Supporting Information

1-Bromoethene-1-Sulfonyl Fluoride (1-Br-ESF), a New SuFEx Clickable Reagent, and the Application for Regioselective Construction of 5-Sulfonylfluoro Isoxazoles

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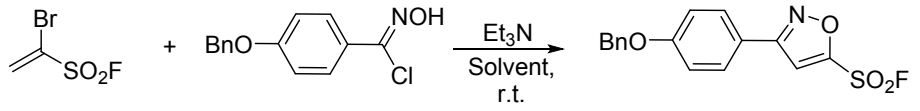
1. General considerations

All reactions were carried out under an air atmosphere. Unless otherwise specified, NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a 500 MHz (for ^1H), 471 MHz (for ^{19}F), or 126 MHz (for ^{13}C) spectrometer. The chemical shifts converted to the TMS scale ($CDCl_3$: δ H = 7.26 ppm, δ C = 77.16 ppm; DMSO-d_6: δ H = 2.50 ppm, δ C = 39.52 ppm). Data for ^{19}F NMR was reported in terms of chemical shift (ppm) relative to added internal standard ($CFCl_3$ at 0 ppm). All coupling constants (*J* values) were reported in Hertz (Hz). The HPLC experiments were carried out on a Waters e2695 instrument (column: J&K, RP-C18, 5 μm, 4.6 × 150 mm), and the yields of the products were determined by using the corresponding pure compounds as the external standards. The following abbreviations are used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Melting points are reported uncorrected. MS experiments were performed on a TOF-Q ESI or CI/EI instrument. Reagents used in the reactions were all purchased from commercial sources and used without further purification.

2. Optimization of the reaction conditions

Table 1 Screening of solvents [a]

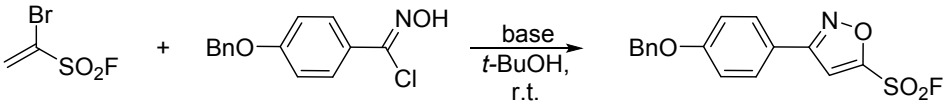


2 **3b** **4b**

Entry	Solvent	Et_3N (mmol)	Yield [b] (%)
1	DCM	0.5	16
2	Toluene	0.5	16
3	DMF	0.5	2
4	H_2O	0.5	0
5	THF	0.5	6
6	1,4-Dioxane	0.5	1
7	MeOH	0.5	0
8	Acetone	0.5	12
9	EtOH	0.5	0
10	DMSO	0.5	5
11	***t*-BuOH**	**0.5**	**20**

Conditions: [a] **3b** (1.5 equiv., 0.15 mmol, 39 mg), **2** (1.0 equiv., 0.1 mmol, 18.9 mg), triethylamine (5 equiv., 0.5 mmol, 50 mg), solvent (2 mL) were mixed in a tube; [b] the yield was determined by HPLC using **4b** as the external standard. [$t_{\mathbf{4b}}$ = 9.416 min, λ_{max} = 240.5 nm, methanol / water = 80 : 20 (v / v)].

Table 2 Screening of inorganic base [a]



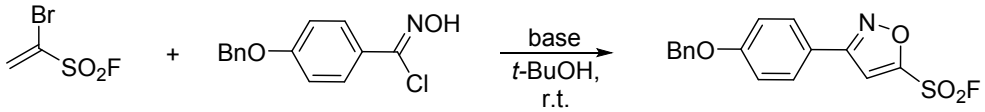
2 **3b** **4b**

Entry	Base (mmol)	Yield [b] (%)
1	$NaHCO_3$	<1
2	$NaHSO_3$	n.d.
3	NaOAc	9
4	NaH_2PO_4	n.d.
5	$KHCO_3$	n.d.
6	K_3PO_4	5

7	K_2HPO_4	n.d.
8	KH_2PO_4	n.d.
9	KF	<1
10	$NaCO_3$	<1
11	$KHSO_4$	n.d.
12	K_2CO_3	<1
13	KOAc	1
14	KHF_2	n.d.
15	$Na_3PO_4{\cdot}12H_2O$	n.d.
16	LiOAc	6

Conditions: [a] **3b** (1.5 equiv., 0.15 mmol, 39 mg), **2** (1.0 equiv., 0.1 mmol, 18.9 mg), base (5 equiv., 0.5 mmol), *t*-BuOH (2 mL) were mixed in a tube; [b] the yield was determined by HPLC using **4b** as the external standard. [$t_{\mathbf{4b}}$ = 9.416 min, λ_{max} = 240.5 nm, methanol / water = 80 : 20 (v / v)].

Table 3 Screening of organic base [a]

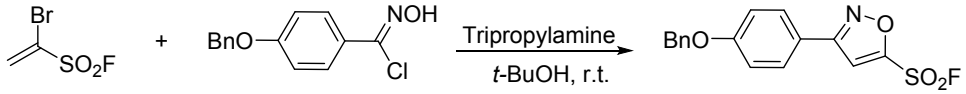


2 **3b** **4b**

Entry	Base (mmol)	Yield [b] (%)
1	TMEDA	20
2	**Tripropylamine**	**39**
3	DABCO	<1
4	Et_3N	20
5	DIPEA	14
6	DBU	12

Conditions: [a] **3b** (1.5 equiv., 0.75 mmol, 130 mg), **2** (1.0 equiv., 0.5 mmol, 95 mg), base (5 equiv., 2.5 mmol), *t*-BuOH (2 mL) were mixed in a tube; [b] isolated yield.

Table 4 Screening of reaction ratio [a]

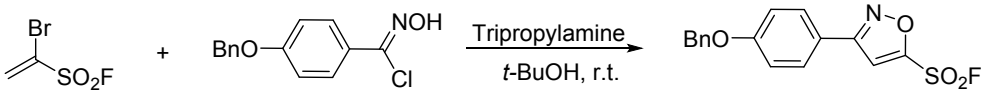


2 **3b** **4b**

Entry	**3b** (mmol)	**2** (mmol)	Yield (%) [b]
1	0.5	0.5	16
2	0.5	1.0	38
3	0.5	1.5	37
4	0.5	2.0	47
5	0.5	2.5	32
6 [c]	0.5	2.0	55
7 [d]	**0.5**	**2.0**	**57**

Conditions: [a] **3b** (0.5 mmol, 130 mg), **2**, tripropylamine (2.5 mmol, 358 mg), *t*-BuOH (4 mL) were mixed in a tube; [b] isolated yield; [c] tripropylamine was dissolved in another 2 mL *t*-BuOH and added to the reaction mixture dropwise; [d] **2** was dissolved in another 2 mL *t*-BuOH and added to the reaction mixture dropwise.

Table 5 Screening of loading of base [a]



2 **3b** **4b**

Entry	Tripropylamine (mmol)	Yield (%) [b]
1	0.5	32
2	1.0	62
3	**1.25**	**57**
4	**1.5**	**61**
5	2	39
6[c]	**1.25**	**80**

Conditions: [a] **3b (**0.5 mmol, 130 mg**)**, **2** (2.0 mmol, 378 mg), tripropylamine, *t*-BuOH (4 mL) were mixed in a tube; [b] isolated yield; [c] **2** was dissolved in another 2 mL *t*-BuOH and added to the reaction mixture dropwise.

3. General procedure for synthesis of starting materials

3.1 General procedure for synthesis of starting chlorooximes 3

3a-3u were prepared according to the literature,[1-4] All homemade starting materials are identical to those reported regarding the ^{1}H and ^{13}C NMR and melting points (if applicable).

3.2 General procedure for synthesis of 1-bromoethene-1-sulfonyl fluoride 2

Ethenesulfonyl fluoride,[5] 33 g (300 mmol) was dissolved in 300 mL CH_2Cl_2 and placed in a 500 mL round-bottom flask equipped with a stirred bar under the irradiation of 50 W white light. To the flask was added 96 g (600 mmol, 31 mL) bromine in three portions in 30 minutes, the reaction was stirred for about 12-16 hours. When the flask was swirled, the temperature rose rapidly to about 45 ^{o}C, the flask was cooled under ice-bath to maintain the temperature at near 25 ^{o}C. The reaction was monitored by TLC using $KMnO_4$ as chromogenic agent. After the ethenesulfonyl fluoride was completely consumed, the mixture turned dark orange, the solution was washed with sodium thiosulfate solution until the color turned light yellow. Then dried over anhydrous Na_2SO_4, and concentrated to dryness. The residue was dissolved in 250 mL dry ether, and the mixture was cooled to -50 ^{o}C. A solution of 31 g (300 mmol) of triethylamine in 60 mL dry ether was added in 30 minutes blow -40 ^{o}C. The mixture reacted vigorously to precipitate triethylamine hydrobromide. After warming slowly to room temperature with stirring, dilute sulfuric acid was added and the layers were separated. The layers were washed with acid, water and saturated sodium chloride solution, dried with anhydrous Na_2SO_4, concentrated to dryness. The residue was purified by reduced pressure distillation. The product weighed 41.4 g, 73 %.

4. General procedure for synthesis of 4, 7, 12 and 13

4.1 General procedure for synthesis of 4

An oven-dried reaction tube (20 mL) was charged with chlorooximes (**3**, 1.0 mmol), tripropylamine (358 mg, 2.5 mmol, 2.5 equiv.), 5 mL *t*-BuOH, the reaction mixture was stirred at room temperature. Then 1-bromoethene-1-sulfonyl fluoride (**2**, 756 mg, 4.0 mmol, 4.0 equiv.) dissolved in another 5 mL *t*-BuOH was added dropwise for a period of 30 minutes. The resulting mixture was stirred at room temperature for 1-2 h with monitoring by TLC. The solution was washed with water and extracted with dichloromethane (3 × 10 mL), the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. The residue was purified through silica gel chromatography using a mixture of ethyl acetate and petroleum ether from 5 % ethyl acetate / petroleum ether to 20 % ethyl acetate / petroleum ether to afford the desired products **4**.

4.2 General procedure for synthesis of 7

An oven-dried reaction tube (20 mL) was charged with aniline (**6**, 1.0 mmol, 93 mg), 1-bromoethene-1-sulfonyl fluoride (**2**, 2.05 mmol, 388 mg) and HOAc (3 mL). The resulting mixture was stirred at 50 ^oC for 10 h. The solution was washed with water and extracted with dichloromethane (3 × 10 mL), the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. The residue was purified by column chromatography on silica gel using 20 % ethyl acetate / petroleum ether as eluents to give the desired product **7** (264 mg, 94 %).

4.3 General procedure for synthesis of (*Z*)-1-bromo-2-phenylethene-1-sulfonyl fluoride 12

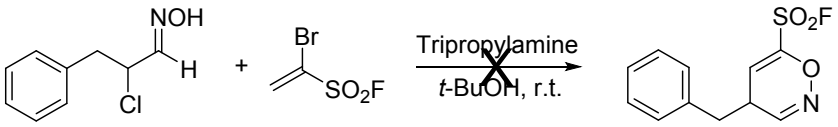
(*E*)-2-phenylethene-1-sulfonyl fluoride,[6] 1.86 g (10 mmol) was dissolved in 10 mL CH_2Cl_2 and placed in a 50 mL round-bottom flask equipped with a stirred bar under the irradiation of 50 W white light. To the flask was added 3.2 g (20 mmol, 1.02 mL) bromine in three portions in 10 minutes and the reaction was stirred for about 12-16 hours. When the flask was swirled, the temperature rose rapidly to about 45 ^oC, the

flask was cooled under ice-bath to maintain the temperature at near 25 °C. The reaction was monitored by TLC using $KMnO_4$ as chromogenic agent. After the (*E*)-2-phenylethene-1-sulfonyl fluoride was completely consumed, the mixture turned dark orange, the solution was washed with sodium thiosulfate solution until the color turned light yellow. Then dried over anhydrous Na_2SO_4, and concentrated to dryness. The residue was dissolved in 10 mL dry ether, and the mixture was cooled to -50 °C. A solution of 1.01 g (10 mmol) of triethylamine in 2 mL dry ether was added dropwise in 10 minutes blow -40 °C. The mixture reacted vigorously to precipitate triethylamine hydrobromide. After warming slowly to room temperature with stirring, dilute sulfuric acid was added and the layers were separated. The layers were washed with acid, water and saturated sodium chloride solution, dried with anhydrous Na_2SO_4 and concentrated to crude product. The pure product was obtained by column chromatography on silica gel using 10 % ethyl acetate / petroleum ether as eluents. Pure product **12** weighed 1.40 g, 53 %.

4.4 General procedure for synthesis of 13

An oven-dried reaction tube (20 mL) was charged with phenylboronic acid (**11**, 1.5 mmol, 183 mg), tri-*o*-tolylphosphine (30 mg, 10 mol%), $Pd_2(dba)_3$(45 mg, 5 mol%), K_3PO_4(425 mg, 2 equiv.), the reaction tube was then capped with a rubber septum and placed under a nitrogen atmosphere (through a needle attached to a vacuum manifold). 5 mL toluene and 1-bromoethene-1-sulfonyl fluoride (**2**, 189 mg, 1.0 mmol, 1.0 equiv.) were then added using syringes. The resulting mixture was stirred at 50 °C for 15-24 h with monitoring by TLC. The solution was concentrated to dryness and purified through silica gel chromatography using 2.5 % ethyl acetate / petroleum ether as eluents to afford the desired product **13** (116 mg, 62 %).

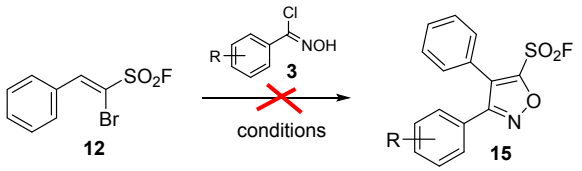
5. Attempt for the synthesis of six-membered ring product 4-benzyl-4H-1,2-oxazine-6-sulfonyl fluoride 17



16 **2** **17**

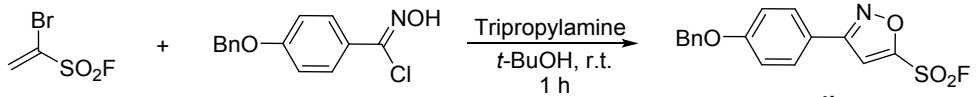
An oven-dried reaction tube (20 mL) was charged with 2-chloro-3-phenylpropanal oxime[7, 8] (**16**, 1.0 mmol), tripropylamine (358 mg, 2.5 mmol, 2.5 equiv.), 5 mL *t*-BuOH, the reaction mixture was stirred at room temperature. Then 1-bromoethene-1-sulfonyl fluoride (**2**, 756 mg, 4.0 mmol, 4.0 equiv.) dissolved in another 5 mL *t*-BuOH was added dropwise for a period of 30 minutes. The resulting mixture was stirred at room temperature for 2 h with monitoring by TLC. It was found that the starting material **16** was consumed completely, while no **17** was observed, only a mixture of many nonisolatable or unidentified products were formed.

6. Attempt for the synthesis of trisubstituted isoxazole 15



An oven-dried reaction tube (20 mL) was charged with chlorooximes (**3**, 0.5 mmol), tripropylamine (179 mg, 1.25 mmol, 2.5 equiv.), 5 mL *t*-BuOH, the reaction mixture was stirred at room temperature. Then (*Z*)-1-bromo-2-phenylethene-1-sulfonyl fluoride (**12**, 530 mg, 2.0 mmol, 4.0 equiv.) dissolved in another 5 mL *t*-BuOH was added dropwise for a period of 30 minutes. The resulting mixture was stirred at room temperature for 12 h with monitoring by TLC, the two starting materials were not consumed at all and no desired **15** was formed. Then the reaction was heated to 60 °C and stirred for another 12 h, still no trisubstituted isoxazole **15** was observed.

7. Multigram scale synthesis of 4b



2
32 mmol, 6.05 g

3b
8 mmol, 2.09 g

4b
2.05 g, 77 %

An oven-dried round-bottom flask (250 mL) was charged with 4-(benzyloxy)-*N*-hydroxybenzimidoyl chloride **3b** (8.0 mmol, 2.09 g), tripropylamine (2.86 g, 20 mmol, 2.5 equiv.), 50 mL *t*-BuOH, the reaction mixture was stirred at room temperature. Then 1-bromoethene-1-sulfonyl fluoride (**2**, 6.05 g, 32.0 mmol, 4.0 equiv.) dissolved in another 50 mL *t*-BuOH was added dropwise for a period of 30 minutes. The resulting mixture was stirred at room temperature for 1 h with monitoring by TLC. The solution was washed with water and extracted with dichloromethane (3 × 80 mL), the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated to dryness. The residue was purified through silica gel chromatography using 20 % ethyl acetate / petroleum ether as eluents to afford the desired product **4b** (77 %, 2.05 g).

8. References

[1] K.-C. Liu, B. R. Shelton, R. K. Howe, *J. Org. Chem.* **1980**, *45*, 3916.

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[3] A. Vörös, Z. Baán, P. Mizsey, Z. Finta, *Org. Process Res. Dev.* **2012**, *16*, 1717.

[4] M. Kocevar, S. Polanc, M. Sollner, M. Tisler, B. Vercek, *Synth. Commun.* **1988**, *18*, 1427.

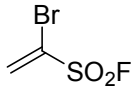
[5] Q. Zheng, J. Dong, K. B. Sharpless, *J. Org. Chem.* **2016**, *81*, 11360.

[6] G.-F. Zha, Q. Zheng, J. Leng, P. Wu, H.-L. Qin, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2017**, *56*, 4849.

[7] T. Borg, J. Danielsson, M. Mohiti, P. Restorp, P. Somfai, *Adv. Synth. Catal.* **2011**, *353*, 2022.

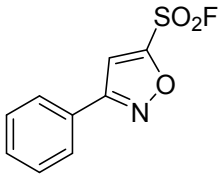
[8] R. Sengupta, S. M. Weinreb, *Synthesis*, **2012**, *44*, 2933.

9. NMR spectra of 2, 4, 7 and 13



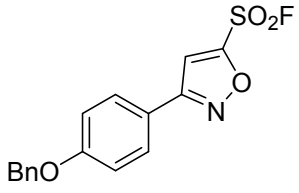
2

1-Bromoethene-1-sulfonyl fluoride (**2**). Colorless liquid, 41.4 g, 220 mmol, 73 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (d, J = 3.7 Hz, 1H), 6.59 (t, J = 4.1 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 48.8 (d, J = 5.4 Hz, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.9 (d, J = 2.2 Hz), 119.4 (d, J = 34.0 Hz). ESI-MS HRMS calculated for $C_2H_3FO_2SBr$ $[M+H]^+$ 188.9016, found 188.9016.



4a

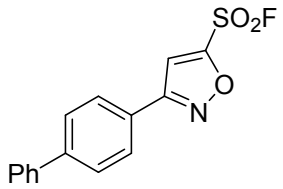
3-Phenylisoxazole-5-sulfonyl fluoride (**4a**). White solid, 188 mg, 83%. M.p. 69-70 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 7.2 Hz, 2H), 7.56–7.52 (m, 3H), 7.47 (s, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 64.0 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3 (s), 158.8 (d, J = 39.0 Hz), 131.8 (s), 129.6 (s), 127.2 (s), 126.4 (s), 110.4 (d, J = 3.5 Hz). ESI-MS HRMS calculated for $C_9H_7FNO_3S$ $[M+H]^+$ 228.0125, found 228.0129.



4b

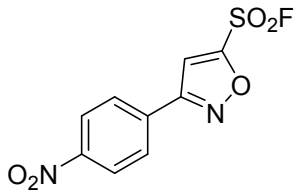
3-(4-(Benzyloxy)phenyl)isoxazole-5-sulfonyl fluoride (**4b**). White solid, 266 mg, 80%. M.p. 131-132 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 2H), 7.46–7.40 (m, 5H), 7.36 (t, J = 7.0 Hz, 1H), 7.10 (d, J = 8.4 Hz, 2H), 5.14 (s, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 63.8 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.9 (s), 161.5 (s),

158.5 (d, J = 38.4 Hz), 136.3 (s), 128.9 (s), 128.7 (s), 128.4 (s), 127.6 (s), 119.0 (s), 115.8 (s), 110.2 (d, J = 3.5 Hz), 70.3 (s). ESI-MS HRMS calculated for $C_{16}H_{13}FNO_4S$ $[M+H]^+$ 334.0544, found 334.0548.



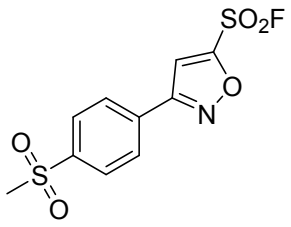
4c

3-([1,1'-Biphenyl]-4-yl)isoxazole-5-sulfonyl fluoride (**4c**). White solid, 236 mg, 78%. M.p. 158-159 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 8.1 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 7.7 Hz, 2H), 7.50–7.48 (m, 3H), 7.42 (t, J = 7.3 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 64.0 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.0 (s), 158.8 (d, J = 38.7 Hz), 144.6 (s), 139.8 (s), 129.2 (s), 128.4 (s), 128.2 (s), 127.6 (s), 127.3 (s), 125.2 (s), 110.4 (d, J = 3.5 Hz). ESI-MS HRMS calculated for $C_{15}H_{11}FNO_3S$ $[M+H]^+$ 304.0438, found 304.0443.



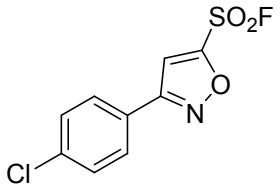
4d

3-(4-Nitrophenyl)isoxazole-5-sulfonyl fluoride (**4d**). White solid, 130 mg, 52%. M.p. 111-112 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, J = 8.7 Hz, 2H), 8.05 (d, J = 8.7 Hz, 2H), 7.57 (s, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 64.4 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.6 (s), 159.9 (d, J = 39.6 Hz), 149.8 (s), 132.2 (s), 128.3 (s), 124.8 (s), 110.3 (d, J = 3.5 Hz). ESI-MS HRMS calculated for $C_9H_6FN_2O_5S$ $[M+H]^+$ 272.9976, found 272.9970.



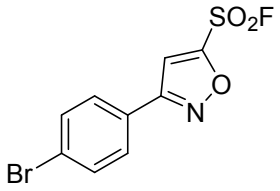
4e

3-(4-(Methylsulfonyl)phenyl)isoxazole-5-sulfonyl fluoride (**4e**). White solid, 136 mg, 45%. M.p. 169-170 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, J = 8.3 Hz, 2H), 8.06 (d, J = 8.3 Hz, 2H), 7.56 (s, 1H), 3.11 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 64.4 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.9 (s), 159.7 (d, J = 39.4 Hz), 143.4 (s), 131.5 (s), 128.7 (s), 128.2 (s), 110.3 (d, J = 3.5 Hz), 44.5 (s). ESI-MS HRMS calculated for $C_{10}H_8FNO_5S_2Na$ $[M+Na]^+$ 327.9720, found 327.9724.



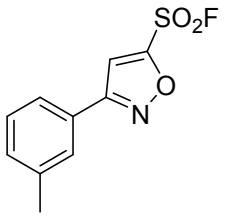
4f

(3-(4-Chlorophenyl)isoxazol-5-yl)fluoro(l1-oxidanyl)-l5-sulfanone (**4f**). White solid, 223 mg, 85%. M.p. 97-98 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.45 (s, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 64.1 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4 (s), 159.1 (d, J = 39.0 Hz), 138.1 (s), 129.9 (s), 128.4 (s), 124.9 (s), 110.2 (d, J = 3.5 Hz). ESI-MS HRMS calculated for ESI-MS HRMS calculated for $C_9H_6FN_2O_5S$ $[M+H]^+$ 261.9735, found 261.9738.



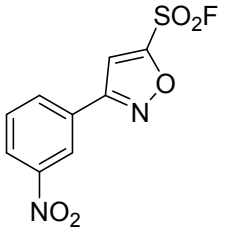
4g

3-(4-Bromophenyl)isoxazole-5-sulfonyl fluoride (**4g**). White solid, 217 mg, 71%. M.p. 96-97 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (q, J = 8.5 Hz, 4H), 7.45 (s, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 64.1 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.5 (s), 159.2 (d, J = 39.2 Hz), 132.9 (s), 128.6 (s), 126.4 (s), 125.3 (s), 110.1 (d, J = 3.5 Hz). ESI-MS HRMS calculated for ESI-MS HRMS calculated for $C_9H_6BrFNO_3S$ $[M+H]^+$ 305.9230, found 305.9232.



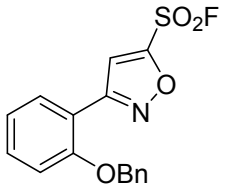
4h

3-(*m*-Tolyl)isoxazole-5-sulfonyl fluoride (**4h**). White solid, 198 mg, 82%. M.p. 129-130 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.61 (d, J = 7.5 Hz, 1H), 7.45 (s, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.36 (d, J = 7.5 Hz, 1H), 2.44 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 63.9 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.5 (s), 158.7 (d, J = 38.7 Hz), 139.5 (s), 132.5 (s), 129.5 (s), 127.7 (s), 126.3 (s), 124.3 (s), 110.5 (d, J = 3.5 Hz), 21.5 (s). ESI-MS HRMS calculated for ESI-MS HRMS calculated for $C_{10}H_9FNO_3S$ $[M+H]^+$ 242.0282, found 242.0279.



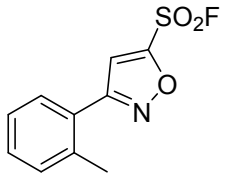
4i

3-(3-Nitrophenyl)isoxazole-5-sulfonyl fluoride (**4i**). White solid, 222 mg, 81%. M.p. 67-68 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.43 (d, J = 8.2 Hz, 1H), 8.22 (d, J = 7.7 Hz, 1H), 7.77 (t, J = 8.0 Hz, 1H), 7.58 (s, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 64.4 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.6 (s), 159.9 (d, J = 39.7 Hz), 149.0 (s), 132.7 (s), 130.9 (s), 128.2 (s), 126.3 (s), 122.3 (s), 110.1 (d, J = 3.5 Hz). ESI-MS HRMS calculated for ESI-MS HRMS calculated for $C_9H_6FN_2O_5S$ $[M+H]^+$ 272.9976, found 272.9974.



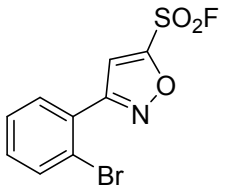
4j

3-(2-(Benzyloxy)phenyl)isoxazole-5-sulfonyl fluoride (**4j**). White solid, 238 mg, 71%. M.p. 73-74 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 9.4 Hz, 1H), 7.65 (s, 1H), 7.49 (t, J = 7.9 Hz, 1H), 7.41-7.37 (m, 5H), 7.12-7.09 (m, 2H), 5.21 (s, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 63.9 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.9 (s), 157.5 (d, J = 38.0 Hz), 156.6 (s), 135.9 (s), 133.0 (s), 129.6 (s), 129.0 (s), 128.7 (s), 127.5 (s), 121.8 (s), 115.7 (s), 114.0 (d, J = 3.5 Hz), 113.3 (s), 71.1 (s). ESI-MS HRMS calculated for ESI-MS HRMS calculated for $C_{16}H_{13}FNO_4S$ $[M+H]^+$ 356.0363, found 356.0366.



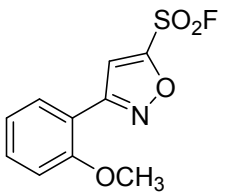
4k

3-(*o*-Tolyl)isoxazole-5-sulfonyl fluoride (**4k**). Yellow oil liquid. 256 mg, 83%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, J = 7.6 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 7.37-7.32 (m, 3H), 2.51 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 64.1 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.9 (s), 158.2 (d, J = 38.7 Hz), 137.4 (s), 131.8 (s), 131.1 (s), 129.7(s), 126.7 (s), 126.0 (s), 112.7 (d, J = 3.5 Hz), 21.3 (s). ESI-MS HRMS calculated for ESI-MS HRMS calculated for $C_{10}H_9FNO_3S$ $[M+H]^+$ 242.0282, found 242.0280.



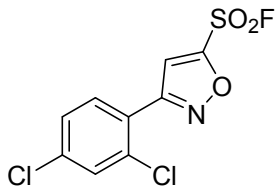
4l

3-(2-Bromophenyl)isoxazole-5-sulfonyl fluoride (**4l**). Yellow oil liquid, 158 mg, 52%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 7.9 Hz, 1H), 7.69 (d, J = 7.4 Hz, 1H), 7.65 (s, 1H), 7.48 (t, J = 7.4 Hz, 1H), 7.42 (t, J = 7.3 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 64.3 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.3 (s), 157.9 (d, J = 39.0 Hz), 134.1 (s), 132.6 (s), 131.6 (s), 128.3 (s), 127.7 (s), 122.3 (s), 113.5 (d, J = 3.5 Hz). ESI-MS HRMS calculated for ESI-MS HRMS calculated for $C_9H_6BrFNO_3S$ $[M+H]^+$ 305.9230, found 305.9233.



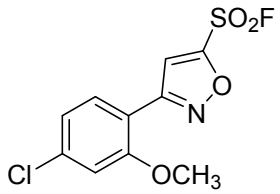
4m

3-(2-Methoxyphenyl)isoxazole-5-sulfonyl fluoride (**4m**). White solid, 229 mg, 90%. M.p. 76-77 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dd, J = 7.7, 1.4 Hz, 1H), 7.70 (d, J = 1.0 Hz, 1H), 7.51 (td, J = 7.8, 1.4 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 7.05 (d, J = 8.4 Hz, 1H), 3.95 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 63.9 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.9 (s), 157.5 (d, J = 38.1 Hz), 157.4 (s), 133.1 (s), 129.5 (s), 121.4 (s), 115.2 (s), 114.0 (d, J = 3.6 Hz), 111.8 (s), 55.8 (s). ESI-MS HRMS calculated for ESI-MS HRMS calculated for $C_{10}H_8FNO_4SNa$ $[M+Na]^+$ 280.0050, found 280.0053.



4n

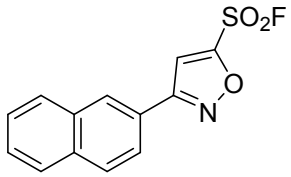
3-(2,4-Dichlorophenyl)isoxazole-5-sulfonyl fluoride (**4n**). Yellow solid, 160 mg, 54%. M.p. 59-60 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 8.4 Hz, 1H), 7.66 (s, 1H), 7.58 (s, 1H), 7.43 (dd, J = 8.4, 1.5 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 64.4 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.1 (s), 158.5 (d, J = 39.2 Hz), 138.4 (s), 133.9 (s), 131.9 (s), 130.9 (s), 128.3 (s), 124.2 (s), 113.1 (d, J = 3.6 Hz). ESI-MS HRMS calculated for ESI-MS HRMS calculated for $C_9H_5Cl_2FNO_3S$ $[M+H]^+$ 295.9346, found 295.9349.



4o

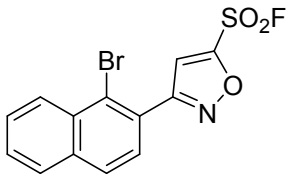
3-(4-Chloro-2-methoxyphenyl)isoxazole-5-sulfonyl fluoride (**4o**). White solid, 155 mg, 53%. M.p. 63-64 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 2.5 Hz, 1H), 7.69 (d, J = 1.0 Hz, 1H), 7.46 (dd, J = 8.9, 2.5 Hz, 1H), 6.99 (d, J = 8.9 Hz, 1H), 3.94 (s, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 64.1 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ

159.9 (s), 158.0 (d, J = 38.4 Hz), 156.0 (s), 132.7 (s), 129.1 (s), 126.7 (s), 116.5 (s), 113.7 (d, J = 3.6 Hz), 113.1 (s), 56.3 (s). ESI-MS HRMS calculated for ESI-MS HRMS calculated for $C_{10}H_8ClFNO_4S$ $[M+H]^+$ 291.9841, found 291.9842.



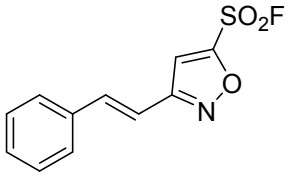
4p

3-(Naphthalen-2-yl)isoxazole-5-sulfonyl fluoride (**4p**). White solid, 195 mg, 70%. M.p. 101-102 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.99-7.90 (m, 4H), 7.62-7.57 (m, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 64.0 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.4 (s), 158.9 (d, J = 38.7 Hz), 134.8 (s), 133.1 (s), 129.6 (s), 128.8 (s), 128.2 (s), 128.1 (s), 127.7 (s), 127.4 (s), 123.7 (s), 123.4 (s), 110.5 (d, J = 3.5 Hz). ESI-MS HRMS calculated for ESI-MS HRMS calculated for $C_{13}H_9FNO_3S$ $[M+H]^+$ 278.0282, found 278.0285.



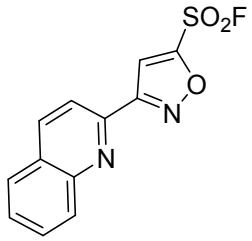
4q

3-(1-Bromonaphthalen-2-yl)isoxazole-5-sulfonyl fluoride (**4q**). White solid, 276 mg, 78%. M.p. 81-82 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.75 (s, 1H), 7.73–7.65 (m, 3H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 64.3 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2 (s), 157.8 (d, J = 38.9 Hz), 135.3 (s), 132.4 (s), 128.8 (s), 128.7 (s), 128.61 (s), 128.57 (s), 128.2 (s), 127.1 (s), 125.8 (s), 124.1 (s), 114.2 (d, J = 3.5 Hz). ESI-MS HRMS calculated for ESI-MS HRMS calculated for $C_{13}H_8BrFNO_3S$ $[M+H]^+$ 355.9387, found 355.9387.



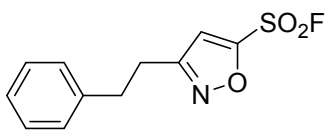
4r

(*E*)-3-styrylisoxazole-5-sulfonyl fluoride (**4r**). White solid, 101 mg, 40%. M.p. 94-95 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 7.1 Hz, 2H), 7.44-7.39 (m, 4H), 7.29 (d, J = 16.5 Hz, 1H), 7.14 (d, J = 16.5 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 63.8 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.5 (s), 158.2 (d, J = 38.7 Hz), 139.5 (s), 134.8 (s), 130.2 (s), 129.2 (s), 127.5 (s), 113.4 (s), 109.6 (d, J = 3.5 Hz). ESI-MS HRMS calculated for ESI-MS HRMS calculated for $C_{11}H_8FNO_3SNa$ $[M+Na]^+$ 276.0101, found 276.0100.



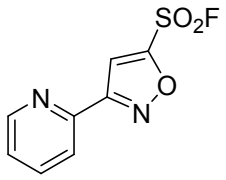
4s

3-(Quinolin-2-yl)isoxazole-5-sulfonyl fluoride (**4s**). White solid, 88 mg, 32%. M.p. 83-84 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, J = 8.5 Hz, 1H), 8.22 (d, J = 8.5 Hz, 1H), 8.15 (d, J = 8.5 Hz, 1H), 8.05 (d, J = 1.3 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.81 (t, J = 7.0 Hz, 1H), 7.66 (t, J = 8.1 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 64.3 (s, 1F). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.5 (s), 158.8 (d, J = 39.0 Hz), 148.2 (s), 145.9 (s), 137.7 (s), 130.7 (s), 130.1 (s), 128.9 (s), 128.4 (s), 128.0 (s), 118.8 (s), 112.0 (d, J = 3.5 Hz). ESI-MS HRMS calculated for $C_{12}H_8FN_2O_3S$ $[M+H]^+$ 279.0234, found 279.0236.



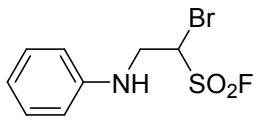
4t

3-Phenethylisoxazole-5-sulfonyl fluoride (**4t**). Yellow oil, 102 mg, 40 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, J = 7.4 Hz, 2H), 7.26 (t, J = 7.3 Hz, 1H), 7.20 (d, J = 7.5 Hz, 2H), 6.83 (s, 1H), 3.13 (t, J = 7.7 Hz, 2H), 3.04 (t, J = 7.4 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 63.8 (s). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2 (s), 158.0 (d, J = 38.4 Hz), 139.3 (s), 128.9 (s), 128.5 (s), 127.0 (s), 112.1 (d, J = 3.5 Hz), 34.0 (s), 27.9 (s). ESI-MS HRMS calculated for $C_{11}H_{11}FNO_3S$ $[M+H]^+$ 256.0438, found 256.0435.



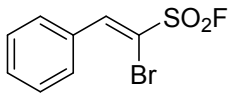
4u

3-(Pyridin-2-yl)isoxazole-5-sulfonyl fluoride (**4u**). Yellow oil, 126 mg, 55 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, J = 4.7 Hz, 1H), 8.14 (d, J = 7.9 Hz, 1H), 7.87 (t, J = 7.3 Hz, 1H), 7.84 (s, 1H), 7.46-7.44 (m, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 64.1 (s). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.2 (s), 158.7 (d, J = 38.9 Hz), 150.4 (s), 146.0 (s), 137.4 (s), 125.9 (s), 122.1 (s), 111.6 (d, J = 3.5 Hz). ESI-MS HRMS calculated for $C_8H_6FN2O_3S$ $[M+H]^+$ 229.0078, found 227.0076.



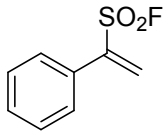
7

1-Bromo-2-(phenylamino)ethane-1-sulfonyl fluoride (**I**). Yellow liquid, 265 mg, 94 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.26 (m, 2H), 6.88 (t, J = 7.4 Hz, 1H), 6.68 (d, J = 7.7 Hz, 2H), 5.21 (t, J = 6.9 Hz, 1H), 4.28 (br, 1H), 4.23 (dd, J = 15.8, 5.5 Hz, 1H), 3.90 (dd, J = 14.9, 6.4 Hz, 1H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 47.1 (s). ^{13}C NMR (126 MHz, DMSO-d_6) δ 146.6 (s), 129.1 (s), 117.2 (s), 112.5 (s), 57.0 (d, J = 11.6 Hz), 46.0 (s). ESI-MS HRMS calculated for $C_8H_{10}BrFNO_2S$ $[M+H]^+$ 281.9594, found 281.9595.



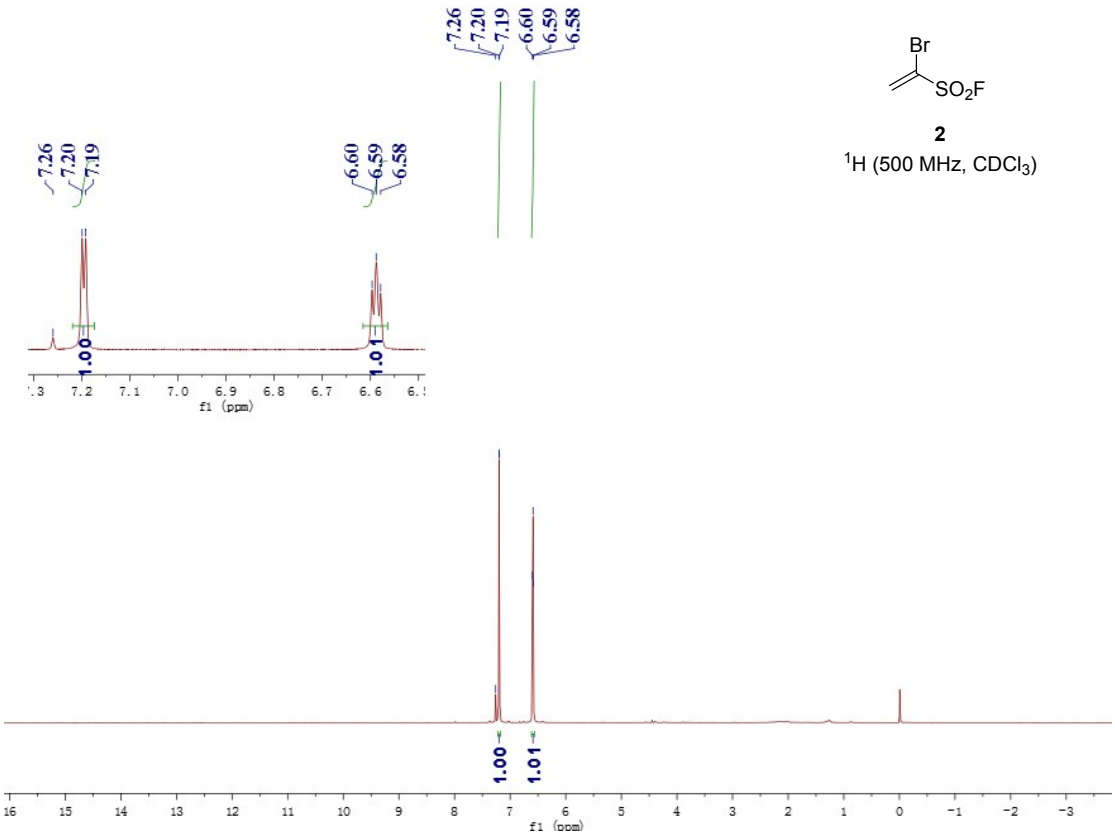
12

(*Z*)-1-bromo-2-phenylethene-1-sulfonyl fluoride (**12**). White solid, 1.40 g, 5.28 mmol, 53 %. M.p. 49-50 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.88 (d, J = 7.7 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.5 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 50.5 (s). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.6 (d, J = 2.0 Hz), 132.5 (s), 130.8 (d, J = 0.7 Hz), 130.8 (s), 129.2 (s), 110.0 (d, J = 32.6 Hz). ESI-MS HRMS calculated for $C_8H_7BrFO_2S$ $[M+H]^+$ 264.9329, found 264.9333.



13

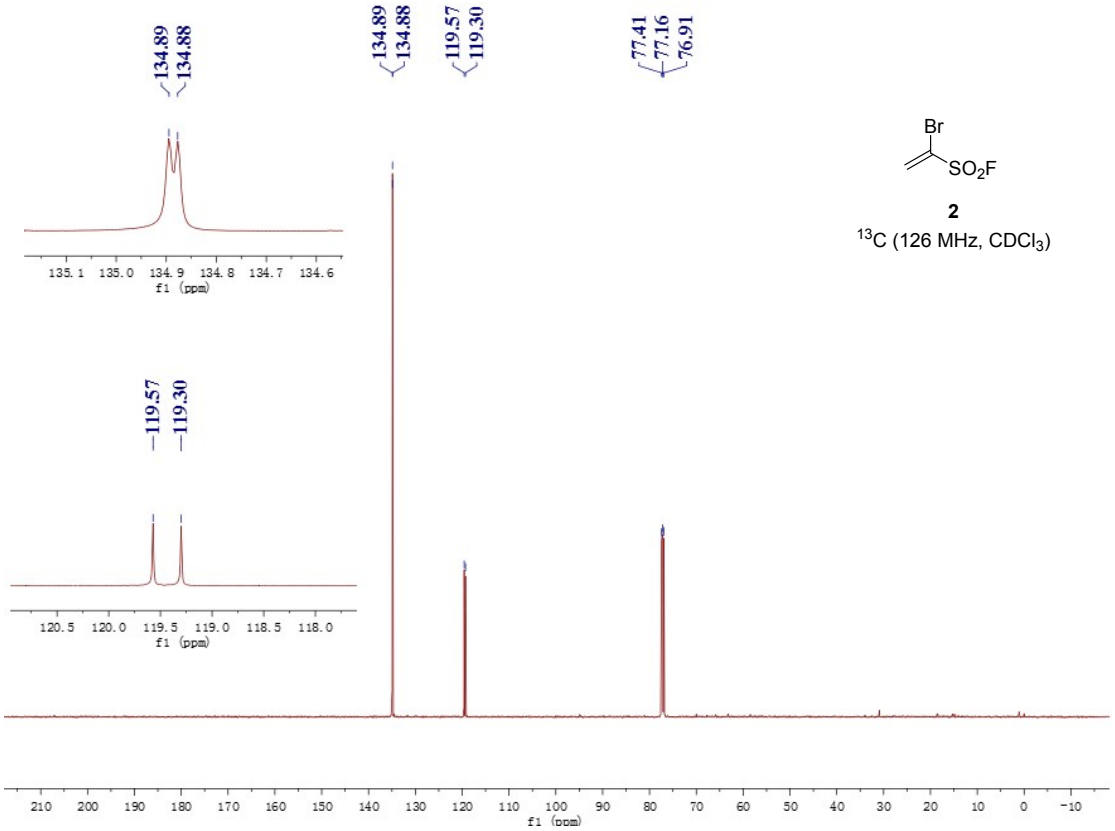
1-Phenylethene-1-sulfonyl fluoride (**13**). Colorless liquid, 112 mg, 62 %. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 7.0 Hz, 2H), 7.51-7.44 (m, 3H), 6.69 (s, 1H), 6.29 (d, J = 6.1 Hz, 2H). ^{19}F NMR (471 MHz, $CDCl_3$) δ 54.5 (d, J = 6.0 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.7 (d, J = 22.9 Hz), 130.6 (s), 130.44 (s), 130.40 (d, J = 2.1 Hz), 129.1 (s), 128.6 (s). ESI-MS HRMS calculated for $C_8H_8FO_2S$ $[M+H]^+$ 187.0224, found 187.0232.



Br
SO_2F

2

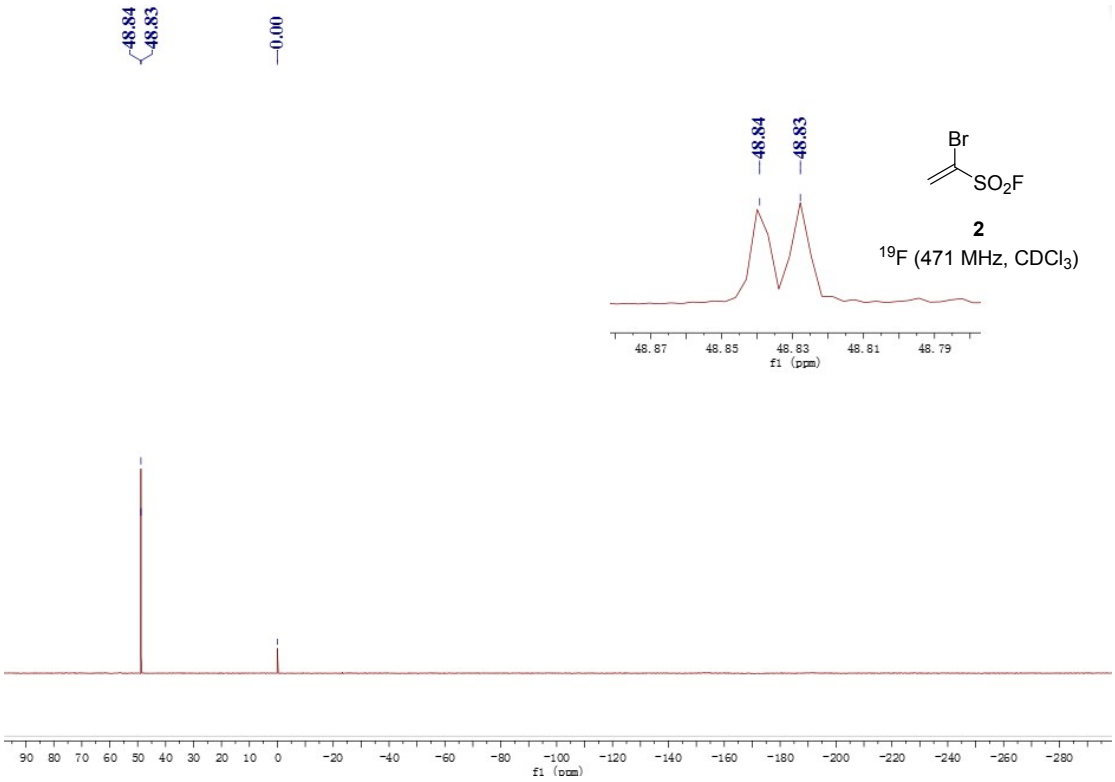
^1H (500 MHz, $CDCl_3$)

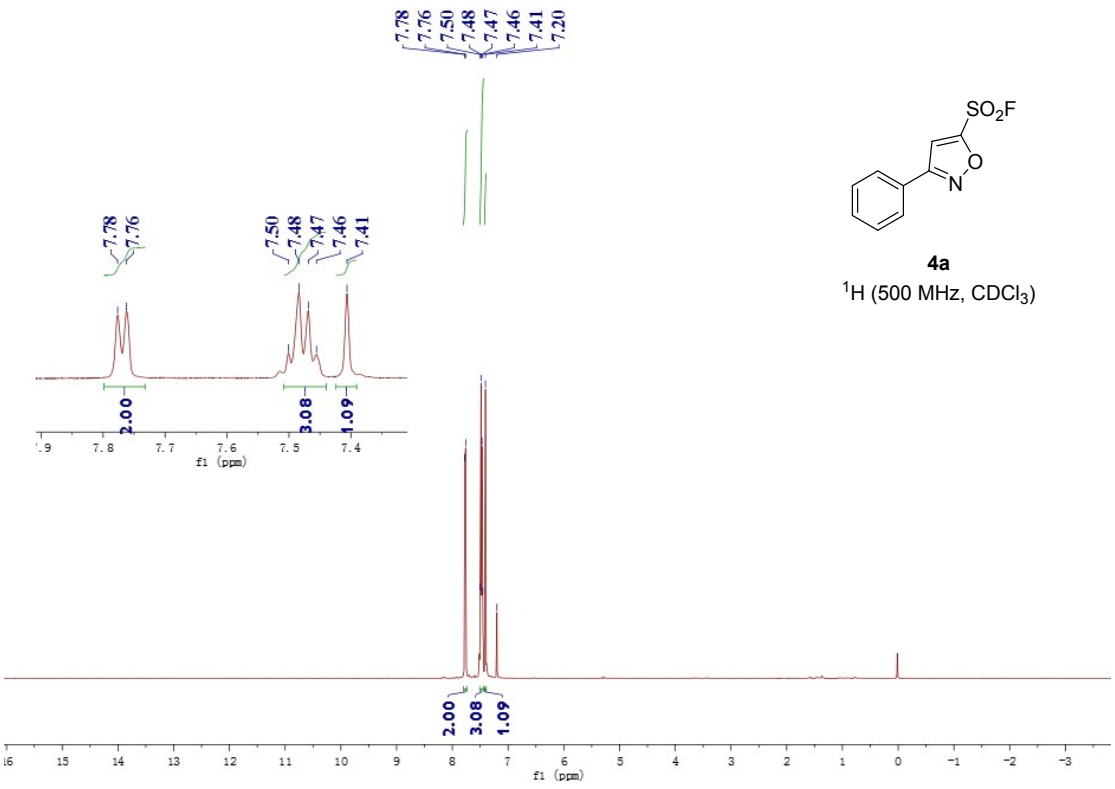


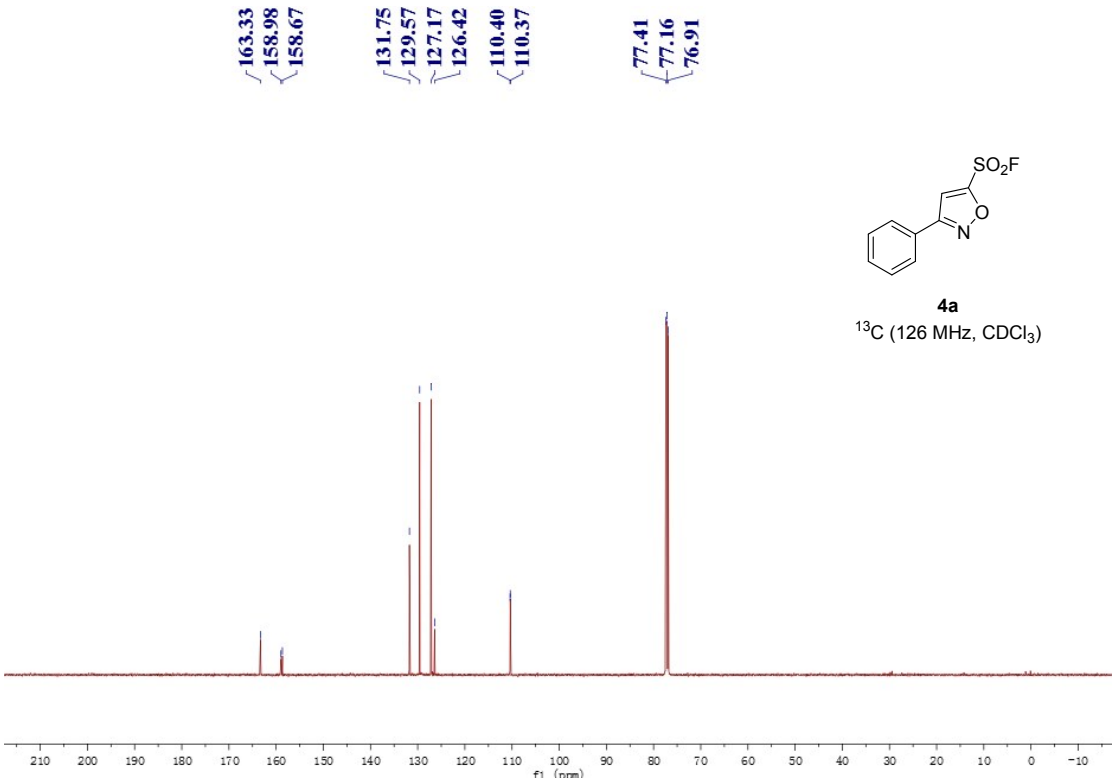
Br
SO_2F

2

^{13}C (126 MHz, $CDCl_3$)

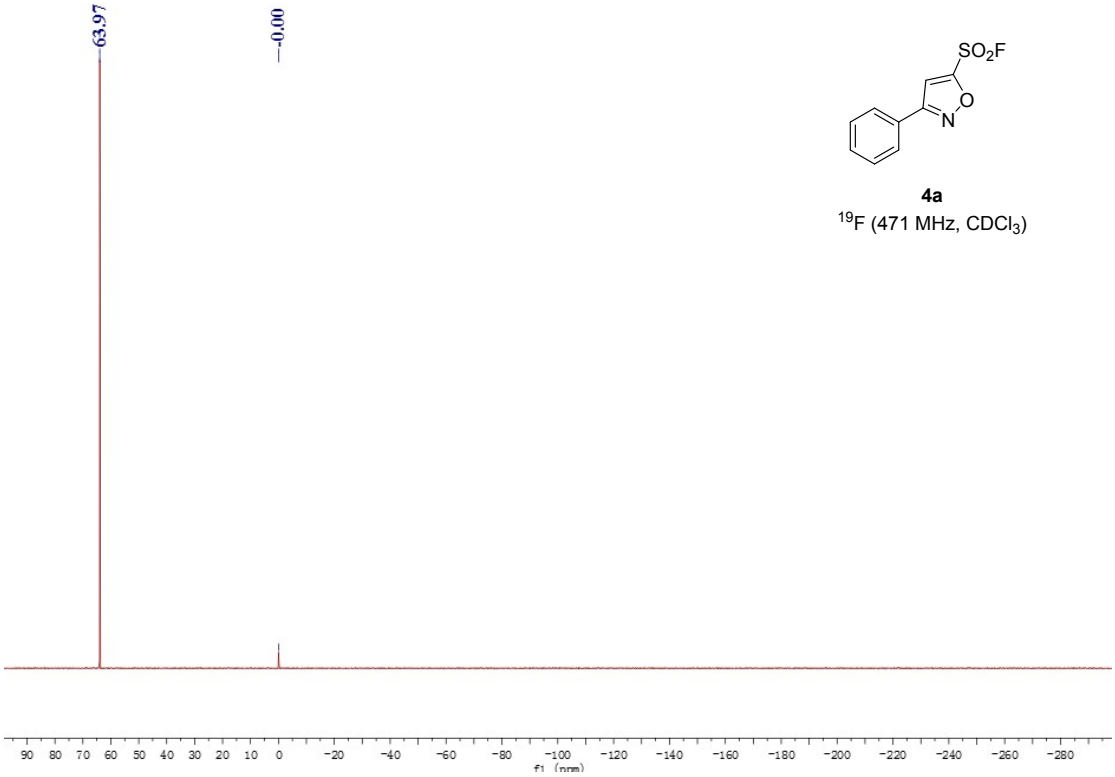

48.84
48.83
0.00
Br
SO2F
2
19F (471 MHz, CDCl3)
f1 (ppm)


7.78
7.76
7.50
7.48
7.47
7.46
7.41
7.20
SO2F
O
N
4a
1H (500 MHz, CDCl3)
2.00
3.08
1.09
f1 (ppm)



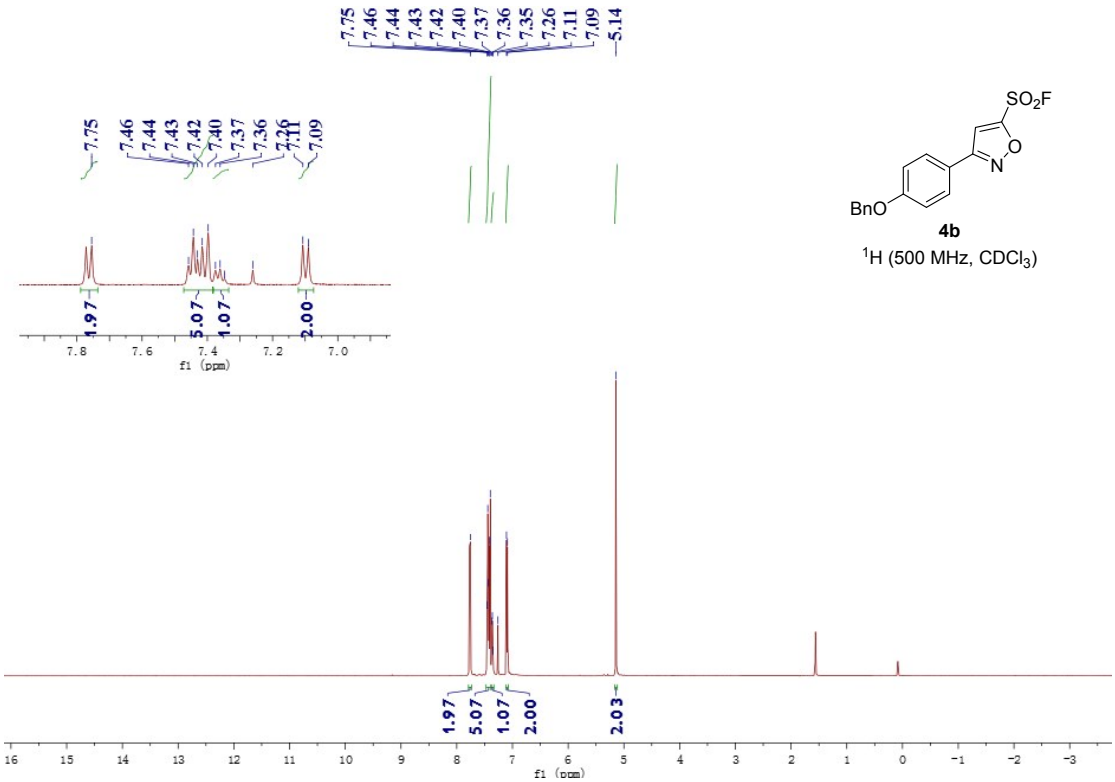
4a

^{13}C (126 MHz, $CDCl_3$)



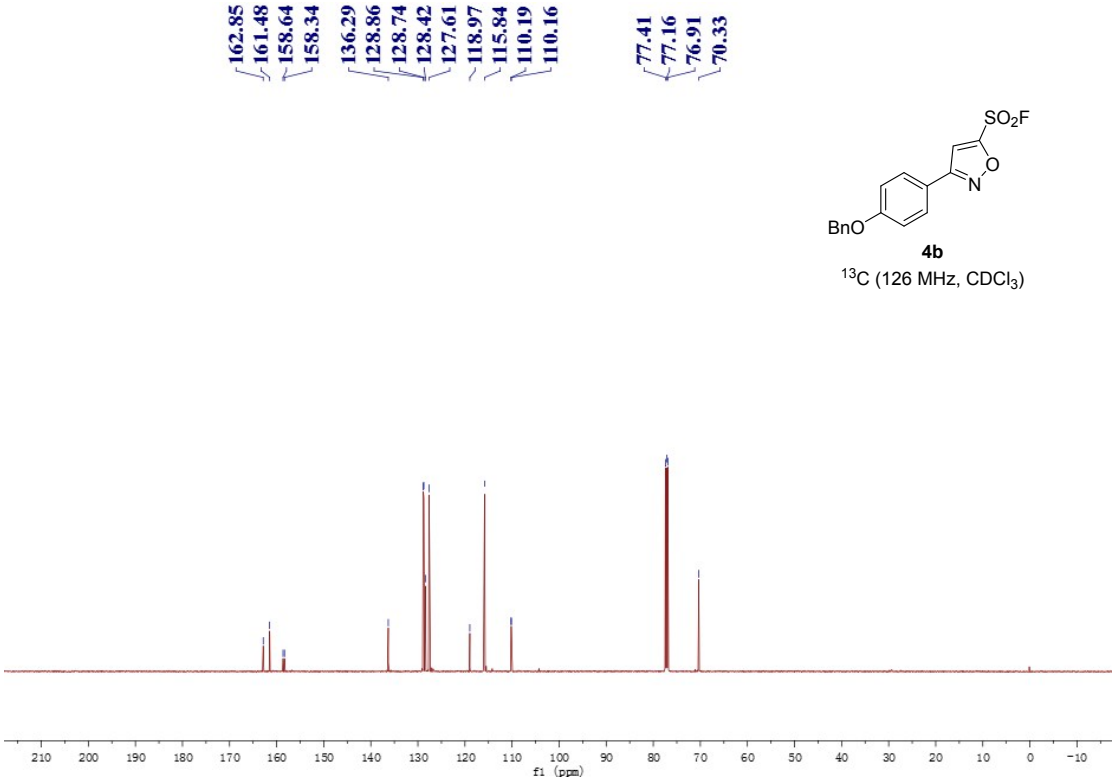
4a

^{19}F (471 MHz, $CDCl_3$)



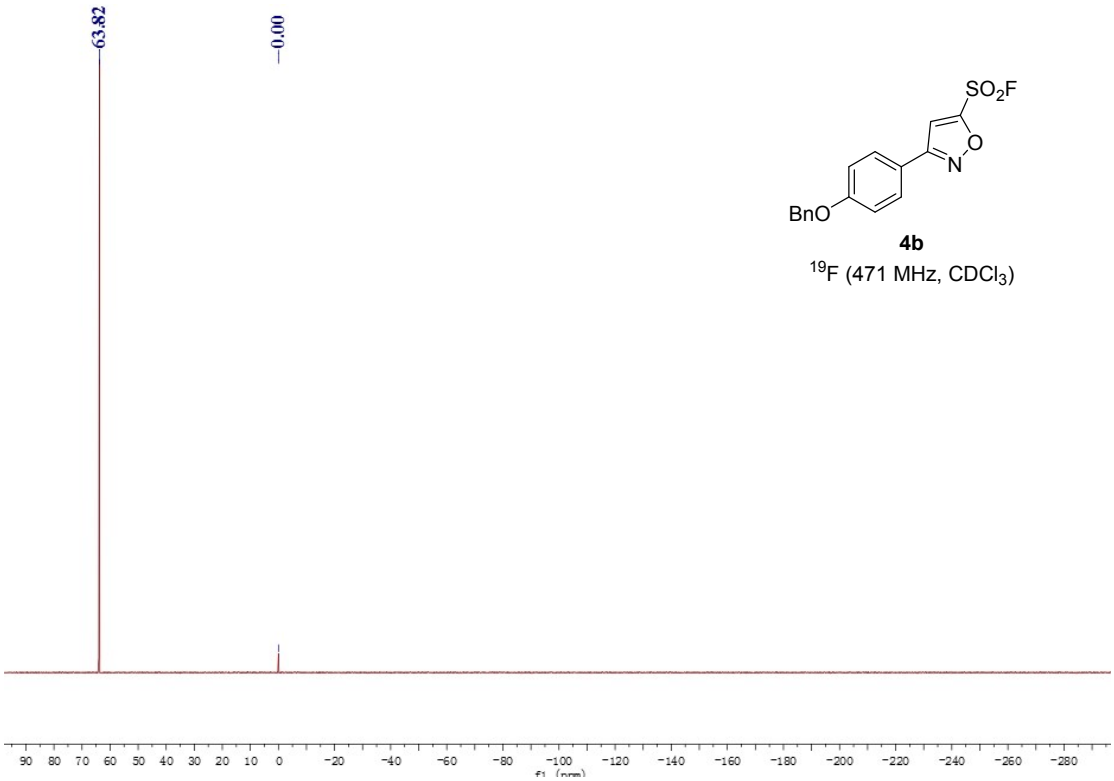
4b

^{1}H (500 MHz, $CDCl_3$)



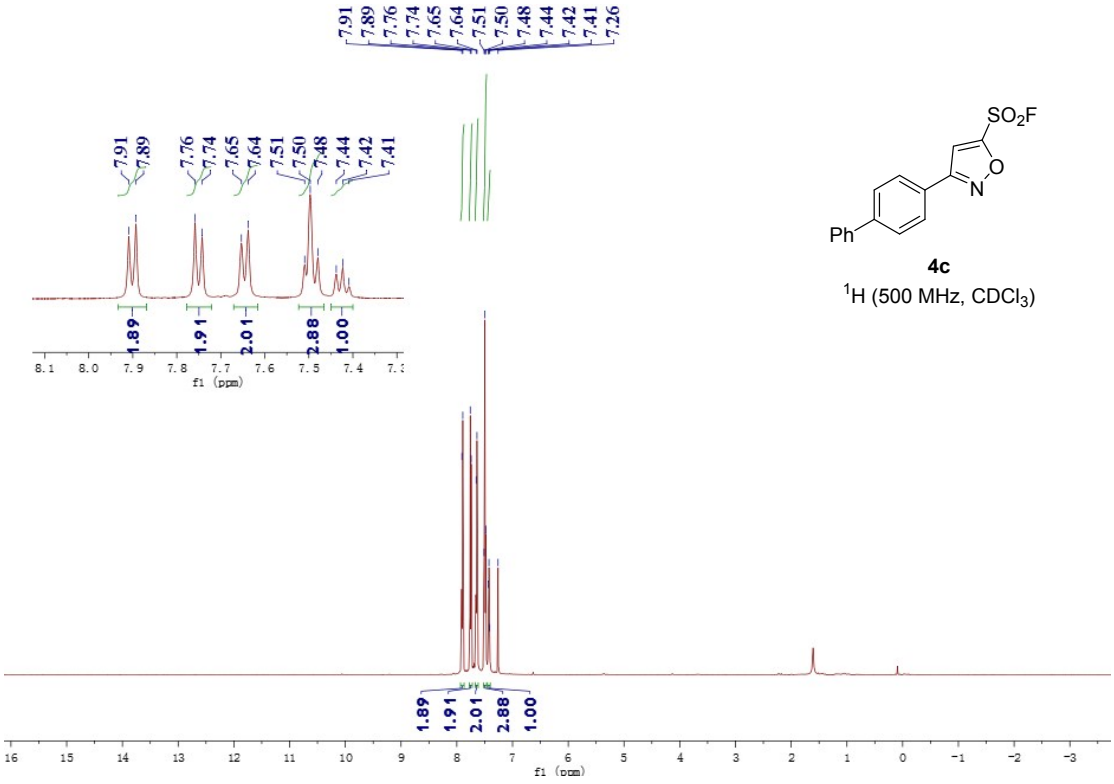
4b

^{13}C (126 MHz, $CDCl_3$)



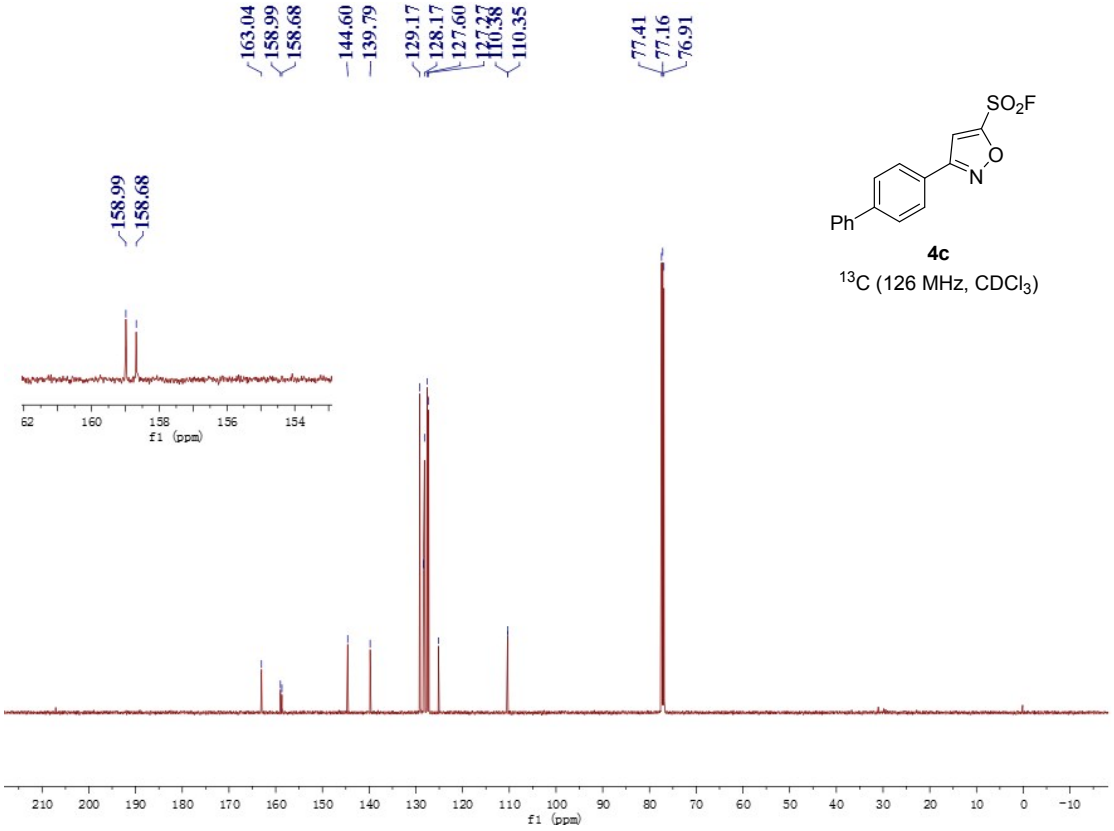
4b

^{19}F (471 MHz, $CDCl_3$)



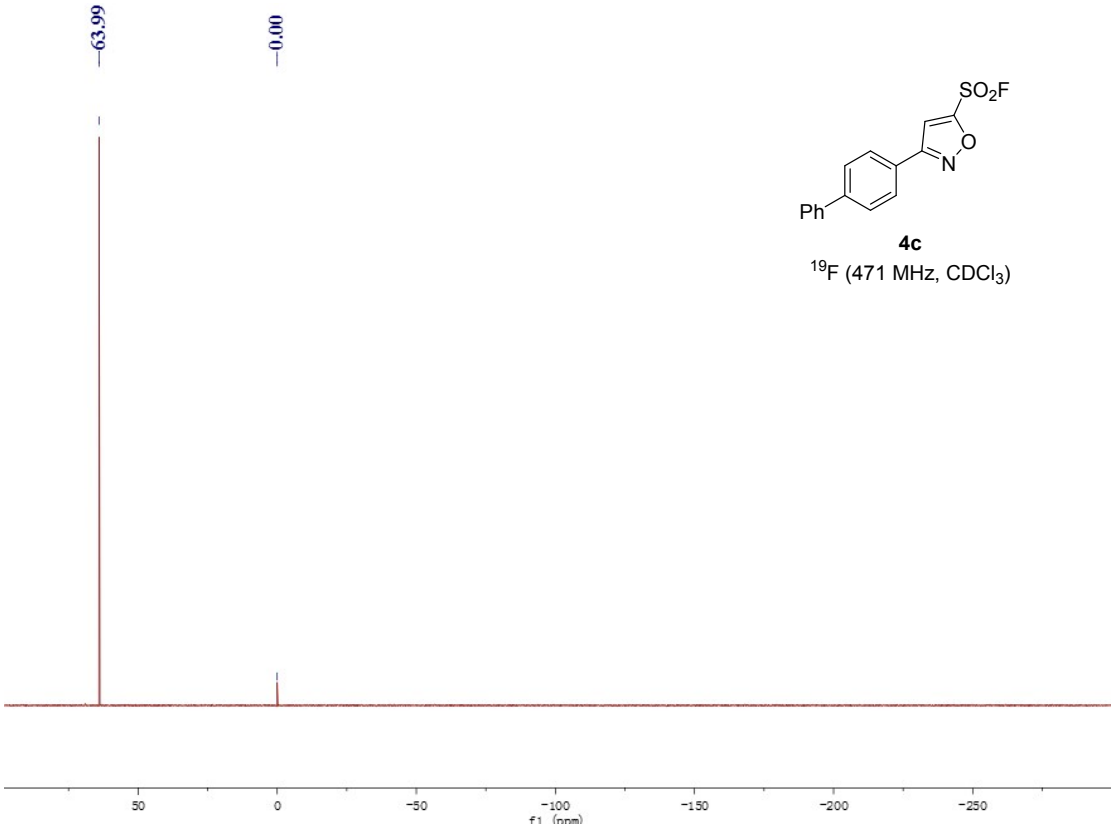
4c

^{1}H (500 MHz, $CDCl_3$)



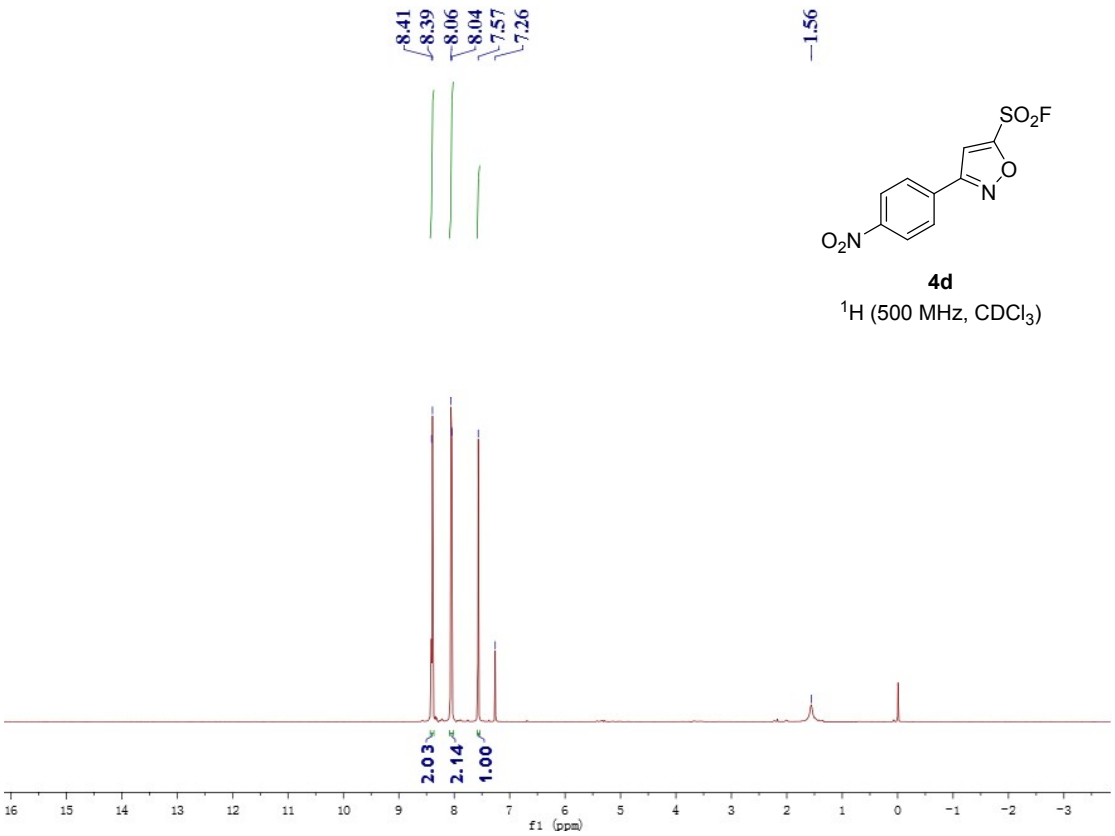
4c

^{13}C (126 MHz, $CDCl_3$)



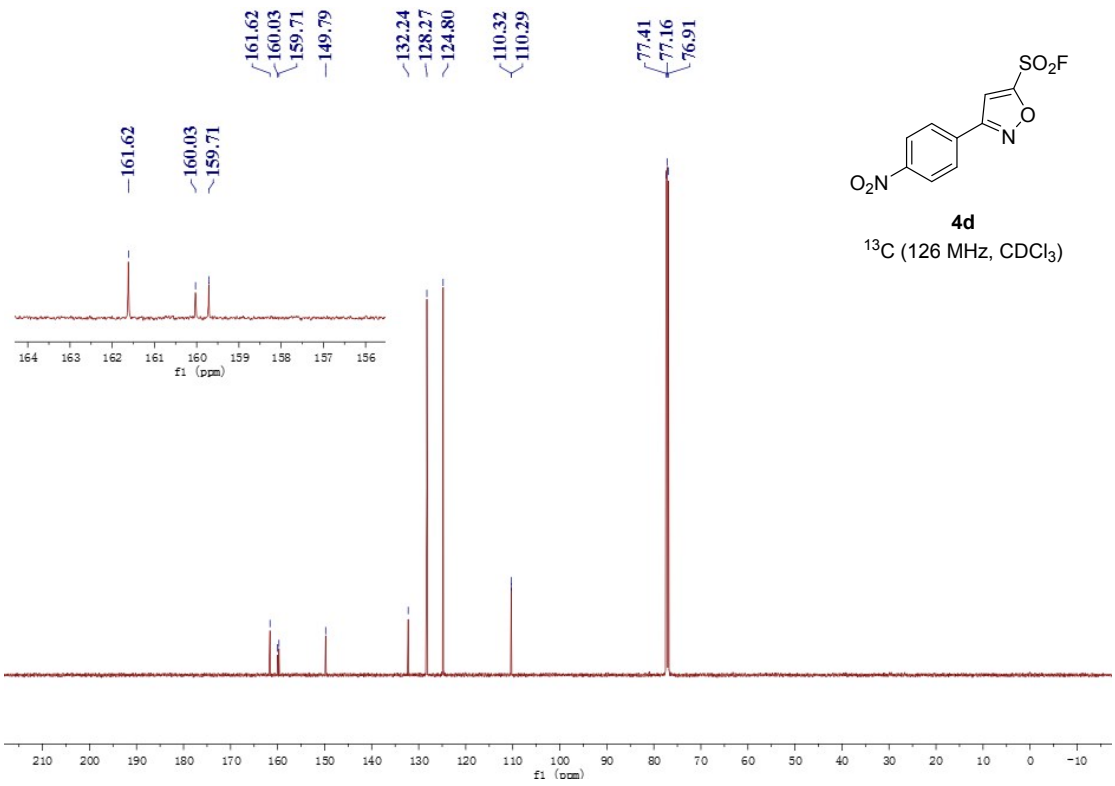
4c

^{19}F (471 MHz, $CDCl_3$)



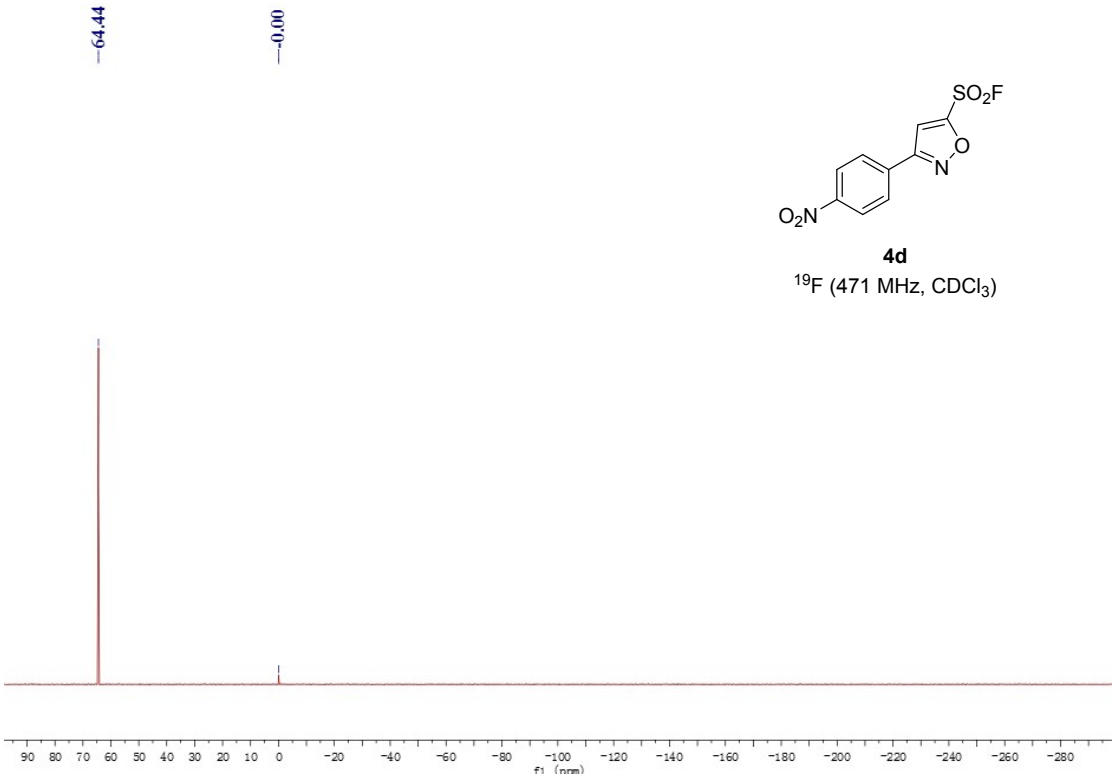
4d

^{1}H (500 MHz, $CDCl_3$)



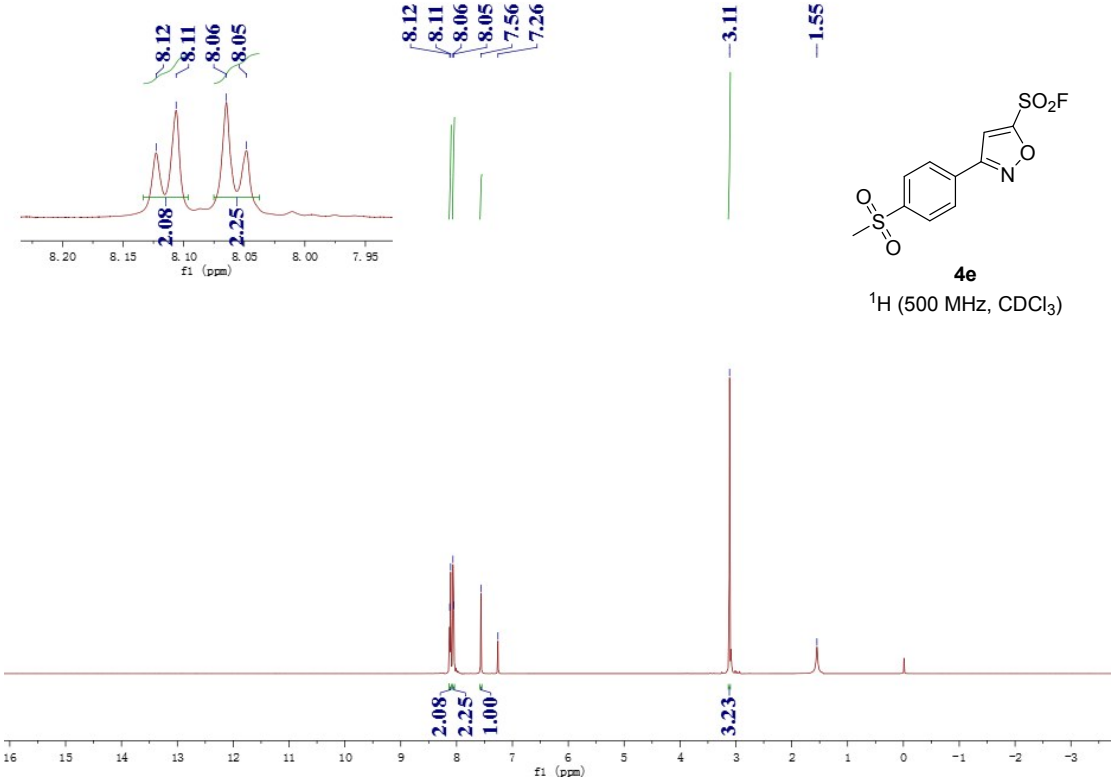
4d

^{13}C (126 MHz, $CDCl_3$)



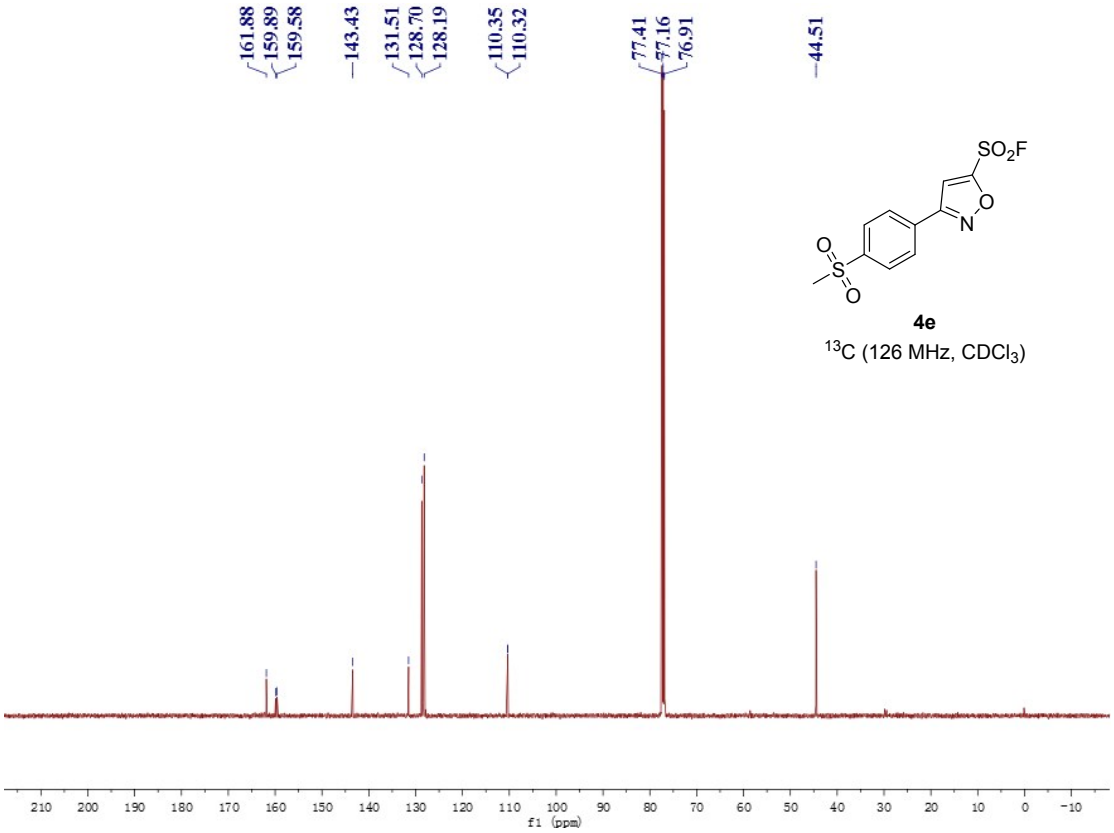
4d

^{19}F (471 MHz, $CDCl_3$)



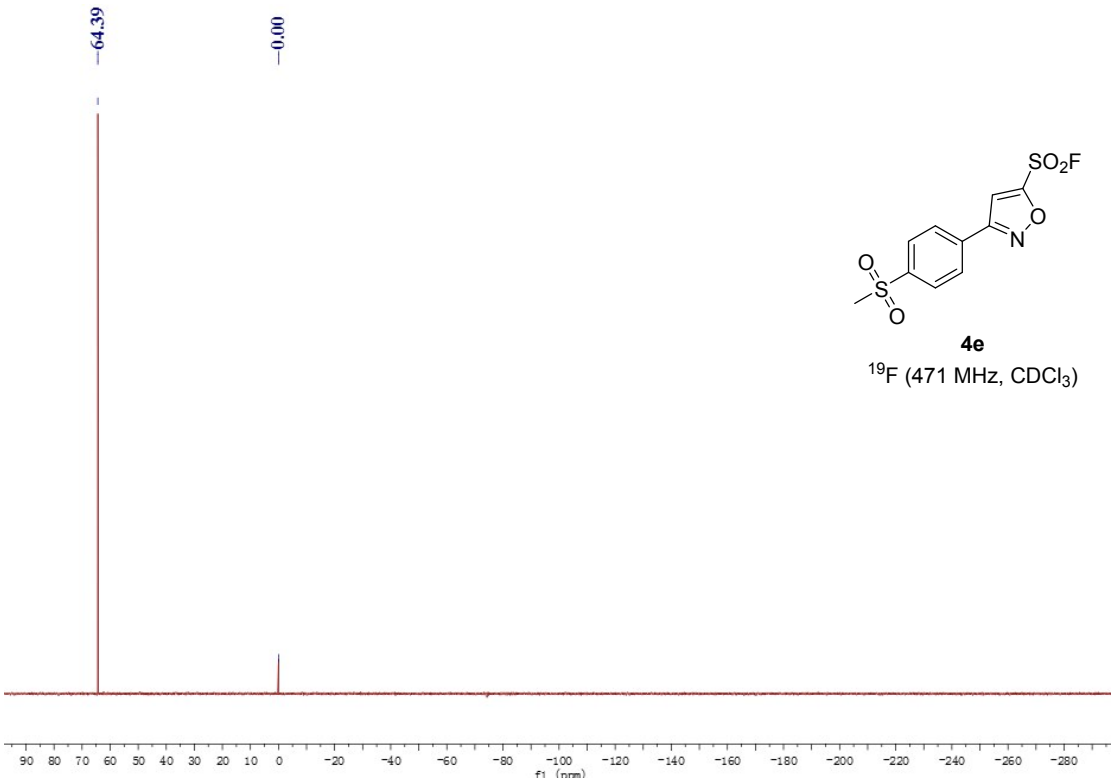
4e

^{1}H (500 MHz, $CDCl_3$)



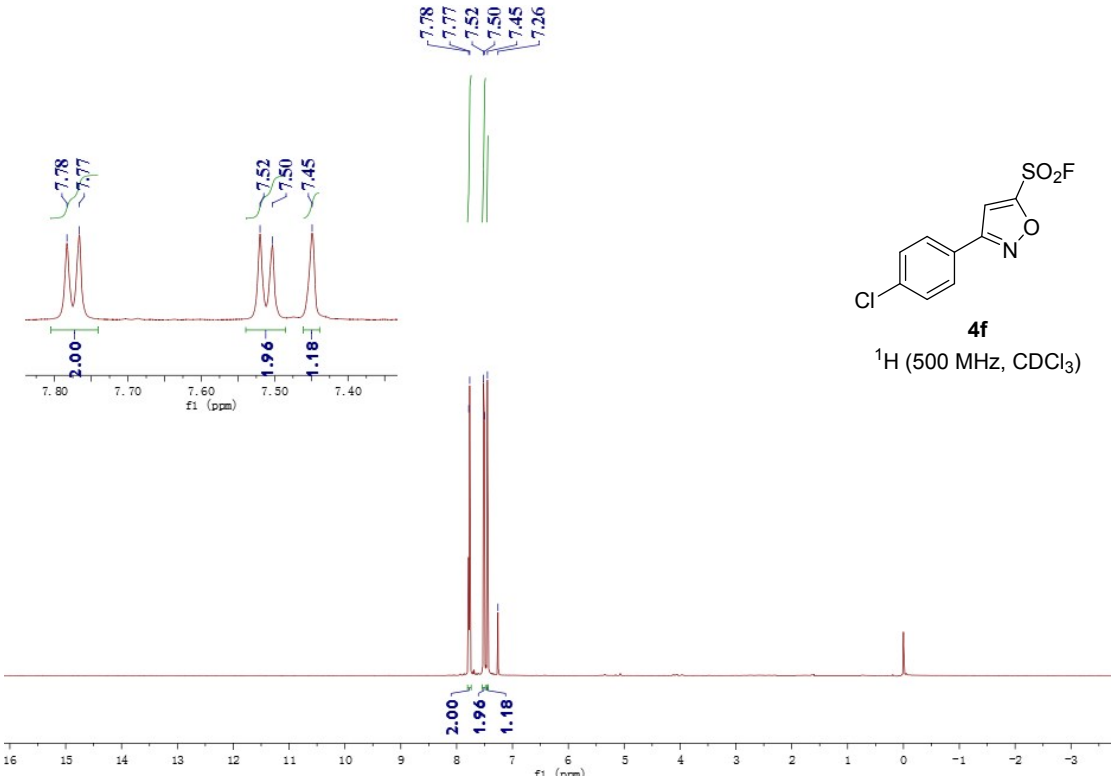
4e

^{13}C (126 MHz, $CDCl_3$)



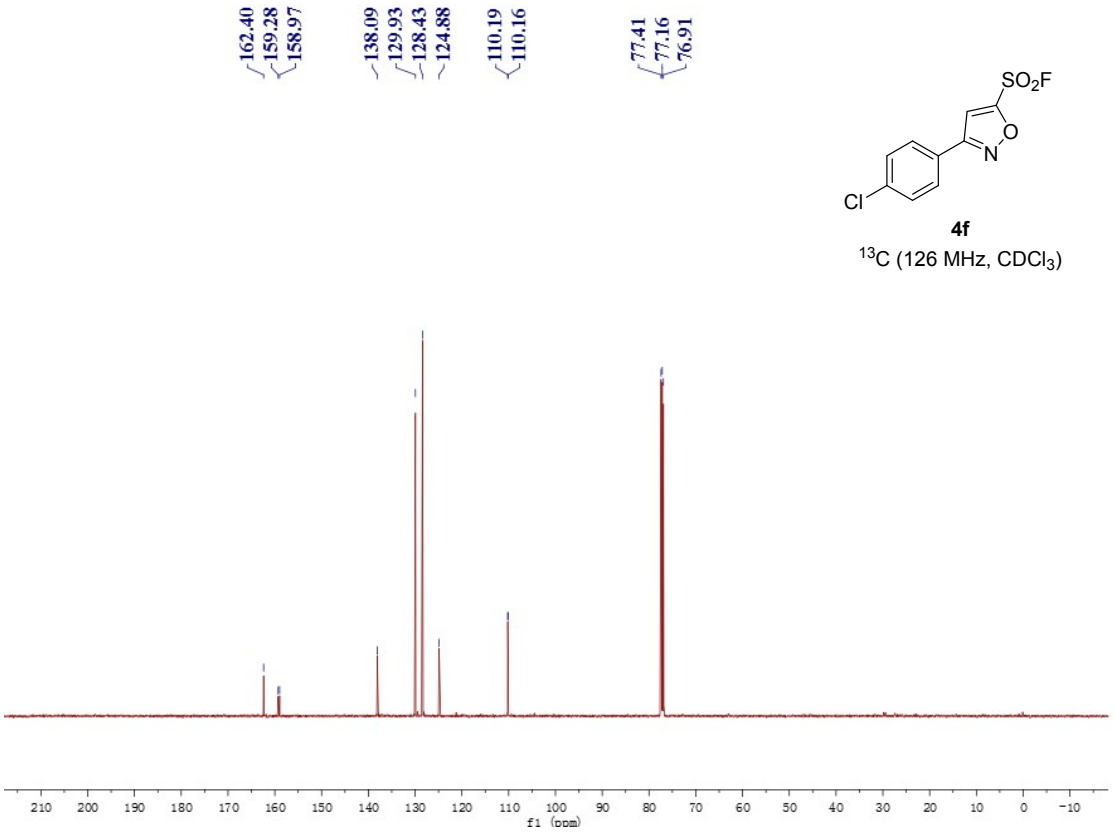
4e

^{19}F (471 MHz, $CDCl_3$)



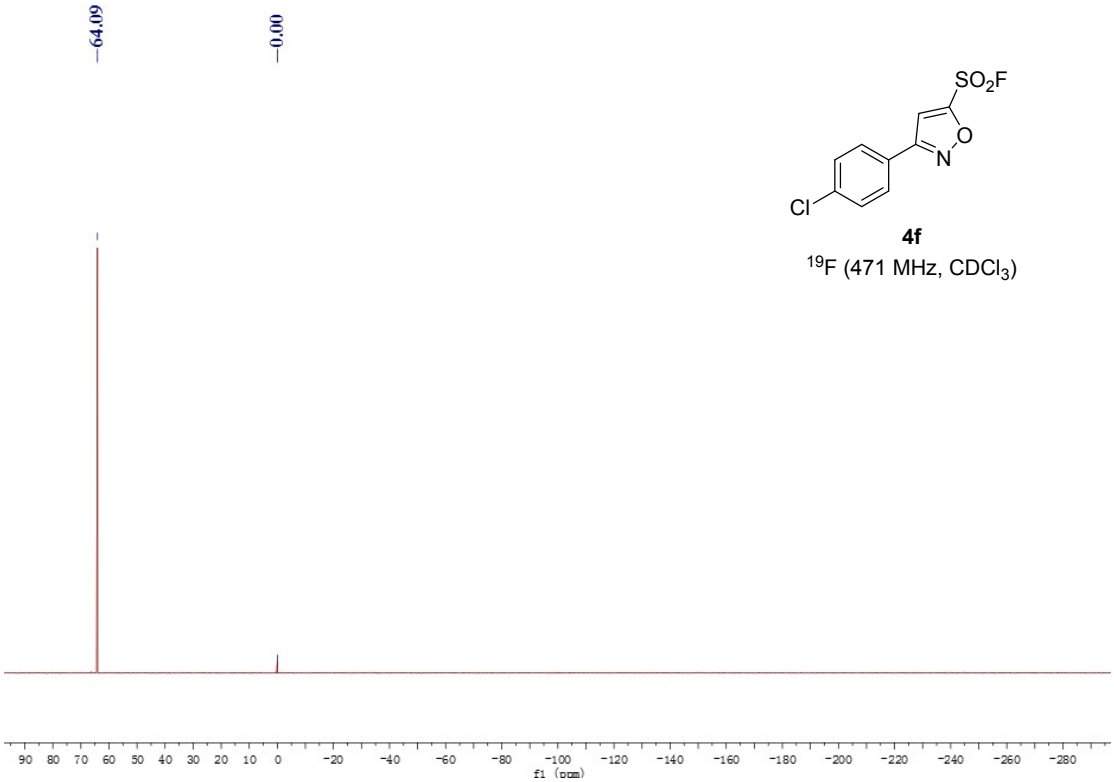
4f

^{1}H (500 MHz, $CDCl_3$)



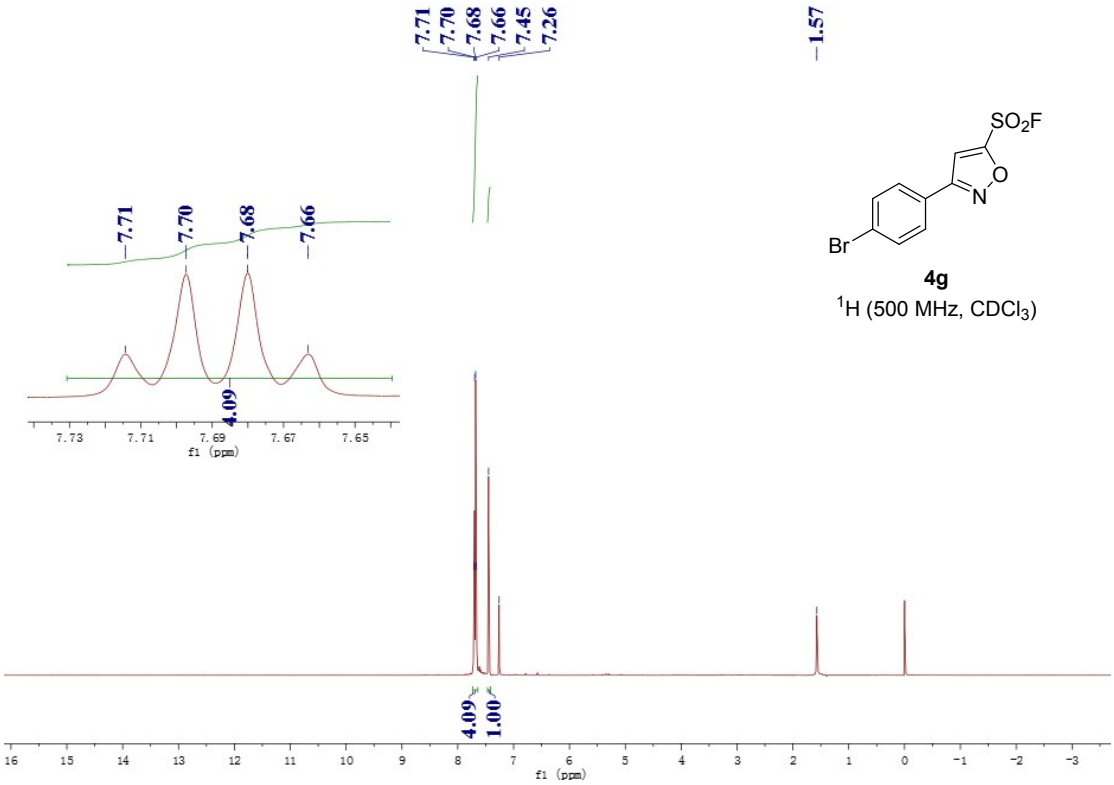
4f

^{13}C (126 MHz, $CDCl_3$)



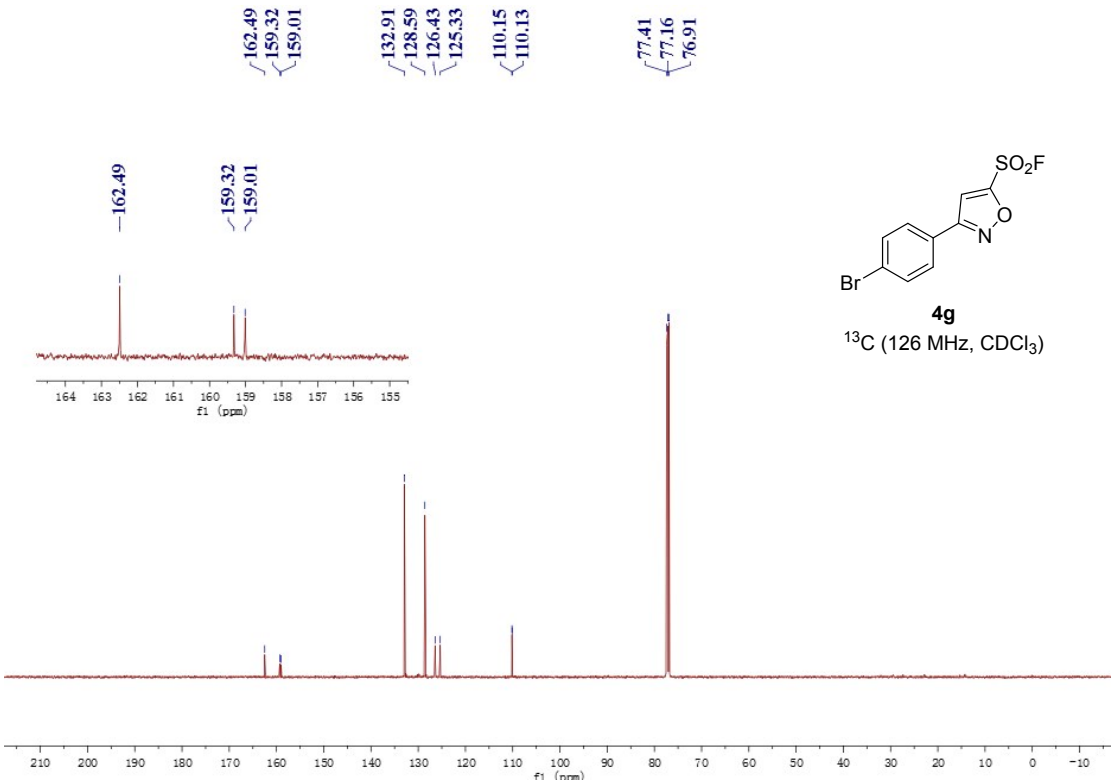
4f

^{19}F (471 MHz, $CDCl_3$)



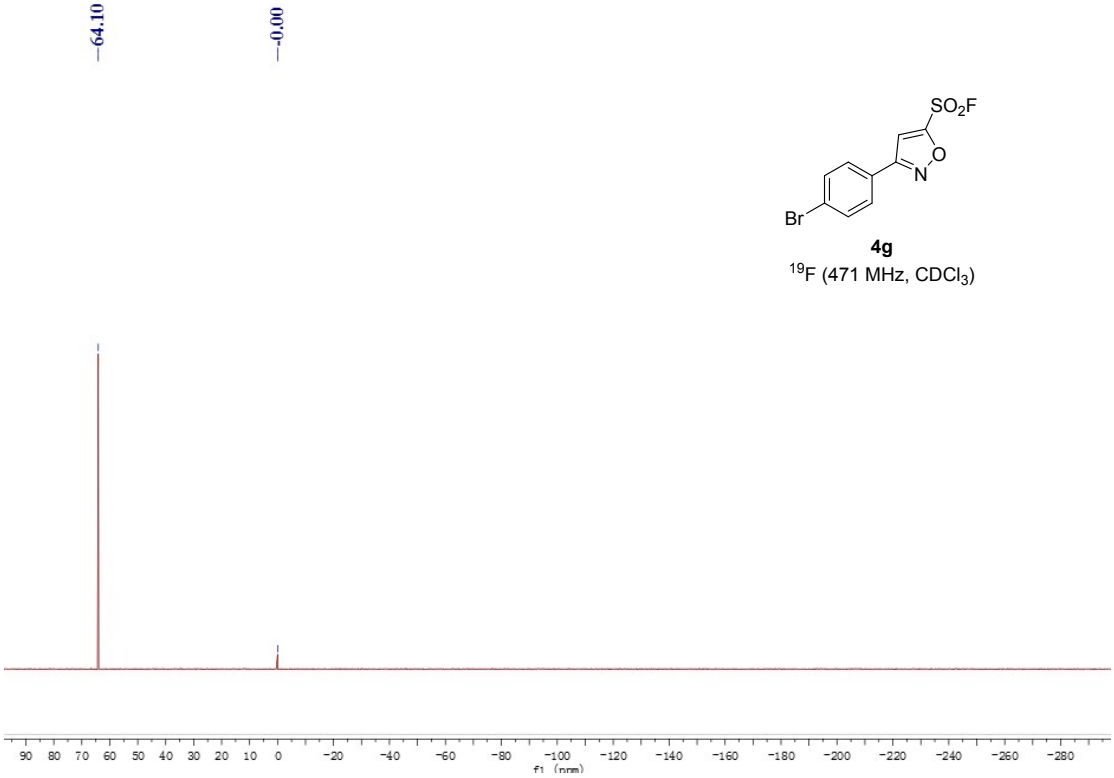
4g

^{1}H (500 MHz, $CDCl_3$)



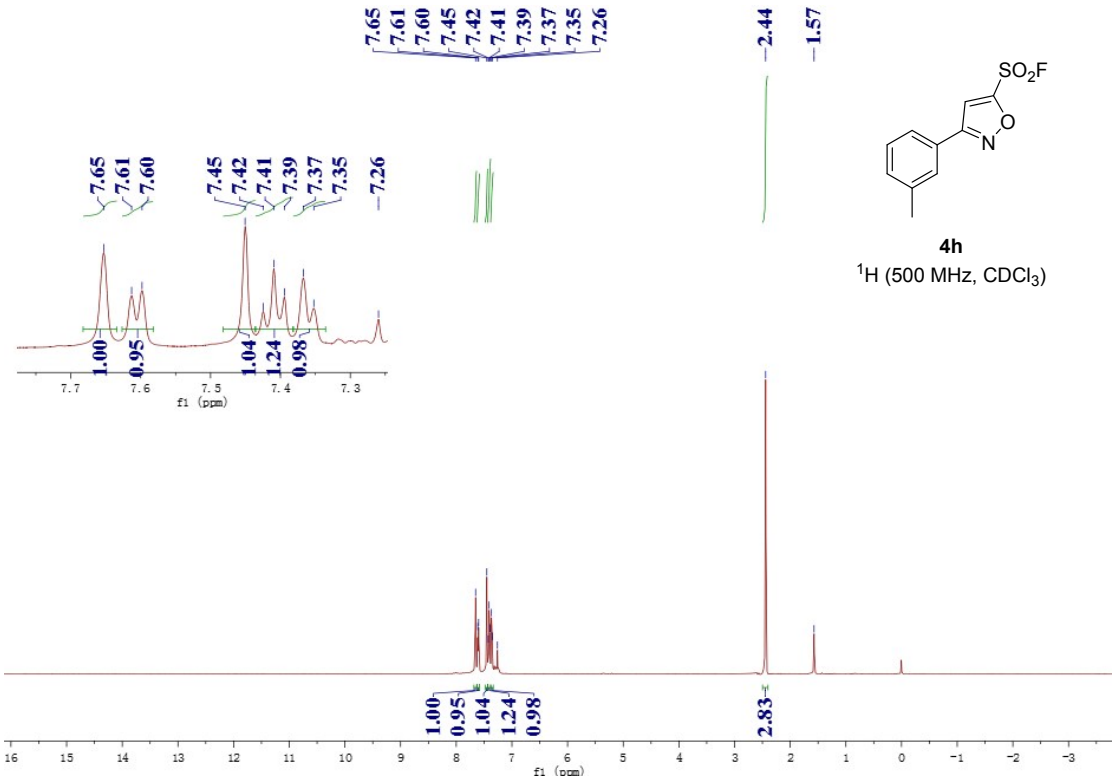
4g

^{13}C (126 MHz, $CDCl_3$)



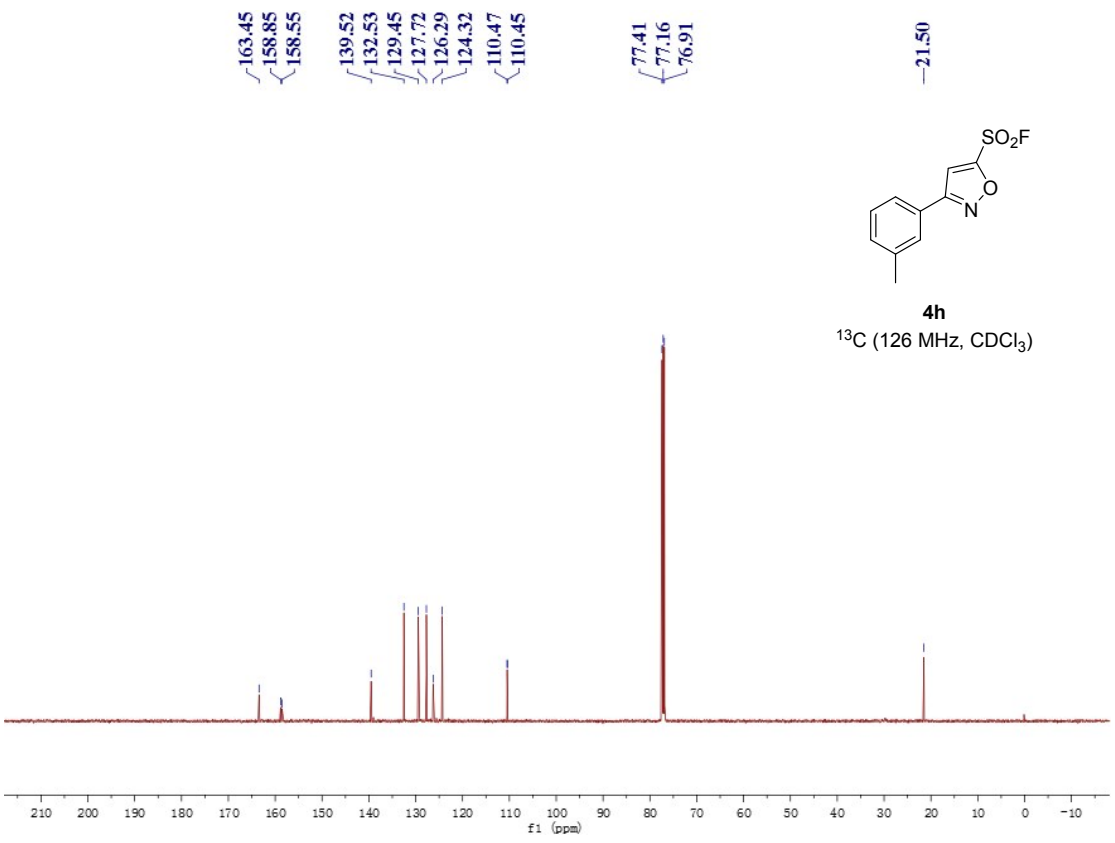
4g

^{19}F (471 MHz, $CDCl_3$)



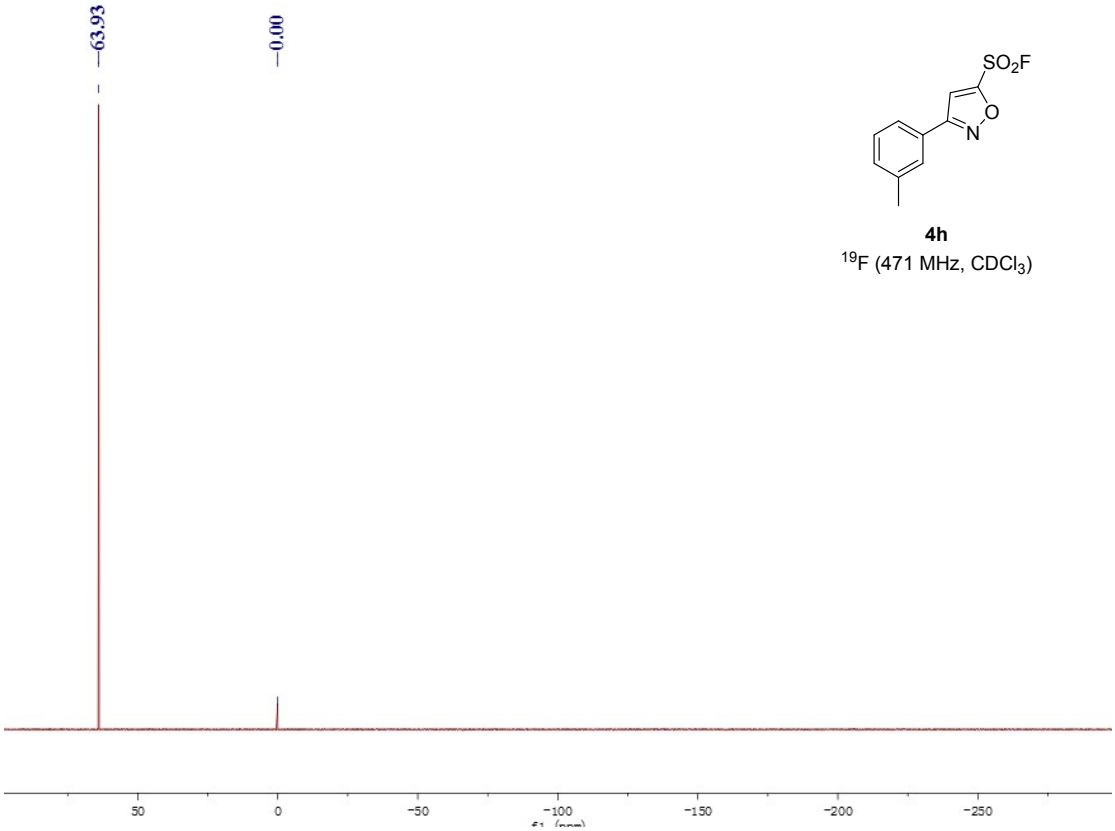
4h

^{1}H (500 MHz, $CDCl_3$)



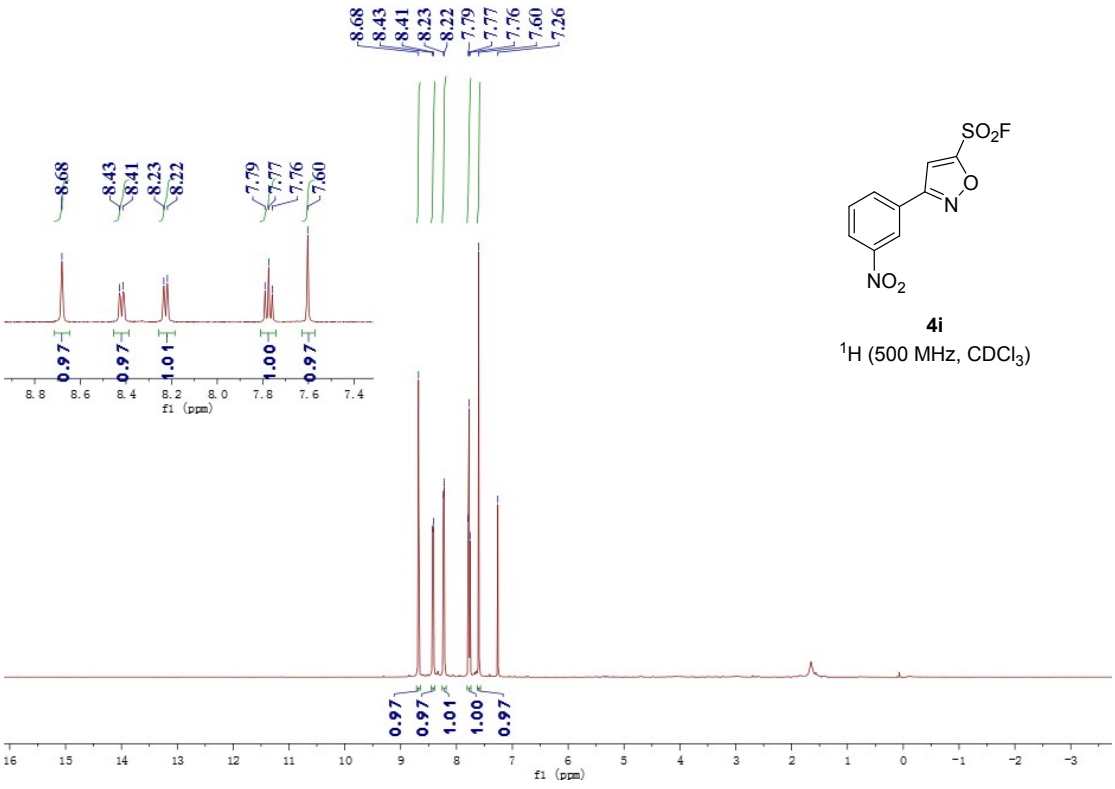
4h

^{13}C (126 MHz, $CDCl_3$)



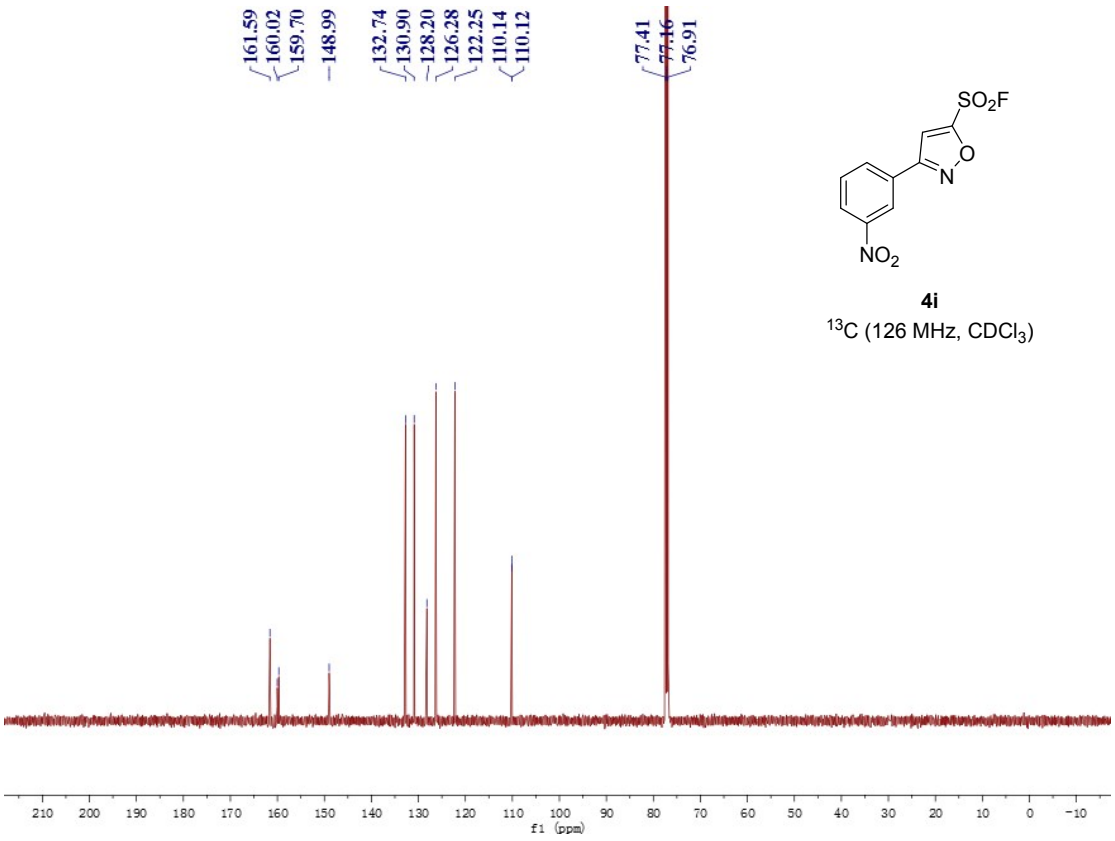
4h

^{19}F (471 MHz, $CDCl_3$)



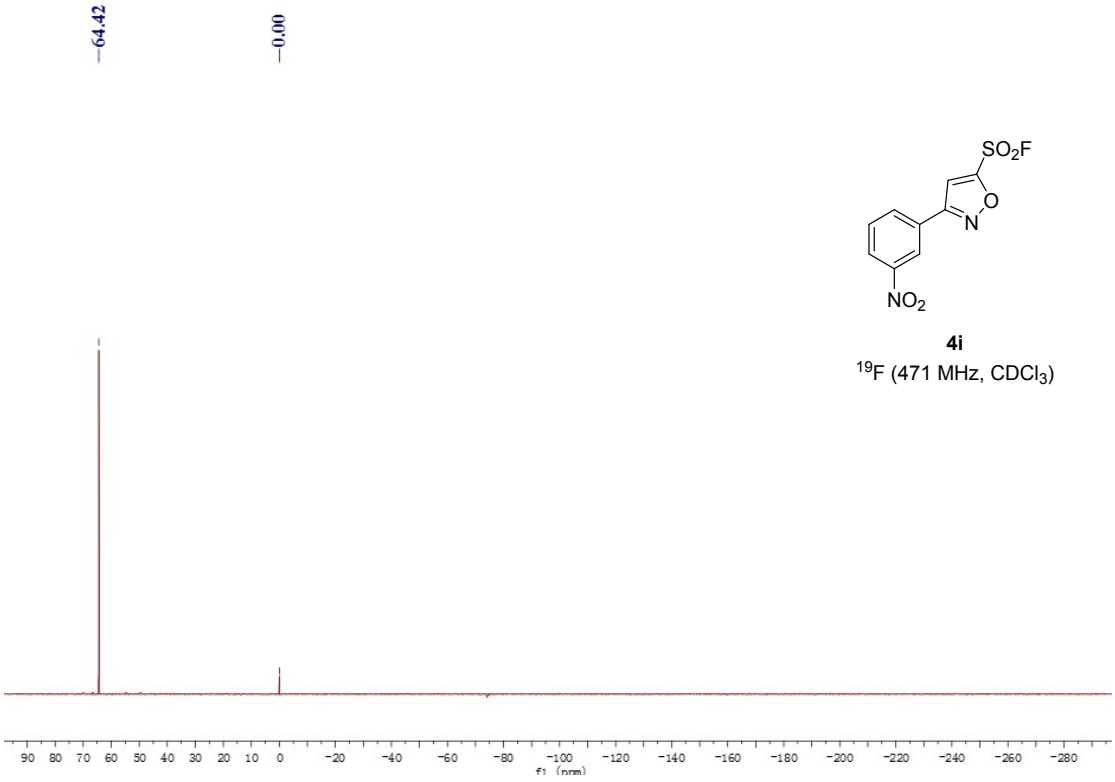
4i

^{1}H (500 MHz, $CDCl_3$)



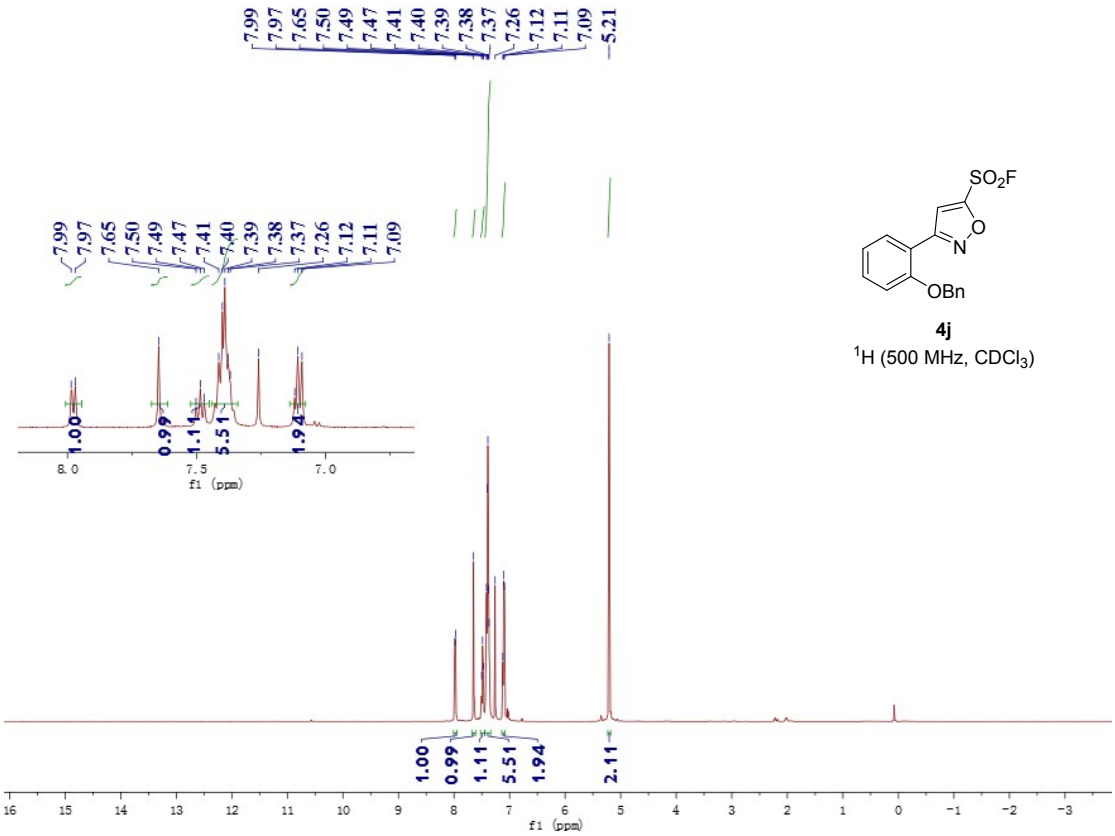
4i

^{13}C (126 MHz, $CDCl_3$)



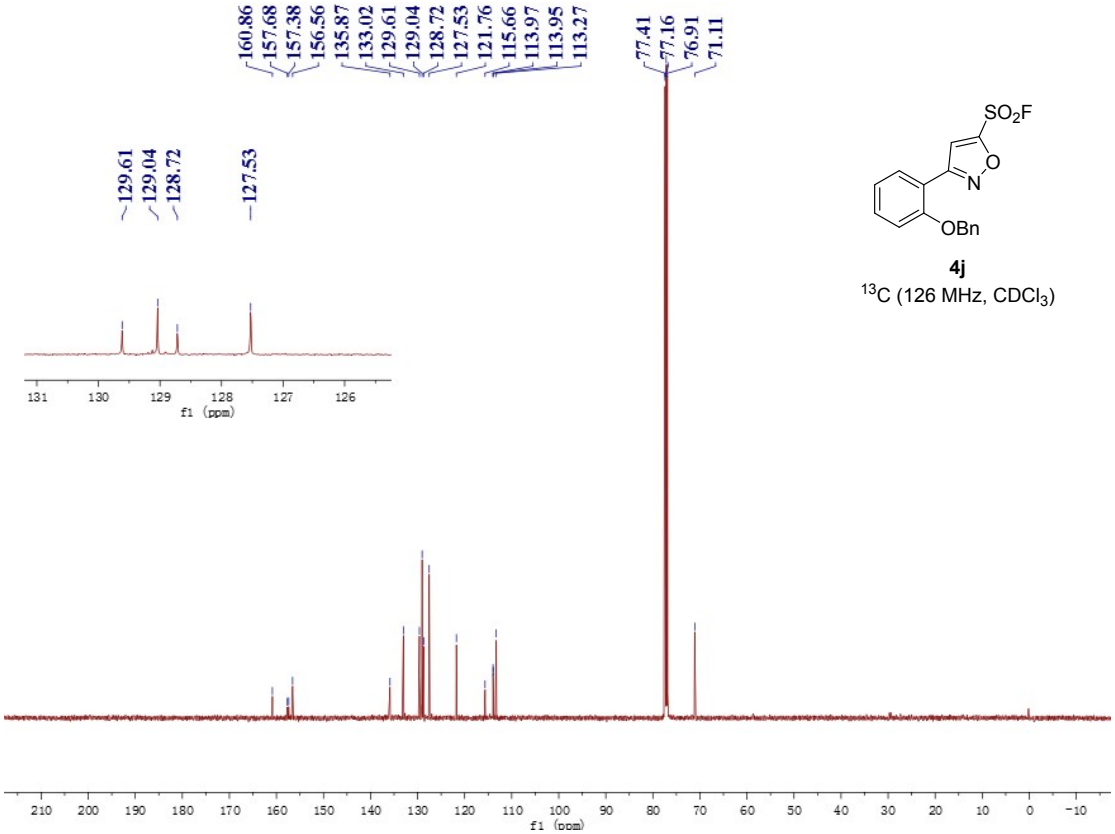
4i

^{19}F (471 MHz, $CDCl_3$)



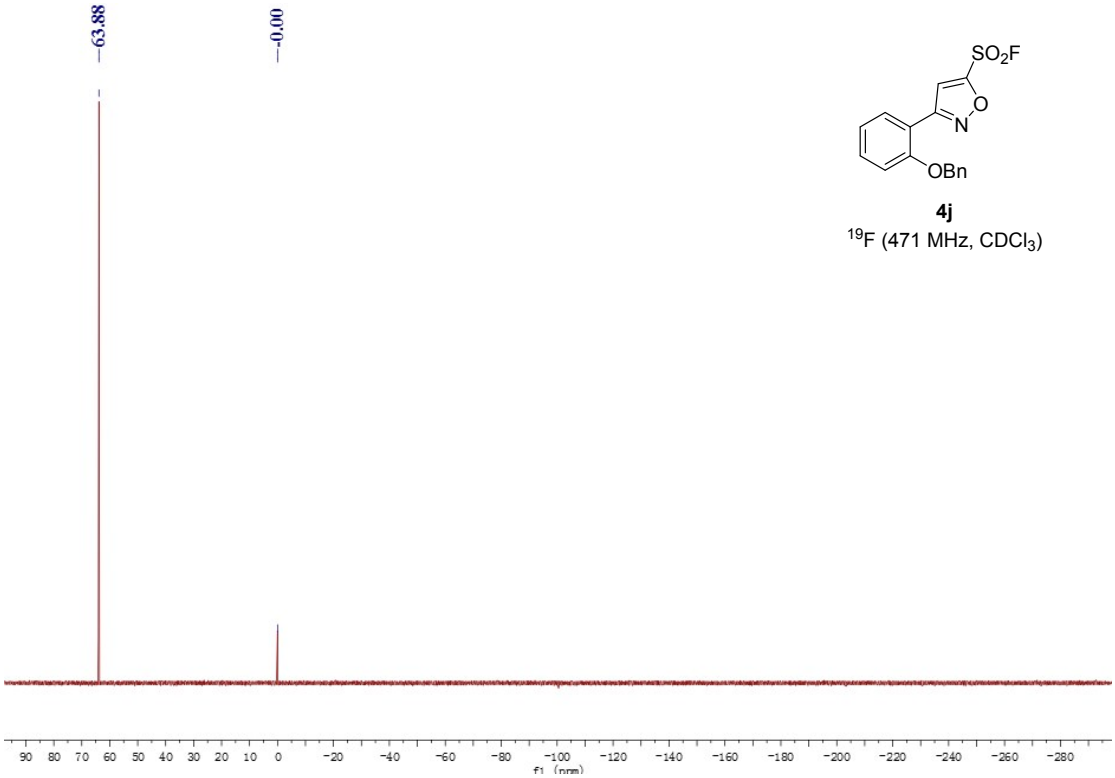
4j

^{1}H (500 MHz, $CDCl_3$)



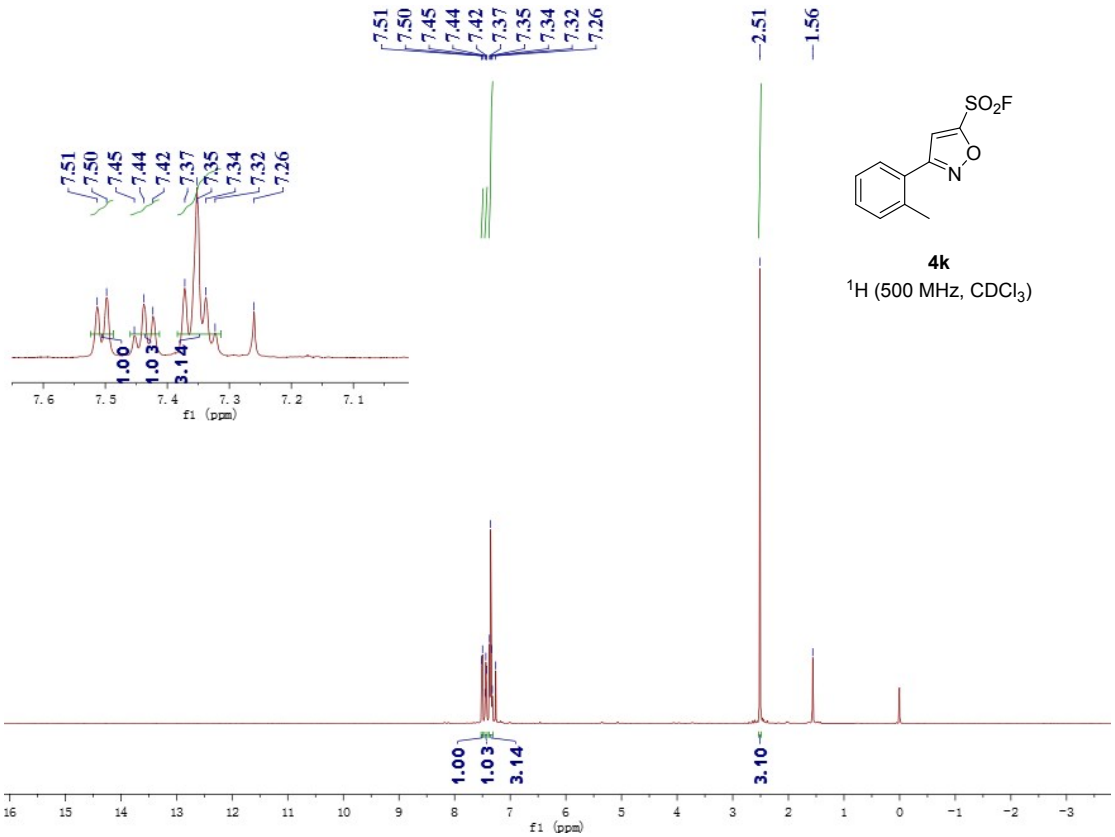
4j

^{13}C (126 MHz, $CDCl_3$)



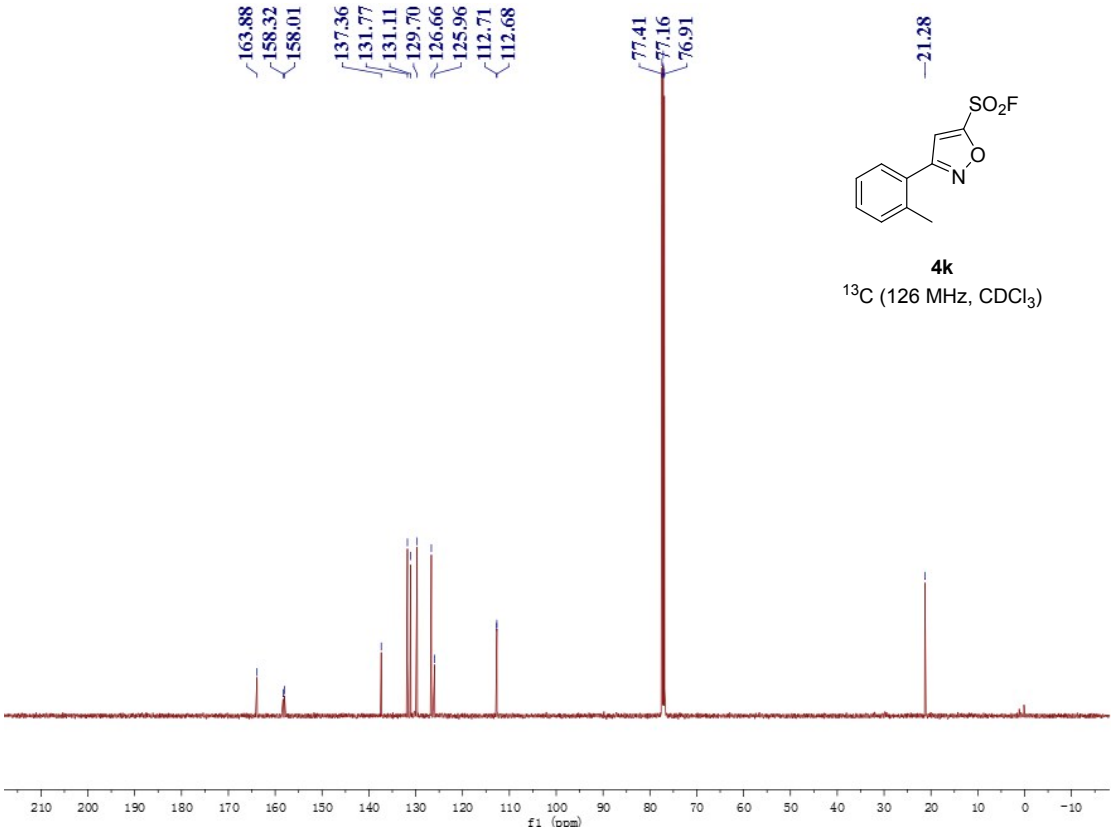
4j

^{19}F (471 MHz, $CDCl_3$)



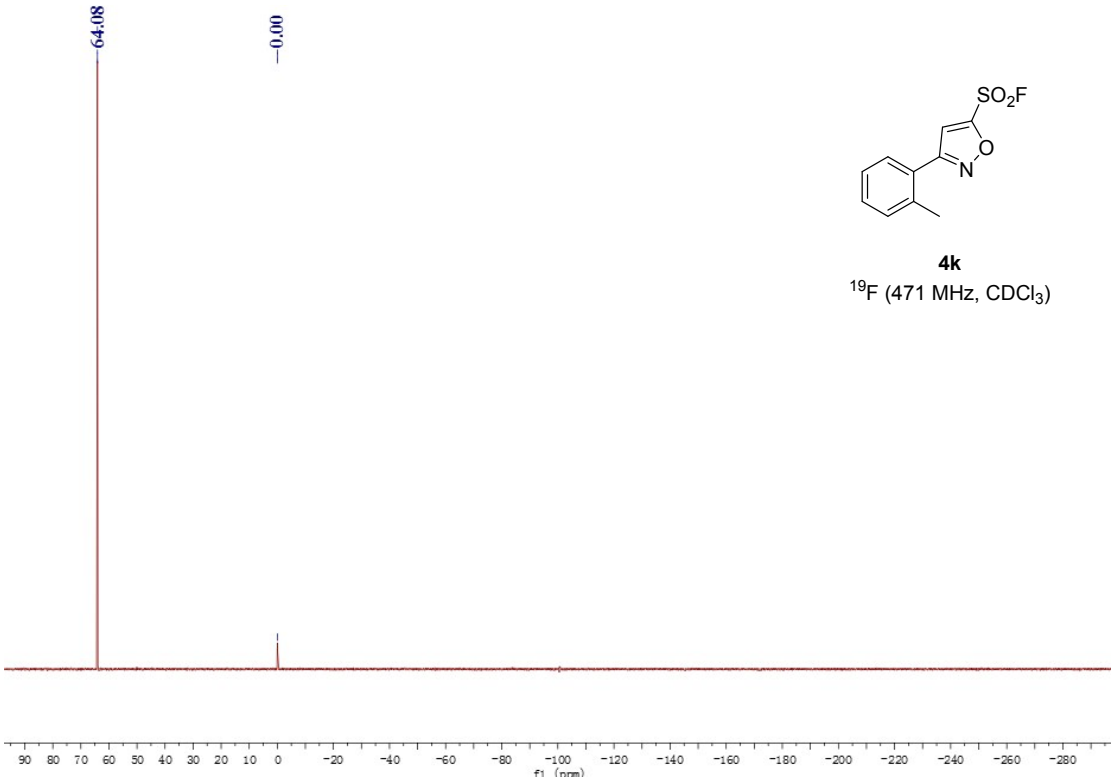
4k

^{1}H (500 MHz, $CDCl_3$)



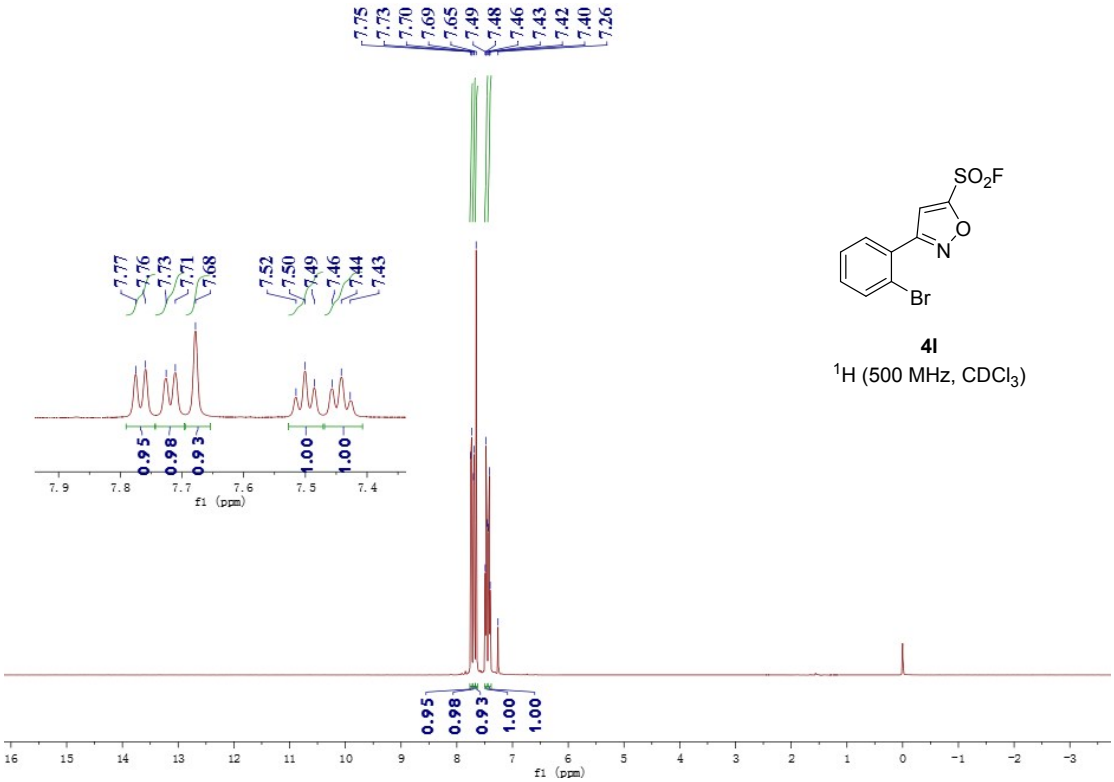
4k

^{13}C (126 MHz, $CDCl_3$)



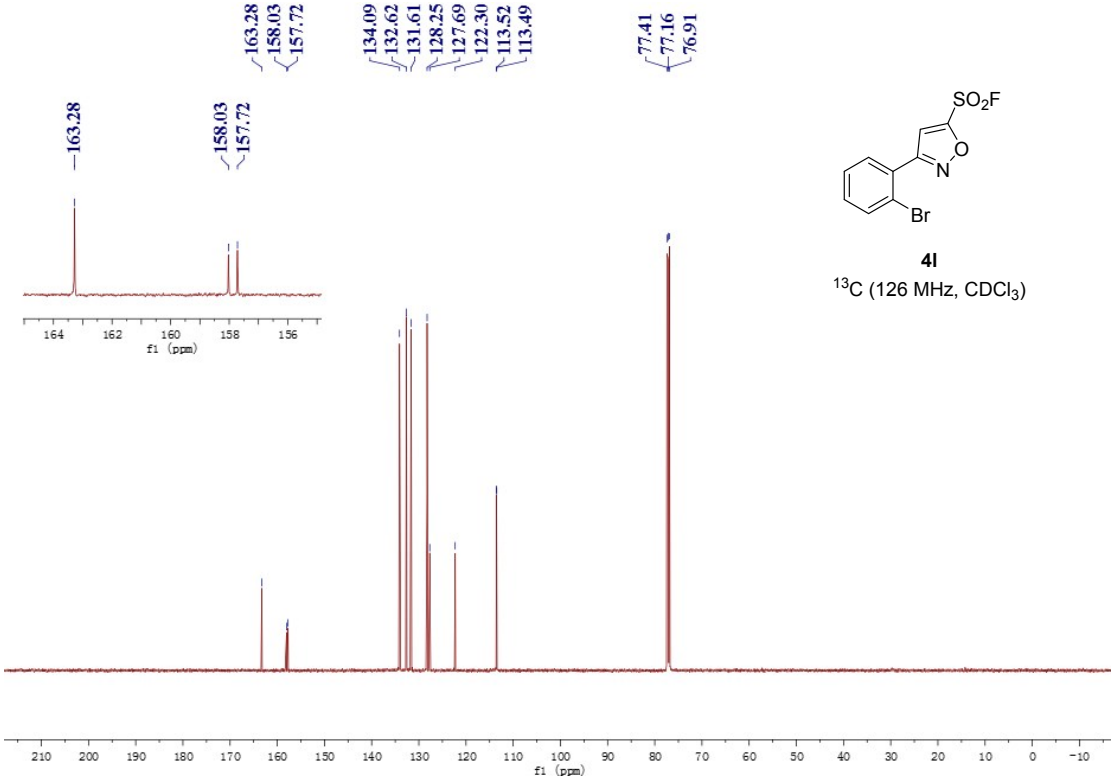
4k

^{19}F (471 MHz, $CDCl_3$)



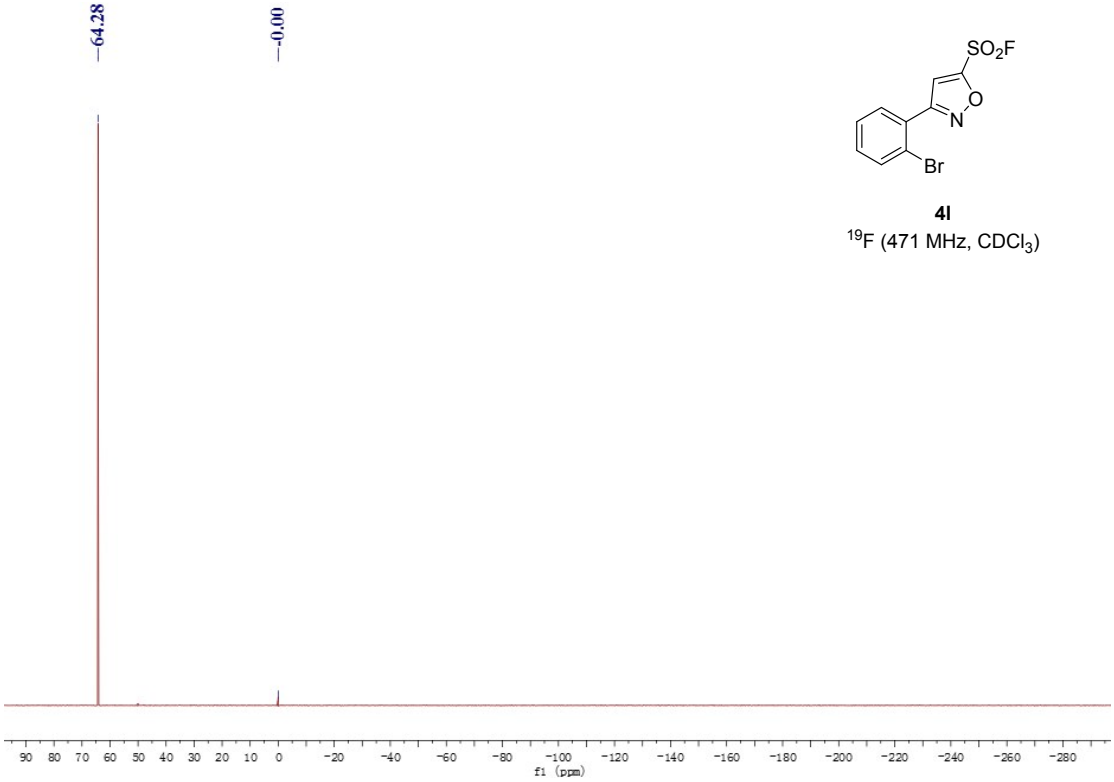
4l

^{1}H (500 MHz, $CDCl_3$)



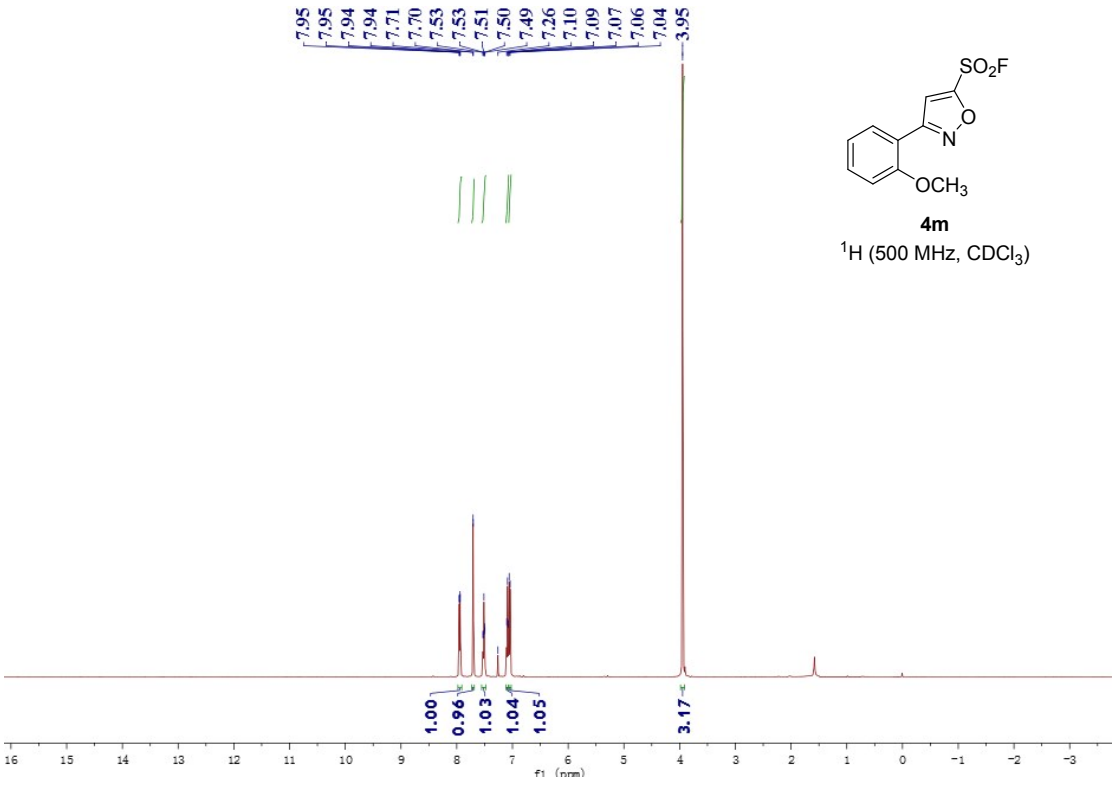
4l

^{13}C (126 MHz, $CDCl_3$)



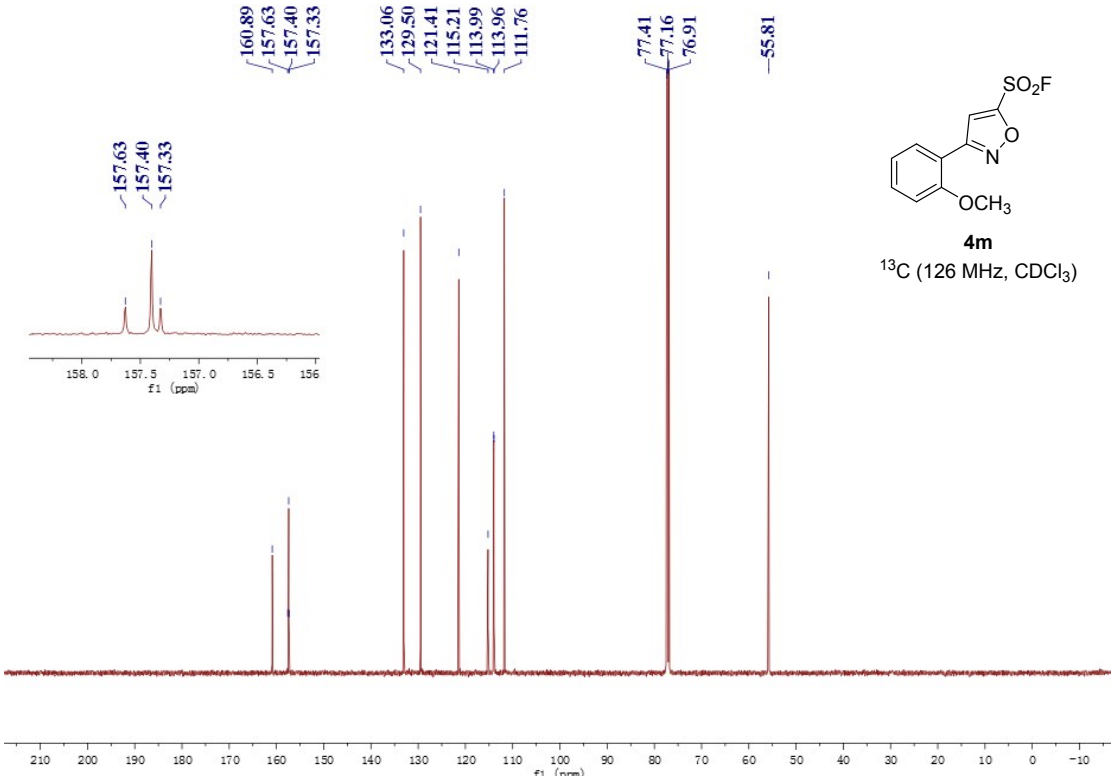
4l

^{19}F (471 MHz, $CDCl_3$)



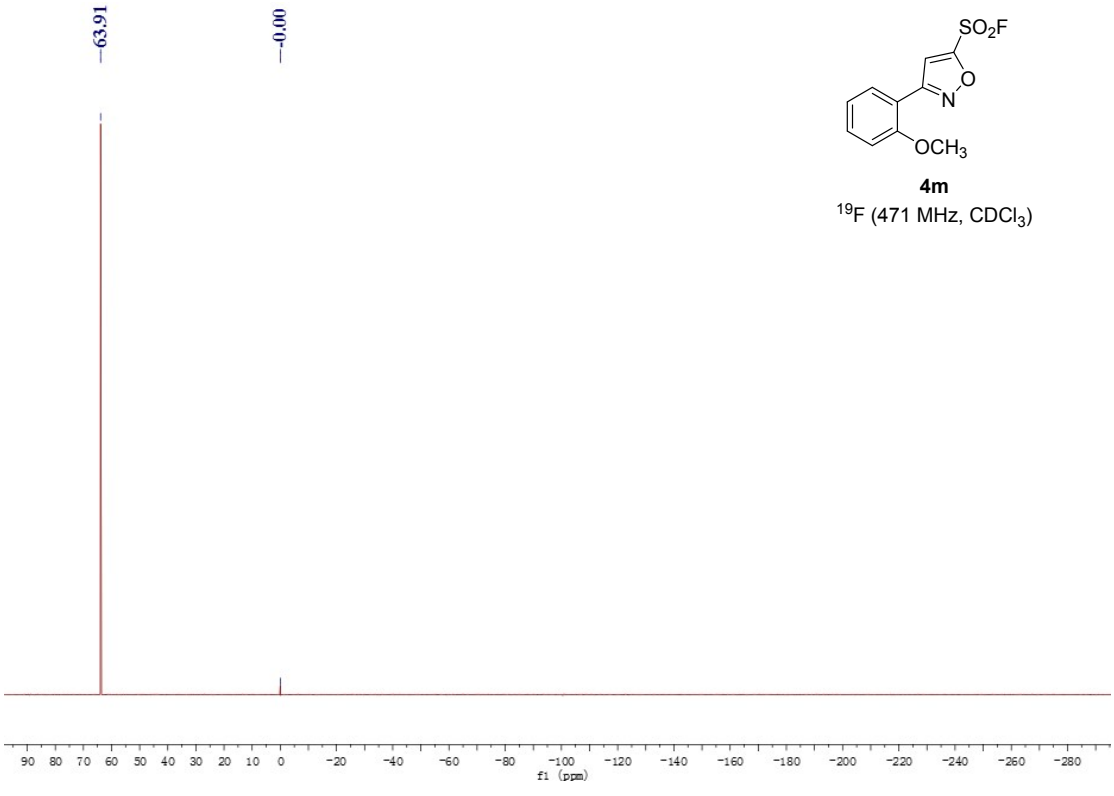
4m

^{1}H (500 MHz, $CDCl_3$)



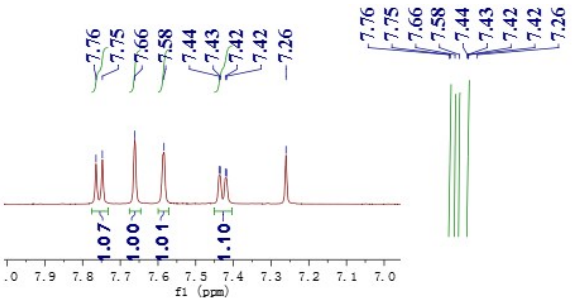
4m

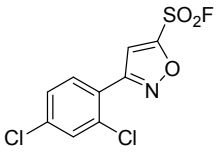
^{13}C (126 MHz, $CDCl_3$)



4m

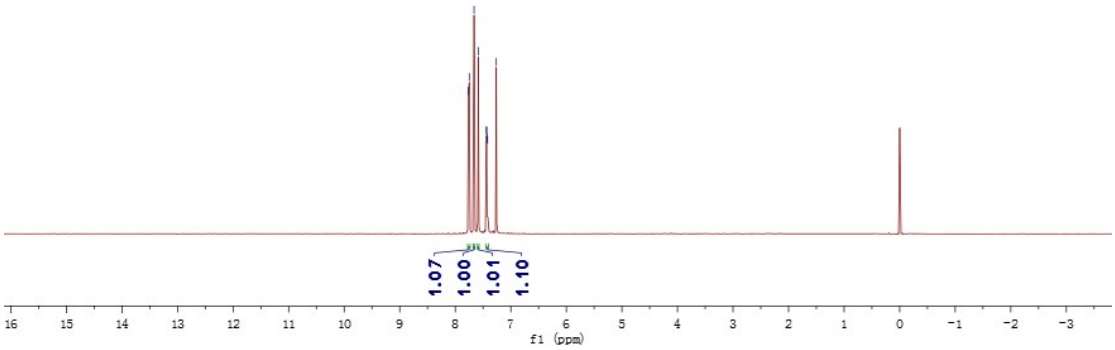
^{19}F (471 MHz, $CDCl_3$)

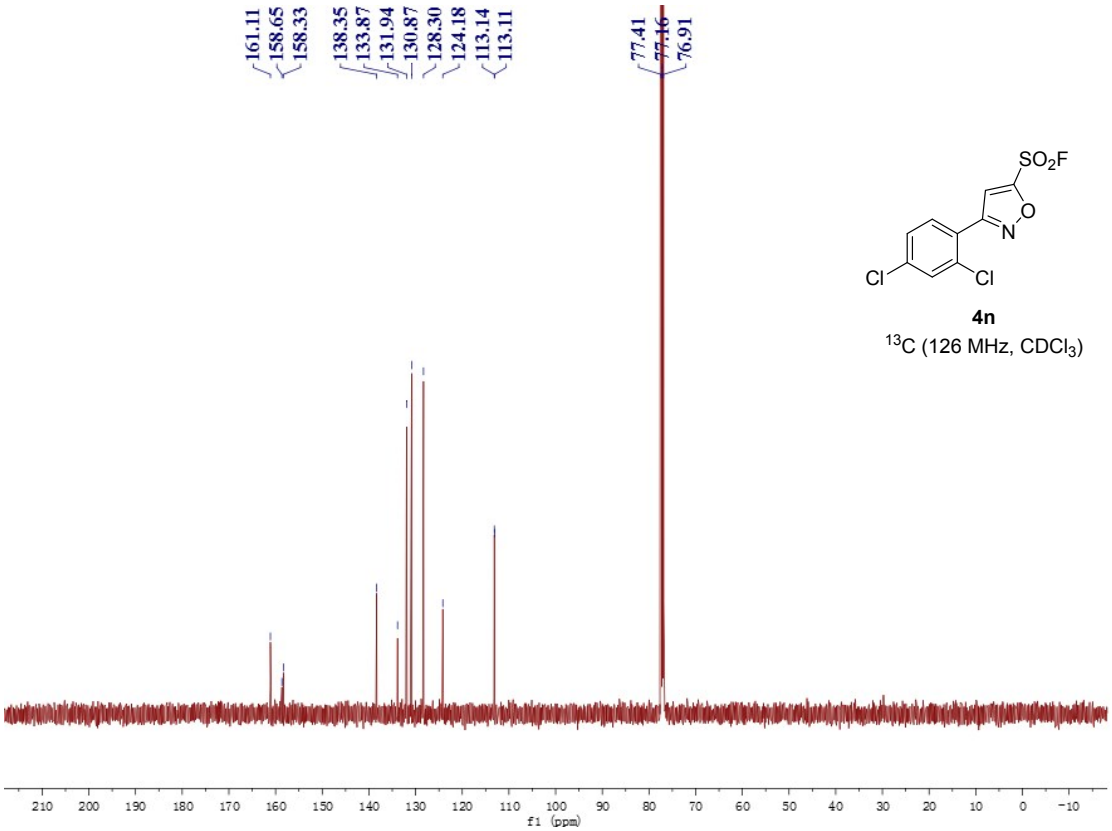




4n

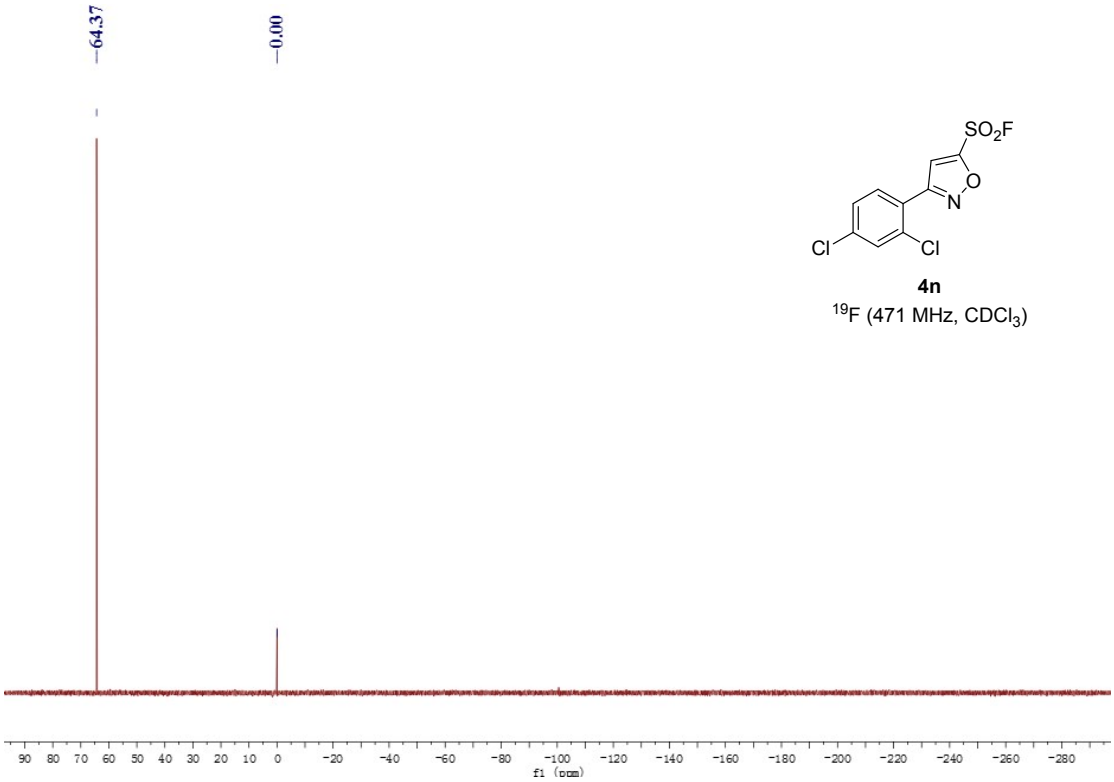
^{1}H (500 MHz, $CDCl_3$)





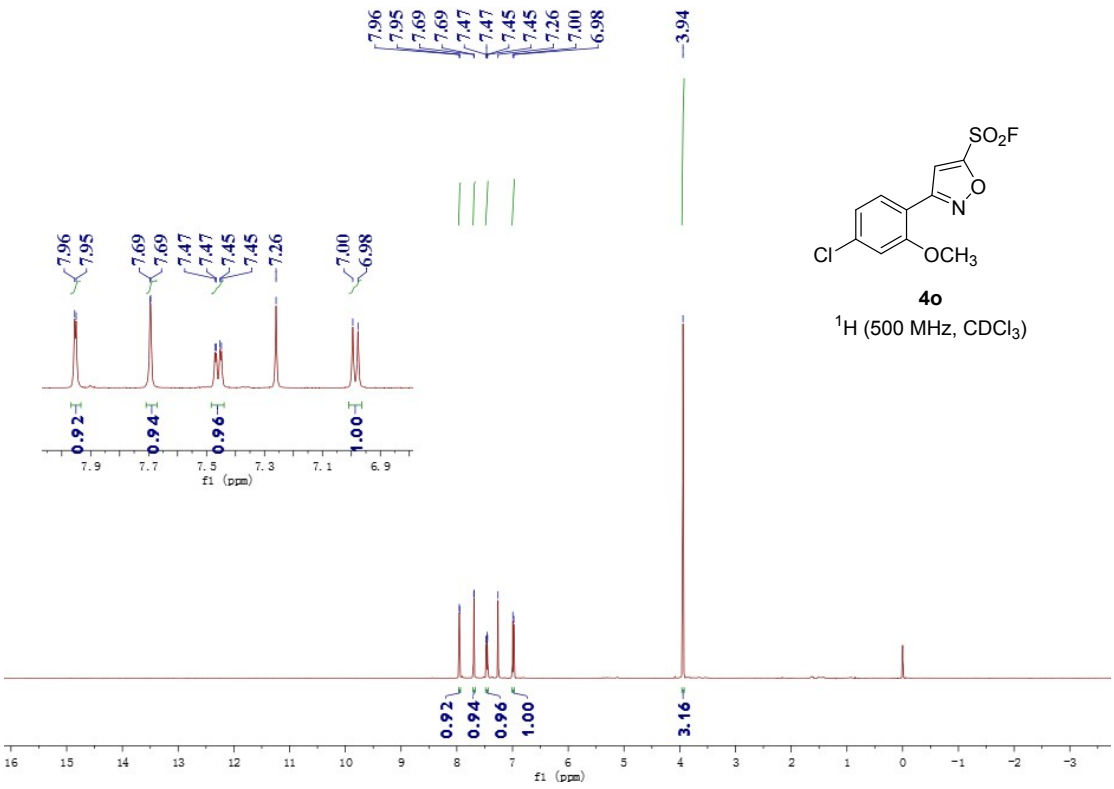
4n

^{13}C (126 MHz, $CDCl_3$)



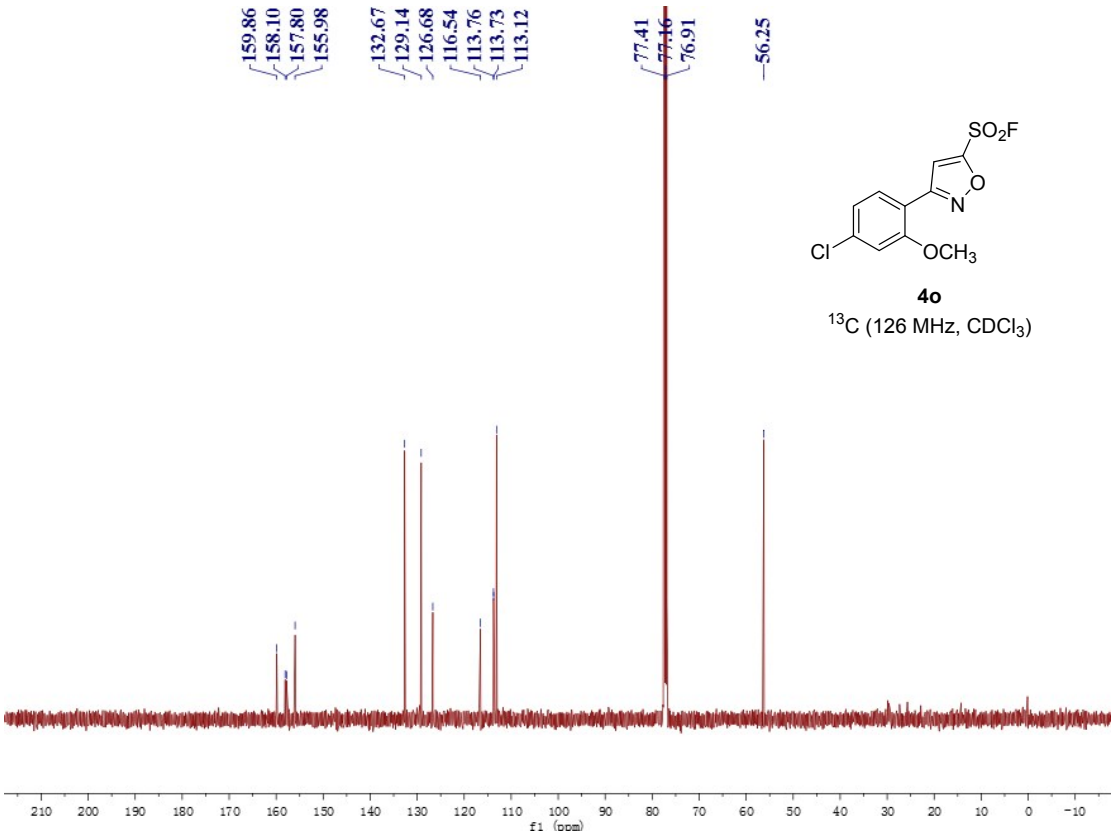
4n

^{19}F (471 MHz, $CDCl_3$)



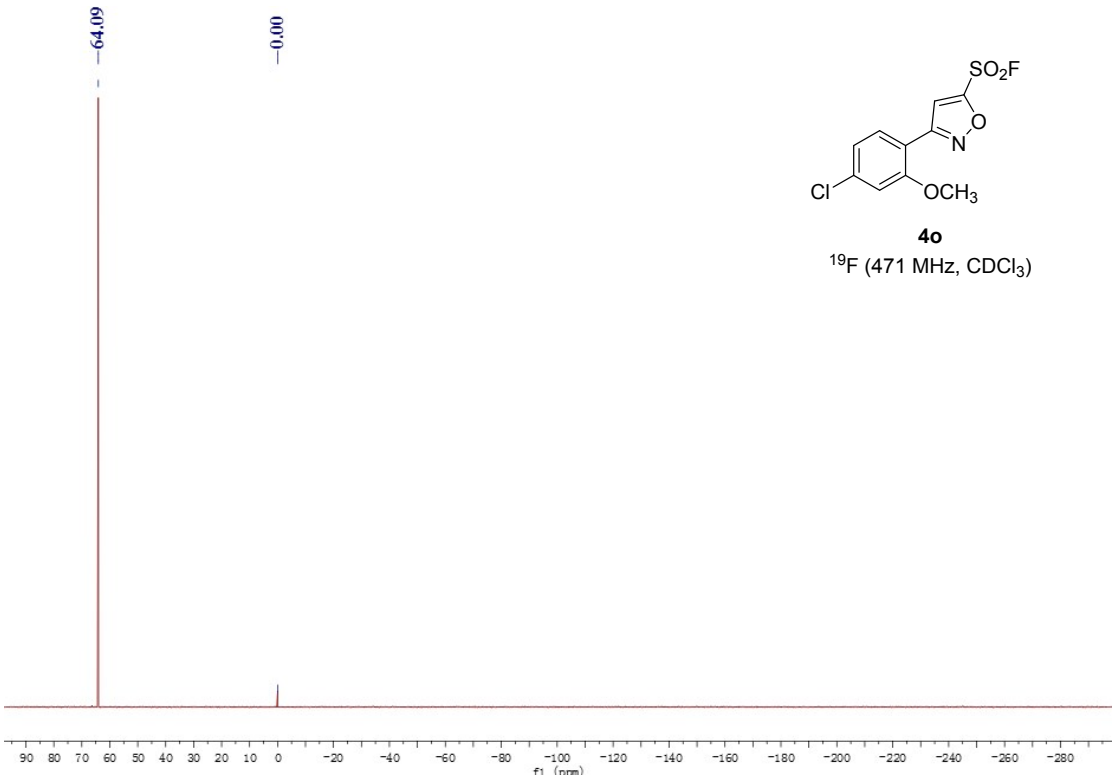
4o

^{1}H (500 MHz, $CDCl_3$)



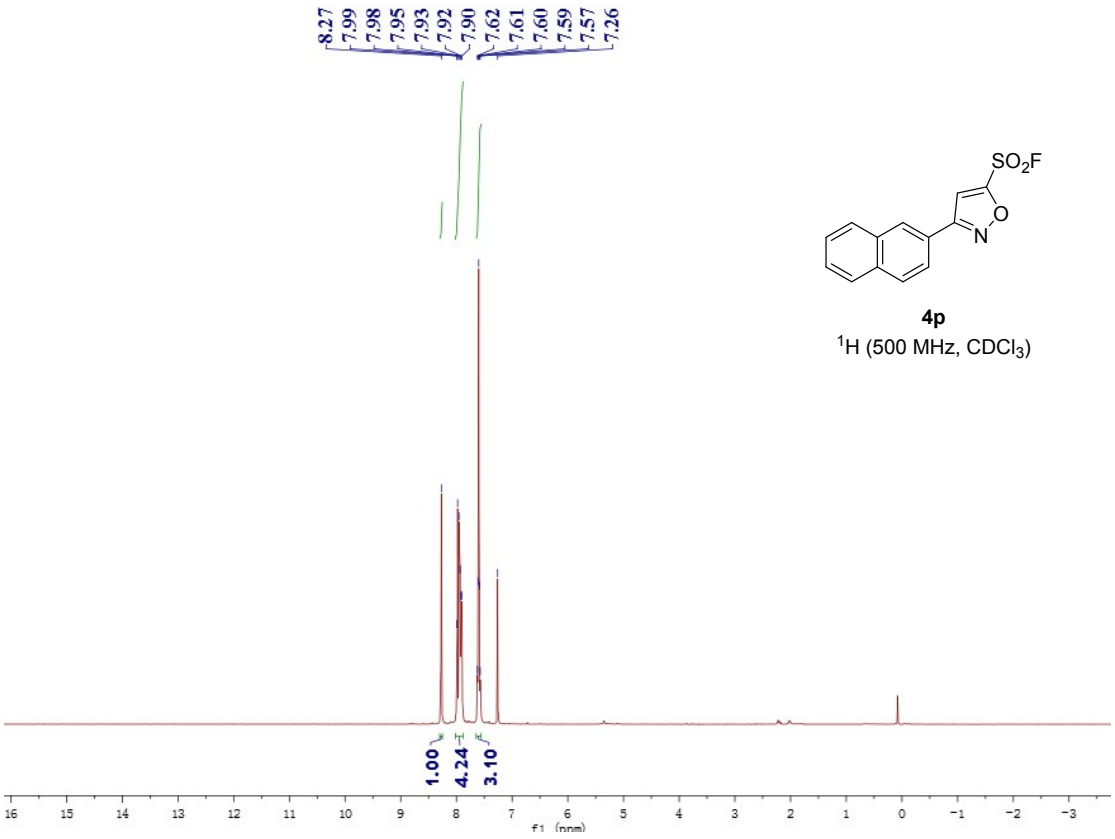
4o

^{13}C (126 MHz, $CDCl_3$)



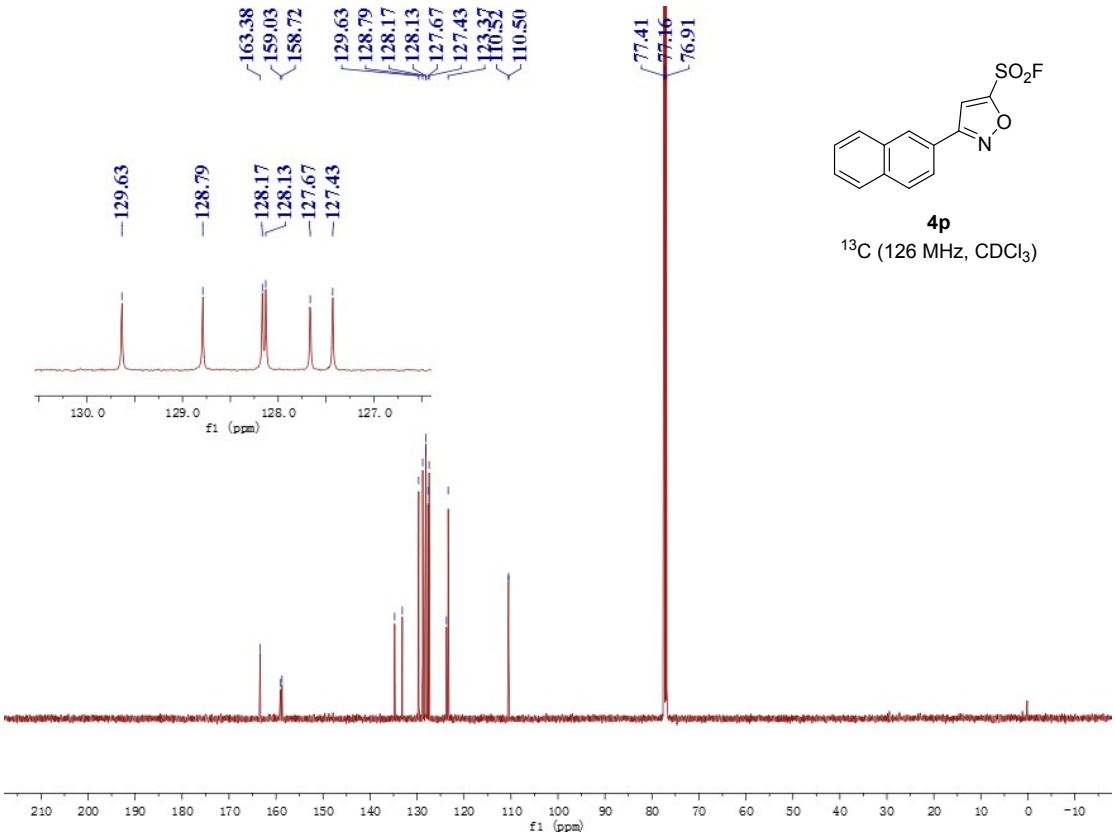
4o

^{19}F (471 MHz, $CDCl_3$)



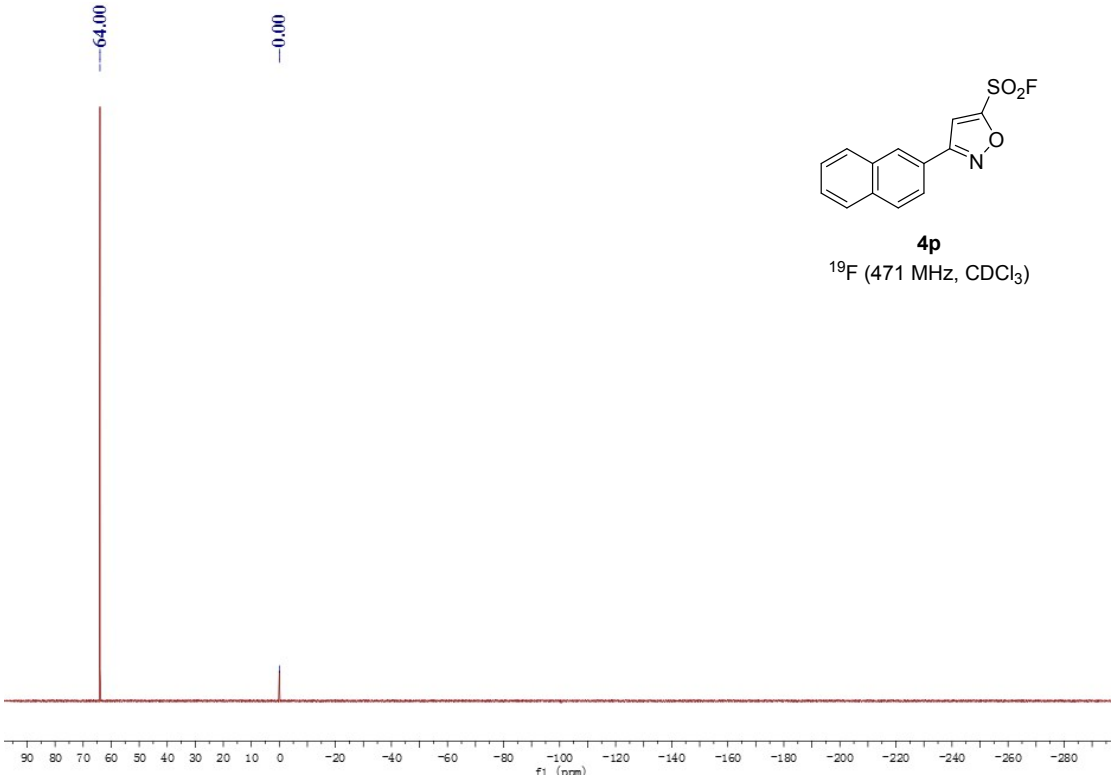
4p

^{1}H (500 MHz, $CDCl_3$)



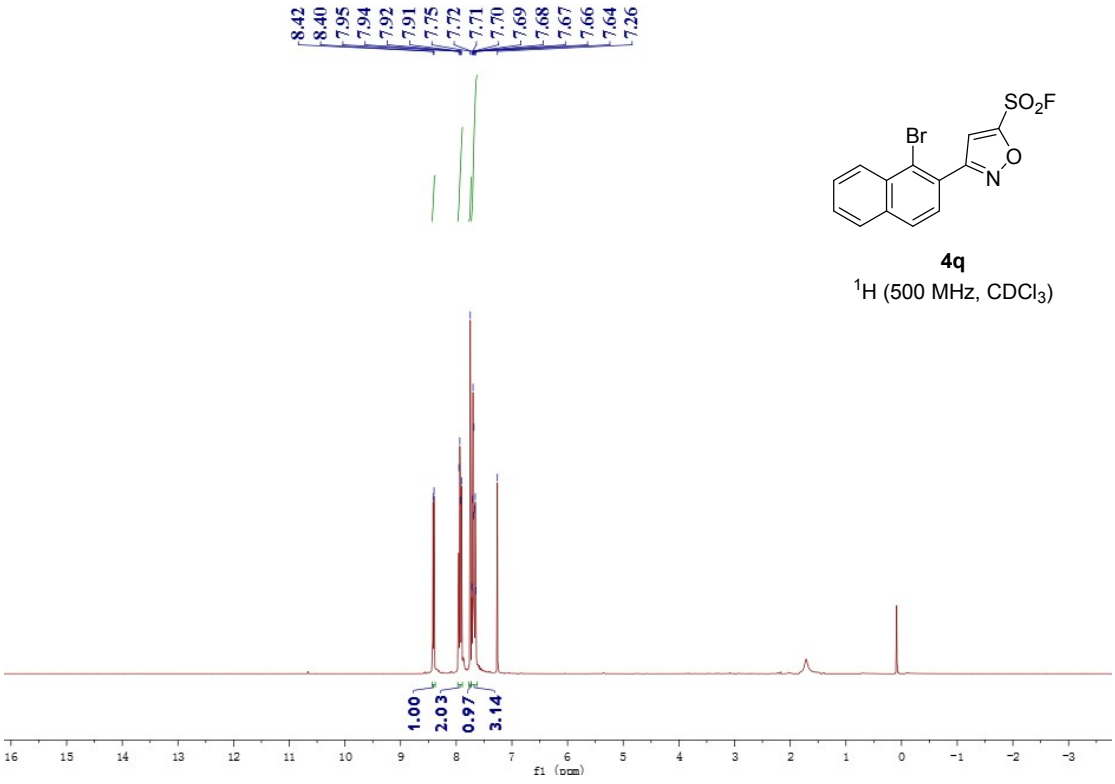
4p

^{13}C (126 MHz, $CDCl_3$)



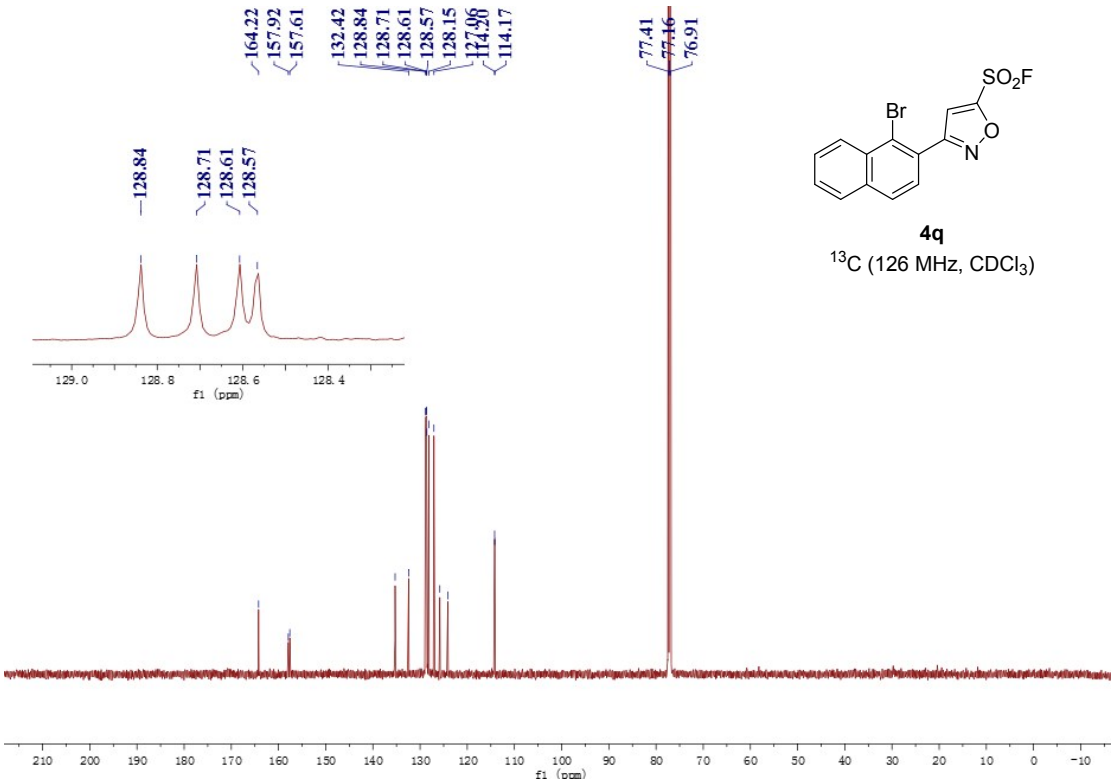
4p

^{19}F (471 MHz, $CDCl_3$)



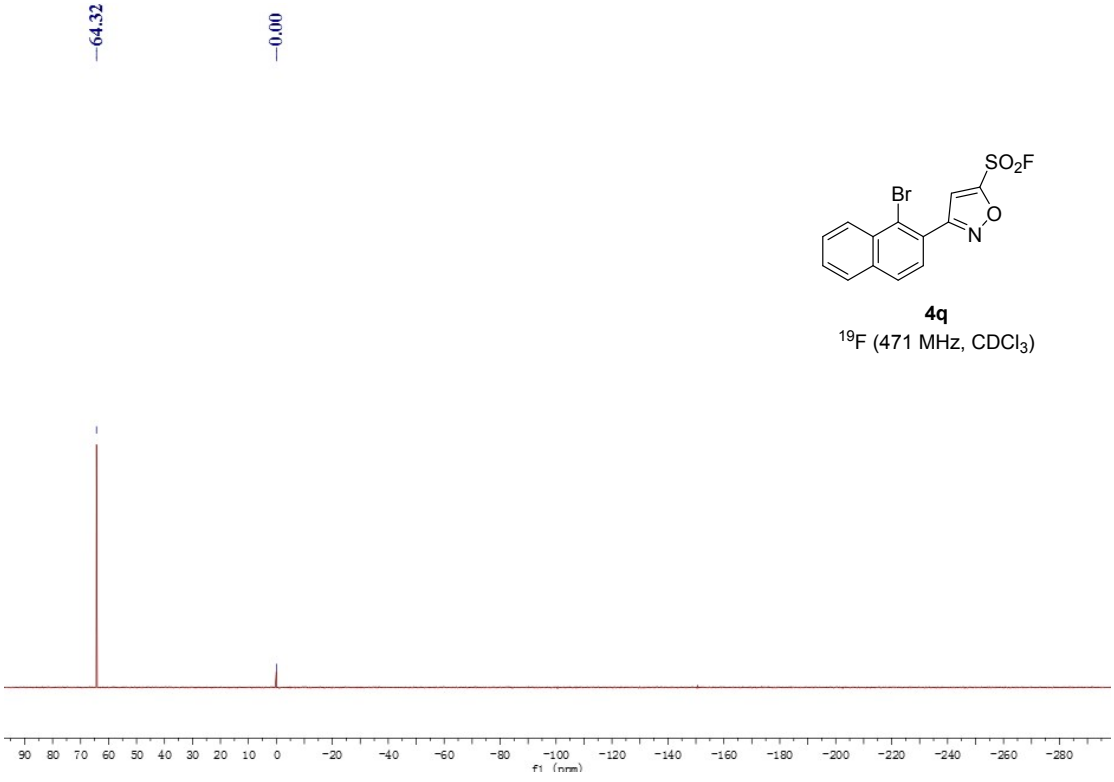
4q

^{1}H (500 MHz, $CDCl_3$)



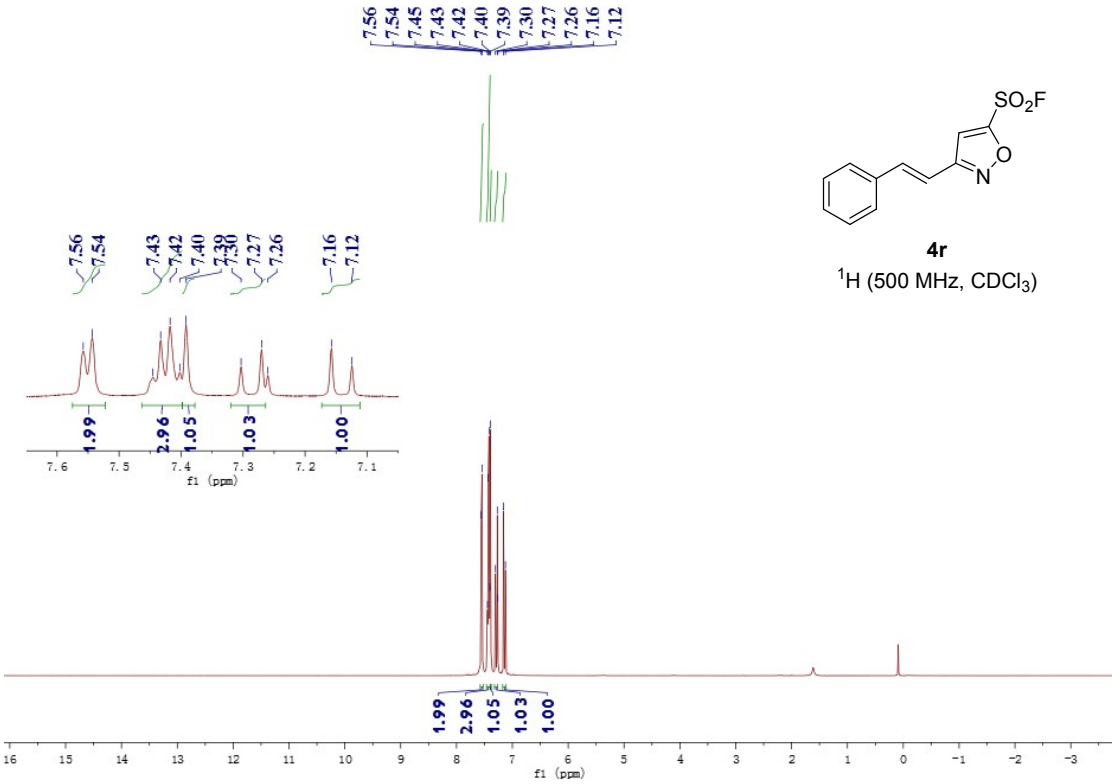
4q

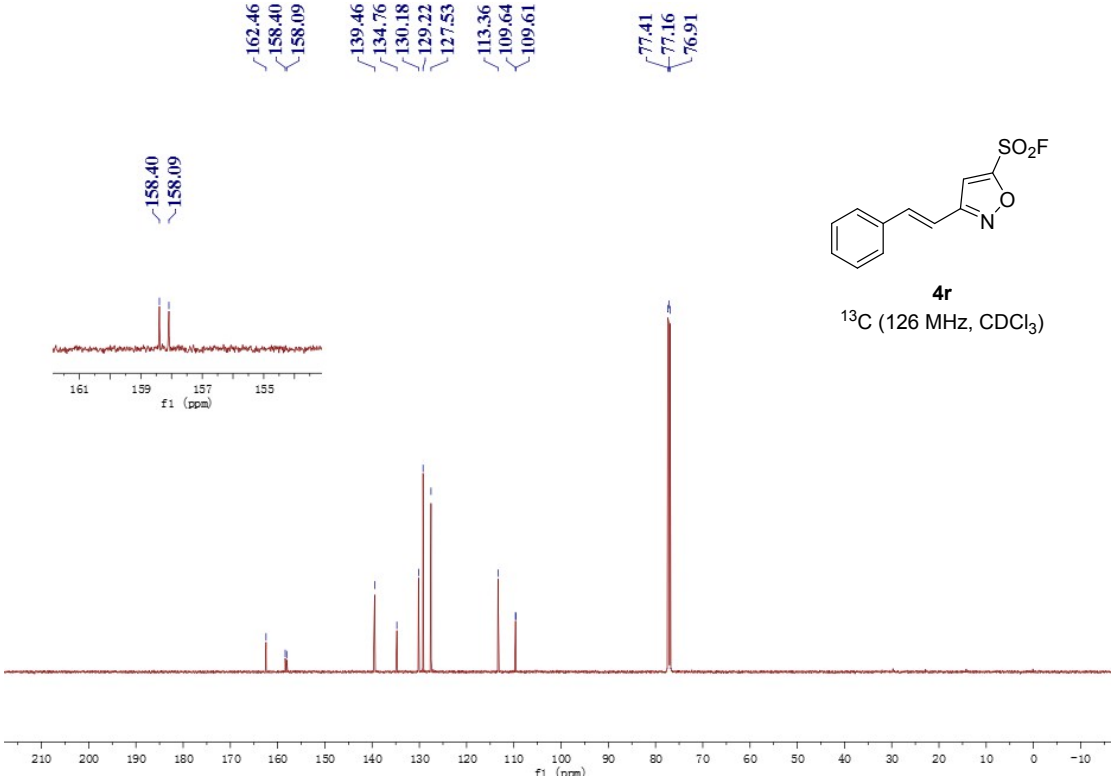
^{13}C (126 MHz, $CDCl_3$)

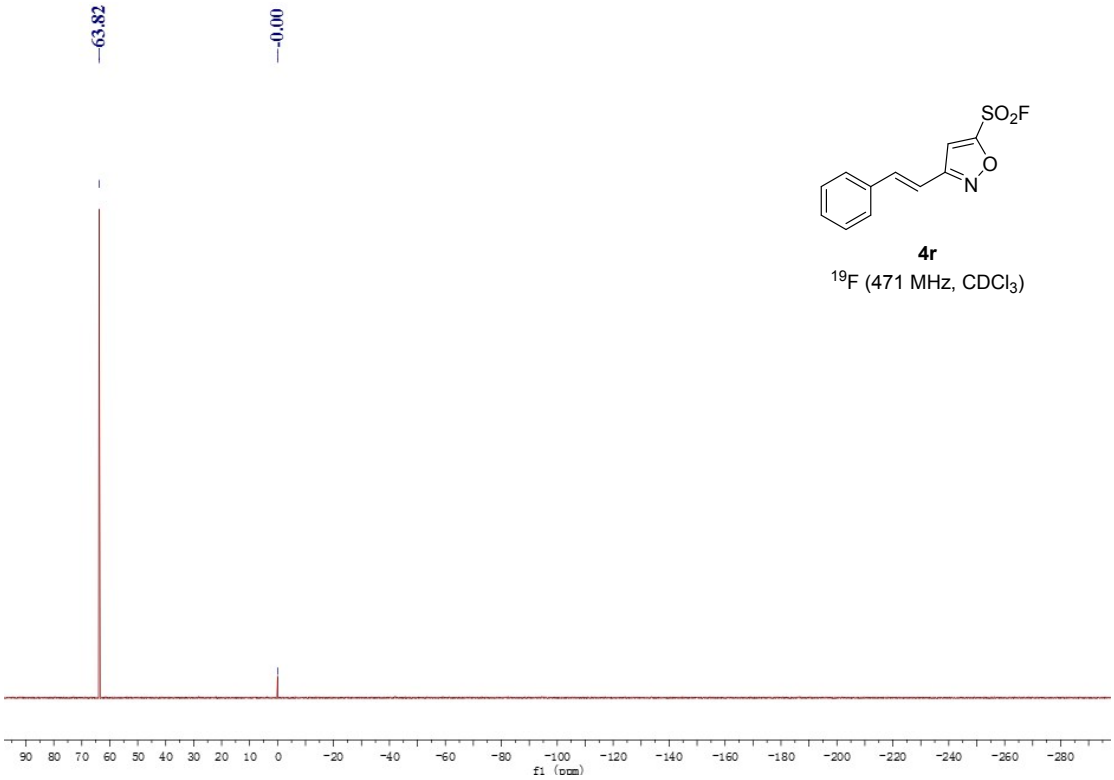


4q

^{19}F (471 MHz, $CDCl_3$)

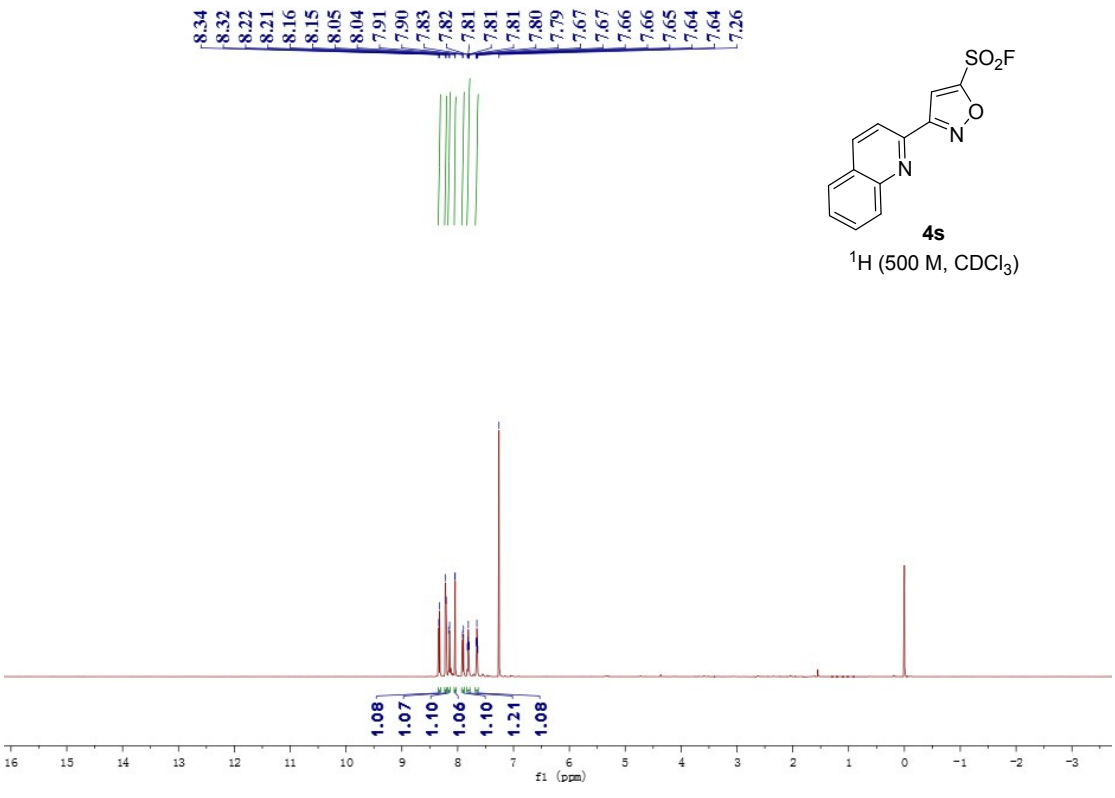

7.56
7.54
7.45
7.43
7.42
7.40
7.39
7.30
7.27
7.26
7.16
7.12
SO2F
O
N
4r
1H (500 MHz, CDCl3)
1.99
2.96
1.05
1.03
1.00
f1 (ppm)


162.46
158.40
158.09
139.46
134.76
130.18
129.22
127.53
113.36
109.64
109.61
77.41
77.16
76.91
SO2F
O
N
4r
13C (126 MHz, CDCl3)
f1 (ppm)



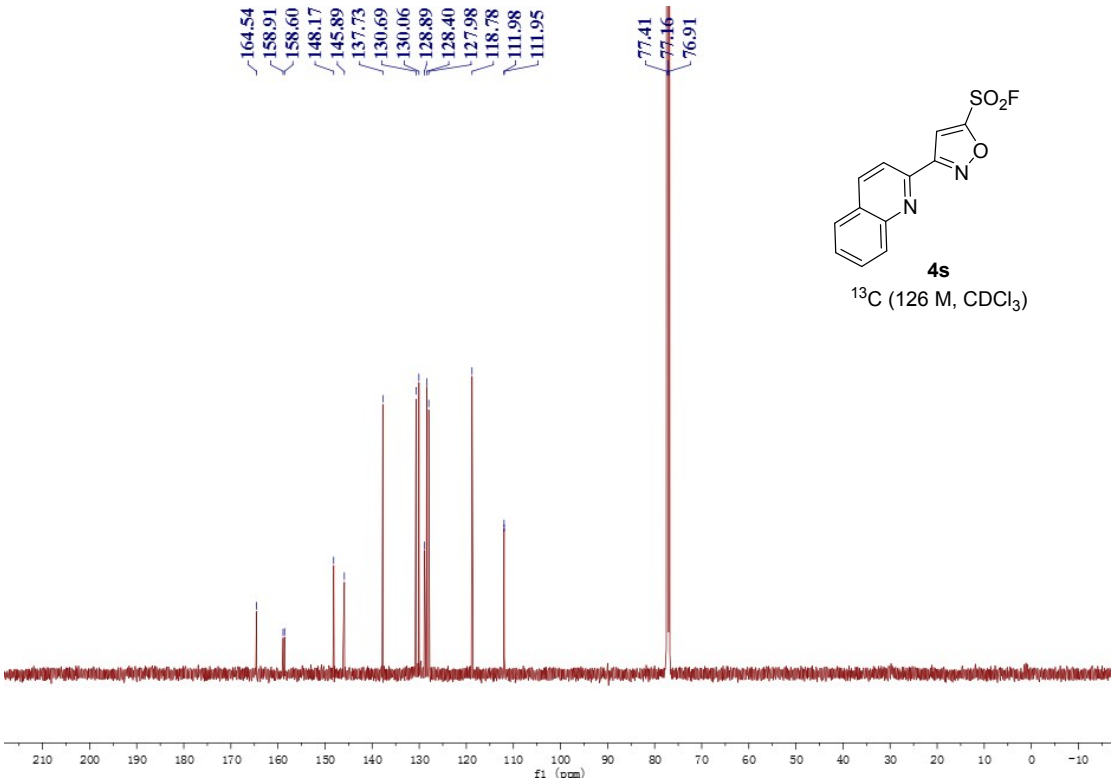
4r

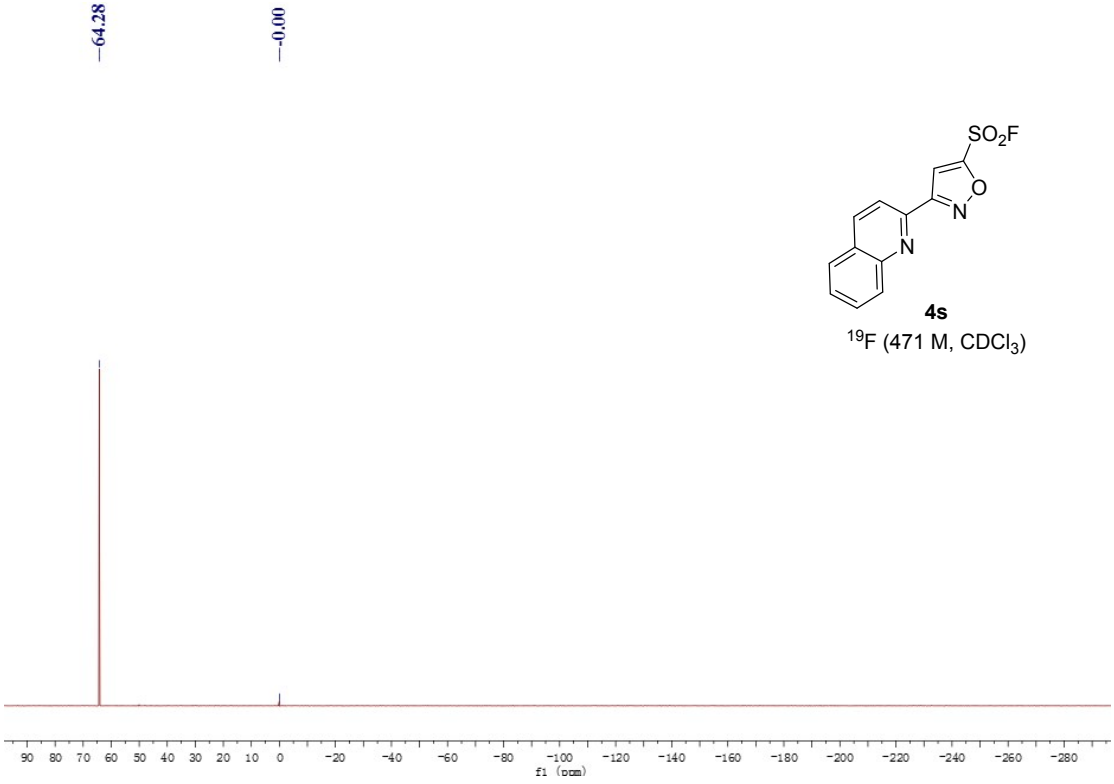
^{19}F (471 MHz, $CDCl_3$)

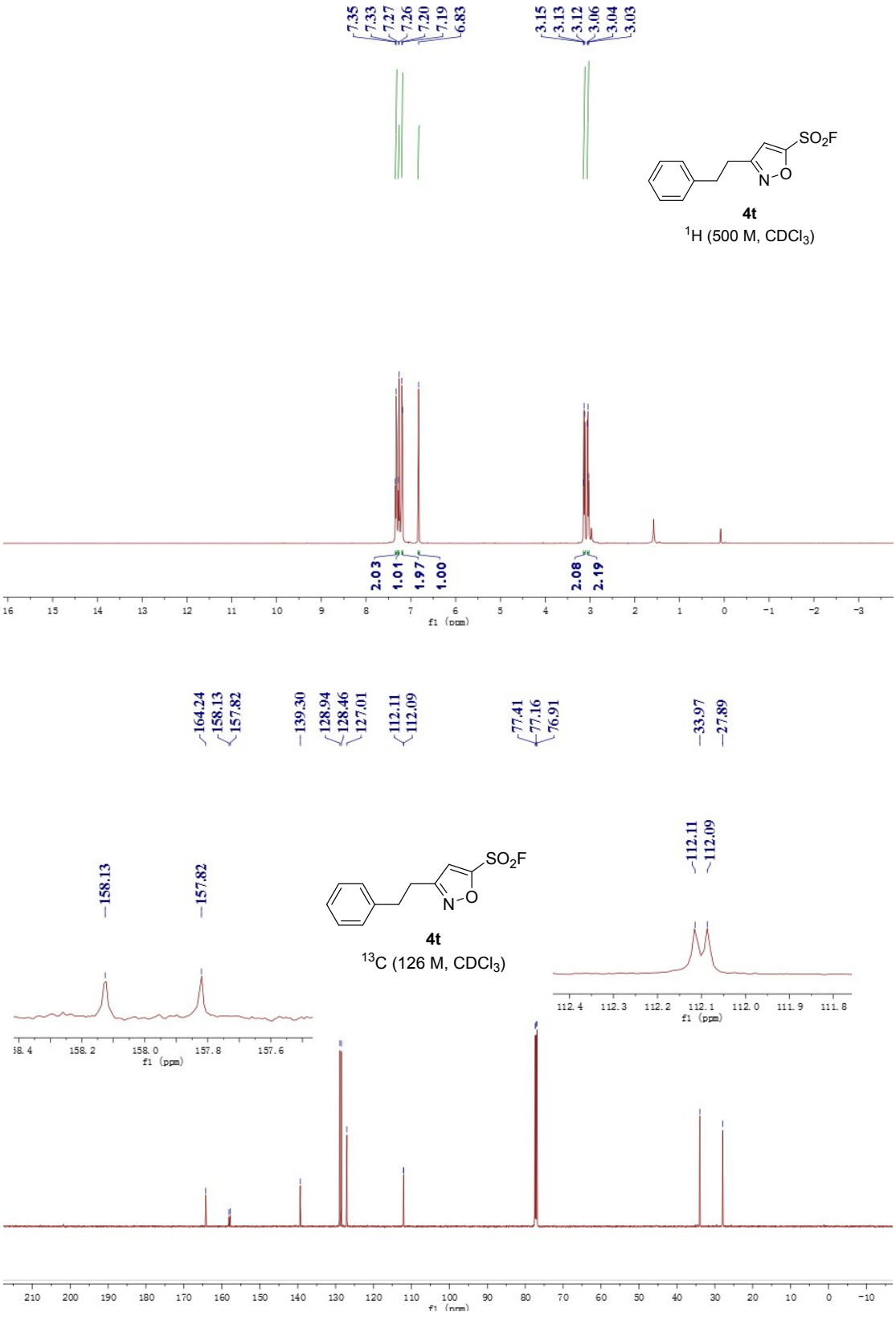


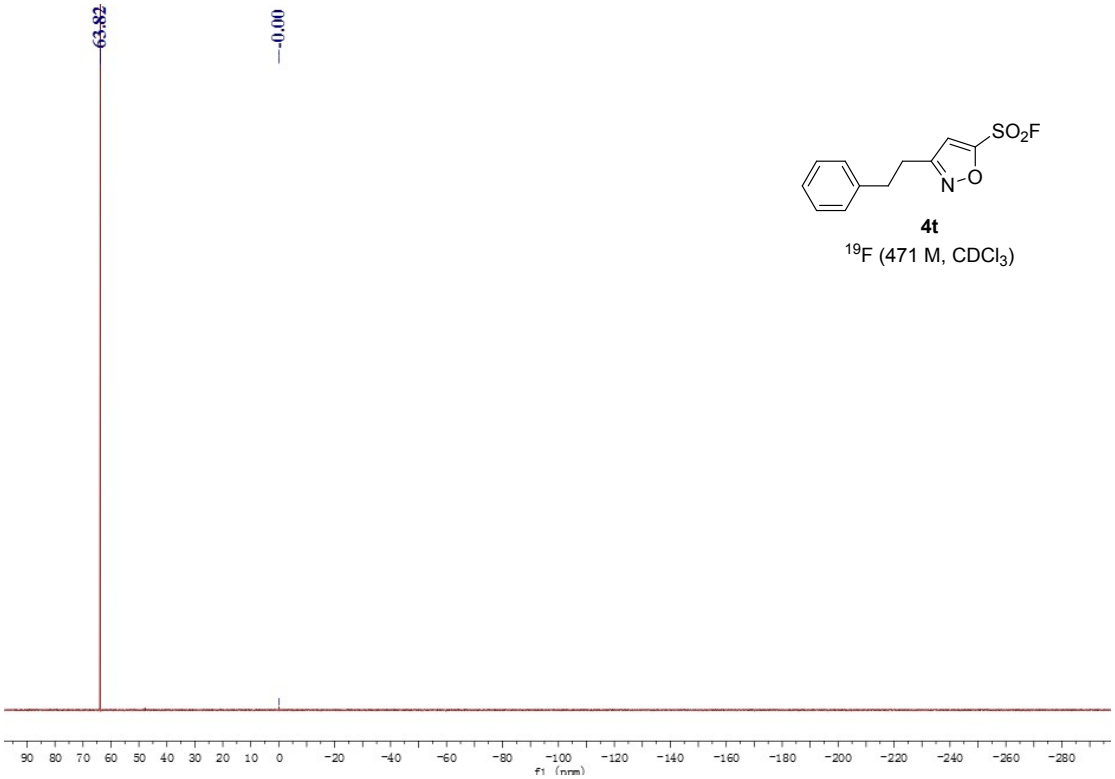
4s

^{1}H (500 M, $CDCl_3$)


164.54
158.91
158.60
148.17
145.89
137.73
130.69
130.06
128.89
128.40
127.98
118.78
111.98
111.95
77.41
77.16
76.91
SO2F
O
N
N
4s
13C (126 M, CDCl3)
f1 (ppm)

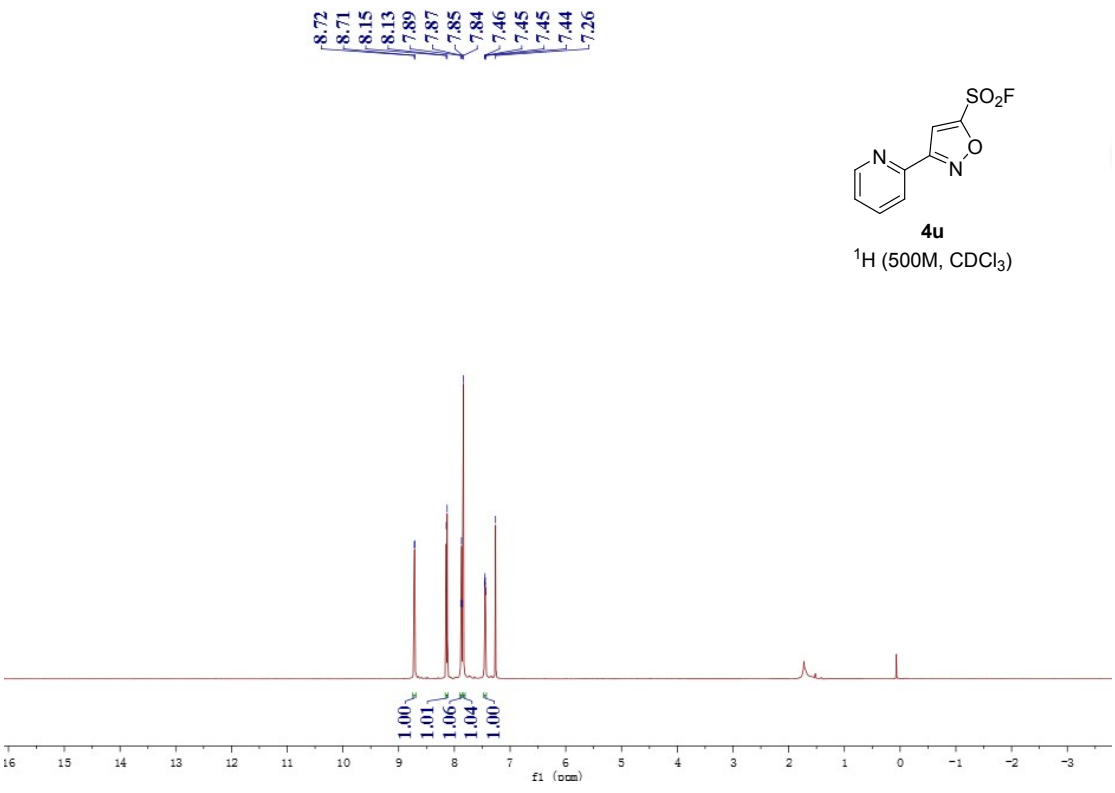

-64.28
-0.00
SO2F
O
N
N
4s
19F (471 M, CDCl3)
f1 (ppm)


7.35
7.33
7.27
7.26
7.20
7.19
6.83
3.15
3.13
3.12
3.06
3.04
3.03
SO2F
N
O
4t
1H (500 M, CDCl3)
2.03
1.01
1.97
1.00
2.08
2.19
f1 (ppm)
164.24
158.13
157.82
139.30
128.94
128.46
127.01
112.11
112.09
77.41
77.16
76.91
33.97
27.89
158.13
157.82
112.11
112.09
SO2F
N
O
4t
13C (126 M, CDCl3)
f1 (ppm)
f1 (ppm)
f1 (ppm)



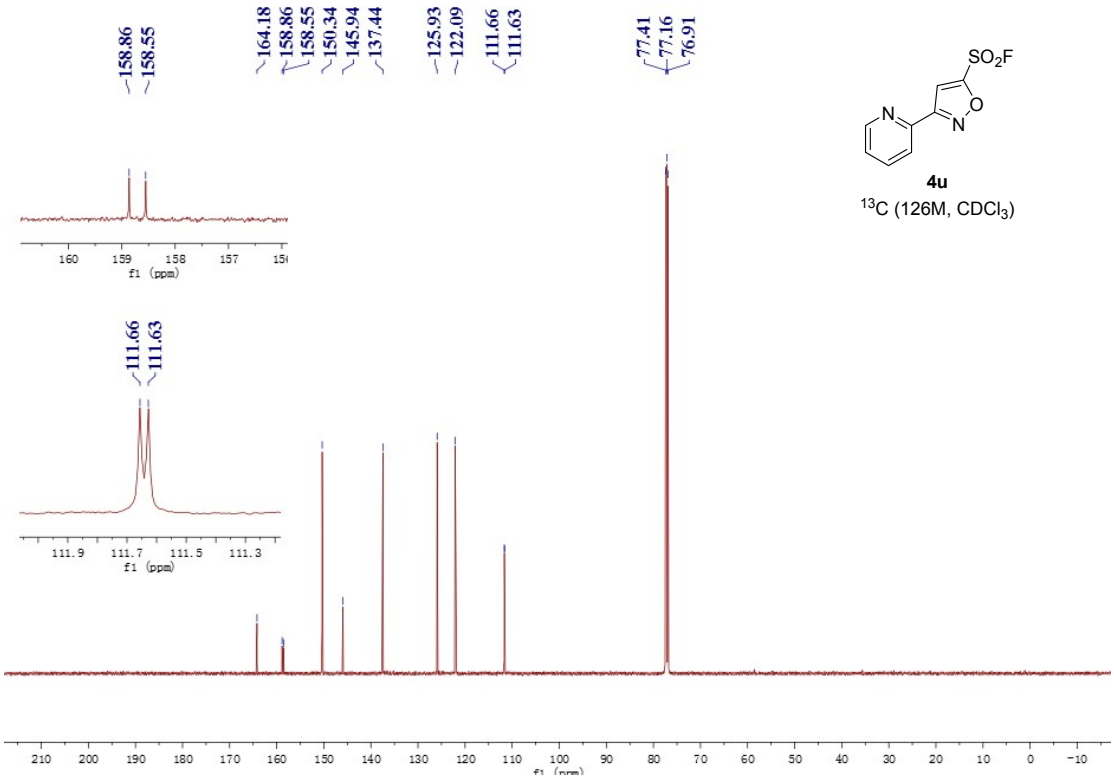
4t

^{19}F (471 M, $CDCl_3$)



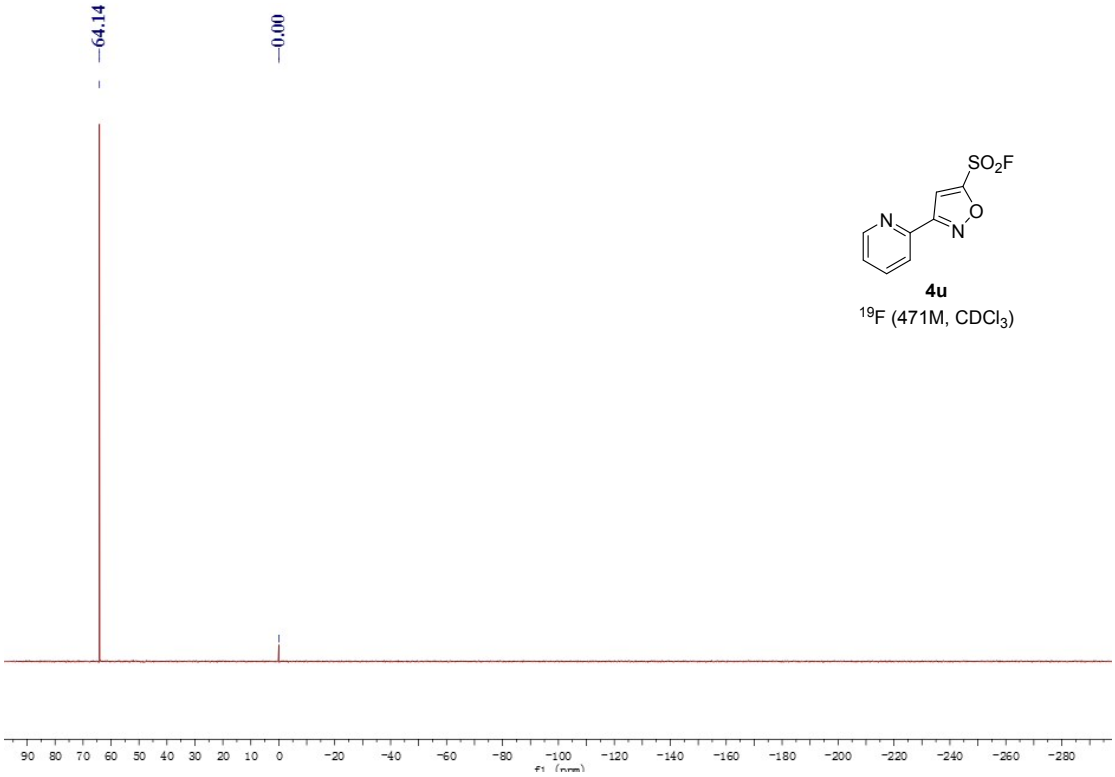
4u

^{1}H (500M, $CDCl_3$)



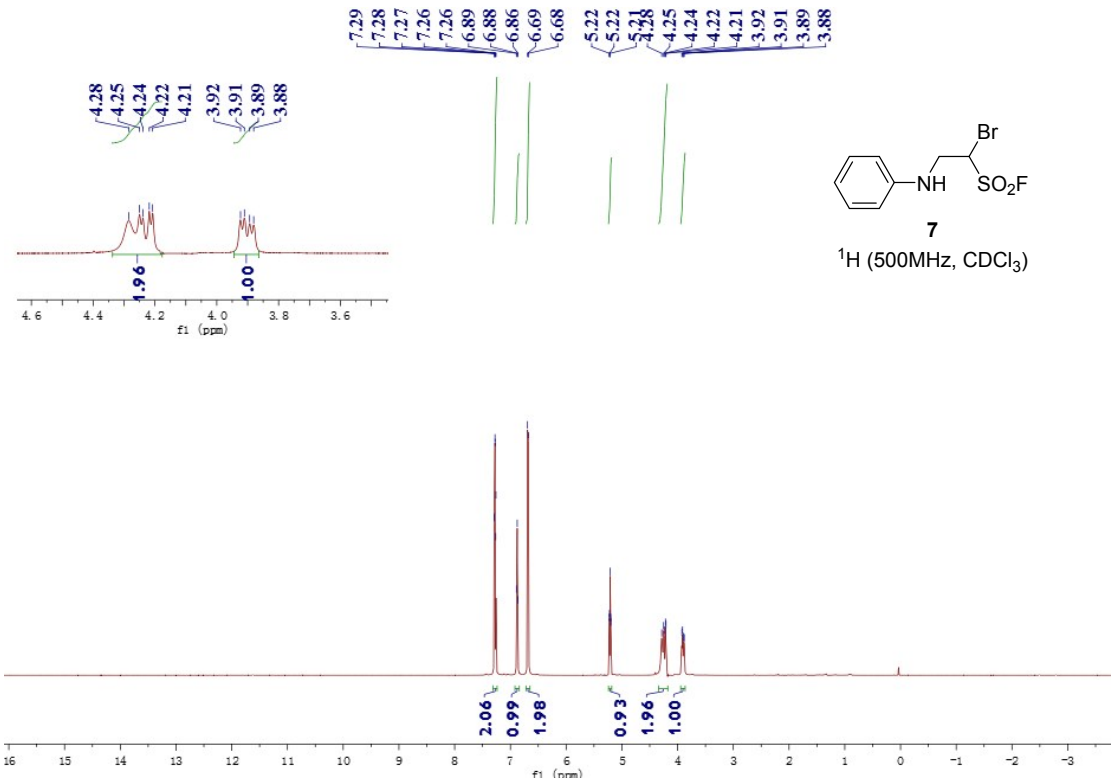
4u

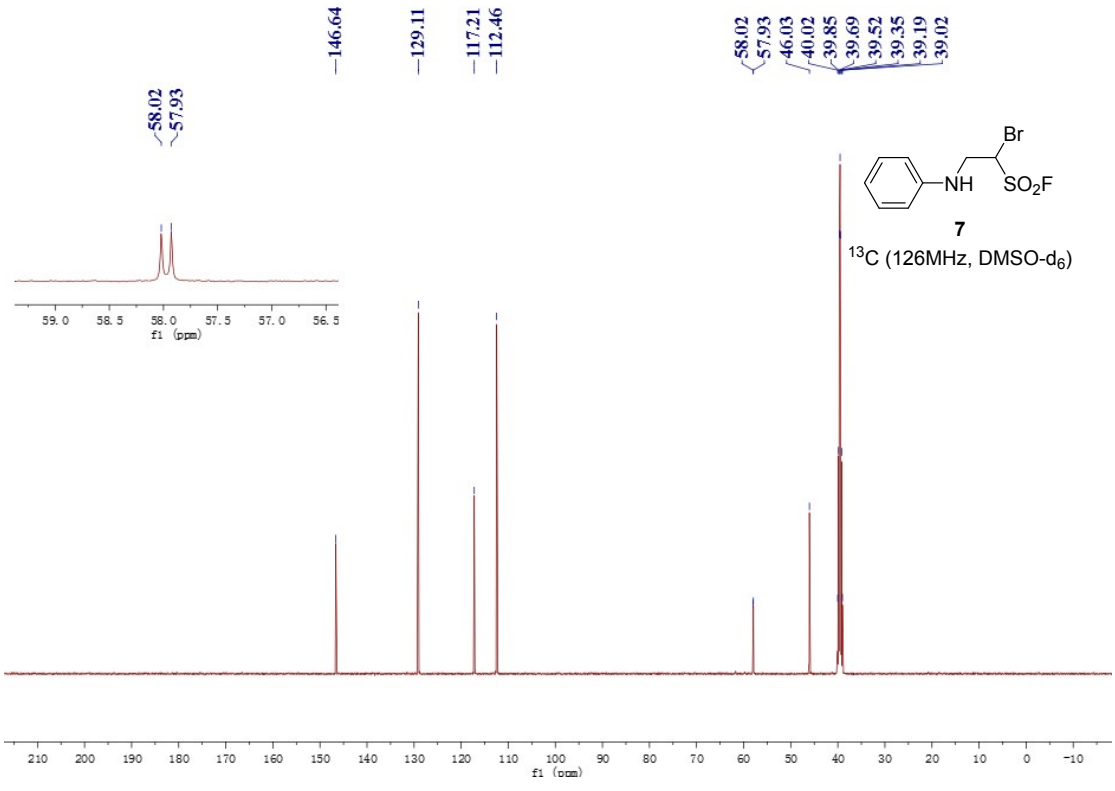
^{13}C (126M, $CDCl_3$)

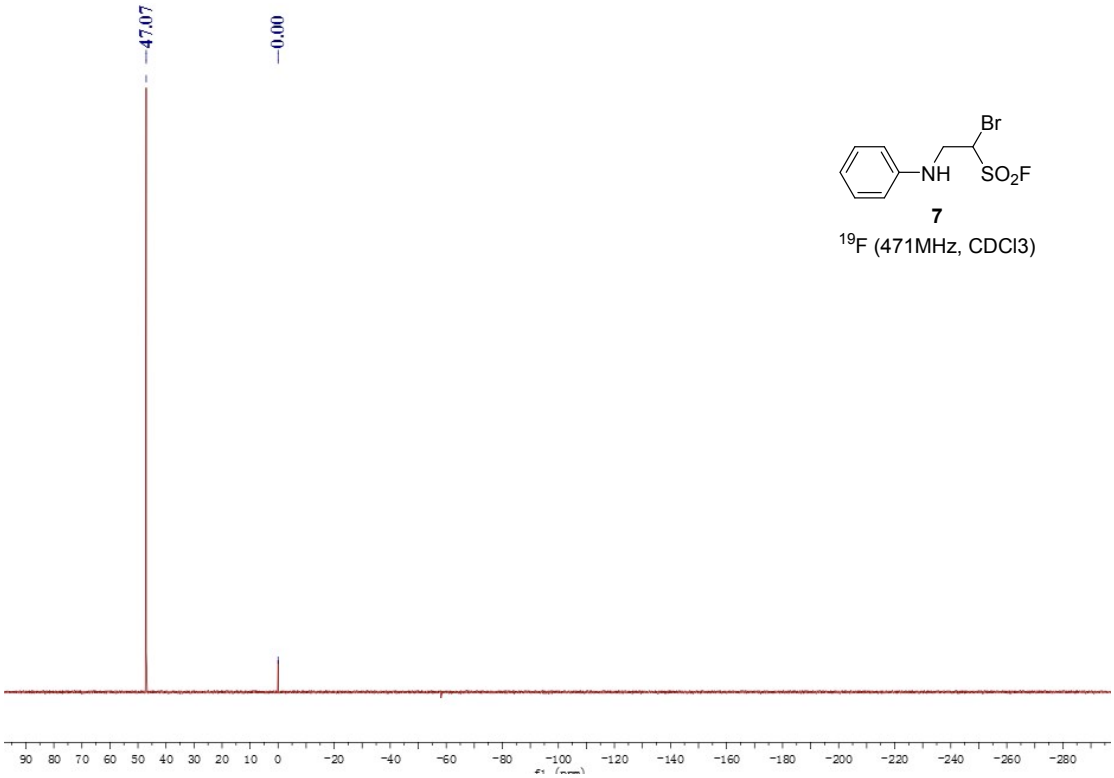


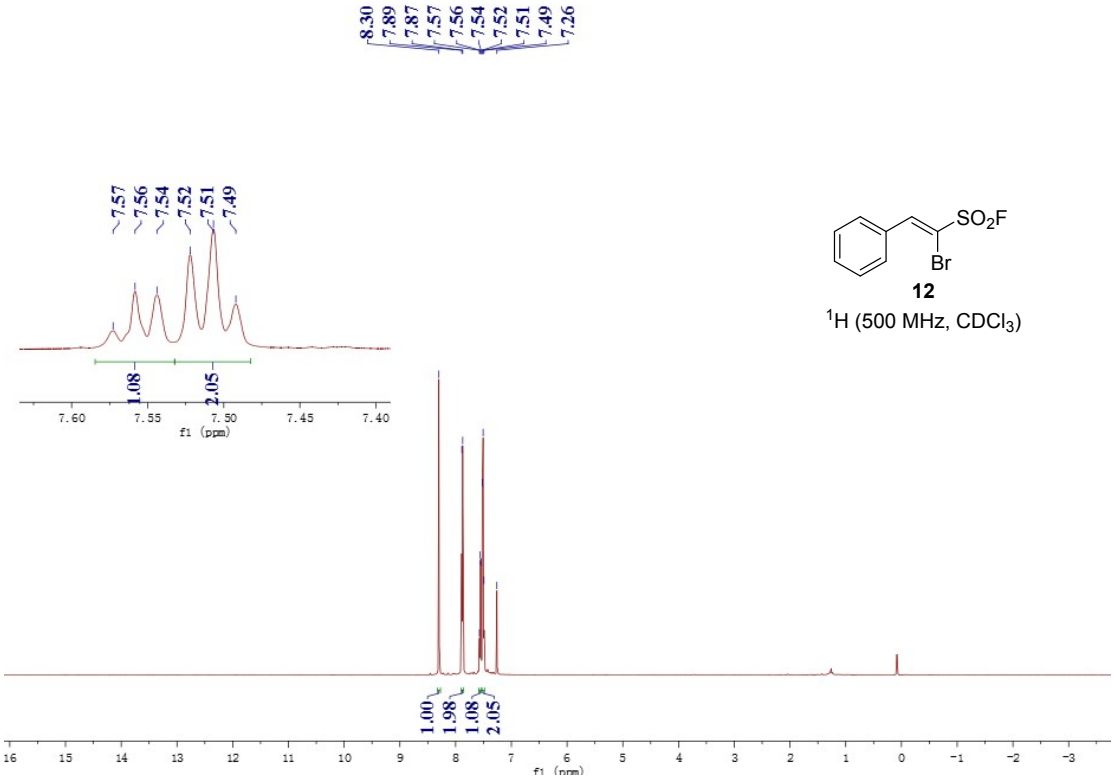
4u

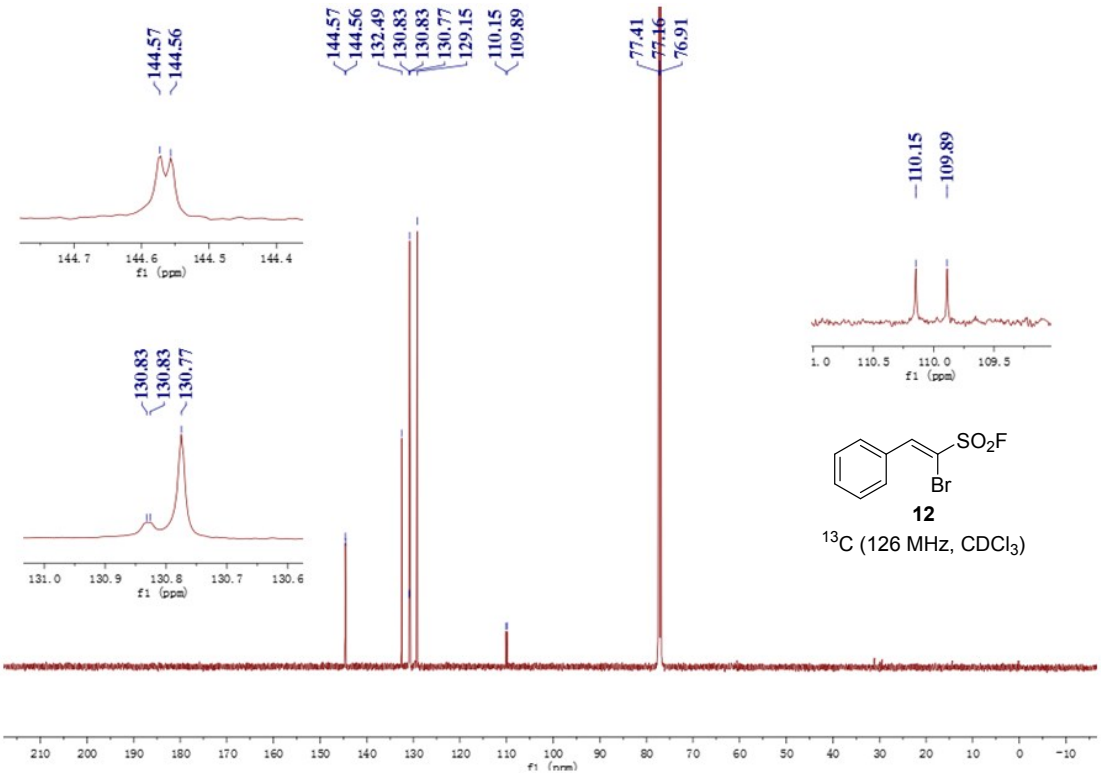
^{19}F (471M, $CDCl_3$)


7.29
7.28
7.27
7.26
7.26
6.89
6.88
6.86
6.69
6.68
5.22
5.22
5.21
4.28
4.25
4.24
4.22
4.21
3.92
3.91
3.89
3.88
1.96
1.00
f1 (ppm)
Br
NH
SO2F
7
1H (500MHz, CDCl3)
2.06
0.99
1.98
0.93
1.96
1.00
f1 (ppm)


146.64
129.11
117.21
112.46
58.02
57.93
46.03
40.02
39.85
39.69
39.52
39.35
39.19
39.02
f1 (ppm)
Br
NH
SO2F
7
13C (126MHz, DMSO-d6)
f1 (ppm)

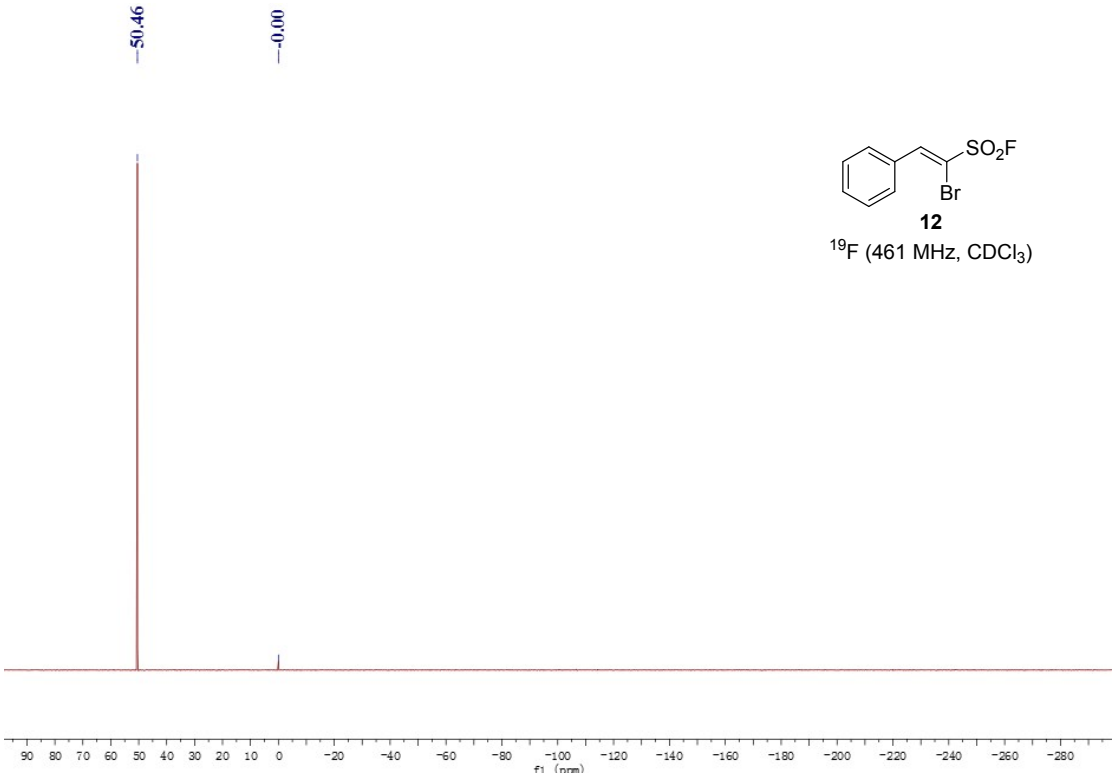

-47.07
-0.00
Br
NH
SO2F
7
19F (471MHz, CDCl3)


8.30
7.89
7.87
7.57
7.56
7.54
7.52
7.51
7.49
7.26
1.08
2.05
1.00
1.98
1.08
2.05
SO2F
Br
12
1H (500 MHz, CDCl3)



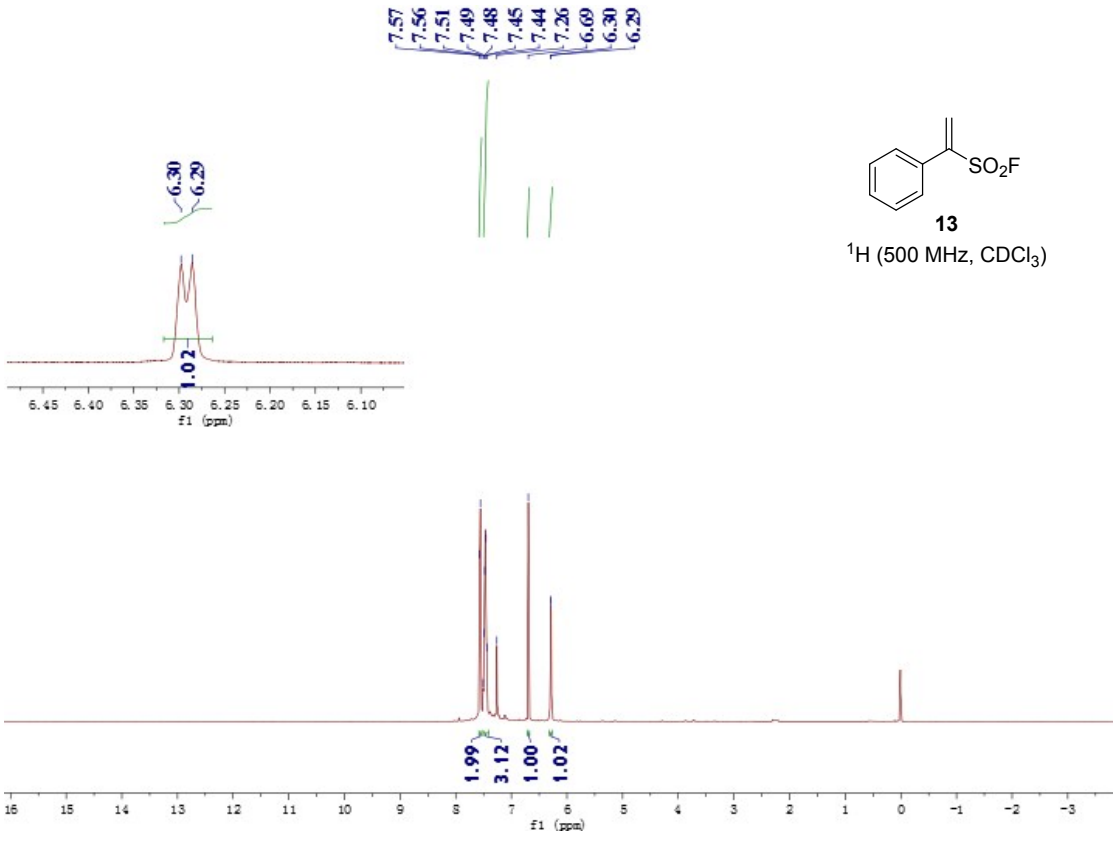
12

^{13}C (126 MHz, $CDCl_3$)



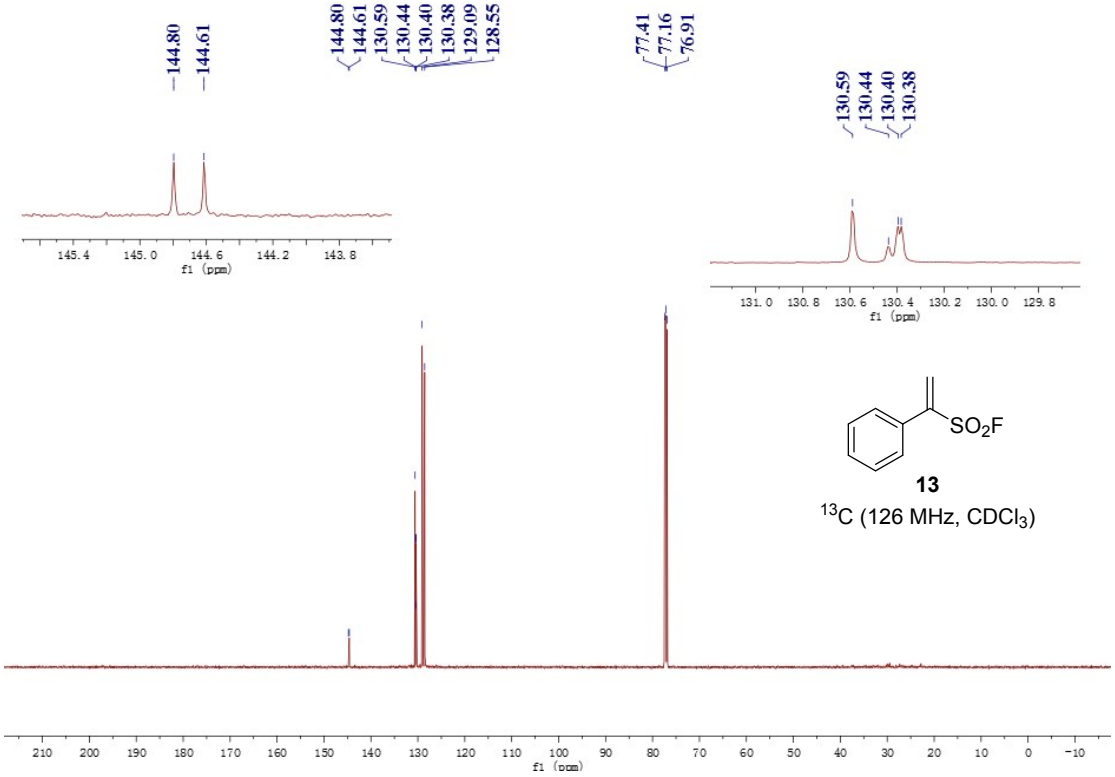
12

^{19}F (461 MHz, $CDCl_3$)



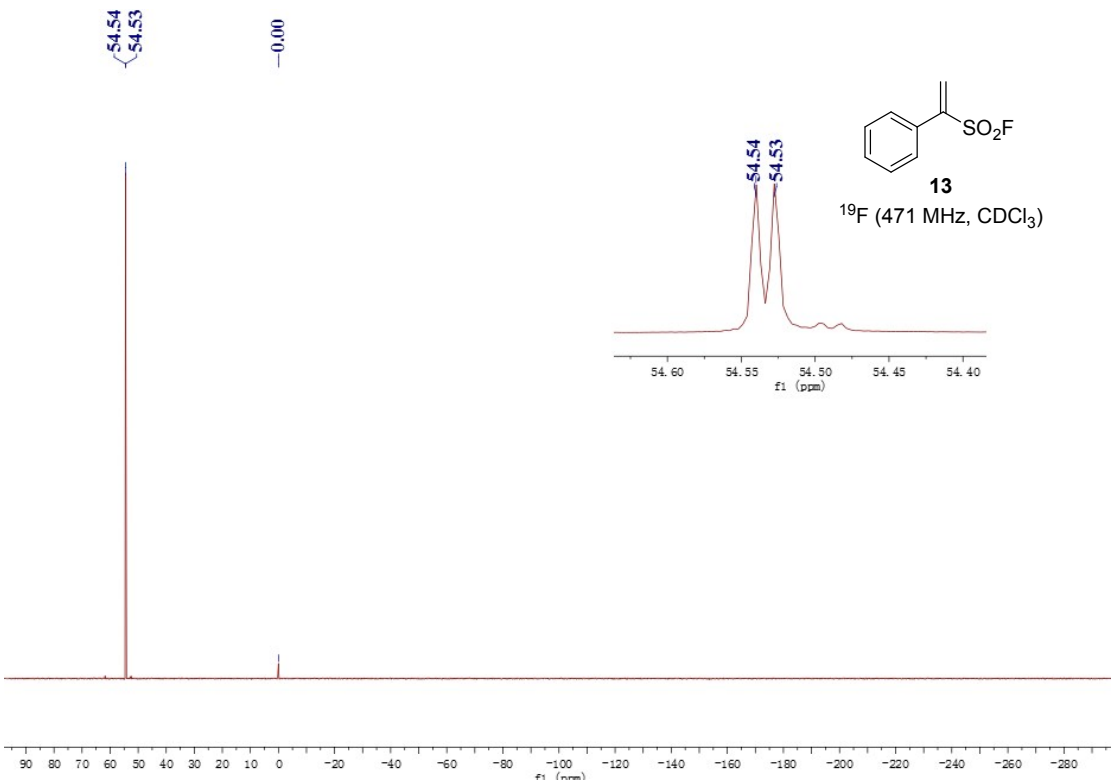
13

^{1}H (500 MHz, $CDCl_3$)



13

^{13}C (126 MHz, $CDCl_3$)



13

^{19}F (471 MHz, $CDCl_3$)

10.Data of Crystal Structure of 3a.

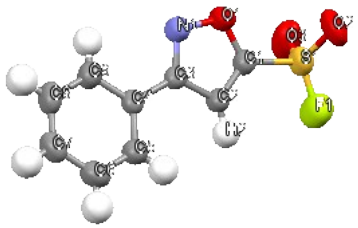


Table 1. Crystal data and structure refinement for 170913b.

Identification code	170913b
Empirical formula	C9 H6 F N O3 S
Formula weight	227.21
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 5.6820(5) A alpha = 70.6000(10) deg.
	b = 7.9839(7) A beta = 77.450(2) deg.
	c = 11.5941(9) A gamma = 86.006(3) deg.
Volume	484.24(7) A^3

Z, Calculated density	2, 1.558 Mg/m^3
Absorption coefficient	0.334 mm^-1
F(000)	232
Crystal size	0.48 x 0.44 x 0.43 mm
Theta range for data collection	2.70 to 25.02 deg.
Limiting indices	-5<=h<=6, -8<=k<=9, -13<=l<=13
Reflections collected / unique	2439 / 1666 [R(int) = 0.0254]
Completeness to theta = 25.02	97.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8698 and 0.8563
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1666 / 0 / 136
Goodness-of-fit on F^2	1.077
Final R indices [I>2sigma(I)]	R1 = 0.0577, wR2 = 0.1773
R indices (all data)	R1 = 0.0711, wR2 = 0.1891

Largest diff. peak and hole	0.411 and -0.327 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 170913b.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
F(1)	5260(5)	1851(4)	5233(3)	108(1)
N(1)	999(5)	3038(5)	1937(3)	68(1)
O(1)	621(4)	2942(4)	3206(2)	71(1)
O(2)	991(6)	1139(5)	5935(2)	100(1)
O(3)	2322(6)	4115(4)	5122(3)	91(1)
S(1)	2872(2)	2260(1)	5090(1)	66(1)
C(1)	2753(6)	2489(4)	3555(3)	51(1)
C(2)	4469(6)	2285(4)	2630(3)	51(1)
C(3)	3273(5)	2665(4)	1612(3)	47(1)
C(4)	4292(5)	2644(4)	323(3)	47(1)
C(5)	6551(6)	1916(5)	47(3)	59(1)
C(6)	7492(7)	1864(5)	-1156(4)	68(1)
C(7)	6177(7)	2558(5)	-2082(3)	68(1)
C(8)	3959(7)	3302(5)	-1822(3)	69(1)
C(9)	2993(6)	3349(5)	-625(3)	58(1)

Table 3. Bond lengths [A] and angles [deg] for 170913b.

F(1)-S(1)	1.405(3)
N(1)-C(3)	1.308(4)
N(1)-O(1)	1.416(4)
O(1)-C(1)	1.348(4)
O(2)-S(1)	1.414(3)
O(3)-S(1)	1.503(3)
S(1)-C(1)	1.744(3)
C(1)-C(2)	1.329(4)
C(2)-C(3)	1.425(4)
C(2)-H(2)	0.9300
C(3)-C(4)	1.485(4)
C(4)-C(5)	1.389(4)
C(4)-C(9)	1.398(4)
C(5)-C(6)	1.394(5)
C(5)-H(5)	0.9300
C(6)-C(7)	1.383(6)
C(6)-H(6)	0.9300
C(7)-C(8)	1.372(5)
C(7)-H(7)	0.9300
C(8)-C(9)	1.389(5)
C(8)-H(8)	0.9300
C(9)-H(9)	0.9300
C(3)-N(1)-O(1)	106.2(3)
C(1)-O(1)-N(1)	106.5(2)

F(1)-S(1)-O(2)	118.9(2)
F(1)-S(1)-O(3)	108.7(2)
O(2)-S(1)-O(3)	107.8(2)
F(1)-S(1)-C(1)	107.86(15)
O(2)-S(1)-C(1)	110.34(17)
O(3)-S(1)-C(1)	101.88(16)
C(2)-C(1)-O(1)	112.3(3)
C(2)-C(1)-S(1)	130.2(3)
O(1)-C(1)-S(1)	117.5(2)
C(1)-C(2)-C(3)	103.6(3)
C(1)-C(2)-H(2)	128.2
C(3)-C(2)-H(2)	128.2
N(1)-C(3)-C(2)	111.3(3)
N(1)-C(3)-C(4)	120.5(3)
C(2)-C(3)-C(4)	128.1(3)
C(5)-C(4)-C(9)	119.1(3)
C(5)-C(4)-C(3)	120.3(3)
C(9)-C(4)-C(3)	120.6(3)
C(4)-C(5)-C(6)	120.3(3)
C(4)-C(5)-H(5)	119.8
C(6)-C(5)-H(5)	119.8
C(7)-C(6)-C(5)	119.8(3)
C(7)-C(6)-H(6)	120.1
C(5)-C(6)-H(6)	120.1
C(8)-C(7)-C(6)	120.2(3)
C(8)-C(7)-H(7)	119.9
C(6)-C(7)-H(7)	119.9
C(7)-C(8)-C(9)	120.6(3)
C(7)-C(8)-H(8)	119.7
C(9)-C(8)-H(8)	119.7

C(8)-C(9)-C(4)	119.9(3)
C(8)-C(9)-H(9)	120.0
C(4)-C(9)-H(9)	120.0

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 170913b.

The anisotropic displacement factor exponent takes the form:

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

	U11	U22	U33	U23	U13	U12
F(1)	104(2)	158(3)	80(2)	-56(2)	-40(2)	23(2)
N(1)	56(2)	102(2)	48(2)	-28(2)	-15(1)	12(2)
O(1)	52(2)	111(2)	50(1)	-29(1)	-12(1)	11(1)
O(2)	103(2)	136(3)	47(2)	-18(2)	5(2)	-25(2)
O(3)	140(3)	77(2)	75(2)	-45(2)	-40(2)	33(2)
S(1)	74(1)	84(1)	44(1)	-27(1)	-14(1)	8(1)
C(1)	53(2)	60(2)	43(2)	-17(1)	-14(1)	1(1)
C(2)	46(2)	66(2)	44(2)	-20(2)	-14(1)	2(1)
C(3)	45(2)	52(2)	46(2)	-15(1)	-13(1)	-2(1)
C(4)	50(2)	50(2)	42(2)	-14(1)	-12(1)	-7(1)
C(5)	53(2)	72(2)	54(2)	-23(2)	-14(2)	1(2)
C(6)	58(2)	85(3)	67(2)	-36(2)	-6(2)	-1(2)
C(7)	74(2)	85(3)	51(2)	-33(2)	-5(2)	-14(2)
C(8)	86(3)	79(2)	47(2)	-18(2)	-25(2)	-6(2)
C(9)	63(2)	66(2)	51(2)	-20(2)	-20(2)	3(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 170913b.

	x	y	z	U(eq)
H(2)	6071	1969	2645	61
H(5)	7442	1460	668	71
H(6)	8998	1366	-1336	82
H(7)	6798	2519	-2884	81
H(8)	3095	3780	-2452	83
H(9)	1484	3849	-454	70

Table 6. Torsion angles [deg] for 170913b.

C(3)-N(1)-O(1)-C(1)	-0.6(4)
N(1)-O(1)-C(1)-C(2)	0.0(4)
N(1)-O(1)-C(1)-S(1)	-179.9(2)
F(1)-S(1)-C(1)-C(2)	2.1(4)
O(2)-S(1)-C(1)-C(2)	-129.3(4)
O(3)-S(1)-C(1)-C(2)	116.5(4)
F(1)-S(1)-C(1)-O(1)	-177.9(3)
O(2)-S(1)-C(1)-O(1)	50.7(3)
O(3)-S(1)-C(1)-O(1)	-63.6(3)
O(1)-C(1)-C(2)-C(3)	0.5(4)
S(1)-C(1)-C(2)-C(3)	-179.5(3)
O(1)-N(1)-C(3)-C(2)	0.9(4)
O(1)-N(1)-C(3)-C(4)	179.9(3)
C(1)-C(2)-C(3)-N(1)	-0.9(4)
C(1)-C(2)-C(3)-C(4)	-179.8(3)
N(1)-C(3)-C(4)-C(5)	-167.3(3)
C(2)-C(3)-C(4)-C(5)	11.5(5)
N(1)-C(3)-C(4)-C(9)	12.5(5)
C(2)-C(3)-C(4)-C(9)	-168.7(3)
C(9)-C(4)-C(5)-C(6)	-1.0(5)
C(3)-C(4)-C(5)-C(6)	178.8(3)
C(4)-C(5)-C(6)-C(7)	0.6(6)
C(5)-C(6)-C(7)-C(8)	0.3(6)
C(6)-C(7)-C(8)-C(9)	-0.9(6)
C(7)-C(8)-C(9)-C(4)	0.4(6)

C(5)-C(4)-C(9)-C(8)	0.5(5)
C(3)-C(4)-C(9)-C(8)	-179.3(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for 170913b [A and deg.].

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