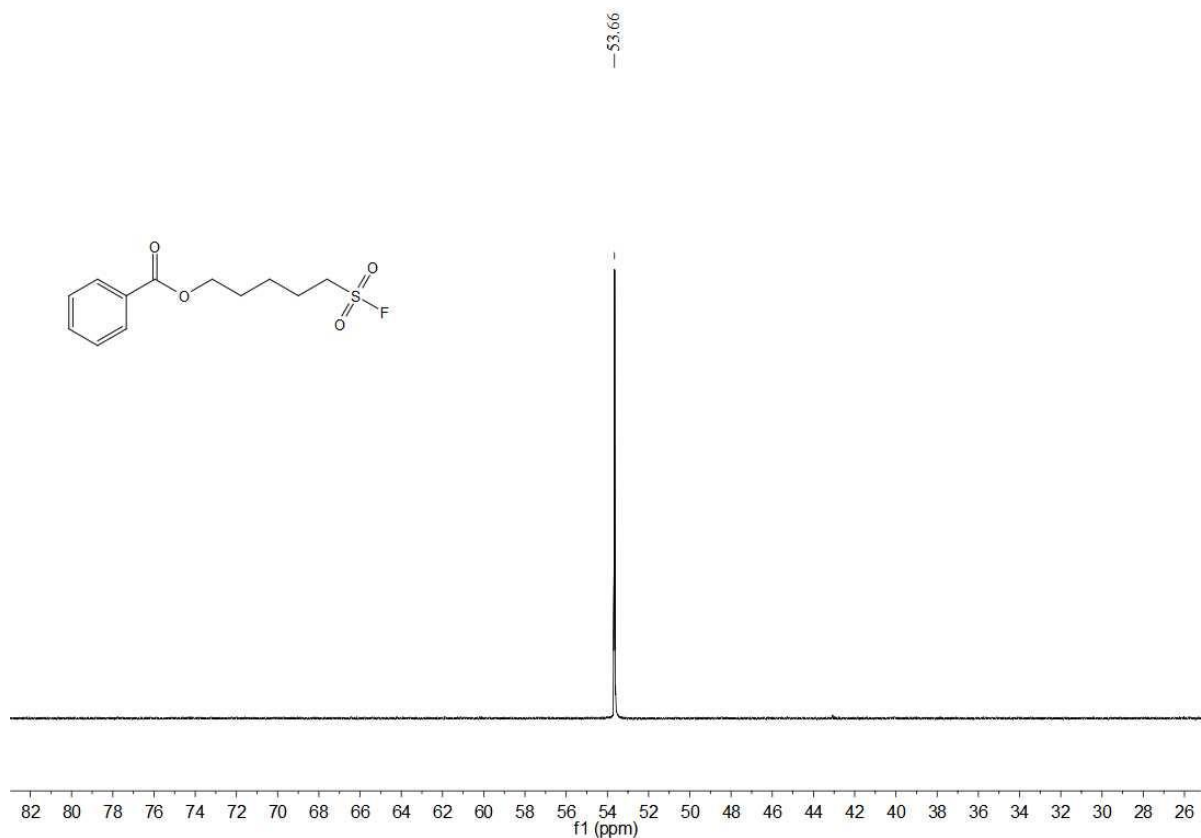
¹H NMR



¹³C NMR

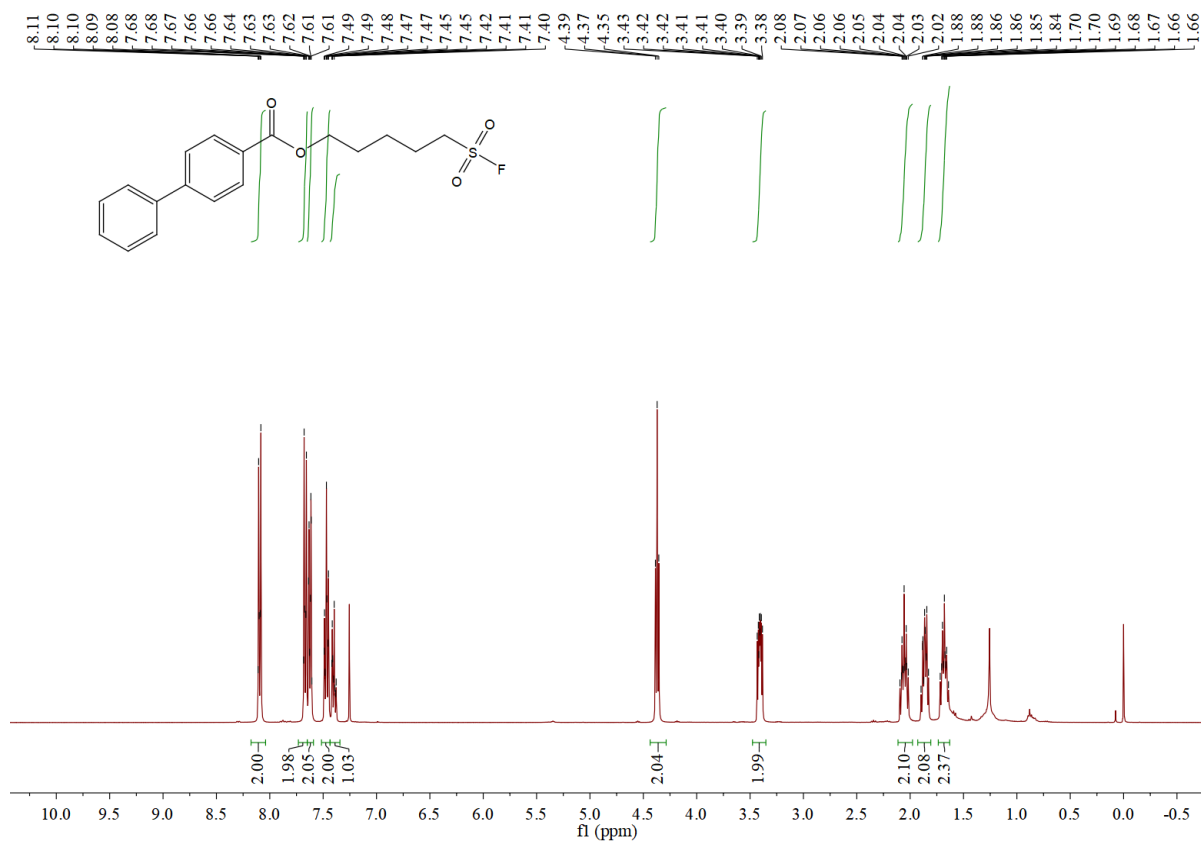


¹⁹F NMR

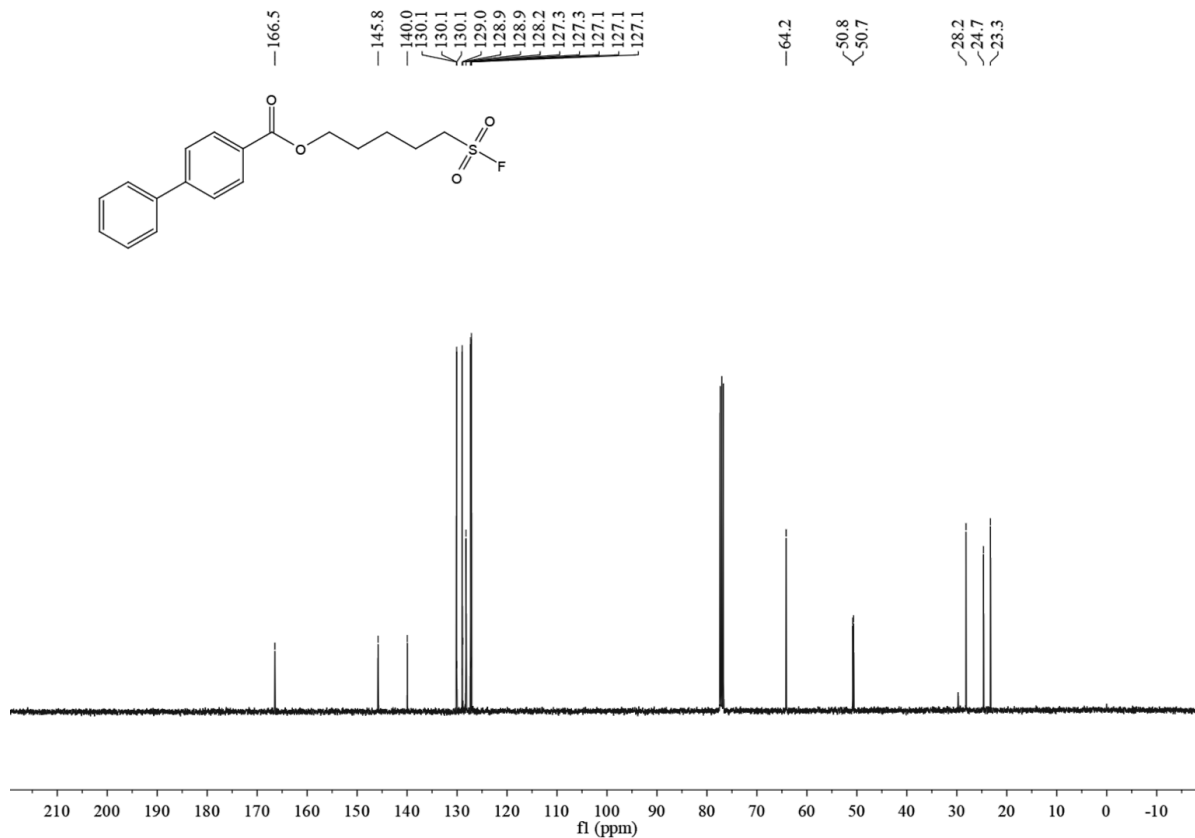


5-(fluorosulfonyl)pentyl [1,1'-biphenyl]-4-carboxylate (4h)

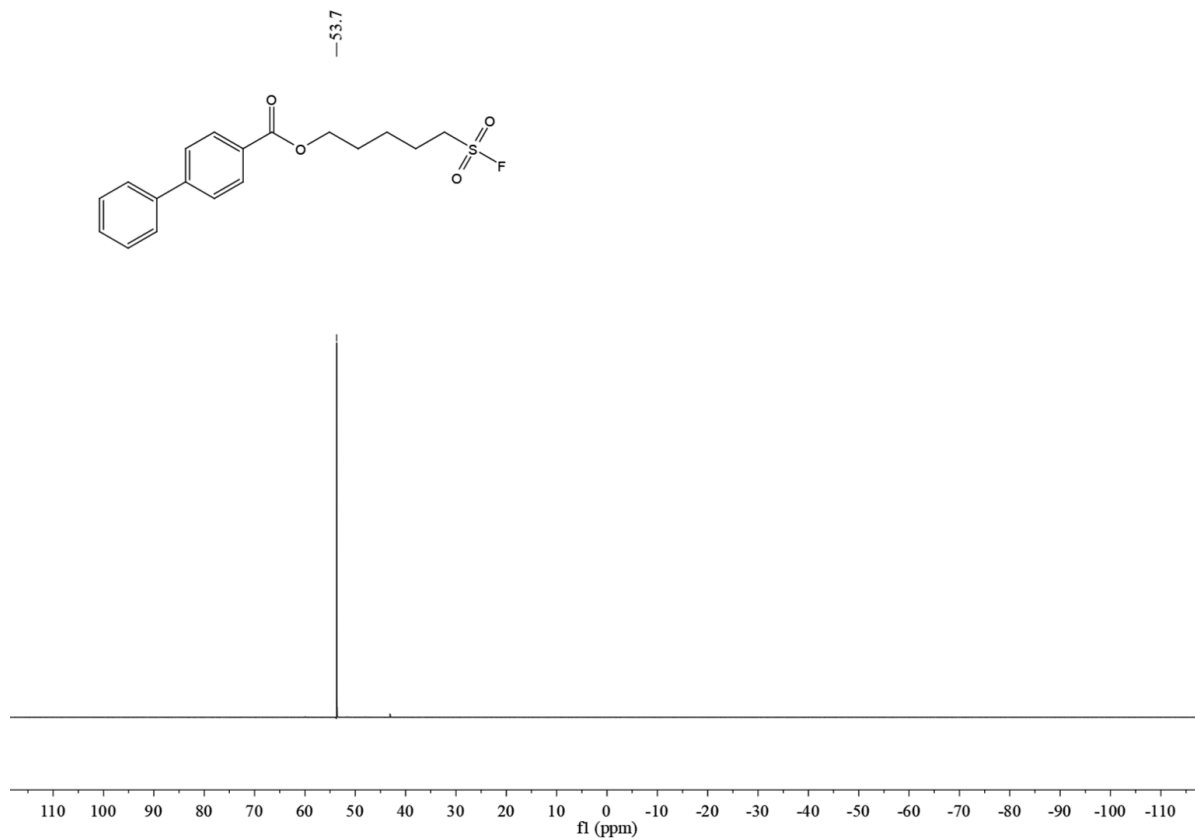
¹H NMR



¹³C NMR

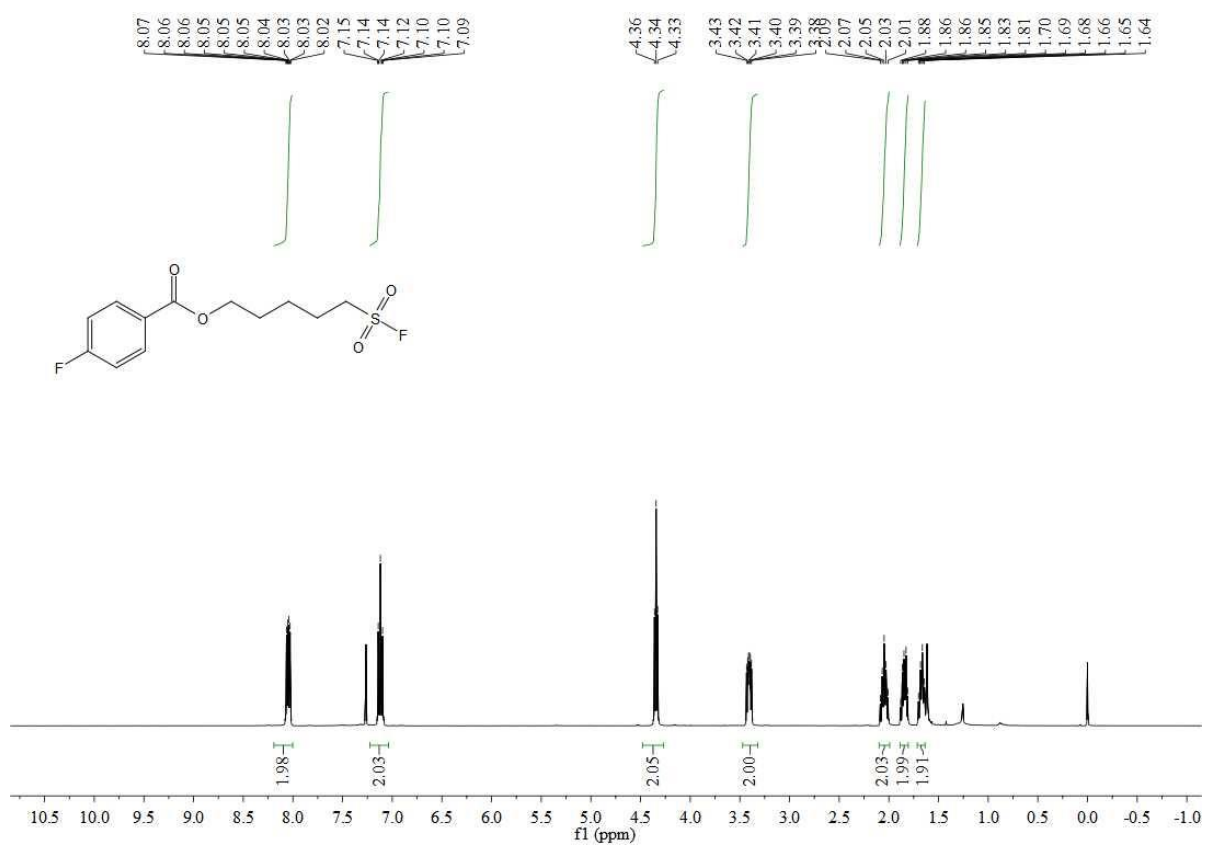


¹⁹F NMR

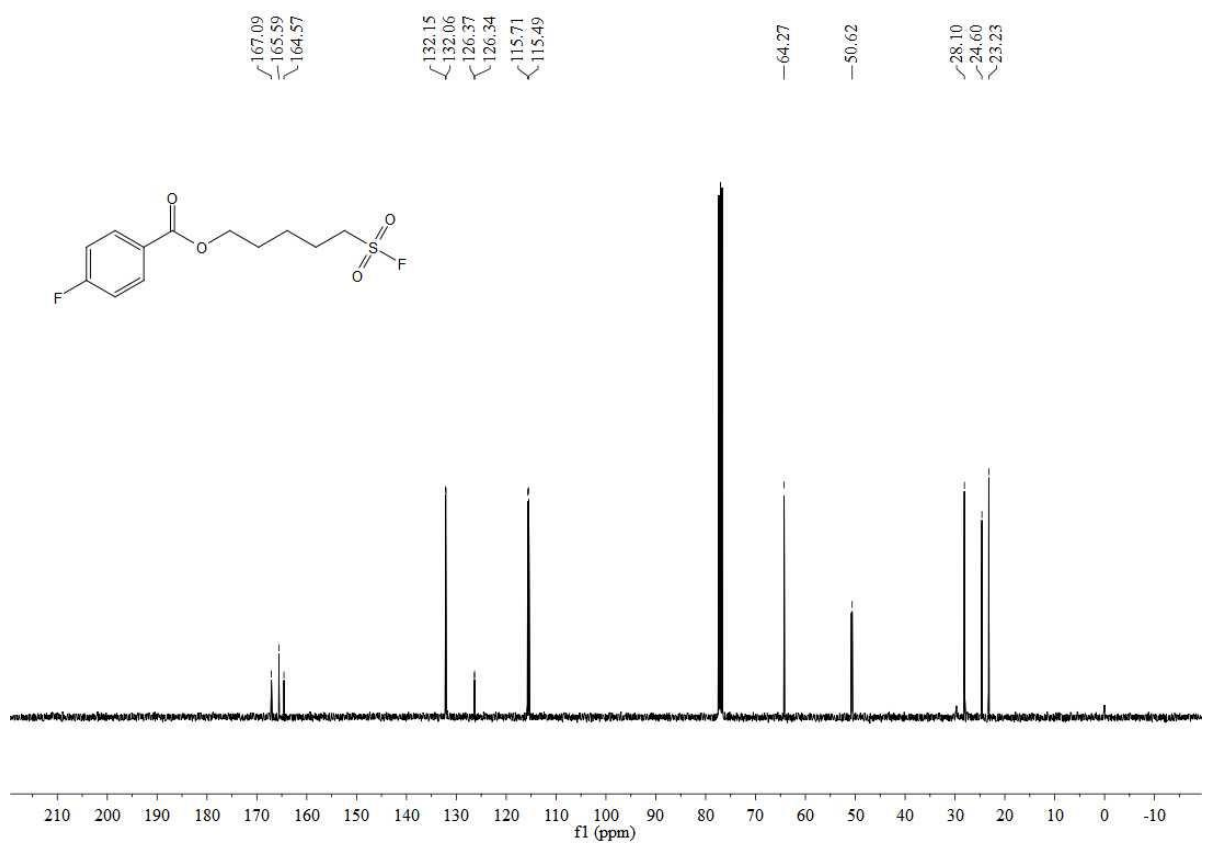


5-(fluorosulfonyl)pentyl 4-fluorobenzoate (2i)

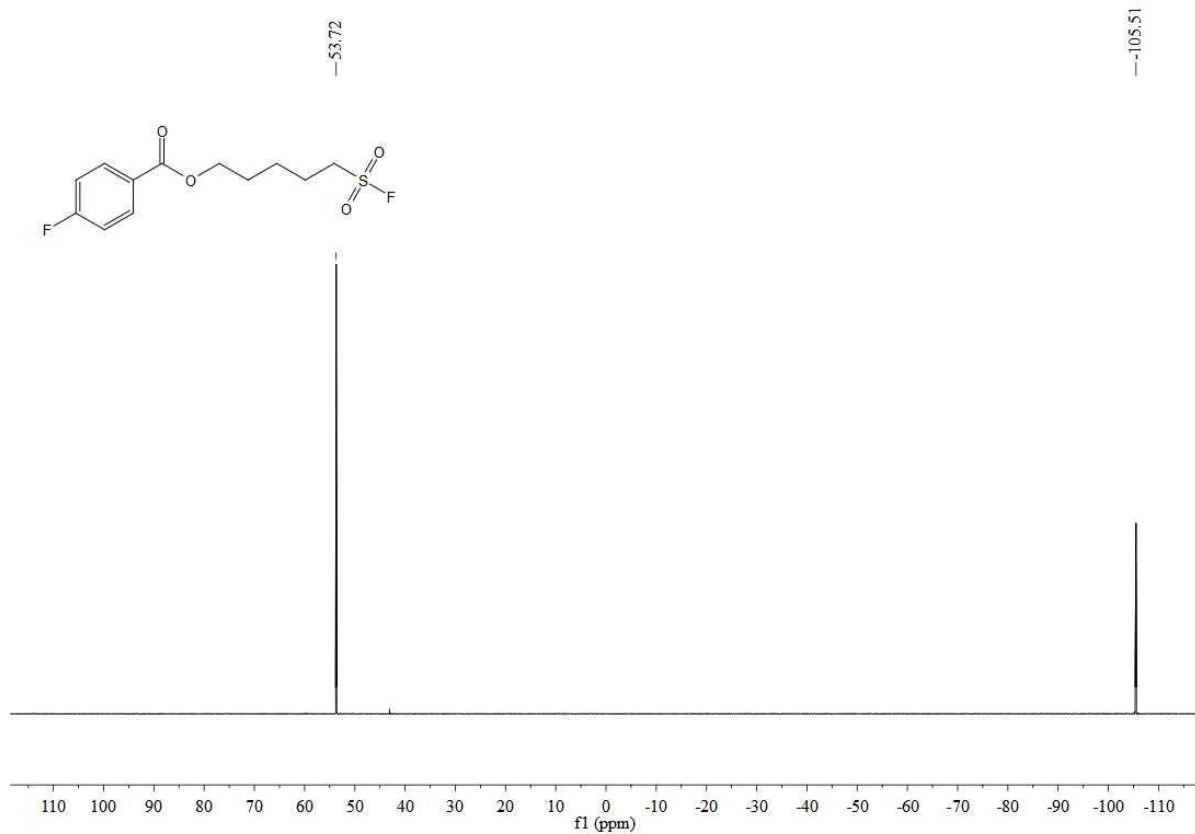
¹H NMR



¹³C NMR

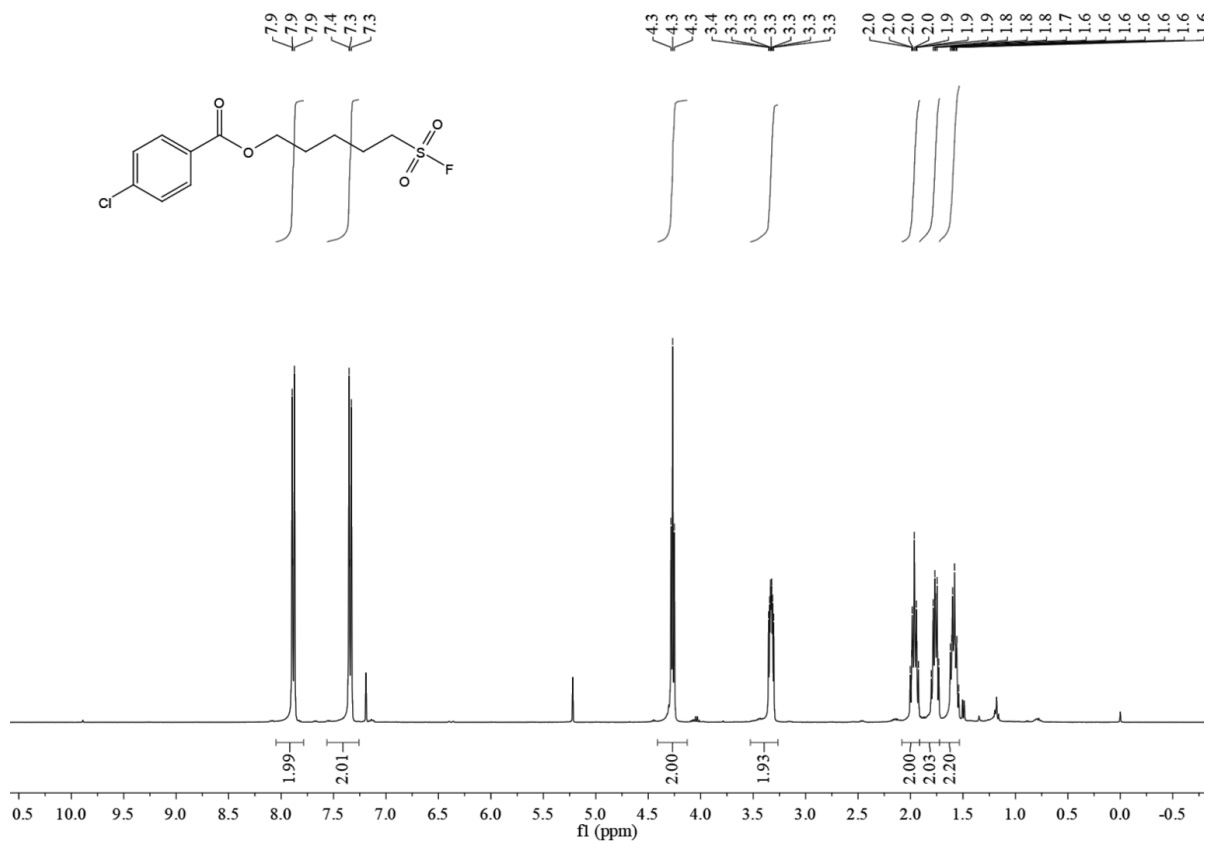


¹⁹F NMR

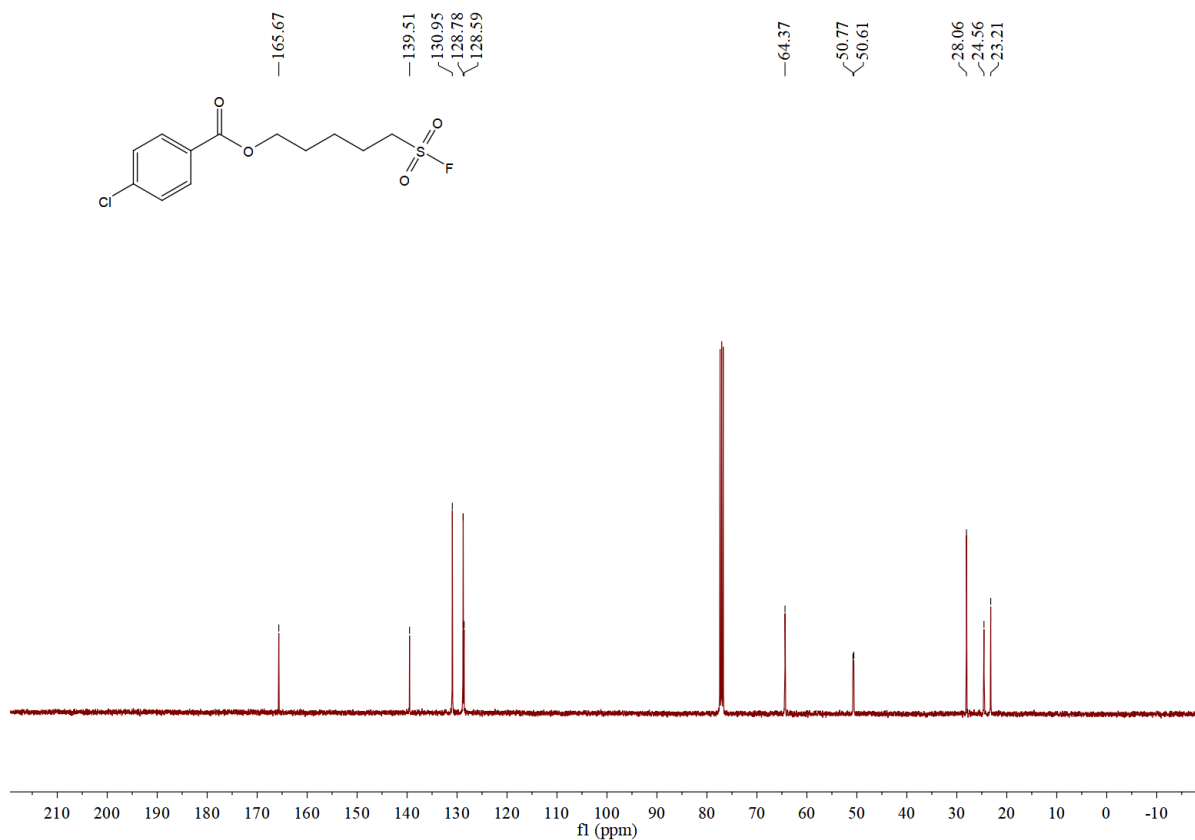


5-(fluorosulfonyl)pentyl 4-chlorobenzoate (**4j**)

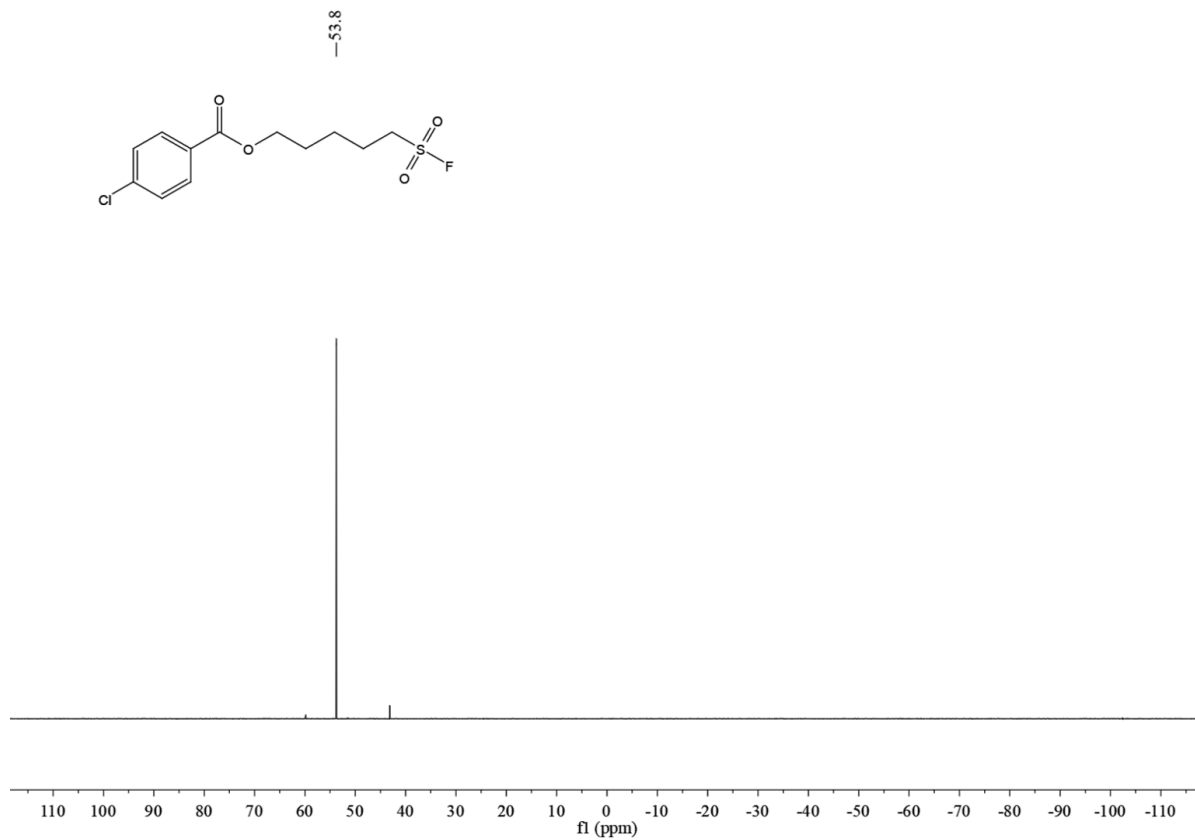
¹H NMR



¹³C NMR

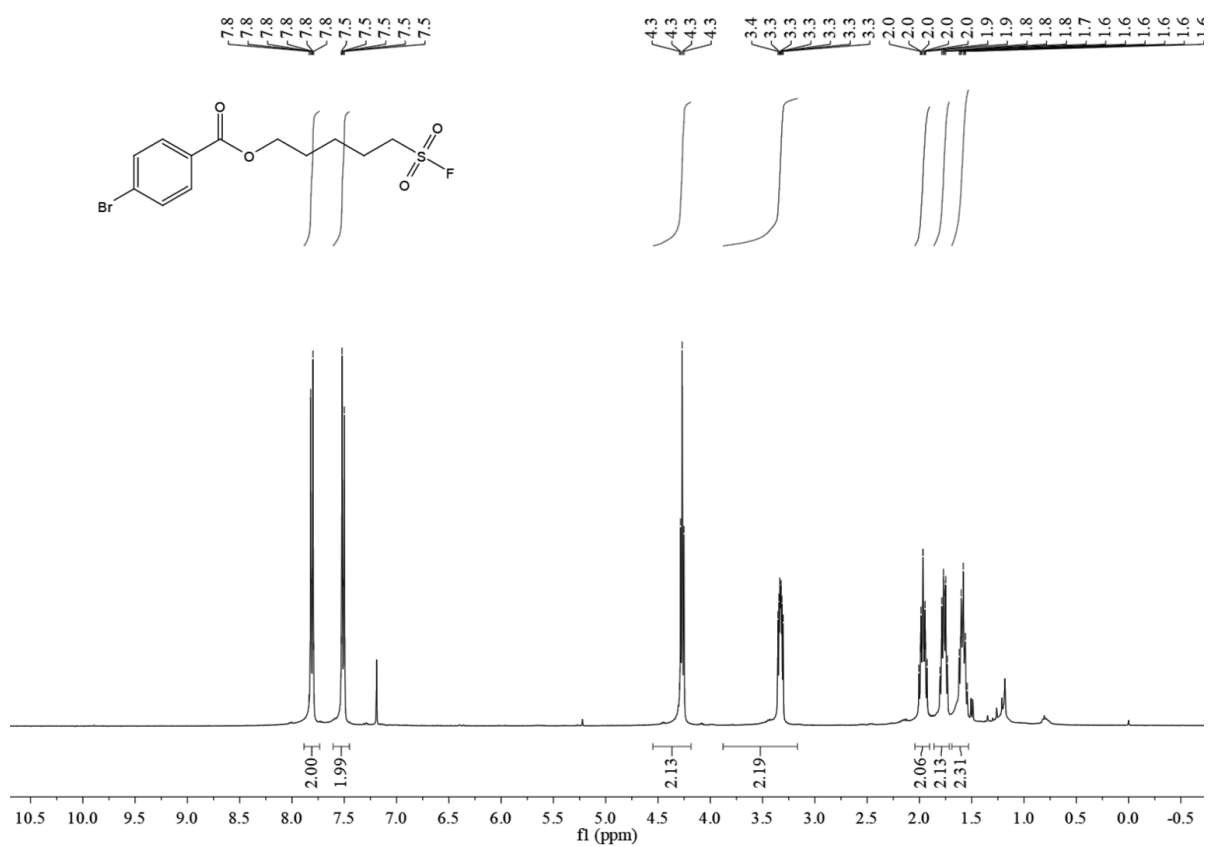


¹⁹F NMR

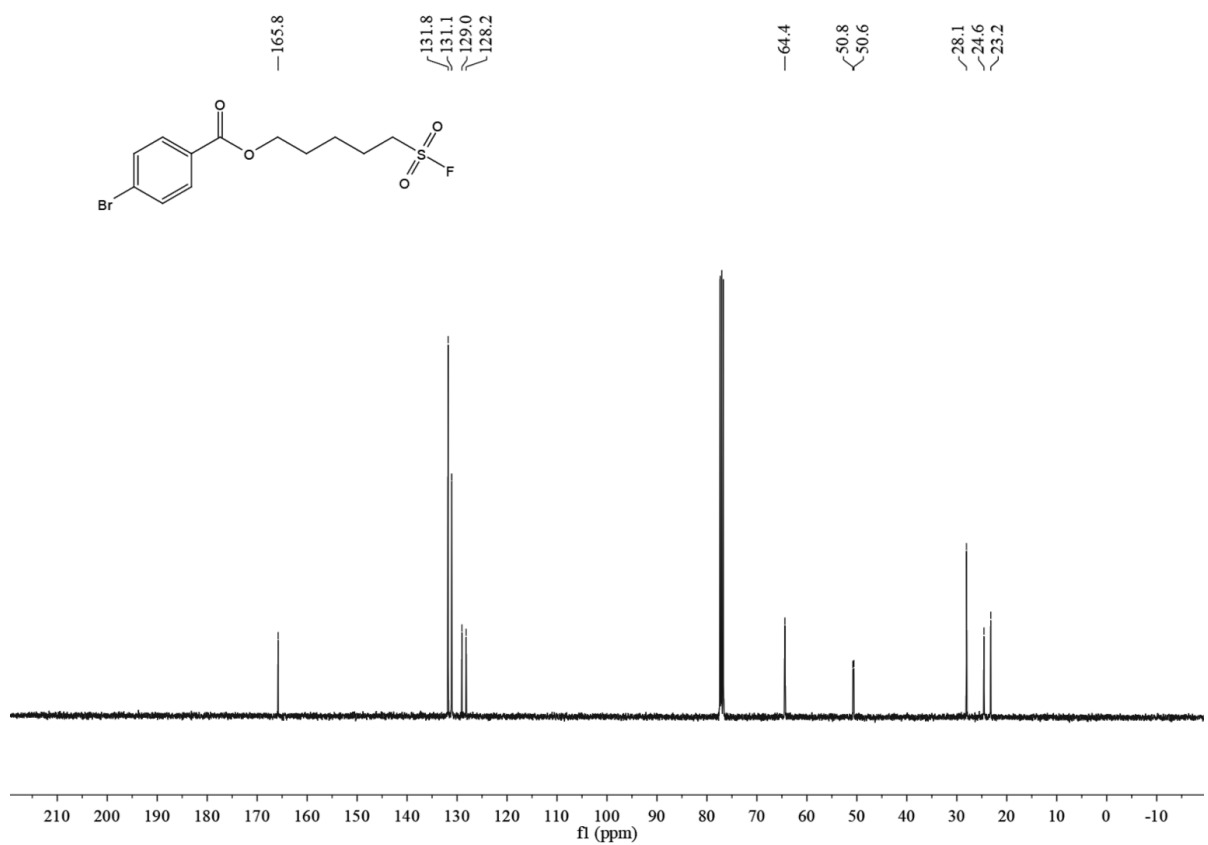


5-(fluorosulfonyl)pentyl 4-bromobenzoate (**4k**)

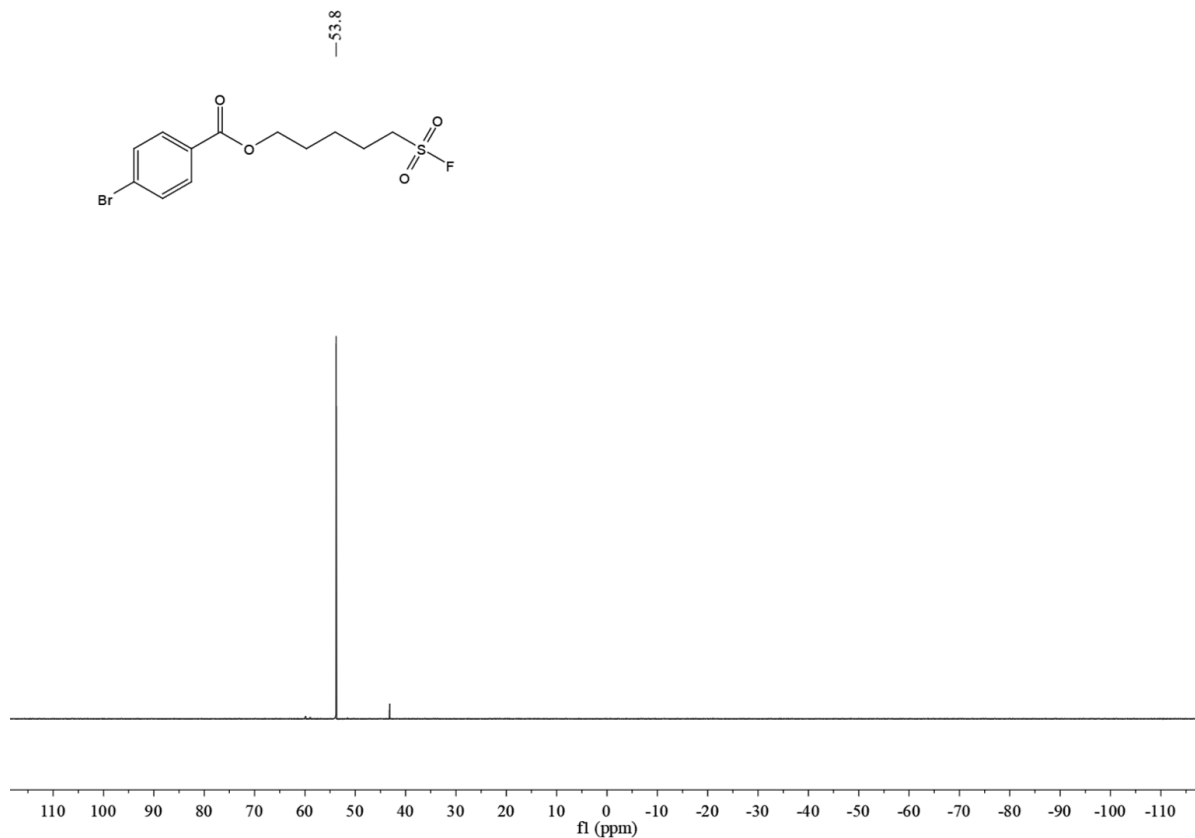
¹H NMR



¹³C NMR

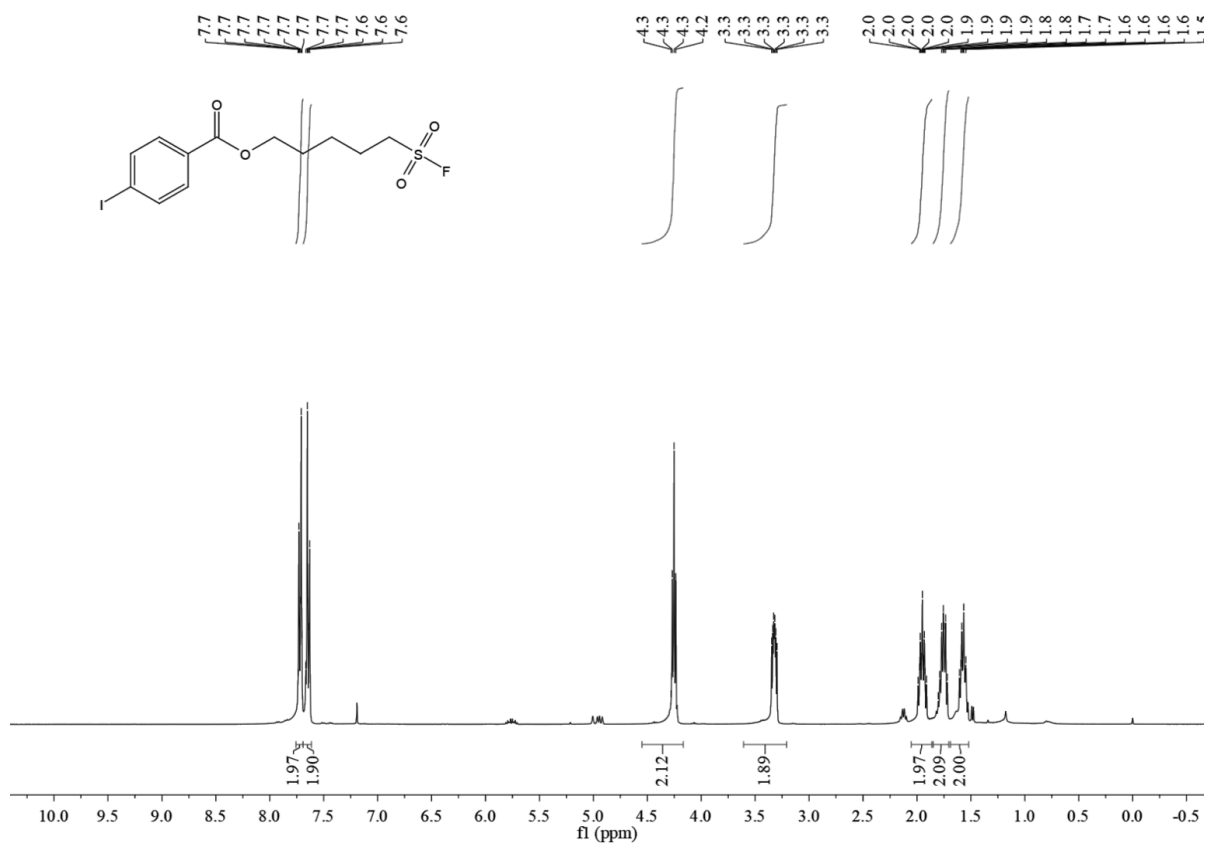


¹⁹F NMR

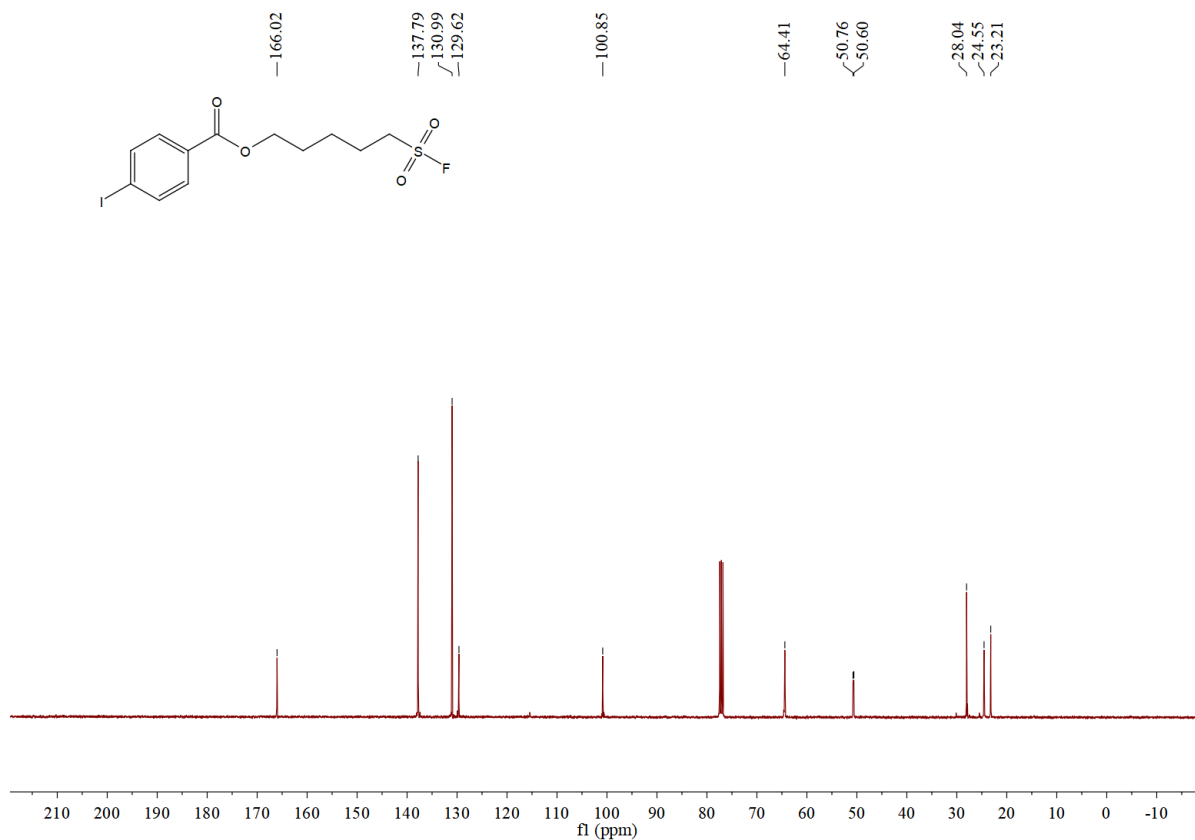


5-(fluorosulfonyl)pentyl 4-iodobenzoate (**4l**)

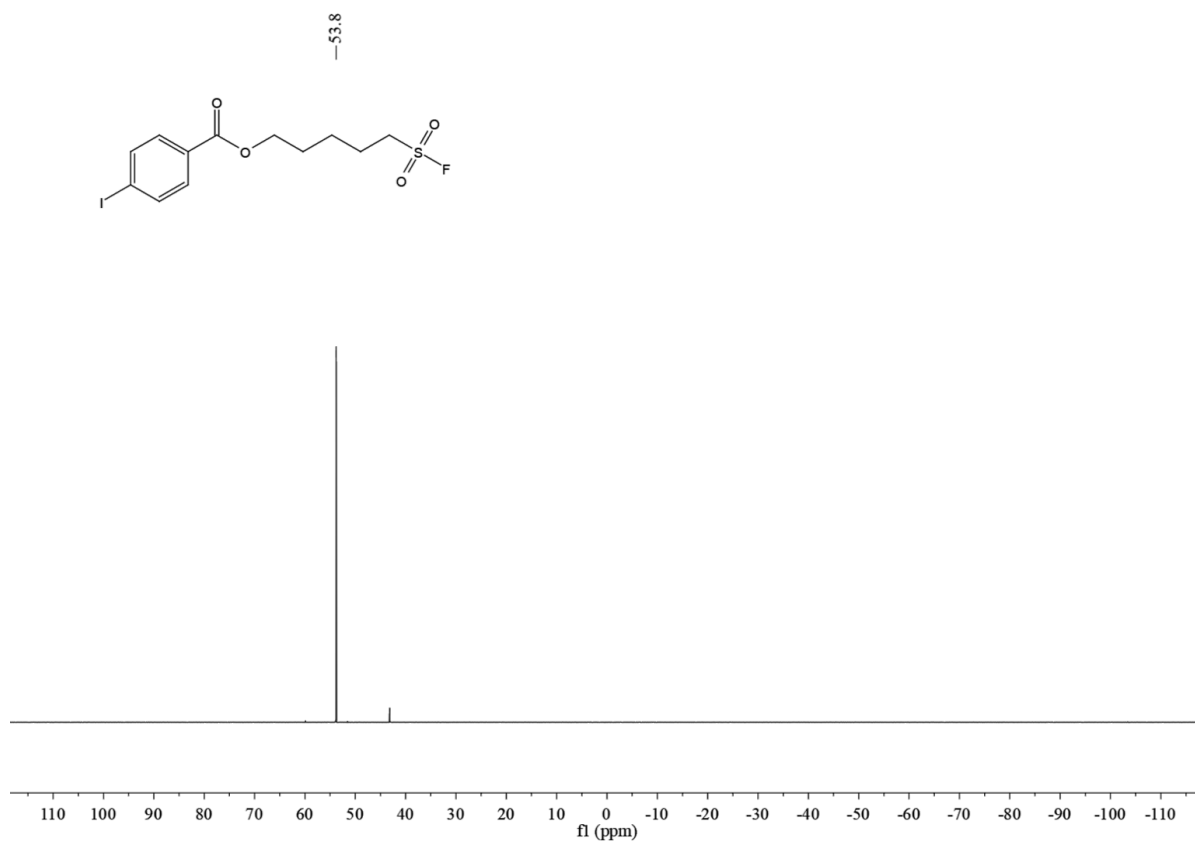
¹H NMR



¹³C NMR

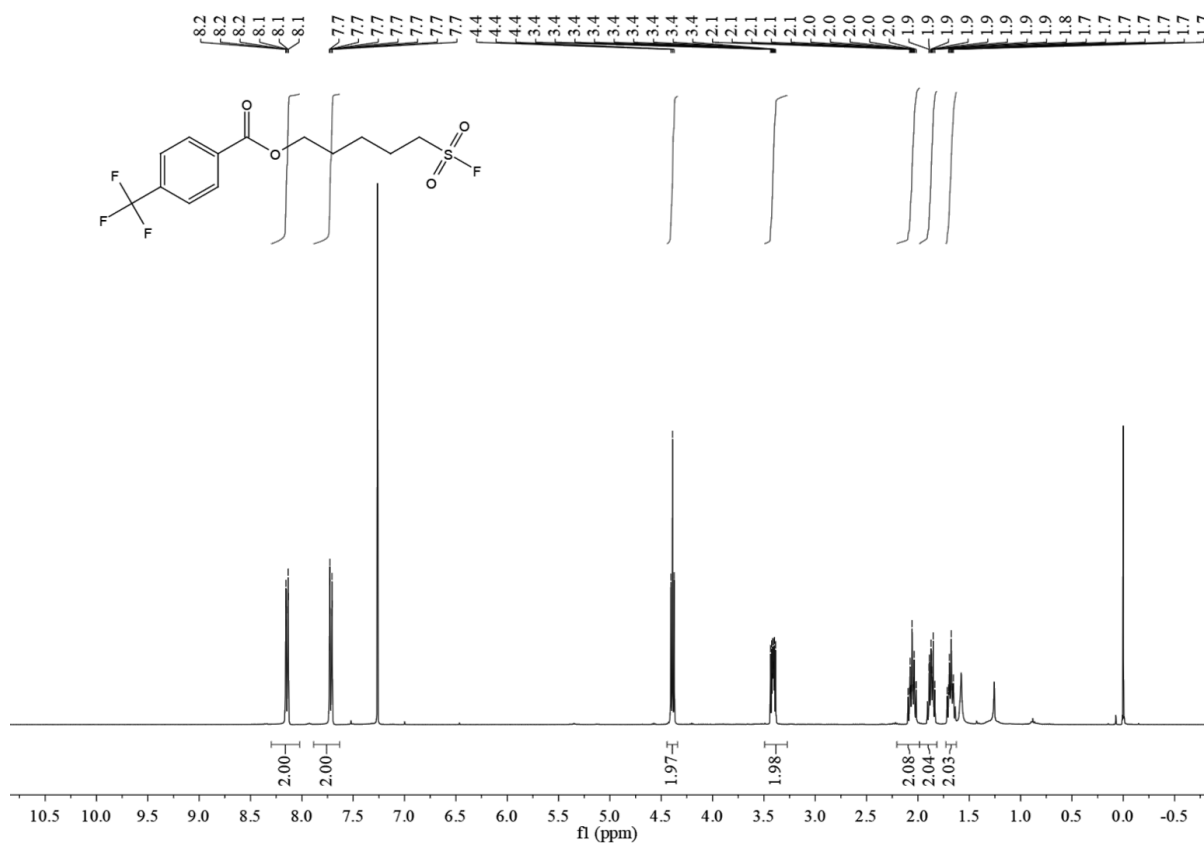


¹⁹F NMR

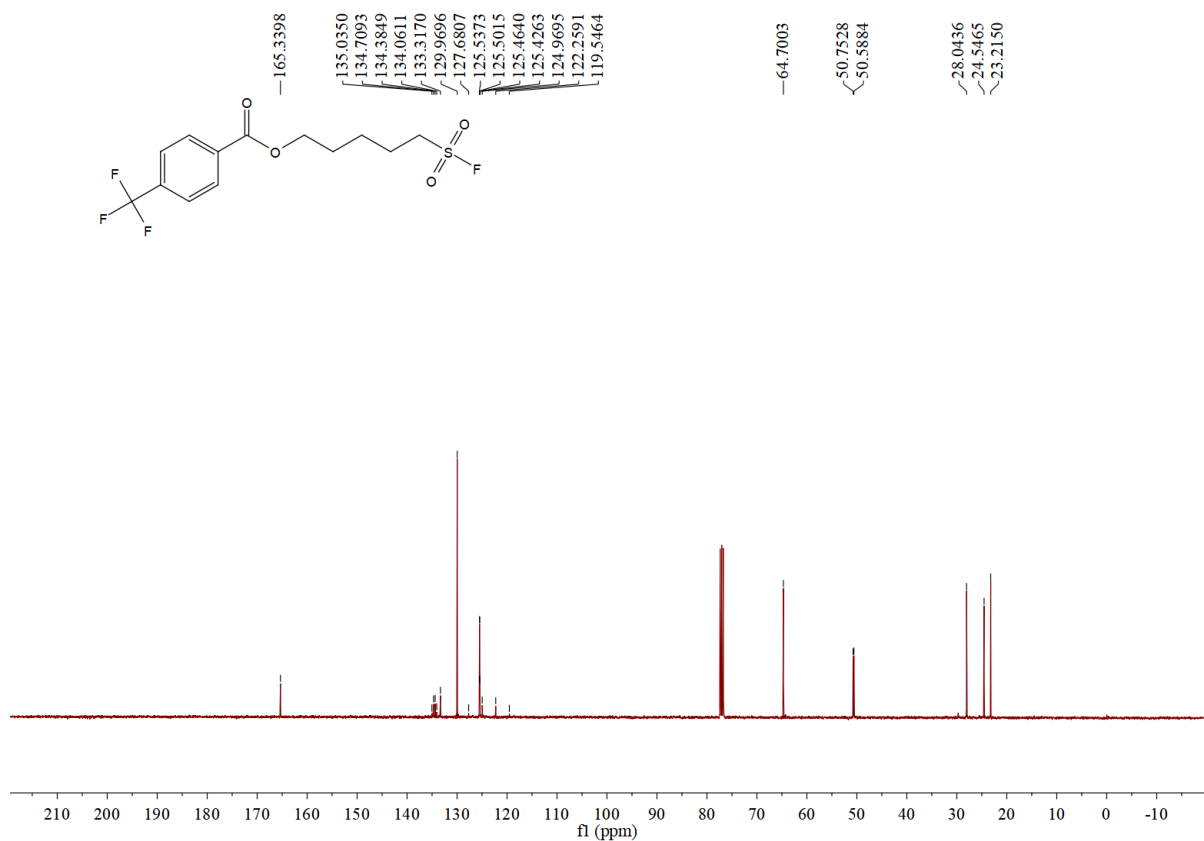


5-(trifluoromethyl)pentyl 4-(trifluoromethyl)benzoate (4m)

¹H NMR



¹³C NMR

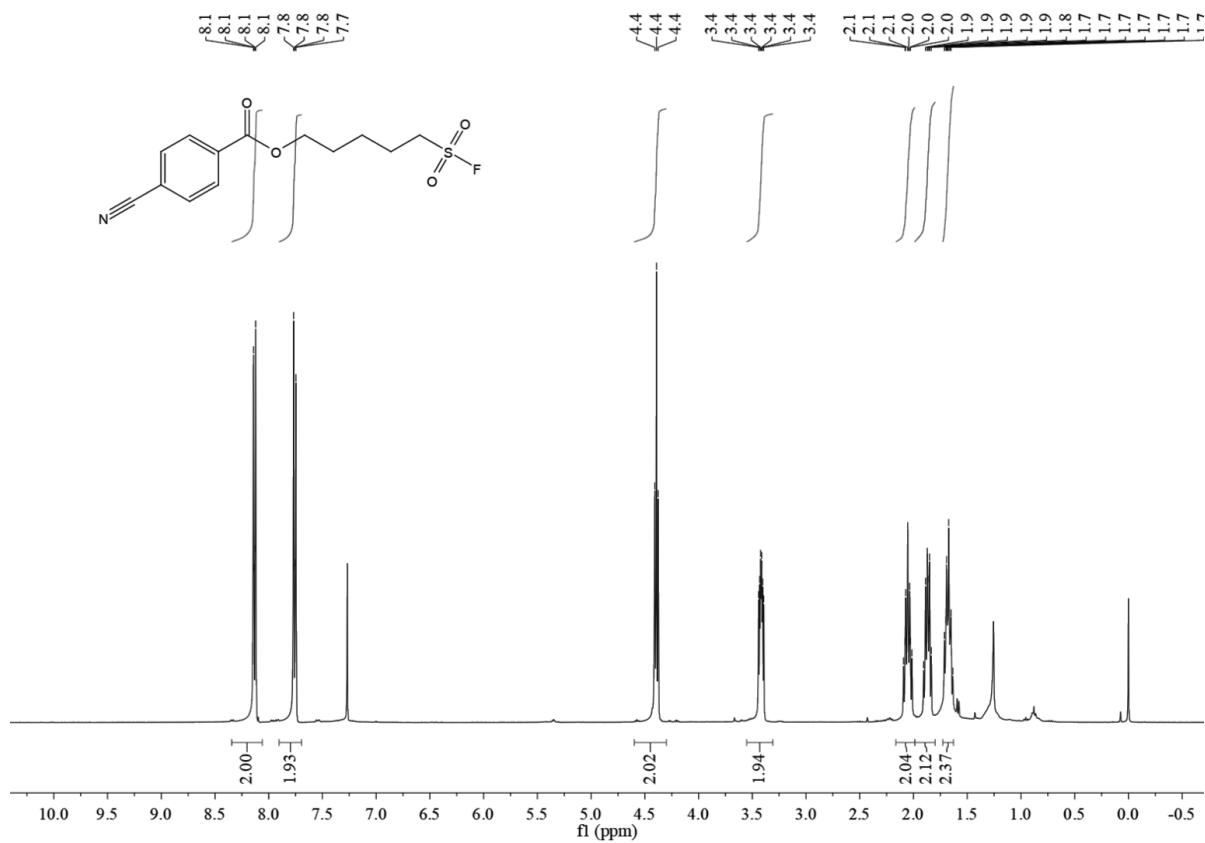


¹⁹F NMR

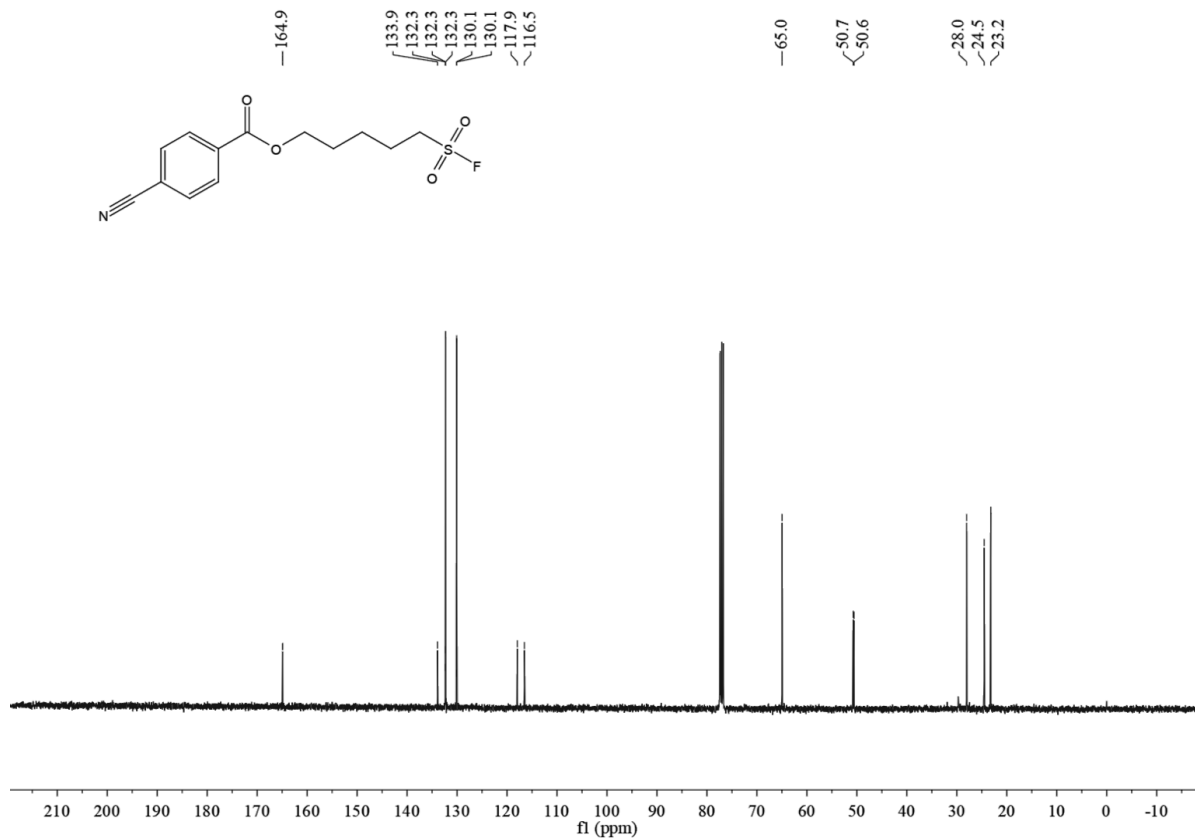


5-(fluorosulfonyl)pentyl 4-cyanobenzoate (**4n**)

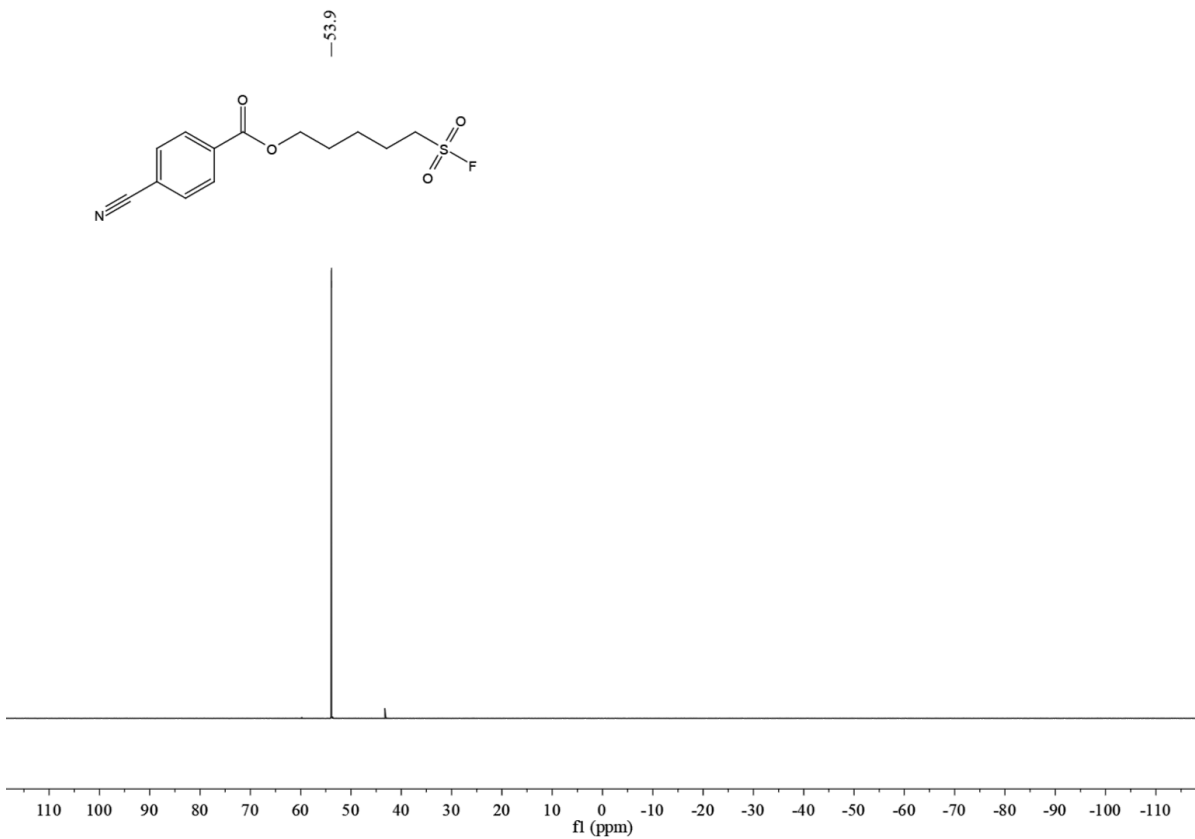
¹H NMR



¹³C NMR

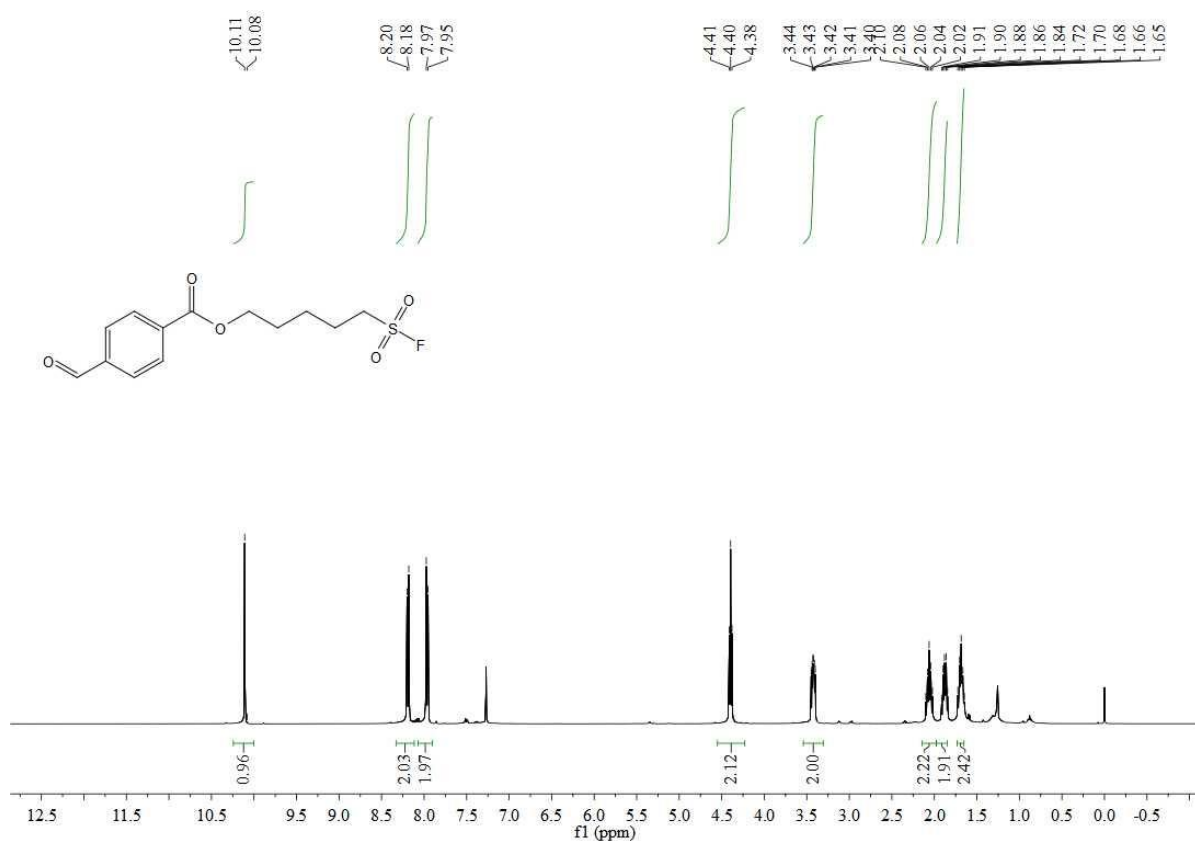


¹⁹F NMR

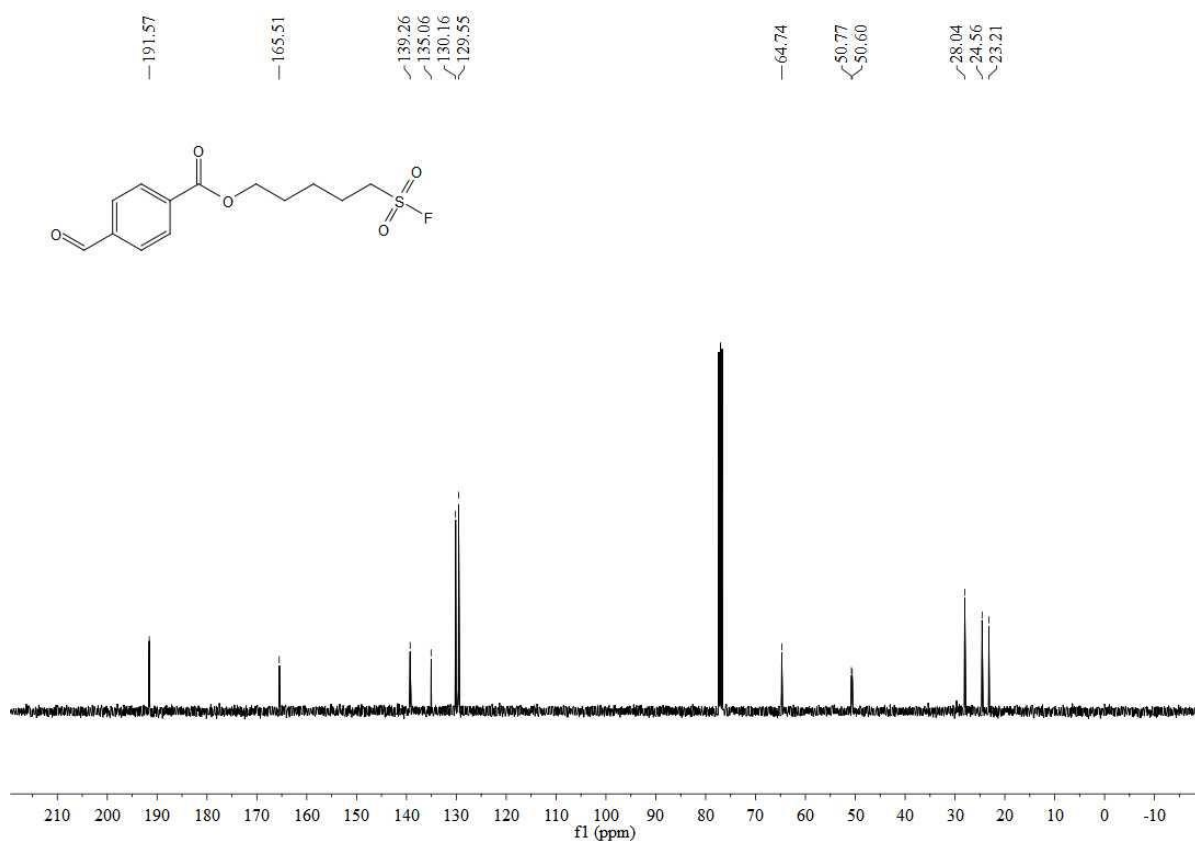


5-(fluorosulfonyl)pentyl 4-formylbenzoate (4o)

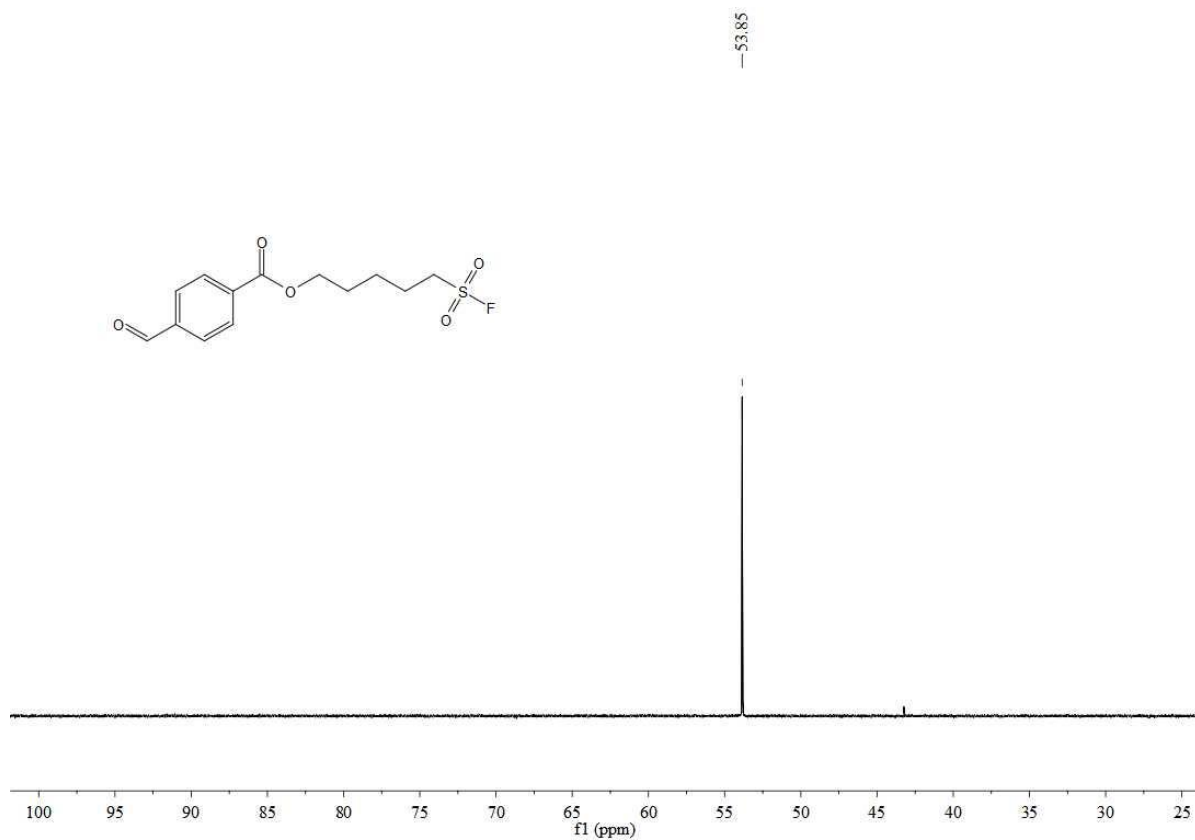
¹H NMR



¹³C NMR

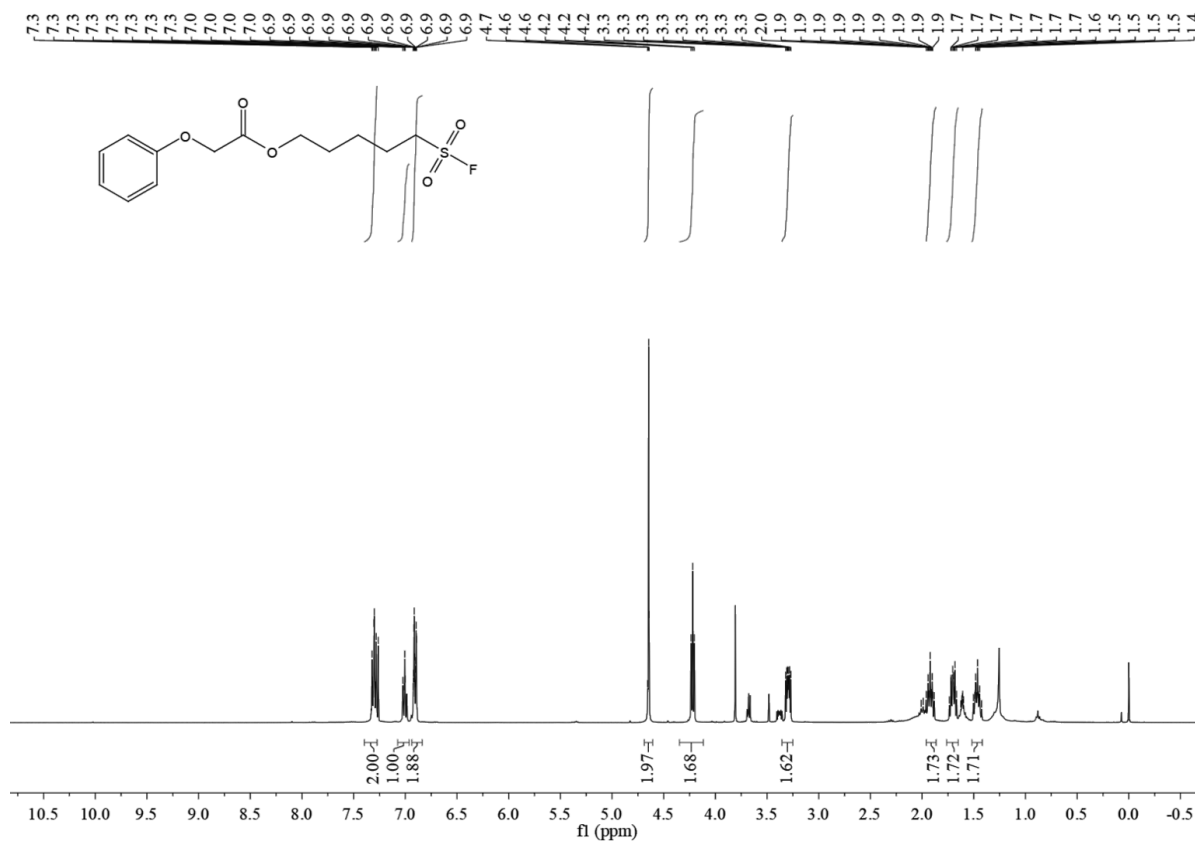


¹⁹F NMR

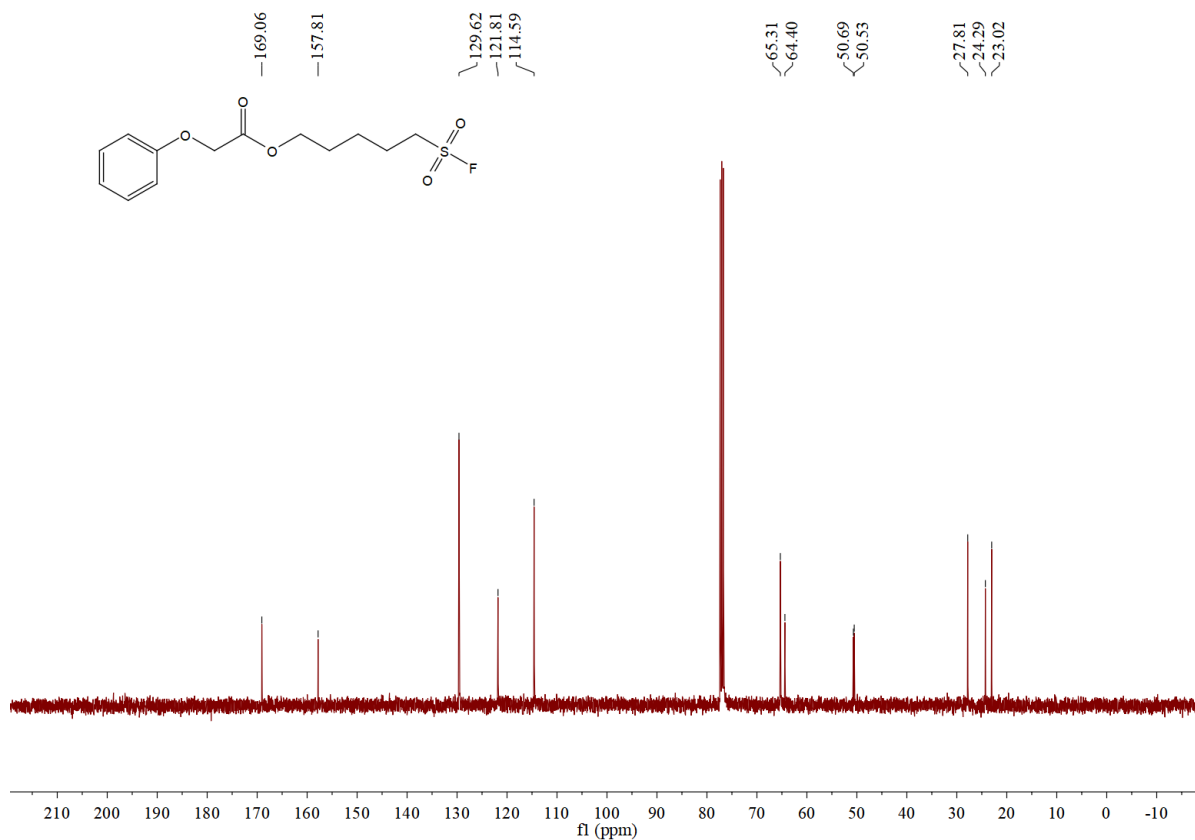


5-(fluorosulfonyl)pentyl 2-phenoxyacetate (4p)

¹H NMR



¹³C NMR

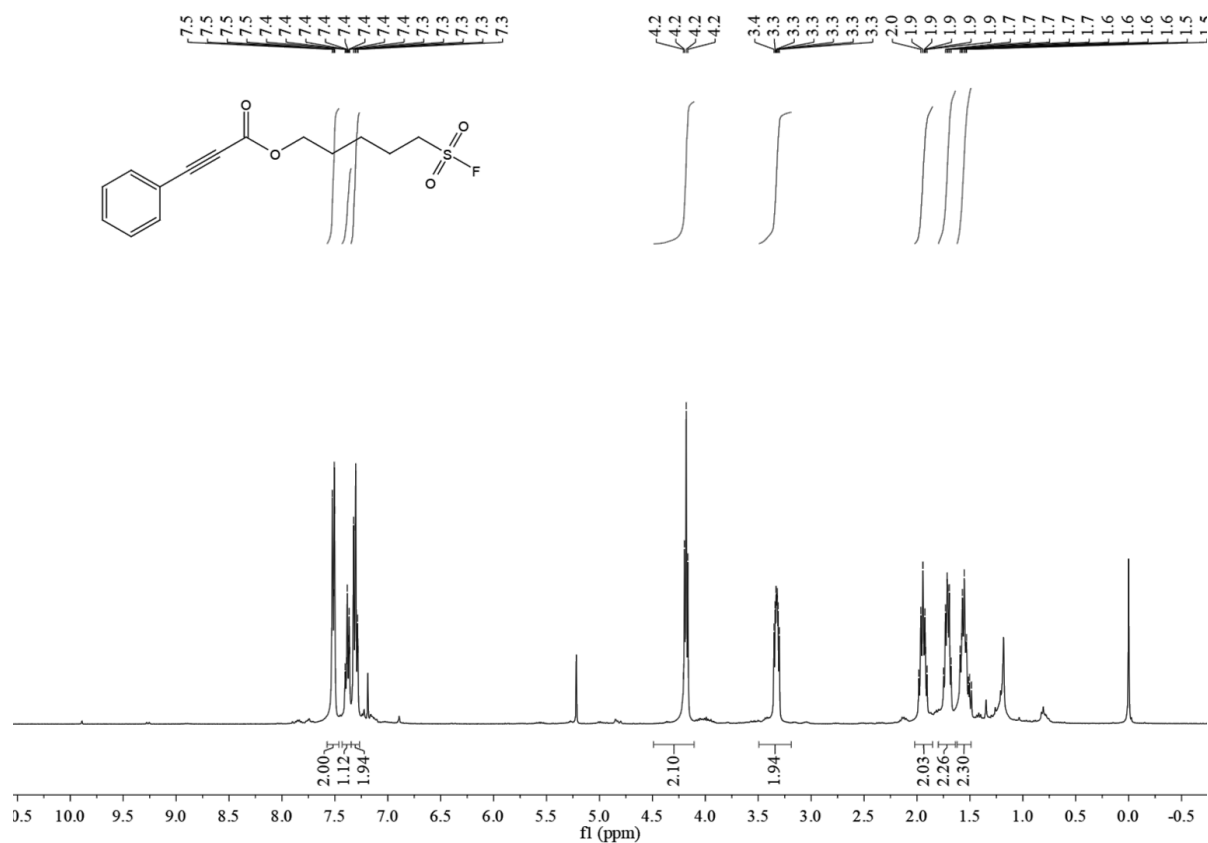


¹⁹F NMR

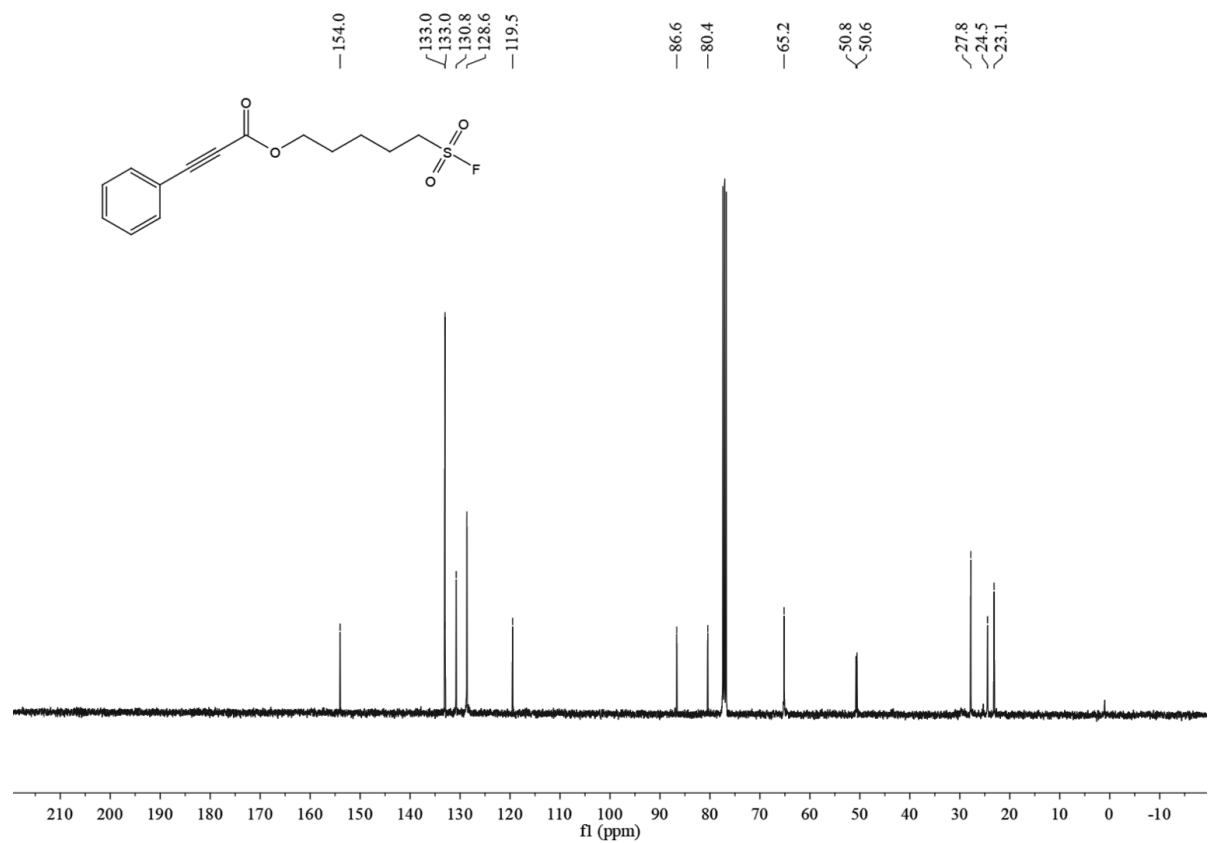


5-(fluorosulfonyl)pentyl 3-phenylpropiolate (**4q**)

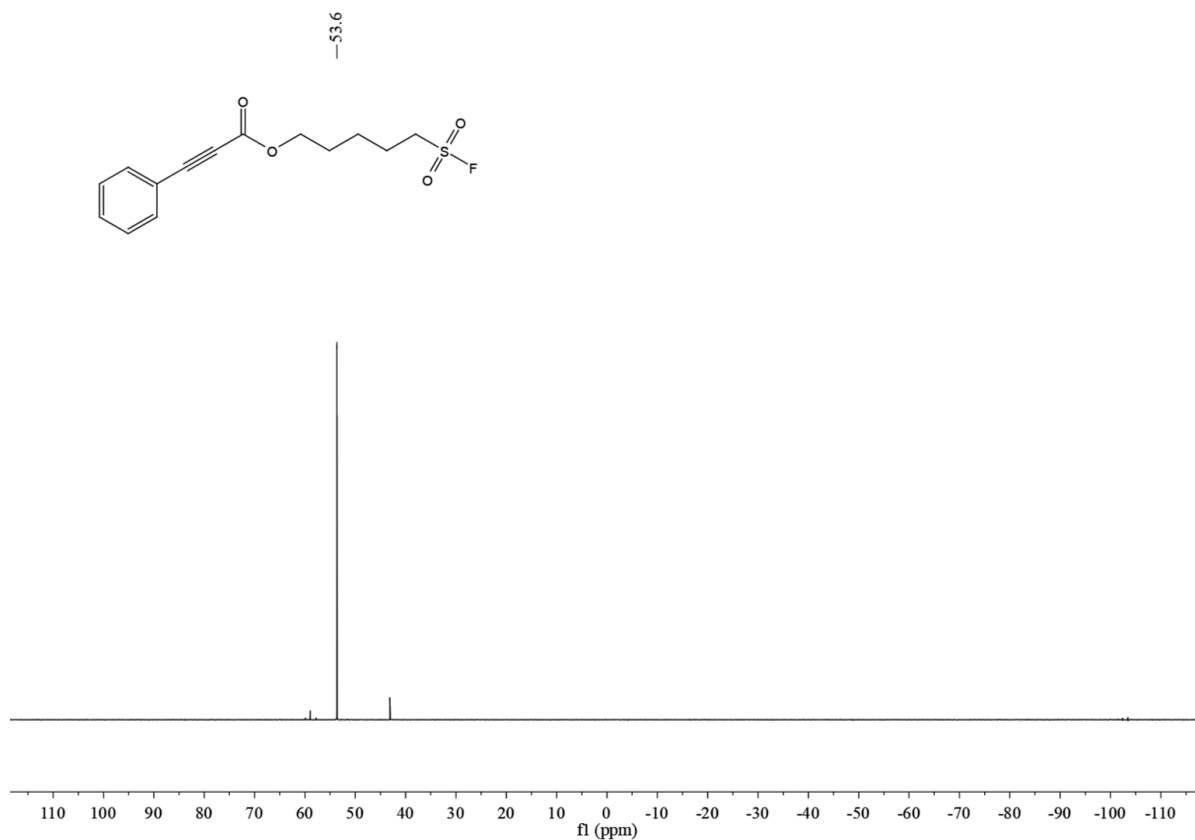
¹H NMR



¹³C NMR

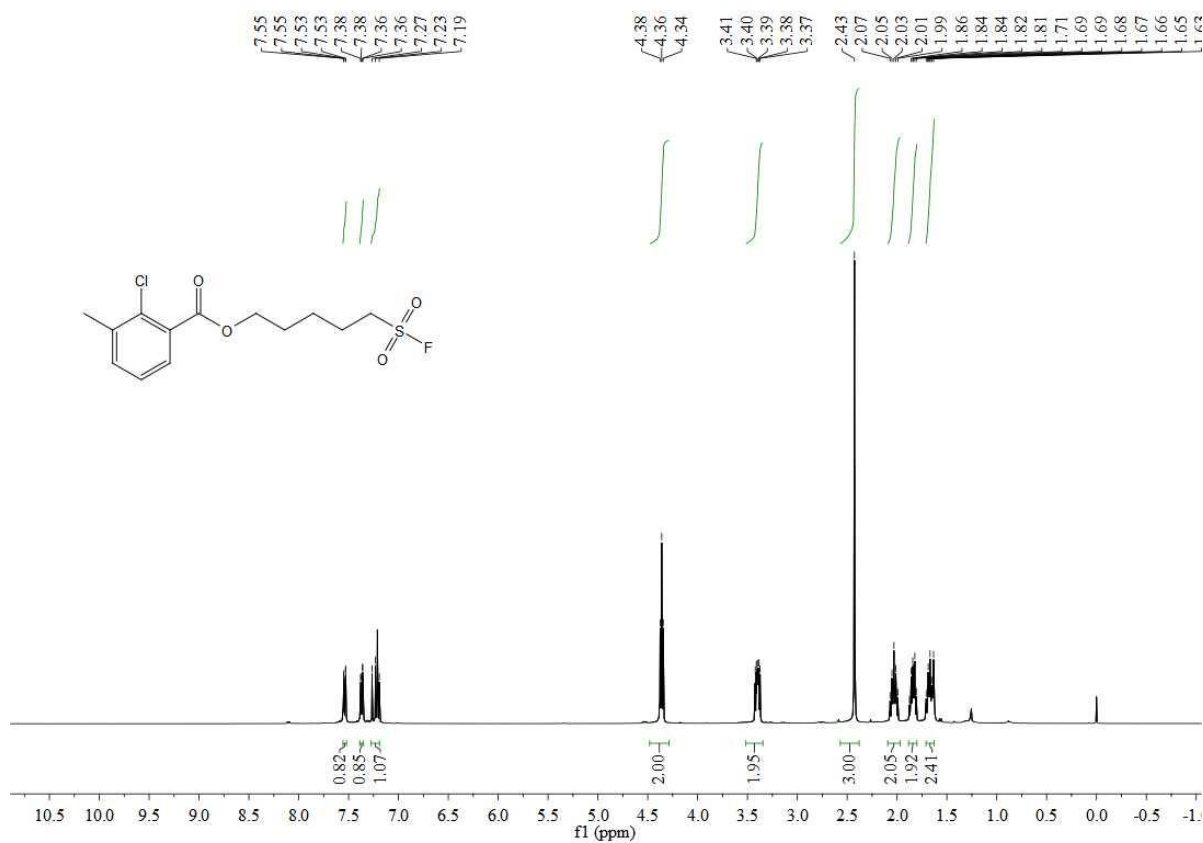


¹⁹F NMR

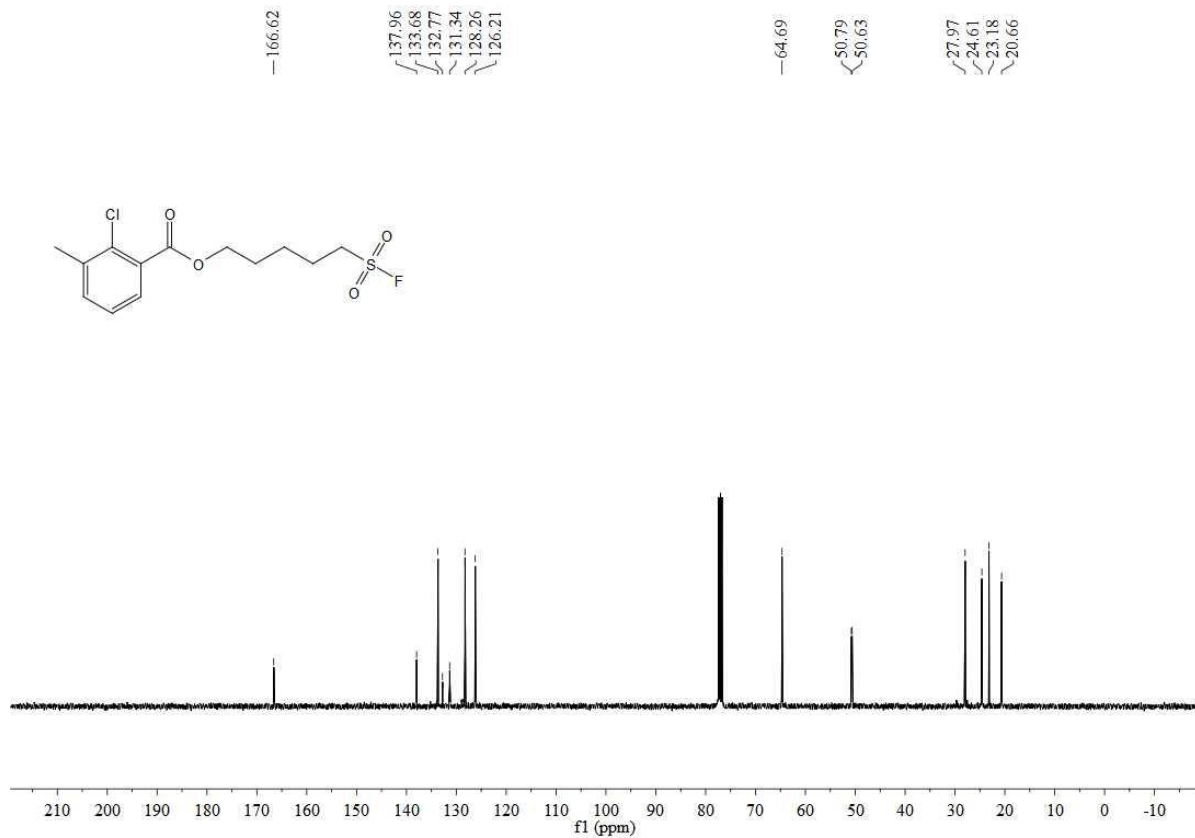


5-(fluorosulfonyl)pentyl 2-chloro-3-methylbenzoate (**4r**)

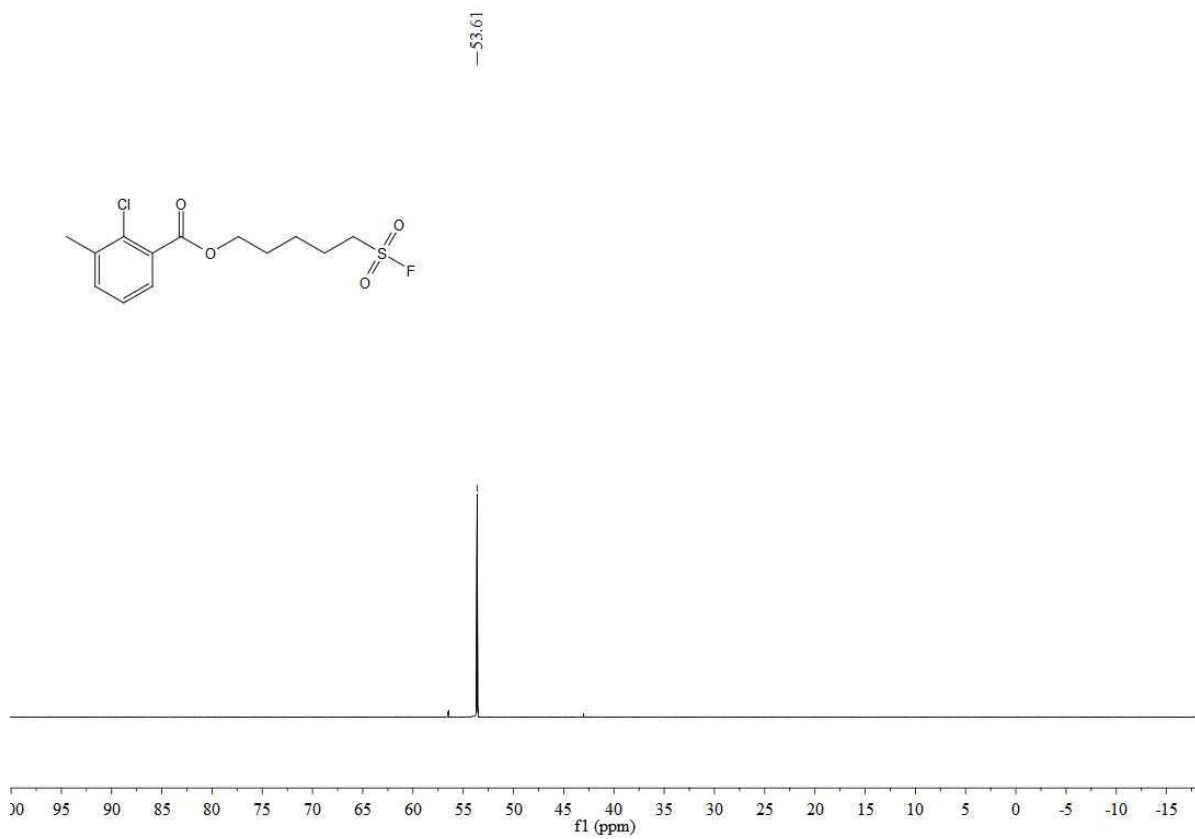
¹H NMR



¹³C NMR

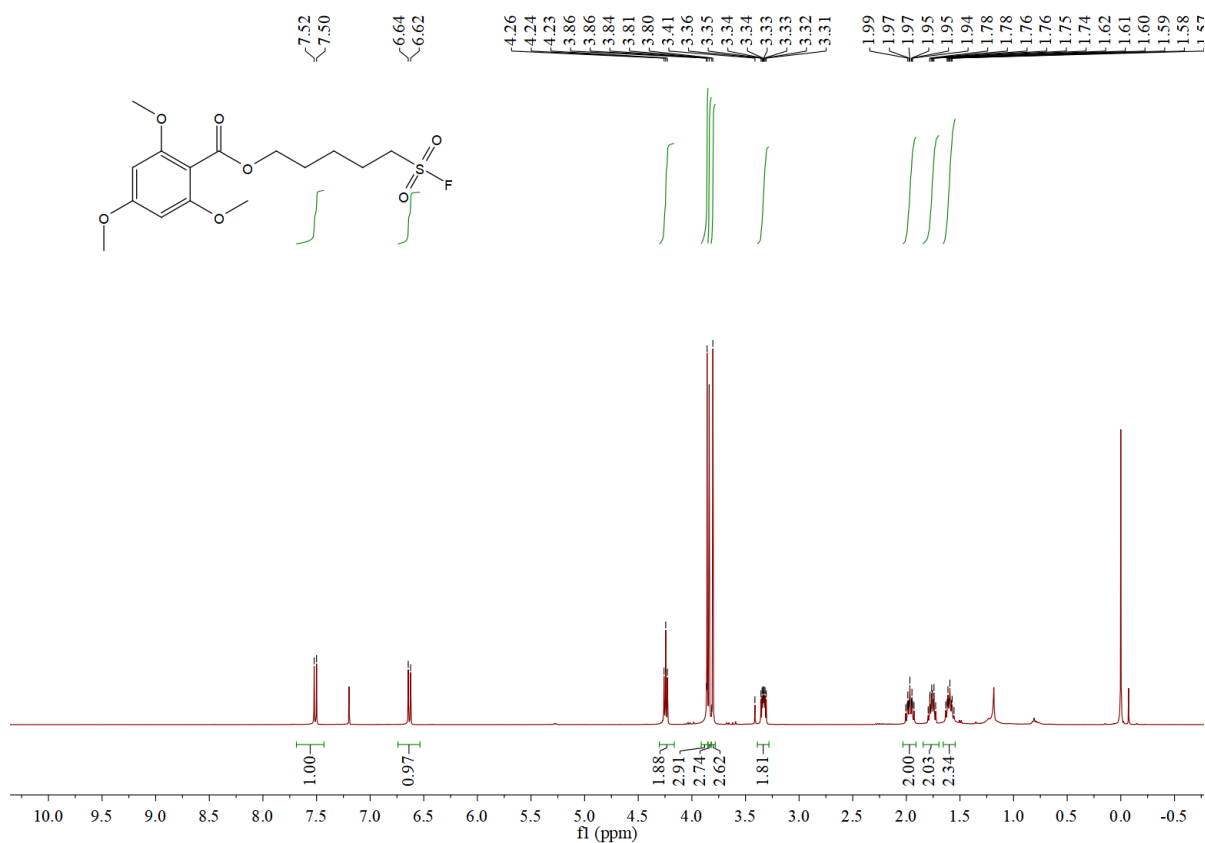


¹⁹F NMR

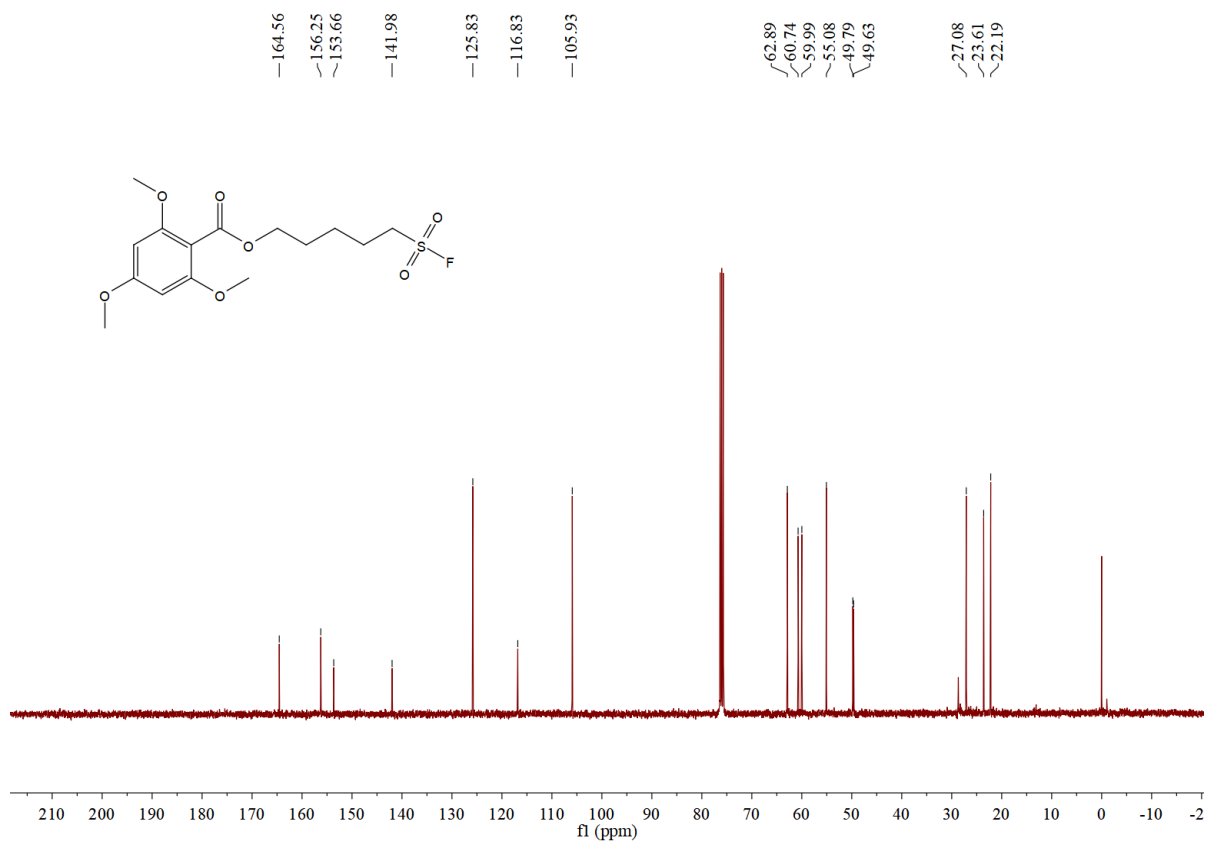


5-(fluorosulfonyl)pentyl 2,4,6-trimethoxybenzoate (4s)

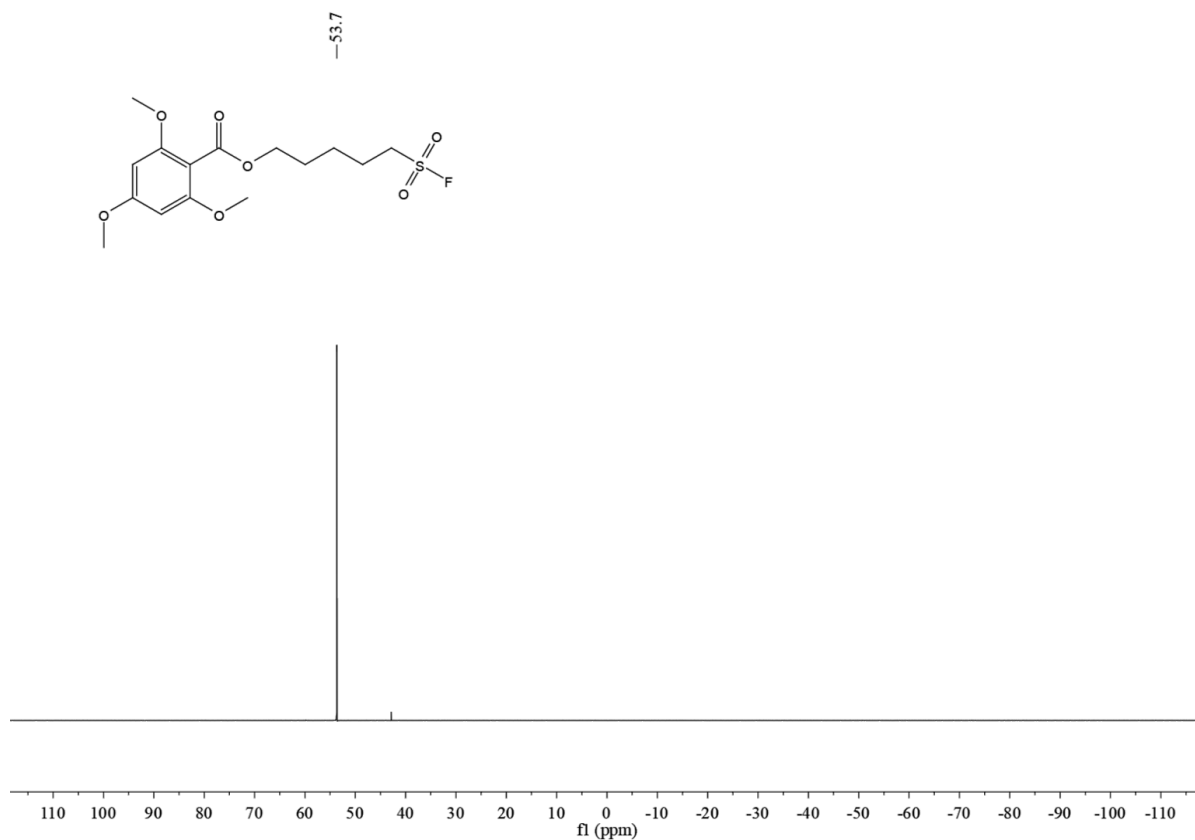
¹H NMR



¹³C NMR

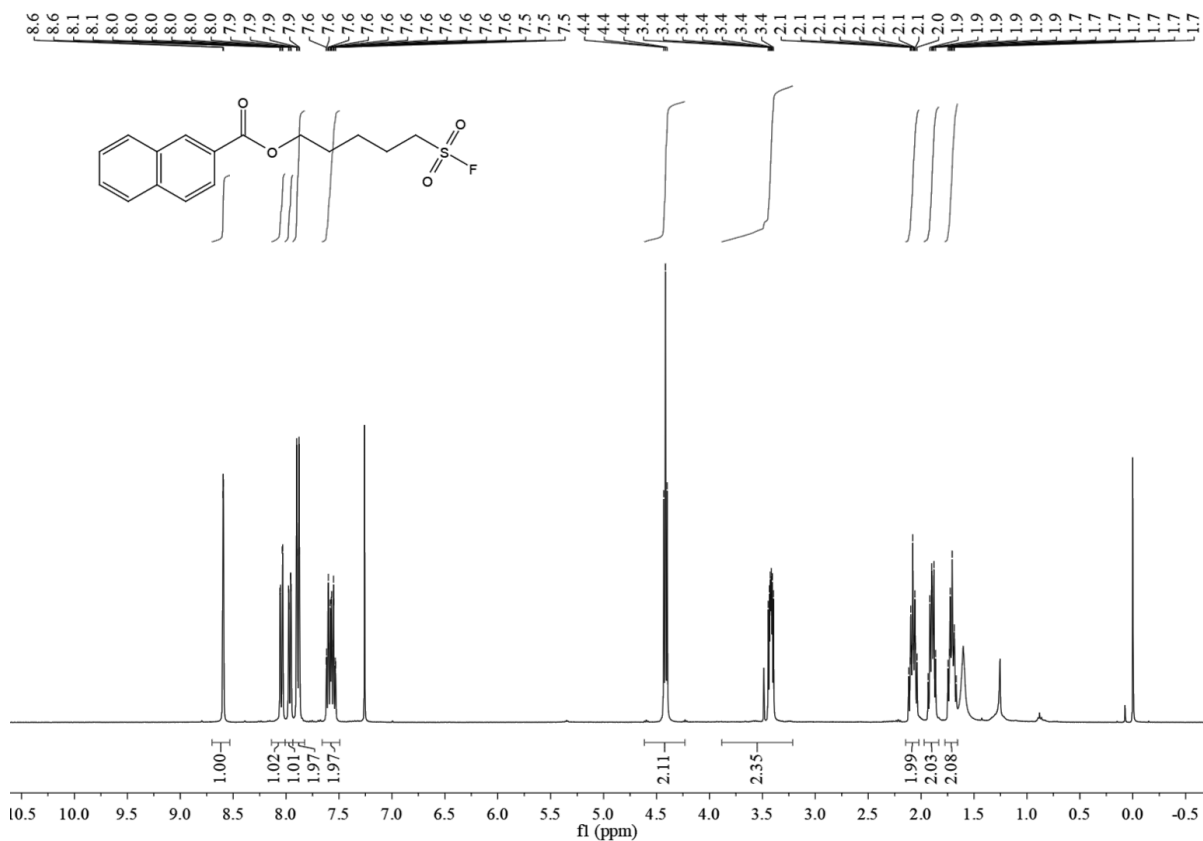


¹⁹F NMR

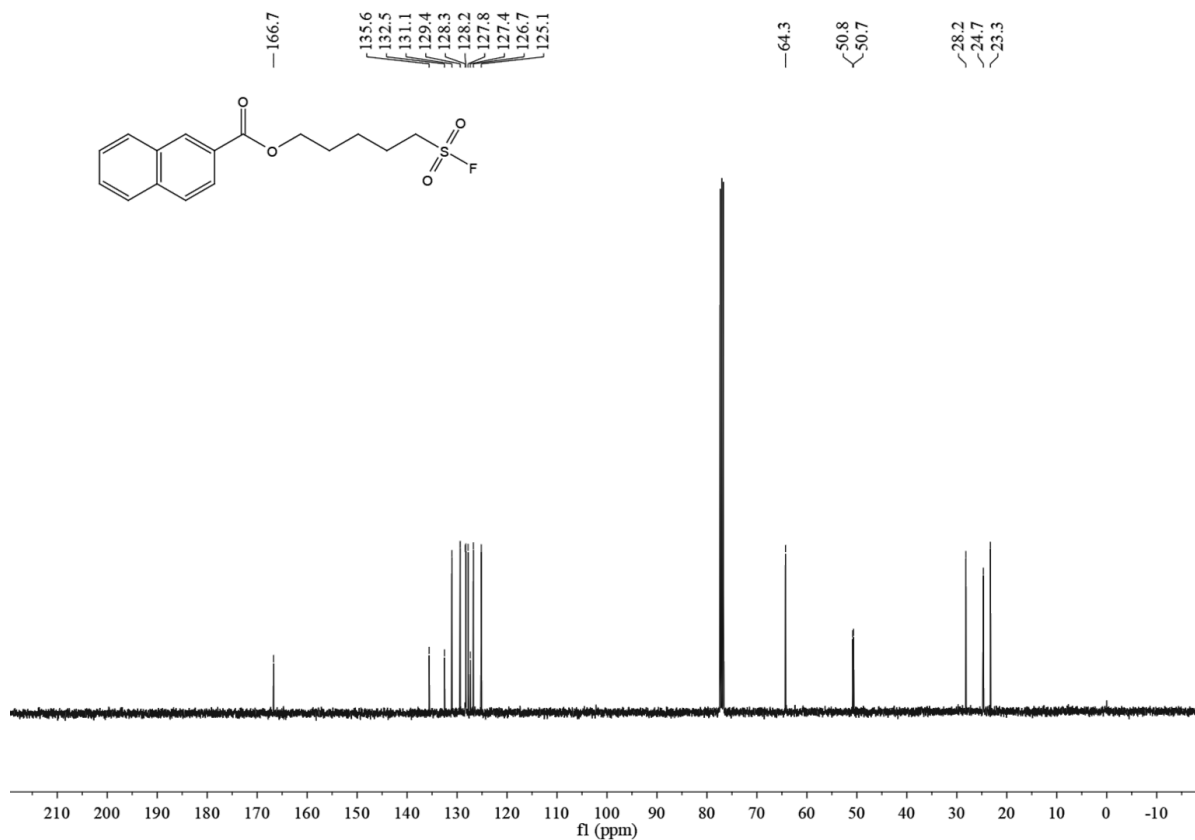


5-(fluorosulfonyl)pentyl 2-naphthoate (4t)

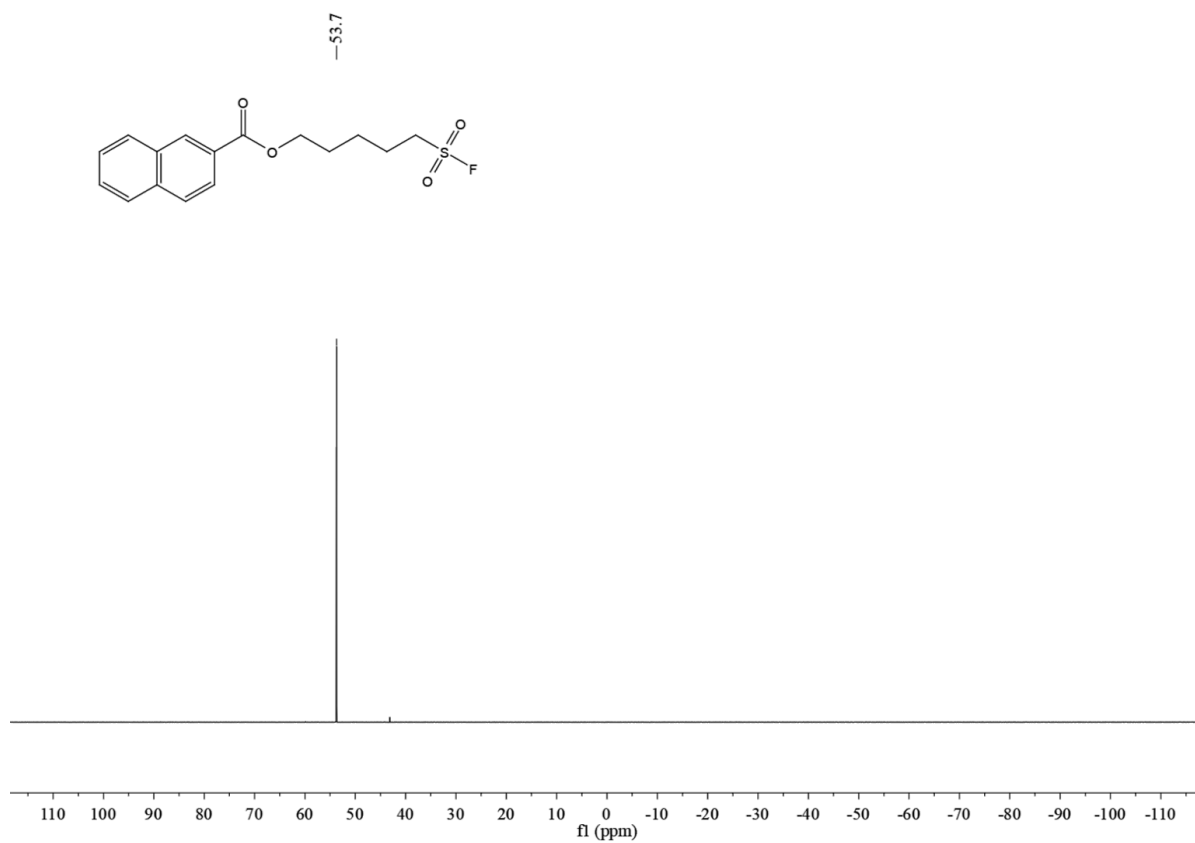
¹H NMR



¹³C NMR

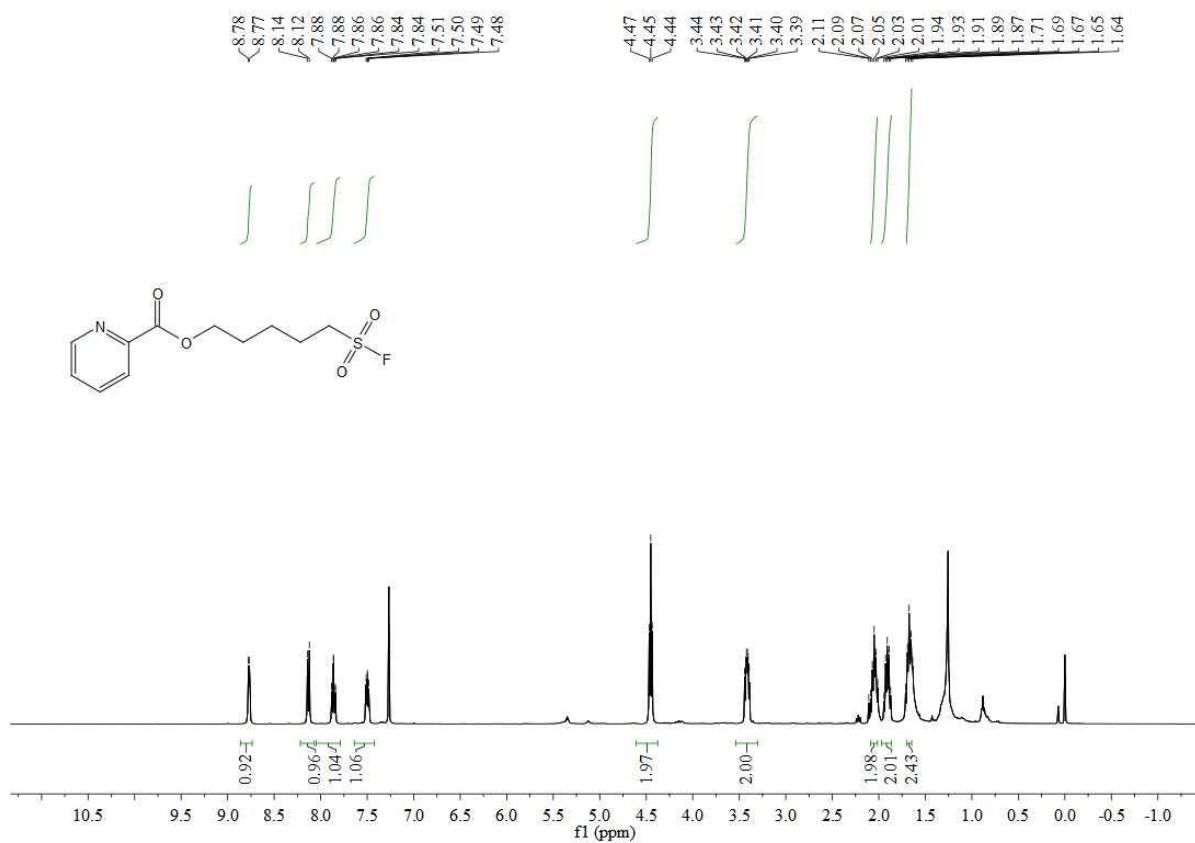


¹⁹F NMR

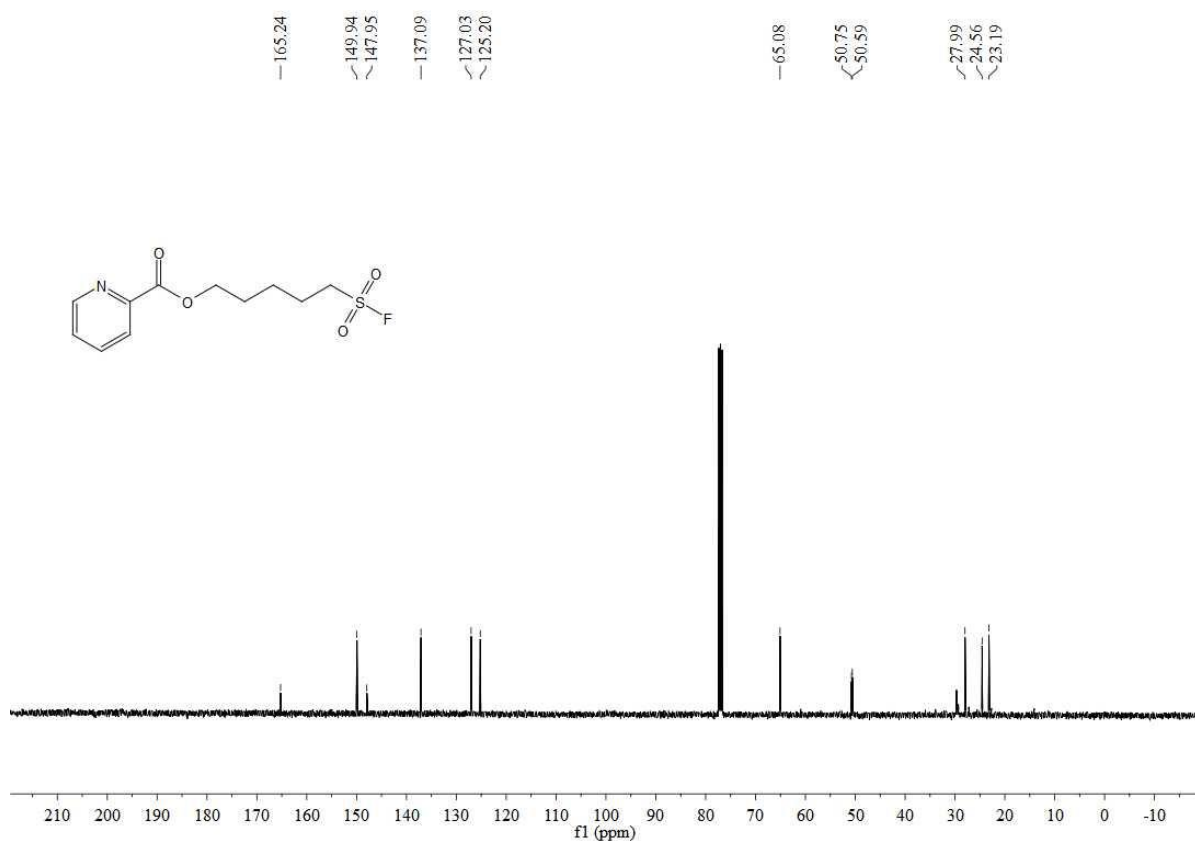


5-(fluorosulfonyl)pentyl picolinate (**4u**)

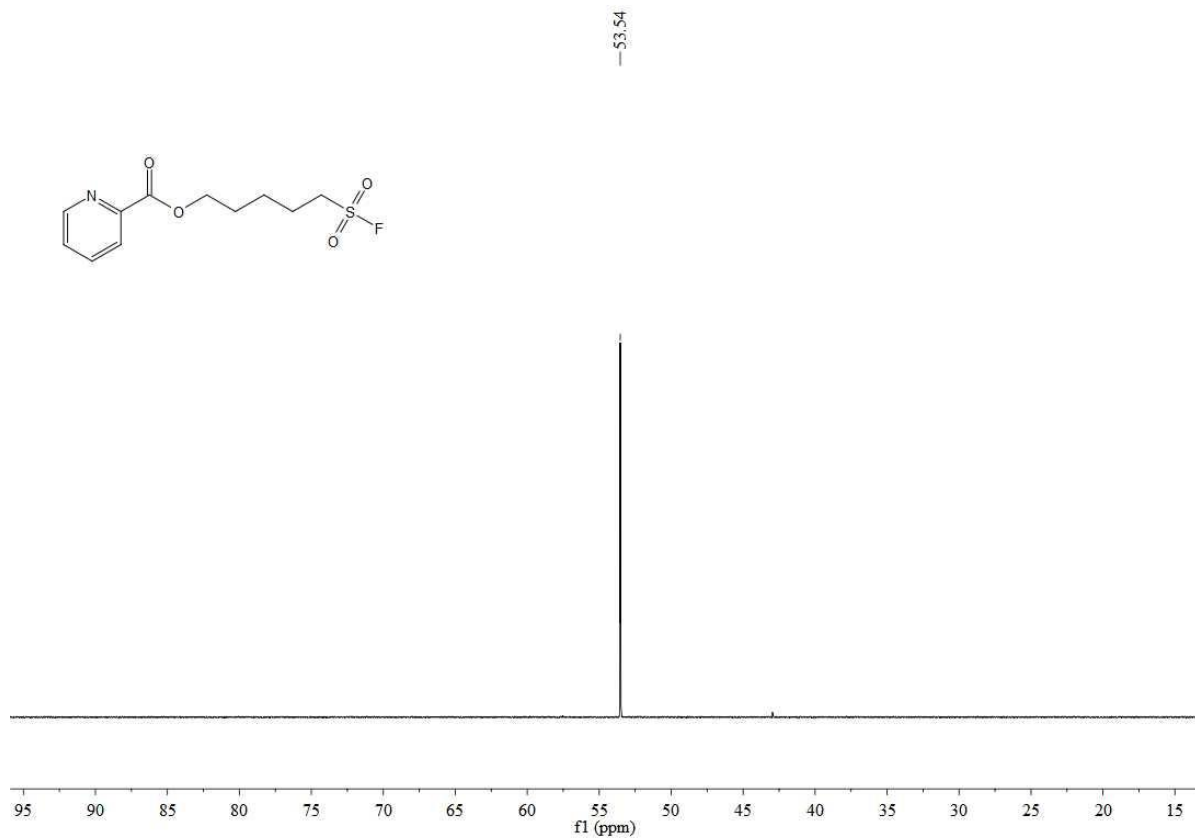
¹H NMR



¹³C NMR

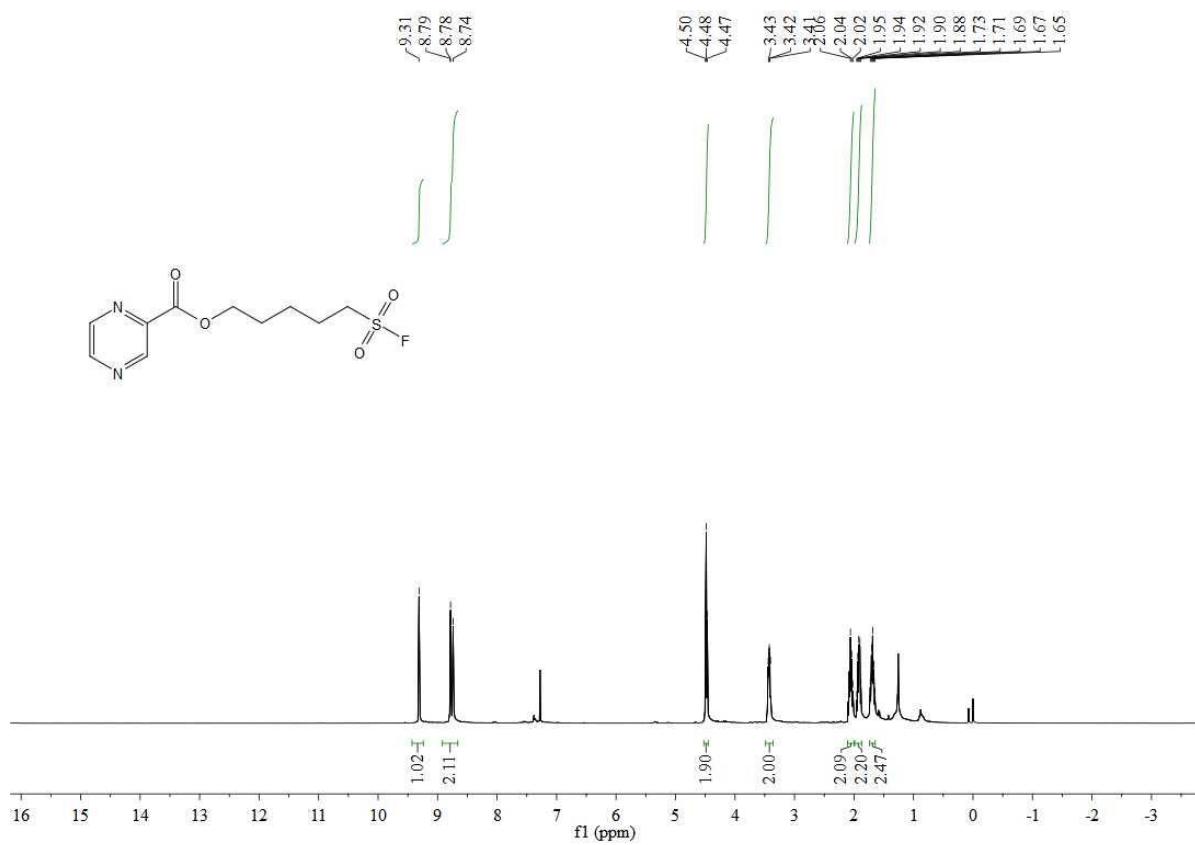


¹⁹F NMR

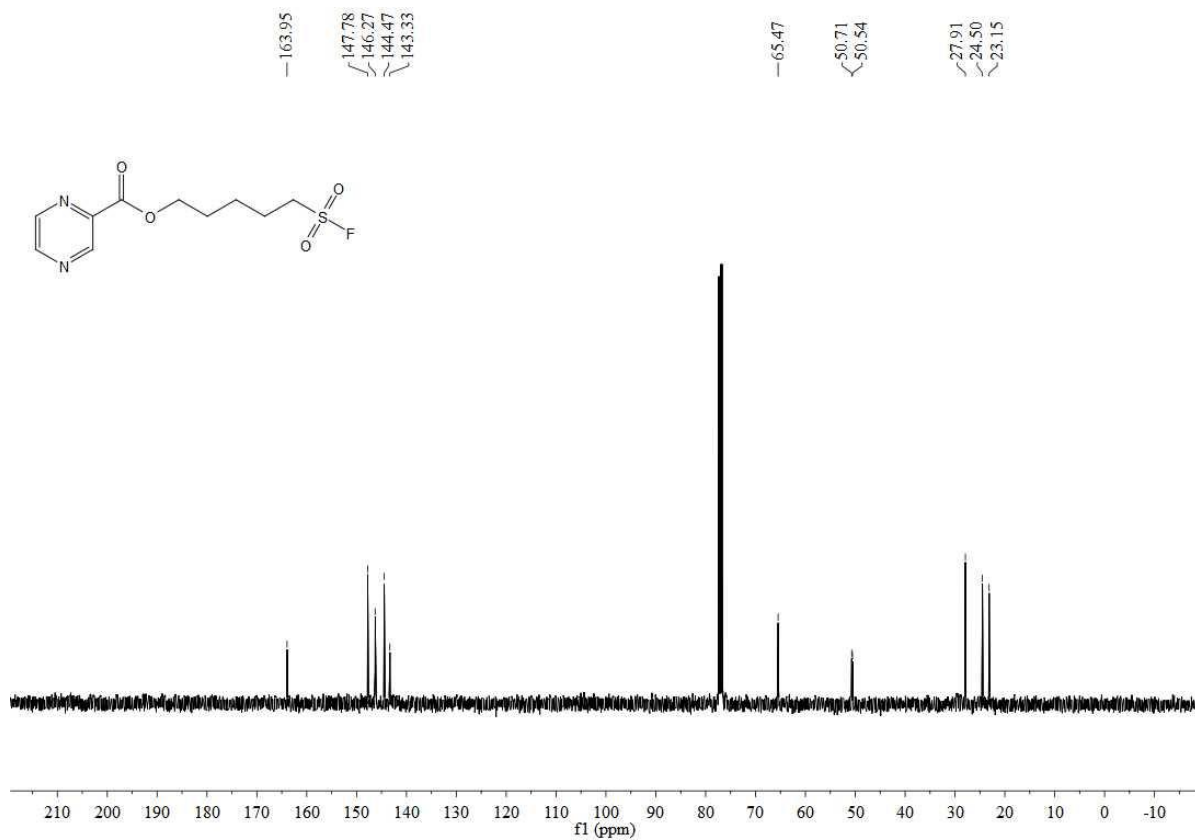


5-(fluorosulfonyl)pentyl pyrazine-2-carboxylate (4v)

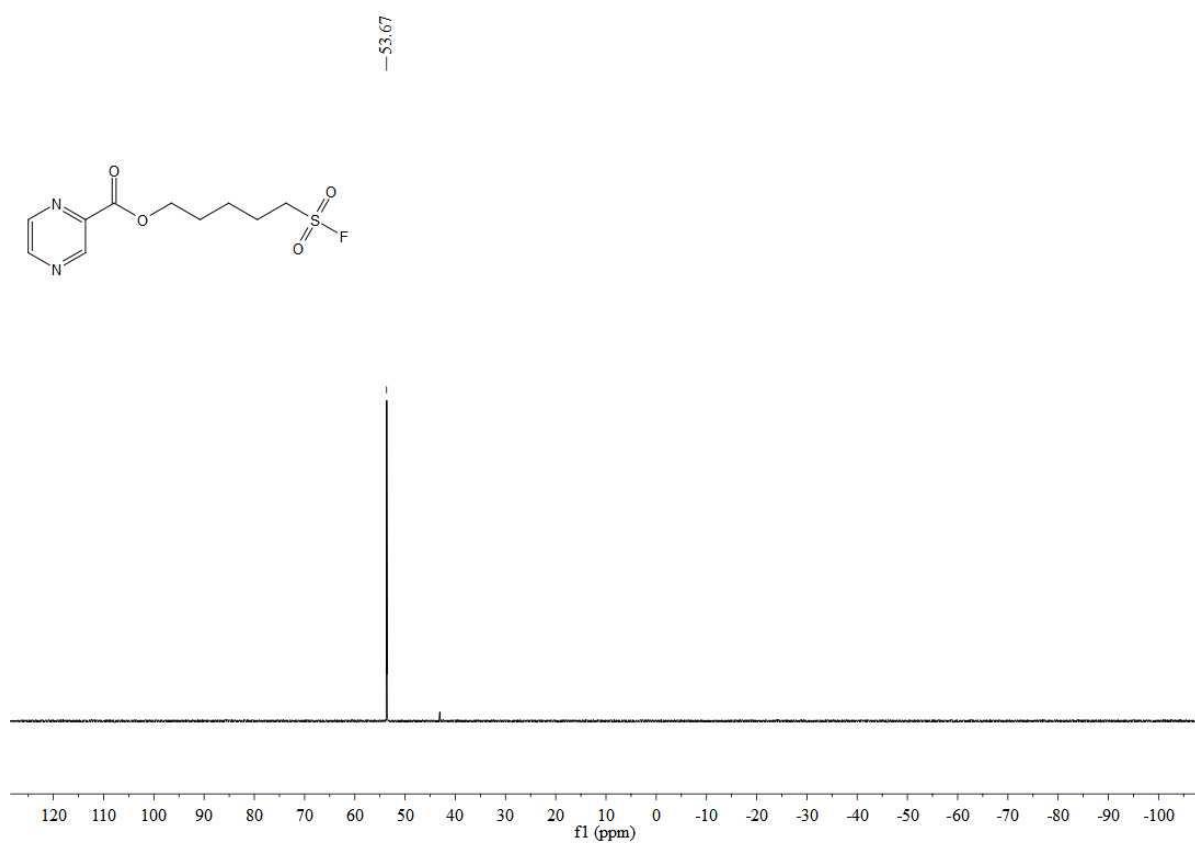
¹H NMR



¹³C NMR

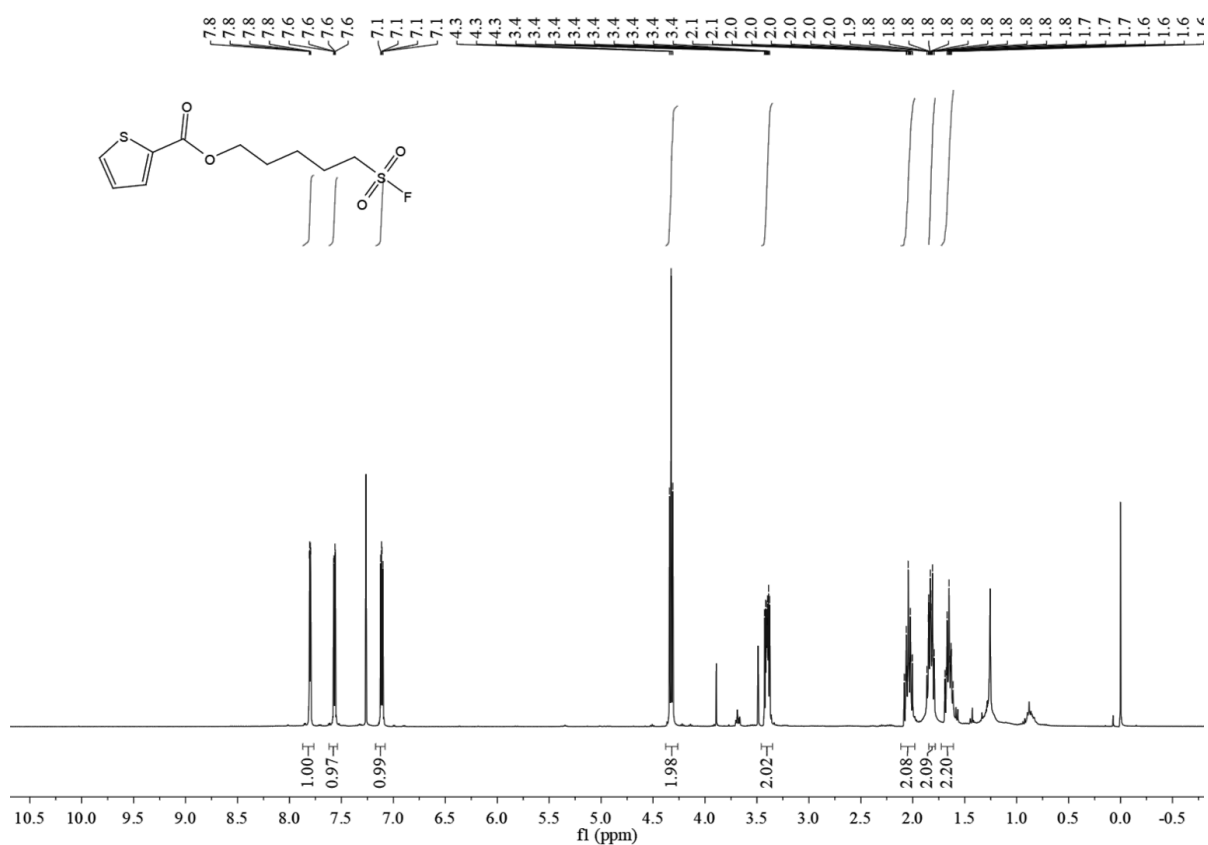


¹⁹F NMR

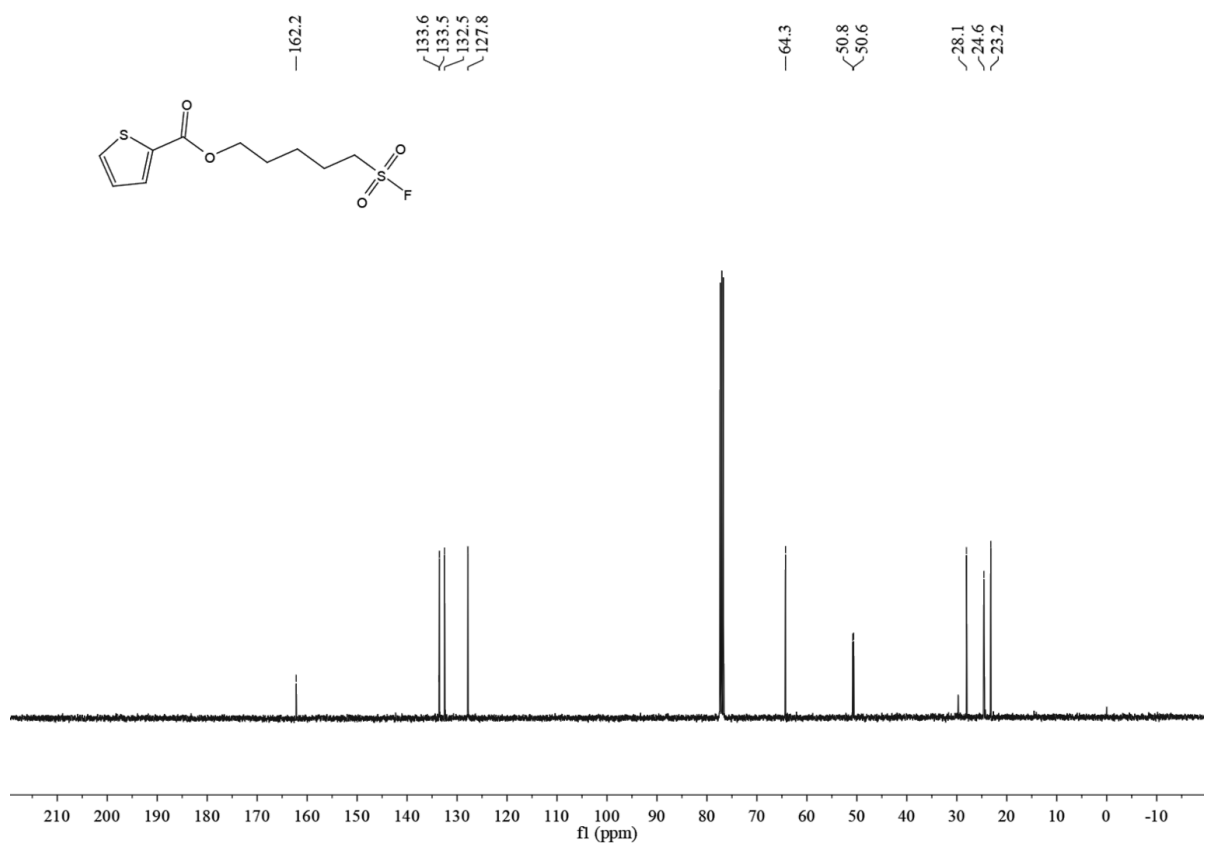


5-(fluorosulfonyl)pentyl thiophene-2-carboxylate (**4w**)

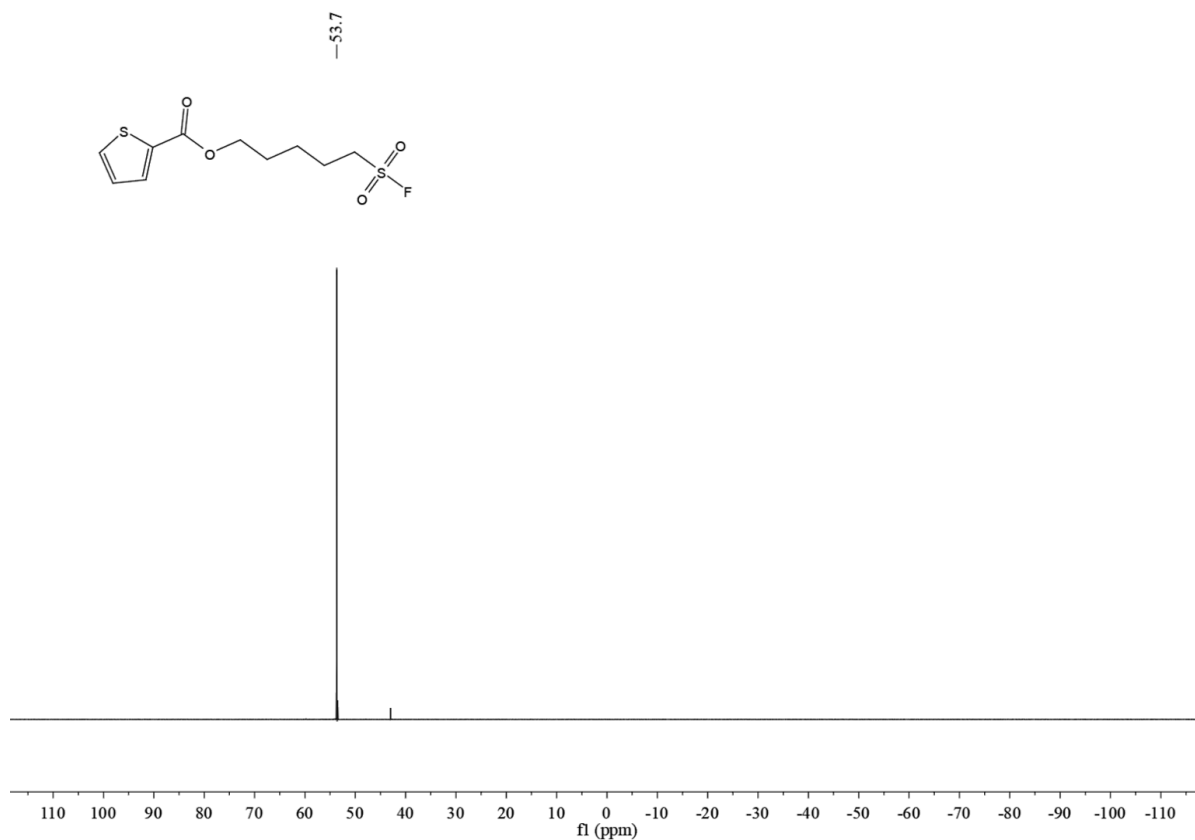
¹H NMR



¹³C NMR

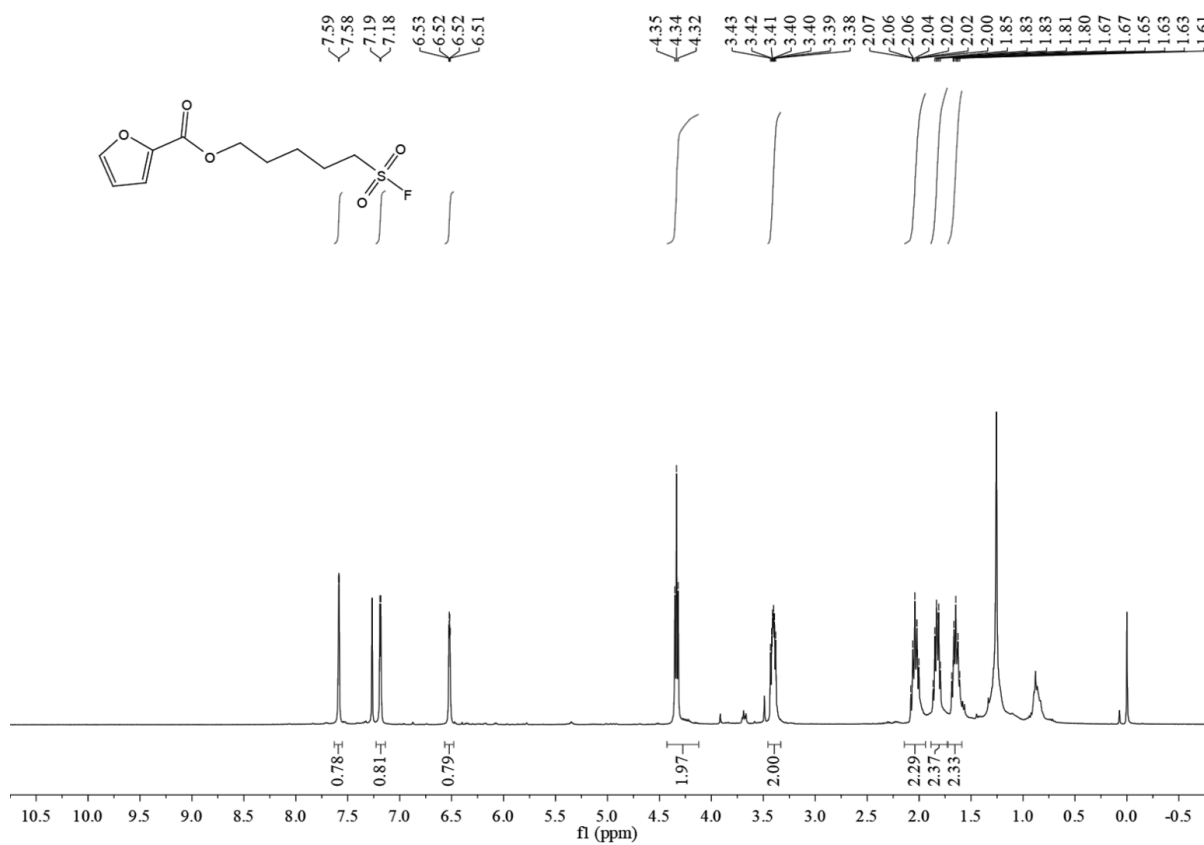


¹⁹F NMR

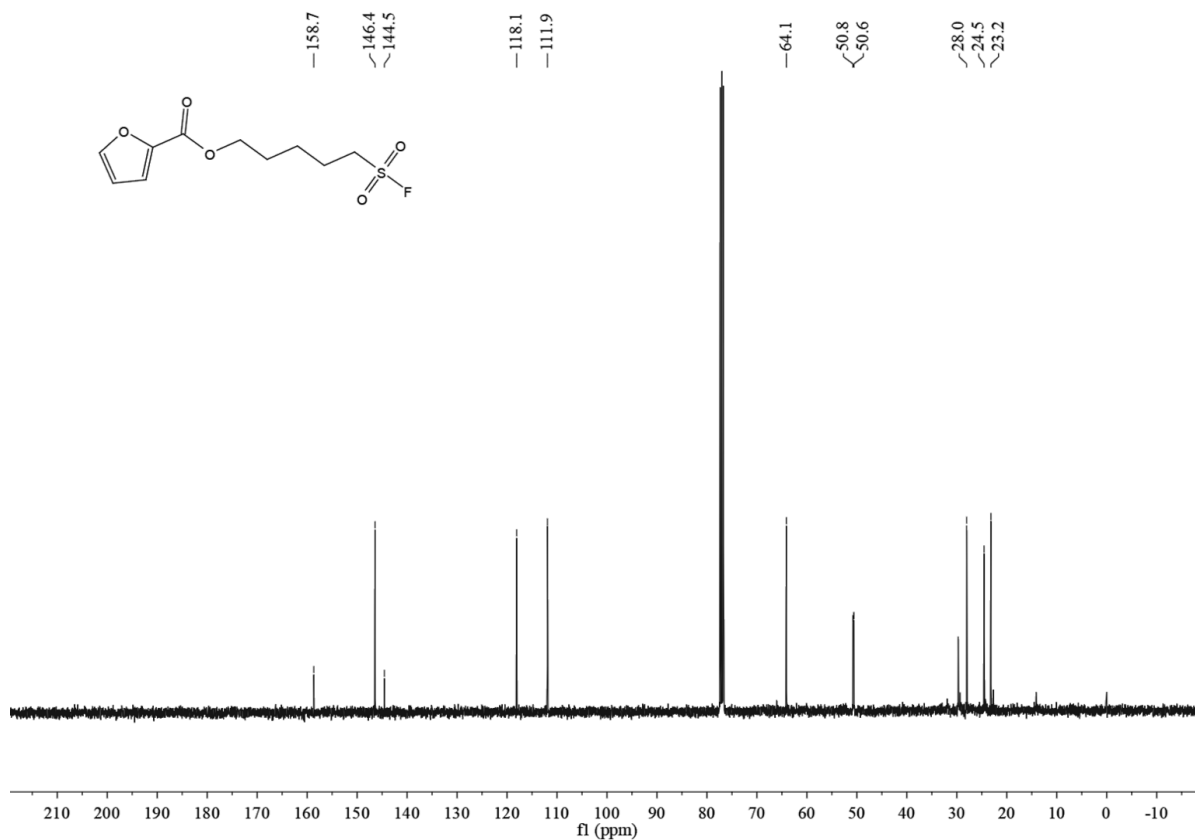


5-(fluorosulfonyl)pentyl furan-2-carboxylate (4x)

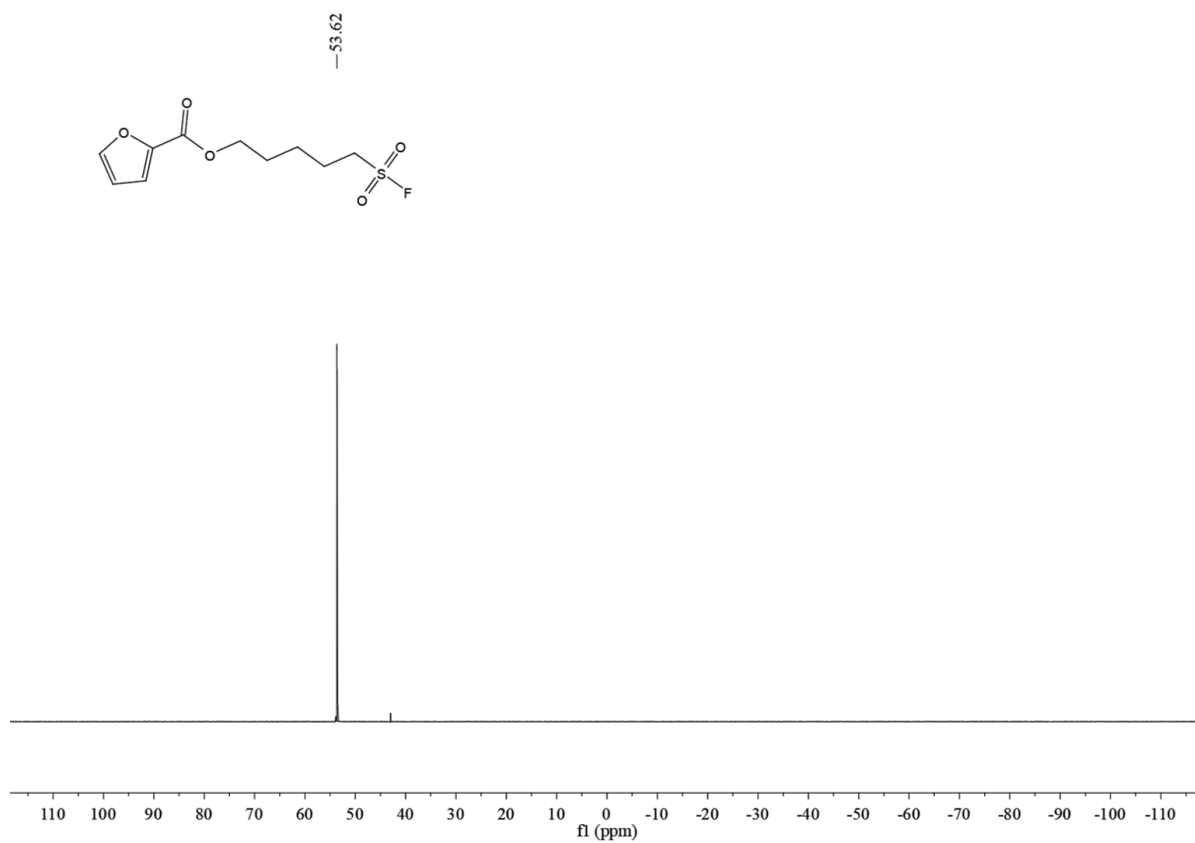
¹H NMR



¹³C NMR

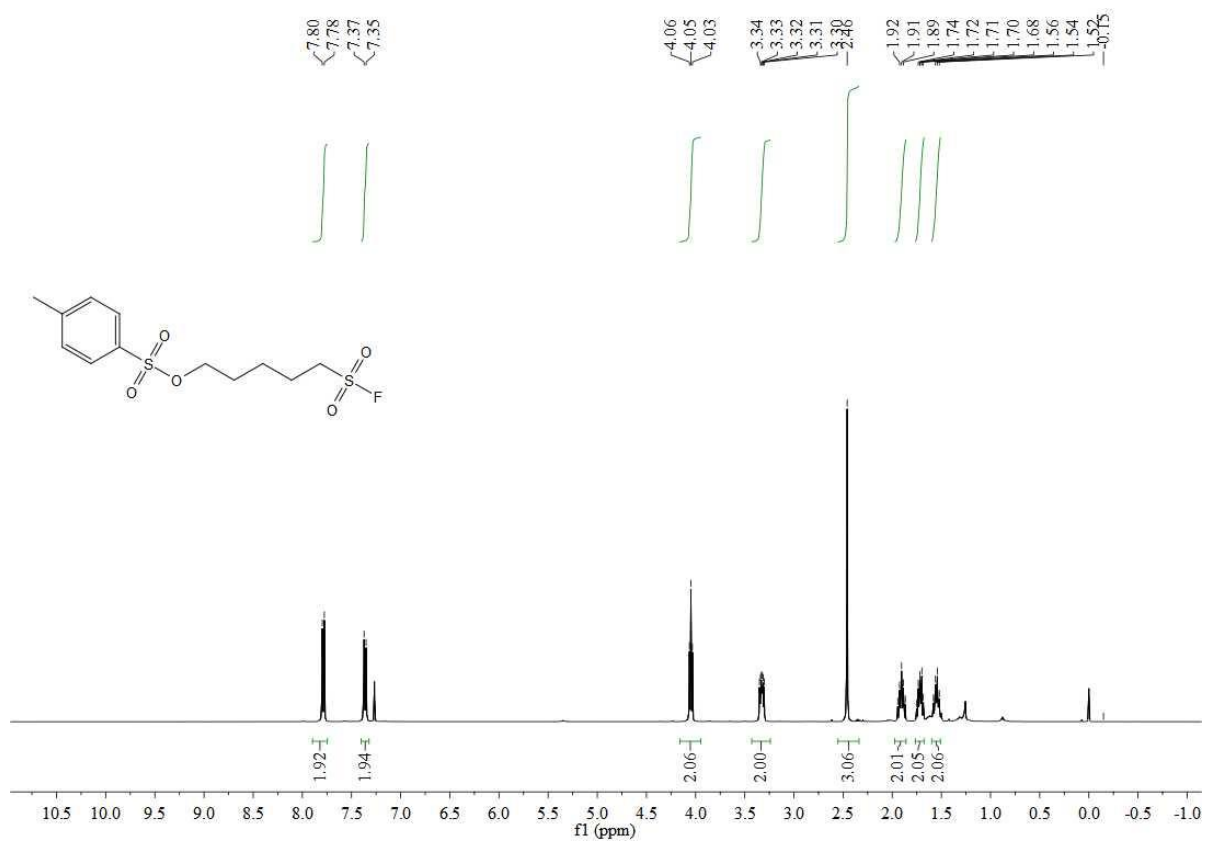


¹⁹F NMR

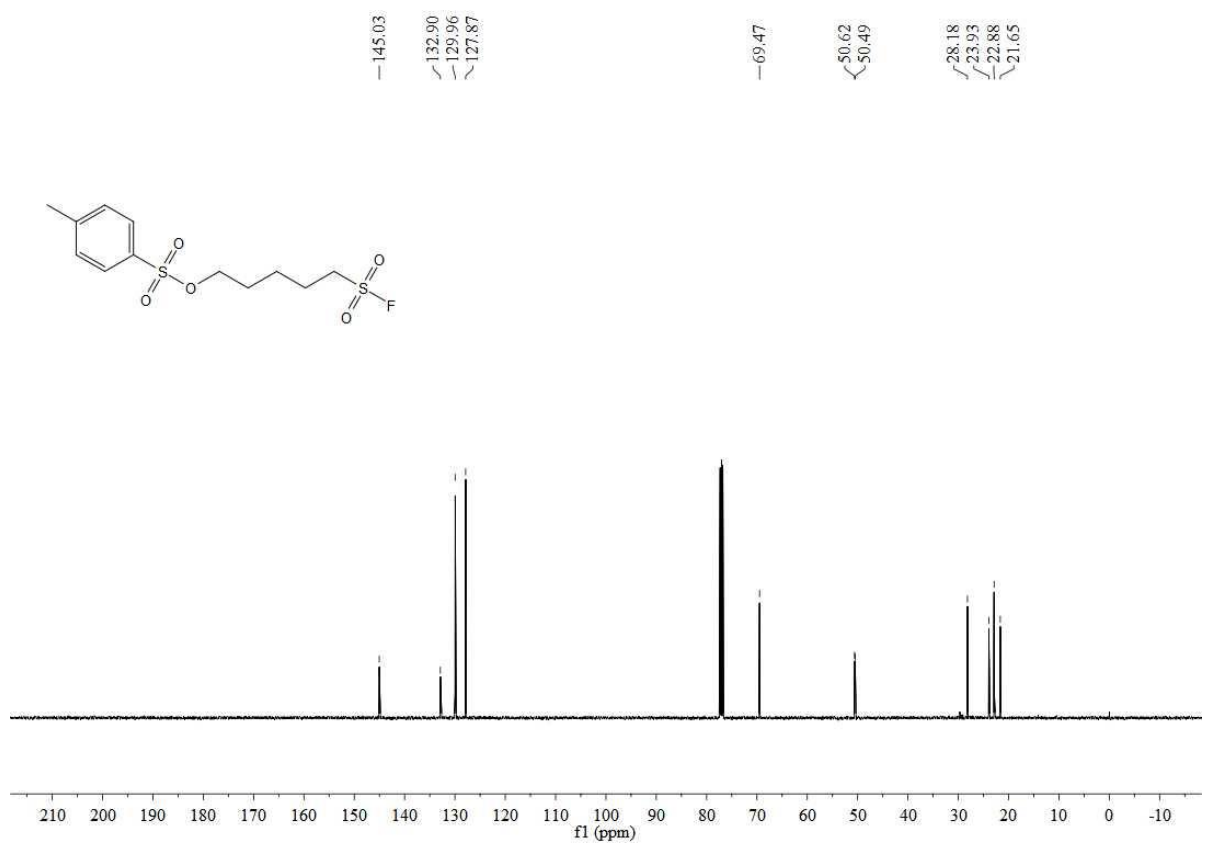


5-(fluorosulfonyl)pentyl 4-methylbenzenesulfonate (**4y**)

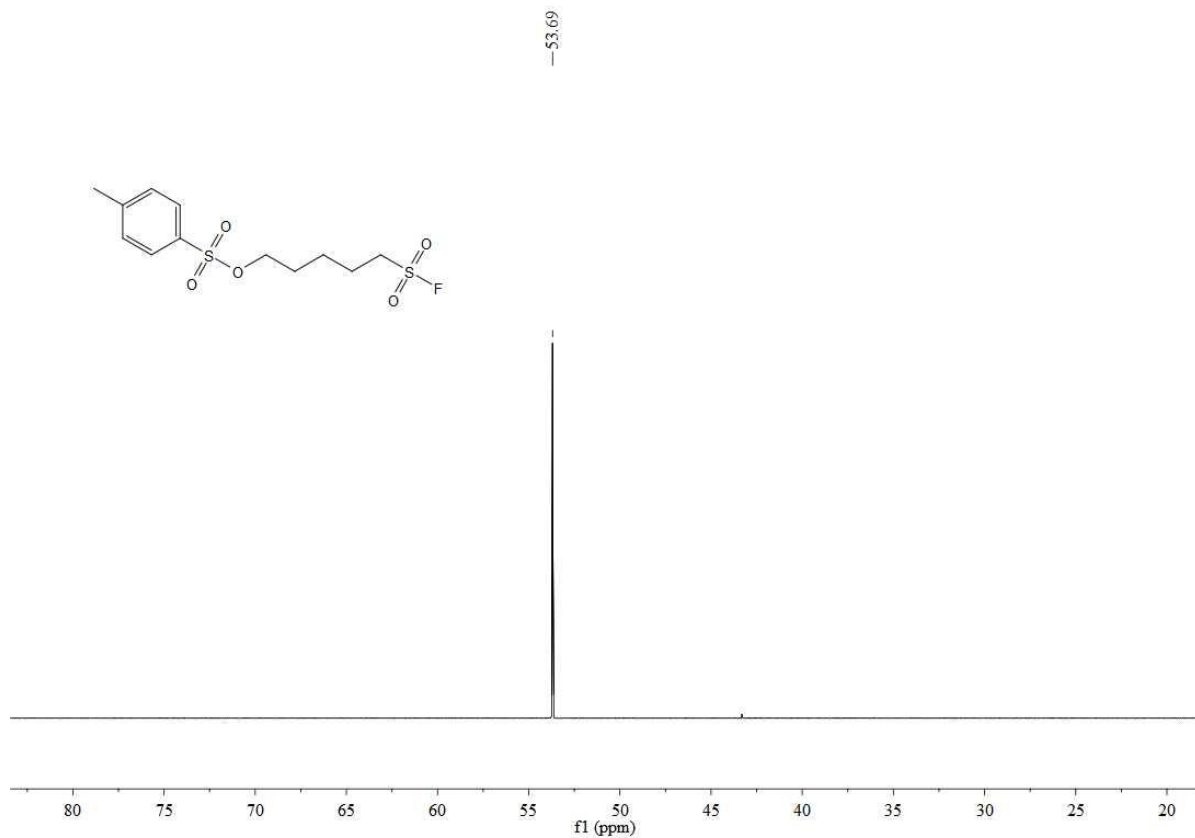
¹H NMR



¹³C NMR

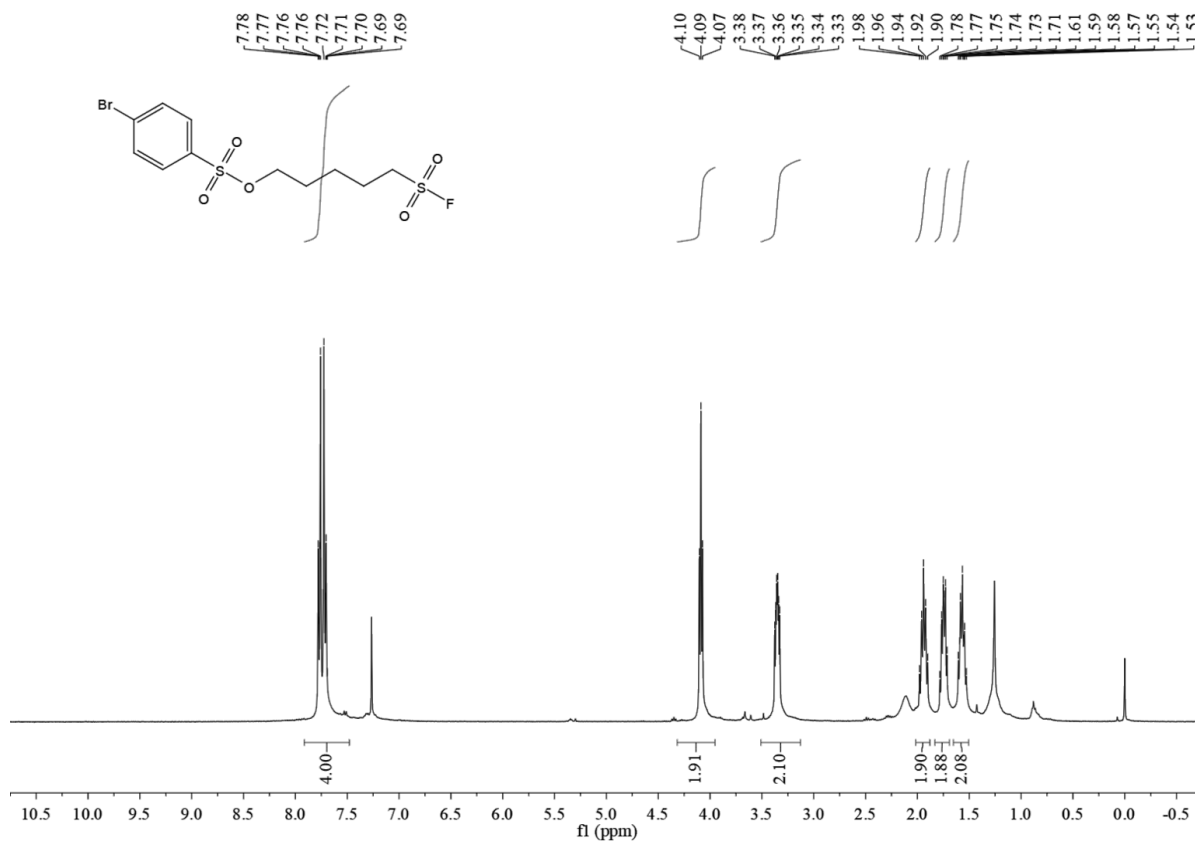


¹⁹F NMR

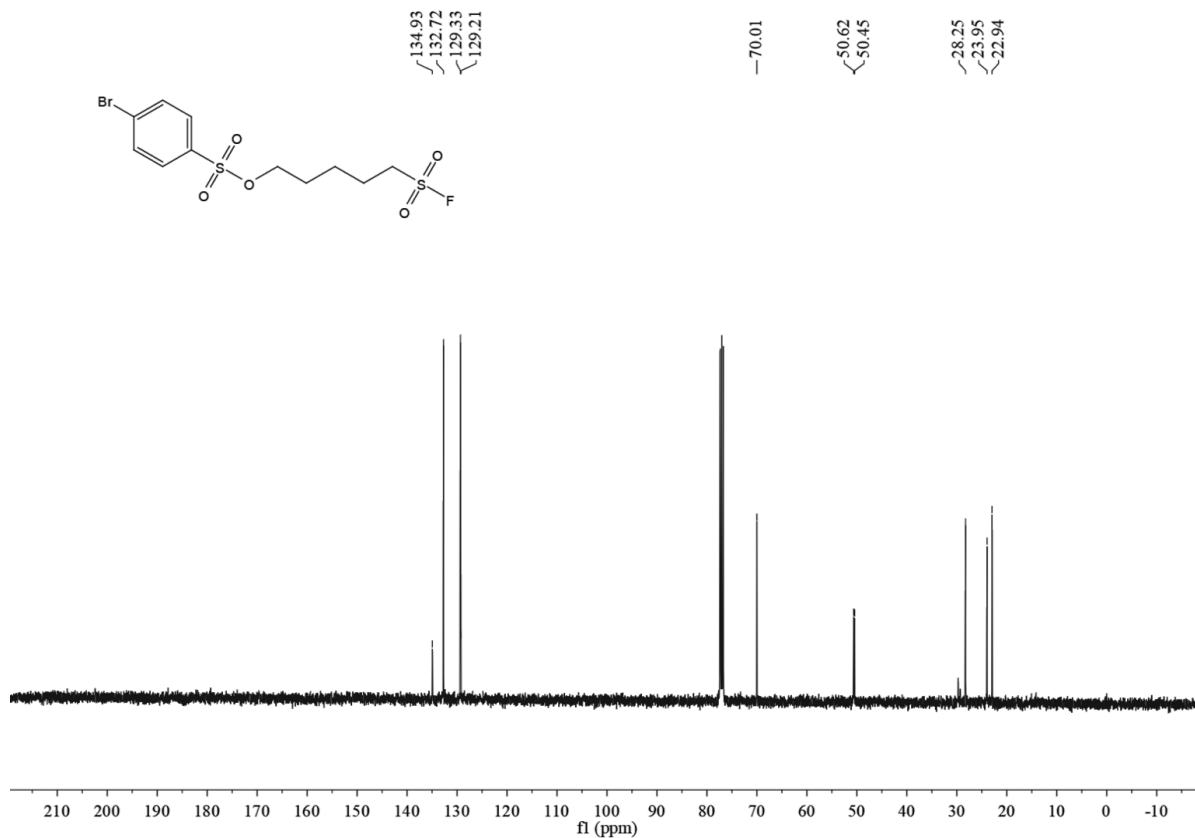


5-(fluorosulfonyl)pentyl 4-bromobenzenesulfonate (**4z**)

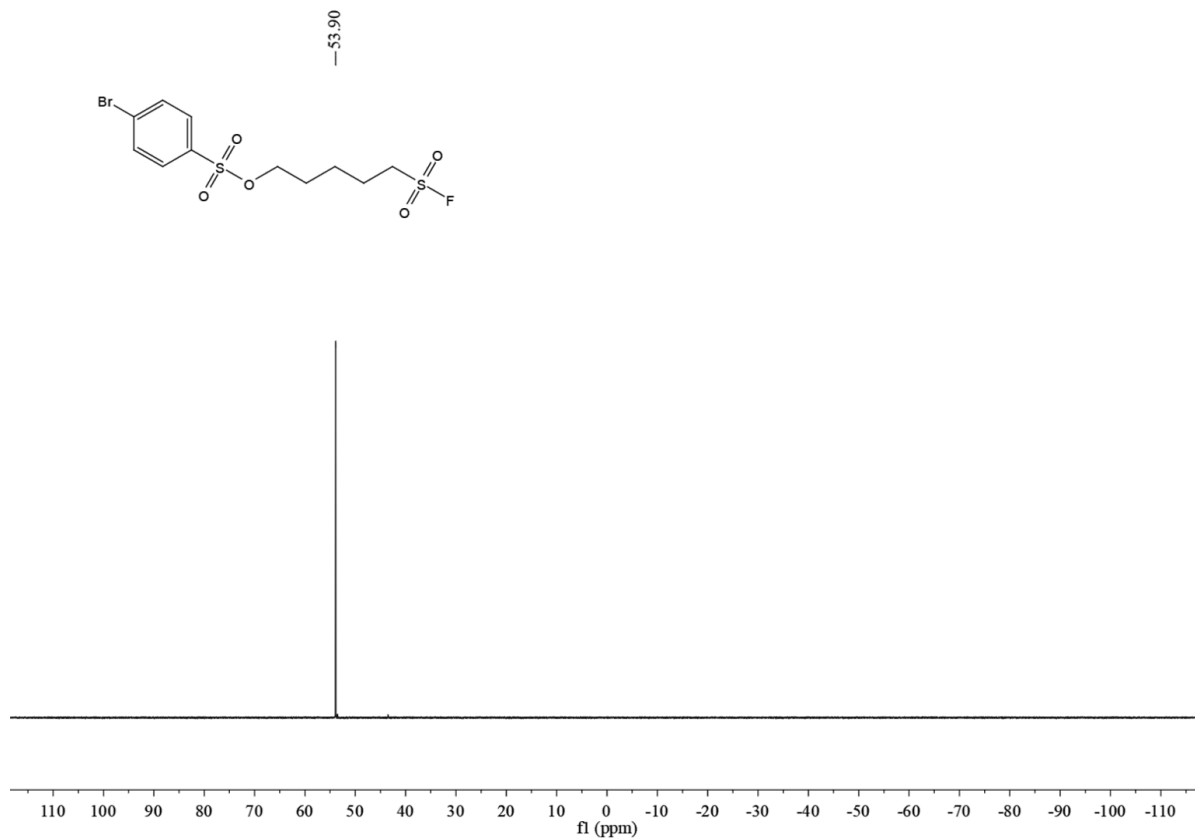
¹H NMR



¹³C NMR

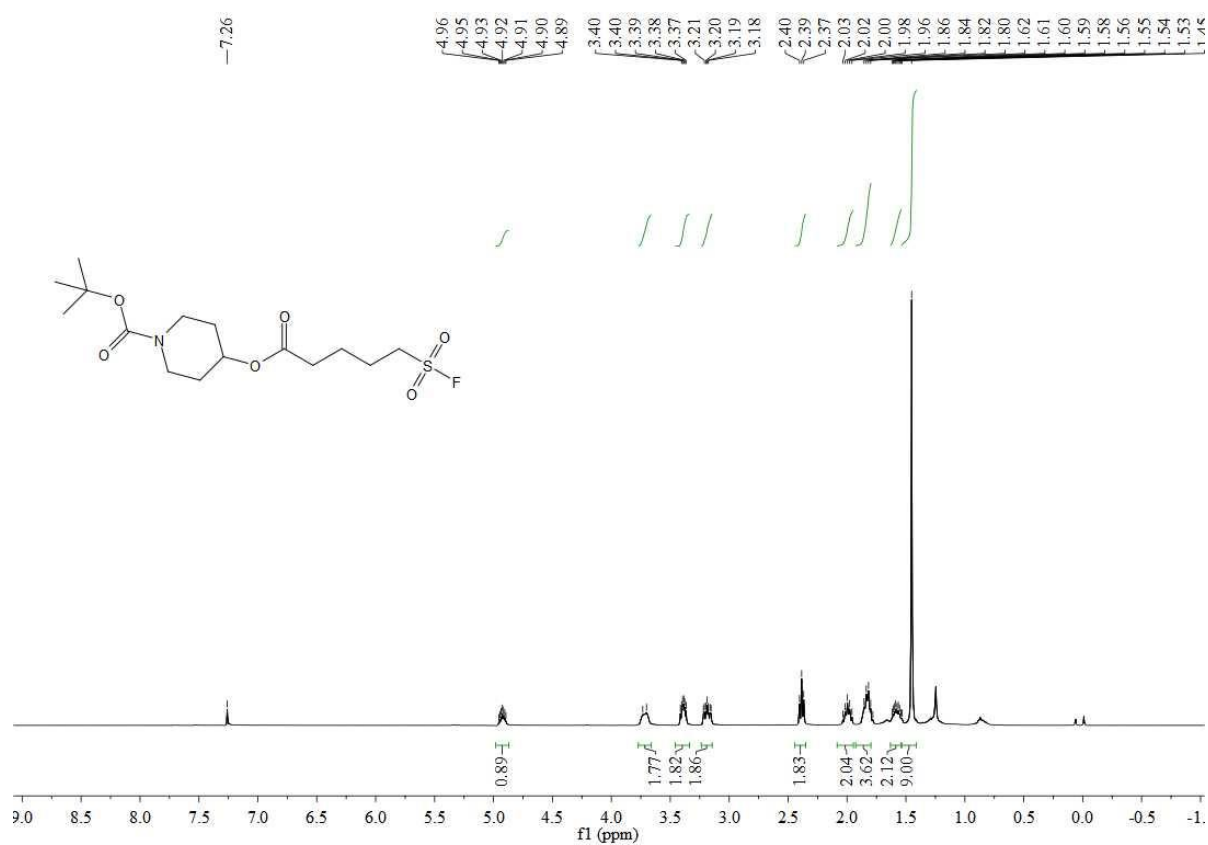


¹⁹F NMR

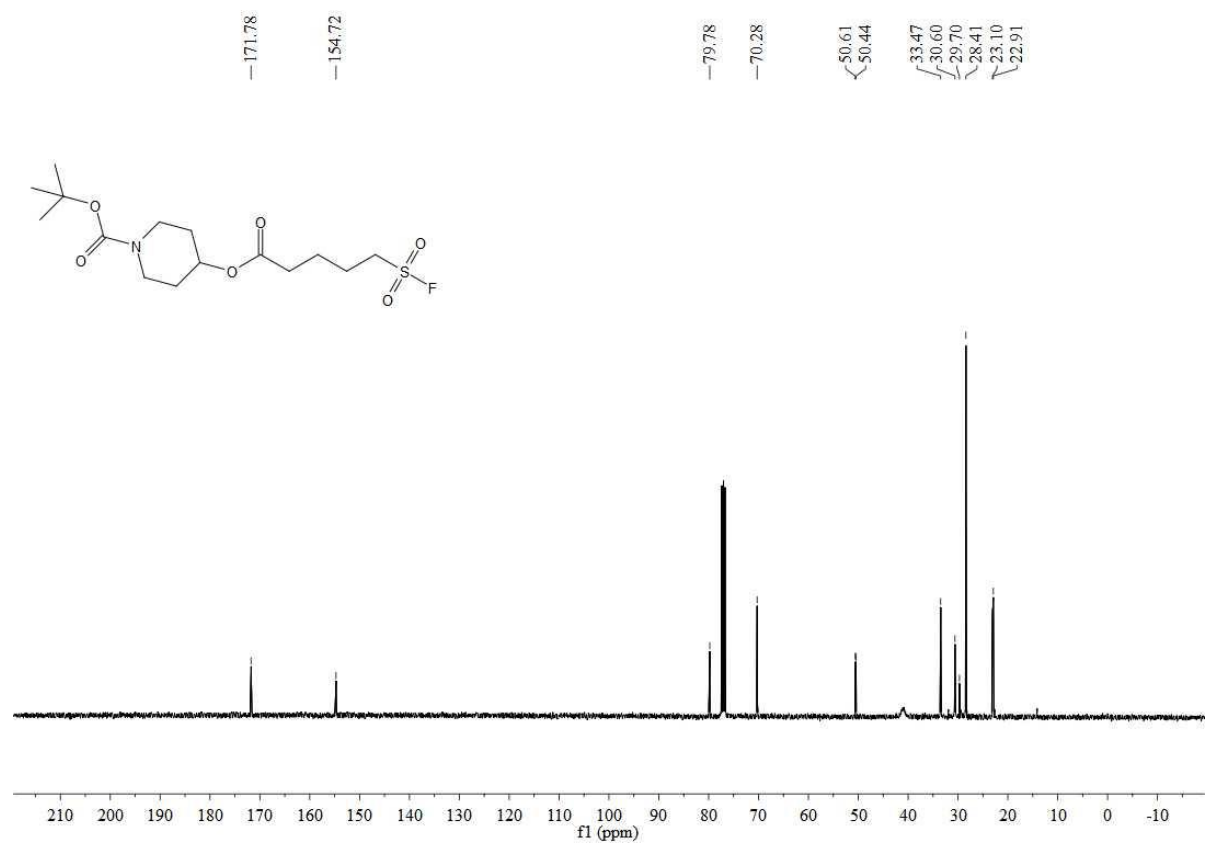


tert-butyl 4-((5-(fluorosulfonyl)pentanoyl)oxy)piperidine-1-carboxylate (**4aa**)

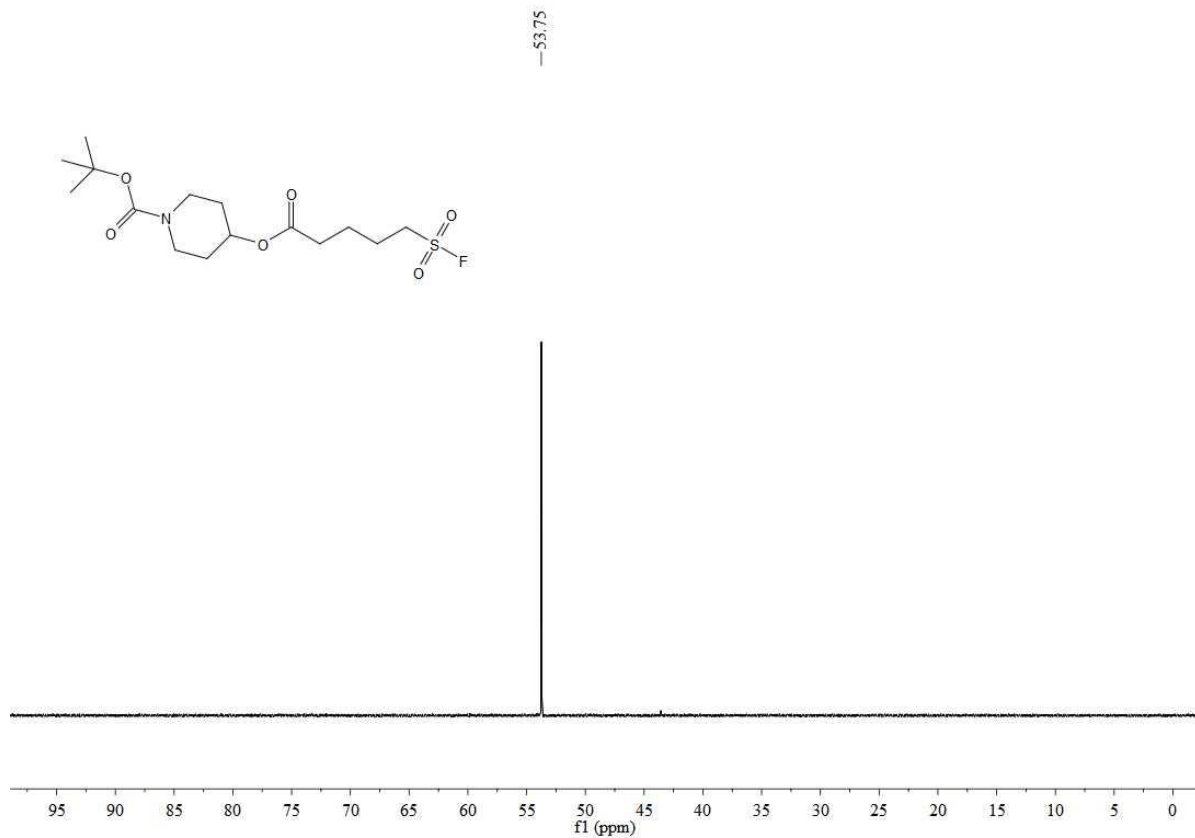
¹H NMR



¹³C NMR

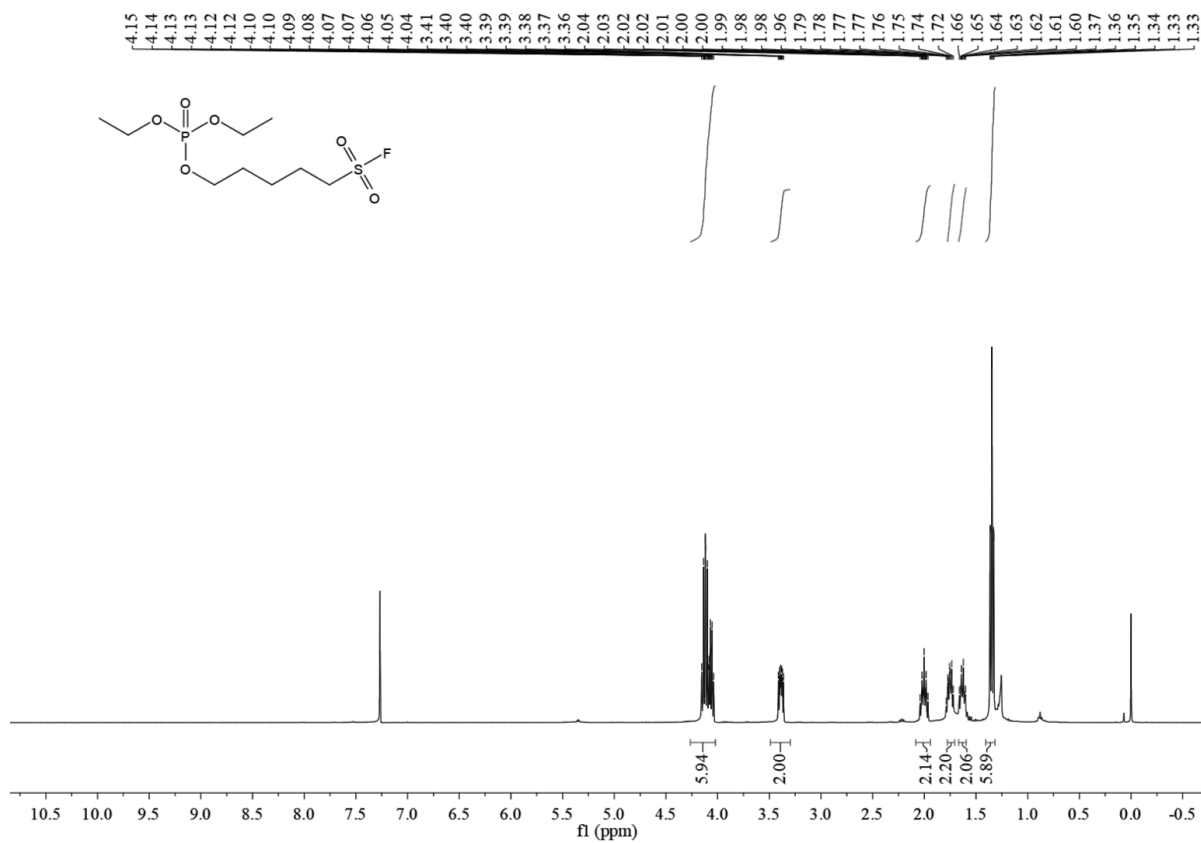


¹⁹F NMR

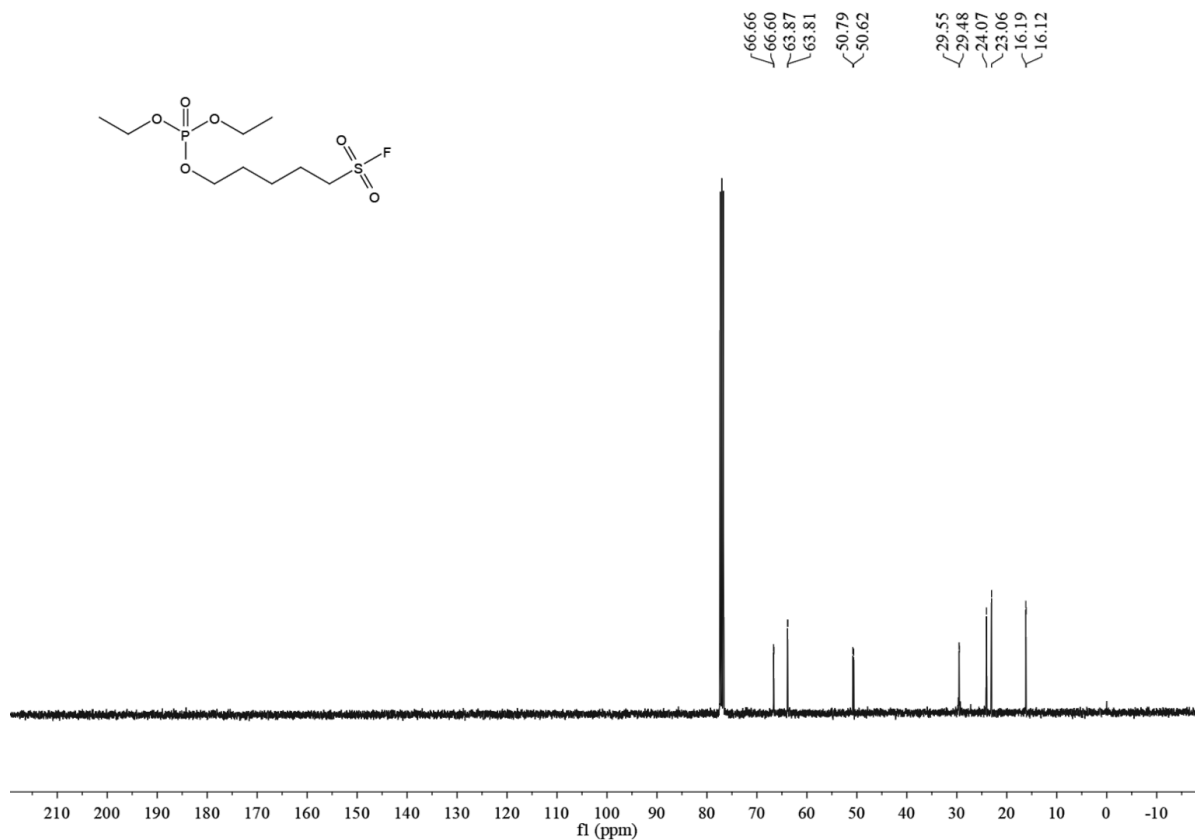


diethyl (5-(fluorosulfonyl)pentyl) phosphate (4ab)

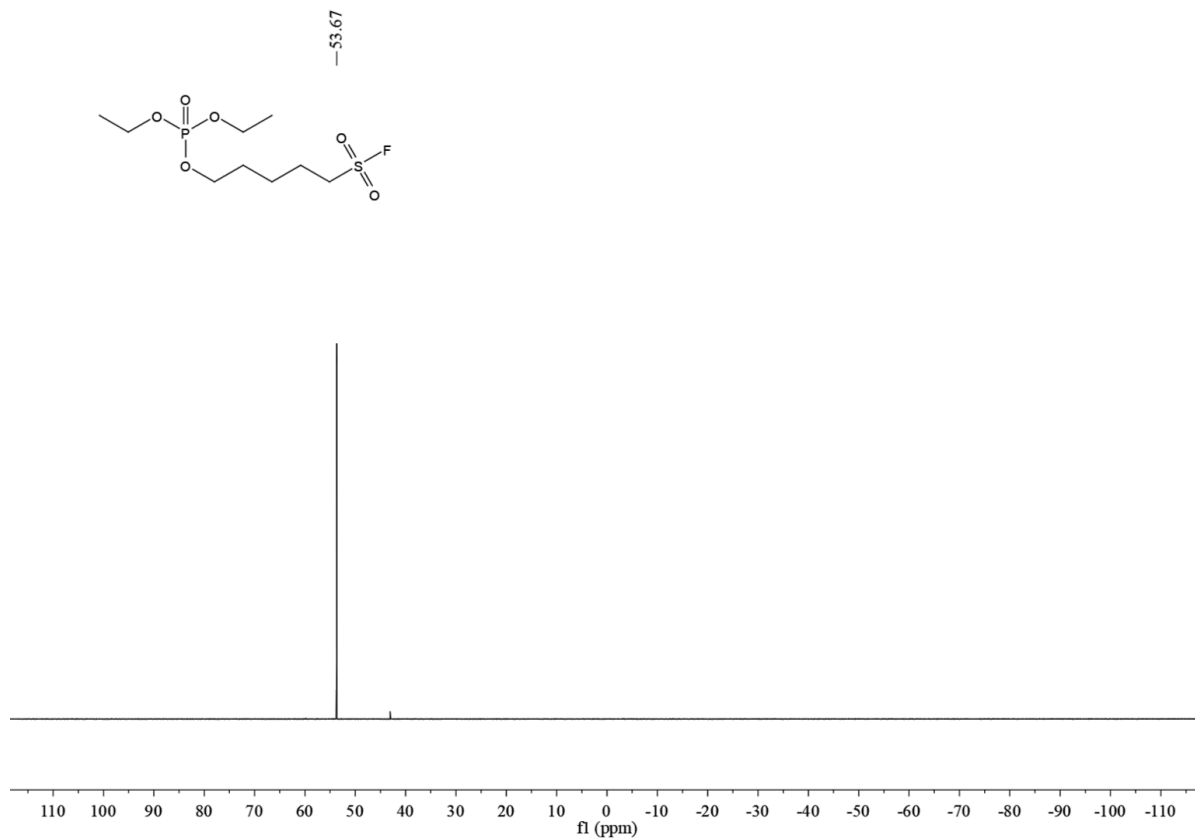
¹H NMR



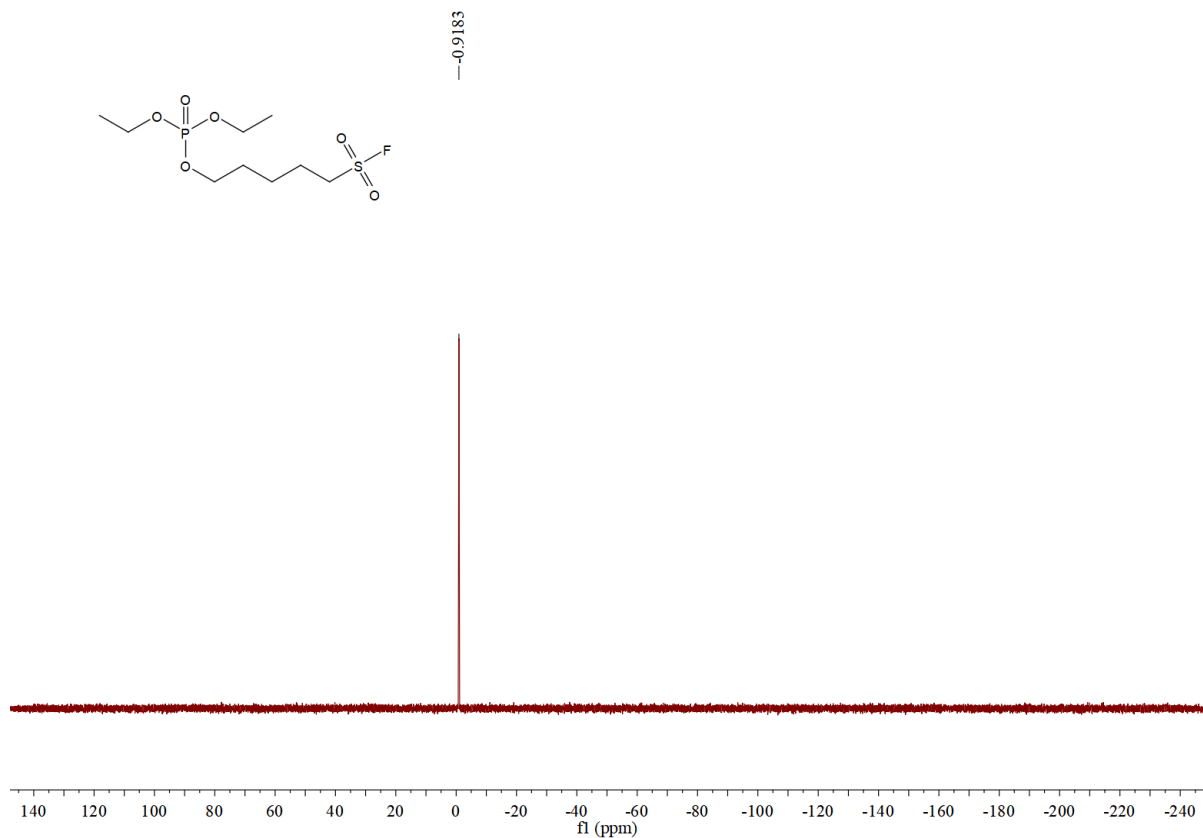
¹³C NMR



¹⁹F NMR

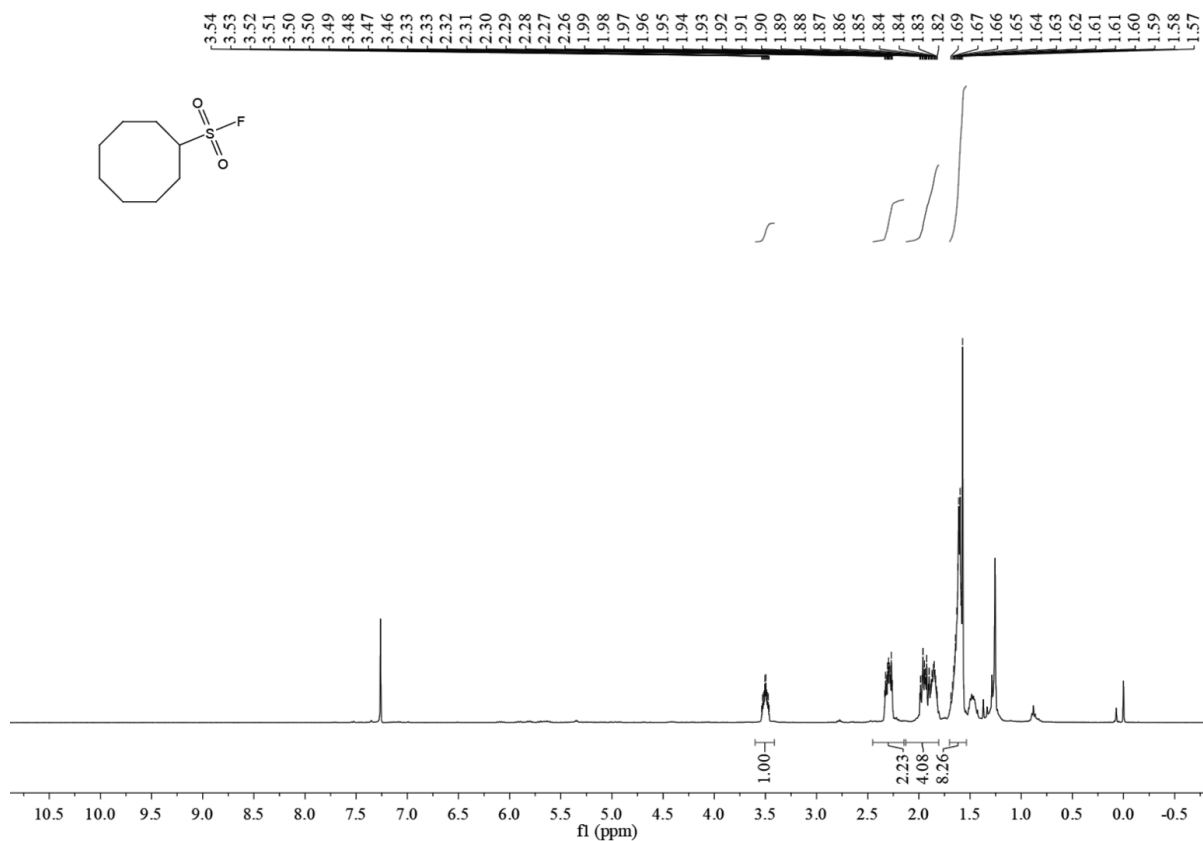


³¹P NMR

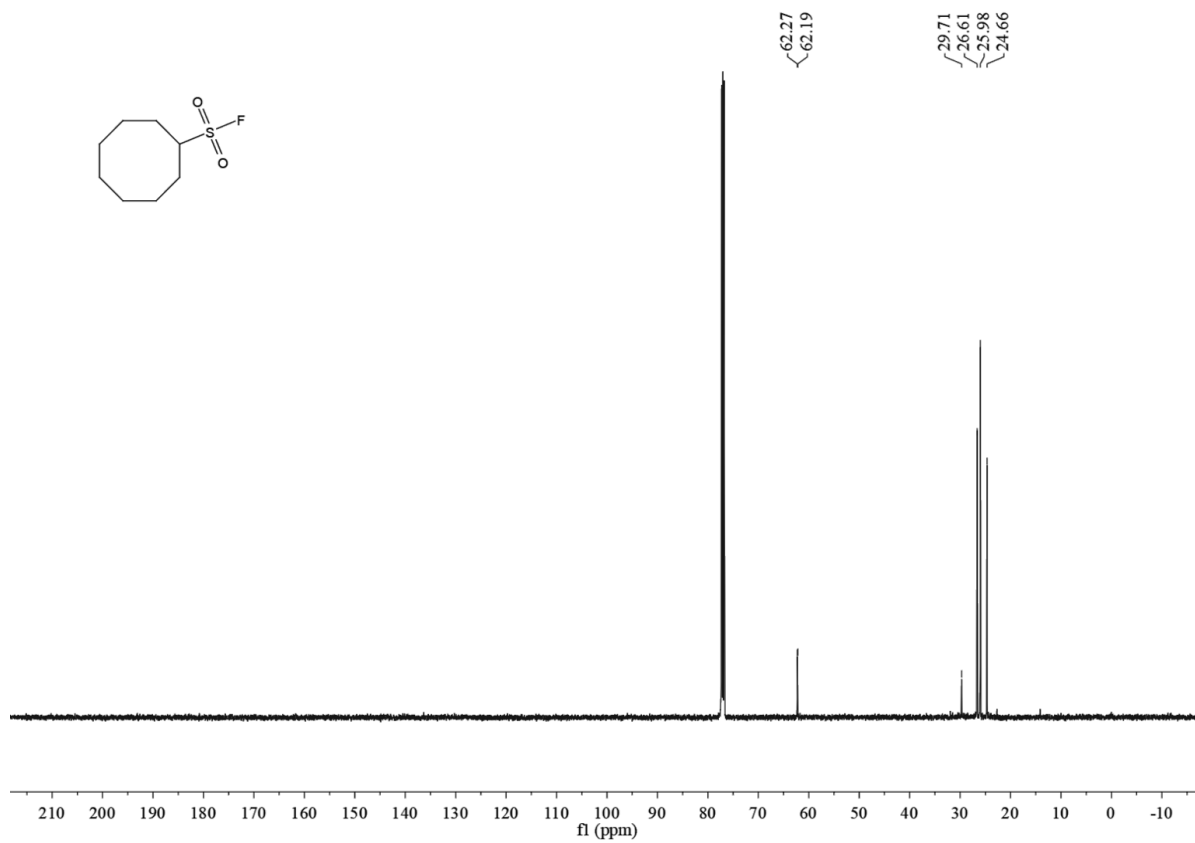


cyclooctanesulfonyl fluoride (4ac)

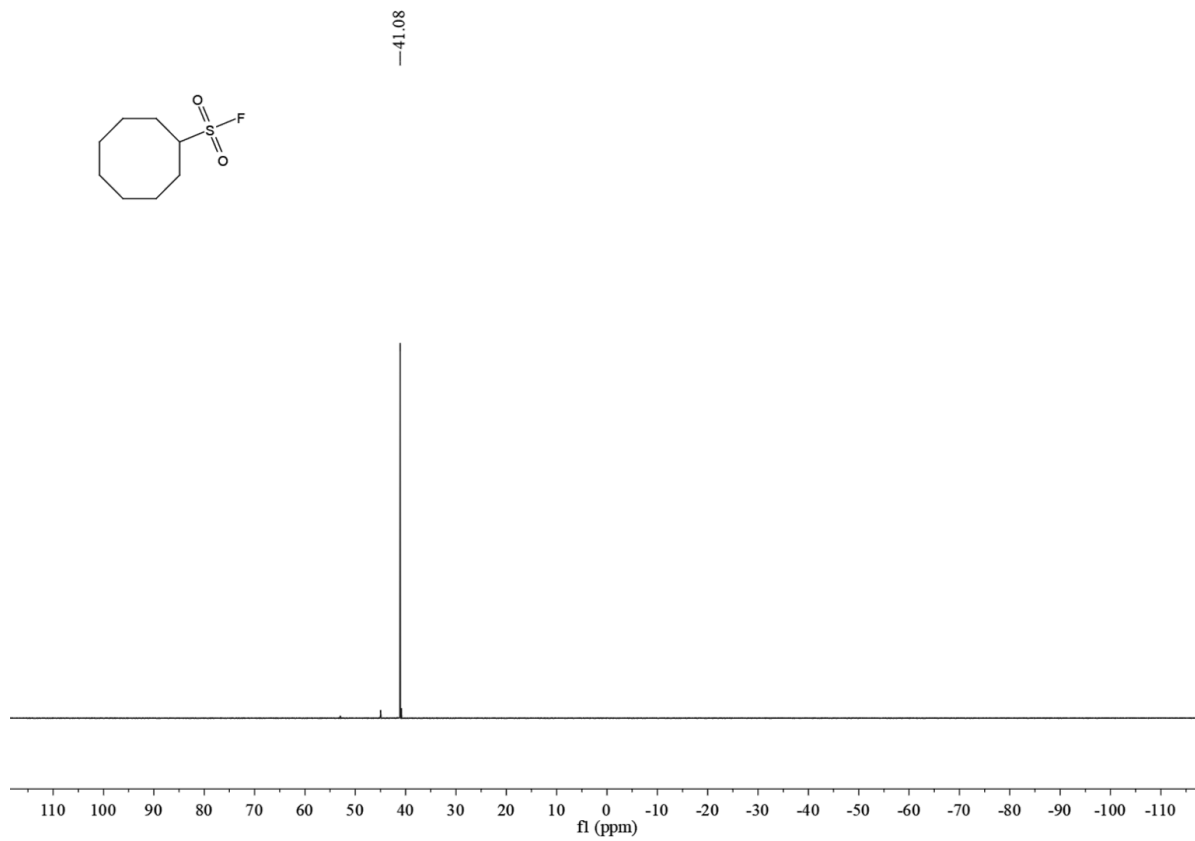
¹H NMR



¹³C NMR

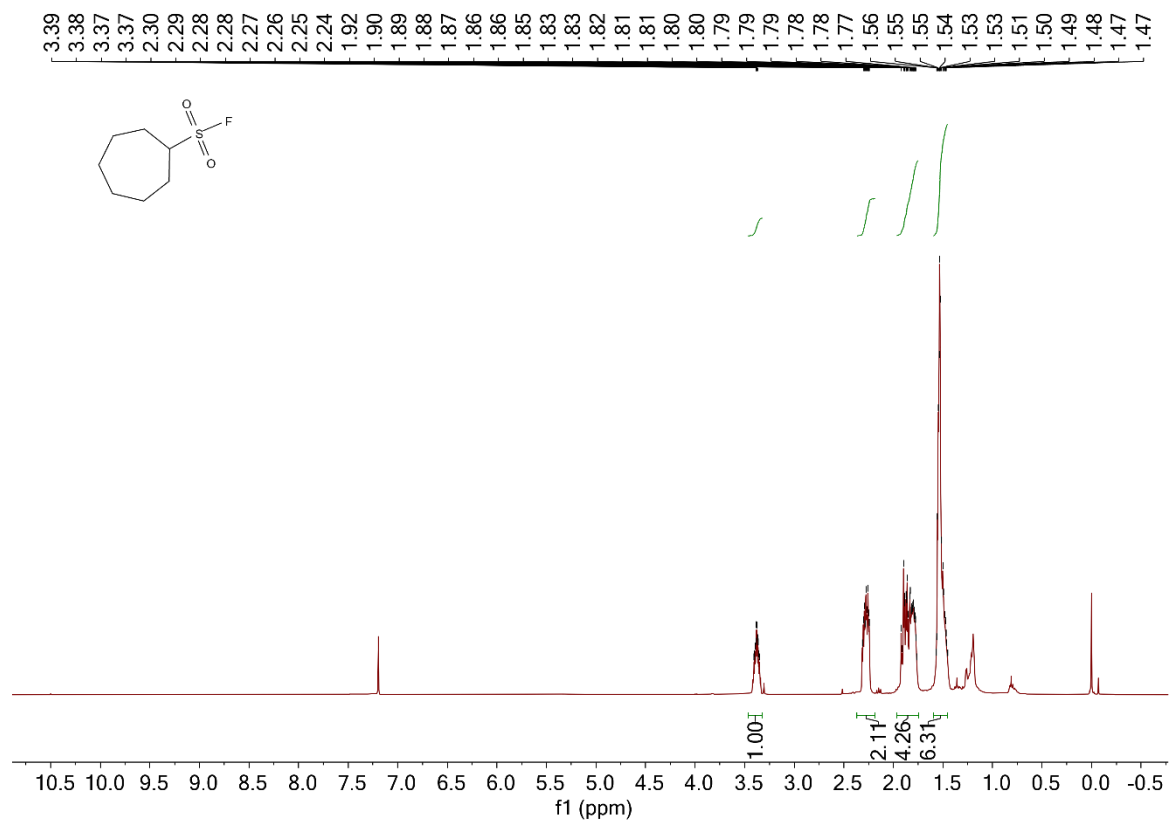


¹⁹F NMR

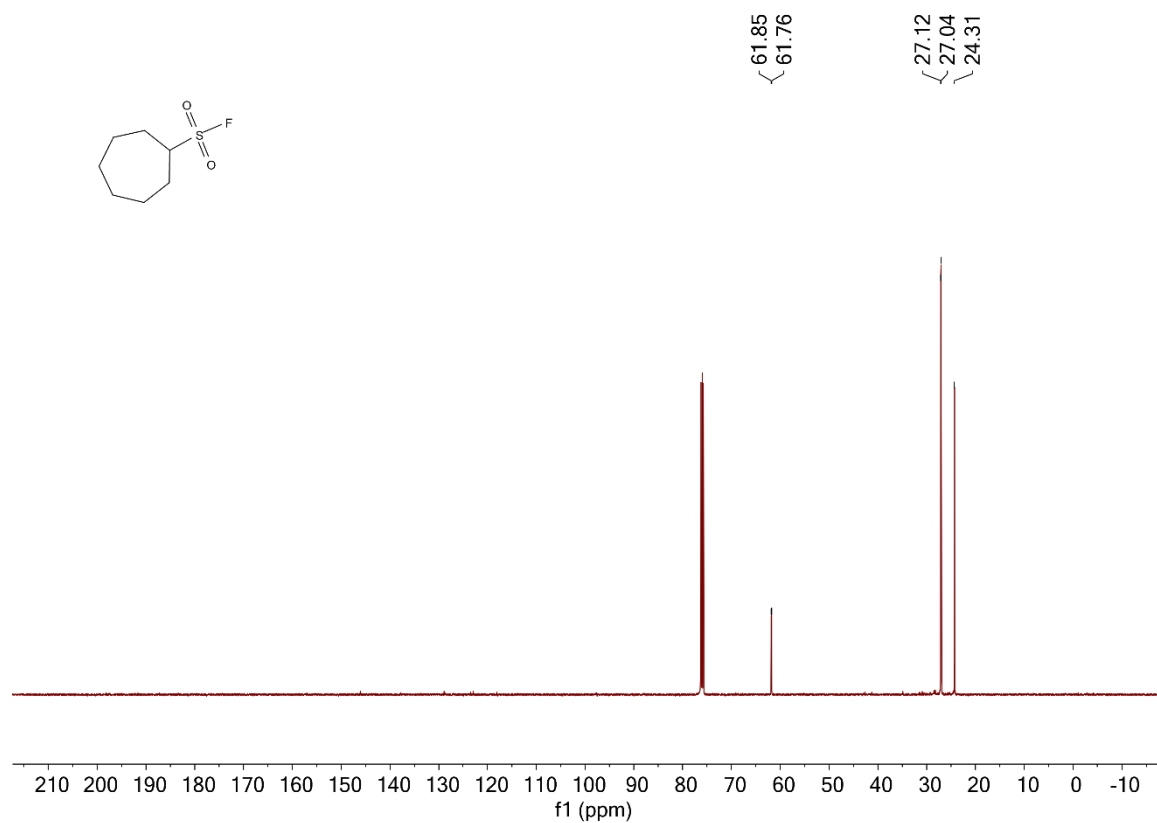


cycloheptanesulfonyl fluoride (4ad)

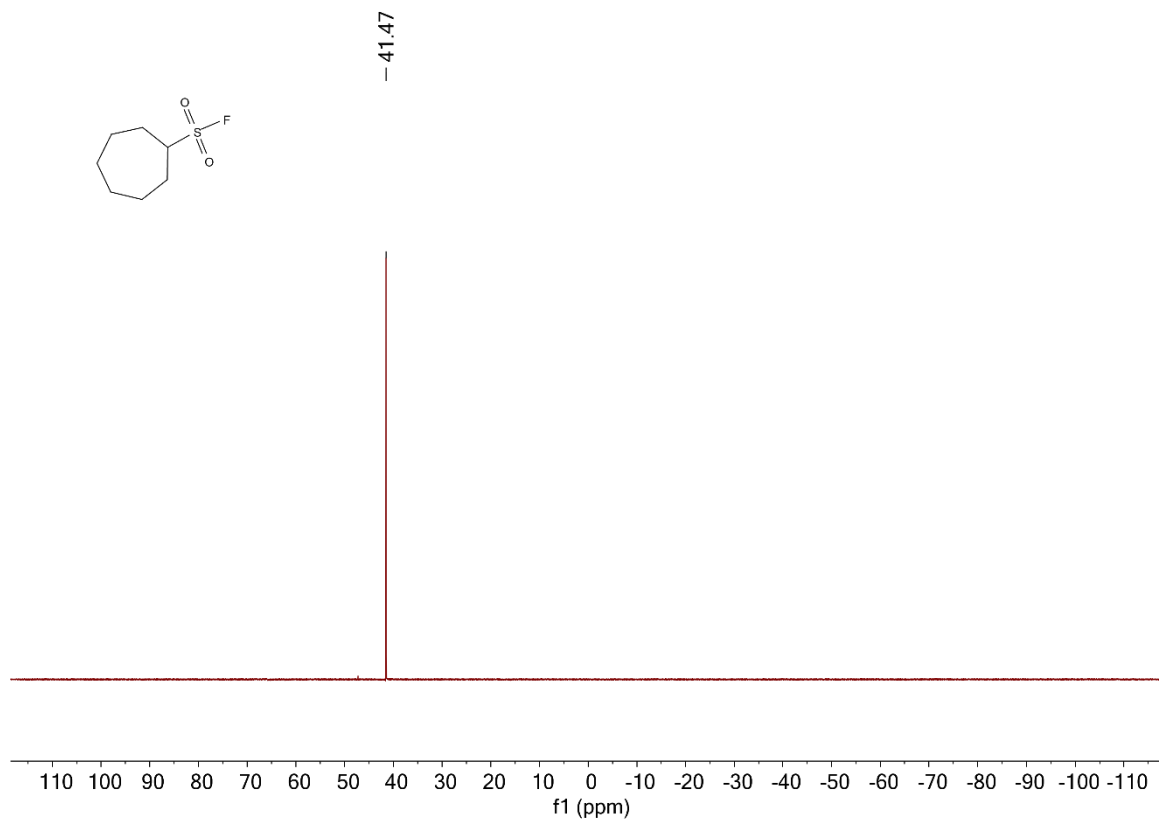
¹H NMR



¹³C NMR

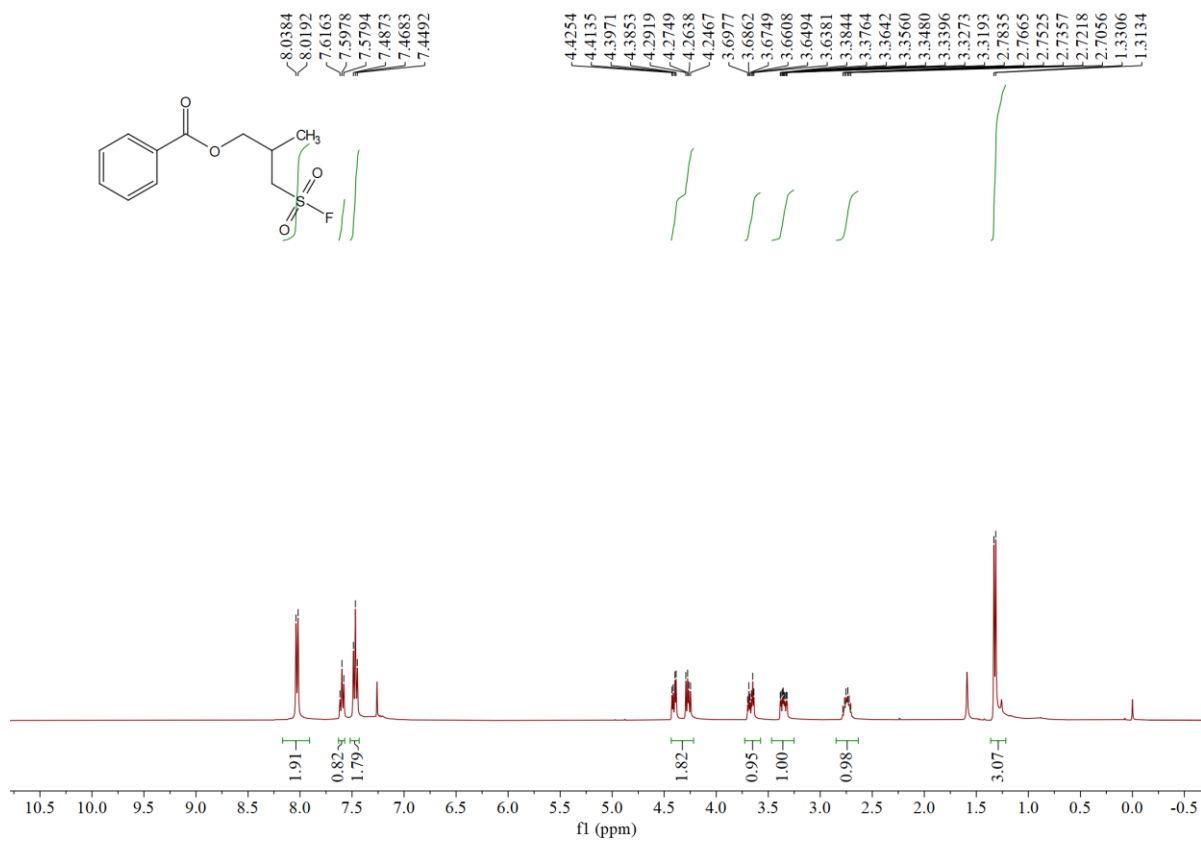


¹⁹F NMR

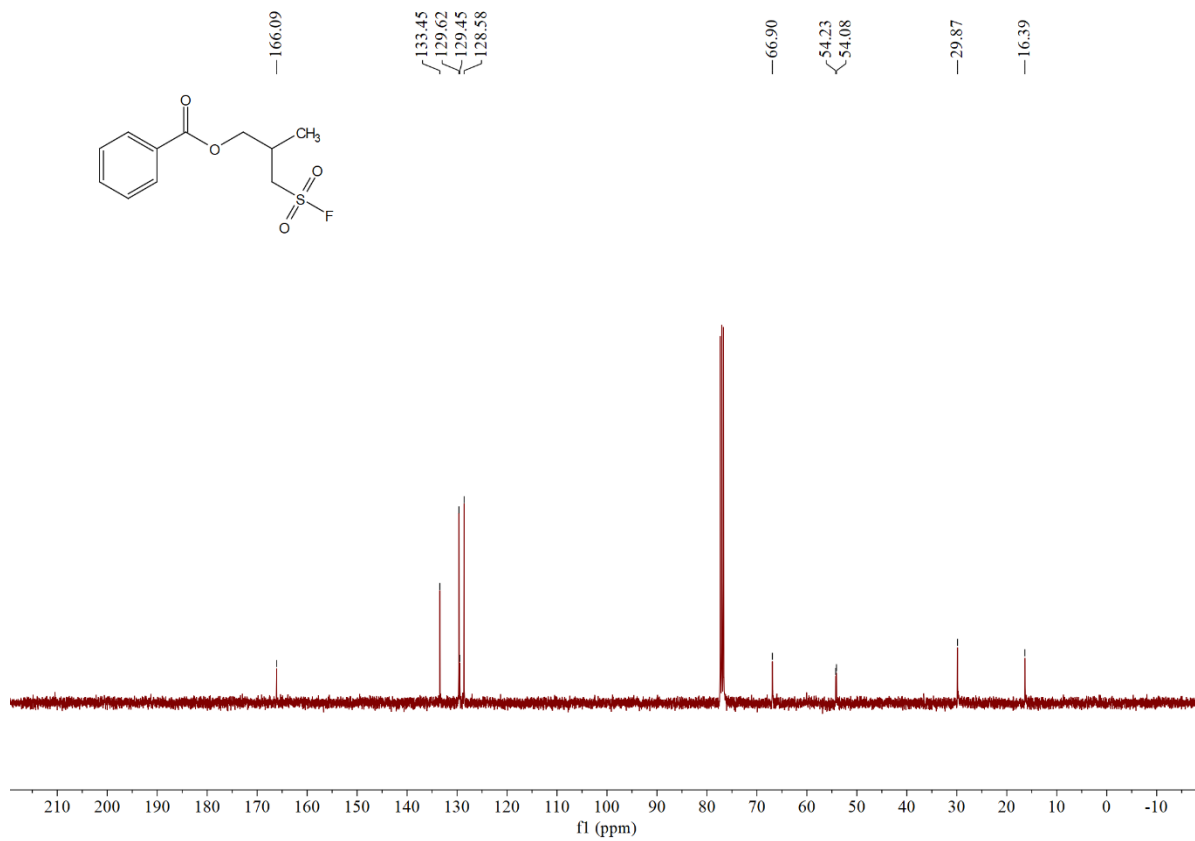


3-(fluorosulfonyl)-2-methylpropyl benzoate (4ae)

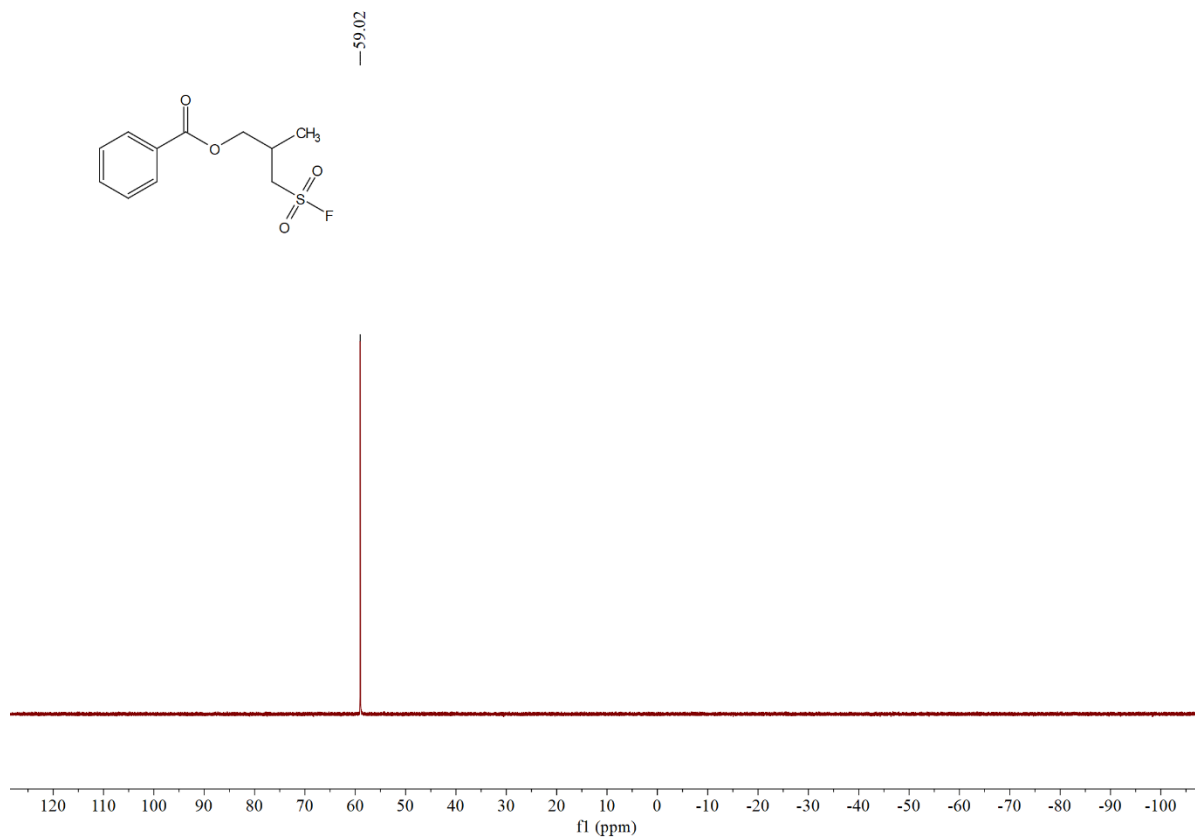
¹H NMR



¹³C NMR

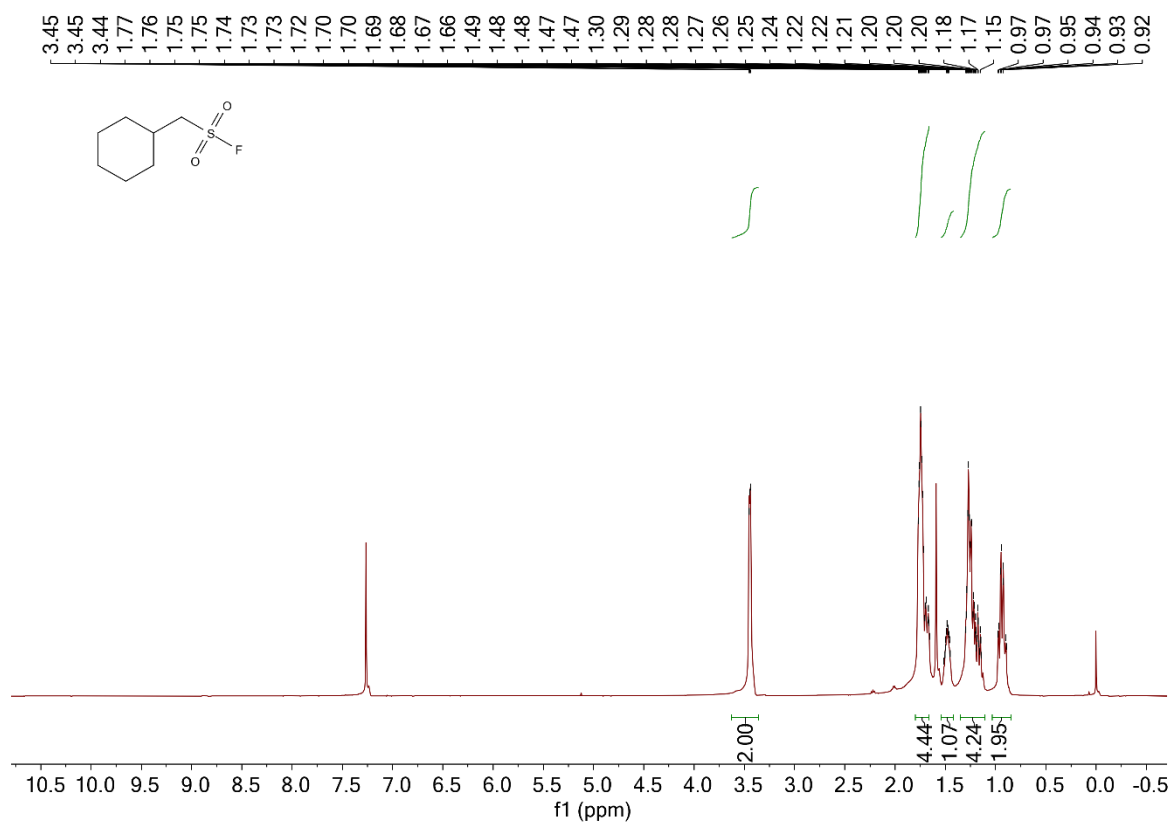


¹⁹F NMR

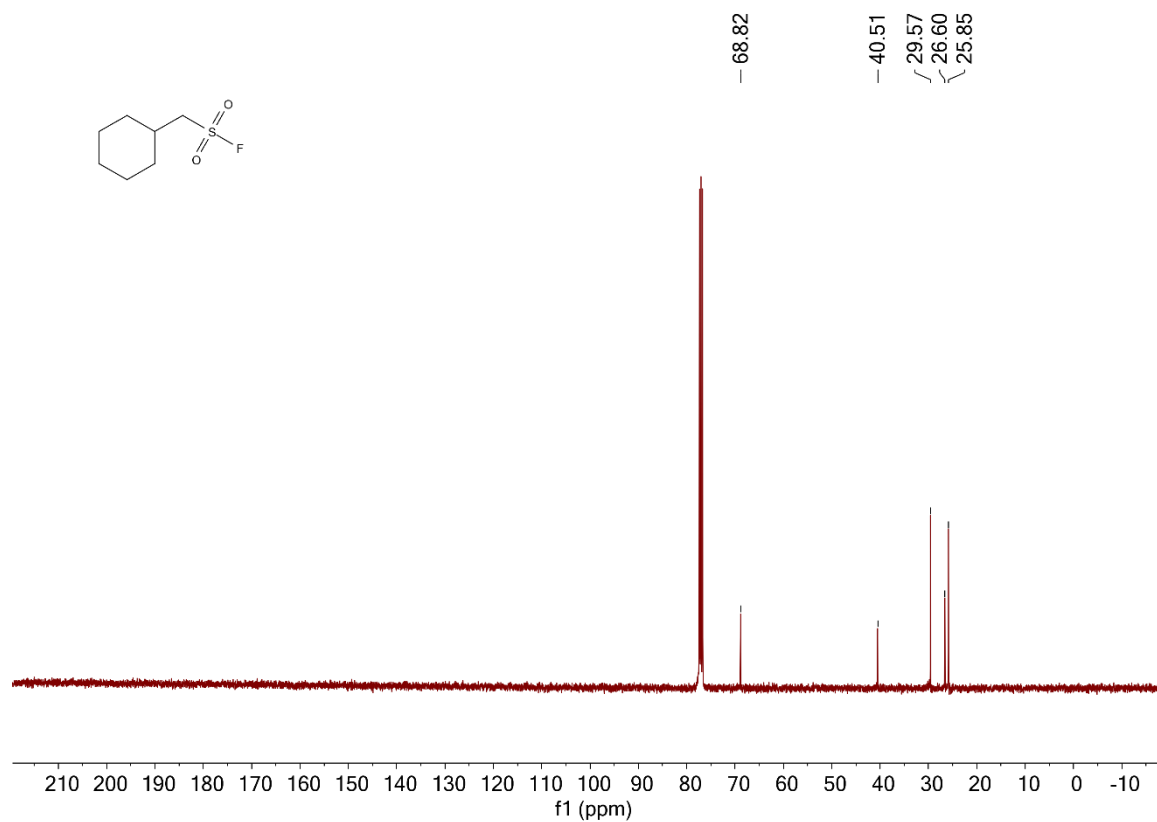


cyclohexylmethanesulfonyl fluoride (4af)

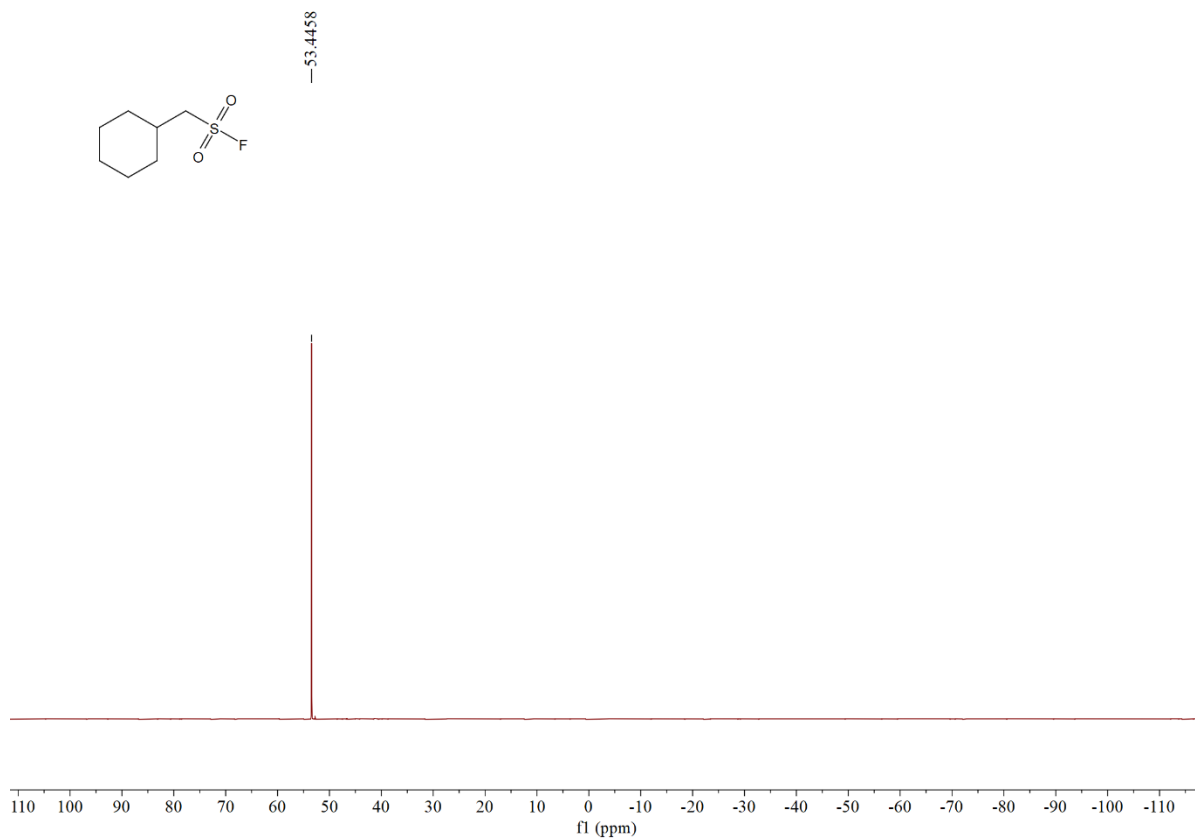
¹H NMR



¹³C NMR

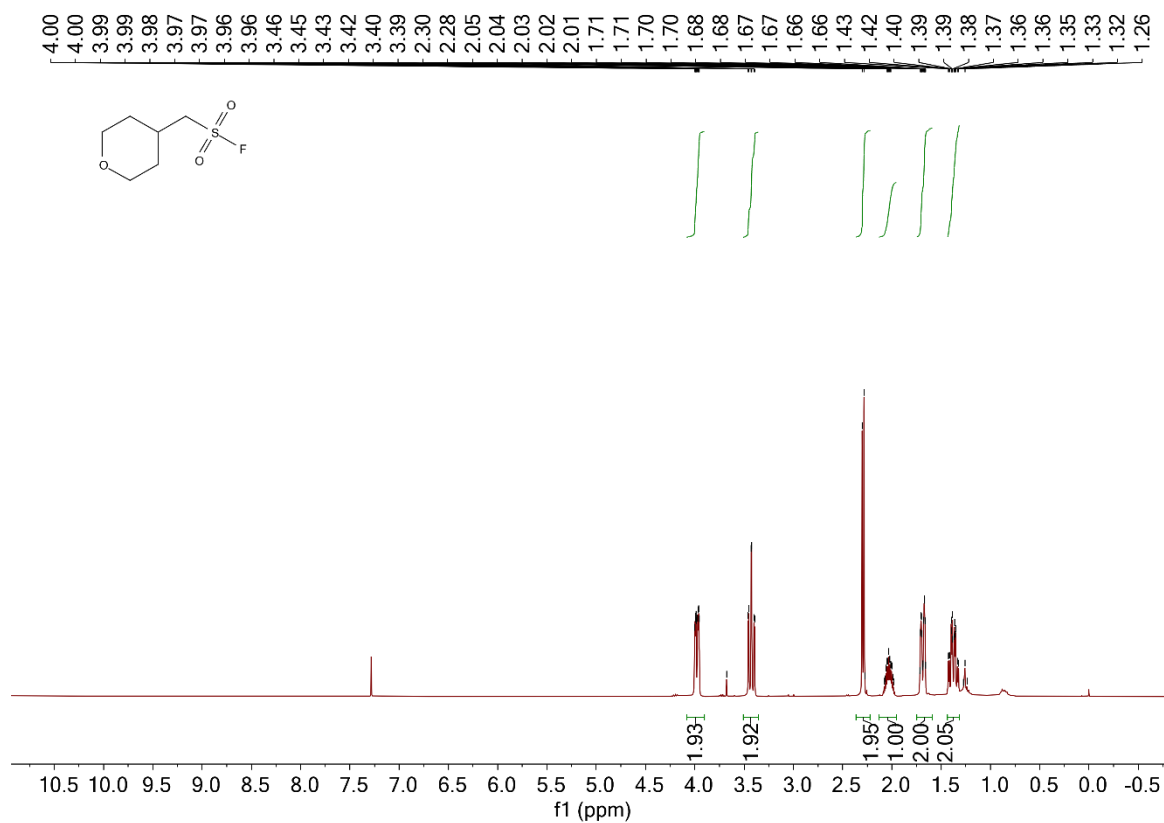


¹⁹F NMR

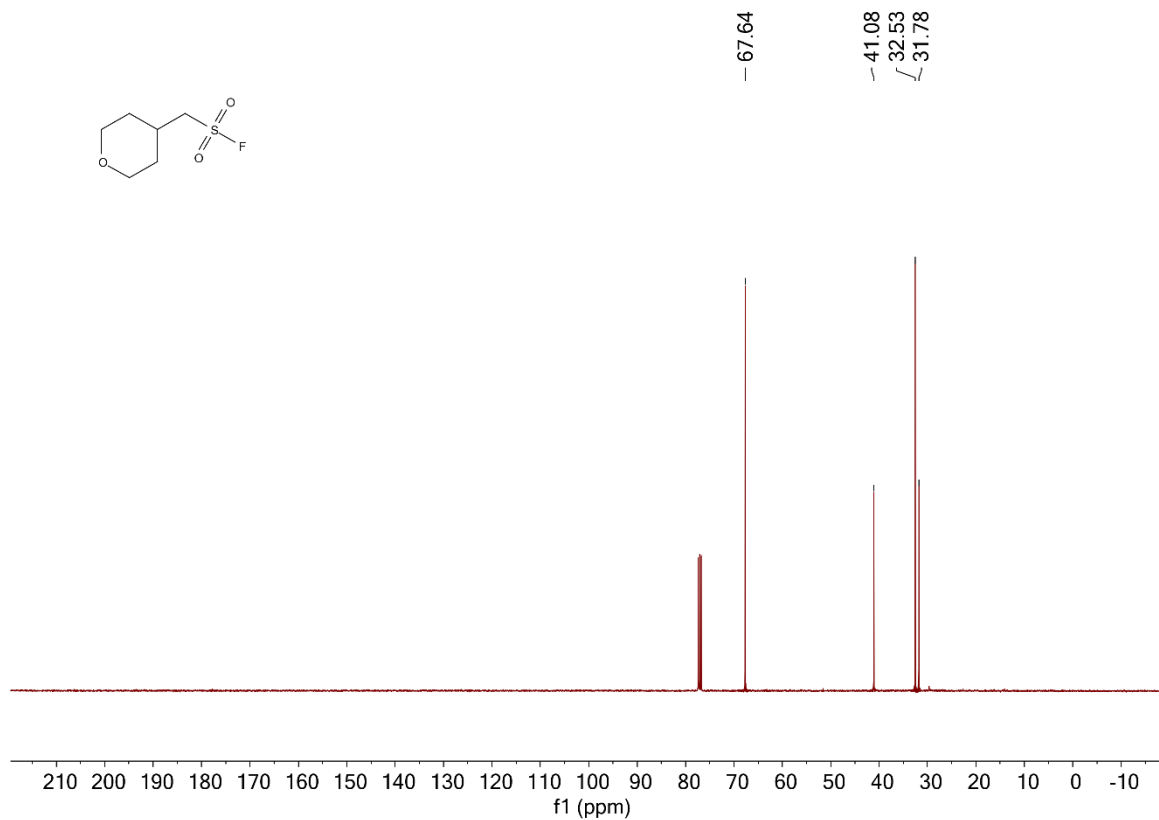
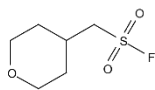


(tetrahydro-2H-pyran-4-yl)methanesulfonyl fluoride (4ag)

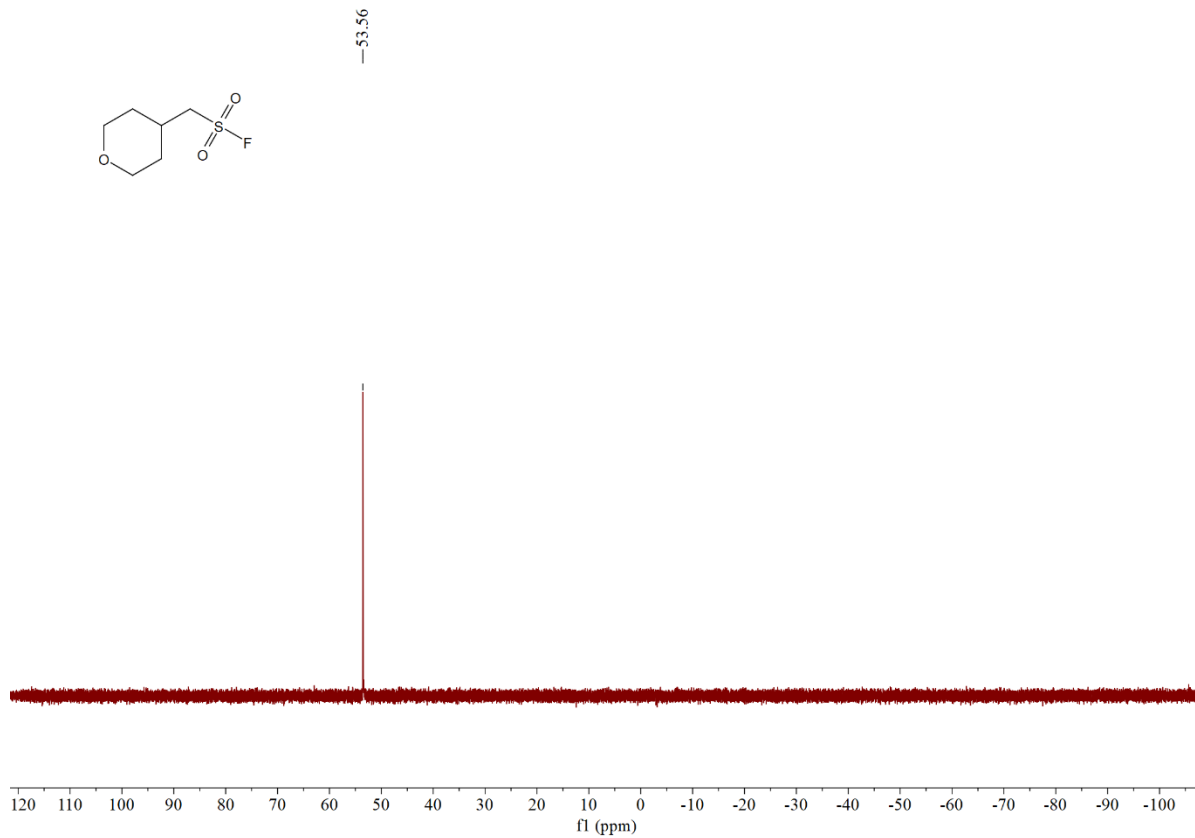
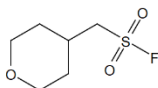
¹H NMR



¹³C NMR

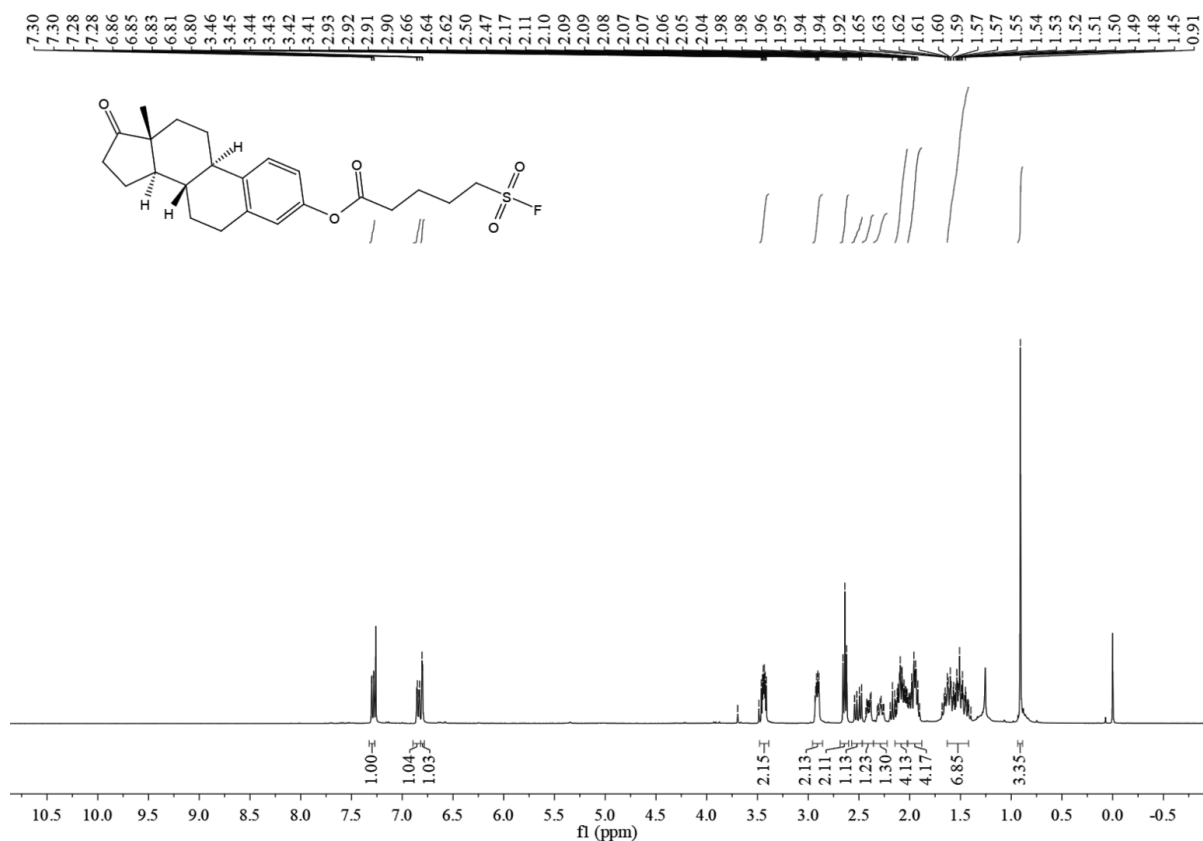


¹⁹F NMR

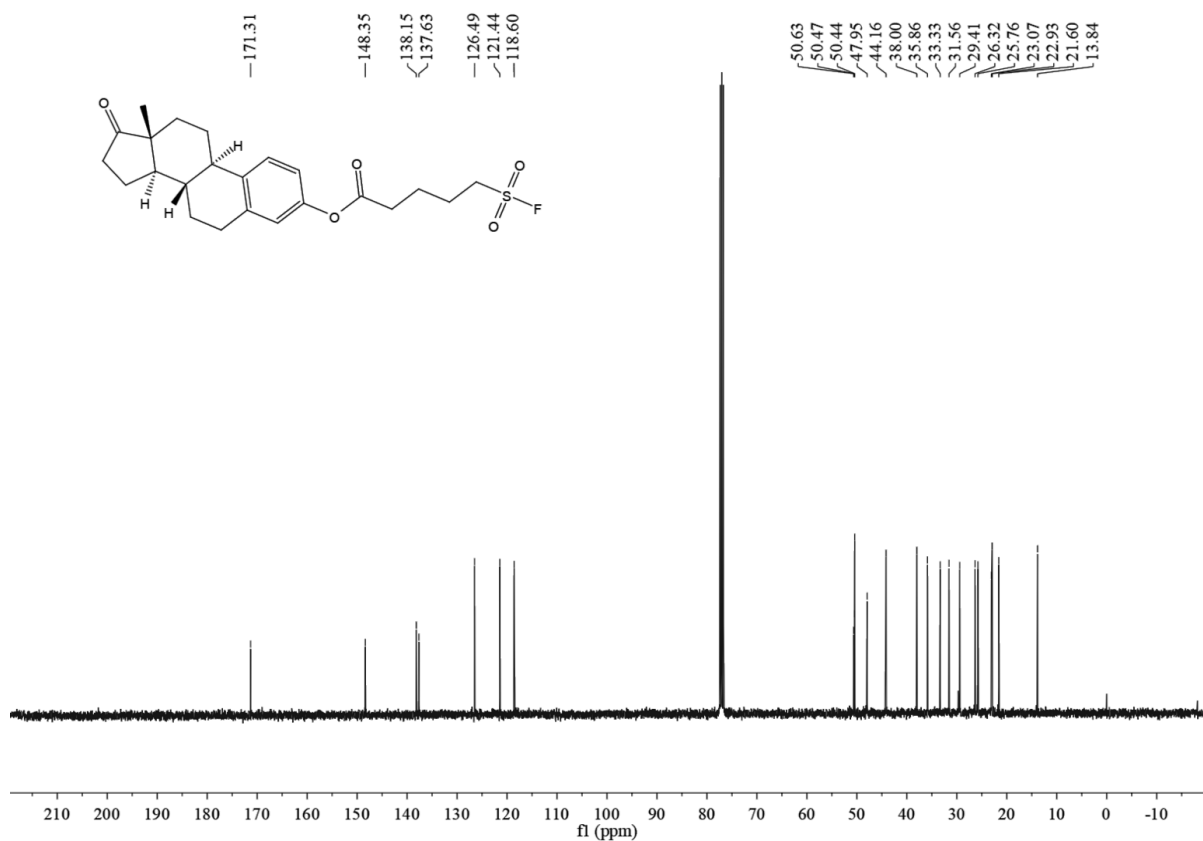


(8*S*,9*R*,13*R*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl 5-(fluorosulfonyl)pentanoate (**4ah**)

¹H NMR



¹³C NMR

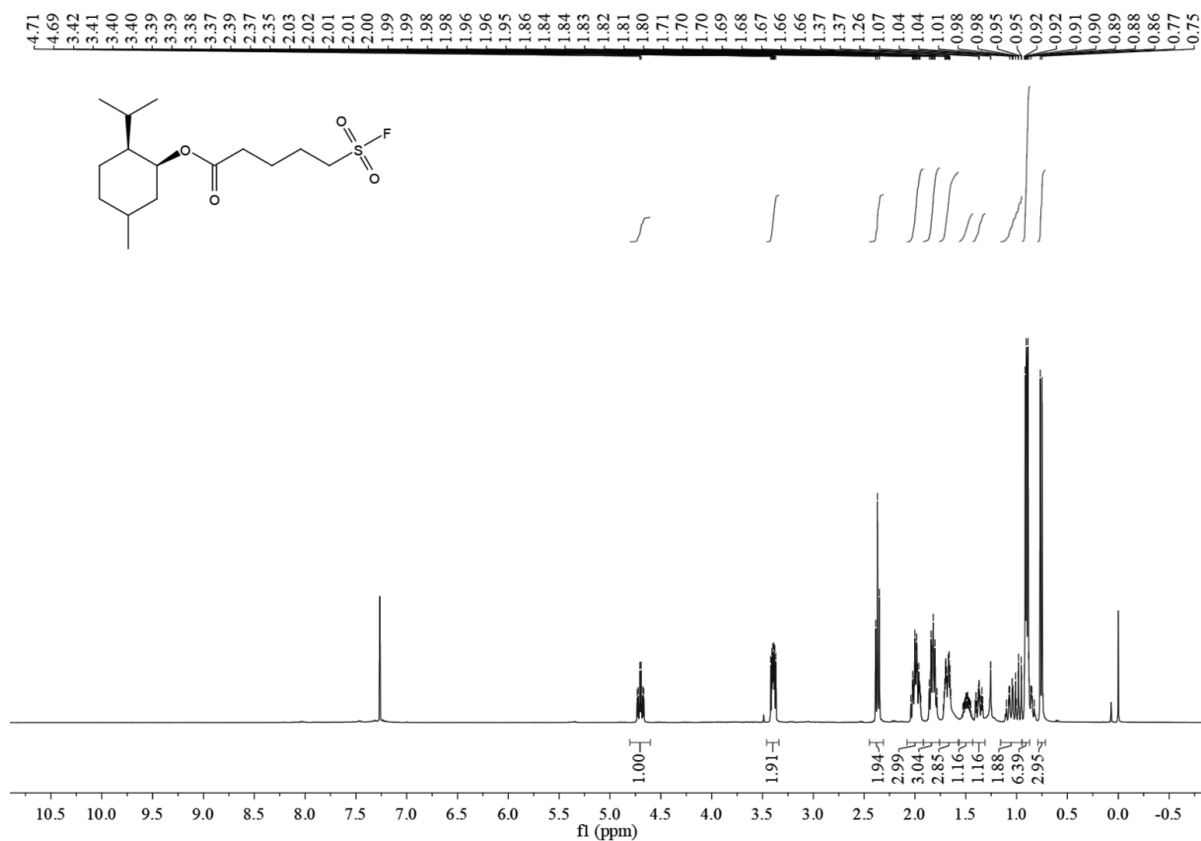


¹⁹F NMR

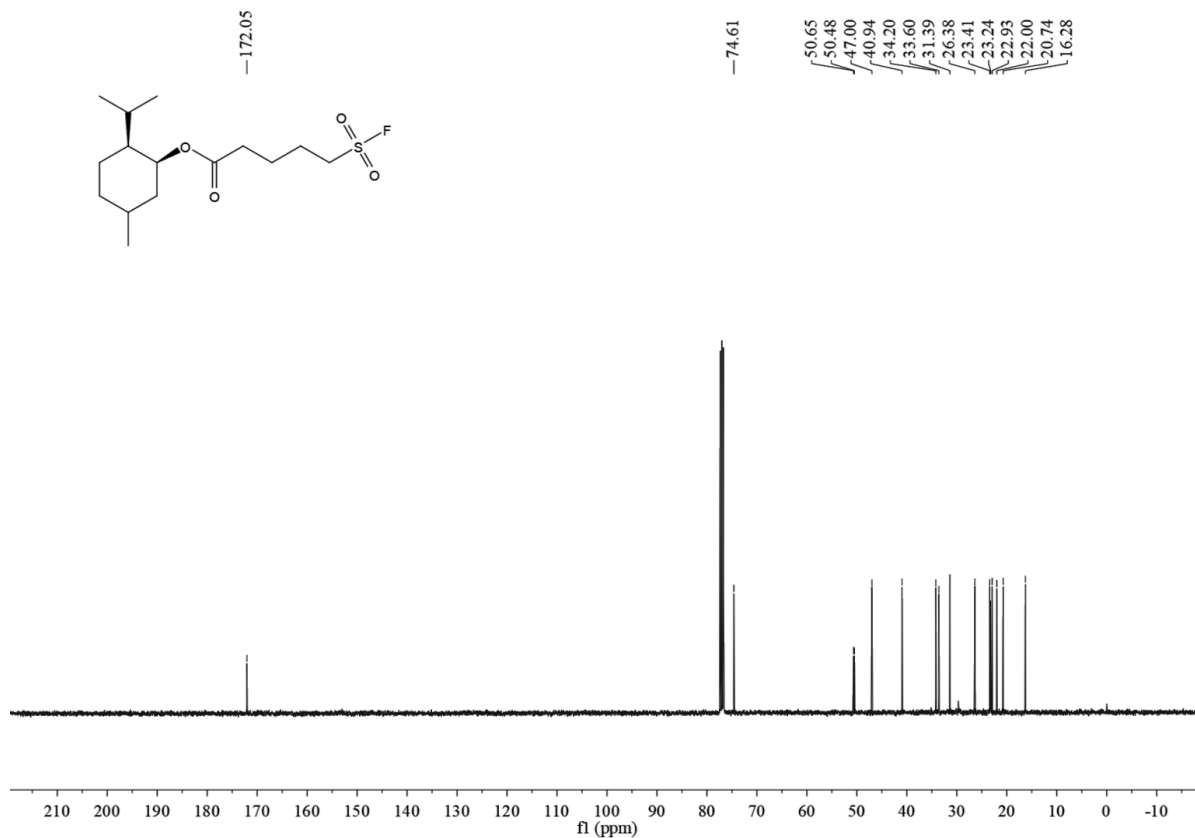


(1*S*,2*S*)-2-isopropyl-5-methylcyclohexyl 5-(fluorosulfonyl)pentanoate (**4ai**)

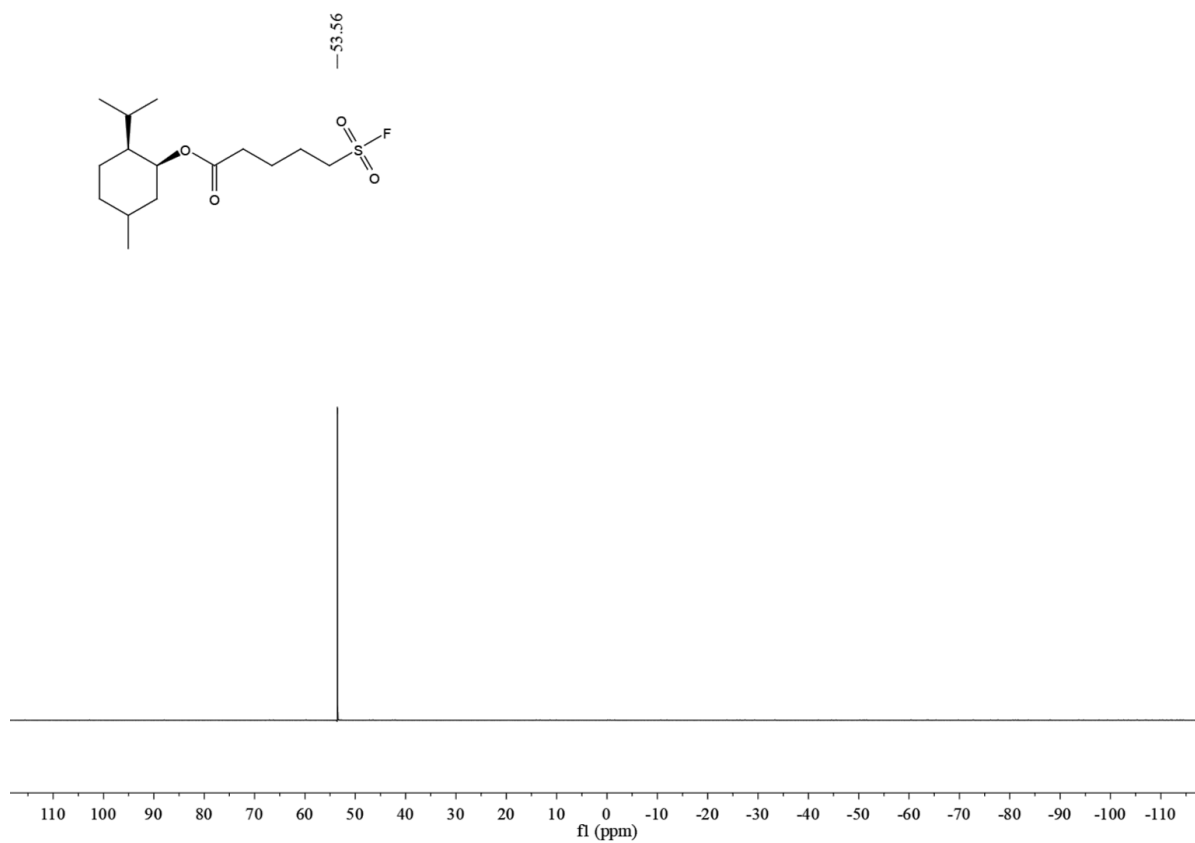
¹H NMR



¹³C NMR

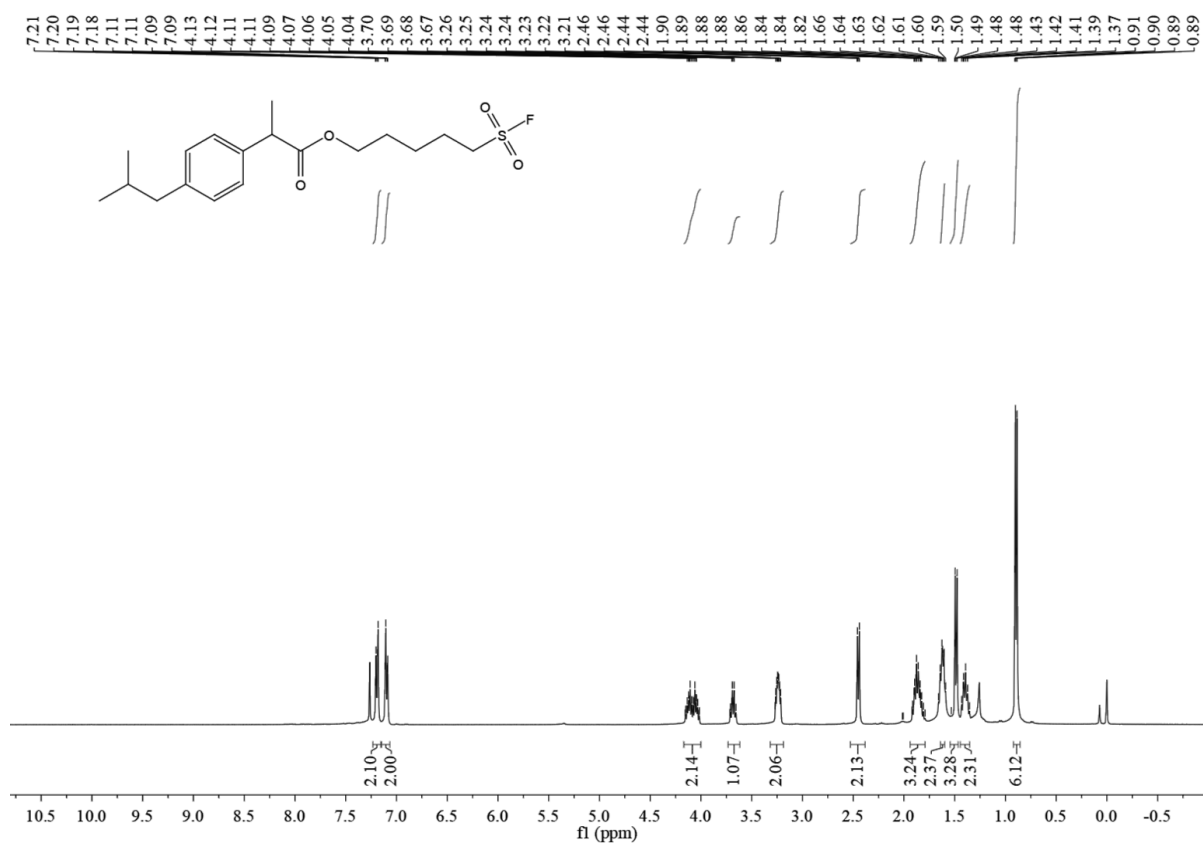


¹⁹F NMR

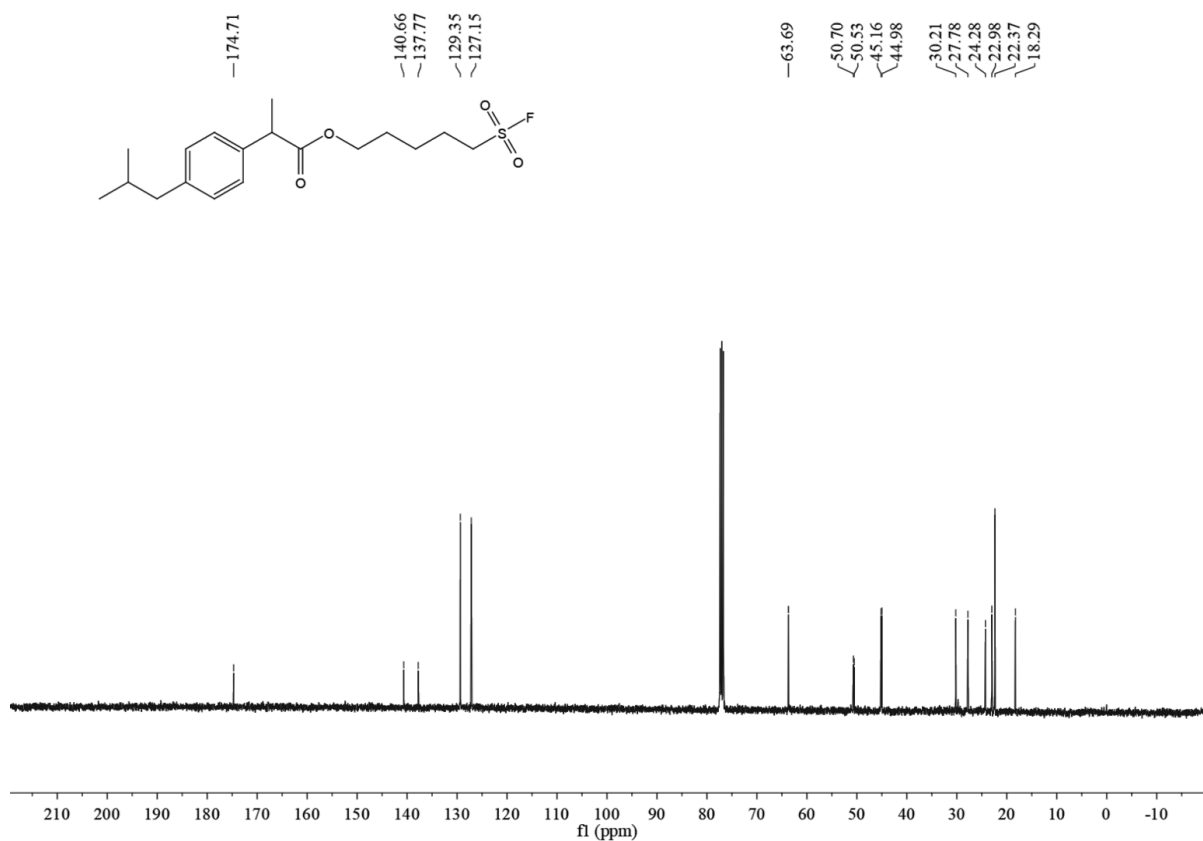


5-(fluorosulfonyl)pentyl 2-(4-isobutylphenyl)propanoate (**4aj**)

¹H NMR



¹³C NMR

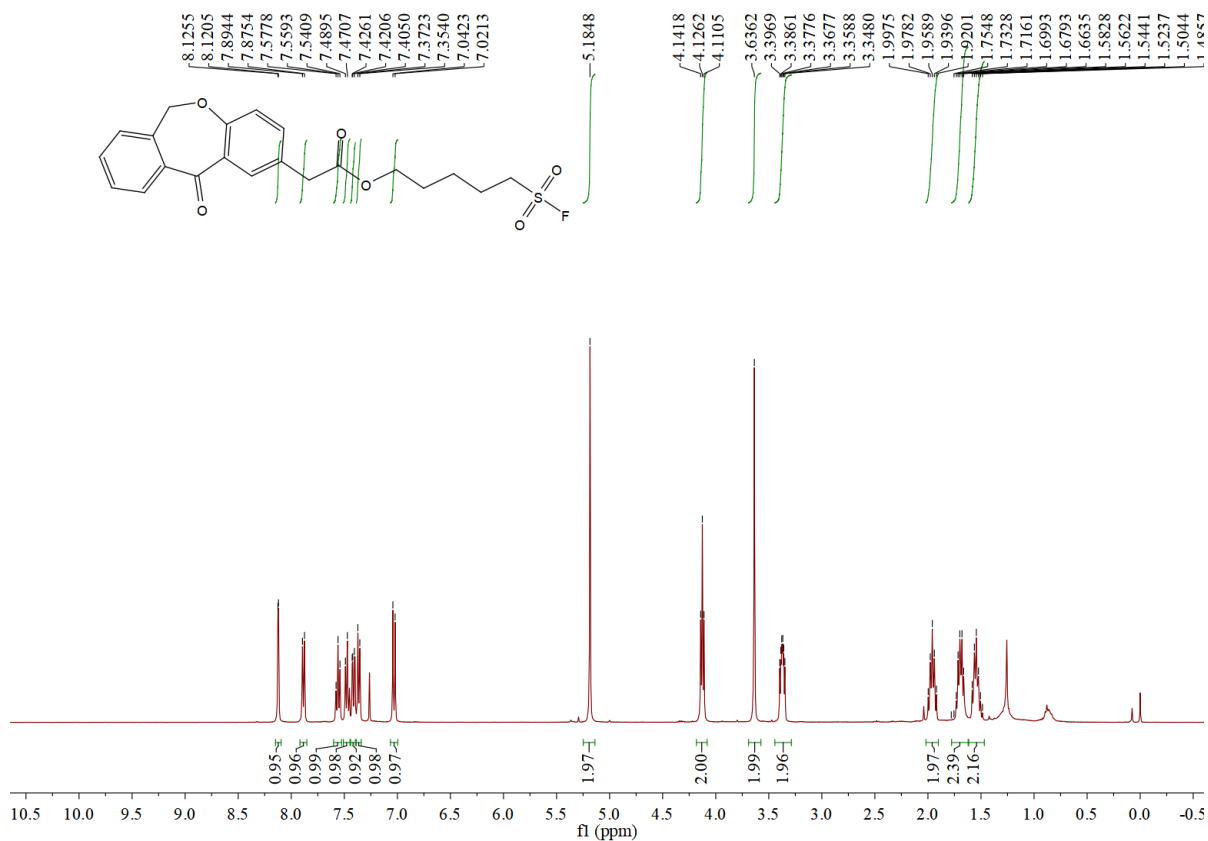


¹⁹F NMR

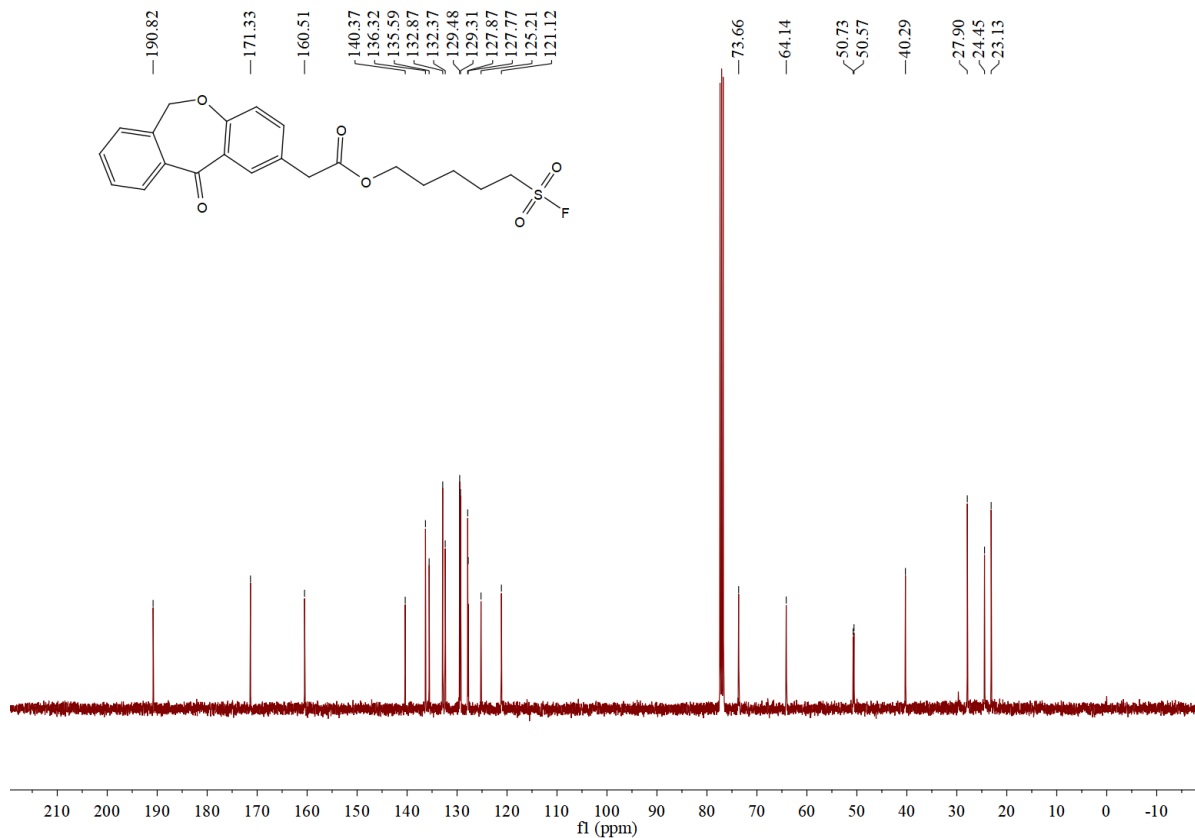


4-(fluorosulfonyl)butyl 2-(11-oxo-6,11-dihydrodibenzo[b,e]oxepin-2-yl)acetate (4ak)

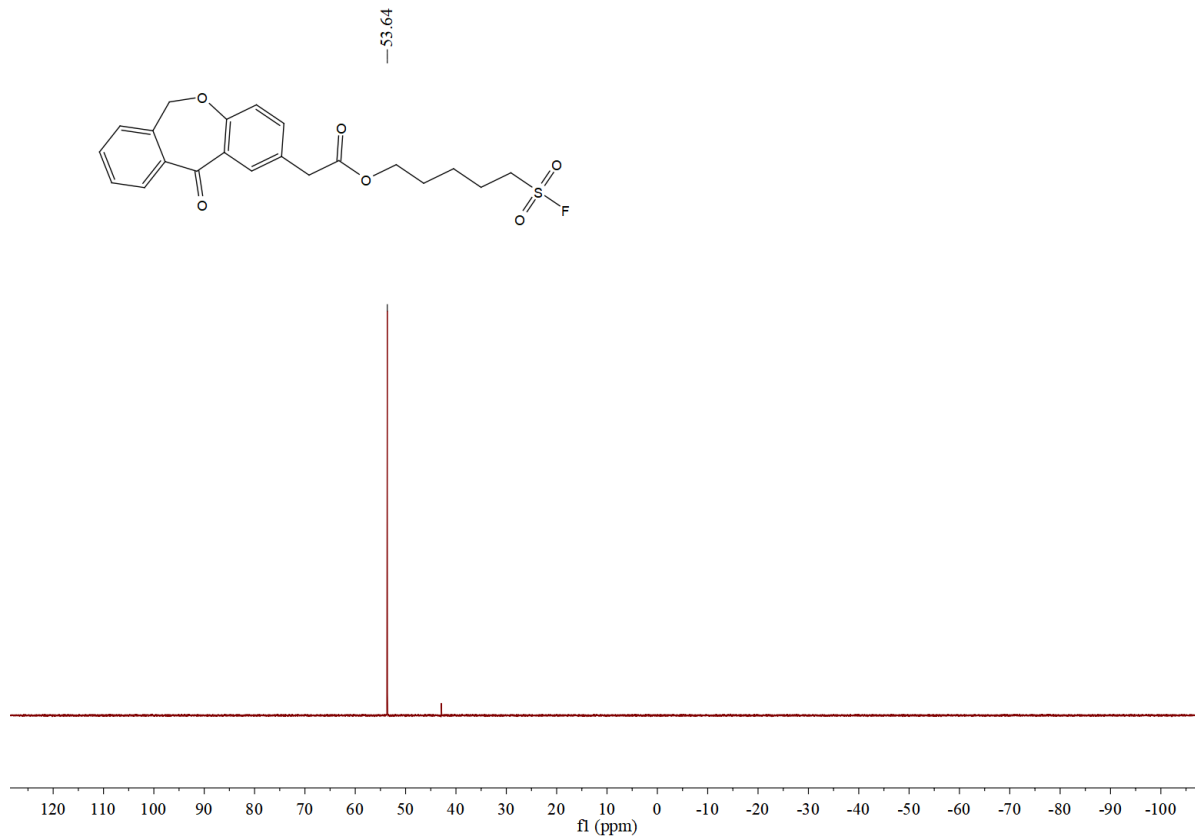
¹H NMR



¹³C NMR

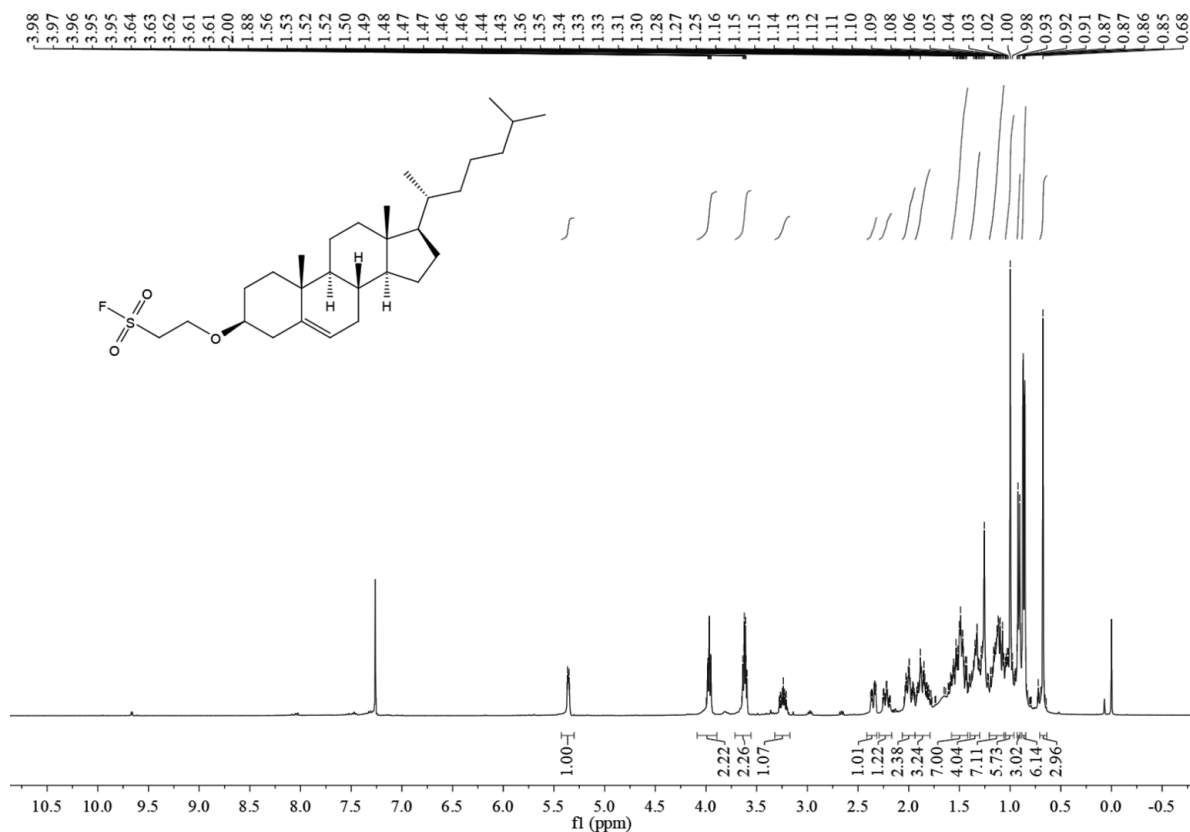


¹⁹F NMR

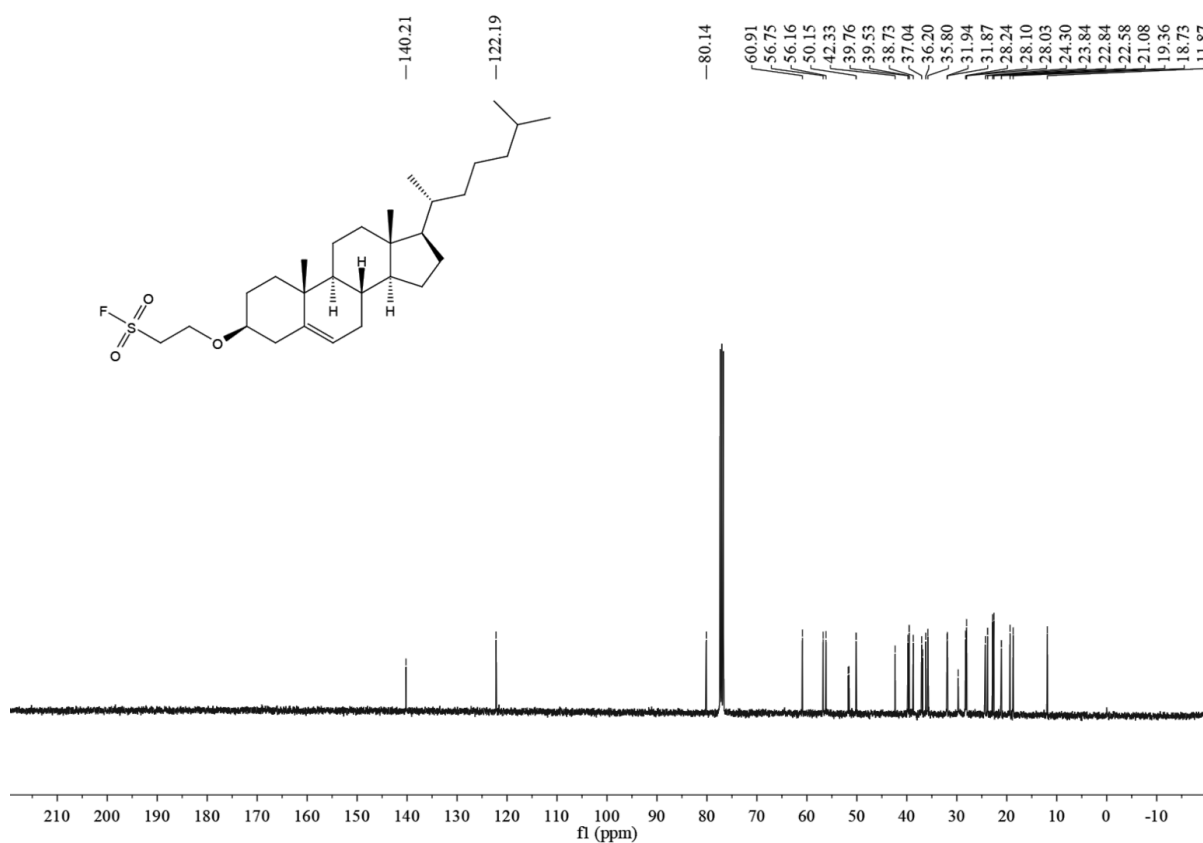


2-(((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)ethane-1-sulfonyl fluoride (**4al**)

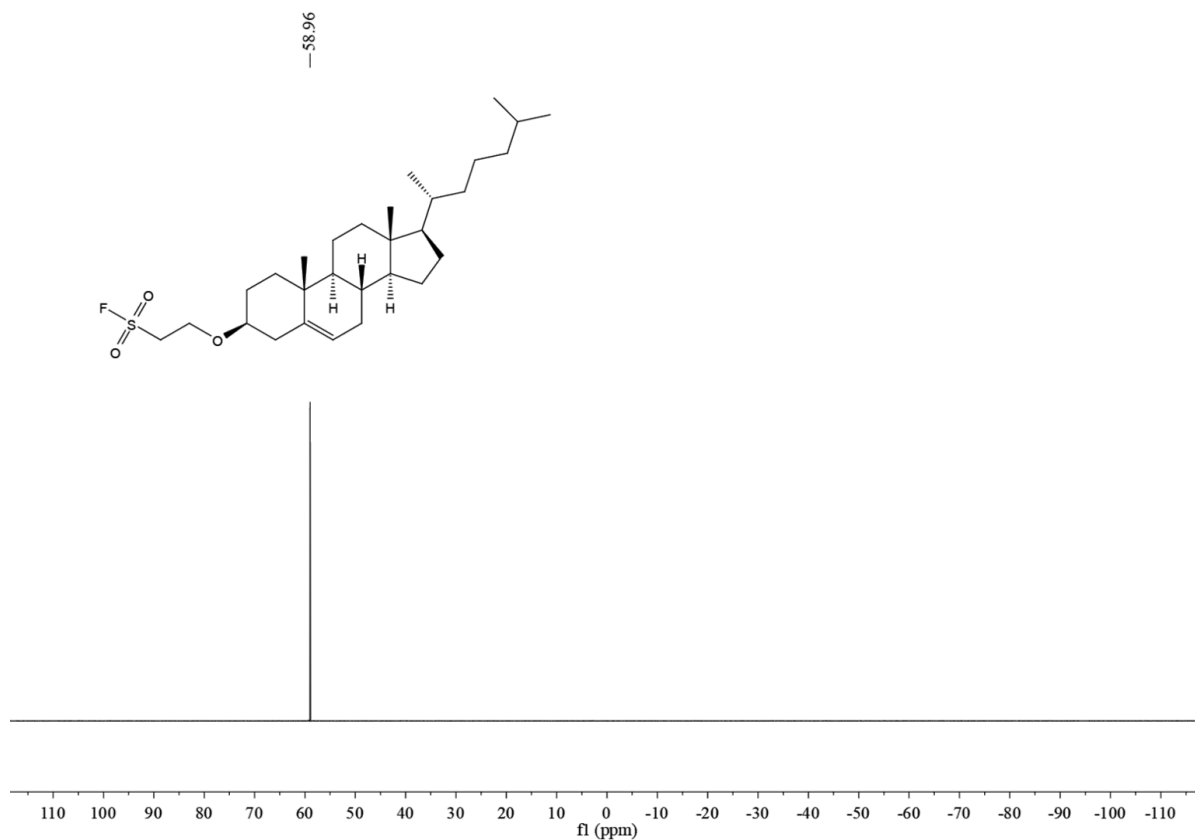
¹H NMR



¹³C NMR

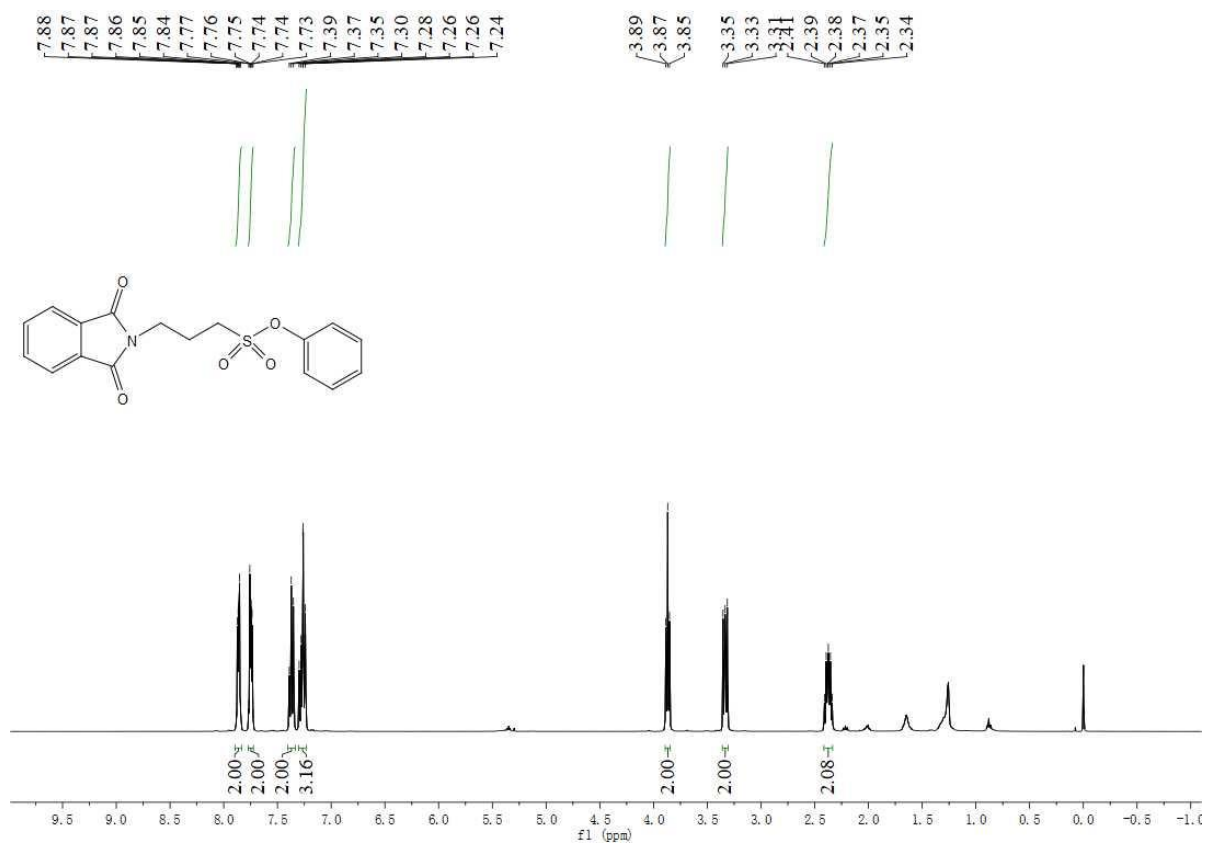


¹⁹F NMR

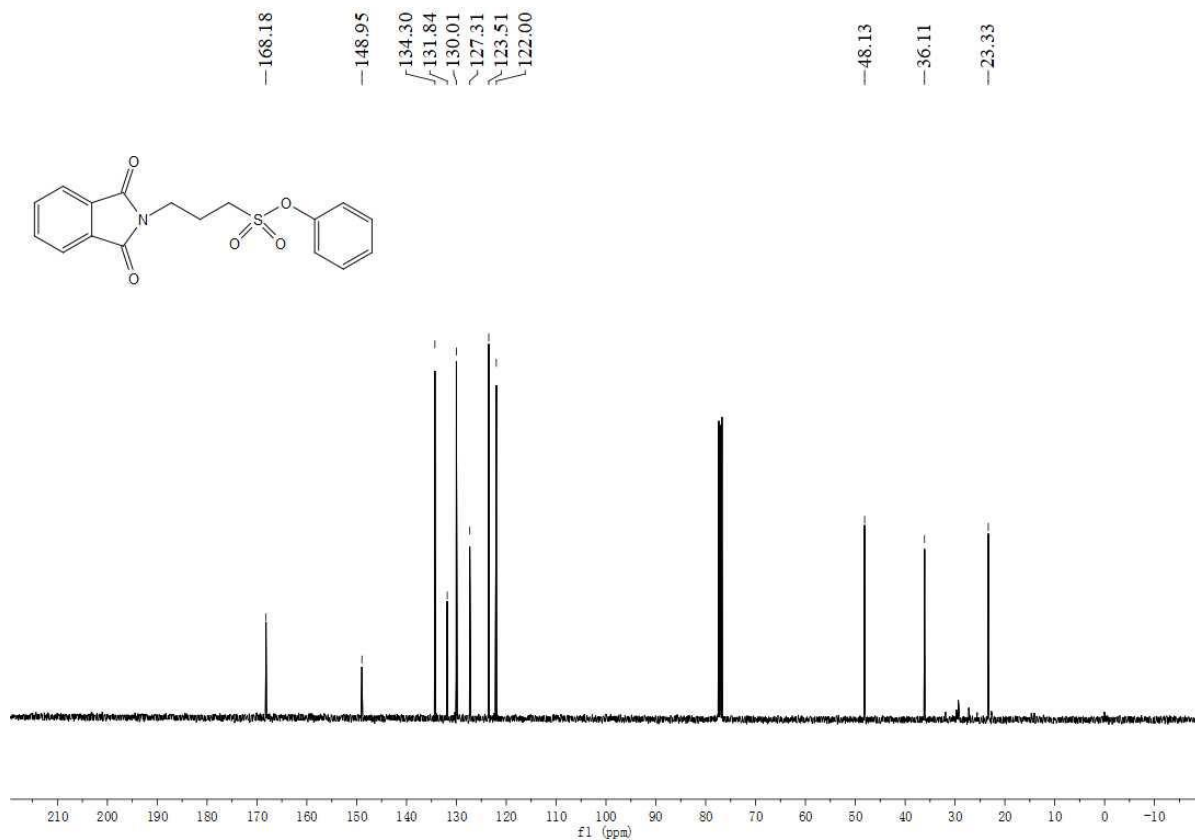


2-(3-(phenylsulfonyl)propyl)isoindoline-1,3-dione (6)

¹H NMR

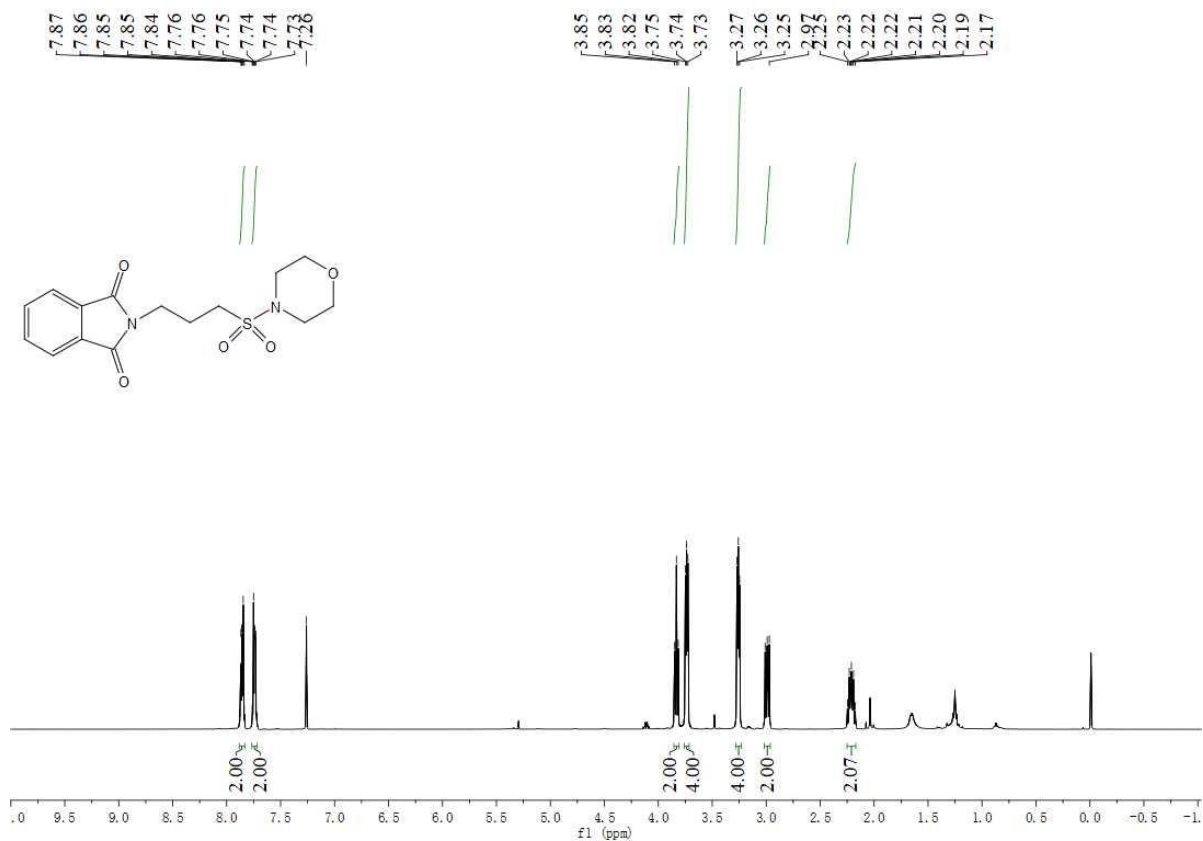


¹³C NMR

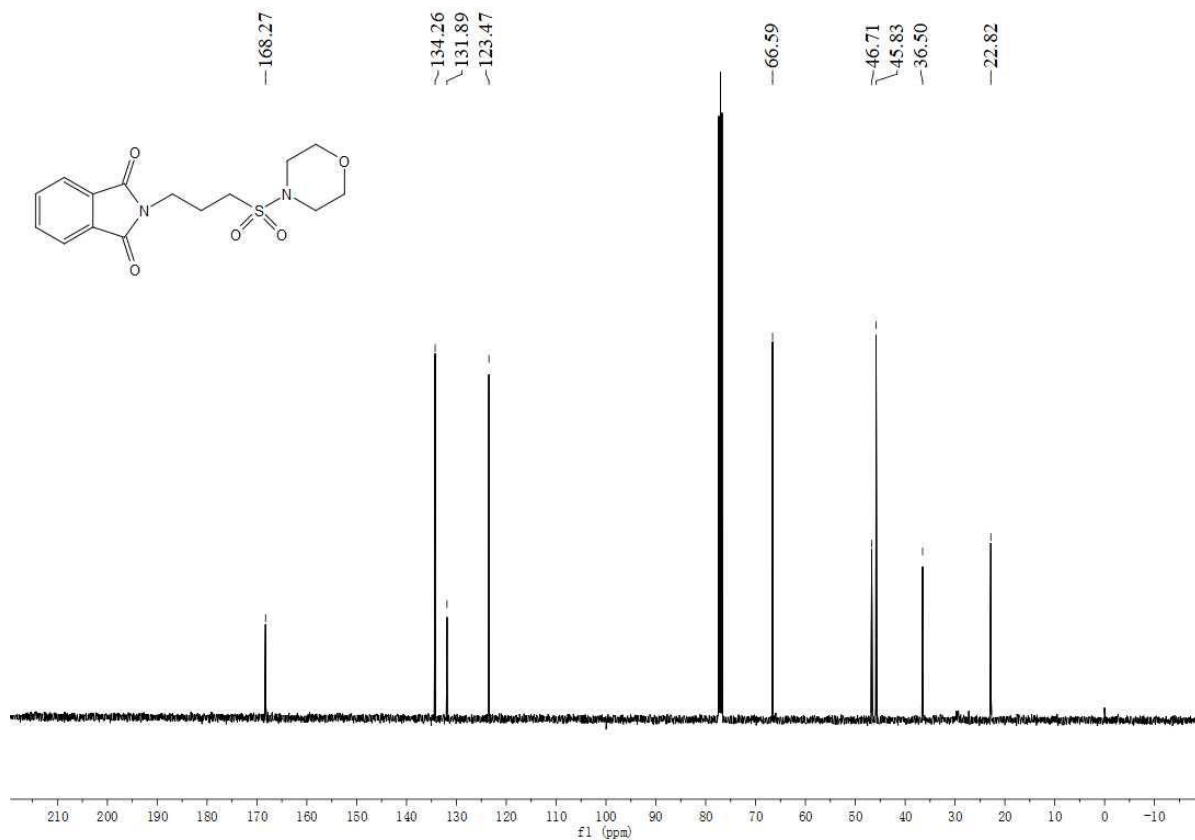


2-(3-(morpholinosulfonyl)propyl)isoindoline-1,3-dione (**8**)

¹H NMR

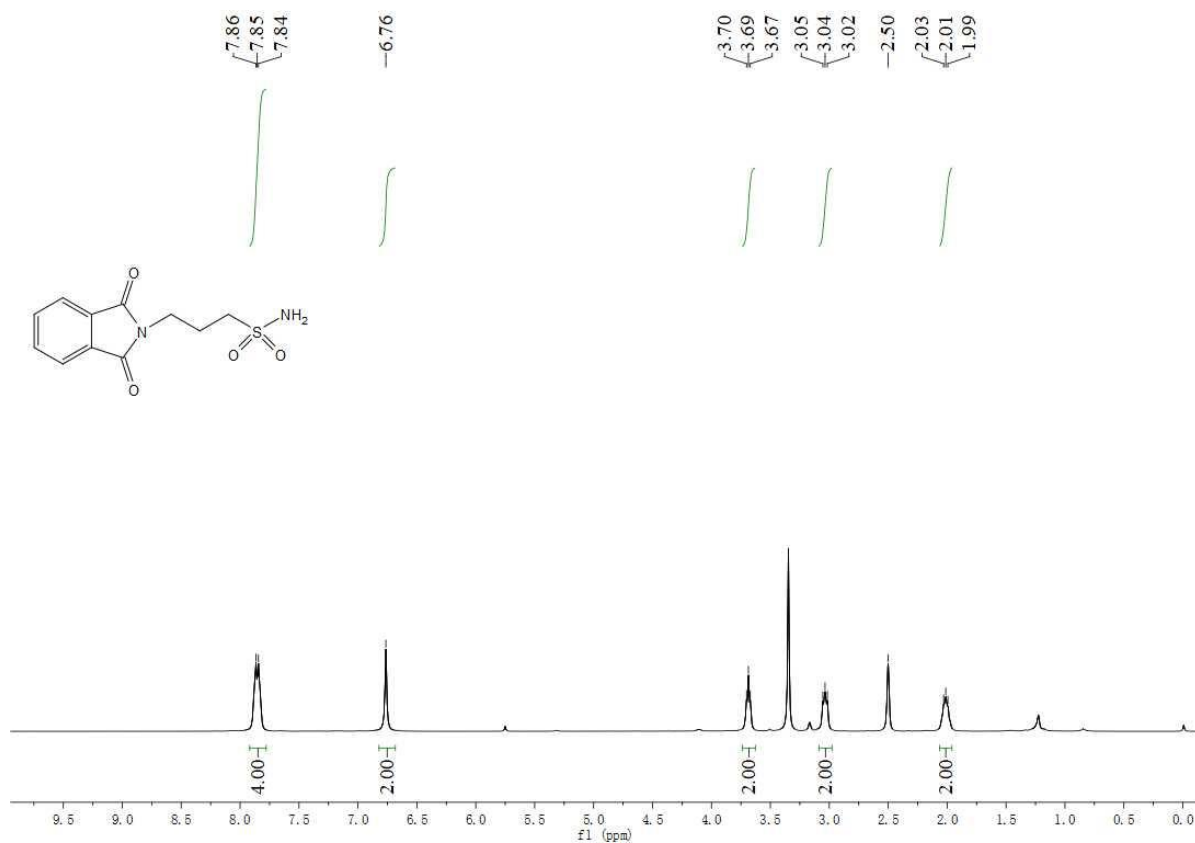


¹³C NMR

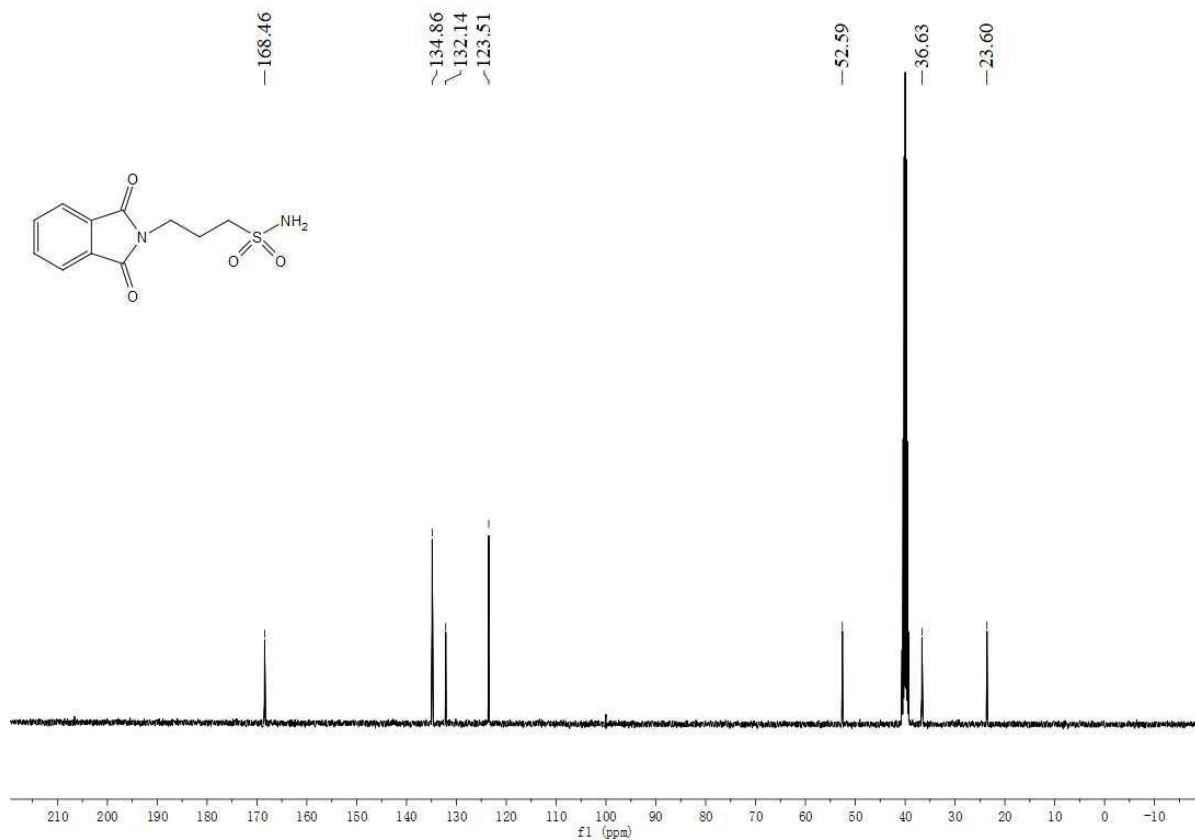


3-(1,3-dioxisoindolin-2-yl)propane-1-sulfonamide (10)

¹H NMR

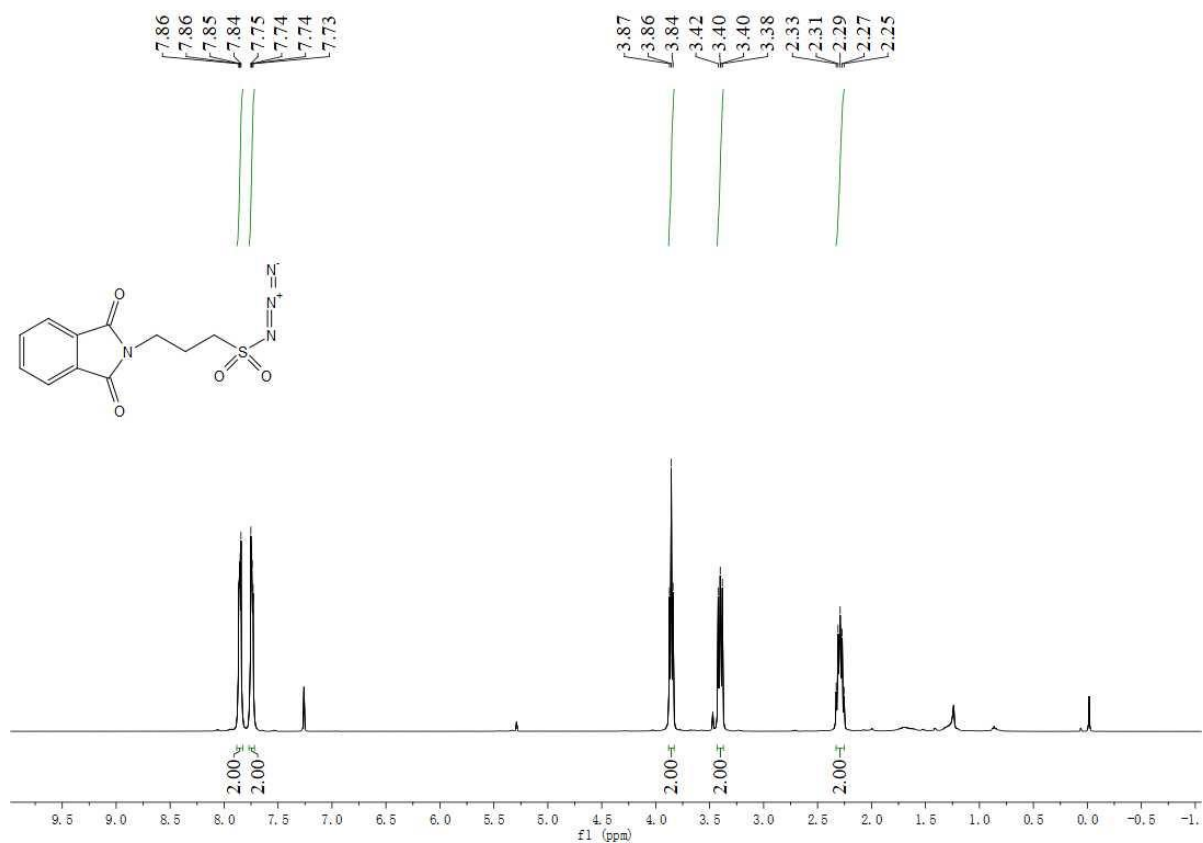


¹³C NMR

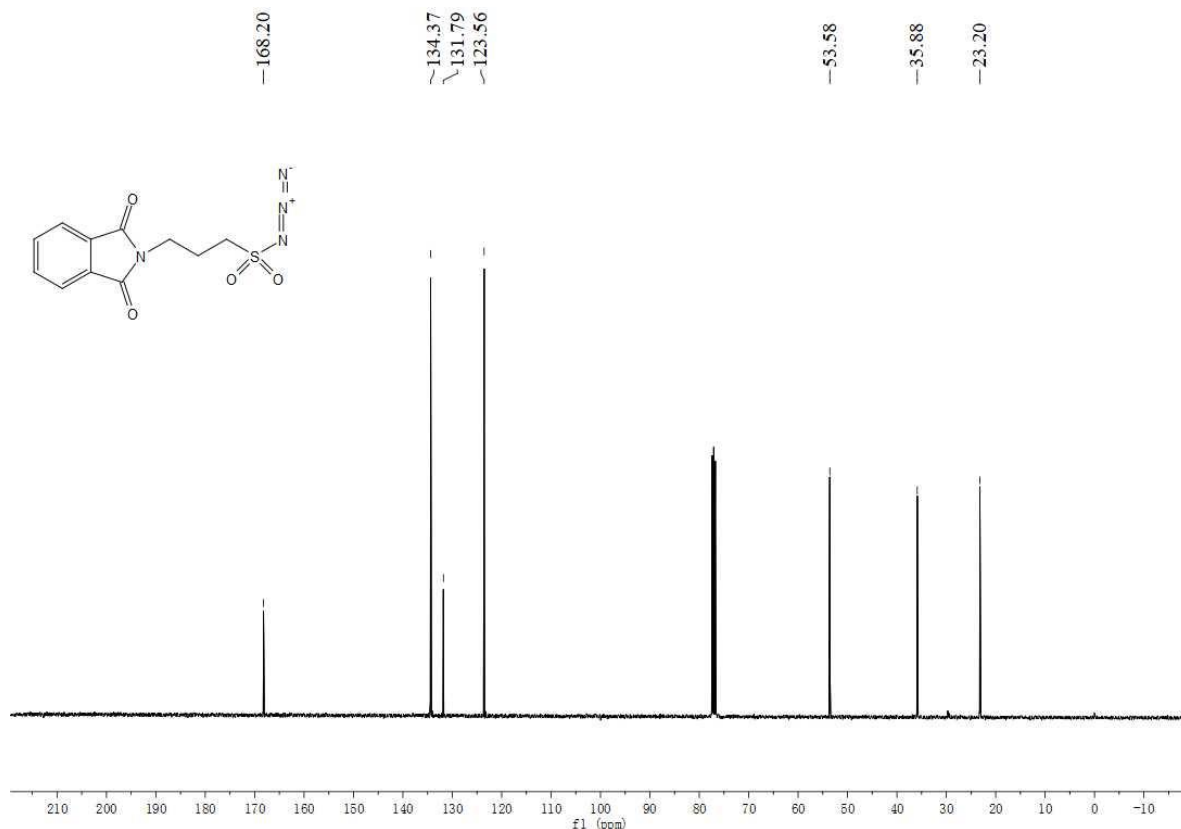


3-(1,3-dioxisoindolin-2-yl)propane-1-sulfonyl azide (12)

¹H NMR

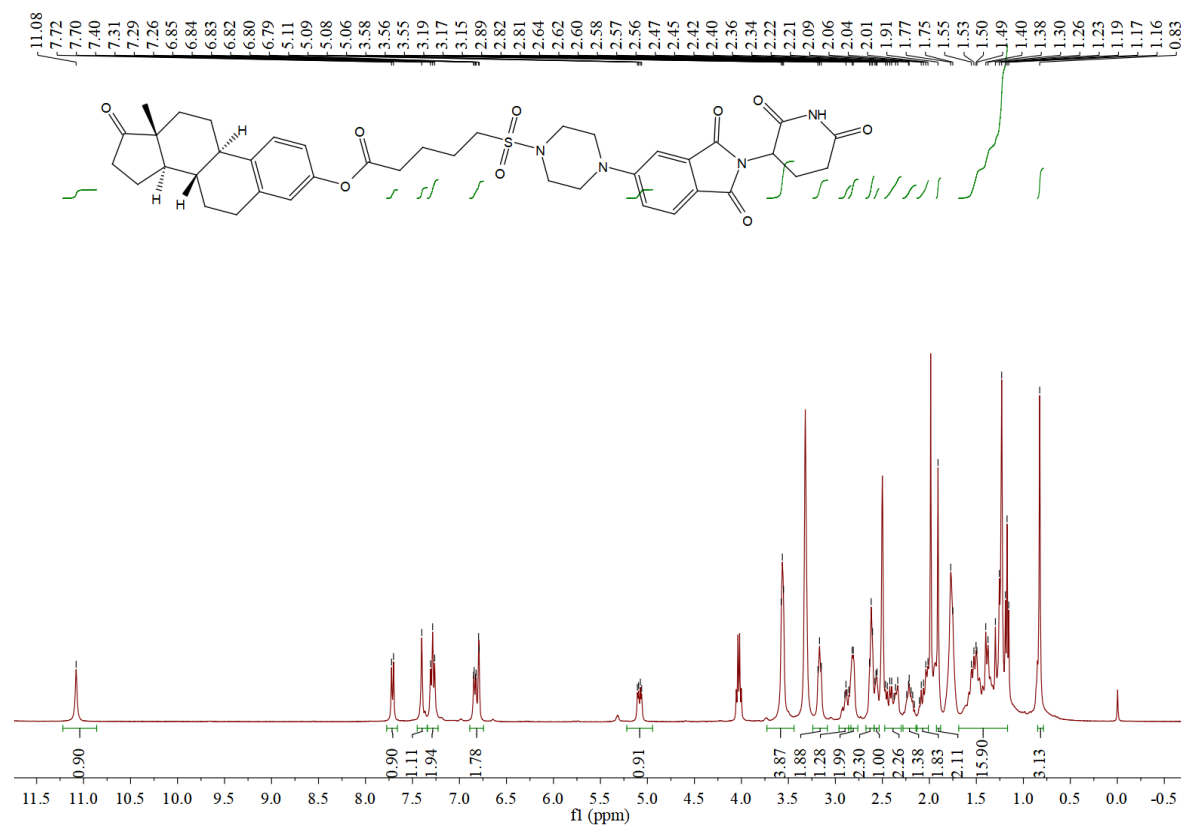


¹³C NMR

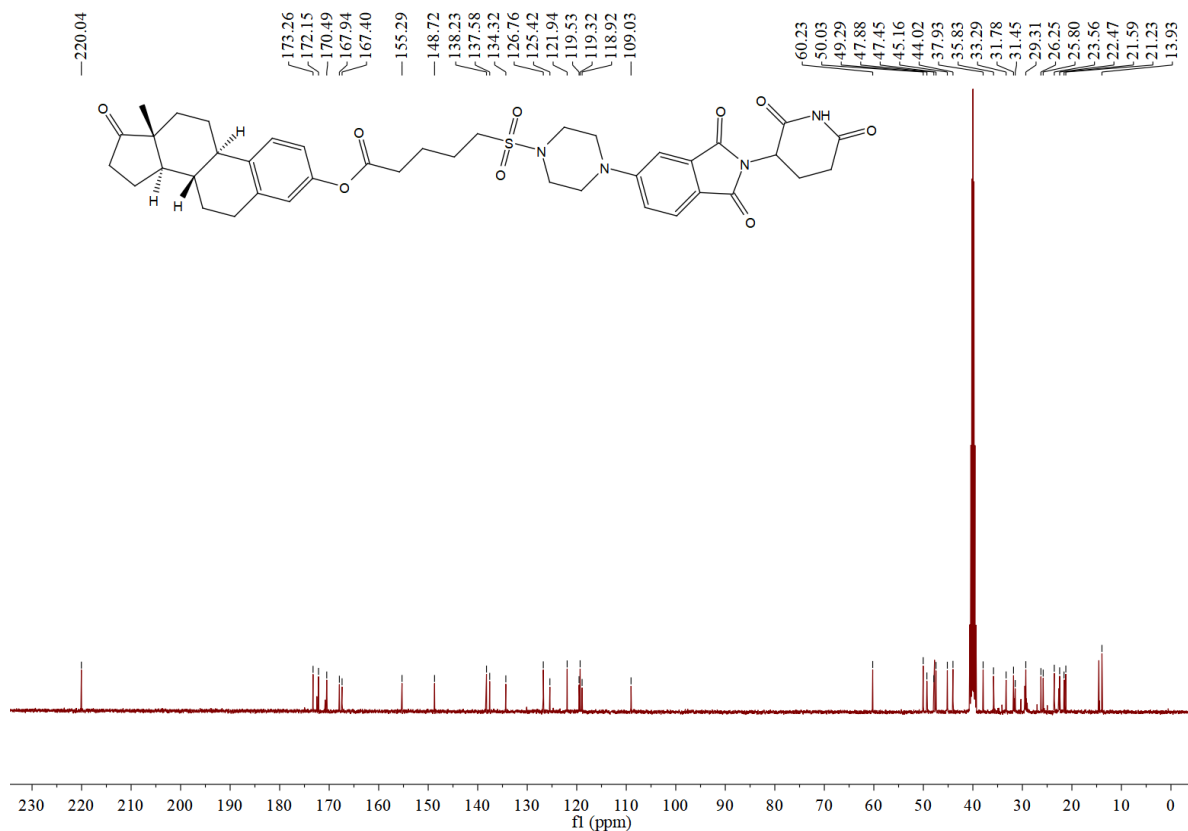


(8*S*,9*R*,13*R*,14*R*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[*a*]phenanthren-3-yl 5-((4-(2-(2,6-dioxopiperidin-3-yl)-1,3-dioxisoindolin-5-yl)piperazin-1-yl)sulfonyl)pentanoate (**14**)

¹H NMR

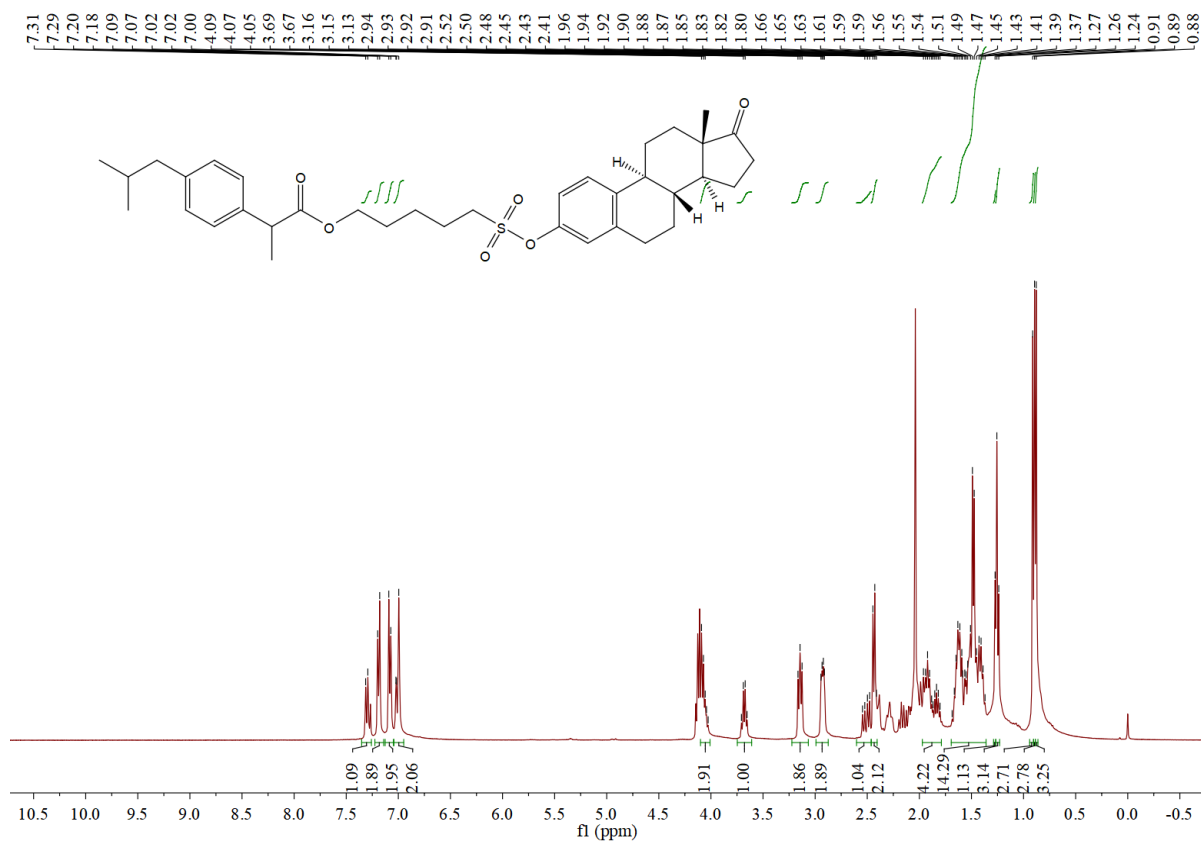


¹³C NMR

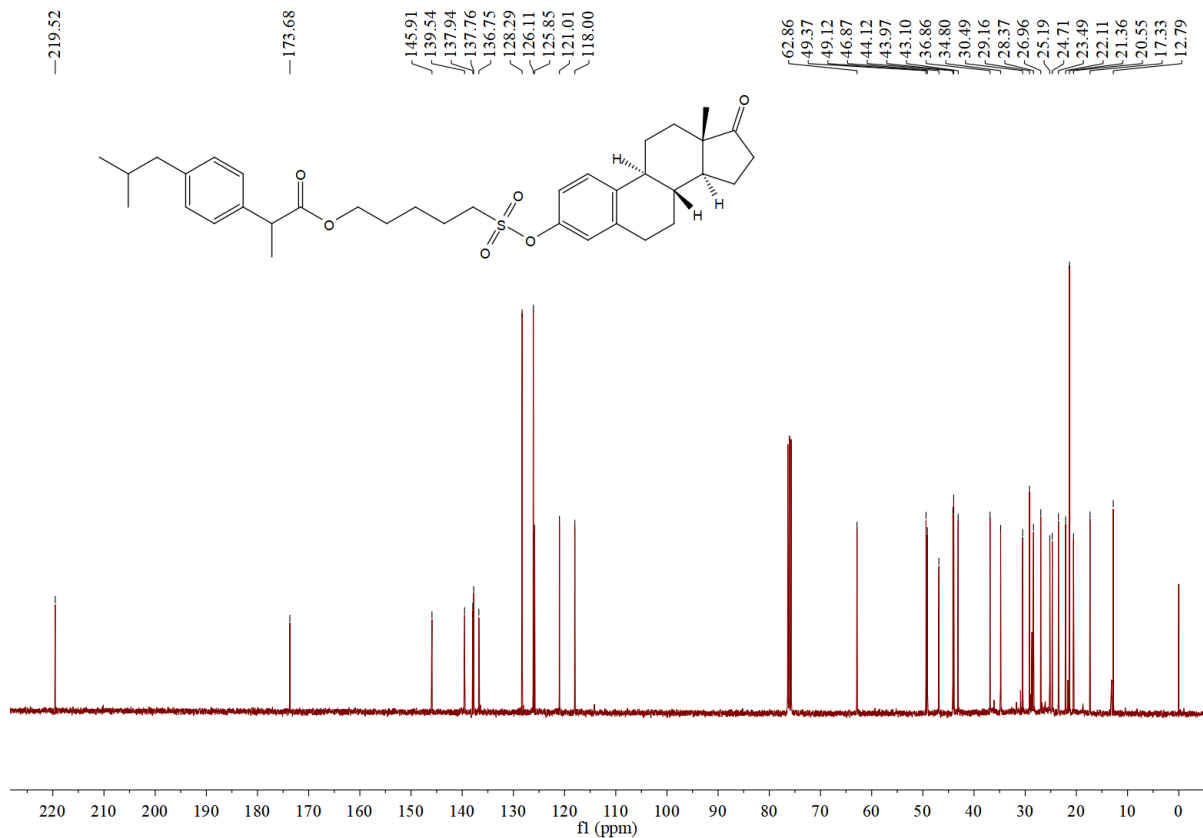


5-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)sulfonyl)pentyl 2-(4-isobutylphenyl)propanoate (**16**)

¹H NMR

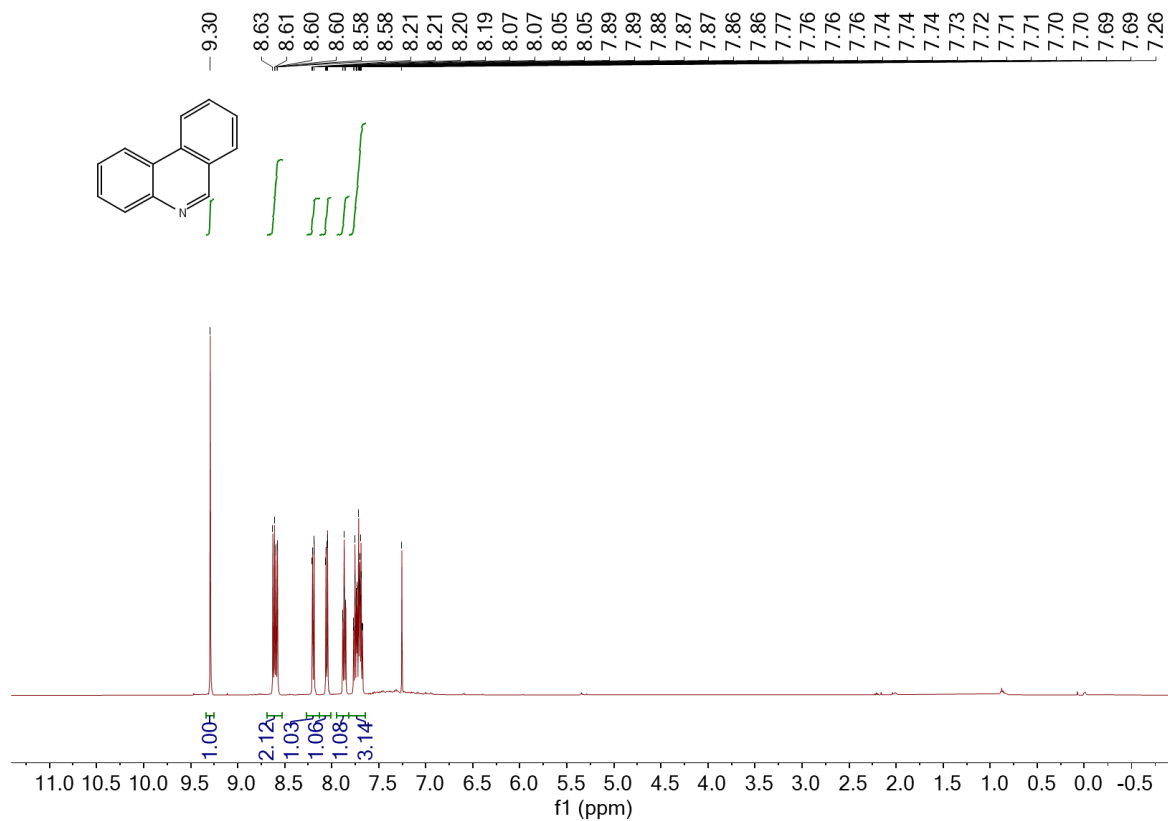


¹³C NMR



Phenanthridine (19)

¹H NMR



¹³C NMR

