Comparative Study of the Reaction of 2-Mercaptobenzimidazole with 2-Bromo-1,3-Diketones under Conventional and Green Conditions: Regioselective Access to N/S-difunctionalized Benzimidazoles and Benzimidazo[2,1-*b*]thiazoles

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SUPPLEMENTARY DATA

General method for preparation of 6-substituted-2-aroyl-3-methylbenzimidazo[2,1-*b*]thiazoles 6(a-n)

1,3-Diketones **3** (1.0 mmol) were ground with N-bromosuccinimide (1.0 mmol) in a dry mortar for 15-30 min, forming a thick paste. The mixture was then transferred to a conical flask and stirred with 15 mL of absolute ethanol under visible-light irradiations. Next, 2-mercaptobenzimidazoles **5** (1.0 mmol) were added and stirred for 30-40 min until completion, monitored by TLC using ethyl acetate-petroleum ether (20:80, v/v). Excess ethanol was removed under reduced pressure and the reaction mixture was neutralized with aqueous sodium bicarbonate. The obtained solid products **6(a-n)** were recrystallized using ethanol and dried, yielding high-purity products.

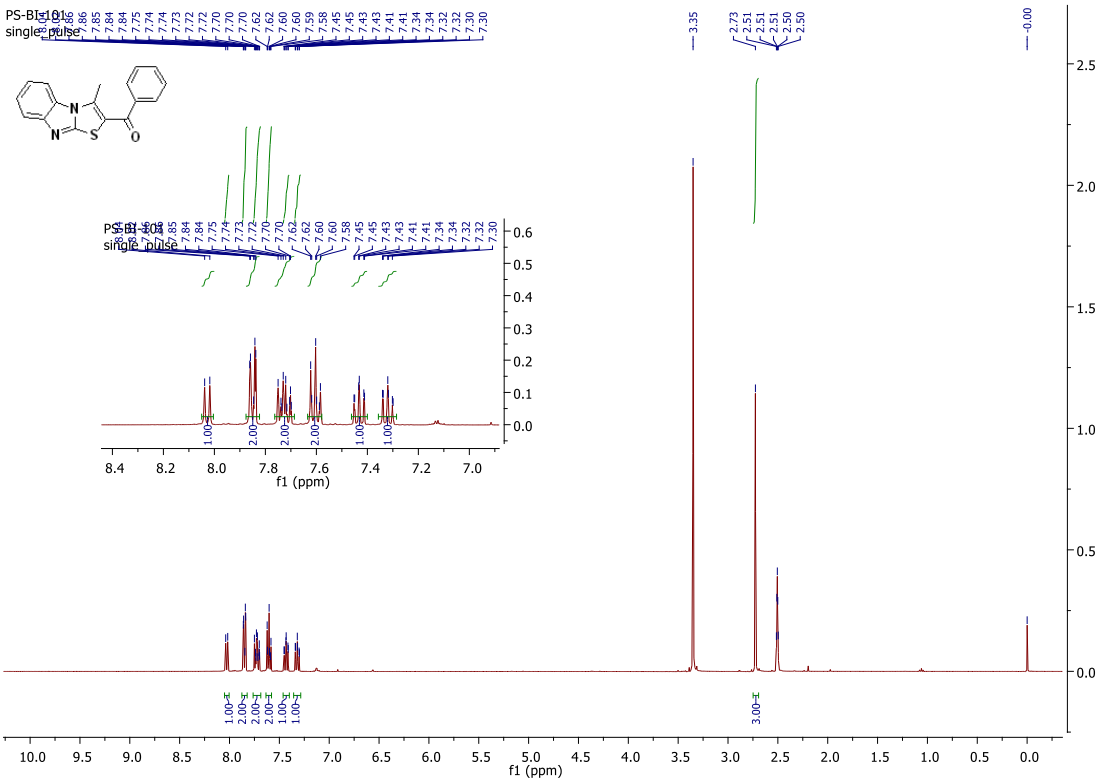
General method for preparation of 2-((1-acetyl-1*H*-benzimidazol-2-yl)thio)-1-arylethan-1-one 10(a-e)

1,3-Diketones **3** (1.0 mmol) were grounded with NBS (1.0 mmol) in a dry mortar for 15-30 min to form a thick paste. Subsequently, 2-mercaptobenzimidazole **5** (1.0 mmol) was added and the reaction mixture was further grounded thoroughly at room temperature for 15-20 min. Reaction progress was monitored by TLC using ethyl acetate-petroleum ether (20:80, v/v). After completion, 30 mL of saturated sodium bicarbonate solution was added and the mixture was filtered to obtain the crude solid. N/S-difunctionalized benzimidazole derivatives **10(a-e)**, were recrystallized from ethanol and dried, yielding high-purity products.

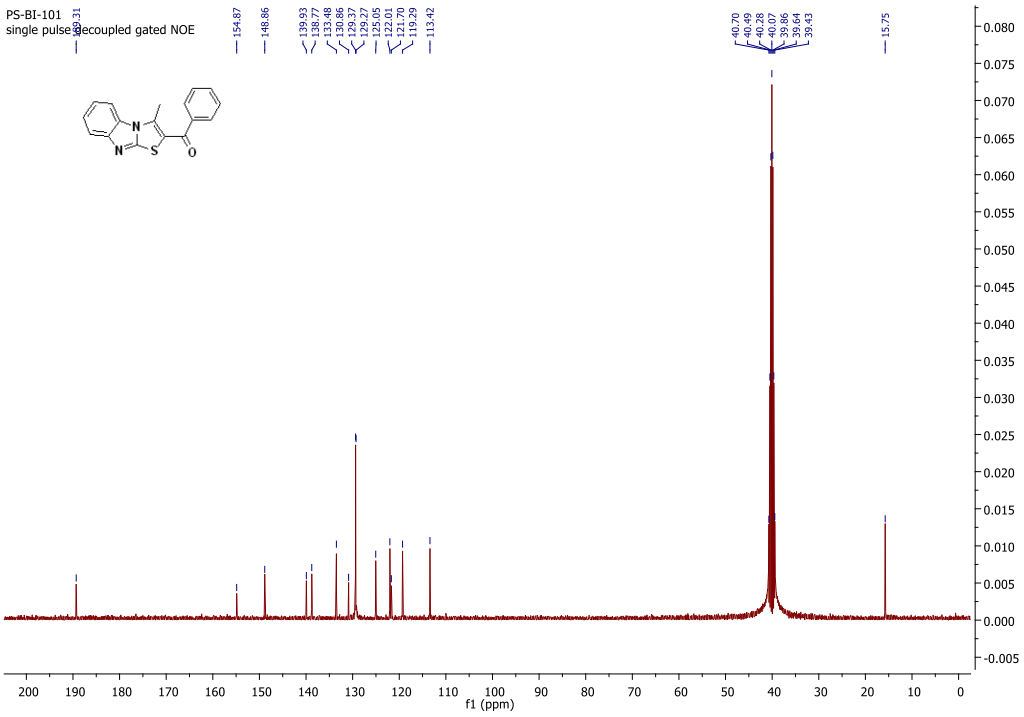
Characterization of Final Compounds

^{1}H NMR, ^{13}C NMR, HSQC, HMBC and HRMS Spectrum of Final Compounds

2-Benzoyl-3-methylbenzo[4,5]imidazo[2,1-b]thiazole (6a)

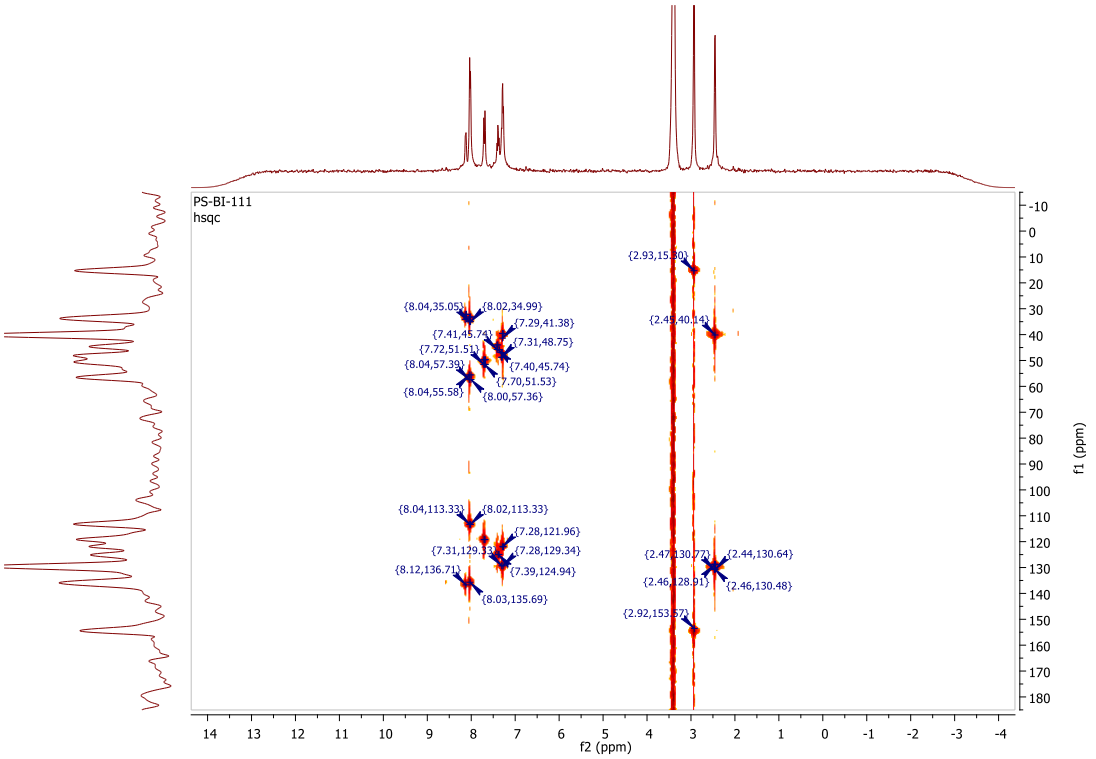


^{1}H NMR spectrum of **6a**

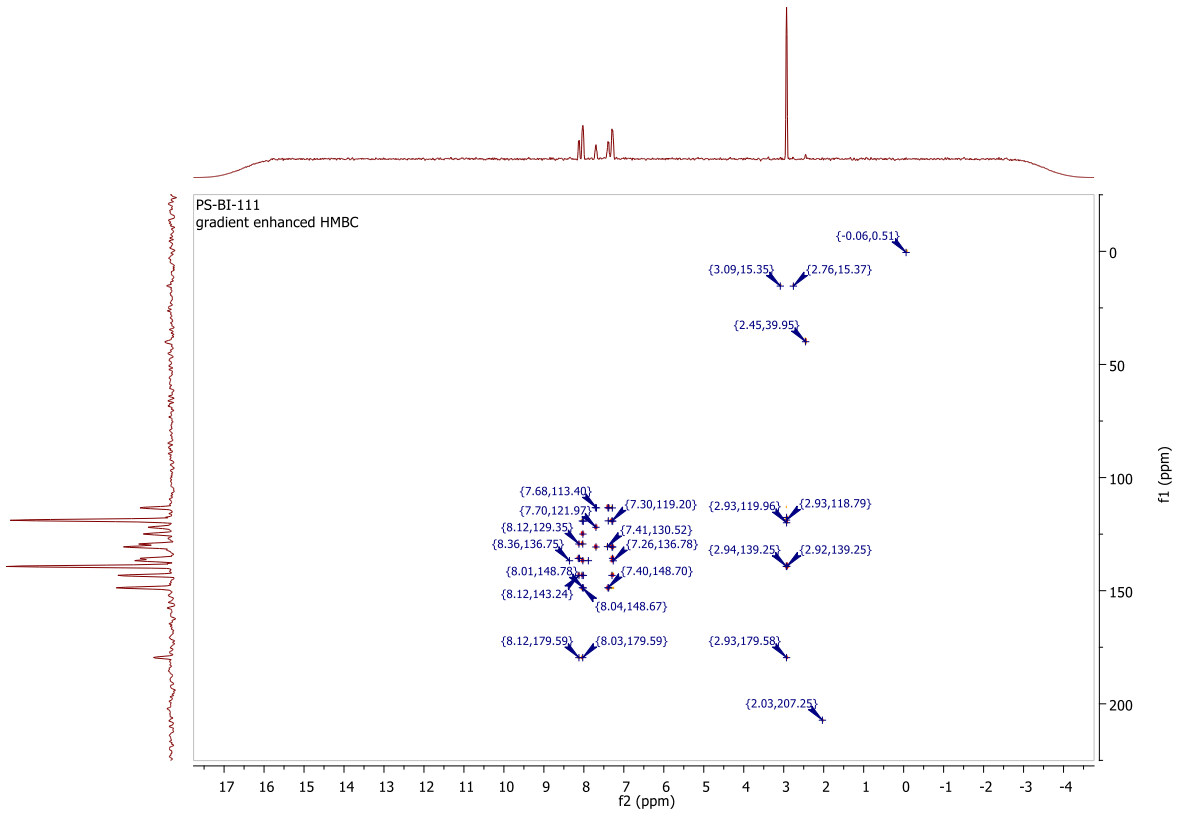


^{13}C NMR spectrum of **6a**

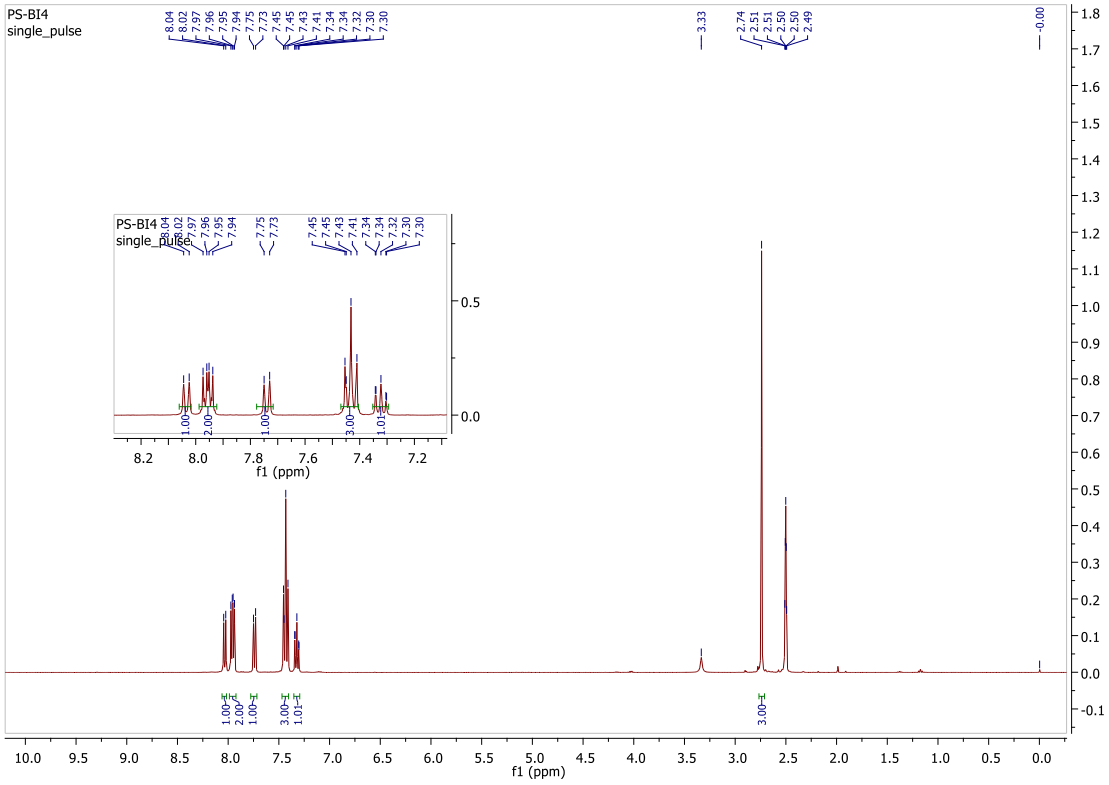
^{1}H-^{13}C HSQC



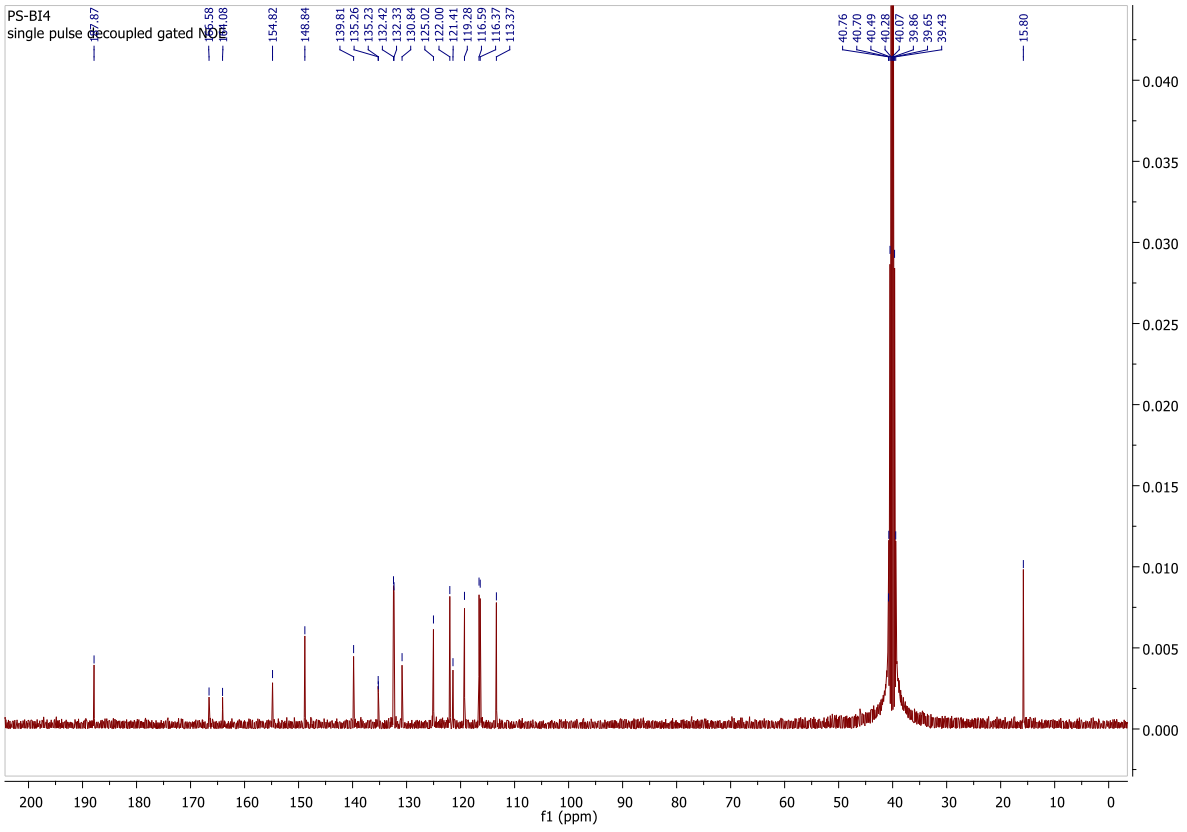
^{1}H-^{13}C HMBC



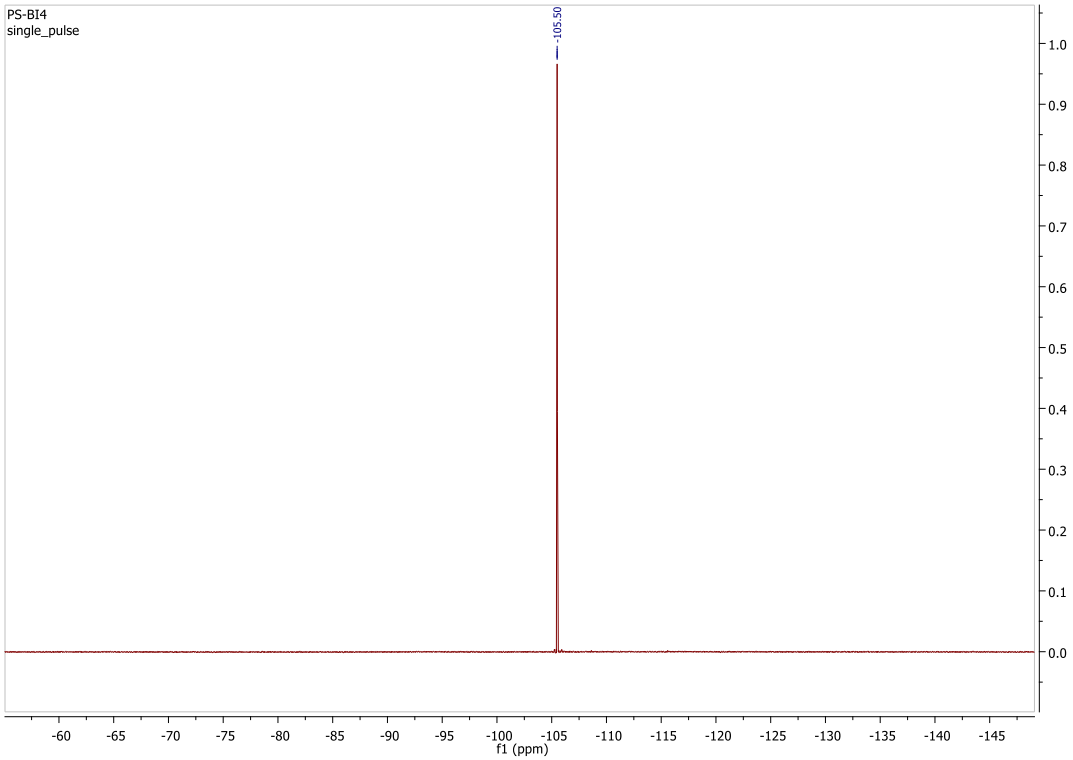
2-(4-Fluorobenzoyl)-3-methylbenzo[4,5]imidazo[2,1-b]thiazole (6b)



^{1}H NMR spectrum of **6b**

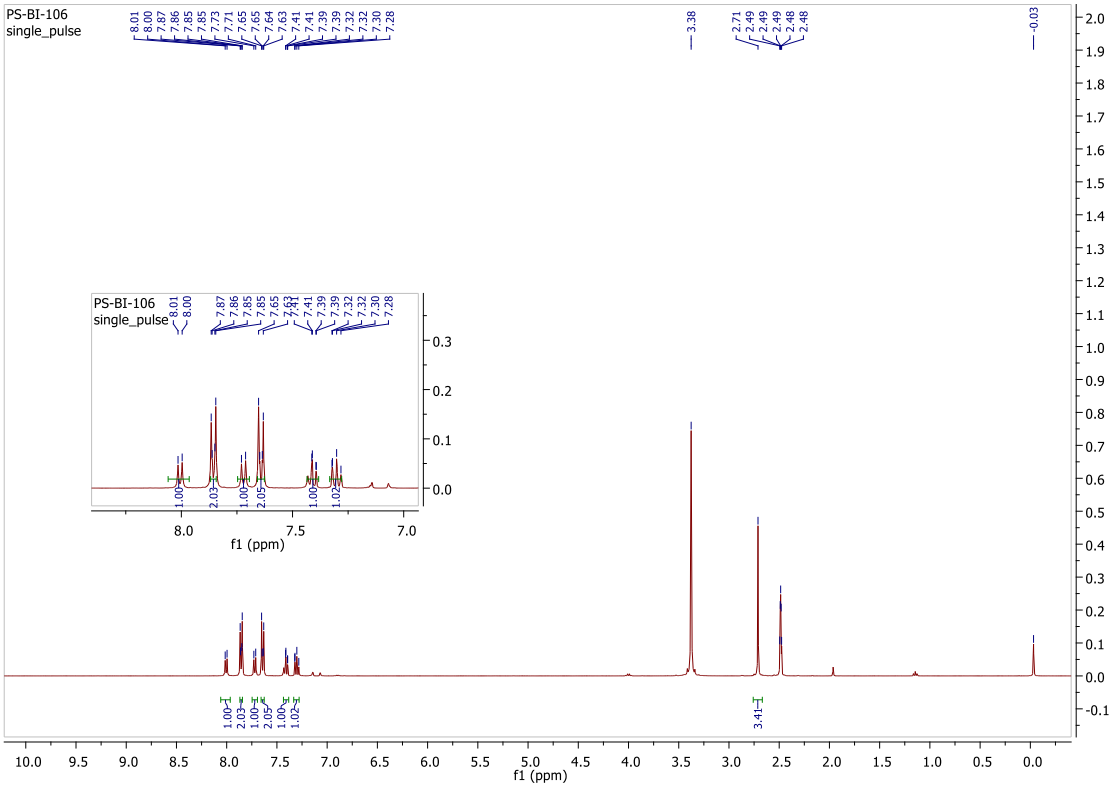


^{13}C NMR spectrum of **6b**

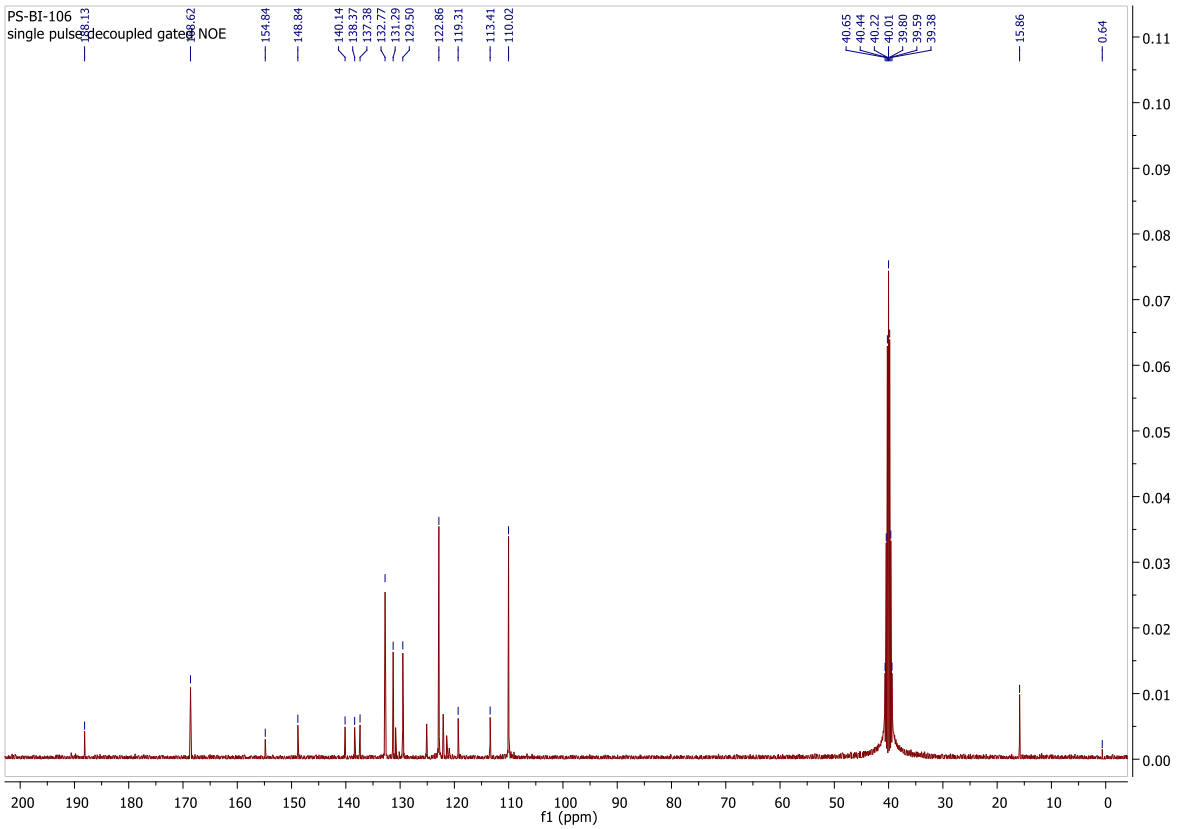


^{19}F NMR spectrum of **6b**

2-(4-Chlorobenzoyl)-3-methylbenzo[4,5]imidazo[2,1-b]thiazole (6c)

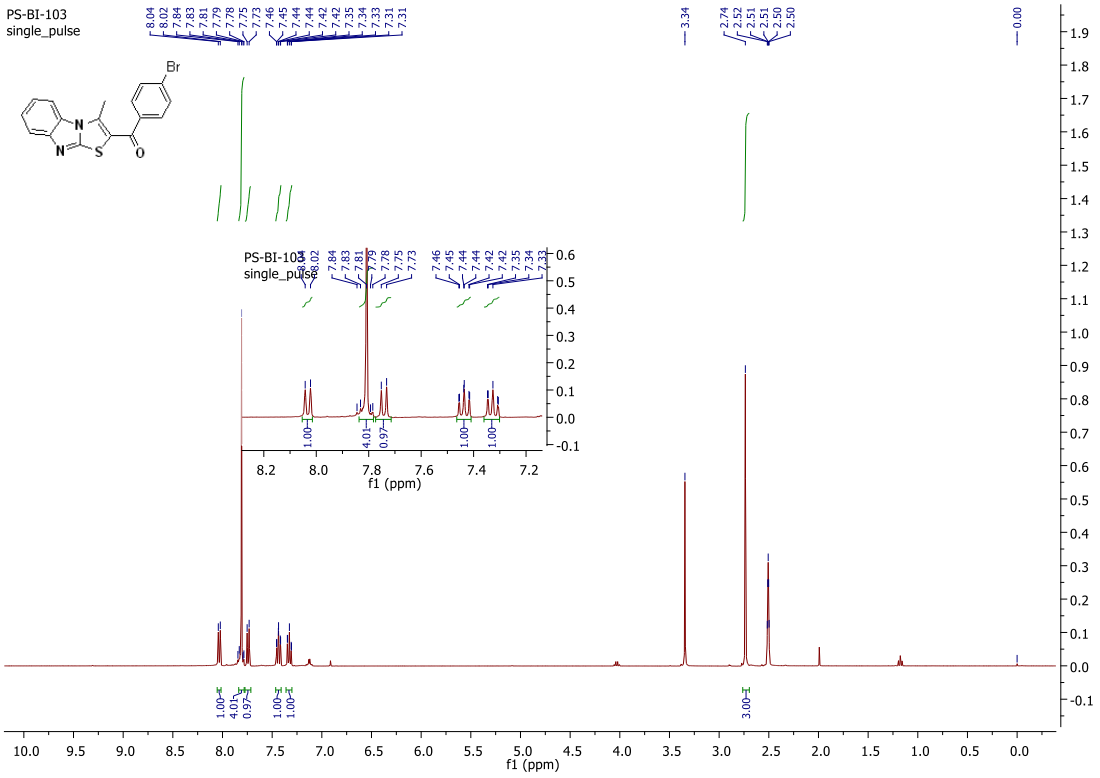


^{1}H NMR spectrum of **6c**

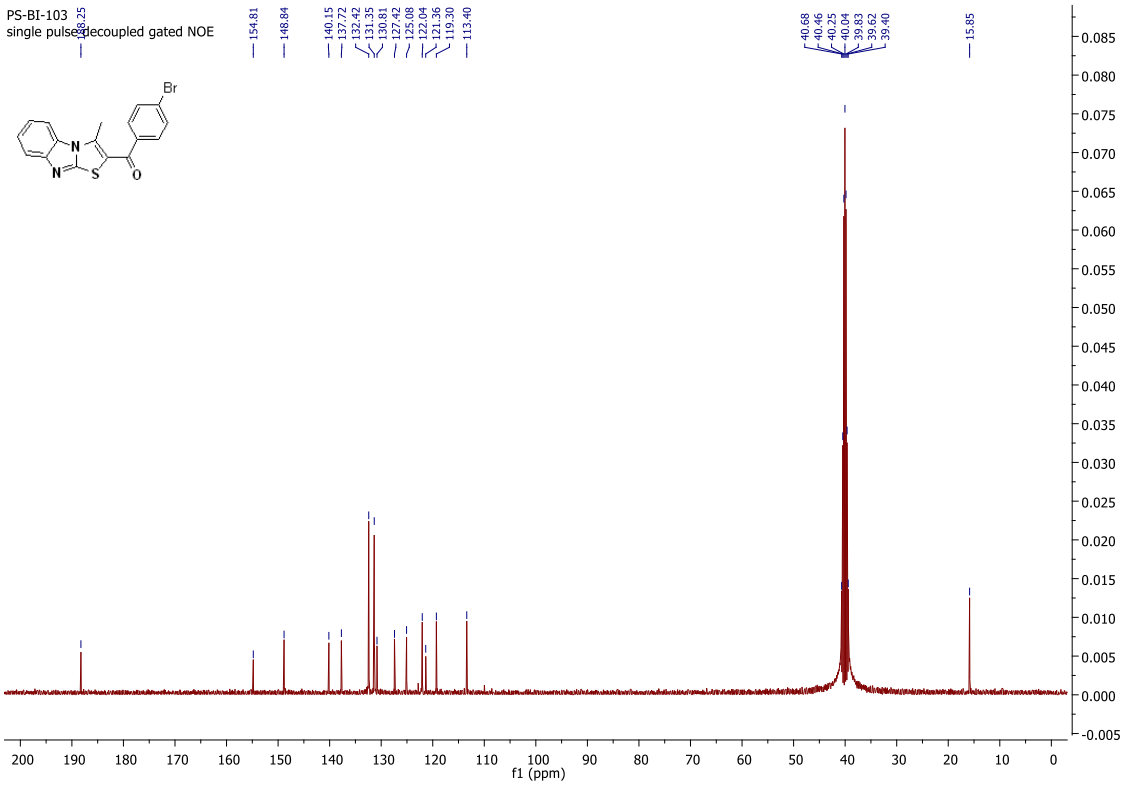


^{13}C NMR spectrum of **6c**

2-(4-Bromobenzoyl)-3-methylbenzo[4,5]imidazo[2,1-b]thiazole (6d)

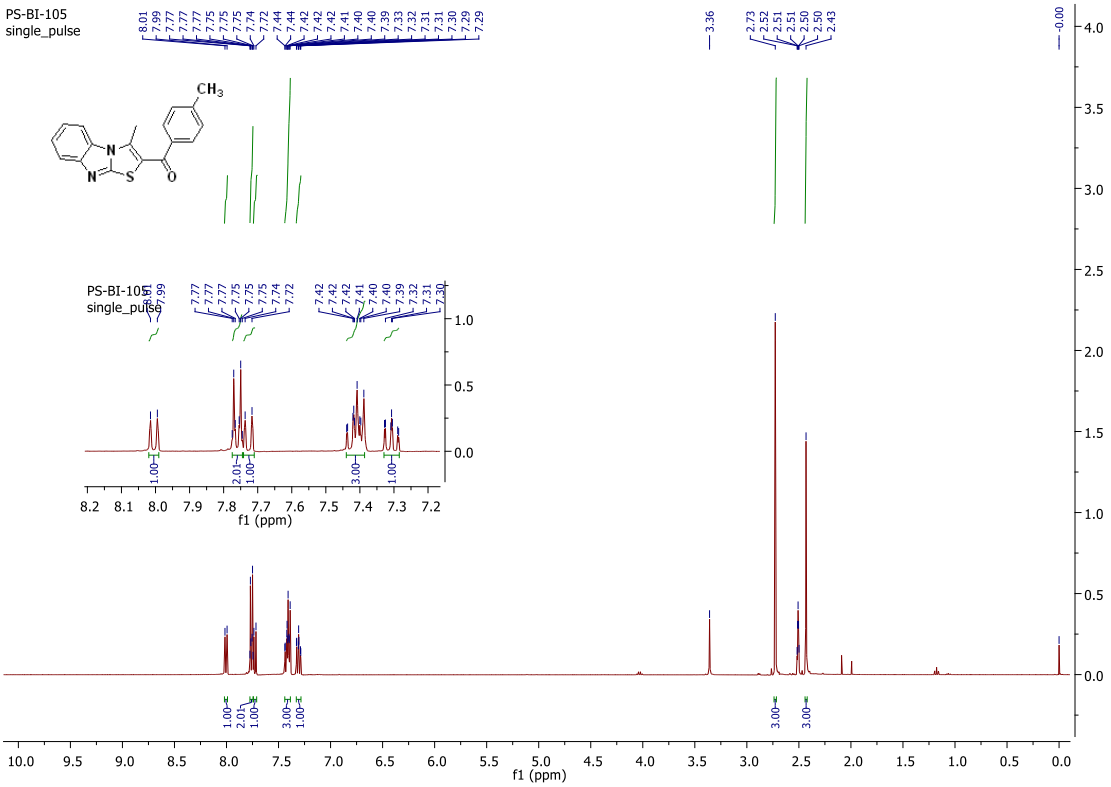


^{1}H NMR spectrum of **6d**

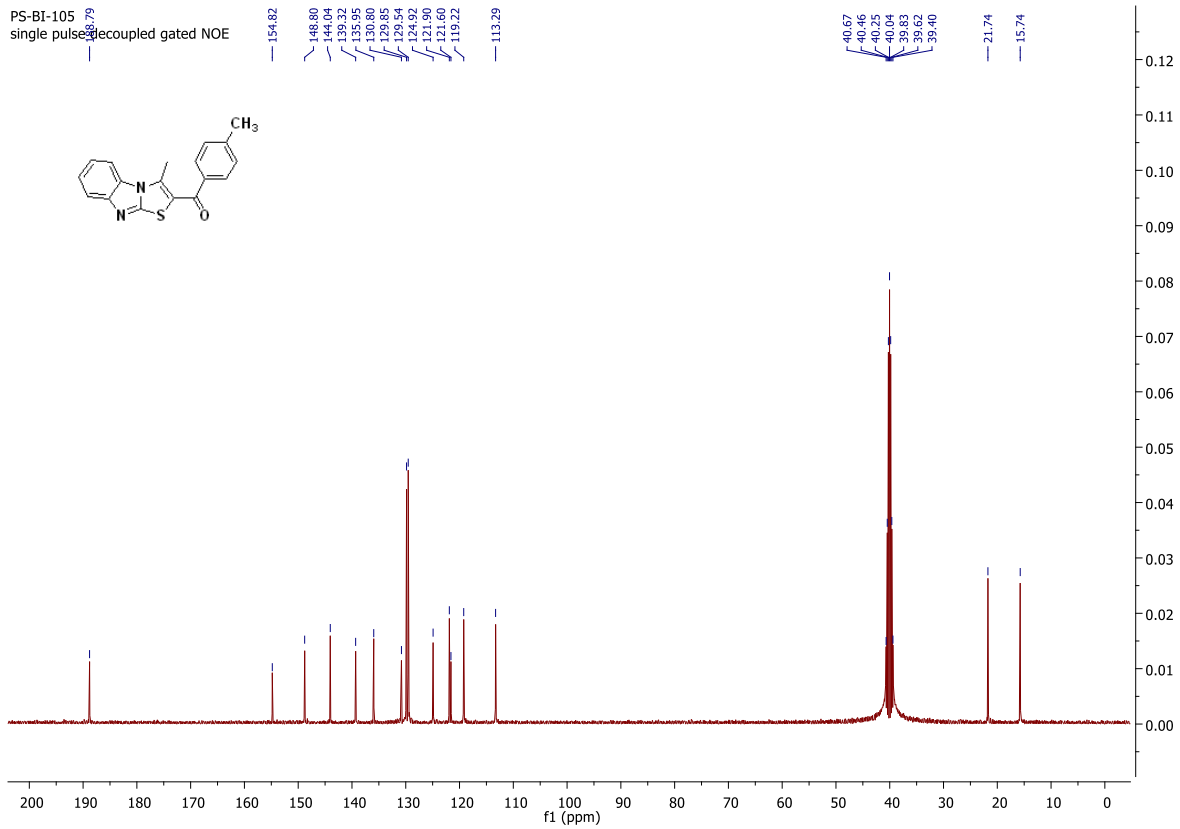


^{13}C NMR spectrum of **6d**

2-(4-Methylbenzoyl)-3-methylbenzo[4,5]imidazo[2,1-b]thiazole (6e)

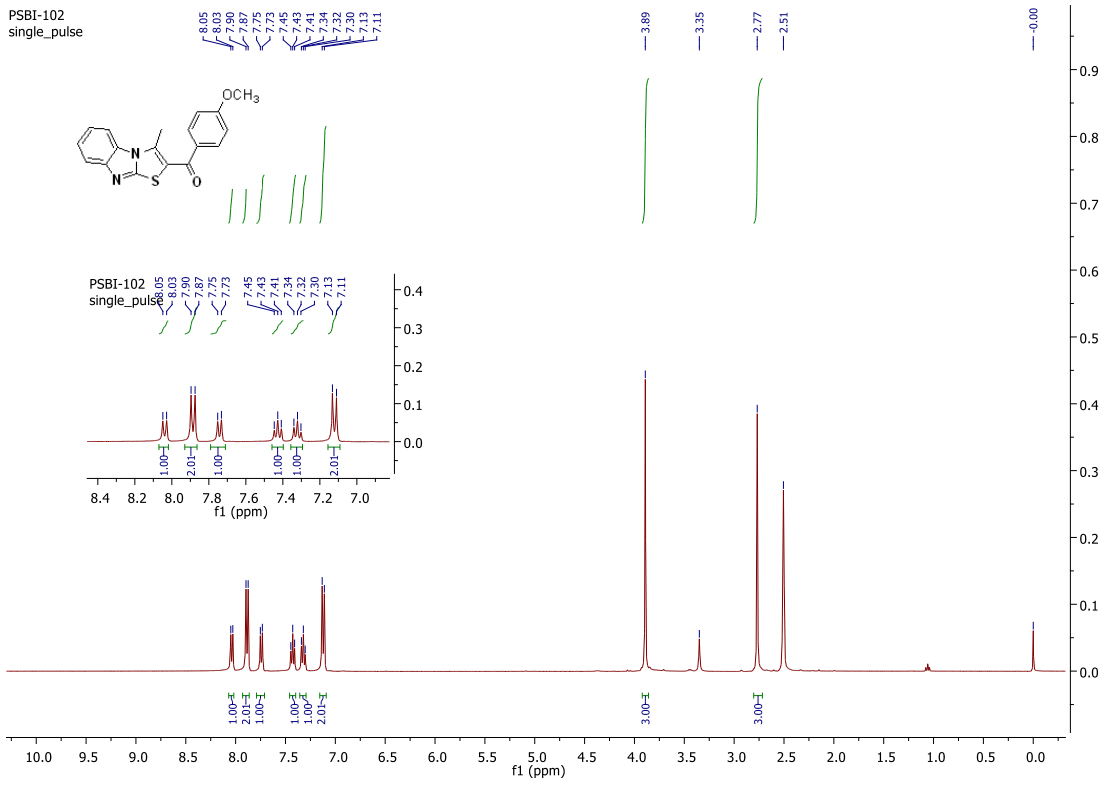


^{1}H NMR spectrum of **6e**

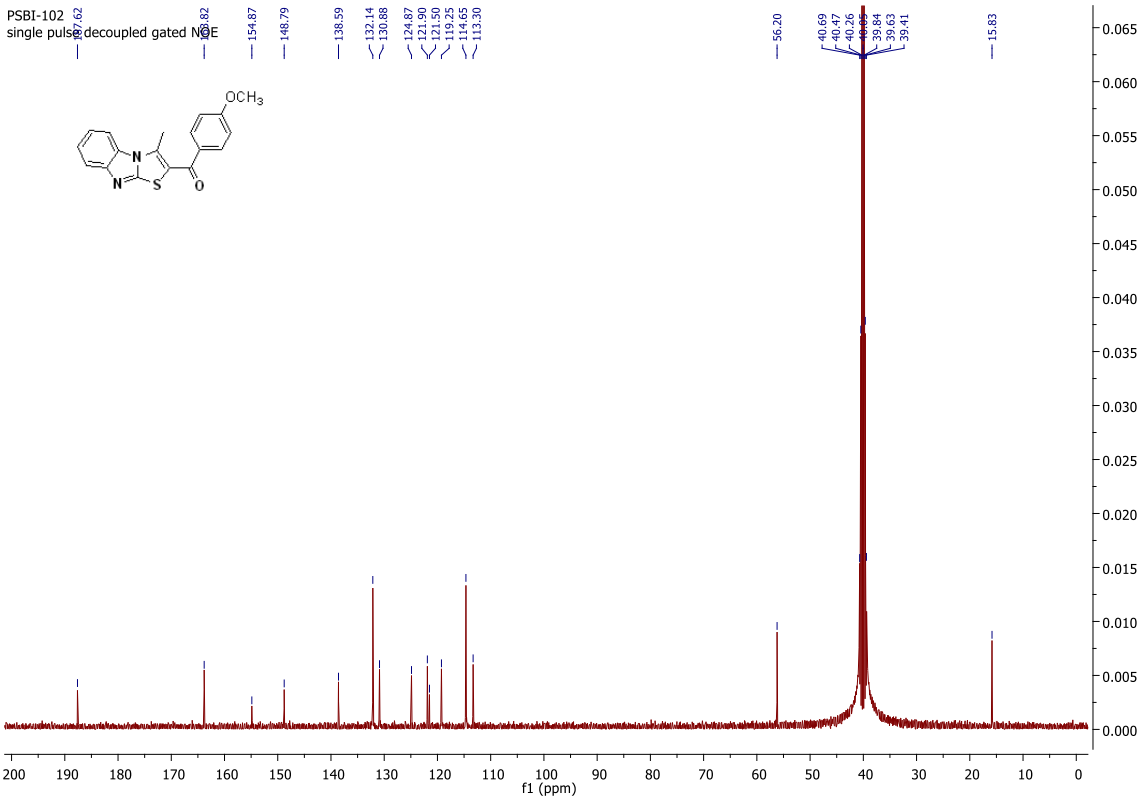


^{13}C NMR spectrum of **6e**

2-(4-Methoxylbenzoyl)-3-methylbenzo[4,5]imidazo[2,1-b]thiazole (6f)

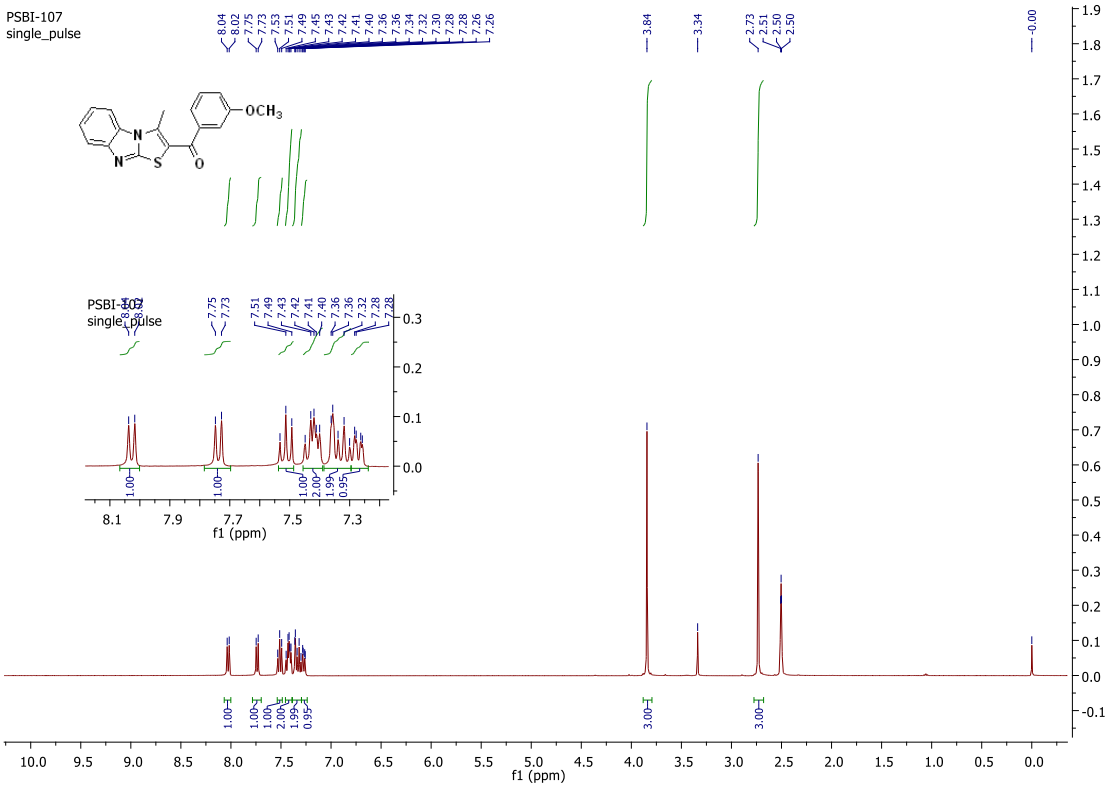


^{1}H NMR spectrum of **6f**

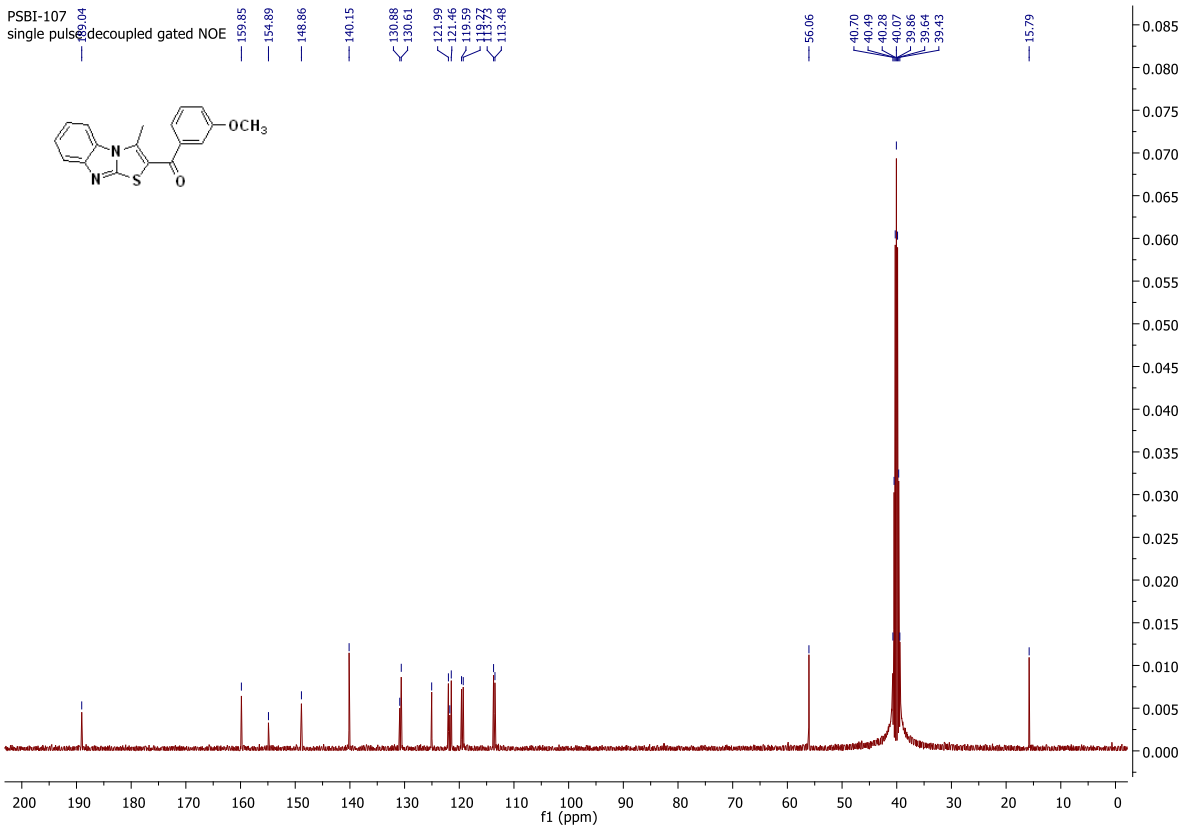


^{13}C NMR spectrum of **6f**

2-(3-Methoxylbenzoyl)-3-methylbenzo[4,5]imidazo[2,1-b]thiazole (6g)

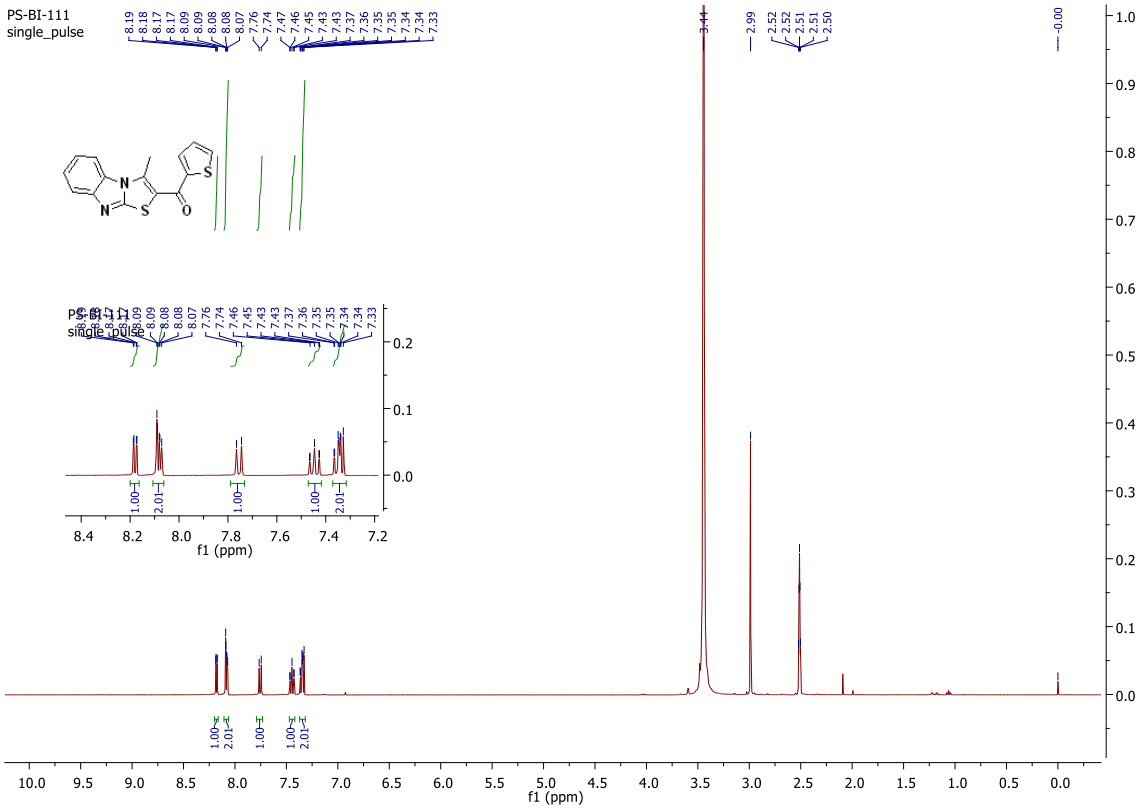


^{1}H NMR spectrum of **6g**

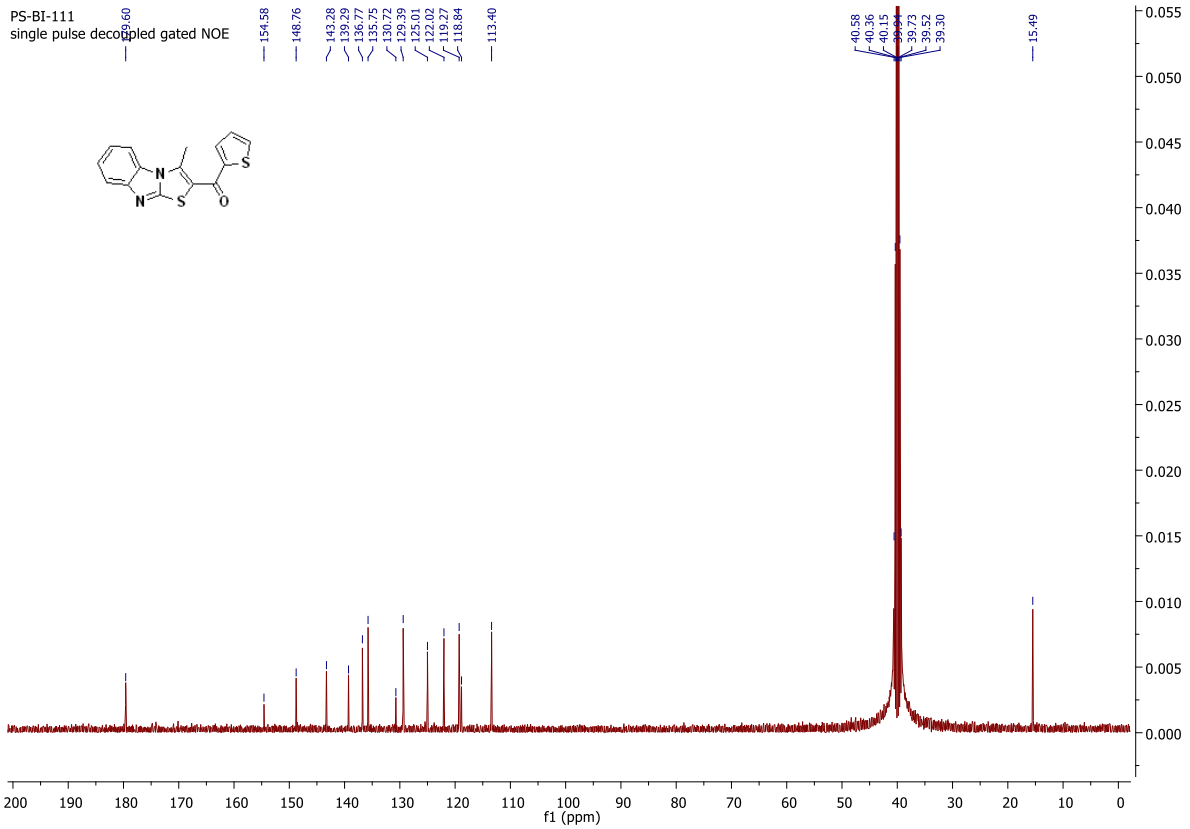


^{13}C NMR spectrum of **6g**

3-Methyl-(2-(2-thiophen)oyl)-benzo[4,5]imidazo[2,1-b]thiazole 6h

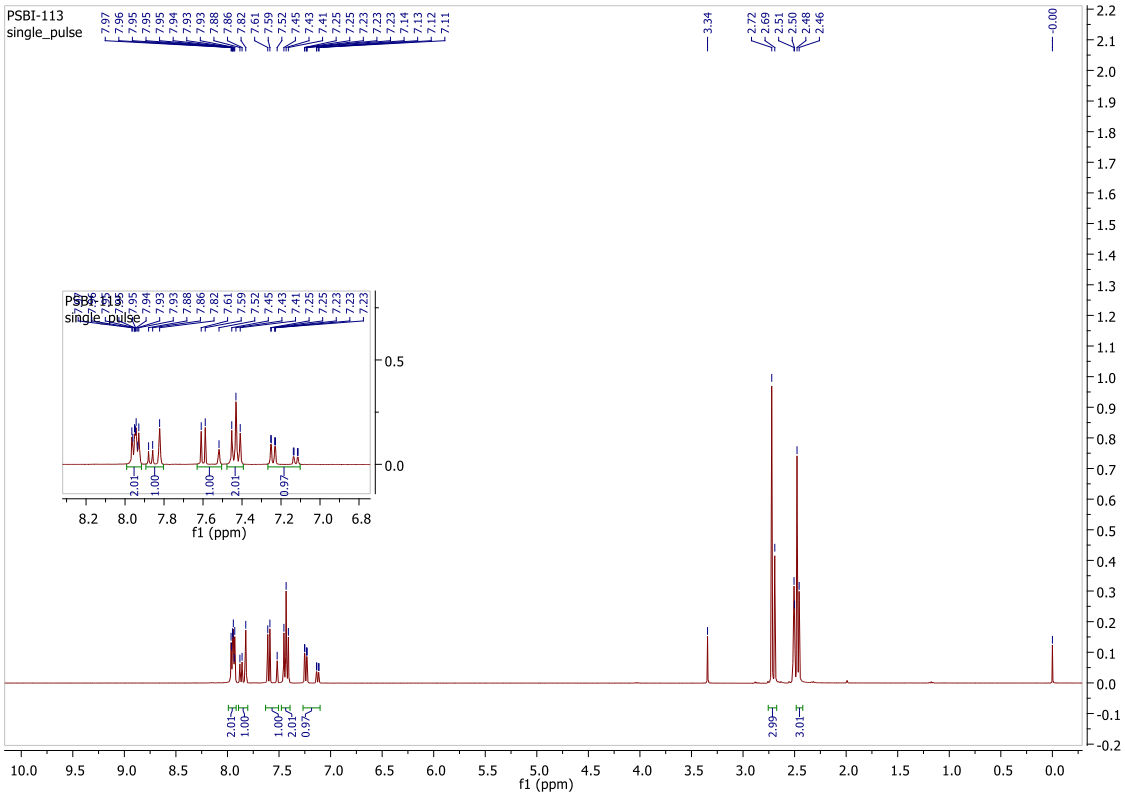


^{1}H NMR spectrum of **6h**

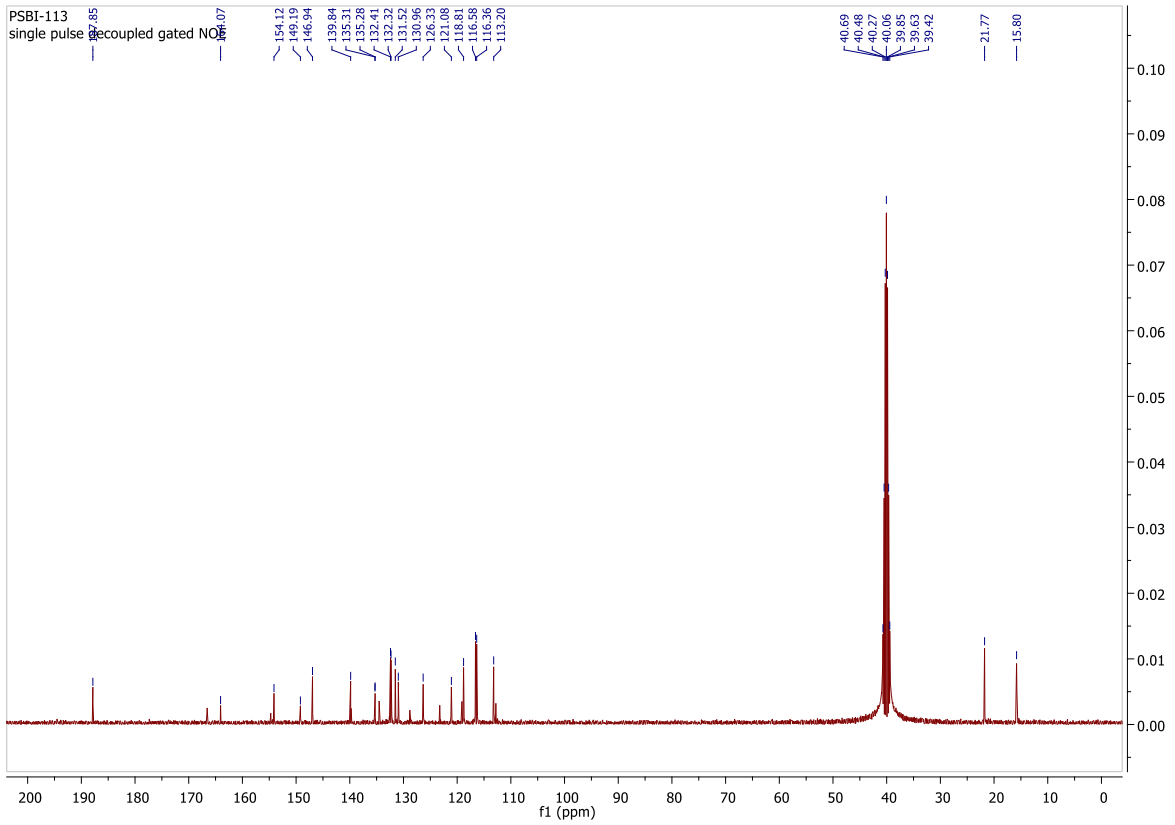


^{13}C NMR spectrum of **6h**

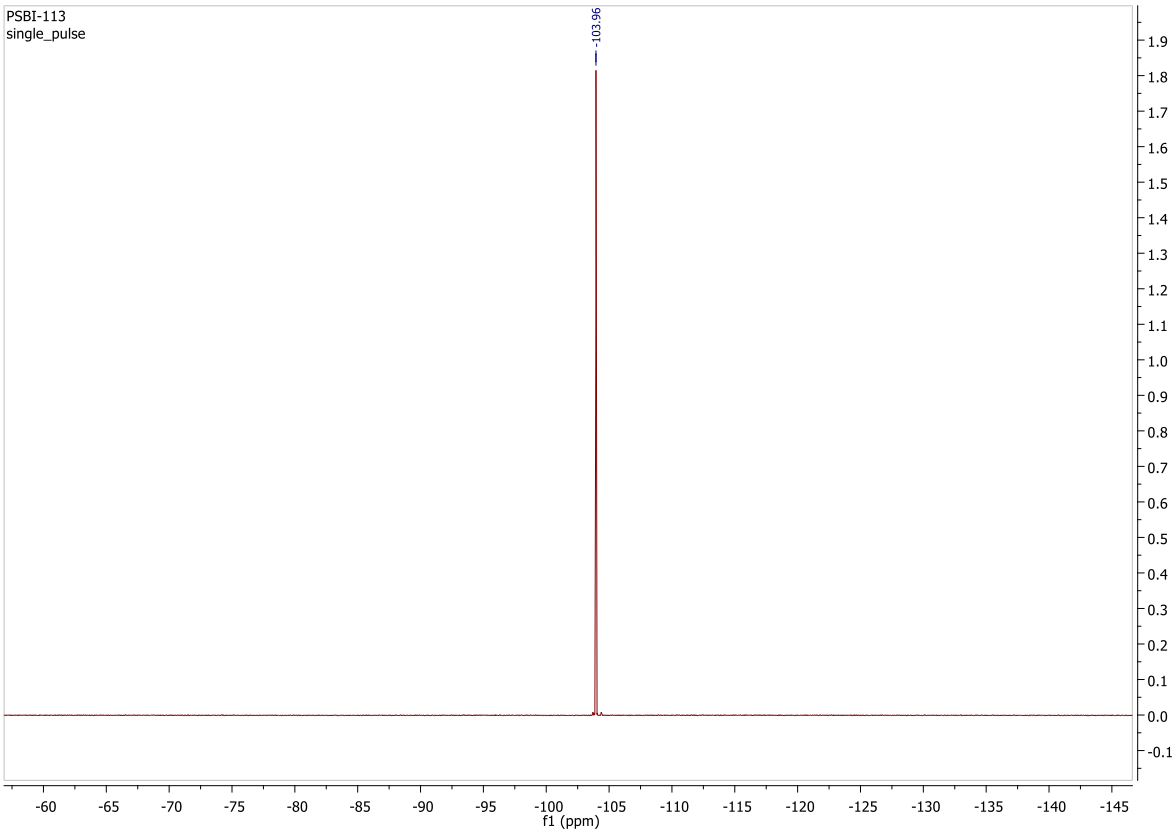
2-(4-Fluorobenzoyl)-3-methyl-6-methylbenzo[4,5]imidazo[2,1-b]thiazole 6i



^{1}H NMR spectrum of **6i**

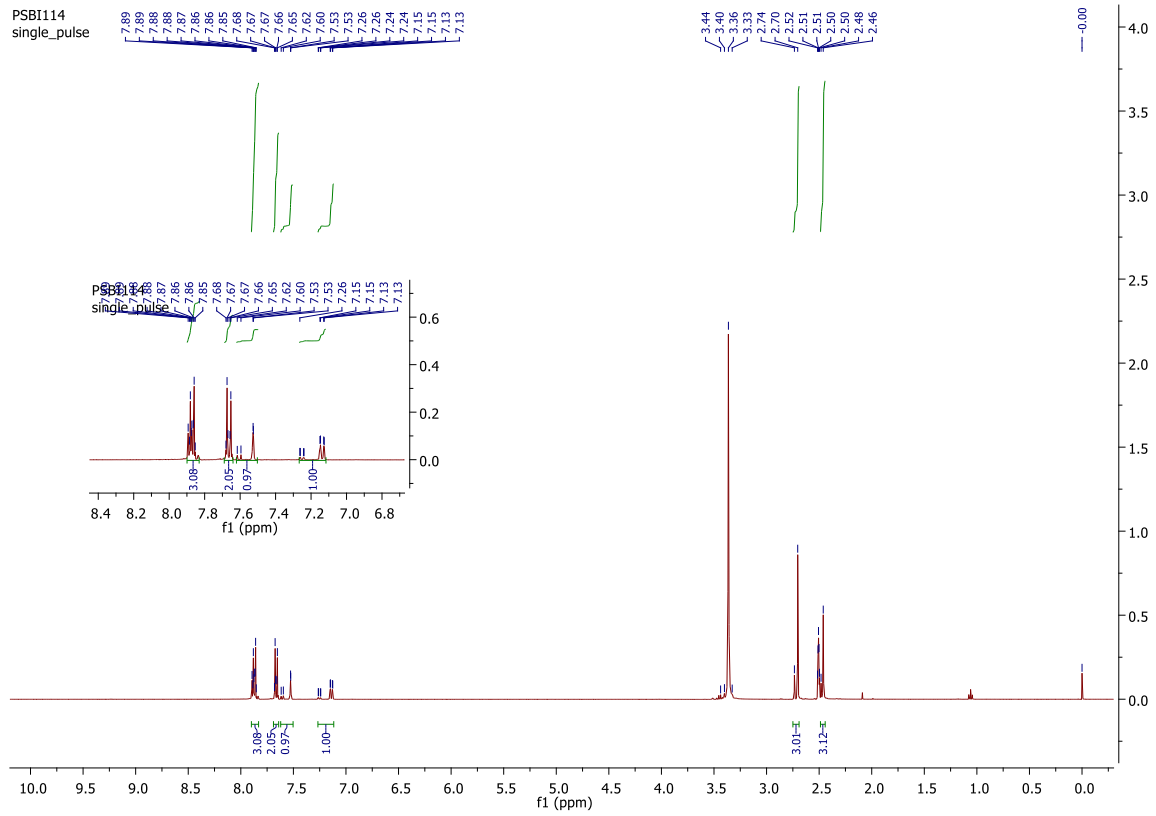


^{13}C NMR spectrum of **6i**

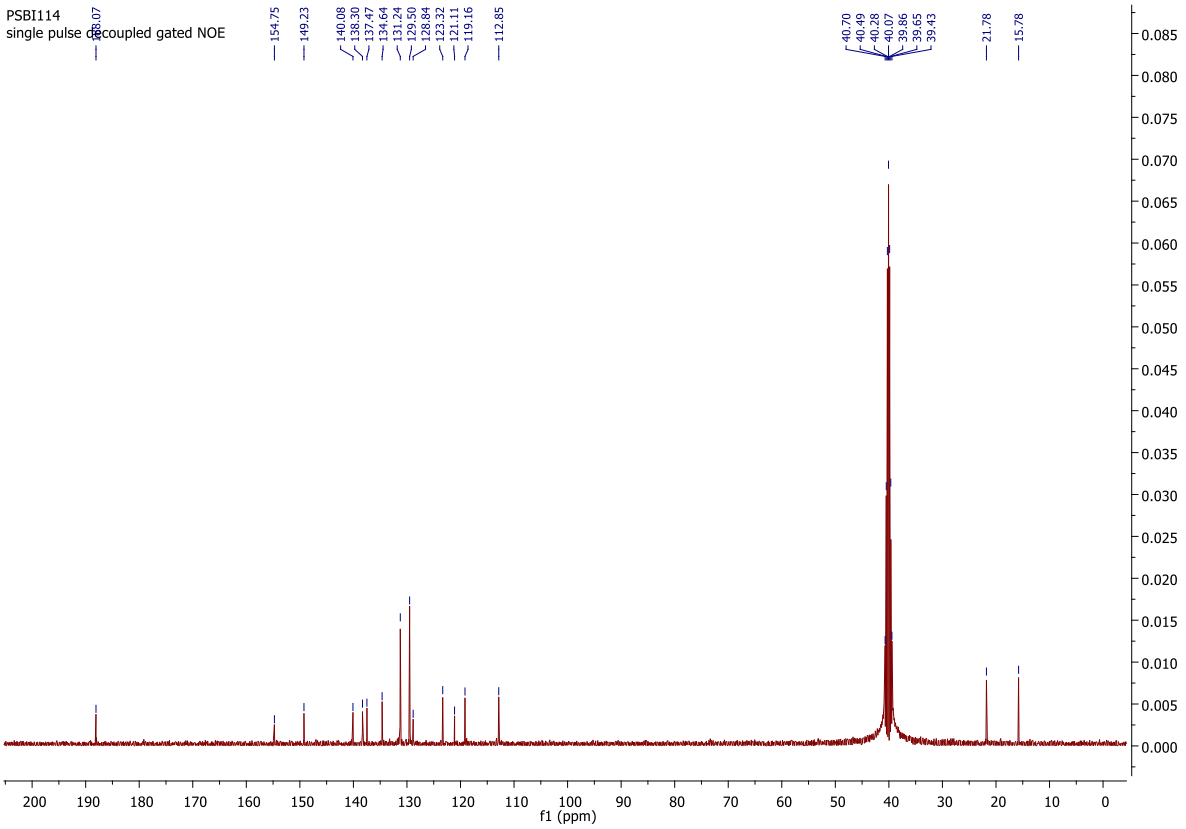


^{19}F NMR spectrum of **6i**

2-(4-Chlorobenzoyl)-3-methyl-6-methylbenzo[4,5]imidazo[2,1-b]thiazole (6j)

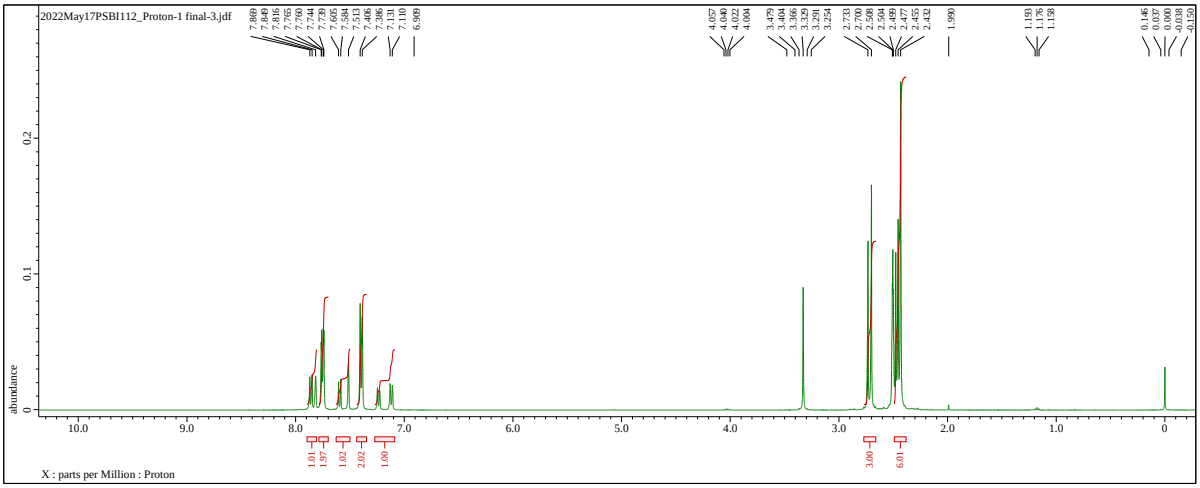


^{1}H NMR spectrum of **6j**

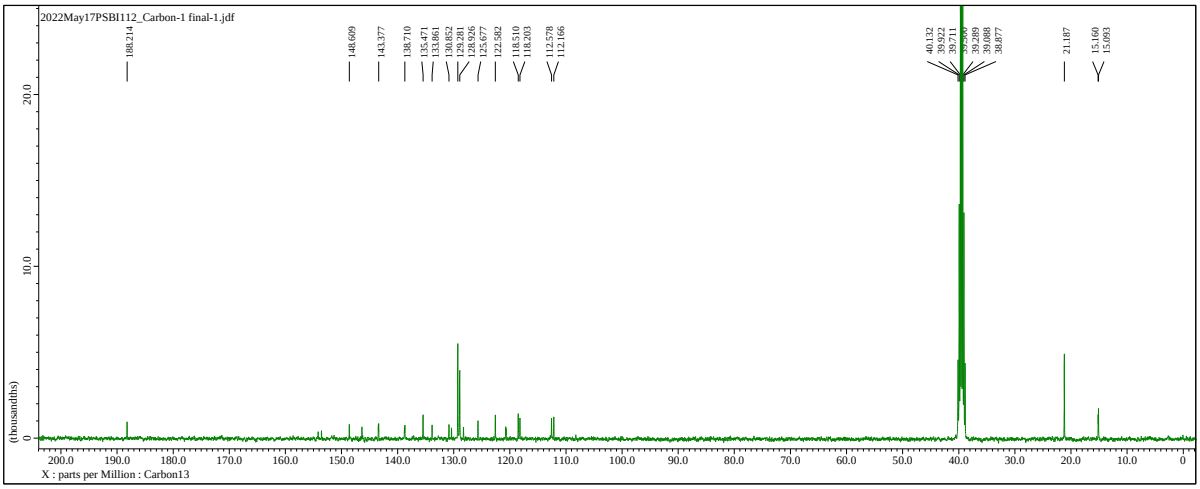


^{13}C NMR spectrum of **6j**

2-(4-Methylbenzoyl)-3-methyl-6-methylbenzo[4,5]imidazo[2,1-b]thiazole (6k)

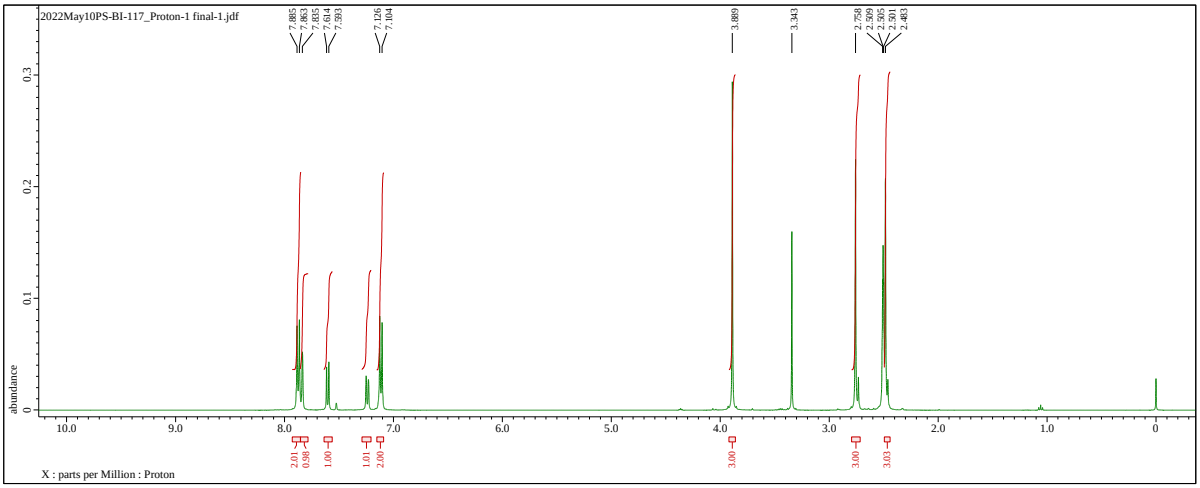


^{1}H NMR spectrum of **6k**

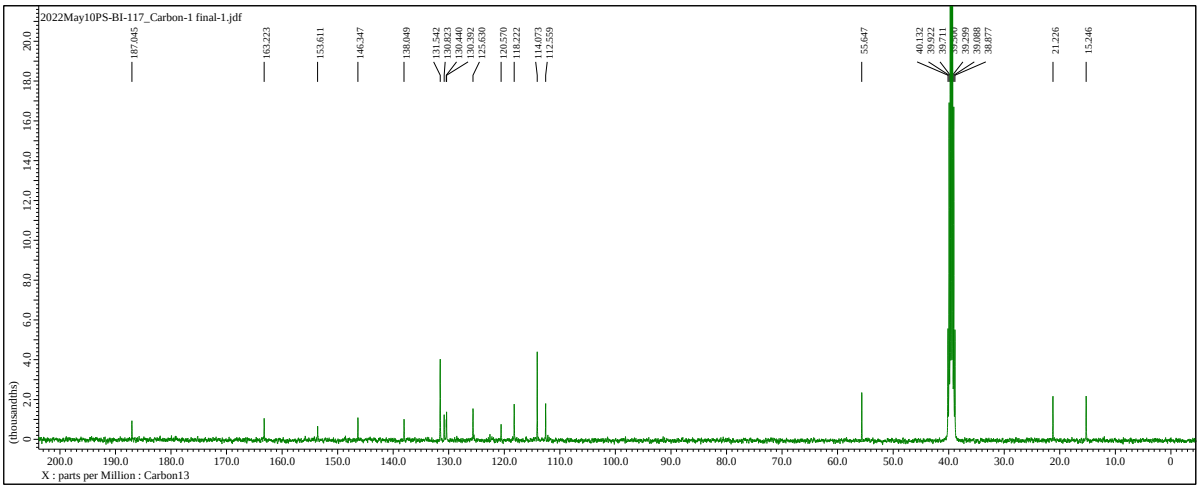


^{13}C NMR spectrum of **6k**

2-(4-Methoxybenzoyl)-3-methyl-6-methylbenzo[4,5]imidazo[2,1-b]thiazole (6l)

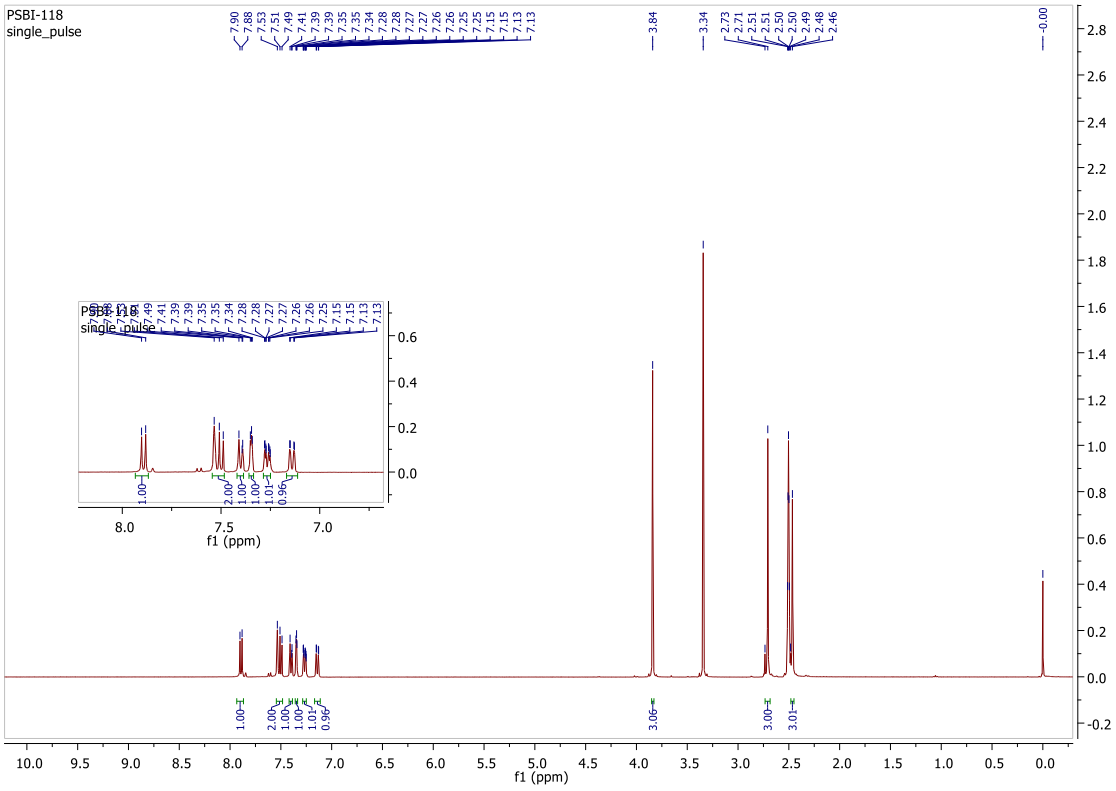


^{1}H NMR spectrum of **6l**

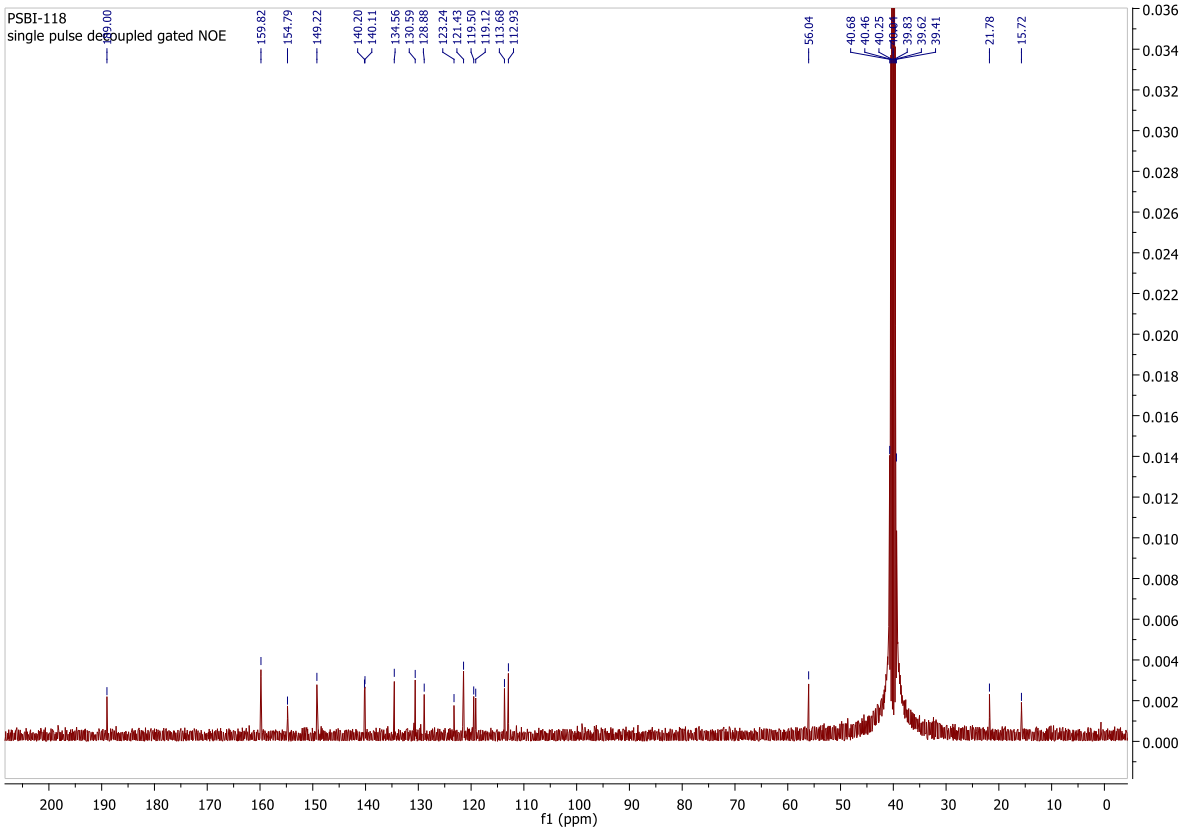


^{13}C NMR spectrum of **6l**

2-(3-Methoxybenzoyl)-3-methyl-6-methylbenzo[4,5]imidazo[2,1-b]thiazole (6m)

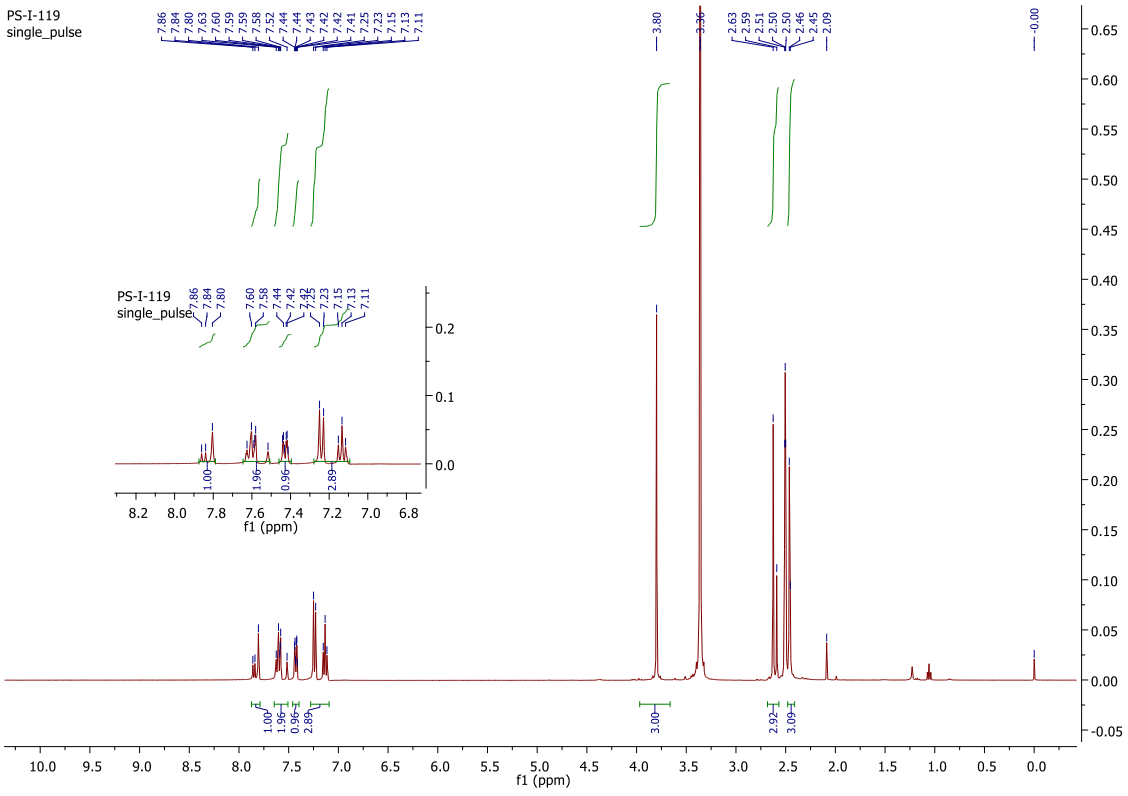


^{1}H NMR spectrum of **6m**

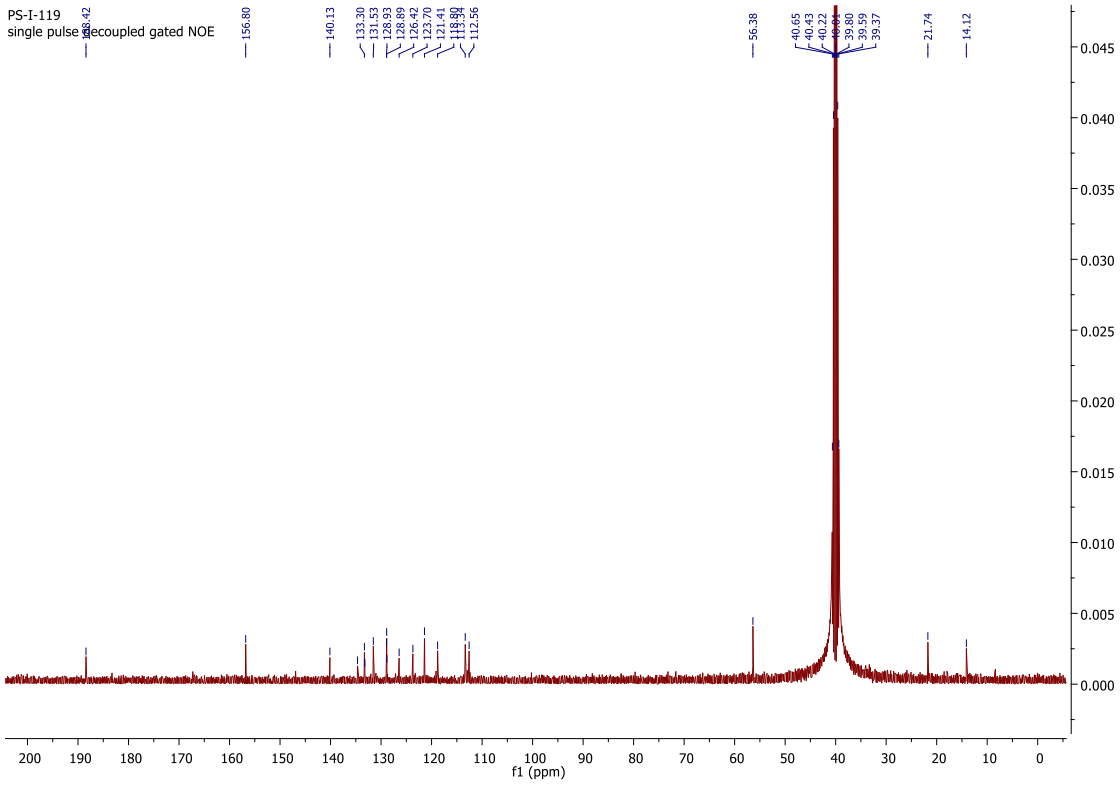


^{13}C NMR spectrum of **6m**

2-(2-Methoxybenzoyl)-3-methyl-6-methylbenzo[4,5]imidazo[2,1-b]thiazole (6n)

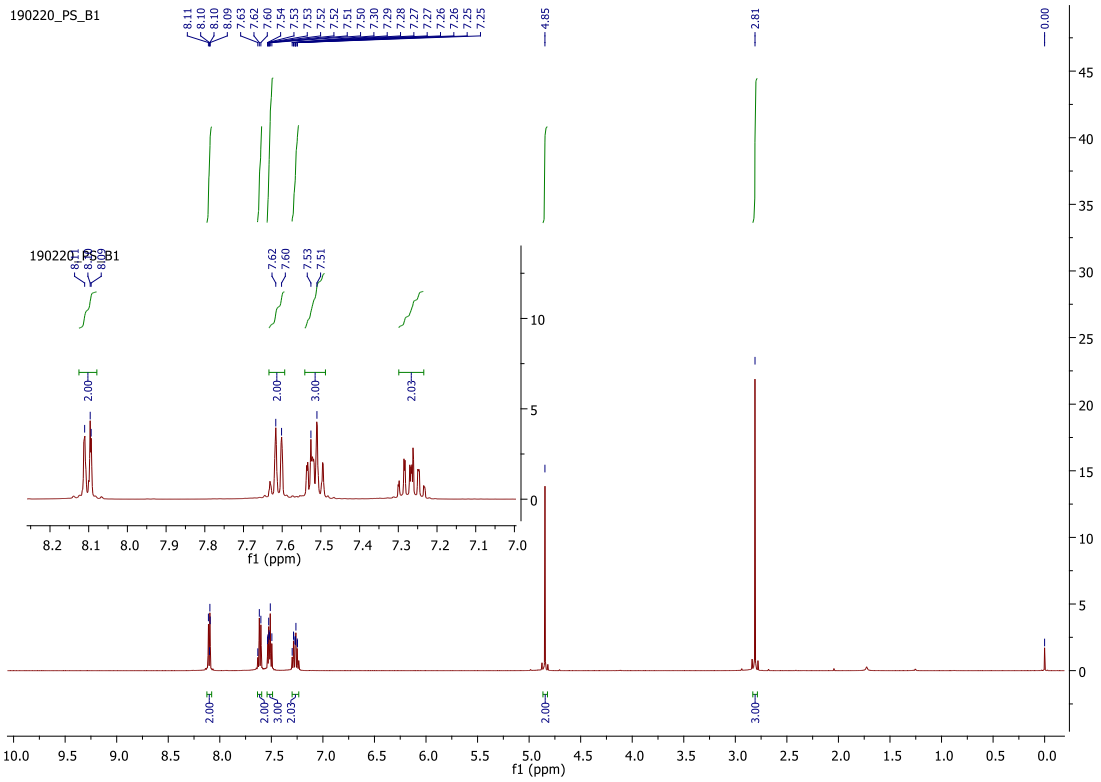


^{1}H NMR spectrum of **6n**

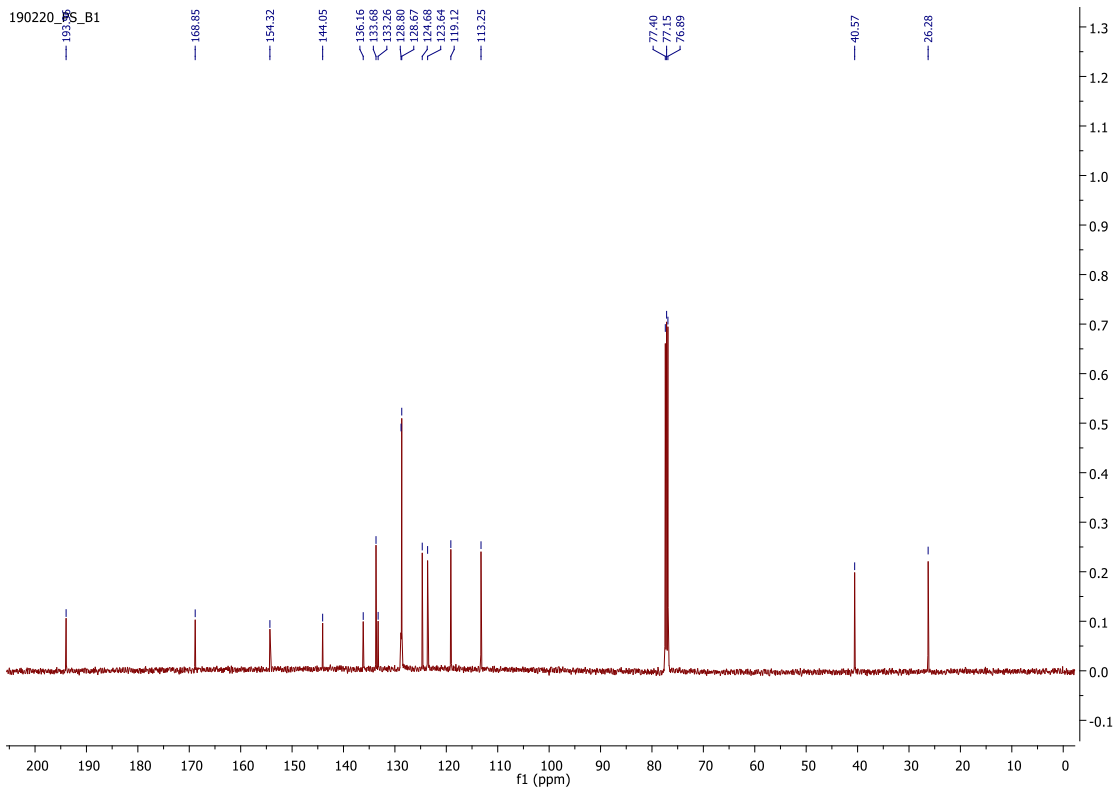


^{13}C NMR spectrum of **6n**

1-Acetyl-2-((2-oxo-2-phenylethyl)thio)benzo[4,5]imidazole (10a)

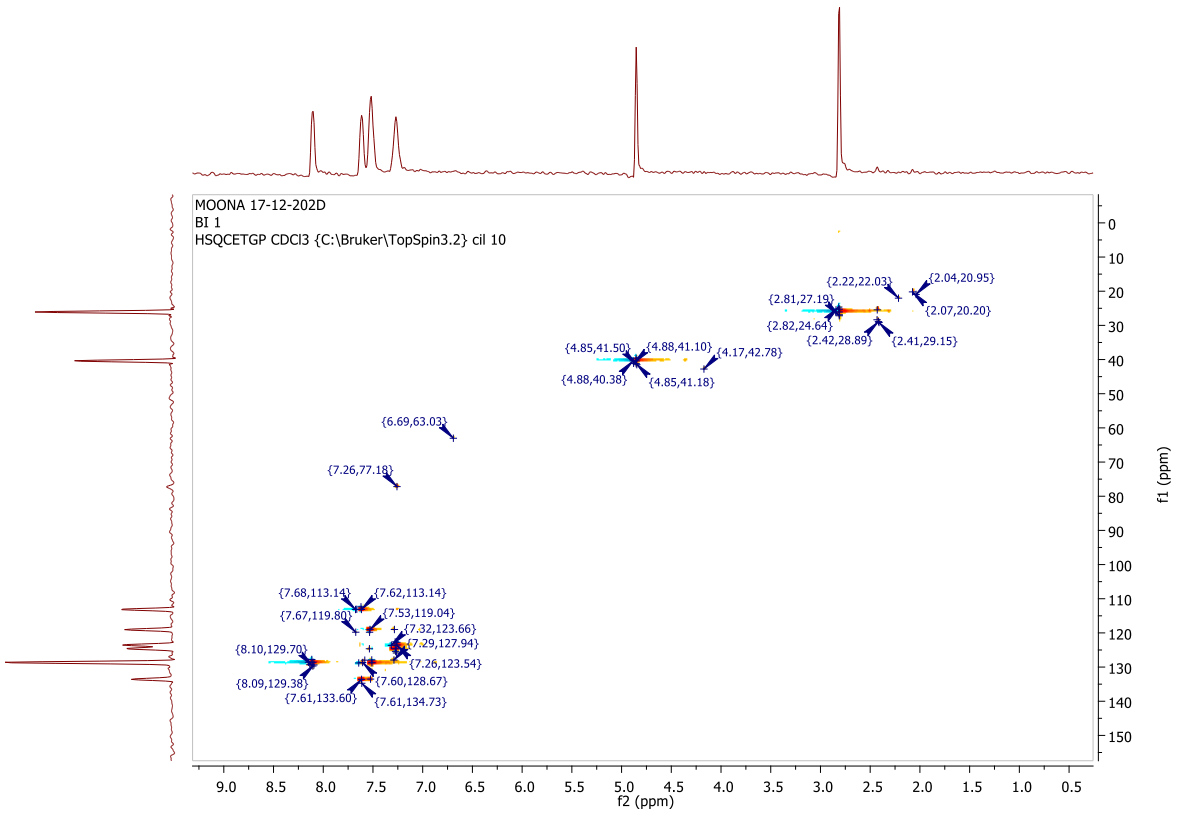


^{1}H NMR spectrum of **10a**



^{13}C NMR spectrum of **10a**

^{1}H-^{13}C HMQC



^{1}H-^{13}C HMBC

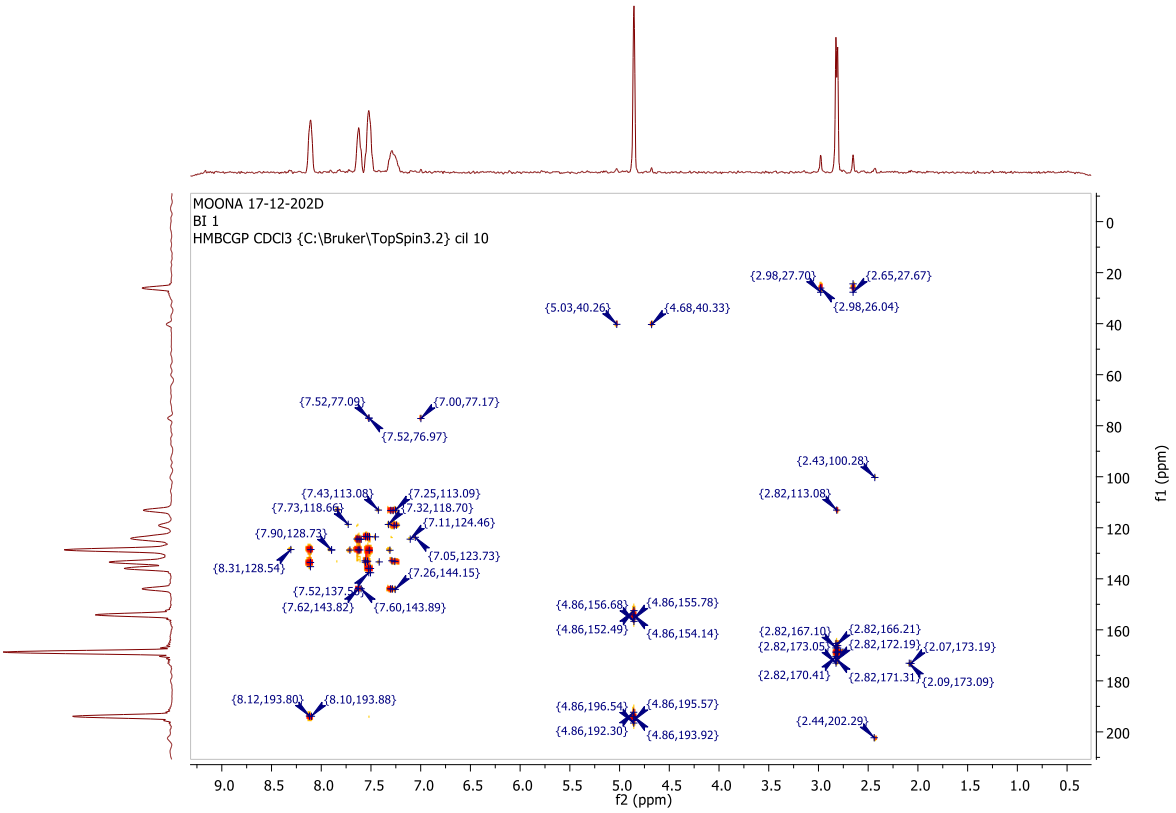
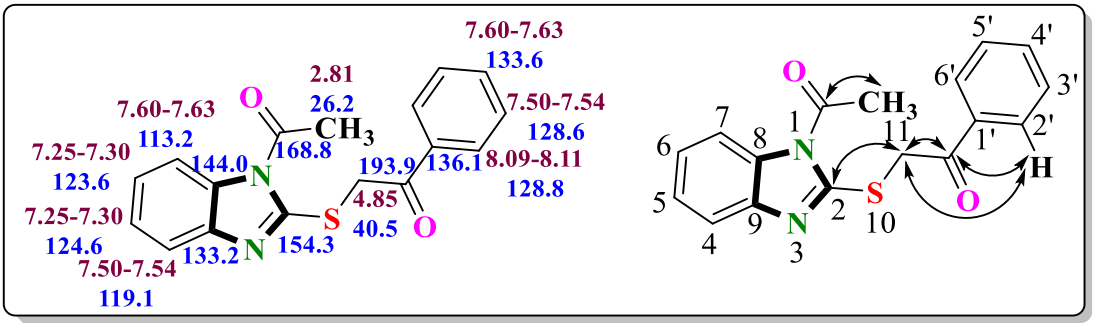


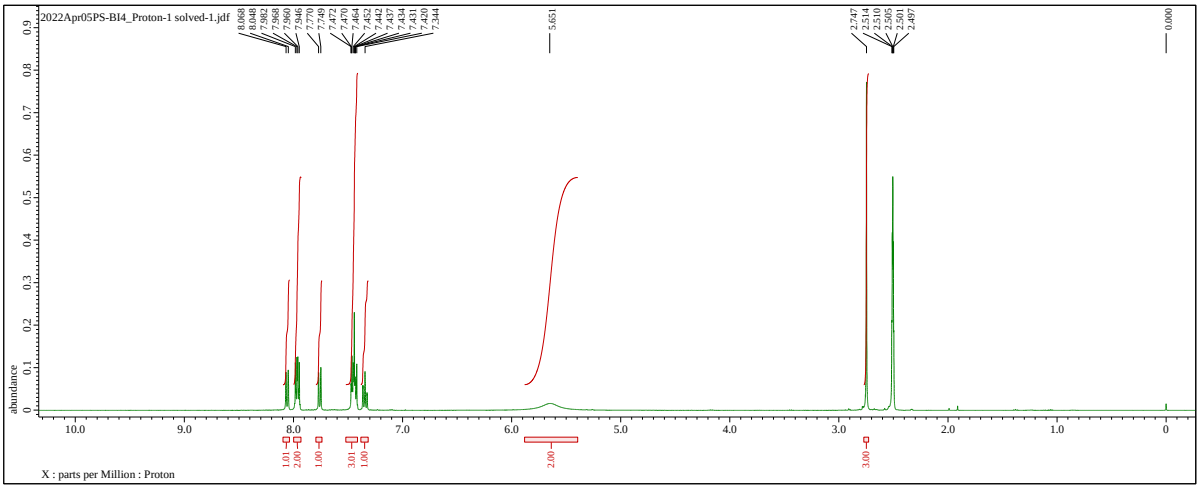
Table 4.2. ^{1}H, ^{13}C and 2D NMR correlations of **10a**.



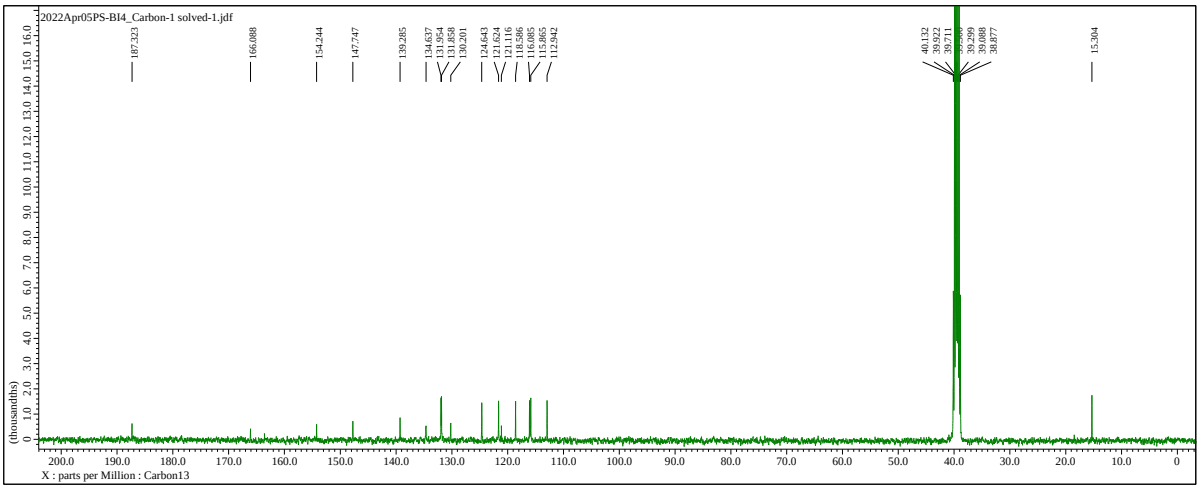
Chemical shifts (δ in ppm)	gs-HSQC	gs-HMBC	Assignments
193.9	---	8.09-8.11 (H2'/H6'), 4.85 (CH_2)	$CH_2COC_6H_5$
168.8	---	2.81 (CH_3)	$COCH_3$
154.3	---	4.85 (CH_2)	C2
144.0	---	7.60-7.63 (H7), 7.25-7.30 (H6), 7.50-7.54 (H4)	C8
136.1	---	8.09-8.11 (H2'/H6'),	C1'

		7.50-7.54 (H3'/H5') 4.85 (CH_2)	
133.6	7.60-7.63 (H4')	8.09-8.11 (H2'/H6'), 7.50-7.54 (H3'/H5')	C4'
128.8	8.09-8.11 (H2'/ H6')	7.50-7.54 (H3'/H5') 7.60-7.63 (H4')	C2'/C6'
128.6	7.50-7.54 (H3'/H5')	8.09-8.11 (H2'/H6'), 7.60-7.63 (H4')	C3'/C5'
124.6	7.25-7.30 (H5)	7.25-7.30 (H6), 7.50-7.54 (H4), 7.60-7.63 (H7)	C5
123.6	7.25-7.30 (H6)	7.25-7.30 (H5), 7.50-7.54 (H4), 7.60-7.63 (H7)	C6
119.1	7.50-7.54 (H4)	7.25-7.30 (H5/H6)	C4
113.2	7.60-7.63 (H7)	7.25-7.30 (H5/H6)	C7
40.5	4.85 (CH_2)	---	CH_2
26.2	2.81 (CH_3)	---	CH_3

1-Acetyl-2-((2-oxo-2-(4-fluorophenyl)ethyl)thio)benzo[4,5]imidazole (10b)

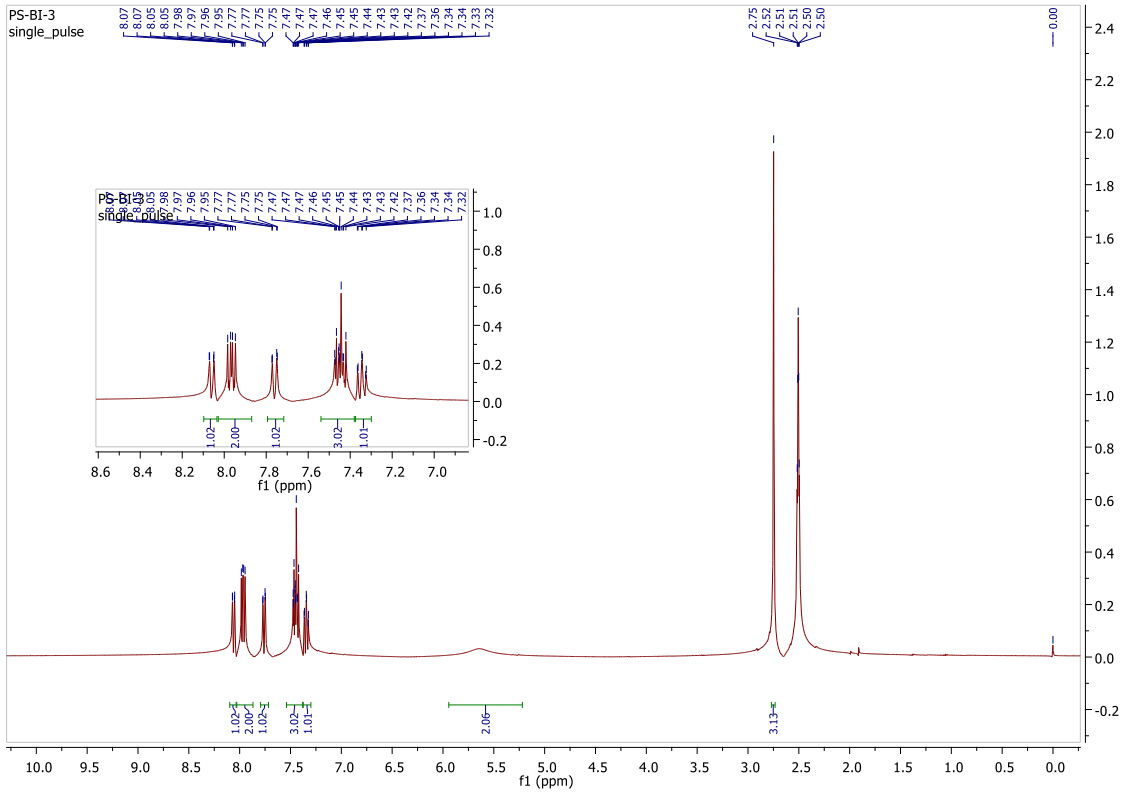


^{1}H NMR spectrum of **10b**

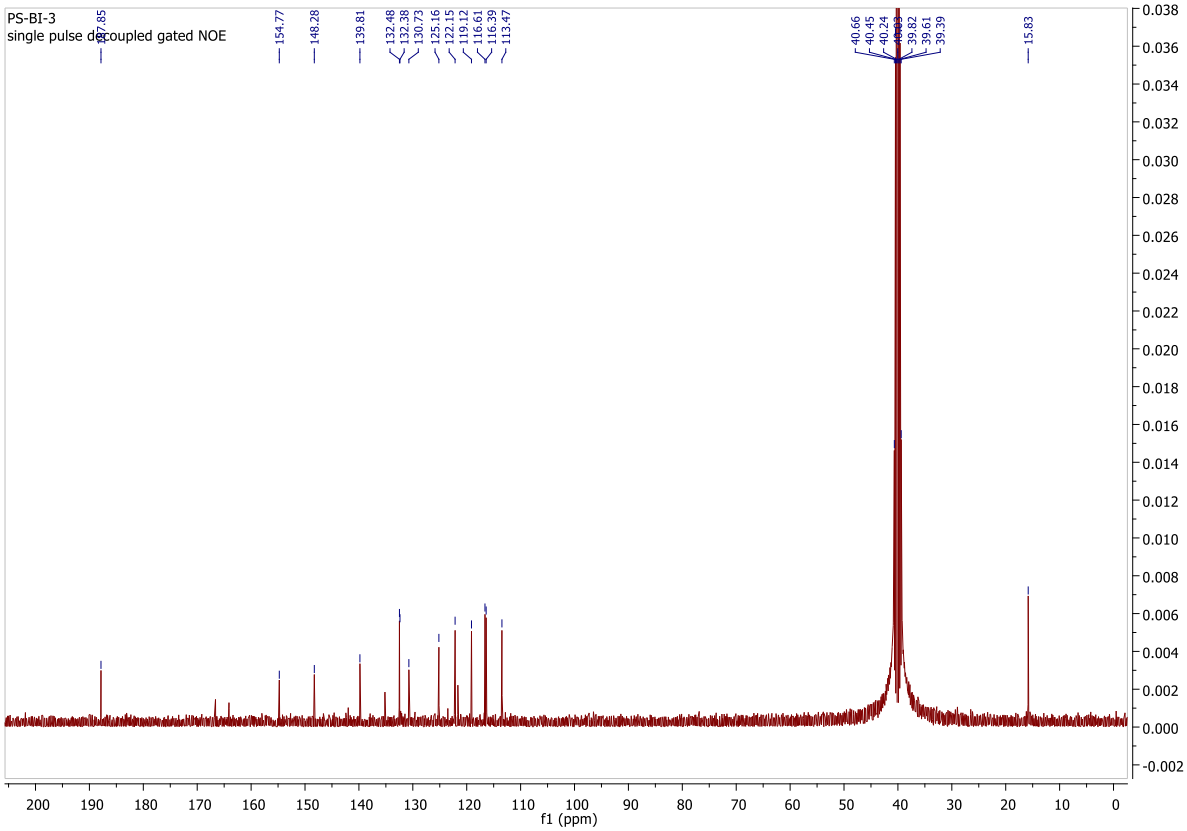


^{13}C NMR spectrum of **10b**

1-Acetyl-2-((2-oxo-2-(4-chlorophenyl)ethyl)thio)benzo[4,5]imidazole (10c)

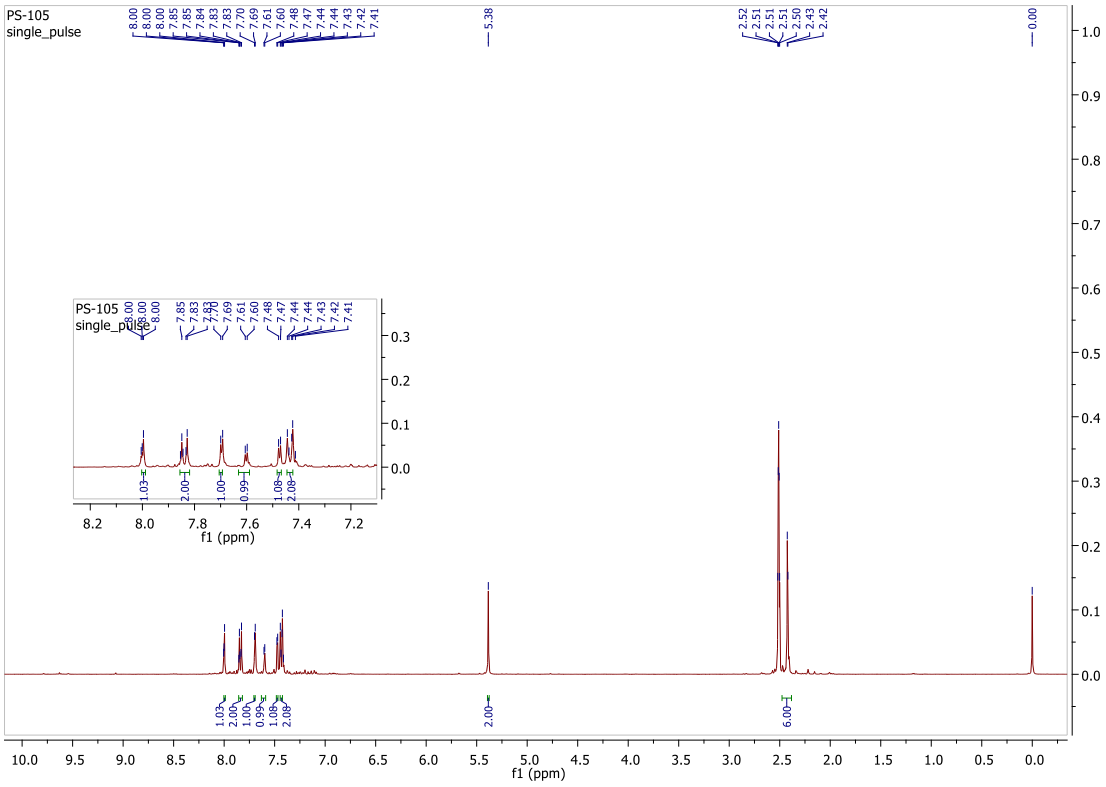


^{1}H NMR spectrum of **10c**

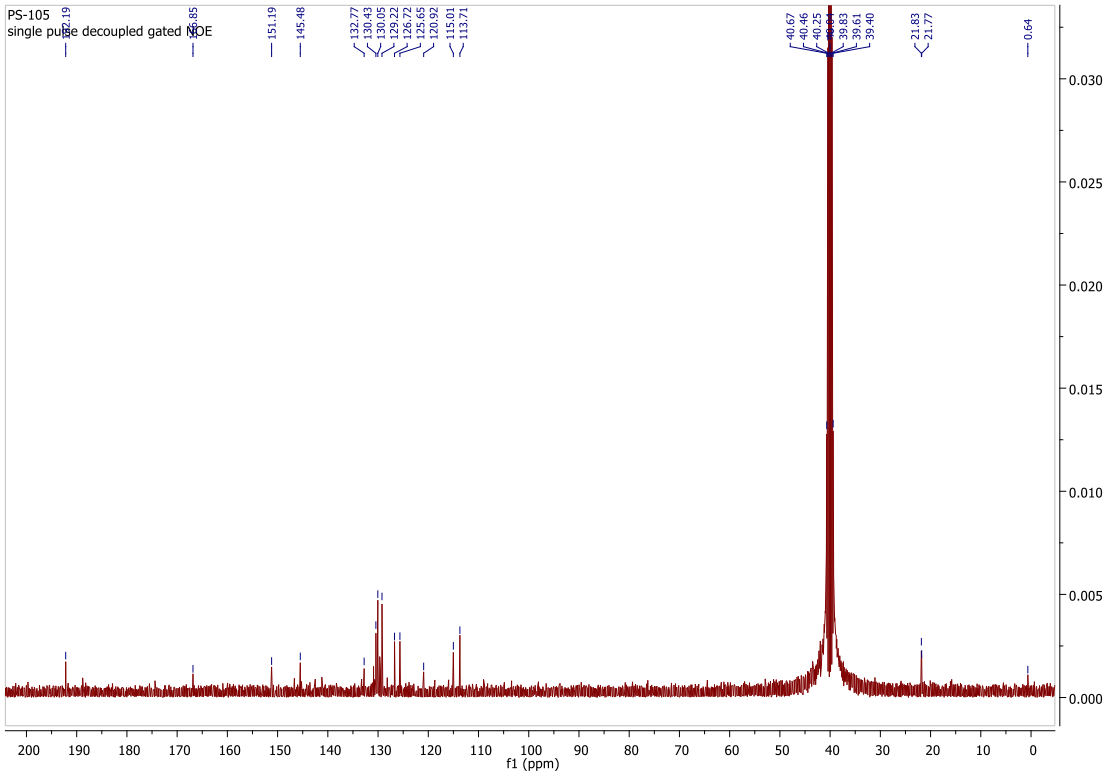


^{13}C NMR spectrum of **10c**

1-Acetyl-2-((2-oxo-2-(4-tolyl)ethyl)thio)benzo[4,5]imidazole (10d)

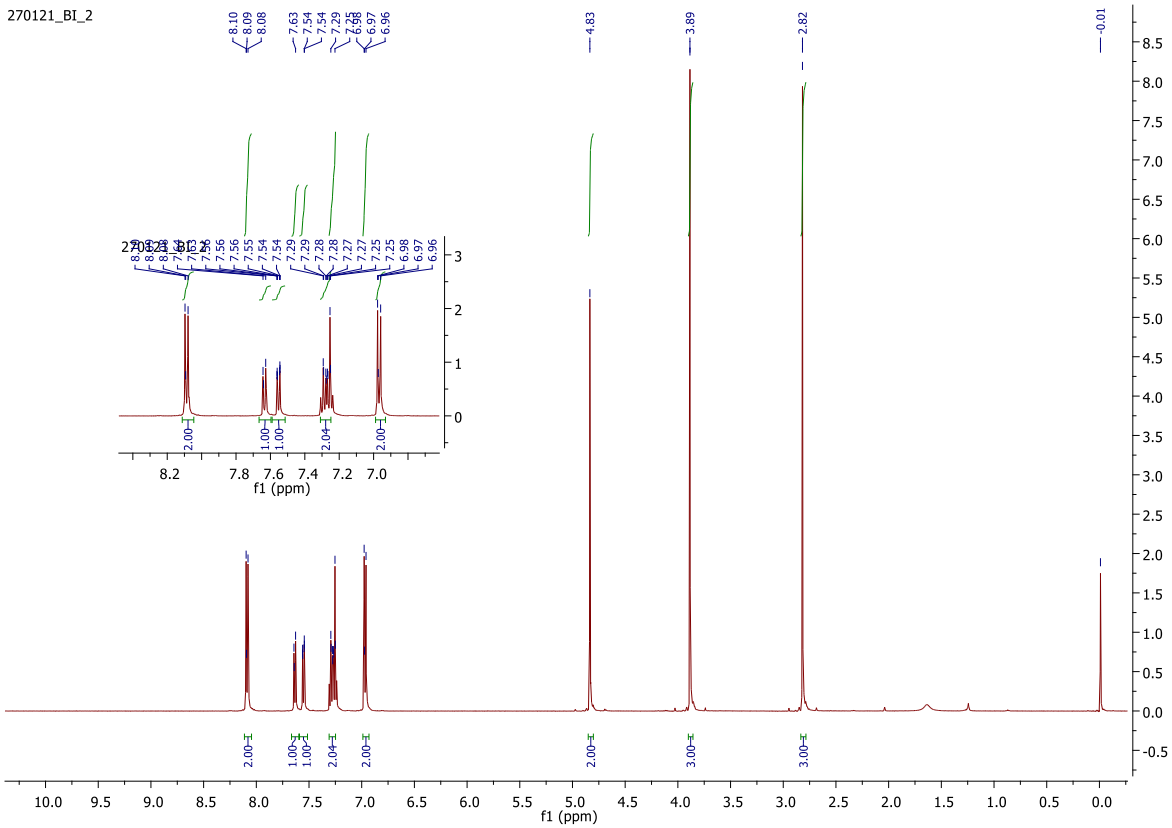


^{1}H NMR spectrum of **10d**

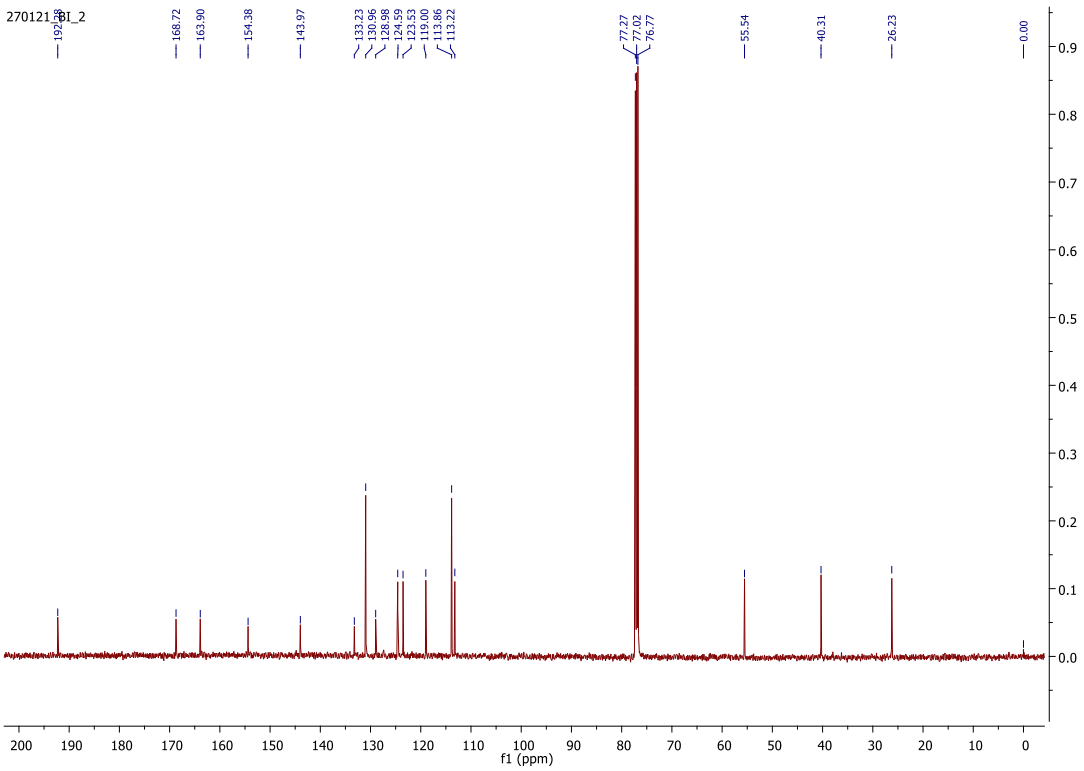


^{13}C NMR spectrum of **10d**

1-Acetyl-2-((2-oxo-2-(4-methoxyphenyl)ethyl)thio)benzo[4,5]imidazole (10e)

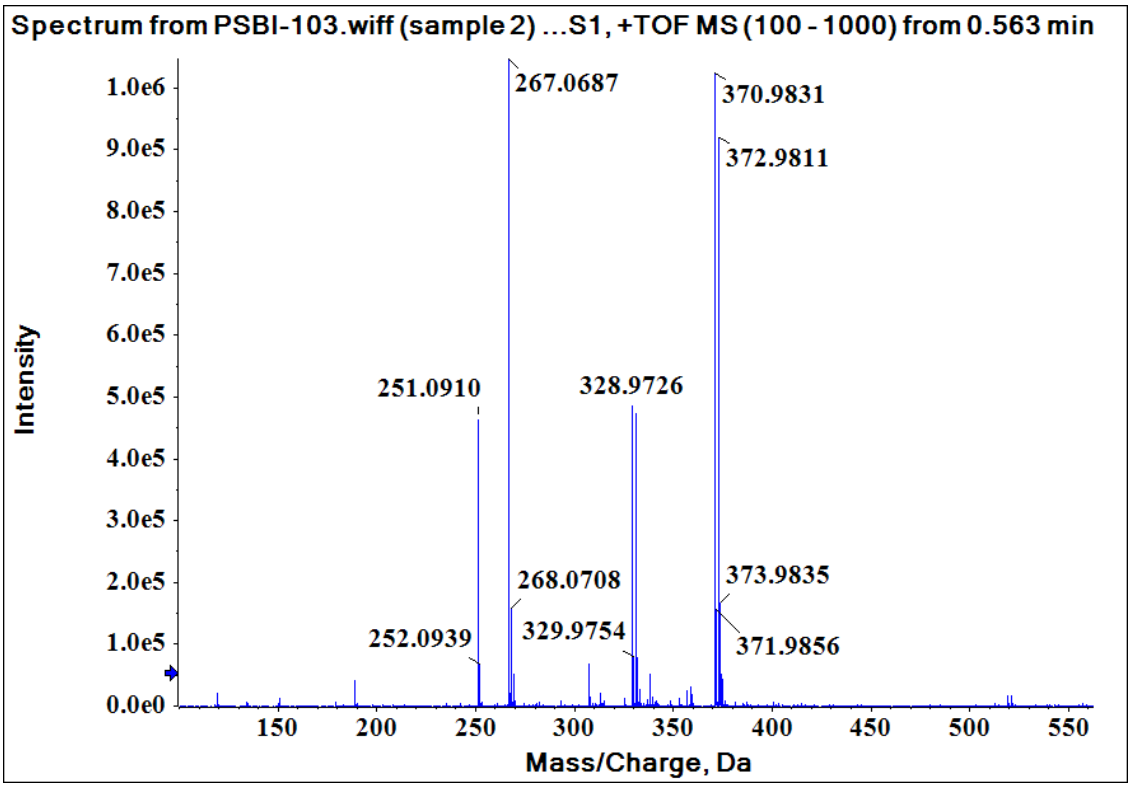


^{1}H NMR spectrum of **10e**

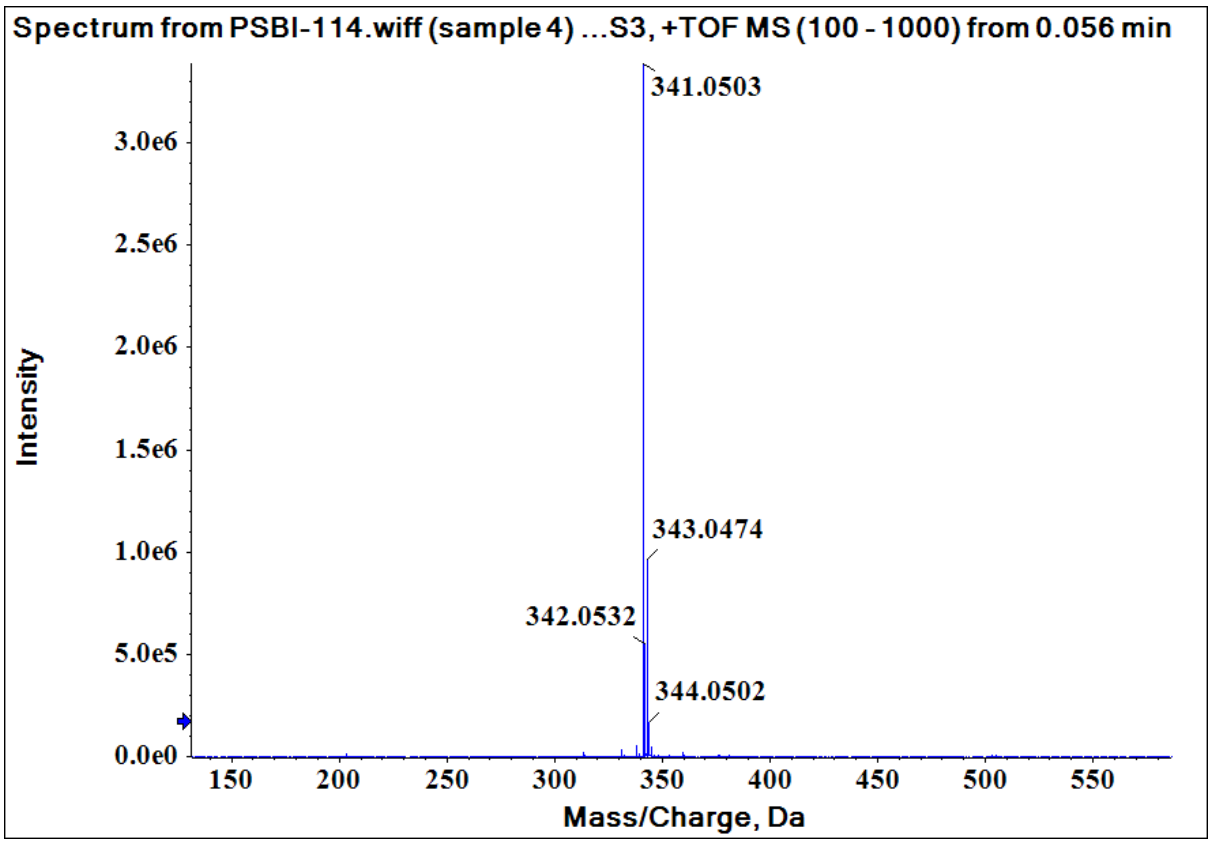


^{13}C NMR spectrum of **10e**

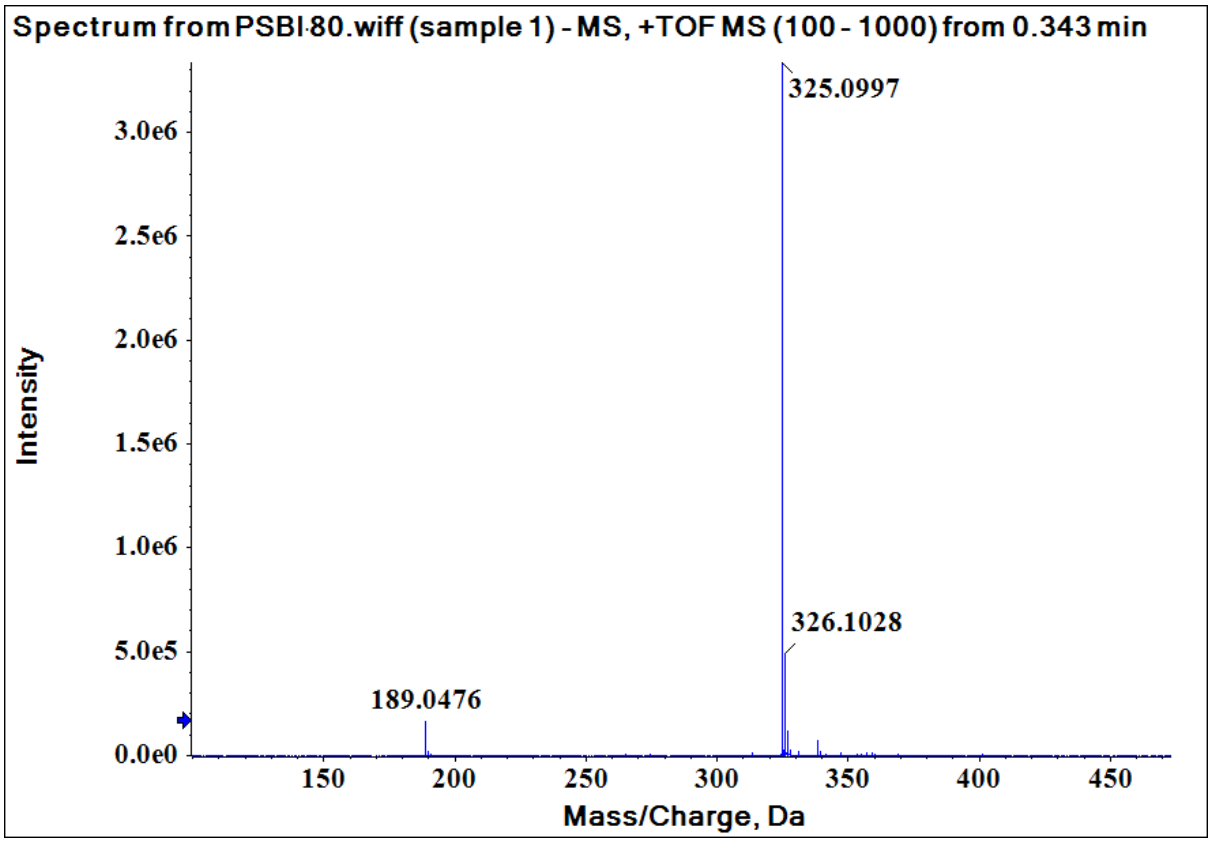
HRMS



HRMS of **6d**



HRMS of **6j**



HRMS of **10d**