Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Photocatalytic Access to Aromatic Keto Sulfonyl Fluorides from Vinyl Fluorosulfates

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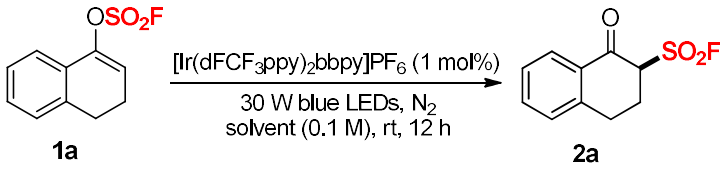
1. General information

All the starting materials were obtained from commercial sources and used without further purification; reactions were carried out in flame-dried glassware under N_2 unless otherwise stated. All solvents were purified and dried according to standard methods prior to use. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on BRUKER 400 MHz spectrometer or JOEL 500 MHz spectrometer in deuterated solvents. ^{1}H NMR chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, coupling constant(s) in Hz, integration). ^{13}C NMR spectra were recorded in deuterated solvent. Chemical shifts are reported in ppm with the internal solvent signal as a standard. ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as the external standard. GC-MS measurements were conducted on a Shimadzu QP2010SE. HRMS were obtained on Waters GCT-TOF. IR measurements were conducted on Nicolet is 50 KBr pelleting method. CPME = Cyclopentyl Methyl Ether, EA = Ethyl Acetate, DCE = 1,2-Dichloroethane.

2. Optimization details

2.1 Optimization of solvents

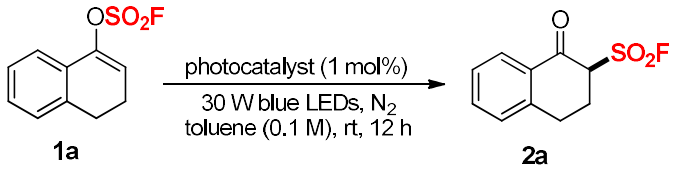


1a 2a

entry[a]	solvent	**2a/1a** (%)[b]
1	Et_2O	6/69
2	THF	18/54
3	DMF	<5/51
4	DCE	<5/69
5	CH_3CN	6/45
6	2-methyl tetrahydrofuran	15/12
7	EA	33/36
8	CPME	6/75
9	EtOH	<5/18
10	DCM	9/60
11	toluene	30/63
12	benzene	<5/66
13	CF_3Ph	<5/48
14	cyclohexane	<5/93
15	1,4-dioxane	21/30
16	H_2O	<5/90
17	toluene:EA (3:1)	21/18
18	toluene:DCM (3:1)	24/18
19	toluene:CH_3CN (3:1)	15/36
20	toluene:acetone (3:1)	21/21

[a]*Reaction conditions*: **1a** (0.2 mmol) and [Ir(dFCF$_3$ppy)$_2$bbpy]PF$_6$ (0.002 mmol, 1 mol%) in solvent (2 mL) irradiated by 30 W blue LEDs for 12 h at room temperature under N_2. [b] Determined by crude ^{19}F NMR analysis with trifluoromethoxybenzene as the internal standard.

2.2 Optimization of photocatalysts



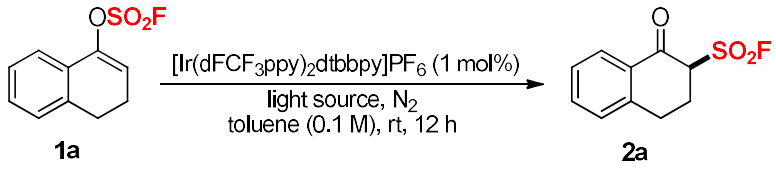
1a 2a

entry[a]	photocatalyst	**2a/1a** (%)[b]
1	[Ir(dFCF$_3$ppy)$_2$bbpy]PF$_6$	30/63
2	*fac*-Ir(ppy)$_3$	<5/93
3	[Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$	48/21

4	$[Ir(ppy)_2dtbbpy]PF_6$	6/75
5	$[Ir(bbpy)_3]PF_6$	6/81
6	$[Ir(dFppy)_2ppy]PF_6$	12/69
7	$[Ir(dFCF_3ppy)_2phen]PF_6$	9/60
8	$[Ru(bpy)_3]Cl_2$	<5/96
9	$[Rh(COD)Cl]_2$	<5/93
10	Eosin Y-Na_2	<5/98
11	4-CzIPN	21/60
12	Eosin B	<5/96
13	9-fluorenone	33/60
14	fluorescein	<5/99

[a]*Reaction conditions*: **1a** (0.2 mmol) and photocatalyst (0.002 mmol, 1 mol%) in toluene (2 mL) irradiated by 30 W blue LEDs for 12 h at room temperature under N_2. [b]Determined by crude ^{19}F NMR analysis with trifluoromethoxybenzene as the internal standard.

2.3 Optimization of light sources

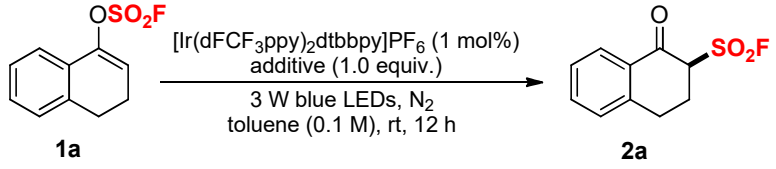


1a **2a**

entry[a]	light source	**2a/1a** (%)[b]
1	30 W blue LEDs	48/21
2	30 W green LEDs	<5/96
3	30 W white LEDs	24/36
4	3 W blue LEDs	48/39

[a]*Reaction conditions*: **1a** (0.2 mmol) and $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (0.002 mmol, 1 mol%) in toluene (2 mL) irradiated by light for 12 h at room temperature under N_2. [b]Determined by crude ^{19}F NMR analysis with trifluoromethoxybenzene as the internal standard.

2.4 Optimization of additives



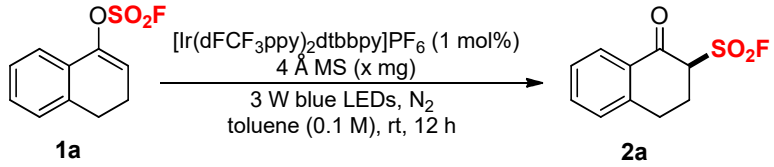
1a **2a**

entry[a]	additive	**2a/1a** (%)[b]
1	Na_2CO_3	78/<5
2	K_2CO_3	51/24
3	Cs_2CO_3	<5/72
4	Na_2HPO_4	63/<5
5	Li_2CO_3	69/<5

6	Li_3PO_4	<5/72
7	$NaHCO_3$	48/<5
8	4 Å MS (88 mg)	81 (78)[c]/9
9	Et_3N	<5/99
10	DBN	<5/96
11	$LiNO_3$	6/75
12	KNO_3	<5/84
13	$KHCO_3$	<5/66
14[d]	Na_2CO_3 and 4 Å MS	78/<5

[a]*Reaction conditions*: **1a** (0.2 mmol), [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$ (0.002 mmol, 1 mol%) and additive (0.2 mmol, 1.0 equiv.) in toluene (2 mL) irradiated by 3 W blue LEDs for 12 h at room temperature under N_2. [b]Determined by crude ^{19}F NMR analysis with trifluoromethoxybenzene as the internal standard. [c]Isolated yield was given in parentheses. [d]Na_2CO_3 (10 mg) and 4 Å MS (44 mg) were added as additives.

2.5 Optimization of the amount of 4 Å MS

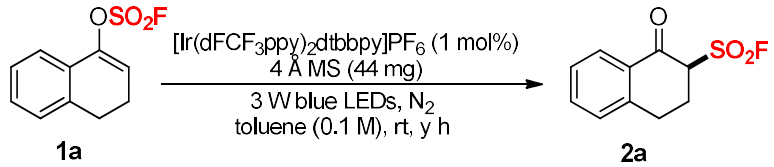


1a **2a**

entry[a]	x	**2a**/**1a** (%)[b]
1	22	60/27
2	44	84/<5
3	88	81/9
4	132	72/<5

[a]*Reaction conditions*: **1a** (0.2 mmol), [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$ (0.002 mmol, 1 mol%) and 4 Å MS in toluene (2 mL) irradiated by 3 W blue LEDs for 12 h at room temperature under N_2. [b]Determined by crude ^{19}F NMR analysis with trifluoromethoxybenzene as the internal standard. [c]Isolated yield was given in parentheses.

2.6 Optimization of reaction time



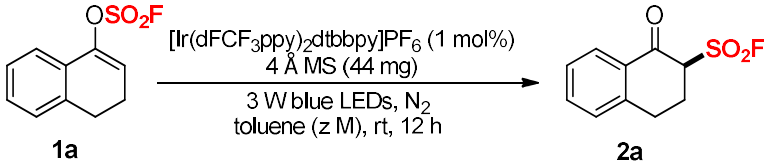
1a **2a**

entry[a]	y	**2a**/**1a** (%)[b]
1	3	24/72
2	6	45/36
3	9	57/29

4	12	84 (81)[c]/<5
5	15	78/<5

[a]*Reaction conditions*: **1a** (0.2 mmol), [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$ (0.002 mmol, 1 mol%) and 4 Å MS (44 mg) in toluene (2 mL) irradiated by 3 W blue LEDs at room temperature under N_2. [b]Determined by crude ^{19}F NMR analysis with trifluoromethoxybenzene as the internal standard. [c]Isolated yield was given in parentheses.

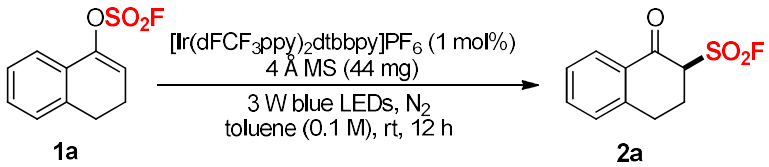
2.7 Optimization of reaction concentration



entry[a]	z	**2a/1a** (%)[b]
1	0.05	72/<5
2	0.1	84 (81)[c]/<5
3	0.2	75/<5

[a]*Reaction conditions*: **1a** (0.2 mmol), [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$ (0.002 mmol, 1 mol%) and 4 Å MS (44 mg) in toluene irradiated by 3 W blue LEDs at room temperature for 12 h under N_2. [b]Determined by crude ^{19}F NMR analysis with trifluoromethoxybenzene as the internal standard. [c]Isolated yield was given in parentheses.

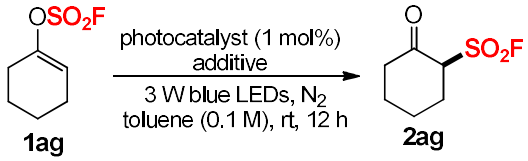
2.8 Control experiments



entry[a]	derivation from the standard conditions	**2a/1a** (%)[b]
1	none	84 (81)[c]/<5
2	in dark	<5/100
3	in the air	<5/84
4	without photocatalyst	<5/100
5	no additive	45/39
6	10 mol% H_2O was added	27/6

[a]*Reaction conditions*: **1a** (0.2 mmol), [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$ (0.002 mmol, 1 mol%) and 4 Å MS (44 mg) in toluene (2 mL) irradiated by 3 W blue LEDs at room temperature for 12 h under N_2. [b]Determined by crude ^{19}F NMR analysis with trifluoromethoxybenzene as the internal standard. [c]Isolated yield was given in parentheses.

2.9 Optimizations of aliphatic substrate **1ag**

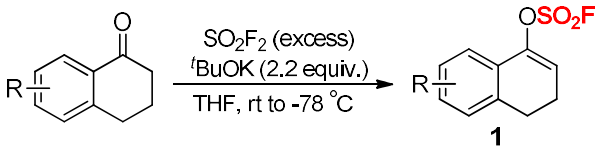


entry[a]	photocatalyst	additive	**1ag/2ag** (%)[b]
1	$[Ir(dFCF_3ppy)_2bbpy]PF_6$	--	<5/100
2	*fac*-$Ir(ppy)_3$	--	<5/100
3	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$	--	<5/100
4	$[Ir(ppy)_2dtbbpy]PF_6$	--	<5/100
5	$[Ru(bpy)_3]Cl_2$	--	<5/100
6	$[Rh(COD)Cl]_2$	--	<5/100
7	9-fluorenone	--	<5/100
8	4-CzIPN	--	<5/100
9	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$	4 Å MS (44 mg)	<5/100
10	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$	Na_2CO_3 (1.0 equiv)	<5/100
11	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$	O_2 (air)	<5/100
12	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$	DDQ (10 mol%)	<5/100
13[c]	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$	--	<5/100

[a]*Reaction conditions*: **1ag** (0.2 mmol) and photocatalyst (0.002 mmol, 1 mol%) in toluene (2 mL) irradiated by 3 W blue LEDs for 12 h at room temperature under N_2. [b]Determined by crude ^{19}F NMR analysis with trifluoromethoxybenzene as the internal standard. [c]Reaction at 80 °C.

3. Synthesis of **1a-1ak**

3.1 General procedure A: synthesis of alkenyl fluorosulfonates[1] (**1a-1aa**, **1ad** and **1af-1ak**)



A flame-dried 25 mL round-bottom flask was equipped with a stirring bar, 3 Å MS, ^{t}BuOK (246 mg, 2.2 mmol, 2.2 equiv.) and ketone[2] (1.0 mmol, 1.0 equiv.). Anhydrous THF (10 mL, 0.1 M) was added and the mixture was stirred at room temperature for 10 mins. Then the reaction was cooled to -78 °C and evacuated until the solvent began boiling. SO_2F_2 gas (approx. 25 mL in size) was introduced with a balloon, and the reaction system was kept stirring at -78 °C for 1.5 h and then warmed

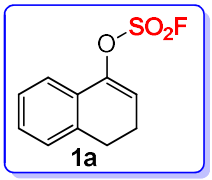
to room temperature. After that, the molecular sieves were removed by filtration and the filtrate was diluted with distilled water (5 mL). The mixture was then extracted with EA (5 mL × 3), and combined organic layers were washed with brine (5 mL) and dried with Na_2SO_4. The residue was concentrated under vacuum and purified by flash column chromatography on silica gel.

3.2 General procedure B: synthesis of alkenyl fluorosulfonates[1] (**1ab**, **1ac** and **1ae**)

To a flame-dried 25 mL round-bottom flask equipped with a stirring bar, anhydrous THF (10 mL, 0.1 M) and ketone[2] (1.0 mmol, 1.0 equiv.) were added. The mixture was cooled to -78 °C, and LDA (1.2 mmol, 1.2 equiv.) was added dropwise over 5 mins. The headspace was evacuated until THF began boiling, and a balloon containing SO_2F_2 gas (approx. 25 mL in size) was introduced. The reaction was then warmed up to 0 °C and stirred for 1 h. Then, the reaction was quenched with sat. NH_4Cl (15 mL) and extracted with EtOAc (5 mL × 3). The combined organic layers were washed with brine (5 mL) and dried over Na_2SO_4. The residue was concentrated under vacuum and purified by flash column chromatography on silica gel.

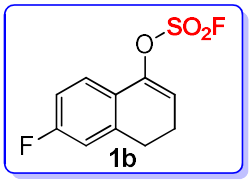
3.3 Characterization of **1a-1ak**

3,4-Dihydronaphthalen-1-yl sulfofluoridate (**1a**)[1]



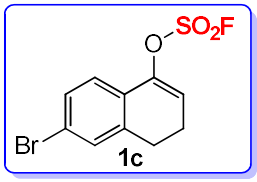
According to general procedure A with 3,4-dihydronaphthalen-1(*2H*)-one, **1a** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 80% yield (182 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.17 (m, 4H), 6.08 (t, *J* = 4.6Hz, 1H), 2.88 (t, *J* = 8.2 Hz, 2H), 2.52 (td, *J* = 8.2, 4.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.1, 136.4, 129.4, 127.9, 127.9, 127.0, 121.2, 117.6, 26.8, 22.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.42 (s); HRMS (ESI) calcd. for $C_{10}H_{10}FO_3S^+$ $[M+H]^+$: 229.0329, found: 229.0330; IR (neat) ν_{max} (cm^{-1}) = 1446, 1264, 1233, 1016, 923, 735, 703, 593.

6-Fluoro-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1b**)



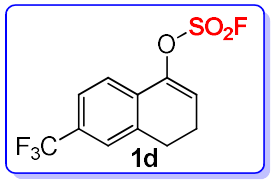
According to general procedure A with 6-fluoro-3,4-dihydronaphthalen-1(*2H*)-one, **1b** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 67% yield (165 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 8.5, 5.5 Hz, 1H), 6.96-6.90 (m, 2H), 6.05 (dt, *J* = 4.6, 2.4 Hz, 1H), 2.87 (t, *J* = 8.2 Hz, 2H), 2.52 (td, *J* = 8.2, 4.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1 (d, *J* = 249.9 Hz), 146.5, 139.2 (d, *J* = 8.0 Hz), 124.3 (d, *J* = 3.0 Hz), 123.2 (d, *J* = 8.7 Hz), 116.7, 115.5 (d, *J* = 22.4 Hz), 113.7 (d, *J* = 22.0 Hz), 27.1, 22.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.41 (s), -111.08 (dd, *J* = 14.3, 8.4 Hz); HRMS (ESI) calcd. for $C_{10}H_9F_2O_3S^+$ $[M+H]^+$: 247.0235, found: 247.0240; IR (neat) ν_{max} (cm^{-1}) = 1495, 1445, 1231, 1062, 1017, 922, 797, 560.

6-Bromo-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1c**)



According to general procedure A with 6-bromo-3,4-dihydronaphthalen-1(*2H*)-one, **1c** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 69% yield (211 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.33-7.32 (m, 1H), 7.19 (d, *J* = 8.3 Hz, 1H), 6.11 (td, *J* = 4.8, 1.5 Hz, 1H), 2.84 (t, *J* = 8.2 Hz, 2H), 2.50 (td, *J* = 8.2, 4.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.4, 138.4, 131.0, 130.1, 127.0, 123.3, 122.8, 118.2, 26.6, 22.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.49 (s); HRMS (ESI) calcd. for $C_{10}H_9BrFO_3S^+$ $[M+H]^+$: 306.9434, found: 306.9438; IR (neat) ν_{max} (cm^{-1}) = 1445, 1232, 1210, 1060, 1018, 911, 793, 570.

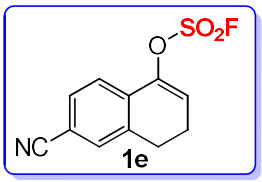
6-(Trifluoromethyl)-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1d**)



According to general procedure A with 6-(trifluoromethyl)-3,4-dihydronaphthalen-1(*2H*)-one, **1d** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 83% yield (246 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54-7.52 (m, 1H), 7.46-7.44 (m, 2H), 6.24 (td, *J* = 4.8, 1.4 Hz, 1H), 2.96 (t, *J* = 8.3 Hz, 2H), 2.59 (td, *J* = 8.3, 4.8 Hz, 2H); ^{13}C NMR (126 MHz,

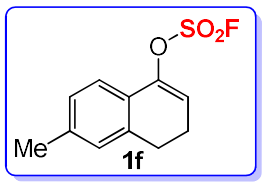
$CDCl_3$) δ 146.1, 137.1, 131.2, 131.2 (q, J = 32.5 Hz), 124.8 (q, J = 3.7 Hz), 124.2 (q, J = 4.0 Hz), 123.9 (q, J = 272.2 Hz), 121.6, 120.4, 26.7, 22.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.54 (s), -62.76 (s); HRMS (ESI) calcd. for $C_{11}H_7F_4O_3S^-$ $[M-H]^-$: 295.0058, found: 295.0062; IR (neat) ν_{max} (cm^{-1}) = 1449, 1331, 1234, 1124, 1017, 921, 734, 541.

6-Cyano-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1e**)



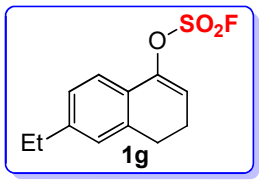
According to general procedure A with 5-oxo-5,6,7,8-tetrahydronaphthalene-2-carbonitrile, **1e** was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate (10 : 1) as eluent and obtained in 57% yield (144 mg, colorless oil). ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, J = 8.0, 1.4 Hz, 1H), 7.48 (s, 1H), 7.43 (d, J = 8.0 Hz, 1H), 6.32 (td, J = 4.8, 1.3 Hz, 1H), 2.95 (t, J = 8.3 Hz, 2H), 2.61 (td, J = 8.3, 4.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.4, 137.2, 131.9, 131.0, 131.0, 121.8, 121.6, 118.3, 112.5, 26.1, 21.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.68 (s); HRMS (ESI) calcd. for $C_{11}H_9FNO_3S^+$ $[M+H]^+$: 254.0282, found: 254.0273; IR (neat) ν_{max} (cm^{-1}) = 2230, 1449, 1264, 1026, 912, 732, 702, 543.

6-Methyl-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1f**)



According to general procedure A with 6-methyl-3,4-dihydronaphthalen-1(*2H*)-one, **1f** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 67% yield (162 mg, colorless oil). ^1H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, J = 7.9 Hz, 1H), 7.03 (d, J = 7.7 Hz, 1H), 6.97 (s, 1H), 5.98 (td, J = 4.8, 1.5 Hz, 1H), 2.79 (t, J = 8.2 Hz, 2H), 2.45 (td, J = 8.2, 4.8 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.4, 139.6, 136.4, 128.9, 127.5, 125.3, 121.2, 116.4, 27.0, 22.3, 21.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.30 (s); HRMS (ESI) calcd. for $C_{11}H_{12}FO_3S^+$ $[M+H]^+$: 243.0486, found: 243.0491; IR (neat) ν_{max} (cm^{-1}) = 1449, 1224, 1162, 1049, 866, 757, 617, 535.

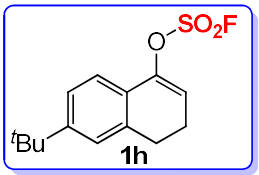
6-Ethyl-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1g**)



According to general procedure A with 6-ethyl-3,4-dihydronaphthalen-1(*2H*)-one, **1g** was purified by

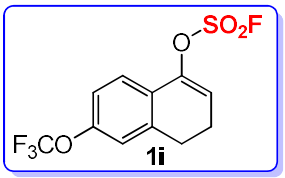
flash column chromatography on silica gel using petroleum ether as eluent and obtained in 76% yield (195 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.02 (s, 1H), 6.00 (td, *J* = 4.7, 1.5 Hz, 1H), 2.84 (t, *J* = 8.2 Hz, 2H), 2.62 (q, *J* = 7.6 Hz, 2H), 2.49 (td, *J* = 7.8, 4.8 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.4, 145.9, 136.5, 127.7, 126.4, 125.6, 121.3, 116.4, 28.8, 27.0, 22.3, 15.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.31 (s); HRMS (ESI) calcd. for $C_{12}H_{14}FO_3S^+$ $[M+H]^+$: 257.0642, found: 257.0649; IR (neat) ν_{max} (cm^{-1}) = 2854, 1444, 1231, 1214, 1013, 921, 796, 561.

6-(tert-Butyl)-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1h**)



According to general procedure A with 6-(*tert*-butyl)-3,4-dihydronaphthalen-1(2*H*)-one, **1h** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 71% yield (201 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 1.5 Hz, 2H), 7.20 (dt, *J* = 1.4, 0.9 Hz, 1H), 6.01 (td, *J* = 4.8, 1.5 Hz, 1H), 2.86 (t, *J* = 8.2 Hz, 2H), 2.49 (td, *J* = 8.2, 4.8 Hz, 2H), 1.31 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.8, 147.4, 136.1, 125.4, 125.2, 123.8, 121.1, 116.6, 34.9, 31.3, 27.3, 22.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.21 (s); HRMS (ESI) calcd. for $C_{14}H_{18}FO_3S^+$ $[M+H]^+$: 285.0955, found: 285.0960; IR (neat) ν_{max} (cm^{-1}) = 1446, 1214, 1013, 921, 871, 796, 561.

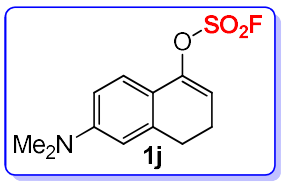
6-(Trifluoromethoxy)-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1i**)



According to general procedure A with 6-(trifluoromethoxy)-3,4-dihydronaphthalen-1(*2H*)-one, **1i** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 38% yield (119 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.5 Hz, 1H), 7.10 (d, *J* = 8.5 Hz, 1H), 7.05 (s, 1H), 6.13 (td, *J* = 4.7, 1.2 Hz, 1H), 2.90 (t, *J* = 8.2 Hz, 2H), 2.55 (td, *J* = 8.2, 4.8 Hz, 2H);^{13}C NMR (126 MHz, $CDCl_3$) δ 149.6 (q, *J* = 1.7 Hz), 146.2, 138.7, 126.6, 122.8, 120.5, 120.5 (q, *J* = 257.8 Hz), 119.1, 118.1, 26.9, 22.0; ^{19}F NMR (471 MHz, $CDCl_3$)

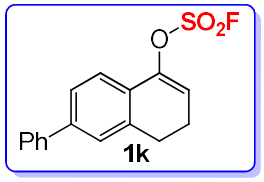
δ 39.42 (s), -57.69 (s); HRMS (ESI) calcd. for $C_{11}H_9F_4O_4S^+$ $[M+H]^+$: 313.0152, found: 313.0158; IR (neat) ν_{max} (cm^{-1}) = 1449, 1263, 1216, 1166, 1018, 733, 703, 556.

6-(Dimethylamino)-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1j**)



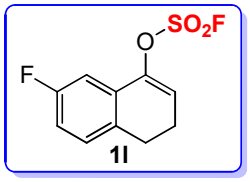
According to general procedure A with 6-(dimethylamino)-3,4-dihydronaphthalen-1(2*H*)-one, **1j** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 67% yield (182 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.3 Hz, 1H), 6.57-6.48 (m, 2H), 5.78 (td, *J* = 4.6, 1.2 Hz, 1H), 2.97 (s, 6H), 2.81 (t, *J* = 8.1 Hz, 2H), 2.45 (td, *J* = 8.1, 4.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.0, 147.8, 138.0, 122.4, 116.4, 111.9, 111.7, 109.8, 40.4, 28.0, 22.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.08; HRMS (ESI) calcd. for $C_{12}H_{15}FNO_3S^+$ $[M+H]^+$: 272.0747, found: 272.0751; IR (neat) ν_{max} (cm^{-1}) = 1609, 1440, 1366, 1227, 1124, 920, 800, 731.

6-Phenyl-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1k**)



According to general procedure A with 6-phenyl-3,4-dihydronaphthalen-1(*2H*)-one, **1k** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 51% yield (155 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.48 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.46-7.41 (m, 4H), 7.38-7.34 (m, 1H), 6.10 (td, *J* = 4.8, 1.4 Hz, 1H), 2.94 (t, *J* = 8.2 Hz, 2H), 2.56 (td, *J* = 8.2, 4.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.1, 142.3, 140.4, 136.9, 129.0, 127.9, 127.2, 127.0, 126.8, 125.7, 121.8, 117.6, 27.1, 22.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.44 (s); HRMS (ESI) calcd. for $C_{16}H_{14}FO_3S^+$ $[M+H]^+$: 305.0642, found: 305.0649; IR (neat) ν_{max} (cm^{-1}) = 1445, 1232, 1015, 925, 797, 731, 698, 573.

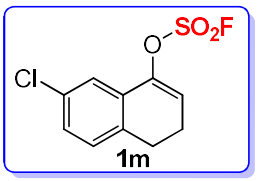
7-Fluoro-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1l**)



According to general procedure A with 7-fluoro-3,4-dihydronaphthalen-1(*2H*)-one, **1l** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 83% yield (204 mg, colorless oil). ^{1}H NMR (500 MHz,

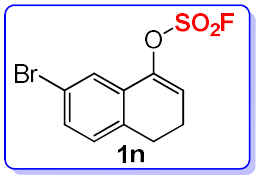
$CDCl_3$) δ 7.14 (dd, *J* = 8.3, 5.4 Hz, 1H), 7.05 (dd, *J* = 9.2, 2.6 Hz, 1H), 6.95 (td, *J* = 8.4, 2.6 Hz, 1H), 6.16 (t, *J* = 4.8, 1H), 2.84 (t, *J* = 8.2 Hz, 2H), 2.53 (td, *J* = 8.2, 4.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9 (d, *J* = 244.8 Hz), 146.2 (d, *J* = 2.5 Hz), 131.8 (d, *J* = 3.3 Hz), 129.6 (d, *J* = 8.2 Hz), 129.4 (d, *J* = 7.9 Hz), 119.0, 115.9 (d, *J* = 21.4 Hz), 108.8 (d, *J* = 24.7 Hz), 26.1, 22.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.50 (s), -114.77 (dd, *J* = 14.5, 8.6 Hz); HRMS (ESI) calcd. for $C_{10}H_9F_2O_3S^+$ $[M+H]^+$: 247.0235, found: 247.0242; IR (neat) ν_{max} (cm^{-1}) = 1584, 1490, 1447, 1229, 1023, 915, 798, 547.

7-Chloro-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1m**)



According to general procedure A with 7-chloro-3,4-dihydronaphthalen-1(*2H*)-one, **1m** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 67% yield (175 mg, colorless oil). ^1H NMR (500 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.27 (d, *J* = 7.4 Hz, 1H), 7.21-7.17 (m, 1H), 6.14 (td, *J* = 4.8, 1.5 Hz, 1H), 3.00 (t, *J* = 8.4 Hz, 2H), 2.6 (td, *J* = 8.4, 4.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.0, 134.6, 132.9, 129.5, 129.3, 129.2, 121.4, 119.0, 26.3, 22.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.52 (s); HRMS (ESI) calcd. for $C_{10}H_7ClFO_3S^-$ $[M-H]^-$: 260.9794, found: 260.9797; IR (neat) ν_{max} (cm^{-1}) = 1449, 1264, 1233, 1023, 923, 735, 591.

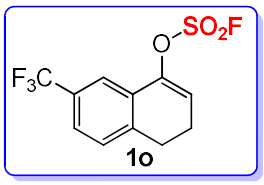
7-Bromo-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1n**)



According to general procedure A with 7-bromo-3,4-dihydronaphthalen-1(*2H*)-one, **1n** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 53% yield (162 mg, colorless oil). ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 1.8 Hz, 1H), 7.36 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.13 (td, *J* = 4.8, 1.4 Hz, 1H), 2.81 (t, *J* = 8.2 Hz, 2H), 2.51 (td, *J* = 8.2, 4.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.8, 135.1, 132.1, 129.7, 129.5, 124.1, 120.6, 119.0, 26.3, 22.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.67 (s); HRMS (ESI) calcd. for

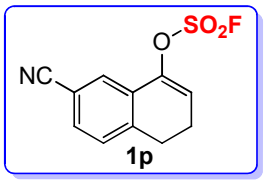
$C_{10}H_9BrFO_3S^+$ $[M+H]^+$: 306.9434, found: 306.9440; IR (n eat) ν_{max} (cm^{-1}) = 1449, 1264, 1234, 1022, 925, 735, 703, 572.

7-(Trifluoromethyl)-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1o**)



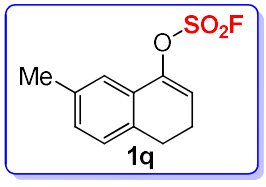
According to general procedure A with 7-(trifluoromethyl)-3,4-dihydronaphthalen-1(*2H*)-one, **1o** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 72% yield (213 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 6.22 (td, *J* = 4.8, 1.5 Hz, 1H), 2.95 (t, *J* = 8.2 Hz, 2H), 2.58 (td, *J* = 8.2, 4.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.0, 140.2, 129.7 (q, *J* = 32.9 Hz), 128.8, 128.5, 126.1 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.1 Hz), 119.4, 118.1 (q, *J* = 10.9 Hz), 26.8, 21.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.61 (s), -62.60 (s); HRMS (ESI) calcd. for $C_{11}H_7F_4O_3S^-$ $[M-H]^-$: 295.0058, found: 295.0061; IR (neat) ν_{max} (cm^{-1}) = 1449, 1321, 1234, 1124, 1075, 921, 734, 541.

7-Cyano-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1p**)



According to general procedure A with 8-oxo-5,6,7,8-tetrahydronaphthalene-2-carbonitrile, **1p** was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate (10 : 1) as eluent and obtained in 47% yield (119 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.57 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.31 (d, *J* = 7.8 Hz, 1H), 6.25 (td, *J* = 4.7, 1.2 Hz, 1H), 2.97 (t, *J* = 8.2 Hz, 2H), 2.60 (td, *J* = 8.2, 4.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.1, 141.5, 132.8, 129.2, 128.9, 124.4, 120.2, 118.3, 111.1, 26.8, 21.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.68 (s); HRMS (ESI) calcd. for $C_{11}H_9FNO_3S^+$ $[M+H]^+$: 254.0282, found: 254.0275; IR (neat) ν_{max} (cm^{-1}) = 2229, 1446, 1233, 1147, 1026, 912, 798, 629.

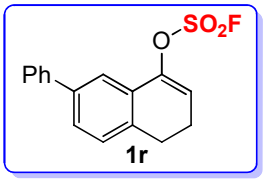
7-Methyl-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1q**)



According to general procedure A with 3,4-dihydronaphthalen-1(*2H*)-one, **1q** was purified by flash column chromatography on silica gel using petroleum ether as

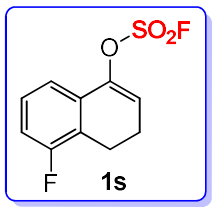
eluent and obtained in 73% yield (177 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (s, 1H), 7.06-7.03 (m, 2H), 6.04 (td, *J* = 4.8, 1.6 Hz, 1H), 2.79 (t, *J* = 8.2 Hz, 2H), 2.46 (td, *J* = 8.2, 4.8 Hz, 2H), 2.32 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.3, 136.7, 133.4, 130.0, 127.8, 127.8, 121.8, 117.4, 26.4, 22.4, 21.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.45 (s); HRMS (ESI) calcd. for $C_{11}H_{12}FO_3S^+$ $[M+H]^+$: 243.0486, found: 243.0493; IR (neat) ν_{max} (cm^{-1}) = 1443, 1225, 1149, 1022, 912, 792, 617, 547.

7-Phenyl-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1r**)



According to general procedure A with 7-methyl-3,4-dihydronaphthalen-1(*2H*)-one, **1r** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 79% yield (240 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 6.8 Hz, 3H), 7.47-7.41 (m, 3H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 6.11 (t, *J* = 4.5 Hz, 1H), 2.88 (t, *J* = 8.2 Hz, 2H), 2.51 (td, *J* = 8.2, 4.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.1, 140.5, 140.3, 135.4, 129.0, 128.4, 128.4, 128.0, 127.7, 127.1, 119.9, 118.1, 26.6, 22.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.61 (s); HRMS (ESI) calcd. for $C_{16}H_{14}FO_3S^+$ $[M+H]^+$: 305.0642, found: 305.0641; IR (neat) ν_{max} (cm^{-1}) = 1445, 1232, 1015, 925, 797, 734, 698, 573.

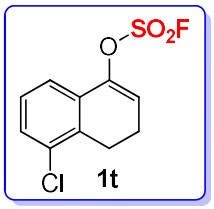
5-Fluoro-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1s**)



According to general procedure A with 5-fluoro-3,4-dihydronaphthalen-1(*2H*)-one, **1s** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 79% yield (194 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (td, *J* = 8.3, 5.8 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 8.6 Hz, 1H), 6.13 (td, *J* = 4.8, 1.5 Hz, 1H), 2.90 (t, *J* = 8.3 Hz, 2H), 2.54 (td, *J* = 8.3, 4.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7 (d, *J* = 244.8 Hz), 146.3 (d, *J* = 5.4 Hz), 129.9 (d, *J* = 5.7 Hz), 127.9 (d, *J* = 8.6 Hz), 122.8 (d, *J* = 19.0 Hz), 118.6, 117.1 (d, *J* = 3.1 Hz), 116.6 (d, *J* = 22.5 Hz), 21.6, 18.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.47 (s), -118.16 (dd, *J* = 8.9, 5.7 Hz); HRMS (ESI) calcd. for

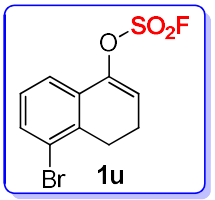
$C_{10}H_9F_2O_3S^+$ $[M+H]^+$: 247.0235, found: 247.0244; IR (neat) ν_{max} (cm^{-1}) = 1446, 1342, 1229, 1102, 949, 911, 727, 576.

5-Chloro-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1t**)



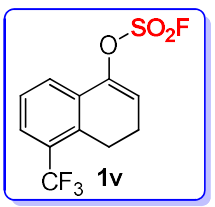
According to general procedure A with 5-chloro-3,4-dihydronaphthalen-1(*2H*)-one, **1t** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 88% yield (231 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.9 Hz, 1H), 6.14 (td, *J* = 4.8, 1.5 Hz, 1H), 3.00 (t, *J* = 8.4 Hz, 1H), 2.54 (td, *J* = 8.4, 4.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.3, 134.0, 133.5, 130.4, 129.8, 127.7, 119.9, 118.5, 23.5, 21.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.52 (s); HRMS (ESI) calcd. for $C_{10}H_9ClFO_3S^+$ $[M+H]^+$: 262.9939, found: 262.9947; IR (neat) ν_{max} (cm^{-1}) = 1446, 1264, 1232, 936, 914, 731, 703, 569.

5-Bromo-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1u**)



According to general procedure A with 5-bromo-3,4-dihydronaphthalen-1(*2H*)-one, **1u** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 64% yield (196 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.1 Hz, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 7.12 (t, *J* = 7.9 Hz, 1H), 6.14 (td, *J* = 4.8, 1.4 Hz, 1H), 3.01 (t, *J* = 8.3 Hz, 2H), 2.56 (td, *J* = 8.4, 4.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.3, 135.7, 133.6, 129.9, 128.1, 124.0, 120.5, 118.4, 26.5, 21.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.54 (s); HRMS (ESI) calcd. for $C_{10}H_9BrFO_3S^+$ $[M+H]^+$: 306.9268, found: 306.9270; IR (neat) ν_{max} (cm^{-1}) = 1447, 1264, 1230, 1143, 912, 729, 703, 565.

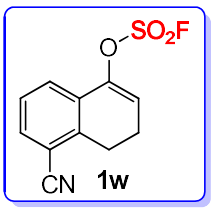
5-(Trifluoromethyl)-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1v**)



According to general procedure A with 5-(trifluoromethyl)-3,4-dihydronaphthalen-1(*2H*)-one, **1v** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 75% yield (222 mg,

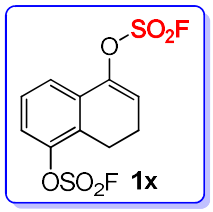
colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 6.22 (td, *J* = 4.8, 1.2 Hz, 1H), 3.05 (t, *J* = 8.2 Hz, 2H), 2.56 (td, *J* = 8.2, 4.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.0, 135.2 (q, *J* = 1.7 Hz), 129.7, 128.8 (q, *J* = 30.3, Hz), 126.9, 126.6 (q, *J* = 5.6 Hz), 124.7, 124.1 (q, *J* = 273.9 Hz) 119.1, 23.3 (q, *J* = 2.2 Hz), 21.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.54 (s), -60.49 (s); HRMS (ESI) calcd. for $C_{11}H_7F_4O_3S^-$ $[M-H]^-$: 295.0058, found: 295.0061; IR (neat) ν_{max} (cm^{-1}) = 1449, 1331, 1234, 1124, 1075, 1017, 921, 734.

5-Cyano-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1w**)



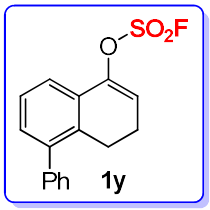
According to general procedure A with 5-oxo-5,6,7,8-tetrahydronaphthalene-1-carbonitrile, **1w** was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate (10 : 1) as eluent and obtained in 44% yield (113 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 6.25 (td, *J* = 4.8, 1.5 Hz, 1H), 3.15 (t, *J* = 8.3 Hz, 2H), 2.64 (td, *J* = 8.3, 4.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.4, 140.1, 132.8, 129.2, 127.6, 125.1, 119.7, 117.0, 112.3, 25.1, 21.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.66 (s); HRMS (ESI) calcd. for $C_{11}H_9FNO_3S^+$ $[M+H]^+$: 254.0282, found: 254.0273; IR (neat) ν_{max} (cm^{-1}) = 2228, 1447, 1226, 1095, 946, 911, 794, 570.

3,4-Dihydronaphthalene-1,5-diyl disulfofluoridate (**1x**)



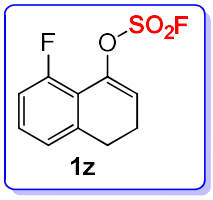
According to general procedure A with 5-hydroxy-3,4-dihydronaphthalen-1(2*H*)-one, **1x** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 43% yield (140 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.30 (m, 3H), 6.24 (td, *J* = 4.8, 1.3 Hz, 1H), 2.99 (t, *J* = 8.3 Hz, 2H), 2.60 (td, *J* = 8.3, 4.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.5, 145.6, 130.7, 128.9, 128.5, 122.1, 121.6, 119.7, 21.3, 20.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.72 (s), 39.30 (s); HRMS (ESI) calcd. for $C_{10}H_9F_2O_6S_2^+$ $[M+H]^+$: 326.9803, found: 326.9801; IR (neat) ν_{max} (cm^{-1}) = 1711, 1444, 1231, 1209, 1012, 912, 797, 708.

5-Phenyl-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1y**)



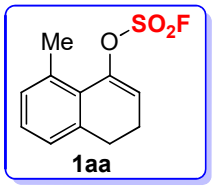
According to general procedure A with 5-phenyl-3,4-dihydronaphthalen-1(*2H*)-one, **1y** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 57% yield (173 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.34 (m, 4H), 7.37-7.19 (m, 4H), 6.13 (td, *J* = 4.8, 1.3 Hz, 1H), 2.82 (t, *J* = 8.1 Hz, 2H), 2.42 (td, *J* = 8.1, 4.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.4, 141.3, 140.7, 133.7, 131.3, 129.3, 128.4, 128.4, 127.4, 126.5, 120.6, 117.8, 24.4, 22.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.53 (s); HRMS (ESI) calcd. for $C_{16}H_{14}FO_3S^+$ $[M+H]^+$: 305.0642, found: 305.0641; IR (neat) ν_{max} (cm^{-1}) = 1232, 1209, 1015, 925, 797, 734, 698, 573.

8-Fluoro-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1z**)



According to general procedure A with 8-fluoro-3,4-dihydronaphthalen-1(*2H*)-one, **1z** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 39% yield (96 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (td, *J* = 8.0, 5.2 Hz, 1H), 6.98 (d, *J* = 7.4 Hz, 1H), 6.95 (dd, *J* = 11.6, 3.1 Hz, 1H), 6.14 (td, *J* = 4.9, 1.4 Hz, 1H), 2.86 (t, *J* = 8.1 Hz, 2H), 2.48 (td, *J* = 8.1, 5.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.7 (d, *J* = 253.7 Hz), 144.5, 139.4 (d, *J* = 1.6 Hz), 130.6 (d, *J* = 9.1 Hz), 123.7 (d, *J* = 3.3 Hz), 120.7 (d, *J* = 1.4 Hz), 115.8 (d, *J* = 8.7 Hz), 115.4 (d, *J* = 22.7 Hz), 27.3 (d, *J* = 2.5 Hz), 22.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.18 (d, *J* = 9.2 Hz), -(116.62-116.67) (m); HRMS (ESI) calcd. for $C_{10}H_9F_2O_3S^+$ $[M+H]^+$: 247.0235, found: 247.0241; IR (neat) ν_{max} (cm^{-1}) = 1654, 1446, 1232, 1213, 993, 886, 785, 559.

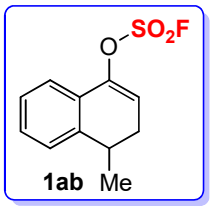
8-Methyl-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1aa**)



According to general procedure A with 8-methyl-3,4-dihydronaphthalen-1(*2H*)-one, **1aa** was purified by flash column chromatography on silica gel using etroleum ether as eluent and obtained in 74% yield (179 mg, colorless oil). ^{1}H NMR

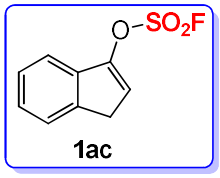
(500 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.4 Hz, 2H), 6.18 (t, *J* = 5.1 Hz, 1H), 2.81 (t, *J* = 7.5 Hz, 2H), 2.49 (s, 3H), 2.40 (td, *J* = 7.4, 2.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.7, 138.5, 133.2, 131.1, 129.0, 127.0, 125.8, 120.3, 28.8, 22.2, 22.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.11 (s); HRMS (ESI) calcd. for $C_{11}H_{12}FO_3S^+$ $[M+H]^+$: 243.0486, found: 243.0491; IR (neat) ν_{max} (cm^{-1}) = 1443, 1225, 1149, 1022, 912, 792, 617, 547.

4-Methyl-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1ab**)



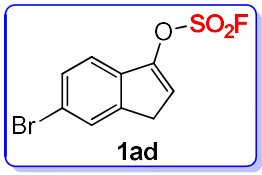
According to general procedure B with 4-methyl-3,4-dihydronaphthalen-1(*2H*)-one, **1ab** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 71% yield (172 mg, colorless oil). ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.7 Hz, 1H), 7.32-7.24 (m, 2H), 7.21 (d, *J* = 7.3 Hz, 1H), 6.03-6.01 (m, 1H), 3.01 (h, *J* = 6.9 Hz, 1H), 2.71-2.64 (m, 1H), 2.31 (ddd, *J* = 17.3, 6.9, 5.4 Hz, 1H), 1.27 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.5, 141.5, 129.7, 127.1, 126.9, 126.8, 121.4, 116.2, 31.6, 30.0, 20.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.49 (s); HRMS (ESI) calcd. for $C_{11}H_{12}FO_3S^+$ $[M+H]^+$: 243.0486, found: 243.0487; IR (neat) ν_{max} (cm^{-1}) = 1702, 1494, 1406, 1203, 1161, 789, 706, 585.

1H-Inden-3-yl sulfofluoridate (**1ac**)



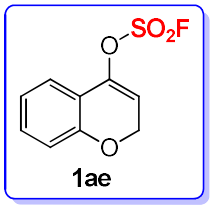
According to general procedure B with 2,3-dihydro-1*H*-inden-1-one **1ac** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 76% yield (163 mg, colorless oil). ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.3 Hz, 1H), 7.44 (d, *J* = 7.1 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.33 (td, *J* = 7.3, 1.2 Hz, 1H), 6.40 (dd, *J* = 3.8, 2.3 Hz, 1H), 3.47 (d, *J* = 2.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 141.4, 136.0, 127.1, 124.6, 118.2, 118.0, 118.0, 34.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ 38.28 (s); HRMS (ESI) calcd. for $C_9H_8FO_3S^+$ $[M+H]^+$: 215.0173, found: 215.0178; IR (neat) ν_{max} (cm^{-1}) = 1449, 1224, 1162, 1049, 868, 807, 757, 535.

6-Bromo-1H-inden-3-yl sulfofluoridate (**1ad**)



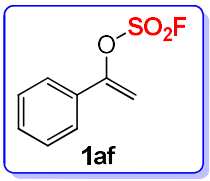
According to general procedure A with 5-bromo-2,3-dihydro-*1H*-inden-1-one, **1ad** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 69% yield (201 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 1.0 Hz, 1H), 7.51 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 6.41 (dd, *J* = 2.0, 1.5 Hz, 1H), 3.47 (d, *J* = 2.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.9, 143.3, 135.1, 130.4, 128.0, 121.5, 119.5, 118.3, 34.8. ^{19}F NMR (471 MHz, $CDCl_3$) δ 38.45 (s); HRMS (ESI) calcd. for $C_9H_5BrFO_3S^-$ [M-H]$^-$: 290.9132, found: 290.9135; IR (neat) ν_{max} (cm^{-1}) = 1465, 1222, 1102, 1049, 886, 807, 757, 556.

2H-Chromen-4-yl sulfofluoridate (**1ae**)



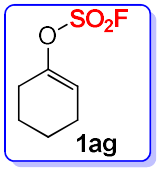
According to general procedure B with chroman-4-one, **1ae** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 67% yield (154 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.22 (m, 2H), 6.96 (td, *J* = 7.6, 1.1 Hz, 1H), 6.84 (d, *J* = 8.1 Hz, 1H), 5.80 (td, *J* = 3.9, 1.4 Hz, 1H), 4.97 (d, *J* = 3.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.2, 143.8, 131.8, 121.9, 121.8, 116.7, 116.4, 109.9, 65.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.99 (s); HRMS (ESI) calcd. for $C_9H_8FO_4S^+$ [M+H]$^+$: 231.0122, found: 231.0123; IR (neat) ν_{max} (cm^{-1}) = 1666, 1446, 1350, 1229, 1189, 1043, 737, 560.

1-Phenylvinyl sulfofluoridate (**1af**)[1]



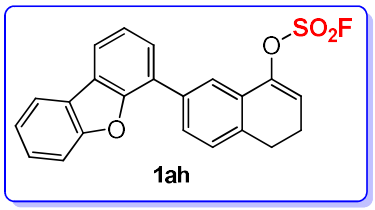
According to general procedure A with acetophenone, **1af** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 45% yield (91 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 1.9 Hz, 1H), 7.54 (d, *J* = 4.3 Hz, 1H), 7.42 (d, *J* = 2.0 Hz, 2H), 7.41 (d, *J* = 1.7 Hz, 1H), 5.64 (d, *J* = 4.1 Hz, 1H), 5.45 (dd, *J* =4.0, 1.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.2, 131.2, 130.5, 129.0, 125.5, 103.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ 40.08.

Cyclohex-1-en-1-yl sulfofluoridate (**1ag**) [1]



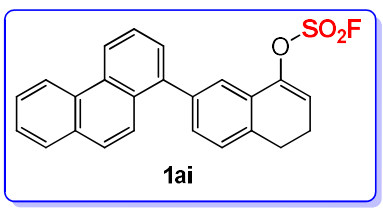
According to general procedure A with cyclohexanone, **1ag** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 71% yield (128 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83-5.81 (m, 1H), 2.35-2.31 (m, 2H), 2.21-2.16 (m, 2H), 1.82-1.77 (m, 2H), 1.63-1.59 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.1, 118.2, 26.4, 23.8, 22.6, 21.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ 38.87.

7-(Dibenzo[b,d]furan-4-yl)-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1ah**)



According to general procedure A with 7-(dibenzo[*b*,*d*]furan-4-yl)-3,4-dihydronaphthalen-1(2*H*)-one, **1ah** was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate (20 : 1) as eluent and obtained in 54% yield (213 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99-7.97 (m, 1H), 7.95-7.93 (m, 2H), 7.81 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.61-7.58 (m, 2H), 7.48-7.44 (m, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.36 (td, *J* = 7.5, 1.0 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 6.17 (td, *J* = 4.7, 1.2 Hz, 1H), 2.96 (t, *J* = 8.2 Hz, 2H), 2.59 (td, *J* = 8.2, 4.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.3, 153.4, 147.2, 135.9, 135.3, 129.6, 128.3, 128.3, 127.5, 126.5, 125.2, 125.0, 124.2, 123.4, 123.0, 121.7, 120.8, 120.1, 118.2, 112.0, 26.7, 22.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.77 (s); HRMS (ESI) calcd. for $C_{22}H_{16}FO_4S^+$ $[M+H]^+$: 395.0748, found: 395.0757; IR (neat) ν_{max} (cm^{-1}) = 1446, 1228, 1189, 1008, 923, 727, 703, 560.

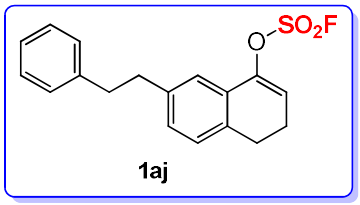
7-(Phenanthren-1-yl)-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1ai**)



According to general procedure A with 7-(phenanthren-3-yl)-3,4-dihydronaphthalen-1(*2H*)-one, **1ai** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 48% yield (194 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (dd, *J* = 3.2, 8.2 Hz, 2H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.62-7.57 (m, 3H), 7.55-7.48 (m, 3H), 7.36 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 6.06

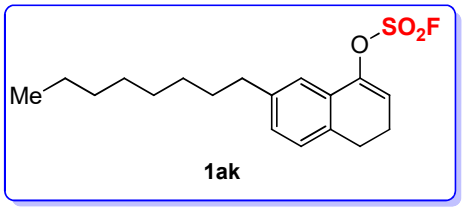
(t, J = 4.5 Hz, 1H), 2.84 (t, J = 8.2 Hz, 2H), 2.45 (td, J = 8.2, 4.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.0, 139.6, 137.9, 135.5, 131.5, 131.0, 130.8, 130.1, 128.8, 128.8, 128.0, 128.0, 127.7, 127.7, 127.0, 126.9, 126.7, 126.7, 123.1, 122.8, 122.6, 118.2, 26.6, 22.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.70 (s); HRMS (ESI) calcd. for $C_{24}H_{15}FO_3S^-$ [M-H]$^-$: 403.0810, found: 403.0821; IR (neat) ν_{max} (cm^{-1}) = 1446, 1264, 1233, 1059, 921, 735, 703, 563.

7-Phenethyl-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1aj**)



According to general procedure A with 7-phenethyl-3,4-dihydronaphthalen-1(*2H*)-one, **1aj** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 61% yield (203 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.26 (m, 2H), 7.23-7.14 (m, 4H), 7.12-7.04 (m, 2H), 6.08 (td, J = 4.8, 1.5 Hz, 1H), 2.91 (s, 4H), 2.84 (t, J = 8.2 Hz, 2H), 2.51 (td, J = 8.2, 4.8 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.3, 141.5, 140.7, 134.0, 129.5, 128.6, 128.5, 128.0, 127.9, 126.1, 121.3, 117.5, 37.9, 37.6, 26.5, 22.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.58 (s); HRMS (ESI) calcd. for $C_{18}H_{16}FO_3S^-$ [M-H]$^-$: 331.0810, found: 331.0812; IR (neat) ν_{max} (cm^{-1}) = 1689, 1447, 1407, 1264, 1205, 731, 701, 579.

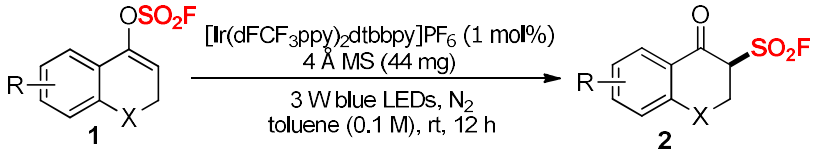
7-Octyl-3,4-dihydronaphthalen-1-yl sulfofluoridate (**1ak**)



According to general procedure A with 7-octyl-3,4-dihydronaphthalen-1(*2H*)-one, **1ak** was purified by flash column chromatography on silica gel using petroleum ether as eluent and obtained in 67% yield (228 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 (s, 1H), 7.07 (d, J = 1.1 Hz, 2H), 6.05 (td, J = 4.8, 1.4 Hz, 1H), 2.82 (t, J = 8.2 Hz, 2H), 2.58 (td, J = 7.8 Hz, 2H), 2.48 (td, J = 8.2, 4.8 Hz, 2H), 1.60-1.56 (m, 2H), 1.32-1.26 (m, 10H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.4, 141.9, 133.6, 129.4, 127.9, 127.8, 121.3, 117.4, 35.8, 32.0, 31.7, 29.6, 29.4, 27.1, 26.6, 22.8, 22.4, 14.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ 39.44 (s); HRMS (ESI) calcd. for $C_{18}H_{26}FO_3S^+$

$[M+H]^+$: 341.1581, found: 341.1589; IR (neat) ν_{max} (cm^{-1}) = 2925, 1446, 1233, 1149, 1022, 913, 795, 548.

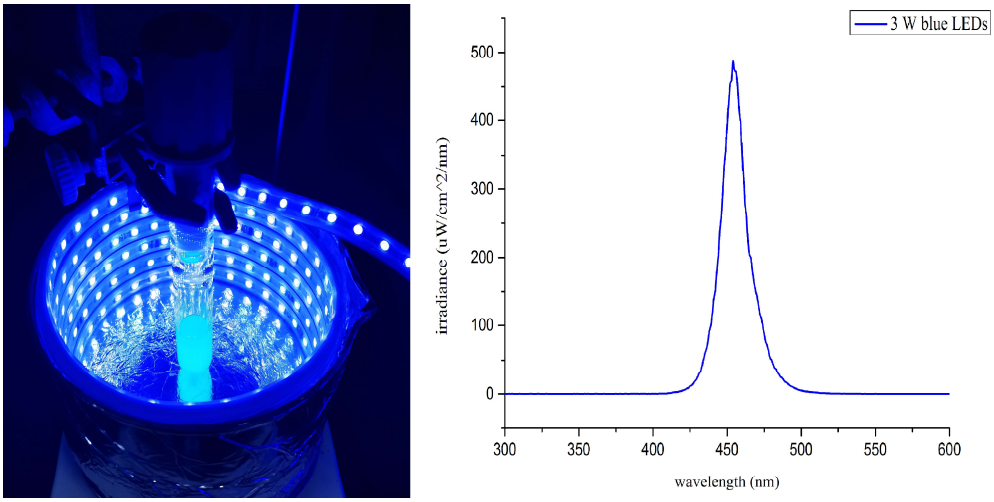
4. General procedure C: synthesis of **2a-2ak**



To a 10 mL sealed tube equipped with a rubber septum and magnetic stirring bar, **1** (0.2 mmol), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (2 mg, 0.002 mmol, 1 mol%) and 4 Å MS (44 mg) were added. The tube was evacuated and backfilled with N_2 for three times, and added with toluene (2.0 mL, 0.1 M). The mixture was stirred and irradiated by 3 W blue LEDs for 12 hours at room temperature. After the reaction complet (monitored by TLC), the crude mixture was purified directly by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) as eluent to give **2**.

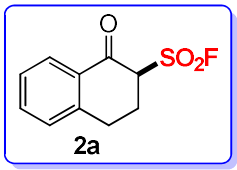
Photoinduced reactor were conducted in circular photo-reactors, which was 3 watts per 30 centimeters. The emission spectra of the blue LEDs were recorded on an Ocean Optics HR4000CG-UVNIR spectrometer. The spectra was normalised to 1.0 at the maximum (453 nm) (Fig. S1).

Fig. S1 photo-reactor and reaction setup.



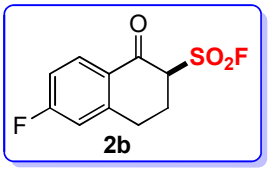
4.1 Characterization of **2a-2ah**

1-Oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2a**)



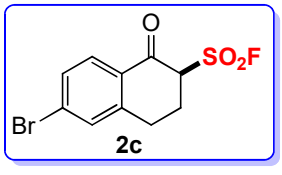
According to general procedure C with **1a**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2a** in 81% yield (37 mg, yellow oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.8 Hz, 1H), 7.59 (td, *J* = 7.6, 1.3 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.7 Hz, 1H), 4.53 (dd, *J* = 9.7, 4.9 Hz, 1H), 3.29 (dt, *J* = 17.2, 5.4 Hz, 1H), 3.14 (ddd, *J* = 17.1, 9.2, 4.8 Hz, 1H), 2.87-2.66 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.4, 142.8, 135.3, 130.9 (d, *J* = 2.7 Hz), 129.1, 128.6, 127.7, 67.7 (d, *J* = 10.9 Hz), 26.9, 25.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.44 (s); HRMS (ESI) calcd. for $C_{10}H_{10}FO_3S^+$ $[M+H]^+$: 229.0329, found: 229.0333; IR (neat) ν_{max} (cm^{-1}) = 1687, 1600, 1404, 1264, 777, 733, 593, 546.

6-Fluoro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2b**)



According to general procedure C with **1b**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2b** in 79% yield (39 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 8.7, 5.9 Hz, 1H), 7.08 (td, *J* = 8.5, 2.2 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 1H), 4.55 (dd, *J* = 9.5, 5.0 Hz, 1H), 3.28 (dt, *J* = 17.2, 5.5 Hz, 1H), 3.14 (ddd, *J* = 17.2, 8.8, 4.8 Hz, 1H), 2.83-2.71 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.0, 166.7 (d, *J* = 259.3 Hz), 146.1 (d, *J* = 9.7 Hz), 131.9 (d, *J* = 10.3 Hz), 127.6 (dd, *J* = 5.0, 2.5 Hz), 115.7 (d, *J* = 13.2 Hz), 115.6 (d, *J* = 12.8 Hz), 67.3 (d, *J* = 11.1 Hz), 26.9, 25.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.80 (s), -100.50 (dd, *J* = 14.6, 8.4 Hz); HRMS (ESI) calcd. for $C_{10}H_9F_2O_3S^+$ $[M+H]^+$: 247.0235, found: 247.0236; IR (neat) ν_{max} (cm^{-1}) = 1687, 1607, 1584, 1405, 1253, 1203, 785, 538.

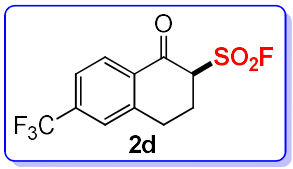
6-Bromo-1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2c**)



According to general procedure C with **1c**: the crude product was purified by flash column chromatography on silica gel

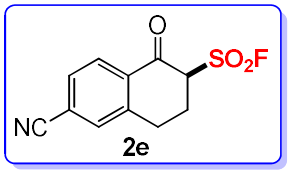
using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2c** in 86% yield (53 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.50 (s, 1H), 4.50 (dd, *J* = 8.8, 5.3 Hz, 1H), 3.28 (dt, *J* = 17.3, 5.9 Hz, 1H), 3.10 (ddd, *J* = 17.3, 8.3, 5.1 Hz, 1H), 2.82-2.71 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.5, 144.2, 132.0, 131.4, 131.0, 130.2, 129.7 (d, *J* = 2.5 Hz), 67.1 (d, *J* = 11.2 Hz), 26.4, 25.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.95 (s); HRMS (ESI) calcd. for $C_{10}H_7BrFO_3S^-$ [M-H]$^-$: 304.9289, found: 304.9290; IR (neat) ν_{max} (cm^{-1}) = 1687, 1587, 1405, 1205, 778, 603, 557.

1-Oxo-6-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2d**)



According to general procedure C with **1d**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2d** in 72% yield (43 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 8.7 Hz, 1H), 7.60 (s, 1H), 4.56 (dd, *J* = 8.9, 5.2 Hz, 1H), 3.38 (dt, *J* = 17.4, 5.8 Hz, 1H), 3.20 (ddd, *J* = 17.4, 8.4, 5.1 Hz, 1H), 2.86-2.78 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.6, 143.3, 136.3 (q, *J* = 32.9 Hz), 133.3-133.2 (m), 129.4, 126.3 (q, *J* = 3.7 Hz), 124.5 (q, *J* = 3.5 Hz), 123.3 (q, *J* = 273.2 Hz), 67.2 (d, *J* = 11.7 Hz), 26.7, 25.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ 57.06 (s), -63.43 (s); HRMS (ESI) calcd. for $C_{11}H_7F_4O_3S^-$ [M-H]$^-$: 295.0058, found: 295.0062; IR (neat) ν_{max} (cm^{-1}) = 1686, 1603, 1405, 1202, 1189, 921, 781, 609, 544.

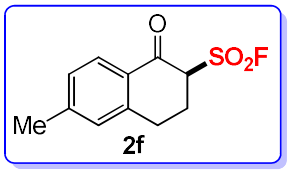
6-Cyano-1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2e**)



According to general procedure C with **1e**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (5 : 1 : 0.2, v : v) to afford **2e** in 59% yield (30 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.66 (s, 1H), 4.57 (dd, *J* = 8.6, 5.3 Hz, 1H), 3.37 (dt, *J* = 17.4, 5.9 Hz, 1H), 3.18 (ddd, *J* = 17.5, 7.9, 5.3 Hz, 1H), 2.89-2.73 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.3, 143.2, 133.6 (d, *J* = 2.3 Hz), 133.0 (d, *J* = 3.6 Hz), 131.0, 129.4, 118.4, 117.5, 66.9 (d, *J* = 11.9 Hz), 26.3, 24.9; ^{19}F NMR (471

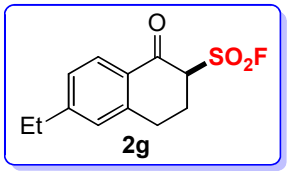
MHz, $CDCl_3$) δ 57.20 (s); HRMS (ESI) calcd. for $C_{11}H_7FNO_3S^-$ [M-H]$^-$: 252.0136, found: 252.0138; IR (neat) ν_{max} (cm^{-1}) = 2228, 1685, 1603, 1405, 1202, 1189, 781, 609.

6-Methyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2f**)



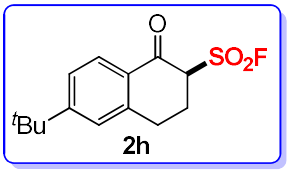
According to general procedure C with **1f**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2f** in 85% yield (41 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 7.10 (s, 1H), 4.49 (dd, *J* = 9.4, 5.0 Hz, 1H), 3.23 (dt, *J* = 17.1, 5.6 Hz, 1H), 3.10 (ddd, *J* = 17.1, 8.9, 4.9 Hz, 1H), 2.81-2.67 (m, 2H), 2.41 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.9, 146.8, 142.8, 129.5, 128.8, 128.7, 128.6 (d, *J* = 2.6 Hz), 67.7 (d, *J* = 10.6 Hz), 26.8, 25.6, 22.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.54 (s); HRMS (ESI) calcd. for $C_{11}H_{10}FO_3S^-$ [M-H]$^-$: 241.0340, found: 241.0342; IR (neat) ν_{max} (cm^{-1}) = 1683, 1607, 1403, 1235, 1201, 780, 610, 552.

6-Ethyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2g**)



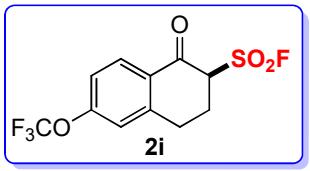
According to general procedure C with **1g**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2g** in 72% yield (37 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.12 (s, 1H), 4.50 (dd, *J* = 9.1, 5.0 Hz, 1H), 3.24 (dt, *J* = 15.9, 4.9 Hz, 1H), 3.10 (ddd, *J* = 12.2, 9.1, 4.5 Hz, 1H), 2.80-2.76 (m, 1H), 2.71-2.67 (m, 3H), 1.26 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.0, 152.8, 143.0, 128.8 (d, *J* = 2.7 Hz), 128.7, 128.3, 127.6, 67.8 (d, *J* = 10.5 Hz), 29.2, 26.9, 25.6, 15.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.41 (s); HRMS (ESI) calcd. for $C_{12}H_{14}FO_3S^+$ [M+H]$^+$: 257.0642, found: 257.0637; IR (neat) ν_{max} (cm^{-1}) = 1685, 1603, 1405, 1202, 1189, 781, 609, 544.

6-(Tert-butyl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2h**)



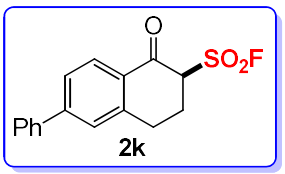
According to general procedure C with **1h**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2h** in 87% yield (49 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.42 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.27 (d, *J* = 9.6 Hz, 1H), 4.50 (dd, *J* = 9.5, 5.0 Hz, 1H), 3.27 (dt, *J* = 17.0, 5.5 Hz, 1H), 3.11 (ddd, *J* = 17.0, 9.0, 4.8 Hz, 1H), 2.81-2.71 (m, 2H), 1.34 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.9, 159.6, 142.7, 128.7, 128.6 (d, *J* = 2.7 Hz), 125.8, 125.2, 67.7 (d, *J* = 10.4 Hz), 35.5, 31.0, 27.1, 25.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.50 (s); HRMS (ESI) calcd. for $C_{14}H_{16}FO_3S^-$ [M-H]$^-$: 283.0810, found: 283.0813; IR (neat) ν_{max} (cm^{-1}) = 1685, 1603, 1405, 1202, 815, 781, 609, 545.

1-Oxo-6-(trifluoromethoxy)-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2i**)



According to general procedure C with **1i**: The crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2i** in 68% yield (42 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.7 Hz, 1H), 7.21 (d, *J* = 9.1 Hz, 1H), 7.14 (s, 1H), 4.56 (dd, *J* = 9.3, 5.0 Hz, 1H), 3.31 (dt, *J* = 17.4, 5.6 Hz, 1H), 3.16 (ddd, *J* = 17.4, 8.8, 4.9 Hz, 1H), 2.85-2.79 (m, 1H), 2.78-2.71 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.1, 154.0 (q, *J* = 1.7 Hz), 145.3, 131.2, 129.1 (d, *J* = 2.6 Hz), 120.3 (q, *J* = 259.9 Hz), 119.9 (q, *J* = 1.0 Hz), 119.5 (q, *J* = 3.3 Hz), 67.2 (d, *J* = 11.3 Hz), 26.9, 25.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.68 (s), -57.35 (s); HRMS (ESI) calcd. for $C_{11}H_7F_4O_4S^-$ [M-H]$^-$: 311.0007, found: 311.0014; IR (neat) ν_{max} (cm^{-1}) = 1691, 1609, 1141, 1253, 1201, 1117, 810, 567.

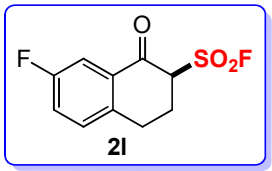
1-Oxo-6-phenyl-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2k**)



According to general procedure C with **1k**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2k** in 69% yield (42 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ

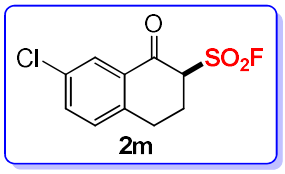
8.16 (d, J = 8.2 Hz, 1H), 7.66-7.56 (m, 3H), 7.53-7.39 (m, 4H), 4.54 (dd, J = 9.2, 5.1 Hz, 1H), 3.35 (dt, J = 17.0, 5.6 Hz, 1H), 3.18 (ddd, J = 17.0, 8.7, 4.9 Hz, 1H), 2.95-2.71 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.0, 148.0, 143.2, 139.3, 129.7 (d, J = 2.4 Hz), 129.3, 129.2, 129.0, 128.9, 127.4, 126.6, 67.6 (d, J = 10.7 Hz), 27.0, 25.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.71 (s); HRMS (ESI) calcd. for $C_{16}H_{12}FO_3S^-$ [M-H]$^-$: 305.0642, found: 305.0650; IR (neat) ν_{max} (cm^{-1}) = 1685, 1603, 1405, 1202, 815, 781, 609, 544.

7-Fluoro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2l**)



According to general procedure C with **1l**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2l** in 70% yield (34 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, J = 8.7 Hz, 1H), 7.32-7.30 (m, 2H), 4.53 (dd, J = 9.4, 5.0 Hz, 1H), 3.27 (dt, J = 17.1, 5.6 Hz, 1H), 3.11 (ddd, J = 17.0, 8.7, 4.8 Hz, 1H), 2.84-2.78 (m, 1H), 2.77-2.69 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.6, 161.9 (d, J = 248.7 Hz), 138.6 (d, J = 2.9 Hz), 132.4 (dd, J = 6.7, 2.6 Hz), 131.1 (d, J = 7.3 Hz), 122.9 (d, J = 22.3 Hz), 114.5 (d, J = 22.6 Hz), 67.2 (d, J = 11.4 Hz), 26.1, 25.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.79 (s), -112.90 (dd, J = 13.5, 7.1 Hz); HRMS (ESI) calcd. for $C_{10}H_7F_2O_3S^-$ [M-H]$^-$: 245.0089, found: 245.0090; IR (neat) ν_{max} (cm^{-1}) = 1702, 1494, 1406, 1242, 1203, 1161, 789, 585.

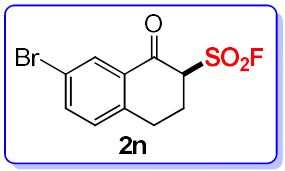
7-Chloro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2m**)



According to general procedure C with **1m**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2m** in 83% yield (44 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, J = 2.3 Hz, 1H), 7.54 (dd, J = 8.3, 2.3 Hz, 1H), 7.28 (d, J = 8.3 Hz, 1H), 4.52 (dd, J = 9.3, 5.0 Hz, 1H), 3.27 (dt, J = 17.3, 5.7 Hz, 1H), 3.10 (ddd, J = 17.3, 8.7, 4.9 Hz, 1H), 2.84-2.78 (m, 1H), 2.27-2.69 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.4, 141.0, 135.3, 134.1, 132.1 (d, J = 2.5 Hz), 130.7, 128.1, 67.2 (d, J = 11.3 Hz), 26.2,

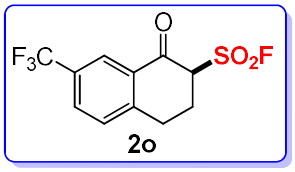
25.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.86 (s); HRMS (ESI) calcd. for $C_{10}H_7ClFO_3S^-$ [M-H]$^-$: 260.9794 found: 260.9796; IR (neat) ν_{max} (cm^{-1}) = 1690, 1477, 1406, 1308, 1202, 850, 781, 577.

7-Bromo-1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2n**)



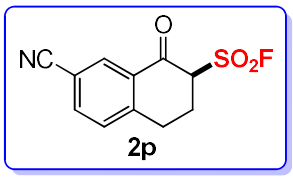
According to general procedure C with **1n**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2n** in 63% yield (39 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 2.2 Hz, 1H), 7.69 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.21 (d, *J* = 8.2 Hz, 1H), 4.51 (dd, *J* = 9.0, 5.1 Hz, 1H), 3.25 (dt, *J* = 17.3, 5.8 Hz,1H), 3.07 (ddd, *J* = 17.3, 8.5, 4.9 Hz, 1H), 2.83-2.77 (m, 1H), 2.76-2.70 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.2, 141.5, 138.1, 132.3 (d, *J* = 2.5 Hz), 131.3, 130.9, 121.8, 67.1 (d, *J* = 11.3 Hz), 26.3, 25.2 ; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.97 (s); HRMS (ESI) calcd. for $C_{10}H_7BrFO_3S^-$ [M-H]$^-$: 304.9289, found: 304.9297; IR (neat) ν_{max} (cm^{-1}) = 1687, 1587, 1405, 1202, 1186, 778, 603, 557.

1-Oxo-7-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2o**)



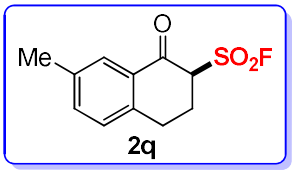
According to general procedure C with **1o**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2o** in 59% yield (35 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.82 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 4.57 (dd, *J* = 8.6, 5.2 Hz, 1H), 3.38 (dt, *J* = 17.5, 5.9 Hz, 1H), 3.20 (ddd, *J* = 17.6, 7.8, 5.4 Hz, 1H), 2.87-2.75 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.3, 146.2, 131.4 (q, *J* = 3.4 Hz), 131.2 (d, *J* = 2.6 Hz), 130.6 (q, *J* = 33.6 Hz), 130.1, 125.8 (q, *J* = 3.9 Hz), 123.4 (q, *J* = 272.4 Hz), 67.0 (d, *J* = 11.5 Hz), 26.6, 25.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ 57.11 (s), -62.91 (s); HRMS (ESI) calcd. for $C_{11}H_7F_4O_3S^-$ [M-H]$^-$: 295.0058, found: 295.0061; IR (neat) ν_{max} (cm^{-1}) = 1694, 1620, 1407, 1203, 1123, 1073, 784, 570.

7-Cyano-1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2p**)



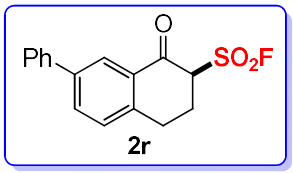
According to general procedure C with **1p**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (5 : 1 : 0.2, v : v) to afford **2p** in 57% yield (29 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.84 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 4.55 (dd, *J* = 7.7, 5.9 Hz, 1H), 3.40 (dt, *J* = 17.7, 6.0 Hz, 1H), 3.19 (dt, *J* = 17.8, 6.3 Hz, 1H), 2.89-2.74 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.6, 147.1, 137.3, 132.8, 131.6 (d, *J* = 2.4 Hz), 130.4, 117.4, 112.5, 66.7 (d, *J* = 11.8 Hz), 26.7, 24.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ 57.44 (s); HRMS (ESI) calcd. for $C_{11}H_7FNO_3S^-$ [M-H]$^-$: 252.0136, found: 252.0141; IR (neat) ν_{max} (cm^{-1}) = 2230, 1699, 1581, 1410, 1203, 808, 772, 550.

7-Methyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2q**)



According to general procedure C with **1q**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2q** in 77% yield (37 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.39 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 4.51 (dd, *J* = 9.8, 4.9 Hz, 1H), 3.22 (dt, *J* = 17.1, 5.5 Hz, 1H), 3.08 (ddd, *J* = 17.0, 9.2, 4.8 Hz, 1H), 2.81-2.75 (m, 1H), 2.72-2.65 (m, 1H), 2.37 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.6, 140.0, 137.6, 136.4, 130.7 (d, *J* = 2.5 Hz), 129.0, 128.5, 67.8 (d, *J* = 10.6 Hz), 26.4, 25.6, 21.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.40 (s); HRMS (ESI) calcd. for $C_{11}H_{11}FO_3SNa^+$ [M+Na]$^+$: 265.0305, found: 265.0309; IR (neat) ν_{max} (cm^{-1}) = 1447, 1225, 1078, 945, 910, 792, 732, 569.

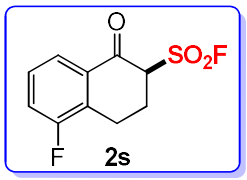
1-Oxo-7-phenyl-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2r**)



According to general procedure C with **1r**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2r** in 79% yield (48 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.55 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.48-7.41 (m, 4H), 7.30-7.28 (m, 2H), 4.54 (dd, *J* = 9.8, 4.9 Hz, 1H), 3.14 (dt, *J* = 17.5, 5.4 Hz, 1H), 3.01-2.94 (ddd,

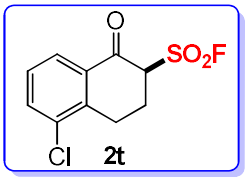
J = 17.5, 9.2, 4.7 Hz, 1H), 2.73-2.66 (m, 1H), 2.65-2.58 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.7, 142.4, 140.3, 139.5, 136.5, 131.4 (d, J = 2.5 Hz), 129.1, 128.7, 128.1, 128.0, 127.5, 67.5 (d, J = 10.9 Hz), 25.6, 25.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.56 (s); HRMS (ESI) calcd. for $C_{16}H_{12}FO_3S^-$ [M-H]$^-$: 303.0497, found: 303.0504; IR (neat) ν_{max} (cm^{-1}) = 1684, 1406, 1264, 1202, 780, 732, 700, 560.

5-Fluoro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2s**)



According to general procedure C with **1s**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2s** in 71% yield (35 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 7.6 Hz, 1H), 7.41-7.33 (m, 2H), 4.54 (dd, J = 9.3, 4.9 Hz, 1H), 3.32 (dt, J = 17.8, 5.6 Hz, 1H), 3.08 (ddd, J = 17.8, 8.5, 5.8 Hz, 1H), 2.86-2.80 (m, 1H), 2.80-2.71 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.5 (d, J = 3.5 Hz), 159.8 (d, J = 248.0 Hz), 132.5 (dd, J = 3.3, 3.1 Hz), 129.8 (d, J = 18.2 Hz), 128.6 (d, J = 8.0 Hz), 124.2 (d, J = 3.5 Hz), 121.8 (d, J = 21.6 Hz), 67.1 (d, J = 11.5 Hz), 24.6, 19.6 (d, J = 4.1 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.71 (s), -115.94 (dd, J = 8.4, 5.8 Hz); HRMS (ESI) calcd. for $C_{10}H_7F_2O_3S^-$ [M-H]$^-$: 245.0089, found: 245.0089; IR (neat) ν_{max} (cm^{-1}) = 1692, 1610, 1407, 1263, 1201, 793, 734, 702.

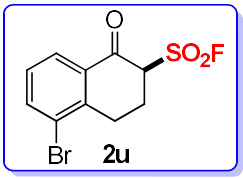
5-Chloro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2t**)



According to general procedure C with **1t**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2t** in 87% yield (46 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 7.4 Hz, 1H), 7.67 (d, J = 7.9 Hz, 1H), 7.36 (t, J = 7.9 Hz, 1H), 4.54 (dd, J = 9.8, 4.8 Hz, 1H), 3.39 (dt, J = 18.1, 5.6 Hz, 1H), 3.13 (ddd, J = 18.1, 8.9, 5.2 Hz, 1H), 2.87-2.81 (m, 1H), 2.77-2.70 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.9, 140.2, 135.8, 134.4, 132.6 (d, J = 2.7 Hz), 128.4, 127.2, 66.8 (d, J = 11.8 Hz), 24.6, 24.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.50 (s); HRMS (ESI) calcd. for $C_{10}H_7ClFO_3S^-$ [M-H]$^-$:

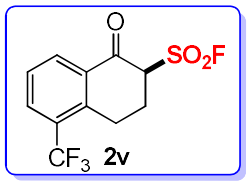
260.9794, found: 260.9797; IR (neat) ν_{max} (cm^{-1}) = 1685, 1588, 1403, 1199, 1140, 766, 731, 561.

5-Bromo-1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2u**)



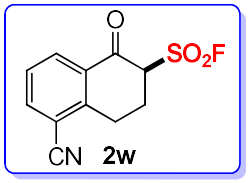
According to general procedure C with **1u**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2u** in 58% yield (35 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.86 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.30 (t, *J* = 7.9 Hz, 1H), 4.52 (dd, *J* = 9.7, 4.9 Hz, 1H), 3.37 (dt, *J* = 18.1, 5.6 Hz, 1H), 3.12 (ddd, *J* = 18.1, 8.8, 5.2 Hz, 1H), 2.94-2.61 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.9, 141.8, 139.1, 132.8 (d, *J* = 2.6 Hz), 128.8, 127.9, 124.9, 66.7 (d, *J* = 11.9 Hz), 27.5, 24.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.50 (s); HRMS (ESI) calcd. for $C_{10}H_9BrFO_3S^+$ $[M+H]^+$: 306.9434, found: 306.9439; IR (neat) ν_{max} (cm^{-1}) = 1694, 1588, 1404, 1199, 1127, 730, 611, 555.

1-Oxo-5-(trifluoromethyl)-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2v**)



According to general procedure C with **1v**: the crude product was purified by flash column chromatography on silica gel using petroleum ether: ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2v** in 60% yield (36 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.9 Hz, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 4.56 (dd, *J* = 9.8, 4.9 Hz, 1H), 3.51 (dt, *J* = 18.0, 5.4 Hz, 1H), 3.27 (ddd, *J* = 18.0, 9.1, 4.7 Hz, 1H), 2.92-2.65 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.5, 141.1 (q, *J* = 1.3 Hz), 132.5 (q, *J* = 1.7 Hz), 132.4 (d, *J* = 5.6 Hz), 132.3 (q, *J* = 33.7 Hz), 129.4 (q, *J* = 30.7 Hz), 127.7, 123.7 (q, *J* = 274.1 Hz), 66.9 (d, *J* = 12.1 Hz), 24.7, 23.5 (q, *J* = 2.5 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.76 (s), -61.03 (s); HRMS (ESI) calcd. for $C_{11}H_8F_4O_3SNa^+$ $[M+Na]^+$: 319.0022, found: 319.0013; IR (neat) ν_{max} (cm^{-1}) = 1694, 1410, 1329, 1307, 1175, 787, 737, 552.

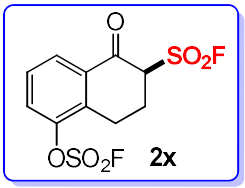
5-Cyano-1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2w**)



According to general procedure C with **1w**: the crude product was purified by flash column chromatography on silica gel using

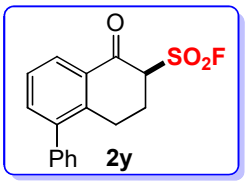
petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2w** in 62% yield (31 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 7.9 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 4.60 (dd, *J* = 9.1, 5.1 Hz, 1H), 3.55 (dt, *J* = 18.0, 5.7 Hz, 1H), 3.33 (ddd, *J* = 18.0, 8.4, 5.1 Hz, 1H), 2.97-2.74 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.0, 145.7, 138.8, 132.8, 131.8 (d, *J* = 2.5 Hz), 128.3, 116.2, 113.4, 66.7 (d, *J* = 12.1 Hz), 25.3, 24.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.98 (s); HRMS (ESI) calcd. for $C_{11}H_7FNO_3S^-$ [M-H]$^-$: 252.0136, found: 252.0139; IR (neat) ν_{max} (cm^{-1}) = 2230, 1699, 1581, 1410, 1203, 808, 772, 550.

6-(Fluorosulfonyl)-5-oxo-5,6,7,8-tetrahydronaphthalen-1-yl sulfofluoridate (**2x**)



According to general procedure C with **1x**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2x** in 49% yield (32 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.68 (dt, *J* = 8.2, 1.4 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 4.58 (dd, *J* = 9.6, 4.9 Hz, 1H), 3.41 (dt, *J* = 17.9, 5.6 Hz, 1H), 3.18 (ddd, *J* = 18.1, 9.0, 5.1 Hz, 1H), 2.92-2.82 (m, 1H), 2.81-2.73 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.9, 147.6, 135.2, 133.2 (d, *J* = 2.6 Hz), 129.1, 129.0, 127.6, 66.7 (d, *J* = 12.2 Hz), 24.4, 21.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.81 (s), 40.05 (s); HRMS (ESI) calcd. for $C_{10}H_7F_2O_6S_2^-$ [M-H]$^-$: 324.9658, found: 324.9666; IR (neat) ν_{max} (cm^{-1}) = 1447, 1232, 1199, 1180, 956, 910, 729, 553.

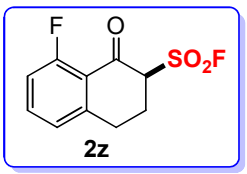
1-Oxo-5-phenyl-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2y**)



According to general procedure C with **1y**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2y** in 57% yield (35 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.55 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.50-7.39 (m, 4H), 7.30-7.28 (m, 2H), 4.54 (dd, *J* = 9.8, 4.9 Hz, 1H), 3.14 (dt, *J* = 17.5, 5.4 Hz, 1H), 2.97 (ddd, *J* = 17.5, 9.1, 4.7 Hz, 1H), 2.73-2.66 (m, 1H), 2.65-2.58 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.7, 142.4, 140.3, 139.5, 136.5, 131.4 (d, *J* = 2.5 Hz), 129.1, 128.7, 128.0, 127.9,

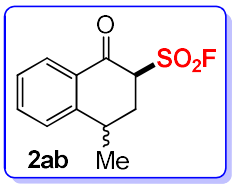
127.5, 67.5 (d, J = 10.9 Hz), 25.6, 25.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.56 (s); HRMS (ESI) calcd. for $C_{16}H_{14}FO_3S^+$ $[M+H]^+$: 305.0642, found: 305.0635; IR (neat) ν_{max} (cm^{-1}) = 1702, 1494, 1406, 1203, 1161, 889, 789, 585.

8-Fluoro-1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2z**)



According to general procedure C with **1z**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2z** in 33% yield (16 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (td, J = 8.0, 5.1 Hz, 1H), 7.11 (d, J = 7.7 Hz, 1H), 7.06 (dd, J = 10.9, 8.3 Hz, 1H), 4.52 (dd, J = 9.0, 5.3 Hz, 1H), 3.32 (dt, J = 17.3, 5.8 Hz, 1H), 3.13 (ddd, J = 17.3, 8.6, 5.0 Hz, 1H), 2.82-2.69 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.8, 162.9 (d, J = 269.6 Hz), 144.7, 136.5 (d, J = 10.7 Hz), 124.8 (d, J = 4.0 Hz), 120.0 (dd, J = 5.2, 2.6 Hz), 116.0 (d, J = 21.3 Hz), 68.3 (d, J = 10.9 Hz), 26.9 (d, J = 2.1 Hz), 25.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.97 (s), -108.65 (dd, J = 11.0, 5.2 Hz); HRMS (ESI) calcd. for $C_{10}H_7F_2O_3S^-$ $[M-H]^-$: 245.0089, found: 245.0093; IR (neat) ν_{max} (cm^{-1}) = 1687, 1607, 1405, 1253, 1201, 785, 614, 538.

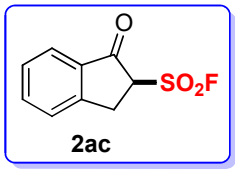
4-Methyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2ab**)



According to general procedure C with **1ab**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2ab** in 51% yield (25 mg, colorless oil, major : minor = 1.5 : 1 as determined by crude ^{19}F NMR). ^{1}H NMR (500 MHz, $CDCl_3$) major: δ 8.06 (td, J = 7.4, 6.8, 1.4 Hz, 1H), 7.62 (td, J = 7.5, 1.4 Hz, 1H), 7.38-7.35 (m, 2H), 4.62 (dd, J = 14.1, 4.3 Hz, 1H), 3.27 (dp, J = 11.9, 6.6 Hz, 1H), 2.83-2.78 (m, 1H), 2.34 (dt, J = 14.0, 12.6 Hz, 1H), 1.47 (d, J = 7.2 Hz, 3H); minor: δ 8.06 (td, J = 7.4, 6.8, 1.4 Hz, 1H), 7.65 (td, J = 8.0, 1.3 Hz, 1H), 7.45 (d, J = 7.9 Hz, 1H), 7.41-7.38 (m, 1H), 4.70 (dd, J = 10.7, 4.9 Hz, 1H), 3.46 (td, J = 12.5, 6.5 Hz, 1H), 2.82-2.79 (m, 1H), 2.57 (dtd, J = 13.7, 5.2, 2.2 Hz, 1H), 1.54 (d, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 186.2 (185.4), 147.7 (146.7), 135.6 (135.5), 130.7 (d, J = 3.5 Hz) (129.9 (d, J = 2.7

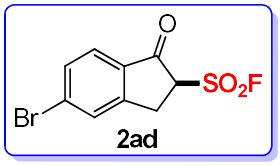
Hz)), 128.6 (128.4), 128.2 (127.6), 127.6 (126.7), 68.2 (d, J = 11.5 Hz) (65.1 (d, J = 10.8 Hz)), 33.8 (32.0) 31.9 (30.8), 21.3 (20.0); ^{19}F NMR (471 MHz, $CDCl_3$) minor: 56.28 (s), major: 54.68 (s); HRMS (ESI) calcd. for $C_{11}H_{10}FO_3S^-$ [M-H]$^-$: 241.0340, found: 241.0343; IR (neat) ν_{max} (cm^{-1}) = 1690, 1600, 1402, 1264, 1191, 732, 702, 589.

1-Oxo-2,3-dihydro-1H-indene-2-sulfonyl fluoride (**2ac**)



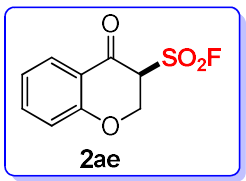
According to general procedure C with **1ac**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2ac** in 90% yield (42 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 7.8 Hz, 1H), 7.74 (dd, J = 7.5, 1.0 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 4.58 (ddd, J = 7.6, 5.2, 1.4 Hz, 1H), 3.75 (dd, J = 6.3, 4.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.7, 150.9, 137.0, 134.4 (d, J = 3.0 Hz), 129.0, 126.7, 125.6, 64.4 (d, J = 13.9 Hz), 29.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ 54.17 (s); HRMS (ESI) calcd. for $C_9H_6FO_3S^-$ [M-H]$^-$: 231.0021, found: 213.0027; IR (neat) ν_{max} (cm^{-1}) = 1721, 1403, 1366, 1180, 816, 734, 699, 586.

5-Bromo-1-oxo-2,3-dihydro-1H-indene-2-sulfonyl fluoride (**2ad**)



According to general procedure C with **1ad**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2ad** in 76% yield (44 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80-7.71 (m, 2H), 7.65 (d, J = 8.3 Hz, 1H), 4.54 (td, J = 6.4, 0.9 Hz, 1H), 3.73 (d, J = 6.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.5, 152.2, 133.3 (d, J = 3.0 Hz), 132.8, 132.7, 130.1, 126.7, 64.3 (d, J = 14.4 Hz), 28.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.95 (s); HRMS (ESI) calcd. for $C_9H_5BrFO_3S^-$ [M-H]$^-$: 290.9132, found: 290.9137; IR (neat) ν_{max} (cm^{-1}) = 1721, 1594, 1403, 1203, 998, 811, 789, 582.

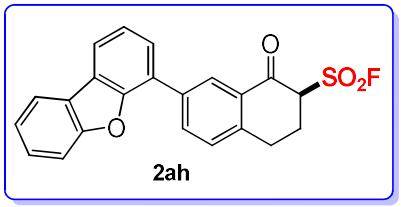
4-Oxochroman-3-sulfonyl fluoride (**2ae**)



According to general procedure C with **1ae**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v)

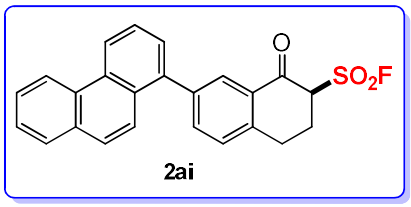
to afford **2ae** in 57% yield (26 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.61 (ddd, *J* = 8.7, 7.2, 1.8 Hz, 1H), 7.16-7.13 (m, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 5.09 (dd, *J* = 12.8, 4.7 Hz, 1H), 4.86 (ddd, *J* = 12.8, 5.1, 4.2 Hz, 1H), 4.51 (td, *J* = 4.4, 2.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.1, 161.1, 138.1, 128.3, 123.2, 119.8 (d, *J* = 1.3 Hz), 118.5, 66.2, 64.7 (d, *J* = 12.6 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ 59.80 (s); HRMS (ESI) calcd. for $C_9H_8FO_4S^+$ $[M+H]^+$: 231.0122, found: 231.0114; IR (neat) ν_{max} (cm^{-1}) = 1684, 1478, 1413, 1264, 1208, 731, 702, 586.

7-(Dibenzo[b,d]furan-4-yl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2ah**)



According to general procedure C with **1ah**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (8 : 1 : 0.2, v : v) to afford **2ah** in 40% yield (32 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 1.6 Hz, 1H), 8.19 (dd, *J* = 8.0, 1.8 Hz, 1H), 8.02-7.97 (m, 2H), 7.64-7.59 (m, 2H), 7.53-7.43 (m, 3H), 7.41-7.36 (m, 1H), 4.59 (dd, *J* = 9.3, 5.1 Hz, 1H), 3.39 (dt, *J* = 17.1, 5.4 Hz, 1H), 3.21 (ddd, *J* = 17.2, 8.8, 5.0 Hz, 1H), 2.93-2.75 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.3, 156.3, 153.3, 142.0, 136.3, 135.6, 131.3 (d, *J* = 2.2 Hz), 129.5, 128.5, 127.6, 126.7, 125.3, 124.1, 124.0, 123.5, 123.2, 120.9, 120.7, 112.1, 67.7 (d, *J* = 10.8 Hz), 26.7, 25.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.66 (s); HRMS (ESI) calcd. for $C_{22}H_{16}FO_4S^+$ $[M+H]^+$: 395.0748, found: 395.0749; IR (neat) ν_{max} (cm^{-1}) = 1719, 1609, 1446, 1264, 1233, 730, 703, 581.

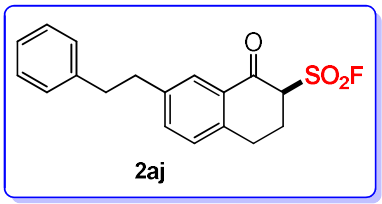
1-Oxo-7-(phenanthren-1-yl)-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2ai**)



According to general procedure C with **1ai**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (8 : 1 : 0.2, v : v) to afford **2ai** in 48% yield (39 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (d, *J* = 8.3 Hz,

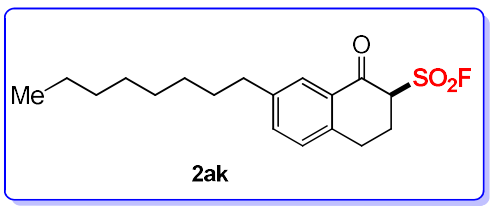
1H), 8.71 (d, J = 8.3 Hz, 1H), 8.29 (d, J = 1.9 Hz, 1H), 7.87 (s, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.75 (dd, J = 7.8, 2.0 Hz, 1H), 7.71-7.65 (m, 2H), 7.65-7.60 (m, 2H), 7.53 (t, J = 1.2 Hz, 1H), 7.42 (d, J = 7.9 Hz, 1H), 4.56 (dd, J = 9.2, 5.2 Hz, 1H), 3.38 (dt, J = 17.1, 5.5 Hz, 1H), 3.20 (ddd, J = 17.1, 8.6, 5.0 Hz, 1H), 2.91-2.76 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.3, 141.8, 140.6, 137.0, 136.8, 131.4, 131.0 (d, J = 2.2 Hz), 130.8, 130.6, 130.3, 129.7, 129.2, 128.9, 128.1, 127.2, 127.2, 126.9, 126.9, 126.4, 123.2, 122.7, 67.7 (d, J = 10.8 Hz), 26.7, 25.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.81 (s); HRMS (ESI) calcd. for $C_{24}H_{18}FO_3S^+$ $[M+H]^+$: 405.0955, found: 405.0949; IR (neat) ν_{max} (cm^{-1}) = 1655, 1445, 1264, 1231, 1023, 727, 703, 563.

1-Oxo-7-phenethyl-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2aj**)



According to general procedure C with **1aj**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2aj** in 65% yield (43 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 1.6 Hz, 1H), 7.34 (dd, J = 7.8, 1.8 Hz, 1H), 7.27 (t, J = 7.4 Hz, 2H), 7.21-7.15 (m, 4H), 4.49 (dd, J = 9.6, 5.0 Hz, 1H), 3.23 (dt, J = 17.1, 5.5 Hz, 1H), 3.07 (ddd, J = 17.0, 9.0, 4.8 Hz, 1H), 2.97-2.88 (m, 4H), 2.81-2.66 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.5, 141.5, 141.1, 140.5, 135.8, 130.8 (d, J = 2.4 Hz), 129.1, 128.6, 128.5, 128.0, 126.3, 67.7 (d, J = 10.7 Hz), 37.6, 37.3, 26.5, 25.6; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.56 (s); HRMS (ESI) calcd. for $C_{18}H_{16}FO_3S^-$ $[M-H]^-$: 331.0810, found: 331.0817; IR (neat) ν_{max} (cm^{-1}) = 1655, 1446, 1233, 1218, 1013, 923, 735, 563.

7-Octyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonyl fluoride (**2ak**)

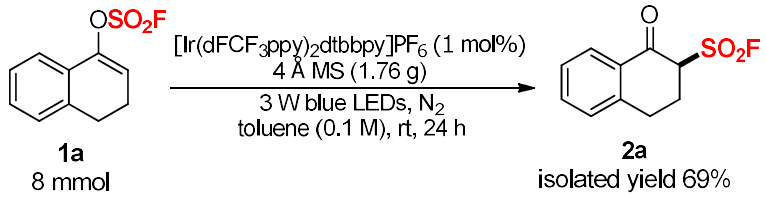


According to general procedure C with **1ak**: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) to afford **2ak** in 57% yield (39 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 1.7 Hz, 1H), 7.40 (dd, J = 7.8, 1.9 Hz, 1H), 7.21 (d, J = 7.9 Hz,

1H), 4.51 (dd, J = 9.8, 4.9 Hz, 1H), 3.23 (dt, J = 17.0, 5.4 Hz, 1H), 3.09 (ddd, J = 17.0, 9.3, 4.7 Hz, 1H), 2.81-2.75 (m, 1H), 2.73-2.68 (m, 1H), 2.63 (t, J = 7.8 Hz, 2H), 1.63-1.57 (m, 2H), 1.30-1.26 (m, 10H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 185.6, 142.7, 140.2, 135.8, 130.7 (d, J = 2.4 Hz), 129.0, 127.9, 67.8 (d, J = 10.6 Hz), 35.4, 32.0, 31.3, 29.5, 29.3, 29.2, 26.5, 25.6, 22.8, 14.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ 56.41 (s); HRMS (ESI) calcd. for $C_{18}H_{24}FO_3S^-$ $[M-H]^-$: 339.1436 found: 339.1444; IR (neat) ν_{max} (cm^{-1}) = 1695, 1610, 1243, 1120, 1095, 873, 733, 703.

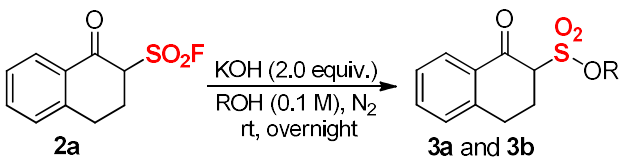
5. Gram-scale synthesis and derivatizations of **2a**

5.1 Gram-scale experiment



To a 150 mL sealed tube equipped with a rubber septum and a magnetic stirring bar, **1a** (1.82 g, 8 mmol, 1.0 equiv.), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (93 mg, 0.08 mmol, 1 mol%) and 4 Å MS (1.76 g) were added. The tube was evacuated and backfilled with N_2 for three times, and toluene (80 mL, 0.1 M) were added. The mixture was stirred and irradiated by 3 W blue LEDs for 24 hours at room temperature. After the reaction was complete (monitored by TLC), the crude mixture was concentrated under vacuum and purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate : AcOH (10 : 1 : 0.2, v : v) as eluent to give **2a** in 69% yield (1.26 g, colorless oil).

5.2 General procedure D: synthesis of **3a** and **3b**

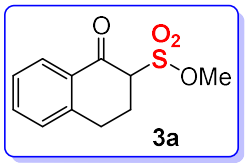


To a solution of **2a** (46 mg, 0.2 mmol) in alcohols (2 mL, 0.1 M) was added KOH (22 mg, 0.4 mmol, 2.0 equiv.). After stirring at room temperature overnight, the

resulting mixture was concentrated in *vacuo* and the residue was purified by flash column chromatography to afford the corresponding sulfonate.

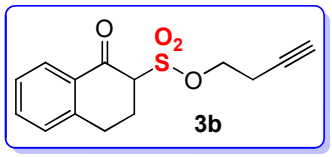
5.3 Characterization of **3a** and **3b**

Methyl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonate (**3a**)



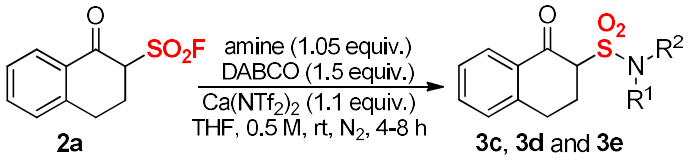
According to general procedure D with methanol: the crude product was filter with silica gel pad without purification to afford **3a** in 95% yield (43.2 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.9 Hz, 1H), 7.55 (td, *J* = 7.6, 1.3 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 4.24 (dd, *J* = 6.5, 5.3 Hz, 1H), 4.03 (s, 3H), 3.39 (ddd, *J* = 17.0, 9.2, 4.8 Hz, 1H), 3.01 (dt, *J* = 17.1, 5.6 Hz, 1H), 2.81-2.55 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.7, 143.5, 134.8, 131.4, 129.0, 128.2, 127.3, 65.7, 57.6, 26.3, 25.2; HRMS (ESI) calcd. for $C_{11}H_{13}O_4S^+$ $[M+H]^+$: 241.0529, found: 241.0519; IR (neat) ν_{max} (cm^{-1}) = 1685, 1599, 1355, 1302, 1171, 985, 780, 703.

But-3-yn-1-yl 1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonate (**3b**)



According to general procedure D with but-3-yn-1-ol: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate (10 : 1, v : v) to afford **3b** in 72% yield (40.0 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.9 Hz, 1H), 7.54 (td, *J* = 7.5, 1.2 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 4.46 (dt, *J* = 9.8, 6.9 Hz, 1H), 4.39 (dt, *J* = 9.8, 6.9 Hz, 1H), 4.26 (dd, *J* = 6.9, 5.5 Hz, 1H), 3.34 (ddd, *J* = 17.0, 8.0, 5.2 Hz, 1H), 3.01 (dt, *J* = 17.1, 5.9 Hz, 1H), 2.72-2.63 (m, 4H), 2.03 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.7, 143.4, 134.8, 131.4, 129.0, 128.2, 127.3, 78.6, 71.0, 69.2, 66.4, 26.5, 25.3, 19.9; HRMS (ESI) calcd. for $C_{14}H_{15}O_4S^+$ $[M+H]^+$: 279.0686, found: 279.0693; IR (neat) ν_{max} (cm^{-1}) = 1683, 1599, 1357, 1170, 971, 891, 732, 590.

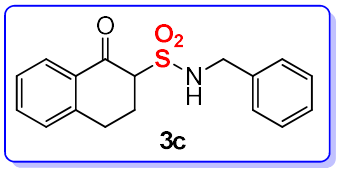
5.4 General procedure E:[3] synthesis of **3c**, **3d** and **3e**



To a flame-dried 25 mL round-bottom-flask equipped with a stirring bar, $Ca(NTf_2)_2$ (132 mg, 0.22 mmol, 1.1 equiv.), DABCO (34 mg, 0.3 mmol, 1.5 equiv.) and **2a** (46 mg, 0.2 mmol, 1.0 equiv.) were added and the flask was evacuated and backfilled with N_2 for three times. The amine (0.21 mmol, 1.05 equiv.) was added followed with dry THF (0.3 mL, 0.5 M). The solution was stirred at room temperature and monitored by TLC. Once full consumption of the starting material was reached, NH_4Cl (sat. 5 mL) was added and the resulting mixture was extracted using EtOAc (15 mL × 3). The combined organic phases were washed with brine and dried over $MgSO_4$. The residue was concentrated under vacuum and purified by flash column chromatography to afford the corresponding sulfonamide.

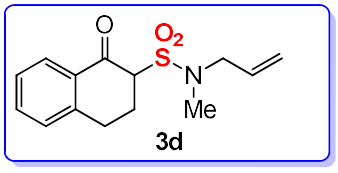
5.5 Characterization of **3c**, **3d** and **3e**

N-Benzyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonamide (**3c**) [1]



According to general procedure E with phenylmethanamine: the crude product was purified flash column chromatography on by silica gel using petroleum ether : ethyl acetate (20 : 1, v : v) to afford **3c** in 92% yield (58 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.52 (td, *J* = 7.5, 1.4 Hz, 1H), 7.39-7.37 (m, 2H), 7.34-7.30 (m, 3H), 7.29-7.24 (m, 2H), 5.51 (dd, *J* = 7.0, 6.3 Hz, 1H), 4.42 (dd, *J* = 13.9, 7.4 Hz, 1H), 4.32 (dd, *J* = 13.9, 5.5 Hz, 1H), 3.88 (dd, *J* = 9.3, 5.2 Hz, 1H), 3.24 (ddd, *J* = 16.8, 6.4, 4.7 Hz, 1H), 2.94 (ddd, 16.8, 9.2, 4.7 Hz, 1H), 2.69-2.56 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.8, 144.0, 136.6, 134.8, 131.5, 129.0, 128.9, 128.2, 128.1, 128.0, 127.3, 65.7, 47.8, 27.2, 24.4.

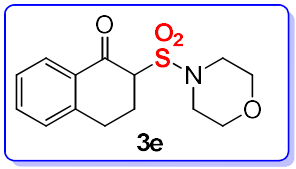
N-Allyl-N-methyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-sulfonamide (**3d**)



According to general procedure E with *N*-methylprop-2-en-1-amine: the crude product was purified flash column chromatography on by silica gel

using petroleum ether : ethyl acetate (10 : 1, v : v) to afford **3d** in 55% yield (44 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.52 (td, *J* = 7.5, 1.4 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.7 Hz, 1H), 5.81 (ddt, *J* = 16.6, 10.1, 6.2 Hz, 1H), 5.29 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.23 (dq, *J* = 10.2, 1.3 Hz, 1H), 4.07 (t, *J* = 4.8 Hz, 1H), 3.93 (dd, *J* = 15.3, 5.9 Hz, 1H), 3.73 (dd, *J* = 15.3, 6.5 Hz, 1H), 3.52 (ddd, *J* = 16.5, 11.3, 4.7 Hz, 1H), 2.90 (s, 4H), 2.85-2.71 (m, 1H), 2.56 (ddt, *J* = 14.4, 11.2, 5.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.2, 144.2, 134.6, 133.2, 131.7, 129.1, 127.9, 127.0, 118.8, 65.5, 53.6, 34.8, 26.2, 25.4; HRMS (ESI) calcd. for $C_{14}H_{18}NO_3S^+$ $[M+H]^+$: 280.1002, found: 280.1009; IR (neat) ν_{max} (cm^{-1}) = 1678, 1599, 1453, 1330, 1141, 987, 920, 732.

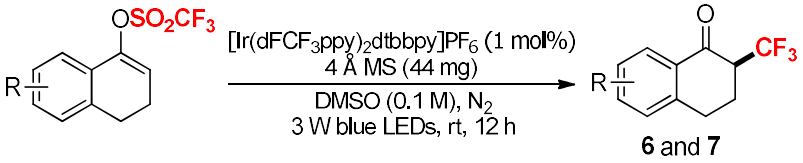
2-(Morpholinosulfonyl)-3,4-dihydronaphthalen-1(2H)-one (**3e**)



3e

According to general procedure E with morpholine: the crude product was purified flash column chromatography on by silica gel using petroleum ether : ethyl acetate (20 : 1, v : v) to afford **3e** in 79% yield (47 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.9 Hz, 1H), 7.54-7.51 (td, *J* = 7.6, 1.2 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 4.04 (t, *J* = 5.0 Hz, 1H), 3.77-3.69 (m, 4H), 3.51-3.42 (m, 3H), 3.39-3.34 (m, 2H), 2.93 (dt, *J* = 17.1, 4.8 Hz, 1H), 2.77 (dq, *J* = 14.1, 4.7 Hz, 1H), 2.60-2.53 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 189.9, 143.9, 134.6, 131.7, 129.1, 128.0, 127.1, 66.9, 65.7, 46.5, 26.3, 25.6; HRMS (ESI) calcd. for $C_{14}H_{18}NO_4S^+$ $[M+H]^+$: 291.0951, found: 291.0958; IR (neat) ν_{max} (cm^{-1}) = 1678, 1341, 1263, 1148, 956, 730, 702, 572.

6. General procedure F: synthesis of **6** and **7**

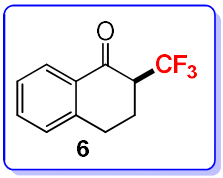


6 and **7**

To a 10 mL sealed tube equipped with a rubber septum and a magnetic stirring bar, 3,4-dihydronaphthalen-1-yl triflate[4] (0.2 mmol), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (2 mg, 0.002 mmol, 1 mol%) and 4 Å MS (44 mg) were added. The tube was evacuated and

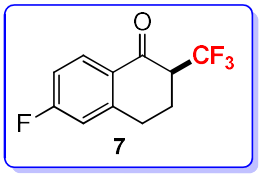
backfilled with N_2 for three times, and DMSO (2 mL, 0.1 M) were added. The mixture was stirred and irradiated by 3 W blue LEDs for 12 hours at room temperature. After the reaction was complete (monitored by TLC), the crude mixture was purified directly by flash column chromatography on silica gel using petroleum ether : ethyl acetate (40 : 1, v : v) as eluent to give **6** and **7**.

2-(Trifluoromethyl)-3,4-dihydronaphthalen-1(2H)-one (**6**)[5]



According to general procedure F: the crude product was purified by flash column chromatography on silica gel using petroleum ether : ethyl acetate (40 : 1, v : v) to afford **6** in 67% yield (32 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.53 (td, *J* = 7.5, 1.4 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.7 Hz, 1H), 3.27 (dtd, *J* = 17.7, 8.8, 4.5 Hz, 1H), 3.15-3.04 (m, 2H), 2.50 (dt, *J* = 13.7, 4.6 Hz, 1H), 2.32-2.25 (m, 1H); ^{19}F NMR (471 MHz, $CDCl_3$) δ -67.42 (d, *J* = 8.6 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.4, 143.2, 134.3, 132.0 (q, *J* = 1.7 Hz), 128.9, 127.8, 127.1, 125.2 (q, *J* = 279.7 Hz), 50.9 (q, *J* = 25.6 Hz), 27.6, 23.5; IR (neat) ν_{max} (cm^{-1}) = 1692, 1598, 1328, 1178, 1079, 1011, 751, 553.

6-Fluoro-2-(trifluoromethyl)-3,4-dihydronaphthalen-1(2H)-one (**7**)

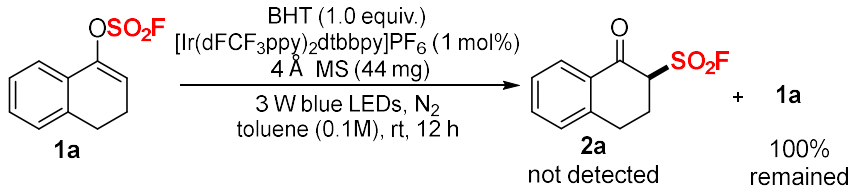


According to general procedure F: the crude product was purified flash column chromatography on by silica gel using petroleum ether : ethyl acetate (40 : 1, v : v) to afford **7** in 78% yield (38 mg, colorless oil). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.8, 5.9 Hz, 1H), 7.01 (td, *J* = 8.5, 2.5 Hz, 1H), 6.95 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.27 (dtd, *J* = 17.6, 8.8, 4.5 Hz, 1H), 3.15-3.04 (m, 2H), 2.50 (dt, *J* = 13.8, 4.7 Hz, 1H), 2.31-2.23 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.9, 166.2 (d, *J* = 257.1 Hz), 146.4 (d, *J* = 9.3 Hz), 131.1 (d, *J* = 10.1 Hz), 128.6 (q, *J* = 2.5 Hz), 125.1 (q, *J* = 279.9 Hz), 115.2 (d, *J* = 21.6 Hz), 115.0 (d, *J* = 22.2 Hz), 50.7 (q, *J* = 25.7 Hz), 27.7, 23.3 (q, *J* = 2.5 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -67.42 (d, *J* = 8.9 Hz), -103.02 (dd, *J* = 14.5, 7.8 Hz); HRMS (ESI) calcd. for $C_{11}H_8F_4ONa^+$ $[M+Na]^+$: 255.0403 found: 255.0397; IR (neat) ν_{max} (cm^{-1}) = 1702, 1494, 1406, 1203, 1161, 900, 789, 585.

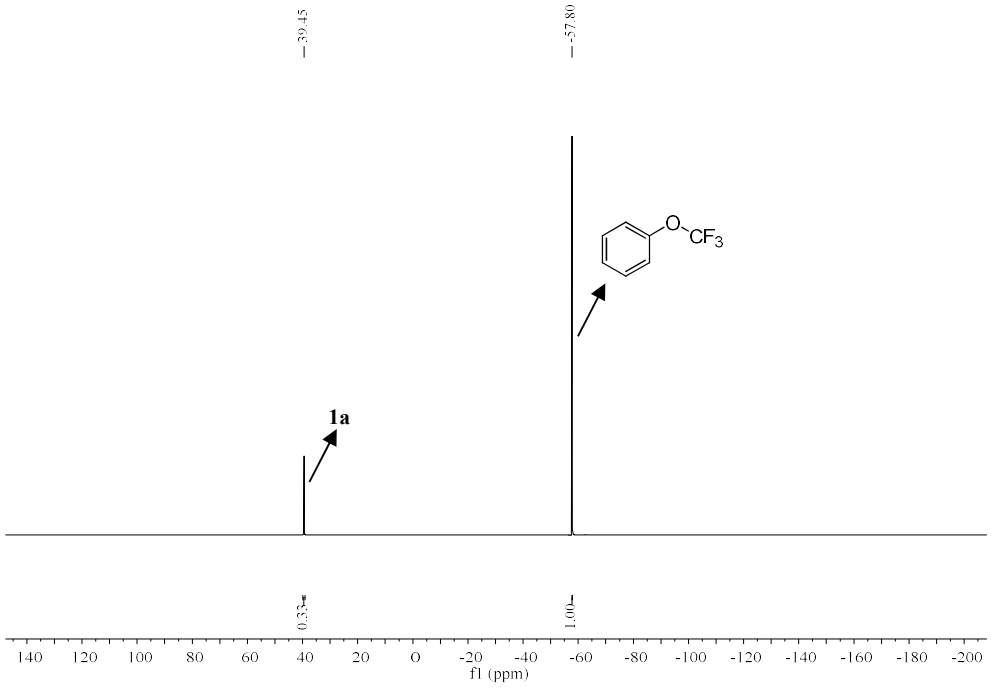
7. Mechanism studies

7.1 Radical capture experiments

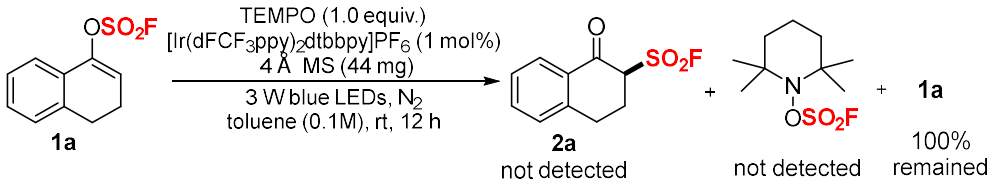
7.1.1 Radical capture experiment with BHT



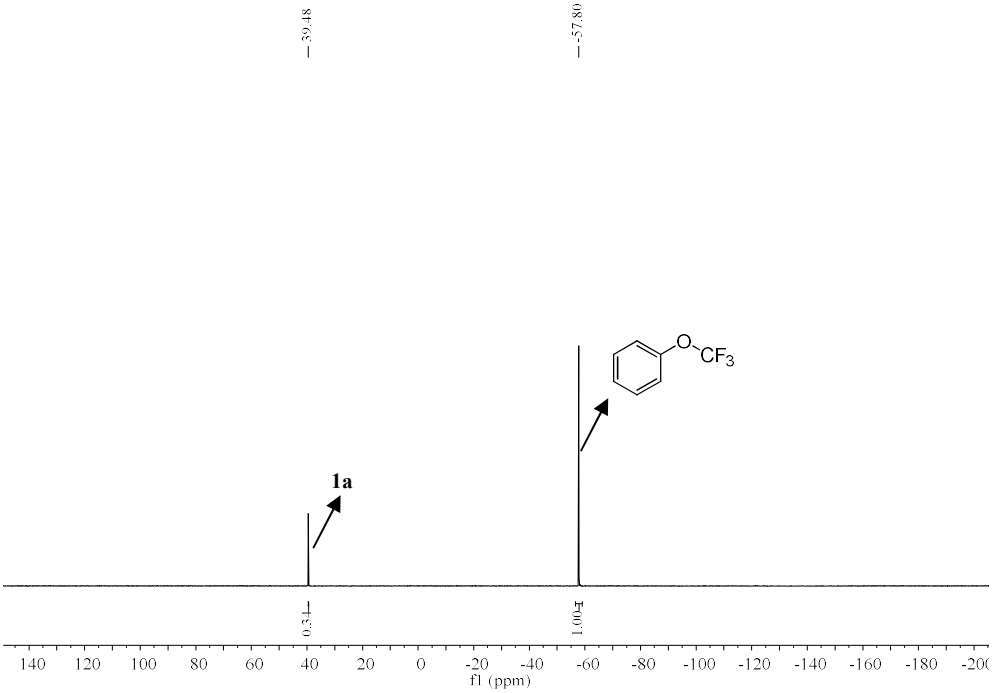
To a 10 mL sealed tube equipped with a rubber septum and magnetic stirring bar, **1a** (46 mg, 0.2 mmol), [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$ (2 mg, 0.002 mmol, 1 mol%), BHT (44 mg, 0.2 mmol, 1.0 equiv.) and 4 Å MS (44 mg) were added. The tube was evacuated and backfilled with N_2 for three times, and added with toluene (2.0 mL, 0.1 M). The mixture was stirred and irradiated by 3 W blue LEDs for 12 hours at room temperature. After that, the system was detected by crude ^{19}F NMR with trifluoromethoxybenzene (32.4 mg, 0.2 mmol) as the internal standard.



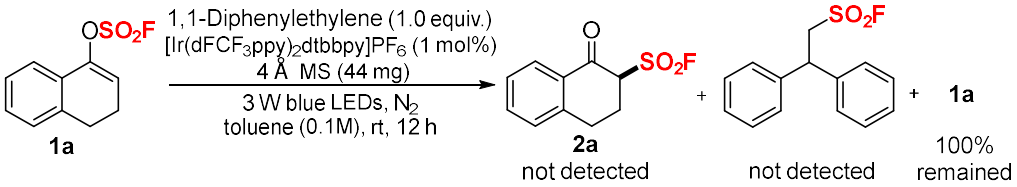
7.1.2 Radical capture experiment with TEMPO



To a 10 mL sealed tube equipped with a rubber septum and magnetic stirring bar, **1a** (46 mg, 0.2 mmol), [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$ (2 mg, 0.002 mmol, 1 mol%), TEMPO (31 mg, 0.2 mmol, 1.0 equiv.) and 4 Å MS (44 mg) were added. The tube was evacuated and backfilled with N_2 for three times, and added with toluene (2.0 mL, 0.1 M). The mixture was stirred and irradiated by 3 W blue LEDs for 12 hours at room temperature. After that, the system was detected by crude ^{19}F NMR with trifluoromethoxybenzene (32.4 mg, 0.2 mmol) as the internal standard.

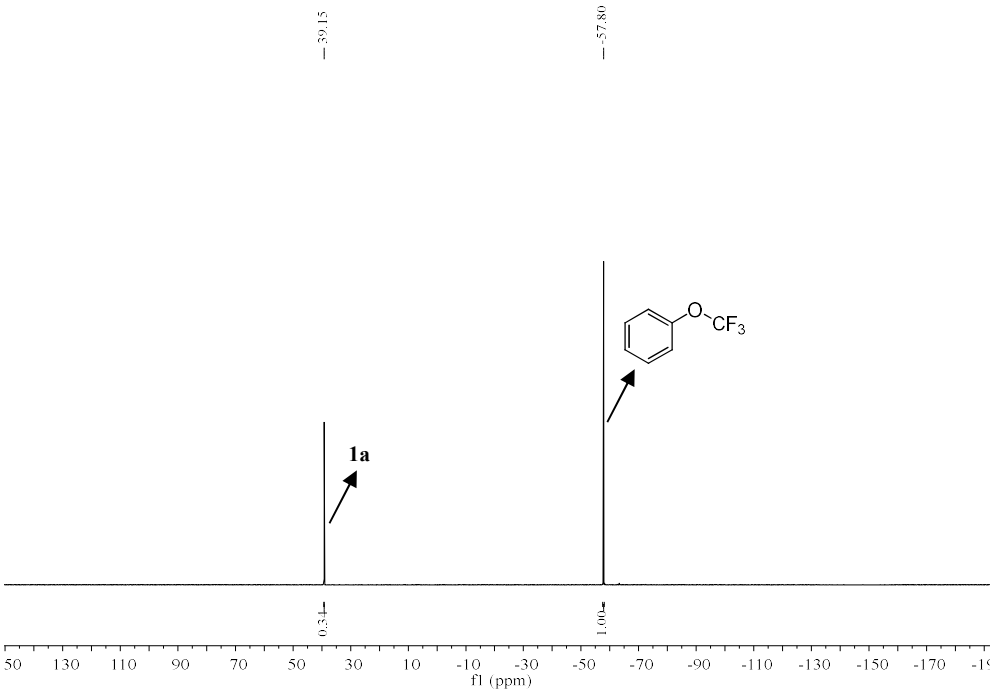


7.1.3 Radical capture experiment with 1,1-diphenylethylene

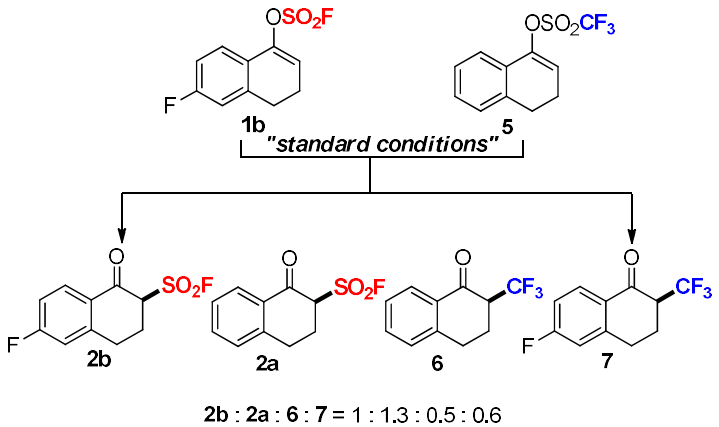


To a 10 mL sealed tube equipped with a rubber septum and magnetic stirring bar, **1a** (46 mg, 0.2 mmol), [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$ (2 mg, 0.002 mmol, 1 mol%),

1,1-diphenylethylene (36 mg, 0.2 mmol, 1.0 equiv.) and 4 Å MS (44 mg) were added. The tube was evacuated and backfilled with N_2 for three times, and added with toluene (2.0 mL, 0.1 M). The mixture was stirred and irradiated by 3 W blue LEDs for 12 hours at room temperature. After that, the system was detected by crude ^{19}F NMR with trifluoromethoxybenzene (32.4 mg, 0.2 mmol) as the internal standard.



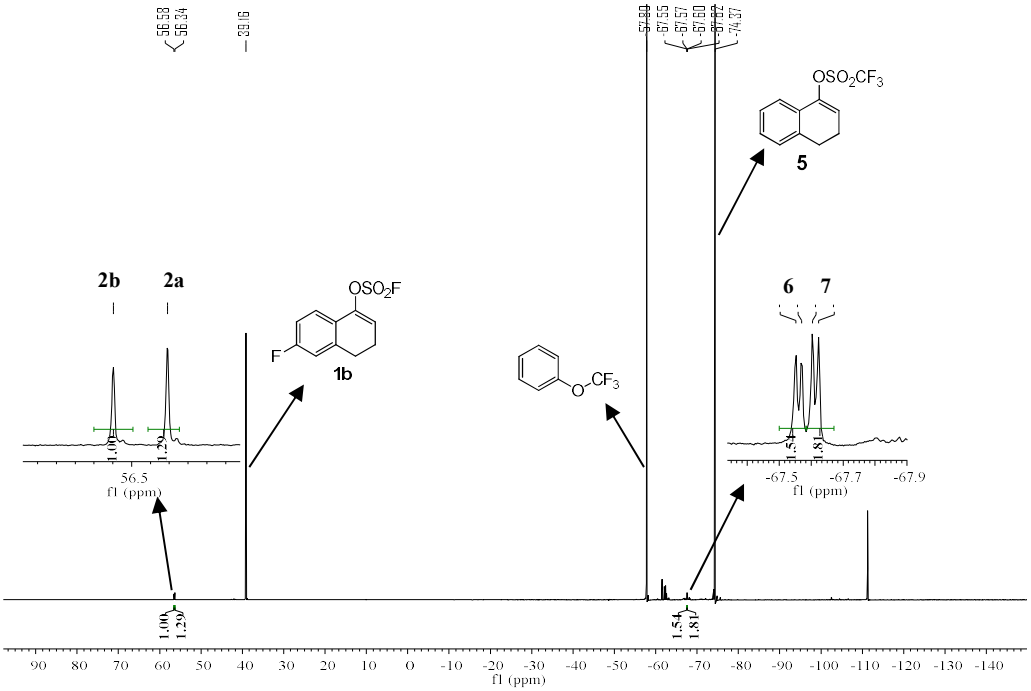
7.2 Cross-over reaction



2b : 2a : 6 : 7 = 1 : 1.3 : 0.5 : 0.6

To a 10 mL sealed tube equipped with a rubber septum and a magnetic stirring bar, **1b** (25 mg, 0.1 mmol), **5**[4] (28 mg, 0.1 mmol), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (2 mg, 0.002 mmol, 1 mol%) and 4 Å MS (44 mg) were added. The tube was evacuated and backfilled with N_2 for three times, and added with toluene (2.0 mL, 0.1 M). The

mixture was stirred and irradiated by 3 W blue LEDs for 12 hours at room temperature. The ratio of **2b** to **2a** to **6** to **7** (1:1.3:0.5:0.6) were determined by crude ^{19}F NMR with trifluoromethoxybenzene (32.4 mg, 0.2 mmol) as the internal standard.

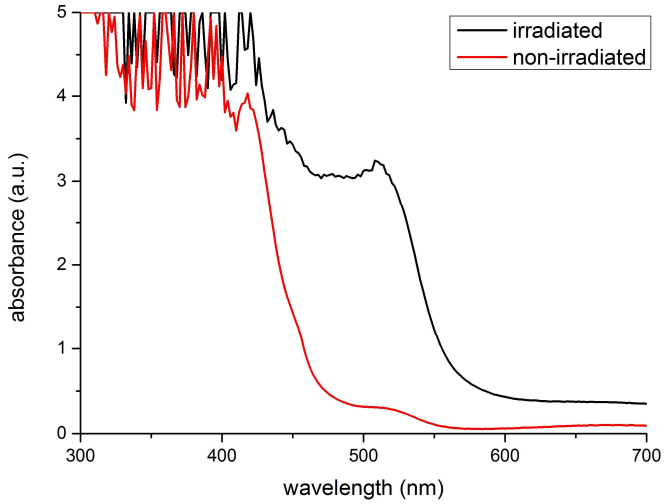


7.3 Determination of the photon quantum yield[6]

Determination of the light intensity at 436 nm: the photon flux of the spectrophotometer was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4. Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90.0 seconds at λ = 436 nm with an emission slit width at 10.0 nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm (Fig. S2). A non-irradiated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculated using eq 1.

$$\text{mol } Fe^{2+} = \frac{V \cdot \triangle A}{1 \cdot \varepsilon} \qquad (1)$$

Fig. S2 Absorbance of the ferrioxalate actinometer solution.



Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and ε is the molar absorptivity at 510 nm (11,100 L mol^{-1} cm^{-1}). The photon flux can be calculated using eq 2.

$$\text{photo flux} = \frac{\text{mol } Fe^{2+}}{\Phi \cdot t \cdot f} \qquad (2)$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.01 for a 0.15 M solution at λ = 436 nm), t is the time (90.0 s), and *f* is the fraction of light absorbed at λ = 436 nm (0.9998, *vide infra*). The photon flux was calculated (average of three experiments) to be 6.81 × 10^{-9} einstein s^{-1}.

Sample calculation:

$$\text{mol } Fe^{2+} = \frac{0.00235\text{L} \cdot 2.92206}{1.000\text{cm} \cdot 11100 \text{ L mol}^{-1}\text{cm}^{-1}} = 6.19 \times 10^{-7} \ mol$$

$$\text{photo flux} = \frac{6.19 \times 10^{-7} \text{ mol}}{1.01 \cdot 90.0 \ s \cdot 0.9998} = 6.81 \times 10^{-9} \ einstein \ s^{-1}$$

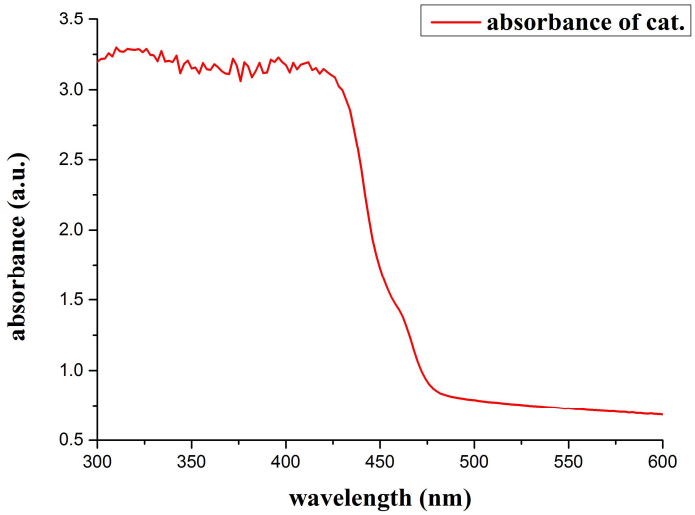
Determination of fraction of light absorbed at 436 nm for the ferrioxalate solution: the absorbance of the above ferrioxalate solution at 436 nm was measured to

be 2.92206. The fraction of light absorbed f by this solution was calculated using eq 3, where A is the measured absorbance at 436 nm.

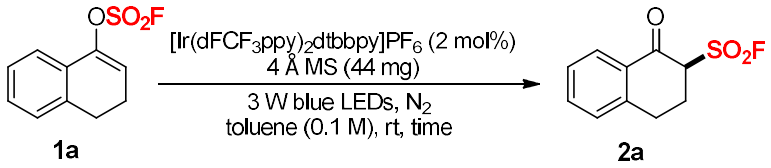
$$f = 1 - 10^{-A} \qquad (3)$$

The absorbance at 436 nm for a 2.0 $\times 10^{-4}$ M solution is >3 indicating the fraction of light absorbed is >0.999 (Fig. S3).

Fig. S3 Absorbance of catalyst.



Determination of reaction time



The tube was charged with **1a** (46 mg, 0.2 mmol, 1.0 equiv.), 4 Å MS (44 mg), [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$ (4 mg, 0.004 mmol, 2 mol%) and toluene (2.0 mL, 0.1 M). The sample was stirred at room temperature and irradiated (λ = 436 nm) for 7200 s (2 h). After irradiation, trifluoromethoxybenzene (32 mg, 0.2 mmol, 1.0 equiv.) was added as the internal standard. Yield of product formed was determined by ^{19}F NMR is 21%. The quantum yield was determined. Essentially all incident light (f > 0.999,

vide infra) is absorbed by the [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$ at the reaction conditions described above.

$$\Phi = \frac{\text{product}}{\text{flux} \cdot \text{t} \cdot \text{f}} \qquad (4)$$

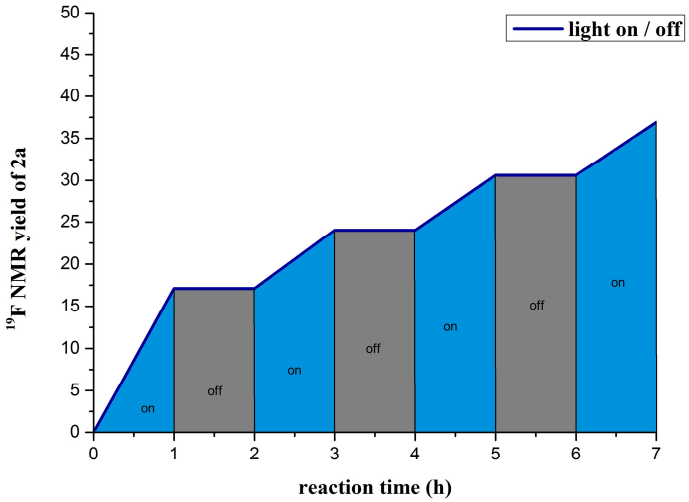
Sample quantum yield calculation:

$$\Phi = \frac{4.2 \times 10^{-5}\ \text{mol}}{6.81 \times 10^{-9}\ \text{einstein}\ \text{s}^{-1} \cdot 7200\ \text{s} \cdot 1.00} = 0.8611$$

7.4 Light on-off experiments

A tube was equipped with a stirring bar and charged with **1a** (46 mg, 0.2 mmol, 1.0 equiv.), [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$ (2 mg, 0.002 mmol, 1 mol%), 4 Å MS (44 mg) trifluoromethoxybenzene (32 mg, 0.2 mmol, 1.0 equiv.) and toluene (2.0 mL, 0.1 M). The reaction was stirred at room temperature and the reaction was alternatively irradiated with 3 W blue LEDs and kept in the dark in 1 hour intervals. Yield of **2a** was determined by crude ^{19}F NMR with trifluoromethoxybenzene as the internal standard (Fig. S4).

Fig. S4 Line chart of light on-off experiments.



7.5. Luminescence quenching of [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$ by **1a**

Fig. S5 Emission quenching of [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$ by **1a** (0.1 M) after irradiation at 460 nm. [Ir] = 0.001M in toluene.

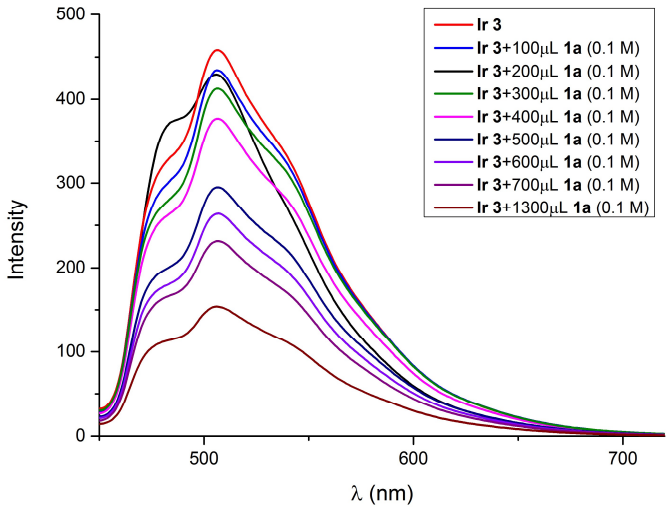


Fig. S6 Stern-Volmer plot for the emission quenching of [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$ by **1a** (0.1 M).

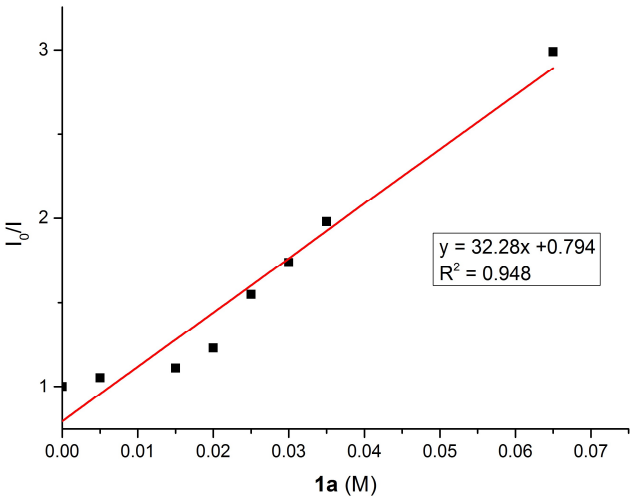


Fig. S7 Emission quenching of [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$ and 4 Å MS by **1a** (0.1 M) after irradiation at 460 nm. [Ir] = 0.001M, 4 Å MS (44 mg) in toluene.

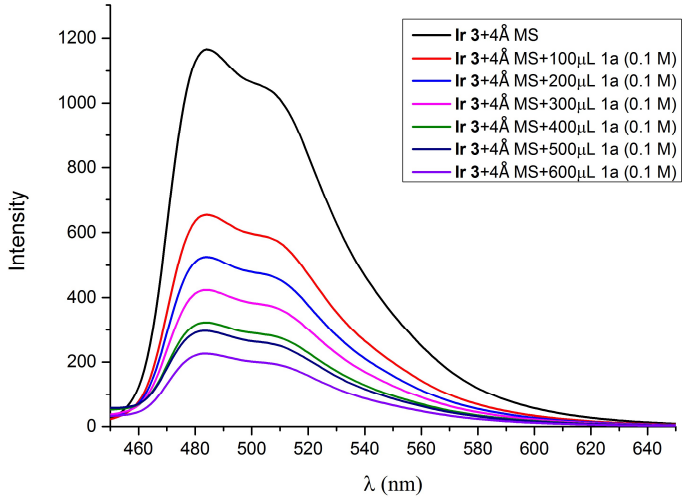


Fig. S8 Stern-Volmer plot for the emission quenching of [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$ and 4 Å MS by **1a** (0.1 M).

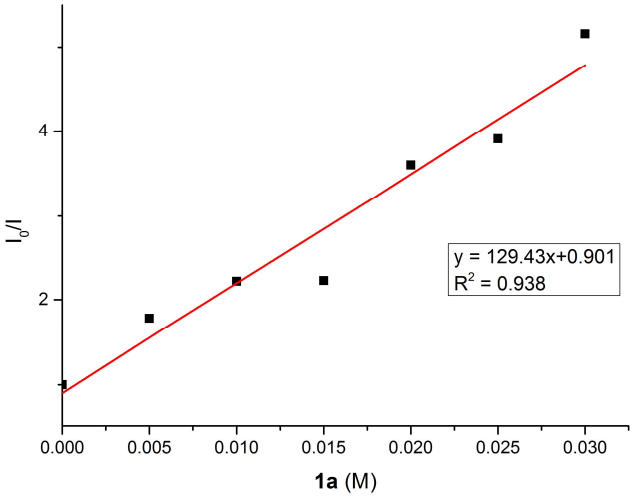


Fig. S9 Emission quenching of $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ and Na_2CO_3 by **1a** (0.1 M) after irradiation at 460 nm. [Ir] = 0.001 M, Na_2CO_3 = 0.1 M toluene.

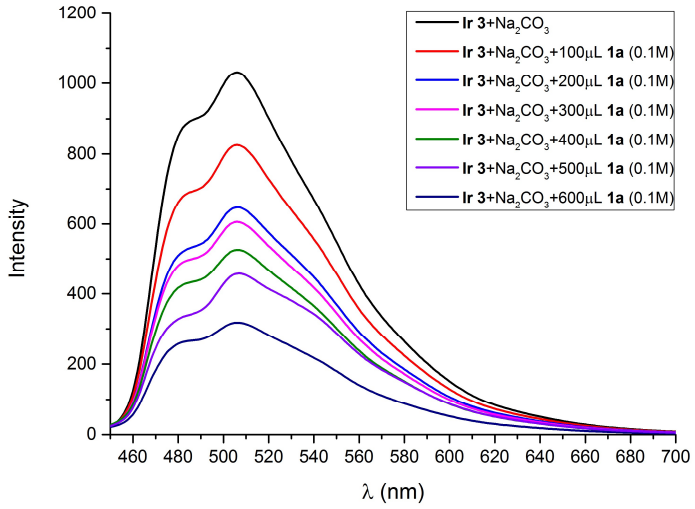
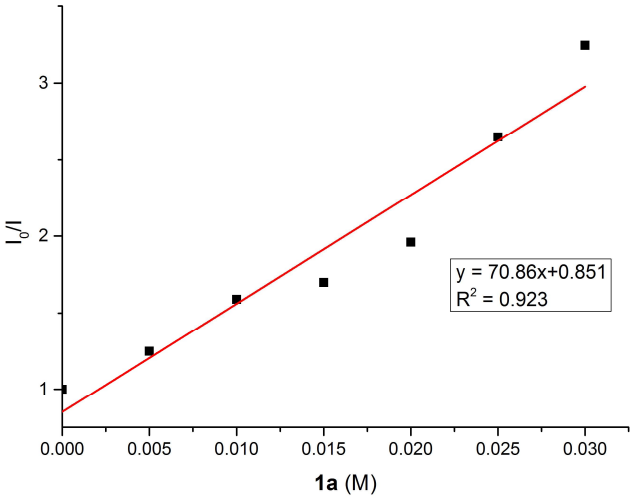
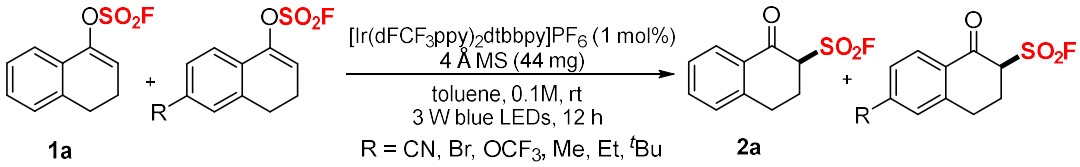


Fig. S10 Stern-Volmer plot for the emission quenching of $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ and Na_2CO_3 by **1a** (0.1 M).

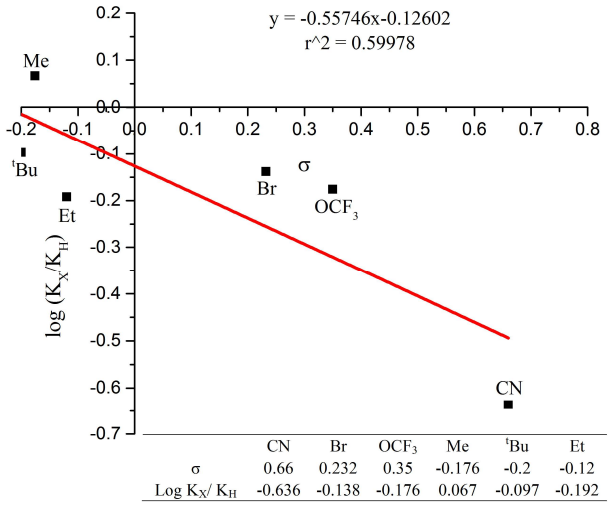


7.6 Hammett equation



To a flame dried sealing tube equipped with a stirring bar, 4 Å MS (44 mg) and [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$ (2 mg, 0.002 mmol, 1 mol%), **1a** (22 mg, 0.1 mmol) and other substrates (0.1 mmol) (R = CN, Br, OCF$_3$, Me, Et, ^{t}Bu) were added respectively. Toluene (2 mL) was added afterwards. The mixture were irradiated by 3 W blue LEDs for 12 h at room temperature, and then monitored by crude ^{19}F NMR. The electronic effect on the aromatic ring of styrene is significant and a negative ρ value (-0.55746) in Hammett plot was given in below, which means a cation or radical cation intermediate formed during the reaction process (Fig. S11).

Fig. S11 Hammett plot of para-substituents in aromatic rings.

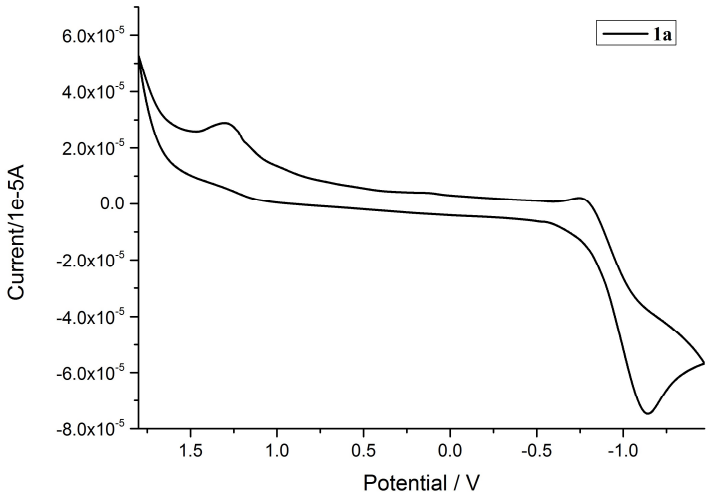


	CN	Br	OCF_3	Me	^{t}Bu	Et
σ	0.66	0.232	0.35	-0.176	-0.2	-0.12
Log K_X/ K_H	-0.636	-0.138	-0.176	0.067	-0.097	-0.192

7.7 Cyclic voltammetry experiment

General information: cyclic voltammetry (CV) experiments were conducted in a 10 mL glass vial fitted with a glassy carbon working electrode (3 mm in diameter), a platinum wire auxiliary electrode and SCE reference electrode. Current was reported in A, while all potentials were reported in V against the Fc^{+}/Fc redox couple. The scan rate was 0.1 V/s.

Fig. S12 Cyclic voltammetry curve of substrate **1a**



Cyclic voltammograms of **1a** (0.1 mmol) in acetonitrile (MeCN) containing 5 mmol $^{n}Bu_4NPF_6$ as the electrolyte.

7.8 DFT Calculations on the triplet energies of substrate **1a**[7]

In order to clarify the initiation mechanism, we applied DFT calculations on the triplet energy of enol fluorosulflate **1a**. The reported triplet energy of $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ is 251 kJ/mol. [8] The calculated triplet energy of **1a**, in which the two SOMOs are mainly localized on the C=C (Fig. S12) is 100 kJ/mol. The calculated decomposition energy of vinyl fluorosulfate **1a** into enol radical and fluorosulfinyl radical is 134 kJ/mol, which are much lower than the triplet energy of $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (Scheme S1). The DFT calculations show that the energy transfer from the excited photocatalyst to substrate is possible.

Scheme S1 Triplet energy of **1a** and [Ir(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$.

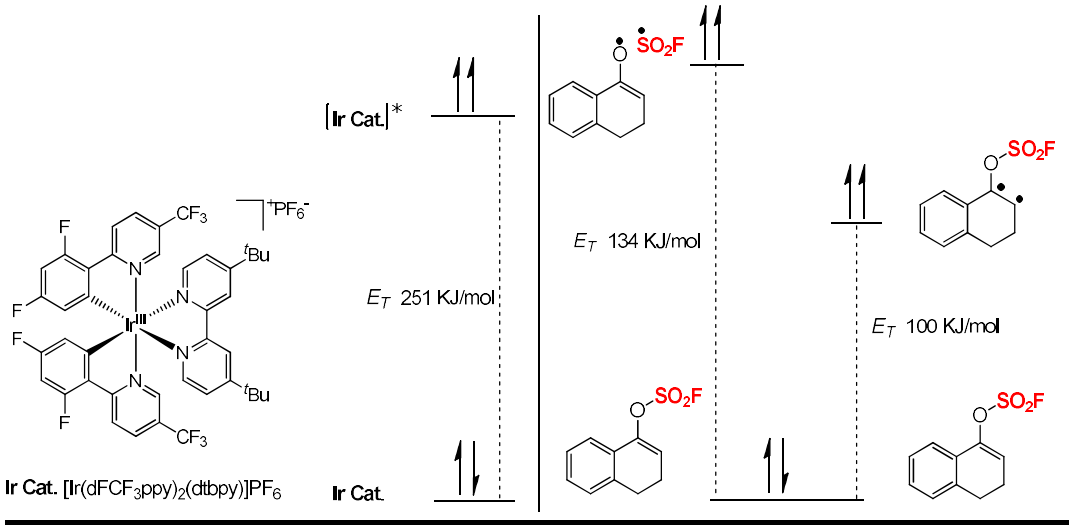
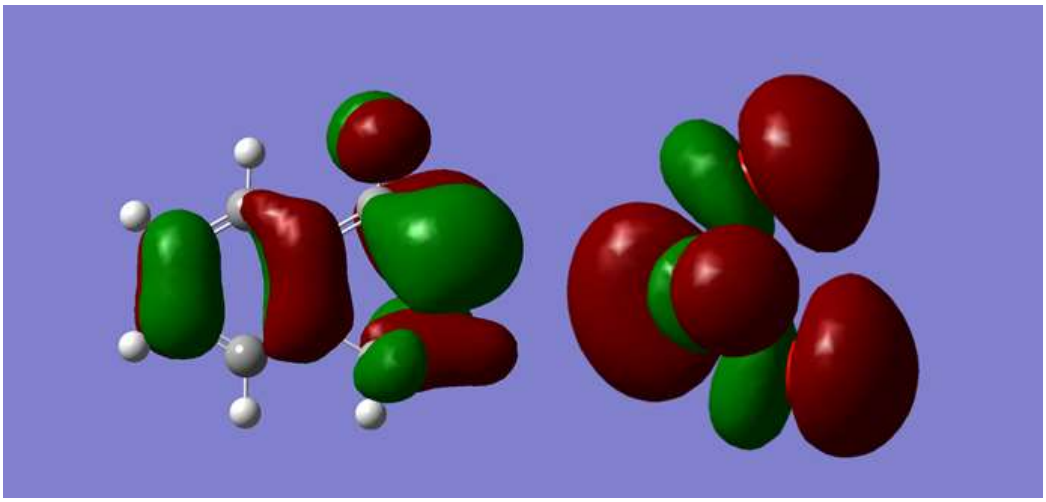


Fig. S13 SOMOs of the triplet state of **1a** by B3LYP/ 6-31+g(d,p).guess=(mix,always) nosymm



Computational methods:

All calculations were calculated using the Gaussian 09 package[9]. The geometries of catalyst and substrate were optimized, without imposing symmetry constraints, at the B3LYP density functional level using the 6-31+g(d,p) basis set. The minima were confirmed with all real frequencies.

Energies and Cartesian coordinates of all structures:

3,4-dihydronaphthalen-1-yl sofluoroulfate **1a**

Ground state: singlet Opt at B3LYP/6-31-31+g(d,p) nosymm

SCF Done: E(RB3LYP) = -1110.146288 A.U.

C	-5.13800000	-2.63700000	-0.41200000
C	-6.16200000	-3.04700000	-1.14100000
C	-7.19000000	-2.23700000	-1.33300000
C	-7.20100000	-1.01500000	-0.78100000
C	-6.18400000	-0.52700000	-0.02300000
C	-5.15300000	-1.41000000	0.11200000
C	-8.40000000	-0.05000000	-1.08200000
C	-8.60300000	1.00400000	0.01200000
C	-7.30800000	1.48000000	0.55000000
C	-6.17600000	0.70100000	0.50100000
F	-5.50300000	3.99800000	0.54900000
H	-4.28600000	-3.30300000	-0.25200000
H	-6.15300000	-4.04300000	-1.58800000
H	-8.02100000	-2.57500000	-1.95600000
H	-4.27600000	-1.13400000	0.70900000
H	-9.35400000	-0.59800000	-1.24600000
H	-8.18200000	0.43900000	-2.05900000
H	-9.20500000	1.85300000	-0.38500000
H	-9.19200000	0.60100000	0.86600000
H	-7.53700000	2.49500000	0.97400000
O	-5.02000000	1.26900000	1.06700000
O	-3.67800000	3.16000000	2.21100000
O	-5.98900000	2.87800000	2.85700000
S	-5.02900000	2.79600000	1.72200000

Triplet at Opt B3LYP/6-31+g(d,p) guess=(mix,always) nosymm

SCF Done: E(RB3LYP) = -1110.108260 A.U.

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C	-7.19000000	-2.23700000	-1.33300000
C	-7.20100000	-1.01500000	-0.78100000
C	-6.18400000	-0.52700000	-0.02300000
C	-5.15300000	-1.41000000	0.11200000
C	-8.40000000	-0.05000000	-1.08200000
C	-8.60300000	1.00400000	0.01200000
C	-7.30800000	1.48000000	0.55000000
C	-6.17600000	0.70100000	0.50100000
F	-5.50300000	3.99800000	0.54900000
H	-4.28600000	-3.30300000	-0.25200000
H	-6.15300000	-4.04300000	-1.58800000
H	-8.02100000	-2.57500000	-1.95600000
H	-4.27600000	-1.13400000	0.70900000
H	-9.35400000	-0.59800000	-1.24600000
H	-8.18200000	0.43900000	-2.05900000
H	-9.20500000	1.85300000	-0.38500000
H	-9.19200000	0.60100000	0.86600000
H	-7.53700000	2.49500000	0.97400000
O	-5.02000000	1.26900000	1.06700000
O	-3.67800000	3.16000000	2.21100000
O	-5.98900000	2.87800000	2.85700000
S	-5.02900000	2.79600000	1.72200000

Enol radical

Doublet Opt at B3LYP/6-31+g(d,p) guess=(mix,always) nosymm

SCF Done: E(RB3LYP) = -461.704720 A.U.

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C	-7.20100000	-1.01500000	-0.78100000
C	-6.18400000	-0.52700000	-0.02300000
C	-5.15300000	-1.41000000	0.11200000
C	-8.40000000	-0.05000000	-1.08200000
C	-8.60300000	1.00400000	0.01200000
C	-7.30800000	1.48000000	0.55000000
C	-6.17600000	0.70100000	0.50100000
H	-4.28600000	-3.30300000	-0.25200000
H	-6.15300000	-4.04300000	-1.58800000
H	-8.02100000	-2.57500000	-1.95600000
H	-4.27600000	-1.13400000	0.70900000
H	-9.35400000	-0.59800000	-1.24600000
H	-8.18200000	0.43900000	-2.05900000
H	-9.20500000	1.85300000	-0.38500000
H	-9.19200000	0.60100000	0.86600000
H	-7.53700000	2.49500000	0.97400000
O	-5.02000000	1.26900000	1.06700000

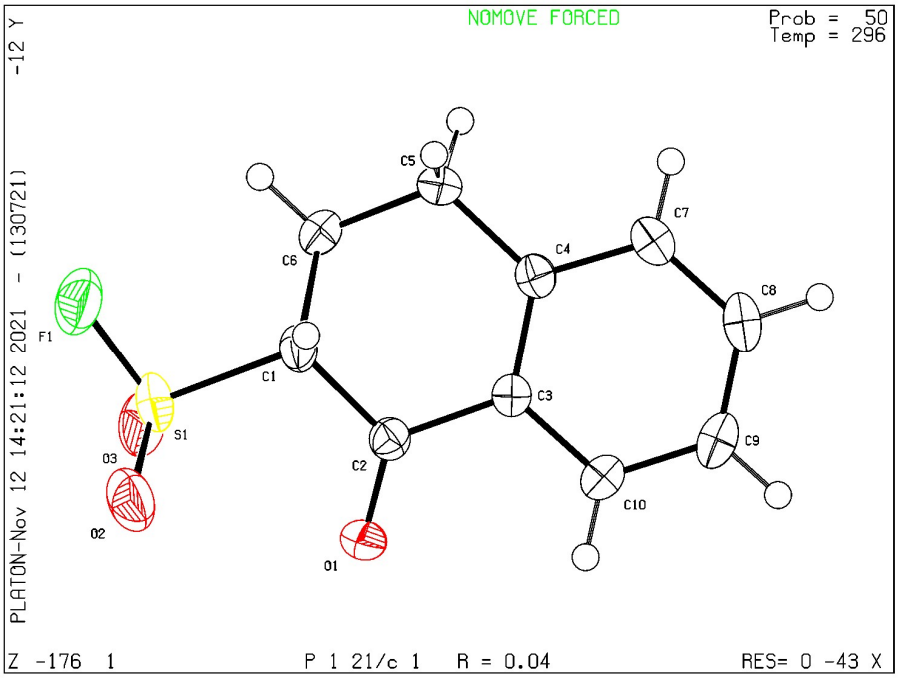
Fluorosulfonyl radical

Doublet Opt at B3LYP/6-31+g(d,p) guess=(mix,always) nosymm

SCF Done: E(RB3LYP) = -648.390661 A.U.

F	-5.50300000	3.99800000	0.54900000
O	-3.67800000	3.16000000	2.21100000
O	-5.98900000	2.87800000	2.85700000
S	-5.02900000	2.79600000	1.72200000

8. X-ray crystal data for **2a**



Thermal ellipsoids are set at 50% probability.

Crystal data and structure refinement for **2a** (CCDC: 2142067)

Empirical formula	$C_{10}H_9FO_3S$
Formula weight	228.23
Temperature/K	296
Cryst Crystal system al system	monoclinic
Identification code	**2a**
Space group	$P2_1/c$
a/Å	10.2088(6)
b/Å	11.1724(5)
c/Å	8.9589(5)
α/°	90
β/°	108.436(2)
γ/°	90
Volume/Å^3	969.38(9)
Z	4
ρ_{calcg}/cm^3	1.564
μ/mm^{-1}	0.331
F(000)	472.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	MoK\α (λ = 0.71073)
2Θ range for data collection/°	2.78 to 24.99
Index ranges	-12<=h<=12; -12<=k<=12; -10<l=10

Reflections collected	15025
Independent reflections	1711 [R_{int} = 0.0332, Rsigma = 0.0193]
Data/restraints/parameters	1711/0/136
Goodness-of-fit on F^2	1.044
Final R indices [I >= 2σ (I)]	R_1 = 0.0367, wR_2 = 0.0935
Final R indices (all data)	R_1 = 0.0444, wR_2 = 0.0976
Largest diff. peak/hole / e $Å^{-3}$	0.453/-0.335

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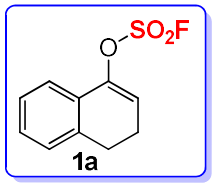
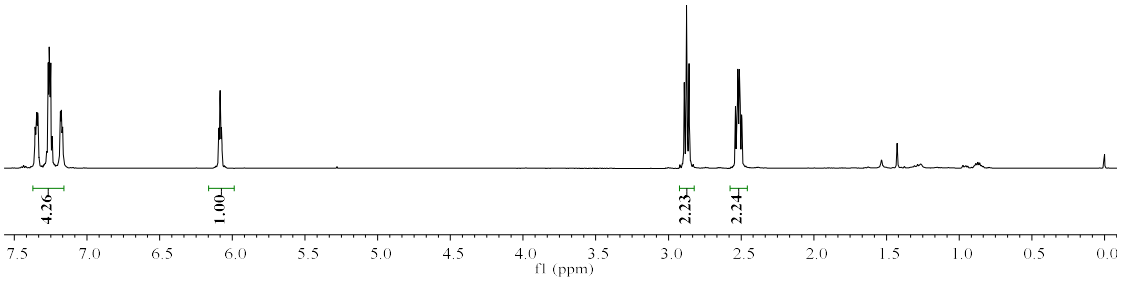
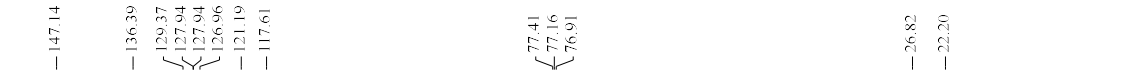
10. Spectra

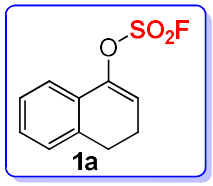
^{1}H NMR (500 MHz, $CDCl_3$) for **1a**

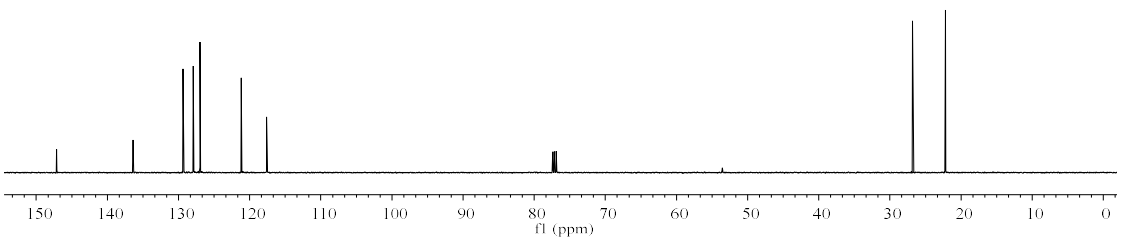




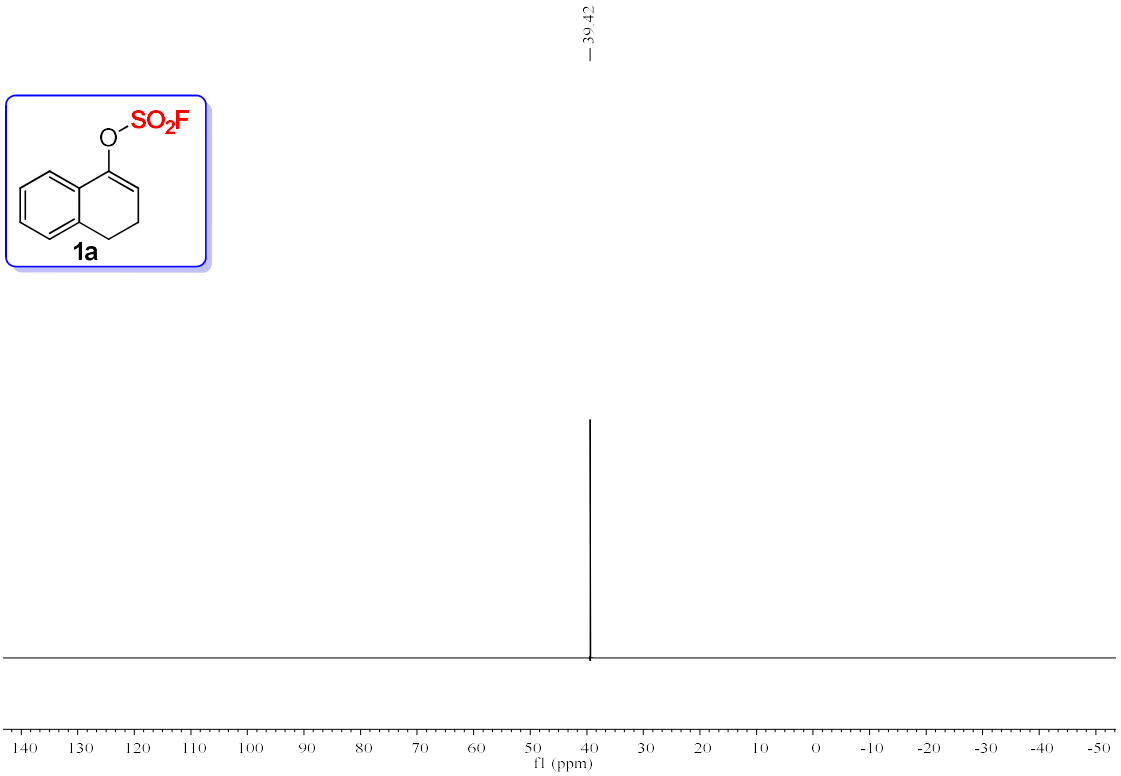
^{13}C NMR (126 MHz, $CDCl_3$) for **1a**



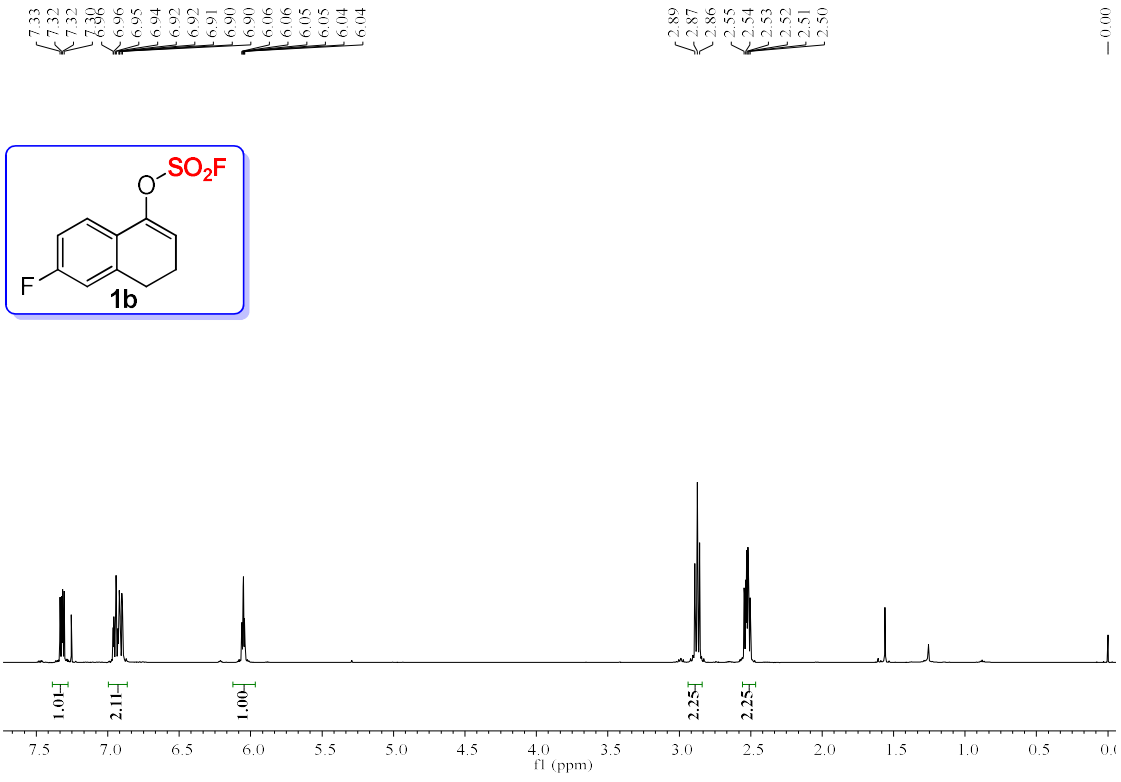




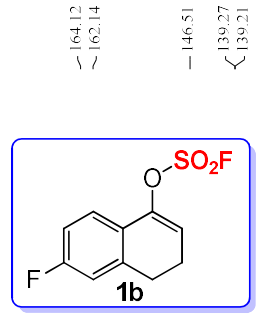
^{19}F NMR (471 MHz, $CDCl_3$) for **1a**



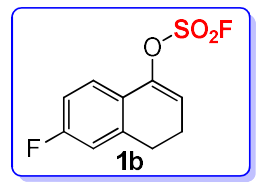
^{1}H NMR (500 MHz, $CDCl_3$) for **1b**



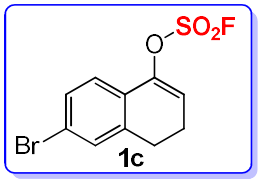
^{13}C NMR (126 MHz, $CDCl_3$) for **1b**

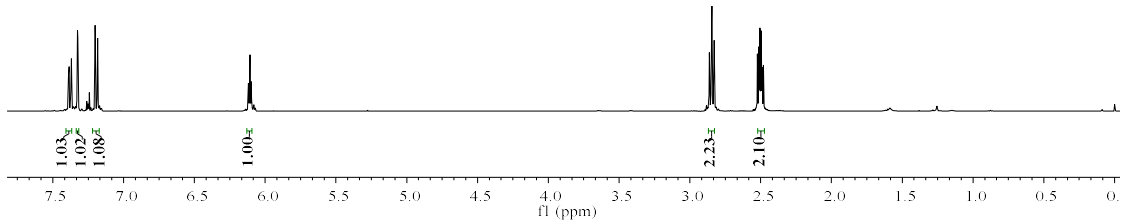


^{19}F NMR (471 MHz, $CDCl_3$) for **1b**

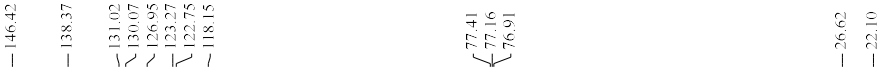


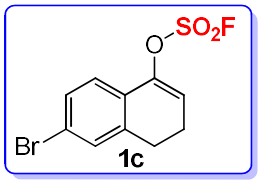
^{1}H NMR (500 MHz, $CDCl_3$) for **1c**

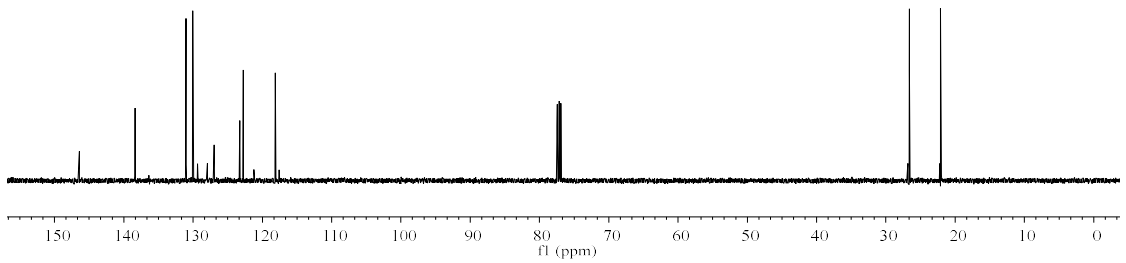




^{13}C NMR (126 MHz, $CDCl_3$) for **1c**







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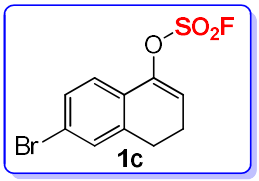
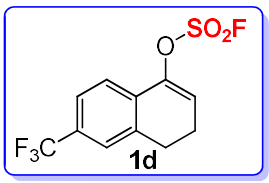
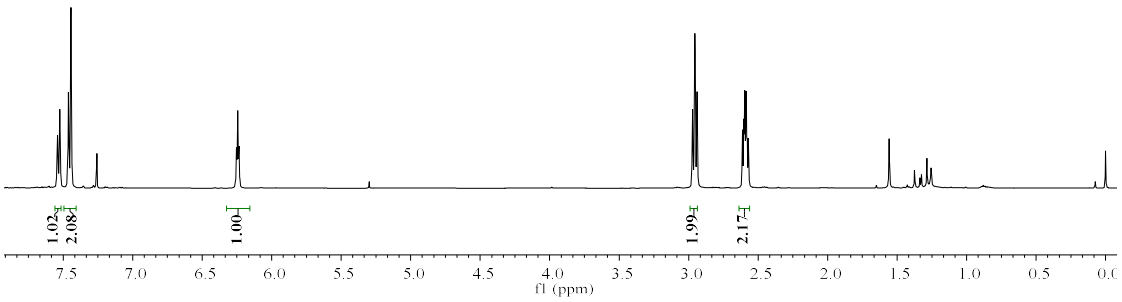


^{1}H NMR (500 MHz, $CDCl_3$) for **1d**





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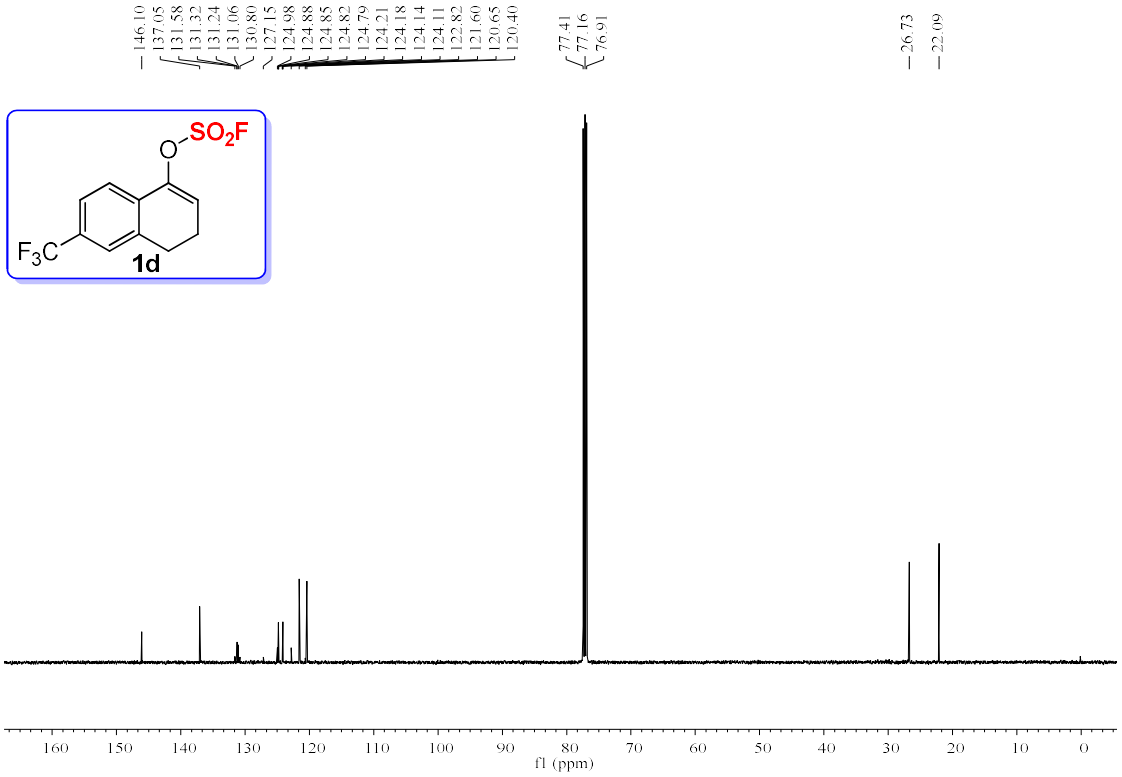
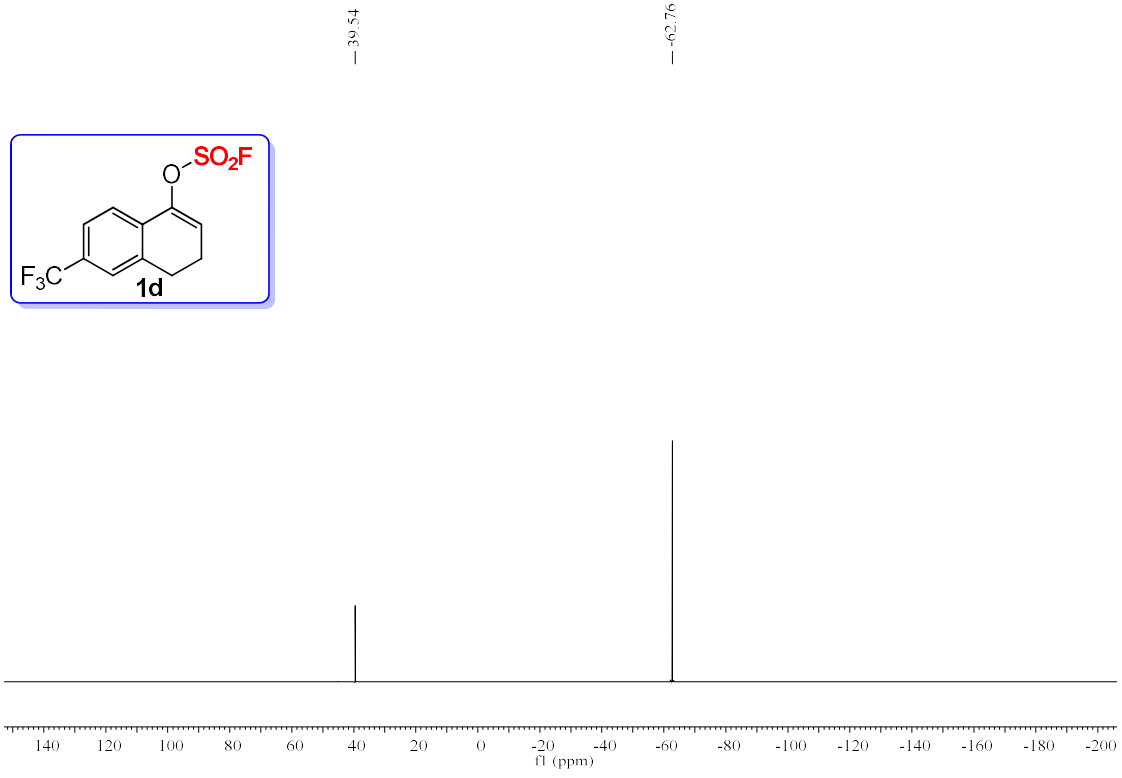
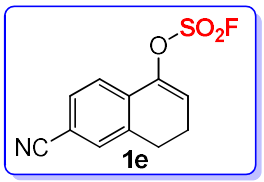
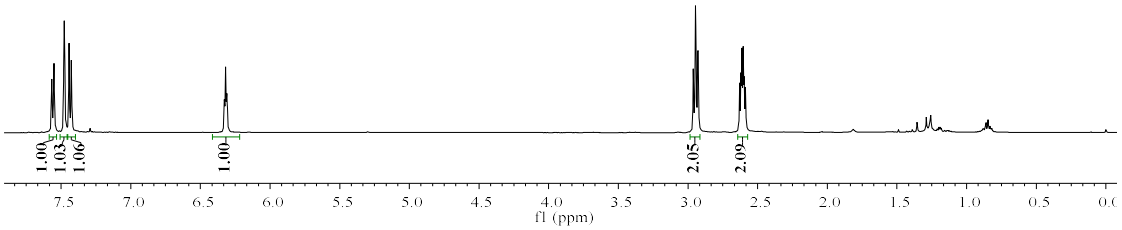


^{19}F NMR (471 MHz, $CDCl_3$) for **1d**

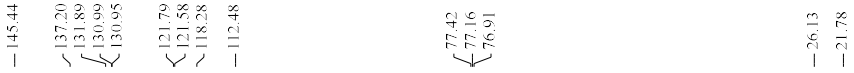


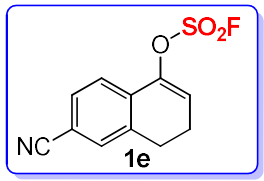
^{1}H NMR (500 MHz, $CDCl_3$) for **1e**

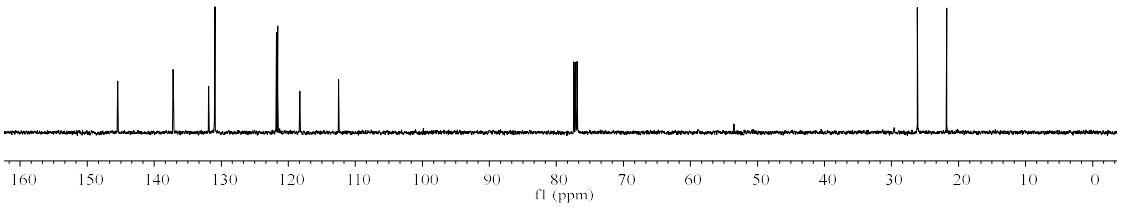




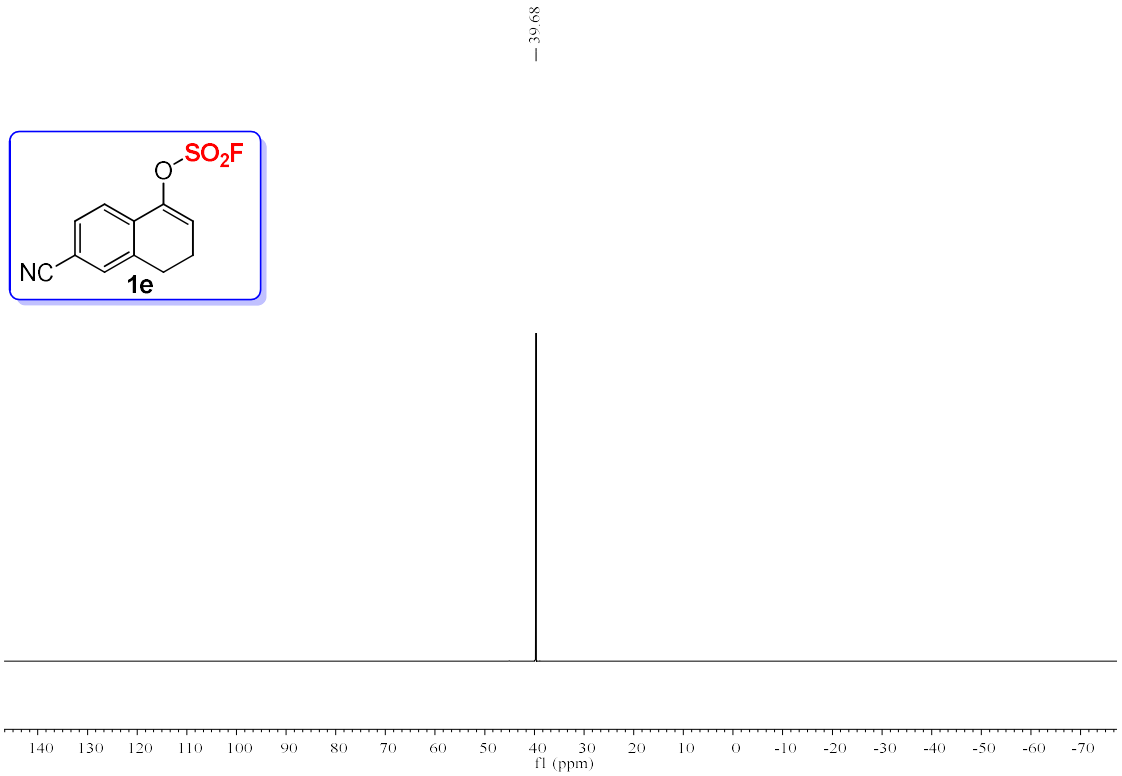
^{13}C NMR (126 MHz, $CDCl_3$) for **1e**



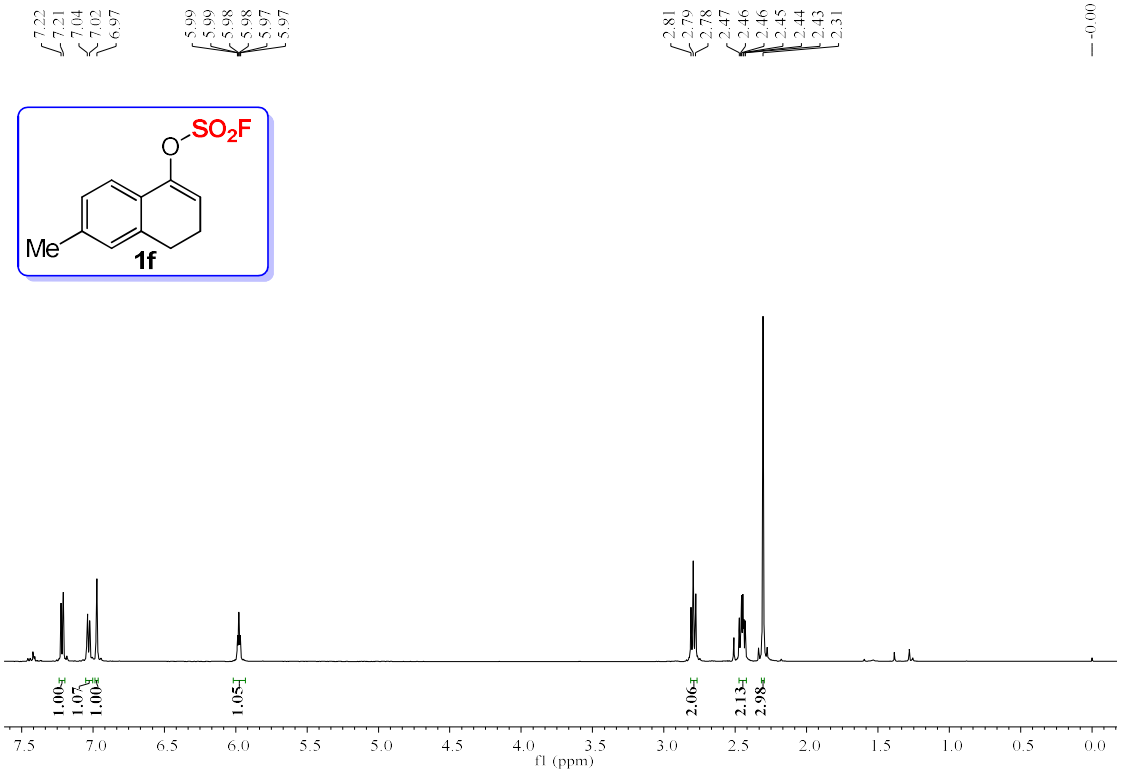




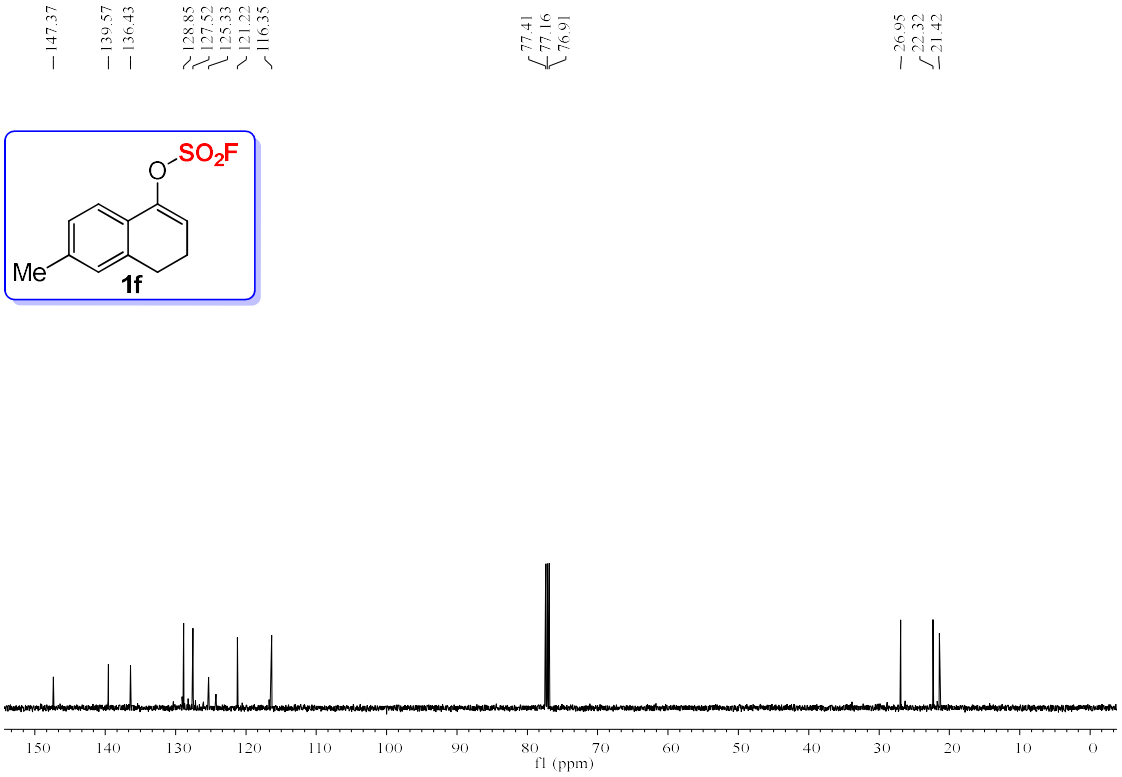
^{19}F NMR (471 MHz, $CDCl_3$) for **1e**



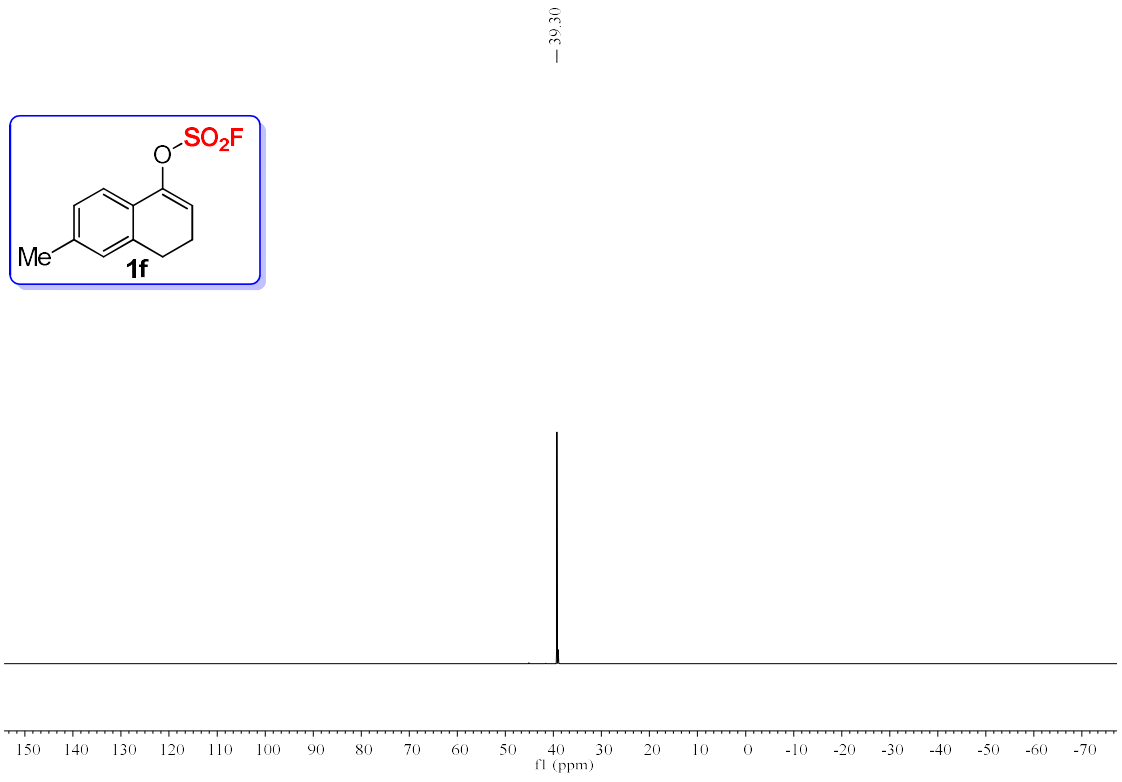
^{1}H NMR (500 MHz, $CDCl_3$) for **1f**



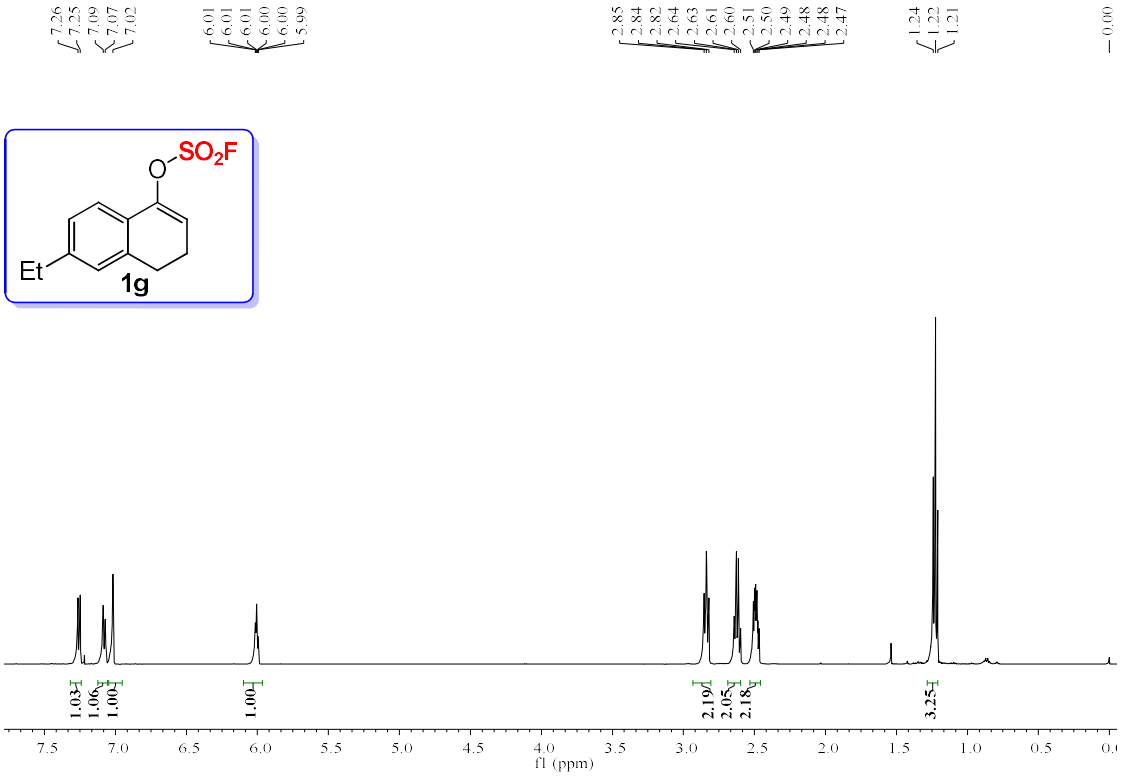
^{13}C NMR (126 MHz, $CDCl_3$) for **1f**



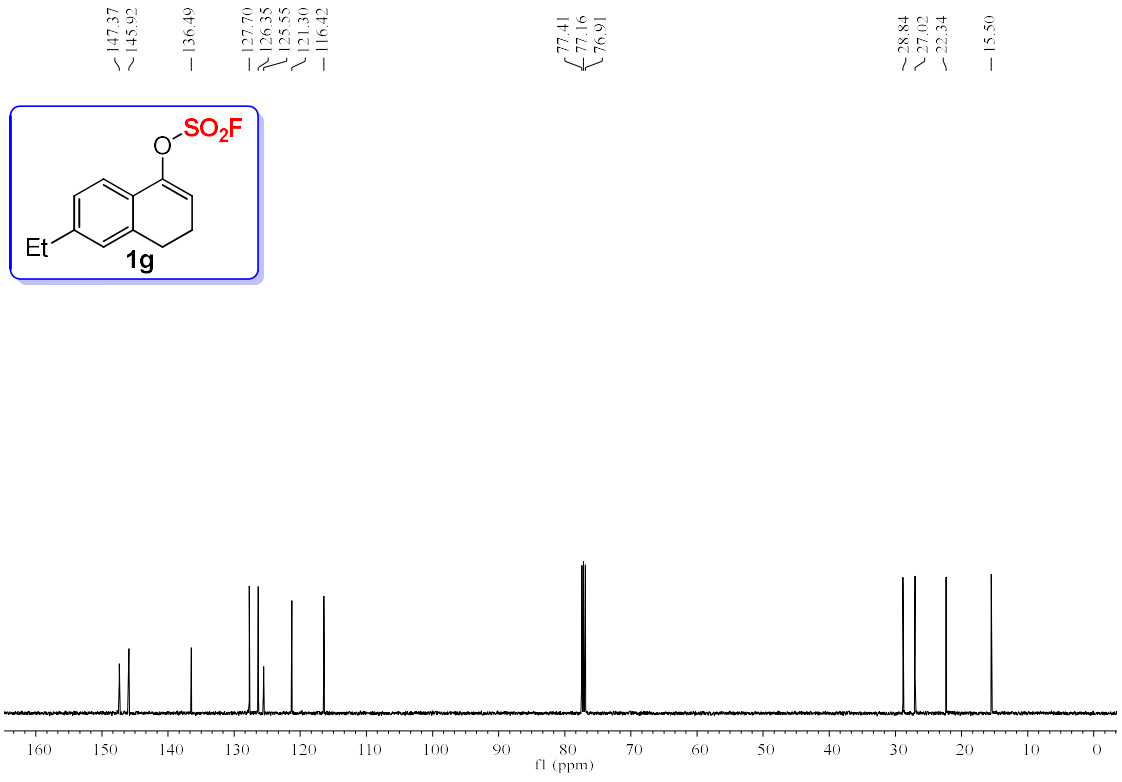
^{19}F NMR (471 MHz, $CDCl_3$) for **1f**



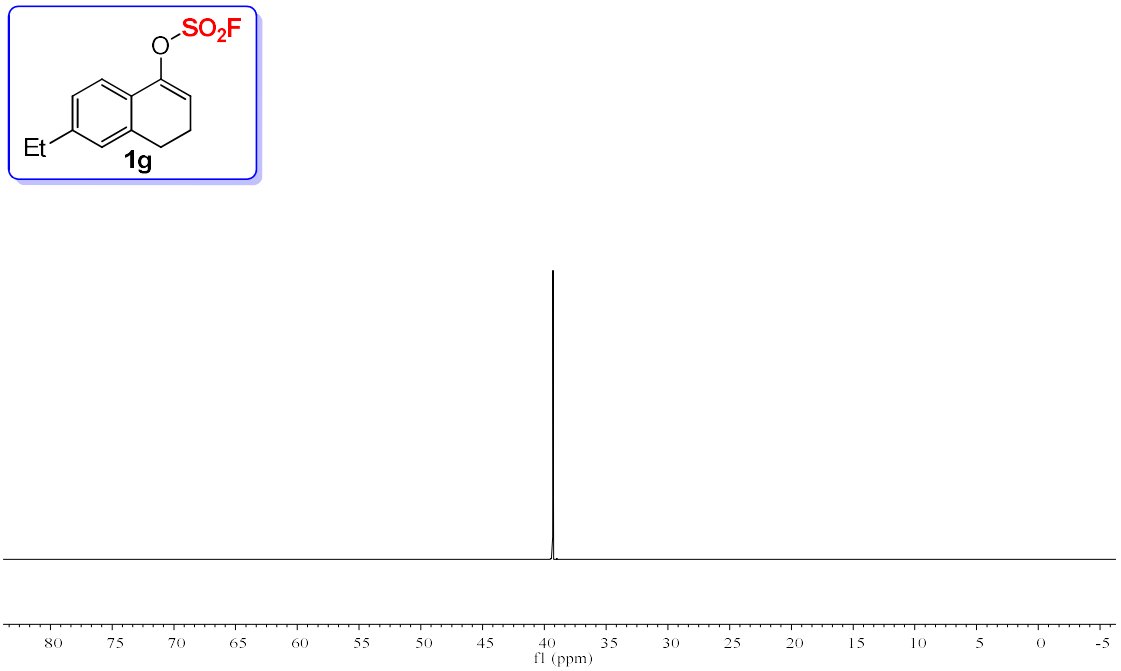
^{1}H NMR (500 MHz, $CDCl_3$) for **1g**



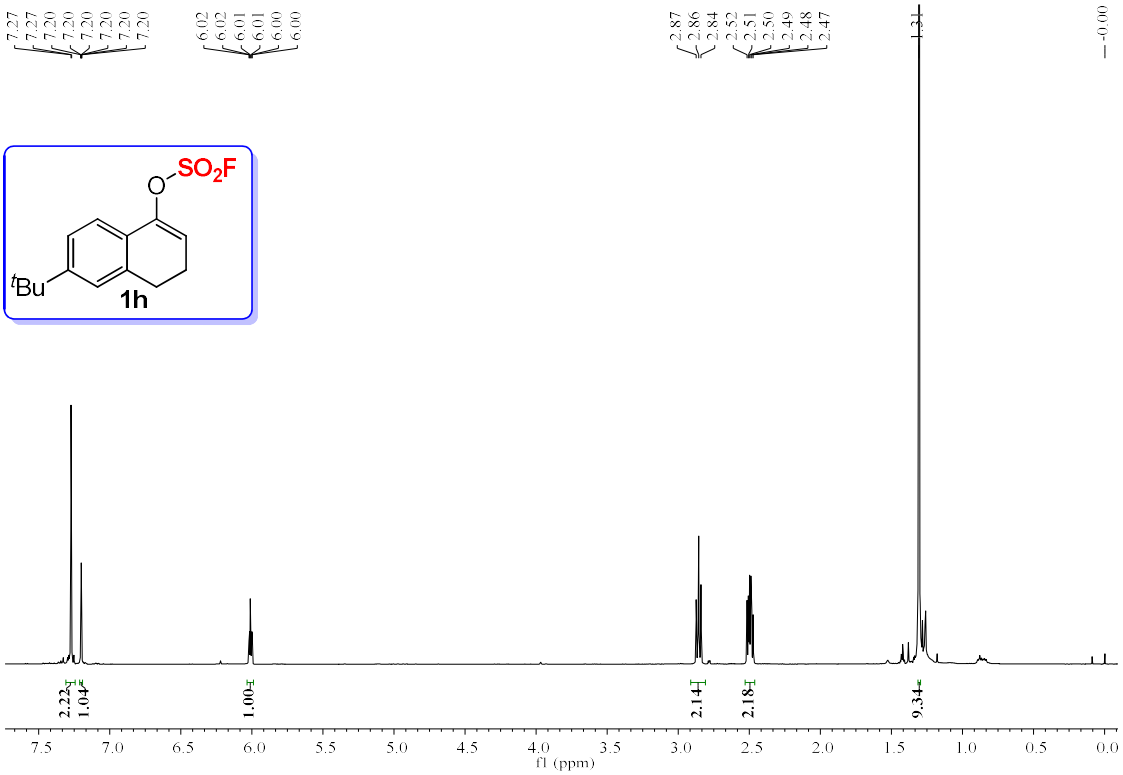
^{13}C NMR (126 MHz, $CDCl_3$) for **1g**



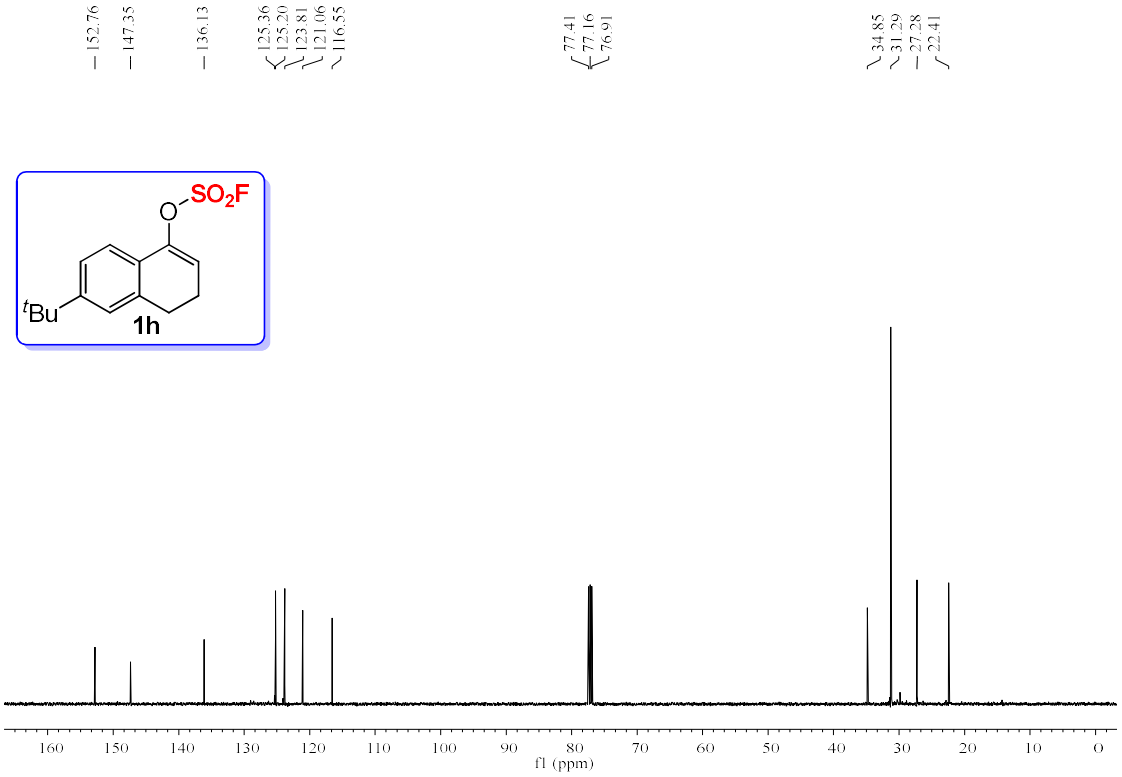
^{19}F NMR (471 MHz, $CDCl_3$) for **1g**



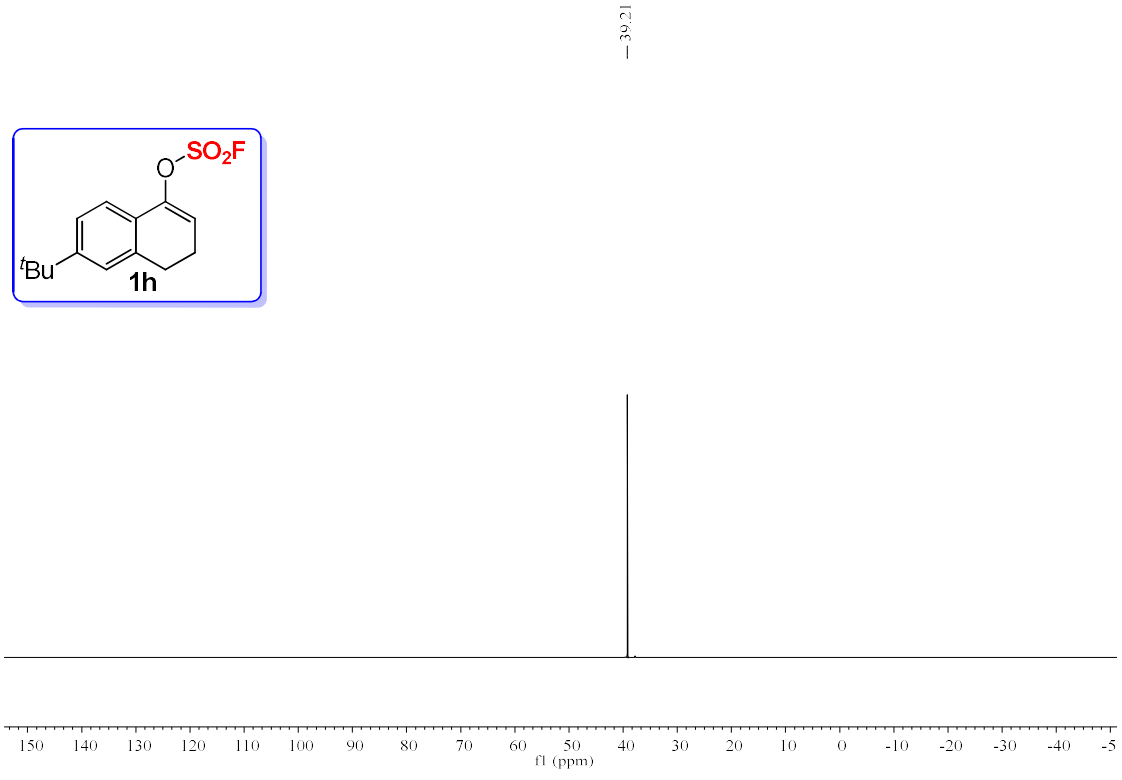
^{1}H NMR (500 MHz, $CDCl_3$) for **1h**



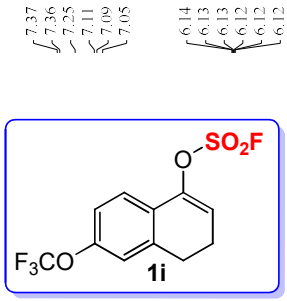
^{13}C NMR (126 MHz, $CDCl_3$) for **1h**

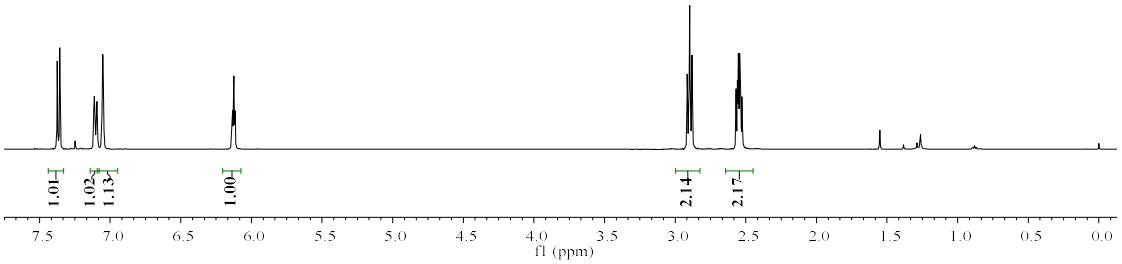


^{19}F NMR (471 MHz, $CDCl_3$) for **1h**

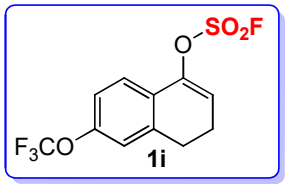


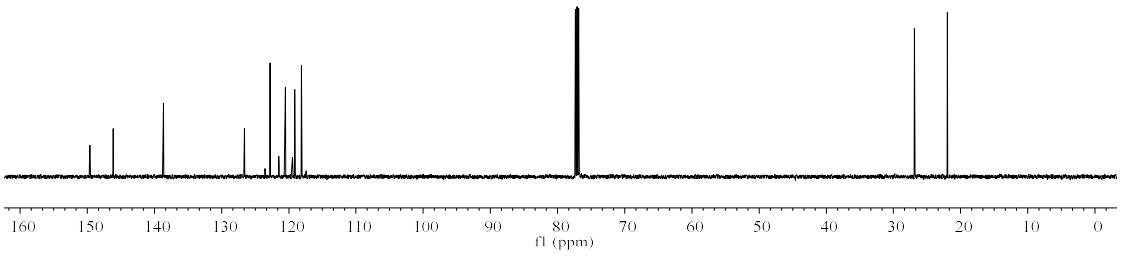
^{1}H NMR (500 MHz, $CDCl_3$) for **1i**



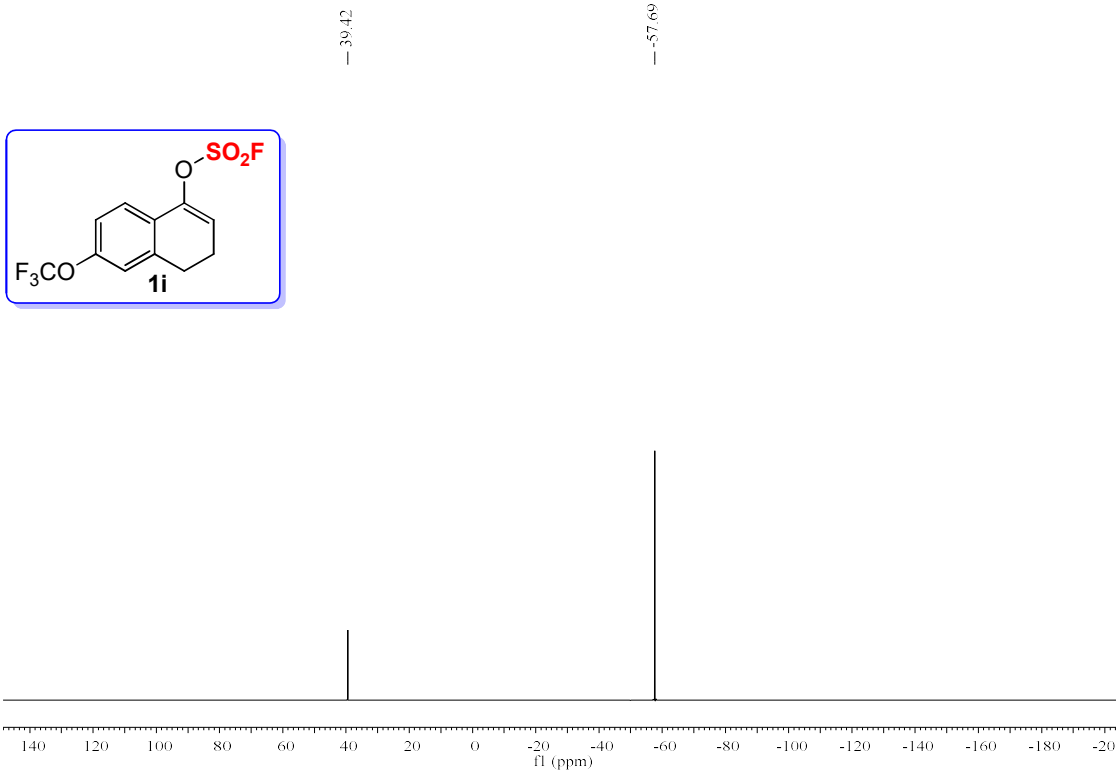


^{13}C NMR (126 MHz, $CDCl_3$) for **1i**

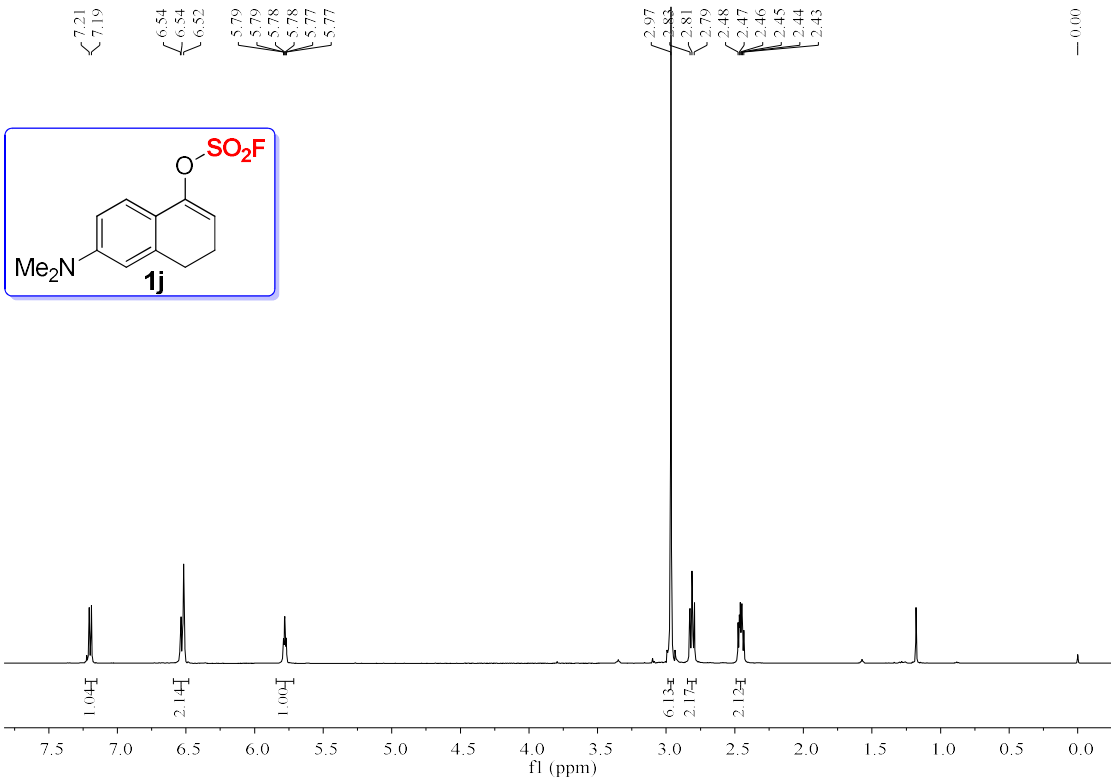




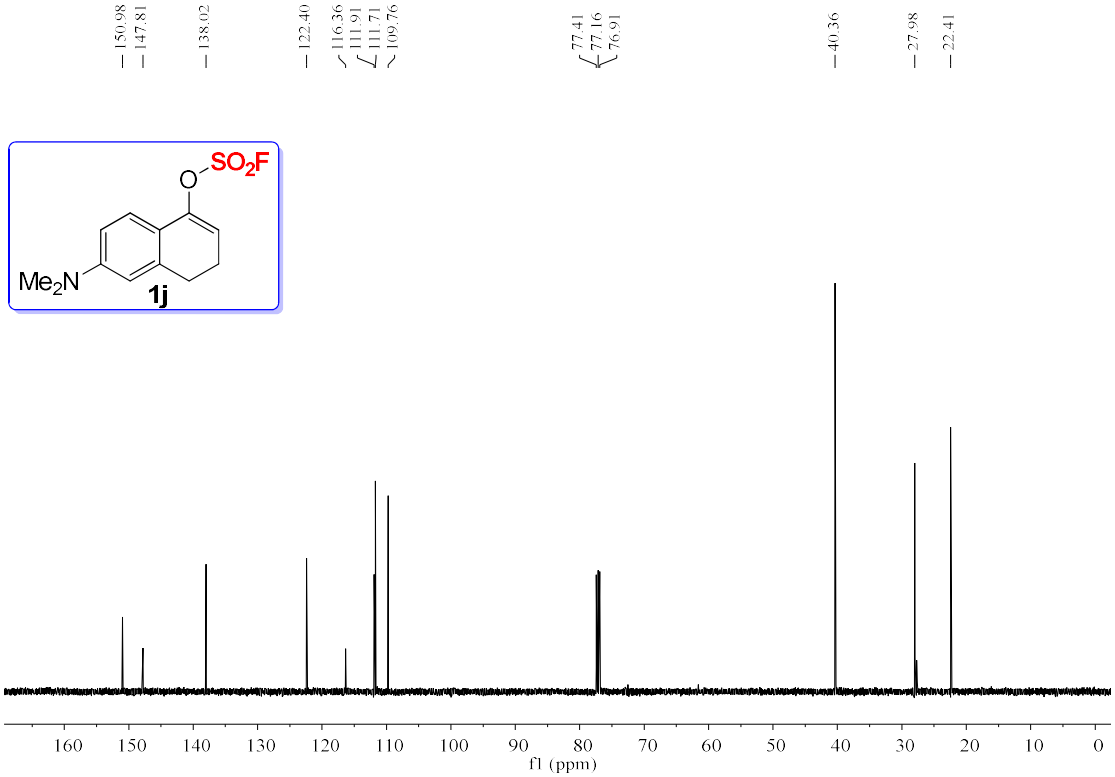
^{19}F NMR (471 MHz, $CDCl_3$) for **1i**



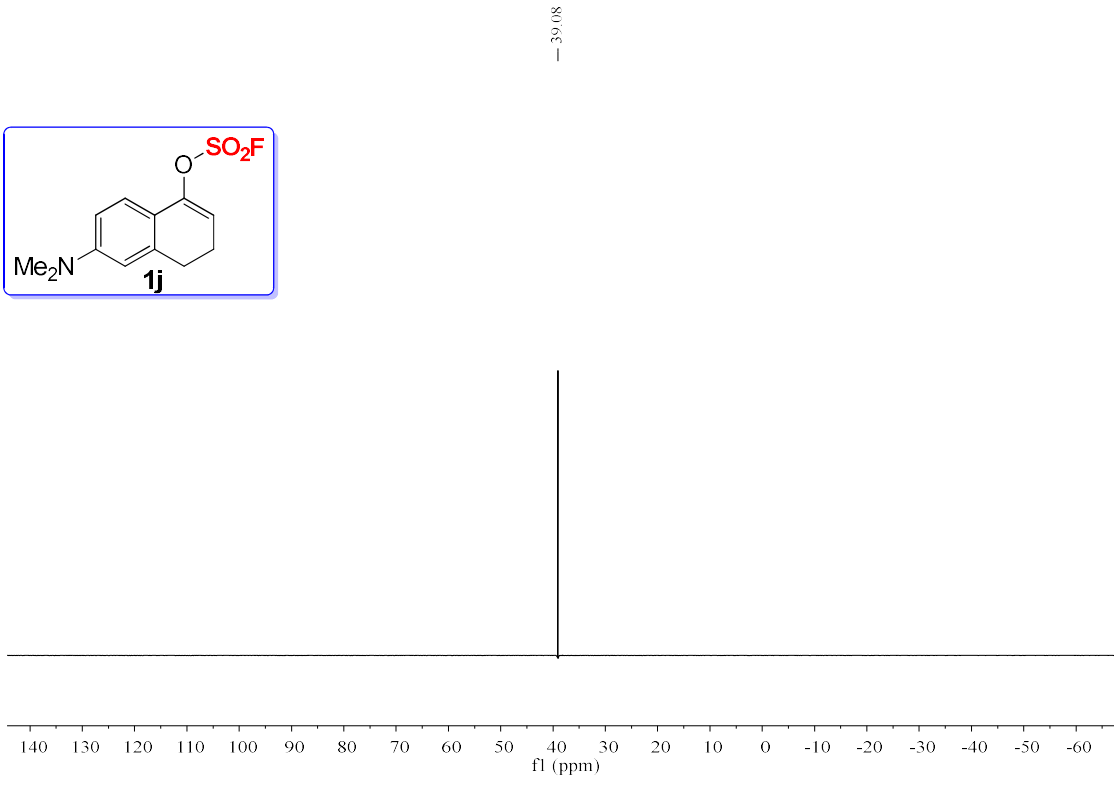
^{1}H NMR (500 MHz, $CDCl_3$) for **1j**



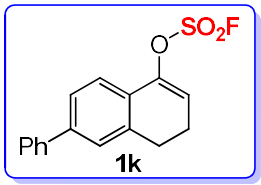
^{13}C NMR (126 MHz, $CDCl_3$) for **1j**

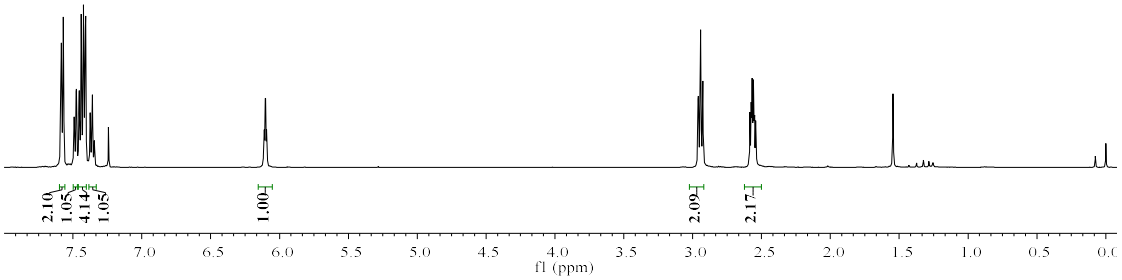


^{19}F NMR (471 MHz, $CDCl_3$) for **1j**



^{1}H NMR (500 MHz, $CDCl_3$) for **1k**





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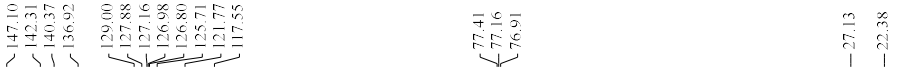
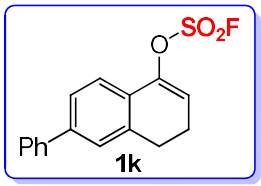
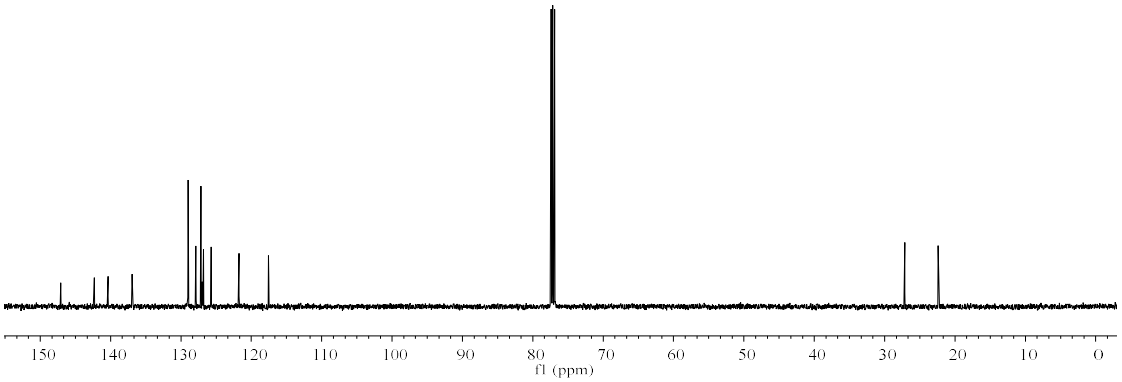
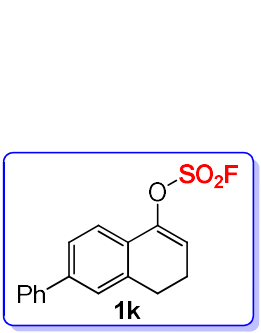






^{19}F NMR (471 MHz, $CDCl_3$) for **1k**



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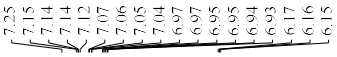
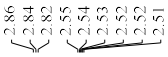
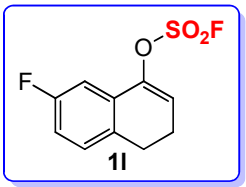
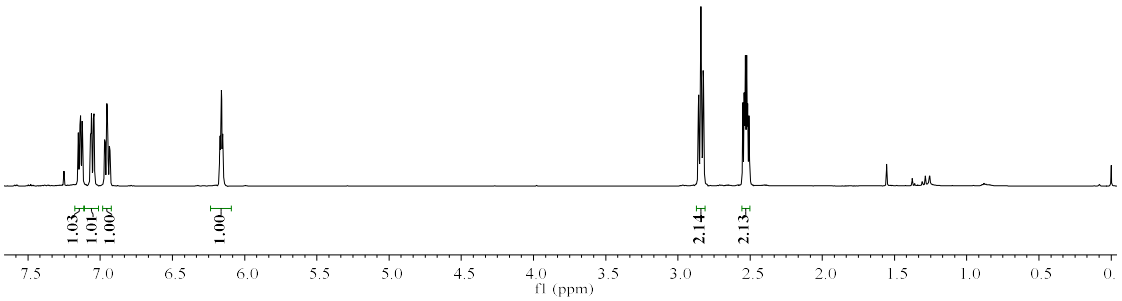
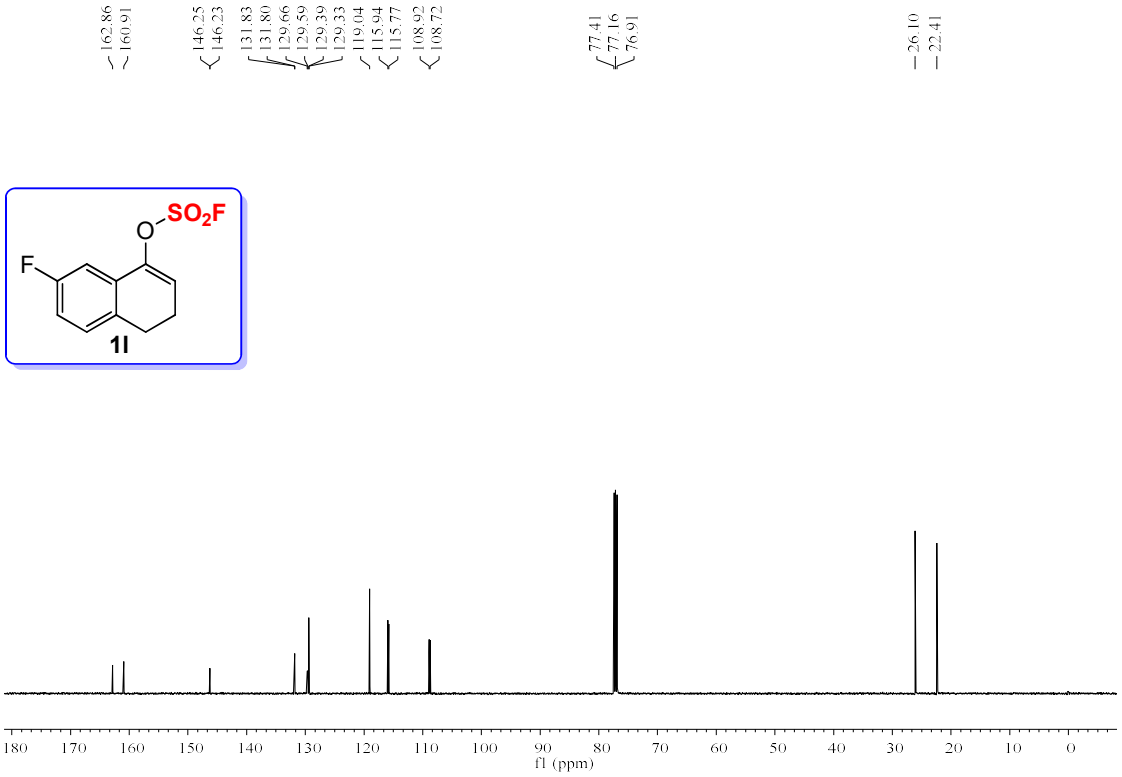




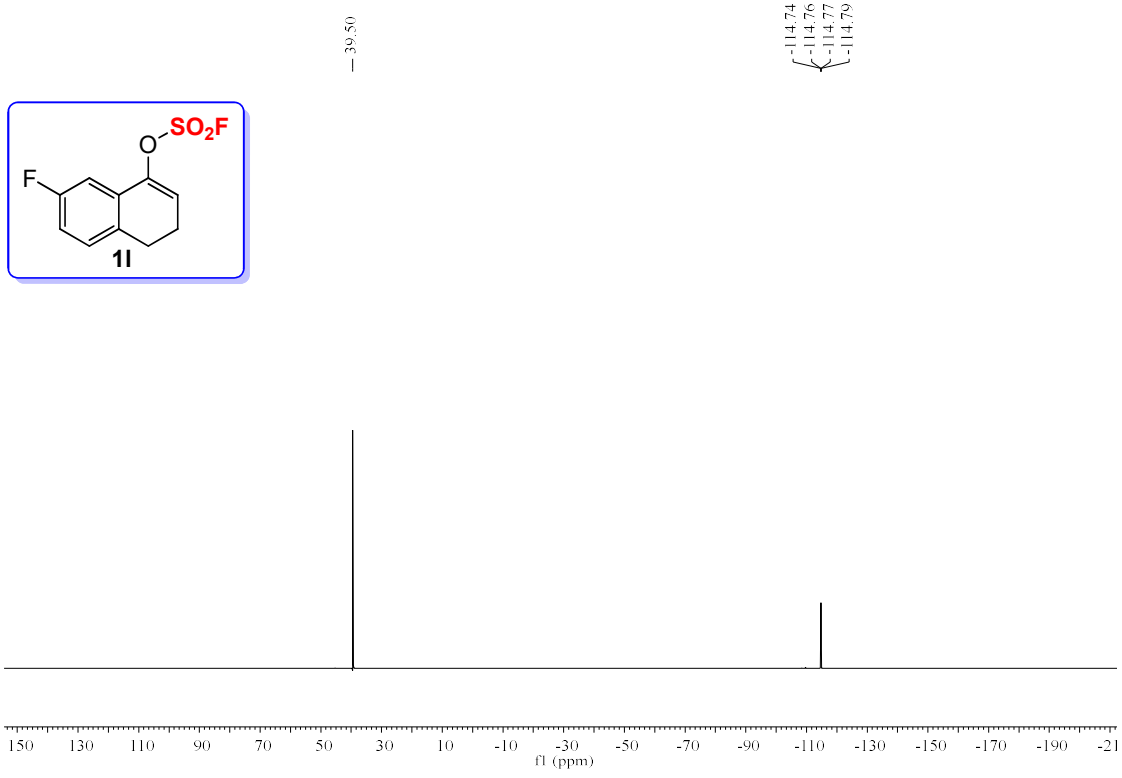




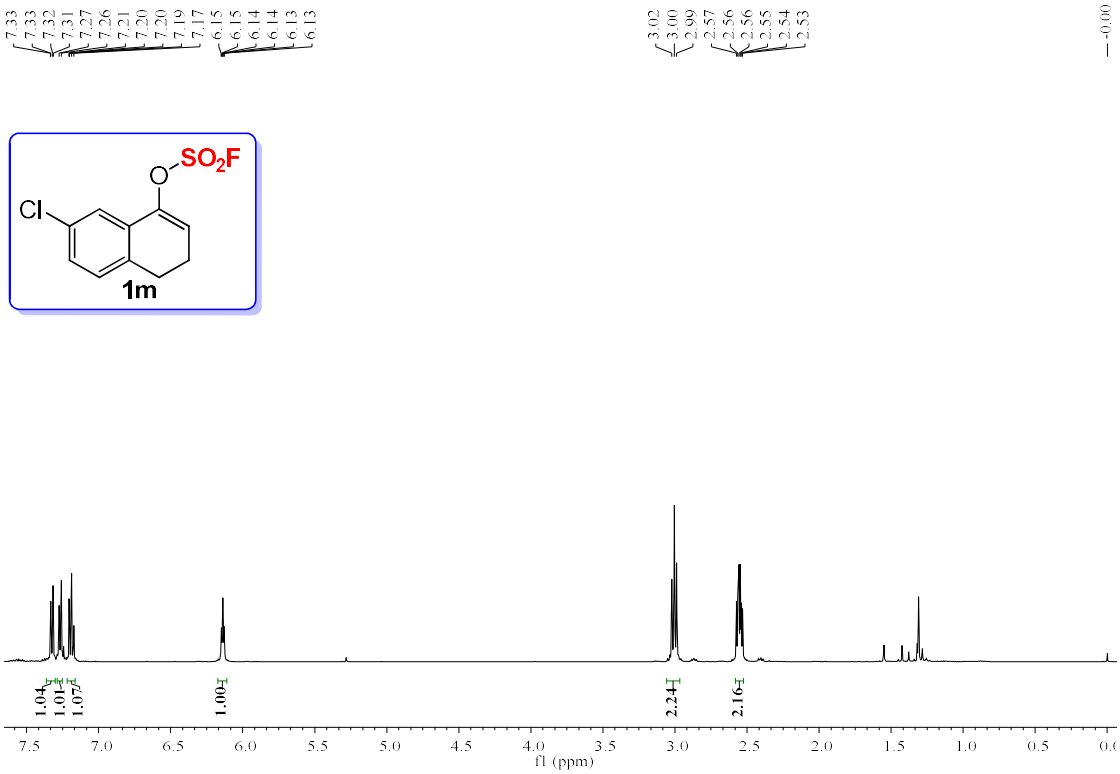
^{13}C NMR (126 MHz, $CDCl_3$) for **1l**



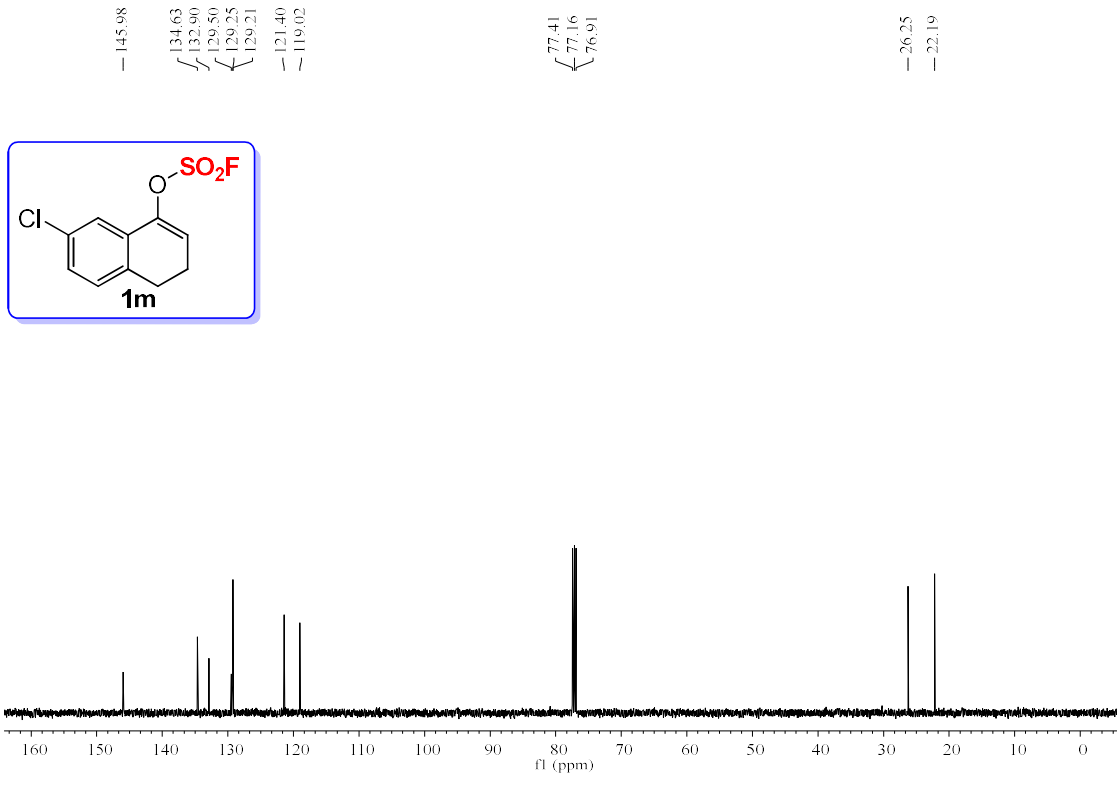
^{19}F NMR (471 MHz, $CDCl_3$) for **1l**



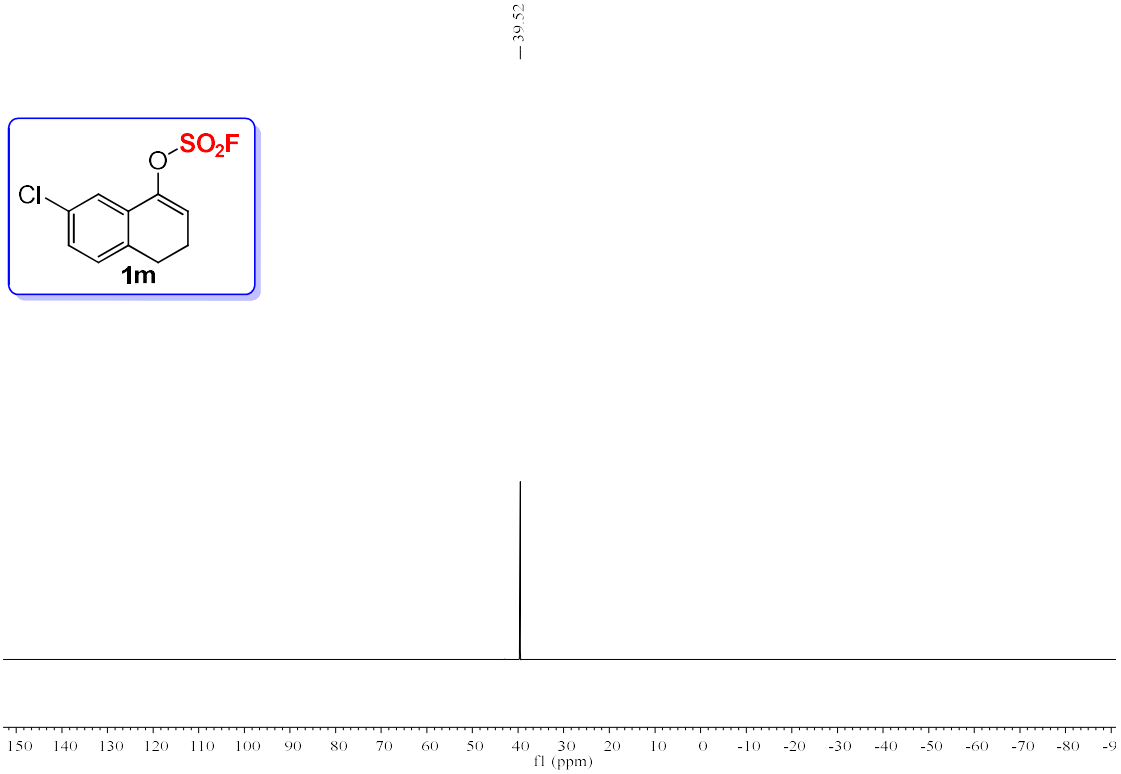
^{1}H NMR (500 MHz, $CDCl_3$) for **1m**



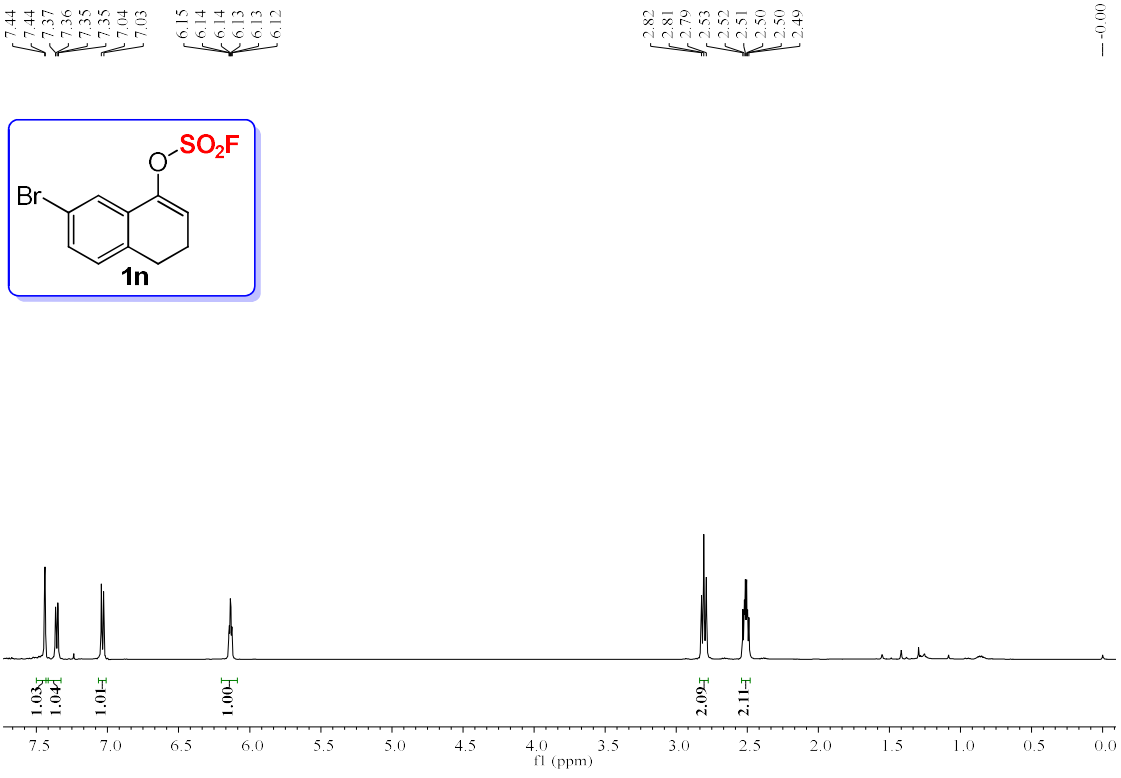
^{13}C NMR (126 MHz, $CDCl_3$) for **1m**



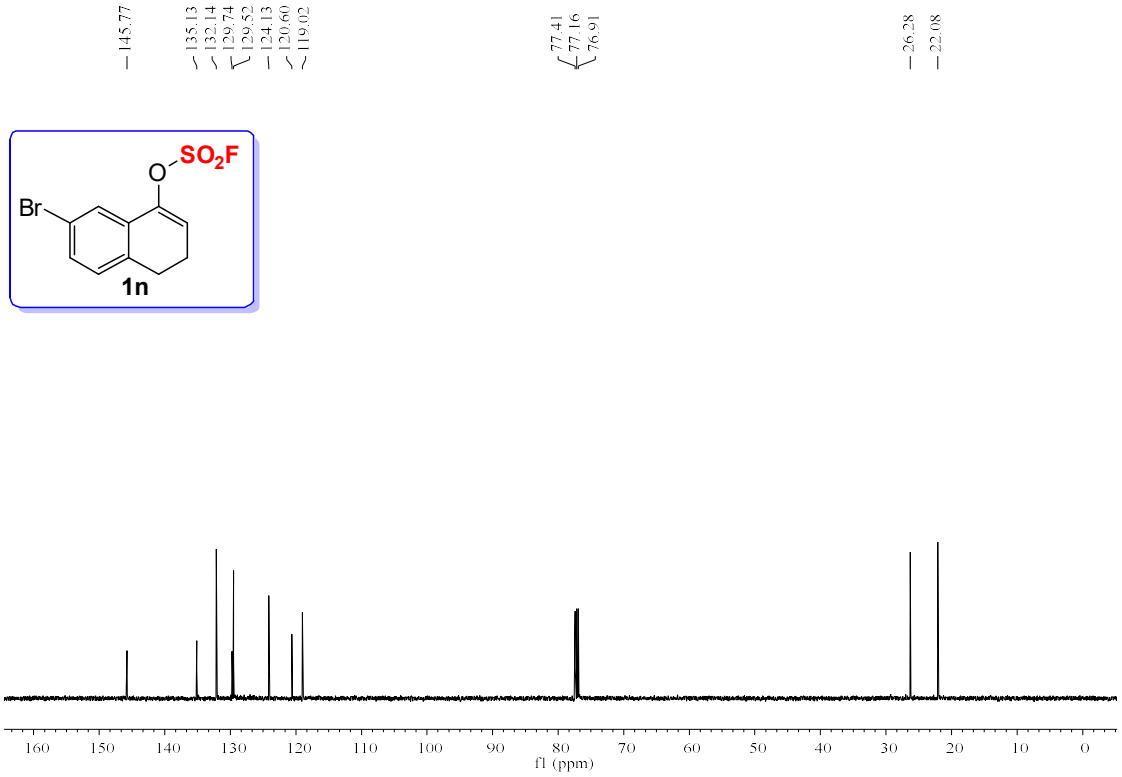
^{19}F NMR (471 MHz, $CDCl_3$) for **1m**



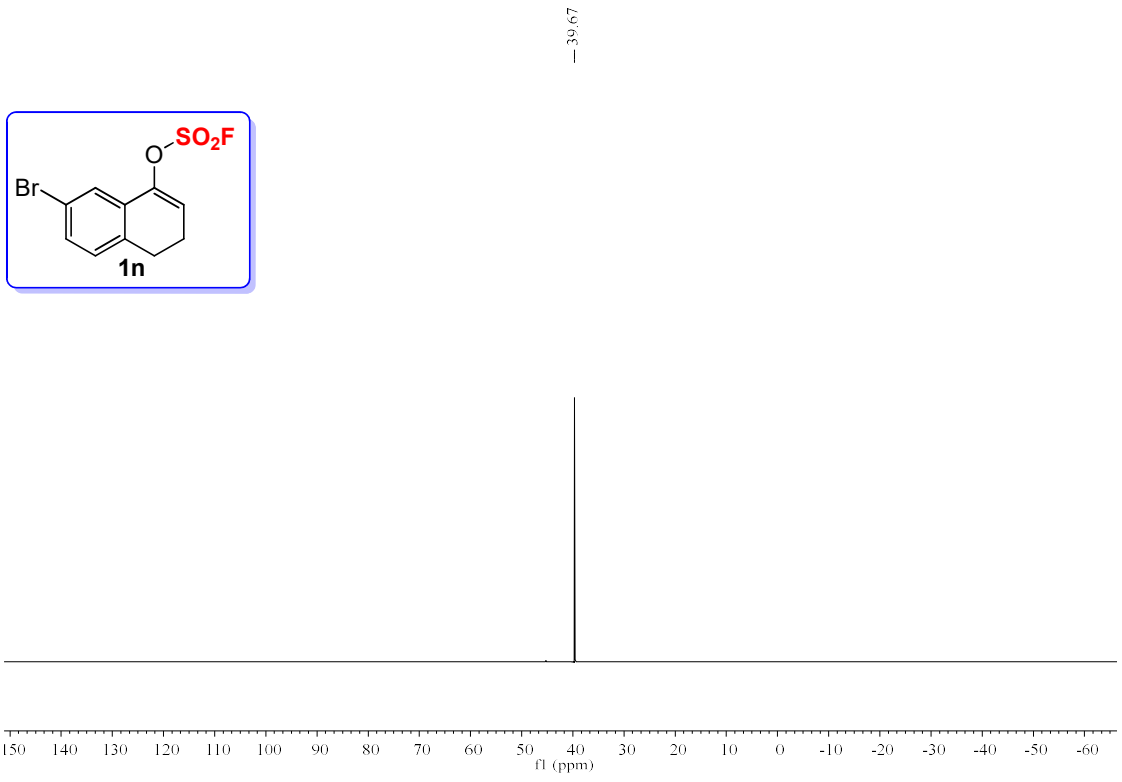
^{1}H NMR (500 MHz, $CDCl_3$) for **1n**



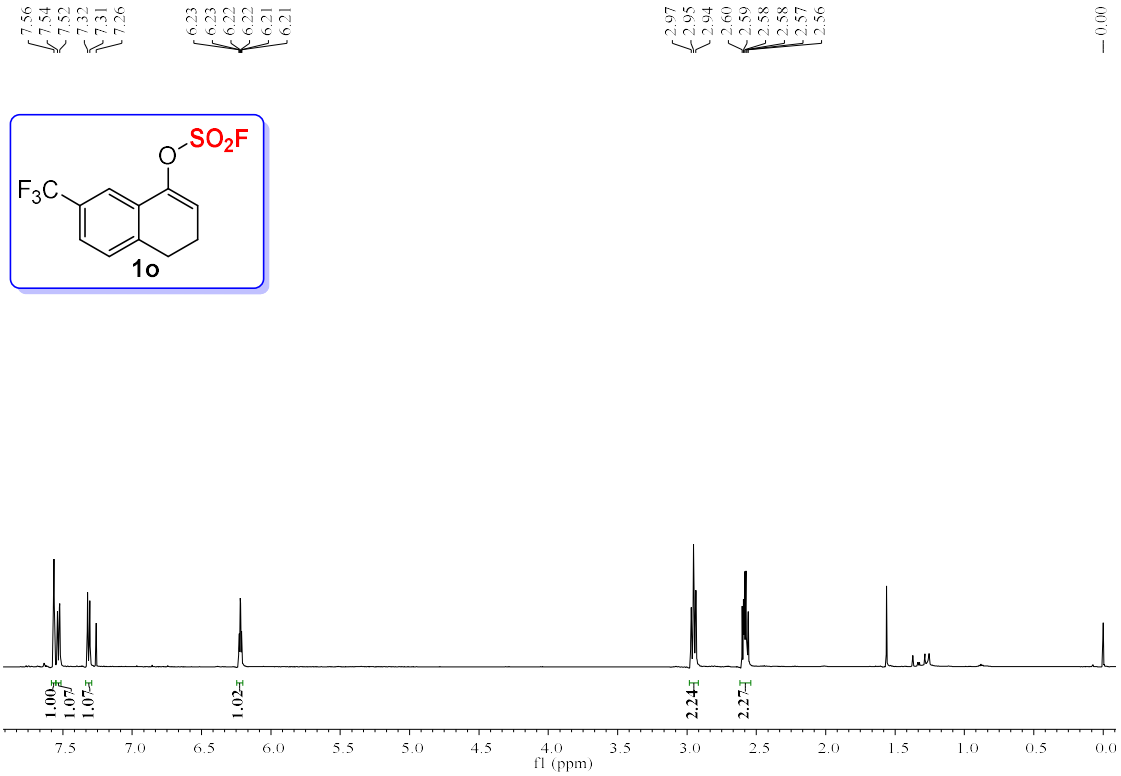
^{13}C NMR (126 MHz, $CDCl_3$) for **1n**



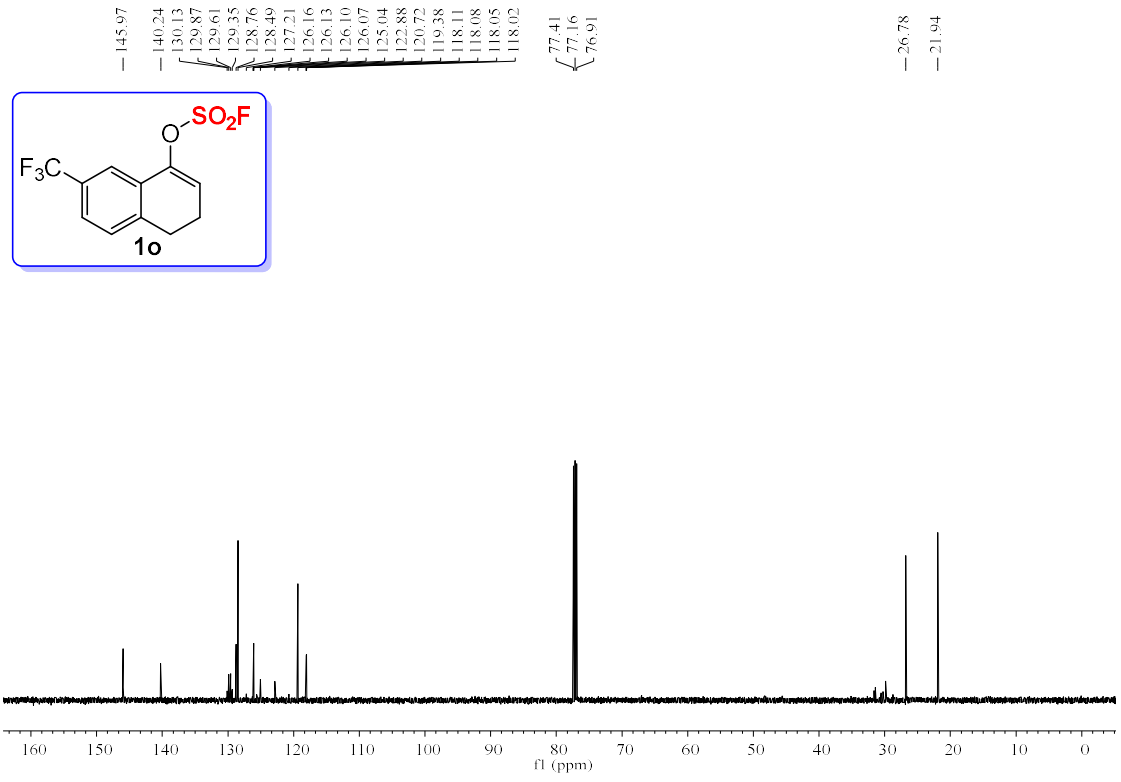
^{19}F NMR (471 MHz, $CDCl_3$) for **1n**



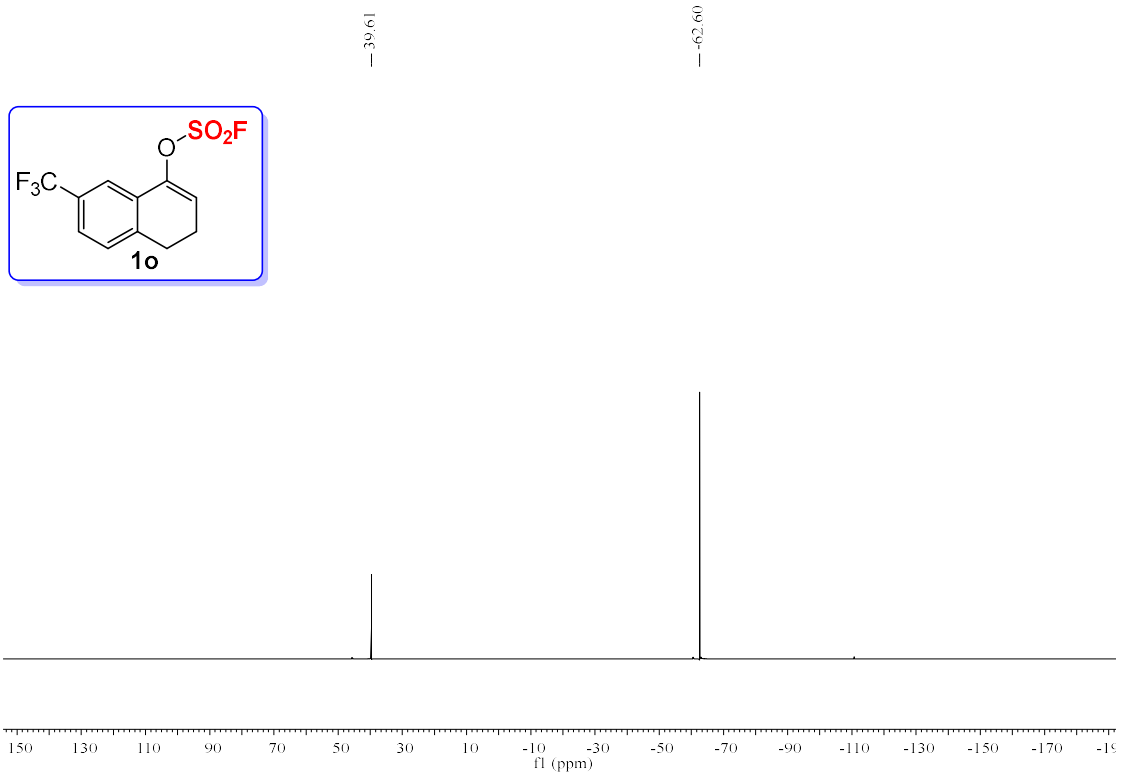
^{1}H NMR (500 MHz, $CDCl_3$) for **1o**



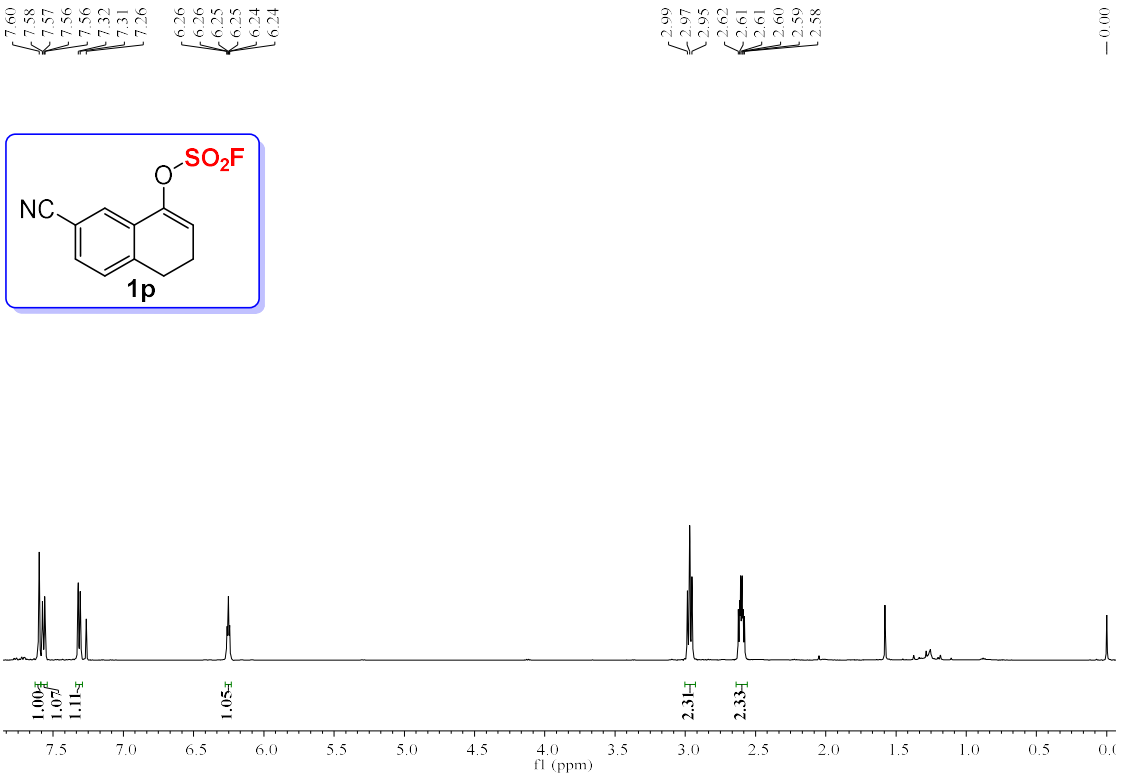
^{13}C NMR (126 MHz, $CDCl_3$) for **1o**



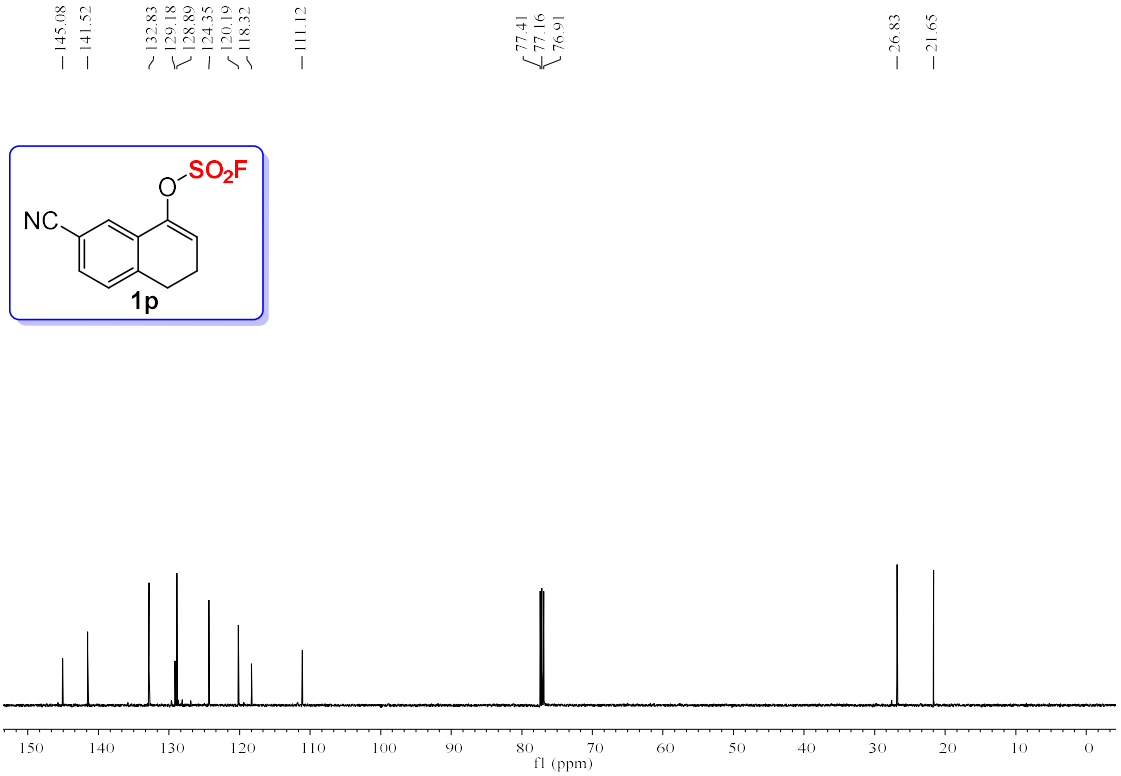
^{19}F NMR (471 MHz, $CDCl_3$) for **1o**



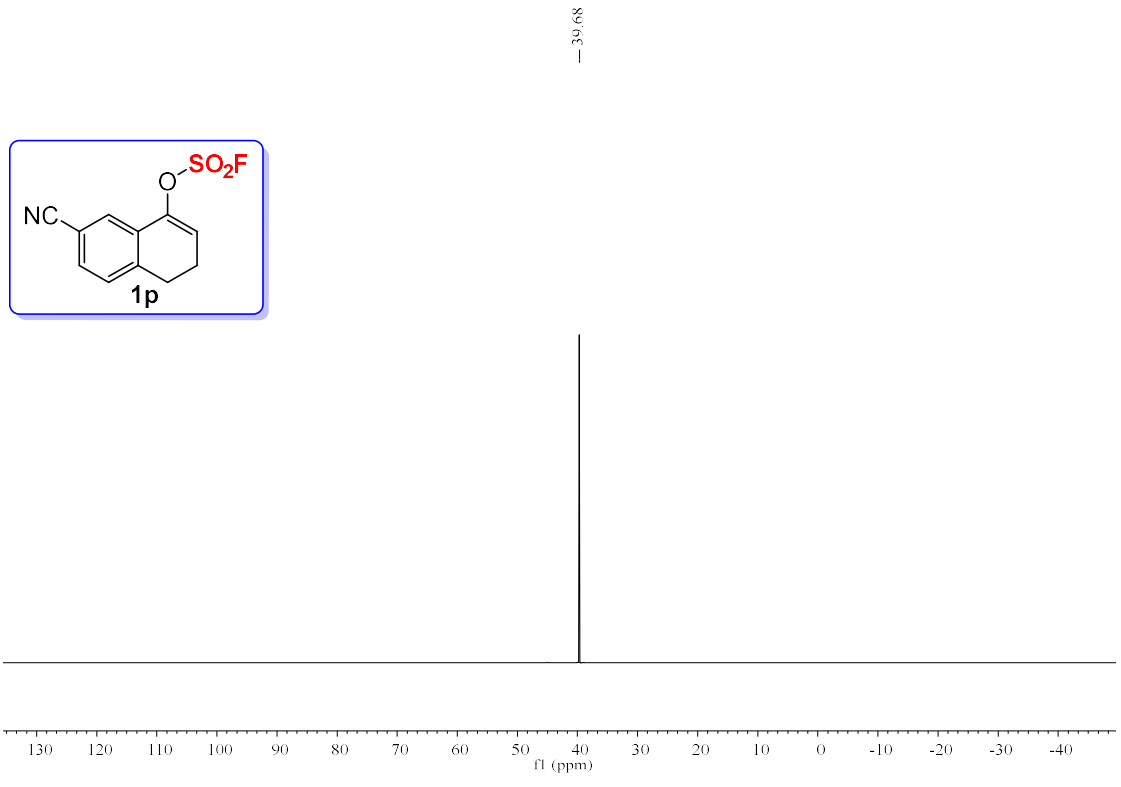
^{1}H NMR (500 MHz, $CDCl_3$) for **1p**



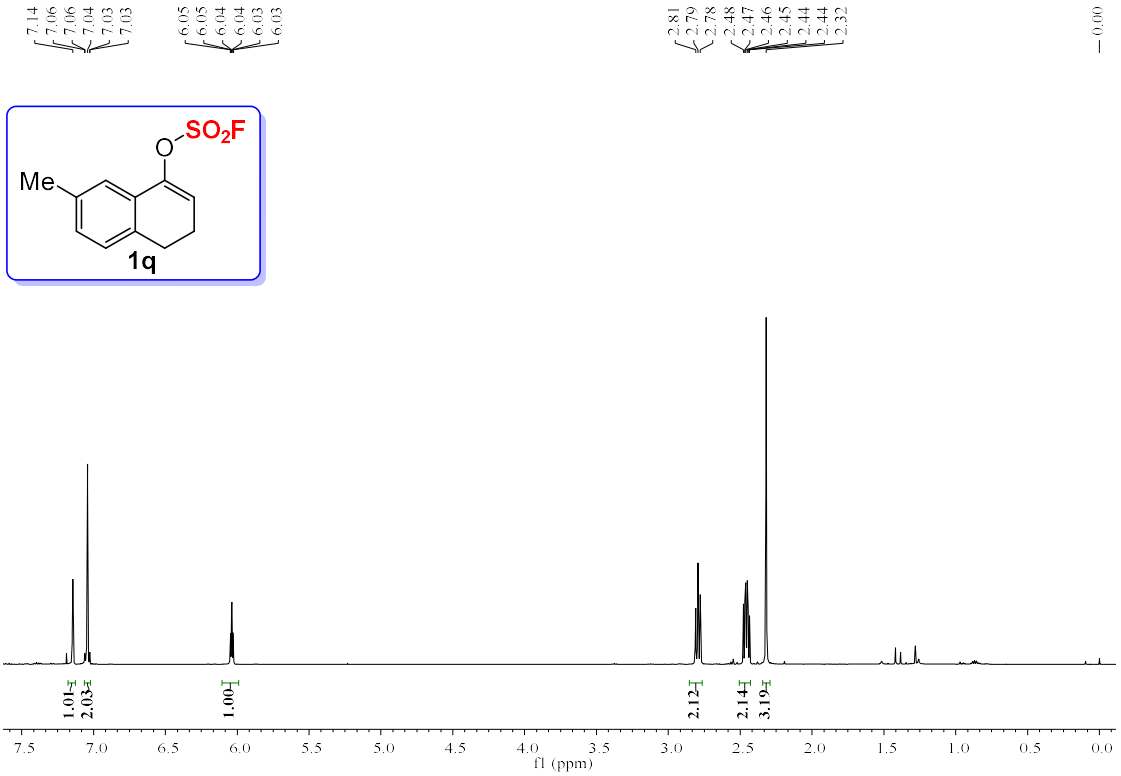
^{13}C NMR (126 MHz, $CDCl_3$) for **1p**



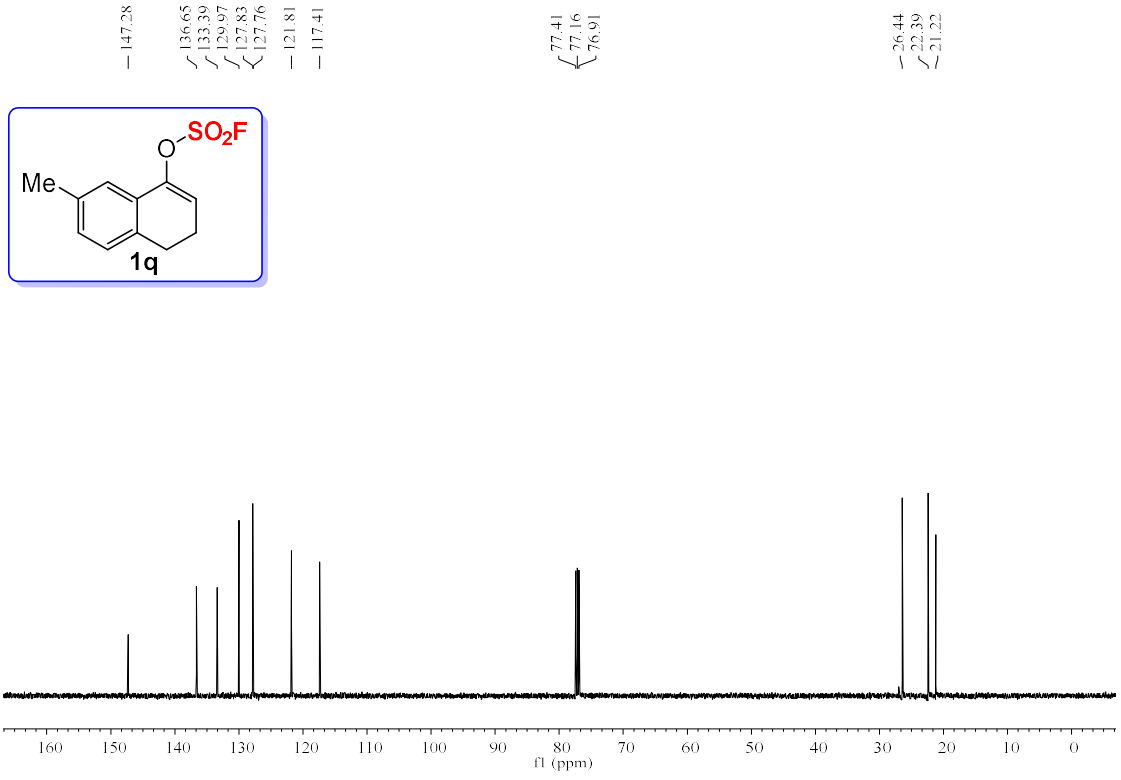
^{19}F NMR (471 MHz, $CDCl_3$) for **1p**



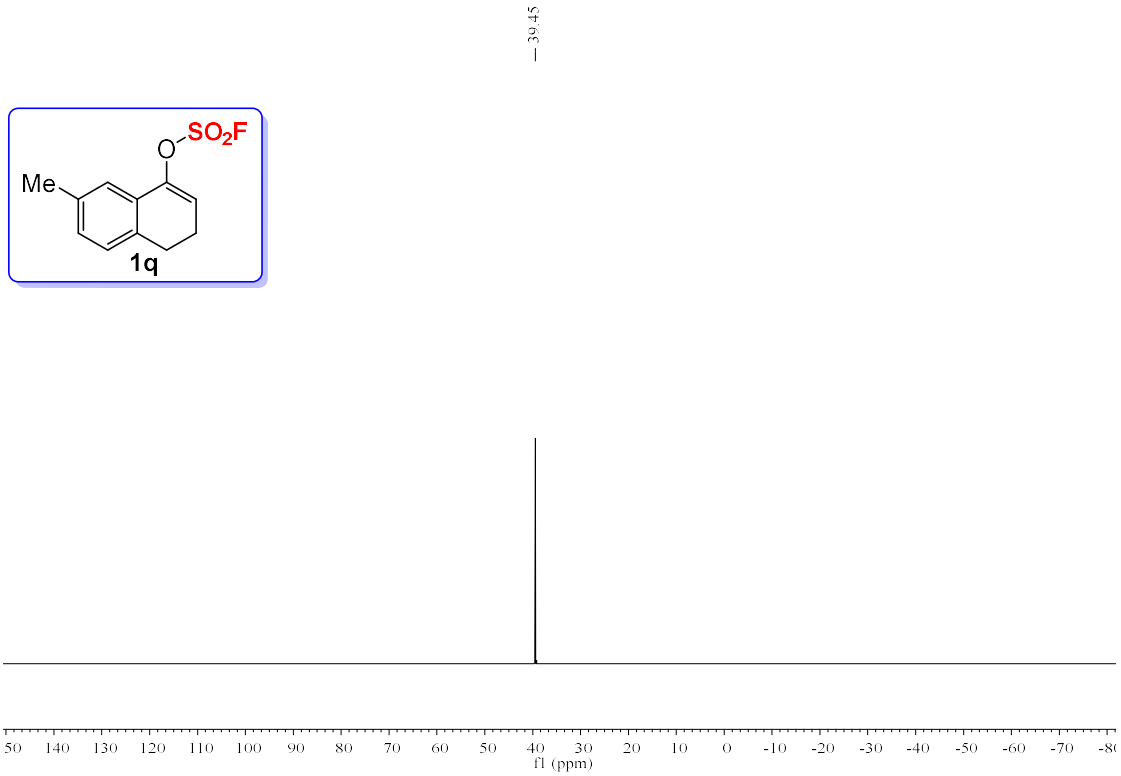
^{1}H NMR (500 MHz, $CDCl_3$) for **1q**



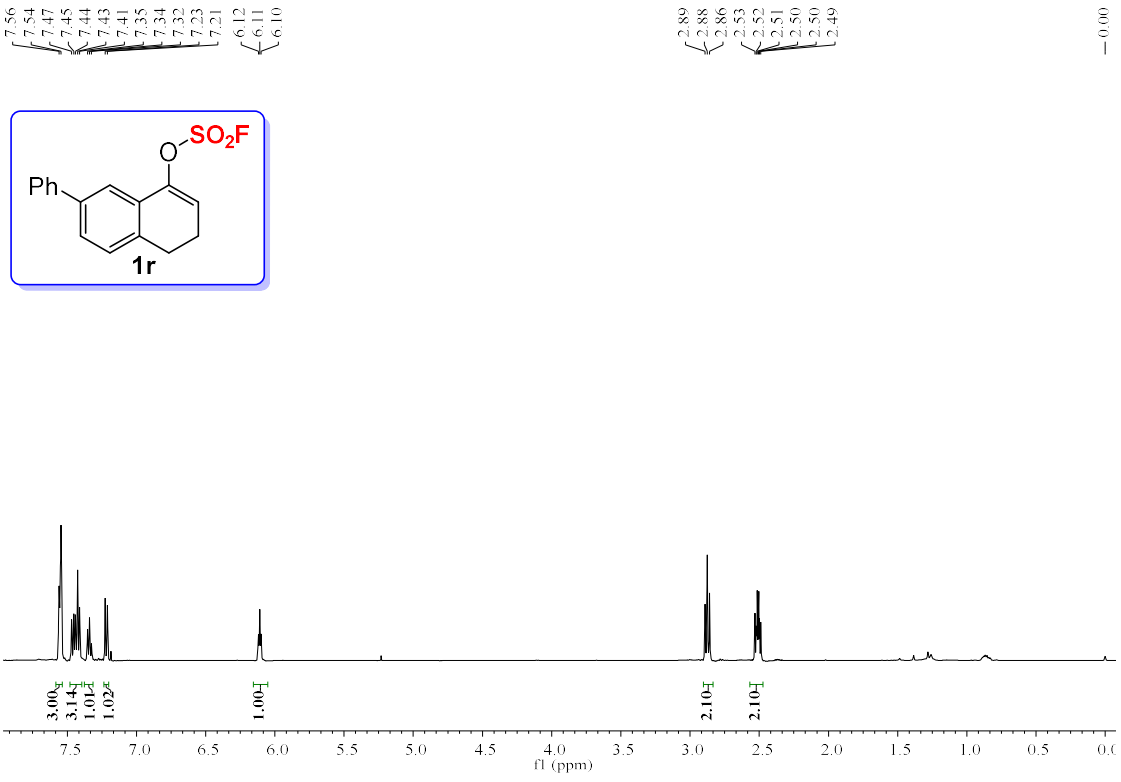
^{13}C NMR (126 MHz, $CDCl_3$) for **1q**



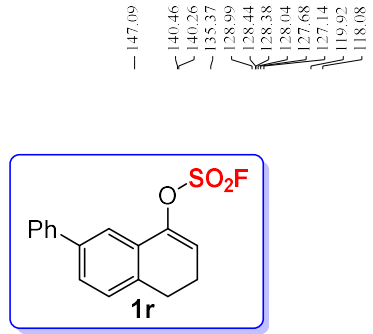
^{19}F NMR (471 MHz, $CDCl_3$) for **1q**

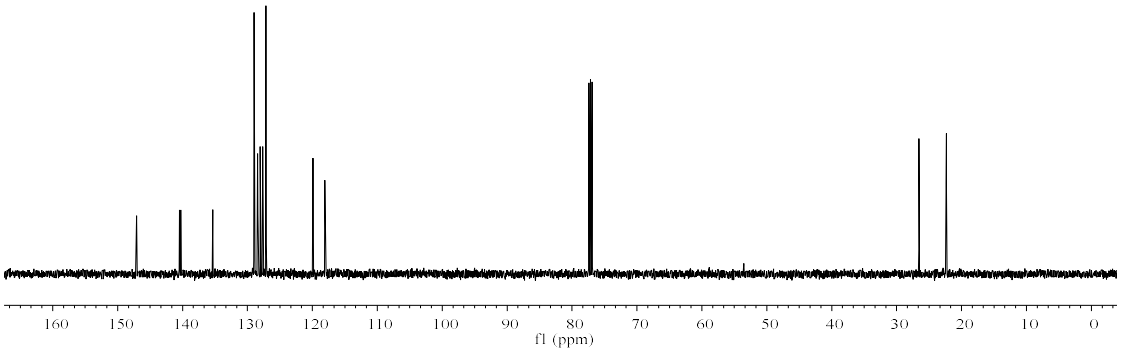


^{1}H NMR (500 MHz, $CDCl_3$) for **1r**

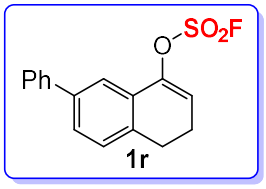


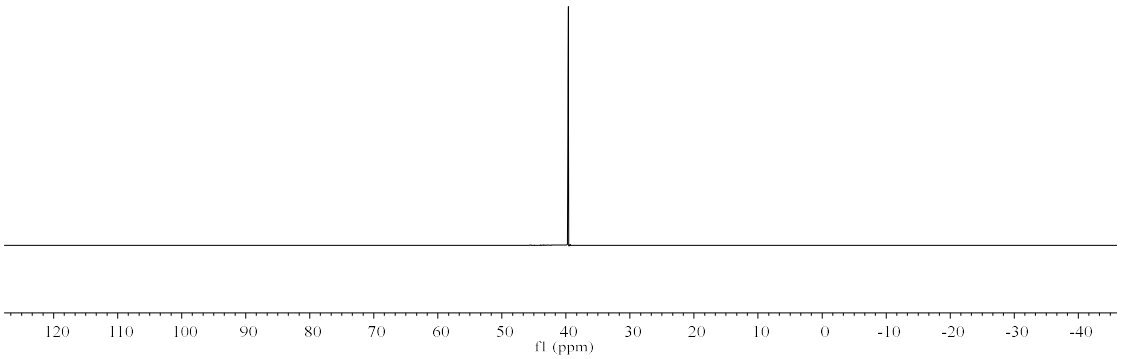
^{13}C NMR (126 MHz, $CDCl_3$) for **1r**



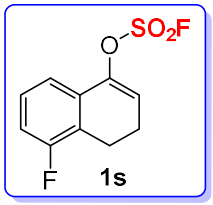


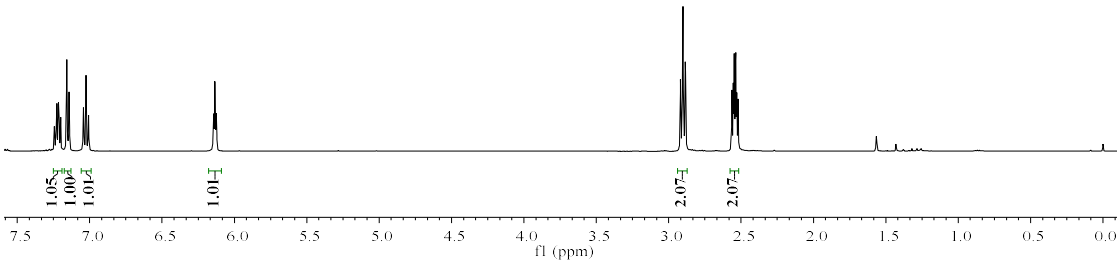
^{19}F NMR (471 MHz, $CDCl_3$) for **1r**



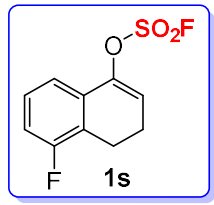


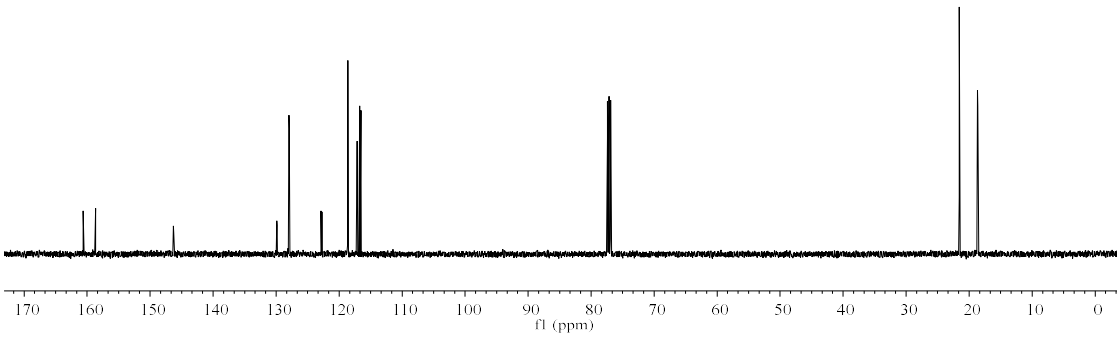
^{1}H NMR (500 MHz, $CDCl_3$) for **1s**



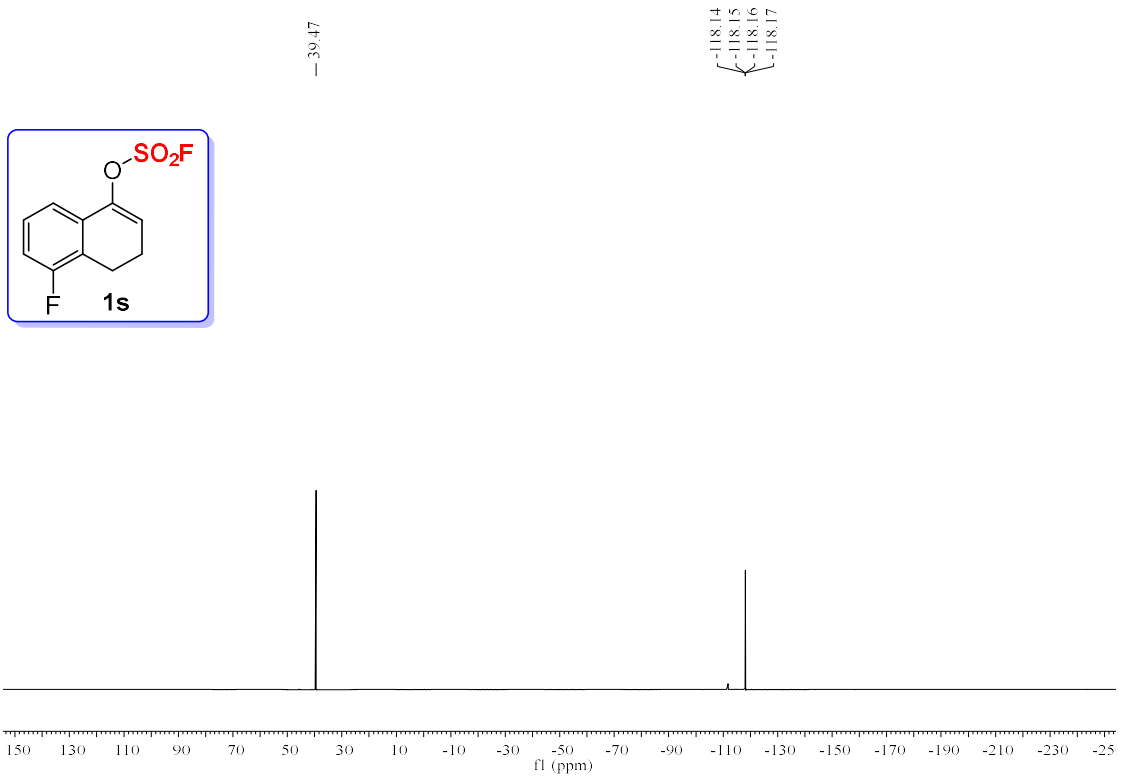


^{13}C NMR (126 MHz, $CDCl_3$) for **1s**

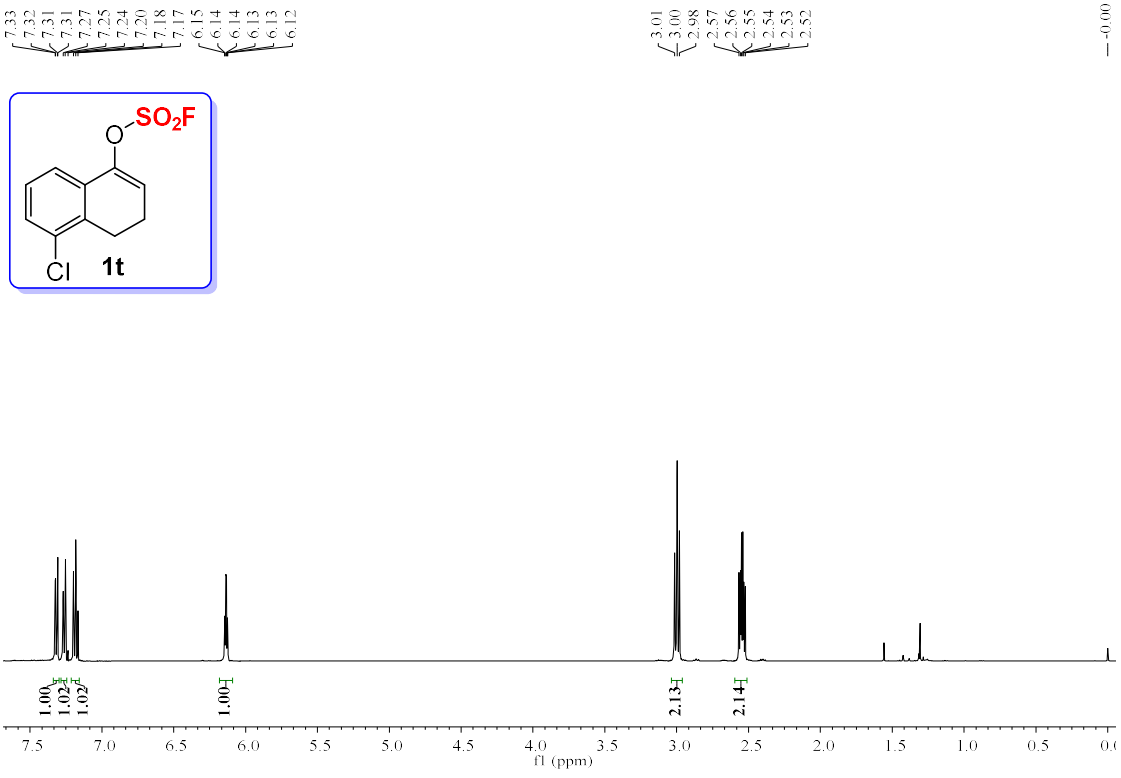




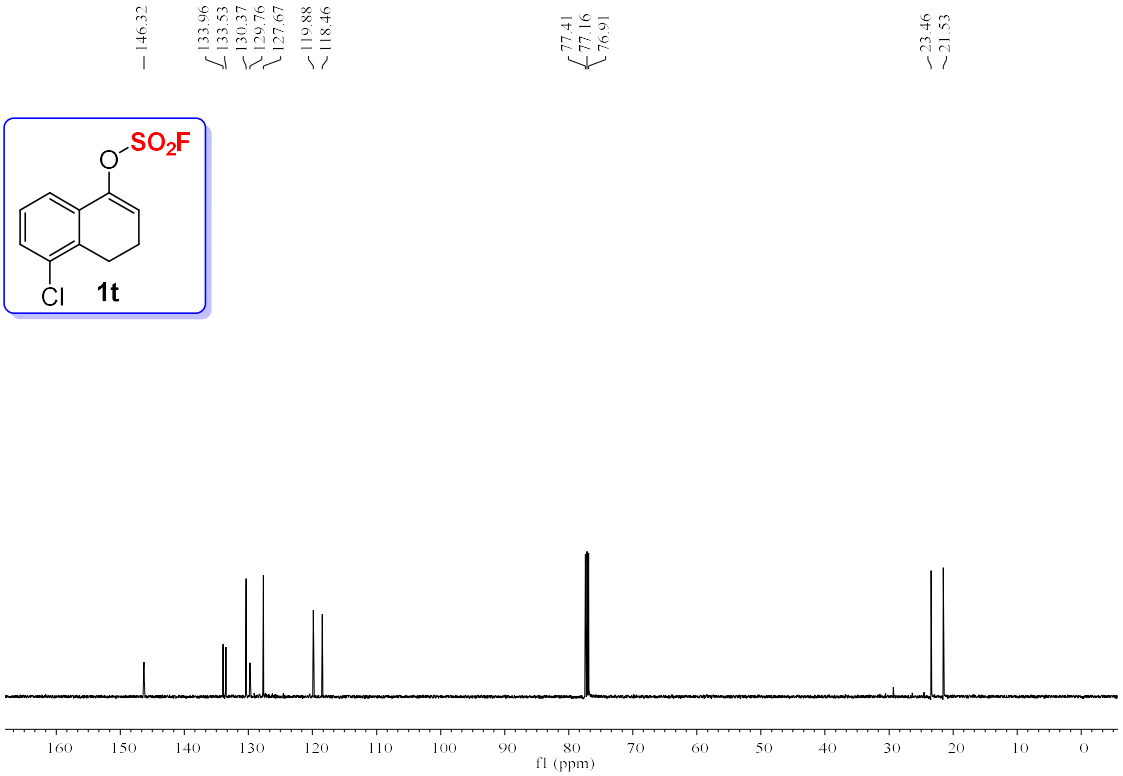
^{19}F NMR (471 MHz, $CDCl_3$) for **1s**



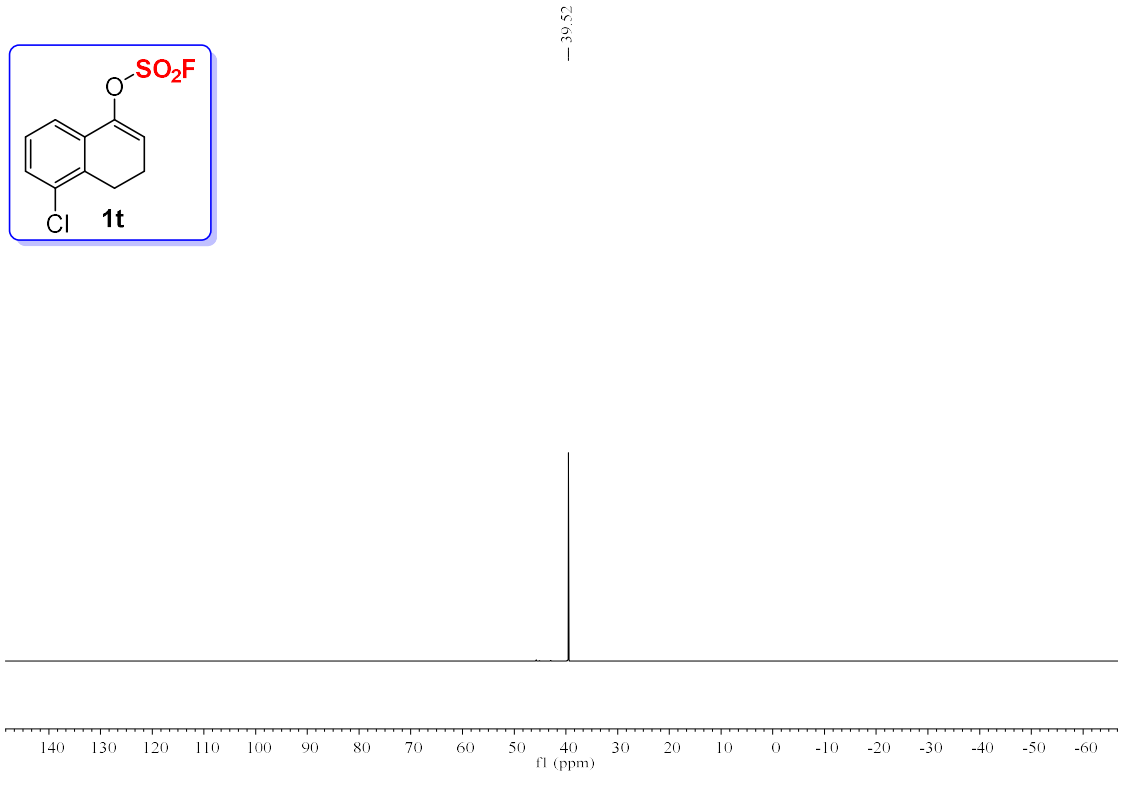
^{1}H NMR (500 MHz, $CDCl_3$) for **1t**



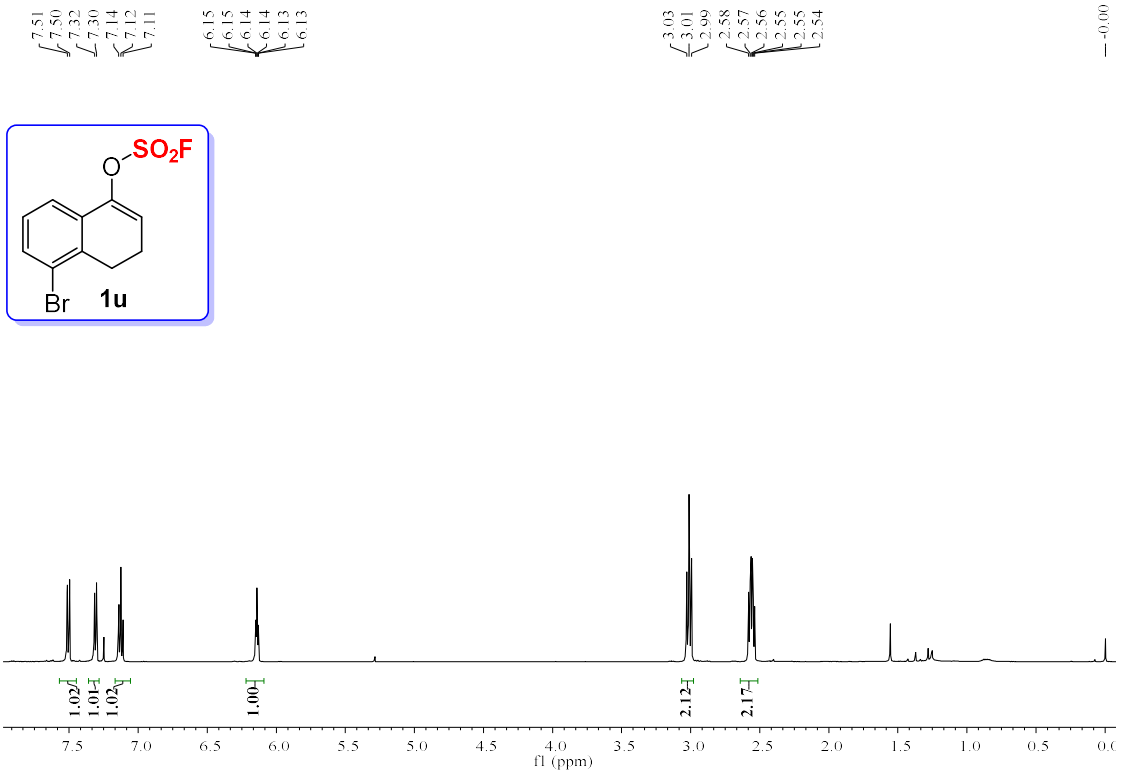
^{13}C NMR (126 MHz, $CDCl_3$) for **1t**



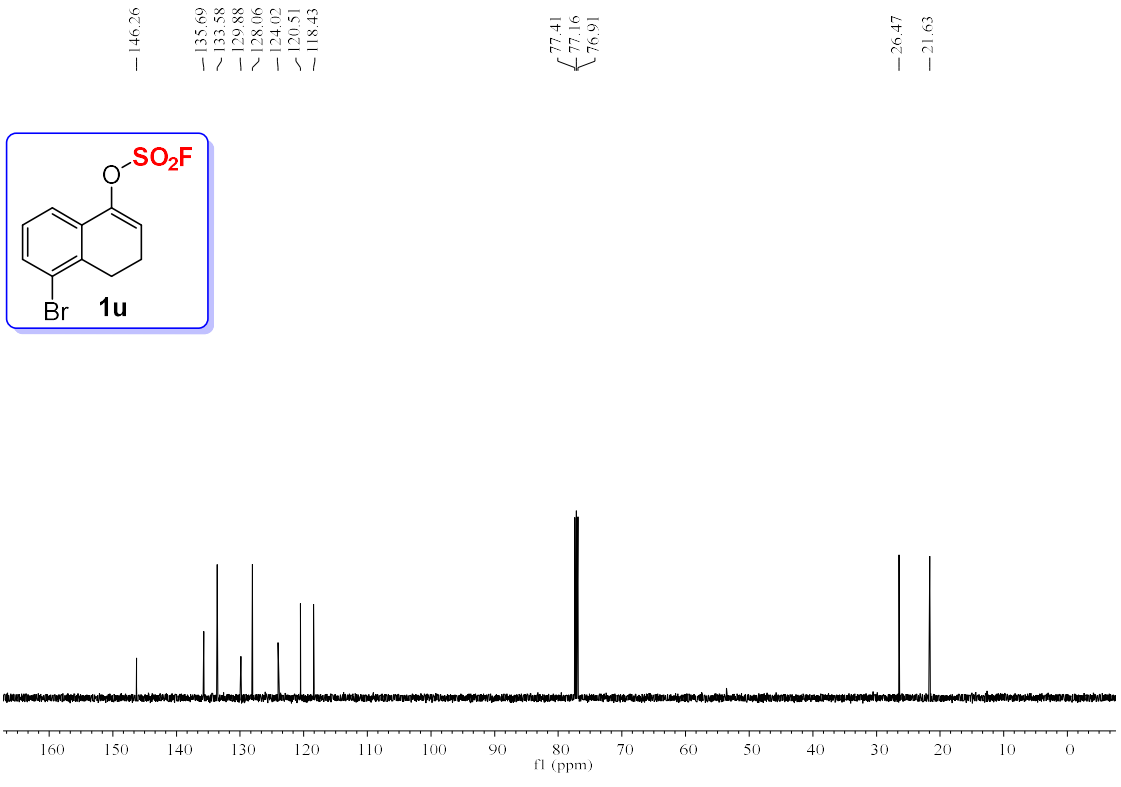
^{19}F NMR (471 MHz, $CDCl_3$) for **1t**



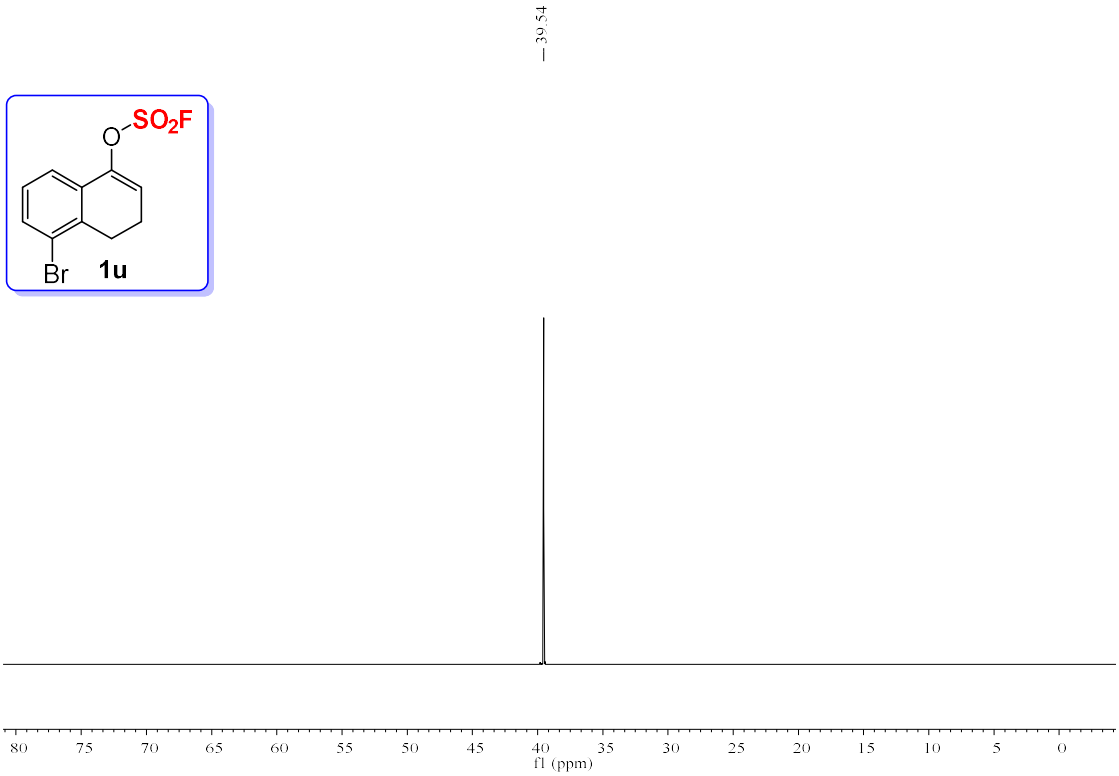
^{1}H NMR (500 MHz, $CDCl_3$) for **1u**



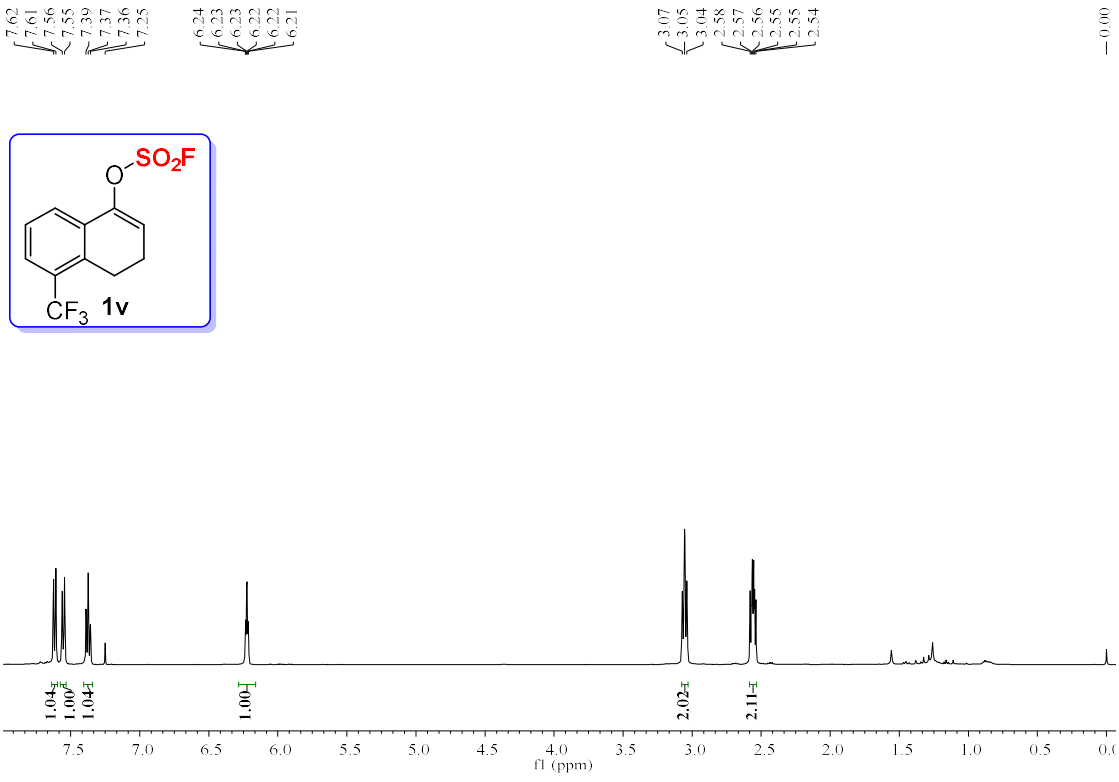
^{13}C NMR (126 MHz, $CDCl_3$) for **1u**



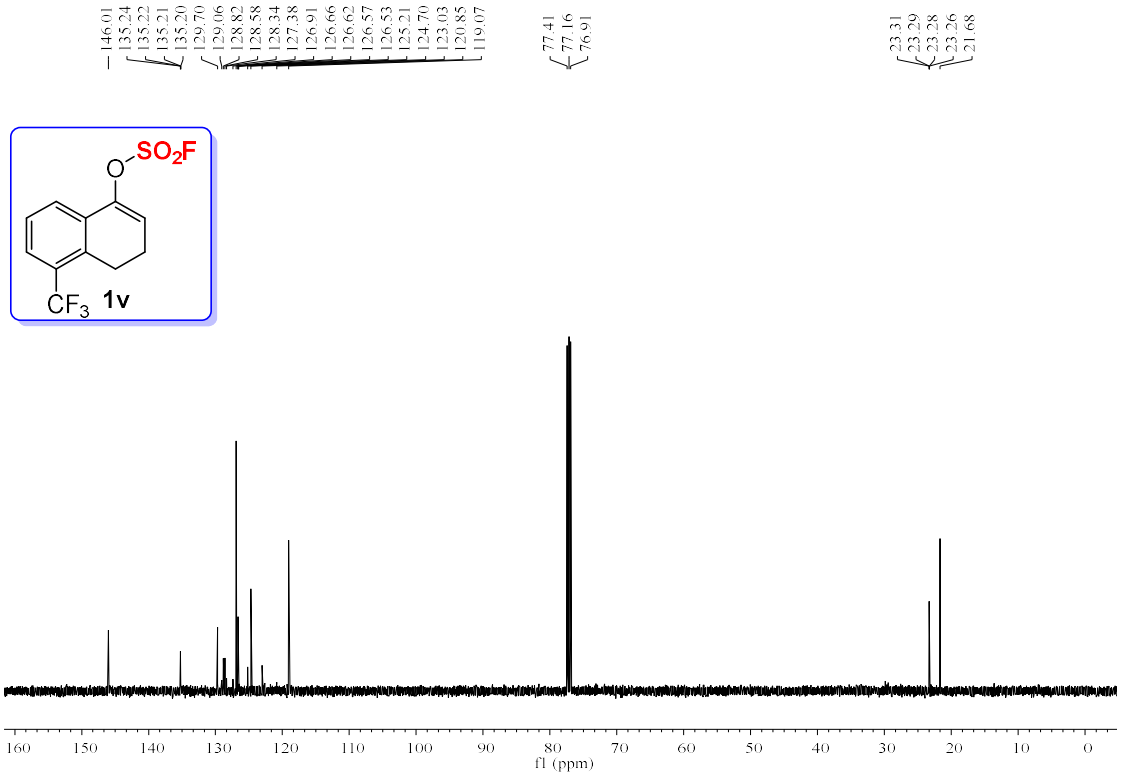
^{19}F NMR (471 MHz, $CDCl_3$) for **1u**



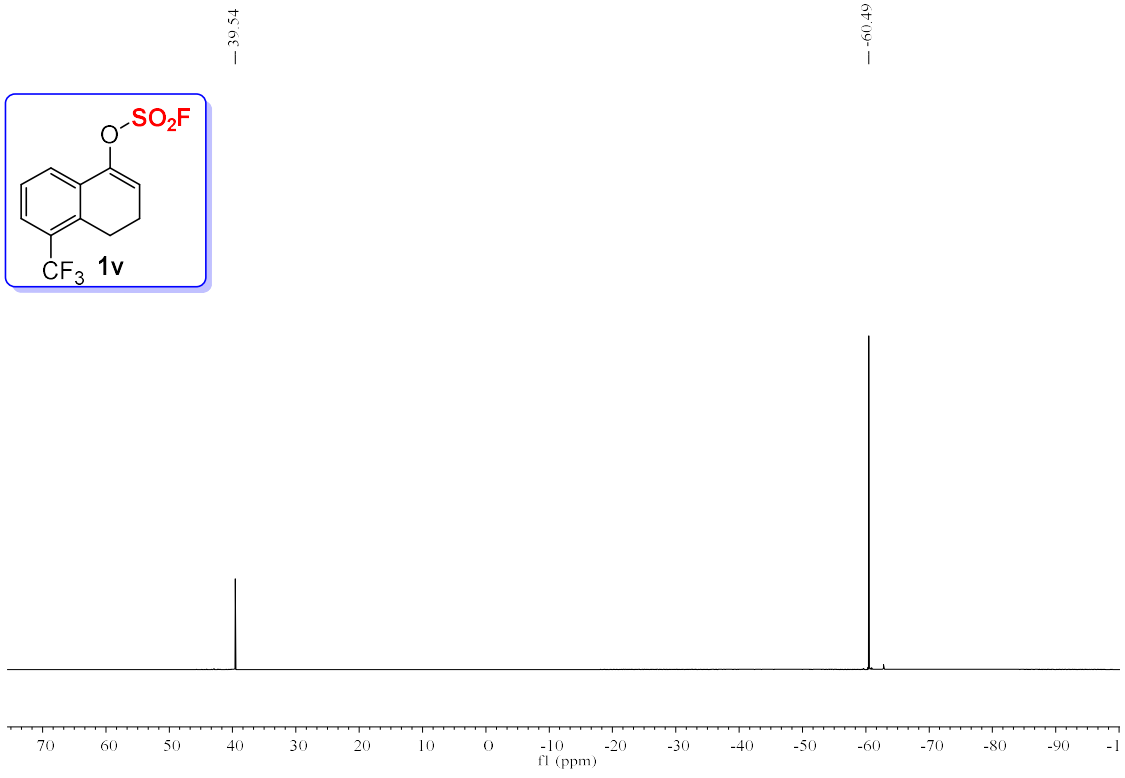
^{1}H NMR (500 MHz, $CDCl_3$) for **1v**



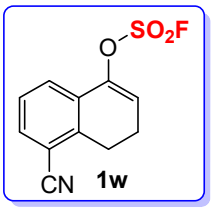
^{13}C NMR (126 MHz, $CDCl_3$) for **1v**

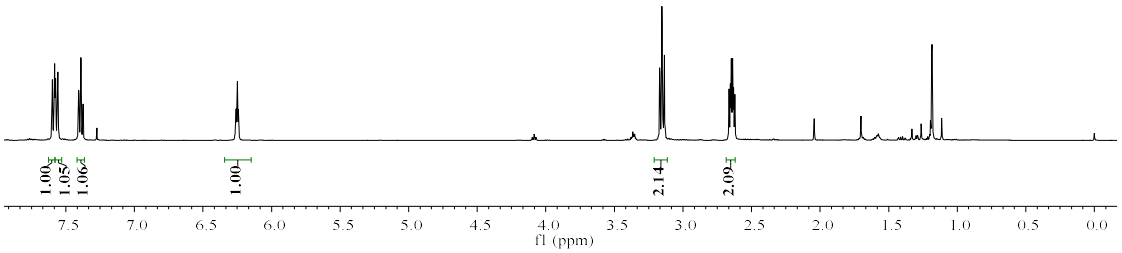


^{19}F NMR (471 MHz, $CDCl_3$) for **1v**

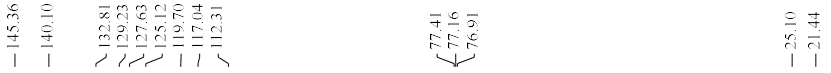


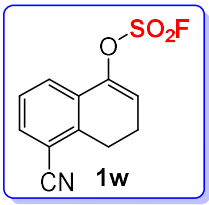
^{1}H NMR (500 MHz, $CDCl_3$) for **1w**

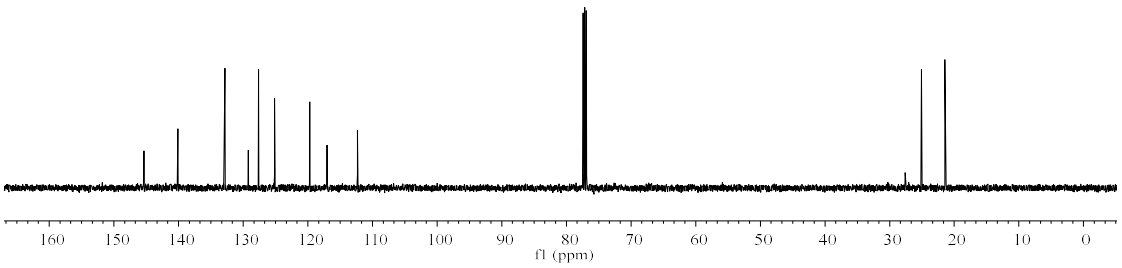




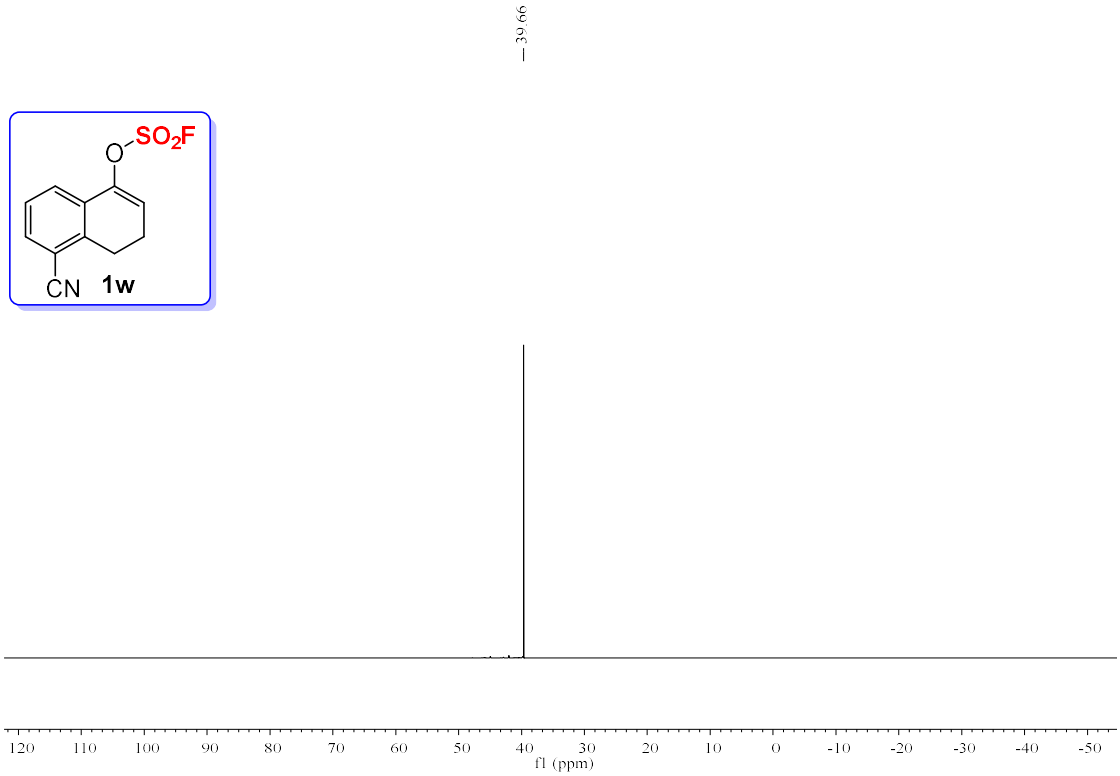
^{13}C NMR (126 MHz, $CDCl_3$) for **1w**



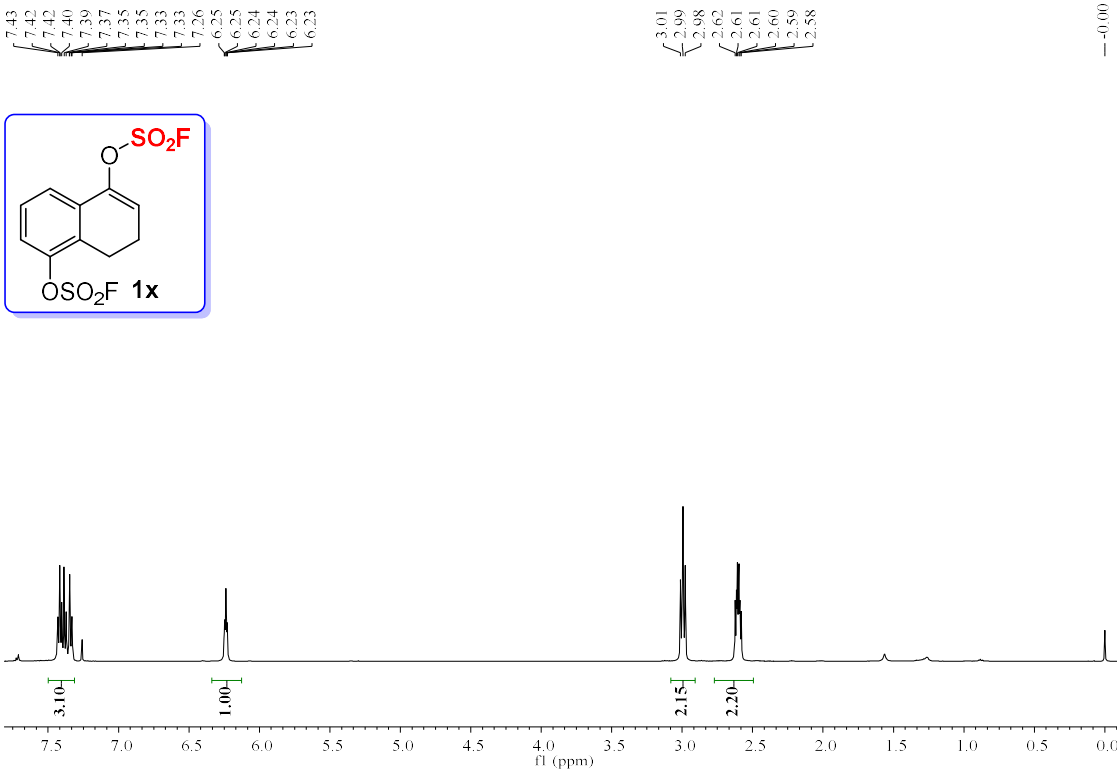




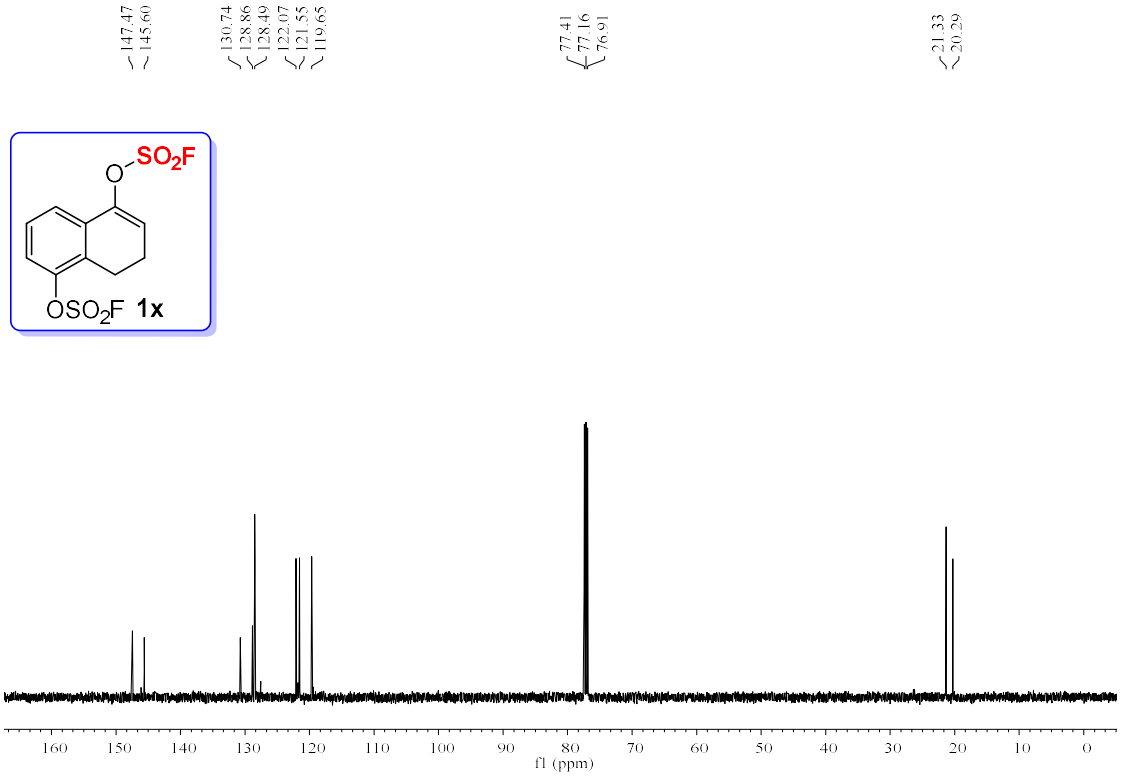
^{19}F NMR (471 MHz, $CDCl_3$) for **1w**



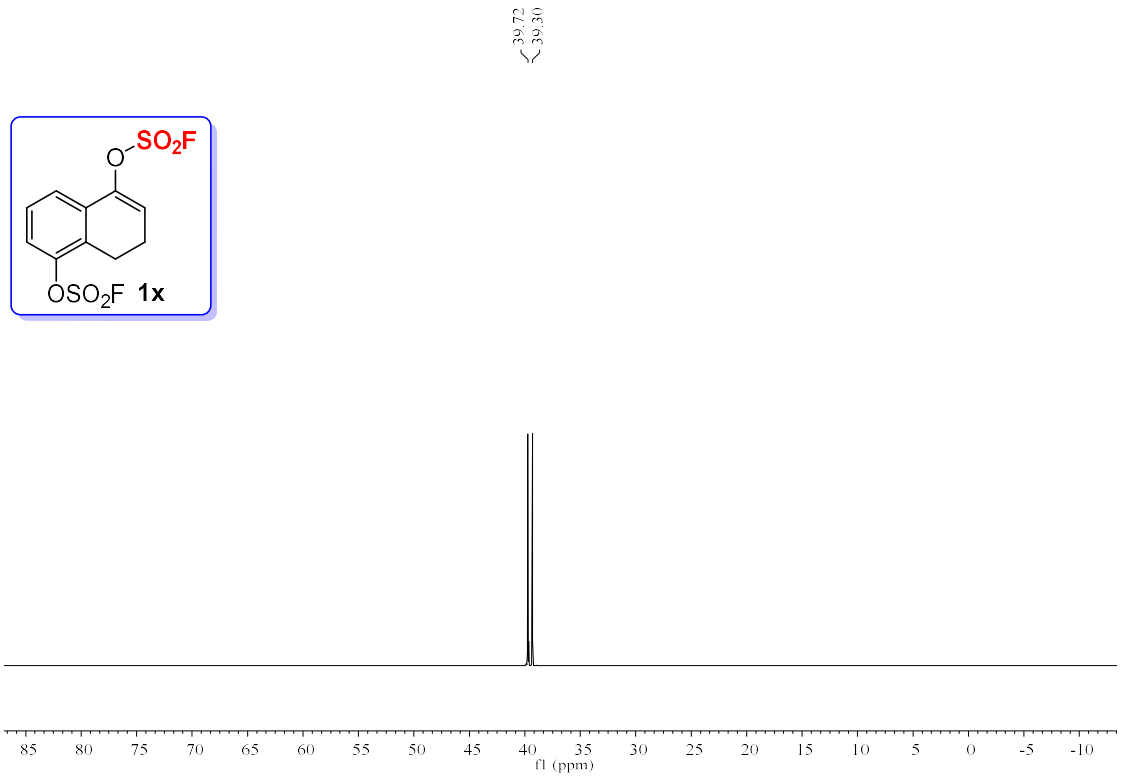
^{1}H NMR (500 MHz, $CDCl_3$) for **1x**



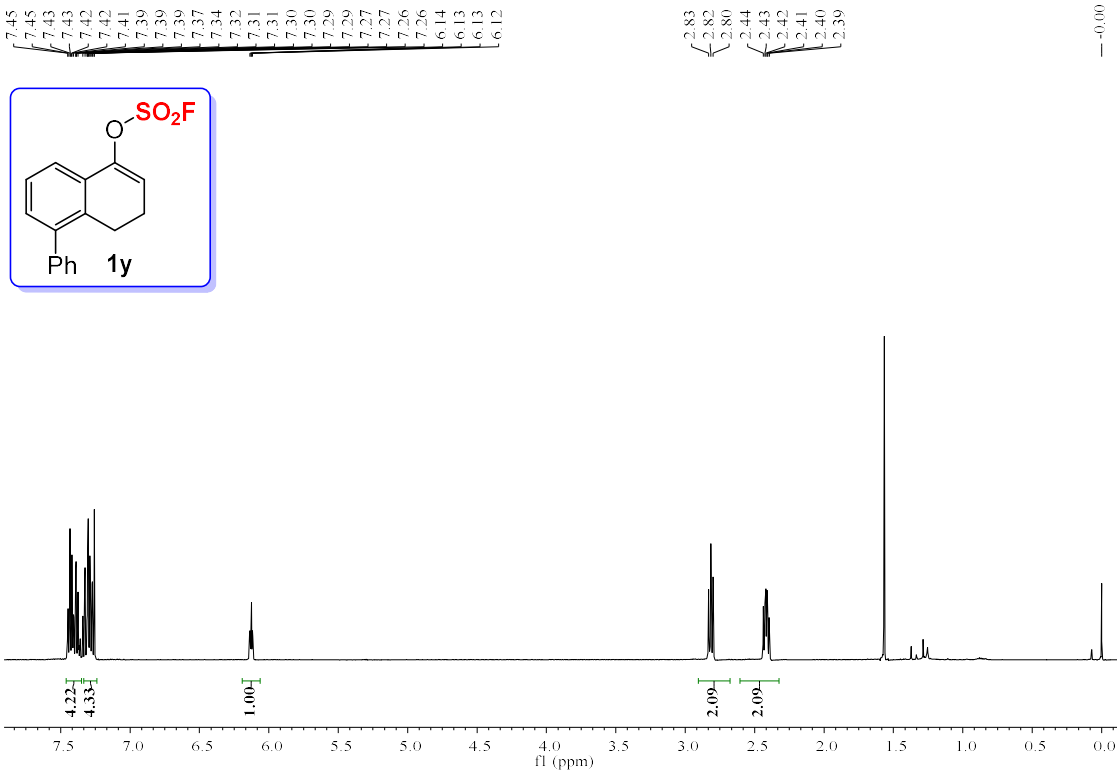
^{13}C NMR (126 MHz, $CDCl_3$) for **1x**



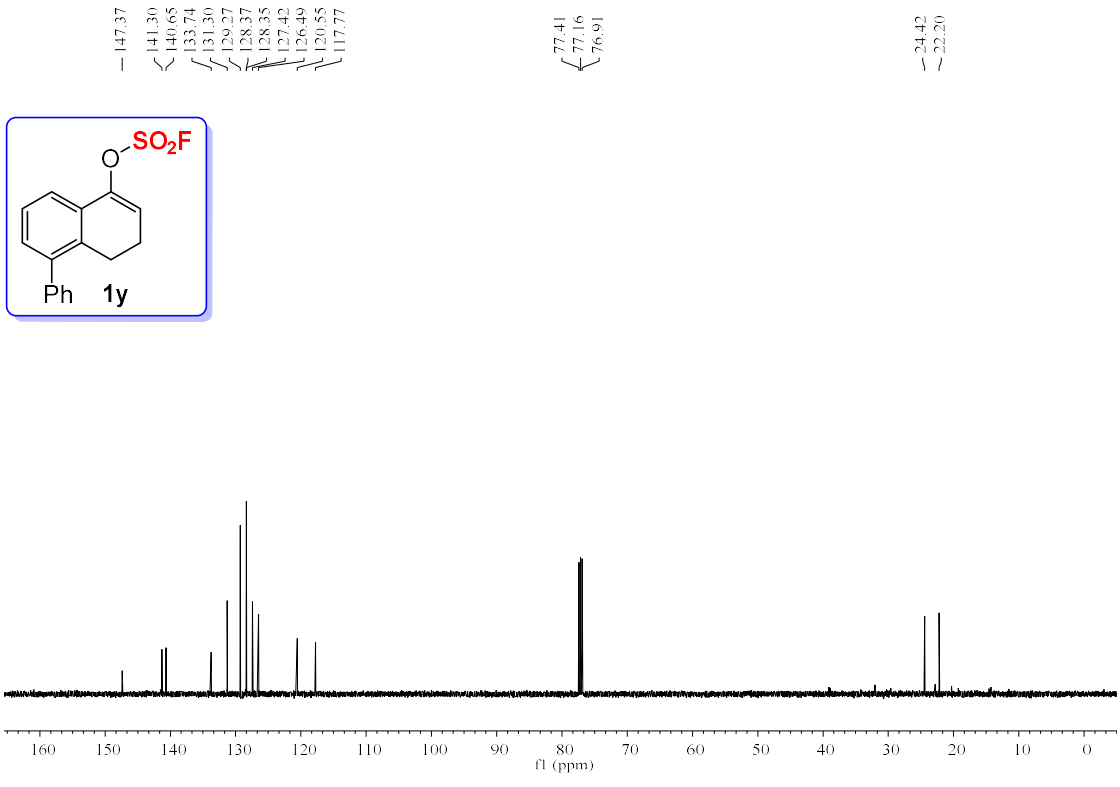
^{19}F NMR (471 MHz, $CDCl_3$) for **1x**



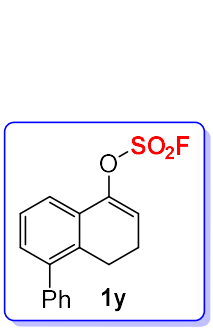
^{1}H NMR (500 MHz, $CDCl_3$) for **1y**



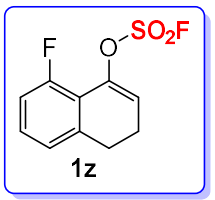
^{13}C NMR (126 MHz, $CDCl_3$) for **1y**

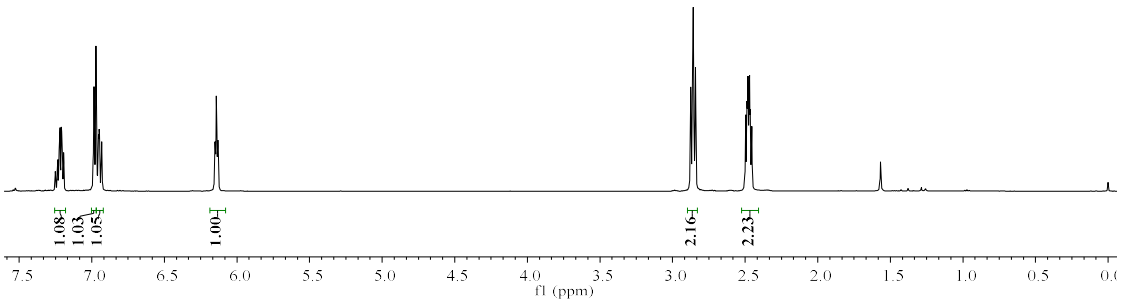


^{19}F NMR (471 MHz, $CDCl_3$) for **1y**

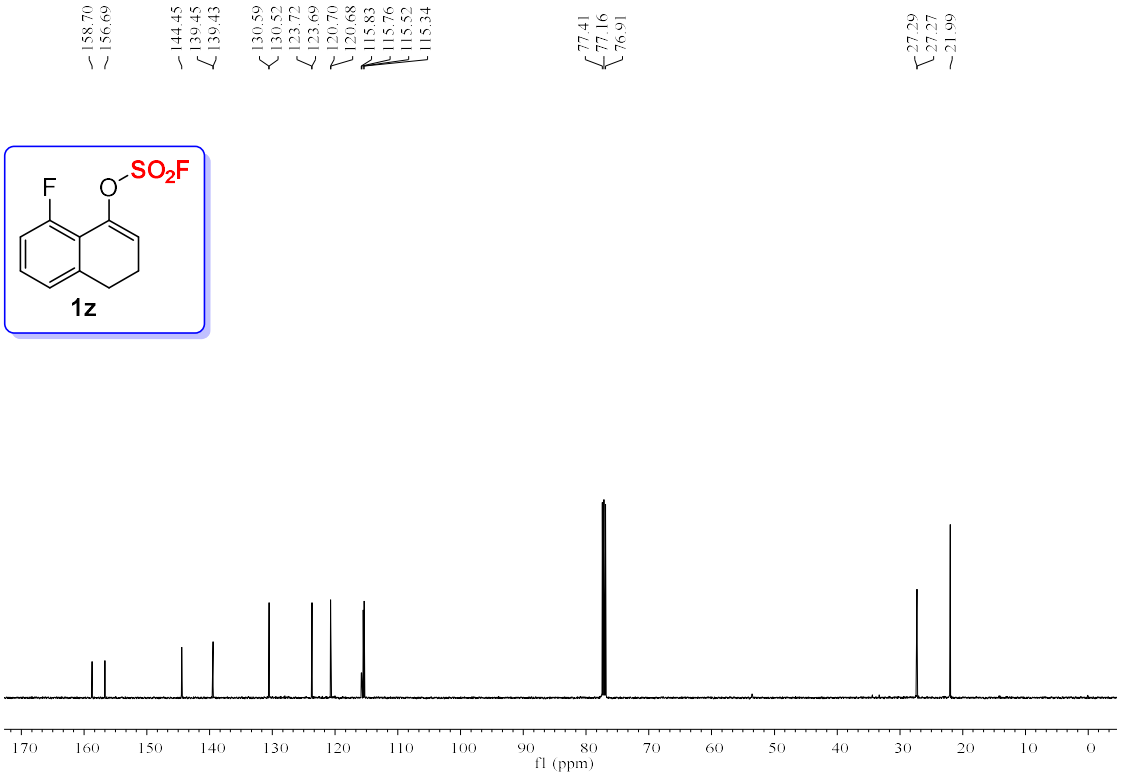


^{1}H NMR (500 MHz, $CDCl_3$) for **1z**

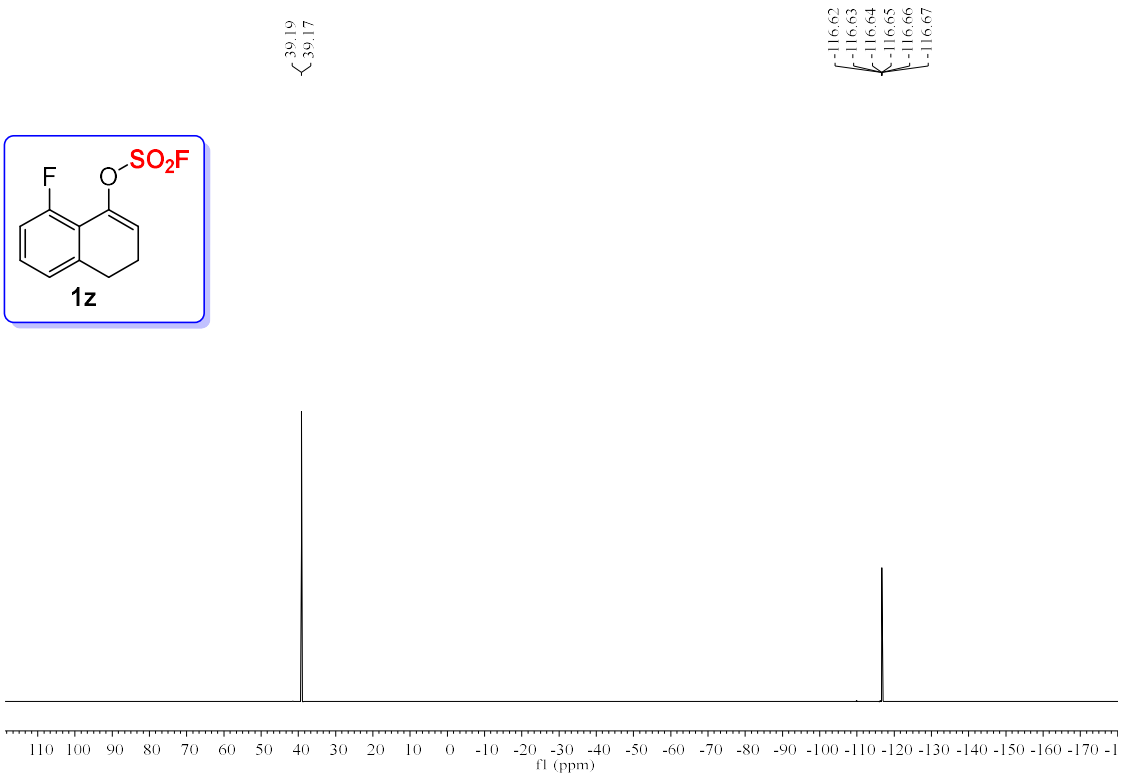




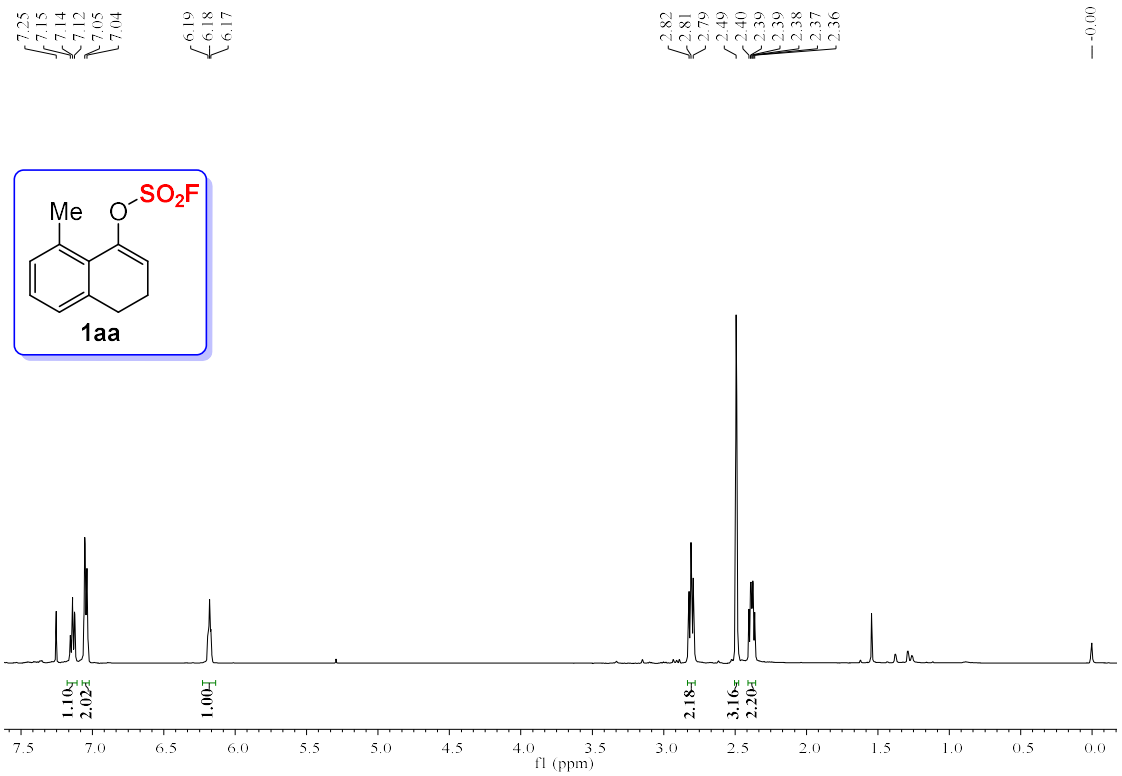
^{13}C NMR (126 MHz, $CDCl_3$) for **1z**



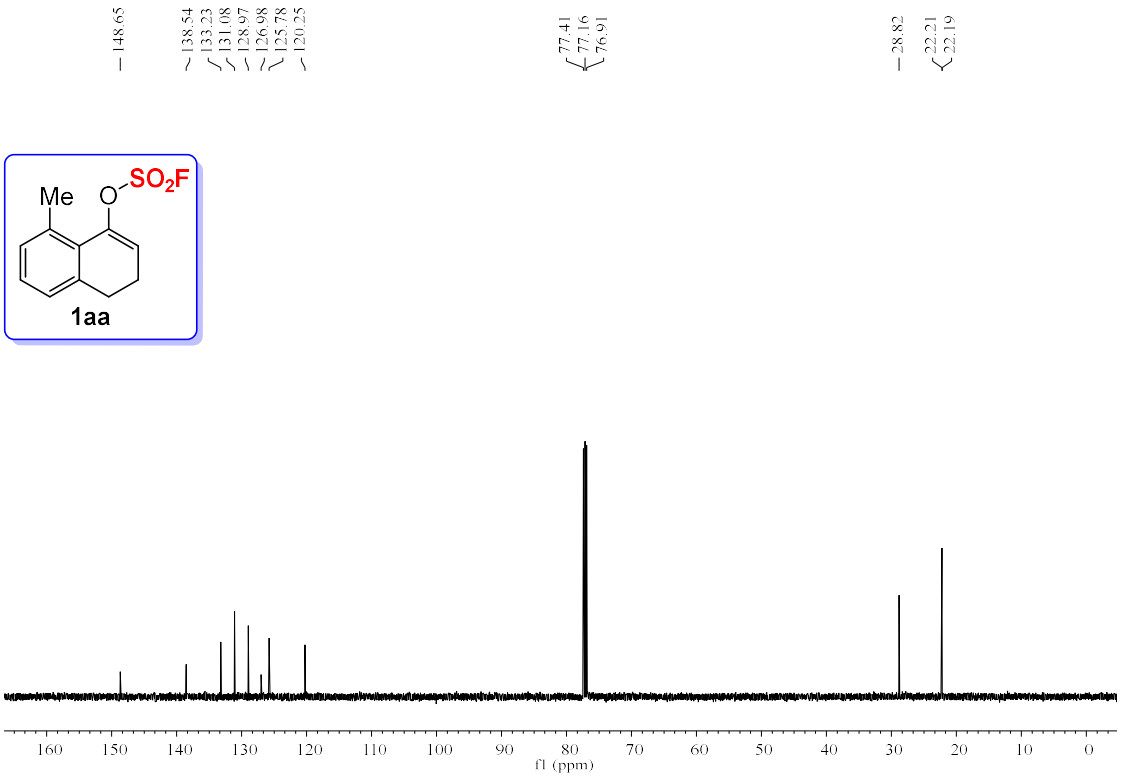
^{19}F NMR (471 MHz, $CDCl_3$) for **1z**



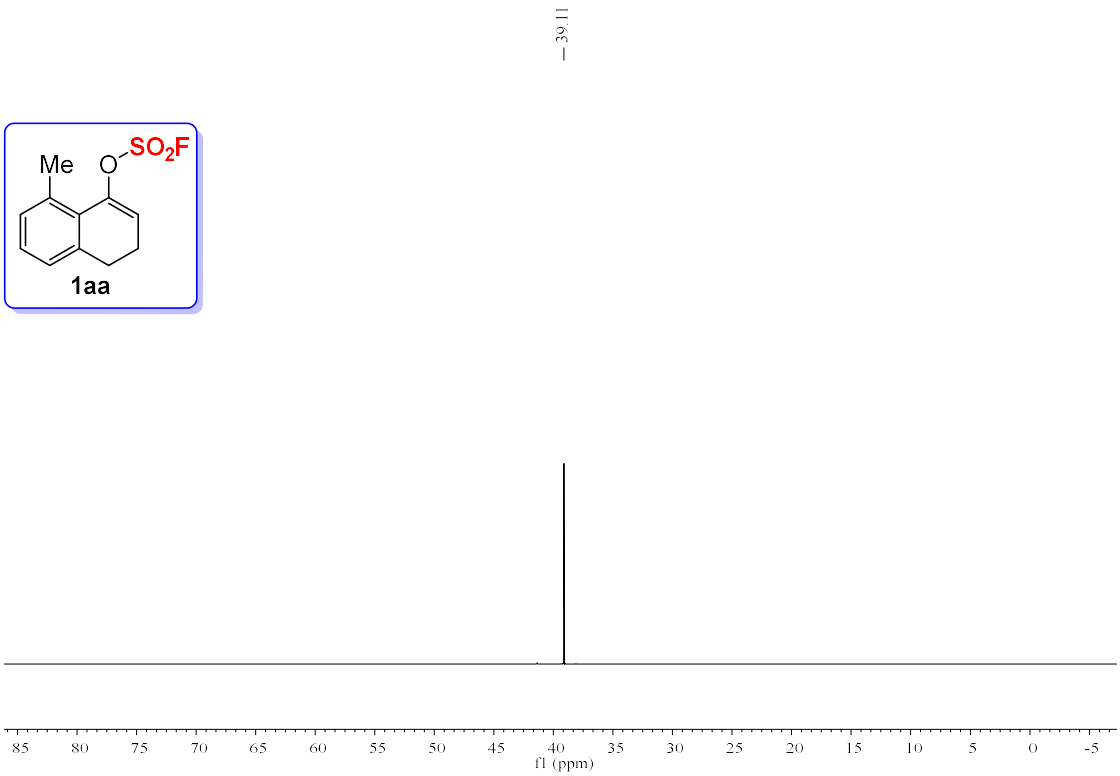
^{1}H NMR (500 MHz, $CDCl_3$) for **1aa**



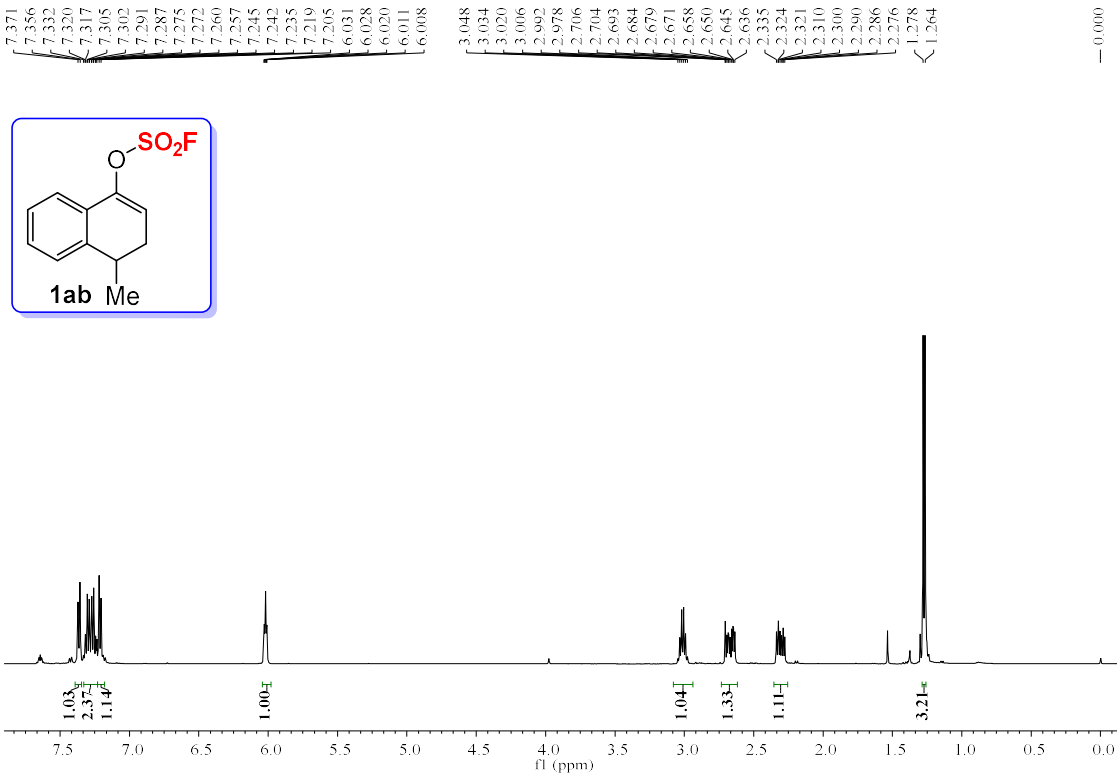
^{13}C NMR (126 MHz, $CDCl_3$) for **1aa**



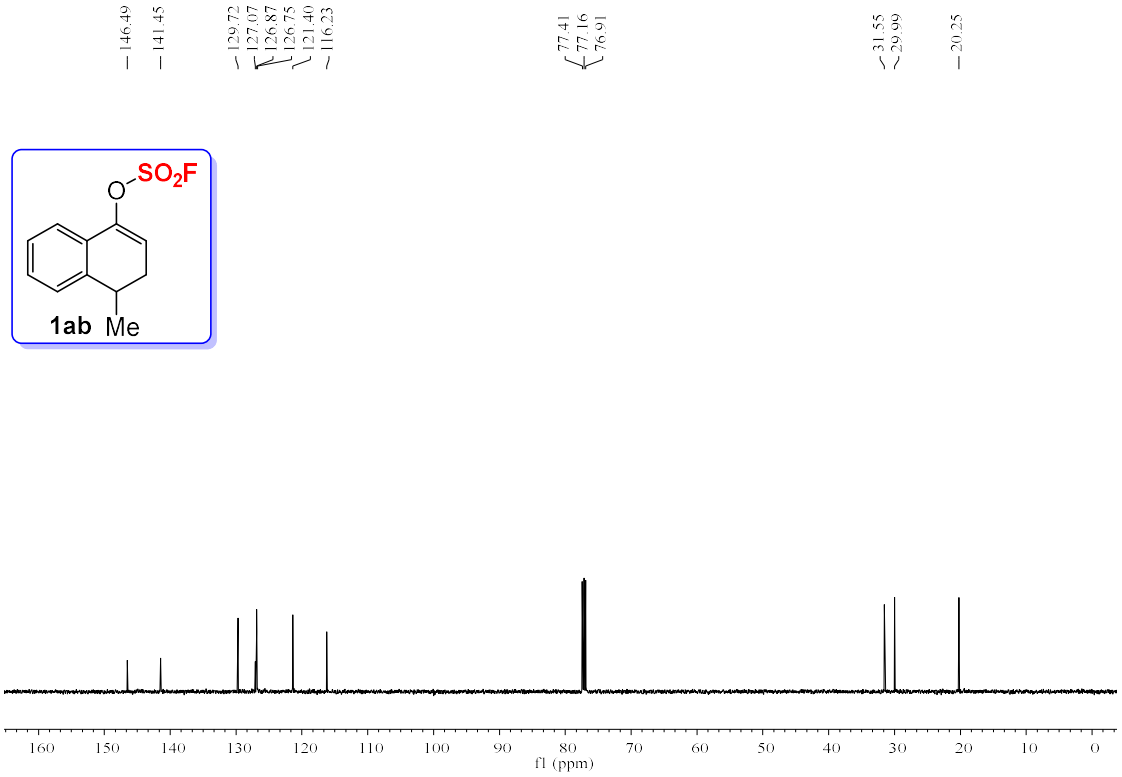
^{19}F NMR (471 MHz, $CDCl_3$) for **1aa**



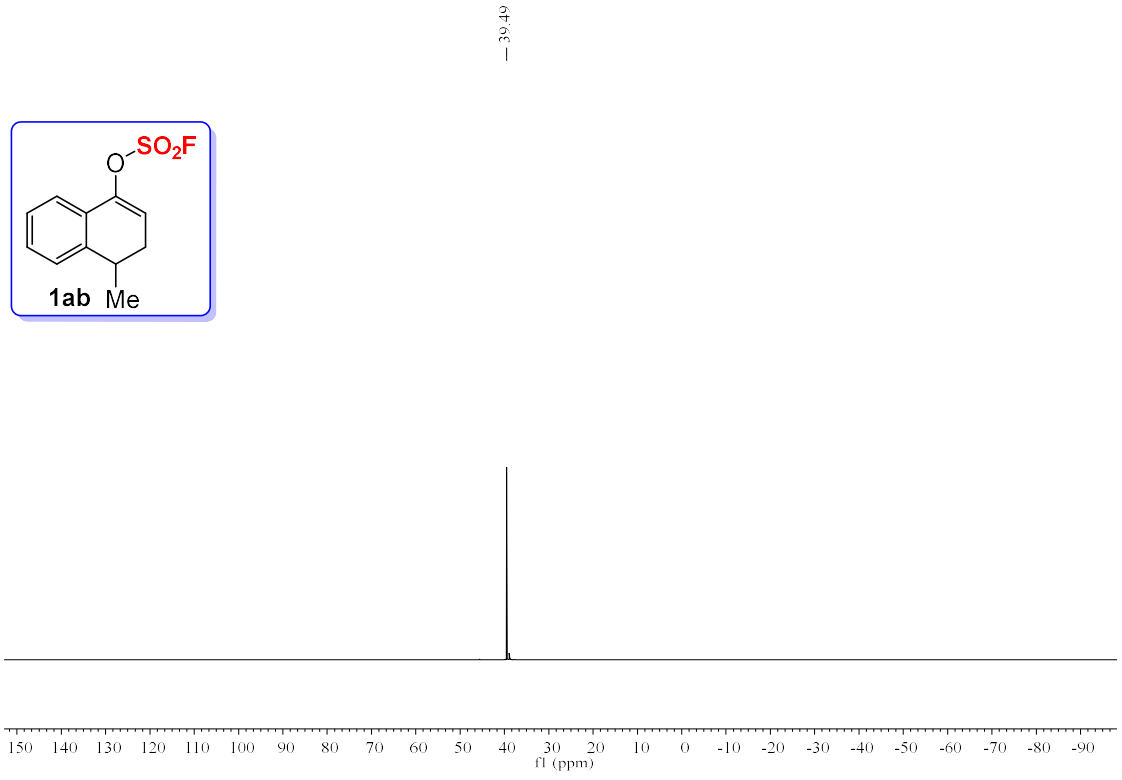
^{1}H NMR (500 MHz, $CDCl_3$) for **1ab**



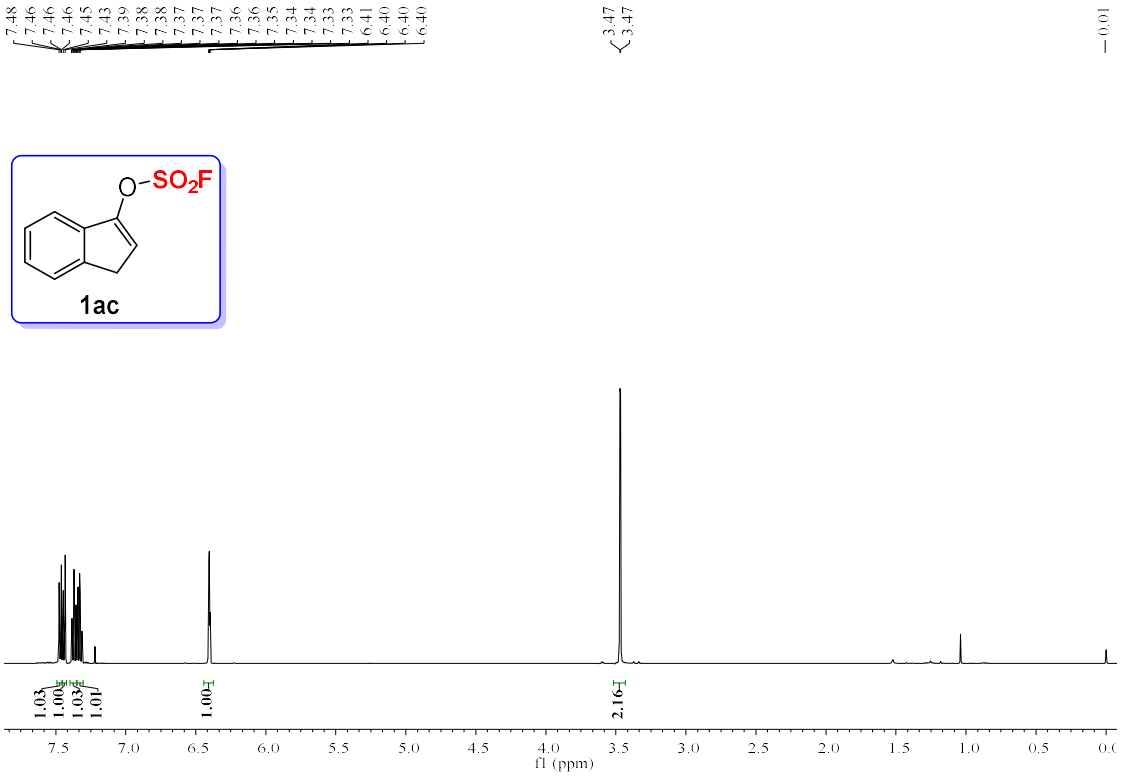
^{13}C NMR (126 MHz, $CDCl_3$) for **1ab**



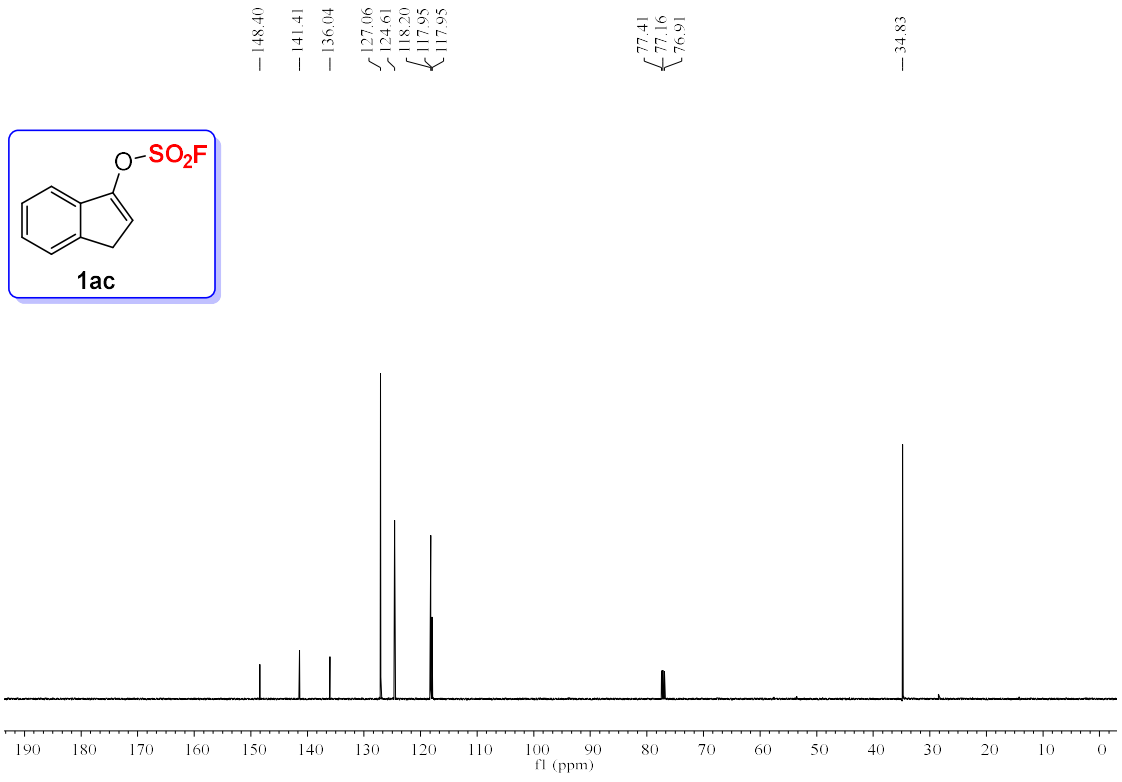
^{19}F NMR (471 MHz, $CDCl_3$) for **1ab**



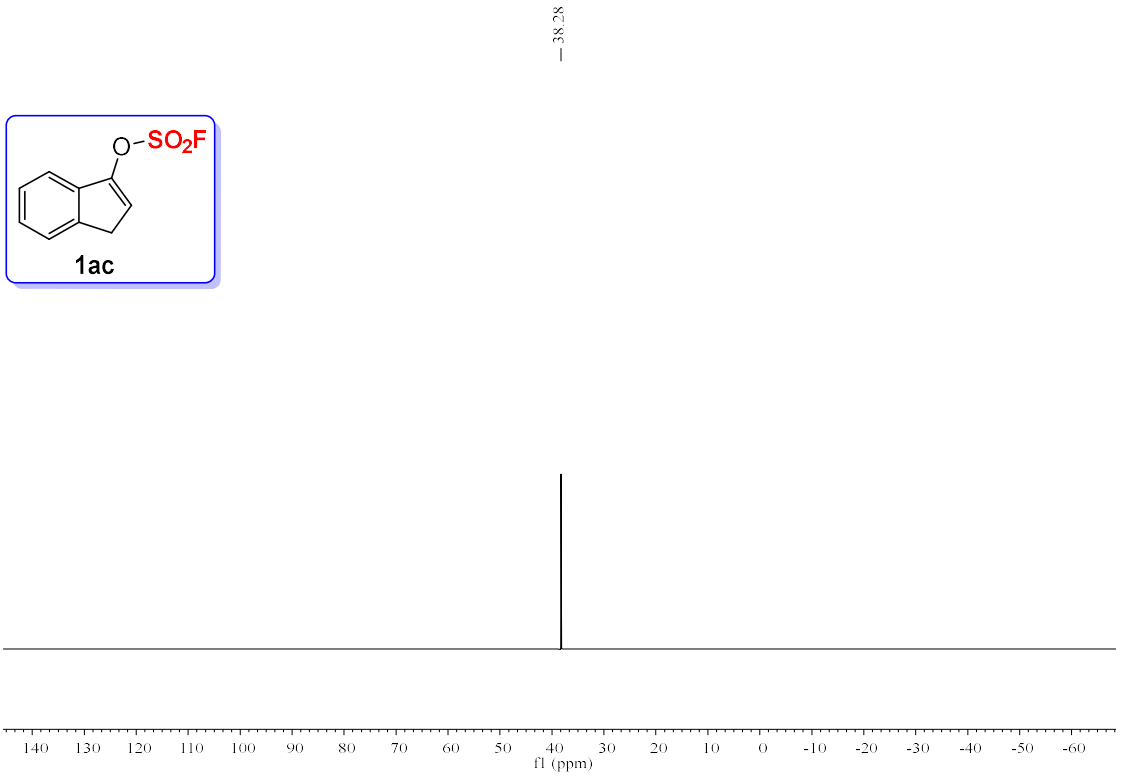
^{1}H NMR (500 MHz, $CDCl_3$) for **1ac**



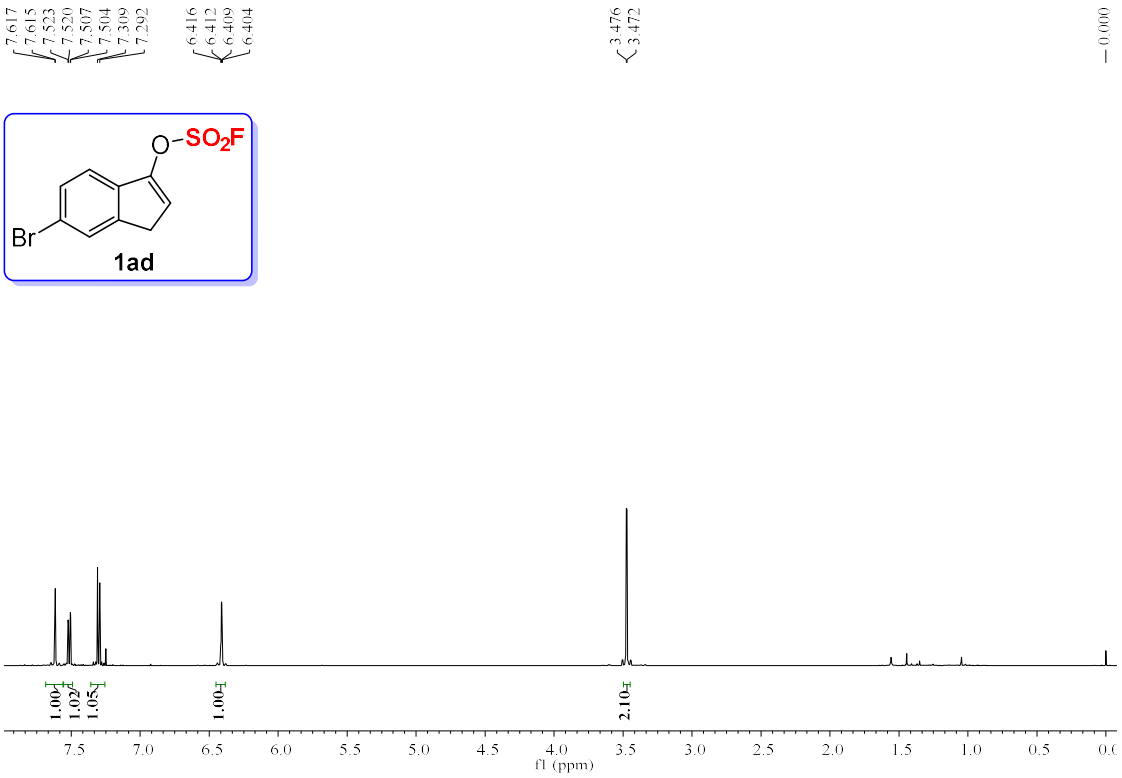
^{13}C NMR (126 MHz, $CDCl_3$) for **1ac**



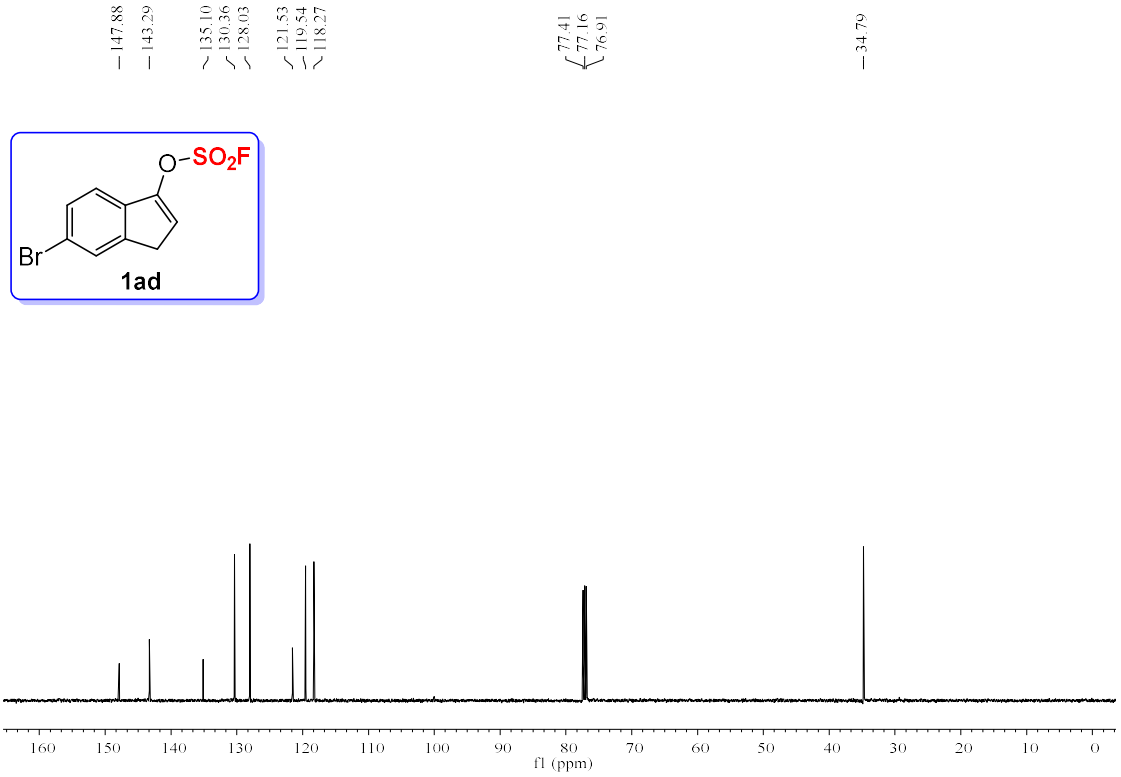
^{19}F NMR (471 MHz, $CDCl_3$) for **1ac**



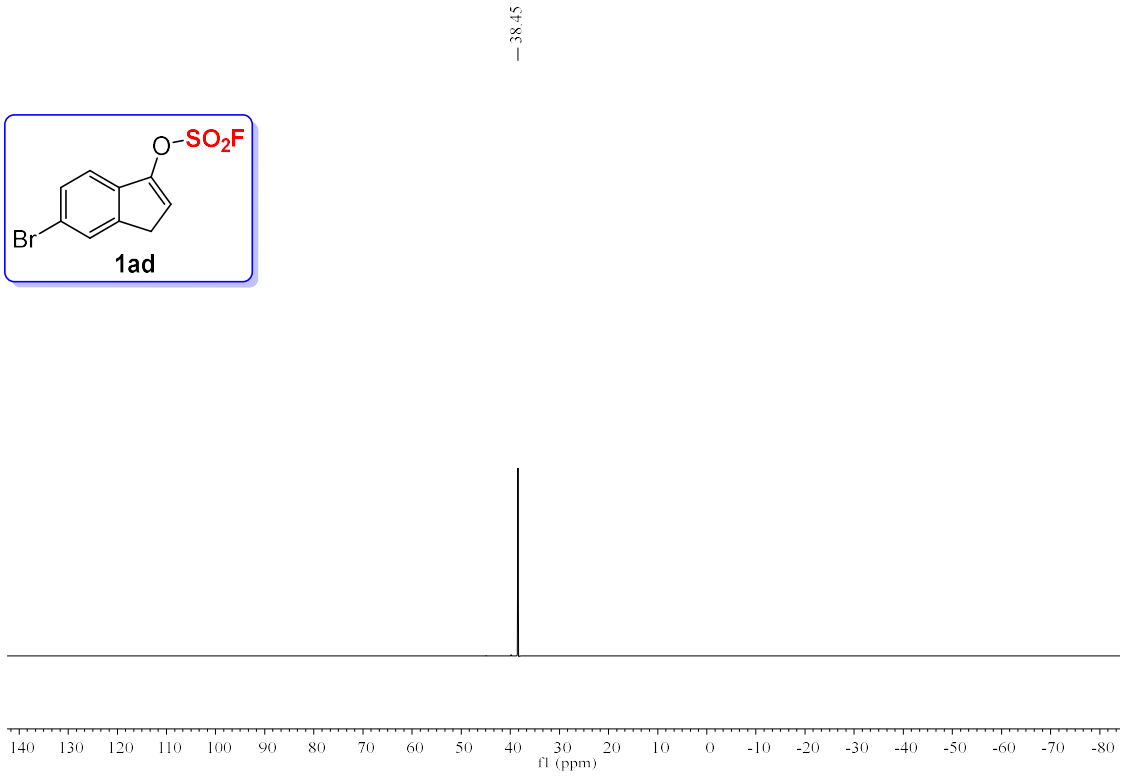
^{1}H NMR (500 MHz, $CDCl_3$) for **1ad**



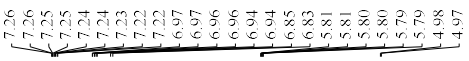
^{13}C NMR (126 MHz, $CDCl_3$) for **1ad**

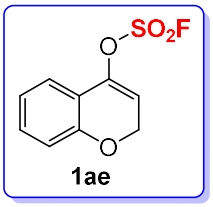


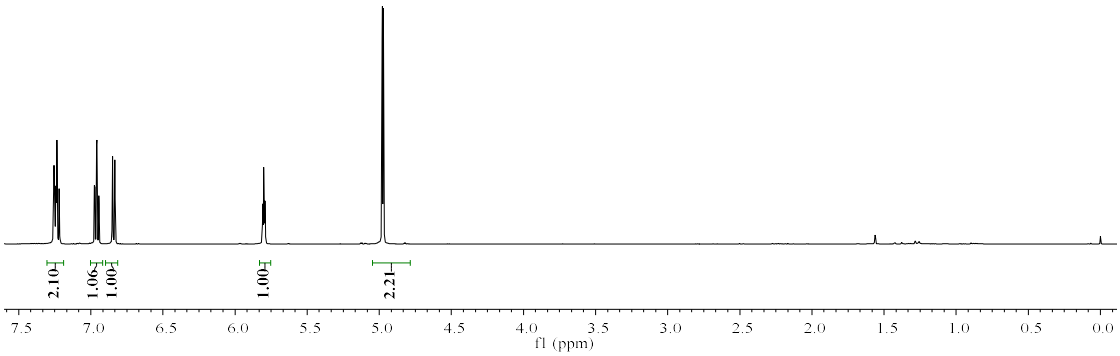
^{19}F NMR (471 MHz, $CDCl_3$) for **1ad**



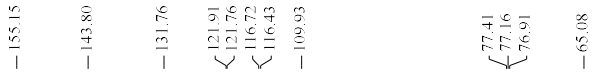
^{1}H NMR (500 MHz, $CDCl_3$) for **1ae**

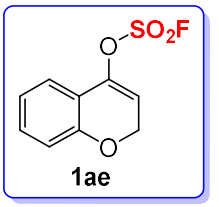


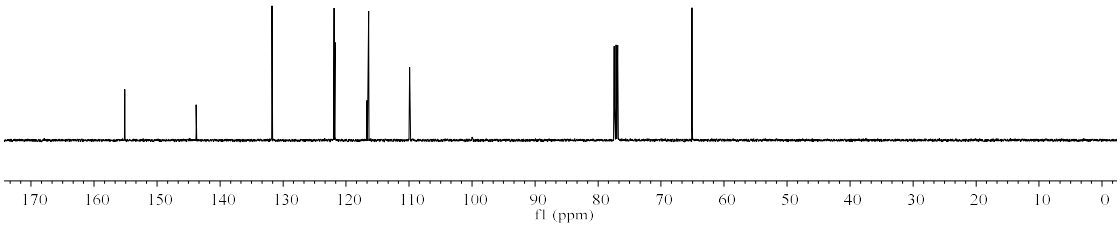




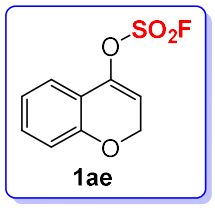
^{13}C NMR (126 MHz, $CDCl_3$) for **1ae**



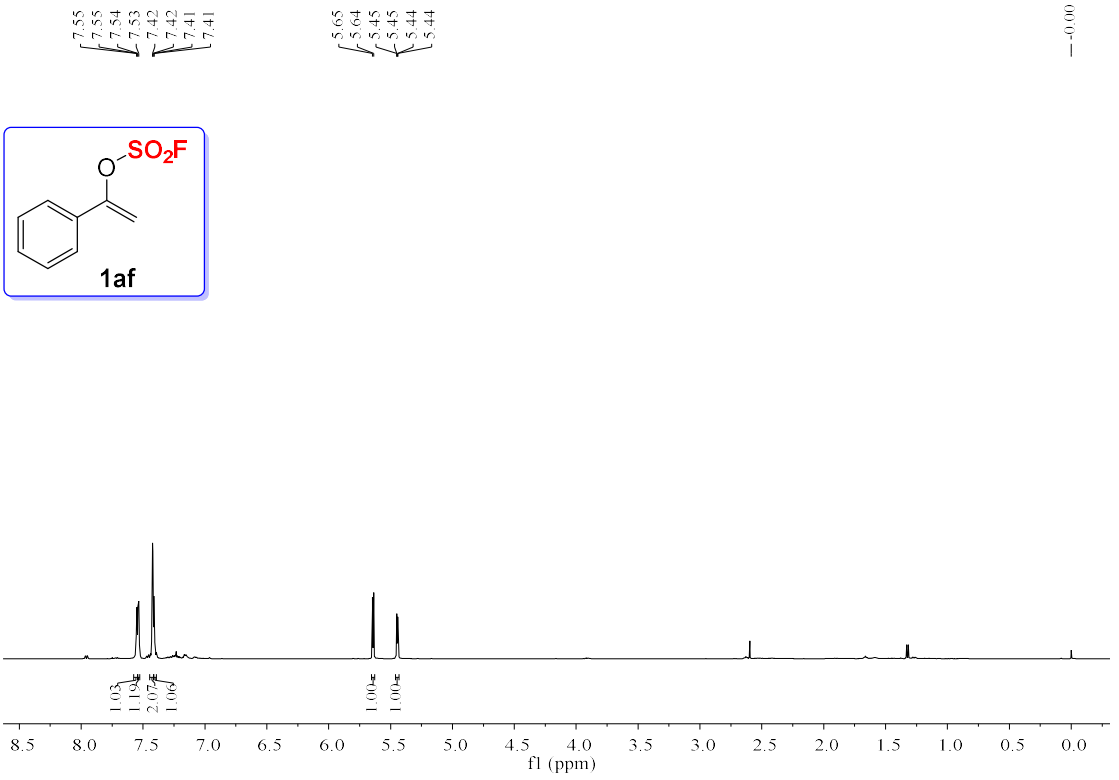




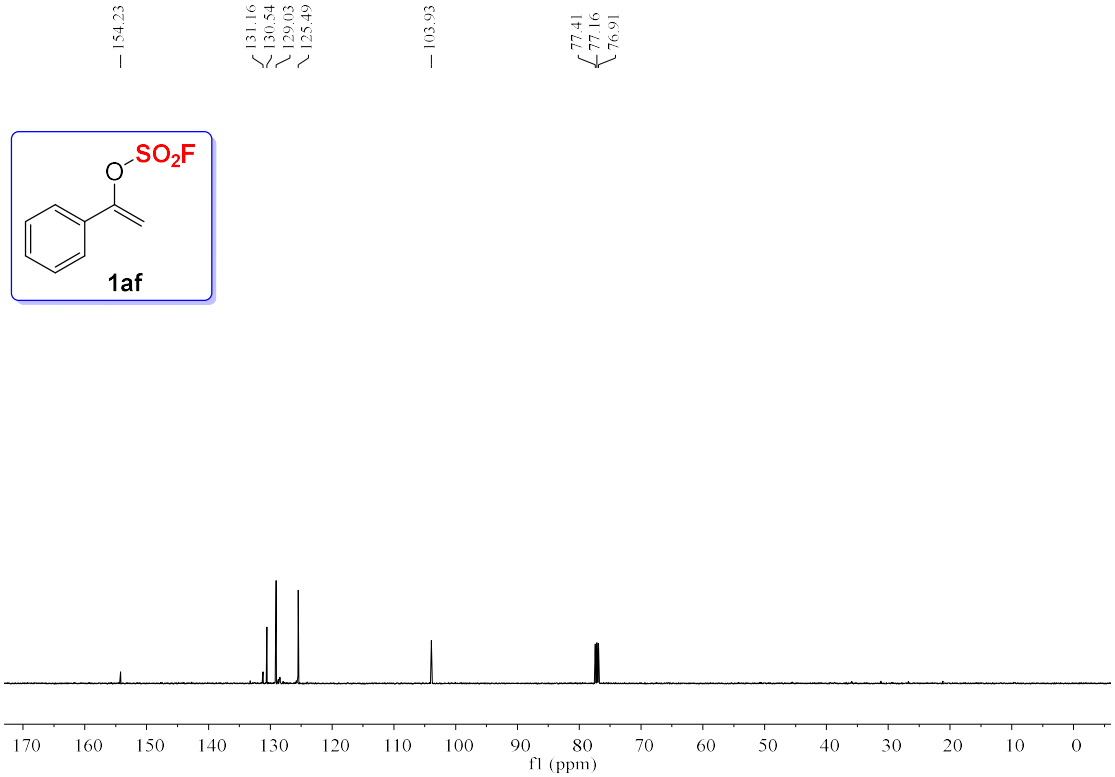
^{19}F NMR (471 MHz, $CDCl_3$)for **1ae**



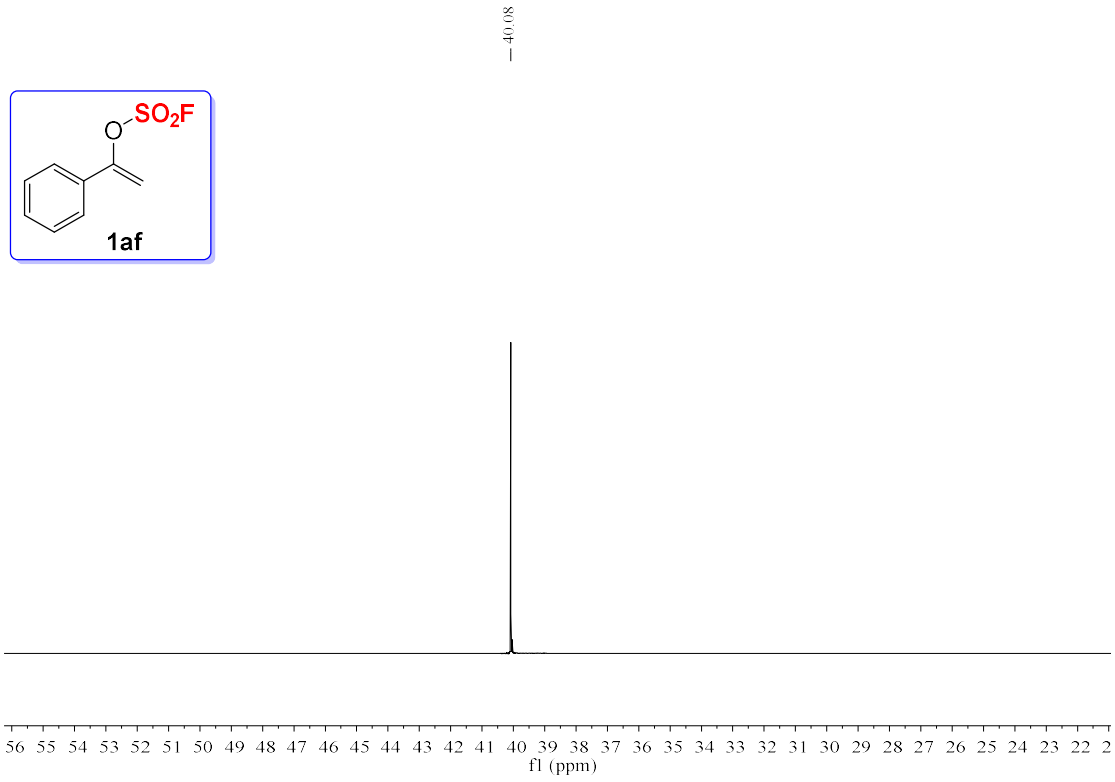
^{1}H NMR (500 MHz, $CDCl_3$) for **1af**



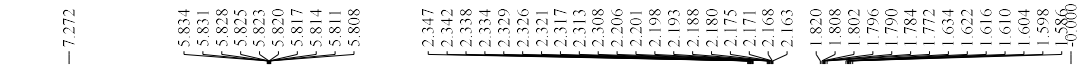
^{13}C NMR (126 MHz, $CDCl_3$) for **1af**

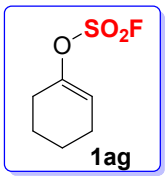


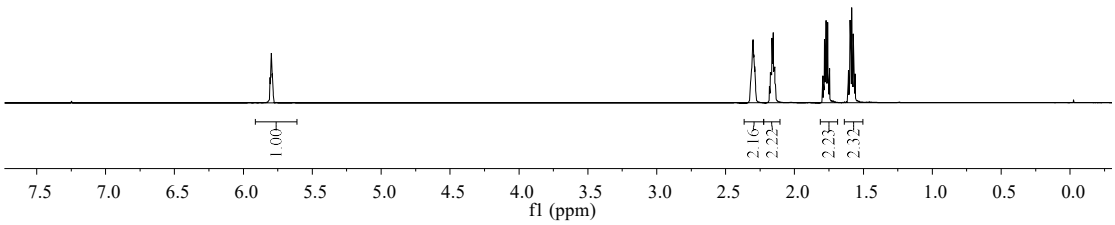
^{19}F NMR (471 MHz, $CDCl_3$) for **1af**



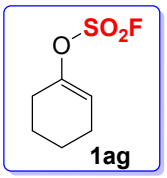
^{1}H NMR (500 MHz, $CDCl_3$) for **1ag**

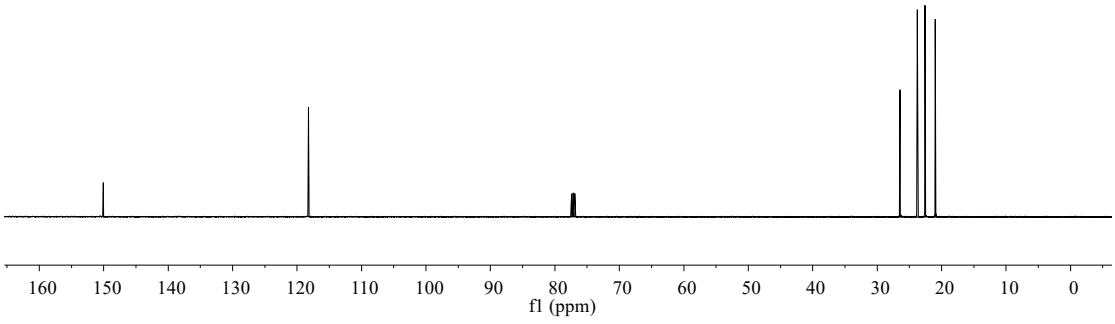




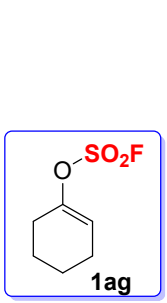


^{13}C NMR (126 MHz, $CDCl_3$) for **1ag**

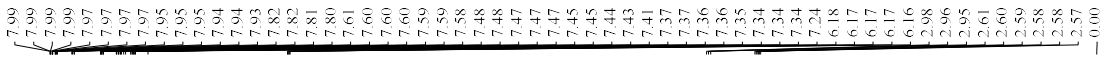


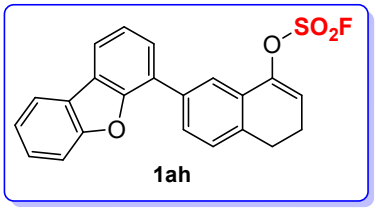


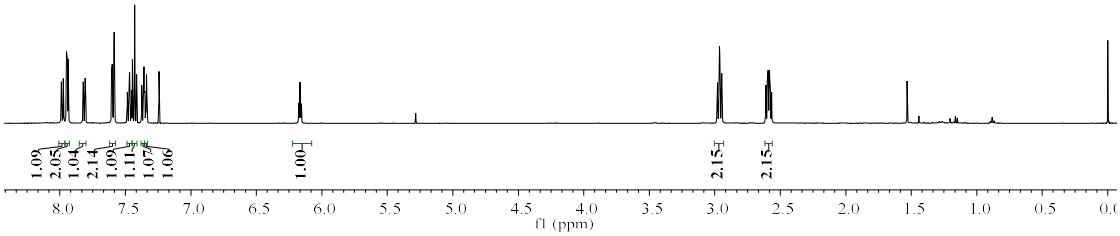
^{19}F NMR (471 MHz, $CDCl_3$) for **1ag**



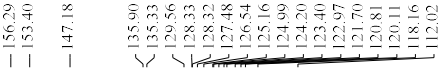
^{1}H NMR (500 MHz, $CDCl_3$) for **1ah**

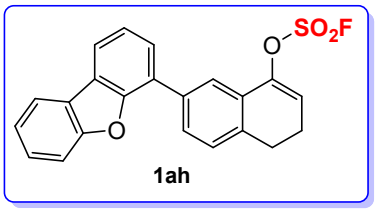


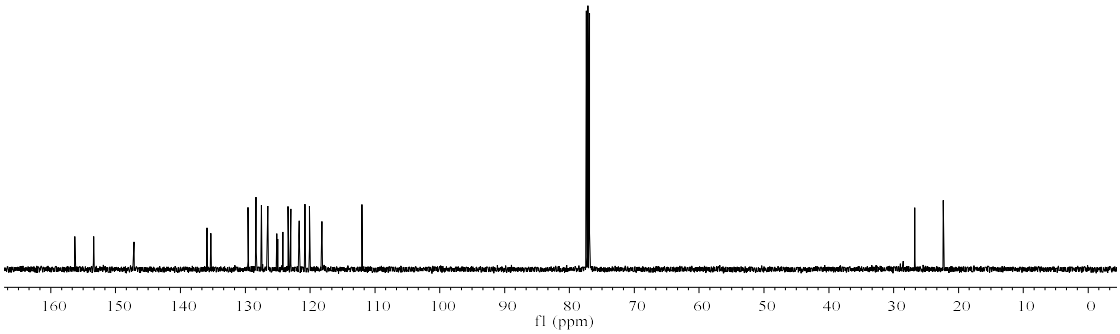




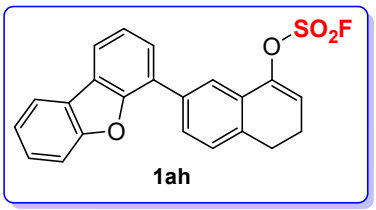
^{13}C NMR (126 MHz, $CDCl_3$) for **1ah**

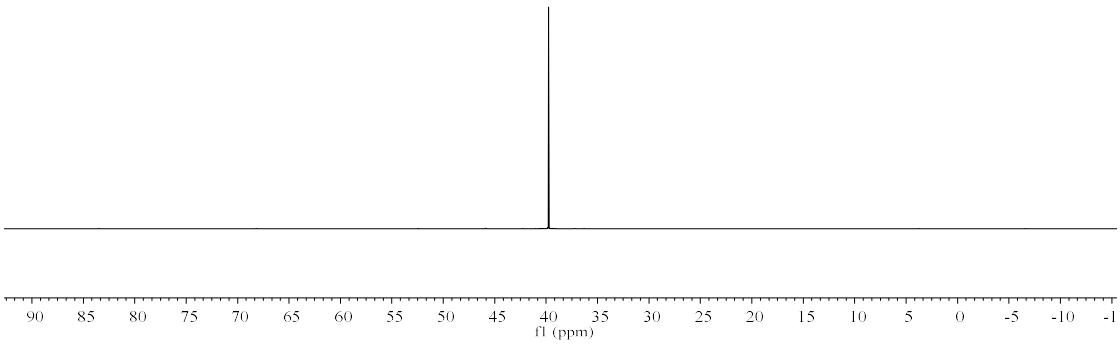




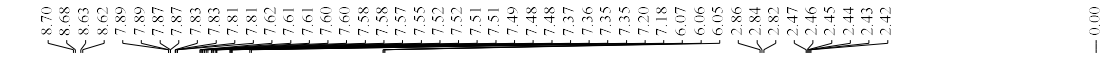


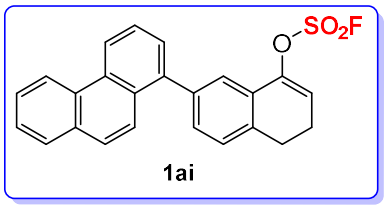
^{19}F NMR (471 MHz, $CDCl_3$) for **1ah**

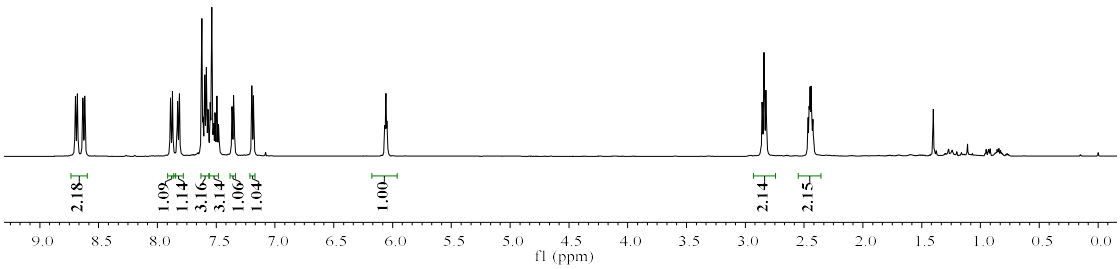




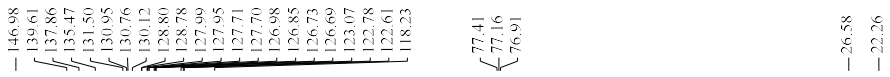
^{1}H NMR (500 MHz, $CDCl_3$) for **1ai**

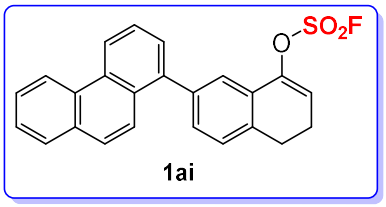


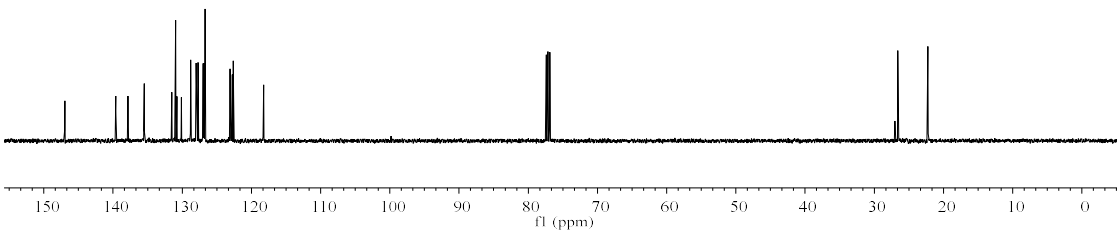




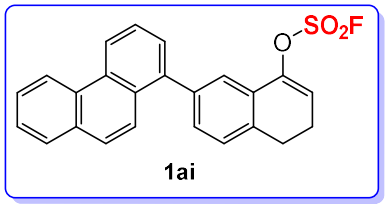
^{13}C NMR (126 MHz, $CDCl_3$) for **1ai**



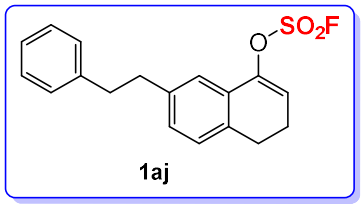


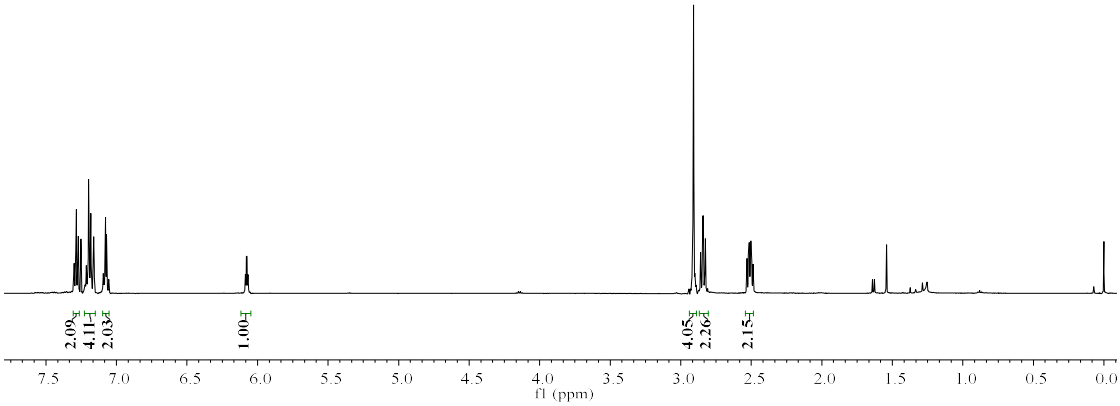


^{19}F NMR (471 MHz, $CDCl_3$) for **1ai**

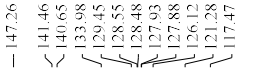


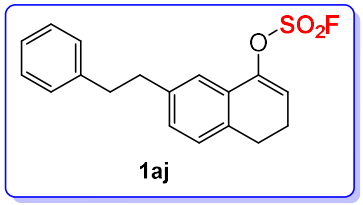
^{1}H NMR (500 MHz, $CDCl_3$) for **1aj**

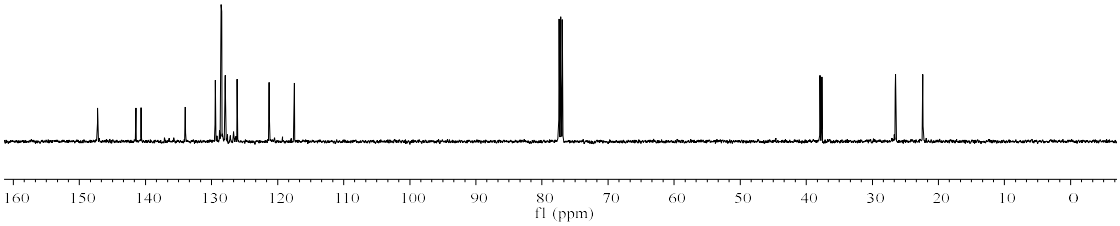




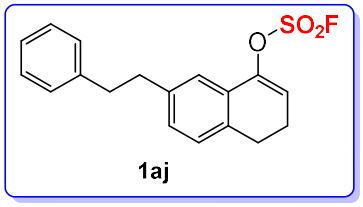
^{13}C NMR (126 MHz, $CDCl_3$) for **1aj**

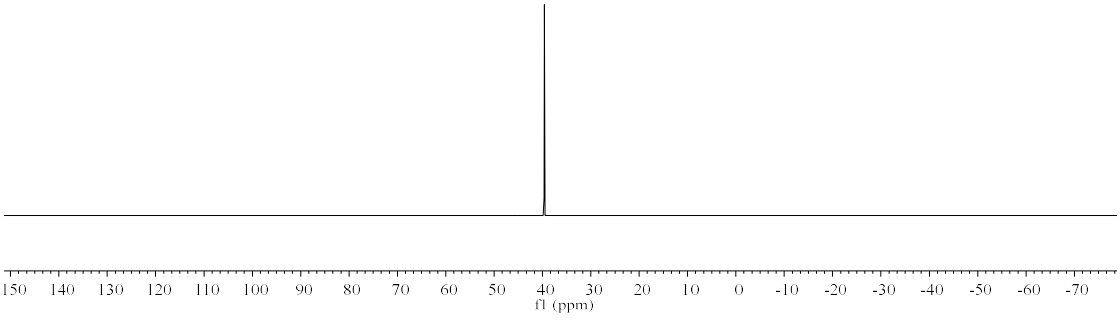




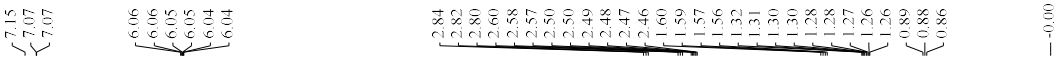


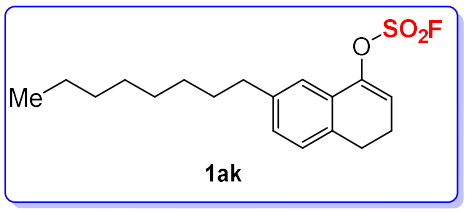
^{19}F NMR (471 MHz, $CDCl_3$) for **1aj**

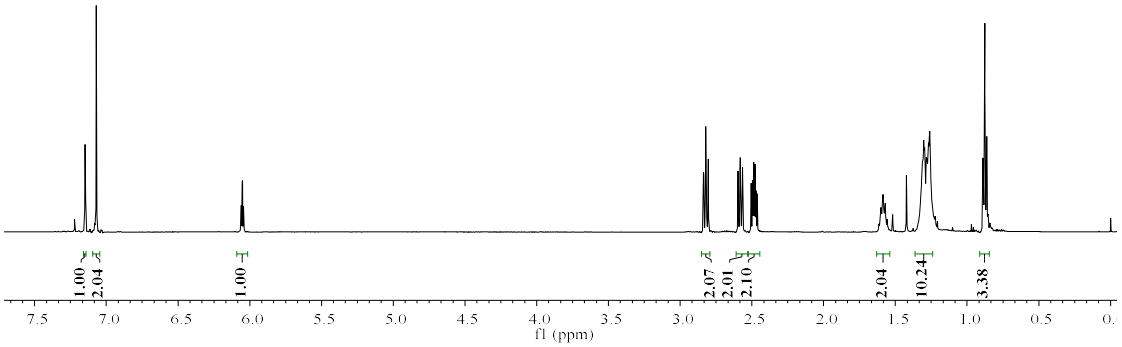




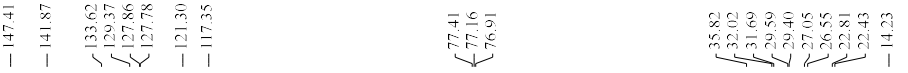
^{1}H NMR (500 MHz, $CDCl_3$) for **1ak**

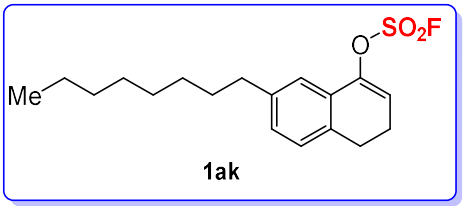


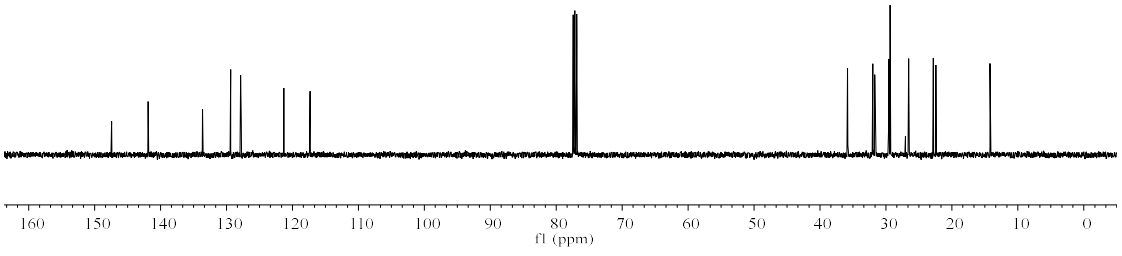




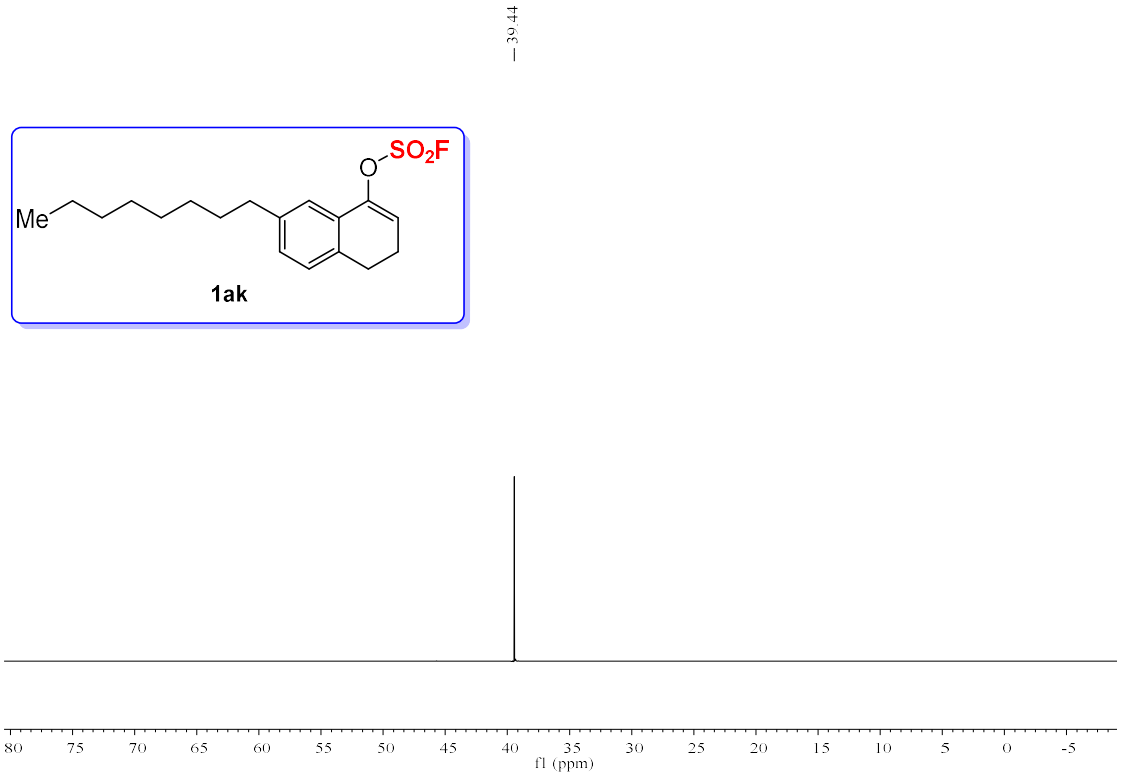
^{13}C NMR (126 MHz, $CDCl_3$) for **1ak**



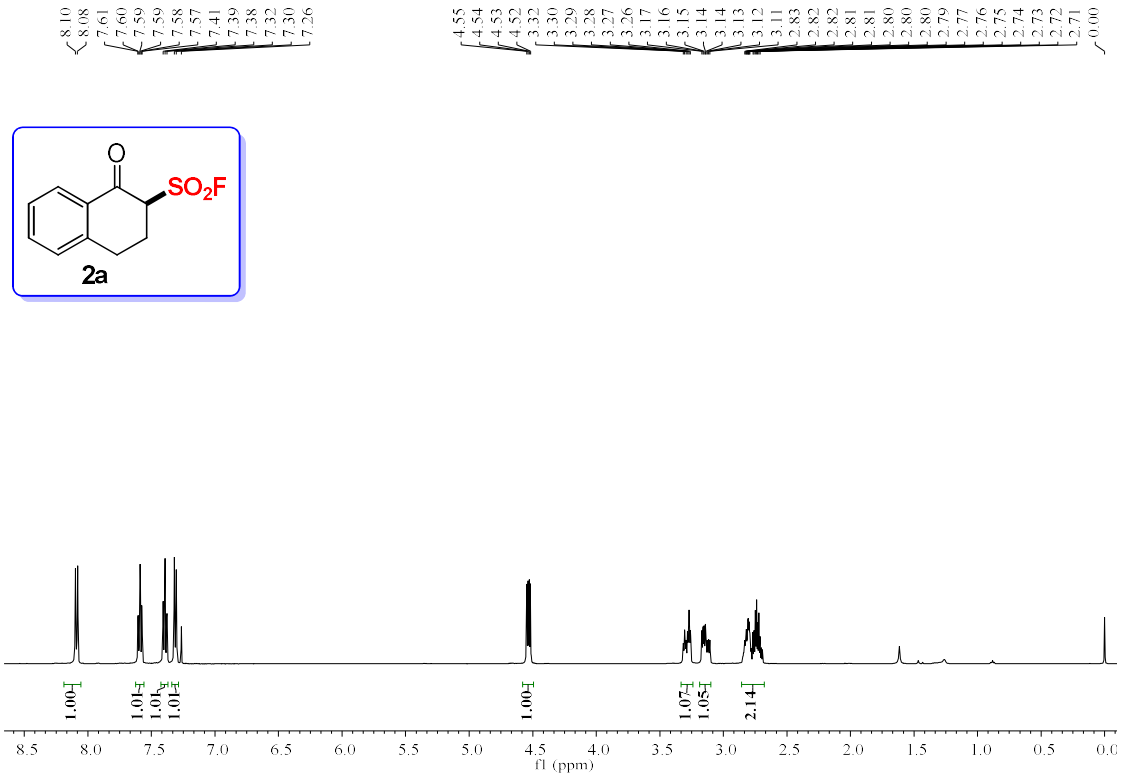




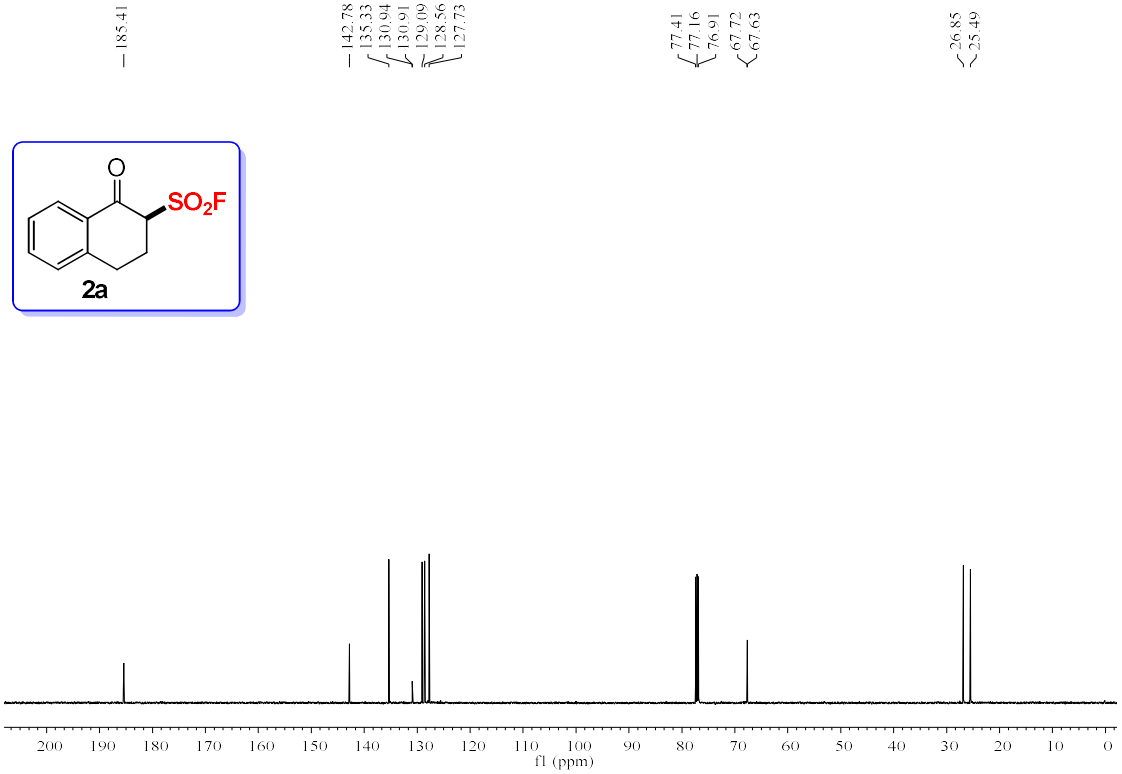
^{19}F NMR (471 MHz, $CDCl_3$) for **1ak**



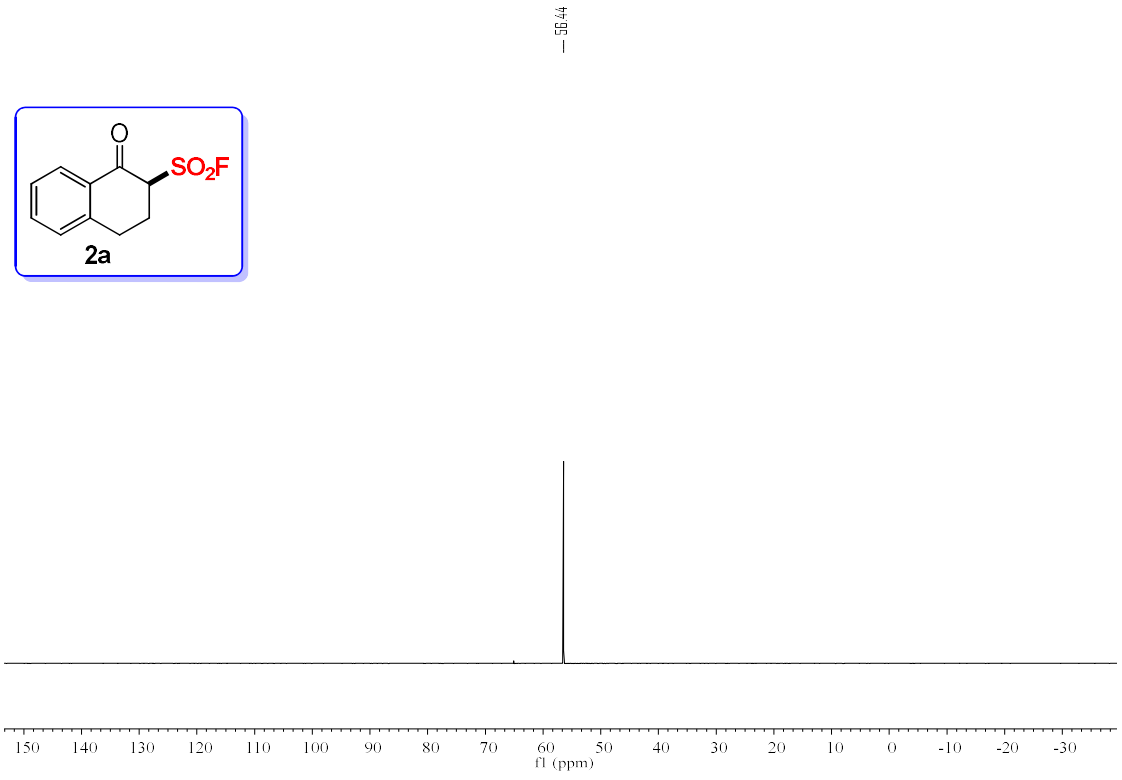
^{1}H NMR (500 MHz, $CDCl_3$) for **2a**



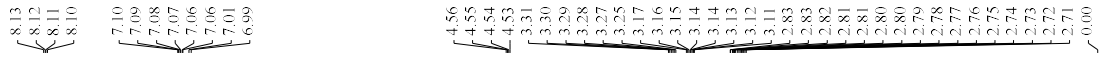
^{13}C NMR (126 MHz, $CDCl_3$) for **2a**

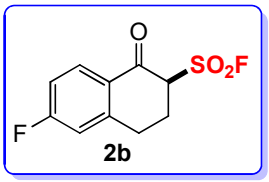


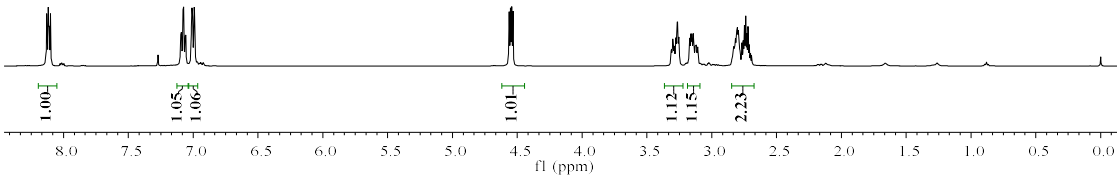
^{19}F NMR (471 MHz, $CDCl_3$) for **2a**



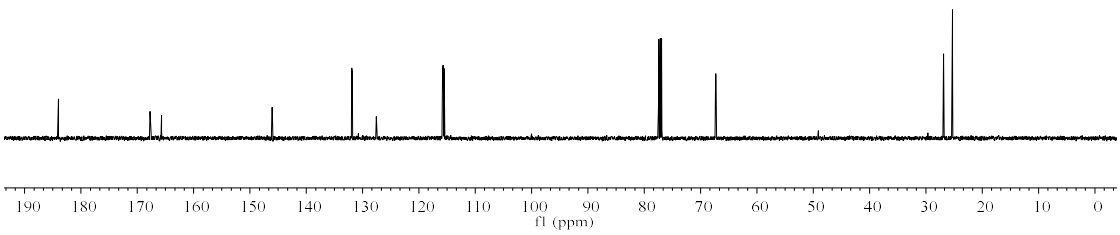
^{1}H NMR (500 MHz, $CDCl_3$) for **2b**



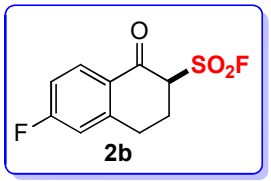




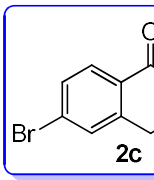
^{13}C NMR (126 MHz, $CDCl_3$) for **2b**



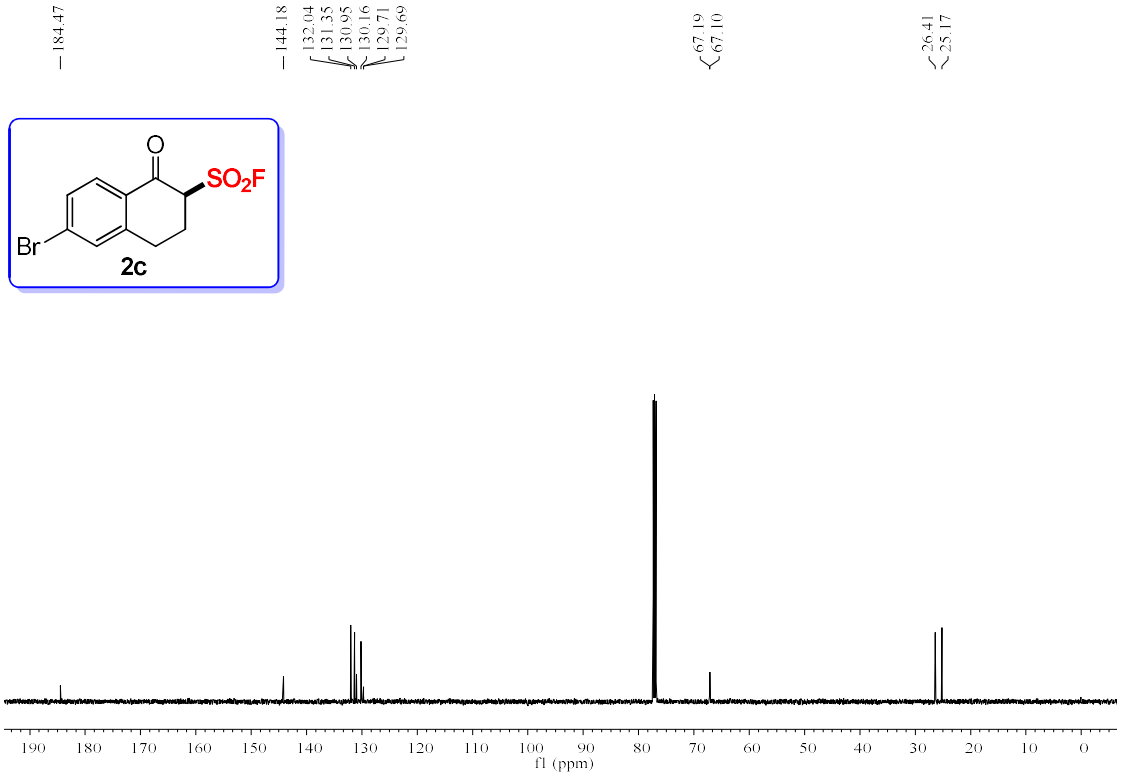
^{19}F NMR (471 MHz, $CDCl_3$) for **2b**



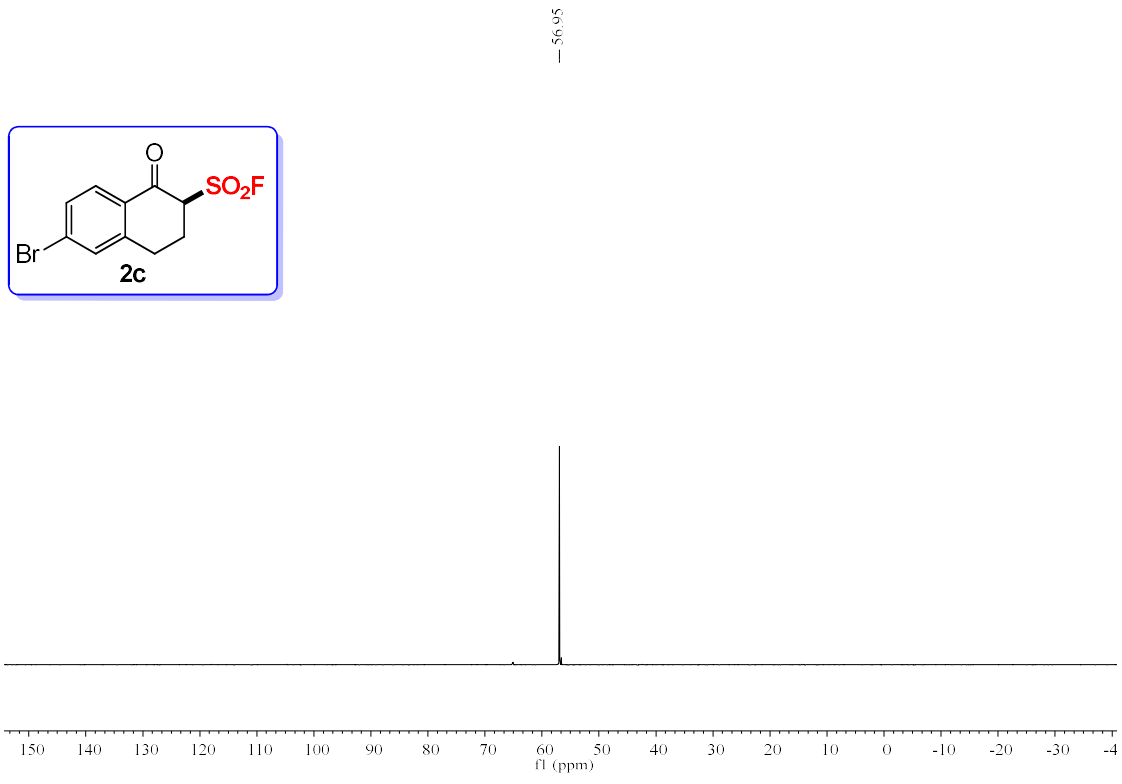
^{1}H NMR (500 MHz, $CDCl_3$) for **2c**



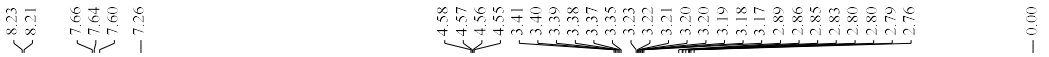
^{13}C NMR (126 MHz, $CDCl_3$) for **2c**

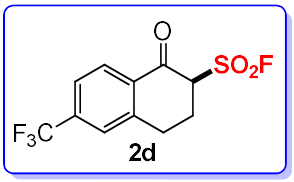


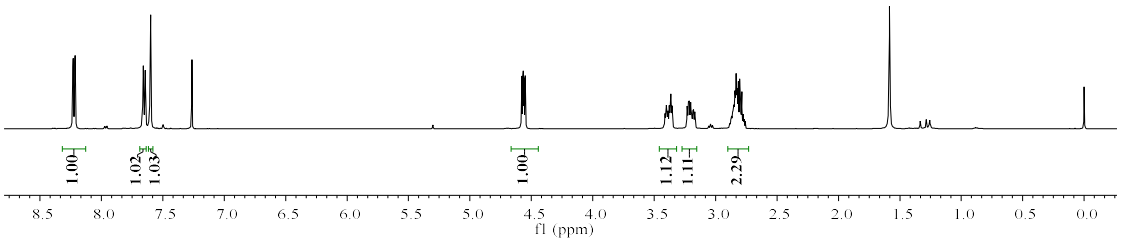
^{19}F NMR (471 MHz, $CDCl_3$) for **2c**



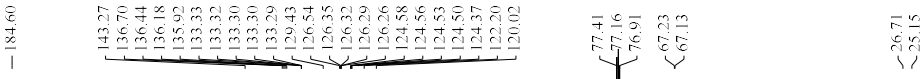
^{1}H NMR (500 MHz, $CDCl_3$) for **2d**

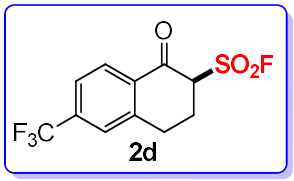


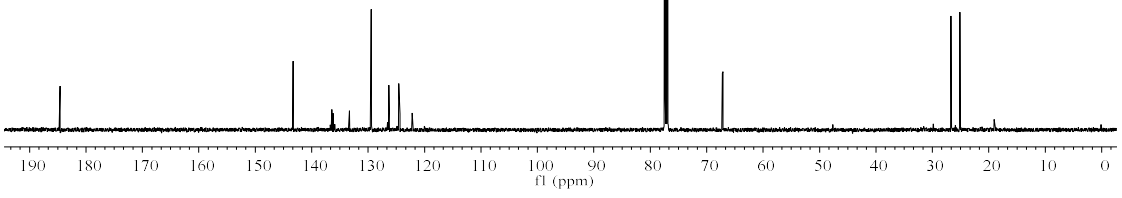




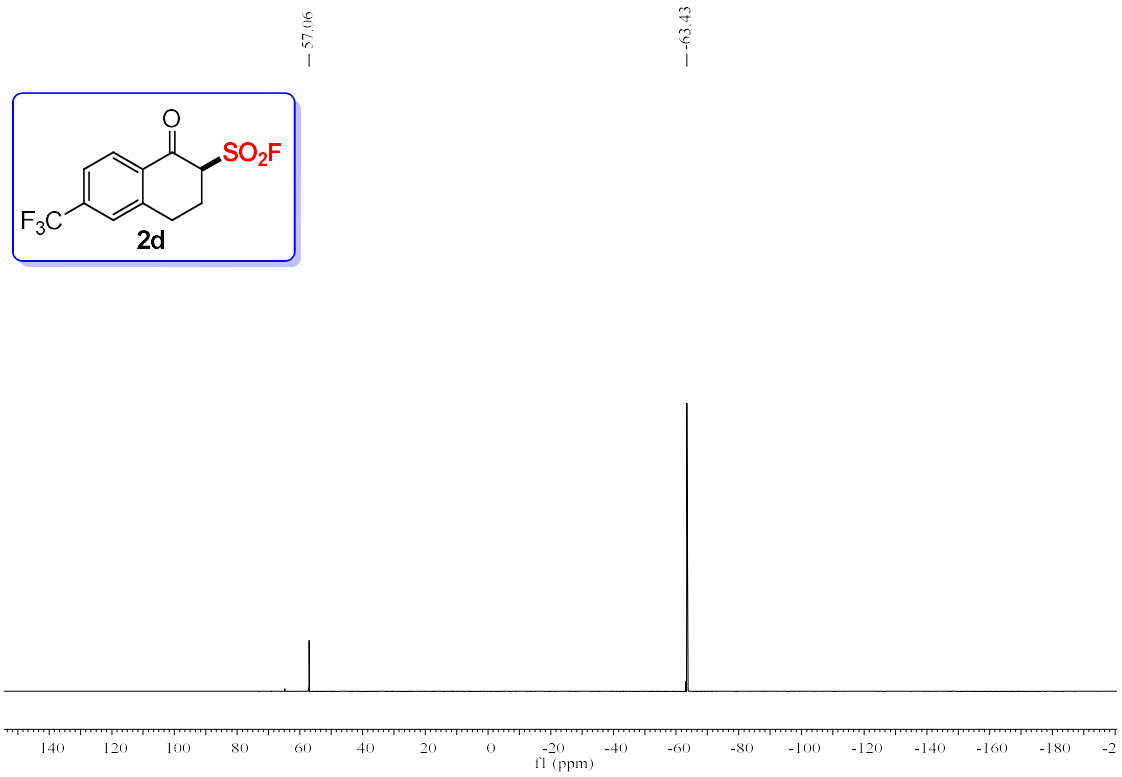
^{13}C NMR (126 MHz, $CDCl_3$) for **2d**



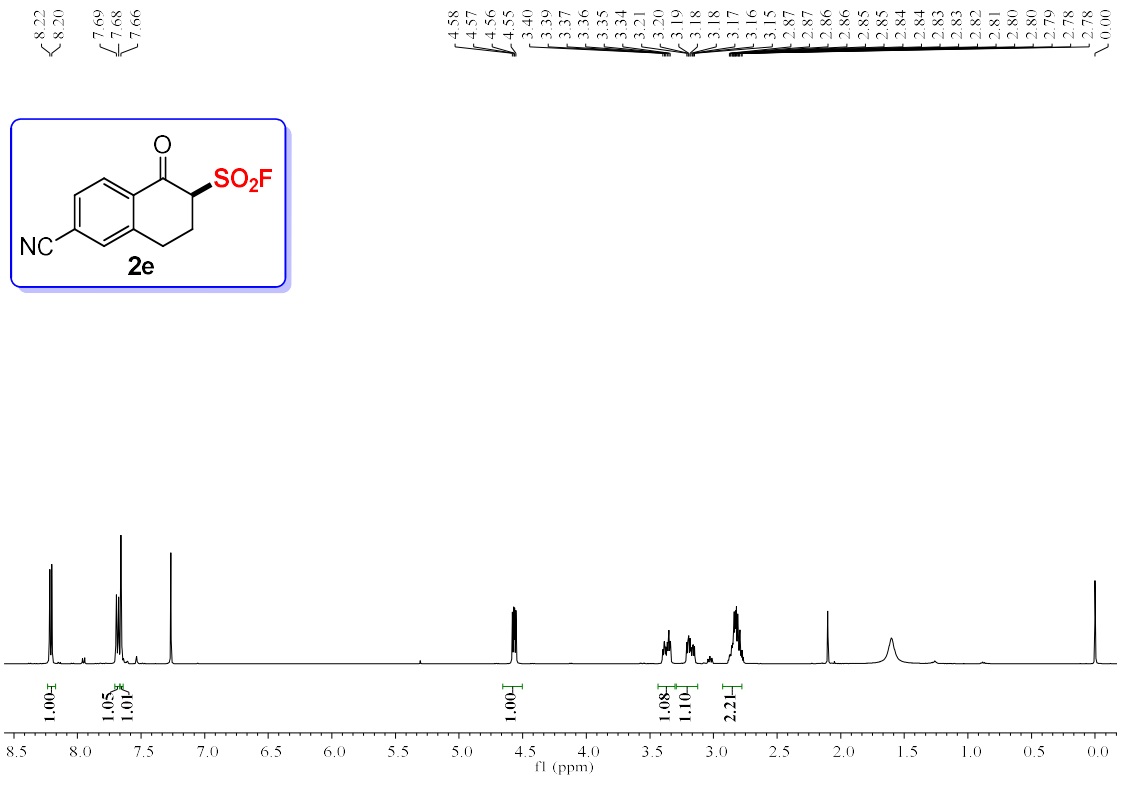




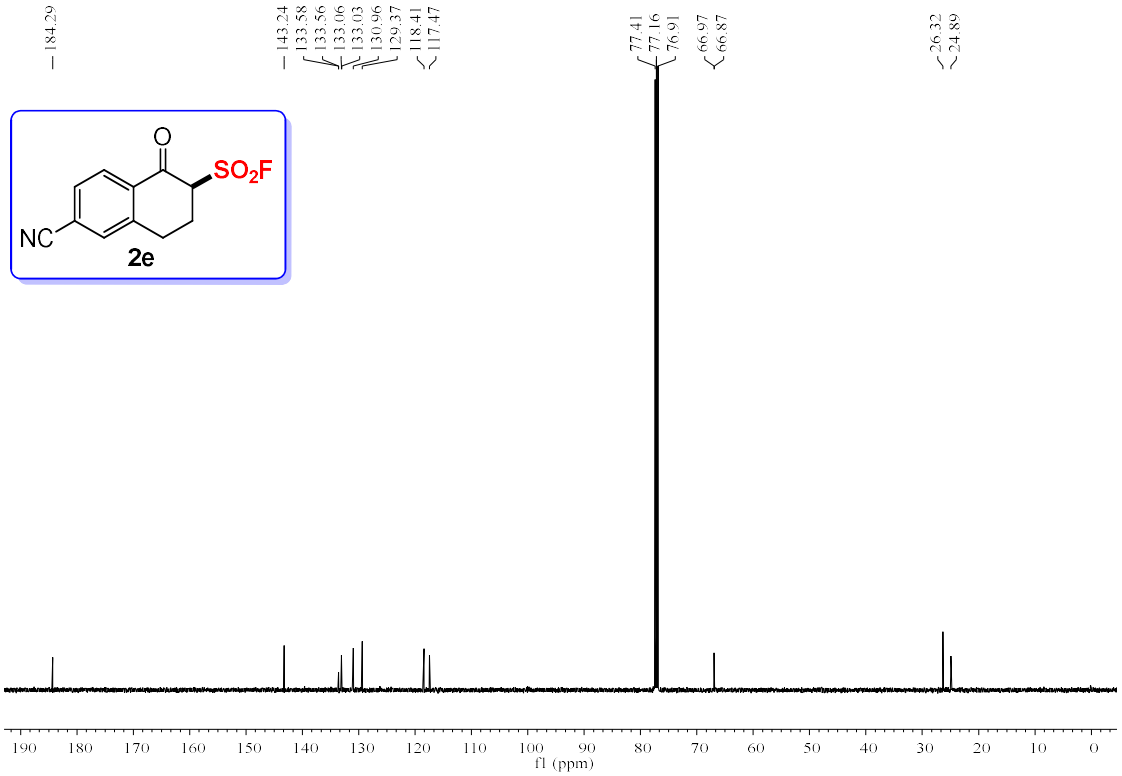
^{19}F NMR (471 MHz, $CDCl_3$) for **2d**



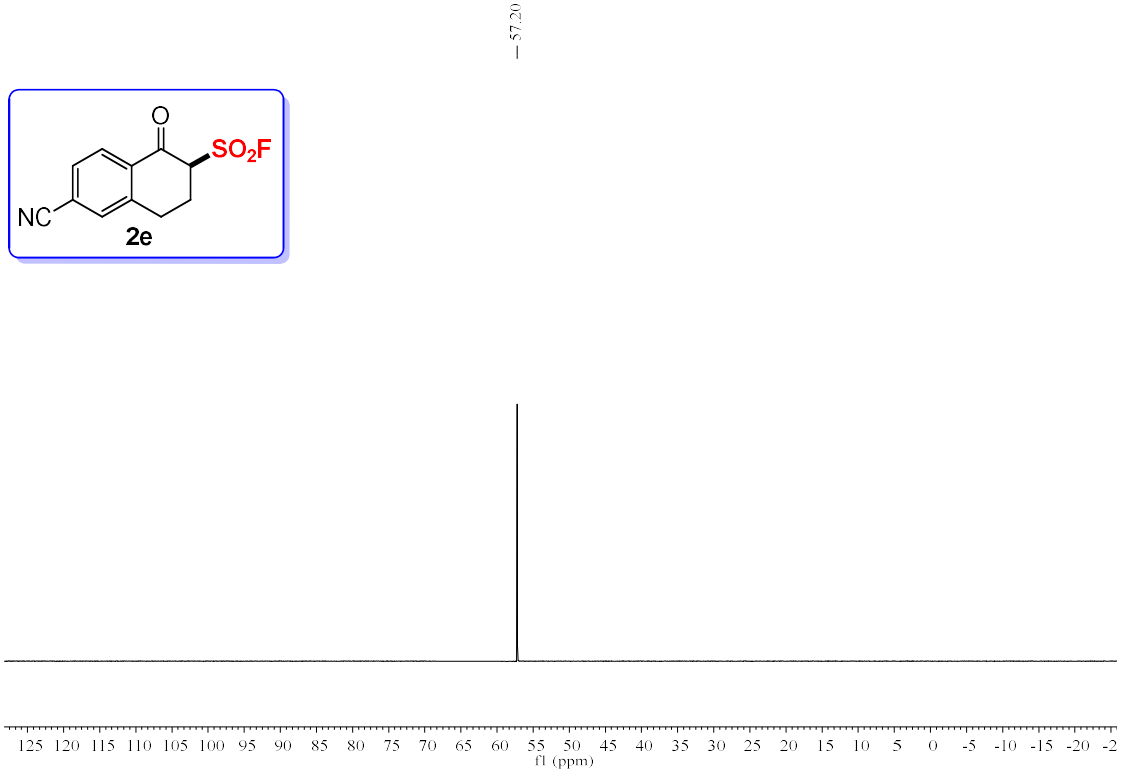
^{1}H NMR (500 MHz, $CDCl_3$) for **2e**



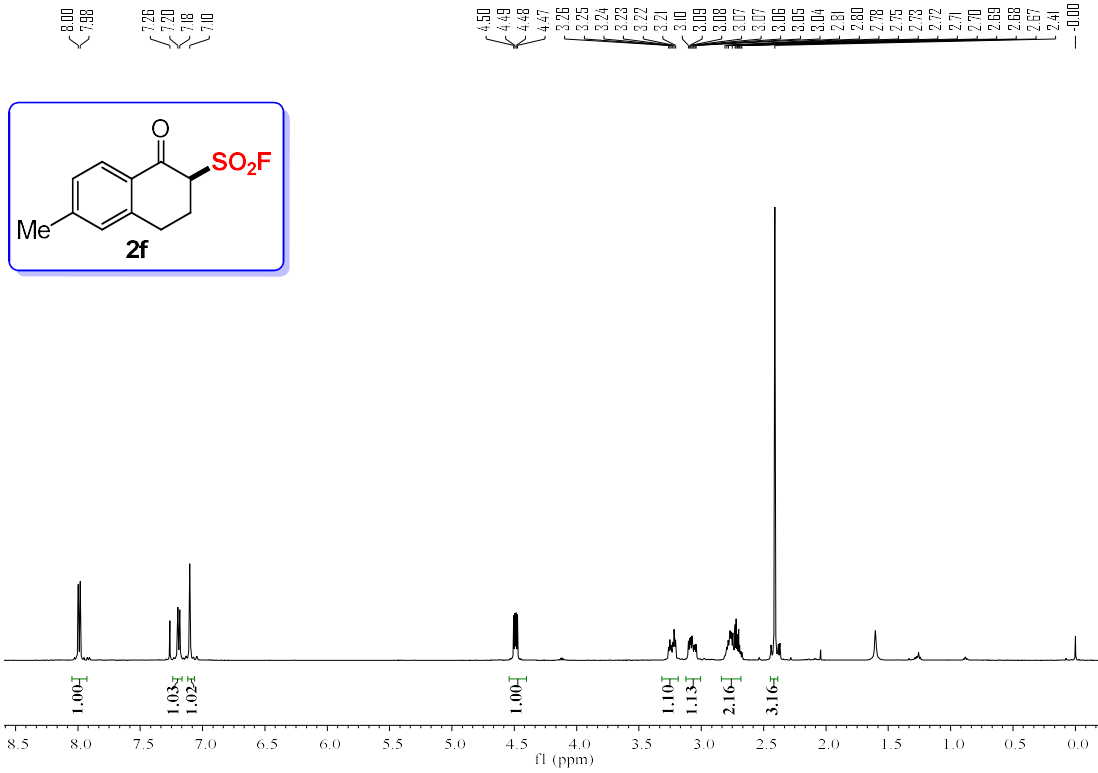
^{13}C NMR (126 MHz, $CDCl_3$) for **2e**



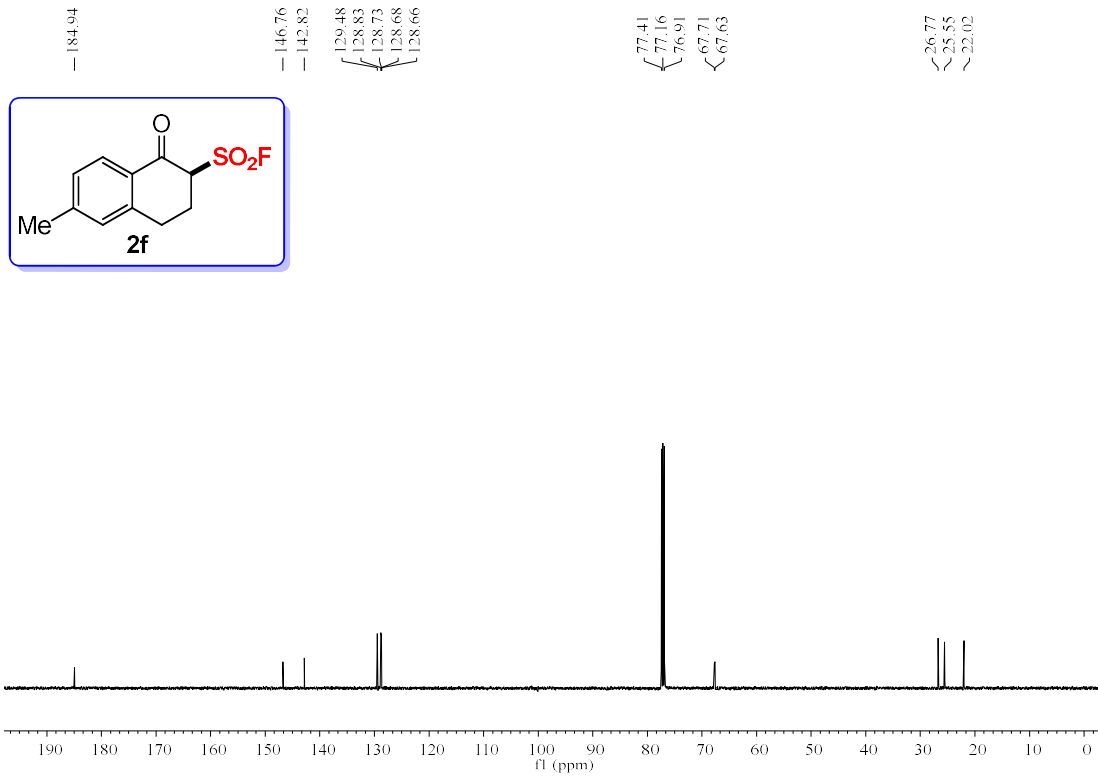
^{19}F NMR (471 MHz, $CDCl_3$) for **2e**



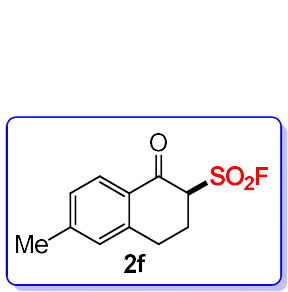
^{1}H NMR (500 MHz, $CDCl_3$) for **2f**



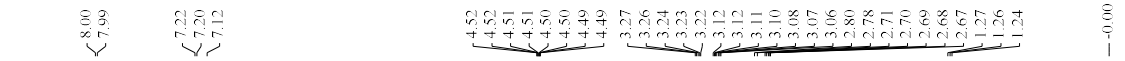
^{13}C NMR (126 MHz, $CDCl_3$) for **2f**

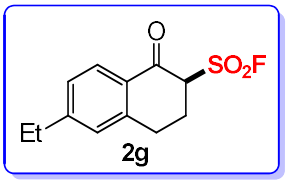


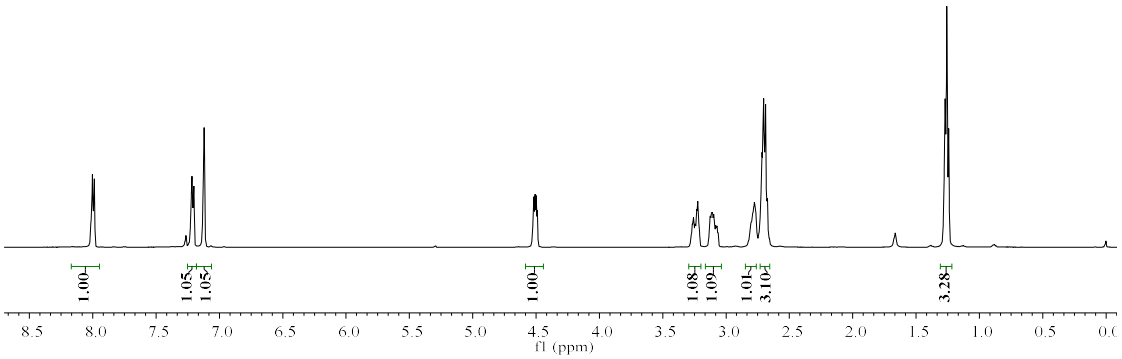
^{19}F NMR (471 MHz, $CDCl_3$) for **2f**



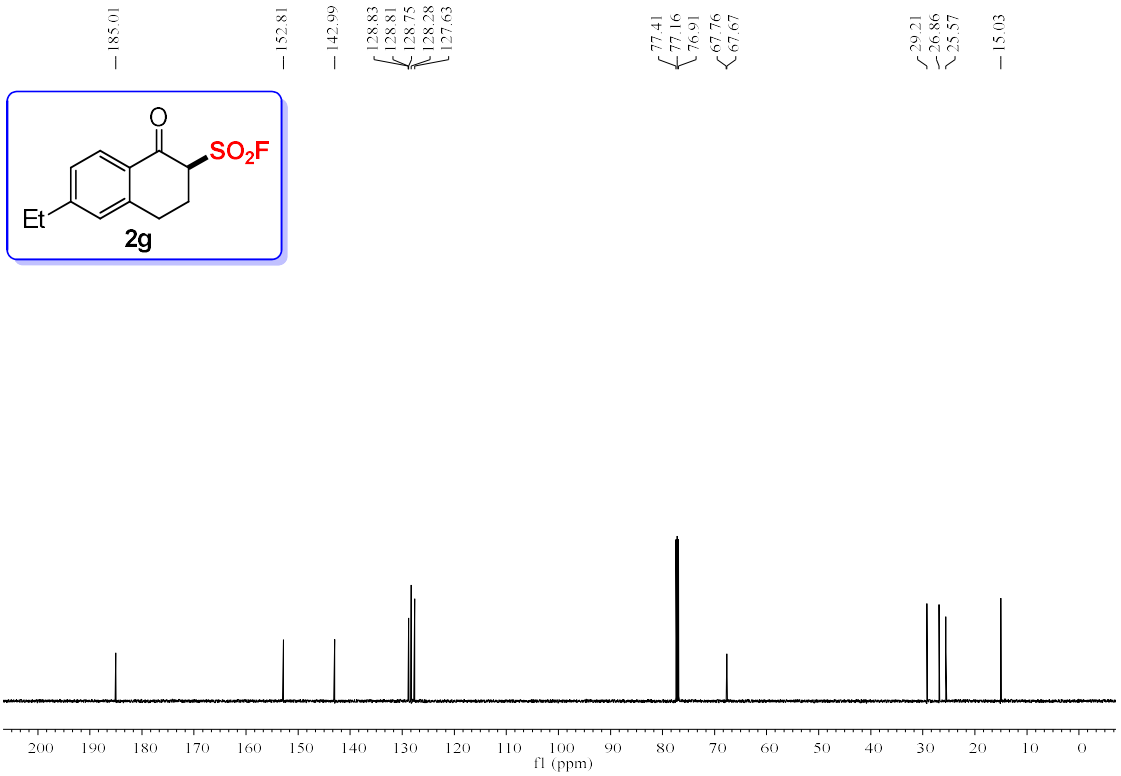
^{1}H NMR (500 MHz, $CDCl_3$) for **2g**



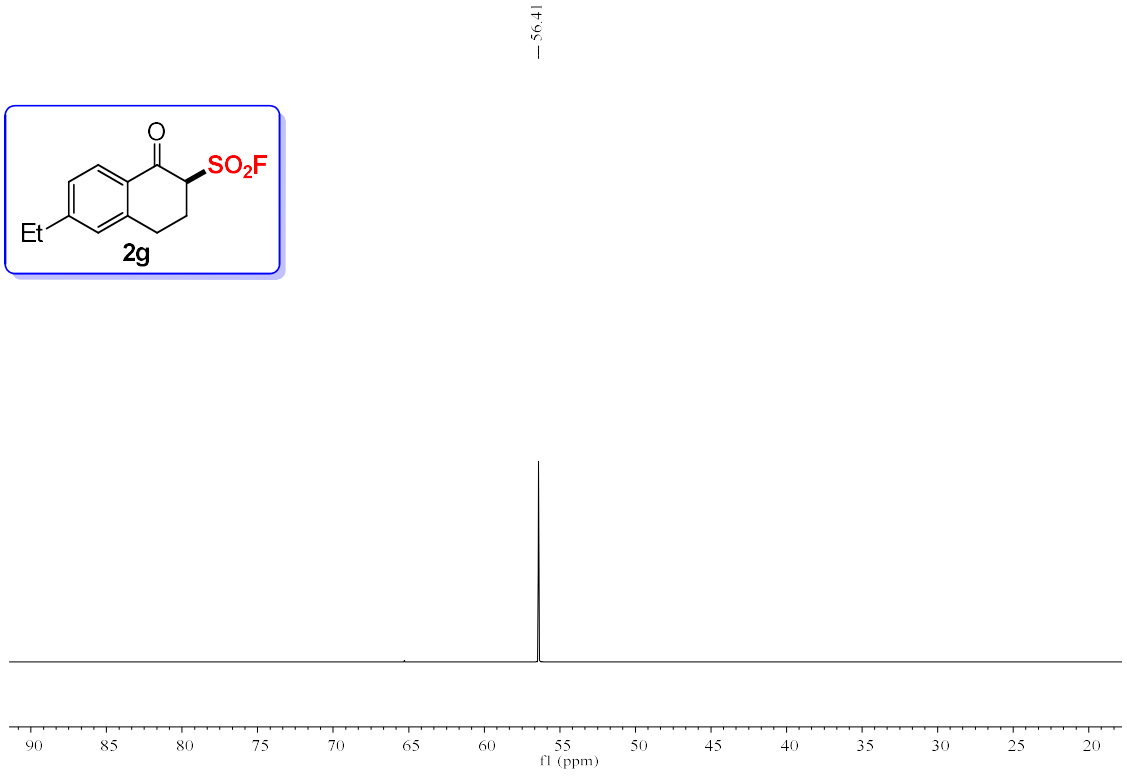




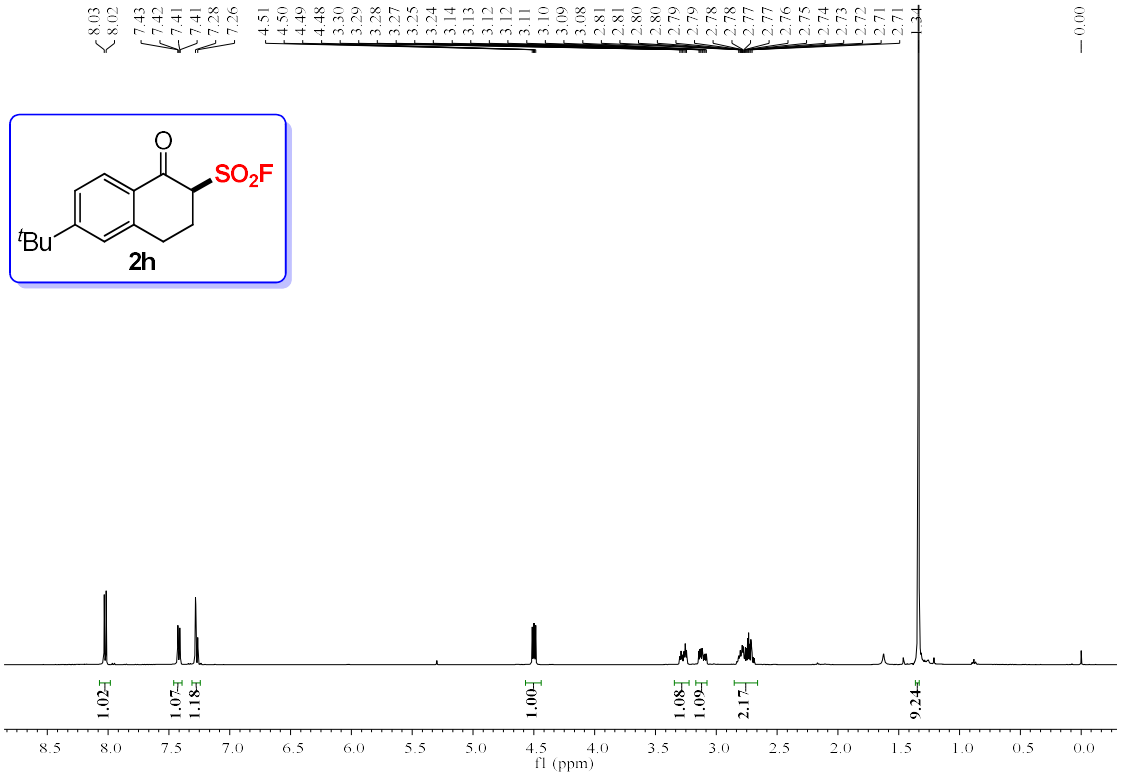
^{13}C NMR (126 MHz, $CDCl_3$) for **2g**



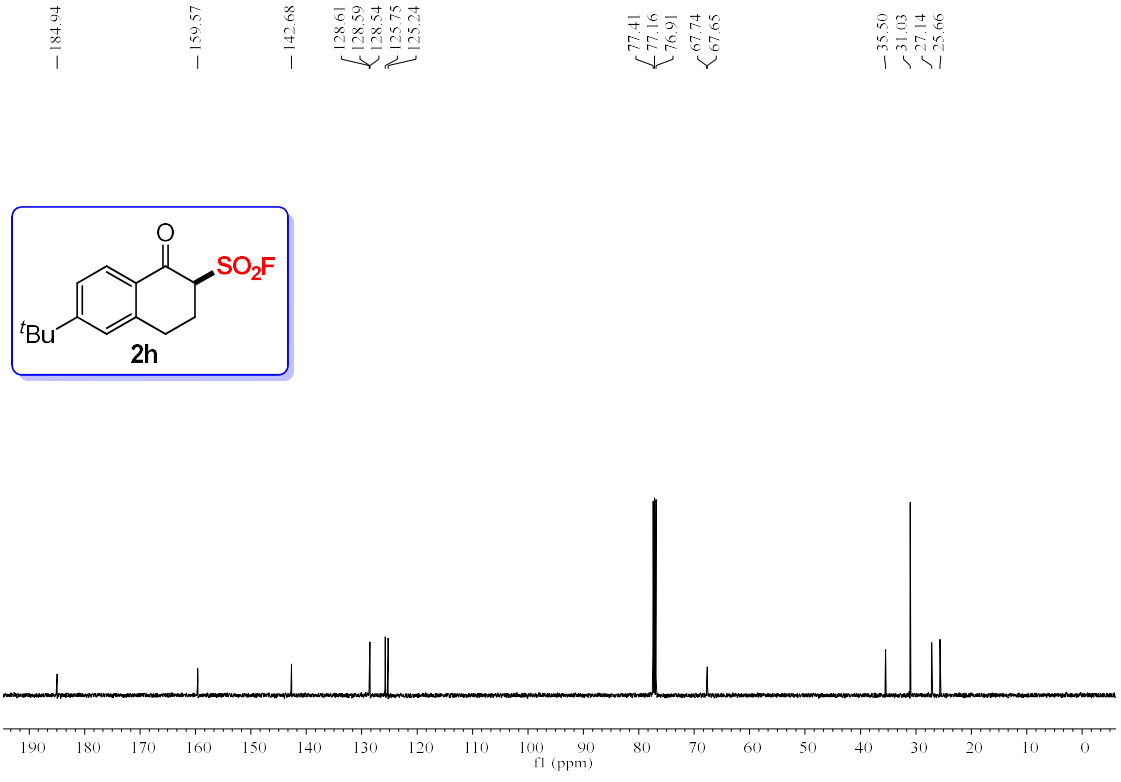
^{19}F NMR (471 MHz, $CDCl_3$) for **2g**



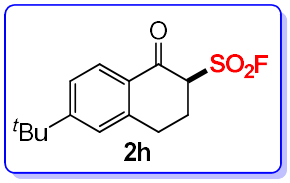
^{1}H NMR (500 MHz, $CDCl_3$) for **2h**



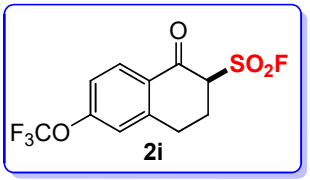
^{13}C NMR (126 MHz, $CDCl_3$) for **2h**



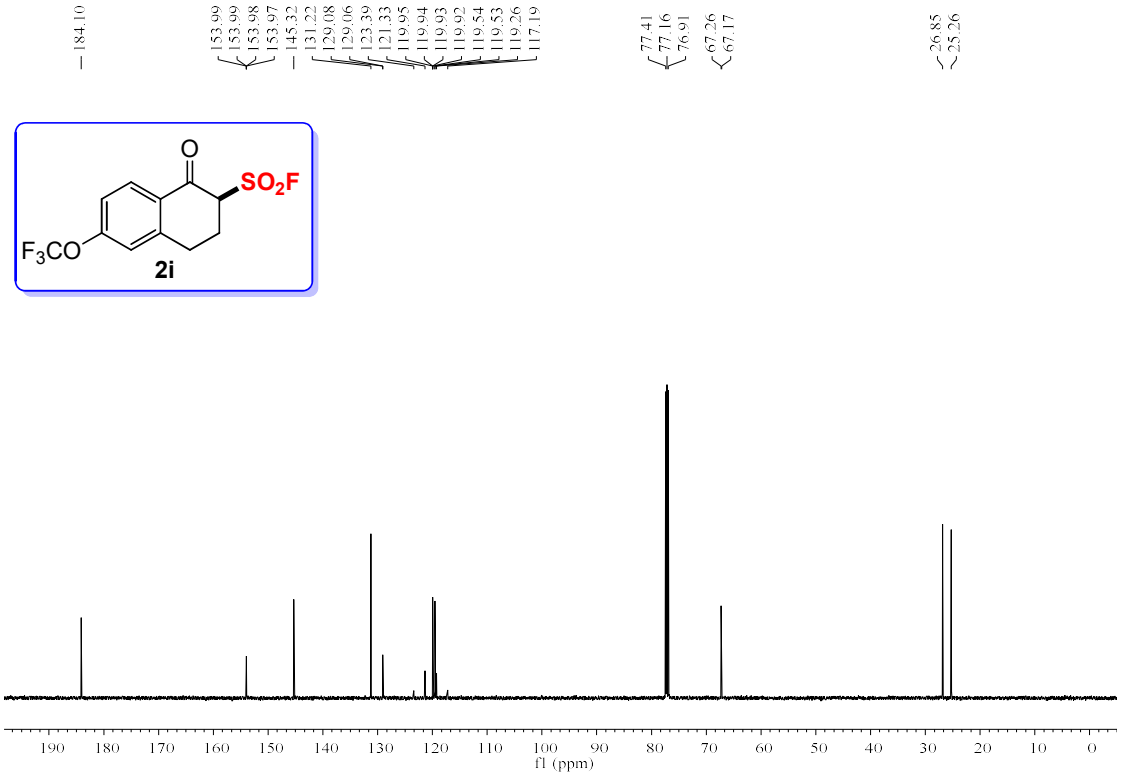
^{19}F NMR (471 MHz, $CDCl_3$) for **2h**



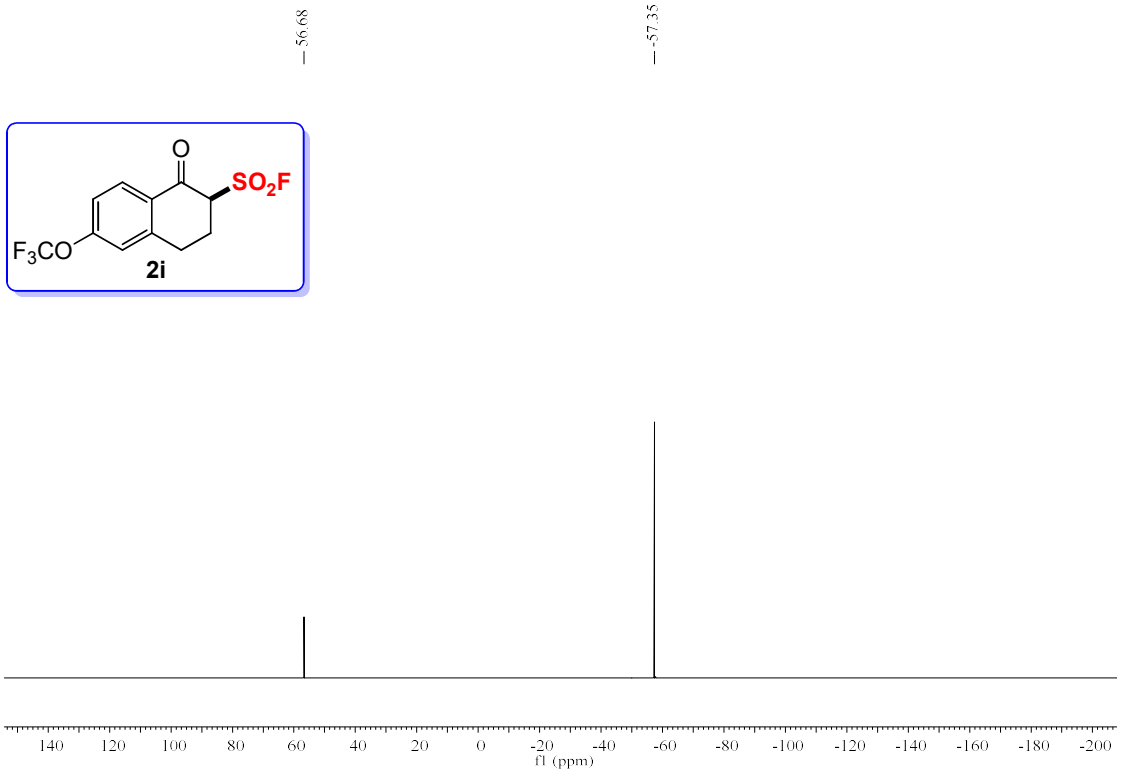
^{1}H NMR (500 MHz, $CDCl_3$) **2i**



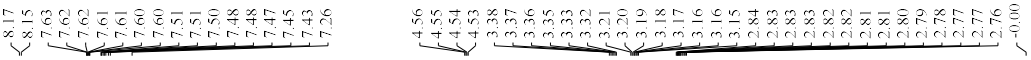
^{13}C NMR (126 MHz, $CDCl_3$) for **2i**

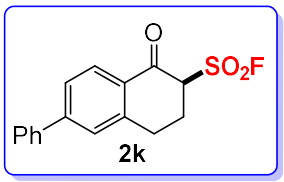


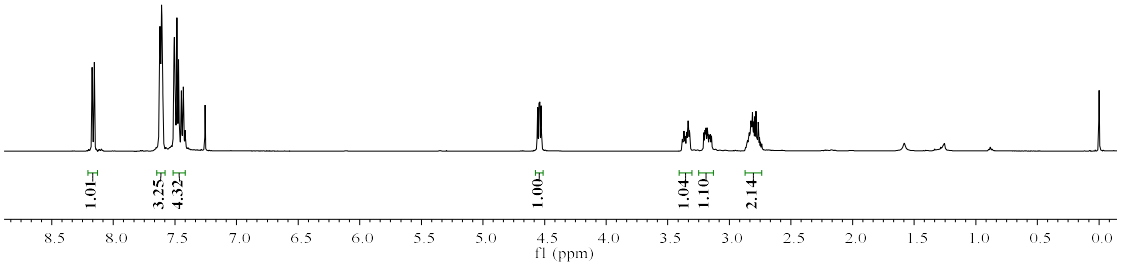
^{19}F NMR (471 MHz, $CDCl_3$) for **2i**



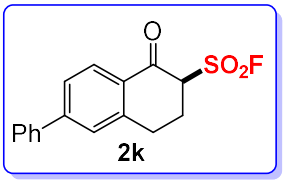
^{1}H NMR (500 MHz, $CDCl_3$) for **2k**

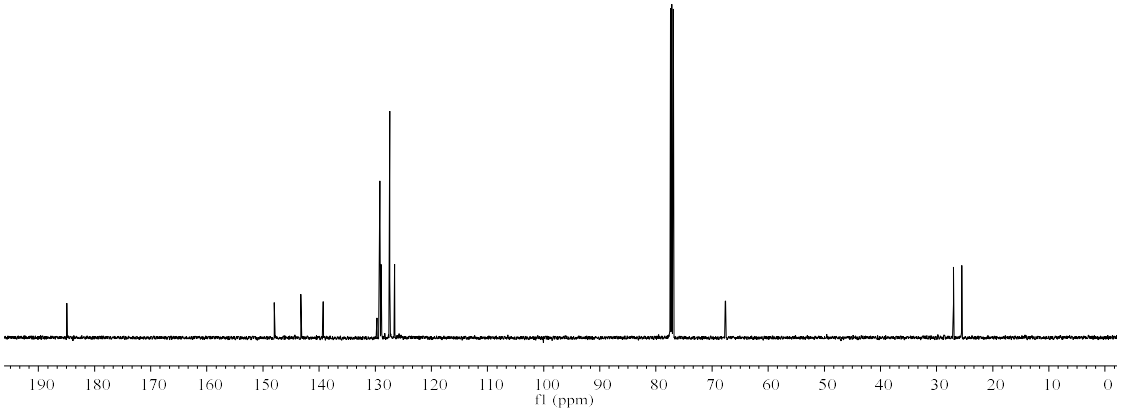




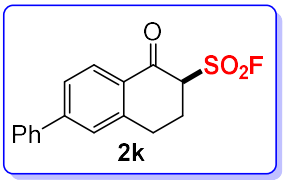


^{13}C NMR (126 MHz, $CDCl_3$) for **2k**

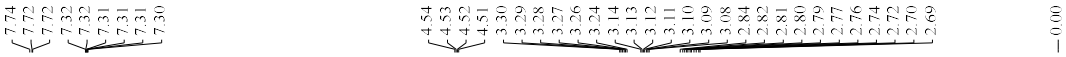


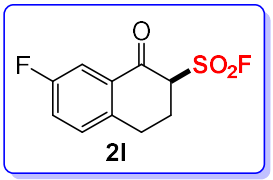


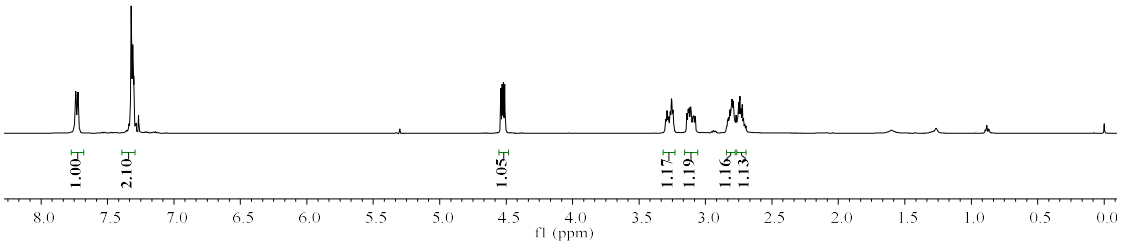
^{19}F NMR (471 MHz, $CDCl_3$) for **2k**



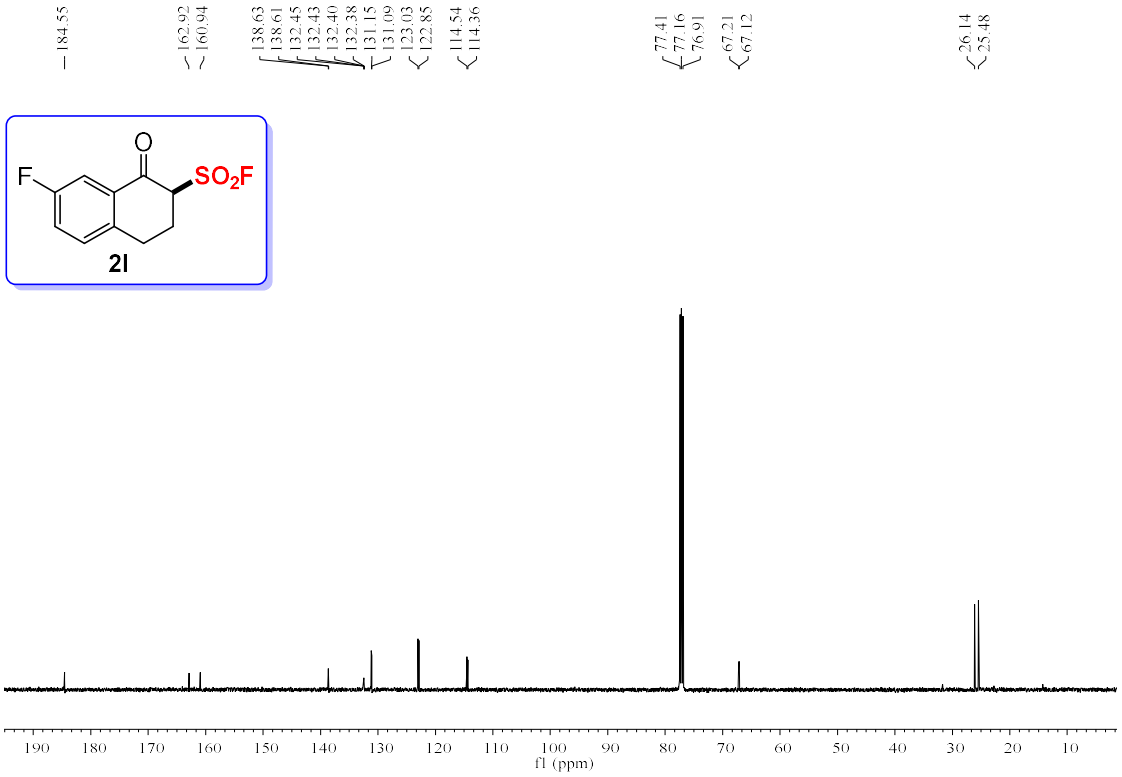
^{1}H NMR (500 MHz, $CDCl_3$) for **2l**



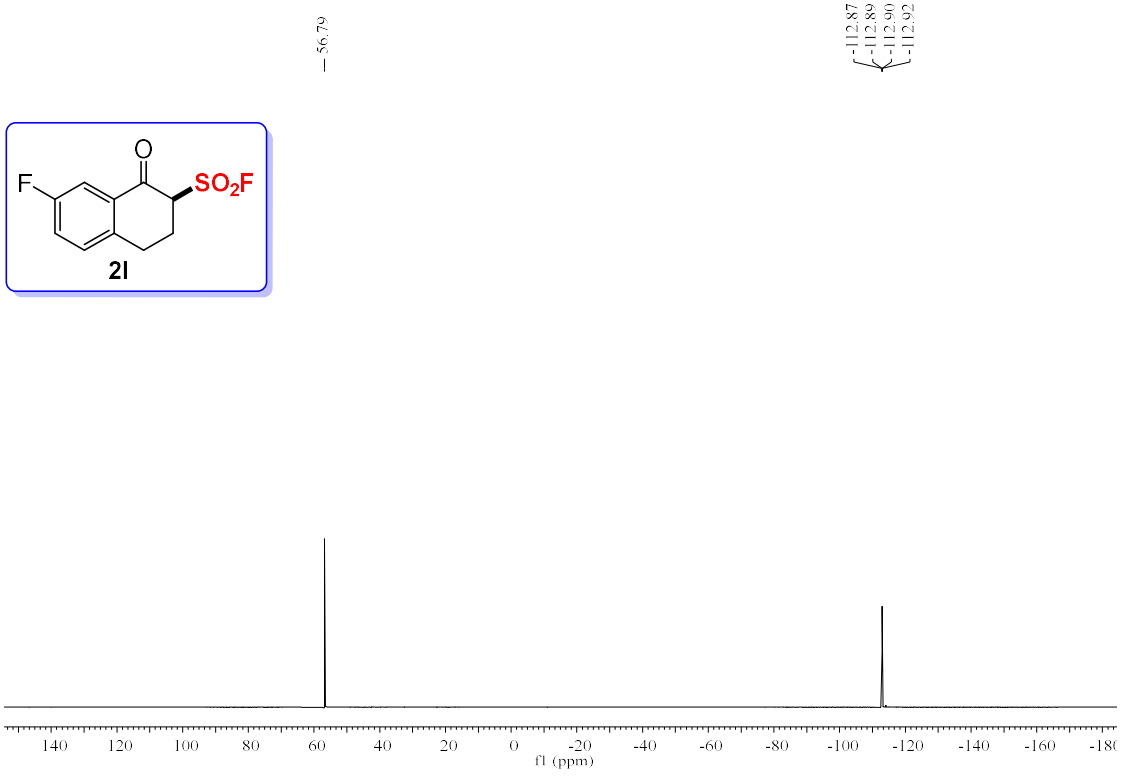




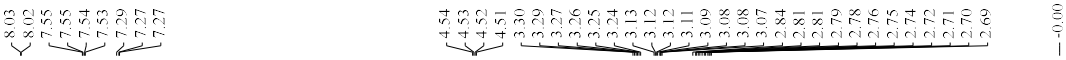
^{13}C NMR (126 MHz, $CDCl_3$) for **2l**

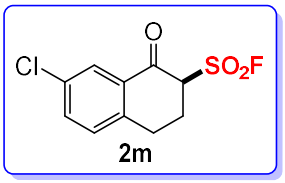


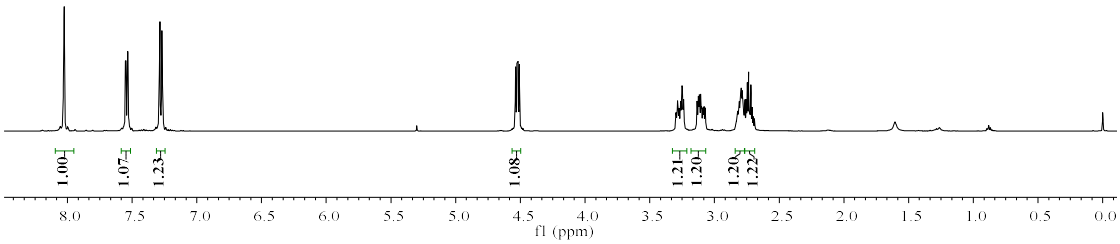
^{19}F NMR (471 MHz, $CDCl_3$) for **2l**



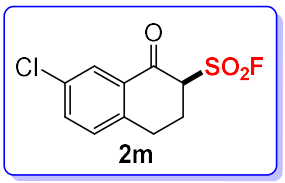
^{1}H NMR (500 MHz, $CDCl_3$) for **2m**

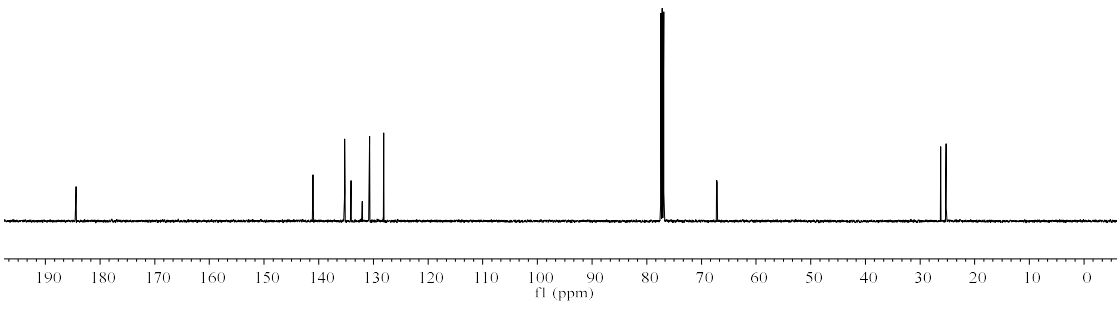




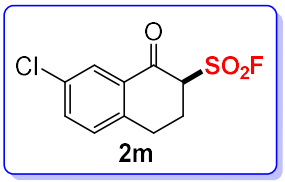


^{13}C NMR (126 MHz, $CDCl_3$) for **2m**

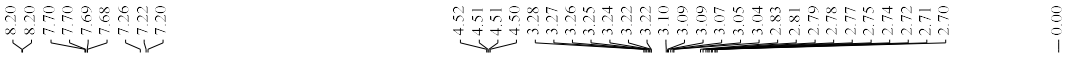


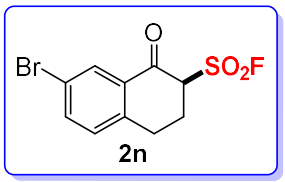


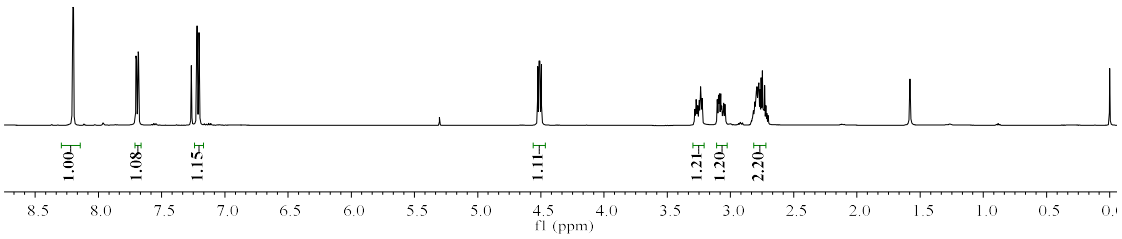
^{19}F NMR (471 MHz, $CDCl_3$) for **2m**



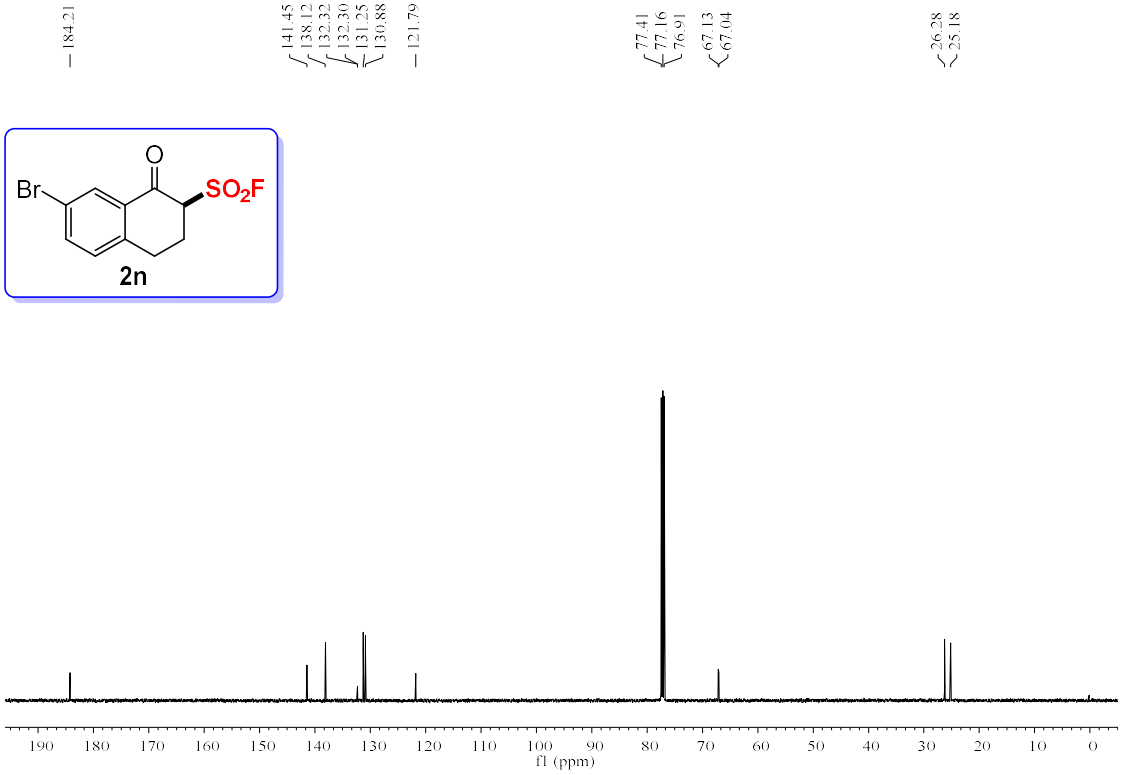
^{1}H NMR (500 MHz, $CDCl_3$) for **2n**



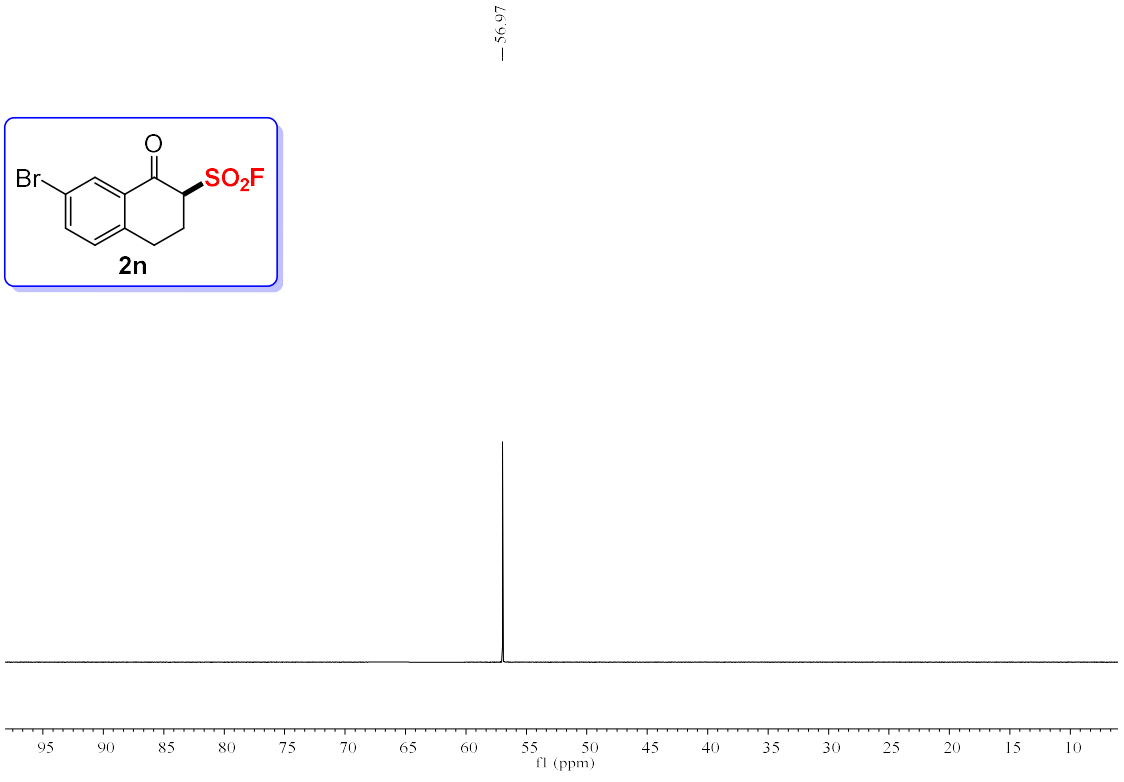




^{13}C NMR (126 MHz, $CDCl_3$) for **2n**



^{19}F NMR (471 MHz, $CDCl_3$) for **2n**



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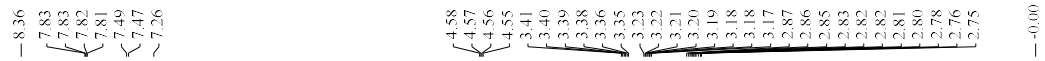
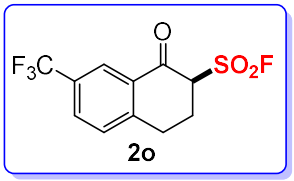
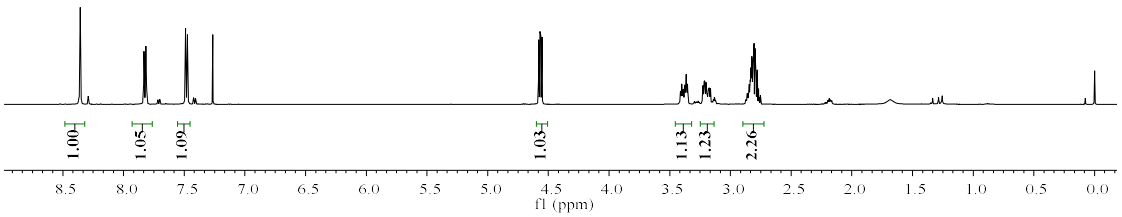
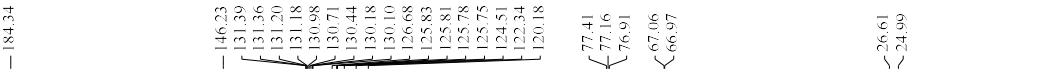
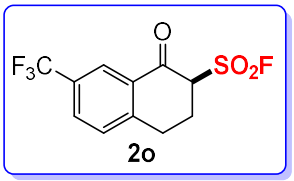




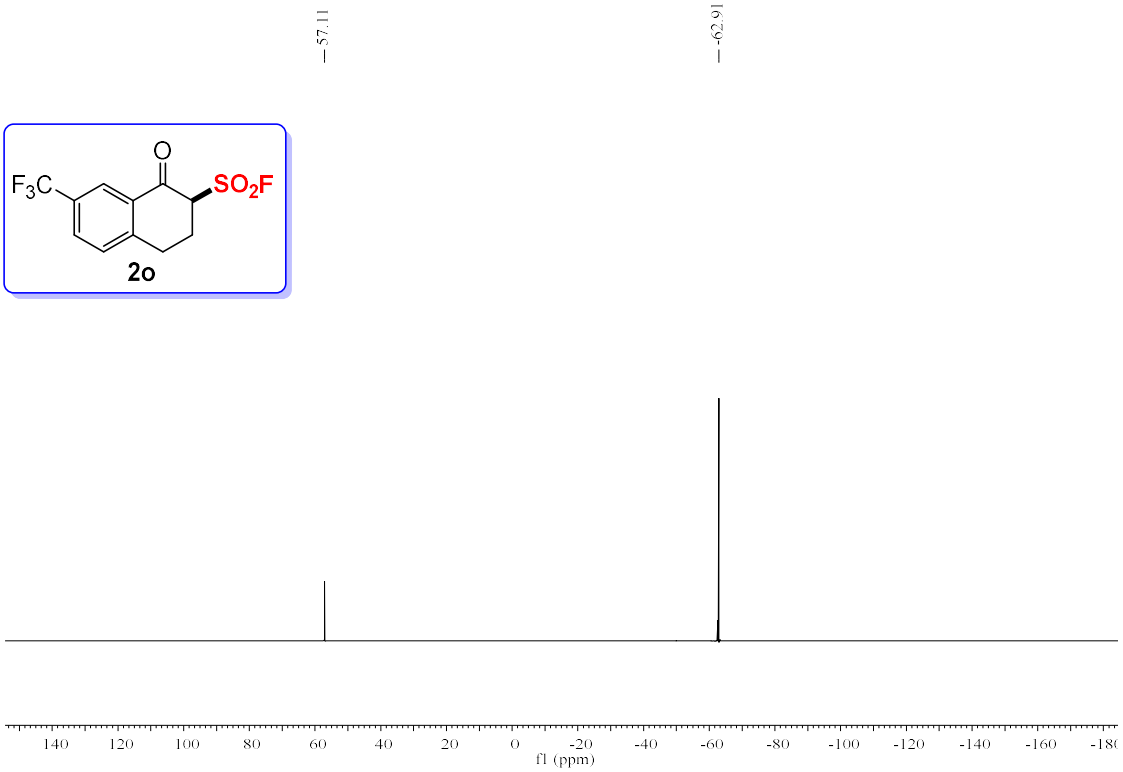


^{13}C NMR (126 MHz, $CDCl_3$) for **2o**





^{19}F NMR (471 MHz, $CDCl_3$) for **2o**



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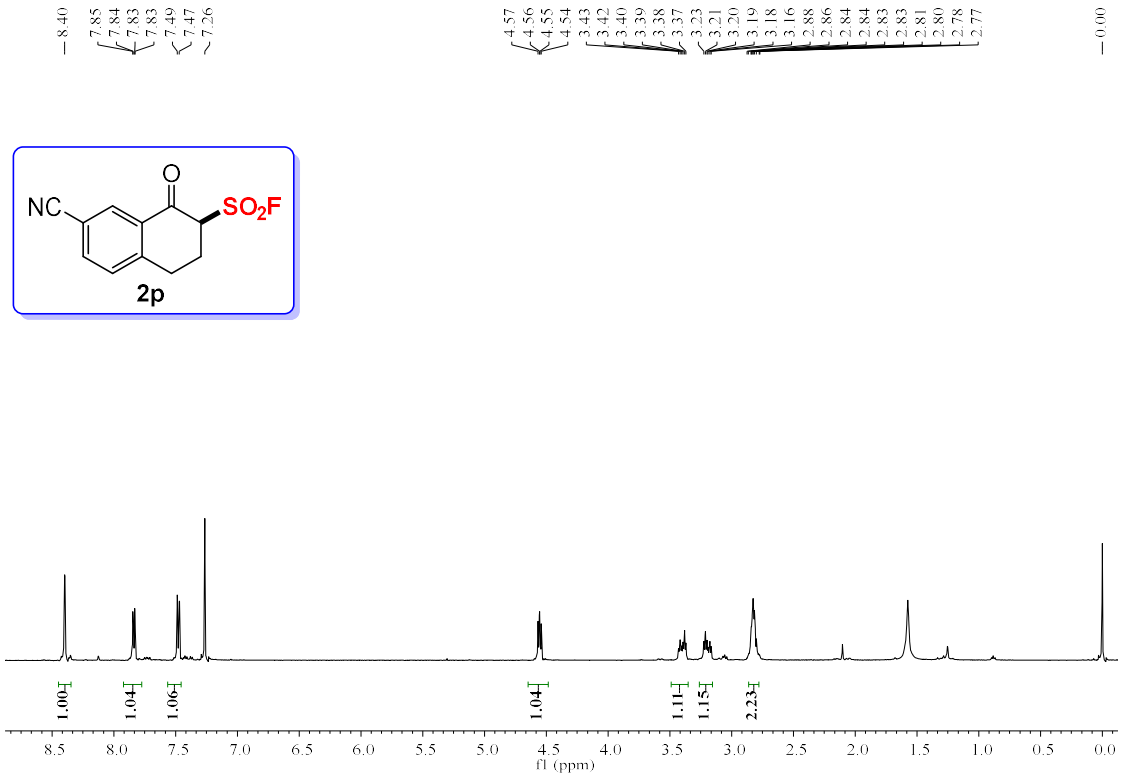
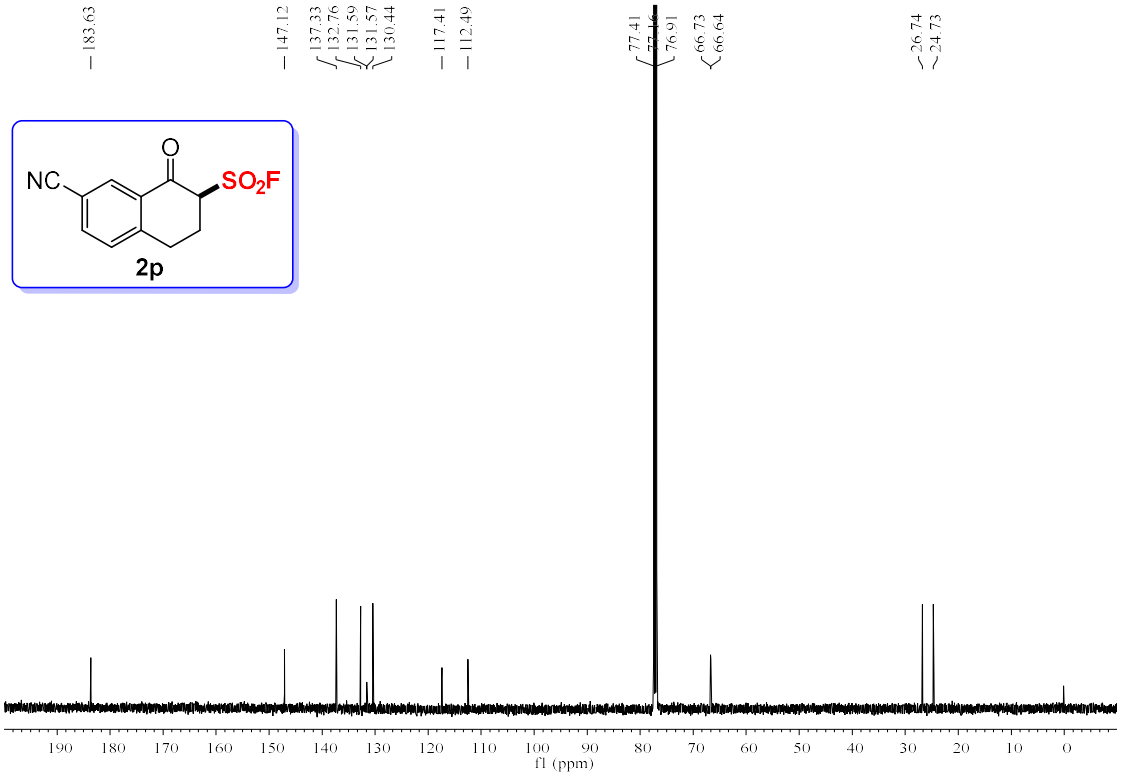
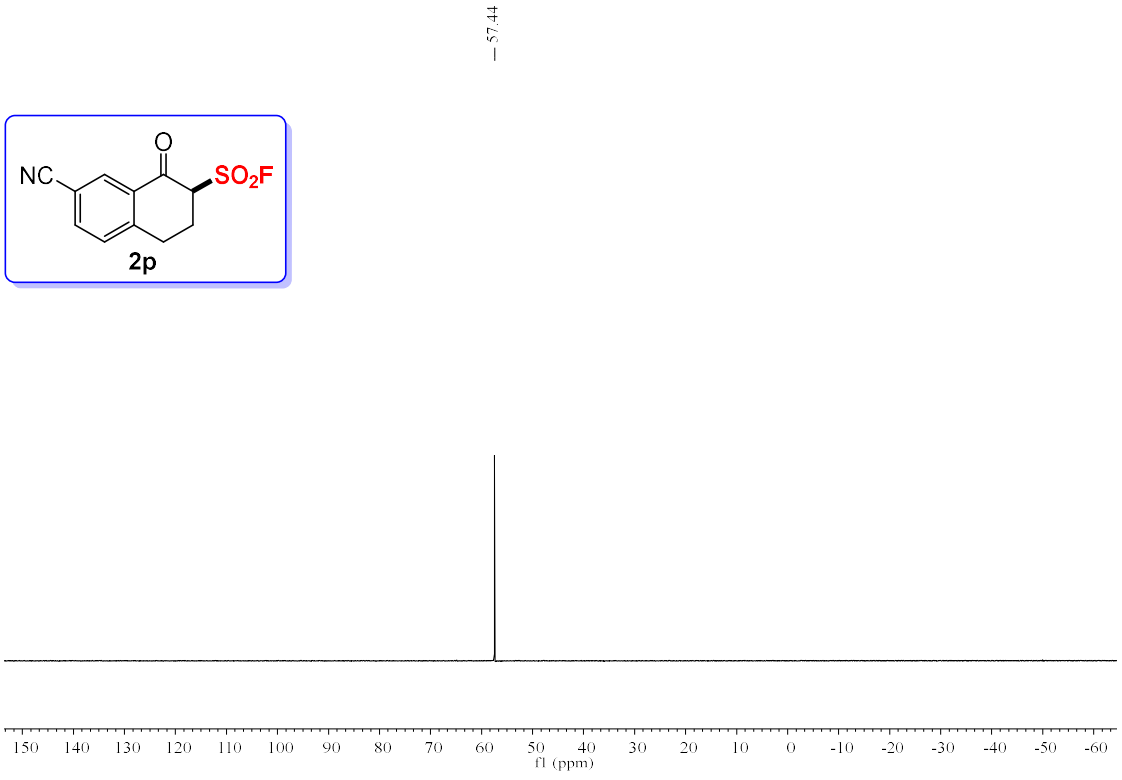


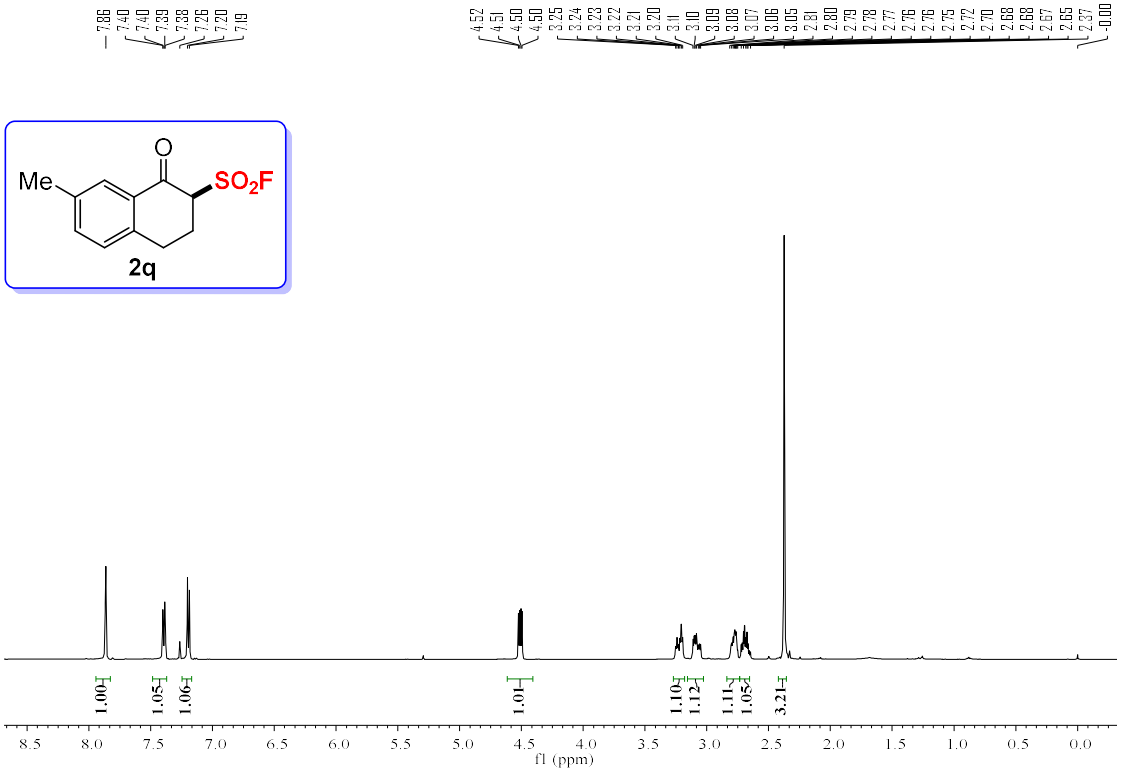
^{13}C NMR (126 MHz, $CDCl_3$) for **2p**



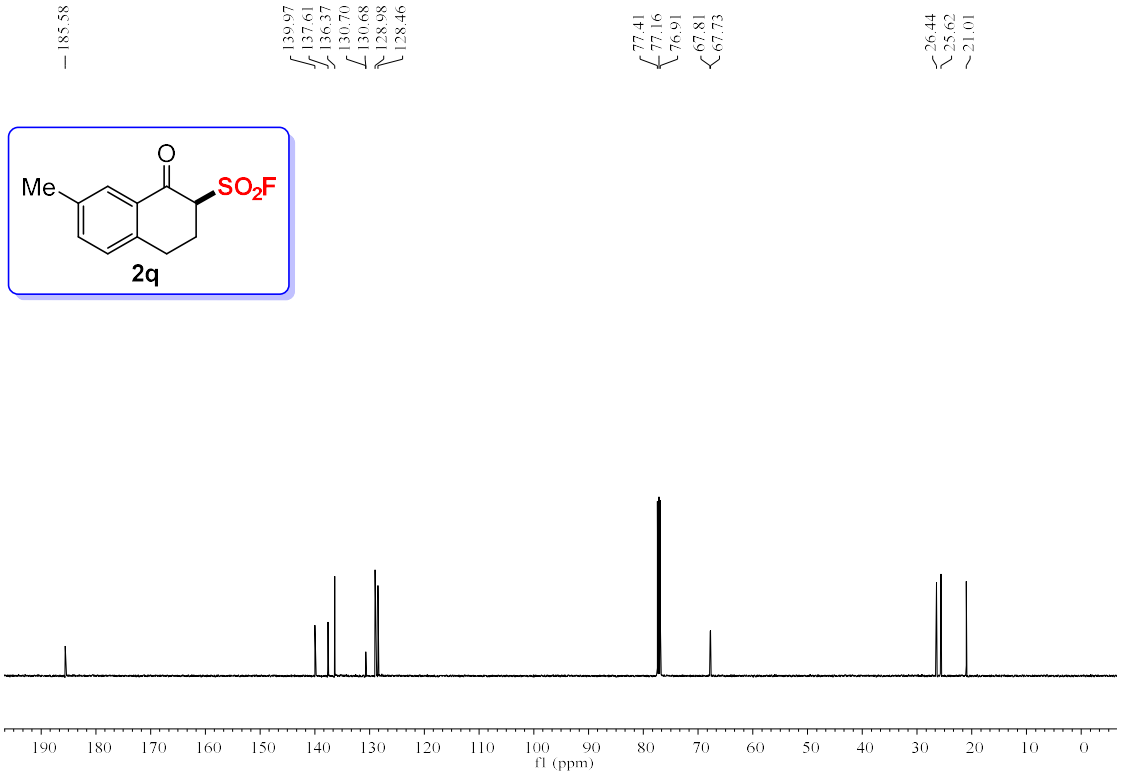
^{19}F NMR (471 MHz, $CDCl_3$) for **2p**



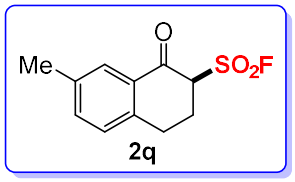
^{1}H NMR (500 MHz, $CDCl_3$) for **2q**



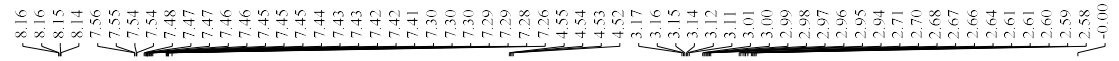
^{13}C NMR (126 MHz, $CDCl_3$) for **2q**

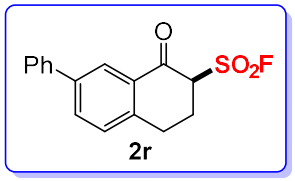


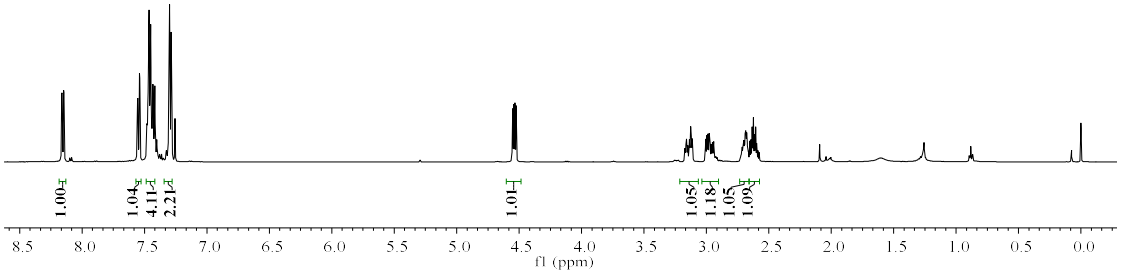
^{19}F NMR (471 MHz, $CDCl_3$) for **2q**



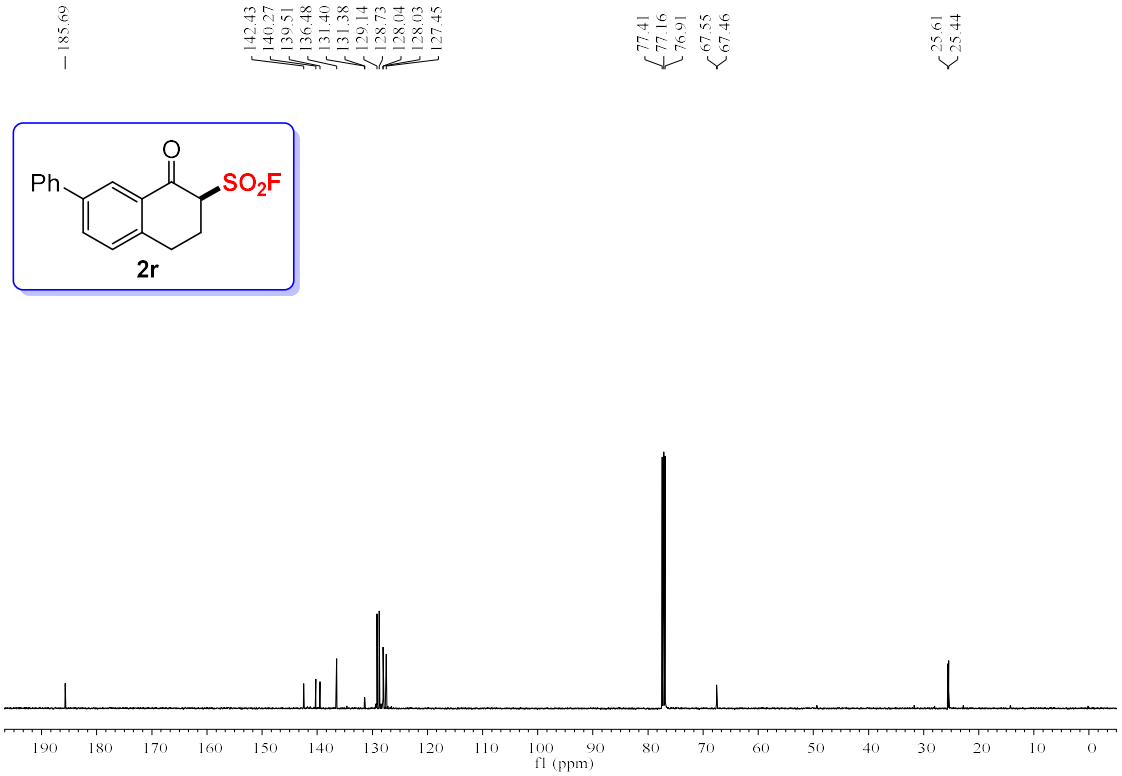
^{1}H NMR (500 MHz, $CDCl_3$) for **2r**



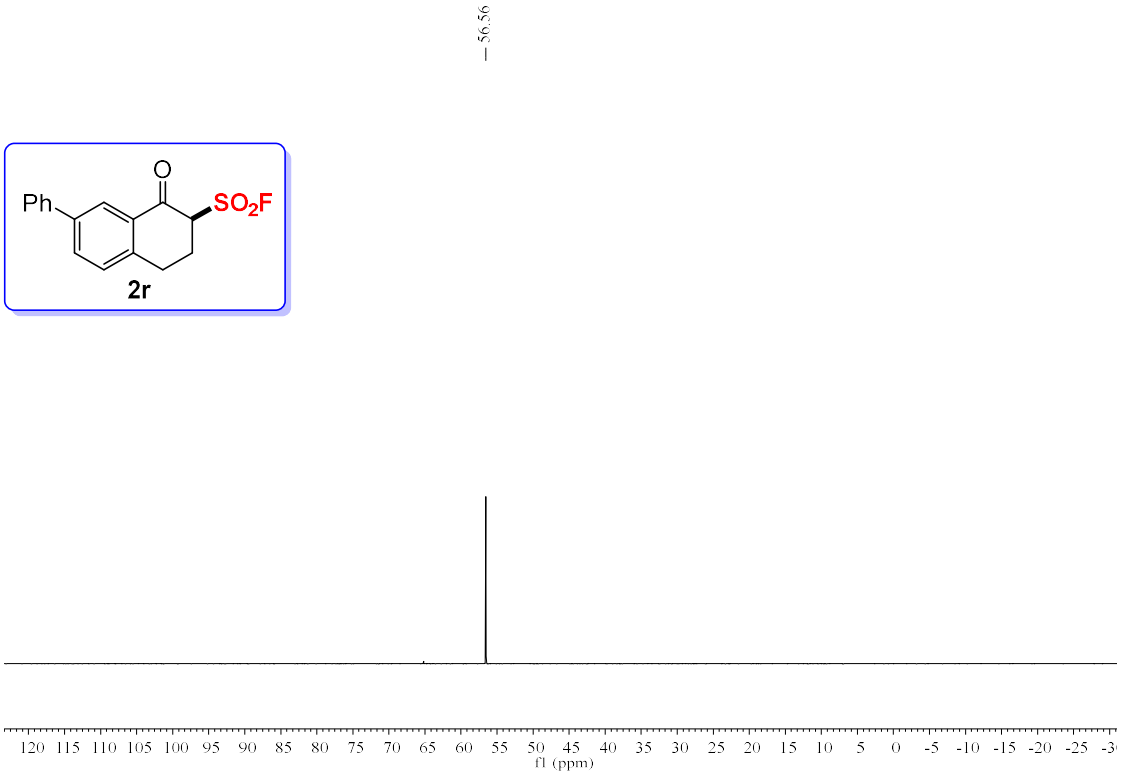




^{13}C NMR (126 MHz, $CDCl_3$) for **2r**



^{19}F NMR (471 MHz, $CDCl_3$) for **2r**



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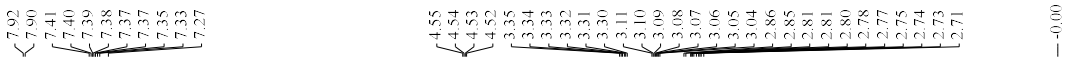
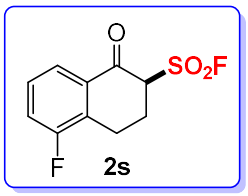
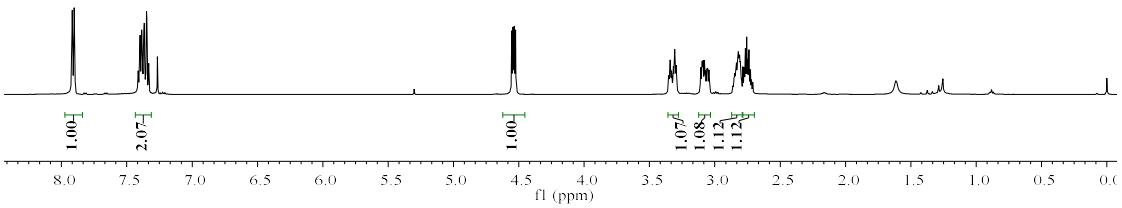
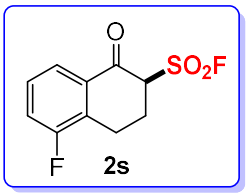
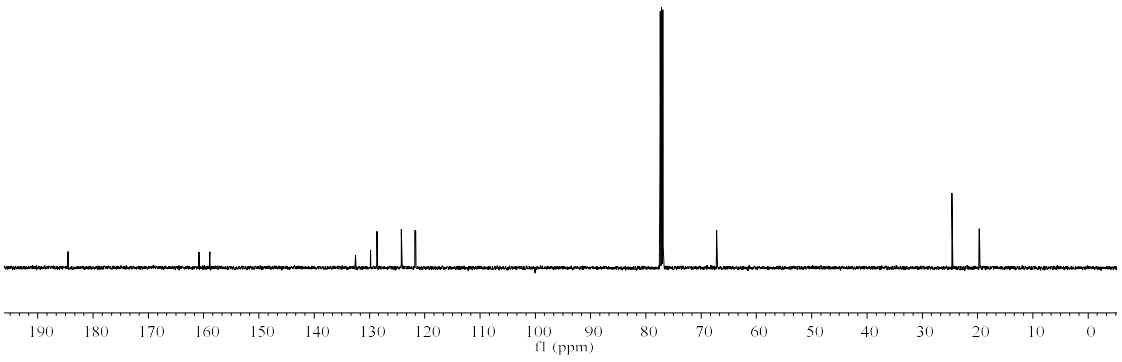




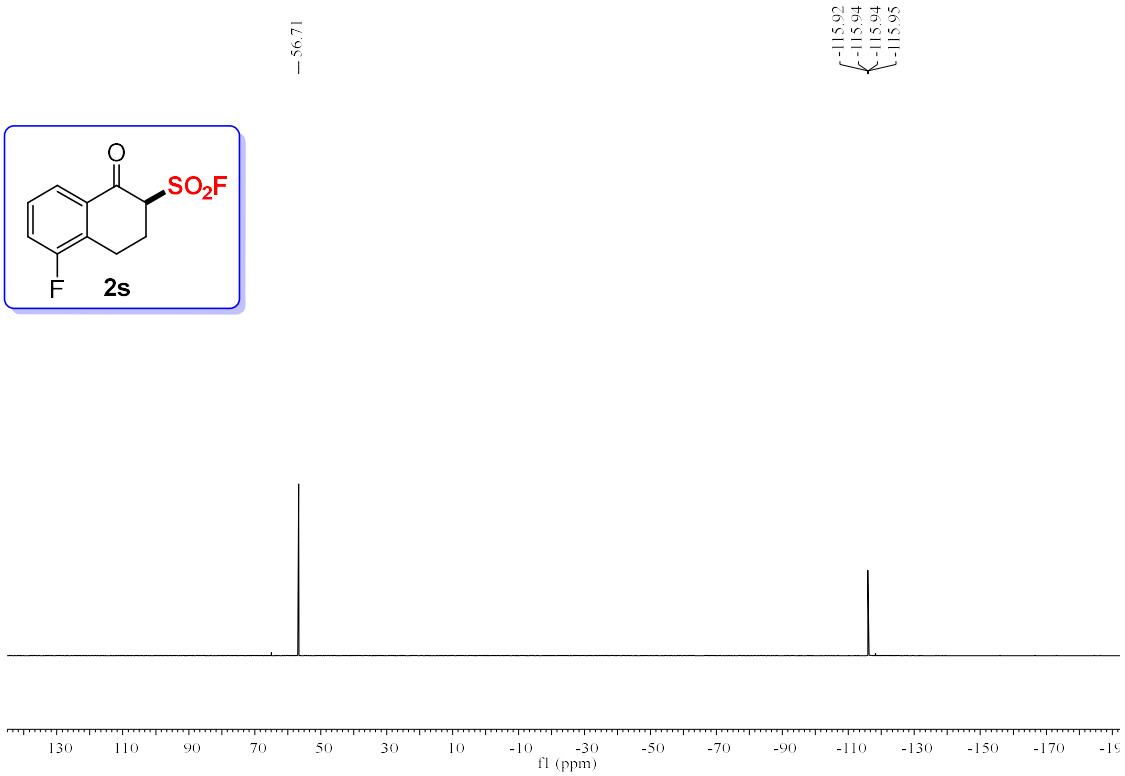


^{13}C NMR (126 MHz, $CDCl_3$) for **2s**

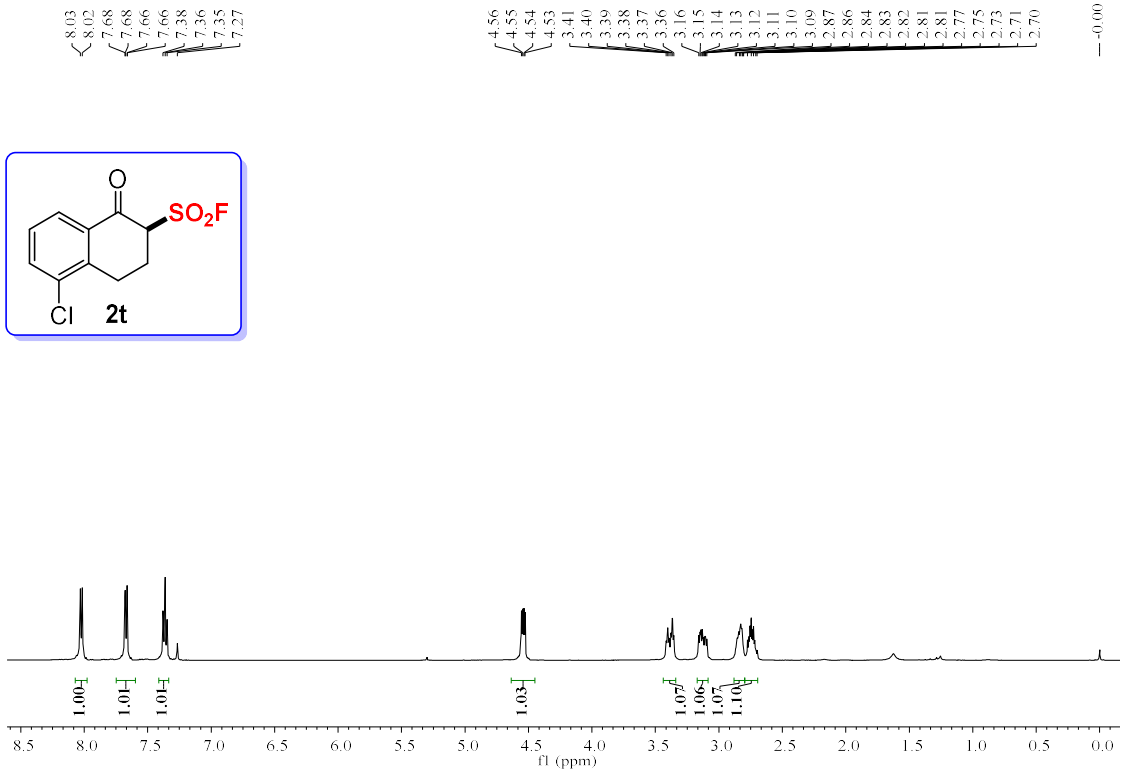




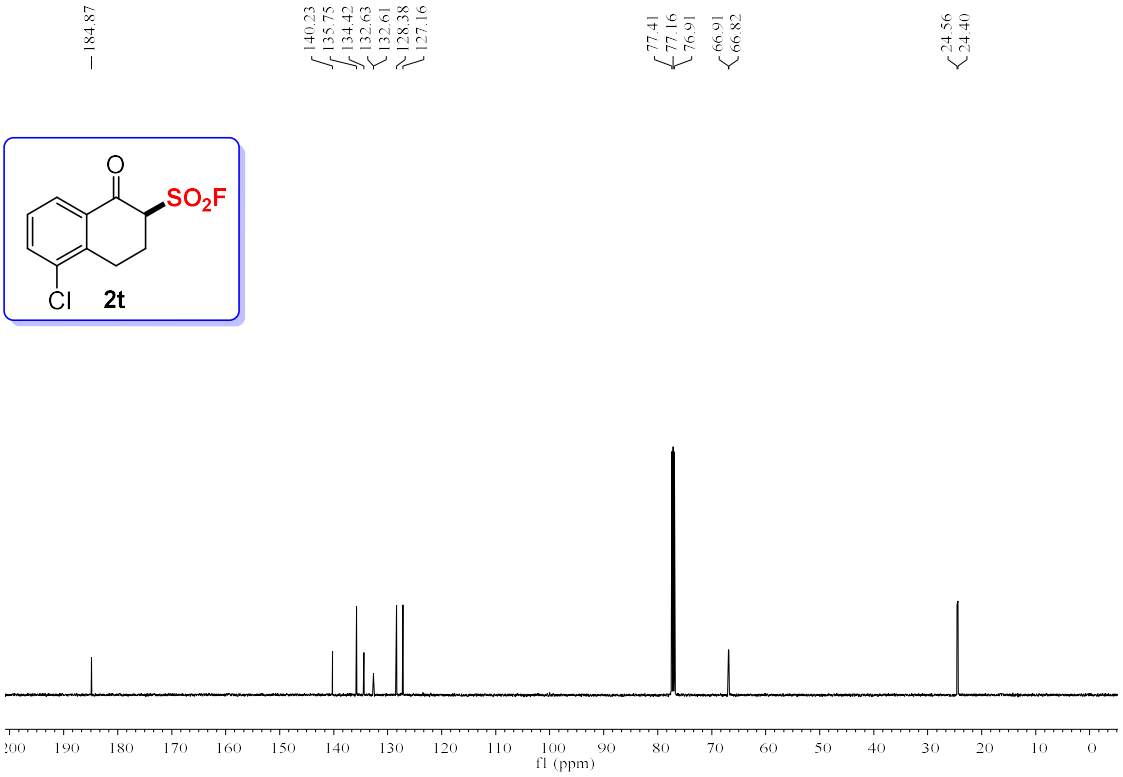
^{19}F NMR (471 MHz, $CDCl_3$) for **2s**



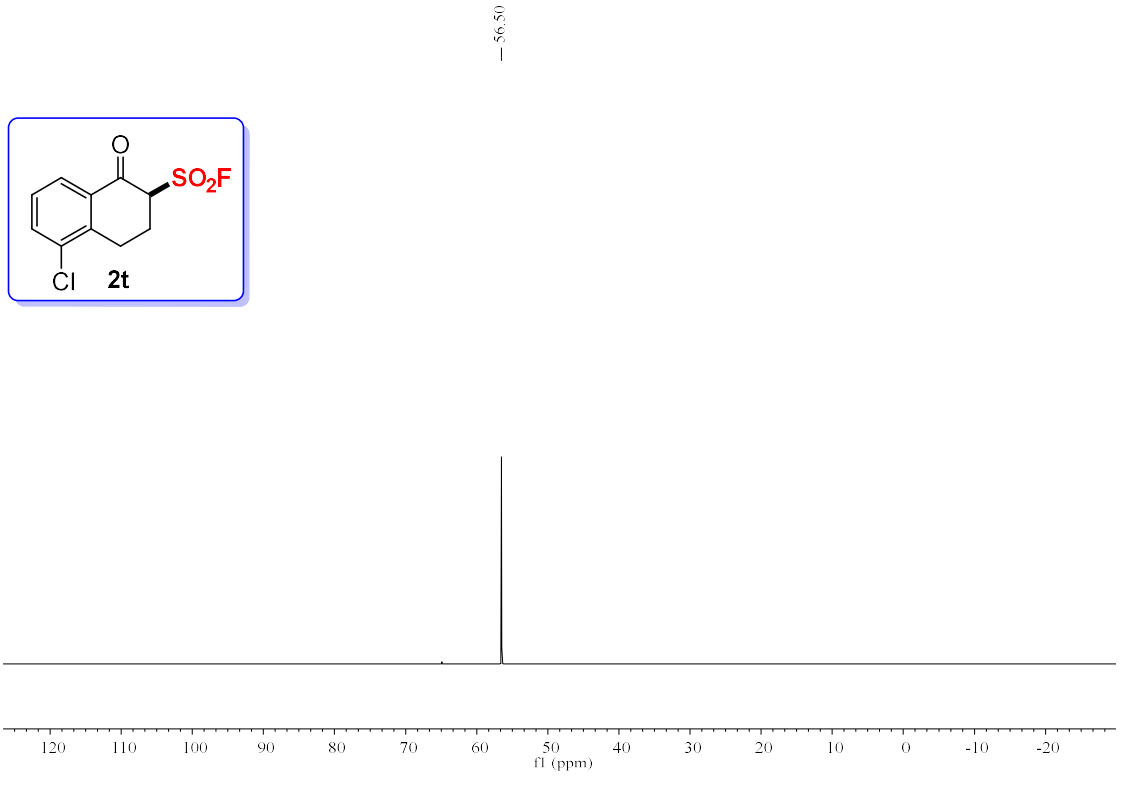
^{1}H NMR (500 MHz, $CDCl_3$) for **2t**



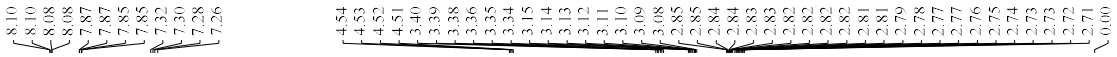
^{13}C NMR (126 MHz, $CDCl_3$) for **2t**

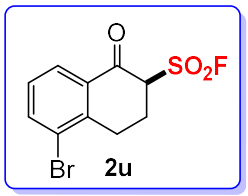


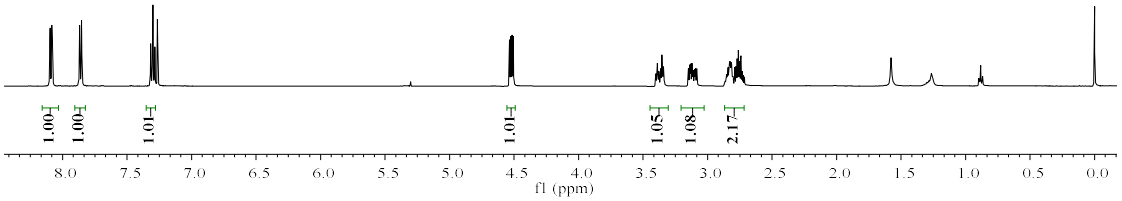
^{19}F NMR (471 MHz, $CDCl_3$) for **2t**



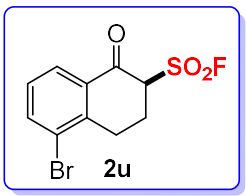
^{1}H NMR (500 MHz, $CDCl_3$) for **2u**

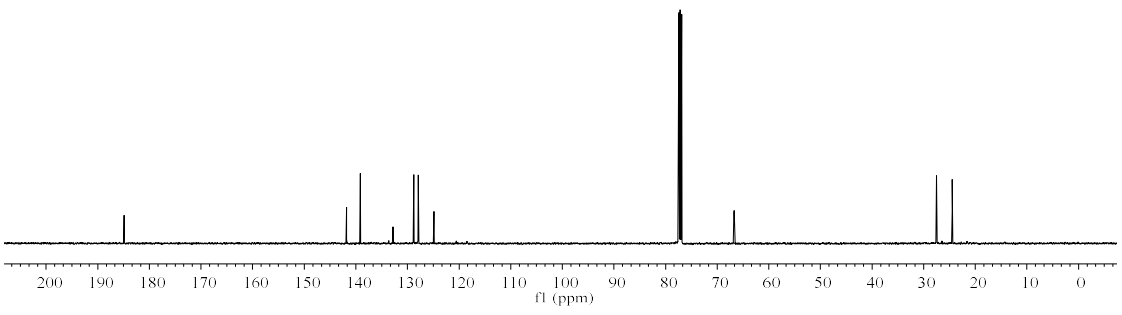




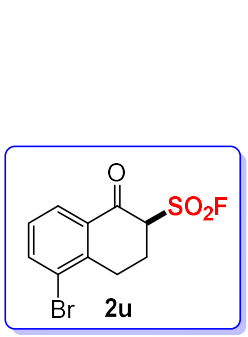


^{13}C NMR (126 MHz, $CDCl_3$) for **2u**

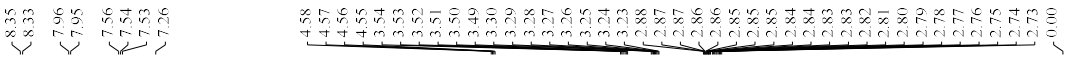


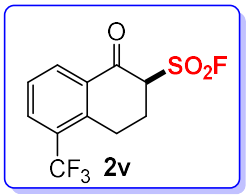


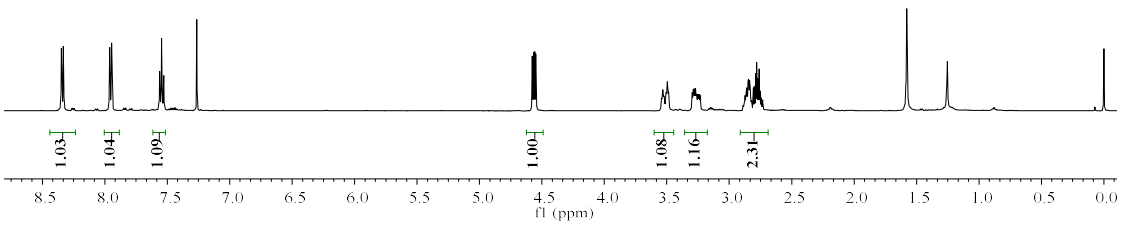
^{19}F NMR (471 MHz, $CDCl_3$) for **2u**



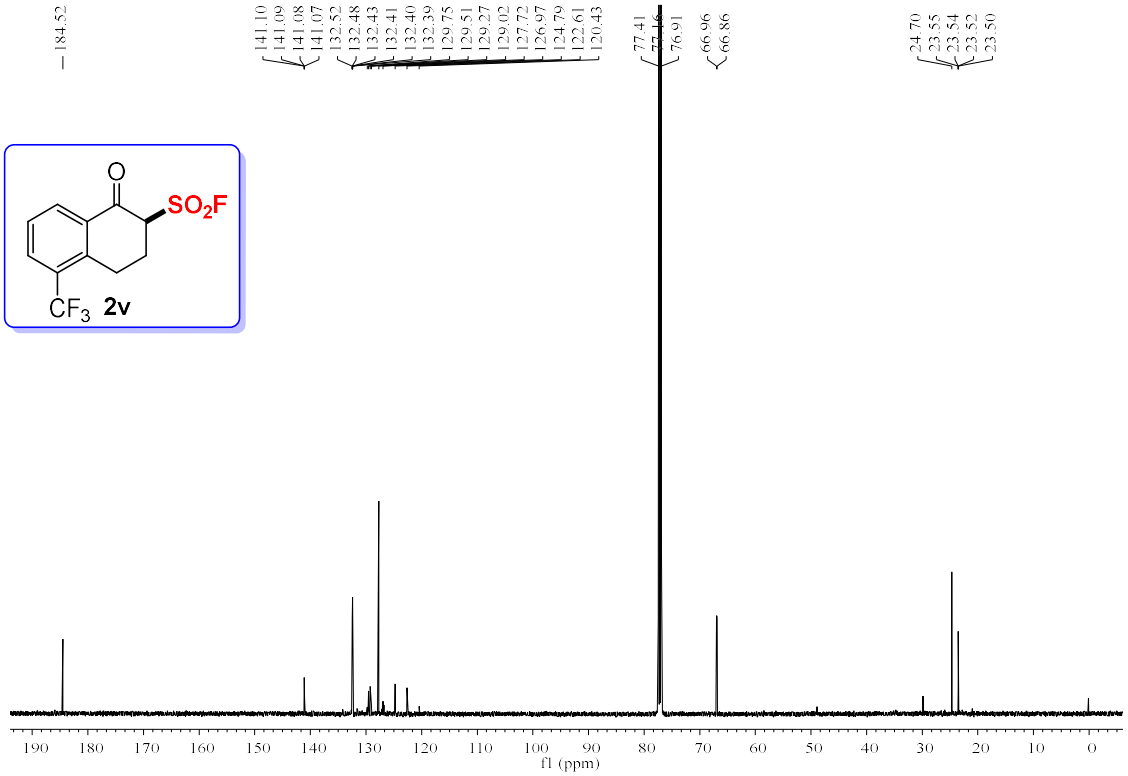
^{1}H NMR (500 MHz, $CDCl_3$) for **2v**



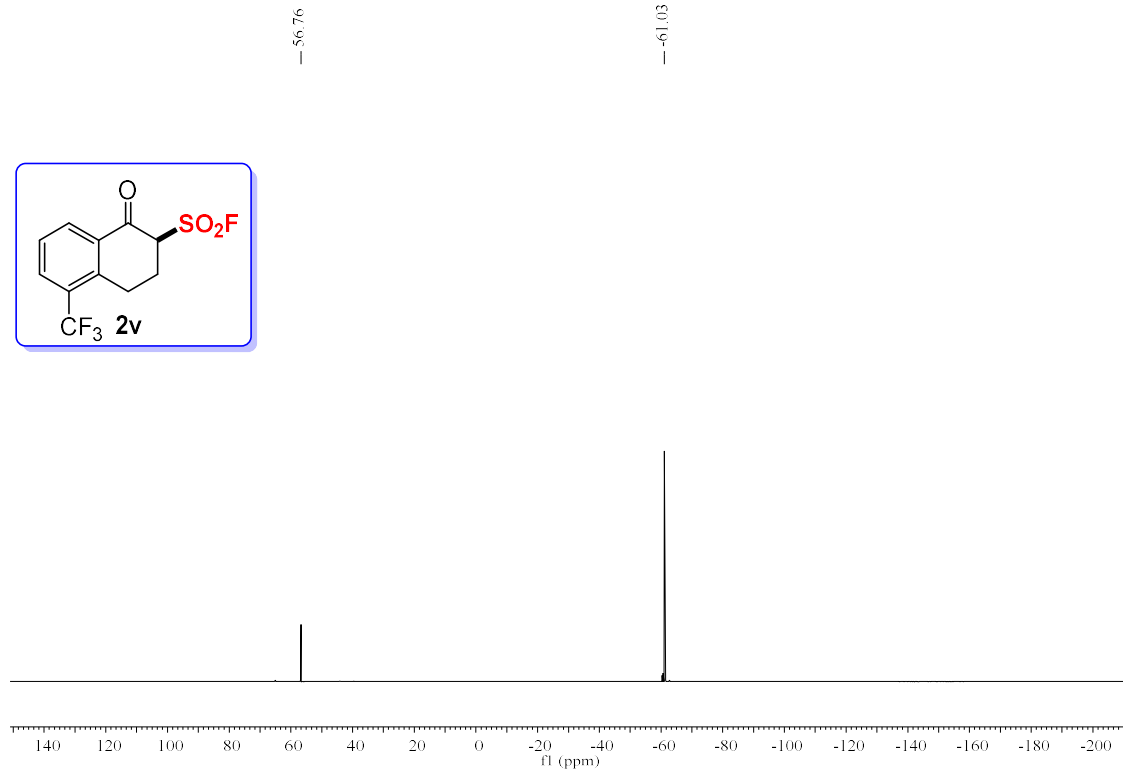




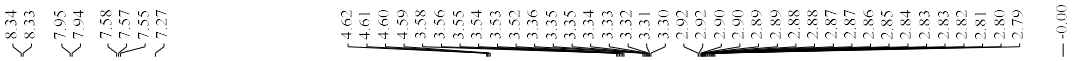
^{13}C NMR (126 MHz, $CDCl_3$) for **2v**

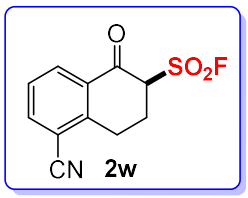


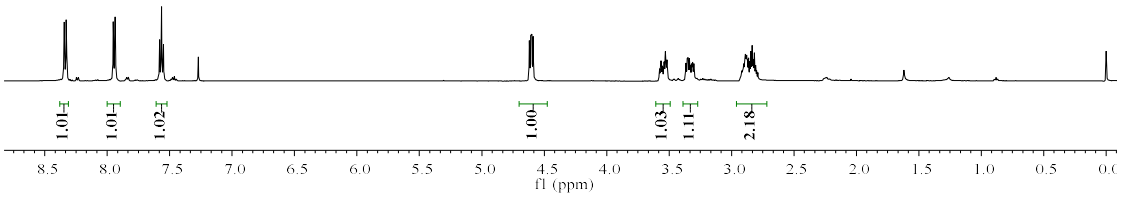
^{19}F NMR (471 MHz, $CDCl_3$) for **2v**



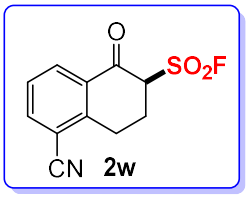
^{1}H NMR (500 MHz, $CDCl_3$) for **2w**

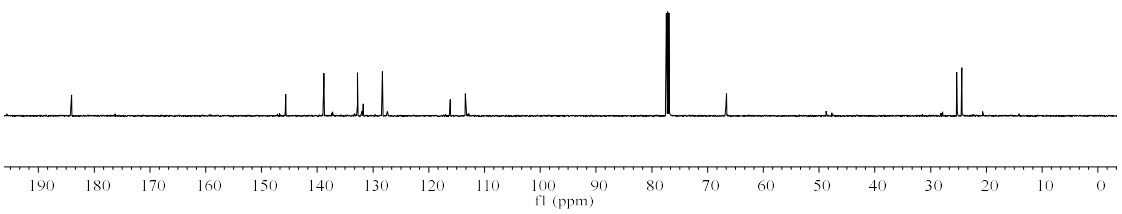




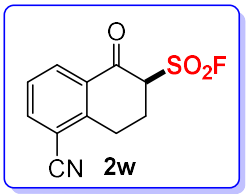


^{13}C NMR (126 MHz, $CDCl_3$) for **2w**

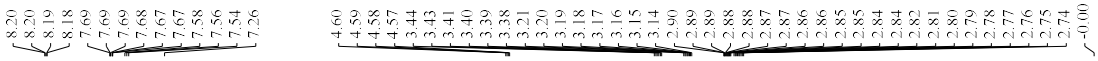


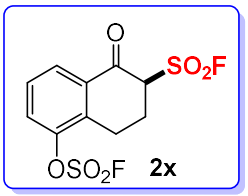


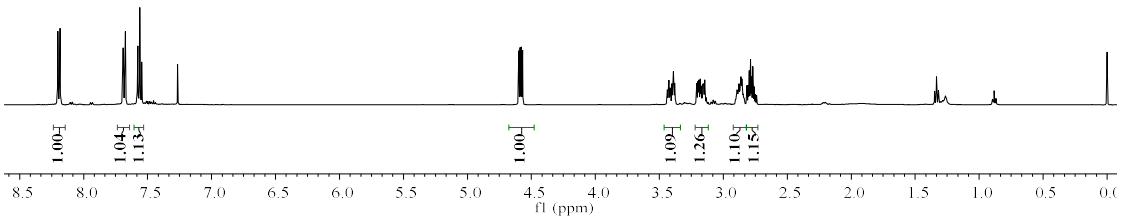
^{19}F NMR (471 MHz, $CDCl_3$) for **2w**



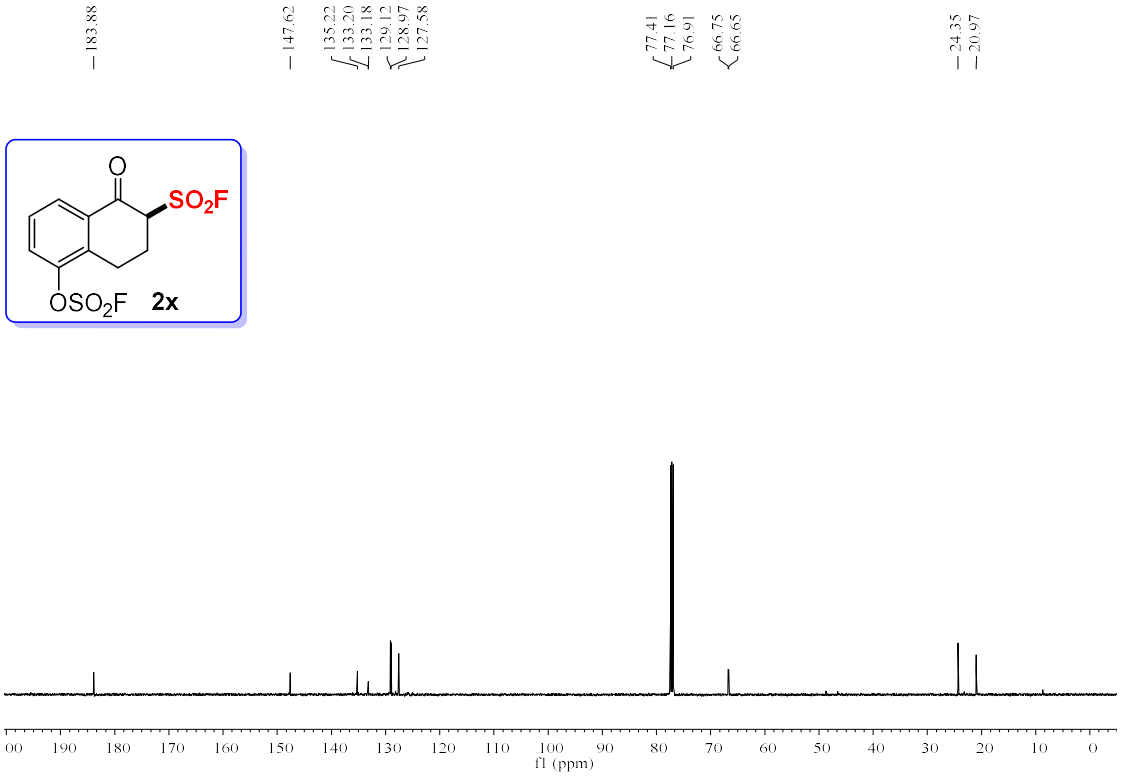
^{1}H NMR (500 MHz, $CDCl_3$) for **2x**



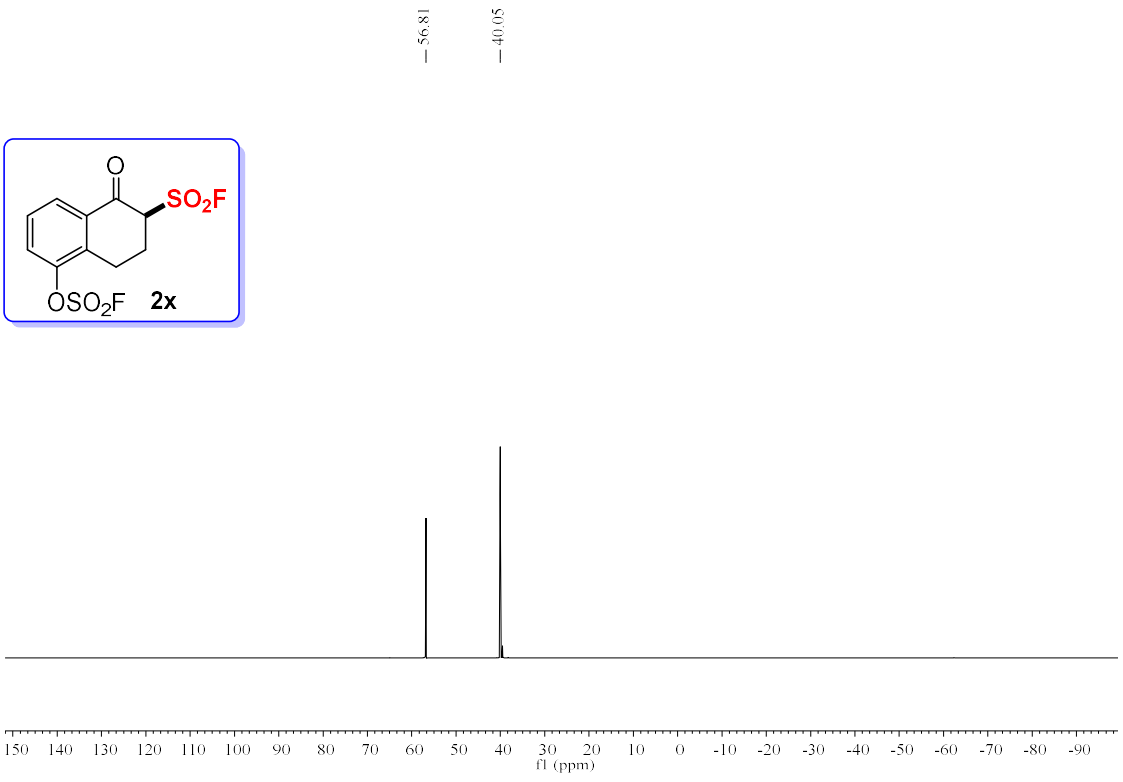




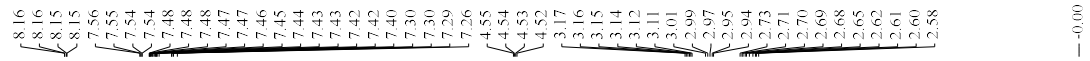
^{13}C NMR (126 MHz, $CDCl_3$) for **2x**

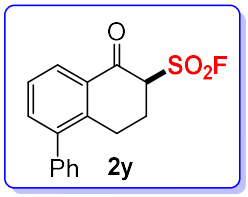


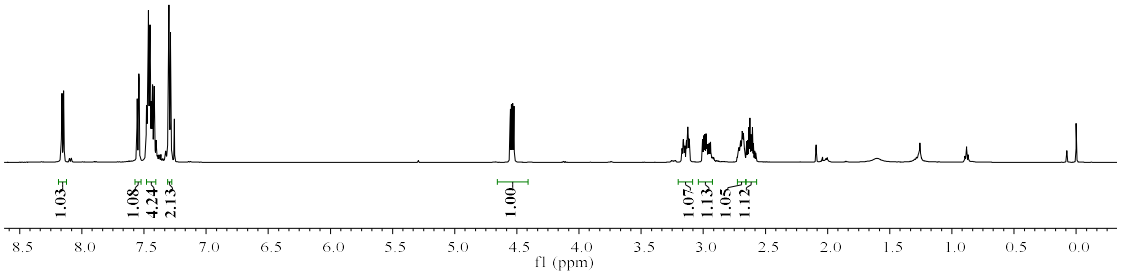
^{19}F NMR (471 MHz, $CDCl_3$) for **2x**



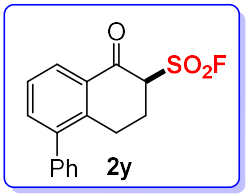
^{1}H NMR (500 MHz, $CDCl_3$) for **2y**

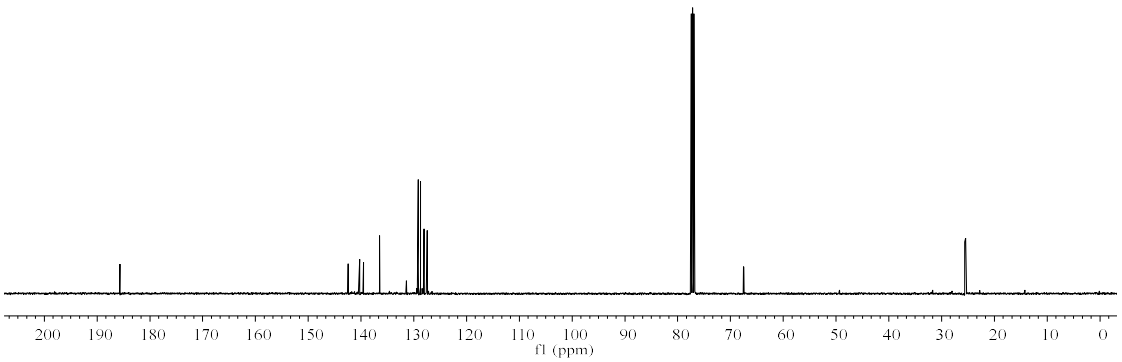




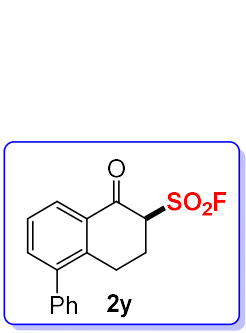


^{13}C NMR (126 MHz, $CDCl_3$) for **2y**





^{19}F NMR (471 MHz, $CDCl_3$) for **2y**



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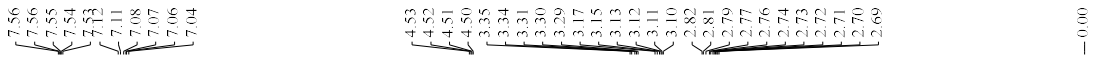
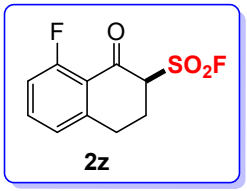
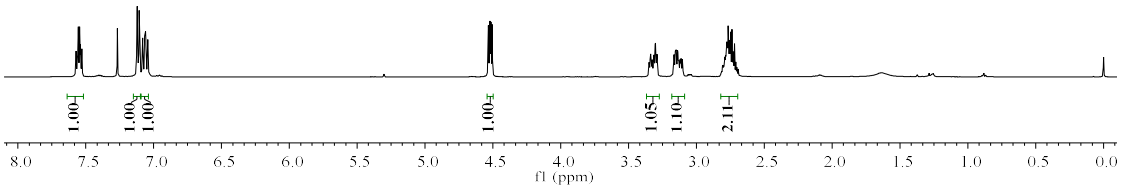
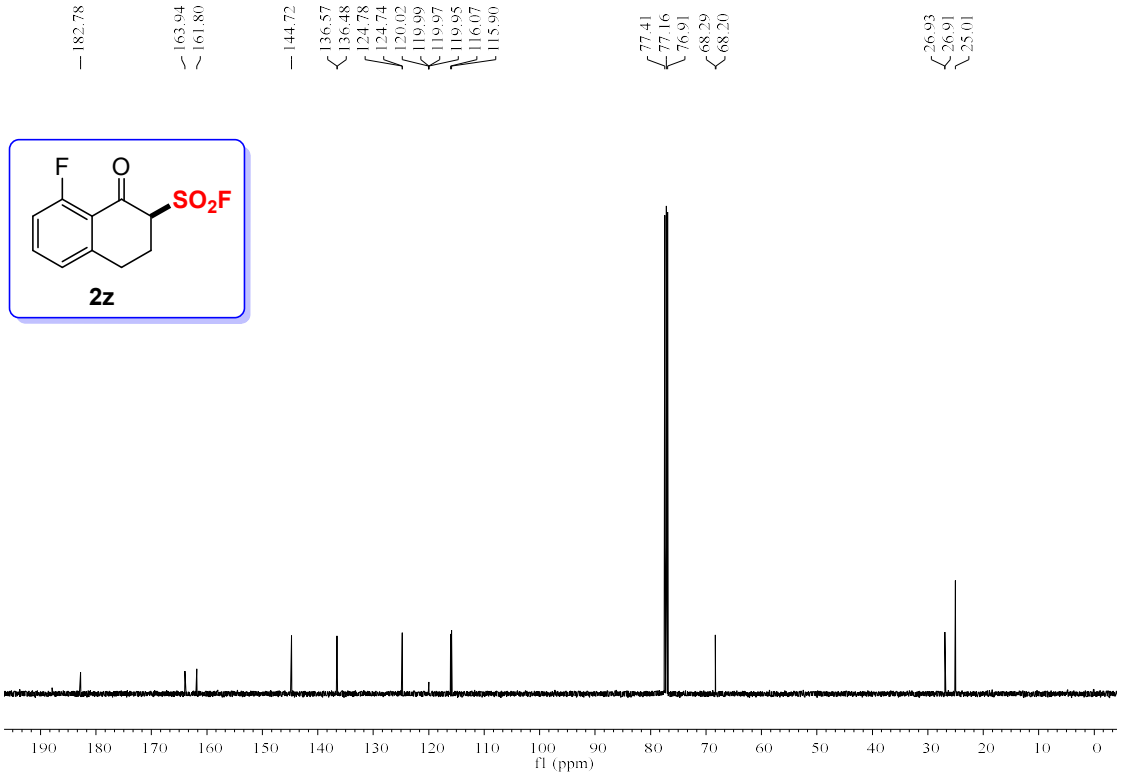


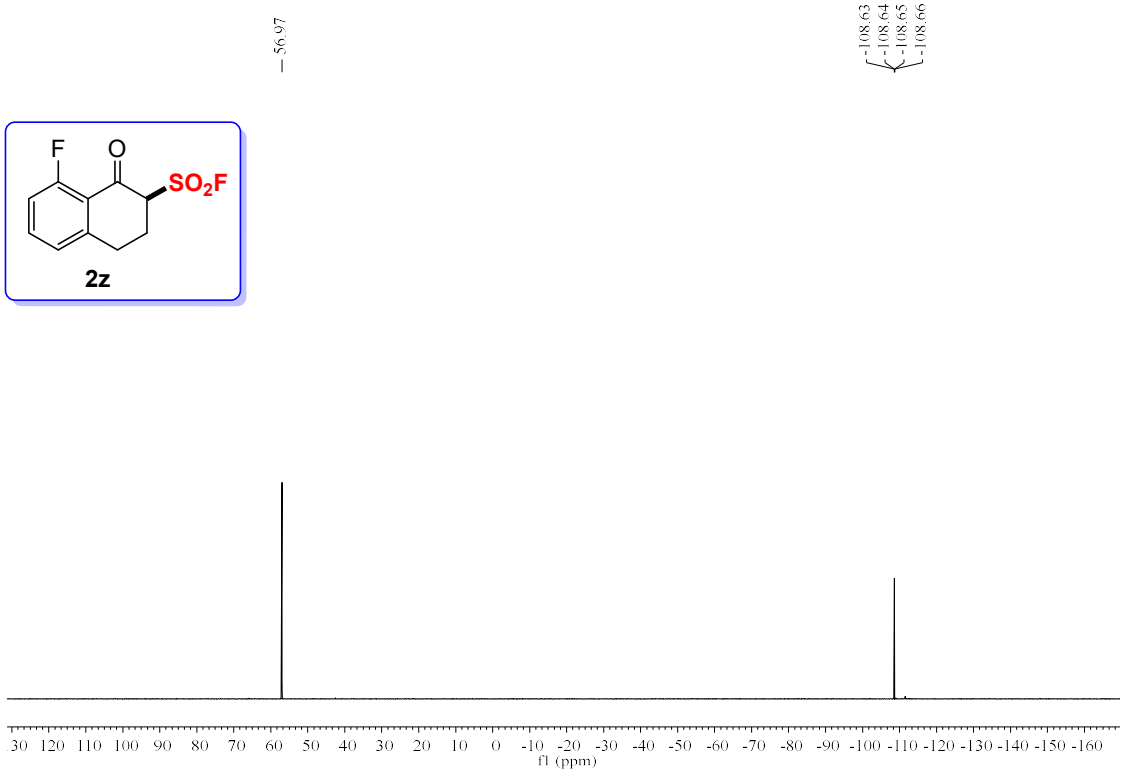




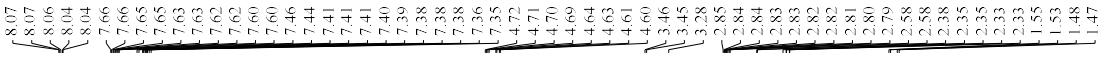
^{13}C NMR (126 MHz, $CDCl_3$) for **2z**

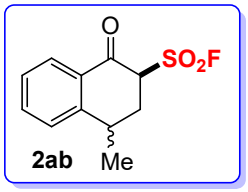


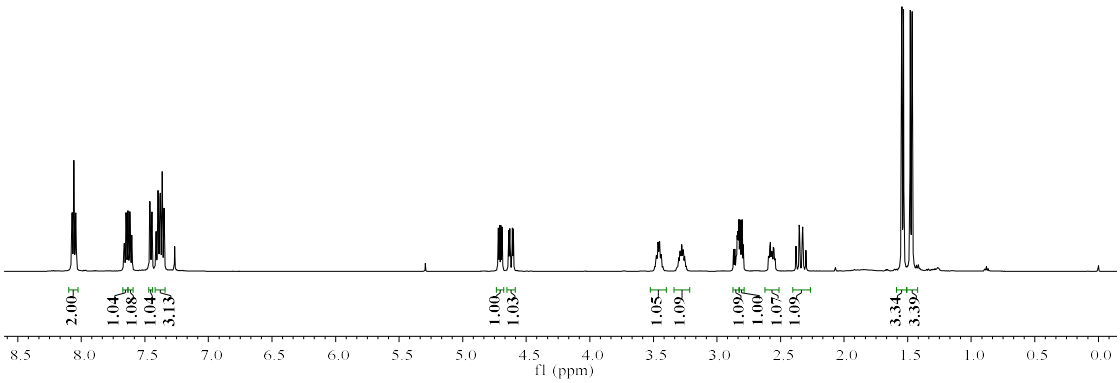
^{19}F NMR (471 MHz, $CDCl_3$) for **2z**



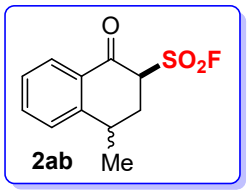
^{1}H NMR (500 MHz, $CDCl_3$) for **2ab**

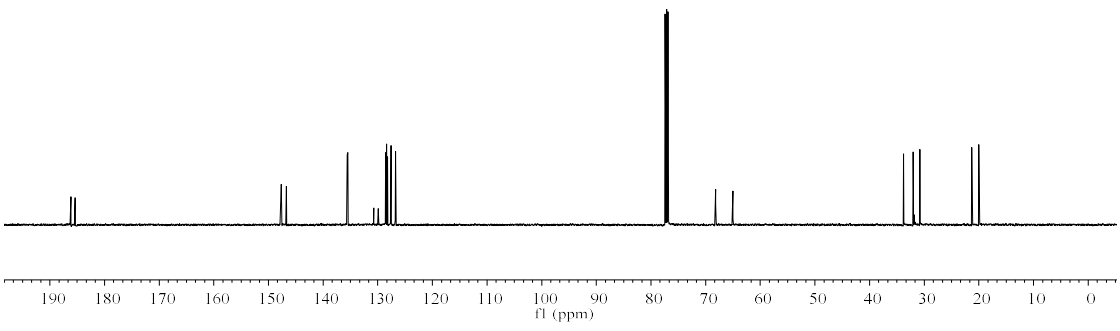




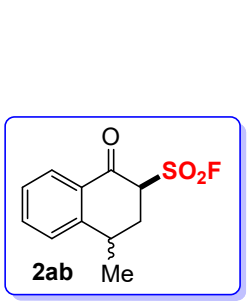


^{13}C NMR (126 MHz, $CDCl_3$) for **2ab**

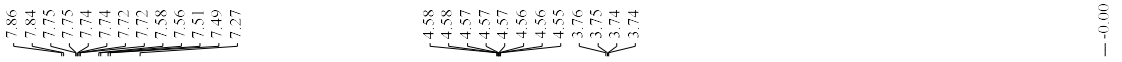


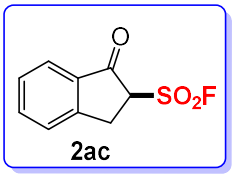


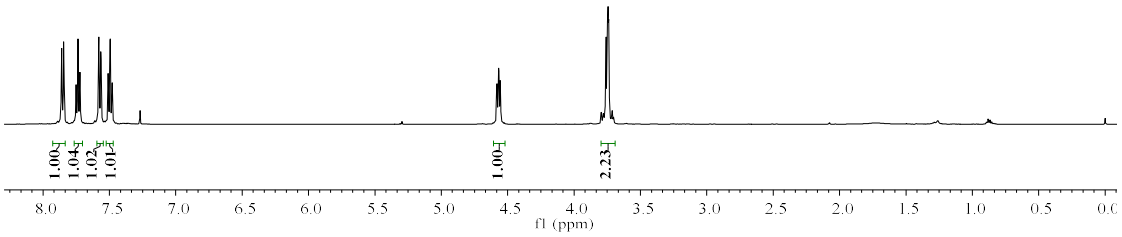
^{19}F NMR (471 MHz, $CDCl_3$) for **2ab**



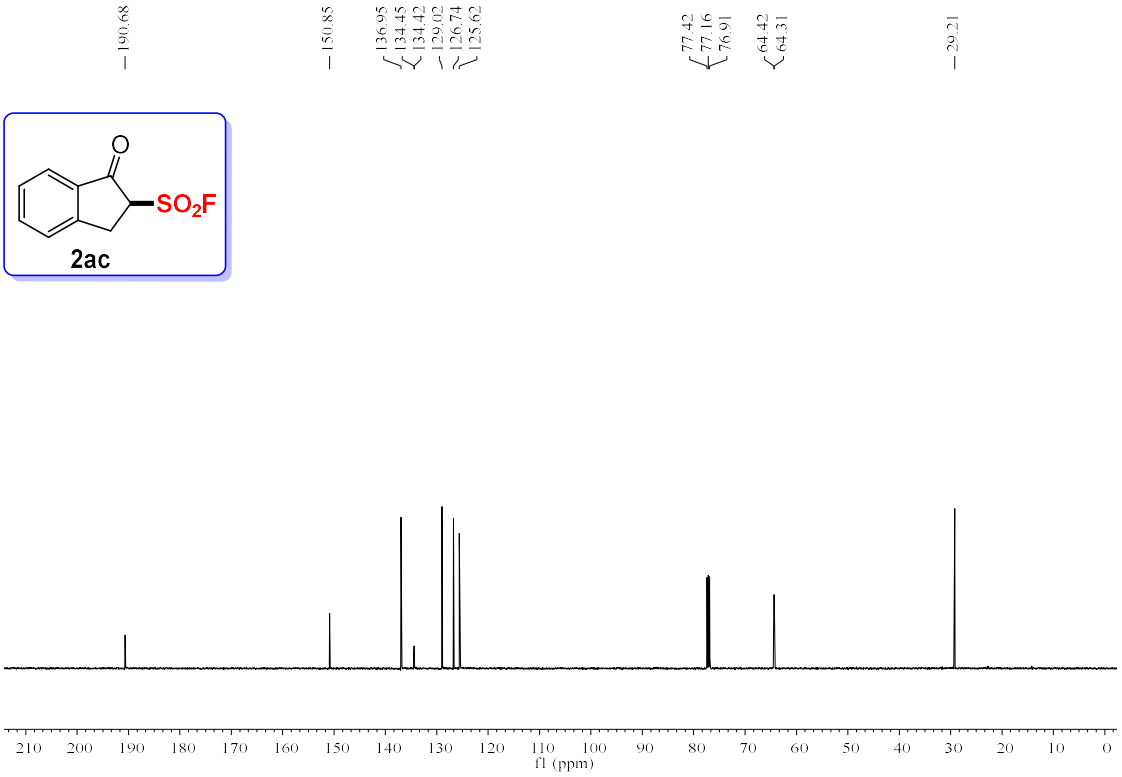
^{1}H NMR (500 MHz, $CDCl_3$) for **2ac**



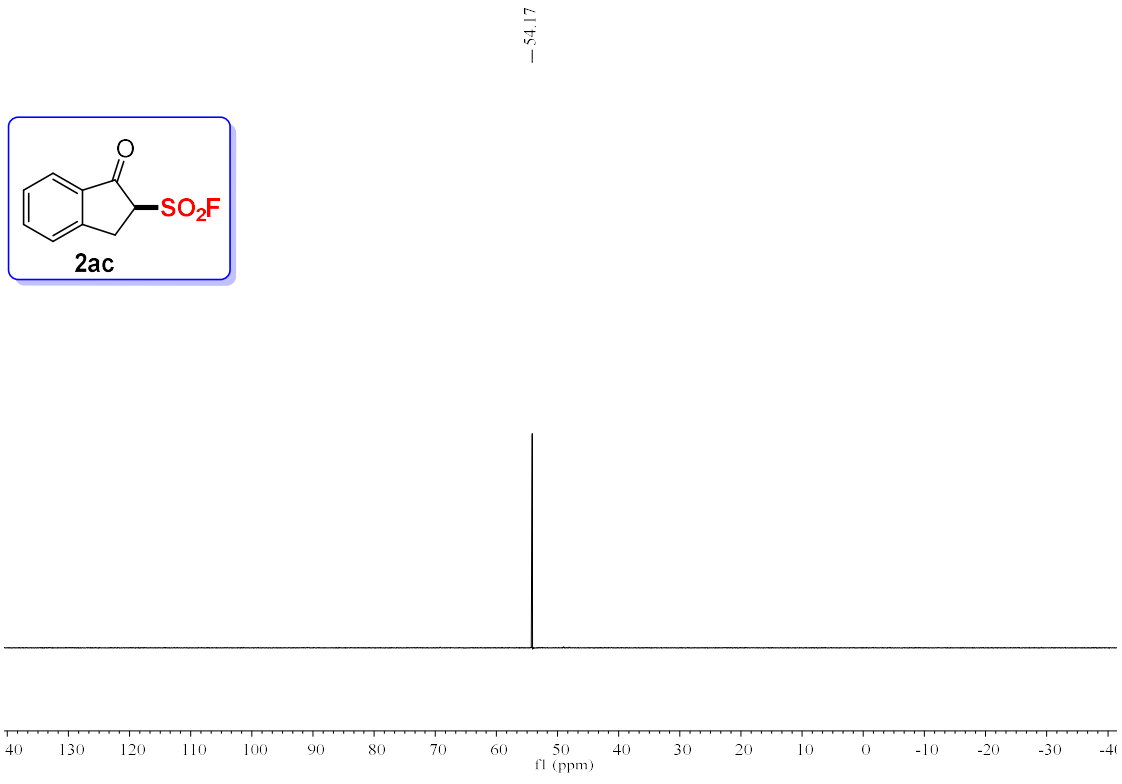




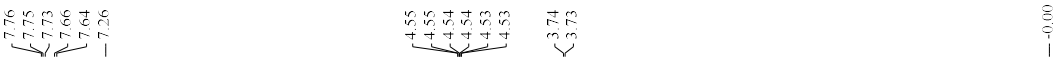
^{13}C NMR (126 MHz, $CDCl_3$) for **2ac**

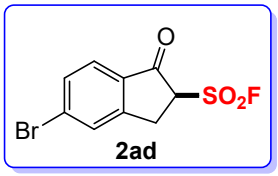


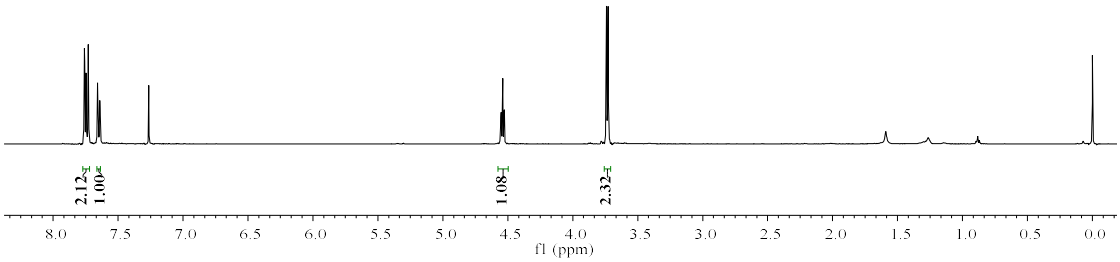
^{19}F NMR (471 MHz, $CDCl_3$) for **2ac**



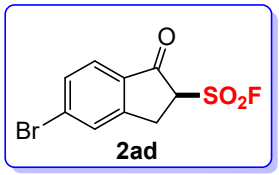
^{1}H NMR (500 MHz, $CDCl_3$) for **2ad**

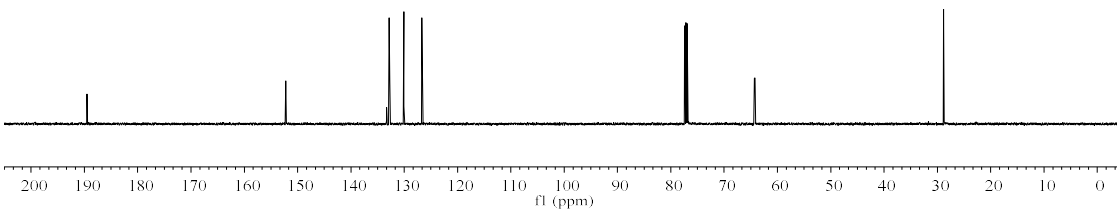




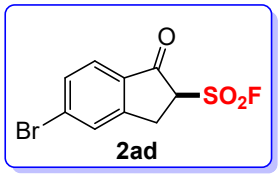


^{13}C NMR (126 MHz, $CDCl_3$) for **2ad**

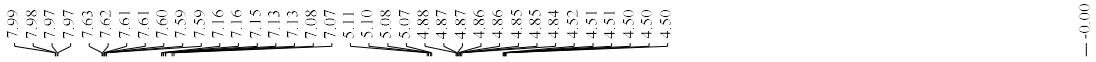


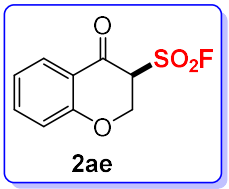


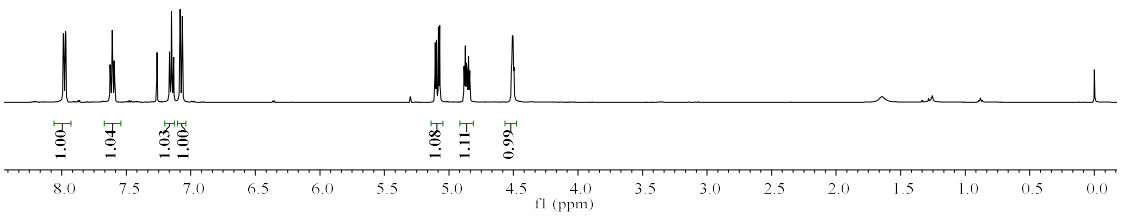
^{19}F NMR (471 MHz, $CDCl_3$) for **2ad**



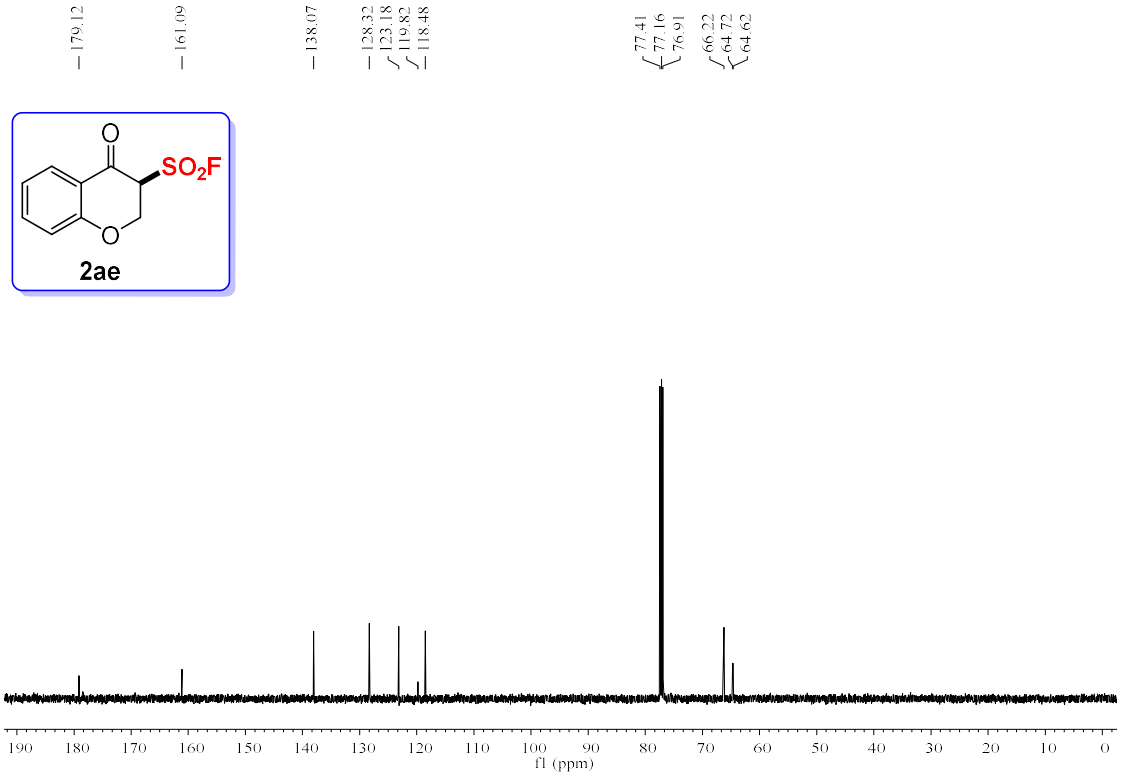
^{1}H NMR (500 MHz, $CDCl_3$) for **2ae**



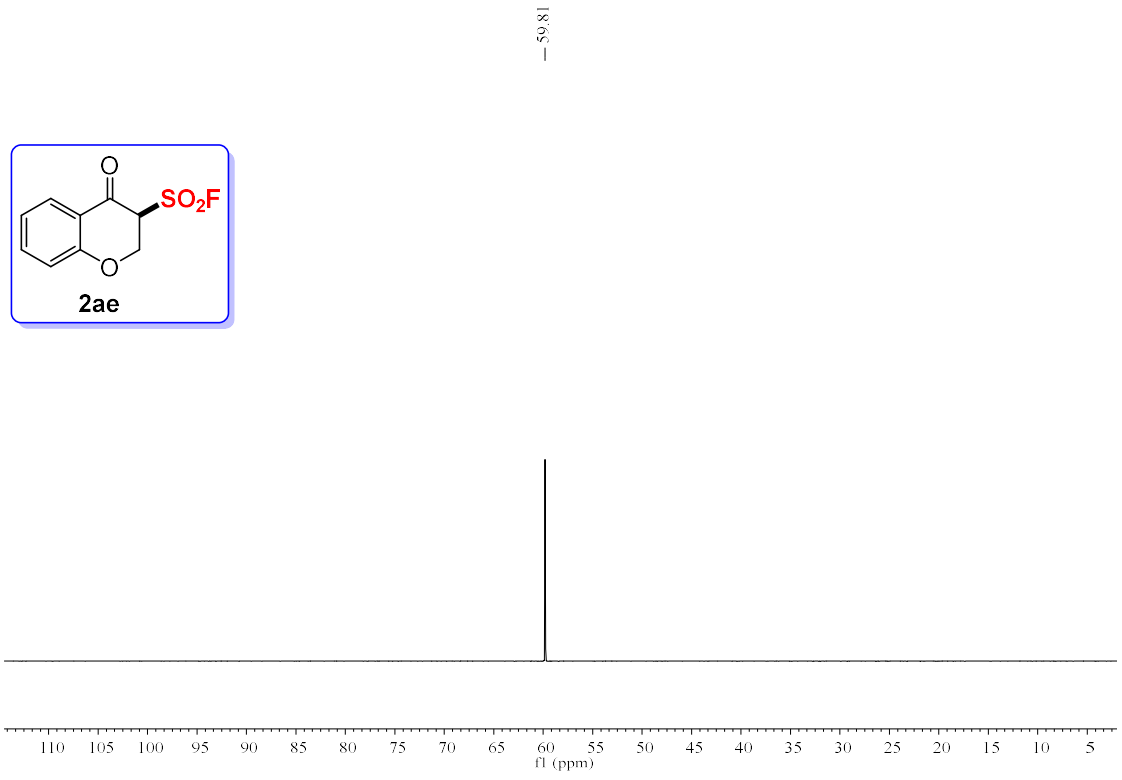




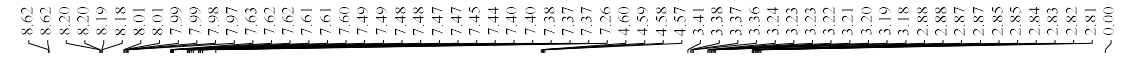
^{13}C NMR (126 MHz, $CDCl_3$) for **2ae**

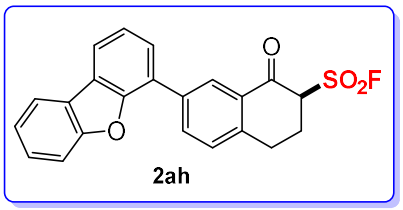


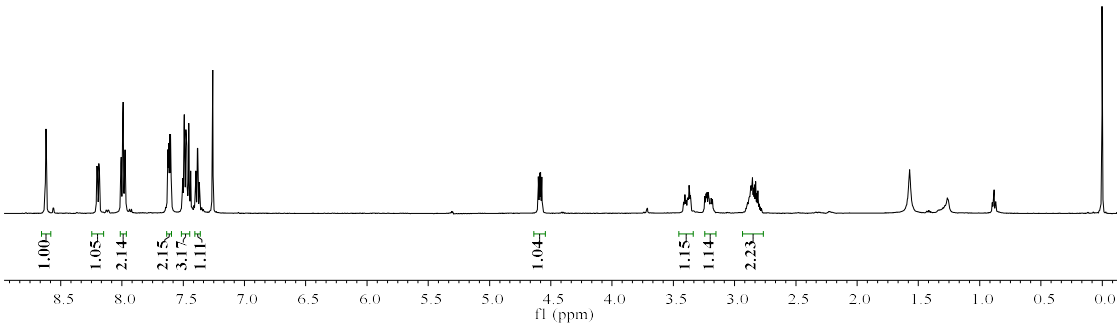
^{19}F NMR (471 MHz, $CDCl_3$) for **2ae**



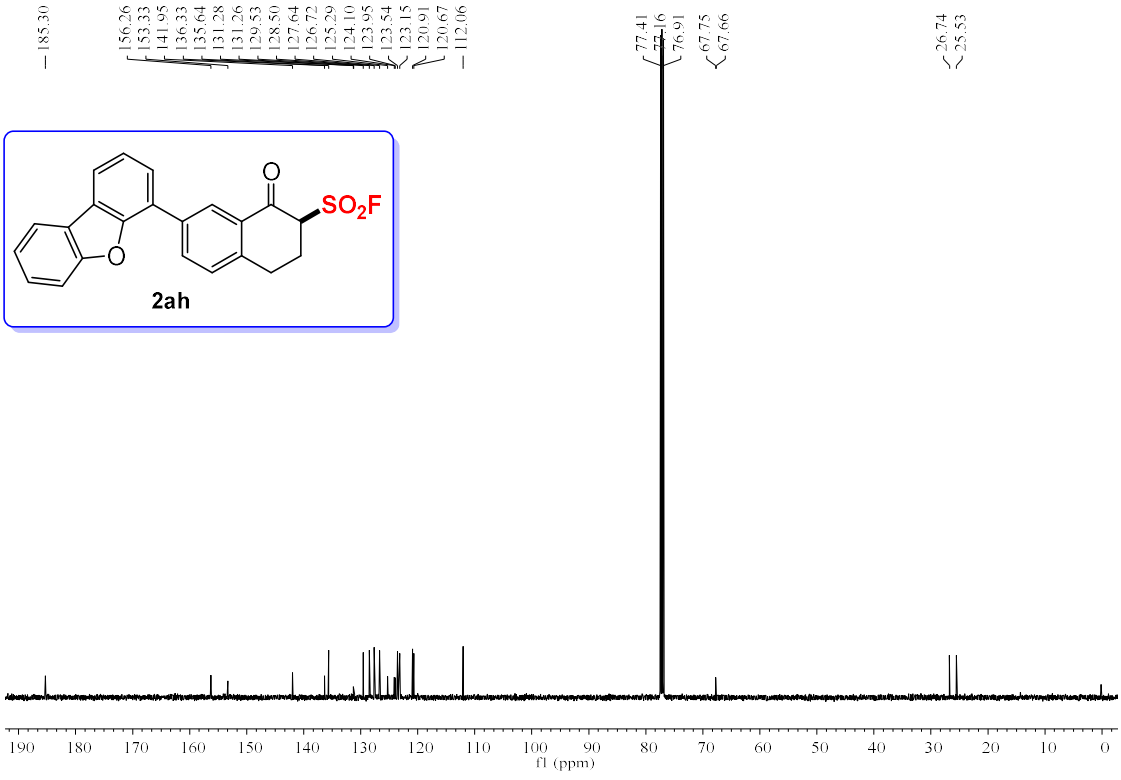
^{1}H NMR (500 MHz, $CDCl_3$) for **2ah**



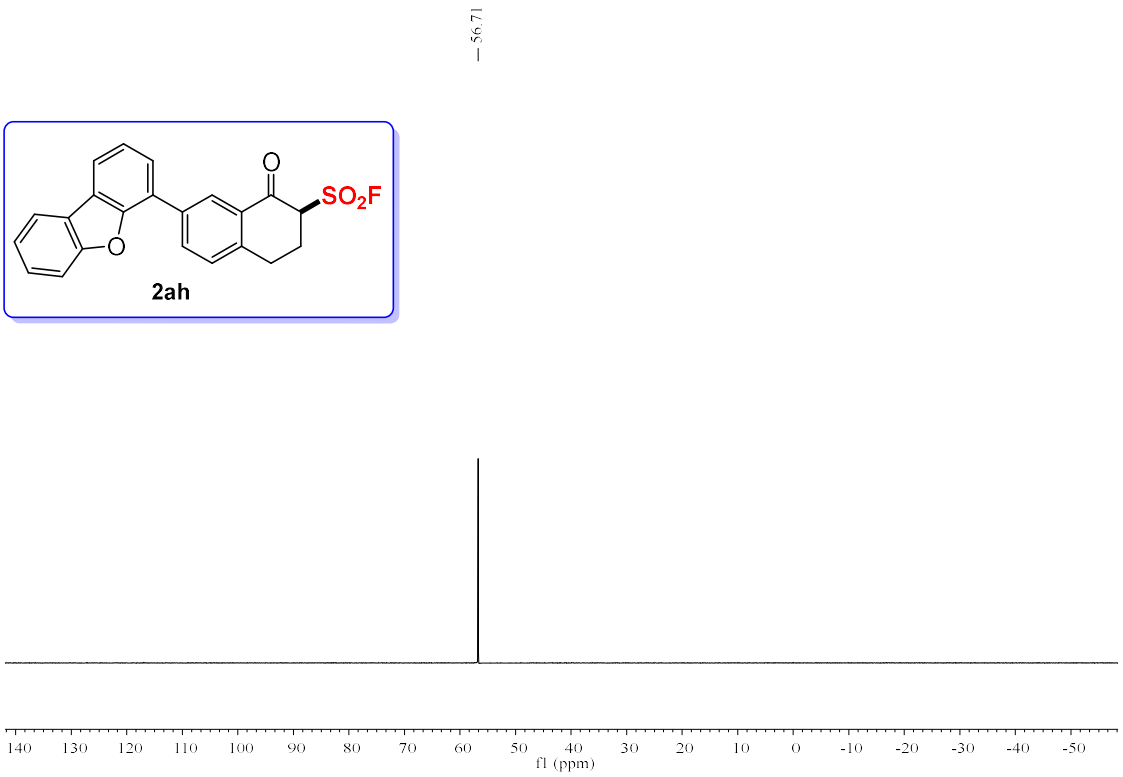




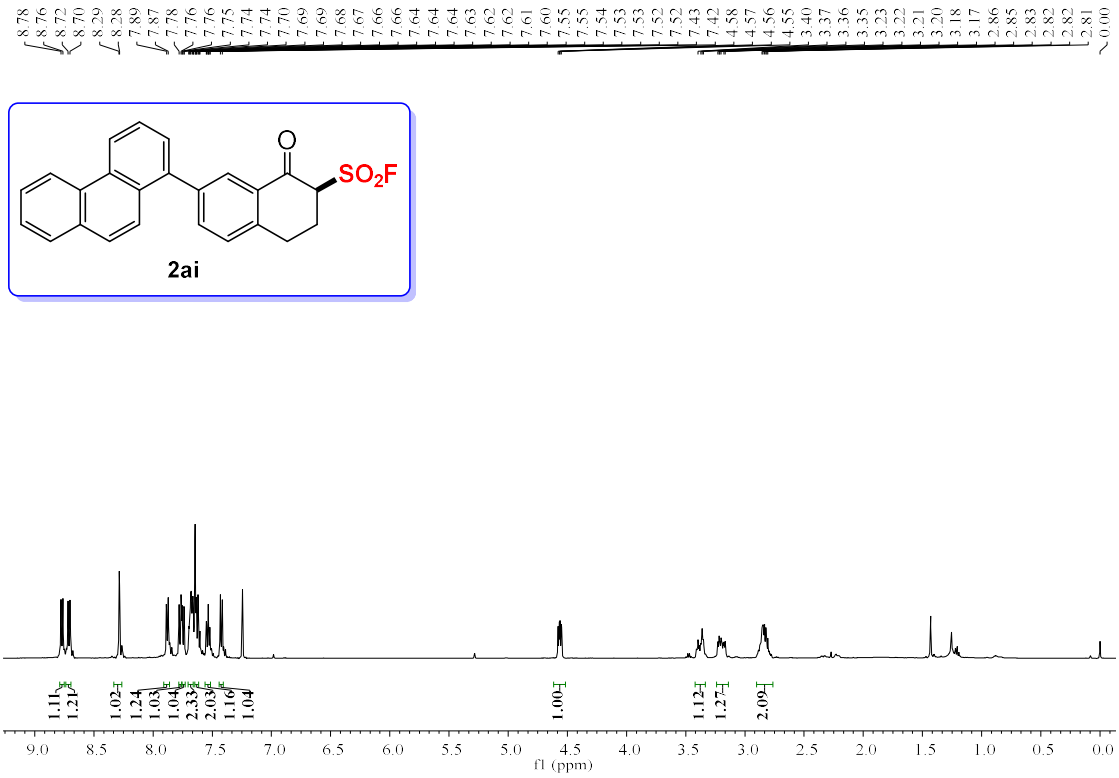
^{13}C NMR (126 MHz, $CDCl_3$) for **2ah**



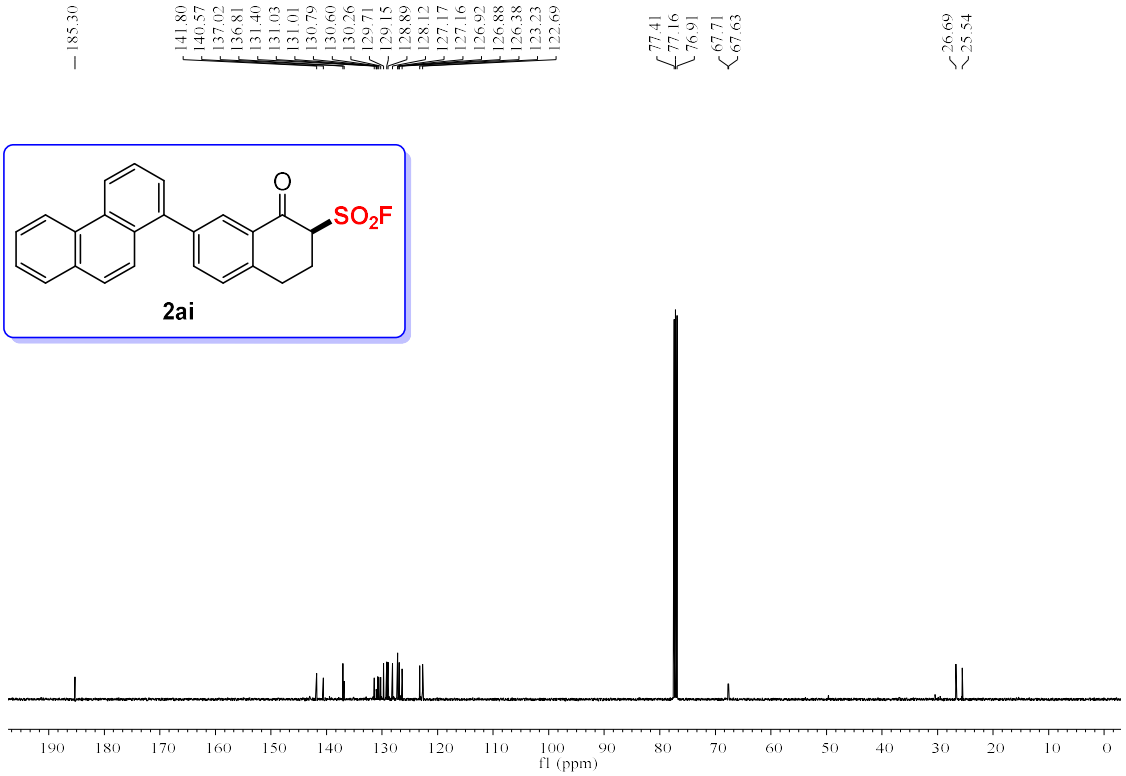
^{19}F NMR (471 MHz, $CDCl_3$) for **2ah**



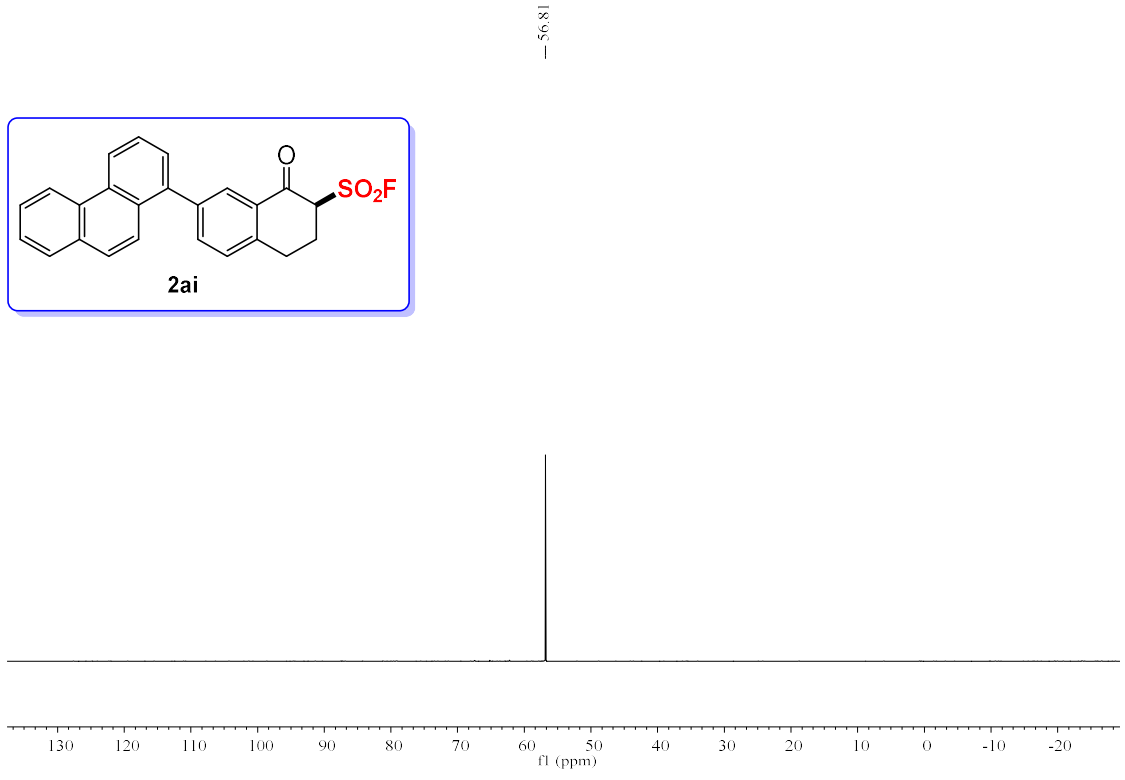
^{1}H NMR (500 MHz, $CDCl_3$) for **2ai**



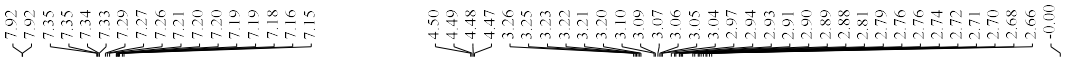
^{13}C NMR (126 MHz, $CDCl_3$) for **2ai**

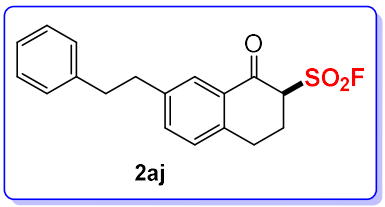


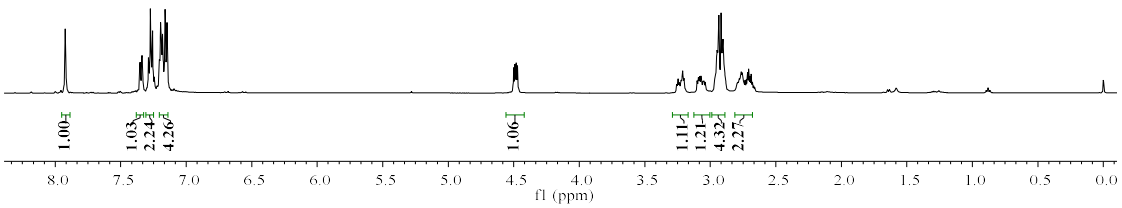
^{19}F NMR (471 MHz, $CDCl_3$) for **2ai**



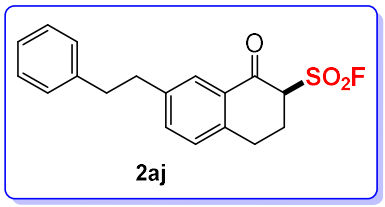
^{1}H NMR (500 MHz, $CDCl_3$) for **2aj**

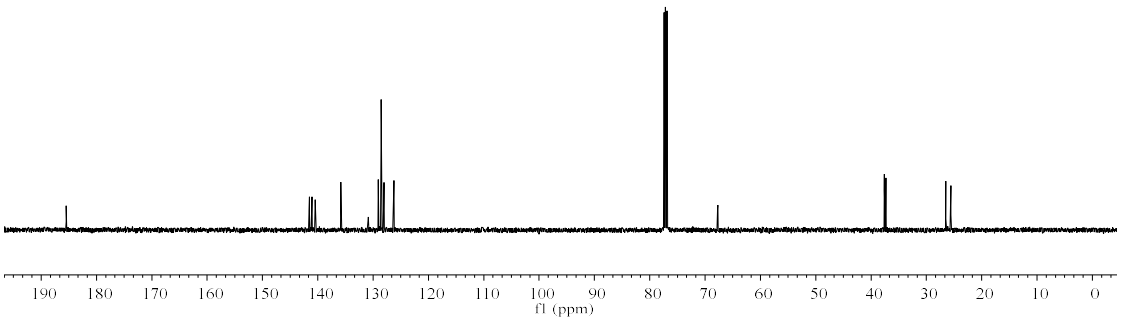




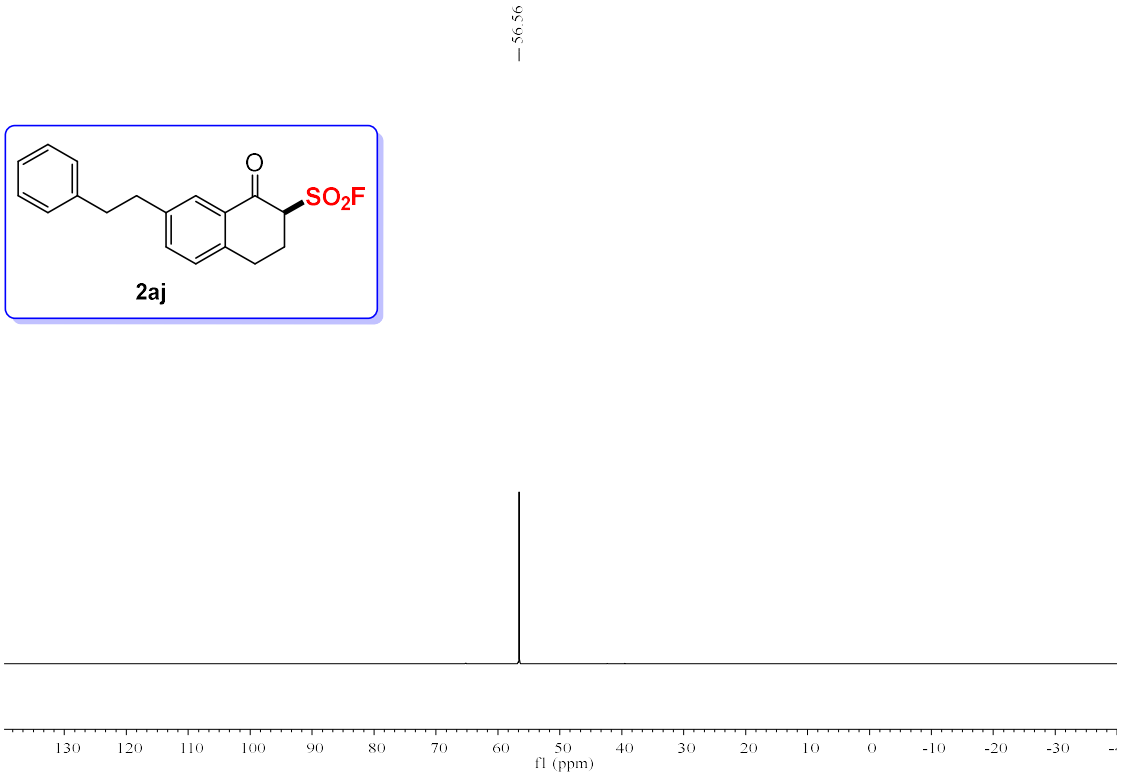


^{13}C NMR (126 MHz, $CDCl_3$) for **2aj**

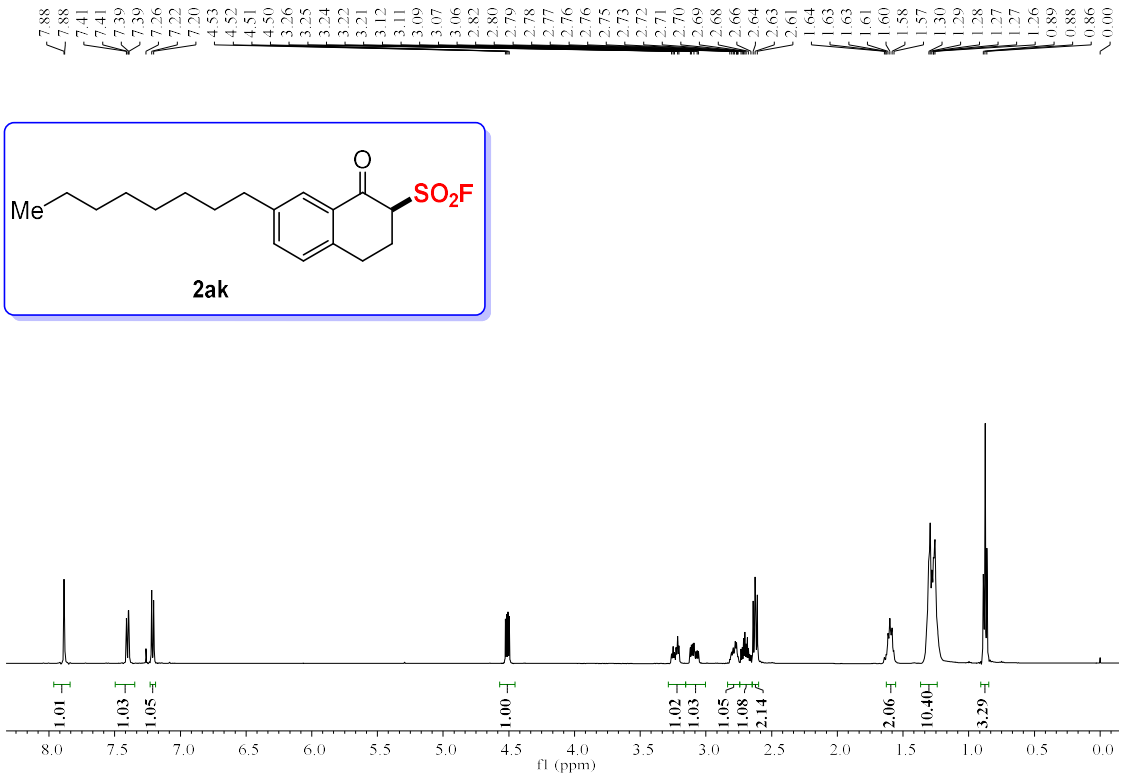




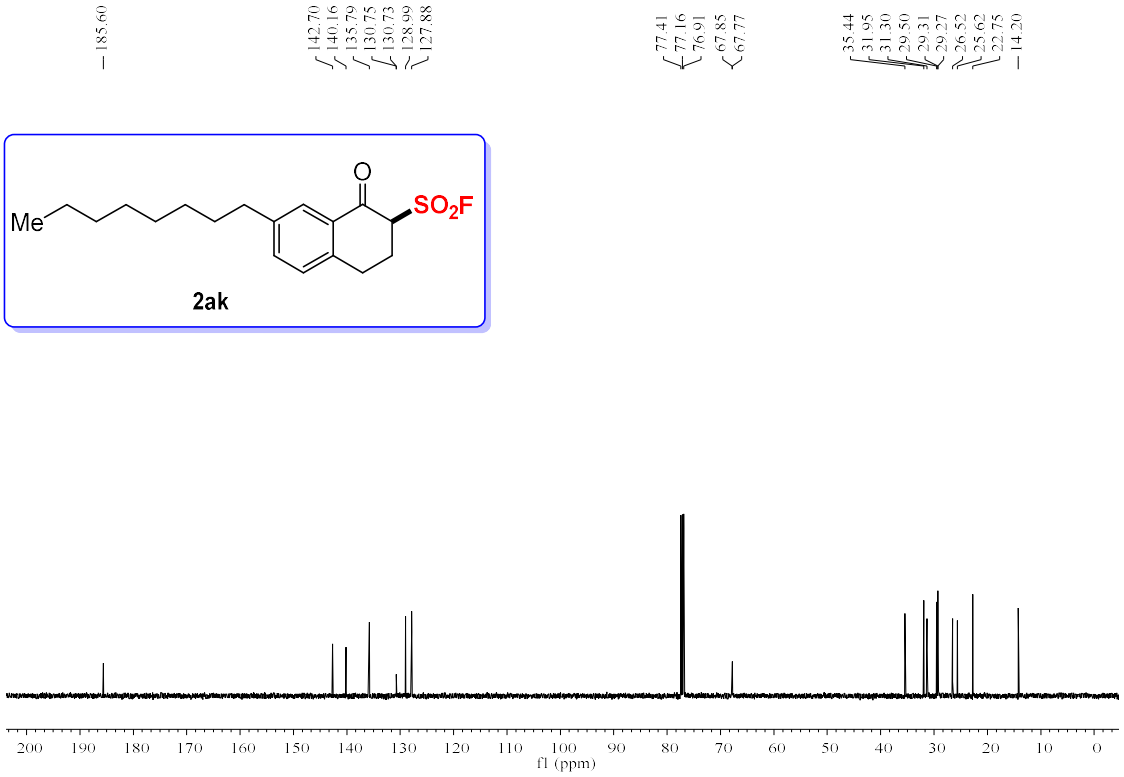
^{19}F NMR (471 MHz, $CDCl_3$) for **2aj**



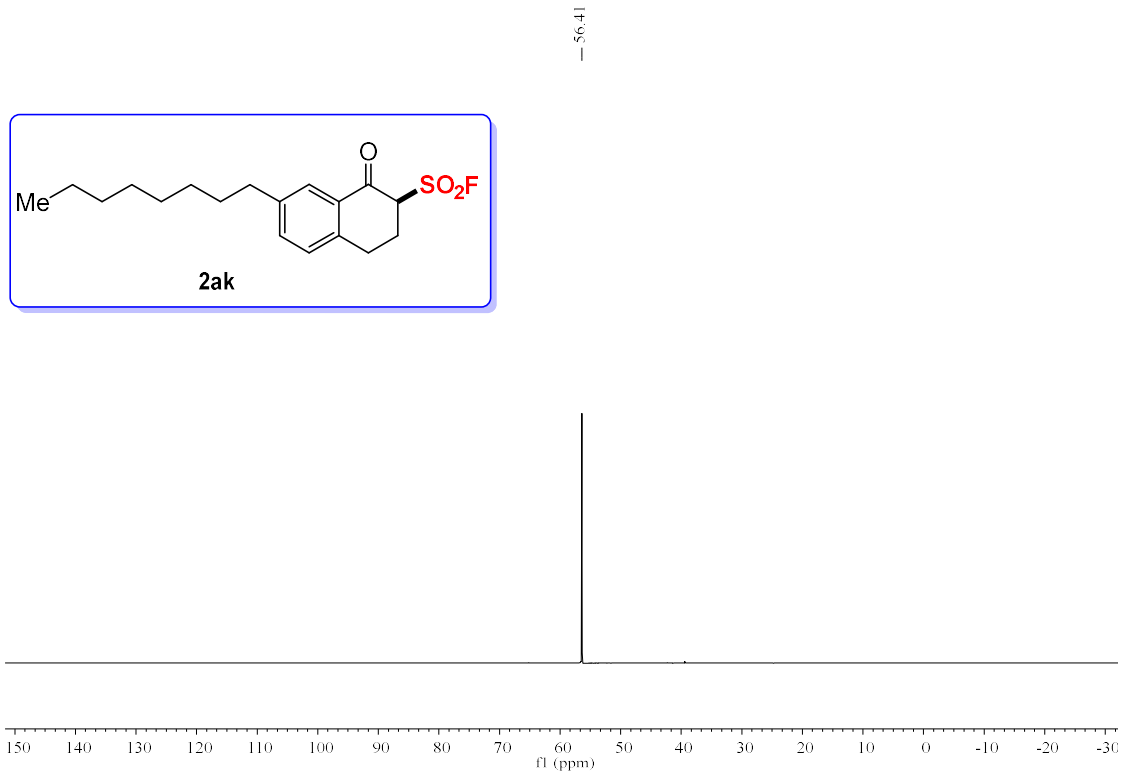
^{1}H NMR (500 MHz, $CDCl_3$) for **2ak**



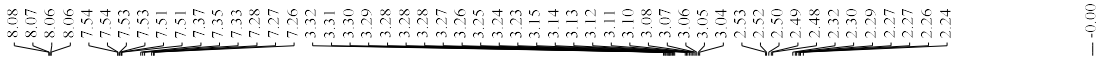
^{13}C NMR (126 MHz, $CDCl_3$) for **2ak**

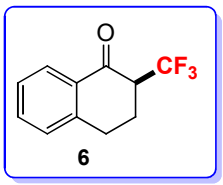


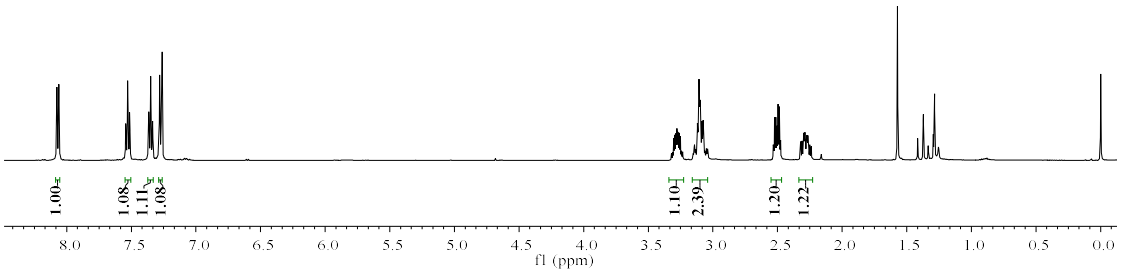
^{19}F NMR (471 MHz, $CDCl_3$) for **2ak**



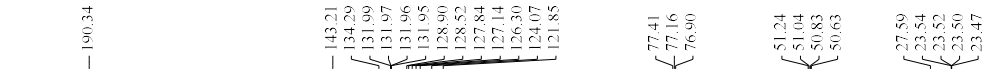
^{1}H NMR (500 MHz, $CDCl_3$) for **6**

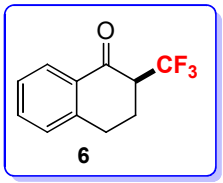


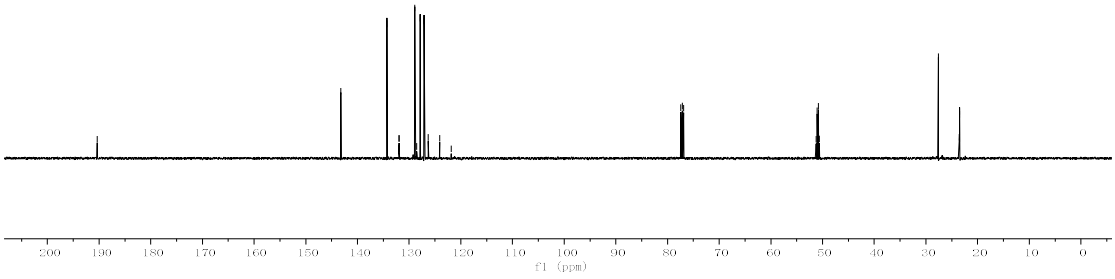




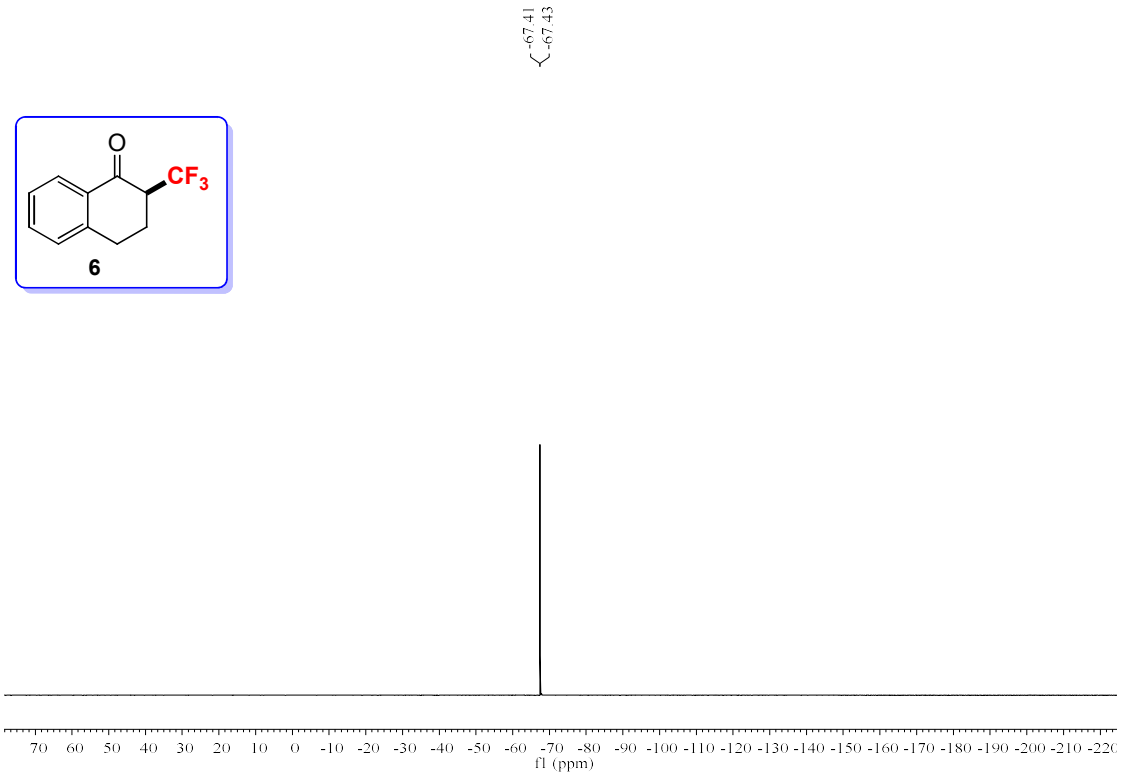
^{13}C NMR (126 MHz, $CDCl_3$) for **6**



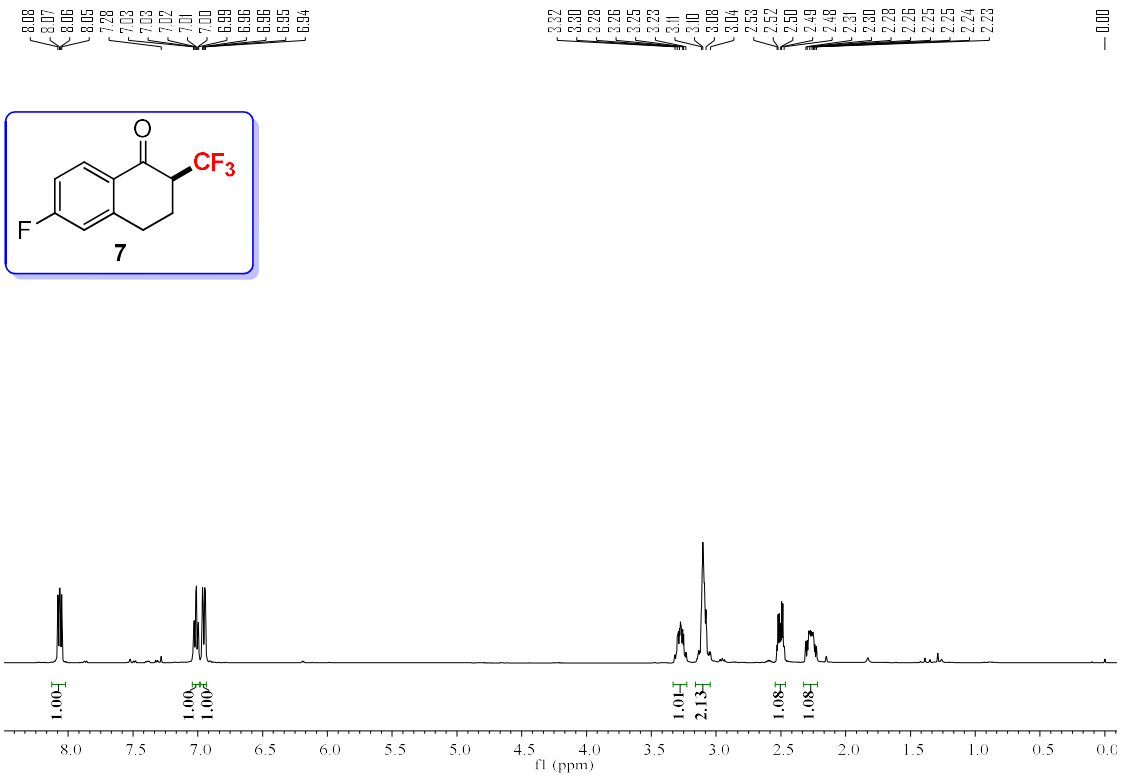




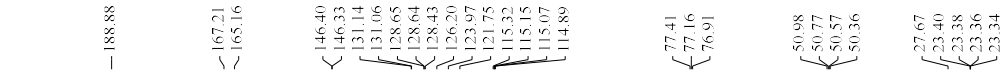
^{19}F NMR (471 MHz, $CDCl_3$) for **6**

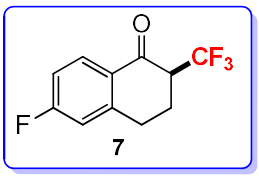


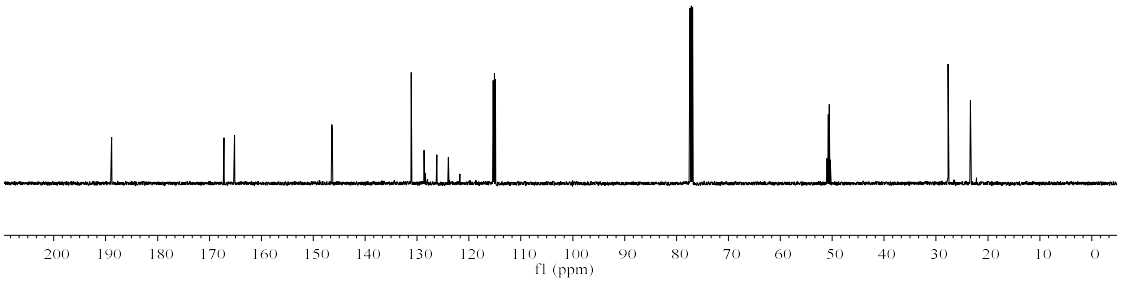
^{1}H NMR (500 MHz, $CDCl_3$) for **7**



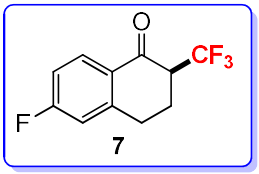
^{13}C NMR (126 MHz, $CDCl_3$) for **7**

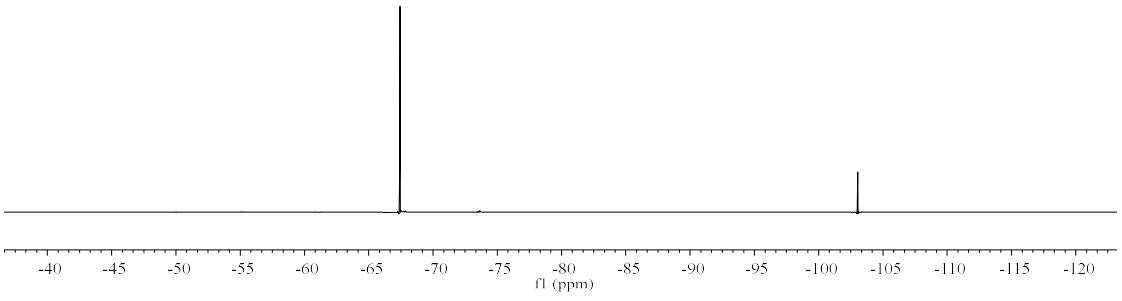




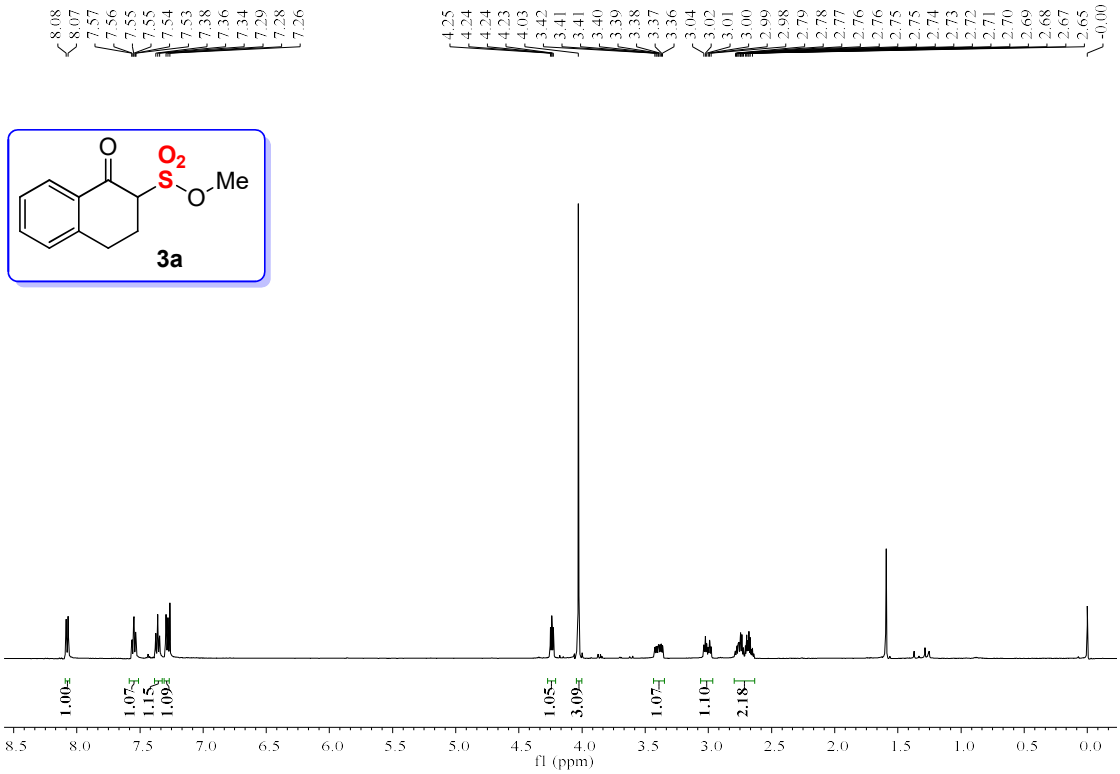


^{19}F NMR (471 MHz, $CDCl_3$) for **7**

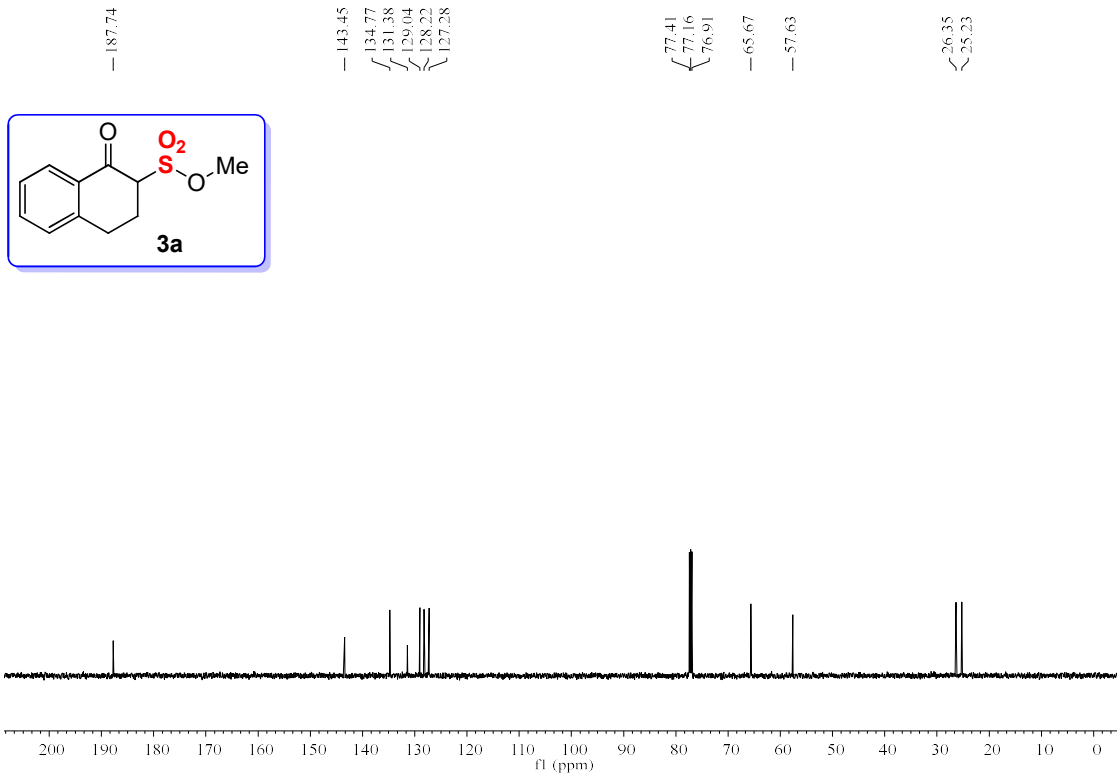




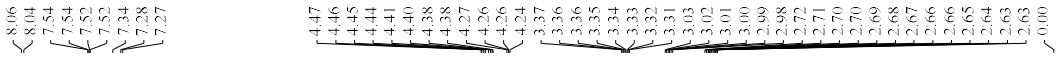
^{1}H NMR (500 MHz, $CDCl_3$) for **3a**

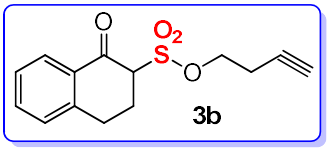


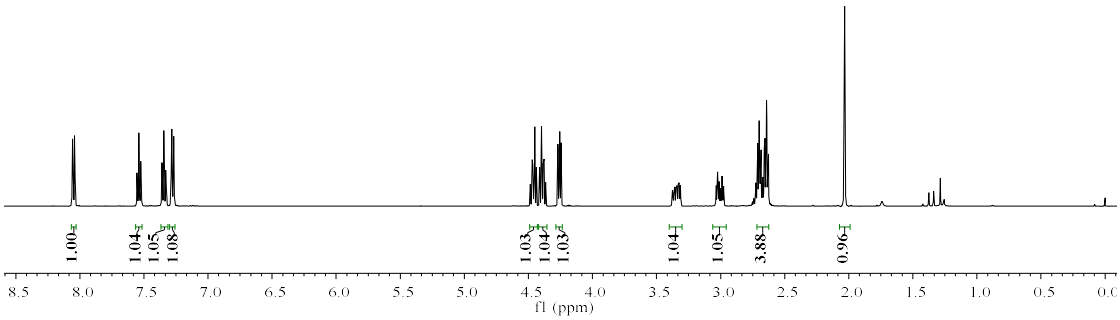
^{13}C NMR (126 MHz, $CDCl_3$) for **3a**



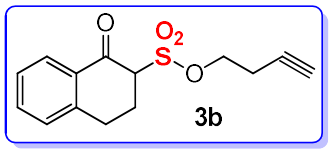
^{1}H NMR (500 MHz, $CDCl_3$) for **3b**

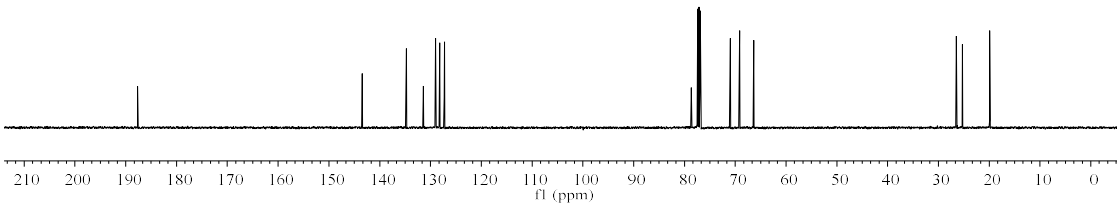




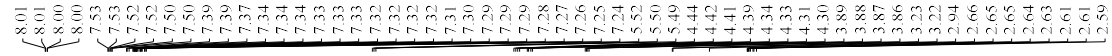


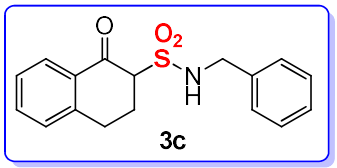
^{13}C NMR (126 MHz, $CDCl_3$) for **3b**

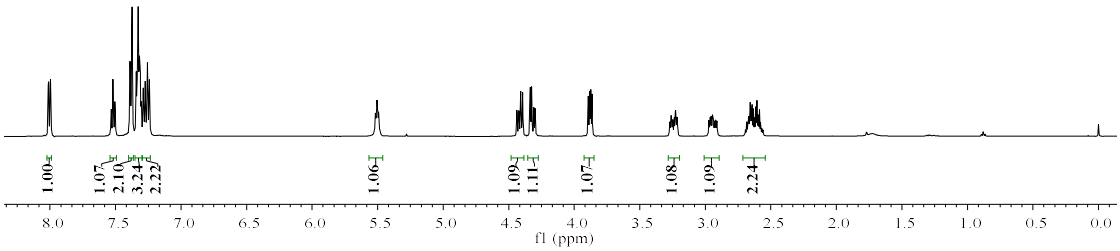




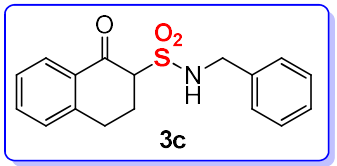
^{1}H NMR (500 MHz, $CDCl_3$) for **3c**

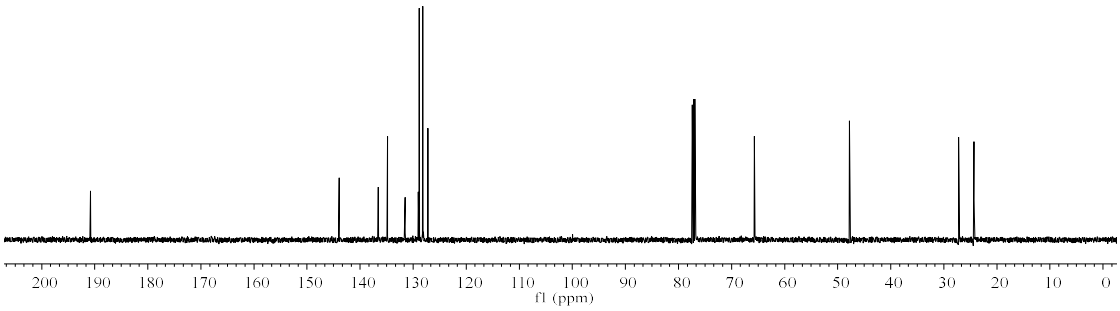




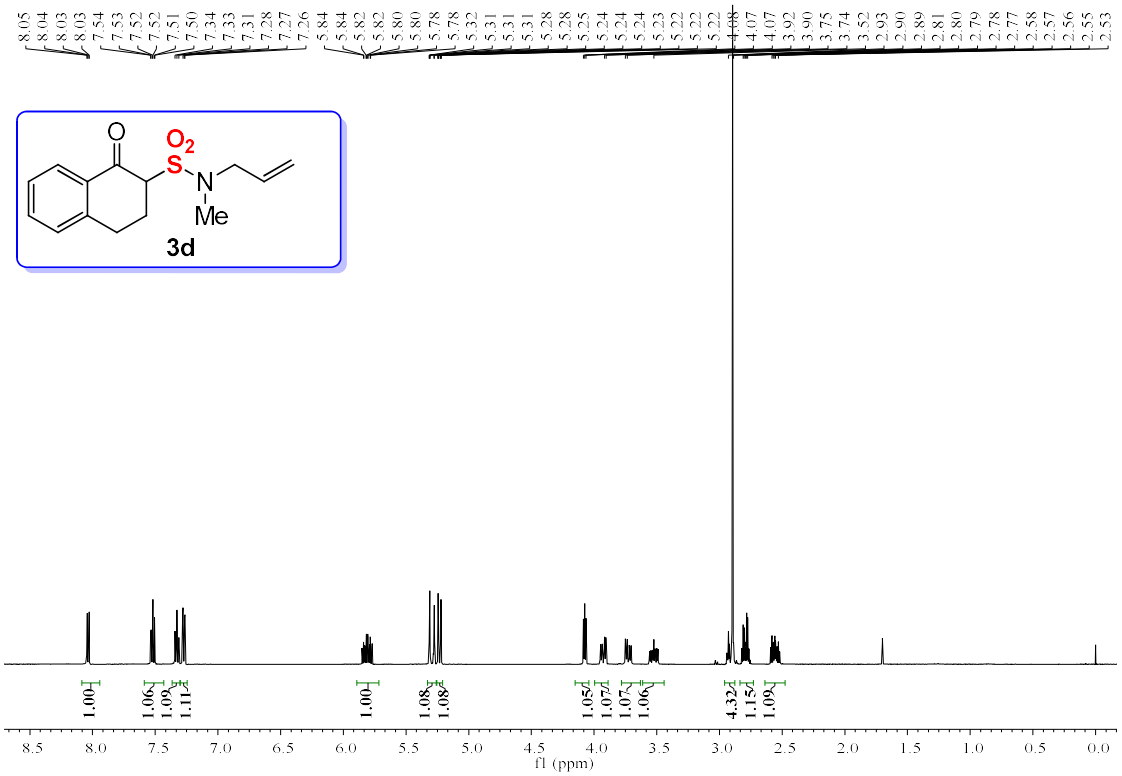


^{13}C NMR (126 MHz, $CDCl_3$) for **3c**

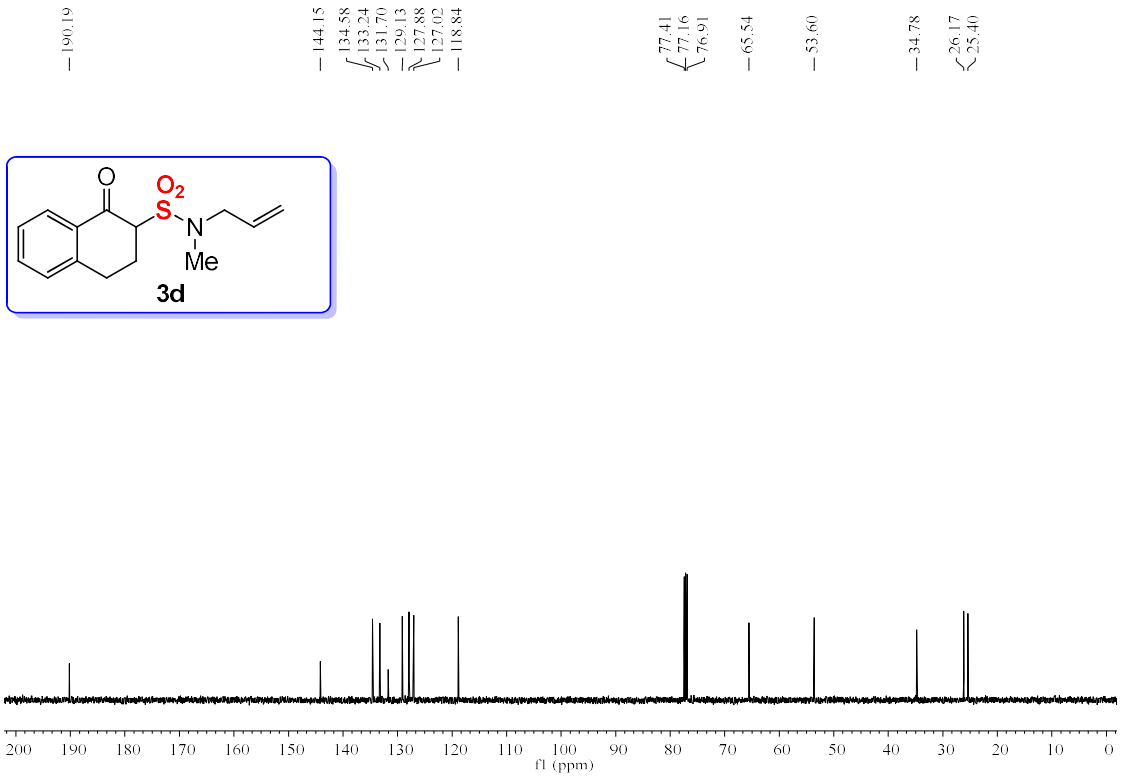




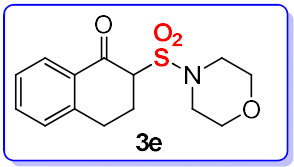
^{1}H NMR (500 MHz, $CDCl_3$) for **3d**

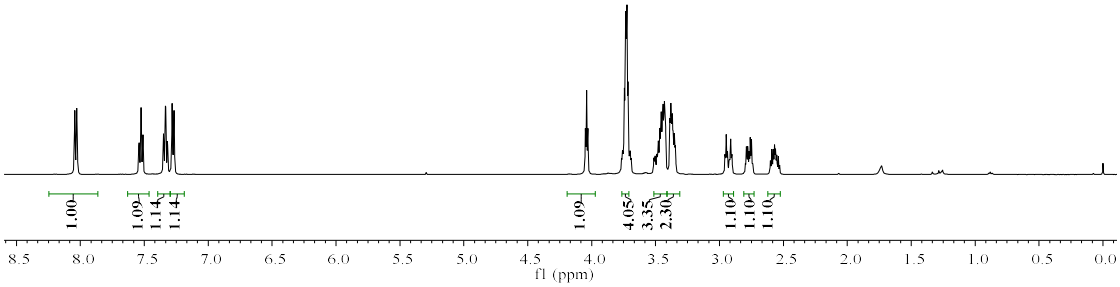


^{13}C NMR (126 MHz, $CDCl_3$) for **3d**



^{1}H NMR (500 MHz, $CDCl_3$) for **3e**





^{13}C NMR (126 MHz, $CDCl_3$) for **3e**