

Supporting Information

SO₂F₂ Mediated Transforming Pyrozolones to Pyrazolyl Fluorosulfates

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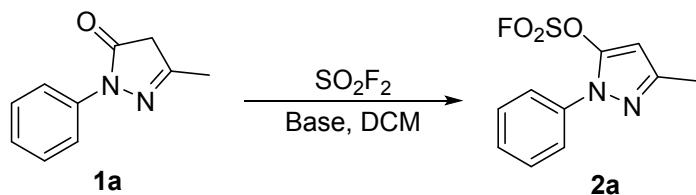
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1. General considerations.

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



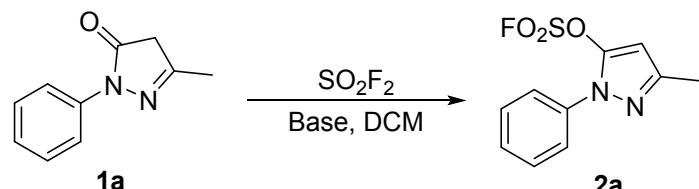
Entry	Base	Conversion (%) ^b	Yield (%) ^c
1	Et ₃ N	58	46
2	DBU	73	n.d.
3	DABCO	78	70
4	TMEDA	66	58
5	DIPEA	96	95 (93) ^d

^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

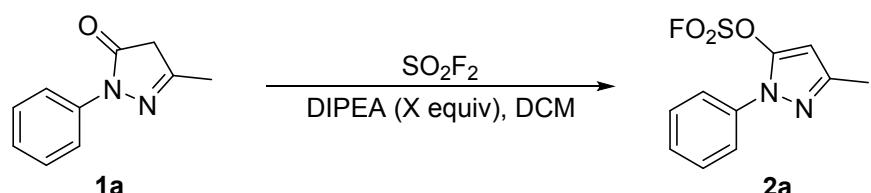


Entry	Base	Conversion (%) ^b	Yield (%) ^c
1	Na ₂ CO ₃	23	n.d.
2	NaHCO ₃	21	21
3	K ₂ CO ₃	38	38
4	KHCO ₃	58	58
5	NaOH	59	35
6	Cs ₂ CO ₃	51	29
7	K ₃ PO ₄	67	67
8	KOAc	n.d.	n.d.
9	CsF	70	69
10	Na ₃ PO ₄	16	n.d.

^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)].

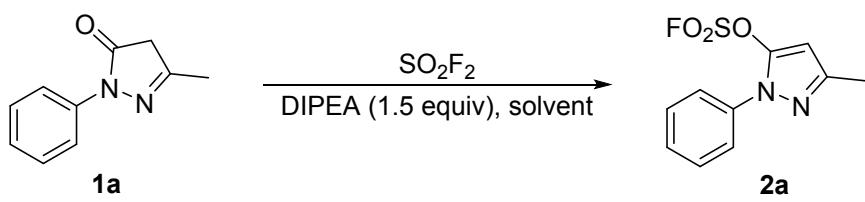
Table 3 Screening the amount of DIPEA ^a



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

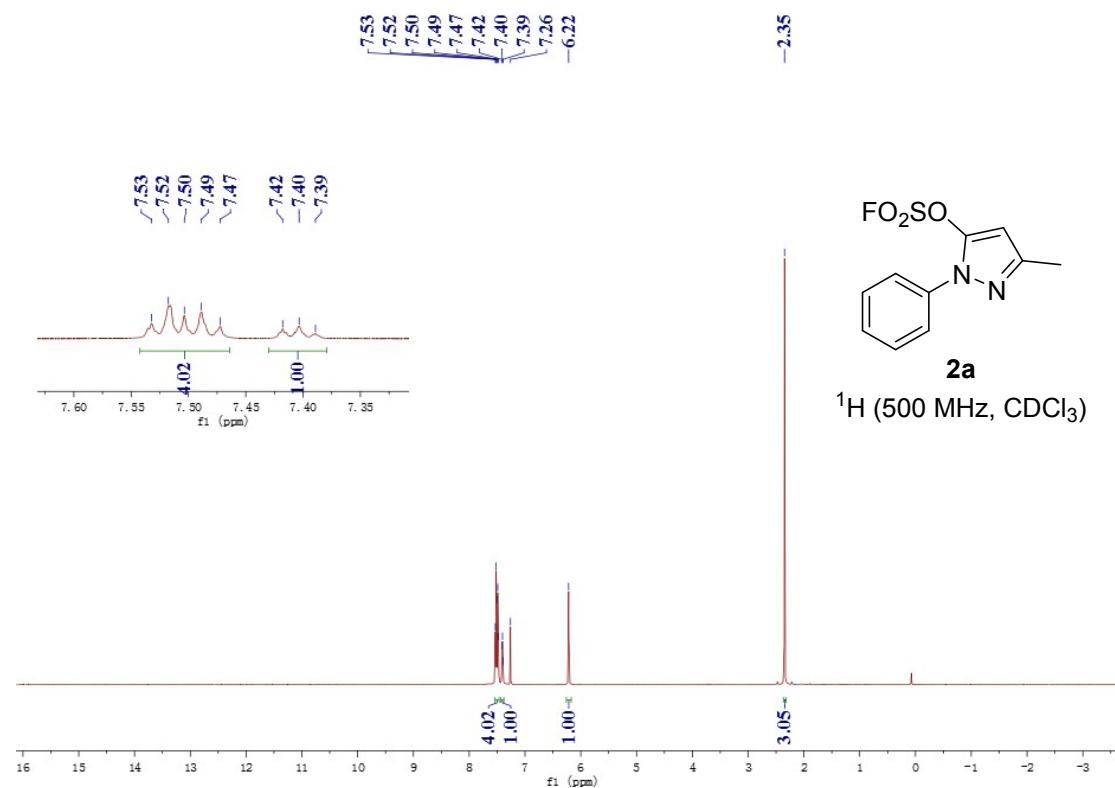


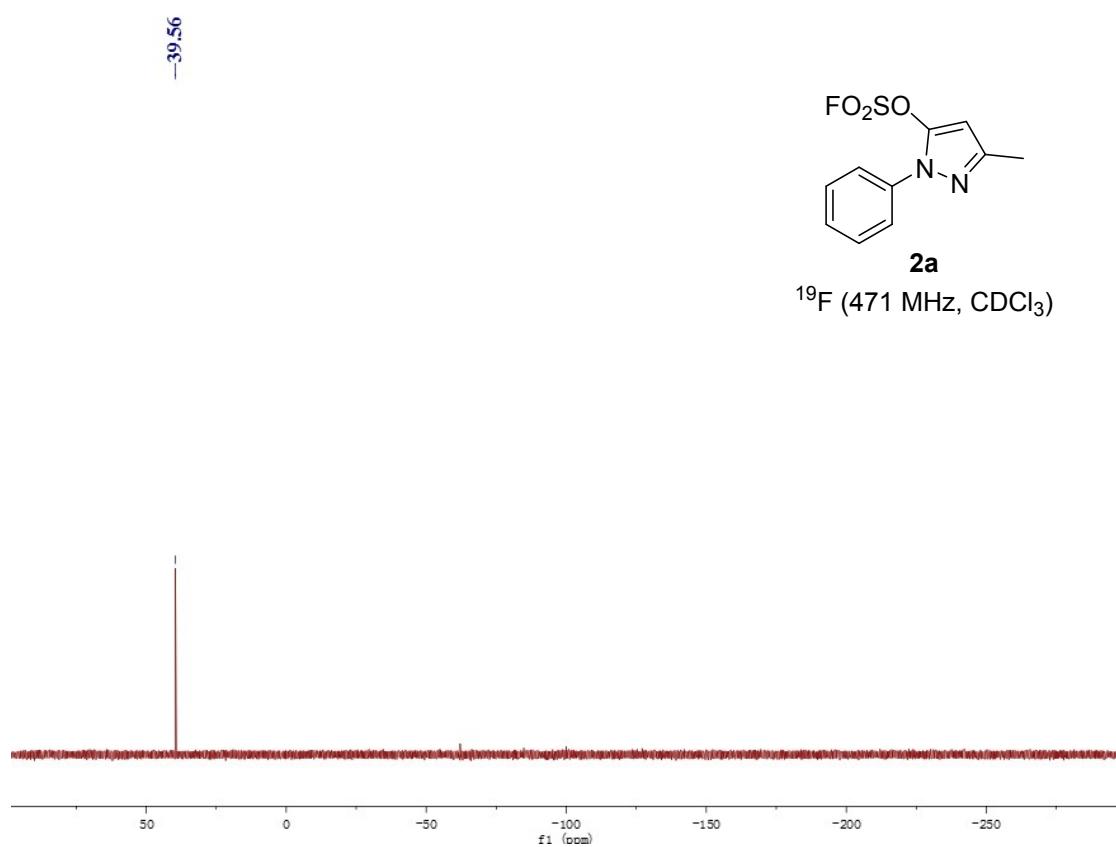
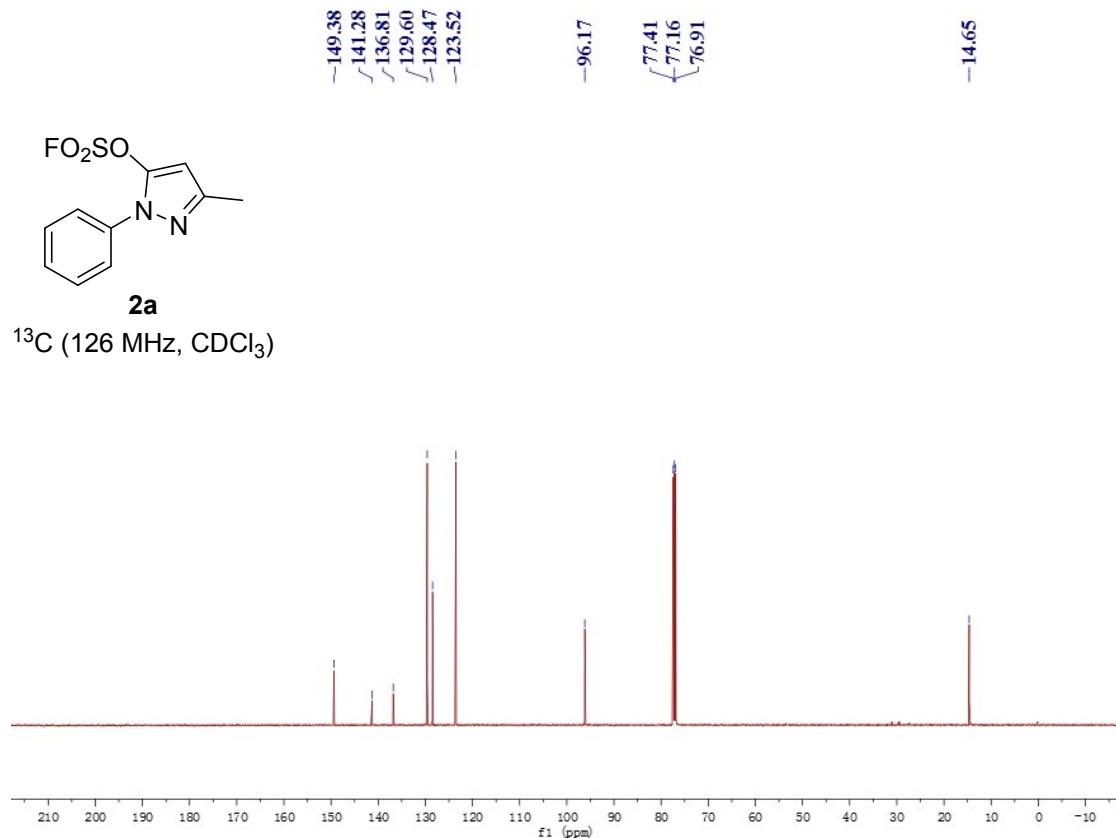
Entry	Solvent	Conversion (%) ^b	Yield (%) ^c
1	DCM	95	93
2	DMSO	96	70
3	MeOH	n.d.	n.d.
4	Toluene	51	45
5	Dioxane	59	34
6	DMF	91	91

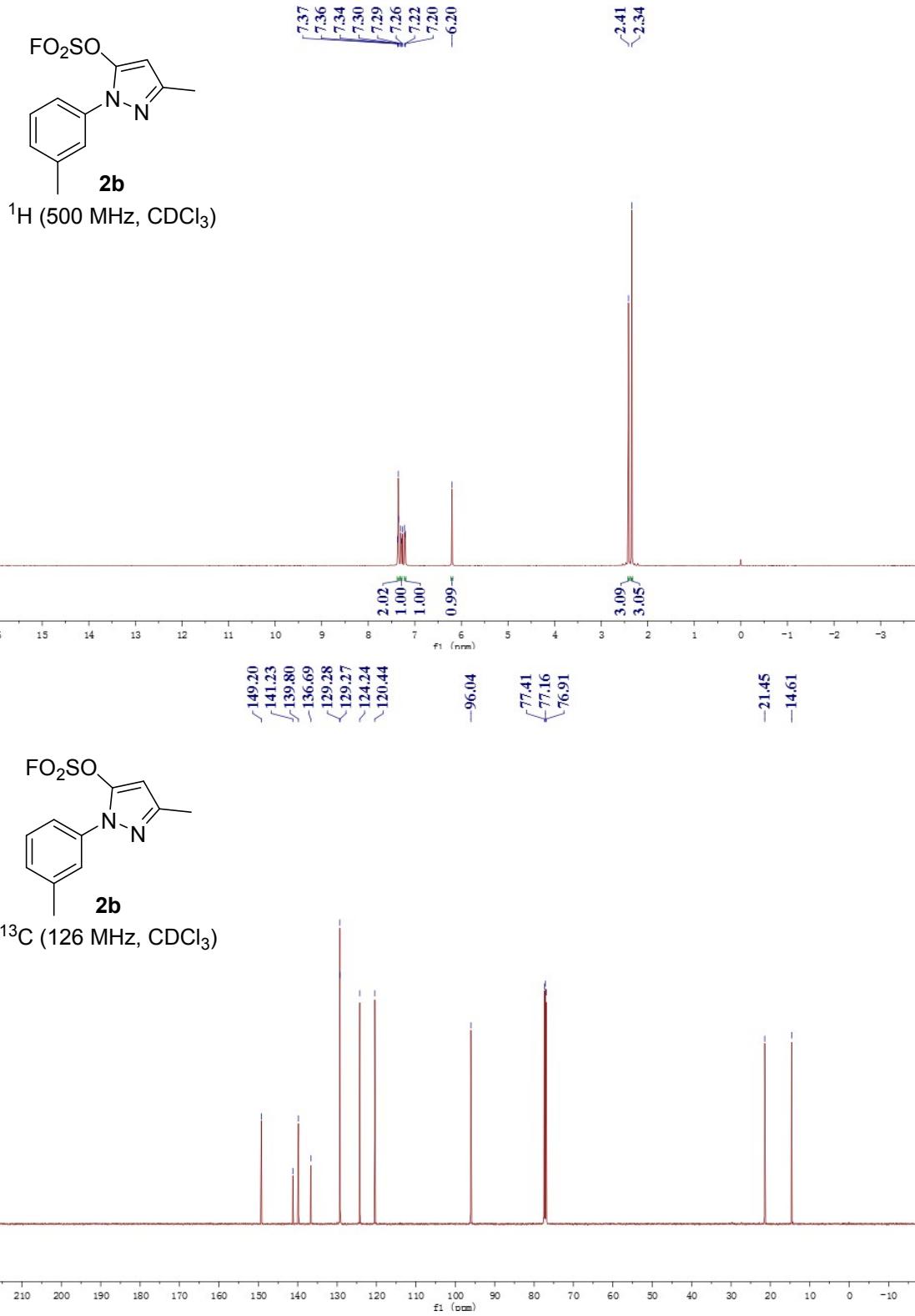
7	THF	n.d.	n.d.
8	CH ₃ CN	95	91
9	Acetone	n.d.	n.d.
10	NMP	95	83
11	H ₂ O	65	46

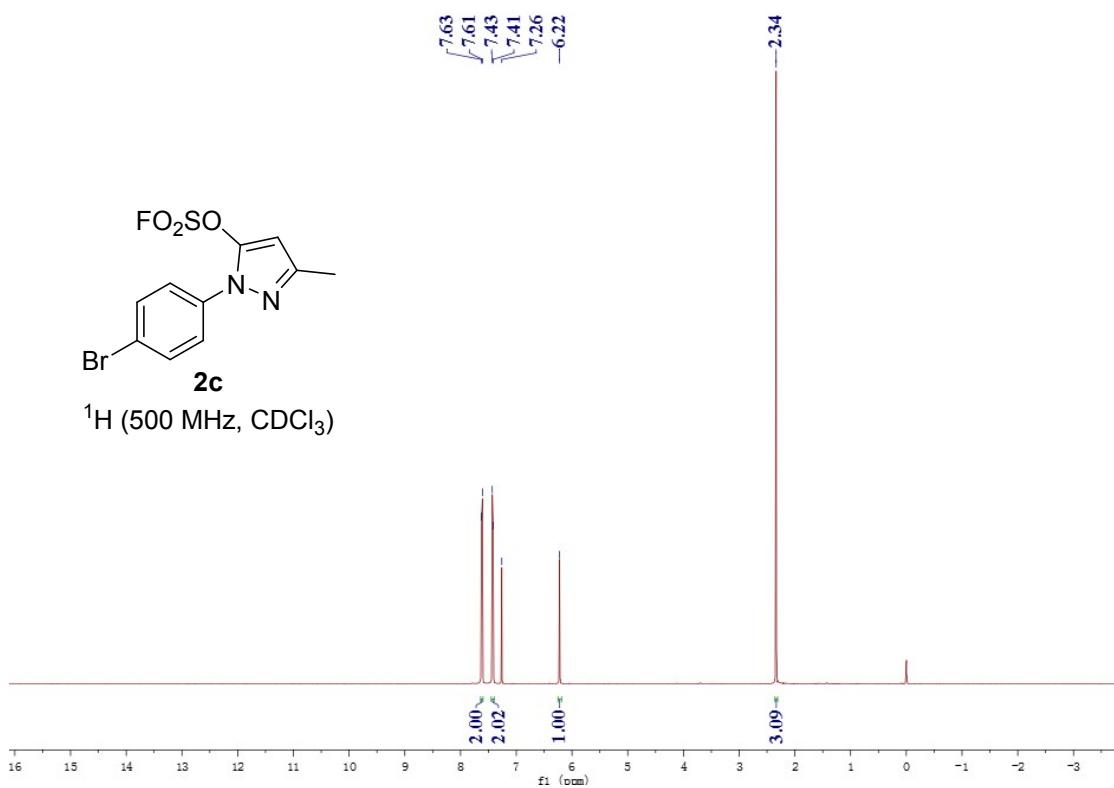
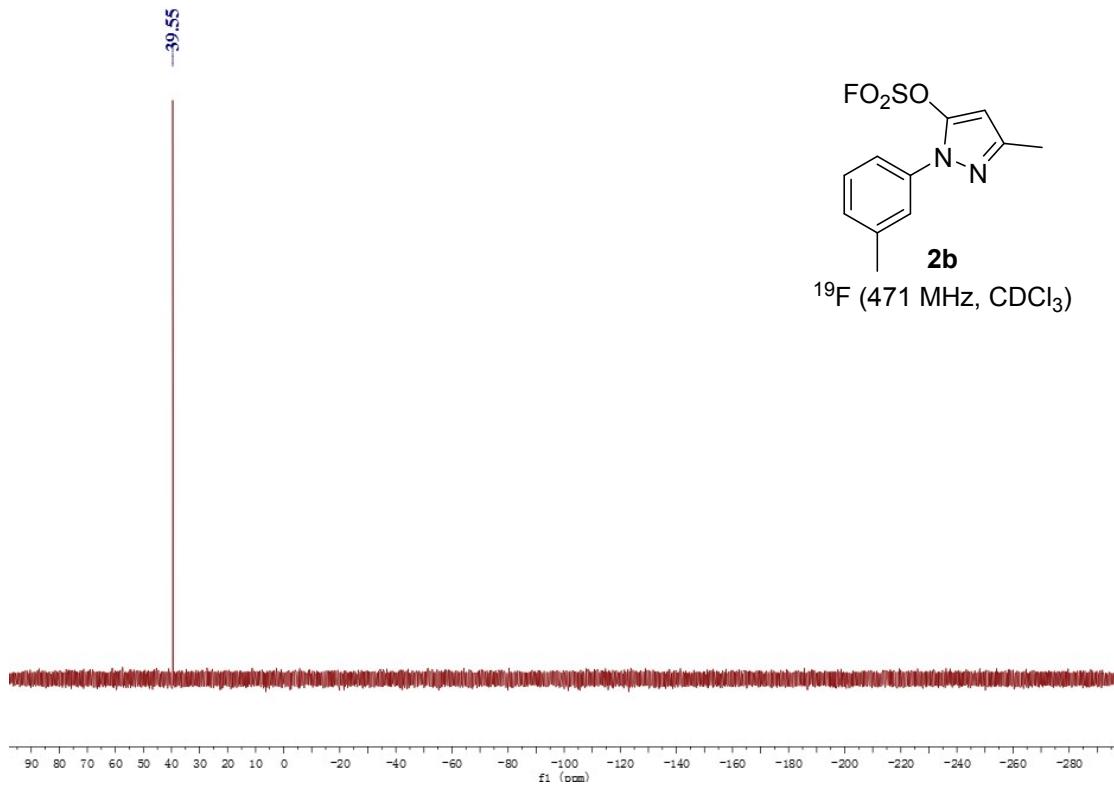
^a Reaction conditions: **1a** (0.1 mmol), DIPEA (0.15 mmol, 1.5 equiv.) and solvent (1.5 mL) were mixed in a tube with a SO₂F₂ balloon and reacted at room temperature for 10 h. ^b The conversion was determined by HPLC using **1a** as the external standard. [t_{1a} = 2.670 min, λ_{max} = 240.5 nm, methanol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

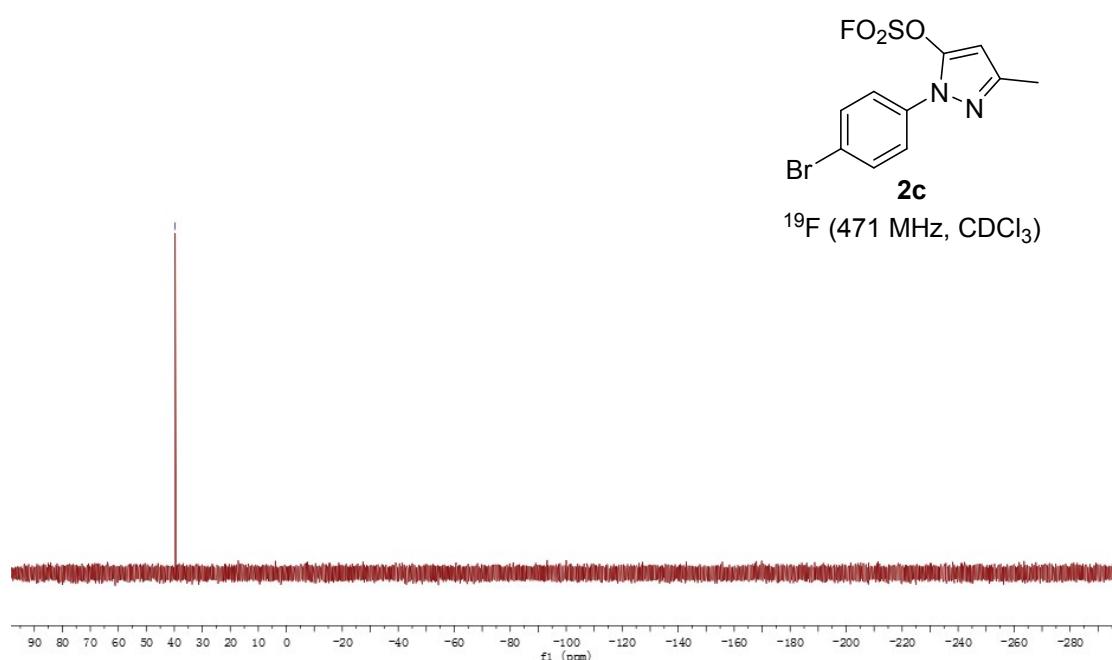
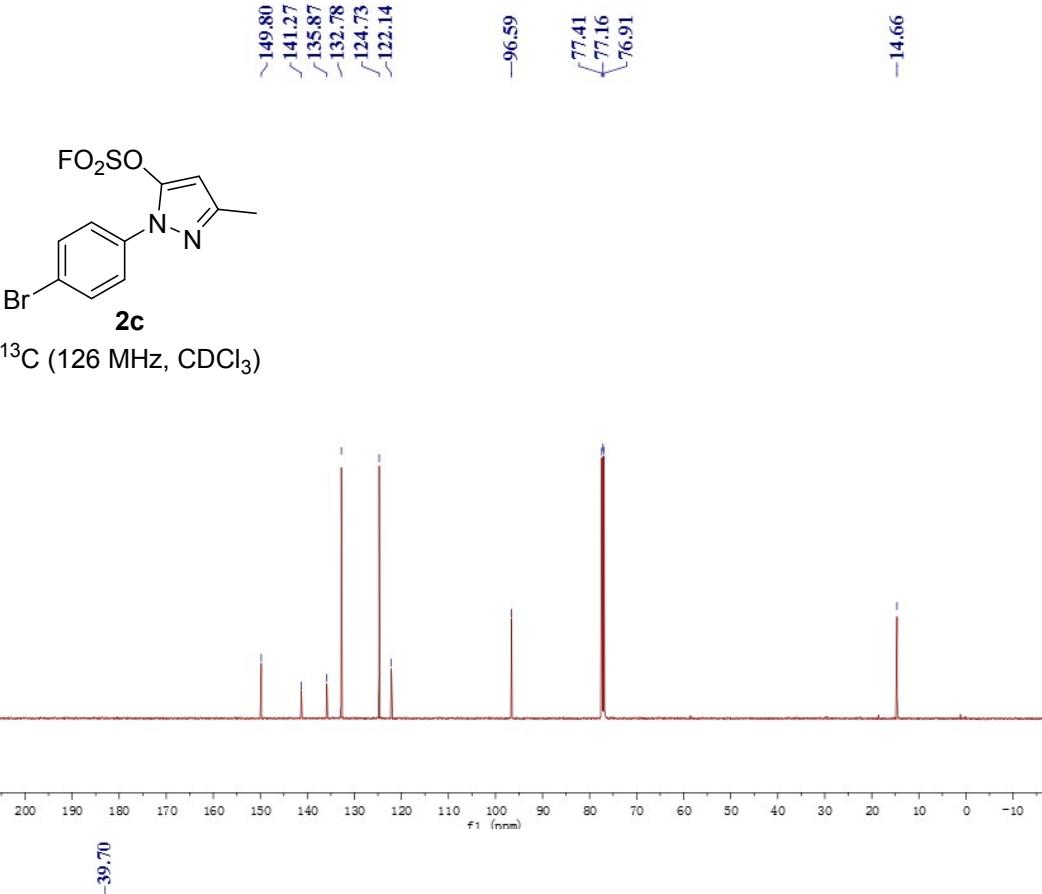
3. NMR spectra of **2**, **3**, **4**, **5**, **6** and **8**.

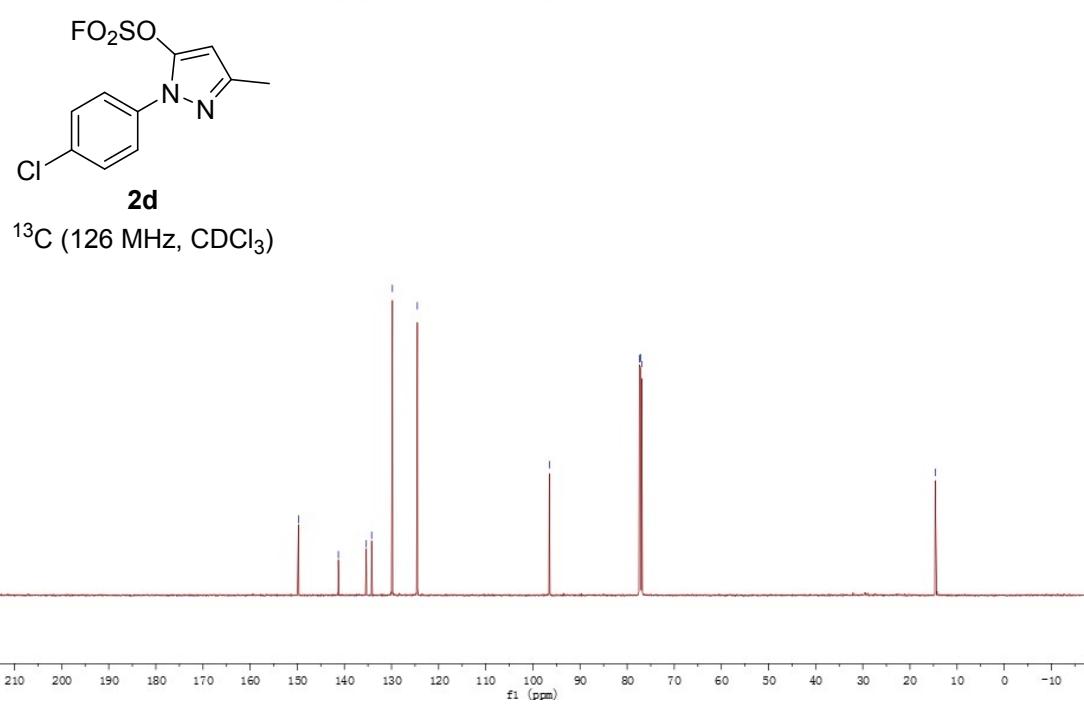
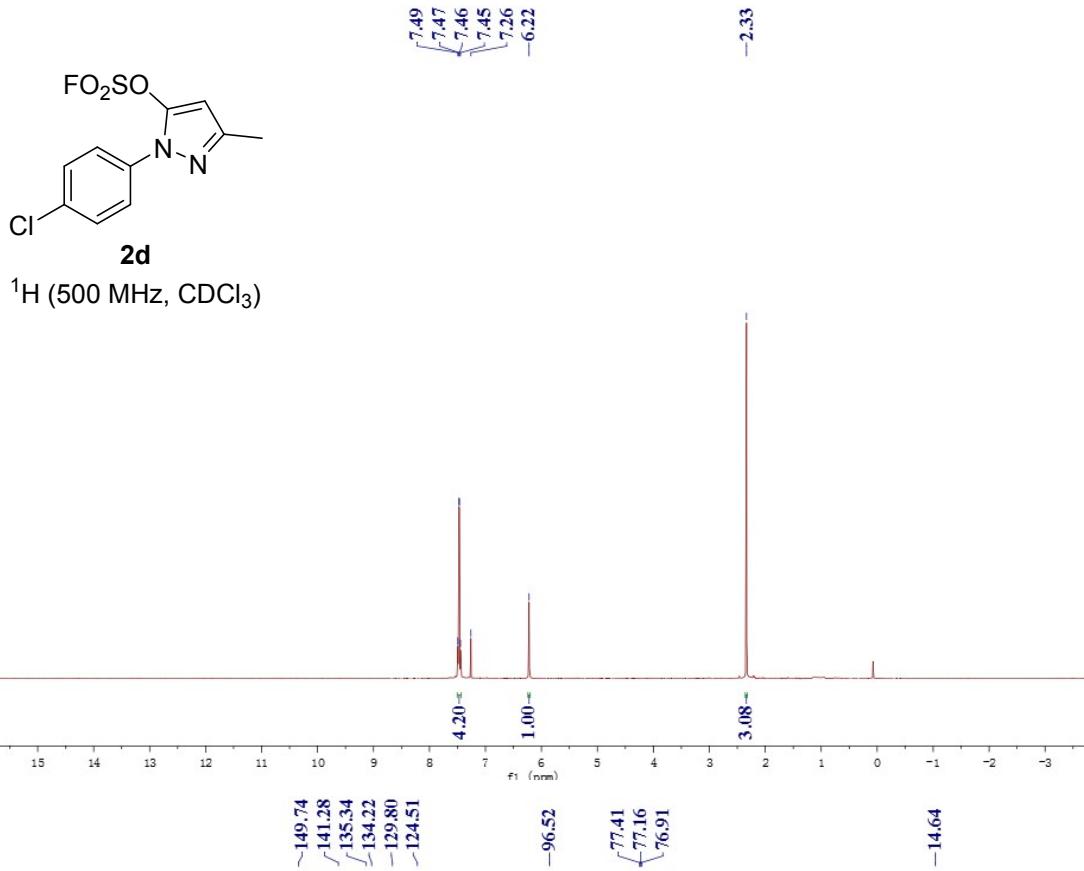




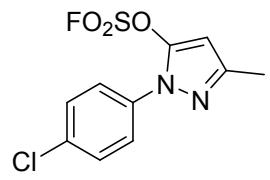




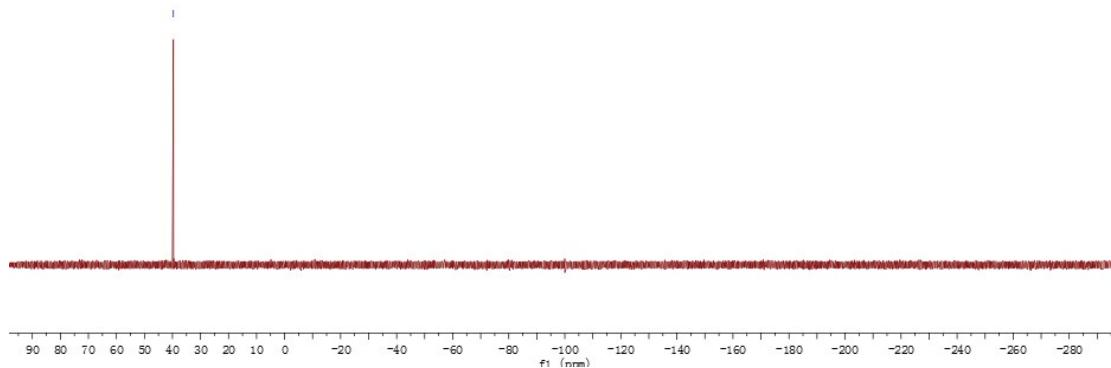




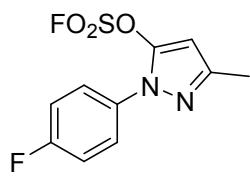
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¹⁹F (471 MHz, CDCl₃)

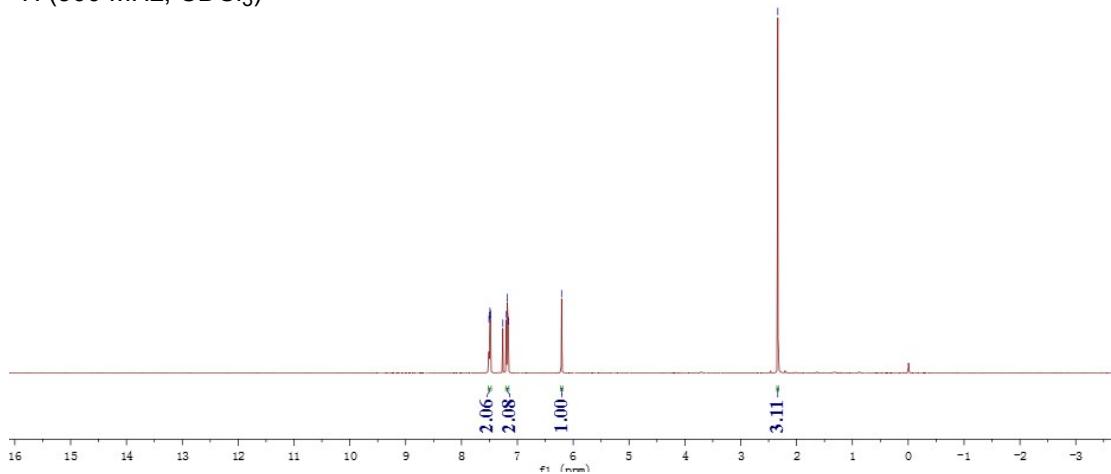


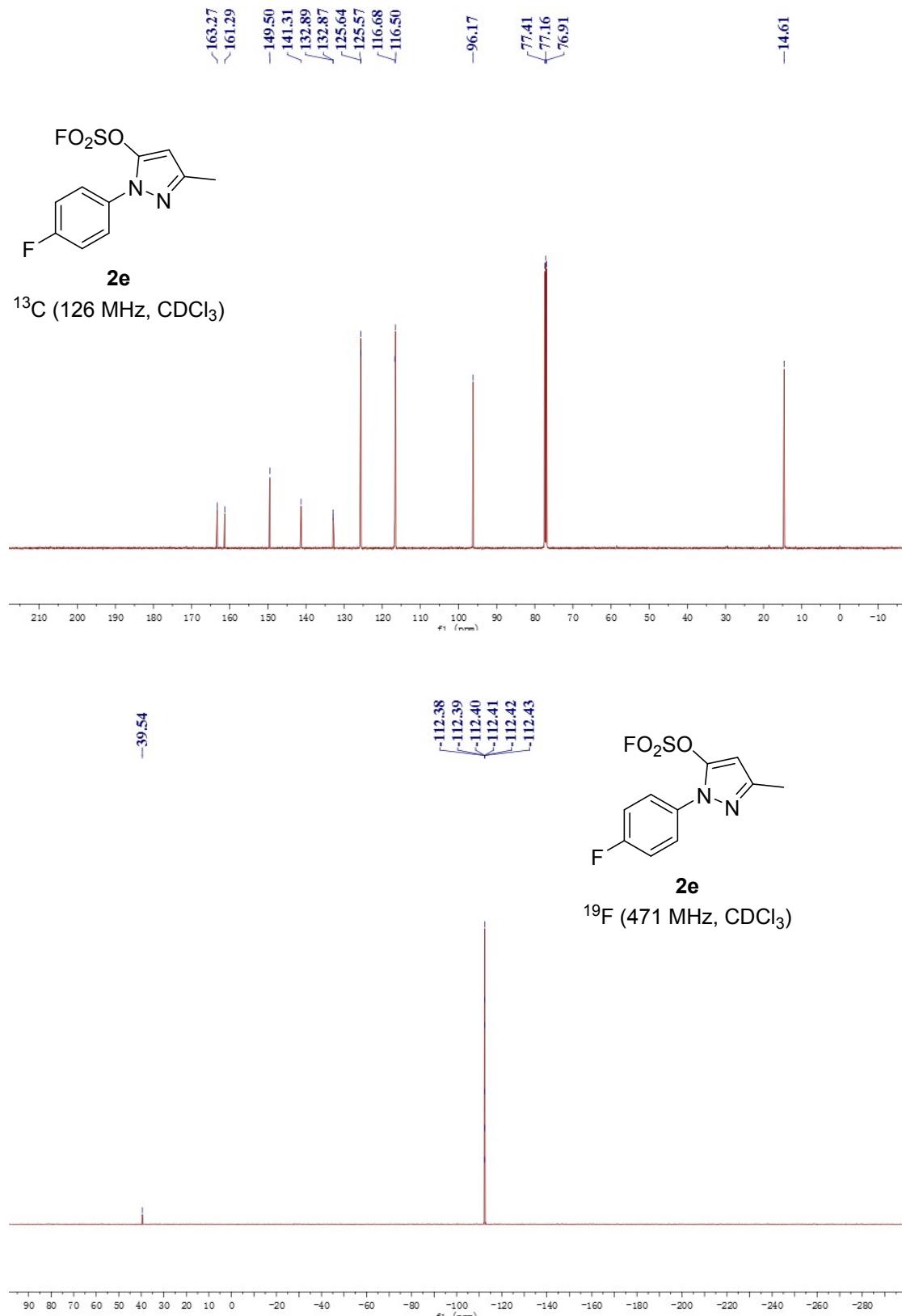
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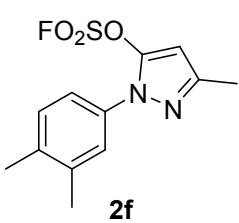


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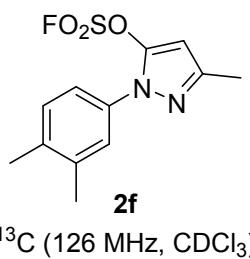
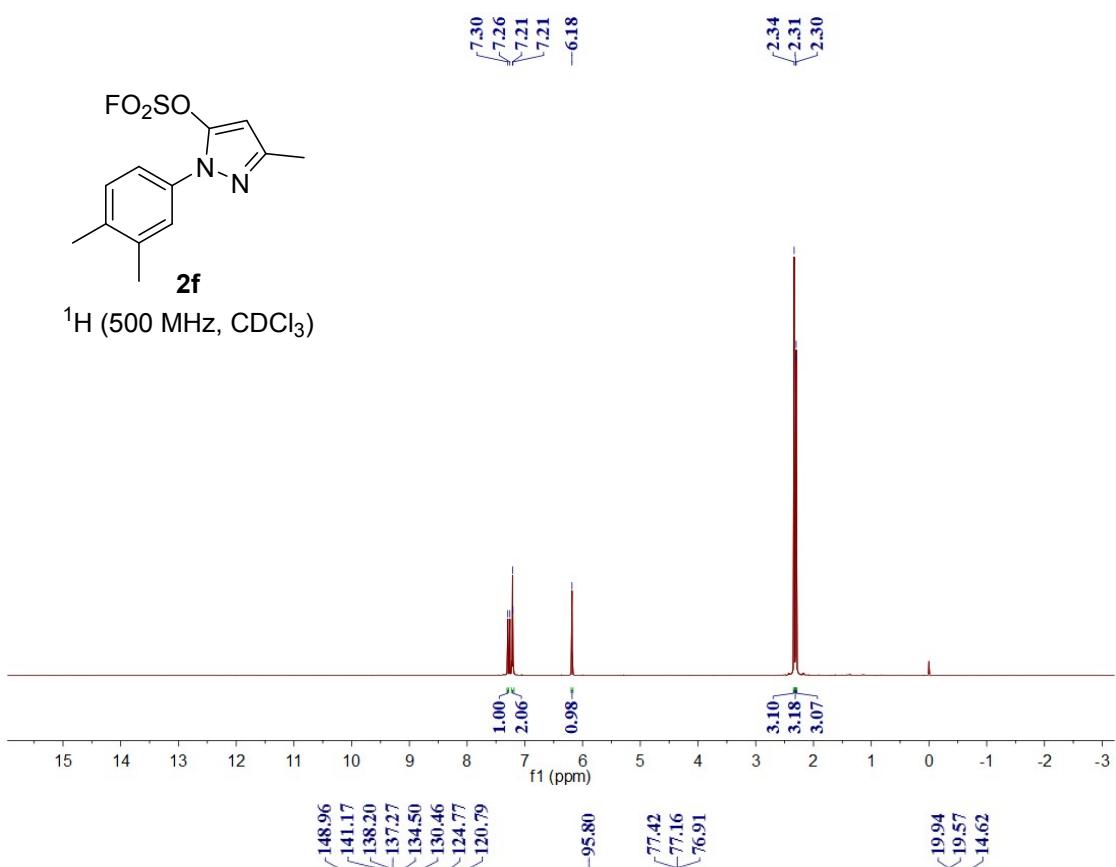
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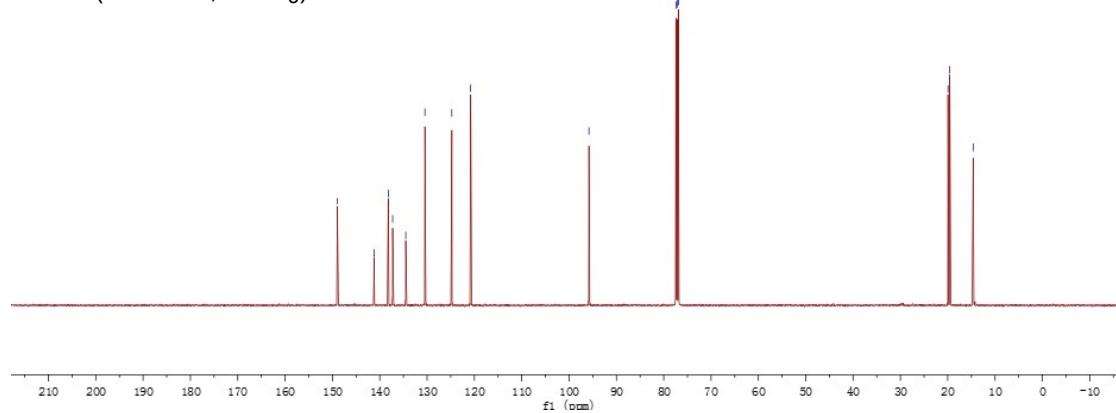




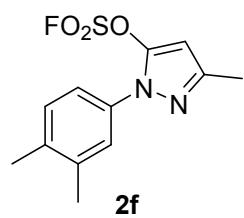
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¹³C (126 MHz, CDCl₃)

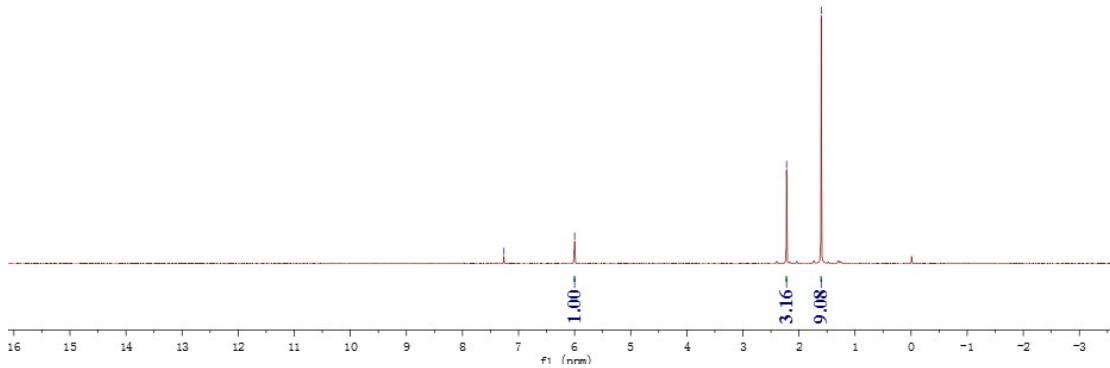
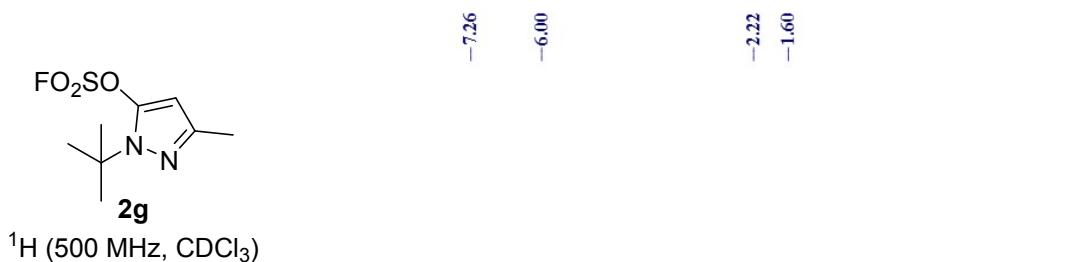
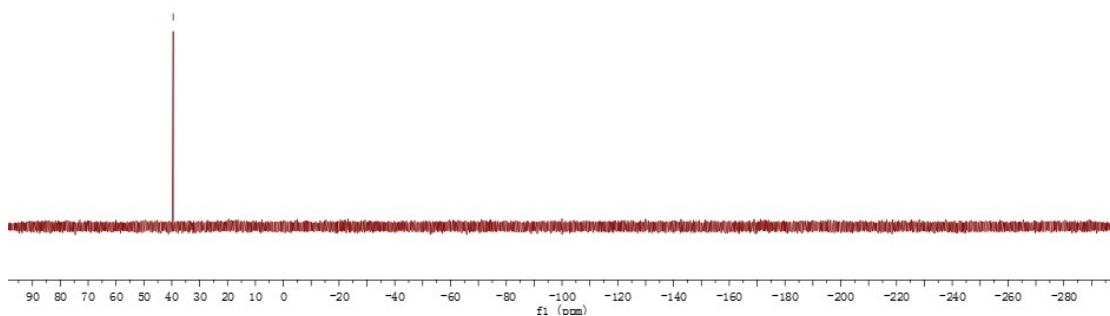


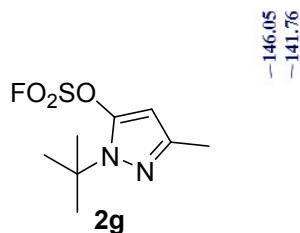
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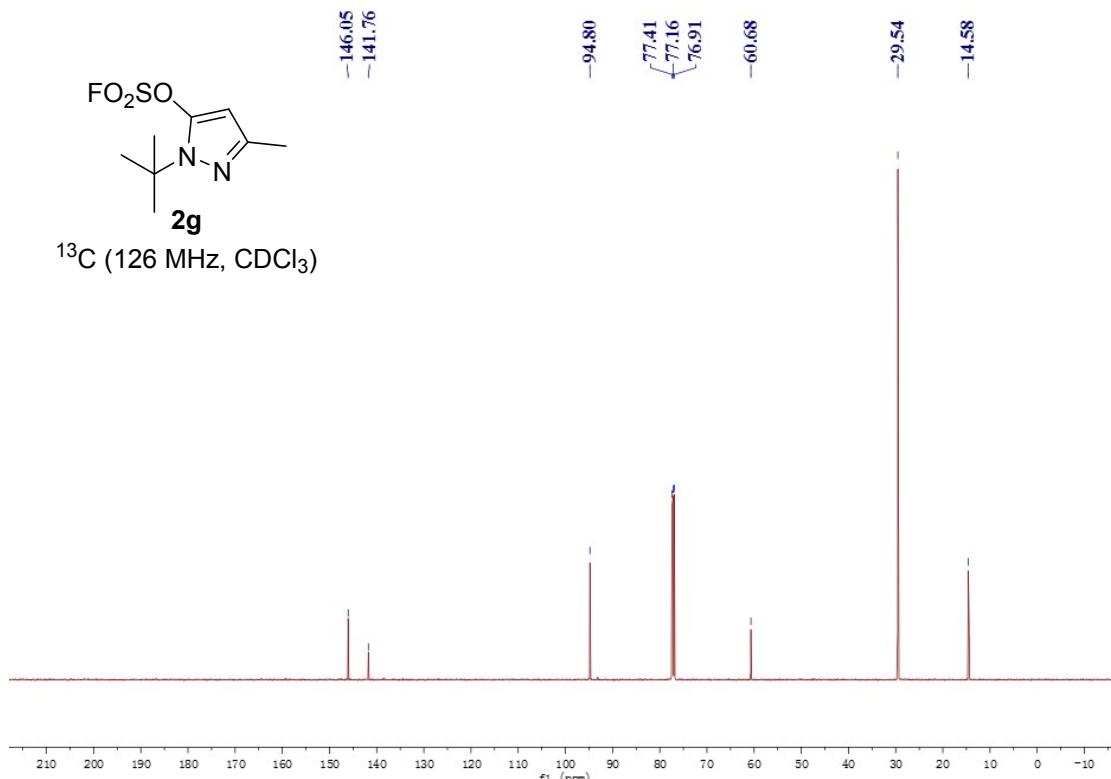
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¹⁹F (471 MHz, CDCl₃)

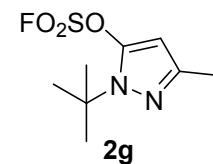




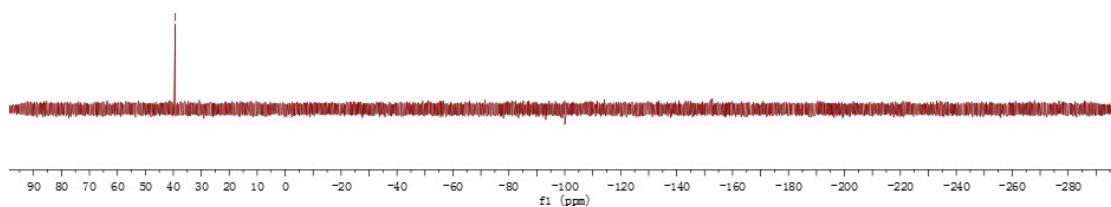
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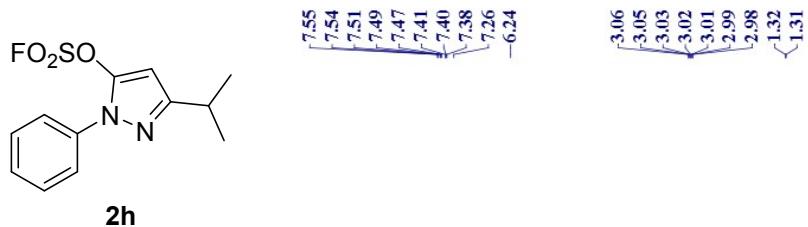


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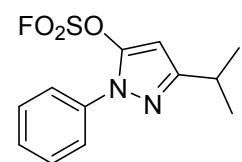
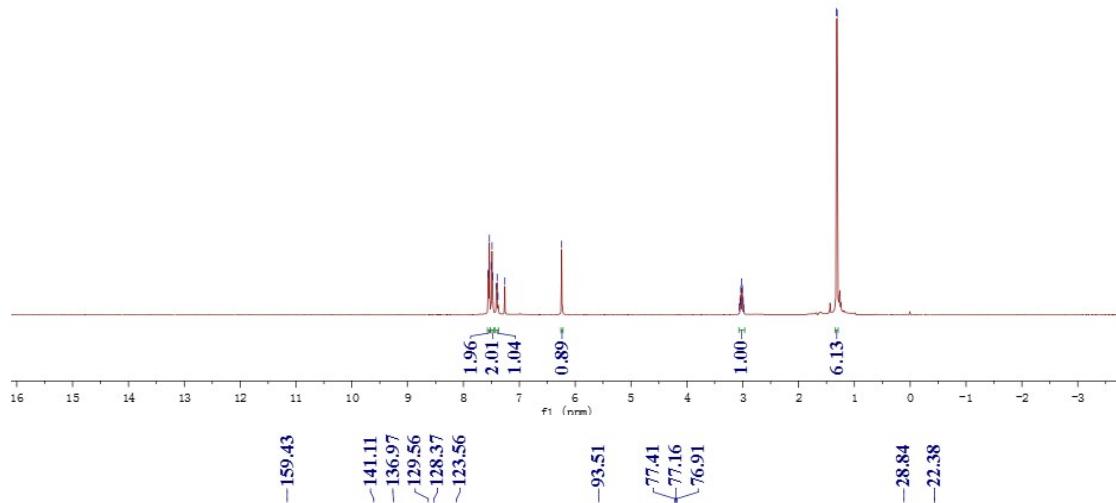


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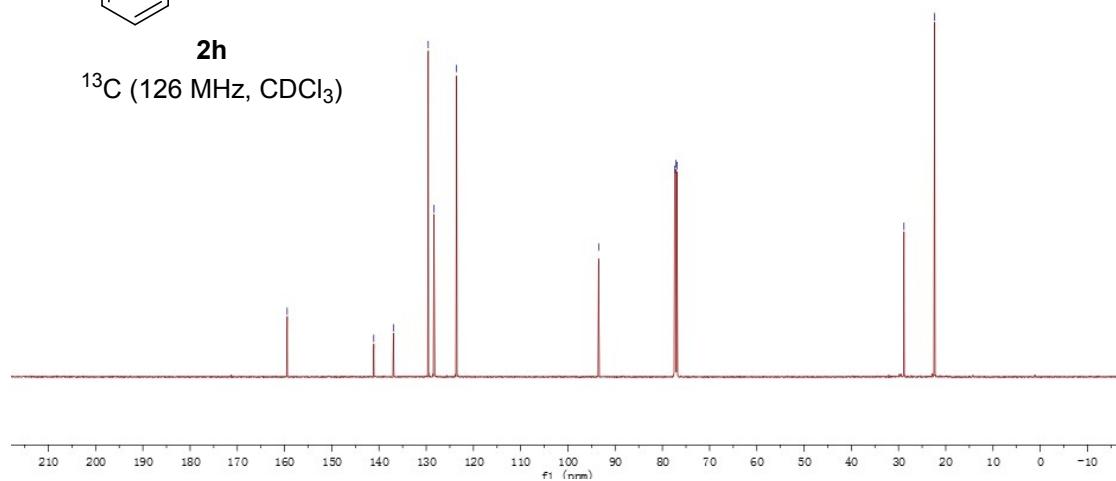




¹H (500 MHz, CDCl₃)



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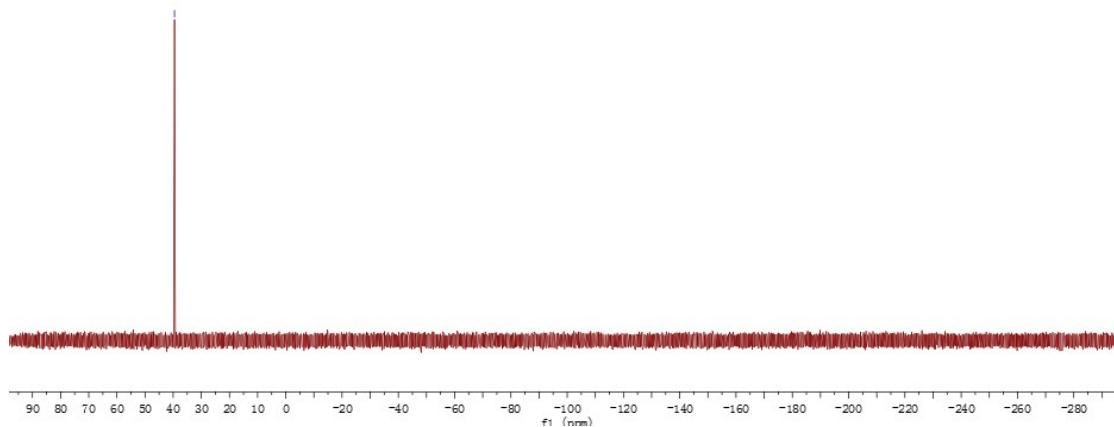


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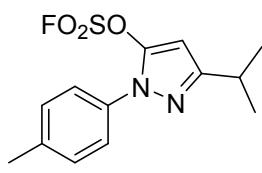


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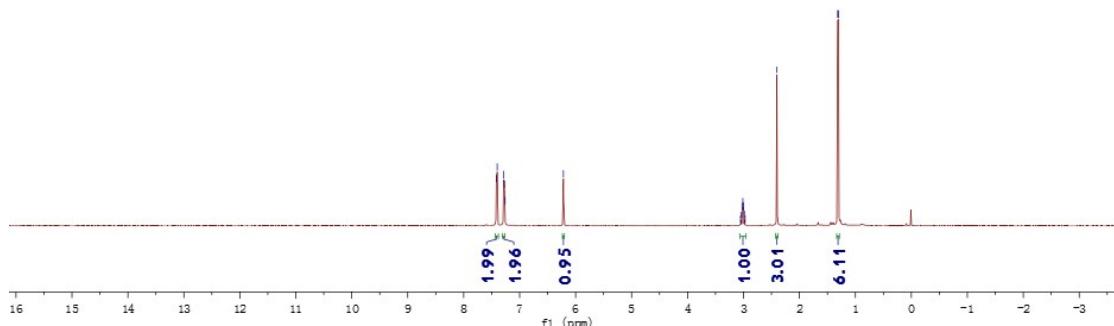


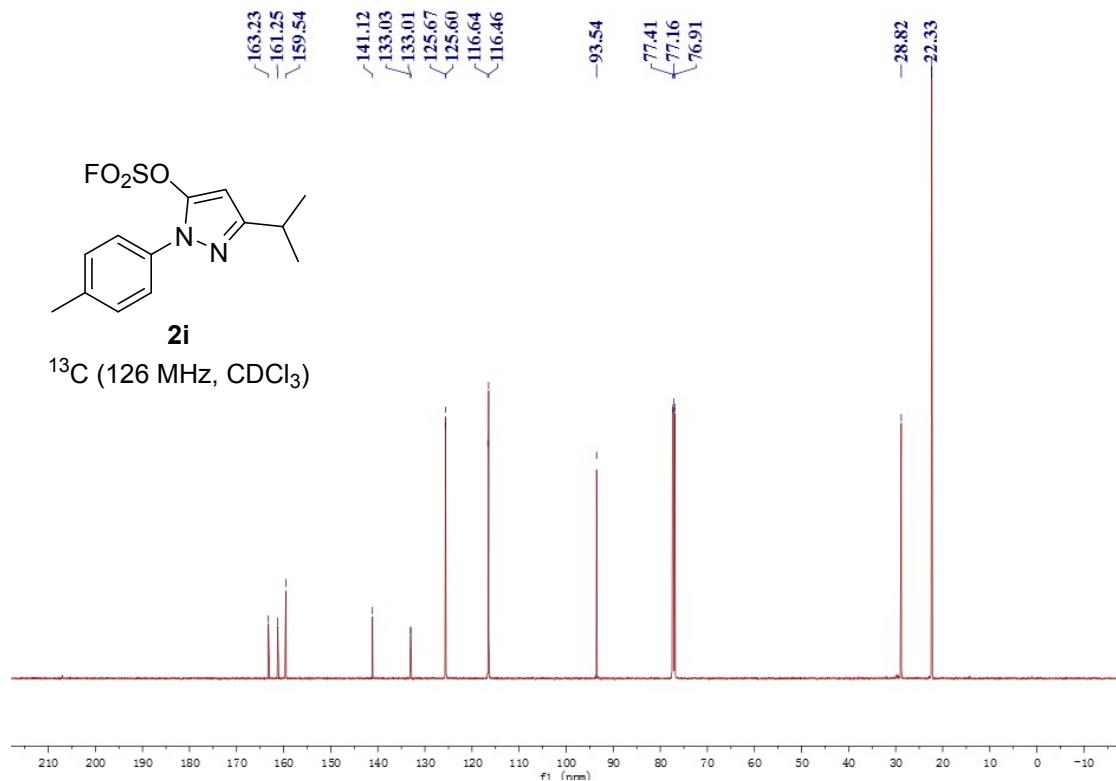
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1.30



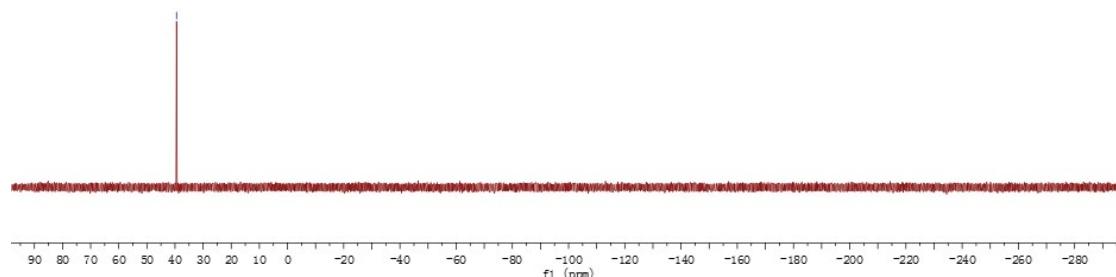
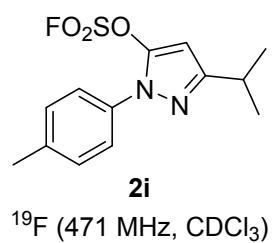
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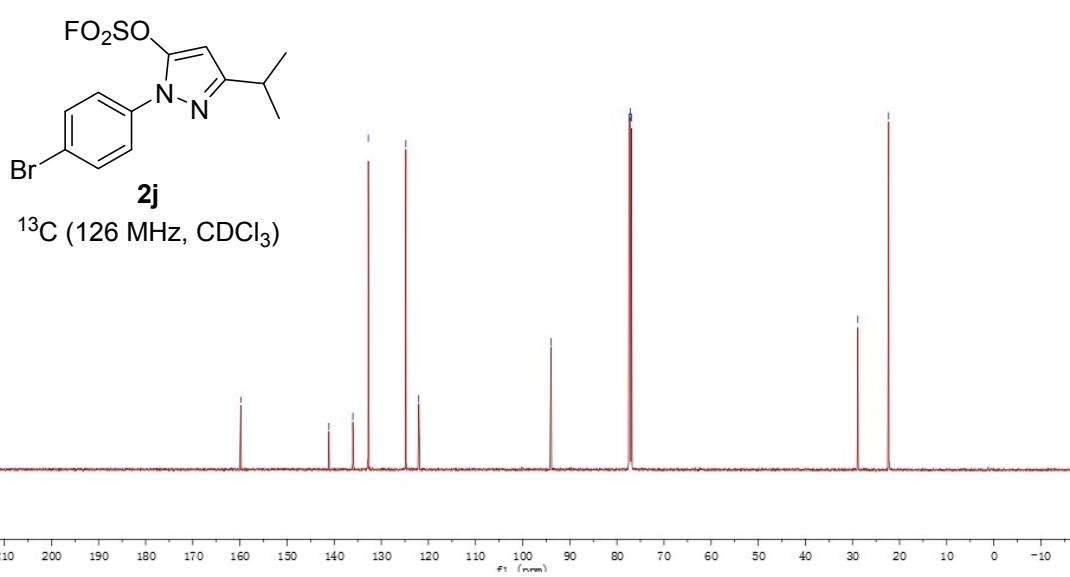
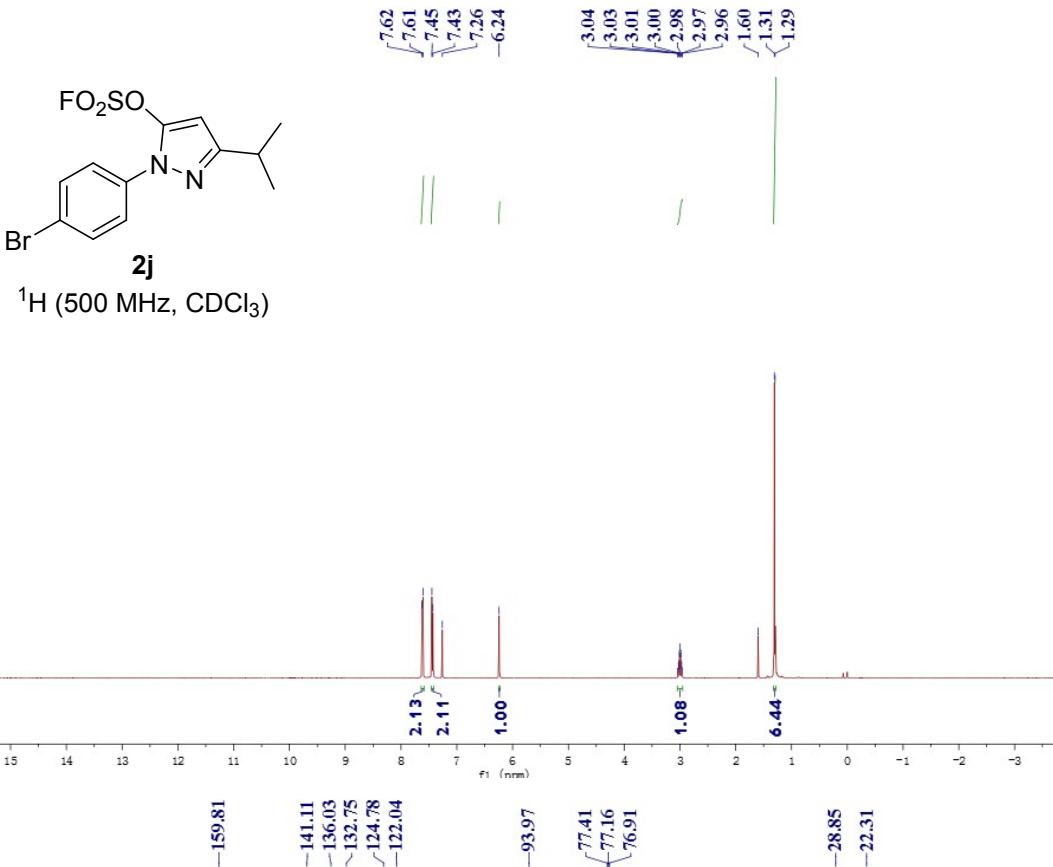
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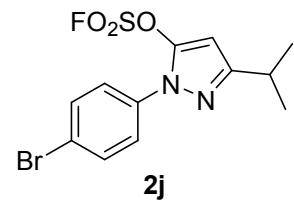


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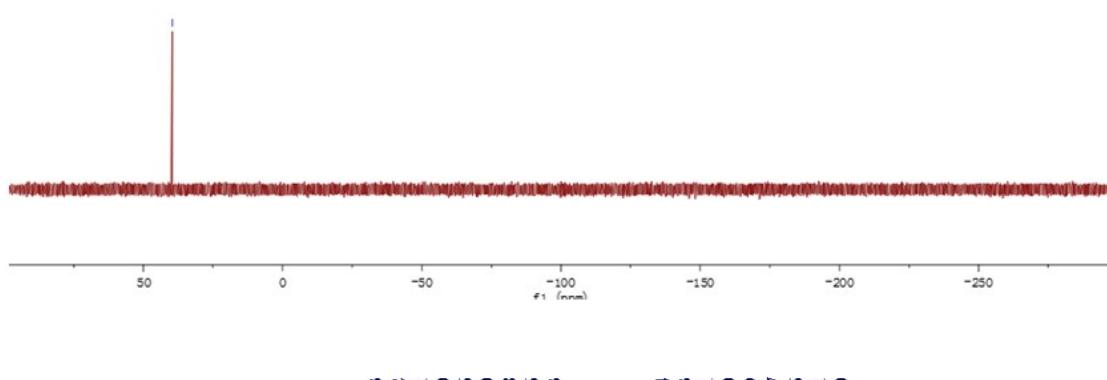




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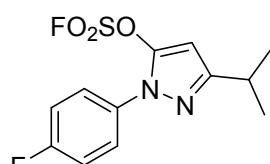


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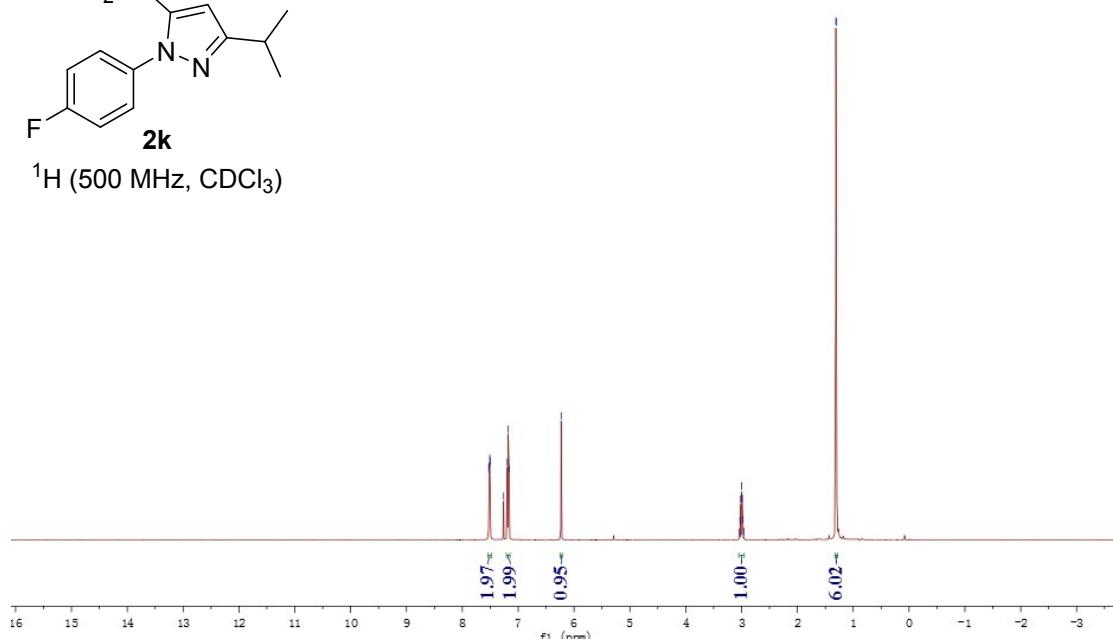


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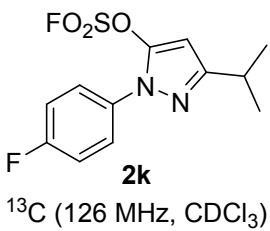
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1.31
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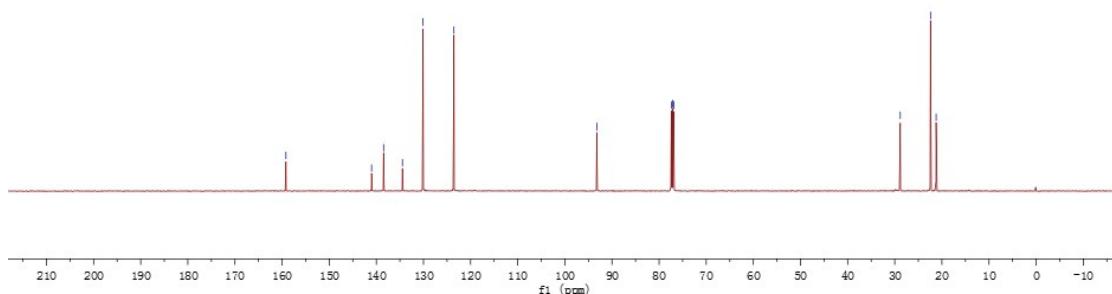
¹H (500 MHz, CDCl₃)



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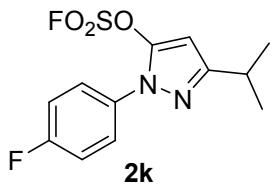


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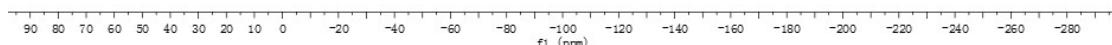


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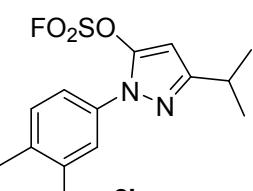
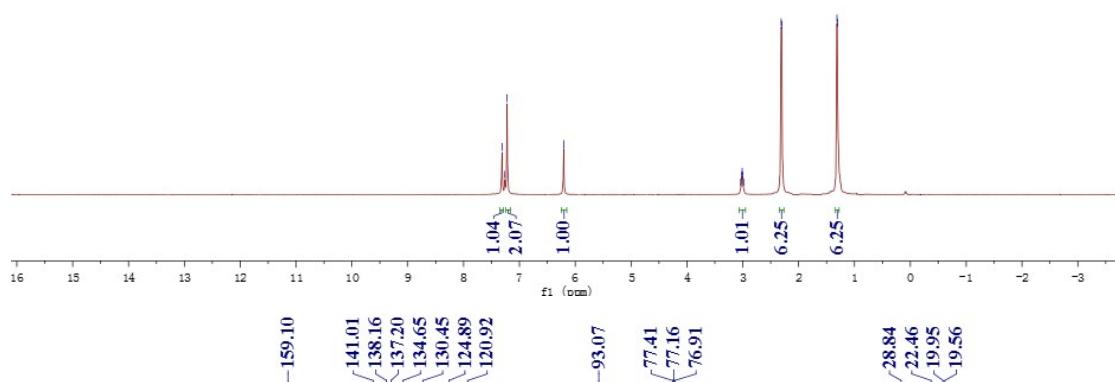


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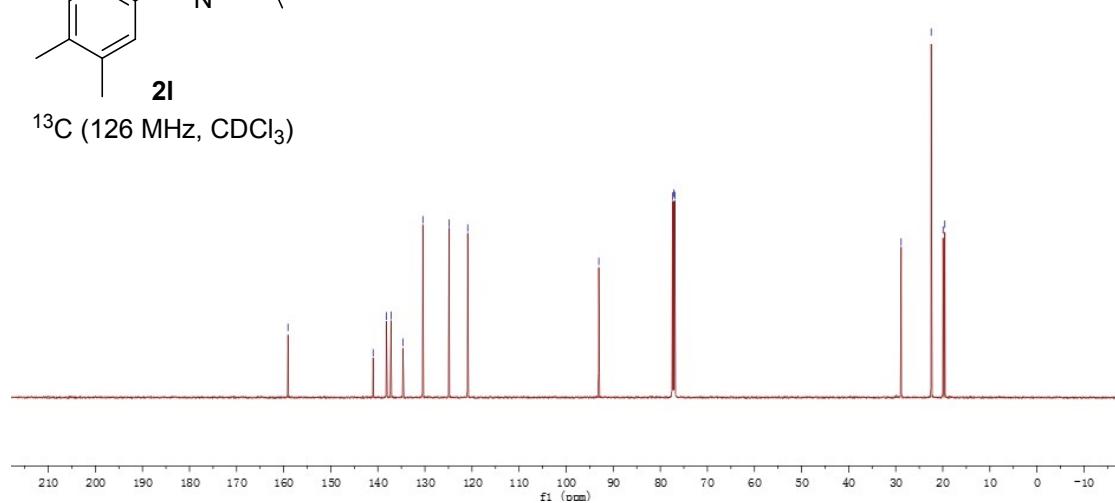




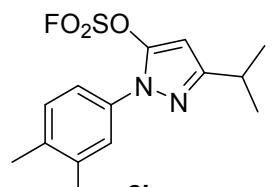
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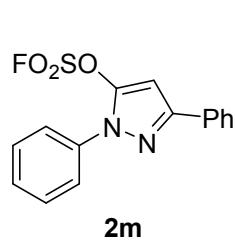
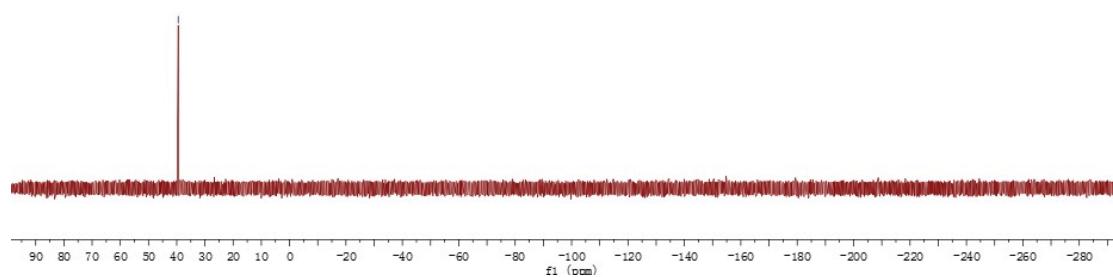
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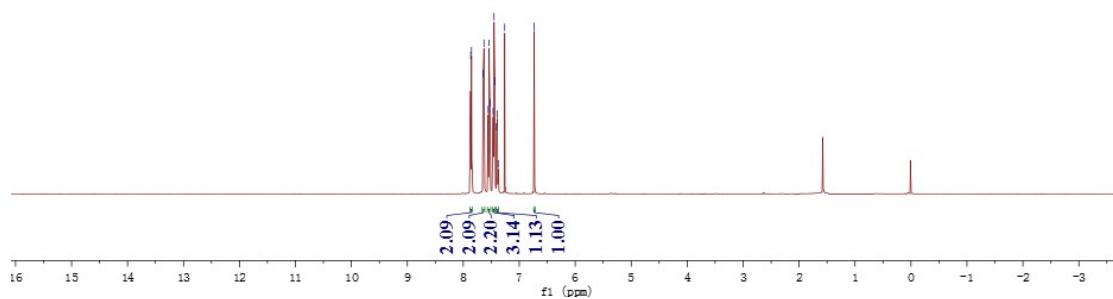
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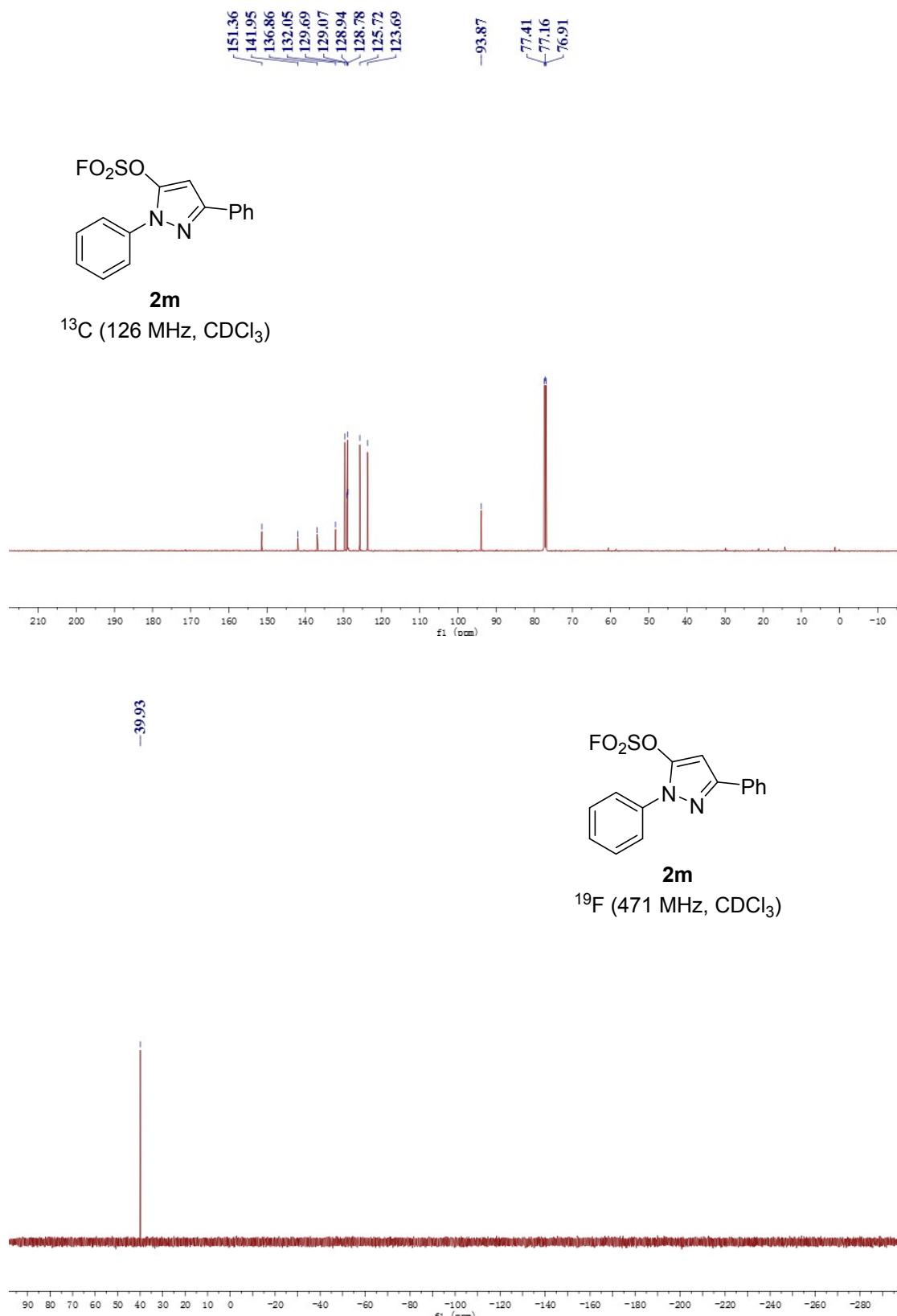


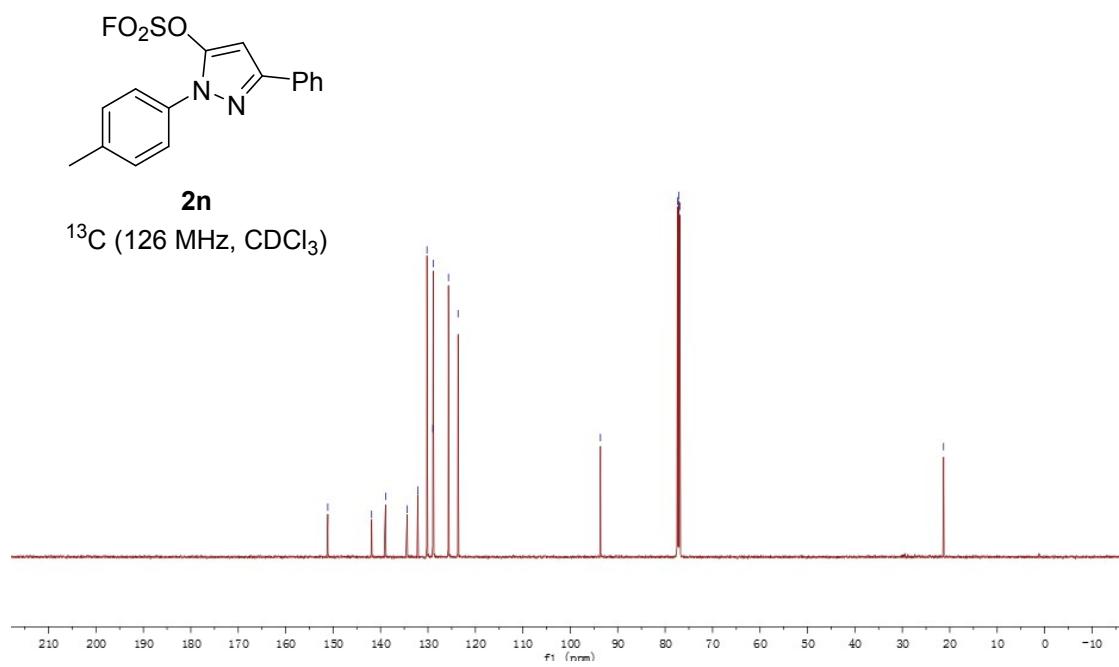
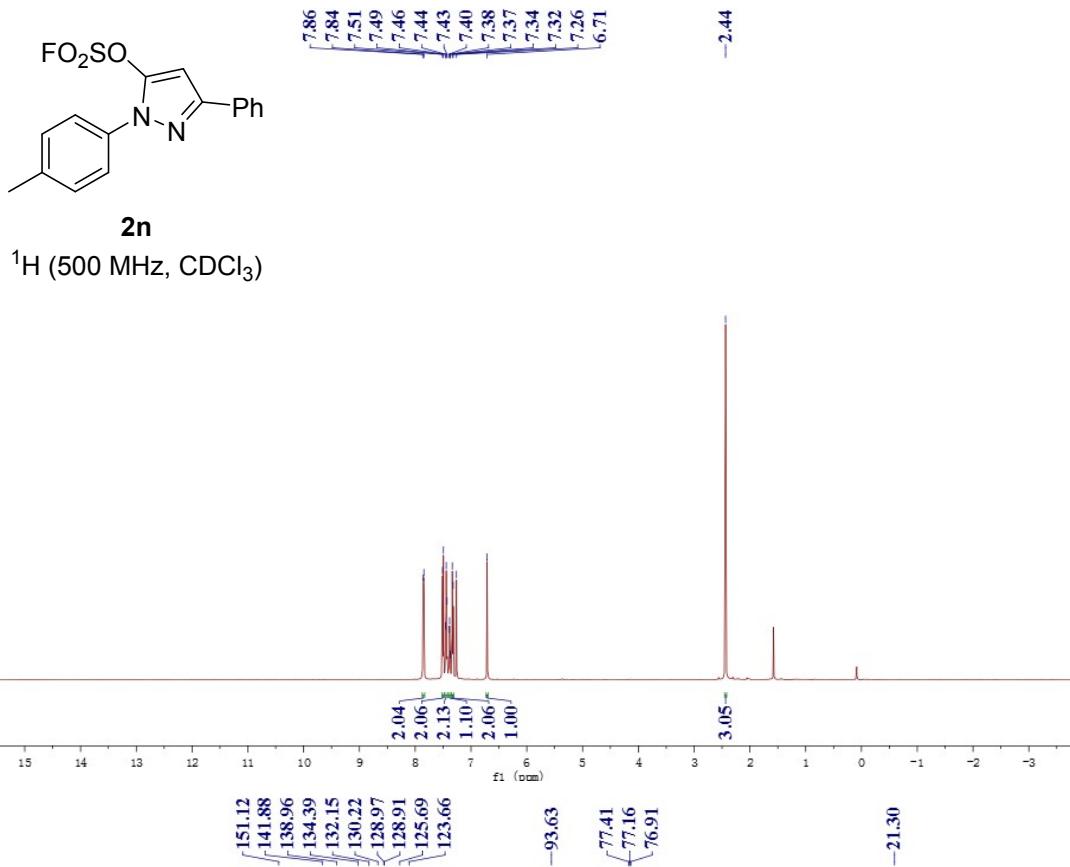
¹⁹F (471 MHz, CDCl₃)



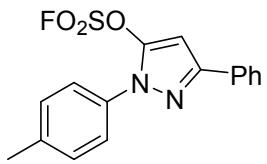
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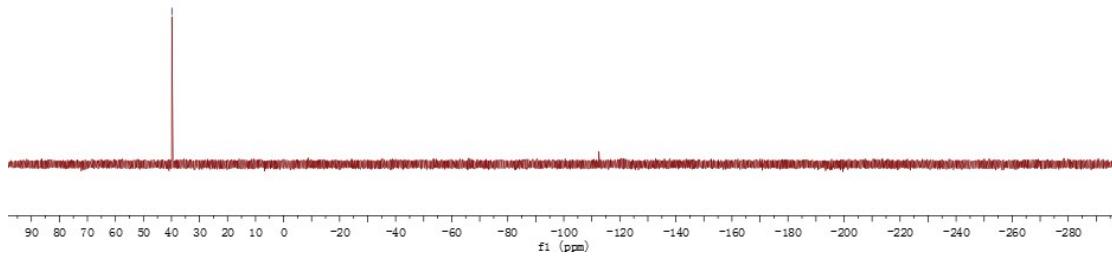


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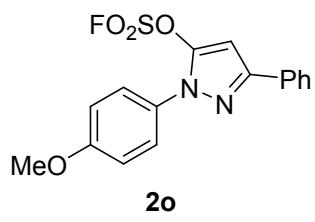


2n

^{19}F (471 MHz, CDCl_3)

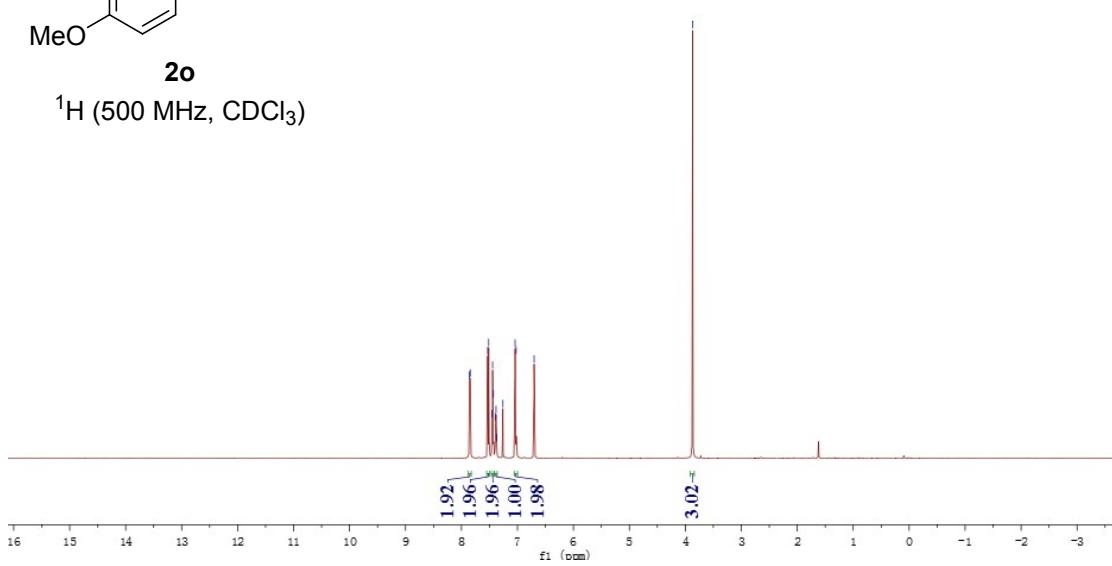


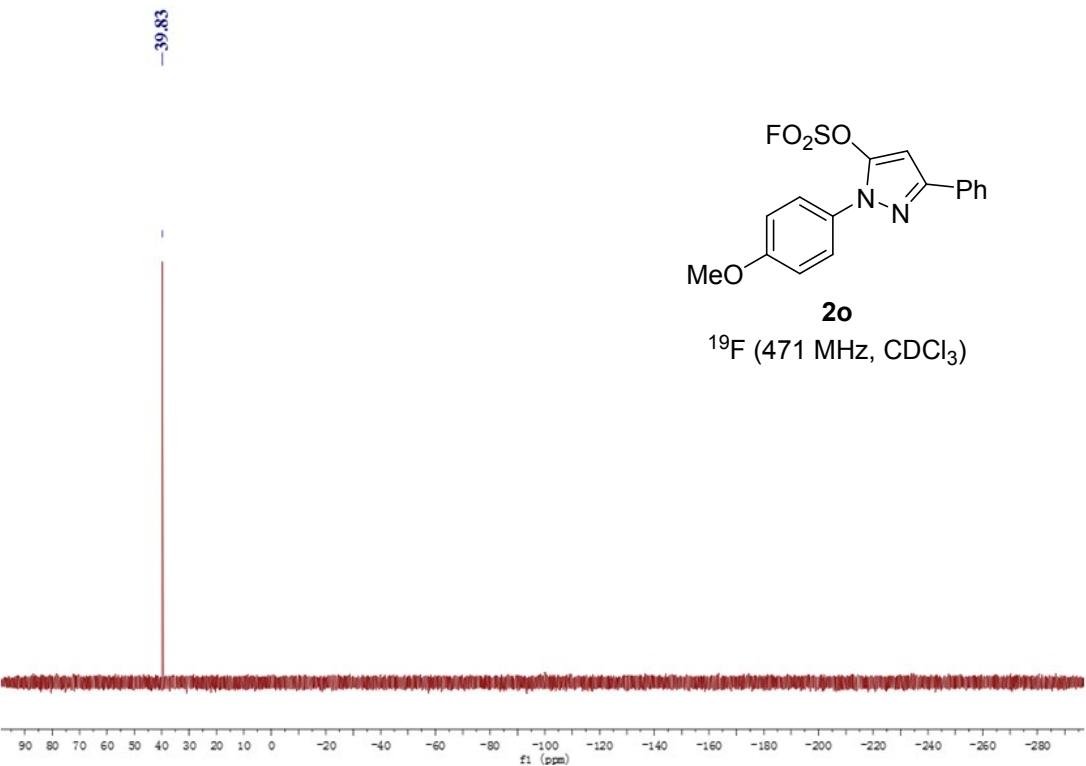
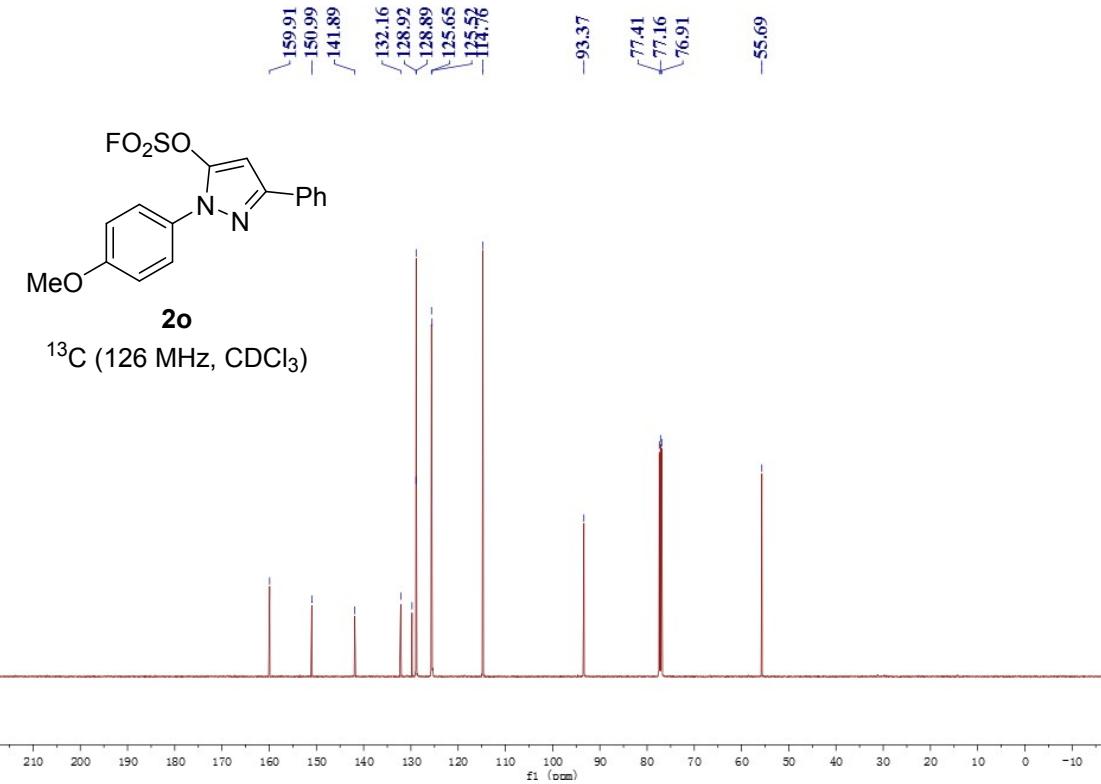
7.86
7.84
7.53
7.51
7.46
7.44
7.43
7.40
7.38
7.37
7.26
7.04
7.02
6.70
-3.87

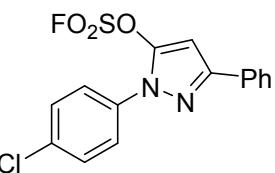


2o

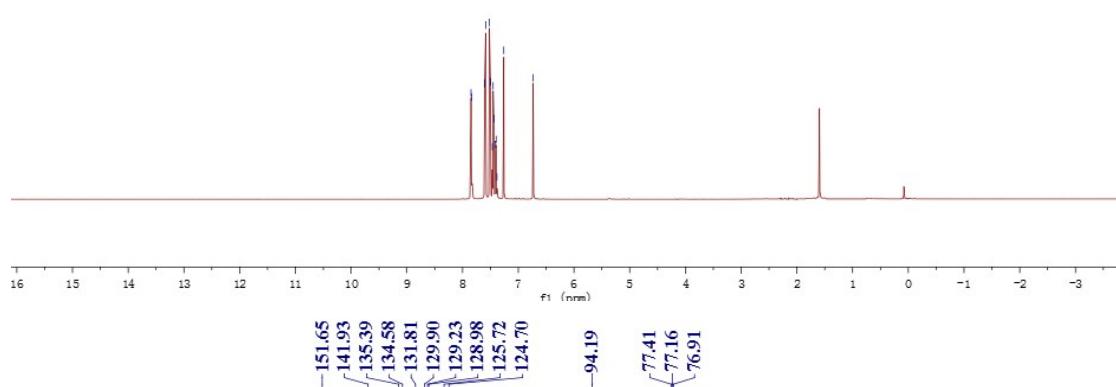
^1H (500 MHz, CDCl_3)







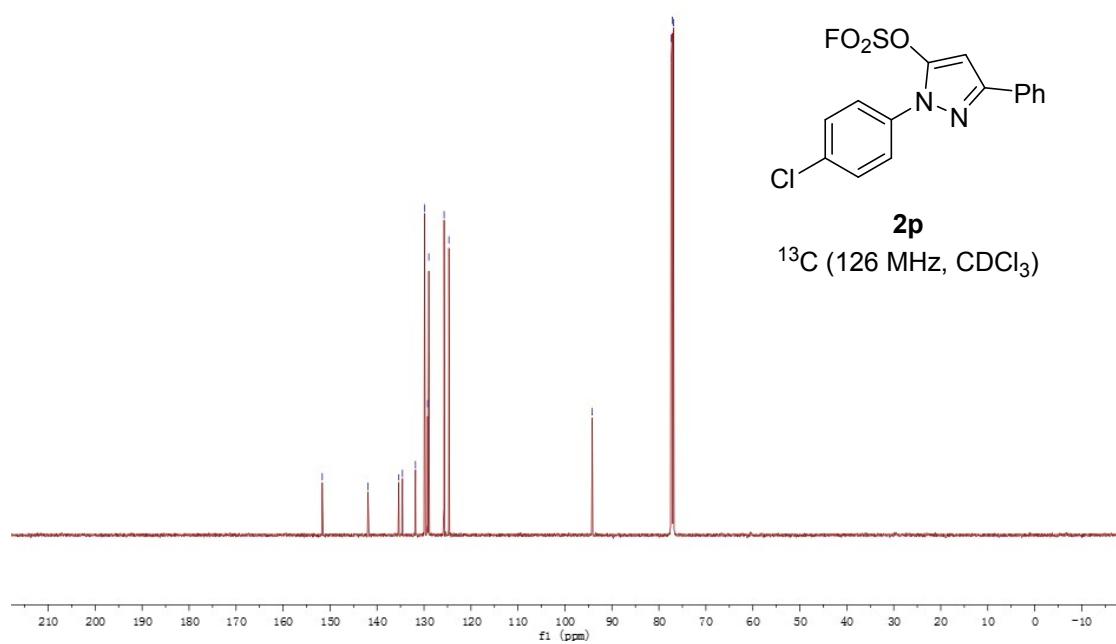
^1H (500 MHz, CDCl_3)



—151.65
—141.93
—135.39
—134.58
—131.81
—129.90
—129.23
—128.98
—125.72
—124.70
—94.19
—77.41
—77.16
—76.91



^{13}C (126 MHz, CDCl_3)

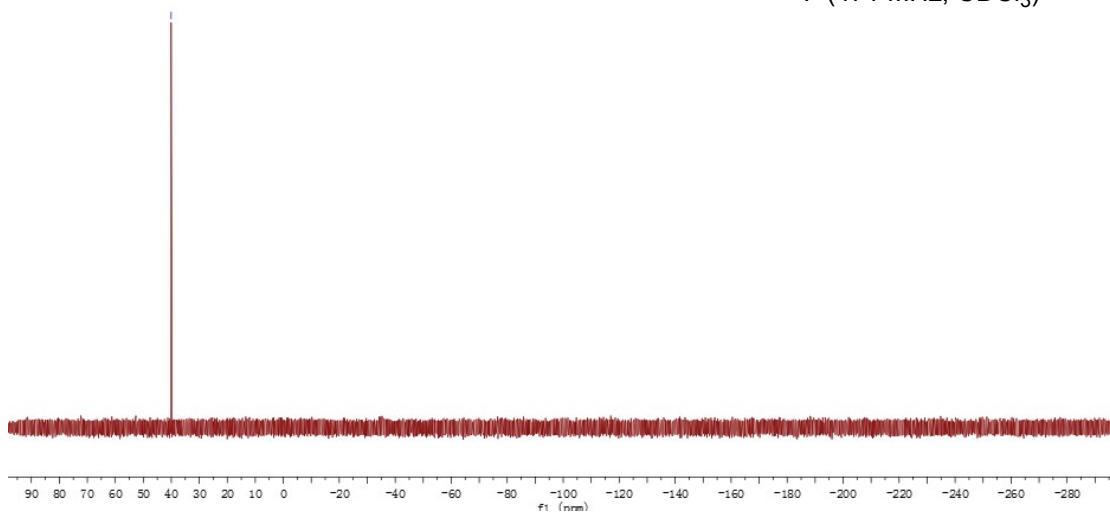


-40.06

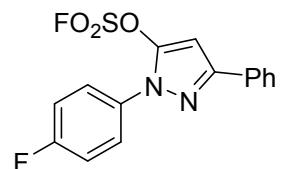


2p

¹⁹F (471 MHz, CDCl₃)

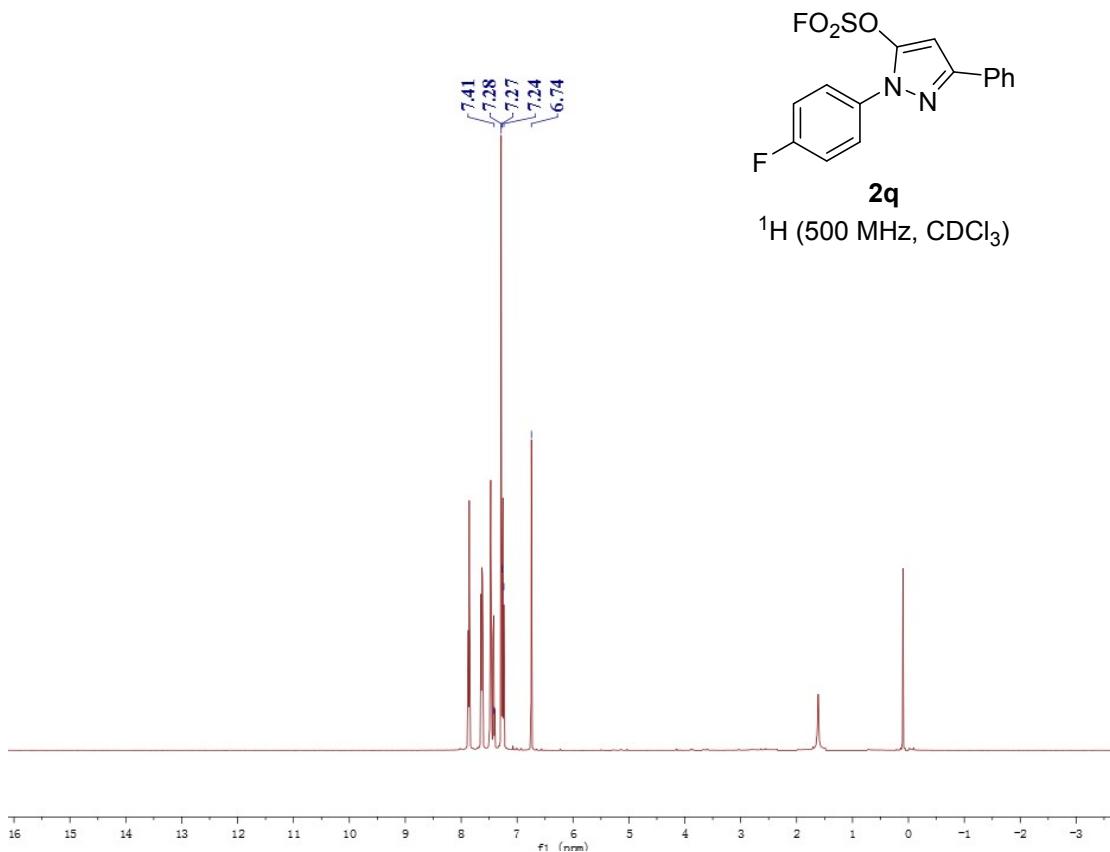


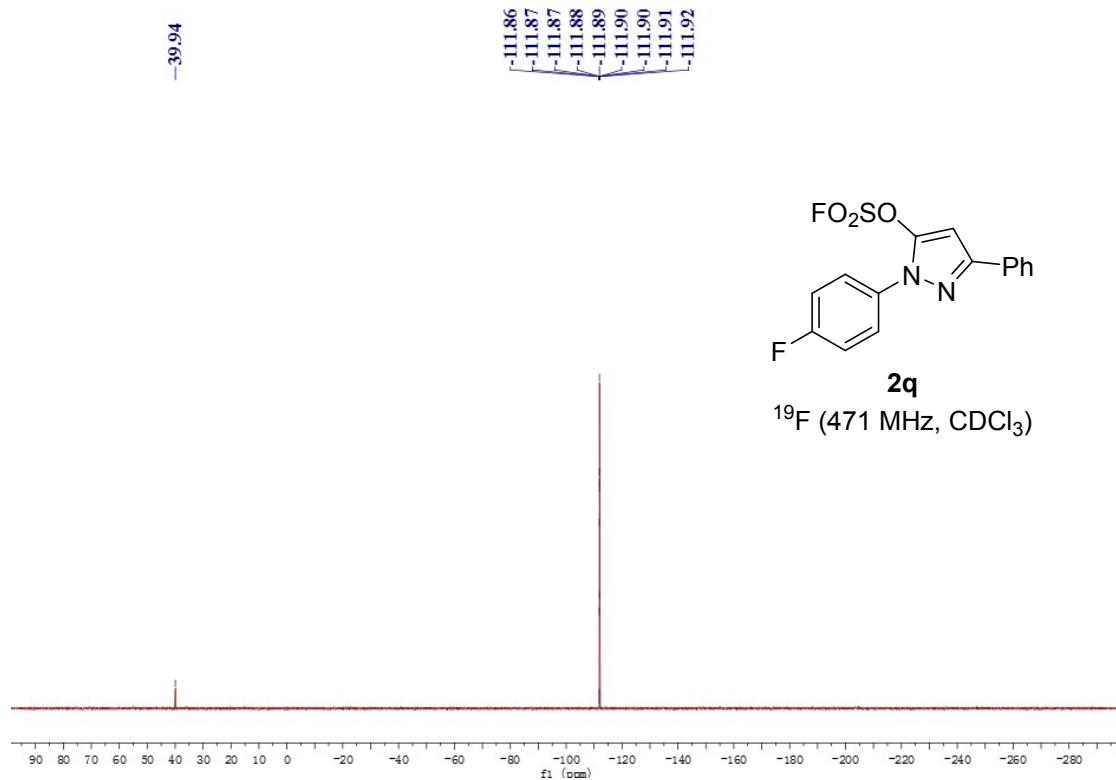
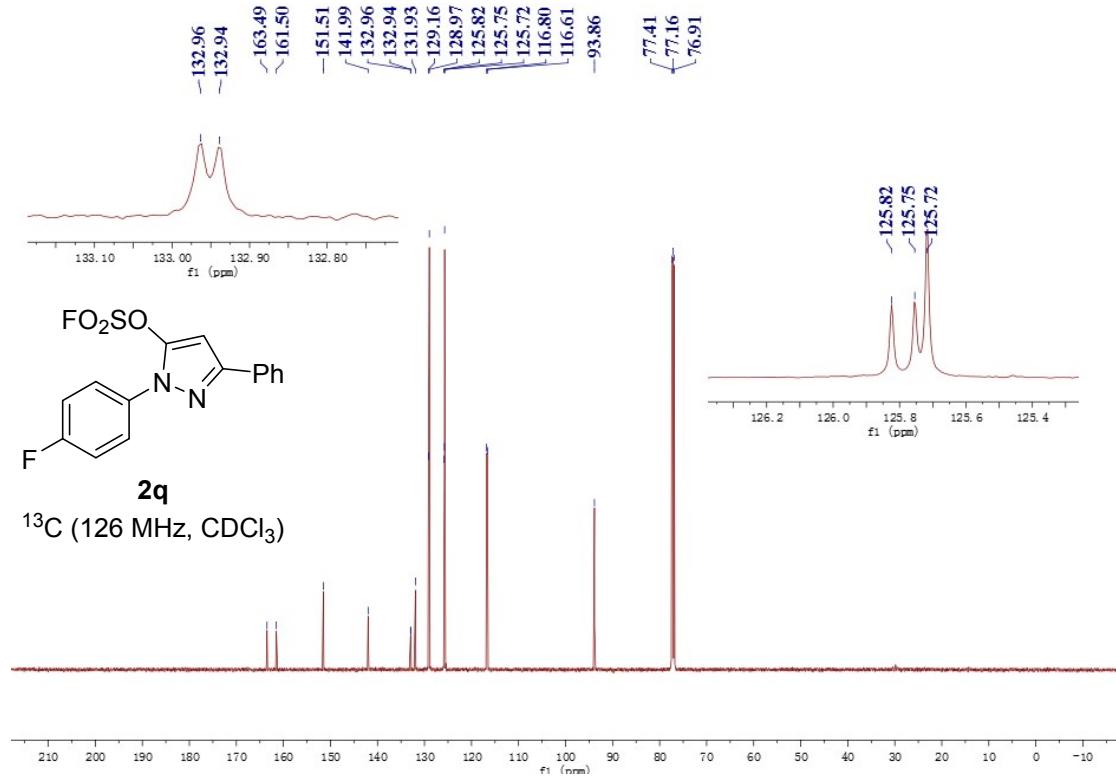
7.41
7.28
7.27
7.24
6.74

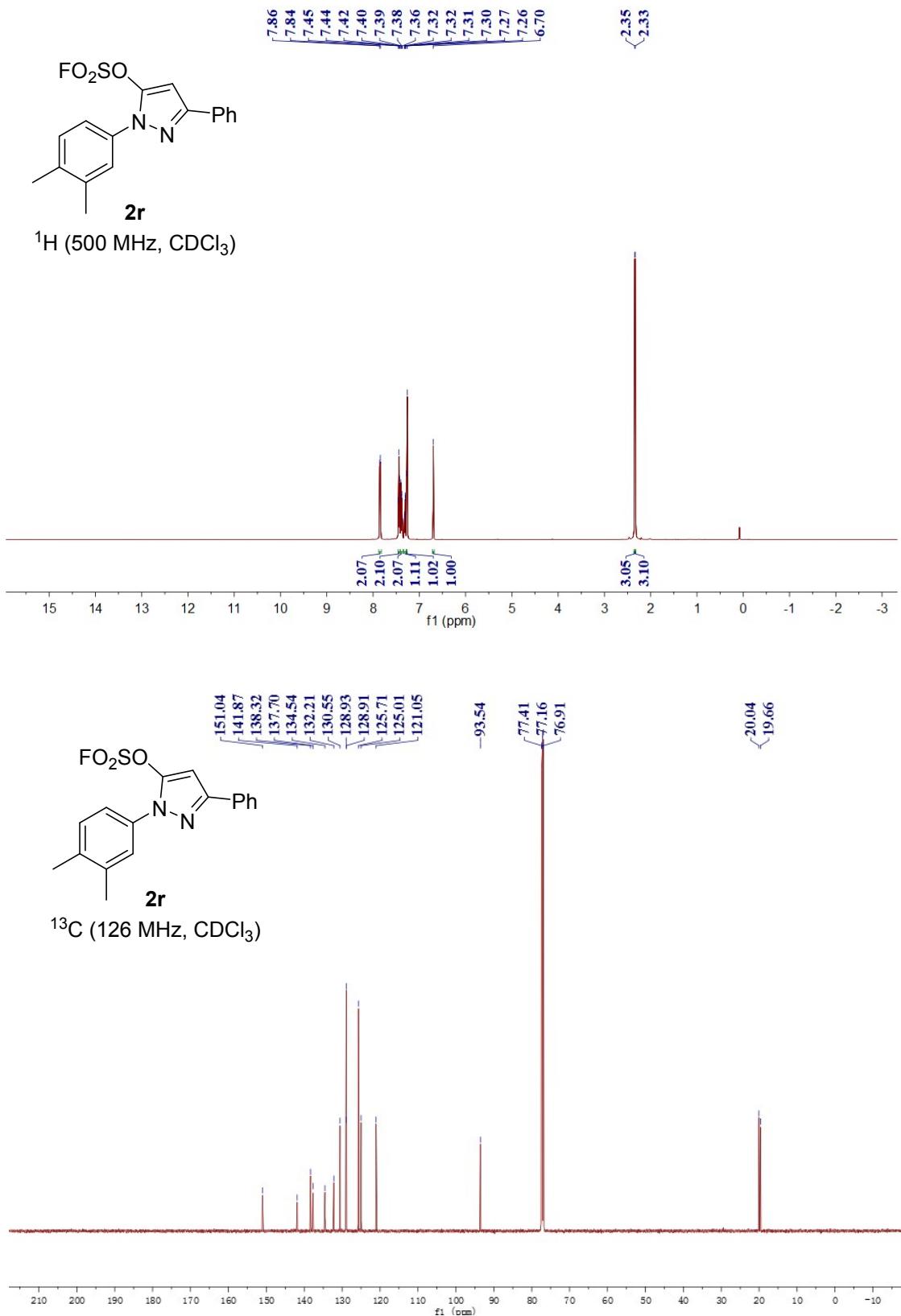


2q

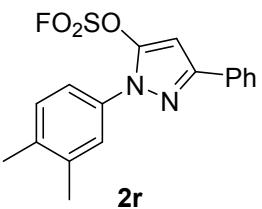
¹H (500 MHz, CDCl₃)



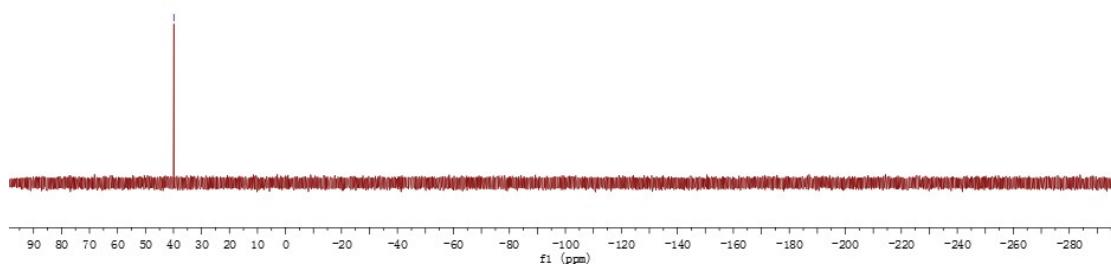




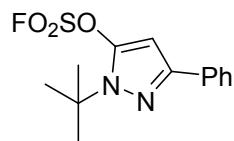
-39.88



¹⁹F (471 MHz, CDCl₃)

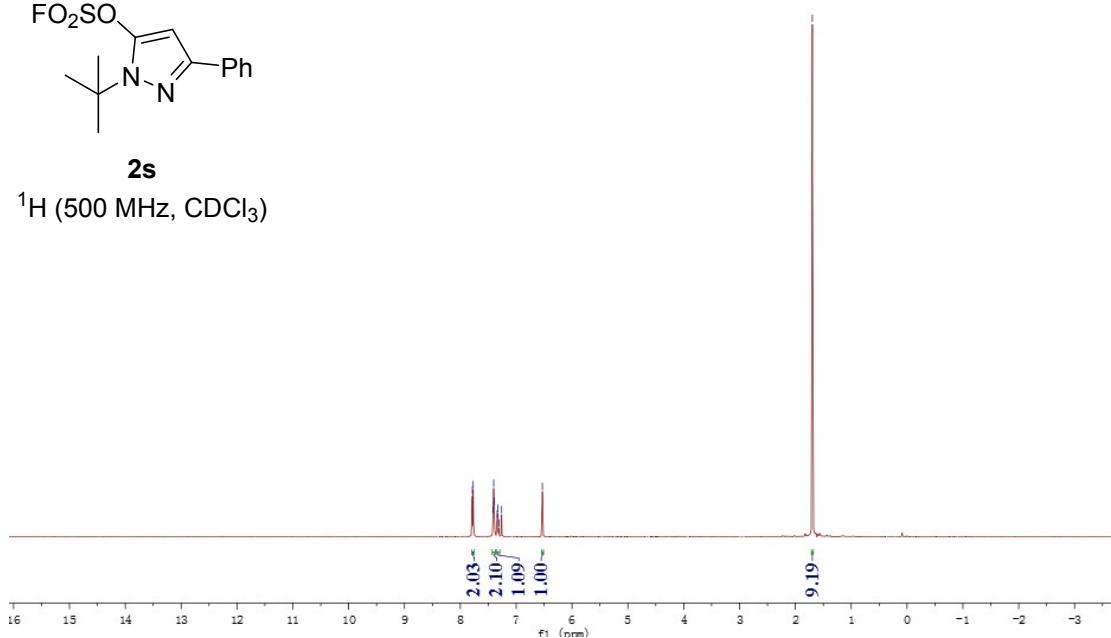


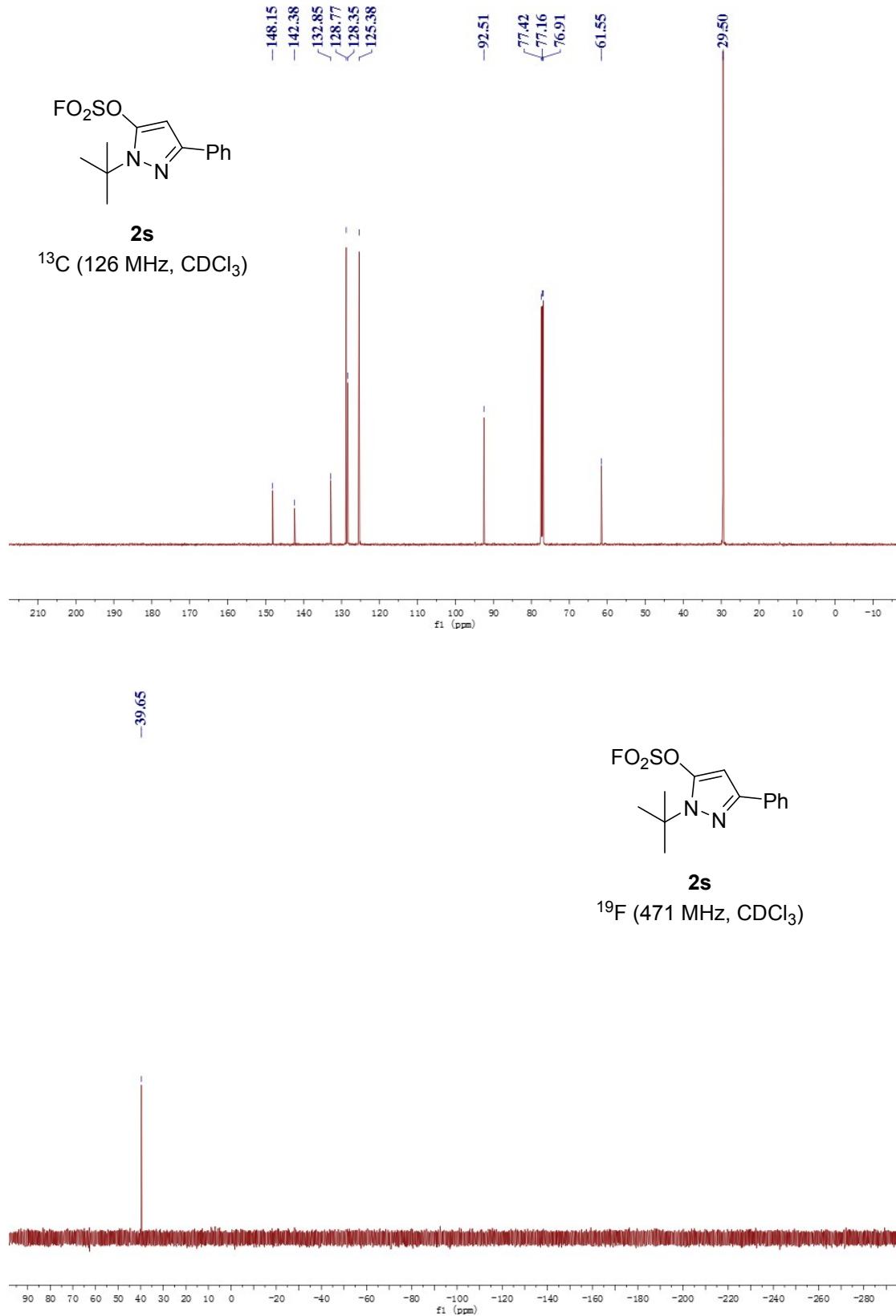
7.78
7.77
7.42
7.40
7.39
7.34
7.33
7.31
7.26
6.53
-1.70

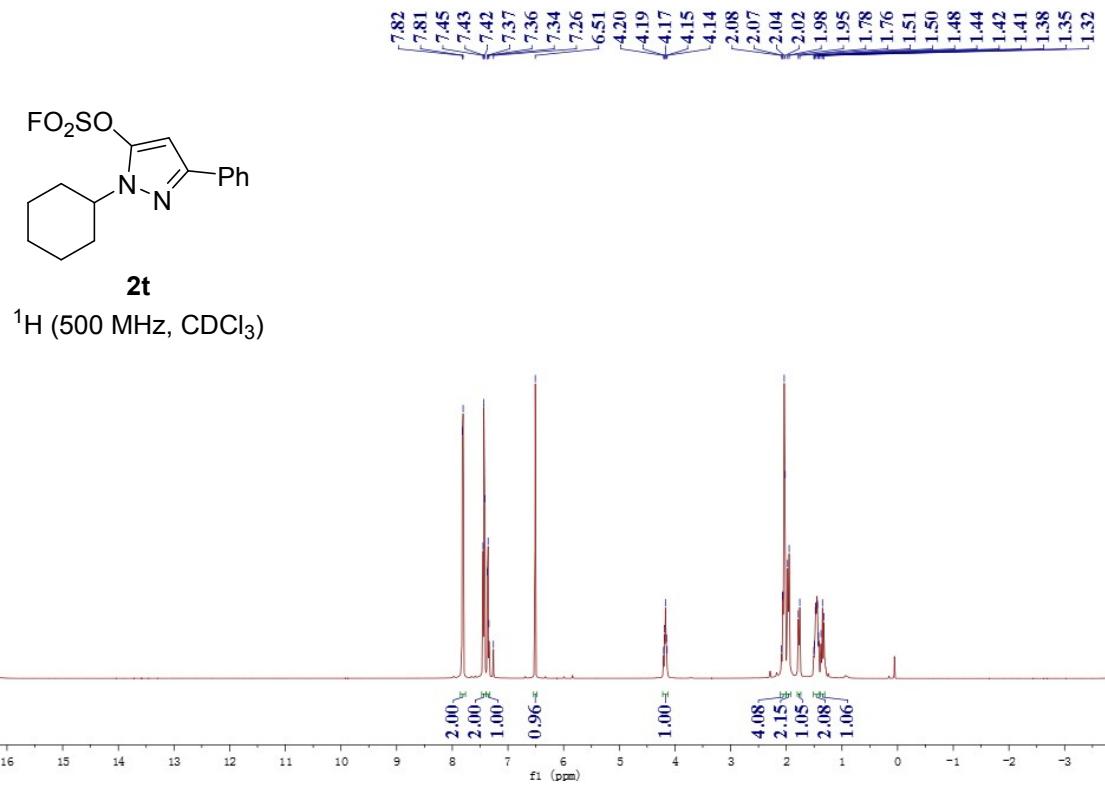


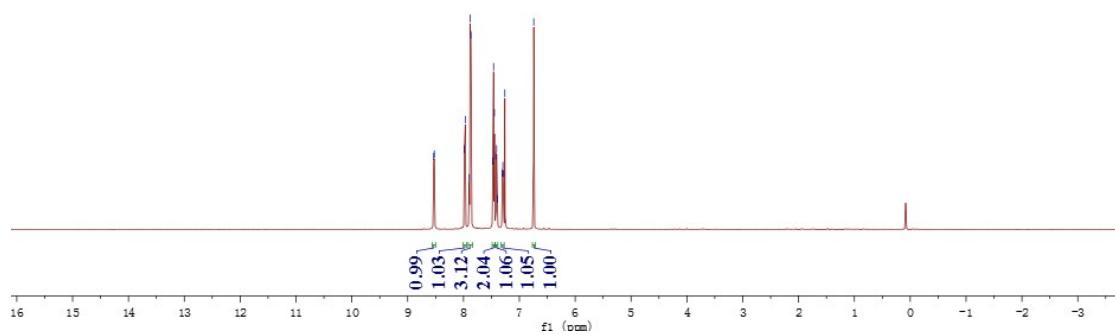
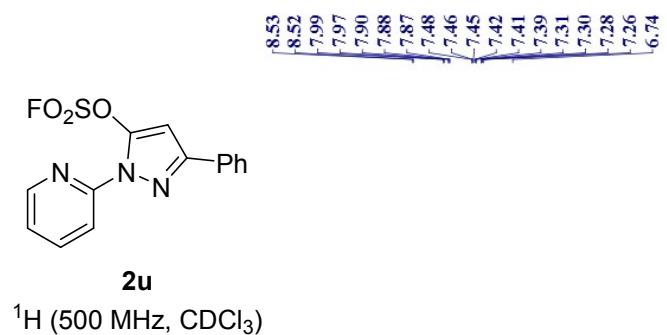
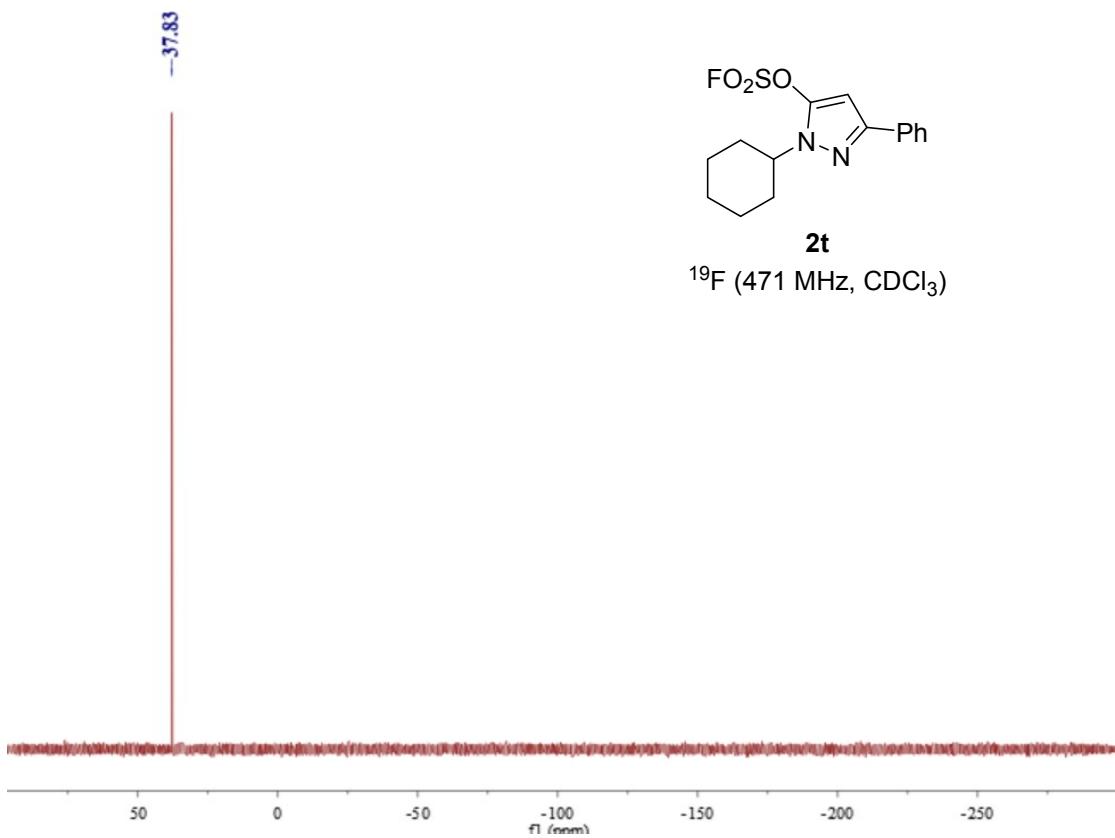
2s

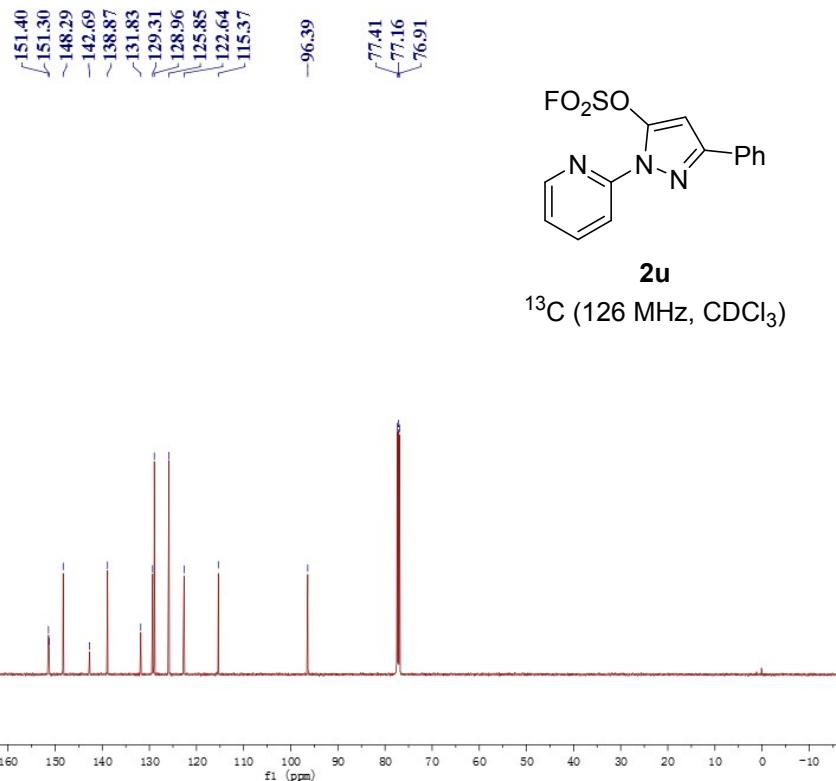
¹H (500 MHz, CDCl₃)



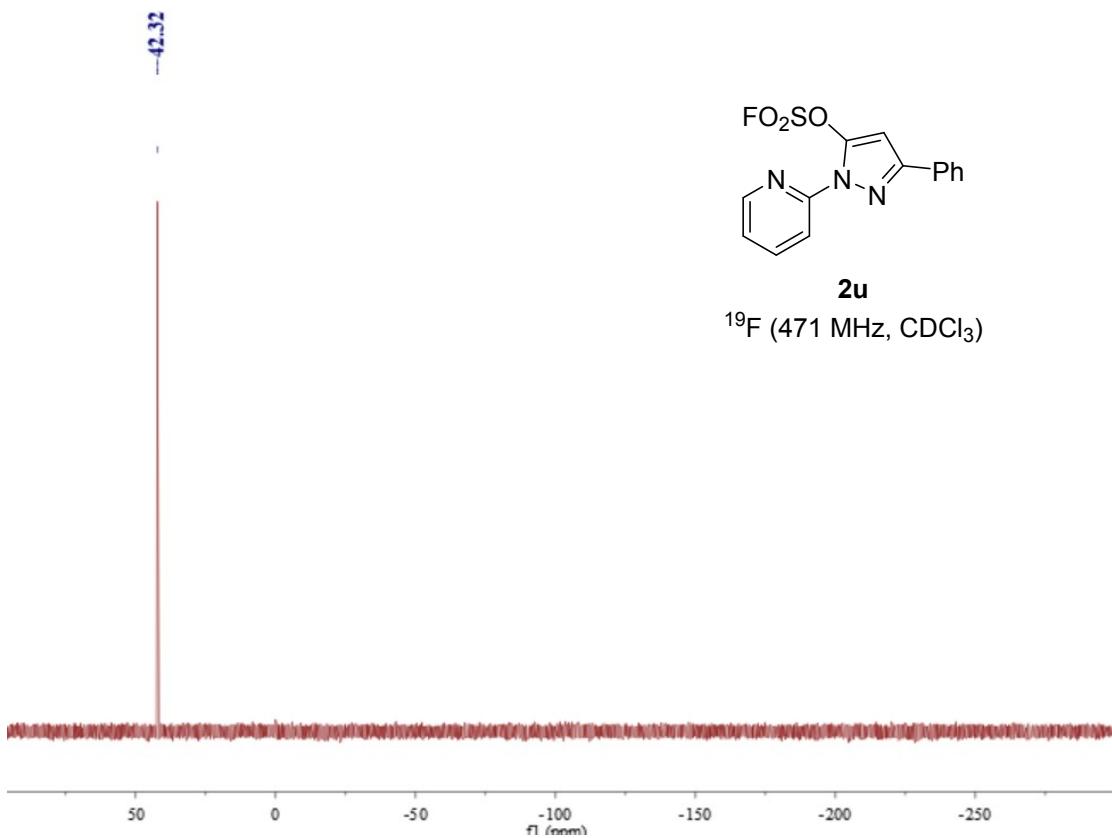


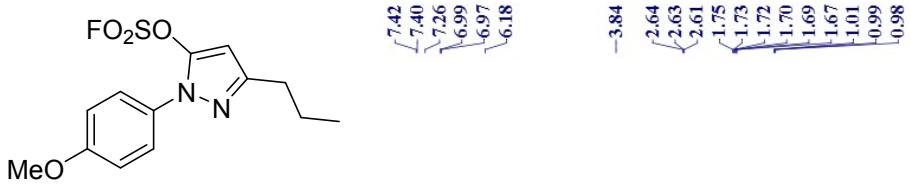




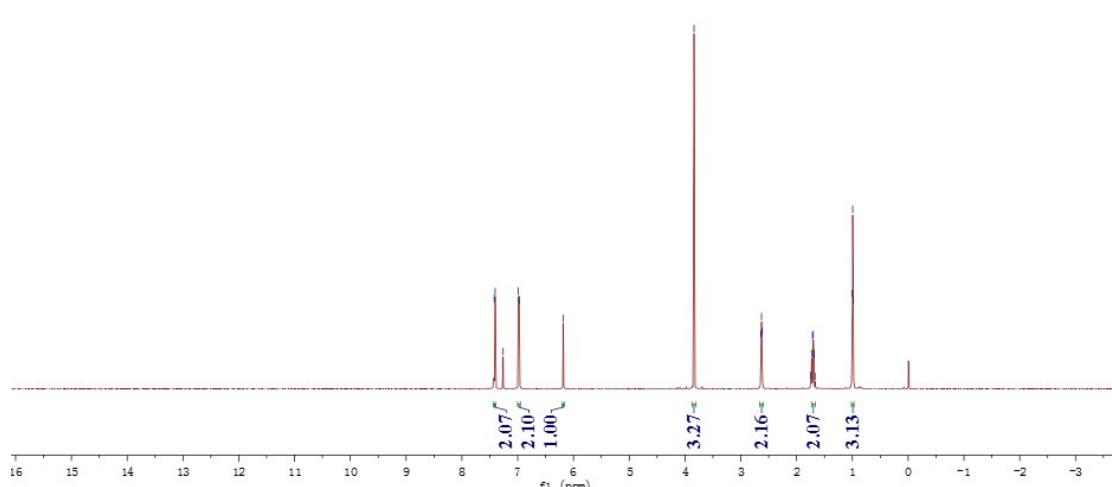


^{19}F (471 MHz, CDCl_3)

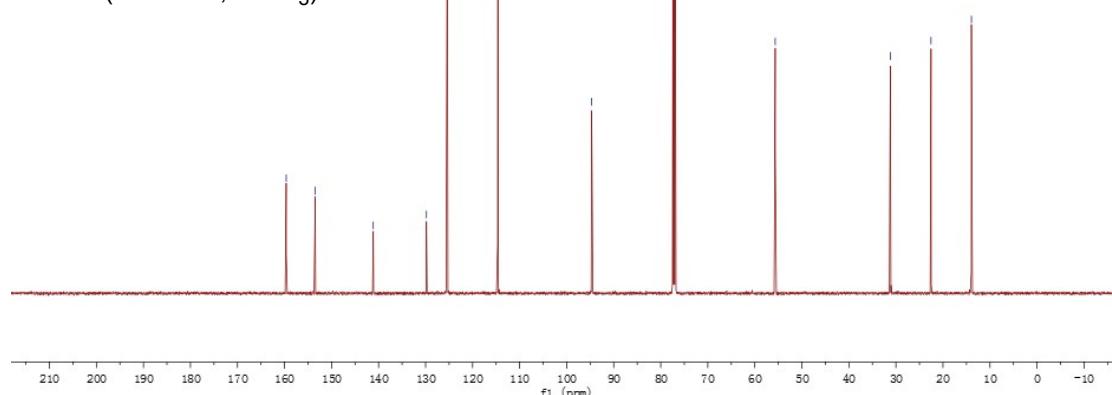




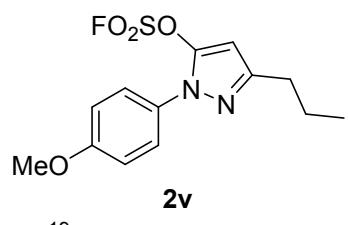
¹H (500 MHz, CDCl₃)



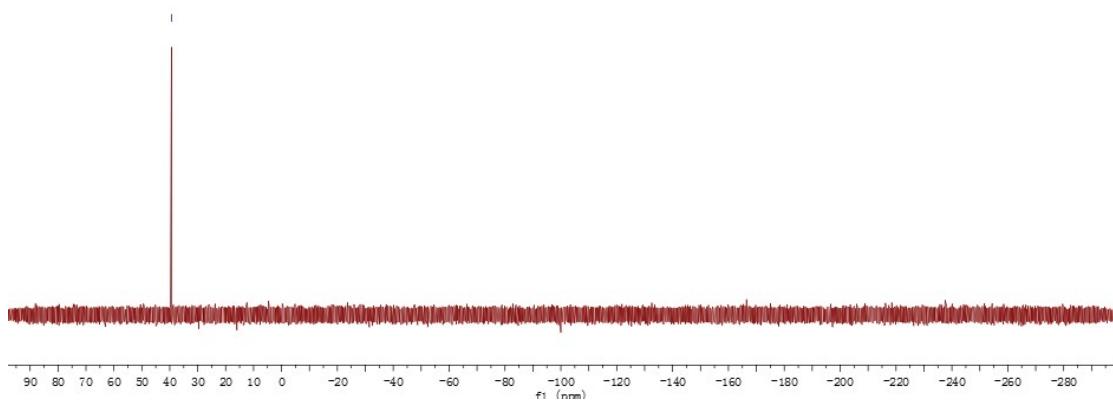
2v
¹³C (126 MHz, CDCl₃)



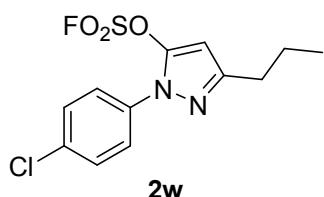
-39.41



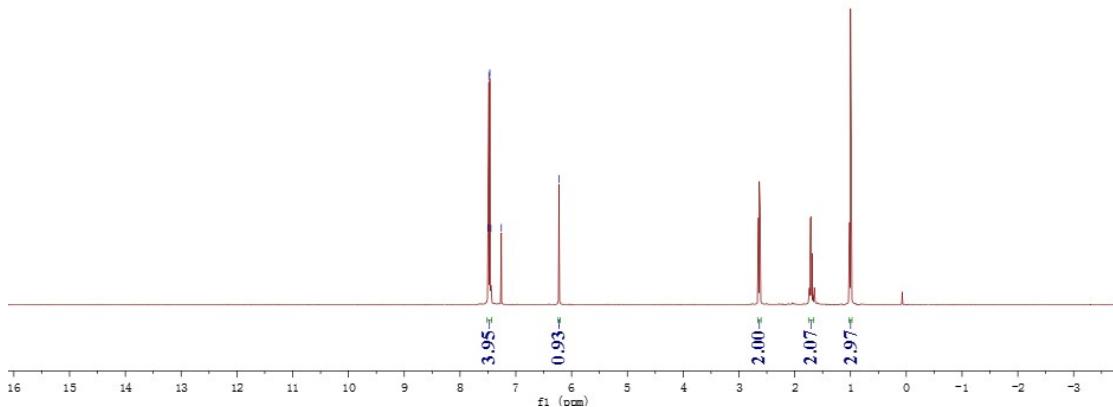
¹⁹F (471 MHz, CDCl₃)

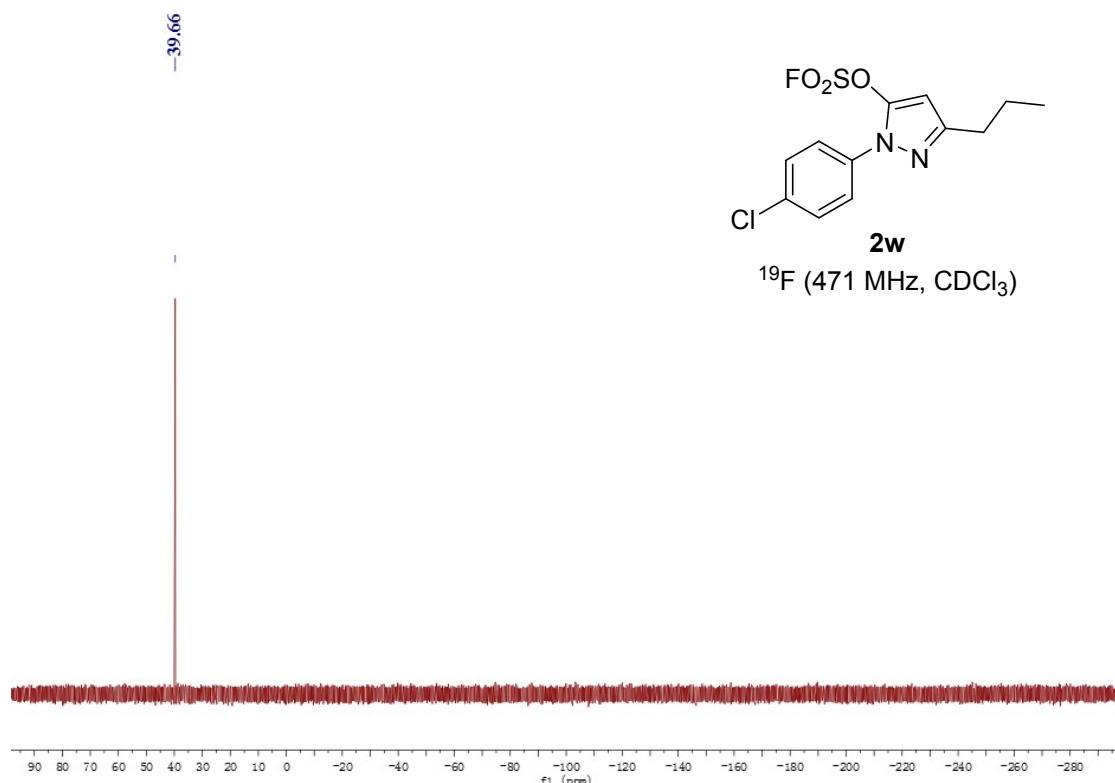
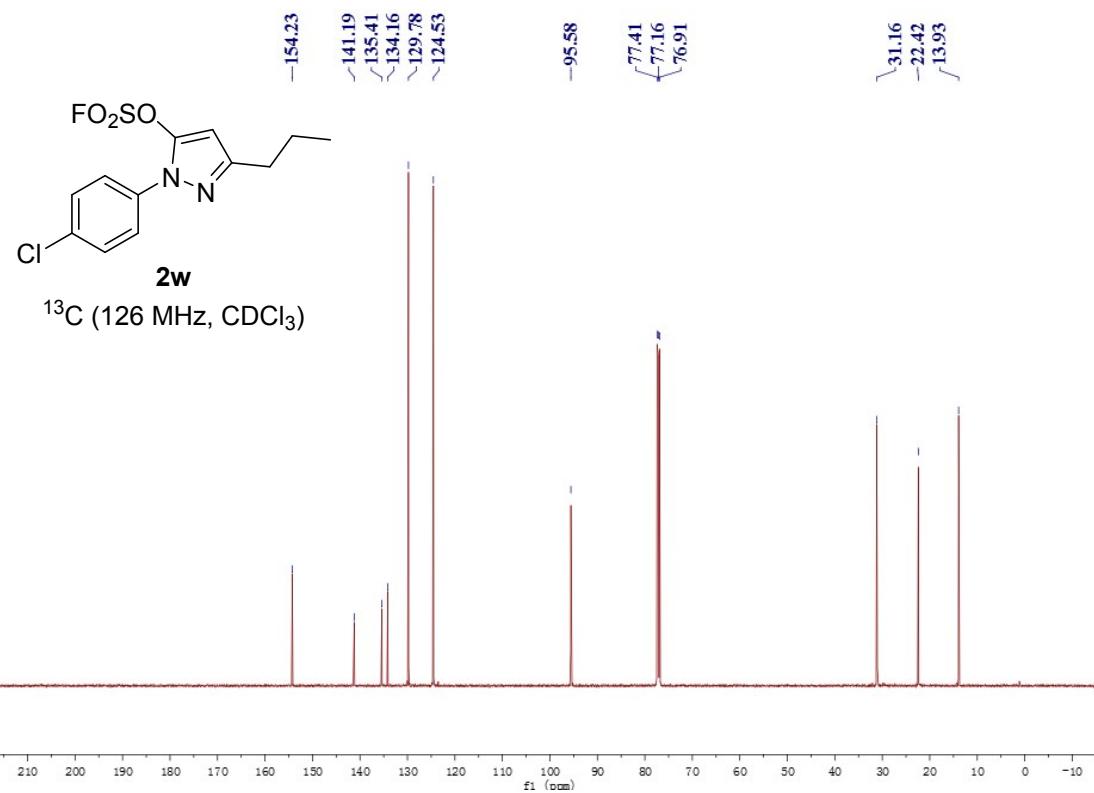


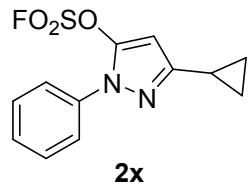
7.50
7.48
7.47
7.45
7.26
7.23



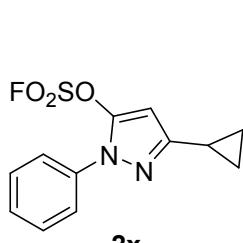
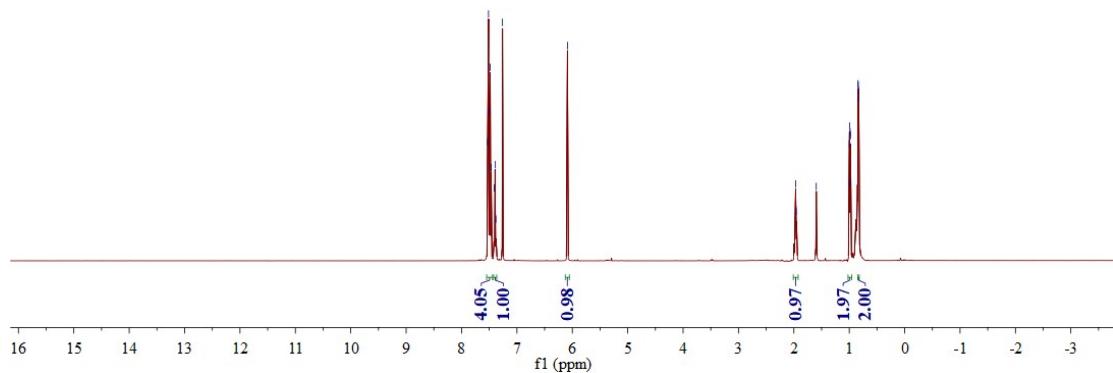
¹H (500 MHz, CDCl₃)



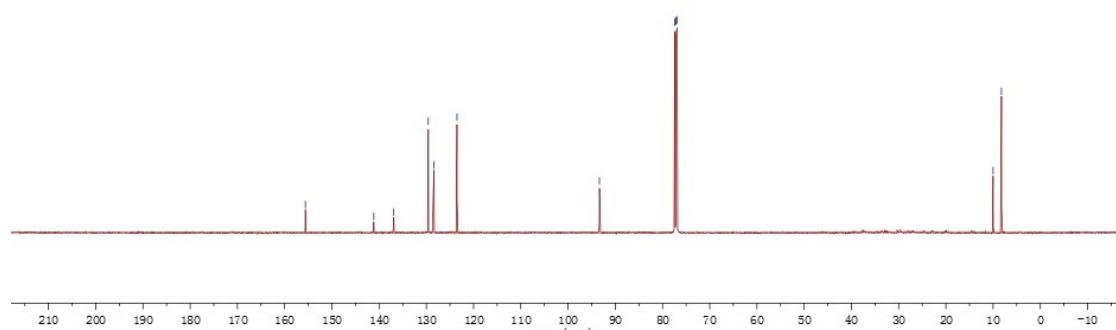




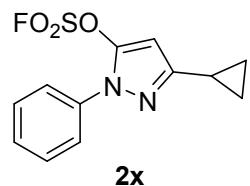
^1H (500 MHz, CDCl_3)



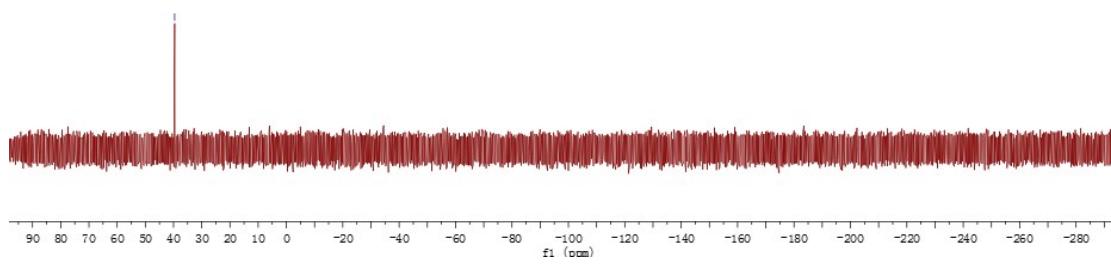
^{13}C (126 MHz, CDCl_3)



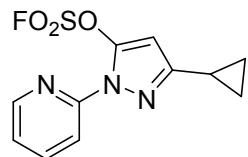
-39.60



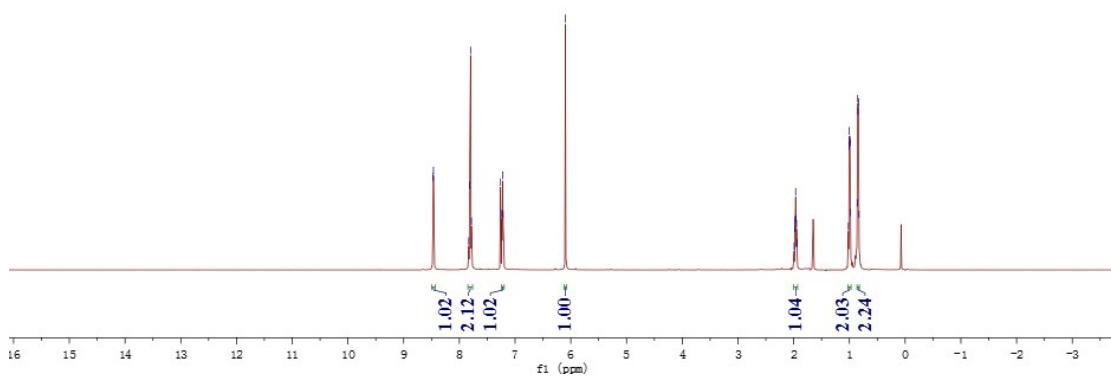
^{19}F (471 MHz, CDCl_3)

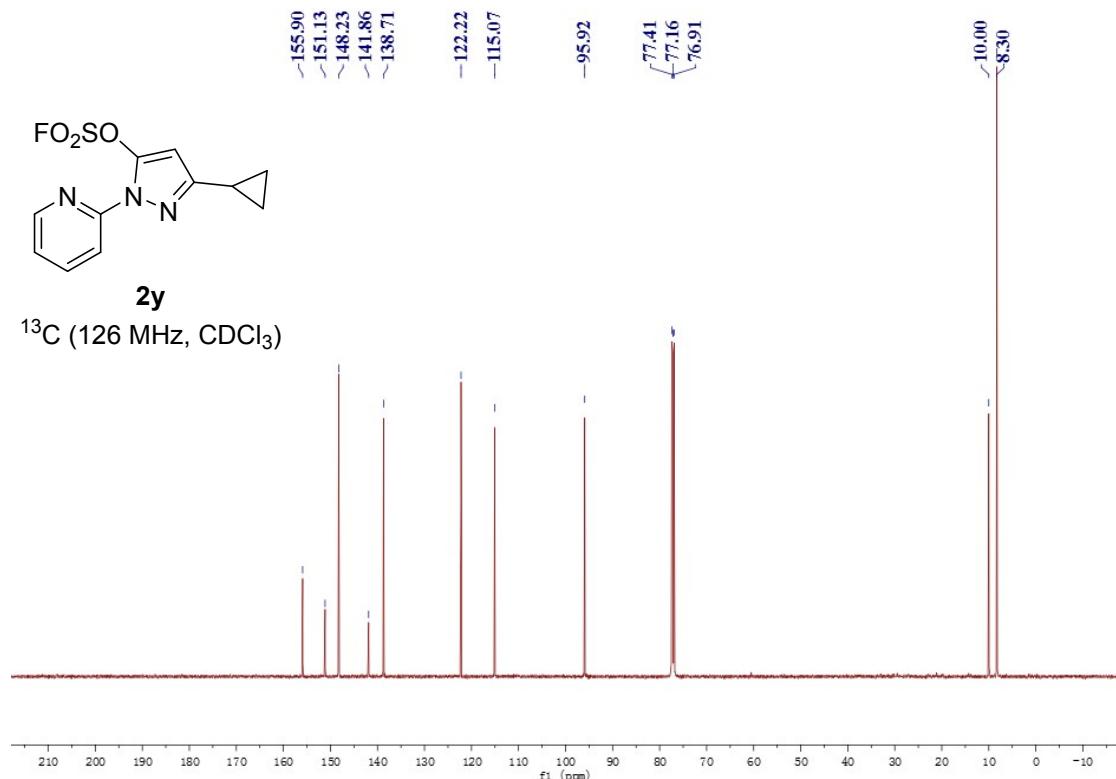


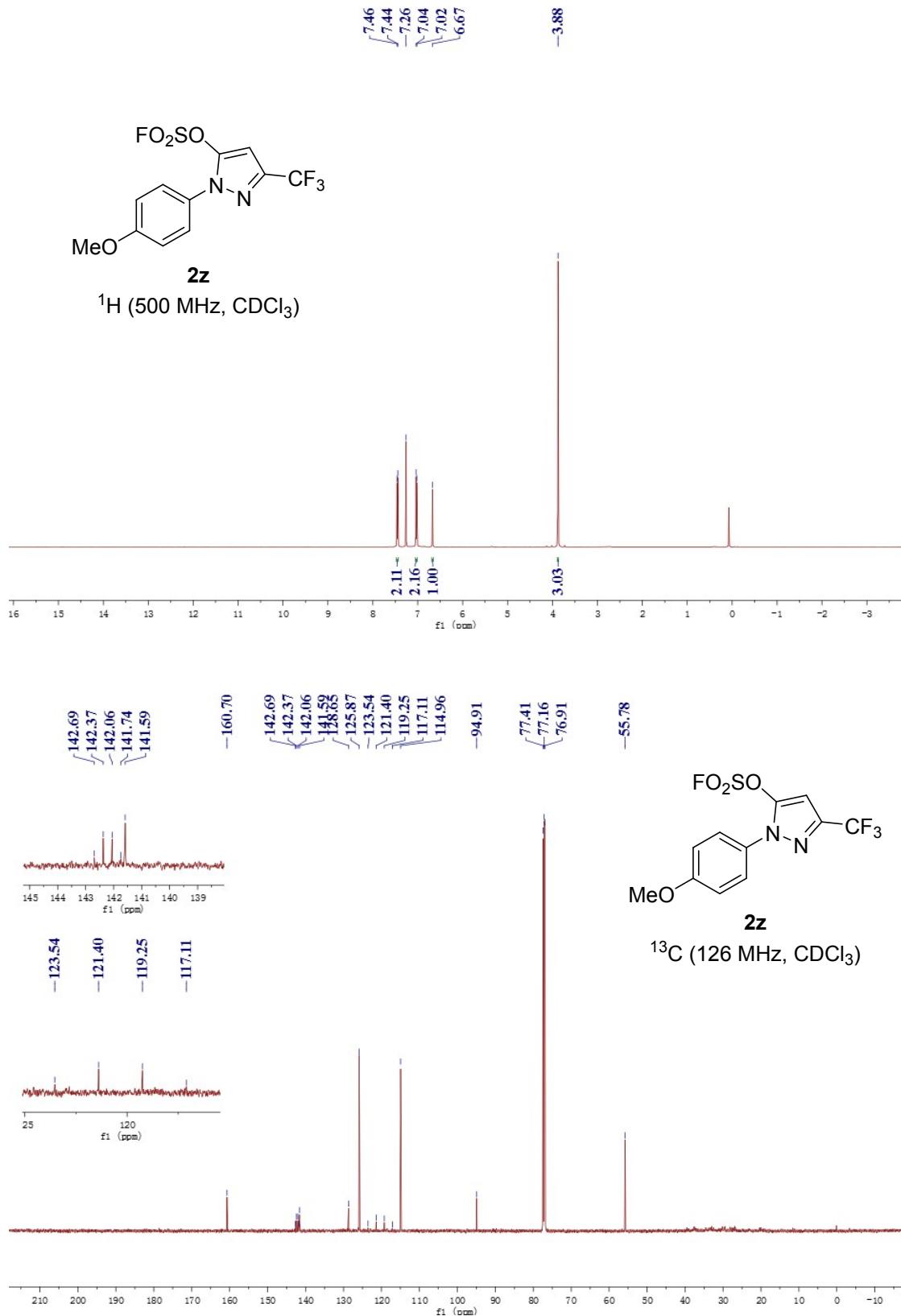
8.47
8.46
7.83
7.82
7.80
7.78
7.26
7.24
7.23
7.22
6.10
1.99
1.98
1.98
1.97
1.96
1.95
1.94
1.02
1.01
1.00
0.99
0.99
0.98
0.86
0.85
0.84
0.83

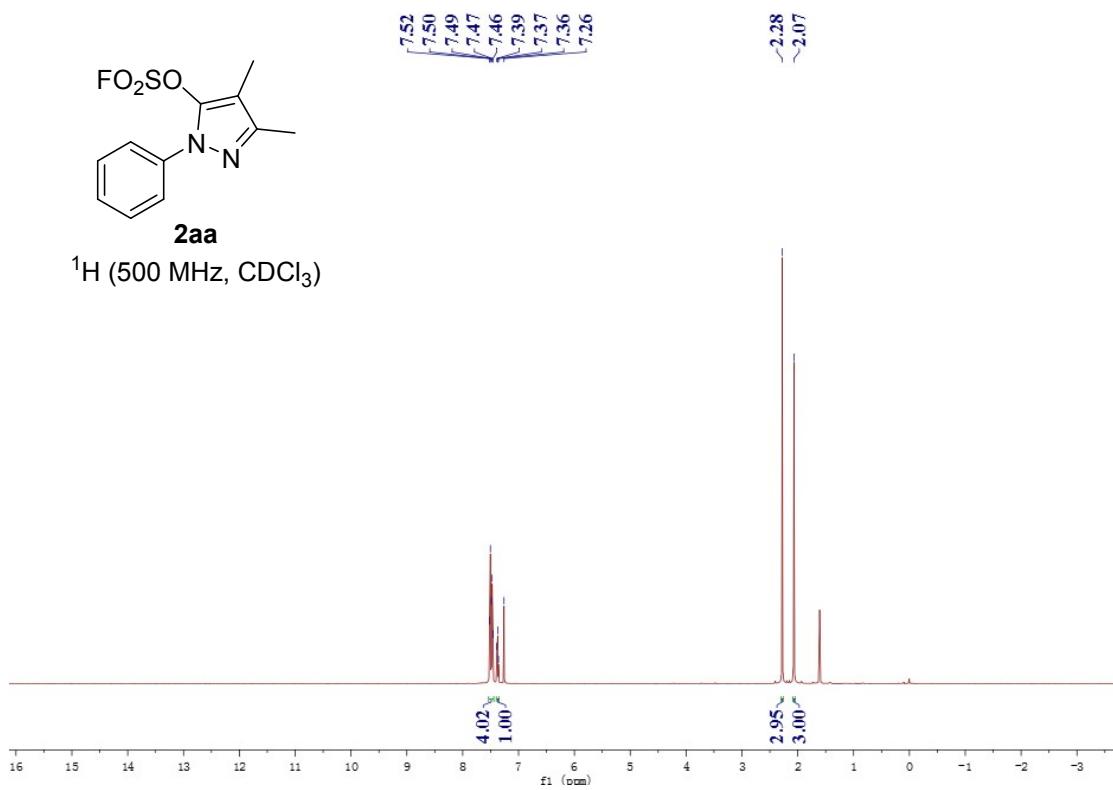
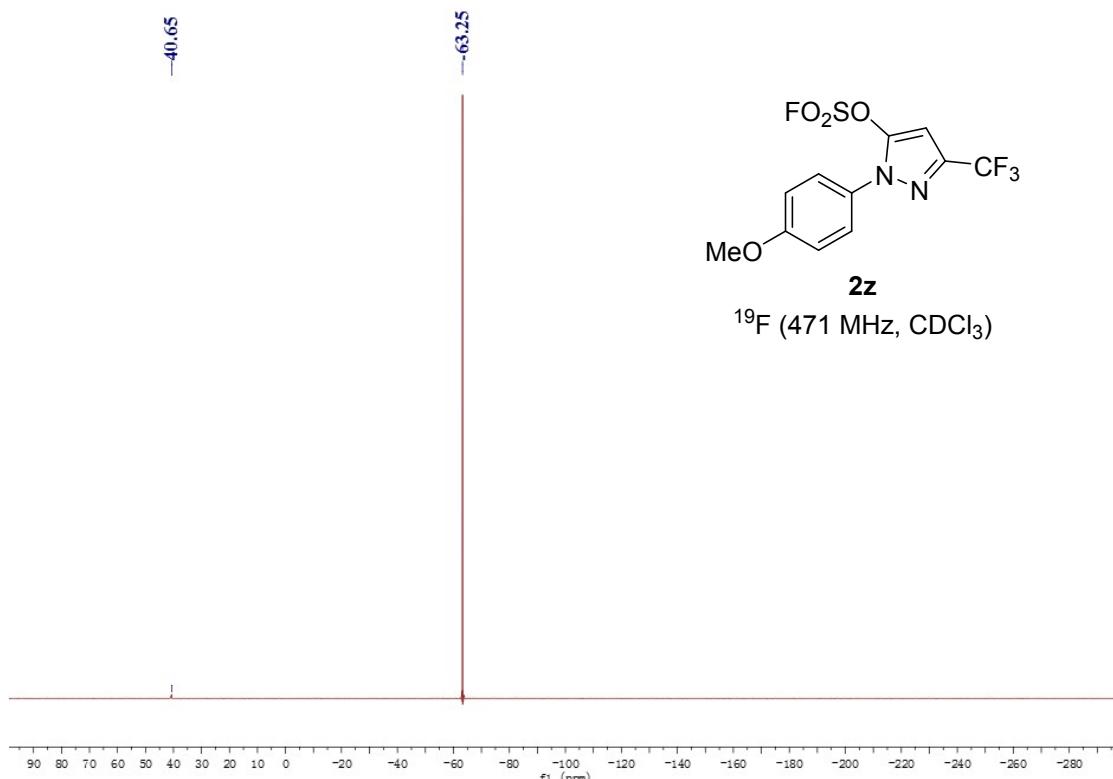


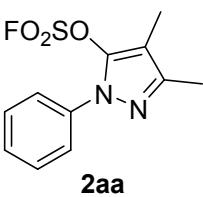
^1H (500 MHz, CDCl_3)



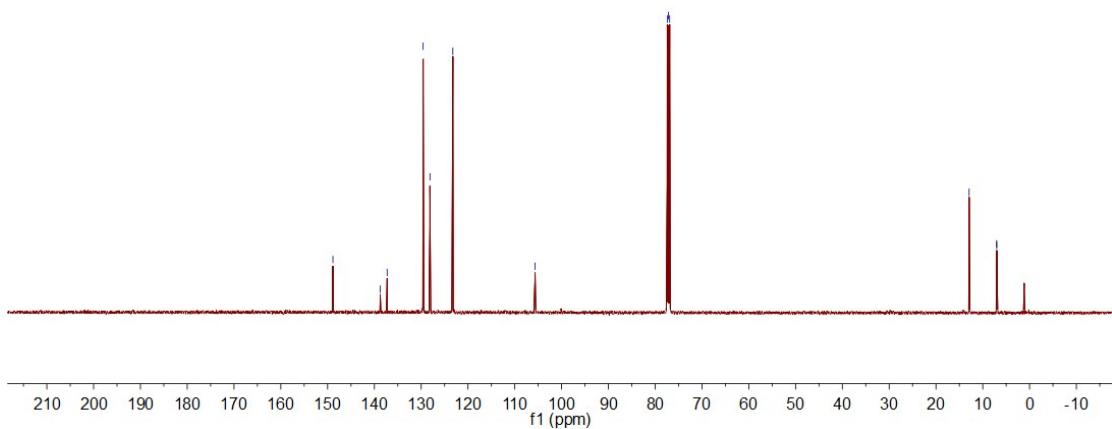




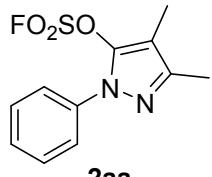




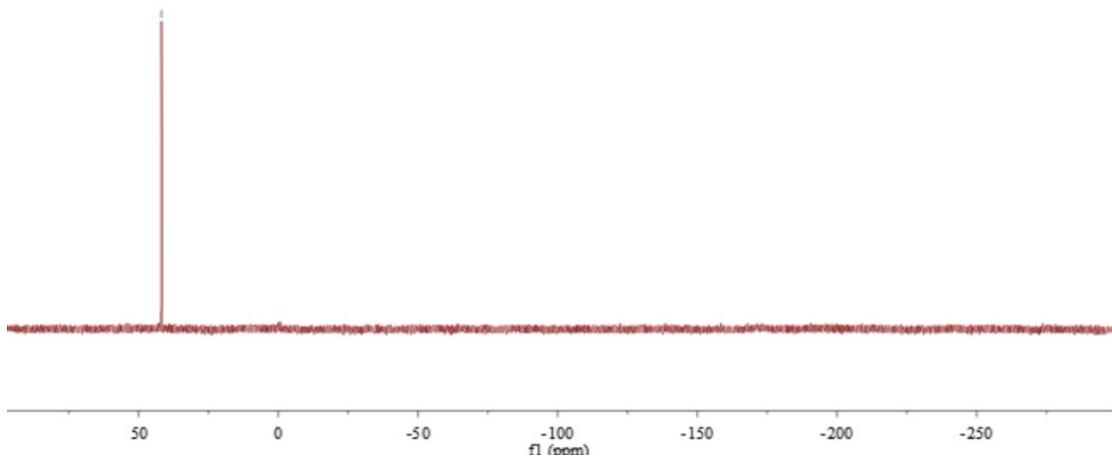
^{13}C (126 MHz, CDCl_3)

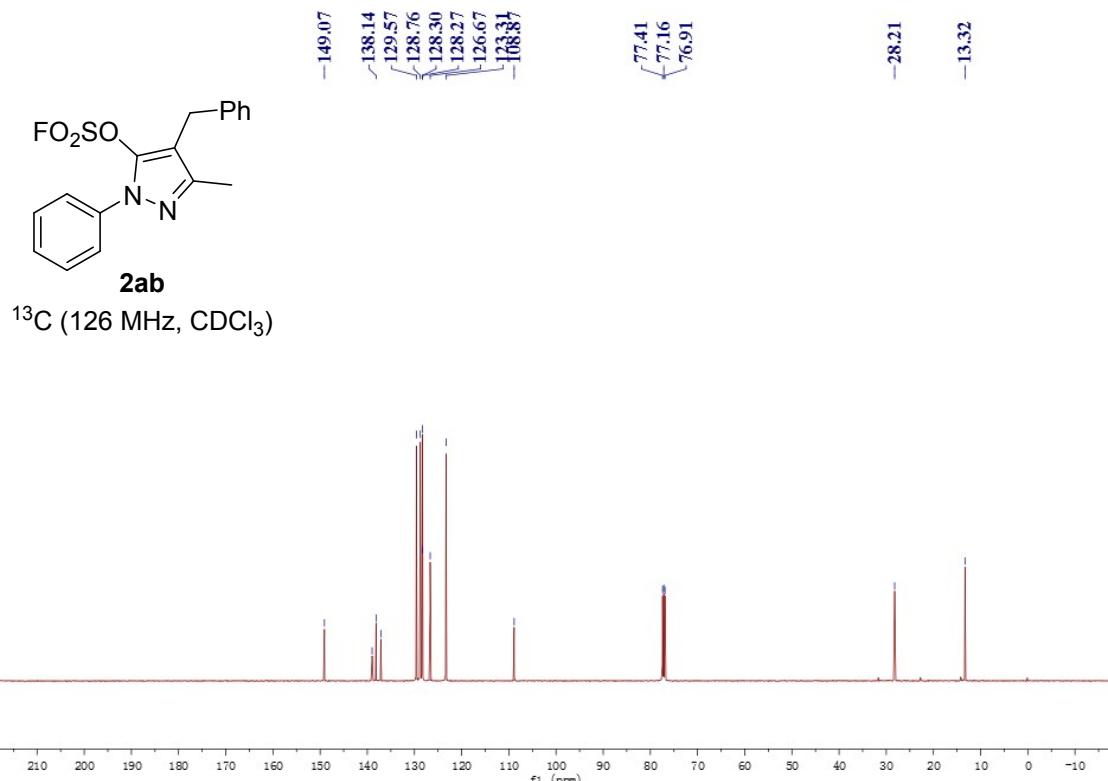
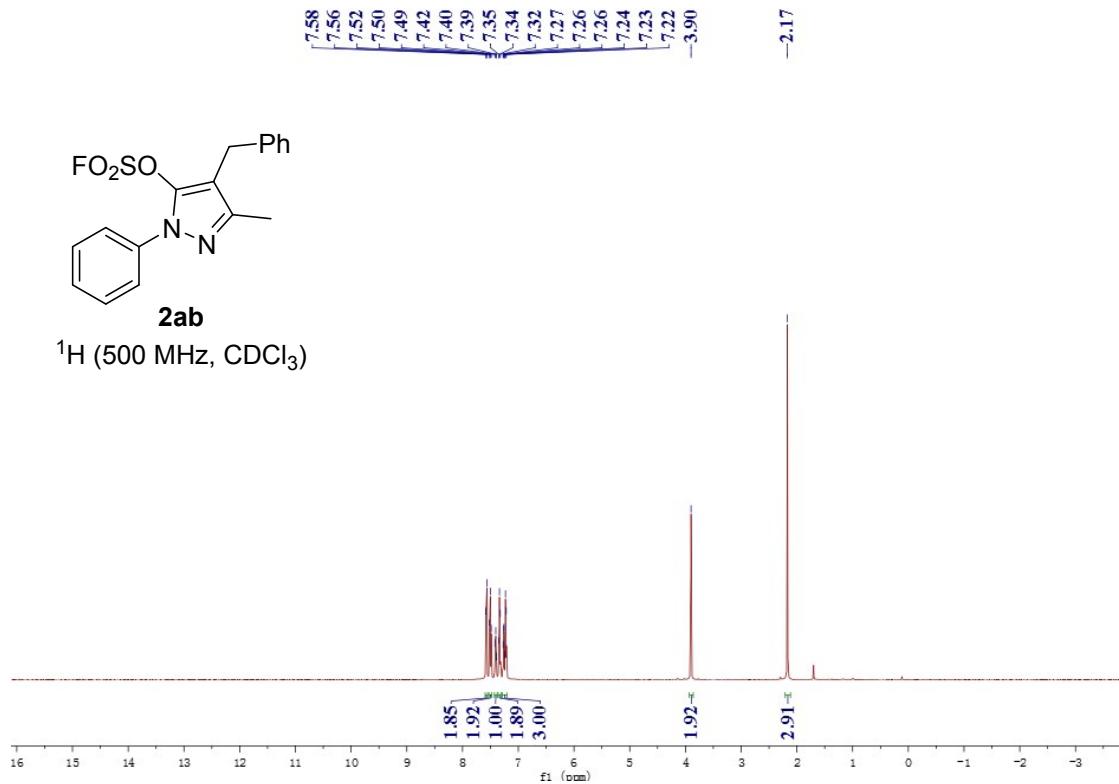


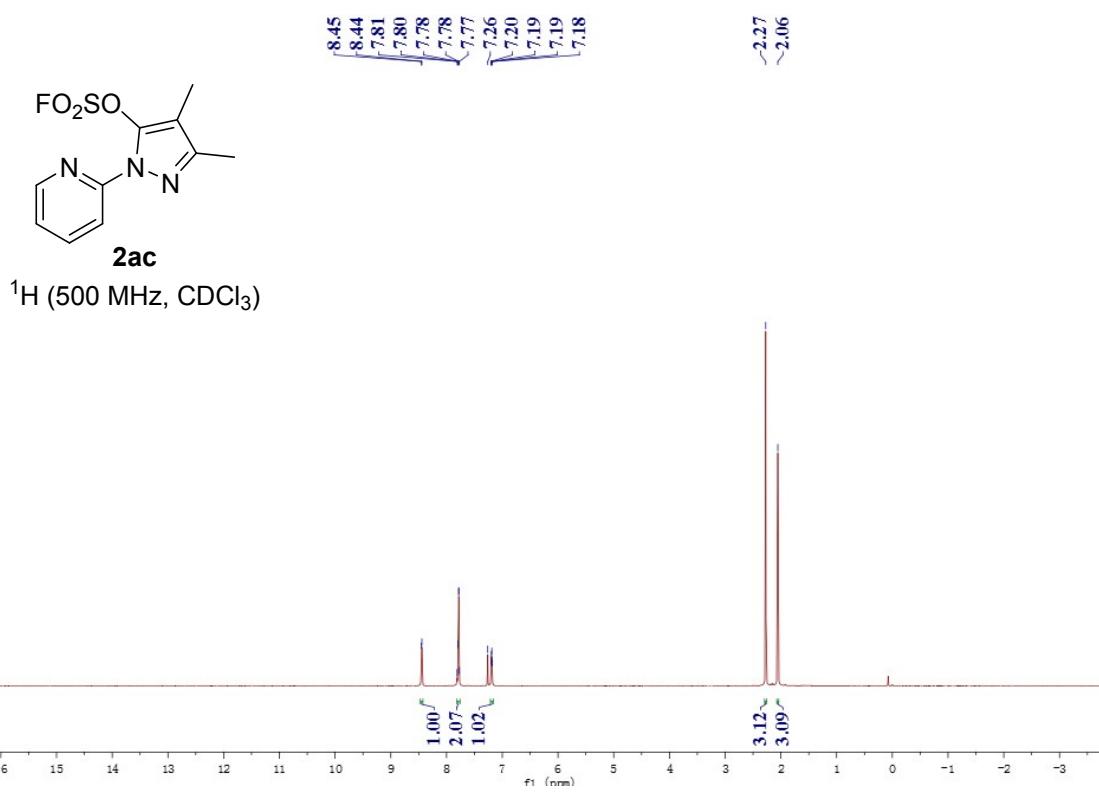
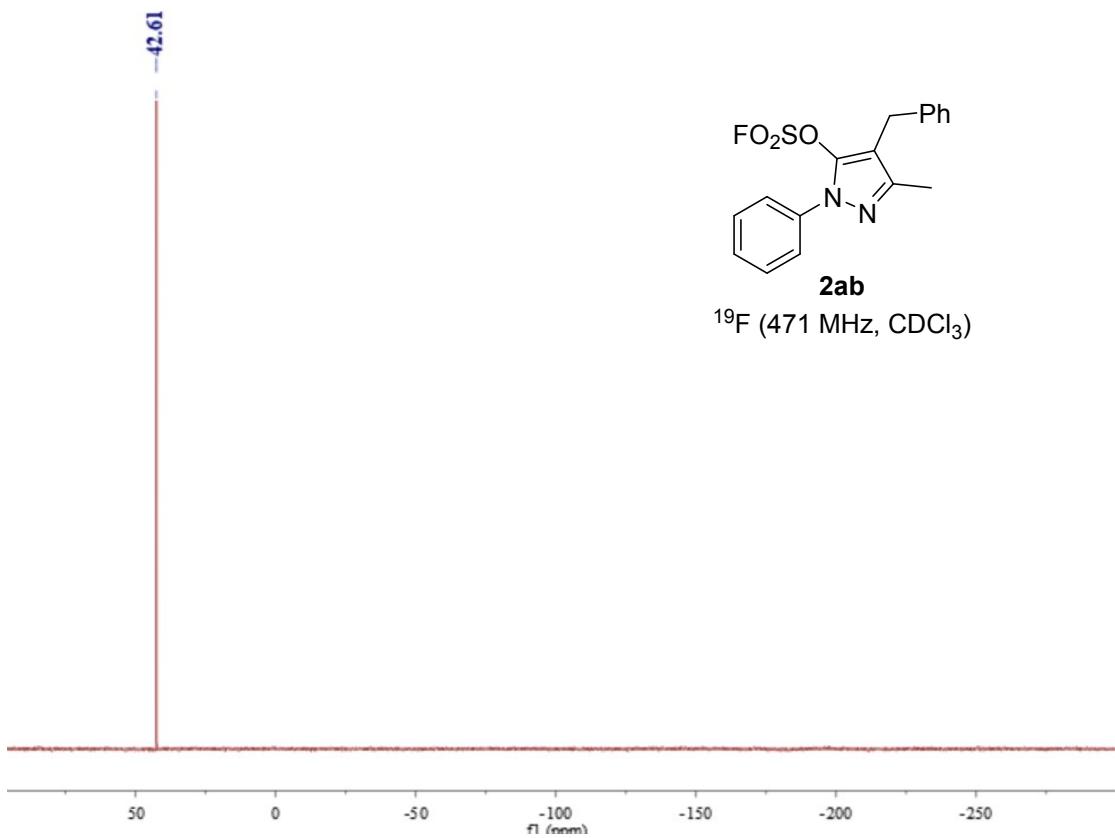
-41.96

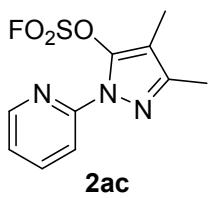


^{19}F (471 MHz, CDCl_3)

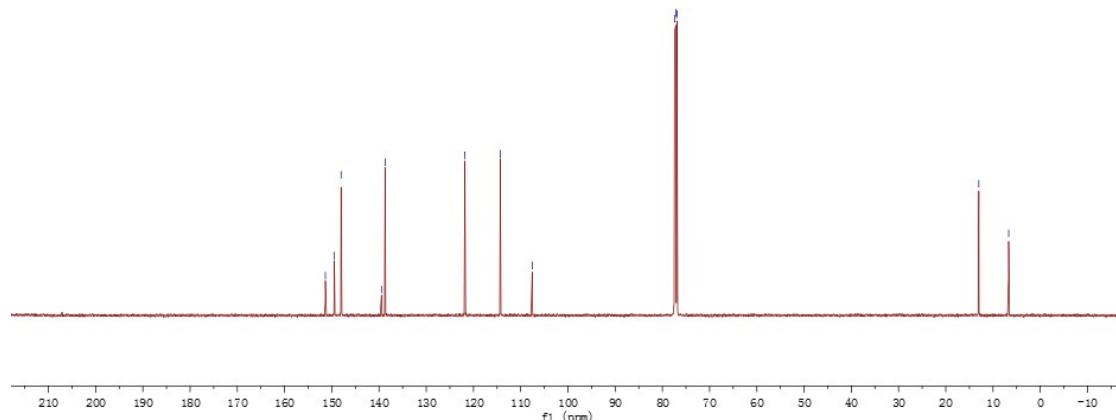




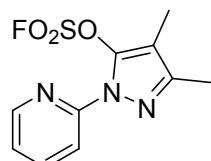




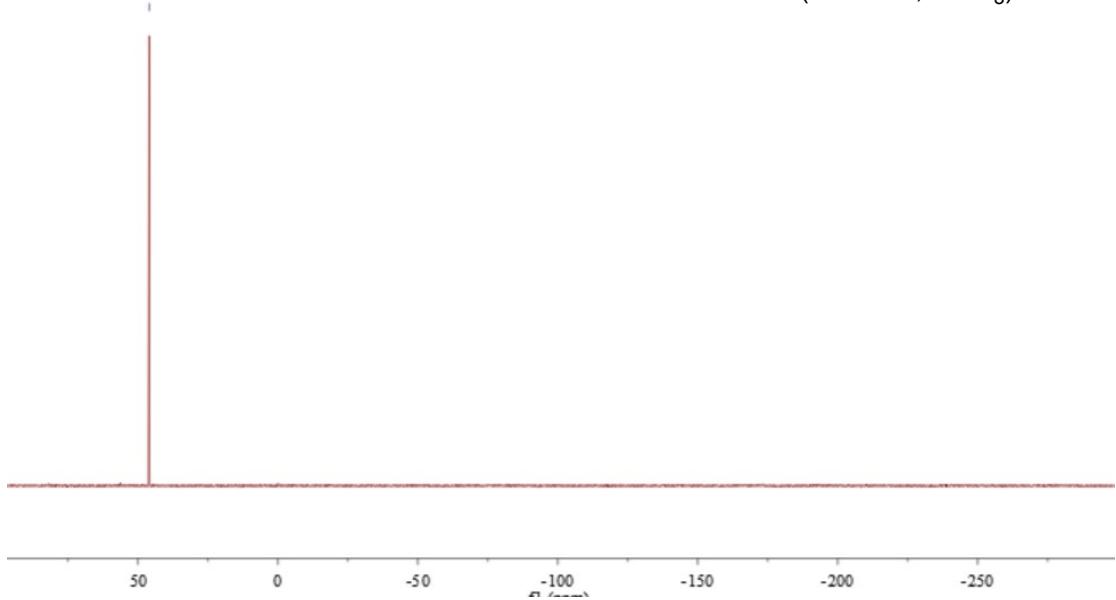
^{13}C (126 MHz, CDCl_3)

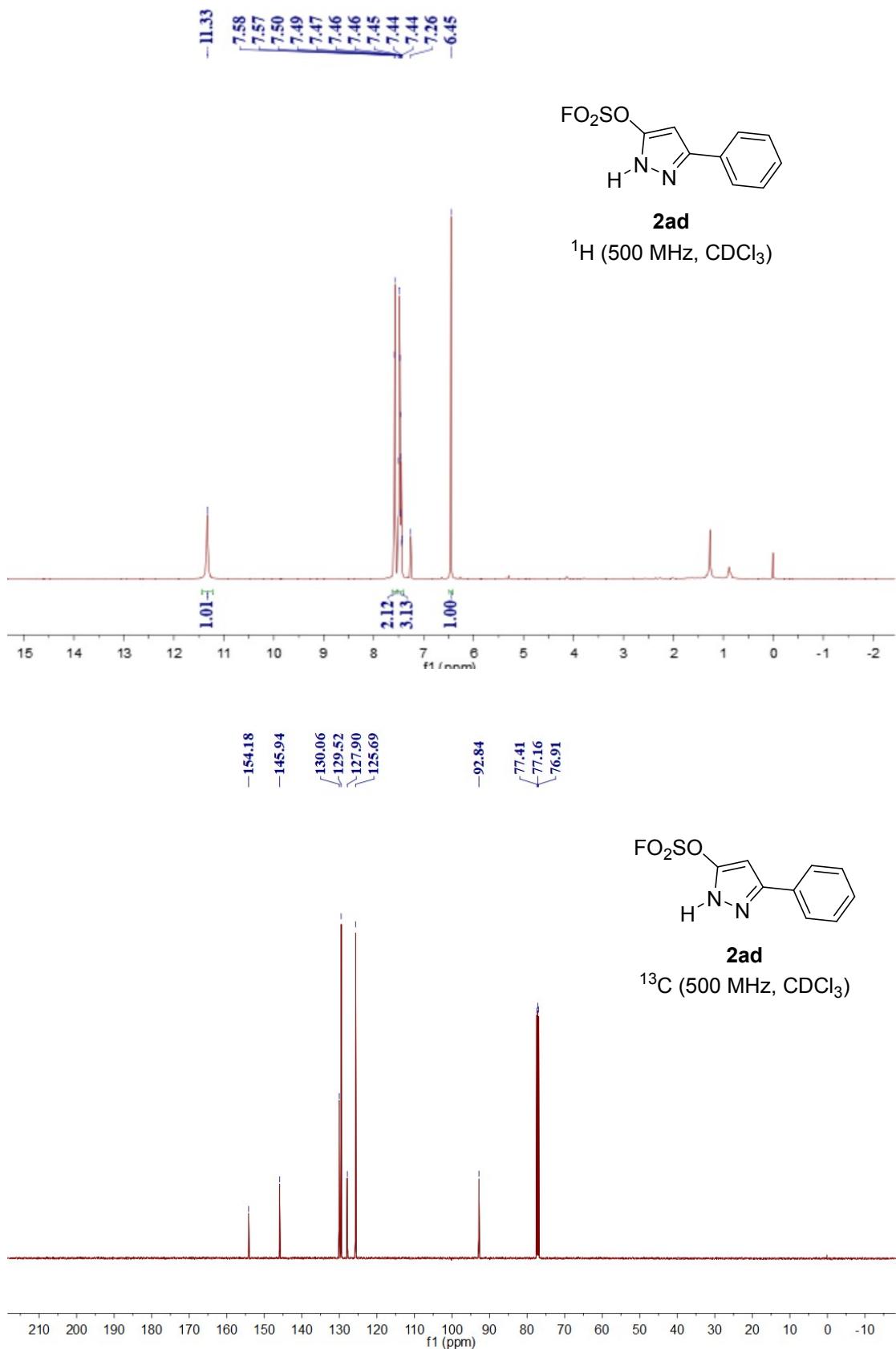


-46.14

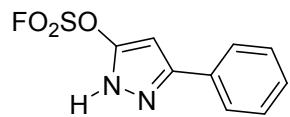


^{19}F (471 MHz, CDCl_3)



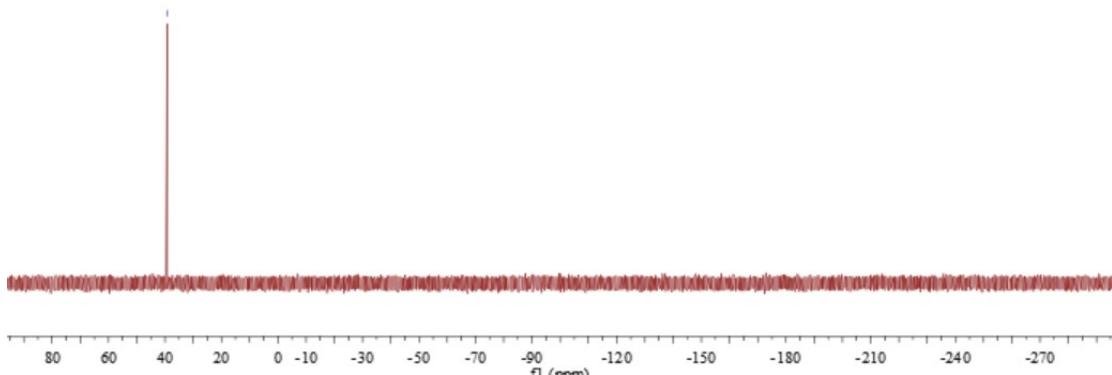


-39.23



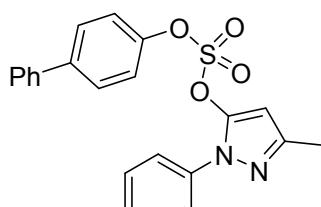
2ad

^{19}F (471 MHz, CDCl_3)



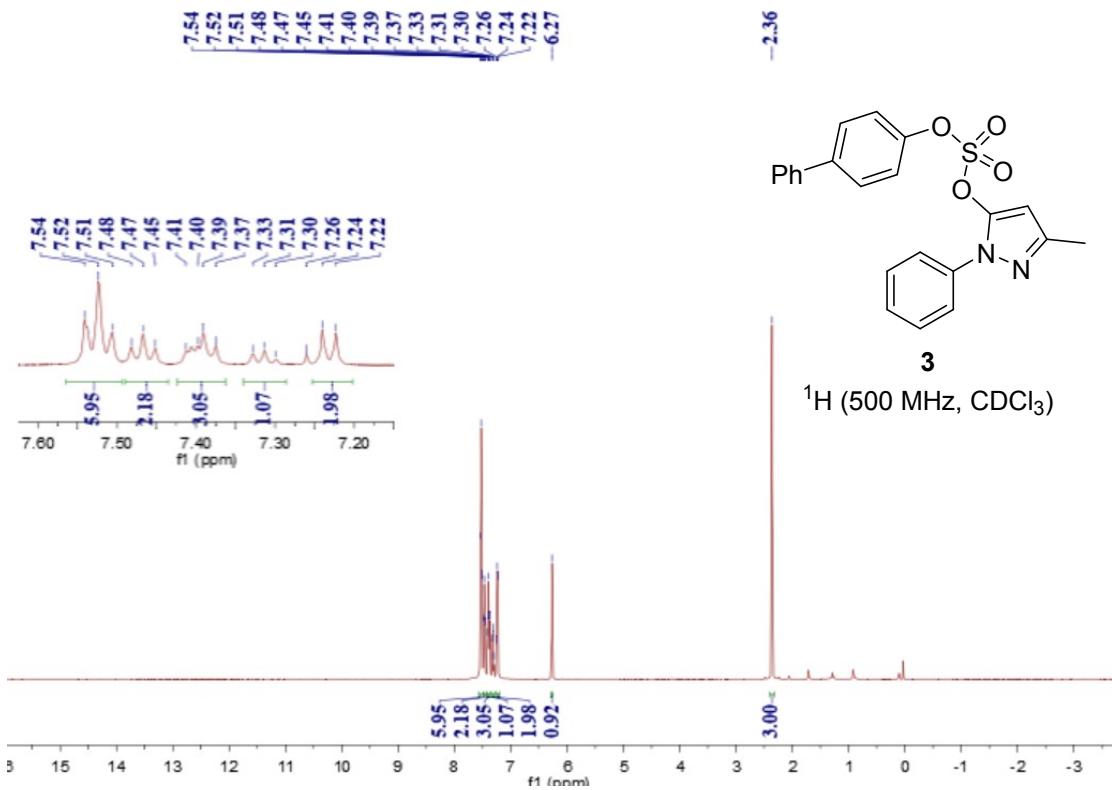
7.54
7.52
7.51
7.48
7.47
7.45
7.41
7.40
7.39
7.37
7.33
7.31
7.30
7.26
7.24
7.22
7.21
7.20

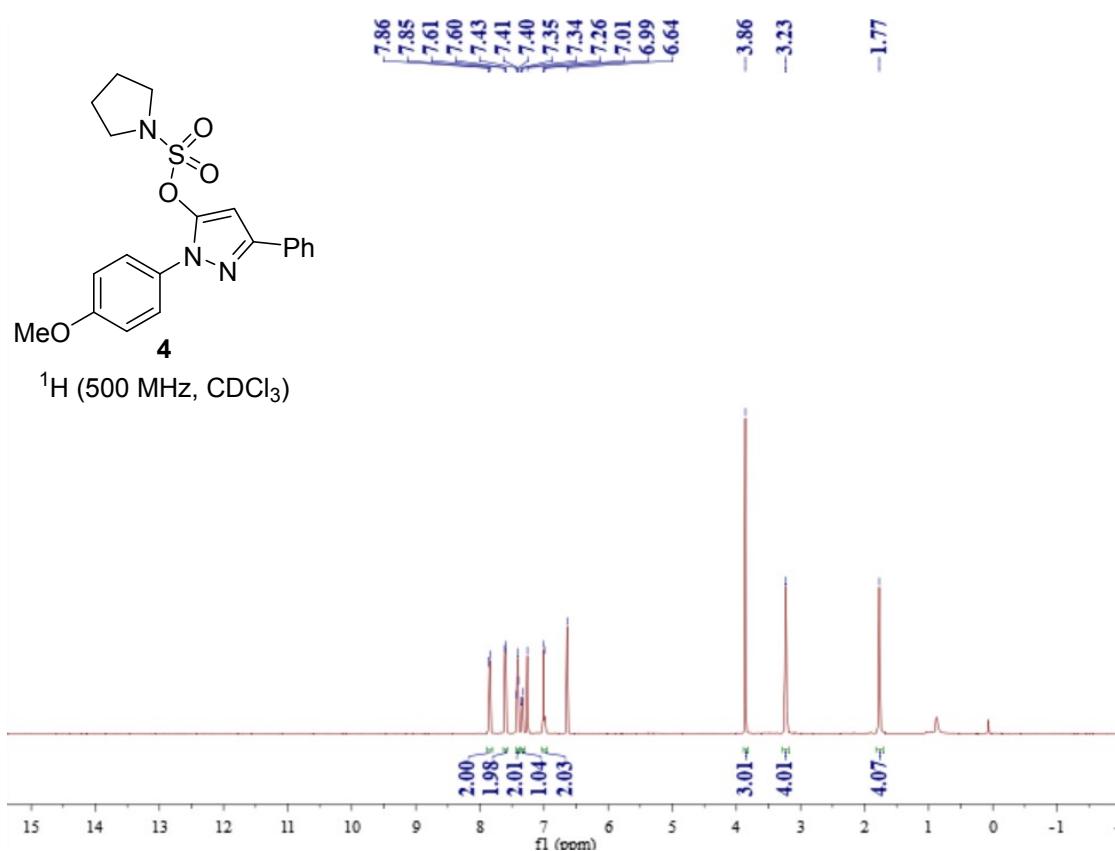
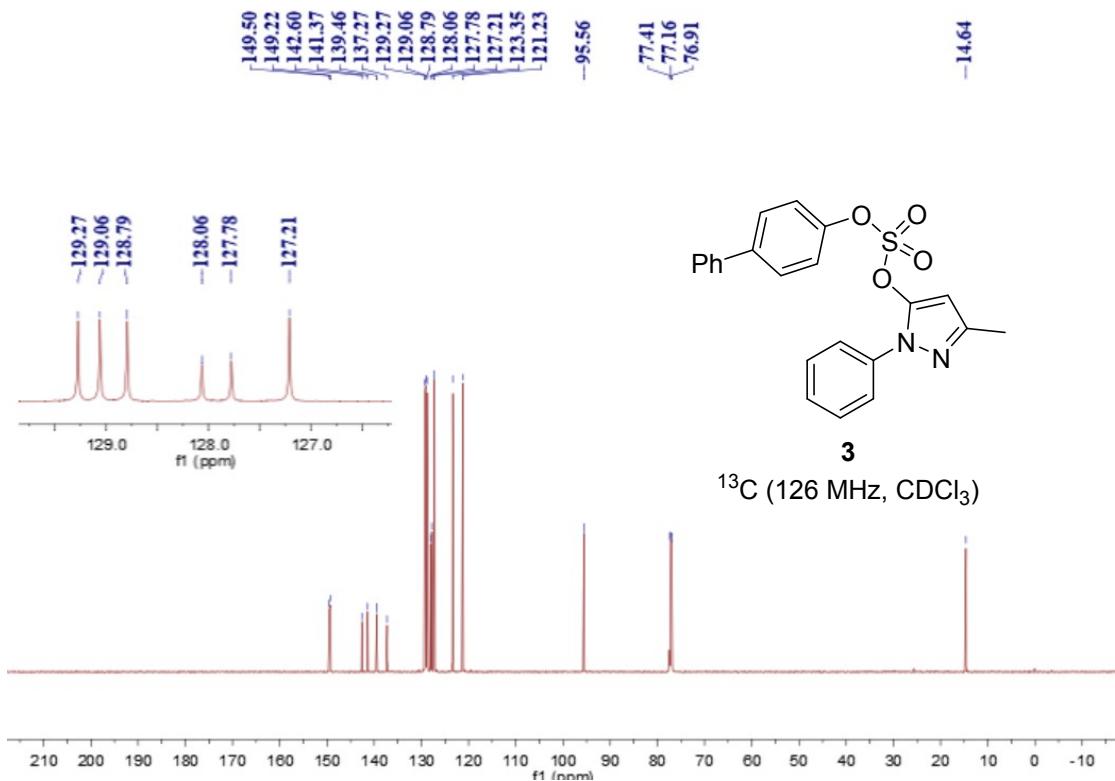
-2.36

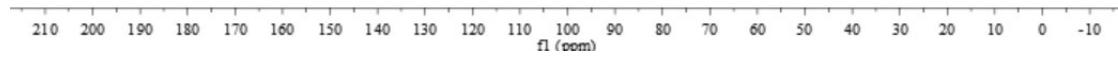
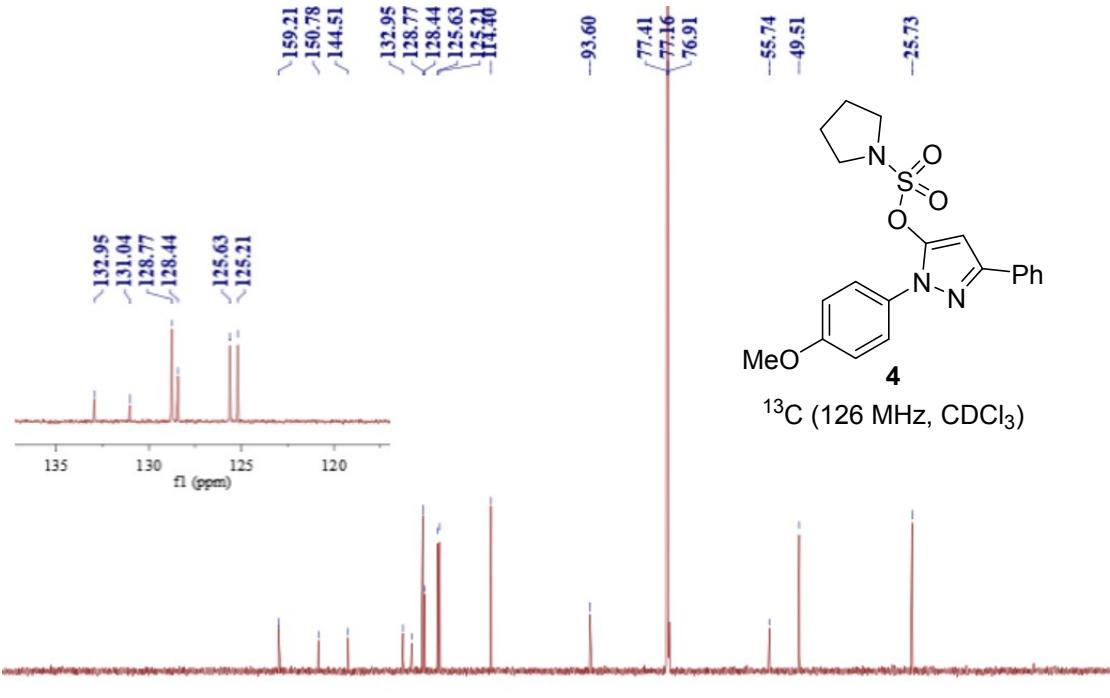


3

^1H (500 MHz, CDCl_3)







5
 ^1H (500 MHz, CDCl_3)

