

Supporting Information

A general protocol for stereoselective construction of enaminyll sulfonyl fluorides

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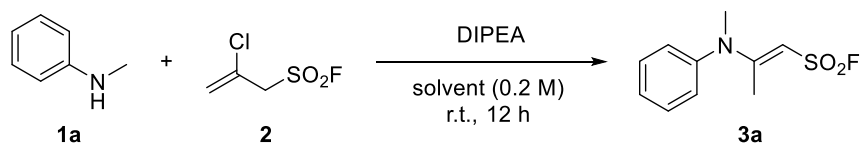
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1. General Information

All reactions were carried out under an air atmosphere unless otherwise specified. Reagents used in the reactions were all purchased from commercial sources and used without further purification. Unless otherwise specified, NMR spectra were recorded in CDCl₃ or DMSO-*d*₆ on a 500 MHz (for ¹H), 471 MHz (for ¹⁹F), and 126 MHz (for ¹³C) Bruker Avance spectrometer, and were internally referenced to solvent residual signals (note: CDCl₃: δ H = 7.264 ppm, δ C = 77.16 ppm; DMSO-*d*₆: δ H = 2.500 ppm, δ C = 39.52 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All chemical shifts were reported in ppm relative to TMS (0 ppm) as internal standards. The HPLC experiments were carried out on a Waters e2695 instrument (column: J&K, RP-C18, 5 μ m, 4.6 \times 150 mm), and the yields of the products were determined by using the corresponding pure compounds as the external standards. Melting points of the products were measured on a micro melting point apparatus (SGW X-4) and uncorrected. HRMS experiments were performed on a TOF-Q ESI or CI/EI instrument. The coupling constants were reported in Hertz (Hz). The product spots on the thin layer chromatography (TLC) were visualized under ultraviolet light (254 nm or 365 nm) followed by staining with potassium permanganate or phosphomolybdic acid.

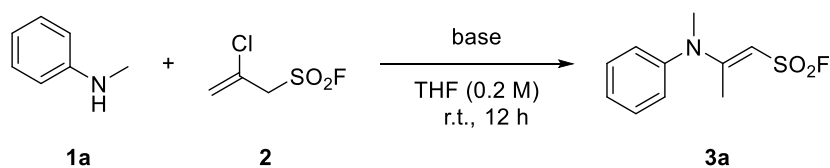
2. Optimization of the Reaction Conditions

Table S1 Screening the Solvent^a



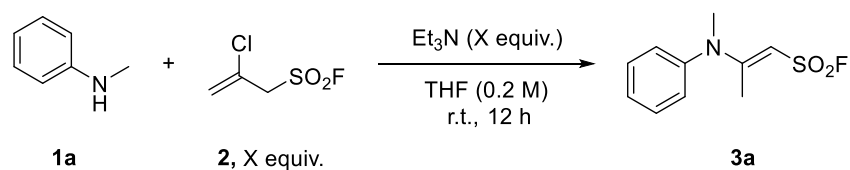
Entry	Solvent	Yield (3a , %) ^b
1	CH ₃ CN	62
2	EtOH	35
3	DMSO	71
4	DMF	72
5	Acetone	67
6	1,4-Dioxane	63
7	THF	79
8	DCM	53
9	Toluene	45
10	H ₂ O	N.D.

^aReaction conditions: a mixture of *N*-Methylaniline (**1a**, 21 mg, 0.2 mmol, 1.0 equiv.), CESF (**2**, 32 mg, 0.2 mmol, 1.0 equiv.) and DIPEA (26 mg, 0.2 mmol, 1.0 equiv.) in solvent (1.0 mL) was stirred at r.t. for 12 h under air. ^bThe yield was determined by HPLC using pure **3a** as the external standard ($t_R = 3.981$ min, $\lambda_{max} = 264.2$ nm, water/methanol =30:70 (v/v)). N.D. = Not detectable.

Table S2 Screening the base^a

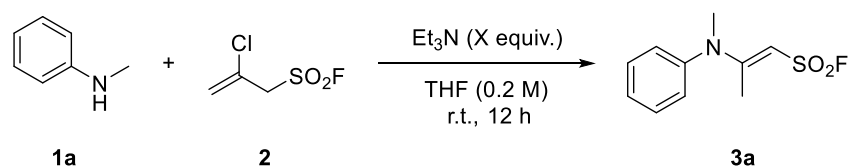
Entry	Base	Yield (3a , %) ^b
1	DIPEA	79
2	DABCO	52
3	DBU	34
4	TMEDA	87
5	Et₃N	93
6	Tripropylamine	47
7	NaHCO ₃	11
8	K ₂ CO ₃	64
9	Cs ₂ CO ₃	76

^aReaction conditions: a mixture of *N*-Methylaniline (**1a**, 21 mg, 0.2 mmol, 1.0 equiv.), CESF (**2**, 32 mg, 0.2 mmol, 1.0 equiv.) and base (0.2 mmol, 1.0 equiv.) in THF (1.0 mL) was stirred at r.t. for 12 h under air. ^bThe yield was determined by HPLC using pure **3a** as the external standard ($t_R = 3.981$ min, $\lambda_{max} = 264.2$ nm, water/methanol = 30: 70 (v/v)). N.D. = Not detectable.

Table S3 Screening the loading of CESF (**2**)^a

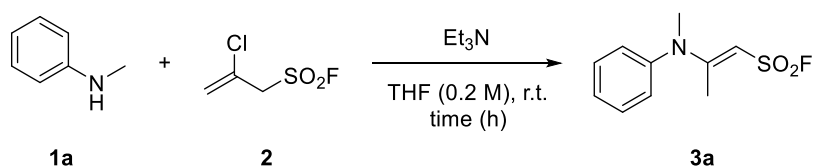
Entry	X equiv.	Yield (3a , %) ^b
1	1.0	93
2	1.2	97
3	1.5	95
4	2.0	97

^aReaction conditions: a mixture of *N*-Methylaniline (**1a**, 21 mg, 0.2 mmol, 1.0 equiv.), CESF (**2**, X equiv.) and Et_3N (X equiv.) in THF (1.0 mL) was stirred at r.t. for 12 h under air. ^bThe yield was determined by HPLC using pure **3a** as the external standard ($t_{\text{R}} = 3.981$ min, $\lambda_{\text{max}} = 264.2$ nm, water/methanol = 30:70 (v/v)). N.D. = Not detectable.

Table S4 Screening the loading of base^a

Entry	Et ₃ N (X equiv.)	Yield (3a , %) ^b
1	1.2	97
2	1.4	96
3	1.6	94

^aReaction conditions: a mixture of *N*-Methylaniline (**1a**, 21 mg, 0.2 mmol, 1.0 equiv.), CESF (**2**, 38 mg, 0.24 mmol, 1.2 equiv.) and Et₃N (X equiv.) in THF (1.0 mL) was stirred at r.t. for 12 h under air. ^bThe yield was determined by HPLC using pure **3a** as the external standard (*t*_R = 3.981 min, λ_{max} = 264.2 nm, water/methanol = 30:70 (v/v)). N.D. = Not detectable.

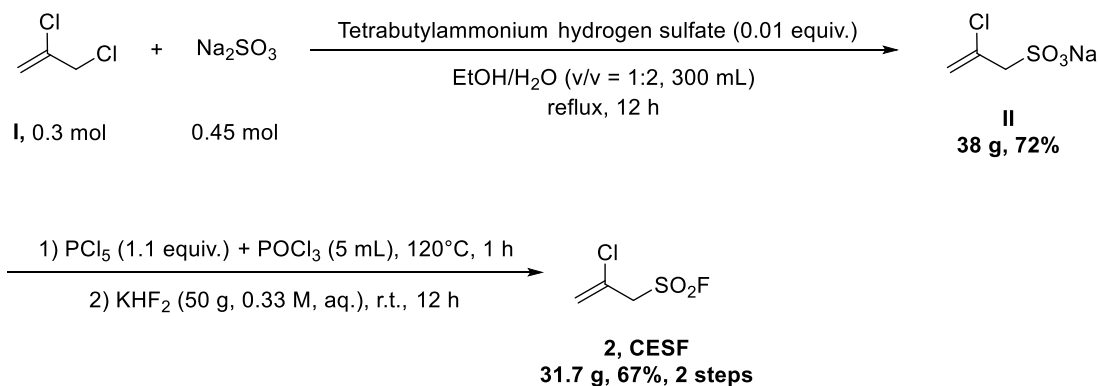
Table S5 Screening the time of reaction^a

Entry	Time (h)	Yield (3a , %) ^b
1	0.5	81
2	1.0	89
3	2.0	94
4	3.0	96
5	6.0	96

^aReaction conditions: a mixture of *N*-Methylaniline (**1a**, 21 mg, 0.2 mmol, 1.0 equiv.), CESF (**2**, 38 mg, 0.24 mmol, 1.2 equiv.) and Et_3N (25 mg, 0.24 mmol, 1.2 equiv.) in THF (1.0 mL) was stirred at r.t. for the corresponding time under air. ^bThe yield was determined by HPLC using pure **3a** as the external standard ($t_{\text{R}} = 3.981$ min, $\lambda_{\text{max}} = 264.2$ nm, water/methanol =30:70 (v/v)). N.D. = Not detectable.

3. Experimental Procedures

3.1 Preparation of 2-chloroprop-2-ene-1-sulfonyl fluoride (CESF)^{[1][2]}

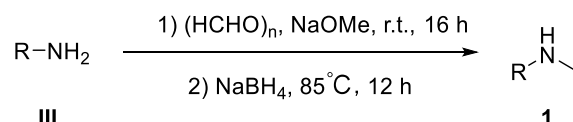


Step 1: 1,2-Dichloro-2-propene (33 g, 0.3 mol), Na₂SO₃ (56 g, 0.45 mol, 1.5 equiv.) and tetrabutylammonium hydrogen sulfate (1.0 g, 0.003 mol, 0.01 equiv.) were added to a solution of EtOH and H₂O (v/v = 1:2, 300 mL) with stirring and heating. The mixture was then refluxed for 12 h and the solvent evaporated in vacuo. To the residue was added EtOH (250 mL), and the mixture was refluxed with stirring for 1 h. After removing some insoluble material by filtration of the hot mixture, the filtrate was cooled. The crystalline sodium 2-chloro-2-propene-1-sulfonate was collected by filtration: 38.0 g (0.216 mol, 72%).

Step 2: A mixture of this sodium salt (38.0 g, 0.216 mol) and PCl₅ (49.5 g, 0.238 mol, 1.1 equiv.) was stirred vigorously until the mixture liquified. The solids remaining on the walls of the bottle were rinsed with phosphorus oxychloride (5 mL), then the mixture was rapidly heated to 120 °C for 1 hour, cooled, and poured onto ice with vigorous stirring. Kept the reaction mixture stirring at low temperature and extracted with CH₂Cl₂ (50 mL). The organic phase was washed with ice water, 5% NaHCO₃ solution (2×100 mL), then dried, and evaporated in vacuo. The evaporated 2-chloro-2-propene sulfonyl chloride was added dropwise to the solution of KHF₂ (50 g, 0.33 M) with stirring for 12 hours. The reaction mixture was further extracted with CH₂Cl₂ (2×25 mL), then dried, and evaporated in vacuo. 2-Chloroprop-2-ene-1-sulfonyl fluoride (CESF) was distilled under reduced pressure to give colorless oil 31.7 g (**2**, 67%, 2 steps). ¹H NMR (500 MHz, CDCl₃) δ 5.75 (dd,

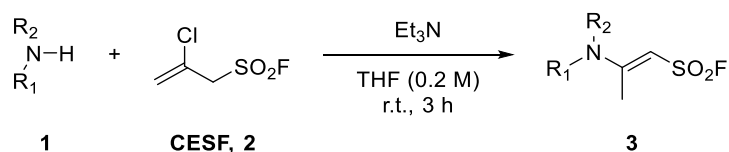
$J_1 = 2.4$ Hz, $J_2 = 1.0$ Hz, 1H), 5.72 (d, $J = 2.5$ Hz, 1H), 4.33 (dd, $J_1 = 3.8$ Hz, $J_2 = 0.8$ Hz, 2H). ^{19}F NMR (471 MHz, CDCl_3) δ 56.4 (s, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 126.6, 123.6 (d, $J = 1.5$ Hz), 59.3 (d, $J = 19.4$ Hz). HRMS-ESI (m/z) calcd. for $[\text{C}_3\text{H}_5\text{ClFO}_2\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 158.9677, found: 158.9674.

3.2 Preparation of amine substrates (**1**)^[3]



Compound **1b** was taken as an example to illustrate the preparation process of the substrate: p-methylaniline (0.53 g, 5 mmol) was added to the methanol solution (10 ml) containing sodium methanol (1.71 g, 30 mmol) in drops, and the mixed solution was continuously stirred for 0.5 h. The methanol solution (5 mL) of paraformaldehyde (0.32 g, 10 mmol) was added to the above mixture by drop and stirred for 16 h at room temperature. Sodium borocyanide (0.2 g, 5 mmol) was added to the mixture in proportion, and the reaction was heated and kept reflux for 6 h. The reaction was detected by TLC. After the reaction, the solution was concentrated under vacuum to remove the solvent. Water (50 mL) was added to the residue and the reaction mixture was extracted with ethyl acetate (3×20 mL). The extracts were dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate (10:1) as eluents to give the desired product **1b** as a white solid, 526 mg, 87% yield. The synthesis of amine substrates (**1c-1u**) can be referred to the above process.^{[4][5]} Amine substrates (**1a**, **1v**, **1w**, **1aa-1ad**) were all purchased from commercial sources and used without further purification.

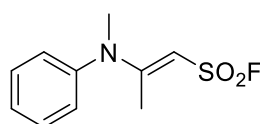
3.3 General procedure for preparation of N-ESF (**3**)



An oven-dried reaction tube (20 mL) equipped with a magnetic stirring bar was charged with amines (**1**, 1.0 mmol, 1.0 equiv.), CESF (**2**, 189 mg, 1.2 mmol, 1.2

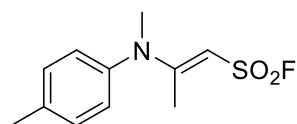
equiv.) and 4.0 mL THF. Then, trimethylamine (122 mg, 1.2 mmol, 1.2 equiv.) dissolved in THF (1.0 mL) was added dropwise to the above solution and the solution slowly became turbid. The mixture was stirred at room temperature for 3 h under an air atmosphere monitored by TLC. After the reaction was completed, water (20 mL) was added to the mixture and the reaction mixture was extracted with ethyl acetate (3×10 mL). The extracts were dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluents to give the desired product **3**.

4. Characterization



3a

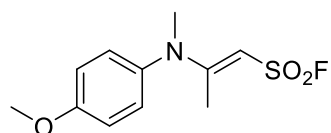
(E)-2-(methyl(phenyl)amino)prop-1-ene-1-sulfonyl fluoride (**3a**). White solid, 219 mg, 96% yield. M.p. 74–76 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. ¹H NMR (500 MHz, CDCl₃) δ 7.45 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.0 Hz, 1H), 7.14 (d, *J* = 8.5 Hz, 2H), 5.06 (s, 1H), 3.26 (s, 3H), 2.19 (s, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ 72.3 (s, 1F). ¹³C NMR (126 MHz, CDCl₃) δ 162.6, 144.6, 130.3, 128.5, 127.0, 85.7 (d, *J* = 24.3 Hz), 41.6, 17.8. HRMS-ESI (m/z) calcd. for [C₁₀H₁₃FNO₂S]⁺ ([M+H]⁺): 230.0646, found: 230.0645.



3b

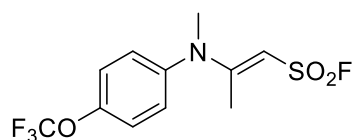
(E)-2-(methyl(*p*-tolyl)amino)prop-1-ene-1-sulfonyl fluoride (**3b**). White solid, 228 mg, 94% yield. M.p. 81–83 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. ¹H NMR (500 MHz, CDCl₃) δ

7.24 (d, $J = 8.0$ Hz, 2H), 7.01 (d, $J = 8.0$ Hz, 2H), 5.03 (s, 1H), 3.24 (s, 3H), 2.39 (s, 3H), 2.18 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ 72.3 (s, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 162.8, 142.0, 138.6, 130.8, 126.7, 85.3 (d, $J = 24.1$ Hz), 41.7, 21.2, 17.8. **HRMS-ESI** (m/z) calcd. for $[\text{C}_{11}\text{H}_{15}\text{FNO}_2\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 244.0802, found: 244.0795.



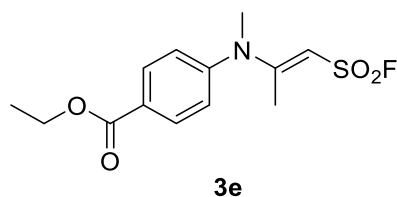
3c

(E)-2-((4-methoxyphenyl)(methyl)amino)prop-1-ene-1-sulfonyl fluoride (**3c**). White solid, 241 mg, 93% yield. M.p. 69–71 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. ^1H NMR (500 MHz, CDCl_3) δ 7.04 (d, $J = 9.0$ Hz, 2H), 6.93 (d, $J = 9.0$ Hz, 2H), 5.02 (s, 1H), 3.83 (s, 3H), 3.23 (s, 3H), 2.18 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ 72.3 (s, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 162.9, 159.2, 137.2, 127.9, 115.2, 85.1 (d, $J = 24.2$ Hz), 55.6, 41.7, 17.7. **HRMS-ESI** (m/z) calcd. for $[\text{C}_{11}\text{H}_{15}\text{FNO}_3\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 260.0751, found: 260.0752.

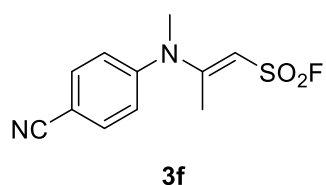


3d

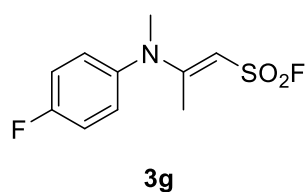
(E)-2-(methyl(4-(trifluoromethoxy)phenyl)amino)prop-1-ene-1-sulfonyl fluoride (**3d**). White solid, 278 mg, 89% yield. M.p. 51–53 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. ^1H NMR (500 MHz, CDCl_3) δ 7.31 (d, $J = 8.5$ Hz, 2H), 7.20 (d, $J = 8.5$ Hz, 2H), 5.09 (s, 1H), 3.26 (s, 3H), 2.20 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ 72.1 (s, 1F), -58.0 (s, 3F). ^{13}C NMR (126 MHz, CDCl_3) δ 162.3, 148.7 (d, $J = 2.0$ Hz), 142.9, 128.8, 122.7, 120.5 (q, $J = 258.8$ Hz), 87.1 (d, $J = 24.7$ Hz), 41.7, 17.9. **HRMS-ESI** (m/z) calcd. for $[\text{C}_{11}\text{H}_{12}\text{F}_4\text{NO}_3\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 314.0469, found: 314.0476.



methyl (E)-4-((1-(fluorosulfonyl)prop-1-en-2-yl)(methyl)amino)benzoate (3e). White solid, 243 mg, 85% yield. M.p. 84–86 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. ¹H NMR (500 MHz, CDCl₃) δ 8.13 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.5 Hz, 2H), 5.13 (s, 1H), 4.41 (q, *J* = 7.0 Hz, 2H), 3.28 (s, 3H), 2.20 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ 72.0 (s, 1F). ¹³C NMR (126 MHz, CDCl₃) δ 165.5, 161.9, 148.3, 131.6, 130.5, 127.1, 87.6 (d, *J* = 24.8 Hz), 61.6, 41.5, 18.0, 14.4. HRMS-ESI (m/z) calcd. for [C₁₃H₁₇FNO₄S]⁺ ([M+H]⁺): 302.0857, found: 302.0858.

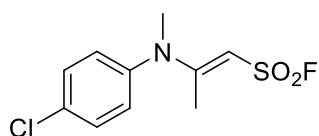


(E)-2-((4-cyanophenyl)(methyl)amino)prop-1-ene-1-sulfonyl fluoride (3f). Light yellow solid, 175 mg, 69% yield. M.p. 119–121 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 5:1 (v/v) as eluent. ¹H NMR (500 MHz, CDCl₃) δ 7.78 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 5.18 (s, 1H), 3.29 (s, 3H), 2.22 (s, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ 71.9 (s, 1F). ¹³C NMR (126 MHz, CDCl₃) δ 161.5, 148.3, 134.2, 128.2, 117.7, 112.3, 88.9 (d, *J* = 25.2 Hz), 41.5, 17.9. HRMS-ESI (m/z) calcd. for [C₁₁H₁₂FN₂O₂S]⁺ ([M+H]⁺): 255.0598, found: 255.0605.



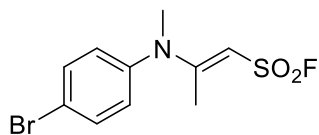
(E)-2-((4-fluorophenyl)(methyl)amino)prop-1-ene-1-sulfonyl fluoride (3g). White solid,

212 mg, 86% yield. M.p. 61–63 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.16 – 7.13 (m, 4H), 5.05 (s, 1H), 3.24 (s, 3H), 2.18 (s, 3H). $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ 72.2 (s, 1F), -112.1 (m, 1F). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 162.8 (d, $J = 49.3$ Hz), 161.0, 140.6 (d, $J = 3.5$ Hz), 128.9 (d, $J = 8.7$ Hz), 117.2 (d, $J = 23.1$ Hz), 86.3 (d, $J = 24.4$ Hz), 41.7, 17.8. **HRMS-ESI** (m/z) calcd. for $[\text{C}_{10}\text{H}_{12}\text{F}_2\text{NO}_2\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 248.0551, found: 248.0545.



3h

(E)-2-((4-chlorophenyl)(methyl)amino)prop-1-ene-1-sulfonyl fluoride (**3h**). White solid, 236 mg, 90% yield. M.p. 77–79 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.43 (d, $J = 8.5$ Hz, 2H), 7.09 (d, $J = 8.7$ Hz, 2H), 5.07 (s, 1H), 3.24 (s, 3H), 2.19 (s, 3H). $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ 72.1 (s, 1F). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 162.3, 143.0, 134.4, 130.5, 128.5, 86.8 (d, $J = 24.6$ Hz), 41.6, 17.8. **HRMS-ESI** (m/z) calcd. for $[\text{C}_{10}\text{H}_{12}\text{ClFNO}_2\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 264.0256, found: 264.0259.

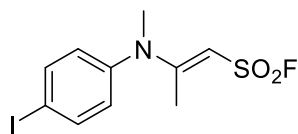


3i

(E)-2-((4-bromophenyl)(methyl)amino)prop-1-ene-1-sulfonyl fluoride (**3i**). Yellow solid, 278 mg, 91% yield. M.p. 96–98 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.58 (d, $J = 8.5$ Hz, 2H), 7.03 (d, $J = 8.5$ Hz, 2H), 5.08 (s, 1H), 3.24 (s, 3H), 2.19 (s, 3H). $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ 72.1 (s, 1F). $^{13}\text{C NMR}$ (126

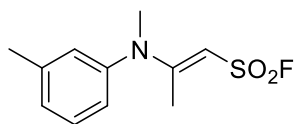
MHz, CDCl₃) δ 162.2, 143.6, 133.5, 128.8, 122.3, 86.9 (d, $J = 24.6$ Hz), 41.6, 17.8.

HRMS-ESI (m/z) calcd. for [C₁₀H₁₂BrFNO₂S]⁺ ([M+H]⁺): 307.9751, found: 307.9759.



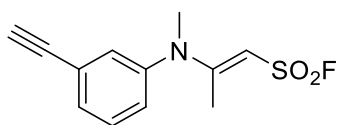
3j

(*E*)-2-((4-iodophenyl)(methyl)amino)prop-1-ene-1-sulfonyl fluoride (**3j**). Purple solid, 322 mg, 91% yield. M.p. 124–126 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **¹H NMR** (500 MHz, CDCl₃) δ 7.80 – 7.77 (m, 2H), 6.91 – 6.88 (m, 2H), 5.08 (s, 1H), 3.23 (s, 3H), 2.19 (s, 3H). **¹⁹F NMR** (471 MHz, CDCl₃) δ 72.1 (s, 1F). **¹³C NMR** (126 MHz, CDCl₃) δ 162.1, 144.3, 139.5, 129.0, 93.7, 87.0 (d, $J = 24.8$ Hz), 41.5, 17.9. **HRMS-ESI** (m/z) calcd. for [C₁₀H₁₂FINO₂S]⁺ ([M+H]⁺): 355.9612, found: 355.9617.



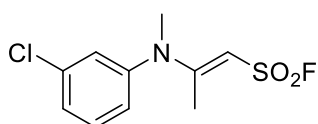
3k

(*E*)-2-(methyl(*m*-tolyl)amino)prop-1-ene-1-sulfonyl fluoride (**3k**). White solid, 230 mg, 95% yield. M.p. 84–86 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. **¹H NMR** (500 MHz, CDCl₃) δ 7.32 (t, $J = 7.7$ Hz, 1H), 7.18 (d, $J = 7.6$ Hz, 1H), 6.94 – 6.91 (m, 2H), 5.04 (s, 1H), 3.24 (s, 3H), 2.38 (s, 3H), 2.19 (s, 3H). **¹⁹F NMR** (471 MHz, CDCl₃) δ 72.3 (s, 1F). **¹³C NMR** (126 MHz, CDCl₃) δ 162.7, 144.5, 140.5, 130.0, 129.2, 127.5, 123.9, 85.3 (d, $J = 24.1$ Hz), 41.6, 21.4, 17.8. **HRMS-ESI** (m/z) calcd. for [C₁₁H₁₅FNO₂S]⁺ ([M+H]⁺): 244.0802, found: 244.0798.



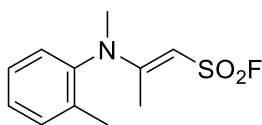
3l

(*E*)-2-((3-ethynylphenyl)(methyl)amino)prop-1-ene-1-sulfonyl fluoride (**3l**). White solid, 222 mg, 92% yield. M.p. 88–90 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.48 (d, $J = 7.5$ Hz, 1H), 7.40 (t, $J = 8.0$ Hz, 1H), 7.26 (s, 1H), 7.13 (d, $J = 8.0$ Hz, 1H), 5.06 (s, 1H), 3.23 (s, 3H), 3.16 (s, 1H), 2.18 (s, 3H). $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ 72.2 (s, 1F). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 162.3, 144.6, 132.1, 130.6, 130.4, 127.7, 124.5, 86.6 (d, $J = 24.4$ Hz), 82.0, 79.3, 41.5, 17.8. **HRMS-ESI** (m/z) calcd. for $[\text{C}_{12}\text{H}_{13}\text{FNO}_2\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 254.0646, found: 254.0637.



3m

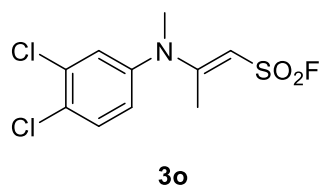
(*E*)-2-((3-chlorophenyl)(methyl)amino)prop-1-ene-1-sulfonyl fluoride (**3m**). White solid, 236 mg, 90% yield. M.p. 108–110 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.42 – 7.36 (m, 2H), 7.17 (t, $J = 2.0$ Hz, 1H), 7.07 – 7.04 (m, 1H), 5.09 (s, 1H), 3.25 (s, 3H), 2.20 (s, 3H). $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ 72.1 (s, 1F). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 162.2, 145.6, 135.7, 131.3, 128.8, 127.5, 125.5, 87.0 (d, $J = 24.7$ Hz), 41.5, 17.8. **HRMS-ESI** (m/z) calcd. for $[\text{C}_{10}\text{H}_{12}\text{ClFNO}_2\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 264.0256, found: 264.0256.



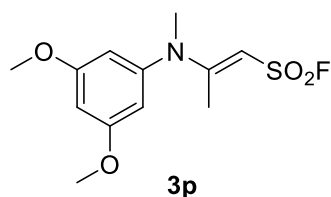
3n

(*E*)-2-(methyl(*o*-tolyl)amino)prop-1-ene-1-sulfonyl fluoride (**3n**). White solid, 225 mg,

93% yield. M.p. 73–75 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.32 (t, $J = 7.7$ Hz, 1H), 7.18 (d, $J = 7.6$ Hz, 1H), 6.94 – 6.91 (m, 2H), 5.04 (s, 1H), 3.24 (s, 3H), 2.38 (s, 3H), 2.19 (s, 3H). $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ 72.3 (s, 1F). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 162.7, 144.5, 140.5, 130.0, 129.2, 127.5, 123.9, 85.3 (d, $J = 24.1$ Hz), 41.6, 21.4, 17.8. **HRMS-ESI** (m/z) calcd. for $[\text{C}_{11}\text{H}_{15}\text{FNO}_2\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 244.0802, found: 244.0798.

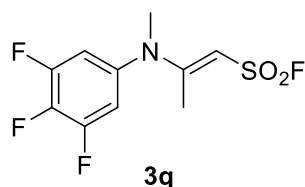


(E)-2-((3,4-dichlorophenyl)(methyl)amino)prop-1-ene-1-sulfonyl fluoride (**3o**). White solid, 264 mg, 89% yield. M.p. 102–104 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.54 (d, $J = 8.5$ Hz, 1H), 7.29 (d, $J = 2.5$ Hz, 1H), 7.03 (dd, $J_1 = 8.5$ Hz, $J_2 = 2.5$ Hz, 1H), 5.11 (s, 1H), 3.24 (s, 3H), 2.21 (s, 3H). $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ 72.0 (s, 1F). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 161.9, 143.7, 134.2, 133.0, 131.9, 129.3, 126.7, 88.0 (d, $J = 24.8$ Hz), 41.6, 17.8. **HRMS-ESI** (m/z) calcd. for $[\text{C}_{10}\text{H}_{11}\text{Cl}_2\text{FNO}_2\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 297.9866, found: 297.9875.

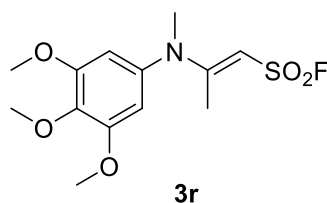


(E)-2-((3,5-dimethoxyphenyl)(methyl)amino)prop-1-ene-1-sulfonyl fluoride (**3p**). White solid, 271 mg, 94% yield. M.p. 141–143 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 6.45 (t, $J = 2.5$ Hz, 1H), 6.26 (d, $J = 2.5$ Hz, 2H), 5.06 (s, 1H), 3.80 (s, 6H), 3.23 (s, 3H), 2.23 (s, 3H). $^{19}\text{F NMR}$ (471 MHz, CDCl_3)

δ 72.2 (s, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 162.5, 161.9, 146.1, 105.3, 100.3, 85.6 (d, $J = 24.2$ Hz), 55.7, 41.4, 17.7. **HRMS-ESI** (m/z) calcd. for $[\text{C}_{12}\text{H}_{17}\text{FNO}_4\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 290.0857, found: 290.0863.

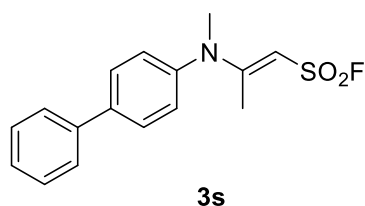


(*E*)-2-(methyl(3,4,5-trifluorophenyl)amino)prop-1-ene-1-sulfonyl fluoride (**3q**). White solid, 219 mg, 83% yield. M.p. 89–91 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. ^1H NMR (500 MHz, CDCl_3) δ 6.88 – 6.85 (m, 2H), 5.11 (s, 1H), 3.23 (s, 3H), 2.21 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ 71.9 (s, 1F), -130.39 (dd, $J_1 = 20.3$, $J_2 = 7.1$ Hz, 2F), -158.52 – -158.62 (m, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 161.8, 151.8 (dq, $J_1 = 254.8$ Hz, $J_2 = 5.04$ Hz), 140.0 (dt, $J_1 = 255.7$ Hz, $J_2 = 15.0$ Hz), 139.8 – 139.6 (m), 112.5 (dd, $J_1 = 16.8$ Hz, $J_2 = 5.7$ Hz), 88.7 (d, $J = 25.2$ Hz), 41.5, 17.7. **HRMS-ESI** (m/z) calcd. for $[\text{C}_{10}\text{H}_{10}\text{F}_4\text{NO}_2\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 284.0363, found: 284.0359.

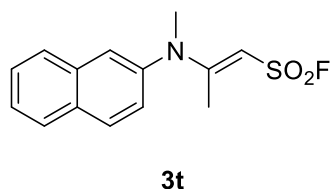


(*E*)-2-(methyl(3,4,5-trimethoxyphenyl)amino)prop-1-ene-1-sulfonyl fluoride (**3r**). White solid, 303 mg, 95% yield. M.p. 156–158 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. ^1H NMR (500 MHz, CDCl_3) δ 6.34 (s, 2H), 5.04 (s, 1H), 3.86 (s, 3H), 3.85 (s, 6H), 3.24 (s, 3H), 2.23 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ 72.3 (s, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 162.7, 154.2, 140.1, 138.1, 104.3, 85.5 (d, $J = 24.3$ Hz), 61.1, 56.5, 41.6, 17.7. **HRMS-ESI** (m/z) calcd. for $[\text{C}_{13}\text{H}_{19}\text{FNO}_5\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 320.0962,

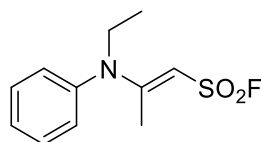
found: 320.0957.



(E)-2-([1,1'-biphenyl]-4-yl(methyl)amino)prop-1-ene-1-sulfonyl fluoride (**3s**). White solid, 280 mg, 92% yield. M.p. 131–133 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.66 (d, $J = 8.5$ Hz, 2H), 7.59 (d, $J = 7.0$ Hz, 2H), 7.48 (t, $J = 8.0$ Hz, 2H), 7.40 (t, $J = 7.5$ Hz, 1H), 7.21 (d, $J = 8.5$ Hz, 2H), 5.11 (s, 1H), 3.30 (s, 3H), 2.25 (s, 3H). $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ 72.3 (s, 1F). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 162.6, 143.6, 141.5, 139.8, 129.1, 128.9, 128.1, 127.4, 127.2, 86.1 (d, $J = 24.2$ Hz), 41.7, 18.0. **HRMS-ESI** (m/z) calcd. for $[\text{C}_{16}\text{H}_{17}\text{FNO}_2\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 306.0959, found: 306.0964.

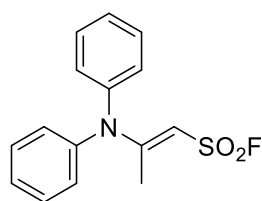


(E)-2-(methyl(naphthalen-2-yl)amino)prop-1-ene-1-sulfonyl fluoride (**3t**). White solid, 253 mg, 91% yield. M.p. 121–123 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.99 – 7.88 (m, 3H), 7.67 (s, 1H), 7.63 – 7.61 (m, 2H), 7.31 – 7.24 (m, 1H), 5.18 (s, 1H), 3.39 (s, 3H), 2.29 (s, 3H). $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ 72.4 (s, 1F). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 162.7, 141.8, 133.7, 132.6, 130.5, 128.0, 128.0, 127.4, 127.3, 125.7, 124.6, 86.0 (d, $J = 24.1$ Hz), 41.7, 18.0. **HRMS-ESI** (m/z) calcd. for $[\text{C}_{14}\text{H}_{15}\text{FNO}_2\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 280.0802, found: 280.0798.



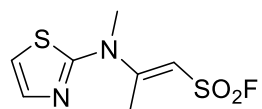
3u

(E)-2-(ethyl(phenyl)amino)prop-1-ene-1-sulfonyl fluoride (**3u**). White solid, 217 mg, 95% yield. M.p. 79–81 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.62 (t, $J = 7.5$ Hz, 2H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.27 (d, $J = 7.0$ Hz, 2H), 5.17 (s, 1H), 3.80 (q, $J = 7.0$ Hz, 2H), 2.35 (s, 3H), 1.36 (t, $J = 7.5$ Hz, 3H). $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ 72.6 (s, 1F). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 162.0, 142.8, 130.3, 128.6, 127.9, 84.8 (d, $J = 23.9$ Hz), 48.4, 17.7, 12.0. **HRMS-ESI** (m/z) calcd. for $[\text{C}_{11}\text{H}_{15}\text{FNO}_2\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 244.0802, found: 244.0792.



3v

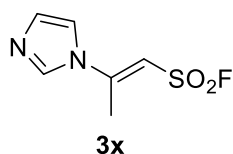
(E)-2-(diphenylamino)prop-1-ene-1-sulfonyl fluoride (**3v**). White solid, 198 mg, 68% yield. M.p. 103–105 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.45 (t, $J = 7.5$ Hz, 4H), 7.35 (t, $J = 7.5$ Hz, 2H), 7.27 (d, $J = 7.0$ Hz, 4H), 5.12 (s, 1H), 2.36 (s, 3H). $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ 71.9 (s, 1F). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 163.0, 143.3, 130.3, 128.2, 127.9, 90.9 (d, $J = 24.4$ Hz), 18.5. **HRMS-ESI** (m/z) calcd. for $[\text{C}_{15}\text{H}_{15}\text{FNO}_2\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 292.0802, found: 292.0811.



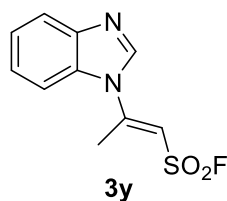
3w

(E)-2-(methyl(thiazol-2-yl)amino)prop-1-ene-1-sulfonyl fluoride (**3w**). Light yellow

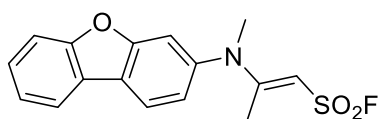
solid, 186 mg, 79% yield. M.p. 158–160 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 3:1 (v/v) as eluent. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.60 (d, $J = 3.6$ Hz, 1H), 7.31 (d, $J = 3.6$ Hz, 1H), 5.57 (s, 1H), 3.37 (s, 3H), 2.36 (s, 3H). $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ 71.4 (s, 1F). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 164.4, 161.3, 140.4, 119.8, 93.1 (d, $J = 25.4$ Hz), 41.4, 17.8. **HRMS-ESI** (m/z) calcd. for $[\text{C}_7\text{H}_{10}\text{FN}_2\text{O}_2\text{S}_2]^+$ ($[\text{M}+\text{H}]^+$): 237.0162, found: 237.0165.



(*E*)-2-(1*H*-imidazol-1-yl)prop-1-ene-1-sulfonyl fluoride (**3x**). Light yellow solid, 154 mg, 81% yield. M.p. 135–137 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 5:1 (v/v) as eluent. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.93 (s, 1H), 7.25 (t, $J = 1.6$ Hz, 1H), 7.21 (d, $J = 1.5$ Hz, 1H), 6.54 (s, 1H), 2.74 (s, 3H). $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ 67.0 (s, 1F). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 151.1 (d, $J = 2.7$ Hz), 135.6, 132.5, 116.6, 108.6 (d, $J = 29.5$ Hz), 17.0. **HRMS-ESI** (m/z) calcd. for $[\text{C}_6\text{H}_8\text{FN}_2\text{O}_2\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 191.0285, found: 191.0285.



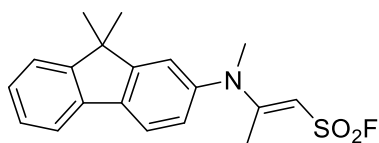
(*E*)-2-(1*H*-benzo[*d*]imidazol-1-yl)prop-1-ene-1-sulfonyl fluoride (**3y**). Light yellow solid, 134 mg, 56% yield. M.p. 158–160 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 5:1 (v/v) as eluent. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.18 (s, 1H), 7.87 (dd, $J = 7.6, 1.9$ Hz, 1H), 7.67 – 7.64 (m, 1H), 7.49 – 7.40 (m, 2H), 6.76 (s, 1H), 2.90 (s, 3H). $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ 70.0 (s, 1F). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 151.9 (d, $J = 2.4$ Hz), 145.1, 140.7, 131.6, 125.7, 125.0, 121.9, 112.4, 110.8 (d, $J = 29.2$ Hz), 18.5. **HRMS-ESI** (m/z) calcd. for $[\text{C}_{10}\text{H}_{10}\text{FN}_2\text{O}_2\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 241.0442, found: 241.0443.



3z

(E)-2-((dibenzo[*b,d*]furan-3-yl(methyl)amino)prop-1-ene-1-sulfonyl fluoride (**3u**).

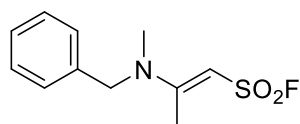
Light yellow solid, 293 mg, 92% yield. M.p. 154–156 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 7:1 (v/v) as eluent. ¹H NMR (500 MHz, CDCl₃) δ 7.99 (dd, *J*₁ = 13.5 Hz, *J*₂ = 8.5 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.42 – 7.37 (m, 2H), 7.13 (dd, *J*₁ = 8.5 Hz, *J*₂ = 2.0 Hz, 1H), 5.14 (s, 1H), 3.34 (s, 3H), 2.24 (s, 3H). ¹⁹F NMR (471 MHz, CDCl₃) δ 72.2 (s, 1F). ¹³C NMR (126 MHz, CDCl₃) δ 162.6, 157.2, 156.5, 143.3, 128.2, 124.6, 123.5, 123.3, 121.9, 121.8, 121.0, 112.1, 110.8, 86.5 (d, *J* = 24.6 Hz), 42.0, 18.0. HRMS-ESI (m/z) calcd. for [C₁₆H₁₅FNO₃S]⁺ ([M+H]⁺): 320.0751, found: 320.0755.



3aa

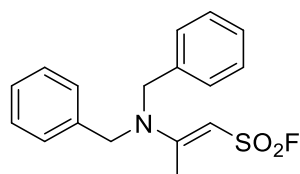
(E)-2-((9,9-dimethyl-9H-fluoren-2-yl)(methyl)amino)prop-1-ene-1-sulfonyl fluoride

(**3t**). Light yellow solid, 314 mg, 91% yield. M.p. 115–117 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. ¹H NMR (500 MHz, CDCl₃) δ 7.77 – 7.73 (m, 2H), 7.48 – 7.46 (m, 1H), 7.38 – 7.37 (m, 2H), 7.19 (d, *J* = 2.0 Hz, 1H), 7.10 (dd, *J*₁ = 8.0 Hz, *J*₂ = 2.0 Hz, 1H), 5.13 (s, 1H), 3.32 (s, 3H), 2.24 (s, 3H), 1.51 (s, 6H). ¹⁹F NMR (471 MHz, CDCl₃) δ 72.4 (s, 1F). ¹³C NMR (126 MHz, CDCl₃) δ 162.7, 155.8, 153.9, 143.5, 139.5, 137.8, 128.1, 127.4, 125.8, 122.6, 121.3, 121.2, 120.4, 85.5 (d, *J* = 24.2 Hz), 47.3, 41.9, 27.1, 18.0. HRMS-ESI (m/z) calcd. for [C₁₉H₂₁FNO₂S]⁺ ([M+H]⁺): 346.1272, found: 346.1265.



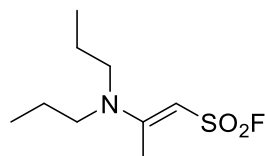
3ab

(*E*)-2-(benzyl(methyl)amino)prop-1-ene-1-sulfonyl fluoride (**3aa**). White solid, 192 mg, 79% yield. M.p. 94–96 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.39 (t, $J = 8.0$ Hz, 2H), 7.33 (t, $J = 7.0$ Hz, 1H), 7.11 (d, $J = 7.0$ Hz, 2H), 5.01 (s, 1H), 4.57 (s, 2H), 2.98 (s, 3H), 2.43 (s, 3H). $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ 73.0 (s, 1F). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 162.8, 129.3, 128.2, 126.3, 84.2 (d, $J = 24.2$ Hz), 55.9, 39.2, 16.4. **HRMS-ESI** (m/z) calcd. for $[\text{C}_{11}\text{H}_{15}\text{FNO}_2\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 244.0802, found: 244.0812.



3ac

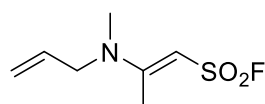
(*E*)-2-(dibenzylamino)prop-1-ene-1-sulfonyl fluoride (**3ab**). White solid, 277 mg, 87% yield. M.p. 105–107 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.40 (t, $J = 8.0$ Hz, 4H), 7.34 (t, $J = 7.5$ Hz, 2H), 7.14 (d, $J = 7.1$ Hz, 4H), 5.16 (s, 1H), 4.57 (s, 4H), 2.52 (s, 3H). $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ 73.0 (s, 1F). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 162.9, 134.7, 129.4, 128.2, 126.4, 85.4 (d, $J = 24.3$ Hz), 54.0, 16.6. **HRMS-ESI** (m/z) calcd. for $[\text{C}_{17}\text{H}_{19}\text{FNO}_2\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 320.1117, found: 320.1115.



3ad

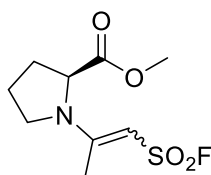
(*E*)-2-(dipropylamino)prop-1-ene-1-sulfonyl fluoride (**3ac**). White solid, 187 mg, 84%

yield. M.p. 47–49 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 4.83 (s, 1H), 3.18 (t, $J = 7.5$ Hz, 4H), 2.34 (s, 3H), 1.66 – 1.59 (m, 4H), 0.93 (t, $J = 7.5$ Hz, 6H). $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ 73.1 (s, 1F). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 161.5, 82.0 (d, $J = 23.7$ Hz), 52.9, 16.2, 11.3. **HRMS-ESI** (m/z) calcd. for $[\text{C}_9\text{H}_{19}\text{FNO}_2\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 224.1115, found: 224.1120.



3ae

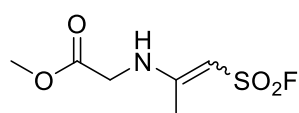
(*E*)-2-(allyl(methyl)amino)prop-1-ene-1-sulfonyl fluoride (**3ad**). White solid, 194 mg, 75% yield. M.p. 46–48 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 5.79 – 5.72 (m, 1H), 5.27 (d, $J = 10.5$ Hz, 1H), 5.12 (d, $J = 17.0$ Hz, 1H), 4.91 (s, 1H), 3.93 (s, 2H), 2.95 (s, 3H), 2.35 (s, 3H). $^{19}\text{F NMR}$ (471 MHz, CDCl_3) δ 72.9 (s, 1F). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 162.6, 131.3, 117.7, 83.4 (d, $J = 23.7$ Hz), 54.9, 38.8, 16.0. **HRMS-ESI** (m/z) calcd. for $[\text{C}_7\text{H}_{13}\text{FNO}_2\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 194.0646, found: 194.0651.



3af

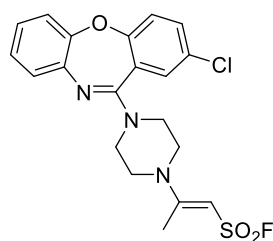
Methyl(*Z/E*) (1-(fluorosulfonyl)prop-1-en-2-yl)glycinate (**3af**). White solid, 202 mg, 81% yield. M.p. 66–68 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. $^1\text{H NMR}$ (500 MHz, $\text{DMSO}-d_6$) δ 5.06 (s, 2.2H), 4.92 – 4.79 (m, 2.2H), 4.70 (s, 1H), 4.44 (dd, $J = 8.9, 2.3$ Hz, 1H), 3.71 (d, $J = 6.0$ Hz, 9.6H), 3.64 – 3.58 (m, 1H), 3.39 – 3.37 (m, 3.21H), 3.29 – 3.24 (m, 2.2H), 2.37 (s, 3H), 2.27 – 2.24 (m, 1H), 2.22 (s, 6.62H), 2.22 – 2.16 (m, 2.25H),

2.16 – 1.76 (m, 10.23H). **¹⁹F NMR** (471 MHz, DMSO-*d*₆) δ 75.2 (s, 1F), 75.1 (s, 1F). **¹³C NMR** (126 MHz, DMSO-*d*₆) δ 172.3, 171.4, 162.3, 161.7, 82.3 (d, *J* = 22.1 Hz), 81.7 (d, *J* = 22.3 Hz), 61.4, 53.2, 52.9, 49.9, 49.8, 30.4, 30.4, 23.4, 23.2, 17.6, 17.1. **HRMS-ESI** (*m/z*) calcd. for [C₉H₁₅FNO₄S]⁺ ([M+H]⁺): 252.0700, found: 252.0698.



3ag

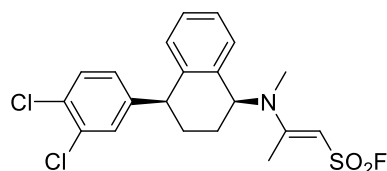
Methyl(Z/E) (1-(fluorosulfonyl)prop-1-en-2-yl) glycinate (3ag). White solid, 184 mg, 87% yield. M.p. 41–43 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 5:1 (v/v) as eluent. **¹H NMR** (500 MHz, DMSO-*d*₆) δ 8.24 (t, *J* = 6.0 Hz, 1H), 7.65 (s, 0.1H), 5.06 (s, 0.1H), 5.04 (s, 1H), 4.21 (d, *J* = 5.8 Hz, 0.2H), 4.03 (d, *J* = 6.0 Hz, 2H), 3.71 (s, 0.3H), 3.70 (s, 3H), 2.24 (s, 3H), 2.05 – 1.89 (m, 0.3H). **¹⁹F NMR** (471 MHz, DMSO-*d*₆) δ 75.0 (s, 1F), 73.2 (s, 1F). **¹³C NMR** (126 MHz, DMSO-*d*₆) δ 170.4, 169.3, 164.1, 163.6, 80.2 (d, *J* = 22.3 Hz), 77.6 (d, *J* = 20.6 Hz), 52.7, 52.5, 45.1, 44.7, 20.0, 19.1. **HRMS-ESI** (*m/z*) calcd. for [C₆H₁₁FNO₄S]⁺ ([M+H]⁺): 212.0387, found: 212.0381.



3ah

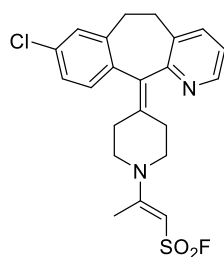
(E)-2-(4-(2-chlorodibenzo[b,f][1,4]oxazepin-11-yl)piperazin-1-yl)prop-1-ene-1-sulfonyl fluoride (3ah). White solid, 379 mg, 87% yield. M.p. 185–187 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 3:1 (v/v) as eluent. **¹H NMR** (500 MHz, CDCl₃) δ 7.44 – 7.42 (m, 1H), 7.31 (d, *J* = 2.5 Hz, 1H), 7.22 (d, *J* = 8.5 Hz, 1H), 7.16 – 7.02 (m, 4H), 5.09 (s, 1H), 3.61 (s, 4H), 3.49 (s, 4H), 2.38 (s, 3H). **¹⁹F NMR** (471 MHz, CDCl₃) δ 73.0 (s, 1F). **¹³C NMR** (126 MHz,

CDCl₃) δ 162.1, 159.5, 158.3, 151.8, 139.7, 133.2, 130.6, 128.8, 127.2, 126.1, 125.4, 124.5, 123.1, 120.4, 86.4 (d, $J = 24.5$ Hz), 46.1, 16.6. **HRMS-ESI** (m/z) calcd. for [C₂₀H₂₀Cl₁FN₃O₃S]⁺ ([M+H]⁺): 436.0892, found: 436.0892.



3ai

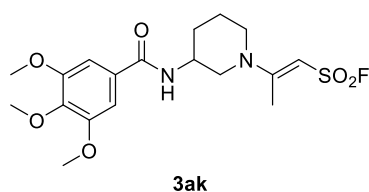
(*E*)-2-(((1*S*,4*S*)-4-(3,4-dichlorophenyl)-1,2,3,4-tetrahydronaphthalen-1-yl)(methyl)amino)prop-1-ene-1-sulfonyl fluoride (**3ai**). White solid, 358 mg, 84% yield. M.p. 176–178 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 3:1 (v/v) as eluent. ¹H NMR (500 MHz, CDCl₃) δ 7.38 – 7.27 (m, 3H), 7.10 – 7.03 (m, 3H), 6.70 (d, $J = 8.5$ Hz, 1H), 5.18 – 5.03 (m, 2H), 4.25 (t, $J = 4.0$ Hz, 1H), 2.64 (s, 3H), 2.53 (s, 3H), 2.34 – 2.28 (m, 1H), 2.13 – 2.10 (m, 1H), 1.85 – 1.77 (m, 1H). ¹⁹F NMR (471 MHz, CDCl₃) δ 73.2 (s, 1F). ¹³C NMR (126 MHz, CDCl₃) δ 162.4, 146.4, 138.1, 135.0, 132.7, 131.5, 130.7, 128.5, 128.2, 128.0, 126.7, 84.6 (d, $J = 24.1$ Hz), 58.4, 42.7, 34.5, 30.0, 23.0, 16.1. **HRMS-ESI** (m/z) calcd. for [C₂₀H₂₁Cl₂FNO₂S]⁺ ([M+H]⁺): 428.0649, found: 428.0645.



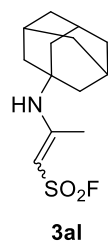
3aj

(*E*)-2-(4-(8-chloro-5,6-dihydro-11*H*-benzo[5,6]cyclohepta[1,2-*b*]pyridin-11-ylidene)piperidin-1-yl)prop-1-ene-1-sulfonyl fluoride (**3aj**). White solid, 341 mg, 79% yield. M.p. 159–161 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 3:1 (v/v) as eluent. ¹H NMR (500 MHz, CDCl₃) δ 8.39 (dd, $J = 3.5, 1.5$ Hz, 1H), 7.46 – 7.44 (m, 1H), 7.19 – 7.10 (m, 4H), 4.94 (s, 1H),

3.61 – 3.52 (m, 2H), 3.37 – 3.23 (m, 4H), 2.89 – 2.76 (m, 2H), 2.62 – 2.56 (m, 1H), 2.45 – 2.37 (m, 2H), 2.33 (s, 3H). ^{19}F NMR (471 MHz, CDCl_3) δ 73.4 (s, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 161.4, 156.2, 146.7, 137.9, 137.3, 135.7, 134.4, 133.4, 130.2, 129.1, 126.3, 122.6, 83.9 (d, $J = 24.1$ Hz), 46.7, 46.6, 46.5, 46.4, 31.6, 31.5, 29.5, 16.5. **HRMS-ESI** (m/z) calcd. for $[\text{C}_7\text{H}_{13}\text{FNO}_2\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 433.1147, found: 433.1147.

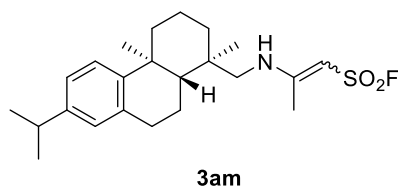


(*E*)-2-(3-(3,4,5-trimethoxybenzamido)piperidin-1-yl)prop-1-ene-1-sulfonyl fluoride (**3ak**). White solid, 379 mg, 91% yield. M.p. 177–179 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 10:1 (v/v) as eluent. ^1H NMR (500 MHz, CDCl_3) δ 7.0 (s, 2H), 6.29 (d, $J = 7.0$ Hz, 1H), 5.12 (s, 1H), 4.05 – 4.00 (m, 1H), 3.94 – 3.91 (m, 1H), 3.87 (s, 6H), 3.85 (s, 3H), 3.59 – 3.56 (m, 1H), 3.15 – 3.09 (m, 1H), 2.33 (s, 3H), 2.13 – 2.09 (m, 1H), 1.87 – 1.82 (m, 1H), 1.75 – 1.64 (m, 2H). ^{19}F NMR (471 MHz, CDCl_3) δ 73.6 (s, 1F). ^{13}C NMR (126 MHz, CDCl_3) δ 167.3, 162.0, 153.3, 141.2, 129.4, 104.5, 84.8 (d, $J = 22.9$ Hz), 61.0, 56.4, 51.6, 47.7, 46.8, 29.6, 21.1, 16.6. **HRMS-ESI** (m/z) calcd. for $[\text{C}_7\text{H}_{13}\text{FNO}_2\text{S}]^+$ ($[\text{M}+\text{H}]^+$): 417.1490, found: 417.1493.



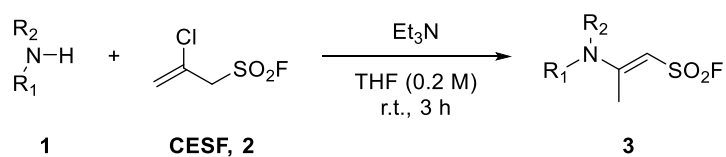
(*Z/E*)-2-(adamantan-1-ylamino)prop-1-ene-1-sulfonyl fluoride (**3al**). White solid, 196 mg, 72% yield. M.p. 196–198 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 3:1 (v/v) as eluent. ^1H NMR (500 MHz, CDCl_3) δ 7.15 (s, 0.65H), 5.18 (s, 1H), 4.54 (s, 1H), 4.48 (d, $J = 3.5$ Hz, 0.64H), 2.26

(s, 3H), 2.16 – 2.14 (m, 6.92H), 1.95 – 1.94 (m, 9.91H), 1.74 – 1.65 (m, 11.36H). ¹⁹F NMR (471 MHz, CDCl₃) δ 72.4 (s, 1F), 72.3 (s, 1F). ¹³C NMR (126 MHz, CDCl₃) δ 162.3, 158.5, 83.8 (d, *J* = 24.1 Hz), 78.2 (d, *J* = 23.6 Hz), 54.9, 54.0, 43.4, 41.2, 36.1, 36.0, 29.6, 29.4, 22.1, 22.0. HRMS-ESI (m/z) calcd. for [C₁₃H₂₁FNO₂S]⁺ ([M+H]⁺): 274.1272, found: 274.1272.



(*Z/E*)-2-((((1*R*,4*aS*,10*aR*)-7-isopropyl-1,4*a*-dimethyl-1,2,3,4,4*a*,9,10,10*a*-octahydrophenanthren-1-yl)methyl)amino)prop-1-ene-1-sulfonyl fluoride (**3am**). White solid, 341 mg, 84% yield. M.p. 116–118 °C. Purification by column chromatography on silica gel using petroleum ether / ethyl acetate = 2:1 (v/v) as eluent. ¹H NMR (500 MHz, CDCl₃) δ 7.30 (t, *J* = 6.0 Hz, 2.39H), 7.20 – 7.17 (m, 3.37H), 7.04 – 7.00 (m, 3.37H), 6.94 – 6.90 (m, 3.38H), 4.99 (s, 1H), 4.71 (s, 1H), 4.62 (d, *J* = 3.5 Hz, 2.35H), 3.25 – 3.21 (m, 2.32H), 3.02 – 2.81 (m, 14.34H), 3.38 – 2.30 (m, 6.58H), 2.01 – 2.00 (m, 7.0H), 1.85 – 1.70 (m, 13.54H), 1.59 – 1.55 (m, 3.4H), 1.52 – 1.48 (m, 1.01 H), 1.47 – 1.39 (m, 6.90 H), 1.27 – 1.22 (m, 34.10H), 1.03 (s, 2.98H), 1.00 (s, 7.06H). ¹⁹F NMR (471 MHz, CDCl₃) δ 72.9 (s, 1F), 72.7 (s, 1F). ¹³C NMR (126 MHz, CDCl₃) δ 162.1, 161.4, 146.8, 146.7, 146.2, 145.9, 134.4, 134.3, 127.1, 127.0, 124.4, 124.3, 124.2, 124.2, 82.4 (d, *J* = 25.6 Hz), 77.78 (d, *J* = 23.9 Hz), 55.3, 54.6, 46.7, 45.9, 38.3, 38.3, 38.0, 37.7, 37.6, 37.2, 36.5, 36.3, 33.6, 30.2, 29.9, 25.5, 25.3, 24.1, 24.1, 20.5, 19.4, 19.2, 19.1, 18.6, 18.5, 18.1, 18.0. HRMS-ESI (m/z) calcd. for [C₇H₁₃FNO₂S]⁺ ([M+H]⁺): 408.2367, found: 408.2369.

5. Procedure for Scale-up Reaction of *N*-ESF (**3**)



An oven-dried reaction tube (50 mL) equipped with a magnetic stirring bar was charged with amines (**1**, 6.0 mmol, 1.0 equiv.) and CESF (**2**, 1.14 g, 7.2 mmol, 1.2 equiv.), 30.0 mL THF. After stirring evenly, trimethylamine (0.73 g, 7.2 mmol, 1.2 equiv.) was added to the above solution slowly with stirring, and the mixed solution became turbid slowly. The mixture was stirred at room temperature under an air atmosphere for 3 h monitored by TLC. After the reaction was completed, water (50 mL) was added to the mixture and the reaction mixture was extracted with ethyl acetate (3×20 mL). The extracts were dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as eluents to afford the target product **3**.

6. NOESY of (*E*)-2-(methyl(phenyl)amino)prop-1-ene-1-sulfonyl fluoride (**3a**)

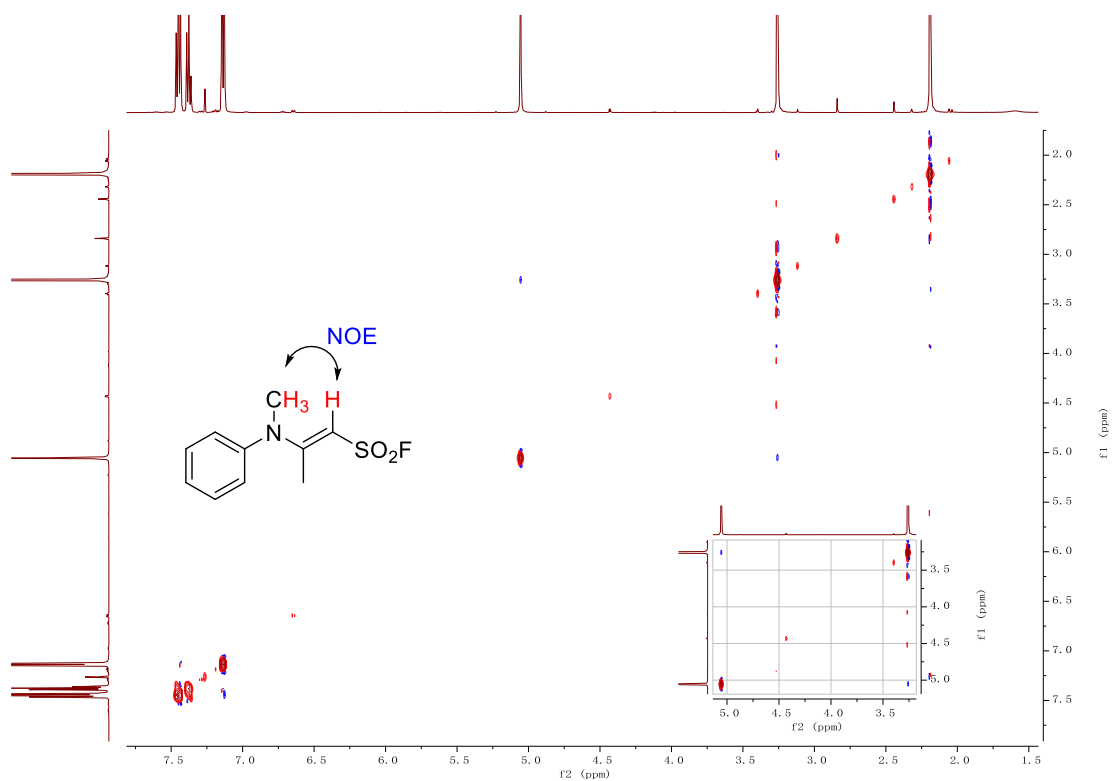


Figure S1 NOESY spectrum of compound **3a** (in CDCl₃)

7. References

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8. NMR Spectra

