

Supporting Information for

A cascade trisulfur radical anion ($S_3^{\bullet-}$) addition / electron de-tosylation process for the synthesis of 1,2,3-thiadiazoles and isothiazoles

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Optimization of The Reaction Conditions

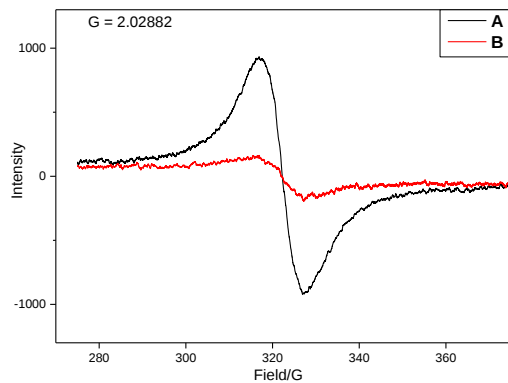
Table S1. Optimization of the reaction conditions^a

entry	base	time	solvent	yield (%) ^b
1		1.5h	DMF	43
2	K ₂ CO ₃	10min	DMF	52
3	K ₃ PO ₄	10min	DMF	40
4	NaHCO ₃	1h	DMF	53
5	Et ₃ N	10min	DMF	42
6	DIPEA	1h	DMF	41
7	Cs ₂ CO ₃	7min	DMF	42
8	DBU	1.5h	DMF	52
9	EtONa	2h	DMF	48
10	Ba ₂ CO ₃	1h	DMF	36
11	LiCO ₃	1h	DMF	59
12	KOH	10min	DMF	32
13	K ₂ CO ₃	1h	THF	0
14	K ₂ CO ₃	1h	1,4-dioxane	19
15	K ₂ CO ₃	10min	toluene	0
16	K ₂ CO ₃	0.5h	DMSO	48
17	K ₂ CO ₃	1h	EtOH	22
18	K ₂ CO ₃	2h	EtOAc	39
19 ^c	K ₂ CO ₃	1.5h	DMF	52
20 ^d	K ₂ CO ₃	10min	DMF	55
21 ^e	K ₂ CO ₃	1h	DMF	43
22 ^f	K ₂ CO ₃	17min	DMF	53
23 ^g	S+KOH	0.5h	DMF	messy
24^h	K₂CO₃	0.5h	DMF	66
25 ⁱ	K ₂ CO ₃	1h	DMF	50
26 ^j	K ₂ CO ₃	0.5h	DMF	52

^aReaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol), base (0.3 mmol) and solvent (1.5mL) at 100 °C. The time of the reaction was according to TLC. ^bYields were determined by LC analysis using biphenyl as the internal standard. ^cBase (K₂CO₃ 0.15 mmol). ^dBase

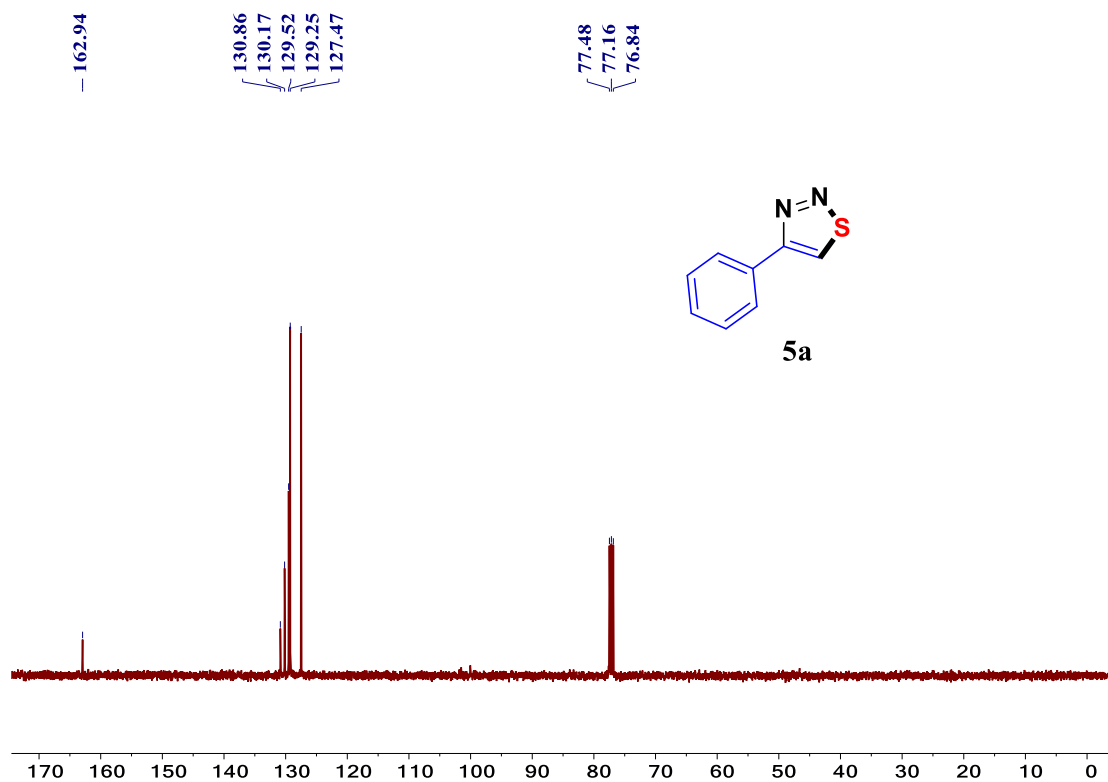
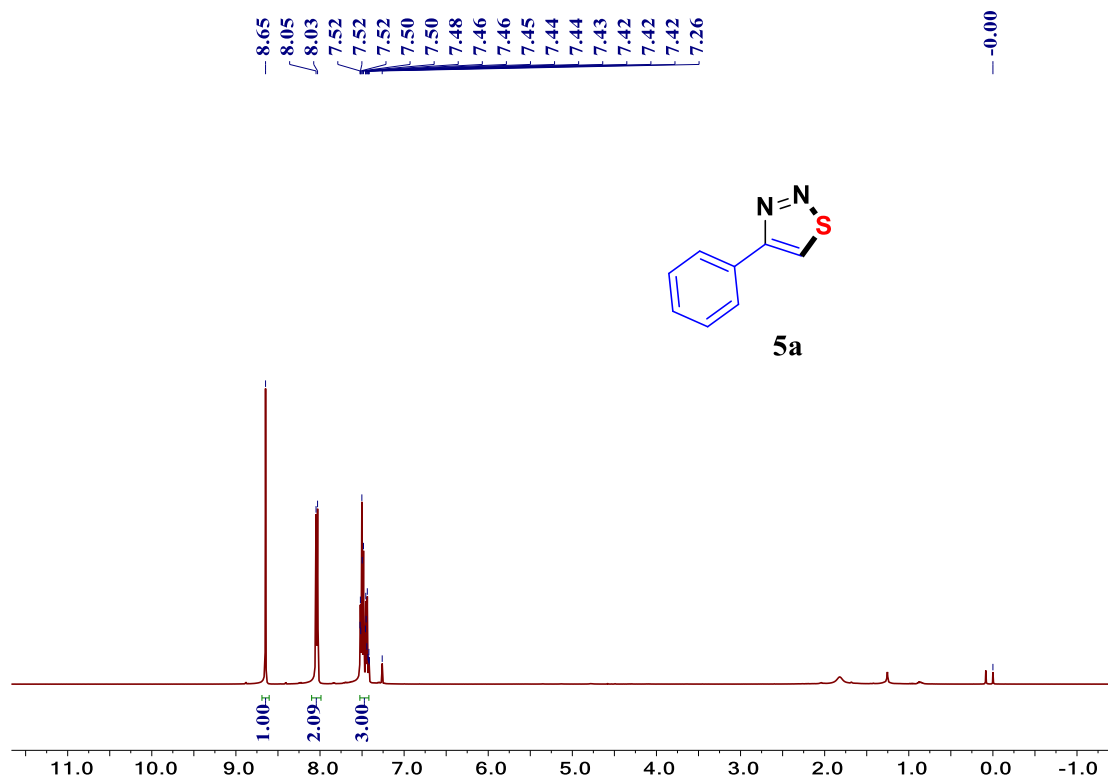
(K_2CO_3 0.6 mmol). ^eTemperature = 60 °C. ^fTemperature = 80 °C. ^gSulfur reagent (S, 0.9 mmol), base (KOH, 0.15 mmol). ^hBase (K_2CO_3 0.15 mmol), 130 °C. ⁱSulfur reagent (K_2S , 0.45 mmol), base (K_2CO_3 0.15 mmol), 130 °C. ^jSulfur reagent (K_2S , 0.75 mmol), base (K_2CO_3 0.15 mmol), 130 °C.

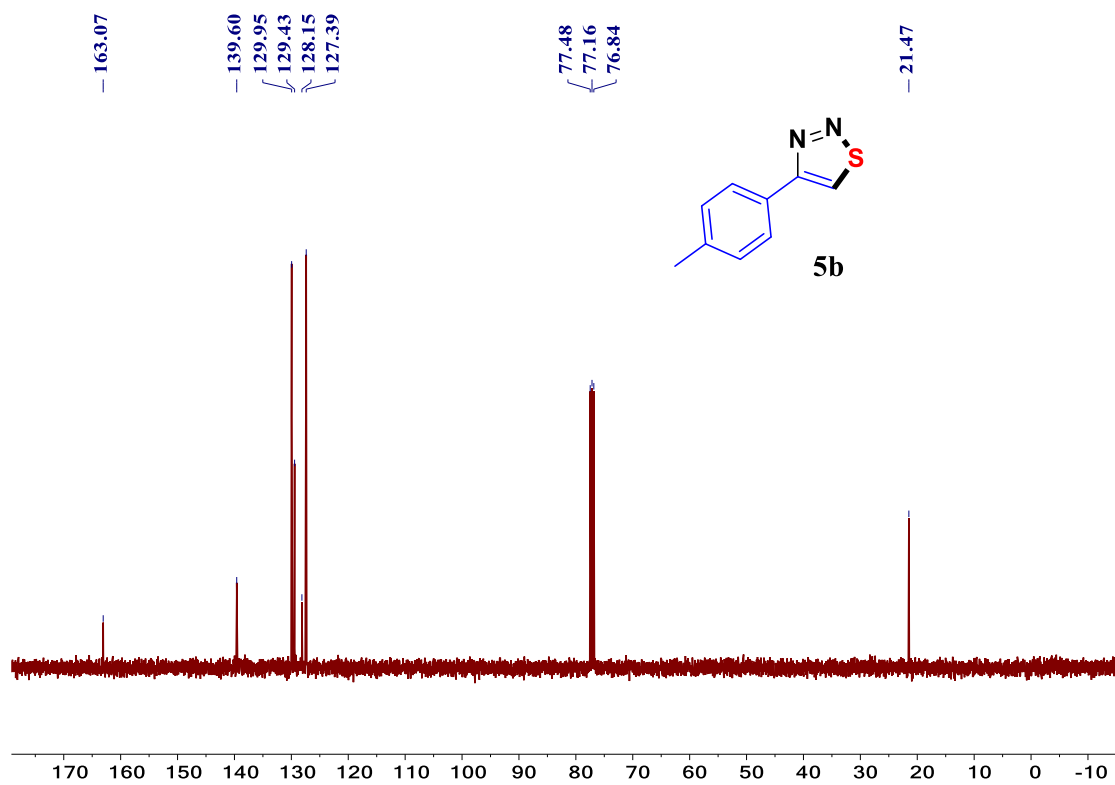
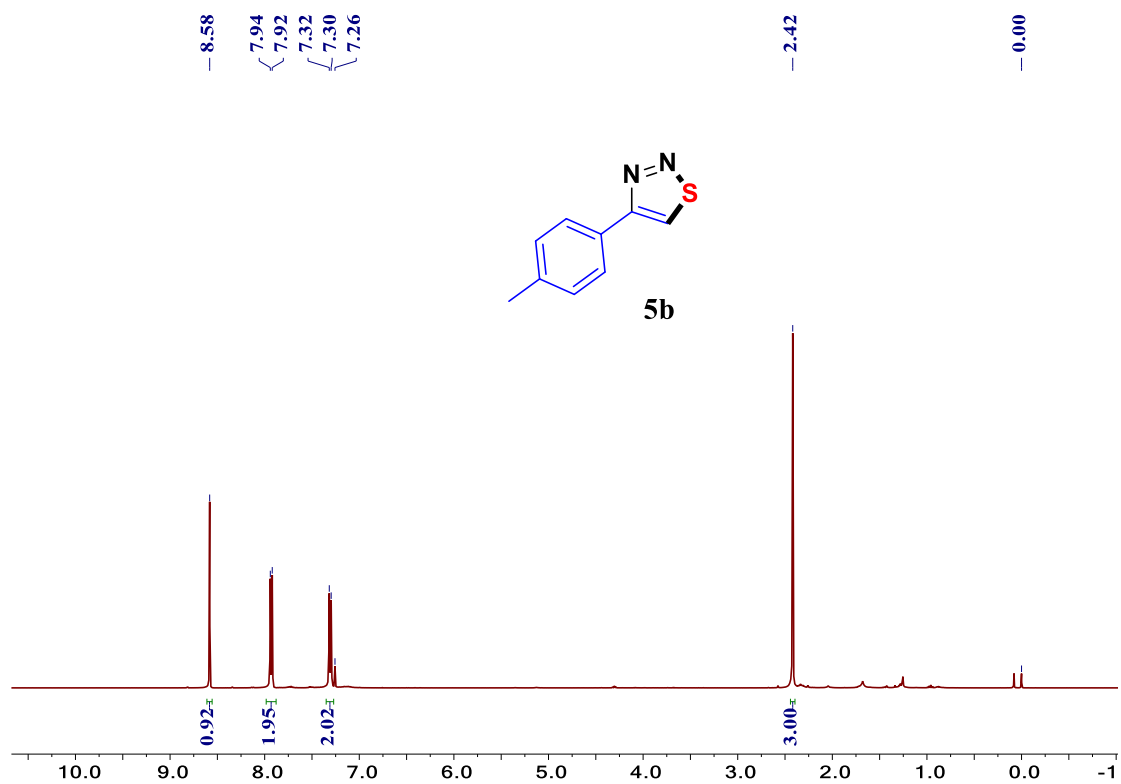
Figure S1. ESR studies of K_2S in different conditions.

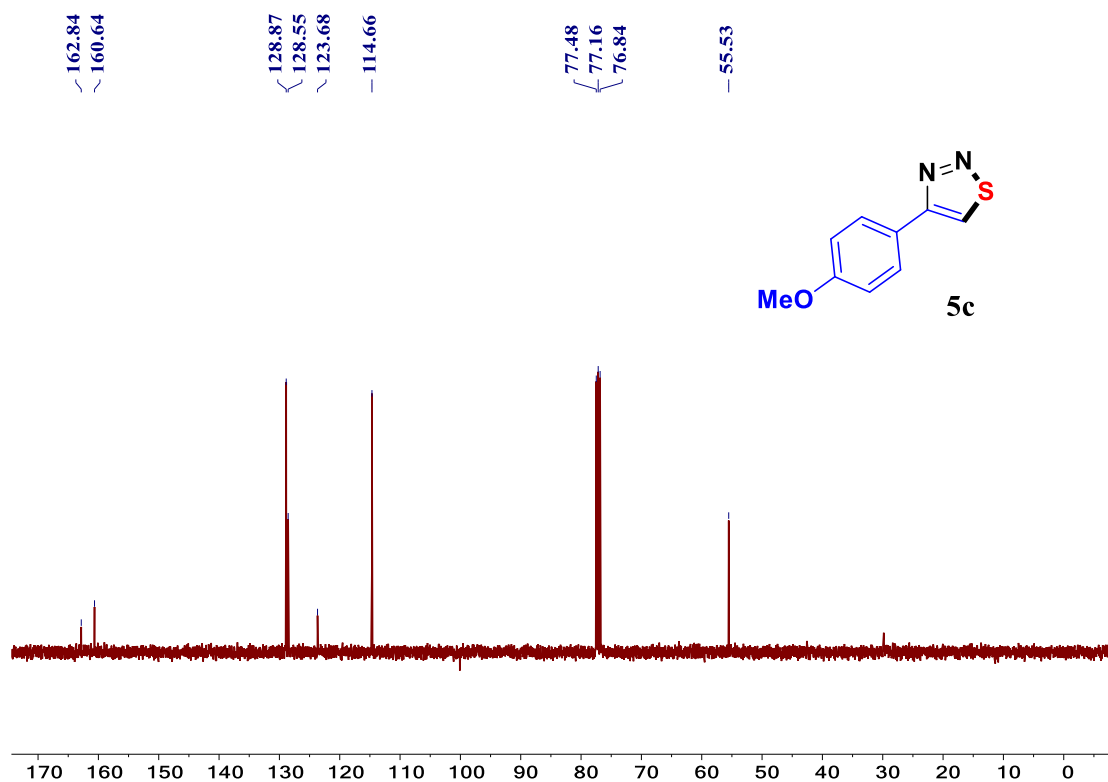
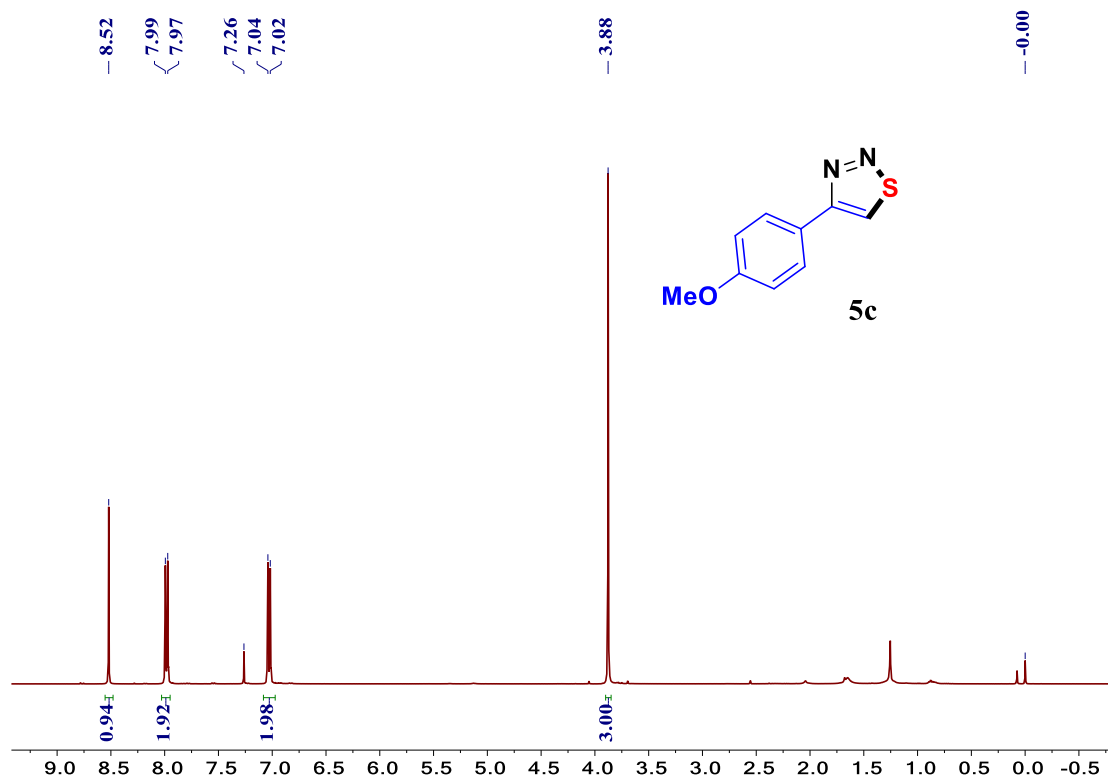


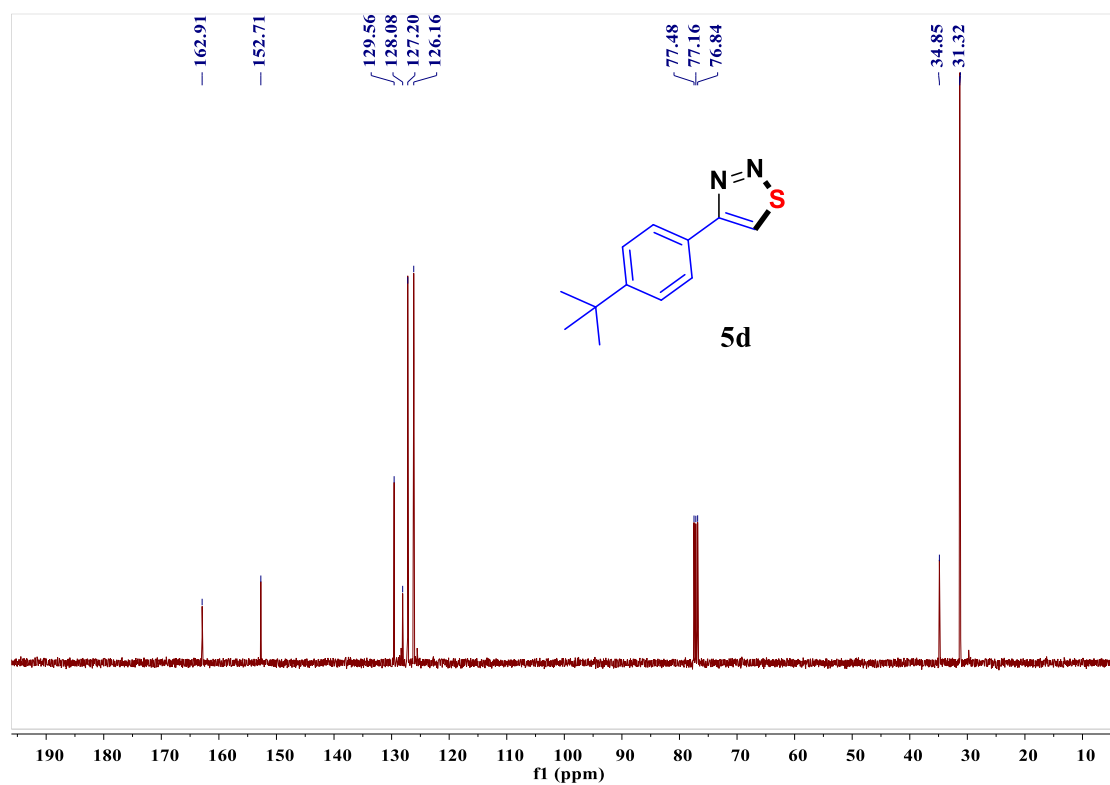
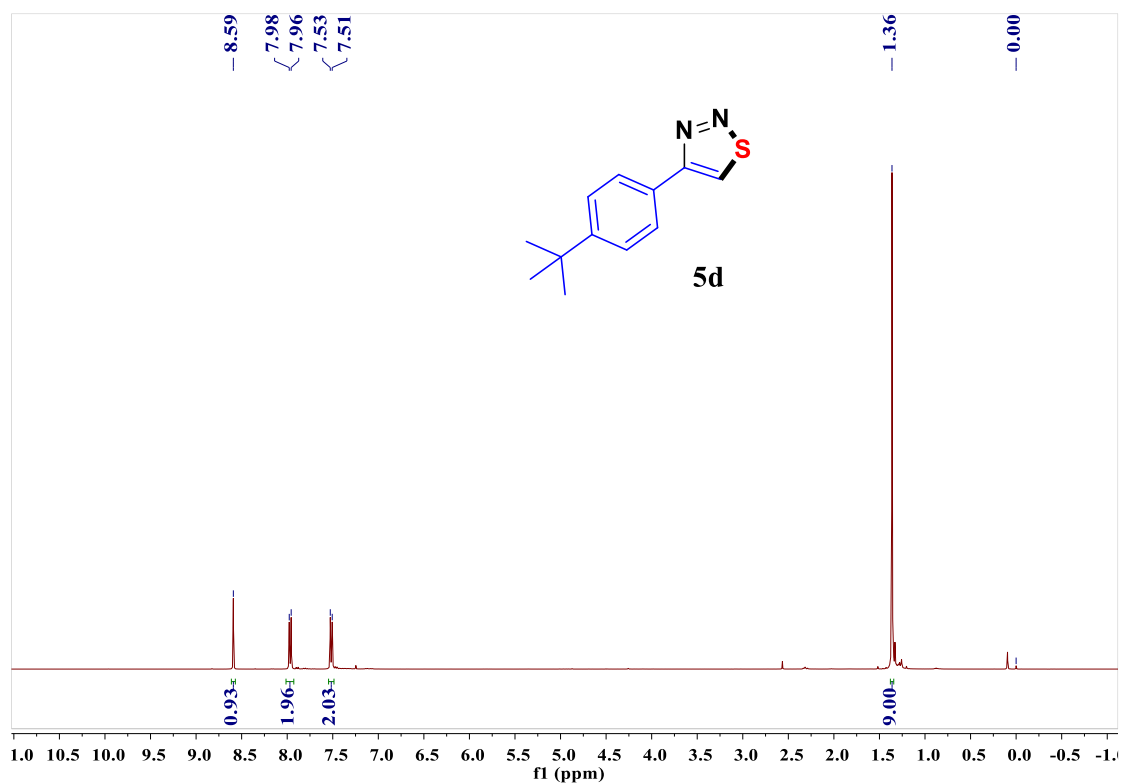
Condition **A**: K_2S (0.6 mmol) in 2 mL DMF at room temperature. Condition **B**: K_2S (0.6 mmol) and K_2CO_3 (0.15 mmol) in 2 mL DMF at room temperature.

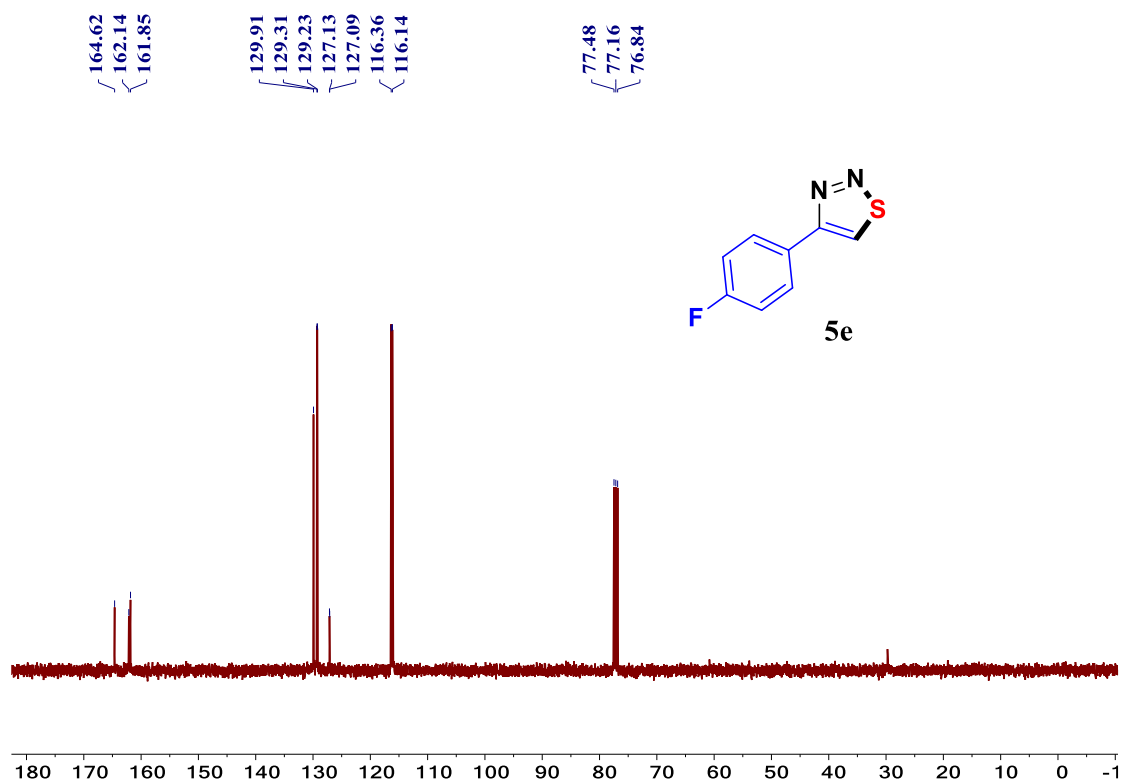
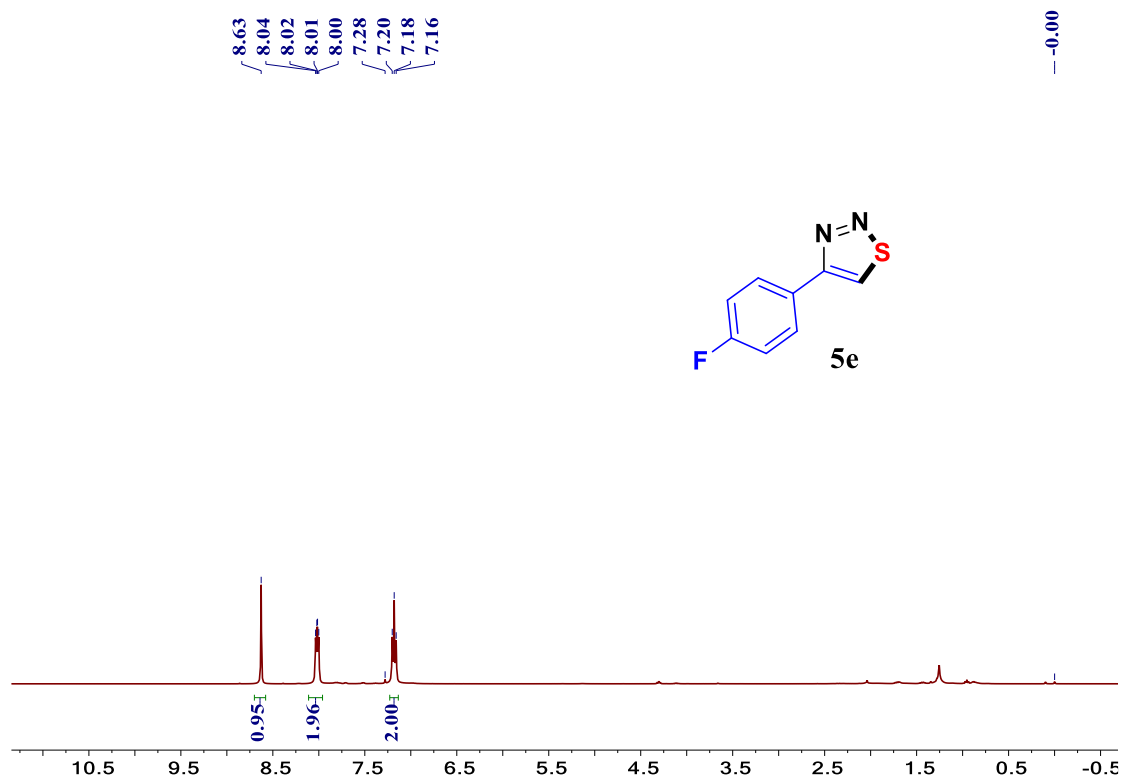
Spectroscopic Data for Products

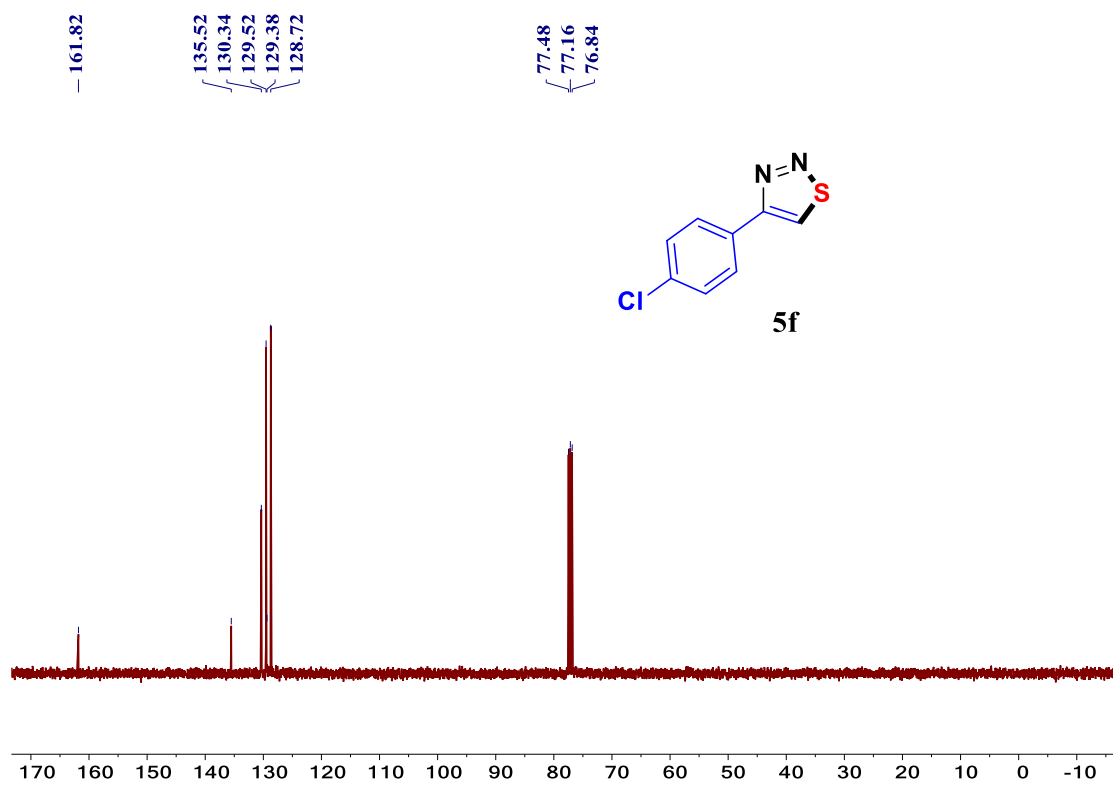
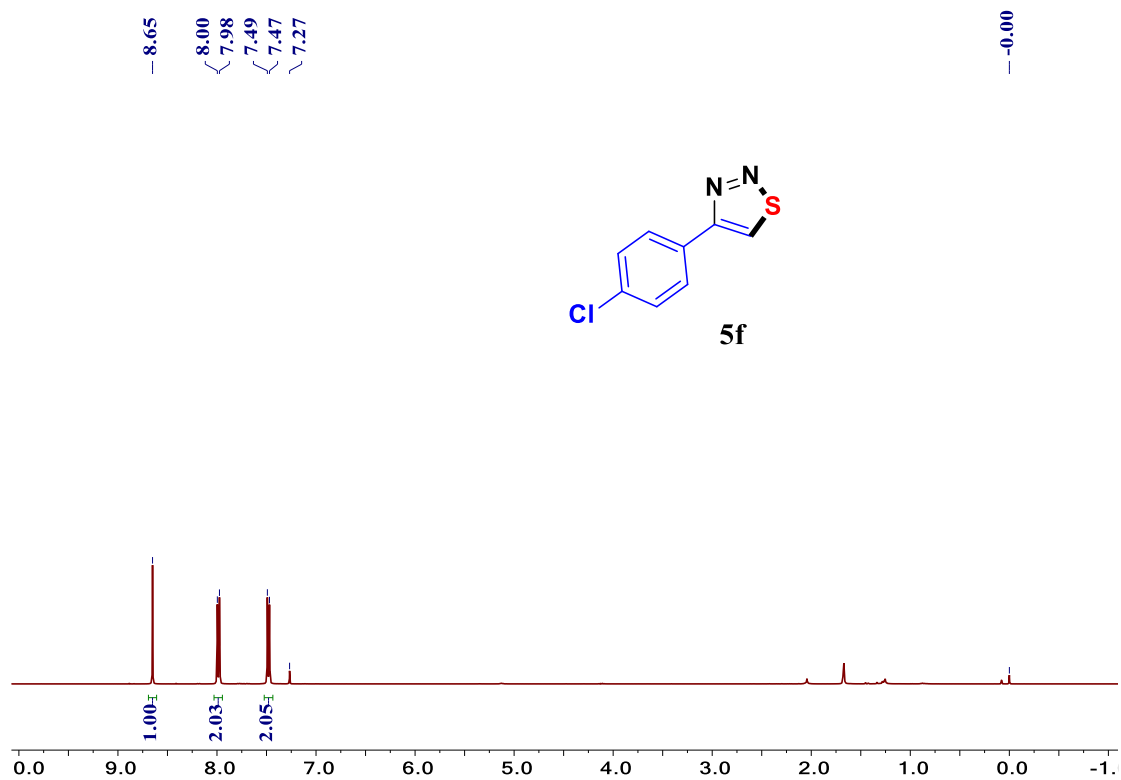


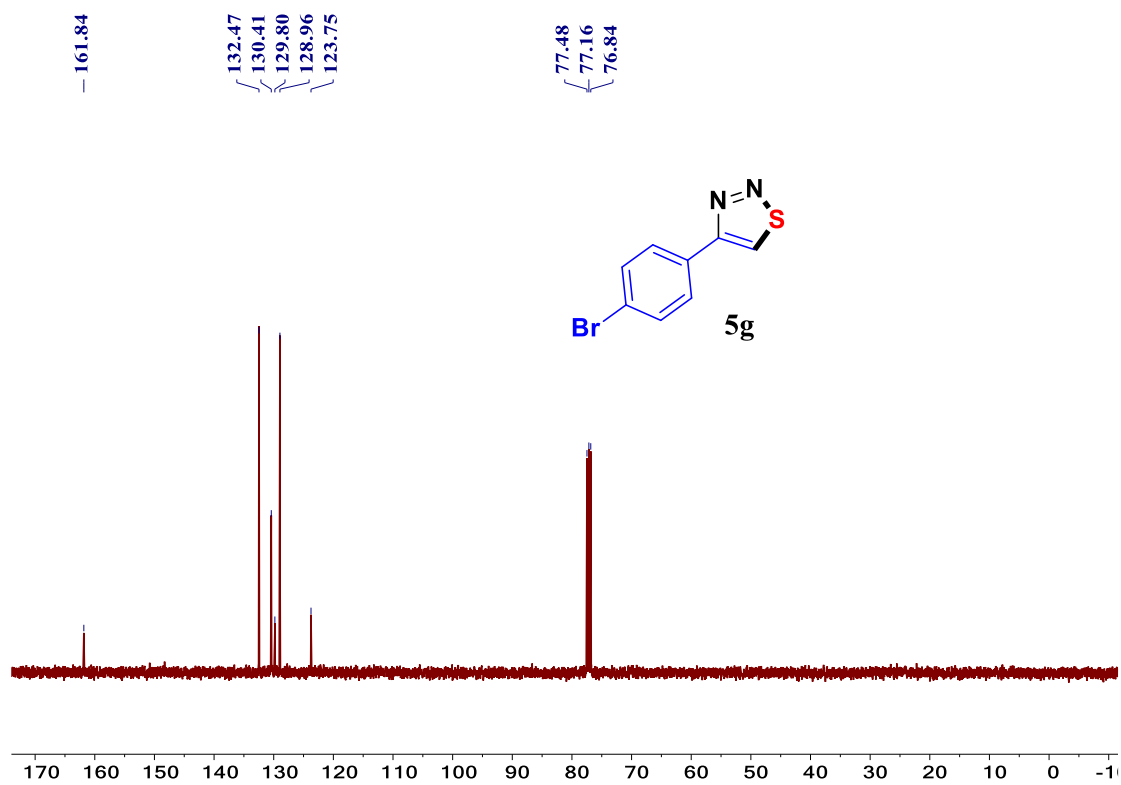
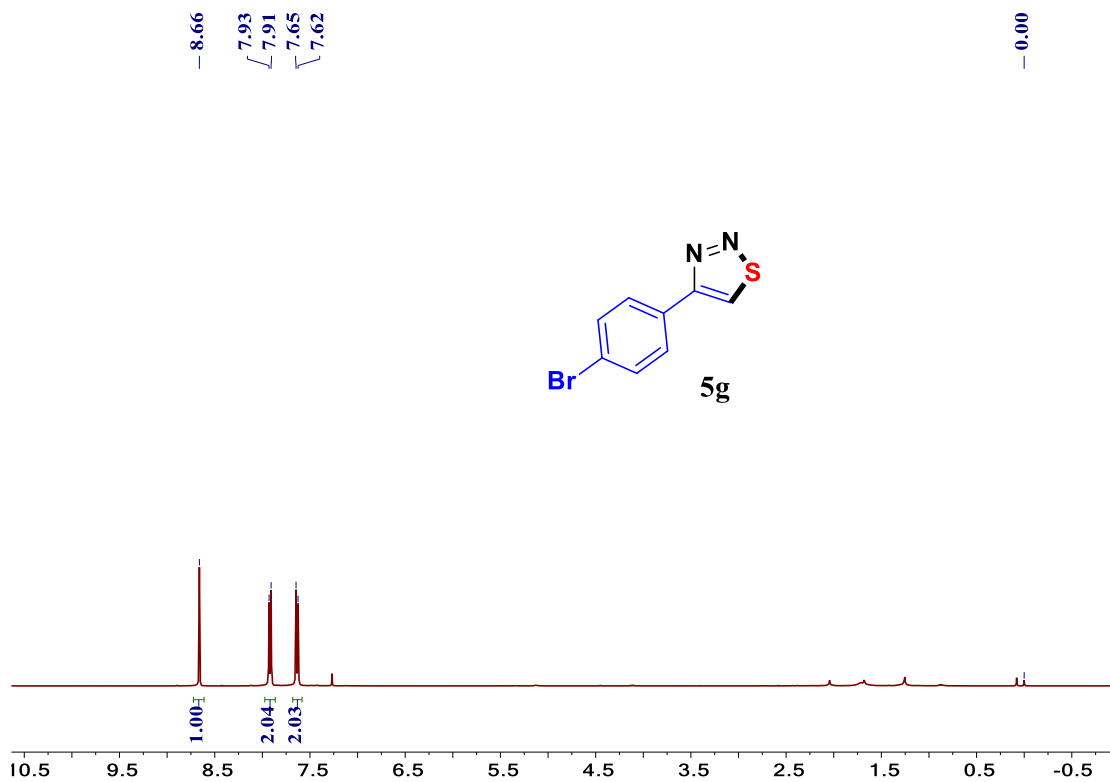


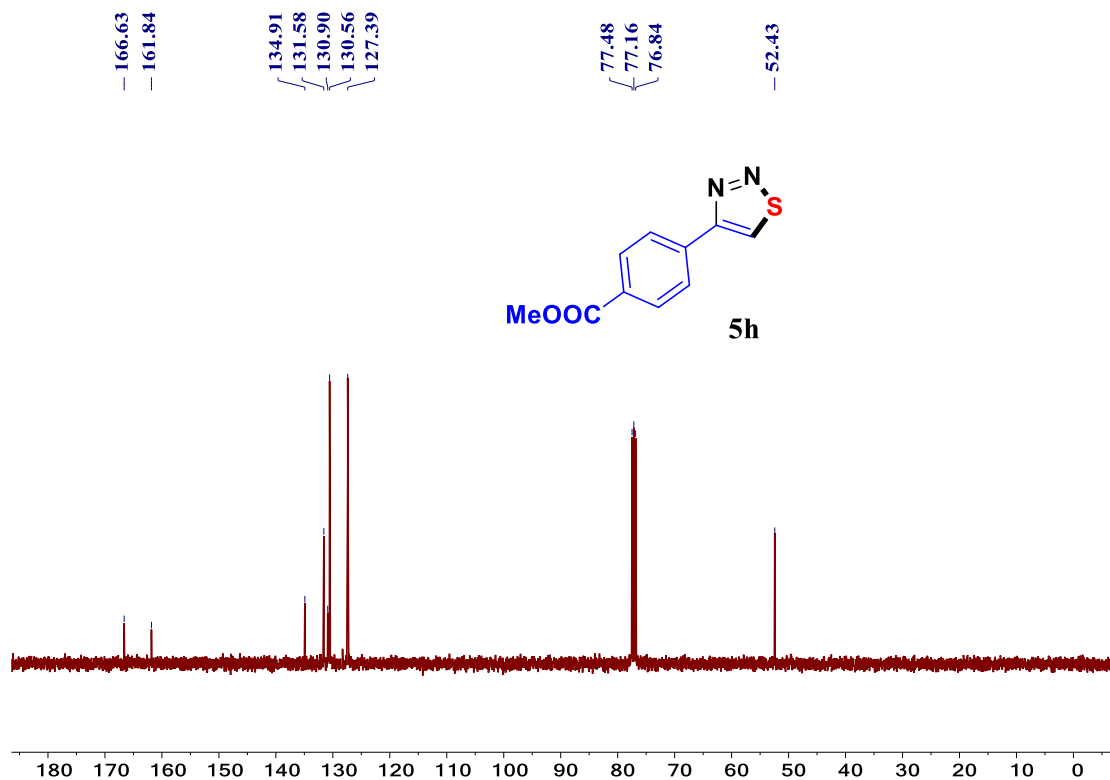
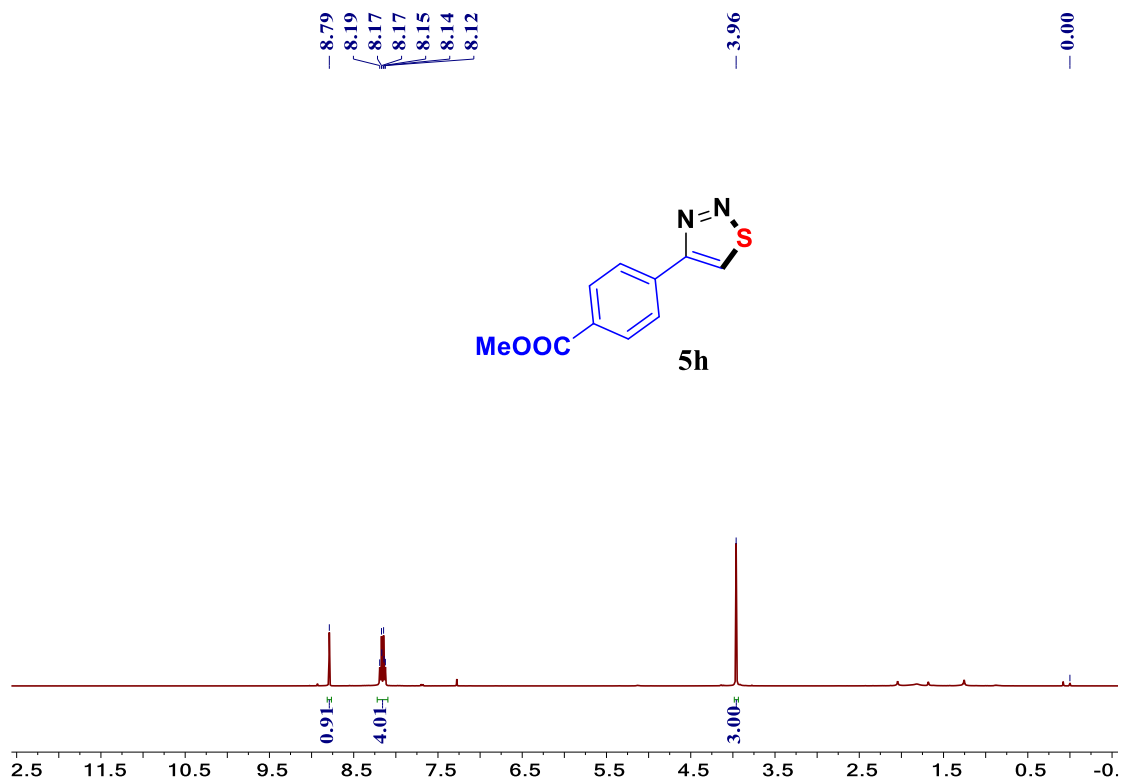


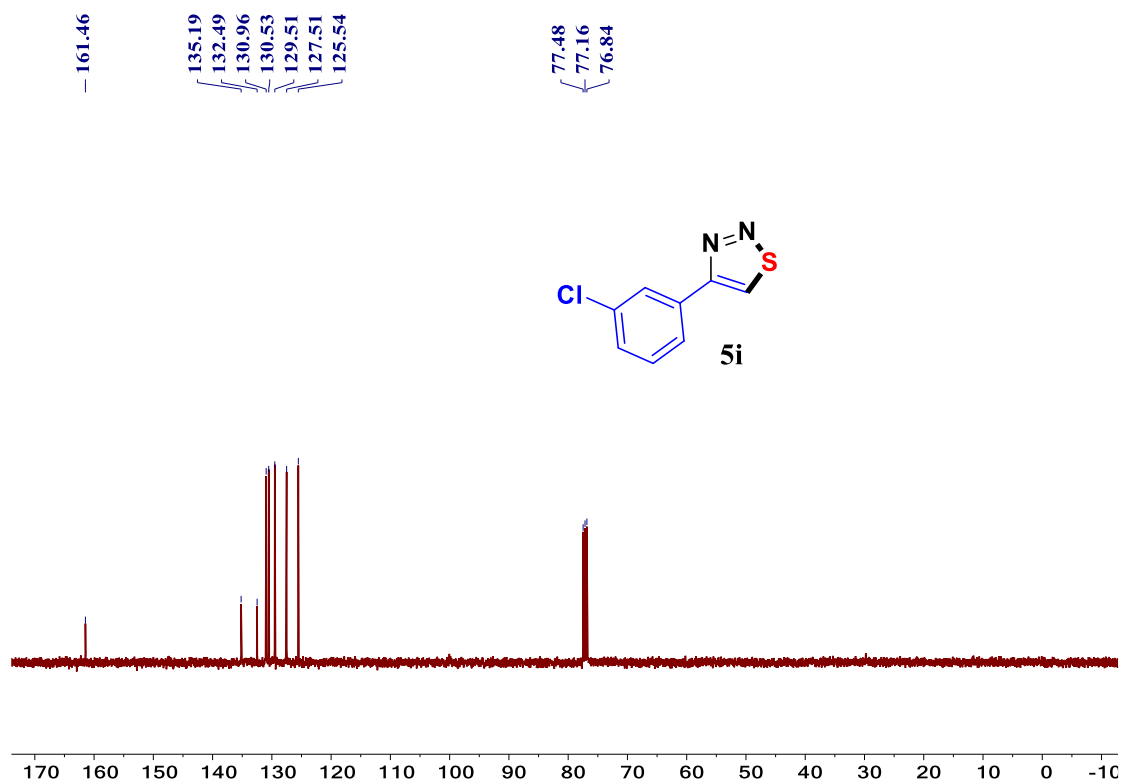
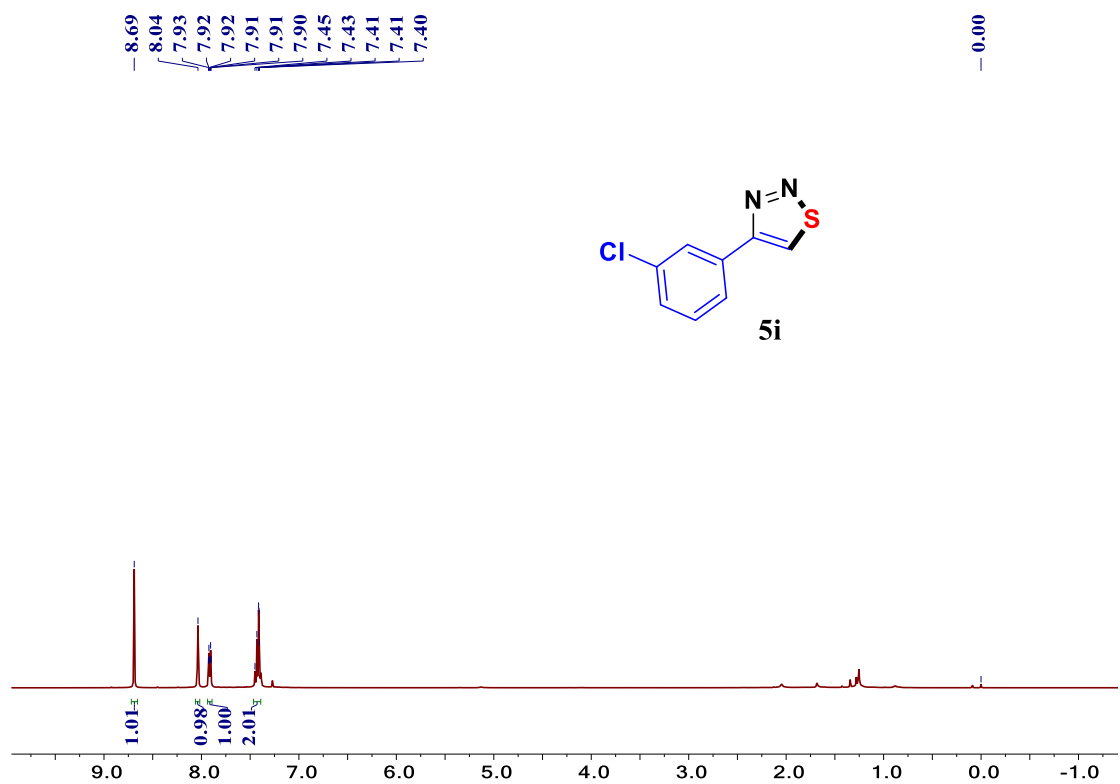


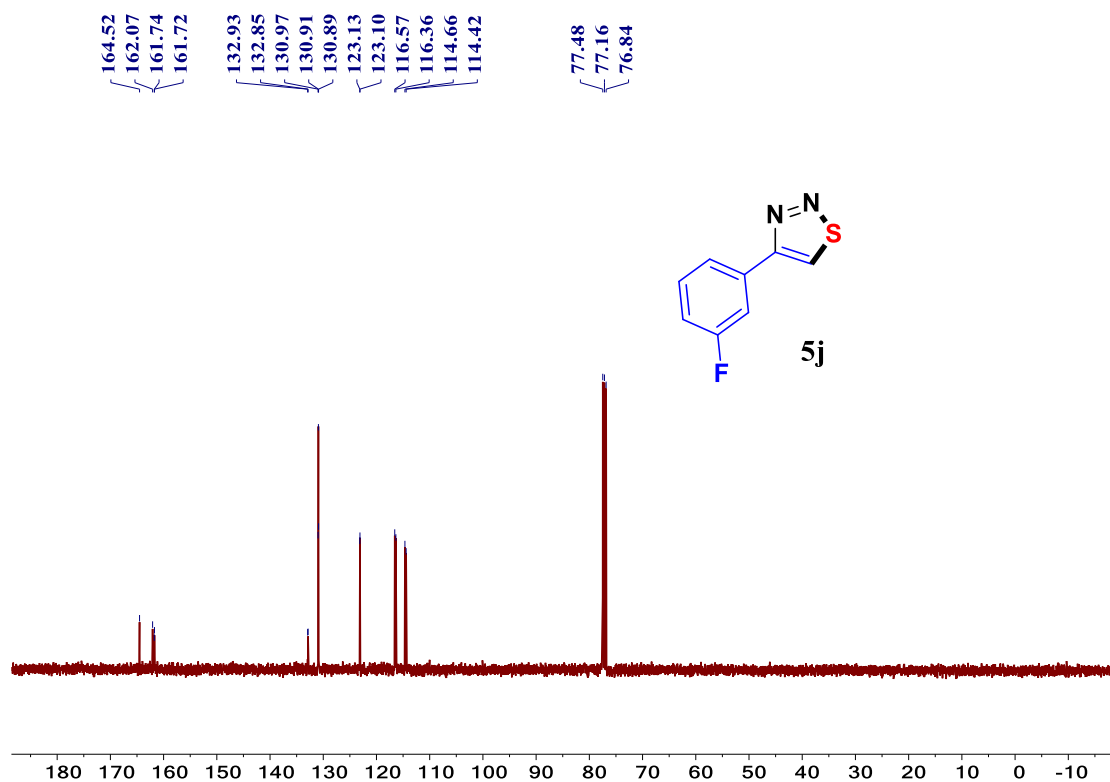
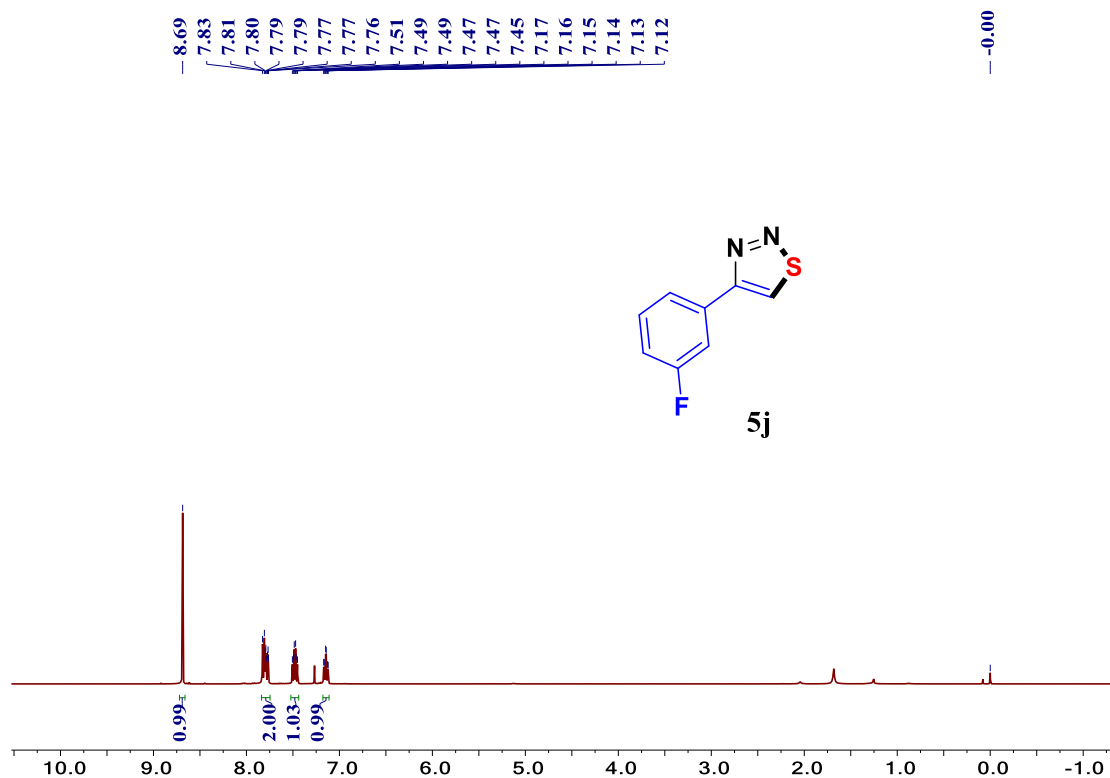


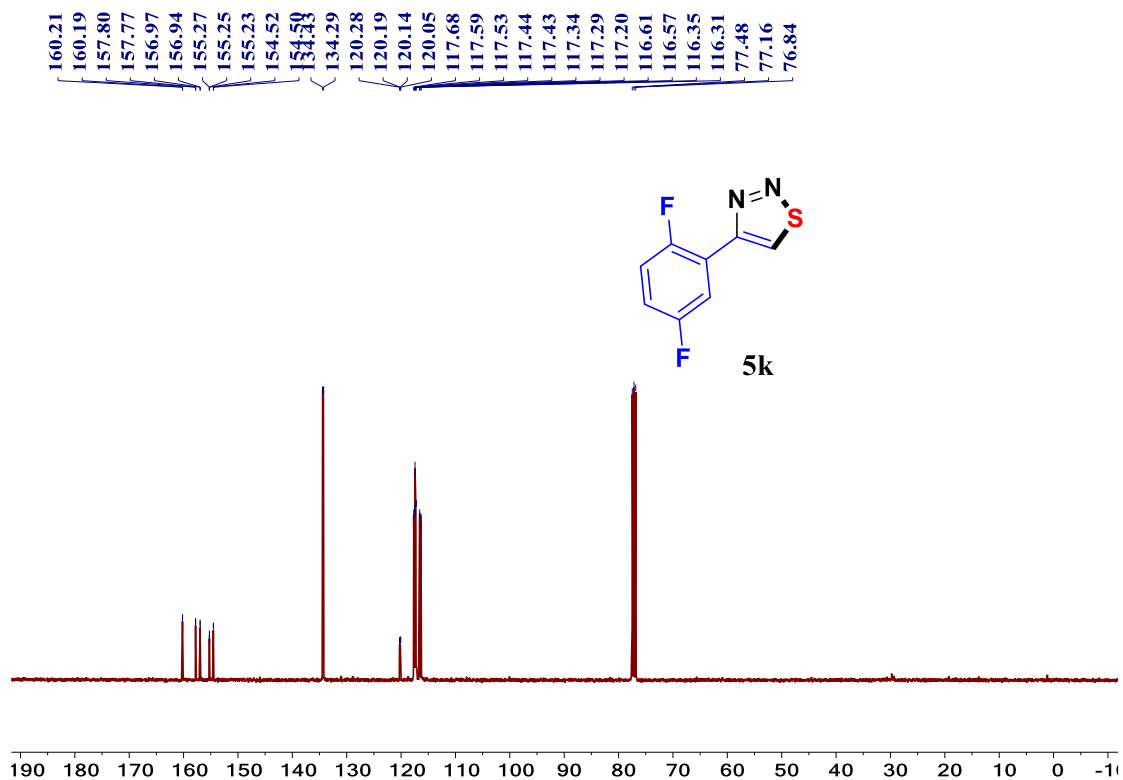
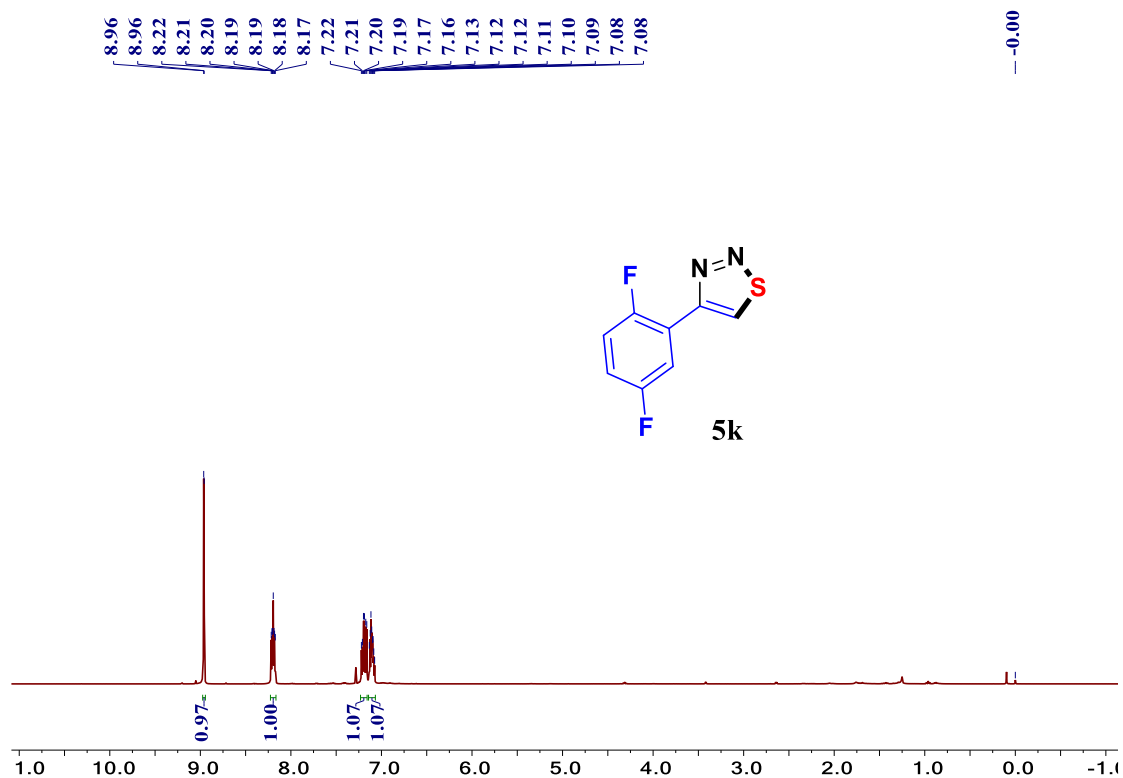


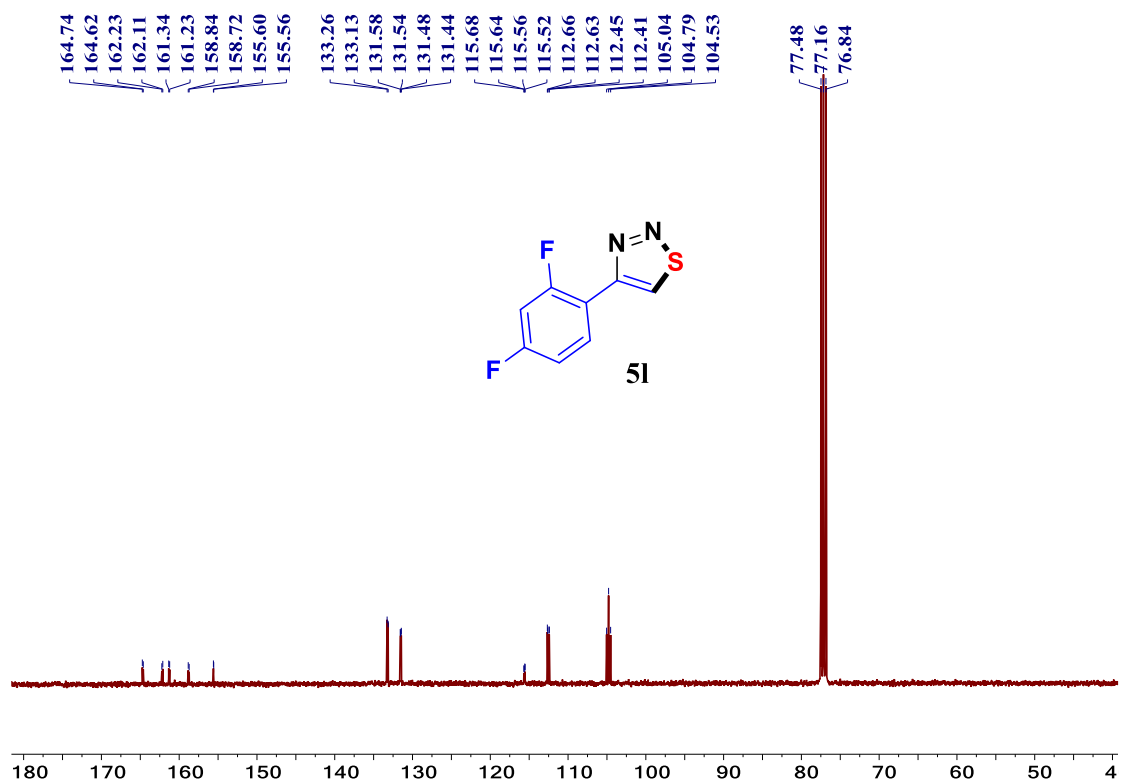
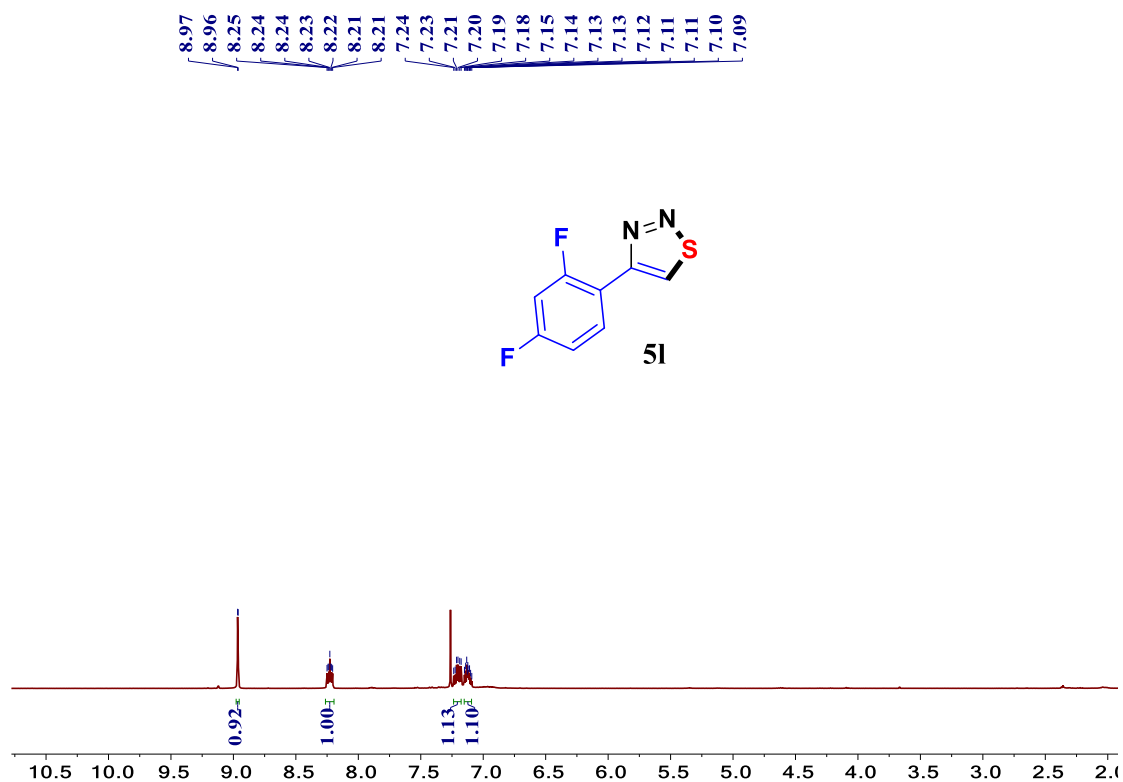


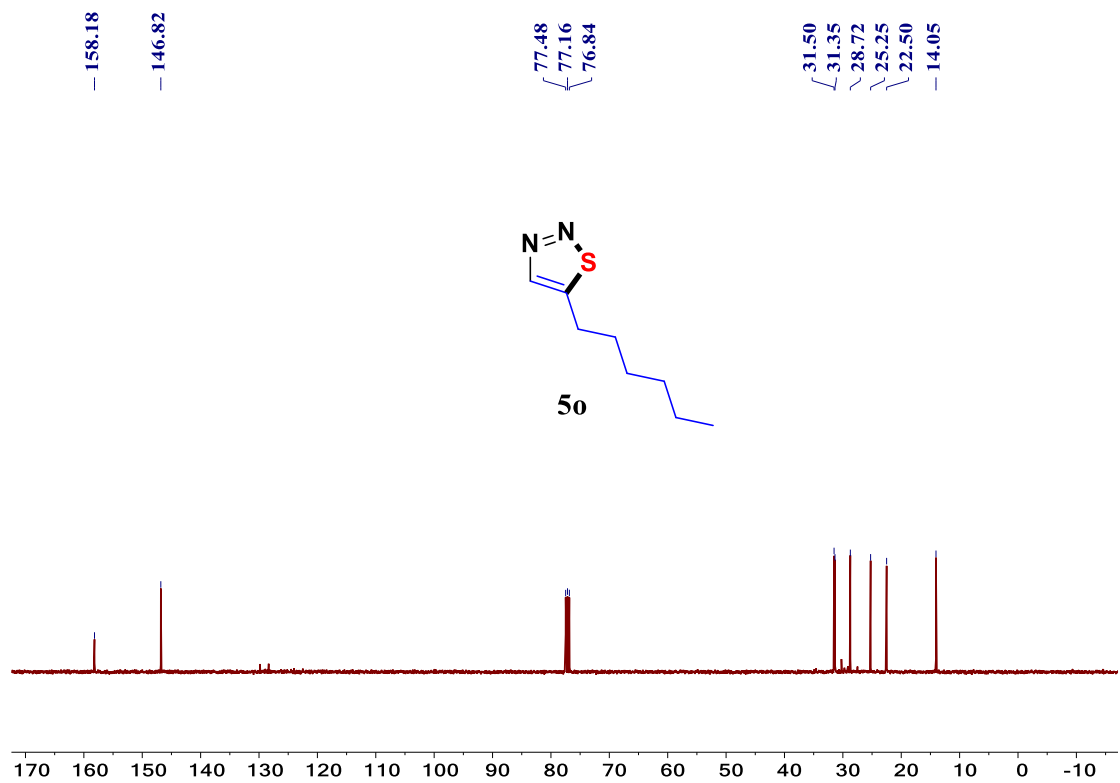
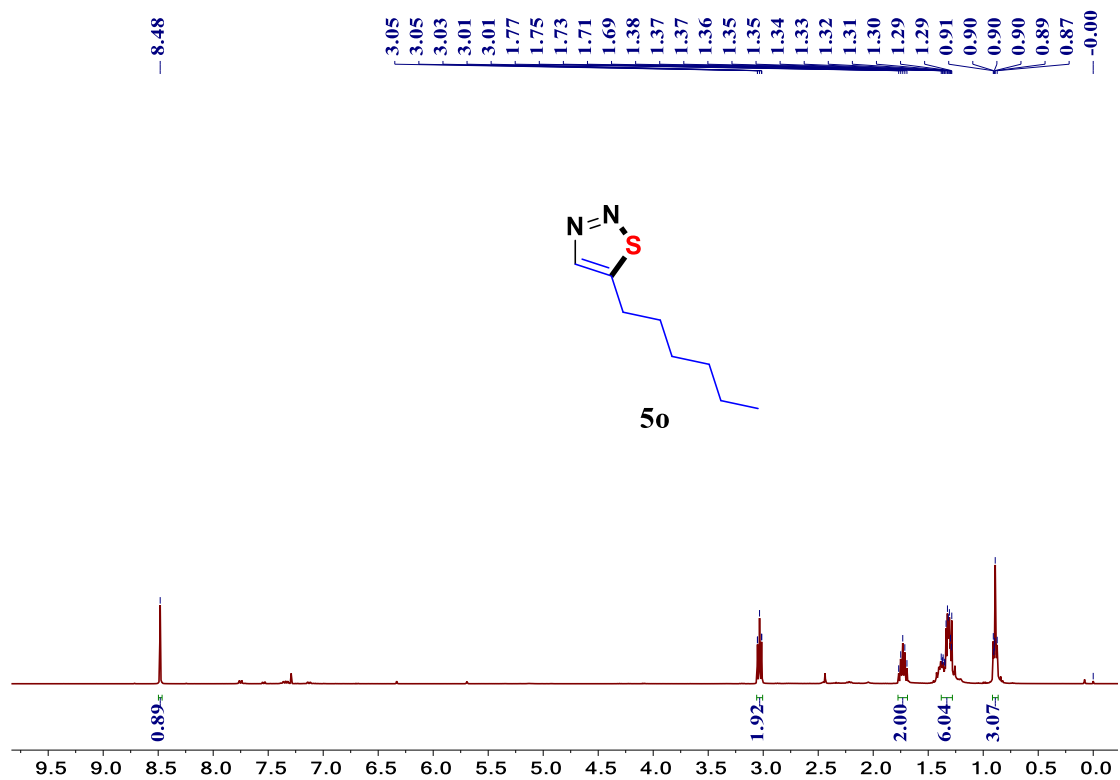


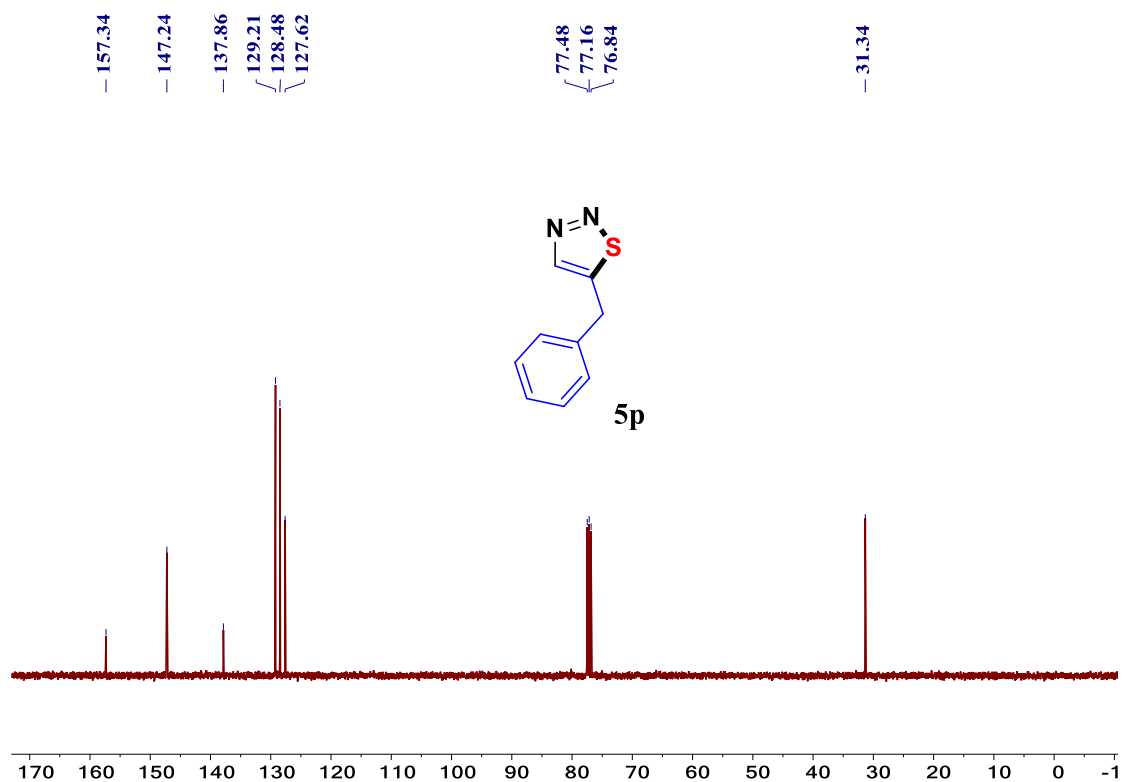
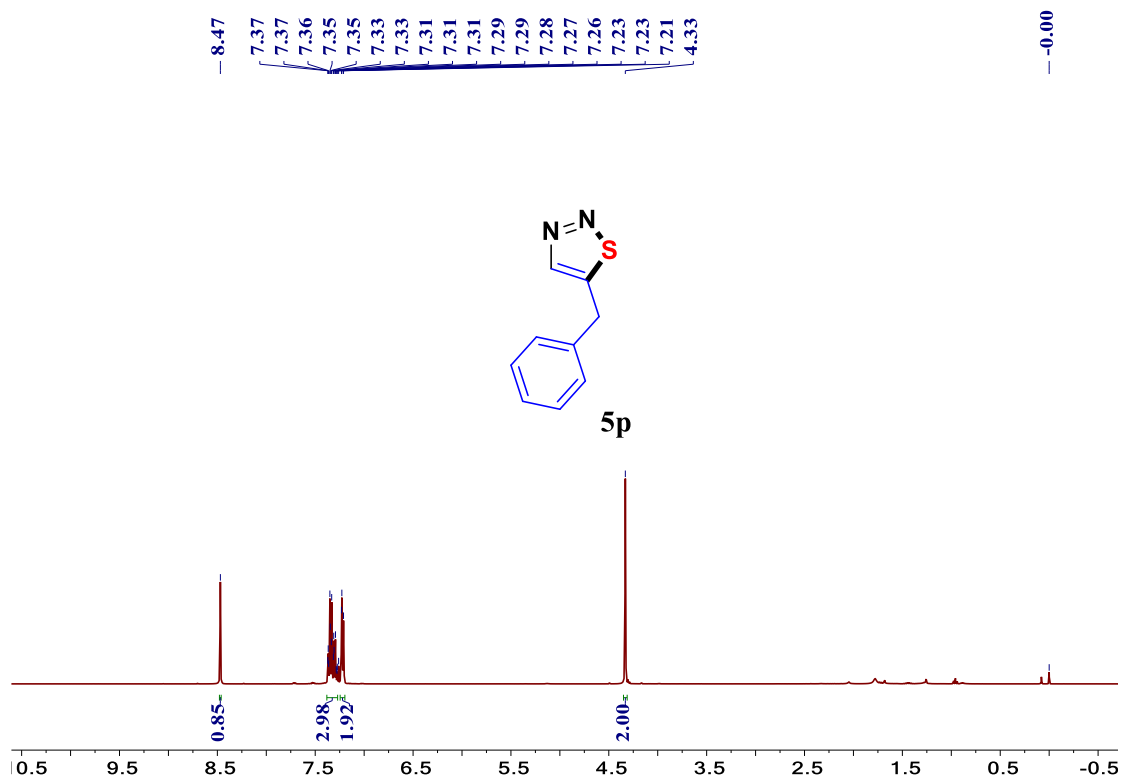


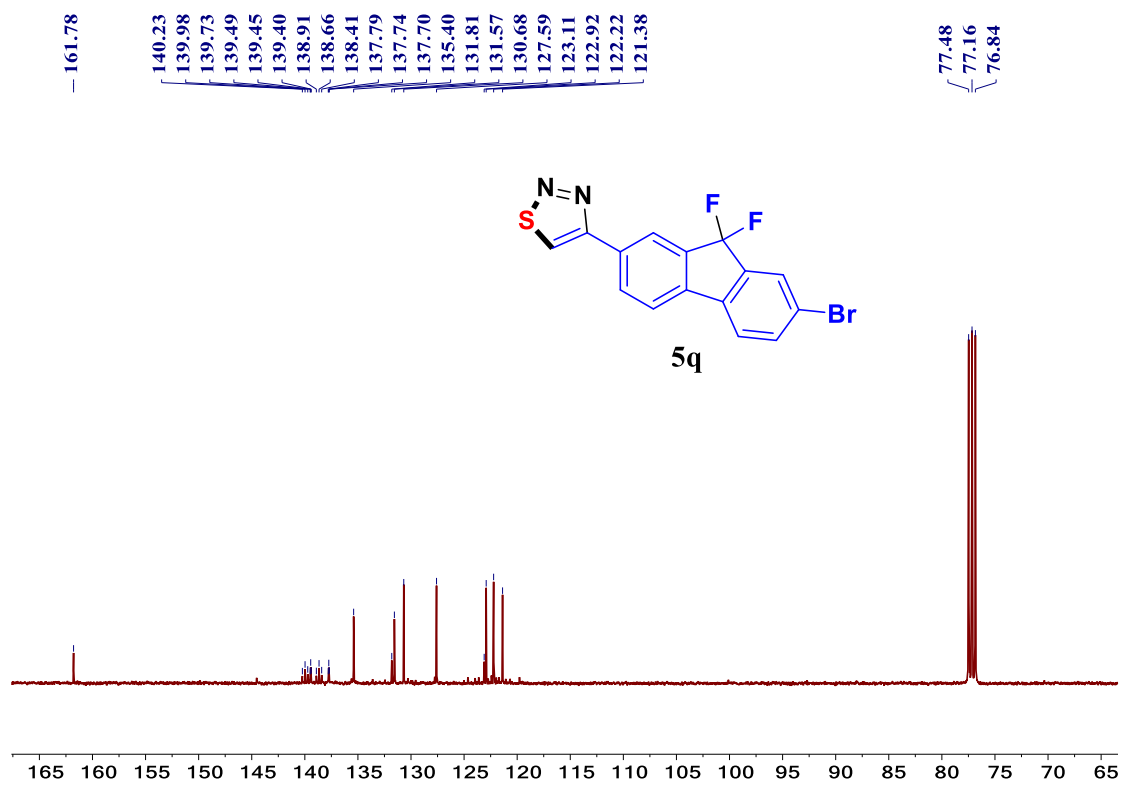
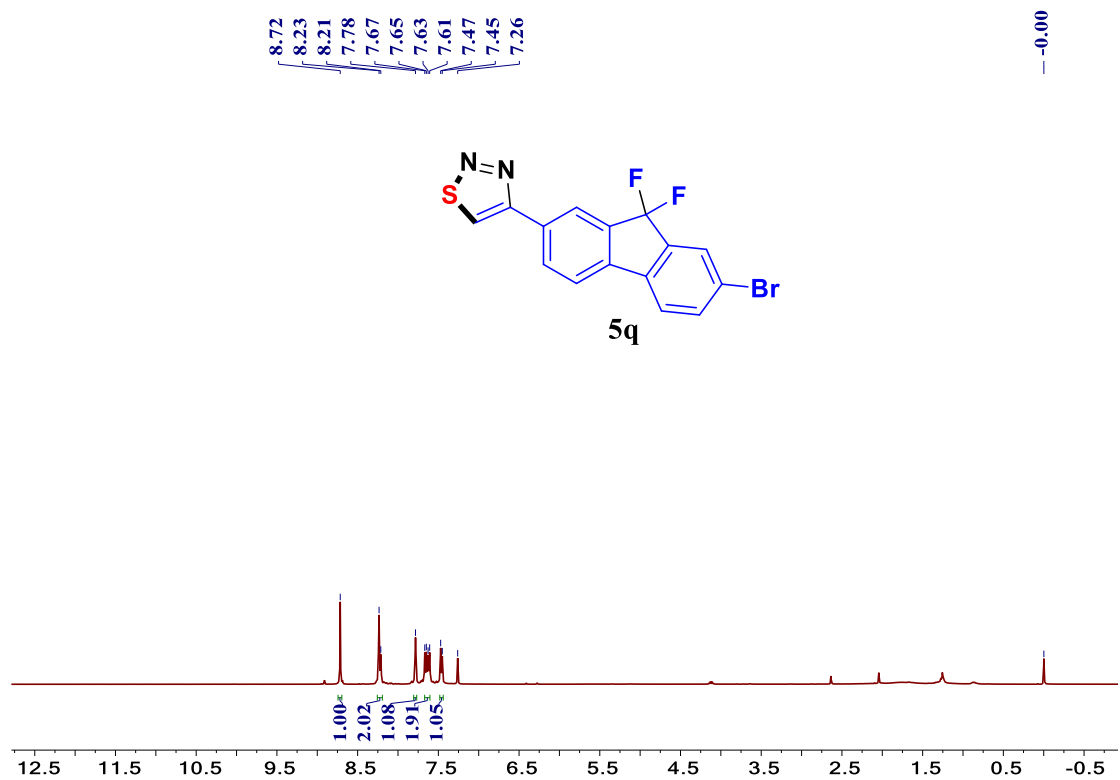


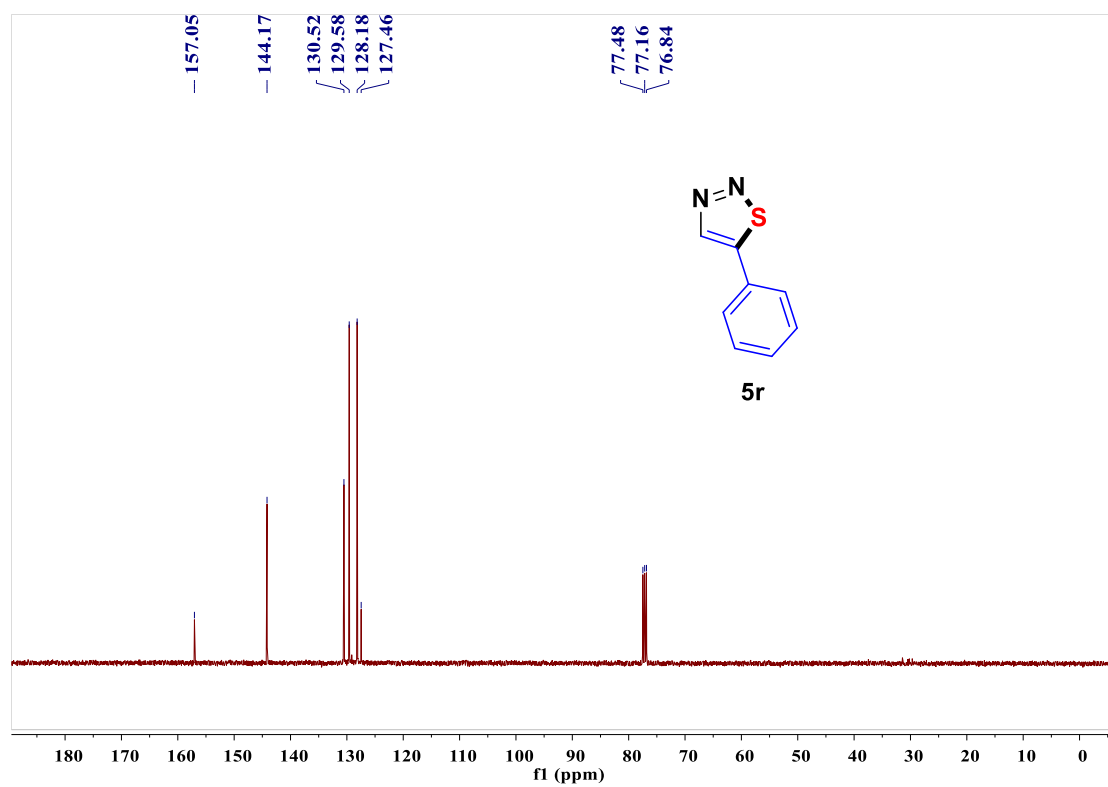
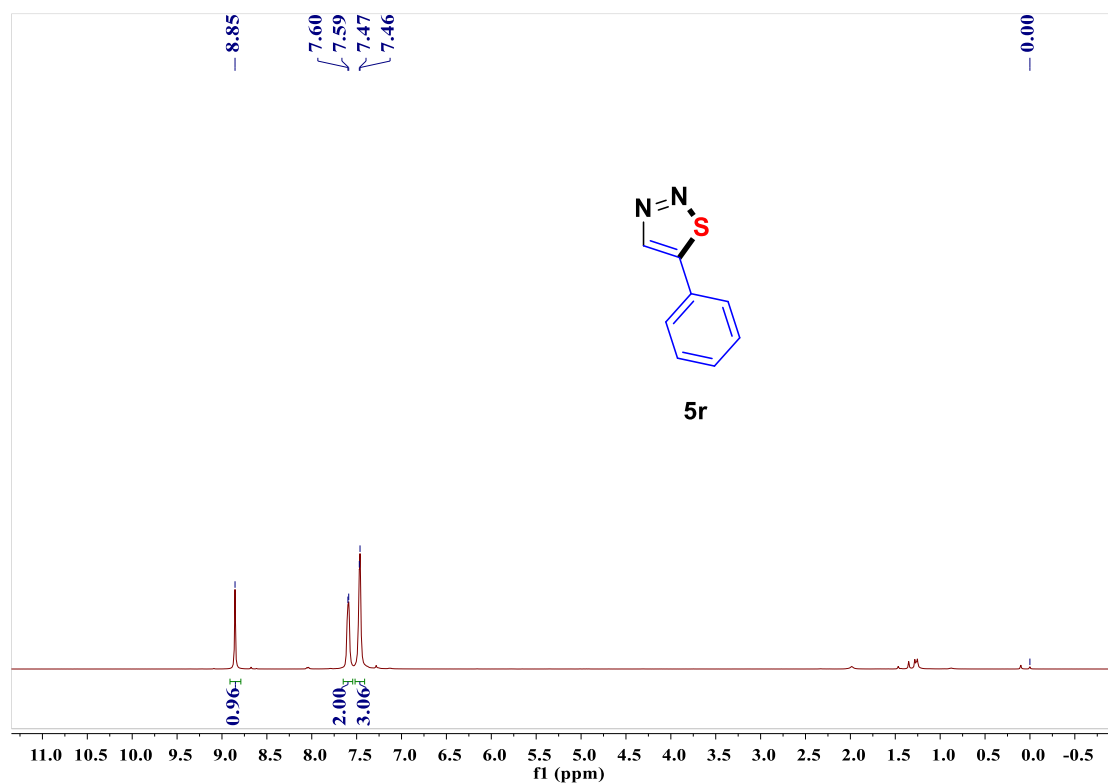


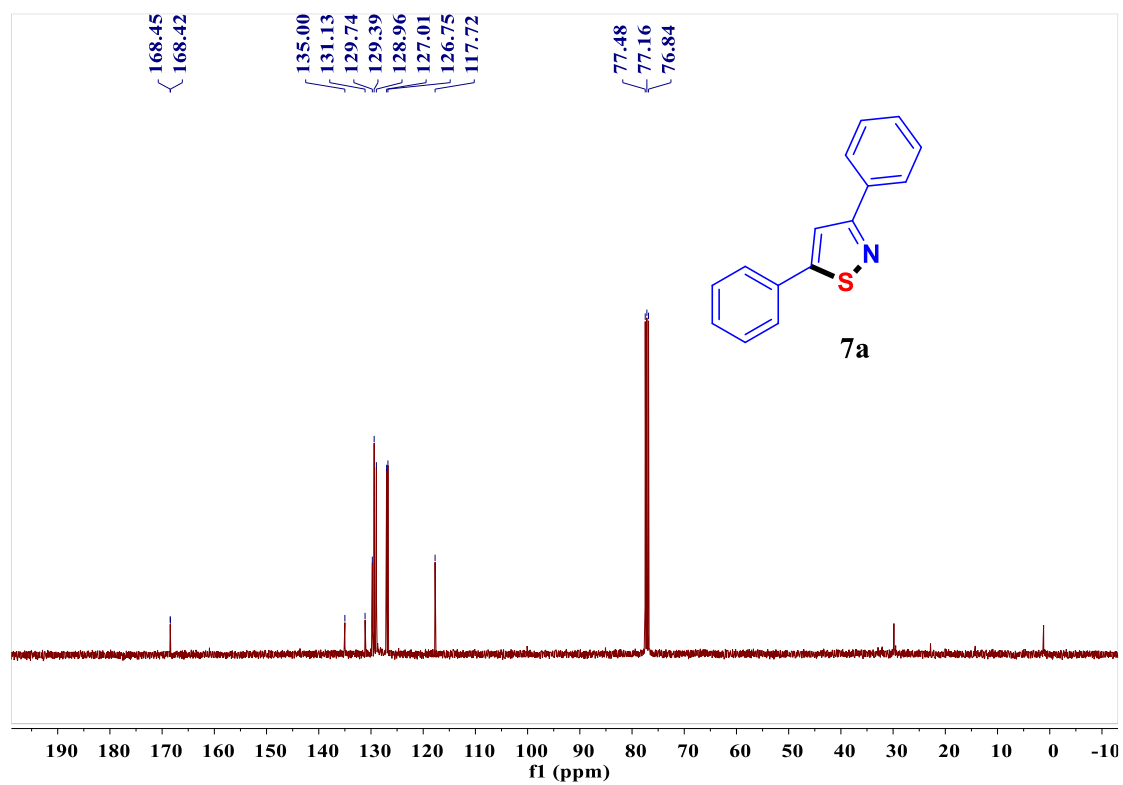
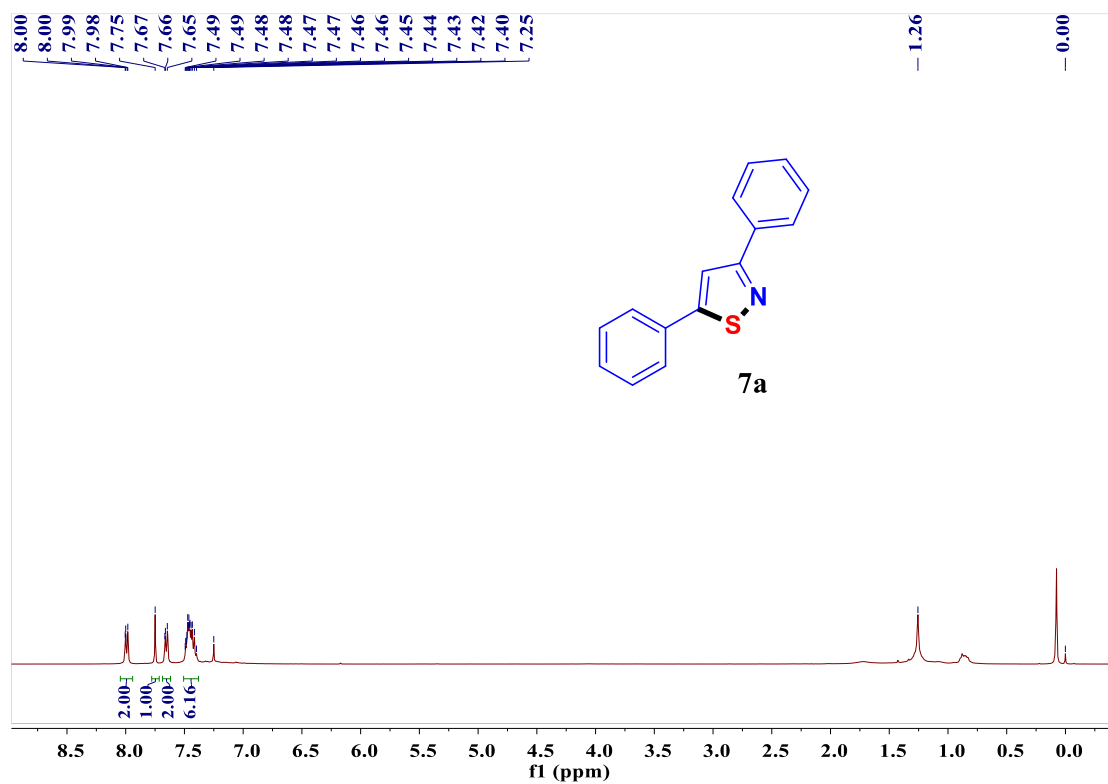












3-(4-(tert-butyl)phenyl)-5-phenylisothiazole (7b)

