

Supporting Information

SO₂F₂ Mediated Transforming Pyrozonones to Pyrazolyl Fluorosulfates

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Table of content

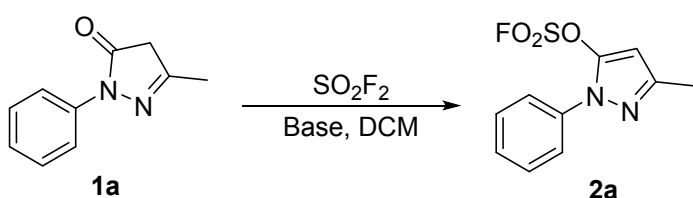
1. General considerations.....	S2
2. Optimization of the reaction conditions.....	S2
3. NMR spectra of 2 , 3 , 4 , 5 , 6 and 8	S5

1. General considerations.

All reactions were carried out under an air atmosphere. Unless otherwise specified, NMR spectra were recorded in CDCl₃ on a 500 MHz (for ¹H), 471 MHz (for ¹⁹F), or 126 MHz (for ¹³C) spectrometer. The chemical shifts converted to the TMS scale (CDCl₃: δ H = 7.26 ppm, δ C = 77.16 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

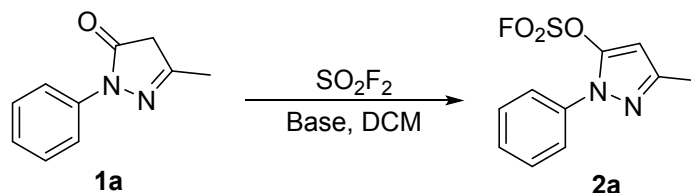
Table 1 Screening of organic bases^a

			
Entry	Base	Conversion (%) ^b	Yield (%) ^c
1	Et ₃ N	58	46
2	DBU	73	n.d.
3	DABCO	78	70
4	TMEDA	66	58
5	DIPEA	96	95 (93) ^d

^a Reaction conditions: **1a** (0.1 mmol), base (0.3 mmol, 3 equiv.) and DCM (1.5 mL) were mixed in a tube with a SO₂F₂ balloon and reacted at room temperature for 10 h. ^b The conversion was determined by HPLC using **1a** as the external standard. [*t*_{1a} = 2.670 min, λ_{max} = 240.5 nm, methanol / water = 70 : 30 (v / v)]. ^c The yield was

determined by HPLC using **2a** as the external standard. [t_{2a} = 8.020 min, $\lambda_{\max}$ = 241.7 nm, methanol / water = 70 : 30 (v / v)]. ^d Isolated yield of 1 mmol reaction scale.

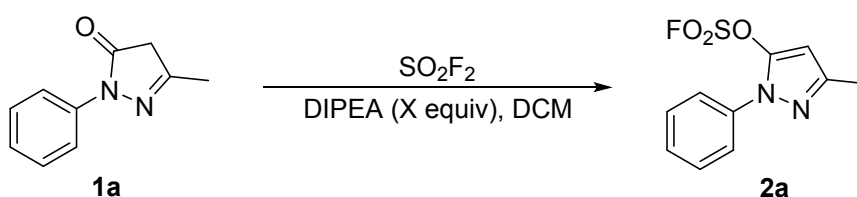
Table 2 Screening of inorganic bases ^a



Entry	Base	Conversion (%) ^b	Yield (%) ^c
1	Na ₂ CO ₃	23	n.d.
2	NaHCO ₃	21	21
3	K ₂ CO ₃	38	38
4	KHCO ₃	58	58
5	NaOH	59	35
6	Cs ₂ CO ₃	51	29
7	K ₃ PO ₄	67	67
8	KOAc	n.d.	n.d.
9	CsF	70	69
10	Na ₃ PO ₄	16	n.d.

^a Reaction conditions: **1a** (0.1 mmol), base (0.3 mmol, 3 equiv.) and DCM (1.5 mL) were mixed in a tube with a SO₂F₂ balloon and reacted at room temperature for 10 h. ^b The conversion was determined by HPLC using **1a** as the external standard. [t_{1a} = 2.670 min, $\lambda_{\max}$ = 240.5 nm, methanol / water = 70 : 30 (v / v)]. ^c The yield was determined by HPLC using **2a** as the external standard. [t_{2a} = 8.020 min, $\lambda_{\max}$ = 241.7 nm, methanol / water = 70 : 30 (v / v)].

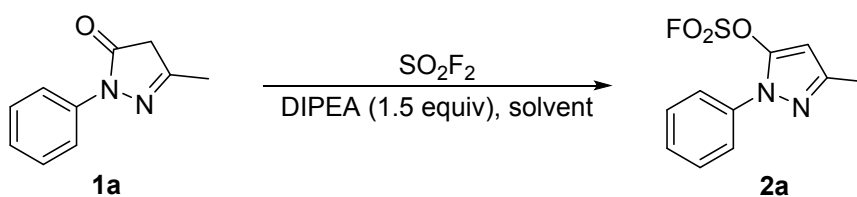
Table 3 Screening the amount of DIPEA ^a



Entry	X (equiv.)	Conversion (%) ^b	Yield (%) ^c
1	0	n.d.	n.d.
2	0.05	24	12
3	0.1	38	25
4	0.2	48	40
5	0.5	69	61
6	1.0	92	85
7	1.5	95	93
4	2.0	94	94
5	2.5	94	94
6	3.0	96	95

^a Reaction conditions: **1a** (0.1 mmol), DIPEA (X equiv.) and DCM (1.5 mL) were mixed in a tube with a SO₂F₂ balloon and reacted at room temperature for 10 h. ^b The conversion was determined by HPLC using **1a** as the external standard. [*t*_{1a} = 2.670 min, λ_{max} = 240.5 nm, methanol / water = 70 : 30 (v / v)]. ^c The yield was determined by HPLC using **2a** as the external standard. [*t*_{2a} = 8.020 min, λ_{max} = 241.7 nm, methanol / water = 70 : 30 (v / v)].

Table 4 Screening of solvents ^a

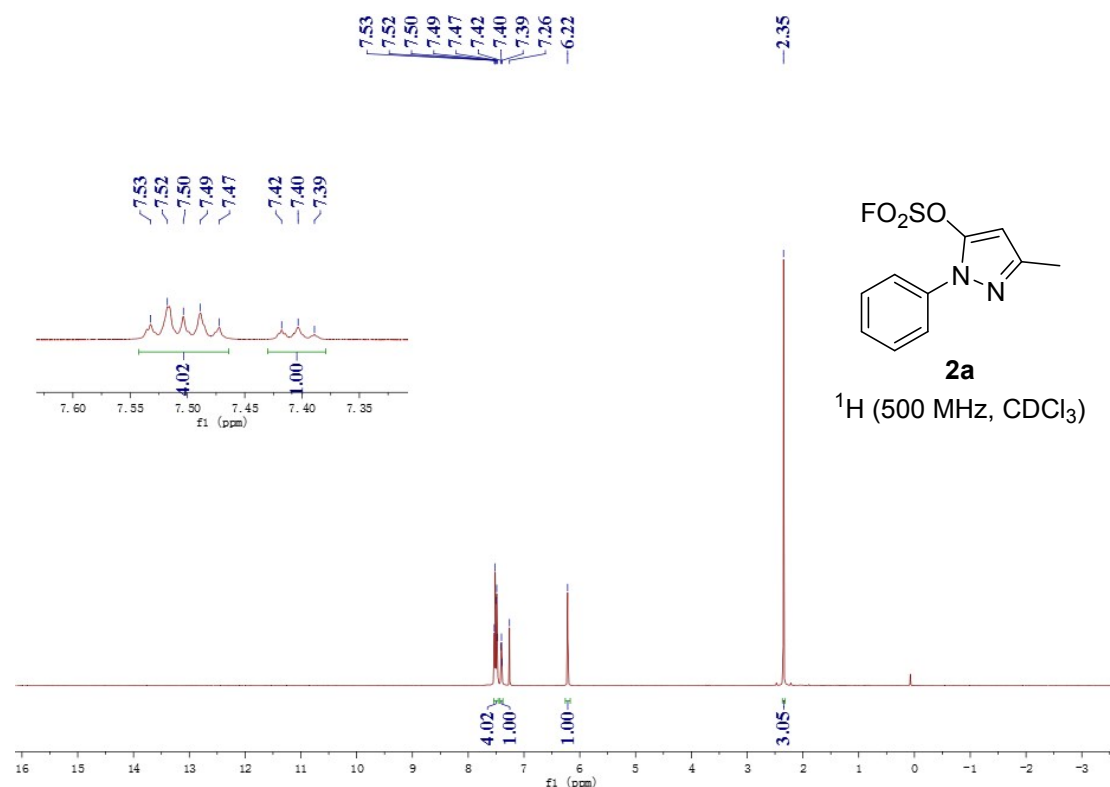


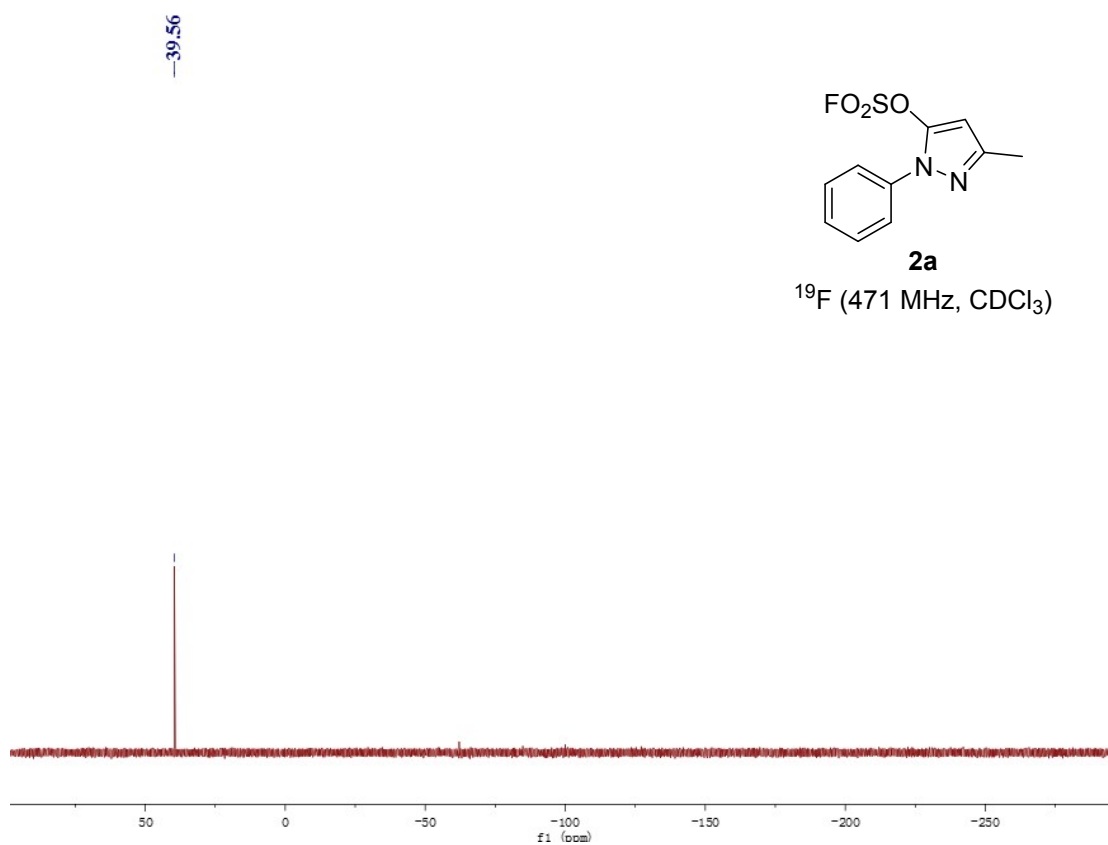
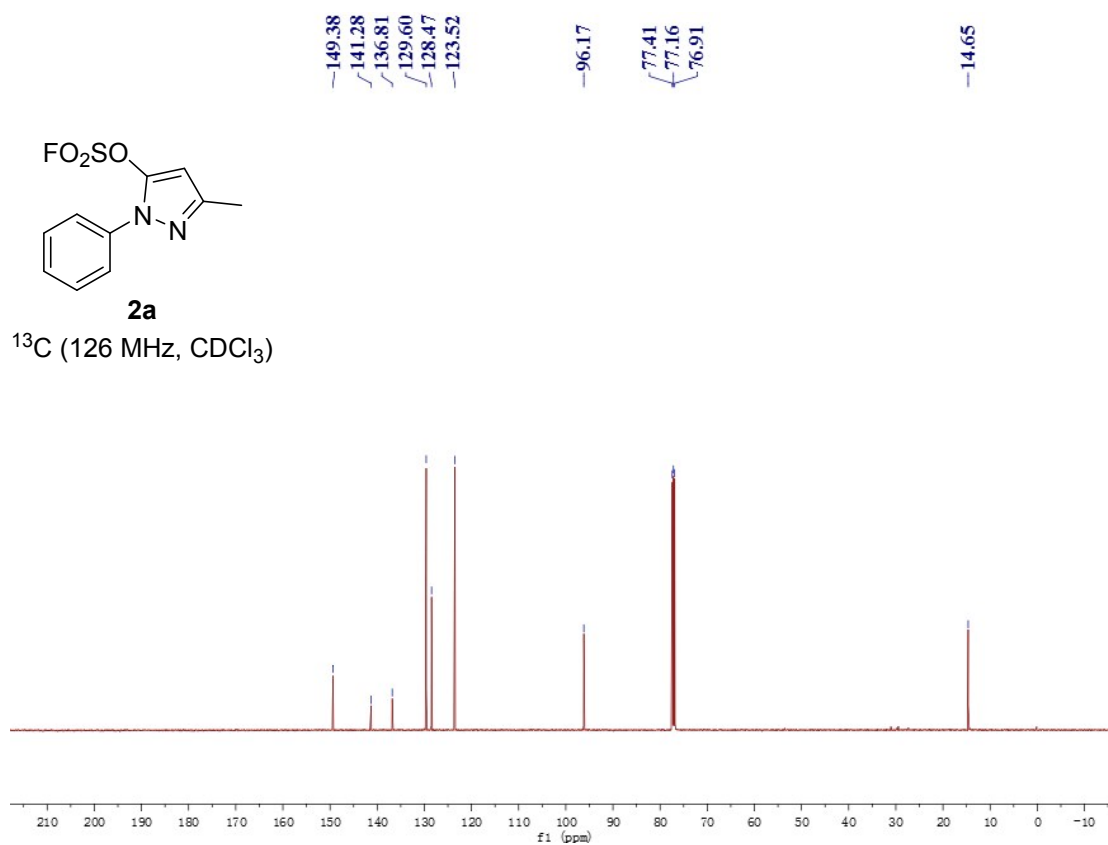
Entry	Solvent	Conversion (%) ^b	Yield (%) ^c
1	DCM	95	93
2	DMSO	96	70
3	MeOH	n.d.	n.d.
4	Toluene	51	45
5	Dioxane	59	34
6	DMF	91	91

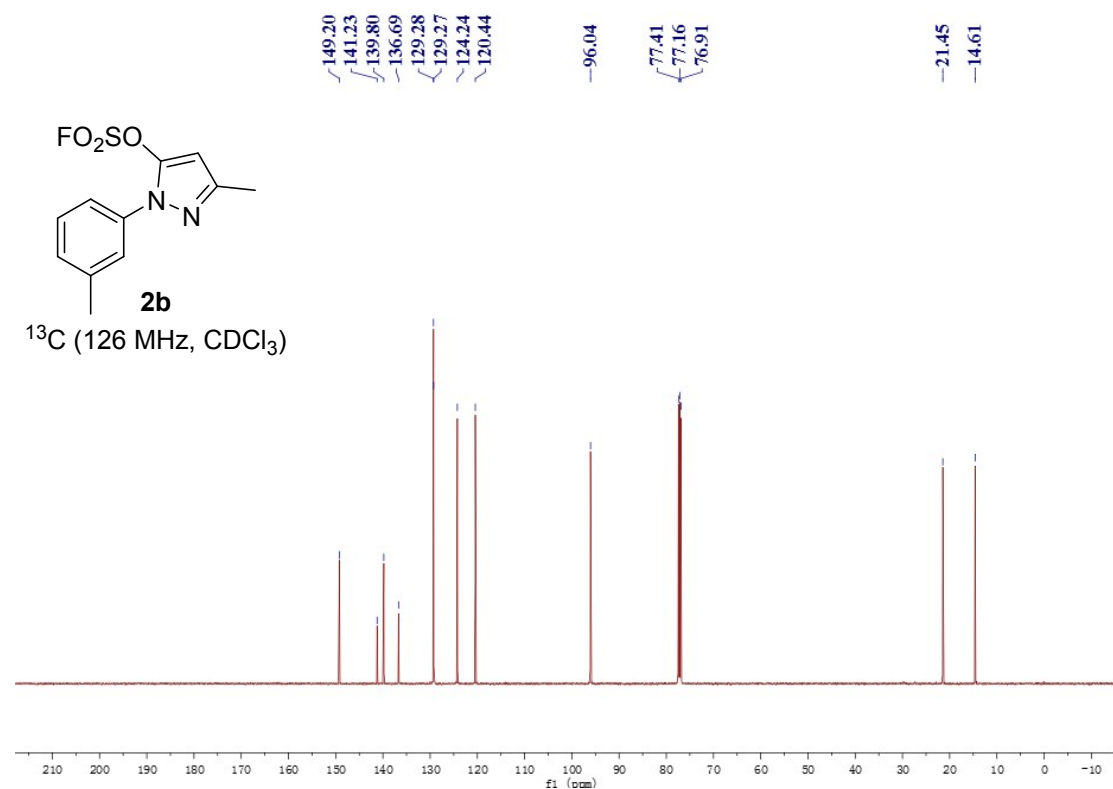
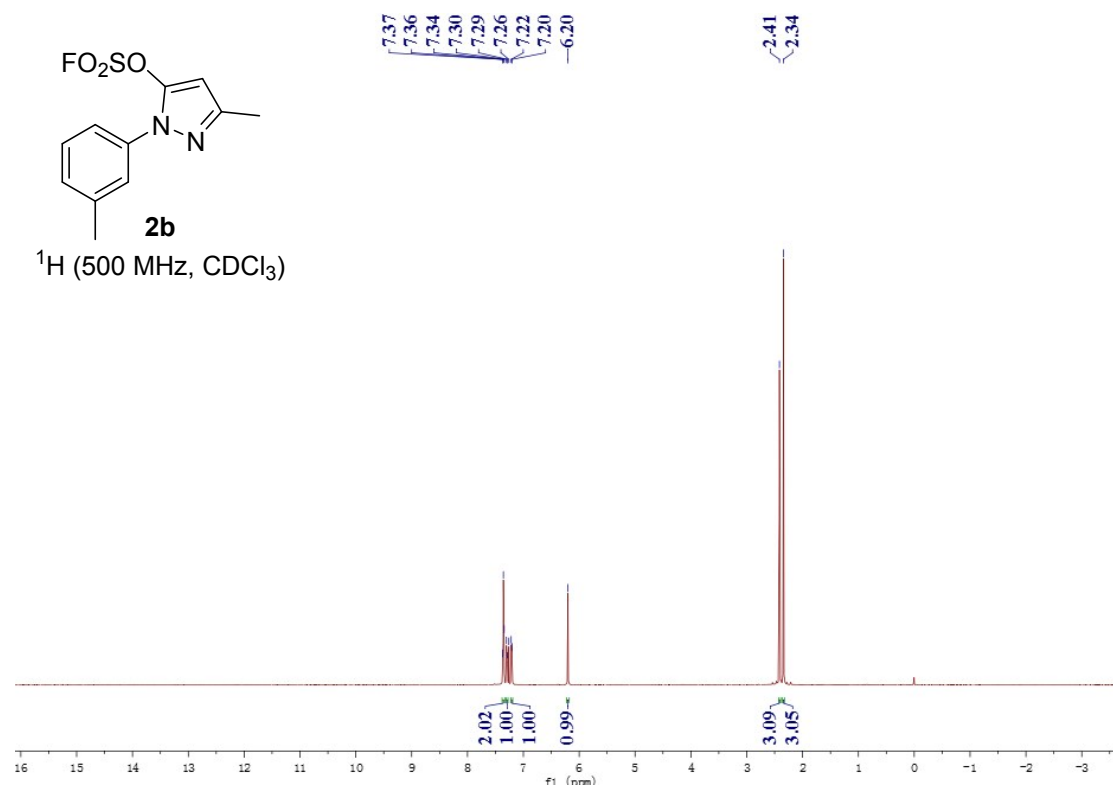
7	THF	n.d.	n.d.
8	CH ₃ CN	95	91
9	Acetone	n.d.	n.d.
10	NMP	95	83
11	H ₂ O	65	46

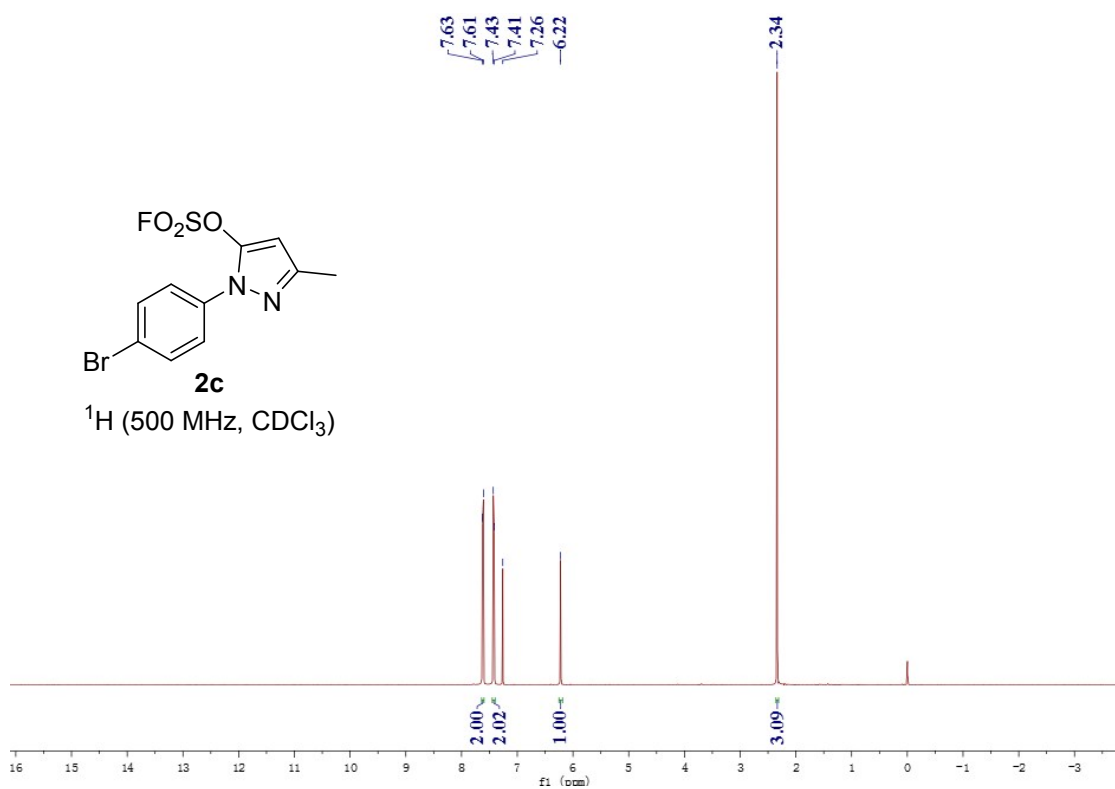
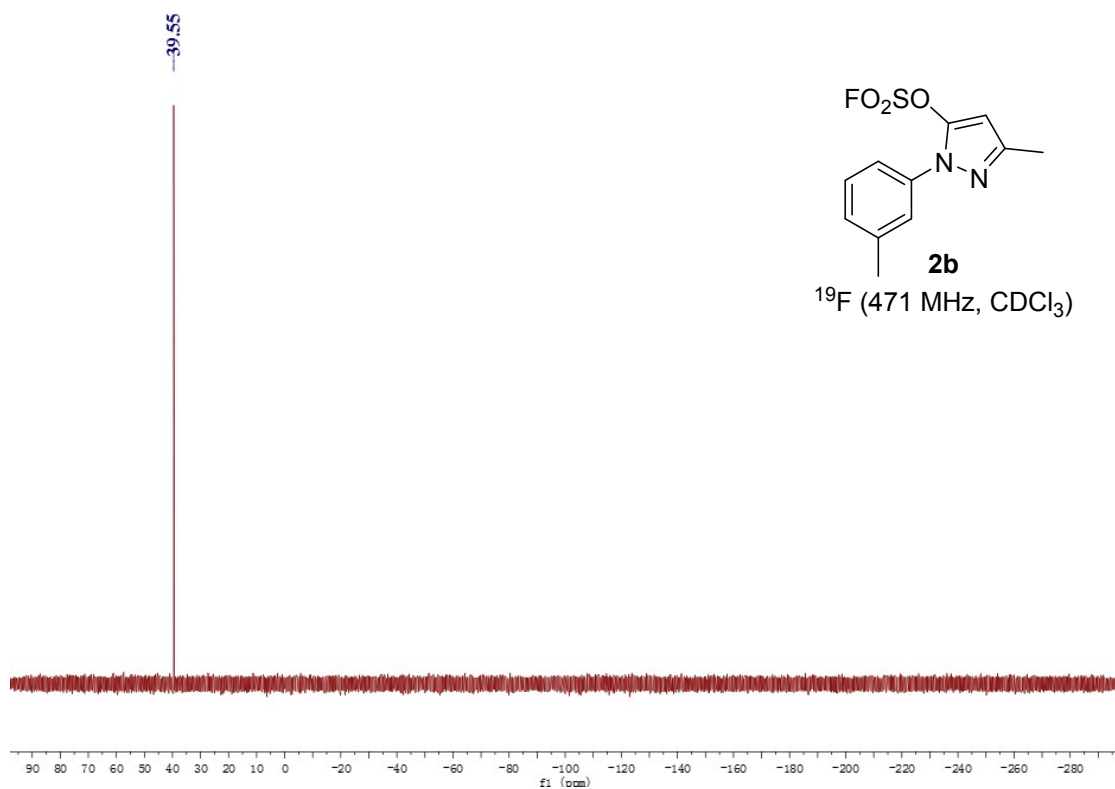
^a Reaction conditions: **1a** (0.1 mmol), DIPEA (0.15 mmol, 1.5 equiv.) and solvent (1.5 mL) were mixed in a tube with a SO₂F₂ balloon and reacted at room temperature for 10 h. ^b The conversion was determined by HPLC using **1a** as the external standard. [*t*_{1a} = 2.670 min, λ_{max} = 240.5 nm, methanol / water = 70 : 30 (v / v)]. ^c The yield was determined by HPLC using **2a** as the external standard. [*t*_{2a} = 8.020 min, λ_{max} = 241.7 nm, methanol / water = 70 : 30 (v / v)].

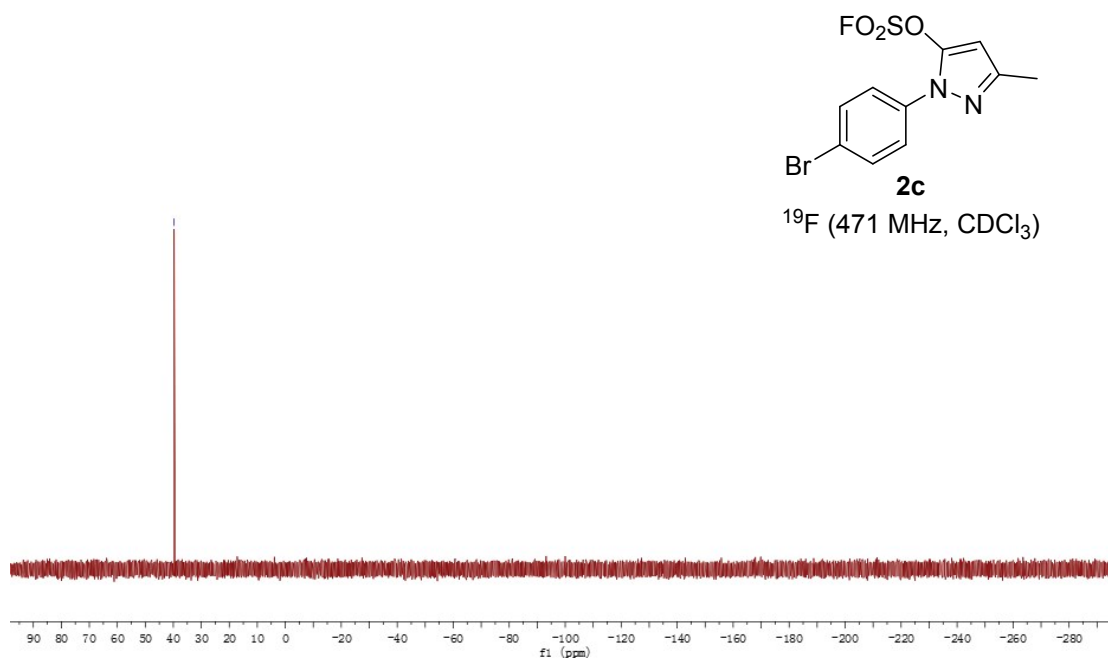
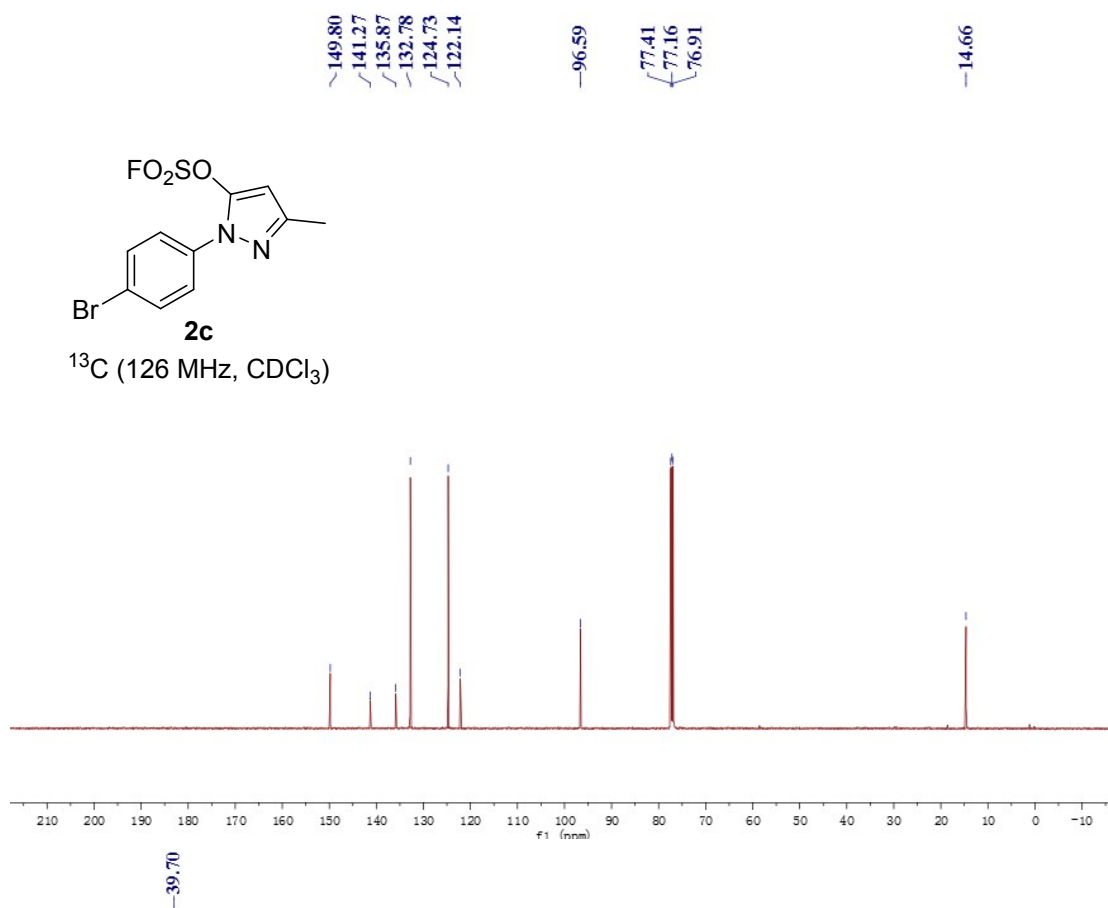
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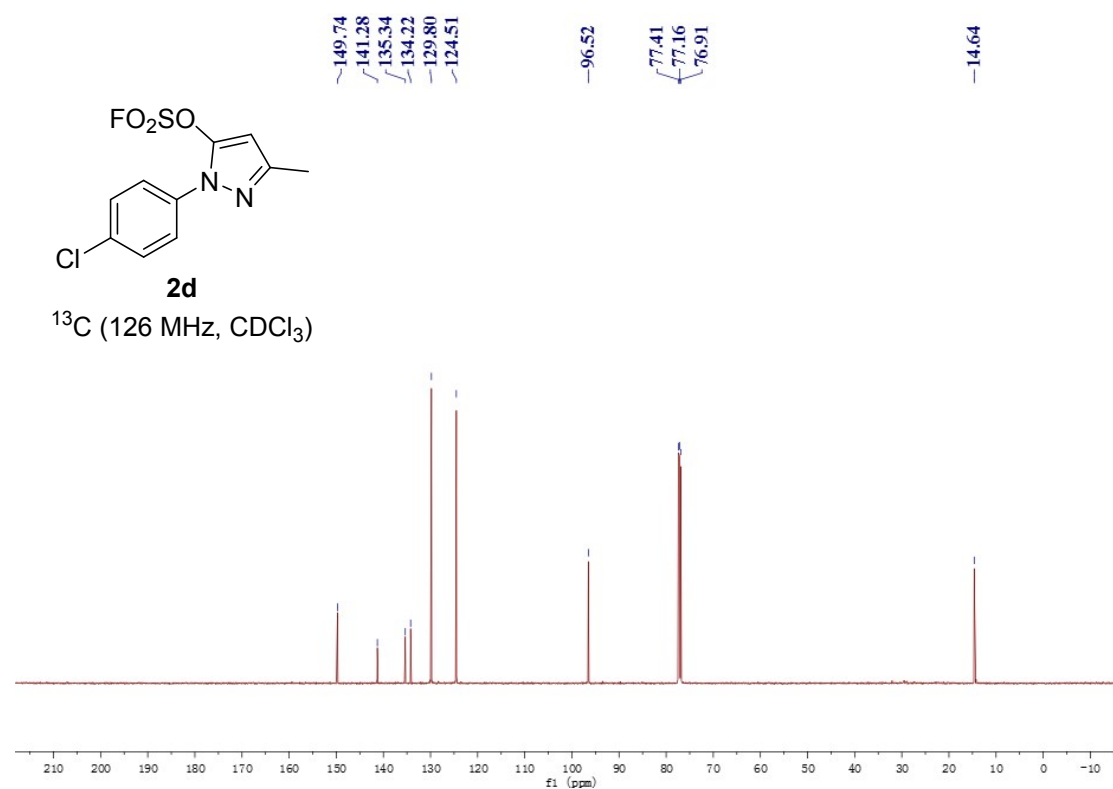
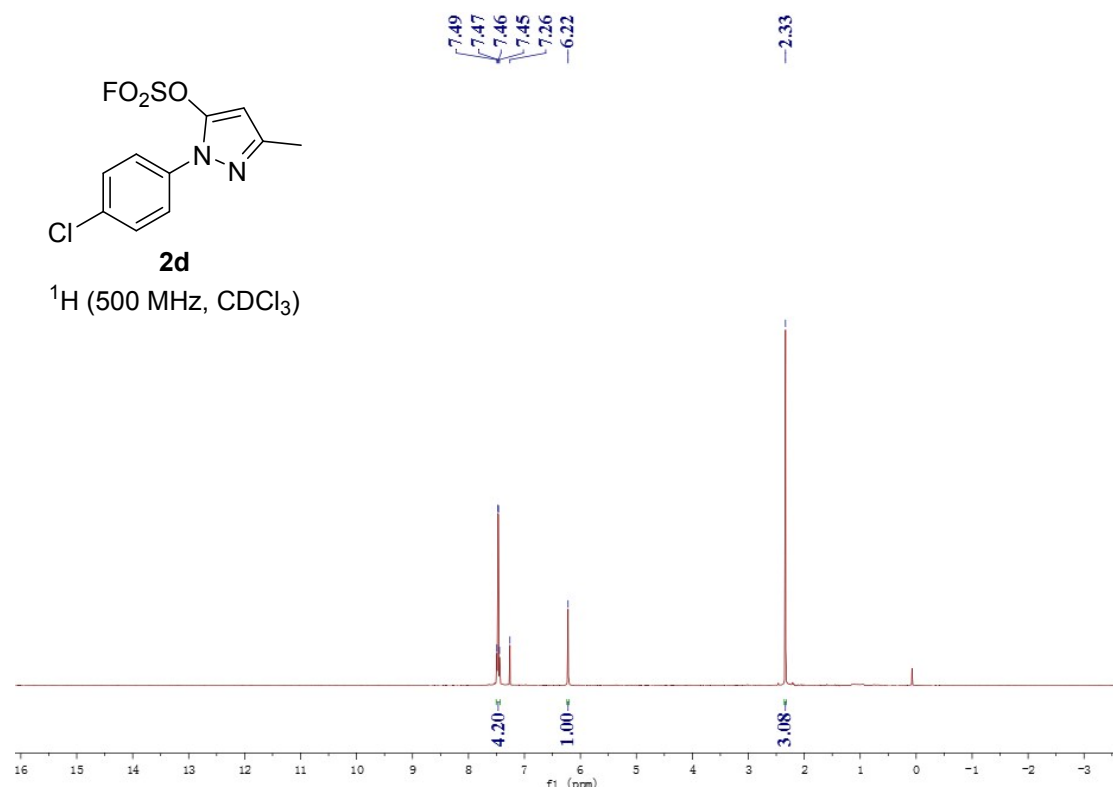


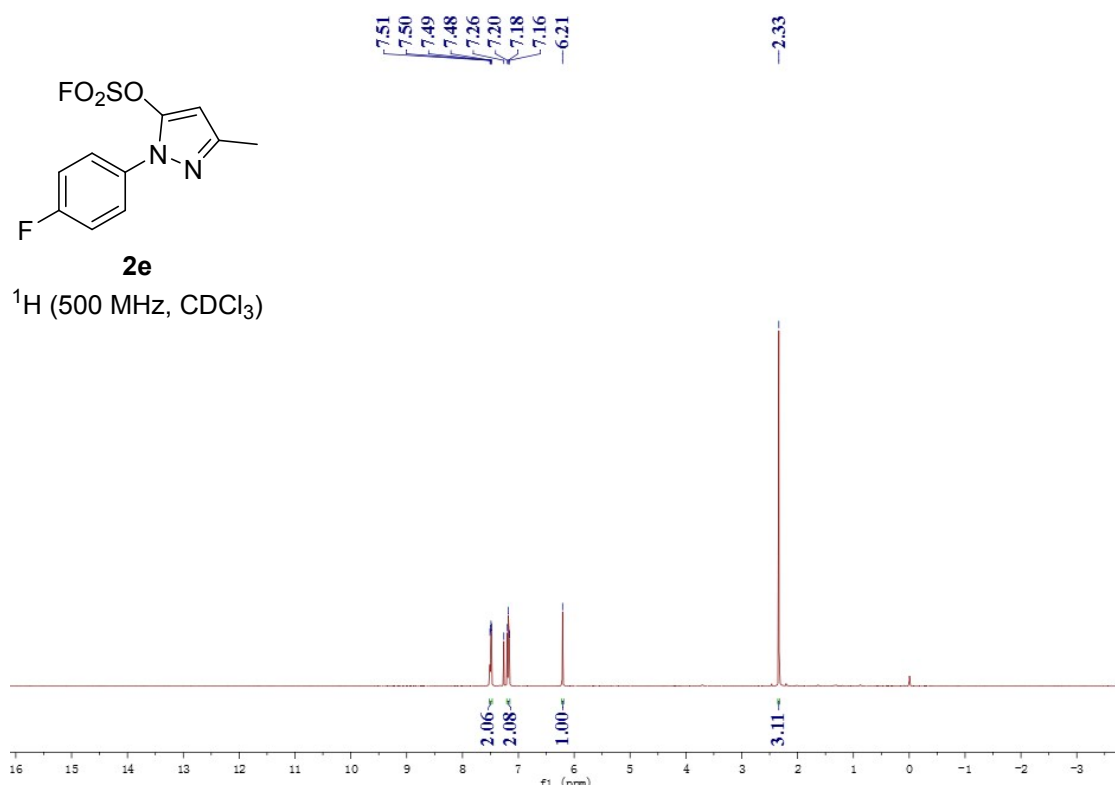
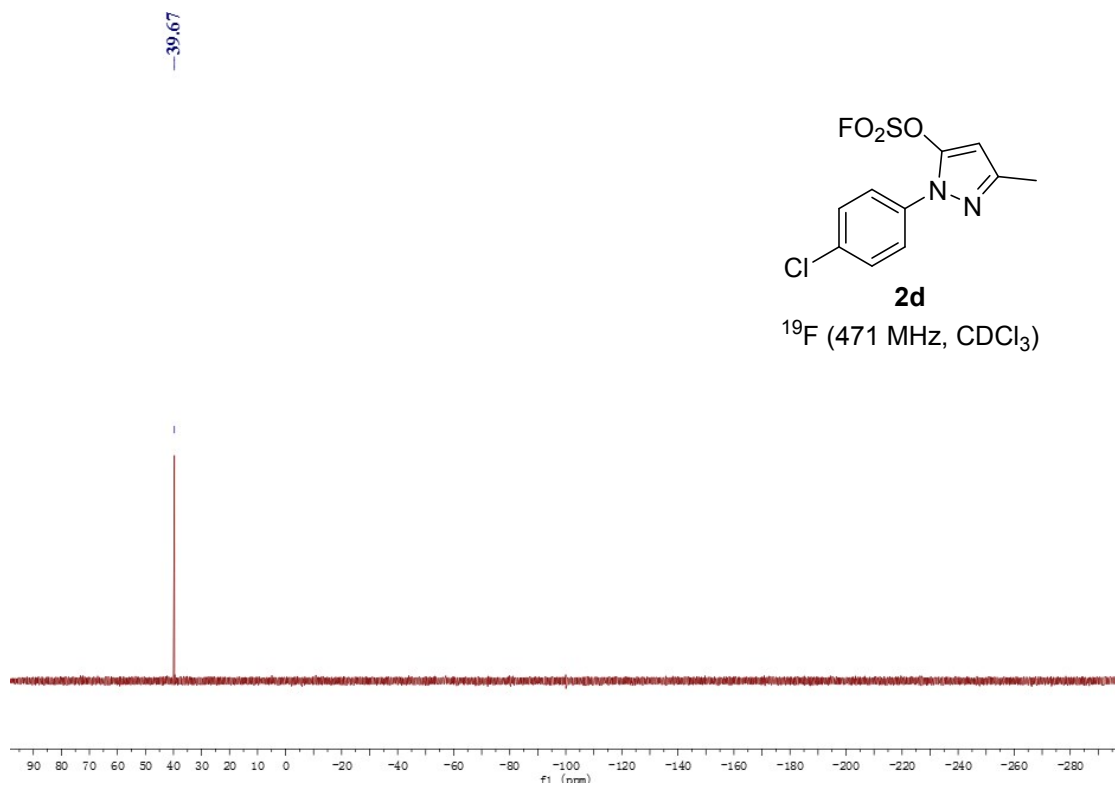


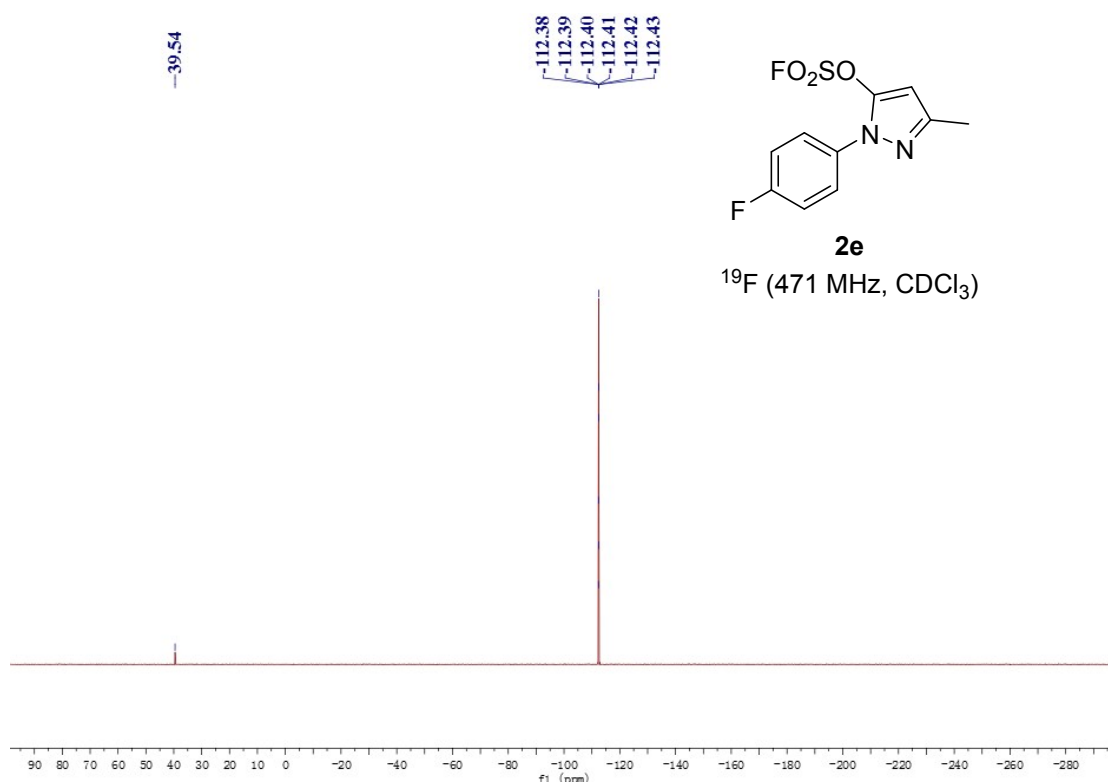
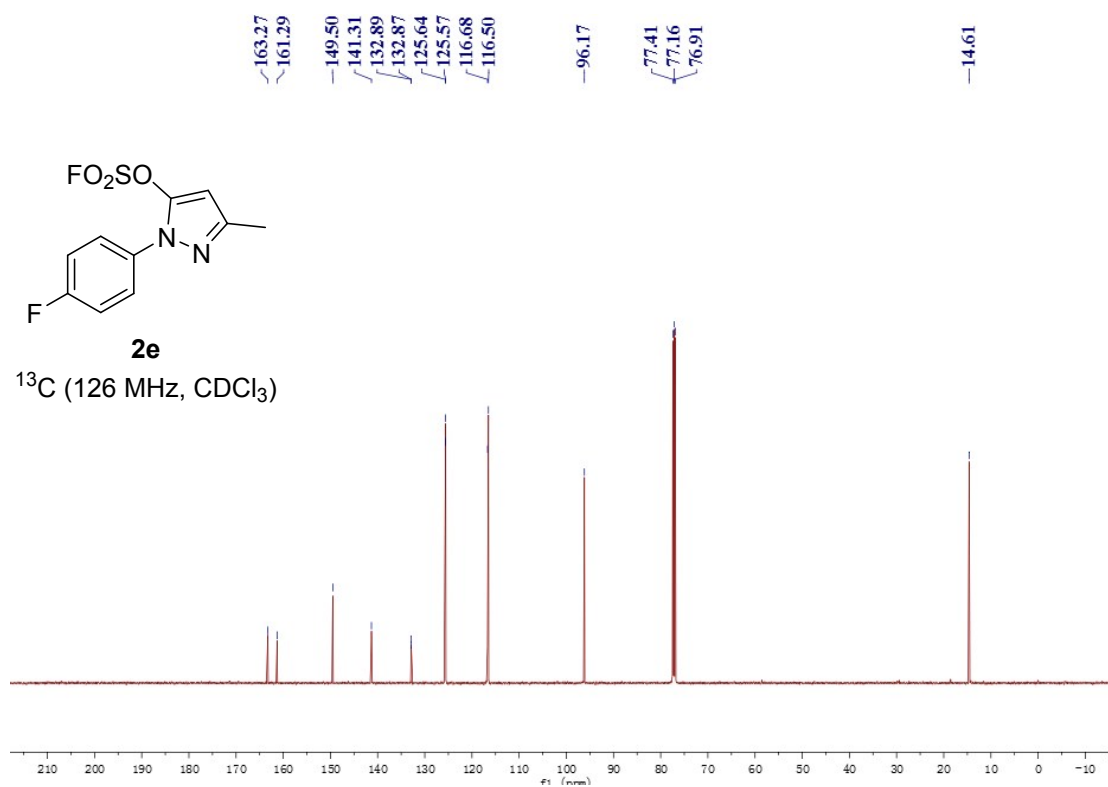


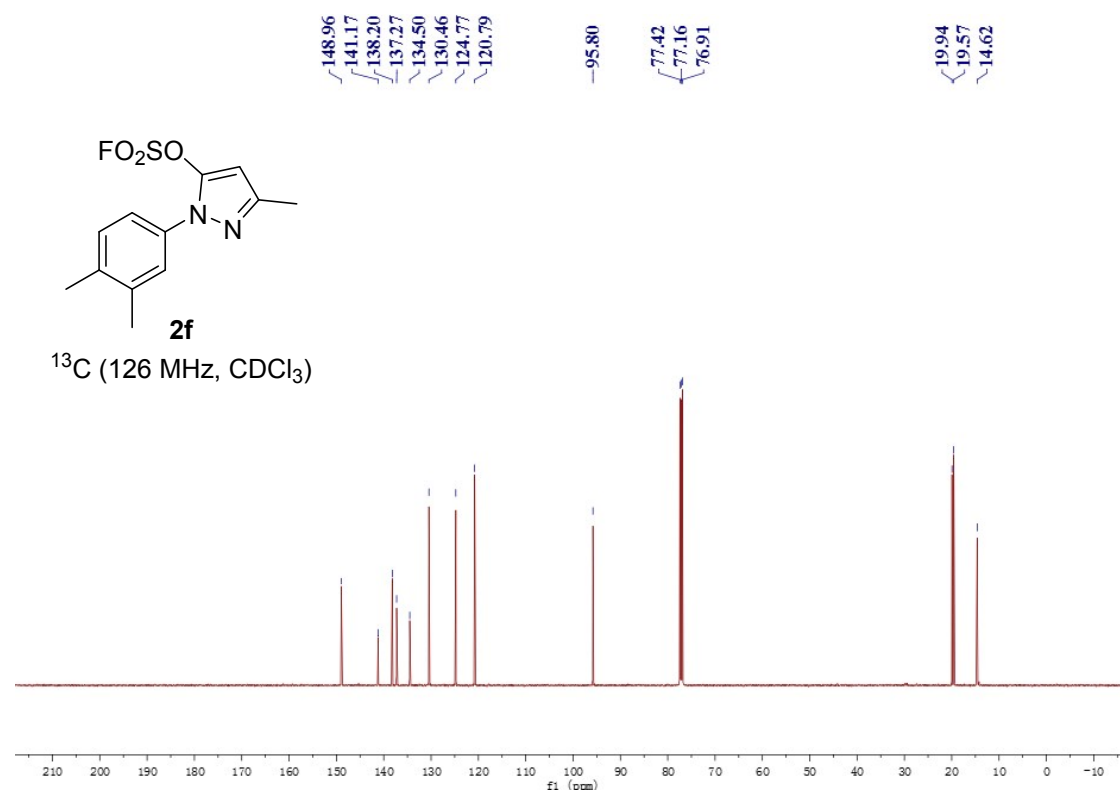
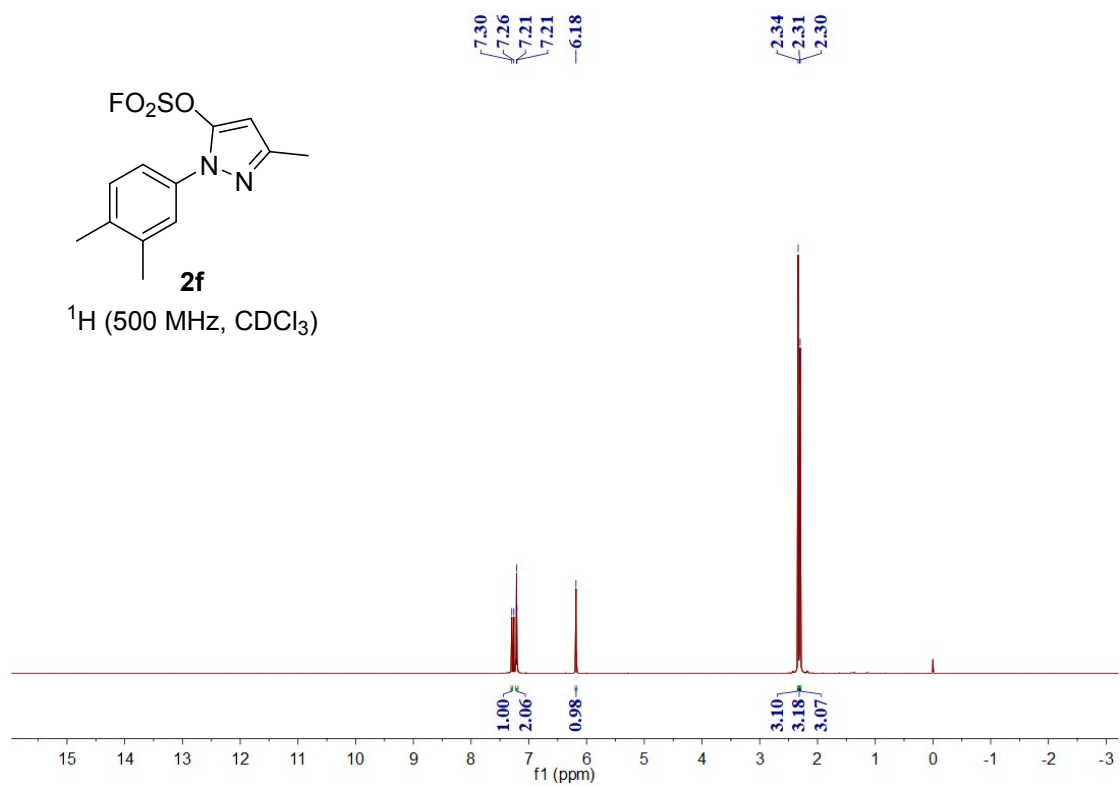


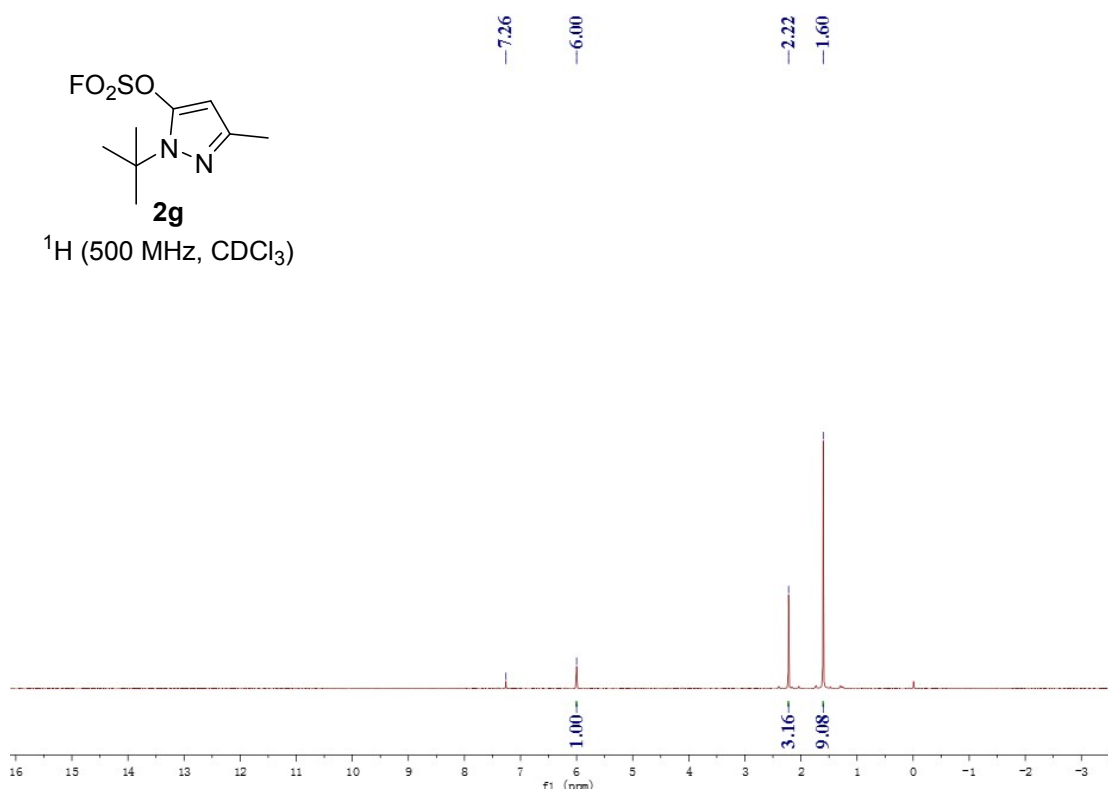
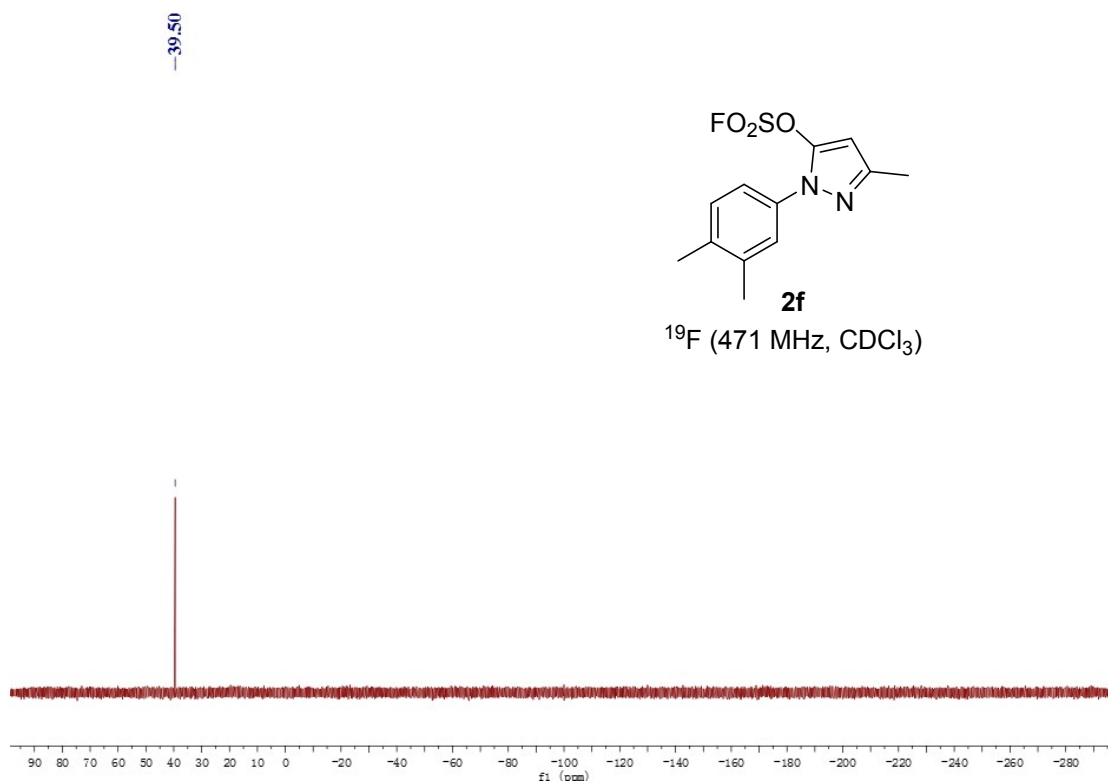


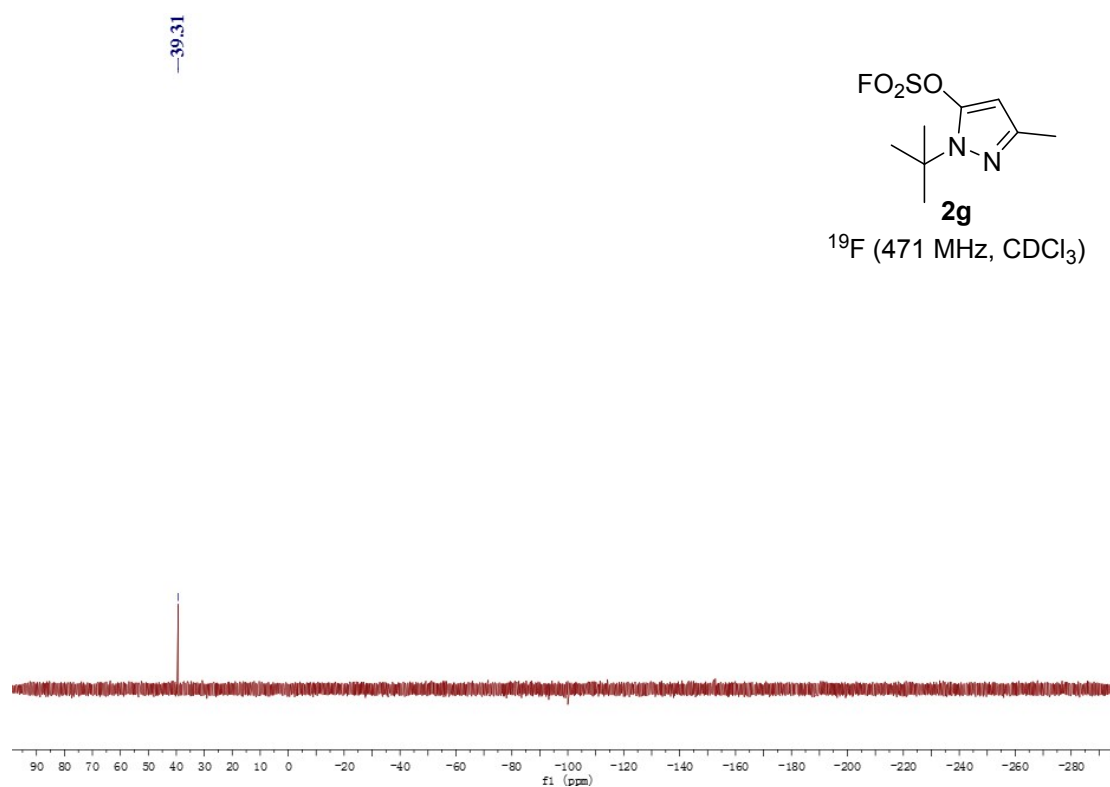
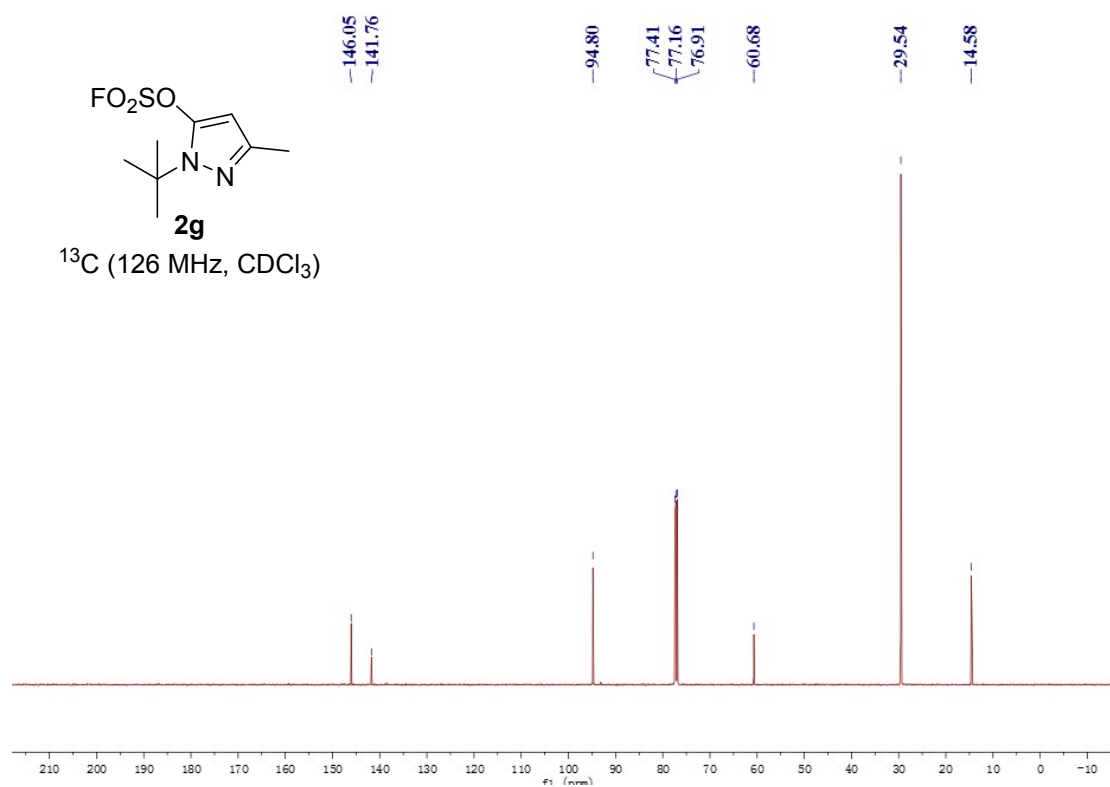


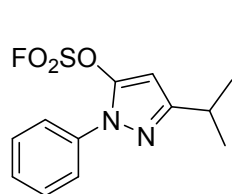






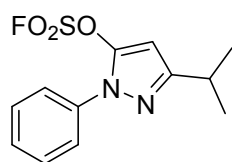
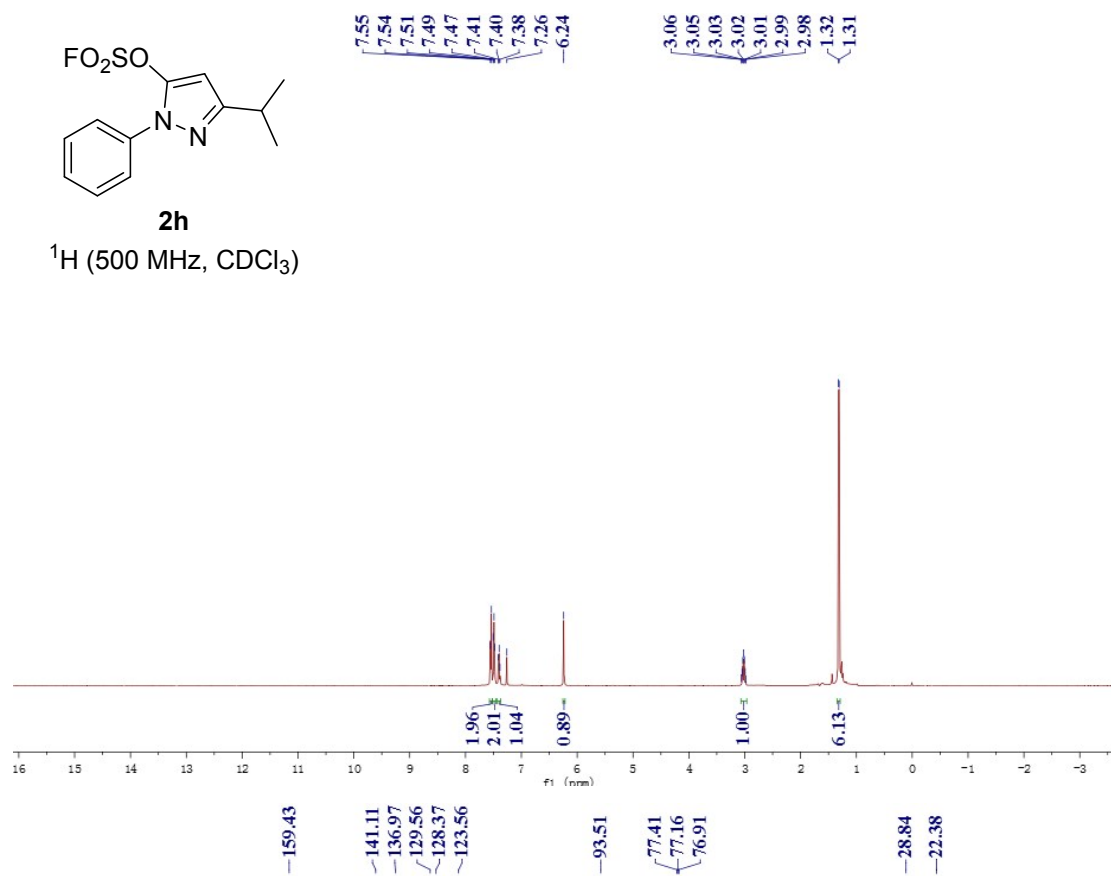






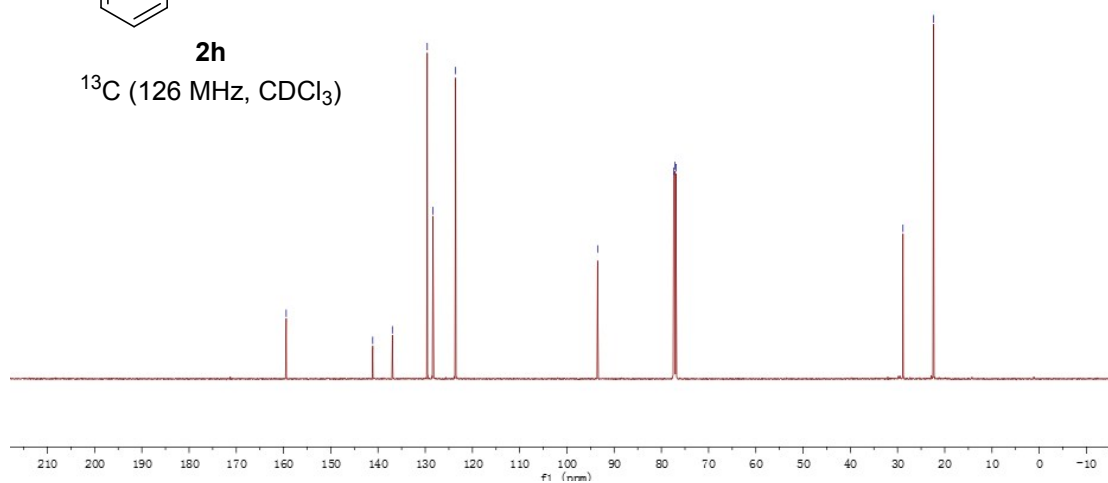
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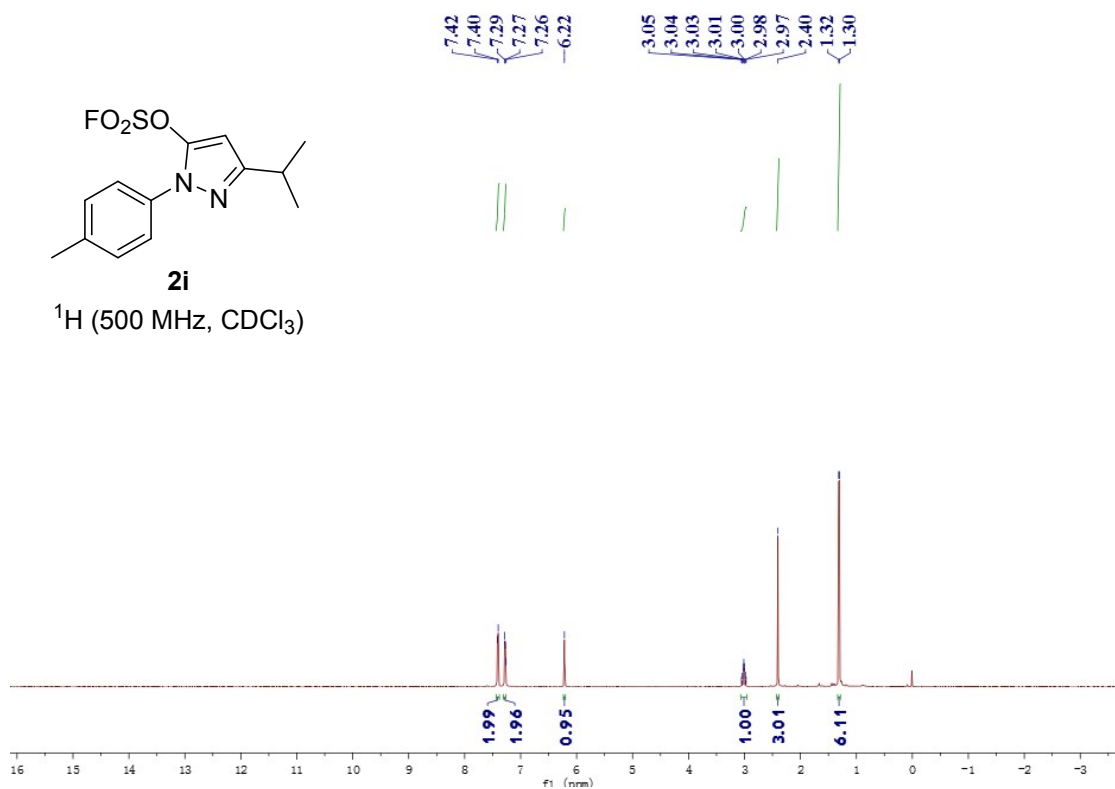
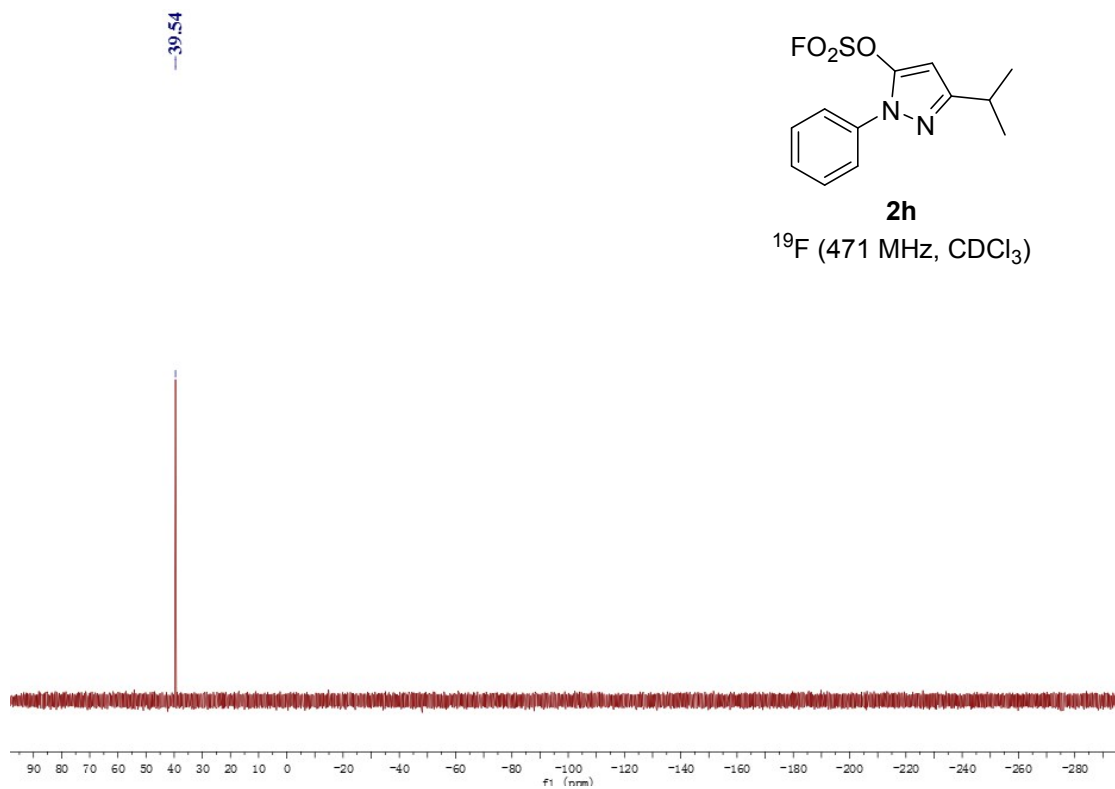
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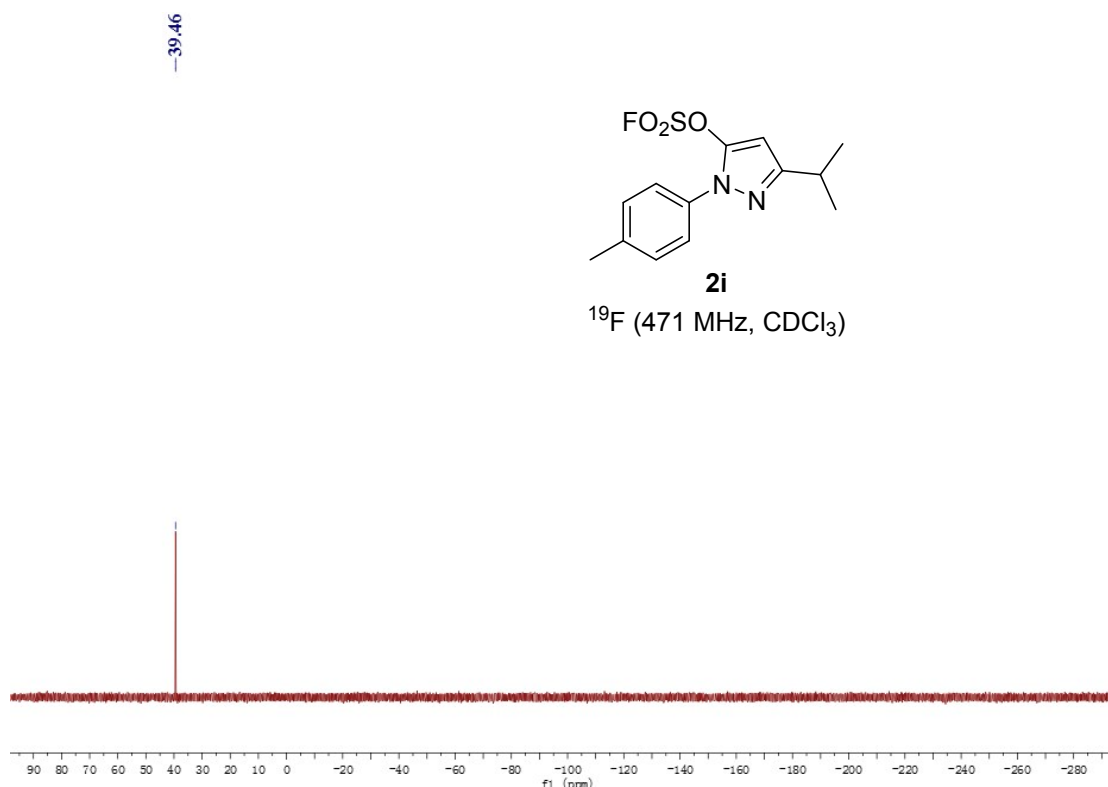
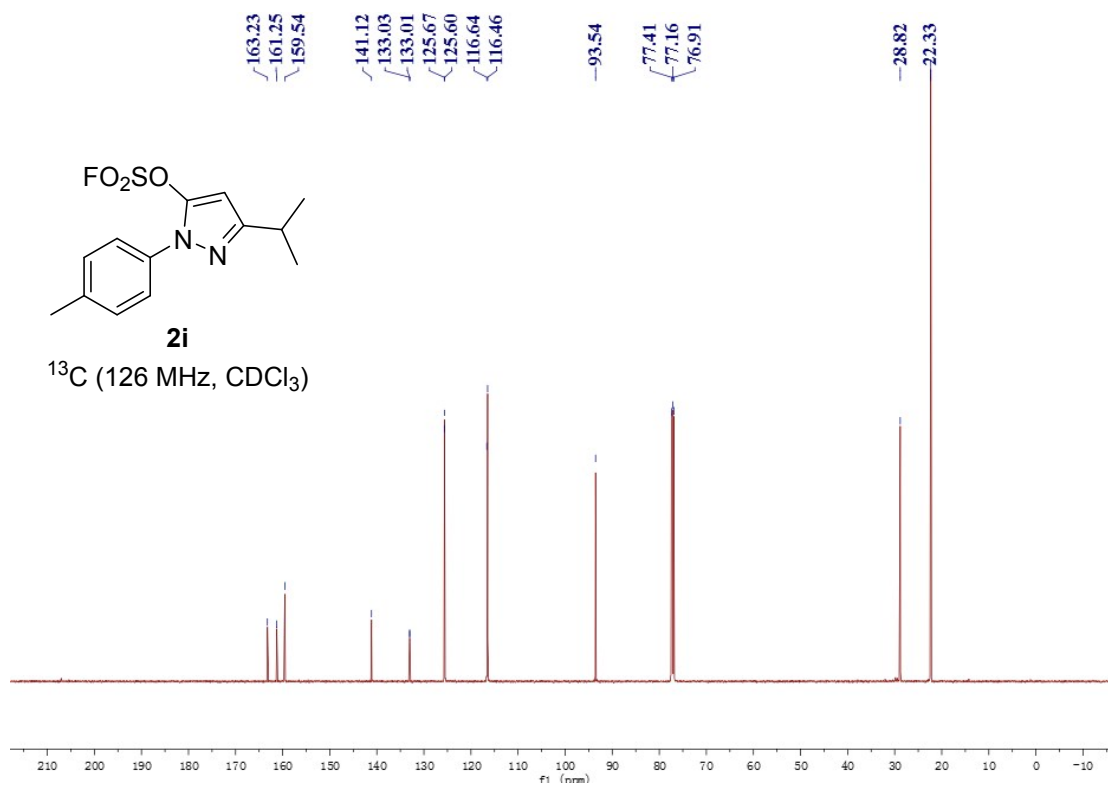


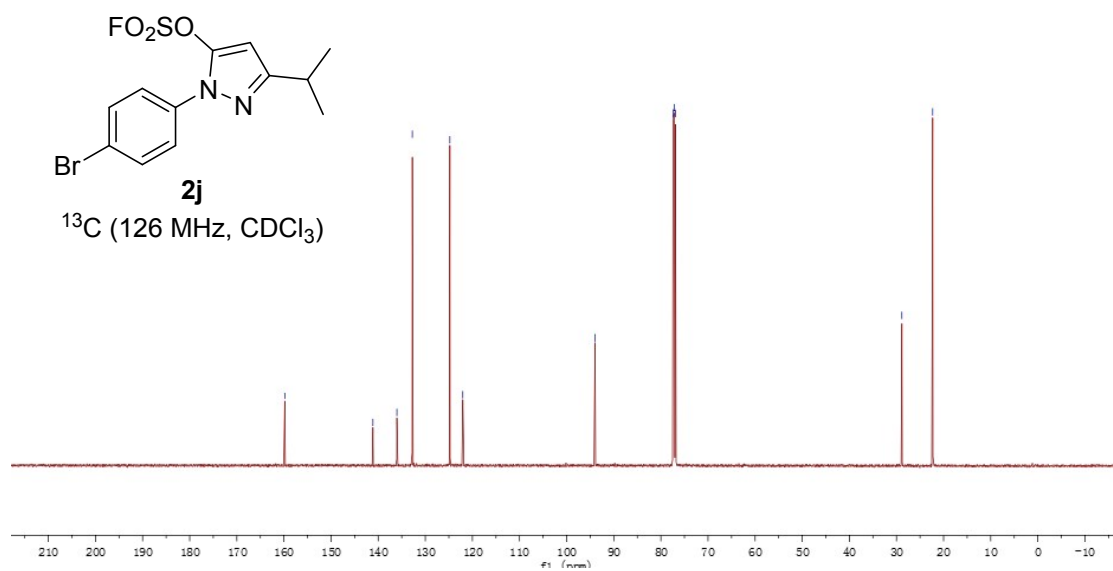
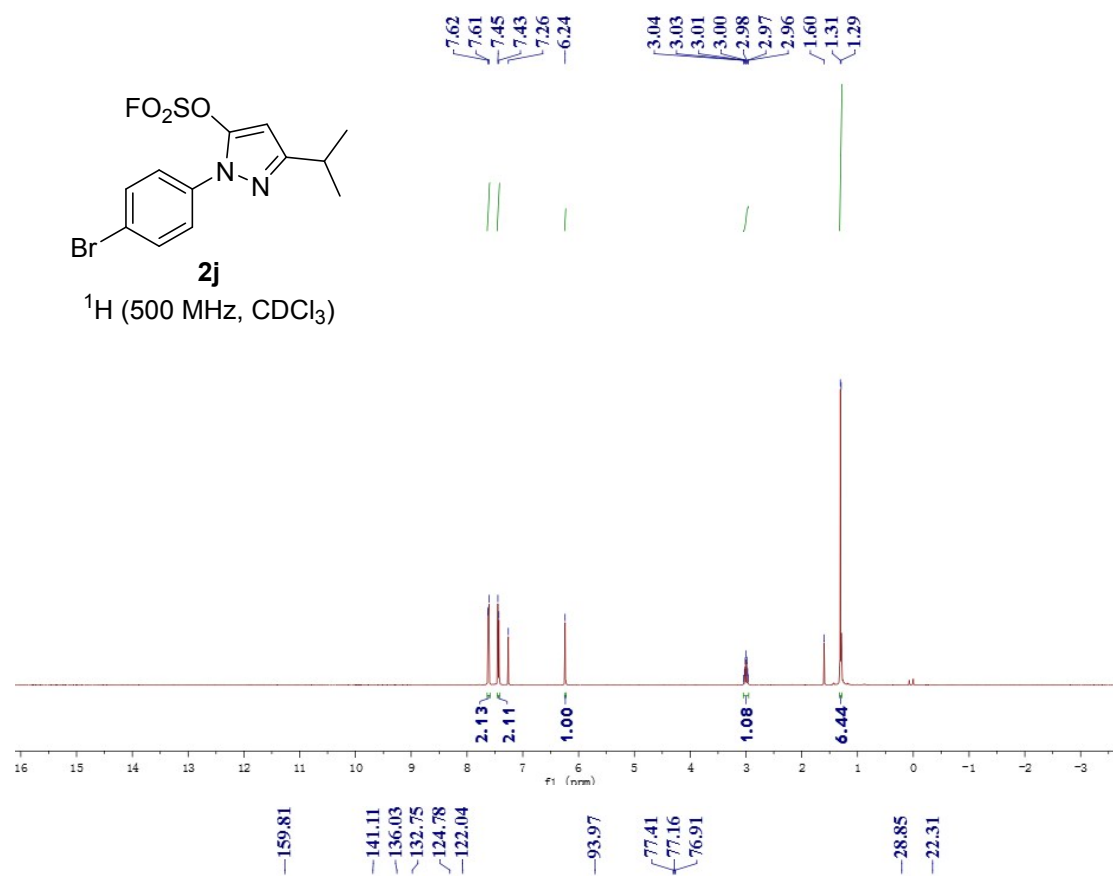
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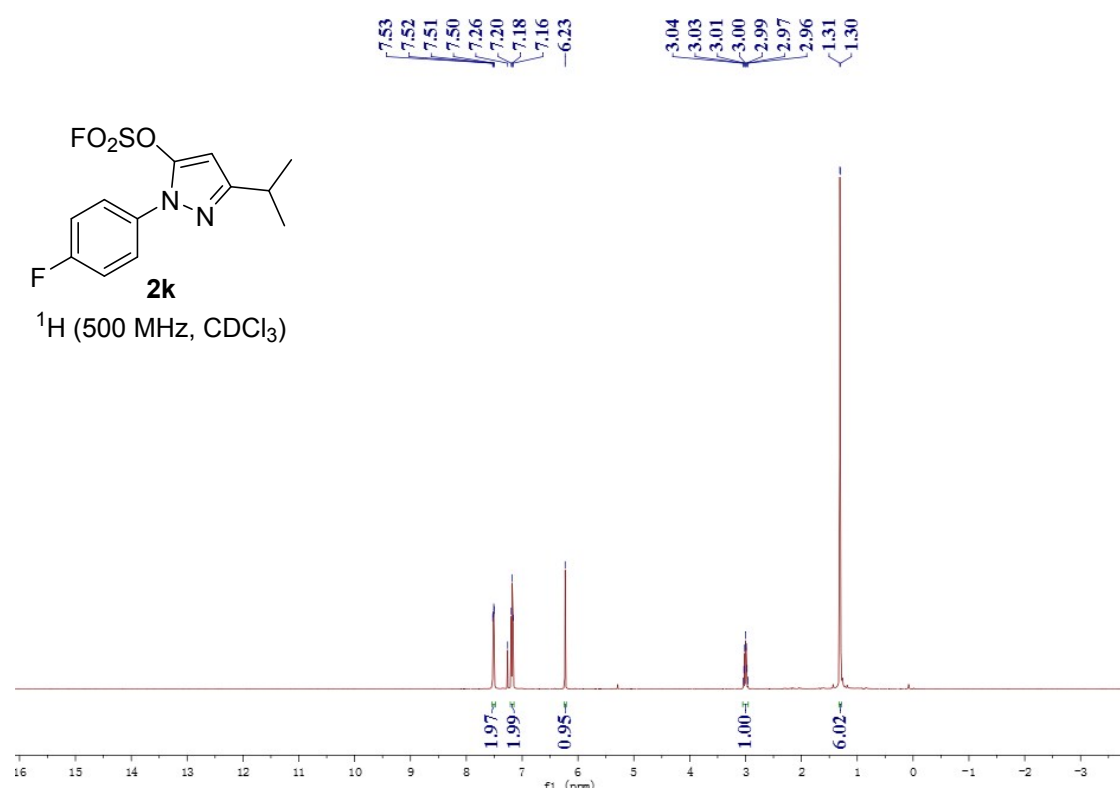
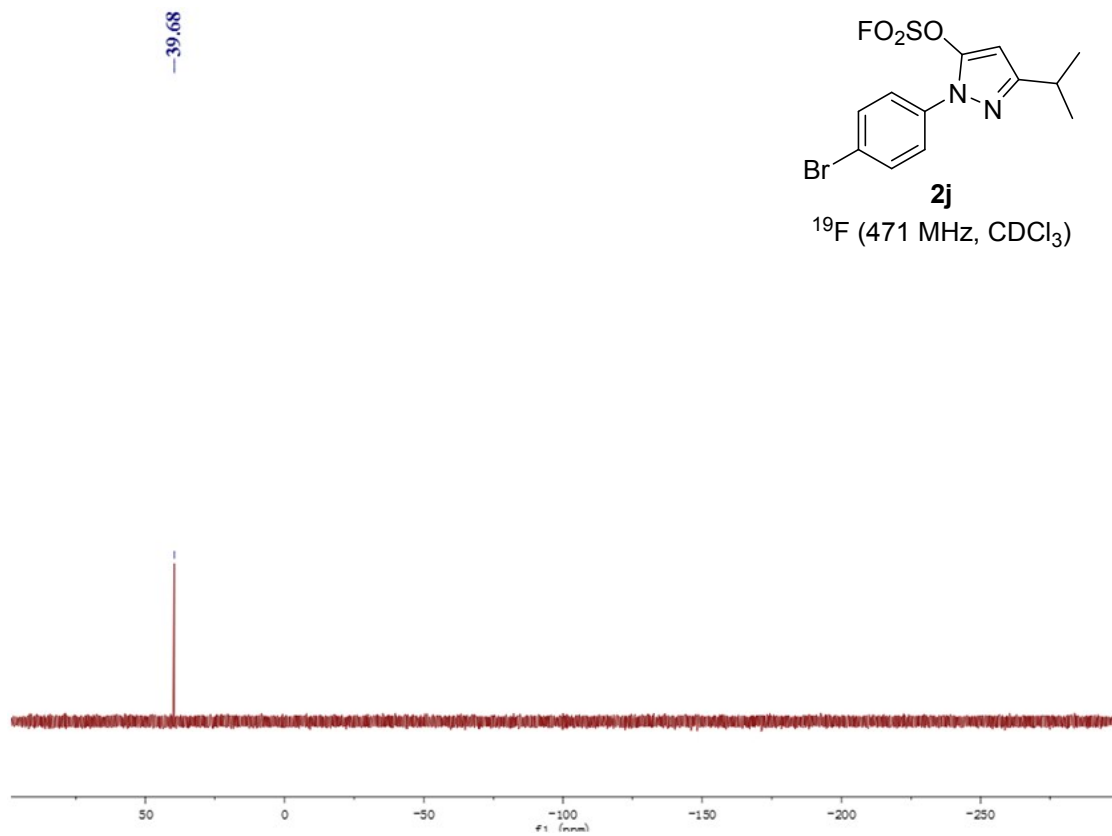
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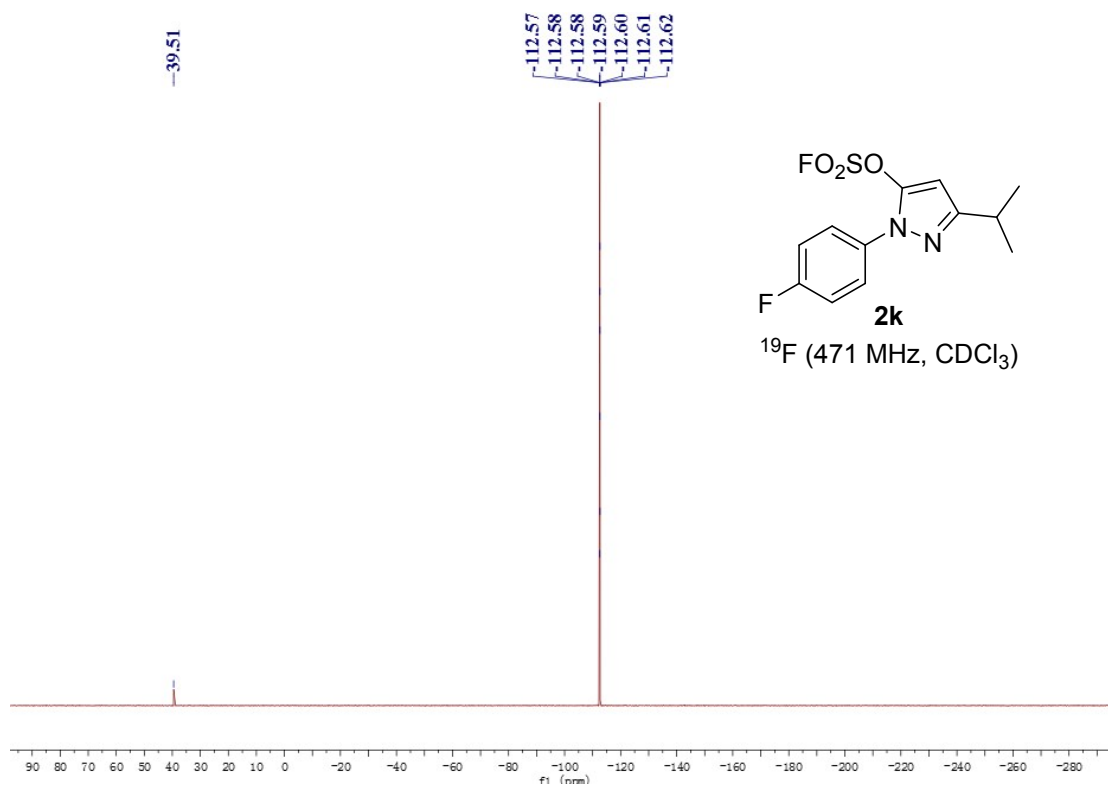
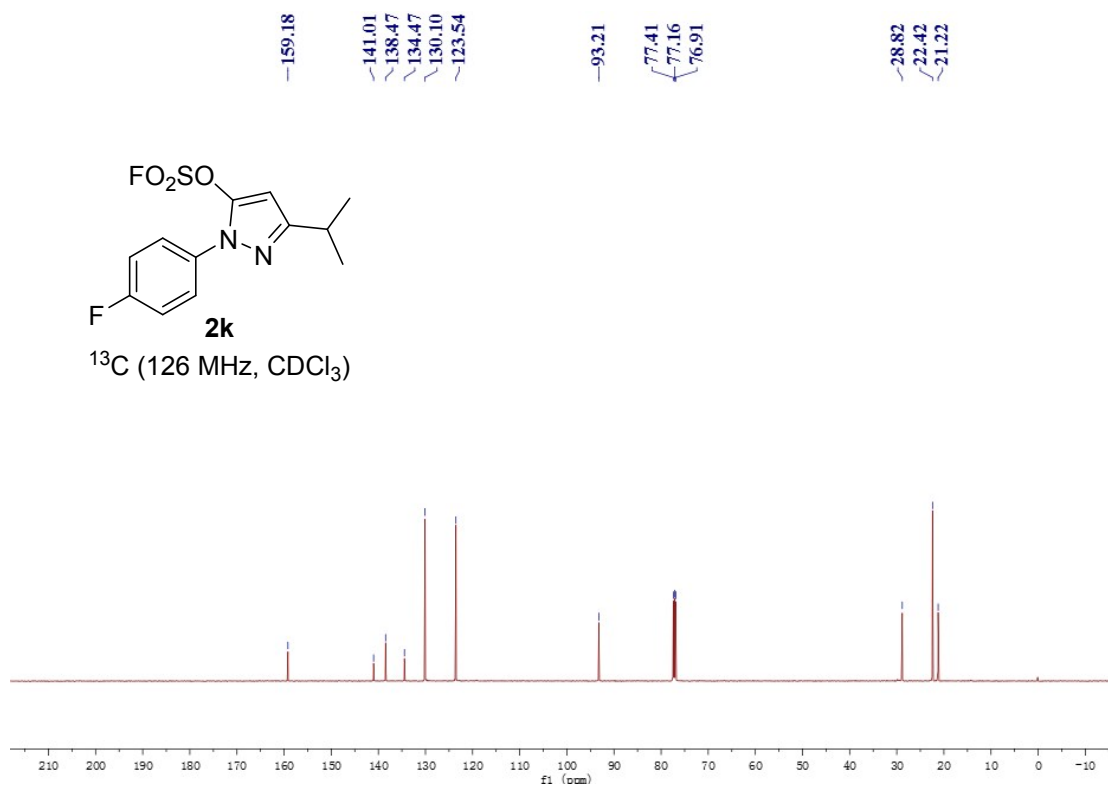


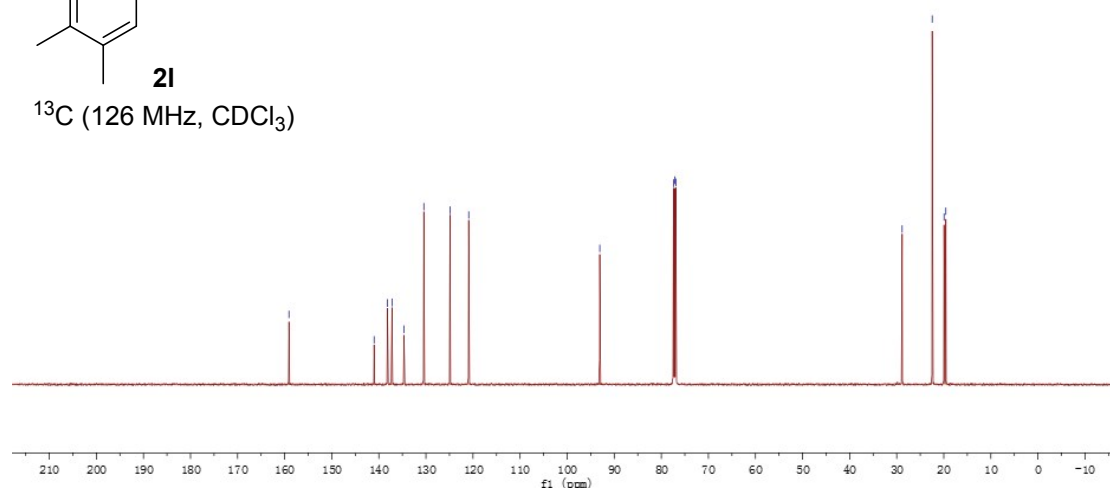
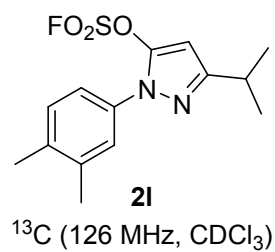
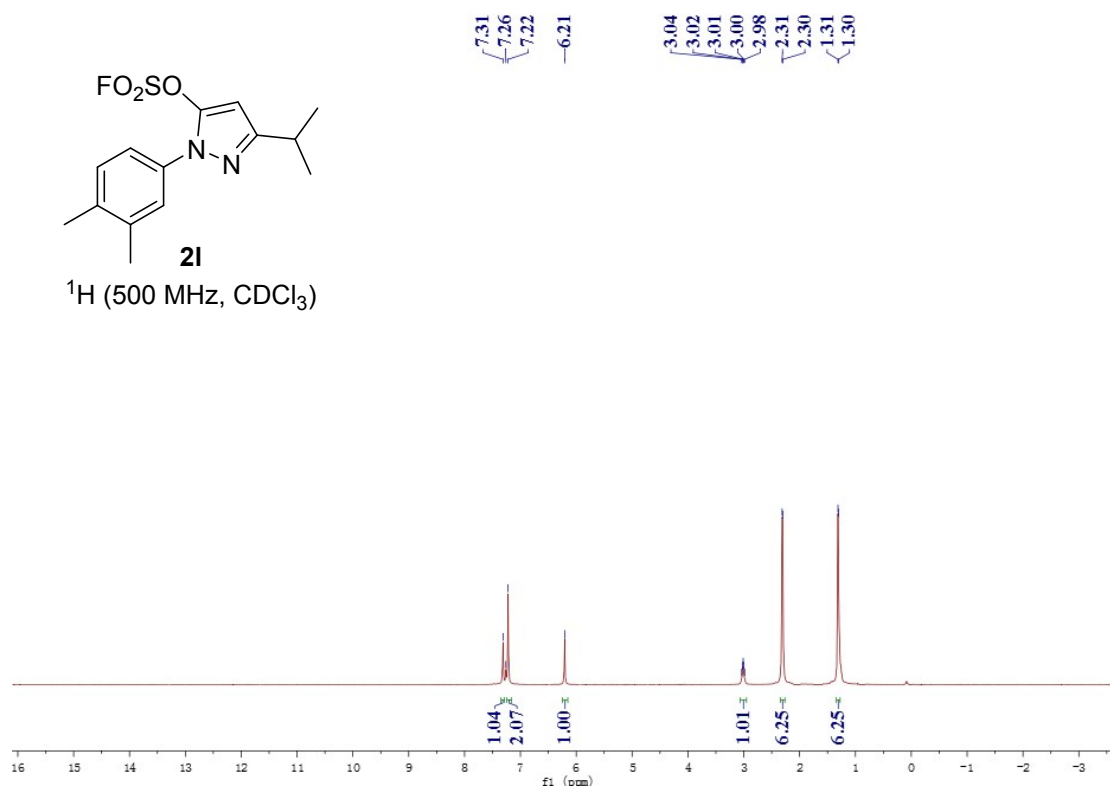
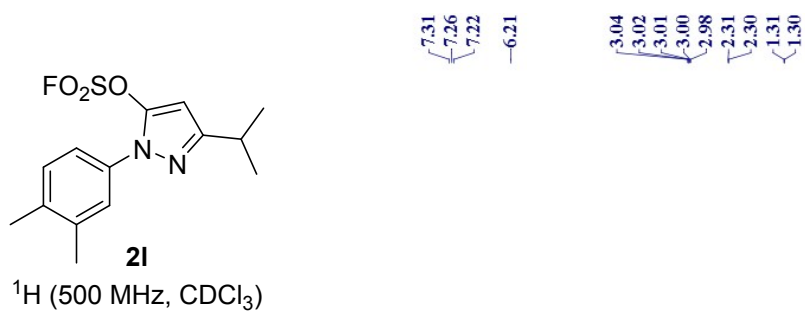


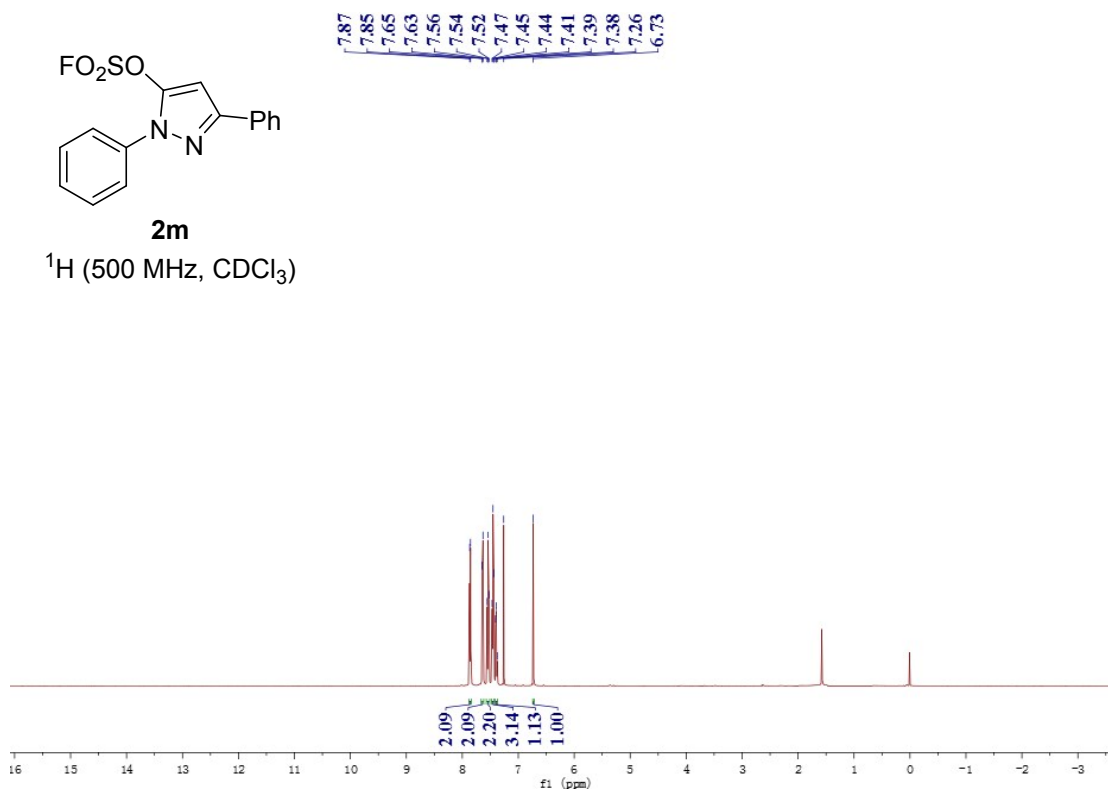
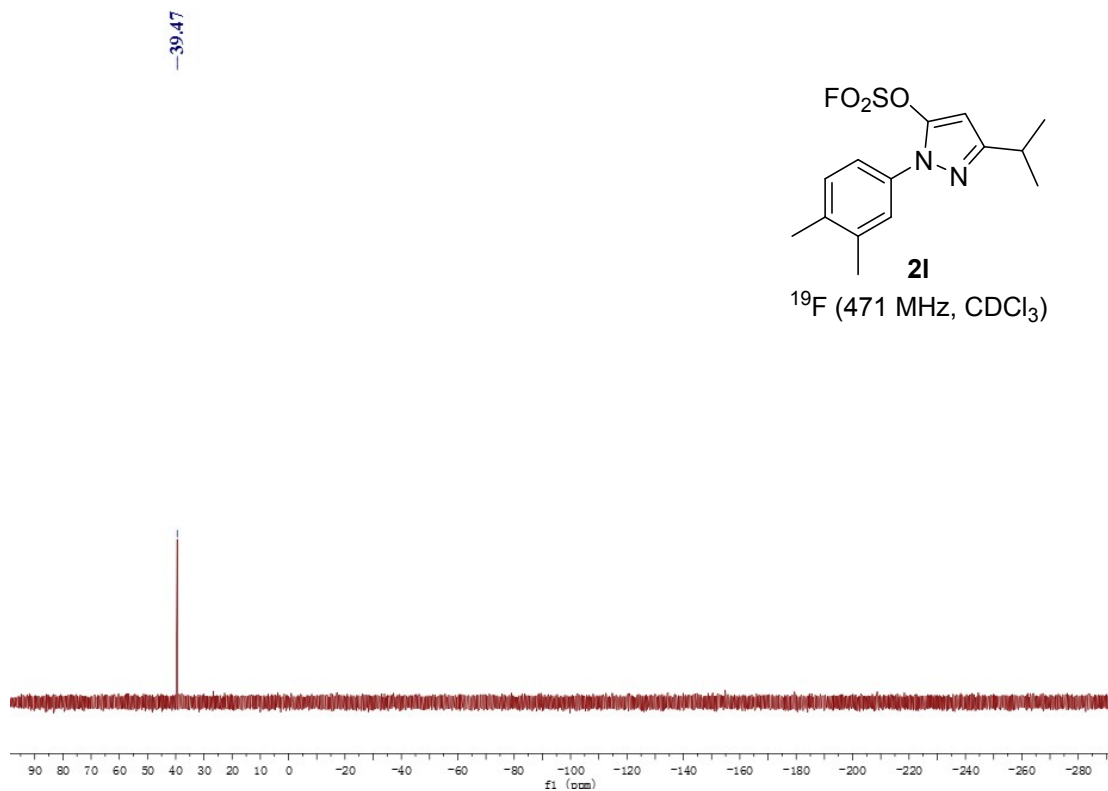


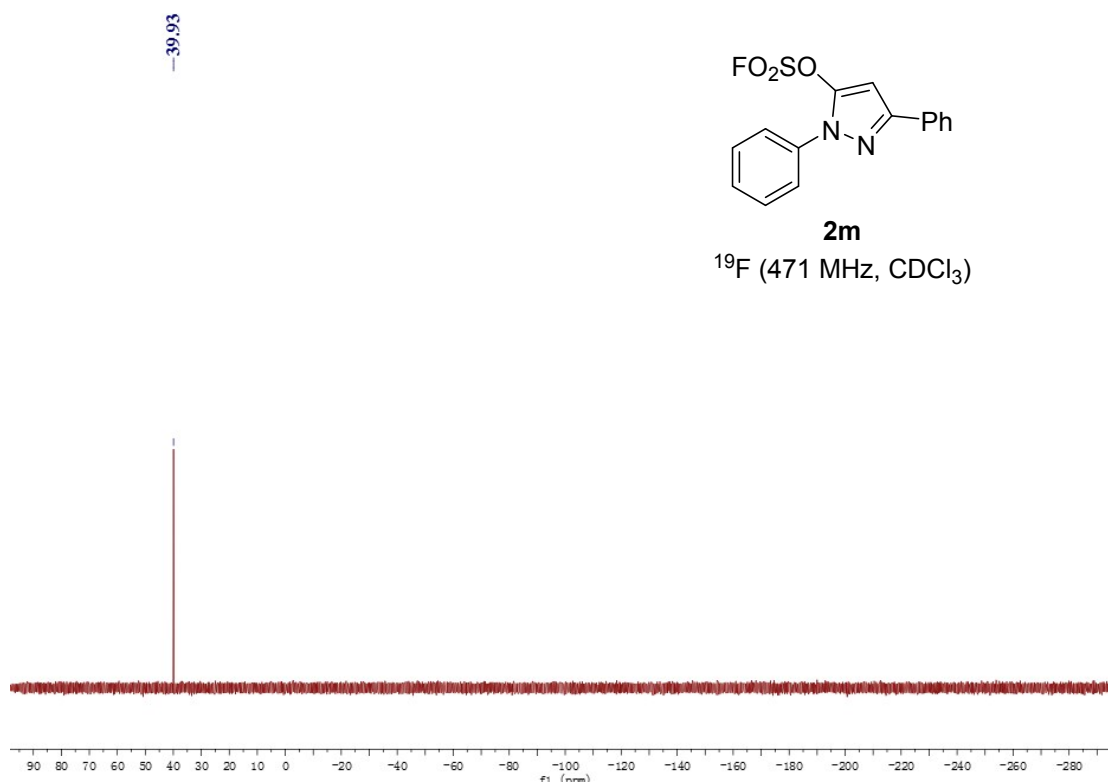
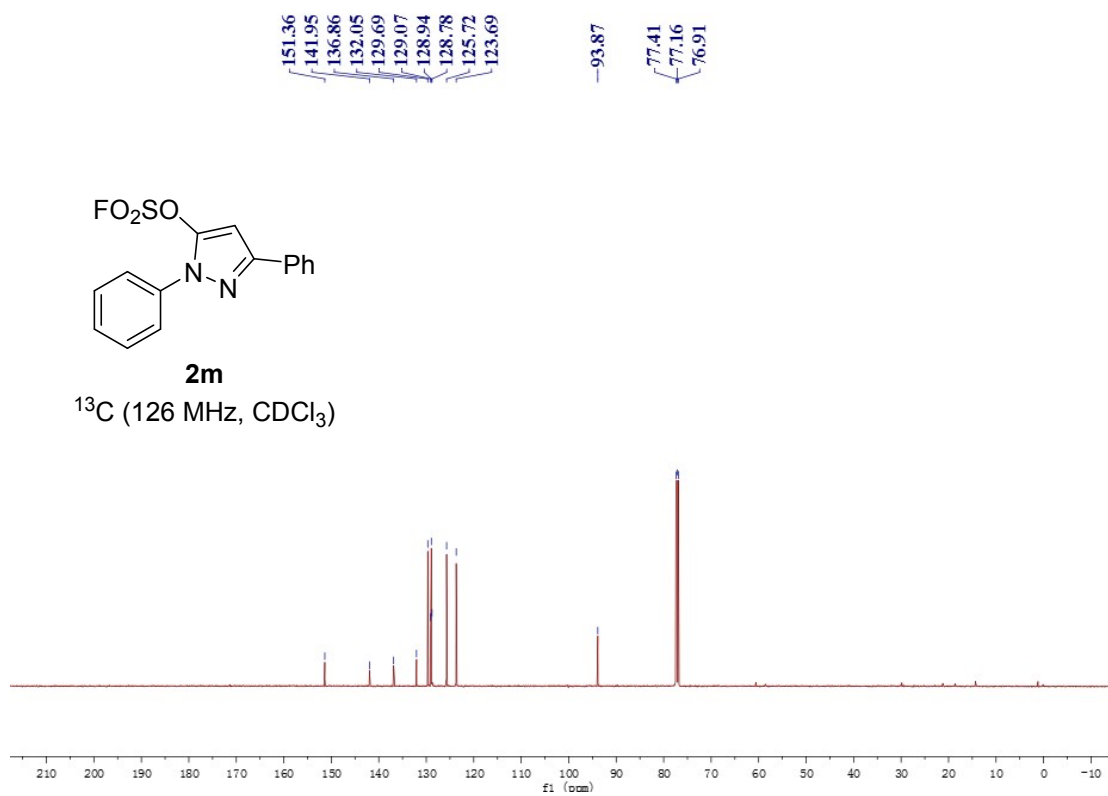


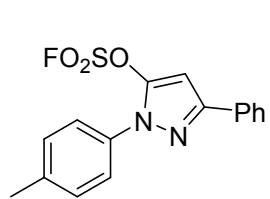






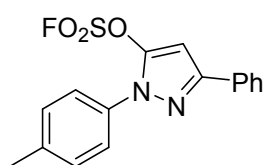
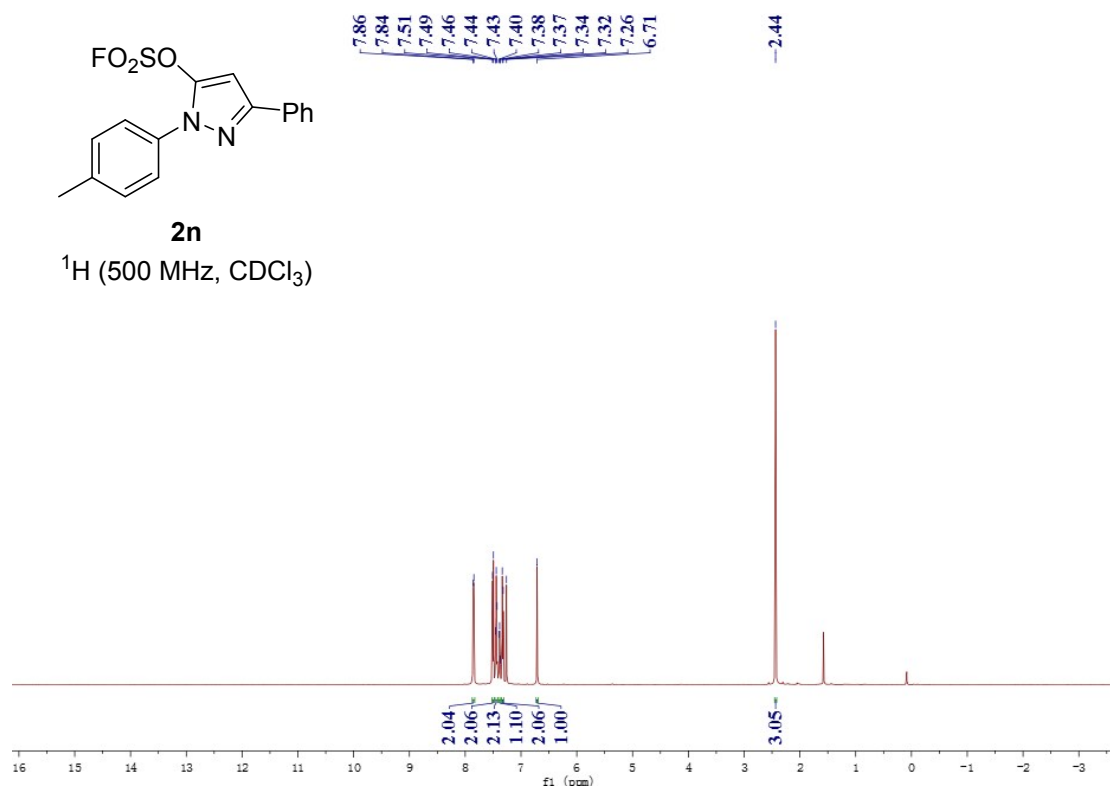






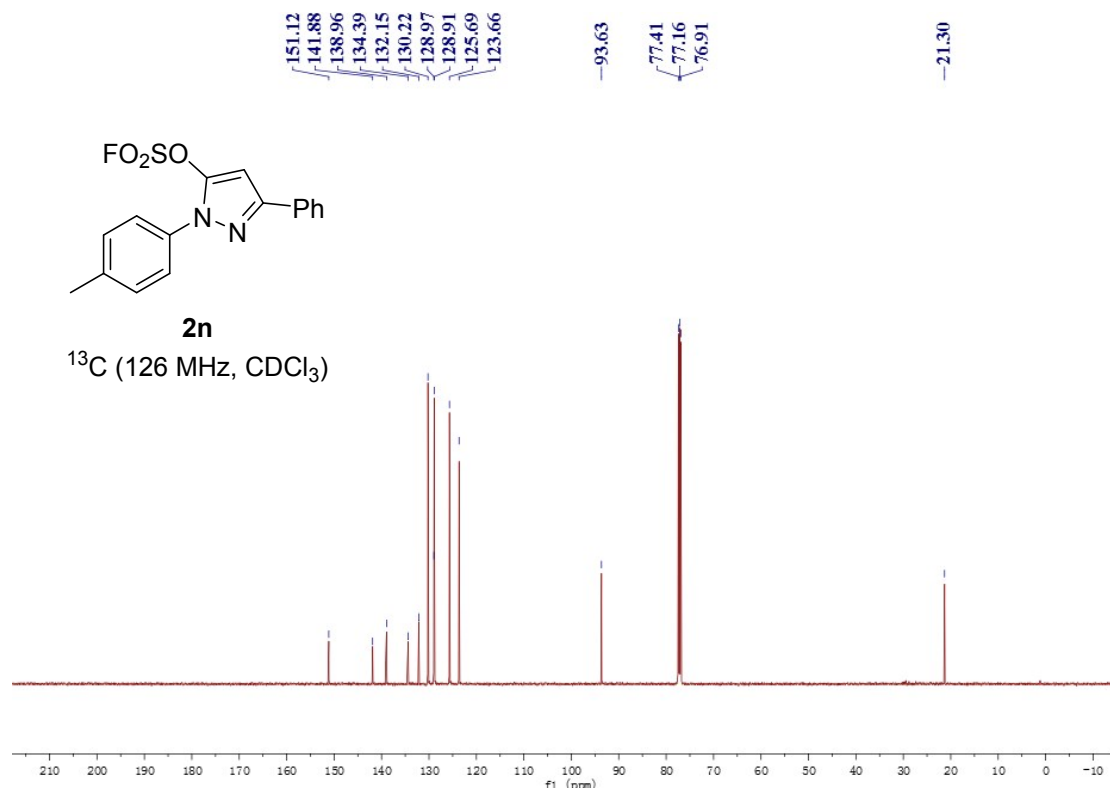
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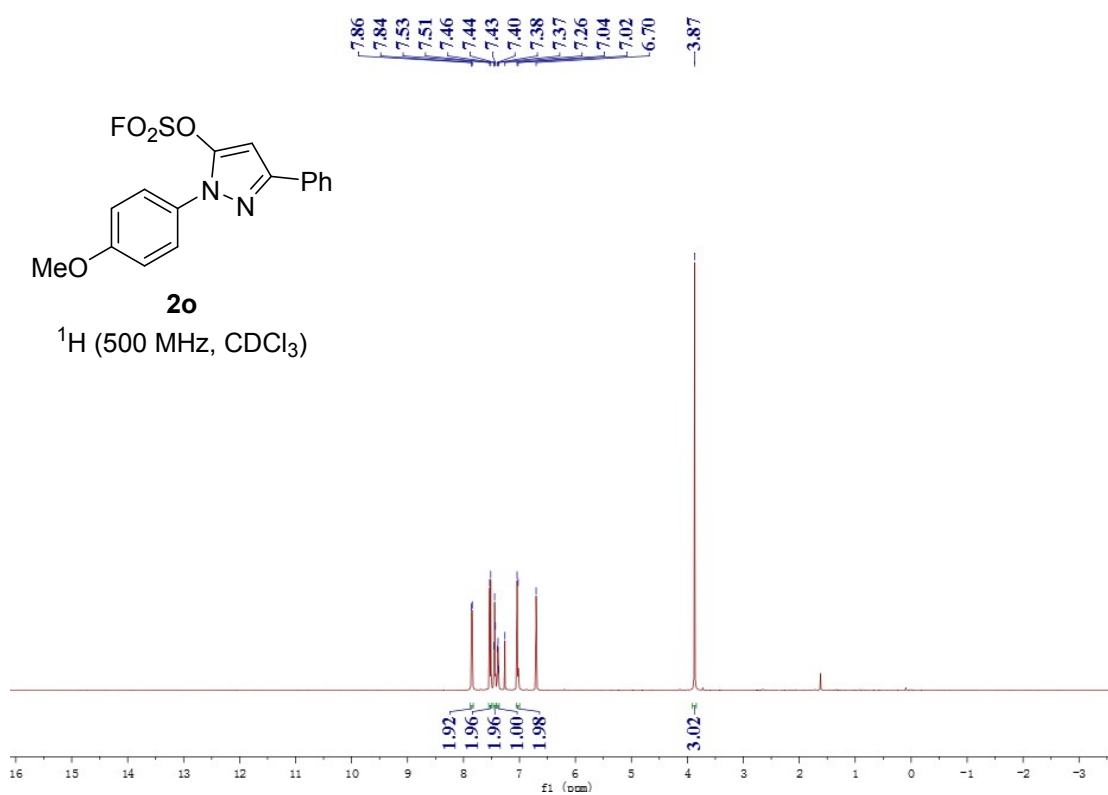
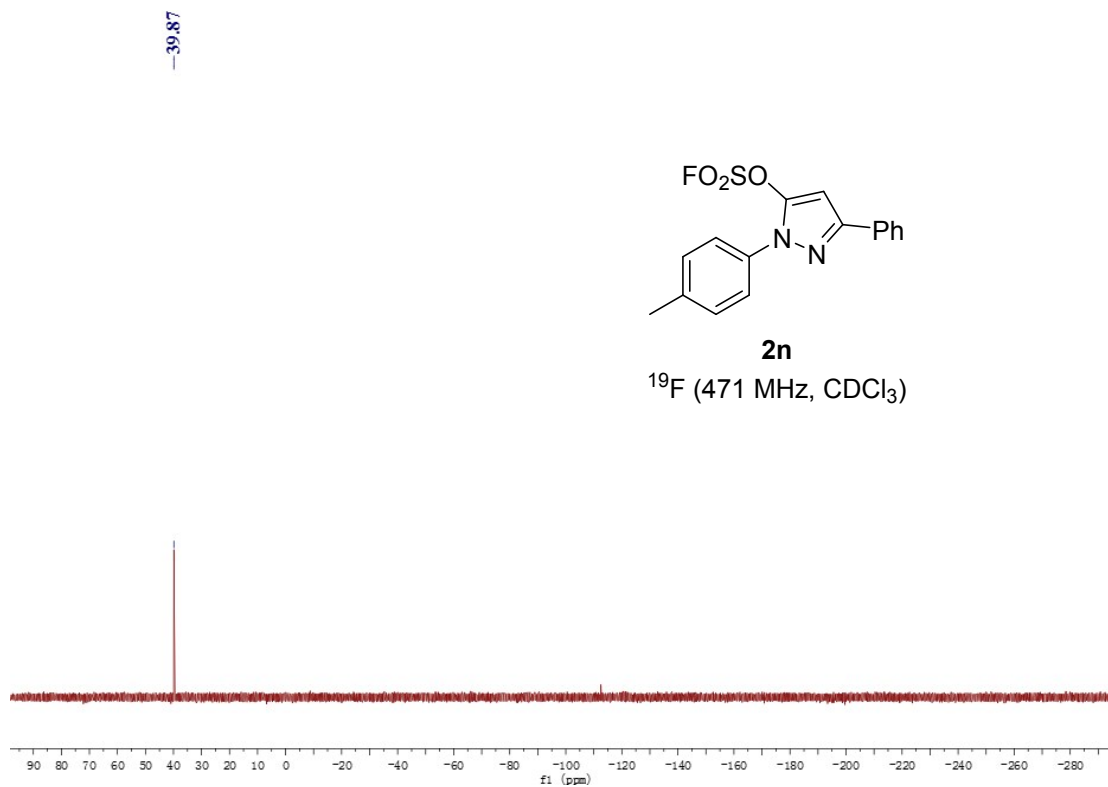
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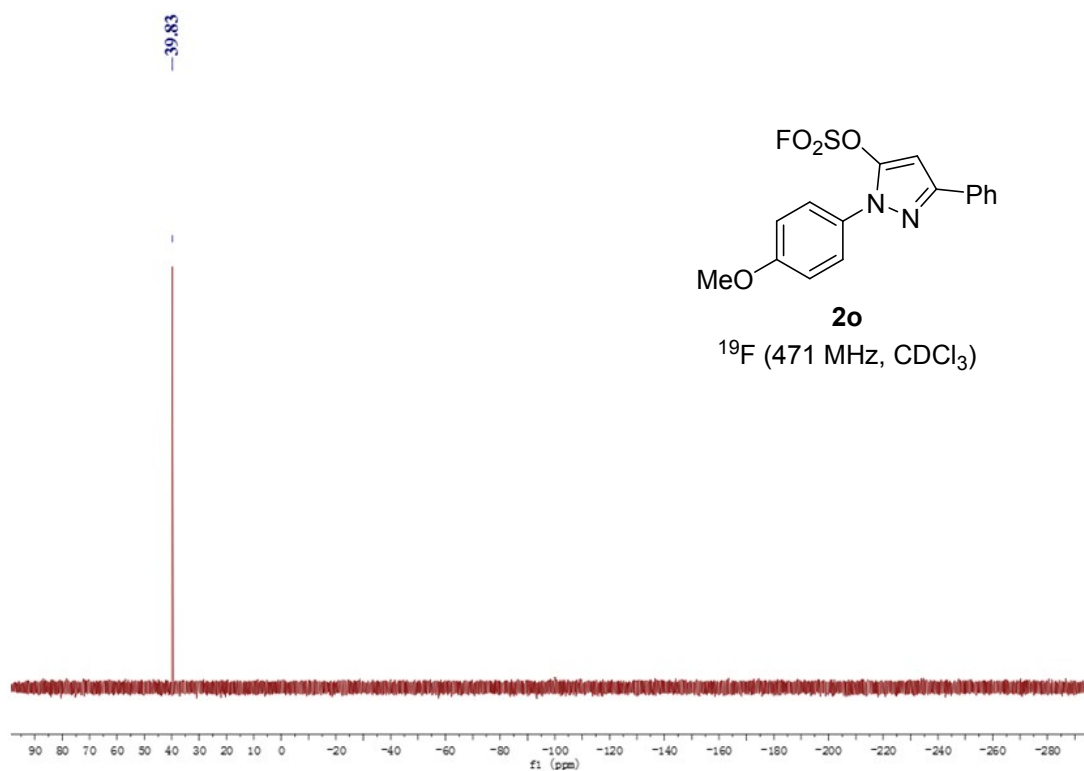
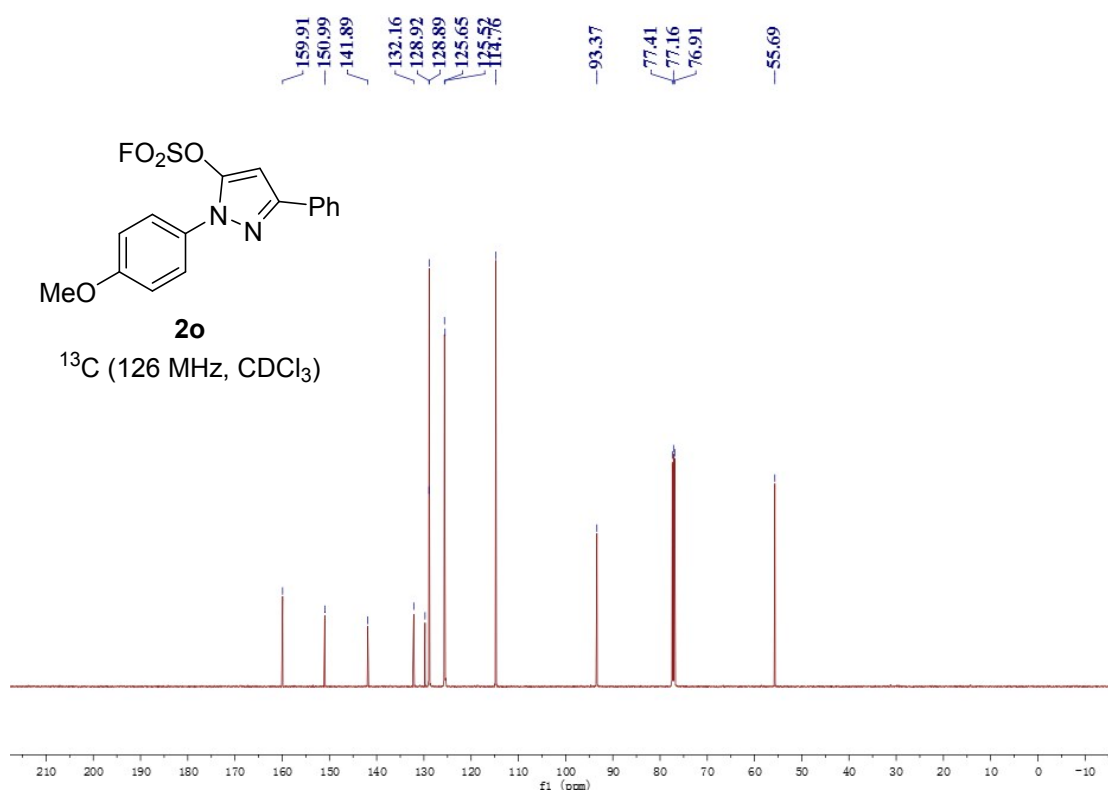


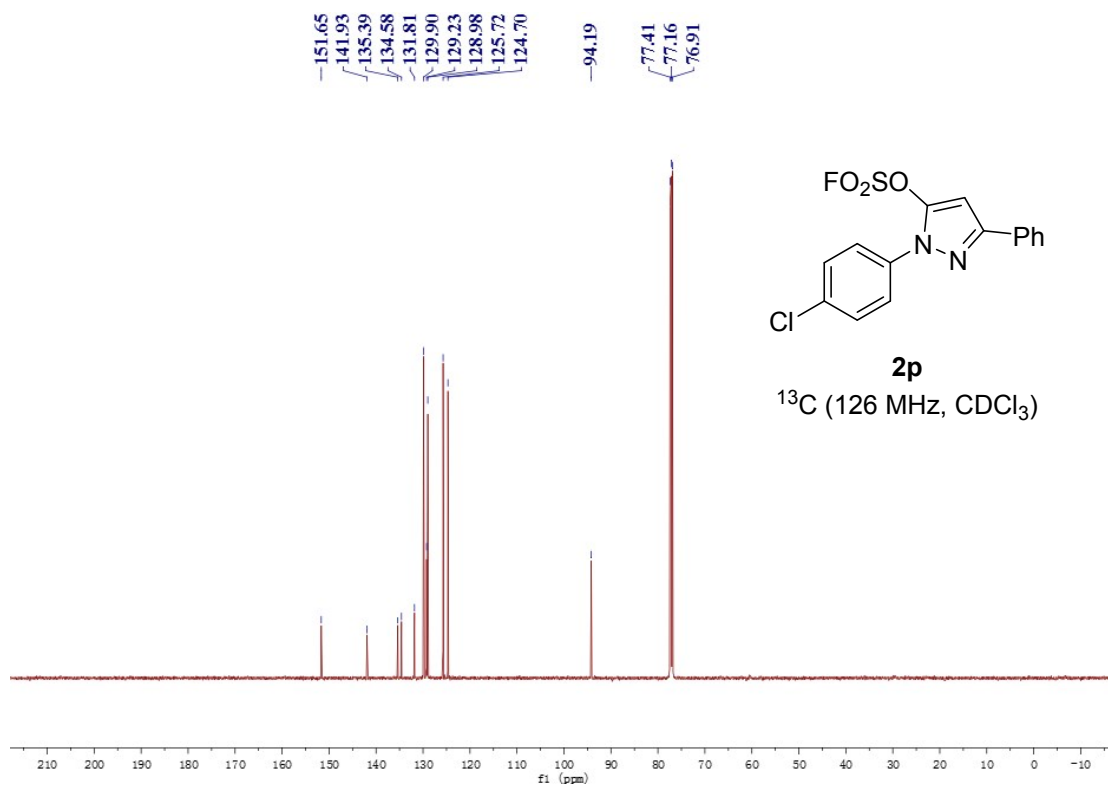
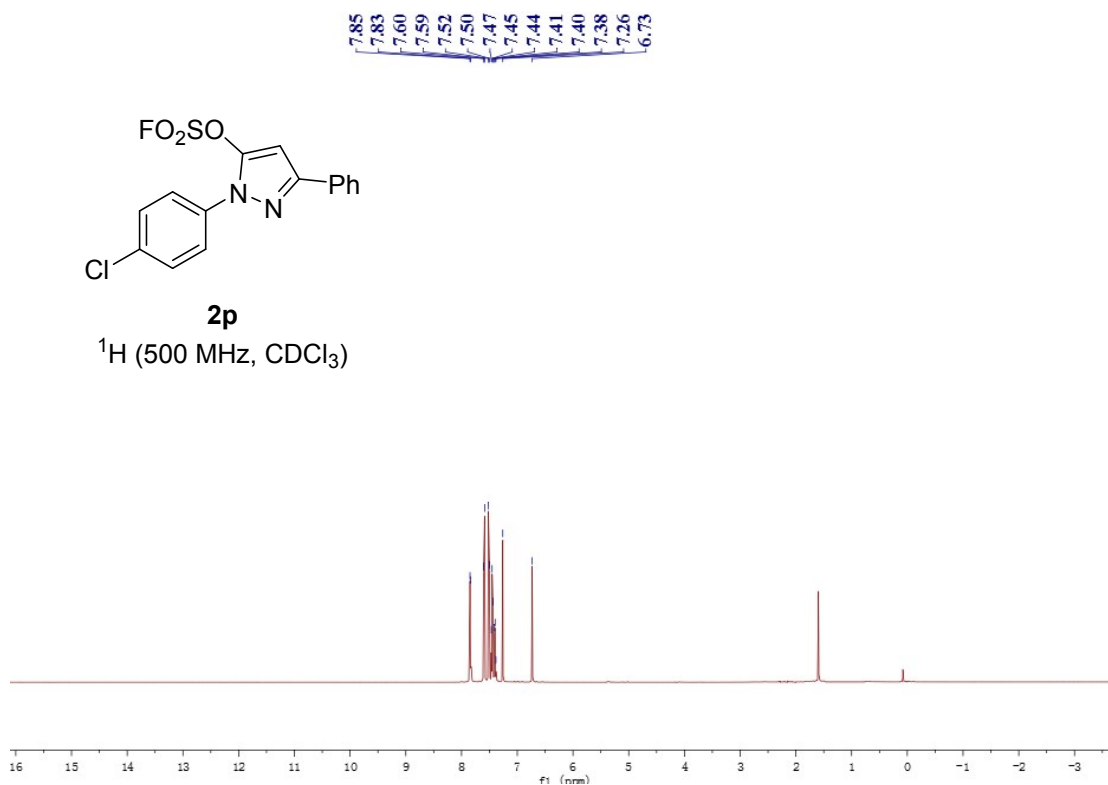
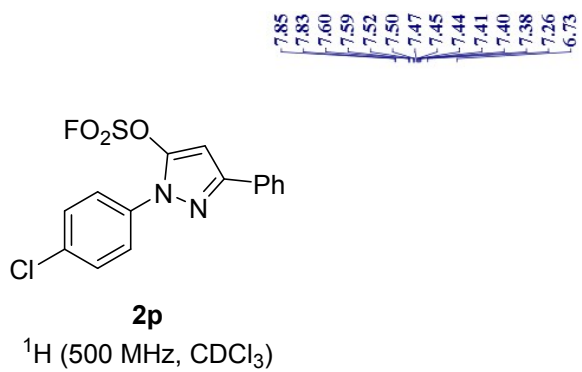
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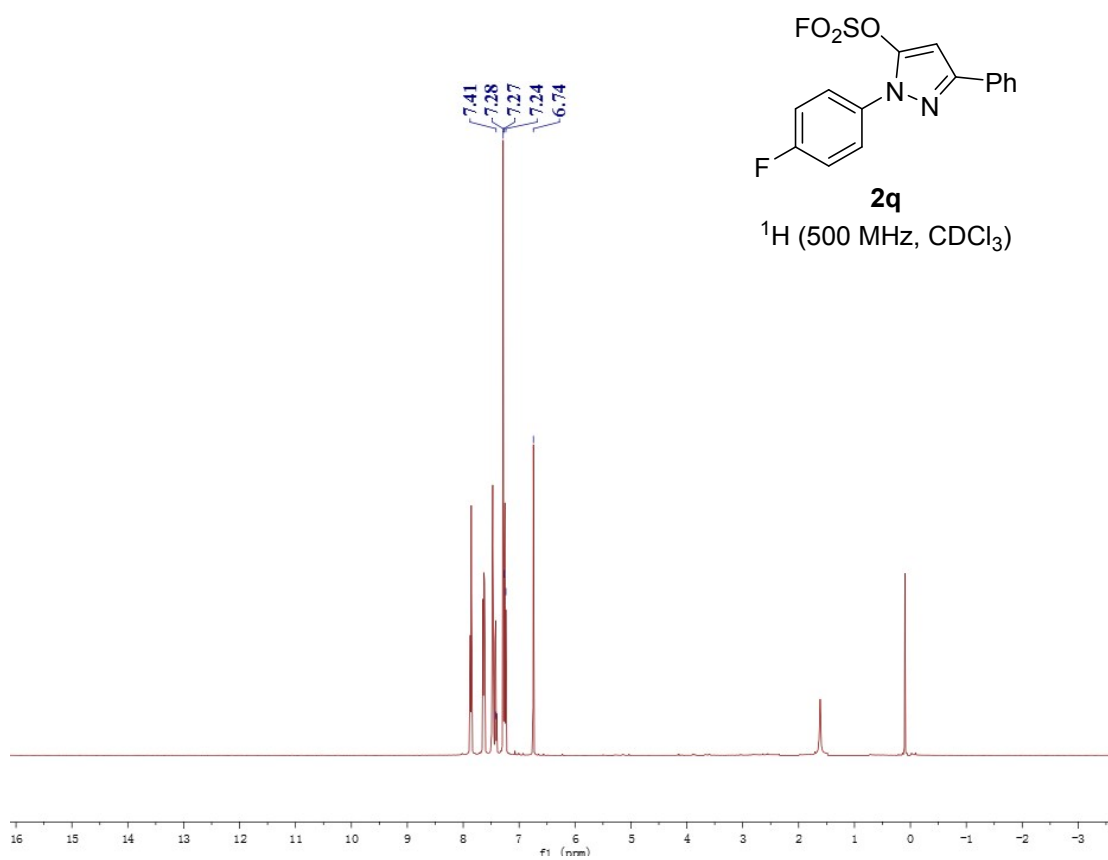
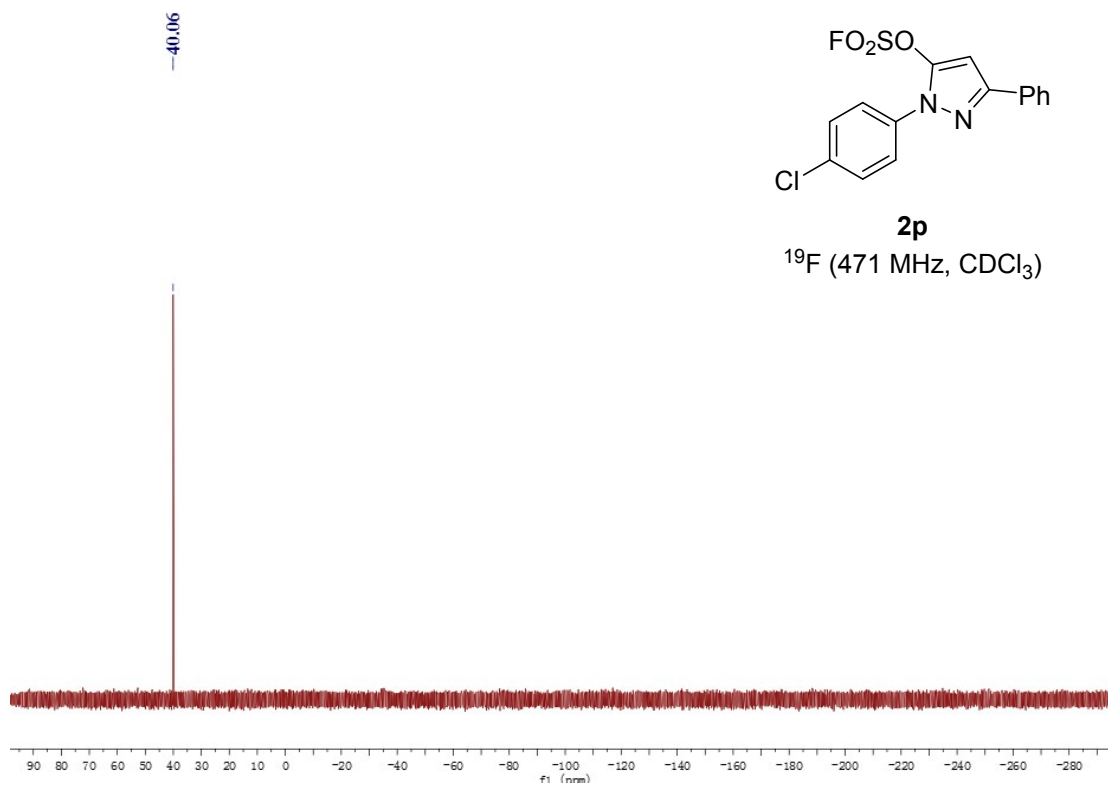
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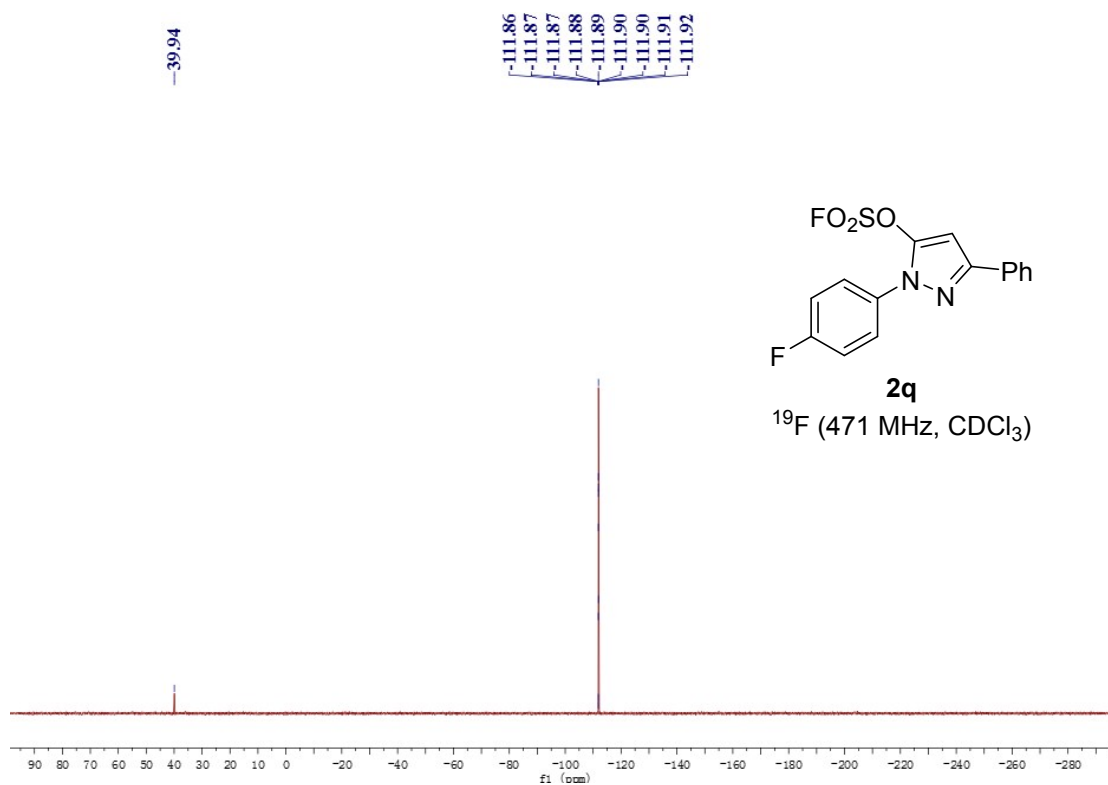
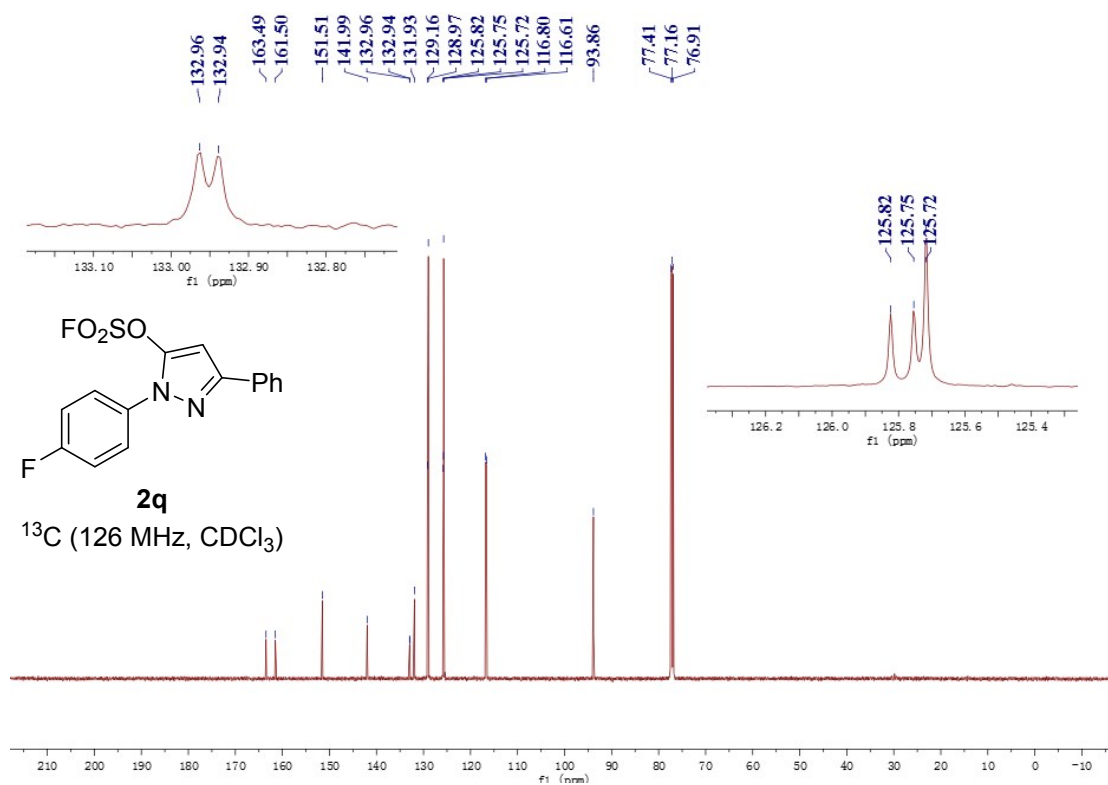


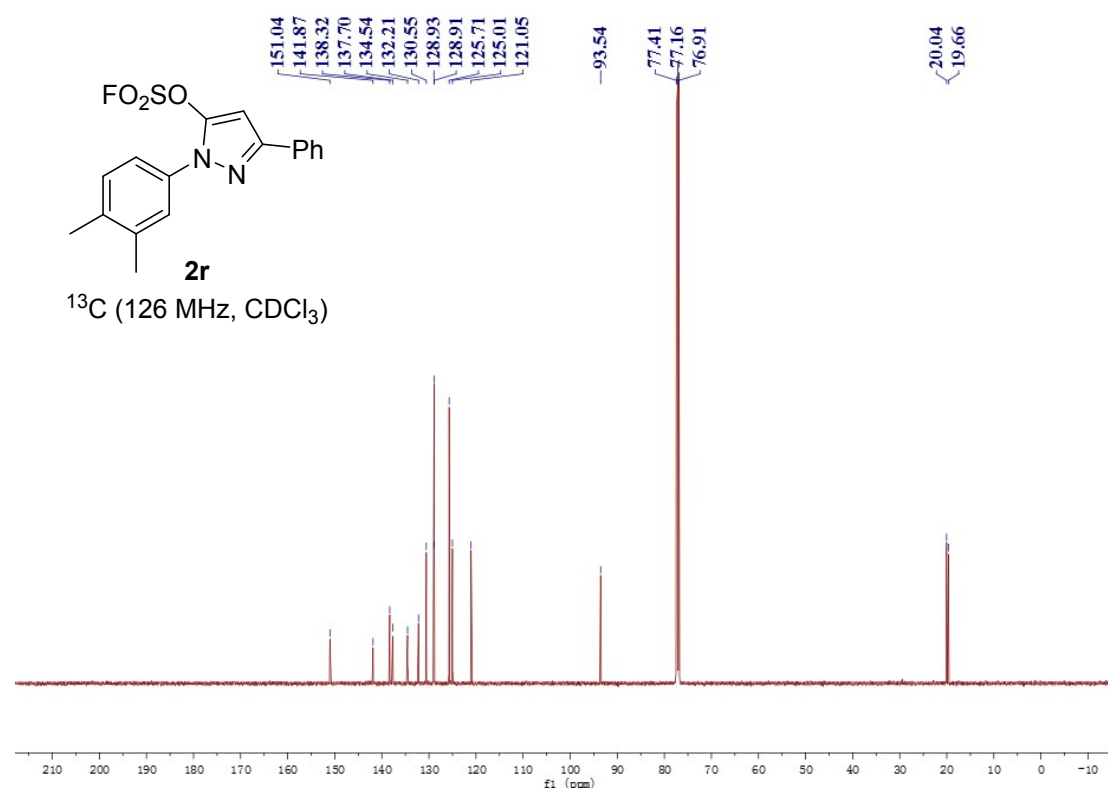
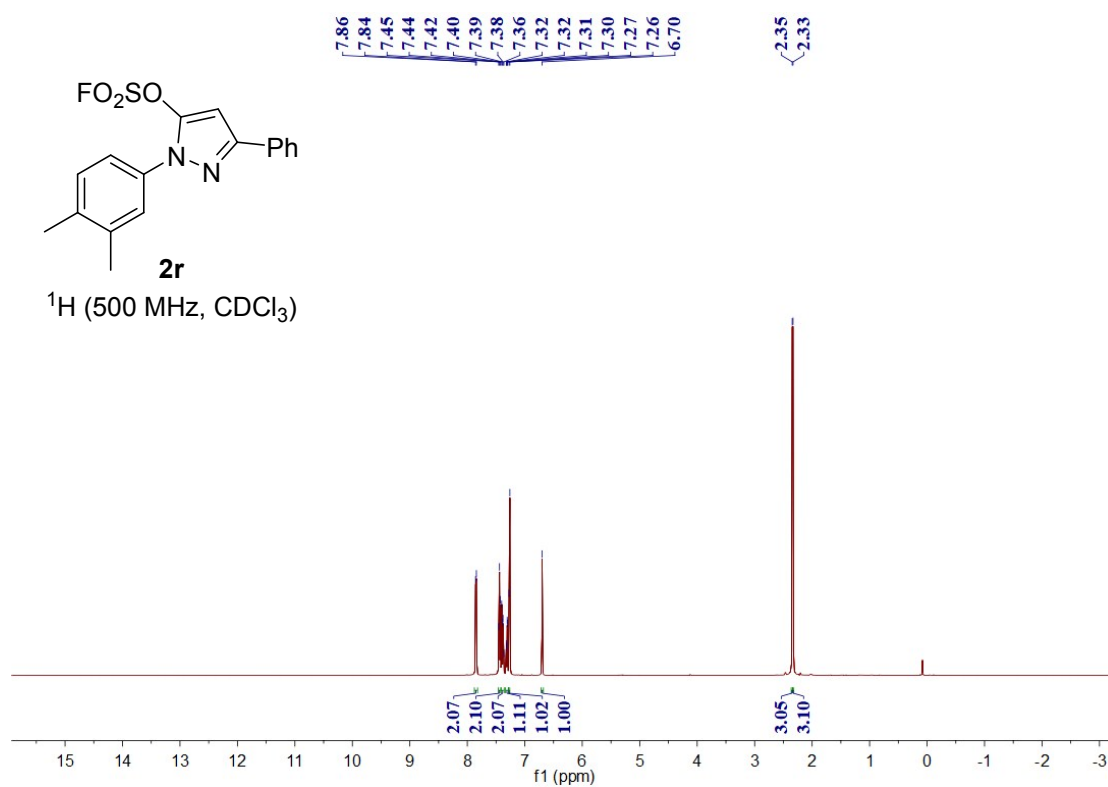


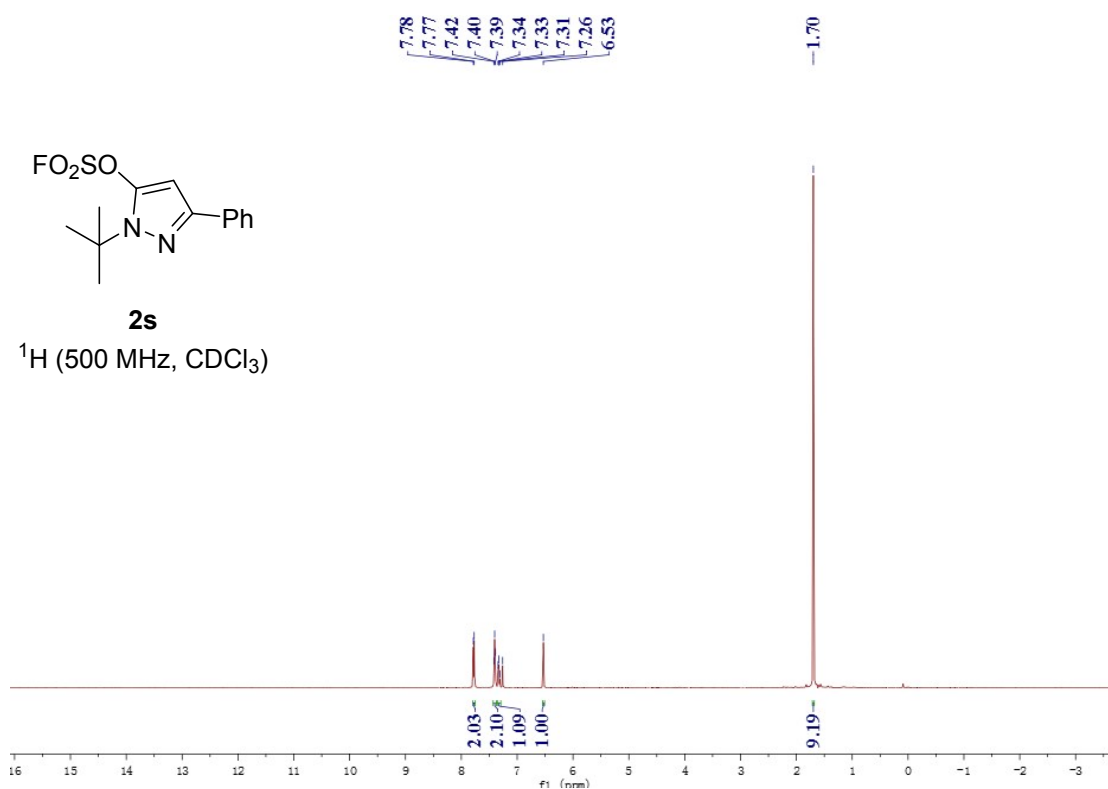
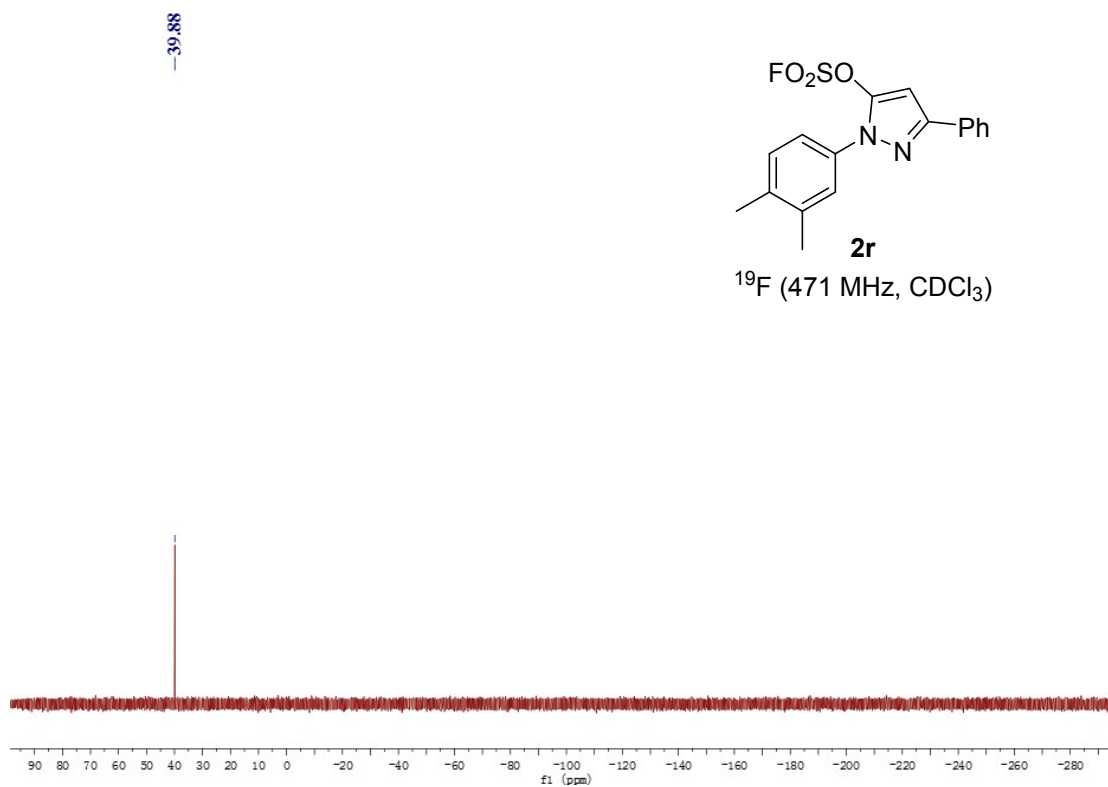


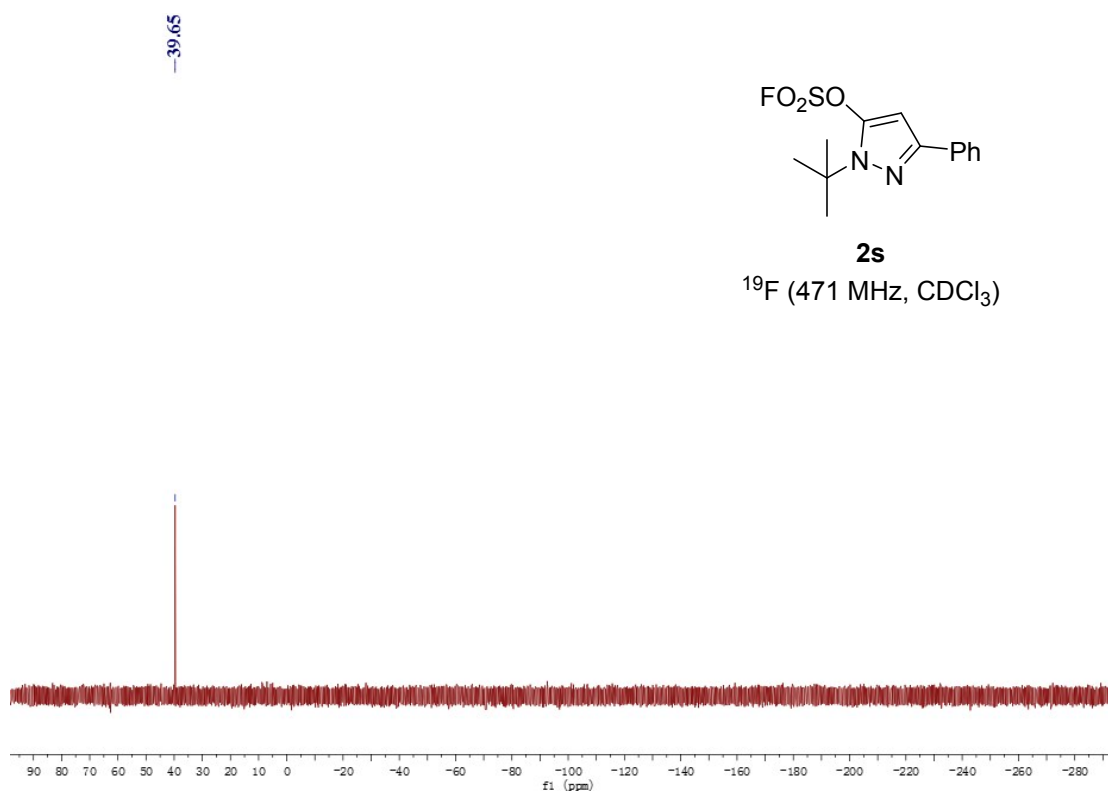
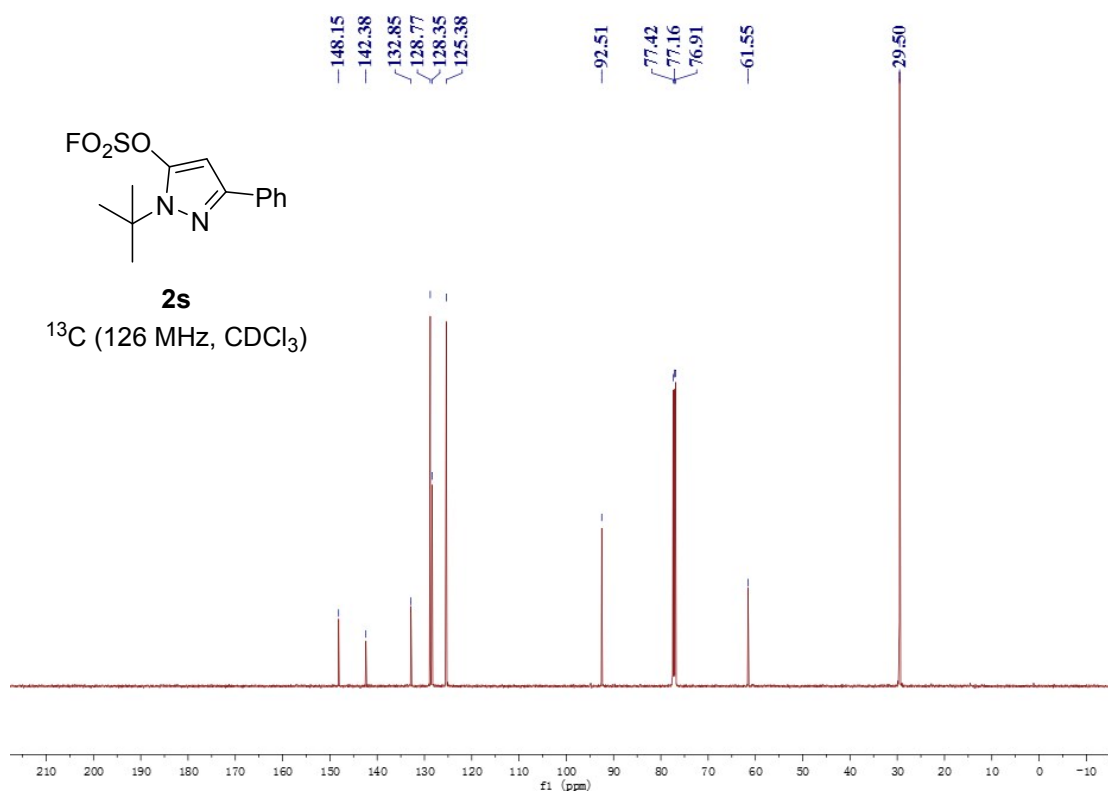


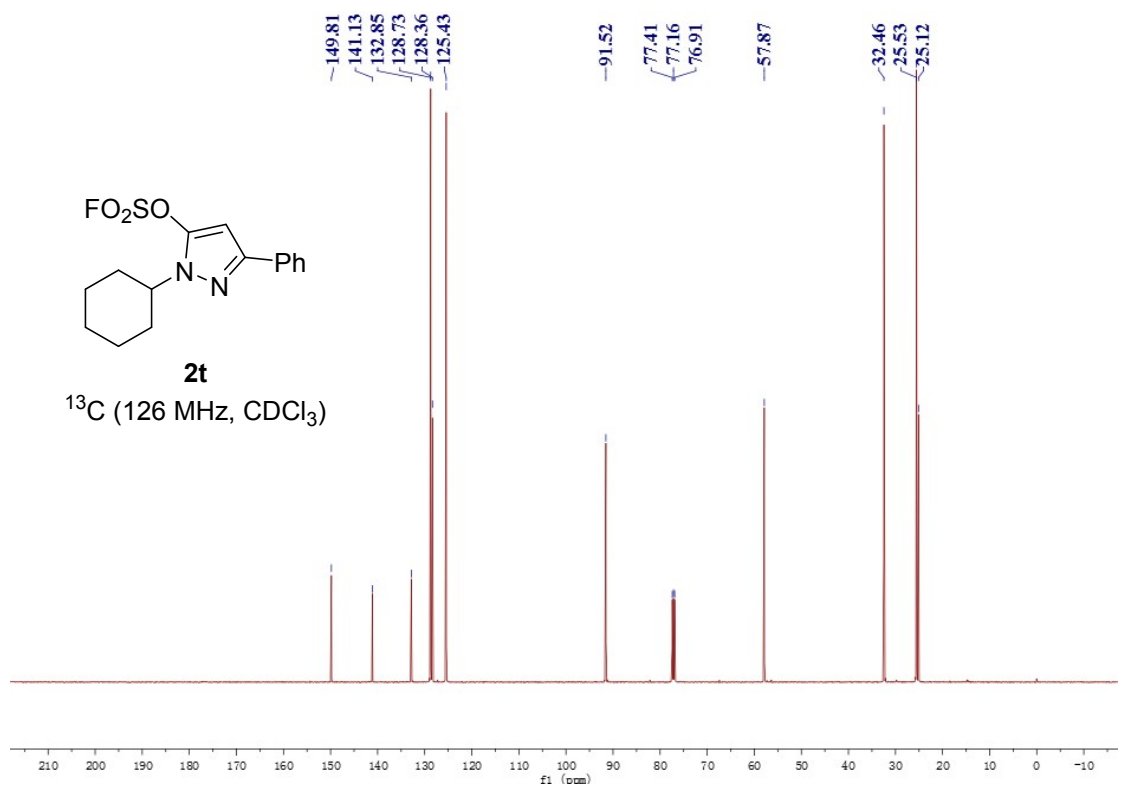
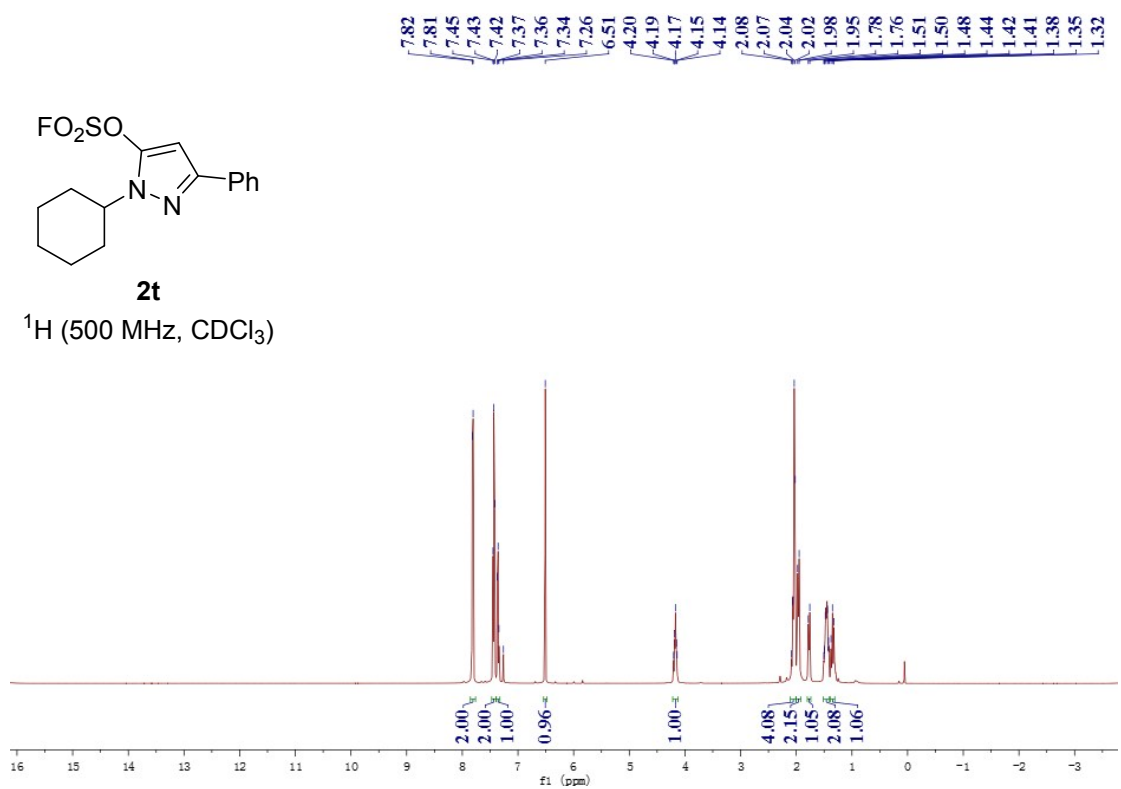


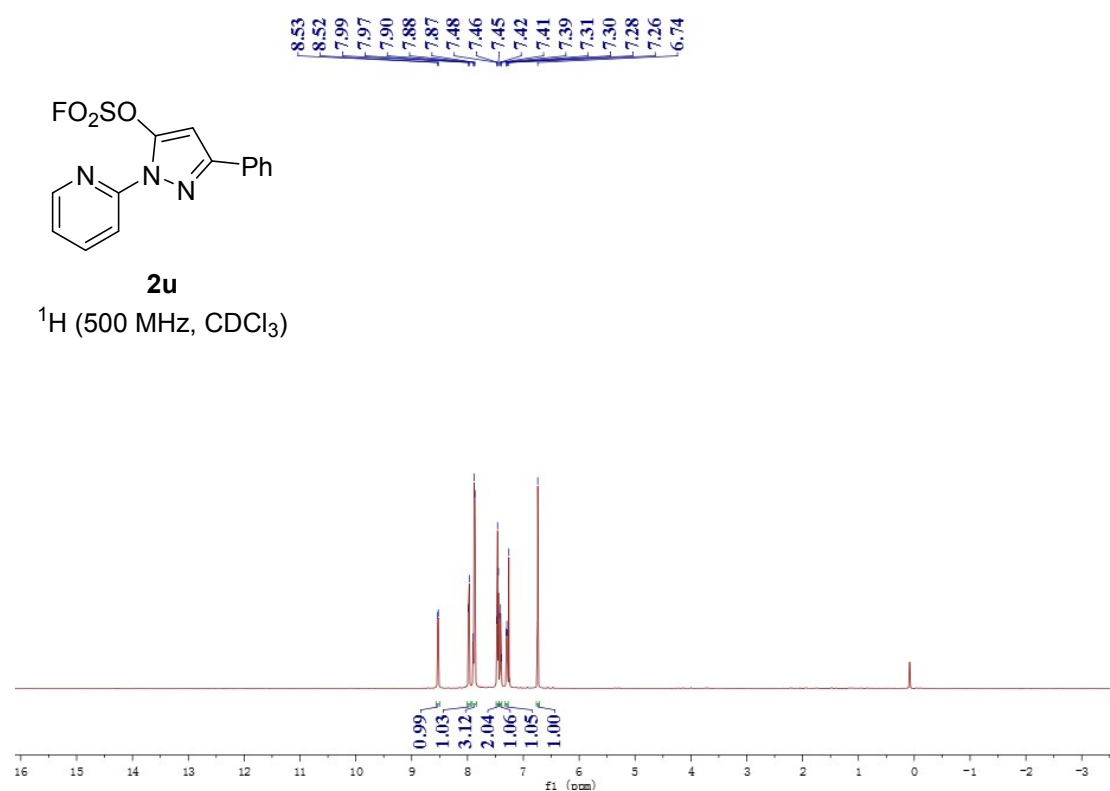
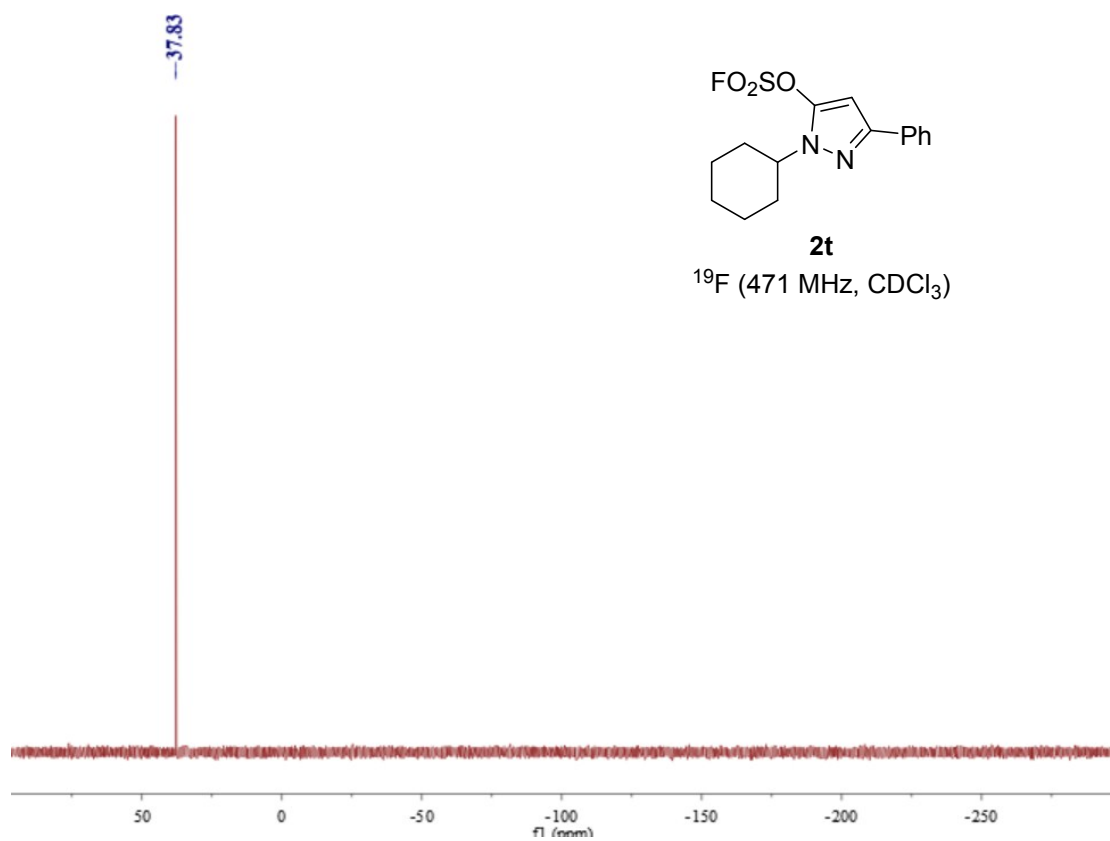


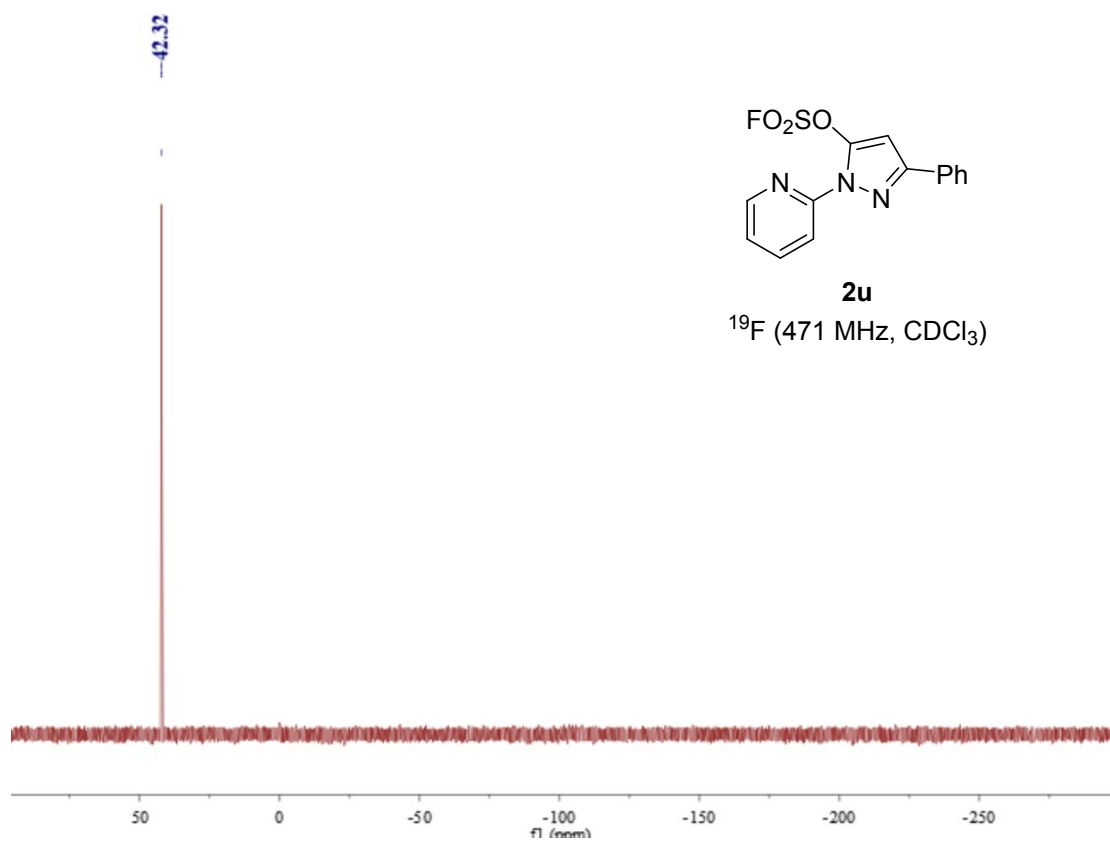
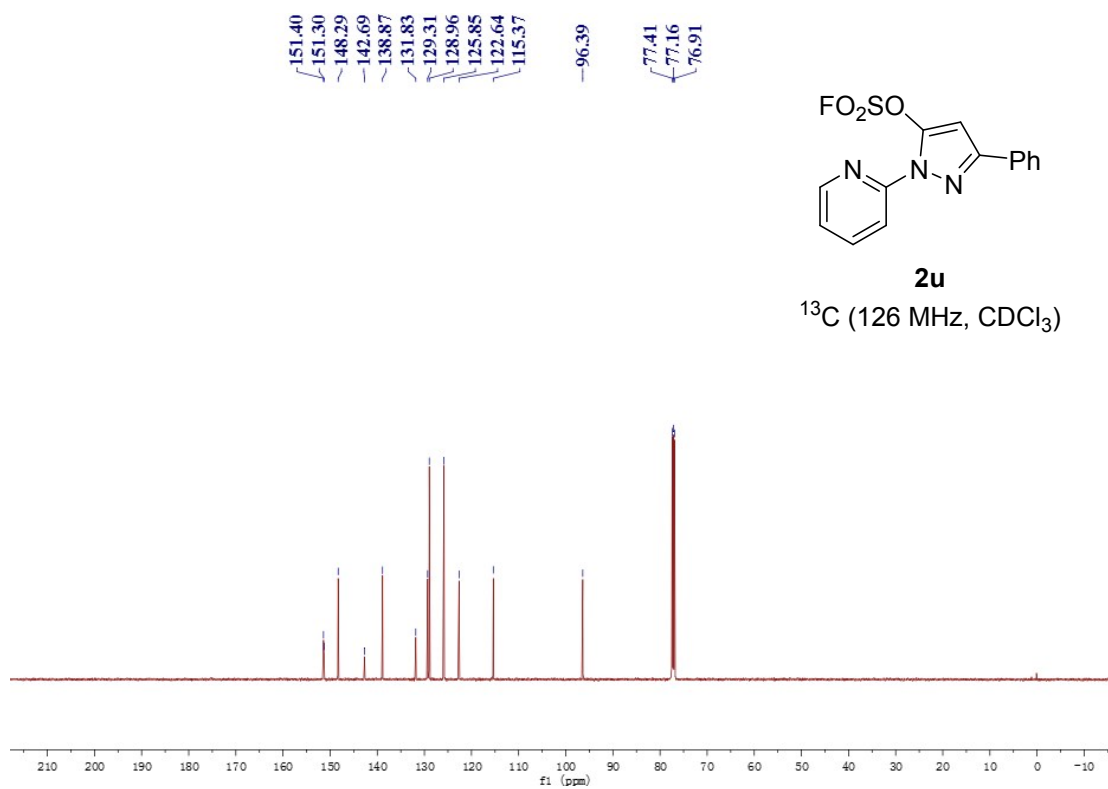


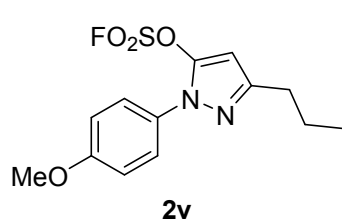




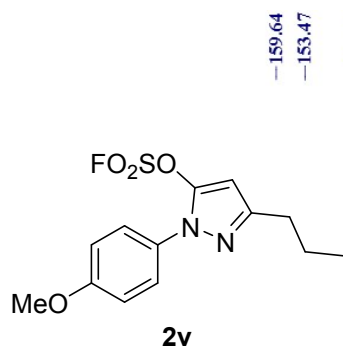
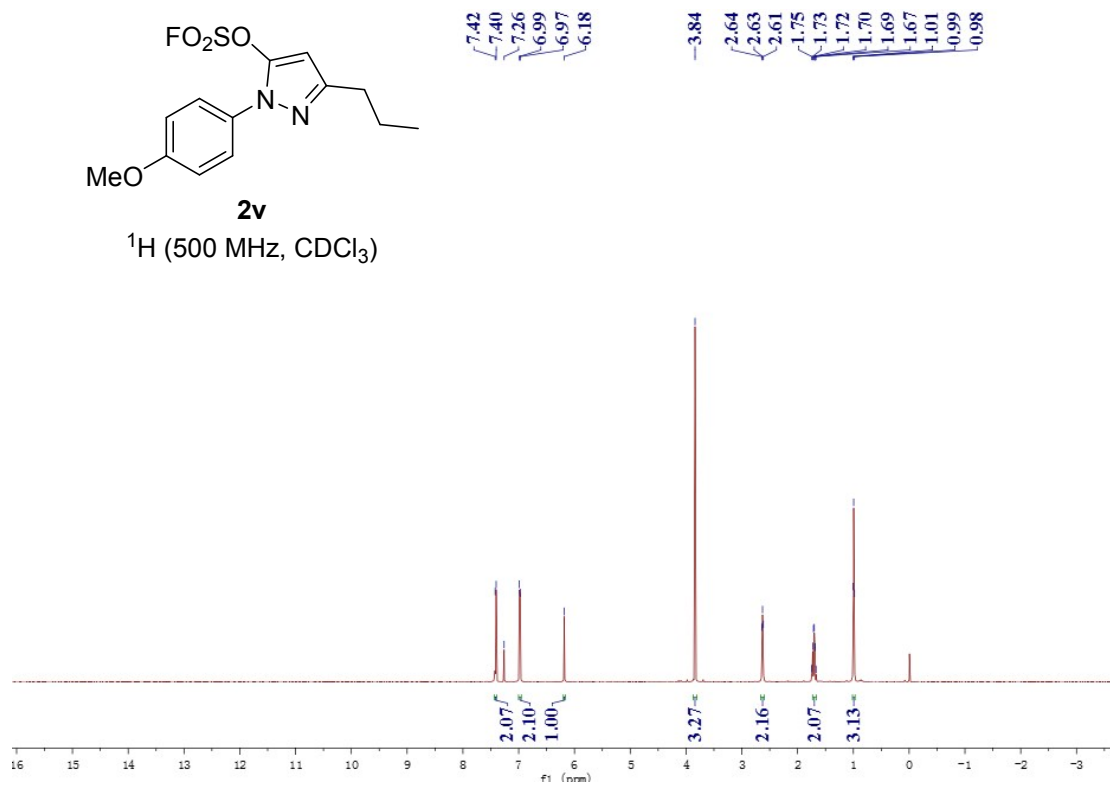








^1H (500 MHz, CDCl_3)



^{13}C (126 MHz, CDCl_3)

