Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Rhodium(III)-catalyzed Oxidative Coupling of *N*-Methoxybenzamides and Ethenesulfonyl fluoride: a C-H Bond Activation Strategy for the Preparation of 2-Aryl ethenesulfonyl fluorides and Sulfonyl fluoride Substituted γ-Lactams.

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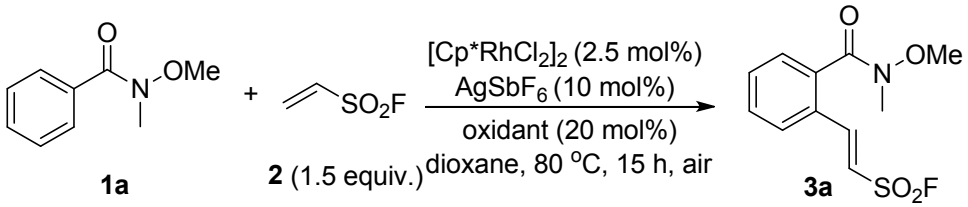
1. General considerations

All reactions were carried out under an air atmosphere. Unless otherwise specified, NMR spectra were recorded in $CDCl_3$ on a 500 MHz (for ^1H), 471 MHz (for ^{19}F), and 126 MHz (for ^{13}C) spectrometer. All chemical shifts were reported in ppm relative to TMS (^1H NMR, 0 ppm) as internal standards. The HPLC experiments were carried out on a Waters e2695 instrument (column: J&K, RP-C18, 5 μm, 4.6 × 150 mm), and the yields of the products were determined by using the corresponding pure compounds as the external standards. Ethenesulfonyl fluoride[1] and N-methoxybenzamides[2] were prepared according to literature. Melting points of the products were measured on a micro melting point apparatus (SGW X-4) and uncorrected. HRMS experiments were performed on a TOF-Q ESI or CI/EI instrument. Reagents used in the reactions were all purchased from commercial sources and used without further purification.

2. Screening the optimized conditions for oxidative coupling of 1a or 6a with 2

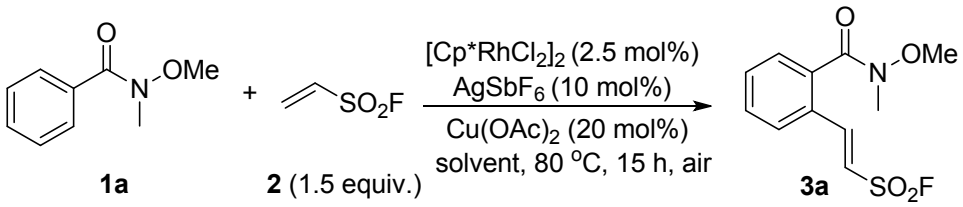
Table 1 The reaction of **1a** with **2** in the presence of different oxidants [a]



Entry	oxidant	Yield (%) [b]
1	$Cu(OAc)_2$	48
2	CuO	trace
3	CuI	trace
4	AgOTf	trace
5	Ag_2CO_3	trace
6	AgTFA	trace
7	Ag_2O	trace
8	$K_2S_2O_8$	trace

[a] Reaction conditions: A mixture of **1a** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), oxidant (20 mol%) and dioxane (2.0 mL) was reacted at 80 °C for 15h. [b] The yield was determined by HPLC using **3a** (t_R = 8.879 min, λ_{max} = 270 nm, water / methanol = 50 : 50 (v / v)) as the external standard.

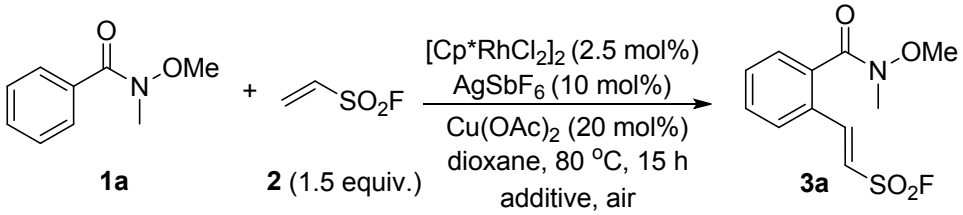
Table 2 The reaction of **1a** with **2** in the presence of different solvents. [a]



Entry	solvent	Yield (%) [b]
1	DCE	53
2	THF	50
3	HFIP	19
4	dioxane	48
5	AcOH	14
6	acetone	34

[a] Reaction conditions: A mixture of **1a** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), $Cu(OAc)_2$ (20 mol%) in solvent (2.0 mL) was reacted at 80 °C for 15h. [b] The yield was determined by HPLC using **3a** (t_R = 8.879 min, λ_{max} = 270 nm, water / methanol = 50 : 50 (v / v)) as the external standard.

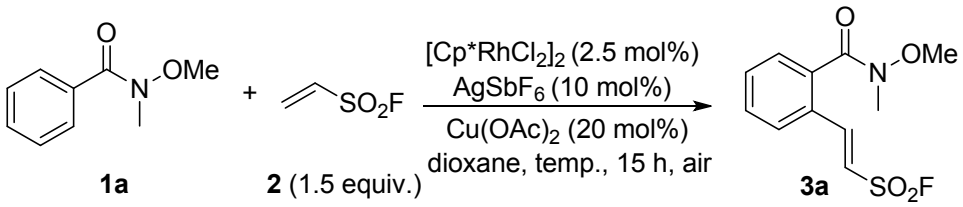
Table 3 The reaction of **1a** with **2** in the presence of different additives. [a]



Entry	Additive	Yield (%) [b]
1	1 equiv. AcOH	9
2	1 equiv. NaOPiv	trace
3	1 equiv. K_3PO_4	trace
4	1 equiv. Cs_2CO_3	trace
5	20 mol% Pyridine	trace
6	20 mol% 2-Picoline	trace
7	20 mol% 2,6-Lutidine	trace

[a] Reaction conditions: A mixture of **1a** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), $Cu(OAc)_2$ (20 mol%) and additive in 1,4-dioxane (2.0 mL) was reacted at 80 °C for 15h. [b] The yield was determined by HPLC using **3a** (t_R = 8.879 min, λ_{max} = 270 nm, water / methanol = 50 : 50 (v / v)) as the external standard.

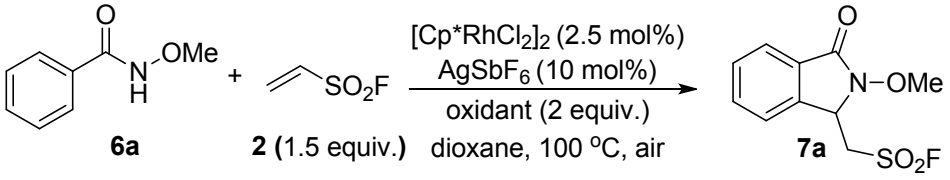
Table 4 The reaction of **1a** with **2** under different temperatures. [a]



Entry	Temp (°C)	Yield (%) [b]
1	80	48
2[c]	80	90
3	100	92
4	120	75
5[d]	100	trace
6[e]	100	trace

[a] Reaction conditions: A mixture of **1a** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), $Cu(OAc)_2$ (20 mol%) in 1,4-dioxane (2.0 mL) was reacted at different temperature for 15h. [b] The yield was determined by HPLC using **3a** (t_R = 8.879 min, λ_{max} = 270 nm, water / methanol = 50 : 50 (v / v)) as the external standard. [c] $AgSbF_6$ (1.0 equiv.) was used. [d] Without $Cu(OAc)_2$. [e] Without $AgSbF_6$.

Table 5 The reaction of **6a** with **2** in the presence of different oxidants [a]

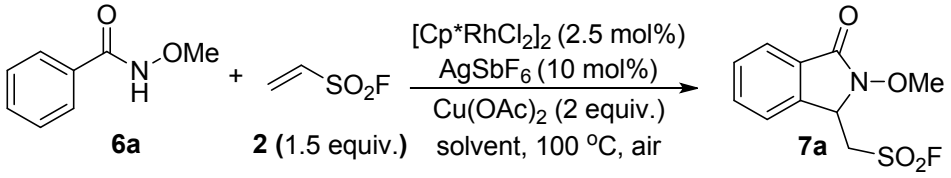


Entry	oxidant	Yield (%) [b]
1	$Cu(OAc)_2$	52
2	CuO	trace
3	CuI	trace
4	CuF_2	38
5	AgOTf	40
6	Ag_2CO_3	trace
7	AgF	trace
8	AgTFA	trace
9	Ag_2O	trace
10	DDQ	trace
11	m-CPBA	trace
12	$K_2S_2O_8$	trace
13[c]	$Cu(OAc)_2$	84

[a] Reaction conditions: A mixture of **6a** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), oxidant (2 equiv.) in dioxane (2.0 mL) was reacted at 100 °C for 15h. [b] The yield was determined by HPLC using **7a** (t_R = 4.592 min, λ_{max} = 230 nm, water / methanol = 50 : 50 (v / v)) as the external

standard. [c] $Cu(OAc)_2$ (20 mol%) was used.

Table 6 The reaction of **6a** with **2** in the presence of different solvents [a]

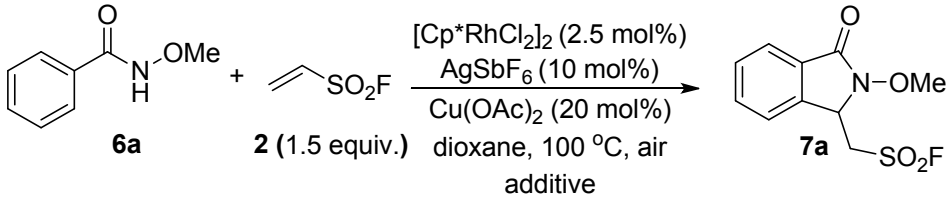


6a **2** (1.5 equiv.) **7a**

Entry	solvent	Yield (%) [b]
1	dioxane	52
2	toluene	28
3	DMF	trace
4	DMSO	trace
5	THF	57
6	DCE	53
7	MeCN	trace

[a] Reaction conditions: A mixture of **6a** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), Cu(OAc) (0.4 mmol, 2 equiv.) in solvent (2.0 mL) was reacted at 100 °C for 15h. [b] The yield was determined by HPLC using **7a** (t_R = 4.592 min, λ_{max} = 230 nm, water / methanol = 50 : 50 (v / v)) as the external standard.

Table 7 The reaction of **6a** with **2** in the presence of different additives [a]

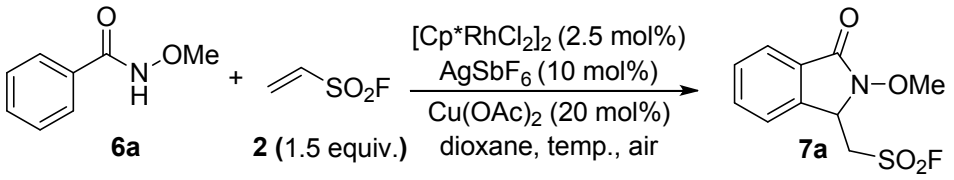


6a **2** (1.5 equiv.) **7a**

Entry	additive	Yield (%) [b]
1	10 mol% PPh_3	35
2	10 mol% DPPP	trace
3	10 mol% bpy	trace
4	10 mol% 1,10-Phen	38
5	1 equiv. AcOH	47
6	1 equiv. TFA	41
7	1 equiv. $NaHCO_3$	trace
8	1 equiv. NaOAc	trace
9	1 equiv. Pyridine	59
10	1 equiv Et_3N	trace

[a] Reaction conditions: A mixture of **6a** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), Cu(OAc) (20 mol%) and additive in dioxane (2.0 mL) was reacted at 100 °C for 15h. [b] The yield was determined by HPLC using **7a** (t_R = 4.592 min, λ_{max} = 230 nm, water / methanol = 50 : 50 (v / v)) as the external standard.

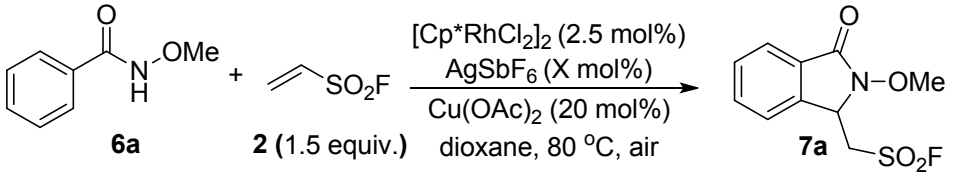
Table 8 The reaction of **6a** with **2** in the presence of different temperature [a]



Entry	Temp. (°C)	Yield (%) [b]
1	100	84
2	120	61
3	80	90
4	60	50

[a] Reaction conditions: A mixture of **6a** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), Cu(OAc) (20 mol%) in dioxane (2.0 mL) was reacted at different temperature for 15h. [b] The yield was determined by HPLC using **7a** (t_R = 4.592 min, λ_{max} = 230 nm, water / methanol = 50 : 50 (v / v)) as the external standard.

Table 9 The reaction of **5a** with **2** in the presence of different $AgSbF_6$ loading [a]

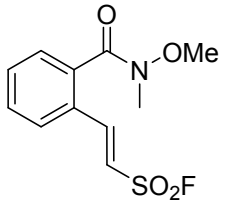


Entry	X	Yield (%) [b]
1	10	84
2	25	80
3	100	95

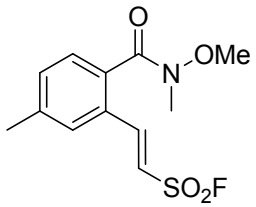
[a] Reaction conditions: A mixture of **6a** (0.2 mmol, 1.0 equiv.), **2** (0.3 mmol, 1.5 equiv.), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (X mol%), Cu(OAc) (20 mol%) in dioxane (2.0 mL) was reacted at 80 °C for 15h. [b] The yield was determined by HPLC using **7a** (t_R = 4.592 min, λ_{max} = 230 nm, water / methanol = 50 : 50 (v / v)) as the external standard.

3. Procedures for the synthesis of 3

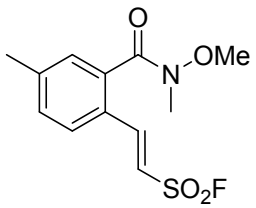
An oven-dried screw cap test tube was charged with *N*-methoxy-*N*-methylbenzamide (**1**, 0.5 mmol), ethenesulfonyl fluoride (ESF, **2**, 0.75 mmol, 1.5 equiv.), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), $Cu(OAc)_2$ (20 mol%) and 1,4-dioxane (5 mL) under an air atomosphere. The resulting mixture was stirred at 100 °C for 15 h before concentrating under vacuum. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluents to give the desired product (**3**).



(*E*)-2-(2-(methoxy(methyl)carbamoyl)phenyl)ethenesulfonyl fluoride (**3a**). Petroleum ether / ethyl acetate = 5 : 1 (v /v) as eluent for column chromatography. Yellow oil, 123.0 mg, 90% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 15.5 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.56-7.47 (m, 3H), 6.87 (d, *J* = 15.5 Hz, 1H), 3.42 (s, 3H), 3.36 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.8 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5 (s), 146.0 (d, *J* = 2.0 Hz), 136.6 (s), 131.8 (s), 130.1 (s), 128.6 (s), 128.0 (s), 127.4 (s), 120.2 (d, *J* = 27.7 Hz), 61.3 (s), 32.7 (s). HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{11}H_{12}FNO_4SNa$: 296.0363, found: 296.0359.

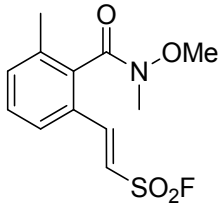


(*E*)-2-(2-(methoxy(methyl)carbamoyl)-5-methylphenyl)ethenesulfonyl fluoride (**3b**). Petroleum ether / ethyl acetate = 5 : 1 (v /v) as eluent for column chromatography. White solid, 104.9 mg, 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 15.5 Hz, 1H), 7.43 (s, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 15.4 Hz, 1H), 3.45 (s, 3H), 3.35 (s, 3H), 2.43 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.9 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7 (s), 146.3 (d, *J* = 1.3 Hz), 140.4 (s), 133.8 (s), 132.6 (s), 128.6 (s), 128.1 (s), 127.9 (s), 119.8 (d, *J* = 28.6 Hz), 61.3 (s), 32.8 (s), 21.3 (s). Mp 98-100 ^{o}C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{14}FNO_4SNa$: 310.0520, found: 310.0520.

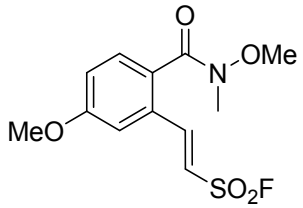


(*E*)-2-(2-(methoxy(methyl)carbamoyl)-4-methylphenyl)ethenesulfonyl fluoride (**3c**). Petroleum ether / ethyl acetate = 5 : 1 (v /v) as eluent for column chromatography. White solid, 99.1 mg, 69% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 15.5 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.28 (s, 1H), 6.82 (d, J = 15.6 Hz, 1H), 3.34 (br, 6H), 2.43 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 62.1 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9 (s), 146.0 (d, *J* = 2.0 Hz), 143.0 (s), 136.8 (s), 130.9 (s), 128.5 (s), 127.4 (s), 125.7 (s), 118.9 (d, *J* = 30.2 Hz), 61.3 (s), 32.6 (s), 21.5 (s).

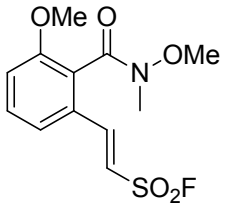
Mp 80-82 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{14}FNO_4SNa$: 310.0520, found: 310.0515.



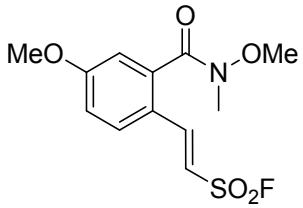
(*E*)-2-(2-(methoxy(methyl)carbamoyl)-3-methylphenyl)ethenesulfonyl fluoride (**3d**). Petroleum ether / ethyl acetate = 5 : 1 (v /v) as eluent for column chromatography. White solid, 90.5 mg, 63% yield. The product were obtained as two rotational isomers. Major : minor = 1 : 0.25. Major: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 15.4 Hz, 1H), 7.45-7.44 (m, 1H), 7.37-7.36 (m, 2H), 6.86 (dd, *J* = 15.4, 2.2 Hz, 1H), 3.41 (s, 3H), 3.36 (s, 3H), 2.34 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.9 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3 (s), 146.3 (d, *J* = 2.8 Hz), 137.1 (s), 136.1 (s), 133.7 (s), 129.3 (s), 127.8 (s), 124.6 (s), 120.0 (d, *J* = 28.2 Hz), 61.4 (s), 32.5 (s), 19.2 (s). Minor: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 15.5 Hz, 0.25H), 7.45-7.44 (m, 0.36H), 7.40-7.39 (m, 0.56H), 6.92 (dd, *J* = 15.5, 1.9 Hz, 0.26H), 3.94 (s, 0.75H), 3.01 (s, 0.73H), 2.37 (s, 0.81H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.8 (s, 0.23F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.9 (s), 145.1 (d. *J* = 2.7 Hz), 136.2 (s), 136.1 (s), 134.3 (s), 130.0 (s), 127.9 (s), 125.4 (s), 121.0 (d, *J* = 28.5 Hz), 61.0 (s), 35.7 (s), 18.9 (s). Mp 77-79 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{14}FNO_4SNa$: 310.0520, found: 310.0515.



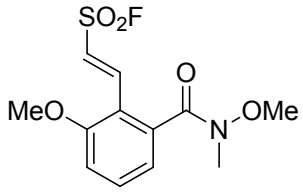
(*E*)-2-(5-methoxy-2-(methoxy(methyl)carbamoyl)phenyl)ethenesulfonyl fluoride (**3e**). Petroleum ether / ethyl acetate = 3 : 1 (v /v) as eluent for column chromatography. Yellow solid, 110.7 mg, 73% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 15.4 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.07 (s, 1H), 7.06 (d, *J* = 11.6 Hz, 1H), 6.83 (d, *J* = 15.3 Hz, 1H), 3.88 (s, 3H), 3.46 (s, 3H), 3.34 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.9 (s). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2 (s), 160.7 (s), 146.3 (s), 130.5 (s), 123.0 (s), 128.7 (s), 120.2 (d, *J* = 28.2 Hz), 117.2 (s), 112.4 (s), 61.2 (s), 55.6 (s), 33.3 (s). Mp 89-92 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{14}FNO_5SNa$: 326.0469, found: 326.0465.



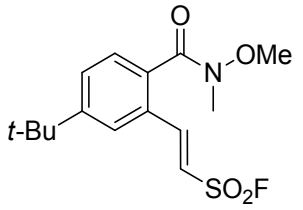
(*E*)-2-(3-methoxy-2-(methoxy(methyl)carbamoyl)phenyl)ethenesulfonyl fluoride (**3f**). Petroleum ether / ethyl acetate = 3 : 1 (v /v) as eluent for column chromatography. White solid, 109.2 mg, 72% yield. The product were obtained as two rotational isomers. Major : minor = 1 : 0.28. Major: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 15.5 Hz, 1H), 7.42 (t, *J* = 8.1 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 8.3 Hz, 1H), 6.88 (dd, *J* = 15.5, 1.9 Hz, 1H), 3.86 (s, 3H), 3.41 (s, 3H), 3.39 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.8 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1 (s), 156.4 (s), 145.6 (d, *J* = 2.4 Hz), 130.5 (s), 129.1 (s), 127.0 (s), 120.7 (d, *J* = 28.3 Hz), 119.4 (s), 114.4 (s), 61.4 (s), 56.2 (s), 32.4 (s). Minor: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 15.5 Hz, 0.28H), 7.42 (t, *J* = 8.1 Hz, 0.36H), 7.19 (d, *J* = 7.8 Hz, 0.39H), 7.07 (d, *J* = 8.3 Hz, 0.34H), 6.94 (d, *J* = 15.6 Hz, 0.32H), 3.89 (s, 0.93H), 3.86 (s, 1.06H), 3.05 (s, 0.81H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.7 (s, 0.28F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1 (s), 144.8 (s), 131.3 (s), 129.5 (s), 126.0 (s), 121.4 (d, *J* = 28.2 Hz), 119.9 (s), 114.5 (s), 60.9 (s), 35.8 (s). Theoretically, there should be twelve peaks, due to the compact overlaying, it is difficult to specify the overlaying peaks. Mp 129-131 ^{o}C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{14}FNO_5SNa$: 326.0469, found: 326.0464.



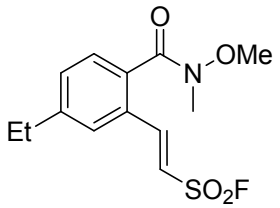
(*E*)-2-(4-methoxy-2-(methoxy(methyl)carbamoyl)phenyl)ethenesulfonyl fluoride (**3g**). Petroleum ether / ethyl acetate = 3 : 1 (v /v) as eluent for column chromatography. Yellow solid, 51.6 mg, 34% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 15.4 Hz, 1H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 1H), 6.96 (s, 1H), 6.72 (d, *J* = 15.3 Hz, 1H), 3.88 (s, 3H), 3.41 (br, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 62.6 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4 (s), 162.4 (s), 145.6 (d, *J* = 4.6 Hz), 138.9 (s), 129.4 (s), 120.7 (s), 116.9 (d, *J* = 28.1 Hz), 116.0 (s), 113.0 (s), 61.4 (s), 55.8 (s), 32.5 (s). Mp 102-104 ^{o}C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{14}FNO_5SNa$: 326.0469, found: 326.0467.



(*E*)-2-(2-methoxy-6-(methoxy(methyl)carbamoyl)phenyl)ethenesulfonyl fluoride (**3h**). Petroleum ether / ethyl acetate = 3 : 1 (v /v) as eluent for column chromatography. Yellow oil, 54.6 mg, 36% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 15.3 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.26 (d, *J* = 15.3 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 2H), 3.97 (s, 3H), 3.39 (s, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.6 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.2 (s), 159.3 (s), 141.9 (d, *J* = 2.0 Hz), 139.2 (s), 132.9 (s), 121.7 (d, *J* = 24.6 Hz), 119.4 (s), 112.0 (s), 100.0 (s), 61.4 (s), 56.0 (s), 32.5 (s). HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{14}FNO_5SNa$: 326.0469, found: 326.0466.

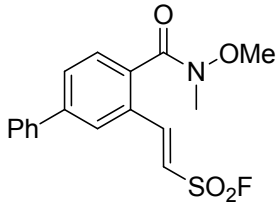


(*E*)-2-(5-(tert-butyl)-2-(methoxy(methyl)carbamoyl)phenyl)ethenesulfonyl fluoride (**3i**). Petroleum ether / ethyl acetate = 5 : 1 (v /v) as eluent for column chromatography. White solid, 107.1 mg, 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 15.5 Hz, 1H), 7.58 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 6.87 (d, *J* = 15.2 Hz, 1H), 3.47 (s, 3H), 3.35 (s, 3H), 1.35 (s, 9H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 62.0 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.5 (s), 153.6 (s), 146.7 (s), 133.8 (s), 129.1 (s), 128.3 (s), 127.9 (s), 124.4 (s), 119.8 (d, *J* = 28.6 Hz), 61.3 (s), 35.0 (s), 31.2 (s), 31.1 (s). Mp 82-83 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{15}H_{20}FNO_4SNa$: 352.0989, found: 352.0985.

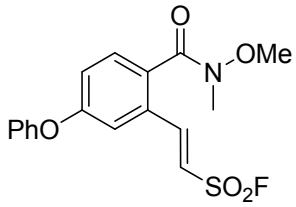


(*E*)-2-(5-ethyl-2-(methoxy(methyl)carbamoyl)phenyl)ethenesulfonyl fluoride (**3j**). Petroleum ether / ethyl acetate = 5 : 1 (v /v) as eluent for column chromatography. White solid, 78.3 mg, 52% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 15.5 Hz, 1H), 7.43 (s, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 15.4 Hz, 1H), 3.46 (s, 3H), 3.34 (s, 3H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.9 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6 (s), 146.6 (s), 146.3 (s), 134.0 (s), 131.5 (s), 128.6 (s), 128.2 (s), 126.8 (s), 119.8 (d, *J* =

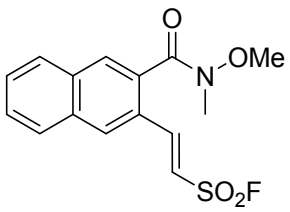
27.4 Hz), 61.3 (s), 33.1 (s), 28.6 (s), 15.1 (s). Mp 85-87 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{13}H_{16}FNO_4SNa$: 324.0676, found: 324.0674.



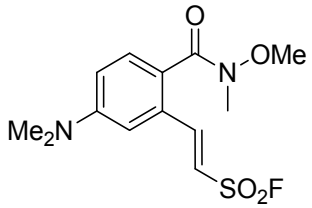
(*E*)-2-(4-(methoxy(methyl)carbamoyl)-[1,1'-biphenyl]-3-yl)ethenesulfonyl fluoride (**3k**). Petroleum ether / ethyl acetate = 5 : 1 (v /v) as eluent for column chromatography. White solid, 118.8 mg, 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 15.5 Hz, 1H), 7.80 (d, *J* = 1.1 Hz, 1H), 7.75 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.61-7.57 (m, 3H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 6.94 (d, *J* = 15.5 Hz, 1H), 3.50 (s, 3H), 3.39 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.9 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4 (s), 146.1 (s), 143.3 (s), 139.0 (s), 135.1 (s), 130.3 (s), 129.2 (s), 129.2 (s), 128.7 (s), 128.5 (s), 127.2 (s), 126.1 (s), 120.5 (d, *J* = 28.1 Hz), 61.4 (s), 33.0 (s). Mp 116-117 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{17}H_{16}FNO_4SNa$: 372.0676, found: 372.0671.



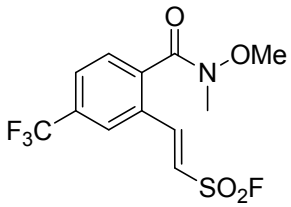
(*E*)-2-(2-(methoxy(methyl)carbamoyl)-5-phenoxyphenyl)ethenesulfonyl fluoride (**3l**). Petroleum ether / ethyl acetate = 3 : 1 (v /v) as eluent for column chromatography. White solid, 124.2 mg, 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 15.5 Hz, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 1.9 Hz, 1H), 7.12 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.05 (d, *J* = 7.7 Hz, 2H), 6.76 (dd, *J* = 15.4, 1.7 Hz, 1H), 3.48 (s, 3H), 3.35 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.9 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0 (s), 159.1 (s), 155.4 (s), 145.6 (s), 130.7 (s), 130.7 (d, *J* = 3.1 Hz), 130.3 (s), 130.1 (s), 124.9 (s), 120.9 (s), 120.7 (d, *J* = 28.5 Hz), 119.9 (s), 116.1 (s), 61.3 (s), 32.9 (s). Mp 118-120 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{17}H_{16}FNO_5SNa$: 388.0625, found: 388.0621.



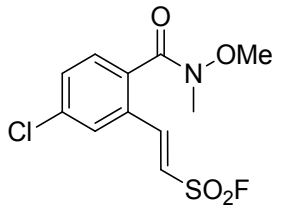
(*E*)-2-(3-(methoxy(methyl)carbamoyl)naphthalen-2-yl)ethenesulfonyl fluoride (**3m**). Petroleum ether / ethyl acetate = 3 : 1 (v /v) as eluent for column chromatography. White solid, 111.5 mg, 69% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.02 (d, *J* = 15.5 Hz, 1H), 7.98 (s, 1H), 7.90 (d, *J* = 9.6 Hz, 2H), 7.65-7.60 (m, 2H), 6.95 (dd, *J* = 15.4, 1.3 Hz, 1H), 3.45 (s, 3H), 3.40 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 62.0 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7 (s), 146.7 (s), 133.8 (s), 132.9 (s), 132.4 (s), 129.2 (s), 129.0 (s), 128.7 (s), 128.3 (s), 128.3 (s), 128.1 (s), 126.2 (s), 119.9 (d, *J* = 28.1 Hz), 61.3 (s), 33.2 (s). Mp 121-122 ^{o}C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{15}H_{14}FNO_4SNa$: 346.0520, found: 346.0517.



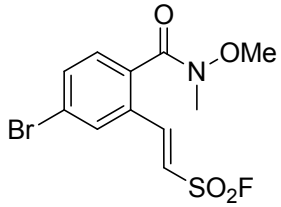
(*E*)-2-(5-(dimethylamino)-2-(methoxy(methyl)carbamoyl)phenyl)ethenesulfonyl fluoride (**3n**). Petroleum ether / ethyl acetate = 2 : 1 (v /v) as eluent for column chromatography. Orange solid, 117.0 mg, 74% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 15.4 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 1H), 6.83-6.74 (m, 3H), 3.47 (s, 3H), 3.29 (s, 3H), 3.02 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 62.0 (s). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.9 (s), 151.1 (s), 148.1 (d, *J* = 2.0 Hz), 130.4 (s), 129.9 (s), 122.9 (s), 119.0 (d, *J* = 27.7 Hz), 114.5 (s), 109.4 (s), 61.1 (s), 40.1 (s), 33.7 (s). Mp 90-91 ^{o}C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{13}H_{17}FN_2O_4SNa$: 339.0785, found: 339.0781.



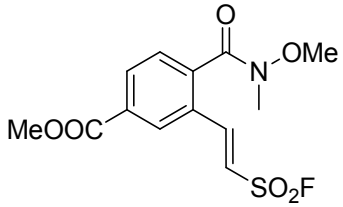
(*E*)-2-(2-(methoxy(methyl)carbamoyl)-5-(trifluoromethyl)phenyl)ethenesulfonyl fluoride (**3o**). Petroleum ether / ethyl acetate = 5 : 1 (v /v) as eluent for column chromatography. White solid, 99.0 mg, 58% yield.^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 14.2 Hz, 1H), 7.86 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 15.4 Hz, 1H), 3.40 (s, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.6 (s, 1F), -63.1 (s, 3F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4 (s), 144.3 (s), 139.7 (s), 132.4 (q, *J* = 33.4 Hz), 129.6 (s), 128.7 (s), 128.1 (s), 124.3 (s), 123.1 (q, *J* = 273.2 Hz), 122.3 (d, *J* = 30.0 Hz), 61.5 (s), 32.5 (s). Mp 95-97 ^{o}C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{11}F_4NO_4SNa$: 364.0237, found: 364.0234.



(*E*)-2-(5-chloro-2-(methoxy(methyl)carbamoyl)phenyl)ethenesulfonyl fluoride (**3p**). Petroleum ether / ethyl acetate = 5 : 1 (v /v) as eluent for column chromatography. White solid, 110.8 mg, 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 15.5 Hz, 1H), 7.60 (s, 1H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 6.89 (d, *J* = 15.4 Hz, 1H), 3.44 (s, 3H), 3.35 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.7 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5 (s), 144.6 (s), 136.3 (s), 134.7 (s), 131.6 (s), 130.5 (s), 129.5 (s), 127.3 (s), 121.6 (d, *J* = 28.8 Hz), 61.4 (s), 32.7 (s). Mp 92-94 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{11}H_{11}ClFNO_4SNa$: 329.9974, found: 329.9973, 331.9945.

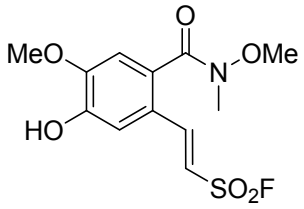


(*E*)-2-(5-bromo-2-(methoxy(methyl)carbamoyl)phenyl)ethenesulfonyl fluoride (**3q**). Petroleum ether / ethyl acetate = 5 : 1 (v /v) as eluent for column chromatography. Yellow solid, 142.6 mg, 81% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 15.5 Hz, 1H), 7.76 (s, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 6.88 (d, *J* = 15.6 Hz, 1H), 3.44 (s, 3H), 3.36 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.8 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6 (s), 144.5 (s), 135.2 (s), 134.5 (s), 130.7 (s), 130.2 (s), 129.6 (s), 124.3 (s), 121.6 (d, *J* = 29.0 Hz), 61.5 (s), 32.7 (s). Mp 93-95 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{11}H_{11}BrFNO_4SNa$: 373.9468, found: 373.9466, 375.9448.

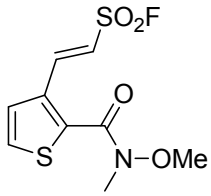


(*E*)-methyl 3-(2-(fluorosulfonyl)vinyl)-4-(methoxy(methyl)carbamoyl)benzoate (**3r**). Petroleum ether / ethyl acetate = 3 : 1 (v /v) as eluent for column chromatography. White solid, 129.2 mg, 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 15.5 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 15.3 Hz, 1H), 3.97 (s, 3H), 3.39 (s, 6H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.7 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.8 (s), 165.3 (s), 144.9 (s), 140.4 (s), 132.3 (s),

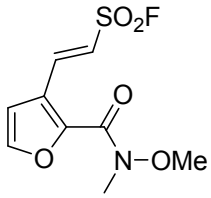
131.8 (s), 129.0 (s), 128.5 (s), 128.2 (s), 121.5 (d, J = 26.7 Hz), 61.5 (s), 52.7 (s), 32.5 (s). Mp 110-112 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{13}H_{14}FNO_6SNa$: 354.0418, found: 354.0415.



(*E*)-2-(5-hydroxy-4-methoxy-2-(methoxy(methyl)carbamoyl)phenyl)ethenesulfonyl fluoride (**3s**). Petroleum ether / ethyl acetate = 2 : 1 (v /v) as eluent for column chromatography. Brown solid, 87.8 mg, 55% yield. ^{1}H NMR (500 MHz, DMSO-d6) δ 9.76 (s, 1H), 7.66 (s, 2H), 7.39 (s, 1H), 7.09 (s, 1H), 3.88 (s, 3H), 3.52 (s, 3H), 3.25 (s, 3H). ^{19}F NMR (471 MHz, DMSO-d6) δ 63.0 (s, 1F). ^{13}C NMR (126 MHz, DMSO-d6) δ 172.5 (s), 156.3 (s), 153.0 (s), 150.8 (s), 135.3 (s), 126.2 (s), 122.2 (d, J = 25.5 Hz), 118.9 (d, J = 6.1 Hz), 115.9 (s), 66.1 (s), 61.3 (s), 38.4 (s). Mp 88-89 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{14}FNO_6SNa$: 324.0418, found: 324.0414.

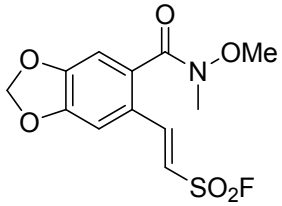


(*E*)-2-(2-(methoxy(methyl)carbamoyl)thiophen-3-yl)ethenesulfonyl fluoride (**3t**). Petroleum ether / ethyl acetate = 2 : 1 (v /v) as eluent for column chromatography. White solid, 93.6 mg, 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, J = 15.6 Hz, 1H), 7.54 (d, J = 5.3 Hz, 1H), 7.30 (d, J = 5.3 Hz, 1H), 6.75 (d, J = 15.6 Hz, 1H), 3.71 (s, 3H), 3.37 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 62.5 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.7 (s), 142.5 (d, J = 2.6 Hz), 138.2 (s), 133.5 (s), 130.9 (s), 125.7 (s), 119.8 (d, J = 28.1 Hz), 61.8 (s), 33.1 (s). Mp 100-101 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_9H_{10}FNO_4S_2Na$: 301.9928, found: 301.9924.



(*E*)-2-(2-(methoxy(methyl)carbamoyl)furan-3-yl)ethenesulfonyl fluoride (**3u**). Petroleum ether / ethyl acetate = 2 : 1 (v /v) as eluent for column chromatography. White solid, 110.5 mg, 84% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, J = 15.6 Hz, 1H), 7.53 (d, J = 1.7 Hz, 1H), 6.75 (d, J = 15.6 Hz, 1H), 6.70 (d, J = 1.7 Hz, 1H), 3.82 (s, 3H), 3.34 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 62.2 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3 (s), 146.9 (s), 144.6 (s), 139.5 (s), 124.3 (s), 120.4 (d, J = 28.7

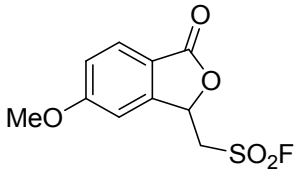
Hz), 109.2 (s), 62.2 (s), 33.7 (s). Mp 95-97 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_9H_{10}FNO_5SNa$: 286.0156, found: 286.0152.



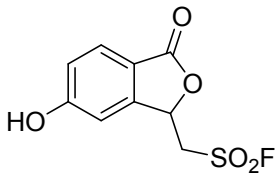
(*E*)-2-(6-(methoxy(methyl)carbamoyl)benzo[d][1,3]dioxol-5-yl)ethenesulfonyl fluoride (**3v**). Petroleum ether / ethyl acetate = 2 : 1 (v /v) as eluent for column chromatography. Yellow oil, 71.4 mg, 45% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 15.4 Hz, 1H), 7.27 (d, *J* = 15.3 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.18 (s, 2H), 3.49 (s, 3H), 3.34 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.9 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7 (s), 149.0 (s), 147.6 (s), 140.6 (s), 129.9 (s), 122.3 (d, *J* = 28.0 Hz), 122.1 (s), 111.9 (s), 110.9 (s), 102.6 (s), 61.3 (s), 33.2 (s). HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{12}H_{12}FNO_6SNa$: 340.0262, found: 340.0258.

4. Procedures for the synthesis of 5

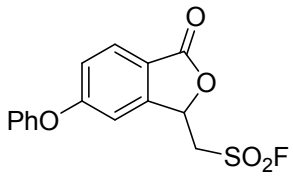
An oven-dried screw cap test tube was charged with *N*-methoxy-*N*-methylbenzamide (**1**, 0.5 mmol), ethenesulfonyl fluoride (ESF, **2**, 0.75 mmol, 1.5 equiv.), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (0.5 mmol, 1 equiv.), $Cu(OAc)_2$ (20 mol%) and 1,4-dioxane (5 mL) under an air atomosphere. The resulting mixture was stirred at 100 °C for 15 h before concentrating under vacuum. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluents to give the desired products (**5**).



(6-Methoxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)methanesulfonyl fluoride (**5a**). Petroleum ether / ethyl acetate = 3 : 1 (v /v) as eluent for column chromatography. White solid, 98.9 mg, 76% yield. ^{1}H NMR (500 MHz, DMSO-d6) δ 7.79 (d, *J* = 8.5 Hz, 1H), 7.44 (s, 1H), 7.18 (d, *J* = 8.5 Hz, 1H), 6.03 (d, *J* = 8.5 Hz, 1H), 5.02 (dd, *J* = 15.1, 9.6 Hz, 1H), 4.61 (dd, *J* = 15.2, 9.4 Hz, 1H), 3.89 (s, 3H). ^{19}F NMR (471 MHz, DMSO) δ 61.0 (d, *J* = 9.8 Hz, 1F). ^{13}C NMR (126 MHz, DMSO-d6) δ 169.0 (s), 165.0 (s), 149.8 (s), 127.2 (s), 118.0 (s), 117.7 (s), 107.9 (s), 74.3 (s), 56.5 (s), 53.9 (d, *J* = 13.8 Hz). Mp 175-177 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{10}H_9FO_5SNa$: 283.0047, found: 283.0047.



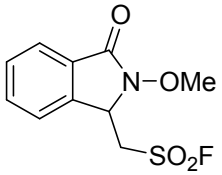
(6-Hydroxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)methanesulfonyl fluoride (**5b**). Petroleum ether / ethyl acetate = 2 : 1 (v /v) as eluent for column chromatography. White solid, 83.7 mg, 68% yield. ^{1}H NMR (500 MHz, DMSO-d6) δ 10.86 (s, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.13 (s, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 5.95 (d, *J* = 9.0 Hz, 1H), 4.97 (dd, *J* = 15.0, 10.2 Hz, 1H), 4.57 (dd, *J* = 15.2, 9.3 Hz, 1H). ^{19}F NMR (471 MHz, DMSO-d6) δ 61.4 (d, *J* = 10.1 Hz, 1F). ^{13}C NMR (126 MHz, DMSO-d6) δ 169.1 (s), 163.9 (s), 149.8 (s), 127.5 (s), 118.6 (s), 116.1 (s), 109.6 (s), 74.0 (s), 54.0 (d, *J* = 13.5 Hz). Mp 213-214 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_9H_7FO_5SNa$: 268.9890, found: 268.9891.



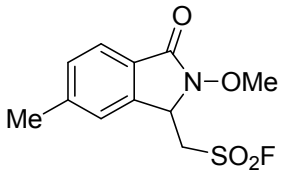
(3-Oxo-6-phenoxy-1,3-dihydroisobenzofuran-1-yl)methanesulfonyl fluoride (**5c**). Petroleum ether / ethyl acetate = 2 : 1 (v /v) as eluent for column chromatography. White solid, 106.4 mg, 66% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.5 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.19 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 7.04 (s, 1H), 5.85 (dd, *J* = 8.0, 3.2 Hz, 1H), 3.94 (ddd, *J* = 15.2, 8.3, 3.5 Hz, 1H), 3.78 (dd, *J* = 15.3, 8.1 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.2 (d, *J* = 8.2 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0 (s), 164.2 (s), 154.6 (s), 148.0 (s), 130.5 (s), 128.2 (s), 125.7 (s), 120.6 (s), 120.2 (s), 119.1 (s), 109.9 (s), 73.3 (s), 54.6 (d, *J* = 17.5 Hz). Mp 118-120 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{15}H_{11}FO_5SNa$: 345.0203, found: 345.0200.

5. Procedures for the synthesis of 7

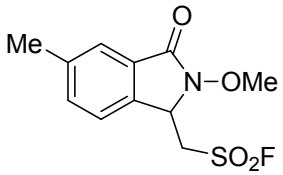
An oven-dried screw cap test tube was charged with *N*-methoxybenzamide (**6**, 0.5 mmol), ethenesulfonyl fluoride (ESF, **2**, 0.75 mmol, 1.5 equiv.), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (0.5 mmol, 1 equiv.), $Cu(OAc)_2$ (20 mol%) and 1,4-dioxane (5 mL) under an air atomosphere. The resulting mixture was stirred at 80 °C for 15 h before concentrating under vacuum. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluents to give the desired products (**7**).



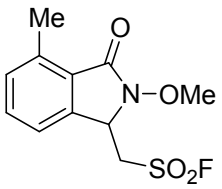
(2-Methoxy-3-oxoisoindolin-1-yl)methanesulfonyl fluoride (**7a**). Petroleum ether / ethyl acetate = 3 : 1 (v /v) as eluent for column chromatography. Yellow solid, 118.0 mg, 91% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 1H), 7.69-7.63 (m, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 5.25 (dd, *J* = 6.4, 4.3 Hz, 1H), 4.14 (dt, *J* = 15.2, 3.6 Hz, 1H), 4.03 (s, 3H), 3.74 (dt. *J* = 15.3, 4.8 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.6 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.8 (s), 138.7 (s), 133.2 (s), 130.1 (s), 129.3 (s), 124.4 (s), 123.4 (s), 64.2 (s), 54.6 (s), 52.2 (d, *J* = 16.8 Hz). Mp 89-90 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{10}H_{10}FNO_4SNa$: 282.0207, found: 282.0205.



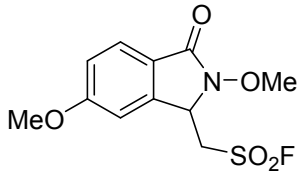
(2-Methoxy-6-methyl-3-oxoisoindolin-1-yl)methanesulfonyl fluoride (**7b**). Petroleum ether / ethyl acetate = 3 : 1 (v /v) as eluent for column chromatography. Yellow solid, 106.6 mg, 78% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.8 Hz, 1H), 7.42 (s, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 5.19 (t, *J* = 4.8 Hz, 1H), 4.11 (dt, *J* = 15.0, 3.2 Hz, 1H), 4.01 (s, 3H), 3.73 (dt, *J* = 15.1, 4.9 Hz, 1H), 2.48 (s, 3H). ^{19}F NMR (471 Hz, $CDCl_3$) δ 61.5 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.2 (s), 144.4 (s), 139.2 (s), 131.0 (s), 126.5 (s), 124.3 (s), 123.7 (s), 64.2 (s), 54.6 (s), 52.4 (d, *J* = 16.8 Hz), 22.1 (s). Mp 123-124 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{11}H_{12}FNO_4SNa$: 296.0363, found: 296.0360.



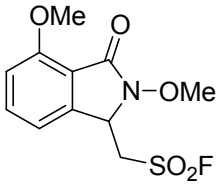
(2-Methoxy-5-methyl-3-oxoisoindolin-1-yl)methanesulfonyl fluoride (**7c**). Petroleum ether / ethyl acetate = 3 : 1 (v /v) as eluent for column chromatography. Yellow solid, 103.9 mg, 76% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 5.18 (t, *J* = 5.0 Hz, 1H), 4.10 (dt, *J* = 15.2, 3.5 Hz, 1H), 3.99 (s, 3H), 3.75 (dt, *J* = 15.0, 4.9 Hz, 1H), 2.42 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.8 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1 (s), 140.4 (s), 135.9 (s), 134.1 (s), 129.2 (s), 124.5 (s), 123.1 (s), 64.1 (s), 54.5 (s), 52.3 (d, *J* = 16.5 Hz), 21.4 (s). Mp 114-116 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{11}H_{12}FNO_4SNa$: 296.0363, found: 296.0358.



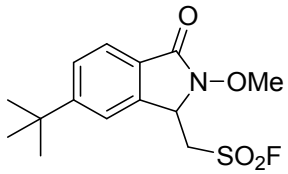
(2-Methoxy-4-methyl-3-oxoisoindolin-1-yl)methanesulfonyl fluoride (**7d**). Petroleum ether / ethyl acetate = 3 : 1 (v /v) as eluent for column chromatography. Brown solid, 60.1 mg, 44% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (t, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 5.17 (t, *J* = 5.2 Hz, 1H), 4.08 (dt, *J* = 15.1, 3.7 Hz, 1H), 4.00 (s, 3H), 3.76 (dt, *J* = 15.2, 5.3 Hz, 1H), 2.67 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.7 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4 (s), 139.4 (s), 138.9 (s), 132.7 (s), 131.9 (s), 126.2 (s), 120.6 (s), 64.1 (s), 54.3 (s), 52.6 (d, *J* = 16.5 Hz), 17.2 (s). Mp 89-91 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{11}H_{12}FNO_4SNa$: 296.0363, found: 296.0358.



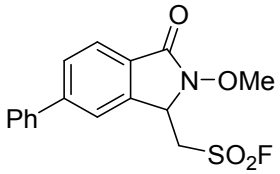
(2,6-Dimethoxy-3-oxoisoindolin-1-yl)methanesulfonyl fluoride (**7e**). Petroleum ether / ethyl acetate = 2 : 1 (v /v) as eluent for column chromatography. Yellow solid, 94.0 mg, 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.5 Hz, 1H), 7.11 (s, 1H), 7.05 (d, *J* = 8.5 Hz, 1H), 5.17 (dd, *J* = 6.4, 4.3 Hz, 1H), 4.13 (dt, *J* = 15.2, 3.3 Hz, 1H), 3.99 (s, 3H), 3.88 (s, 3H), 3.73 (dt, *J* = 15.1, 5.0 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.5 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6 (s), 164.0 (s), 141.3 (s), 126.1 (s), 121.2 (s), 116.5 (s), 108.4 (s), 64.3 (s), 55.9 (s), 54.7 (s), 52.4 (d, *J* = 16.9 Hz). Mp 128-129 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{11}H_{12}FNO_5SNa$: 312.0312, found: 312.0308.



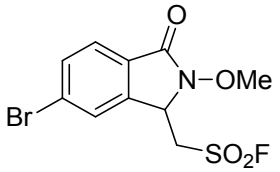
(2,4-Dimethoxy-3-oxoisoindolin-1-yl)methanesulfonyl fluoride (**7f**). Petroleum ether / ethyl acetate = 2 : 1 (v /v) as eluent for column chromatography. Yellow solid, 92.6 mg, 64% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (t, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 5.15 (t, *J* = 5.0 Hz, 1H), 4.09 (dt, *J* = 15.2, 3.8 Hz, 1H), 4.00 (s, 3H), 3.98 (s, 3H), 3.74 (dt, *J* = 15.2, 5.3 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.7 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.9 (s), 157.8 (s), 141.3 (s), 135.1 (s), 116.2 (s), 115.1 (s), 112.2 (s), 64.1 (s), 56.1 (s), 54.5 (s), 52.5 (d, *J* = 16.7 Hz). Mp 120-122 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{11}H_{12}FNO_5SNa$: 312.0312, found: 312.0308.



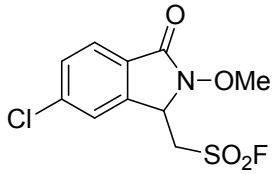
(6-(Tert-butyl)-2-methoxy-3-oxoisoindolin-1-yl)methanesulfonyl fluoride (**7g**). Petroleum ether / ethyl acetate = 3 : 1 (v /v) as eluent for column chromatography. Brown solid, 99.4 mg, 63% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 1H), 7.63 (s, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 5.22 (t, *J* = 5.2 Hz, 1H), 4.14 (dt, *J* = 15.0, 3.5 Hz, 1H), 4.00 (s, 3H), 3.74 (dt, *J* = 15.4, 5.6 Hz, 1H), 1.35 (s, 9H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.7 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1 (s), 157.7 (s), 138.9 (s), 127.4 (s), 126.4 (s), 124.1 (s), 120.3 (s), 64.2 (s), 54.7 (s), 52.5 (d, *J* = 16.7 Hz), 35.7 (s), 31.2 (s). Mp 121-123 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{14}H_{18}FNO_4SNa$: 338.0833, found: 338.0828.



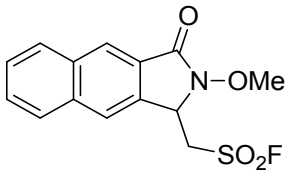
(2-Methoxy-3-oxo-6-phenylisoindolin-1-yl)methanesulfonyl fluoride (**7h**). Petroleum ether / ethyl acetate = 3 : 1 (v /v) as eluent for column chromatography. White solid, 87.2 mg, 52% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.9 Hz, 1H), 7.83 (s, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 5.30 (dd, *J* = 6.4, 4.3 Hz, 1H), 4.18 (dt, *J* = 15.1, 3.5 Hz, 1H), 4.04 (s, 3H), 3.78 (dt, *J* = 15.1, 5.5 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.7 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.9 (s), 146.7 (s), 139.6 (s), 139.5 (s), 129.2 (s), 129.1 (s), 128.7 (s), 127.8 (s), 127.4 (s), 124.8 (s), 122.0 (s), 64.3 (s), 54.7 (s), 52.3 (d, *J* = 17.0 Hz). Mp 116-117 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{16}H_{14}FNO_4SNa$: 358.0520, found: 358.0516.



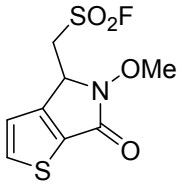
(6-Bromo-2-methoxy-3-oxoisoindolin-1-yl)methanesulfonyl fluoride (**7i**). Petroleum ether / ethyl acetate = 3 : 1 (v /v) as eluent for column chromatography. Yellow solid, 52.4 mg, 31% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.76-7.71 (m, 2H), 5.22 (dd, *J* = 6.1, 4.0 Hz, 1H), 4.15-4.09 (m, 1H), 4.02 (s, 3H), 3.77-3.71 (m, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.6 (s). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.9 (s), 140.4 (s), 133.7 (s), 128.2 (s), 128.0 (s), 126.9 (s), 125.9 (s), 64.4 (s), 54.2 (s), 51.9 (d, *J* = 17.4 Hz). Mp 150-152 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{10}H_9BrFNO_4SNa$: 359.9312, found: 359.9312, 361.9290.



(6-Chloro-2-methoxy-3-oxoisoindolin-1-yl)methanesulfonyl fluoride (**7j**). Petroleum ether / ethyl acetate = 3 : 1 (v /v) as eluent for column chromatography. Yellow solid, 54.3 mg, 37% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 1H), 7.65 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 5.22 (dd, *J* = 6.7, 3.9 Hz, 1H), 4.15 (dt, *J* = 5.9, 3.3 Hz, 1H), 4.03 (s, 3H), 3.74 (dt, *J* = 15.0, 5.5 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.6 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.8 (s), 140.3 (s), 139.8 (s), 130.8 (s), 127.7 (s), 125.8 (s), 124.0 (s), 64.4 (s), 54.3 (s), 51.9 (d, *J* = 17.4 Hz). Mp 153-155 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{10}H_9ClFNO_4SNa$: 315.9817, found: 315.9816, 317.9784.

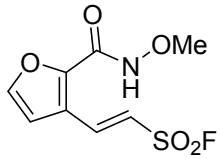


(2-Methoxy-3-oxo-2,3-dihydro-1H-benzo[f]isoindol-1-yl)methanesulfonyl fluoride (**7k**). Petroleum ether / ethyl acetate = 2 : 1 (v /v) as eluent for column chromatography. Yellow solid, 92.8 mg, 60% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.09 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.67 – 7.61 (m, 2H), 5.41 (t, *J* = 5.7 Hz, 1H), 4.22 (dt, *J* = 15.0, 3.0 Hz, 1H), 4.08 (s, 3H), 3.79 (dt, *J* = 15.3, 5.4 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.6 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.3 (s), 135.4 (s), 133.5 (s), 133.4 (s), 129.6 (s), 128.7 (s), 128.6 (s), 127.7 (s), 126.1 (s), 125.3 (s), 123.1 (s), 64.2 (s), 54.4 (s), 52.8 (d, *J* = 16.6 Hz). Mp 181-182 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{14}H_{12}FNO_4SNa$: 332.0363, found: 332.0360.



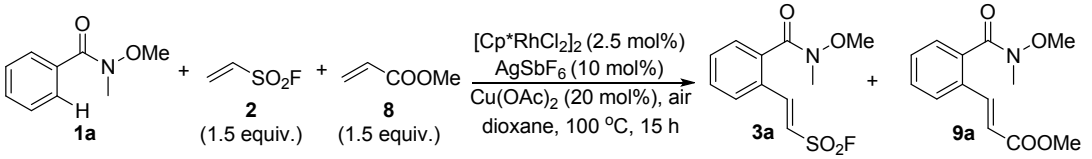
(5-Methoxy-6-oxo-5,6-dihydro-4H-thieno[2,3-c]pyrrol-4-yl)methanesulfonyl fluoride (**7l**). Petroleum ether / ethyl acetate = 2 : 1 (v /v) as eluent for column chromatography. Yellow oil, 54.4 mg, 41% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 4.9 Hz, 1H), 7.25 (d, *J* = 4.8 Hz, 1H), 5.14 (dd, *J* = 8.7, 3.5 Hz, 1H), 4.19 (dt, *J* = 14.9, 3.7 Hz, 1H), 4.01 (s, 3H), 3.64 (ddd, *J* = 14.8, 8.7, 4.2 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 61.1 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.8 (s), 148.6 (s),

136.8 (s), 132.7 (s), 122.2 (d, J = 1.8 Hz), 64.9 (s), 55.1 (s), 51.8 (d, J = 17.1 Hz). HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_8H_8FNO_4S_2$: 287.9771, found: 287.9770.



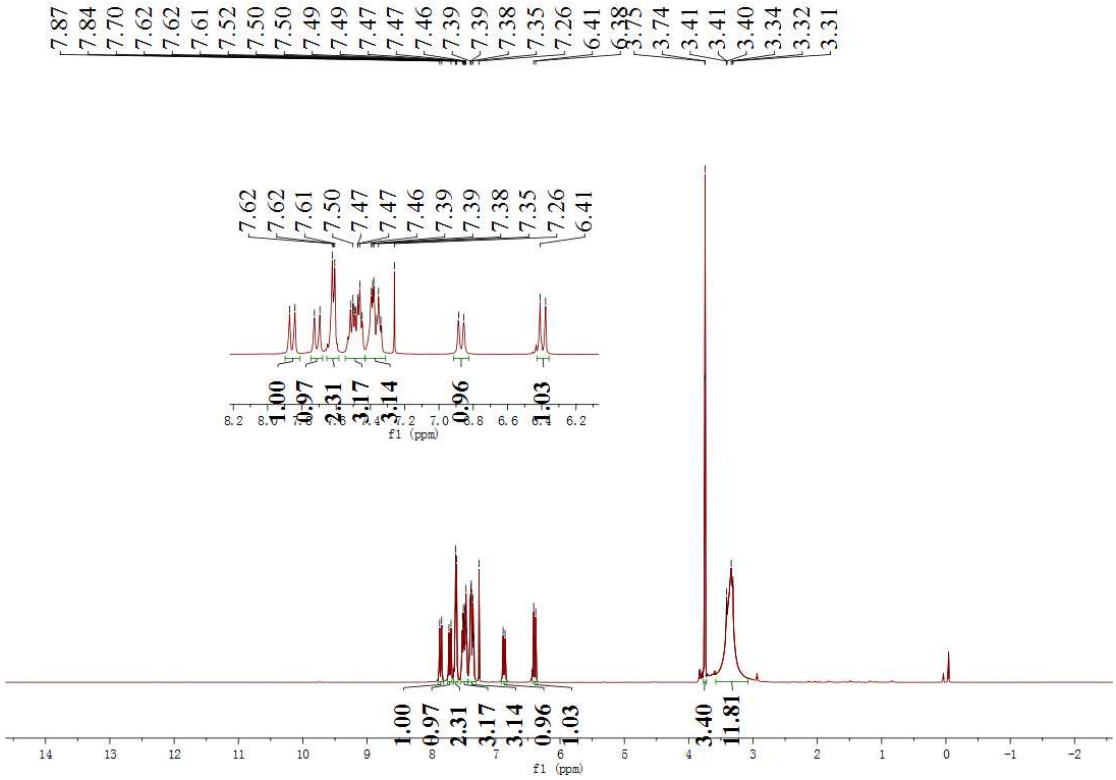
(*E*)-2-(2-(methoxycarbamoyl)furan-3-yl)ethenesulfonyl fluoride (**7m**). Petroleum ether / ethyl acetate = 2 : 1 (v /v) as eluent for column chromatography. White solid, 47.3 mg, 38% yield (reaction temperature was 80 °C); 79.7 mg, 64% yield (reaction temperature was 100 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.17 (s, 1H), 8.51 (d, J = 15.6 Hz, 1H), 7.48 (s, 1H), 6.91 (d, J = 15.7 Hz, 1H), 6.73 (s, 1H), 3.89 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 62.0 (s). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4 (s), 144.6 (s), 144.5 (s), 138.8 (s), 138.2 (s), 122.0 (d, J = 29.2 Hz), 110.3 (s), 65.2 (s). Mp 138-139 °C. HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_8H_8FNO_5SNa$: 271.9999, found: 271.9996.

6. Competition reaction between methyl acrylate and ESF as coupling paterners in the Rh(III)-catalyzed C-H coupling reaction.

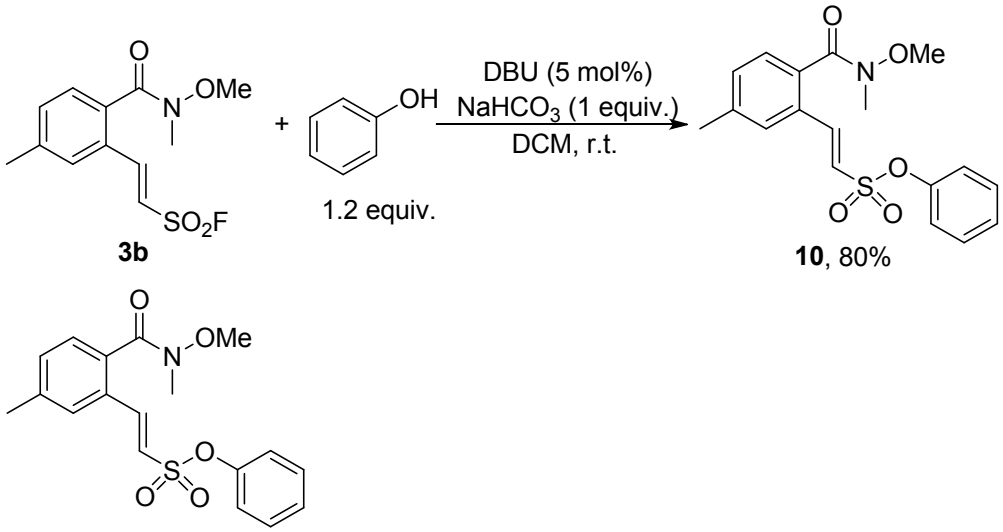


An oven-dried screw cap test tube was charged with *N*-methoxy-*N*-methylbenzamide (**1a**, 0.5 mmol), ethenesulfonyl fluoride (ESF, **2**, 0.75 mmol, 1.5 equiv.), methyl acrylate (**8**, 0.75 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), $AgSbF_6$ (10 mol%), $Cu(OAc)_2$ (20 mol%) and 1,4-dioxane (5 mL) under an air atomosphere. The resulting mixture was stirred at 100 °C for 15 h before concentrating under vacuum. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluents to give a mixture of **3a** and **9a**.

The chemical shifts of two olefin protons of **3a** are 7.88 ppm and 6.87 ppm. The chemical shifts of two olefin protons of **9a** are 7.73 ppm and 6.41 ppm.[3] The ratio of **3a** and **9a** is 1:1 from the ^{1}H NMR.



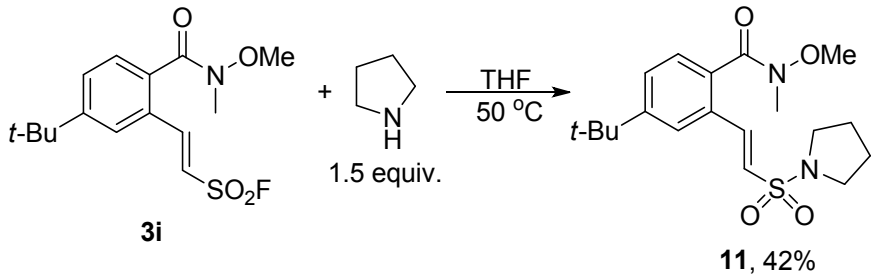
7. Diverse derivations of 3

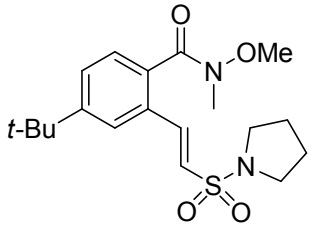


(*E*)-phenyl 2-(2-(methoxy(methyl)carbamoyl)-5-methylphenyl)ethenesulfonate (**10**)

A mixture of **3b** (0.1 mmol, 1 equiv.), phenol (0.12 mmol, 1.2 equiv.), DBU (5 mol%) and $NaHCO_3$ (0.1 mmol, 1 equiv.) in dichloromethane (2 mL) was stirred at r.t. for 24 h. Upon completion, the reaction mixture was concentrated in vacuo and purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 2 : 1 (v / v) as the eluent to afford the desired product **10** as a colorless oil (28.9 mg, 80% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 15.5 Hz, 1H), 7.38-7.24 (m, 8H), 6.84 (d, *J* = 15.5 Hz, 1H), 3.35 (s, 3H), 3.25 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0 (s), 149.6 (s), 143.6 (s), 140.2 (s), 133.5 (s), 131.8 (s), 129.9 (s), 129.2 (s), 127.8 (s), 127.8 (s), 127.2 (s), 122.7 (s), 122.4 (s), 61.2 (s), 32.6 (s),

21.3 (s). HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{18}H_{19}NNaO_5S$: 384.0879, found: 384.0883.

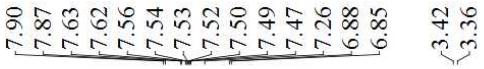


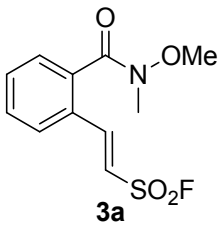


(*E*)-4-(tert-butyl)-N-methoxy-N-methyl-2-(2-(pyrrolidin-1-ylsulfonyl)vinyl)benzamide (**11**).

A mixture of **3i** (0.2 mmol, 1 equiv.) and tetrahydro pyrrole (0.3 mmol, 1.5 equiv.) in THF (2 mL) was stirred at 50 °C for 6 hours. Upon completion, the reaction mixture was concentrated in vacuo and purified by column chromatography on silica gel using petroleum ether / ethyl acetate = 1 : 1 (v / v) as the eluent to afford the desired product **11** as a colorless oil (32.0 mg, 42% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55-7.52 (m, 2H), 7.46 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 1H), 6.69 (d, *J* = 15.5 Hz, 1H), 3.49 (s, 3H), 3.37-3.27 (m, 7H), 1.90-1.88 (m, 4H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.3 (s), 153.2 (s), 140.6 (s), 132.9 (s), 130.2 (s), 127.4 (s), 127.4 (s), 124.1 (s), 123.1 (s), 61.3 (s), 47.9 (s), 34.9 (s), 32.9 (s), 31.1 (s), 25.7 (s). HRMS ESI (m/z): $[M+Na]^+$ calcd for $C_{19}H_{28}N_2NaO_4S$: 403.1668, found: 403.1663.

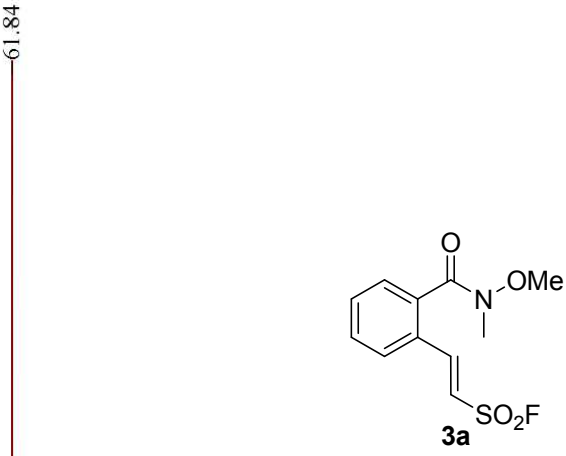
8. NMR spectra of 3, 5, 7, 10 and 11





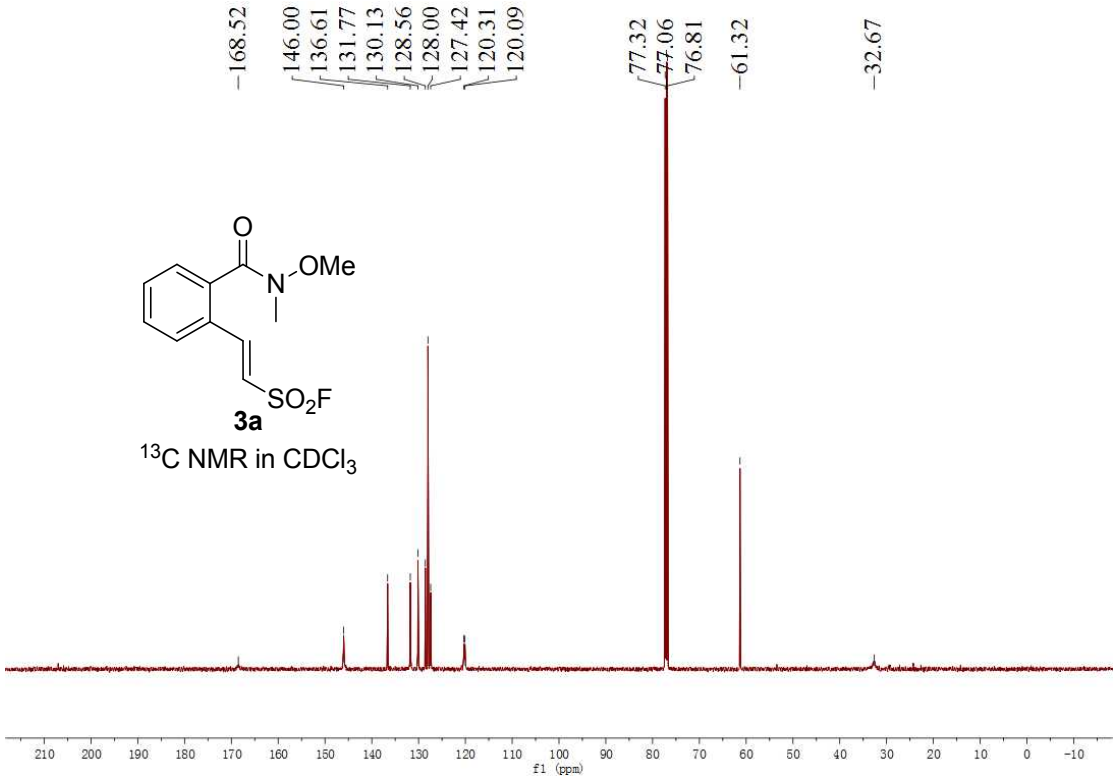
3a

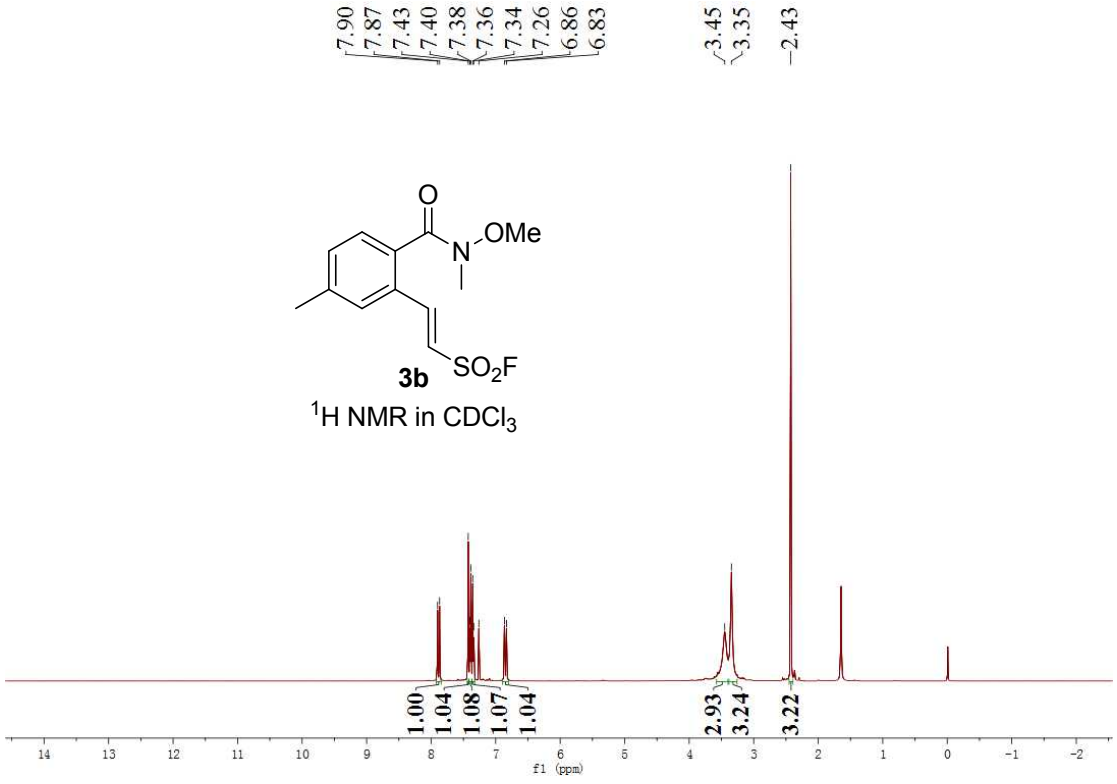
^{1}H NMR in $CDCl_3$

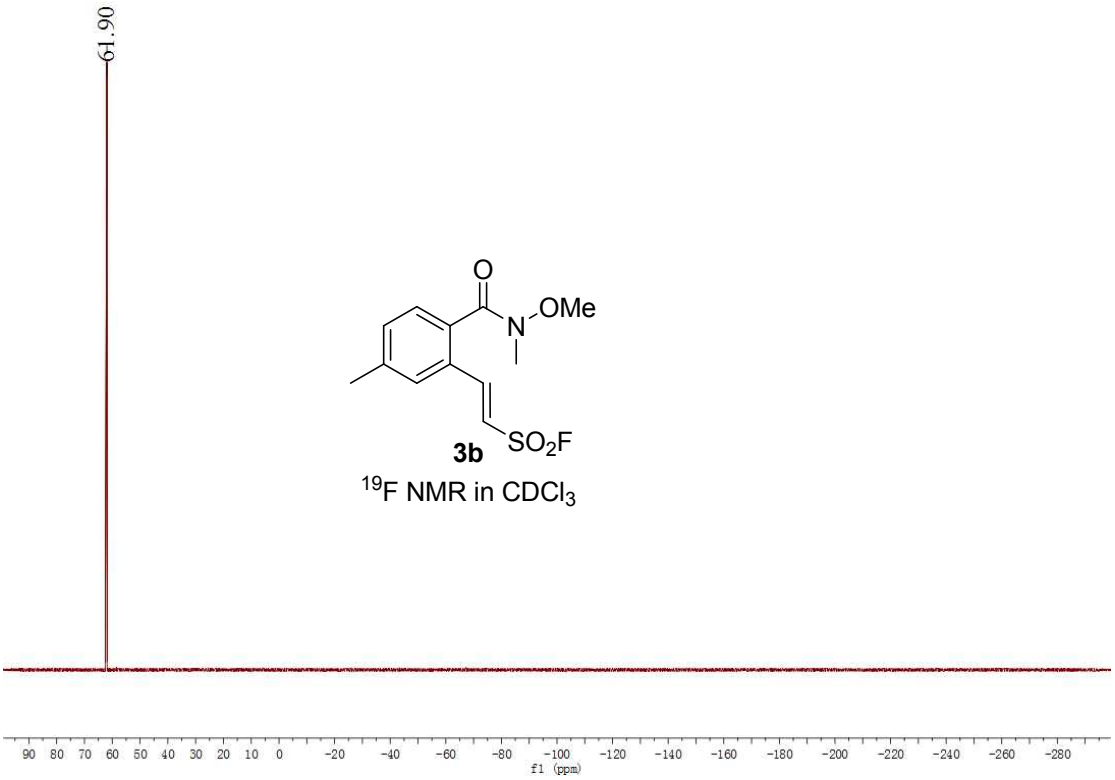


3a

^{19}F NMR in $CDCl_3$

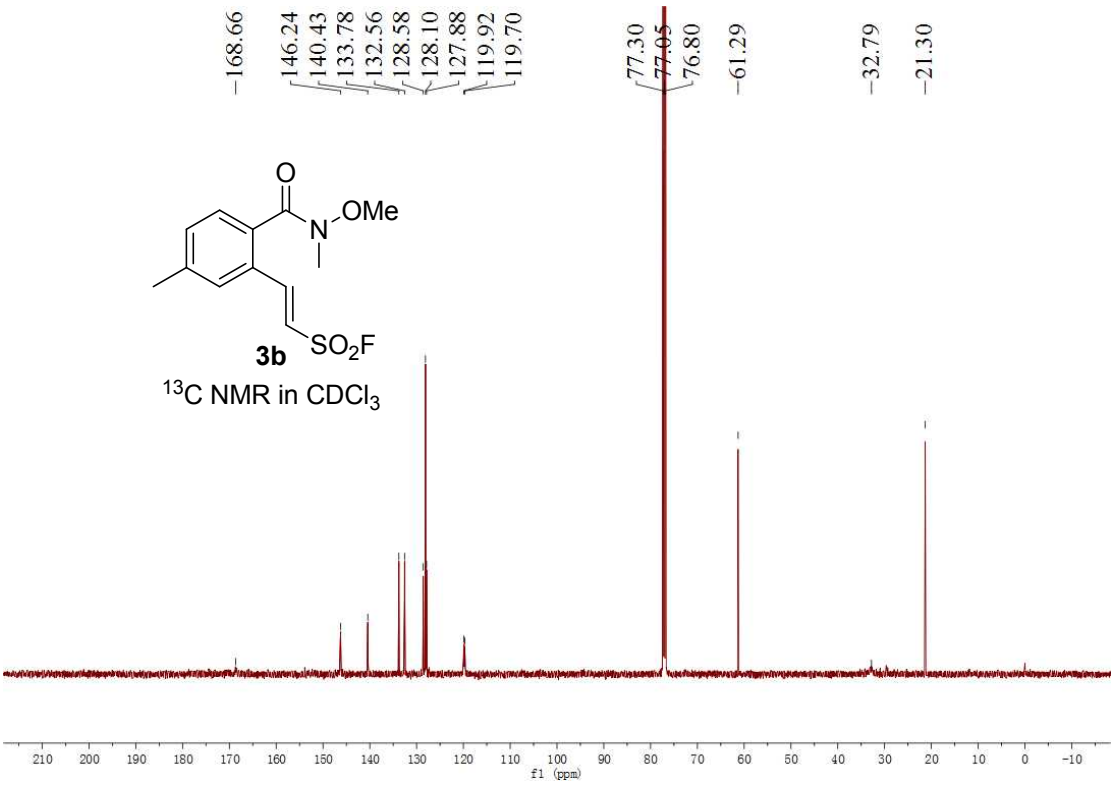

168.52
146.00
136.61
131.77
130.13
128.56
128.00
127.42
120.31
120.09
77.32
77.06
76.81
61.32
32.67
O
N
OMe
SO2F
3a
13C NMR in CDCl3
f1 (ppm)


7.90
7.87
7.43
7.40
7.38
7.36
7.34
7.26
6.86
6.83
3.45
3.35
2.43
O
N
OMe
SO2F
3b
1H NMR in CDCl3
1.00
1.04
1.08
1.07
1.04
2.93
3.24
3.22
f1 (ppm)



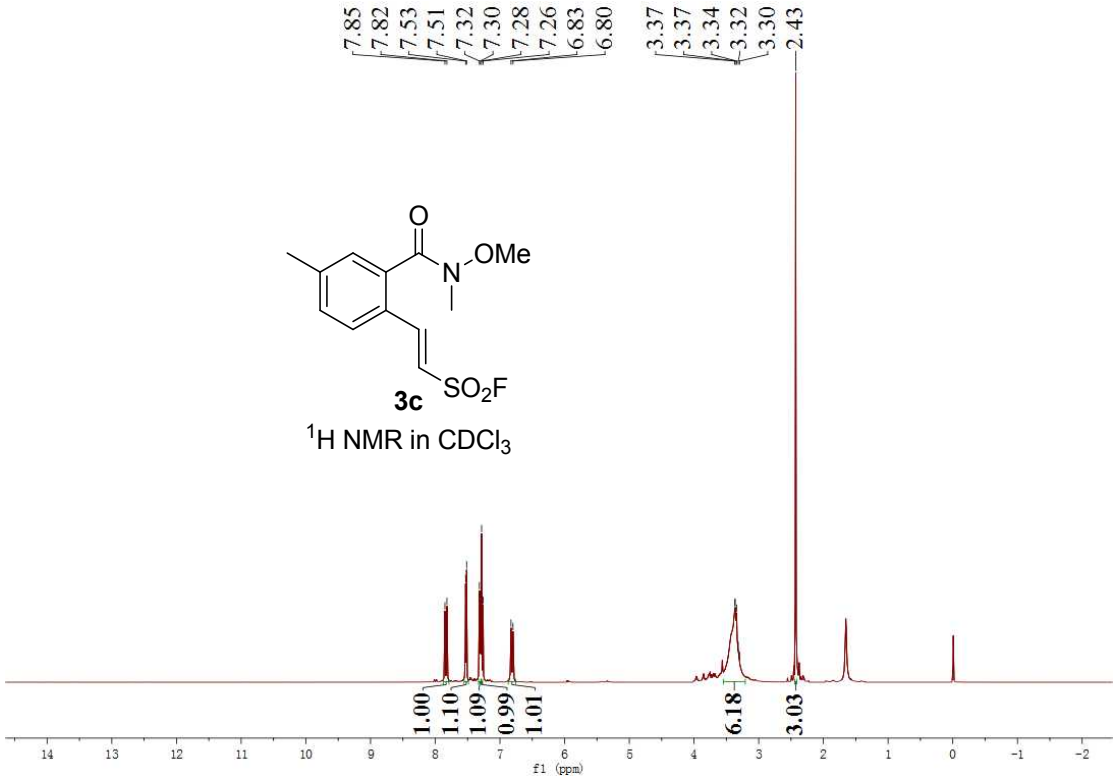
3b

^{19}F NMR in $CDCl_3$



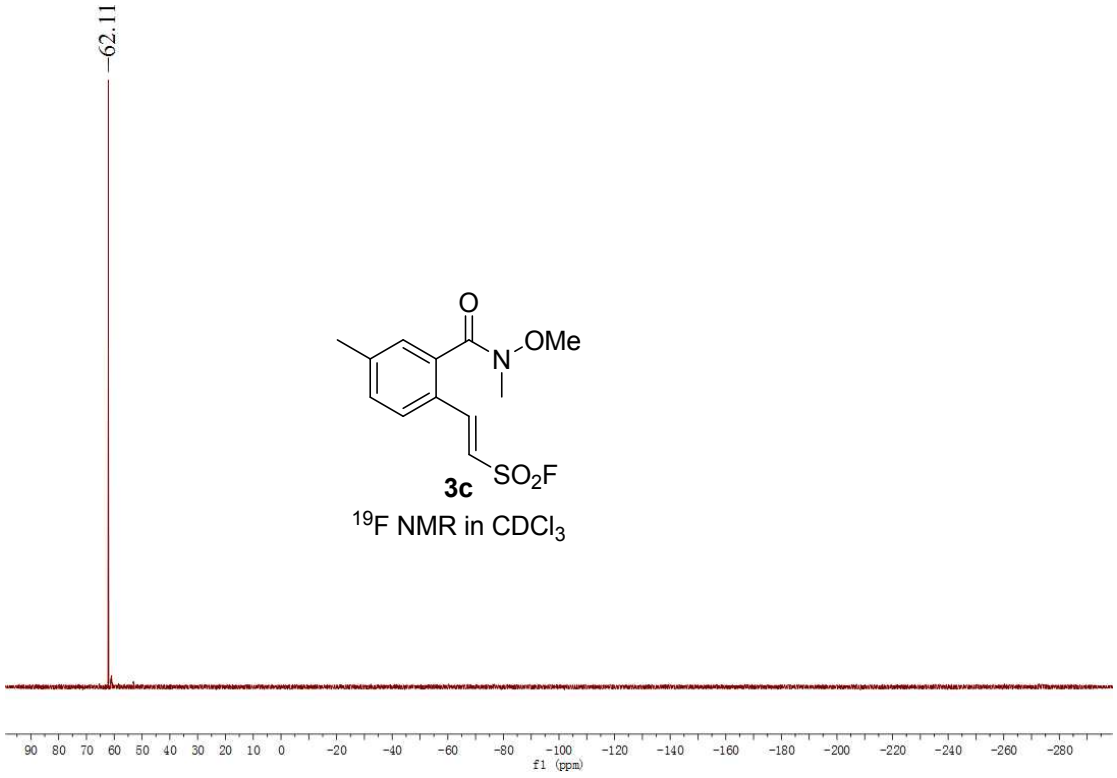
3b

^{13}C NMR in $CDCl_3$



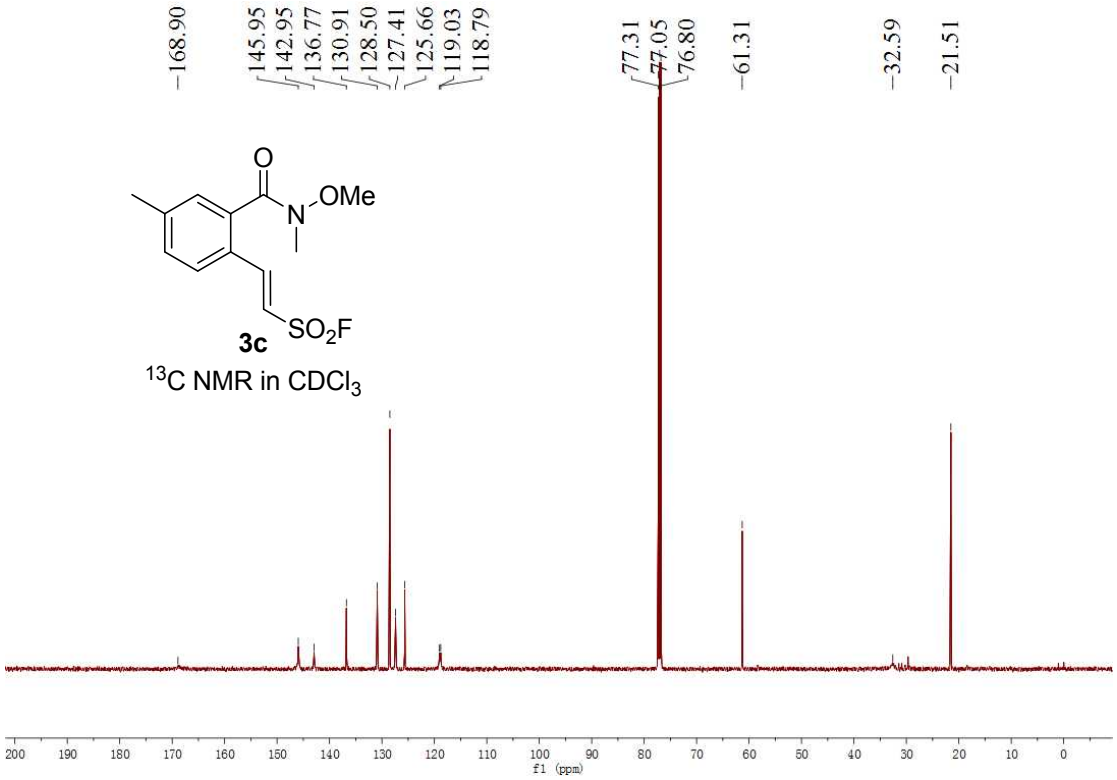
3c

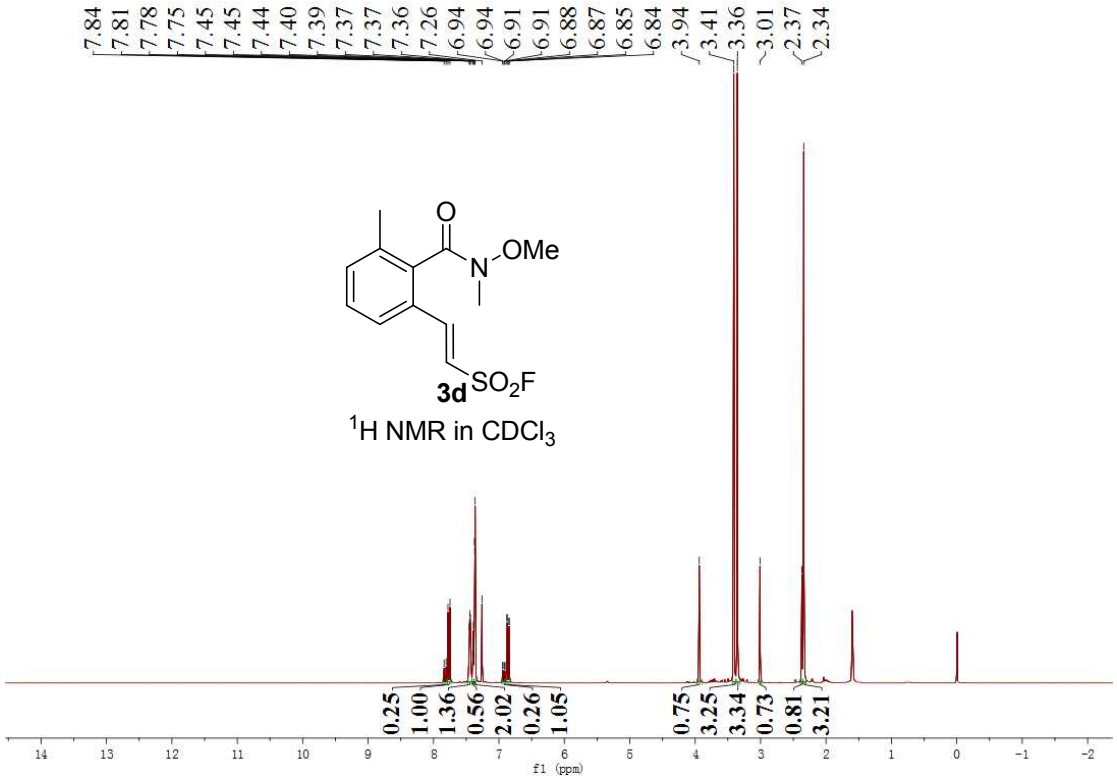
^{1}H NMR in $CDCl_3$

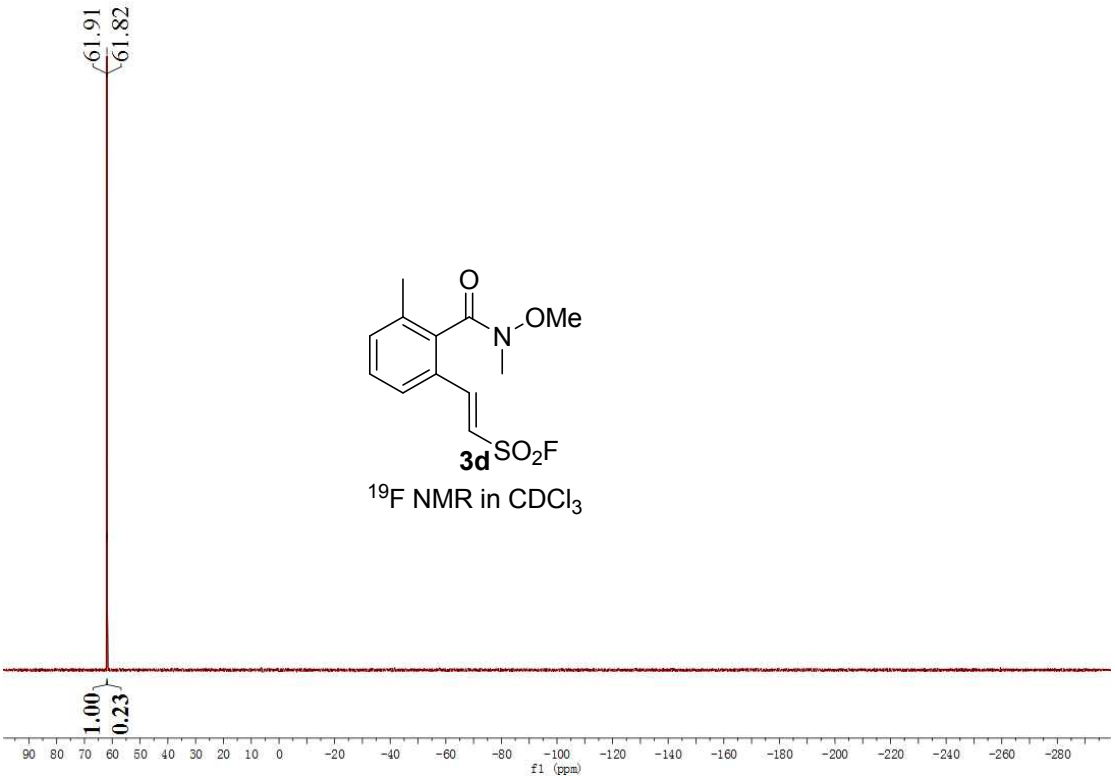


3c

^{19}F NMR in $CDCl_3$

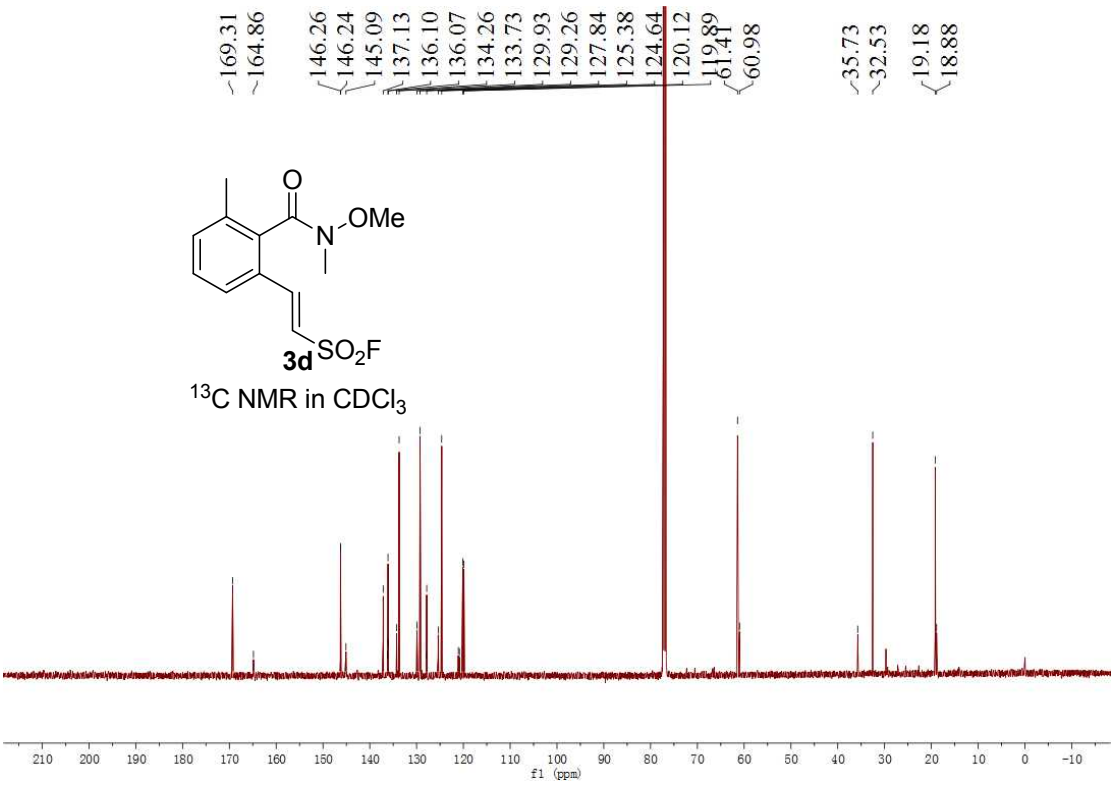

168.90
145.95
142.95
136.77
130.91
128.50
127.41
125.66
119.03
118.79
77.31
77.05
76.80
61.31
32.59
21.51
O
N
OMe
SO2F
3c
13C NMR in CDCl3
f1 (ppm)


7.84
7.81
7.78
7.75
7.45
7.45
7.44
7.40
7.39
7.37
7.37
7.36
7.26
6.94
6.94
6.91
6.91
6.88
6.87
6.85
6.84
3.94
3.41
3.36
3.01
2.37
2.34
O
N
OMe
SO2F
3d
1H NMR in CDCl3
0.25
1.00
1.36
0.56
2.02
0.26
1.05
0.75
3.25
3.34
0.73
0.81
3.21
f1 (ppm)



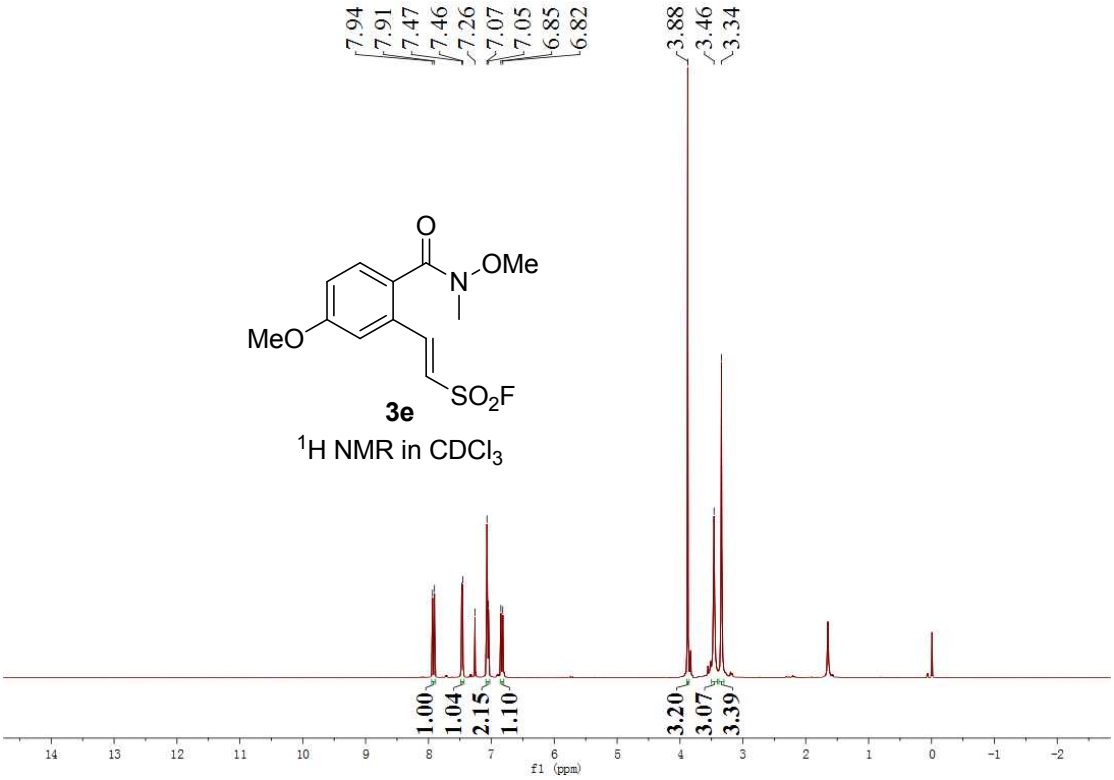
3d

^{19}F NMR in $CDCl_3$



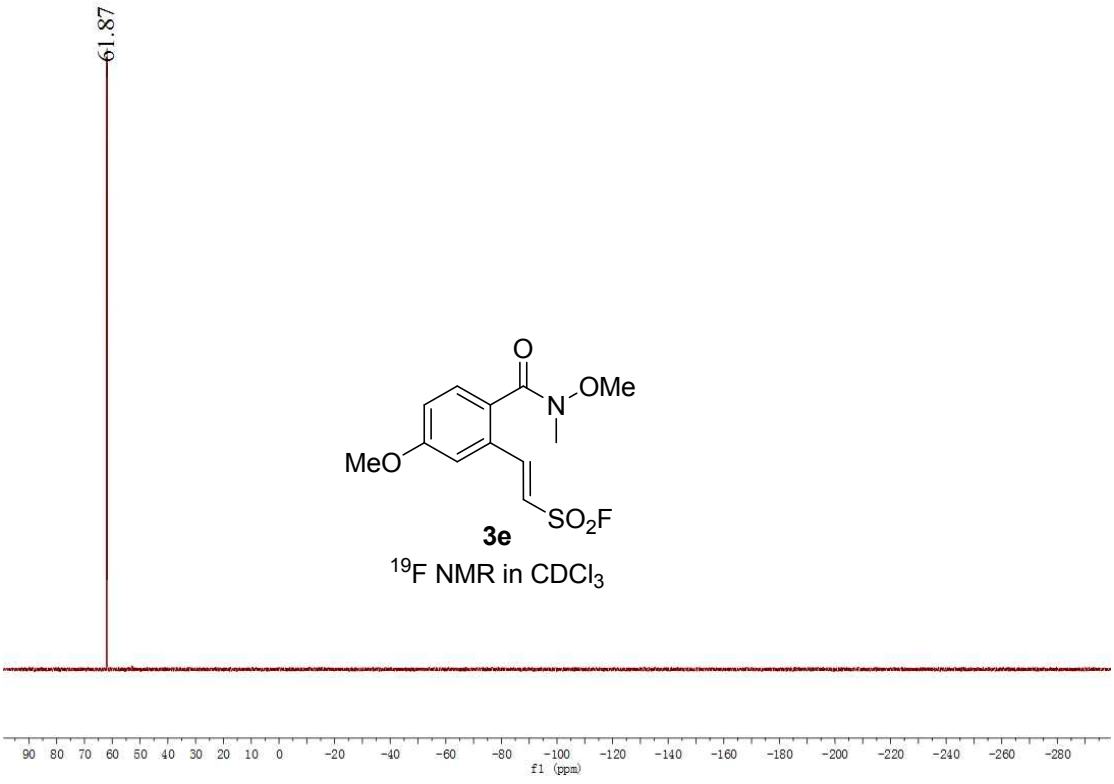
3d

^{13}C NMR in $CDCl_3$



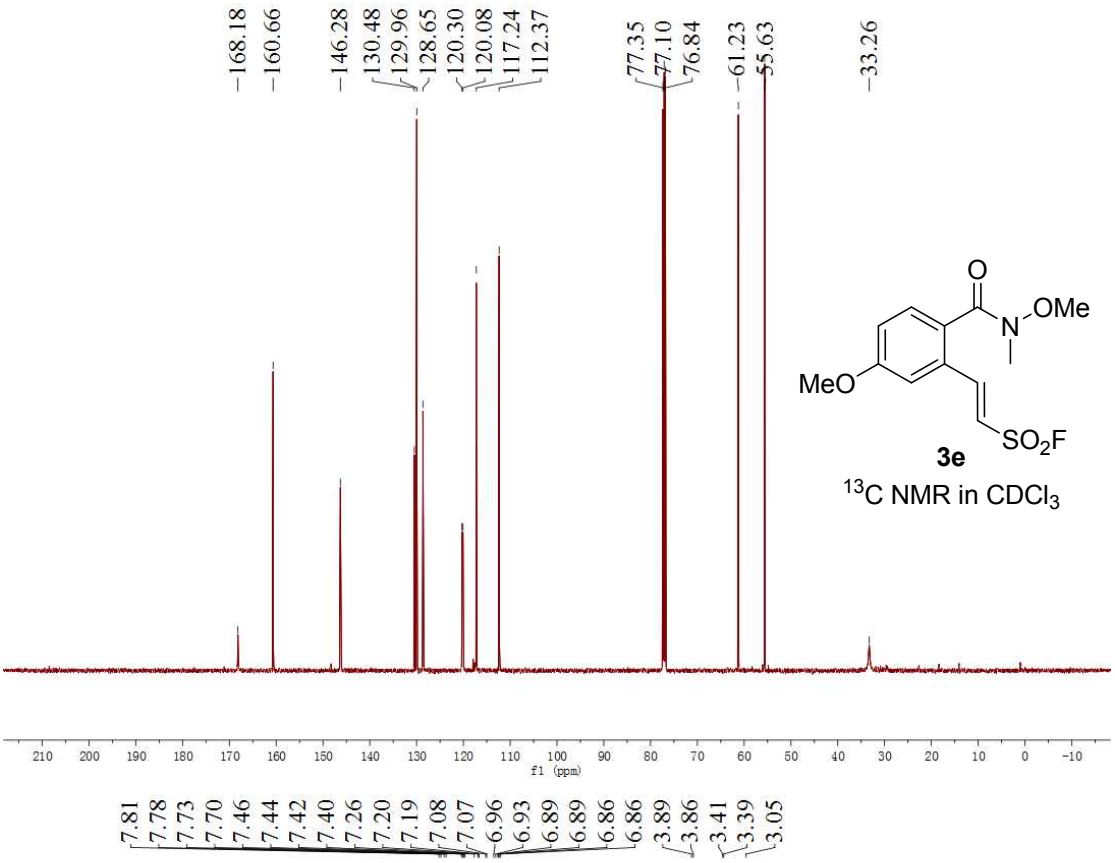
3e

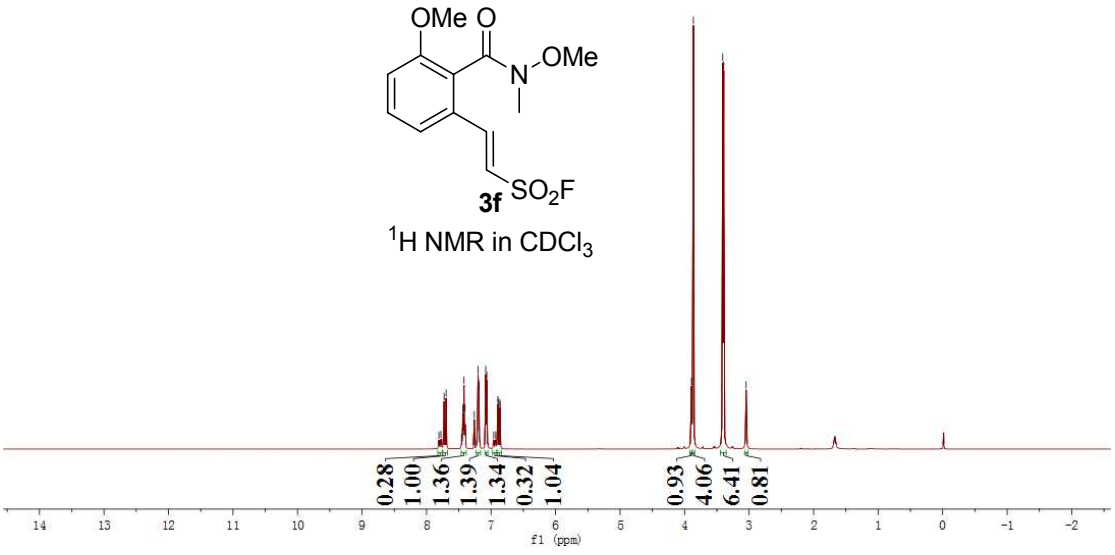
^{1}H NMR in $CDCl_3$

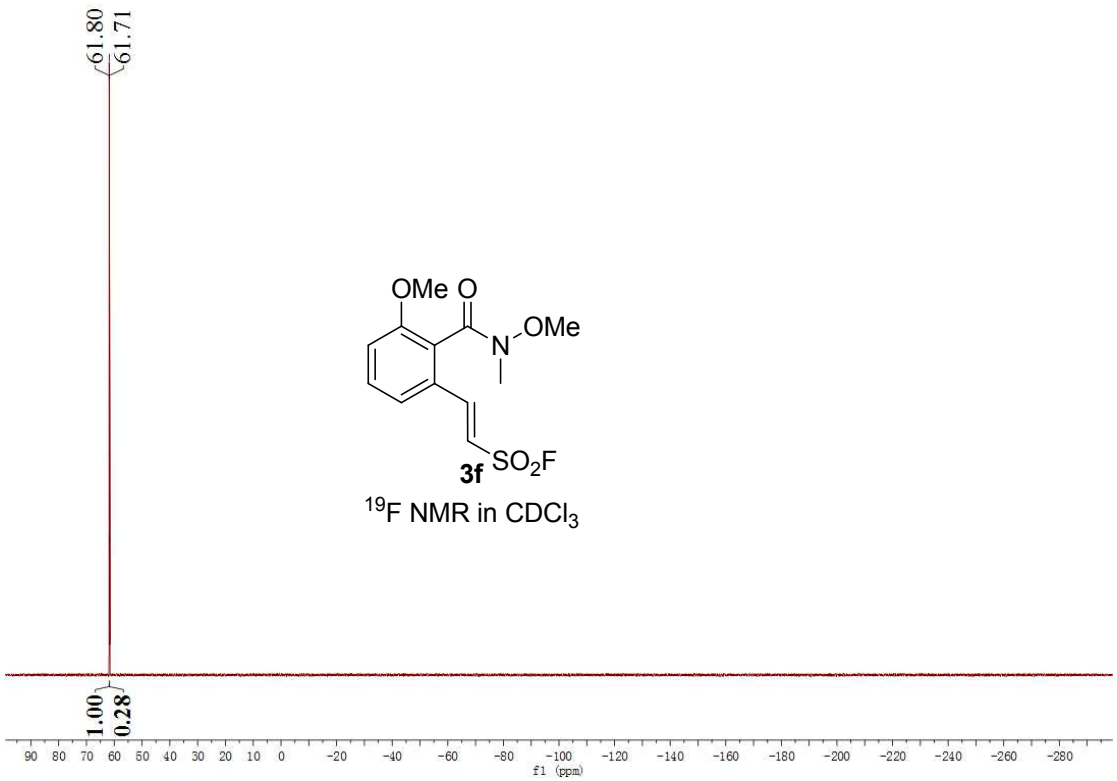


3e

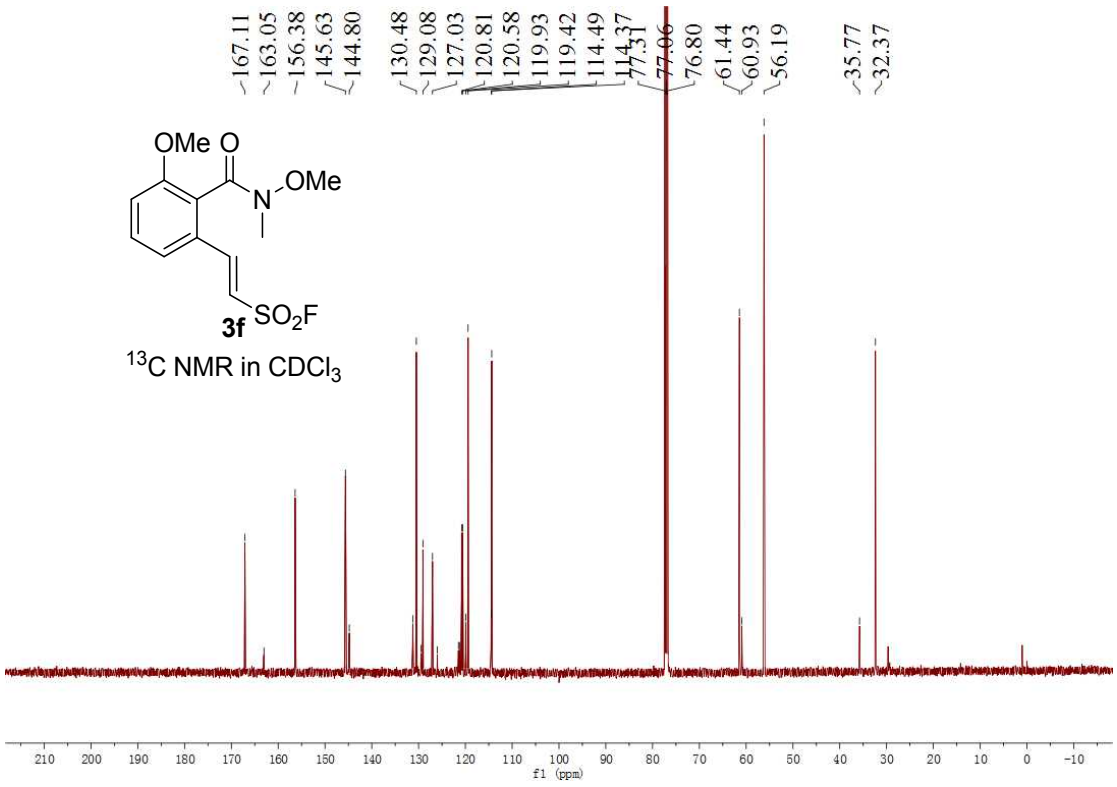
^{19}F NMR in $CDCl_3$


168.18
160.66
146.28
130.48
129.96
128.65
120.30
120.08
117.24
112.37
77.35
77.10
76.84
61.23
55.63
33.26
O
N
OMe
MeO
SO2F
3e
13C NMR in CDCl3
f1 (ppm)
7.81
7.78
7.73
7.70
7.46
7.44
7.42
7.40
7.26
7.20
7.19
7.08
7.07
6.96
6.93
6.89
6.89
6.86
6.86
3.89
3.86
3.41
3.39
3.05

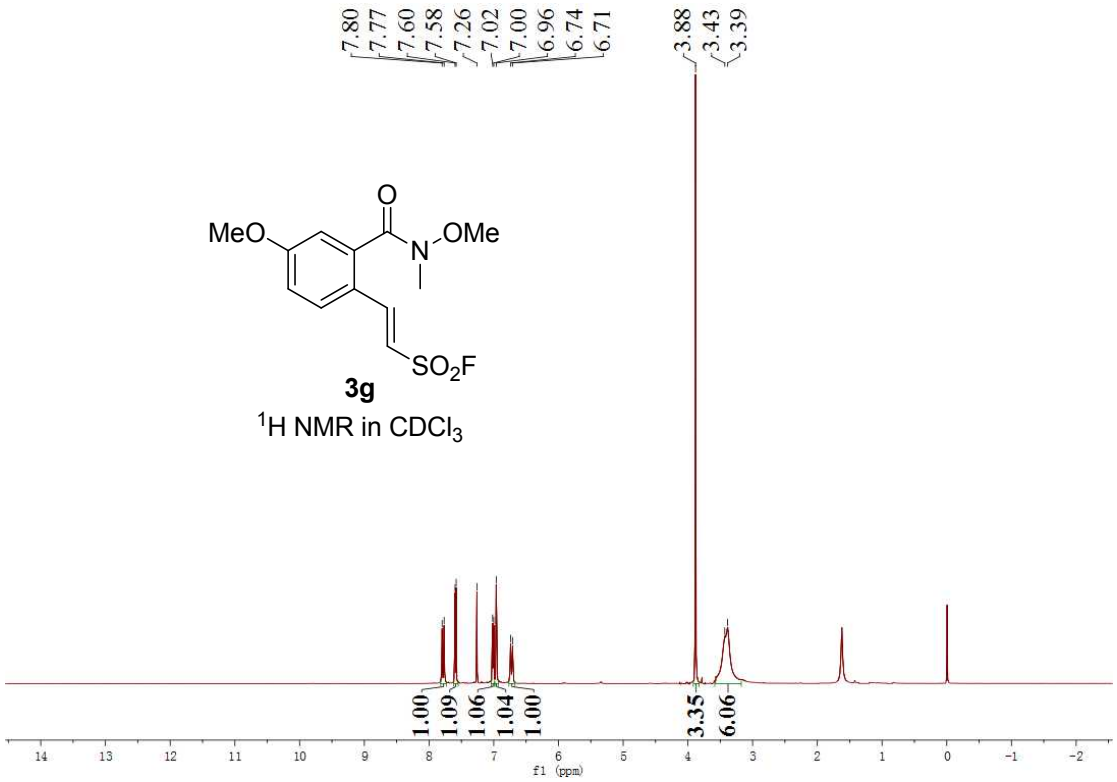

OMe
O
N
OMe
SO2F
3f
1H NMR in CDCl3
0.28
1.00
1.36
1.39
1.34
0.32
1.04
0.93
4.06
6.41
0.81
f1 (ppm)



^{19}F NMR in $CDCl_3$

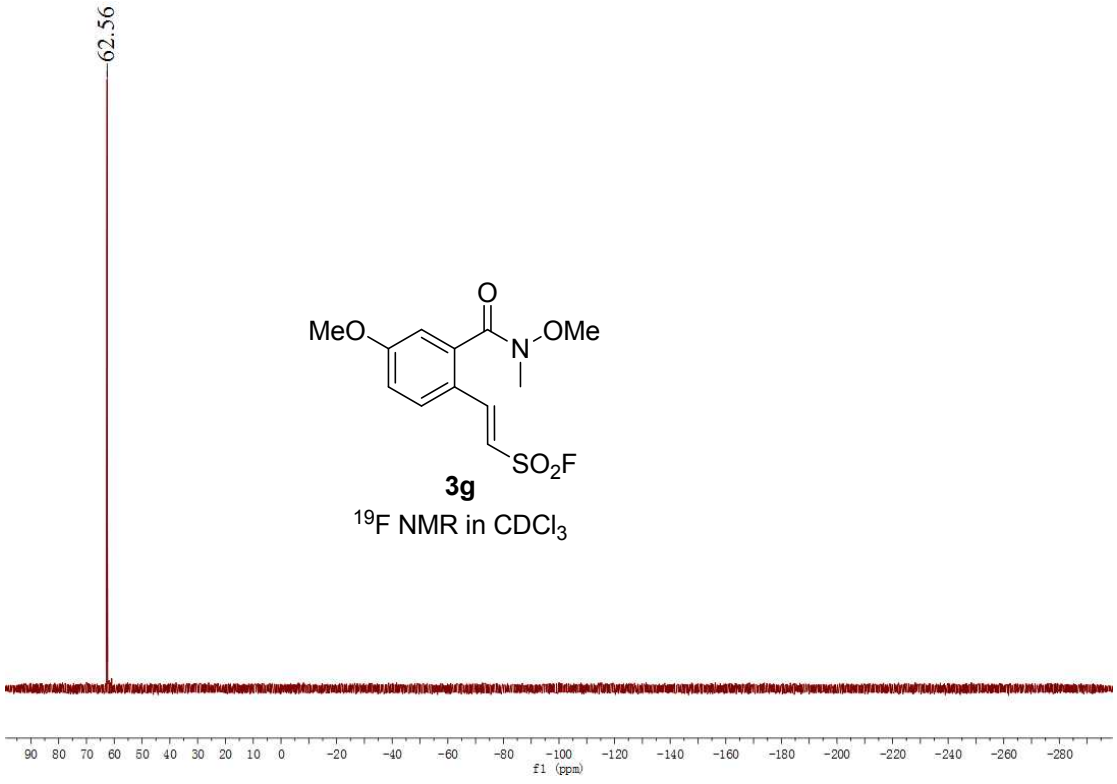


^{13}C NMR in $CDCl_3$



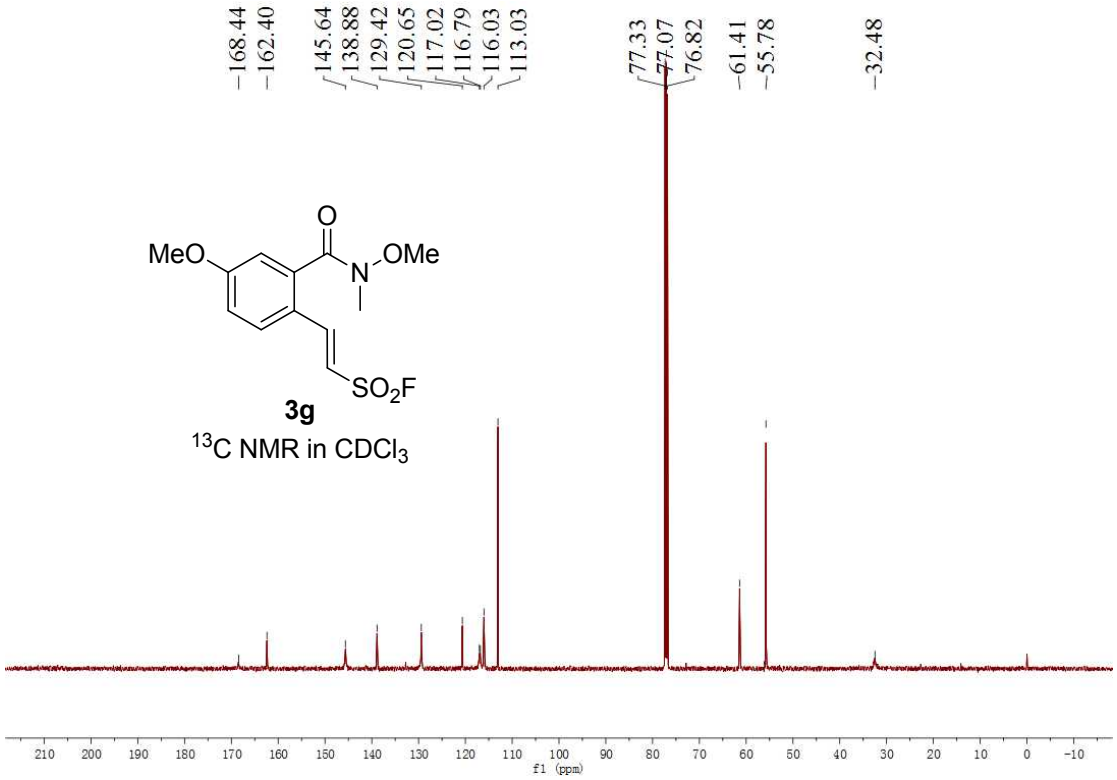
3g

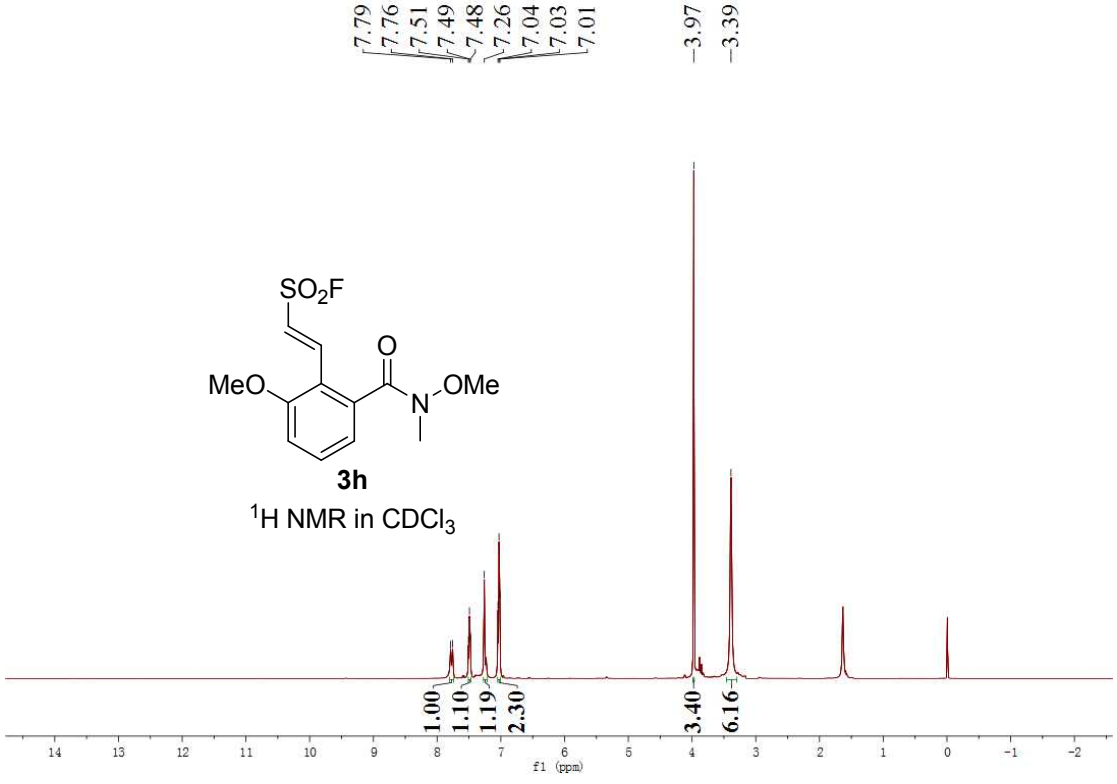
^{1}H NMR in $CDCl_3$

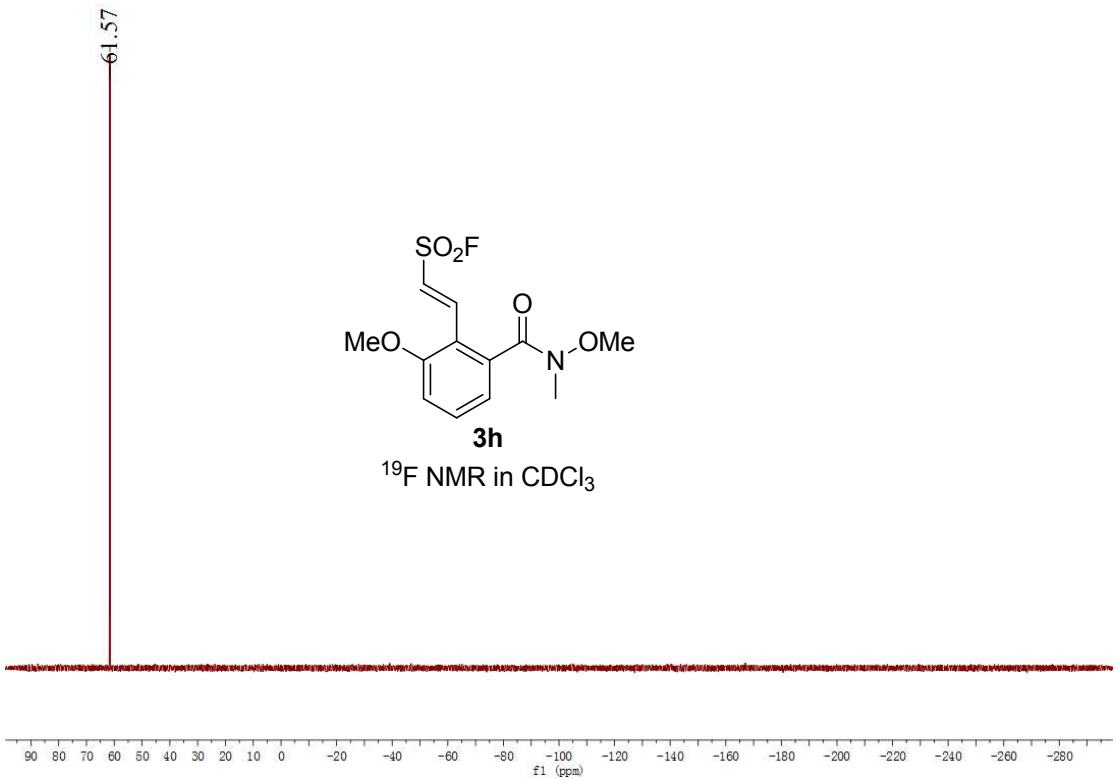


3g

^{19}F NMR in $CDCl_3$

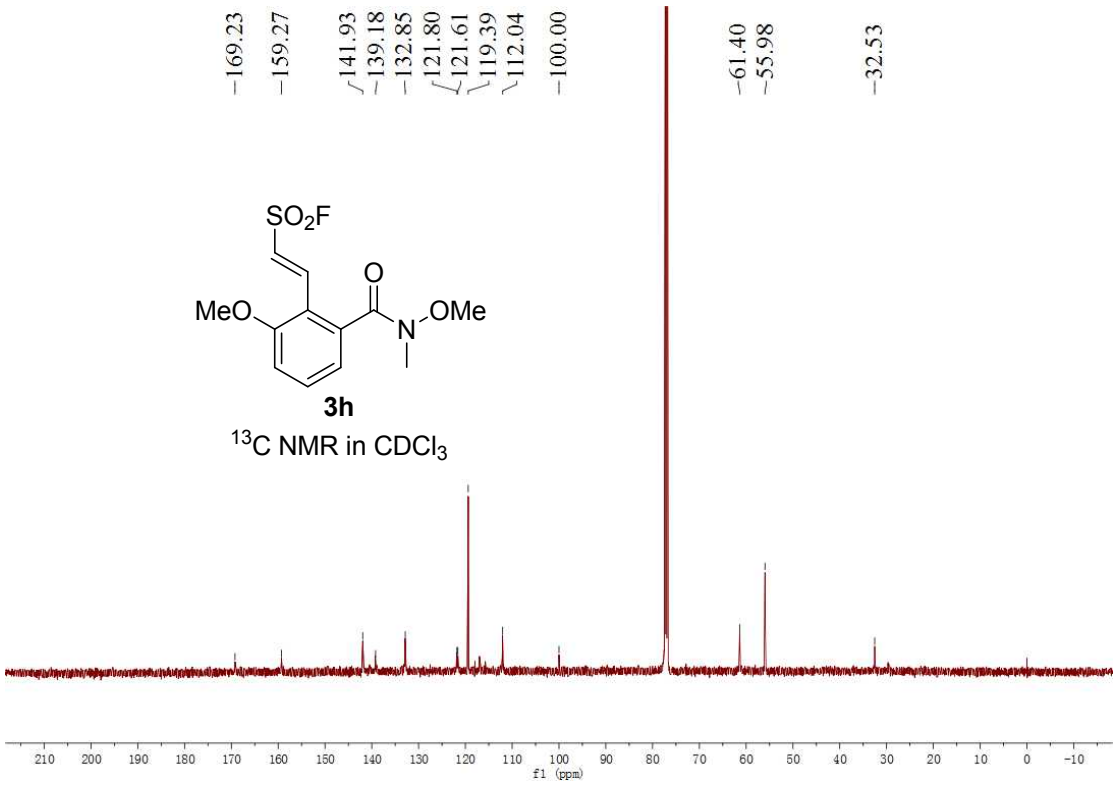

168.44
162.40
145.64
138.88
129.42
120.65
117.02
116.79
116.03
113.03
77.33
77.07
76.82
61.41
55.78
32.48
MeO
O
N
OMe
SO2F
3g
13C NMR in CDCl3
f1 (ppm)


7.79
7.76
7.51
7.49
7.48
7.26
7.04
7.03
7.01
3.97
3.39
SO2F
MeO
O
N
OMe
3h
1H NMR in CDCl3
1.00
1.10
1.19
2.30
3.40
6.16
f1 (ppm)



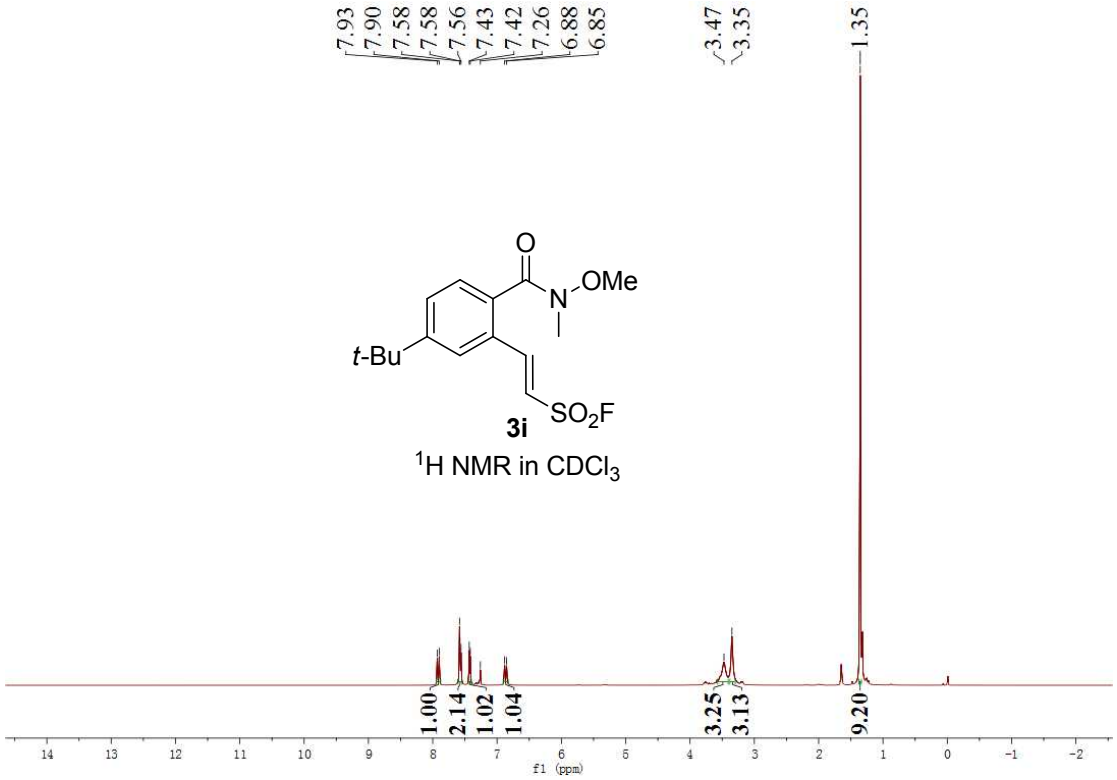
3h

^{19}F NMR in $CDCl_3$



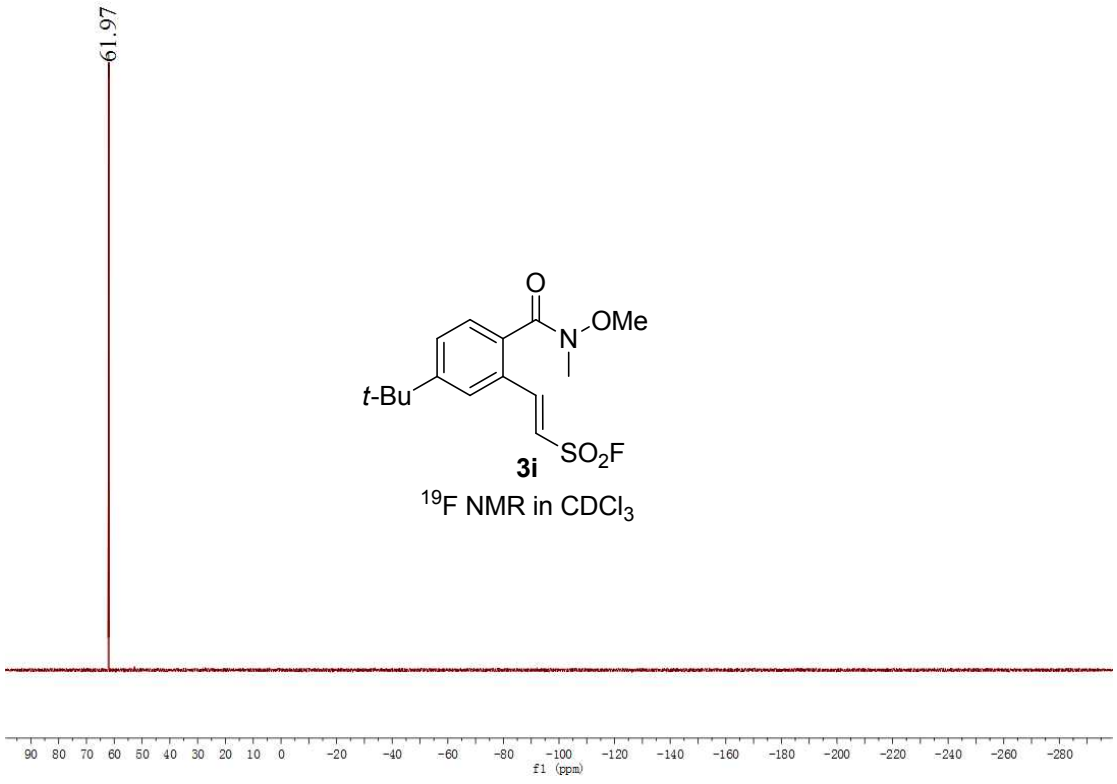
3h

^{13}C NMR in $CDCl_3$



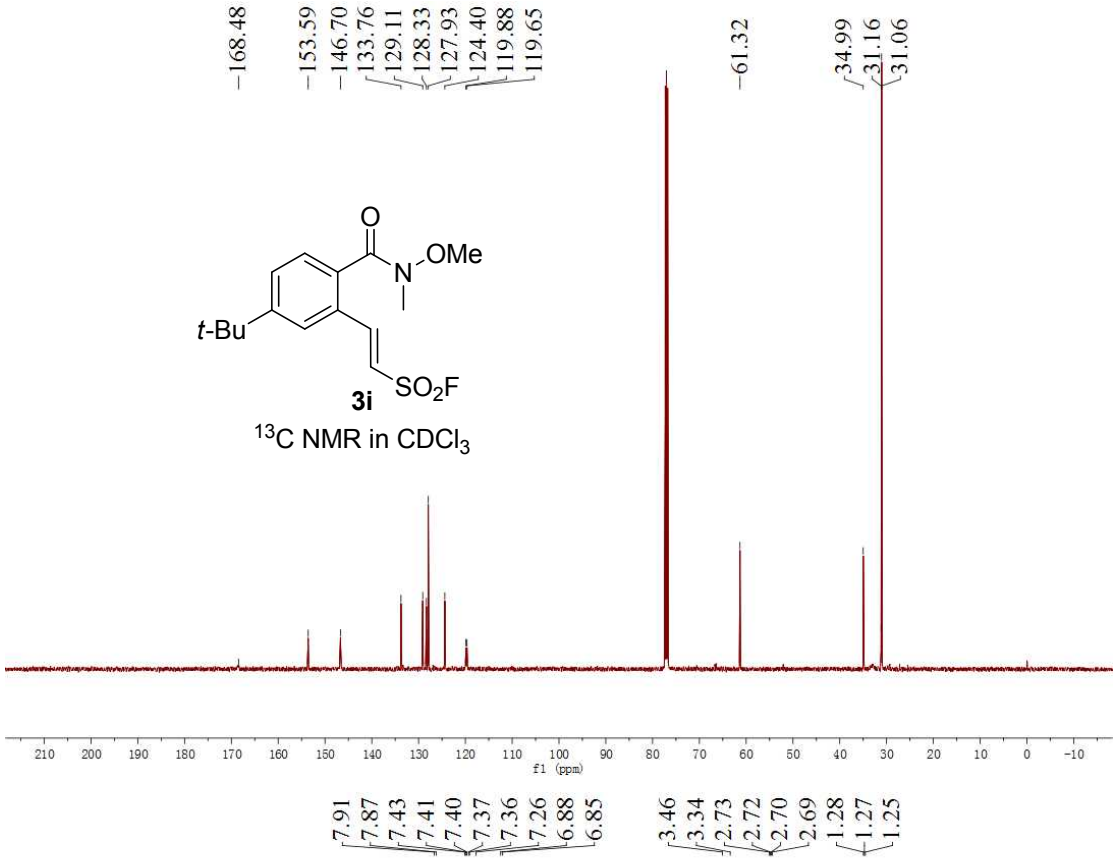
3i

^{1}H NMR in $CDCl_3$



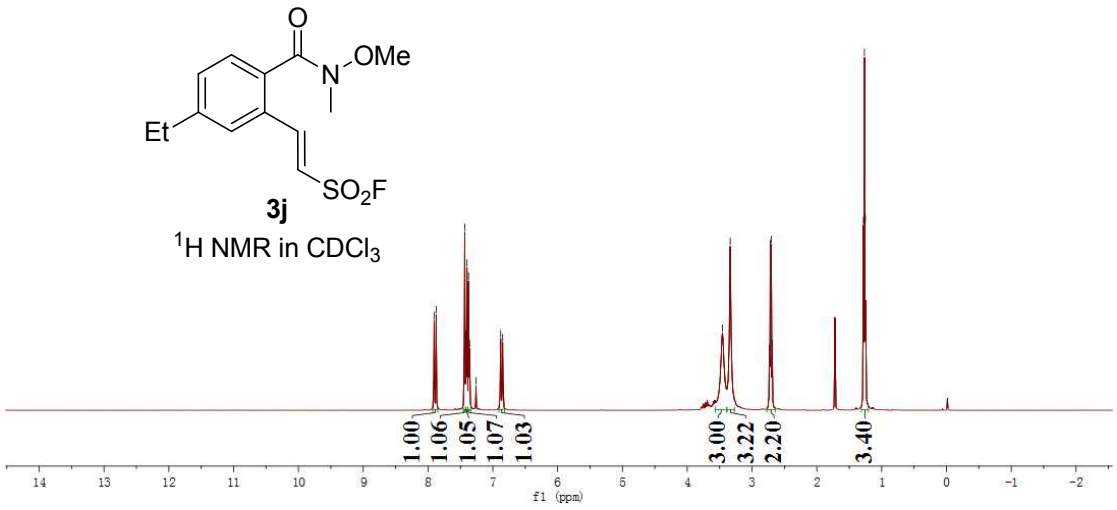
3i

^{19}F NMR in $CDCl_3$



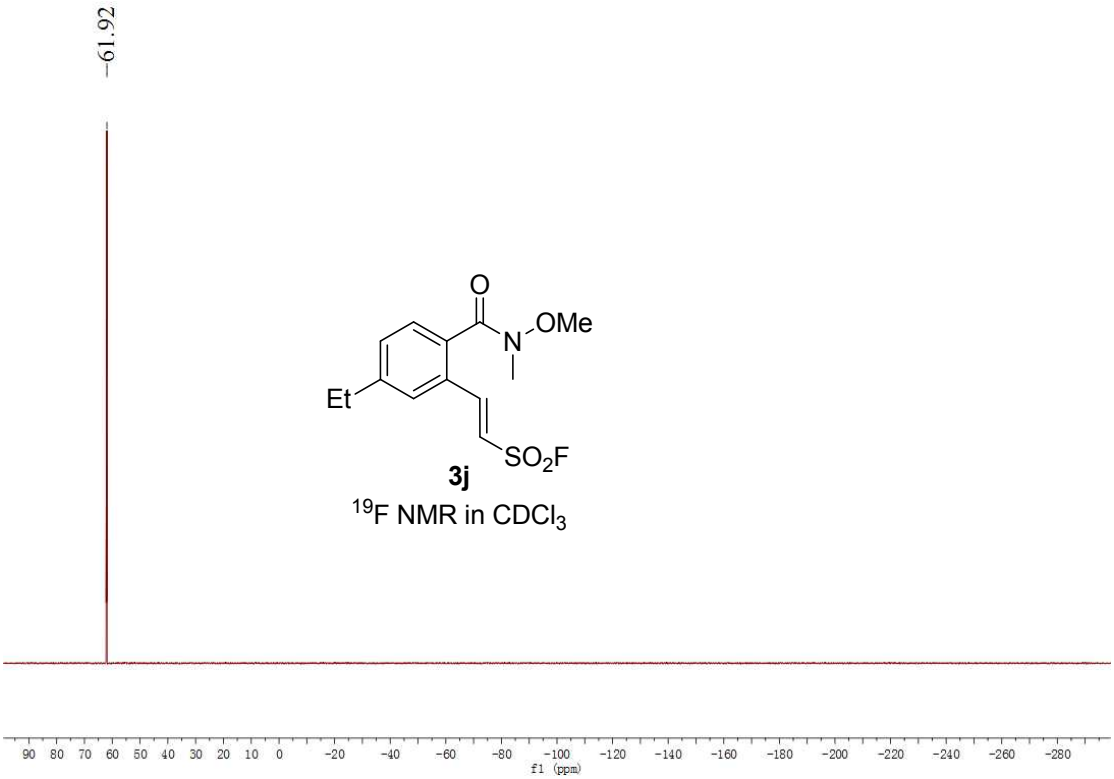
3i

^{13}C NMR in $CDCl_3$



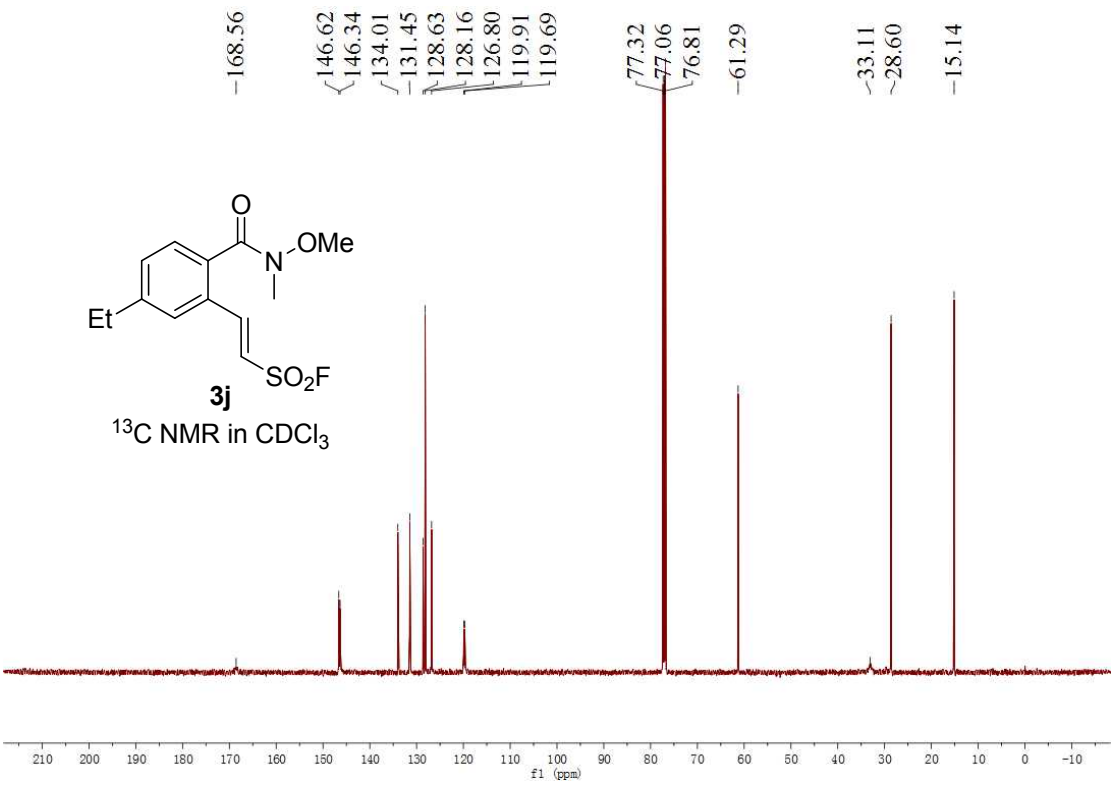
3j

^{1}H NMR in $CDCl_3$



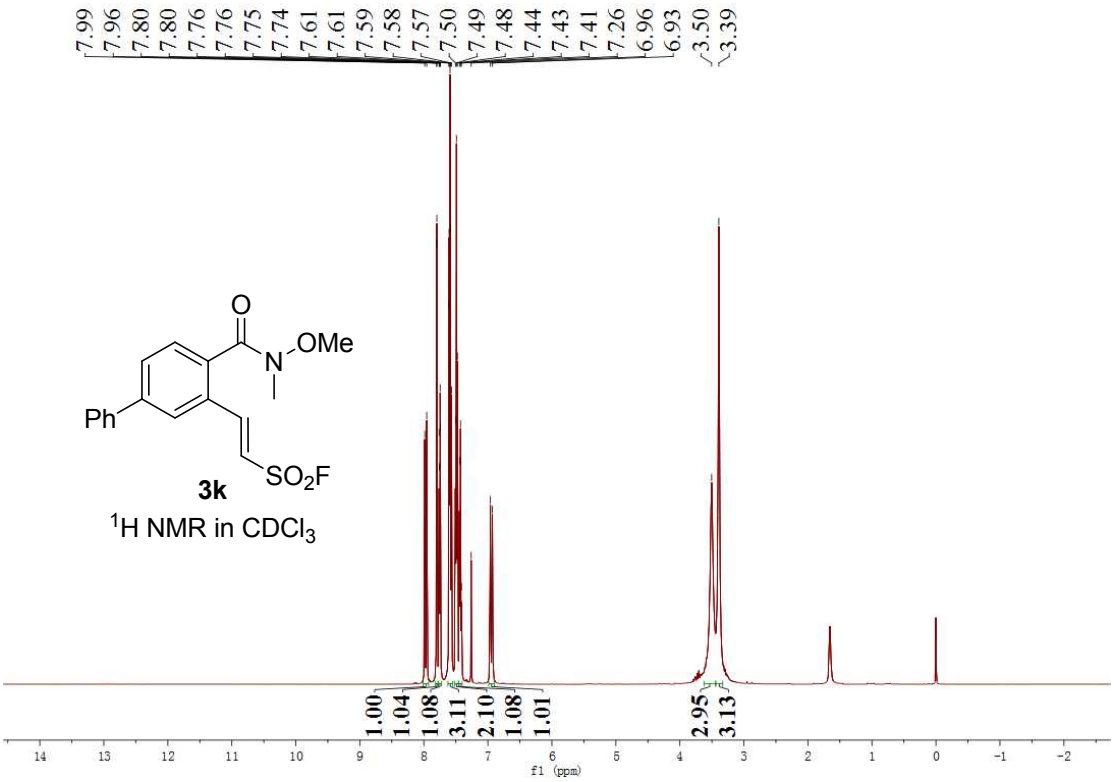
3j

^{19}F NMR in $CDCl_3$



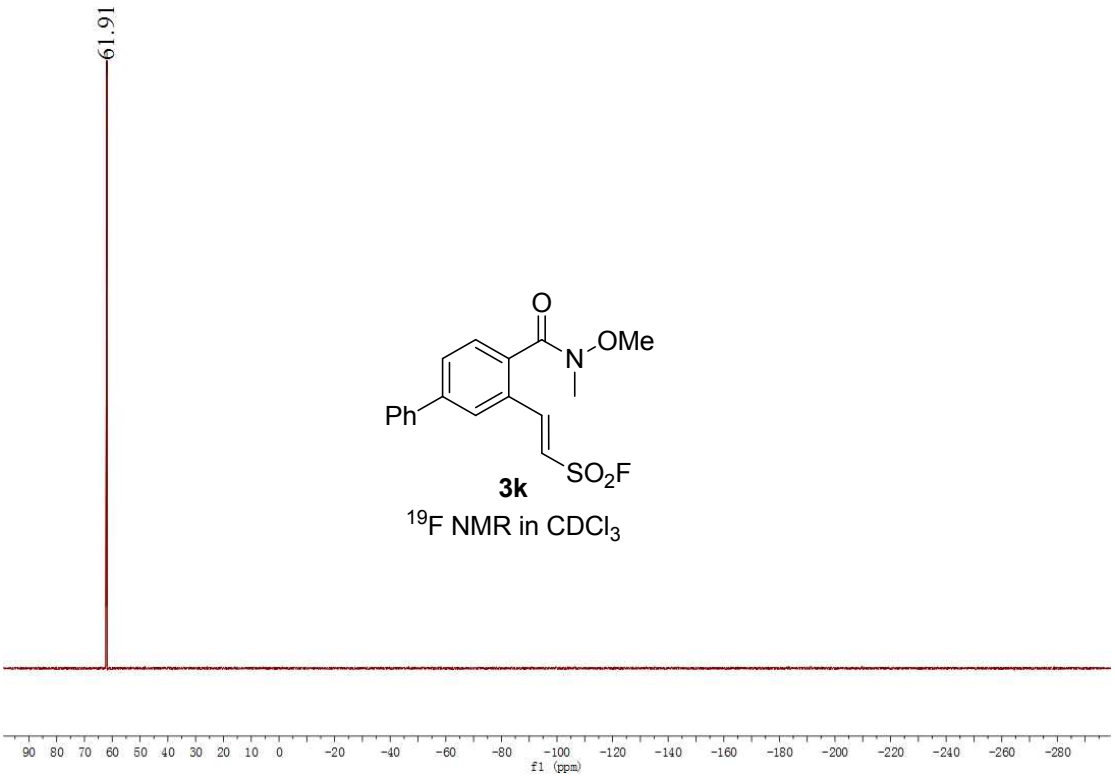
3j

^{13}C NMR in $CDCl_3$



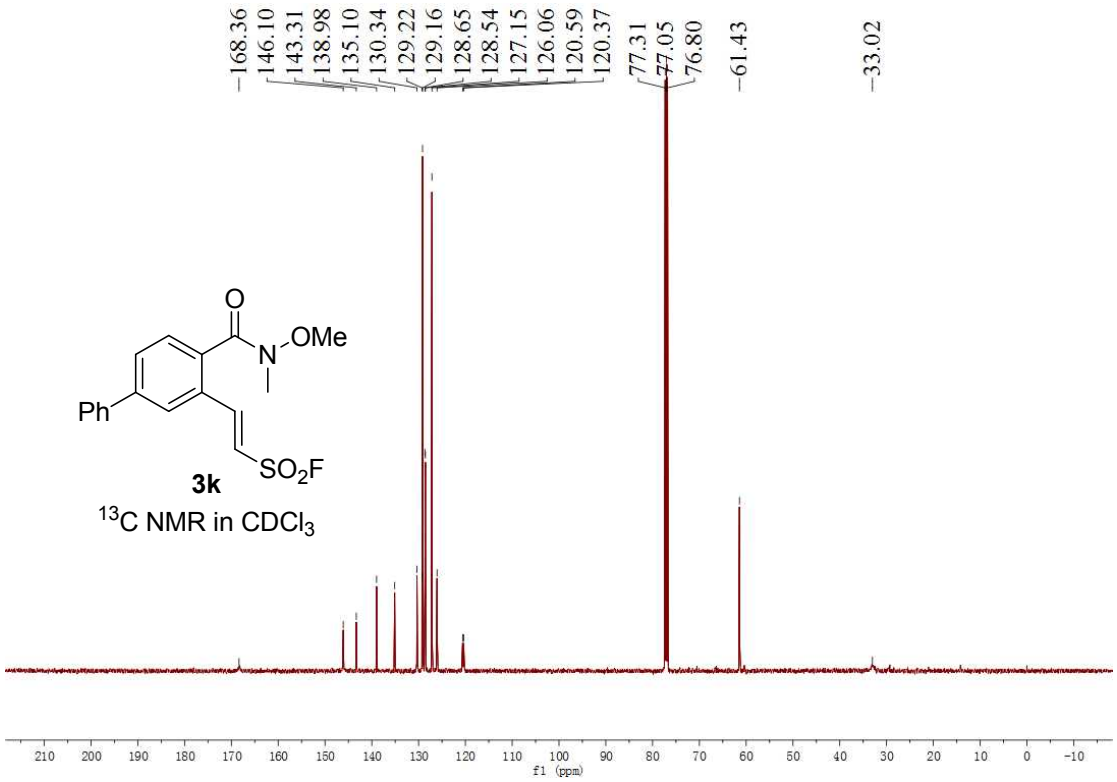
3k

^{1}H NMR in $CDCl_3$



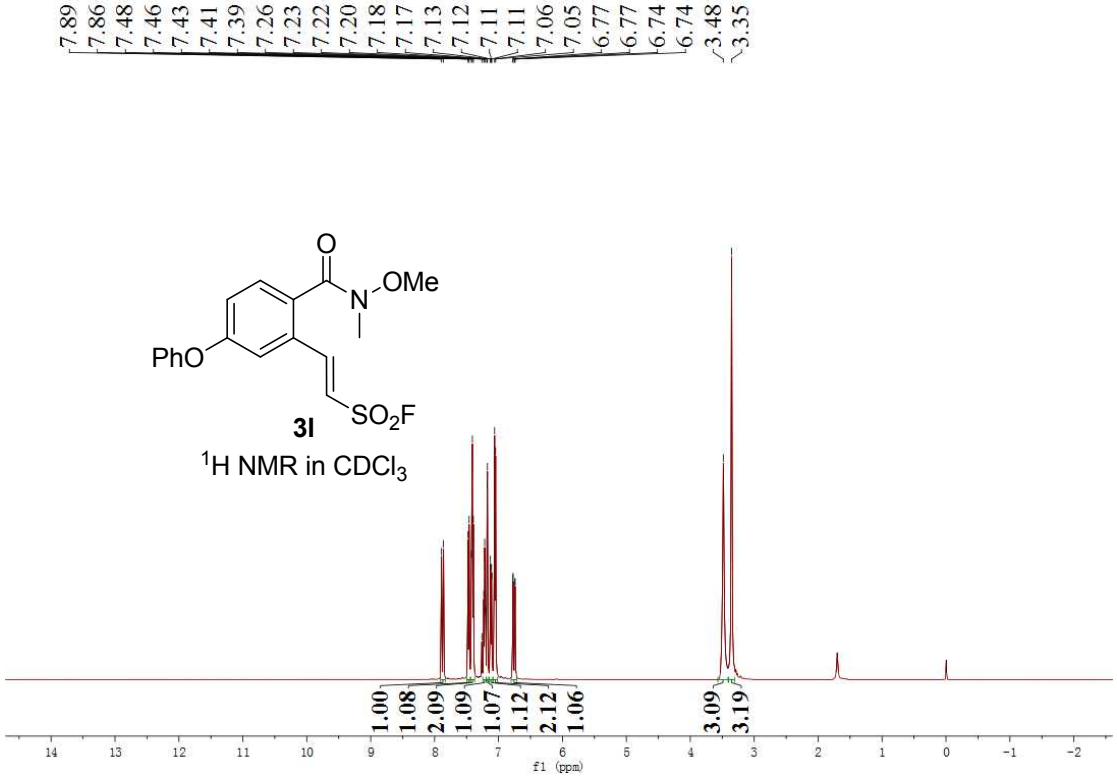
3k

^{19}F NMR in $CDCl_3$



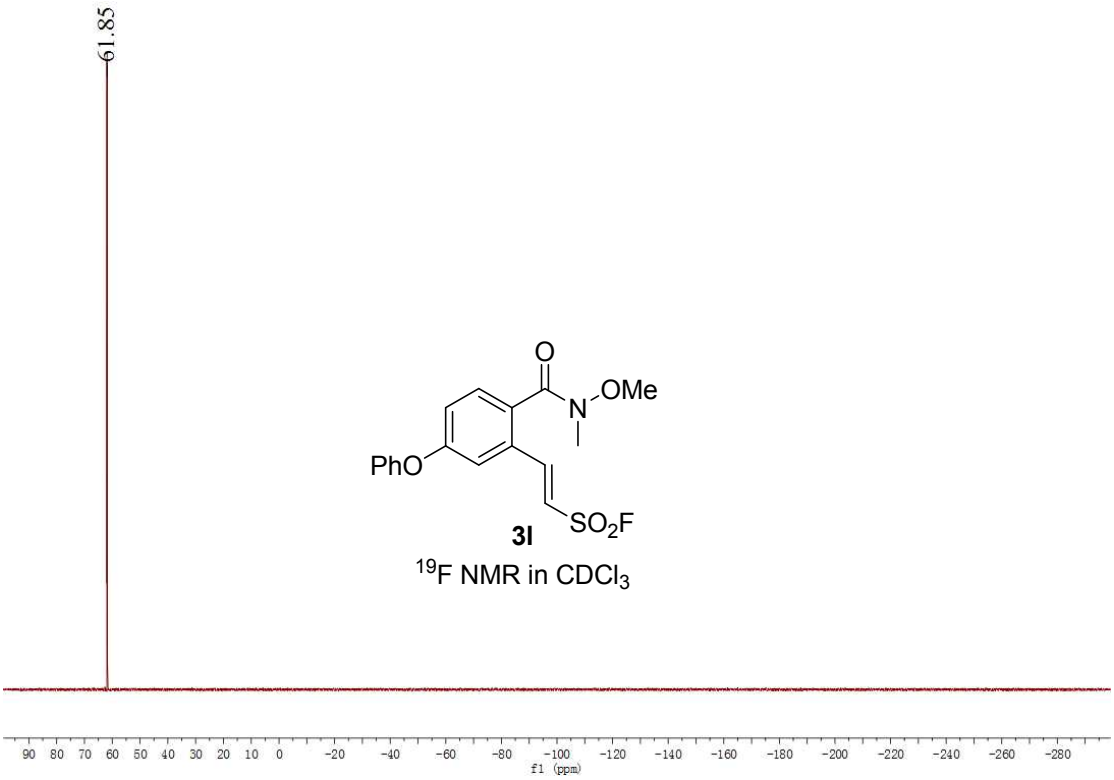
3k

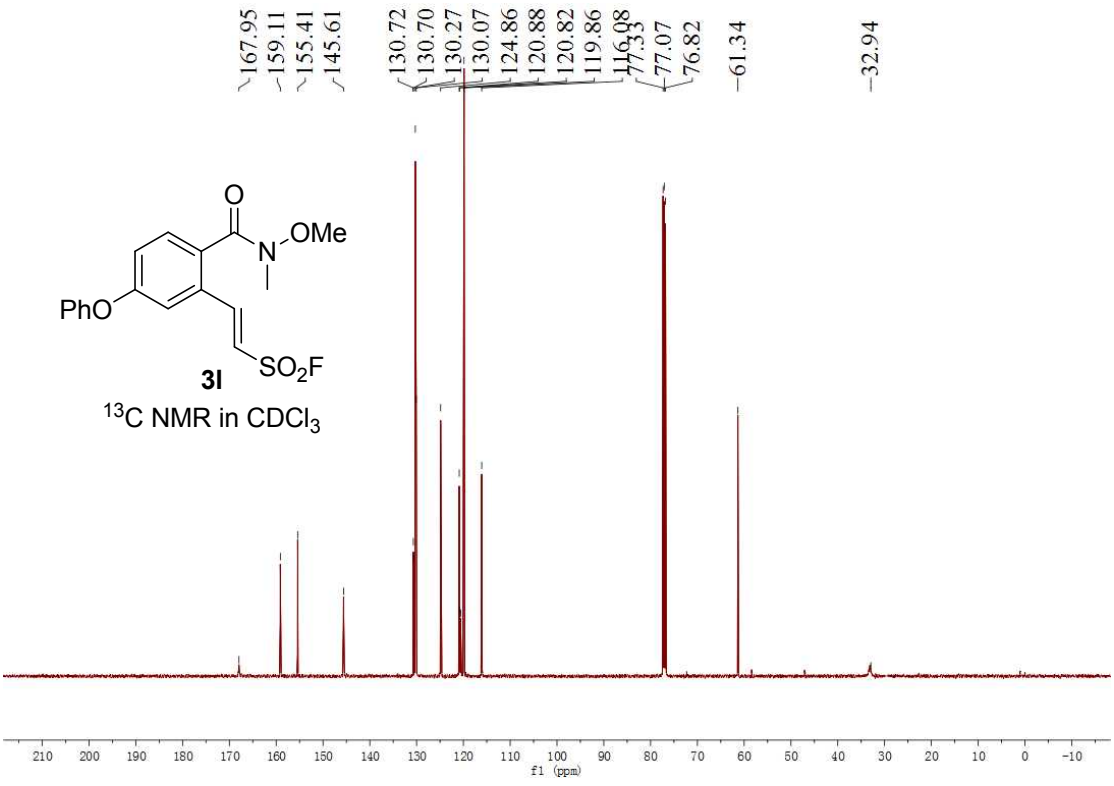
^{13}C NMR in $CDCl_3$

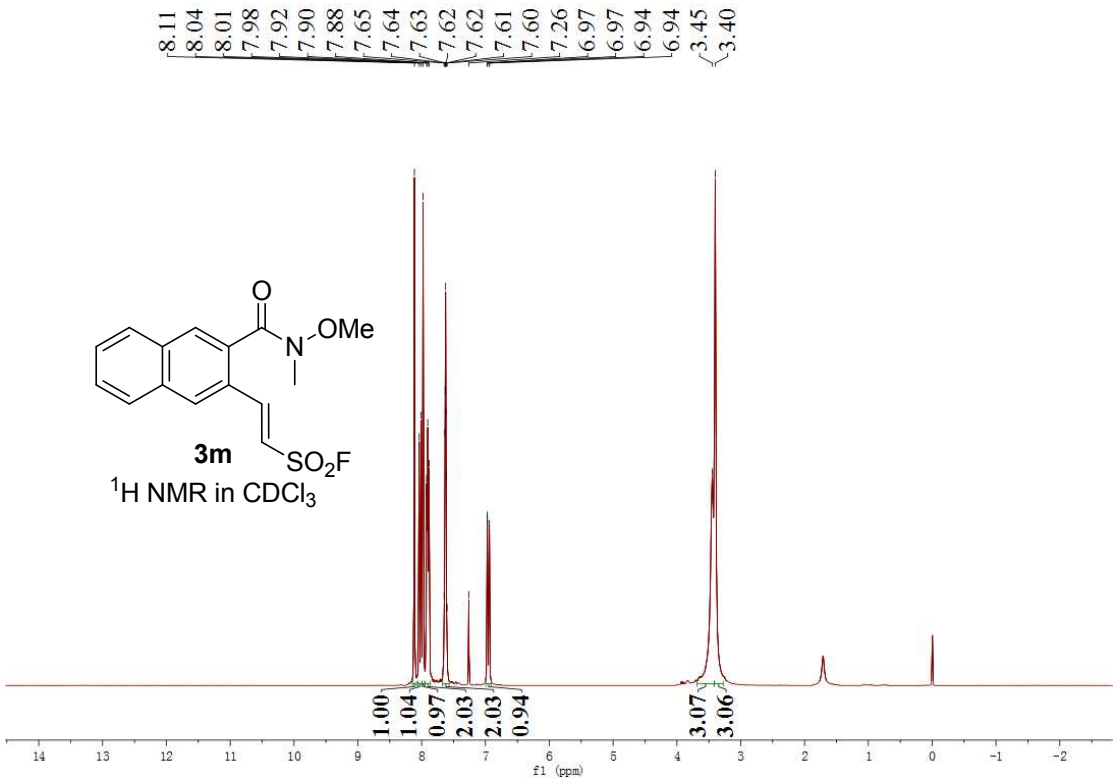


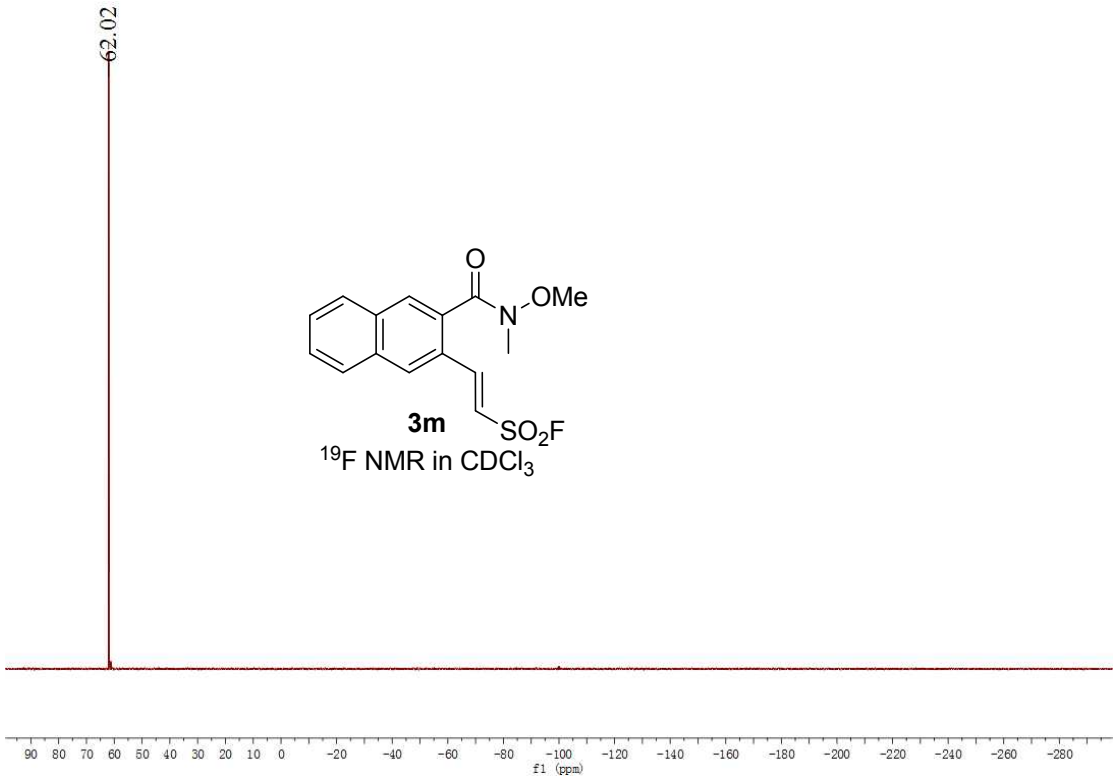
3l

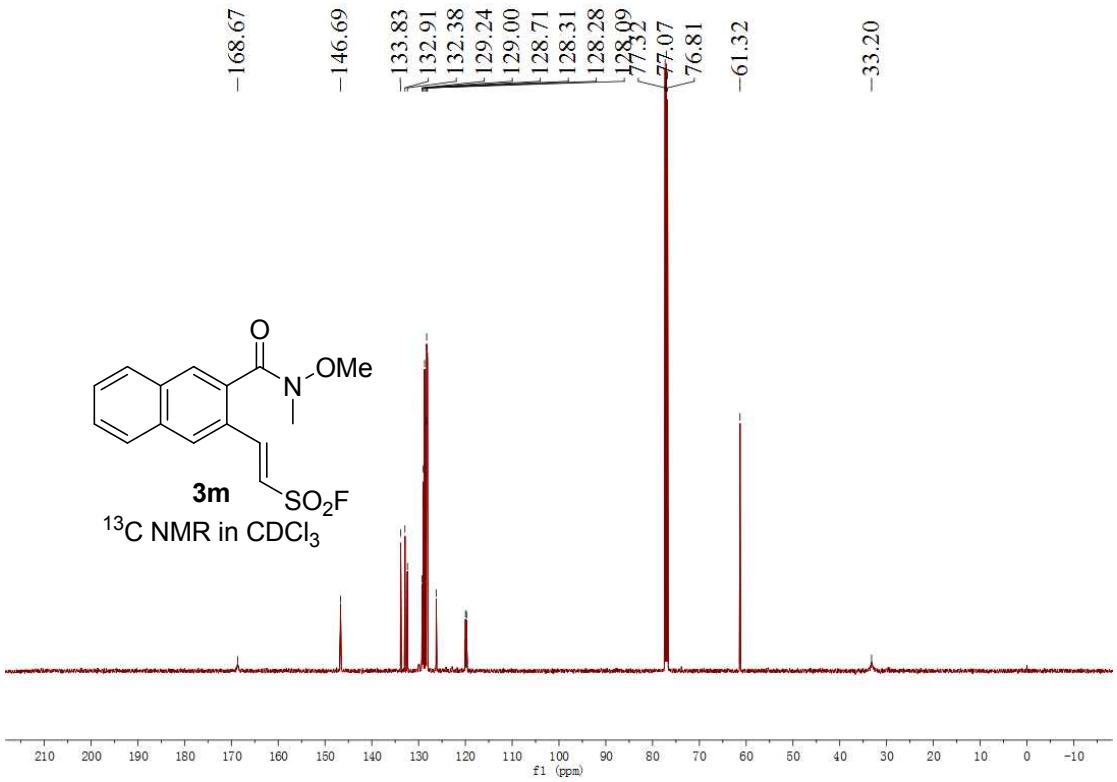
^{1}H NMR in $CDCl_3$

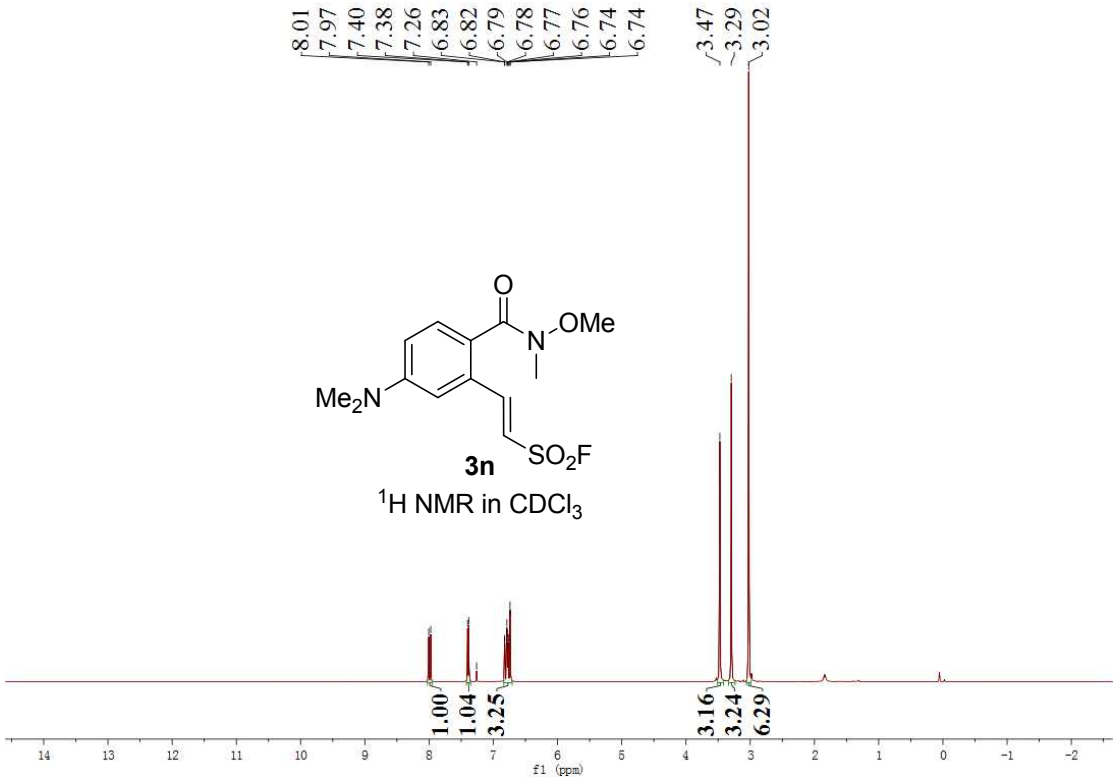

61.85
O
N
OMe
PhO
SO2F
3l
19F NMR in CDCl3
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)

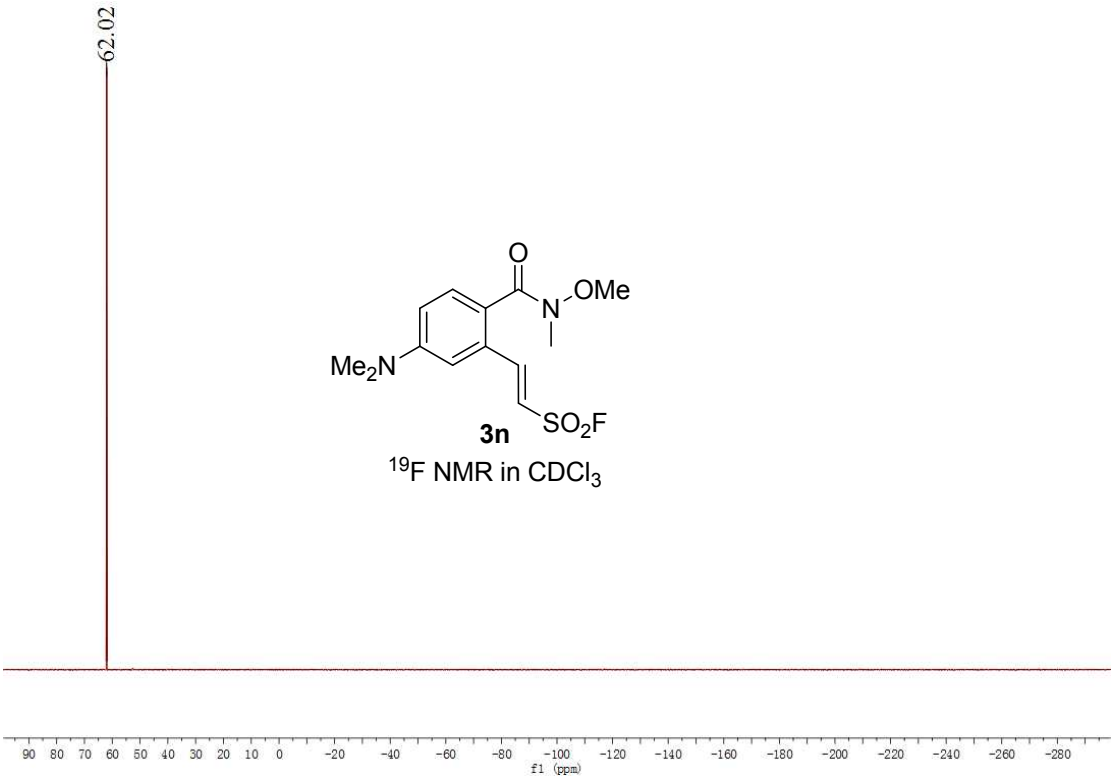

167.95
159.11
155.41
145.61
130.72
130.70
130.27
130.07
124.86
120.88
120.82
119.86
116.08
77.33
77.07
76.82
61.34
32.94
O
N
OMe
PhO
SO2F
3l
13C NMR in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

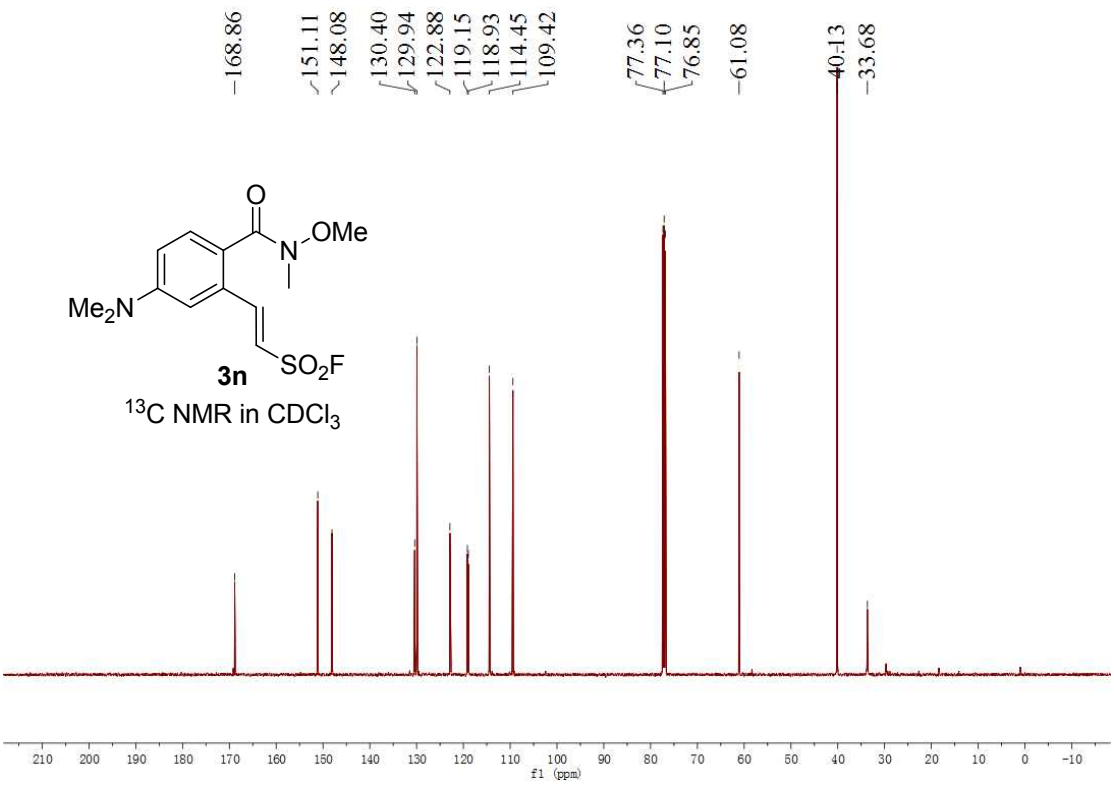

8.11
8.04
8.01
7.98
7.92
7.90
7.88
7.65
7.64
7.63
7.62
7.62
7.61
7.60
7.26
6.97
6.97
6.94
6.94
3.45
3.40
O
N
OMe
SO2F
3m
1H NMR in CDCl3
1.00
1.04
0.97
2.03
2.03
0.94
3.07
3.06
f1 (ppm)

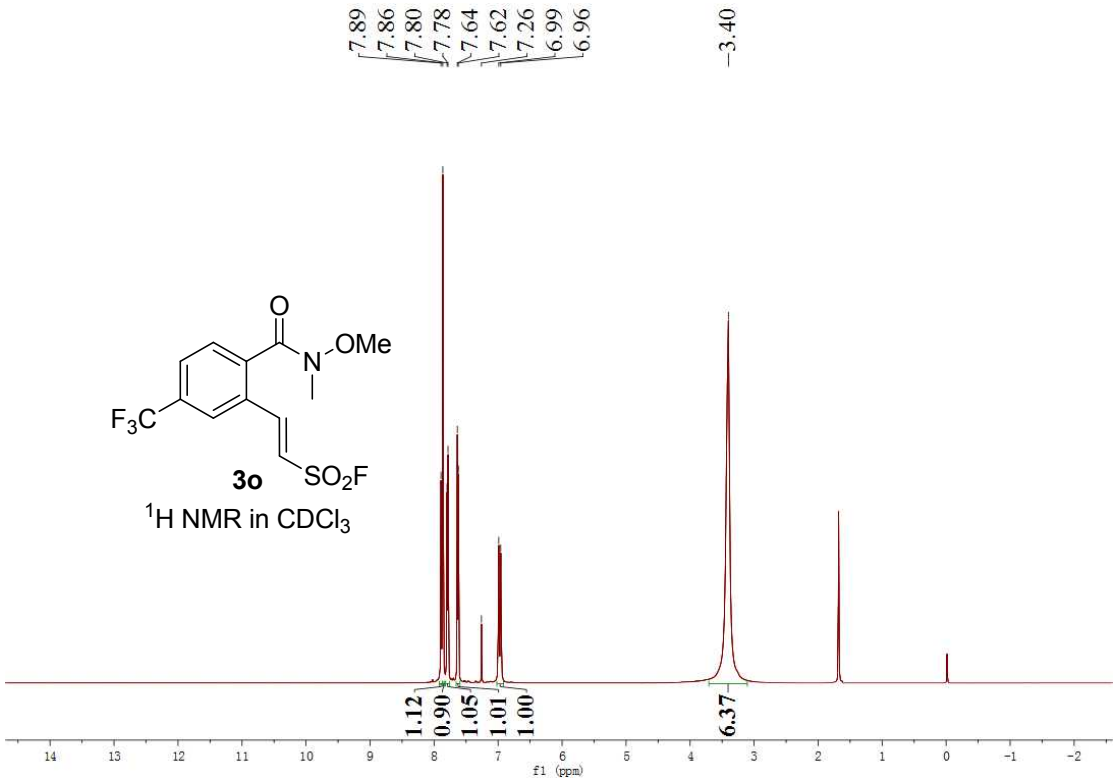

62.02
O
N
OMe
SO2F
3m
19F NMR in CDCl3
f1 (ppm)

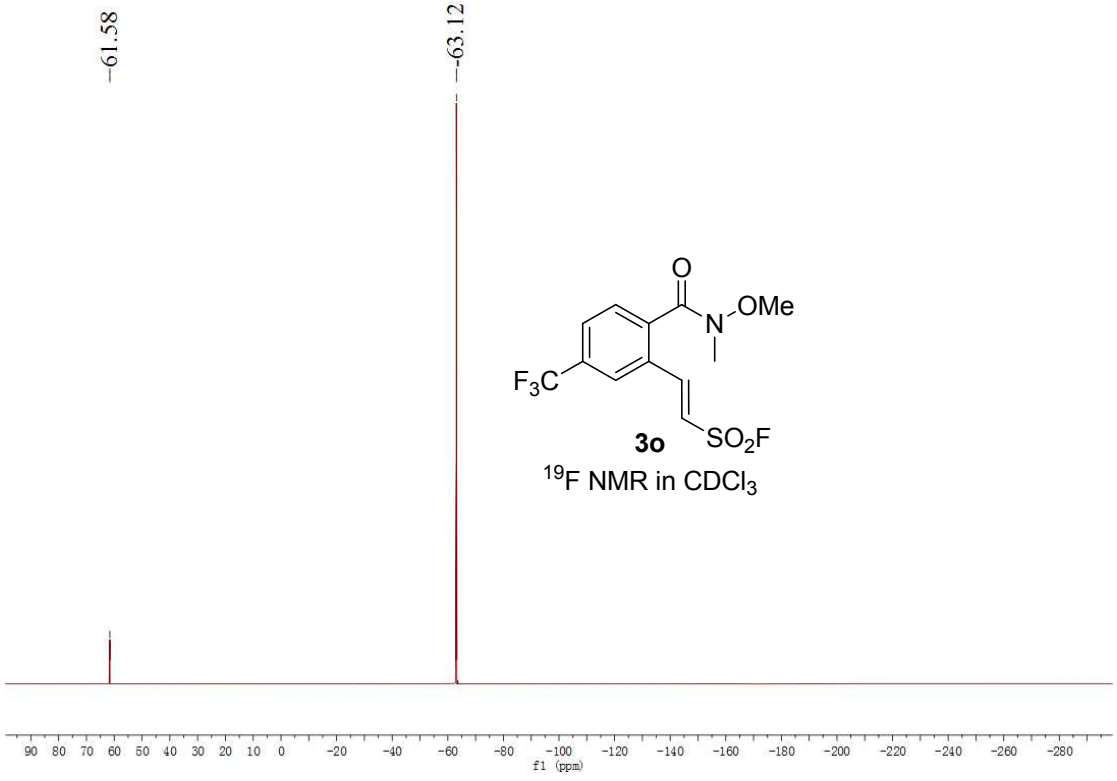

168.67
146.69
133.83
132.91
132.38
129.24
129.00
128.71
128.31
128.28
128.09
77.32
77.07
76.81
61.32
33.20
O
N
OMe
SO2F
3m
13C NMR in CDCl3
f1 (ppm)

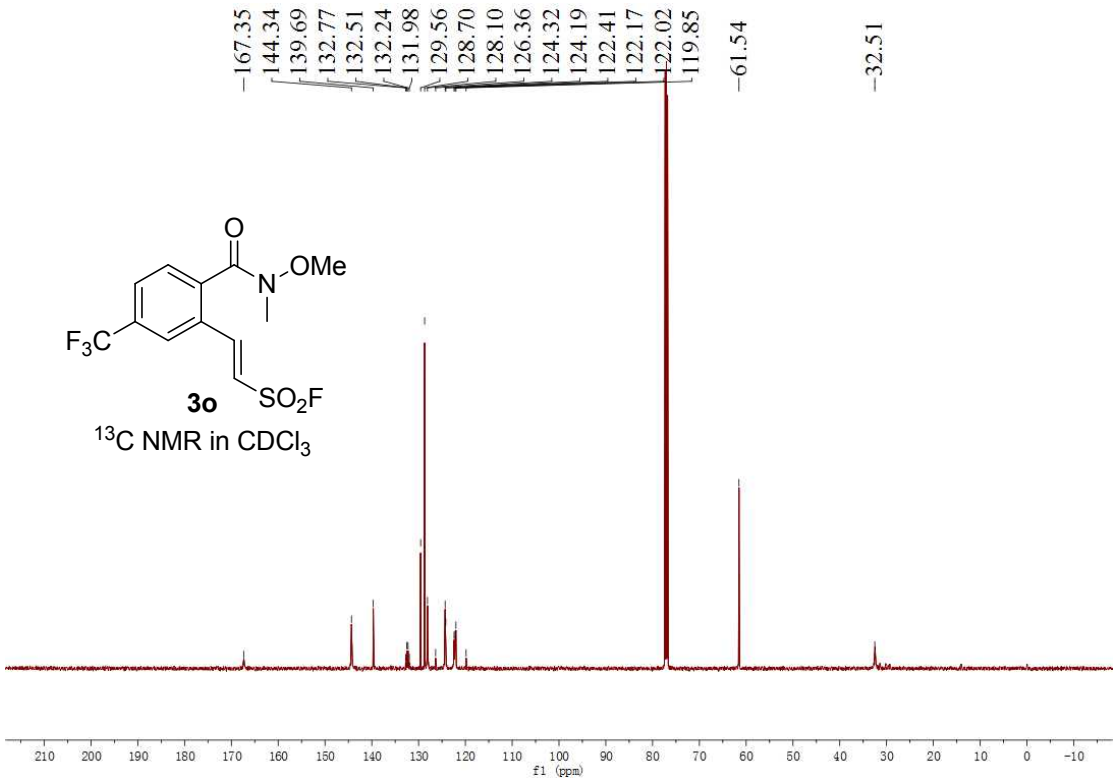

8.01
7.97
7.40
7.38
7.26
6.83
6.82
6.79
6.78
6.77
6.76
6.74
6.74
3.47
3.29
3.02
O
N
OMe
Me2N
SO2F
3n
1H NMR in CDCl3
1.00
1.04
3.25
3.16
3.24
6.29
f1 (ppm)

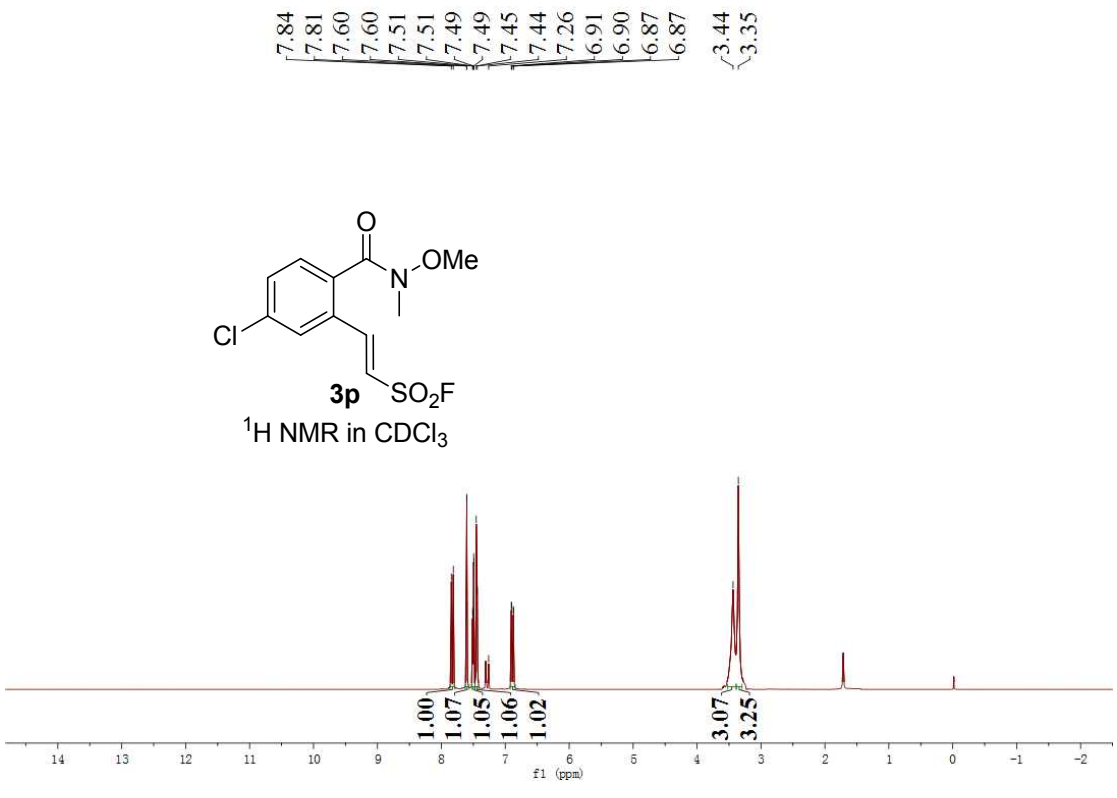

62.02
O
N
OMe
Me2N
SO2F
3n
19F NMR in CDCl3
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)

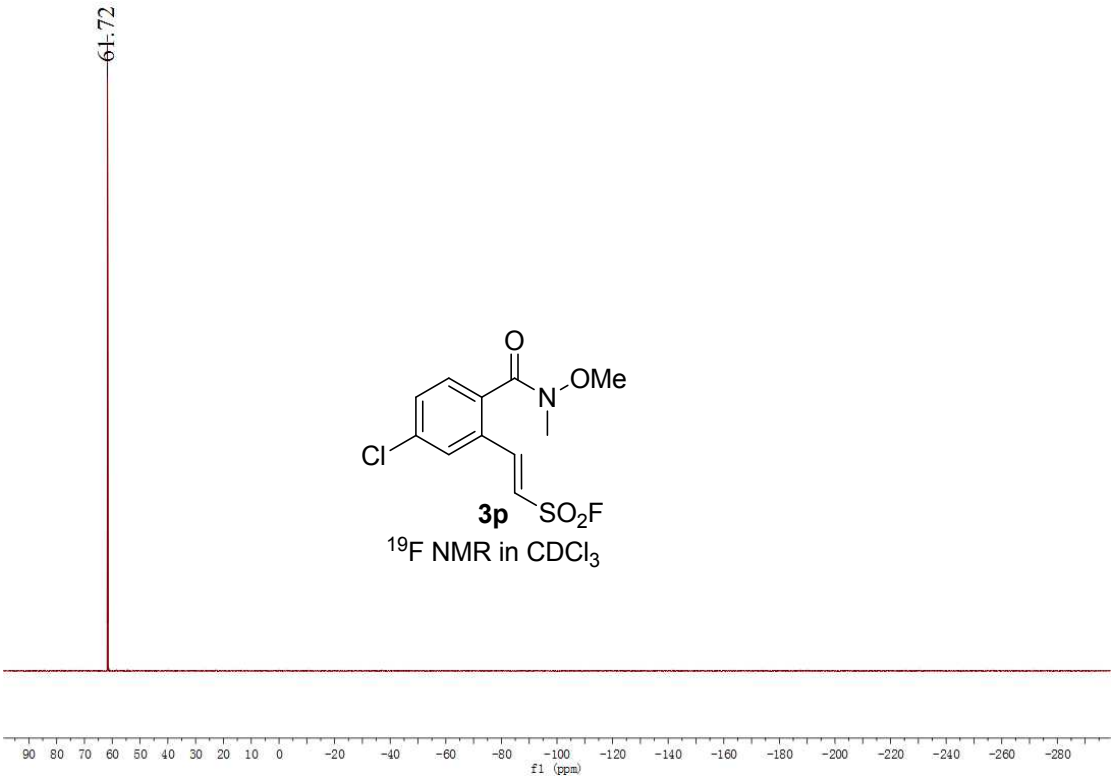

168.86
151.11
148.08
130.40
129.94
122.88
119.15
118.93
114.45
109.42
77.36
77.10
76.85
61.08
40.13
33.68
O
N
OMe
Me2N
SO2F
3n
13C NMR in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

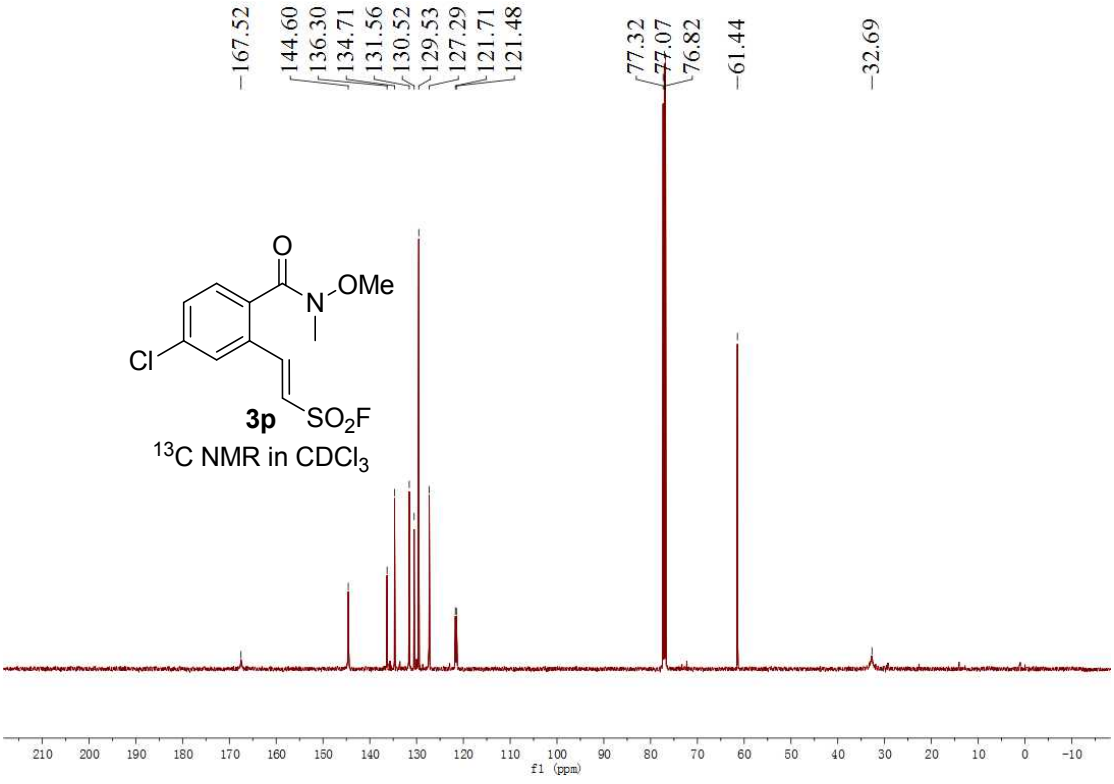

7.89
7.86
7.80
7.78
7.64
7.62
7.26
6.99
6.96
3.40
O
N
OMe
F3C
SO2F
3o
1H NMR in CDCl3
1.12
0.90
1.05
1.01
1.00
6.37
f1 (ppm)

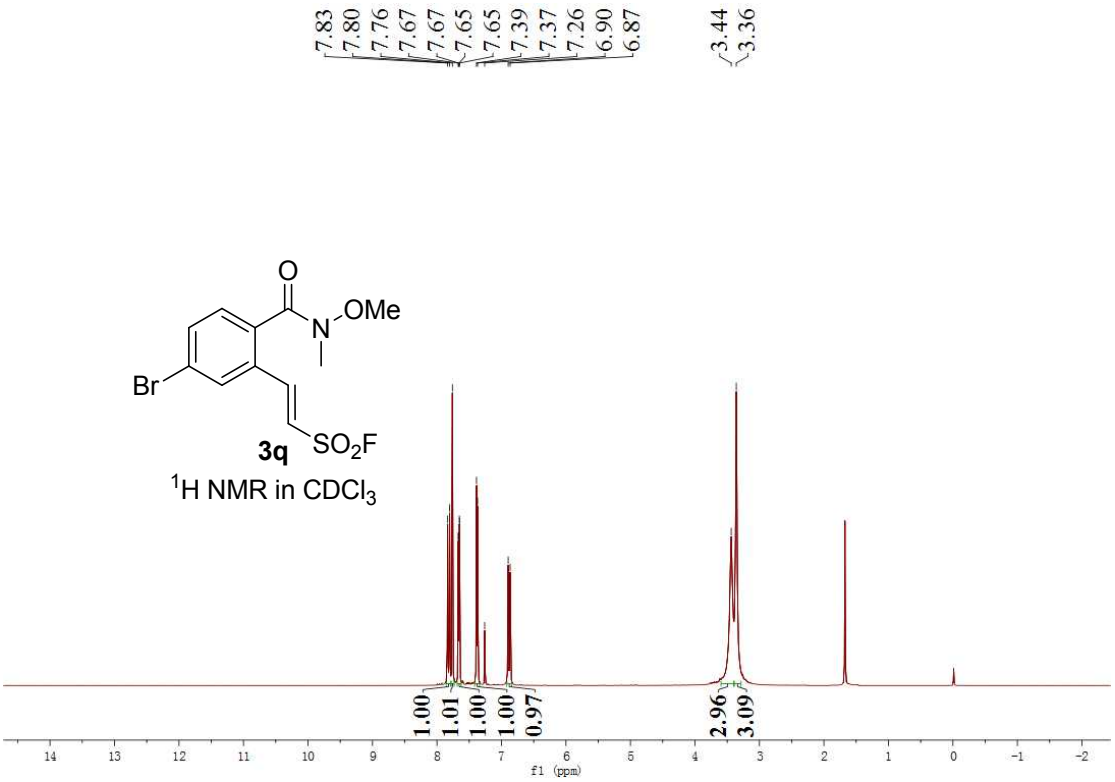

-61.58
-63.12
O
N
OMe
F3C
SO2F
3o
19F NMR in CDCl3
f1 (ppm)


167.35
144.34
139.69
132.77
132.51
132.24
131.98
129.56
128.70
128.10
126.36
124.32
124.19
122.41
122.17
122.02
119.85
61.54
32.51
O
N
OMe
F3C
SO2F
3o
13C NMR in CDCl3
f1 (ppm)


7.84
7.81
7.60
7.60
7.51
7.51
7.49
7.49
7.45
7.44
7.26
6.91
6.90
6.87
6.87
3.44
3.35
O
N
OMe
Cl
SO2F
3p
1H NMR in CDCl3
1.00
1.07
1.05
1.06
1.02
3.07
3.25
f1 (ppm)


61.72
O
N
OMe
Cl
3p
SO2F
19F NMR in CDCl3
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)


167.52
144.60
136.30
134.71
131.56
130.52
129.53
127.29
121.71
121.48
77.32
77.07
76.82
61.44
32.69
O
N
OMe
Cl
3p
SO2F
13C NMR in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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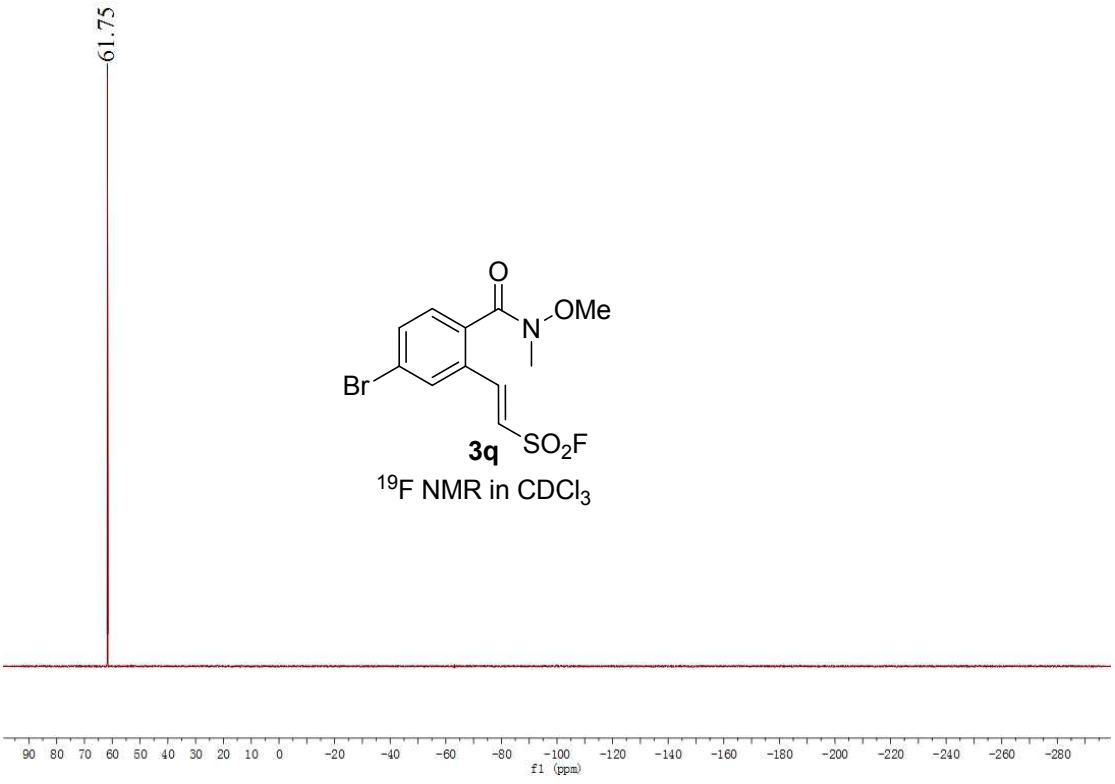
7.80
7.76
7.67
7.67
7.65
7.65
7.39
7.37
7.26
6.90
6.87
3.44
3.36
O
N
OMe
Br
SO2F
3q
1H NMR in CDCl3
1.00
1.01
1.00
1.00
0.97
2.96
3.09
f1 (ppm)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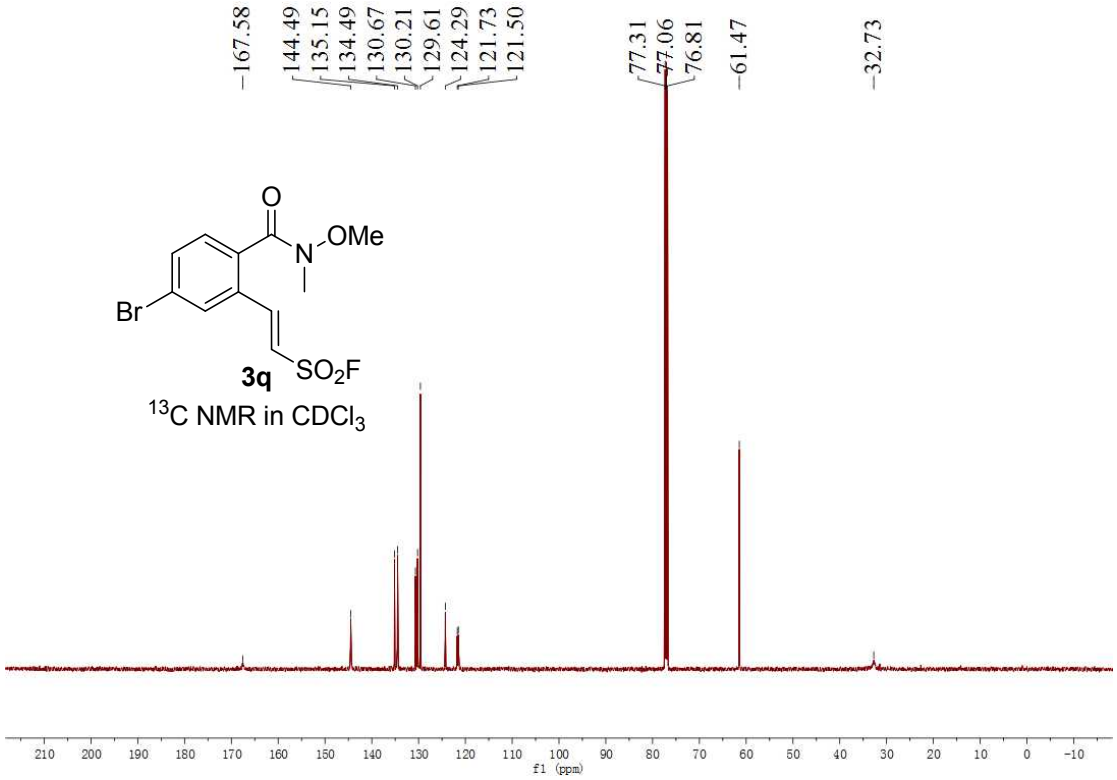
Br
SO2F
3q
19F NMR in CDCl3
f1 (ppm)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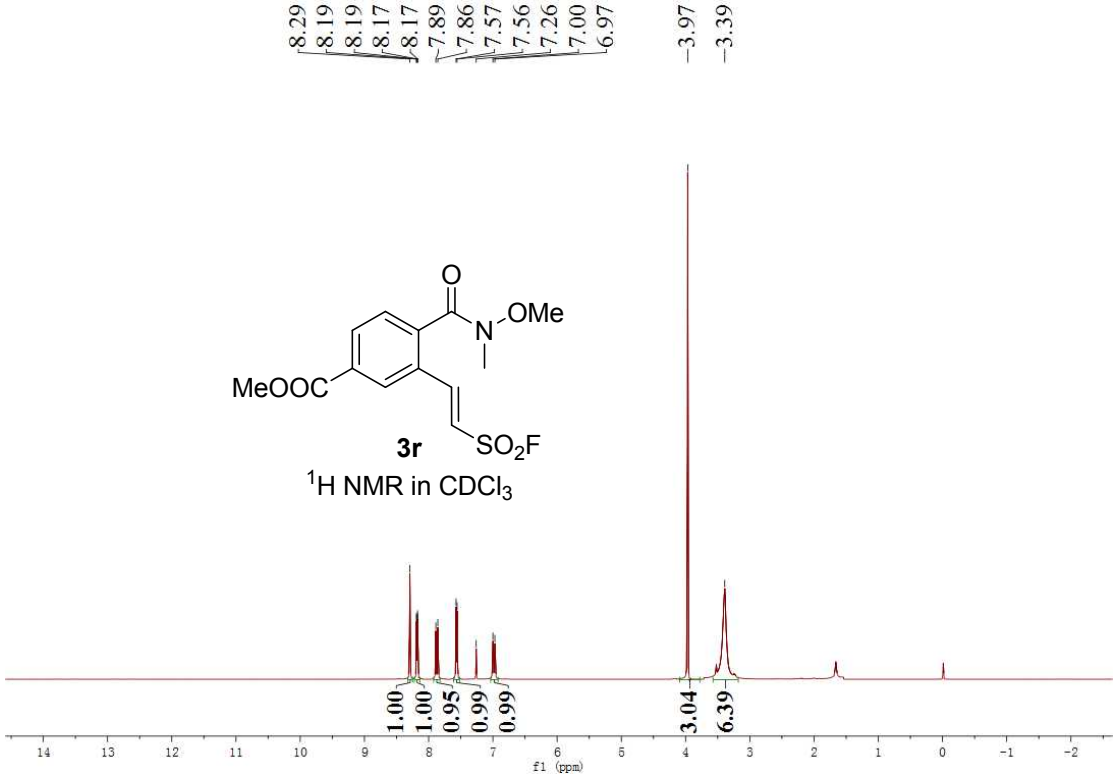
144.49
135.15
134.49
130.67
130.21
129.61
124.29
121.73
121.50
77.31
77.06
76.81
61.47
32.73
O
N
OMe
Br
SO2F
3q
13C NMR in CDCl3
f1 (ppm)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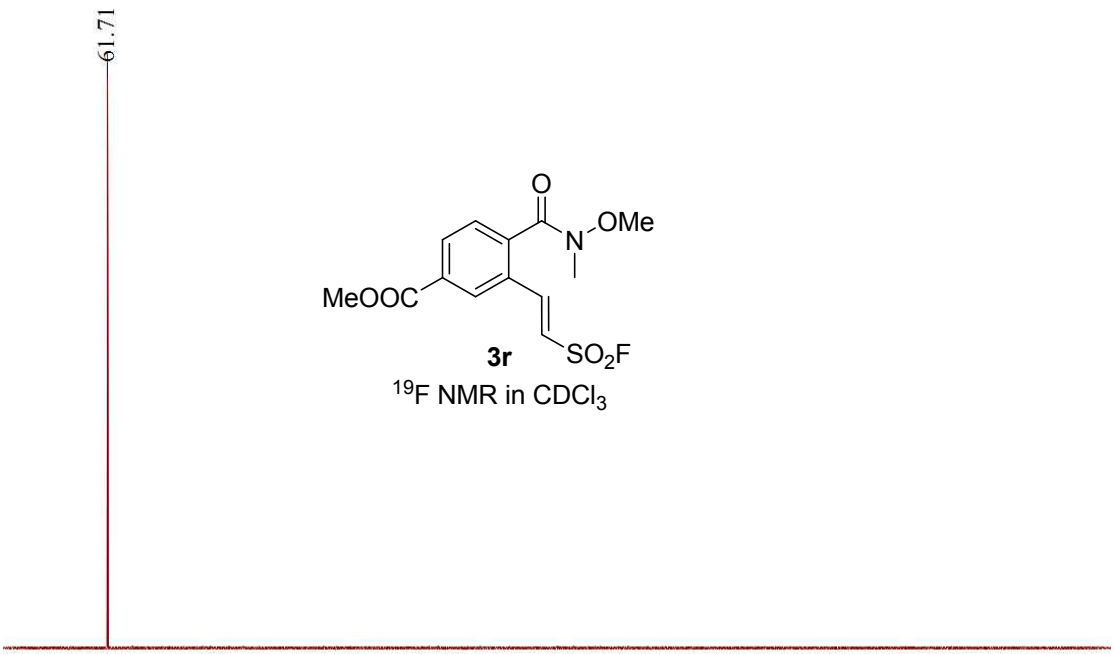
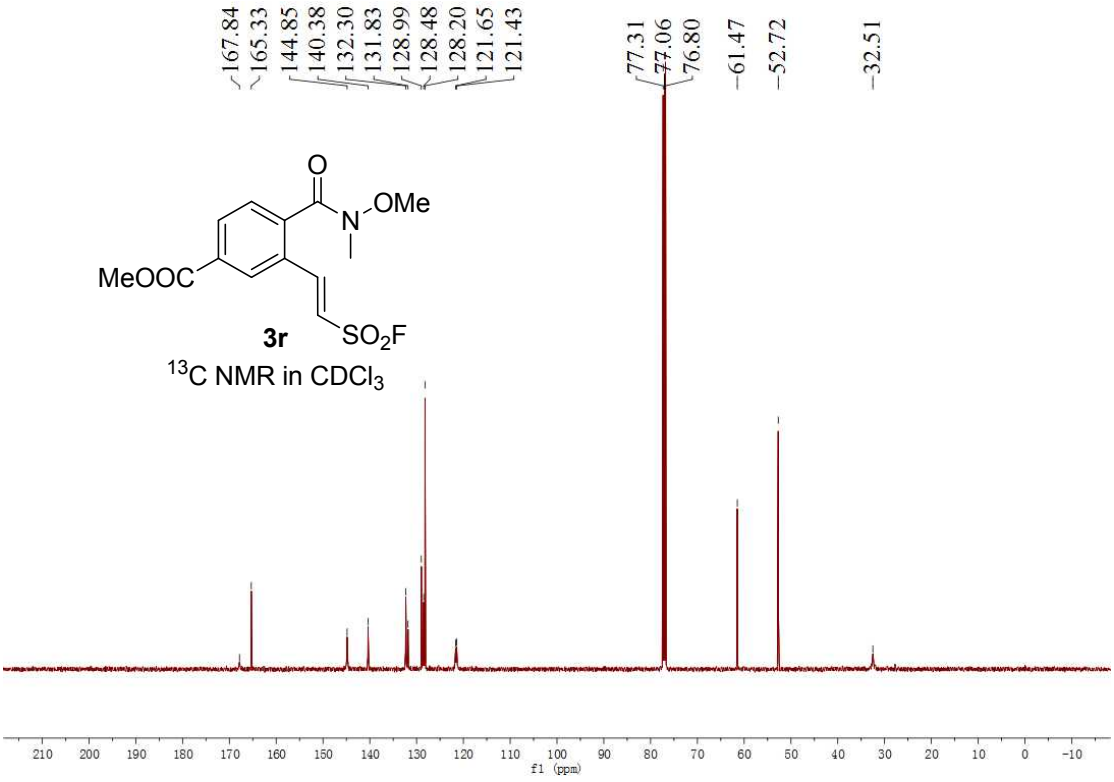
8.19
8.19
8.17
8.17
7.89
7.86
7.57
7.56
7.26
7.00
6.97
3.97
3.39
O
N
OMe
MeOOC
SO2F
3r
1H NMR in CDCl3
1.00
1.00
0.95
0.99
0.99
3.04
6.39
f1 (ppm)


61.71
O
N
OMe
MeOOC
SO2F
3r
19F NMR in CDCl3
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)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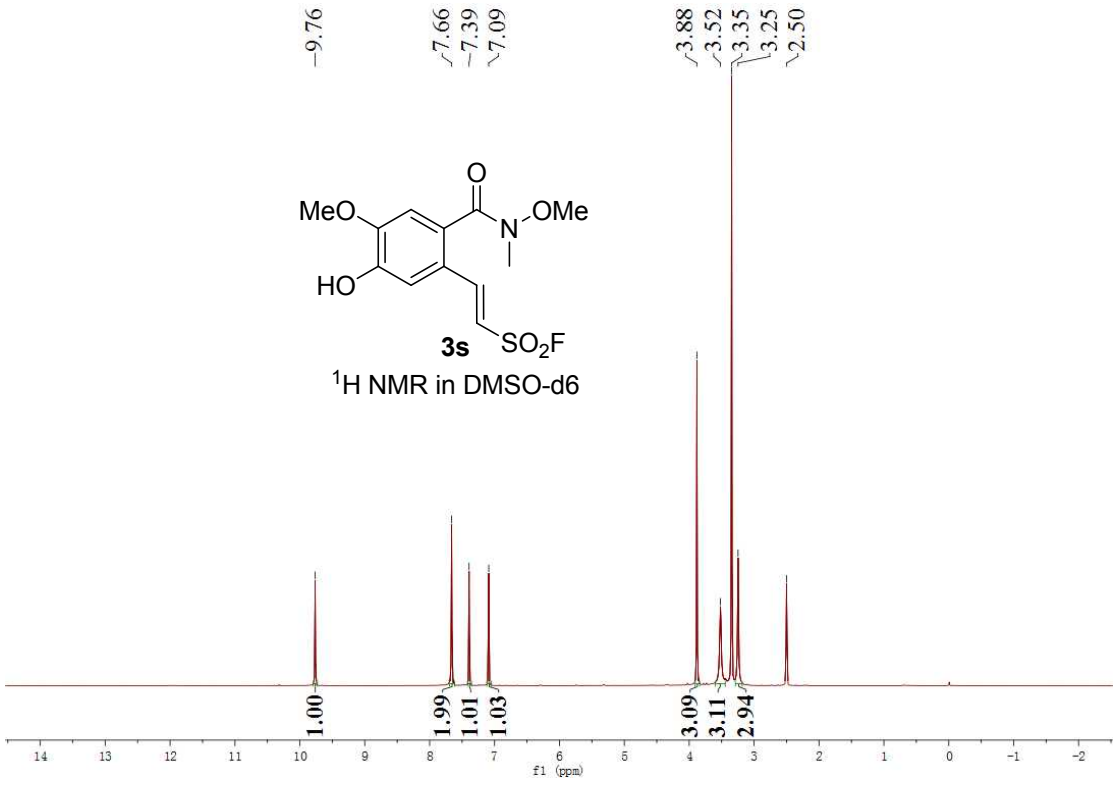
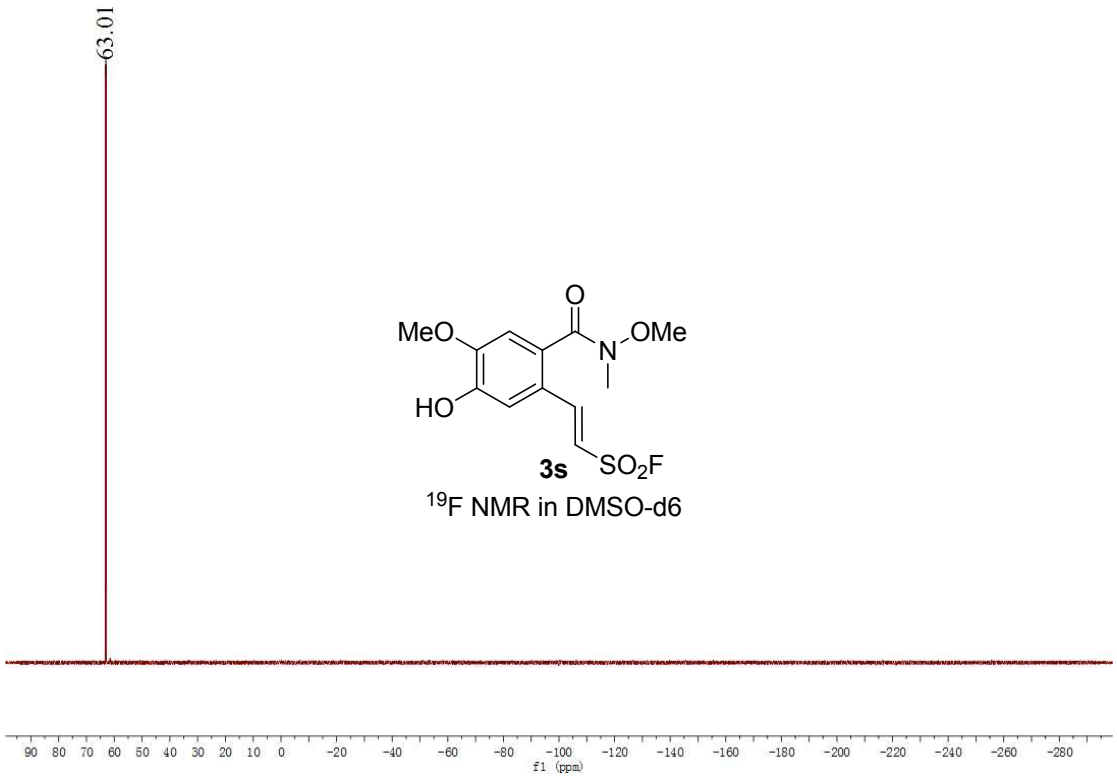
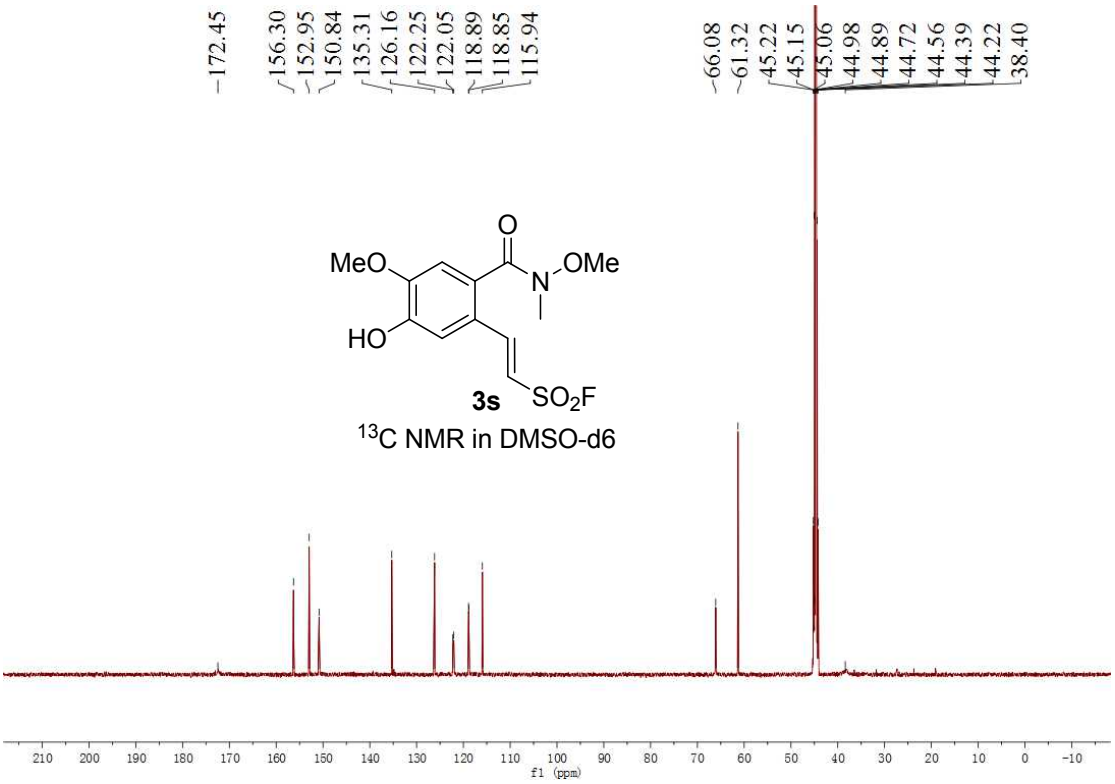
165.33
144.85
140.38
132.30
131.83
128.99
128.48
128.20
121.65
121.43
77.31
77.06
76.80
61.47
52.72
32.51
O
N
OMe
MeOOC
SO2F
3r
13C NMR in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

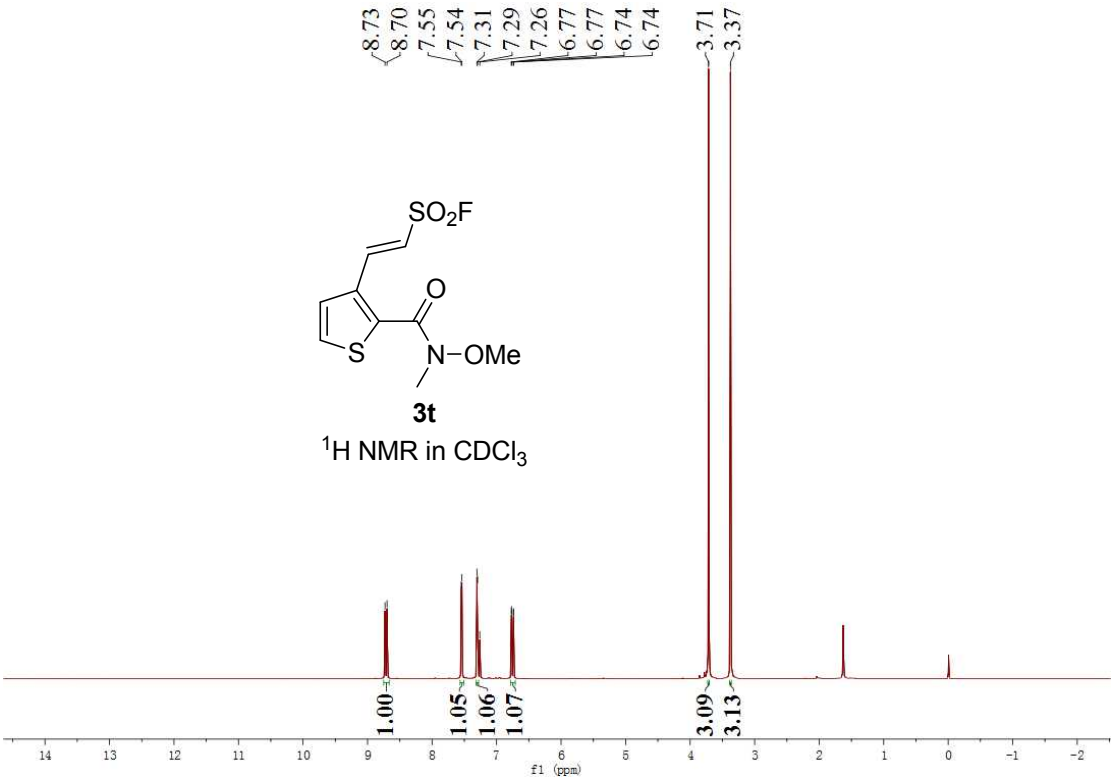


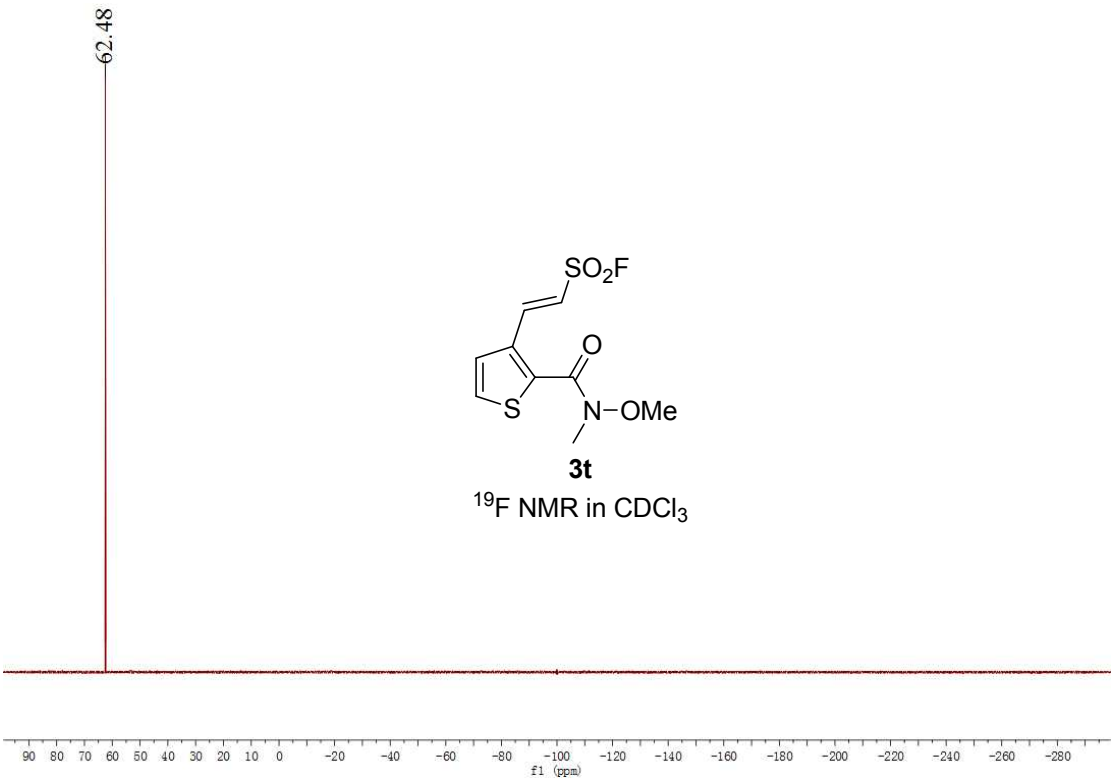
^{1}H NMR in DMSO-d6

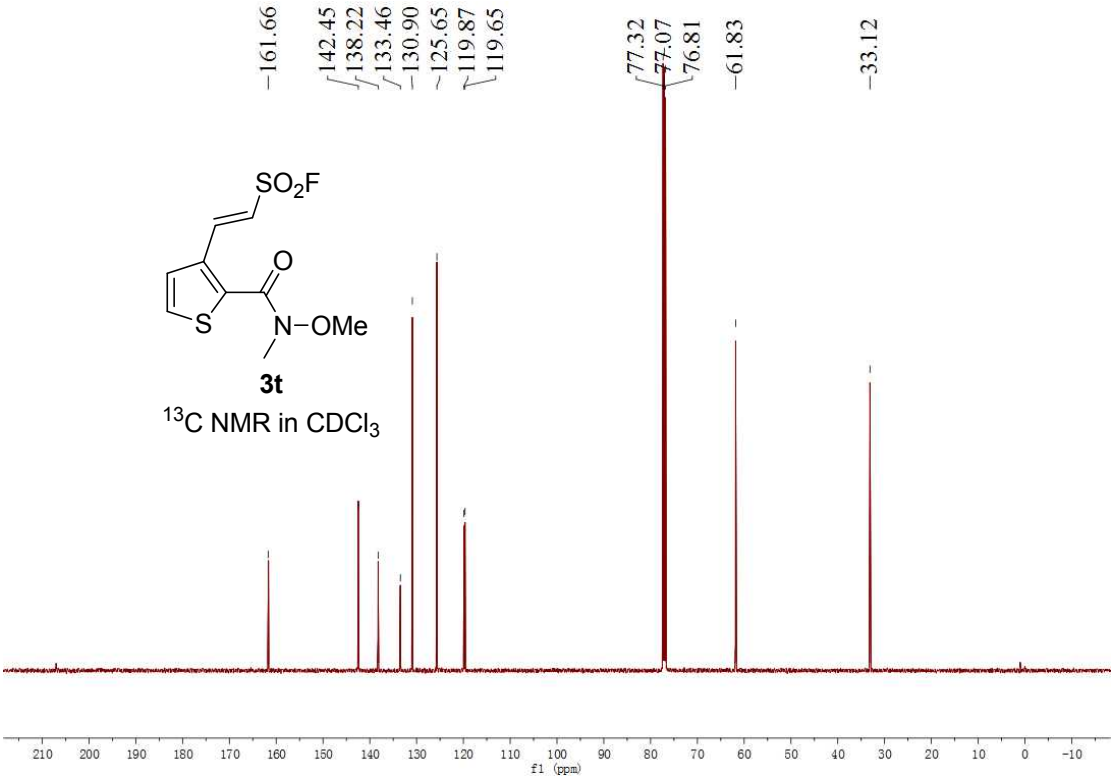


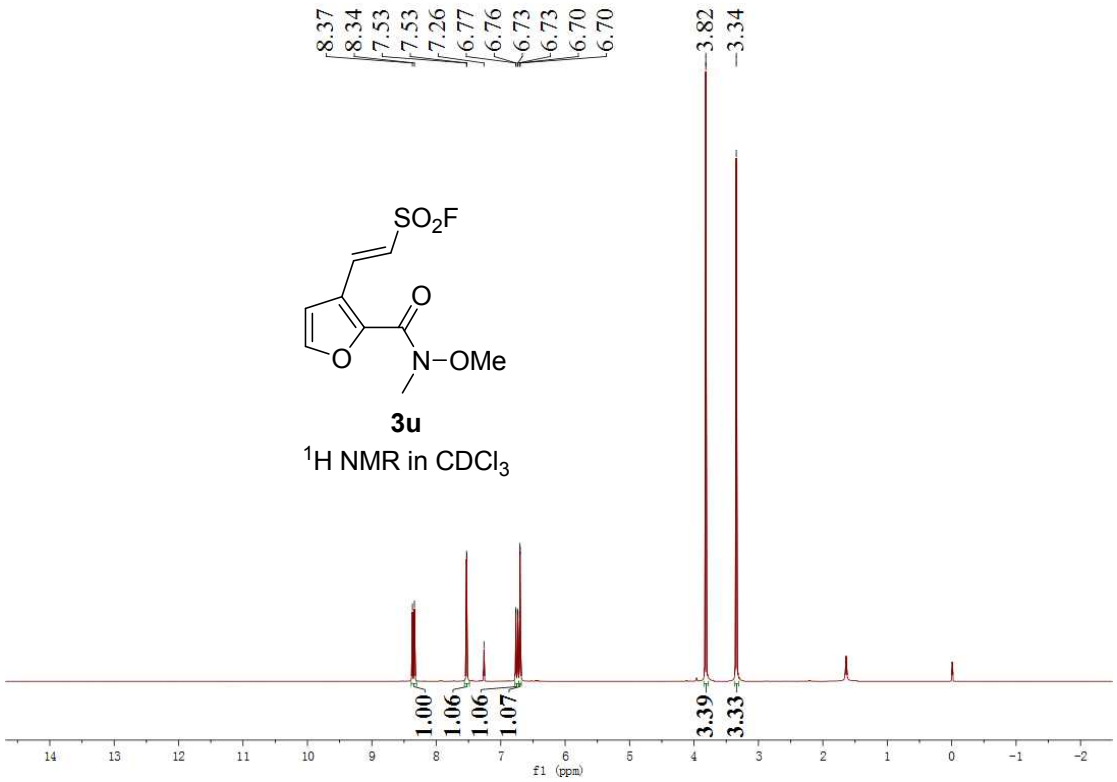
^{19}F NMR in DMSO-d6


172.45
156.30
152.95
150.84
135.31
126.16
122.25
122.05
118.89
118.85
115.94
66.08
61.32
45.22
45.15
45.06
44.98
44.89
44.72
44.56
44.39
44.22
38.40
MeO
HO
O
N
OMe
SO2F
3s
13C NMR in DMSO-d6
f1 (ppm)


8.73
8.70
7.55
7.54
7.31
7.29
7.26
6.77
6.77
6.74
6.74
3.71
3.37
SO2F
O
S
N−OMe
3t
1H NMR in CDCl3
1.00
1.05
1.06
1.07
3.09
3.13
f1 (ppm)

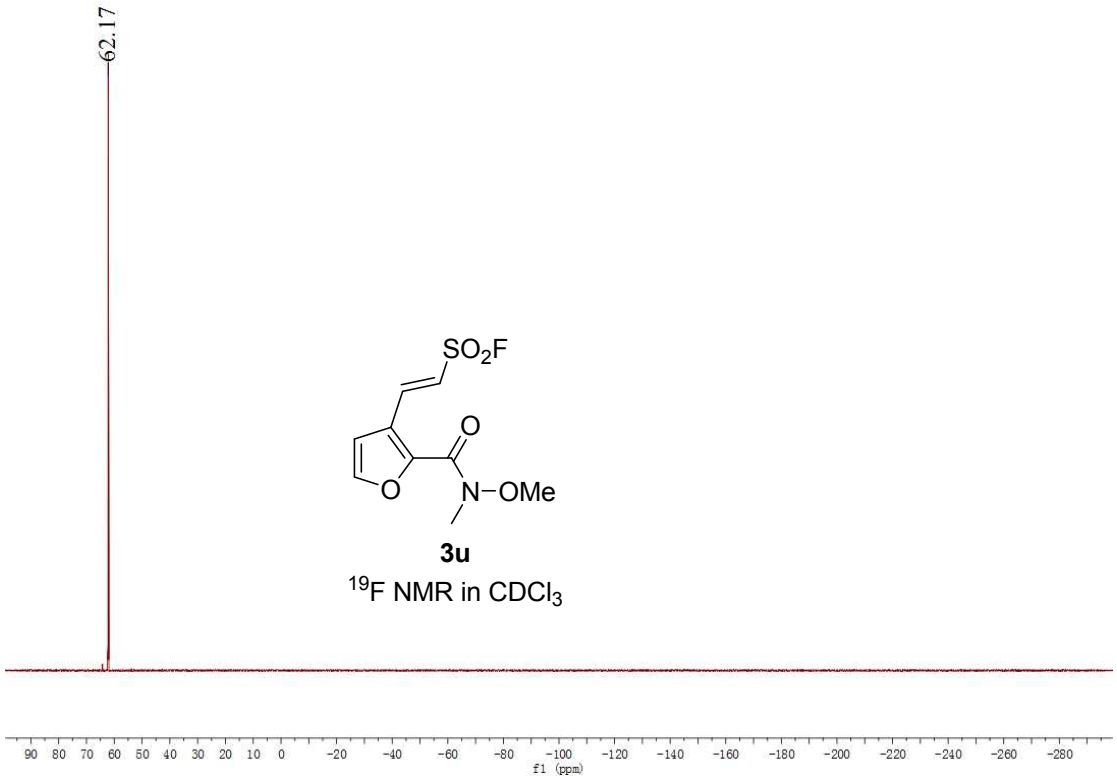

62.48
SO2F
O
S
N−OMe
3t
19F NMR in CDCl3
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)


161.66
142.45
138.22
133.46
130.90
125.65
119.87
119.65
77.32
77.07
76.81
61.83
33.12
SO2F
O
S
N−OMe
3t
13C NMR in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



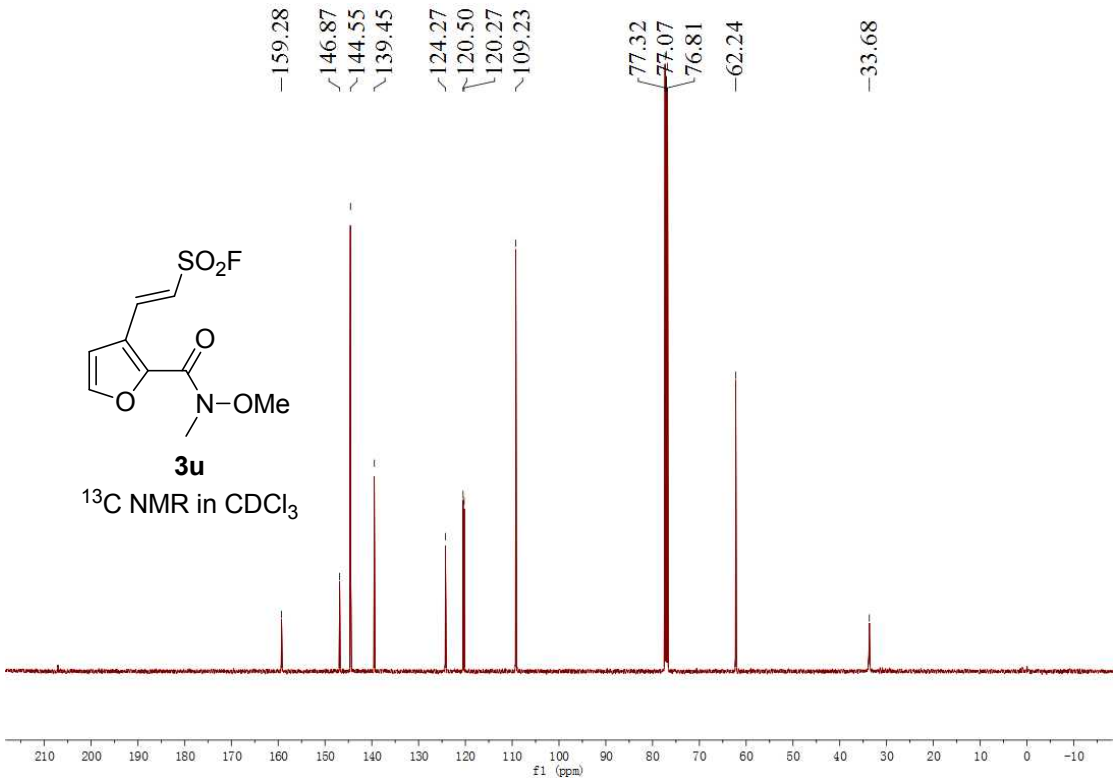
3u

^{1}H NMR in $CDCl_3$



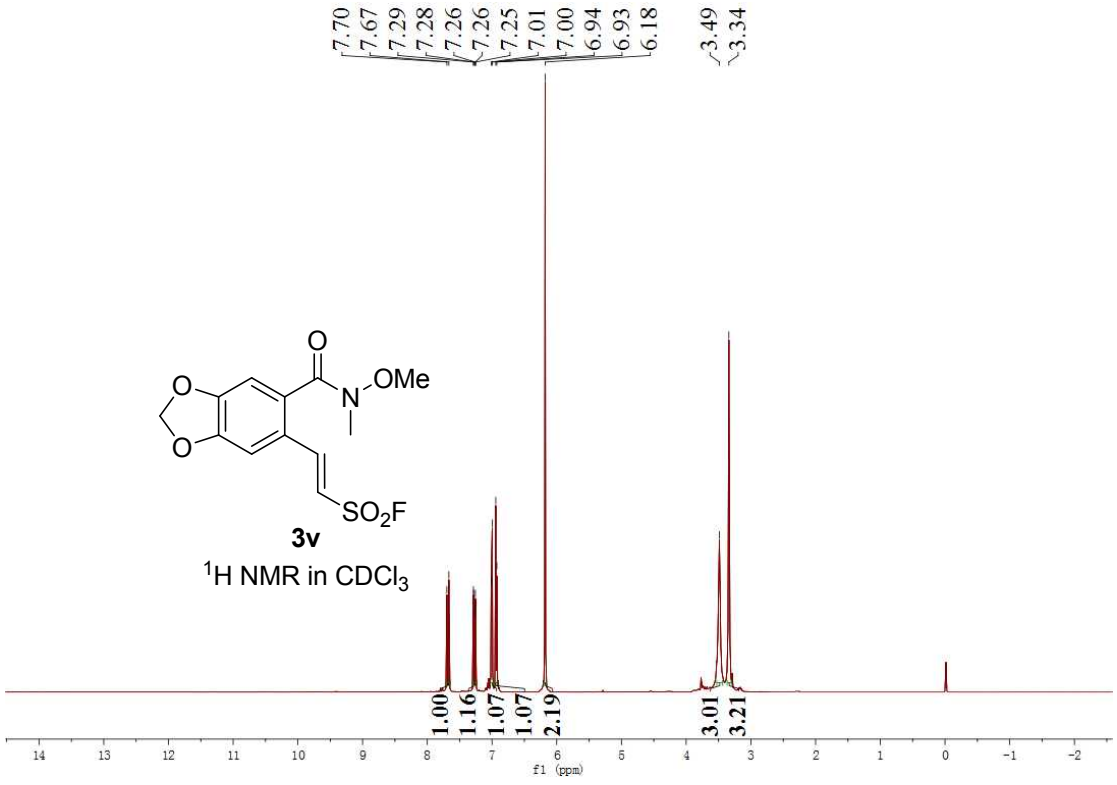
3u

^{19}F NMR in $CDCl_3$



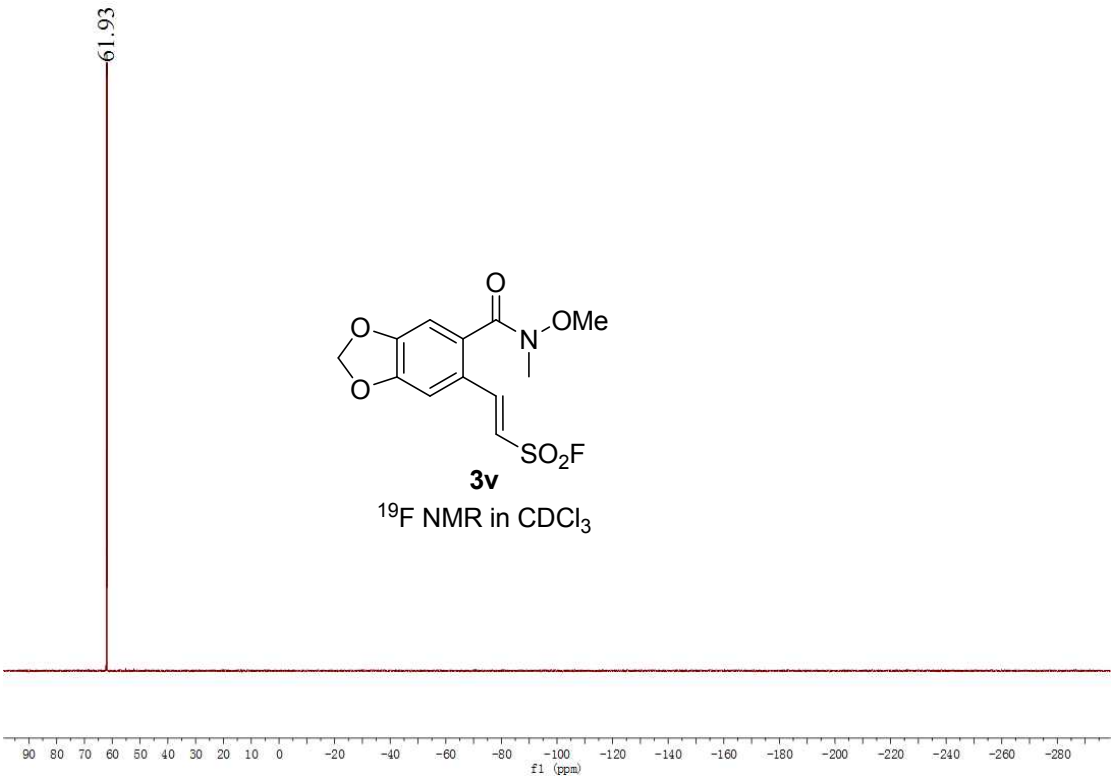
3u

^{13}C NMR in $CDCl_3$



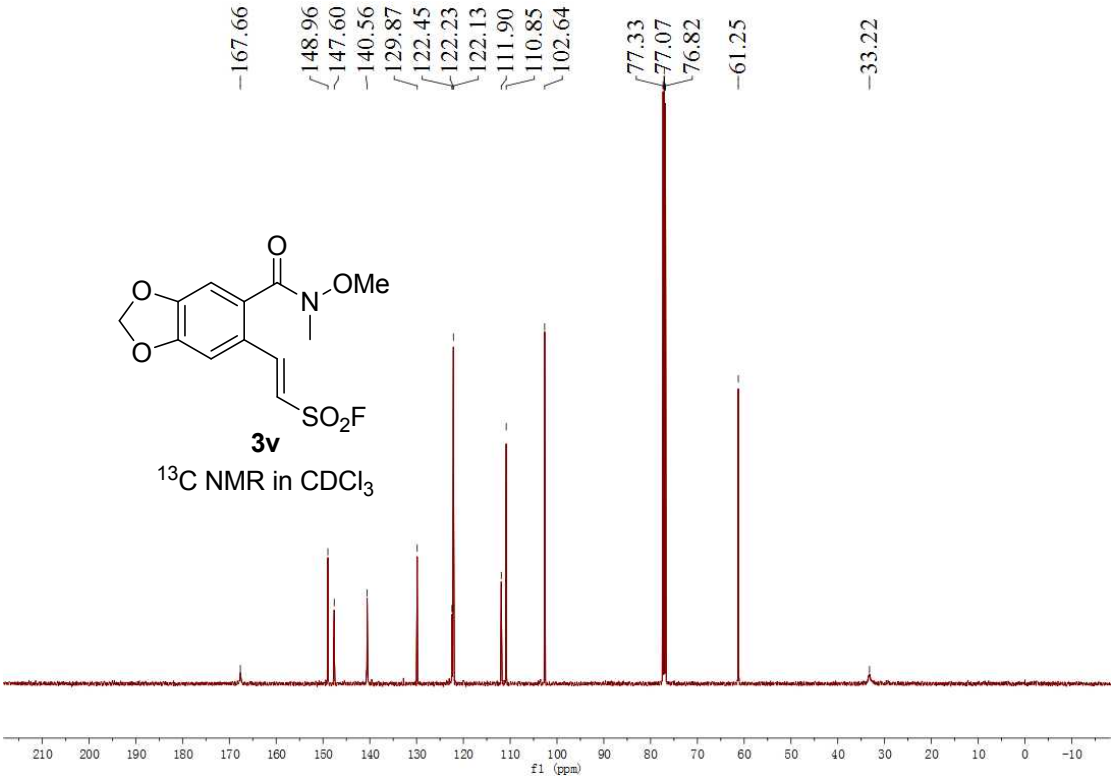
3v

^{1}H NMR in $CDCl_3$



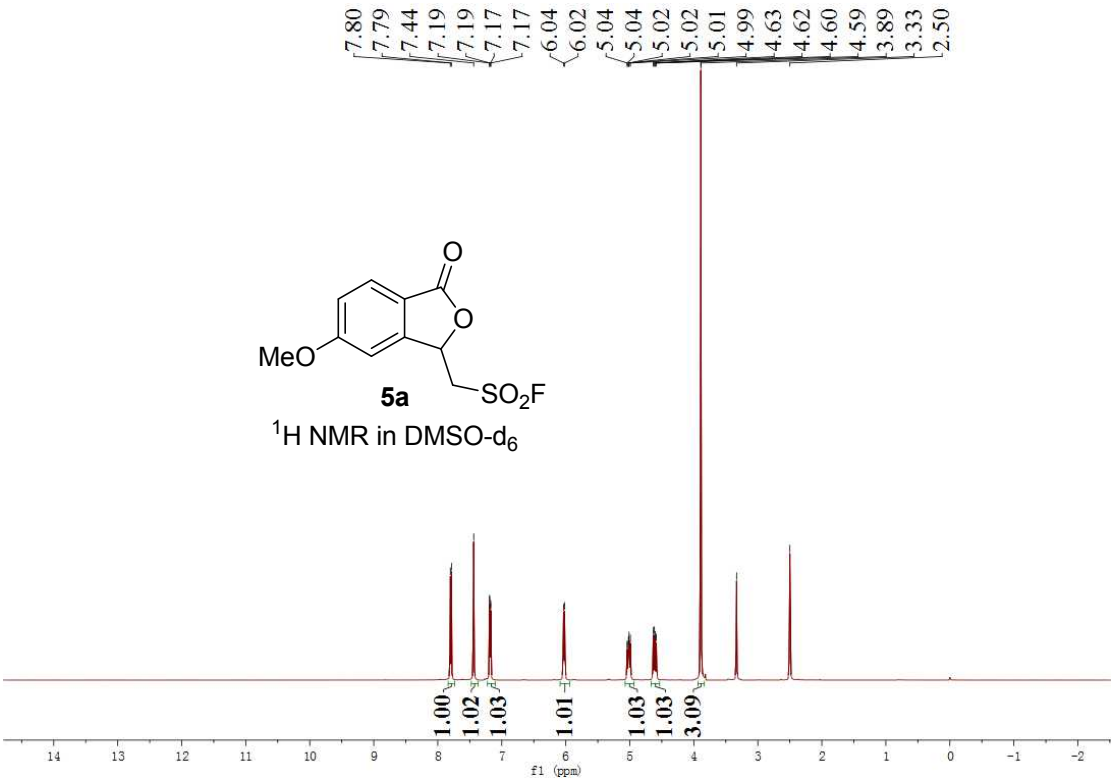
3v

^{19}F NMR in $CDCl_3$



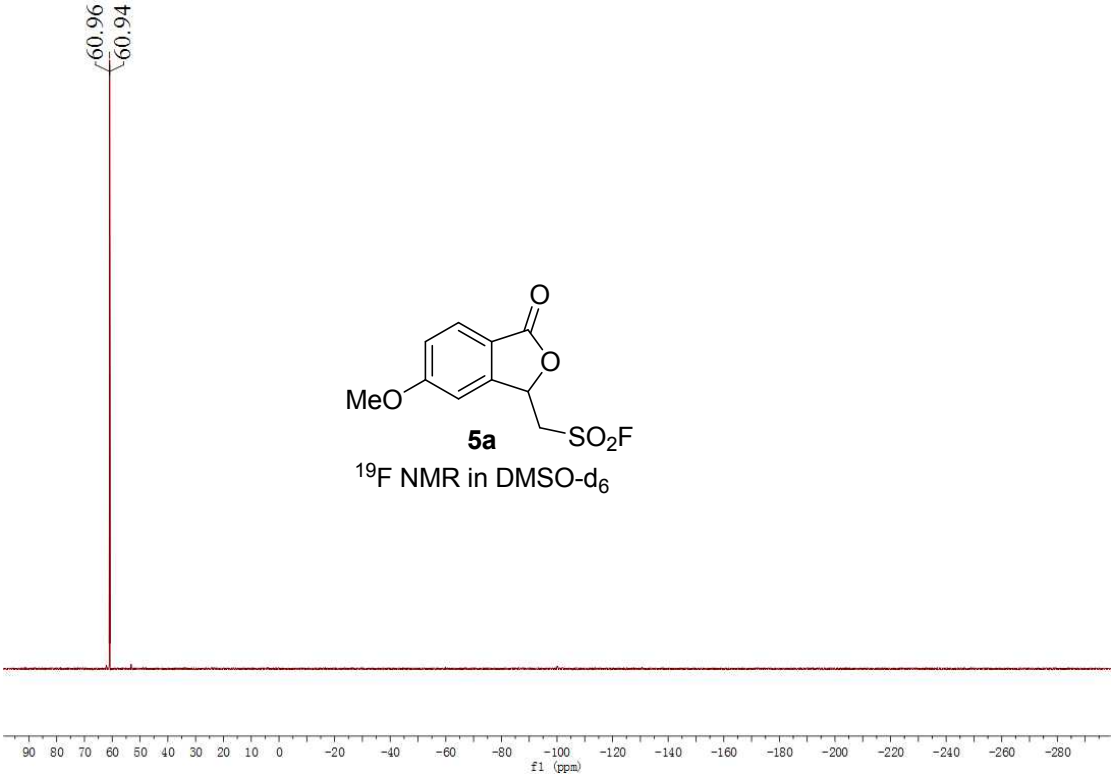
3v

^{13}C NMR in $CDCl_3$



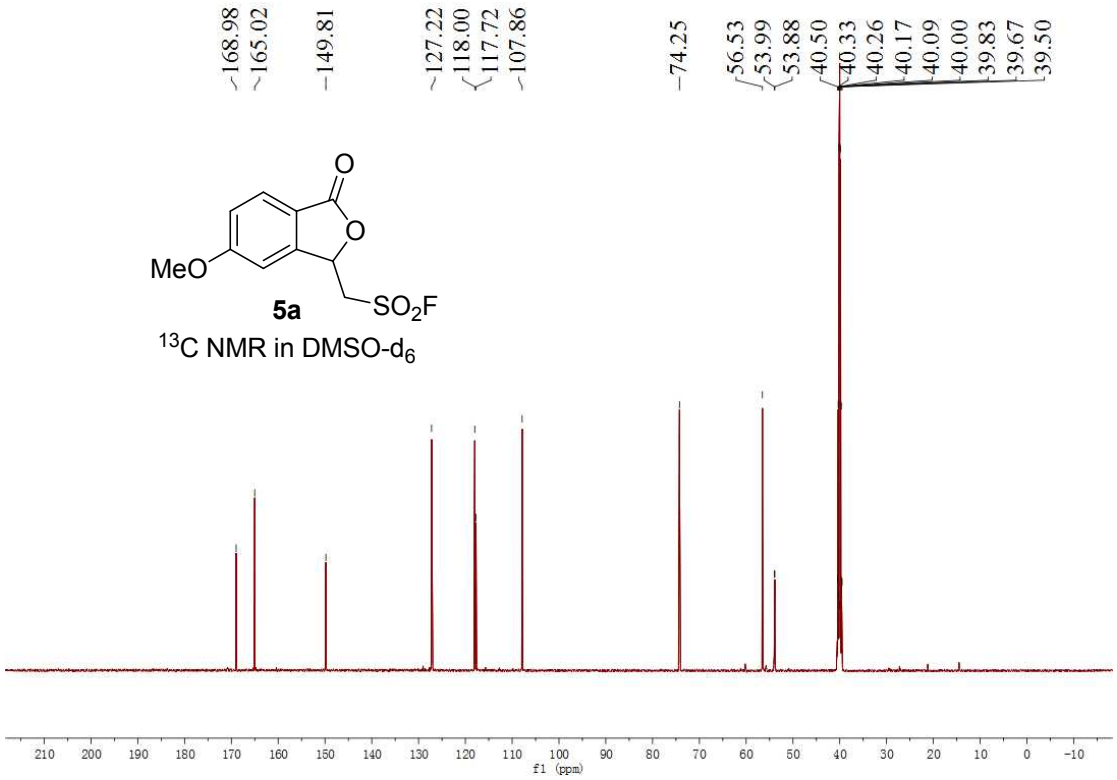
5a

^{1}H NMR in DMSO-d_6



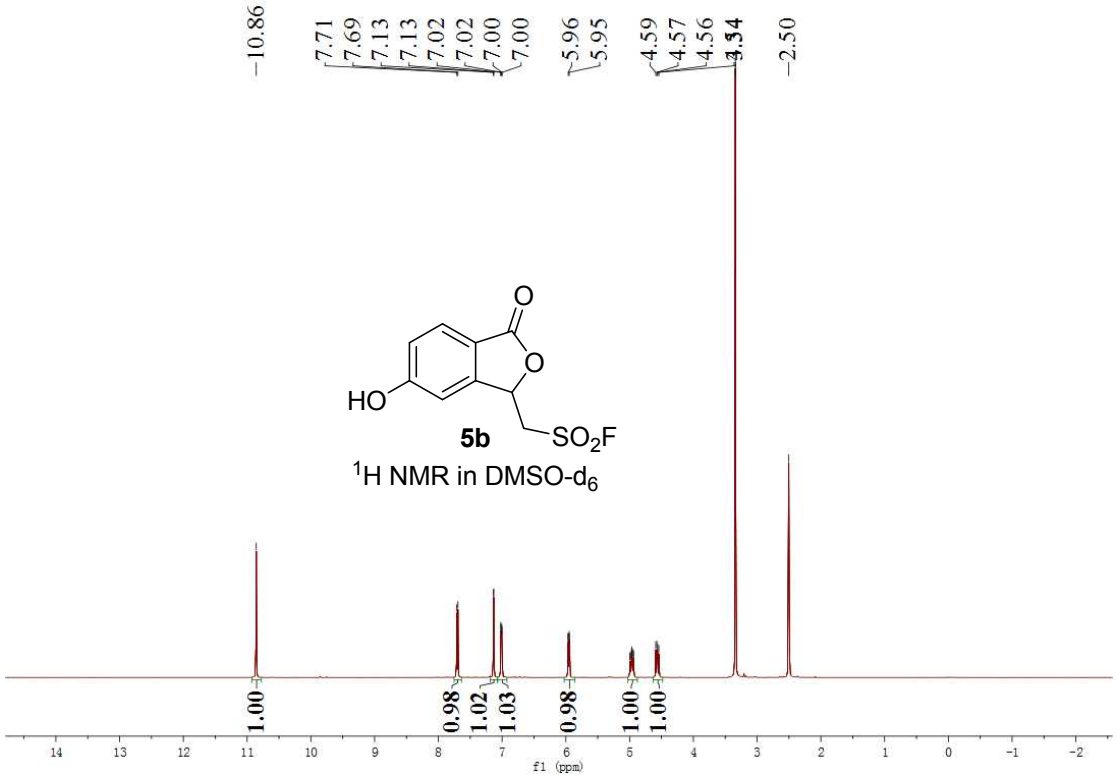
5a

^{19}F NMR in DMSO-d_6



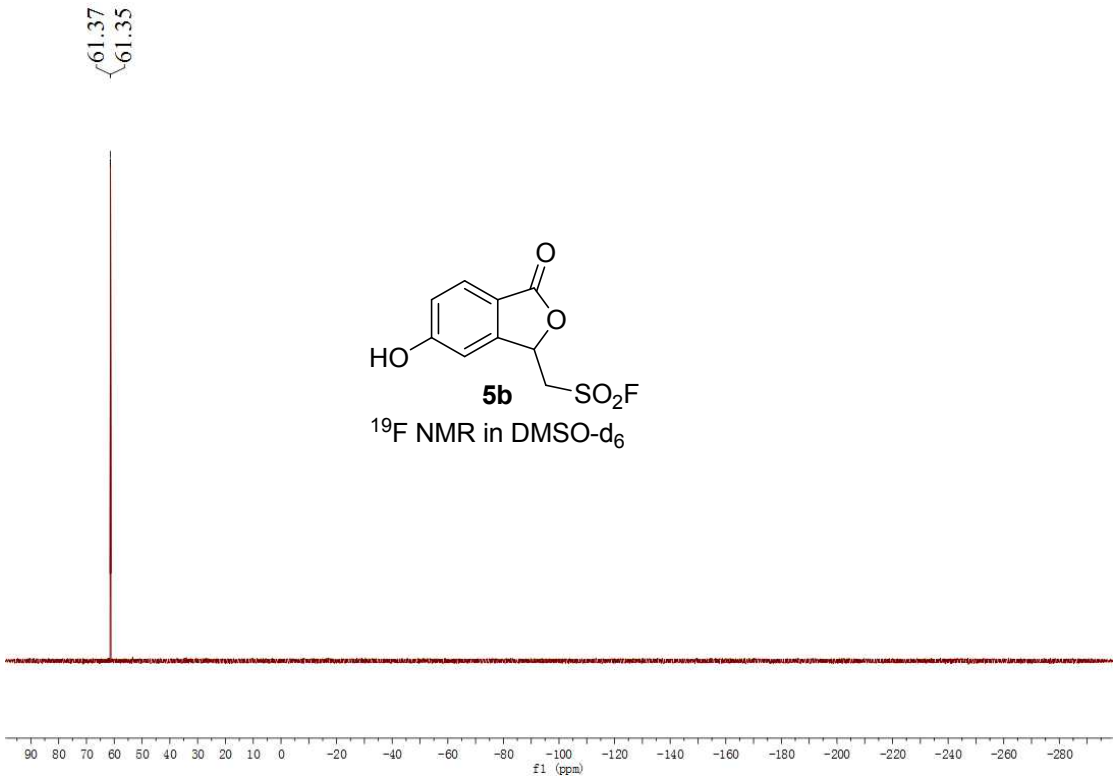
5a

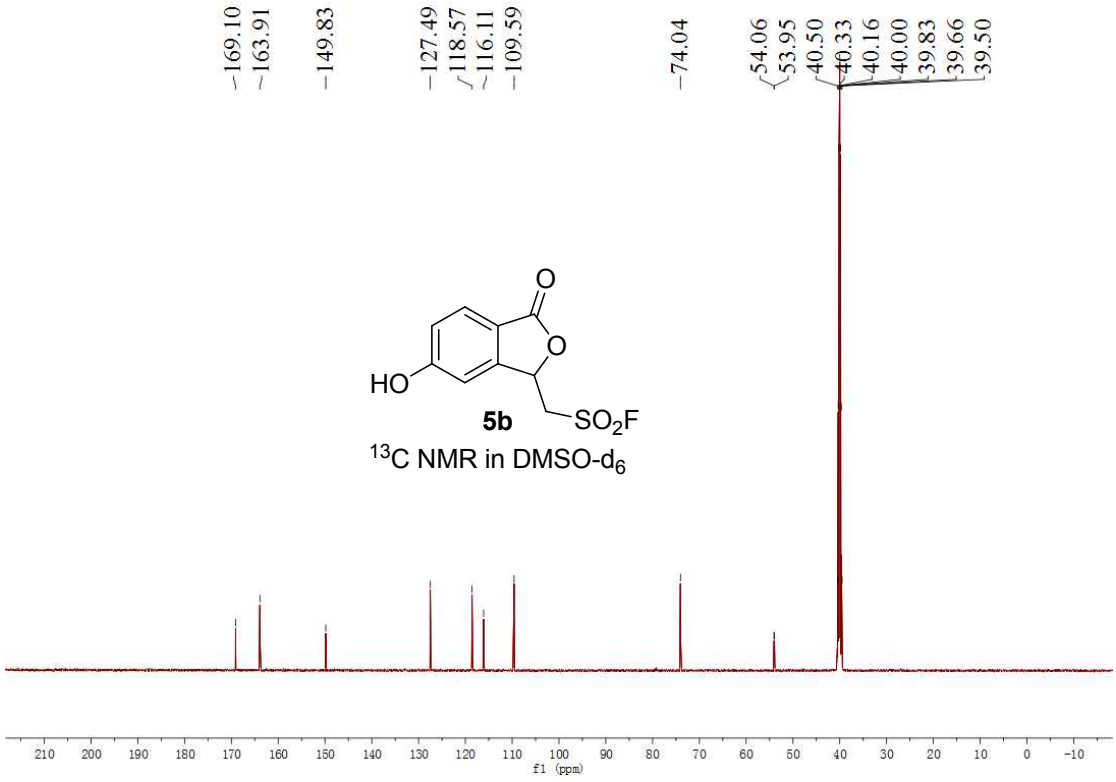
^{13}C NMR in DMSO-d_6

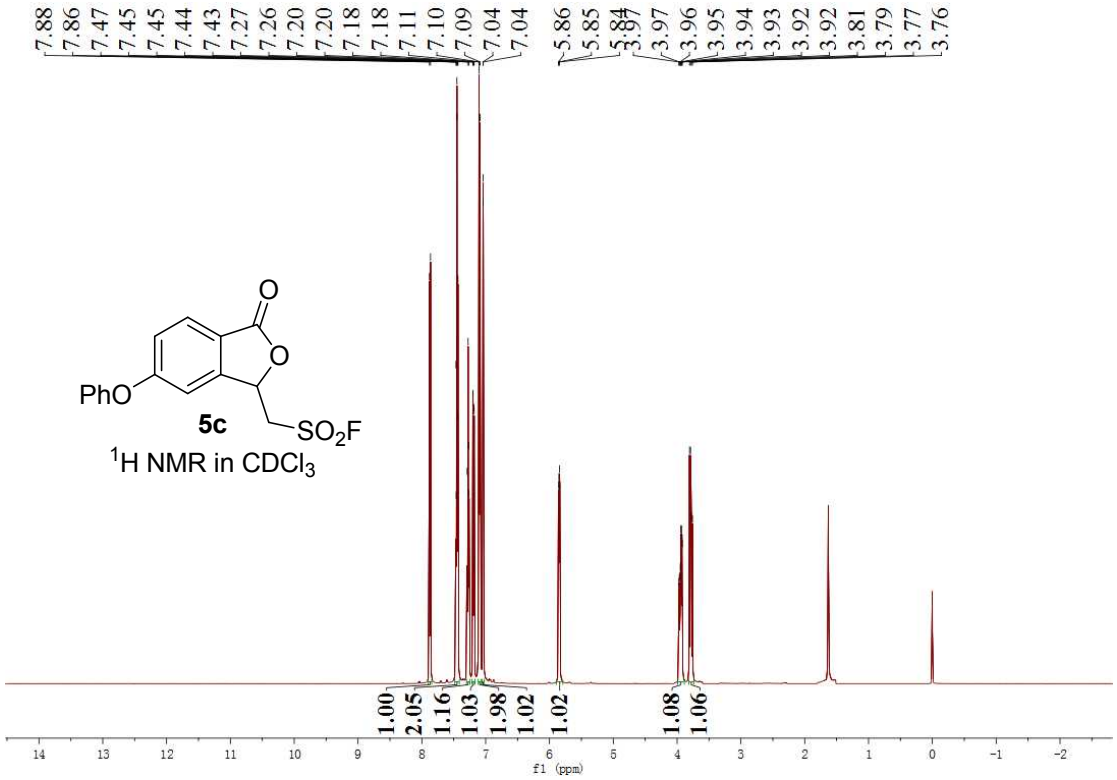


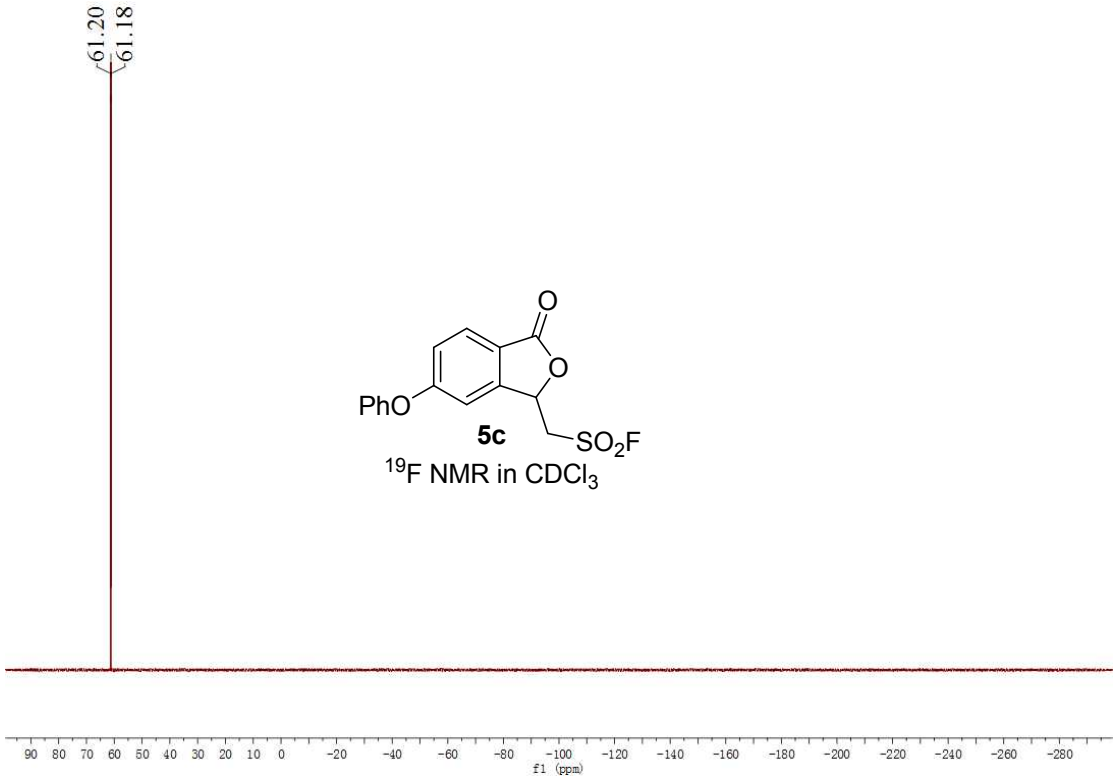
5b

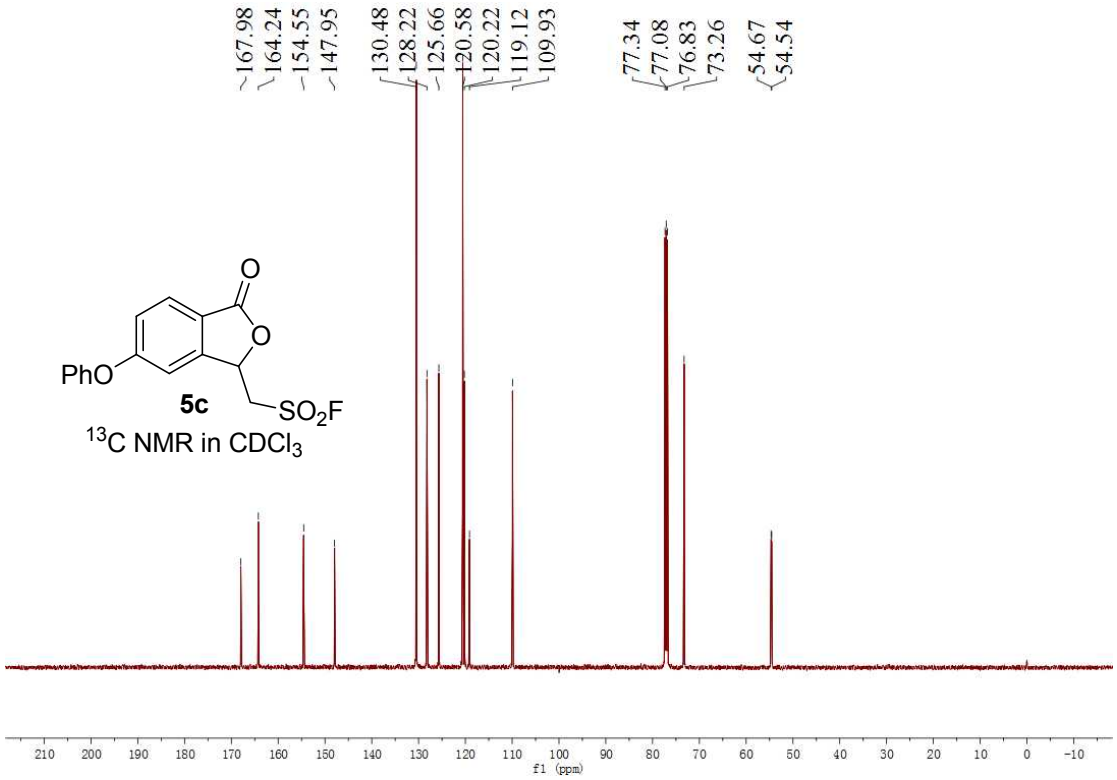
^{1}H NMR in DMSO-d_6

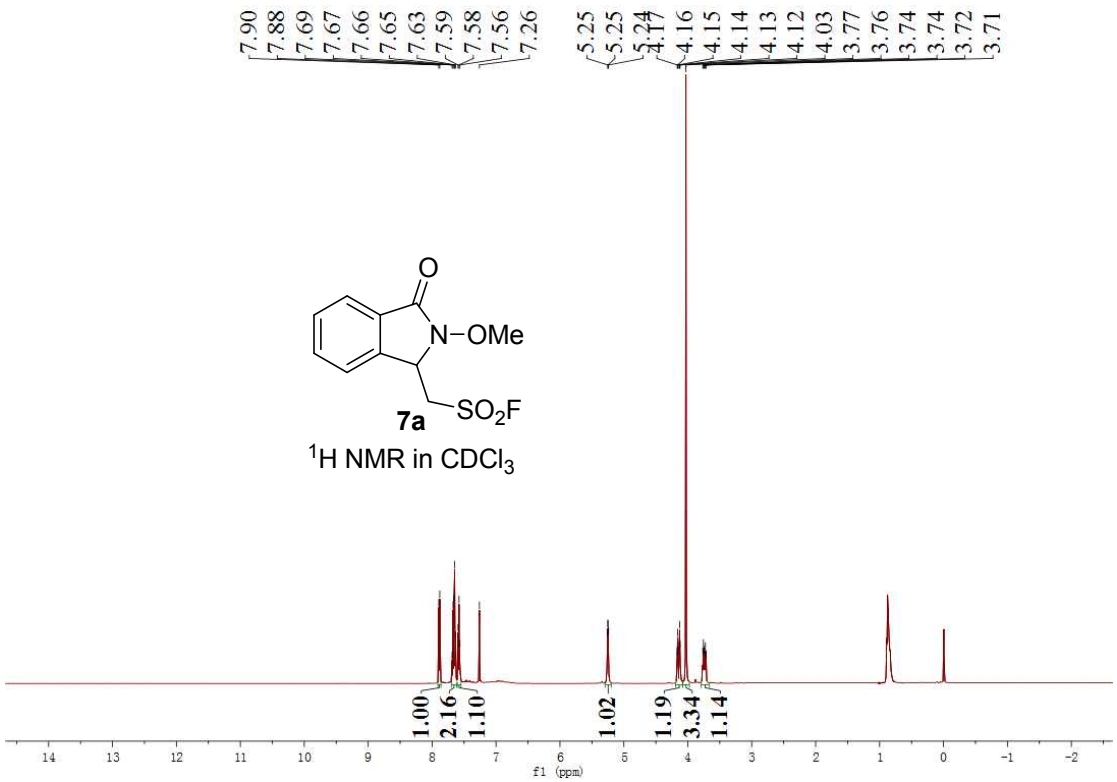

61.37
61.35
O
O
HO
SO2F
5b
19F NMR in DMSO-d6
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)

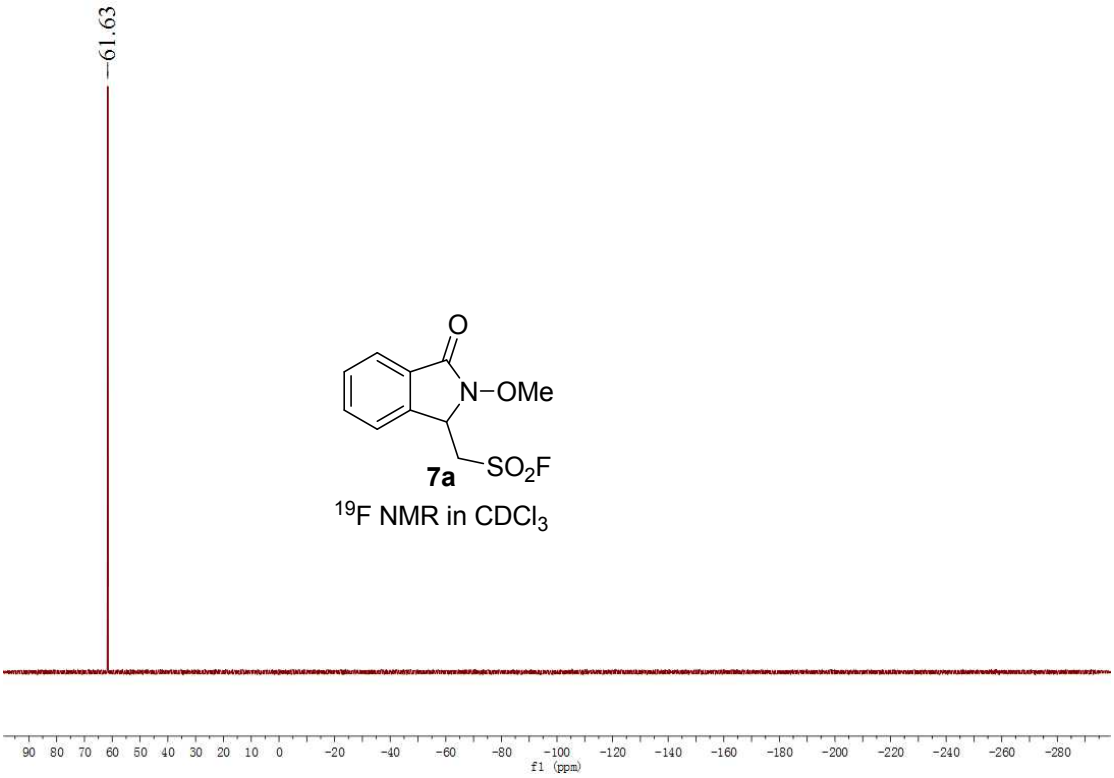

169.10
163.91
149.83
127.49
118.57
116.11
109.59
74.04
54.06
53.95
40.50
40.33
40.16
40.00
39.83
39.66
39.50
O
O
HO
SO2F
5b
13C NMR in DMSO-d6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

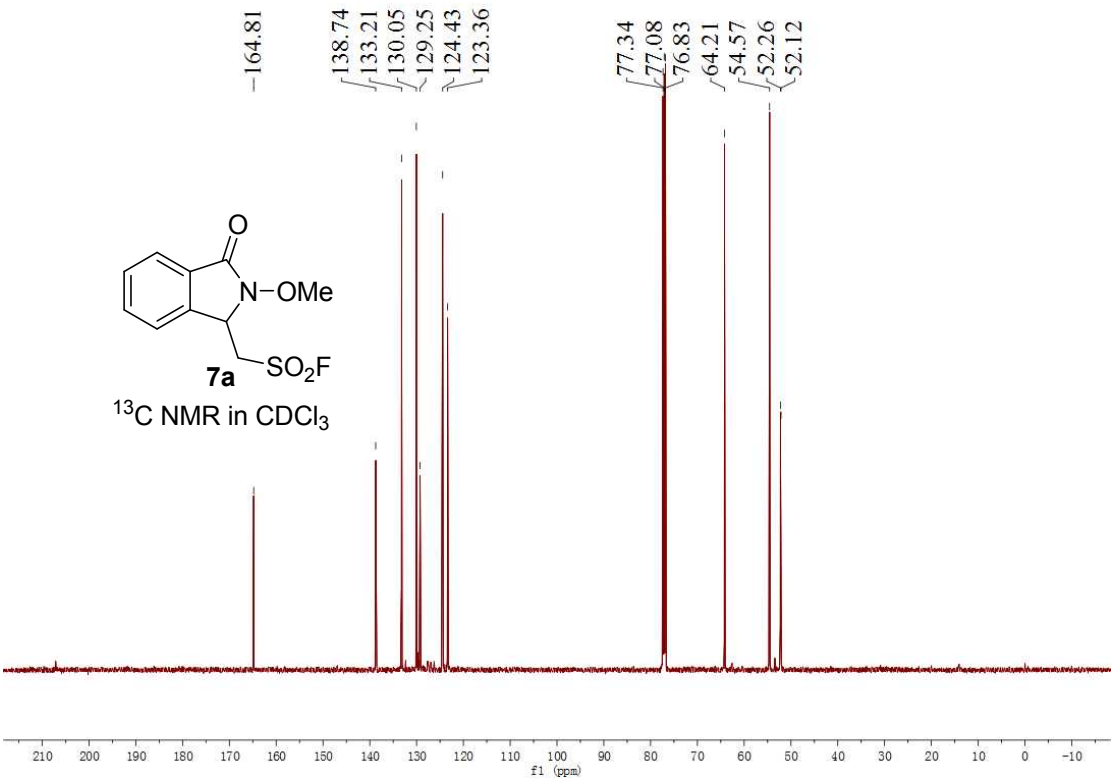

7.88
7.86
7.47
7.45
7.45
7.44
7.43
7.27
7.26
7.20
7.20
7.18
7.18
7.11
7.10
7.09
7.04
7.04
5.86
5.85
5.84
3.97
3.97
3.96
3.95
3.94
3.93
3.92
3.92
3.81
3.79
3.77
3.76
O
O
PhO
SO2F
5c
1H NMR in CDCl3
1.00
2.05
1.16
1.03
1.98
1.02
1.02
1.08
1.06
f1 (ppm)

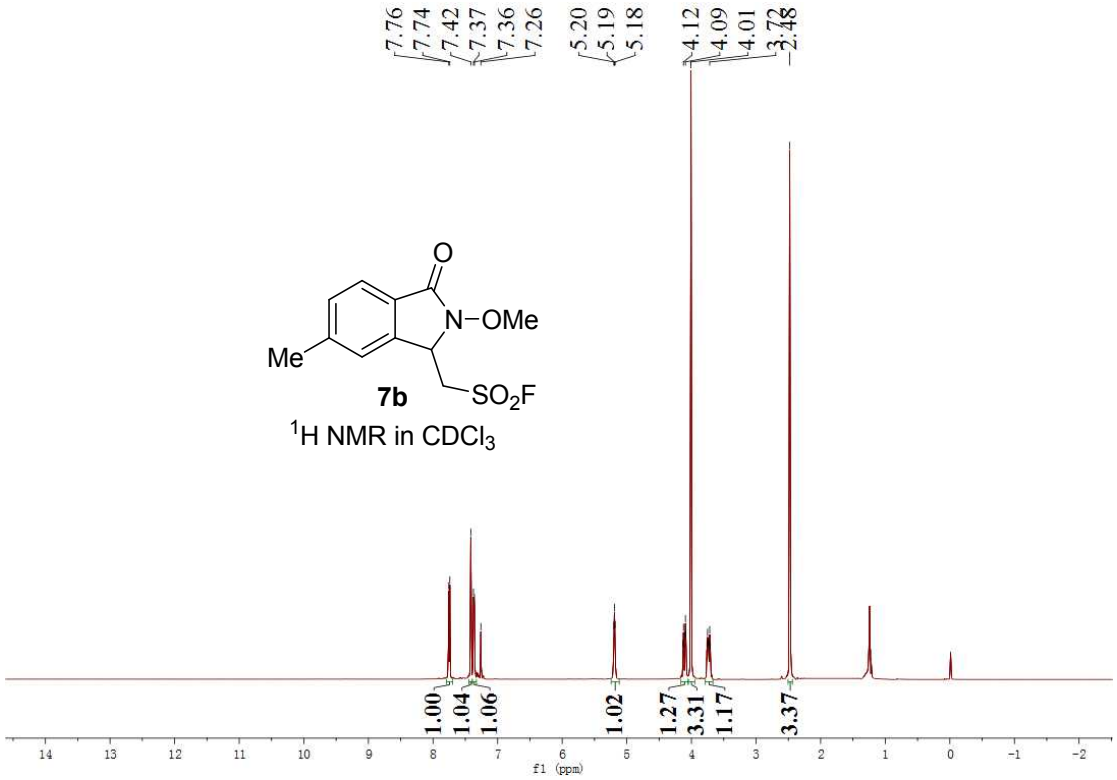

61.20
61.18
O
O
PhO
SO2F
5c
19F NMR in CDCl3
f1 (ppm)


167.98
164.24
154.55
147.95
130.48
128.22
125.66
120.58
120.22
119.12
109.93
77.34
77.08
76.83
73.26
54.67
54.54
O
O
PhO
SO2F
5c
13C NMR in CDCl3
f1 (ppm)


7.90
7.88
7.69
7.67
7.66
7.65
7.63
7.59
7.58
7.56
7.26
5.25
5.25
5.24
4.17
4.16
4.15
4.14
4.13
4.12
4.03
3.77
3.76
3.74
3.74
3.72
3.71
O
N−OMe
SO2F
7a
1H NMR in CDCl3
1.00
2.16
1.10
1.02
1.19
3.34
1.14
f1 (ppm)

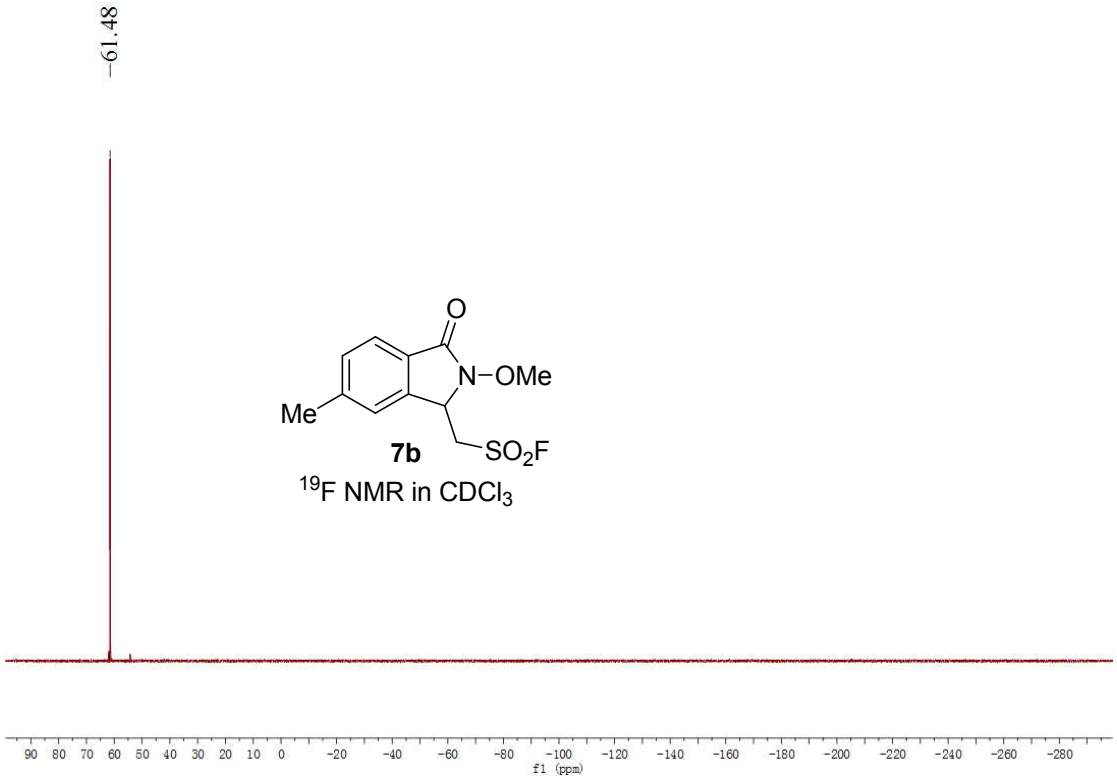

-61.63
O
N−OMe
SO2F
7a
19F NMR in CDCl3
f1 (ppm)


-164.81
138.74
133.21
130.05
129.25
124.43
123.36
77.34
77.08
76.83
64.21
54.57
52.26
52.12
O
N−OMe
SO2F
7a
13C NMR in CDCl3
f1 (ppm)



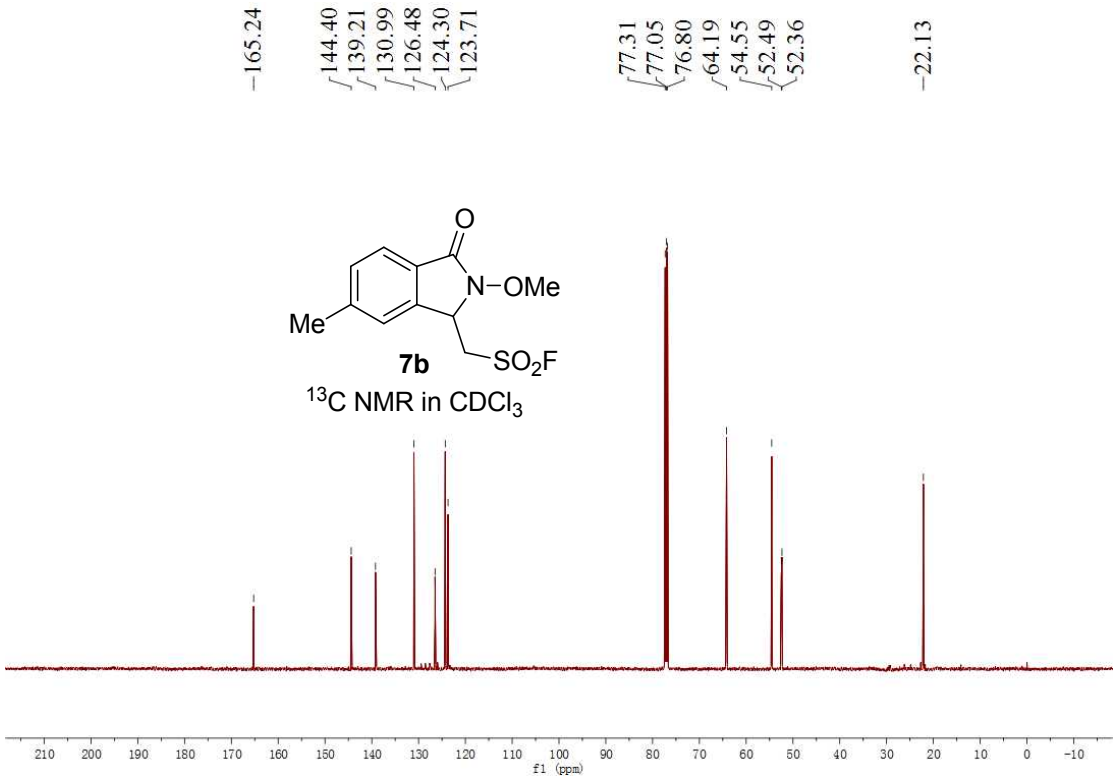
7b

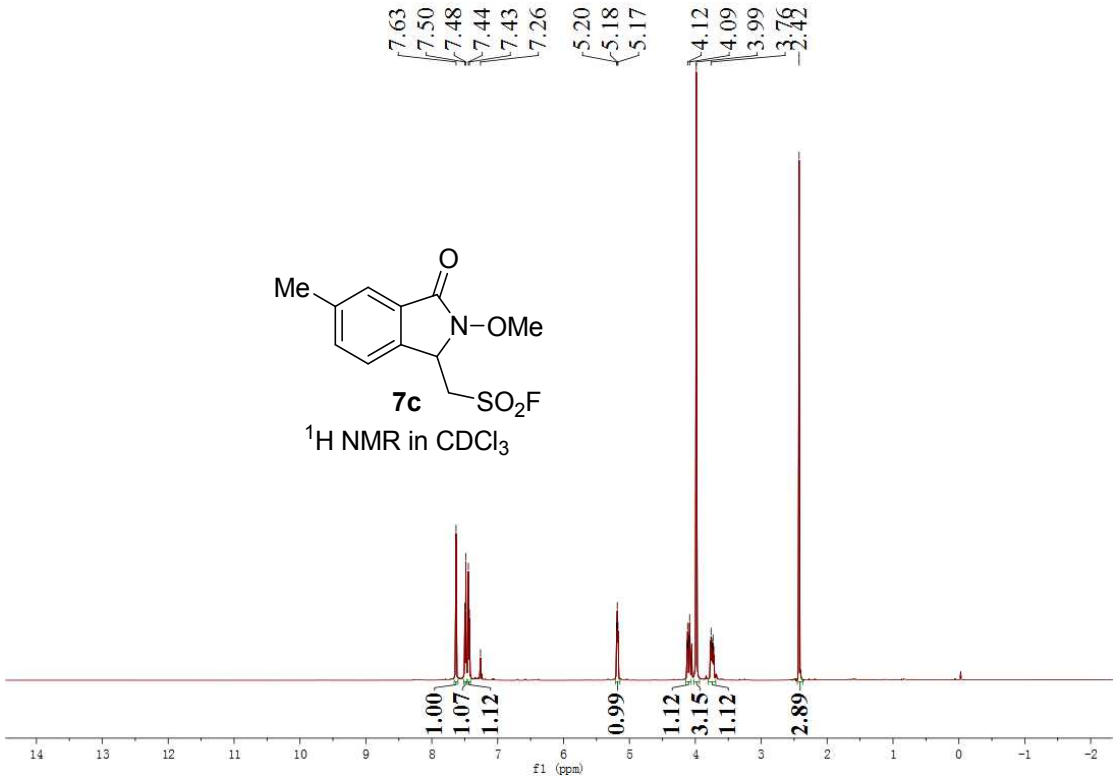
^{1}H NMR in $CDCl_3$

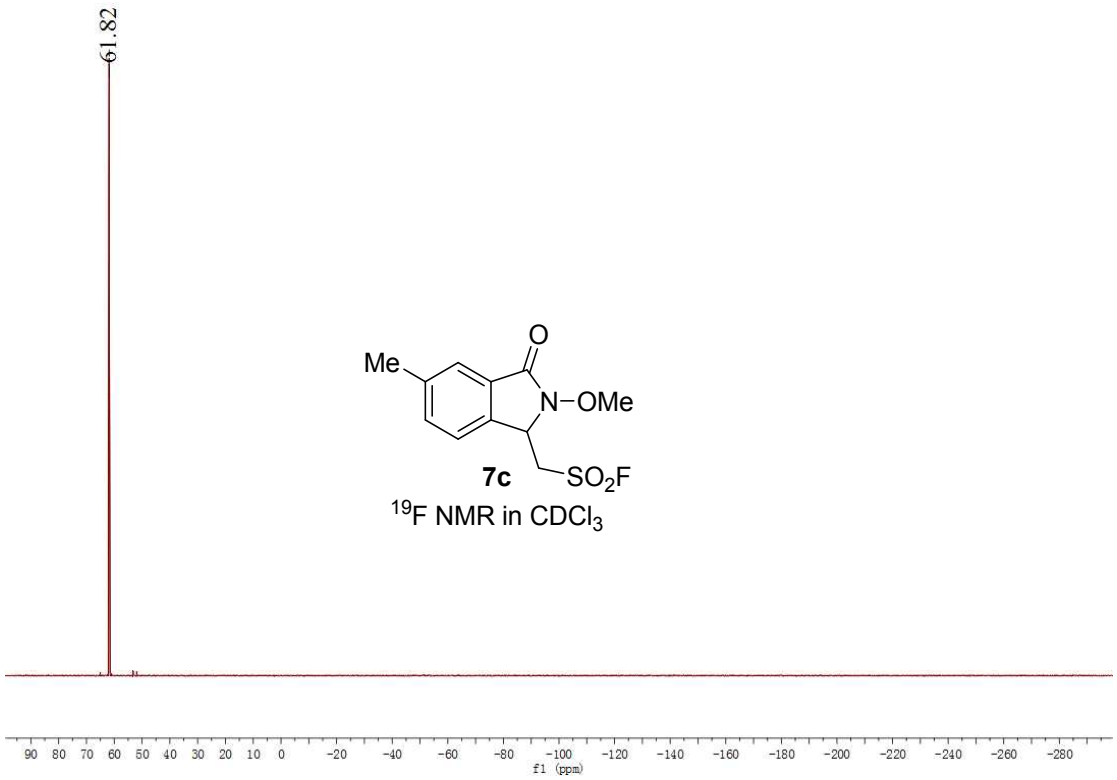


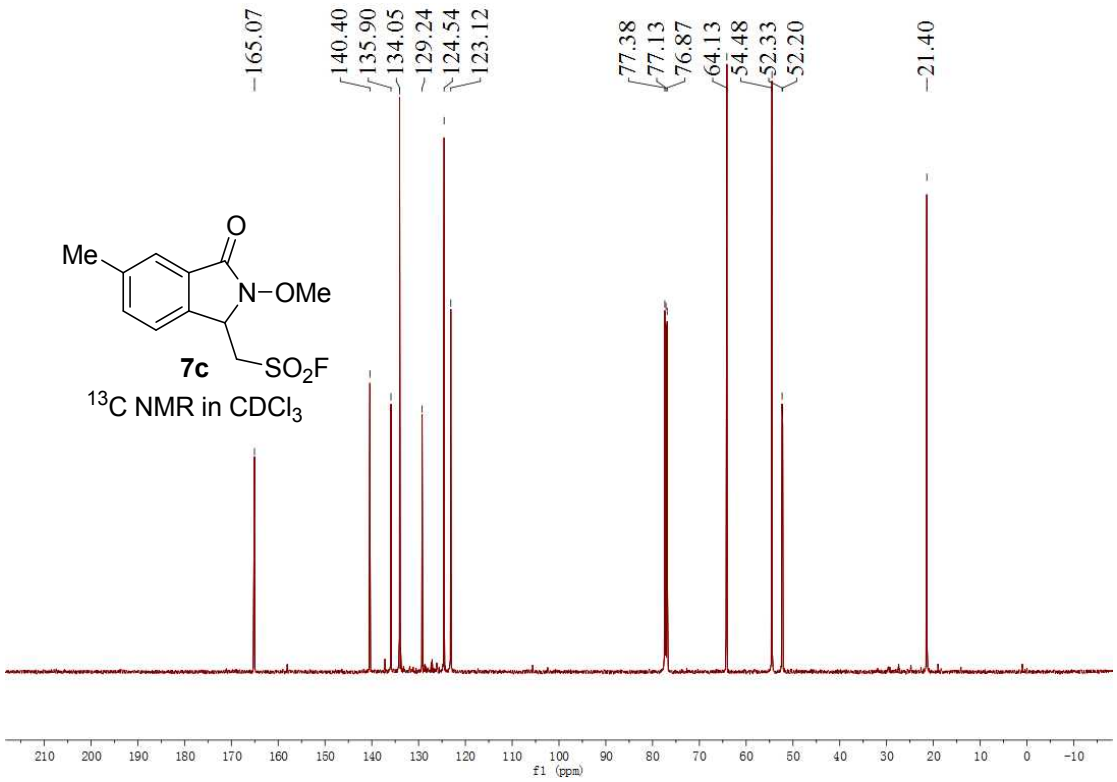
7b

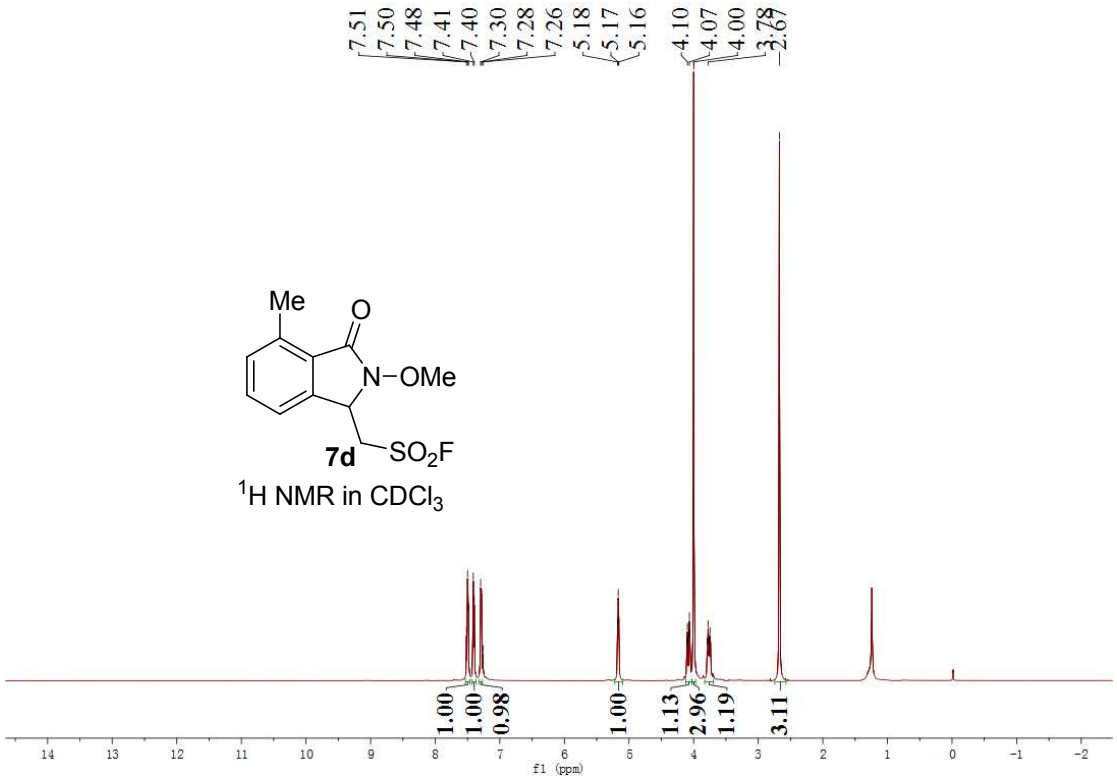
^{19}F NMR in $CDCl_3$

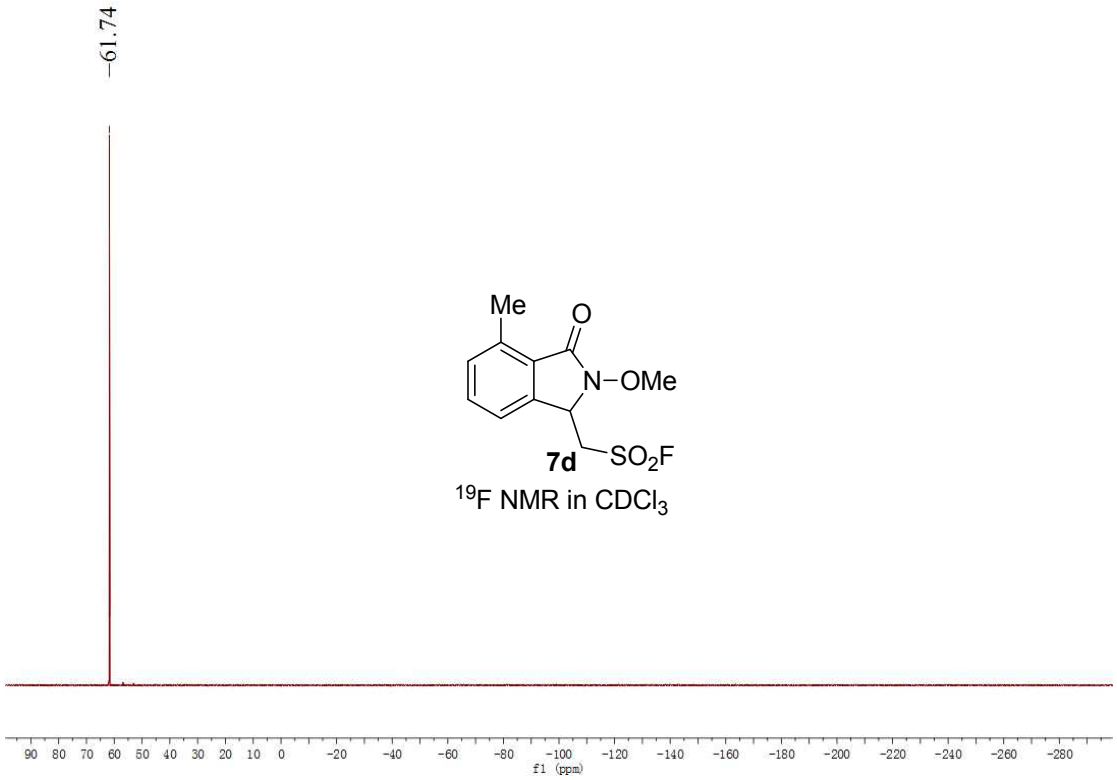

165.24
144.40
139.21
130.99
126.48
124.30
123.71
77.31
77.05
76.80
64.19
54.55
52.49
52.36
22.13
O
N−OMe
Me
SO2F
7b
13C NMR in CDCl3
f1 (ppm)

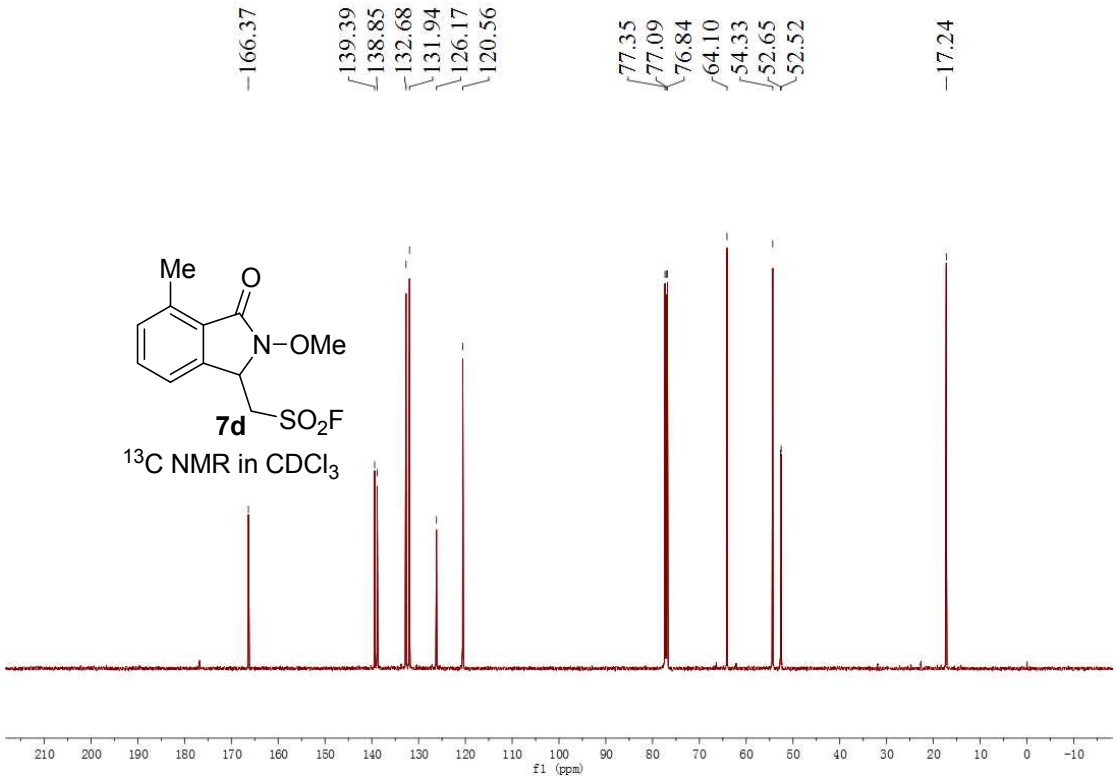

7.63
7.50
7.48
7.44
7.43
7.26
5.20
5.18
5.17
4.12
4.09
3.99
3.76
2.42
O
Me
N−OMe
SO2F
7c
1H NMR in CDCl3
1.00
1.07
1.12
0.99
1.12
3.15
1.12
2.89
f1 (ppm)

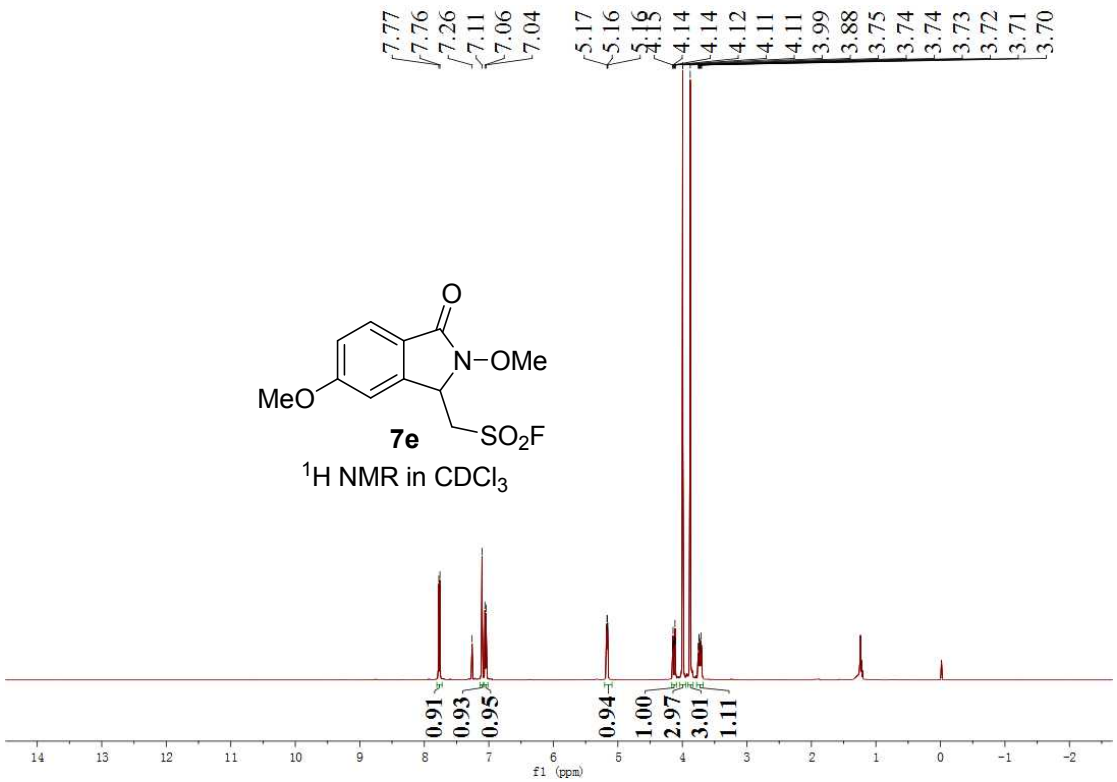

61.82
Me
O
N−OMe
SO2F
7c
19F NMR in CDCl3
f1 (ppm)

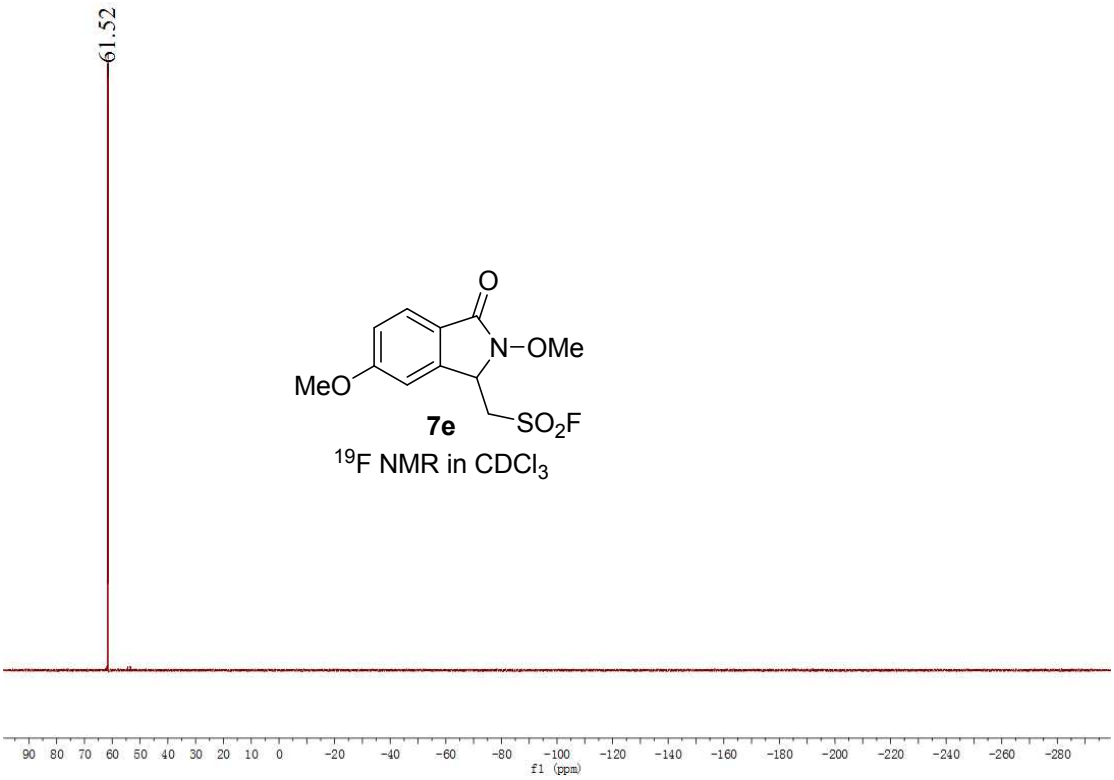

165.07
140.40
135.90
134.05
129.24
124.54
123.12
77.38
77.13
76.87
64.13
54.48
52.33
52.20
21.40
Me
O
N−OMe
SO2F
7c
13C NMR in CDCl3
f1 (ppm)

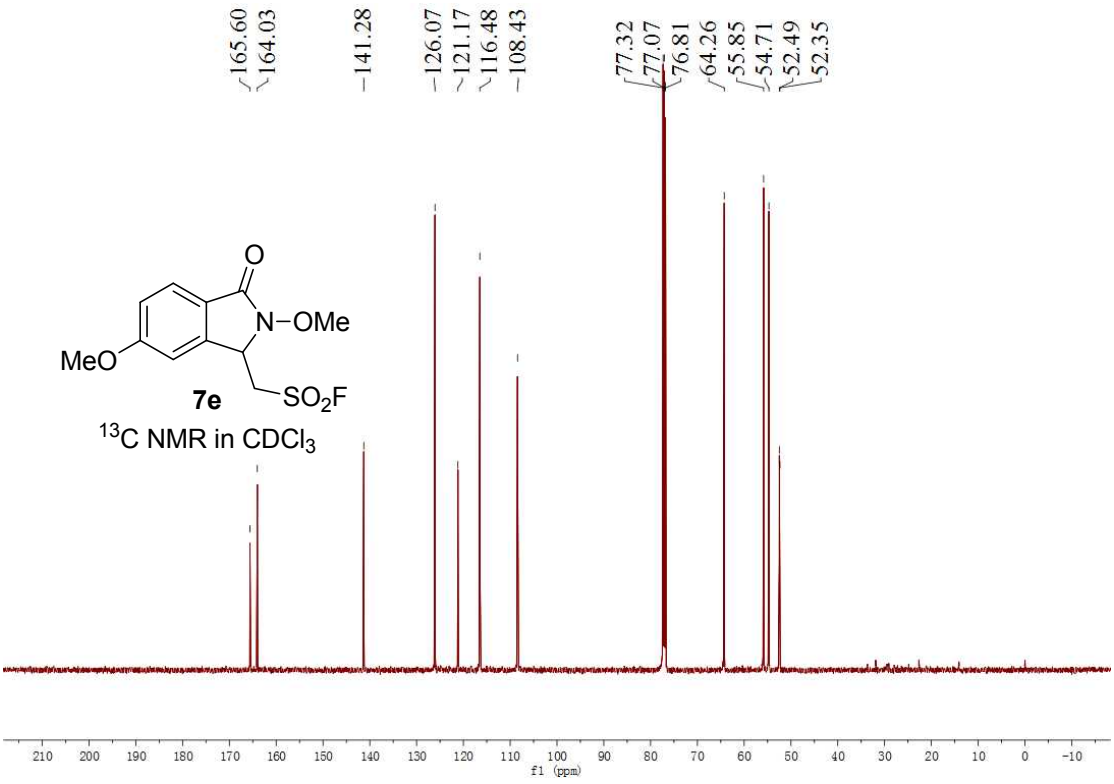

7.51
7.50
7.48
7.41
7.40
7.30
7.28
7.26
5.18
5.17
5.16
4.10
4.07
4.00
3.78
3.67
Me
O
N−OMe
SO2F
7d
1H NMR in CDCl3
1.00
1.00
0.98
1.00
1.13
2.96
1.19
3.11
f1 (ppm)

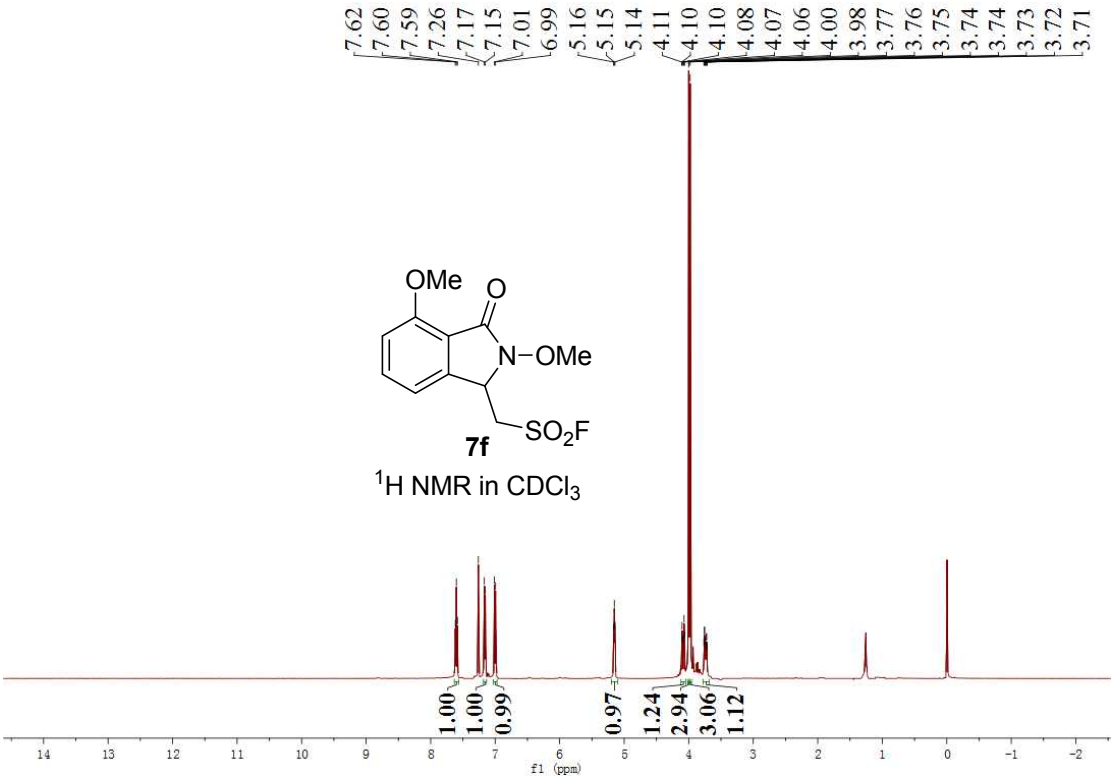

−61.74
Me
O
N−OMe
SO2F
7d
19F NMR in CDCl3
f1 (ppm)

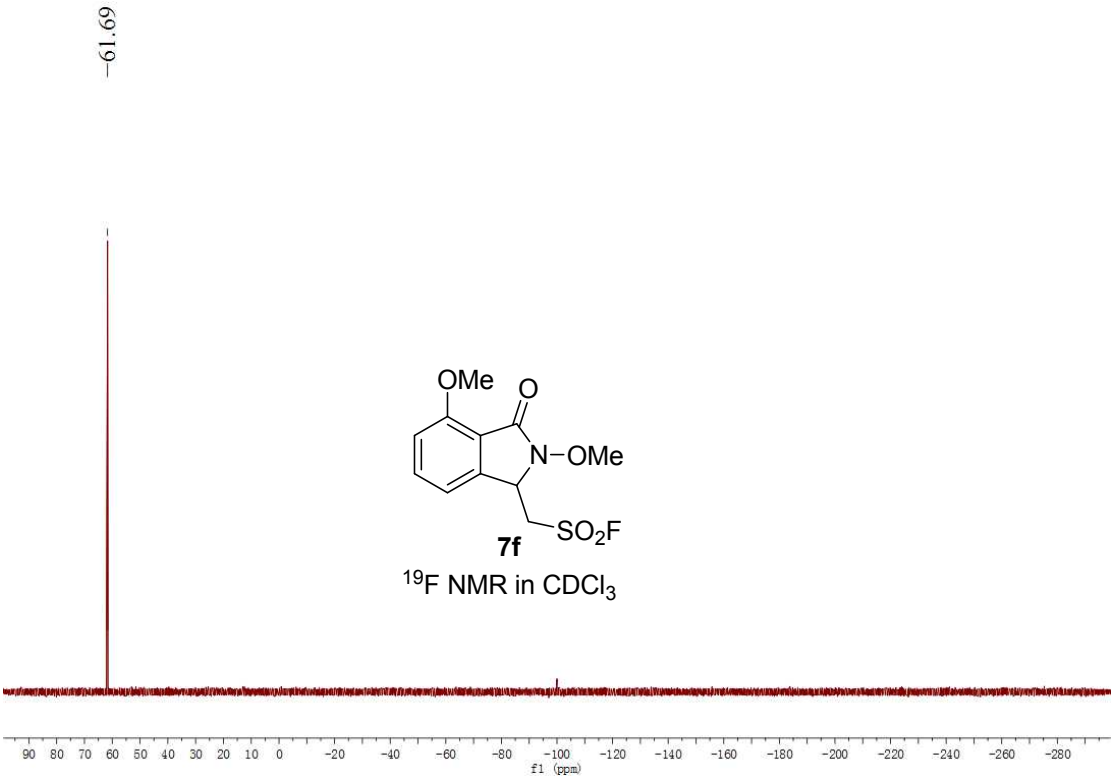

166.37
139.39
138.85
132.68
131.94
126.17
120.56
77.35
77.09
76.84
64.10
54.33
52.65
52.52
17.24
Me
O
N−OMe
SO2F
7d
13C NMR in CDCl3
f1 (ppm)

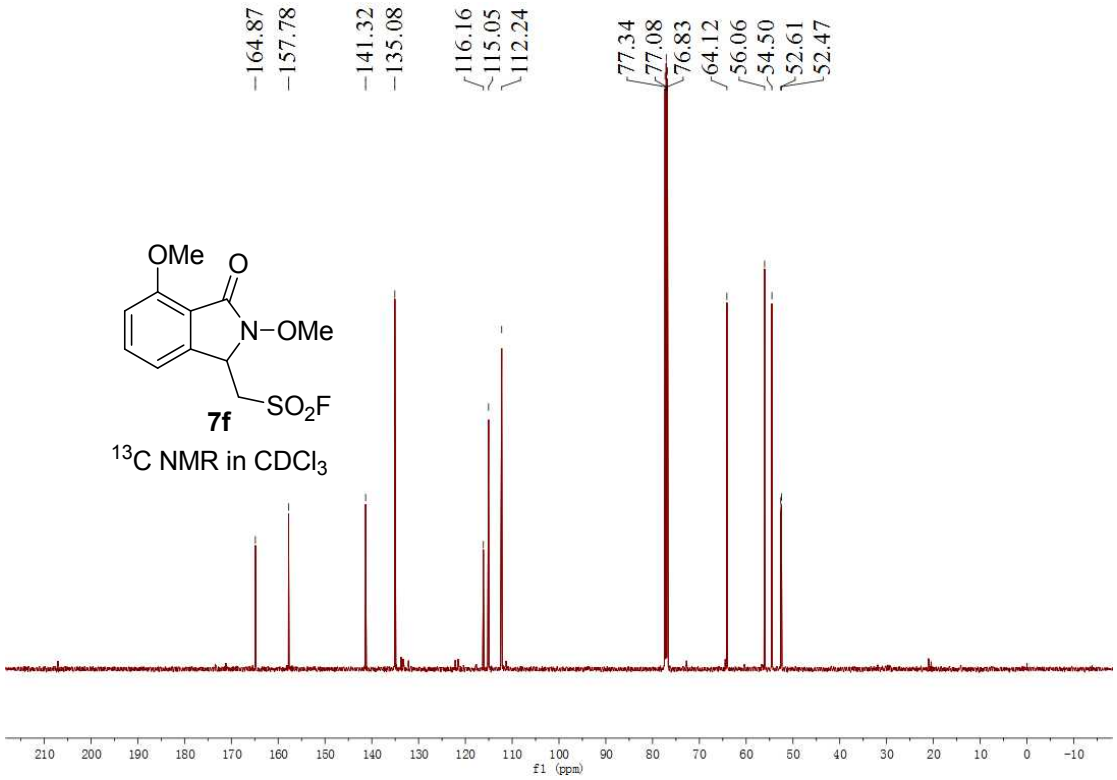

7.77
7.76
7.26
7.11
7.06
7.04
5.17
5.16
4.14
4.14
4.12
4.11
4.11
3.99
3.88
3.75
3.74
3.74
3.73
3.72
3.71
3.70
O
N−OMe
MeO
SO2F
7e
1H NMR in CDCl3
0.91
0.93
0.95
0.94
1.00
2.97
3.01
1.11
f1 (ppm)

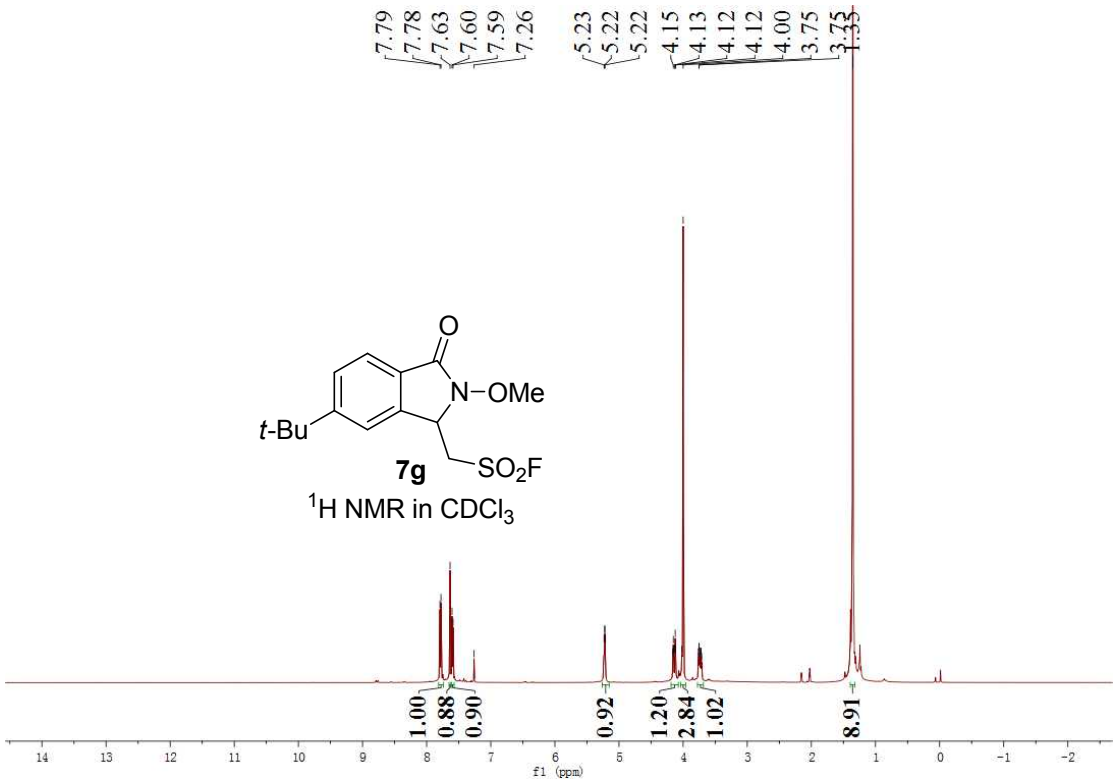

61.52
O
N−OMe
MeO
SO2F
7e
19F NMR in CDCl3
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)

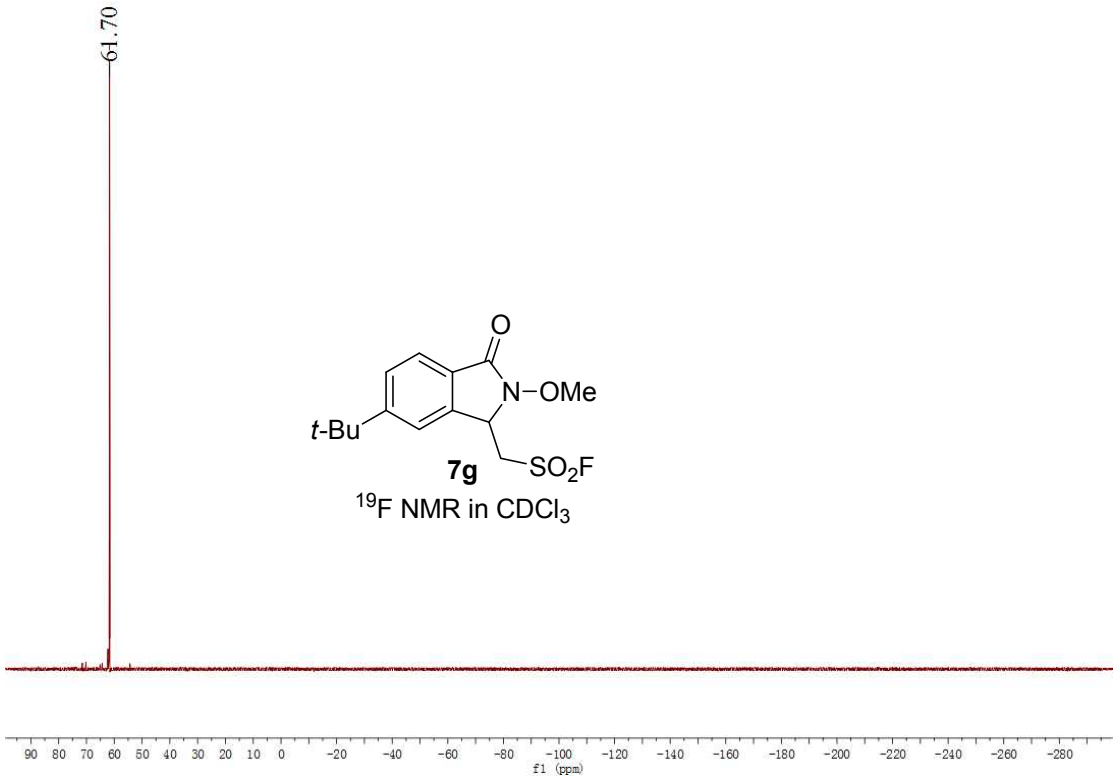

165.60
164.03
141.28
126.07
121.17
116.48
108.43
77.32
77.07
76.81
64.26
55.85
54.71
52.49
52.35
O
N−OMe
MeO
SO2F
7e
13C NMR in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

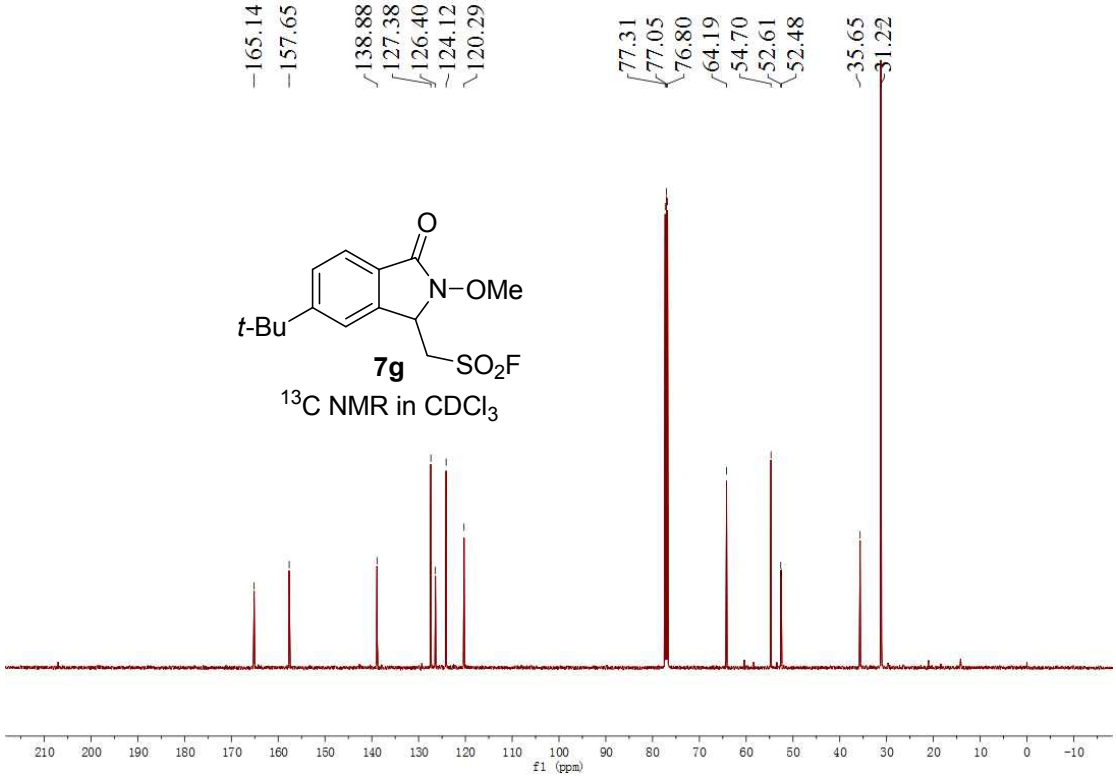

7.62
7.60
7.59
7.26
7.17
7.15
7.01
6.99
5.16
5.15
5.14
4.11
4.10
4.10
4.08
4.07
4.06
4.00
3.98
3.77
3.76
3.75
3.74
3.74
3.73
3.72
3.71
OMe
O
N−OMe
SO2F
7f
1H NMR in CDCl3
1.00
1.00
0.99
0.97
1.24
2.94
3.06
1.12
f1 (ppm)

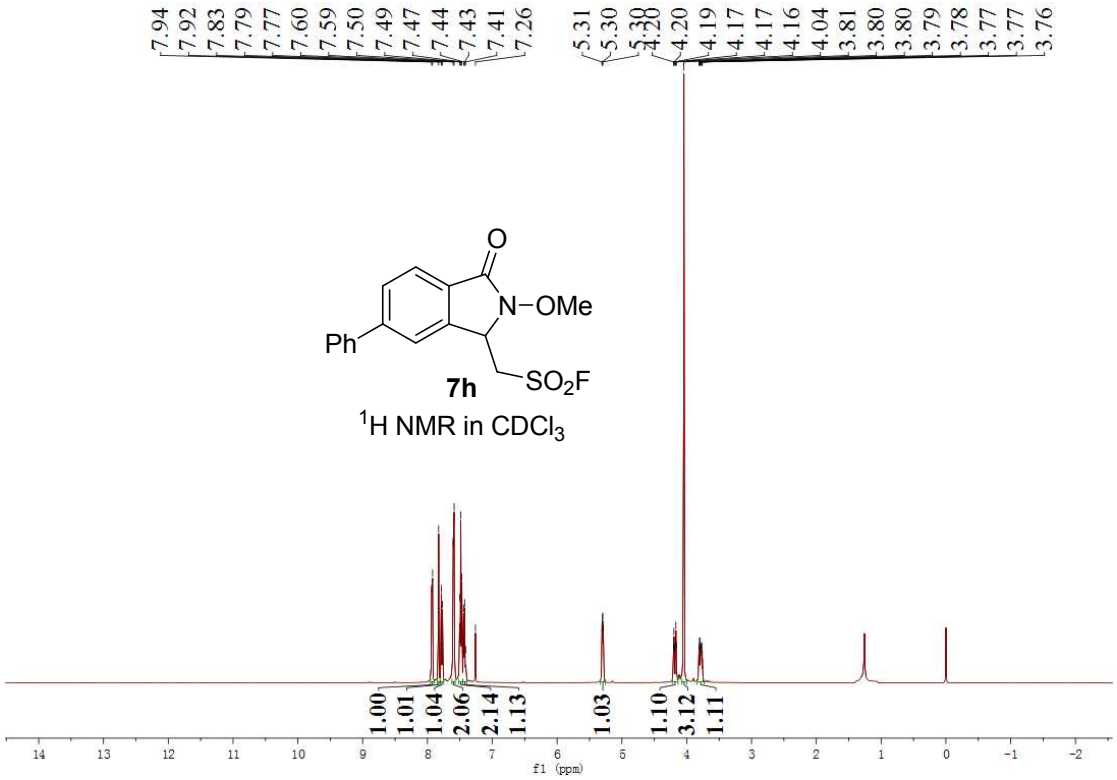

−61.69
OMe
O
N−OMe
SO2F
7f
19F NMR in CDCl3
f1 (ppm)


164.87
157.78
141.32
135.08
116.16
115.05
112.24
77.34
77.08
76.83
64.12
56.06
54.50
52.61
52.47
OMe
O
N−OMe
SO2F
7f
13C NMR in CDCl3
f1 (ppm)


7.79
7.78
7.63
7.60
7.59
7.26
5.23
5.22
5.22
4.15
4.13
4.12
4.12
4.00
3.75
3.75
1.33
O
N−OMe
t-Bu
SO2F
7g
1H NMR in CDCl3
1.00
0.88
0.90
0.92
1.20
2.84
1.02
8.91
f1 (ppm)

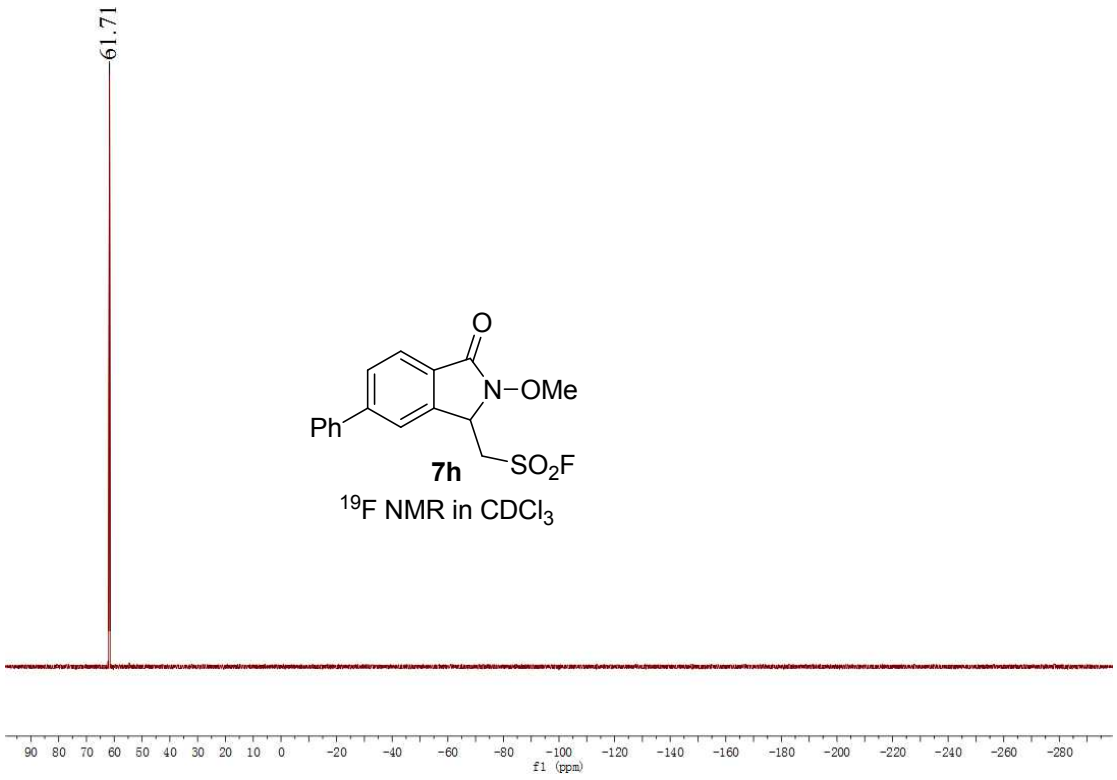

61.70
O
N−OMe
t-Bu
SO2F
7g
19F NMR in CDCl3
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)


165.14
157.65
138.88
127.38
126.40
124.12
120.29
77.31
77.05
76.80
64.19
54.70
52.61
52.48
35.65
31.22
O
N−OMe
t-Bu
SO2F
7g
13C NMR in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



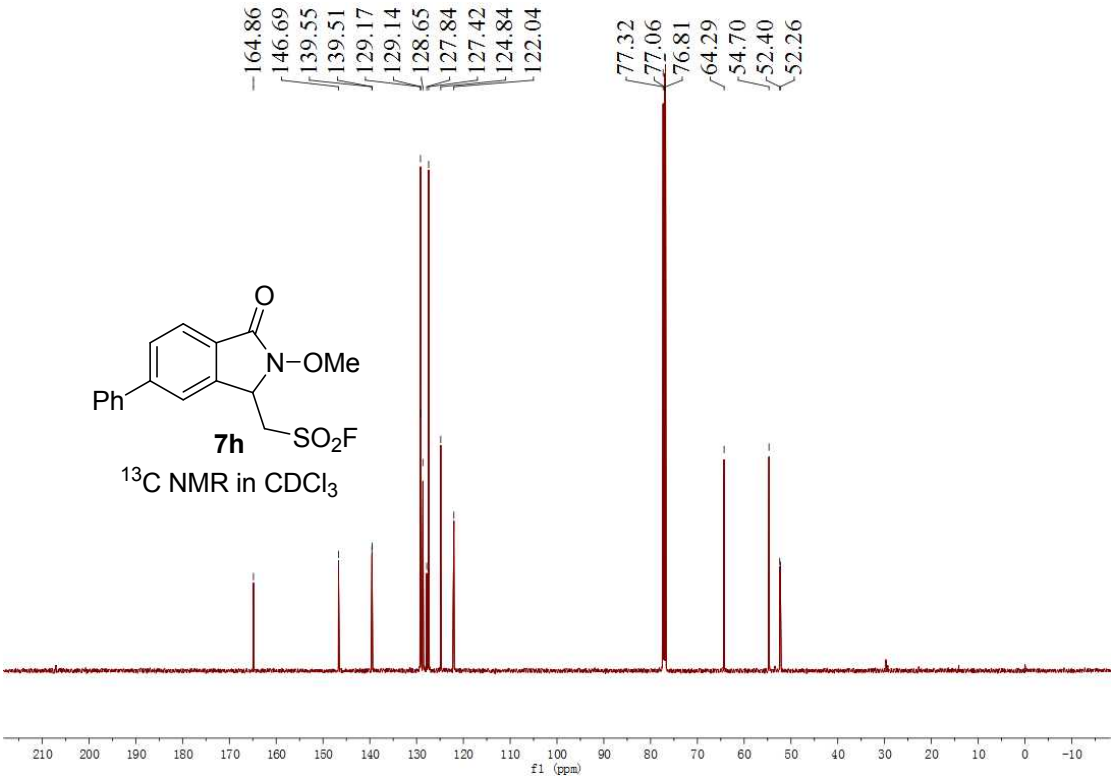
7h

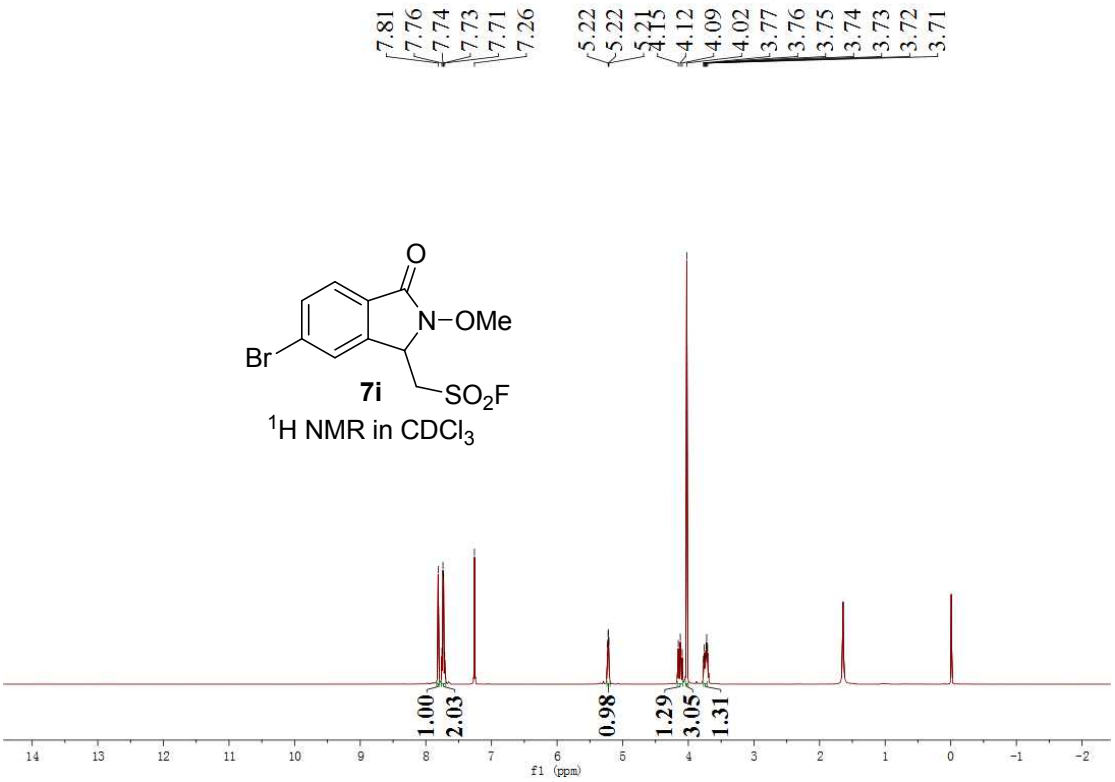
^{1}H NMR in $CDCl_3$

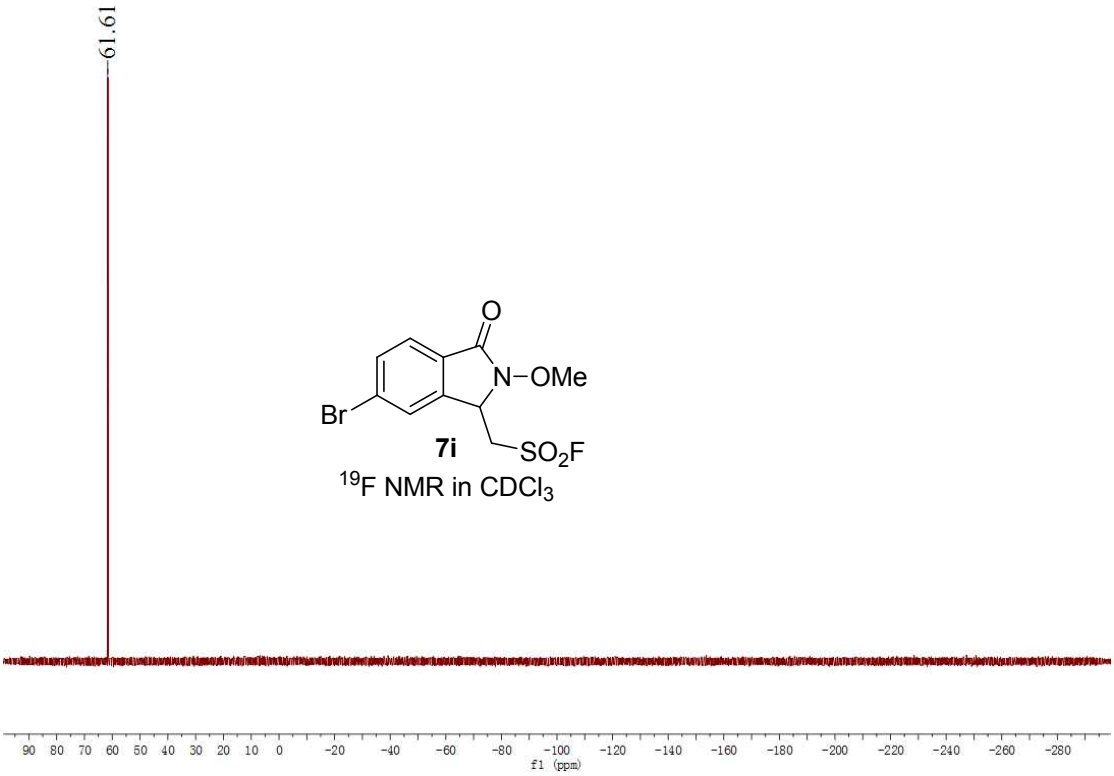


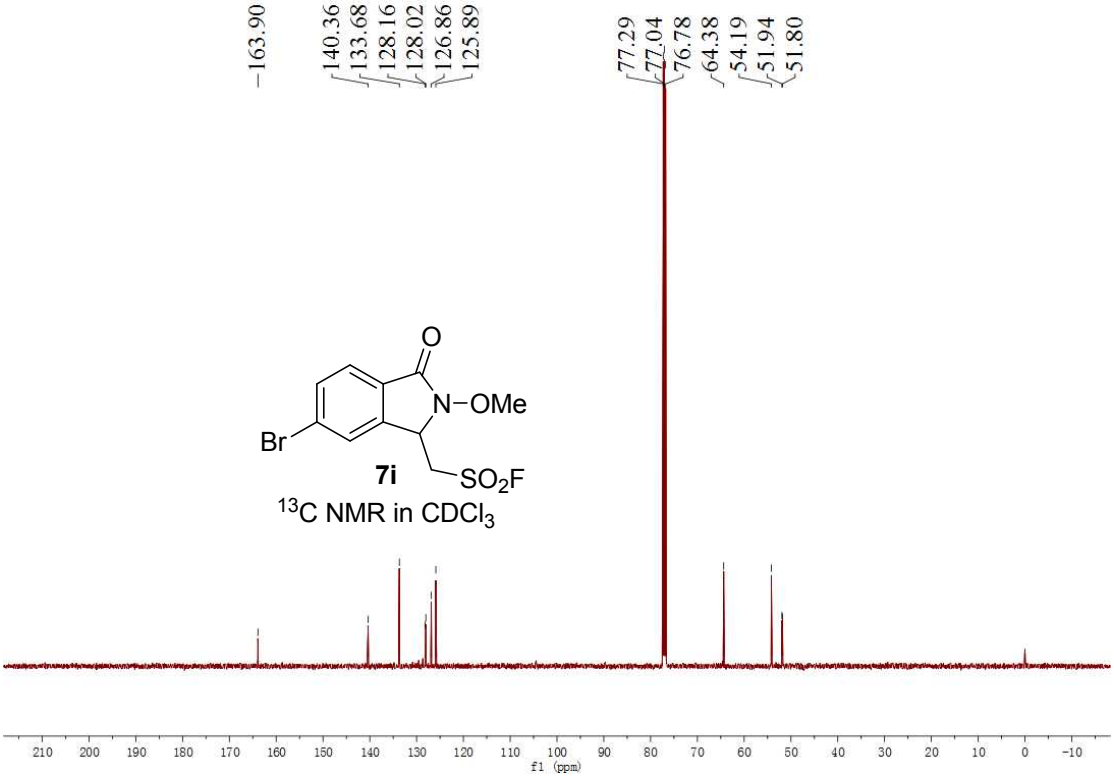
7h

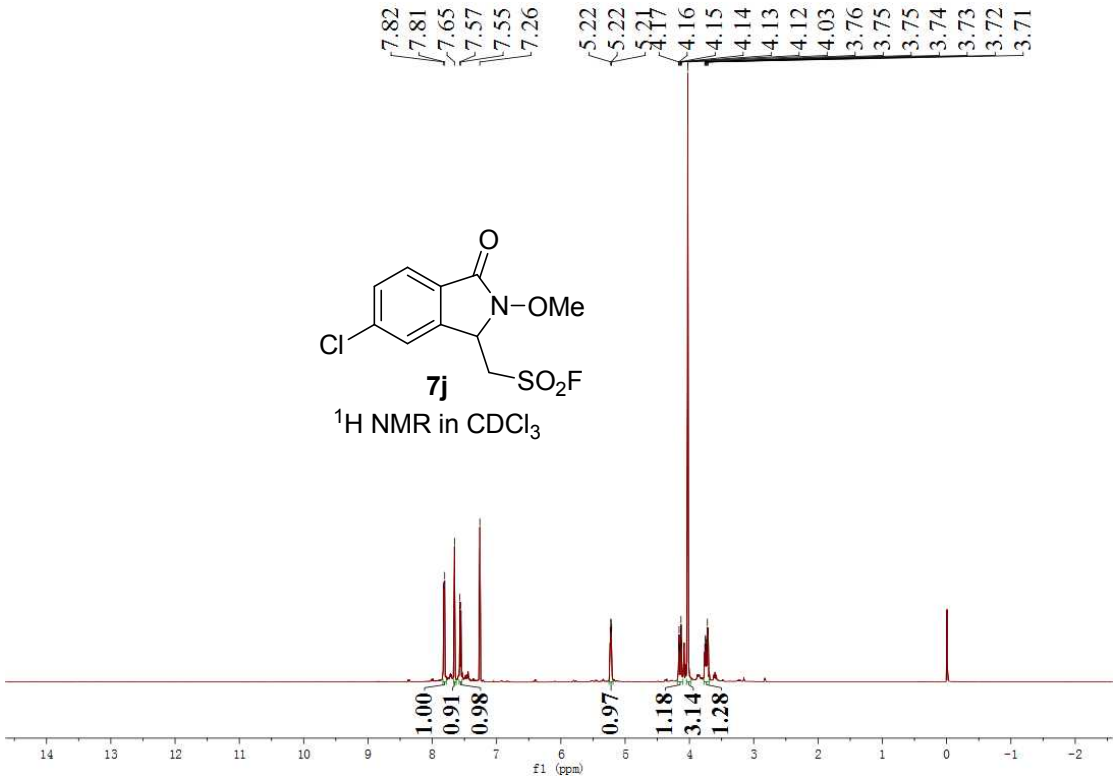
^{19}F NMR in $CDCl_3$

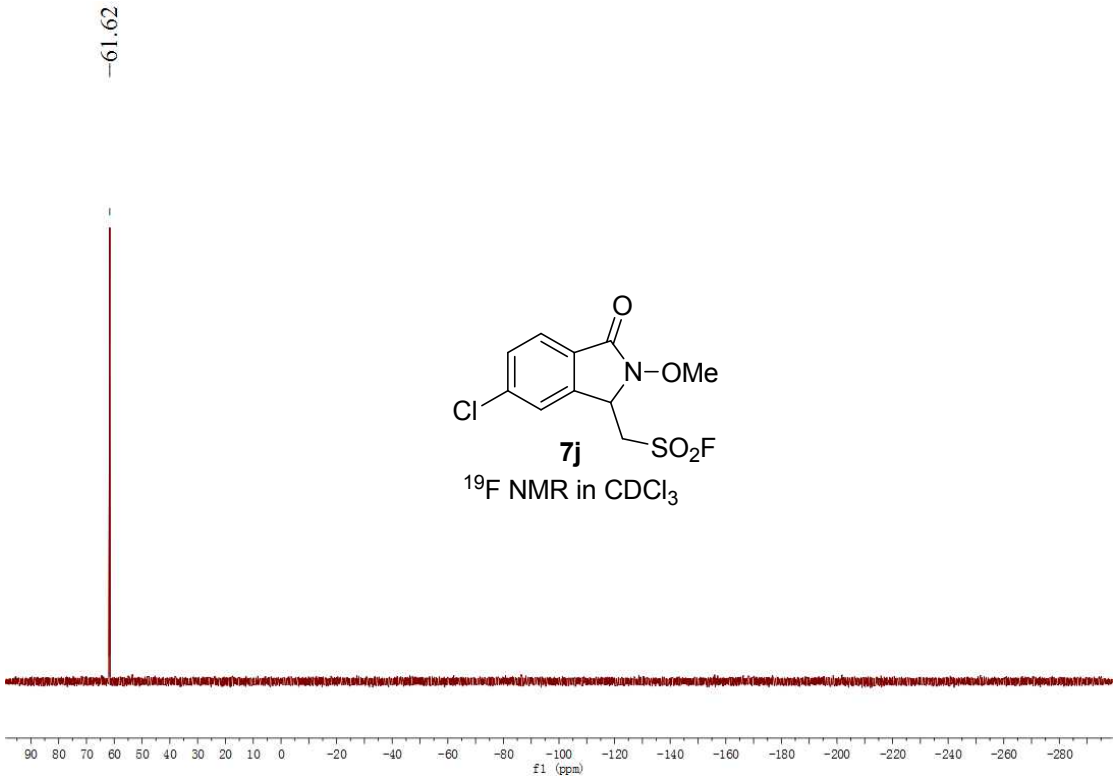

164.86
146.69
139.55
139.51
129.17
129.14
128.65
127.84
127.42
124.84
122.04
77.32
77.06
76.81
64.29
54.70
52.40
52.26
O
N−OMe
Ph
SO2F
7h
13C NMR in CDCl3
f1 (ppm)

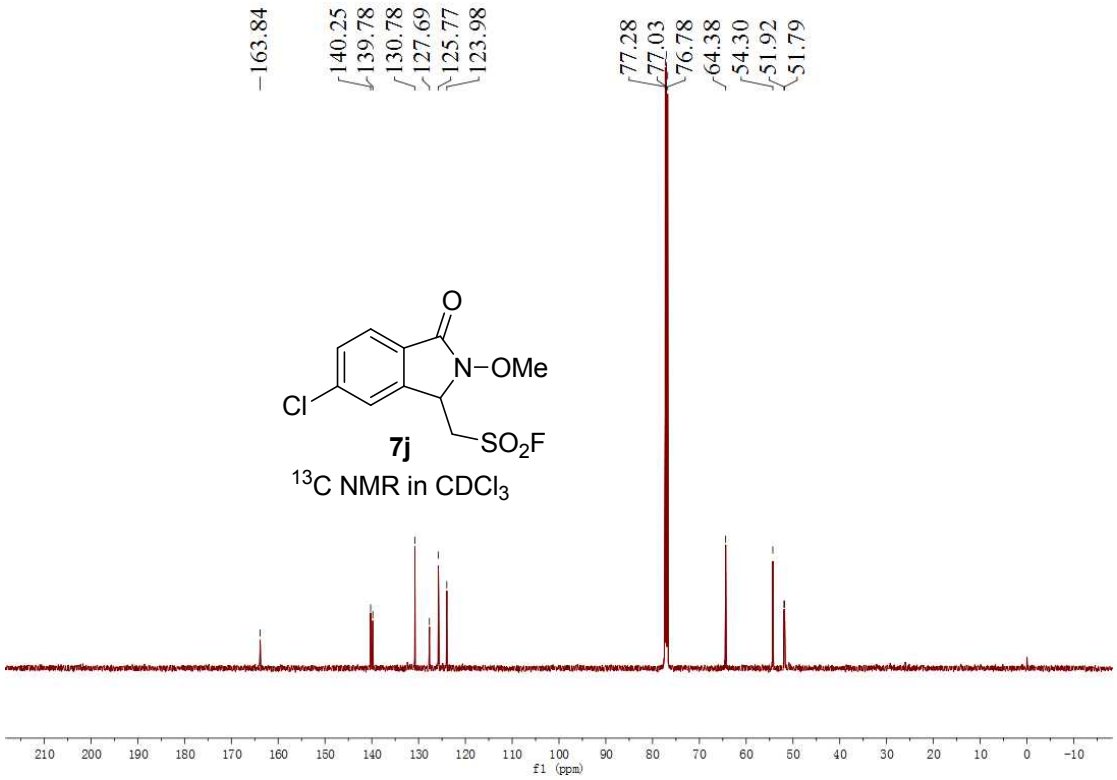

7.81
7.76
7.74
7.73
7.71
7.26
5.22
5.22
4.12
4.09
4.02
3.77
3.76
3.75
3.74
3.73
3.72
3.71
O
N−OMe
Br
SO2F
7i
1H NMR in CDCl3
1.00
2.03
0.98
1.29
3.05
1.31
f1 (ppm)

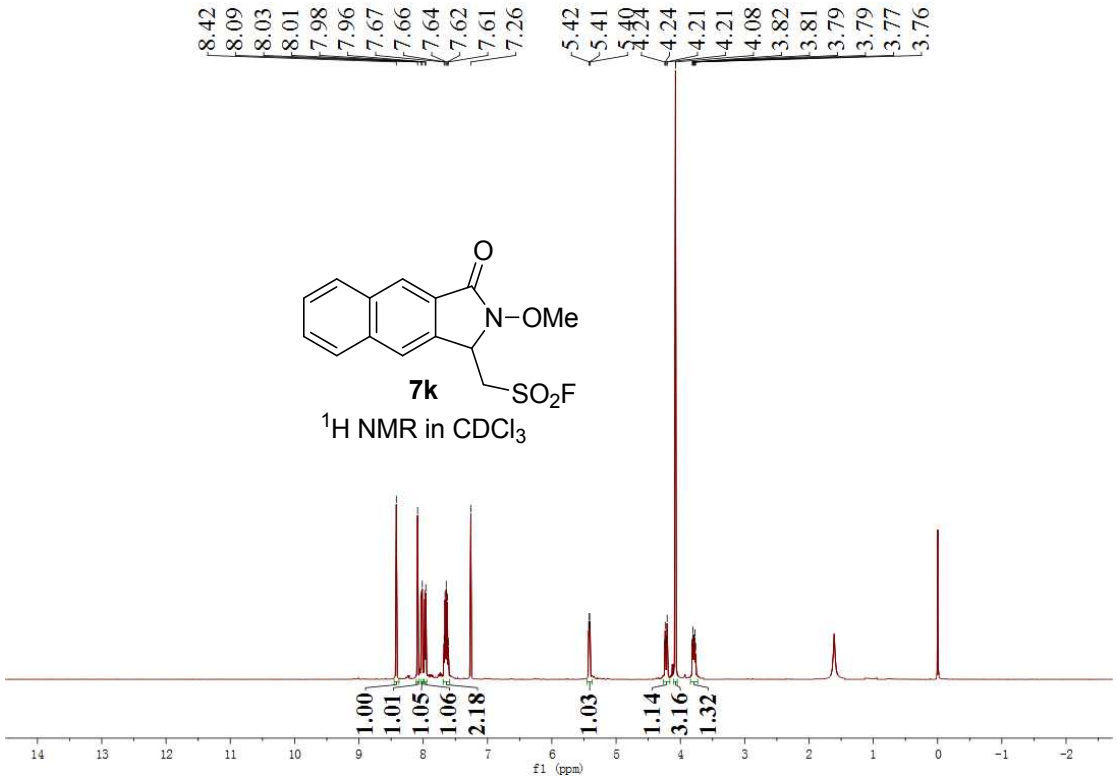

-61.61
O
N−OMe
Br
SO2F
7i
19F NMR in CDCl3
f1 (ppm)

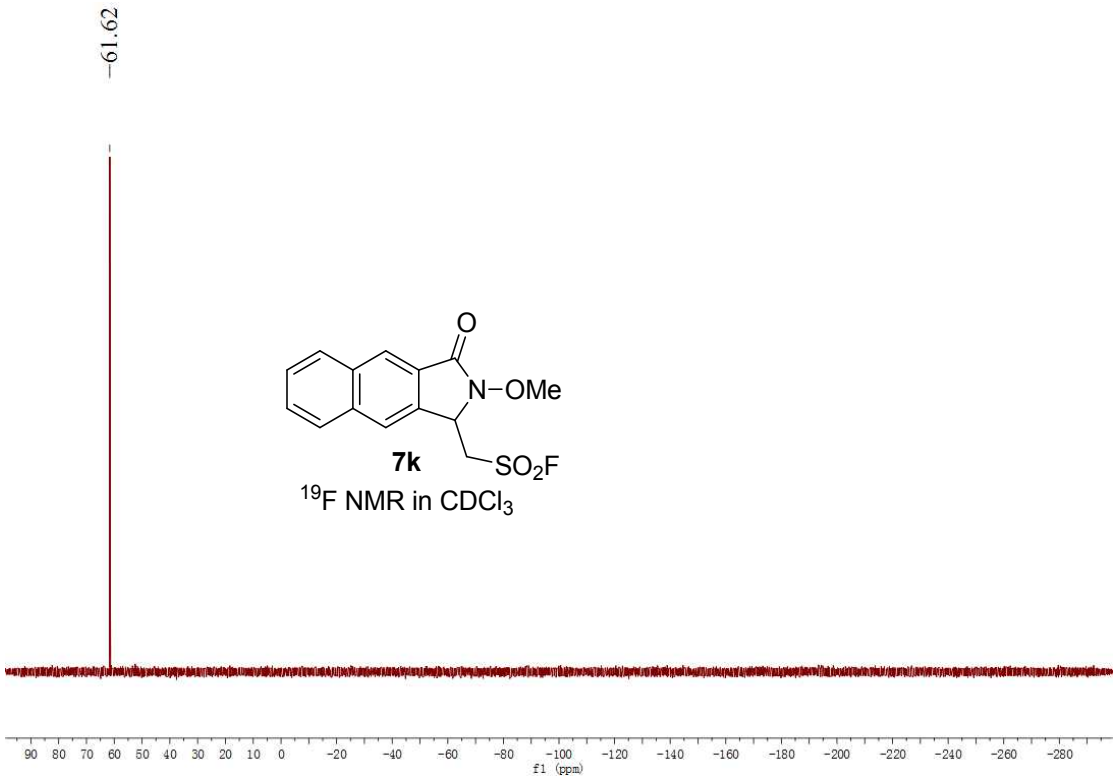

-163.90
140.36
133.68
128.16
128.02
126.86
125.89
77.29
77.04
76.78
64.38
54.19
51.94
51.80
O
N−OMe
Br
SO2F
7i
13C NMR in CDCl3
f1 (ppm)

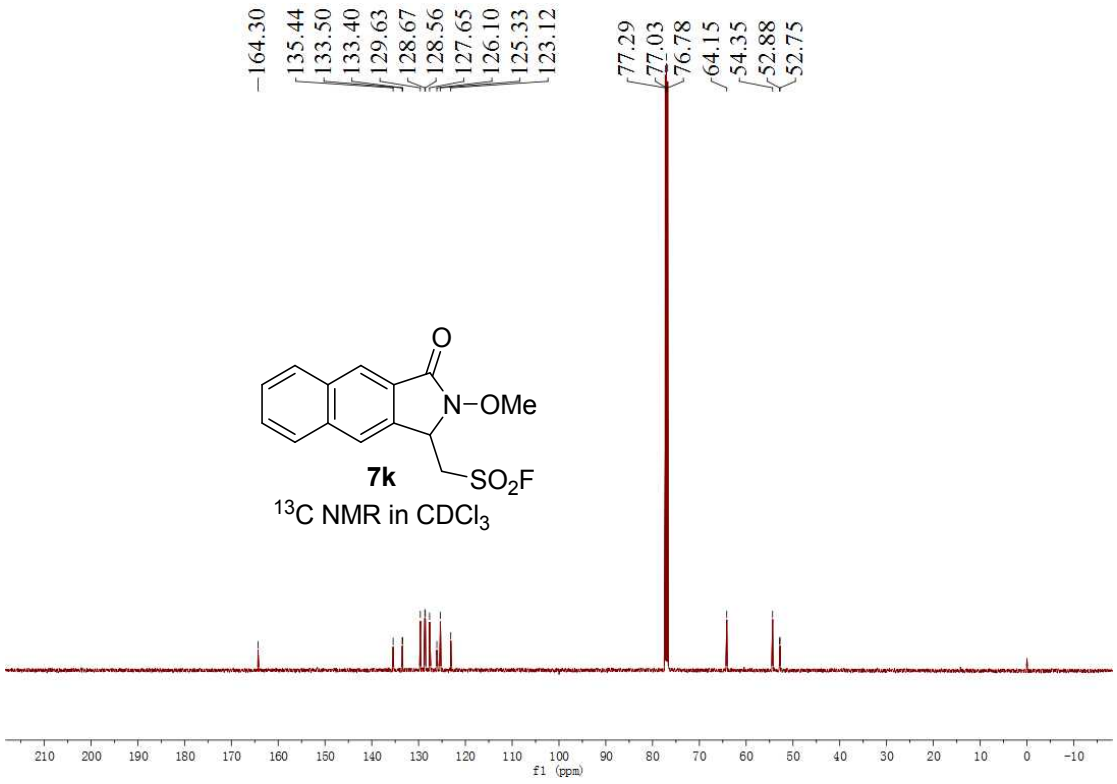

7.82
7.81
7.65
7.57
7.55
7.26
5.22
5.22
5.21
4.17
4.16
4.15
4.14
4.13
4.12
4.03
3.76
3.75
3.75
3.74
3.73
3.72
3.71
O
N−OMe
Cl
SO2F
7j
1H NMR in CDCl3
1.00
0.91
0.98
0.97
1.18
3.14
1.28
f1 (ppm)

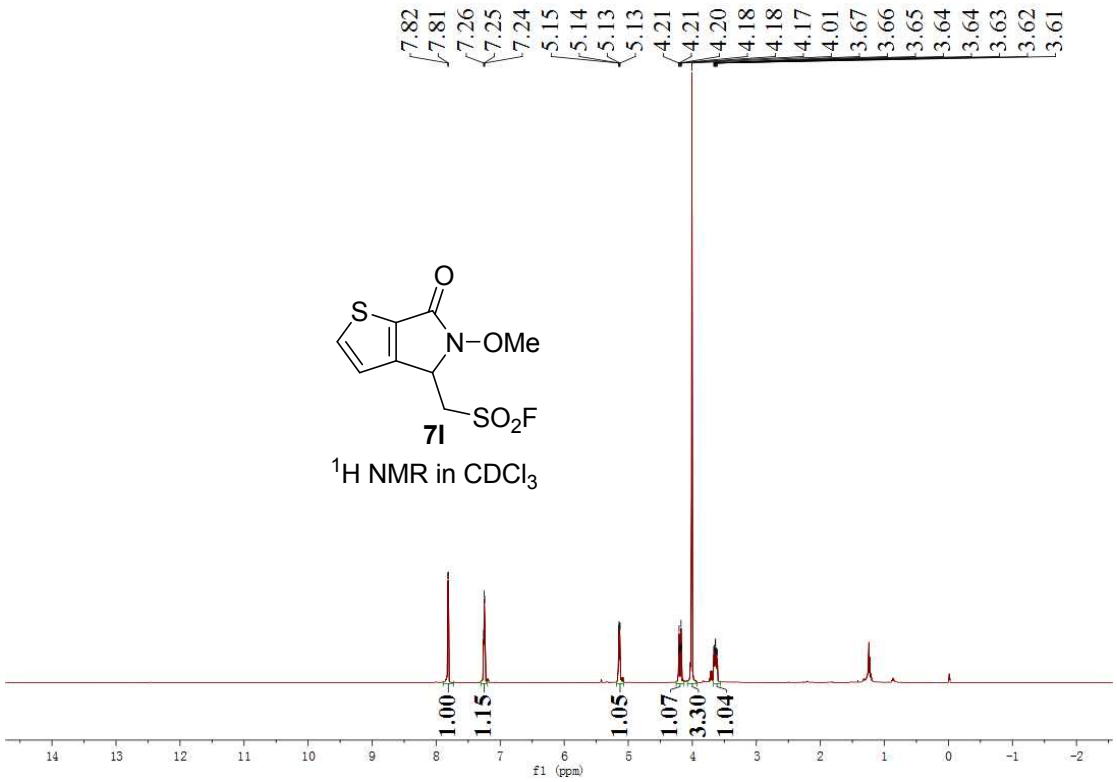

−61.62
O
N−OMe
Cl
SO2F
7j
19F NMR in CDCl3
f1 (ppm)


163.84
140.25
139.78
130.78
127.69
125.77
123.98
77.28
77.03
76.78
64.38
54.30
51.92
51.79
O
N−OMe
Cl
SO2F
7j
13C NMR in CDCl3
f1 (ppm)


8.42
8.09
8.03
8.01
7.98
7.96
7.67
7.66
7.64
7.62
7.61
7.26
5.42
5.41
5.40
4.24
4.21
4.21
4.08
3.82
3.81
3.79
3.79
3.77
3.76
O
N−OMe
SO2F
7k
1H NMR in CDCl3
1.00
1.01
1.05
1.06
2.18
1.03
1.14
3.16
1.32
f1 (ppm)

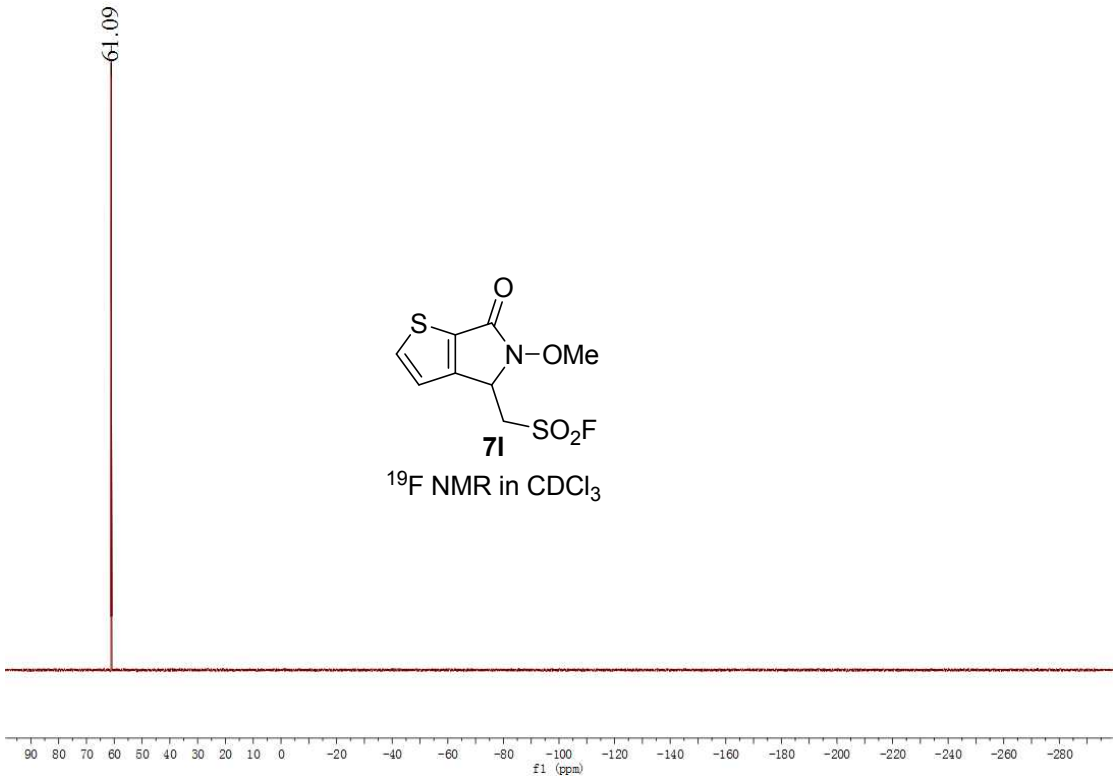

-61.62
O
N−OMe
SO2F
7k
19F NMR in CDCl3
90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280
f1 (ppm)


164.30
135.44
133.50
133.40
129.63
128.67
128.56
127.65
126.10
125.33
123.12
77.29
77.03
76.78
64.15
54.35
52.88
52.75
O
N−OMe
SO2F
7k
13C NMR in CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



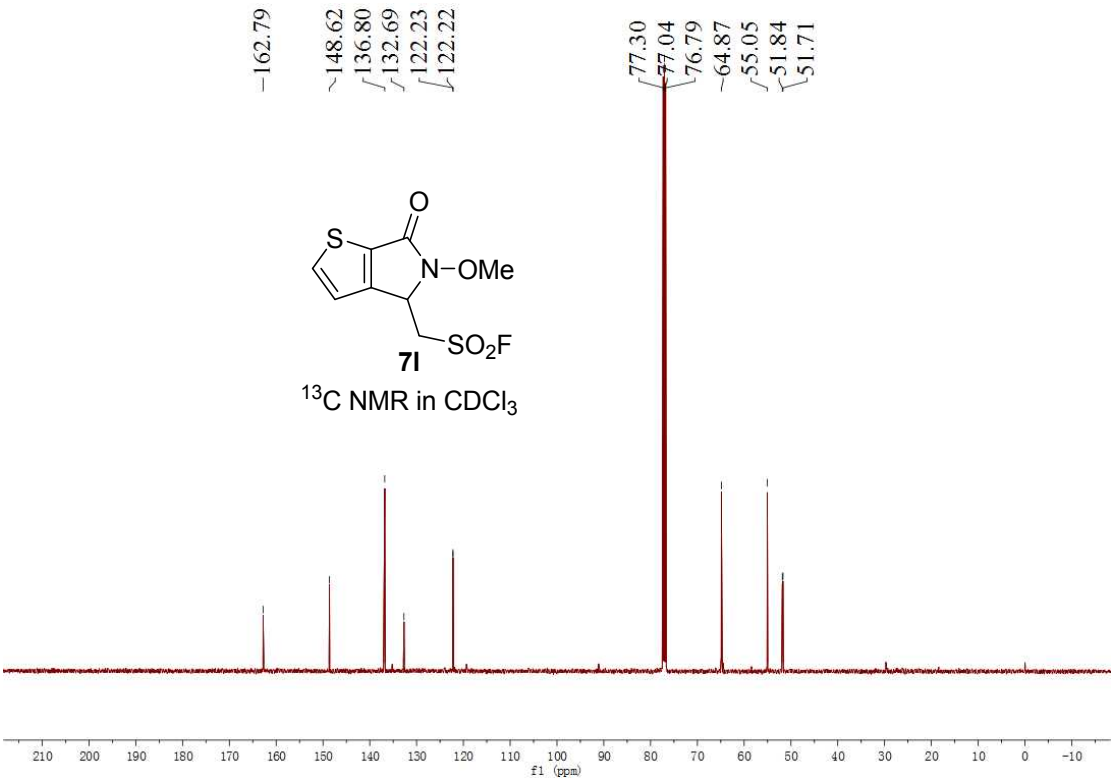
7l

^{1}H NMR in $CDCl_3$



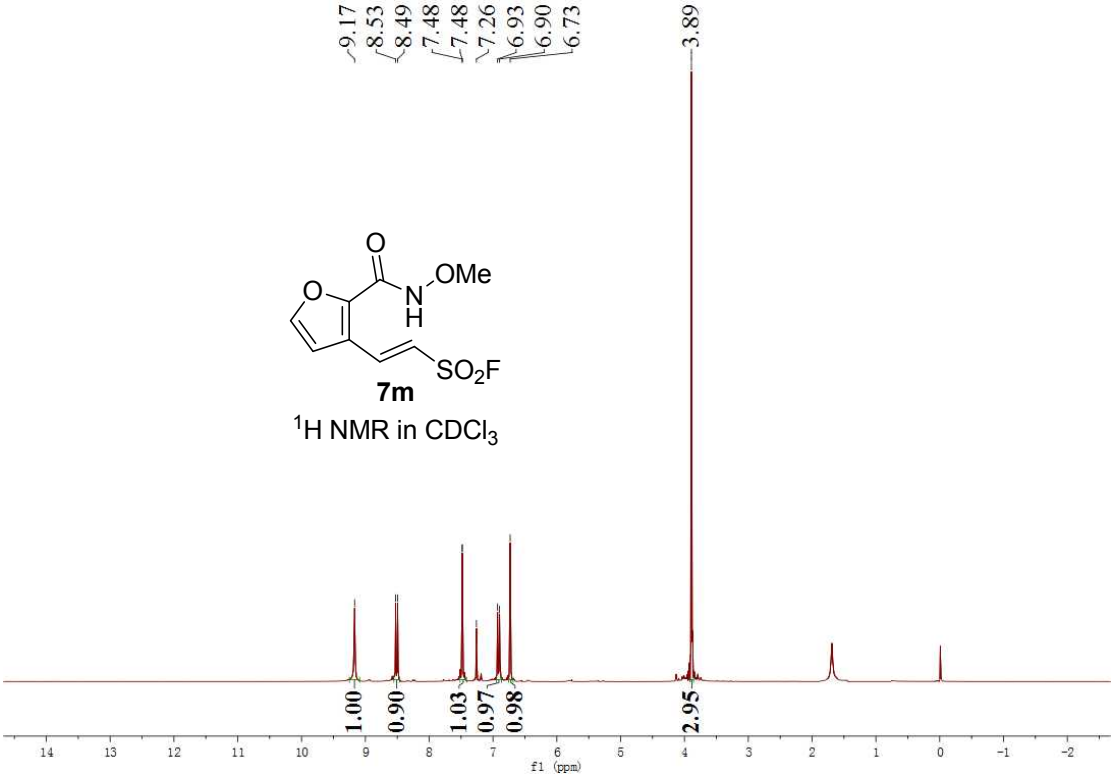
7l

^{19}F NMR in $CDCl_3$



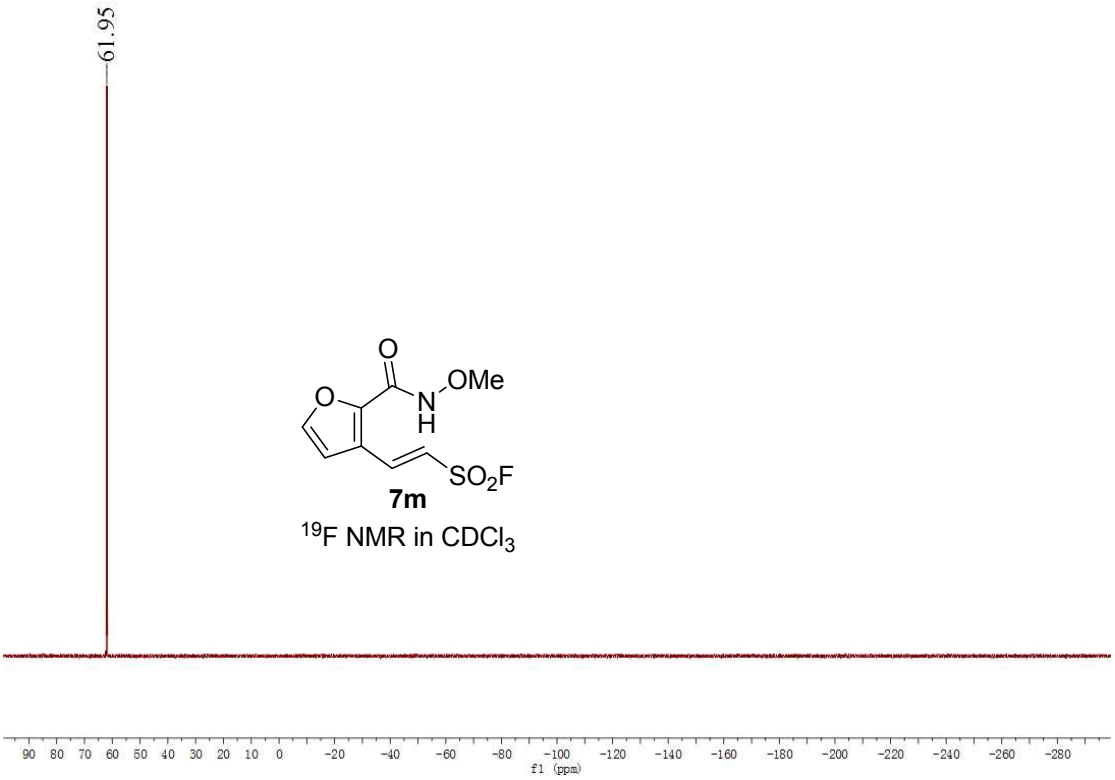
7l

^{13}C NMR in $CDCl_3$



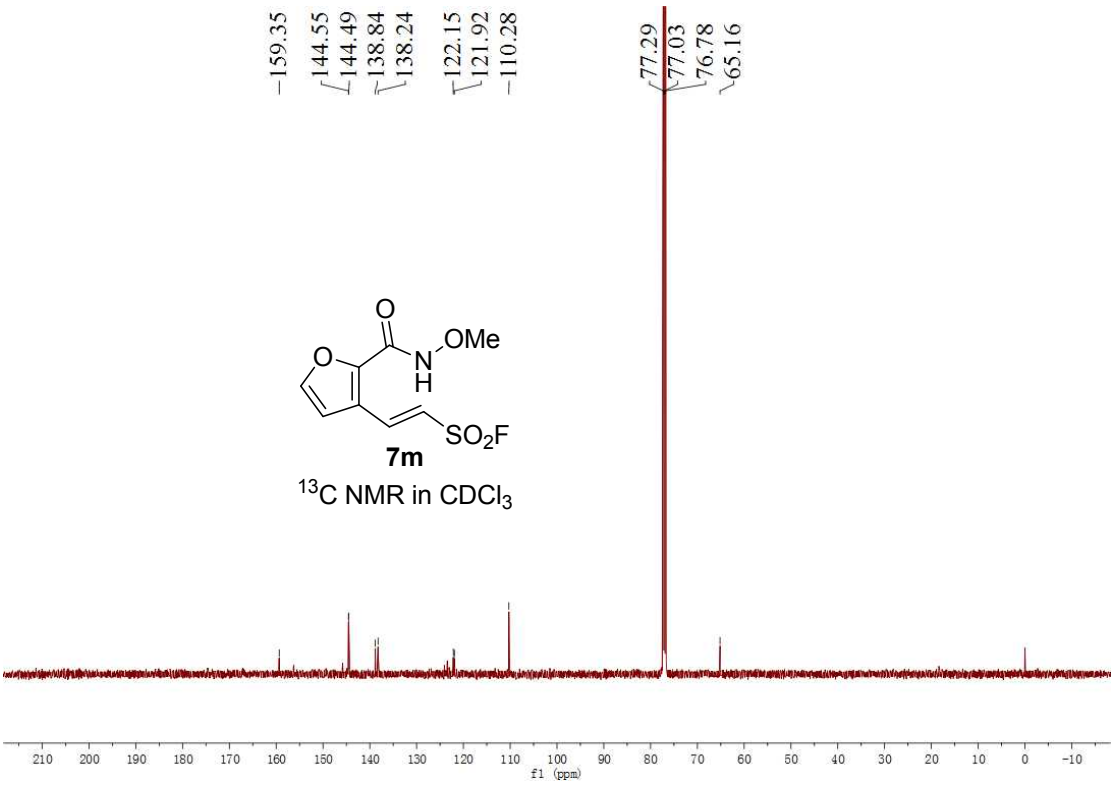
7m

^{1}H NMR in $CDCl_3$



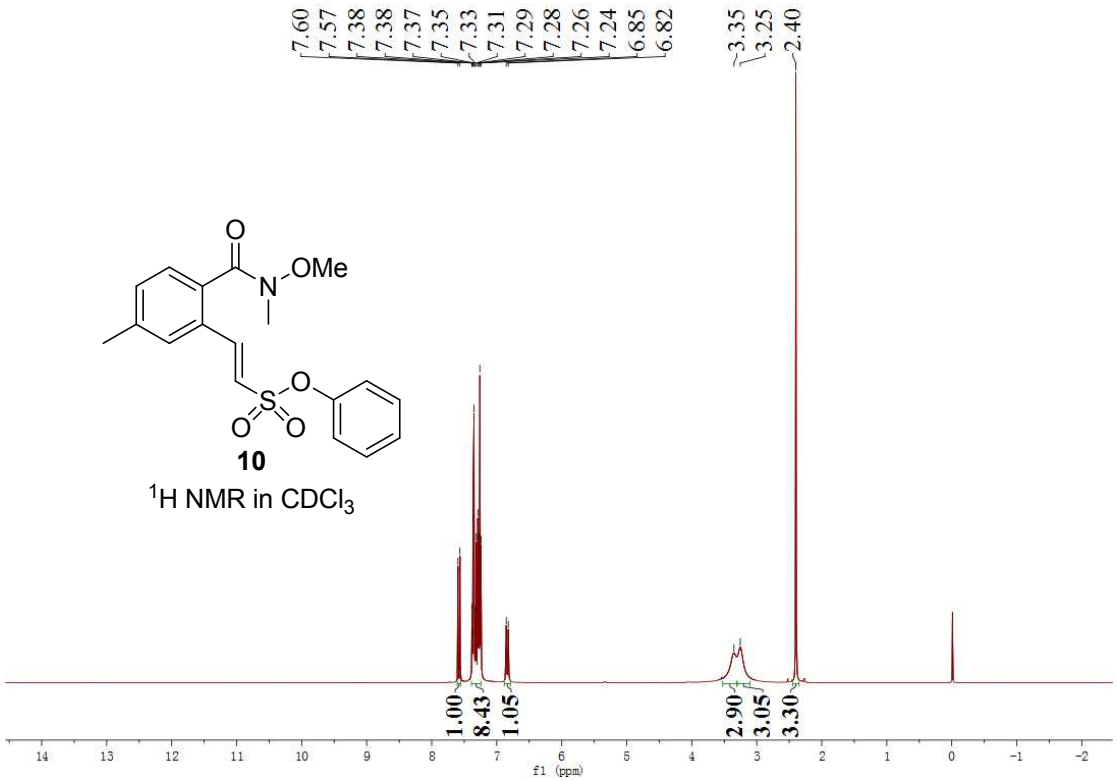
7m

^{19}F NMR in $CDCl_3$



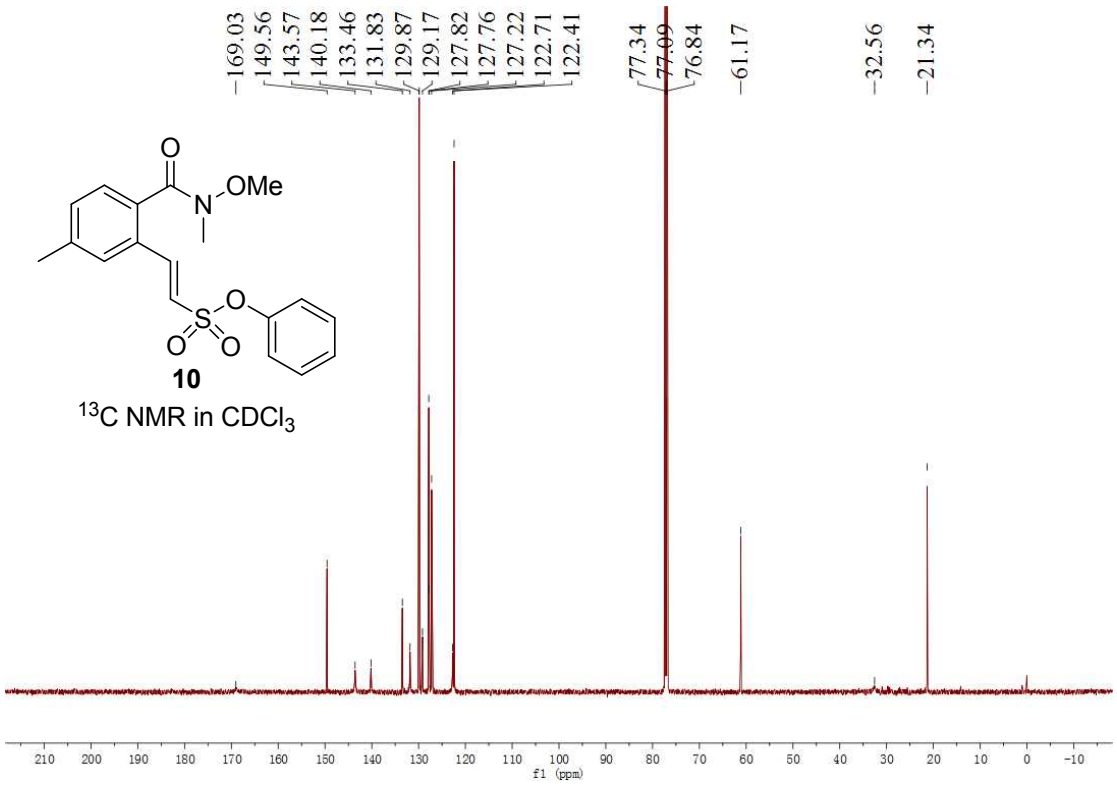
7m

^{13}C NMR in $CDCl_3$



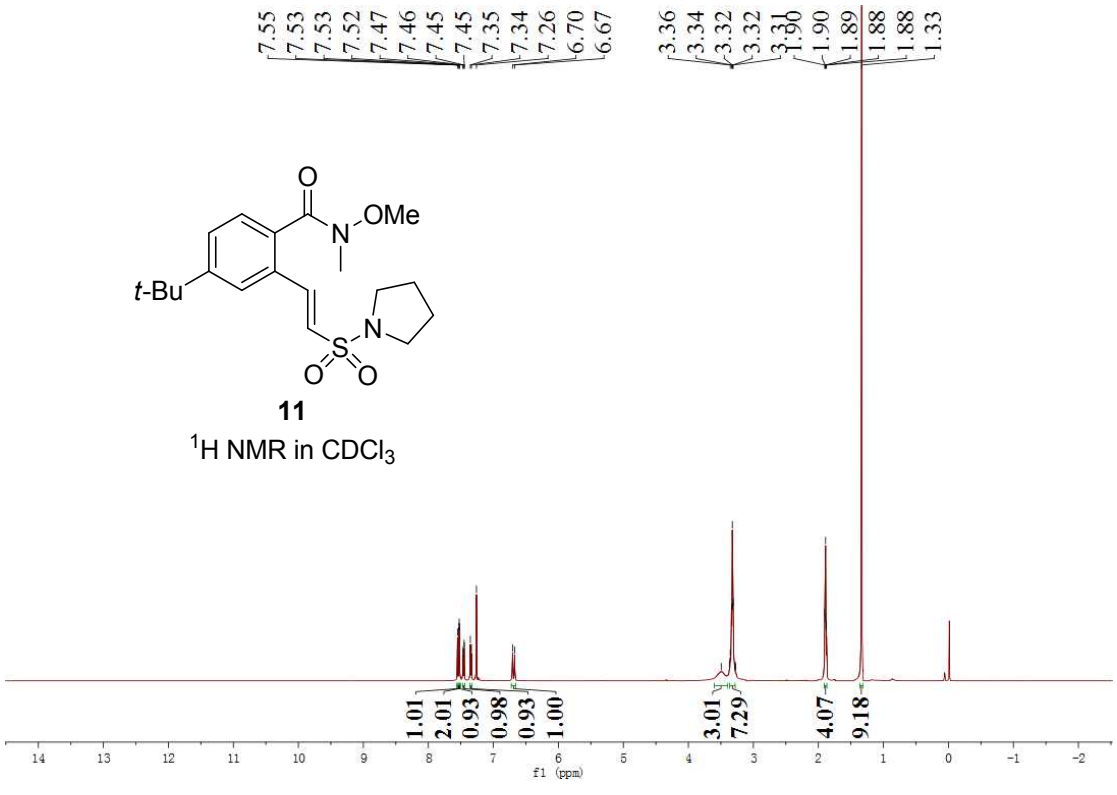
10

^{1}H NMR in $CDCl_3$



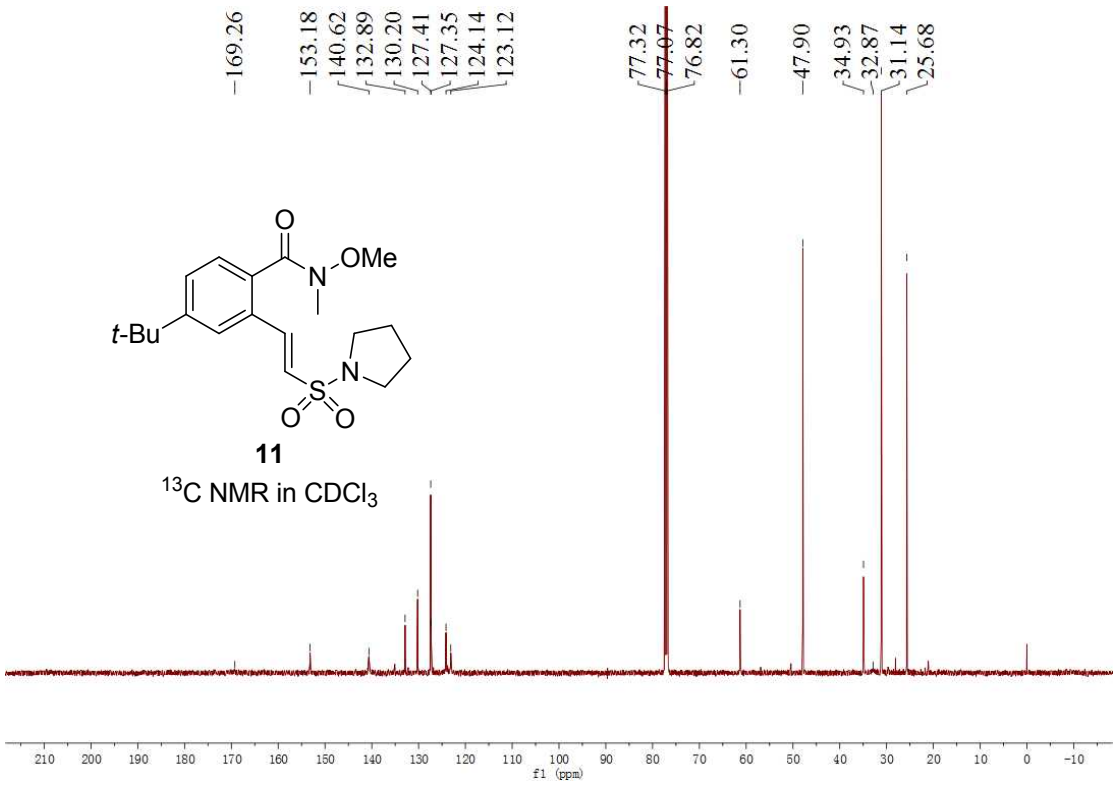
10

^{13}C NMR in $CDCl_3$



11

^{1}H NMR in $CDCl_3$



11

^{13}C NMR in $CDCl_3$

9. Data of crystal structures

9.1 Data of crystal structure for **5c**.

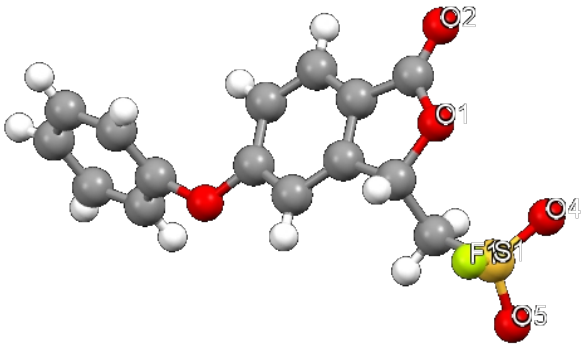


Table 1. Crystal data and structure refinement for 170906f.

Identification code	170906f
Empirical formula	C15 H11 F O5 S
Formula weight	322.30
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 8.6492(9) A alpha = 90 deg.
	b = 6.7929(8) A beta = 98.112(2) deg.

c = 25.645(3) A gamma = 90 deg.

Volume	1491.7(3) A^3
Z, Calculated density	4, 1.435 Mg/m^3
Absorption coefficient	0.248 mm^-1
F(000)	664
Crystal size	0.42 x 0.40 x 0.35 mm
Theta range for data collection	3.10 to 25.02 deg.
Limiting indices	-10<=h<=10, -8<=k<=8, -5<=l<=30
Reflections collected / unique	2570 / 2570 [R(int) = 0.0000]
Completeness to theta = 25.02	98.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9182 and 0.9029

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2570 / 0 / 200
Goodness-of-fit on F^2	1.053
Final R indices [I>2sigma(I)]	R1 = 0.0813, wR2 = 0.2160
R indices (all data)	R1 = 0.1039, wR2 = 0.2291
Largest diff. peak and hole	0.351 and -0.398 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 170906f.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(4)	7330(6)	7871(9)	11016(2)	100(2)
O(1)	7415(4)	9537(5)	9913(1)	53(1)
O(2)	8862(4)	12054(5)	9697(2)	61(1)
O(3)	8863(7)	4339(6)	8199(2)	91(2)
F(1)	5021(5)	6488(8)	10551(2)	104(2)
O(5)	7021(7)	4405(9)	10990(2)	113(2)
S(1)	6630(2)	6233(2)	10702(1)	58(1)
C(1)	8385(6)	10420(7)	9599(2)	46(1)
C(2)	8645(5)	9065(7)	9189(2)	44(1)
C(3)	9538(6)	9262(8)	8782(2)	55(1)
C(4)	9636(7)	7730(9)	8445(2)	61(2)

C(5)	8796(7)	5988(8)	8509(2)	59(1)
C(6)	7901(6)	5765(7)	8905(2)	53(1)
C(7)	7837(5)	7350(7)	9243(2)	43(1)
C(8)	7029(6)	7553(7)	9724(2)	45(1)
C(9)	7619(6)	6089(7)	10148(2)	46(1)
C(10)	9485(7)	4397(9)	7727(2)	60(2)
C(11)	8937(8)	5588(10)	7321(3)	80(2)
C(12)	9566(11)	5472(12)	6850(3)	91(2)
C(13)	10662(11)	4130(12)	6797(3)	93(2)
C(14)	11203(10)	2925(12)	7202(3)	97(3)
C(15)	10641(8)	3080(10)	7676(2)	77(2)

Table 3. Bond lengths [A] and angles [deg] for 170906f.

O(4)-S(1)	1.455(4)
O(1)-C(1)	1.378(6)
O(1)-C(8)	1.455(6)
O(2)-C(1)	1.198(6)
O(3)-C(5)	1.379(6)
O(3)-C(10)	1.392(6)
F(1)-S(1)	1.402(4)
O(5)-S(1)	1.461(5)
S(1)-C(9)	1.760(5)
C(1)-C(2)	1.440(7)
C(2)-C(7)	1.376(6)
C(2)-C(3)	1.391(7)
C(3)-C(4)	1.361(8)
C(3)-H(3)	0.9300
C(4)-C(5)	1.410(8)
C(4)-H(4)	0.9300
C(5)-C(6)	1.370(7)
C(6)-C(7)	1.389(7)
C(6)-H(6)	0.9300

C(7)-C(8)	1.507(6)
C(8)-C(9)	1.508(7)
C(8)-H(8)	0.9800
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-C(11)	1.351(9)
C(10)-C(15)	1.362(9)
C(11)-C(12)	1.395(10)
C(11)-H(11)	0.9300
C(12)-C(13)	1.336(11)
C(12)-H(12)	0.9300
C(13)-C(14)	1.353(11)
C(13)-H(13)	0.9300
C(14)-C(15)	1.375(9)
C(14)-H(14)	0.9300
C(15)-H(15)	0.9300

C(1)-O(1)-C(8)	109.8(4)
C(5)-O(3)-C(10)	122.0(4)
F(1)-S(1)-O(4)	112.2(3)
F(1)-S(1)-O(5)	113.2(3)
O(4)-S(1)-O(5)	108.7(4)
F(1)-S(1)-C(9)	111.2(2)
O(4)-S(1)-C(9)	106.2(3)

O(5)-S(1)-C(9)	104.9(3)
O(2)-C(1)-O(1)	120.0(5)
O(2)-C(1)-C(2)	131.3(5)
O(1)-C(1)-C(2)	108.6(4)
C(7)-C(2)-C(3)	120.1(4)
C(7)-C(2)-C(1)	109.5(4)
C(3)-C(2)-C(1)	130.4(4)
C(4)-C(3)-C(2)	119.5(5)
C(4)-C(3)-H(3)	120.2
C(2)-C(3)-H(3)	120.2
C(3)-C(4)-C(5)	119.3(5)
C(3)-C(4)-H(4)	120.3
C(5)-C(4)-H(4)	120.3
C(6)-C(5)-O(3)	114.3(4)
C(6)-C(5)-C(4)	122.2(5)
O(3)-C(5)-C(4)	123.4(4)
C(5)-C(6)-C(7)	117.0(4)
C(5)-C(6)-H(6)	121.5
C(7)-C(6)-H(6)	121.5
C(2)-C(7)-C(6)	121.9(4)
C(2)-C(7)-C(8)	107.8(4)
C(6)-C(7)-C(8)	130.2(4)
O(1)-C(8)-C(7)	104.2(4)
O(1)-C(8)-C(9)	109.4(4)

C(7)-C(8)-C(9)	112.4(4)
O(1)-C(8)-H(8)	110.2
C(7)-C(8)-H(8)	110.2
C(9)-C(8)-H(8)	110.2
C(8)-C(9)-S(1)	113.0(3)
C(8)-C(9)-H(9A)	109.0
S(1)-C(9)-H(9A)	109.0
C(8)-C(9)-H(9B)	109.0
S(1)-C(9)-H(9B)	109.0
H(9A)-C(9)-H(9B)	107.8
C(11)-C(10)-C(15)	120.1(5)
C(11)-C(10)-O(3)	123.4(6)
C(15)-C(10)-O(3)	116.4(6)
C(10)-C(11)-C(12)	119.7(7)
C(10)-C(11)-H(11)	120.1
C(12)-C(11)-H(11)	120.1
C(13)-C(12)-C(11)	119.7(7)
C(13)-C(12)-H(12)	120.1
C(11)-C(12)-H(12)	120.1
C(12)-C(13)-C(14)	120.5(6)
C(12)-C(13)-H(13)	119.7
C(14)-C(13)-H(13)	119.7
C(13)-C(14)-C(15)	120.3(7)
C(13)-C(14)-H(14)	119.8

C(15)-C(14)-H(14)	119.8
C(10)-C(15)-C(14)	119.4(7)
C(10)-C(15)-H(15)	120.3
C(14)-C(15)-H(15)	120.3

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 170906f.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
O(4)	86(3)	142(5)	78(3)	-68(3)	34(2)	-61(3)
O(1)	62(2)	41(2)	59(2)	-7(2)	18(2)	-1(2)
O(2)	68(2)	35(2)	76(2)	-3(2)	1(2)	-9(2)
O(3)	144(4)	57(3)	91(3)	-22(2)	81(3)	-30(3)
F(1)	75(2)	152(4)	91(3)	-20(3)	34(2)	-21(3)
O(5)	130(5)	126(5)	91(3)	63(3)	43(3)	17(4)
S(1)	57(1)	76(1)	46(1)	-7(1)	18(1)	-16(1)
C(1)	45(3)	36(3)	54(3)	1(2)	-1(2)	-2(2)
C(2)	44(3)	37(3)	51(3)	2(2)	3(2)	-10(2)
C(3)	59(3)	49(3)	59(3)	3(2)	13(3)	-18(2)
C(4)	66(3)	65(4)	56(3)	-3(3)	25(3)	-19(3)

C(5)	75(4)	48(3)	60(3)	-6(2)	33(3)	-17(3)
C(6)	67(3)	45(3)	50(3)	-7(2)	20(2)	-21(2)
C(7)	46(3)	40(3)	42(2)	-1(2)	7(2)	-9(2)
C(8)	47(3)	42(3)	47(3)	-10(2)	13(2)	-9(2)
C(9)	50(3)	42(3)	49(3)	-2(2)	16(2)	-4(2)
C(10)	79(4)	55(3)	54(3)	-13(3)	30(3)	-19(3)
C(11)	71(4)	68(4)	100(5)	2(4)	17(4)	5(3)
C(12)	133(7)	86(5)	52(3)	13(3)	-1(4)	-8(5)
C(13)	144(7)	77(5)	67(4)	-8(4)	52(5)	-9(5)
C(14)	115(6)	84(5)	107(6)	11(5)	65(5)	24(5)
C(15)	95(5)	77(4)	64(4)	6(3)	30(3)	7(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 170906f.

	x	y	z	U(eq)
H(3)	10065	10432	8739	66
H(4)	10250	7832	8177	73
H(6)	7360	4604	8945	63
H(8)	5897	7417	9627	54
H(9A)	8724	6317	10259	55
H(9B)	7502	4770	10003	55
H(11)	8142	6482	7355	95
H(12)	9224	6326	6574	110
H(13)	11057	4024	6479	111
H(14)	11959	1987	7160	117
H(15)	11047	2292	7959	92

Table 6. Torsion angles [deg] for 170906f.

C(8)-O(1)-C(1)-O(2)	-178.5(4)
C(8)-O(1)-C(1)-C(2)	1.1(5)
O(2)-C(1)-C(2)-C(7)	179.9(5)
O(1)-C(1)-C(2)-C(7)	0.3(5)
O(2)-C(1)-C(2)-C(3)	0.0(9)
O(1)-C(1)-C(2)-C(3)	-179.5(5)
C(7)-C(2)-C(3)-C(4)	-1.6(8)
C(1)-C(2)-C(3)-C(4)	178.3(5)
C(2)-C(3)-C(4)-C(5)	1.6(9)
C(10)-O(3)-C(5)-C(6)	168.6(6)
C(10)-O(3)-C(5)-C(4)	-14.5(10)
C(3)-C(4)-C(5)-C(6)	-1.2(10)
C(3)-C(4)-C(5)-O(3)	-177.8(6)
O(3)-C(5)-C(6)-C(7)	177.6(5)
C(4)-C(5)-C(6)-C(7)	0.7(9)
C(3)-C(2)-C(7)-C(6)	1.1(8)
C(1)-C(2)-C(7)-C(6)	-178.8(5)
C(3)-C(2)-C(7)-C(8)	178.3(5)
C(1)-C(2)-C(7)-C(8)	-1.6(5)

C(5)-C(6)-C(7)-C(2)	-0.6(8)
C(5)-C(6)-C(7)-C(8)	-177.1(5)
C(1)-O(1)-C(8)-C(7)	-2.0(5)
C(1)-O(1)-C(8)-C(9)	118.5(4)
C(2)-C(7)-C(8)-O(1)	2.1(5)
C(6)-C(7)-C(8)-O(1)	179.0(5)
C(2)-C(7)-C(8)-C(9)	-116.2(5)
C(6)-C(7)-C(8)-C(9)	60.7(7)
O(1)-C(8)-C(9)-S(1)	67.3(4)
C(7)-C(8)-C(9)-S(1)	-177.4(3)
F(1)-S(1)-C(9)-C(8)	41.4(5)
O(4)-S(1)-C(9)-C(8)	-80.8(5)
O(5)-S(1)-C(9)-C(8)	164.2(4)
C(5)-O(3)-C(10)-C(11)	-58.2(9)
C(5)-O(3)-C(10)-C(15)	125.8(7)
C(15)-C(10)-C(11)-C(12)	-0.4(10)
O(3)-C(10)-C(11)-C(12)	-176.2(6)
C(10)-C(11)-C(12)-C(13)	2.7(12)
C(11)-C(12)-C(13)-C(14)	-2.1(13)
C(12)-C(13)-C(14)-C(15)	-0.7(13)
C(11)-C(10)-C(15)-C(14)	-2.3(11)
O(3)-C(10)-C(15)-C(14)	173.7(7)
C(13)-C(14)-C(15)-C(10)	2.9(12)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 170906f [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

9.2 Data of crystal structure for **7i**.

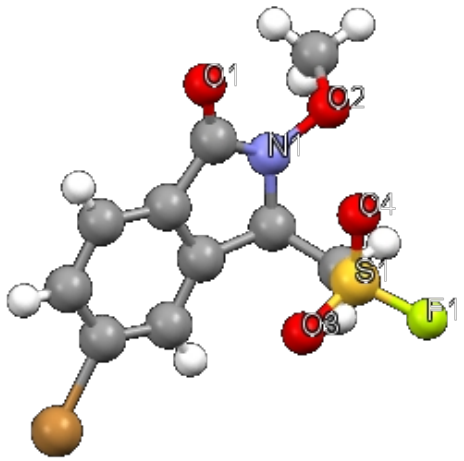


Table 1. Crystal data and structure refinement for 170526e.

Identification code	170526e
Empirical formula	C10 H9 Br F N O4 S
Formula weight	338.15

Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 8.7382(6) A alpha = 90 deg. b = 5.8569(4) A beta = 91.1410(10) deg. c = 23.8346(18) A gamma = 90 deg.
Volume	1219.58(15) A^3
Z, Calculated density	4, 1.842 Mg/m^3
Absorption coefficient	3.560 mm^-1
F(000)	672
Crystal size	0.40 x 0.30 x 0.23 mm
Theta range for data collection	2.50 to 25.02 deg.

Limiting indices	-10<=h<=9, -6<=k<=6, -28<=l<=20
Reflections collected / unique	5749 / 2143 [R(int) = 0.0441]
Completeness to theta = 25.02	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4948 and 0.3301
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2143 / 0 / 164
Goodness-of-fit on F^2	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0397, wR2 = 0.0926
R indices (all data)	R1 = 0.0627, wR2 = 0.0996
Largest diff. peak and hole	0.540 and -0.433 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 170526e.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	9087(1)	13223(1)	478(1)	65(1)
F(1)	5730(5)	8440(5)	2955(1)	112(1)
N(1)	3051(3)	8412(5)	1345(1)	47(1)
O(1)	3187(3)	5201(5)	794(1)	55(1)
O(2)	1812(3)	7716(5)	1658(1)	48(1)
O(3)	7010(4)	8309(7)	2116(2)	102(1)
O(4)	4784(5)	6005(5)	2246(2)	114(2)
S(1)	5528(1)	8047(2)	2342(1)	52(1)
C(1)	3683(4)	7039(7)	955(2)	40(1)
C(2)	5057(4)	8308(6)	780(2)	36(1)
C(3)	6088(4)	7808(7)	366(2)	45(1)

C(4)	7281(4)	9281(7)	280(2)	46(1)
C(5)	7406(4)	11222(7)	601(2)	43(1)
C(6)	6396(4)	11778(6)	1016(2)	41(1)
C(7)	5212(4)	10285(6)	1100(1)	36(1)
C(8)	3923(4)	10412(6)	1515(2)	39(1)
C(9)	4404(4)	10394(6)	2133(2)	46(1)
C(10)	420(5)	8374(8)	1382(2)	65(1)

Table 3. Bond lengths [A] and angles [deg] for 170526e.

Br(1)-C(5)	1.906(4)
F(1)-S(1)	1.486(3)
N(1)-C(1)	1.355(5)
N(1)-O(2)	1.387(4)
N(1)-C(8)	1.451(5)
O(1)-C(1)	1.220(4)
O(2)-C(10)	1.424(5)
O(3)-S(1)	1.421(3)
O(4)-S(1)	1.378(3)
S(1)-C(9)	1.756(4)
C(1)-C(2)	1.479(5)
C(2)-C(3)	1.380(5)
C(2)-C(7)	1.392(5)
C(3)-C(4)	1.372(5)
C(3)-H(3)	0.9300
C(4)-C(5)	1.374(5)
C(4)-H(4)	0.9300
C(5)-C(6)	1.377(5)
C(6)-C(7)	1.372(5)

C(6)-H(6)	0.9300
C(7)-C(8)	1.515(4)
C(8)-C(9)	1.522(5)
C(8)-H(8)	0.9800
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-H(10A)	0.9600
C(10)-H(10B)	0.9600
C(10)-H(10C)	0.9600

C(1)-N(1)-O(2)	121.8(3)
C(1)-N(1)-C(8)	116.8(3)
O(2)-N(1)-C(8)	119.9(3)
N(1)-O(2)-C(10)	110.0(3)
O(4)-S(1)-O(3)	117.5(3)
O(4)-S(1)-F(1)	110.2(3)
O(3)-S(1)-F(1)	105.3(3)
O(4)-S(1)-C(9)	111.9(2)
O(3)-S(1)-C(9)	108.4(2)
F(1)-S(1)-C(9)	102.35(18)
O(1)-C(1)-N(1)	126.3(3)
O(1)-C(1)-C(2)	129.8(3)
N(1)-C(1)-C(2)	103.9(3)
C(3)-C(2)-C(7)	120.7(3)

C(3)-C(2)-C(1)	129.8(3)
C(7)-C(2)-C(1)	109.5(3)
C(4)-C(3)-C(2)	118.8(4)
C(4)-C(3)-H(3)	120.6
C(2)-C(3)-H(3)	120.6
C(3)-C(4)-C(5)	119.3(3)
C(3)-C(4)-H(4)	120.4
C(5)-C(4)-H(4)	120.4
C(4)-C(5)-C(6)	123.4(4)
C(4)-C(5)-Br(1)	118.4(3)
C(6)-C(5)-Br(1)	118.2(3)
C(7)-C(6)-C(5)	116.8(4)
C(7)-C(6)-H(6)	121.6
C(5)-C(6)-H(6)	121.6
C(6)-C(7)-C(2)	121.0(3)
C(6)-C(7)-C(8)	129.5(3)
C(2)-C(7)-C(8)	109.5(3)
N(1)-C(8)-C(7)	99.9(3)
N(1)-C(8)-C(9)	113.4(3)
C(7)-C(8)-C(9)	115.9(3)
N(1)-C(8)-H(8)	109.1
C(7)-C(8)-H(8)	109.1
C(9)-C(8)-H(8)	109.1
C(8)-C(9)-S(1)	115.0(3)

C(8)-C(9)-H(9A)	108.5
S(1)-C(9)-H(9A)	108.5
C(8)-C(9)-H(9B)	108.5
S(1)-C(9)-H(9B)	108.5
H(9A)-C(9)-H(9B)	107.5
O(2)-C(10)-H(10A)	109.5
O(2)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
O(2)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 170526e.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	60(1)	55(1)	82(1)	21(1)	26(1)	-6(1)
F(1)	183(4)	98(3)	54(2)	9(2)	-13(2)	24(2)
N(1)	49(2)	45(2)	47(2)	-5(2)	19(2)	-10(2)
O(1)	63(2)	40(2)	63(2)	-9(2)	6(1)	-5(1)
O(2)	44(1)	54(2)	48(2)	14(1)	14(1)	-1(1)
O(3)	68(2)	128(4)	109(3)	45(3)	24(2)	30(2)
O(4)	118(3)	31(2)	191(4)	17(2)	-72(3)	-6(2)
S(1)	67(1)	41(1)	47(1)	6(1)	1(1)	0(1)
C(1)	46(2)	38(2)	36(2)	5(2)	4(2)	6(2)
C(2)	44(2)	31(2)	33(2)	2(2)	3(2)	4(2)
C(3)	55(2)	41(2)	40(2)	-6(2)	5(2)	10(2)

C(4)	48(2)	50(2)	39(2)	-1(2)	14(2)	9(2)
C(5)	45(2)	43(2)	43(2)	15(2)	11(2)	6(2)
C(6)	55(2)	30(2)	38(2)	6(2)	10(2)	2(2)
C(7)	45(2)	31(2)	33(2)	5(2)	10(2)	6(2)
C(8)	48(2)	26(2)	42(2)	4(2)	14(2)	5(2)
C(9)	61(2)	37(2)	39(2)	0(2)	18(2)	-1(2)
C(10)	51(2)	75(3)	69(3)	5(3)	2(2)	9(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 170526e.

	x	y	z	U(eq)
H(3)	5976	6494	150	54
H(4)	7998	8969	7	55
H(6)	6510	13101	1228	49
H(8)	3312	11783	1438	46
H(9A)	3489	10419	2356	55
H(9B)	4972	11781	2214	55
H(10A)	428	9992	1317	98
H(10B)	-428	7988	1614	98
H(10C)	322	7587	1030	98

Table 6. Torsion angles [deg] for 170526e.

C(1)-N(1)-O(2)-C(10)	-91.5(4)
C(8)-N(1)-O(2)-C(10)	102.7(4)
O(2)-N(1)-C(1)-O(1)	7.5(6)
C(8)-N(1)-C(1)-O(1)	173.8(4)
O(2)-N(1)-C(1)-C(2)	-173.1(3)
C(8)-N(1)-C(1)-C(2)	-6.9(4)
O(1)-C(1)-C(2)-C(3)	4.1(7)
N(1)-C(1)-C(2)-C(3)	-175.2(4)
O(1)-C(1)-C(2)-C(7)	-177.0(4)
N(1)-C(1)-C(2)-C(7)	3.7(4)
C(7)-C(2)-C(3)-C(4)	0.7(5)
C(1)-C(2)-C(3)-C(4)	179.6(4)
C(2)-C(3)-C(4)-C(5)	-0.8(6)
C(3)-C(4)-C(5)-C(6)	0.6(6)
C(3)-C(4)-C(5)-Br(1)	179.3(3)
C(4)-C(5)-C(6)-C(7)	-0.3(6)
Br(1)-C(5)-C(6)-C(7)	-179.0(3)
C(5)-C(6)-C(7)-C(2)	0.1(5)
C(5)-C(6)-C(7)-C(8)	-179.6(4)

C(3)-C(2)-C(7)-C(6)	-0.4(5)
C(1)-C(2)-C(7)-C(6)	-179.4(3)
C(3)-C(2)-C(7)-C(8)	179.4(3)
C(1)-C(2)-C(7)-C(8)	0.4(4)
C(1)-N(1)-C(8)-C(7)	7.0(4)
O(2)-N(1)-C(8)-C(7)	173.5(3)
C(1)-N(1)-C(8)-C(9)	-117.0(4)
O(2)-N(1)-C(8)-C(9)	49.5(4)
C(6)-C(7)-C(8)-N(1)	175.8(4)
C(2)-C(7)-C(8)-N(1)	-4.0(4)
C(6)-C(7)-C(8)-C(9)	-62.1(5)
C(2)-C(7)-C(8)-C(9)	118.2(3)
N(1)-C(8)-C(9)-S(1)	58.7(4)
C(7)-C(8)-C(9)-S(1)	-56.0(4)
O(4)-S(1)-C(9)-C(8)	-59.1(4)
O(3)-S(1)-C(9)-C(8)	72.0(3)
F(1)-S(1)-C(9)-C(8)	-177.0(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 170526e [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

10. References

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[3] D. C. Fabry, J. Zoller, S. Raja, and M. Rueping, *Angew. Chem. Int. Ed.* **2014**, *53*, 10228.