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Graphical Abstract

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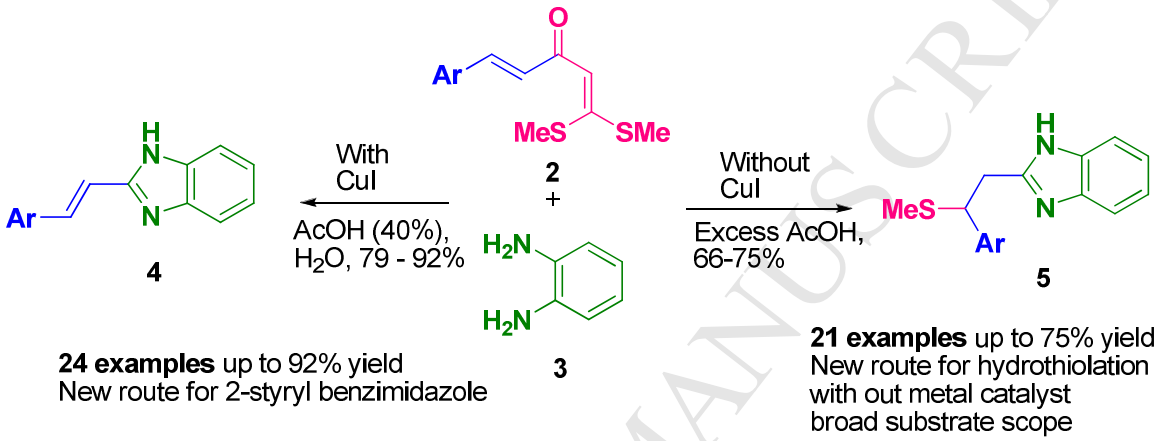

α-Aroylidineketene Dithioacetal Chemistry: CuI Catalyzed Synthesis of 2-Styryl benzimidazoles Enroute to Regioselective Hydrothiolation

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Abstract: Reactivity of *α*-aroylidineketene dithioacetals **2** was investigated to synthesize novel 2-styrylbenzimidazole derivatives **4** and their hydrothiolated product 2-(2-(methylthio)-2-arylethyl)-1*H*-benzo[*d*]imidazoles **5** has been reported**.** Compound **4** and **5** were synthesized by cyclocondensation of *α*-aroylidineketene dithioacetals **2** and *o*-phenylene diamine (OPD) **3** in the presence and absence of copper catalyst. Regioselective one-pot tandem hydrothiolation of olefin functionality in **4** was achieved under AcOH conditions.

1. Introduction

Functionalized ketene dithioacetals are readily accessible versatile synthons[1] and their chemistry has received considerable attention for several years.[2] *α*-aroylidineketene dithioacetals and related compounds with the basic structural unit Z-CH=C(SR)$_2$ possess a push pull alkene functionality accompanied with both nucleophilic and electrophilic characters (Z=COAr, COCH=CHAr etc). This complementary electronic nature of the functionalized ketene dithioacetals has been utilized in the assembly of novel heterocycles.[1-2]

Recently, we reported,[3] the synthesis of 2-arylbenzimidazole by cyclocondensation of *α*-aroylketene dithioacetals[4] (AKDTA) with OPD **3** under AcOH (cat.)/H_2O media. On this account, we got interested to examine the reactivity of *α*-aroylidineketene dithioacetal **2** by treating with **3** under similar cyclocondensation conditions. Interestingly, compound **4** was

Keywords: *α*-aroylidineketene dithioacetals; 2-styryl benzimidazole; *o*-phenylene diamine; regioselective hydrothiolation; copper iodide; acetic acid

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obtained as major along with a 25% of byproduct, which has been identified as hydrothiolated product of **4**. Hydrothiolation across the C=C bond is a key transformation of significant interest in organic chemistry.[5] It constitutes a key role in biochemical synthesis of biologically active compounds.[6] A large number of bioactive organo-sulphur compounds are known as valuable feedstock chemicals finding utility as synthetic intermediates and functional materials.[7]

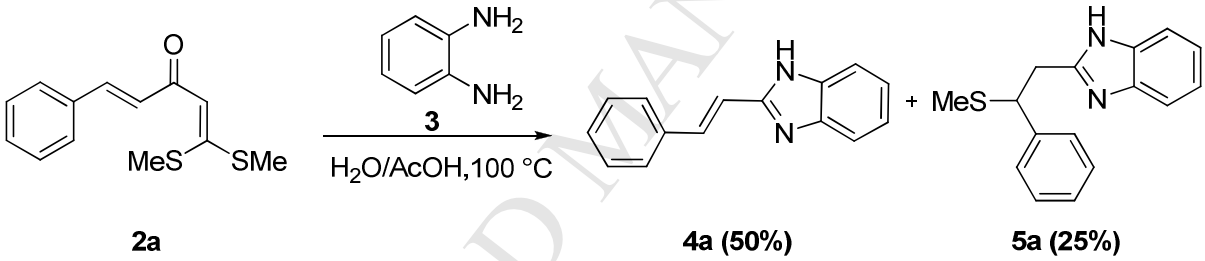
On the other hand, benzimidazoles are important class of compounds that found significant interest in contemporary organic synthesis[8], and medicinal chemistry.[9] A series of cyano and amino substituted derivatives of 2-styryl benzimidazoles and benzimidazo[1,2-*α*]quinolines have been evaluated for their biological activity in DNA and RNA binding ability[9]. Currently, only few reports are available in the literature for the synthesis of 2-styryl benzimidazoles. Most of the previous syntheses of 2-styryl benzimidazoles involved the condensation of 1,2-phenylenediamine with either cinnamaldehyde in the presence of $Yb(OTf)_3$[10], $TiCl_4$[11], $FePO_4$[12], and KI/DMF-H_2O[13] or cinnamic acid under relatively harsh condition such as PPA[14], ethylene glycol[15], glycerol[16], 4N HCl[17] and H_2SO_4-ethylene glycol.[18] Another related method by Okumara *et al*. included condensation of 1,2-phenylenediamine with cinnamoyl chloride in toluene under reflux conditions.[19] Alternative methods of 2-styryl benzimidazole synthesis includes steps such as Philips condensation followed by reaction of the 2-methyl benzimidazole intermediate with various aromatic aldehydes;[20] reactions of *α*,*β*, unsaturated ester with $AlMe_3$-Toluene under reflux conditions[21] (24h); and oxidative C-N coupling reaction of N^1-Benzyl (substituted benzene)-1,2-diamines using TEMPO as oxidant.[22] However, none of the classical methods exhibited broad substrate scope and utilized milder reaction conditions. Here in for the first time we report the synthesis of 2-styryl benzimidazoles from *α*-aroylidineketene dithioacetals under milder reaction conditions.

Besides, substituted benzimidazoles incorporated with alkyl/aryl sulfide functionalities are known to possess high anthelmintic activity against intestinal nematodes in human as well as in animals.[23,24] Additionally, the sulfides could be useful synthons for preparation of sulfones which are key synthetic intermediates [23,24] and potential bioactive compounds.[23-25] Although, there are few reports on hydrothiolation of *α*,*β*-unsaturated carbonyl compounds using various catalysts [26,27] to the best of our knowledge there are no reports on hydrothiolation of olefin functionality as in compound **4**. In the present work, the different reactivity of *α*-

aroylidineketene dithioacetals **2** compared to *α*-aroylketene dithioacetals were exploited which led to unprecedented formation of **5** besides the expected product **4**. This finding gave us scope to diverge from this point and establish methodologies for selective synthesis of 2-styryl benzimidazoles **4** and regioselective hydrothiolation product **5**.

2. Results and discussion

The selected substrates **2a-y** were prepared by aldol condensation of 4,4-bis(methylthio)but-3-en-2-one **1** with various aryl aldehydes under basic conditions (Table 1, see SI).[28] At the onset of our studies, the cyclocondensation of readily prepared **2a** and **3** in the presence of acetic acid (50 mol%) in water at 100 ^{o}C was investigated. We observed that the expected product 2-styryl benzimidazole **4a** was obtained only 50% yield along with a by-product that formed in 25% yield (Scheme 1). The by-product was identified as 2-(2-(methylthio)-2-arylethyl)-1*H*-benzo[*d*]imidazole **5a** which resulted from regioselective hydrothiolation of **4a**. Compounds **4a**&**5a** were confirmed by ^{1}H&^{13}C NMR spectrum.



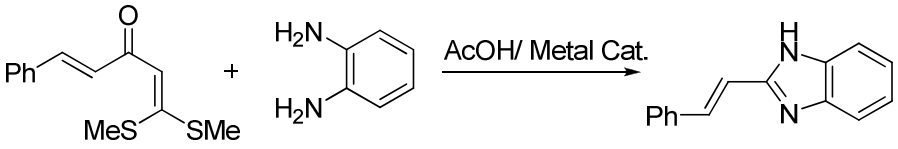
2a **4a (50%)** **5a (25%)**

Scheme 1. Reaction of *α*-aroylidineketene dithioacetal **2a** and OPD **3** in the presence of AcOH (cat)

In order to modulate the selective synthesis of **4a**, several reaction conditions using various metal catalysts in AcOH/H_2O media were explored (Table 1). Interestingly, in the presence of copper iodide (CuI, 5 mol%) the cyclocondensation of **2a** and **3** in AcOH/water (Table 1, entry 1) led to isolation of compound **4a** in 89% yield. When the same reaction was conducted under microwave conditions, **4a** was isolated in 87% yield (Table 1, entry 2). Further, the formation of **4a** increased to 92% yield by increasing the amount (10 mol%) of copper iodide (Table 1, entry 3). Additionally, when other copper salts such as CuBr or $Cu(OTf)_2$ were employed instead of copper iodide, the yields of **4a** was reduced to 75 & 87% (Table 1, entries 6-7). On the other hand, when $ZnCl_2$ was used as catalyst, compounds **4a** was obtained in 59% yield along with 35% of **5a** (Table 1, entry 8). In addition to Cu

catalysts, the cyclocondensation was explored using other metal catalysts such as $Yb(OTf)_3$, Ag(OTf), and $In(OTf)_3$ to afford **4a** in 84-89% yields (Table 1, entries 9-12).

Table 1. Optimization of the selective synthesis of 2-styrylbenzimidazole **4a** in one-pot cyclocondensation between **2a** & **3**



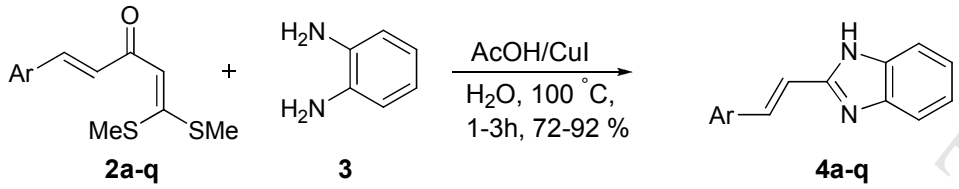
2a **3** **4a**

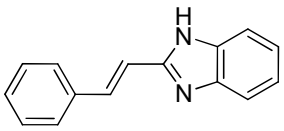
Entry	Solvent	Catalyst	Temp. (^oC)	Time (min)	Yield (%)
1	H_2O	CuI/AcOH (5/50)	100	180	89
2	H_2O	CuI/AcOH (5/50)	100	5	87[a,c]
3	**H_2O**	**CuI/AcOH (10/50)**	**100**	**180**	**92**
4	MeCN	CuI/AcOH (10/50)	70	120	85
5	H_2O	CuI (10)	100	18	-[c,d]
6	DMF	CuBr (10)	100	210	75[b]
7	MeCN	$Cu(OTf)_2$ (10)	70	180	87[b]
8	EtOH	$ZnCl_2$ (20)	90	180	59[b]
9	MeCN	$Yb(OTf)_3$ (10)	70	180	84[b]
10	DMF	$Yb(OTf)_3$ (10)	100	180	86[b]
11	MeCN	Ag(OTf) (10)	70	150	89[b]
12	MeCN	$In(OTf)_3$ (10)	70	180	86[b]
13	MeCN	$InCl_3$ (10)	70	180	--[d]

[a] trace of 2-methyl benzimidazole was isolated.; [b] minor amount of unreacted **2** was recovered& these reactions performed without acetic acid. [c] Under microwave (MW), [d] No reaction.

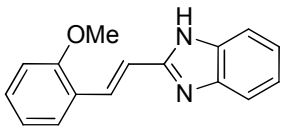
There was no improvement towards the yield of **4a** even the catalysts were used in stoichiometric amounts. Notably, in the absence of AcOH, the cyclocondensation and thereby formation of **4a** was not observed (Table 1, entry 5). The reason could be that AcOH in this reaction is acting as a catalyst as well as co-solvent. Following the optimized conditions (AcOH and CuI in H_2O at 100 ºC for 3 h Table 1, entry 3), the cyclocondensation was explored for synthesis of **4b-q** (Table 2).

Table 2. Synthesis of 2-styryl benzimidazoles **4a-q** from cyclocondensation of **3** and wide range of α- aroylidineketene dithioacetals **2a-q** using the optimized conditions[a]

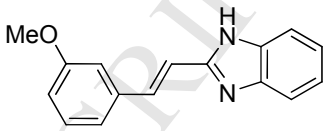




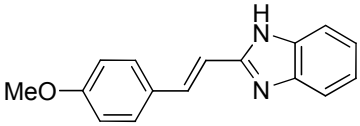
4a (92%)



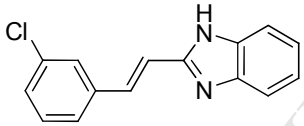
4b (83%)



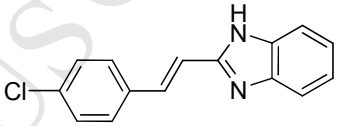
4c (80%)



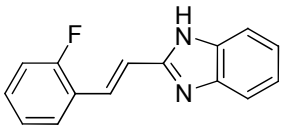
4d (87%)



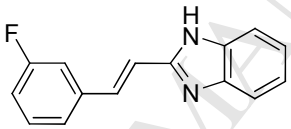
4e (85%)



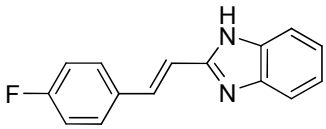
4f (84%)



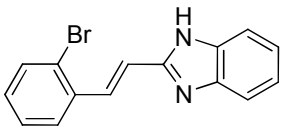
4g (89%)



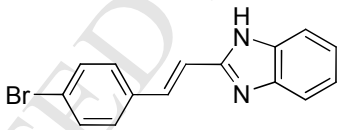
4h (86%)



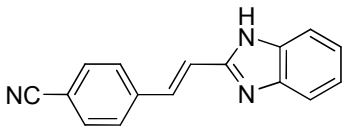
4i (87%)



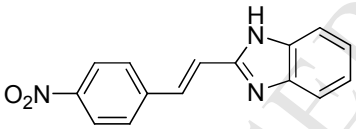
4j (85%)



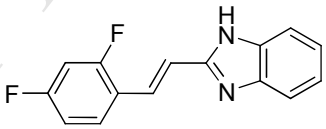
4k (83%)



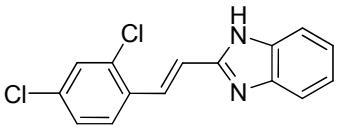
4l (88%)



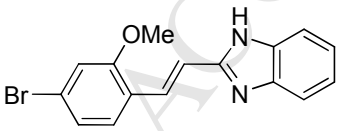
4m (89%)



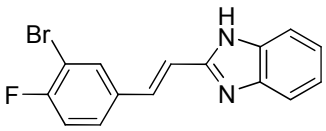
4n (91%)



4o (90%)



4p (84%)



4q (82%)

[a] Optimized Reaction conditions: **2** (1mol), **3** (1mol), 50 mol% AcOH, 10mol% CuI, Water (5mL), reflux, 100 ºC, 1-2.5 h. Isolated yields refer to **2.**

It was observed that variants of **2a** incorporating substitution of phenyl rings with Cl, F, Br and electron withdrawing as well as donating groups underwent cyclocondensation smoothly in excellent yields (79-92%). The structure of **4g**[29a] & **4n**[29b] was confirmed on the basis of single crystal x-ray (Figure. 1).

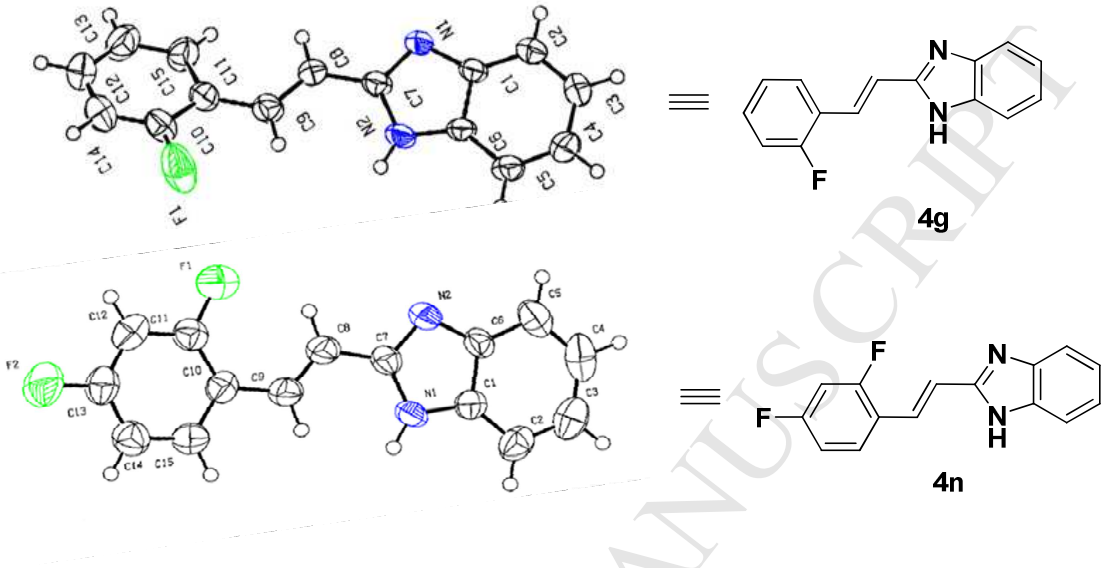
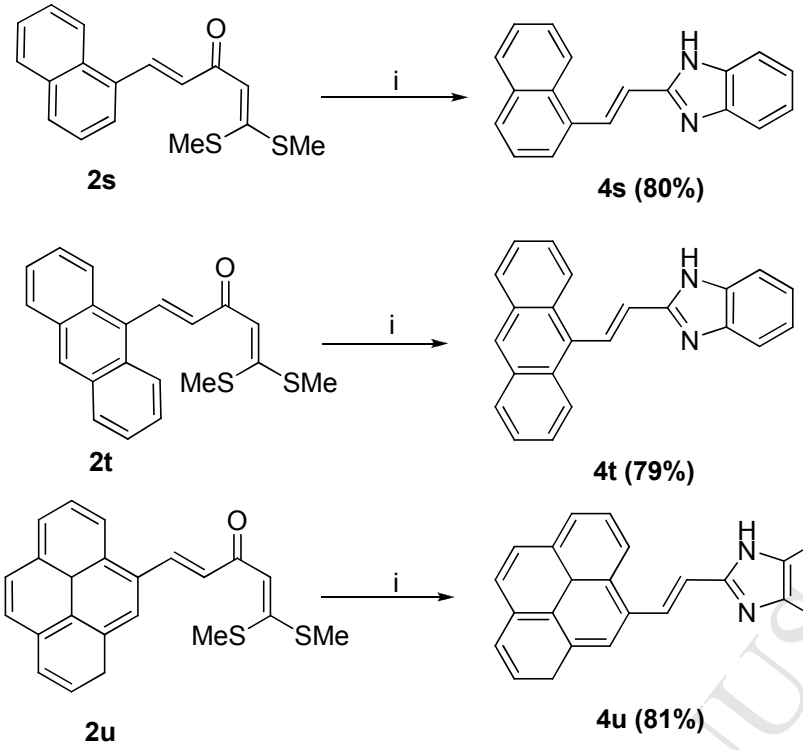


Figure 1. X-ray Crystal structures of 2-styryl benzimidazoles **4g & 4n**

As a further variation of phenyl ring in **2a**, we introduced polyaryls such as naphthalene, anthracene & pyrene molecules and corresponding transformations were observed from **2s-u** to **4s-u** in good yields (Scheme 2).

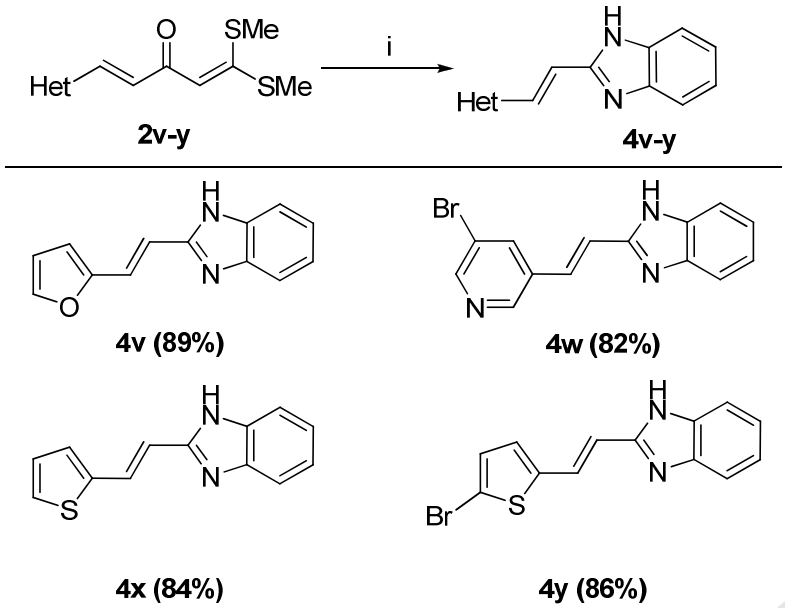


Reaction Condition: (i) **2** (1mol), **3** (1mol), 50 mol% AcOH, 10 mol% CuI, Water (5mL), reflux, 100 ºC, 1-2.5 h. Isolated yields refer to **2.**

Scheme 2. Substrate scope for the synthesis of 2-styryl benzimidazole **4s-u**

Further, the cyclocondensation was extended to the heteroaryl substrates **2v-y** which resulted in synthesis of **4v-y** in 82-89% yields (Table 3). Overall, inclusive cyclocondensation of **2** and **3**, in all these transformations, we did not find the formation **5** in the presence of copper catalyst.

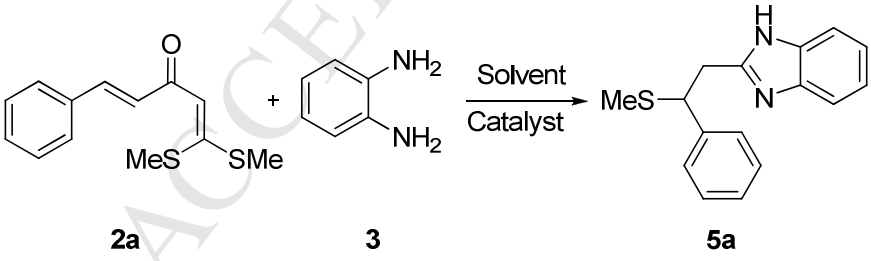
Table 3. Substrate scope in the synthesis of compounds **4v-y**[a] from reaction of **3** and *α*-heteroaroylidineketene dithioacetals **2v-y**



(i) **2** (1mol), **3** (1mol), 50 mol% AcOH, 10 mol%, CuI, Water (5mL), reflux, 100 ºC, 1-2.5 h. Isolated yields refer to **2**.

On the contrary, optimization of cyclocondensation reaction aimed at achieving selective one-pot synthesis of **5a** seemed a very challenging task. In this regard, we envisaged that cyclocondensation **2a** with OPD **3** in the presence of acetic acid initially results in formation of compound **4a** along with MeSH and further reaction of these two intermediates leads to the formation of **5a**. The formation of **5a** was investigated by exploring several reaction conditions.

Table 4. Optimization of the selective synthesis of **5a** during one-pot tandem hydrothiolation



Entry	Solvent	Acid catalyst	Temp (^oC)	Time (min)	Yield (%)
1	H_2O	AcOH[a] (50)	80	120	25
2	EtOH	AcOH (50)	90	120	28
3	MeCN	AcOH (50)	70	120	28
4	EtOH	AcOH (50)	90	120	34

5	H_2O	*p*-TsOH (50)	80	50	25
6	EtOH	L-Proline (50)	90	120	25
7	EtOH	HCl (0.1M, 50)	90	60	30
8	None	AcOH (50)	100	3	38
9	H_2O	AcOH (50)	80	5	21[b]
10	H_2O	AcOH (50)	80	5	25[b]
11	H_2O	*p*-TsOH (50)	80	3	22[b]
12	H_2O	HCl (0.1M)	80	5	24[b]
13	None	HCOOH (50)	80	10	30[b]
14	H_2O	H_2SO4 (0.1M)	80	5	28[b]
15	None	AcOH (100)	RT	72 h	-[a,c]
16	None	AcOH (50)	100	60	30
17	None	AcOH (60)	100	50	40
18	None	AcOH (80)	100	25	40
19	None	AcOH (100)	100	25	45
20	**None**	**AcOH (10Vol)**	**110**	**15 h**	**75**

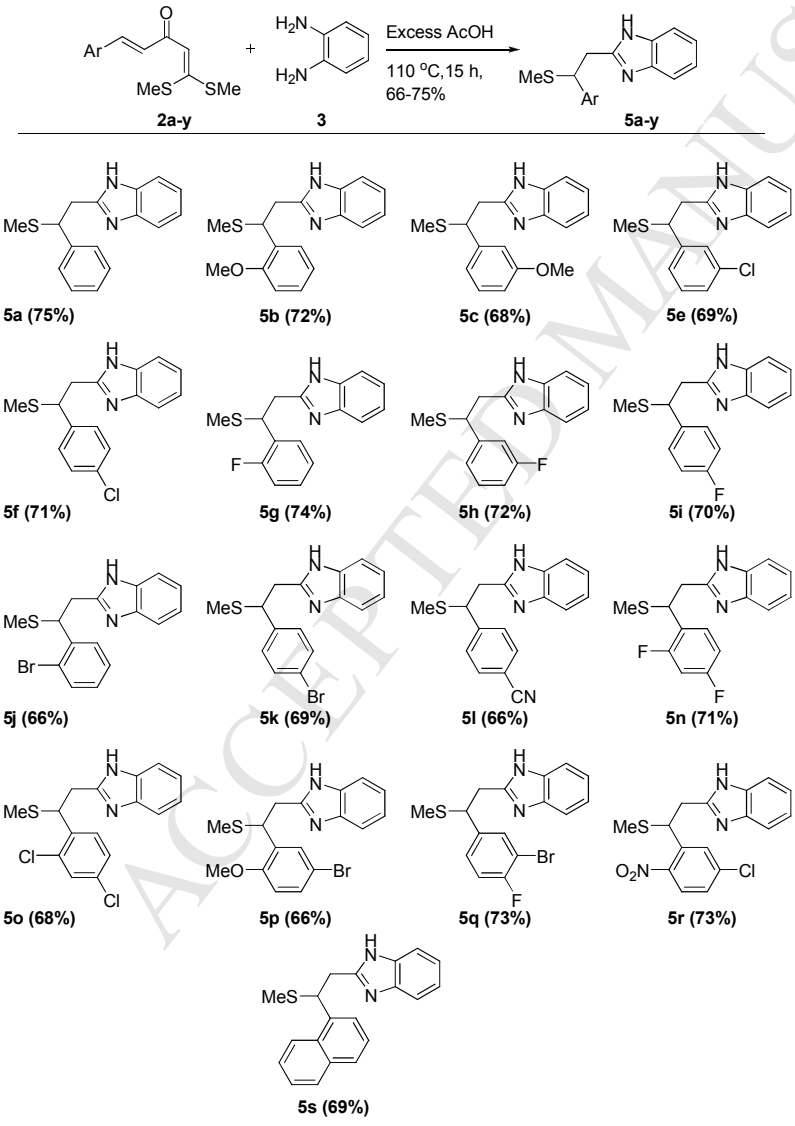
[a]products **5a** accompanied with <10% of 2-methyl benzimidazole as a side product by the reaction of AcOH and **3** under heating. [b] Under microwave (MW) condition. [c] Unreacted **2** was recovered.

An initial attempt towards the optimization includes the reaction of **2a** and OPD **3** at 100 ^oC in presence of catalytic amount of acetic acid (50 mol%) in ethanol/acetonitrile to afford **5a** in 28-34% yields (Table 4, entries 2-4). The similar cyclocondensation was performed using other acid catalysts such as *p*-TsOH and L-proline, the yields of **5a** formation did not improve whereas in presence of HCl the yields increased up to 38% (Table 4, entries 5-7). Further, the reactions were performed in water/EtOH with microwave irradiation at 80-100 ^oC for 3-10 min in the presence of acid catalysts such as *p*-TsOH, HCl, HCOOH, sulphuric acid to yield **5a** with 21-38% yield (Table 4, entries 8-14). The hydrothiolation product **5a** was not observed when the reaction was performed in excess AcOH at room temperature (Table 4, entry 15). Interestingly, the formation of hydrothiolation product **5a** increased to 45% yield upon increasing the amount of AcOH from 50 to 100 mol % (Table 4, entries 16-19).

On this account, the further reaction was carried out with excess of AcOH (~10 vol) in prolonged heating (15h) at 110 ^oC, wherein the formation of **5a** was dramatically increased to 75% yield and conditions involved were considered as optimized conditions (Table 4, entry 20). It was assumed that during the cyclocondensation of **2a** and **3**, the *in situ* eliminated MeSH might be dissolved in excess of AcOH consequently the formation of **5a** was

predominant. Though the AcOH was taken as excess, we could not control the evaporation of MeSH due its high volatile nature and it was acquired that it might have been escaped from the reaction medium. Only the dissolved MeSH in AcOH reacts further with olefin **4** to give **5**. This could be the reason to obtain **5** as the major product though the formation of **4** (<10%) was unavoidable as it is the intermediate for **5**. Following the optimized reaction conditions (Table 4, entry 20) the one-pot tandem hydrothiolation was extended to various substrates **2a-y** (Table 5). This novel hydrothiolation reaction displayed high functional group tolerance and proved to be a general protocol for the synthesis of thioethers.

Table 5. Synthesis of compounds **5a-y** under optimized conditions *via* one-pot Tandem hydrothiolation[a]



[a] Optimized Reaction conditions: **2** (1mol), **3** (1mol), excess AcOH, reflux, 110 °C, 5h.

Isolated yields refer to **2**These tandem hydrothiolation included several variants of *α*-aroylidineketene dithioacetal **2** bearing modifications in substitution of phenyl ring at *ortho*, *meta* and *para* positions were explored to afford regioselective product **5** in good yields. The hydrothiolation reaction with naphthyl variant of **2a** resulted in the formation of **5s** in 69% yields. Compounds **5b-s** were confirmed by ^{1}H,^{13}C NMR and LC-MS analysis. Additional to support of the analytical data, the structure of these compounds were confirmed on the basis of single-crystal X-ray structural analysis of a representative product **5l** of the series (Figure 2).[29c]

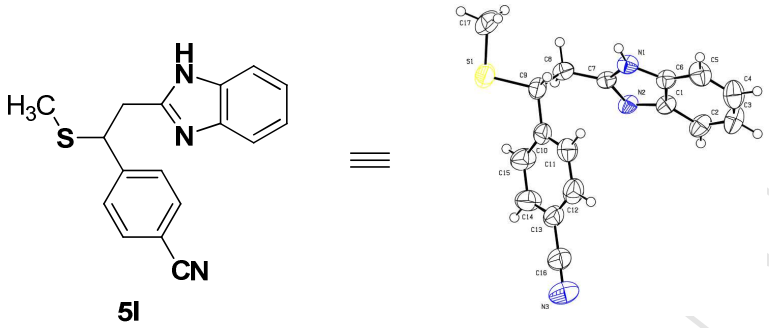
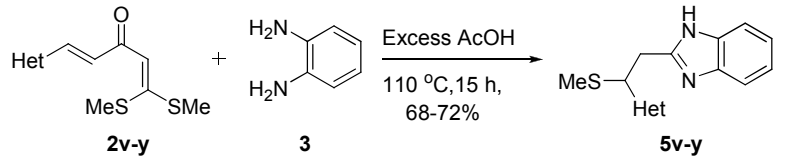
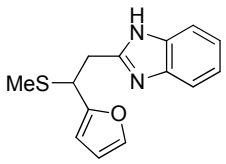


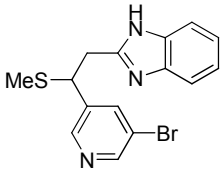
Figure 2. X-ray Crystal structure of **5l**

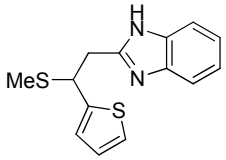
The regioselective hydrothiolation was examined further using various *α*-heteroaroylidineketene dithioacetals **2v-y** incorporating heterocycles such as 2-furyl, 5-bromo-3-pyridinyl, 2-thienyl and 5-bromo-2-thienyl in instead of phenyl ring of **2** under optimized reaction conditions to furnish **5v-y** in good yields (Table 6). This suggests that the methodology has broad scope and can be extended to wide range of substrates.

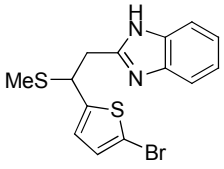
Table 6. Synthesis of **5v-y** during one-pot Tandem hydrothiolation reaction of **3** and *α*-heteroaroylidineketene dithioacetals **2v-y**[a]





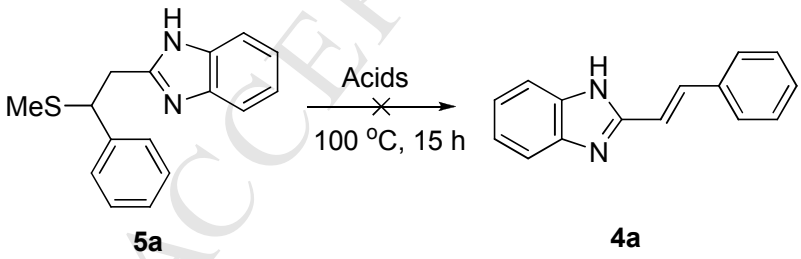






[a] Optimized Reaction conditions: **2** (1mol), **3** (1mol), excess AcOH, reflux, 110 °C, 15h.

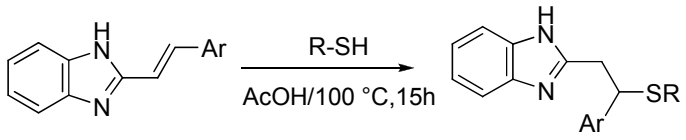
In order to propose the probable mechanism and validate our initial hypothesis on the formation of **4** and **5**, the dehydrothiolation was attempted. The obvious possibility was that either **4** or **5** formed first in the reaction which would further transform to other compound. In this direction, dehydrothiolation of **5a** in presence of several acids such as AcOH, HCOOH, HCl (0.1 M), H_2SO_4 (0.1 M) and *p*-TsOH.H_2O at 100 °C was attempted (Scheme 3). However, the dehydrothiolation was not successful to yield **4a** under acidic condition at 100 °C. It is therefore likely that the formation of olefin **4** precedes the formation of product **5** in the reaction medium.



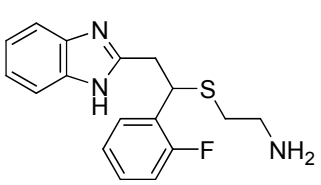
Scheme 3. Attempted elimination of MeSH

The above hypothesis is further supported by the fact that **4g** and **4n** when reacted with 2-aminoethane thiol and thiophenol in AcOH respectively to afford the corresponding regioselective hydrothiolation products **8a** and **8b** (Table 7). As expected, the reaction of **4g** proceeded expeditiously to yield **8a** with no trace of aza Michael adduct product.

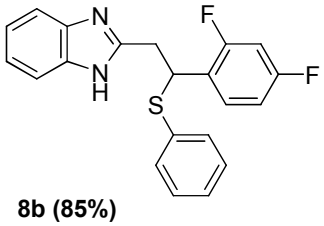
Table 7. Regioselective hydrothiolation of **4g&n** in presence of AcOH[a]



4g&n **8a&b**



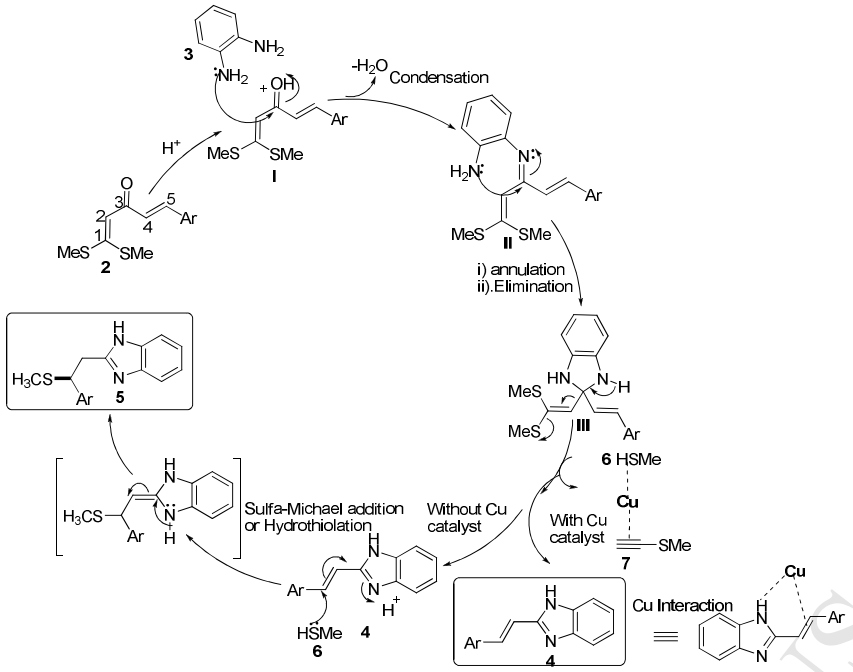
8a (87%)



8b (85%)

[a] Optimized Reaction conditions: **2** (1mol), **3** (1mol), excess AcOH, reflux, 110 ºC, 15h. Isolated yields refer to **2.**

On the basis of above experimental results, we propose a plausible mechanism for formation of **4** and **5** as depicted in Scheme 4, which also highlights on appropriate selectivity of the products in presence/absence of CuI. It is likely that initially oxygen of the carbonyl group in **2** gets protonated followed by nucleophilic addition of amine group of **3** at C-1 position to give imine **II**. The imine **II** further cyclizes to afford 2-(2,2-bis(methylthio)vinyl)-2-phenyl-2,3-dihydro-1*H*-benzo[*d*]imidazole (**III**), which rapidly degrades to more stable 2-styrylbenzimidazole **4** by concomitant elimination of ethynyl(methyl)sulfane **7** and MeSH **6**. At this stage, presence of CuI in the reaction medium is supposed to be determining outcome of the reaction products. In presence of Cu catalyst, the hydrothiolation of **4** would be inhibited since MeSH is likely to be trapped by the Cu atom thereby leading to selective formation of compound **4**. Based on a literature report,[30] we anticipated that copper would likely to form a complex with sulphur atom of thiol source thereby making the nucleophile unavailable for further Michael-type addition. On the other hand, in the absence of CuI or any copper salts, the *in situ* generated MeSH **6** would react with **4** *via* sulfa-Michael addition under acidic conditions leading to hydrothiolated product **5**.



Scheme 4. Plausible mechanism proposed for the formation and selectivity of of **4** & **5** during reaction of **2** and **3**

In conclusion, we have demonstrated selective routes for the synthesis of 2-styryl benzimidazoles **4** and their hydrothiolated products **5** through optimization of the initial reaction involving **2** and OPD **3**. Selective synthesis of **4** was accomplished under acidic conditions in presence of copper catalyst while that of **5** was a catalyst-free transformation. Further, based on these results a plausible mechanism was proposed for the transformation of **2** and **3** under acidic conditions in the presence and absence of copper (I) salts. The current work describes the potential of α-aroylidineketene dithioacetal as key synthetic intermediates. It is worth to highlight here that our new strategy would provide a simple alternative method for the hydrothiolation of broad range of substrates in the absence of metal catalysts.

Acknowledgements

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Experimental Section

General Consideration

The melting points reported in the work are uncorrected. Unless stated otherwise, solvents and chemicals were obtained from commercial sources and used without further purification. The ^{1}H and ^{13}CNMR spectra of the new compounds were measured at 400MHz or 300MHz and 100MHz or 75MHz (mentioned in respective NMR data itself) respectively using Bruker NMR instrument in DMSO-d_6 or $CDCl_3$. Chemical shifts are reported in parts per million (δ), coupling constants (J values) are reported in Hertz (Hz) relative to tetramethylsilane. Spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), m (multiplet) dd (doublet of doublets), td (triplet of doublets) bs (broad singlet). Elemental analysis was recorded on Thermofinnigan flash 2000 organic elemental CHNS analyser.

General procedure for the synthesis of 1,1-bis(methylthio)-5-arylpenta-1,4-dien-3-one (2a-y)

To a solution of 4,4-bis(methylthio)but-3-en-2-one (1mol) in ethanol (10ml) was added NaOH (1.5mol) and aryl aldehyde (1.1mol) under constant stirring. After the starting material was consumed as indicated by TLC, the reaction mixture was poured into ice water and the resulting solid was filtered, washed well with water (20 ml). The solid material obtained was crystallized from ethanol to furnish 81-99% of 1,1-bis(methylthio)-5-arylpenta-1,4-dien-3-one as a yellow solid.

(*E*)-1,1-bis(methylthio)-5-phenylpenta-1,4-dien-3-one 2a:[28] Pale yellow solid (2.5g, 81%); M.pt.150 ^{0}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.68 (dd, *J* = 2 Hz, 8 Hz, 2H), 7.48 (d, *J* = 16 Hz, 1H), 7.38 - 7.44 (m, 3H), 7.07 (d, *J* = 16 Hz, 1H), 6.49 (s, 1H), 3.72 (s, 3H), 2.57 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 183.5, 164.5, 140.4, 135.5, 130.4, 129.4, 128.6, 114.0, 17.2, 14.8; LC-MS calcd.m/z: 250, found 251 $[(M+1)]^{+}$.

(*E*)-5-(2-methoxyphenyl)-1,1-bis(methylthio)-penta-1,4-dien-3-one 2b: Yellow solid (2.9g, 85%); M.pt.116 ^{0}C; [Found: C, 59.92; H, 5.71. $C_{14}H_{16}O_2S_2$ requires C, 59.97; H, 5.75]; IR (ATR KBr cell, cm^{-1}) 1645, 1541; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.72 (d, *J* = 16 Hz, 1H), 7.66 (d, *J* = 6.4 Hz, 1H), 7.39 - 7.35 (m, 1H), 7.08 (s, 1H), 7.05 (d, *J* = 6.4 Hz, 1H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.42 (s, 1H), 3.85 (s, 3H), 2.55 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 183.7, 164.2, 158.4, 135.2, 131.9, 128.5, 128.3, 123.8, 121.1, 114.6, 112.2, 56.1, 17.2, 14.8; LC-MS calcd.m/z 280, found 281 $[(M+1)]^{+}$.

(*E*)-5-(3-methoxyphenyl)-1,1-bis(methylthio)-penta-1,4-dien-3-one 2c: Pale yellow solid (3.1g, 90%); M.pt.114 ^{0}C; [Found: C, 59.94; H, 5.70. $C_{14}H_{16}O_2S_2$ requires C, 59.97; H, 5.75]; IR (ATR KBr cell, cm^{-1}) 1771, 1684, 1577; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 7.44 (d, *J* = 16 Hz, 1H), 7.32 (t, *J* = 8 Hz, 1H), 7.24 - 7.22 (m, 2H), 7.06 (d, *J* = 16.4 Hz, 1H), 6.96 - 6.94 (m, 1H), 6.48 (s, 1H), 3.78 (s, 3H), 2.56 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ_C: 183.6, 164.6, 160.1, 140.4, 136.9, 130.4, 128.9, 121.2, 116.4, 114.0, 113.2, 55.7, 17.3, 14.8; LC-MS calcd.m/z 280, found 281 [(M+1)]$^+$.

(*E*)-5-(4-methoxyphenyl)-1,1-bis(methylthio)-penta-1,4-dien-3-one 2d:[28] Yellow solid (3.1g, 90%); M.pt 104-106 ^{0}C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 7.64 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 15.9 Hz, 1H), 6.98 (d, *J* = 8 Hz, 2H), 6.93 (d, *J* = 16 Hz, 1H), 6.45 (s, 1H), 3.79 (s, 3H), 2.56 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ_C: 183.7, 163.5, 161.3, 140.4, 130.3, 128.0, 126.2, 114.9, 114.2, 55.8, 17.2, 14.8; LC-MS calcd.m/z 280, found 281 [(M+1)]$^+$.

(*E*)-5-(3-chlorophenyl)-1,1-bis(methylthio)penta-1,4-dien-3-one 2e:[28] Pale yellow solid (2.9g, 85%); M.pt. 136 ^{0}C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 7.79 (s, 1H), 7.65 - 7.62 (m, 1H), 7.47 - 7.43 (m, 3H), 7.17 (d, *J* = 16 Hz, 1H), 6.49 (s, 1H), 2.57 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ_C: 183.3, 165.2, 138.6, 137.8, 134.2, 131.2, 130.1, 129.9, 127.9, 127.3, 113.9, 17.3, 14.8; LC-MS calcd. m/z: 284, found 285 [(M+1)]$^+$.

(*E*)-5-(4-chlorophenyl)-1,1-bis(methylthio)penta-1,4-dien-3-one 2f:[28] Yellow solid (3.4g, 99%); M.pt.144 ^{0}C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 7.69 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.43 (s, 1H), 7.07 (d, *J* = 16 Hz, 1H), 6.47 (s, 1H), 2.48 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ_C: 182.8, 164.4, 138.4, 134.3, 133.9, 129.7, 128.9, 128.8, 113.4, 16.7, 14.3; LC-MS calcd.m/z: 284, found 285 [(M+1)]$^+$.

(*E*)-5-(2-fluorophenyl)-1,1-bis(methylthio)-penta-1,4-dien-3-one 2g:[28] Pale yellow solid (3g, 92%); M.pt.109 ^{0}C; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 7.79 (t, *J* = 8 Hz, 1H), 7.53 (d, *J* = 16.4 Hz, 1H), 7.46 - 7.42 (m, 1H), 7.29 - 7.23 (m, 2H), 7.15 (d, *J* = 15.6 Hz, 1H), 6.47 (s, 3H), 2.57 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ_C: 183.7, 166.1, 163.1, 159.7, 133.8, 131.1, 130.9, 129.8, 129.4, 124.3, 123.3, 123.2, 116.2, 115.9, 113.1, 17.2, 15.1; UPLC-MS calcd. m/z 268, found 269[(M+1)]$^+$.

(*E*)-5-(3-fluorophenyl)-1,1-bis(methylthio)-penta-1,4-dien-3-one 2h: Pale yellow solid (2.9g, 90%); M.pt.124 ^{0}C; [Found: C, 58.15; H, 4.83. $C_{13}H_{13}FOS_2$ requires C, 58.18; H, 4.88]; IR (ATR KBr cell, cm^{-1}) 1630, 1500, 1420; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 7.56 - 7.42 (m, 4H), 7.24 - 7.20 (m, 1H), 7.13 (d, *J* = 16.4 Hz, 2H), 6.47 (s, 1H), 2.57 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ_C: 183.0, 166.2, 139.3, 130.1, 130.0, 123.9, 116.4, 116.2, 113.9, 113.7, 112.9, 17.0, 14.8; UPLC-MS calcd.m/z 268, found 269 [(M+1)]$^{+}$.

(*E*)-5-(4-fluorophenyl)-1,1-bis(methylthio)-penta-1,4-dien-3-one 2i: Pale yellow solid (3.0g, 92%); M.pt.116-118 ^{0}C; [Found: C, 58.10; H, 4.81. $C_{13}H_{13}FOS_2$ requires C, 58.18; H, 4.88]; IR (ATR KBr cell, cm^{-1}) 1640, 1598, 1465; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 7.74 (t, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 16.4 Hz, 1H), 7.25 (t, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 16.4 Hz, 2H), 6.46 (s, 1H), 2.55 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ_C: 183.5, 165.7, 162.3, 139.7, 129.9, 129.7, 127.0, 115.9, 115.6, 113.1, 17.2, 15.0; LC-MS calcd.m/z 268, found 269 [(M+1)]$^{+}$.

(*E*)-5-(2-bromophenyl)-1,1-bis(methylthio)-penta-1,4-dien-3-one 2j: Pale yellow solid (3.57g, 88%); M.pt.108 ^{0}C; [Found: C, 47.38; H, 3.92. $C_{13}H_{13}BrOS_2$ requires C, 47.42; H, 3.98]; IR (ATR KBr cell, cm^{-1}) 2986, 1646, 1585; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 7.88 (dd, *J* = 1.56 Hz, 7.84 Hz, 1H), 7.73 (d, *J* = 6.44 Hz, 1H), 7.70 (s, 1H), 7.46 (t, *J* = 6.96 Hz, 1H), 7.35 (td, *J* = 1.64 Hz, 7.88 Hz, 1H), 7.16 (d, *J* = 15.7 Hz, 1H), 6.48 (s, 1H), 2.58 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ_C: 182.8, 166.0, 137.9, 134.9, 133.7, 131.9, 131.3, 128.7, 128.4, 125.3, 114.3, 17.3, 14.9; LC-MS calcd.m/z 329, found 330 [(M+1)]$^{+}$.

(*E*)-5-(4-bromophenyl)-1,1-bis(methylthio)-penta-1,4-dien-3-one 2k: Pale yellow solid (3.45g, 85%); M.pt.148-150 ^{0}C; [Found: C, 47.35; H, 3.94. $C_{13}H_{13}BrOS_2$ requires C, 47.42; H, 3.98]; IR (ATR KBr cell, cm^{-1}) 2914, 1741, 1645, 1580; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 7.63 - 7.59 (m, 4H), 7.44 (d, *J* = 16 Hz, 1H), 7.08 (d, *J* = 15.6 Hz, 2H), 6.47 (s, 1H), 2.56 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ_C: 183.2, 166.1, 139.5, 134.1, 131.8, 129.3, 127.7, 123.8, 113.0, 17.2, 15.0; LC-MS calcd.m/z 329, found 330 [(M+1)]$^{+}$.

(*E*)-4-(5,5-bis(methylthio)-3-oxopenta-1,4-dienyl)benzonitrile 2l: Pale yellow solid (3.02g, 89%); M.pt.218 ^{0}C; [Found: C, 61.01; H, 4.73, N, 5.02. $C_{14}H_{13}NOS_2$ requires C, 61.06; H, 4.76; N, 5.09]; IR (ATR KBr cell, cm^{-1}) 2200, 1630, 1580; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 7.86 - 7.84 (m, 4H), 7.51 (d, *J* = 16 Hz, 1H), 7.22 (d, *J* = 16.4 Hz, 1H), 6.50 (s, 1H), 2.57

(s, 3H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 182.2, 167.0, 139.2, 137.9, 132.0, 130.1, 127.9, 112.5, 112.1, 16.8, 14.6; LC-MS calcd.m/z 275, found 276 $[(M+1)]^+$.

(*E*)-1,1-bis(methylthio)-5-(4-nitrophenyl)-penta-1,4-dien-3-one 2m: Pale yellow solid (3.38g, 93%); M.pt. 224-226 ^{0}C; [Found: C, 52,82; H, 4.38, N, 4.70. $C_{13}H_{13}NO_3S_2$ requires C, 52.86; H, 4.44; N, 4.74]; IR (ATR KBr cell, cm^{-1}) 1644, 1584, 1508, 1467; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 8.26 (d, *J* = 8.8 Hz, 2H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.58 (d, *J* = 16 Hz, 1H), 7.29 (d, *J* = 16 Hz, 1H), 6.54 (s, 1H), 2.59 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 182.6, 166.3, 135.3, 135.0, 133.9, 132.3, 131.8, 129.9, 129.4, 128.4, 114.2, 17.3, 14.8; LC-MS calcd.m/z 295, found 296 $[(M+1)]^+$.

(*E*)-5-(2,4-difluorophenyl)-1,1-bis(methylthio)penta-1,4-dien-3-one 2n:[28] Pale yellow solid (3.1g, 88%); M.pt.152-154 ^{0}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.89 (q, *J* = 15.6 Hz, 1H), 7.47 (d, *J* = 15.6 Hz, 1H), 7.31 - 7.35 (m, 1H), 7.18 - 7.15 (m, 1H), 7.11 (d, *J* = 16 Hz, 1H), 6.45 (s, 1H), 2.56 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 182.5, 165.1, 164.3, 164.1, 162.1, 161.6, 159.5, 130.4, 130.3, 130.5, 119.5, 119.4, 113.6, 112.5, 112.3, 112.2, 104.8, 104.3, 16.7, 14.3; LC-MS calcd. m/z 286, found 287 $[(M+1)]^+$.

(*E*)-5-(2,4-dichlorophenyl)-1,1-bis(methylthio)penta-1,4-dien-3-one 2o:[28] Pale yellow solid (3.9g, 99%); M.pt.126 ^{0}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.69 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.50 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 6.17 (s, 1H), 5.55 (s, 1H), 5.31 - 5.27 (m, 1H), 2.45 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 182.6, 166.3, 135.3, 135.0, 133.9, 132.3, 131.8, 129.9, 129.4, 128.4, 114.3, 17.3, 14.8; LC-MS calcd.m/z 319, found 320 $[(M+1)]^+$.

(*E*)-5-(5-bromo-2-methoxyphenyl)-1,1-bis(methylthio)penta-1,4-dien-3-one 2p:[28] Pale yellow solid (3.85g, 87%); M.pt.156-158 ^{0}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.88 (s, 1H), 7.61 (d, *J* = 15.6 Hz, 1H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.15 (d, *J* = 16.4 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 1H), 6.44 (s, 1H), 3.86 (s, 3H), 2.56 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 183.3, 165.0, 157.4, 134.0, 133.2, 130.1, 129.9, 126.1, 114.6, 112.8, 56.5, 17.2, 14.8; LC-MS calcd.m/z 359, found 360 $[(M+1)]^+$.

***(E)*-5-(3-bromo-4-fluorophenyl)-1,1-bis(methylthio)-penta-1,4-dien-3-one 2q:** Pale yellow solid (3.73g, 87%); M.pt.135-137 ^{0}C; [Found: C, 44.92; H, 3.42. $C_{13}H_{12}BrFOS_2$: C, 44.96; H, 3.48]; IR (ATR KBr cell, cm^{-1}) 1604, 1440; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H:

8.08 (d, *J* = 16 Hz, 2H), 7.74 - 7.71 (m, 1H), 7.45 - 7.38 (m, 2H), 7.10 (d, *J* = 16 Hz, 1H), 6.45 (s, 1H), 2.55 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 182.7, 166.4, 137.8, 132.7, 132.3, 128.6, 127.9, 116.6, 116.3, 112.8, 109.4, 109.1, 17.0, 14.8; LC-MS calcd. m/z 347, found 348 $[(M+1)]^+$.

(*E*)-5-(2-chloro-5-nitrophenyl)-1,1-bis(methylthio)penta-1,4-dien-3-one 2r: Pale yellow solid (3.79g, 93%); M.pt.158 ^{0}C; [Found: C, 47.30; H, 3.65, N, 4.20. $C_{13}H_{12}ClNO_3S_2$ requires C, 47.34; H, 3.67; N, 4.25]; IR (ATR KBr cell, cm^{-1}) 1650, 1560, 1480; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 8.65 (s, 1H), 8.20 (d, *J* = 8.8 Hz, 1H), 7.83 (d, *J* = 8.8 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.44 (d, *J* = 8 Hz, 1H), 6.54 (s, 1H), 2.58 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 182.2, 167.1, 147.3, 140.4, 134.7, 133.6, 133.0, 132.0, 125.6, 122.6, 114.5, 17.4, 14.9; LC-MS calcd. m/z 329, found 330 $[(M+1)]^+$.

(*E*)-1,1-bis(methylthio)-5-(naphthalene-1-yl)penta-1,4-dien-3-one 2s: Pale yellow solid (3.37g, 91%); M.pt.104 ^{0}C; [Found: C, 67.92; H, 5.30.$C_{17}H_{16}OS_2$: C, 67.96; H, 5.37]; IR (ATR KBr cell, cm^{-1}) 2981, 1645, 1509, 1484; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 8.28 (t, *J* = 15.2 Hz, 2H), 7.99 (t, *J* = 8 Hz, 1H), 7.93 (d, *J* = 4.2 Hz, 1H), 7.64 - 7.54 (m, 3H), 7.14 (d, *J* = 16 Hz, 1H), 6.57 (s, 1H), 2.59 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 183.4, 165.1, 136.6, 133.8, 132.3, 131.5, 131.2, 130.6, 129.2, 127.5, 126.7, 126.2, 125.3, 123.7, 114.1, 17.3, 14.8; LC-MS calcd.m/z: 300, found 301 $[(M+1)]^+$.

(*E*)-5-(anthracen-9-yl)-1,1-bis(methylthio)penta-1,4-dien-3-one 2t: Yellow solid (3.97g, 92%); M.pt.102-104 ^{0}C; [Found: C, 71.92; H, 5.10.$C_{21}H_{18}OS_2$: C, 71.96; H, 5.18]; IR (ATR KBr cell, cm^{-1}) 1650, 1570; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 8.68 (s, 1H), 8.39 (d, *J* = 16.4 Hz, 1H), 8.21 (d, *J* = 8 Hz, 2H), 8.12 (d, *J* = 8.4 Hz, 2H), 7.58 - 7.54 (m, 4H), 6.88 (d, *J* = 16.4 Hz, 1H), 6.61 (s, 1H), 2.56 (s, 3H), 2.48 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 183.9, 167.6, 139.1, 136.8, 132.0, 131.4, 130.2, 129.5, 128.5, 126.8, 126.3, 126.0, 114.0, 18.0, 15.9; LC-MS calcd.m/z: 350, found 351 $[(M+1)]^+$.

(*E*)-1,1-bis(methylthio)-5-(pyren-1-yl)penta-1,4-dien-3-one 2u: Brown solid (3.87g, 84%); M.pt.162-168 ^{0}C; [Found: C, 73.71; H, 4.80.$C_{23}H_{18}OS_2$: C, 73.76; H, 4.84]; IR (ATR KBr cell, cm^{-1}) 1638, 1577; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 8.60 (d, *J* = 13.6 Hz, 2H), 8.51 - 8.41 (m, 2H), 8.39 - 8.14 (m, 8H), 8.10 (t, *J* = 8 Hz, 1H), 7.38 (d, *J* = 15.2 Hz, 1H), 6.64 (s, 1H), 2.62 (s, 6H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 194.0, 183.4, 165.1, 132.4, 131.3, 131.0, 130.9, 130.7, 129.6, 129.3, 128.9, 128.7, 127.7, 127.6, 127.2, 126.9, 126.4, 126.1,

125.6, 125.2, 124.7, 124.6, 124.3, 123.0, 122.8, 114.3, 17.1, 14.7; LC-MS calcd.m/z: 374, found 375 $[(M+1)]^+$.

(*E*)-5-(furan-2-yl)-1,1-bis(methylthio)penta-1,4-dien-3-one 2v:[28] Low melting solid (2.6g, 87%); ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.81 (s, 1H), 7.29 (d, J = 15.6 Hz, 1H), 6.86 (s, 1H), 6.75 (d, J = 15.6 Hz, 1H), 6.61 - 6.60 (m, 2H), 6.43 (s, 1H), 2.54 (s, 3H), 2.42 (s, 3H),^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 183.1, 164.4, 151.7, 145.8, 127.4, 125.7, 115.7, 114.1, 113.3, 17.2, 14.8; LC-MS calcd.m/z 240, found 241 $[(M+1)]^+$.

(*E*)-5-(5-bromopyridin-3-yl)-1,1-bis(methylthio)penta-1,4-dien-3-one 2w:[28] Pale yellow solid (3.3g, 82%); M.pt.146 ^{0}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 8.82 (s, 1H), 8.67 (s, 1H), 8.41 (s, 1H), 7.45 (d, J = 16.0 Hz, 1H), 7.29 (d, J = 16.0 Hz, 1H), 6.46 (s, 1H), 2.57 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 182.8, 166.0, 151.2, 148.5, 137.0, 135.2, 133.4, 132.0, 121.1, 113.8, 17.3, 14.8; LC-MS calcd.m/z 329 found 330 $[(M+1)]^+$.

(*E*)-1,1-bis(methylthio)-5-(thiphen-2-yl)-penta-1,4-dien-3-one 2x:[28] Brown solid (2.71g, 86%); M.pt. 90 ^{0}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.89 (s, 1H), 7.59 - 7.61 (m, 1H), 7.49 (d, J = 16.0 Hz, 1H), 7.48 (s, 1H), 6.86 (d, J = 15.6 Hz, 1H), 6.42 (s, 1H), 2.55 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 164.4, 145.8, 142.5, 127.4, 125.7, 115.7, 114.1, 113.7, 113.3, 110.7, 107.3, 56.0, 17.2, 14.8; LC-MS calcd.m/z 256, found 257 $[(M+1)]^+$.

(*E*)-5-(5-bromothiophen-2-yl)-1,1-bis(methylthio)-penta-1,4-dien-3-one 2y: Brown solid (3.55g, 86%); M.pt. 99 ^{0}C; [Found: C, 39.35; H, 3.28. $C_{11}H_{11}BrOS_3$ requires C, 39.40; H, 3.31]; IR (ATR KBr cell, cm^{-1}) 1798, 1633, 1574, 1453; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.55 (d, J = 15.6 Hz, 1H), 7.28 (dd, J = 4 Hz, 21.2 Hz, 2H), 6.71 (d, J = 15.6 Hz, 1H), 6.43 (s, 1H), 2.55 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 183.7, 166.1, 133.8, 131.1, 130.9, 129.8, 129.3, 123.2, 115.9, 113.1, 17.2, 15.0; LC-MS calcd.m/z 335, found 336 $[(M+1)]^+$.

General procedure for the preparation of (*E*)-aryl-1*H*-benzo[*d*]-benzimidazole (4a-y)

To a solution of (*E*)-1,1-bis(methylthio)-5-arylpenta-1,4-dien-3-one (1mol) in water (5mL) was added 1,2-phenylenediamine (1mol) followed by glacial acetic acid (0.05mol). Finally, CuI (10 mol%) was added to the mixture. The reaction was stirred magnetically reflux at 100 ºC for the indicated time (Table 5). After completion of the reaction (monitored by TLC), the

product was extracted with ethyl acetate (15mL) and purified by column chromatography (silica gel) using ethyl acetate/petroleum ether mixture as a gradient elution to afford product (**4a-y**).

(*E*)-2-styryl-1*H*-benzo[*d*]imidazole 4a:[31] Off white solid (0.24g, 92%); M.pt.205-206 ^{0}C; R_f = 0.29 (hexane/ethylacetate 7:3); ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.58 (s, 1H), 7.54 - 7.66 (m, 4H), 7.57 - 7.43 (m, 3H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 8 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 151.2, 138.9, 135.6, 134.8, 128.5,* 126.6, 122.2, 116.9, 114.6; LC-MS calcd.m/z 220, found 221 $[(M+1)]^+$. *[Two carbon signals merged together]

(*E*)-2-(2-methoxystyryl)-1*H*-benzo[*d*]imidazole 4b:[32] Off white solid (0.22g, 83%); M.pt.186-188 ^{0}C; R_f = 0.25 (hexane/ethylacetate 7:3); [Found: C, 76.71; H, 5.60; N, 11.15. $C_{16}H_{14}N_2O$ requires C, 76.78; H, 5.64; N, 11.19]; IR (ATR KBr cell, cm^{-1}) 3042, 2384, 1645, 1570, 1402; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.58 (s, 1H), 7.87 (d, *J* = 16.8 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 1H), 7.48 (s, 2H), 7.35 (t, *J* = 8.4 Hz, 1H), 7.32 - 6.98 (m, 5H), 3.90 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 157.6, 151.8, 130.6, 129.6, 127.6, 124.7, 121.3, 118.5, 112.1, 56.1; LC-MS calcd.m/z 250, found 251 $[(M+1)]^+$.

(*E*)-2-(3-methoxystyryl)-1*H*-benzo[*d*]imidazole 4c:[32] Off white solid (0.21g, 80%); M.pt.175-177 ^{0}C; R_f = 0.23 (hexane/ethylacetate 7:3); [Found: C, 76.75; H, 5.58; N, 11.11. $C_{16}H_{14}N_2O$ requires C, 76.78; H, 5.64; N, 11.19]; IR (ATR KBr cell, cm^{-1}) 3053, 2366, 1645, 1589, 1417; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.57 (s, 1H), 7.61 (d, *J* = 16.8 Hz, 2H), 7.46 (d, *J* = 8 Hz, 1H), 7.35 (t, *J* = 8 Hz, 1H), 7.24 - 7.14 (m, 5H), 6.93 (d, *J* = 8.4 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 156.7, 151.4, 132.7, 129.6, 128.0, 127.1, 122.6, 120.0, 114.4, 113.0, 56.5; LC-MS calcd.m/z 250, found 251 $[(M+1)]^+$.

(*E*)-2-(4-methoxystyryl)-1*H*-benzo[*d*]imidazole 4d:[32] Off white solid (0.23g, 87%); M.pt.184-186 ^{0}C; R_f = 0.21 (hexane/ethylacetate 7:3); [Found: C, 76.72; H, 5.60; N, 11.15. $C_{16}H_{14}N_2O$ requires C, 76.78; H, 5.64; N, 11.19]; IR (ATR KBr cell, cm^{-1}) 3049, 2348, 1635, 1574, 1480, 1258, 743; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.57 (s, 1H), 7.88 (d, *J* = 16.8 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 1H), 7.49 (bs, 2H), 7.35 (t, *J* = 6.8 Hz, 1H), 7.20 (d, *J* = 16.8 Hz, 1H), 7.51 - 7.14 (m, 2H), 7.09 (t, *J* = 8.4 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 157.1, 151.4, 130.1, 129.2, 127.1, 124.2, 121.9, 120.8, 118.0, 111.6, 55.6; LC-MS calcd.m/z 250, found 251 $[(M+1)]^+$.

(*E*)-2-(3-chlorostyryl)-1*H*-benzo[*d*]imidazole 4e:[32,33] Off white solid (0.228g, 85%); M.pt.229-230 ^{0}C; R_f = 0.32 (hexane/ethylacetate 7:3); [Found: C, 70.67; H, 4.30; N, 10.97. $C_{15}H_{11}ClN_2$ requires C, 70.73; H, 4.35; N, 11.00]; IR (ATR KBr cell, cm^{-1}). 3049, 1665, 1427, 742; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H:, 12.60 (s, 1H), 7.74 (s, 1H), 7.64 - 7.58 (m, 3H), 7.49 - 7.38 (m, 3H), 7.29 (d, *J* = 16.4 Hz, 1H), 7.21 - 7.10 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ_C: 150.4, 138.1, 133.8, 132.6, 130.7, 128.4, 126.4, 125.7, 122.7, 119.4; LC-MS calcd. m/z 254, found 255 [(M+1)]$^+$.

(*E*)-2-(4-chlorostyryl)-1*H*-benzo[*d*]imidazole 4f:[32,33] Off white solid (0.225g, 84%); M.pt.239-241 ^{0}C; R_f = 0.40 (hexane/ethylacetate 7:3); [Found: C, 70.70; H, 4.35; N, 10.95. $C_{15}H_{11}ClN_2$ requires C, 70.73; H, 4.35; N, 11.00]; IR (ATR KBr cell, cm^{-1}) 3049, 1650, 1430, 746; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 12.60 (s, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.65 - 7.57 (m, 2H), 7.48 (d, *J* = 8.4 Hz, 3H), 7.22 (d, *J* = 16.4 Hz, 3H), 7.19 - 7.13 (m, 4H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ_C: 151.4, 136.2, 134.7, 129.4, 129.3, 127.5, 122.1, 118.2; LC-MS calcd.m/z 254, found 255 [(M+1)]$^+$.

(*E*)-2-(2-fluorostyryl)-1*H*-benzo[*d*]imidazole 4g:[32] Off white solid (0.237g, 89%); M.pt.180-182 ^{0}C; R_f = 0.32 (hexane/ethylacetate 7:3); [Found: C, 75.58; H, 4.58; N, 11.71. $C_{15}H_{11}FN_2$ requires C, 75.62; H, 4.65; N, 11.76]; IR (ATR KBr cell, cm^{-1}) 3012, 2178, 1482, 1419, 1225, 1023, 963; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 12.76 (s, 1H), 7.85 (t, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 16.4 Hz, 1H), 7.54 (s, 2H), 7.42 (q, *J* = 7.2 Hz, 1H), 7.32 - 7.26 (m, 3H), 7.19 - 7.16 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ_C: 161.7, 158.4, 150.7, 138.7, 129.5, 129.4, 127.2, 127.1, 126.7, 123.9, 123.4, 123.2, 121.9, 119.3, 115.1, 114.4; LC-MS calcd. m/z 238, found 239 [(M+1)]$^+$.

(*E*)-2-(3-fluorostyryl)-1*H*-benzo[*d*]imidazole 4h:[32] Off white solid (0.229g, 86%); M.pt.216-218 ^{0}C; R_f = 0.36 (hexane/ethylacetate 7:3); [Found: C, 75.55; H, 4.61; N, 11.70. $C_{15}H_{11}FN_2$ requires C, 75.62; H, 4.65; N, 11.76]; IR (ATR KBr cell, cm^{-1}) 3049, 1456, 1320, 1012; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 12.65 (s, 1H), 7.64 (d, *J* = 16.4 Hz, 1H), 7.54 - 7.52 (m, 3H), 7.48 - 7.45 (m, 2H), 7.28 (d, *J* =16.4 Hz, 1H), 7.18 - 7.15 (m, 3H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ_C: 163.8, 163.3, 160.5, 150.0, 138.5, 138.0, 137.7, 132.6, 129.7, 122.0, 121.7, 118.0, 114.2, 112.4, 112.1; LC-MS calcd.m/z 238, found 239 [(M+1)]$^+$.

(*E*)-2-(4-fluorostyryl)-1*H*-benzo[*d*]imidazole 4i: Off white solid (0.23g, 87%); M.pt. 116-118 ^{0}C; R_f = 0.28 (hexane/ethylacetate 7:3); [Found: C, 75.58; H, 4.60; N, 11.72. $C_{15}H_{11}FN_2$

requires C, 75.62; H, 4.65; N, 11.76]; IR (ATR KBr cell, cm^{-1}) 3023, 1575, 1480; ^1H NMR (400 MHz, DMSO-d_6) δ_H: 12.66 (s, 1H), 7.74 - 7.70 (m, 2H), 7.65 (d, *J* = 16.4 Hz, 1H), 7.55 - 7.51 (m, 2H), 7.27 (d, *J* = 8.8 Hz, 2H), 7.19 - 7.15 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 164.0, 161.6, 151.3, 133.5, 132.9, 132.8, 129.6, 129.5, 122.5, 118.1, 116.5, 116.2; LC-MS calcd.m/z 238, found 239 $[(M+1)]^+$.

(*E*)-2-(2-bromostyryl)-1*H*-benzo[*d*]imidazole 4j:[32] Off white solid (0.23g, 85%); M.pt.190-192 ^0C; R_f = 0.30 (hexane/ethylacetate 7:3); [Found: C, 60.19; H, 3.66; N, 9.29. $C_{15}H_{11}BrN_2$ requires C, 60.22; H, 3.71; N, 9.36]; IR (ATR KBr cell, cm^{-1}) 3045, 2456, 1785, 1520; ^1H NMR (400 MHz, DMSO-d_6) δ_H: 12.74 (s, 1H), 7.92 - 7.87 (m, 2H), 7.70 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.49 (q, *J* = 8 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.23 - 7.15 (m, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 150.3, 135.3, 133.0, 131.8, 130.2, 129.4, 128.2, 127.3, 123.5, 122.1, 120.7; LC-MS calcd.m/z 299, found 300 $[(M+1)]^+$.

(*E*)-2-(4-bromostyryl)-1*H*-benzo[*d*]imidazole 4k:[32] Off white solid (0.226g, 83%); M.pt.250-252 ^0C; R_f = 0.25 (hexane/ethylacetate 7:3); [Found: C, 60.15; H, 3.67; N, 9.30. $C_{15}H_{11}BrN_2$ requires C, 60.22; H, 3.71; N, 9.36]; IR (ATR KBr cell, cm^{-1}) 3057, 2364, 1645, 1485, 1427, 968, 738; ^1H NMR (400 MHz, DMSO-d_6) δ_H: 12.60 (s, 1H), 7.63 - 7.57 (m, 6H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 16.8 Hz, 1H), 7.19 - 7.13 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 149.5, 133.8, 131.8, 130.5, 127.3, 120.8, 117.1; LC-MS calcd.m/z 299, found 300 $[(M+1)]^+$.

(*E*)-4-(2-(1*H*-benzo[*d*]imidazol-2-yl)vinyl)benzonitile 4l:[9b,c] Off white solid (0.235g, 88%); M.pt.240-241 ^0C; R_f = 0.13 (hexane/ethylacetate 7:3); [Found: C, 78.29; H, 4.49; N, 17.08. $C_{16}H_{11}N_3$ requires C, 78.35; H, 4.52; N, 17.13]; IR (ATR KBr cell, cm^{-1}) 3525, 3055, 2364, 2224, 1599, 1417, 817, 732; ^1H NMR (400 MHz, DMSO-d_6) δ_H: 12.70 (s, 1H), 7.86 (s, 4H), 7.69 (d, *J* = 18 Hz, 1H), 7.58 - 7.52 (m, 2H), 7.39 (d, *J* = 16.4 Hz, 1H), 7.19 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 151.6, 139.1, 129.1, 128.0, 127.6, 126.8, 126.1, 125.7, 122.5, 117.9, 73.9; LC-MS calcd.m/z 245, found 246 $[(M+1)]^+$.

(*E*)-2-(4-nitrostyryl)-1*H*-benzo[*d*]imidazole 4m:[20b] Pale yellow solid (0.239g, 89%); M.pt.257-258 ^0C; R_f = 0.18 (hexane/ethylacetate 7:3); [Found: C, 67.90; H, 4.14; N, 15.80. $C_{15}H_{11}N_3O_2$ requires C, 67.92; H, 4.18; N, 15.84]; IR (ATR KBr cell, cm^{-1}) 2366, 1591, 1506, 1336, 759; ^1H NMR (400 MHz, DMSO-d_6): δ_H: 12.70 (s, 1H), 8.26 (d, *J* = 8.8 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 16.4 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 7.6

Hz, 1H), 7.45 (d, *J* = 16.8 Hz, 1H), 7.24 - 7.16 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 150.5, 147.3, 142.9, 132.2, 129.4, 128.4, 124.6, 124.4, 122.6; LC-MS calcd.m/z 265, found 266 $[(M+1)]^+$.

(*E*)-2-(2,4-difluorostyryl)-1*H*-benzo[*d*]imidazole 4n: Off white solid (0.244g, 91%); M.pt.218-221 ^{0}C; R_f = 0.30 (hexane/ethylacetate 7:3); [Found: C, 70.28; H, 3.90; N, 10.87. $C_{15}H_{10}F_2N_2$ requires C, 70.31; H, 3.93; N, 10.93]; IR (ATR KBr cell, cm^{-1}) 3310, 1581, 1480; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.67 (s, 1H), 7.94 (q, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 16.8 Hz, 1H), 7.58 - 7.48 (m, 2H), 7.35 (t, *J* = 9.6 Hz, 1H), 7.26 (d, *J* = 16.4 Hz, 1H), 7.17 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 164.3, 162.3, 162.2, 161.0, 159.0, 158.8, 151.0, 129.9, 129.8, 129.7, 125.6, 122.7, 120.7, 120.5, 112.9, 112.7, 105.3, 104.6; LC-MS calcd.m/z 256, found 257 $[(M+1)]^+$.

(*E*)-2-(2,4-dichlorostyryl)-1*H*-benzo[*d*]imidazole 4o:[32] Off white solid (0.245g, 90%); M.pt.240-241 ^{0}C; R_f = 0.37 (hexane/ethylacetate 7:3); [Found: C, 62.28; H, 3.44; N, 9.65. $C_{15}H_{10}Cl_2N_2$ requires C, 62.30; H, 3.49; N, 9.69]; IR (ATR KBr cell, cm^{-1}) 3055, 1641, 1581, 1427, 958, 742; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.77 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 16.4 Hz, 1H), 7.69 (s, 1H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 16 Hz, 1H), 7.23 - 7.15 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 150.7, 134.1, 133.9, 133.2, 129.8, 128.9, 128.5, 128.4, 122.3, 121.9; LC-MS calcd.m/z 289, found 290 $[(M+1)]^+$.

(*E*)-2-(5-bromo-2-methoxystyryl)-1*H*-benzo[*d*]imidazole 4p: Off white solid (0.23g, 84%); M.pt.235-237 ^{0}C; R_f = 0.26 (hexane/ethylacetate 7:3); [Found: C, 58.32; H, 3.94; N, 8.49. $C_{16}H_{13}BrN_2O$ requires C, 58.38; H, 3.98; N, 8.51]; IR (ATR KBr cell, cm^{-1}) 2958, 2360, 1741, 1483, 1259, 1024, 802, 742; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.60 (s, 1H), 7.85 - 7.84 (m, 1H), 7.80 (d, *J* = 16.0 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.50 - 7.45 (m, 2H), 7.27 (d, *J* = 16.6 Hz, 1H), 7.17 - 7.14 (m, 2H), 7.06 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 159.7, 137.2, 134.2, 130.0, 122.1, 119.6, 118.1, 114.7, 111.8, 56.1; LC-MS calcd.m/z 329, found 330 $[(M+1)]^+$.

(*E*)-2-(3-bromo-4-fluorostyryl)-1*H*-benzo[*d*]imidazole 4q: Off white solid (0.225g, 82%); M.pt.170-171 ^{0}C; R_f = 0.29 (hexane/ethylacetate 7:3); [Found: C, 56.77; H, 3.12; N, 8.80. $C_{15}H_{10}BrFN_2$ requires C, 56.81; H, 3.18; N, 8.83]; IR (ATR KBr cell, cm^{-1}) 3566, 2926, 2362, 1743, 1491, 1437, 1257, 810, 732; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.57 (s, 1H), 8.05 -

8.02 (m, 1H), 7.73 - 7.70 (m, 1H), 7.62 - 7.58 (m, 2H), 7.48 - 7.40 (m, 2H), 7.24 (d, *J* = 16.4 Hz, 1H), 7.21 - 7.13 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ_C: 151.1, 144.4, 135.5, 134.9, 133.4, 132.3, 129.4, 123.1, 122.3, 122.1, 119.2, 119.1, 111.6; LC-MS calcd.m/z 317, found 318 $[(M+1)]^+$.

(*E*)-2-(2-(naphthalen-1-yl)vinyl)-1*H*-benzo[*d*]imidazole 4s:[32] Off white solid (0.216g, 80%); M.pt.108-110 ^{0}C; R_f = 0.38 (hexane/ethylacetate 7:3); [Found: C, 84.38; H, 5.15; N, 10.31. $C_{19}H_{14}N_2$ requires C, 84.42; H, 5.22; N, 10.36]; IR (ATR KBr cell, cm^{-1}) 3330, 3140, 1581, 1340; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 12.78 (s, 1H), 8.49 (d, *J* = 16.4 Hz, 1H), 8.41 (d, *J* = 8.4 Hz, 1H), 8.08 - 7.95 (m, 3H), 7.68 - 7.57 (m, 5H), 7.30 (d, *J* = 16 Hz, 1H), 7.20 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d$_6$) δ_C: 151.3, 133.4, 133.0, 131.4, 131.0, 128.7, 128.3, 126.0, 125.7, 125.3, 123.4, 122.2, 119.6, 114.7; LC-MS calcd.m/z 270, found 271 $[(M+1)]^+$.

(*E*)-2-(2-(anthracen-9-yl)vinyl)-1*H*-benzo[*d*]imidazole 4t: Yellow solid (0.216g, 79%); M.pt.210-212 ^{0}C; R_f = 0.50 (hexane/ethylacetate 7:3); [Found: C, 86.18; H, 5.00; N, 8.70. $C_{23}H_{16}N_2$ requires C, 86.22; H, 5.03; N, 8.74]; IR (ATR KBr cell, cm^{-1}) 3470, 3168, 3041, 2348, 1478; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 12.96 (s, 1H), 8.64 (s, 1H), 8.58 (d, *J* = 16.4 Hz, 1H), 8.41 (d, *J* = 8 Hz, 2H), 8.17 (d, *J* = 7.2 Hz, 2H), 7.63 - 7.57 (m, 6H), 7.25 - 7.23 (m, 2H), 7.03 (d, *J* = 16.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ_C: 151.0, 131.5, 131.0, 130.9, 129.4, 129.3, 127.7, 126.9, 126.8, 126.0, 125.7, 122.8; LC-MS calcd.m/z 320, found 321 $[(M+1)]^+$.

(*E*)-2-(2-(pyren-1-yl)vinyl)-1*H*-benzo[*d*]imidazole 4u: Brown solid (0.22g, 81%); M.pt.186-188 ^{0}C; R_f = 0.21 (hexane/ethylacetate 7:3); [Found: C, 87.12; H, 4.64; N, 8.10. $C_{25}H_{16}N_2$ requires C, 87.18; H, 4.68; N, 8.13]; IR (ATR KBr cell, cm^{-1}) 3043, 2924, 2364, 1741, 1629, 1433, 837, 738; ^{1}H NMR (400 MHz, DMSO-d$_6$) δ_H: 12.63 (s, 1H), 8.83 (d, *J* = 16.4 Hz, 1H), 8.75 (d, *J* = 9.2 Hz, 1H), 8.61 (d, *J* = 8 Hz, 1H), 8.34 - 8.33 (m, 4H), 8.22 (s, 2H), 8.12 (t, *J* = 7.6 Hz, 1H), 7.63 (q, *J* = 3.2 Hz, 2H), 7.56 (d, *J* = 16.4 Hz, 1H), 7.24 (q, *J* = 3.2 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ_C: 151.8, 131.6, 131.5, 130.9, 130.8, 130.1, 128.8, 128.6, 128.3, 127.9, 127.0, 126.3, 126.0, 124.7, 124.5, 123.2, 122.8, 120.4; LC-MS calcd.m/z 344, found 345 $[(M+1)]^+$.

(*E*)-2-(2-(furan-2-yl)vinyl)-1*H*-benzo[*d*]imidazole 4v: Off white solid (0.23g, 89%); M.pt.236-238 ^{0}C; R_f = 0.20 (hexane/ethylacetate 7:3); [Found: C, 74.22; H, 4.72; N, 13.30.

$C_{13}H_{10}N_2O$ requires C, 74.27; H, 4.79; N, 13.33]; IR (ATR KBr cell, cm^{-1}), 3320, 1571, 1480; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.54 (s, 1H), 7.78 (s, 1H), 7.48 (d, *J* = 16 Hz, 3H), 7.16 - 7.14 (m, 2H), 6.91 (d, *J* = 16 Hz, 1H), 6.76 (s, 1H), 6.60 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_H: 152.0, 151.0, 144.7, 122.5, 122.3, 115.5, 112.9, 112.3; LC-MS calcd.m/z 210, found 211 $[(M+1)]^+$.

(*E*)-2-(2-(5-bromopyridin-3-yl)vinyl)-1*H*-benzo[*d*]imidazole 4w: Off white solid (0.224g, 82%); M.pt.268-270 ^{0}C; R_f = 0.09 (hexane/ethylacetate 7:3); [Found: C, 56.00; H, 3.31; N, 13.96. $C_{14}H_{10}BrN_3$: C, 56.02; H, 3.36; N, 14.00]; IR (ATR KBr cell, cm^{-1}) 3055, 2364, 1637, 1550, 1429, 1020, 736; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.67 (s, 1H), 8.80 (s, 1H), 8.64 (s, 1H), 8.45 (s, 1H), 7.64 - 7.60 (m, 2H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 16.4 Hz, 1H), 7.23 - 7.15 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 150.6, 150.2, 147.7, 136.0, 134.2, 129.6, 121.9, 121.2; LC-MS calcd.m/z 300, found 301 $[(M+1)]^+$.

(*E*)-2-(2-(thiophen-2-yl)vinyl)-1*H*-benzo[*d*]imidazole 4x: Off white solid (0.22g, 84%); M.pt.225-226 ^{0}C; R_f = 0.24 (hexane/ethylacetate 7:3); [Found: C, 68.98; H, 4.40; N, 12.35. $C_{13}H_{10}N_2S$: C, 69.00; H, 4.45; N, 12.38]; IR (ATR KBr cell, cm^{-1}) 3310, 3025,1545; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.52 (s, 1H), 7.76 (s, 1H), 7.64 (d, *J* = 16.4 Hz, 2H), 7.53 (s, 2H), 7.50 - 7.37 (m, 2H), 7.18 - 7.09 (m, 2H), 7.03 (d, *J* = 16.4 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 150.7, 140.9, 133.3, 132.8, 128.2, 122.9, 121.7, 119.3, 111.1; UPLC-MS calcd.m/z 226, found 227 $[(M+1)]^+$.

(*E*)-2-(2-(5-bromothiophen-2-yl)vinyl)-1*H*-benzo[*d*]imidazole 4y: Off white solid (0.23g, 86%); M.pt.190-192 ^{0}C; R_f = 0.31 (hexane/ethylacetate 7:3); [Found: C, 51.12; H, 2.92; N, 9.15. $C_{13}H_9BrN_2S$ requires C, 51.16; H, 2.97; N, 9.18]; IR (ATR KBr cell, cm^{-1}) 3057, 2922, 2365, 1645, 1427, 968, 738; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.54 (s, 1H), 7.72 (d, *J* = 16 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 6.8 Hz, 1H), 7.25 (dd, *J* = 3.6 Hz, 8.8 Hz 2H), 7.16 (s, 2H), 6.85 (d, *J* = 16 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 150.0, 142.4, 138.6, 130.2, 127.7, 126.3, 121.8, 116.3, 114.3, 112.2; LC-MS calcd.m/z 305, found 306 $[(M+1)]^+$.

General procedure for the preparation of 2-(2-(methylthio)-2-arylethyl)-1*H*-benzo[*d*]imidazole (5a-y)

To a solution of 1,1-bis(methylthio)-5-arylpenta-1,4-dien-3-one (1mol), glacial acetic acid (3mL), was added 1,2-phenylenediamine (1mol) in one portion at room temperature . The reaction mixture was stirred magnetically reflux at 110 ºC for 15h. The reaction mixture was subsequently quenched with saturated aqueous $NaHCO_3$ (20ml). The extracts were combined washed with water, brine and then dried over anhydrous Na_2SO_4. The solvent was removed under vacuum to afford the crude product which was then subjected to column chromatography (silica gel) using ethyl acetate/Petroleum ether mixture as a gradient eluent to furnish pure product (**5a-y**).

2-(2-(methylthio)-2-phenylethyl)-1*H*-benzo[*d*]imidazole 5a: Off white solid, (0.24g, 75%); M.pt.155-157 ^{0}C; R_f = 0.25 (hexane/ethylacetate 7:3); [Found: C, 71.59; H, 5.98; N, 10.41. $C_{16}H_{16}N_2S$ requires C, 71.61.37; H, 6.01; N, 10.44]; IR (ATR KBr cell, cm^{-1}) 3400, 2225, 1599, 1450, 670; ^{1}H NMR (300 MHz, $CDCl_3$) δ_H: 7.52 (s, 1H), 7.34 - 7.26 (m, 5H), 7.24 - 7.21 (m, 2H), 4.24 (t, *J* = 7.5 Hz, 1H), 3.48 (d, *J* = 8.4 Hz, 2H), 1.95 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 152.2, 141.0, 128.7, 127.5, 127.4, 122.3, 50.1, 36.2, 14.5; LC-MS calcd.m/z 268, found 269 $[(M+1)]^+$.

2-(2-(2-methoxyphenyl)-2-(methylthio)ethyl)-1*H*-benzo[*d*]imidazole 5b: Off white solid (0.22g, 72%); M.pt.154-156 ^{0}C; R_f = 0.20 (hexane/ethylacetate 7:3); [Found: C, 68.40; H, 6.05; N, 9.37. $C_{17}H_{18}N_2OS$ requires C, 68.42; H, 6.08; N, 9.39]; IR (ATR KBr cell, cm^{-1}) 3020, 2360, 1598, 1502, 1400, 1198, 728; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.28 (s, 1H), 7.46 (s, 2H), 7.40 (dd, *J* = 1.6 Hz, 7.6 Hz, 1H), 7.25 - 7.18 (m, 1H), 7.13 - 7.08 (m, 2H), 6.99 - 6.93 (m, 2H), 4.85 (t, *J* = 7.6 Hz, 1H), 3.79 (s, 3H), 3.46 - 3.34 (m, 2H), 1.87 (s, 3H); ^{13}C NMR (100MHz, DMSO-d_6) δ_C: 157.5, 156.9, 153.1, 151.8, 130.6, 129.6, 129.5, 128.6, 127.6, 124.7, 121.6, 121.3, 120.8, 112.1, 111.7, 56.1, 41.9, 34.3, 13.7; LC-MS calcd.m/z 298, found 299 $[(M+1)]^+$.

2-(2-(3-methoxyphenyl)-2-(methylthio)ethyl)-1*H*-benzo[*d*]imidazole 5c: Off white solid; (0.217g, 68%); M.pt.160-162 ^{0}C; R_f = 0.18 (hexane/ethylacetate 7:3); [Found: C, 68.37; H, 6.04; N, 9.35. $C_{17}H_{18}N_2OS$ requires C, 68.42; H, 6.08; N, 9.39]; IR (ATR KBr cell, cm^{-1}) 3053, 2366, 1645, 1589, 1417, 1269, 740; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H; 12.24 (s, 1H), 7.44 (s, 2H), 7.22 - 7.02 (m, 1H), 7.10 - 7.07 (m, 2H), 6.94 - 6.91 (m, 2H), 6.78 - 6.76 (m, 1H), 4.43 (t, *J* = 8 Hz, 1H), 3.69 (s, 3H), 3.38 - 3.33 (m, 2H), 1.88 (s, 3H); ^{13}C NMR (100

MHz, DMSO-d_6) δ_C: 159.6, 152.7, 143.4, 129.8, 121.7, 120.3, 113.8, 112.8, 55.4, 49.1, 35.7, 14.2; LC-MS calcd.m/z 298, found 299 $[(M+1)]^+$.

2-(2-(3-chlorophenyl)-2-(methylthio)ethyl)-1*H*-benzo[*d*]imidazole 5e: Off white solid (0.22g, 69%); M.pt.164-166 ^{0}C; R_f = 0.28 (hexane/ethylacetate 7:3); [Found: C, 63.44; H, 4.93; N, 9.20. $C_{16}H_{15}ClN_2S$ requires C, 63.46; H, 4.99; N, 9.25]; IR (ATR KBr cell, cm^{-1}) 3053. 2350, 1589, 1487, 1200, 742; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.24 (s, 1H), 7.46 - 7.43 (m, 3H), 7.33 - 7.31 (m, 2H), 7.28 - 7.25 (m, 1H), 7.10 - 7.08 (m, 2H), 4.48 (t, *J* = 8.0 Hz, 1H), 3.40 (d, *J* = 7.2 Hz, 2H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 152.4, 144.4, 133.4, 130.6, 127.9, 127.6, 126.9, 121.8, 115.1, 48.4, 35.0, 14.9; LC-MS calcd.m/z 302, found 303 $[(M+1)]^+$.

2-(2-(4-chlorophenyl)-2-(methylthio)ethyl)-1*H*-benzo[*d*]imidazole 5f: Off white solid (0.226g, 71%); M.pt.158-160 ^{0}C; R_f = 0.26 (hexane/ethylacetate 7:3);. [Found: C, 63.39; H, 4.93; N, 9.19. $C_{16}H_{15}ClN_2S$ requires C, 63.46; H, 4.99; N, 9.25]; IR (ATR KBr cell, cm^{-1}) 3044, 2300, 1460, 1298, 728; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.22 (s, 1H), 7.43 - 7.33 (m, 6H), 7.10 - 7.07 (m, 2H), 4.47 (t, *J* = 8.0 Hz, 1H), 3.43 - 3.32 (m, 2H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 152.5, 140.8, 132.0, 130.0, 128.8, 122.0, 118.7, 111.3, 48.3, 35.2, 14.1; LC-MS calcd.m/z 302, found 303 $[(M+1)]^+$.

2-(2-(2-fluorophenyl)-2-(methylthio)ethyl)-1*H*-benzo[*d*]imidazole 5g: Off white solid (0.236g, 74%); M.pt.126-128 ^{0}C; R_f = 0.25 (hexane/ethylacetate 7:3); [Found: C, 67.08; H, 5.24; N, 9.73. $C_{16}H_{15}FN_2S$ requires C, 67.11; H, 5.28; N, 9.78]; IR (ATR KBr cell, cm^{-1}) 3042, 1700, 1425, 724; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.30 (s, 1H), 7.54 - 7.50 (m, 2H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.32 - 7.25 (m, 1H), 7.20 - 7.07 (m, 4H), 4.75 (t, *J* = 8 Hz, 1H), 3.52 - 3.42 (m, 2H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 161.5, 159.1, 152.5, 143.7, 134.6, 129.5, 129.4, 129.3, 128.6, 128.5, 124.9, 122.0, 121.4, 118.7, 116.0, 115.8, 111.3, 41.9, 34.0, 13.9; LC-MS calcd.m/z 286, found 287 $[(M+1)]^+$.

2-(2-(3-fluorophenyl)-2-(methylthio)ethyl)-1*H*-benzo[*d*]imidazole 5h: Off white solid (0.230g, 72%); M.pt.142-144 ^{0}C; R_f = 0.21 (hexane/ethylacetate 7:3); [Found: C, 67.06; H, 5.26; N, 9.72. $C_{16}H_{15}FN_2S$ requires C, 67.11; H, 5.28; N, 9.78]; IR (ATR KBr cell, cm^{-1}) 3315, 2364, 1417, 1155, 740; ^{1}H NMR (400 MHz, DMSO-d_6): δ_H: 12.22 (s, 1H), 7.47 (s, 2H), 7.34 (q, *J* = 8 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.10 - 7.08 (m, 2H), 7.04 (td, *J* = 2 Hz, 8.4 Hz, 1H), 4.49 (t, *J* = 8 Hz, 1H), 3.43 - 3.37 (m, 2H), 1.89 (s, 3H); ^{13}C NMR (100 MHz,

DMSO-d_6) δ_C: 163.7, 161.3, 152.5, 144.9, 144.8, 143.7, 134.5, 130.6, 124.3, 122.0, 121.4, 118.7, 114.8, 114.5, 111.4, 48.5, 35.1, 14.1; LC-MS calcd.m/z 286, found 287 $[(M+1)]^+$.

2-(2-(4-fluorophenyl)-2-(methylthio)ethyl)-1*H*-benzo[*d*]imidazole 5i: Off white solid (0.224g, 70%); M.pt.136-138 ^{0}C; R_f = 0.22 (hexane/ethylacetate 7:3); [Found: C, 67.07; H, 5.26; N, 9.75. $C_{16}H_{15}FN_2S$ requires C, 67.11; H, 5.28; N, 9.78]; IR (ATR KBr cell, cm^{-1}) 305, 2364, 1741, 1425, 1020, 732; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.23 (s, 1H), 7.44 - 7.37 (m, 4H), 7.14 - 7.06 (m, 4H), 4.46 (t, *J* = 8 Hz, 1H), 3.37 (d, *J* = 7.6 Hz, 2H), 1.87 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 162.7, 160.3, 152.6, 138.0, 137.9, 130.0, 129.9, 121.7, 115.6, 115.4, 48.3, 35.4, 14.1; LC-MS calcd.m/z 286, found 287 $[(M+1)]^+$.

2-(2-(2-bromophenyl)-2-(methylthio)ethyl)-1*H*-benzo[*d*]imidazole 5j: Off white solid (0.208g, 66%); M.pt.126-128 ^{0}C; R_f = 0.25 (hexane/ethylacetate 7:3); [Found: C, 55.30; H, 4.28; N, 8.01. $C_{16}H_{15}BrN_2S$ requires C, 55.34; H, 4.35; N, 8.07]; IR (ATR KBr cell, cm^{-1}) 2854, 2332, 1450, 798; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.26 (s, 1H), 7.59 (t, *J* = 7.2 Hz, 2H), 7.47 - 7.38 (m, 3H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.09 - 7.08 (m, 2H), 4.87 (t, *J* = 8 Hz, 1H), 3.44 (d, *J* = 8 Hz, 2H), 1.91 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 149.9, 146.0, 138.0, 130.8, 126.9, 126.7, 125.9, 122.2, 119.4, 45.5, 32.3, 11.4; LC-MS calcd.m/z 346, found 347 $[(M+1)]^+$.

2-(2-(4-bromophenyl)-2-(methylthio)ethyl)-1*H*-benzo[*d*]imidazole 5k: Off white solid (0.218g, 69%); M.pt.138-140 ^{0}C; R_f = 0.20 (hexane/ethylacetate 7:3); [Found: C, 55.28; H, 4.31; N, 8.01. $C_{16}H_{15}BrN_2S$ requires C, 55.34; H, 4.35; N, 8.07]; IR (ATR KBr cell, cm^{-1}) 2924, 2362, 1741, 1425, 1155, 740; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.33 (s, 1H), 7.48 (d, *J* = 6.8 Hz, 2H), 7.46 - 7.43 (m, 2H), 7.32 (d, *J* = 6.4 Hz, 2H), 7.11 - 7.08 (m, 2H), 4.45 (t, *J* = 8 Hz, 1H), 3.43 - 3.42 (m, 2H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 152.4, 141.2, 138.7, 132.3, 131.7, 130.3, 129.4, 122.6, 121.8, 120.5, 115.3, 48.3, 35.0, 14.1; LC-MS calcd.m/z 347, found 348 $[(M+1)]^+$.

4-(2-(1*H*-benzo[*d*]imidazol-2-yl)-1-(methylthio)ethyl)benzonitrile 5l: Off white solid (0.210g, 66%); M.pt.170-172 ^{0}C; R_f = 0.06 (hexane/ethylacetate 7:3); [Found: C, 69.52; H, 5.10; N, 14.26. $C_{17}H_{15}N_3S$ requires C, 69.59; H, 5.15; N, 14.32]; IR (ATR KBr cell, cm^{-1}) 3425, 2364, 1427, 744, 557; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.23 (s, 1H), 7.77 (d, *J* = 8 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.43 (s, 2H), 7.10 - 7.07 (m, 2H), 4.56 (t, *J* = 8 Hz, 1H), 3.42 (d, *J* = 7.6 Hz, 2H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 152.2, 147.6,

132.8, 129.2, 121.7, 119.2, 110.3, 48.5, 34.6, 14.0; LC-MS calcd.m/z 293, found 294 $[(M+1)]^+$.

2-(2-(2,4-difluorophenyl)-2-(methylthio)ethyl)-1*H*-benzo[*d*]imidazole 5n: Off white solid (0.226g, 71%); M.pt.210-212 ^{0}C. R_f = 0.24 (hexane/ethylacetate 7:3); [Found: C, 63.08; H, 4.59; N, 9.15. $C_{16}H_{14}F_2N_2S$ requires C, 63.14; H, 4.64; N, 9.20]; IR (ATR KBr cell, cm^{-1}) 2686, 1496, 964, 742; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.24 (s, 1H), 7.56 (t, *J* = 8.4 Hz, 1H), 7.43 (s, 2H), 7.17 (t, *J* = 9.2 Hz, 1H), 7.13 - 7.03 (m, 3H), 4.69 (t, *J* = 7.6 Hz, 1H), 3.45 (t, *J* = 7.6 Hz, 2H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 164.0, 161.8, 161.5, 159.4, 151.0, 144.0, 135.0, 129.7, 125.5, 123.0, 122.2, 120.8, 119.2, 113.0, 112.7, 111.6, 105.2, 105.0, 104.7, 47.2, 35.0, 14.0; LC-MS calcd.m/z 304 found 305 $[(M+1)]^+$.

2-(2-(2,4-dichlorophenyl)-2-(methylthio)ethyl)-1*H*-benzo[*d*]imidazole 5o: Off white solid (0.214g, 68%); M.pt.198-200 ^{0}C; R_f = 0.23 (hexane/ethylacetate 7:3); Found: C, 56.95; H, 4.14; N, 8.26. $C_{16}H_{14}Cl_2N_2S$ requires C, 56.98; H, 4.18; N, 8.31]; IR (ATR KBr cell, cm^{-1}) 2800, 1580, 1453; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.29 (s, 1H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.57 - 7.56 (m, 1H), 7.48 - 7.43 (m, 3H), 7.12 - 7.07 (m, 2H), 4.86 (t, *J* = 8 Hz, 1H), 3.45 (dd, *J* = 3.2 Hz, 8 Hz, 2H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 152.4, 152.2, 137.9, 134.2, 132.7, 132.0, 130.4, 129.5, 129.3, 128.9, 128.0, 121.7, 44.4, 33.9, 13.5; LC-MS calcd.m/z 337, found 338 $[(M+1)]^+$.

2-(2-(5-bromo-2-methoxyphenyl)-2-(methylthio)ethyl)-1*H*-benzo[*d*]imidazole 5p: Off white solid (0.207g, 66%); M.pt.168-170 ^{0}C; R_f = 0.22 (hexane/ethylacetate 7:3); [Found: C, 54.07; H, 4.48; N, 7.39. $C_{17}H_{17}BrN_2OS$ requires C, 54.12; H, 4.54; N, 7.42]; IR (ATR KBr cell, cm^{-1}) 2836. 2348, 1584, 1489, 1407, 1244; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.24 (s, 1H), 7.51 (d, *J* = 2.8 Hz, 1H), 7.45 (s, 2H), 7.37 (dd, *J* = 2.4 Hz, 8.6 Hz, 2H), 7.10 - 7.07 (m, 2H), 6.94 (d, *J* = 8.8 Hz, 1H), 4.78 (t, *J* = 7.6 Hz, 1H), 3.78 (s, 3H), 3.43 (d, *J* = 8.4 Hz, 2H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 156.3, 152.7, 132.3, 131.2, 130.3, 121.6, 118.7, 114.1, 112.4, 56.4, 41.8, 34.1, 13.9; LC-MS calcd.m/z 377, found 378 $[(M+1)]^+$.

2-(2-(3-bromo-4-fluorophenyl)-2-(methylthio)ethyl)-1*H*-benzo[*d*]imidazole 5q: Off white solid (0.230g, 73%); M.pt.174-176 ^{0}C; R_f = 0.26 (hexane/ethylacetate 7:3); Found: C, 52.56; H, 3.82; N, 7.62. $C_{16}H_{14}BrFN_2S$ requires C, 52.61; H, 3.86; N, 7.67]; IR (ATR KBr cell, cm^{-1}) 3055. 1739, 1491, 1429, 2364, 742; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.23 (s, 1H), 7.72 (dd, *J* = 2.4 Hz, 6.8 Hz, 1H), 7.49 - 7.40 (m, 3H), 7.32 (t, *J* = 8.8 Hz, 1H), 7.10 (d, *J* = 4.2 Hz,

2H), 4.49 (t, *J* = 8.8 Hz, 1H), 3.39 (d, *J* = 7.2 Hz, 2H), 1.90 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 158.7, 155.5, 151.7, 139.5, 132.5, 131.6, 128.9, 121.1, 116.5, 116.2, 114.4, 107.9, 107.6, 47.3, 34.6, 13.7; LC-MS calcd.m/z 365, found 366 $[(M+1)]^+$.

2-(2-(2-chloro-5-nitrophenyl)-2-(methylthio)ethyl)-1*H*-benzo[*d*]imidazole 5r: Off white solid (0.230g, 73%); M.pt.168-170 ^{0}C; R_f = 0.13 (hexane/ethylacetate 7:3); Found: C, 55.19; H, 4.01; N, 12.03. $C_{16}H_{14}ClN_3O_2S$ requires C, 55.25; H, 4.06; N, 12.08]; IR (ATR KBr cell, cm^{-1}) 2314, 1694, 1644, 1502; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.27 (s, 1H), 8.39 (d, *J* = 2.4 Hz, 1H), 8.10 (dd, *J* = 2.4 Hz, 8.4 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 2H), 7.45 (s, 1H), 7.09 - 7.10 (m, 2H), 4.96 (t, *J* = 7.6 Hz, 1H), 3.52 (d, *J* = 7.6 Hz, 2H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 151.9, 147.1, 141.0, 140.2, 131.4, 124.0, 123.7, 44.9, 33.9, 13.7; LC-MS calcd.m/z 347 found 348 $[(M+1)]^+$.

2-(2-(methylthio)-2-(naphthalen-1-yl)ethyl)-1*H*-benzo[*d*]imidazole 5s: Off white solid (0.219g, 69%); M.pt.182-184 ^{0}C; R_f = 0.25 (hexane/ethylacetate 7:3); [Found: C, 75.39; H, 5.66; N, 8.78. $C_{20}H_{18}N_2S$ requires C, 75.44; H, 5.70; N, 8.80]; IR (ATR KBr cell, cm^{-1}) 3398, 2364, 1427, 1271, 742; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.36 (s, 1H), 8.32 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 6.4 Hz, 1H), 7.59 (t, *J* = 8 Hz, 1H), 7.52 - 7.42 (m, 2H), 7.08 - 7.06 (m, 4H), 5.33 (s, 1H), 3.62 (d, *J* = 7.6 Hz, 2H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 152.5, 136.0, 133.5, 130.6, 128.8, 127.7, 126.1, 125.6, 125.2, 123.4, 121.3, 47.3, 34.1, 13.2; LC-MS calcd.m/z 318, found 319 $[(M+1)]^+$.

2-(2-(furan-2-yl)-2-(methylthio)ethyl)-1*H*-benzo[*d*]imidazole 5v: Off white solid (0.225g, 70%); M.pt.132-134 ^{0}C; R_f = 0.24 (hexane/ethylacetate 7:3); [Found: C, 65.05; H, 5.40; N, 10.78. $C_{14}H_{14}N_2OS$ requires C, 65.09; H, 5.46; N, 10.84]; IR (ATR KBr cell, cm^{-1}) 2336, 1525, 1428, 969; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.34 (s, 1H), 7.48 - 7.60 (m, 4H), 7.19 - 7.09 (m, 3H), 6.37 - 6.34 (m, 2H), 4.57 (t, *J* = 8 Hz, 1H), 3.50 - 3.34 (m, 2H), 1.96 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 153.6, 152.4, 152.0, 151.0, 144.8, 142.9, 122.3, 121.8, 115.6, 112.4, 110.8, 107.6, 41.7, 33.0, 13.3; LC-MS calcd.m/z 258, found 259 $[(M+1)]^+$.

2-(2-(5-bromopyridin-3-yl)-2-(methylthio)ethyl)-1*H*-benzo[*d*]imidazole 5w: Off white solid (0.227g, 72%); M.pt.148-150 ^{0}C; R_f = 0.05 (hexane/ethylacetate 7:3); [Found: C, 51.69; H, 3.99; N, 12.02. $C_{15}H_{14}BrN_3S$ requires C, 51.73; H, 4.05; N, 12.07]; IR (ATR KBr cell, cm^{-1}) 2456, 1478, 1220; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.25 (s, 1H), 8.56 - 8.54 (m, 2H),

8.12 - 8.11 (m, 1H), 7.46 (s, 2H), 7.12 - 7.10 (m, 2H), 4.54 (d, *J* = 8 Hz, 1H), 3.48 (d, *J* = 7.6 Hz, 2H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 152.1, 149.5, 148.1, 139.9, 138.0, 121.8, 120.6, 118.7, 111.6, 45.7, 34.3, 14.0; LC-MS calcd. m/z 348, found 349 $[(M+1)]^+$.

2-(2-(methylthio)-2-(thiophen-2-yl)ethyl)-1*H*-benzo[*d*]imidazole 5x: Off white solid (0.218g, 68%); M.pt.160 ^{0}C; R_f = 0.20 (hexane/ethylacetate 7:3); [Found: C, 61.24; H, 5.10; N, 10.16. $C_{14}H_{14}N_2S_2$ requires C, 61.28; H, 5.14; N, 10.21]; IR (ATR KBr cell, cm^{-1}) 3024, 1458, 1235, 940; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.23 (s, 1H), 7.48 - 7.46 (m, 3H), 7.38 - 7.37 (m, 1H), 7.14 (dd, *J* = 1.2 Hz, 4.8 Hz, 1H), 7.10 - 7.07 (m, 2H), 4.56 (d, *J* = 8 Hz, 1H), 3.40 (d, *J* = 8 Hz, 2H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ_C: 152.8, 142.4, 129.1, 127.6, 126.8, 126.1, 125.7, 122.5, 121.9, 121.4, 117.9, 111.4, 44.1, 35.0, 13.5; LC-MS calcd.m/z 274, found 275 $[(M+1)]^+$.

2-(2-(5-bromothiophen-2-yl)-2-(methylthio)ethyl)-1*H*-benzo[*d*]imidazole 5y: Off white solid (0.224g, 71%); M.pt.188 ^{0}C; R_f = 0.25 (hexane/ethylacetate 7:3); [Found: C, 47.54; H, 3.68; N, 7.87. $C_{14}H_{13}BrN_2S_2$ requires C, 47.59; H, 3.71; N, 7.93]; IR (ATR KBr cell, cm^{-1}) 3087, 2438, 1789, 1435; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.28 (s, 1H), 7.46 - 7.15 (m, 2H), 7.11 - 7.10 (m, 2H), 6.99 - 6.98 (m, 1H), 6.84 - 6.83 (m, 1H), 4.73 (t, *J* = 7.6 Hz, 1H), 3.43 - 3.36 (m, 2H), 1.99 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 150.9, 147.1, 137.9, 128.5, 125.2, 121.1, 114.0, 110.5, 44.3, 36.0, 13.6; LC-MS calcd.m/z 353, found 354 $[(M+1)]^+$.

Synthesis of 2-(2-(1*H*-benzo[*d*]imidazol-2-yl)-1-(2-fluorophenyl)ethylthio)ethanamine 8a: To a solution of (*E*)-2-(2-fluorostyryl)-1*H*-benzo[*d*]imidazole **4g** (1mol), glacial acetic acid (10 vol), was added and 2-aminoethane thiol (1mol) in one portion at room temperature. The reaction mixture was stirred magnetically reflux at 110 ºC for 15h. The reaction mixture was subsequently quenched with saturated aqueous $NaHCO_3$ (20ml) then extracted with ethyl acetate (15ml). The extracts were combined washed with water, brine and then dried over anhydrous Na_2SO_4. Volatile solvent and reagents were removed by rotary evaporation, and the residue was purified by column chromatography (silica gel) using ethyl acetate/Petroleum ether mixture as a gradient eluent to afford pure product **8a**. Semisolid mixture (0.132g, 87%); R_f = 0.32 (hexane/ethylacetate 7:3); [Found: C, 64.70; H, 5.68; N, 13.29. $C_{17}H_{18}FN_3S$ requires C, 64.74; H, 5.75; N, 13.32]; IR (ATR KBr cell, cm^{-1}) 2961, 1721, 1579, 1423, 1259, 738; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 7.54 - 7.51 (m, 1H), 7.45 - 7.42 (m, 2H), 7.28 - 7.23

(m, 1H), 7.18 - 7.07 (m, 4H), 4.81 (t, *J* = 8 Hz, 1H), 4.53 (s, 2H), 3.44 (dd, *J* = 6.8 Hz, 8 Hz, 2H), 2.66 (t, *J* = 6.8 Hz, 2H), 2.45 - 2.20 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 167.0, 161.5, 158.3, 152.1, 138.6, 131.8, 131.6, 129.2, 129.1, 128.7, 128.5, 124.6, 121.4, 115.7, 115.4, 114.6, 34.4, 32.1, 27.3, 18.9; LC-MS calcd.m/z 315, found 316 $[(M+1)]^+$.

Synthesis of 2-(2-(2,4-difluorophenyl)-2-(phenylthio)ethyl)-1*H*-benzo[*d*]imidazole 8b: This compound was prepared from (*E*)-2-(2,4-difluorostyryl)-1*H*-benzo[*d*]imidazole **4n** (1mol) and thiophenol (1mol) following the above procedure. Off white solid (0.12g, 85%); M.pt.130-132 ^{0}C; R_f = 0.35 (hexane/ethylacetate 7:3); [Found: C, 68.80; H, 4.35; N, 7.58. $C_{21}H_{16}F_2N_2S$ requires C, 68.83; H, 4.40; N, 7.65]; IR (ATR KBr cell, cm^{-1}) 3783, 2359, 1726, 1424, 740; ^{1}H NMR (400 MHz, DMSO-d_6) δ_H: 12.29 (s, 1H), 7.44 - 7.39 (m, 3H), 7.29 - 7.27 (m, 5H), 7.13 - 7.07 (m, 3H), 6.97 (t, *J* = 6.4 Hz, 1H), 5.21 (t, *J* = 8 Hz, 1H), 3.49 (d, *J* = 2 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ_C: 162.0, 160.8, 158.9, 157.5, 150.7, 132.2, 131.5, 129.4, 128.2, 127.0, 124.6, 123.2, 120.5, 110.8, 110.5, 103.4, 103.0, 102.7, 42.7, 33.2; LC-MS calcd.m/z 366, found 367 $[(M+1)]^+$.

Supplementary data:

Copies of ^{1}H&^{13}C NMR spectra for all of the compounds (**2**, **4, 5&8**)

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SUPPORTING INFORMATION

α-Aroylidineketene Dithioacetal Chemistry: CuI Catalyzed Synthesis of 2-Styryl benzimidazoles Enroute to Regioselective Hydrothiolation

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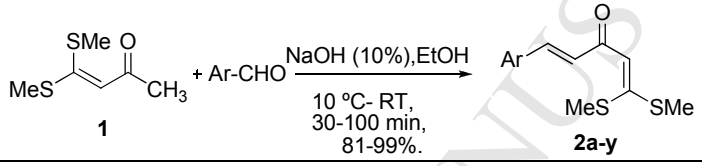
V Copies of ^{1}H&^{13}C NMR of **5a-y** 52
VI Copies of ^{1}H&^{13}C NMR of **8a&b** 73

I General Consideration

The melting points reported in the work are uncorrected. Unless stated otherwise, solvents and chemicals were obtained from commercial sources and used without further purification. The ^{1}H and ^{13}CNMR spectra of the new compounds were measured at 400MHz or 300MHz and 100MHz or 75MHz (mentioned in respective NMR data itself) respectively using Bruker NMR instrument in DMSO-d_6 or $CDCl_3$. Chemical shifts are reported in parts per million (δ), coupling constants (J values) are reported in Hertz (Hz) relative to tetramethylsilane. Spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), m (multiplet) dd (doublet of doublets), td (triplet of doublets) bs (broad singlet). Elemental analysis was recorded on Thermofinnigan flash 2000 organic elemental CHNS analyser.

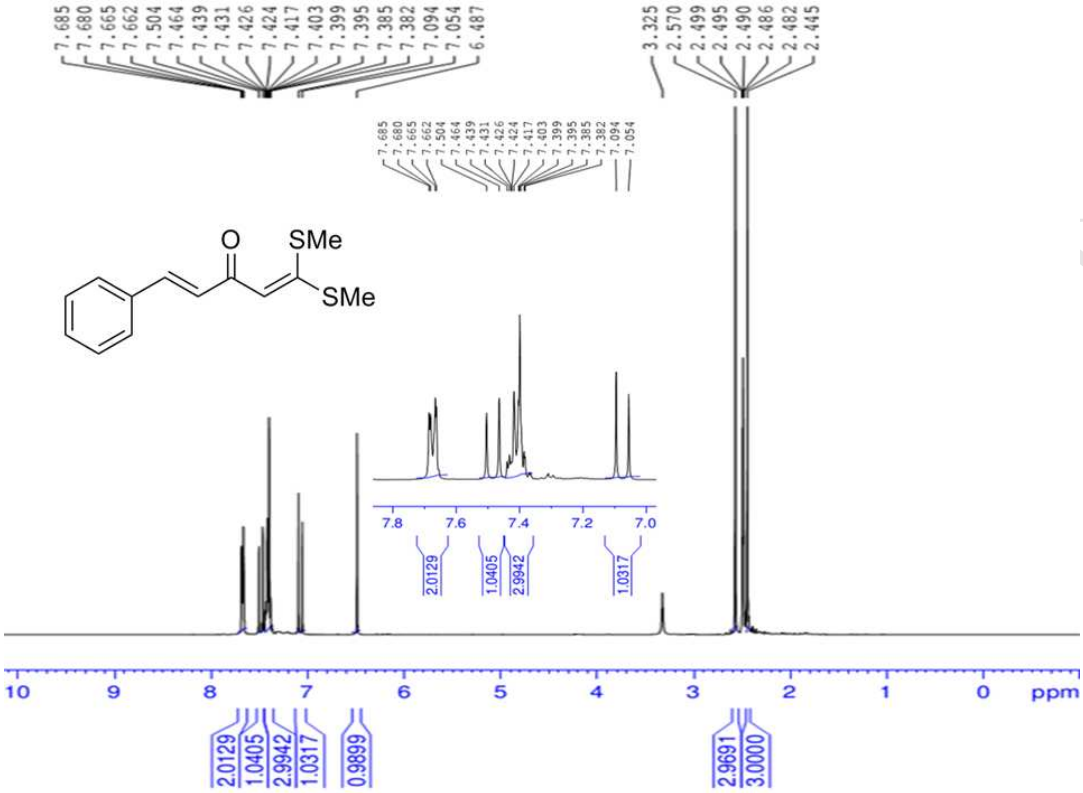
II Table 1: Synthesis of substrates 2a-y[a]



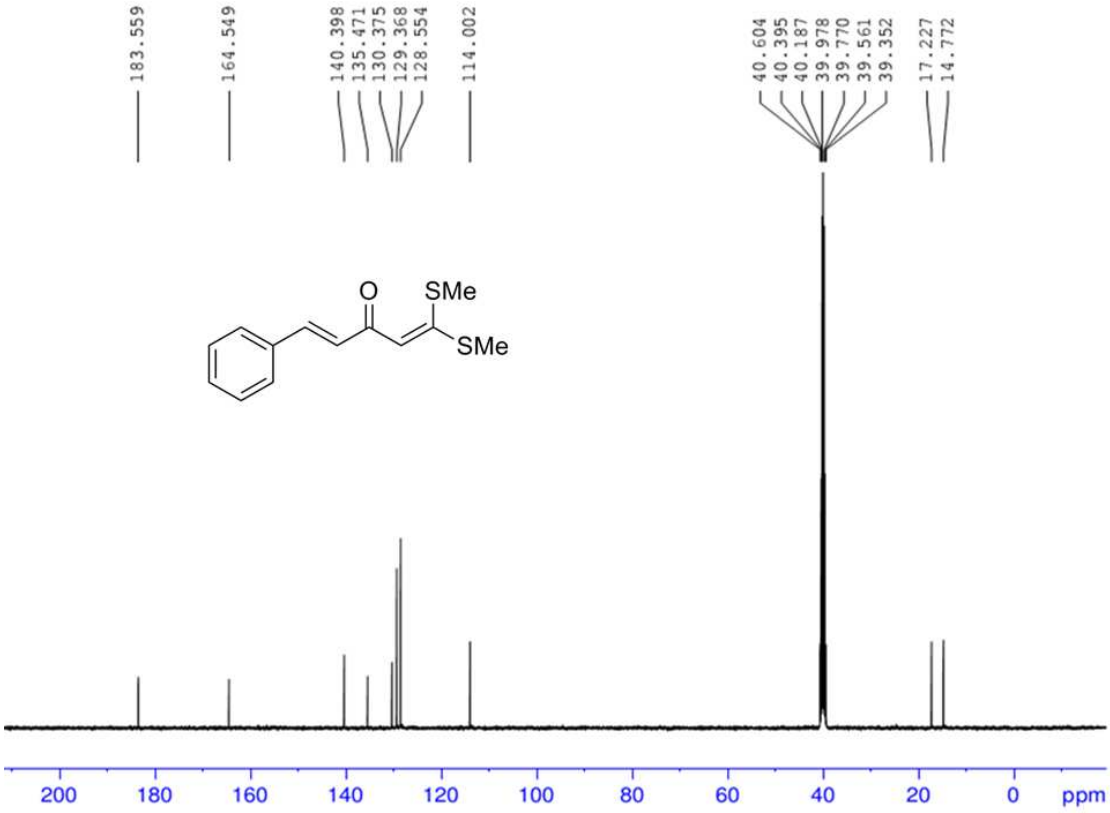
Entry	Ar		Time (min)	Yield[b] %
1	C_6H_5-	**2a**	45	81
2	2-OMe-C_6H_4-	**2b**	20	85
3	3-OMe-C_6H_4-	**2c**	35	90
4	4-OMe-C_6H_4-	**2d**	30	90
5	3-Cl-C_6H_4-	**2e**	45	85
6	4-Cl-C_6H_4-	**2f**	30	99
7	2-F-C_6H_4-	**2g**	45	92
8	3-F-C_6H_4-	**2h**	50	90
9	4-F-C_6H_4-	**2i**	80	92
10	2-Br-C_6H_4	**2j**	30	88
11	4-Br-C_6H_4-	**2k**	40	85
12	4-CN-C_6H_4-	**2l**	90	89
13	4-NO_2-C_6H_4	**2m**	120	93
14	2,4-F_2-C_6H_3-	**2n**	30	88
15	2,4-Cl_2-C_6H_3-	**2o**	30	99
16	2-OMe,5-Br-C_6H_3-	**2p**	40	87
17	3-Br,4-F-C_6H_3-	**2q**	45	87
18	2-Cl,5-NO_2	**2r**	90	93
19	1-Naphthyl	**2s**	100	91
20	9-anthracenyl	**2t**	90	92
21	1-pyrenyl	**2u**	90	84
22	2-Furyl	**2v**	90	87
23	5-Br-C_5H_3N-	**2w**	60	82
24	2-Thienyl	**2x**	60	86
25	5-Br-2-C_4H_3S-	**2y**	90	86

[a]Reaction conditions: **1** (1 mol), Ar-CHO (1.1mol), NaOH (1.5mol), EtOH, 0 ºC - RT, 30-120 min. [b] isolated product yield after recrystallization.

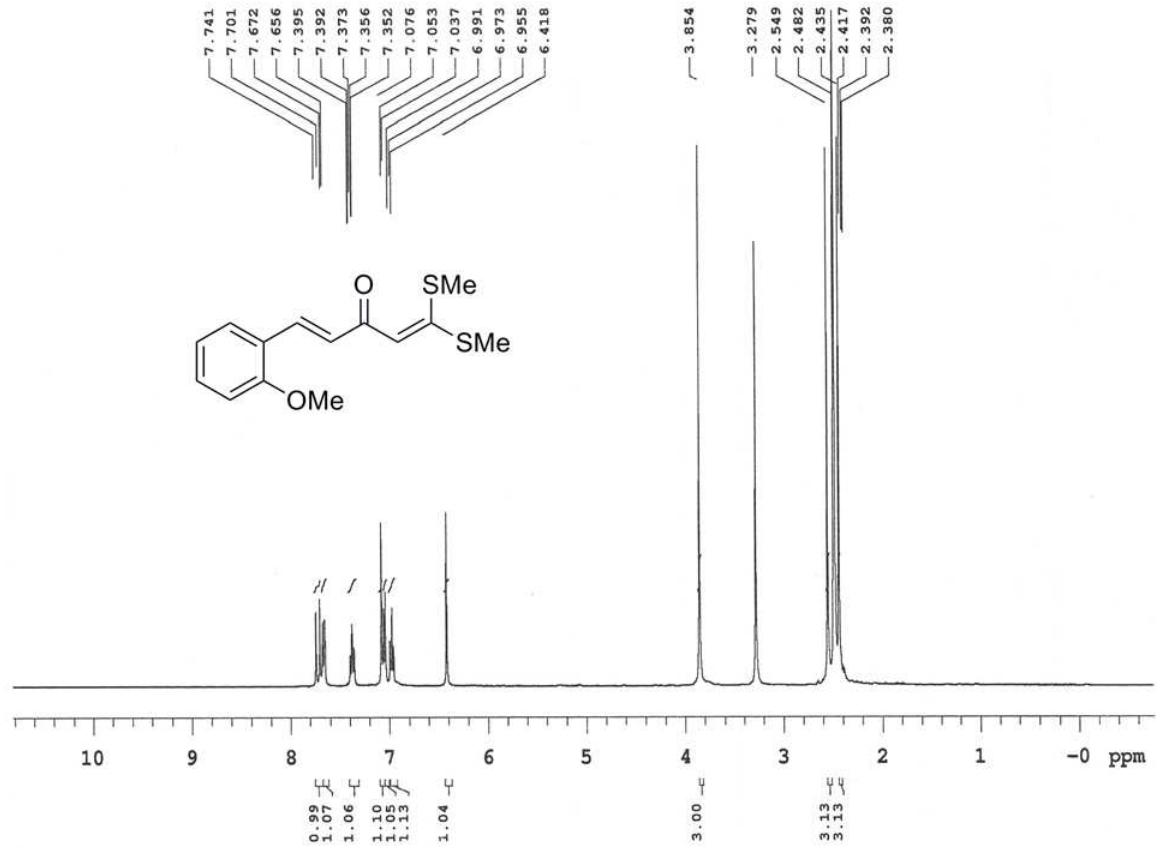
III Copies of ^{1}H NMR&^{13}C NMR spectra 2a-y



(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **2a**



(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **2a**



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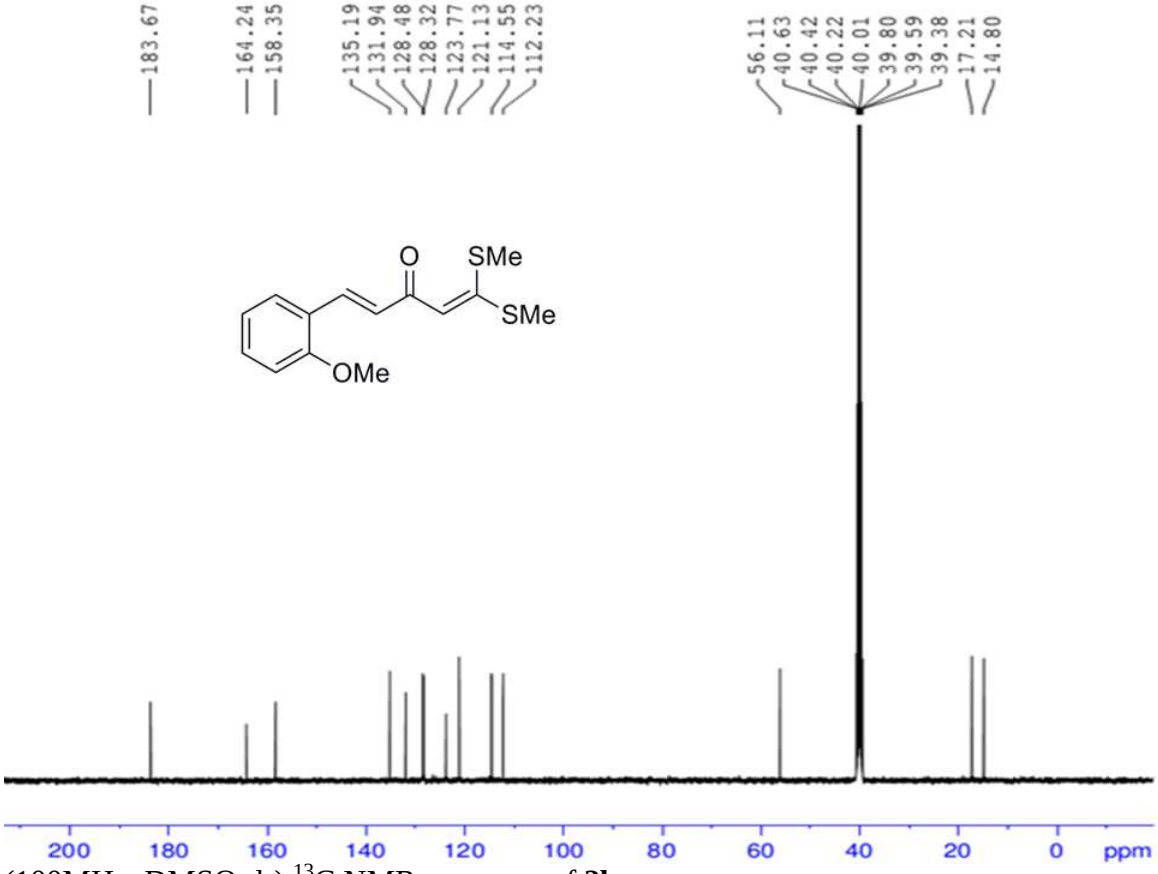

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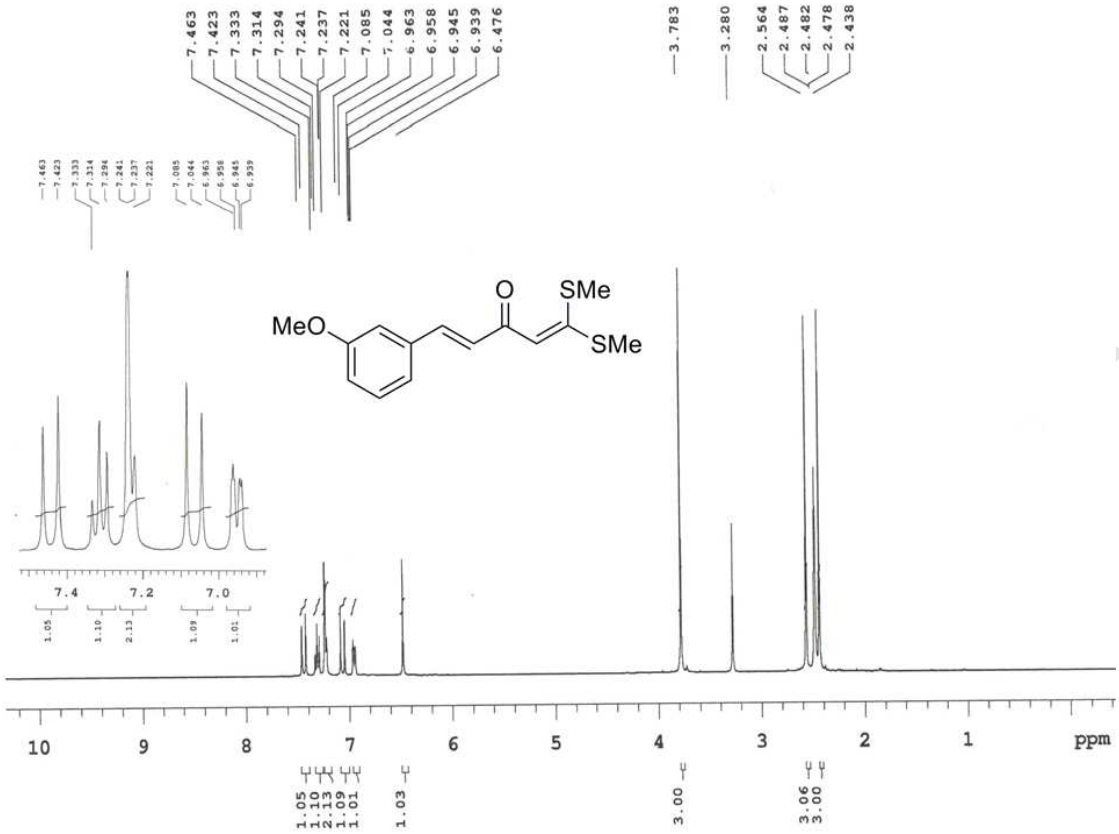

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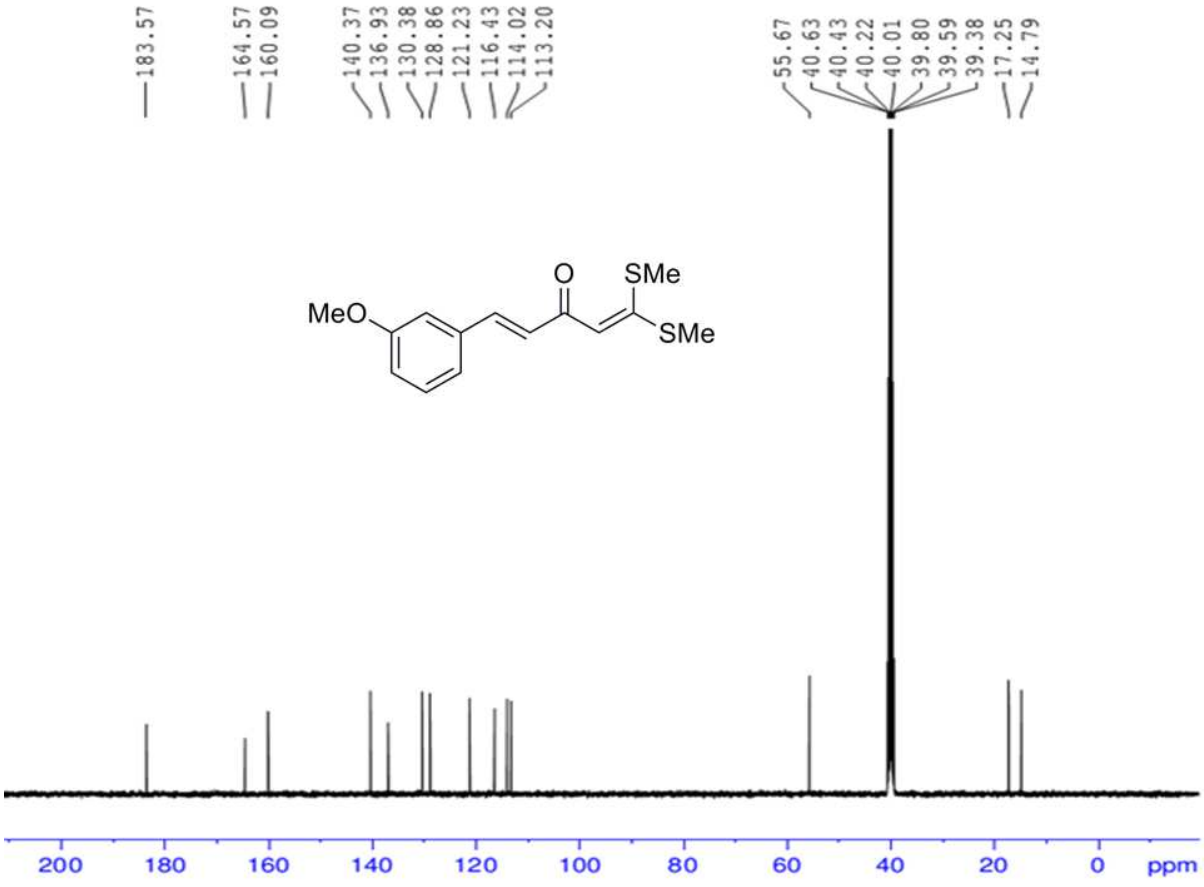

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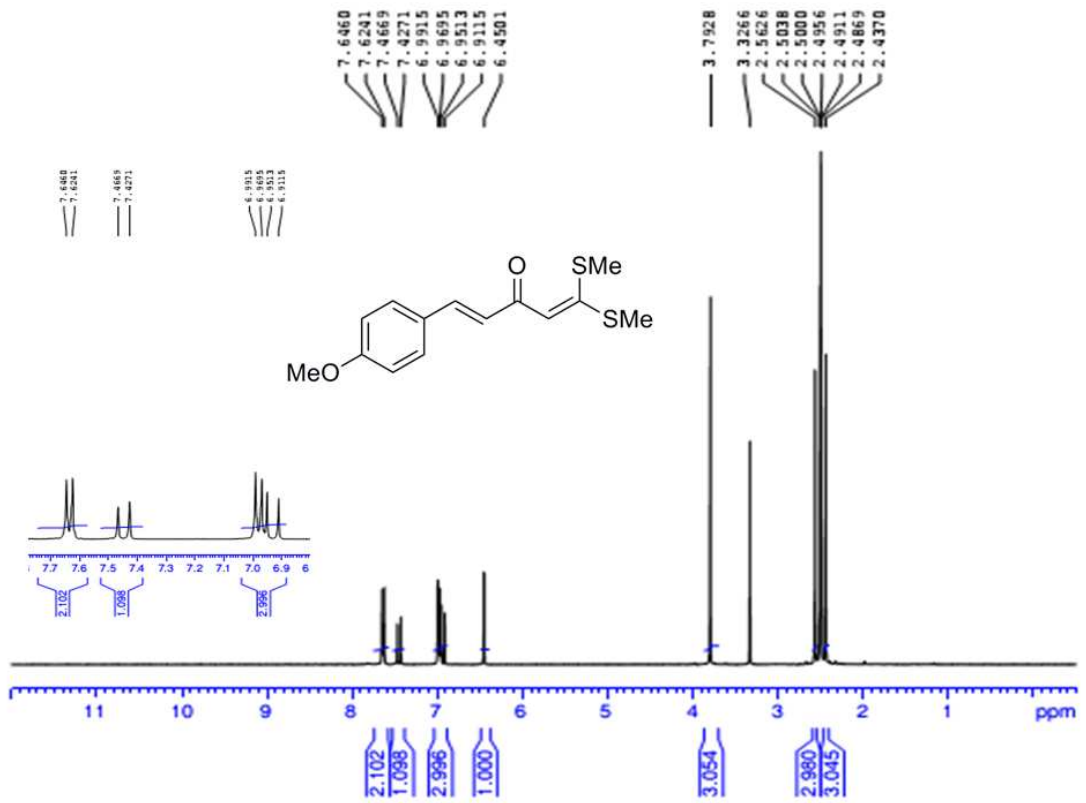

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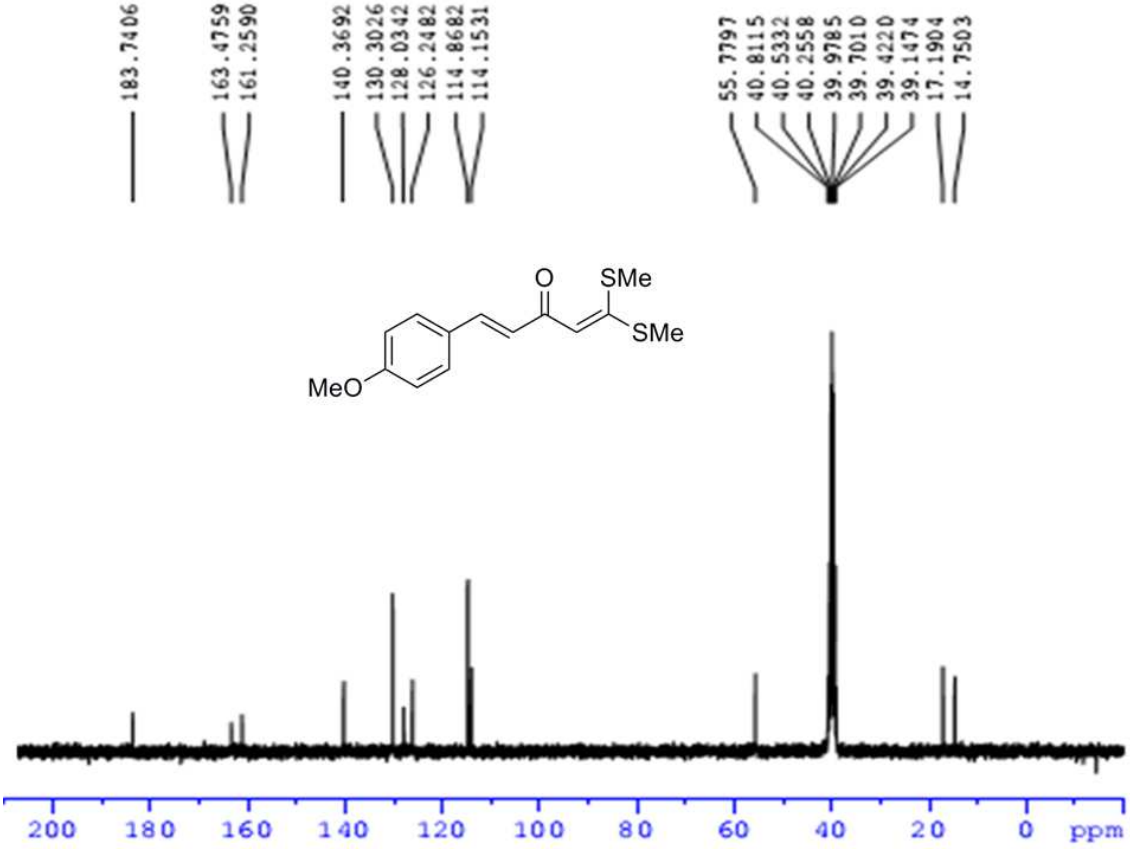

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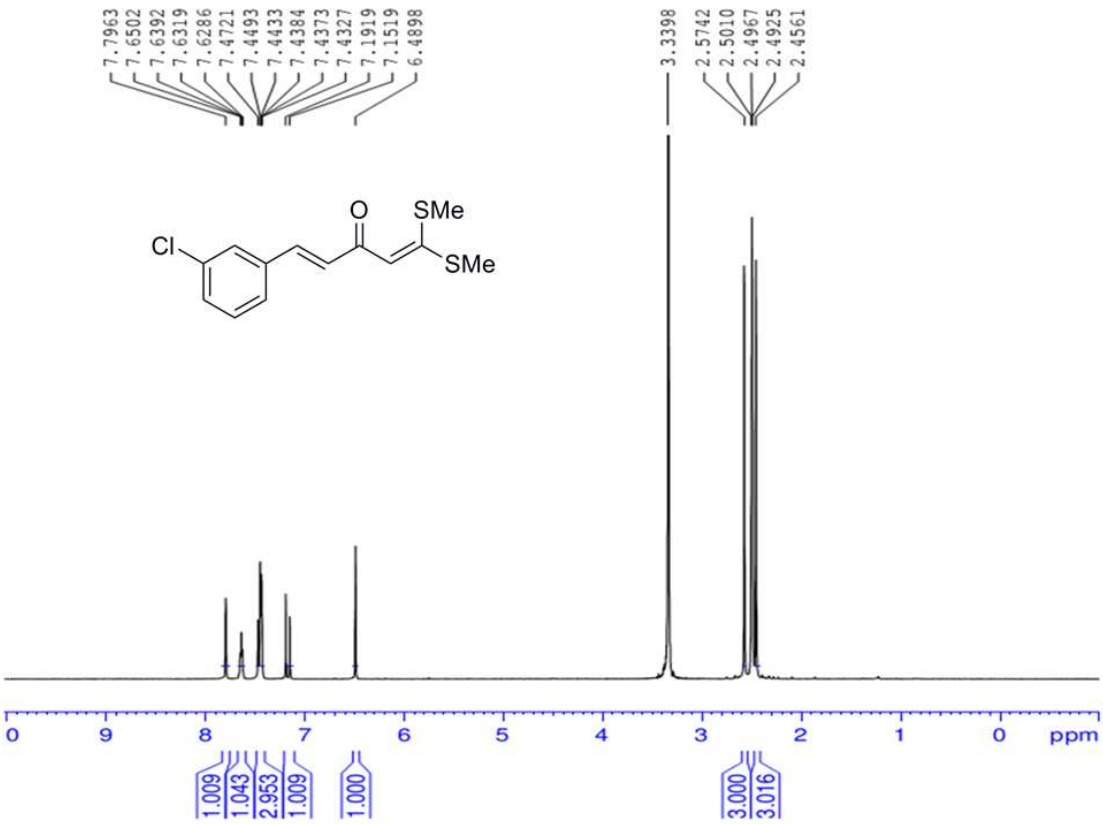

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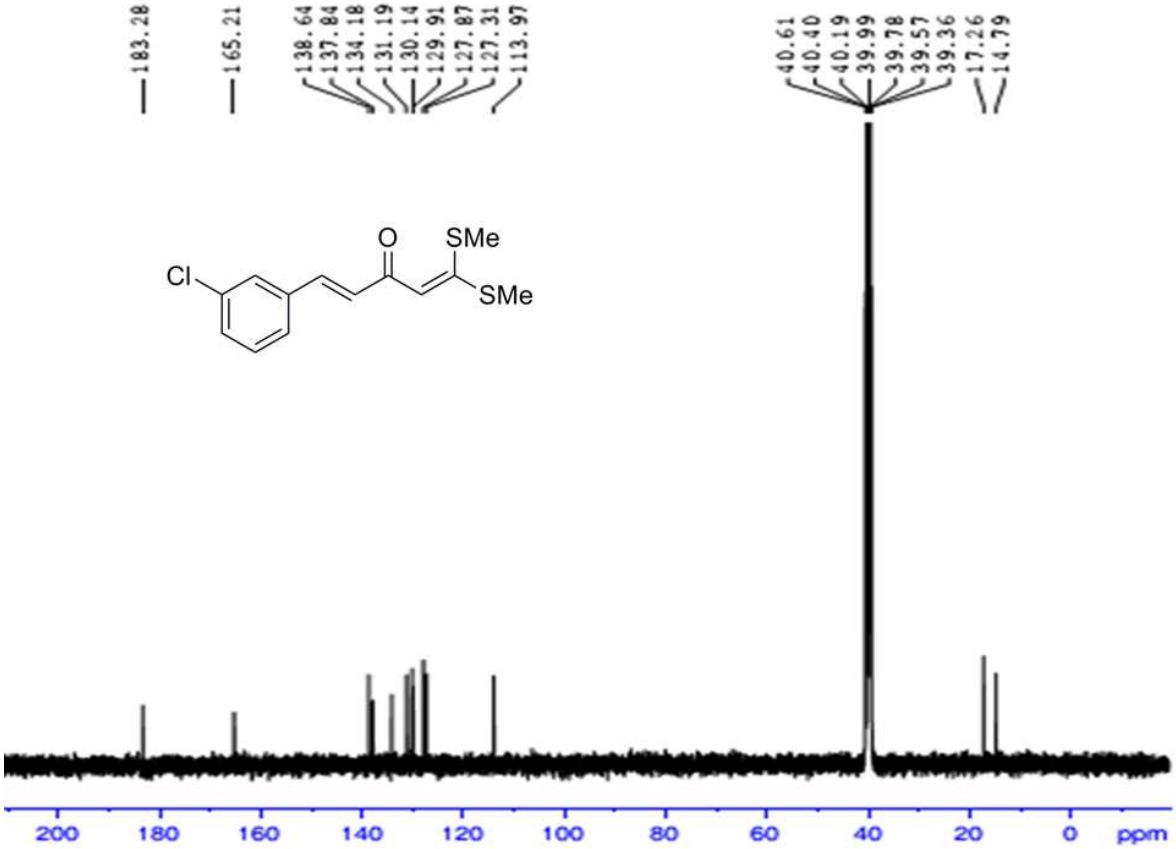

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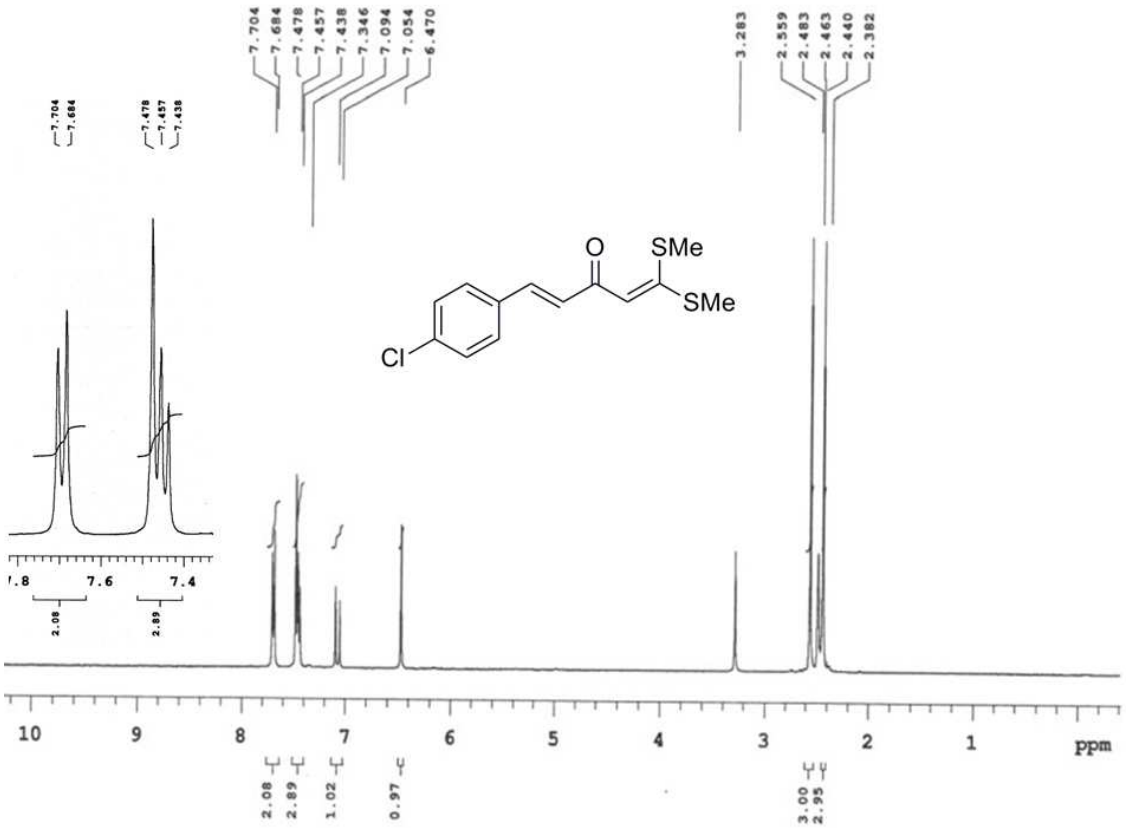

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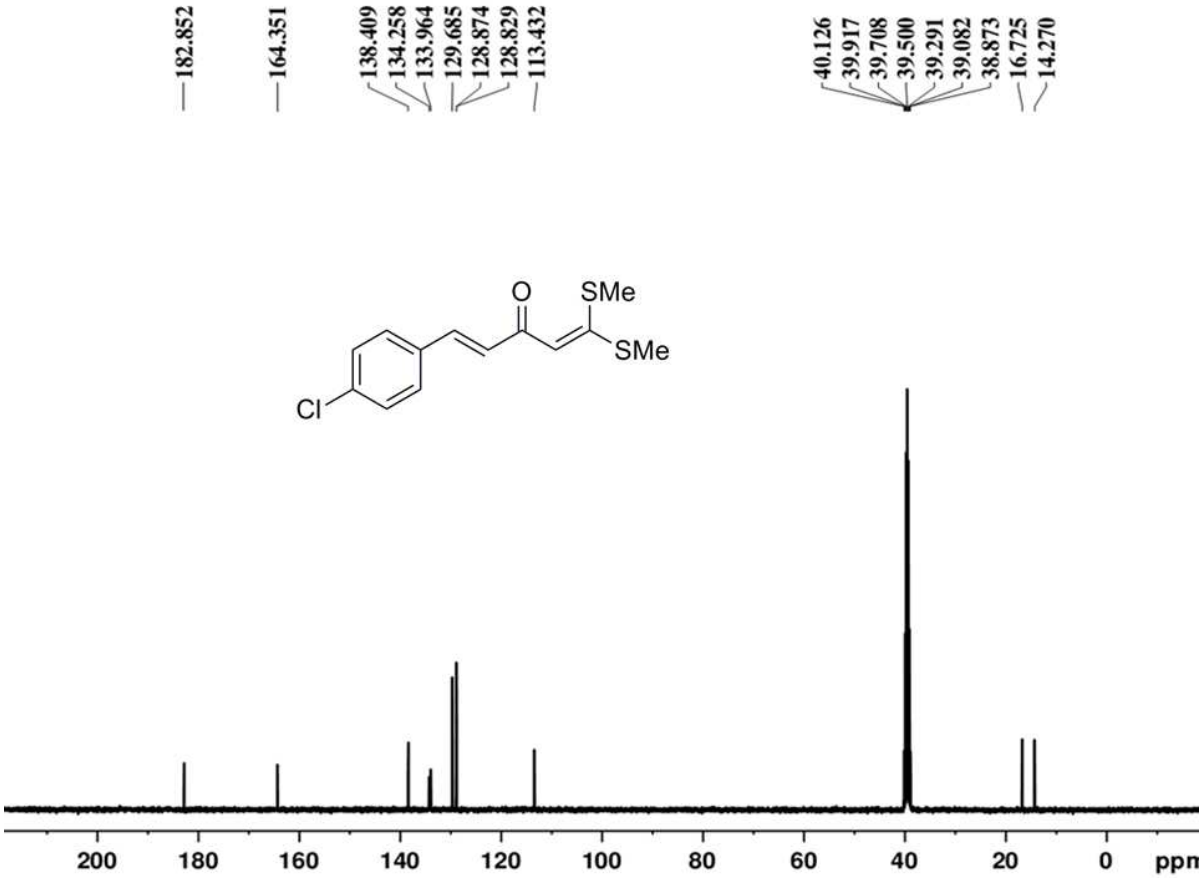

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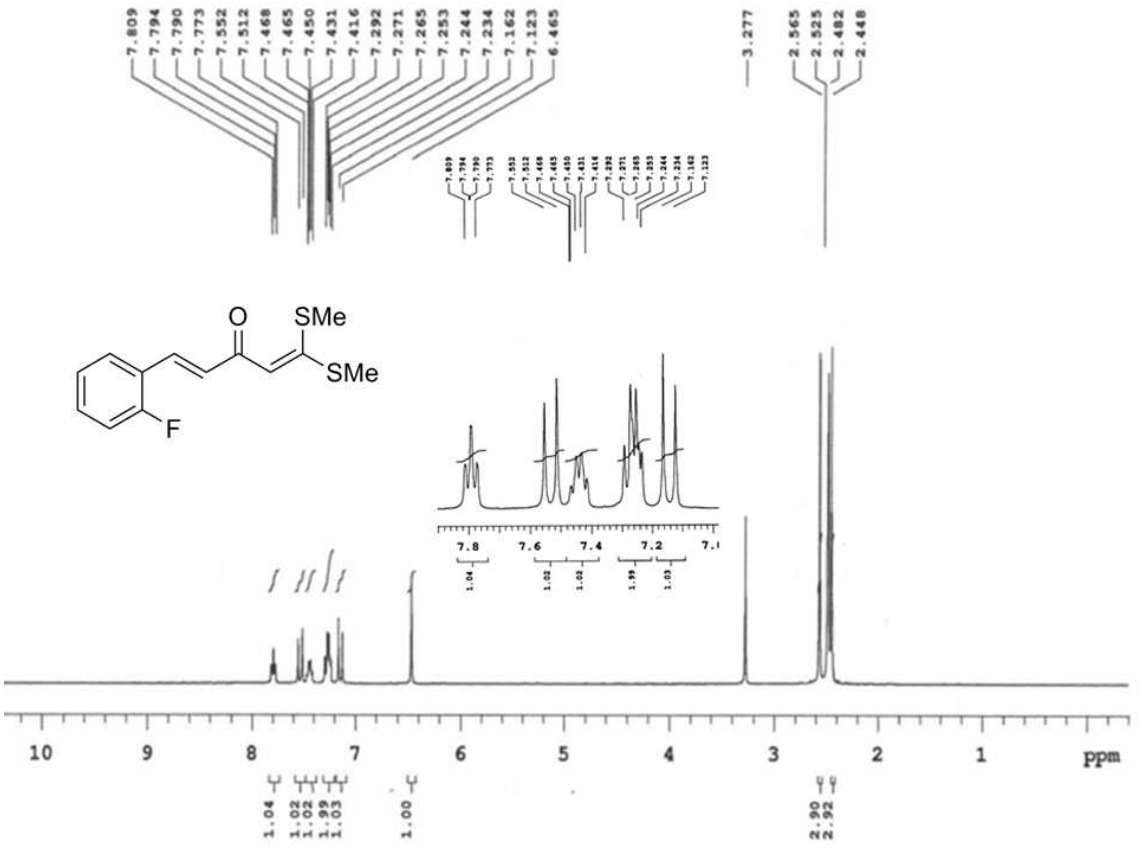

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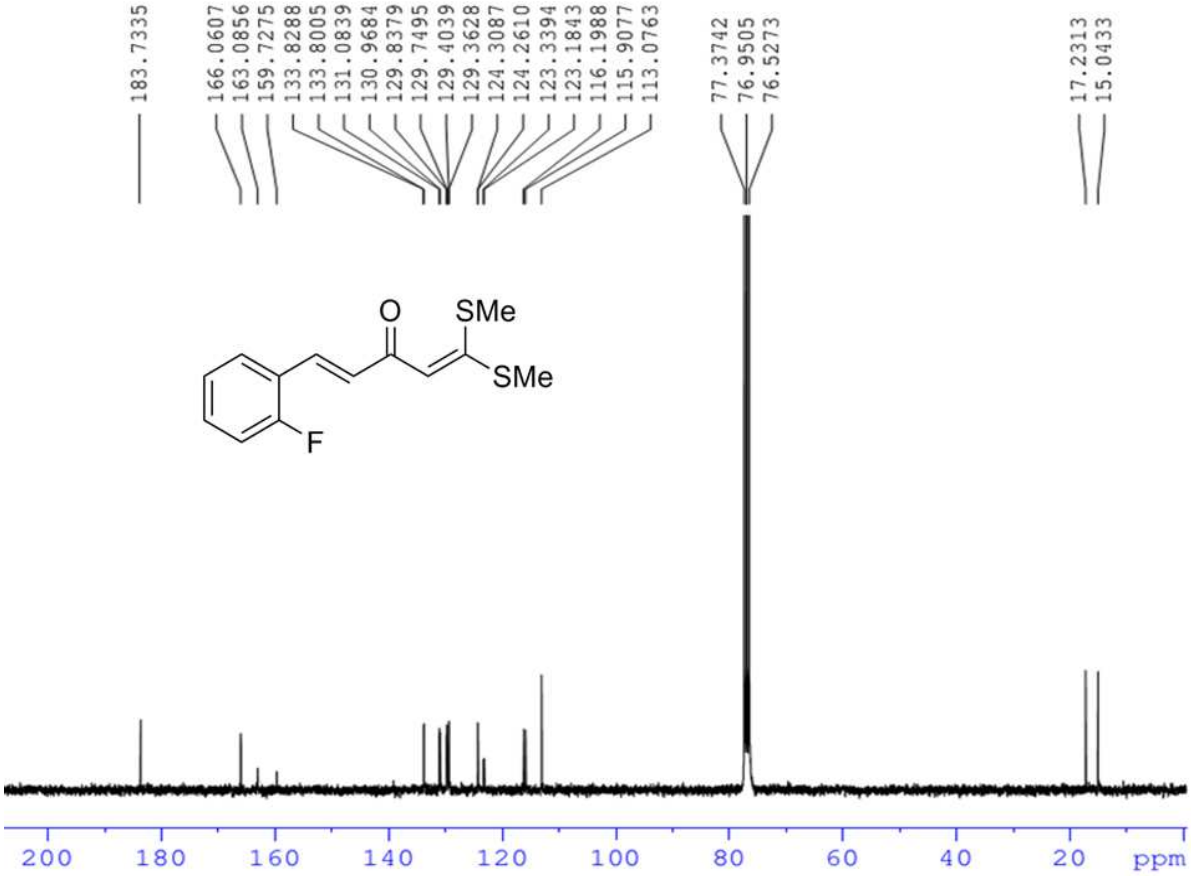

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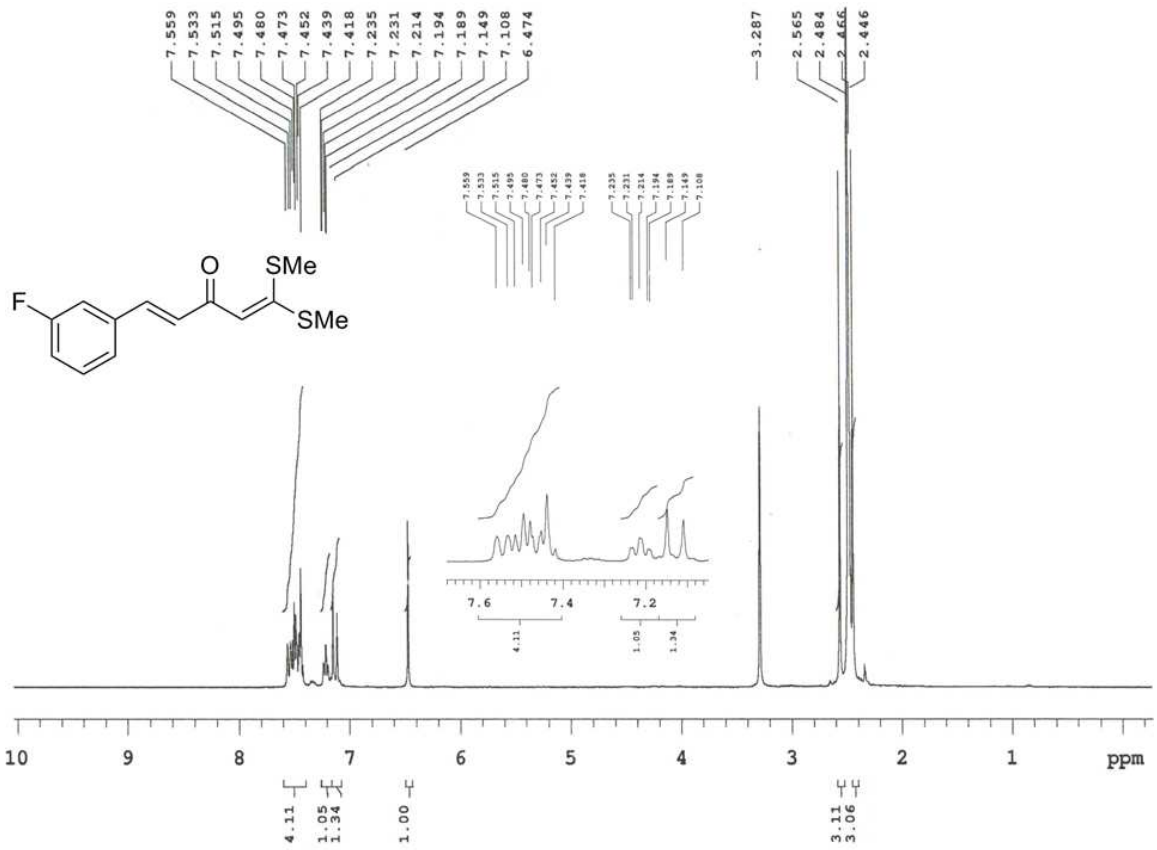

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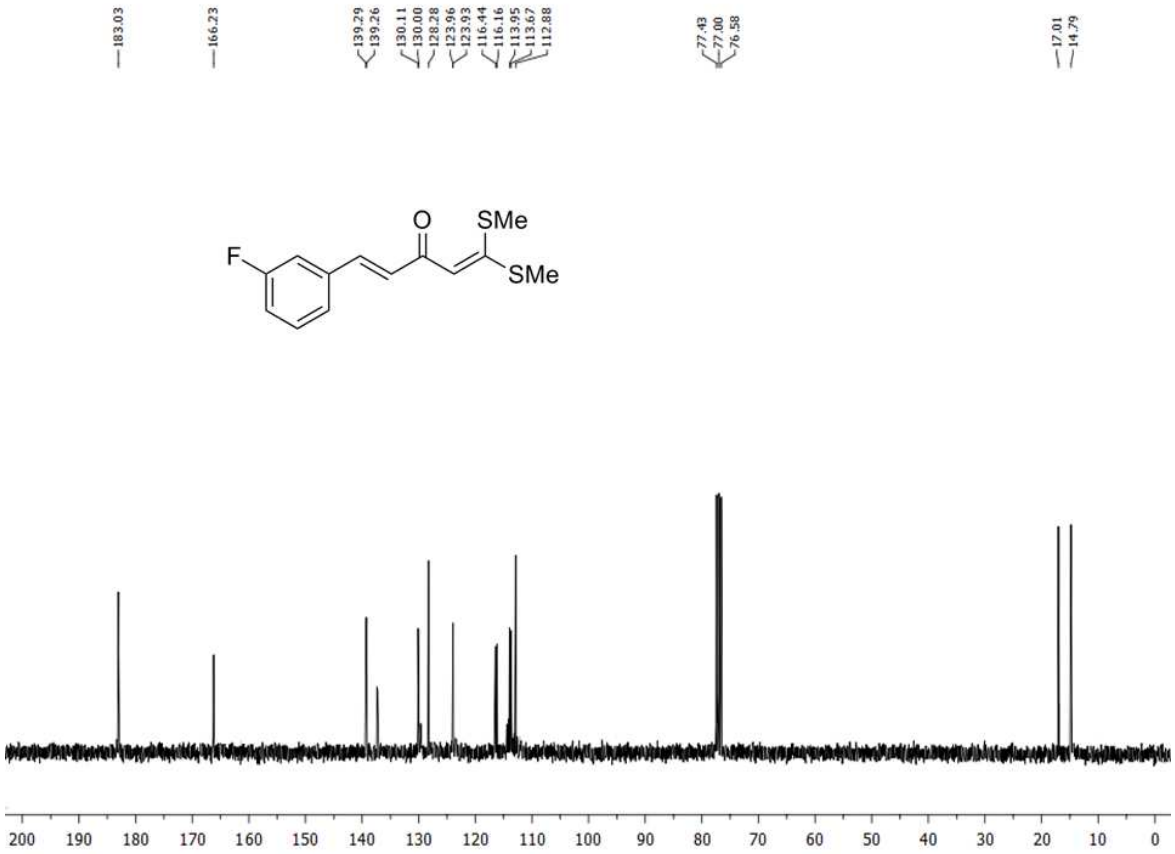

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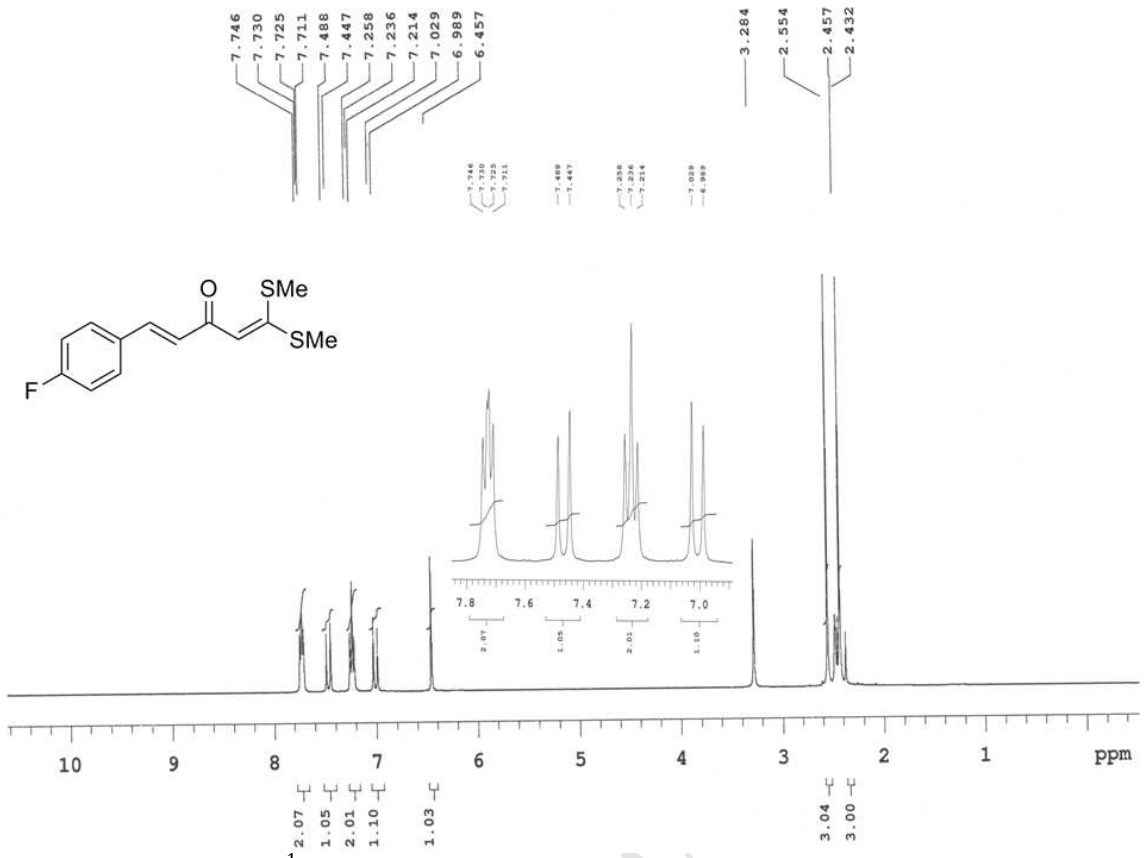

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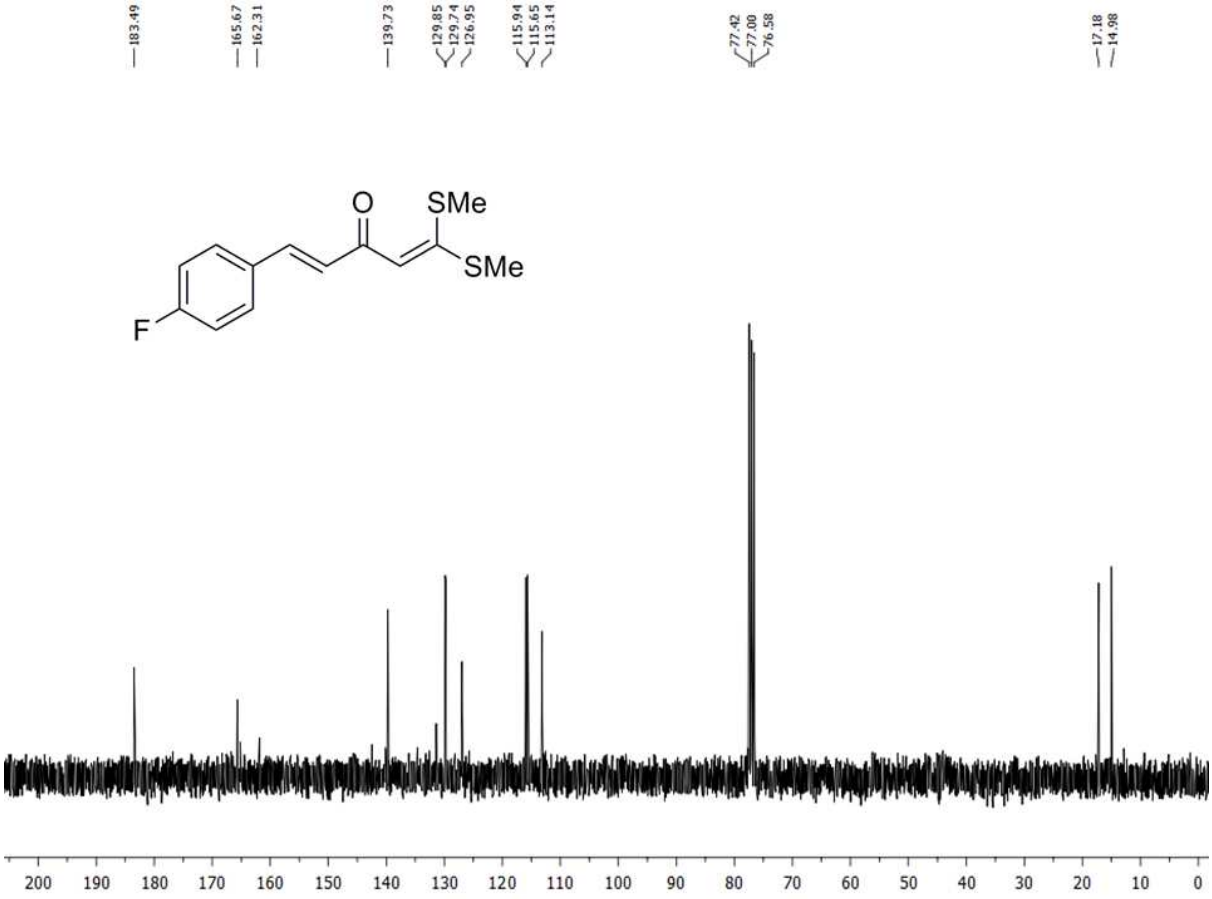

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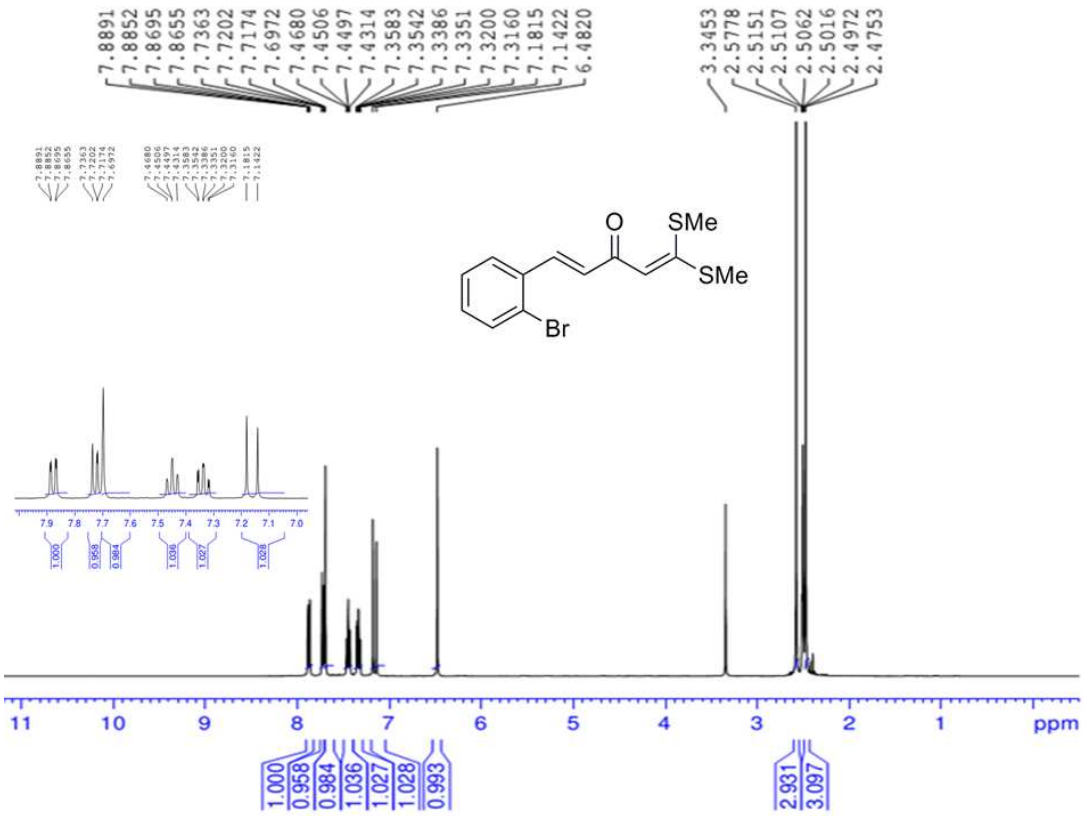

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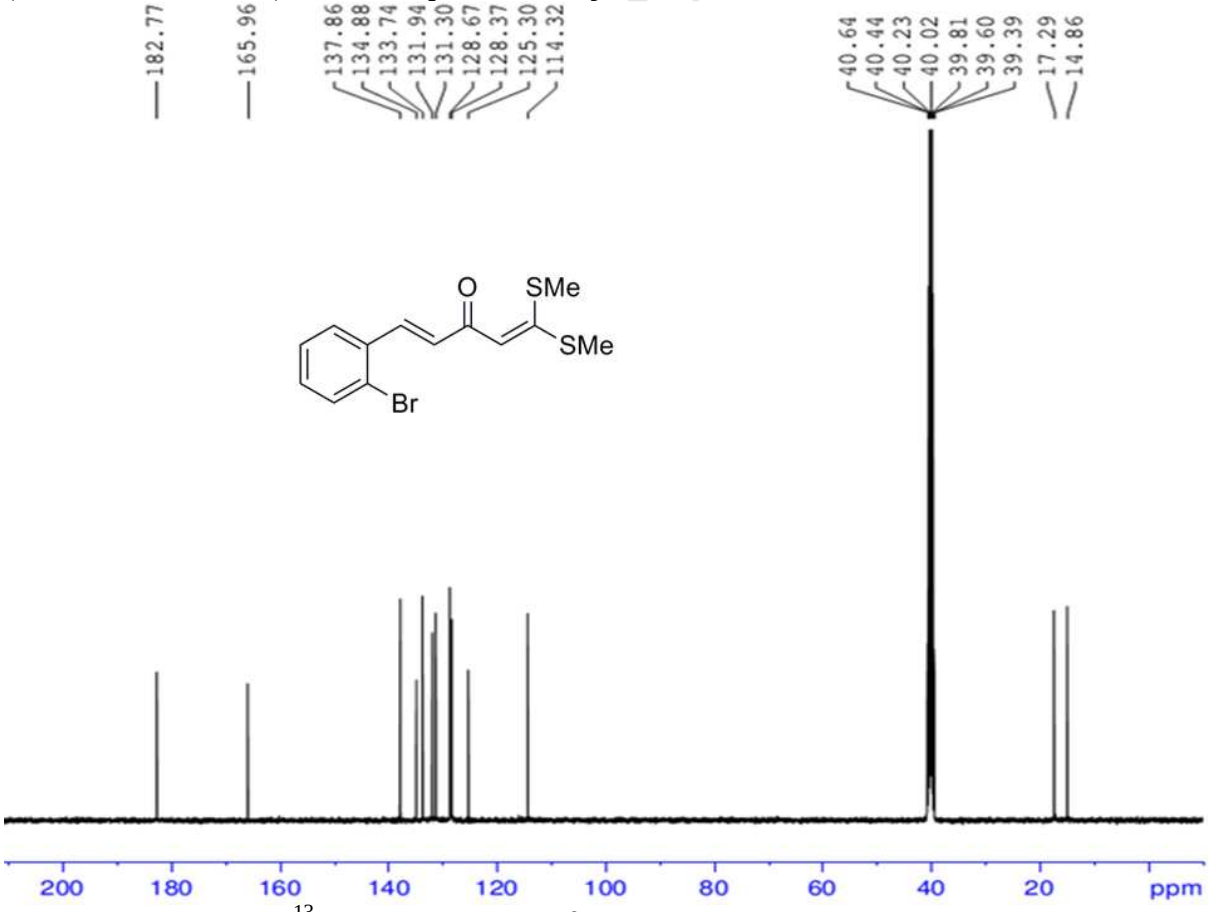

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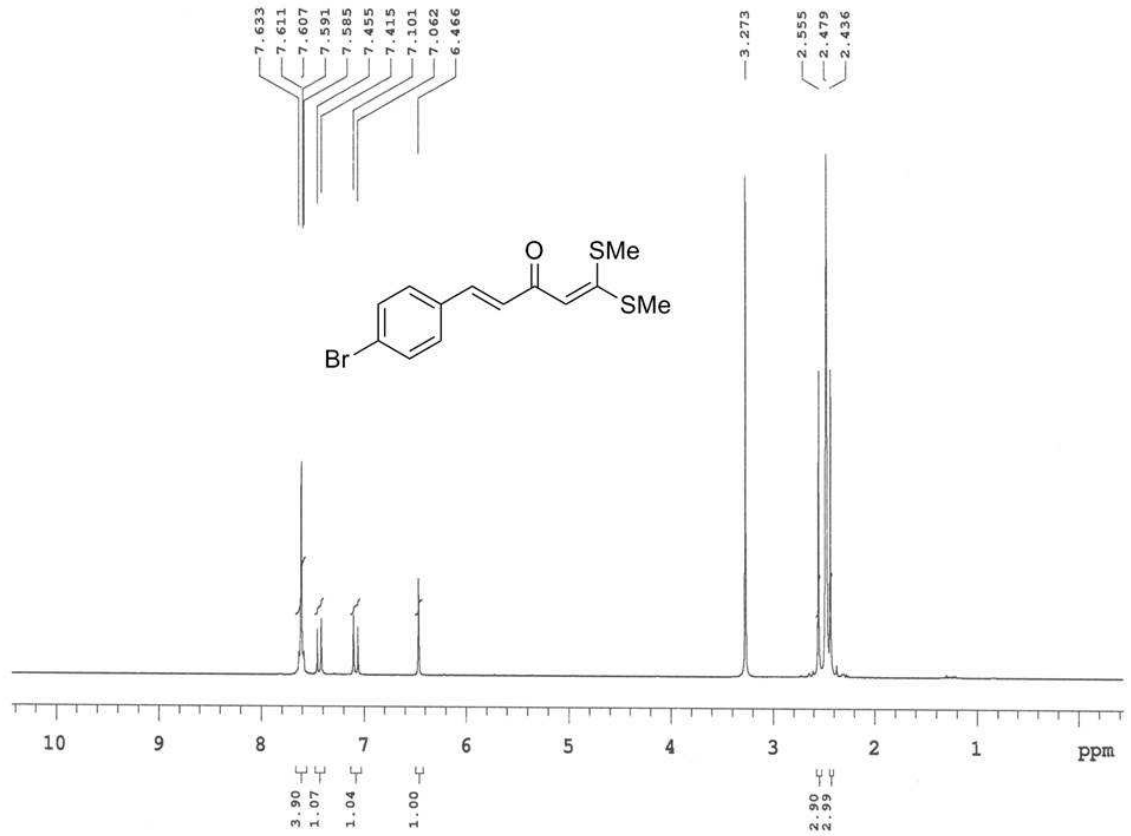

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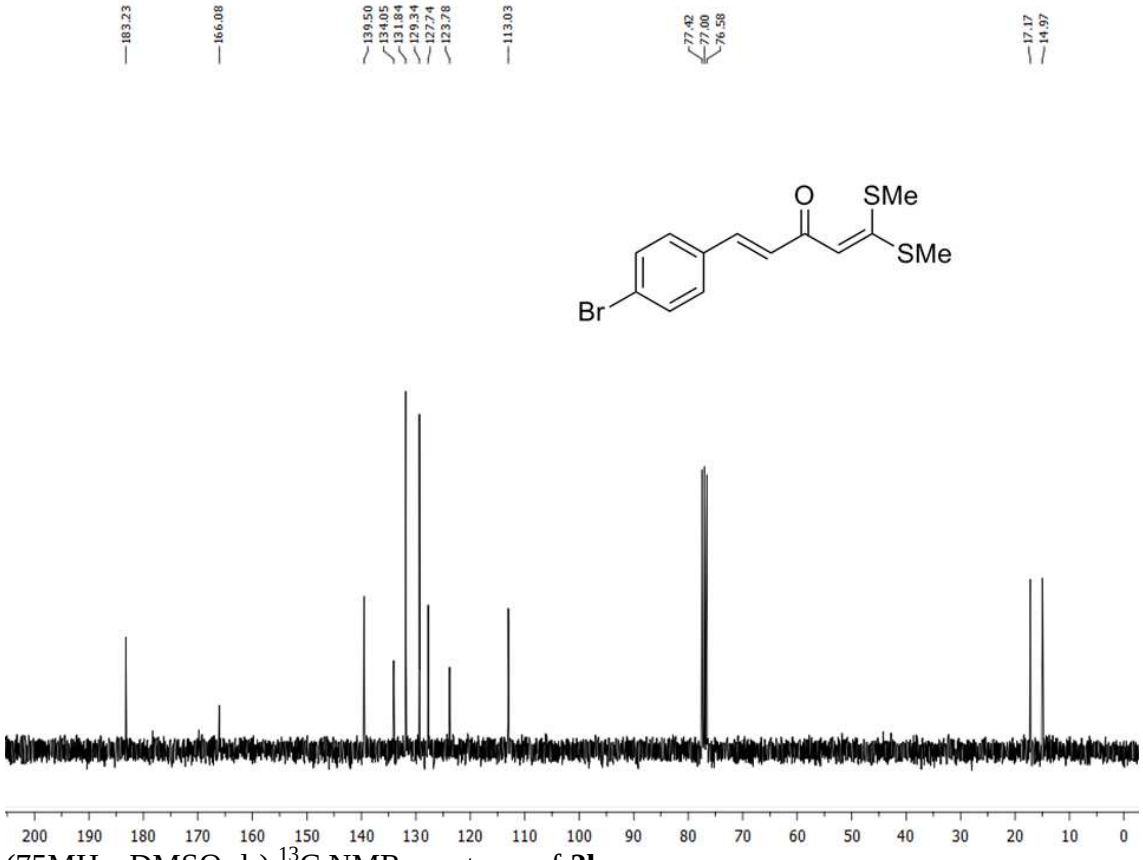

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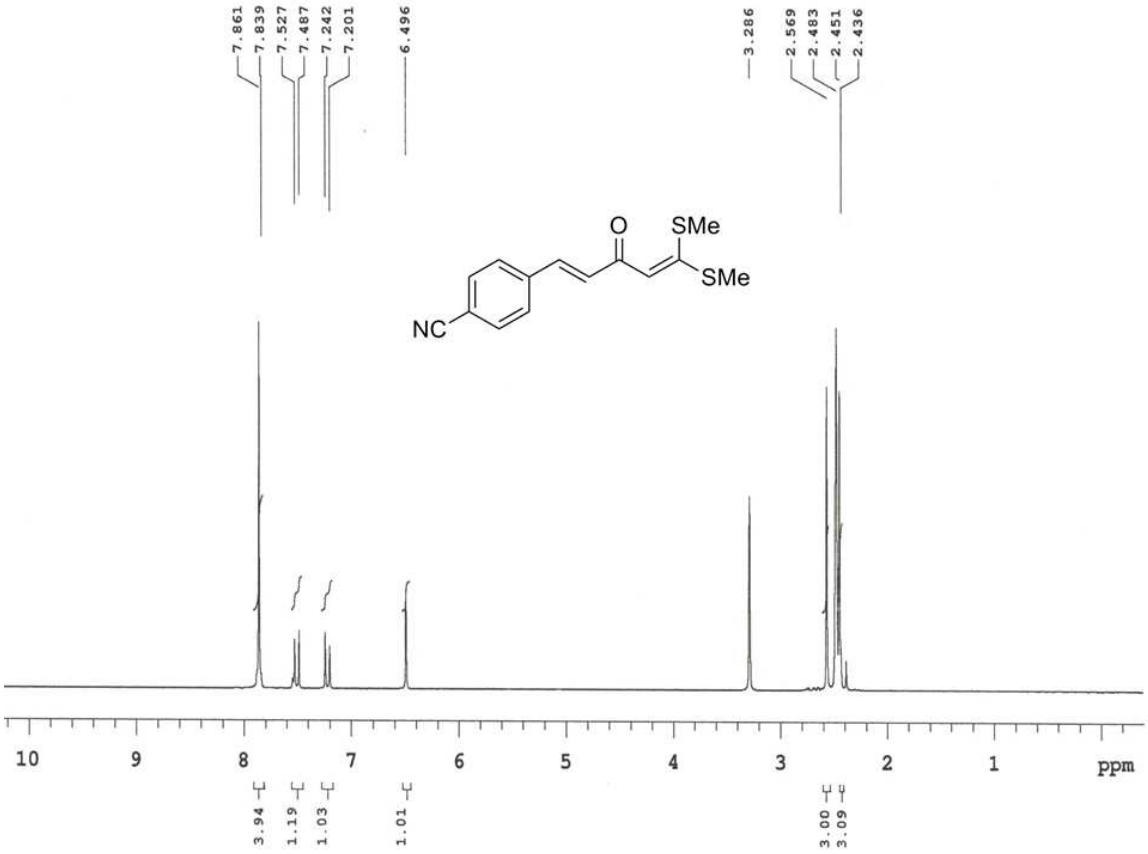

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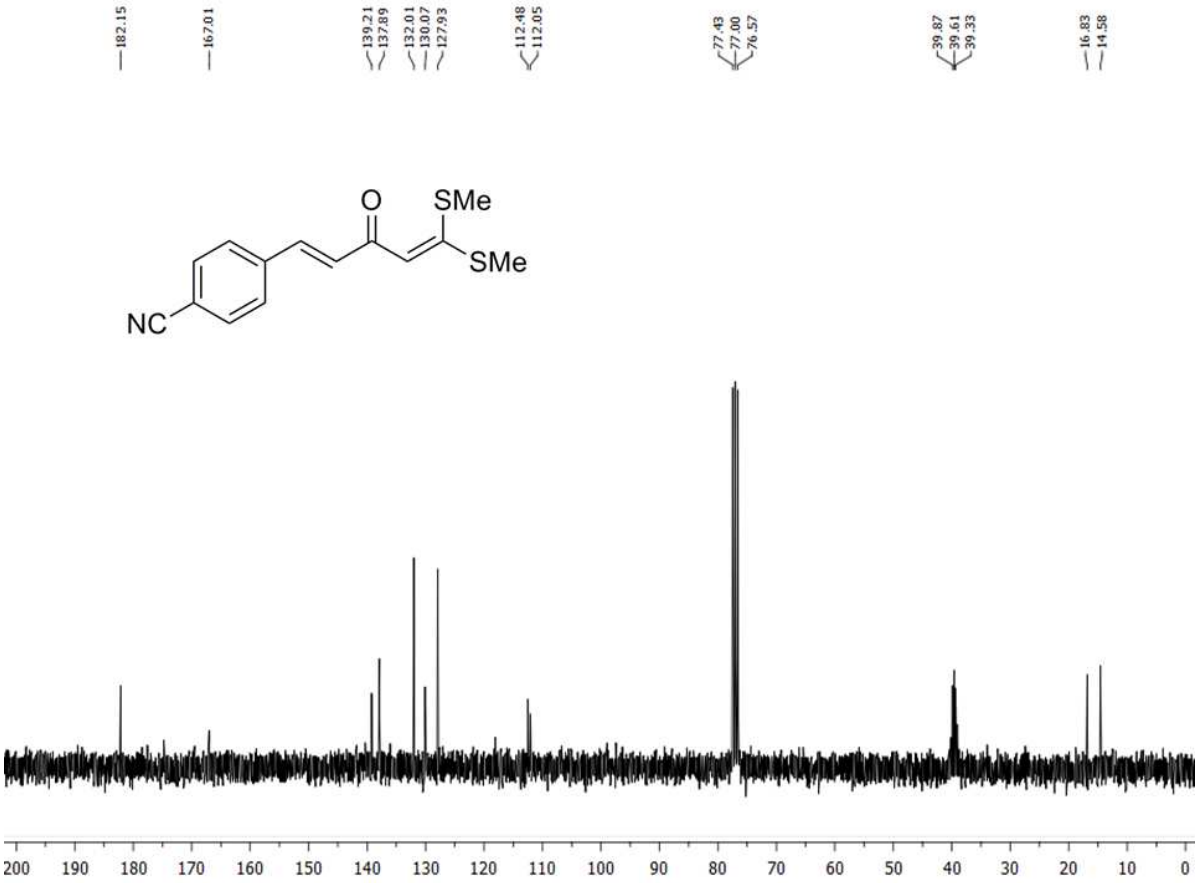

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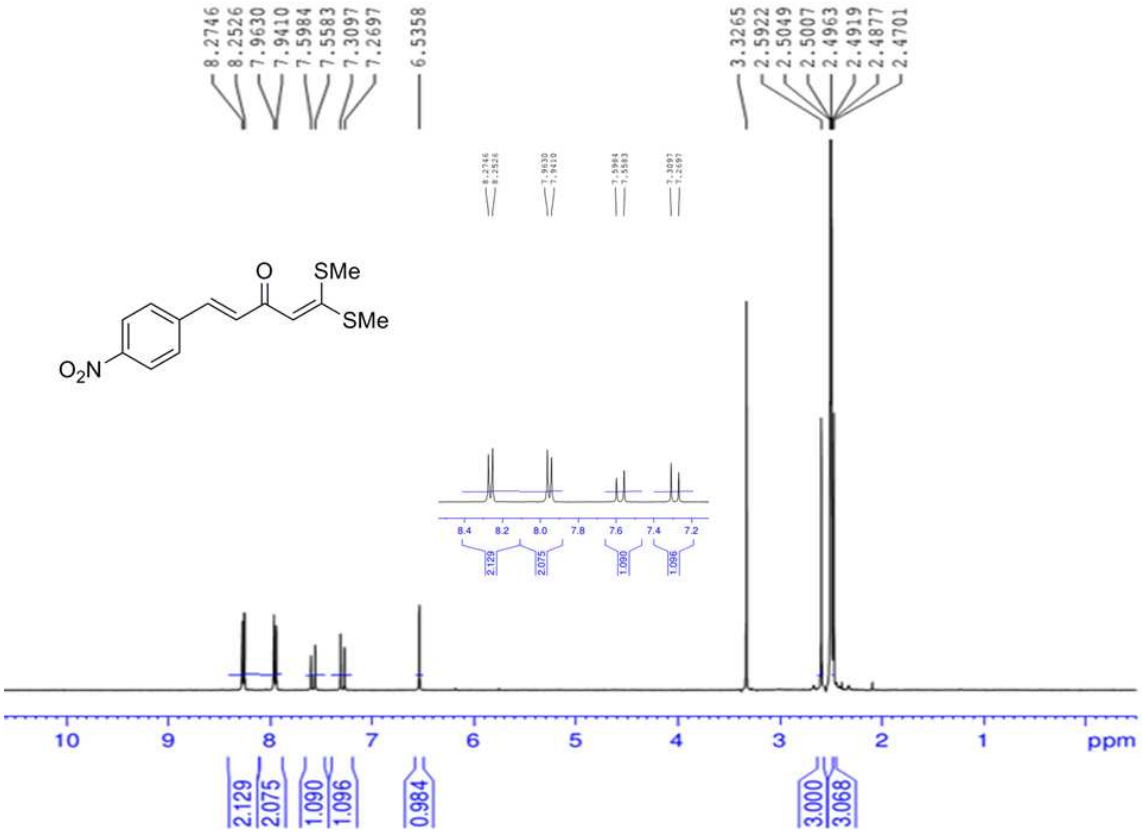

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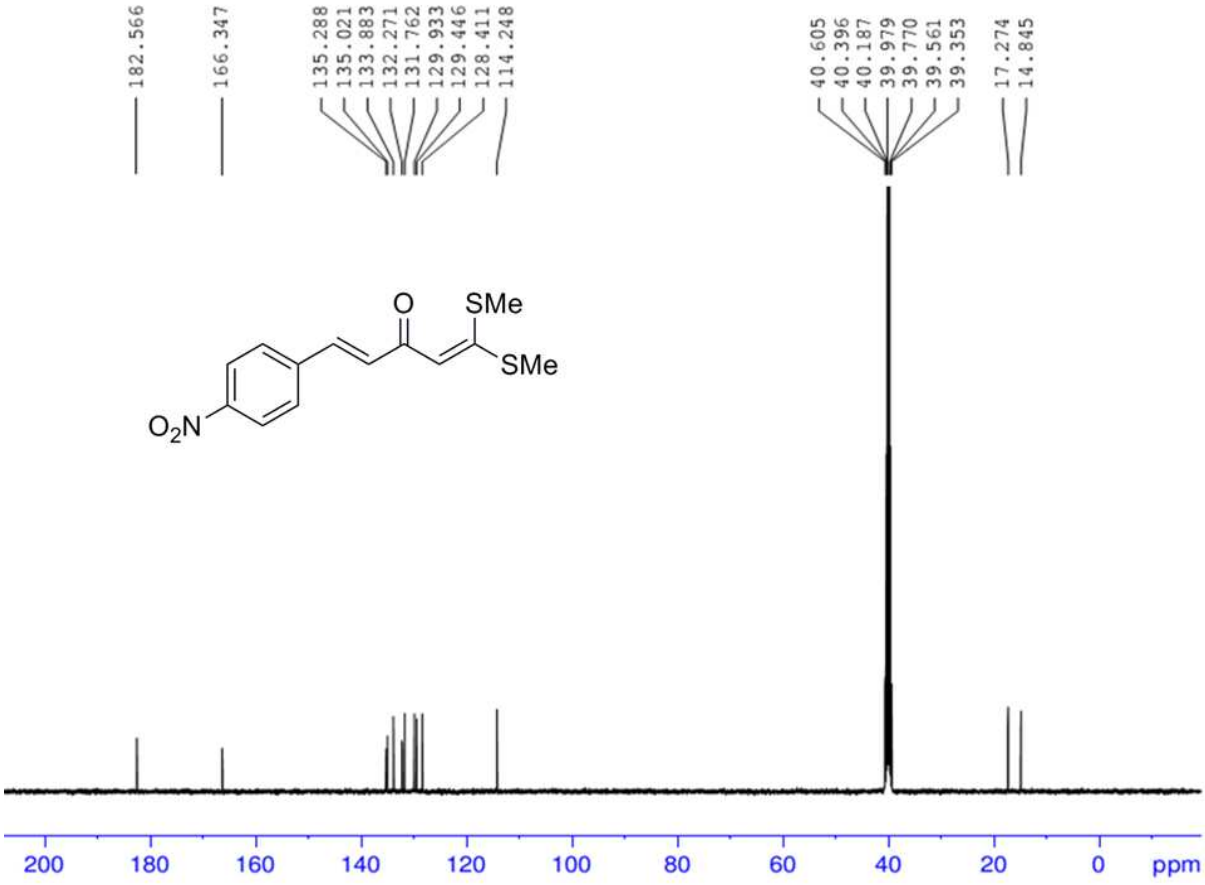

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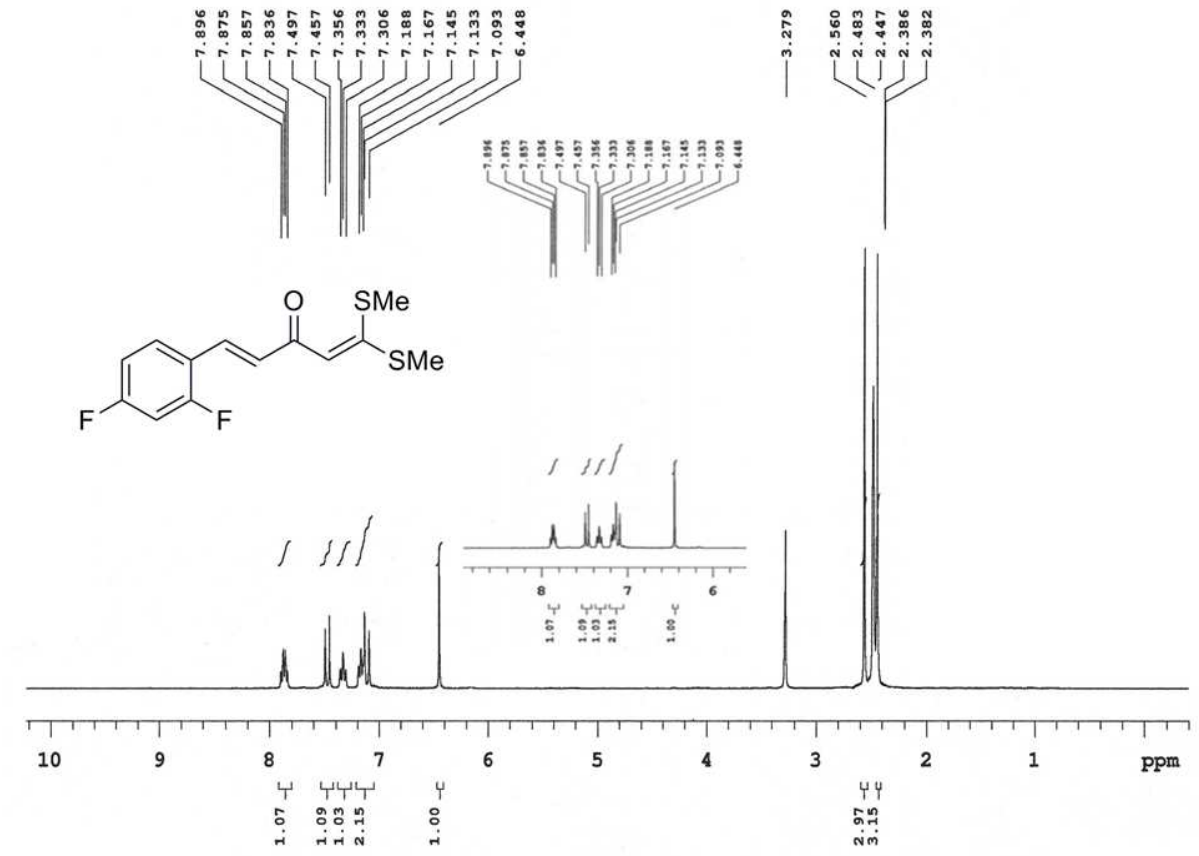
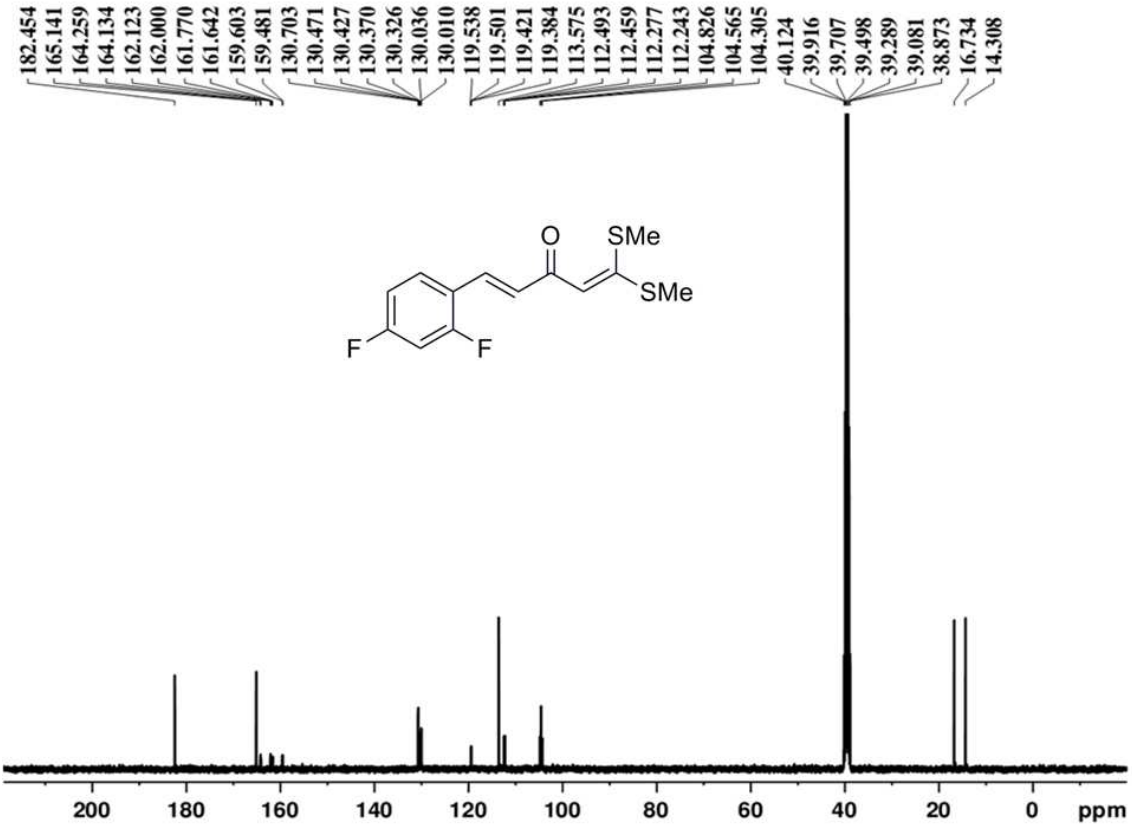
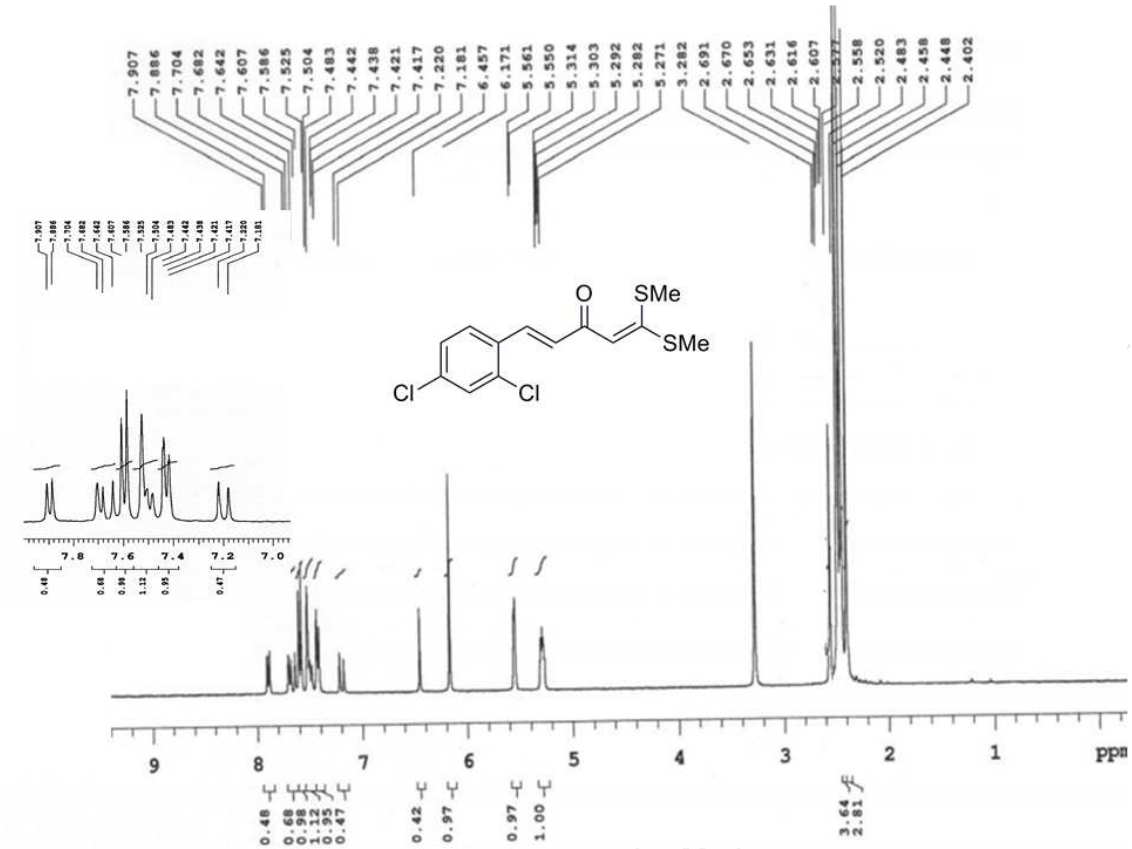


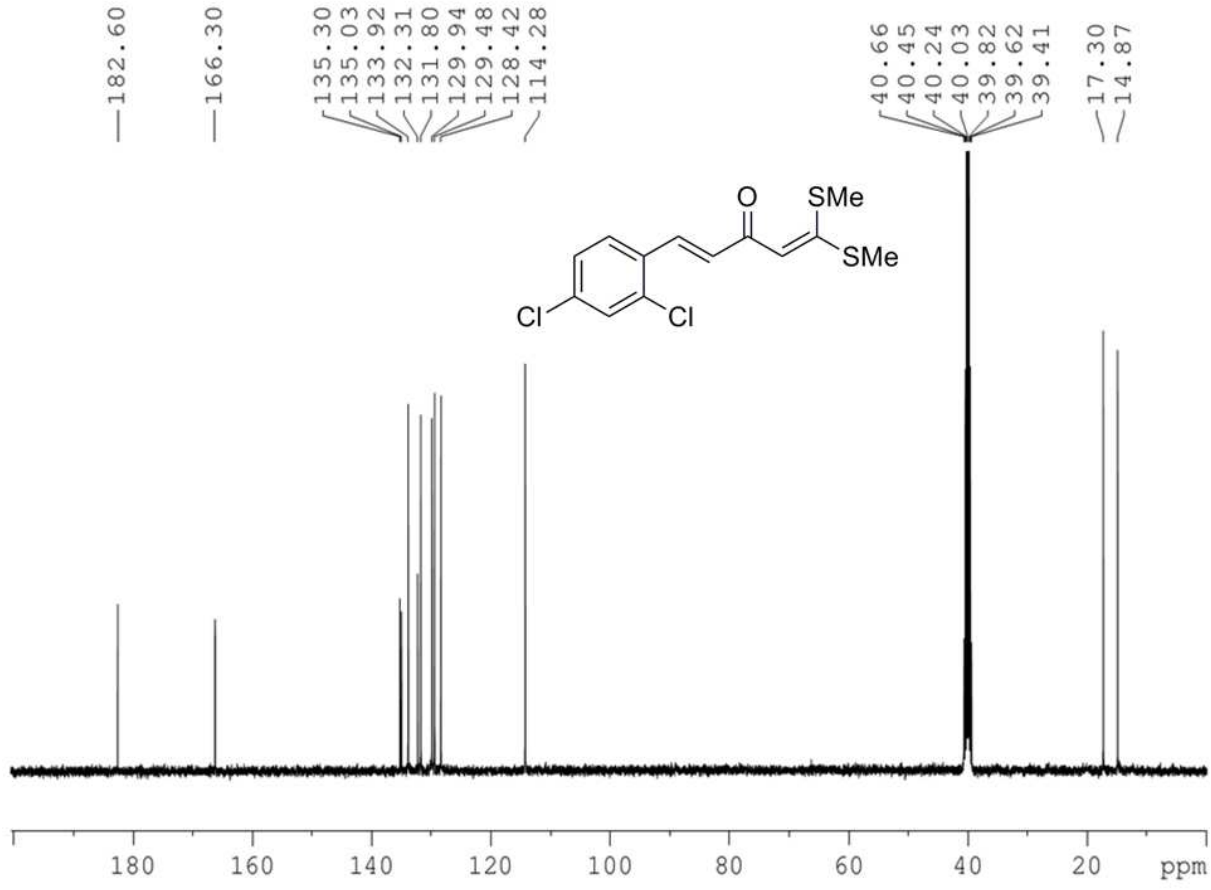
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **2n**



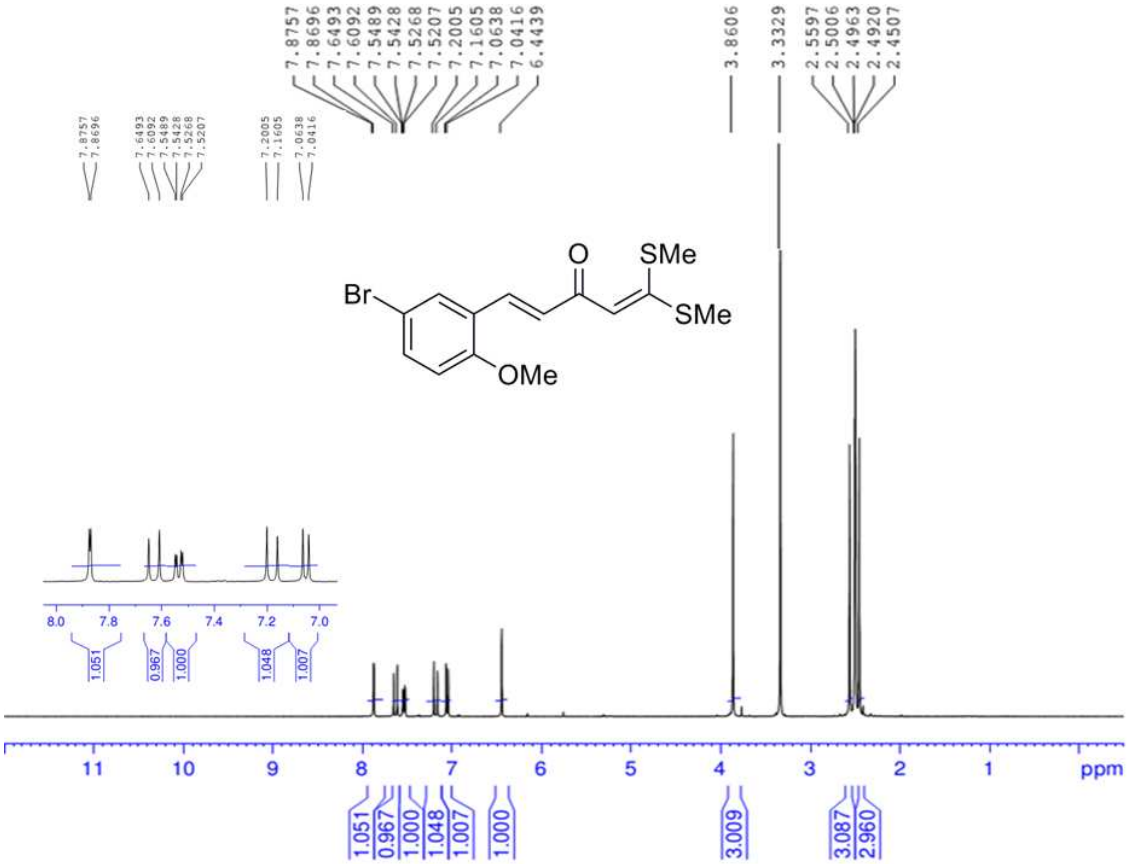
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **2n**



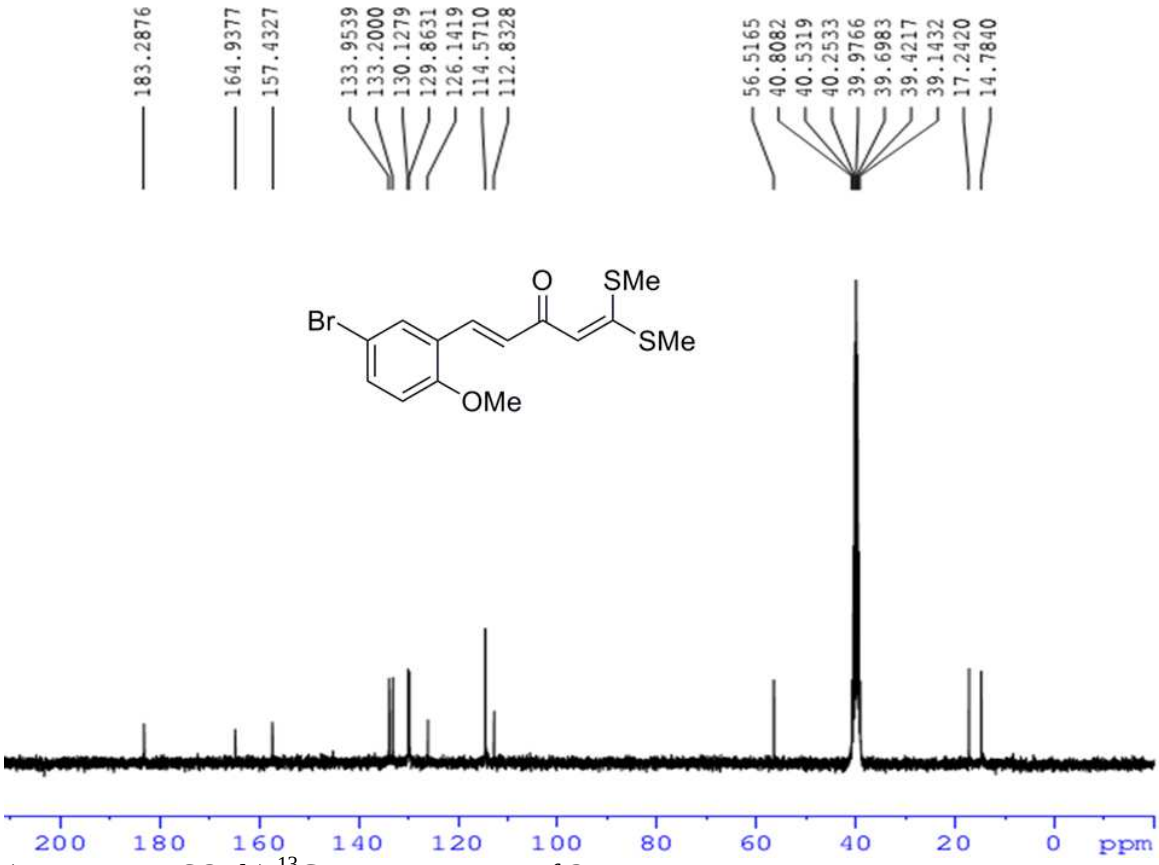
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **2o**



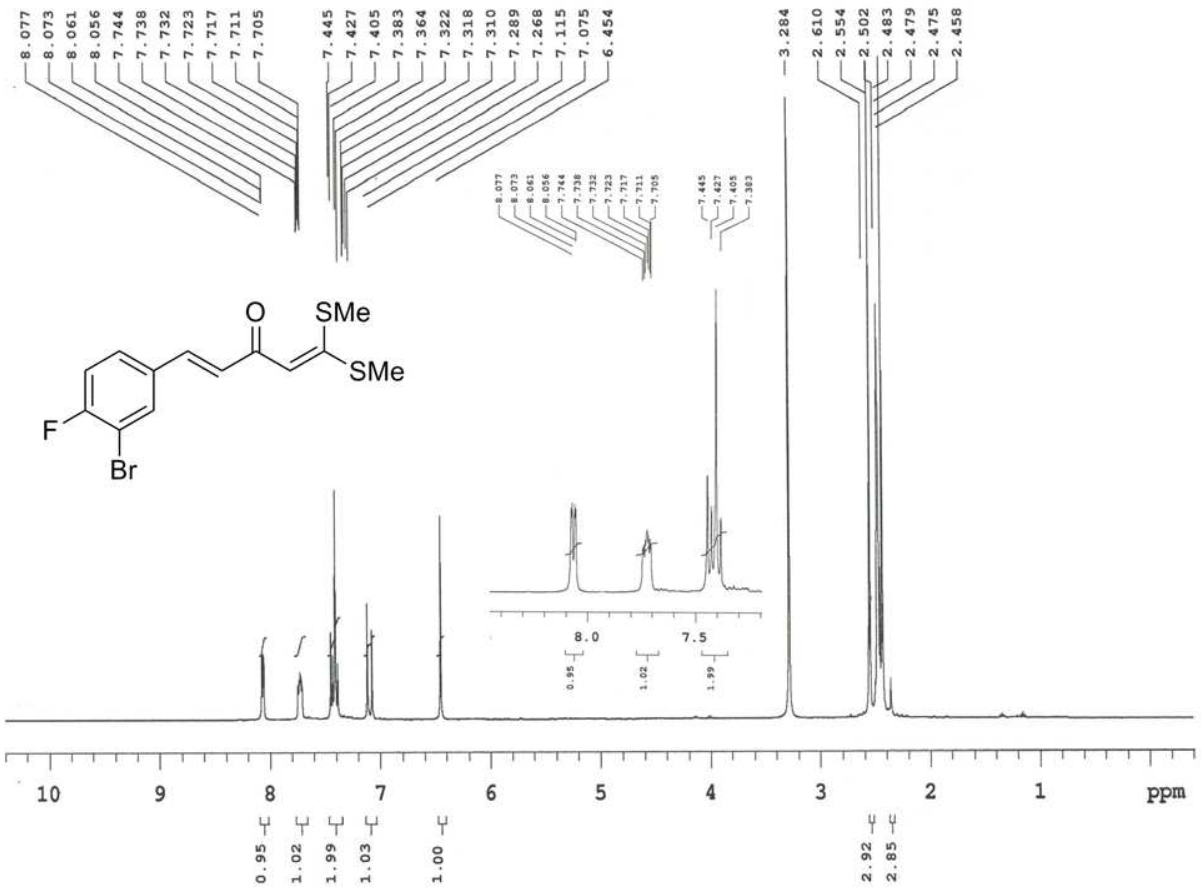
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **2o**



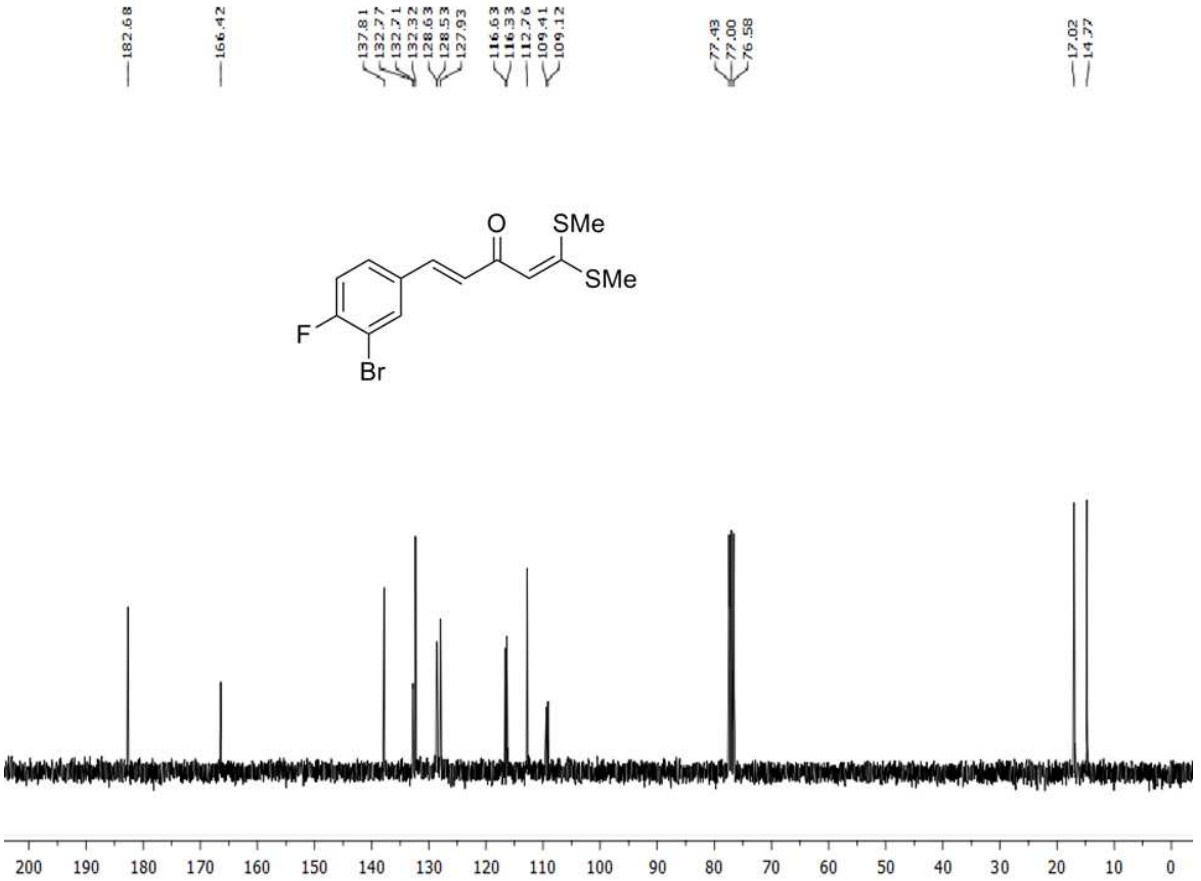
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **2p**



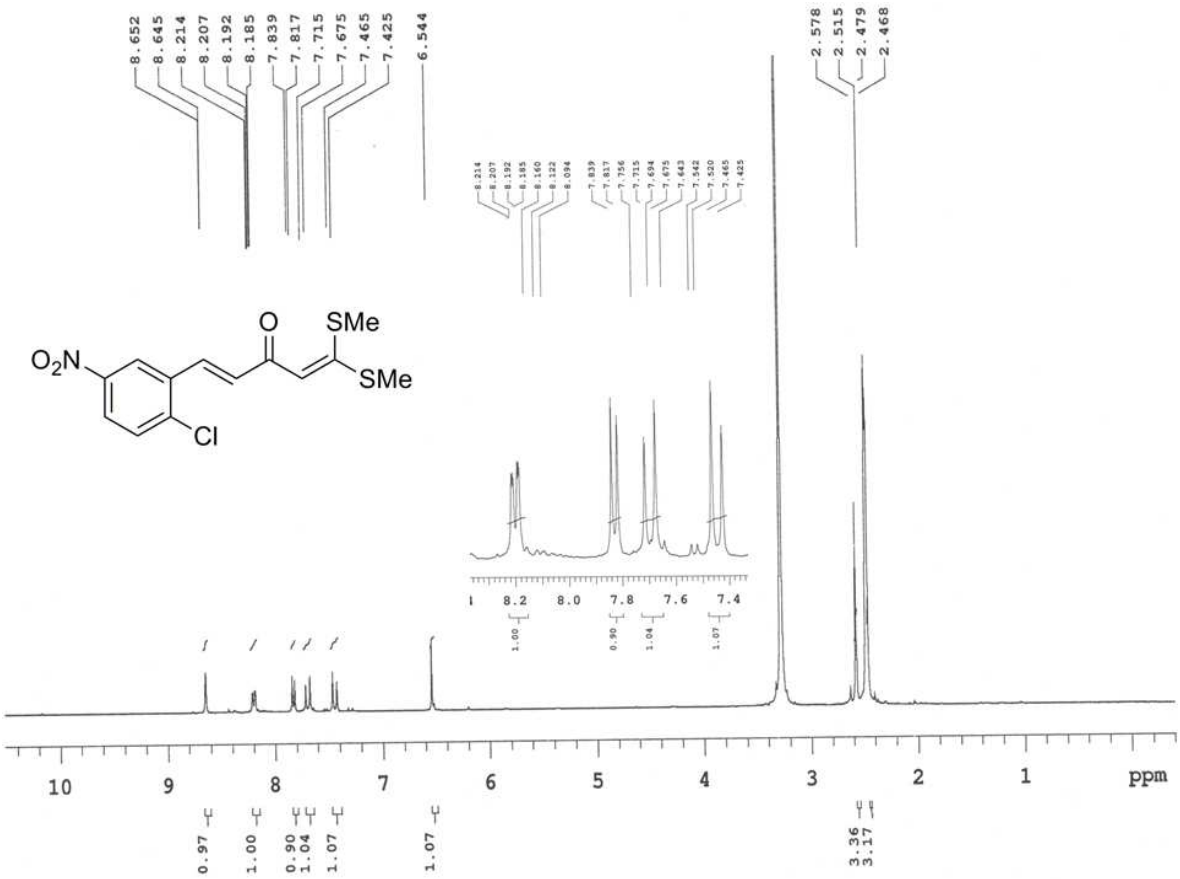
(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **2p**



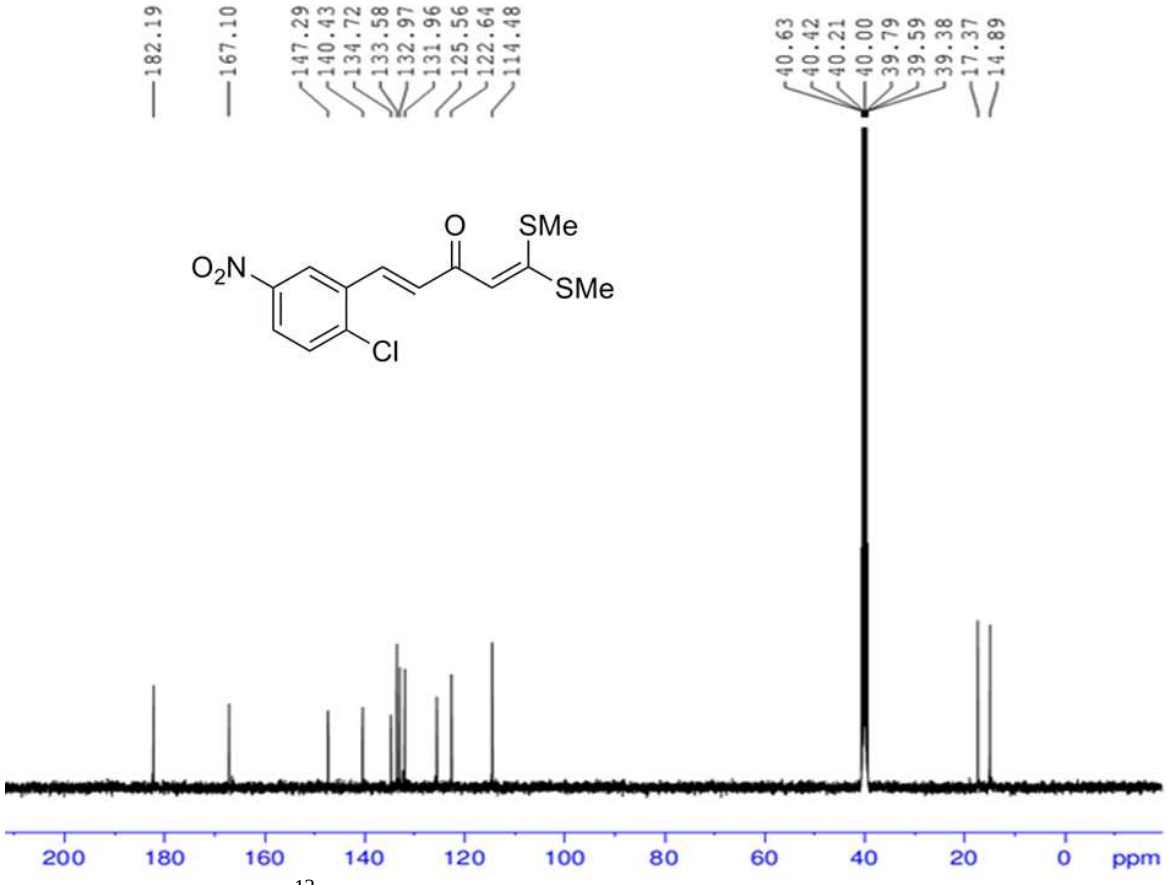
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **2q**



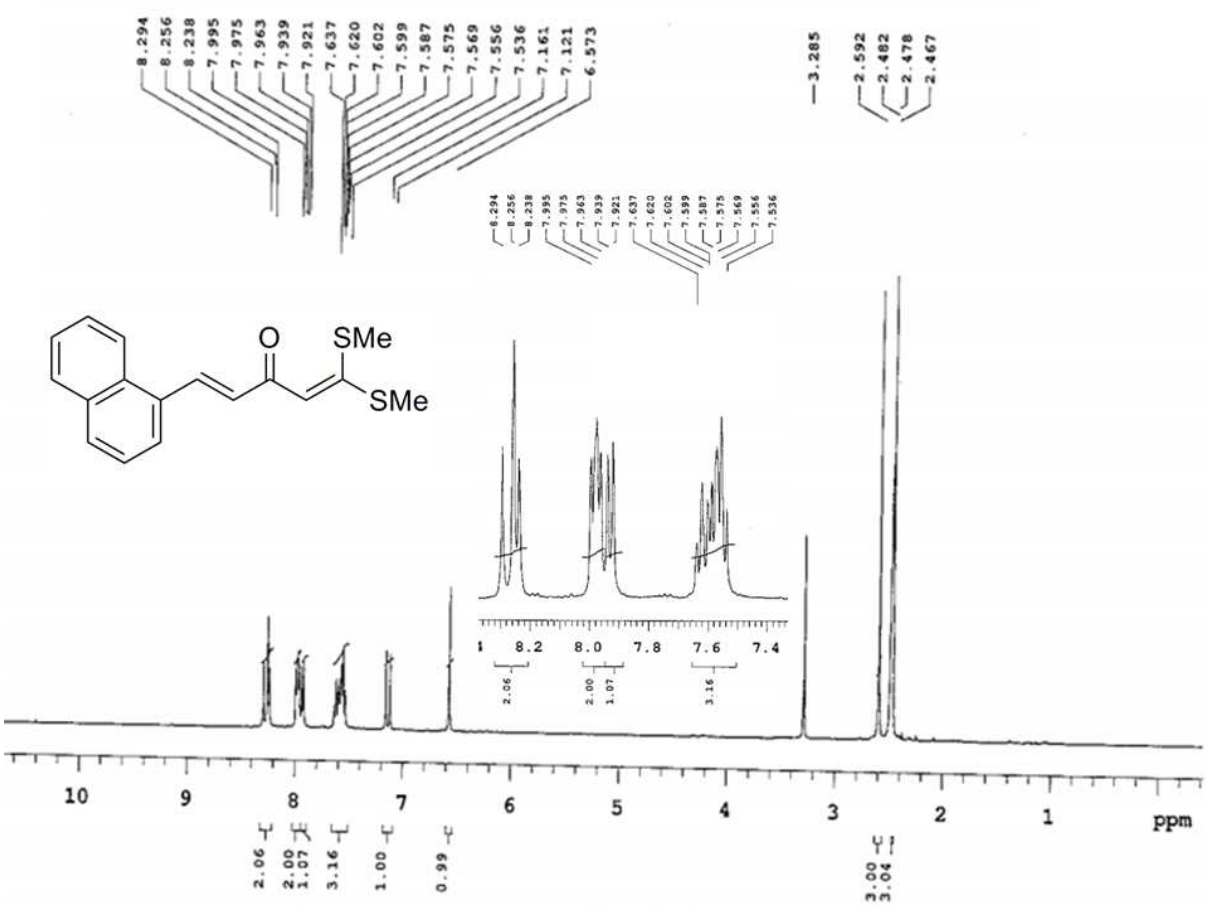
(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **2q**



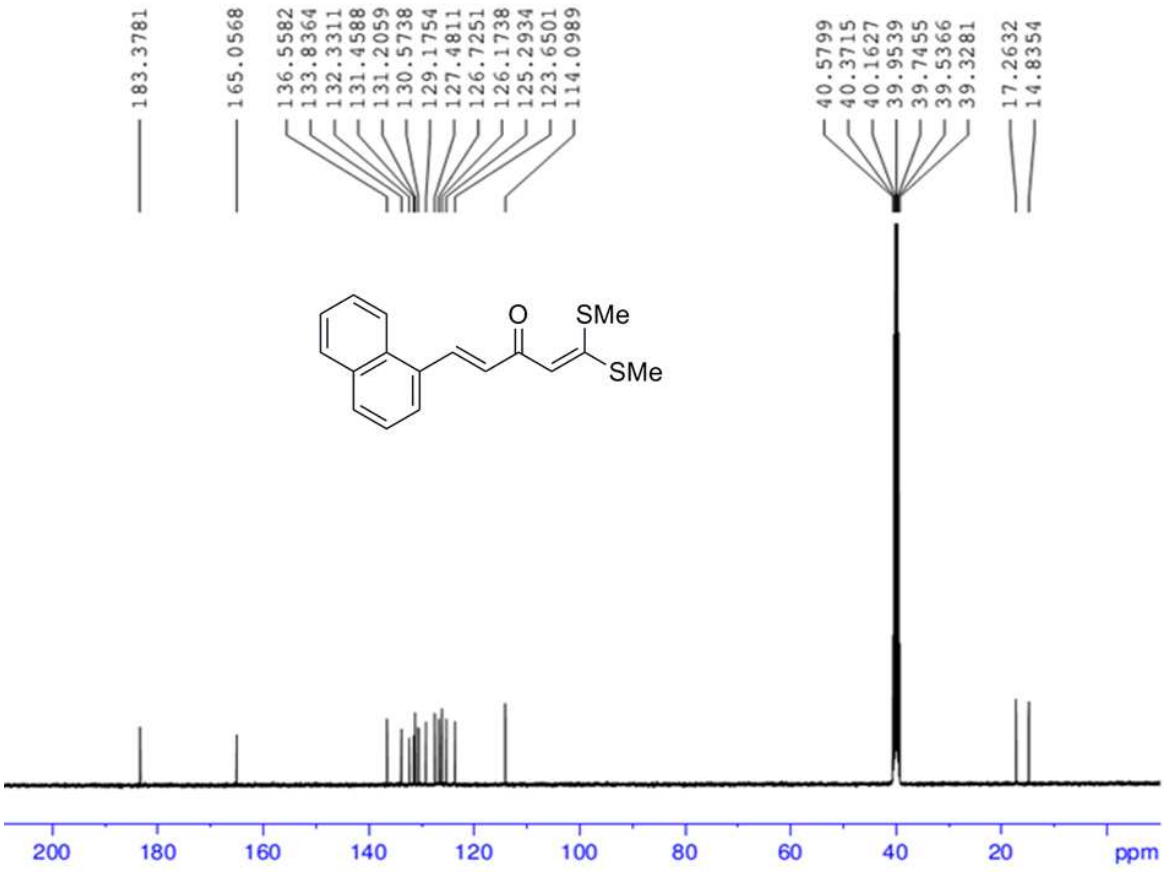
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **2r**



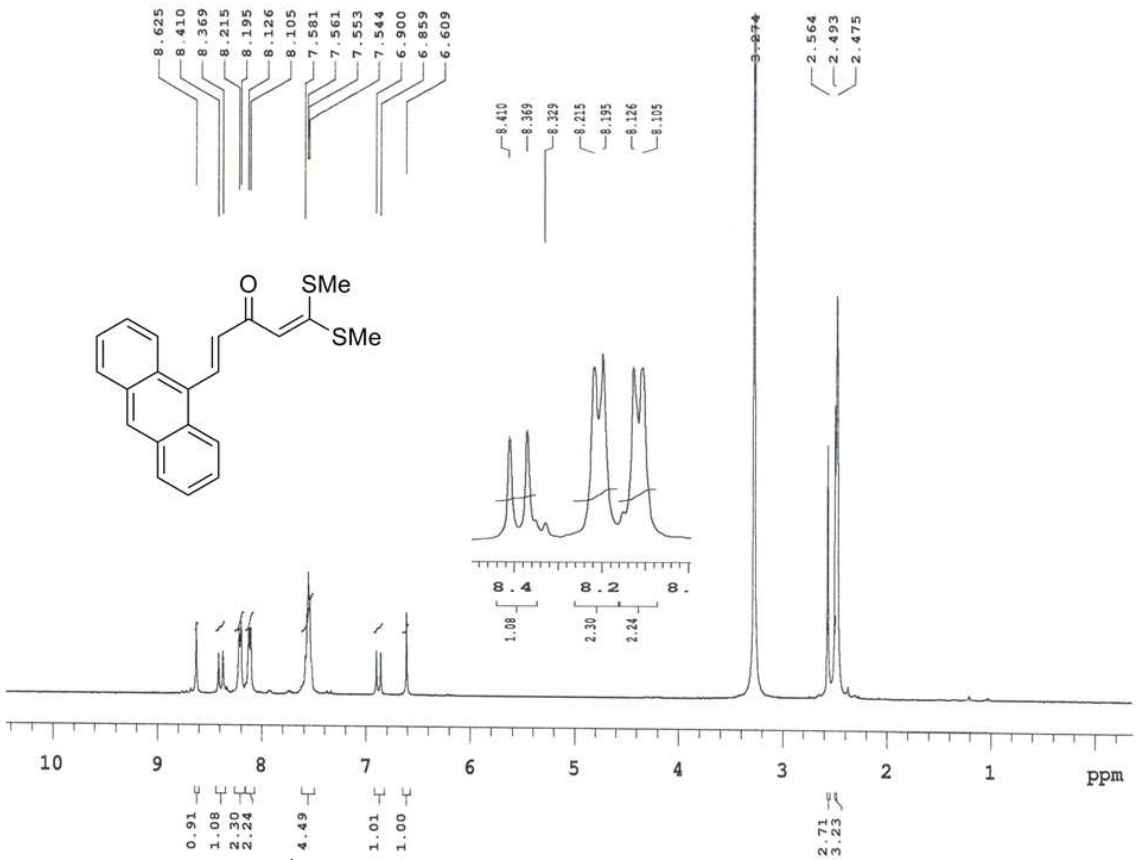
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **2r**



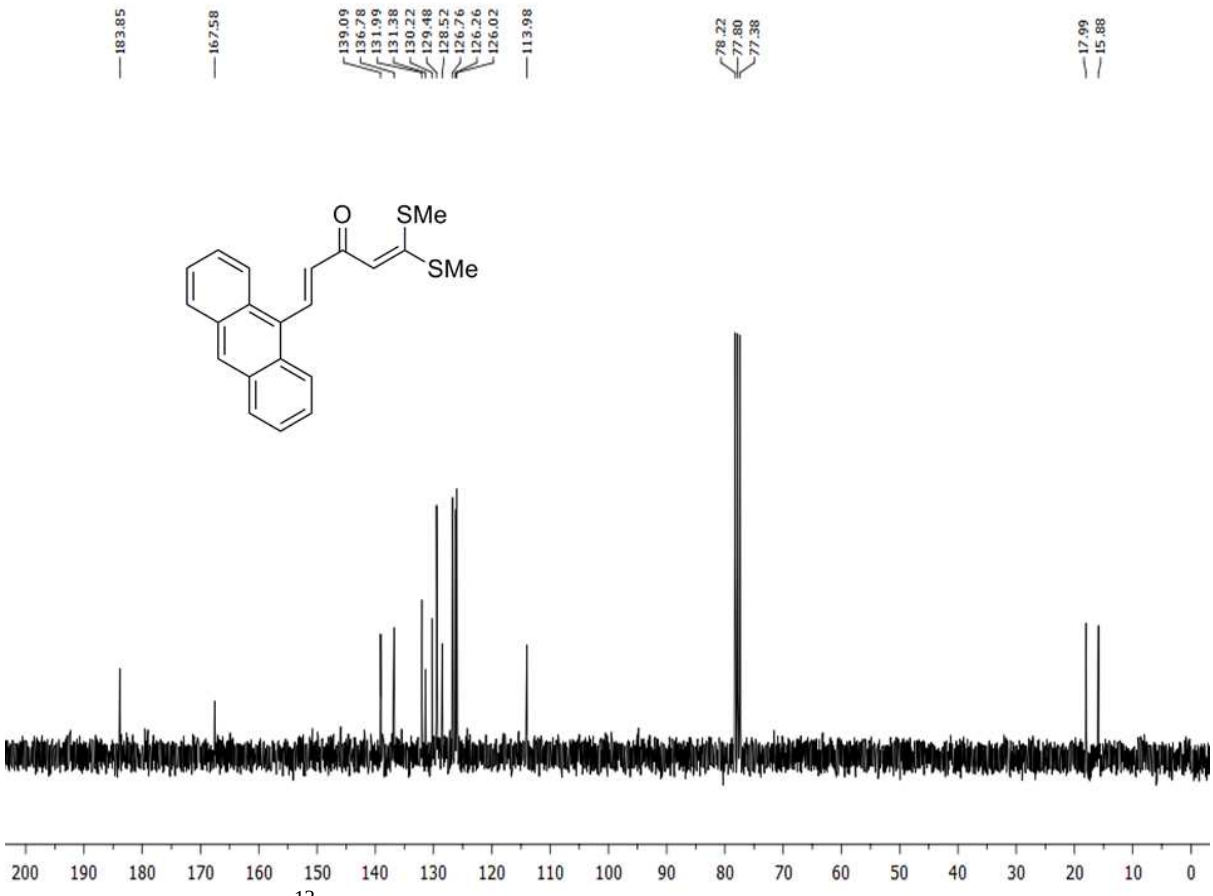
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **2s**



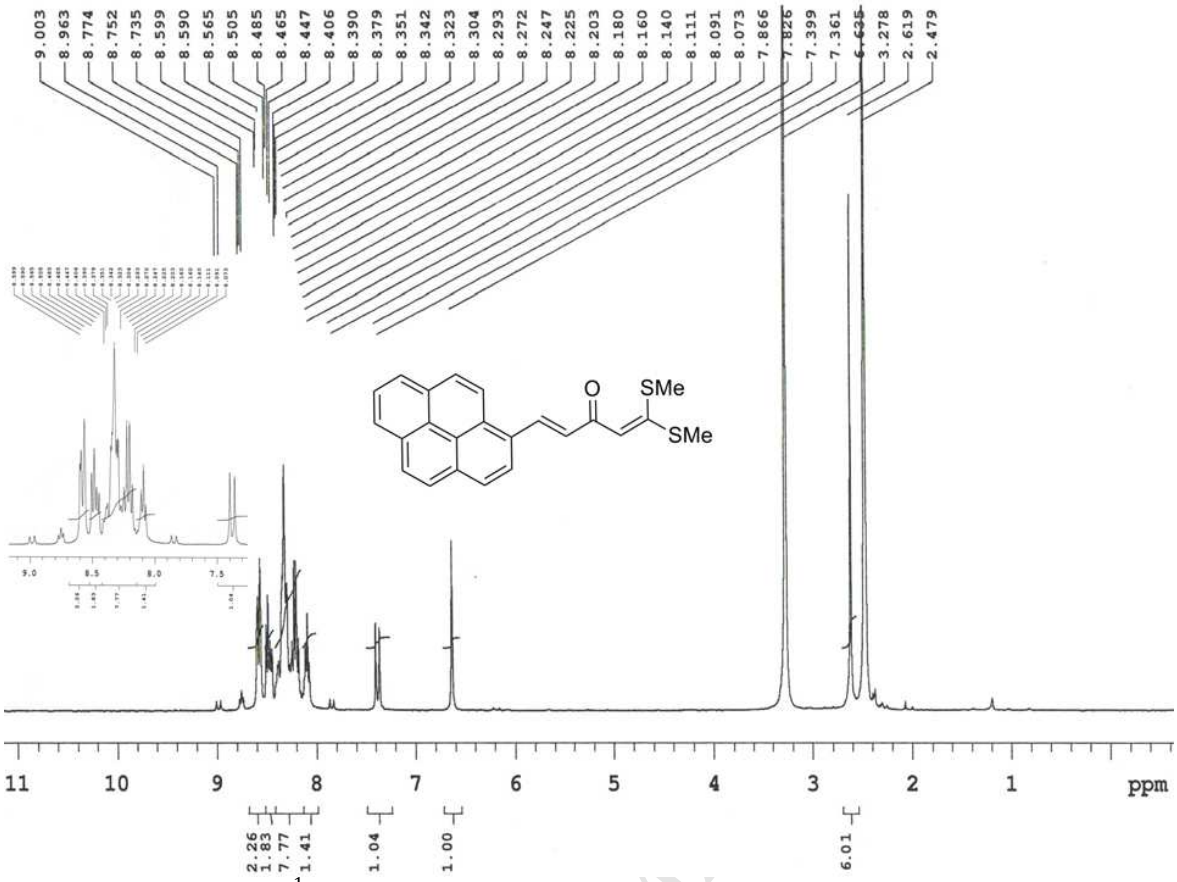
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **2s**



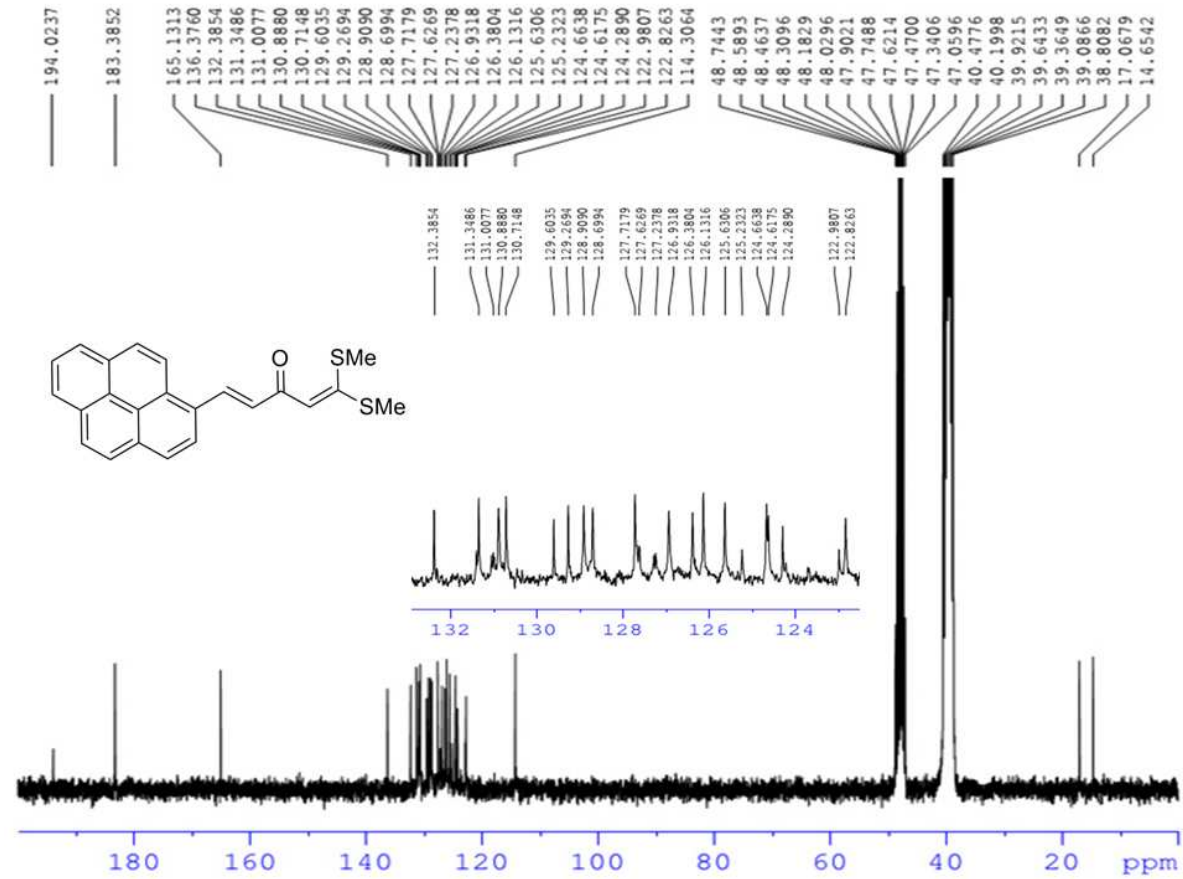
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **2t**



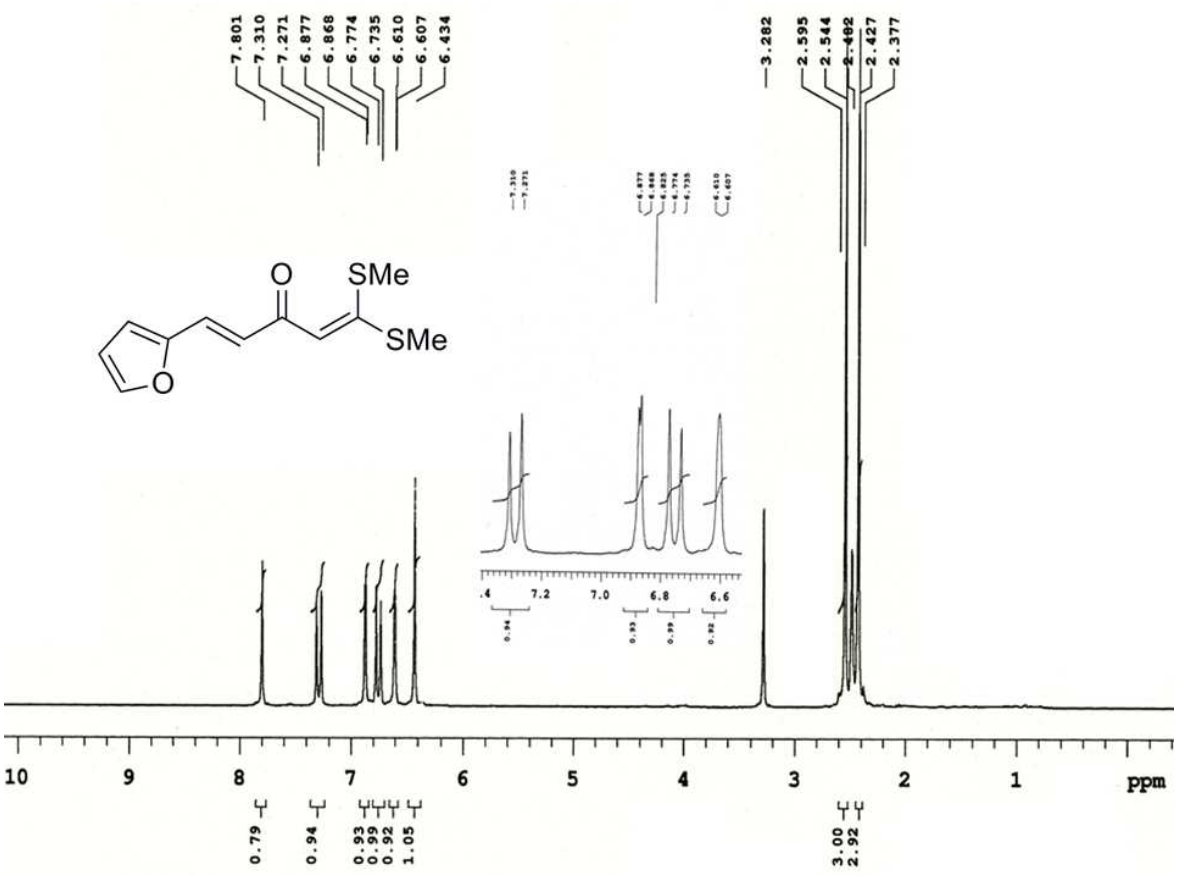
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **2t**



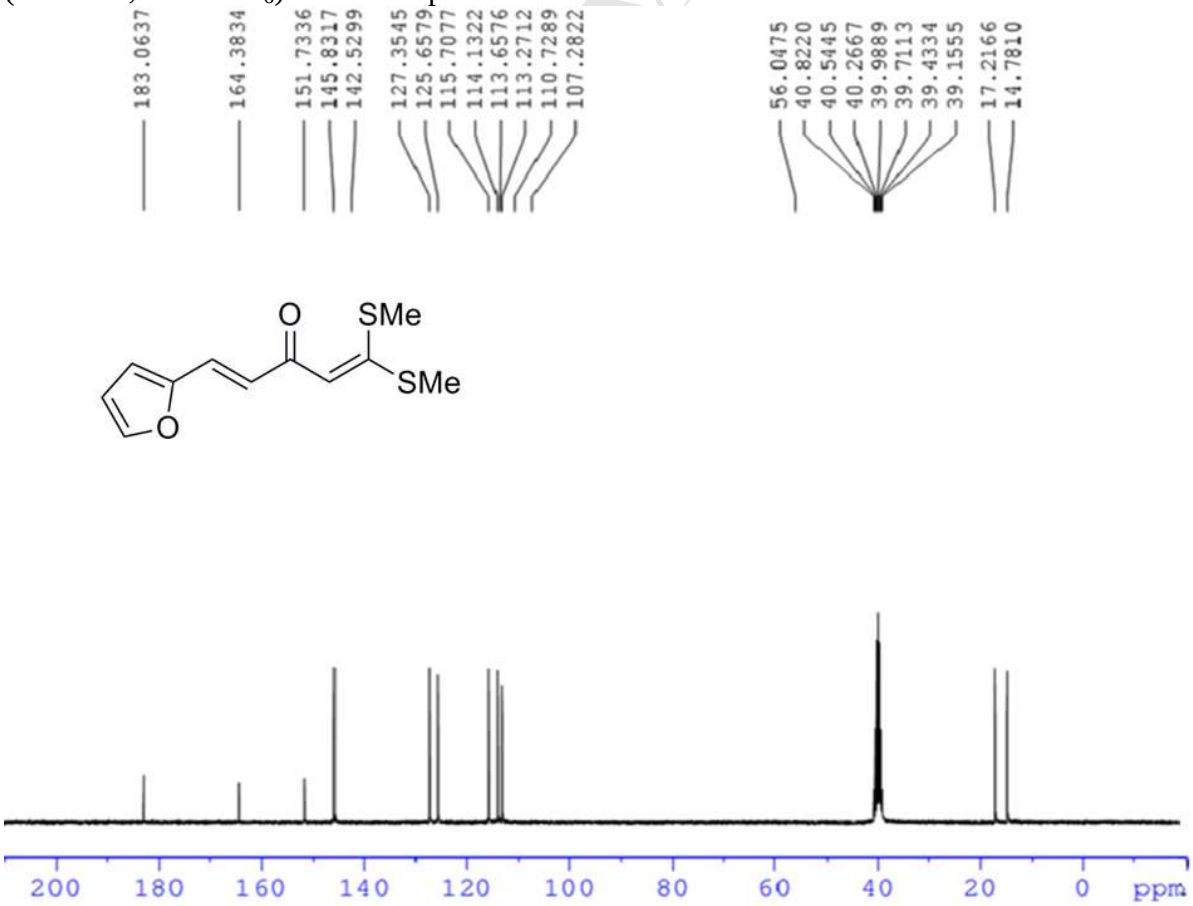
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **2u**



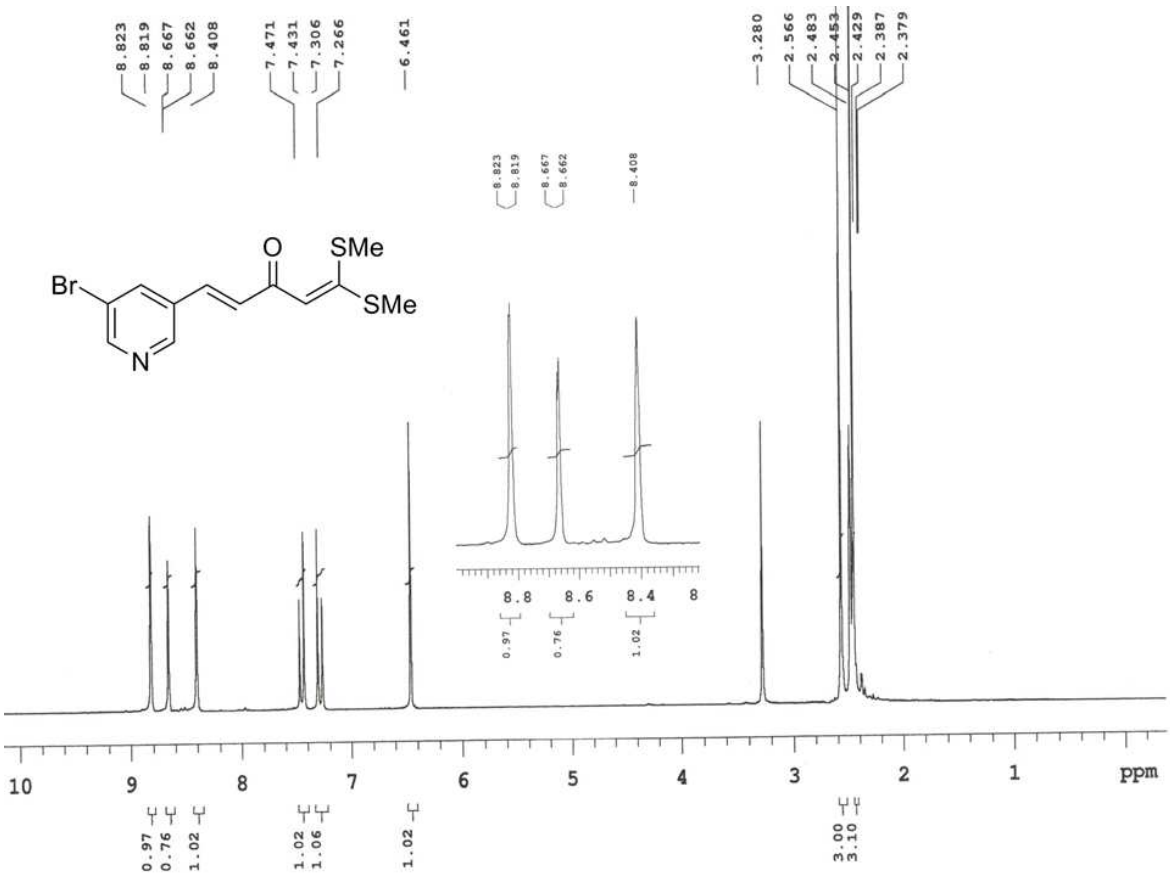
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **2u**



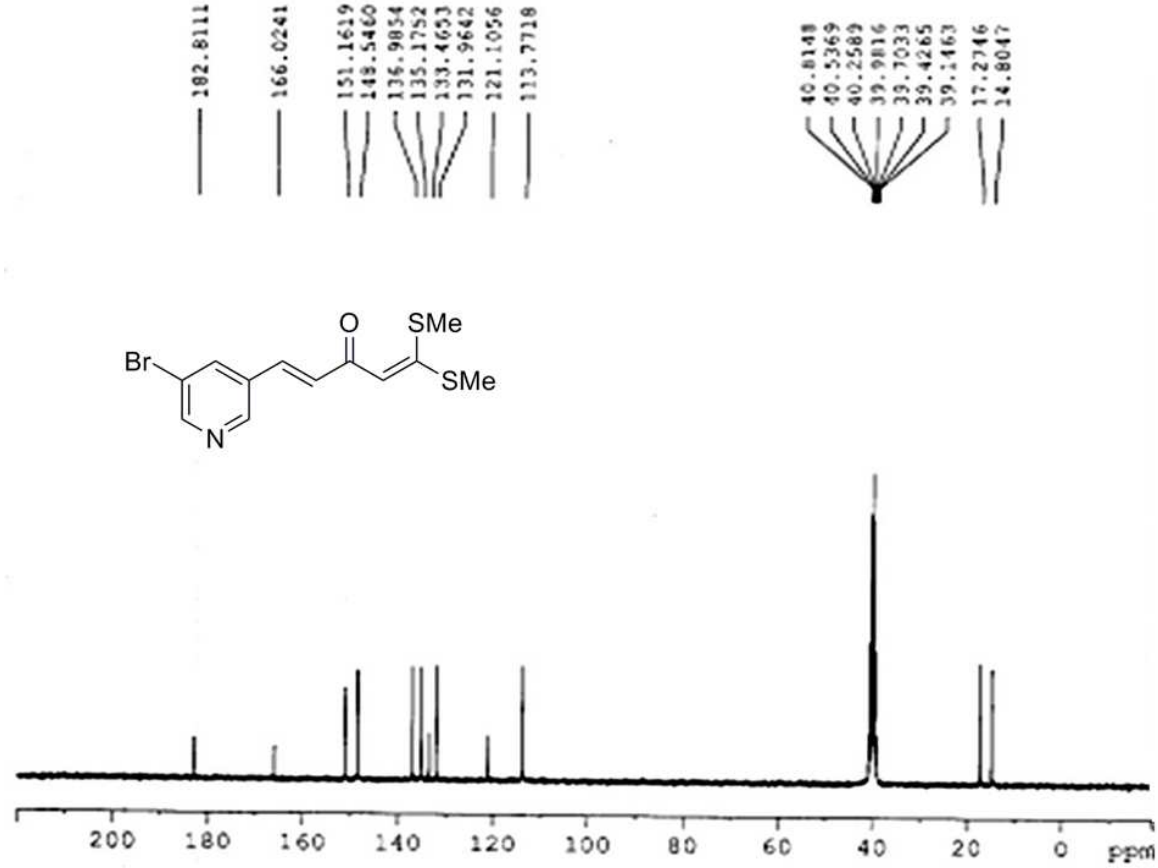
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **2v**



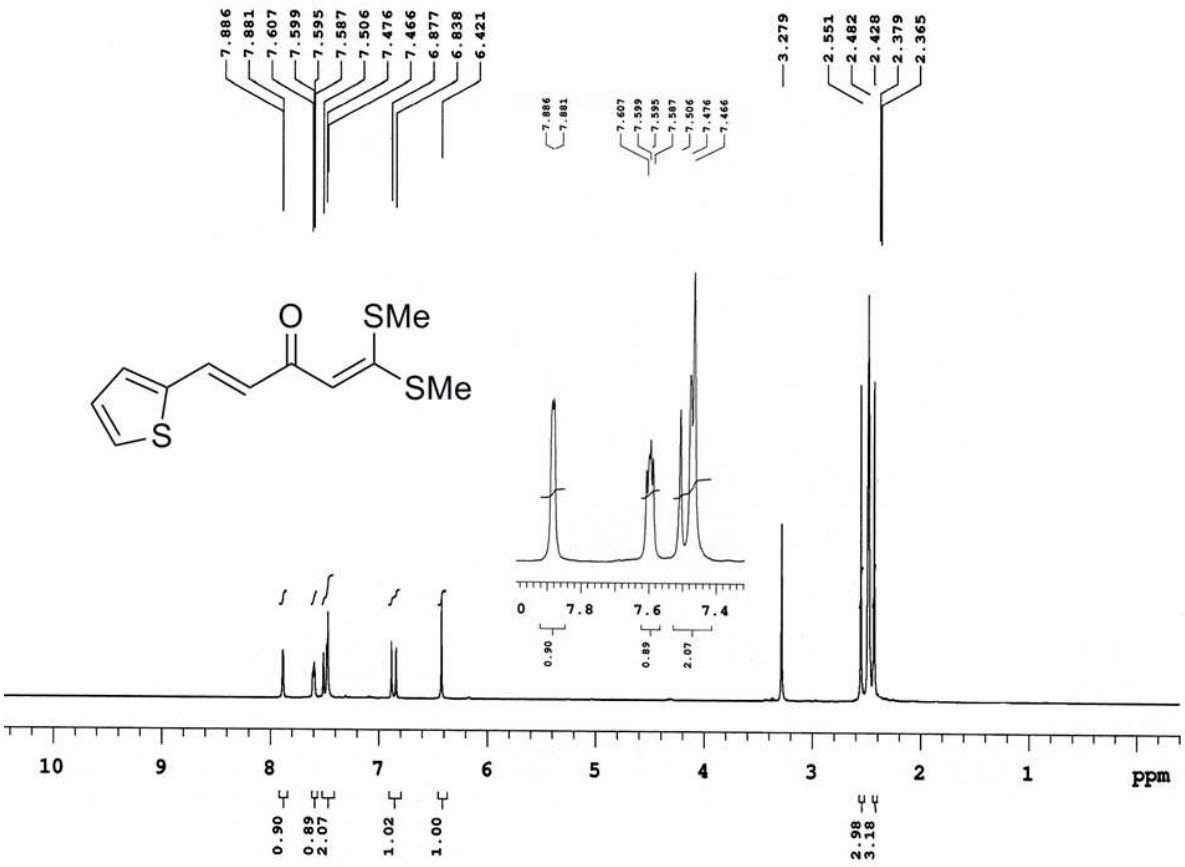
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **2v**



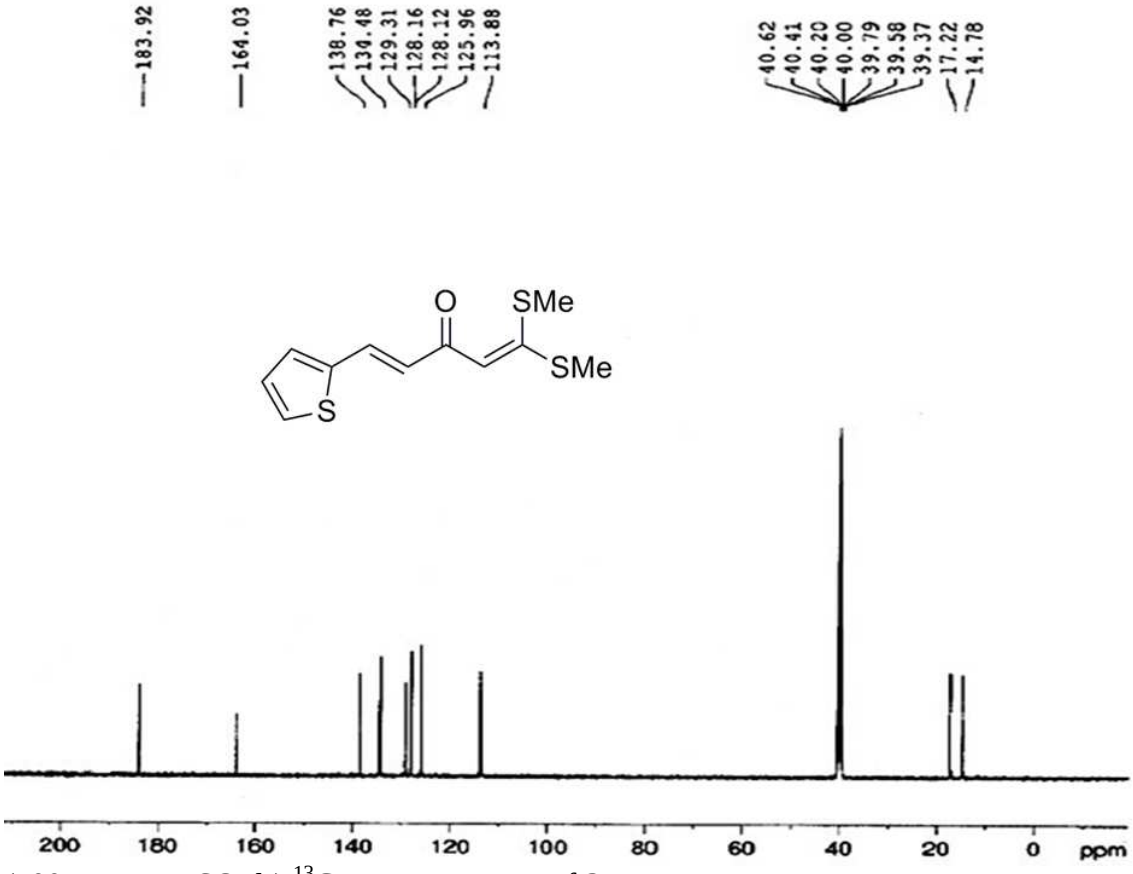
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **2w**



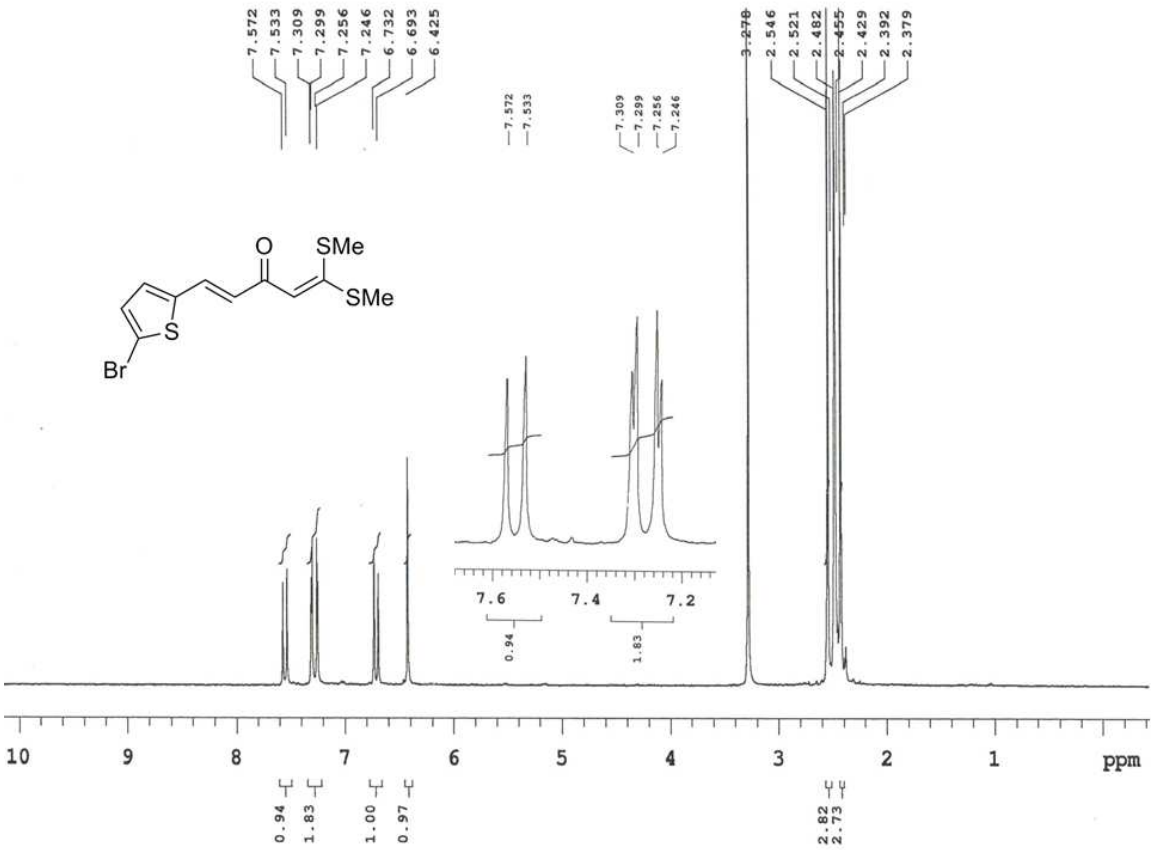
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **2w**



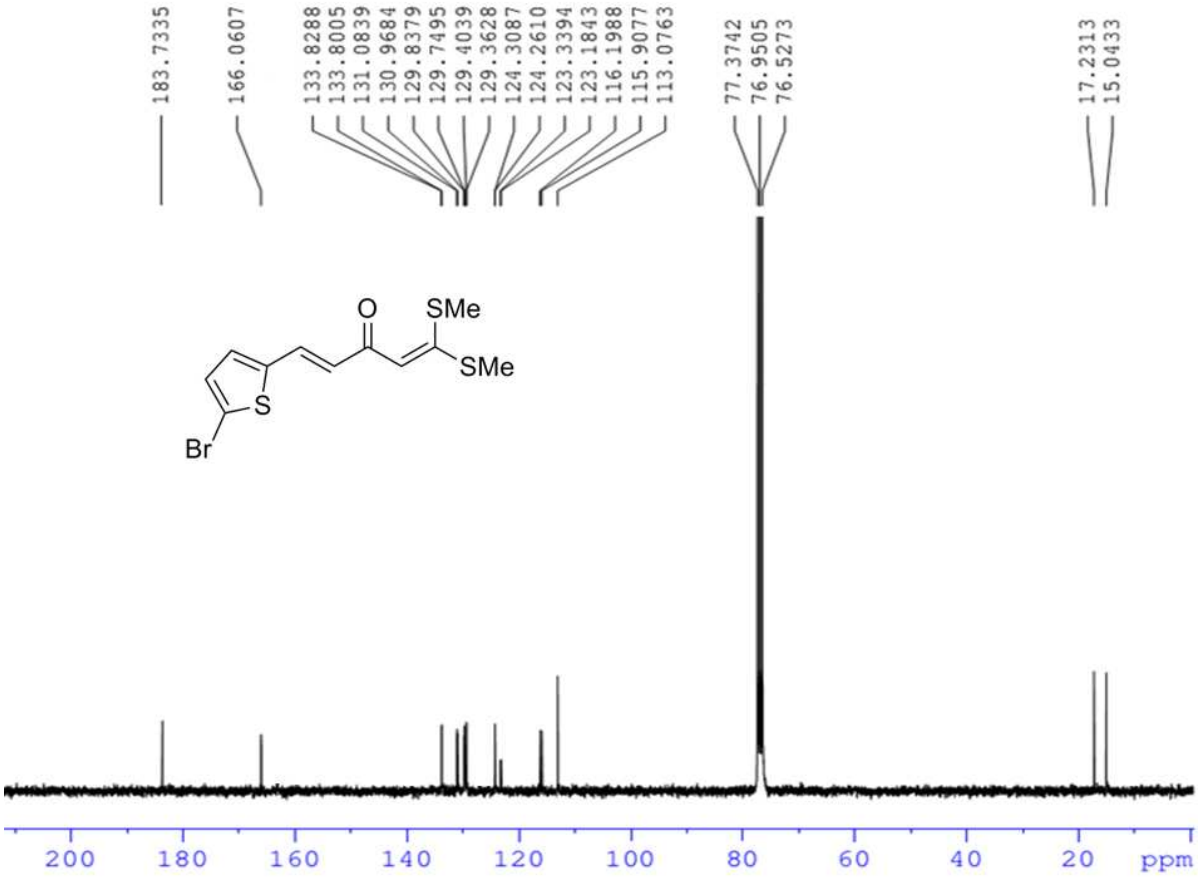
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **2x**



(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **2x**

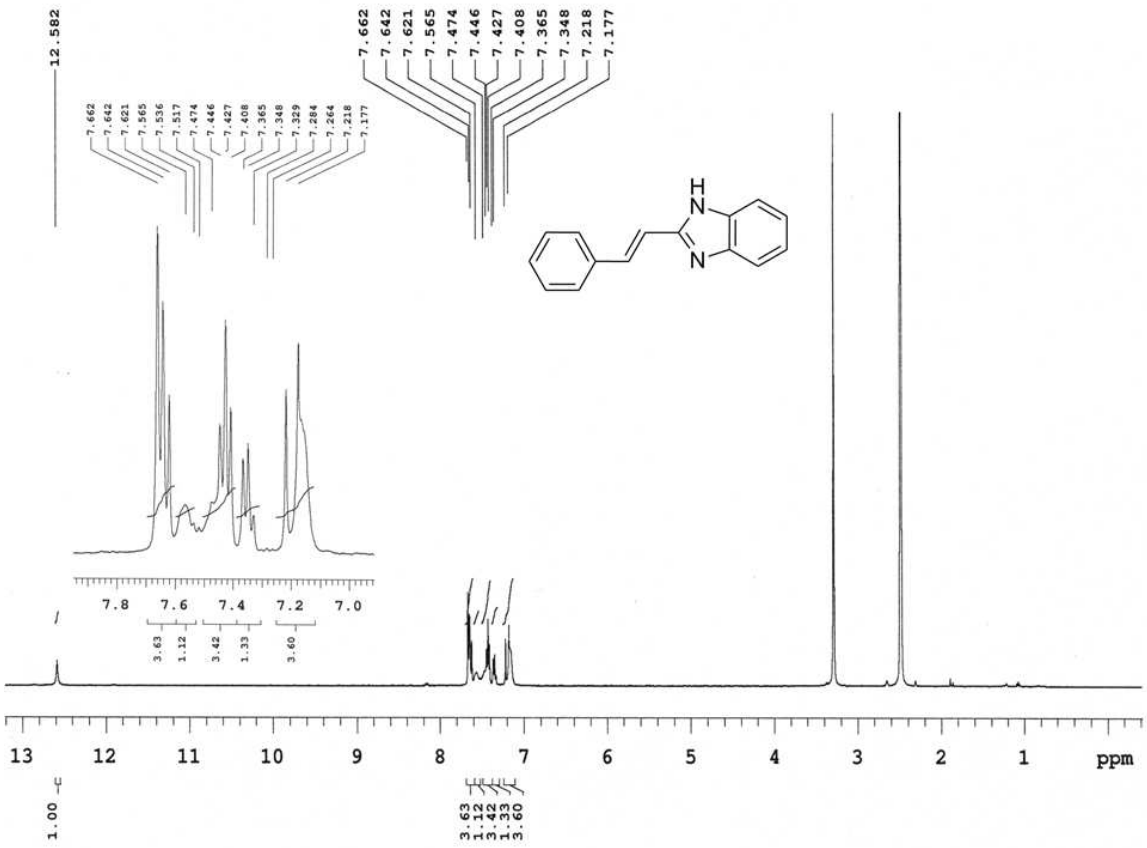


(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **2y**

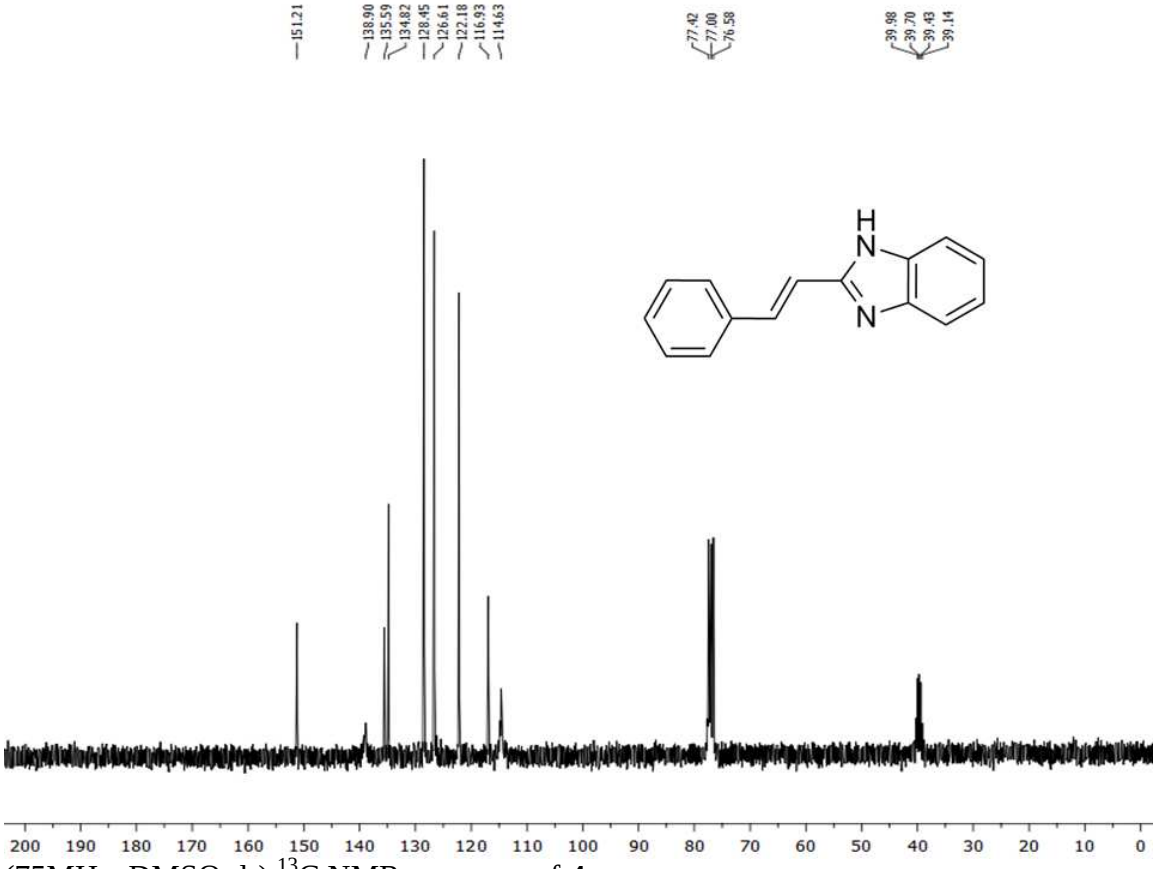


(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **2y**

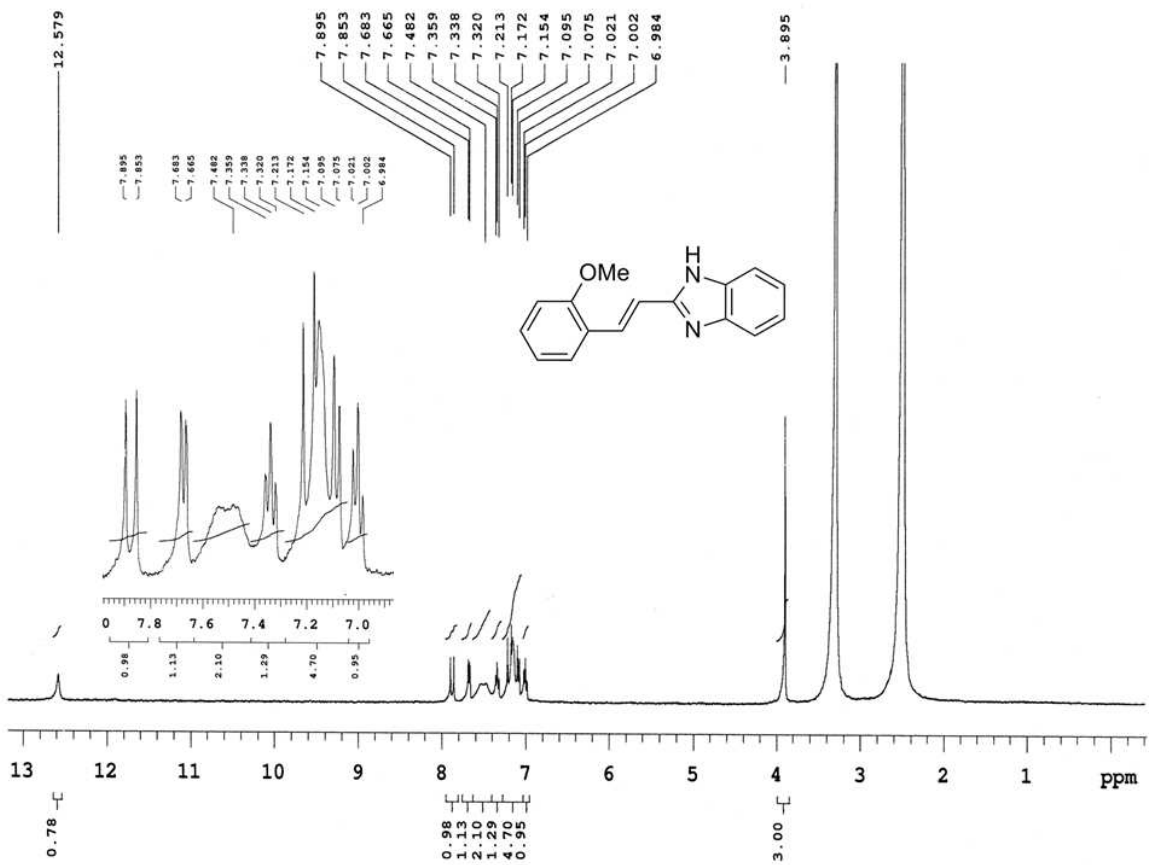
IV Copies of ^{1}H NMR&^{13}C NMR spectra 4a-y



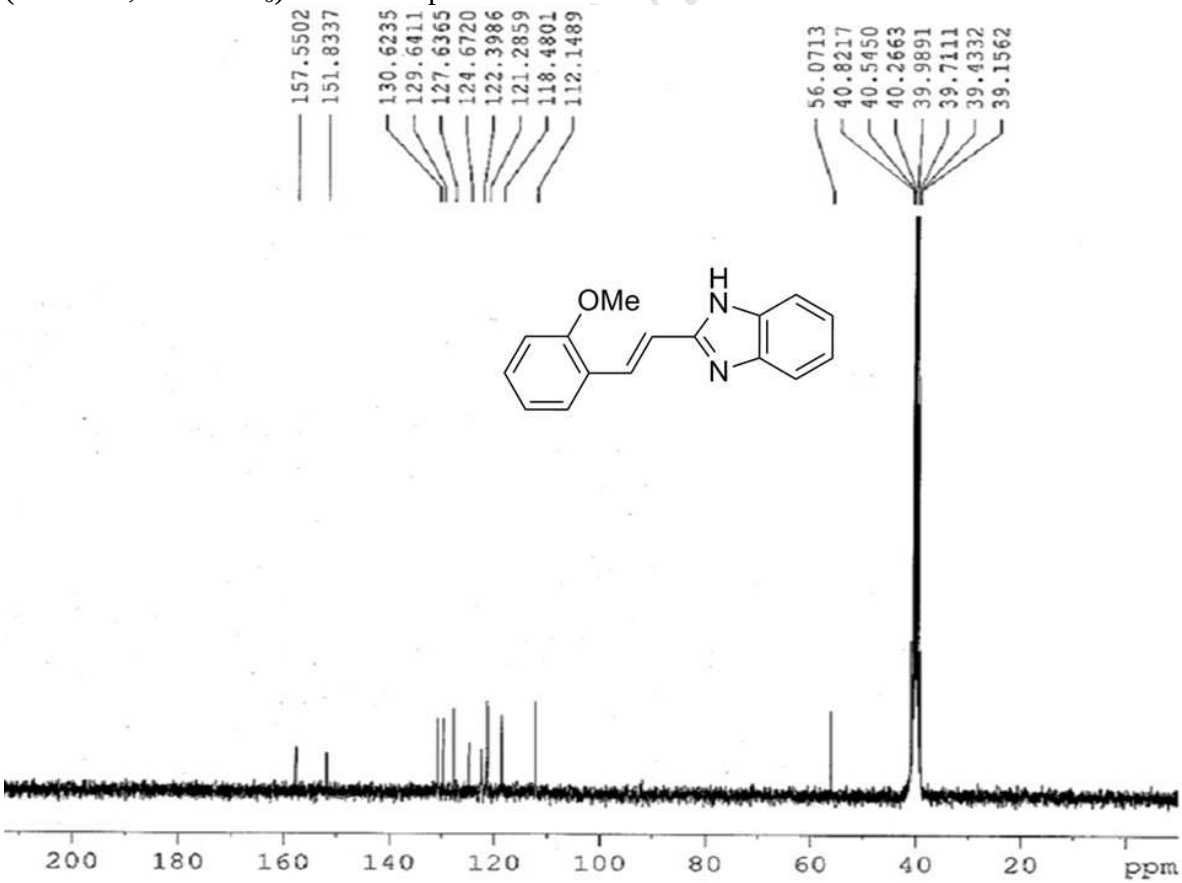
(400MHz, DMSO-d_6) ^{1}H NMR spectrum **4a**



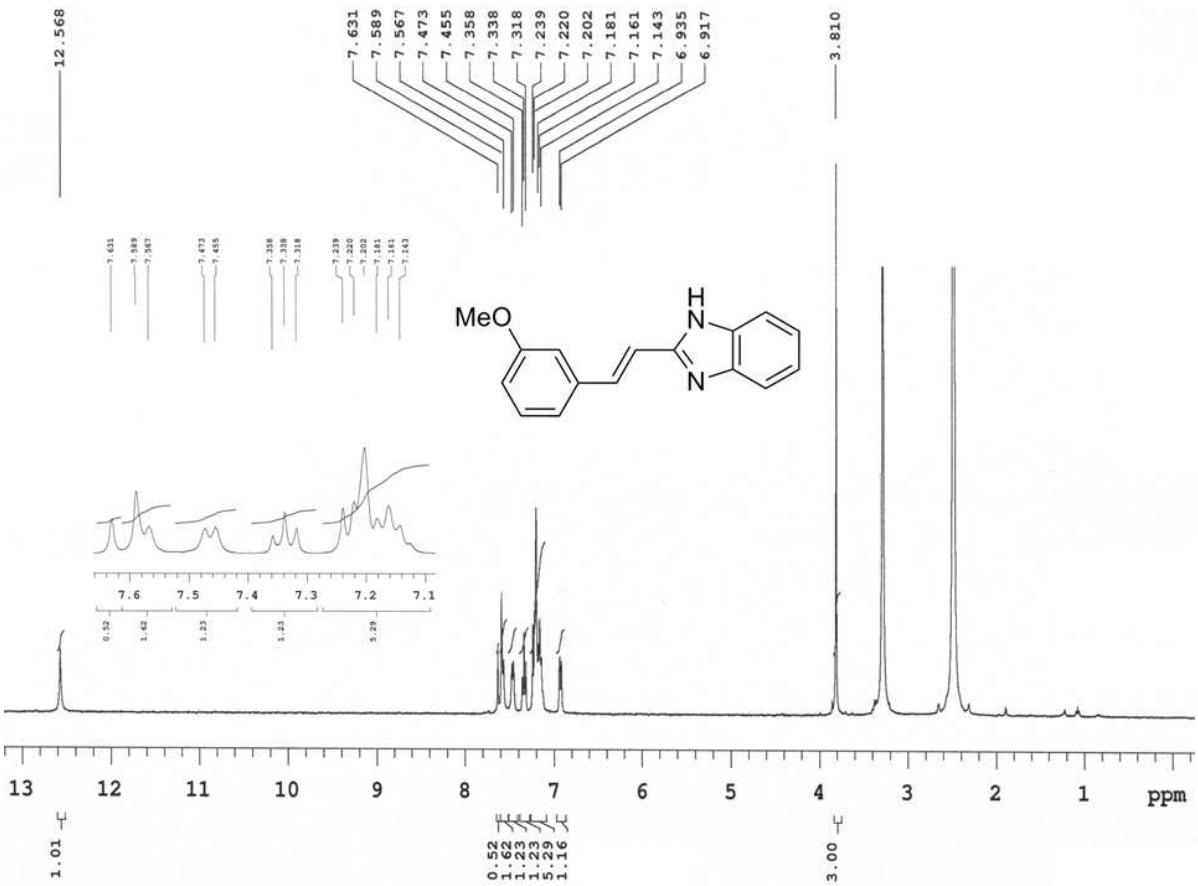
(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **4a**



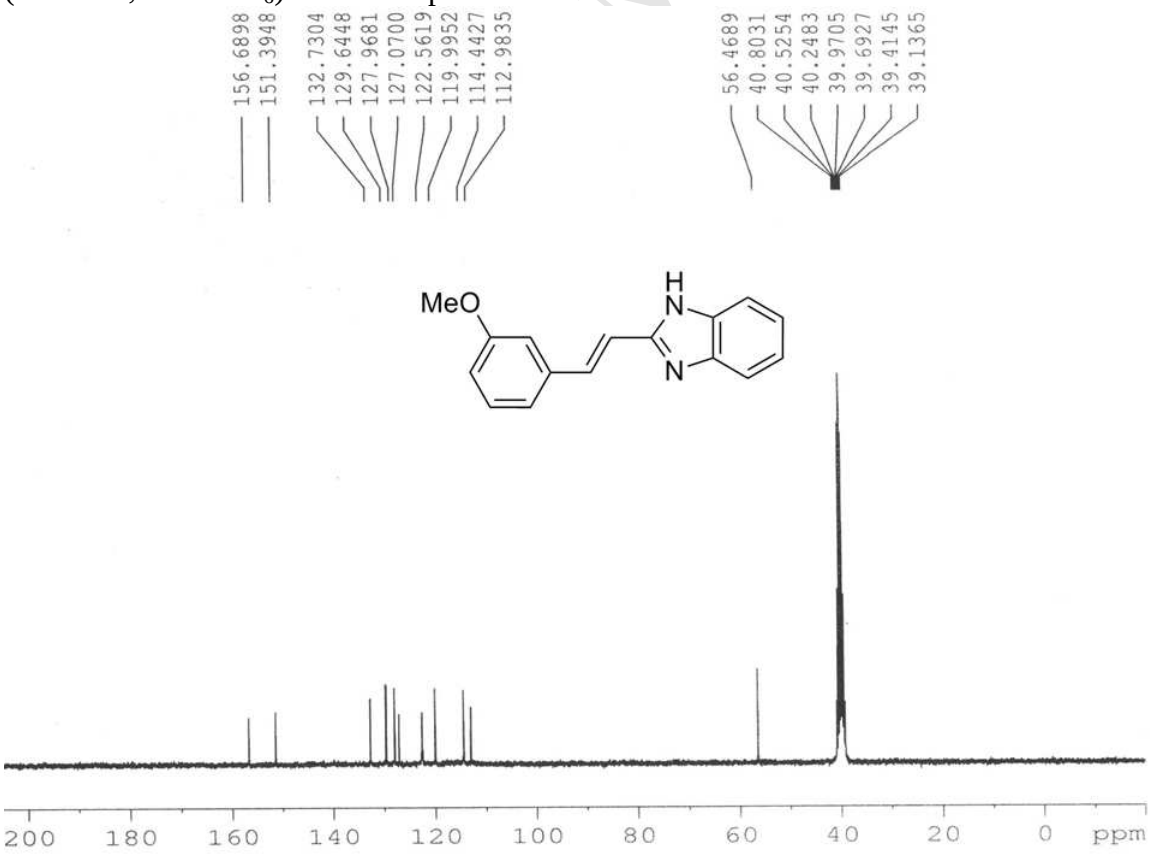
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4b**



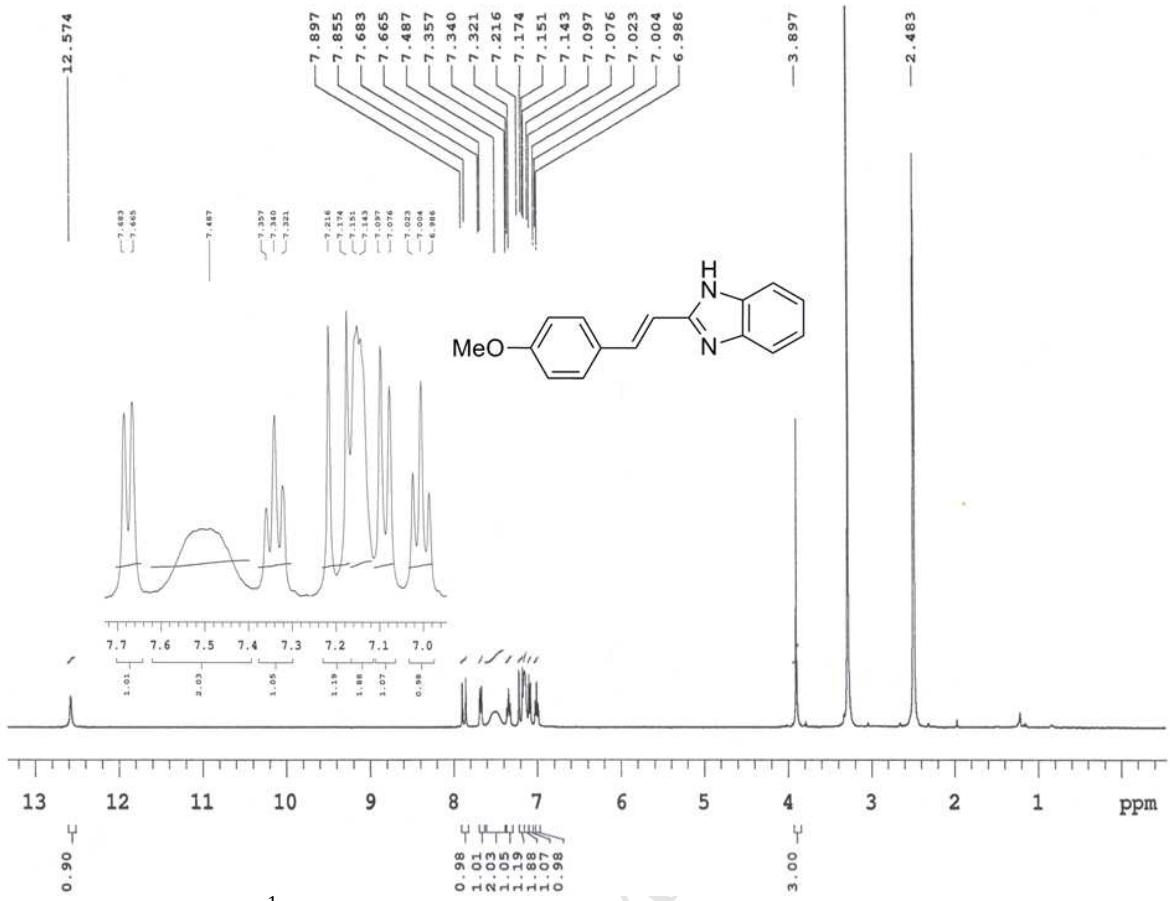
(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **4b**



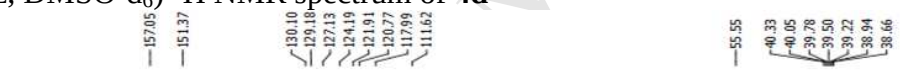
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4c**

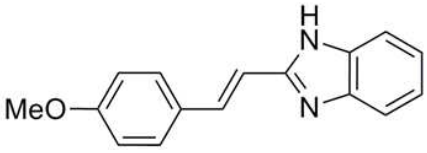


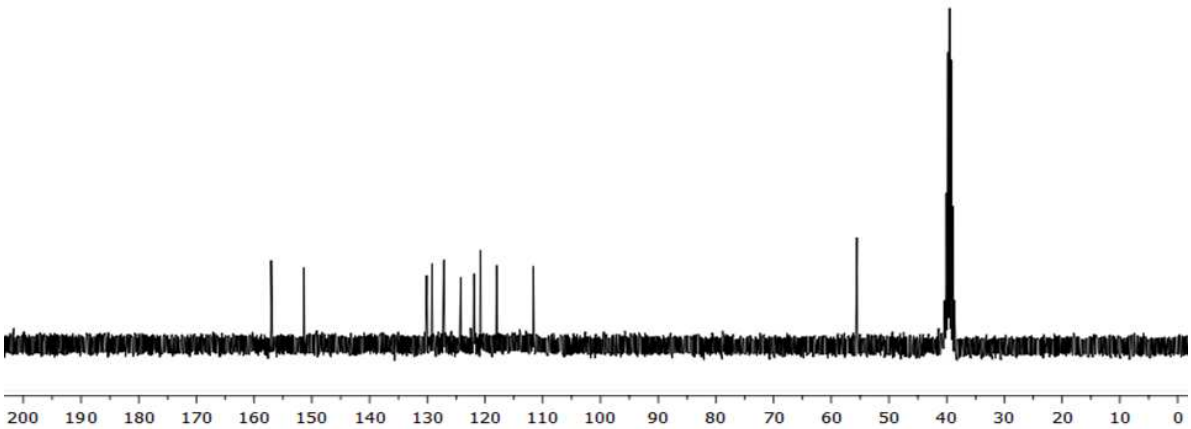
(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **4c**



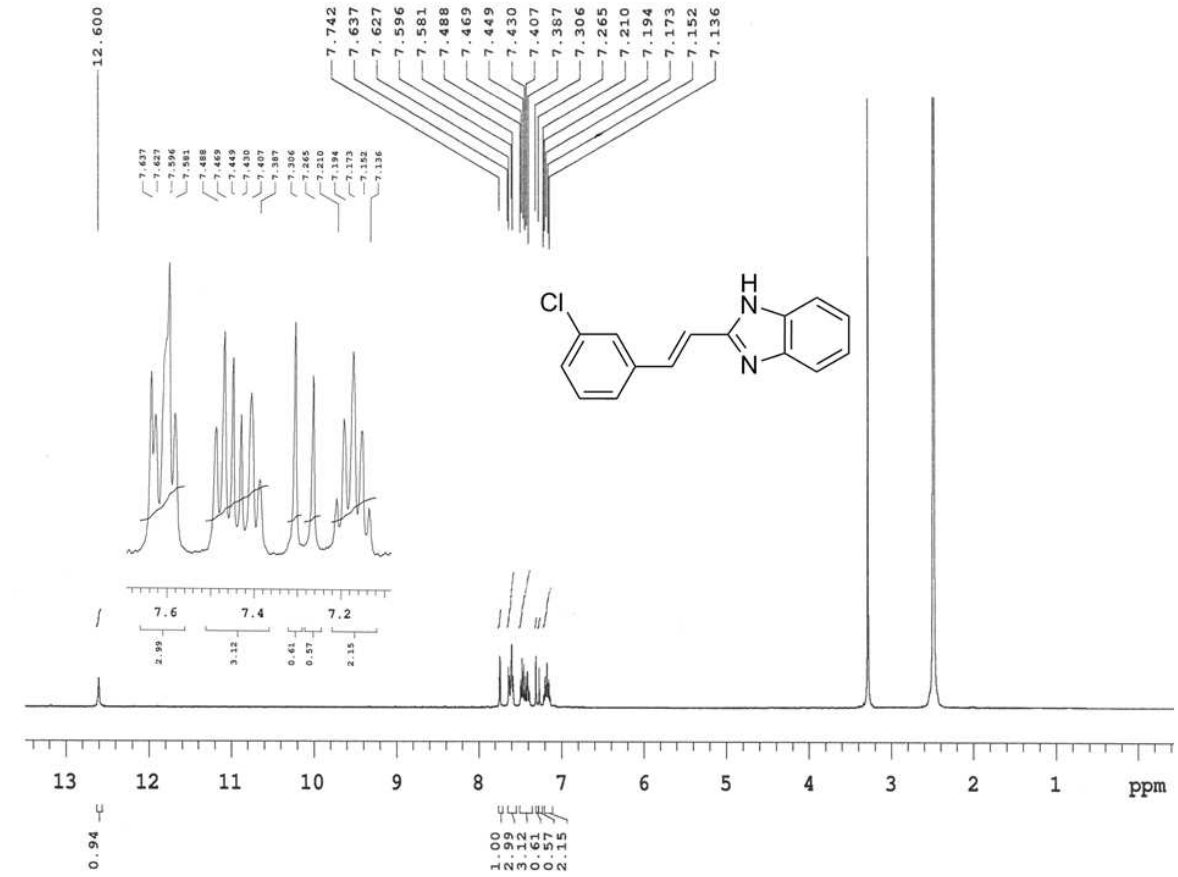
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4d**



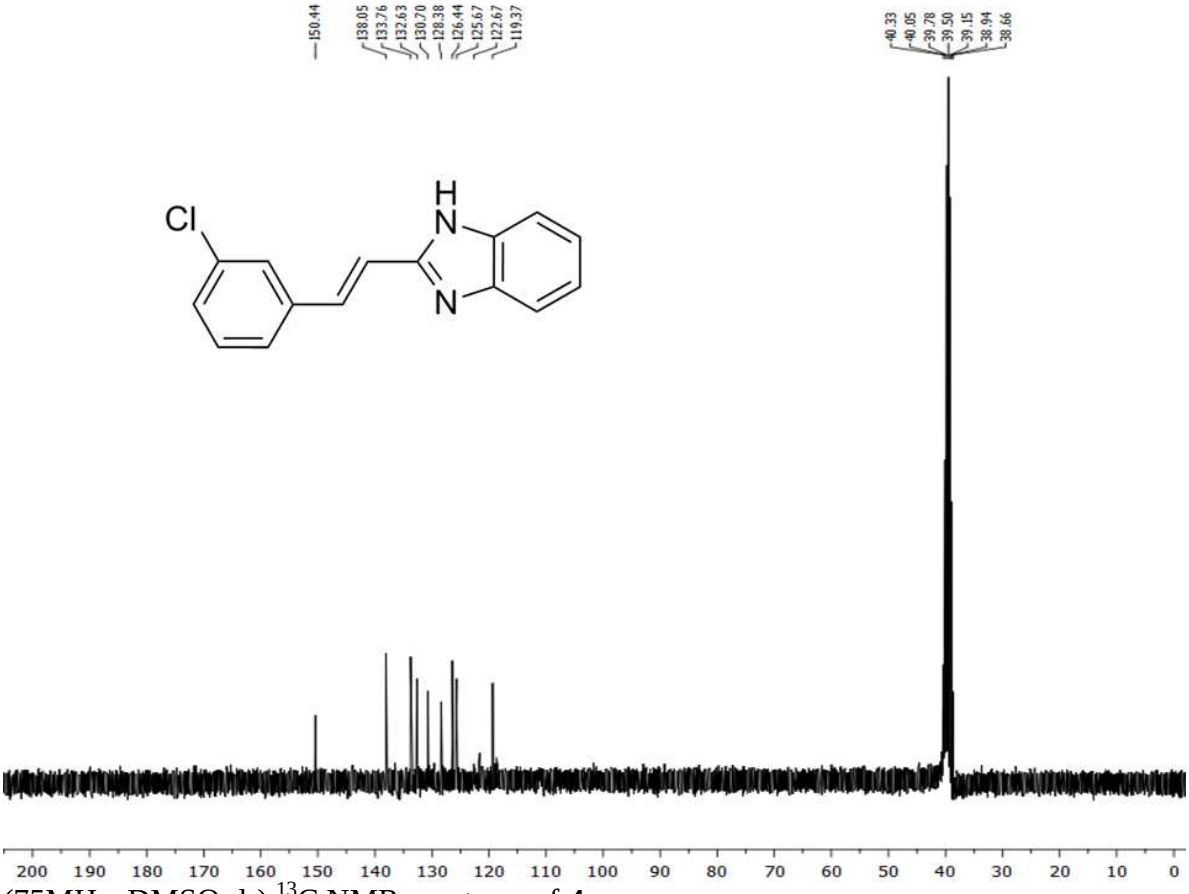




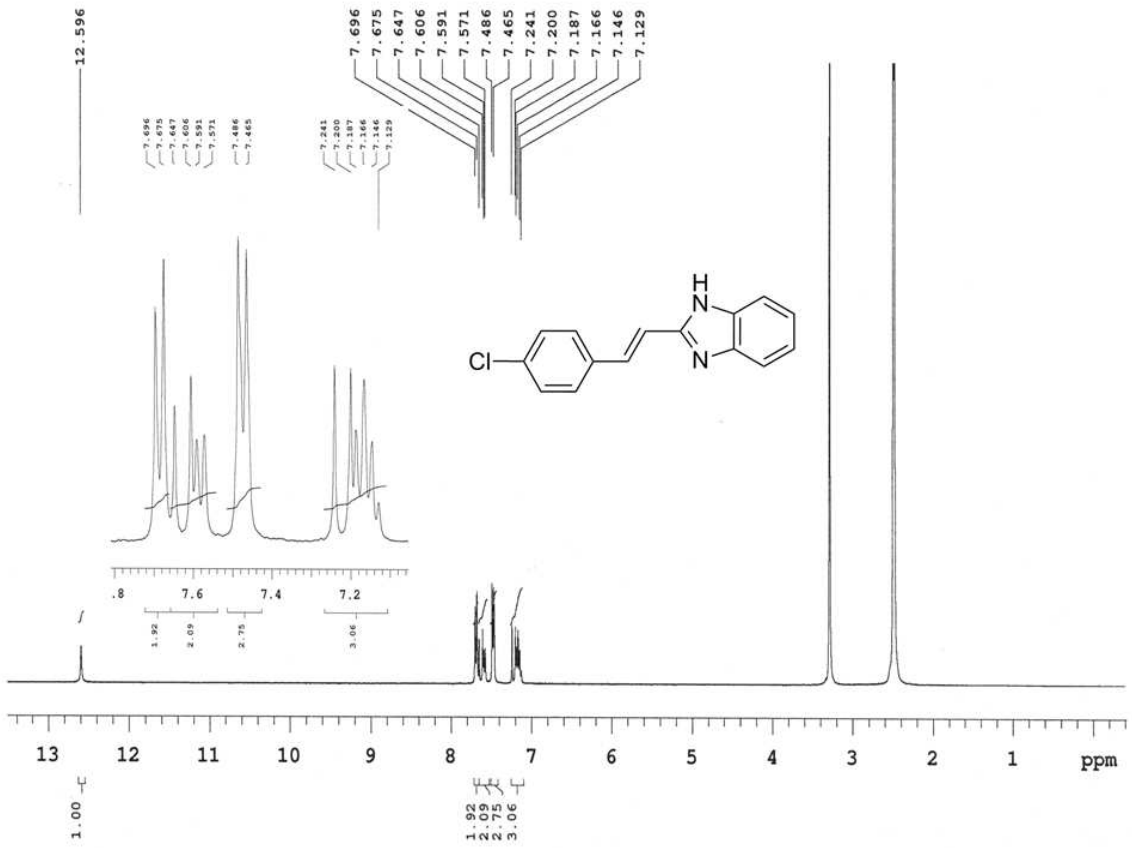
(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **4d**



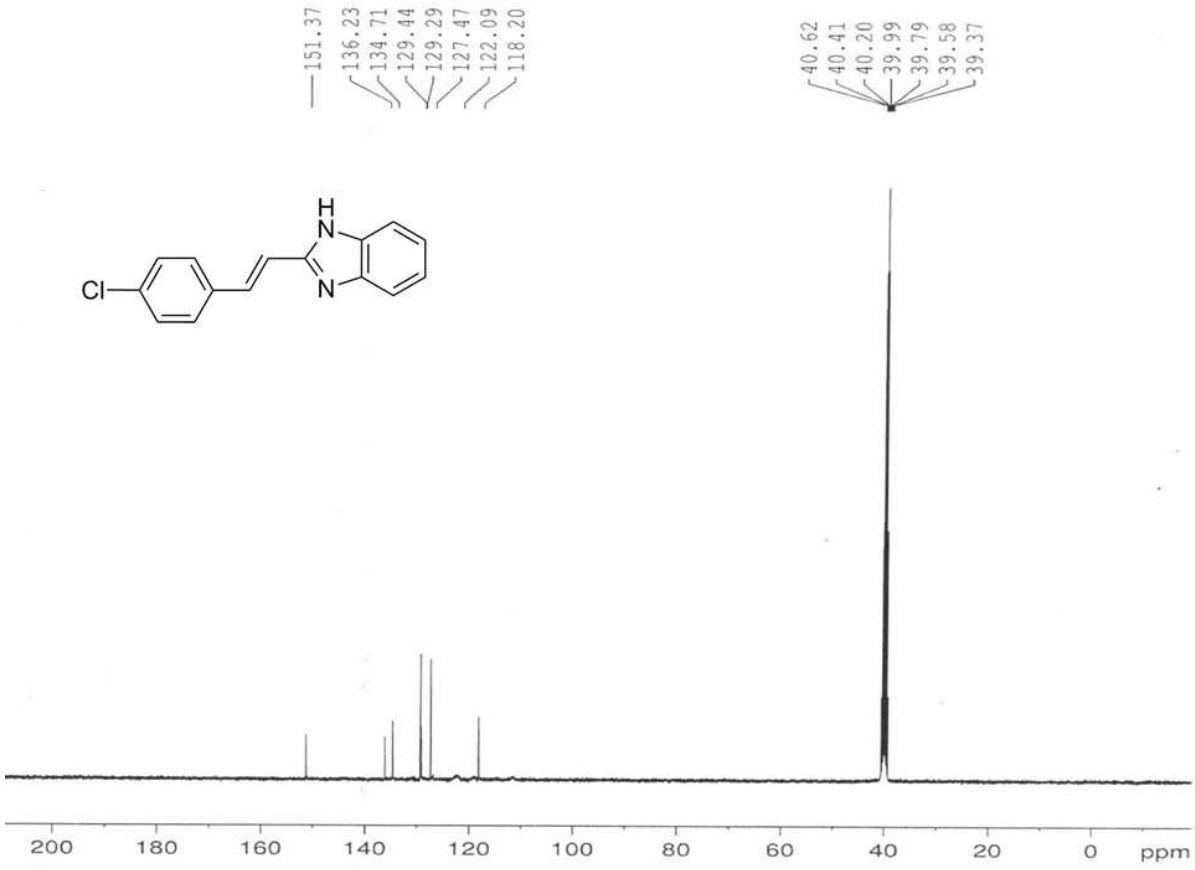
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4e**



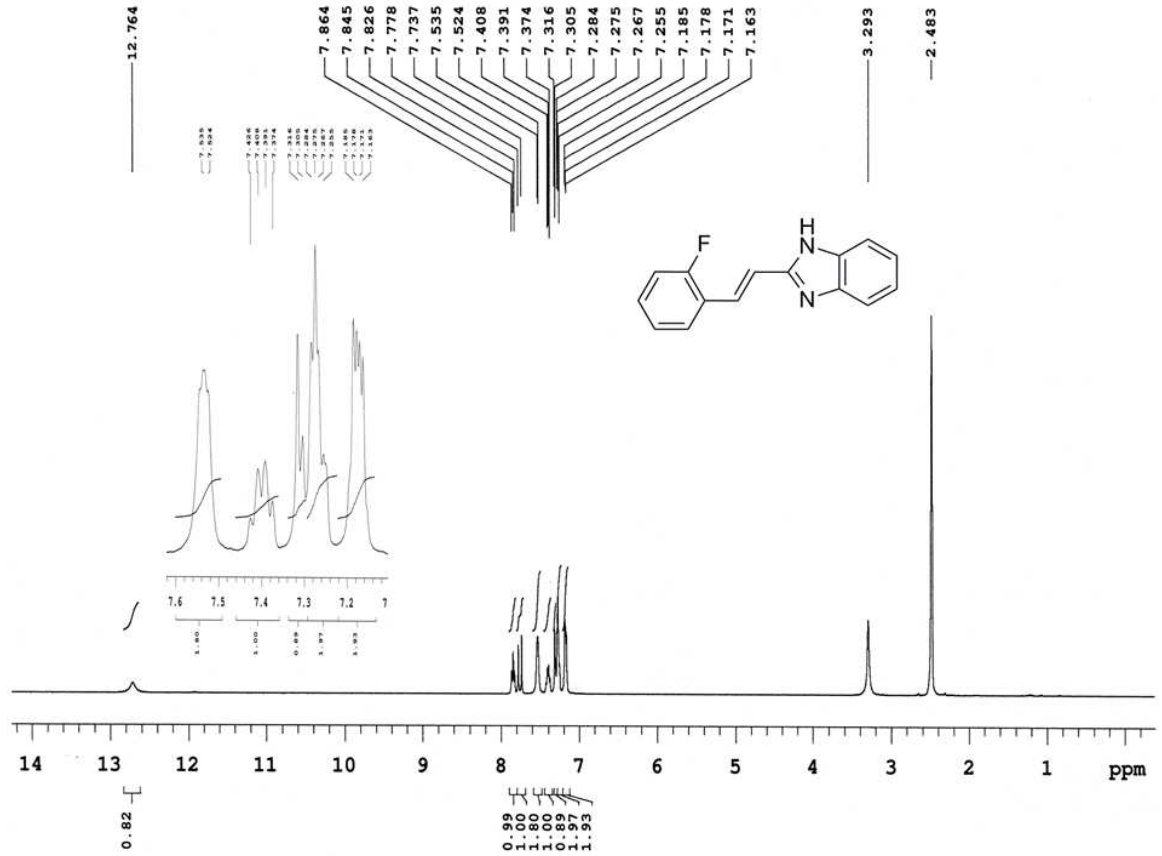
(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **4e**



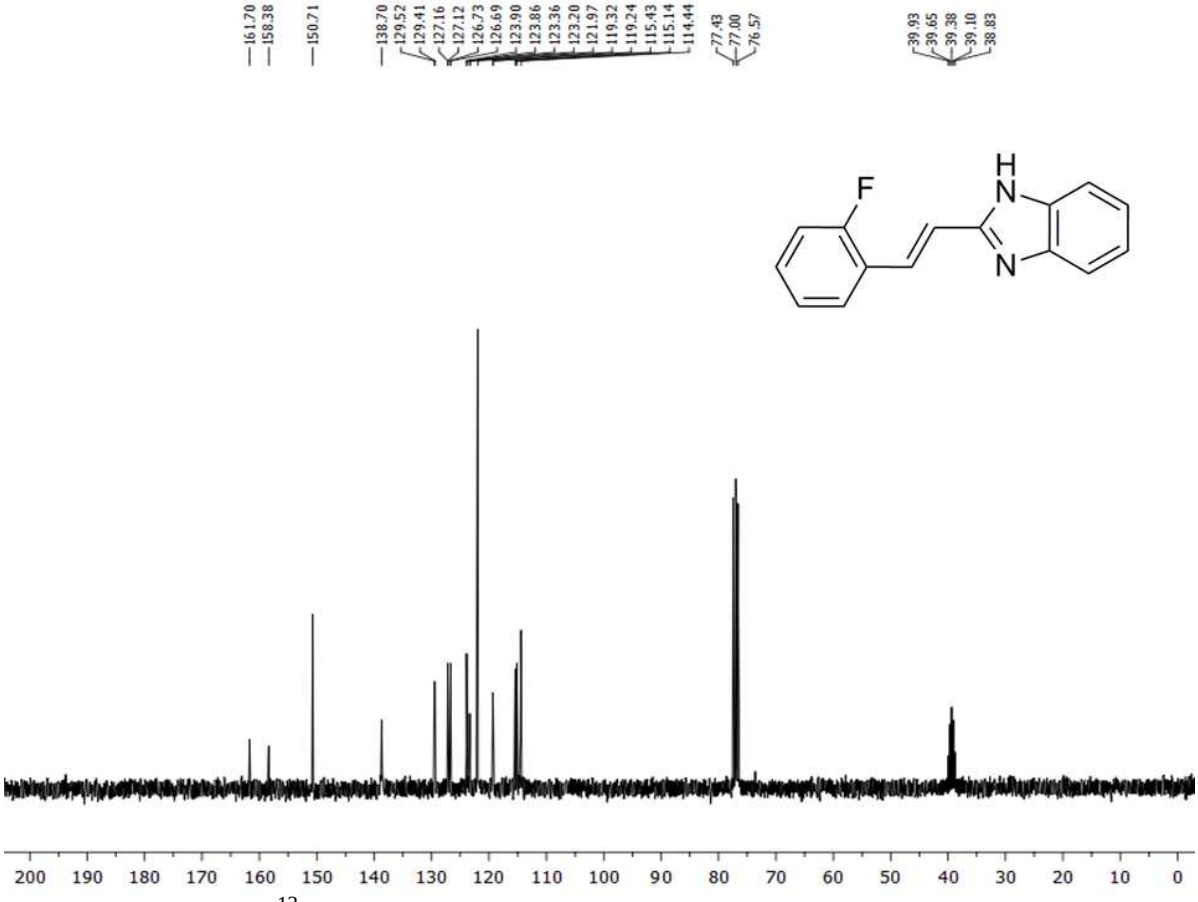
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4f**



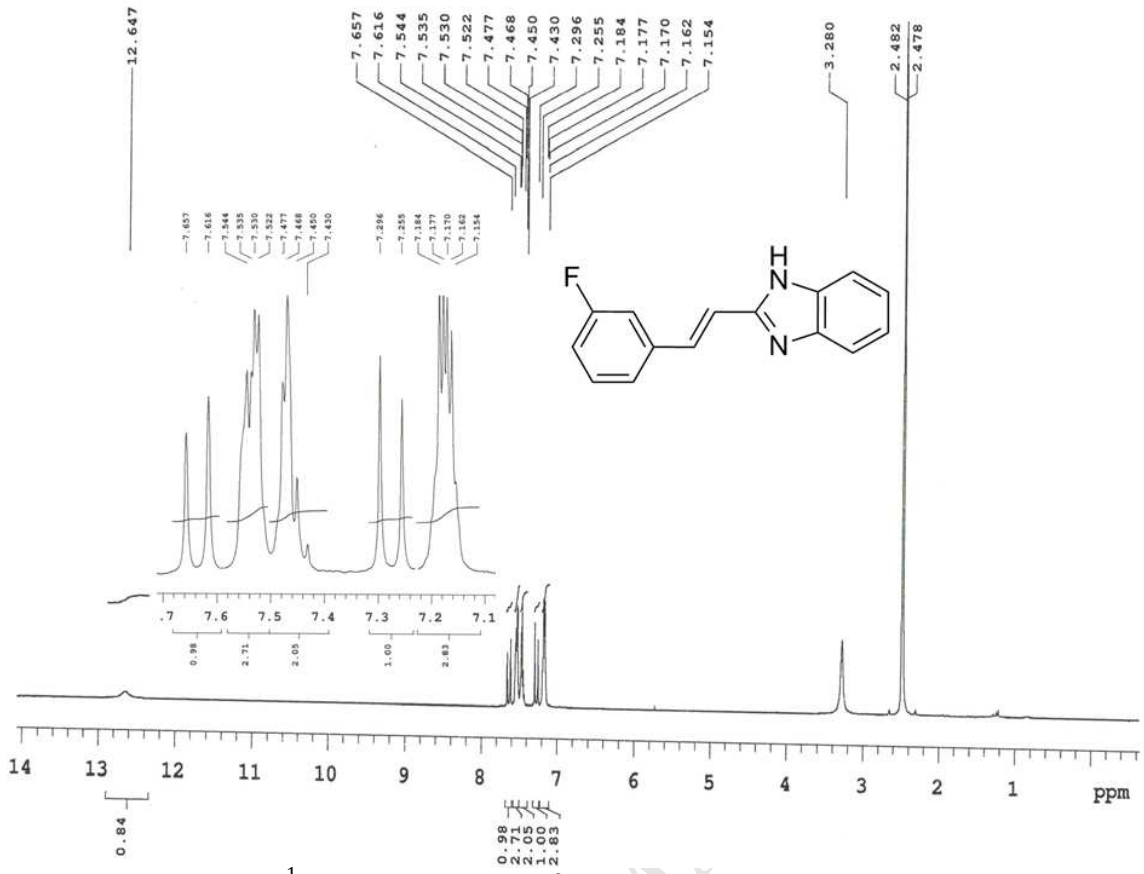
(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **4f**



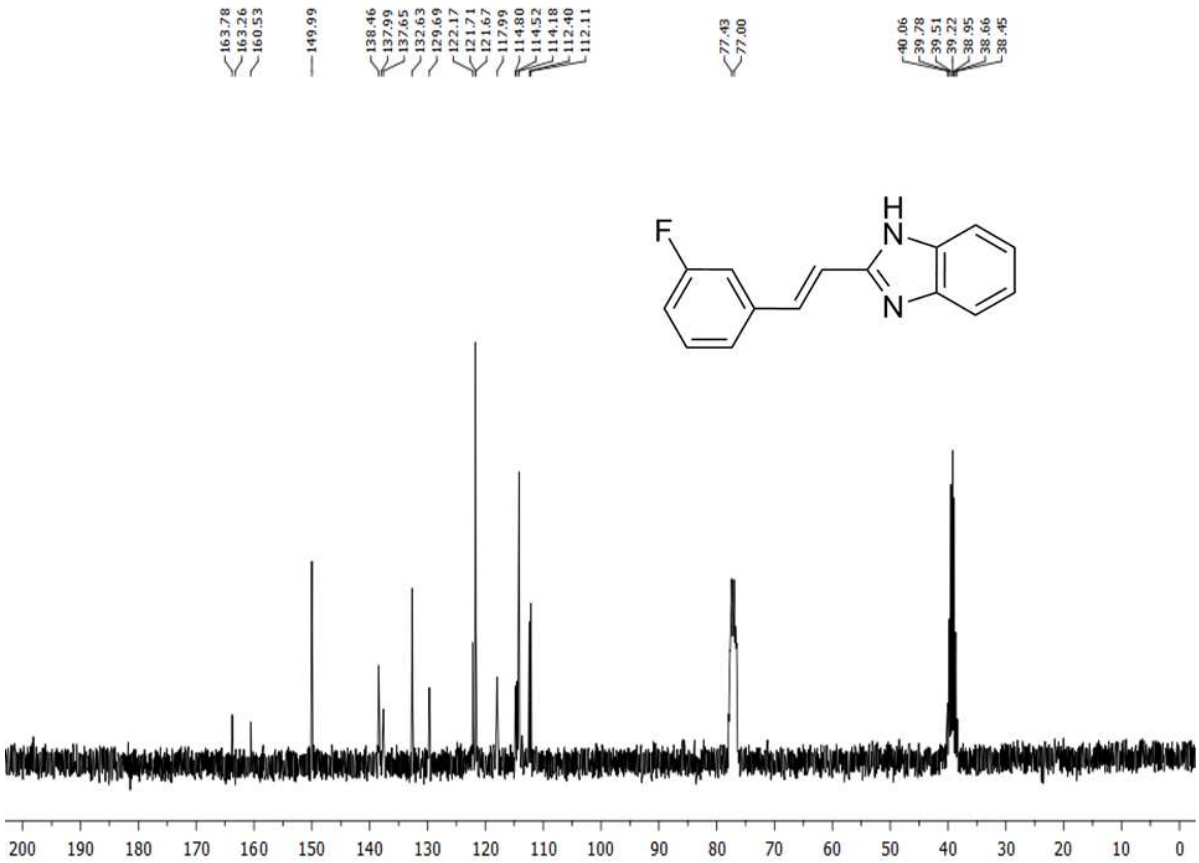
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4g**



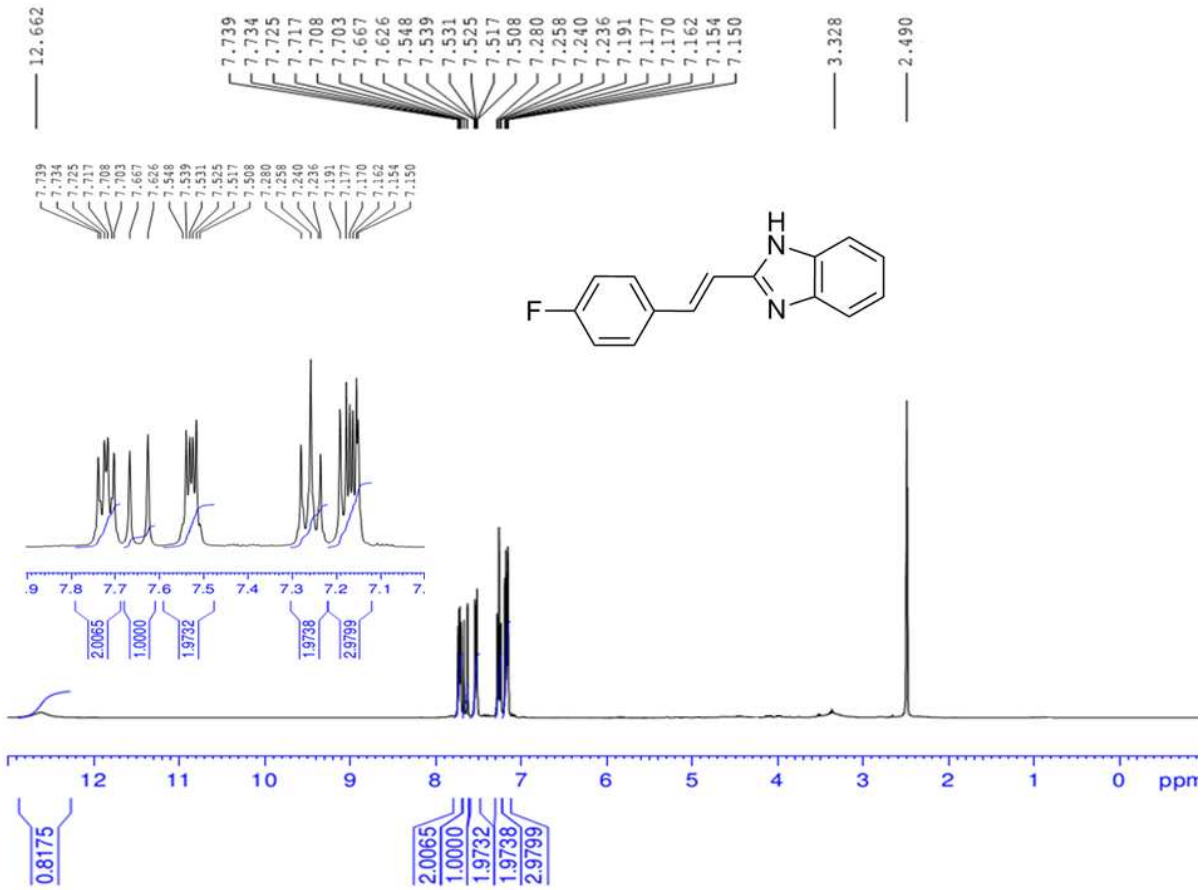
(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **4g**



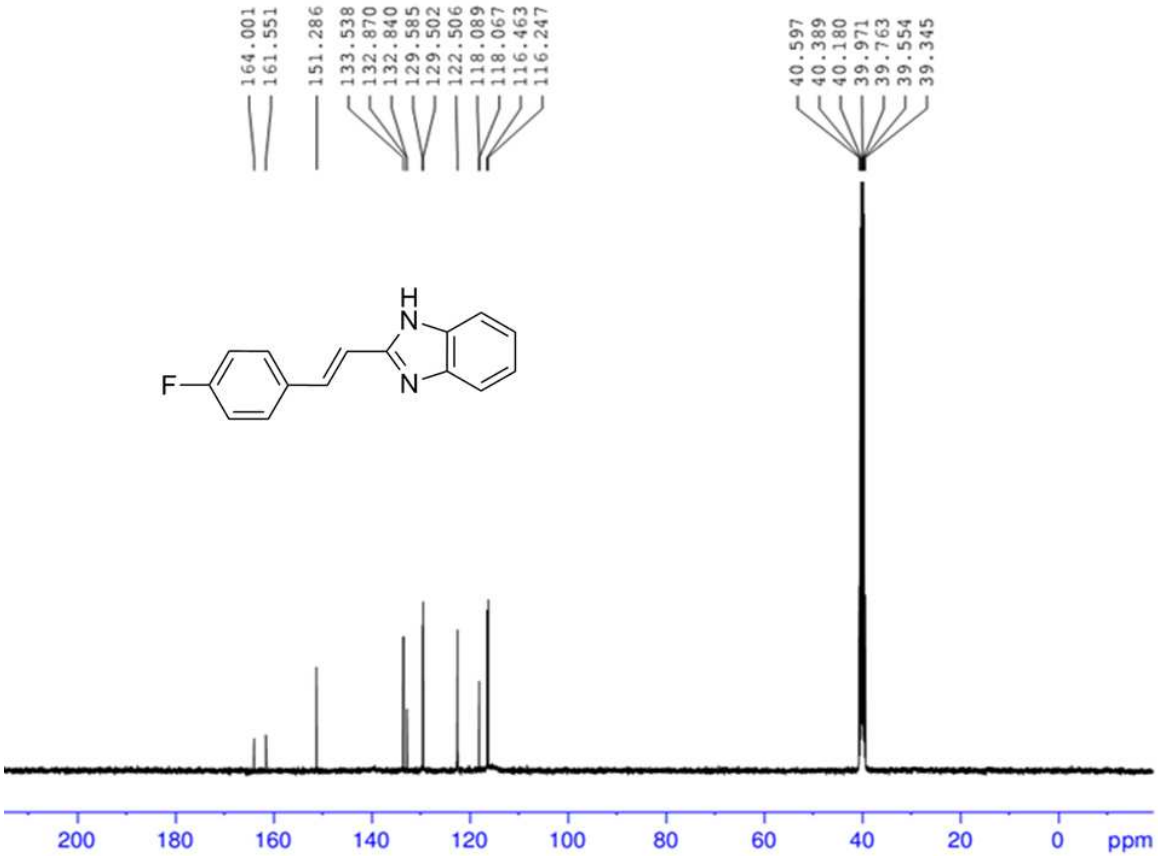
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4h**



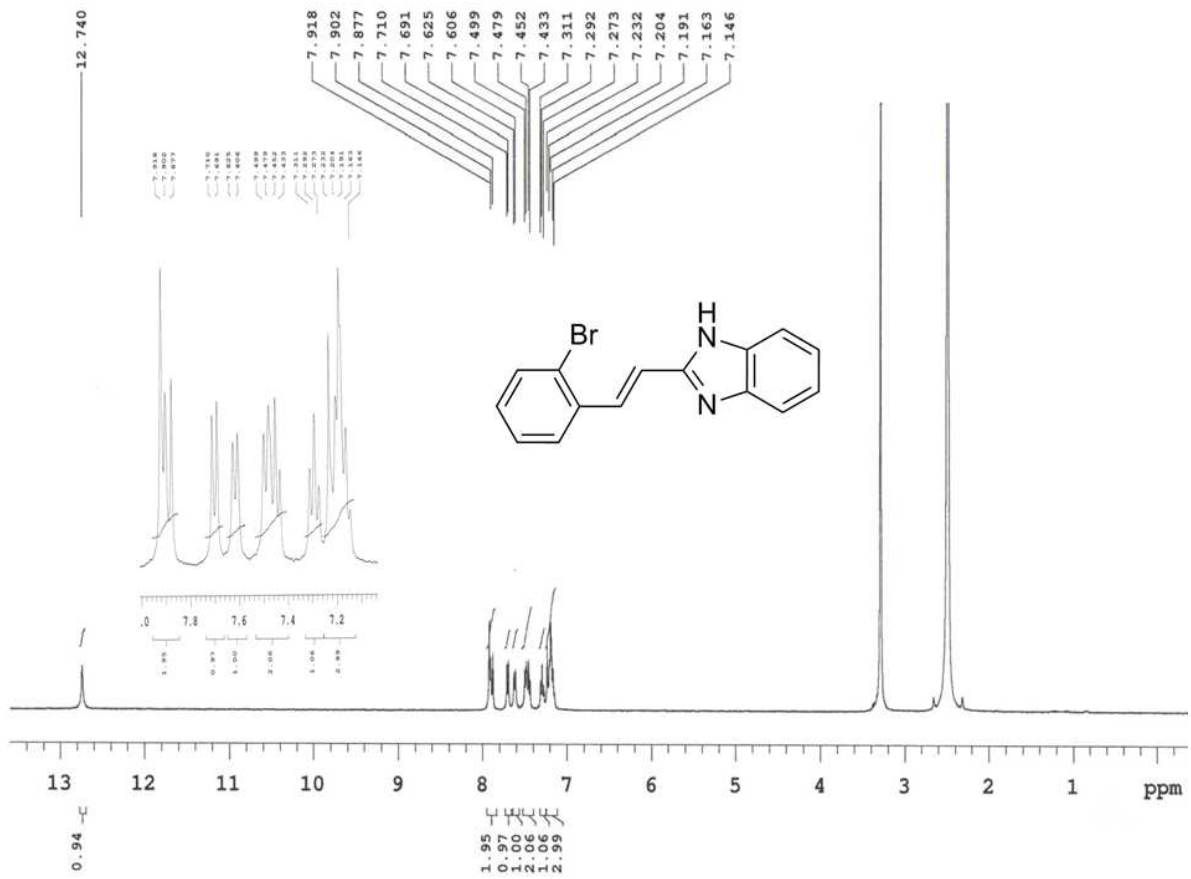
(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **4h**



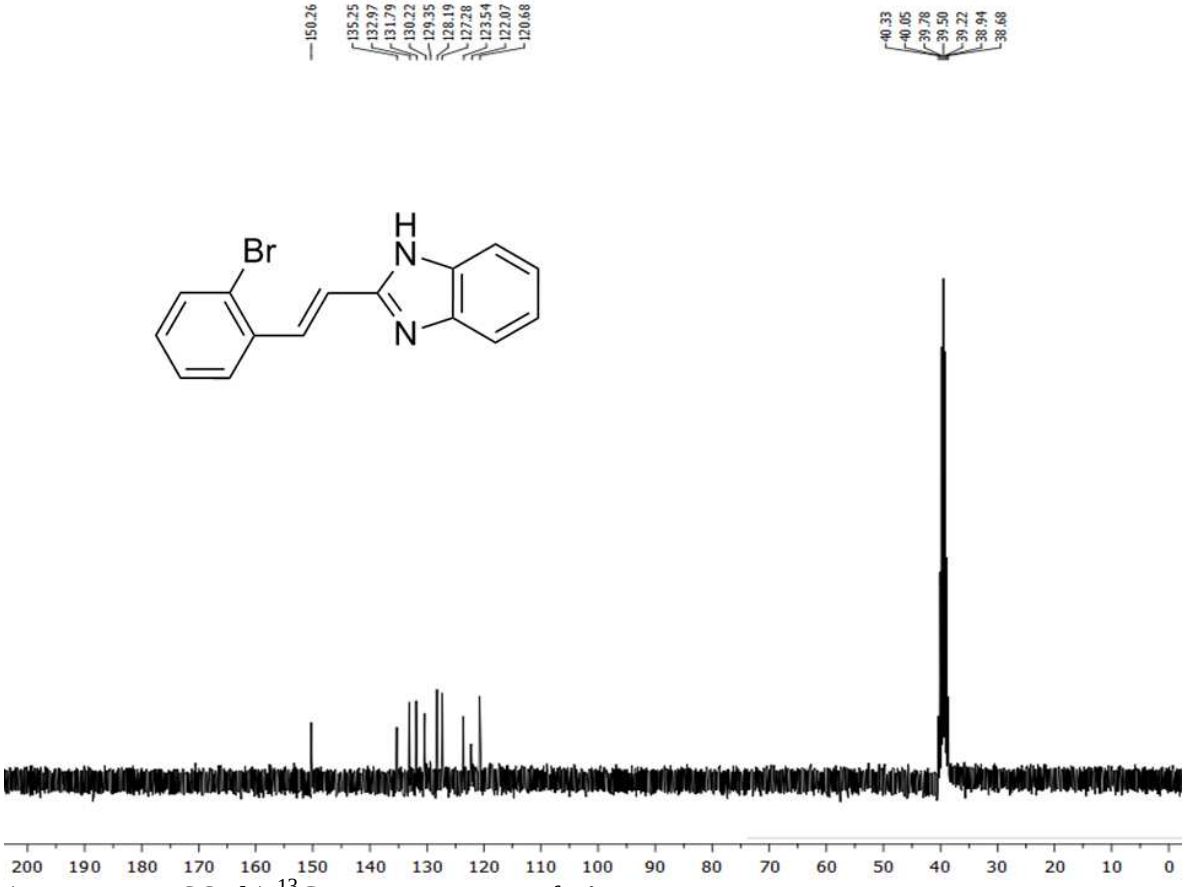
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4i**



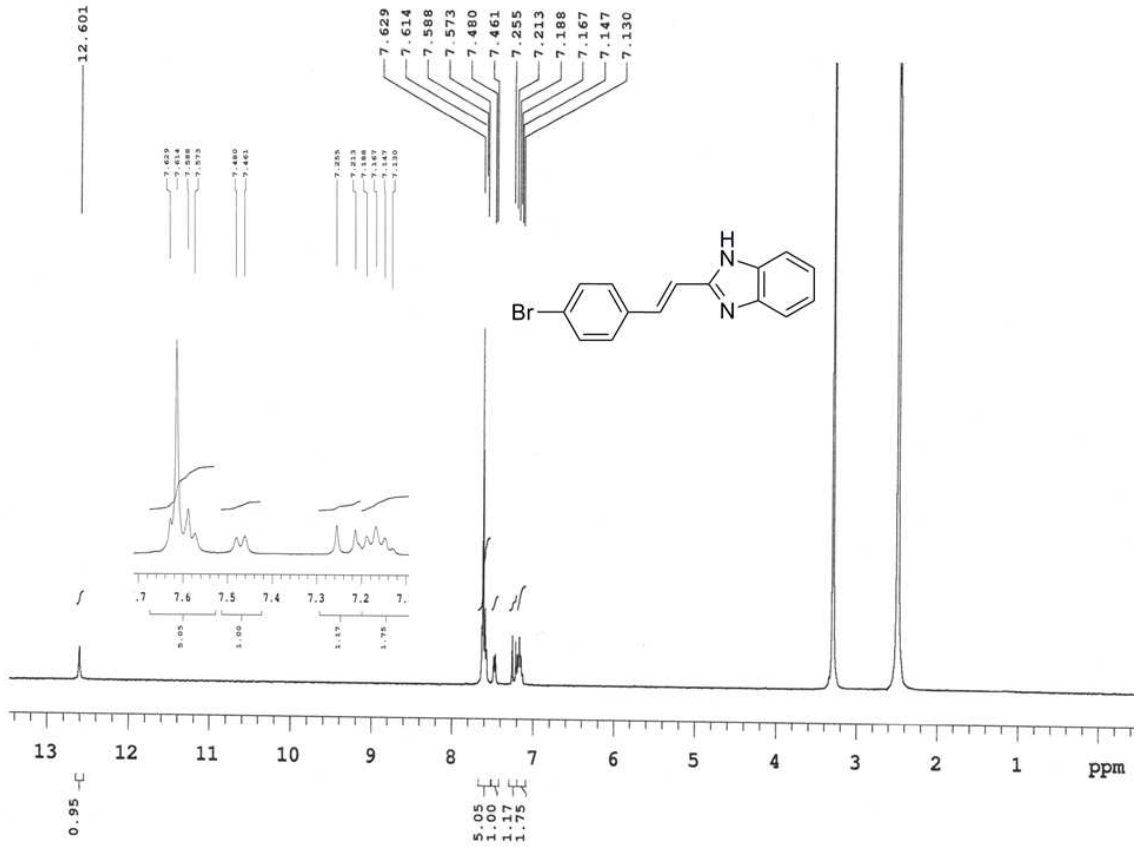
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **4i**



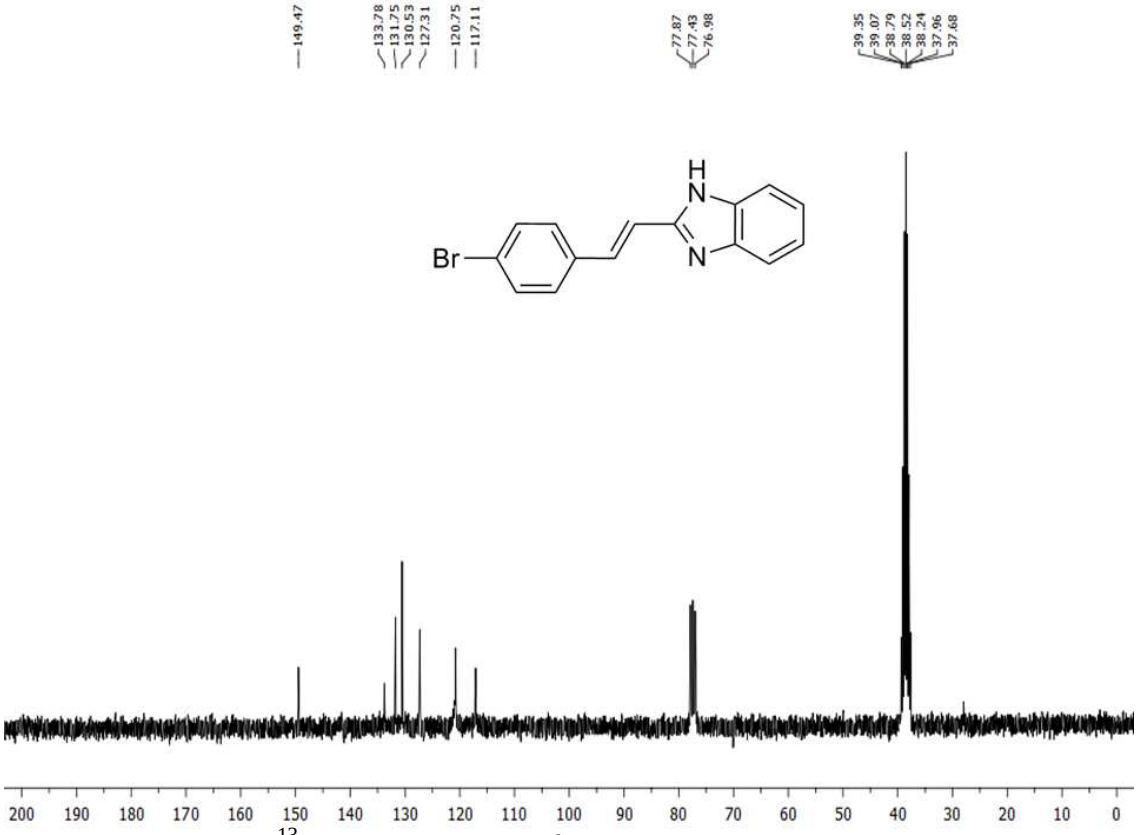
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4j**



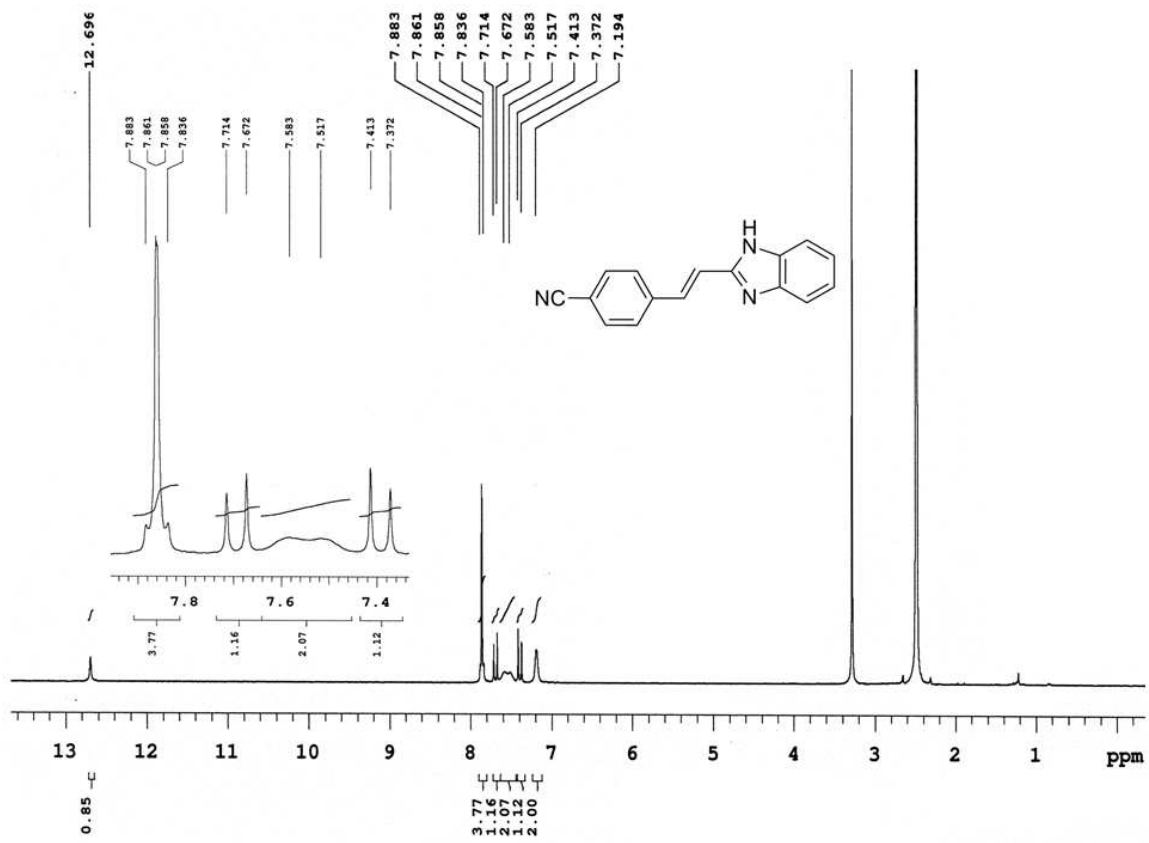
(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **4j**



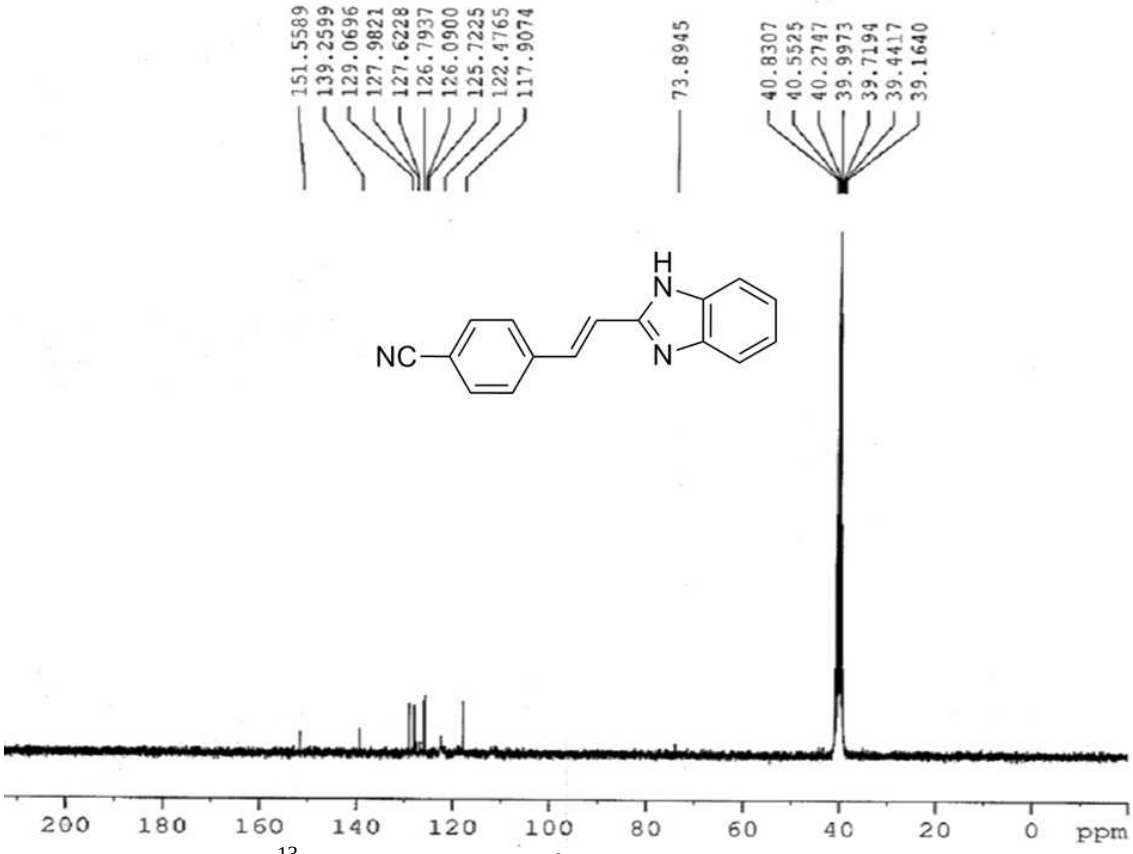
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4k**



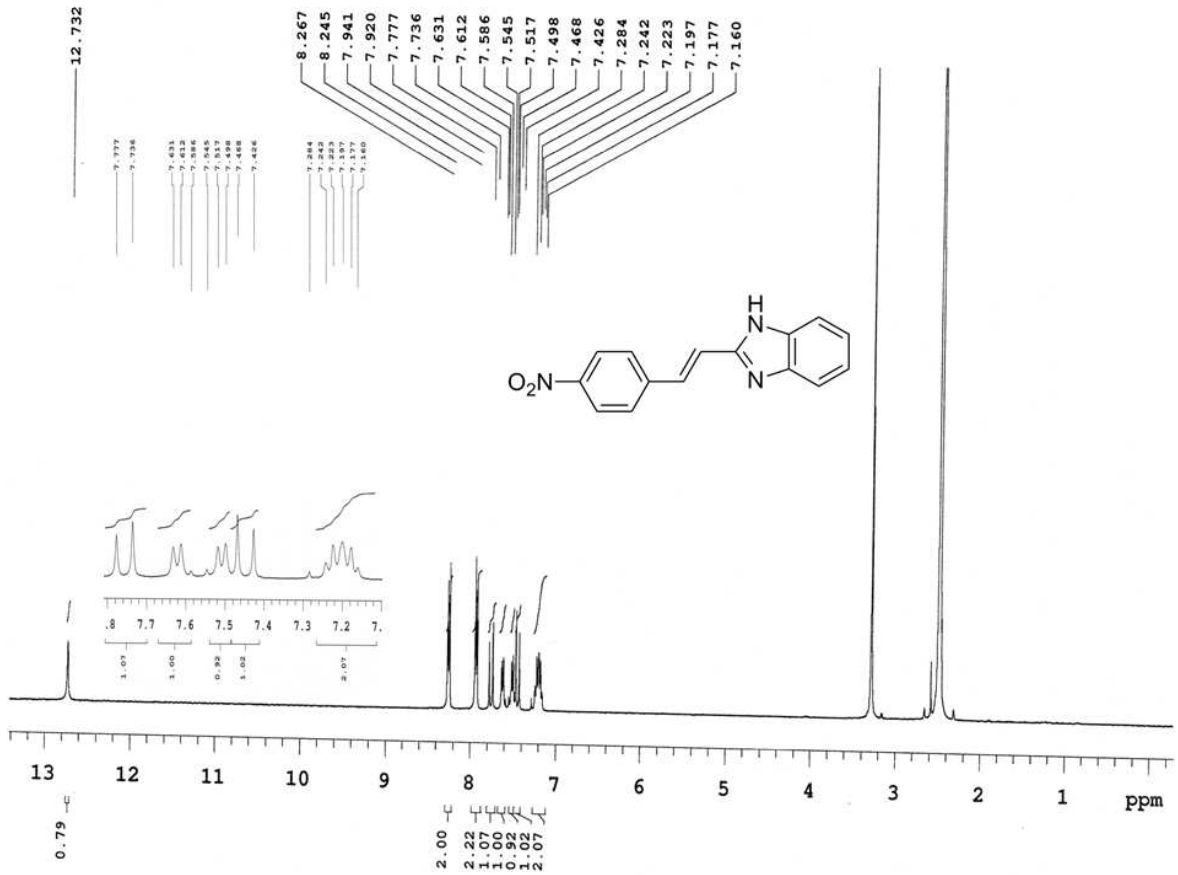
(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **4k**



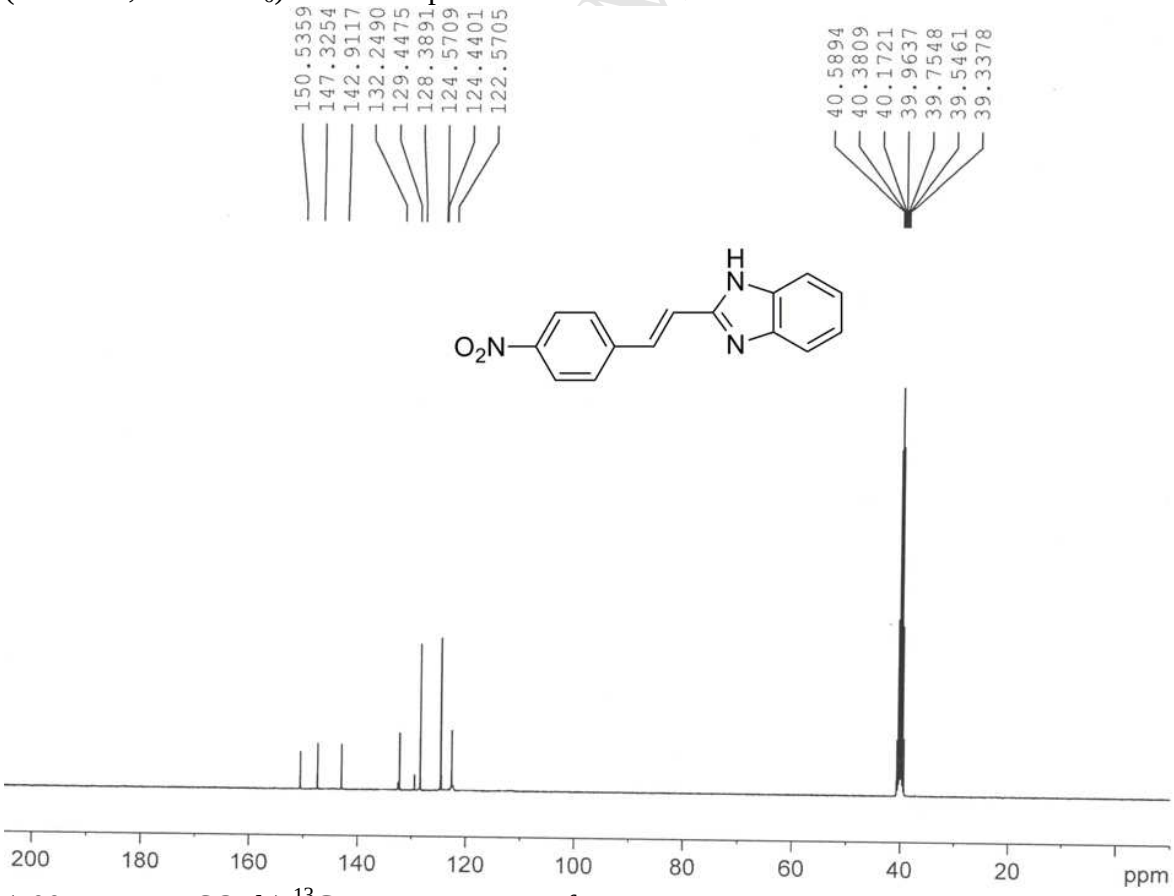
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4l**



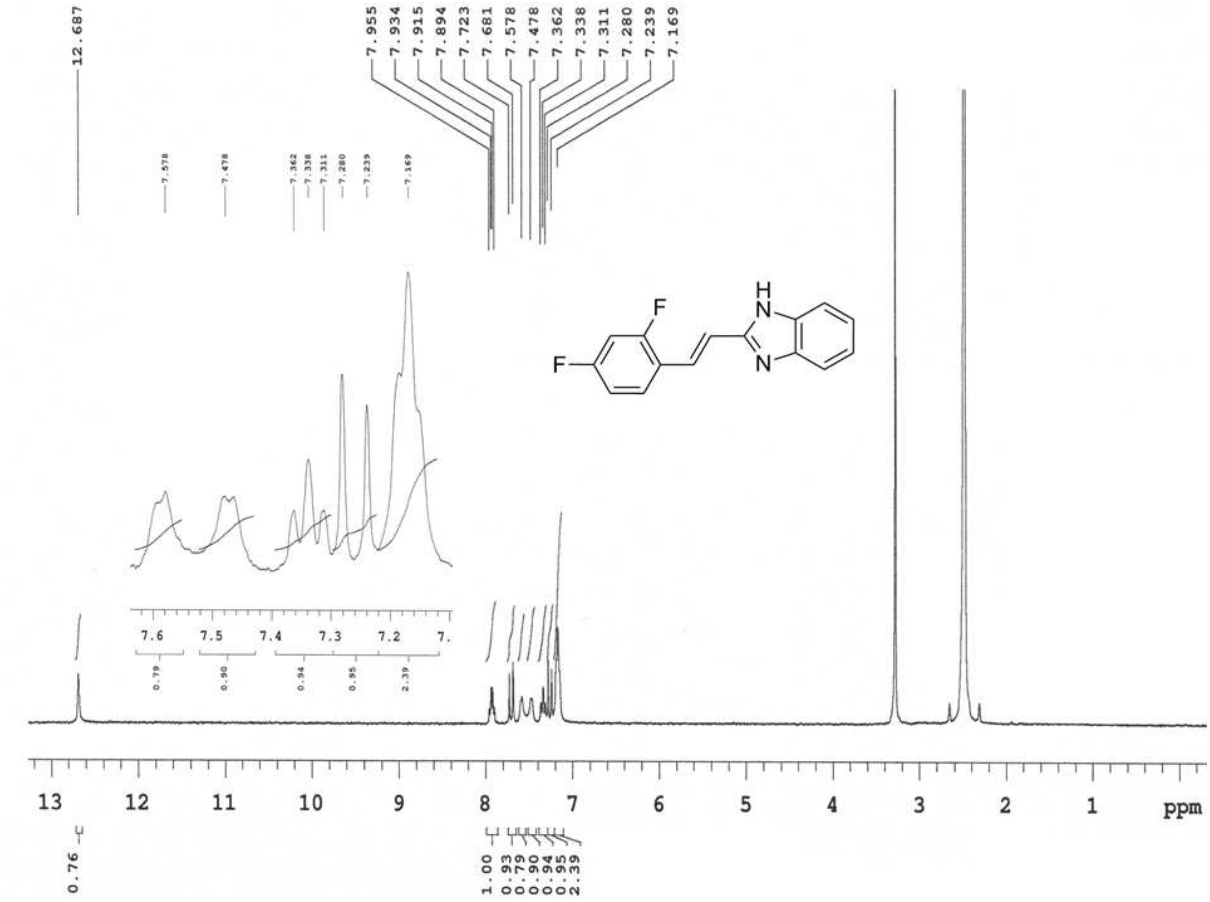
(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **4l**



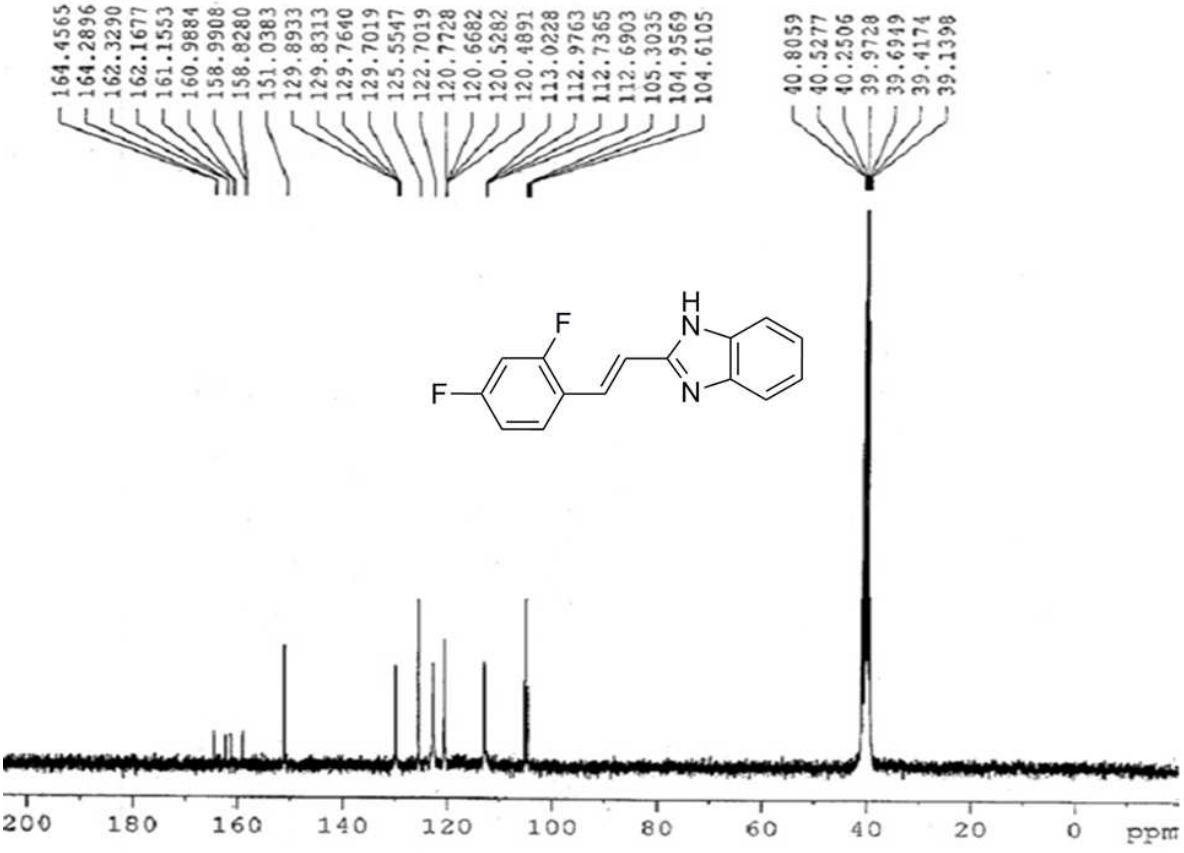
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4m**



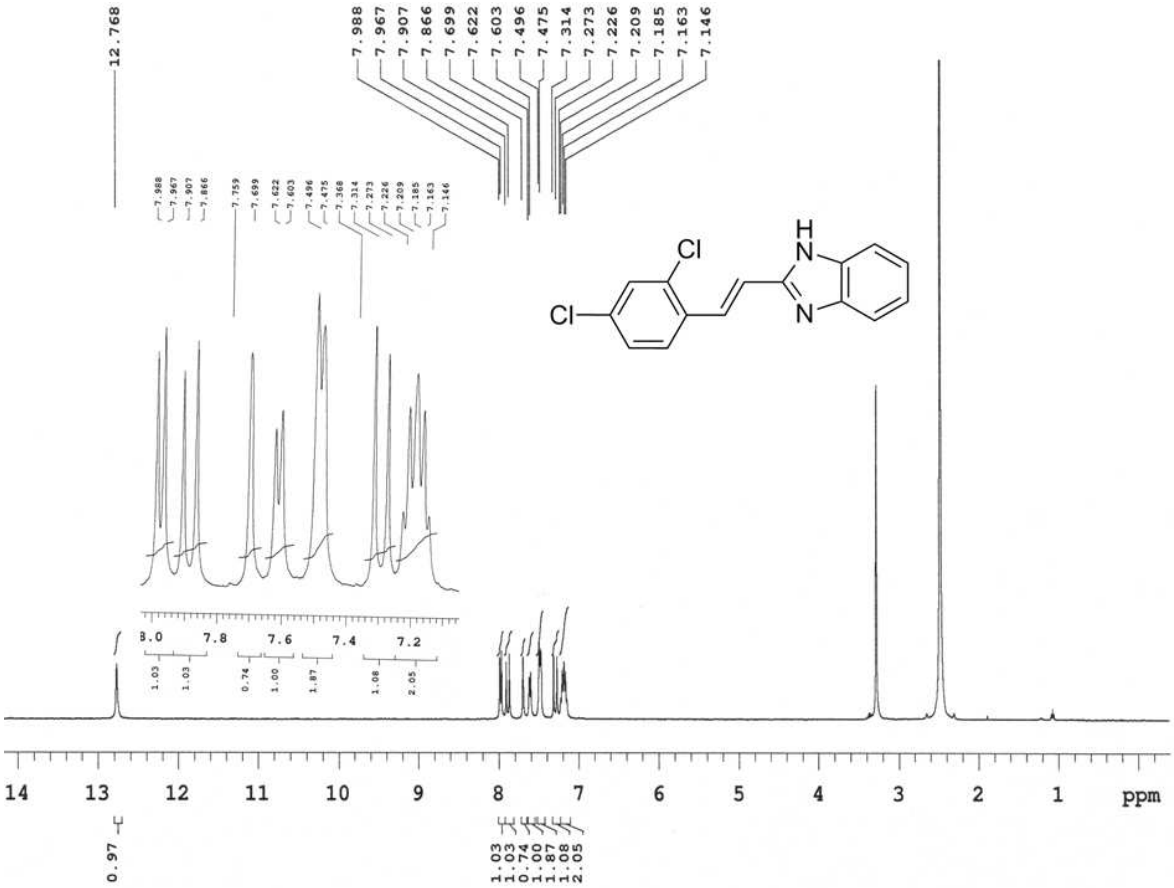
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **4m**



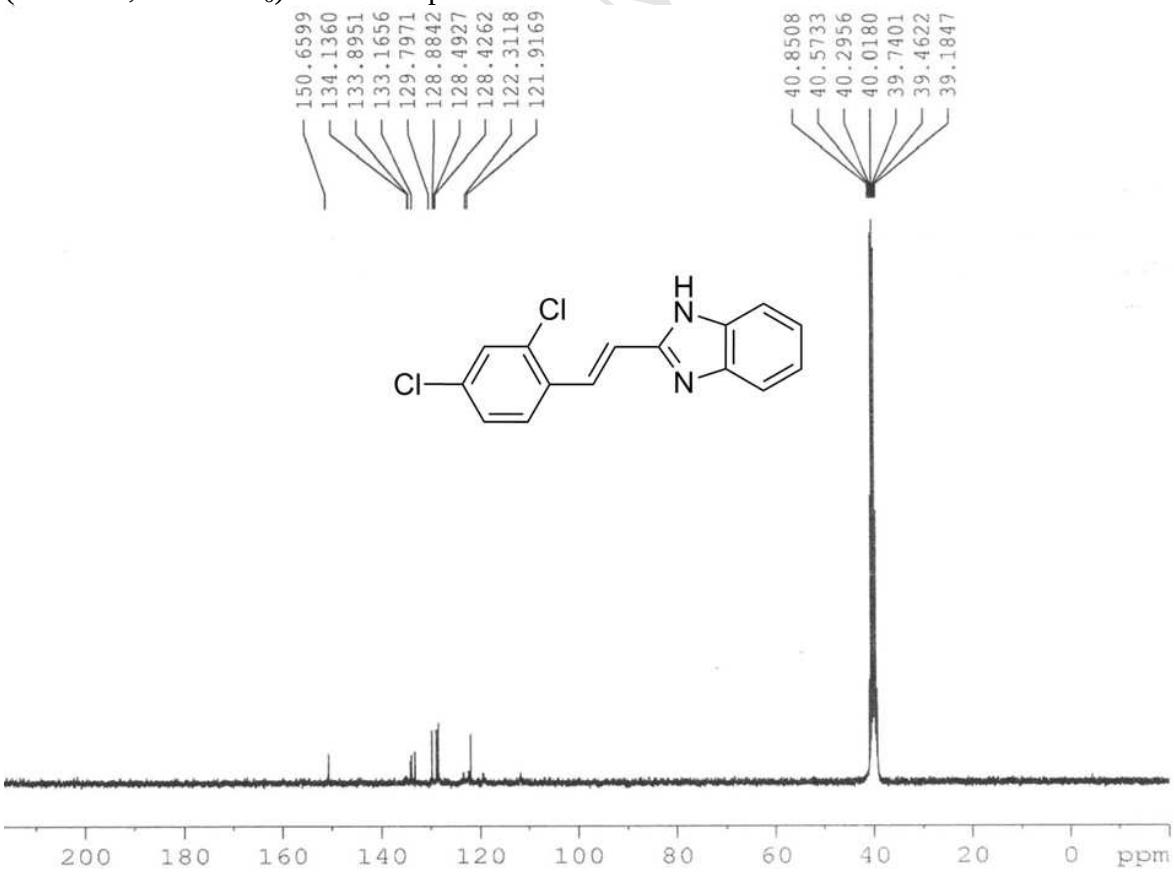
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4n**



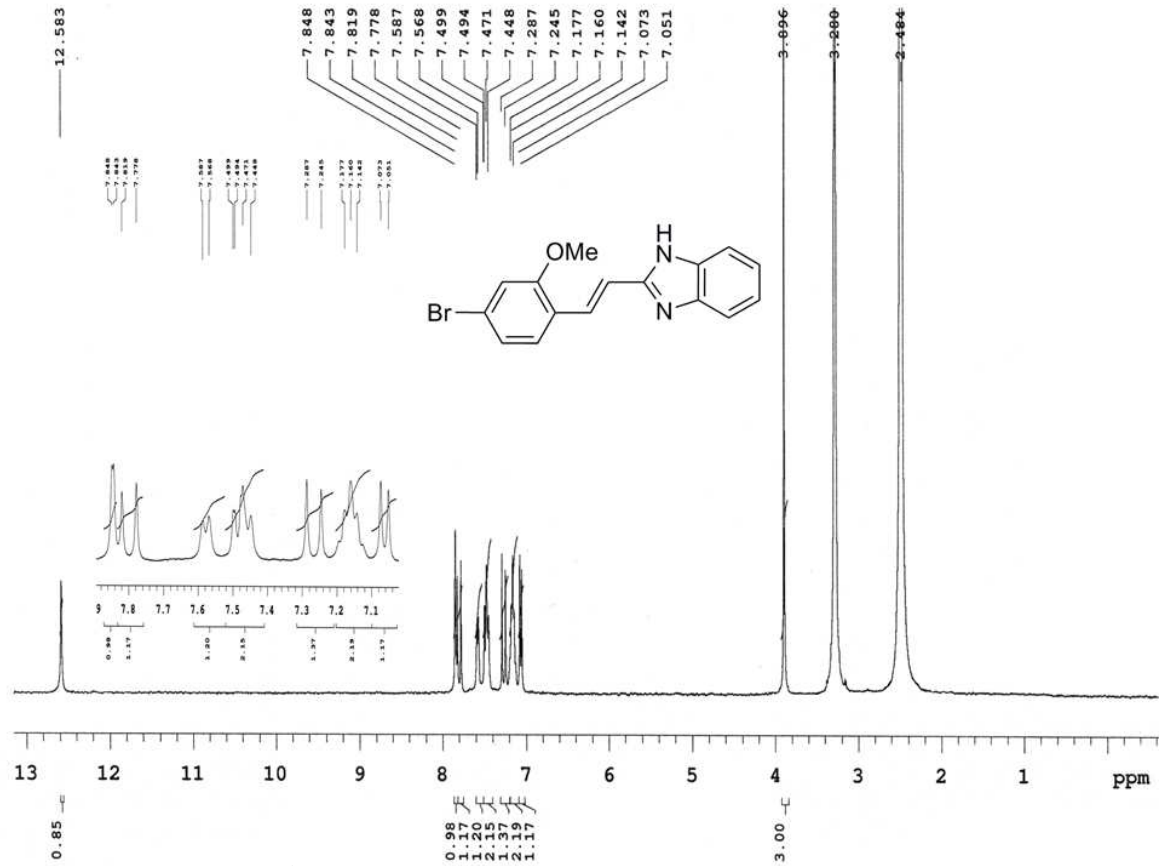
(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **4n**



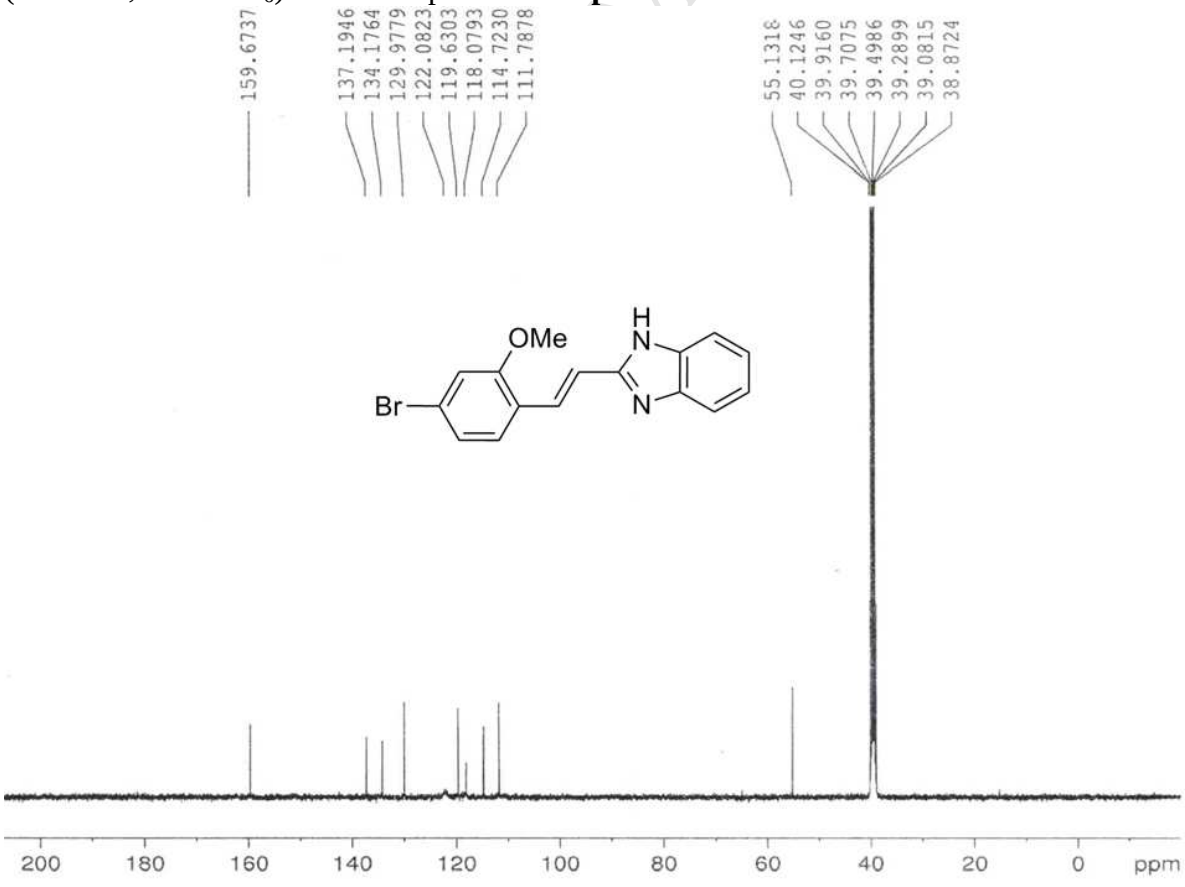
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4o**



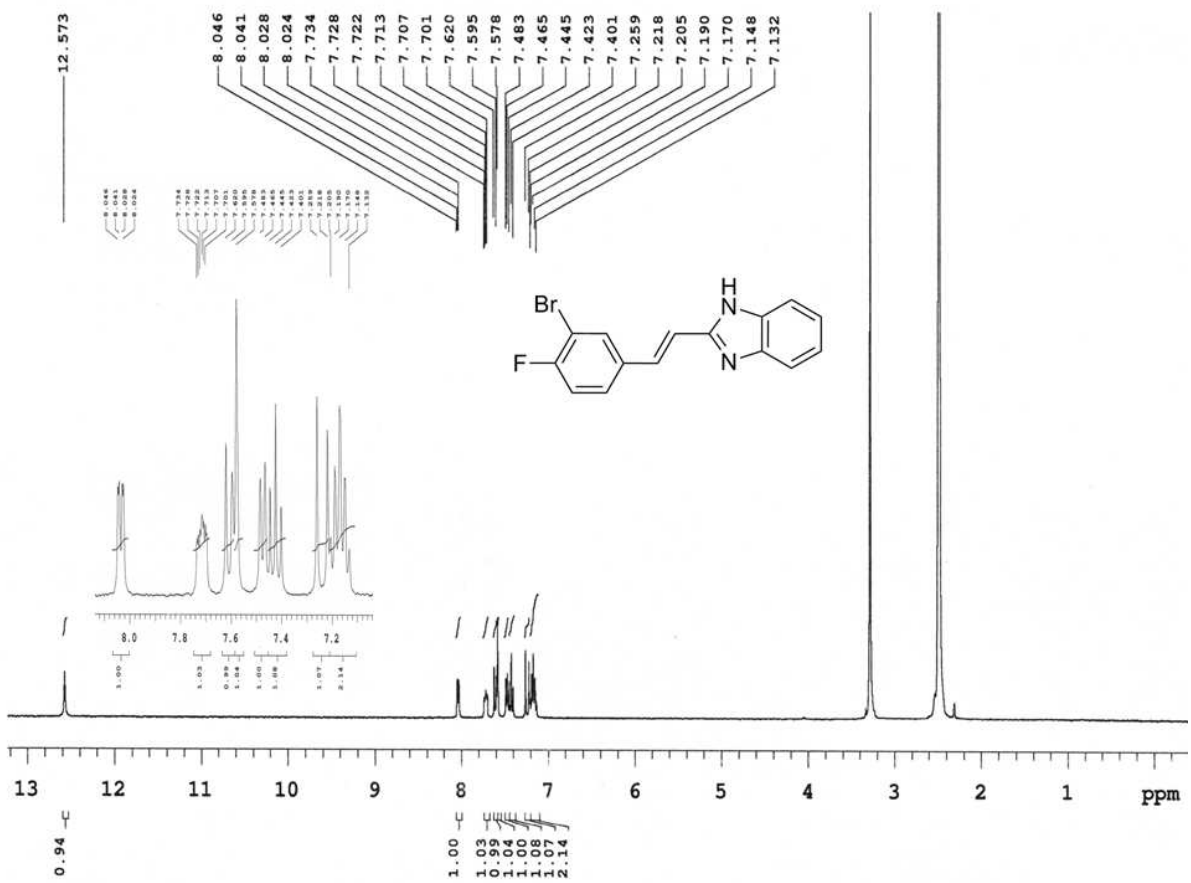
(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **4o**



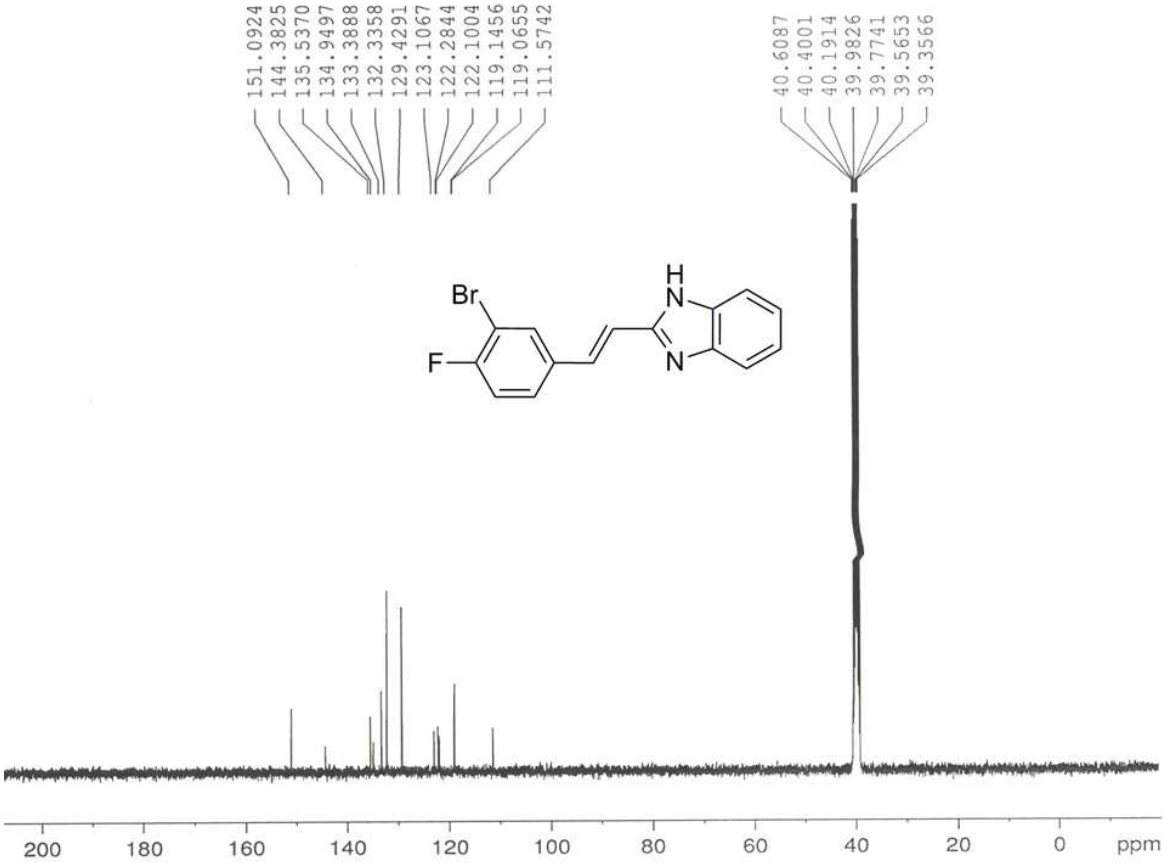
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4p**



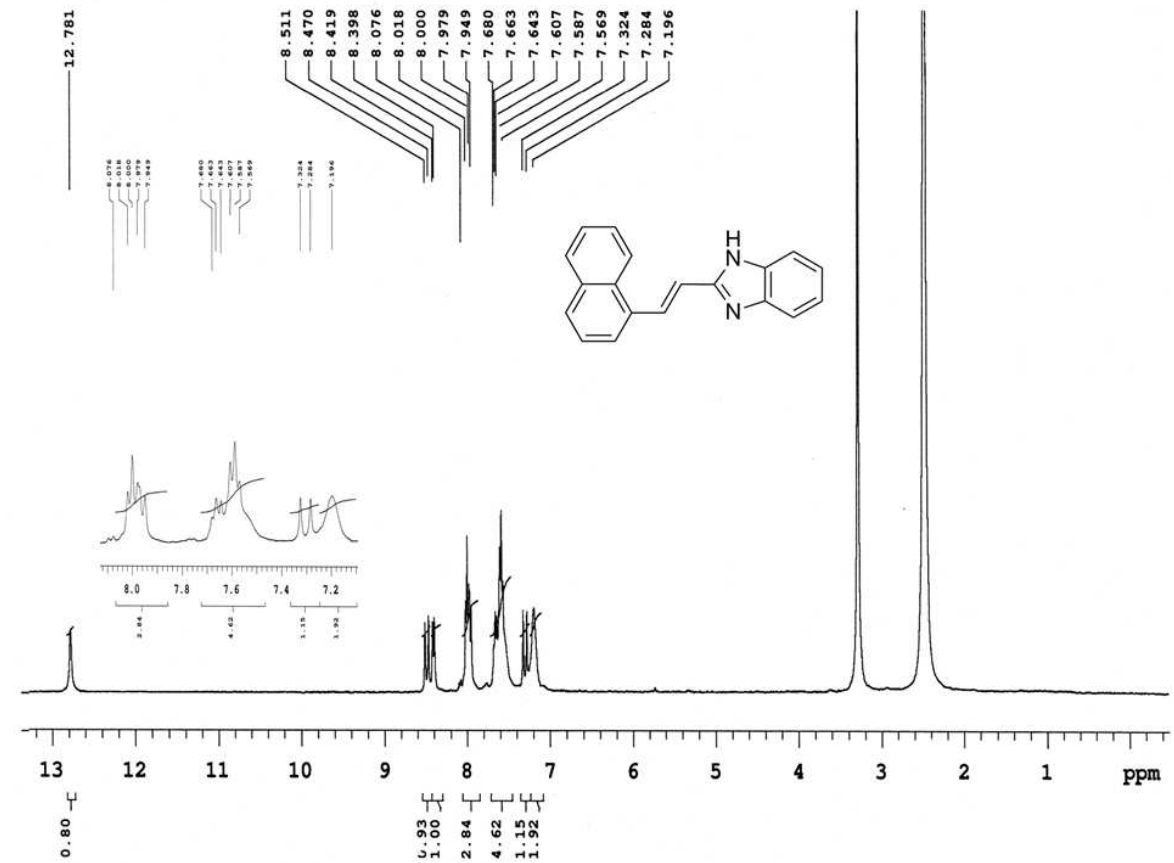
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **4p**



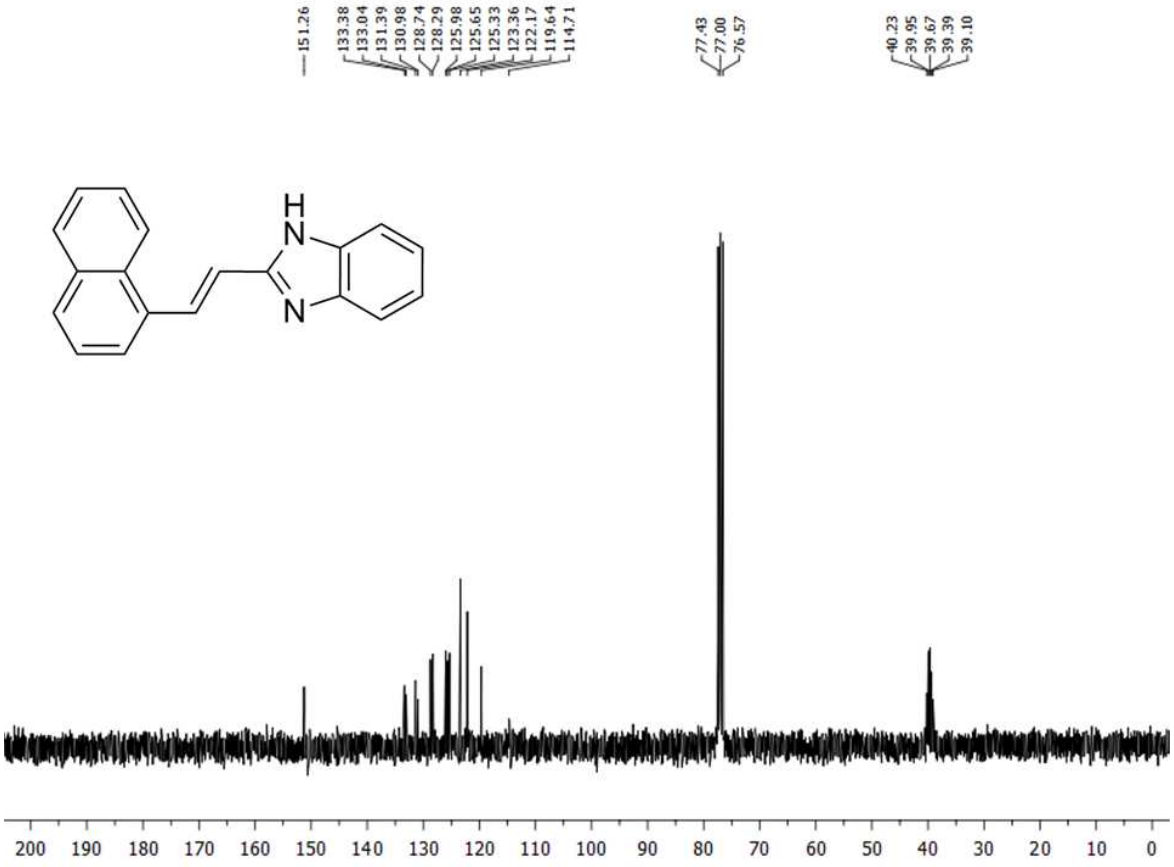
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4q**



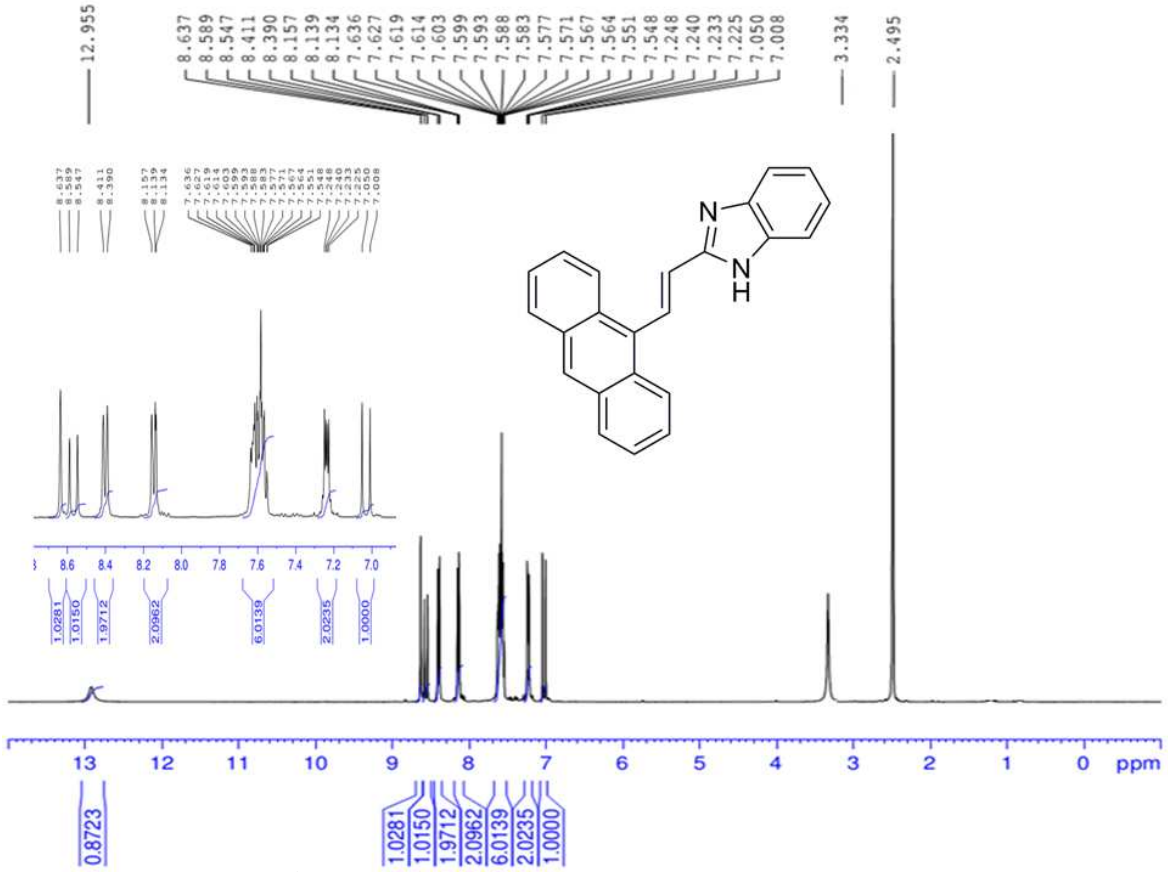
(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **4q**



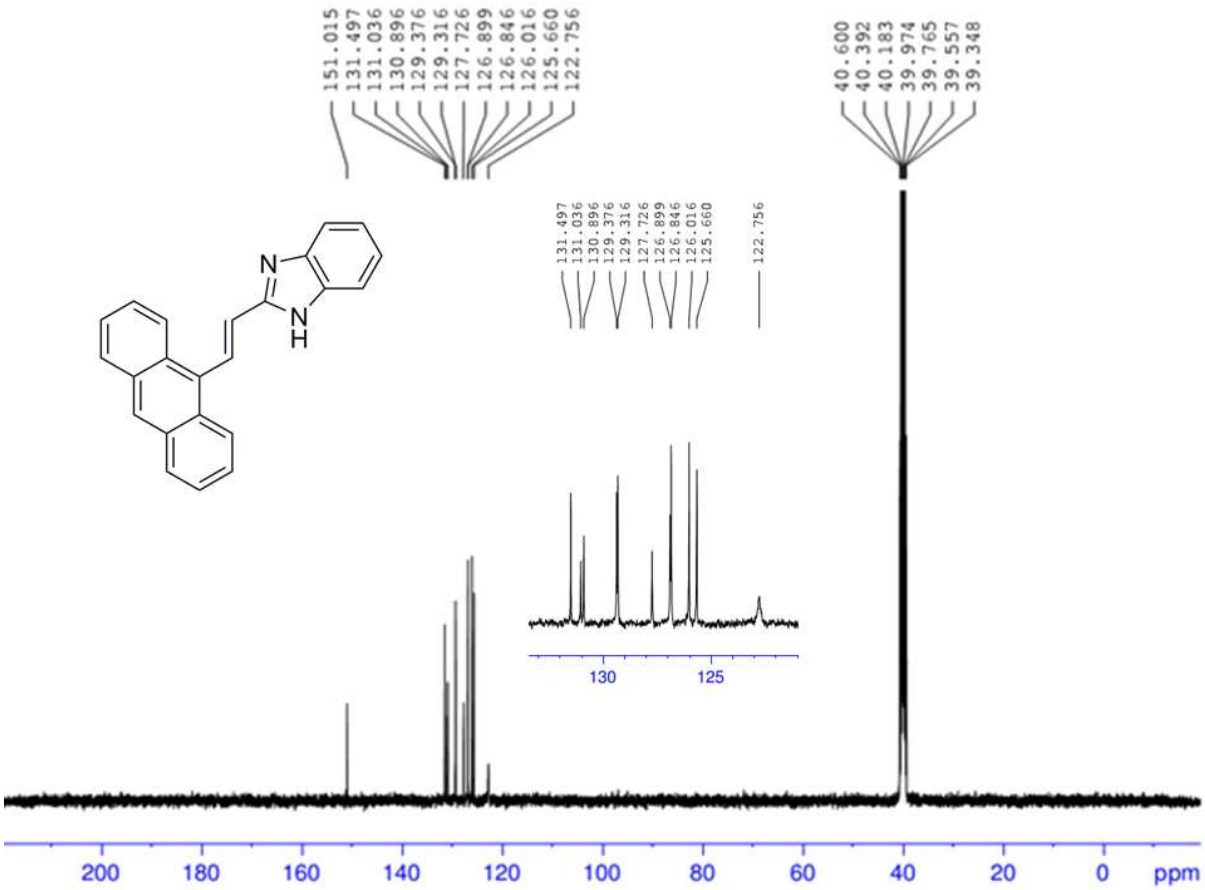
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4s**



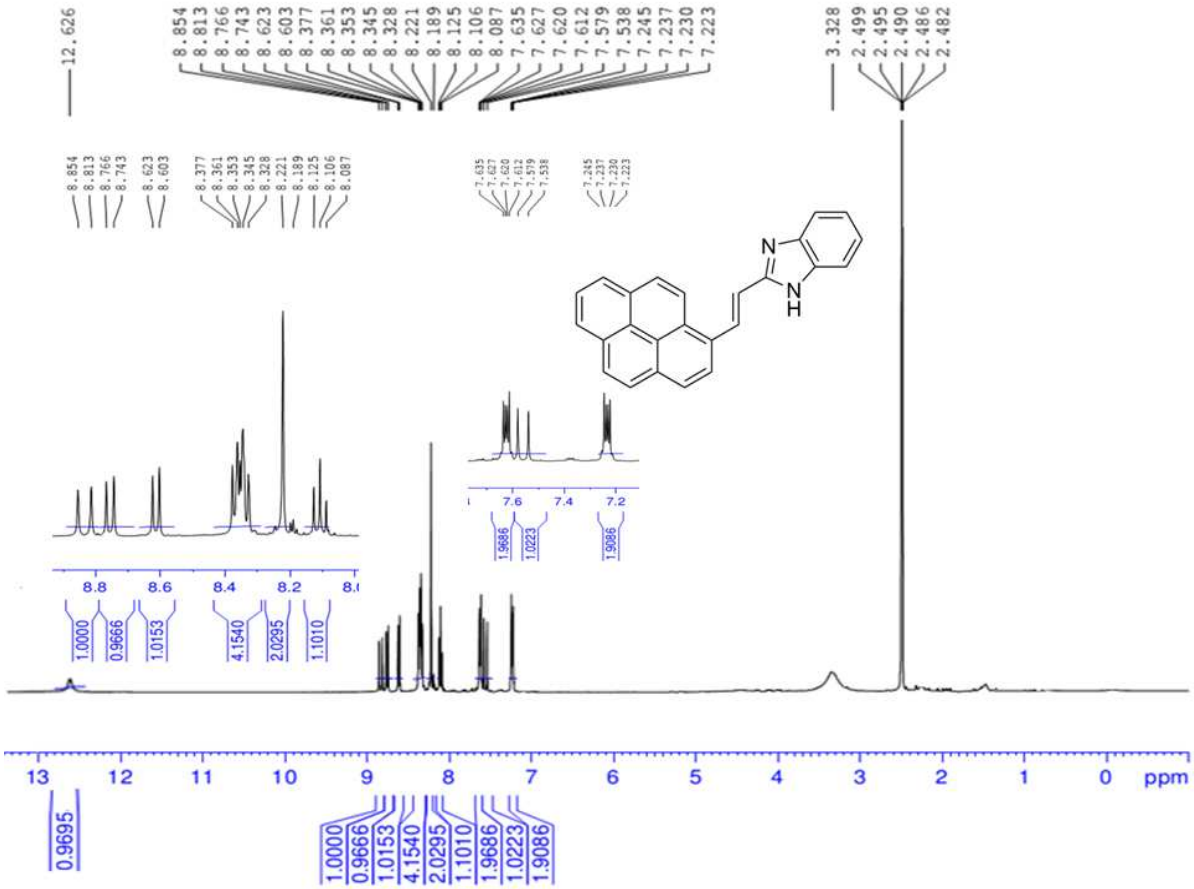
(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **4s**



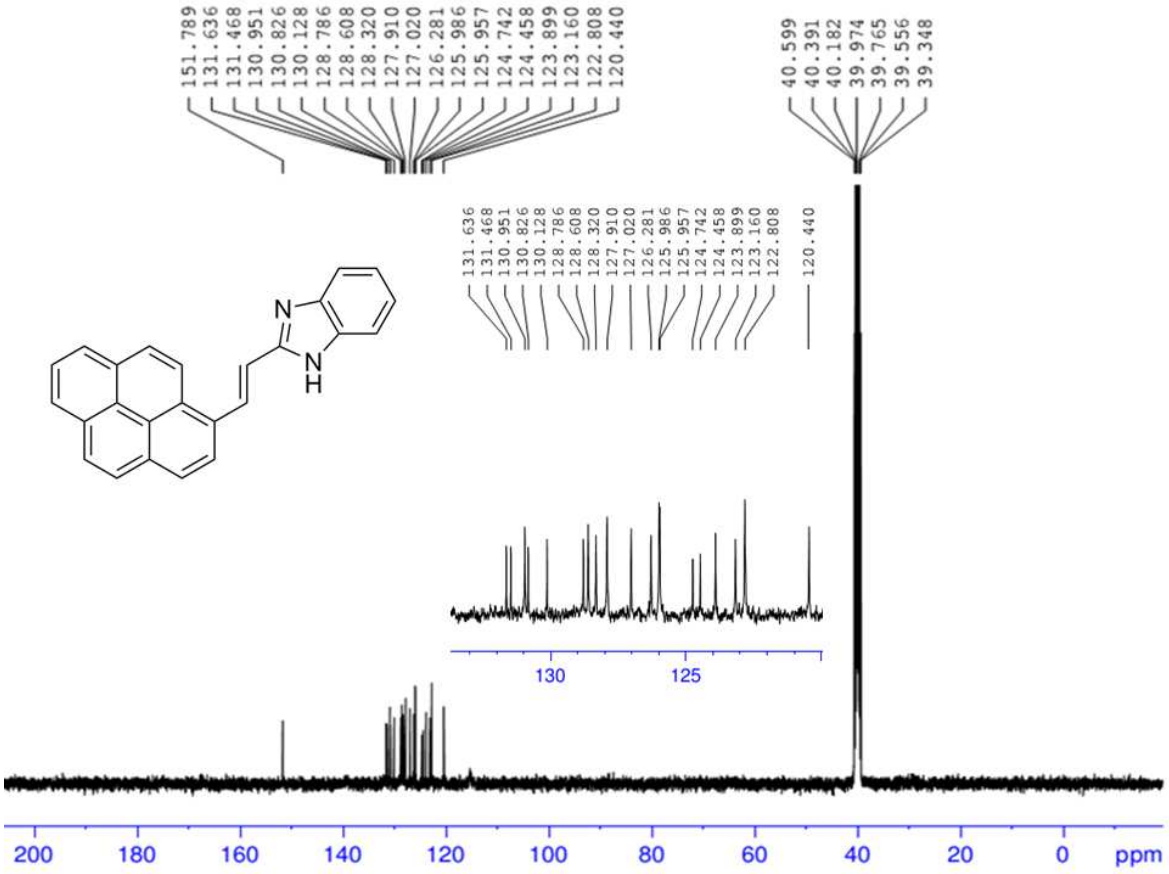
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4t**



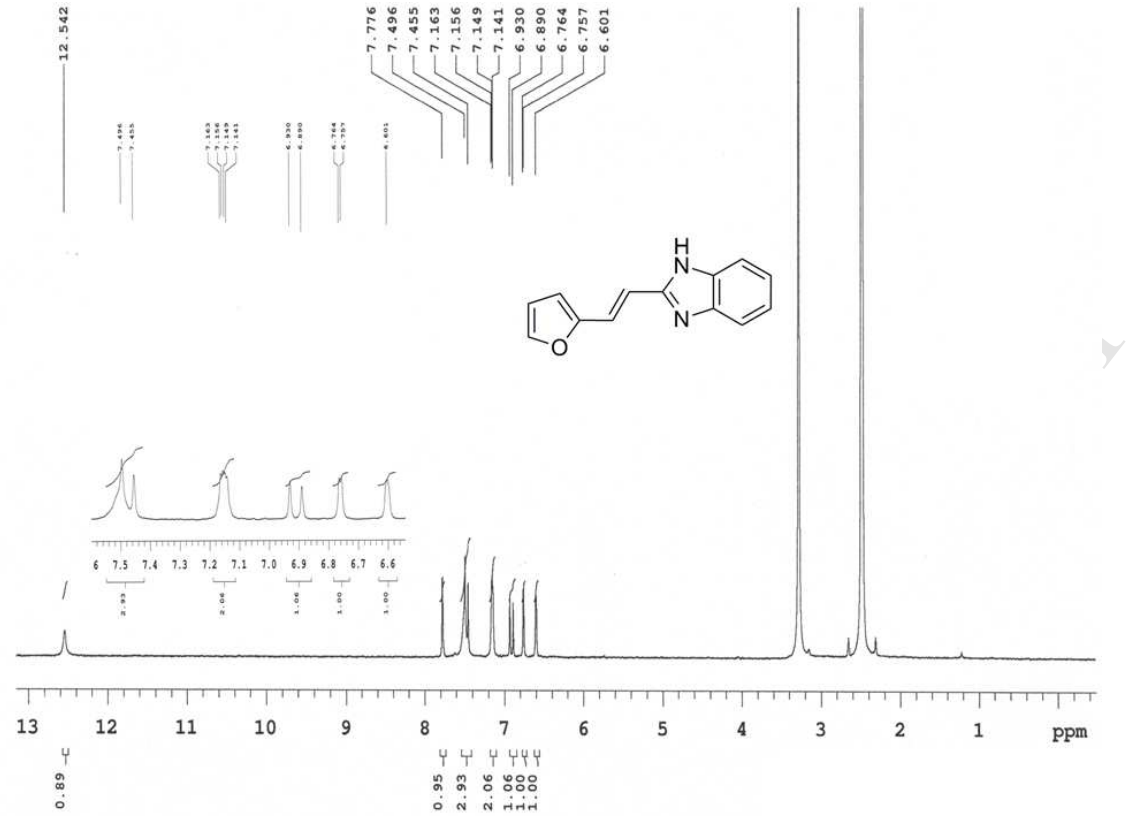
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **4t**



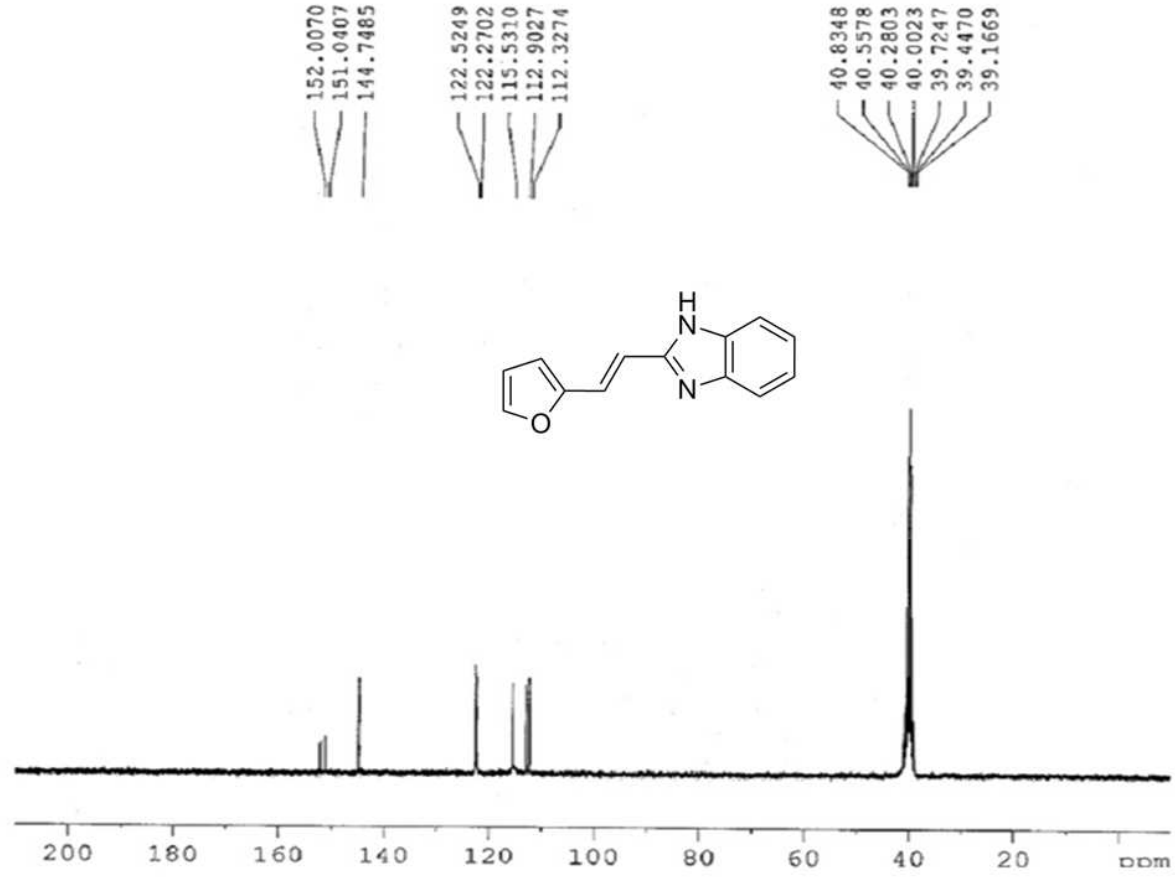
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4u**



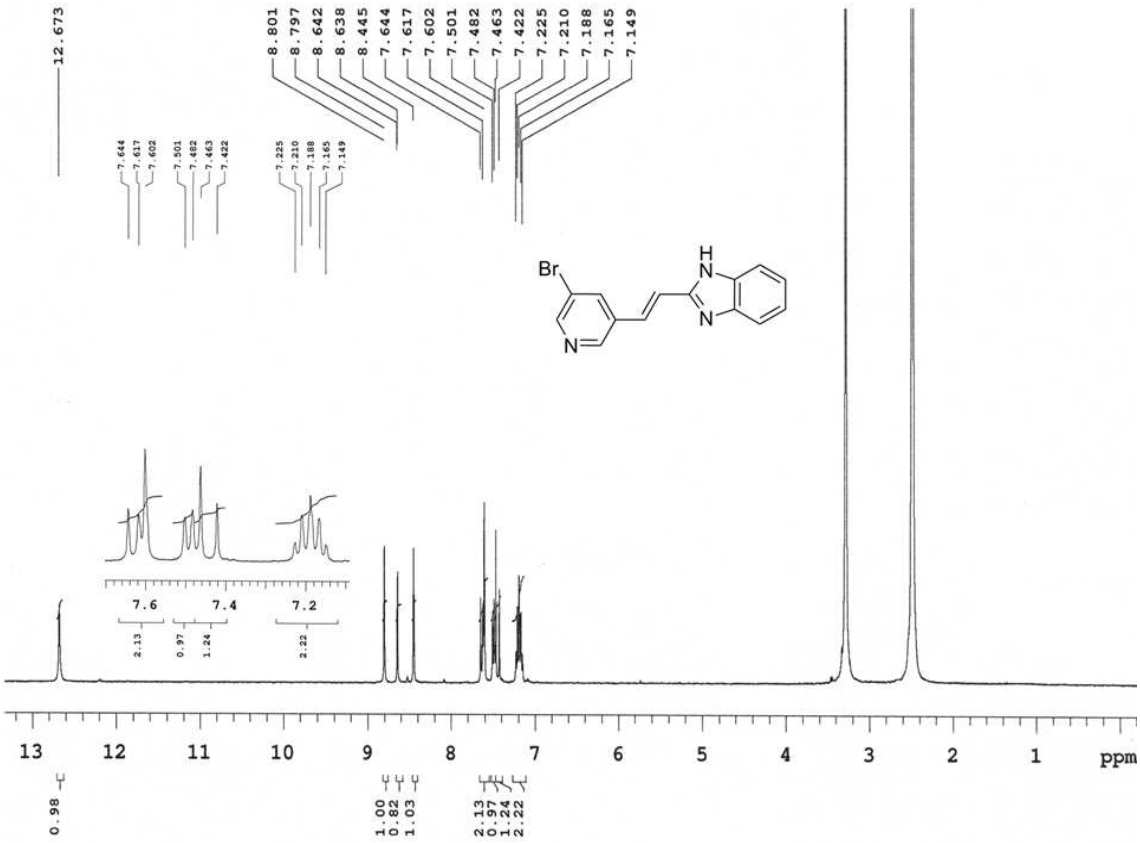
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **4u**



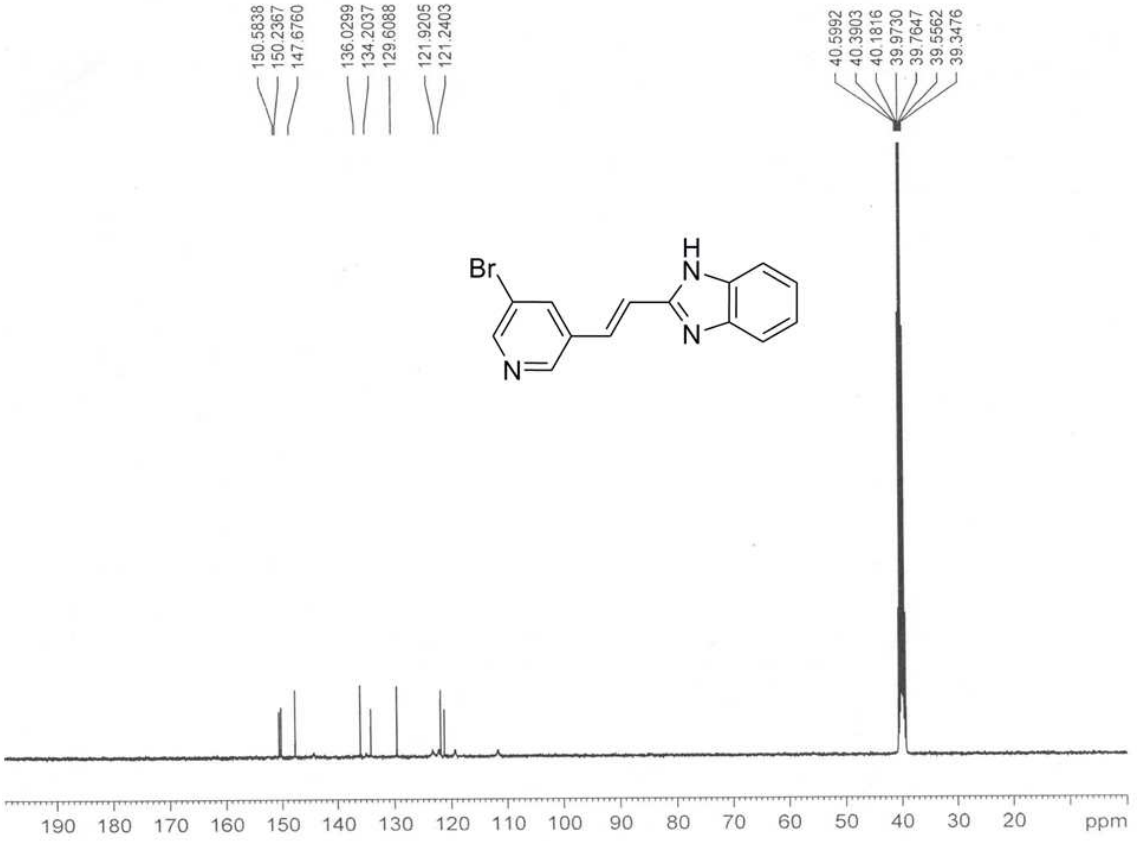
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4v**



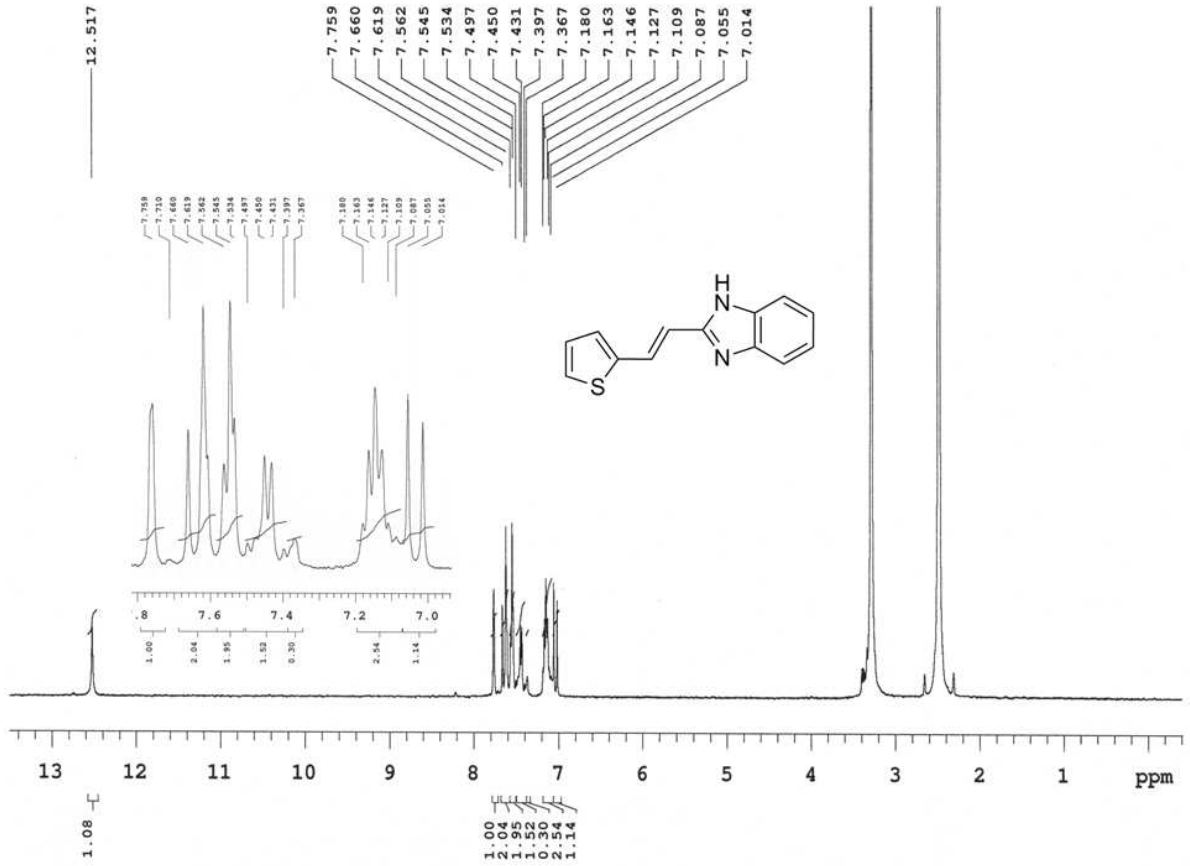
(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **4v**



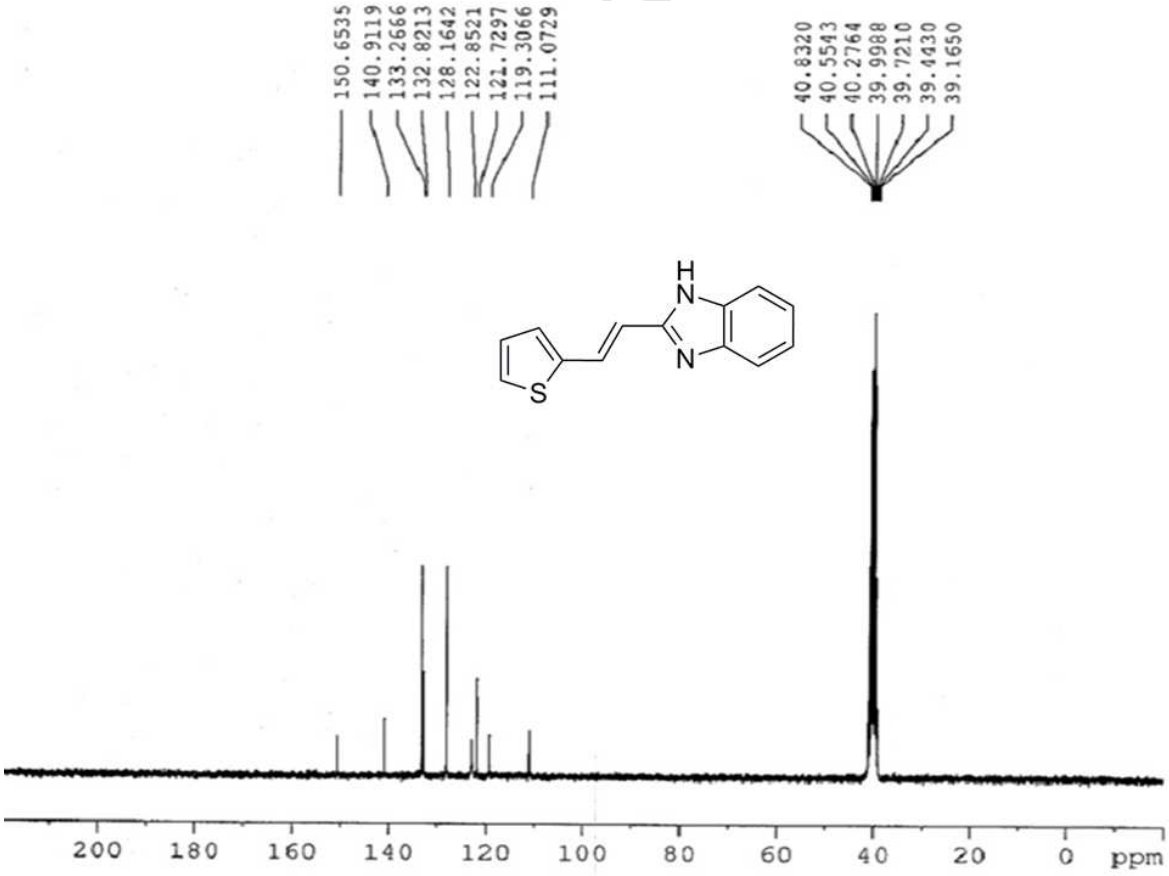
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4w**



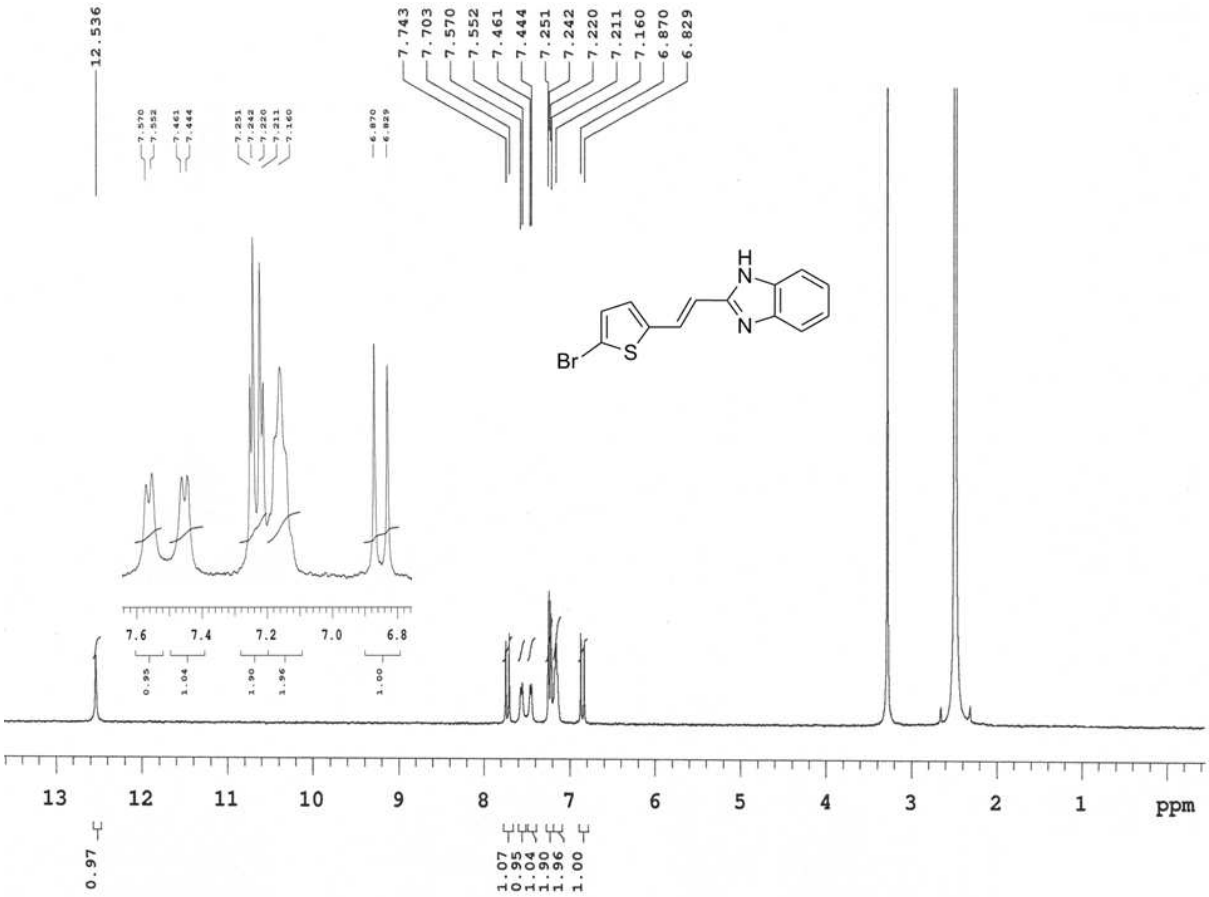
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **4w**



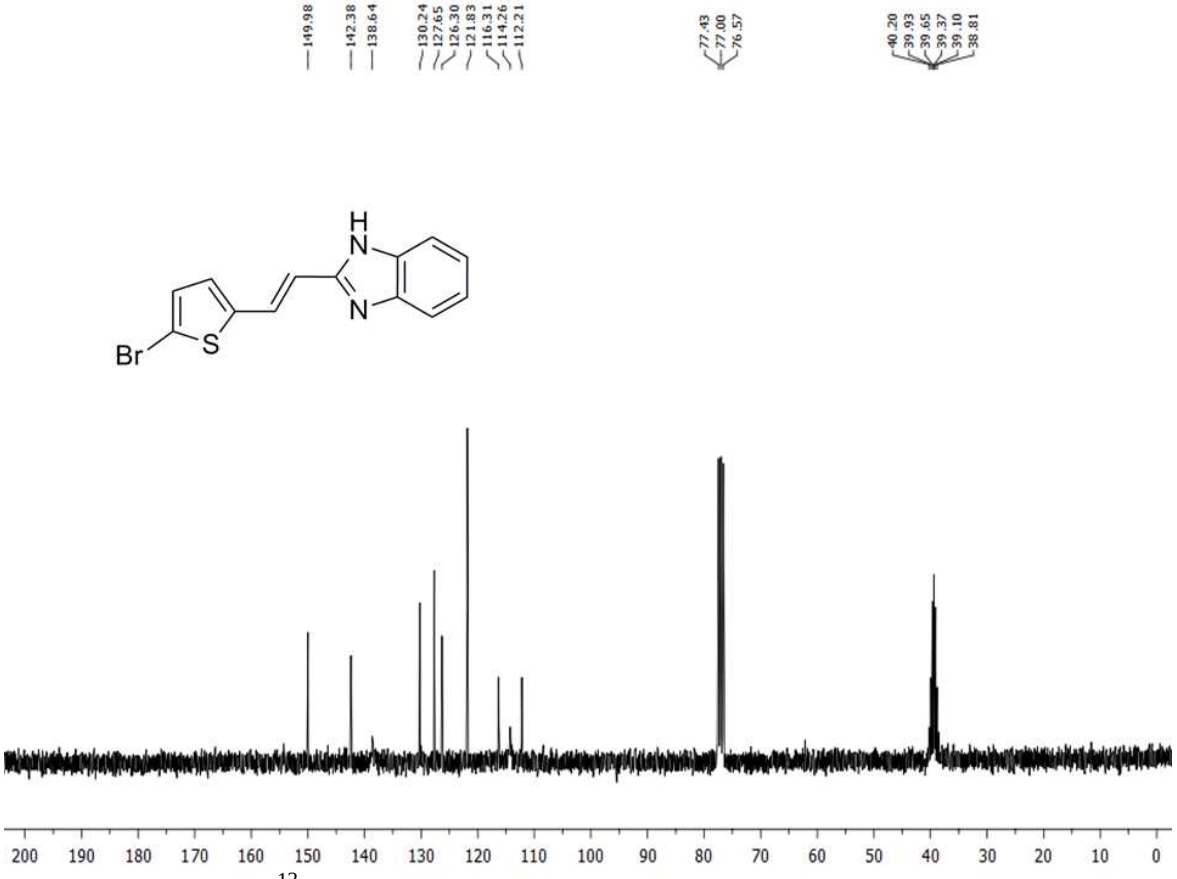
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4x**



(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **4x**

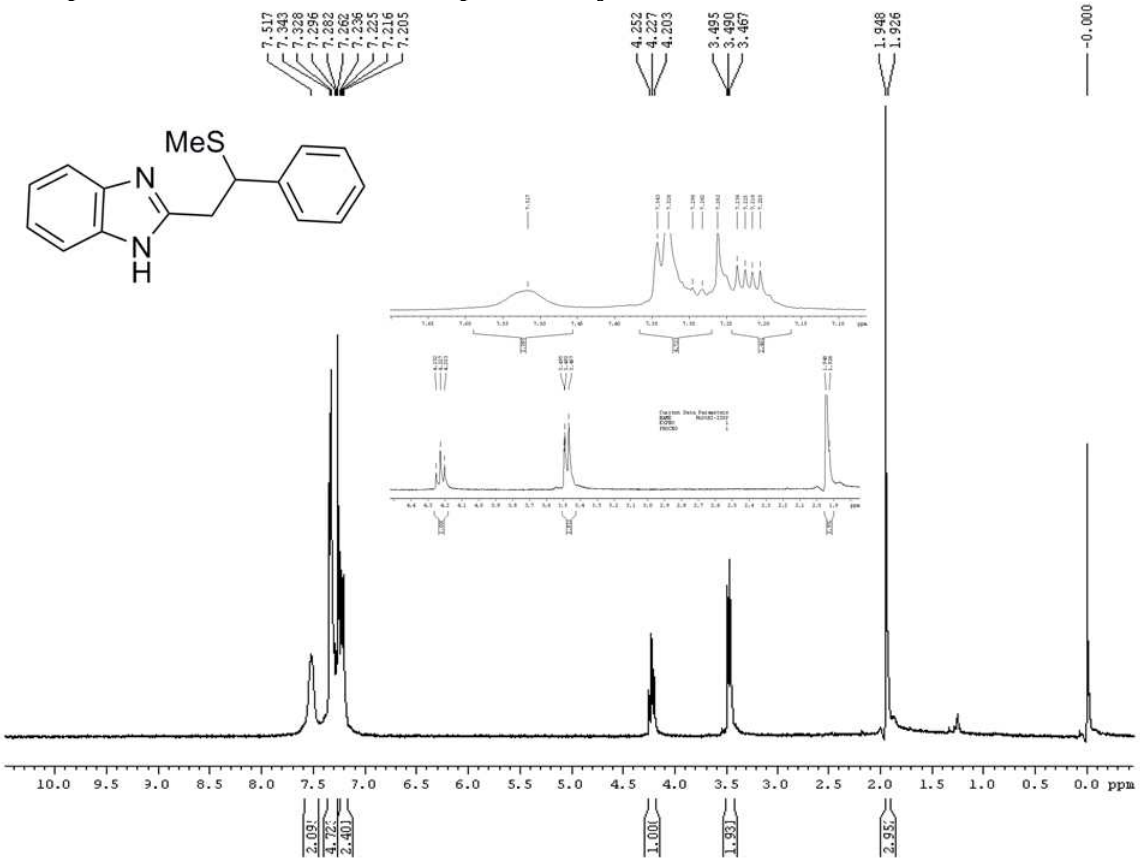


(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **4y**

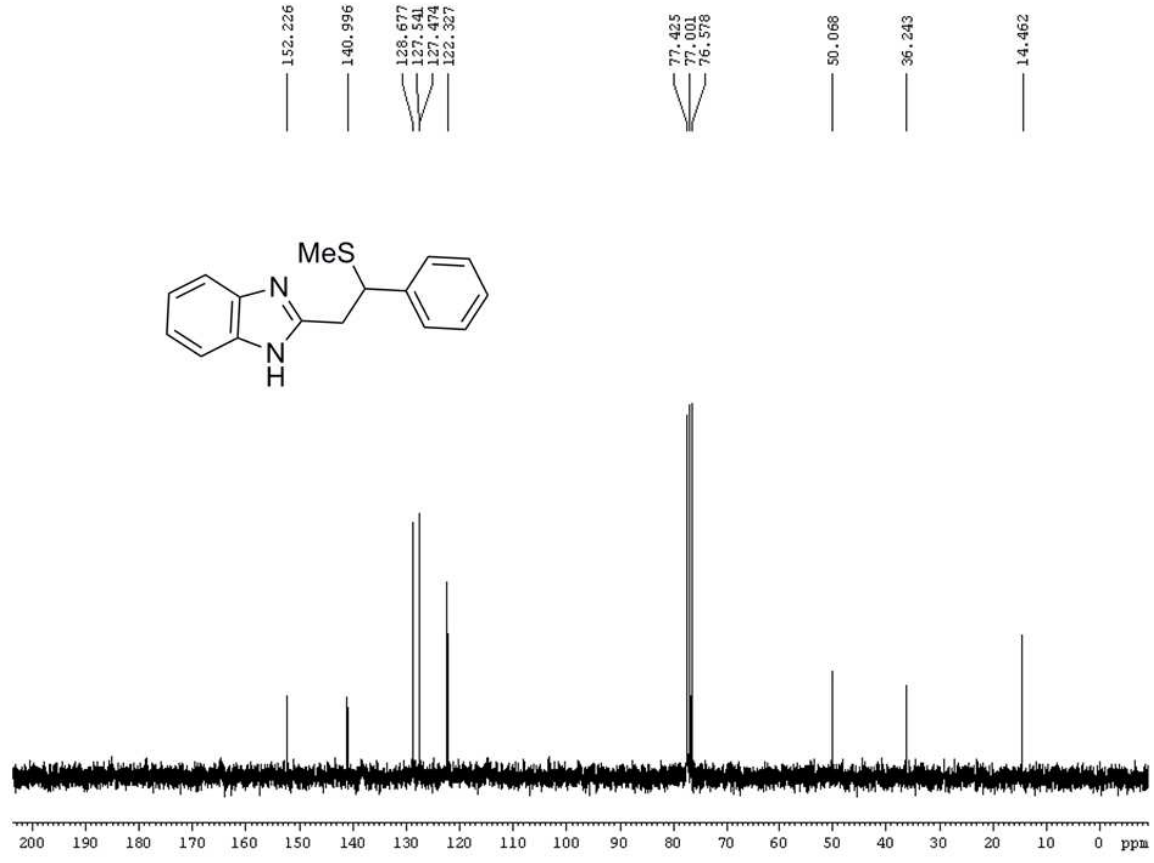


(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **4y**

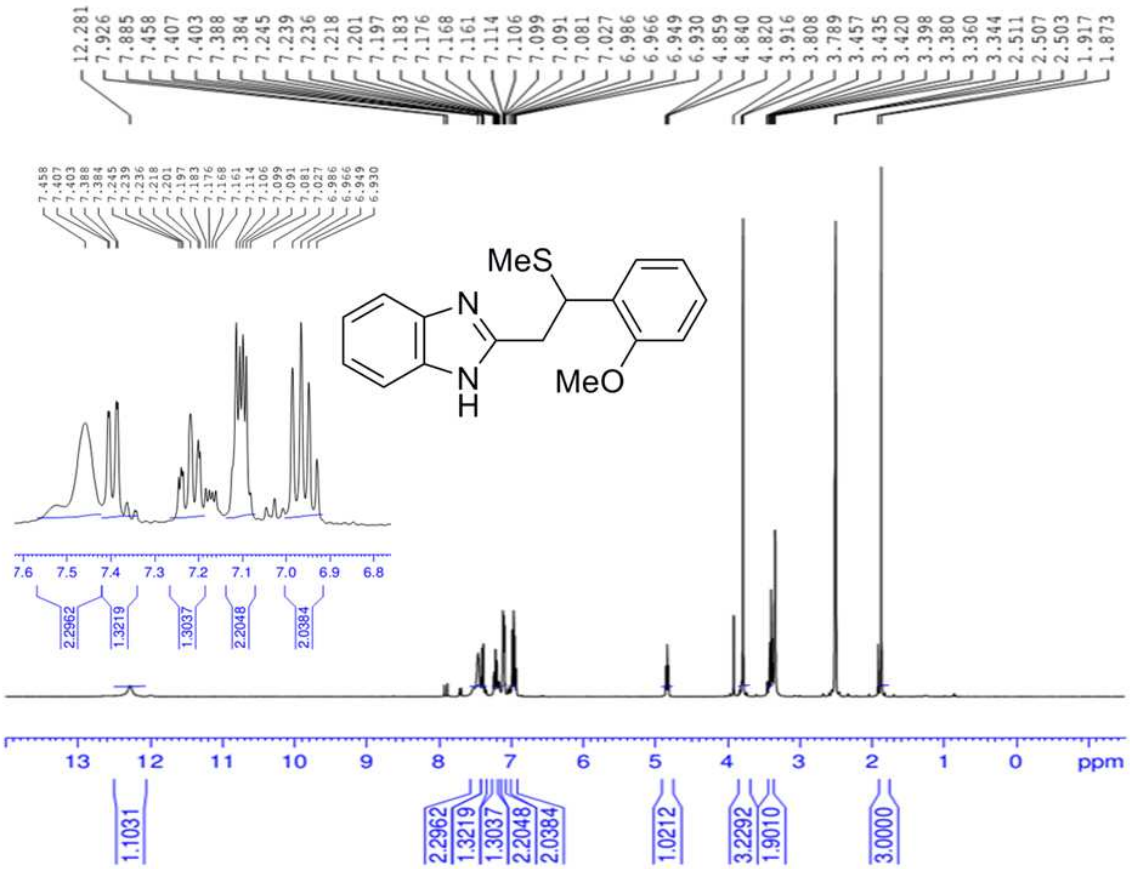
V Copies of ^{1}H NMR&^{13}C NMR spectra 5a-y



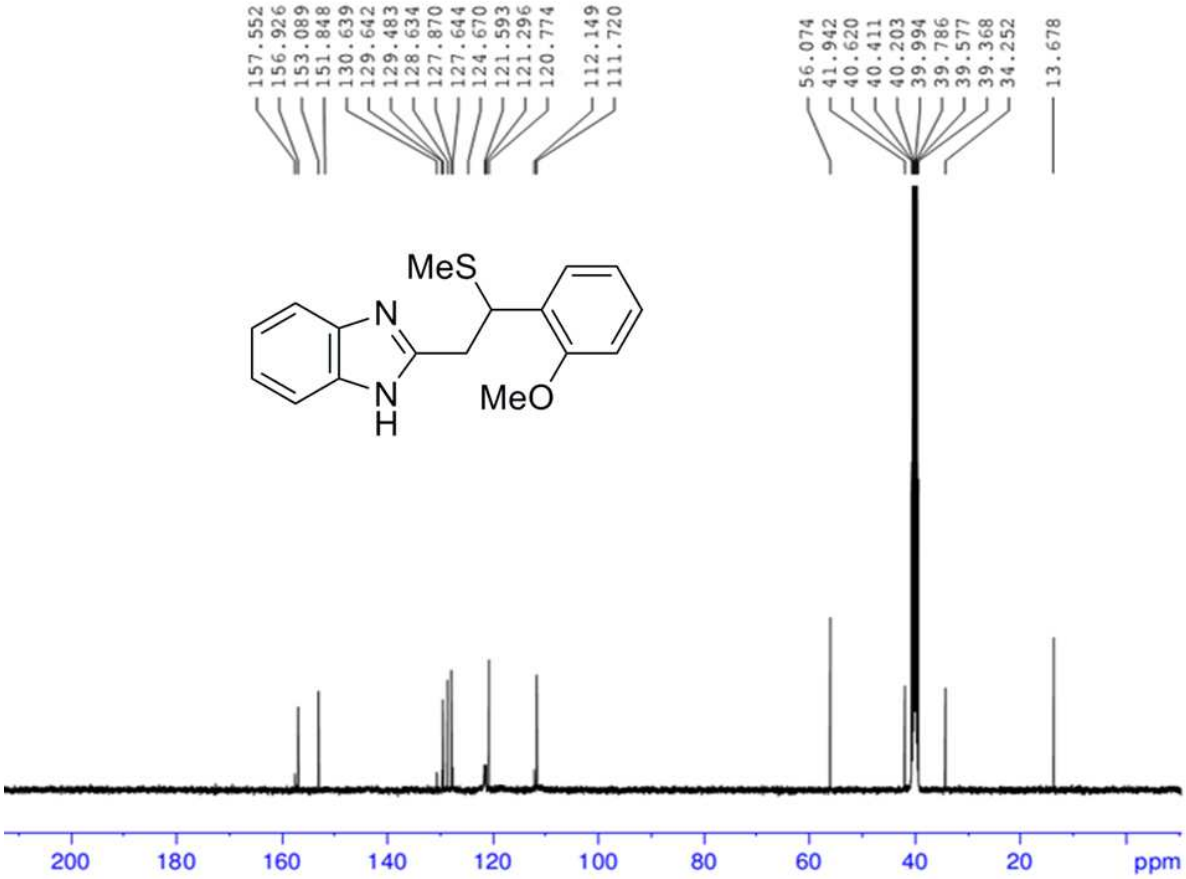
(300MHz, $CDCl_3$) ^{1}H NMR spectrum of **5a**



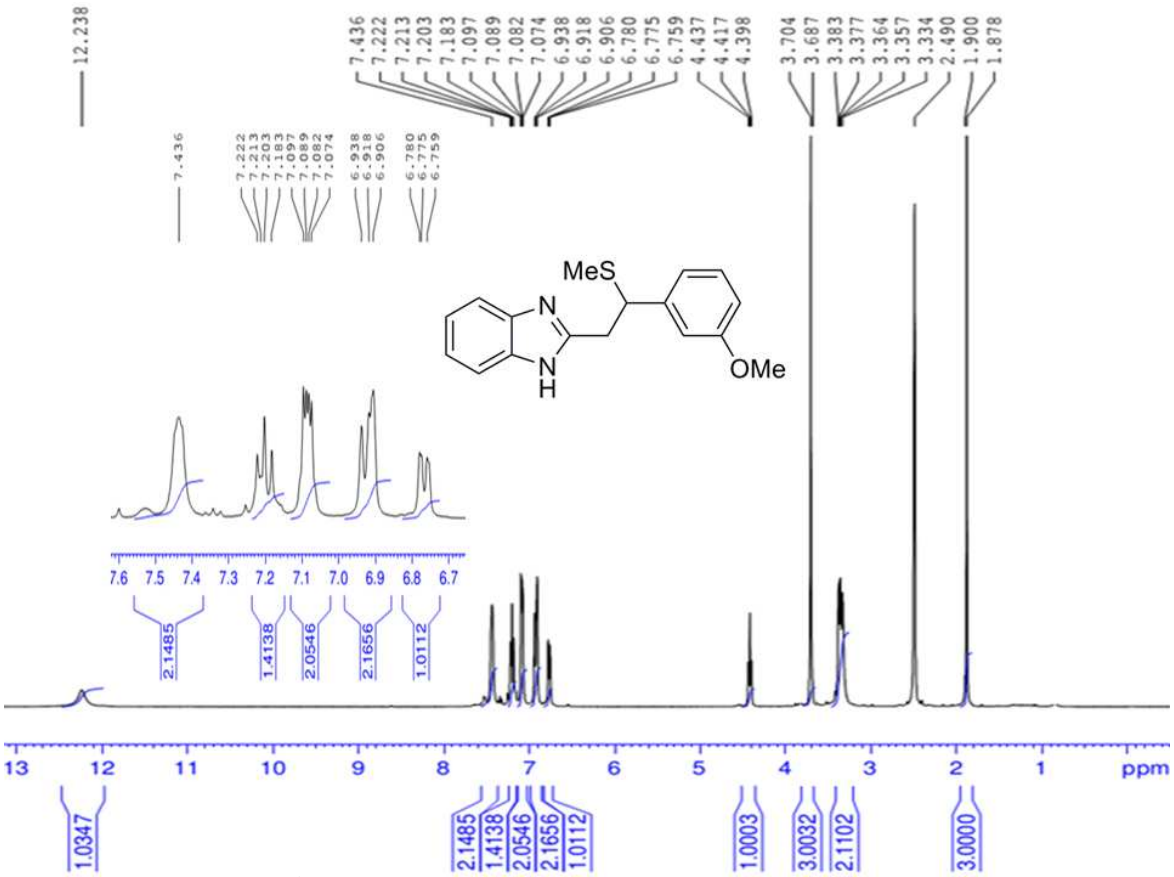
(75MHz, $CDCl_3$) ^{13}C NMR spectrum of **5a**



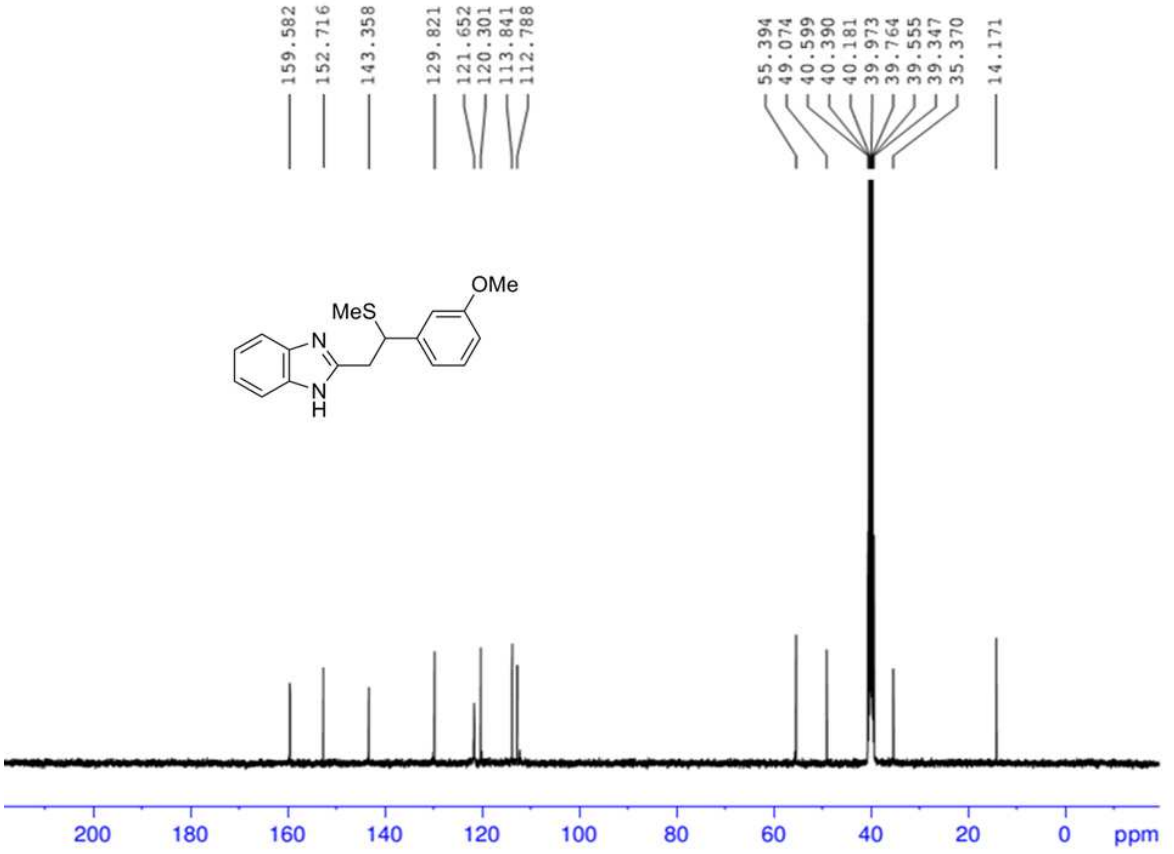
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **5b**



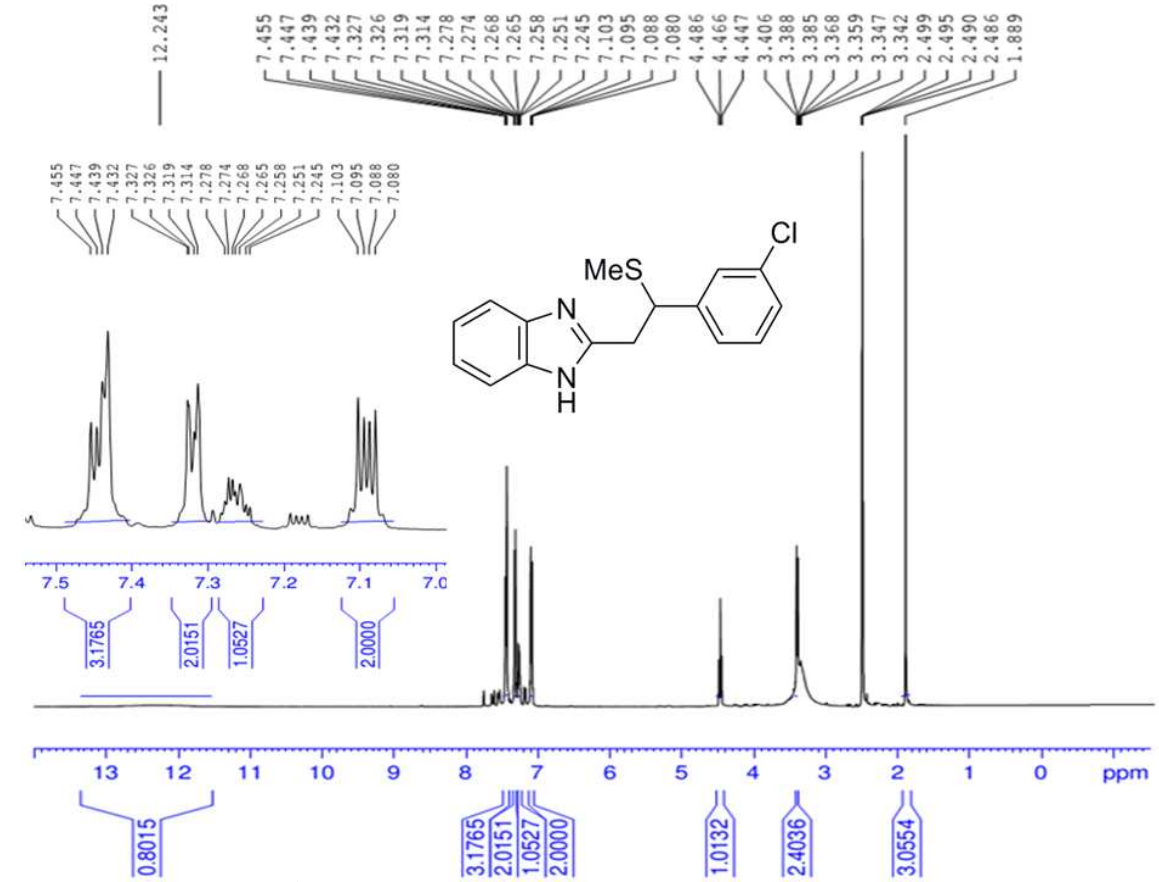
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **5b**



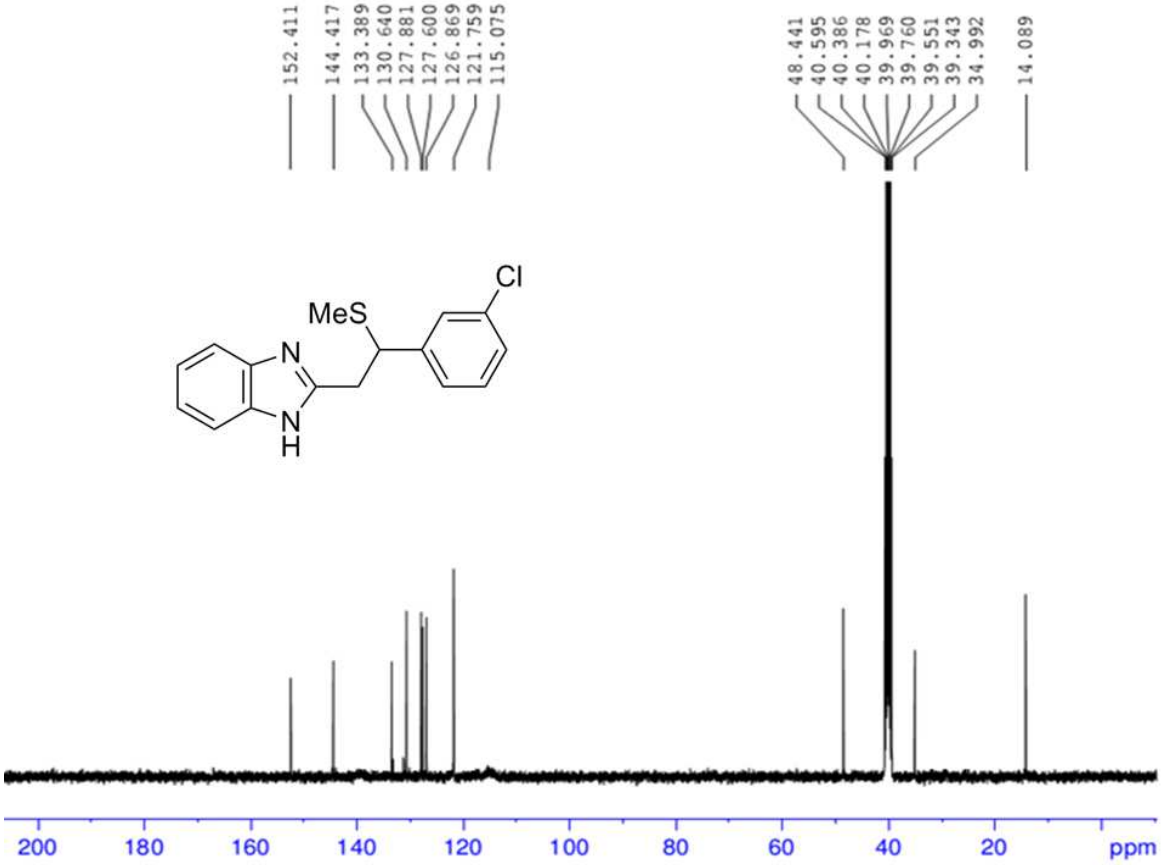
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **5c**



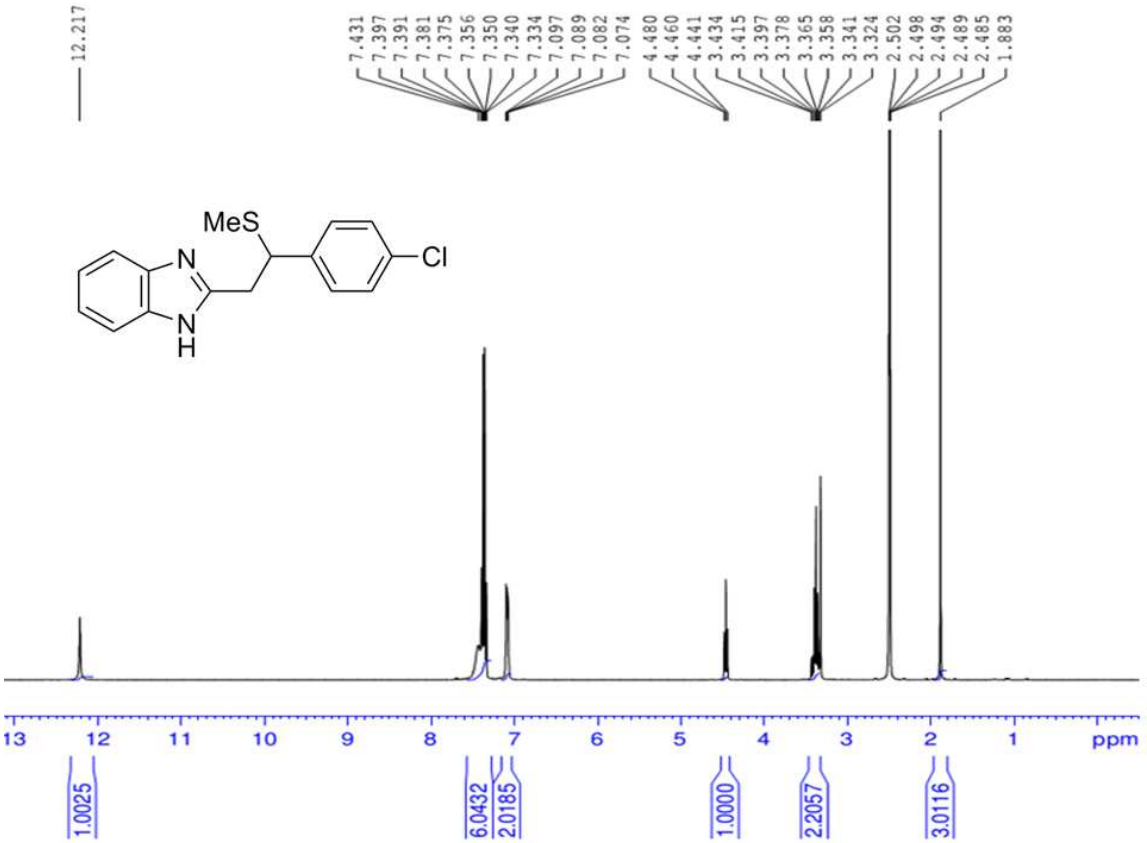
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **5c**



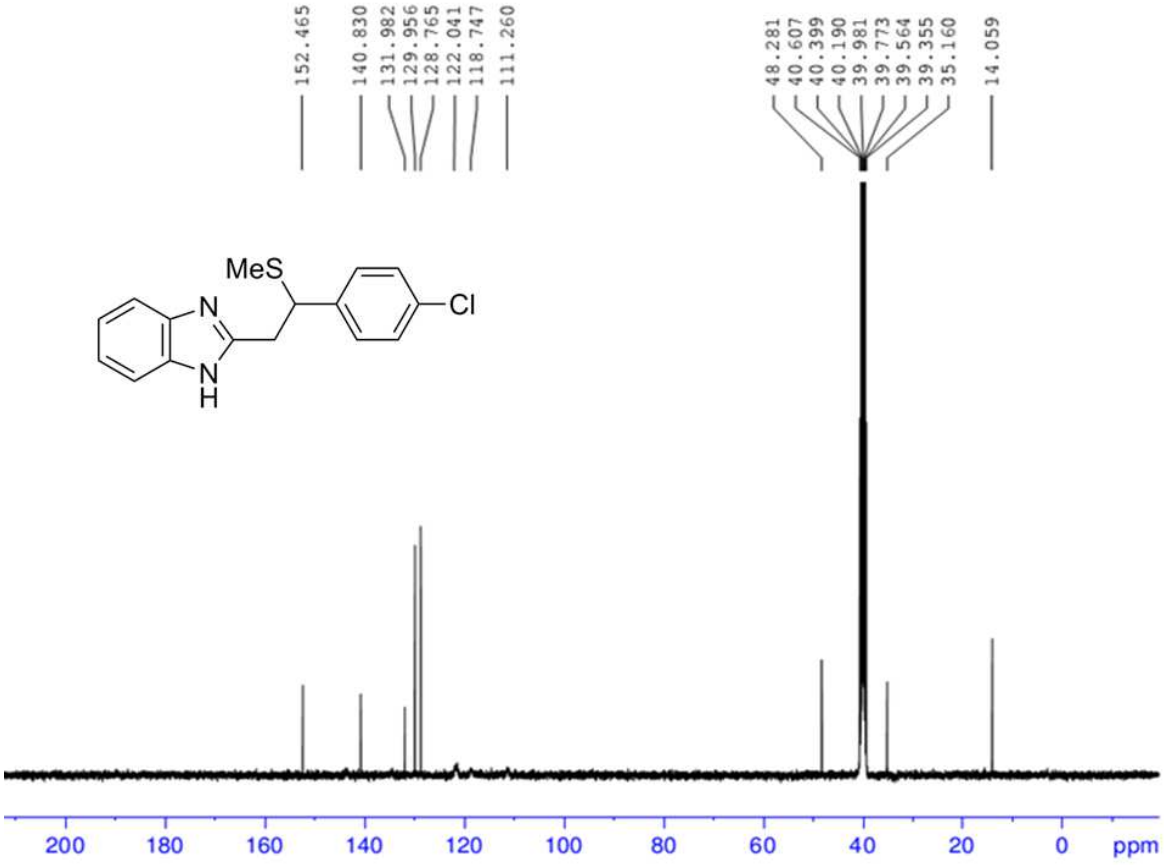
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **5e**



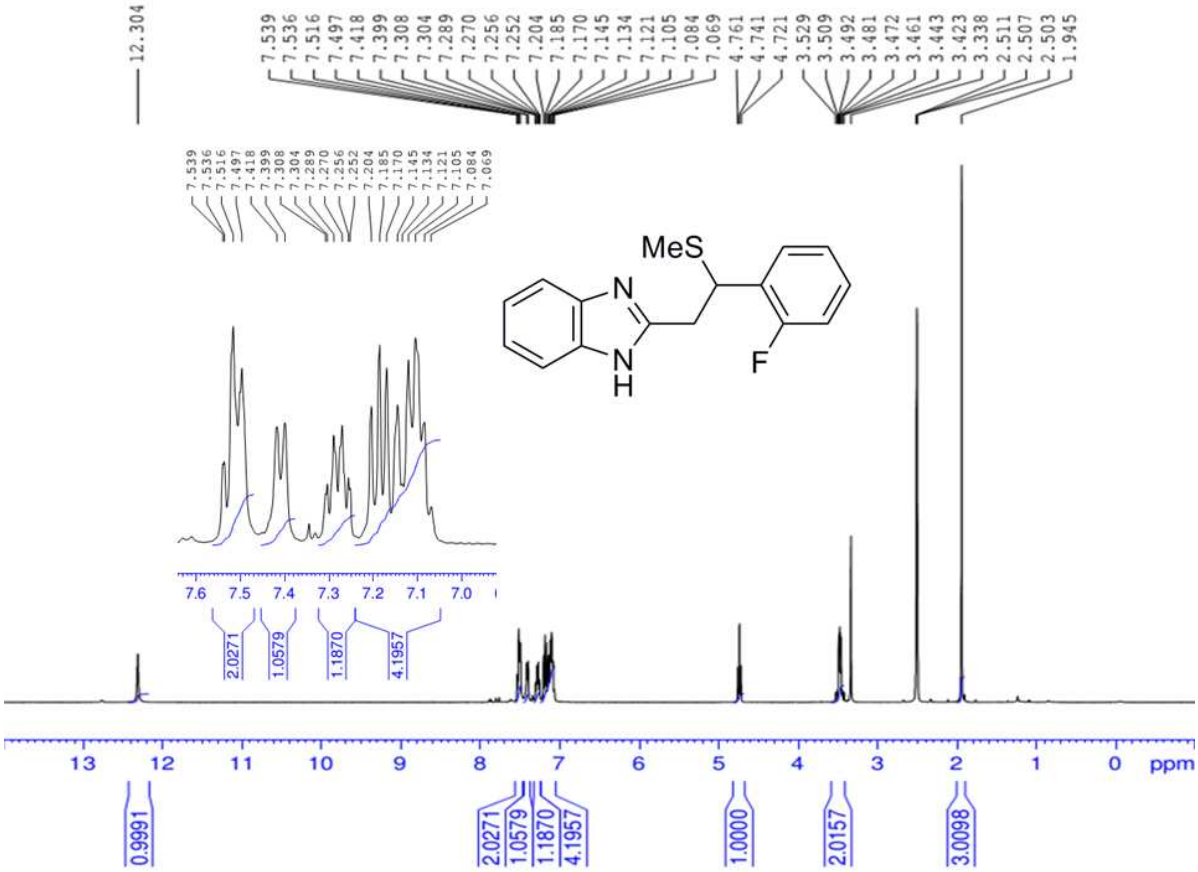
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **5e**



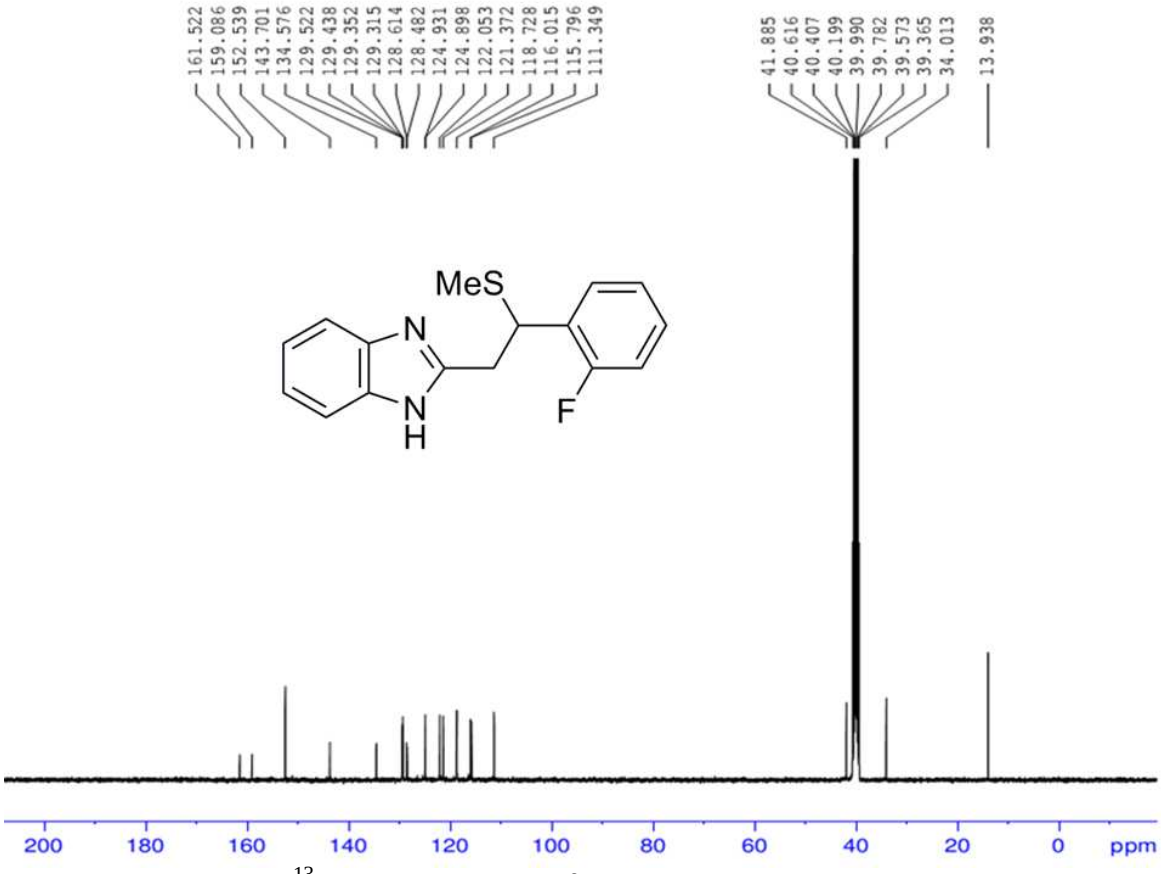
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **5f**



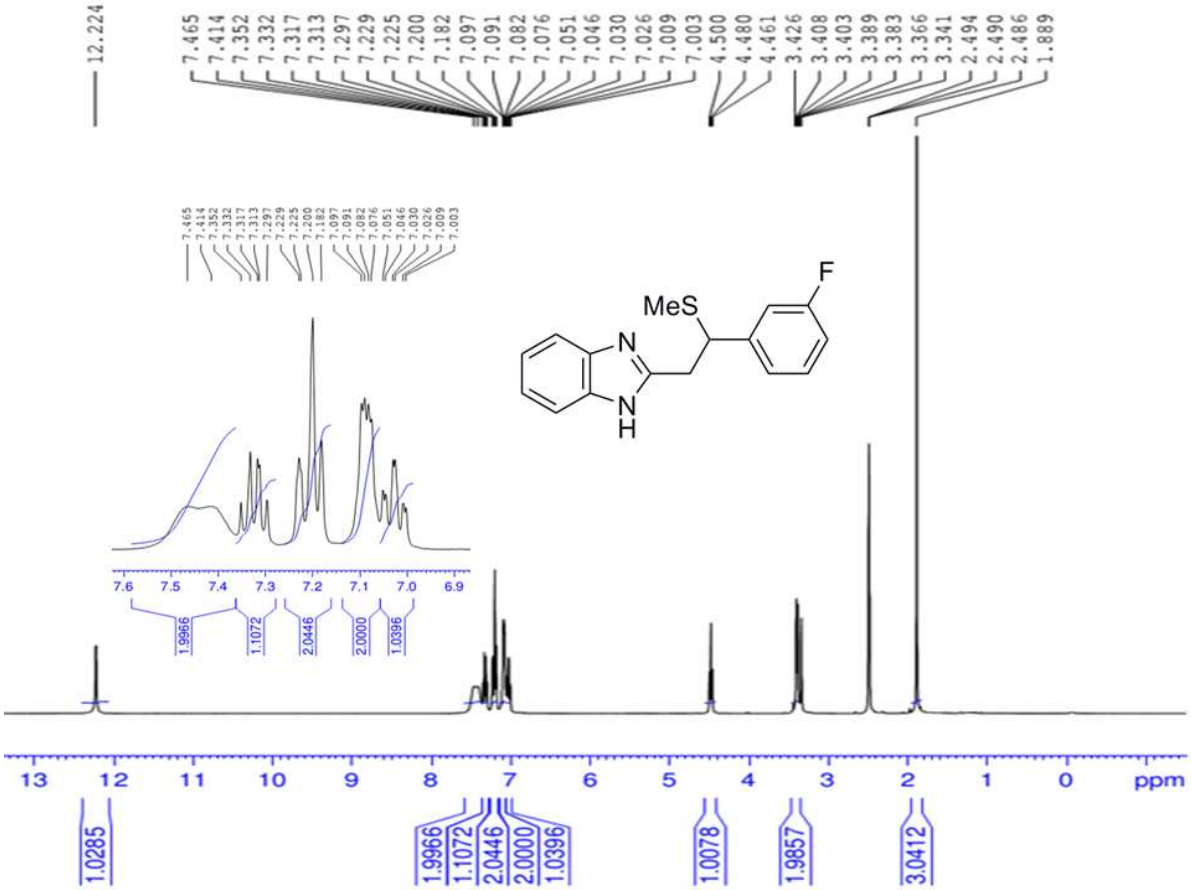
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **5f**



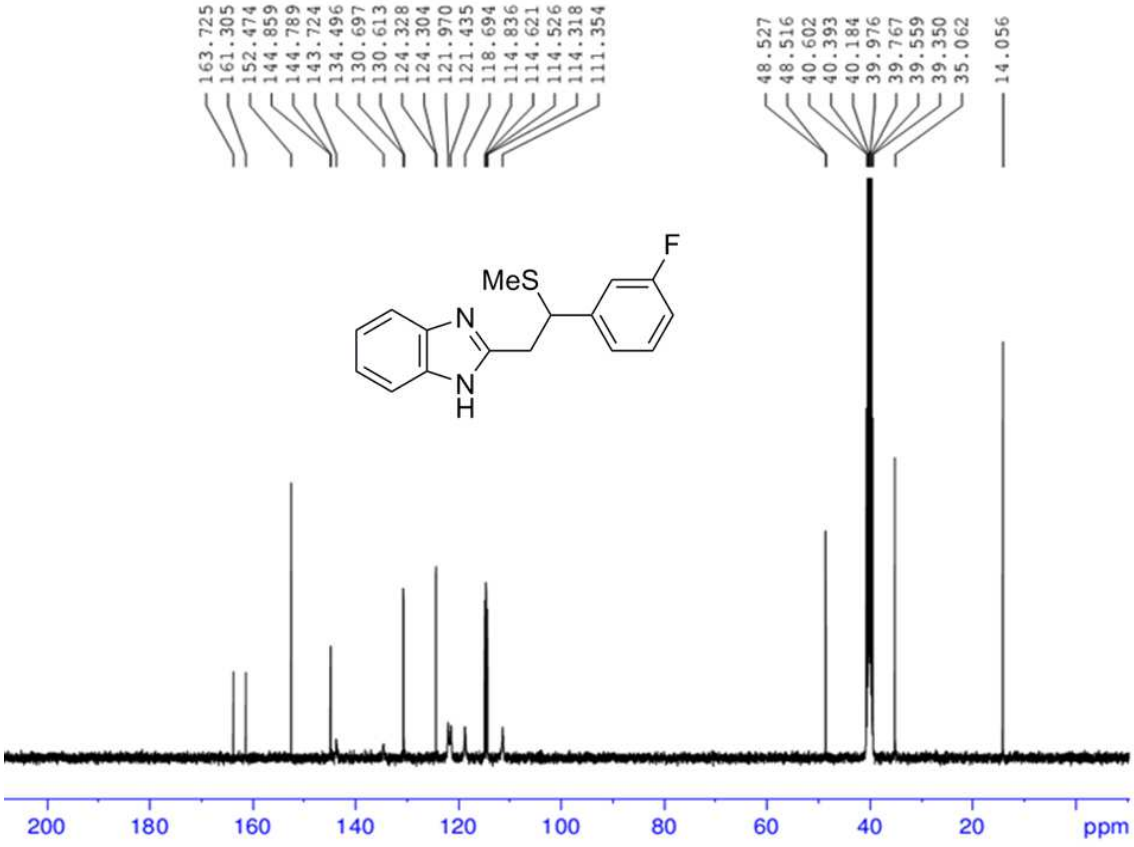
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **5g**



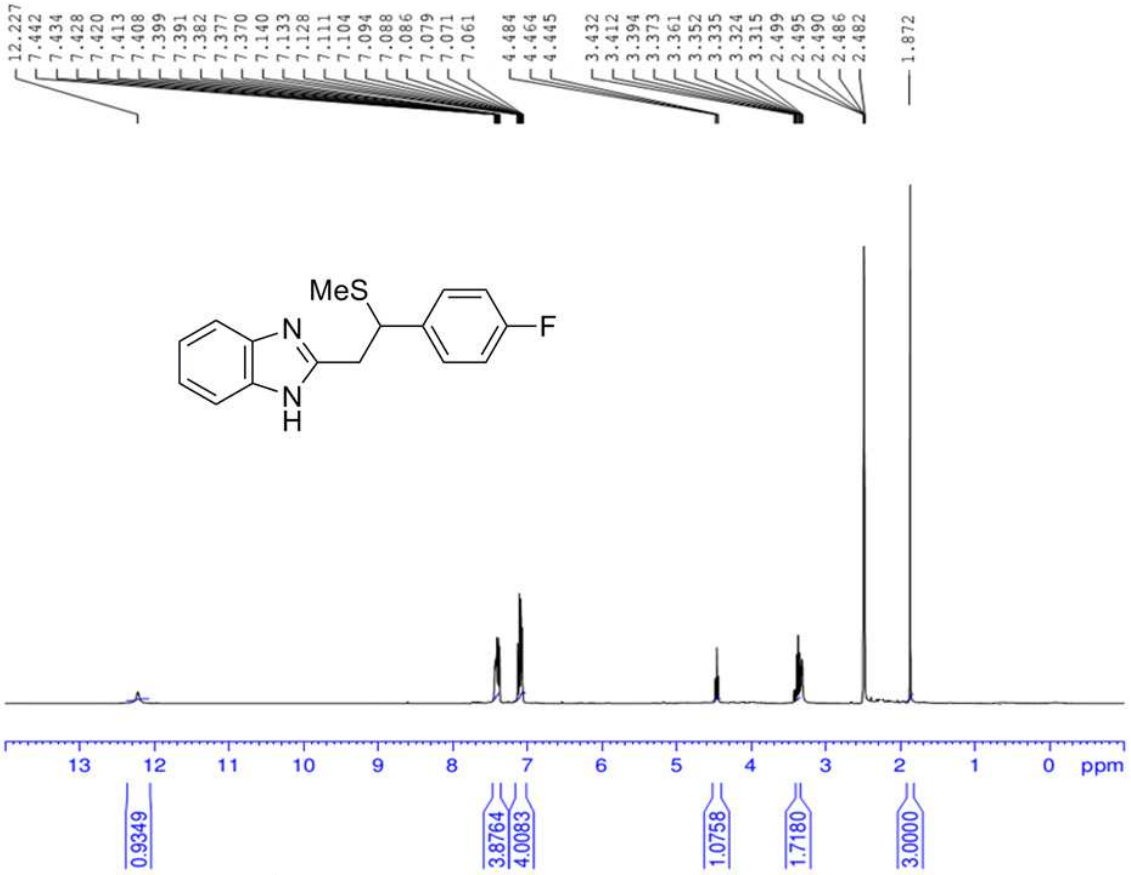
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **5g**



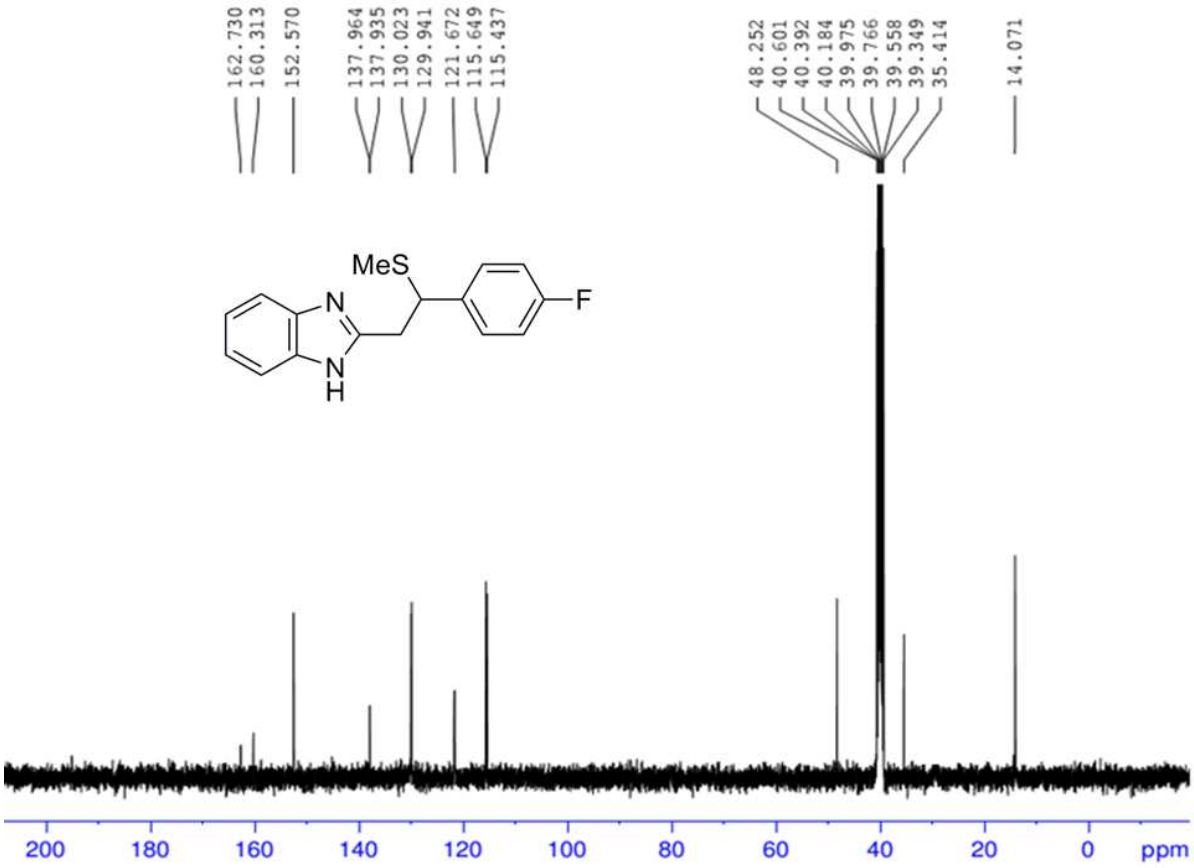
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **5h**



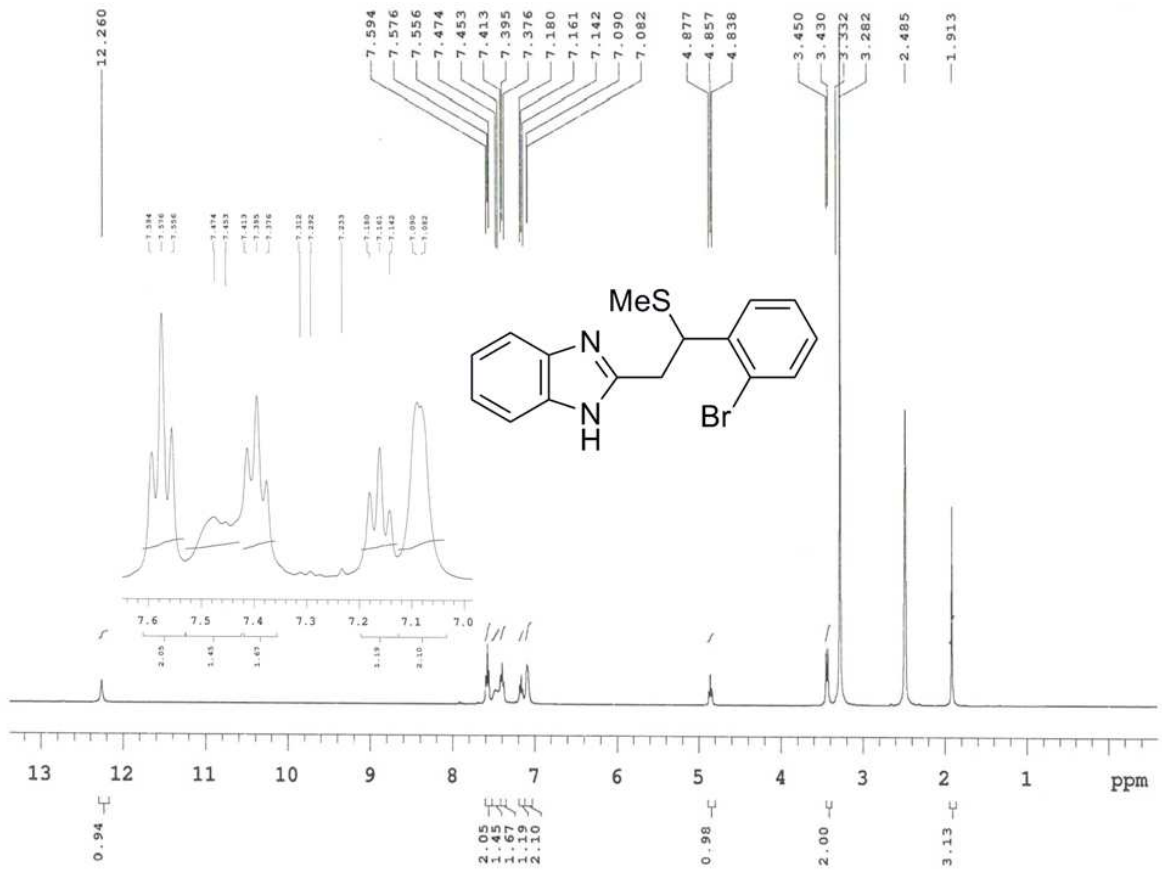
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **5h**



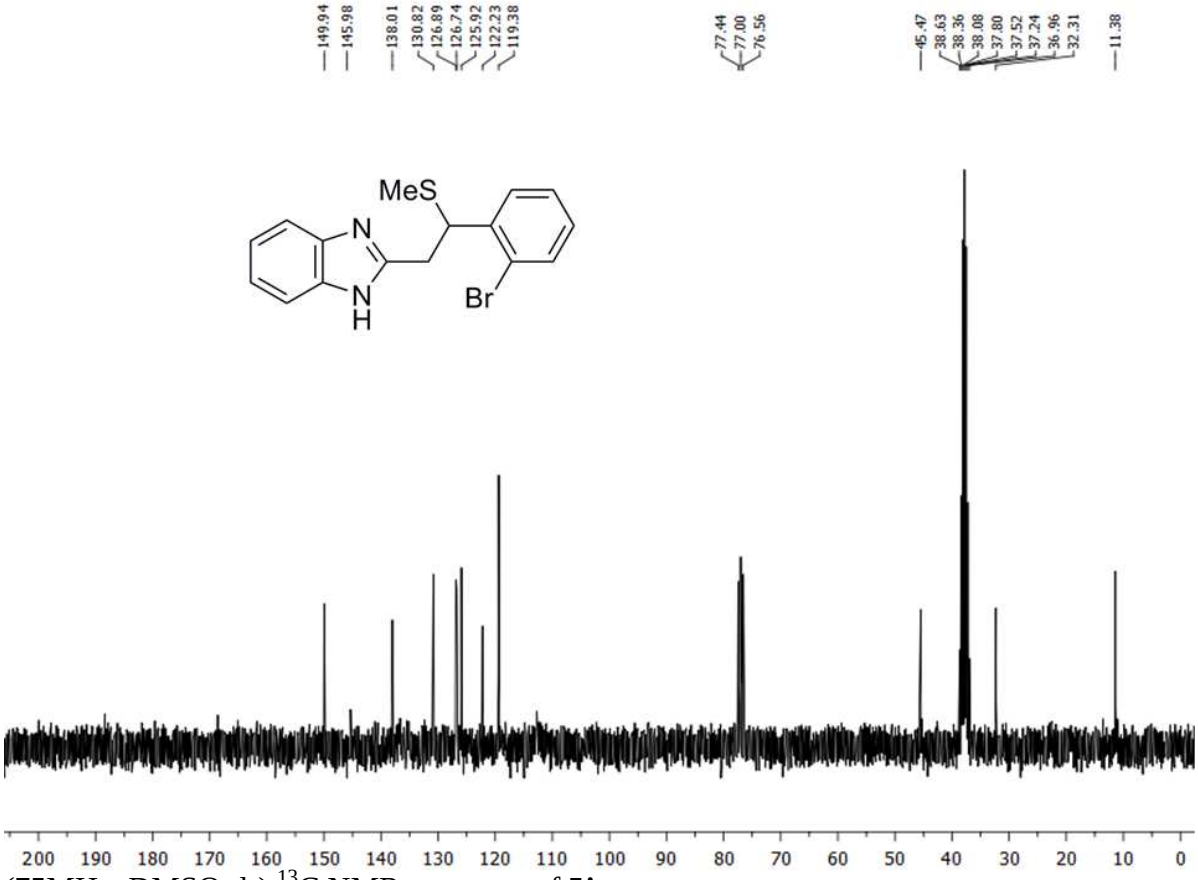
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **5i**



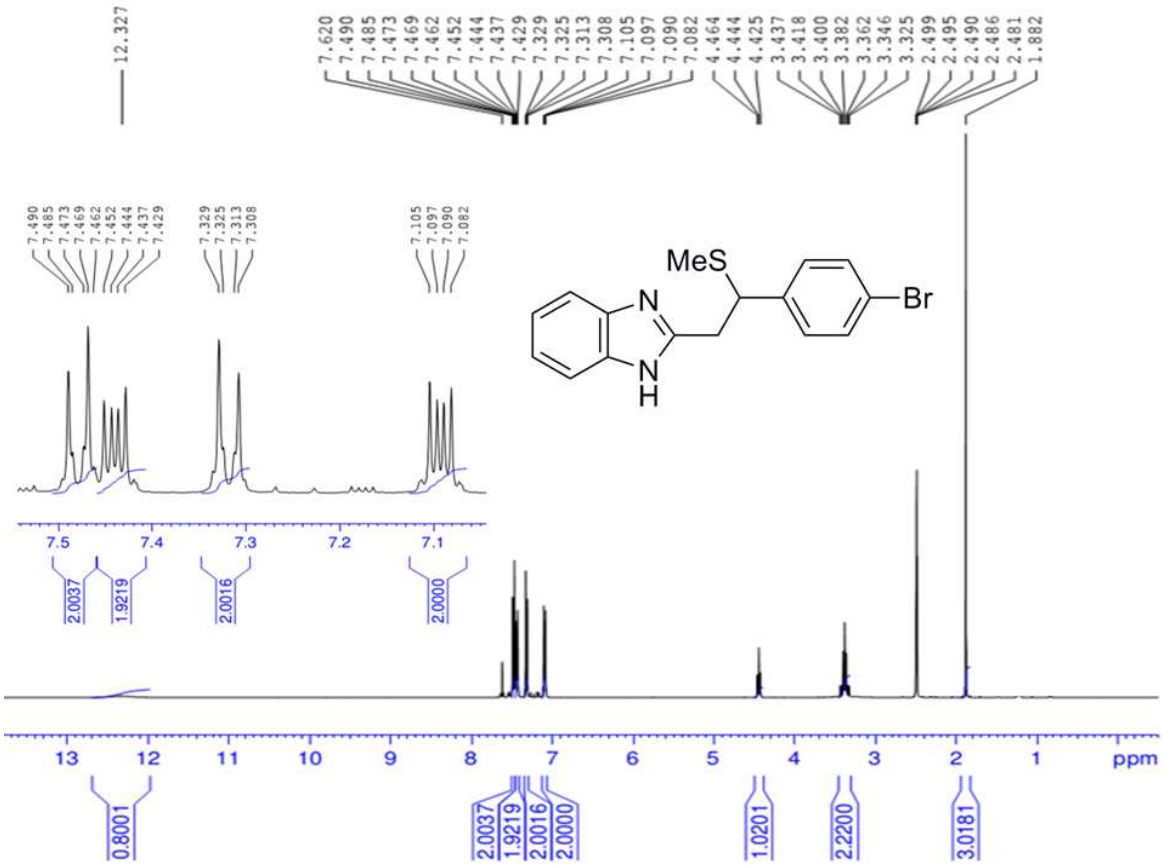
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **5i**



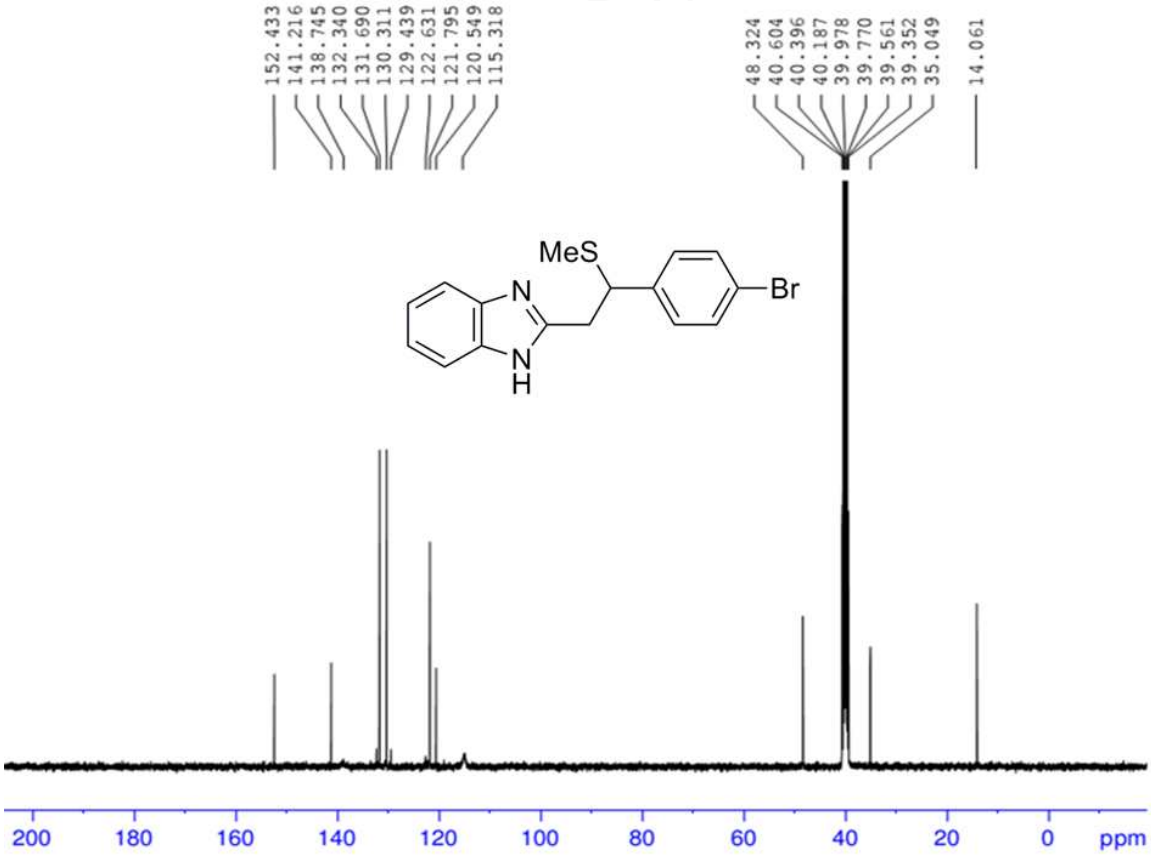
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **5j**



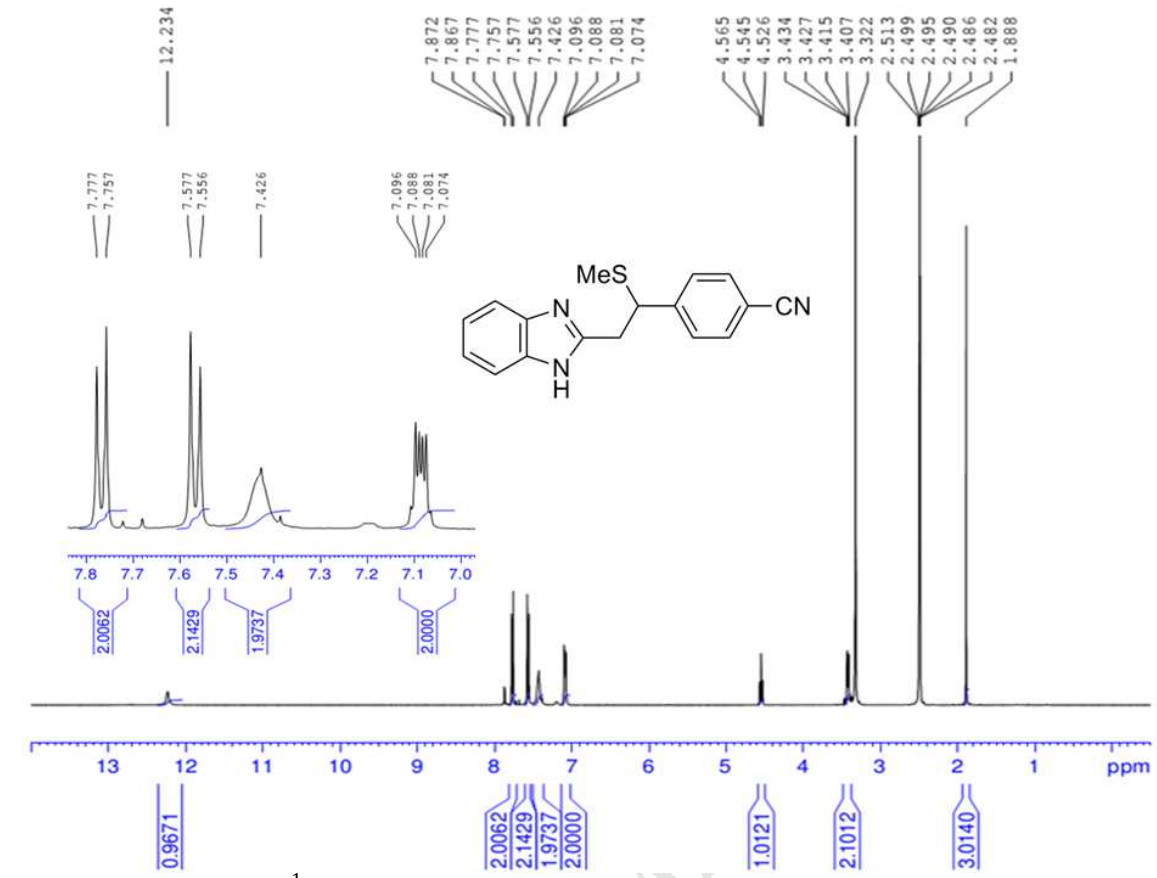
(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **5j**



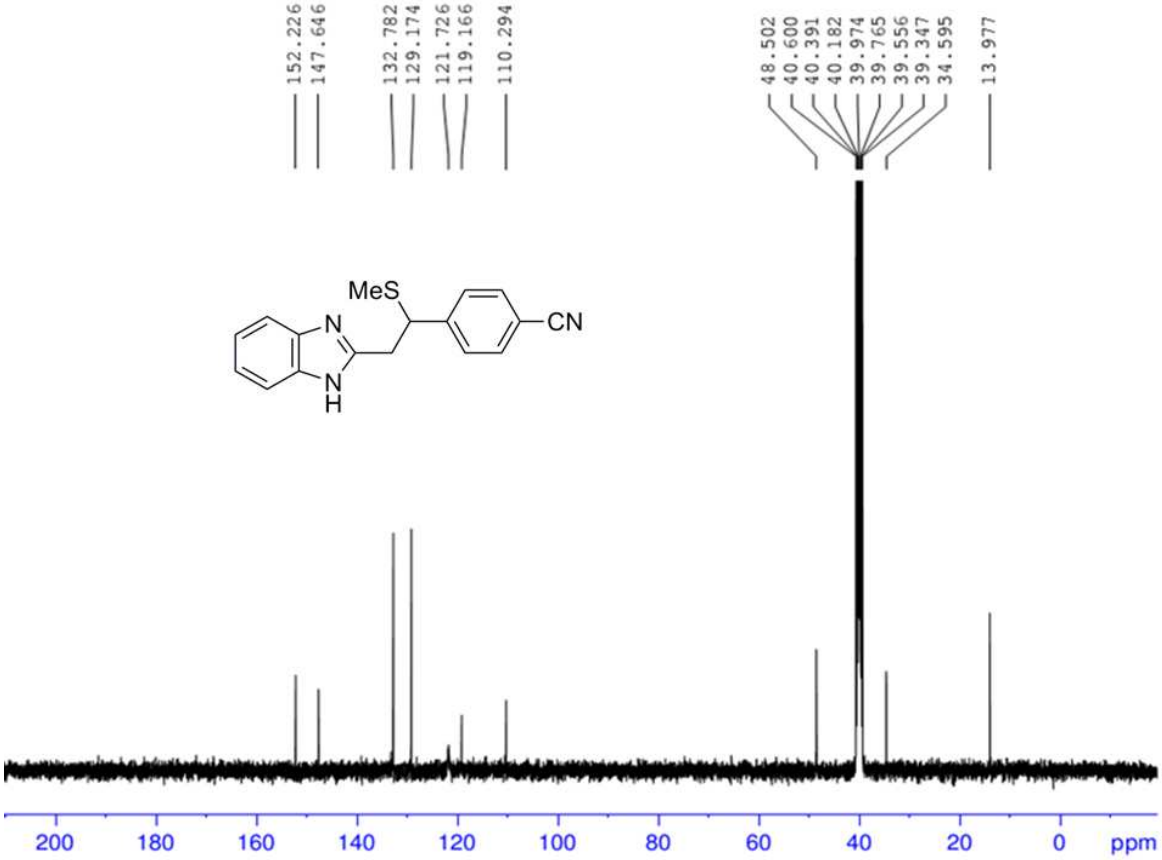
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **5k**



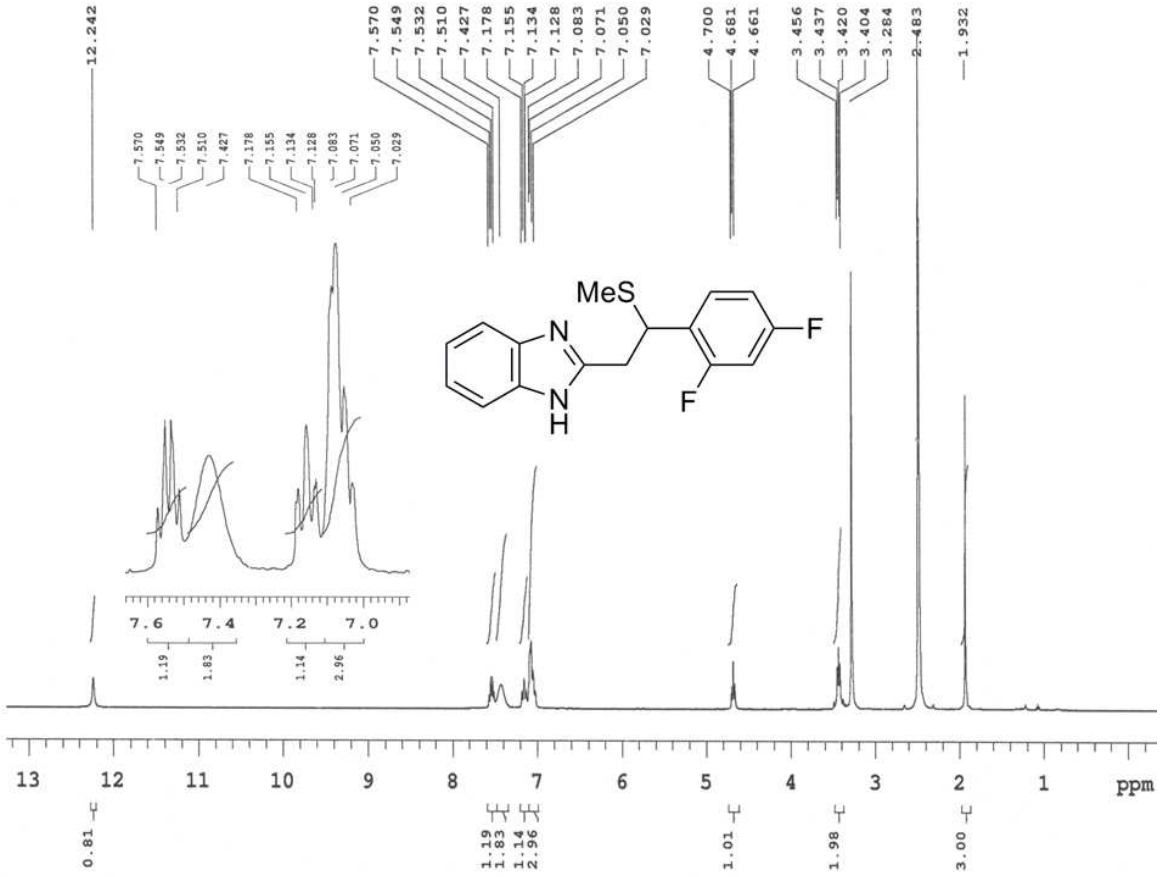
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **5k**



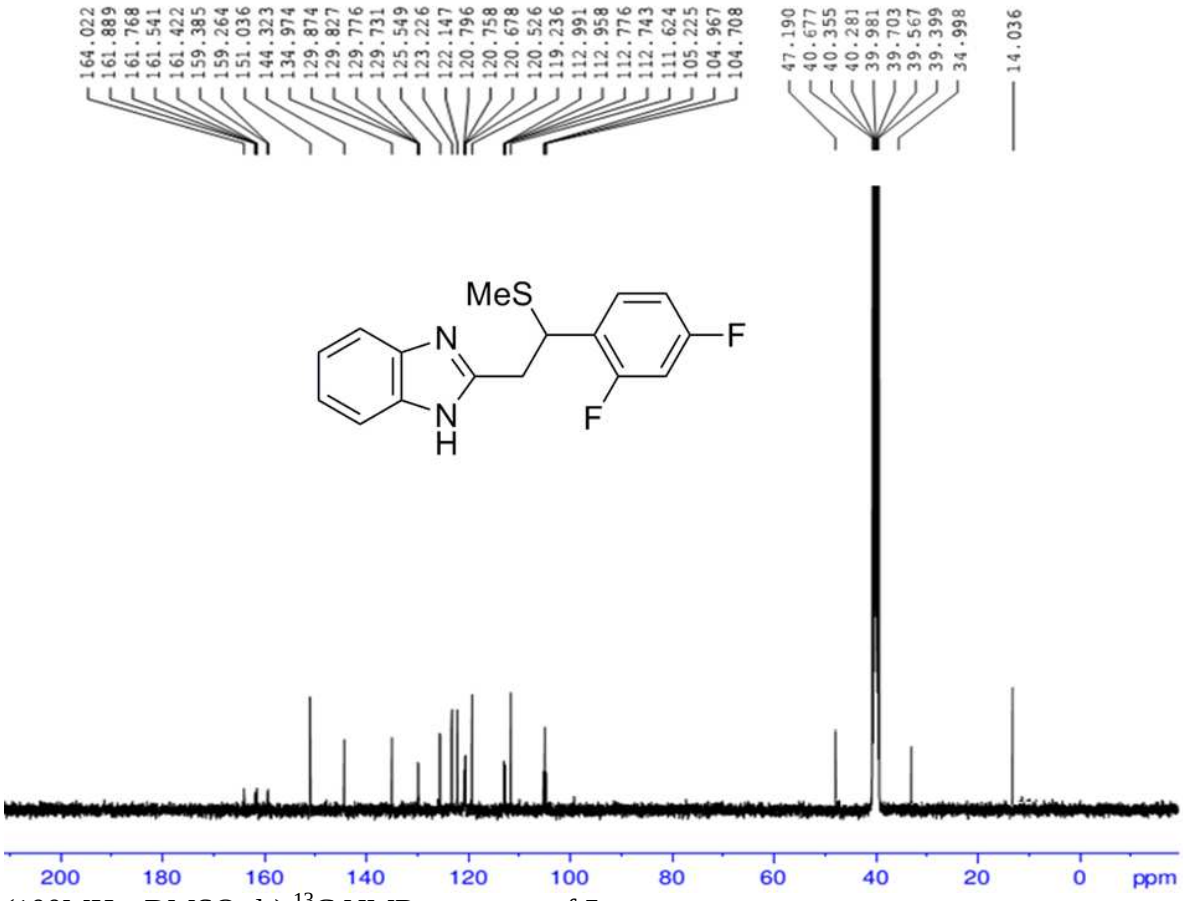
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **5l**



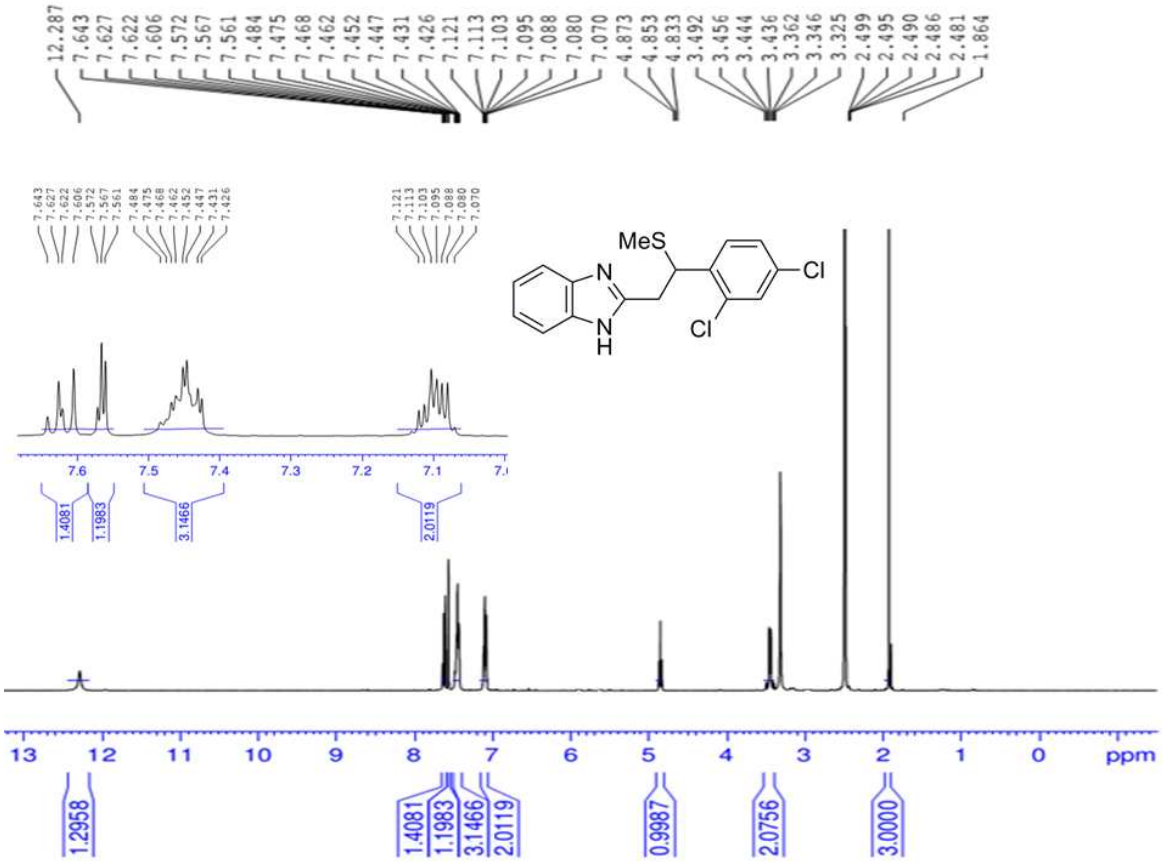
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **5l**



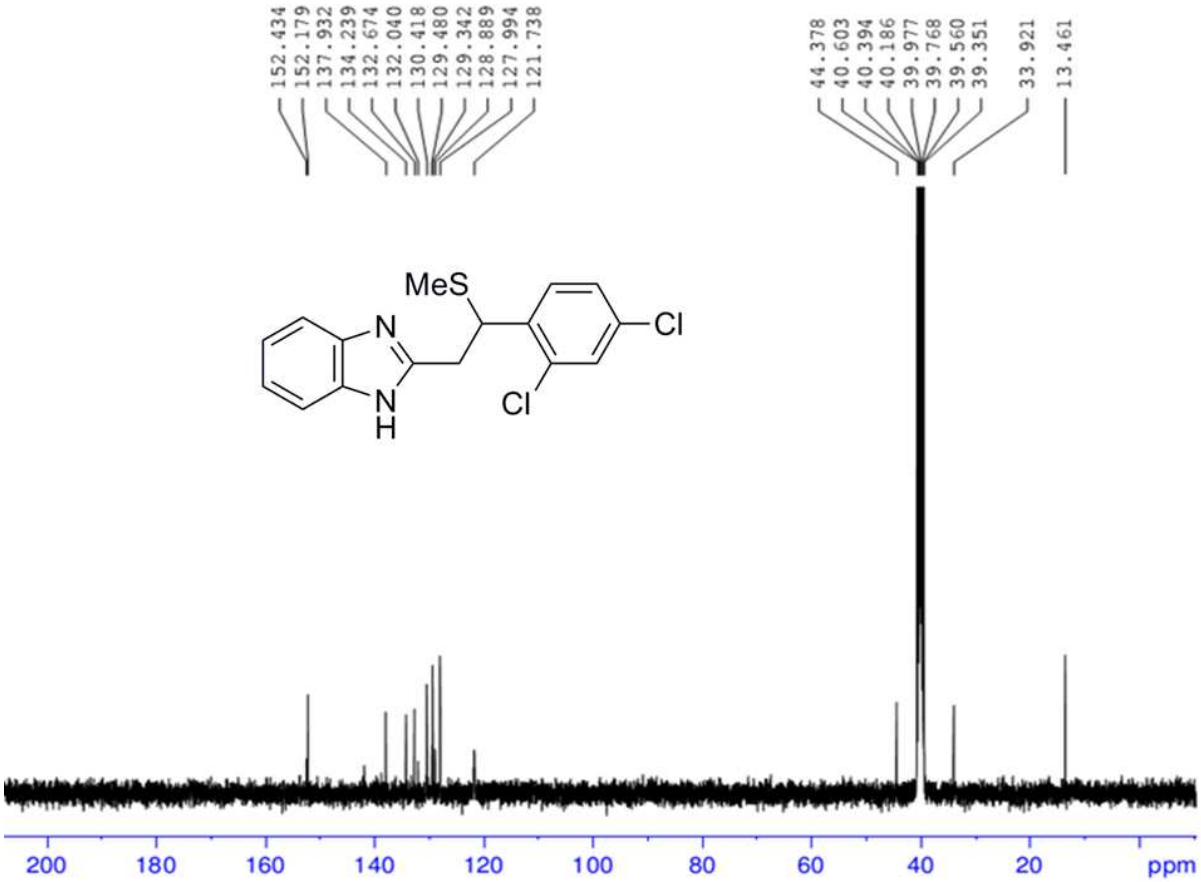
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **5n**



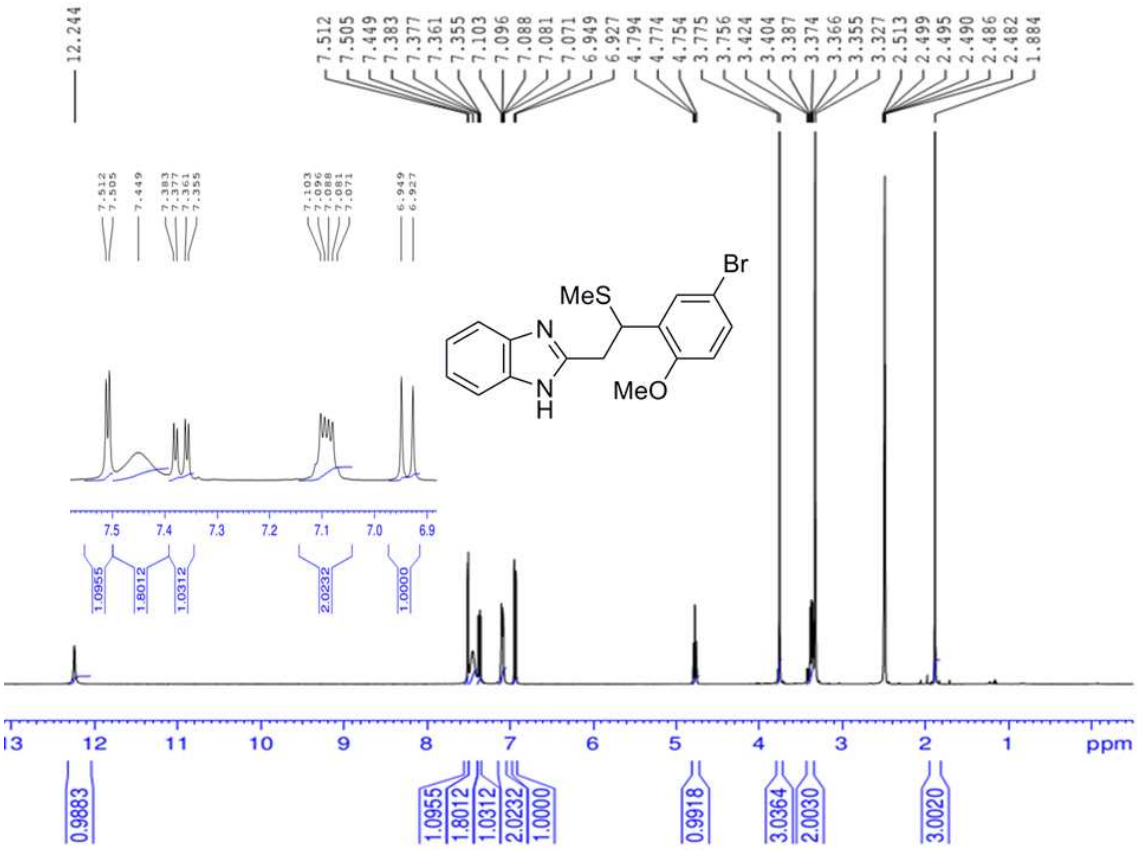
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **5n**



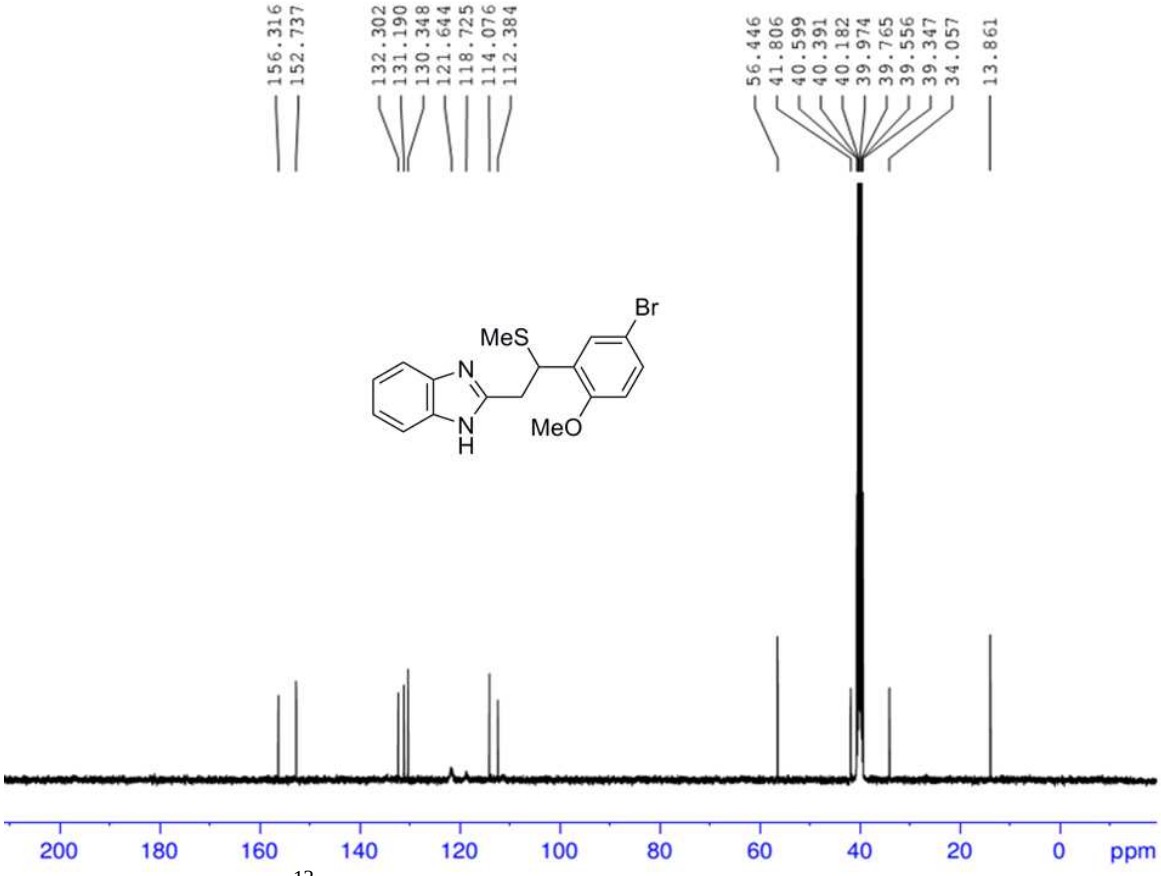
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **5o**



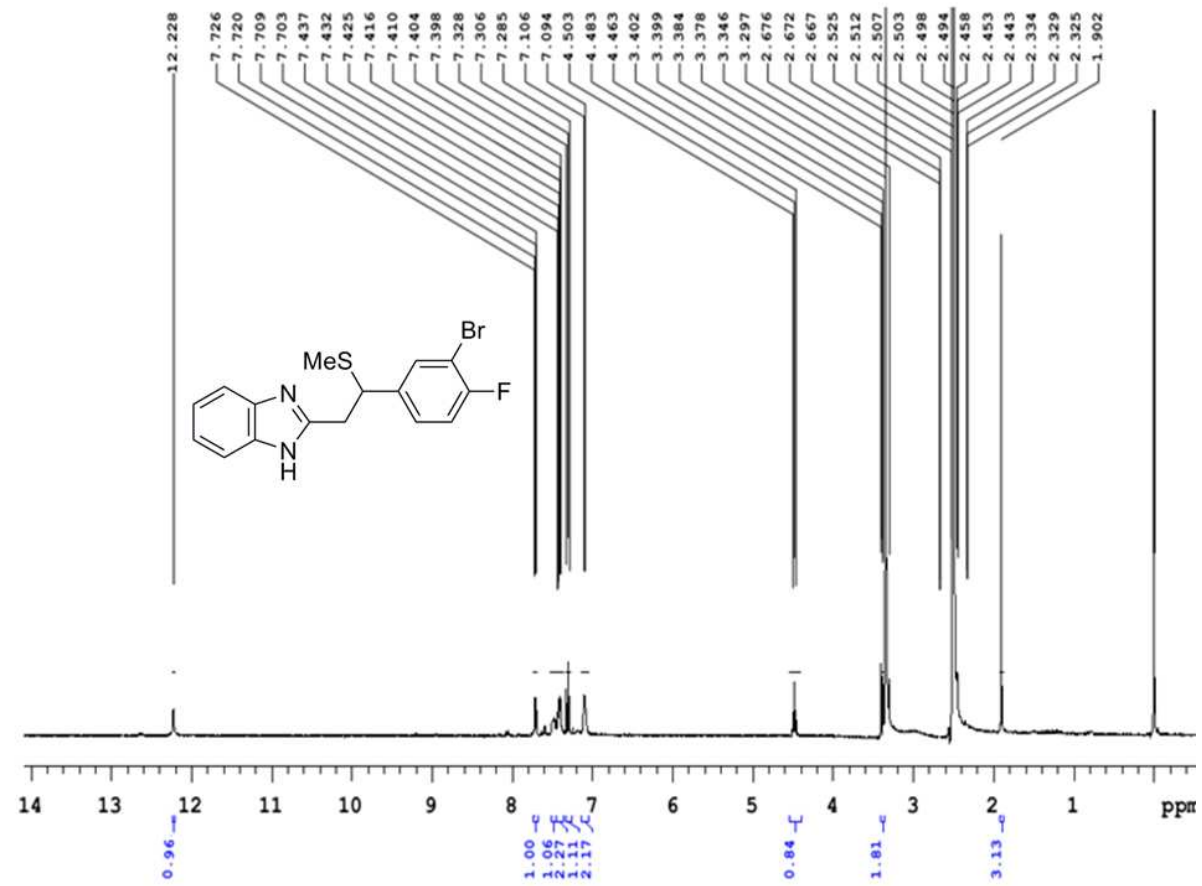
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **5o**



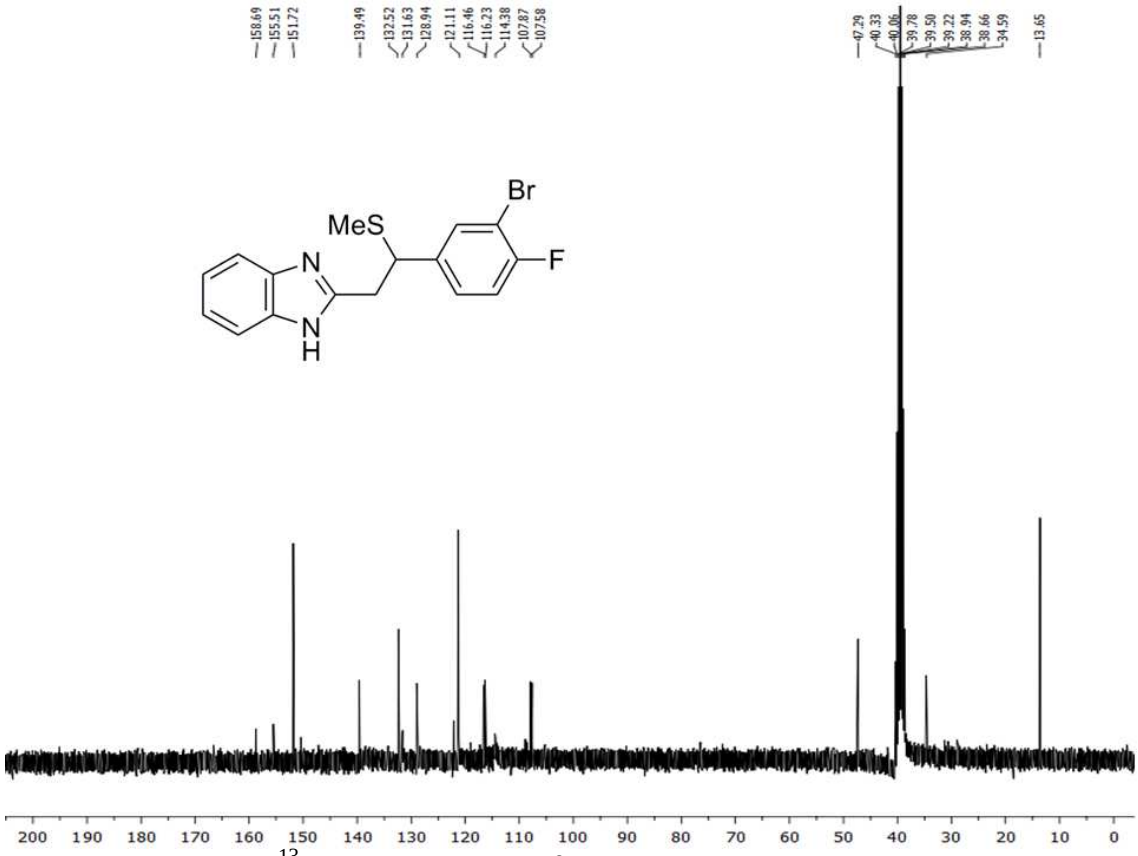
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **5p**



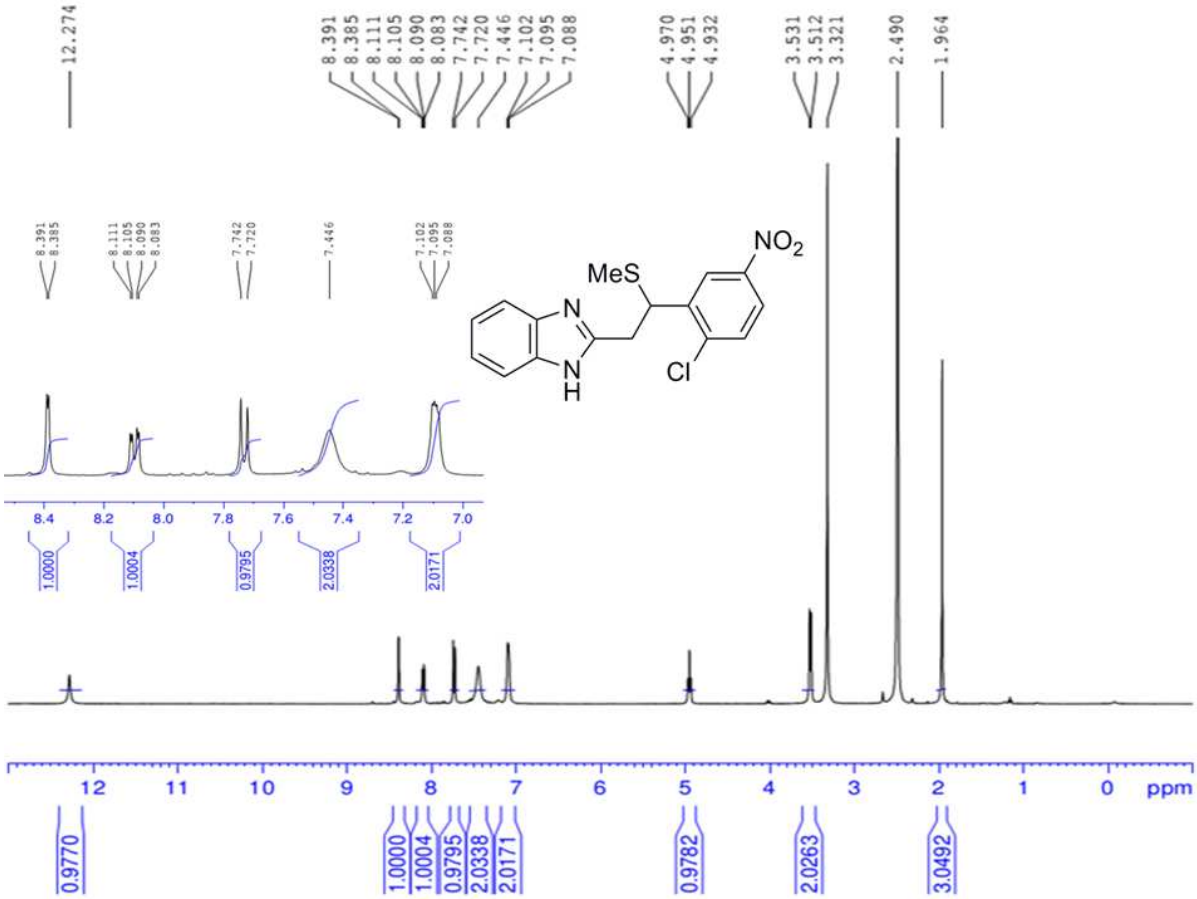
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **5p**



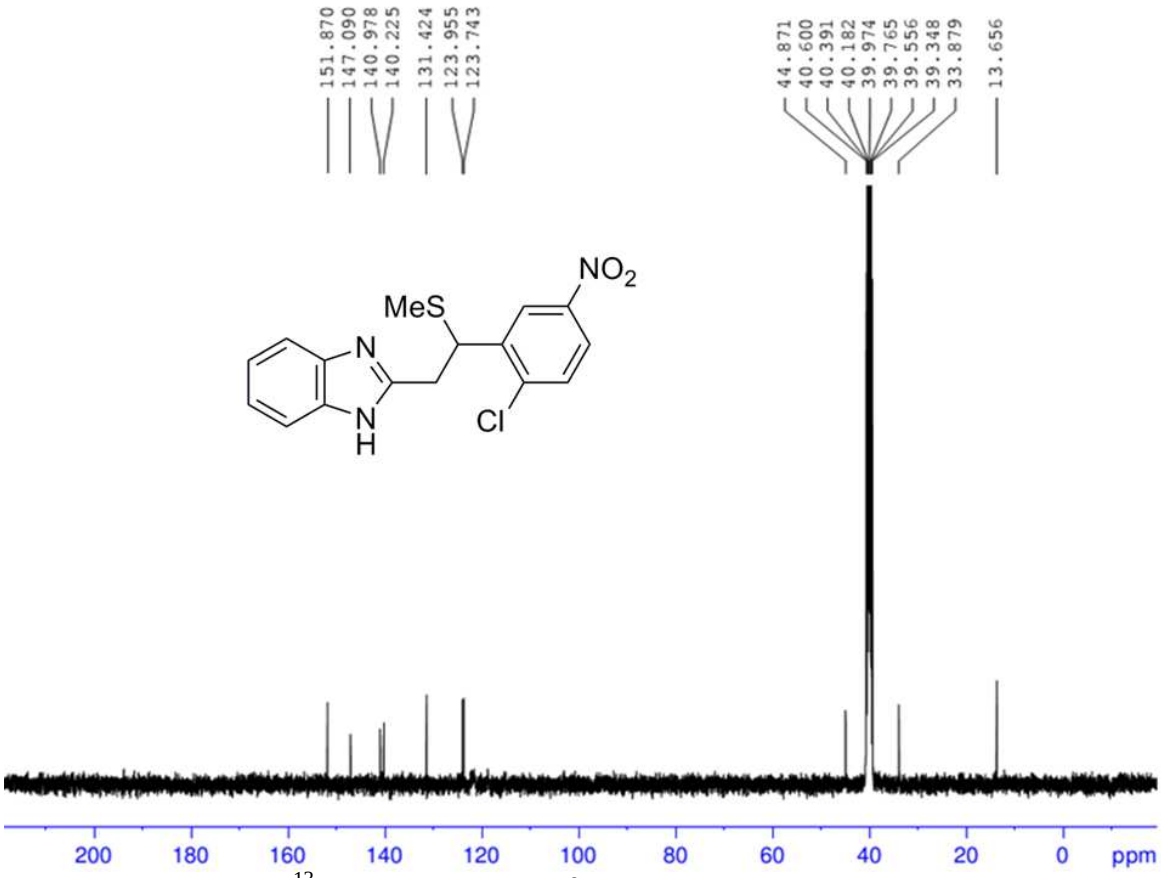
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **5q**



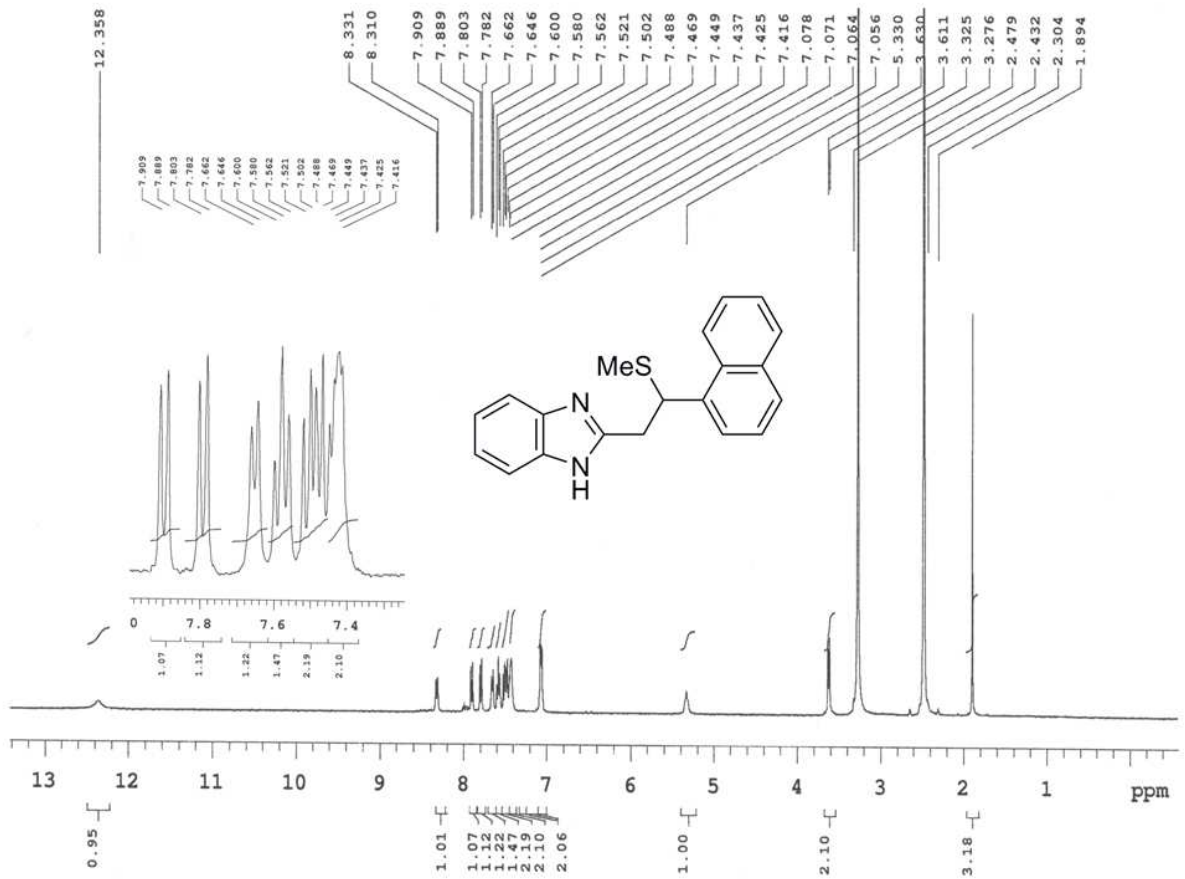
(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **5q**



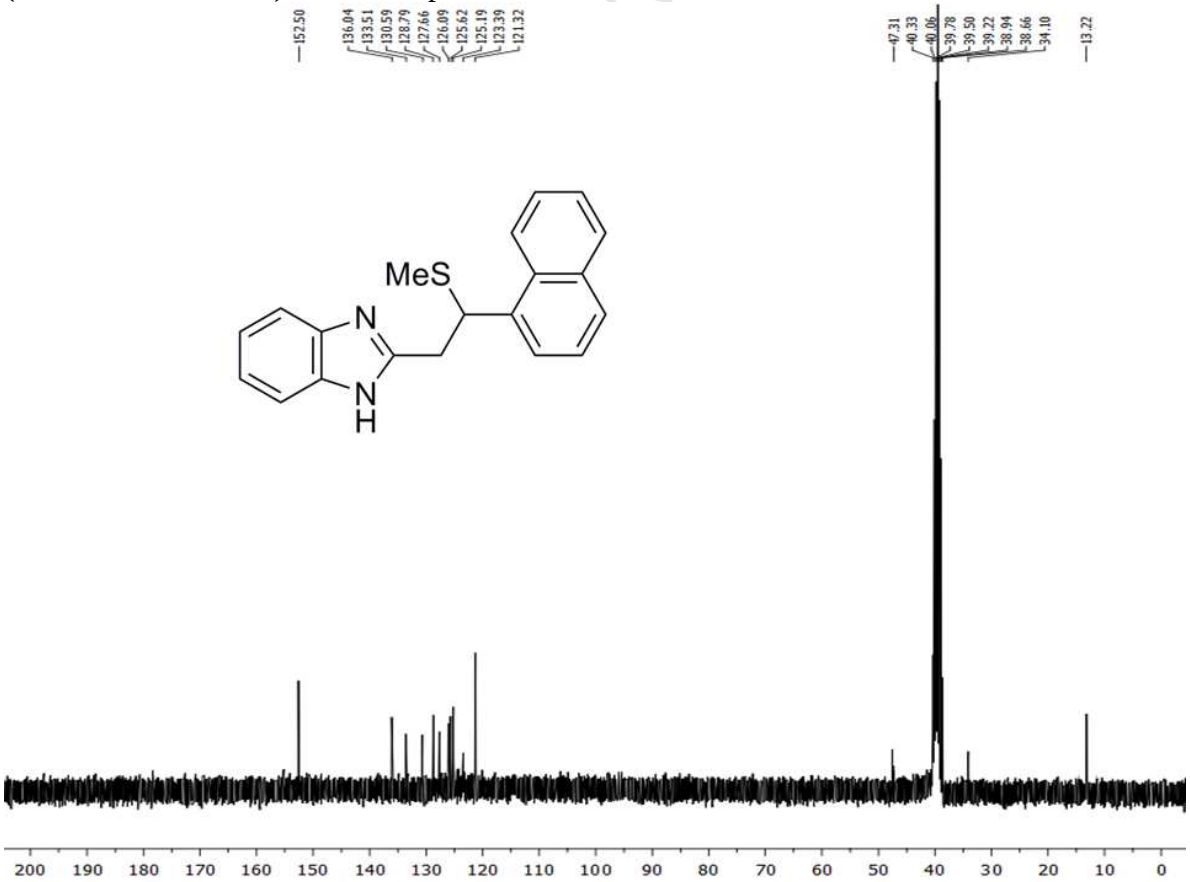
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **5r**



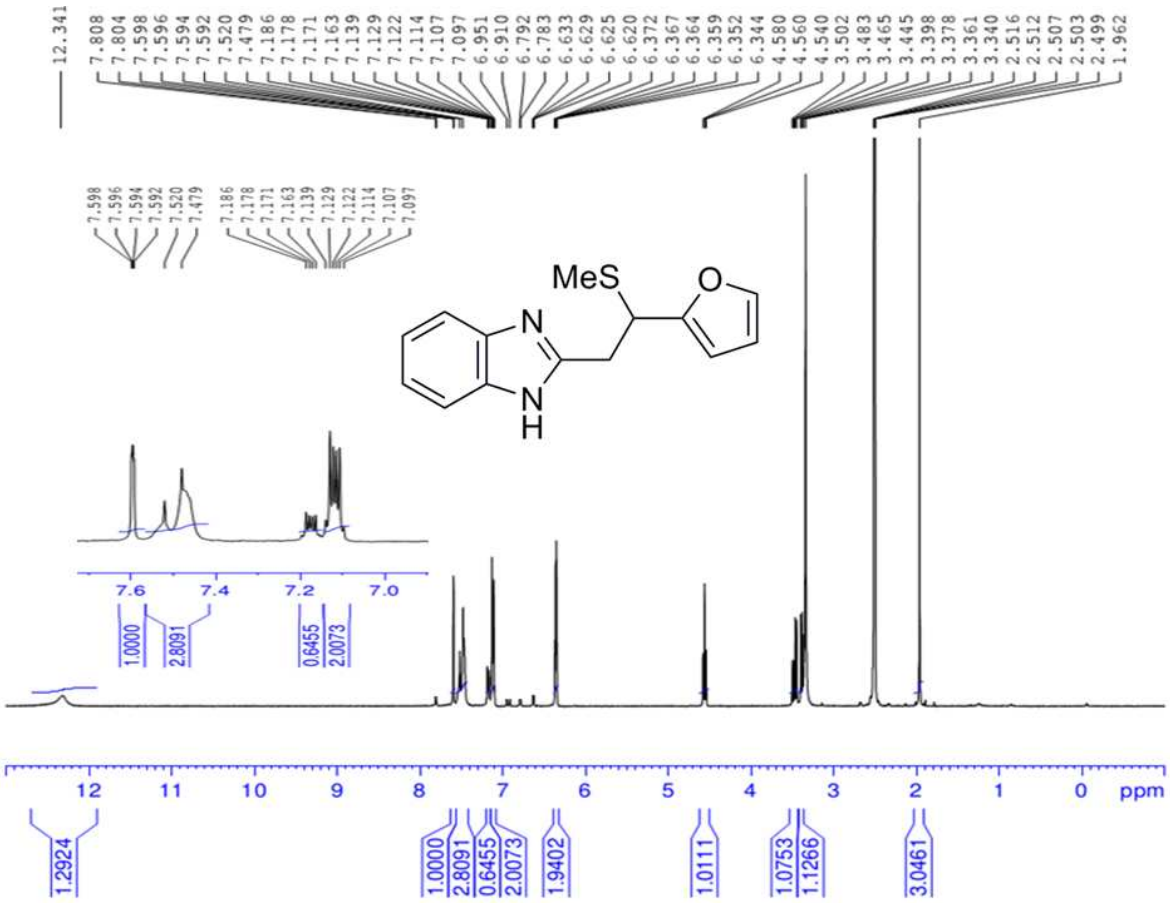
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **5r**



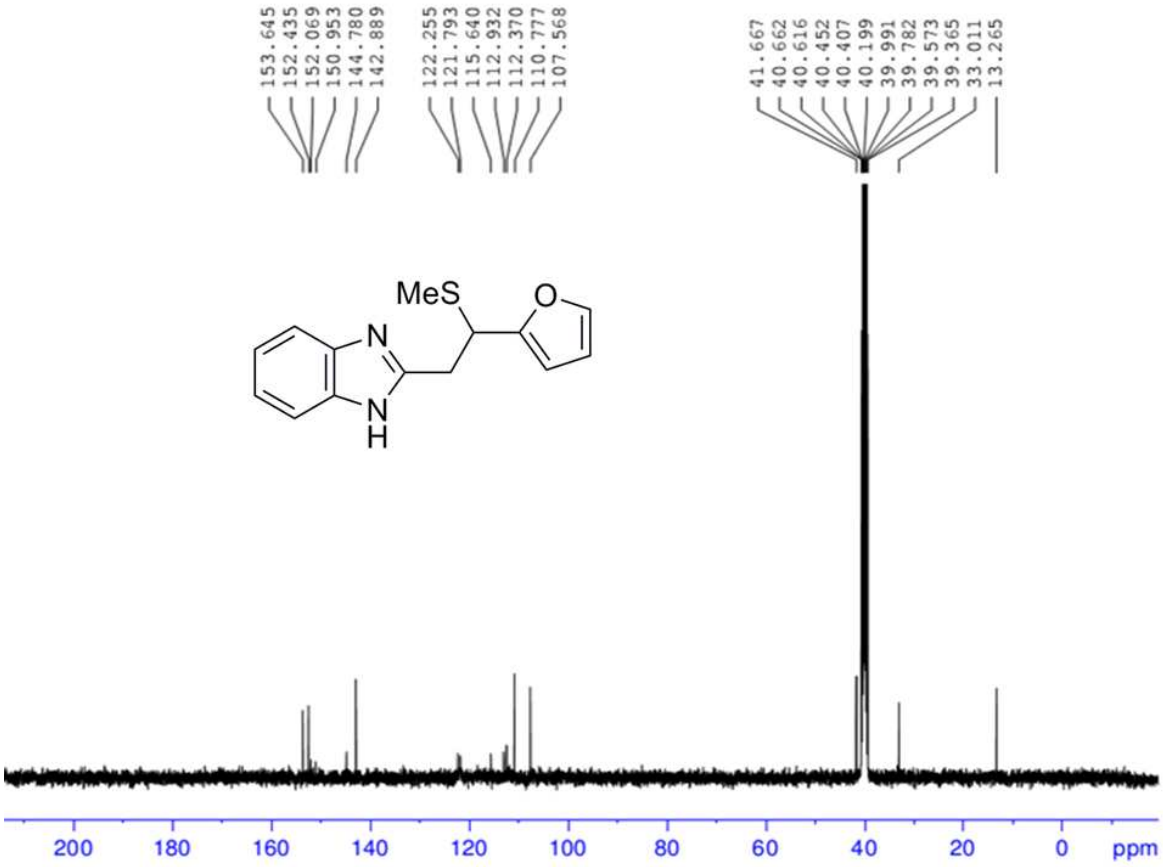
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **5s**



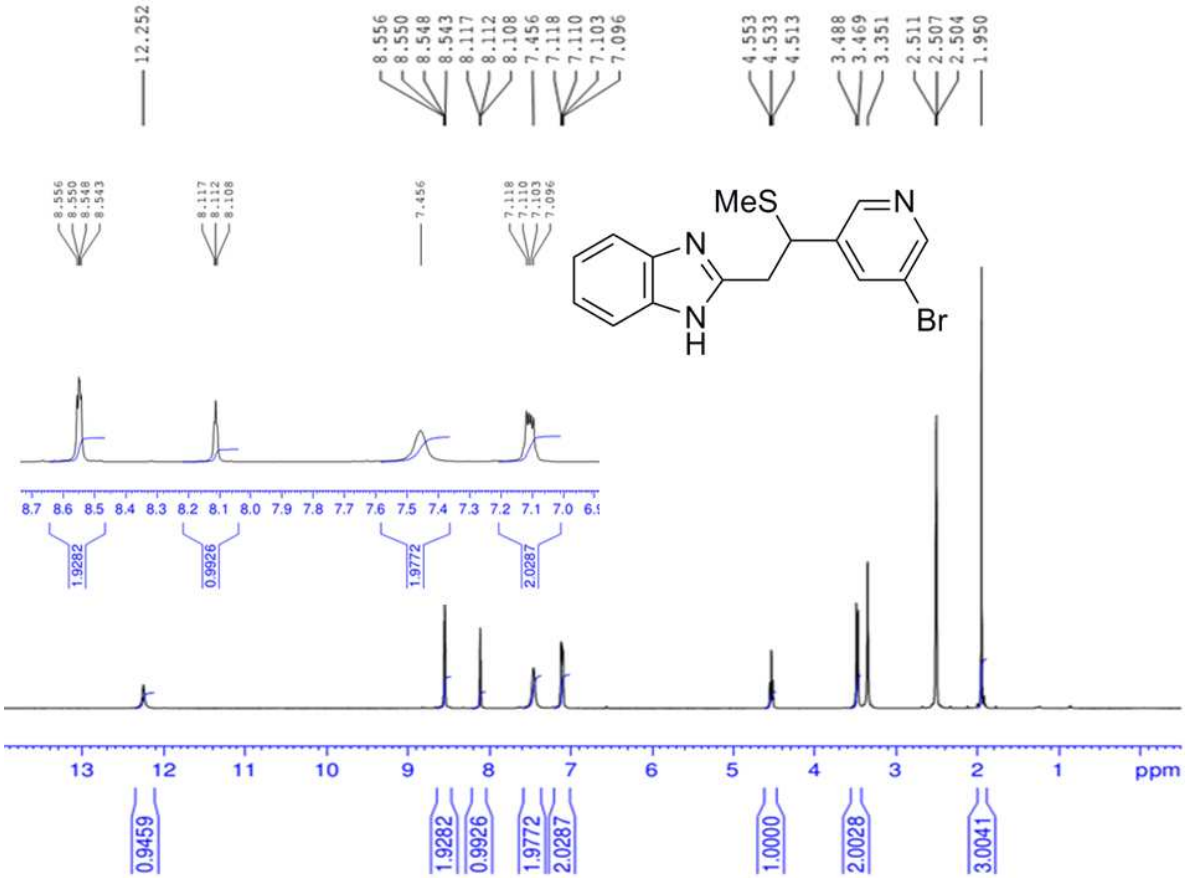
(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **5s**



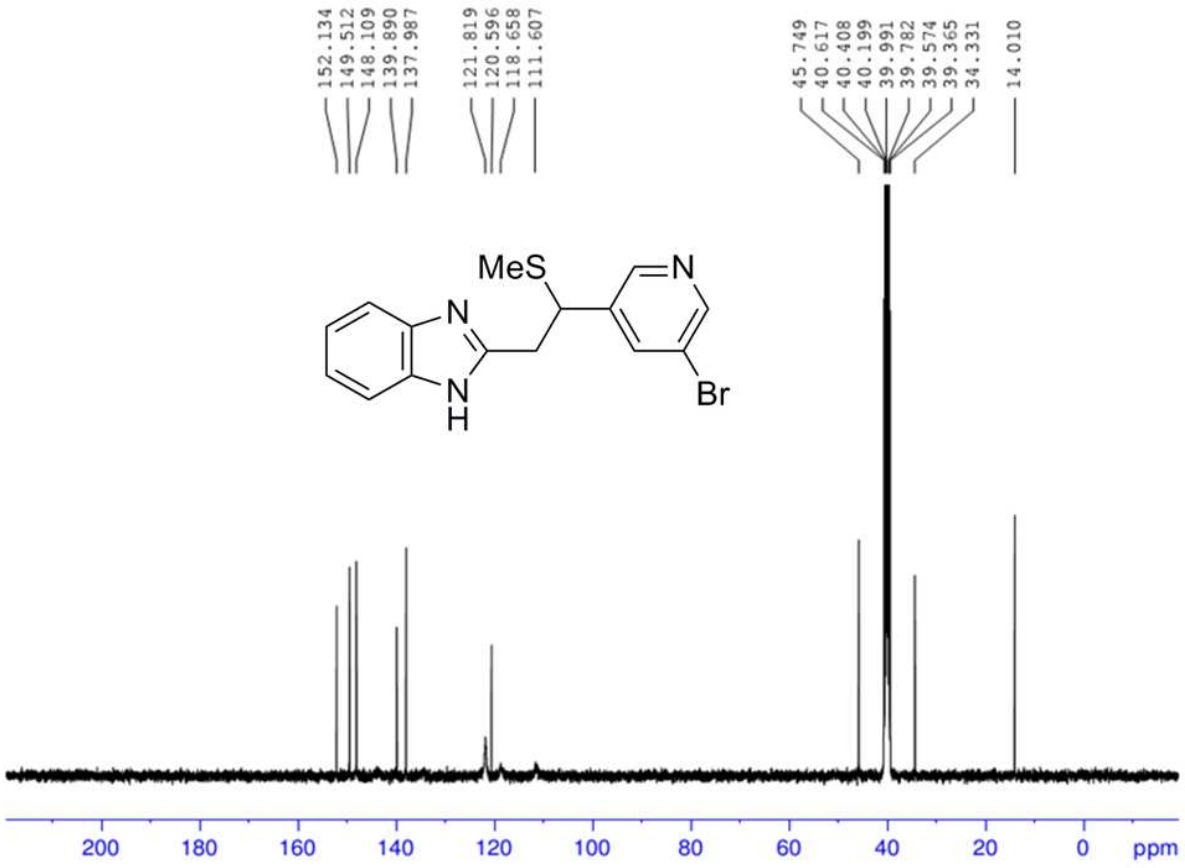
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **5v**



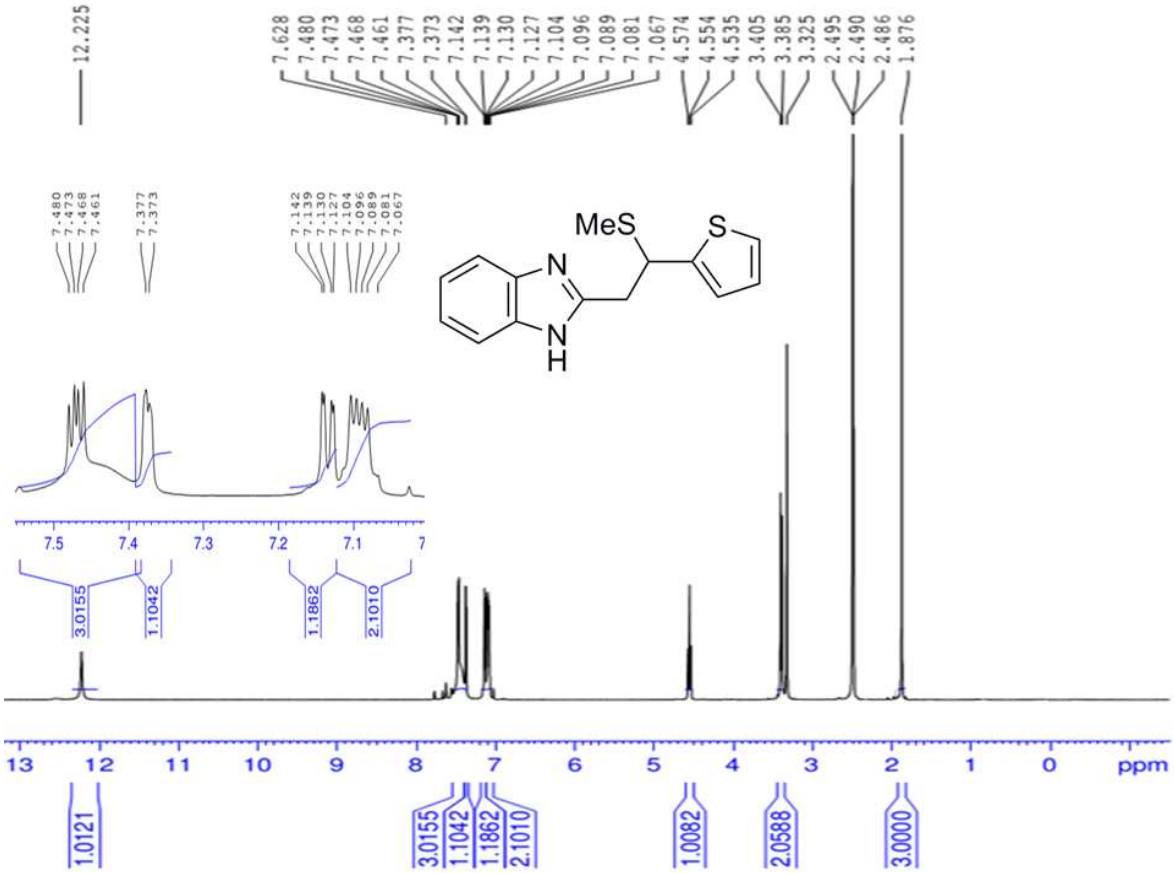
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **5v**



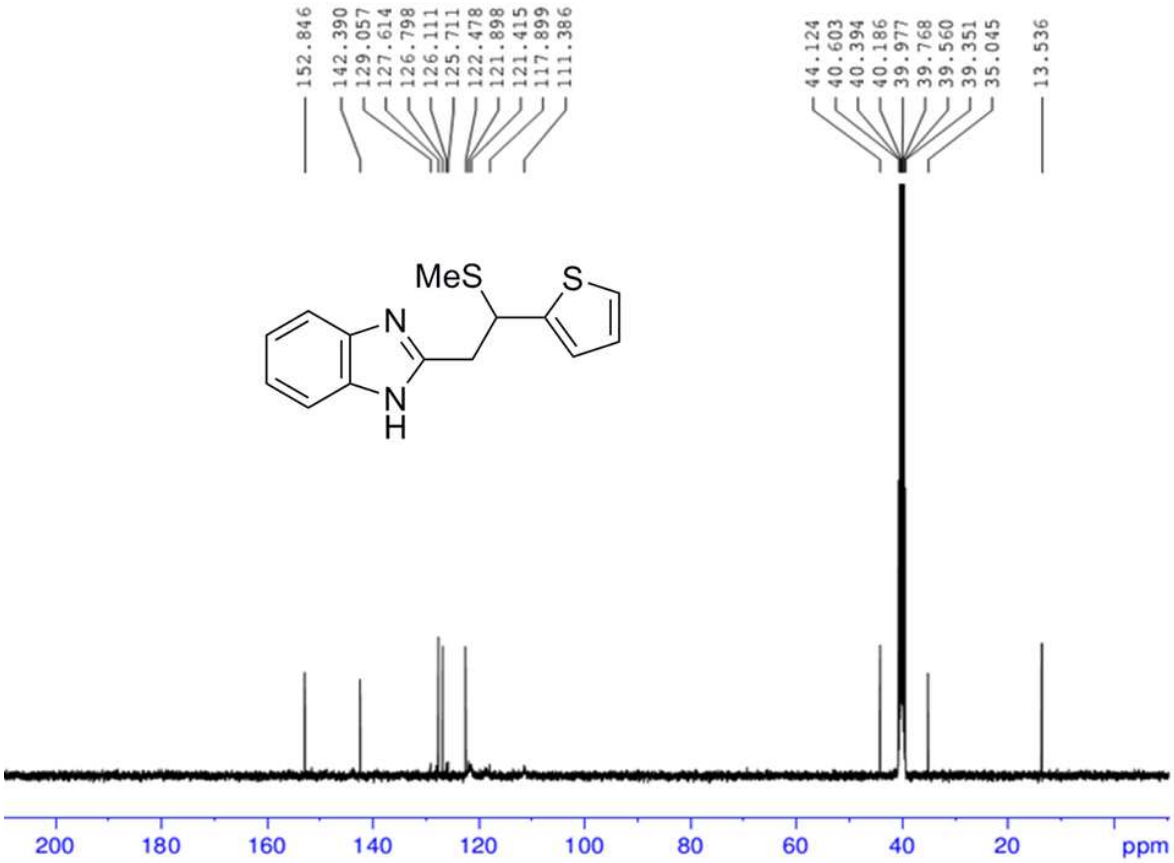
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **5w**



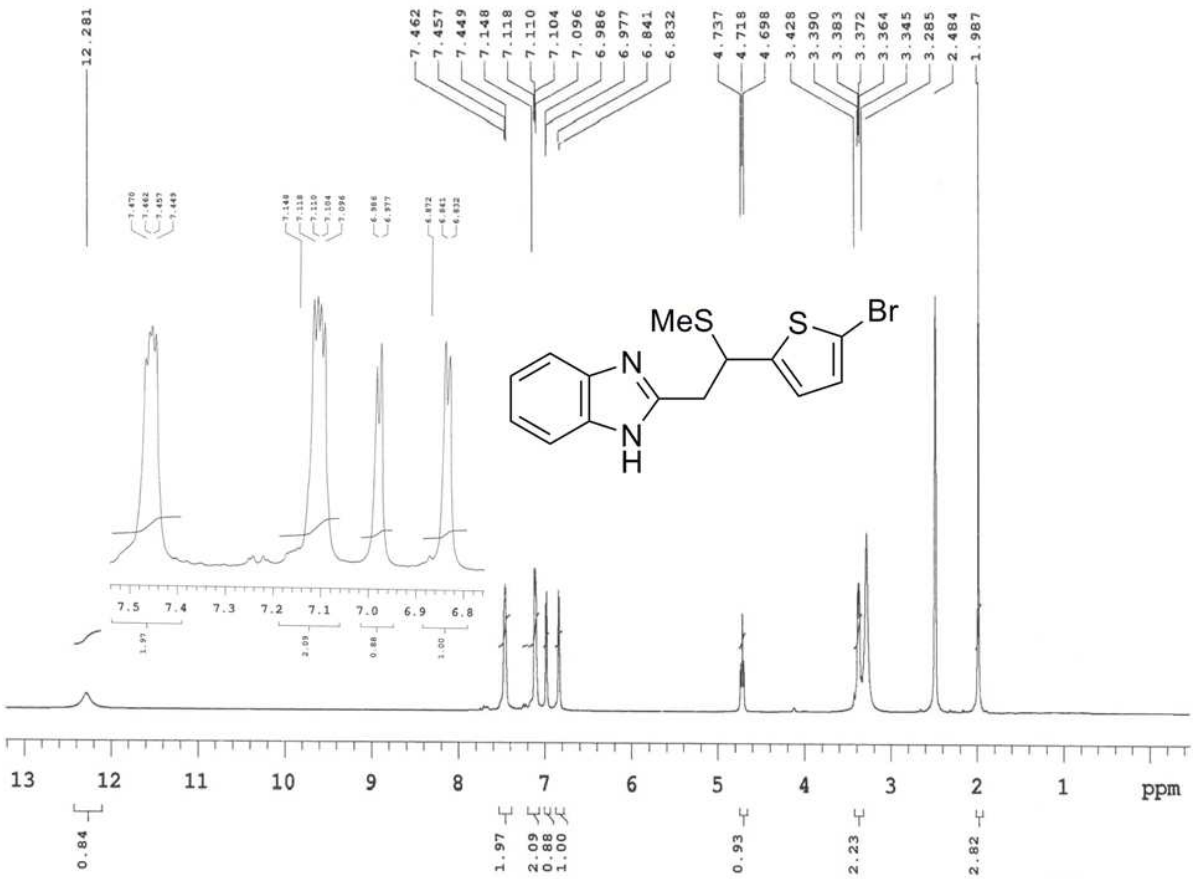
(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **5w**



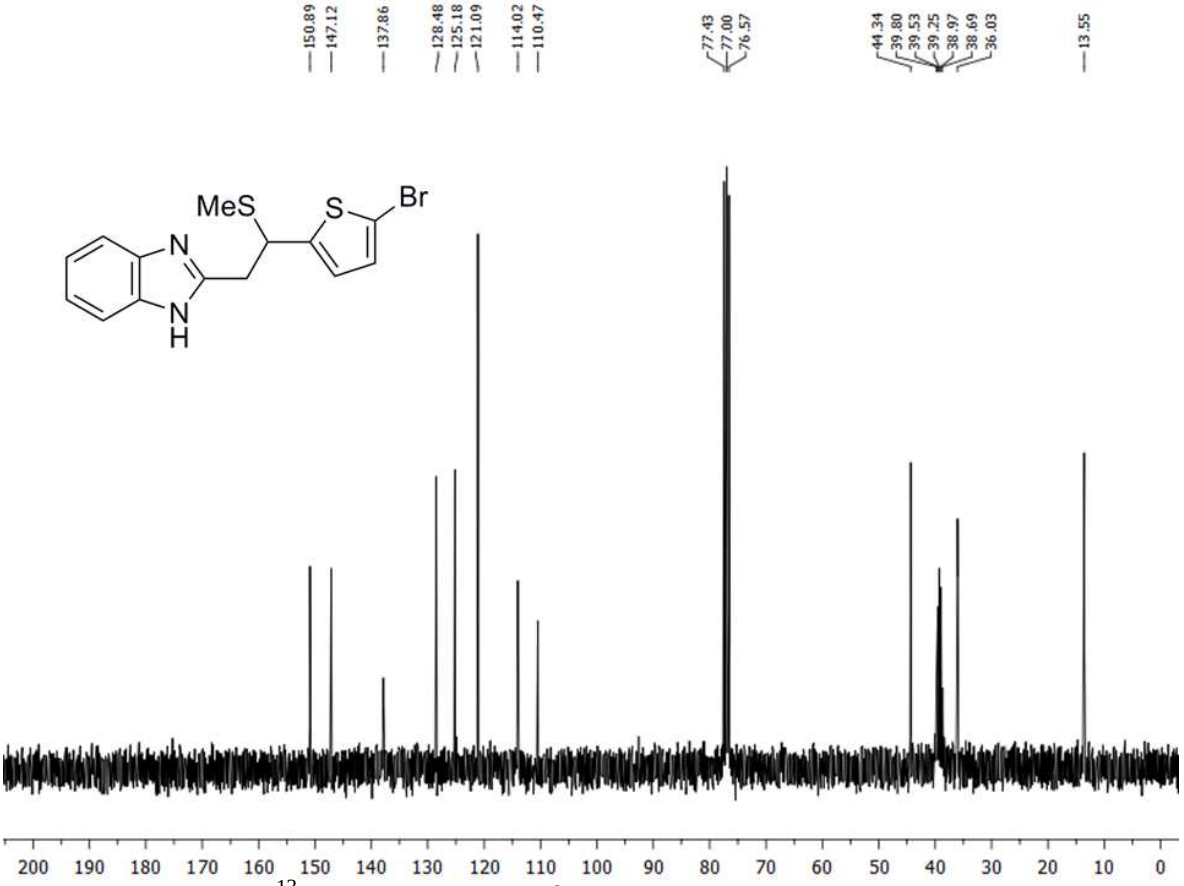
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **5x**



(100MHz, DMSO-d_6) ^{13}C NMR spectrum of **5x**

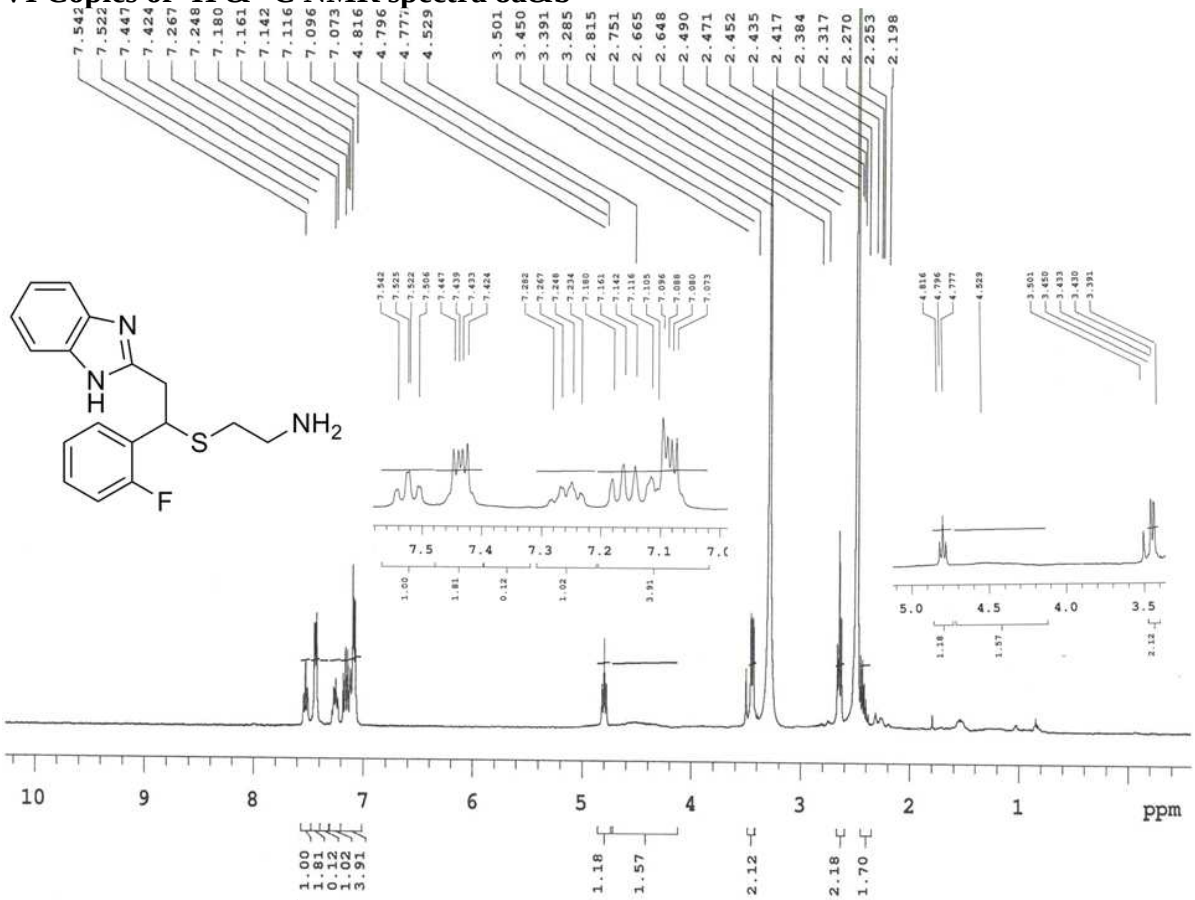


(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **5y**

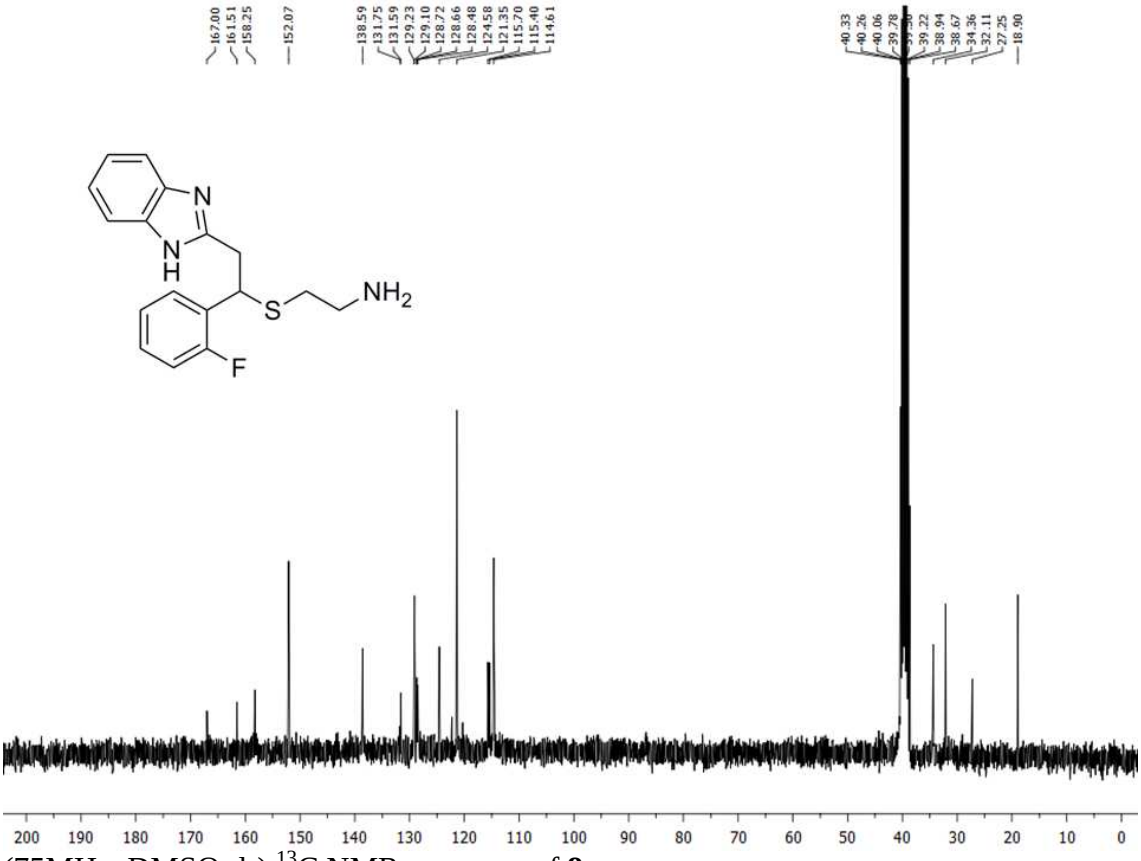


(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **5y**

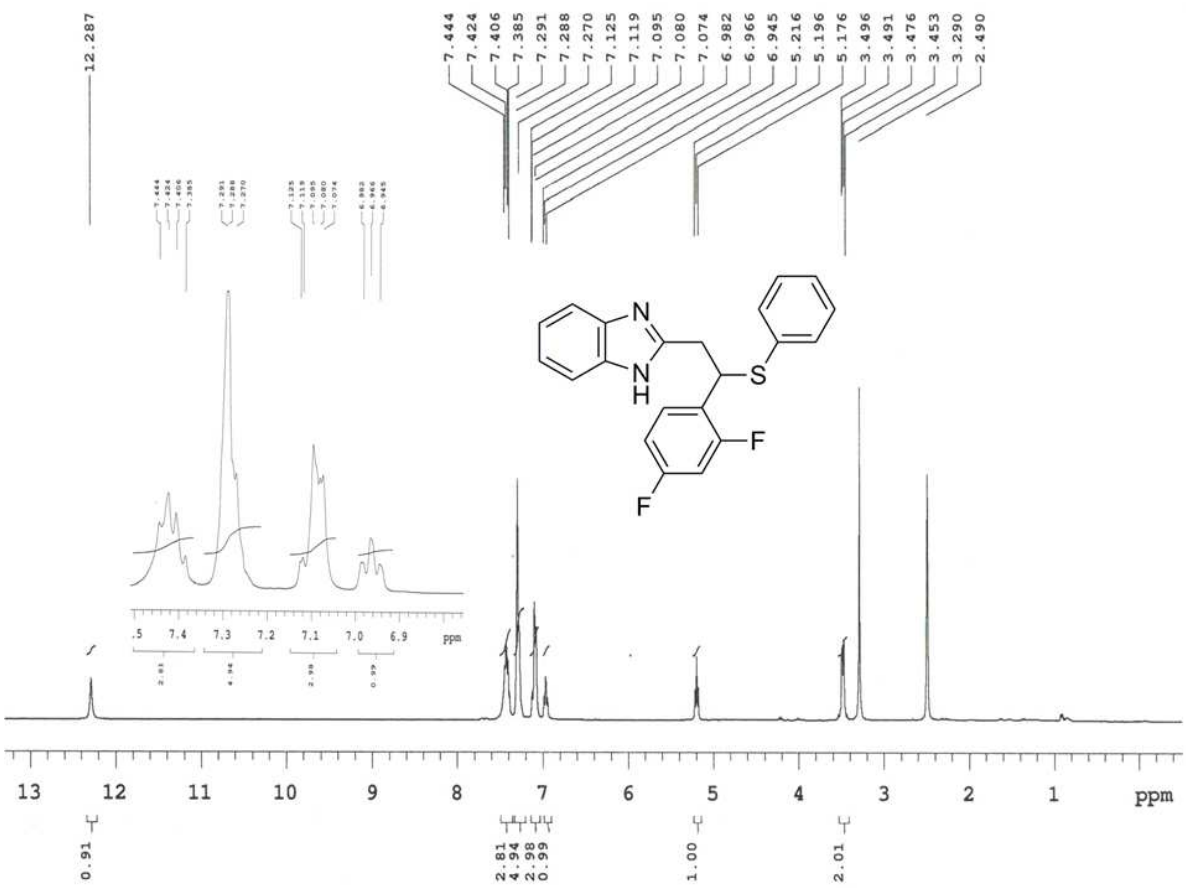
VI Copies of ^{1}H &^{13}C NMR spectra 8a&b



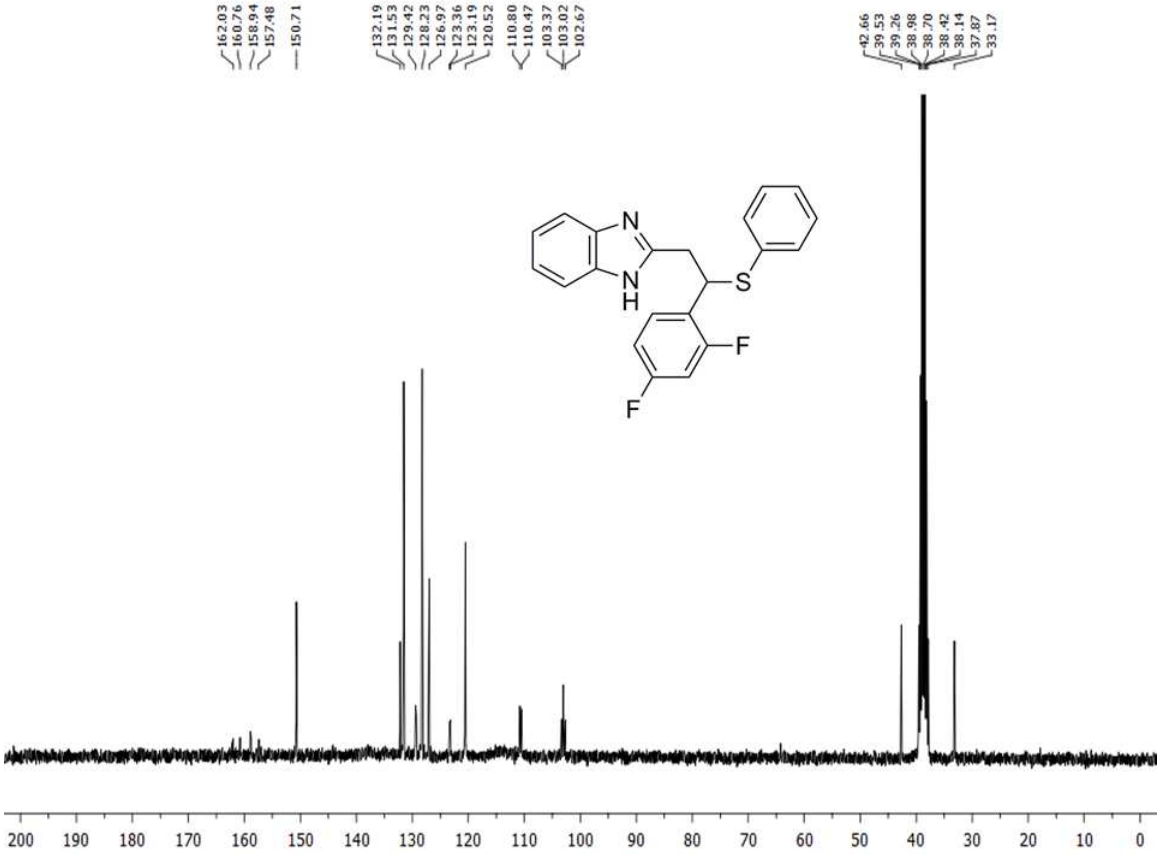
(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **8a**



(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **8a**



(400MHz, DMSO-d_6) ^{1}H NMR spectrum of **8b**



(75MHz, DMSO-d_6) ^{13}C NMR spectrum of **8b**