

SUPPLEMENTARY DATA

for

Visible-light-mediated Regioselective Synthesis of Novel Thiazolo[3,2-*b*][1,2,4]triazoles: Advantageous Synthetic Application of Aqueous Conditions

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General method for preparation of (2-aryl'-6-methylthiazolo[3,2-*b*][1,2,4]triazol-5-yl)(aryl)methanone (6)

To a stirred solution of 1,3-diketone (1.0 eq) in distilled water, 0.178 g of NBS (1.0 eq) was added under visible-light irradiations. Reaction contents were allowed to stir for about 15 minutes. Subsequently, 3-mercapto-1,2,4-triazole (1.0 eq) was added to the reaction mixture and stirred for further 30-40 minutes under the same reaction conditions till the finishing point monitored on TLC. Excess water was distilled off under reduced pressure using a rotatory evaporator; the reaction product was neutralized with an aqueous solution of sodium bicarbonate and extracted with ethyl acetate. Solid obtained after evaporation of ethyl acetate was recrystallized with ethanol, filtered and dried to obtain the product in 73-94% yields.

Characterization of Final Compounds

¹H NMR, ¹³C NMR, HMQC, HMBC Data of Final Compounds

1. (6-methyl-2-phenylthiazolo[3,2-b][1,2,4]triazol-5-yl)(phenyl)methanone (6a)

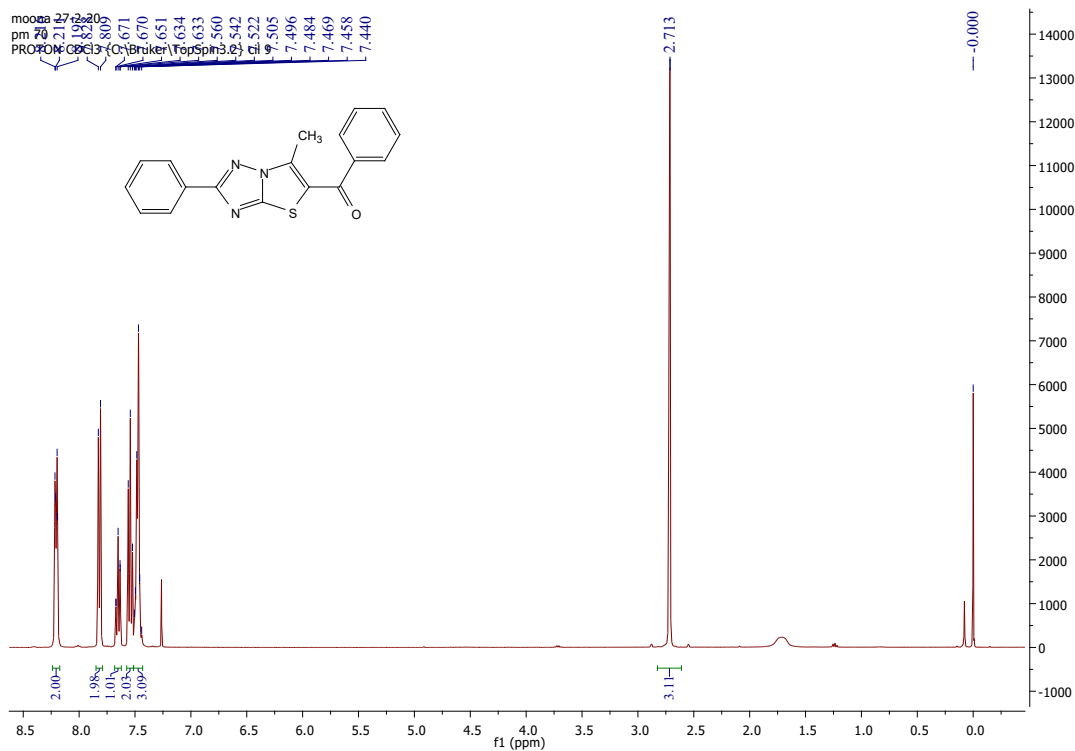


Figure S1a. ¹H NMR spectrum of 6a

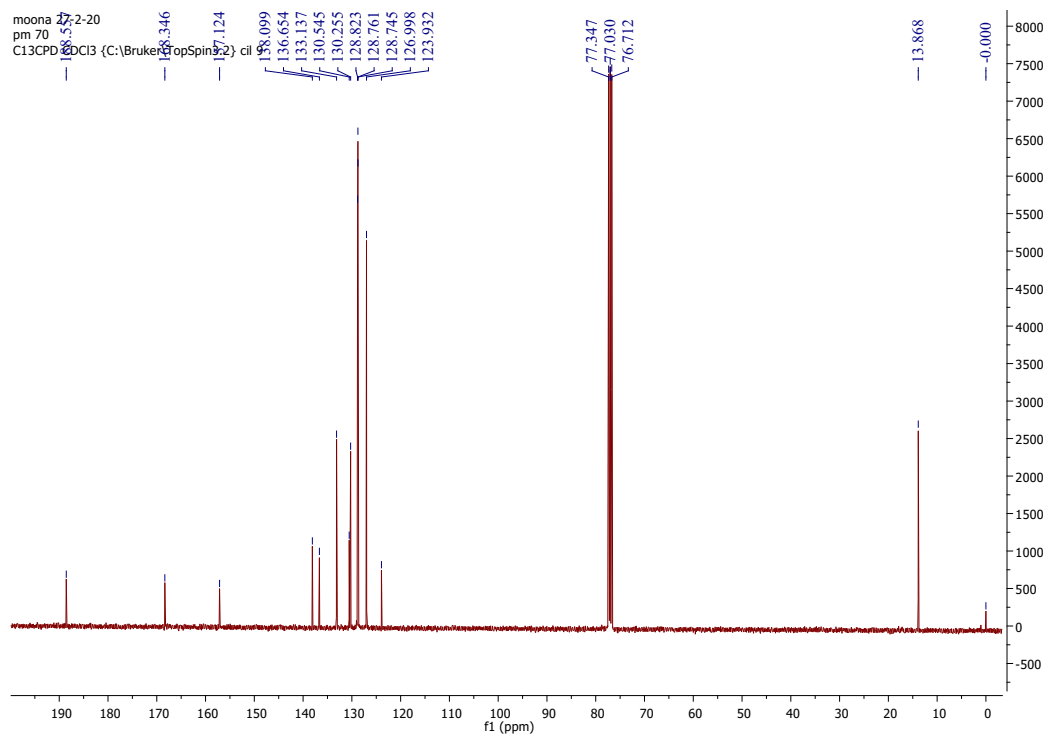


Figure S1b. ¹³C NMR spectrum of 6a

2. (4-fluorophenyl)(6-methyl-2-phenylthiazolo[3,2-b][1,2,4]triazol-5-yl)methanone
(6b)

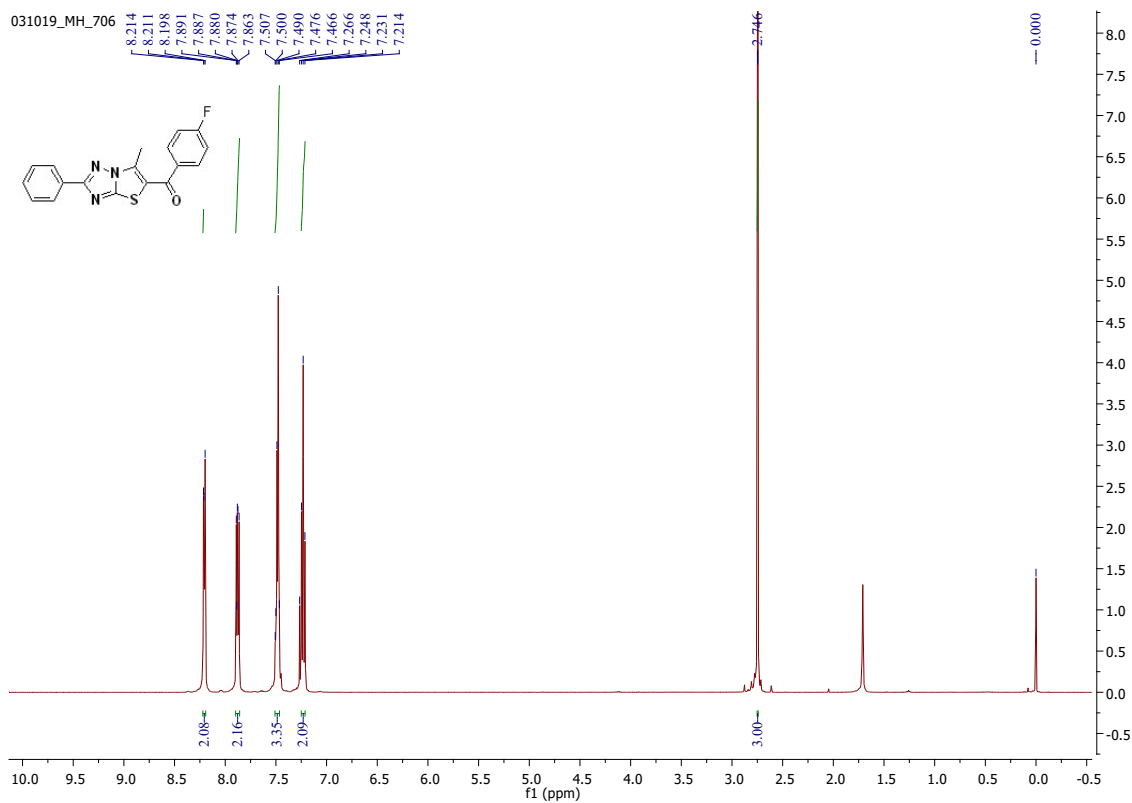


Figure S2a. ¹H NMR spectrum of 6b

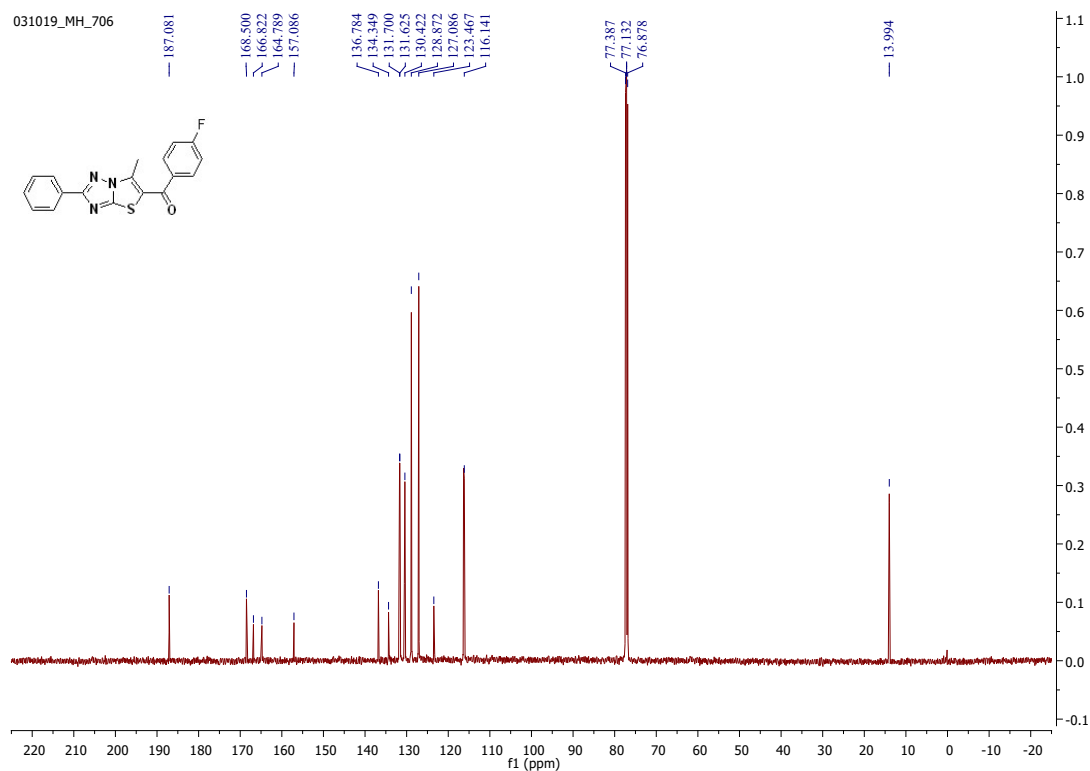


Figure S2b. ¹³C NMR spectrum of 6b

031019_MH_706

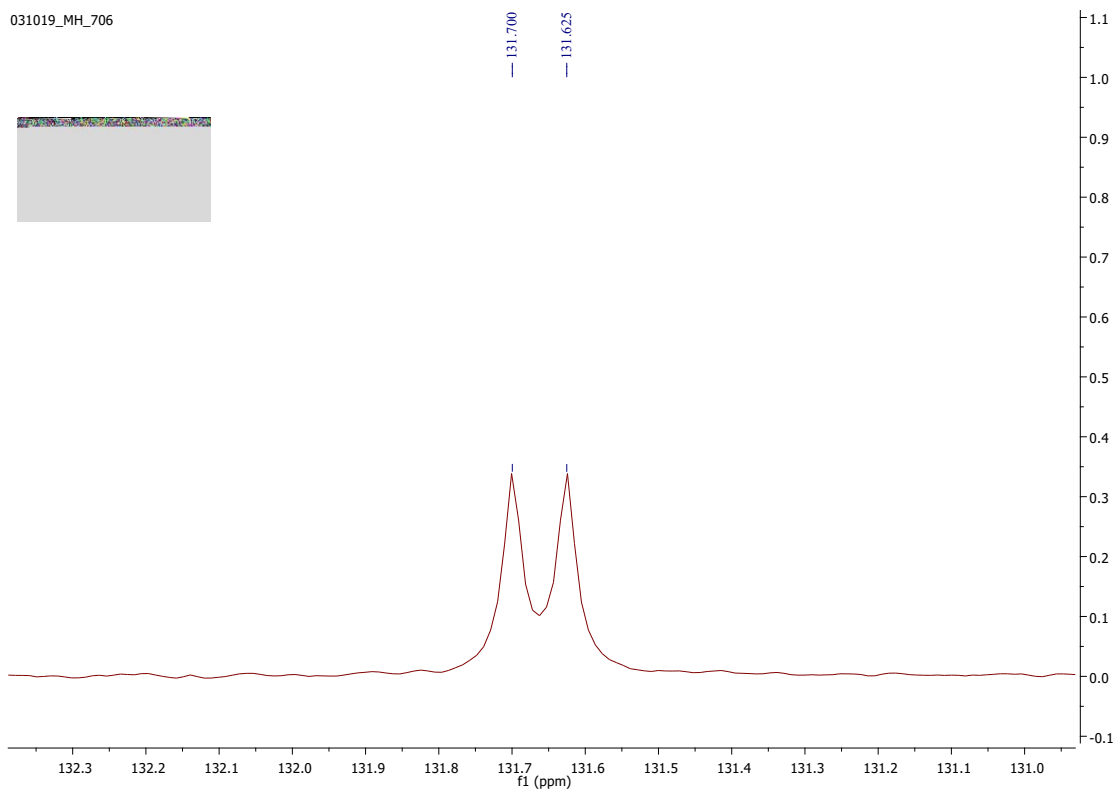


Figure S2c. Zoom ^{13}C NMR spectrum of **6b**

PS-706
single_pulse

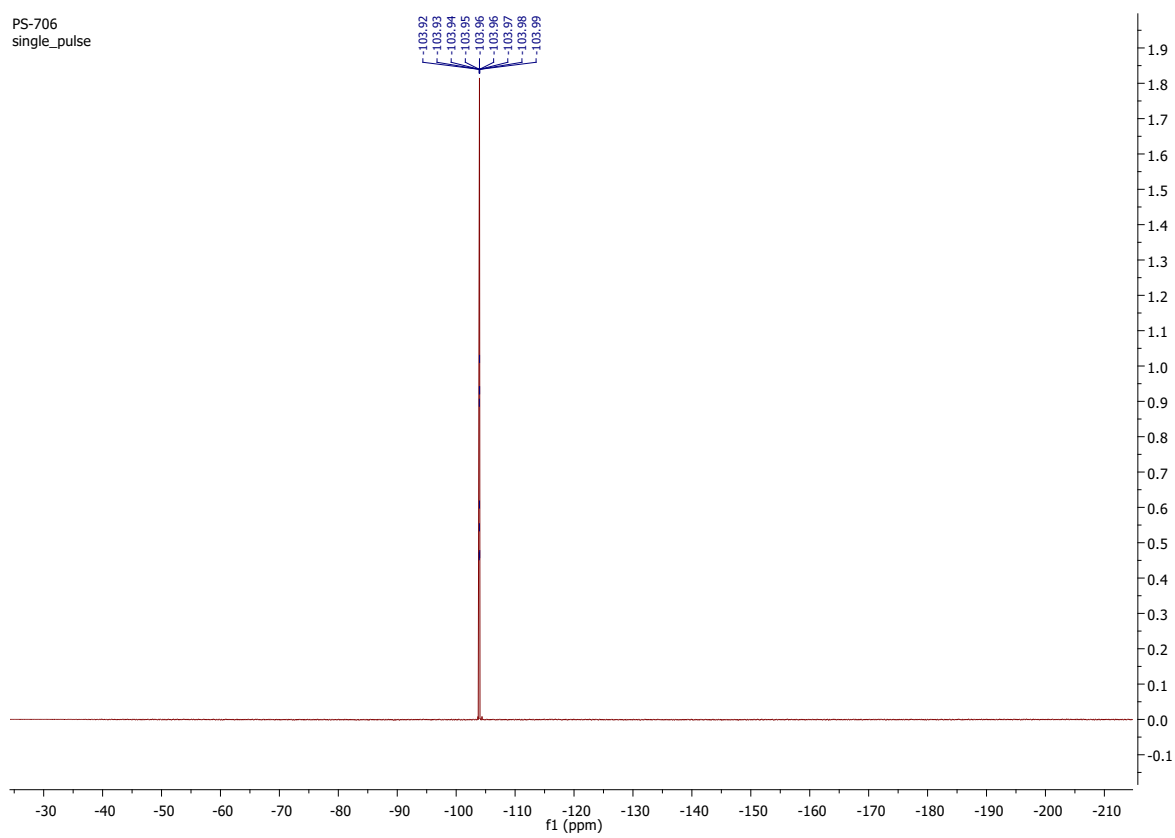


Figure S2d. ^{19}F NMR spectrum of **6b**

3. (4-chlorophenyl)(6-methyl-2-phenylthiazolo[3,2-b][1,2,4]triazol-5-yl)methanone
(6c)

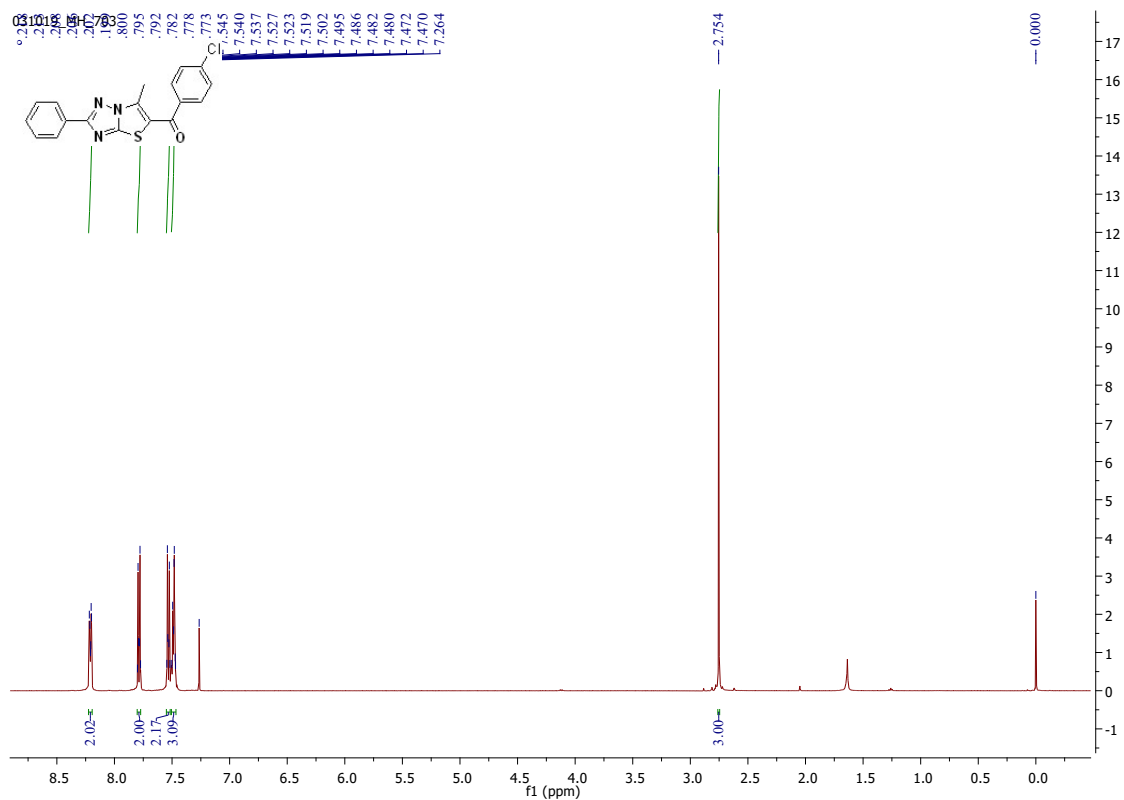


Figure S3a. ¹H NMR spectrum of 6c

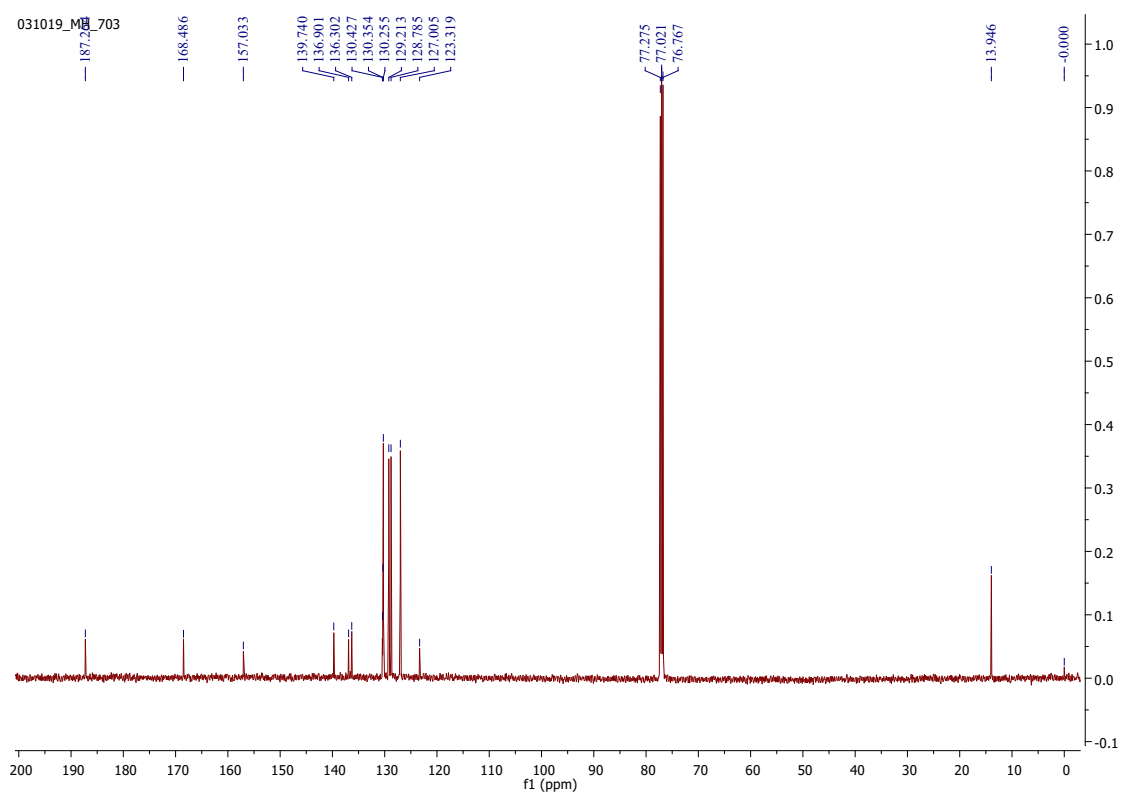


Figure S3b. ¹³C NMR spectrum of 6c

4. (4-bromophenyl)(6-methyl-2-phenylthiazolo[3,2-b][1,2,4]triazol-5-yl)methanone
(6d)

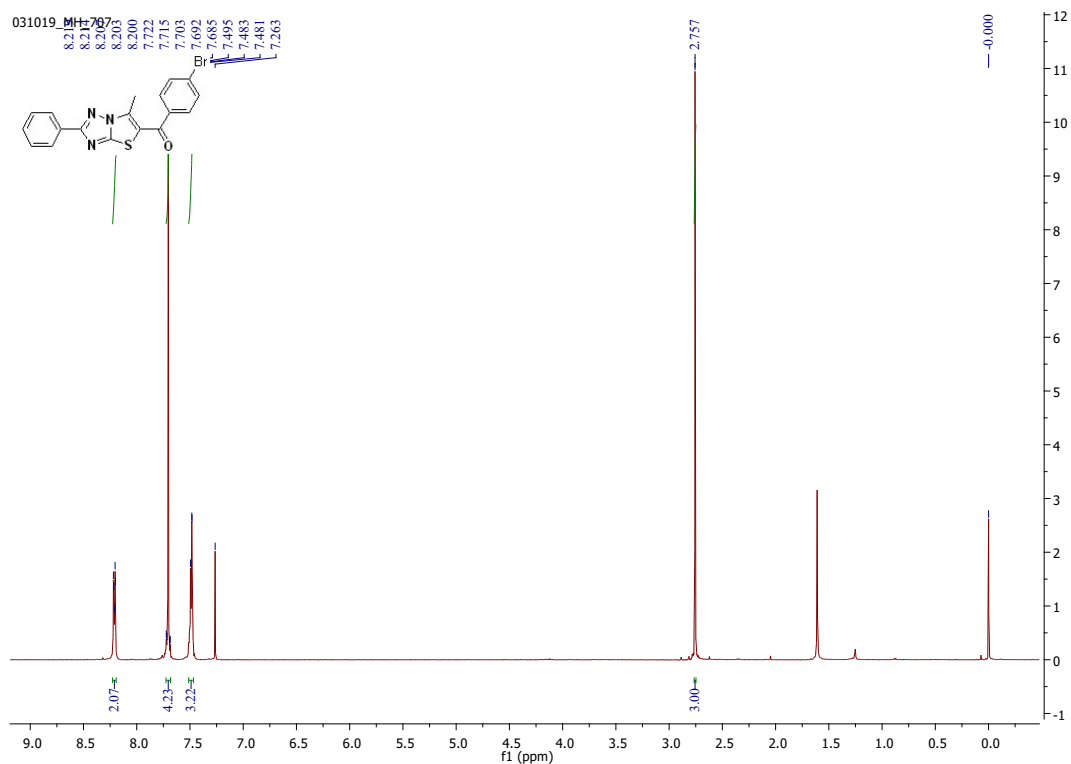


Figure S4a. ¹H NMR spectrum of 6d

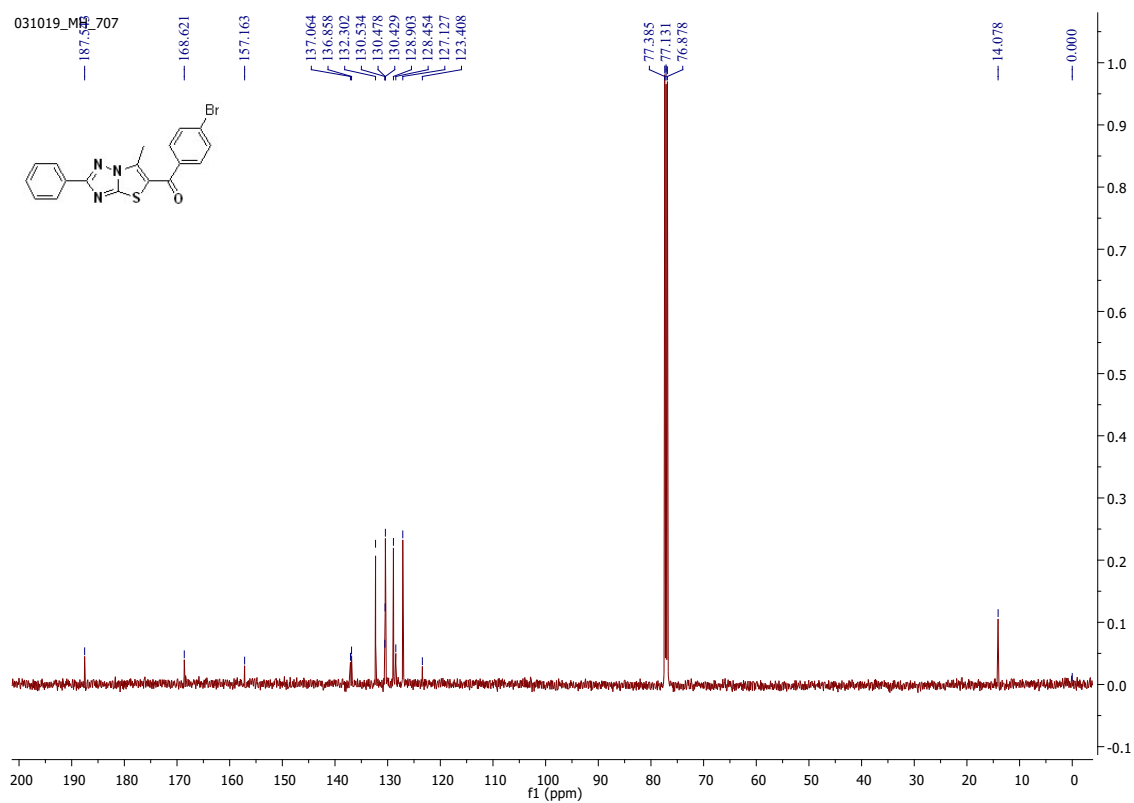


Figure S4b. ¹³C NMR spectrum of 6d

5. (2,4-dichlorophenyl)(6-methyl-2-phenylthiazolo[3,2-b][1,2,4]triazol-5-yl)methanone (6e)

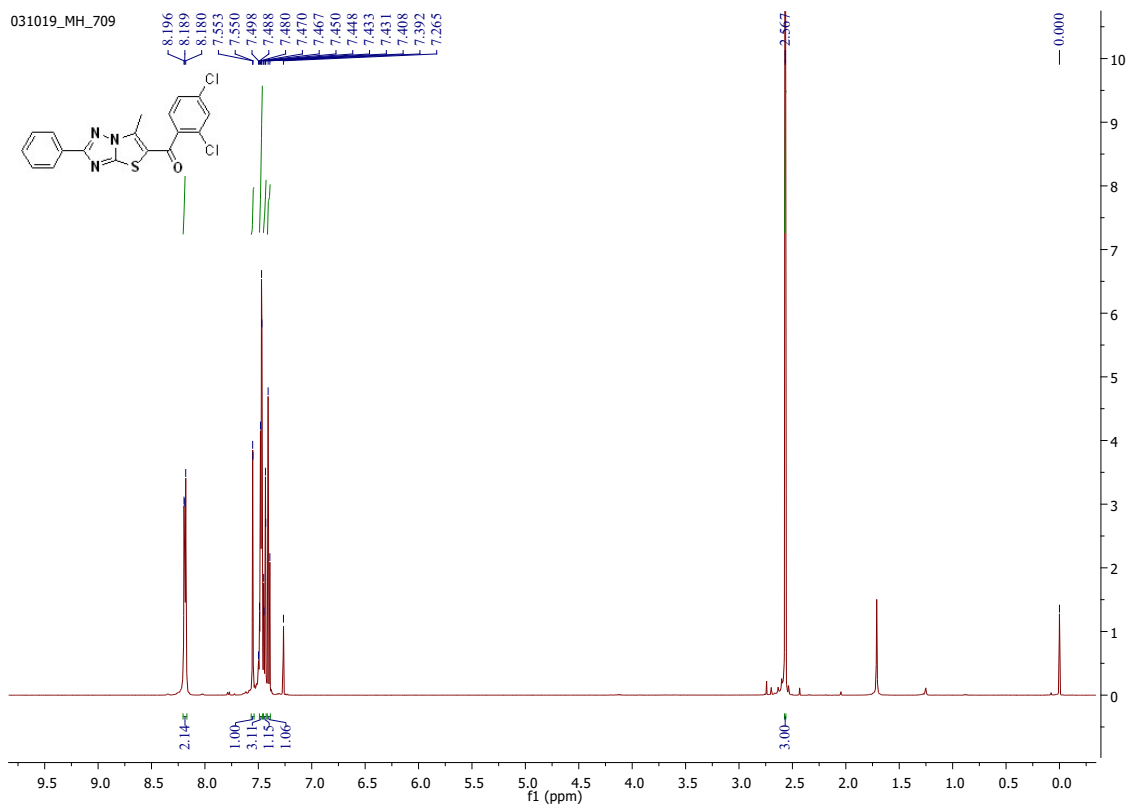


Figure S5a. ¹H NMR spectrum of 6e

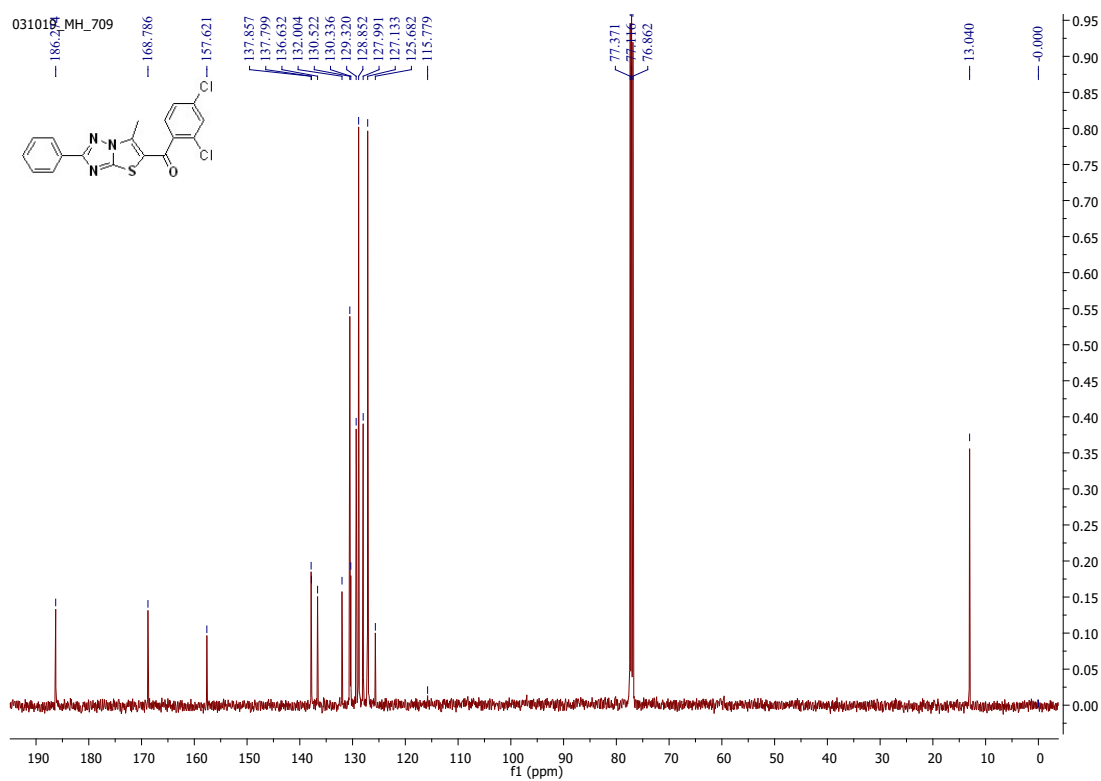


Figure S5b. ¹³C NMR spectrum of 6e

6. (6-methyl-2-phenylthiazolo[3,2-b][1,2,4]triazol-5-yl)(p-tolyl)methanone (6f)

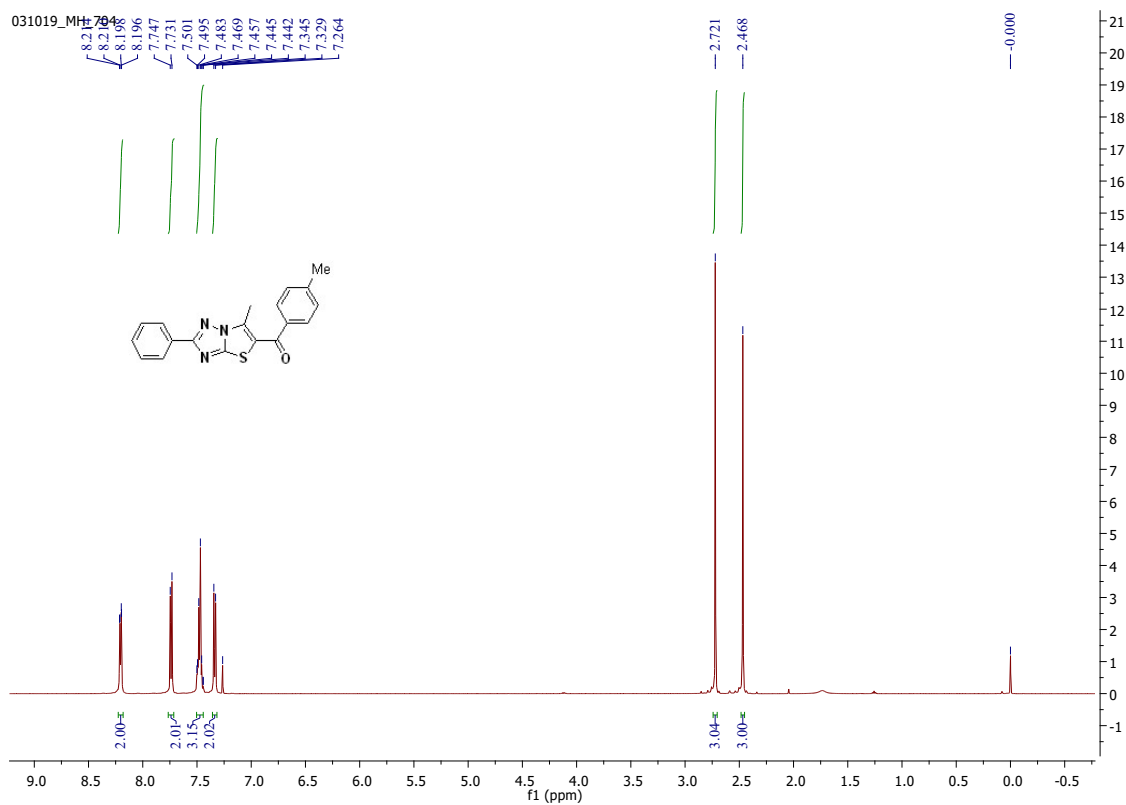


Figure S6a. ¹H NMR spectrum of 6f

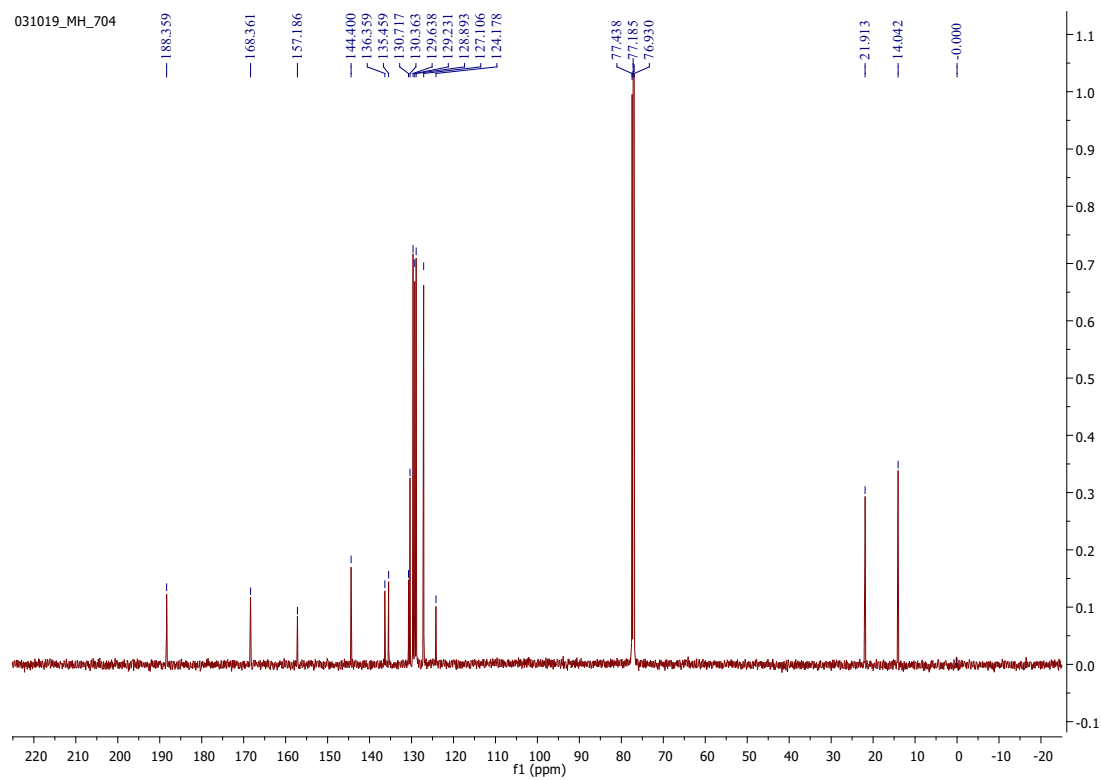


Figure S6b. ¹³C NMR spectrum of 6f

7. (4-methoxyphenyl)(6-methyl-2-phenylthiazolo[3,2-b][1,2,4]triazol-5-yl)methanone (6g)

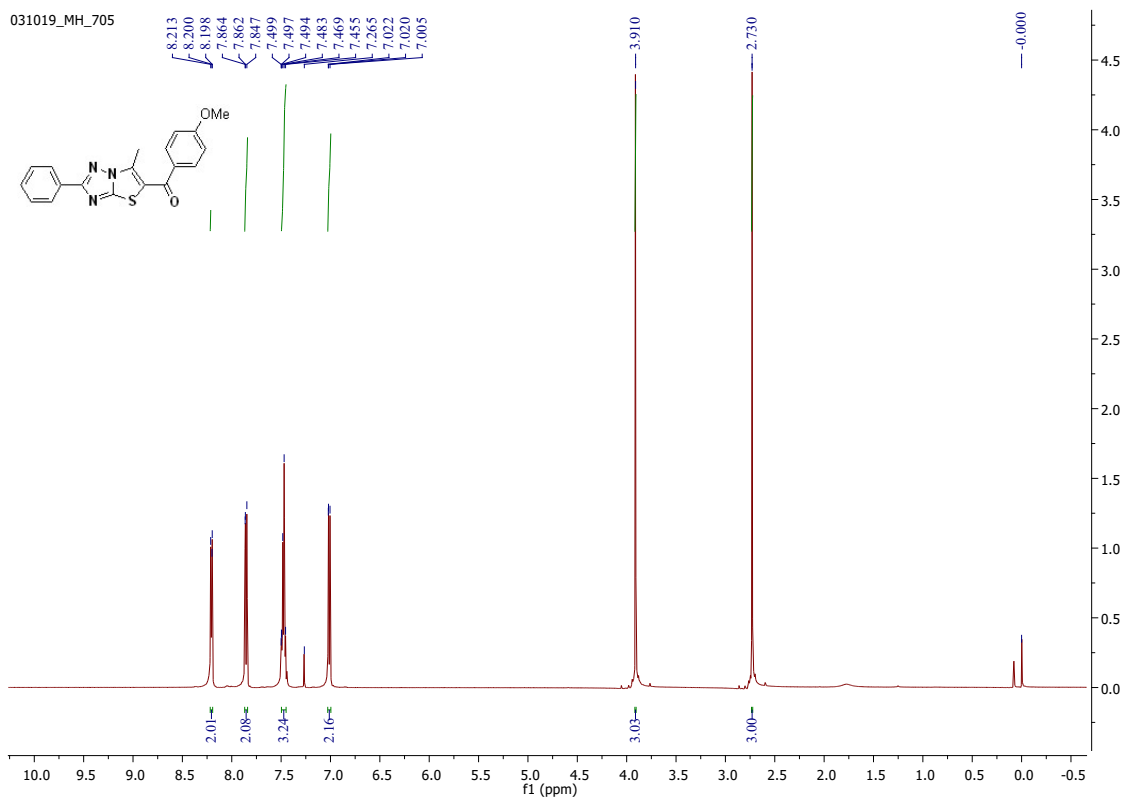


Figure S7a. ¹H NMR spectrum of 6g

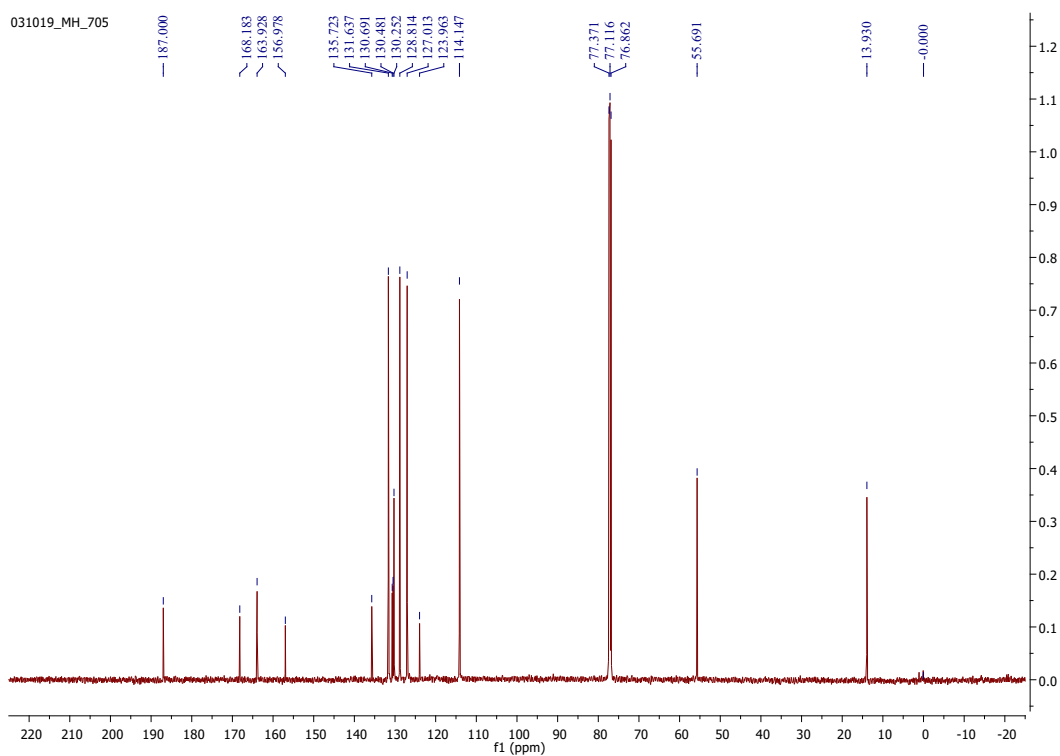


Figure S7b. ¹³C NMR spectrum of 6g

8. (3-methoxyphenyl)(6-methyl-2-phenylthiazolo[3,2-b][1,2,4]triazol-5-yl)methanone (6h)

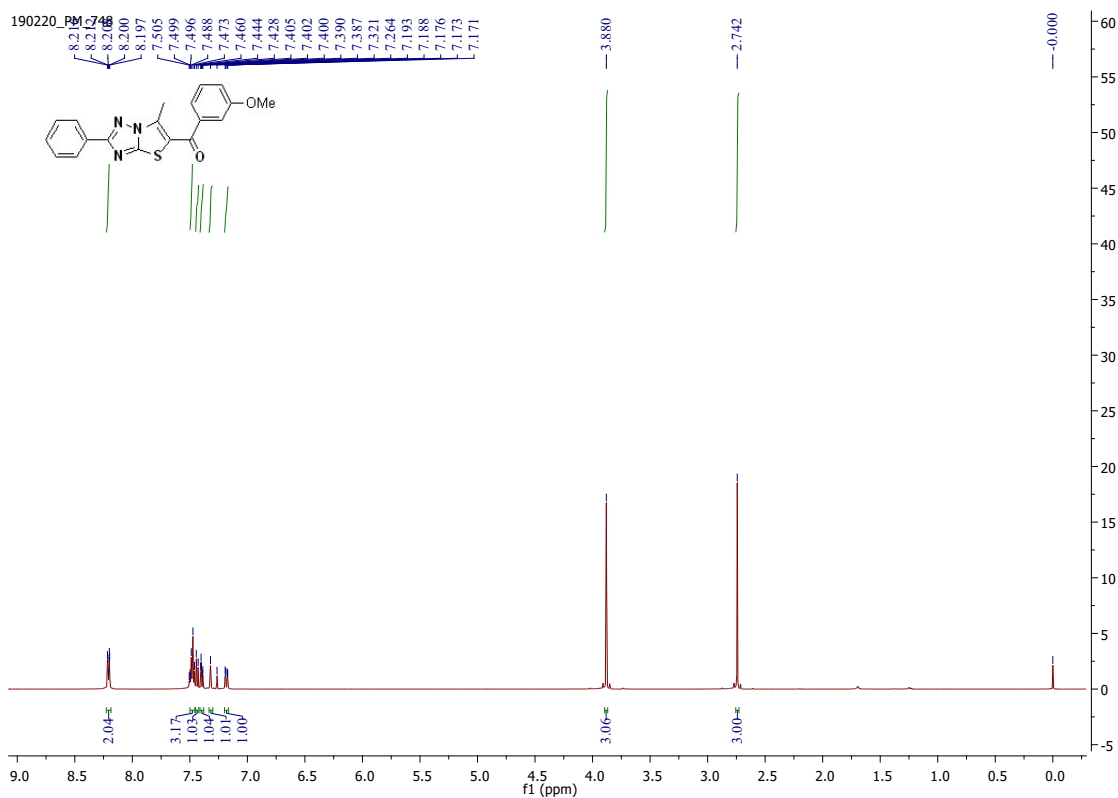


Figure S8a. ¹H NMR spectrum of 6h

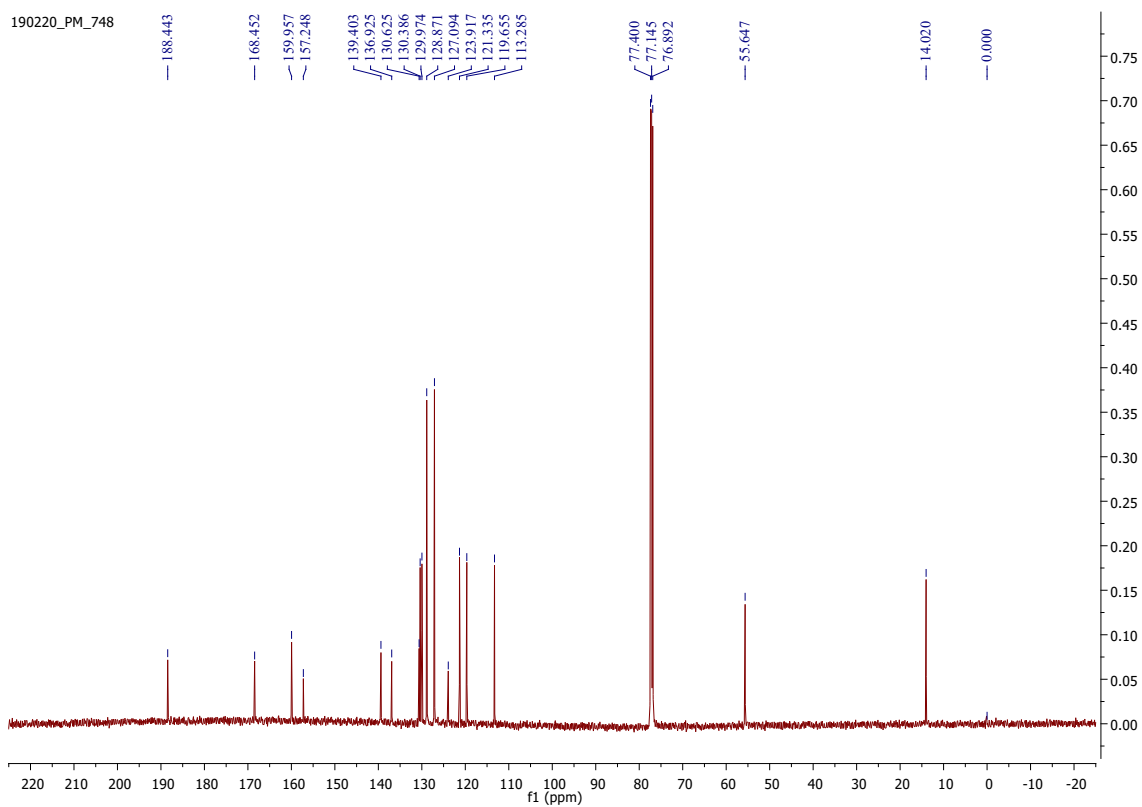


Figure S8b. ¹³C NMR spectrum of 6h

9. (2-methoxyphenyl)(6-methyl-2-phenylthiazolo[3,2-b][1,2,4]triazol-5-yl)methanone (6i)

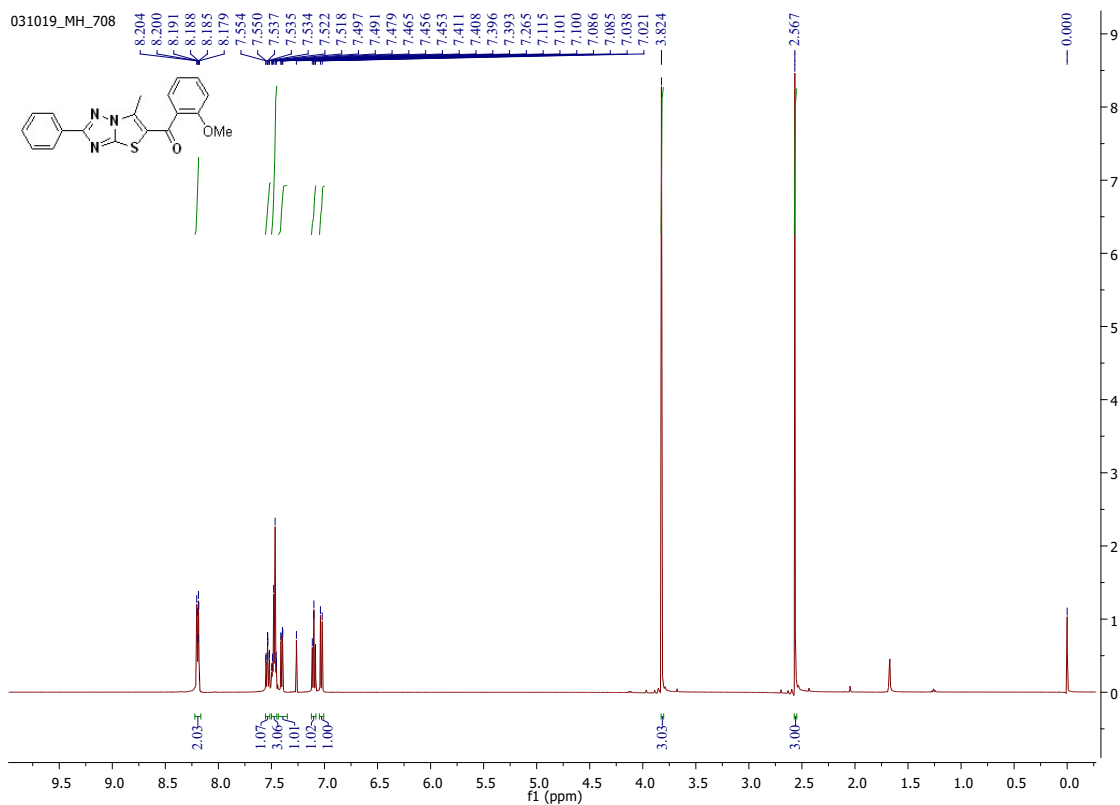


Figure S9a. ¹H NMR spectrum of 6i

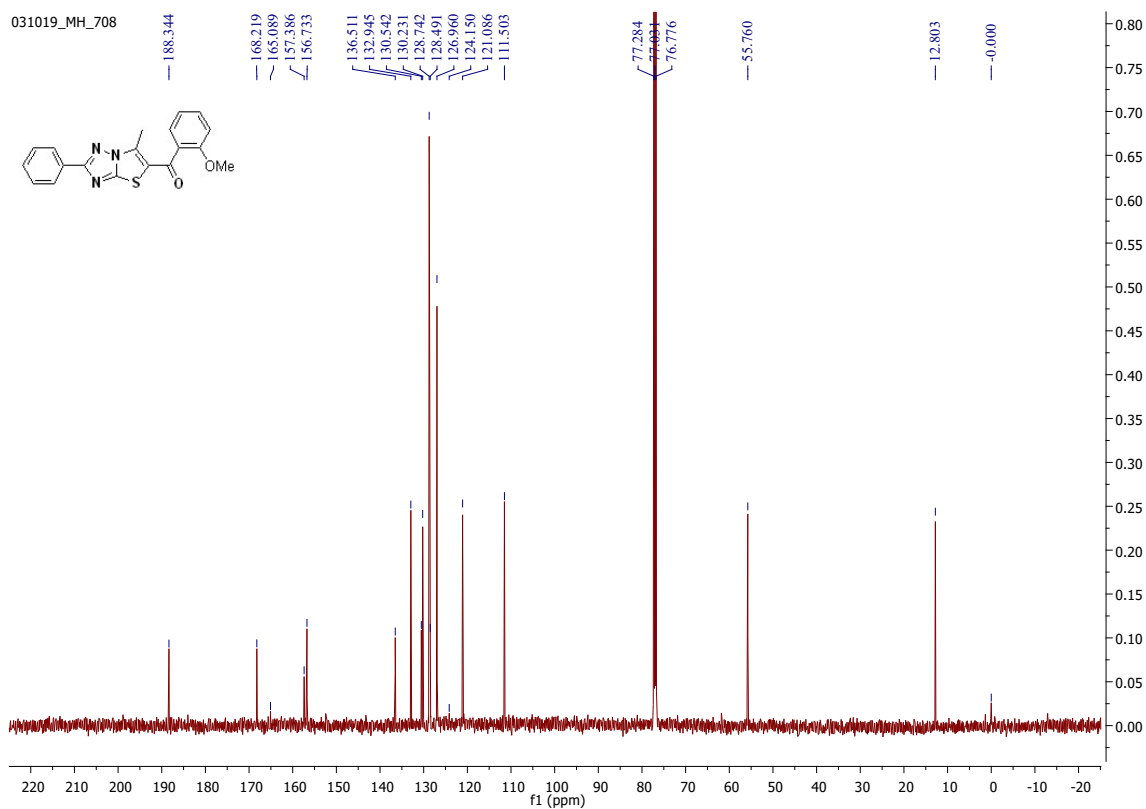


Figure S9b. ¹³C NMR spectrum of 6i

10. (2-(4-methoxyphenyl)-6-methylthiazolo[3,2-b][1,2,4]triazol-5-yl)(phenyl)methanone
(6j)

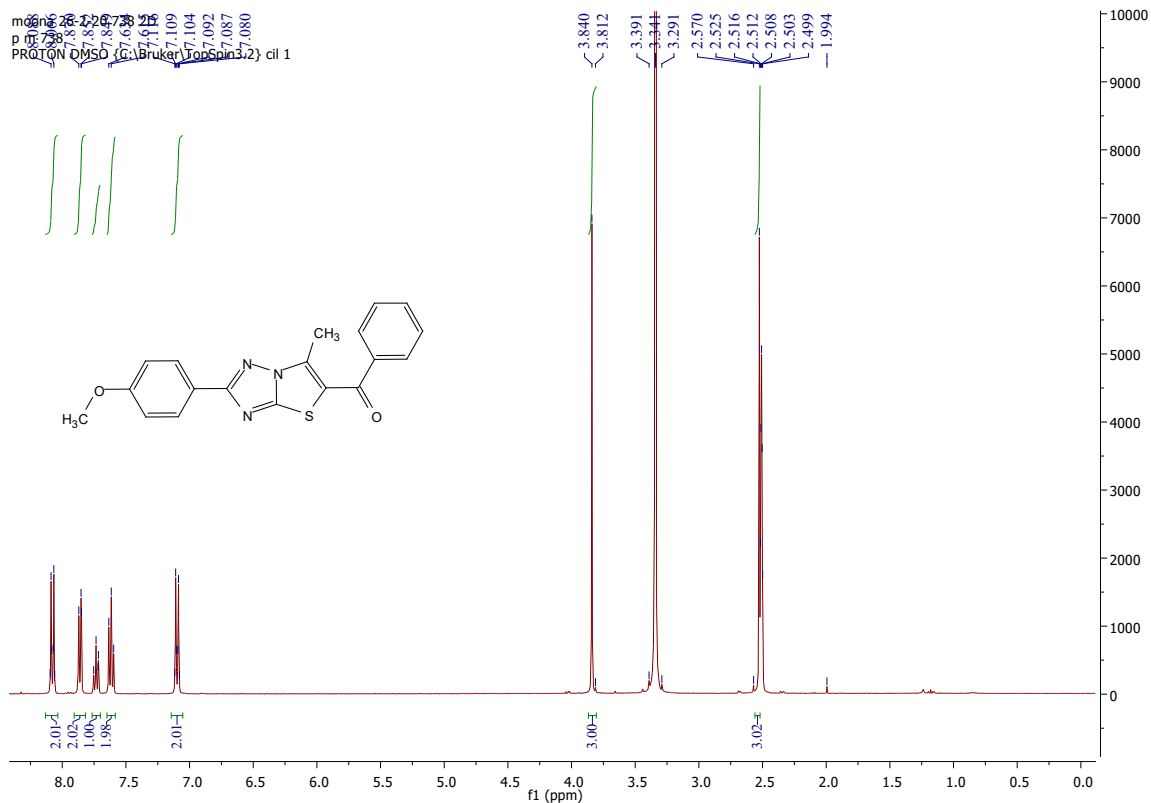


Figure S10a. ¹H NMR spectrum of 6j

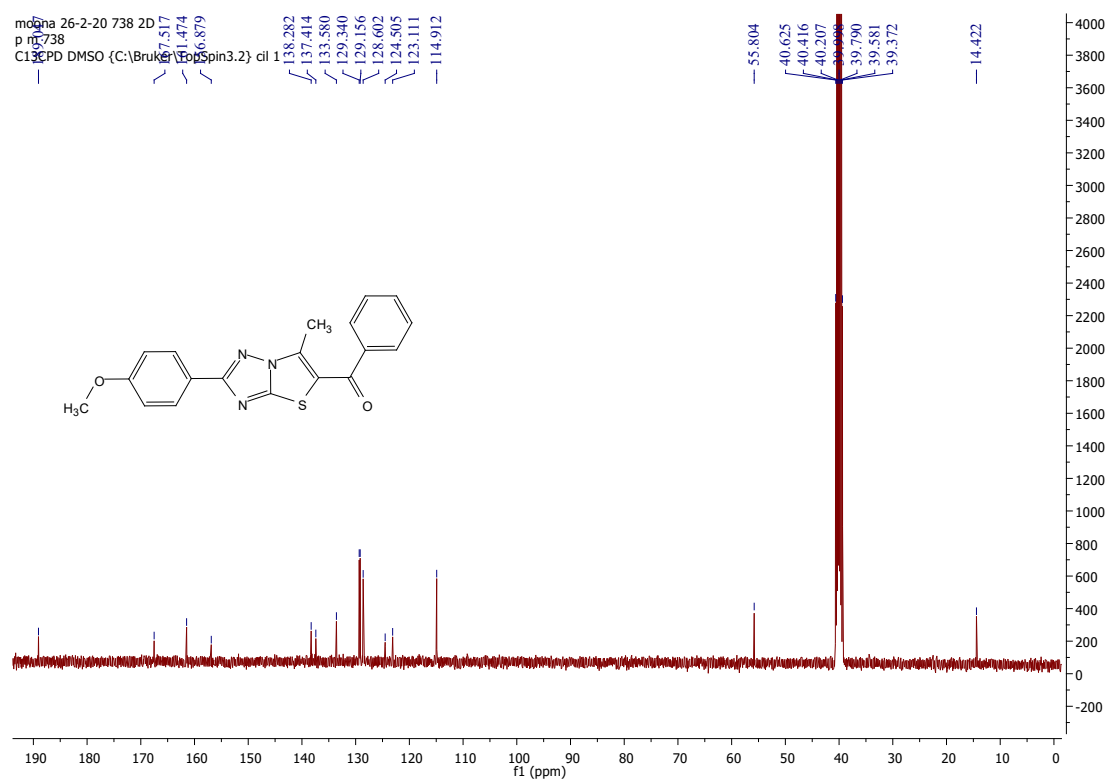


Figure S10b. ¹³C NMR spectrum of 6j

11. (4-fluorophenyl)(2-(4-methoxyphenyl)-6-methylthiazolo[3,2-b][1,2,4]triazol-5-yl)methanone (6k)

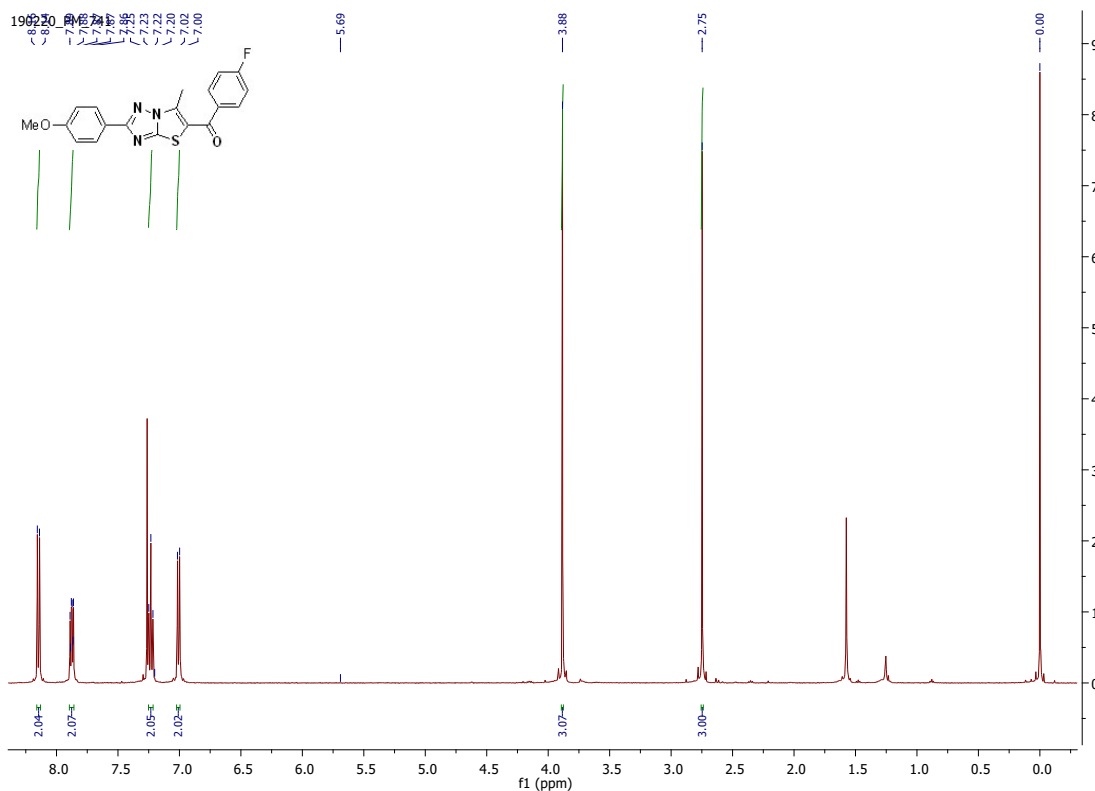


Figure S11a. ¹H NMR spectrum of 6k

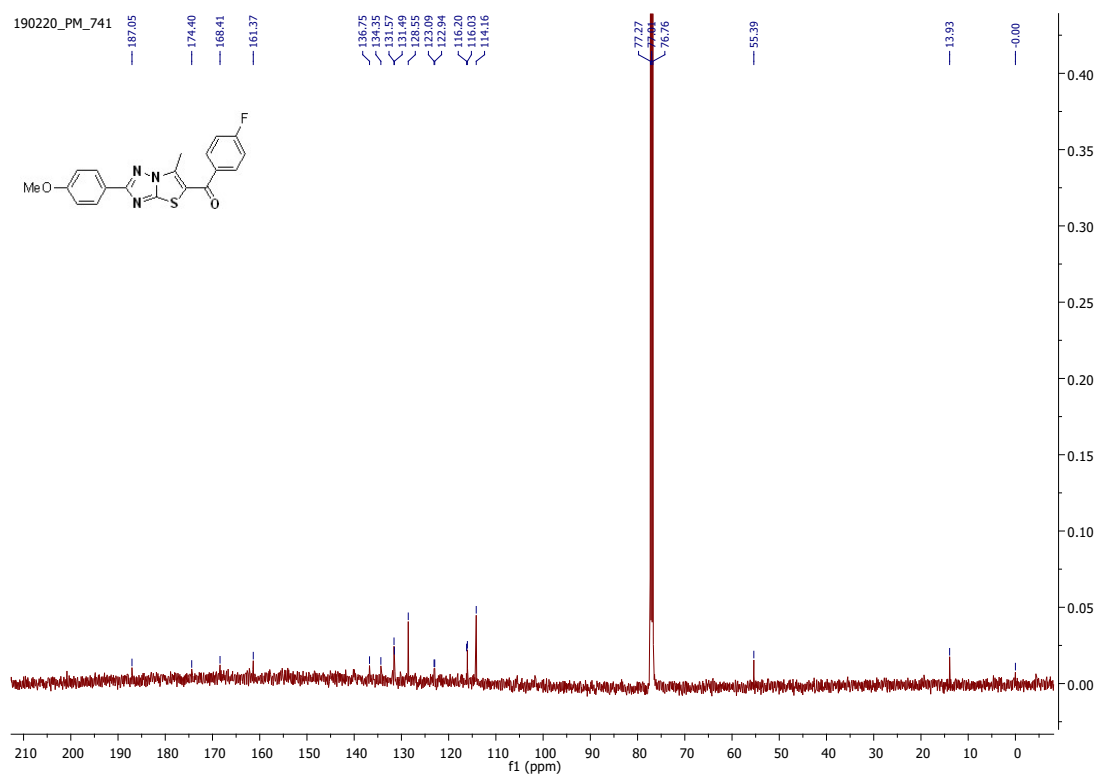


Figure S11b. ¹³C NMR spectrum of 6k

190220_PM_741

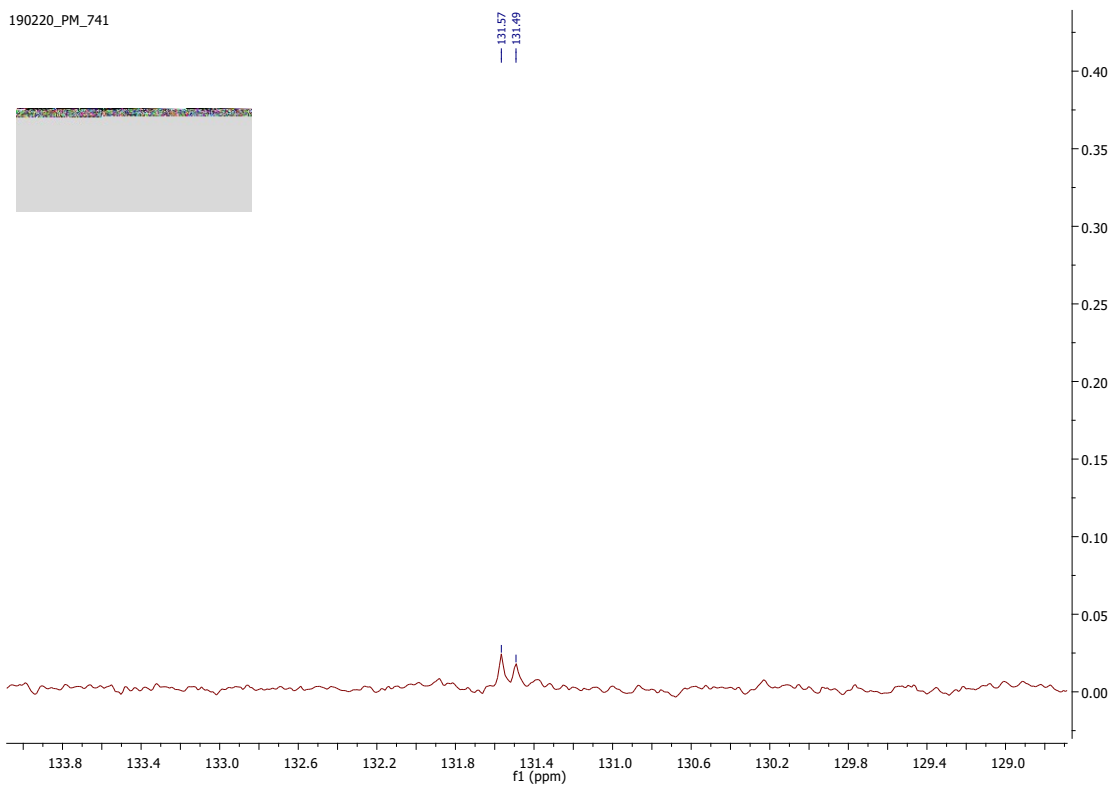


Figure S11c. Zoom ¹³C NMR spectrum of 6k

PS-741
single_pulse

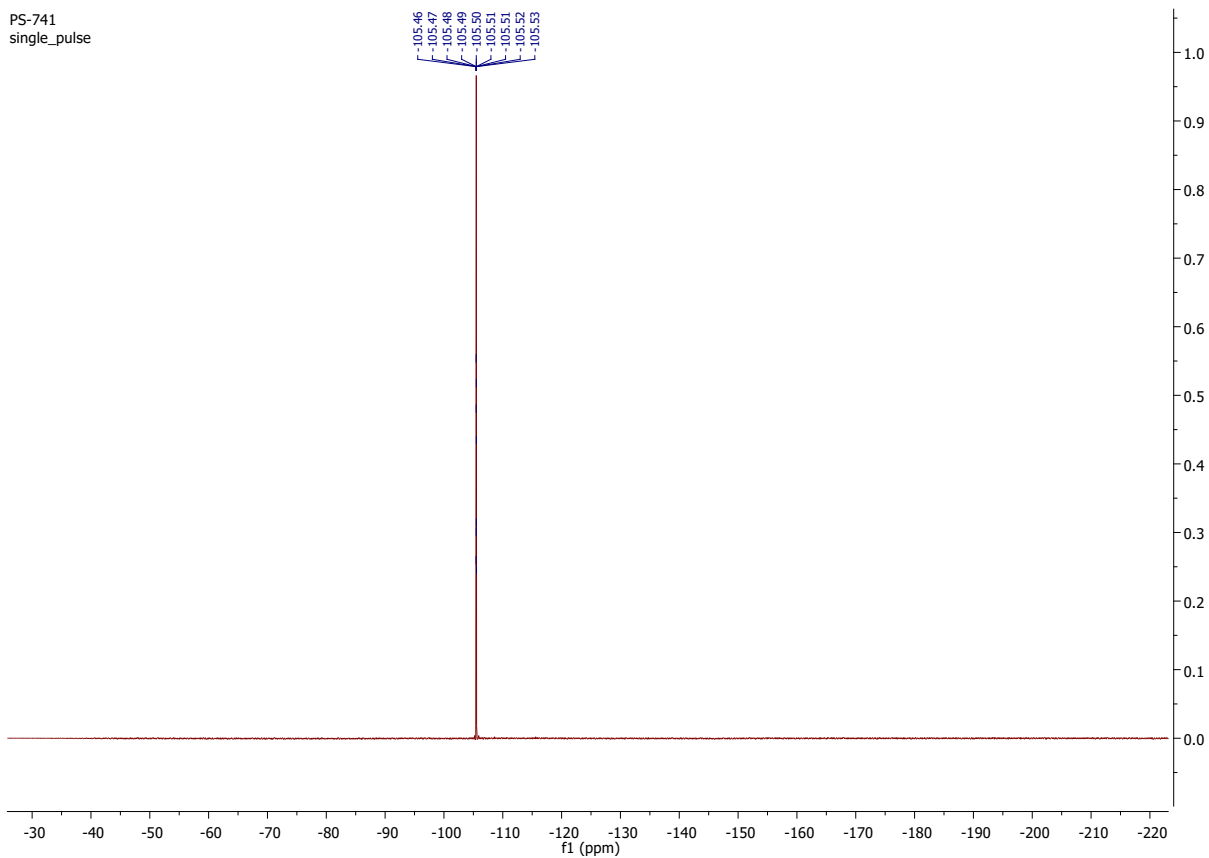


Figure S11d. ¹⁹F NMR spectrum of 6k

12. (4-chlorophenyl)(2-(4-methoxyphenyl)-6-methylthiazolo[3,2-b][1,2,4]triazol-5-yl)methanone (6l)

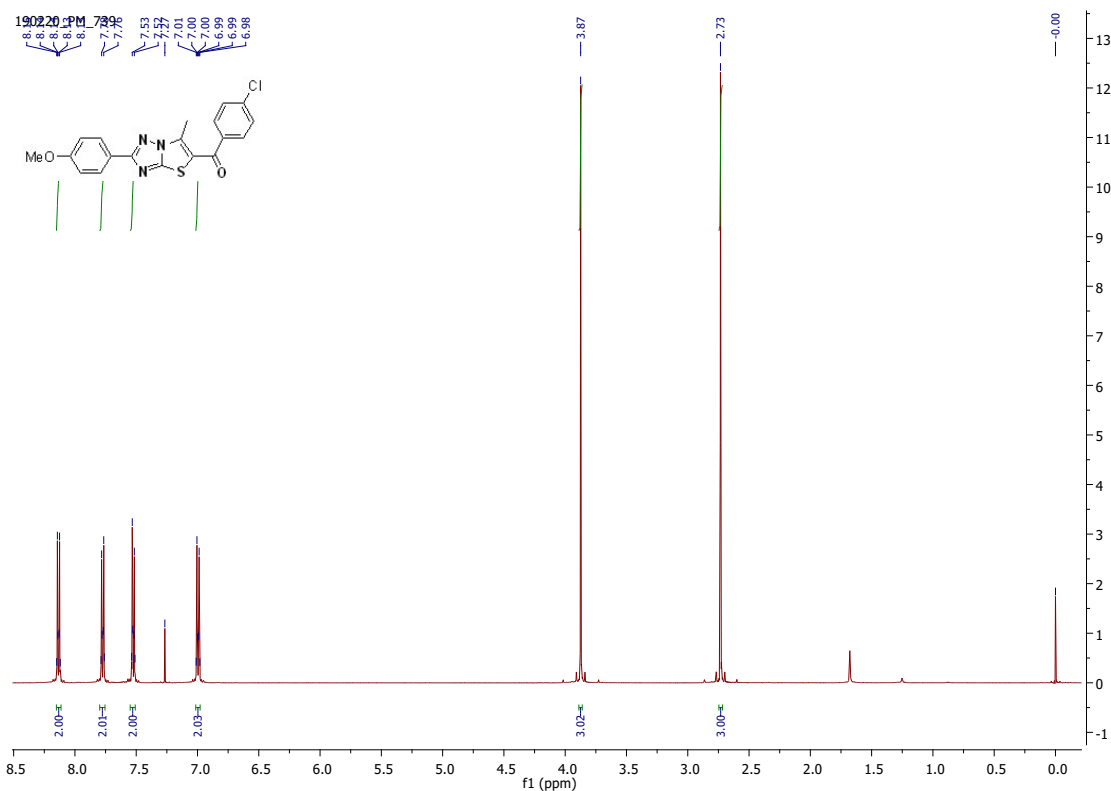


Figure S12a. ¹H NMR spectrum of 6l

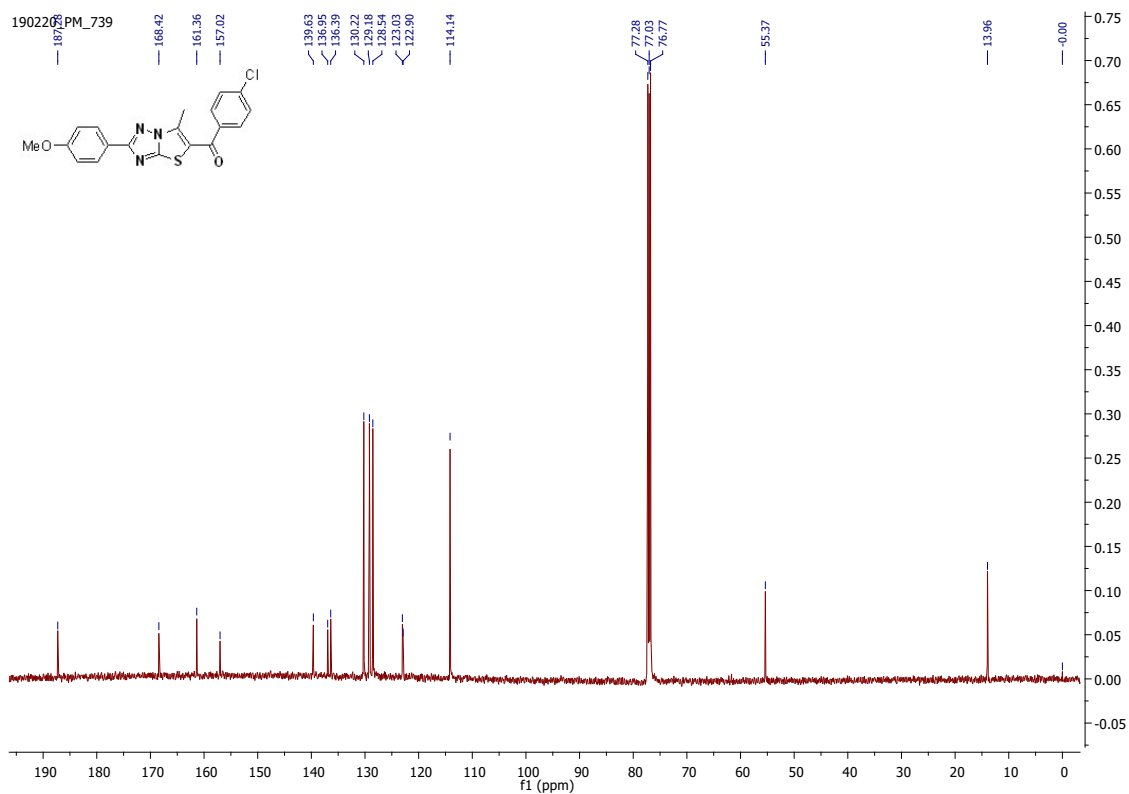


Figure S12b. ¹³C NMR spectrum of 6l

13. (4-bromophenyl)(2-(4-methoxyphenyl)-6-methylthiazolo[3,2-b][1,2,4]triazol-5-yl)methanone (6m)

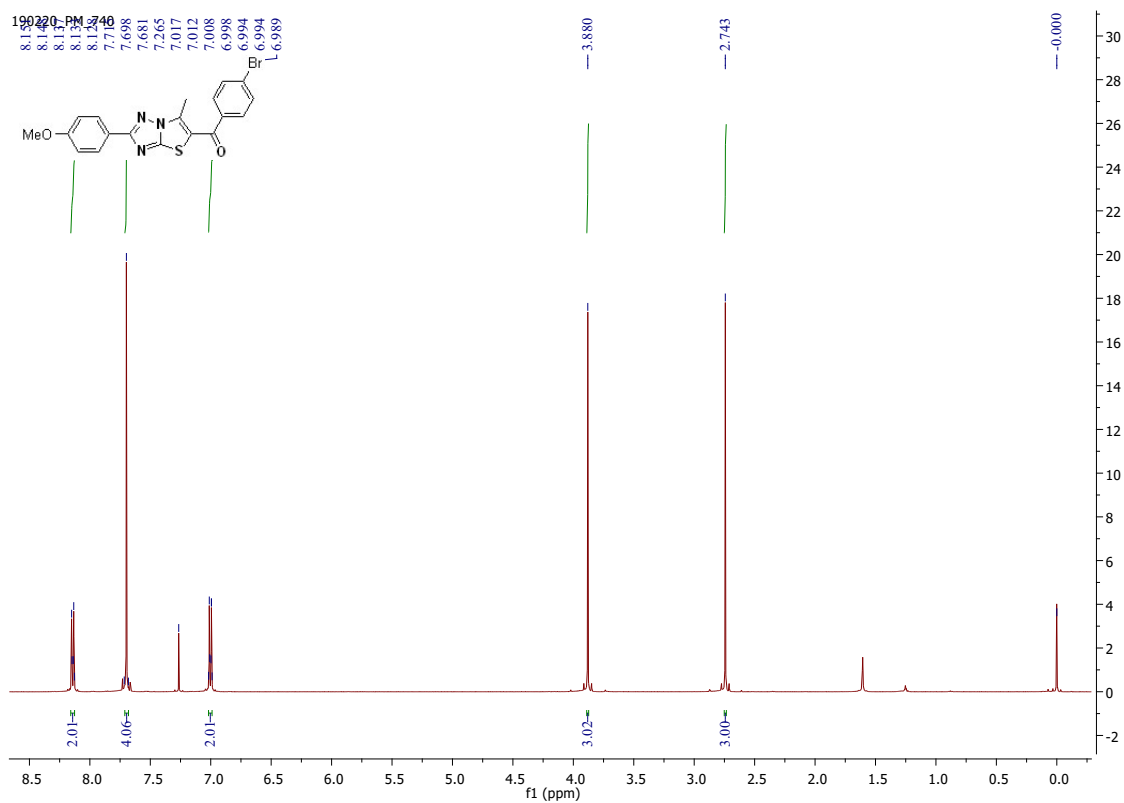


Figure S13a. ¹H NMR spectrum of 6m

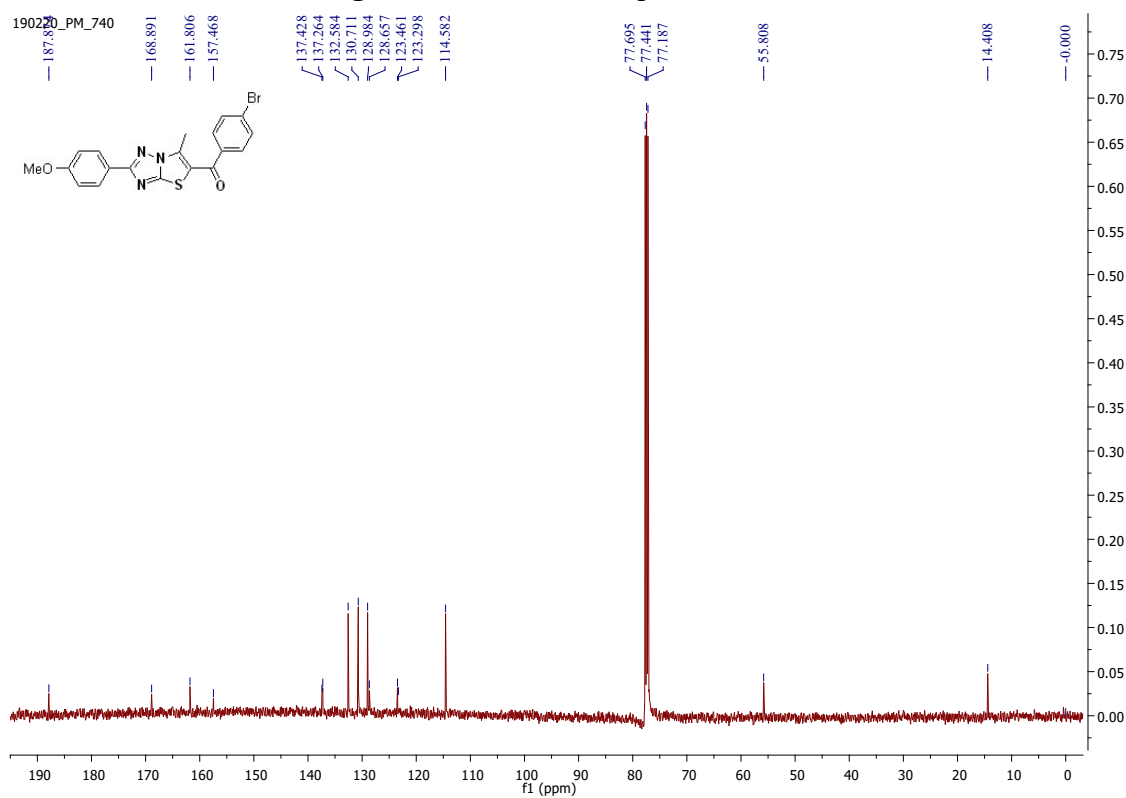


Figure S13b. ¹³C NMR spectrum of 6m

14. (2,4-dichlorophenyl)(2-(4-methoxyphenyl)-6-methylthiazolo[3,2-b][1,2,4]triazol-5-yl)methanone (6n)

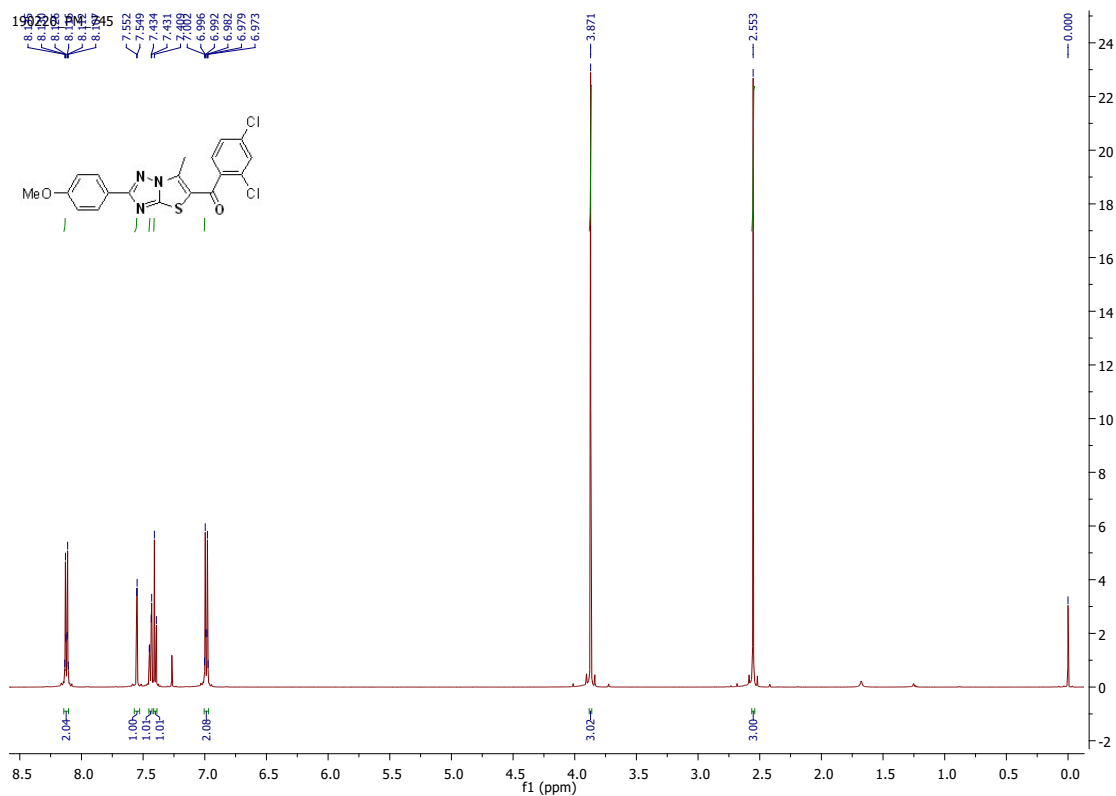


Figure S14a. ¹H NMR spectrum of 6n

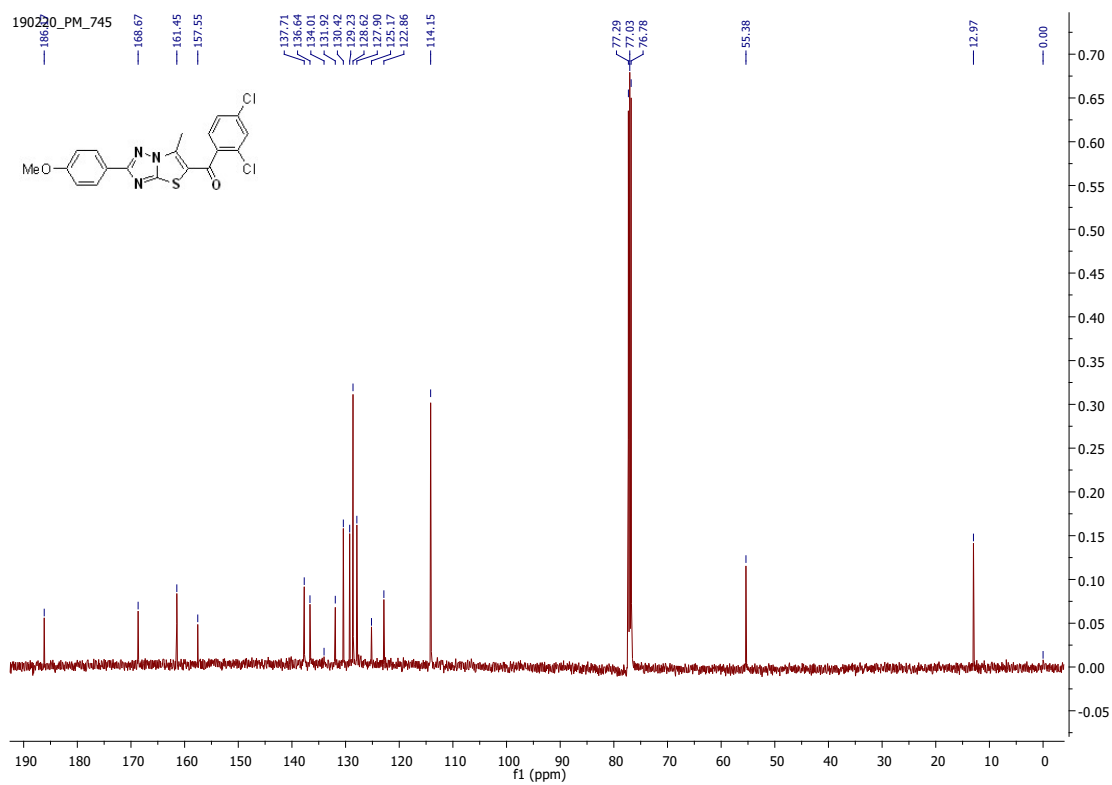


Figure S14b. ¹³C NMR spectrum of 6n

15. (2-(4-methoxyphenyl)-6-methylthiazolo[3,2-b][1,2,4]triazol-5-yl)(p-tolyl)methanone (60)

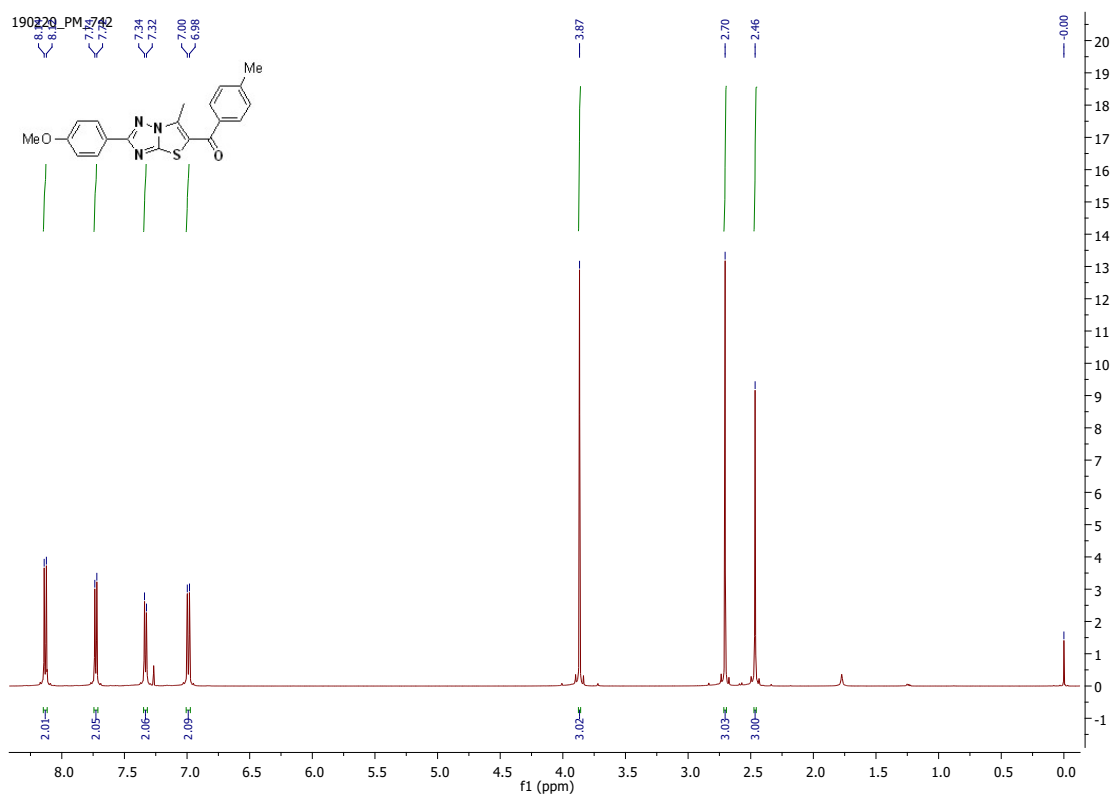


Figure S15a. ¹H NMR spectrum of 60

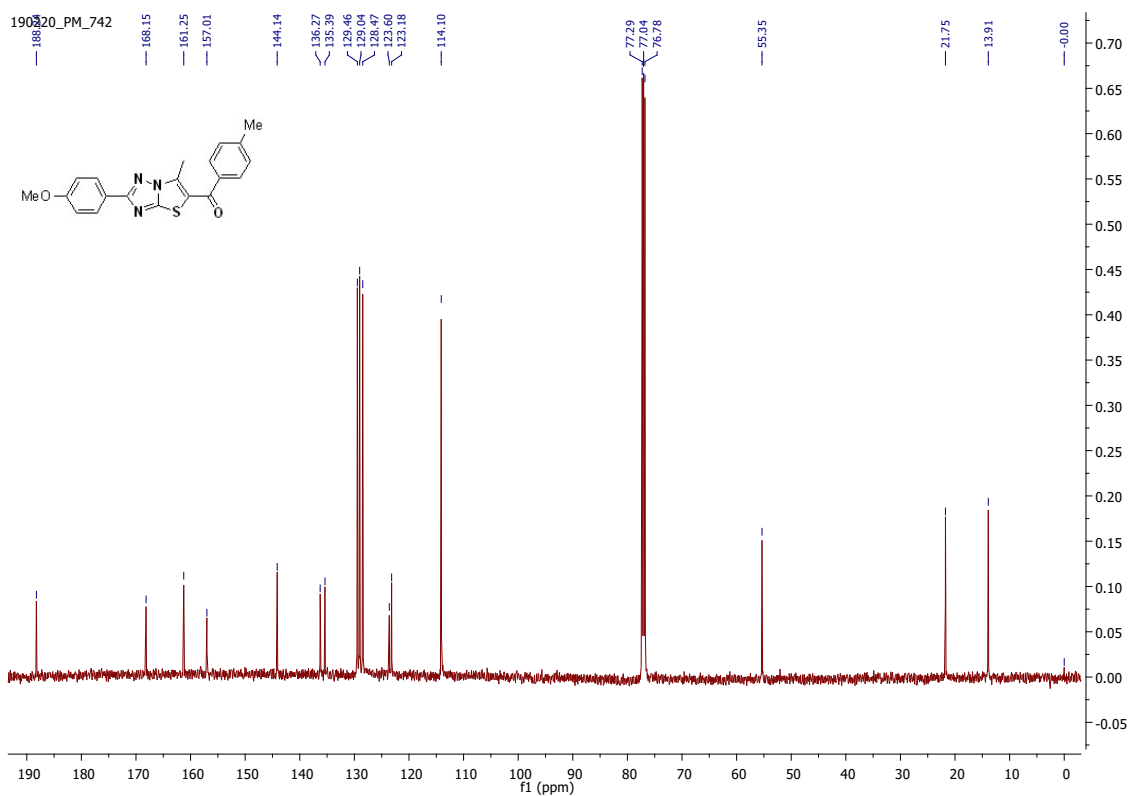


Figure S15b. ¹³C NMR spectrum of 60

16. (4-methoxyphenyl)(2-(4-methoxyphenyl)-6-methylthiazolo[3,2-b][1,2,4]triazol-5-yl)methanone (6p)

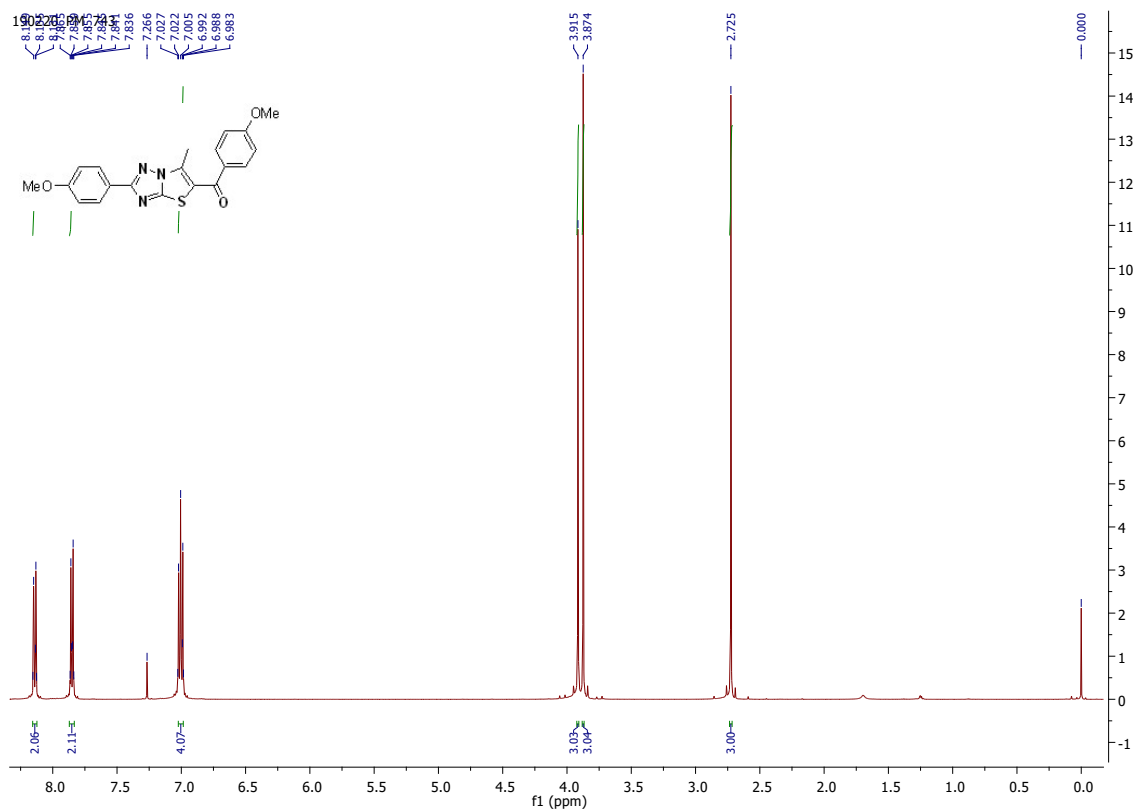


Figure S16a. ¹H NMR spectrum of 6p

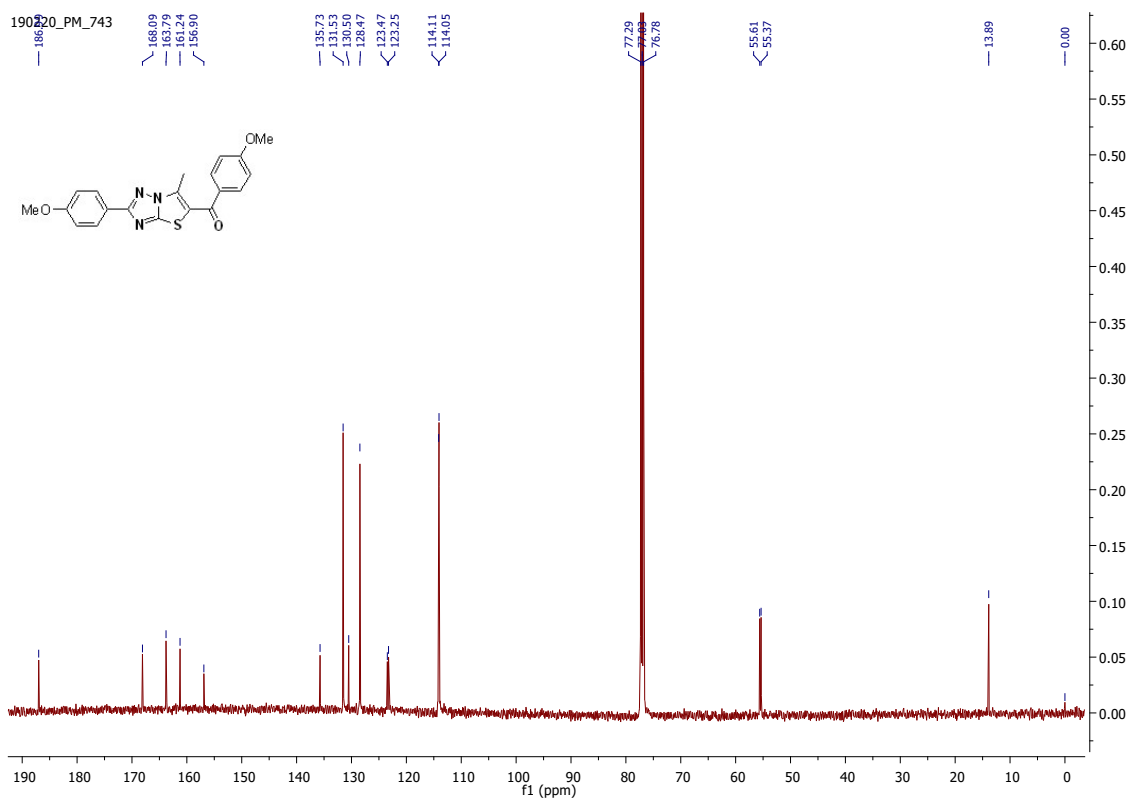


Figure S16b. ¹³C NMR spectrum of 6p

17. (3-methoxyphenyl)(2-(4-methoxyphenyl)-6-methylthiazolo[3,2-b][1,2,4]triazol-5-yl)methanone (6q)

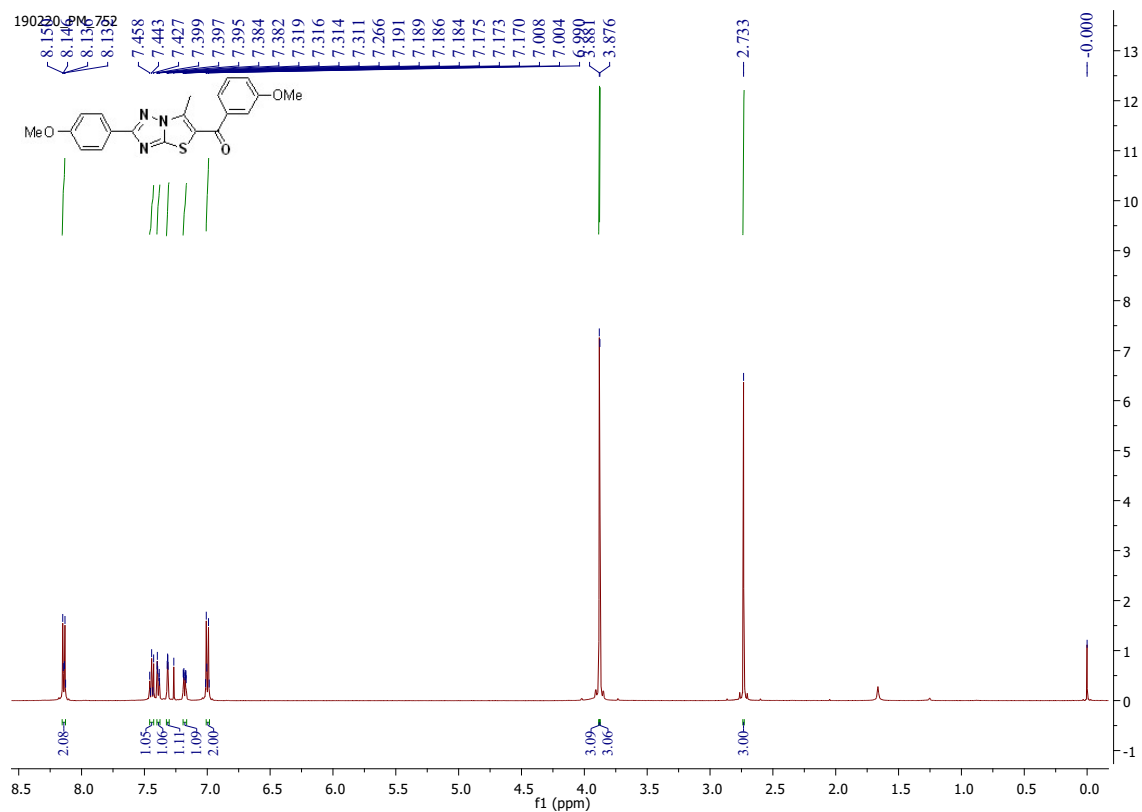


Figure S17a. ¹H NMR spectrum of 6q

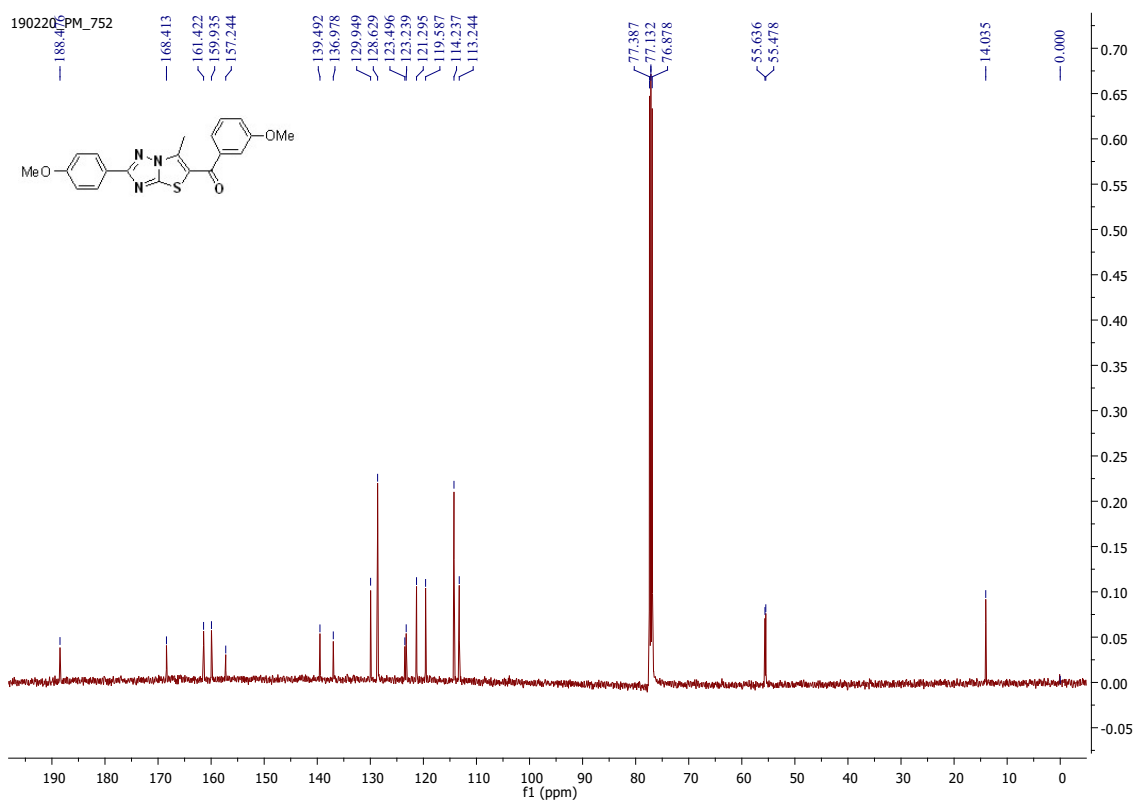


Figure S17b. ¹³C NMR spectrum of 6q

18. (2-(4-methoxyphenyl)-6-methylthiazolo[3,2-b][1,2,4]triazol-5-yl)(thiophen-2-yl)methanone (6r)

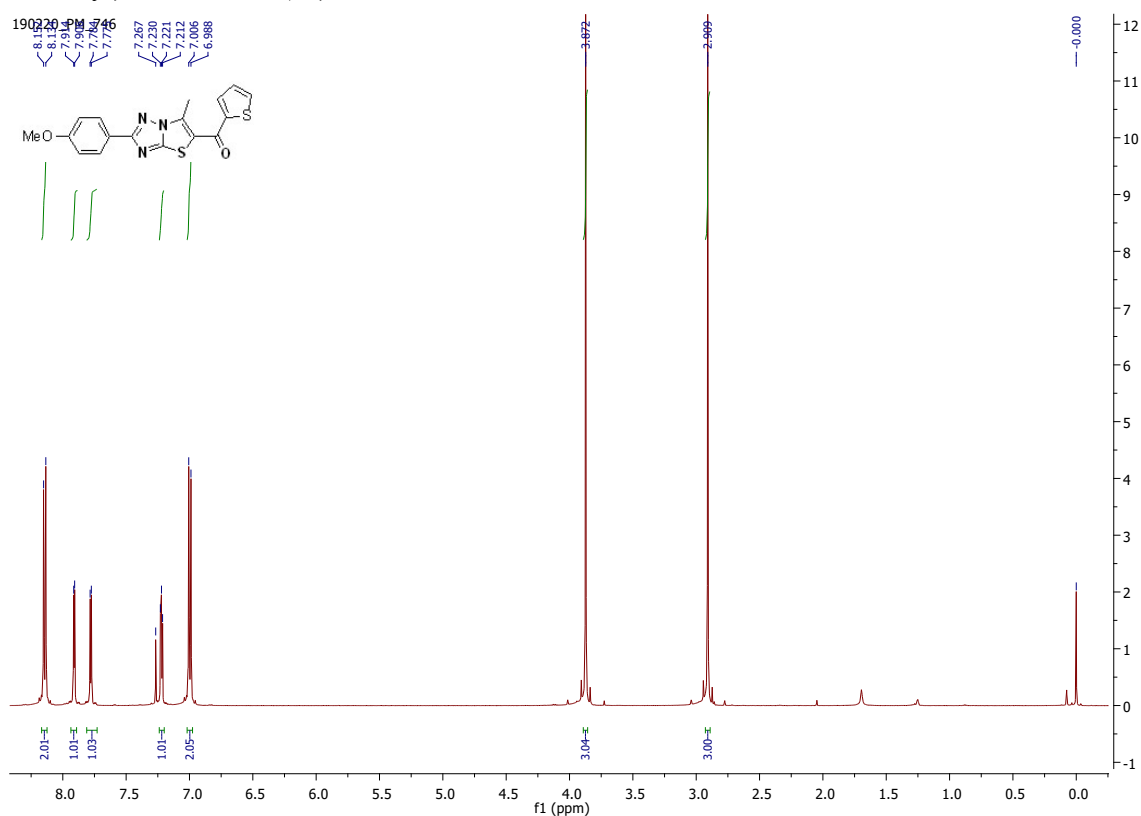


Figure S18a. ¹H NMR spectrum of 6r

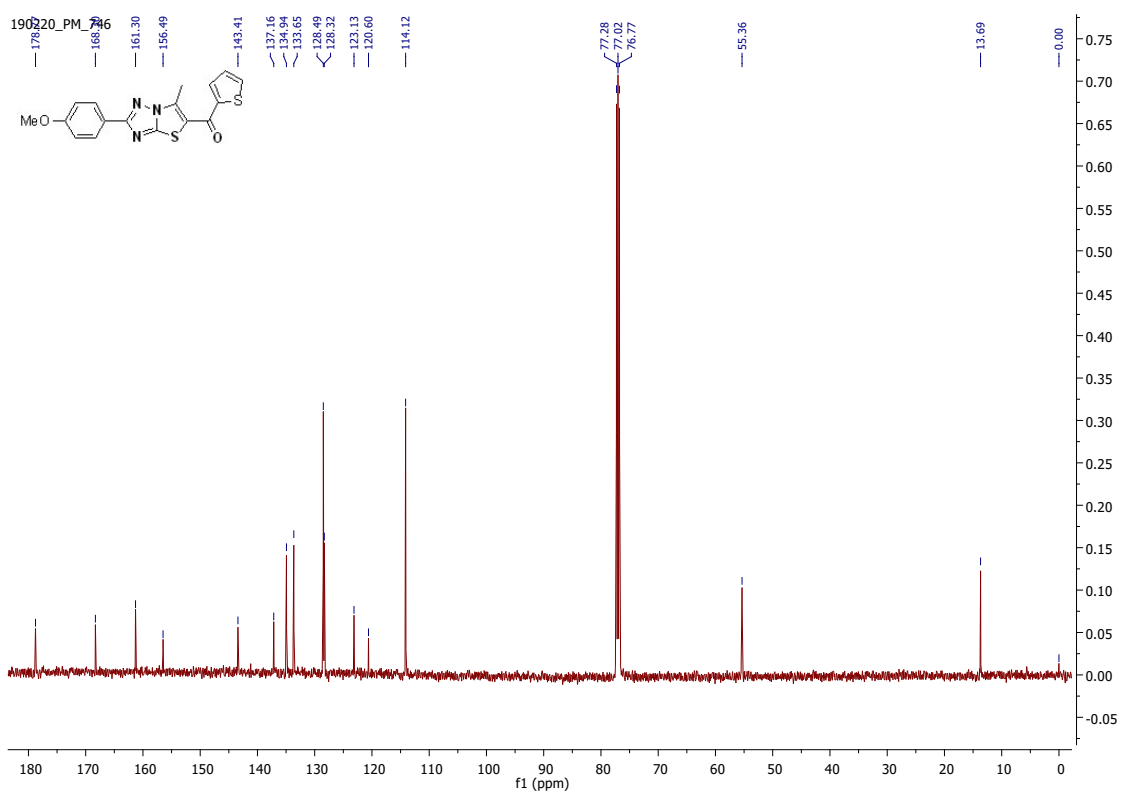


Figure S18b. ¹³C NMR spectrum of 6r

2D NMR (HMBC & HMQC)

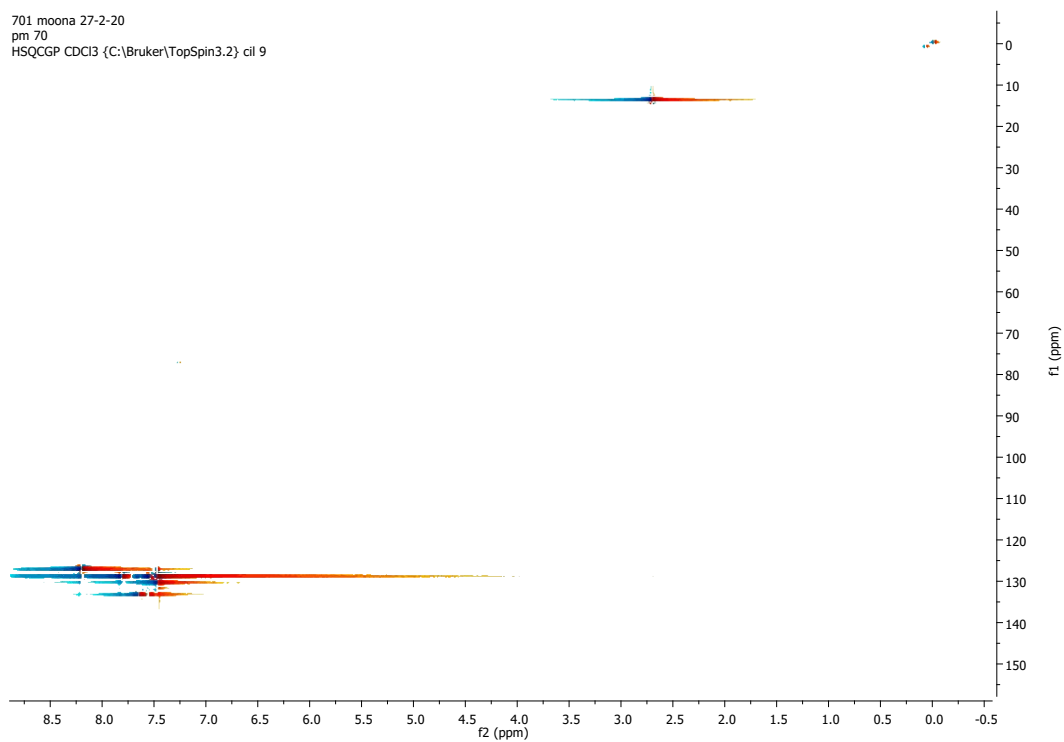


Figure S19a. HMQC of 6a

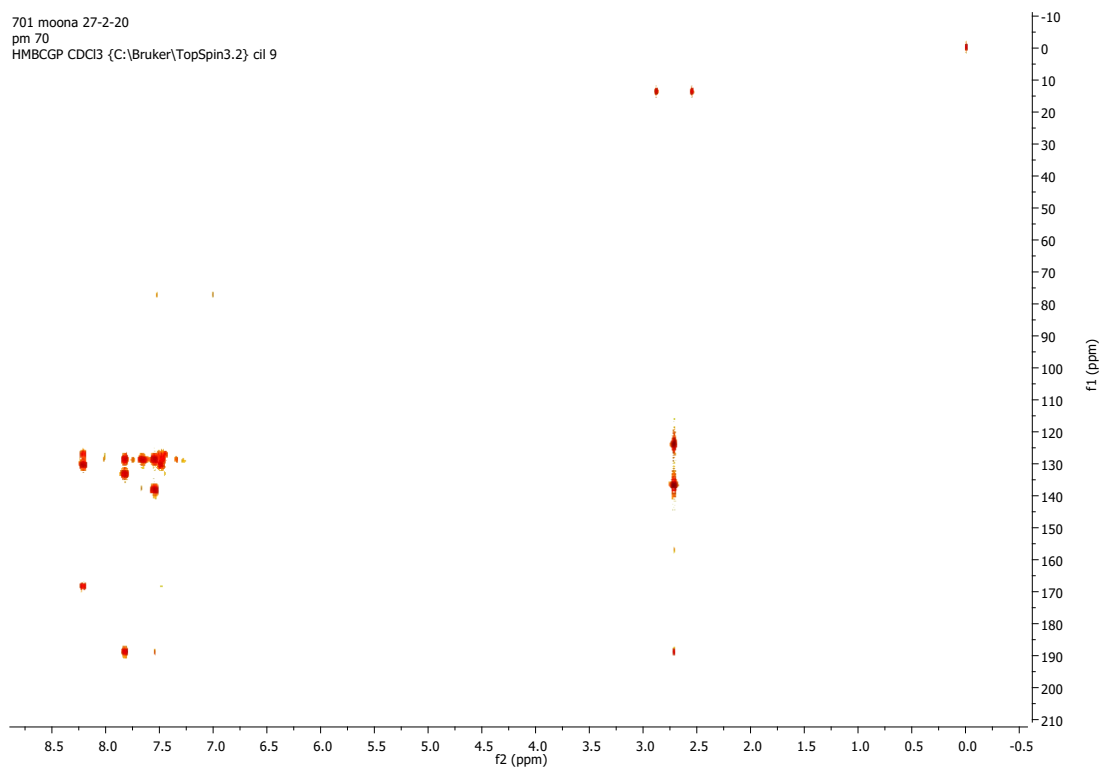
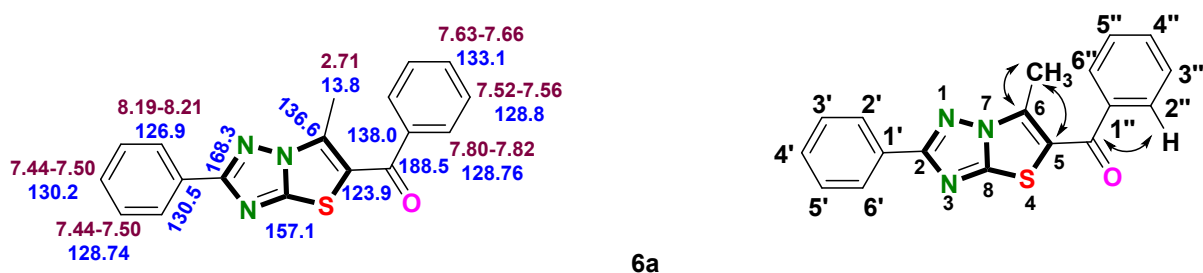


Figure S19b. HMBC of 6a

Table S1. NMR data in CDCl₃, chemical shifts (δ , ppm) and coupling constants (J , Hz) for compound **6a**



6a

Chemical shifts (δ in ppm)	gs-HMQC correlation	gs-HMBC correlation	Assignments
188.5	---	7.80-7.82 (H2''/H6'')	CO
168.3	---	8.19-8.21 (H2'/H6')	C2
157.1	---	---	C8
138.0	---	7.52-7.56 (H3''/H5'')	C1''
136.6	---	2.71 (6-Me)	C6
133.1	7.63-7.67 (H4'')	7.80-7.82 (H2''/H6'')	C4''
130.5	-	7.44-7.50 (H4')	C1'
		7.44-7.50 (H3'/H5')	
130.2	7.44-7.50 (H4')	7.44-7.50 (H3'/H5')	C4'
		8.19-8.21 (H2'/H6')	
128.8	7.52-7.56 (H3''/H5'')	7.80-7.82 (H2''/H6'')	C3''/C5''
128.76	7.80-7.82 (H2''/H6'')	7.52-7.56 (H3''/H5'')	C2''/C6''
		7.63-7.67 (H4'')	
128.74	7.44-7.50 (H3'/H5')	8.19-8.21 (H2'/H6')	C3'/C5'
126.9	8.19-8.21 (H2'/H6')	7.44-7.50 (H3'/H5')	C2'/C6'
123.9		2.71 (6-Me)	C5
13.8	2.71 (6-Me)	123.9 (C5)	6-Me
		136.6 (C6)	

moona 26-2-20
p m 738
HSQC GP DMSO {C:\Bruker\TopSpin3.2} cil 1

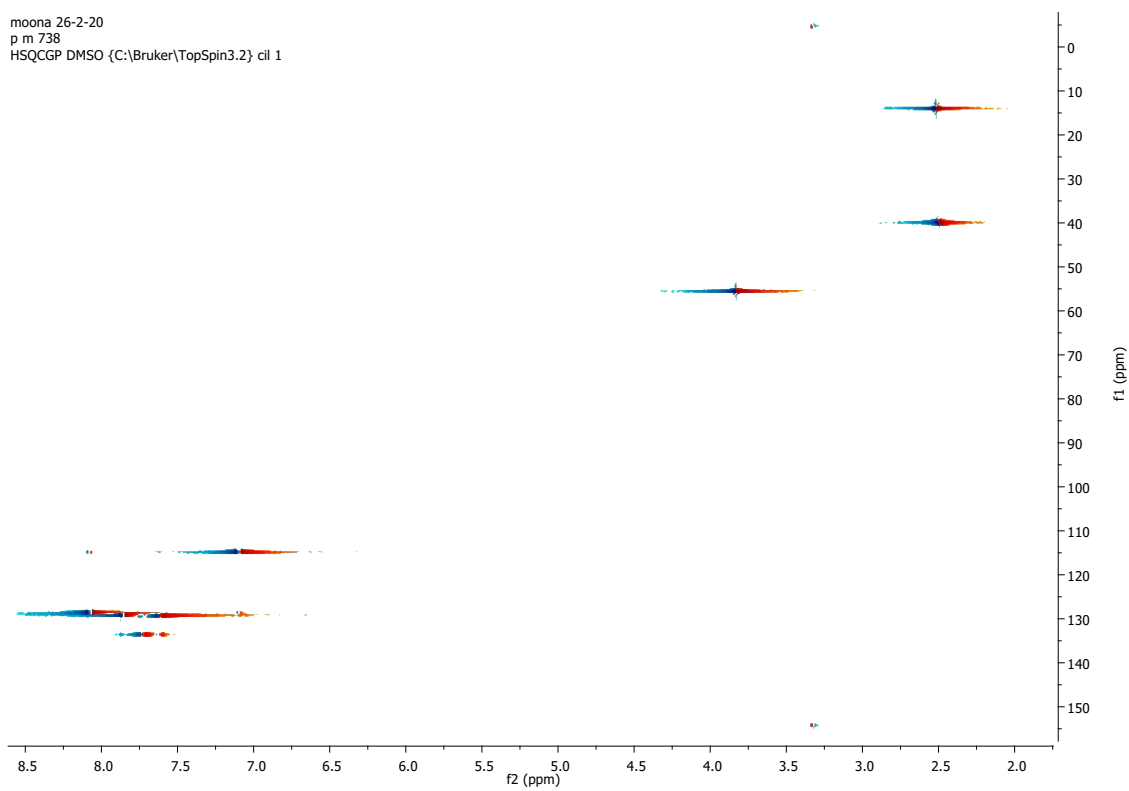


Figure S20a. HMQC of 6j

moona 26-2-20
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HMBC GP DMSO {C:\Bruker\TopSpin3.2} cil 1

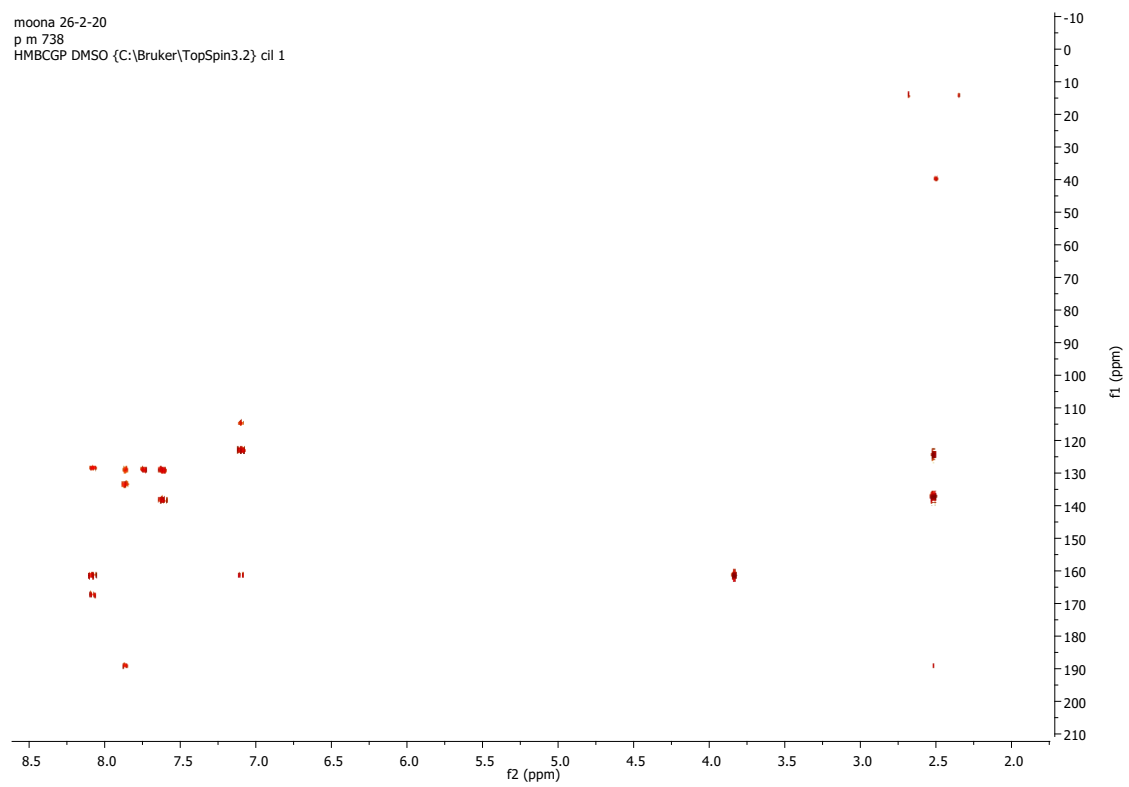
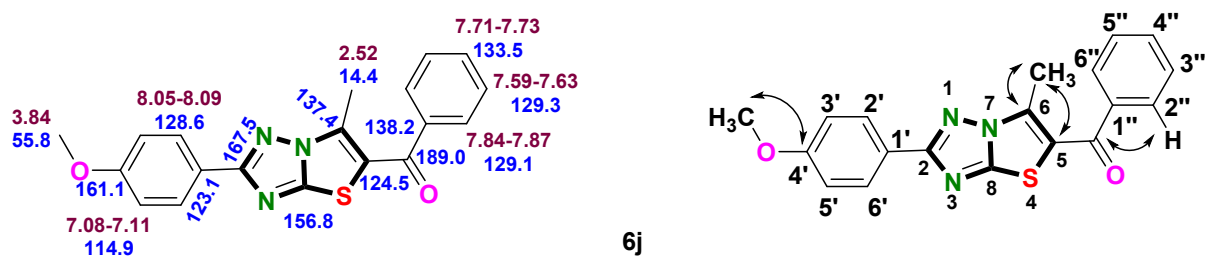


Figure S20b. HMBC of 6j

Table S2. NMR data in CDCl₃, chemical shifts (δ , ppm) and coupling constants (J , Hz) for compound **6j**



Chemical shifts (δ in ppm)	gs-HMQC correlation	gs-HMBC correlation	Assignments
189.0	---	7.84-7.87 (H2''/H6'')	CO
167.5	---	8.05-8.09 (H2'/H6')	C2
161.1	---	8.05-8.09 (H2'/H6') 7.08-7.11 (H3'/H5')	C4'
156.8	---	-	C8
138.2	---	7.59-7.63 (H3''/H5'')	C1''
137.4		2.52 (6-Me)	C6
133.5	7.71-7.75 (H4'')	7.84-7.87 (H2''/H6'')	C4''
129.3	7.59-7.63 (H3''/H5'')	7.71-7.75 (H4'') 7.59-7.63 (H3''/H5'')	C3''/C5''
129.1	7.84-7.87 (H2''/H6'')	7.59-7.63 (H3''/H5'')	C2''/C6''
128.6	8.05-8.09 (H2'/H6')	-	C2'/C6'
124.5		2.52 (6-Me)	C5
123.1		7.08-7.11 (H3'/H5')	C1'
114.9	7.08-7.11 (H3'/H5')	-	C3'/C5'
55.8	3.83 (4-OMePh)	161.1 (C4')	4-OMePh
14.4	2.52 (6-Me)	124.5 (C5) 137.4 (C6)	6-Me

HRMS

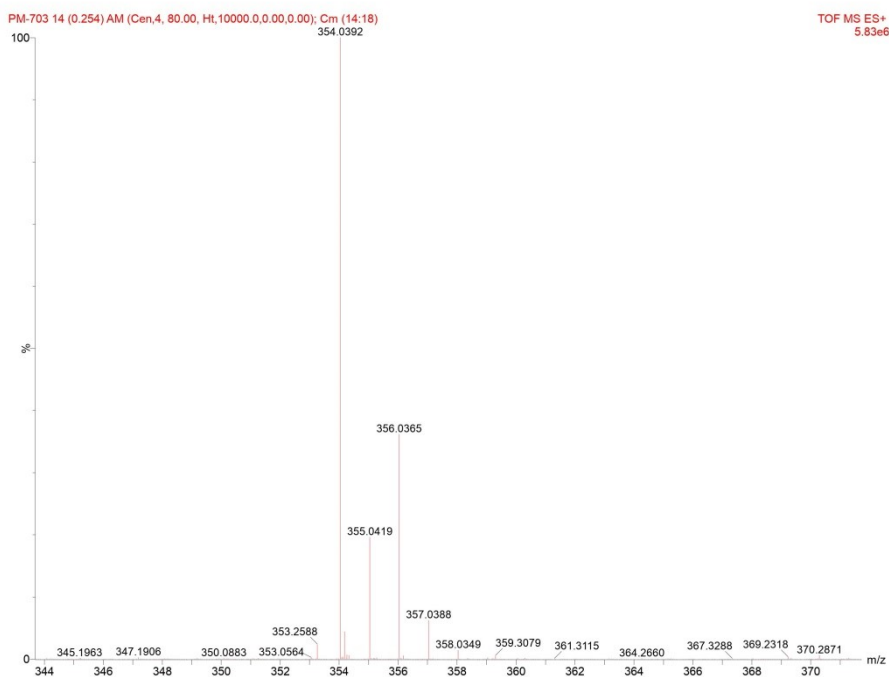


Figure S21. HRMS of *(4-chlorophenyl)(6-methyl-2-phenylthiazolo[3,2-b][1,2,4]triazol-5-yl)methanone (6c)*

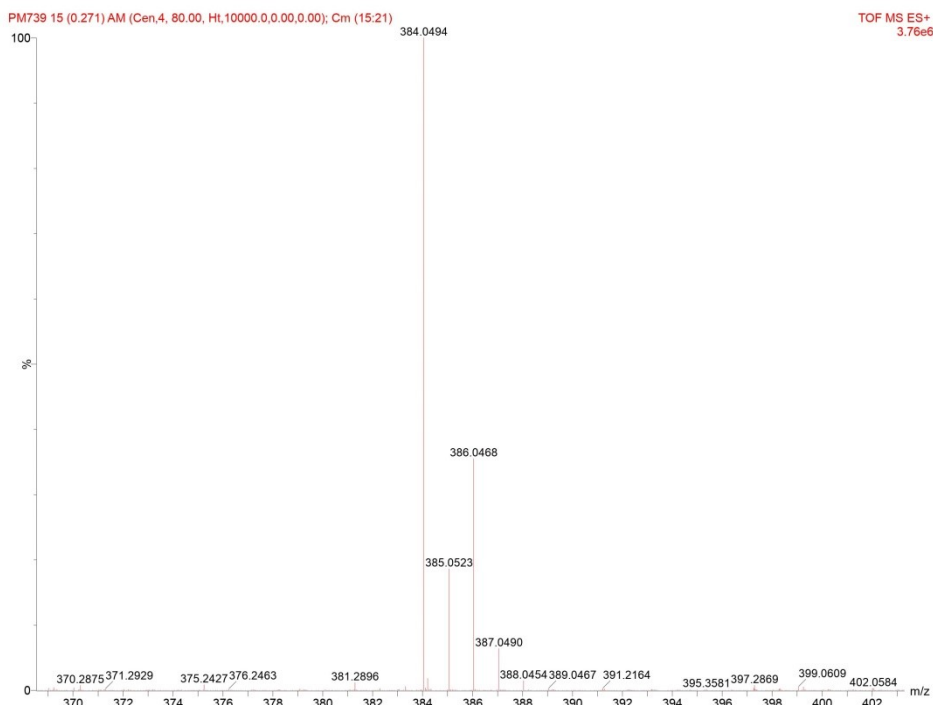


Figure S22. HRMS of *(4-chlorophenyl)(2-(4-methoxyphenyl)-6-methylthiazolo[3,2-b][1,2,4]triazol-5-yl)methanone (6l)*

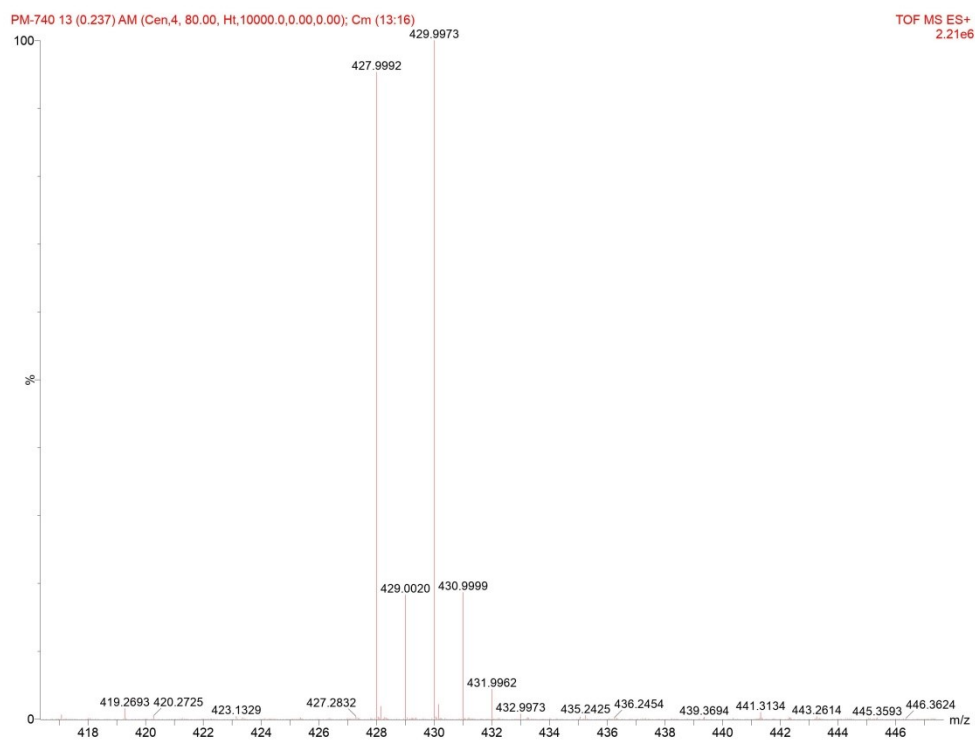


Figure S22. HRMS of *(4-bromophenyl)(2-(4-methoxyphenyl)-6-methylthiazolo[3,2-b][1,2,4]triazol-5-yl)methanone (6m)*

X-ray Crystallographic Data for 6j

Table S3. Bond Lengths for 6j.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S4	C8	1.7226(19)	C5	C9	1.464(3)
S4	C5	1.7804(17)	C5	C6	1.349(3)
N7	C8	1.339(2)	C19	C18	1.388(3)
N7	C6	1.387(2)	C19	C20	1.387(3)
N7	N1	1.370(2)	C9	C10	1.488(3)
O2	C19	1.363(2)	C2	N1	1.329(2)
O2	C22	1.417(3)	C6	C23	1.433(2)
N3	C8	1.313(2)	C15	C10	1.388(3)
N3	C2	1.375(2)	C15	C14	1.378(3)
C16	C21	1.387(3)	C18	C17	1.376(3)
C16	C2	1.469(3)	C10	C11	1.390(3)
C16	C17	1.393(3)	C11	C12	1.382(3)
O1	C9	1.220(2)	C12	C13	1.373(4)
C21	C20	1.390(3)	C13	C14	1.377(3)

Table S4. Bond Angles for 6j.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	S4	C5	89.25(8)	O1	C9	C10	120.35(17)
C8	N7	C6	117.73(15)	C5	C9	C10	121.00(15)
C8	N7	N1	110.80(14)	N3	C2	C16	122.42(16)
N1	N7	C6	131.46(14)	N1	C2	N3	116.14(16)
C19	O2	C22	118.21(16)	N1	C2	C16	121.44(17)
C8	N3	C2	101.75(15)	N7	C6	C23	117.88(15)
N7	C8	S4	110.61(13)	C5	C6	N7	109.45(15)
N3	C8	S4	138.46(14)	C5	C6	C23	132.62(16)
N3	C8	N7	110.93(16)	C14	C15	C10	119.72(19)

C21	C16	C2	121.46(16)	C17	C18	C19	120.98(17)
C21	C16	C17	118.38(17)	C15	C10	C9	121.49(17)
C17	C16	C2	120.15(18)	C15	C10	C11	119.56(18)
C16	C21	C20	121.58(17)	C11	C10	C9	118.80(17)
C9	C5	S4	114.59(13)	C19	C20	C21	119.28(19)
C6	C5	S4	112.93(13)	C12	C11	C10	120.0(2)
C6	C5	C9	132.37(16)	C18	C17	C16	120.38(19)
O2	C19	C18	115.90(16)	C13	C12	C11	120.0(2)
O2	C19	C20	124.69(19)	C12	C13	C14	120.2(2)
C20	C19	C18	119.41(17)	C13	C14	C15	120.5(2)
O1	C9	C5	118.63(17)	C2	N1	N7	100.38(14)