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Supporting Information

A regio- and stereoselective Heck-Matsuda process for construction

of γ-aryl allylsulfonyl fluorides

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1. General Information

All reactions were carried out in oven or flame-dried glassware under air atmosphere. Unless otherwise noted, solvents and reagents were used as purchased without further purification. The reactions were magnetically stirred and monitored by thin layer chromatography. Yields refer to chromatographically and spectroscopically pure compounds. ¹H, ¹⁹F and ¹³C NMR spectra were recorded in CDCl₃ at 500 MHz (¹H NMR), 471 MHz (¹⁹F NMR) and 126 MHz (¹³C NMR) on a Bruker Avance 500 spectrometer. Chemical shifts are reported in parts per million relative to TMS using the residual solvent signal as internal standard (CDCl₃,7.26 and 77.2 ppm) and coupling constants are given in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet.

2. Optimization of the Reaction Conditions. Table S1: Screening the Ligand^a

N ₂ BF ₄ +	SO ₂ F	Pd(OAc) ₂ (5 mol%) ligand (5 mol%) DMF (0.1 M), rt, 4 h	SO ₂ F
1a	2a		3a
Entry		Ligand	Yield(3a , %)
1		dppe	60
2		dppp	59
3		dppb	36
4		dppf	trace
5		PCy ₃	61
6		PPh ₃	66
7		Xantphos	61
8	2-(Diph	enylphosphino)-biphenyl	58
9		/	55

^aReaction conditions: arenediazonium tetrafluoroborate (**1a**, 0.2 mmol), Pd(OAc)₂ (5 mol%) and liagand (5 mol%) were dissolved in DMF (0.1 M, 2.0 mL). Then the prop-2-ene-1-sulfonyl fluoride (0.4 mmol, 2.0 eq.) was added at room temperature. The resulting mixture was stirred for 4 h at room temperature. ^bThe yield was determined by HPLC using pure **3a** as the external standard ($t_R = 6.1 \text{ min}, \lambda_{max} = 258.3 \text{ nm}, \text{ acetonitrile / water } = 80 : 20 (v / v)$)

N ₂ BF ₄ +	SO ₂ F	Pd(OAc) ₂ (5 mol%) <u>PPh₃ (5 mol%)</u> Solvent (0.1 M), rt, 4 h	SO ₂ F
1a	2a		3a
Entry		Solvent	Yield (3a , %) ^b
1		МеОН	71
2		H_2O	trace
3		DMSO	trace
4		DMF	66
5		DMA	51
6		MeCN	trace
7		1,4-dioxane	trace
8		THF	trace
9		Acetone	16

Table S2: Screening the Solvent^a

^aReaction conditions: arenediazonium tetrafluoroborate (**1a**, 0.2 mmol), Pd(OAc)₂ (5 mol%) and PPh₃ (5 mol%) were dissolved in solvent (0.1 M, 2.0 mL). Then the prop-2-ene-1-sulfonyl fluoride (0.4 mmol, 2.0 eq.) was added at room temperature. The resulting mixture was stirred for 4 h at room temperature. ^bThe yield was determined by HPLC using pure **3a** as the external standard ($t_R = 6.1 \text{ min}, \lambda_{max} = 258.3 \text{ nm}, \text{ acetonitrile / water } = 80 : 20 (v / v)$)

N ₂ BF ₄ +	SO ₂ F	Pd(OAc) ₂ (X mol%) PPh ₃ (X mol%) MeOH (0.1 M), rt, 4 h	SO ₂ F
1a	2a		3a
Entry		X (mol%)	Yield (3a , %) ^b
1		1	50
2		2	61
3		3	72
4		5	71
5		10	64

Table S3: Screening of the catalyst loading^a

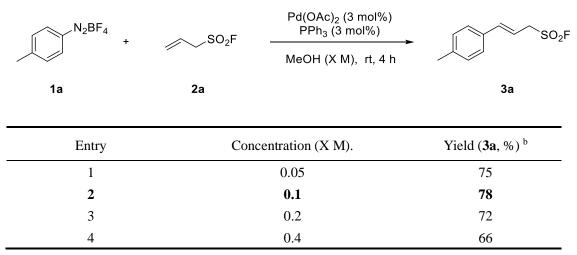
^aReaction conditions: arenediazonium tetrafluoroborate (**1a**, 0.2 mmol), Pd(OAc)₂ (X mol%) and PPh₃ (X mol%) were dissolved in MeOH (0.1 M, 2.0 mL). Then the prop-2-ene-1-sulfonyl fluoride (0.4 mmol, 2.0 eq.) was added at room temperature. The resulting mixture was stirred for 4 h at room temperature. ^bThe yield was determined by HPLC using pure **3a** as the external standard ($t_R = 6.1 \text{ min}, \lambda_{max} = 258.3 \text{ nm}, \text{ acetonitrile / water } = 80 : 20 (v / v)$)

N ₂ BF ₄ +	SO ₂ F	Pd(OAc) ₂ (3 mol%) PPh ₃ (3 mol%)	SO ₂ F
	<i>~</i>	MeOH (0.1 M), rt, 4 h	
1a	2a		3a
Entry		2a (X equiv.)	Yield (3a , %) ^b
1		1.1	78
2		1.2	78
3		1.5	76
4		2.0	72
5		3.0	63

Table S4: Screening of the prop-2-ene-1-sulfonyl fluoride loading^a

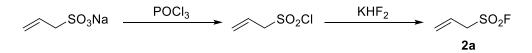
^aReaction conditions: arenediazonium tetrafluoroborate (**1a**, 0.2 mmol), Pd(OAc)₂ (3 mol%) and PPh₃ (3 mol%) were dissolved in MeOH (0.1 M, 2.0 mL). Then the prop-2-ene-1-sulfonyl fluoride (X eq.) was added at room temperature. The resulting mixture was stirred for 4 h at room temperature. ^bThe yield was determined by HPLC using pure **3a** as the external standard ($t_R = 6.1 \text{ min}$, $\lambda_{max} = 258.3 \text{ nm}$, acetonitrile / water = 80 : 20 (v / v))

Table S5: Screening of the reaction concentration^a



^aReaction conditions: arenediazonium tetrafluoroborate (**1a**, 0.2 mmol), Pd(OAc)₂ (3 mol%) and PPh₃ (3 mol%) were dissolved in MeOH (X M). Then the prop-2-ene-1-sulfonyl fluoride (0.22 mmol, 1.1 eq.) was added at room temperature. The resulting mixture was stirred for 4 h at room temperature. ^bThe yield was determined by HPLC using pure **3a** as the external standard ($t_R = 6.1$ min, $\lambda_{max} = 258.3$ nm, acetonitrile / water = 80 : 20 (v / v)).

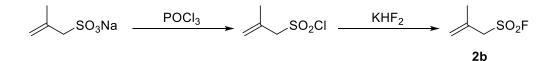
3. General Procedures.3.1 Procedure for the synthesis of prop-2-ene-1-sulfonyl fluoride (2a).



Step 1: Sodium allylsulfonate (100 g, 0.69 mol) and phosphorus oxychloride (329 g, 2.15 mol) were added to a 500 mL flask. The mixture was heated to 120 °C and refluxed for four hours. Then distilled out most of the phosphorus oxychloride. The solution was then poured into 500 mL of ice water and allowed to stand for 10 min in order to hydrolyze the phosphorus oxychloride. prop-2-ene-1-sulfonyl chloride was extracted with three 150 mL portions of methylene chloride. The combined methylene chloride extracts were washed with 200 mL of water, two 100 mL portions of 5% sodium bicarbonate, and finally with 100 mL of water. The solvent was evaporated to give crude prop-2-ene-1-sulfonyl chloride, which was used directly in the next step.

Step 2: KHF₂ (112 g, 1.43 mol) was added to 300 mL water and a nearly saturated KHF₂ solution formed after 1 h, when the solution approached room temperature. At this point, the crude prop-2-ene-1-sulfonyl chloride generated from the previous step was all added to KHF₂ solution. With continued stirring, the mixture was stirred for 2 h at room temperature. The reaction mixture was extracted with three 100 mL portions of methylene chloride, and the combined organic phase was washed with brine, dried over anhydrous Na₂SO₄, and concentrated using a rotary evaporator to give crude prop-2-ene-1-sulfonyl fluoride. Further distillation at 90 °C under reduced pressure with a water pump helped to remove the impurities and gave pure prop-2-ene-1-sulfonyl fluoride as a colorless liquid (52.8 g, 61% yield over two steps).

3.2 Procedure for the synthesis of 2-methylprop-2-ene-1-sulfonyl fluoride (2b).



Step 1: Sodium 2-methylprop-2-ene-1-sulfonate (30 g, 0.19 mol) and phosphorus oxychloride (100 g, 0.65 mol) were added to a 250 mL flask. The mixture was heated to 120 °C and refluxed for 12 h. Then distilled out most of the phosphorus oxychloride. The solution was then poured into

300 mL of ice water and allowed to stand for 10 min in order to hydrolyze the phosphorus oxychloride. 2-methylprop-2-ene-1-sulfonyl chloride was extracted with three 50 mL portions of methylene chloride. The combined methylene chloride extracts were washed with 50 mL of water, two 100 mL portions of 5% sodium bicarbonate, and finally with 50 mL of water. The solvent was evaporated to give crude 2-methylprop-2-ene-1-sulfonyl chloride, which was used directly in the next step.

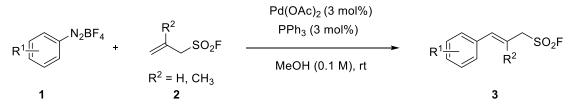
Step 2: KHF₂ (108 g, 1.38 mol) was added to 300 mL water and a nearly saturated KHF₂ solution formed after 1 h, when the solution approached room temperature. At this point, the crude prop-2-ene-1-sulfonyl chloride generated from the previous step was all added to KHF₂ solution. With continued stirring, the mixture was stirred for 12 h at room temperature. The reaction mixture was extracted with three 30 mL portions of methylene chloride, and the combined organic phase was washed with brine, dried over anhydrous Na₂SO₄, and concentrated using a rotary evaporator to give crude 2-methylprop-2-ene-1-sulfonyl fluoride. Further distillation at 120 °C under reduced pressure with a water pump helped to remove the impurities and gave pure 2-methylprop-2-ene-1-sulfonyl fluoride as a colorless liquid (5.6 g, 21% yield over two steps).

3.3 Preparation of aryldiazonium salts:

$$R \xrightarrow{II} NH_{2} NH_{2} NH_{2} NH_{2} R \xrightarrow{II} N_{2}^{+} BF_{4}^{-}$$

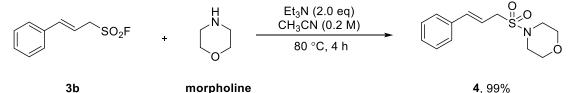
The aniline (10 mmol) was added to a mixture of 50% fluoroboric acid (3 mL) and distilled water (3 mL) in ice bath. To this solution, an ice-cold solution of sodium nitrite (704 mg, 10.2 mmol) in distilled water (3 mL) was added. After stirring for 30 mins, the precipitate was collected on a hirch funnel and washed with small amount of ice-cold distilled water. The solid was dissolved in acetonitrile and precipitated with slow addition of ethyl ether. Solids were obtained after repeat this trituration two to three times.

3.4 General procedure for palladium catalyzed Heck-Matsuda coupling of arenediazonium tetrafluoroborate and allylsulfonyl fluoride.



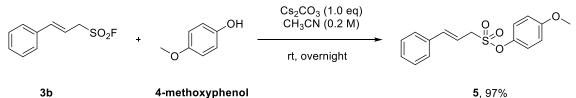
Diazonium tetrafluoroborate (1, 1 mmol), $Pd(OAc)_2$ (3 mol %, 6.7 mg) PPh₃ (3 mol%, 7.9 mg) and MeOH (0.1 M, 10.0 mL) were added to an oven-dried reaction tube (30 mL). Then the allylsulfonyl fluoride (2, 1.1 eq.) was added at room temperature. The resulting mixture was stirred at room temperature. After completion of reaction was monitored by TLC analysis, the mixture was concentrated under reduced pressure. The crude was purified by flash column chromatography with petroleum ether/ethyl acetate (40:1 to 3:1, v/v) to give the corresponding pure product.

3.5 Procedure for synthesis of sulfonamide from morpholine.



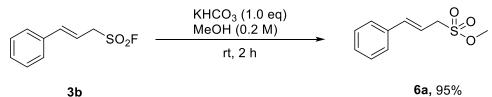
Morpholine (2.0 mmol, 2.0 eq., 174.2 mg) and triethylamine (2.0 mmol, 2.0 eq., 202.4 mg) were added to a stirred solution of (*E*)-3-phenylprop-2-ene-1-sulfonyl fluoride (**3b**, 1.0 mmol, 200.2 mg) dissolved in acetonitrile (2 mL) and the resulting mixture reacted at 80 °C for 4 h. The reaction was concentrated to dryness and the residue was further purified by column chromatography on silica gel by gradient elution with petroleum ether/ethyl acetate (2:1, v/v) as eluent to obtain pure sulfonamide **4** as white solid (265 mg, 99% yield).





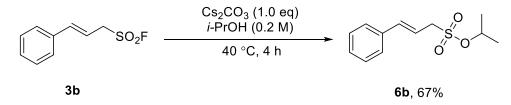
(*E*)-3-phenylprop-2-ene-1-sulfonyl fluoride (**3b**, 1.0 mmol, 200.2 mg), 4-methoxyphenol (1.1 mmol, 1.1 eq., 136.5 mg), cesium carbonate (1.0 mmol, 1.0 eq., 325.8 mg) were added in a solution of acetonitrile (2 mL) and reacted at room temperature for 12 h. The reaction mixture was extracted with ethyl acetate (3×20 mL) and the combined organic layers was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude product was further purified by column chromatography on silica gel by gradient elution with petroleum ether/ethyl acetate (10:1, v/v) as eluent to obtain pure sulfonate **5** as white solid (296 mg, 97% yield).

3.7 Procedure for synthesis of sulfonate from methanol.



(*E*)-3-phenylprop-2-ene-1-sulfonyl fluoride (**3b**, 1.0 mmol, 200.2 mg), KHCO₃ (1.0 mmol, 1.0 eq., 100.1 mg) were added in a solution of methanol (2 mL) and reacted at 25 °C for 2 h. The reaction mixture was extracted with ethyl acetate (3×20 mL) and the combined organic layers was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude product was further purified by column chromatography on silica gel by gradient elution with petroleum ether/ethyl acetate (10:1, v/v) as eluent to obtain pure sulfonate **6a** as white solid (202 mg, 95% yield).

3.8 Procedure for synthesis of sulfonate from isopropanol.



(*E*)-3-phenylprop-2-ene-1-sulfonyl fluoride (**3b**, 1.0 mmol, 200.2 mg), Cs_2CO_3 (1.0 mmol, 1.0 eq., 325.8 mg) were added in a solution of isopropanol (2 mL) and reacted at 40 °C for 4 h. The

reaction mixture was extracted with ethyl acetate $(3 \times 20 \text{ mL})$ and the combined organic layers was dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure. The crude product was further purified by column chromatography on silica gel by gradient elution with petroleum ether/ethyl acetate (10:1, v/v) as eluent to obtain pure sulfonate **6b** as white solid (161 mg, 67% yield).

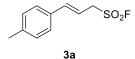
4. Characterization.

Prop-2-ene-1-sulfonyl fluoride (2a). Colorless oil. ¹H NMR (500 MHz, CDCl₃): δ 5.95-5.87 (m, 1H), 5.61 (d, J = 5.2 Hz, 1H), 5.58 (d, J = 12.1 Hz, 1H), 4.09-4.07 (m, 2H). ¹⁹F NMR (471 MHz, CDCl₃): δ 52.0-51.9 (m, -SO₂F). ¹³C NMR (126 MHz, CDCl₃): δ 126.7, 122.2, 55.0 (d, J = 18.2 Hz). ESI-HRMS (m/z) calculated for C₃H₅FO₂S [M+H]⁺ 125.0152, found 125.0154.

SO₂F

2b

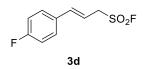
2-methylprop-2-ene-1-sulfonyl fluoride (2b). Colorless oil. ¹H NMR (500 MHz, CDCl₃): δ 5.33-5.32 (m, 1H), 5.25 (s, 1H), 4.04 (dd, $J_1 = 3.3$ Hz, $J_2 = 0.4$ Hz, 2H), 1.99 (s, 3H). ¹⁹F NMR (471 MHz, CDCl₃): δ 54.4 (s, -SO₂F). ¹³C NMR (126 MHz, CDCl₃): δ 131.1, 122.7, 58.7 (d, J =16.4 Hz), 22.1. ESI-HRMS (m/z) calculated for C₄H₇FO₂S [M+H]⁺139.0224, found 139.0224.



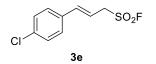
(*E*)-3-(p-tolyl)prop-2-ene-1-sulfonyl fluoride (**3a**). White solid, 155 mg, 72% yield. mp: 70-72°C. ¹H NMR (**500 MHz, CDCl₃**): δ 7.33 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 6.79 (d, *J* = 15.7Hz, 1H), 6.17-6.10 (m, 1H), 4.23-4.21 (m, 2H), 2.37 (s, 3H). ¹⁹F NMR (**471 MHz, CDCl₃**): δ 51.71-51.67 (m, -SO₂F). ¹³C NMR (**126 MHz, CDCl₃**): δ 141.0, 139.5, 132.3, 129.7, 127.0, 111.0, 55.0 (d, *J* = 18.2 Hz), 21.4. **ESI-HRMS** (m/z) calculated for C₁₀H₁₁FO₂S [M+H]⁺ 215.0759, found 215.0761.

(*E*)-3-phenylprop-2-ene-1-sulfonyl fluoride (**3b**). White solid, 138 mg, 69% yield. mp: 49-51°C. ¹H NMR (**500 MHz, CDCl₃**): δ 7.45-7.43 (m, 2H), 7.40-7.33 (m, 3H), 6.83 (d, *J* = 15.9 Hz, 1H), 6.23-6.17 (m, 1H), 4.25-4.23 (m, 2H). ¹⁹F NMR (471 MHz, CDCl₃): δ 52.0-51.9 (m, -SO₂F). ¹³C NMR (126 MHz, CDCl₃): δ 141.1, 135.1, 129.3, 129.0, 127.1, 112.2, 54.8 (d, J = 18.1 Hz). ESI-HRMS (m/z) calculated for C₉H₉FO₂S [M+H]⁺ 201.1160, found 201.1164.

(*E*)-3-(4-methoxyphenyl)prop-2-ene-1-sulfonyl fluoride (**3c**). Yellow solid, 121 mg, 53% yield. mp: 65-68°C. ¹H NMR (**500 MHz, CDCl₃**): δ 7.37 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.76 (d, *J* = 15.7 Hz, 1H), 6.07-6.01 (m, 1H), 4.23-4.20 (m, 1H), 3.83 (s, 3H). ¹⁹F NMR (**471 MHz, CDCl₃**): δ 51.5-51.4 (m, -SO₂F). ¹³C NMR (**126 MHz, CDCl₃**): δ 160.6, 140.6, 128.5, 127.8, 114.4, 109.6, 55.5, 55.0 (d, *J* = 18.2 Hz). **ESI-HRMS** (m/z) calculated for C₁₀H₁₁FO₃S [M+H]⁺ 231.0559, found 231.0562.

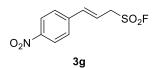


(*E*)-3-(4-fluorophenyl)prop-2-ene-1-sulfonyl fluoride (**3d**). Yellowish solid, 205 mg, 94% yield. mp: 45-47°C. ¹H NMR (**500 MHz, CDCl₃**): δ 7.42-7.39 (m, 2H), 7.08-7.04 (m, 2H), 6.79 (d, *J* = 15.9 Hz, 1H), 6.14-6.08 (m, 1H), 4.24-4.22 (m, 2H). ¹⁹F NMR (**471 MHz, CDCl₃**): δ 51.93-51.92, (m, -SO₂F), -111.5--115.6 (m, -ArF). ¹³C NMR (**126 MHz, CDCl₃**): δ 163.3 (d, *J* = 249.8 Hz), 139.9, 131.3 (d, *J* = 3.7 Hz), 128.8 (d, *J* = 9.1 Hz), 116.0 (d, *J* = 21.8 Hz), 111.9 (d, *J* = 2.7 Hz), 54.7 (d, *J* = 18.1 Hz). **ESI-HRMS** (m/z) calculated for C₉H₈F₂O₂S [M+H]⁺ 219.0965, found 219.0966.

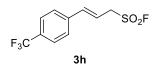


(*E*)-3-(4-chlorophenyl)prop-2-ene-1-sulfonyl fluoride (**3e**). White solid, 208 mg, 89% yield. mp: 74-76°C. ¹H NMR (**500 MHz, CDCl₃**): δ 7.36-7.32 (m, 4H), 6.78 (d, *J* = 15.9 Hz, 1H), 6.20-6.14 (m, 1H), 4.25-4.22 (m, 2H). ¹⁹F NMR (**471 MHz, CDCl₃**): δ 52.15-52.10 (m, -SO₂F). ¹³C NMR (**126 MHz, CDCl₃**): δ 139.8, 135.2, 133.5, 129.2, 128.3, 112.9, 54.7 (d, *J* = 18.1 Hz). **ESI-HRMS** (m/z) calculated for C₉H₈ClFO₂S $[M+H]^+$ 235.0656, found 235.0657.

(*E*)-3-(4-bromophenyl)prop-2-ene-1-sulfonyl fluoride (**3f**). White solid, 218 mg, 78% yield. mp: 87-89°C. ¹H NMR (**500 MHz, CDCl₃**): δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.76 (d *J* = 15.9 Hz, 1H), 6.21-6.15 (m, 1H), 4.24-4.22 (m, 2H). ¹⁹F NMR (**471 MHz, CDCl₃**): δ 52.2-52.1 (m, -SO₂F). ¹³C NMR (**126 MHz, CDCl₃**): δ 139.8, 133.9, 132.1, 128.5, 123.4, 113.0, 54.7 (d, *J* = 18.2 Hz). **ESI-HRMS** (m/z) calculated for C₉H₈BrFO₂S [M+H]⁺ 279.0052, found 279.0002.



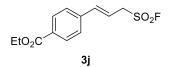
(*E*)-3-(4-nitrophenyl)prop-2-ene-1-sulfonyl fluoride (**3g**). Yellow solid 137 mg, 56% yield. mp: 119-120°C. ¹H NMR (**500 MHz, CDCl₃**): δ 8.23 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 15.7 Hz, 1H), 6.41-6.35 (m, 1H), 4.32-4.29 (m, 2H). ¹⁹F NMR (**471 MHz, CDCl₃**): δ 53.02-52.97 (m, -SO₂F). ¹³C NMR (**126 MHz, CDCl₃**): δ 148.1, 141.1, 138.7, 127.8, 124.3, 117.1, 54.4 (d, *J* = 18.1 Hz). ESI-HRMS (m/z) calculated for C₉H₈FNO₄S [M+H]⁺ 246.0200, found 246.0226.



(*E*)-3-(4-(trifluoromethyl)phenyl)prop-2-ene-1-sulfonyl fluoride (**3h**). yellowish solid, 151 mg, 56% yield. mp: 52-54°C. ¹H NMR (**500** MHz, CDCl₃): δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 15.9 Hz, 1H), 6.33-6.27 (m, 1H), 4.28-4.26 (m, 2H). ¹⁹F NMR (**471** MHz, CDCl₃): δ 52.5 (s, -SO₂F), -62.8 (s, -CF₃). ¹³C NMR (**126** MHz, CDCl₃): δ 139.6, 138.4, 131.1, (q, *J* = 32.7 Hz), 127.3, 126.0 (q, *J* = 3.6 Hz), 124.0 (q, *J* = 272.0 Hz), 115.1, 54.6 (d, *J* = 18.2 Hz).

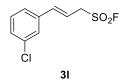
ESI-HRMS (m/z) calculated for $C_{10}H_8F_4O_2S$ [M+H]⁺ 269.0200, found 269.0211.

(*E*)-3-(4-cyanophenyl)prop-2-ene-1-sulfonyl fluoride, white solid (**3i**). 129 mg, 57% yield. mp: 99-101 °C. ¹H NMR (**500 MHz, CDCl₃**): δ 7.66 (d, *J* = 7.9 Hz, 2H), 7.52 (d, *J* = 7.9 Hz, 2H), 6.86 (d, *J* = 15.9 Hz, 1H), 6.36-6.30 (m, 1H), 4.29-4.27 (m, 2H). ¹⁹F NMR (**471 MHz, CDCl₃**): δ 52.9-52.8 (m, -SO₂F). ¹³C NMR (**126 MHz, CDCl₃**): δ 139.3, 139.1, 132.8, 127.6, 118.6, 116.3, 112.7, 54.4 (d, *J* = 19.1 Hz). **ESI-HRMS** (m/z) calculated for C₁₀H₈FNO₂S [M+H]⁺ 226.1860, found 226.1863.



Ethyl (*E*)-4-(3-(fluorosulfonyl)prop-1-en-1-yl)benzoate (**3j**). White solid, 159 mg, 58% yield. mp: 96-98 °C. ¹H NMR (**500 MHz, CDCl₃**): δ 8.03 (d, *J* =7.9 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* =15.9 Hz, 1H), 6.32-6.26 (m, 1H), 4.38 (q, *J* = 7.0 Hz, 2H), 4.28-4.26 (m, 2H), 1.40 (t, *J* =7.0 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃), δ 52.5-52.4 (m, -SO₂F). ¹³C NMR (**126 MHz, CDCl₃**): δ 166.1, 140.0, 139.1, 131.0, 130.1, 126.9, 114.8, 61.2, 54.6 (d, *J* = 19.1 Hz), 14.4. **ESI-HRMS** (m/z) calculated for C₁₂H₁₃FO₄S [M+H]⁺ 273.0545, found 273.0530.

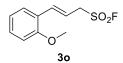
(*E*)-3-(m-tolyl)prop-2-ene-1-sulfonyl fluoride. White solid (**3k**), 133 mg, 62% yield. mp: 32-33°C. ¹**H NMR (500 MHz, CDCl₃):** 7.28-7.22 (m, 3H), 7.16 (d, *J* =7.2 Hz, 1H), 6.80 (d, *J* = 15.7 Hz, 1H), 6.21-6.15 (m, 1H), 4.24-4.22 (m, 2H), 2.37 (s, 3H). ¹⁹**F NMR (471 MHz, CDCl₃)**: δ 51.8-51.7 (m, -SO₂F). ¹³**C NMR (126 MHz, CDCl₃)**: δ 141.2, 138.6, 135.0, 130.1, 128.8, 127.7, 124.3, 111.9, 54.9 (d, *J* = 18.2 Hz), 21.4. **ESI-HRMS** (m/z) calculated for C₁₀H₁₁FO₂S [M+H]⁺ 215.0055, found 214.9909.



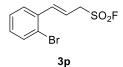
(*E*)-3-(3-chlorophenyl)prop-2-ene-1-sulfonyl fluoride (**3**). Yellowish solid, 210 mg, 89% yield. mp: 44-46 °C. ¹H NMR (**500 MHz, CDCl₃**): δ 7.42 (s, 1H), 7.32-7.29 (m, 3H), 6.77 (d, *J* = 15.8 Hz, 1H), 6.24-6.18 (m, 1H), 4.25-4.23 (m, 2H). ¹⁹F NMR (**471 MHz, CDCl₃**): δ 52.32-52.28 (m, -SO₂F). ¹³C NMR (**126 MHz, CDCl₃**): δ 139.6, 136.8, 135.0, 130.2, 129.3, 127.0, 125.3, 113.9, 54.6 (d, *J* = 18.1 Hz). **ESI-HRMS** (m/z) calculated for C₉H₈ClFO₂S [M+H]⁺ 235.1740, found 235.1741.

(*E*)-3-(3-bromophenyl)prop-2-ene-1-sulfonyl fluoride (**3m**). Yellow solid, 236 mg, 85% yield. mp: 45-47 °C. ¹H NMR (**500 MHz, CDCl₃**): δ 7.57 (s, 1H), 7.46 (d, *J* =7.9 Hz, 1H), δ = 7.34 (d, *J* =7.6 Hz, 1H), 7.24 (t, *J* =7.8 Hz, 1H), 6.76 (d, *J* =15.7 Hz, 1H), 6.23-6.17 (m, 1H), 4.25-4.23 (m, 2H). ¹⁹F NMR (**471 MHz, CDCl₃**): δ 52.35-52.30 (m, -SO₂F). ¹³C NMR (**126 MHz, CDCl₃**): δ 139.5, 137.1, 132.2, 130.5, 129.9, 125.7, 123.1, 113.9, 54.6 (d, *J* = 18.2 Hz). **ESI-HRMS** (m/z) calculated for C₉H₈BrFO₂S [M+H]⁺ 278.9989, found 279.0971.

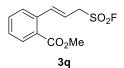
(*E*)-3-(o-tolyl)prop-2-ene-1-sulfonyl fluoride. White soild (**3n**), 141 mg, 66% yield. mp: 36-38°C. ¹H NMR (**500 MHz, CDCl₃**): δ 7.46 (d, *J* =7.4 Hz, 1H), 7.25-7.18 (m, 3H), 7.08 (d, *J* =15.7 Hz, 1H), 6.11-6.05 (m, 1H), 4.28-4.25 (m, 2H), 2.38 (s, 3H). ¹⁹F NMR (**471 MHz, CDCl₃**): δ 51.71-51.67 (m, -SO₂F). ¹³C NMR (**126 MHz, CDCl₃**): δ 139.2, 136.2, 134.3, 130.7, 129.2, 126.5, 126.2, 113.6, 55.0 (d, *J* = 18.2 Hz), 19.8. **ESI-HRMS** (m/z) calculated for C₁₀H₁₁FO₂S [M+H]⁺ 215.0740, found 215.0740.



(*E*)-3-(2-methoxyphenyl)prop-2-ene-1-sulfonyl fluoride (**30**). Colorless oil, 172 mg, 75% yield. ¹H NMR (**500 MHz, CDCl₃**): δ 7.44 (d, *J* =7.7 Hz, 1H), 7.31 (t, *J* =7.7 Hz, 1H), 7.13 (d, *J* =15.8 Hz, 1H), 6.96 (t, *J* =7.5 Hz, 1H), 6.91 (d, *J* =8.4 Hz, 1H), 6.28-6.22 (m, 1H), 4.26-4.23 (m, 2H), 3.87 (s, 3H). ¹⁹F NMR (**471 MHz, CDCl₃**): δ 51.61-51.56 (m, -SO₂F). ¹³C NMR (**126 MHz,** CDCl₃): δ 157.3, 136.3, 130.4, 127.8, 124.0, 120.9, 112.6, 111.2, 55.6, 55.5 (d, *J* = 17.2 Hz). ESI-HRMS (m/z) calculated for C₁₀H₁₁FO₃S [M+H]⁺ 231.0540, found 231.0538.

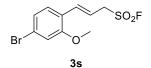


(*E*)-3-(2-bromophenyl)prop-2-ene-1-sulfonyl fluoride (**3p**). White solid, 180 mg, 65% yield. mp: 57-59 °C. ¹H NMR (**500 MHz, CDCl₃**): δ 7.59 (d, *J* =8.1 Hz, 1H), 7.55 (d, *J* =7.8Hz, 1H), 7.33 (t, *J* =7.6 Hz, 1H), 7.22-7.18 (m, 2H), 6.18-6.12 (m, 1H), 4.31-4.28 (m, 2H). ¹⁹F NMR (**471 MHz, CDCl₃**): δ 52.31-51.27 (m, -SO₂F). ¹³C NMR (**126 MHz, CDCl₃**): δ 139.7, 135.1, 133.3, 130.5, 127.9, 127.6, 124.1, 115.3, 54.7 (d, *J* = 18.2 Hz). **ESI-HRMS** (m/z) calculated for C₉H₈BrFO₂S [M+H]⁺ 278.9998, found 279.0918.

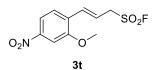


Methyl (E)-2-(3-(fluorosulfonyl)prop-1-en-1-yl)benzoate (**3q**). White solid, 108 mg, 42% yield. mp: 48-50 °C. ¹H NMR (**500 MHz, CDCl₃**): δ 7.97 (d, *J* =7.7 Hz, 1H), 7.69 (d, *J* =15.7 Hz, 1H), 7.57-7.52 (m, 2H), 7.41 (t, *J* =7.5 Hz, 1H), 6.09-6.03 (m, 1H), 4.30-4.28 (m, 2H), 3.91 (s, 3H). ¹⁹F NMR (**471 MHz, CDCl₃**): δ 52.10-52.06 (m, -SO₂F). ¹³C NMR (**126 MHz, CDCl₃**): δ 167.4, 140.4, 137.2, 132.7, 130.9, 128.8, 128.7, 128.0, 114.8, 54.8 (d, *J* = 18.2 Hz), 52.4. **ESI-HRMS** (m/z) calculated for C₁₁H₁₁FO₄S [M+H]⁺ 259.0500, found 259.0504.

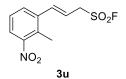
(*E*)-3-(2-methoxy-5-methylphenyl)prop-2-ene-1-sulfonyl fluoride (**3r**). White Solid, 176 mg, 72% yield. mp: 55-57 °C. ¹H NMR (**500** MHz, CDCl₃): δ 7.25 (d, *J* =8.4Hz, 1H), 7.12-7.09 (m, 2H), 6.80 (d, *J* =8.4 Hz, 1H), 6.26-6.20 (m, 1H), 4.25-4.23 (m, 2H), 3.84 (s, 3H), 2.31 (s, 3H). ¹⁹F NMR (**471** MHz, CDCl₃): δ 51.53-51.50 (m, -SO₂F). ¹³C NMR (**126** MHz, CDCl₃): δ 155.3, 136.4, 130.9, 130.1, 128.3, 123.7, 112.3, 111.2, 55.7, 55.5 (d, *J* = 18.2 Hz), 20.5. ESI-HRMS (m/z) calculated for C₁₁H₁₃FO₃S [M+H]⁺ 245.1350, found 245.1355.



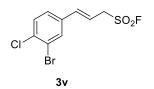
(*E*)-3-(4-bromo-2-methoxyphenyl)prop-2-ene-1-sulfonyl fluoride (**3s**). White solid, 192 mg, 62% yield. mp: 80-82 °C. ¹H NMR (**500 MHz, CDCl₃**): δ 7.26 (d, *J* =8.1 Hz, 1H), 7.07 (d, *J* =8.4 Hz, 1H), 7.01-6.96 (m, 2H), 6.24-6.18 (m, 1H), 4.21-4.20 (m, 2H), 3.84 (s, 3H). ¹⁹F NMR (**471 MHz, CDCl₃**): δ 51.9-51.8 (m, -SO₂F). ¹³C NMR (**126 MHz, CDCl₃**): δ 157.7, 135.4, 128.8, 124.0, 123.8, 123.1, 114.8, 113.3, 55.9, 55.4 (d, *J* = 17.2 Hz). **ESI-HRMS** (m/z) calculated for C₁₀H₁₀BrFO₃S [M+H]⁺ 309.0966, found 309.0970.



(*E*)-3-(2-methoxy-4-nitrophenyl)prop-2-ene-1-sulfonyl fluoride (**3t**). Yellow solid, 187 mg, 68% yield. mp: 98-99 °C. ¹H NMR (**500 MHz, CDCl₃**): δ 7.83 (d, *J* =8.4 Hz, 1H), 7.75 (s, 1H), 7.57 (d, *J* =8.4 Hz, 1H), 7.14 (d, *J* = 15.8 Hz, 1H), 6.45-6.39 (m, 1H), 4.31-4.28 (m, 2H), 3.97 (s, 3H). ¹⁹F NMR (**471 MHz, CDCl₃**): δ 52.7-52.6 (m, -SO₂F). ¹³C NMR (**126 MHz, CDCl₃**): δ 157.4, 148.9, 134.4, 130.4, 128.0, 117.2, 116.1, 106.2, 56.3, 55.0 (d, *J* = 18.2 Hz). **ESI-HRMS** (m/z) calculated for C₁₀H₁₀FNO₅S [M+H]⁺ 276.0400, found 276.0400.



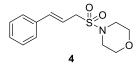
(*E*)-3-(2-methyl-3-nitrophenyl)prop-2-ene-1-sulfonyl fluoride (**3u**). White solid, 178 mg, 69% yield. mp: 69-71 °C. ¹H NMR (**500** MHz, CDCl₃): δ 7.75 (d, *J* =7.9 Hz, 1H), 7.63 (d, *J* =7.7 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 7.12 (d, *J* = 15.6 Hz, 1H), 6.15-6.09 (m, 1H), 4.31-4.29 (m, 2H), 2.46 (s, 3H). ¹⁹F NMR (**471** MHz, CDCl₃): δ 52.50-52.46 (m, -SO₂F). ¹³C NMR (**126** MHz, CDCl₃): δ 151.5, 138.0, 137.6, 130.7, 130.1, 126.9, 124.4, 117.5, 54.5 (d, *J* = 18.2 Hz), 15.4. ESI-HRMS (m/z) calculated for C₁₀H₁₀FNO₄S [M+H]⁺ 260.0424, found 260.0424.



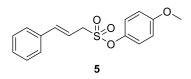
(*E*)-3-(3-bromo-4-chlorophenyl)prop-2-ene-1-sulfonyl fluoride (**3v**). White solid, 197 mg, 63% yield. mp: 61-63 °C. ¹H NMR (**500 MHz, CDCl₃**): δ 7.67 (s, 1H), 7.43 (d, *J* =8.3 Hz, 1H), 7.29 (d, *J* =8.4 Hz, 1H), δ = 6.73 (d, *J* = 15.7 Hz, 1H), 6.22-6.16 (m, 1H), 4.25-4.23 (m, 2H). ¹⁹F NMR (**471 MHz, CDCl₃**): δ 52.53-52.48 (m, -SO₂F). ¹³C NMR (**126 MHz, CDCl₃**): δ 138.5, 135.2, 135.1, 132.1, 130.7, 126.8, 123.1, 114.4, 54.5 (d, *J* = 19.1 Hz). **ESI-HRMS** (m/z) calculated for C₉H₇BrClFO₂S [M+H]⁺ 312.9075, found 312.9073.

3w

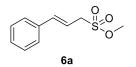
(*E*)-2-methyl-3-phenylprop-2-ene-1-sulfonyl fluoride (**3w**). yellow oil, 95 mg, 44% yield. ¹H NMR (**500 MHz, CDCl₃**): δ 7.41-7.38 (m, 2H), 7.33-7.30 (m, 3H), δ = 6.72 (s, 1H), 4.19 (d, *J* = 3.0 Hz, 2H), 2.12 (d, *J* = 1.1 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃): δ 54.4 (s, -SO₂F). ¹³C NMR (**126 MHz, CDCl₃**): δ 136.7, 136.0, 129.1, 128.5, 127.9, 123.5, 61.5 (d, *J* = 16.3 Hz), 18.2. ESI-HRMS (m/z) calculated for C₁₀H₁₁FO₂S [M+H]⁺ 215.0537, found 215.0536.



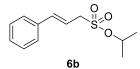
4-(cinnamylsulfonyl)morpholine (**4**). White solid, 265 mg, 99% yield. mp: 116-118 °C. ¹H NMR (**500 MHz, CDCl₃**): δ 7.41-7.39 (m, 2H), 7.37-7.34 (m, 2H), 7.32-7.29 (m, 1H), 6.69 (d, *J* = 15.9 Hz, 1H), 6.26-6.20 (m, 1H), 3.89 (d, *J* = 7.4 Hz, 2H), 3.72-3.71 (m, 4H), 3.35-3.34 (m, 4H). ¹³C NMR (**126 MHz, CDCl₃**): δ 138.5, 135.7, 128.9, 128.8, 126.8, 116.1, 66.8, 54.4, 46.5. **ESI-HRMS** (m/z) calculated for C₁₃H₁₇NO₃S [M+H]⁺ 269.1066, found 268.1061.



4-Methoxyphenyl (*E*)-3-phenylprop-2-ene-1-sulfonate (**5**). White solid, 296 mg, 97% yield. mp: 69-73 °C. ¹H NMR (**500 MHz, CDCl₃**): δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 7.33-7.30 (m, 1H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 6.76 (d, *J* = 15.7 Hz, 1H), 6.30-6.24 (m, 1H), .4.11 (d, *J* = 7.3 Hz, 2H), 3.80 (s, 3H). ¹³C NMR (**126 MHz, CDCl₃**): δ 158.5, 142.8, 139.6, 135.6, 128.91, 128.87, 126.9, 123.3, 115.0, 114.5, 55.8, 54.2. **ESI- HRMS** (m/z) calculated for C₁₆H₁₆O₄S [M+H]⁺ 305.0995, found 309.0904.



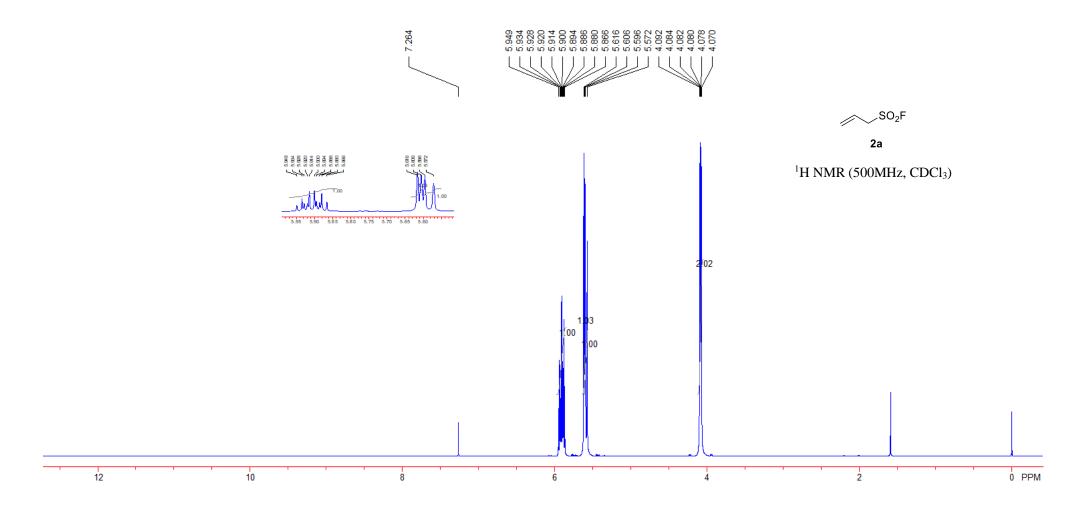
Methyl (*E*)-3-phenylprop-2-ene-1-sulfonate (**6a**). White solid, 202 mg, 95% yield. mp: 44-46 °C. ¹H NMR (**500 MHz, CDCl**₃): δ 7.42 (d, *J* = 7.3 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.31-7.29 (m, 1H), 6.73 (d, *J* = 15.9 Hz, 1H), 6.25-6.19 (m, 1H), .4.01 (d, *J* = 7.5 Hz, 2H), 3.93 (s, 3H). ¹³C NMR (**126 MHz, CDCl**₃) δ 139.1, 135.6, 128.84, 128.82, 126.8, 114.8, 56.4, 54.1. ESI-HRMS (m/z) calculated for C₁₀H₁₂O₃S [M+H]⁺ 213.1084, found 213.1081.

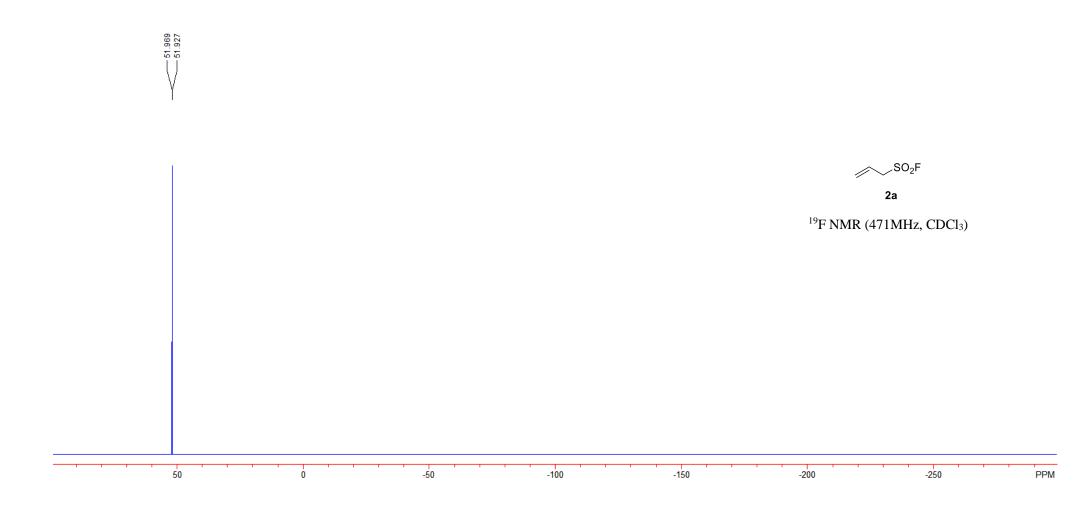


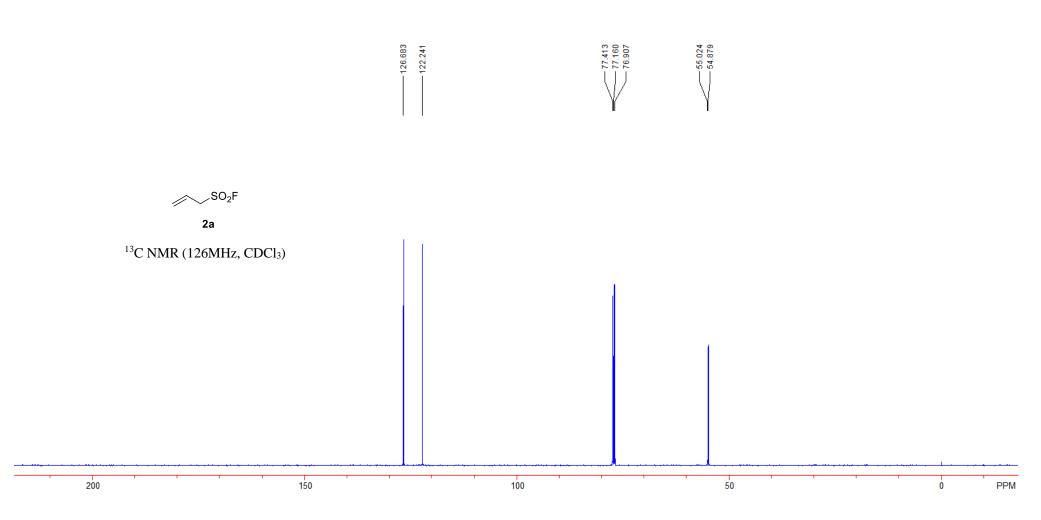
Isopropyl (E)-3-phenylprop-2-ene-1-sulfonate (6b). White solid, 160 mg, 67% yield. mp:

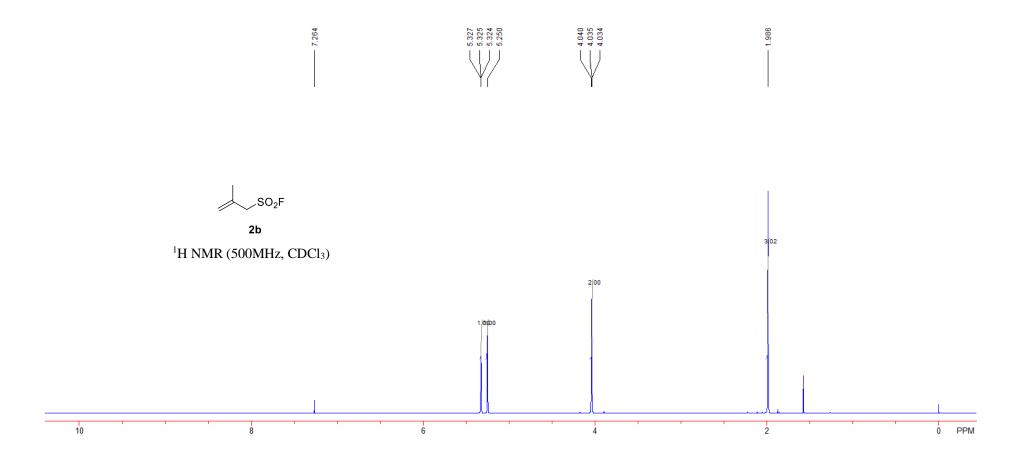
76-78 °C. ¹H NMR (500 MHz, CDCl₃): δ 7.41 (d, J = 7.7 Hz, 2H), 7.35 (t, J = 7.4 Hz, 2H), 7.31-7.29 (m, 1H), 6.71 (d, J = 15.9 Hz, 1H), 6.25-6.19 (m, 1H), 4.99-4.94 (m, 1H), 3.96 (d, J = 7.5 Hz, 2H), 1.41 (d, J = 6.1 Hz, 6H). ¹³C NMR (126 MHz, CDCl₃): δ 138.9, 135.8, 128.9, 128.8, 126.8, 115.4, 77.7, 55.6, 23.3. ESI-HRMS (m/z) calculated for C₁₂H₁₆O₃S [M+H]⁺ 241.1885, found 241.1861.

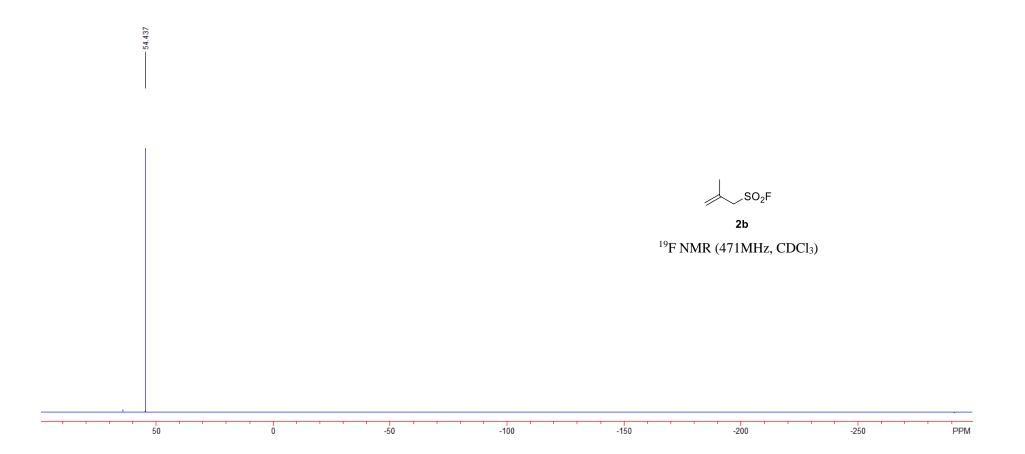
5. NMR spectra.

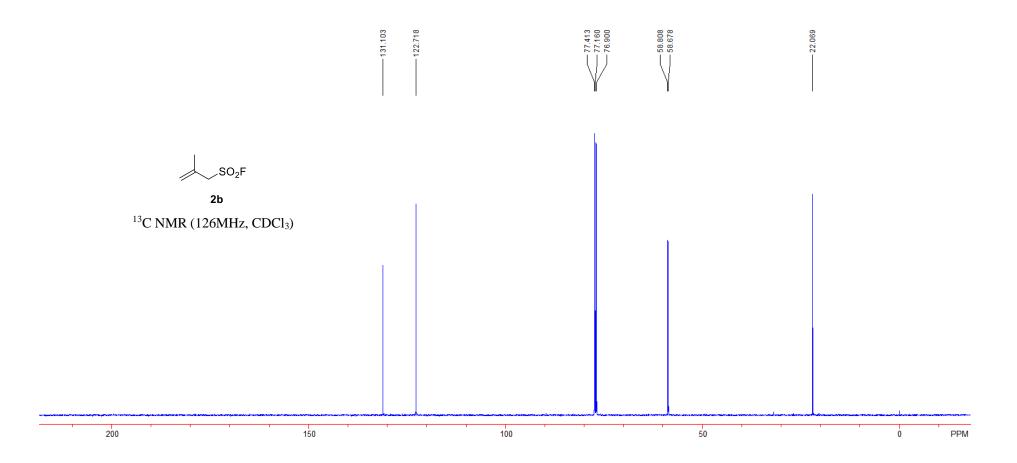


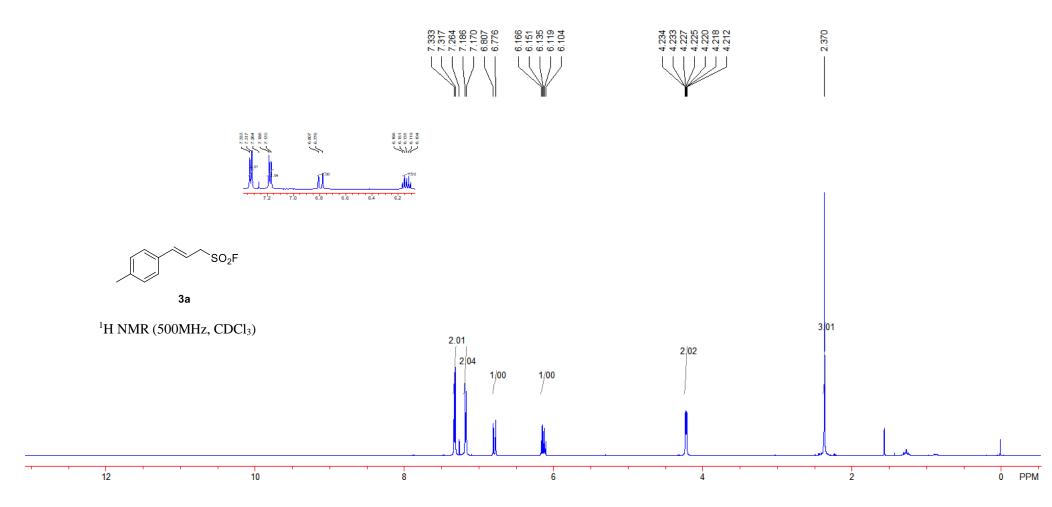


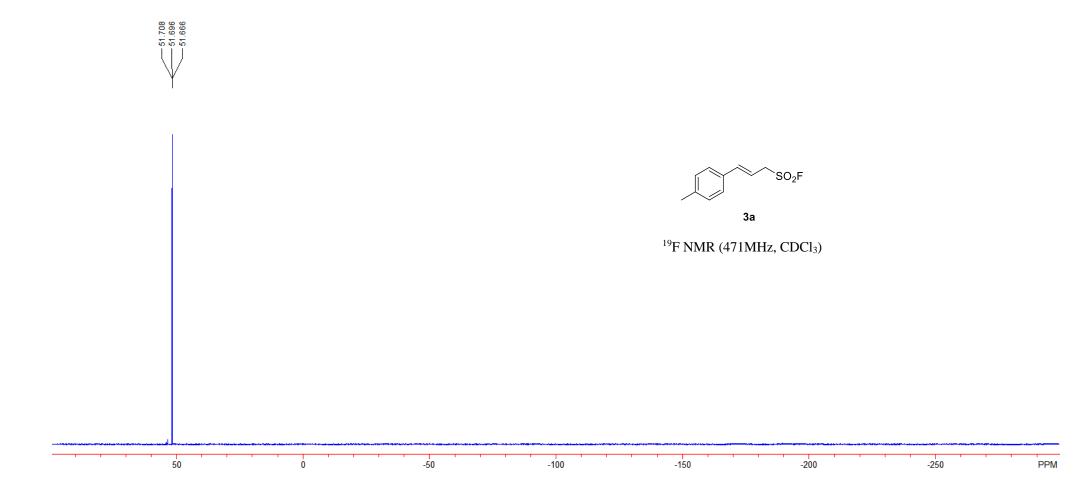


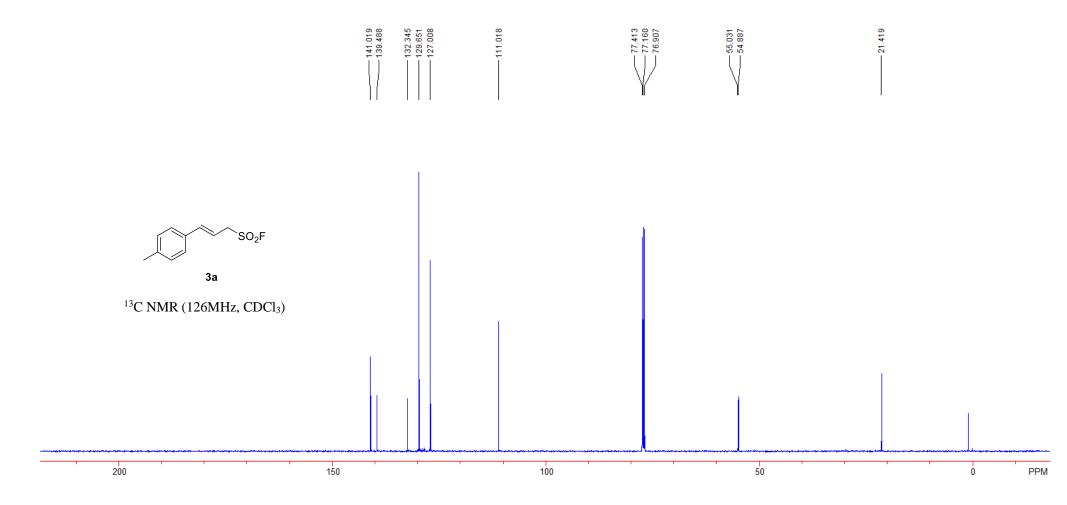


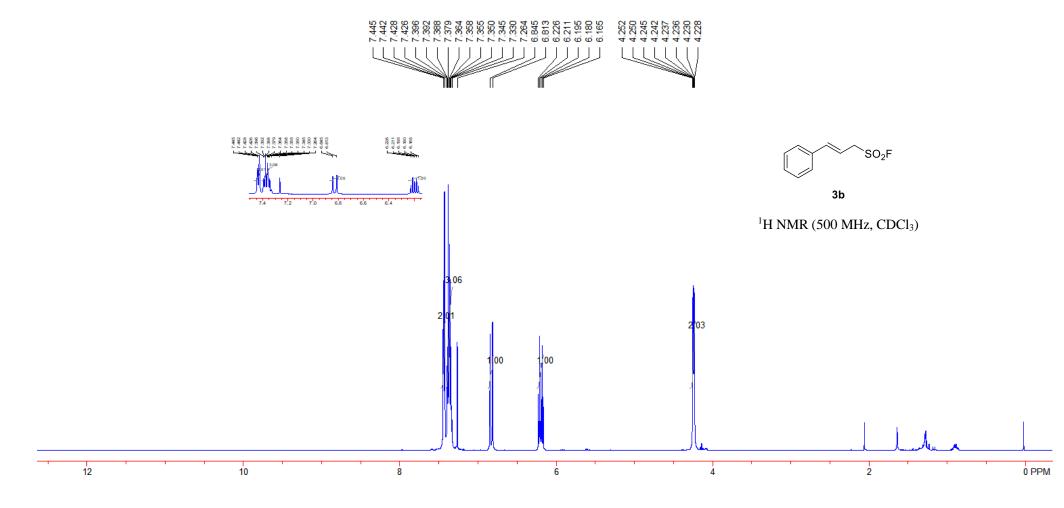


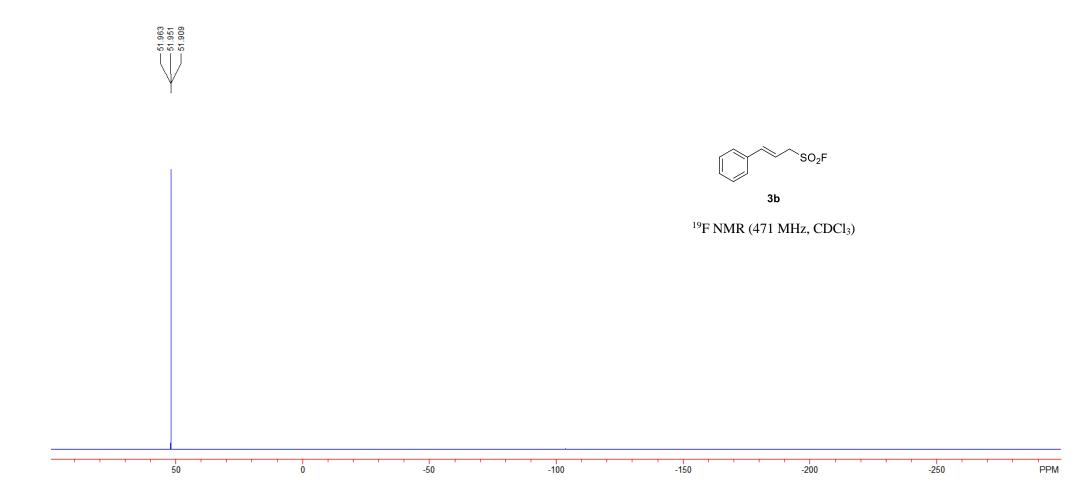


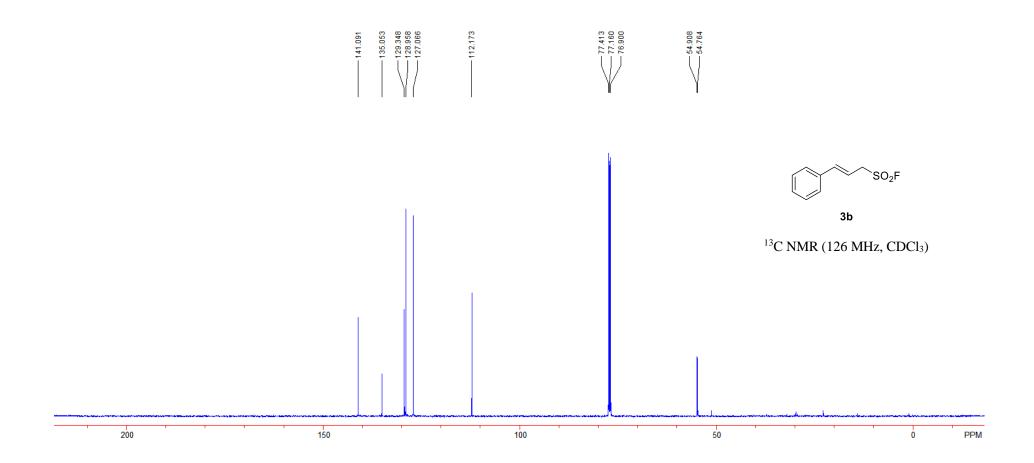


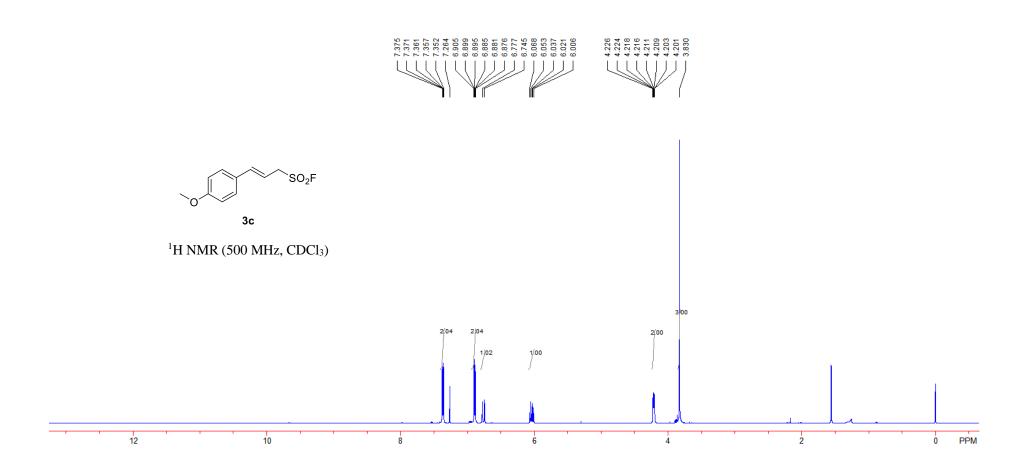


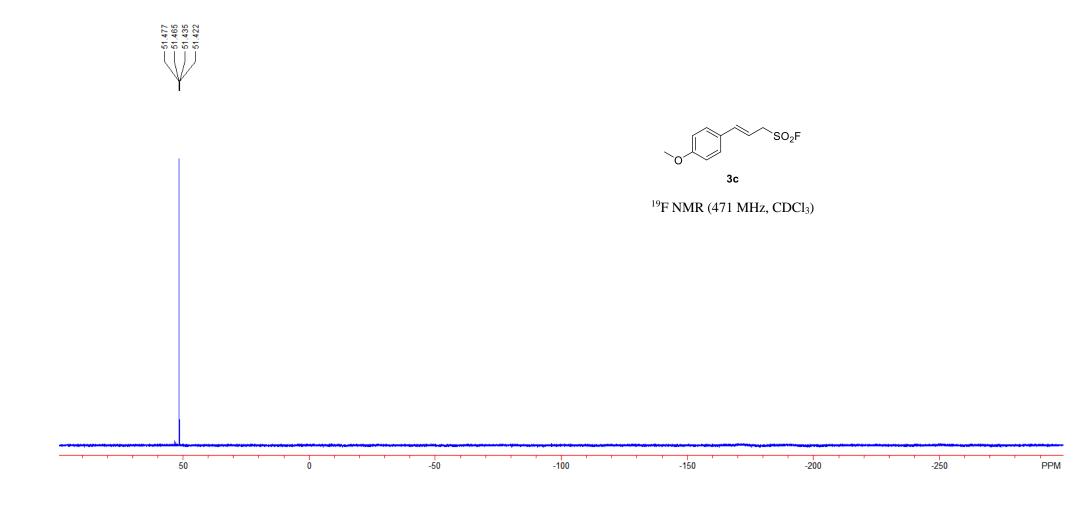


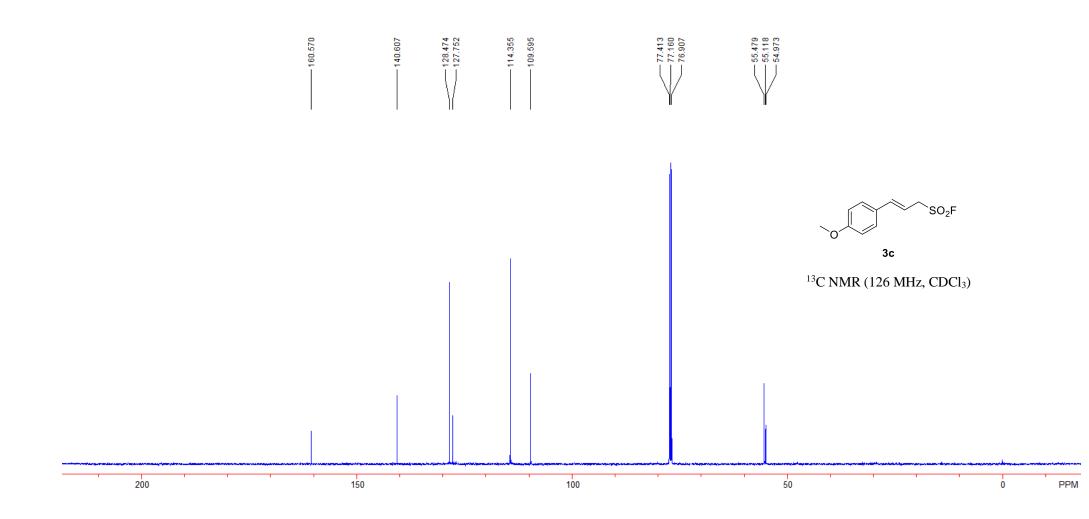


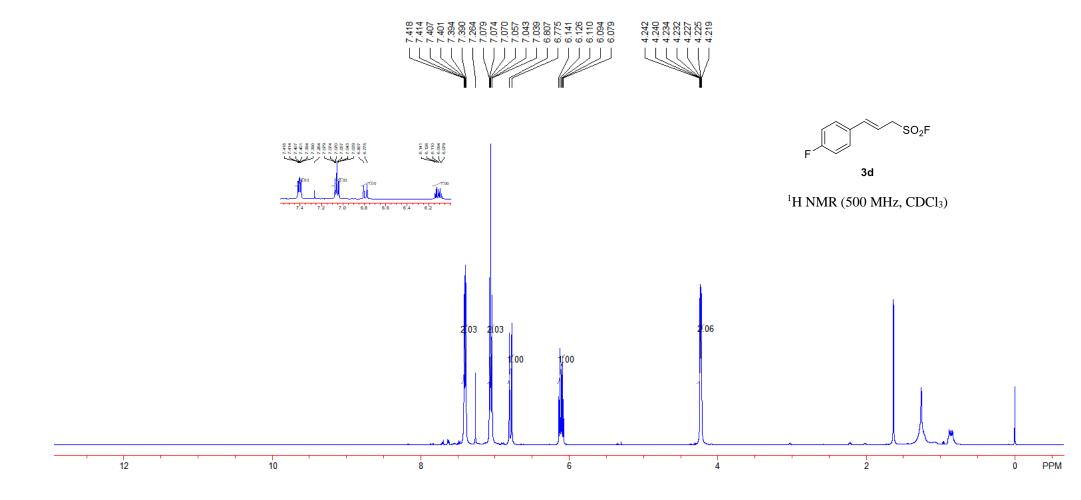


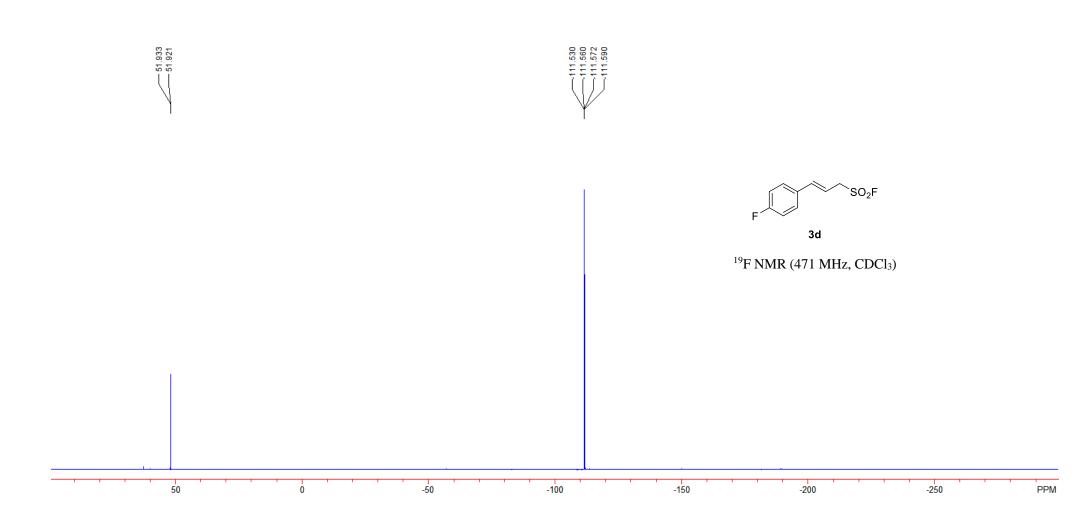


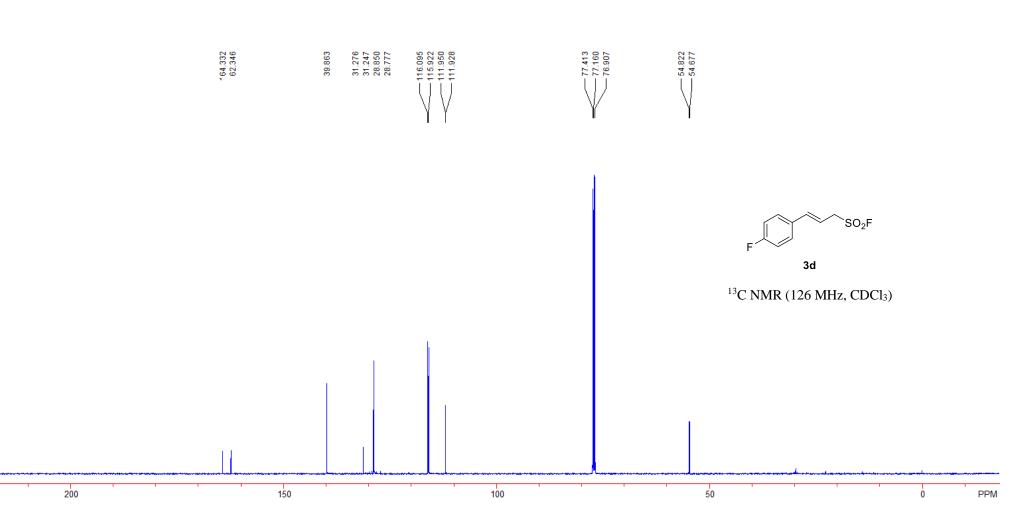


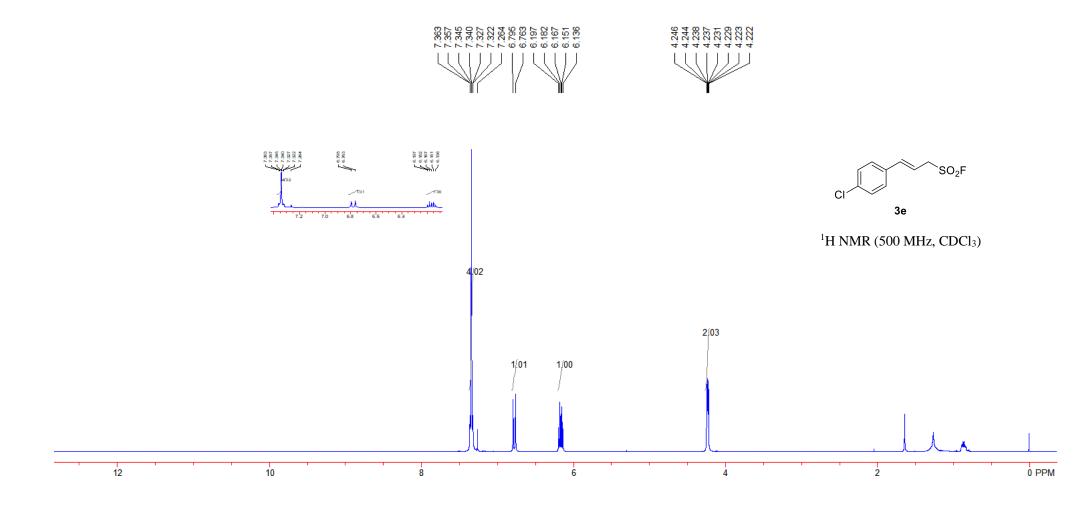


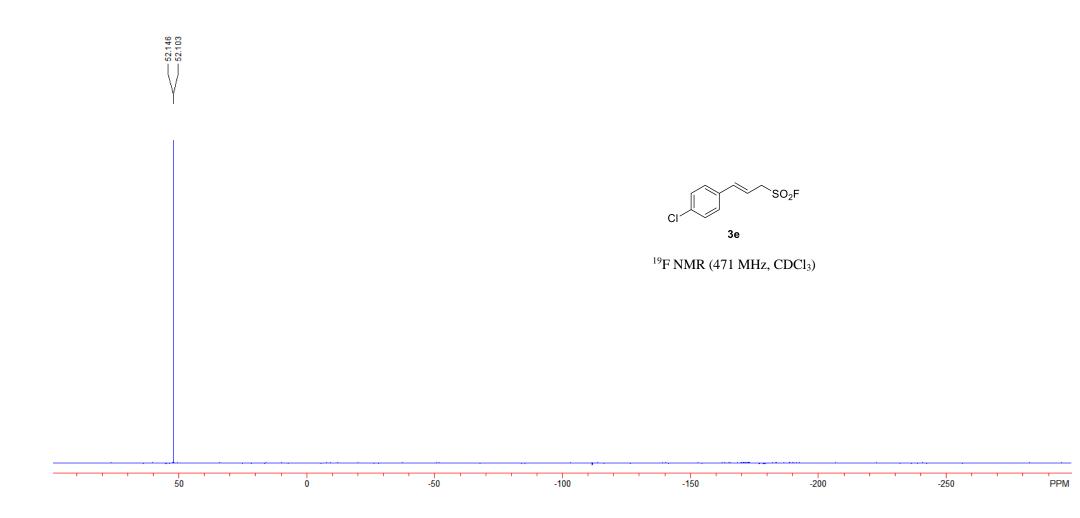


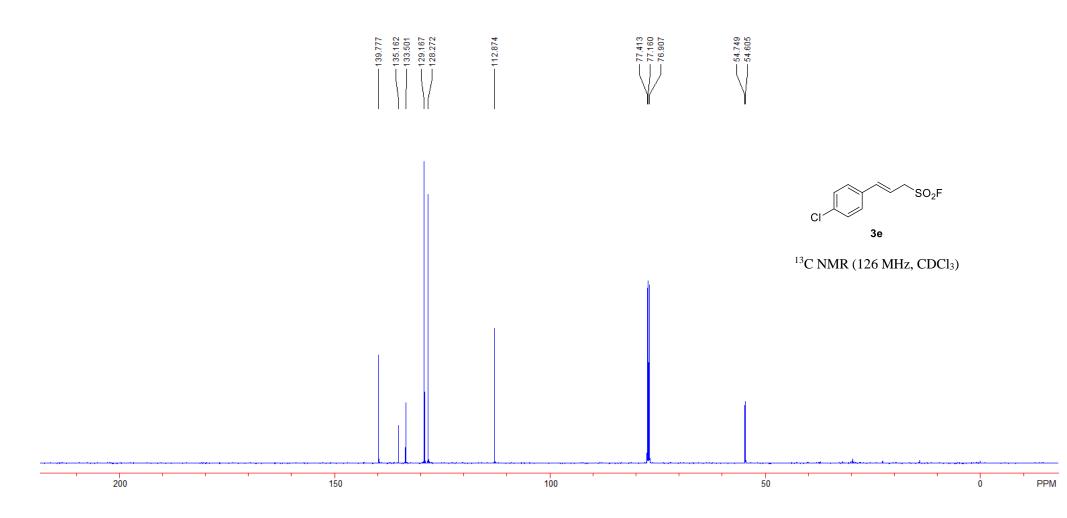


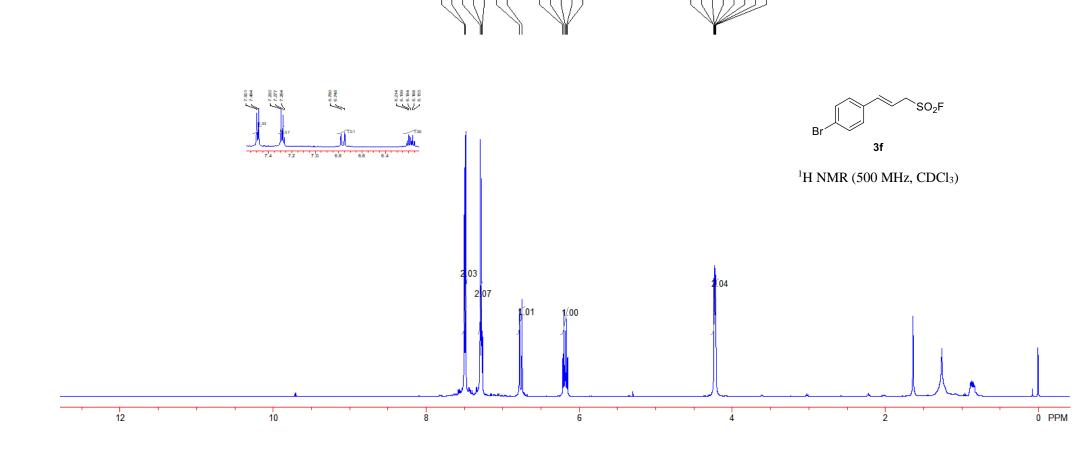








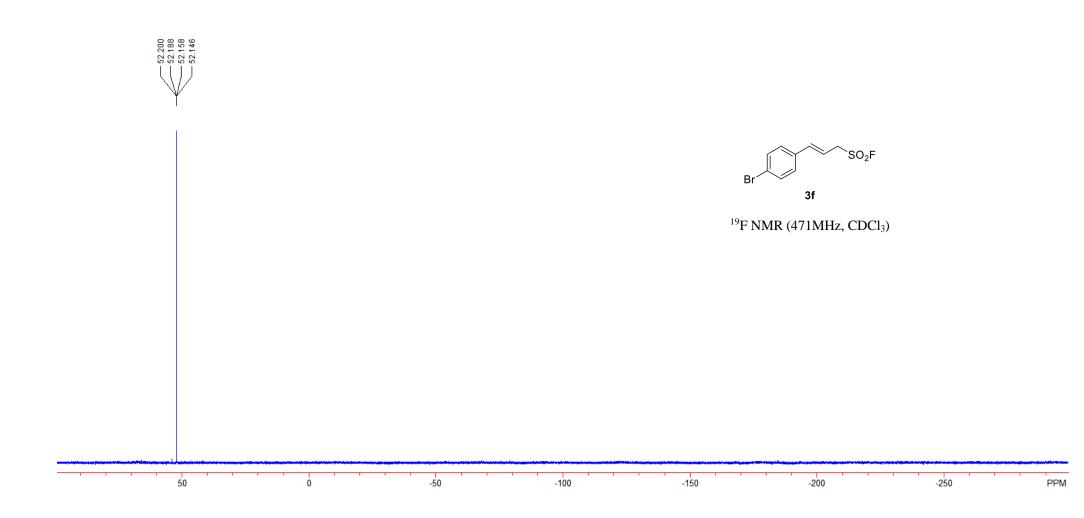


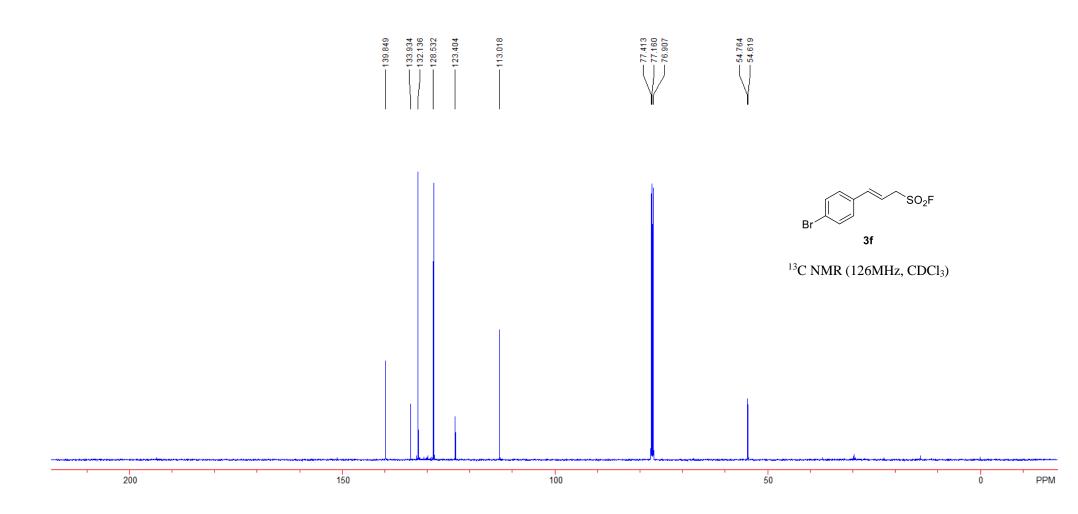


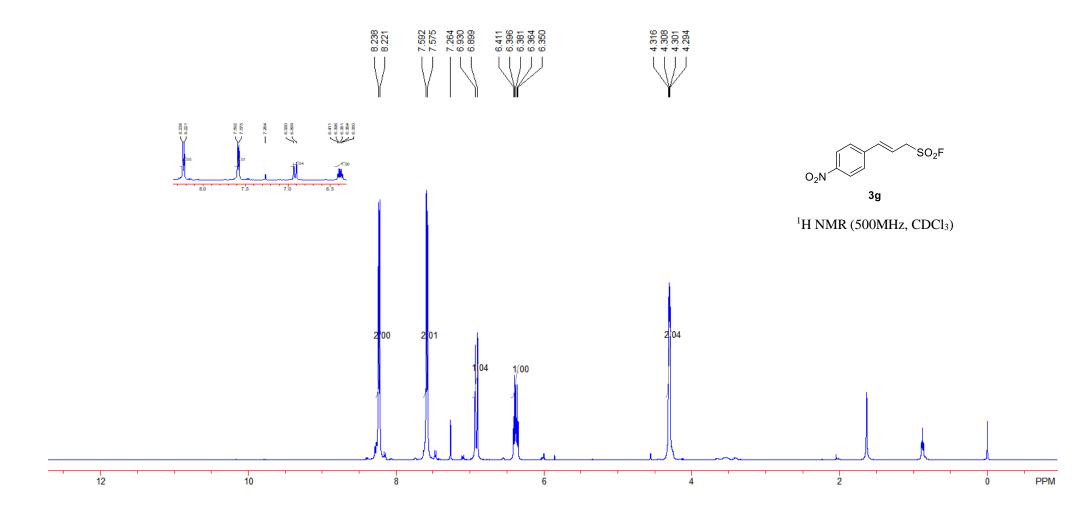
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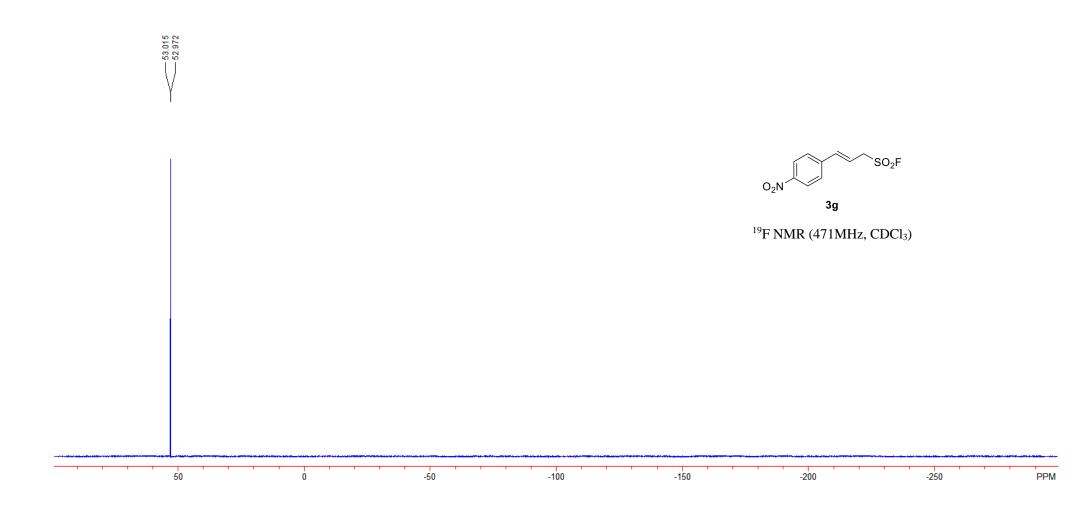
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S42

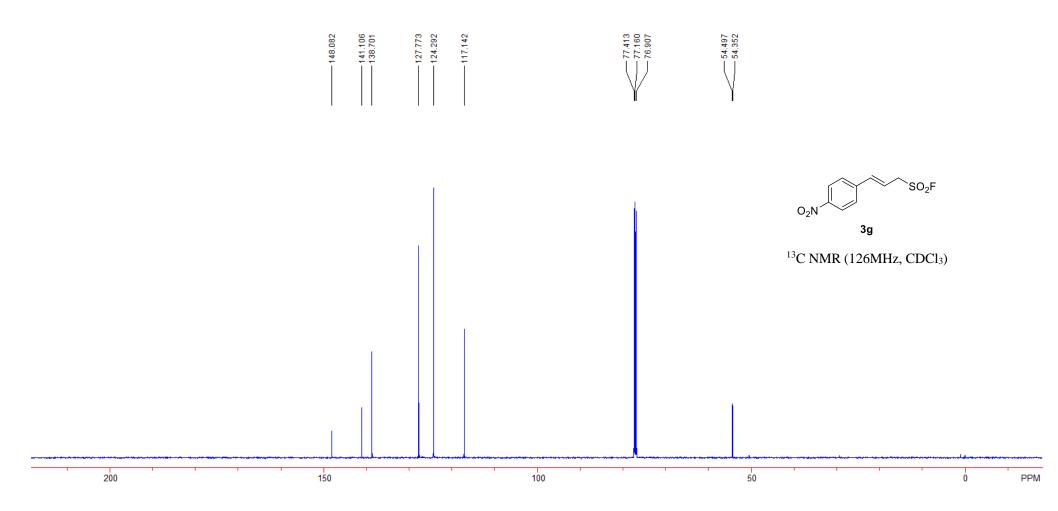


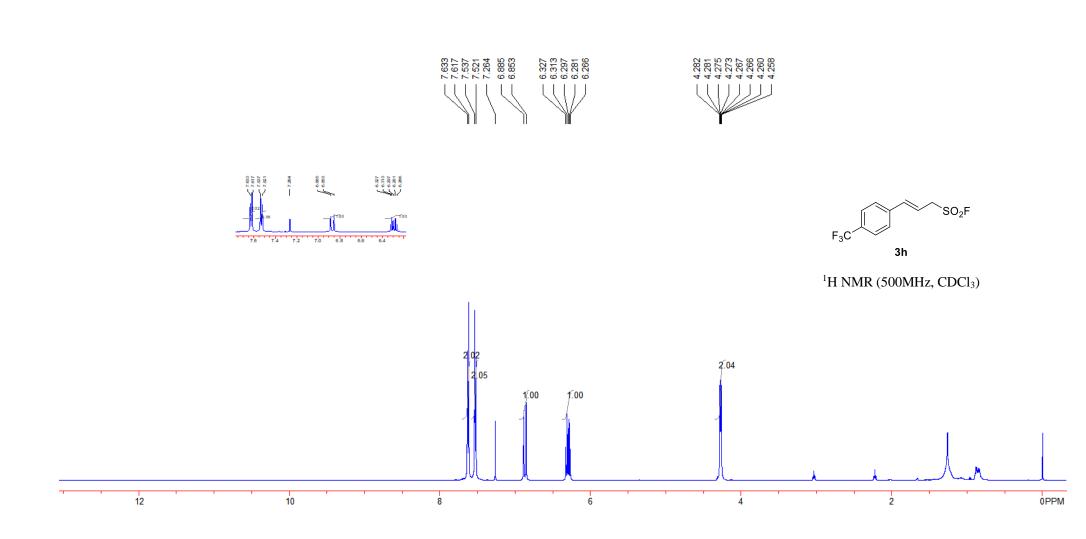


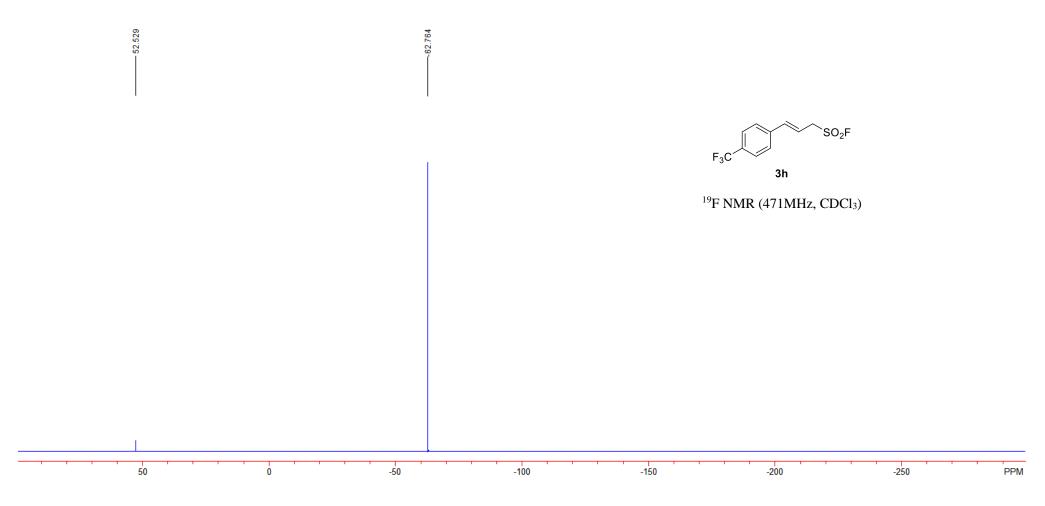


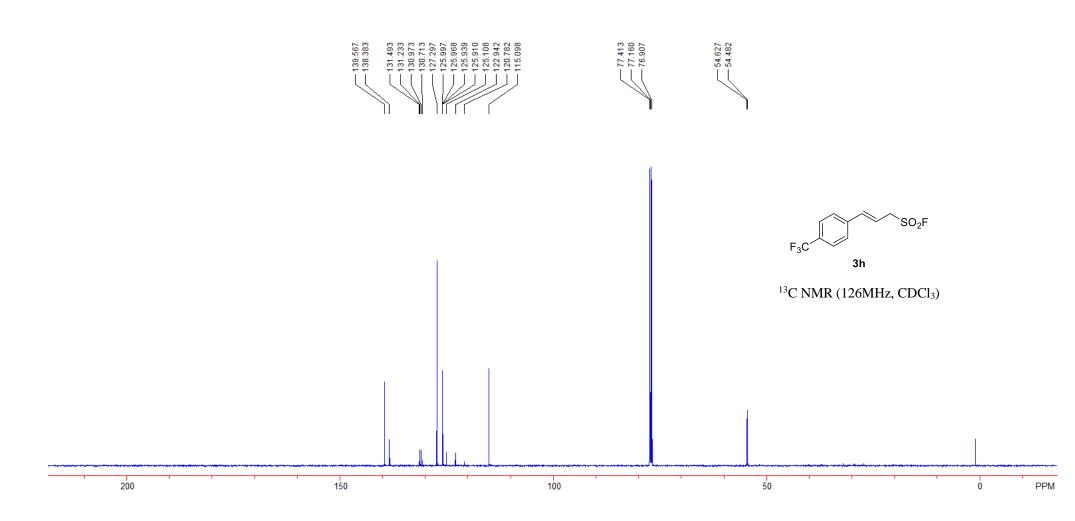


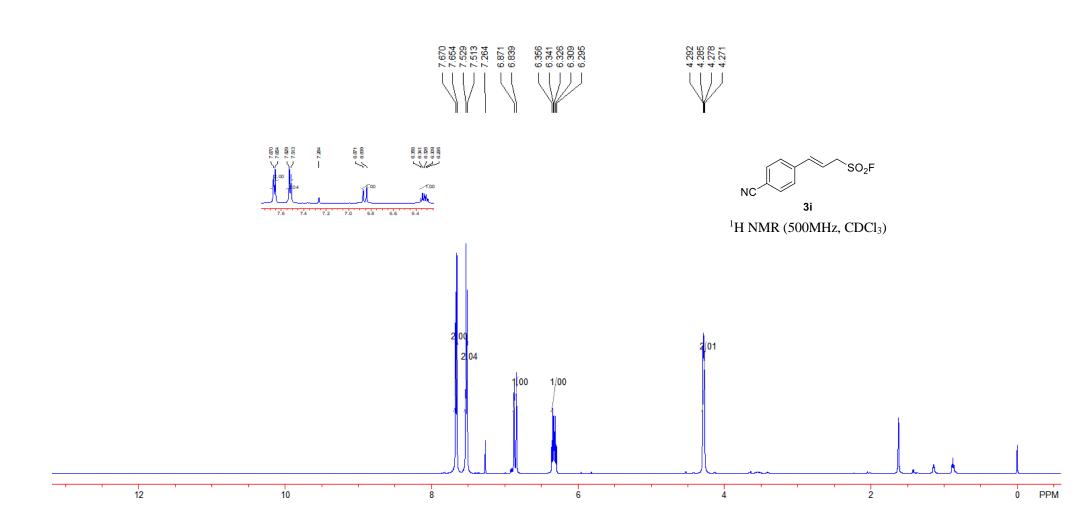


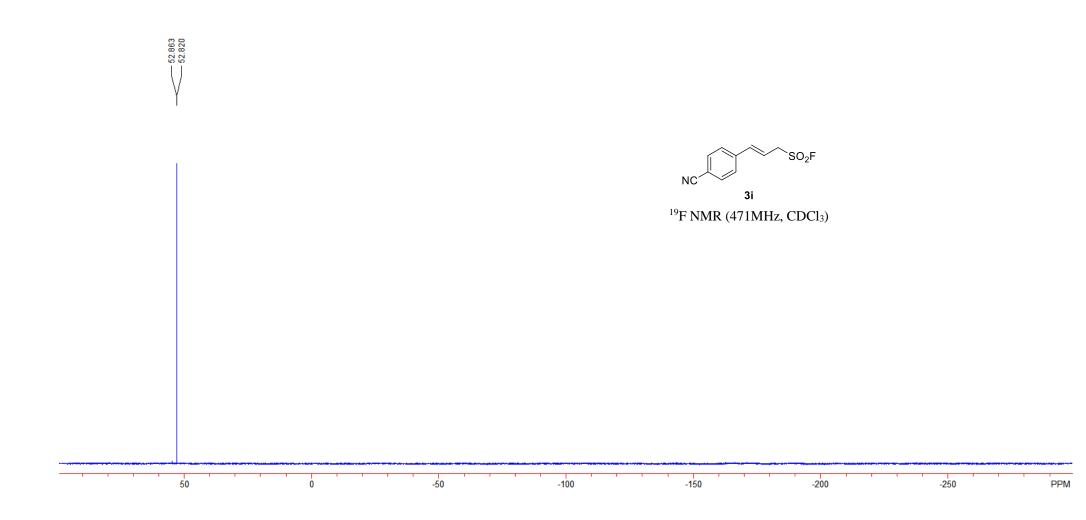


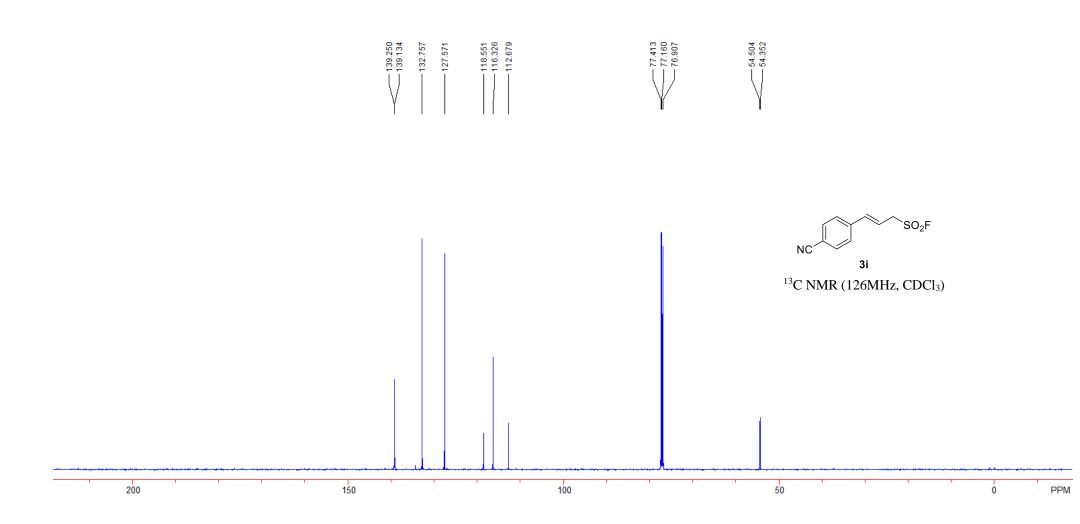


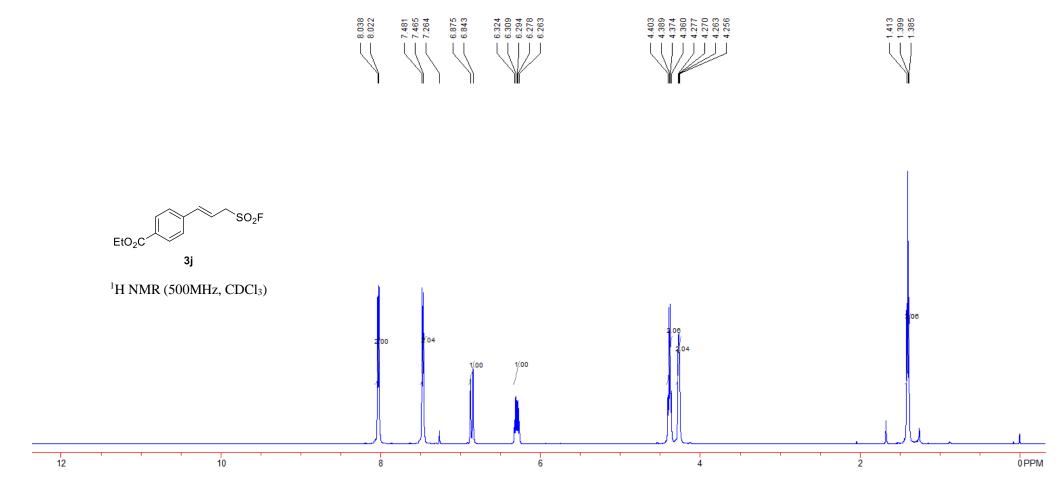


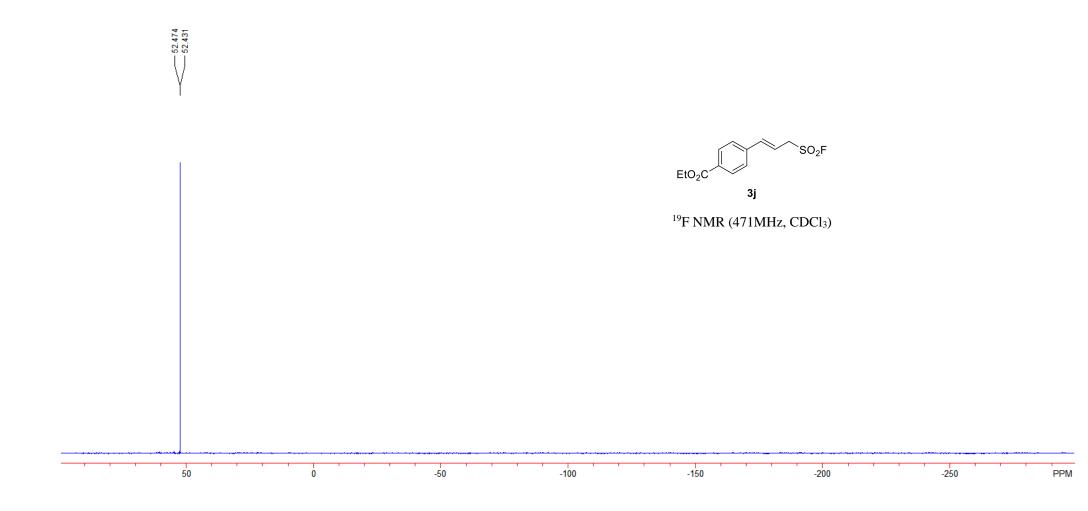


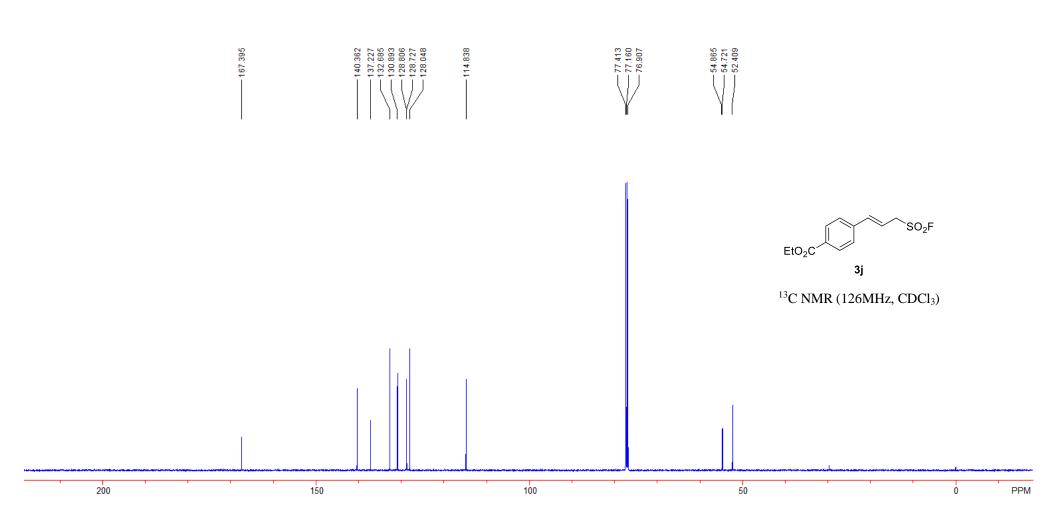


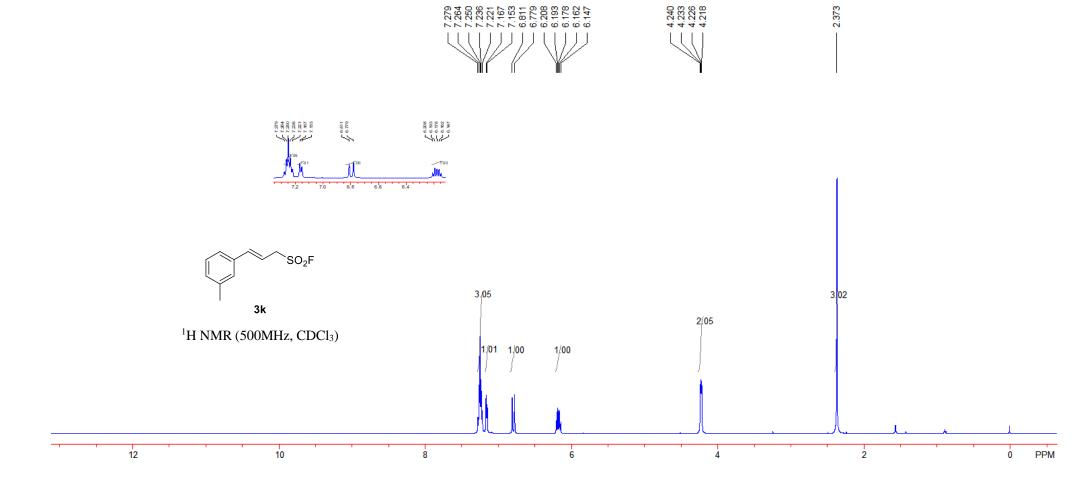


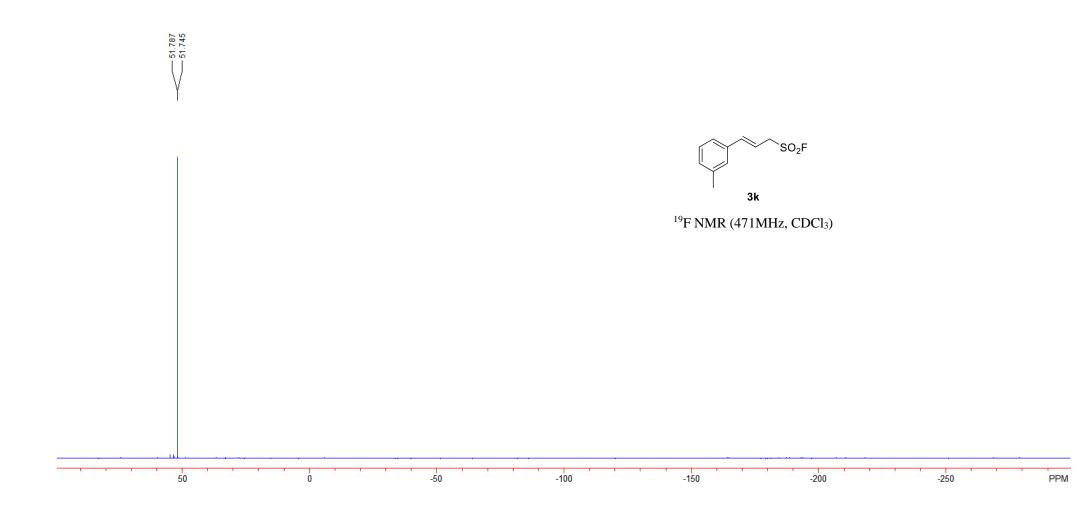


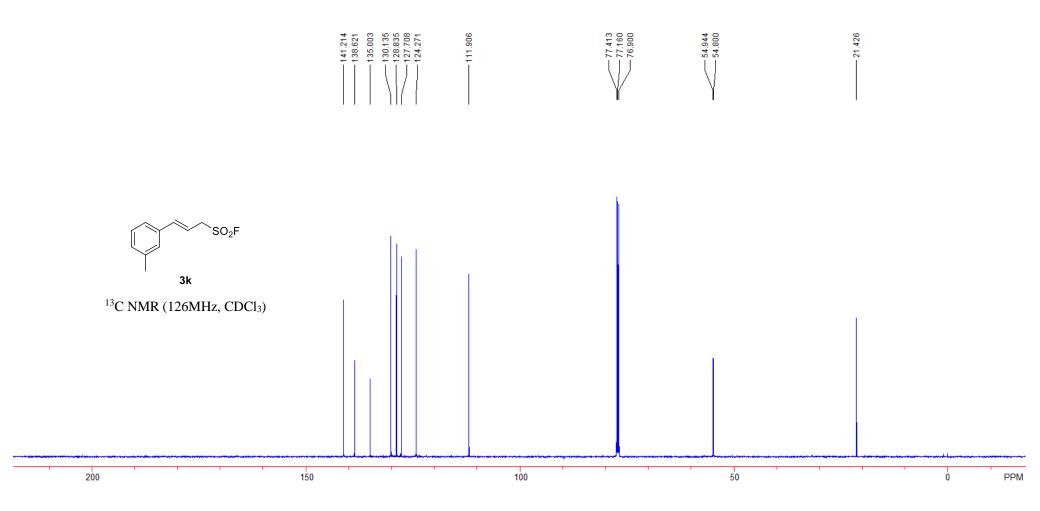


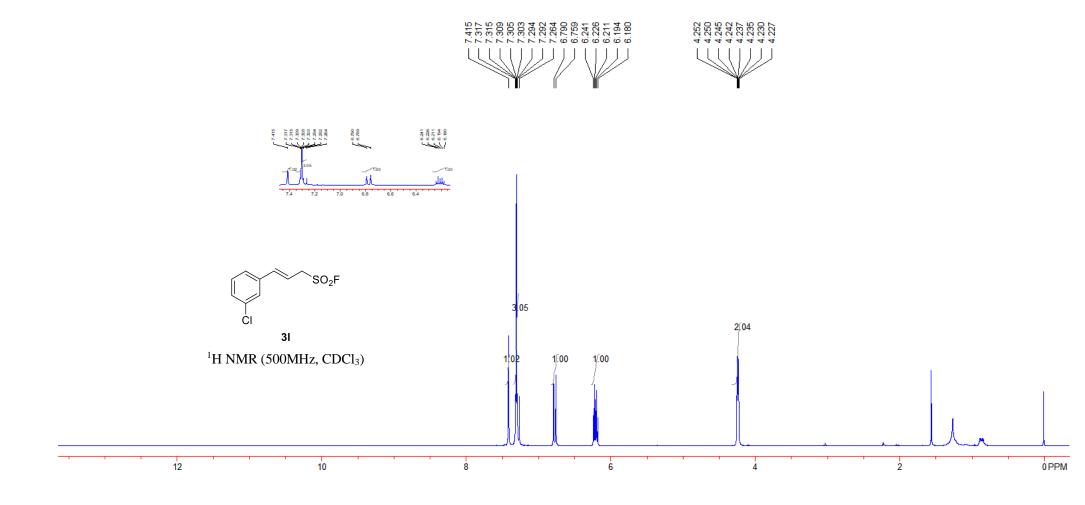


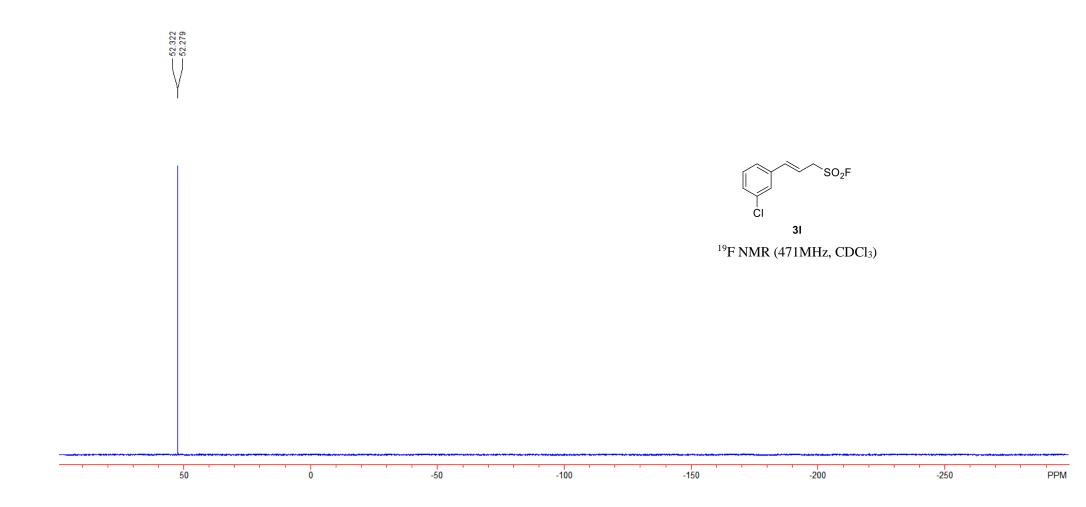


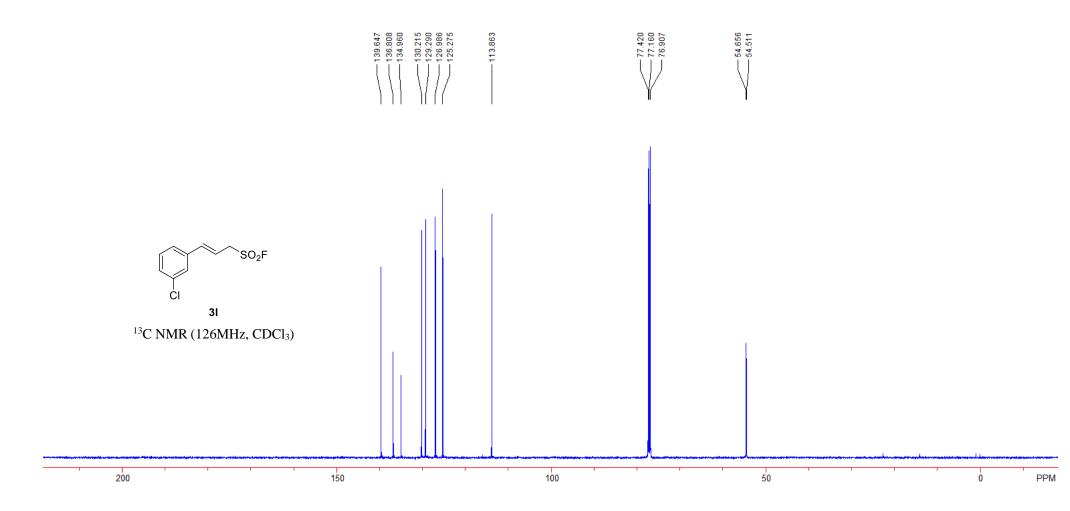


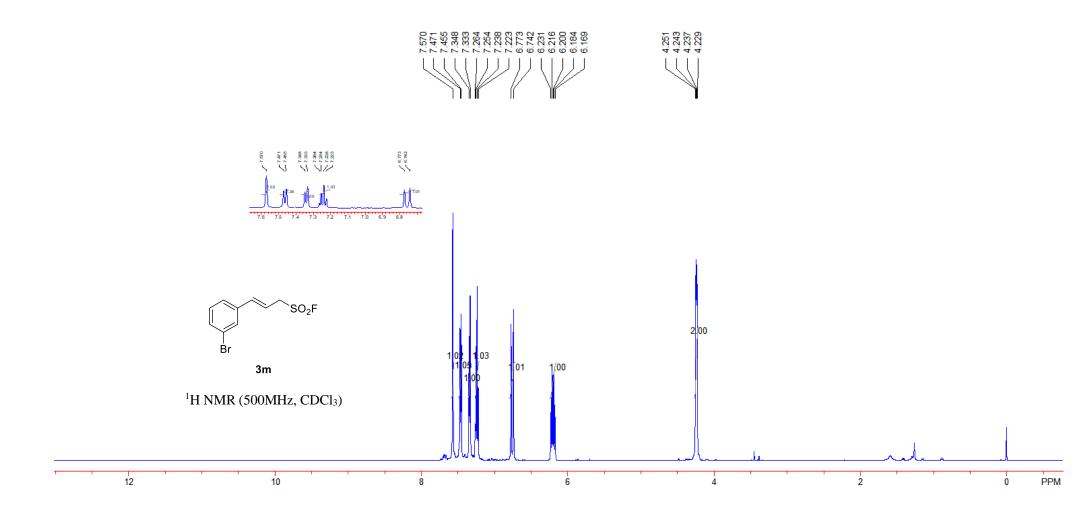


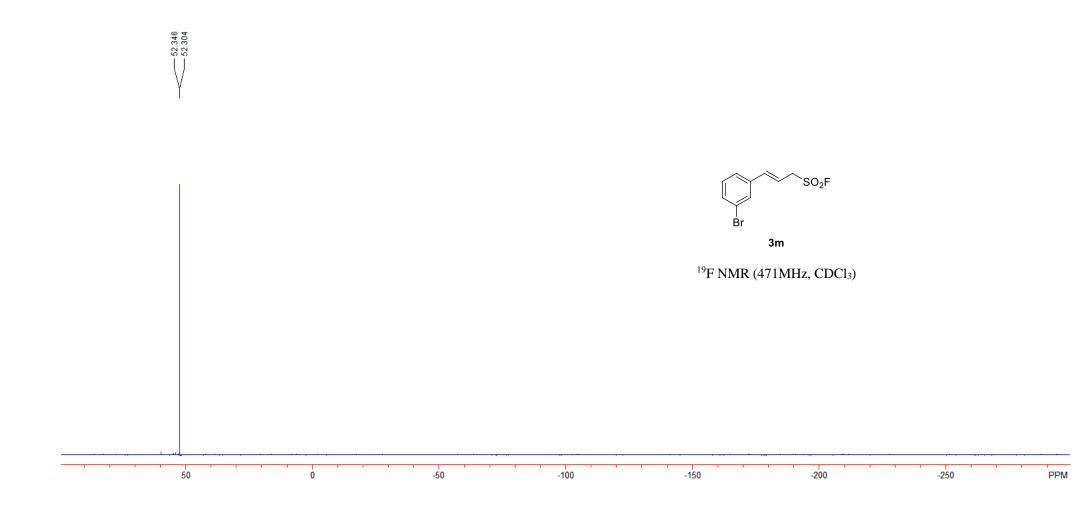


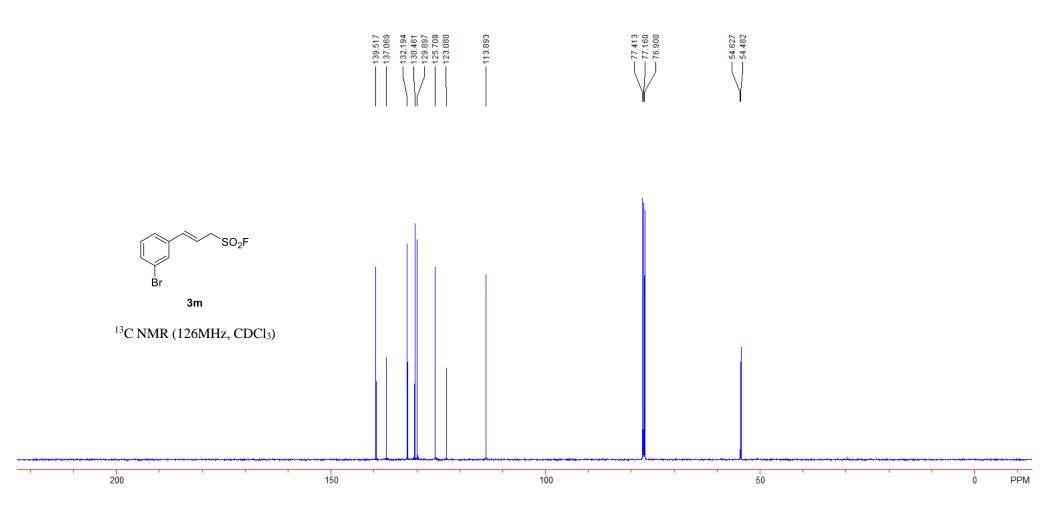


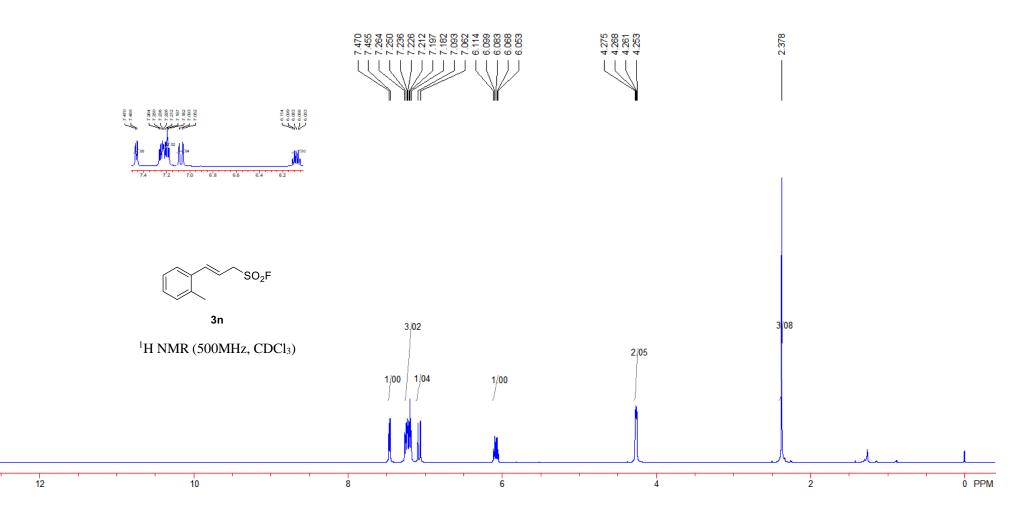


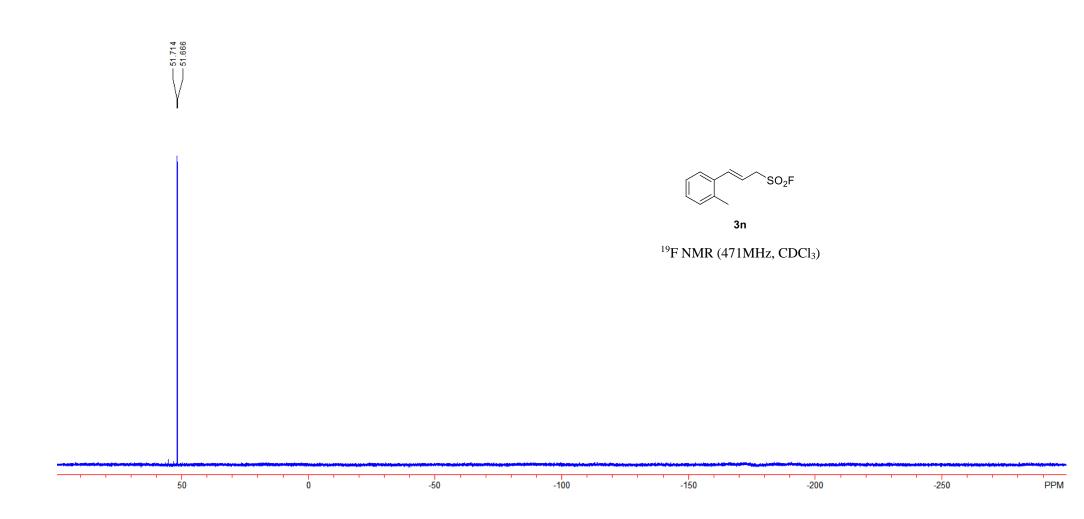


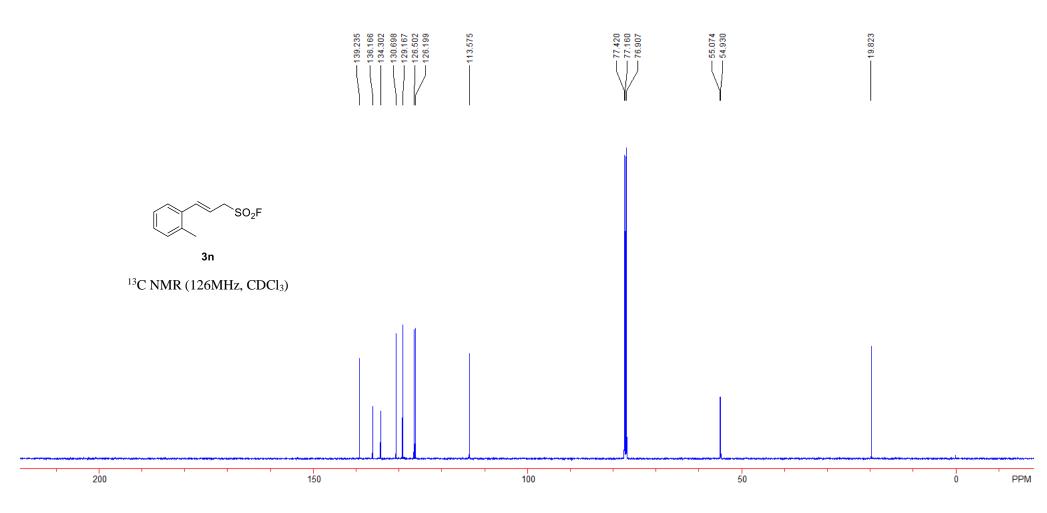


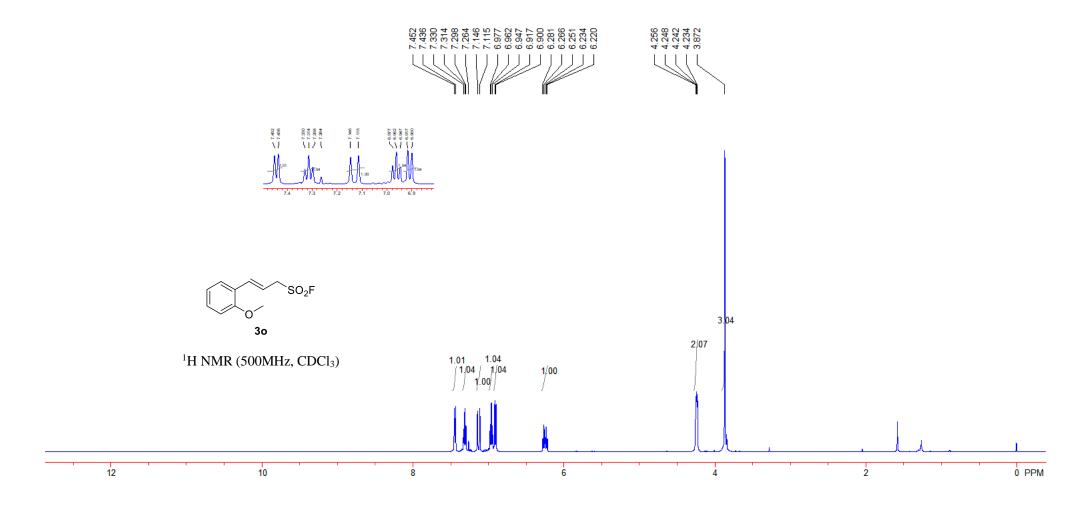


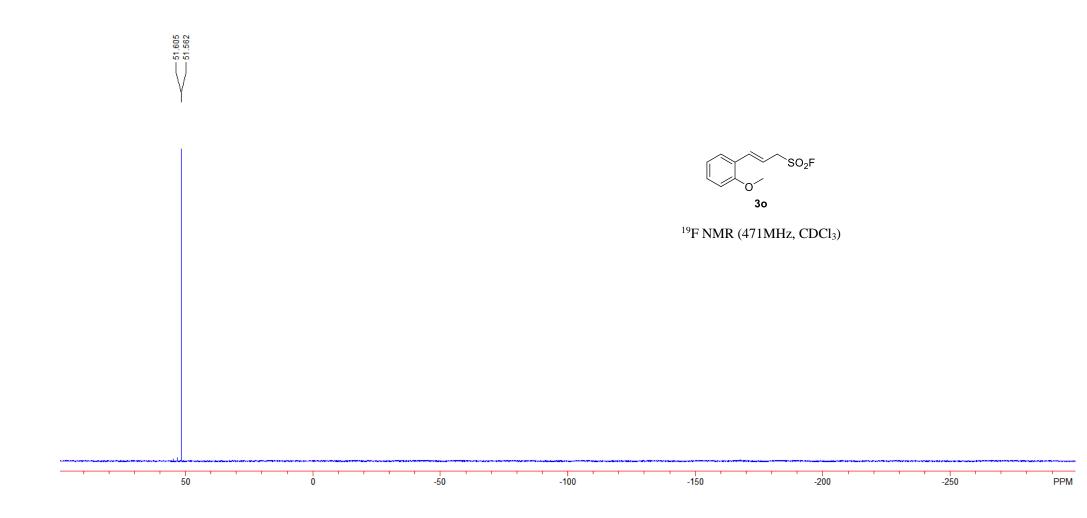


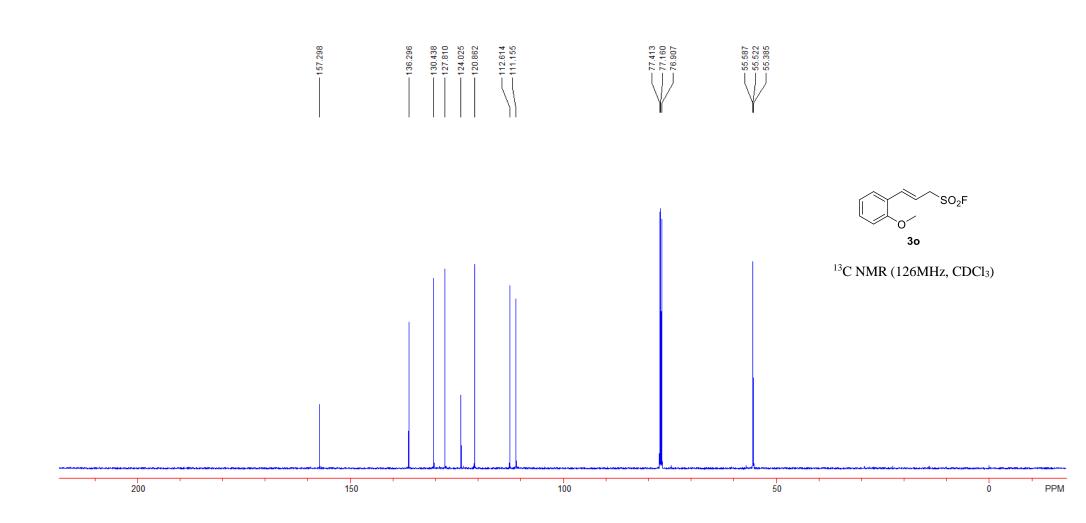


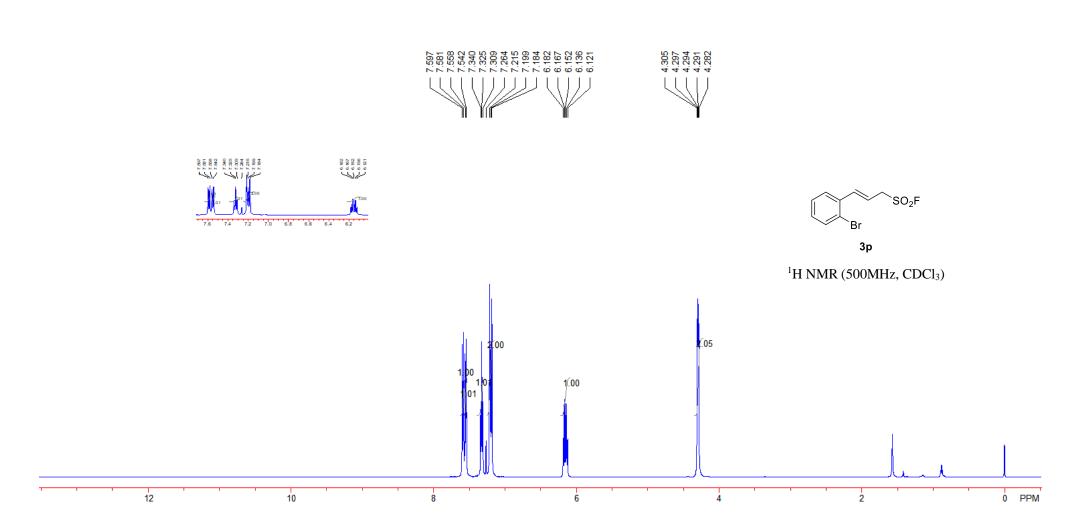


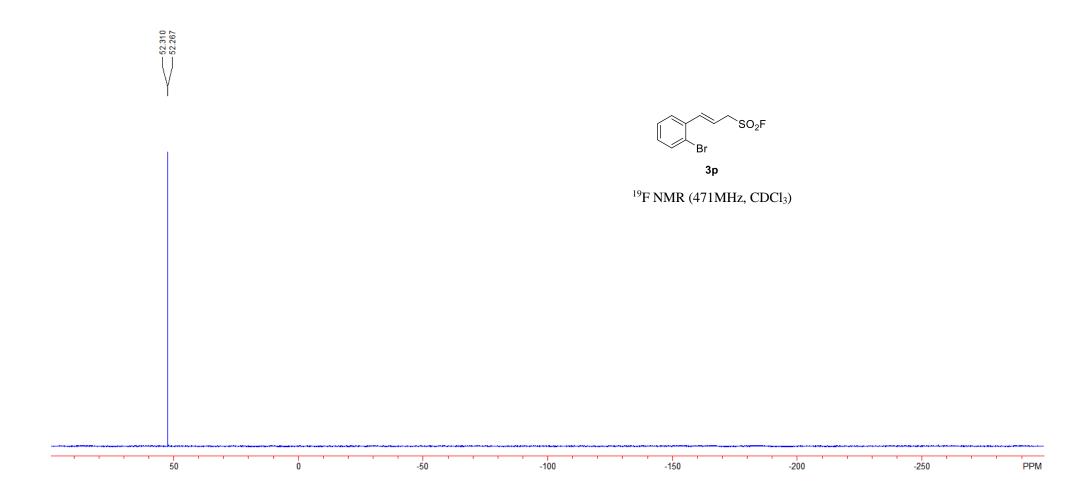


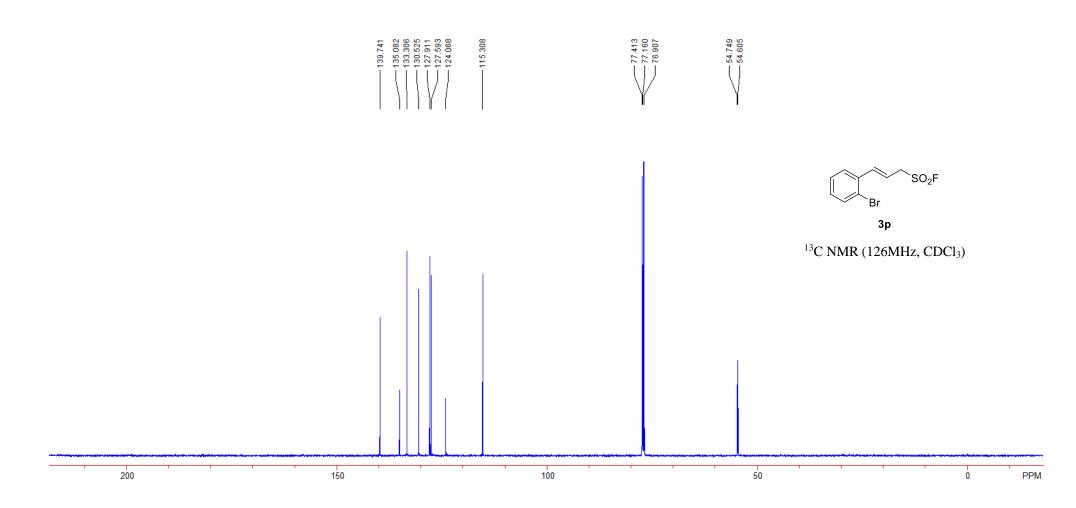


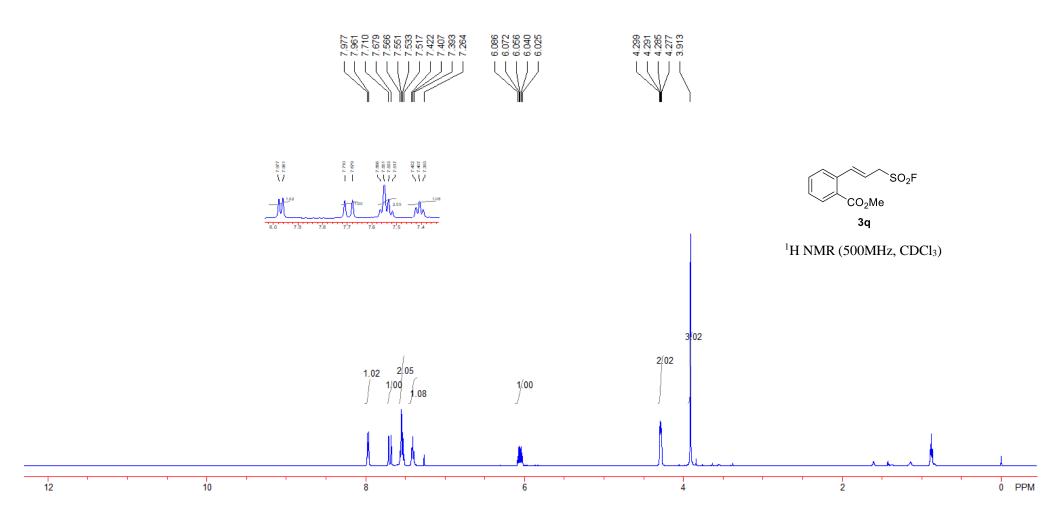


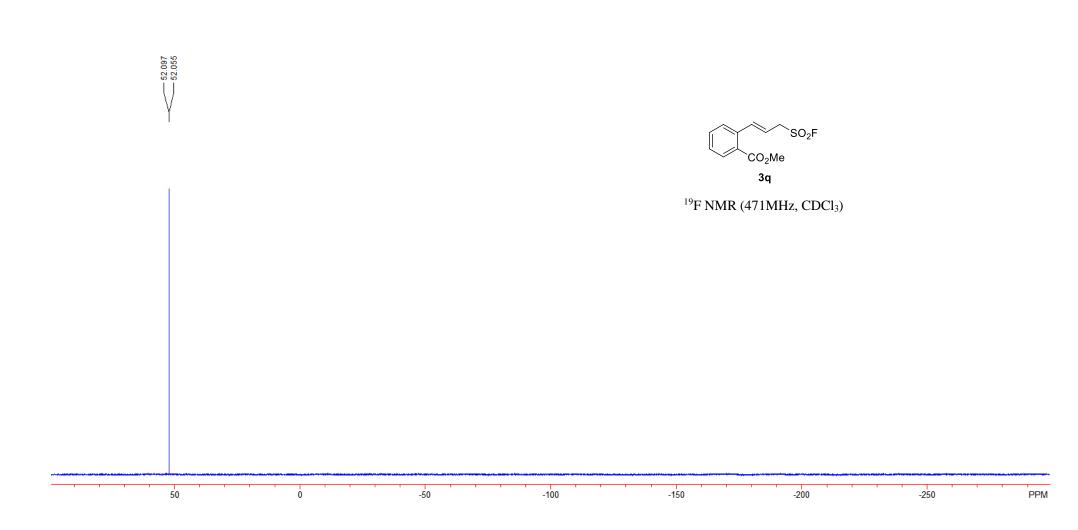


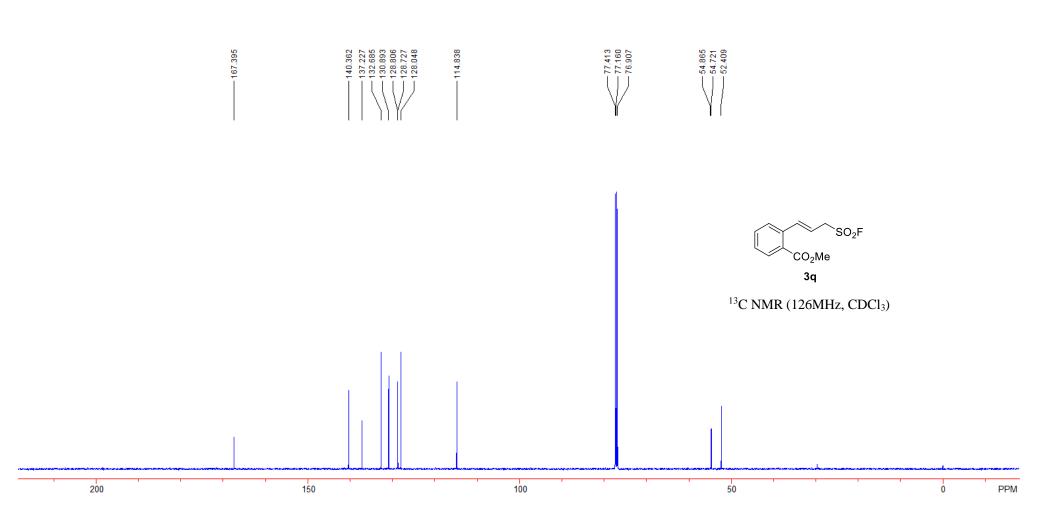


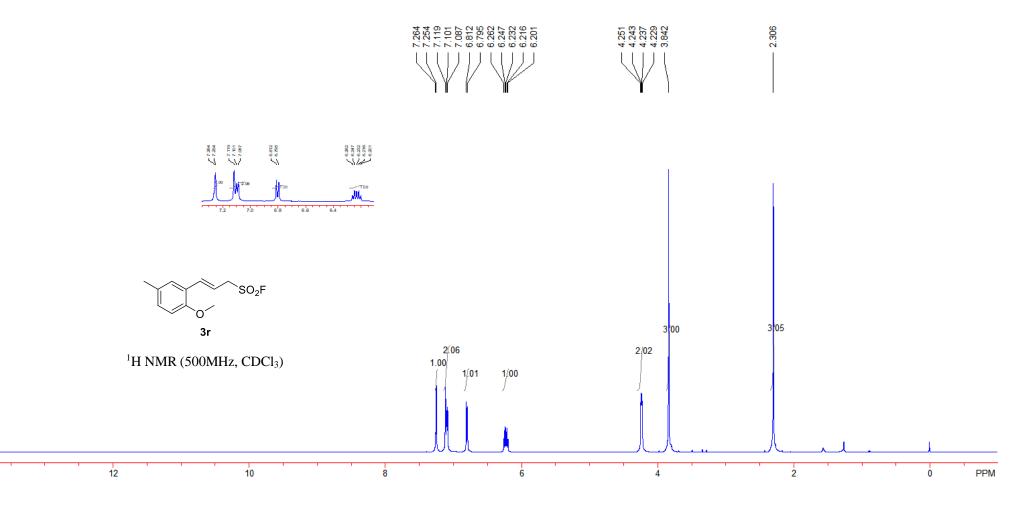


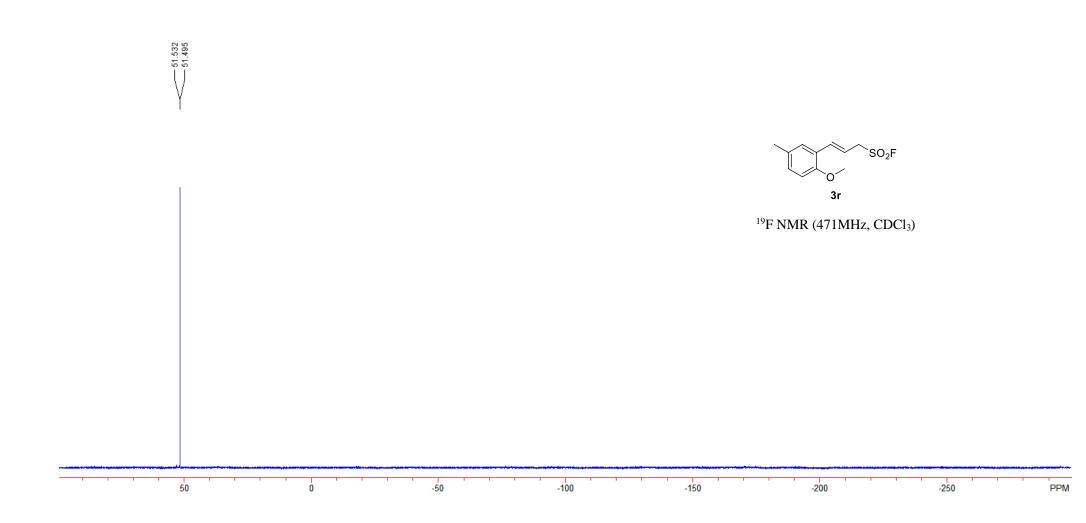


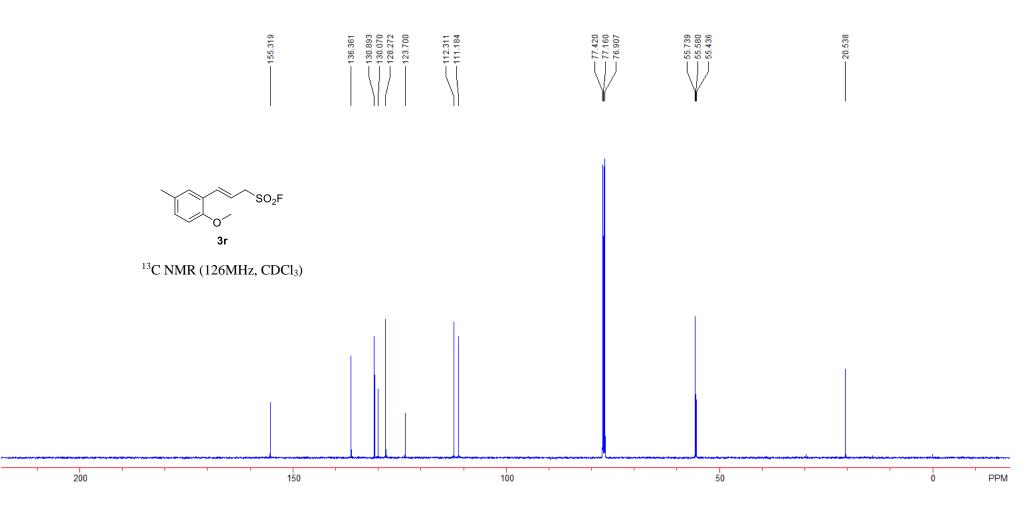


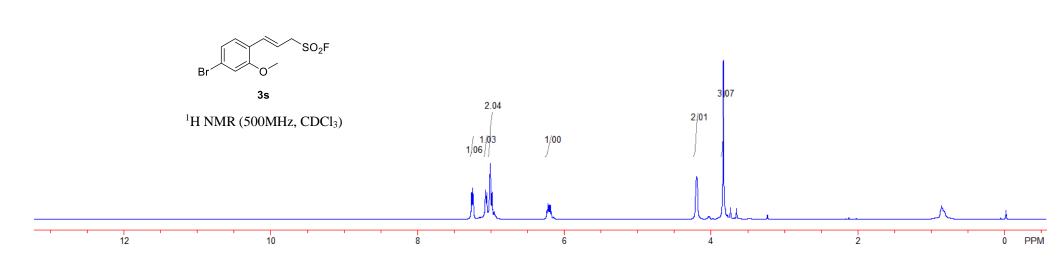


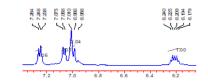


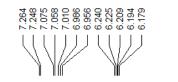




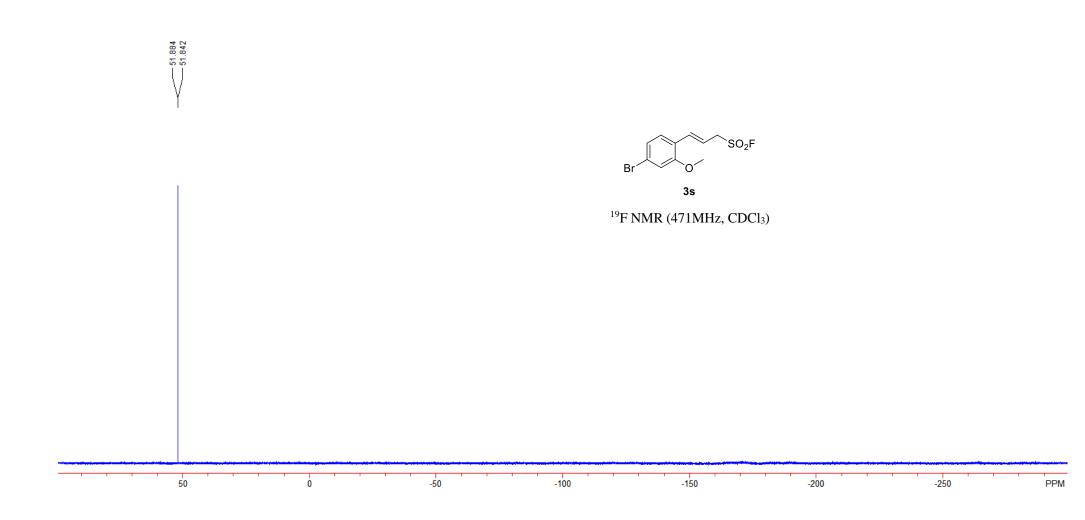


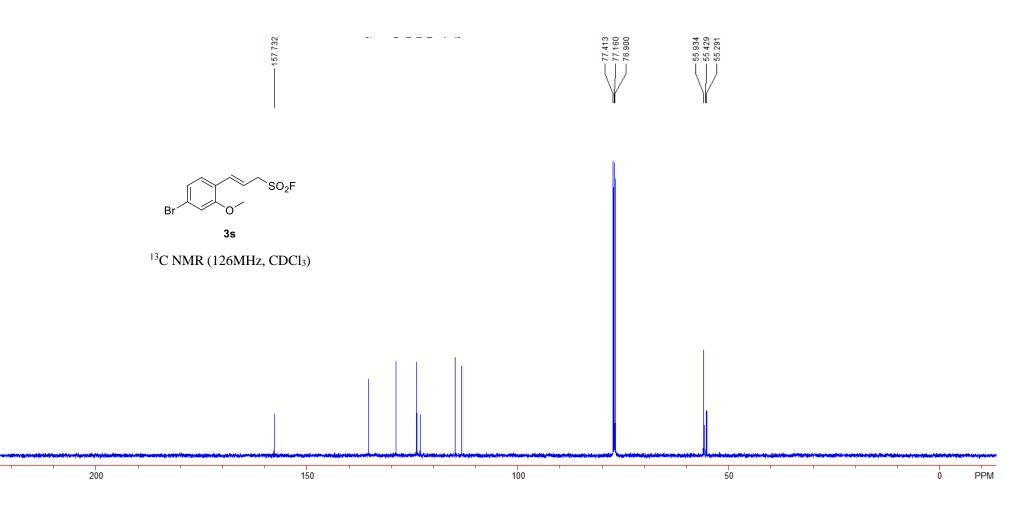


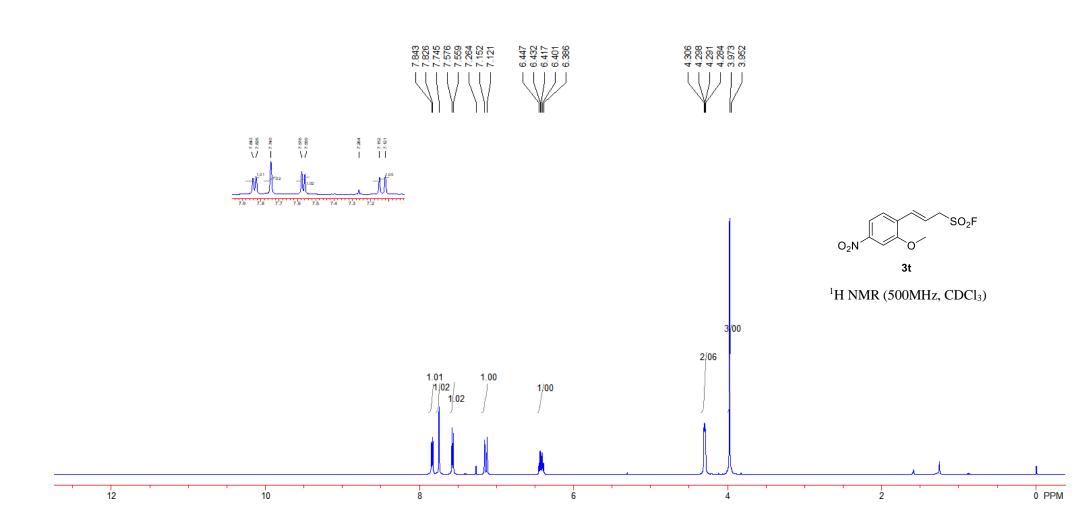


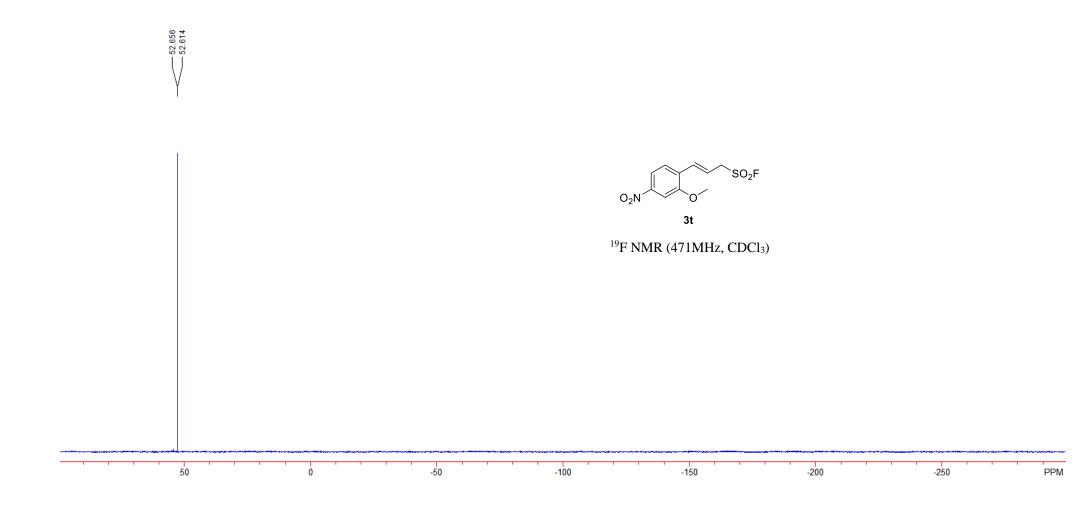


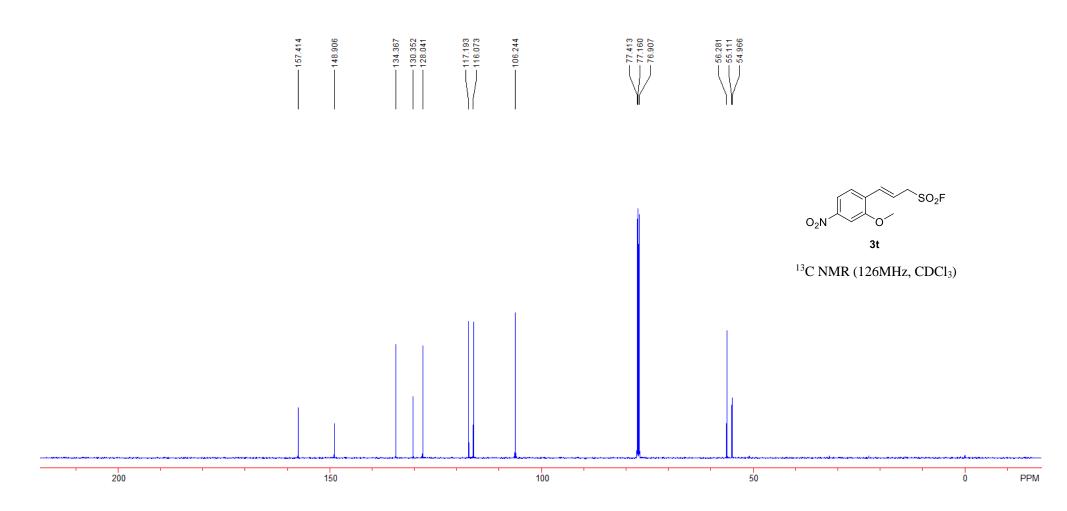


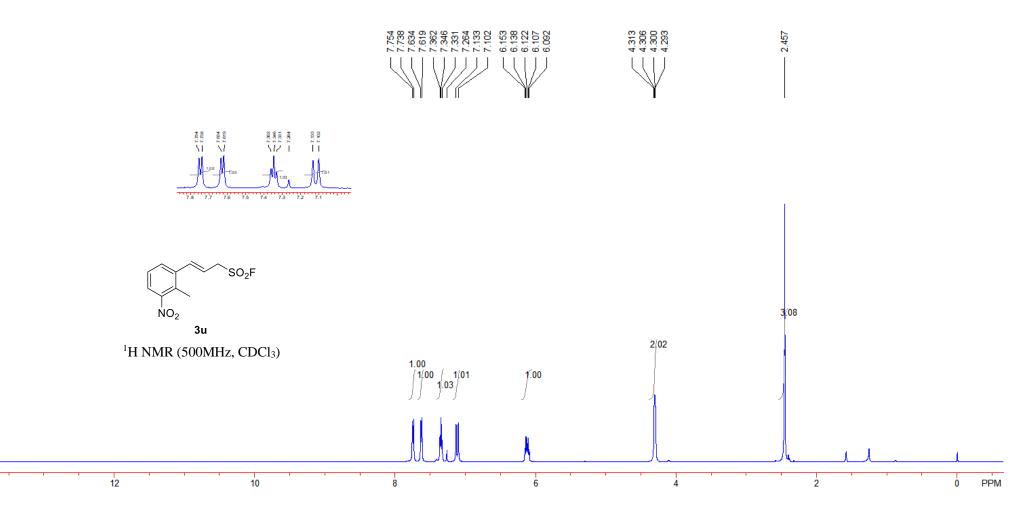


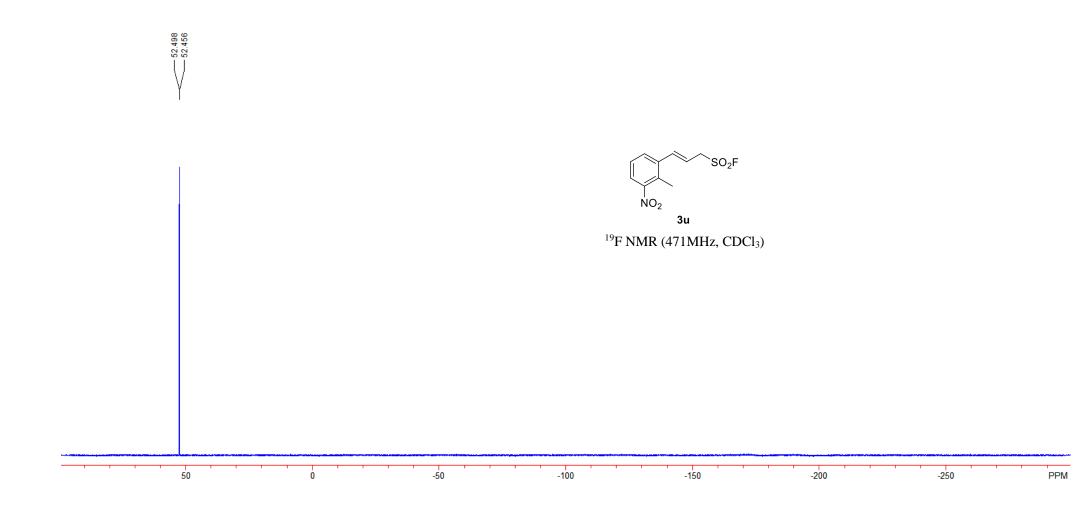


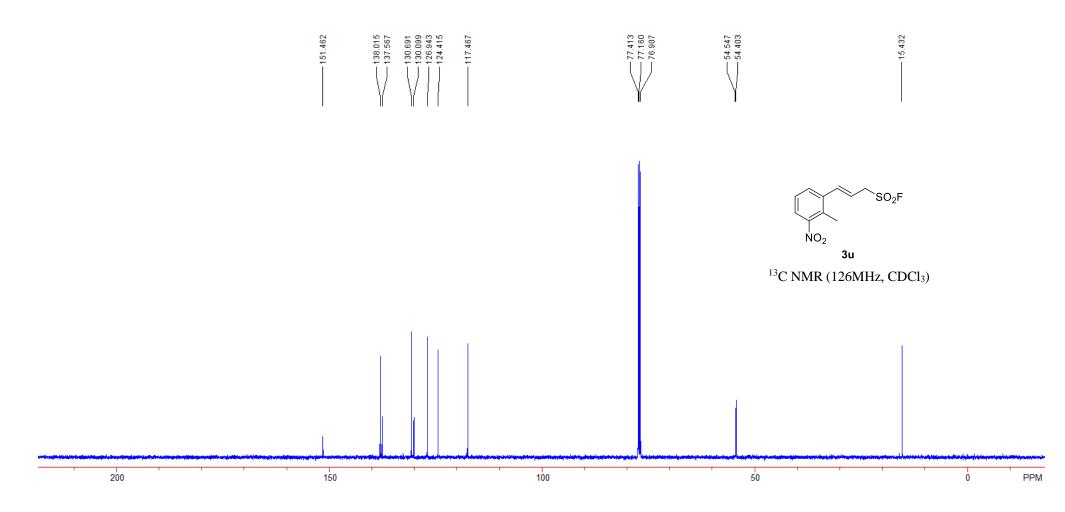


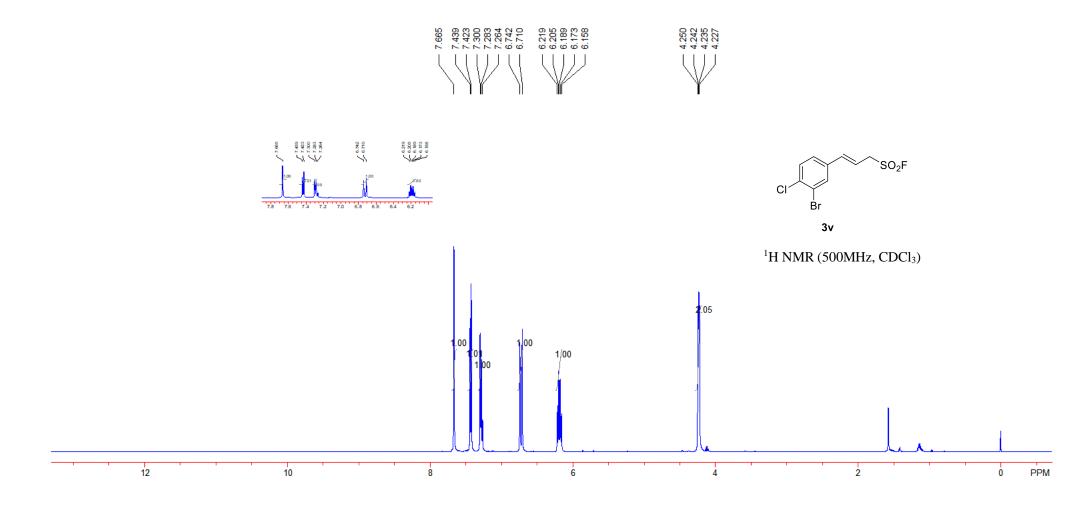


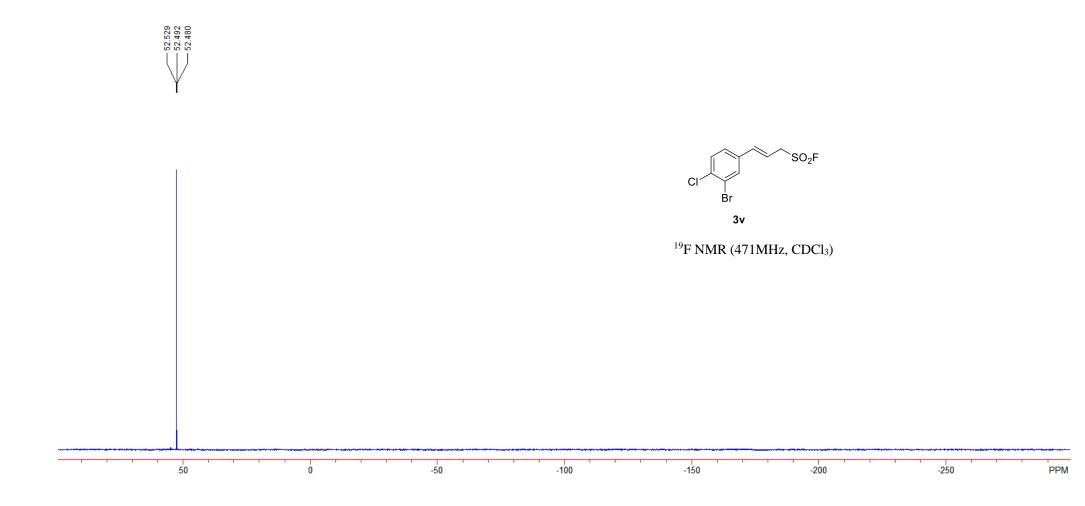


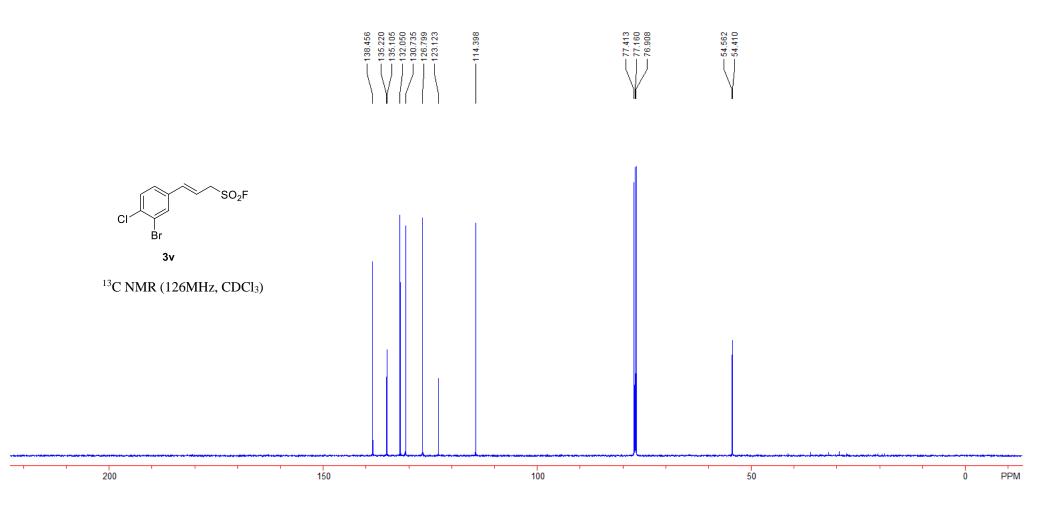


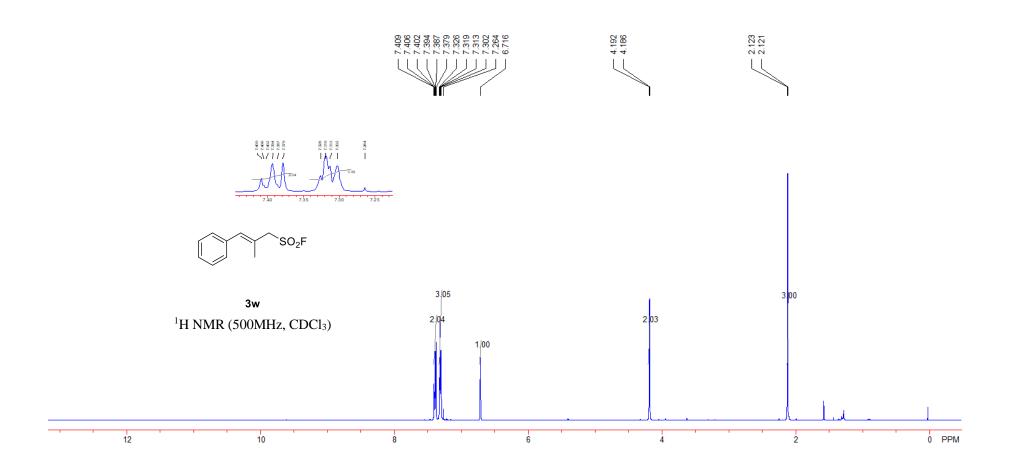


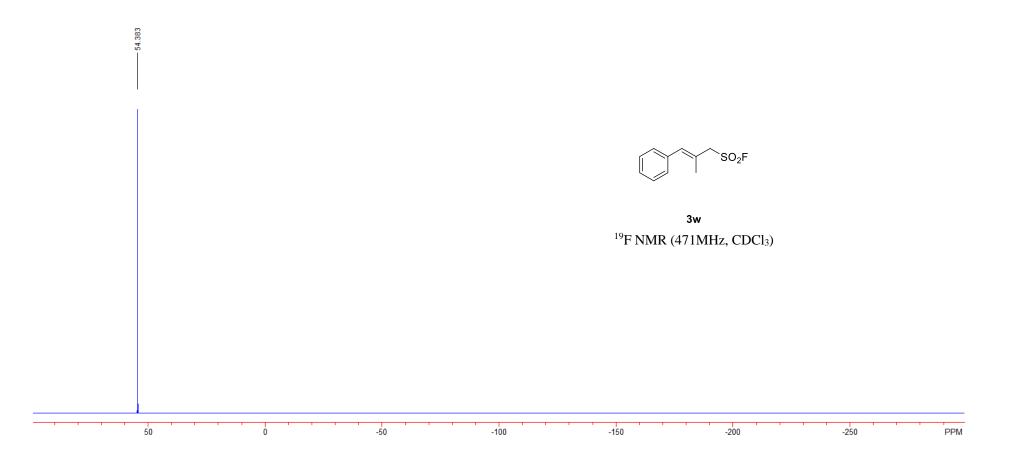


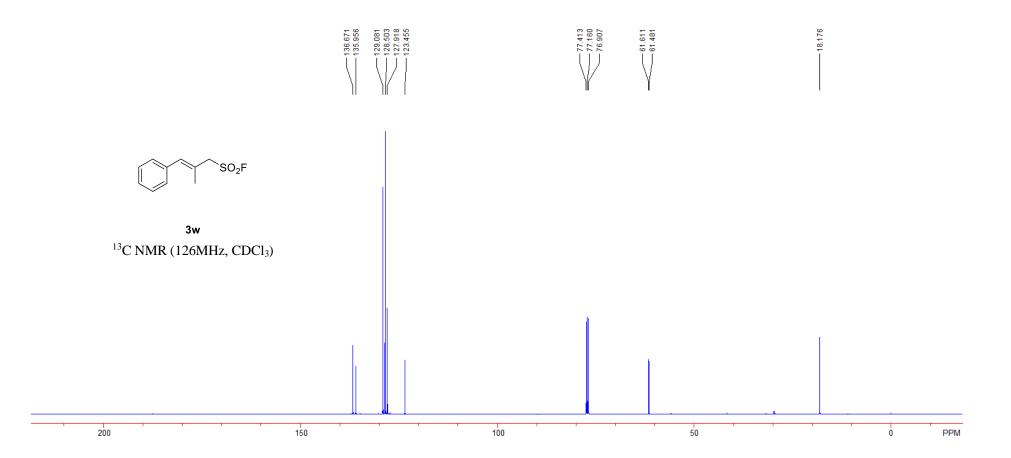


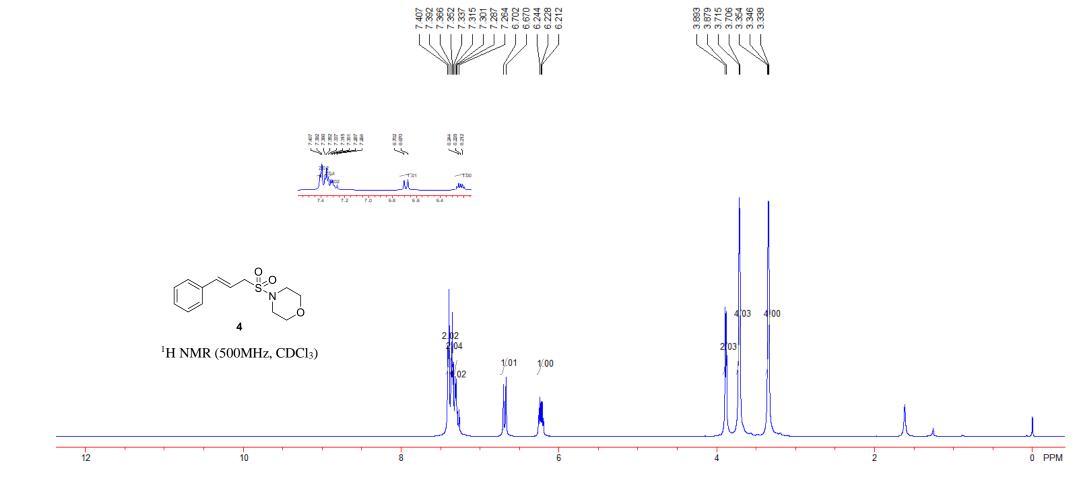


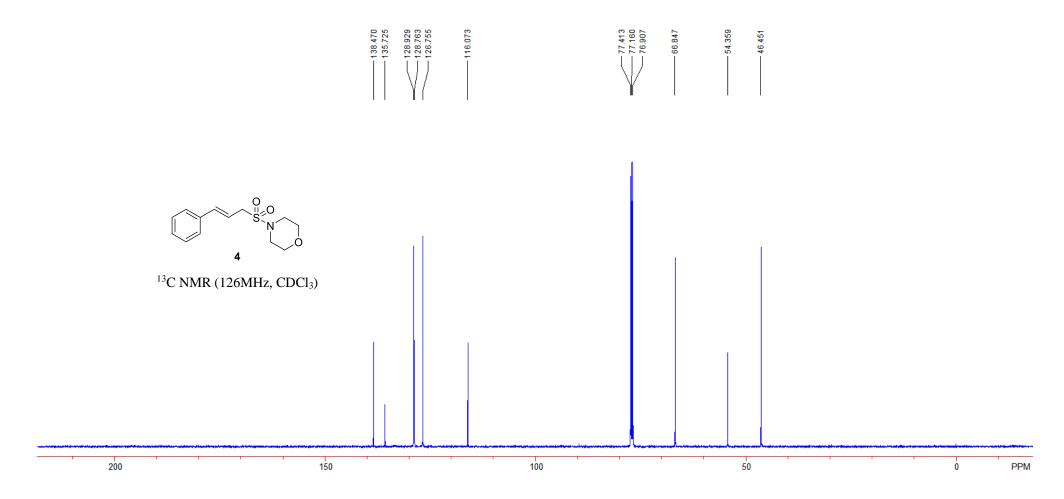


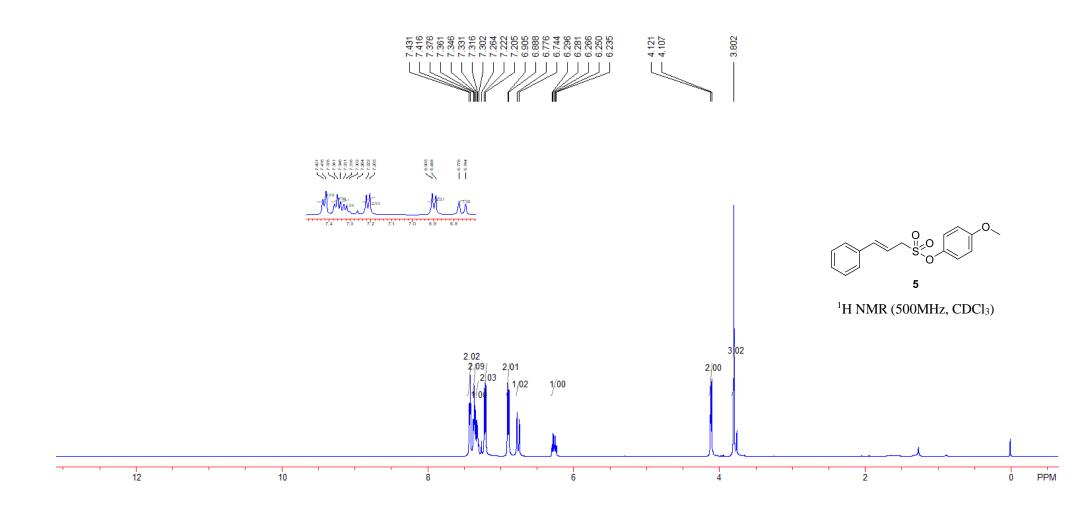


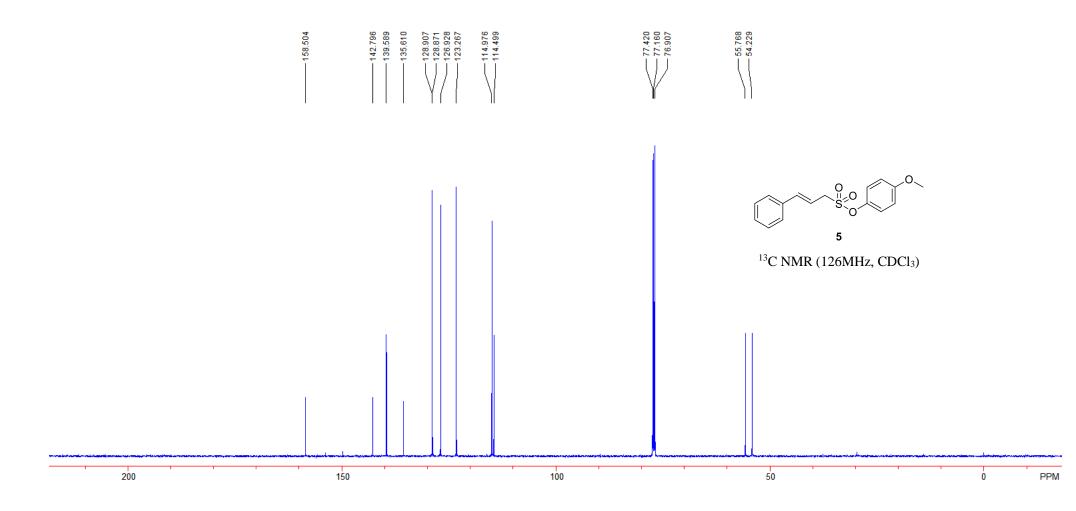


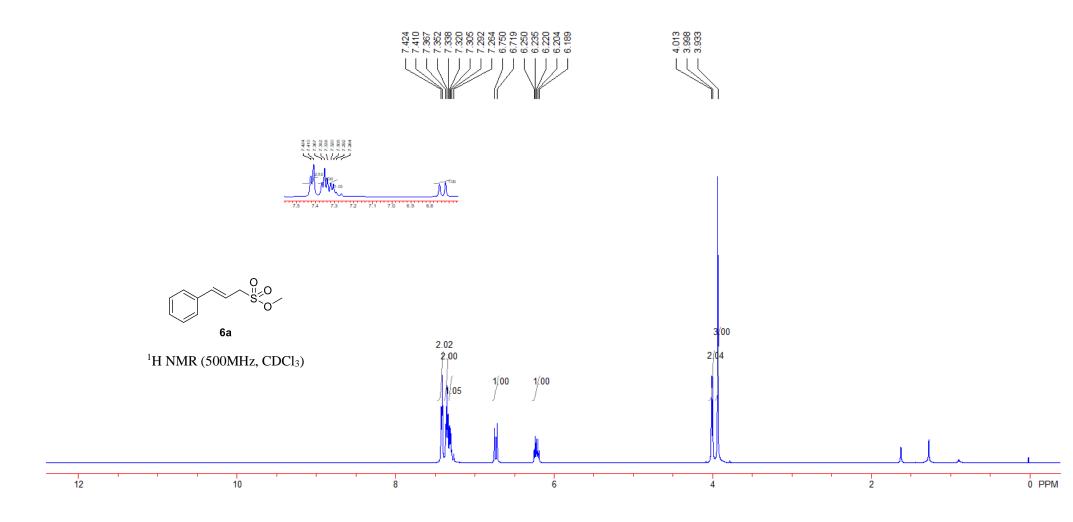


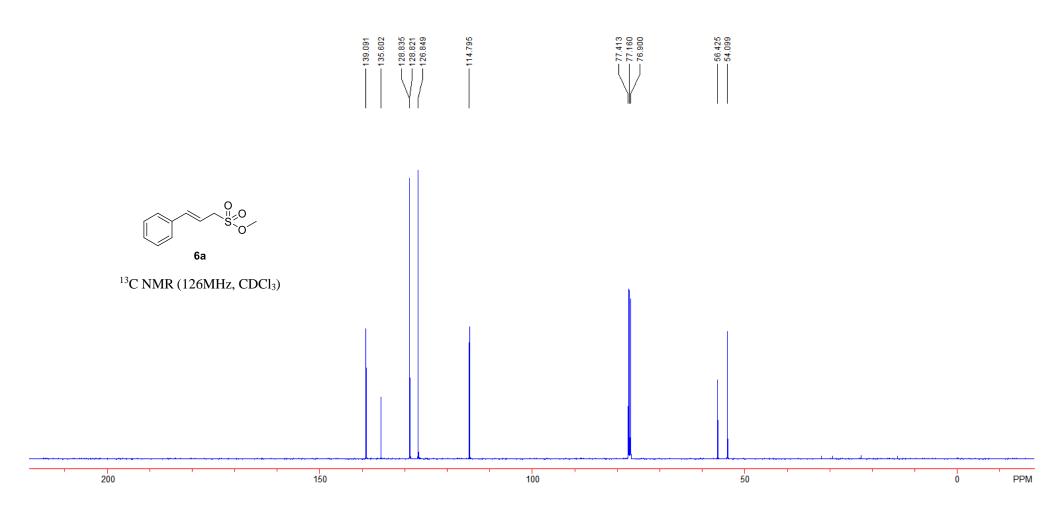


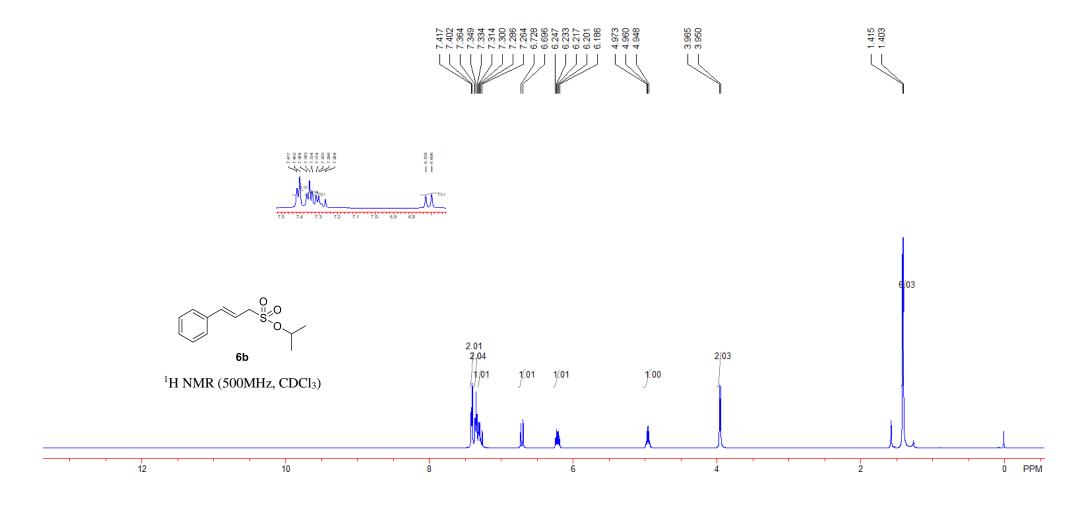


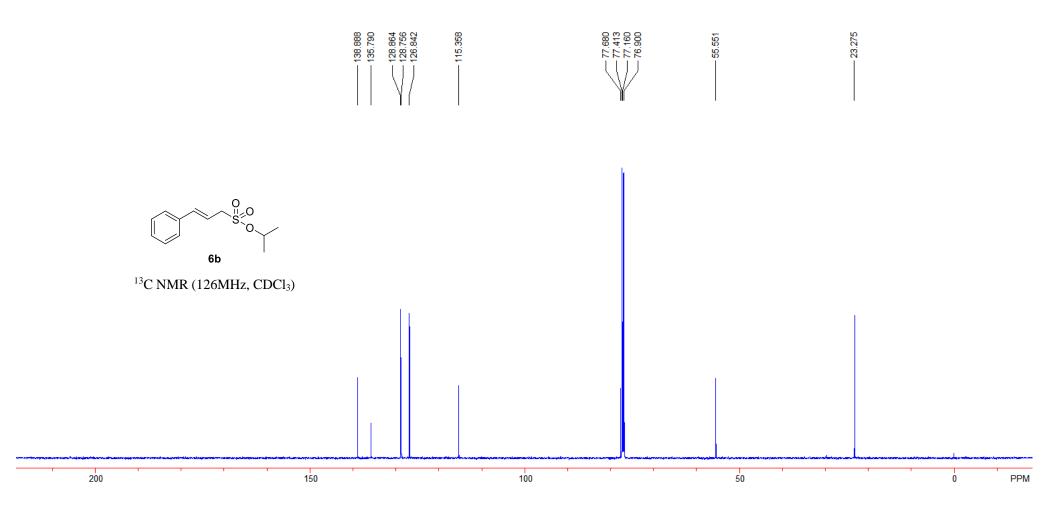




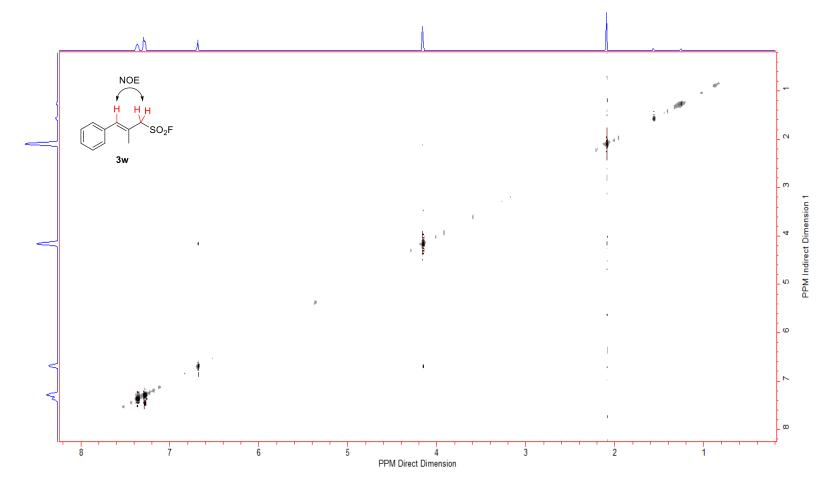












NOESY spectrum of compound 3w (in CDCl₃)