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The Voight reaction on tertiary α-hydroxy ketones

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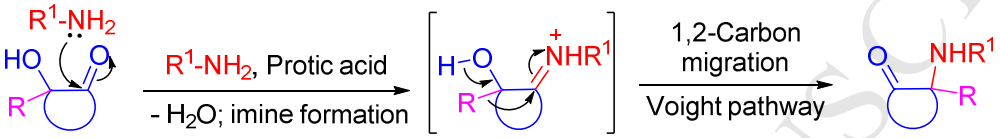
Graphical Abstract



❑ *tert*-α-Hydroxy ketone on phenanthrene, pyrene, acenaphthylene framework;
❑ R = Allyl, propargyl, propyl, benzyl; ❑ Protic acid = HCOOH or PTSA;
❑ R^1 = Benzyl, butyl, phenyl, *S*-(-)-α-methylbenzyl, *R*-(+)-α-methylbenzyl;

Abstract

The Voight reaction is for the transformation of secondary α-hydroxy ketones into corresponding α-amino ketones. Although discovered as early as 1886, it has not enjoyed wide popularity in organic synthesis, as it is applicable to only secondary α-hydroxy ketones. In terms of extending the applications of the reaction, we have shown that the reaction takes place on *tert*-α-hydroxy ketones also, particularly when present on rigid planar molecular frameworks like phenanthrene, pyrene and acenaphthylene. The reaction is not a simple substitution of the hydroxy group with amines, but goes through imine formation followed by 1,2-C migration. The reaction provides good opportunity for the synthesis of optically active α-amino ketones. We have achieved facile synthesis of some chromatographically separable and optically active *tert*-α-amino ketones by employing *S*-(-) or *R*-(+)-α-methylbenzylamines in the Voight amination.

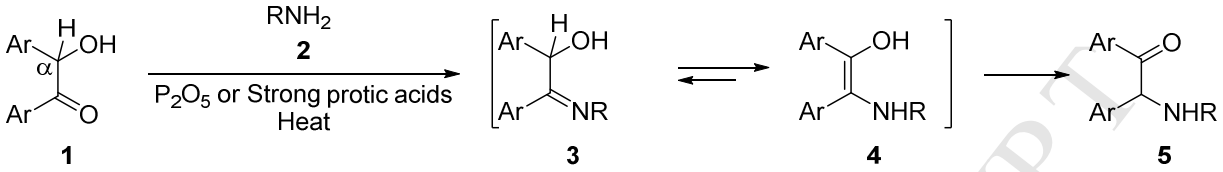
Key words

Voight reaction, α-Hydroxy ketone, *tert*-α-Amino ketone.

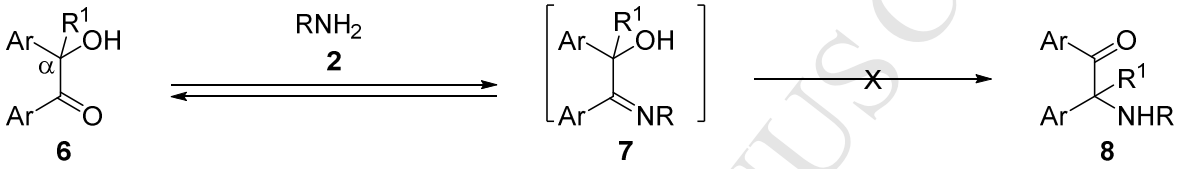
1. Introduction

The Voight reaction, first reported in 1886, is an acid mediated condensation of α-hydroxy ketones **1** with primary **2** (or secondary) amines to form α-amino ketones **5** (Scheme 1).[1] Voight demonstrated phosphorus pentoxide mediated condensation reaction of benzoin and primary amines to form corresponding α-amino ketones. Apart from phosphorus pentoxide, the reaction also worked well in the presence of strong protic acids like hydrochloric acid[2] or trifluoroacetic acid[3] (Scheme 1). Lutz and co-workers probed the mechanism of the reaction in detail and showed that the reaction is not a simple substitution of the secondary hydroxyl group in **1**, but goes through a rearrangement (Scheme 1).[4] According to the proposed mechanism, initially generated imines **3** tautomerize to enol **4** and finally to ketone **5**. Indeed, the reaction of benzoin derivative having electron donating OMe groups at C(4) position of the aryl rings was slower compared to that of simple benzoin owing to lower reactivity of the carbonyl group for the formation of imine intermediate. Lutz has clearly shown that tertiary α-hydroxy ketones **6** e.g. α-methyl and α-phenyl benzoins, do not undergo the Voight reaction (Scheme 2).[4a] In such cases, tautomerization in the intermediate **7** is not possible. In the review article on the Voight reaction Wang stated "In the absence of such α-proton, the reaction becomes the direct replacement of the hydroxyl group by the amino group, which proceeds with difficulty, as supported by the failure of the reaction between amines and α-methyl and α-phenyl benzoins".[1b] Although, α-amino ketones are important synthetic intermediates, the Voight amination reaction did not enjoy wide popularity in organic synthesis as it is restricted to secondary α-hydroxy ketones. However, we

have now discovered that the Voight amination does take place on tertiary α-hydroxy ketones, when the functional group is present on phenanthrene, pyrene or acenaphthylene motif.



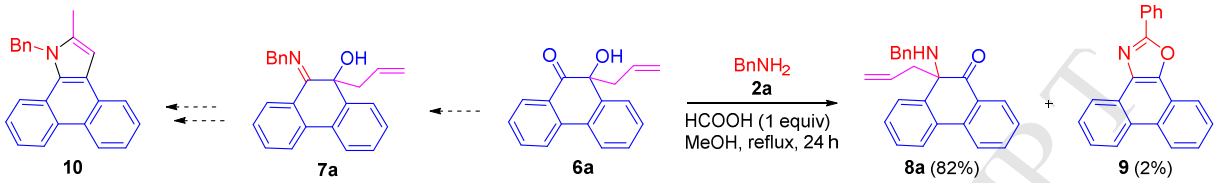
Scheme 1. The Voight reaction on benzoin derivatives **1**.



Scheme 2. The Voight reaction on tertiary α-hydroxy ketones **6**.

While exploring synthesis of polyaryl pyrroles,[5] we attempted to prepare the imine **7a** from 10-allyl-10-hydroxyphenanthren-9(10*H*)-one **6a** and benzylamine **2a** on way to pyrrole appended phenanthrene **10** (Scheme 3). Surprisingly, however, the reaction conducted under standard conditions for imine generation[6] provided α-amino ketone **8a** along with minor amount of oxazole **9**. Vatele and co-workers reported two-step synthesis of tertiary α-amino ketones from aliphatic tertiary α-hydroxy ketones.[7] The tertiary α-hydroxy imines generated in the first-step were heated to 160-170 ^{o}C to force 1,2-migration of the alkyl group. Observation of Vatele reinforced earlier findings of Lutz that α-hydroxy ketones are highly reluctant to undergo the Voight reaction. Our observation that α-amino ketone **8a** was formed under relatively mild conditions is in contrast to earlier observations of Lutz and Vatele. We report herein results from this study for the preparation of several tertiary α-amino ketones located on phenanthrene, pyrene and acenaphthylene platform. We demonstrate that the Voight reaction can be used for

the synthesis of chiral secondary amino ketones by employing optical active primary amines. Furthermore, we report on the accrued mechanistic details of this enigmatic reaction.



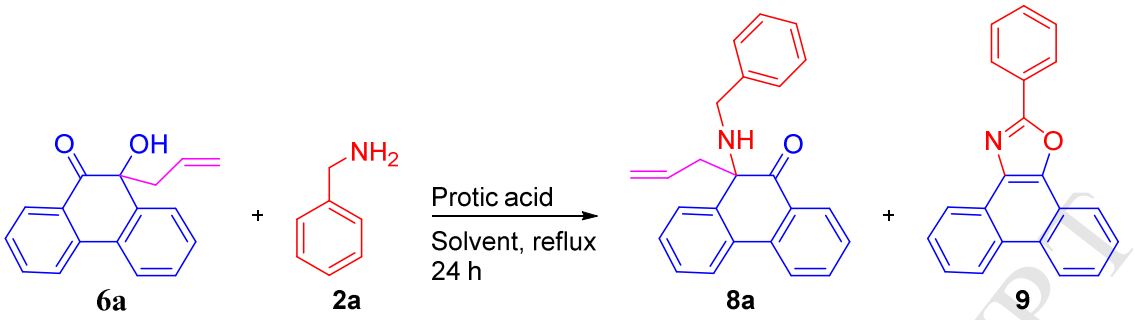
Scheme 3. Formation of the Voight product **8a** and oxazole **9** in the attempted synthesis of pyrrole appended phenanthrene **10**.

2. Results and discussion

2.1. The Voight reaction on symmetrical tertiary α-hydroxy ketones

The Barbier reaction of 9,10-phenanthrenequinone with allyl bromide in the presence of indium metal provided 10-allyl-10-hydroxyphenanthren-9(10*H*)-one **6a**.[8] The formic acid mediated condensation of *tert*-α-hydroxy ketone **6a** with benzylamine **2a** in methanol reflux furnished α-amino ketone **8a** in 82% yield along with minor amount of oxazole **9** (Table 1, entry 1). Formic acid and methanol medium appears to be the best combination for the transformation since other solvents like dimethylformamide (DMF, entry 2) or toluene (entry 3) lowered the yield of **8a**. Similarly, alternate strong acids like trifluoroacetic acid (entry 4) or *p*-toluenesulfonic acid monohydrate (PTSA, entry 5) did not favour the reaction. Benzoic acid in methanol medium (entry 6) or toluene medium (entry 7) did not improve the yield of α-amino ketone **8a**.

Table 1. Optimization of reaction conditions for conversion of α-hydroxy ketone to α-amino ketone.



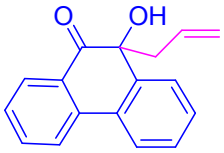
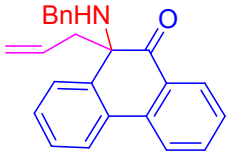
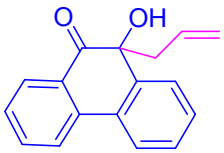
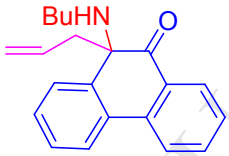
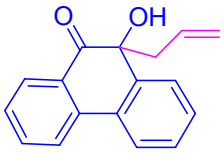
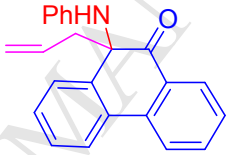
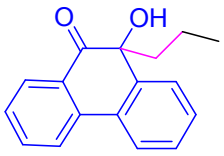
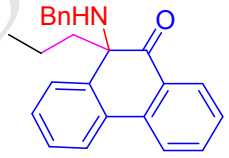
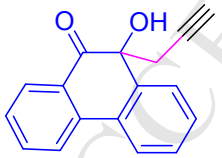
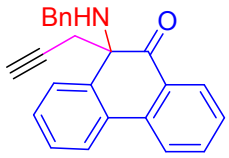
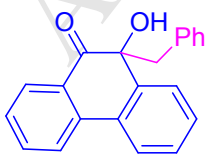
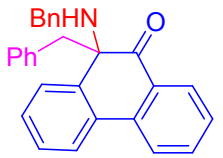
6a + **2a** → **8a** + **9**

Entry	Protic acid	Solvent	Yield of α-amino ketone **8a**	Yield of oxazole **9**
1	**HCOOH**	**MeOH**	**82%**	**2%**
2	HCOOH	DMF	29%	5%
3	HCOOH	Toluene	18%	10%
4	CF_3COOH	Toluene	21%	25%
5	$4\text{-}CH_3C_6H_4SO_3H.H_2O$	Toluene	10%	45%
6	C_6H_5COOH	MeOH	26%	-
7	C_6H_5COOH	Toluene	10%	6%

The generality of the transformation of *tert*-α-hyroxy ketone **6a** into *tert*-α-amino ketone **8a** by condensation with benzylamine **2a** was ascertained by varying the amines **2a-c** and the alkyl group on the C(10) carbon bearing hydroxy group of phenanthrene **6b-d**. The Voight amination reactions worked well in each case to provide *tert*-α-amino ketones **8a-f** in 56-88% yield (Table 2). The reactions with benzylamine **2a** (Table 2, entries 1, 4-6) or butylamine **2b** (entry 2) were conducted in methanol and formic acid. However, the reaction with aniline **2c** required organic solvent soluble *p*-toluenesulfonic acid monohydrate (PTSA) as the acid catalyst and higher boiling toluene as the solvent (entry 3). The transformation did not work when

secondary amines like diethylamine, piperidine or pyrrolidine was employed. The *tert*-α-amino ketones **8a-f** were characterized by IR, ^{1}H NMR, ^{13}C NMR, DEPT-135 NMR and HRMS spectra. In addition, the structures of **8c** and **8f** were unambiguously confirmed by X-ray single crystal structure analysis (Figures 2 and 3).

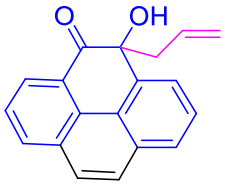
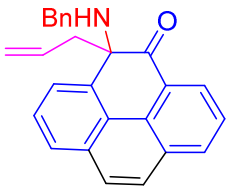
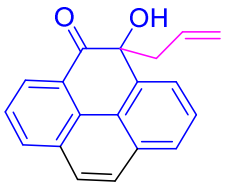
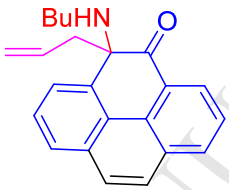
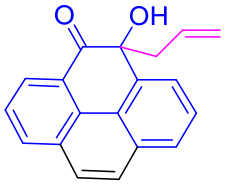
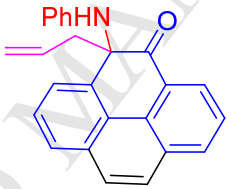
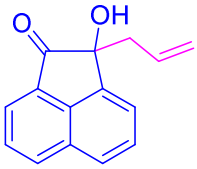
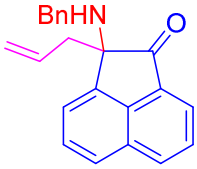
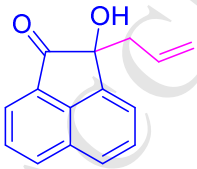
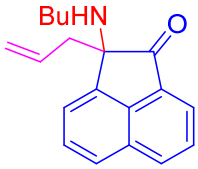
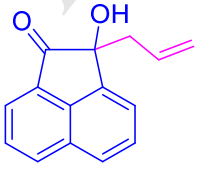
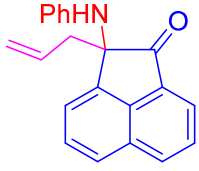
Table 2. Transformation of *tert*-α-hydroxy ketones present on phenanthrene motif **6a-d** to corresponding *tert*-α-amino ketones **8a-f**.

Entry	α-Hydroxy ketone	Amine	α-Amino ketone
1.	 **6a**	$BnNH_2$ **2a**	 **8a** (24 h, 82%)
2.	 **6a**	$BuNH_2$ **2b**	 **8b** (18 h, 86%)
3.	 **6a**	$PhNH_2$ **2c**	 **8c** (24 h, 88%)
4.	 **6b**	$BnNH_2$ **2a**	 **8d** (36 h, 56%)
5.	 **6c**	$BnNH_2$ **2a**	 **8e** (18 h, 75%)
6.	 **6d**	$BnNH_2$ **2a**	 **8f** (36 h, 65%)

Next, we conducted the Voight reaction on *tert*-α-hydroxy ketones present on pyrene motif **11** with three primary amines **2a-c** and the results are gathered in Table 3. 5-Allyl-5-hydroxypyren-4(5*H*)-one **11**, generated by the Barbier reaction on pyrene-4,5-dione[9] was subjected to the Voight reaction with benzylamine **2a** (Table 3, entry 1), butylamine **2b** (entry 2), aniline **2c** (entry 3) to furnish corresponding *tert*-α-amino ketones **12a-c** in good yield. While the first two reactions worked in the presence of formic acid in methanol reflux, the last reaction required PTSA in toluene reflux. Interestingly, in general, the Voight reaction was slower on α-hydroxy ketone functionality present on pyrene motif compared to α-hydroxy ketone on phenanthrene motif.

Our final effort on generalization was directed towards the Voight reaction on *tert*-α-hydroxy ketone functional group present on acenaphthylene framework **13** (see Table 3). The Voight reaction of **13** with three primary amines namely benzylamine **2a**, butylamine **2b** and aniline **2c** worked with facility to provide corresponding *tert*-α-amino ketones **14a-c** in good yield. Similar to the reactions on phenanthrene and pyrene first two examples (entries 4 and 5, Table 3) in this series worked in the presence of formic acid in methanol under reflux and last one worked only when heated in toluene reflux in the presence of PTSA (entry 6). The rate of the reaction of α-hydroxy ketone on acenaphthylene **13** was perceptibly faster than that of α-hydroxy ketone on pyrene **11** and comparable to that of α-hydroxy ketone on phenanthrene **6a**. We made several attempts to synthesize 1-hydroxy-1-allyl-2-naphthalenone to evaluate if the Voight reaction of α-hydroxy ketone on naphthalene skeleton is facile or not. However, even after repeated attempts, we could not succeed in the preparation of 1-hydroxy-1-allyl-2-naphthalenone.[10]

Table 3. Transformation of *tert*-α-hydroxy ketones present on pyrene motif **11,** acenaphthylene motif **13** to corresponding *tert*-α-amino ketones **12a-c** and **14a-c**.

Entry	α-Hydroxyketone	Amine	α-Aminoketone
1.	 **11**	$BnNH_2$ **2a**	 **12a** (28 h, 72%)
2.	 **11**	$BuNH_2$ **2b**	 **12b** (24 h, 76%)
3.	 **11**	$PhNH_2$ **2c**	 **12c** (24 h, 80%)
4.	 **13**	$BnNH_2$ **2a**	 **14a** (22 h, 86%)
5.	 **13**	$BuNH_2$ **2b**	 **14b** (18 h, 88%)
6.	 **13**	$PhNH_2$ **2c**	 **14c** (24 h, 78%)

2.2. Mechanism of the Voight reaction

Generation of *tert*-α-amino ketones **8**, **12** or **14** from condensation of corresponding *tert*-α-hydroxy ketones **6**, **11** or **13** and primary amines **2** could be through the Voight pathway, that is, through initial formation of the imine followed by 1,2-migration of the allyl group. Alternatively, since the protonated hydroxy group is tertiary, benzylic and a good leaving group, substitution through S_N1 pathway is a clear possibility. To probe the mechanism, we synthesized *tert*-α-hydroxy ketones **15** and **16** (Figure 1) from corresponding acenaphthylene-1,2-diones[11] and allyl bromide *via* indium mediated Barbier reaction. The regiochemistry of allylation at C(2) was, according to anticipated electronic characteristics of the carbonyl group influenced by *para*-positioned substituents namely OMe in **15** and NO_2 in **16**. The regiochemistry of allylated products **15** and **16** were confirmed by analysis of ^1H, ^{13}C NMR, DEPT-135 and 2-D NMR (HSQC, HMBC and COSY) spectral data and finally by single crystal X- ray structure analysis (Figures 4 and 5).

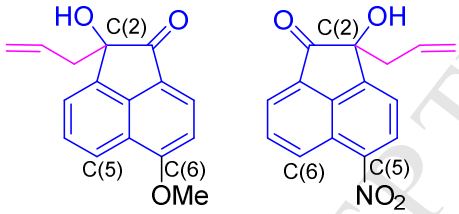
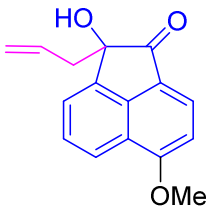
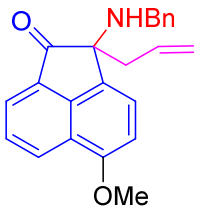
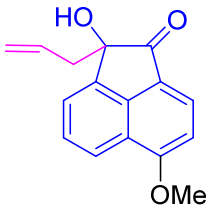
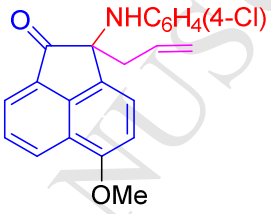
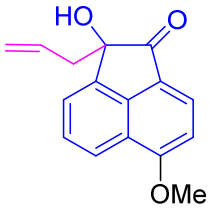
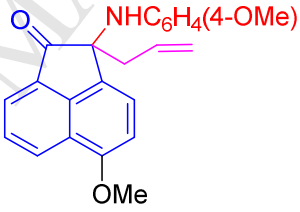
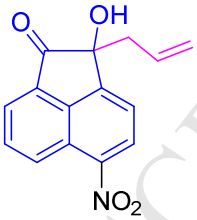
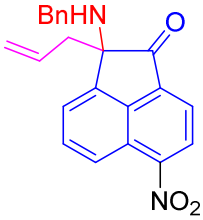


Figure 1. Structure of *tert*-α-hydroxy ketones **15** and **16.**

The Voight reaction of *tert*-α-hydroxy ketone **15** with benzylamine **2a** conducted in methanol reflux in the presence of formic acid furnished *tert*-α-amino ketone **17a** exclusively (Table 4, entry 1). Structure of **17a** and location of the *tert*-amino and the allyl groups was confirmed by ^1H, ^{13}C NMR, DEPT-135 and 2-D NMR (HSQC, HMBC and COSY) spectral

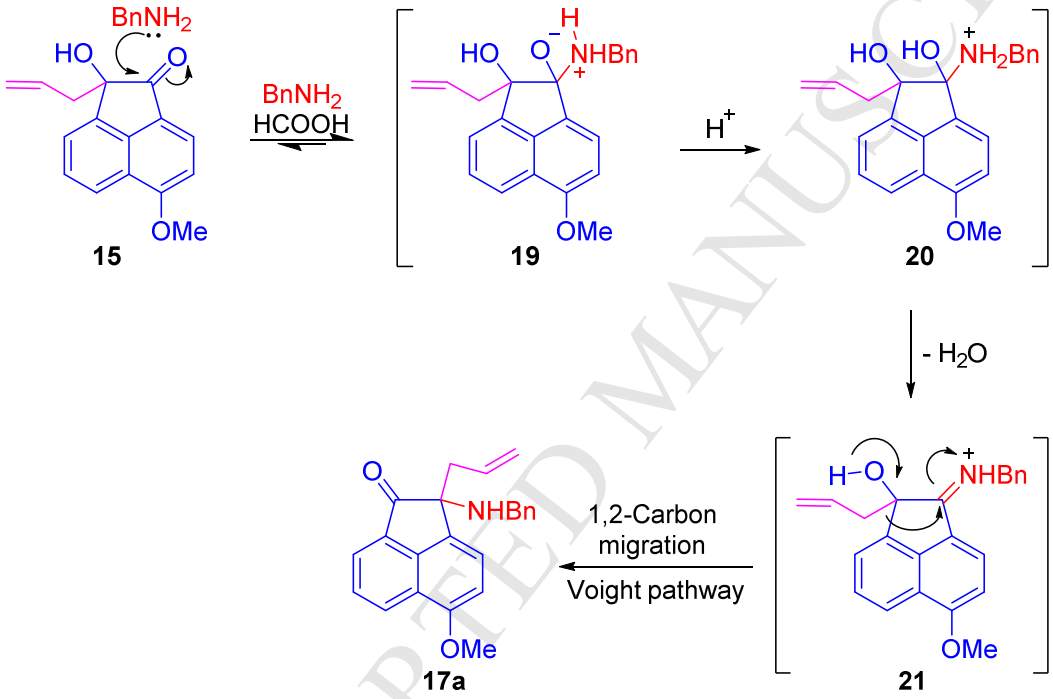
analysis. As anticipated the ^{1}H NMR spectrum of **17a** displayed downfield shifted doublet, now located at δ 8.36 ppm, for C(6)H compared to its parent **15** where it was located at δ 8.06 ppm. From the isolation of **17a** we deduced that the transformation of **15** to **17a** had indeed gone through the Voight pathway, that is initial formation of the imine followed by 1,2-carbon migration. To confirm the Voight pathway, we subjected *tert*-α-hydroxy ketone **16** to reaction with benzylamine in methanol reflux in the presence of formic acid to realize **18** as the exclusive product (entry 4). As anticipated the ^{1}H NMR spectrum of **18** displayed upfield shifted doublet, now located at δ 8.63 ppm, for C(5)H compared to its parent **16** where it was located at δ 9.10 ppm. Since the carbonyl group in **15** is in the *para* position to that of electron-donating methoxy group, reactivity of **15** was lower compared to that of **16**. To evaluate the electronic effect on the benzylamine towards the outcome of the Voight reaction, we conducted two reactions on the *tert*-α-hydroxy ketone **15** with 4-chlorobenzylamine **2d** and 4-methoxybenzylamine **2e** (entries 2 and 3). Although reaction with **2e** was slower, both the reactions respectively provided the Voight products **17b-c** exclusively.

Table 4. Results from the mechanistic probing of the Voight reaction on *tert*-α-hydroxy ketones **15** and **16** with benzylamines.

Entry	α-Hydroxy ketone	Amine	α-Amino ketone
1.	 **15**	$BnNH_2$ **2a**	 **17a** (36 h, 70%)
2.	 **15**	$4\text{-}ClC_6H_4NH_2$ **2d**	 **17b** (42 h, 66%)
3.	 **15**	$4\text{-}OMeC_6H_4NH_2$ **2e**	 **17c** (32 h, 72%)
4.	 **16**	$BnNH_2$ **2a**	 **18** (22 h, 88%)

Based on the results accumulated, we propose a mechanism as given in Scheme 4. In the first step, assisted by protic acid, the primary amine **2** reacts with the keto group in *tert*-α-hydroxy ketone to form the iminium ion **21**, which then undergoes 1,2-carbon migration (rearrangement) to form **17a**. It is interesting to note that 1,2-allyl or propargyl migration appear

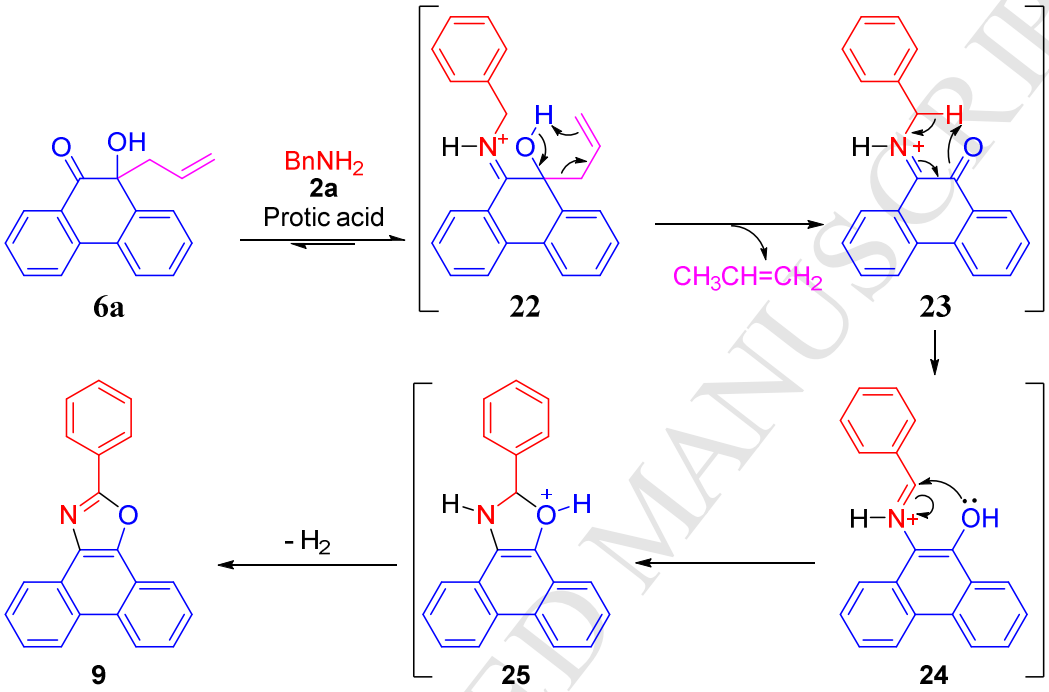
to be more facile compared to propyl migration (see entries 1,4 and 5, Table 2) which could reflect their migratory aptitude. Finally, it is pertinent to note that the Voight reaction did not take place when it was conducted on 2-hydroxy-1,2-diphenylpent-4-en-1-one (Ar = Ph, R^1 = allyl, Scheme 2) with benzylamine **2a**, *n*-butyl amine **2b** or aniline **2c** in the presence of formic acid in methanol reflux or PTSA in toluene reflux. This result indicates that the imine and both the aromatic rings should be planar like in **21** for the Voight reaction to take place.



Scheme 4. Mechanism for the formation of 2-allyl-2-(benzylamino)-6-methoxyacenaphthylen-1(2*H*)-one **17a** from 2-allyl-2-hydroxy-6-methoxyacenaphthylen-1(2*H*)-one **15**.

The plausible mechanism for the formation of oxazole **9** from *tert*-α-hydroxy ketone **6a** is given in Scheme 5. Similar to an earlier case, the first step is the formation of the iminium ion **22**. Subsequent loss of propene via [3,3]-sigmatropic shift leads to the intermediate **23**. An electrocyclic rearrangement initiated by the abstraction of the benzylic hydrogen by the carbonyl

and concomitant restoration of aromatic character of the phenanthrene ring leads to **24**. Formation of dihydrooxazole ring through intra-molecular nucleophilic atatck of the oxygen on the electrophilic carbon of the iminium ion in **24** leads to **25**. Finally, dehydrogenation by aerial oxidation furnishes oxazole **9**.

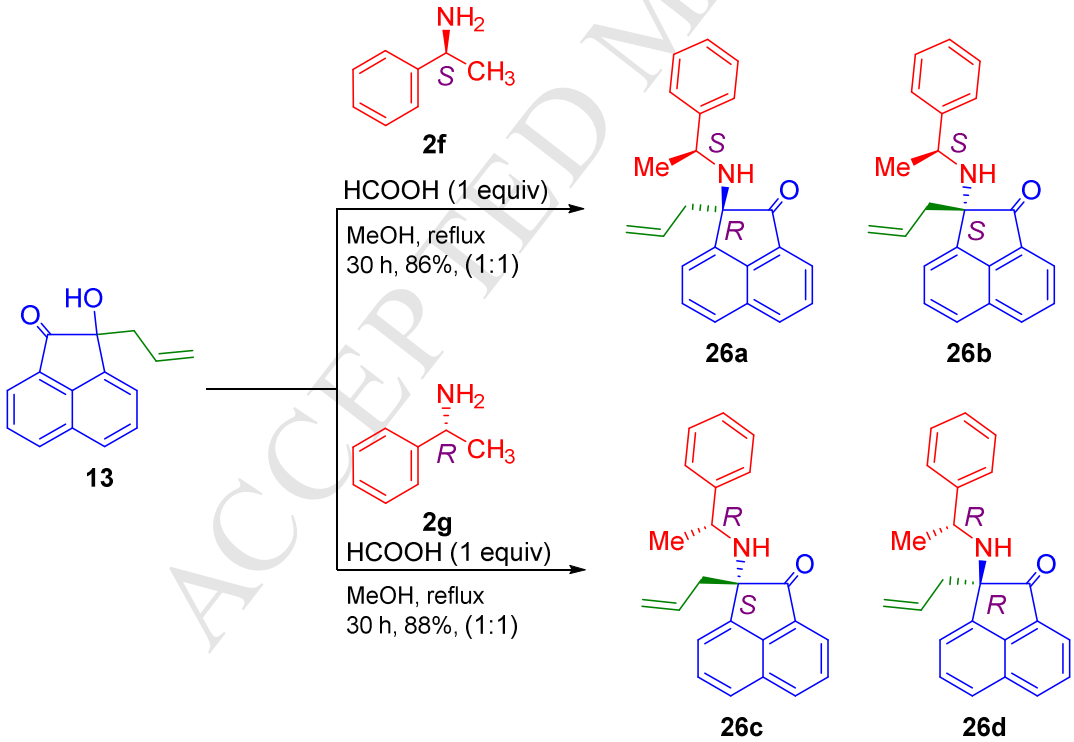


Scheme 5. Mechanism for the formation of oxazole **9** from *tert*-α-hydroxy ketone **6a**.

2.3. The Voight reaction of *tert*-α-hydroxy ketones with chiral amines

The Voight reaction provides unique opportunity for the synthesis of chiral secondary amino ketones by employing commercially available optically active primary amines like *S*-(-)-α-methylbenzylamine **2f** and *R*-(+)-α-methylbenzylamine **2g**. Chiral α-amino ketones are sought-after molecule for their use in stereo selective drug synthesis.[12] The reaction of **13** with *S*-(-)-α-methylbenzylamine **2f** in methanol reflux in the presence of formic acid provided two diastereomers **26a** and **26b** in 1:1 ratio (Scheme 6) which were easily separated by column chromatography and the isomers were characterized independently. The structure of the *S,S*-

isomer **26b** was unambiguously assigned on the basis of single crystal X-ray structure analysis (Figure 6). We attempted selective reductive removal of the ethylbenzene moiety in **26b** by hydrogenolysis using Pd/C (10%) or $Pd(OH)_2/C$ (20%) to check proof-of-the-principle of synthesis of α-amino ketones. Unfortunately, in both the instances, we isolated only the double bond reduced product.[13] Next, we carried out the Voight reaction of **13** with *R*-(+)-α-methylbenzylamine **2f** and the reaction provided the two optically active antipodes **26c** (*R*,*S*) and **26d** (*R*,*R*) in 1:1 ratio (Scheme 6). As to be anticipated for the enantiomeric pairs, the NMR spectra of **26a** and **26c** matched perfectly. Similarly, the NMR spectra of **26b** matched with **26d**. We note that in the ^{1}H NMR spectra, the chemical shift of methine proton of **26b** and **26d** appeared at δ 3.61 ppm, which is in deshielded zone compared to the chemical shift value of δ 3.37 ppm for this proton in **26a** and **26c**.

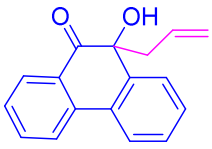
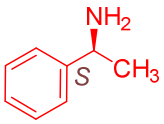
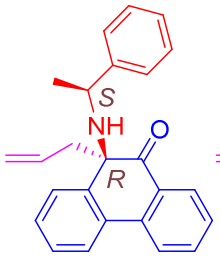
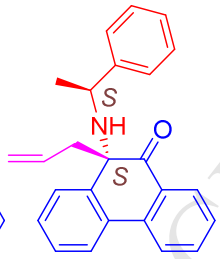
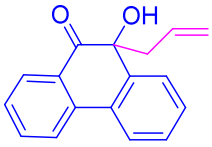
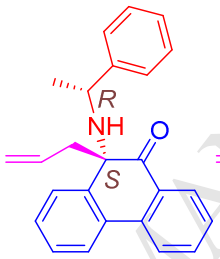
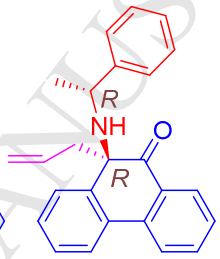
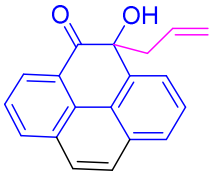
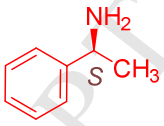
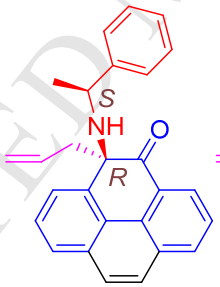
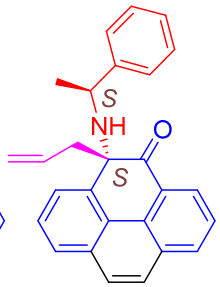
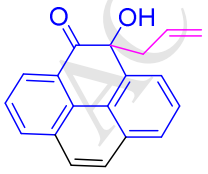
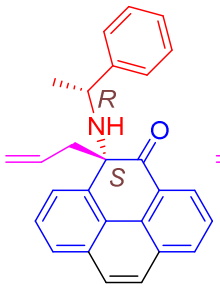
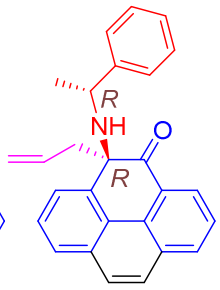


Scheme 6. The Voight reaction of *tert*-α-hydroxy ketone present on acenaphthylene motif **13** with chiral amines **2f-g** to corresponding *tert*-α-amino ketones **26a-d**.

In continuation, we conducted the reaction of *tert*-α-hydroxy ketone present on phenanthrene motif **6a** with *S*-(-)-α-methylbenzylamine **2f** and the reaction provided two chromatographically separable diastereomers **27a** and **27b** in 32:68 ratio (entry 1, Table 5). The isomers were separated and characterized independently. The ratio of the isomers was calculated on the basis of integration of relevant signals in ^{1}H NMR spectra of the reaction mixture. The structure of the isomers was assigned on comparison of ^{1}H and ^{13}C chemical shifts of relevant hydrogen and carbon atoms with those of **26a** and **26b**. Similarly, the reaction of **6a** with *R*-(+)-α-methylbenzylamine **2g** provided optical antipodes **27c** and **27d** in 32:68 ratio (entry 2). Since the final 1,2-C migration step is kinetically controlled, we believe that stereochemistry of the imine intermediate dictates final stereochemical outcome favouring one of the two diasteromers.

Finally, we conducted the Voight reaction with *S*-(-)-α-methylbenzylamine **2f** on *tert*-α-hydroxy ketone **11** present on pyrene motif and the reaction provided chromatographically separable diastereomers **28a** and **28b** in 42:58 ratio (entry 3, Table 5). The reaction of **11** with *R*-(+)-α-methylbenzylamine **2g** under the similar reaction conditions provided the optical antipodes **28c** and **28d** in 42:58 ratio (entry 4). Each isomer was separated and characterized independently. Structures of the isomers were assigned on comparison of the spectra with those derived from acenaphthylene or phenanthrene.

Table 5. Transformation of *tert*-α-hydroxy ketones present on phenanthrene motif **6a**, pyrene motif **11** to corresponding *tert*-α-amino ketones **27a-d** and **28a-d**.

Entry	α-Hydroxy ketone	Amine	α-Amino ketones		Time (h)	Yield (%)	Ratio
1.	 **6a**	 **2f**	 **27a**	 **27b**	32	81	32:68
2.	 **6a**	 **2g**	 **27c**	 **27d**	32	80	32:68
3.	 **11**	 **2f**	 **28a**	 **28b**	36	72	42:58
4.	 **11**	 **2g**	 **28c**	 **28d**	36	72	42:58

3. Conclusion

We have extended scope of the Voight amination for the synthesis of several *tert*-α-amino ketones present on phenanthrene, pyrene and acenaphthylene motif. We have shown that the acid mediated condensation of primary amines and *tert*-α-hydroxy ketones present on rigid planar molecular frameworks takes place readily to provide corresponding *tert*-α-amino ketones. The reaction goes through imine formation followed by 1,2-C migration. It works best with HCOOH in methanol reflux or PTSA in toluene reflux. The reaction has been applied for synthesis of optically active *tert*-α-amino ketones by employing *S*-(-) or *R*-(+)-α-methylbenzylamines.

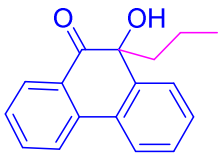
4. Experimental section

4.1. General

All reactions and chromatographic separations were monitored by thin layer chromatography (TLC). Glass plates coated with silica gel GF-254 was used for TLC. Column chromatography was carried on neutral alumina (60-120 mesh, SRL chemicals) or silica gel (100-200 mesh, AVRA synthesis private limited) using increasing percentage of ethyl acetate in hexanes. Melting points were uncorrected and were determined using open-ended capillary tubes on VEEGO VMP-DS instrument. IR spectra were recorded as KBr pellets on a Nicolet-6700 spectrometer. ^{1}H NMR spectra (400 MHz), ^{13}C NMR (100MHz) and DEPT-135 spectra were recorded for ($CDCl_3$ or $CDCl_3$ + CCl_4, 1:1) solutions on Bruker-Avance 400 MHz spectrometer with TMS as internal standard. ^{1}H-NMR data are reported as follows: chemical shift (multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of the doublet, dt = doublet of the triplet, td = triplet of the doublet and br s = broad singlet), coupling constant (*J*) and integrations). Coupling constant *J* values are given in Hz. The ^{13}C NMR spectra were recorded with broadband ^{1}H decoupling. The DEPT-135 NMR spectra were recorded for each sample to

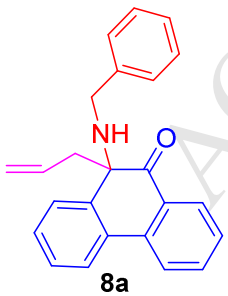
support assigned structure. High resolution mass spectra were recorded on a Water Q-TOF micro mass spectrometer using electron spray ionization mode. The X- ray diffraction measurements were carried out at 298 K on Oxford CrysAlis CCD area detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube (λ = 0.71073 Å). Phenanthrene-9,10-dione, pyrene, acenaphthylene-1,2-dione, formic acid (98-100%), PTSA and benzylamines were procured from commercial sources and used as received. Pyrene-4,5-dione[14] and tertiary α-hydroxy ketones **6a**, **6c**, **6d**, **5**, **7** and 2-hydroxy-1,2-diphenylpent-4-en-1-one were prepared according to literature procedure.[8]

4.2. General procedure for synthesis of α-amino ketones: α-Hydroxy ketone (1 equiv) was taken in a 25 mL two neck round bottom flask and dissolved in dry methanol or dry toluene. To the resulting solution amine (4 equiv) and formic acid or *p*-toluenesulfonic acid monohydrate (1 equiv) was added under a nitrogen atmosphere and stir at room temperature for 10 min. Then, the reaction mixture was refluxed under vigorous stirring. After completion of the reaction (absence of α-hydroxy ketone by TLC) reaction mixture was cooled to room temperature. Methanol or toluene was evaporated under reduced pressure and the crude product was extracted using dichloromethane (30 mL). The organic layer was washed with 0.1 *N* NaOH (2 × 20 mL), 0.01 *N* HCl (2 × 20 mL), brine solution (2 × 20 mL) and then dried over anhydrous sodium sulfate. Then the concentrated crude product was purified by column chromatography using neutral alumina (60-120 mesh SRL chemicals) and increasing amount of ethyl acetate in hexanes (100% hexane to 98% hexane) as eluent.



6b

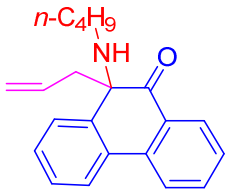
4.2.1. 10-Hydroxy-10-propylphenanthren-9(10*H*)-one (6b): 10-Allyl-10-hydroxyphenanthren-9(10*H*)-one (200.1 mg, 0.80 mmol) was taken in a hydrogenator, dissolved in methanol (5 mL) and then 10% Pd/C (8.6 mg, 0.08 mmol) was added. The reaction was done at 70 psi for 24 h. After completion of starting material in the reaction mixture, filter the Pd/C through celite and concentrated the mother liquor to afford 10-hydroxy-10-propylphenanthren-9(10*H*)-one **6b** (191.6 mg) as a semi solid in 95% yield, R_f (98% Hexane/EtOAc) 0.6; IR (KBr, cm^{-1}) 3489, 3067, 2960, 2934, 2872, 1691, 1600, 1479, 1450, 1385, 1284, 1246, 1199, 1162, 1108, 1072, 1012, 962, 916, 758, 734, 620; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 7.90 (t, *J* = 8.0 Hz, 2H), 7.79-7.75 (m, 1H), 7.73-7.70 (m, 1H), 7.63 (td, *J* = 7.2, 1.6 Hz, 1H), 7.40-7.31 (m, 3H), 4.07 (s, 1H), 1.78-1.60 (m, 2H), 1.34-1.14 (m, 2H), 0.73 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) δ 204.0 (C=O), 141.2 (C), 137.7 (C), 135.0 (CH), 129.09 (CH), 129.05 (C), 128.7 (C), 128.4 (CH), 128.0 (CH), 127.3 (CH), 126.3 (CH), 124.1 (CH), 123.2 (CH), 79.9 (C), 46.9 (CH_2), 17.3 (CH_2), 14.0 (CH_3) ppm; HRMS (ESI) calcd for $C_{17}H_{16}O_2Na$ (M + Na) 275.1048, found 275.1053.



8a

4.2.2. 10-Allyl-10-(benzylamino)phenanthren-9(10*H*)-one (8a): Following the general procedure, the reaction of 10-allyl-10-hydroxyphenanthren-9(10*H*)-one (200.2 mg, 0.80 mmol),

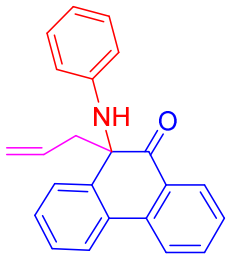
benzylamine (172.3 mg, 3.2 mmol), formic acid (36.8 mg, 0.80 mmol) and methanol (5 mL) afforded 10-allyl-10-(benzylamino)phenanthren-9(10*H*)-one **8a** (222.5 mg) as a light yellow semi solid in 82% yield, R_f (98% Hexane/EtOAc) 0.7; IR (KBr, cm^{-1}) 3351, 3066, 3028, 2924, 2854, 1680, 1600, 1452, 1278, 1219, 1158, 1110, 993, 966, 921, 758, 732, 699, 648; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 8.10 (dd, *J* = 7.8, 1.3 Hz, 1H), 8.06-7.98 (m, 3H), 7.71-7.64 (m, 1H), 7.48-7.34 (m, 5H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.22 (d, *J* = 7.2 Hz, 1H), 5.47-5.36 (m, 1H), 4.89-4.83 (m, 2H), 3.44 (d, *J* = 12.2 Hz, 1H), 3.29 (d, *J* = 12.2 Hz, 1H), 2.53-2.44 (m, 2H), 2.10 (br s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) δ 202.4 (C=O), 140.9 (C), 139.9 (C), 137.5 (C), 134.8 (CH), 131.3 (CH), 131.2 (C), 130.1 (C), 129.6 (CH), 128.5 (CH), 128.43 (CH), 128.41 (CH), 128.0 (CH), 127.6 (CH), 127.1 (CH), 123.8 (CH), 123.2 (CH) , 119.8 (CH_2), 69.3 (C), 49.6 (CH_2), 48.8 (CH_2) ppm; HRMS (ESI) calcd for $C_{24}H_{22}NO$ (M + H) 340.1701, found 340.1700.



8b

4.2.3. 10-Allyl-10-(butylamino)phenanthren-9(10*H*)-one (8b): Following the general procedure, the reaction of 10-allyl-10-hydroxyphenanthren-9(10*H*)-one (200.1 mg, 0.80 mmol), butylamine (234.1 mg, 3.2 mmol), formic acid (36.9 mg, 0.80 mmol) and methanol (5 mL) afforded 10-allyl-10-(butylamino)phenanthren-9(10*H*)-one **8b** (209.9 mg) as a light yellow semi solid in 86% yield, R_f (98% Hexane/EtOAc) 0.7; IR (KBr, cm^{-1}) 3476, 3071, 2957, 2926, 2859, 1678, 1642, 1601, 1475, 1451, 1279, 1223, 1143, 1107, 994, 920, 760, 733, 635; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 8.06 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.01-7.93 (m, 2H), 7.89 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.64 (td, *J* = 8.1, 1.5 Hz, 1H), 7.43-7.33 (m, 3H), 5.44-5.32 (m, 1H), 4.90-4.81 (m,

2H), 2.43 (dd, *J* = 7.4, 3.6 Hz, 2H), 2.35 (br s, 1H), 2.29-2.22 (m, 1H), 2.13-2.06 (m, 1H), 1.49-1.40 (m, 2H), 1.35-1.26 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) δ 202.7 (C=O), 140.2 (C), 137.4 (C), 134.7 (CH), 131.4 (CH), 130.9 (C), 130.0 (C), 129.4 (CH), 128.5 (CH), 128.3 (CH), 127.8 (CH), 127.5 (CH), 123.6 (CH), 123.1 (CH), 119.6 (CH_2), 69.1 (C), 49.6 (CH_2), 44.3 (CH_2), 33.1 (CH_2), 20.6 (CH_2), 14.3 (CH_3) ppm; HRMS (ESI) calcd for $C_{21}H_{24}NO$ (M + H) 306.1858, found 306.1858.



8c

4.2.4. 10-Allyl-10-(phenylamino)phenanthren-9(10*H*)-one (8c): Following the general procedure, the reaction of 10-allyl-10-hydroxyphenanthren-9(10*H*)-one (199.9 mg, 0.80 mmol), aniline (296.1 mg, 3.2 mmol), *p*-toluenesulfonic acid monohydrate (152.0 mg, 0.80 mmol), 4 Å molecular sieves and toluene (5 mL) afforded 10-allyl-10-(phenylamino)phenanthren-9(10*H*)-one **3c** (228.6 mg) as a light yellow color solid in 88% yield, R_f (98% Hexane/EtOAc) 0.6; mp 121-122 °C; IR (KBr, cm^{-1}) 3389, 3064, 3022, 2926, 2855, 1690, 1602, 1502, 1478, 1450, 1432, 1313, 1289, 1256, 1222, 1159, 1024, 993, 923, 754, 734, 691; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 8.13-8.03 (m, 3H), 7.75-7.70 (m, 2H), 7.48-7.36 (m, 2H), 7.33 (td, *J* = 7.7, 1.0 Hz, 1H), 6.93 (t, *J* = 8.1 Hz, 2H), 6.58 (t, *J* = 7.3 Hz, 1H), 6.18 (d, *J* = 7.8 Hz, 2H), 5.63-5.50 (m, 1H), 5.21-5.10 (m, 2H), 4.68 (s, 1H), 2.65-2.52 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) δ 199.6 (C=O), 145.3 (C), 140.6 (C), 137.1 (C), 134.9 (CH), 131.1 (CH), 130.0 (C), 129.82 (C), 129.75 (CH), 128.9 (CH), 128.5 (CH), 128.3 (CH), 128.1 (CH), 127.6 (CH), 124.4

(CH), 123.3 (CH), 121.2 (CH), 118.3 (CH), 115.8 (CH), 66.7 (C), 48.5 (CH_2) ppm; HRMS (ESI) calcd for $C_{23}H_{19}NONa$ (M + Na) 348.1364, found 348.1365.

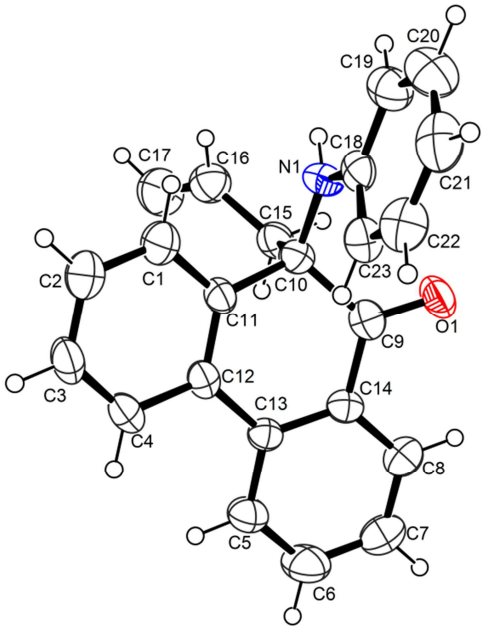
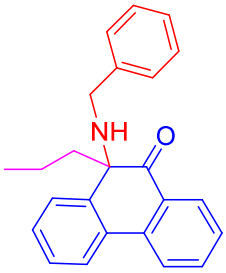


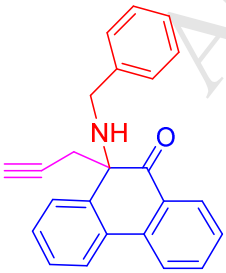
Figure 2. ORTEP diagram of 10-allyl-10-(phenylamino)phenanthren-9(10*H*)-one **8c** (CCDC 1025149) with crystallographic numbering.

Crystal data for 8c: Empirical formula, $C_{23}H_{19}NO$; Formula weight, 325.39; Crystal color, habit: light yellow color, rectangular block; Crystal system, orthorhombic; Crystal dimensions, 0.4 x 0.2 x 0.05 mm^3; Lattice parameters, a = 15.2385(6) Å, b = 23.0797(11) Å, c = 9.9974(6) Å; α = 90.00, β = 90.00, γ = 90.00; V = 3516.1(3) A^3; Space group P2-1; Z = 8; D_{calcd} = 1.229 g/cm^3; F_{000} = 1376; λ(Mo Kα) = 0.7107 Å; R ($I \geq 2\sigma_1$) = 0.0674, wR^2 = 0.1738. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **8c** CCDC # 1025149).



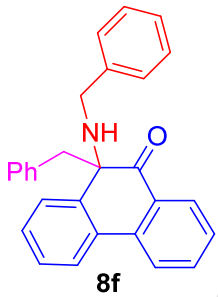
8d

4.2.5. 10-(Benzylamino)-10-propylphenanthren-9(10*H*)-one (8d): Following the general procedure, the reaction of 10-hydroxy-10-propylphenanthren-9(10*H*)-one (199.8 mg, 0.80 mmol), benzylamine (340.8 mg, 3.2 mmol), formic acid (36.6 mg, 0.80 mmol) and methanol (5 mL) afforded 10-(benzylamino)-10-propylphenanthren-9(10*H*)-one **8d** (151.4 mg) as a light yellow semi solid in 56% yield, R_f (98% Hexane/EtOAc) 0.7; IR (KBr, cm^{-1}) 3385, 3063, 3030, 2959, 2930, 2811, 2734, 1702, 1600, 1491, 1453, 1307, 1203, 1166, 1026, 916, 828, 742, 695; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 8.14 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.09-8.01 (m, 3H), 7.71 (td, *J* = 8.1, 1.5 Hz, 1H), 7.47-7.35 (m, 5H), 7.33-7.28 (m, 2H), 7.24 (d, *J* = 7.2 Hz, 1H), 3.41 (d, *J* = 12.1 Hz, 1H), 3.26 (d, *J* = 12.1 Hz, 1H), 1.83 (br s, 1H), 1.77-1.69 (m, 2H), 1.10-0.97 (m, 2H), 0.66 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) δ 204.0 (C=O), 141.0 (C), 140.1 (C), 137.5 (C), 135.0 (CH), 131.1 (C), 130.0 (C), 129.5 (CH), 128.5 (CH), 128.40 (CH), 128.37 (CH), 127.8 (CH), 127.4 (CH), 127.0 (CH), 123.7 (CH), 123.3 (CH), 69.3 (C), 48.9 (CH_2), 48.1 (CH_2), 16.9 (CH_2), 14.2 (CH_3) ppm; HRMS (ESI) calcd for $C_{24}H_{24}NO$ (M + H) 342.1858, found 342.1858.



8e

4.2.6. 10-(Benzylamino)-10-(prop-2-yn-1-yl)phenanthren-9(10*H*)-one (8e): Following the general procedure, the reaction of 10-hydroxy-10-(prop-2-yn-1-yl)phenanthren-9(10*H*)-one (200.1 mg, 0.80 mmol), benzylamine (345.0 mg, 3.2 mmol), formic acid (37.0 mg, 0.80 mmol) and methanol (5 mL) afforded 10-(benzylamino)-10-(prop-2-yn-1-yl)phenanthren-9(10*H*)-one **8e** (212.0 mg) as a light yellow semi solid in 75% yield, R_f (98% Hexane/EtOAc) 0.7; IR (KBr, cm^{-1}) 3292, 3065, 2911, 2855, 3028, 1684, 1601, 1468, 1451, 1275, 1217, 1109, 939, 795, 758, 731, 702; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 8.14 (d, *J* = 7.2 Hz, 1H), 8.08-8.00 (m, 3H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.49-7.40 (m, 3H), 7.38 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.23 (d, *J* = 9.6 Hz, 1H), 3.46 (d, *J* = 12.2 Hz, 1H), 3.31 (d, *J* = 12.2 Hz, 1H), 2.84 (br s, 1H), 2.65 (qd, *J* = 16.5, 2.6 Hz, 2H), 1.88 (t, *J* = 2.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) δ 200.7 (C=O), 140.6 (C), 138.6 (C), 137.4 (C), 135.0 (CH), 131.4 (C), 129.8 (C), 129.7 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 127.8 (CH), 127.1 (CH), 124.0 (CH), 123.2 (CH), 77.9 (CH), 73.0 (C), 67.7 (C), 48.8 (CH_2), 34.9 (CH_2) ppm; HRMS (ESI) calcd for $C_{24}H_{20}NO$ (M + H) 338.1545, found 338.1545.



8f

4.2.7. 10-Benzyl-10-(benzylamino)phenanthren-9(10*H*)-one (8f): Following the general procedure, the reaction of 10-benzyl-10-hydroxyphenanthren-9(10*H*)-one (200.2 mg, 0.66 mmol), benzylamine (285.6 mg, 2.6 mmol), formic acid (31.4 mg, 0.66 mmol) and methanol (5 mL) afforded 10-benzyl-10-(benzylamino)phenanthren-9(10*H*)-one **8f** (168.6 mg) as a solid in 65% yield, R_f (98% Hexane/EtOAc) 0.7; mp 48-49 °C; IR (KBr, cm^{-1}) 3320, 3061, 3028, 1670,

1601, 1495, 1451, 1277, 1123, 1028, 941, 764, 729, 700; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 8.02 (t, *J* = 7.7 Hz, 2H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.45-7.33 (m, 5H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.23-7.17 (m, 1H), 7.00-6.88 (m, 3H), 6.58 (d, *J* = 7.6 Hz, 2H), 3.39 (d, *J* = 12.3 Hz, 1H), 3.30 (d, *J* = 12.3 Hz, 1H), 3.01 (s, 2H), 2.63 (br s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) δ 202.3(C=O), 141.0 (C), 139.3 (C), 137.3 (C), 134.6 (CH), 134.4 (C), 131.7 (C), 130.4 (CH), 129.4 (CH), 128.6 (CH), 128.5 (CH), 128.4 (CH), 128.2 (CH), 128.0 (CH), 127.6 (CH), 127.4 (CH), 127.0 (CH), 126.9 (CH), 123.6 (CH), 123.0 (CH), 70.5 (C), 52.3 (CH_2), 48.8 (CH_2) ppm; HRMS (ESI) calcd for $C_{28}H_{24}NO$ (M + H) 390.1858, found 390.1858.

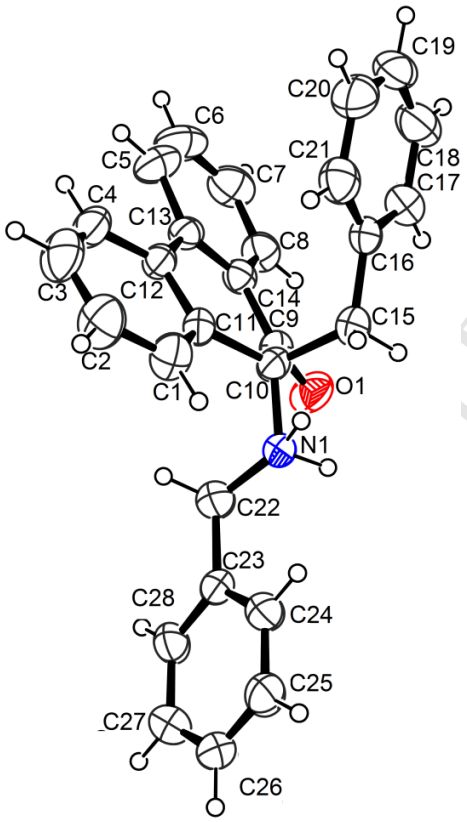
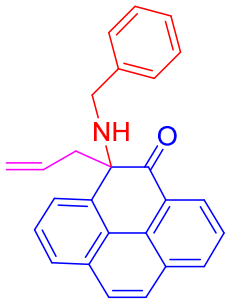


Figure 3. ORTEP diagram of 10-benzyl-10-(benzylamino)phenanthren-9(10*H*)-one **8f** (CCDC 1025150) with crystallographic numbering.

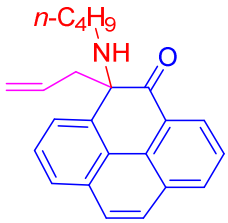
Crystal data for 8f: Empirical formula, $C_{28}H_{23}NO$; Formula weight, 389.47; Crystal color, habit: colorless, plate; Crystal system, triclinic; Crystal dimensions, 0.45 x 025 x 0.20 mm^3; Lattice parameters, a = 8.4602(8) Å, b = 10.6685(10) Å, c = 12.1284(12)Å; α = 80.86(8), β = 76.81(9), γ = 88.58(8); V = 1052.22(18)A^3; Space group P-1; Z = 2; D_{calcd} = 1.229 g/cm^3; F_{000} = 412; λ(Mo Kα) = 0.7107 Å; R ($I \geq 2\sigma_1$) = 0.0619, wR^2 = 0.1478. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **8f** CCDC # 1025150).



12a

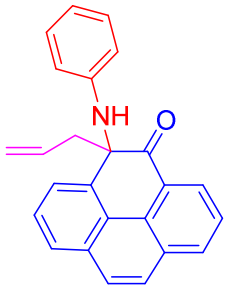
4.2.8. 5-Allyl-5-(benzylamino)pyren-4(5*H*)-one (12a): Following the general procedure, the reaction of 5-allyl-5-hydroxypyren-4(5*H*)-one (100.3 mg, 0.37 mmol), benzylamine (157.8 mg, 1.47 mmol), formic acid (17.2 mg, 0.37 mmol) and methanol (3 mL) afforded 5-allyl-5-(benzylamino)pyren-4(5*H*)-one **12a** (96.4 mg) as a yellow color semi solid in 72% yield, R_f (98% Hexane/EtOAc) 0.7; IR (KBr, cm^{-1}) 3328, 3056, 2958, 2924, 2853, 1677, 1618, 1583, 1494, 1454, 1431, 1341, 1261, 1174, 1117, 1032, 992, 920, 837, 724, 700; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 8.40 (d, *J* = 7.4 Hz, 1H), 8.26 (d, *J* = 7.4 Hz, 1H), 8.13 (d, *J* = 7.9 Hz, 1H), 7.89-7.79 (m, 2H), 7.78-7.69 (m, 3H), 7.37 (d, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.23-7.17 (m, 1H), 5.45-5.32 (m, 1H), 4.84-4.78 (m, 2H), 3.49 (d, *J* = 12.3 Hz, 1H), 3.40 (d, *J* = 12.2 Hz, 1H), 2.64-2.54 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) δ 202.9 (C=O), 140.8 (C), 139.7 (C), 134.1 (CH), 132.1 (C), 131.4 (C), 131.2 (CH), 130.0 (C), 129.0 (C), 128.5 (CH),

128.4 (CH), 128.2 (CH), 128.0 (CH), 127.2 (CH), 127.0 (CH), 127.0 (CH), 126.2 (CH), 126.0 (CH), 119.8 (CH_2), 70.1 (C), 50.2 (CH_2), 48.9 (CH_2) ppm; HRMS (ESI) calcd for $C_{26}H_{22}NO$ (M + H) 364.1701, found 364.1701.



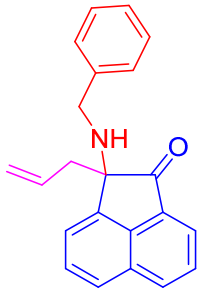
12b

4.2.9. 5-Allyl-5-(butylamino)pyren-4(5*H*)-one (12b): Following the general procedure, the reaction of 5-allyl-5-hydroxypyren-4(5*H*)-one (100.3 mg, 0.37 mmol), *n*-butyl amine (107.3 mg, 1.47 mmol), formic acid (17.4 mg, 0.37 mmol) and methanol (3 mL) afforded 5-allyl-5-(benzylamino)pyren-4(5*H*)-one **12b** (92.2 mg) as a yellow color semi solid in 76% yield, R_f (98% Hexane/EtOAc) 0.7; IR (KBr, cm^{-1}) 3428, 3062, 2958, 2927, 2858, 1675, 1620, 1342, 1260, 1173, 1118, 992, 924, 838, 723; ^1H NMR (400 MHz, $CDCl_3$) δ 8.37 (dd, *J* = 7.4, 1.0 Hz, 1H), 8.14 (d, *J* = 7.9 Hz, 2H), 7.87-7.81 (m, 2H), 7.80-7.70 (m, 3H), 5.39-5.28 (m, 1H), 4.88-4.76 (m, 2H), 2.61-2.51 (m, 2H), 2.36-2.20 (m, 2H), 1.86 (br s, 1H), 1.53-1.43 (m, 2H), 1.35-1.24 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.5 (C=O), 134.2 (CH), 132.0 (C), 131.4 (C), 131.2 (CH), 129.9 (C), 128.9 (C), 128.1 (CH), 128.0 (CH), 127.1 (CH), 127.0 (CH), 126.3 (CH), 126.2 (CH), 125.9 (CH), 125.8 (C), 119.6 (CH), 70.0 (C), 50.2 (CH_2), 44.6 (CH_2), 33.0 (CH_2), 20.5 (CH_2), 14.1 (CH_3) ppm; HRMS (ESI) calcd for $C_{23}H_{24}NO$ (M + H) 330.1858, found 330.1858.



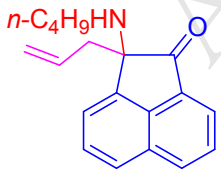
12c

4.2.10. 5-Allyl-5-(phenylamino)pyren-4(5*H*)-one (12c): Following the general procedure, the reaction of 5-allyl-5-hydroxypyren-4(5*H*)-one (100.1 mg, 0.37 mmol), aniline (136.7 mg, 1.47 mmol), *p*-toluenesulfonic acid monohydrate (69.8 mg, 0.37 mmol), 4 Å molecular sieves and toluene (3 mL) afforded 5-allyl-5-(phenylamino)pyren-4(5*H*)-one **12c** (109.3 mg) as a semi solid in 80% yield, R_f (98% Hexane/EtOAc) 0.6; IR (KBr, cm^{-1}) 3398, 3052, 2957, 2927, 2855, 1686, 1603, 1499, 1341, 1314, 1292, 1260, 1120, 1073, 1040, 993, 923, 839, 728, 692; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 8.39 (dd, *J* = 7.4, 1.1 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 7.5 Hz, 1H), 7.91-7.85 (m, 3H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 6.87 (t, *J* = 7.9 Hz, 2H), 6.55 (t, *J* = 7.3 Hz, 1H), 6.26-6.19 (m, 2H), 5.59-5.46 (m, 1H), 5.14-5.06 (m, 2H), 4.89 (s, 1H), 2.71-2.57 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) δ 200.2 (C=O), 145.3 (C), 140.4 (C), 134.2 (CH), 132.6 (C), 131.6 (C), 130.9 (CH), 129.6 (C), 129.0 (CH), 128.8 (C), 128.3 (CH), 128.1 (CH), 127.3 (CH), 127.1 (CH), 126.8 (CH), 126.5 (CH), 125.3 (CH), 124.8 (C), 121.2 (CH_2), 118.3 (CH), 115.7 (CH), 67.4 (C), 48.9 (CH_2) ppm; HRMS (ESI) calcd for $C_{25}H_{19}NONa$ (M + Na) 372.1364, found 372.1369.



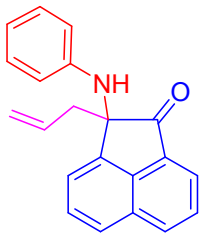
14a

4.2.11. 2-Allyl-2-(benzylamino)acenaphthylen-1(2*H*)-one (14a): Following the general procedure, the reaction of 2-allyl-2-hydroxyacenaphthylen-1(2*H*)-one (100.2 mg, 0.45 mmol), benzylamine (190.9 mg, 1.78 mmol), formic acid (20.6 mg, 0.45 mmol) and methanol (3 mL) afforded 2-allyl-2-(benzylamino)acenaphthylen-1(2*H*)-one **14a** (120.4 mg) as a light yellow semi solid in 86% yield, R_f (98% Hexane/EtOAc) 0.7; IR (KBr, cm^{-1}) 3396, 3064, 2960, 2930, 2869, 1719, 1641, 1600, 1493, 1458, 1433, 1369, 1344, 1274, 1191, 1122, 1094, 1071, 1008, 988, 922, 838, 783, 748, 700, 661; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 8.11 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 7.0 Hz, 1H), 7.88-7.82 (m, 1H), 7.75-7.65 (m, 3H), 7.24-7.13 (m, 5H), 5.61-5.49 (m, 1H), 5.02-4.87 (m, 2H), 3.42 (d, *J* = 12.3 Hz, 1H), 3.22 (d, *J* = 12.3 Hz, 1H), 2.75-2.67 (m, 1H), 2.62-2.54 (m, 1H), 2.29 (br s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) δ 209.2 (C=O), 141.9 (C), 140.3 (C), 139.9 (C), 132.4 (C), 132.0 (CH), 131.8 (CH), 130.9 (C), 128.8 (CH), 128.4 (CH), 128.31 (CH), 128.29 (CH), 127.1 (CH), 124.9 (CH), 121.12 (CH), 121.05 (CH), 119.5 (CH_2), 70.8 (C), 48.6 (CH_2), 43.4 (CH_2) ppm; HRMS (ESI) calcd for $C_{22}H_{20}NO$ (M + H) 314.1545, found 314.1545.



14b

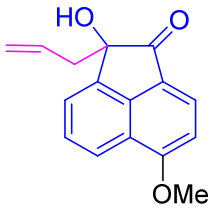
4.2.12. 2-Allyl-2-(butylamino)acenaphthylen-1(2*H*)-one (14b): Following the general procedure, the reaction of 2-allyl-2-hydroxyacenaphthylen-1(2*H*)-one (100.3 mg, 0.45 mmol), butylamine (130.3 mg, 1.78 mmol) and formic acid (20.4 mg, 0.45 mmol) and methanol (3 mL) afforded 2-allyl-2-(butylamino)acenaphthylen-1(2*H*)-one **14b** (109.9 mg) as a light yellow semi solid in 88% yield, R_f (98% Hexane/EtOAc) 0.7; IR (KBr, cm^{-1}) 3317, 3057, 2957, 2928, 2865, 1723, 1640, 1623, 1603, 1492, 1462, 1432, 1367, 1343, 1316, 1293, 1260, 1215, 1191, 1145, 1105, 1055, 1003, 920, 836, 783, 740, 656; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 8.10 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 7.0 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.74-7.64 (m, 2H), 7.60 (d, *J* = 6.9 Hz, 1H), 5.62-5.43 (m, 1H), 4.99 (d, *J* = 16.9 Hz, 1H), 4.88 (d, *J* = 10.1 Hz, 1H), 2.69-2.64 (m, 1H), 2.58-2.52 (m, 1H), 2.27-2.21 (m, 1H), 2.14 (br s, 1H), 2.07-2.01 (m, 1H), 1.37-1.27 (m, 2H), 1.23-1.14 (m, 2H), 0.77 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) δ 209.6 (C=O), 141.8 (C), 140.2 (C), 132.3 (C), 131.8 (CH), 131.8 (CH), 130.8 (C), 128.7 (CH), 128.1 (CH), 124.7 (CH), 120.9 (CH), 120.8 (CH), 119.3 (CH_2), 70.6 (C), 43.8 (CH_2), 43.4 (CH_2), 32.8 (CH_2), 20.2 (CH_2), 14.0 (CH_3) ppm; HRMS (ESI) calcd for $C_{19}H_{22}NO$ (M + H) 280.1701, found 280.1701.



14c

4.2.13. 2-Allyl-2-(phenylamino)acenaphthylen-1(2*H*)-one (14c): Following the general procedure, the reaction of 2-allyl-2-hydroxyacenaphthylen-1(2*H*)-one (100.3 mg, 0.45 mmol), aniline (166.1 mg, 1.78 mmol), *p*-toluenesulfonic acid monohydrate (84.9 mg, 0.45 mmol), 4 Å molecular sieves and toluene (3 mL) afforded 2-allyl-2-(phenylamino)acenaphthylen-1(2*H*)-one

14c (104.4 mg) as a light yellow color semi solid in 78% yield, R_f (98% Hexane/EtOAc) 0.6; IR (KBr, cm^{-1}) 3388, 3054, 2924, 2853, 1725, 1602, 1500, 1463, 1433, 1366, 1342, 1315, 1259, 1213, 1188, 1085, 992, 924, 832, 783, 749, 692; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 8.17 (d, *J* = 8.1 Hz, 1H), 7.97 (d, *J* = 6.9 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.78 (t, *J* = 7.6 Hz, 1H), 7.62 (dd, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 6.8 Hz, 1H), 6.78 (t, *J* = 8.0 Hz, 2H), 6.51 (t, *J* = 7.3 Hz, 1H), 6.02 (d, *J* = 8.5 Hz, 2H), 5.82-5.72 (m, 1H), 5.25-5.14 (m, 2H), 4.57 (s, 1H), 2.72-2.65 (m, 1H), 2.64-2.57 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) δ 206.4 (C=O), 145.2 (C), 140.4 (C), 140.1 (C), 132.4 (CH), 131.5 (CH), 131.2 (C), 129.1 (CH), 128.8 (CH), 128.5 (CH), 125.2 (CH), 122.0 (CH), 121.1 (CH_2), 120.7 (CH), 118.9 (CH), 114.6 (CH), 67.9 (C), 45.0 (CH_2) ppm; HRMS (ESI) calcd for $C_{21}H_{17}NONa$ (M +Na) 322.1208, found 322.1208.



15

4.2.14. 2-Allyl-2-hydroxy-6-methoxyacenaphthylen-1(2*H*)-one (15): A mixture of 5-methoxyacenaphthylene-1,2-dione (501.3 mg, 2.35 mmol), allyl bromide (442.3 mg, 3.65 mmol), indium metal (284.3 mg, 2.47 mmol) and sodium iodide (547.3 mg, 3.65 mmol) in dimethylformamide (10 mL) was stirred at room temperature until the reaction completed (by TLC, 48 h). The reaction mixture was quenched with 0.5 mL of 1 *N* HCl and the organic layer was extracted using dichloromethane (50 mL). The organic layer was washed with water (2 × 50 mL), brine solution (2 × 50 mL) and then dried over anhydrous sodium sulfate. The concentrated crude product was purified by column chromatography using silica (100-200 mesh) and hexane:ethyl acetate 8:2 as eluent to afford 2-allyl-2-hydroxy-6-methoxyacenaphthylen-1(2*H*)-one **15** (372.1 mg) as a crystalline white solid in 62% yield, R_f (98% Hexane/EtOAc) 0.4; mp

148-149 ^{o}C; IR (KBr, cm^{-1}) 3375, 2935, 1690, 1593, 1497, 1452, 1427, 1394, 1335, 1292, 1253, 1177, 1158, 1082, 1050, 1007, 970, 933, 903, 828, 800, 775, 743, 680; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.92 (d, *J* = 7.9 Hz, 1H), 7.65-7.56 (m, 2H), 7.02 (d, *J* = 7.9 Hz, 1H), 5.73-5.60 (m, 1H), 5.09-4.97 (m, 2H), 4.09 (s, 3H), 3.27 (br s, 1H), 2.85-2.76 (m, 1H), 2.68-2.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.6 (C=O), 160.8 (C), 142.9 (C), 138.7 (C), 131.4 (CH), 127.7 (CH), 124.5 (CH), 123.4 (C), 122.3 (C), 121.6 (CH), 121.0 (CH), 120.0 (CH_2), 107.0 (CH), 80.2 (C), 56.3 (CH_2), 43.0 (CH_2). HRMS (ESI) calcd for $C_{16}H_{14}O_3Na$ (M + Na) 277.0841, found 277.0848.

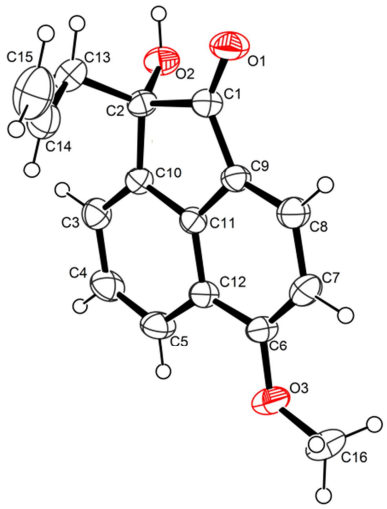
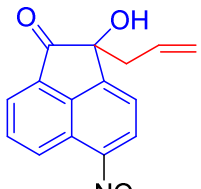


Figure 4. ORTEP diagram of 2-allyl-2-hydroxy-6-methoxyacenaphthylen-1(2*H*)-one **15** (CCDC 1025204) with crystallographic numbering.

Crystal data for 15: Empirical formula, $C_{16}H_{14}O_3$; Formula weight, 254.27; Crystal color, habit: colorless, rectangular block; Crystal system, triclinic; Crystal dimensions, 0.45 x 025 x 0.20 mm^3; Lattice parameters, a = 7.7585(6) Å, b = 8.7350(6) Å, c = 10.7059(8) Å; α = 88.453(6), β = 77.494(6), γ = 66.859(7); V = 649.97(8) A^3; Space group P-1; Z = 2; D_{calcd} = 1.299 g/cm^3; F_{000} = 268; λ(Mo Kα) = 0.7107 Å; R ($I \geq 2\sigma_1$) = 0.0499, wR^2 = 0.1171. Detailed X-ray crystallographic

data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **15** CCDC # 1025204).



16

4.2.15. 2-Allyl-2-hydroxy-5-nitroacenaphthylen-1(2*H*)-one (16): A mixture of 5-nitroacenaphthylene-1,2-dione (200.6 mg, 0.74 mmol), allyl bromide (139.3 mg, 1.15 mmol), indium metal (89.2 mg, 0.77 mmol) and sodium iodide (172.8 mg, 1.15 mmol) in dimethylformamide (5 mL) was stirred at 60 ^{o}C for 4 h. Then the reaction mixture was cooled to room temperature followed by removal of solvent (dimethylformamide) under reduced pressure. Then the reaction mixture was extracted using dichloromethane (30 mL). The organic layer was washed with water (2 × 30 mL), brine solution (2 × 30 mL) and then dried over anhydrous sodium sulfate. The concentrated crude product was purified by column chromatography using silica (100-200 mesh) and hexane:ethyl acetate 8:2 as eluent to afford 2-allyl-2-hydroxy-5-nitroacenaphthylen-1(2*H*)-one **16** (130.7 mg) as a light yellow solid in 55% yield, R_f (98% Hexane/EtOAc) 0.5; mp 46-47 ^{o}C; IR (KBr, cm^{-1}) 3445,1733, 1623, 1523, 1492, 1429, 1336, 1257, 1199, 1172, 1081, 999, 927, 782, 669; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 9.10 (d, *J* = 8.8 Hz, 1H), 8.68 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 6.8 Hz, 1H), 8.04 (t, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 5.70-5.50 (m, 1H), 5.12-5.02 (m, 2H), 3.56 (s, 1H), 2.88-2.78 (m, 1H), 2.73-2.60 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) 203.0 (C=O), 147.3 (C), 143.8 (C), 141.8 (C), 132.4 (CH), 131.1 (C), 130.3 (CH), 130.2 (CH), 127.9 (CH), 124.0 (CH), 123.7 (C), 121.5 (CH_2), 120.1 (CH), 79.1 (C), 43.2 (CH_2) ppm; HRMS (ESI) calcd for $C_{15}H_{11}NO_4Na$ (M + Na) 292.0586, found 292.0586.

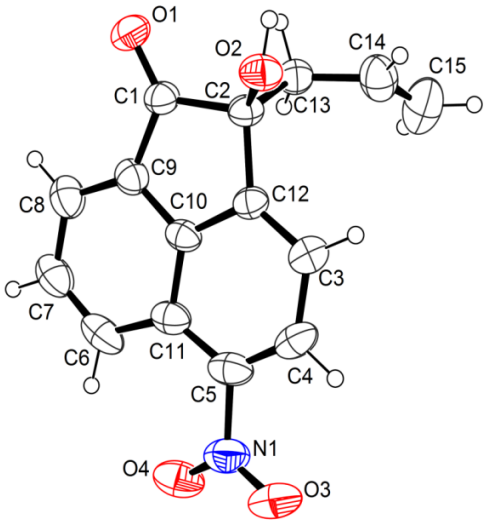
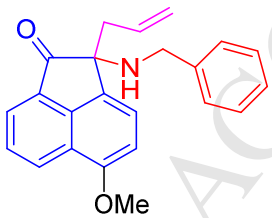


Figure 5. ORTEP diagram of 2-allyl-2-hydroxy-5-nitroacenaphthylen-1(2*H*)-one **16** (CCDC # 1052055) with crystallographic numbering.

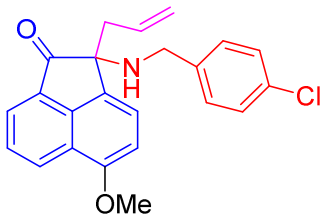
Crystal data for 16: Empirical formula, $C_{15}H_{11}NO_4$; Formula weight, 269.25; Crystal color, habit: colorless, rectangular block; Crystal system, triclinic; Crystal dimensions, 0.45 x 0.30 x 0.20 mm^3; Lattice parameters, 8.0055(17) Å, b = 8.6417(17) Å, c = 10.3601(19) Å; α = 71.724(17), β = 78.571(18), γ = 66.82(2); V = 623.3(2) A^3; Space group P-1; Z = 2; D_{calcd} = 1.435 g/cm^3; F_{000} = 280; λ(Mo Kα) = 0.7107 Å; R ($I \geq 2\sigma_1$) = 0.0820, wR^2 = 0.2778. Detailed X-ray crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **16** CCDC # 1052055).



17a

4.2.16. 2-Allyl-2-(benzylamino)-5-methoxyacenaphthylen-1(2*H*)-one (17a): Following the general procedure, the reaction of 2-allyl-2-hydroxy-6-methoxyacenaphthylen-1(2*H*)-one (100.3 mg, 0.39 mmol), benzylamine (168.6 mg, 1.57 mmol), formic acid (18.2 mg, 0.39 mmol) and

methanol (3 mL) afforded 2-allyl-2-(benzylamino)-5-methoxyacenaphthylen-1(2*H*)-one **17a** (94.8 mg) as a light yellow semi solid in 70% yield, R_f (98% Hexane/EtOAc) 0.6; IR (KBr, cm^{-1}) 3303, 3030, 2855, 1718, 1673, 1602, 1499, 1455, 1427, 1384, 1238, 1152, 1078, 1024, 921, 823, 777, 698; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 8.36 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.92 (dt, *J* = 7.0, 0.7 Hz, 1H), 7.69 (td, *J* = 7.6, 1.1 Hz,, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.25-7.14 (m, 5H), 6.95 (d, *J* = 7.7 Hz, 1H), 5.62-5.49 (m, 1H), 5.02-4.93 (dd, *J* = 18.0, 1.4 Hz, 1H), 4.91-4.84 (dd, *J* = 10.1, 0.8 Hz, 1H), 4.05 (s, 3H), 3.37 (d, *J* = 12.3 Hz, 1H), 3.21 (d, *J* = 12.3 Hz, 1H), 2.73-2.65 (m, 1H), 2.59-2.51 (m, 1H), 2.07 (br s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) δ 209.9 (C=O), 154.7 (C), 143.2 (C), 140.4 (C), 132.1 (CH), 131.9 (C), 131.1 (C), 128.4 (CH), 128.3 (CH), 127.8 (CH), 127.3 (CH), 127.1 (CH), 123.5 (C), 121.7 (CH), 121.6 (CH), 119.3 (CH_2), 106.2 (CH), 70.5 (C), 55.8 (CH_3), 48.5 (CH_2), 43.5 (CH_2) ppm; HRMS (ESI) calcd for $C_{23}H_{22}NO_2$ (M + H) 344.1651, found 344.1658.

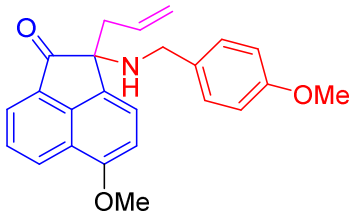


17b

4.2.17. 2-Allyl-2-((4-chlorobenzyl)amino)-5-methoxyacenaphthylen-1(2*H*)-one (17b):

Following the general procedure, the reaction of 2-allyl-2-hydroxy-6-methoxyacenaphthylen-1(2*H*)-one (100.3 mg, 0.39 mmol), 4-chlorobenzylamine (222.1 mg, 1.57 mmol), formic acid (18.3 mg, 0.39 mmol) and methanol (3 mL) afforded 2-allyl-2-((4-chlorobenzyl)amino)-5-methoxyacenaphthylen-1(2H)-one **17b** (98.2 mg) as a light yellow semi solid in 66% yield, R_f (98% Hexane/EtOAc) 0.6; IR (KBr, cm^{-1}) 3306, 3032, 2853, 1718, 1602, 1456, 1429, 1238, 1152, 1024, 923, 821, 777; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 8.36 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.92 (dd, *J* = 7.0, 0.7 Hz, 1H), 7.70 (td, *J* = 7.6, 1.2 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.17

(d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 7.7 Hz, 1H), 5.62-5.50 (m, 1H), 4.98 (dd, *J* = 17.0, 1.5 Hz, 1H), 4.89 (dt, *J* = 10.1, 0.9 Hz, 1H), 4.05 (s, 3H), 3.36 (d, *J* = 12.7 Hz, 1H), 3.17 (d, *J* = 12.6 Hz, 1H), 2.72-2.64 (m, 1H), 2.58-2.50 (m, 1H), 1.83 (br s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) δ 209.7 (C=O), 154.8 (C), 143.2 (C), 139.0 (C), 132.8 (C), 132.0 (CH), 131.8 (C), 130.9 (C), 129.7 (CH), 128.5 (CH), 127.8 (CH), 127.4 (CH), 123.5 (C), 121.8 (CH), 121.7 (CH), 119.5 (CH), 106.1 (CH), 70.4 (C), 55.8 (CH_3), 47.8 (CH_2), 43.5 (CH_2) ppm; HRMS (ESI) calcd for $C_{23}H_{21}ClNO_2$ (M + H) 378.1261, found 378.1260.

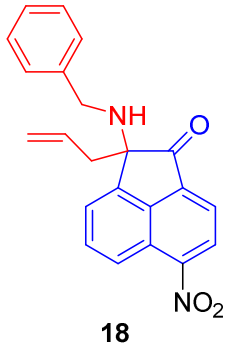


17c

4.2.18. 2-Allyl-2-((4-methoxybenzyl)amino)-5-methoxyacenaphthylen-1(2*H*)-one (17c):

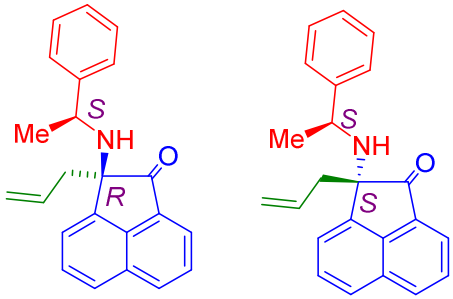
Following the general procedure, the reaction of 2-allyl-2-hydroxy-6-methoxyacenaphthylen-1(2*H*)-one (100.3 mg, 0.39 mmol), 4-methoxy benzylamine (215.8 mg, 1.57 mmol), formic acid (18.5 mg, 0.39 mmol) and methanol (3 mL) afforded 2-allyl-2-((4-methoxybenzyl)amino)-5-methoxyacenaphthylen-1(2*H*)-one **17c** (105.9 mg) as a light yellow semi solid in 72% yield, R_f (98% Hexane/EtOAc) 0.5; IR (KBr, cm^{-1}) 3282, 3072, 3031, 2963, 2932, 2835, 1719, 1611, 1512, 1464, 1425, 1240, 1153, 1024, 922, 822, 776; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 8.36 (dd, *J* = 8.2, 0.6 Hz, 1H), 7.91 (dd, *J* = 7.0, 0.6 Hz, 1H), 7.69 (td, *J* = 7.7, 1.1 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.08 (dd, *J* = 6.8, 1.9 Hz, 2H), 6.96 (d, *J* = 7.7 Hz, 1H), 6.74 (d, *J* = 8.6 Hz, 2H), 5.61-5.49 (m, 1H), 4.97 (dd, *J* = 17.0, 1.4 Hz, 1H), 4.86 (dt, *J* = 9.6, 1.0 Hz, 1H), 4.06 (s, 3H), 3.75 (s, 3H), 3.30 (d, *J* = 12.1 Hz, 1H), 3.15 (d, *J* = 12.0 Hz, 1H), 2.72-2.65 (m, 1H), 2.58-2.50 (m, 1H), 2.03 (br s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) 209.9 (C=O), 158.8

(C), 154.7 (C), 143.2 (C), 132.6 (C), 132.1 (CH), 132.0 (C), 131.3 (C), 129.5 (CH), 127.7 (CH), 127.3 (CH), 123.5 (CH), 121.7 (CH), 121.6 (CH), 119.3 (CH_2), 113.8 (CH), 106.2 (CH), 70.5 (C), 55.8 (CH_3), 55.3 (CH_3), 47.9 (CH_2), 43.5 (CH_2) ppm; HRMS (ESI) calcd for $C_{24}H_{24}NO_3$ (M + H) 374.1756, found 374.1759.



18

4.2.19. 2-Allyl-2-(benzylamino)-6-nitro acenaphthylen-1(2*H*)-one (18): Following the general procedure, the reaction of 2-allyl-2-hydroxy-5-nitro acenaphthylen-1(2*H*)-one (100.2 mg, 0.37 mmol), benzylamine (159.9 mg, 1.49 mmol), formic acid (17.6 mg, 0.37 mmol) and methanol (3 mL) afforded 2-allyl-2-(benzylamino)-6-nitro acenaphthylen-1(2*H*)-one **18** (106.7 mg) as a light yellow semi solid in 88% yield, R_f (98% Hexane/EtOAc) 0.6; IR (KBr, cm^{-1}) 3325, 3078, 2925, 1729, 1663, 1625, 1528, 1458, 1428, 1334, 1258, 1199, 1121, 1023, 924, 857, 801, 786, 749, 699; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 8.63 (dd, *J* = 8.7, 0.6 Hz, 1H), 8.56 (d, *J* = 7.7 Hz, 1H), 7.92-7.86 (m, 2H), 7.76 (d, *J* = 6.8 Hz, 1H), 7.16-7.10 (m, 3H), 7.08-7.05 (m, 2H), 5.47-5.34 (m, 1H), 4.92 (dd, *J* = 17.0, 1.2 Hz, 1H), 4.84 (dt, *J* = 9.9, 0.8 Hz, 1H), 3.35 (d, *J* = 12.3 Hz, 1H), 3.15 (d, *J* = 12.3 Hz, 1H), 2.71-2.63 (m, 1H), 2.59-2.51 (m, 1H), 1.50 (br s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) 207.8 (C=O), 147.6 (C), 142.8 (C), 140.6 (C), 139.7 (C), 137.0 (CH), 132.7 (CH), 131.0 (CH), 128.5 (CH), 128.3 (CH), 127.4 (CH), 126.9 (CH), 123.7 (C), 122.7 (CH), 120.5 (CH_2), 119.6 (CH), 71.0 (C), 48.7 (CH_2), 43.6 (CH_2) ppm; HRMS (ESI) calcd for $C_{22}H_{19}N_2O_3$ (M + H) 359.1396, found 359.1393.



26a and **26b**

4.2.20. (*R*)-2-Allyl-2-(((*S*)-1-phenylethyl)amino)acenaphthylen-1(2*H*)-one (26a) and (*S*)-2-allyl-2-(((*S*)-1-phenylethyl)amino)acenaphthylen-1(2*H*)-one (26b): Following the general procedure, the reaction of 2-allyl-2-hydroxyacenaphthylen-1(2*H*)-one (200.3 mg, 0.89 mmol), *S*-(-)-α-methylbenzylamine (433.3 mg, 3.56 mmol) and formic acid (41.2 mg, 0.89 mmol) and methanol (5 mL) afforded two chromatographically separable diastereomers (*R*)-2-allyl-2-(((*S*)-1-phenylethyl)amino)acenaphthylen-1(2*H*)-one **26a** (125.2 mg) as a yellow liquid and (*S*)-2-allyl-2-(((*S*)-1-phenylethyl)amino)acenaphthylen-1(2*H*)-one **26b** (125.6 mg) as a yellow solid in 1:1 ratio in 86% yield, **26a**: R_f (98% Hexane/EtOAc) 0.7; $[\alpha]_D^{22}$ = -39° (c = 1, methanol); IR (KBr, cm^{-1}) 3324, 3066, 2924, 2858, 1720, 1610, 1539, 1500, 1461, 1368, 1293, 1126, 1001, 1000, 921, 839, 781, 702; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 8.03 (d, *J* = 8.1 Hz, 1H), 7.91 (d, *J* = 6.8 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 6.9 Hz, 1H), 6.94-6.89 (m, 3H), 6.77-6.74 (m, 2H),5.56-5.44 (m, 1H), 4.98-4.85 (m, 2H), 3.36 (q, *J* = 6.6 Hz, 1H), 2.68-2.60 (m, 1H), 2.52-2.44 (m, 1H), 1.20 (d, *J* = 6.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) 210.1 (C=O), 146.9 (C), 141.7 (C), 139.1 (C), 132.6 (C), 132.0 (CH), 131.9 (CH), 130.6 (C), 128.3 (CH), 127.9 (CH), 127.7 (CH), 126.5 (CH), 126.4 (CH), 124.1 (CH), 122.5 (CH), 120.8 (CH), 119.5 (CH_2), 70.6 (C), 54.9 (CH), 44.2 (CH_2), 26.1 (CH_3) ppm; HRMS (ESI) calcd for $C_{23}H_{22}NO$ (M + H) 328.1696, found 328.1710. **26b**: R_f (98% Hexane/EtOAc) 0.5; mp 114-116 ^oC; $[\alpha]_D^{22}$ = -101° (c = 1, methanol); IR (KBr, cm^{-1})

3313, 3053, 2919, 2858, 1713, 1556, 1484, 1440, 1370, 1265, 1200, 1143, 1083, 1001, 927, 844, 793, 776, 705; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 8.01 (dd, *J* = 8.0, 0.7 Hz, 1H), 7.85 (dd, *J* = 8.2, 0.6 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.63 (dd, *J* = 6.8, 0.7 Hz, 1H), 7.59-7.50 (m, 2H), 6.96-6.85 (m, 3H), 6.59-6.55 (m, 2H), 5.54-5.44 (m, 1H), 4.98-4.85 (m, 2H), 3.61 (q, *J* = 6.6 Hz, 1H), 2.68-2.60 (m, 1H), 2.52-2.44 (m, 1H), 1.16 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) 208.0 (C=O), 145.3 (C), 141.5 (C), 140.1 (C), 132.5 (C), 132.1 (CH), 131.3 (CH), 130.8 (C), 128.3 (CH), 128.0 (CH), 127.9 (CH), 127.2 (CH), 127.0 (CH), 124.9 (CH), 121.4 (CH), 120.9 (CH), 119.6 (CH_2), 69.6 (C), 54.8 (CH), 44.3 (CH_2), 24.9 (CH_3) ppm; HRMS (ESI) calcd for $C_{23}H_{22}NO$ (M + H) 328.1696, found 328.1714.

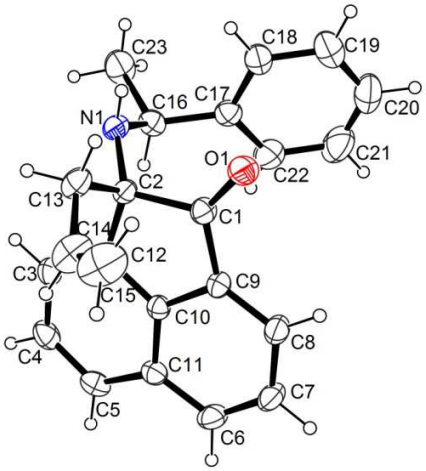
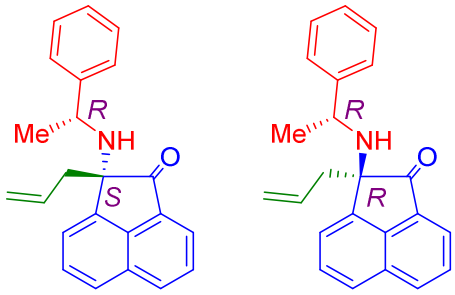


Figure 6. ORTEP diagram of (*S*)-2-allyl-2-(((*S*)-1-phenylethyl)amino)acenaphthylen-1(2*H*)-one **26b** (CCDC # 1052103) with crystallographic numbering.

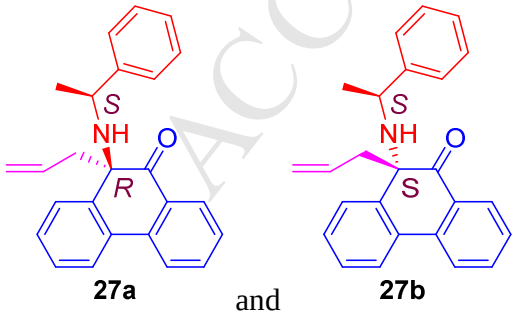
Crystal data for 26b: Empirical formula, $C_{23}H_{21}NO$; Formula weight, 327.41; Crystal color, habit: colorless, rectangular block; Crystal system, orthorhombic; Crystal dimensions, 0.38 x 0.16 x 0.12 mm^3; Lattice parameters, a = 8.8201(4) Å, b = 14.1685(8) Å, c = 14.6717(10) Å; α = 90.00, β = 90.00, γ = 90.00; V = 1833.49(18) A^3; Space group P2-1; Z = 4; D_{calcd} = 1.186 g/cm^3; F_{000} = 696; λ(Mo Kα) = 0.7107 Å; R ($I \geq 2\sigma_1$) = 0.0445, wR^2 = 0.1040. Detailed X-ray

crystallographic data is available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (for compound **26b** CCDC # 1052103).



26c and **26d**

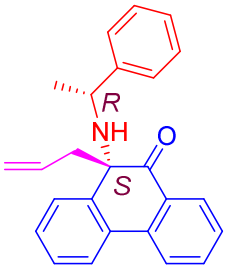
4.2.21. (*S*)-2-Allyl-2-(((*R*)-1-phenylethyl)amino)acenaphthylen-1(2*H*)-one (26c) and (*R*)-2-allyl-2-(((*R*)-1-phenylethyl)amino)acenaphthylen-1(2*H*)-one (26d): Following the general procedure, the reaction of 2-allyl-2-hydroxyacenaphthylen-1(2*H*)-one (200.5 mg, 0.89 mmol), *R*-(+)-α-methylbenzylamine (432.3 mg, 3.56 mmol) and formic acid (40.3 mg, 0.89 mmol) and methanol (5 mL) afforded two chromatographically separable diastereomers (*S*)-2-allyl-2-(((*R*)-1-phenylethyl)amino)acenaphthylen-1(2*H*)-one **26c** (127.9 mg) as a yellow liquid and (*R*)-2-allyl-2-(((*R*)-1-phenylethyl)amino)acenaphthylen-1(2*H*)-one **26d** (127.7 mg) as a yellow solid in 1:1 ratio in 88% yield, **26c**: R_f (98% Hexane/EtOAc) 0.7; $[\alpha]_D^{22}$ = +39° (c = 1, methanol); The IR and NMR spectral data matched with **26a**. **26d:** R_f (98% Hexane/EtOAc) 0.5; $[\alpha]_D^{22}$ = +101° (c = 1, methanol); The IR and NMR spectral data matched with **26b**.



27a and **27b**

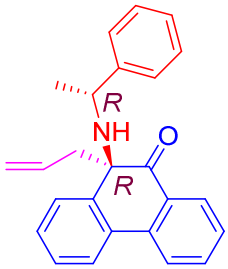
4.2.22. (*R*)-10-Allyl-10-(((*S*)-1-phenylethyl)amino)phenanthren-9(10*H*)-one (27a) and (*S*)-10-allyl-10-(((*S*)-1-phenylethyl)amino)phenanthren-9(10*H*)-one (27b): Following the general procedure, the reaction of 10-allyl-10-hydroxyphenanthren-9(10*H*)-one (200.1 mg, 0.79 mmol), *S*-(-)-α-methylbenzylamine (384.5 mg, 3.16 mmol) and formic acid (36.5 mg, 0.79 mmol) and methanol (5 mL) afforded two chromatographically separable diastereomers (*R*)-10-allyl-10-(((*S*)-1-phenylethyl)amino)phenanthren-9(10*H*)-one **27a** (73.3 mg) and (*S*)-10-allyl-10-(((*S*)-1-phenylethyl)amino)phenanthren-9(10*H*)-one **27b** (153.6 mg) as yellow liquids in 32:68 ratio in 81% yield, **27a**: R_f (98% Hexane/EtOAc) 0.7; $[\alpha]_D^{22}$ = +3° (c = 1, methanol); IR (KBr, cm^{-1}) 3346, 3070, 2924, 2852, 1683, 1609, 1449, 1271, 1086, 1021, 912, 754, 696; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.90 (dd, *J* = 8.0, 0.7 Hz, 1H), 7.71-7.66 (m, 1H), 7.47-7.40 (m, 2H), 7.22-7.16 (m, 1H), 7.12-7.05 (m, 3H), 7.04-7.00 (m, 2H), 6.99-6.94 (m, 1H), 5.36-5.24 (m, 1H), 4.86-4.79 (m, 2H), 3.42 (q, *J* = 6.7 Hz, 1H), 2.52 (d, *J* = 7.4 Hz, 2H), 1.23 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 204.3 (C=O), 146.8 (C), 139.0 (C), 137.6 (C), 134.9 (CH), 131.2 (CH), 130.2 (CH), 129.8 (C), 128.4 (CH), 128.2 (CH), 127.9 (CH), 127.5 (CH), 127.4 (CH), 126.9 (CH), 126.3 (CH), 123.2 (CH), 122.9 (CH), 119.4 (CH_2), 68.6 (C), 55.5 (CH), 50.4 (CH_2), 25.5 (CH_3) ppm; HRMS (ESI) calcd for $C_{25}H_{24}NO$ (M + H) 354.1852, found 354.1859. **27b**: R_f (98% Hexane/EtOAc) 0.5; $[\alpha]_D^{22}$ = -104° (c = 1, methanol); IR (KBr, cm^{-1}) 3337, 3069, 2958, 2924, 2859, 1680, 1628, 1553, 1486, 1448, 1282, 1008, 924, 760, 701; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 8.04-7.94 (m, 3H), 7.75 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.59-7.54 (m, 1H), 7.51-7.46 (m, 1H), 7.45-7.39 (m, 1H), 7.28-7.23 (m, 1H), 6.96-6.89 (m, 3H), 6.83-6.79 (m, 2H), 5.20-5.08 (m, 1H), 4.75-4.65 (m, 2H), 3.68 (q, *J* = 6.8 Hz, 1H), 2.58-2.51 (m, 2H), 1.15 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) 201.7 (C=O), 145.2 (C), 140.8 (C), 136.9 (C), 134.3 (CH), 131.2 (CH), 131.0 (CH),

129.6 (CH), 129.5 (C), 129.0 (CH), 127.89 (CH), 127.86 (CH), 127.8 (CH), 127.7 (CH), 127.5 (CH), 127.0 (CH), 123.2 (C), 122.7 (C), 119.4 (CH_2), 66.0 (C), 54.6 (CH), 51.5 (CH_2), 23.8 (CH_3) ppm; HRMS (ESI) calcd for $C_{25}H_{24}NO$ (M + H) 354.1852, found 354.1863.



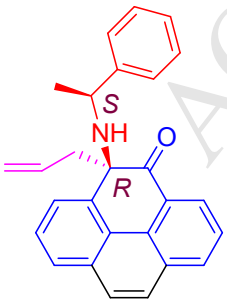
27c

and



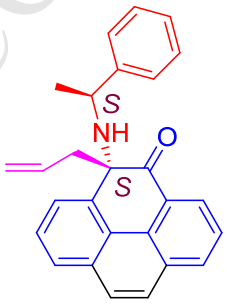
27d

4.2.23. (*S*)-10-Allyl-10-(((*R*)-1-phenylethyl)amino)phenanthren-9(10*H*)-one (27c) and (*R*)-10-allyl-10-(((*R*)-1-phenylethyl)amino)phenanthren-9(10*H*)-one (27d): Following the general procedure, the reaction of 10-allyl-10-hydroxyphenanthren-9(10*H*)-one (200.5 mg, 0.79 mmol), *R*-(+)-α-methylbenzylamine (386.2 mg, 3.16 mmol) and formic acid (36.2 mg, 0.79 mmol) and methanol (5 mL) afforded two chromatographically separable diastereomers (*S*)-10-allyl-10-(((*R*)-1-phenylethyl)amino)phenanthren-9(10*H*)-one **27c** (72.5 mg) and (*R*)-10-allyl-10-(((*R*)-1-phenylethyl)amino)phenanthren-9(10*H*)-one **27d** (152.0 mg) as yellow liquids in 32:68 ratio in 80% yield, **27c**: R_f (98% Hexane/EtOAc) 0.7; $[\alpha]_D^{22}$ = -3° (c = 1, methanol); The IR and NMR spectral data matched with **27a**; **27d**: R_f (98% Hexane/EtOAc) 0.5; $[\alpha]_D^{22}$ = +104° (c = 1, methanol); the IR and NMR spectral data matched with **27b**.



28a

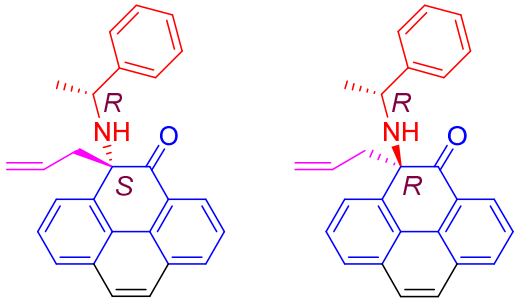
and



28b

4.2.24. (*R*)-5-Allyl-5-(((*S*)-1-phenylethyl)amino)pyren-4(5*H*)-one (28a) and (*S*)-5-allyl-5-(((*S*)-1-phenylethyl)amino)pyren-4(5*H*)-one (28b): Following the general procedure, the reaction of 5-allyl-5-hydroxypyren-4(5*H*)-one (200.1 mg, 0.73 mmol), *S*-(-)-α-methylbenzylamine (357.2 mg, 2.92 mmol) and formic acid (33.2 mg, 0.73 mmol) and methanol (5 mL) afforded two chromatographically separable diastereomers (*R*)-5-allyl-5-(((*S*)-1-phenylethyl)amino)pyren-4(5*H*)-one **28a** (83.3 mg) and (*S*)-5-allyl-5-(((*S*)-1-phenylethyl)amino)pyren-4(5*H*)-one **28b** (115.3 mg) as yellow liquids in 42:58 ratio in 72% yield, **28a**: R_f (98% Hexane/EtOAc) 0.7; $[\alpha]_D^{22}$ = -29° (c = 1, methanol); IR (KBr, cm^{-1}) 3332, 3056, 2923, 2858, 1675, 1539, 1491, 1455, 1270, 1177, 1126, 1069, 993, 923, 838, 758, 715; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 8.43 (dd, *J* = 7.5, 1.3 Hz, 1H), 8.14 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.78-7.72 (m, 3H), 7.65 (dt, *J* = 7.9, 1.1 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.02-6.97 (m, 3H), 6.95-6.90 (m, 2H), 5.30-5.18 (m, 1H), 4.82-4.68 (m, 2H), 3.48 (q, *J* = 6.7 Hz, 1H), 2.62 (d, *J* = 7.2 Hz, 2H), 1.24 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) 204.5 (C=O), 146.9 (C), 138.7 (C), 134.2 (CH), 131.7 (C), 131.5 (C), 131.3 (CH),130.1 (C), 129.0 (C), 128.4 (CH), 128.1 (CH), 127.9 (CH), 127.3 (CH), 127.0 (CH), 126.9 (CH), 126.8 (CH), 126.3 (CH), 126.0 (C), 125.9 (CH), 119.5 (CH_2), 69.5 (C), 55.7 (CH), 51.2 (CH_2), 25.7 (CH_3) ppm; HRMS (ESI) calcd for $C_{27}H_{24}NO$ (M + H) 378.1852, found 378.1859. **28b**: R_f (98% Hexane/EtOAc) 0.5; $[\alpha]_D^{22}$ = -144° (c = 1, methanol); IR (KBr, cm^{-1}) 3321, 3057, 2961, 2921, 2857, 1674, 1611, 1522, 1483, 1448, 1268, 1176, 1131, 1074, 923, 836, 758, 713; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 8.23 (dd, *J* = 7.4, 1.2 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 2H), 7.87 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.82-7.76 (m, 2H), 7.72 (d, *J* = 8.9 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 6.80-6.71 (m, 3H), 6.66-6.61 (m, 2H), 5.12-5.00 (m, 1H), 4.72 (td, *J* = 17.0, 1.0 Hz, 1H), 4.67 (td, *J* = 10.1, 1.0 Hz, 1H), 3.72 (q, *J* = 6.8 Hz, 1H), 2.73-2.60 (m, 2H), 1.15 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C

NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) 202.4 (C=O), 145.0 (C), 140.2 (C), 133.5 (CH), 131.8 (C), 131.16 (CH), 131.15 (C), 129.7 (C),128.4 (C), 127.8 (CH), 127.71 (CH), 127.65 (CH), 127.3 (CH), 127.1 (CH), 126.8 (CH), 126.5 (CH), 126.3 (CH), 126.0 (CH), 125.7 (CH), 119.3 (CH_2), 66.8 (C), 54.6 (CH), 52.2 (CH_2), 23.8 (CH_3) ppm; HRMS (ESI) calcd for $C_{27}H_{24}NO$ (M + H) 378.1852, found 378.1865.



28c and **28d**

4.2.25. (*S*)-5-Allyl-5-(((*R*)-1-phenylethyl)amino)pyren-4(5*H*)-one (28c) and (*R*)-5-allyl-5-(((*R*)-1-phenylethyl)amino)pyren-4(5*H*)-one (28d): Following the general procedure, the reaction of 5-allyl-5-hydroxypyren-4(5*H*)-one (200.3 mg, 0.73 mmol), *R*-(+)-α-methylbenzylamine (356.8 mg, 2.92 mmol) and formic acid (32.9 mg, 0.73 mmol) and methanol (5 mL) afforded two chromatographically separable diastereomers (*S*)-5-allyl-5-(((*R*)-1-phenylethyl)amino)pyren-4(5*H*)-one **28c** (83.6 mg) and (*R*)-5-allyl-5-(((*R*)-1-phenylethyl)amino)pyren-4(5*H*)-one **28d** (124.9 mg) as yellow liquids in 32:68 ratio in 72% yield. **28c**: R_f (98% Hexane/EtOAc) 0.7; $[\alpha]_D^{22}$ = +29° (c = 1, methanol); The IR and NMR spectral data matched with **28a**. **28d:** R_f (98% Hexane/EtOAc) 0.5; $[\alpha]_D^{22}$ = +144° (c = 1, methanol); The IR and NMR spectral data matched with **28b**.

Acknowledgements

H.S.P.R thanks UGC, UGC-SAP, CSIR and DST-FIST. VS thanks UGC for fellowship. We thank CIF, Pondicherry University, and IISC, Bangalore for recording the spectra.

Supporting information

Copies of ^{1}H, ^{13}C NMR, DEPT-135 and HRMS spectra for all newly prepared compounds, 2D NMR (HMBC, HSQC and COSY) spectra of **15**, **17a** and crystal data of **8c**, **8f**, **15**, **16** and **26b**.

References and notes

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[10] See the appendix I in supporting information for further details.

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[13] See the appendix II in supporting information for further details.

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Supporting Information

Voight reaction on tertiary α-hydroxy ketones

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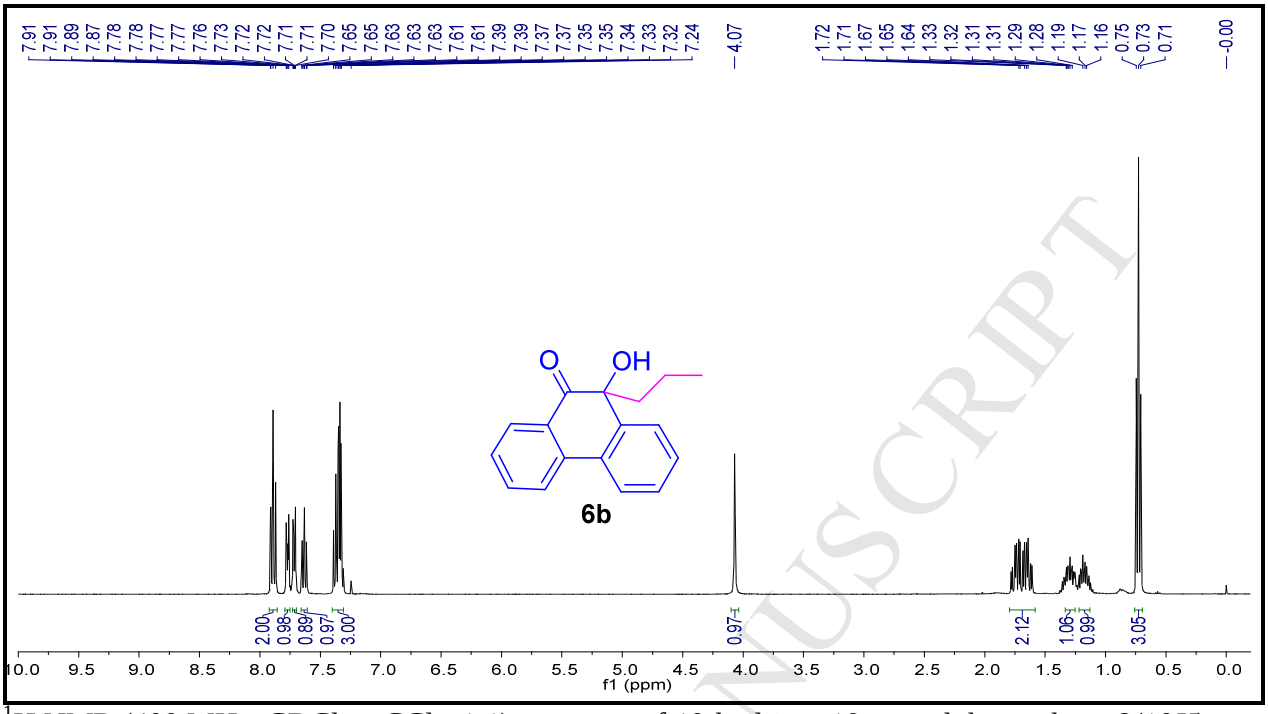
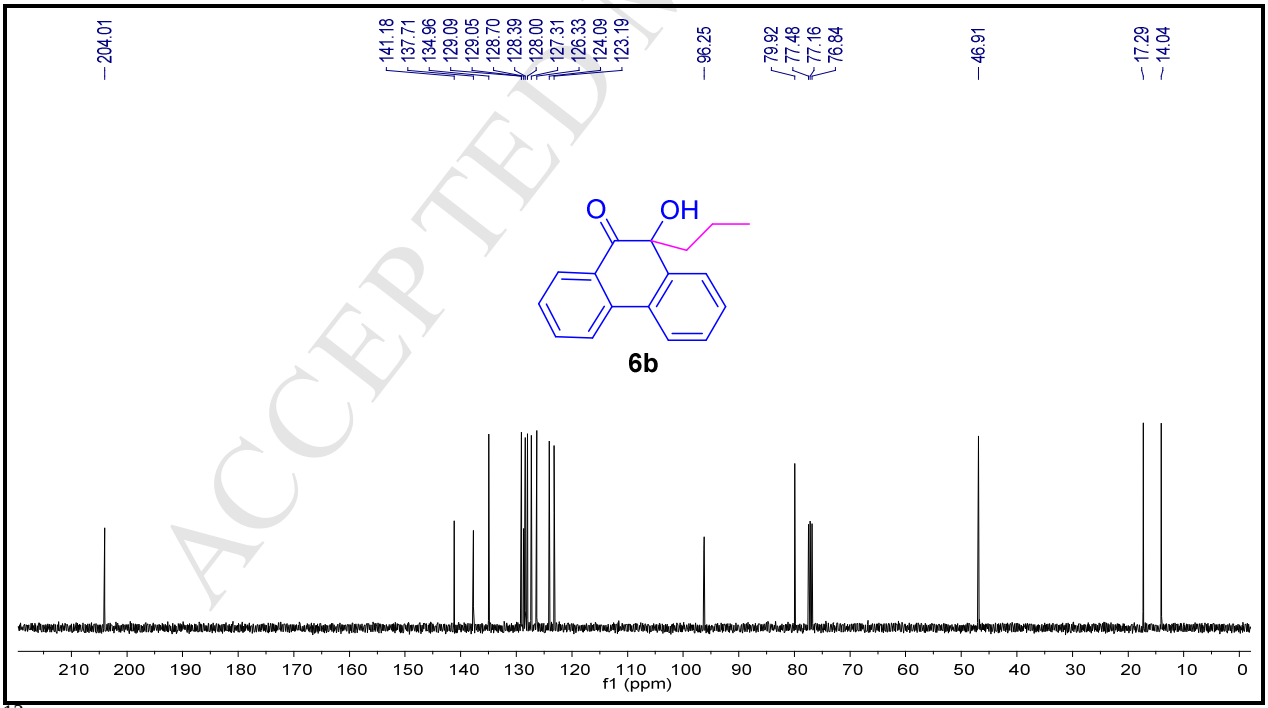
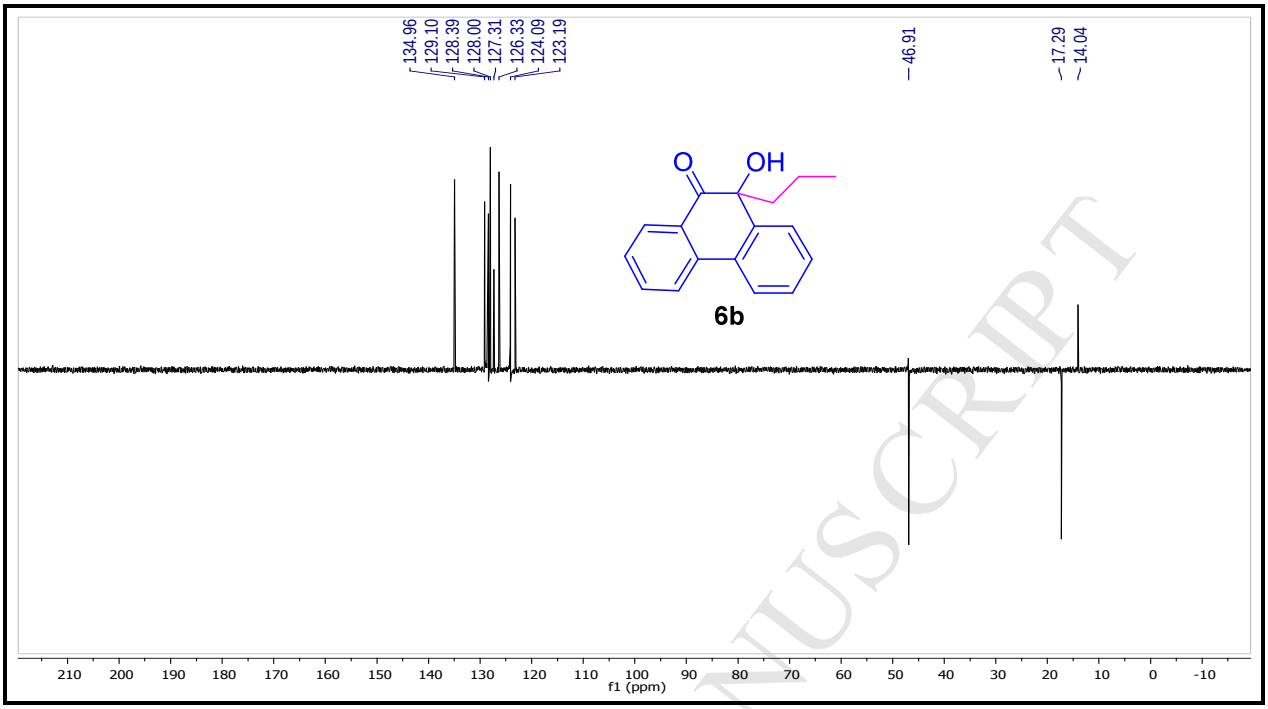


^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 10-hydroxy-10-propylphenanthren-9(10*H*)-one (**6b**).



^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 10-hydroxy-10-propylphenanthren-9(10*H*)-one (**6b**).



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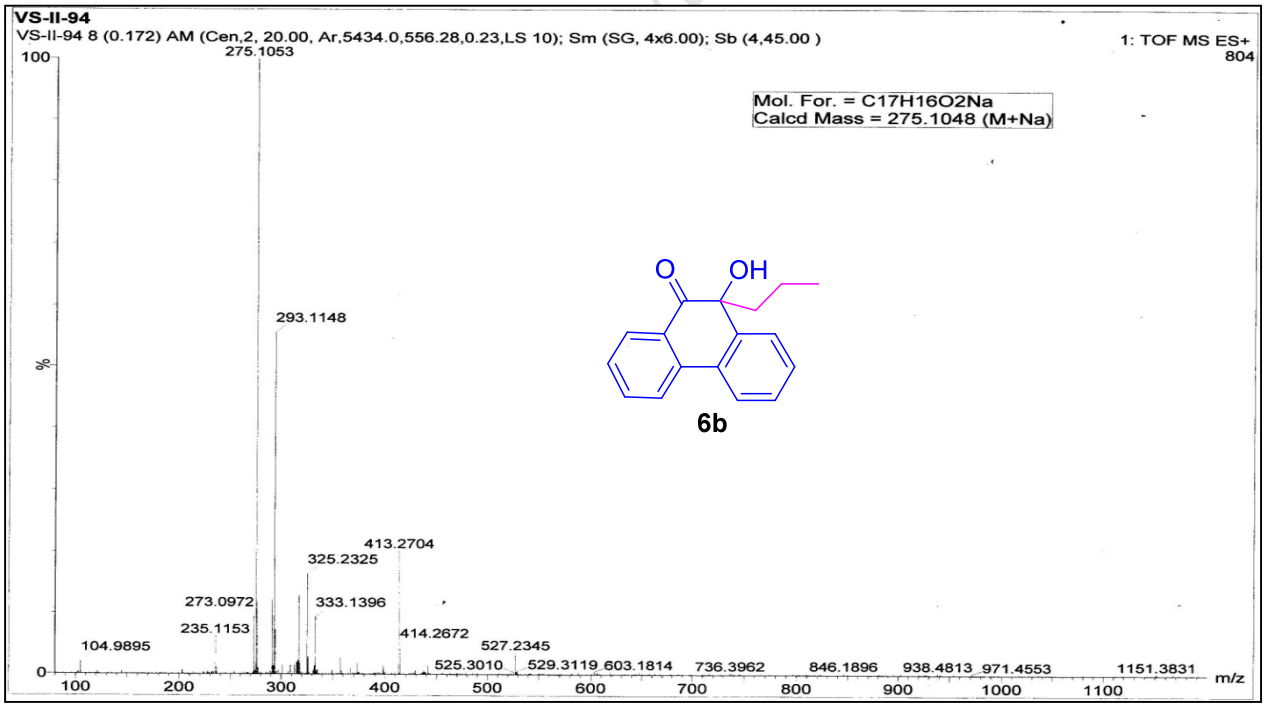
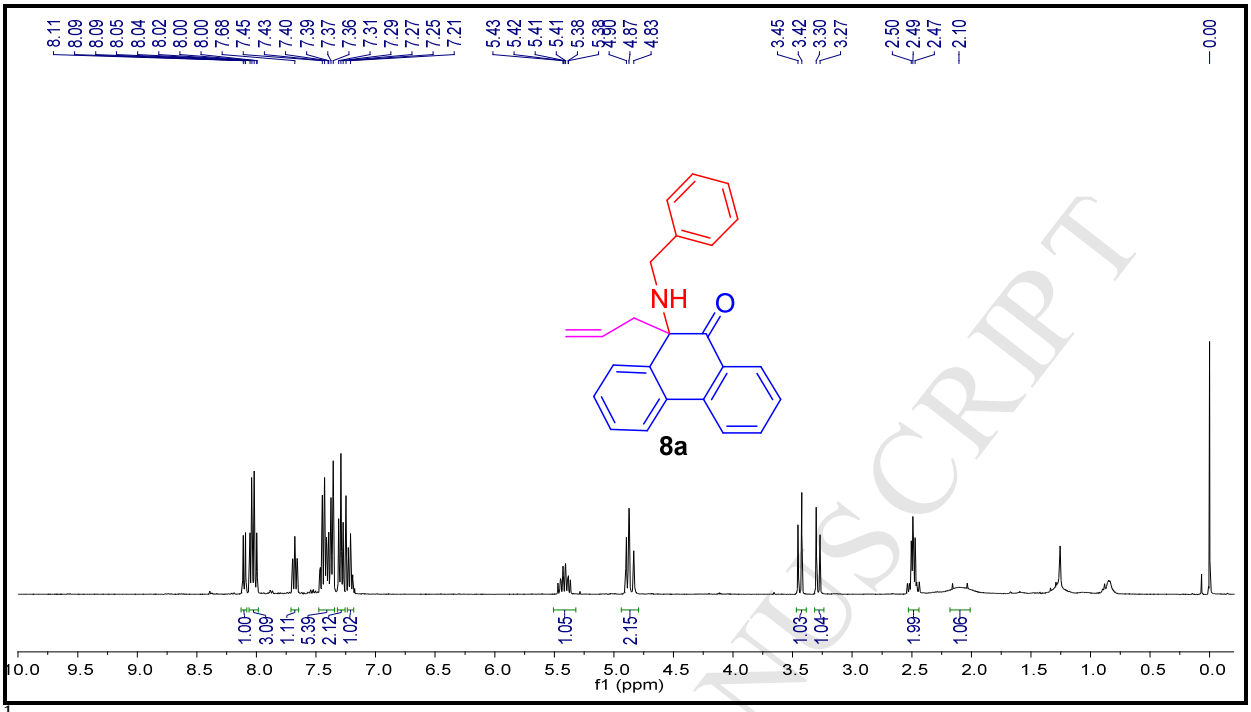
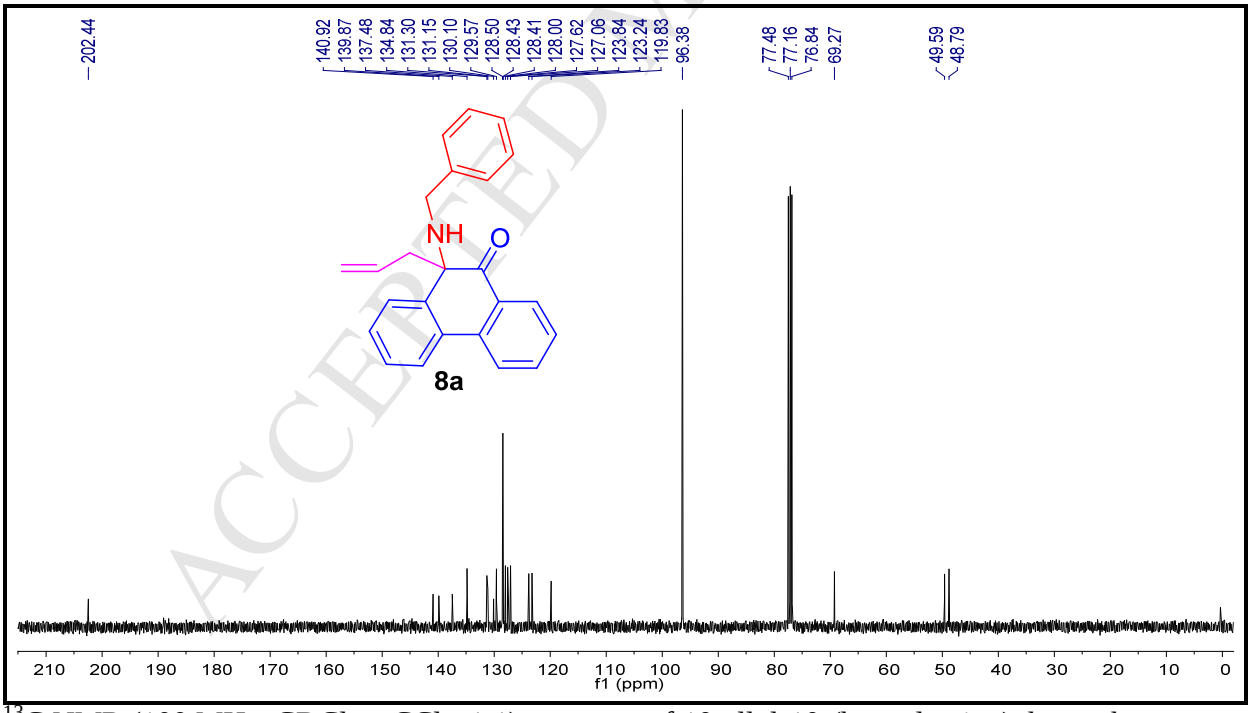


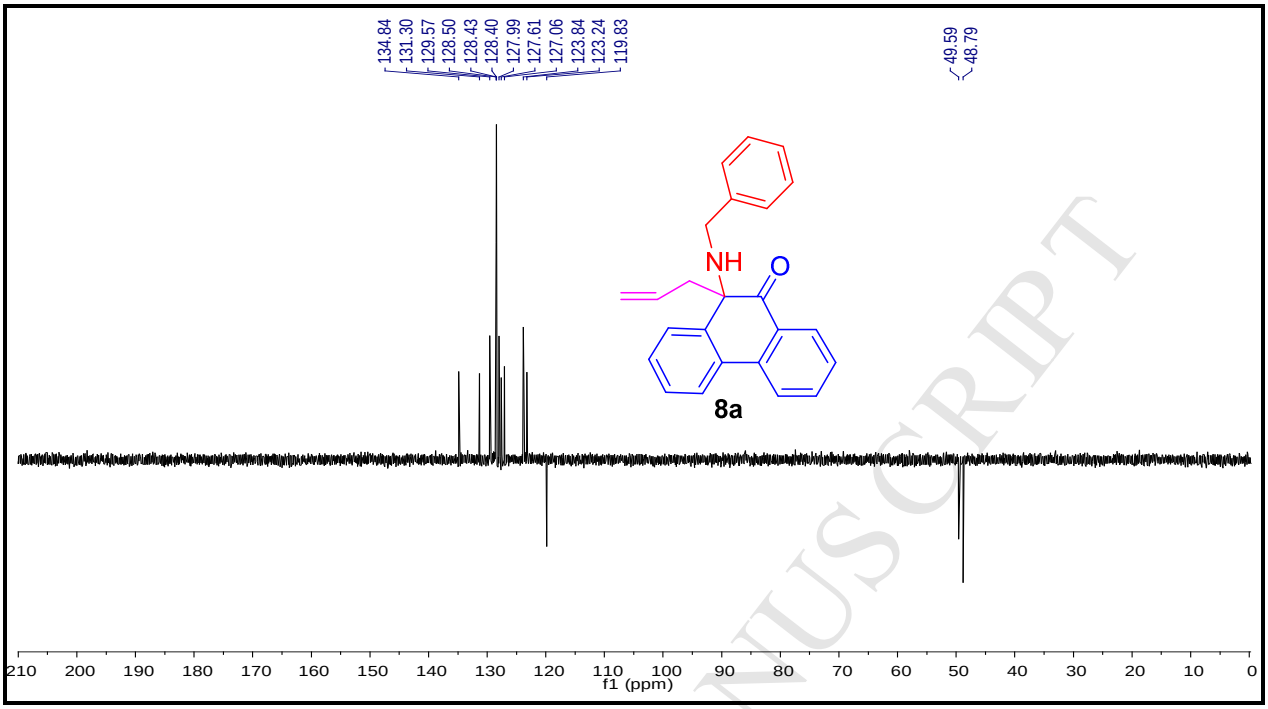
HRMS spectrum of 10-hydroxy-10-propylphenanthren-9(10*H*)-one (**6b**).



^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 10-allyl-10-(benzylamino)phenanthren-9(10*H*)-one (**8a**).



^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 10-allyl-10-(benzylamino)phenanthren-9(10*H*)-one (**8a**).



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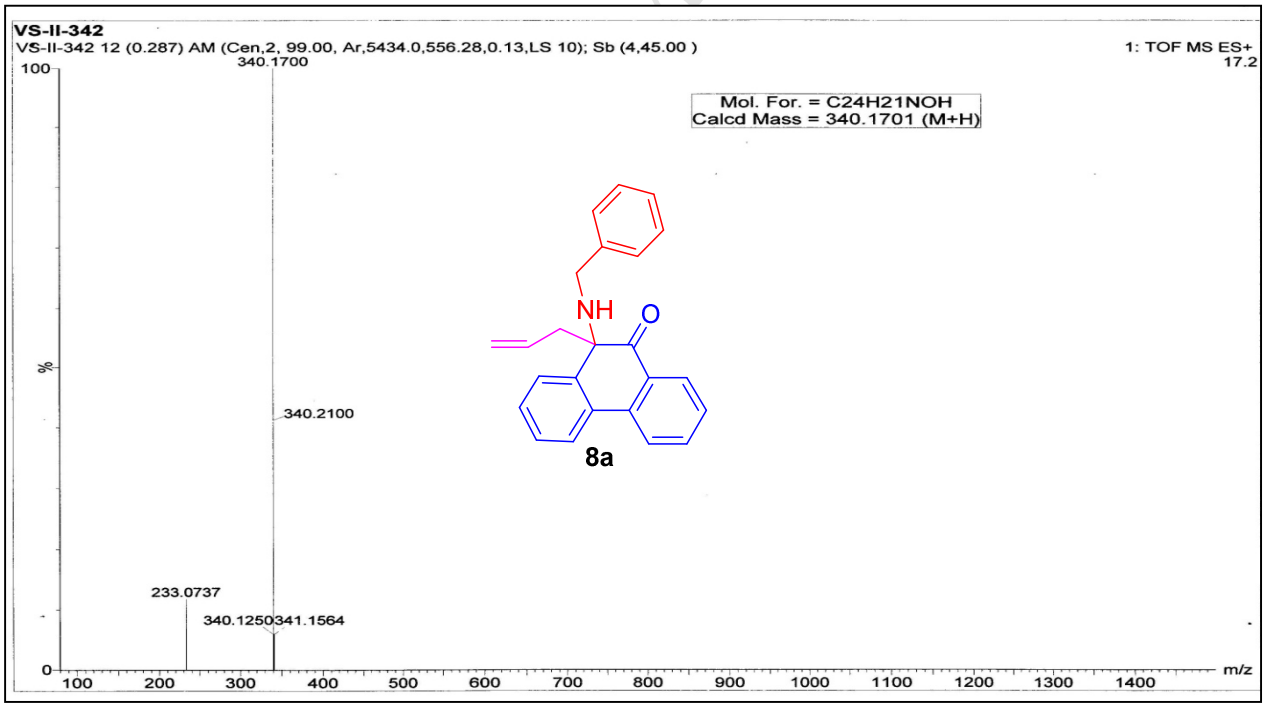
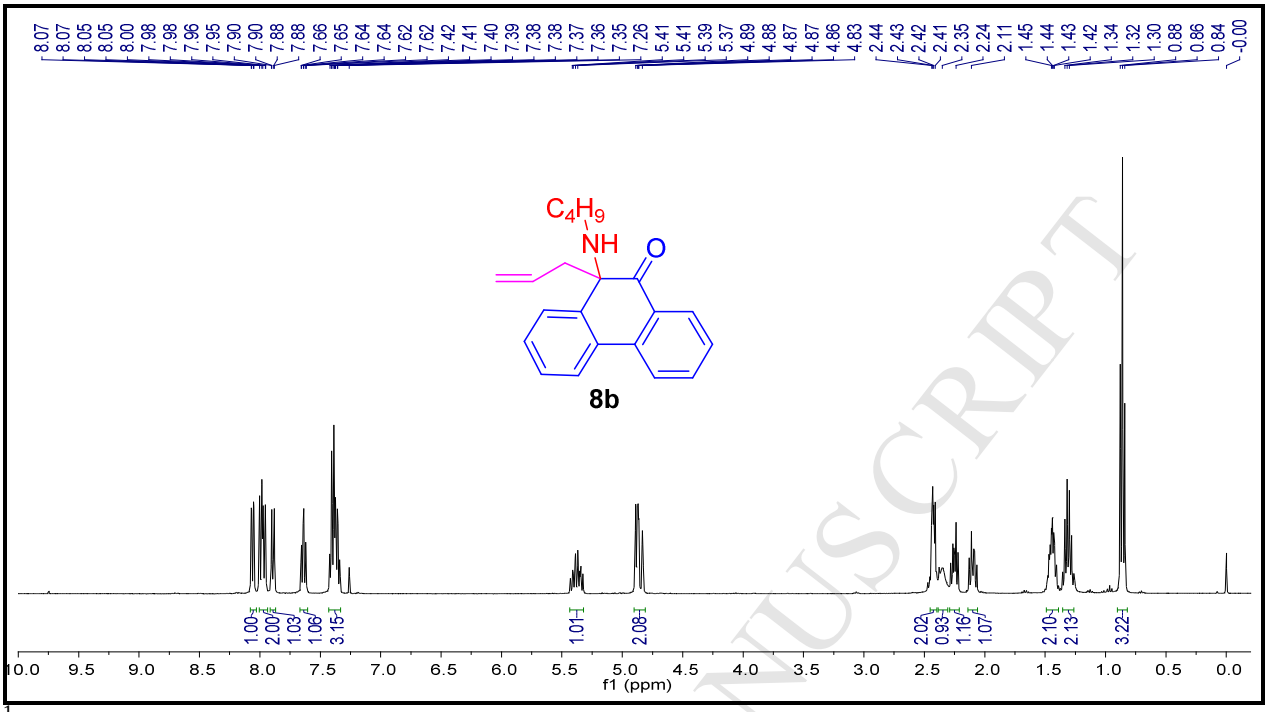
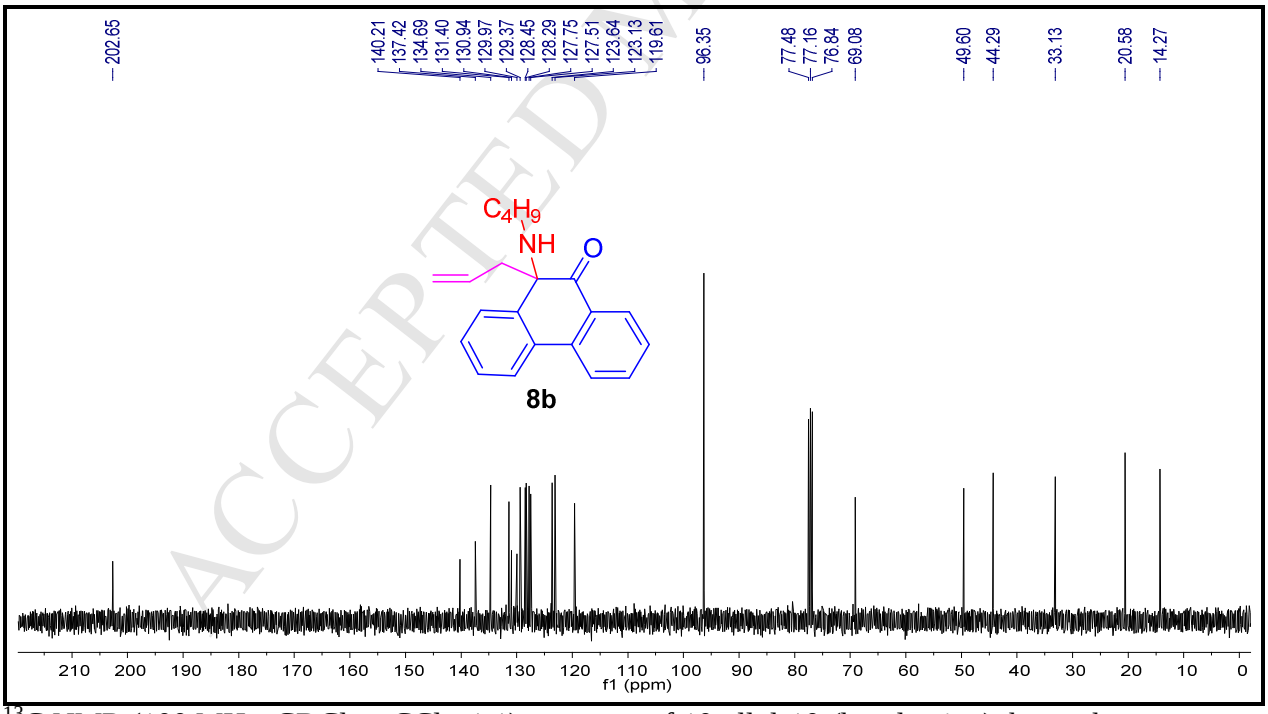


HRMS spectrum of 10-allyl-10-(benzylamino)phenanthren-9(10*H*)-one (**8a**).



^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 10-allyl-10-(butylamino)phenanthren-9(10*H*)-one (**8b**).



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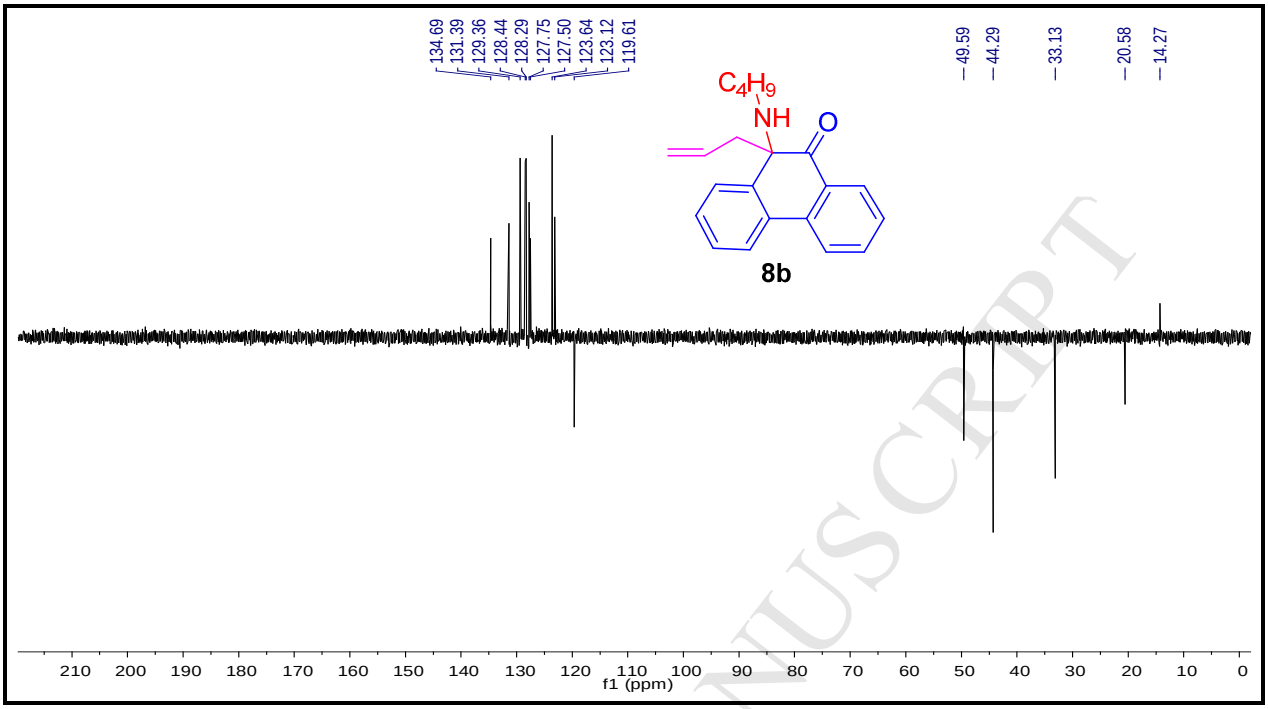
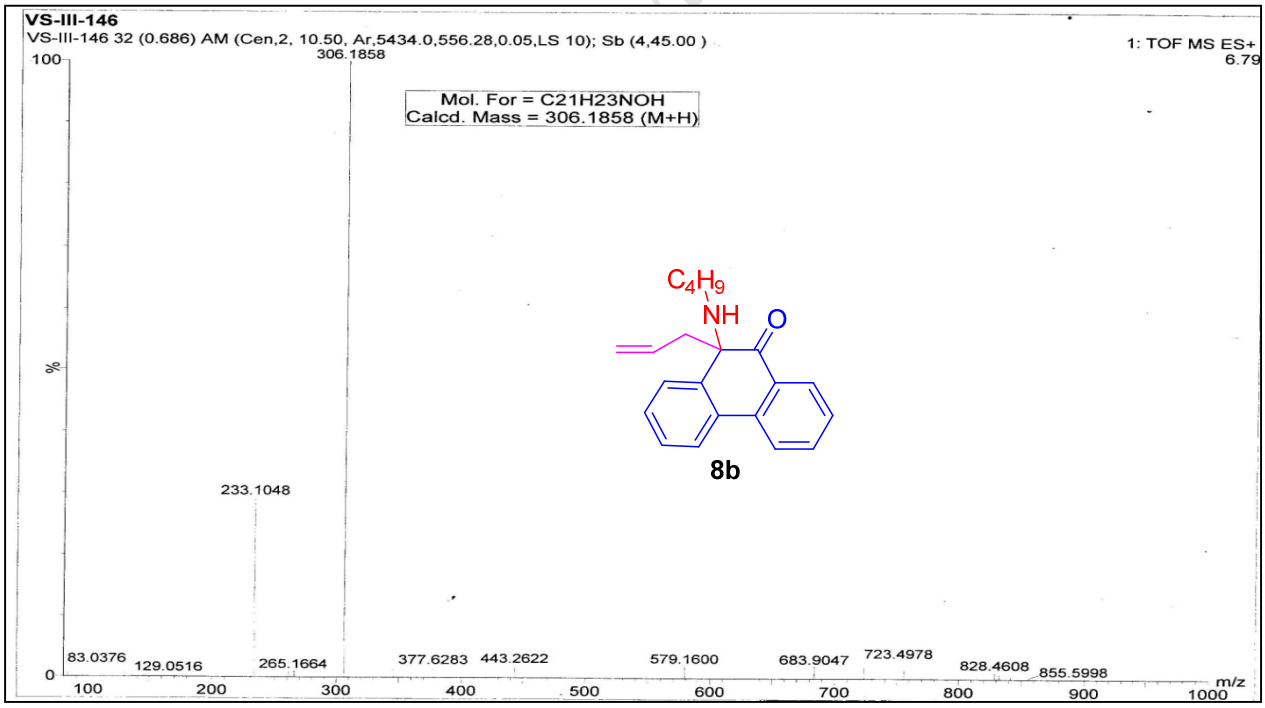
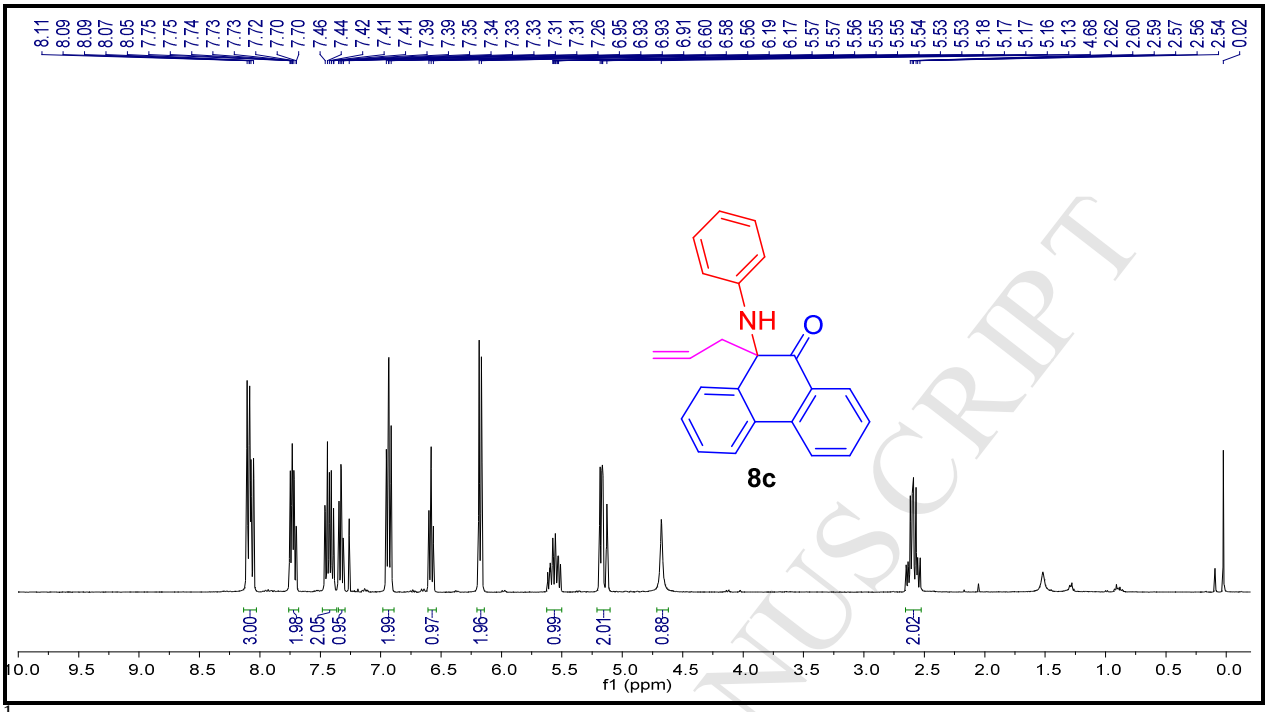


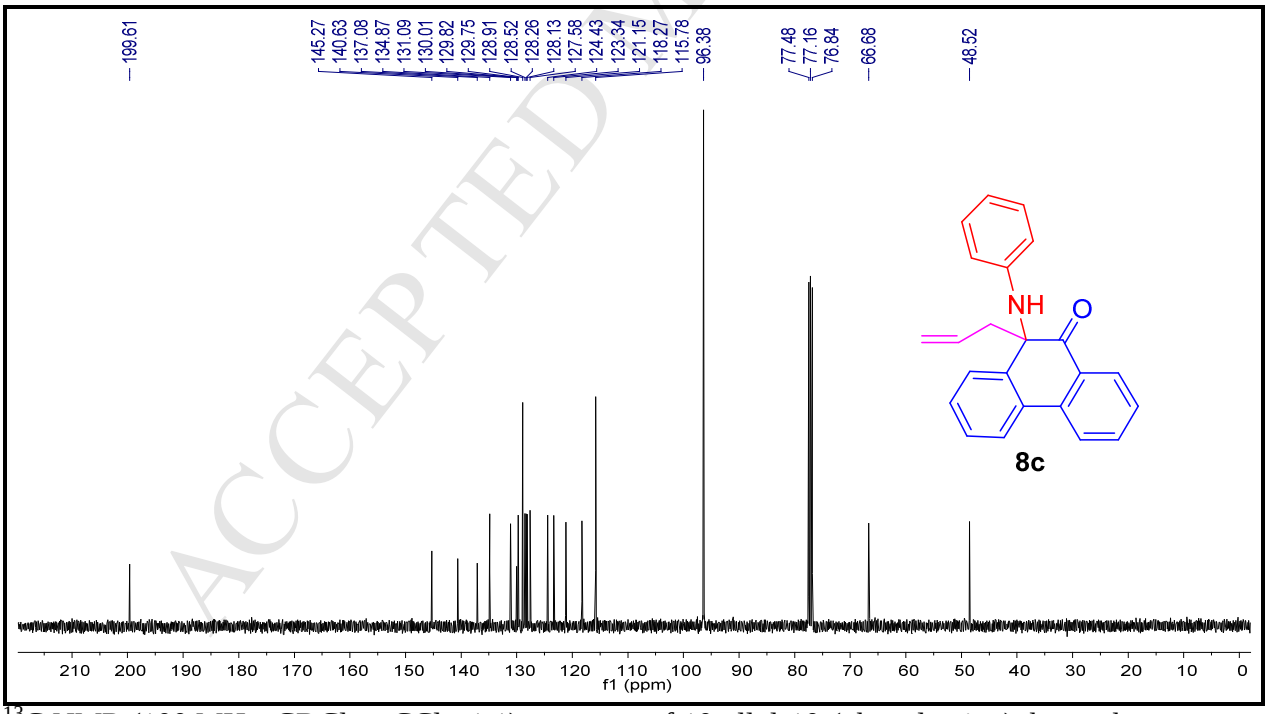
DEPT-135 NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 10-allyl-10-(butylamino)phenanthren-9(10*H*)-one (**8b**).



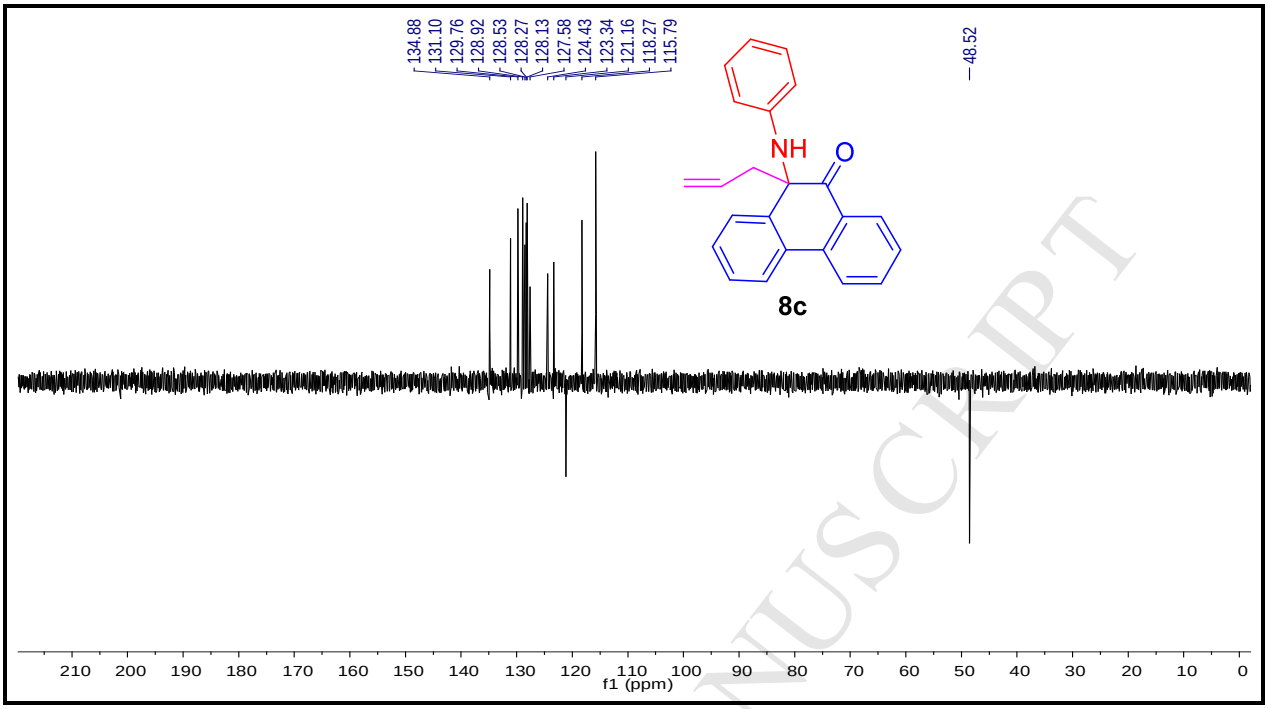
HRMS spectrum of 10-allyl-10-(butylamino)phenanthren-9(10*H*)-one (**8b**).



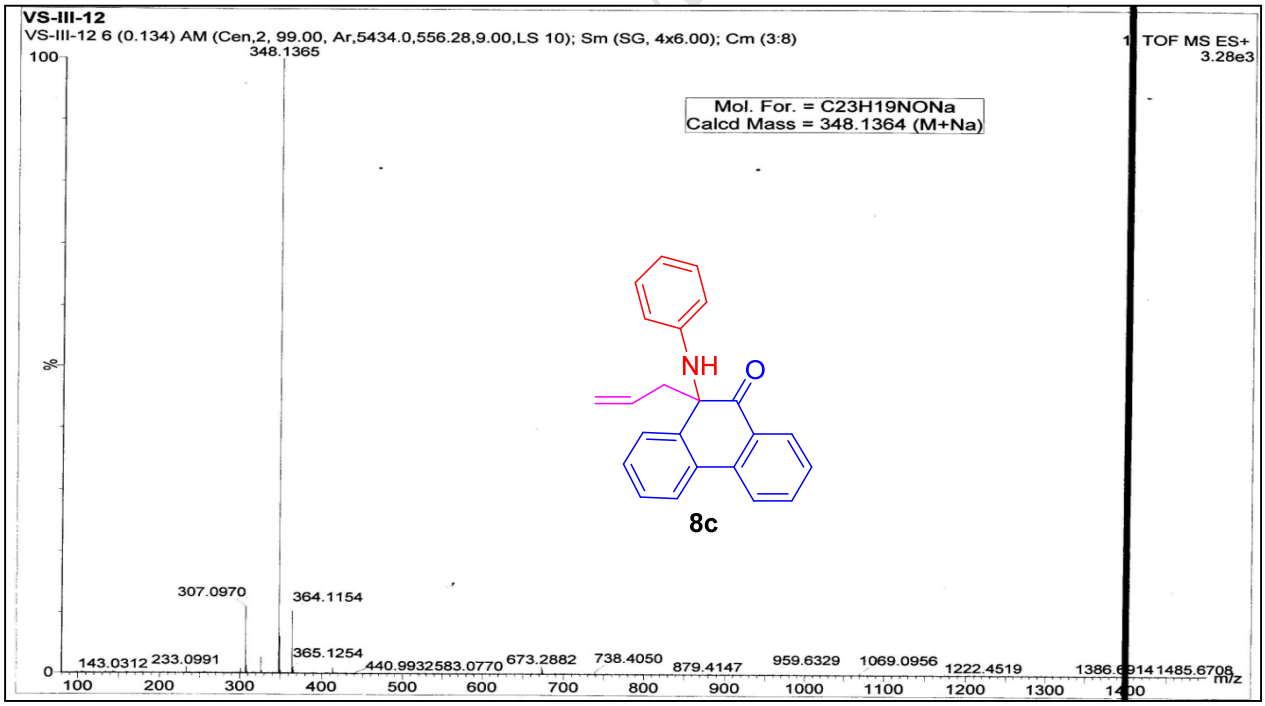
^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 10-allyl-10-(phenylamino)phenanthren-9(10*H*)-one (**8c**).



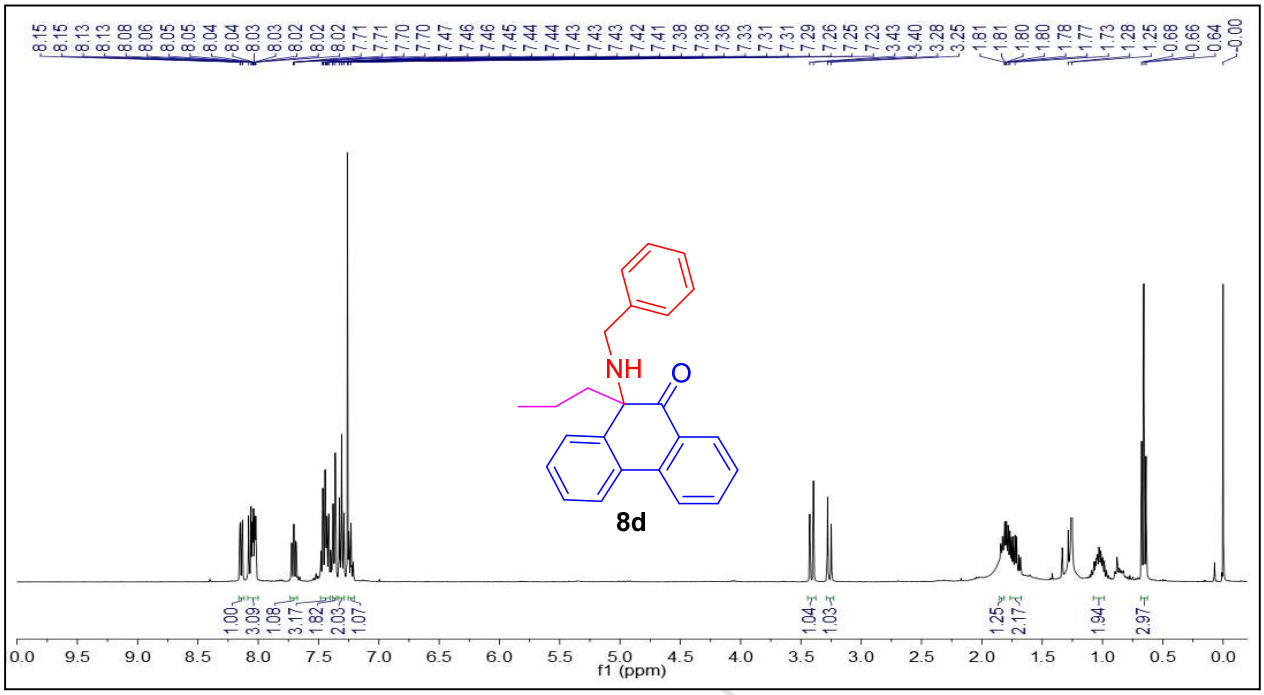
^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 10-allyl-10-(phenylamino)phenanthren-9(10*H*)-one (**8c**).



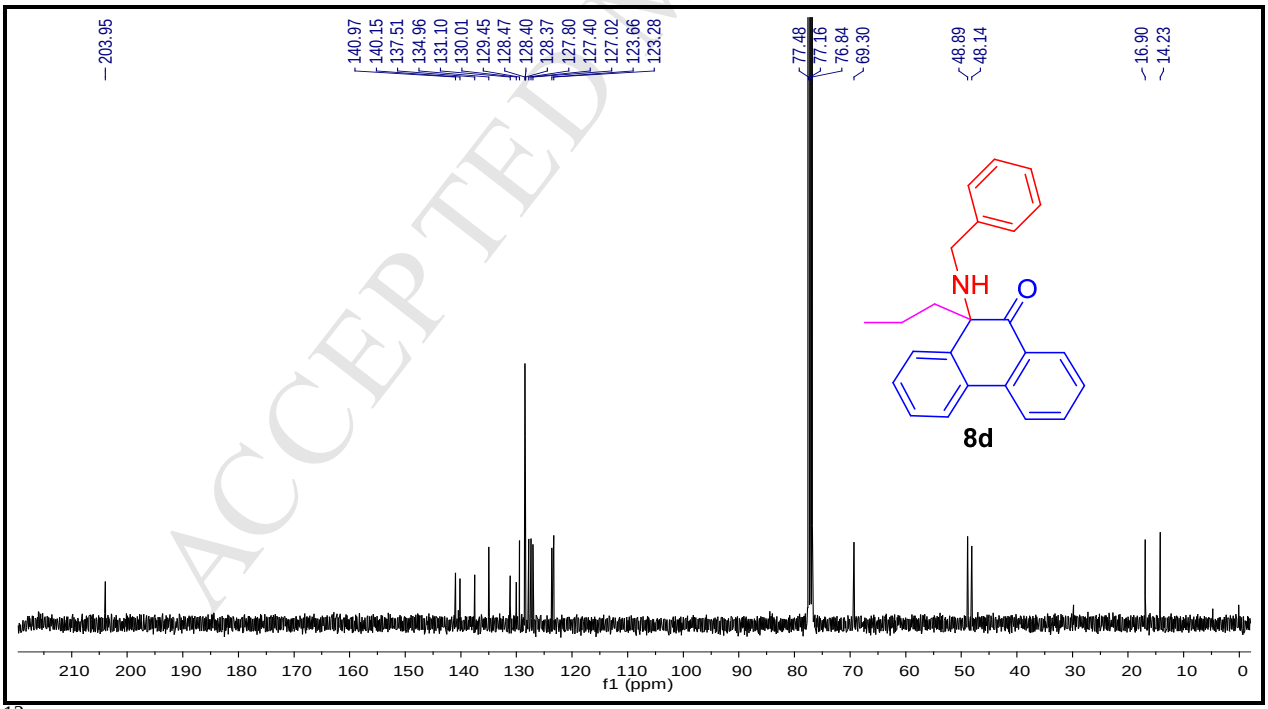
DEPT-135 NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 10-allyl-10-(phenylamino)phenanthren-9(10*H*)-one (**8c**).



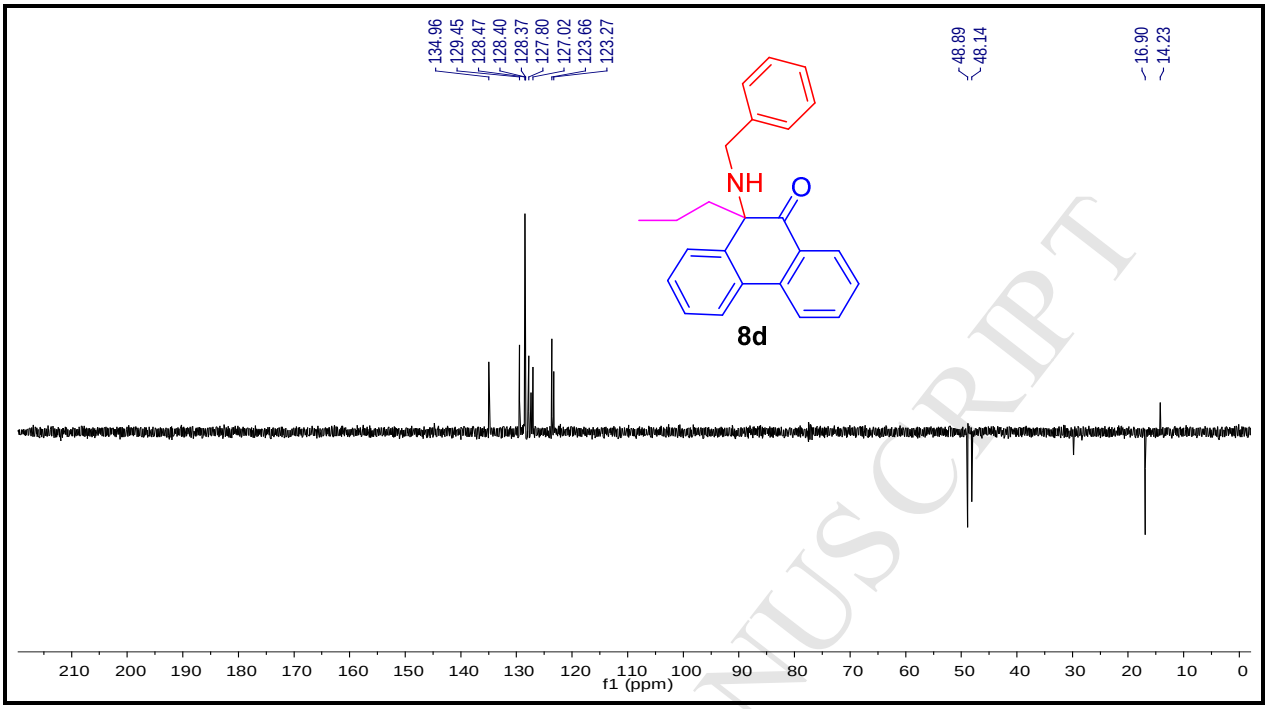
HRMS spectrum of 10-allyl-10-(phenylamino)phenanthren-9(10*H*)-one (**8c**).



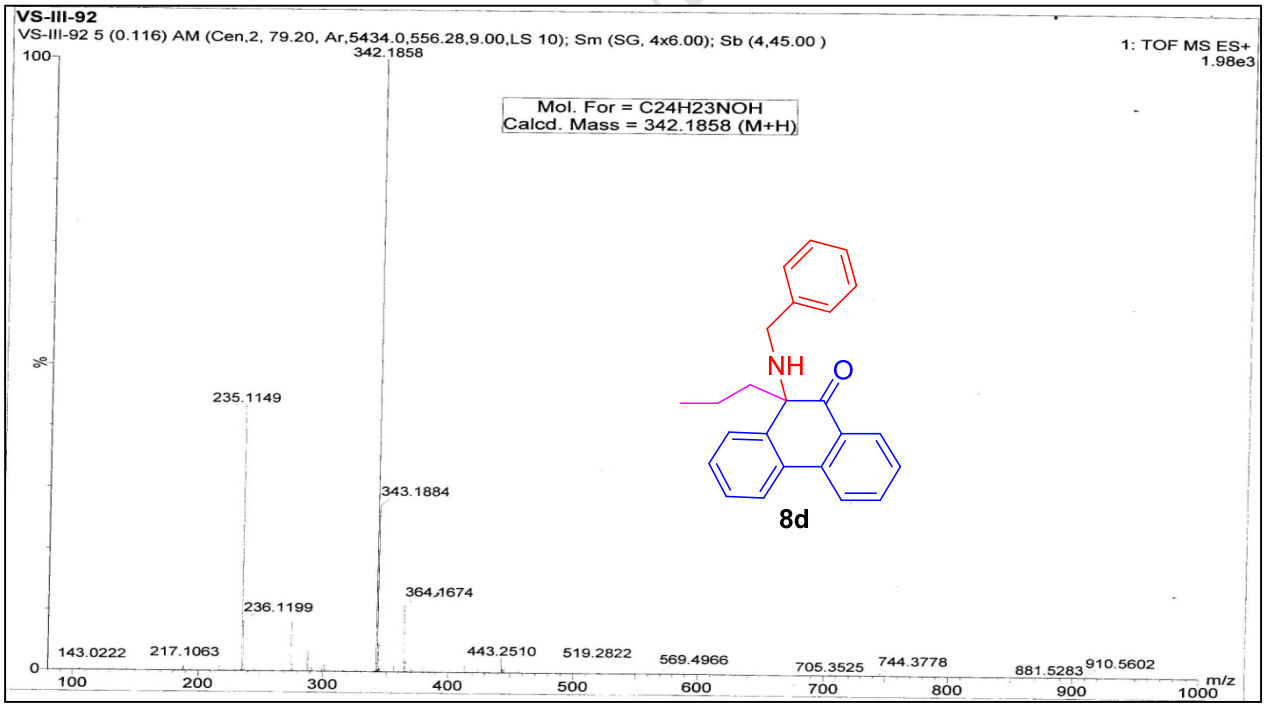
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 10-(benzylamino)-10-propylphenanthren-9(10*H*)-one (**8d**).



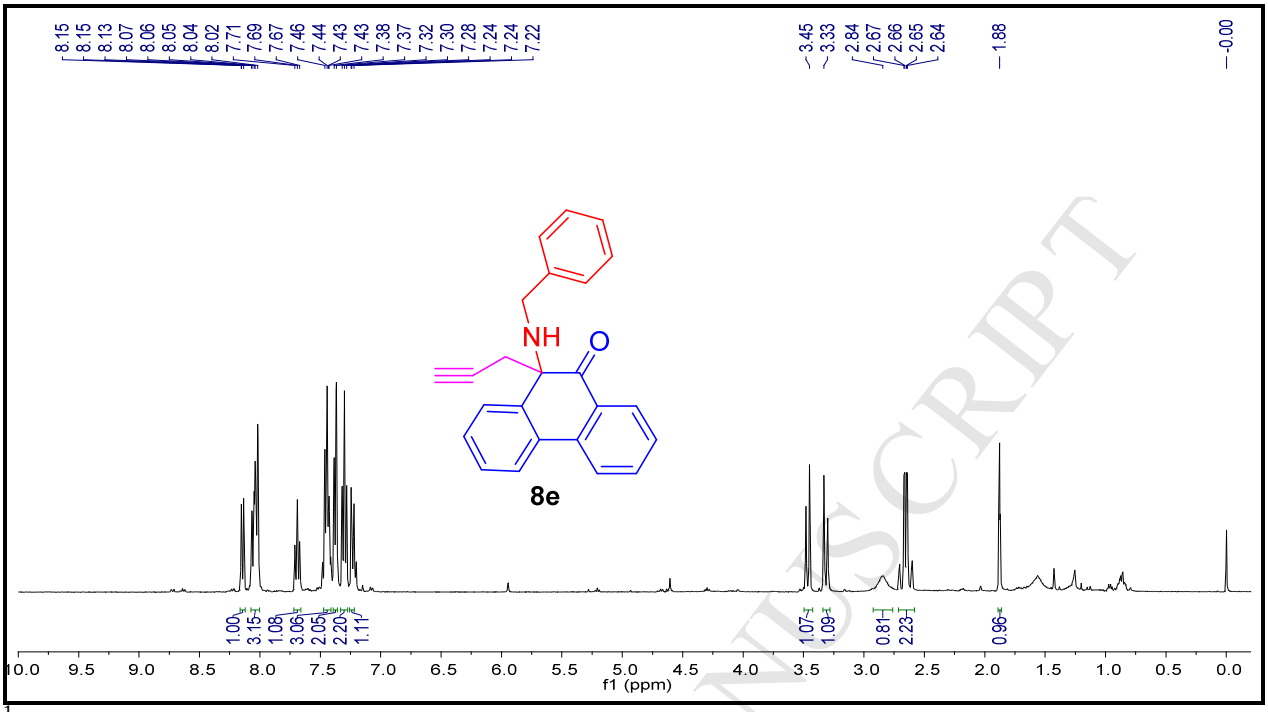
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 10-(benzylamino)-10-propylphenanthren-9(10*H*)-one (**8d**).



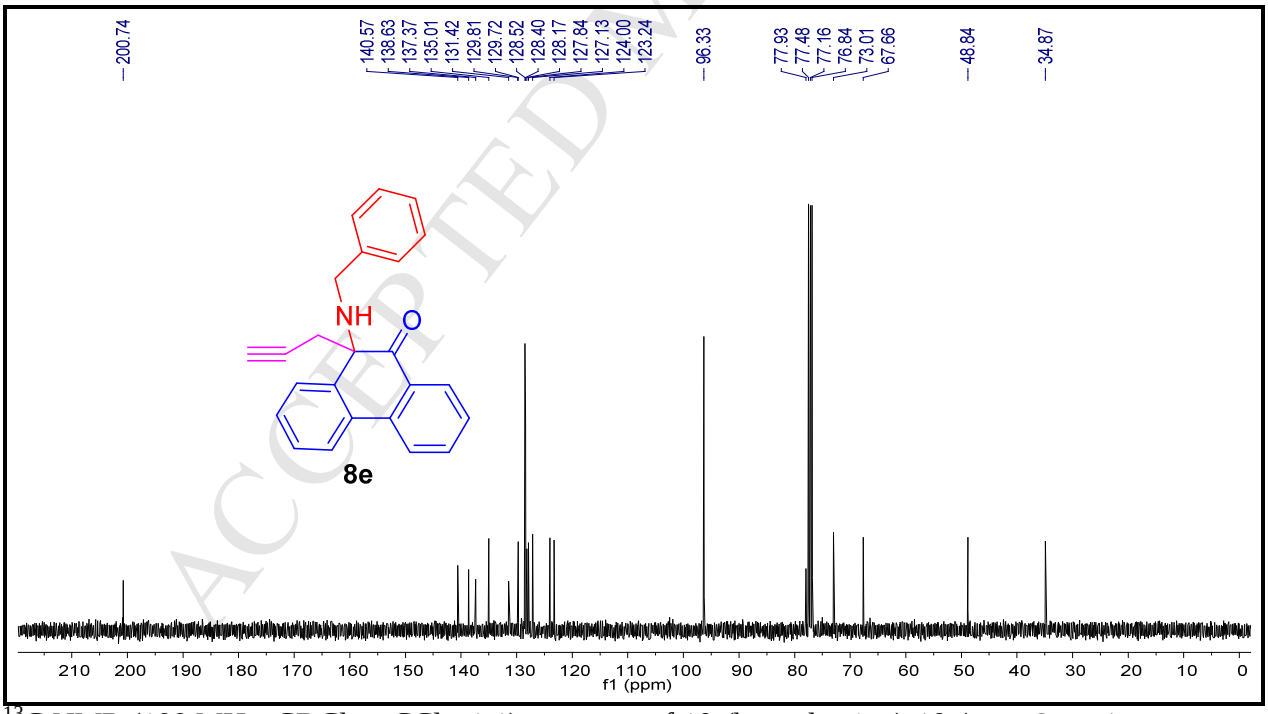
DEPT-135 NMR (100 MHz, $CDCl_3$) spectrum of 10-(benzylamino)-10-propylphenanthren-9(10*H*)-one (**8d**).



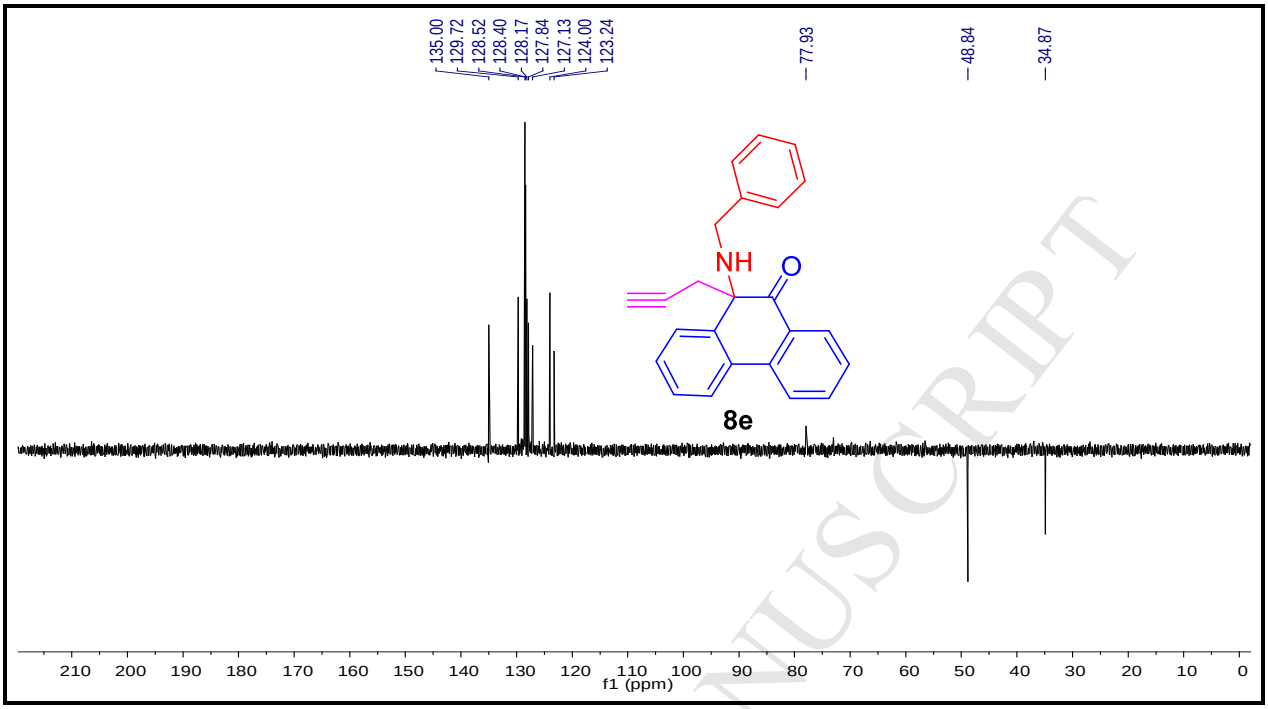
HRMS spectrum of 10-(benzylamino)-10-propylphenanthren-9(10*H*)-one (**8d**).



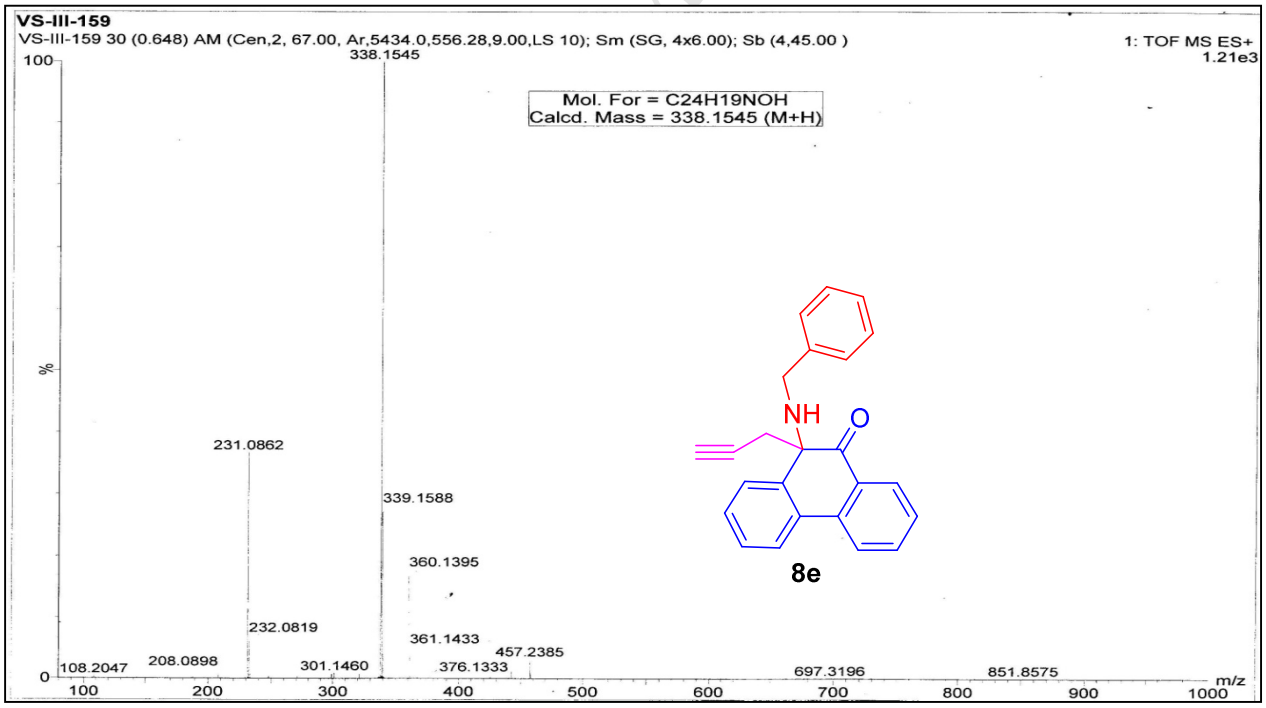
^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 10-(benzylamino)-10-(prop-2-yn-1-yl)phenanthren-9(10*H*)-one (**8e**).



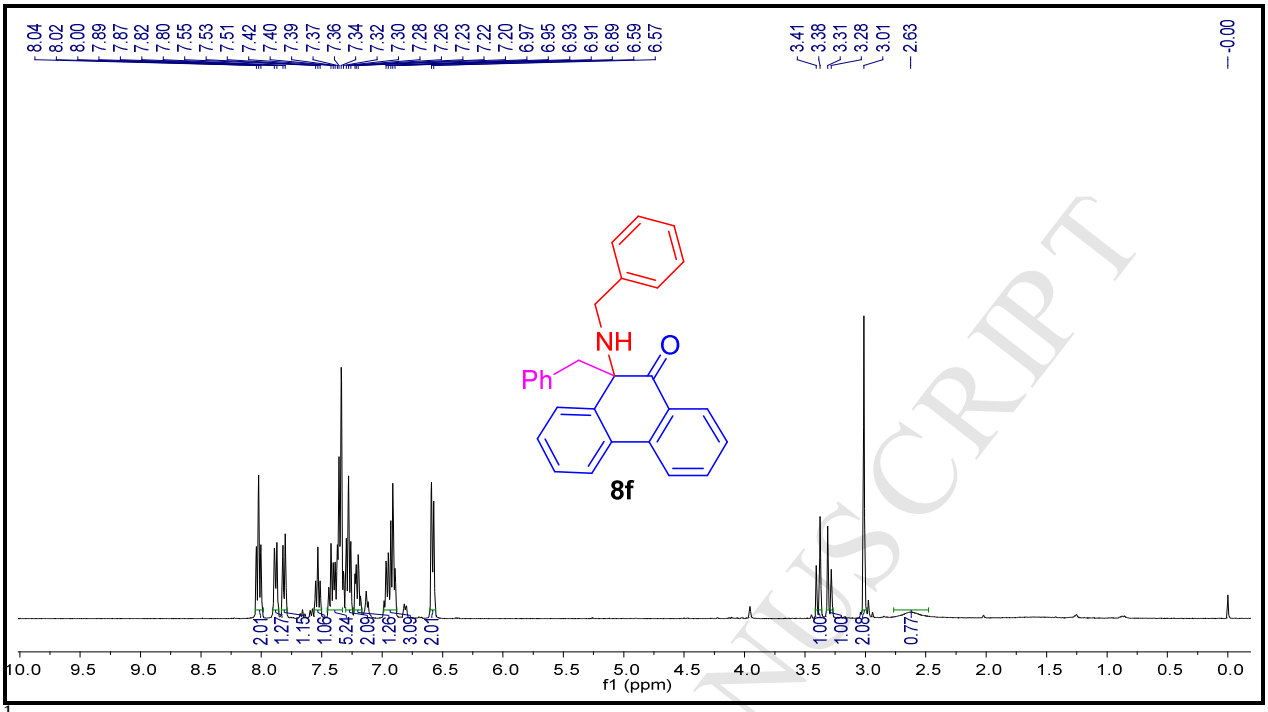
^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 10-(benzylamino)-10-(prop-2-yn-1-yl)phenanthren-9(10*H*)-one (**8e**).



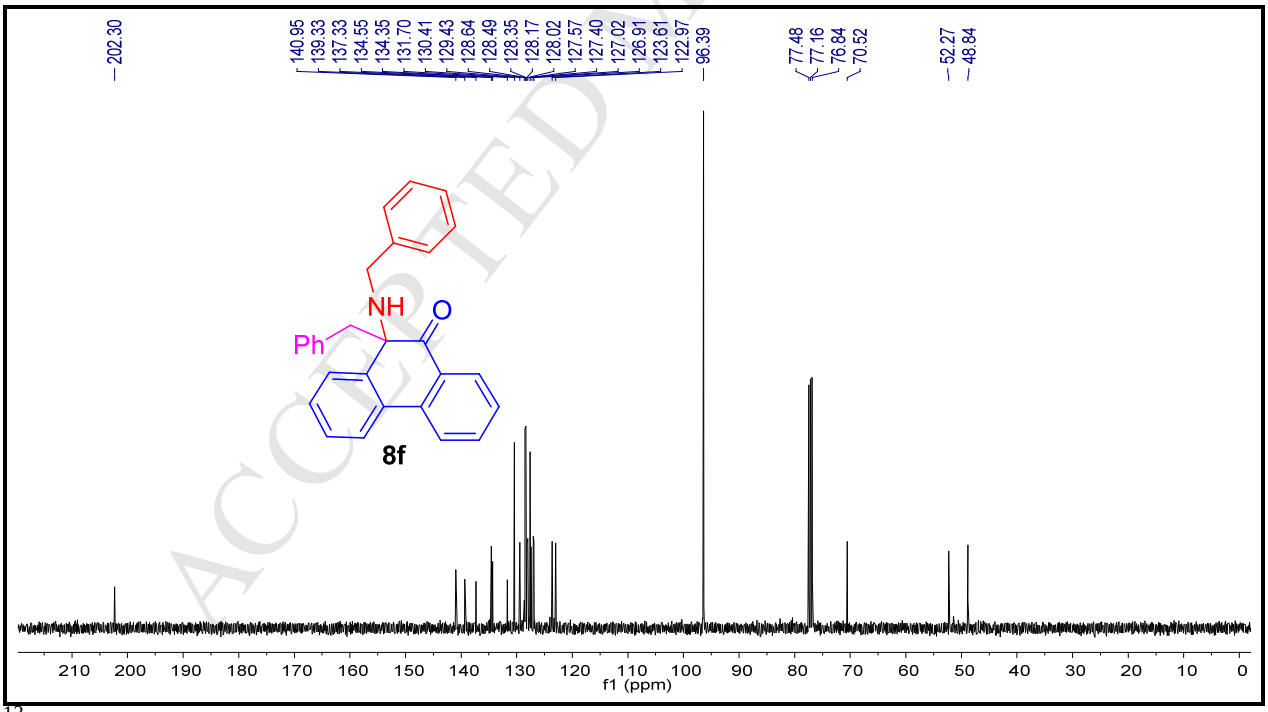
DEPT-135 NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 10-(benzylamino)-10-(prop-2-yn-1-yl)phenanthren-9(10*H*)-one (**8e**).



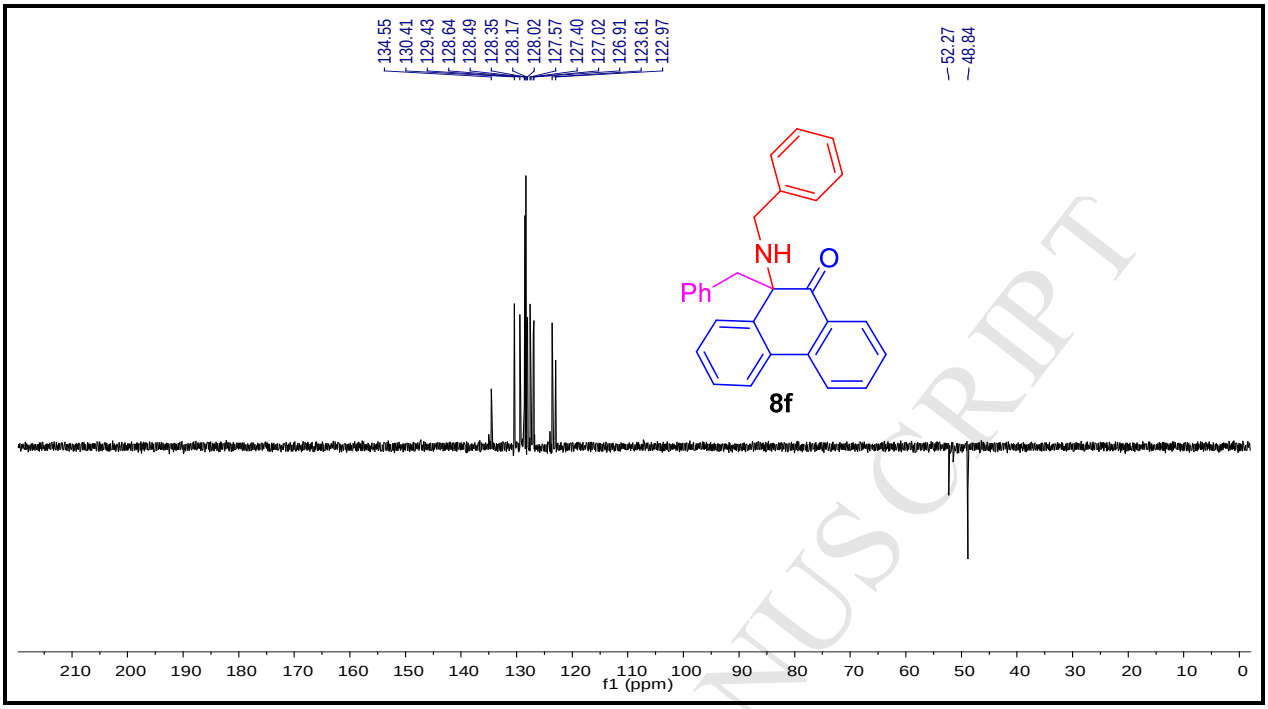
HRMS spectrum of 10-(benzylamino)-10-(prop-2-yn-1-yl)phenanthren-9(10*H*)-one (**8e**).



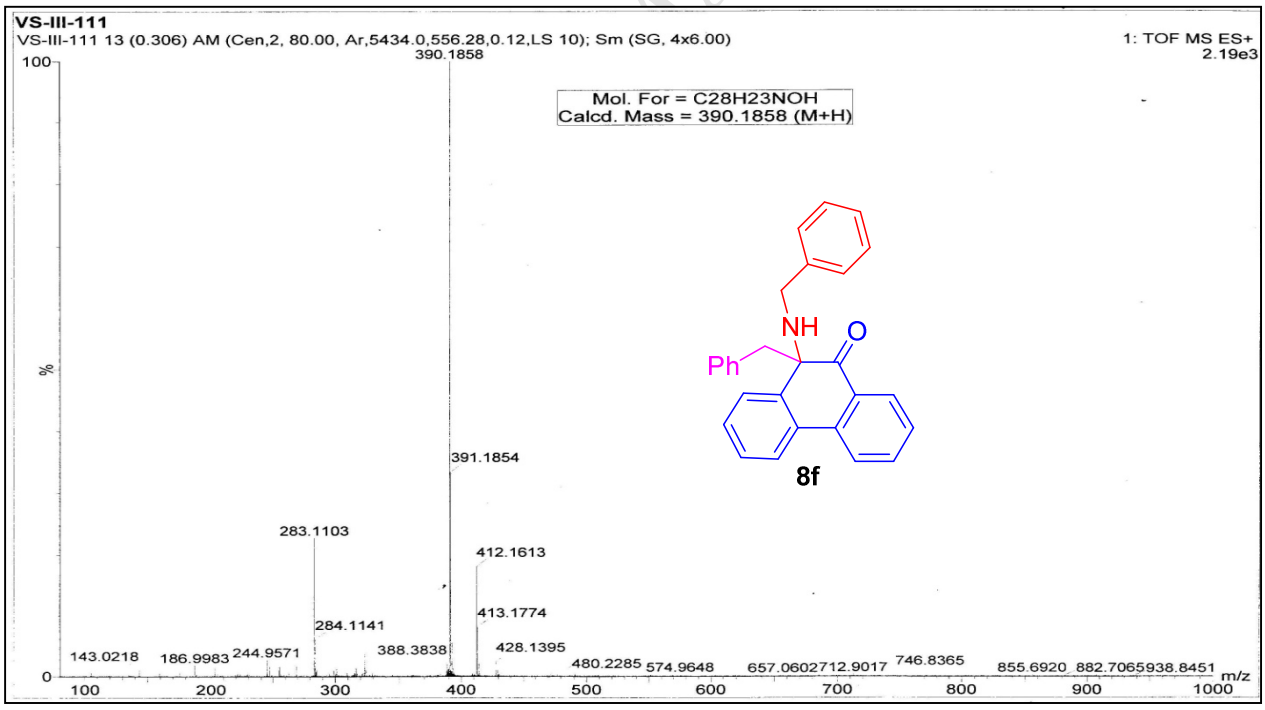
^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 10-benzyl-10-(benzylamino)phenanthren-9(10*H*)-one (**8f**).



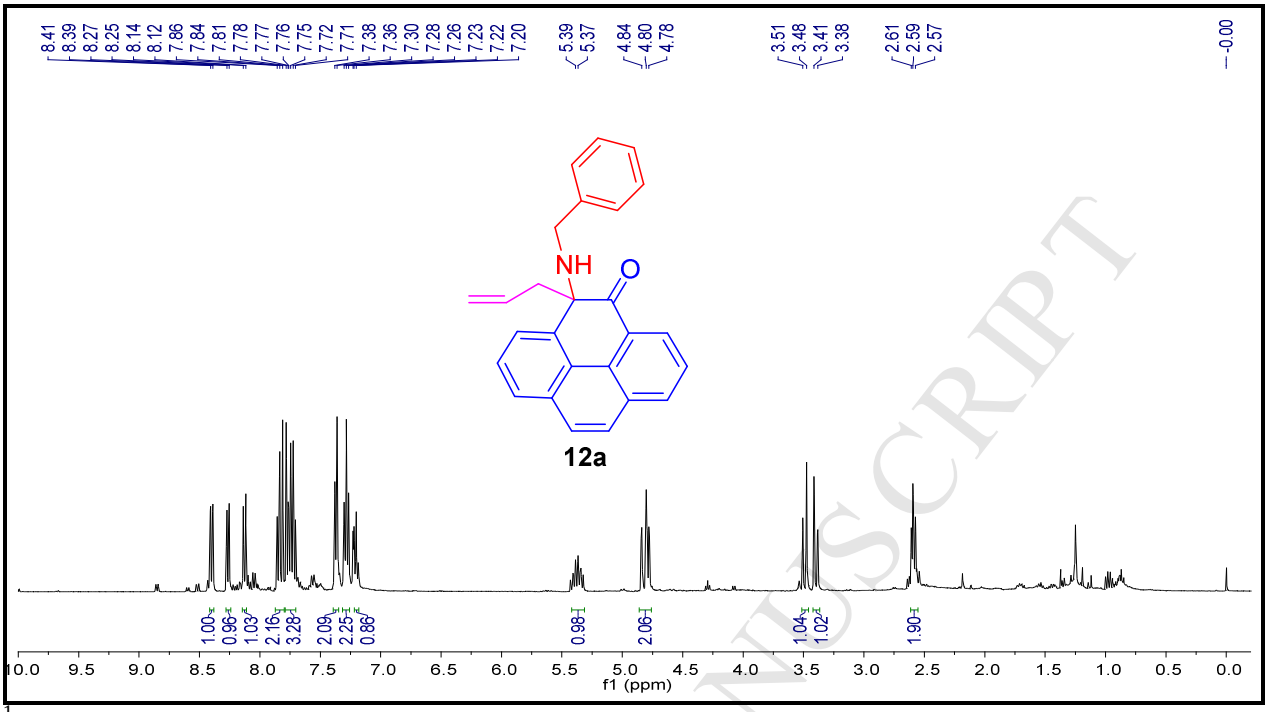
^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 10-benzyl-10-(benzylamino)phenanthren-9(10*H*)-one (**8f**).



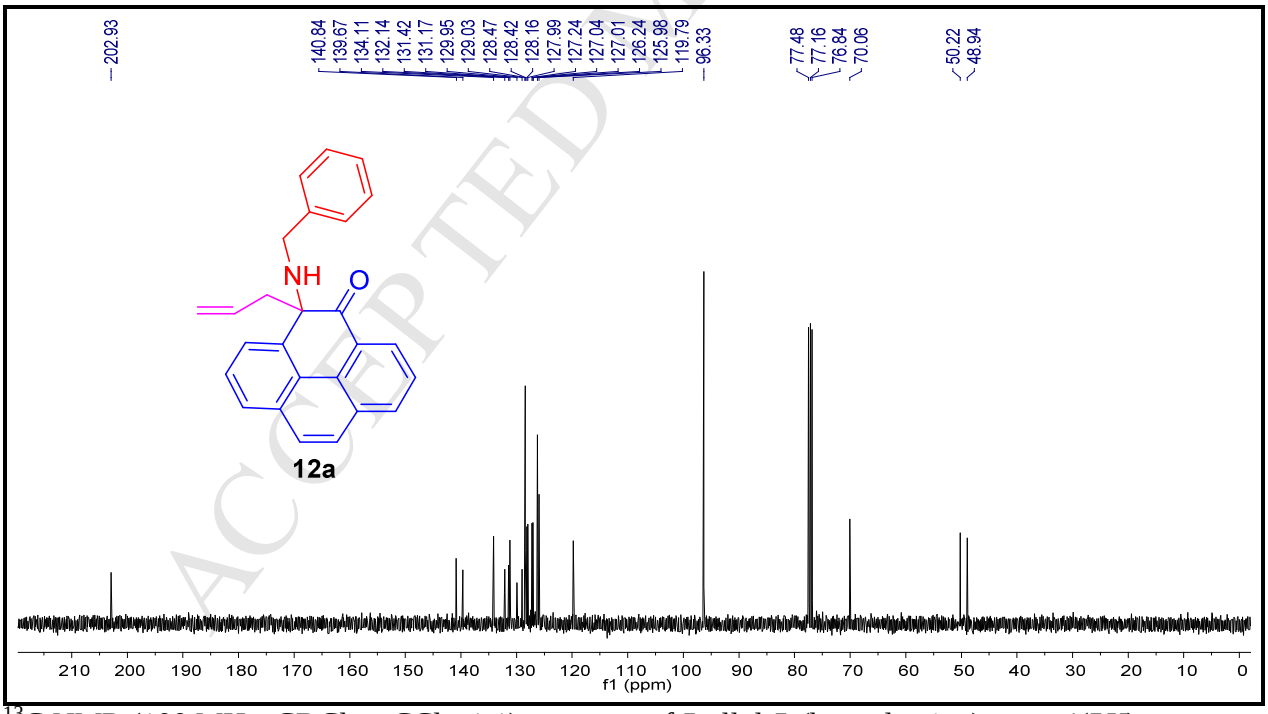
DEPT-135 NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 10-benzyl-10-(benzylamino)phenanthren-9(10*H*)-one (**8f**).



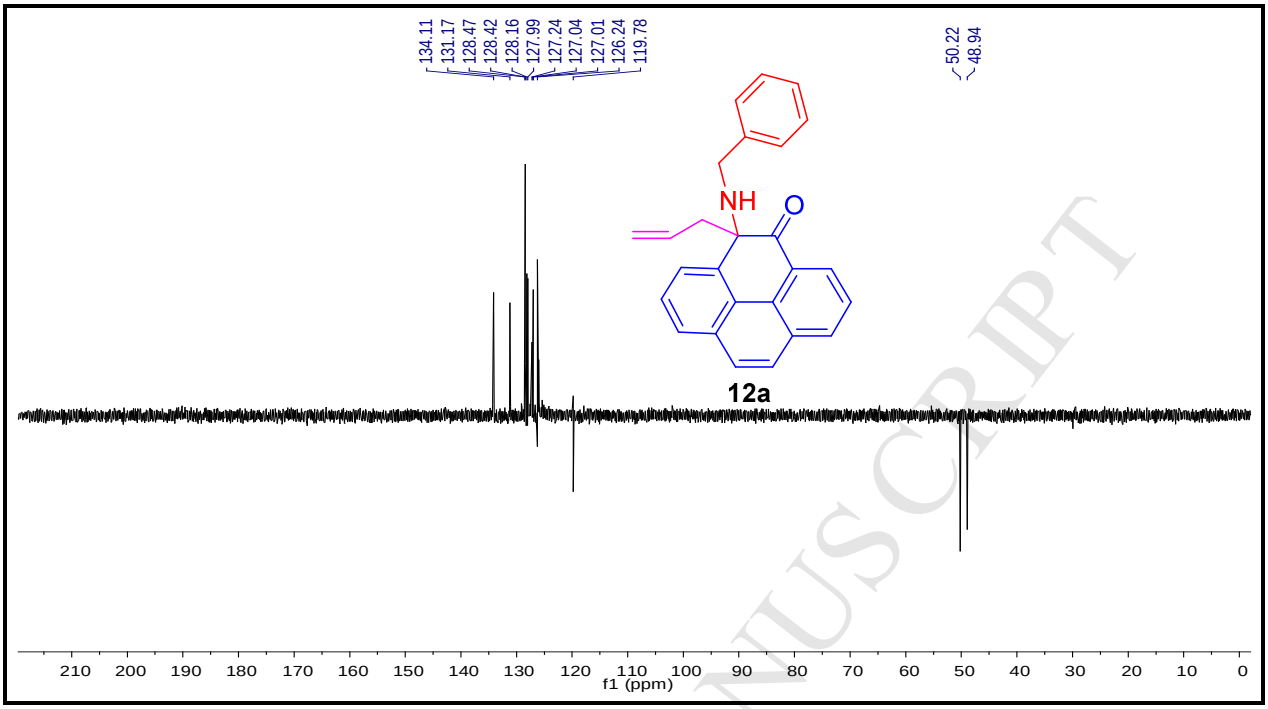
HRMS spectrum of 10-benzyl-10-(benzylamino)phenanthren-9(10*H*)-one (**8f**).



^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 5-allyl-5-(benzylamino)pyren-4(5*H*)-one (**12a**).



^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 5-allyl-5-(benzylamino)pyren-4(5*H*)-one (**12a**).



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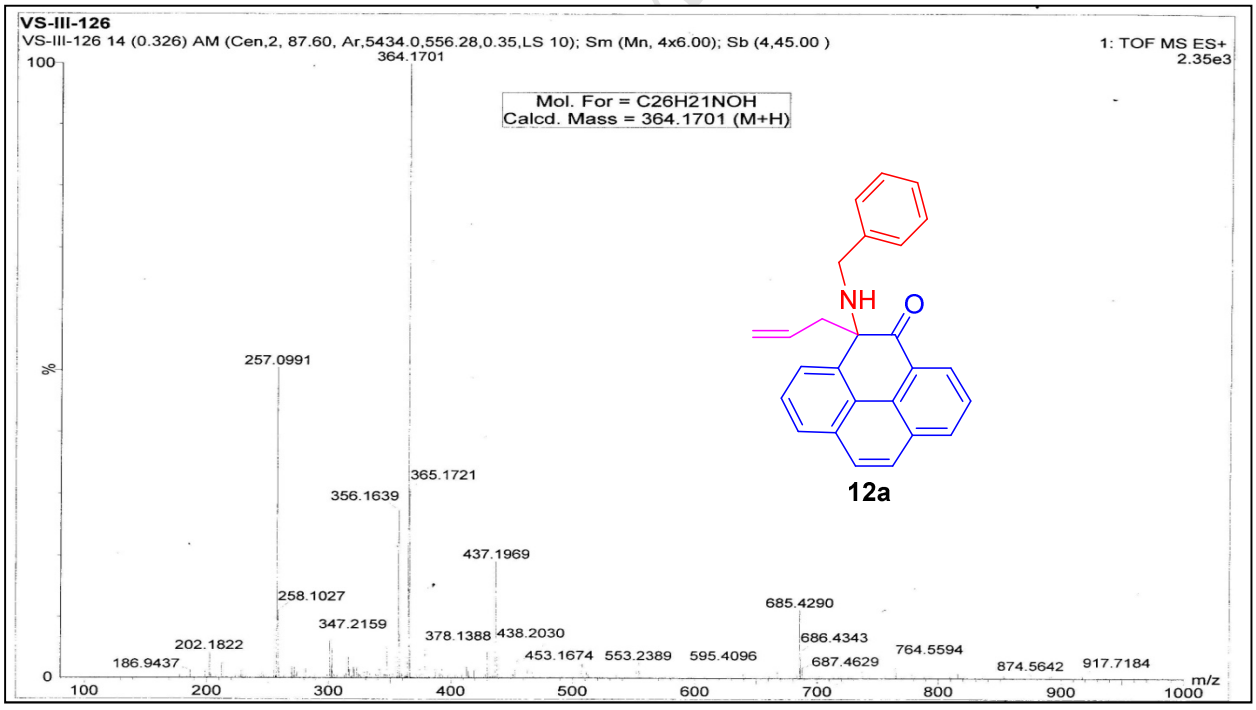
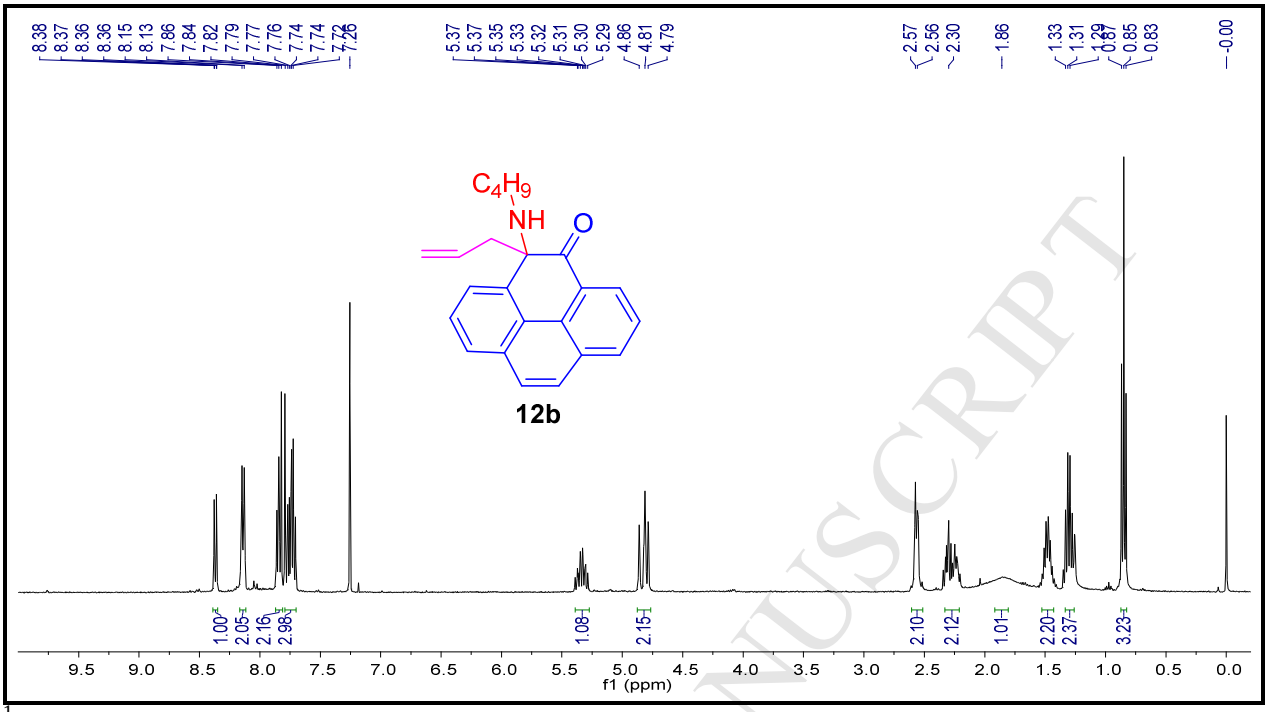


HRMS spectrum of 5-allyl-5-(benzylamino)pyren-4(5*H*)-one (**12a**).



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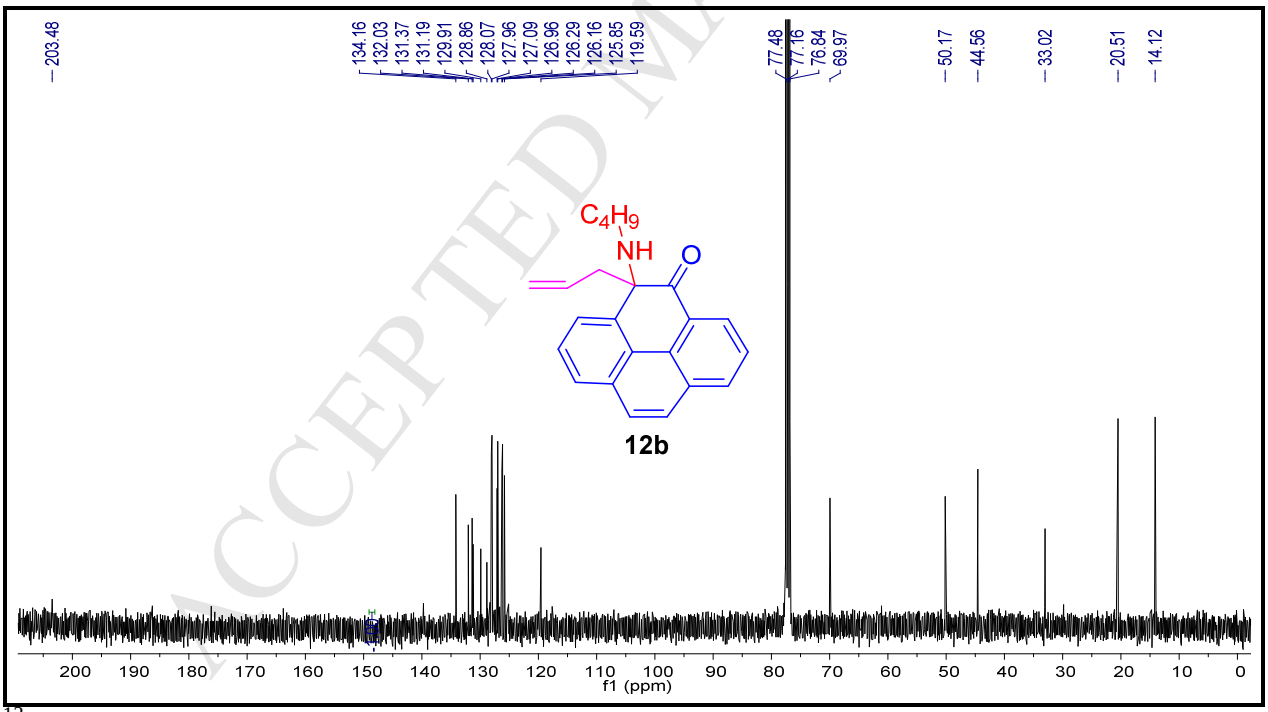
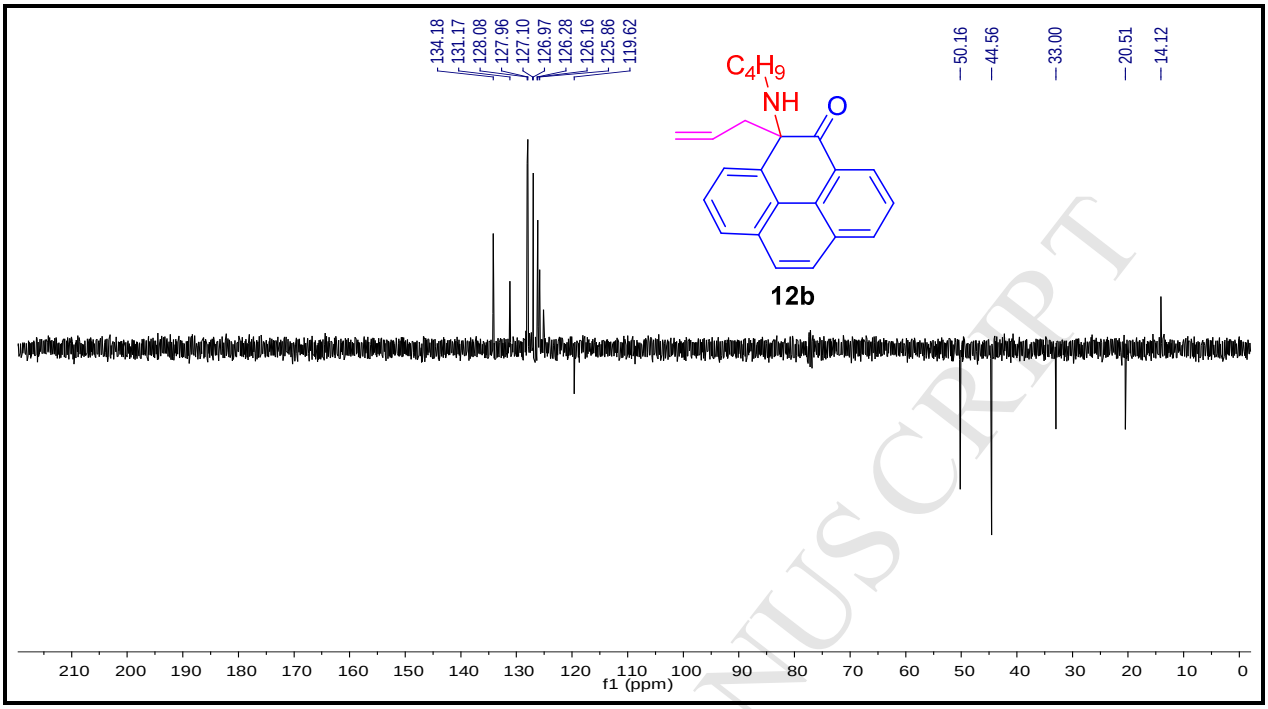
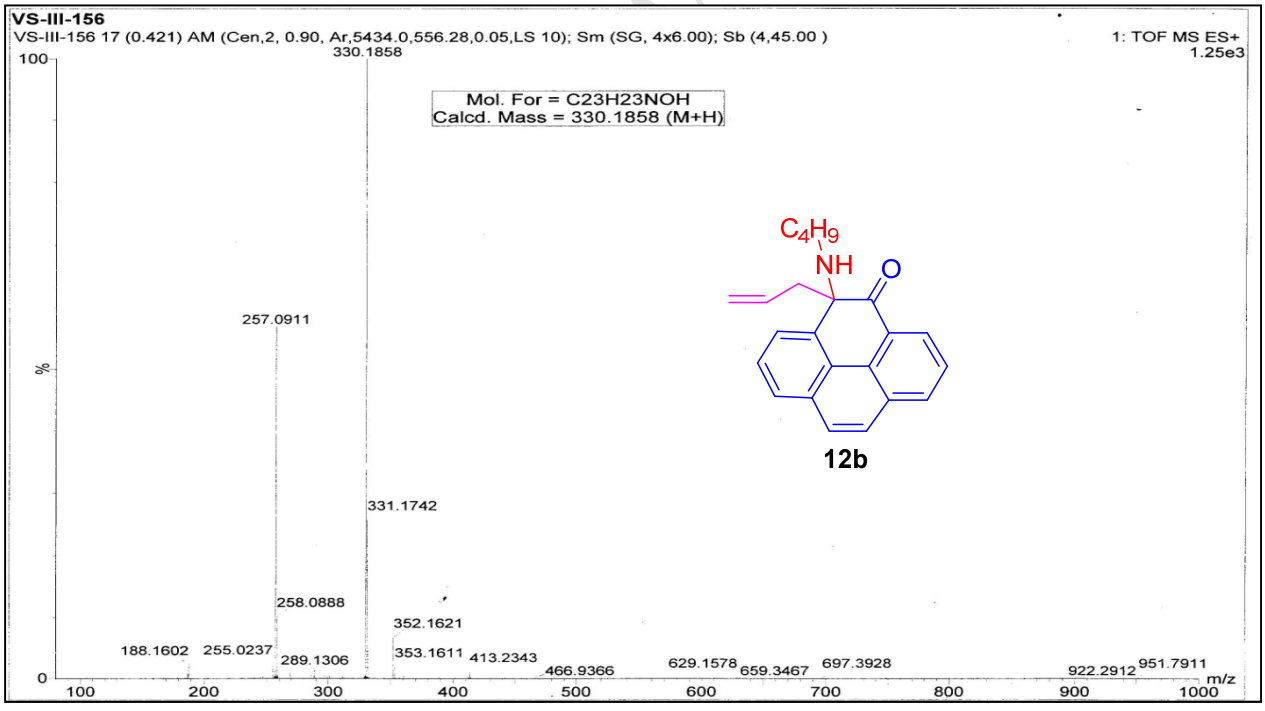


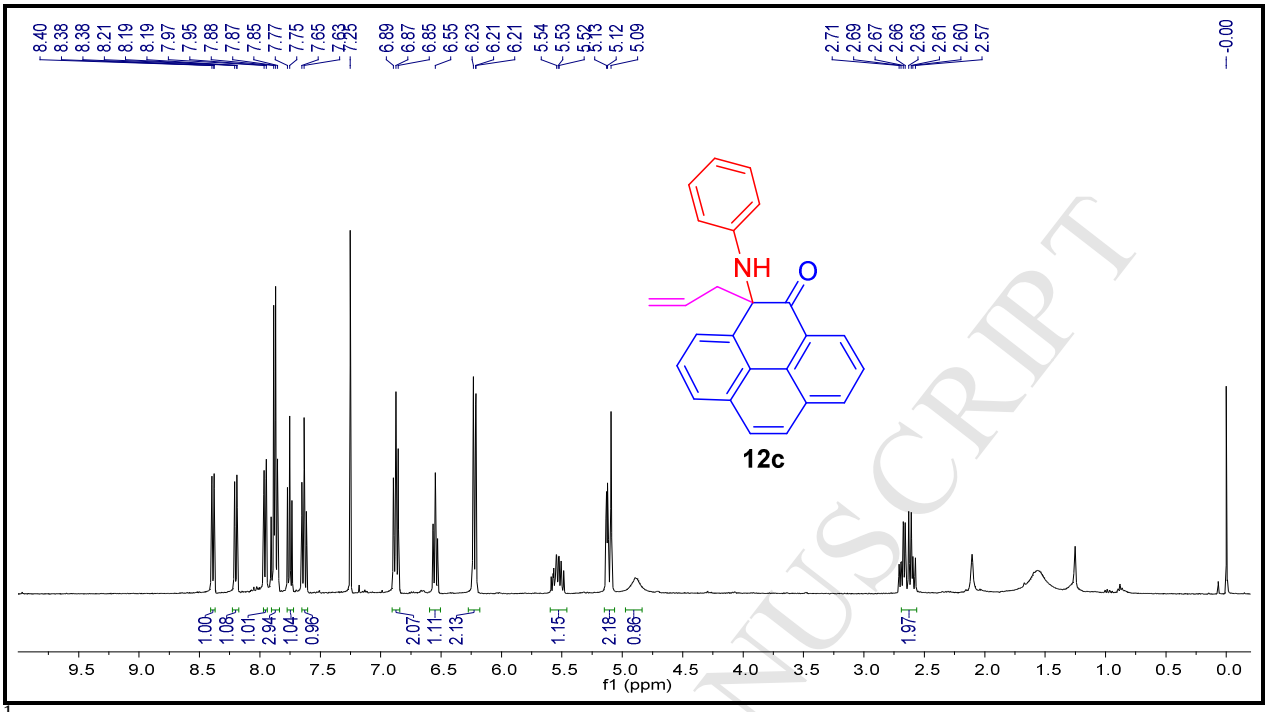
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 5-allyl-5-(butylamino)pyren-4(5*H*)-one (**12b**).



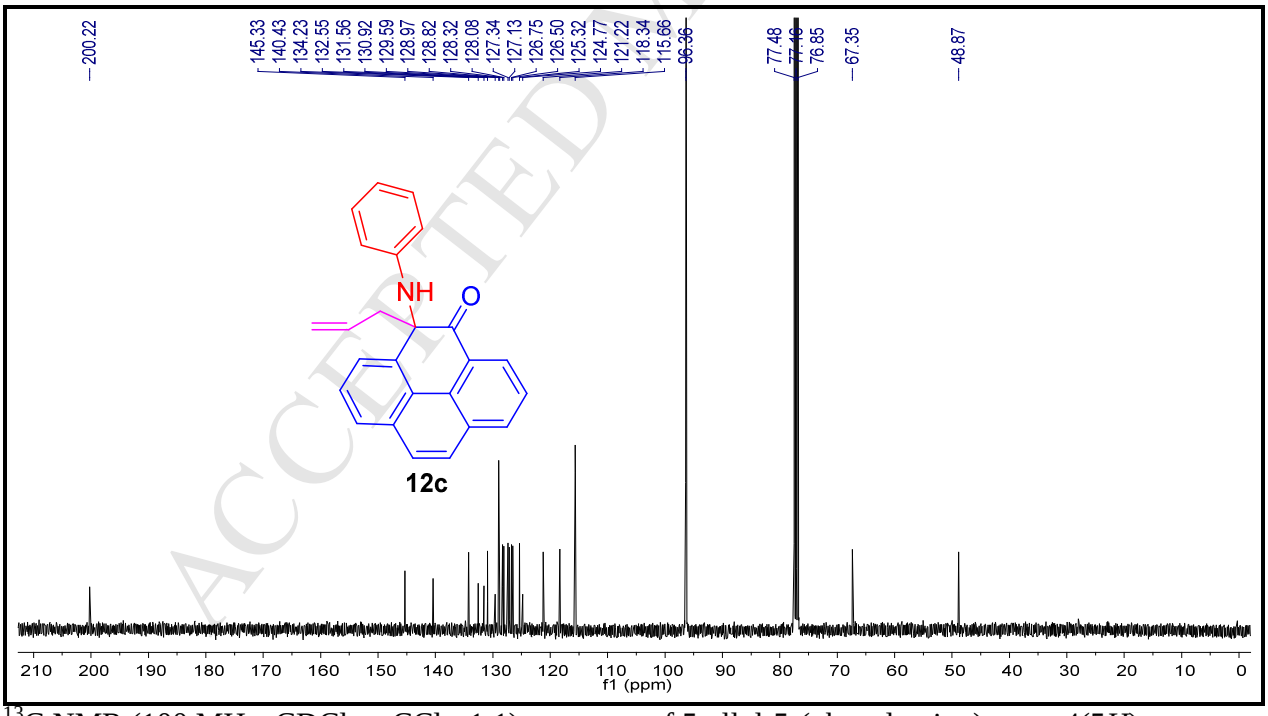
DEPT-135 NMR (100 MHz, $CDCl_3$) spectrum of 5-allyl-5-(butylamino)pyren-4(5*H*)-one (**12b**).



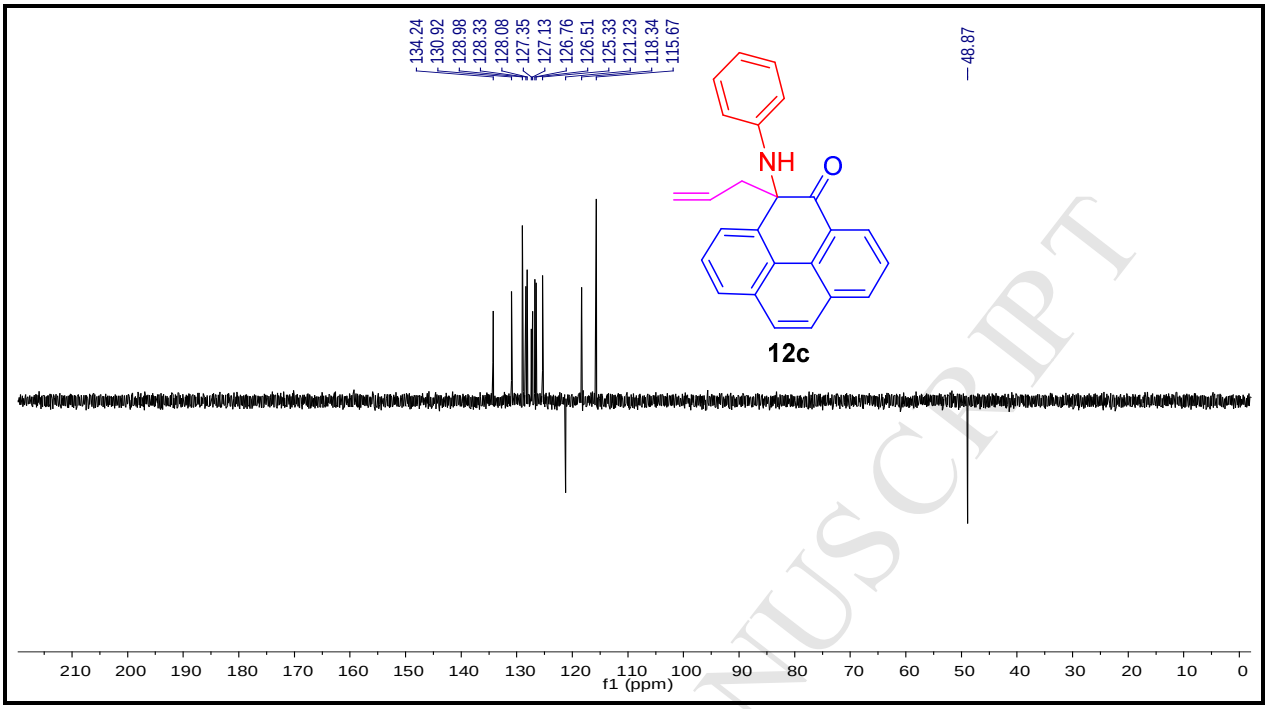
HRMS spectrum of 5-allyl-5-(butylamino)pyren-4(5*H*)-one (**12b**).



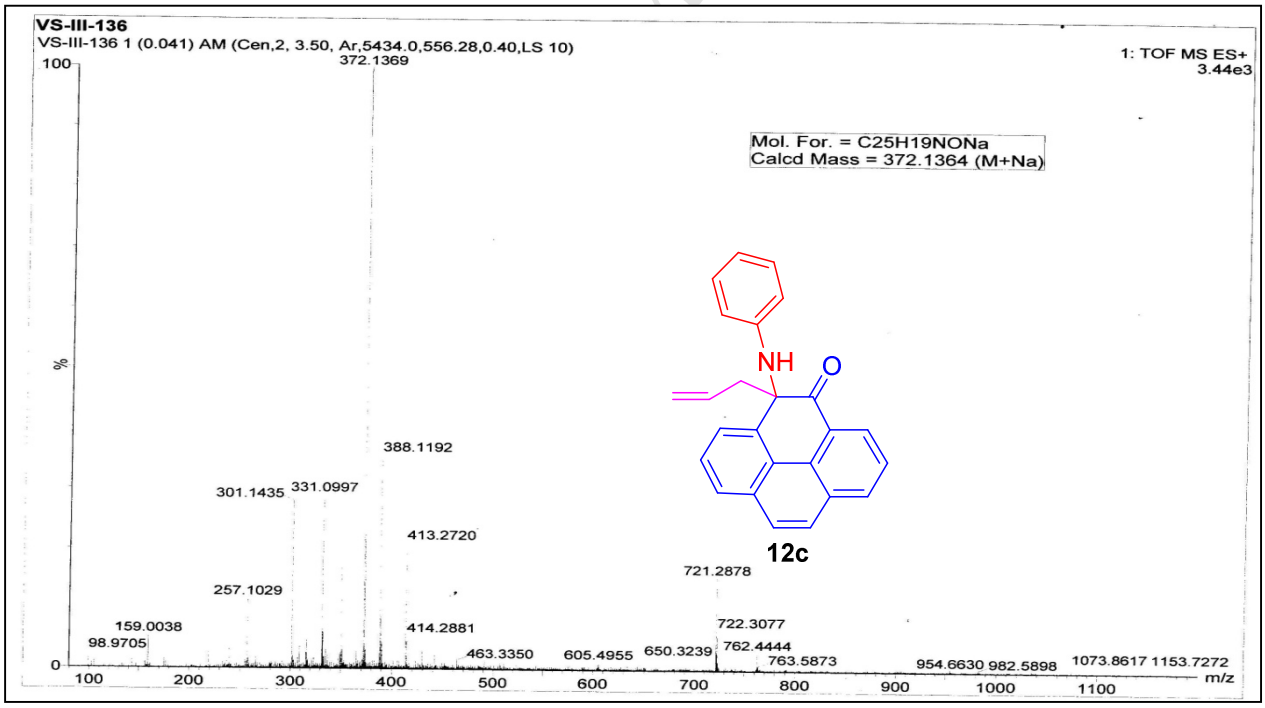
^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 5-allyl-5-(phenylamino)pyren-4(5*H*)-one (**12c**).



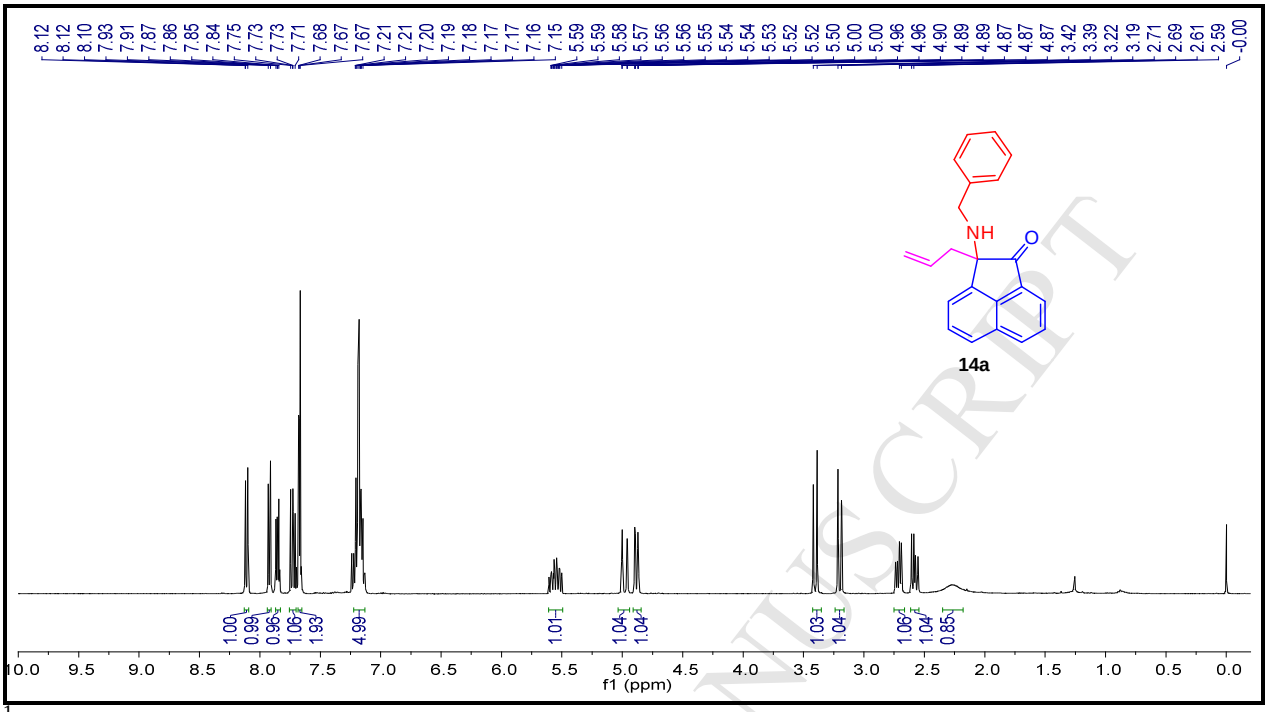
^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 5-allyl-5-(phenylamino)pyren-4(5*H*)-one (**12c**).



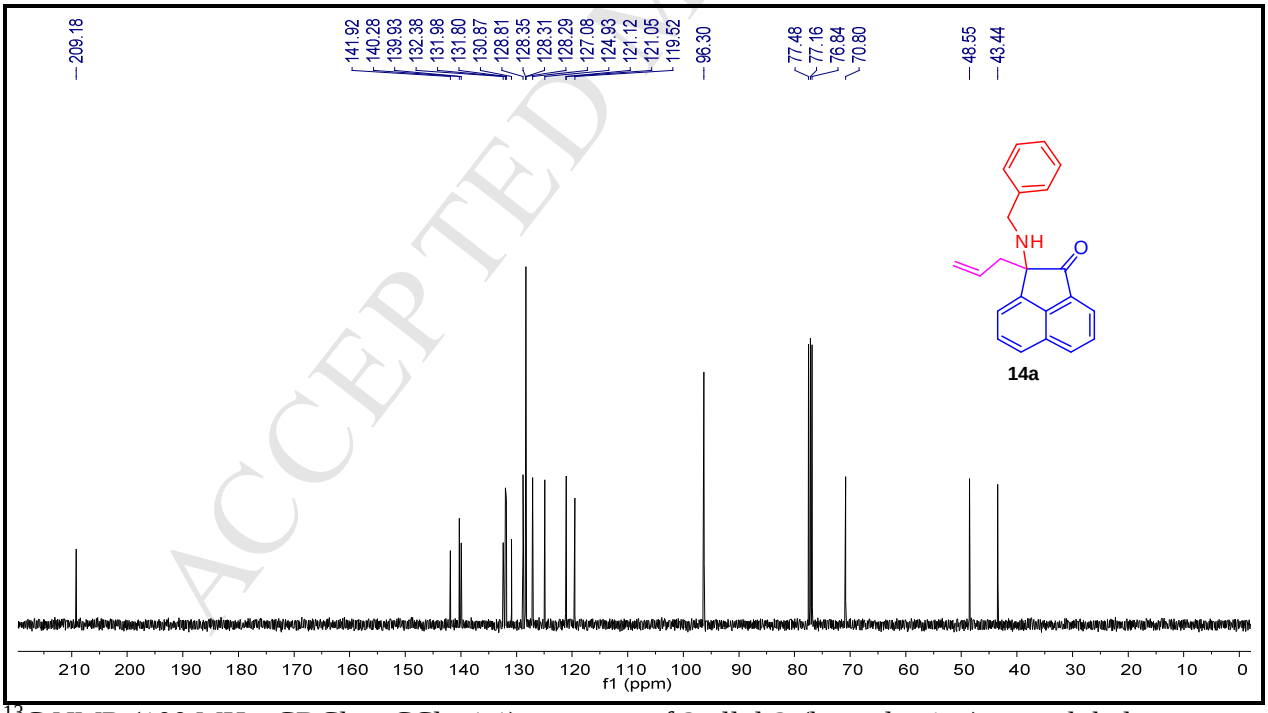
DEPT-135 NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 5-allyl-5-(phenylamino)pyren-4(5*H*)-one (**12c**).



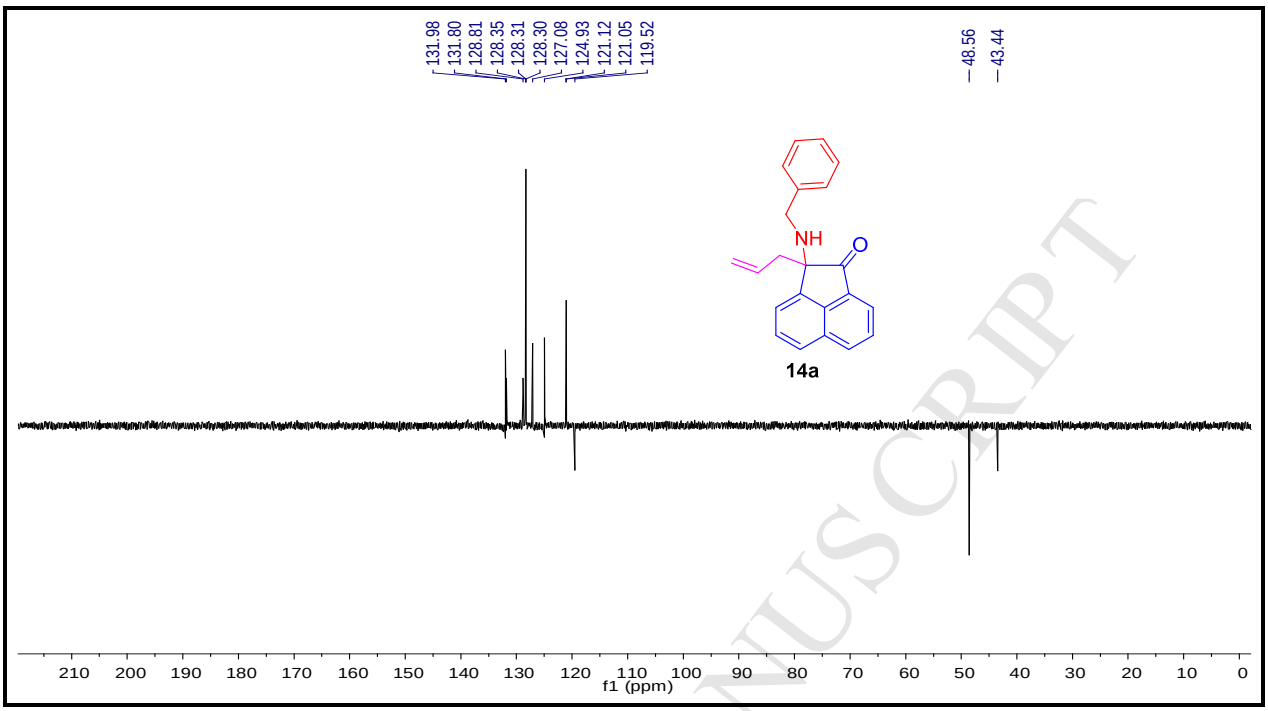
HRMS spectrum of 5-allyl-5-(phenylamino)pyren-4(5*H*)-one (**12c**).



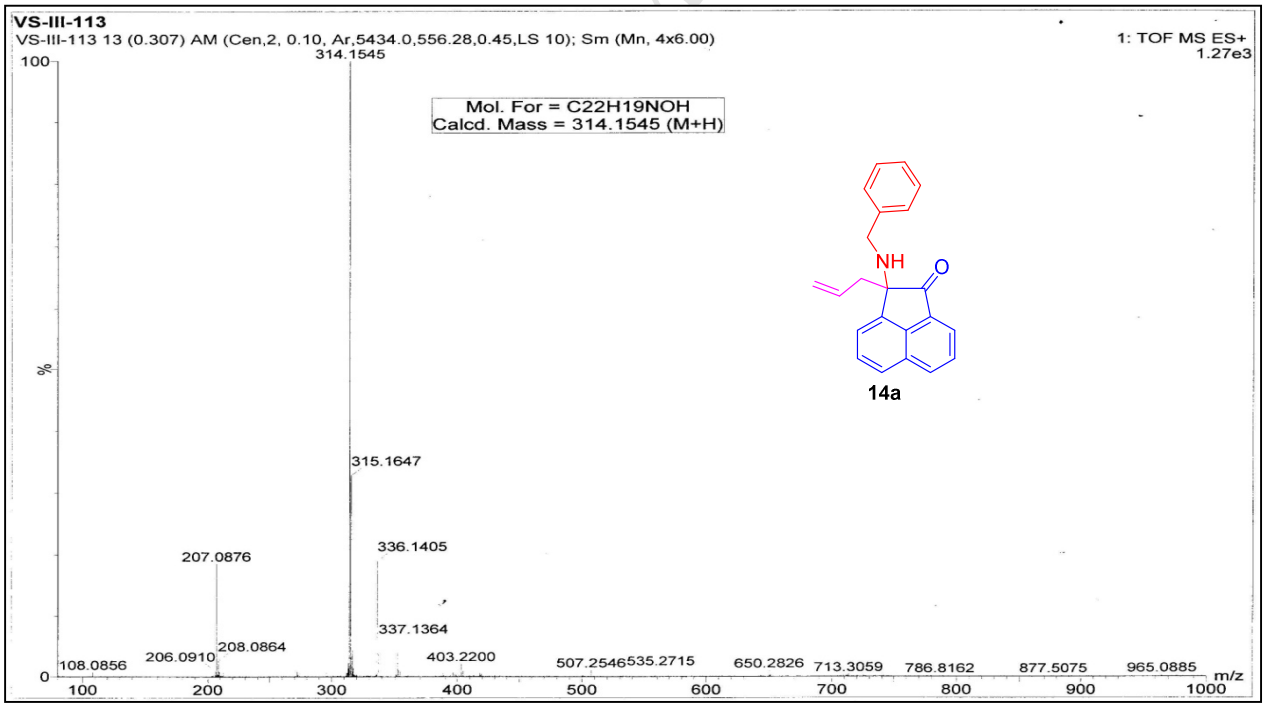
^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-(benzylamino)acenaphthylen-1(2*H*)-one (**14a**).



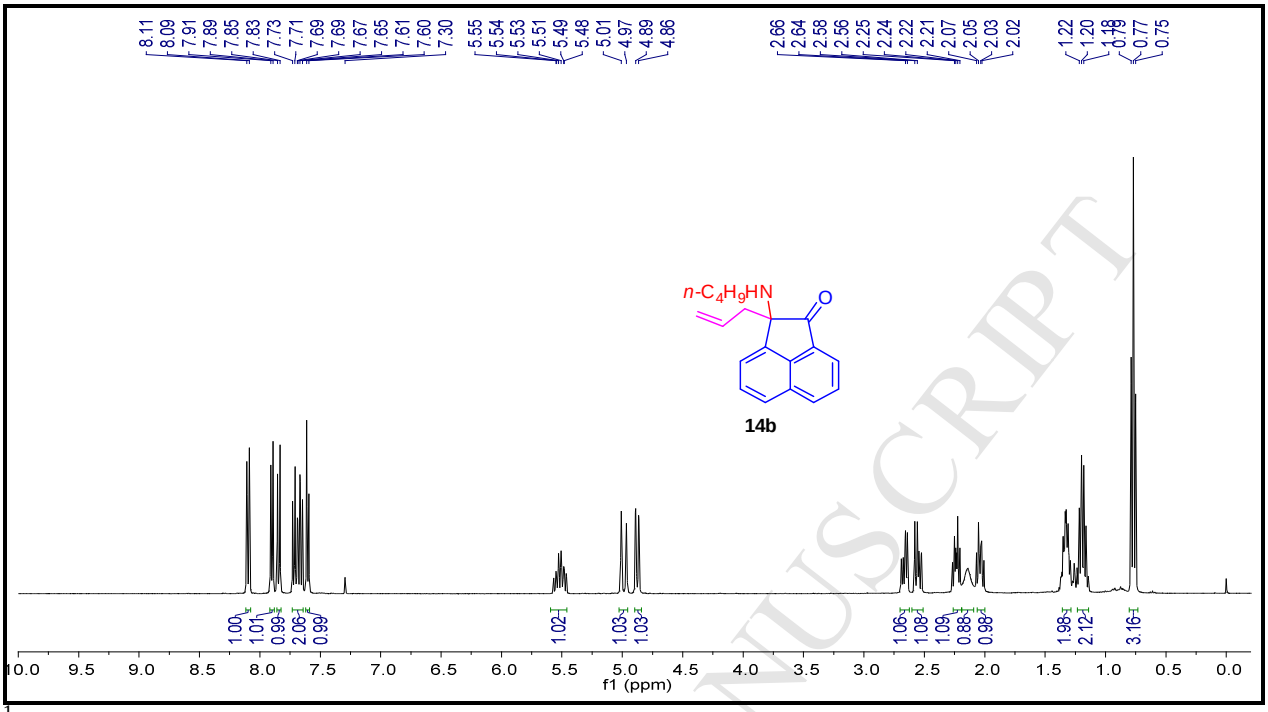
^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-(benzylamino)acenaphthylen-1(2*H*)-one (**14a**).



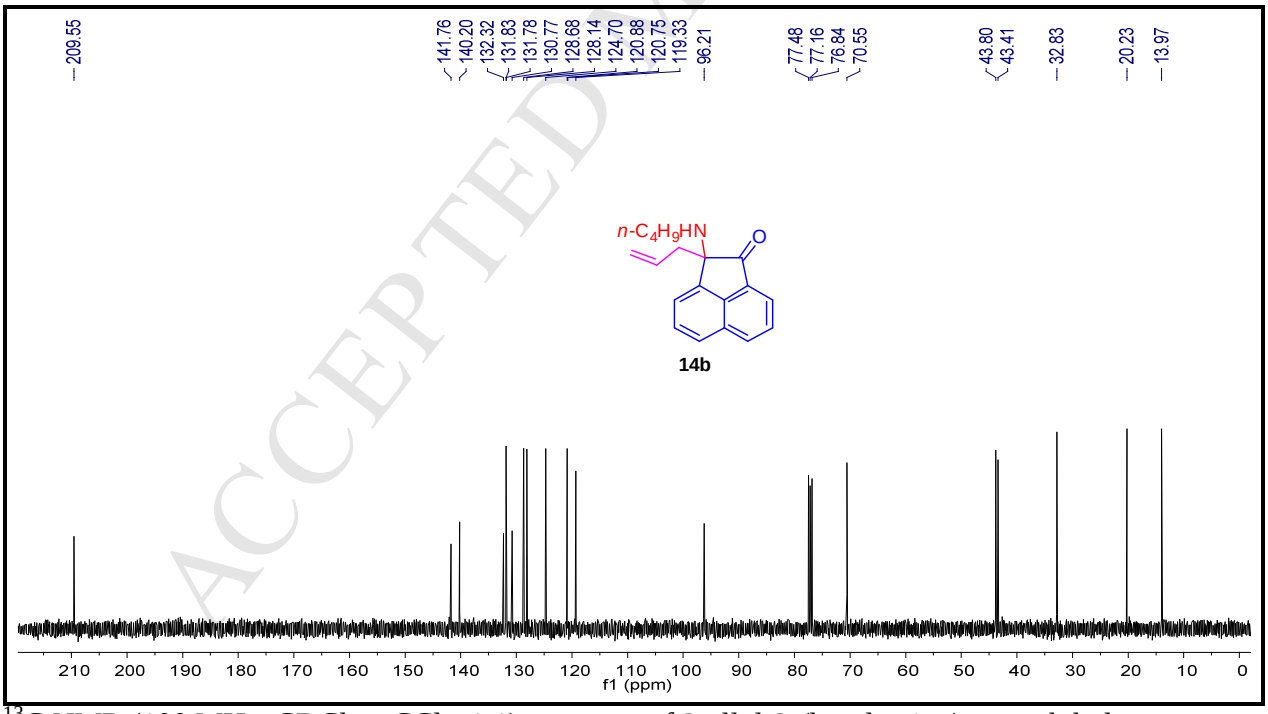
DEPT-135 NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-(benzylamino)acenaphthylen-1(2*H*)-one (**14a**).



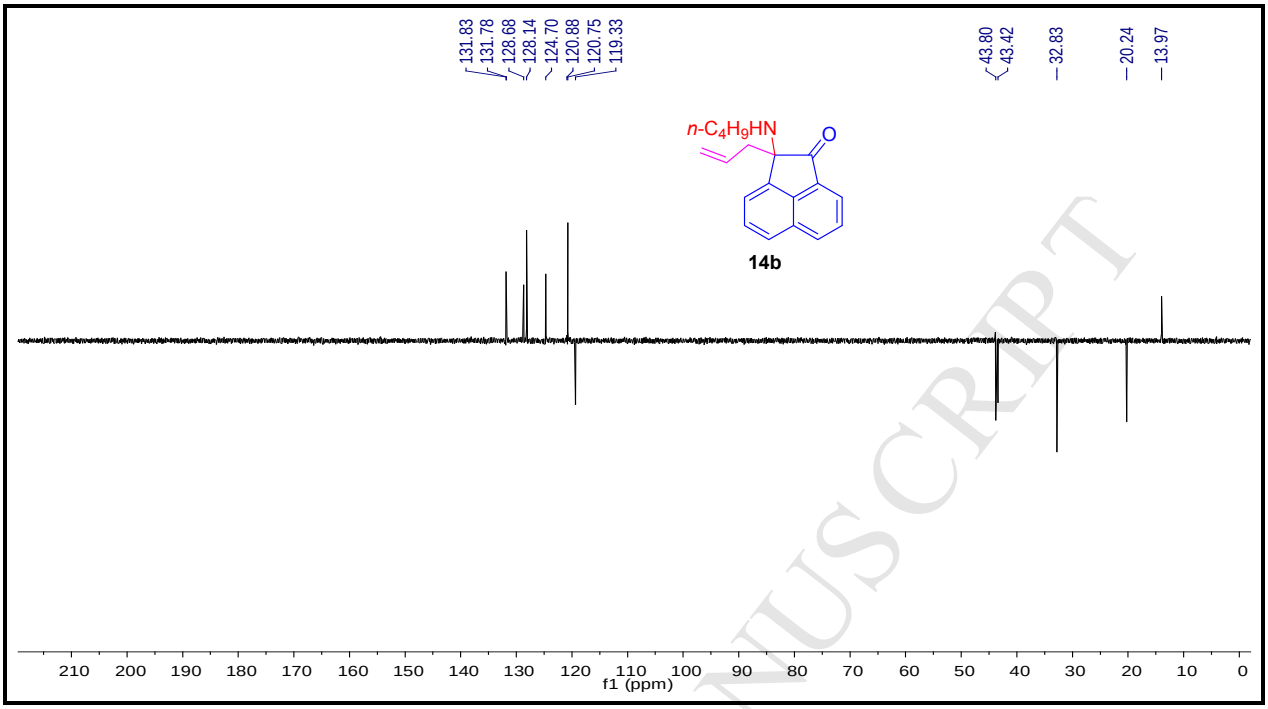
HRMS spectrum of 2-allyl-2-(benzylamino)acenaphthylen-1(2*H*)-one (**14a**).



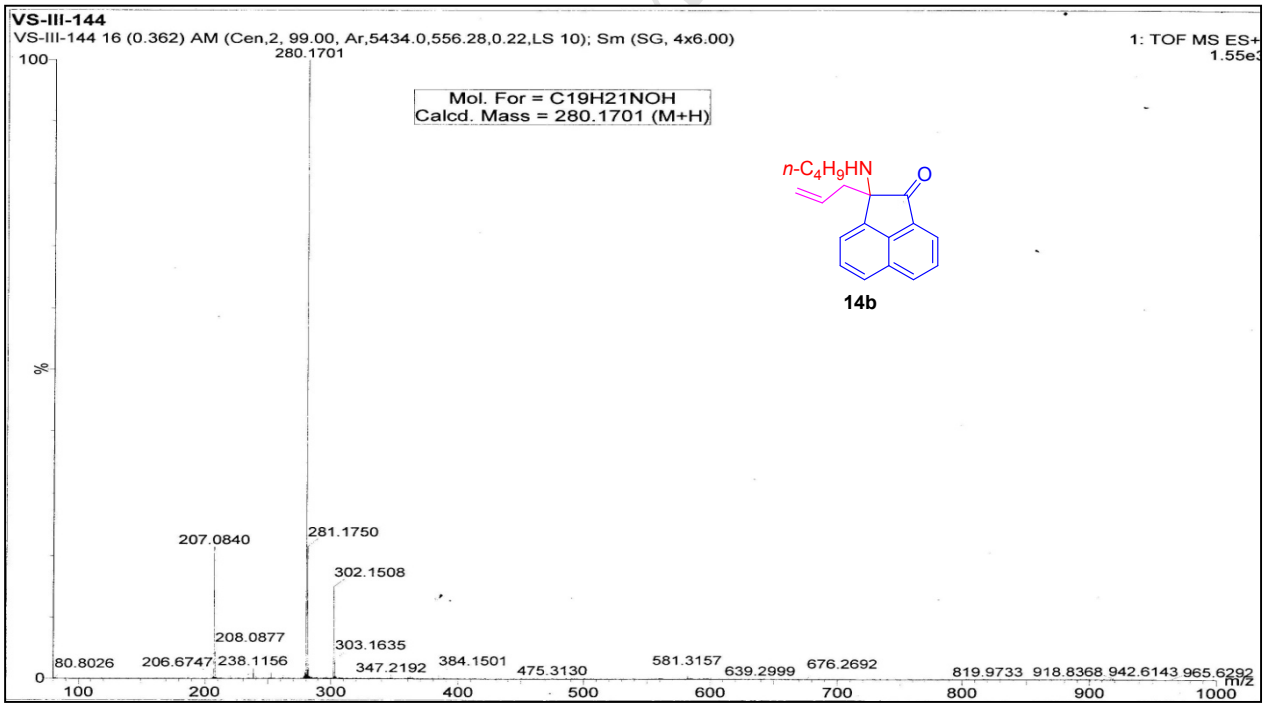
^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-(butylamino)acenaphthylen-1(2*H*)-one (**14b**).



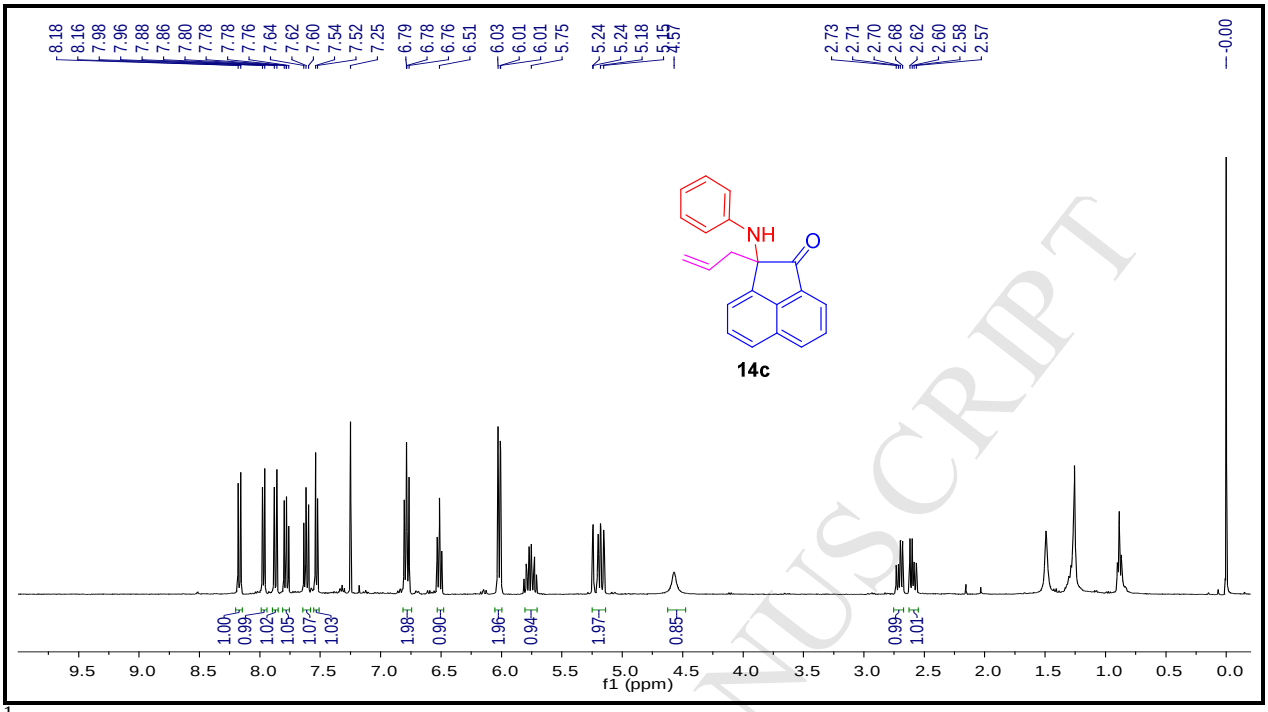
^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-(butylamino)acenaphthylen-1(2*H*)-one (**14b**).



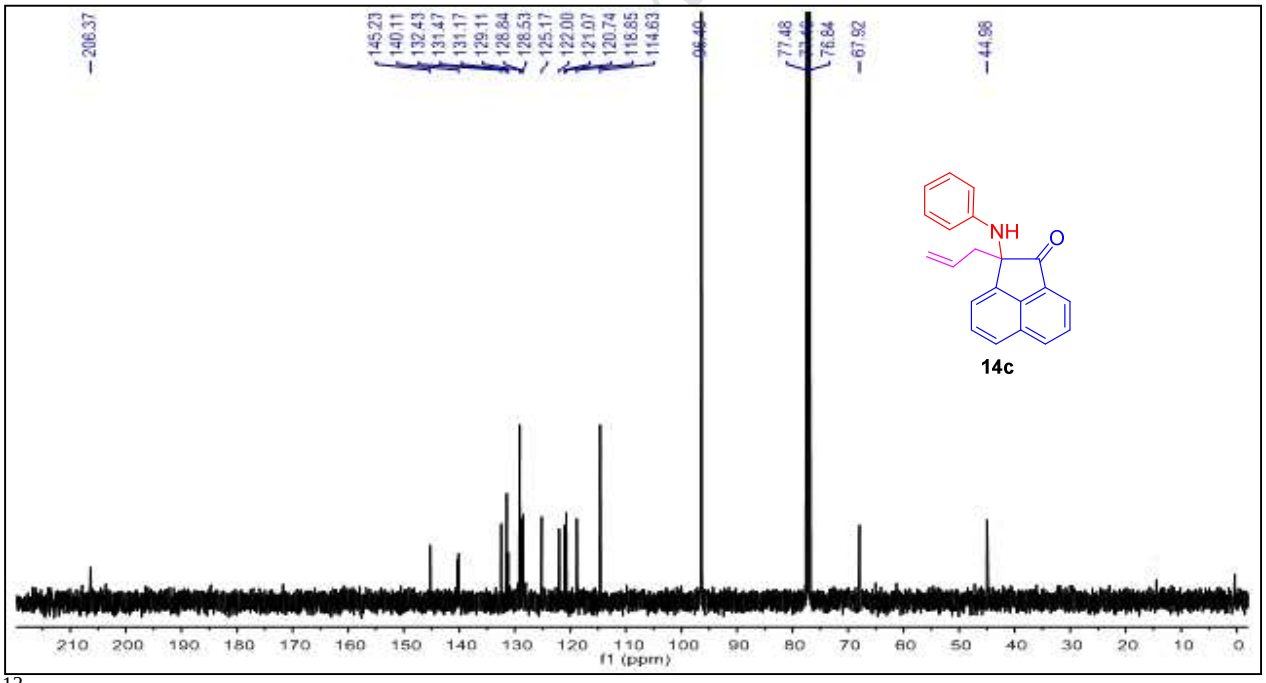
DEPT-135 NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-(butylamino)acenaphthylen-1(2*H*)-one (**14b**).



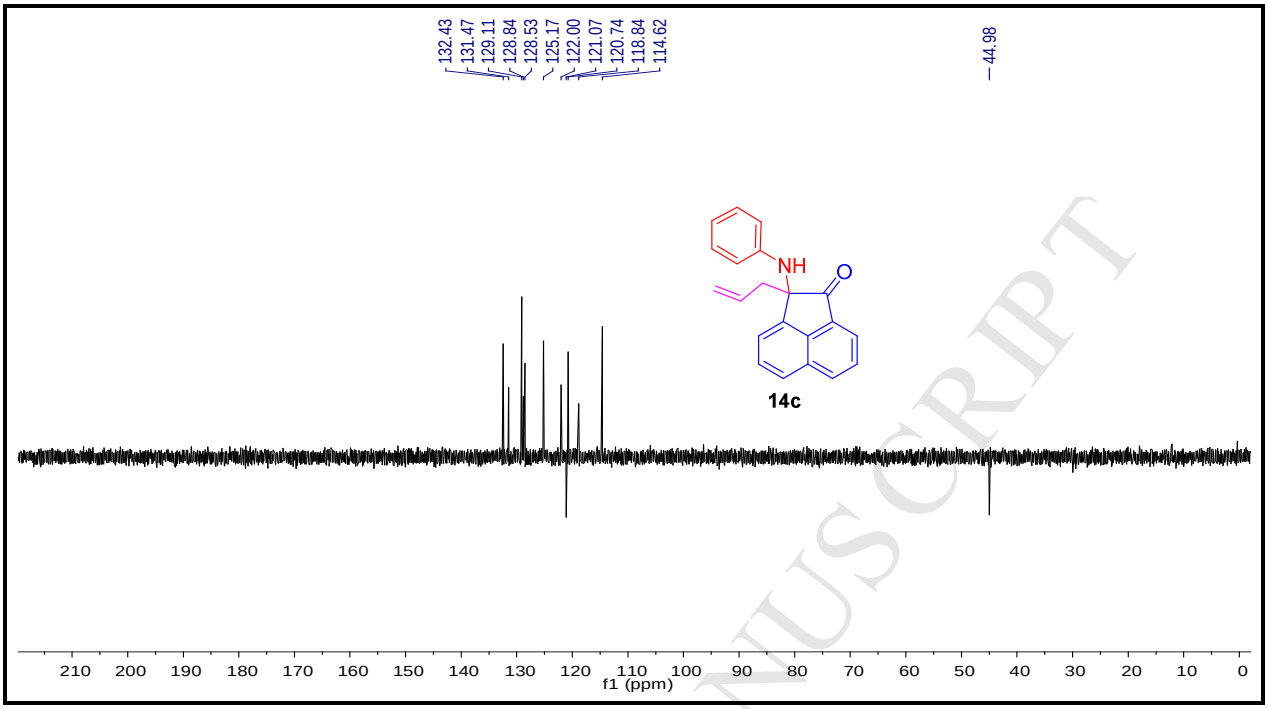
HRMS spectrum of 2-allyl-2-(butylamino)acenaphthylen-1(2*H*)-one (**14b**).



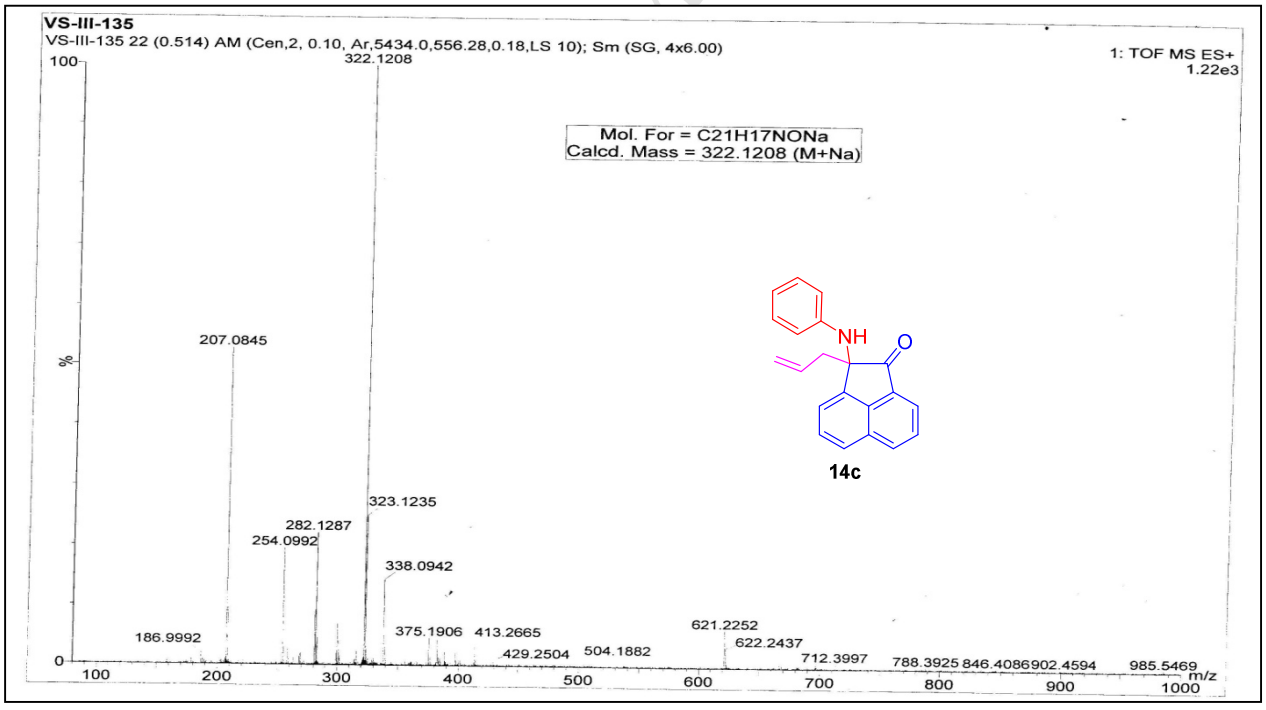
^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-(phenylamino)acenaphthylen-1(2*H*)-one (**14c**).



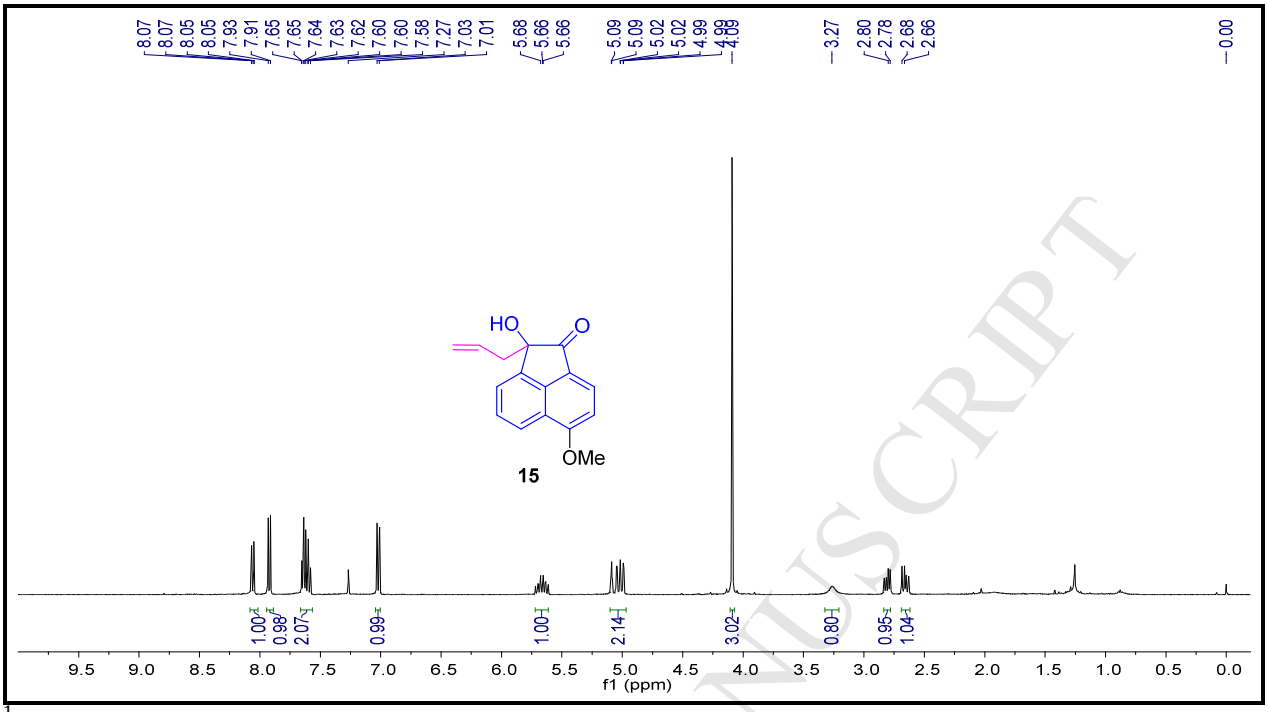
^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-(phenylamino)acenaphthylen-1(2*H*)-one (**14c**).



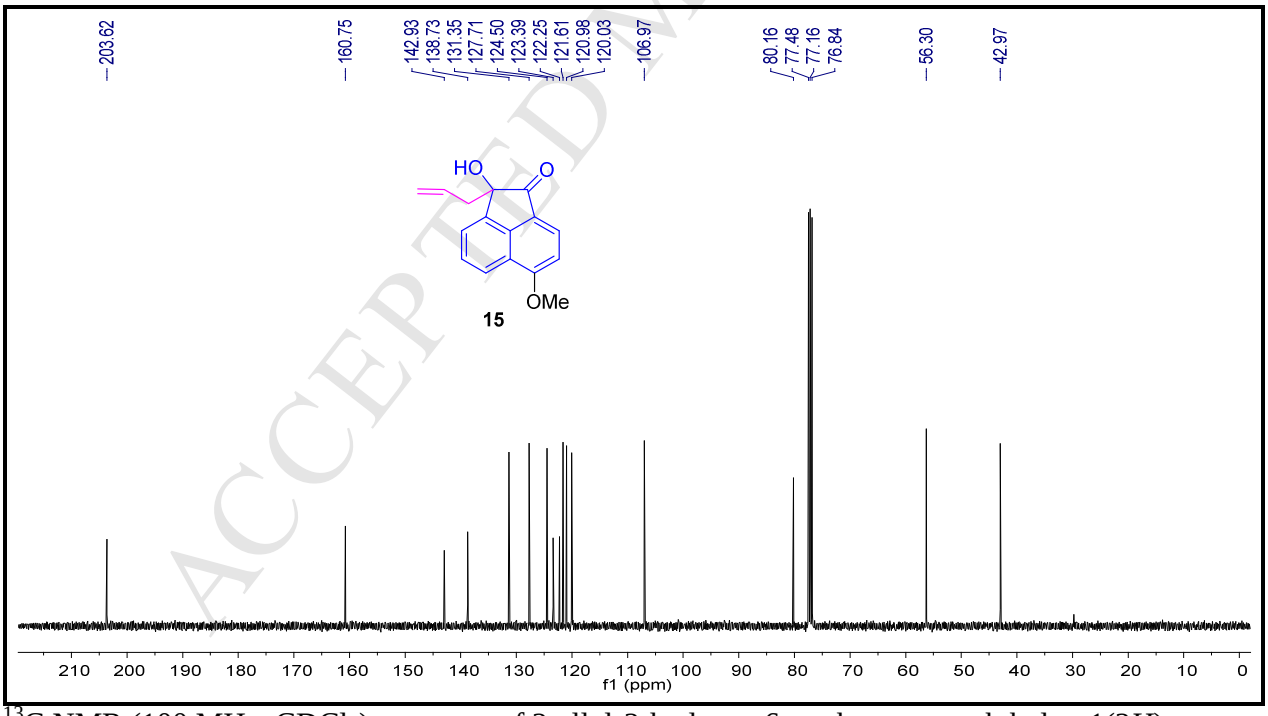
DEPT-135 NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-(phenylamino)acenaphthylen-1(2*H*)-one (**14c**).



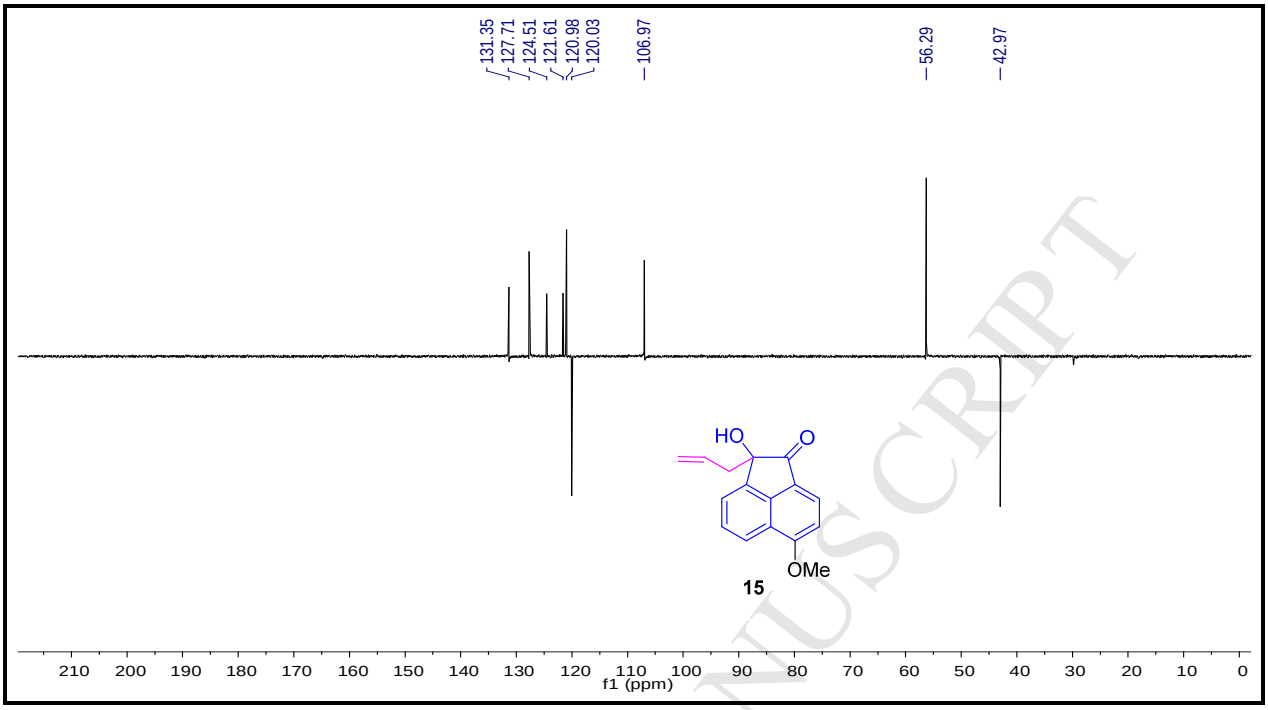
HRMS spectrum of 2-allyl-2-(phenylamino)acenaphthylen-1(2*H*)-one (**14c**).



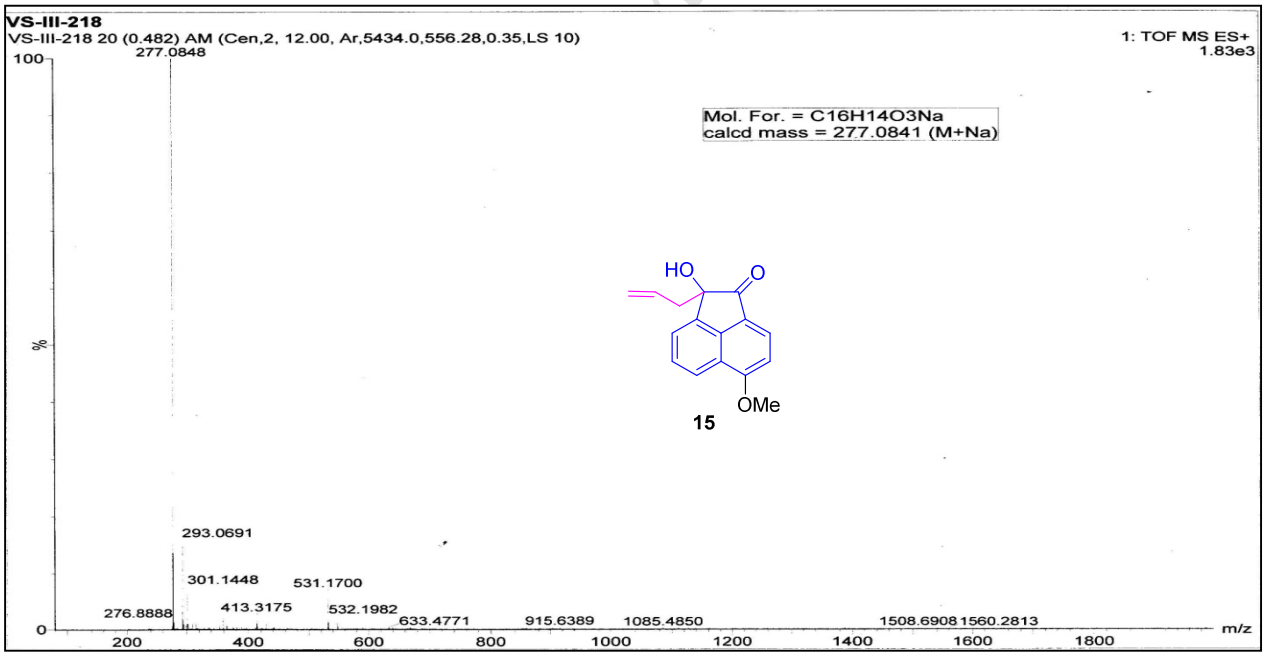
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 2-allyl-2-hydroxy-6-methoxyacenaphthylen-1(2*H*)-one (**15**).



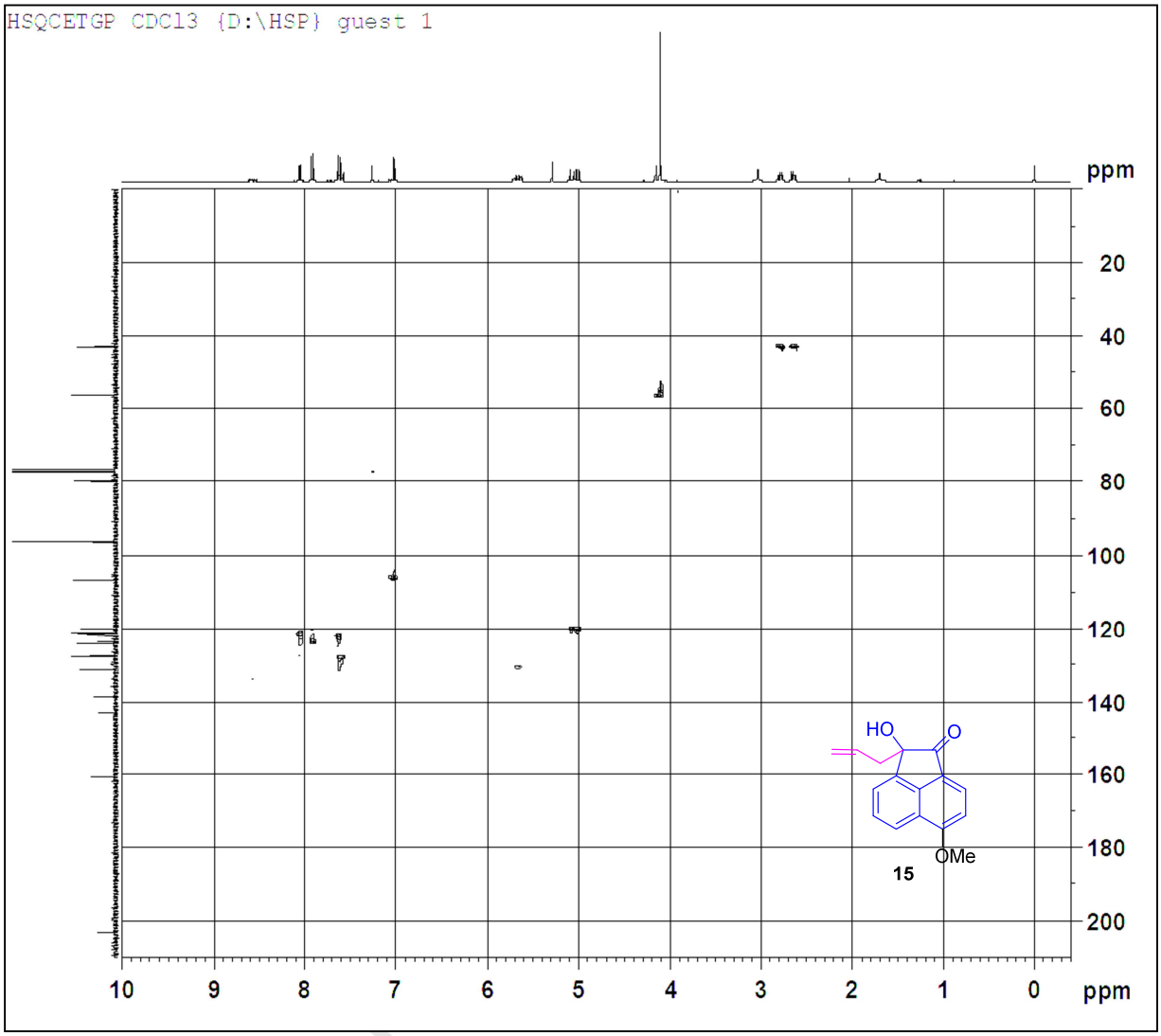
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 2-allyl-2-hydroxy-6-methoxyacenaphthylen-1(2*H*)-one (**15**).



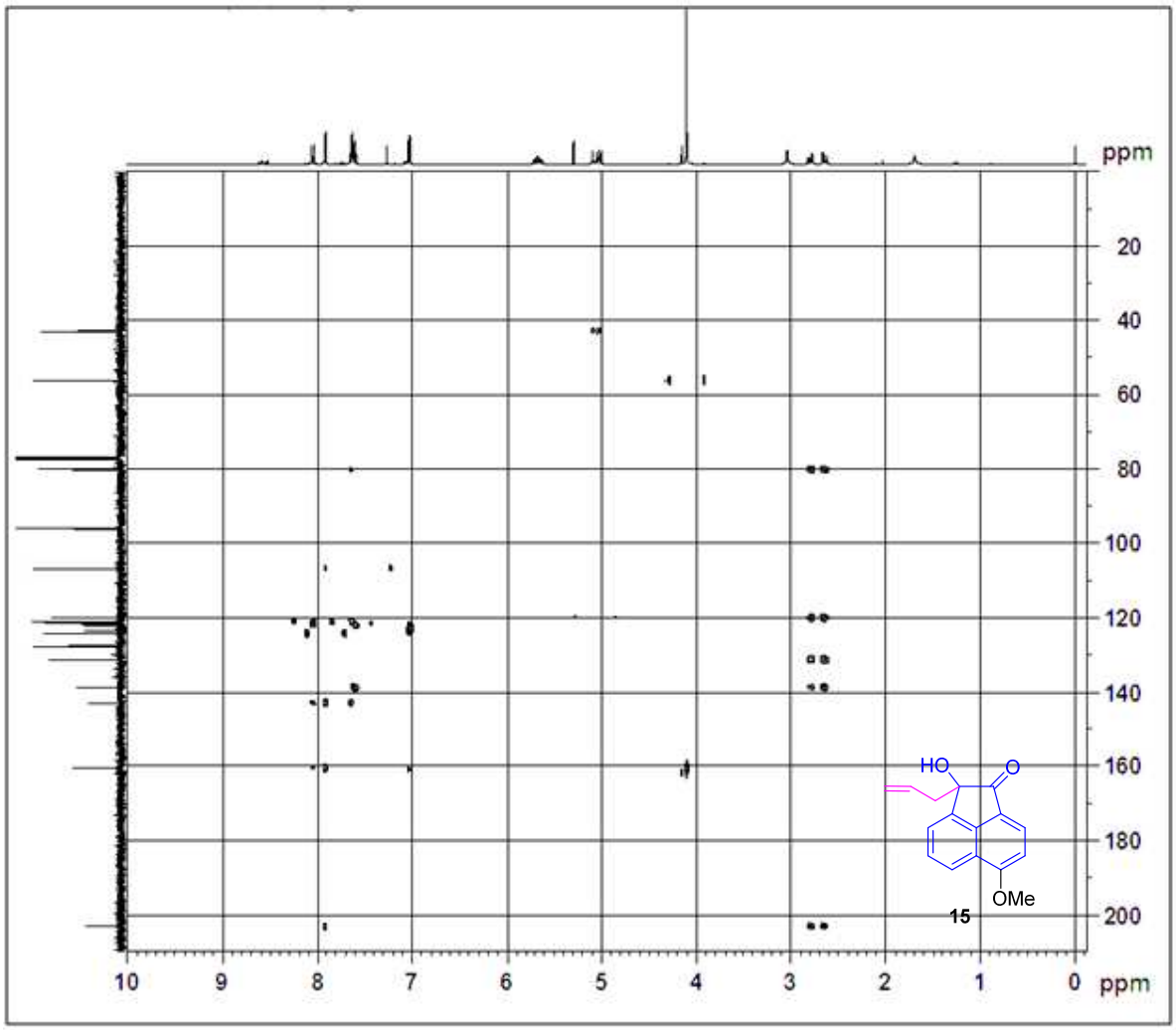
DEPT-135 NMR (100 MHz, $CDCl_3$) spectrum of 2-allyl-2-hydroxy-6-methoxyacenaphthylen-1(2*H*)-one (**15**).



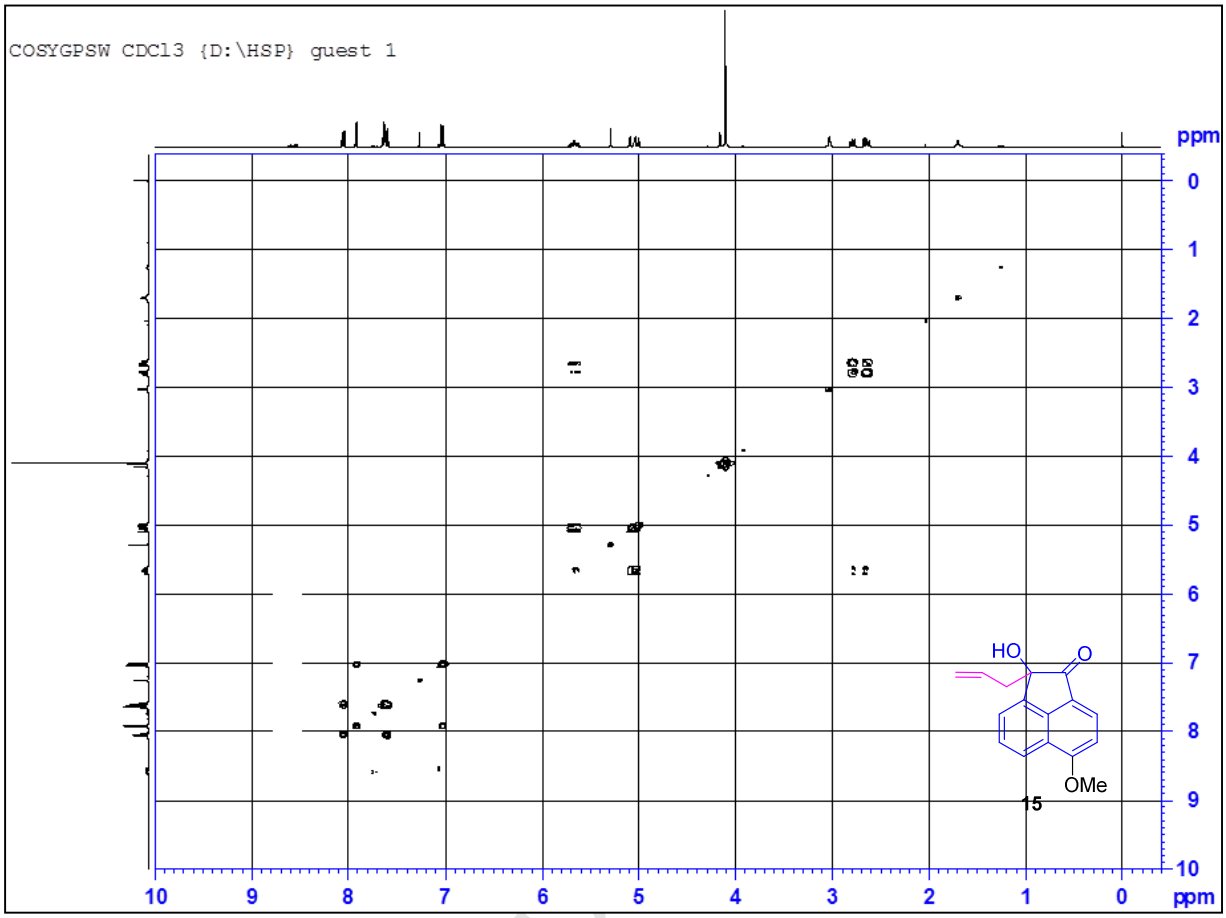
HRMS spectrum of 2-allyl-2-hydroxy-6-methoxyacenaphthylen-1(2*H*)-one (**15**).



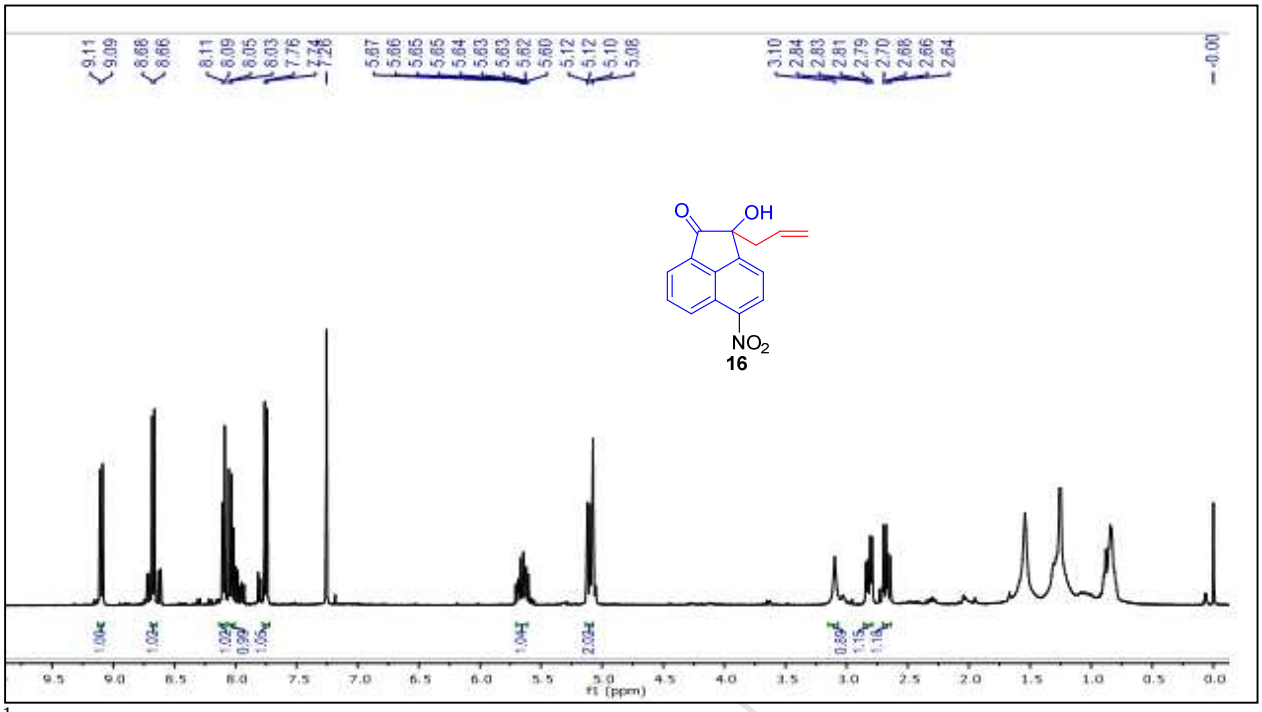
HSQC spectrum of 2-allyl-2-hydroxy-6-methoxyacenaphthylen-1(2*H*)-one (**15**).



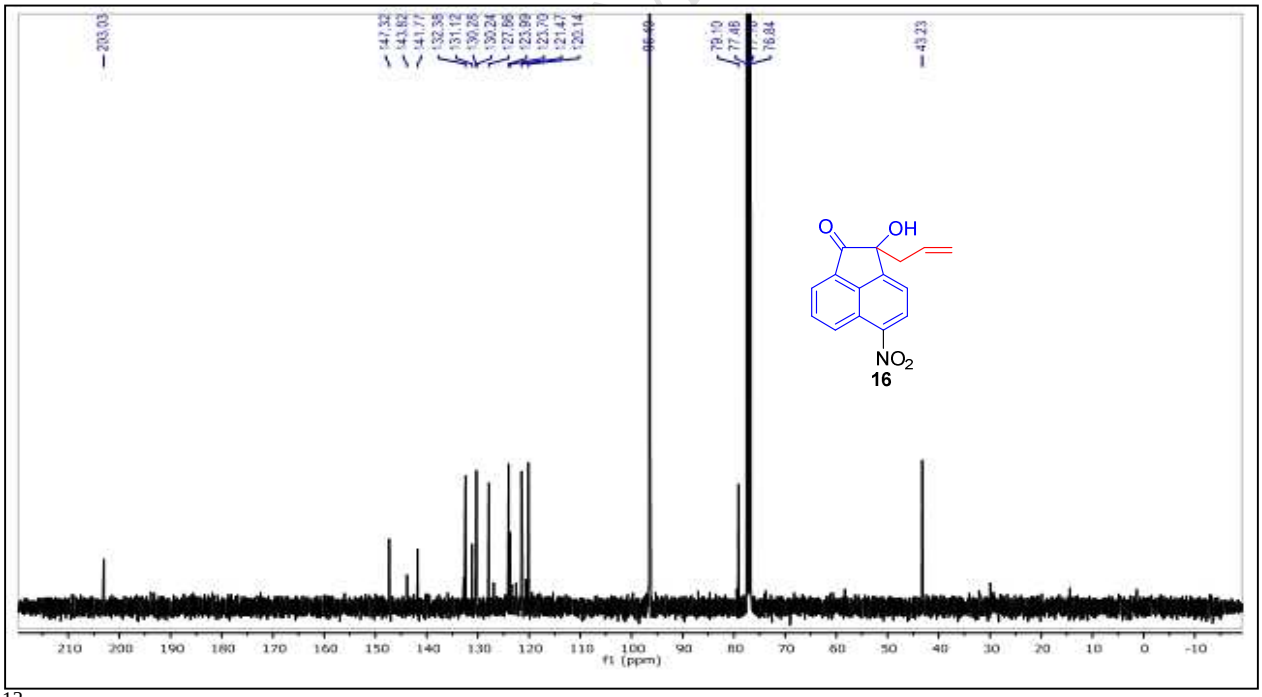
HMBC spectrum of 2-allyl-2-hydroxy-6-methoxyacenaphthylen-1(2*H*)-one (**15**).



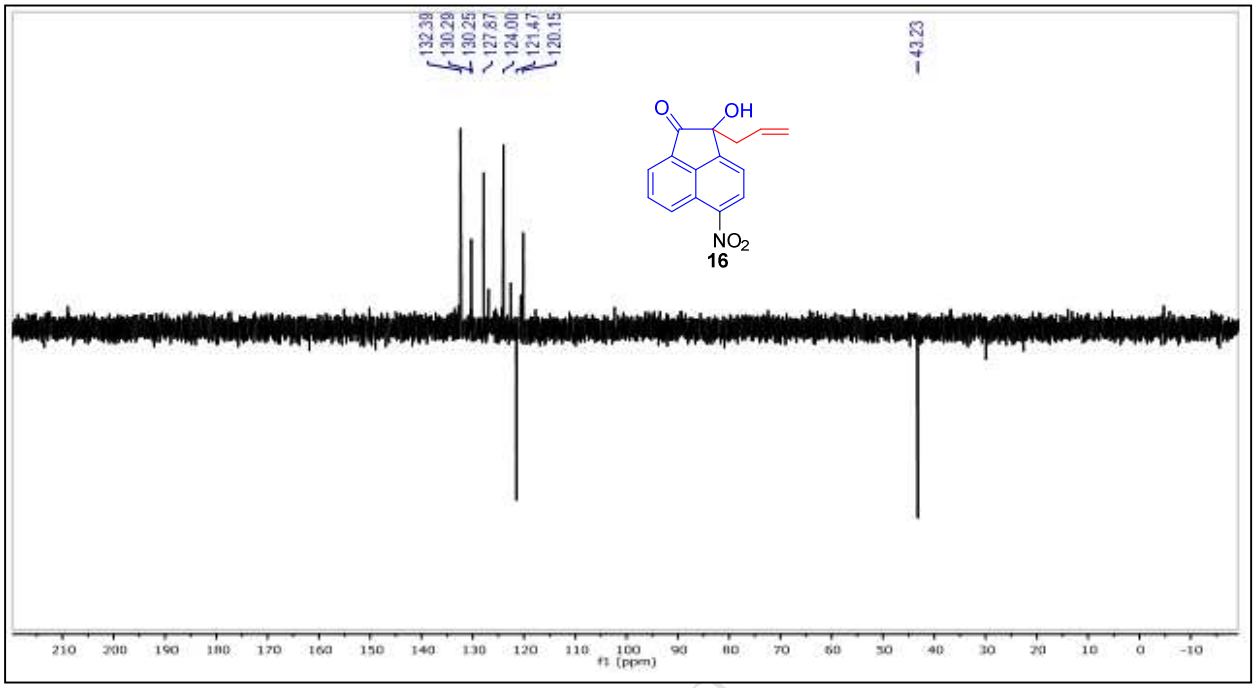
COSY spectrum of 2-allyl-2-hydroxy-6-methoxyacenaphthylen-1(2*H*)-one (**15**).



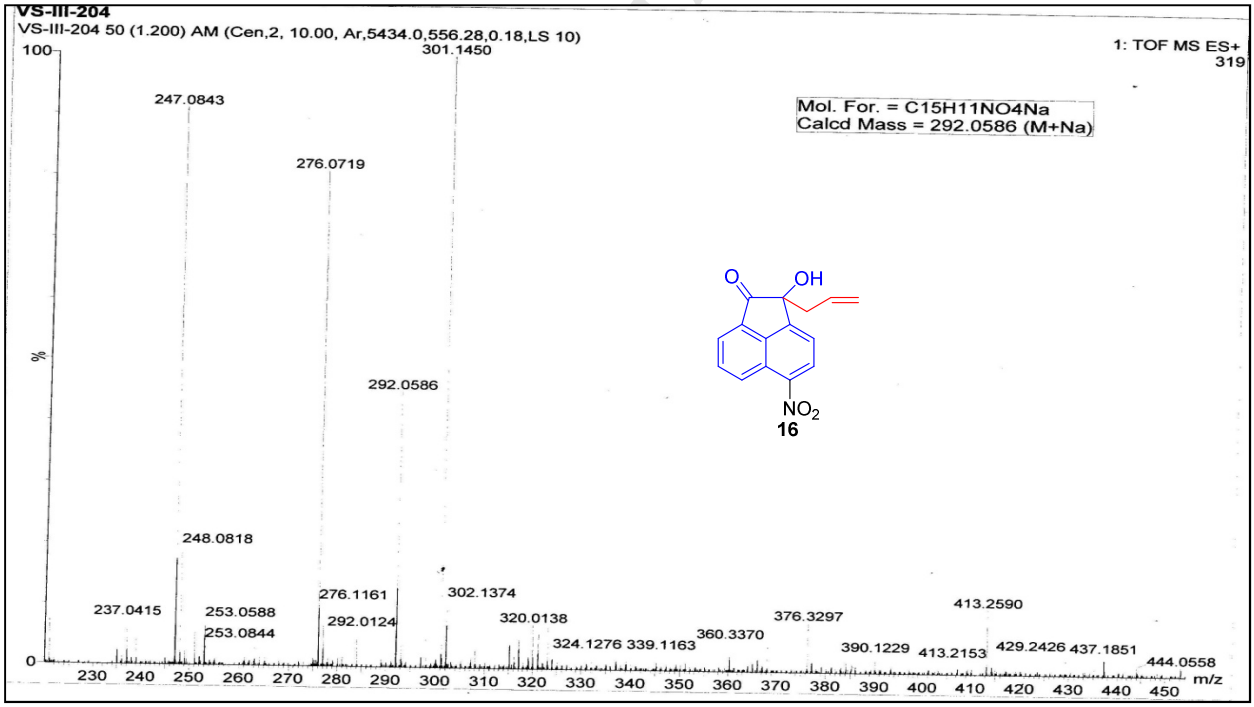
^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-hydroxy-5-nitroacenaphthylen-1(2*H*)-one (**16**).



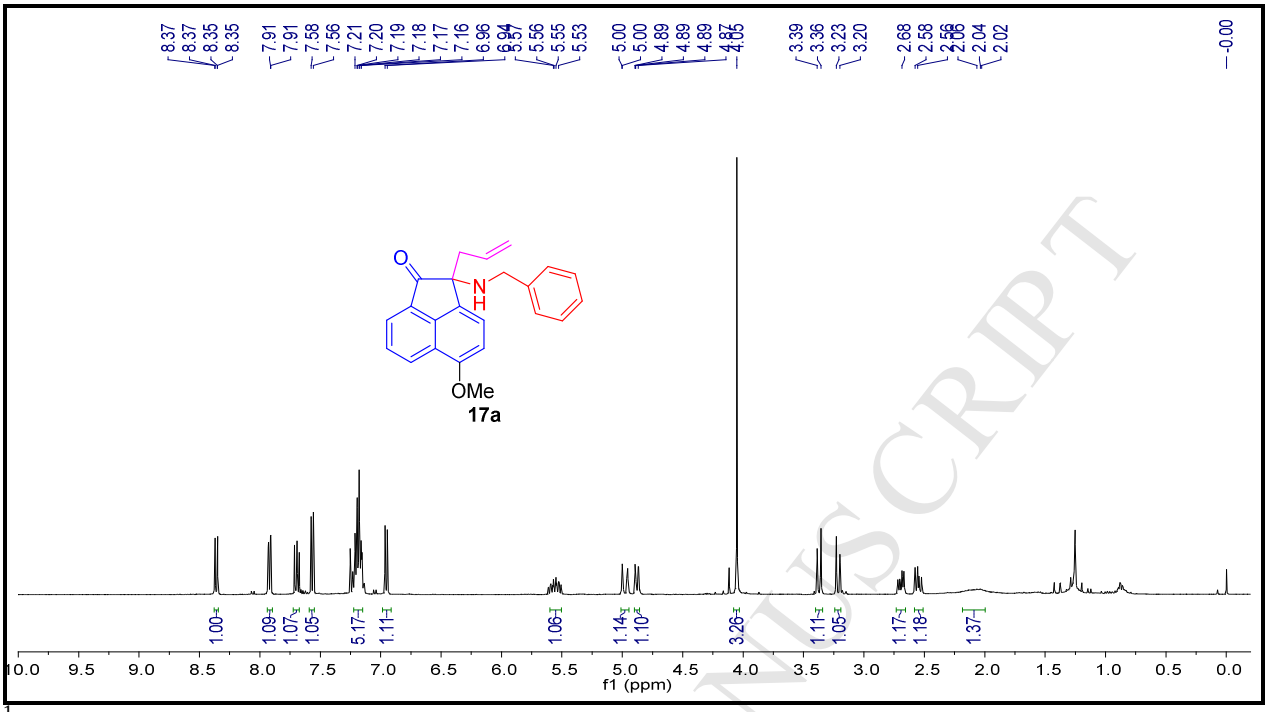
^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-hydroxy-5-nitroacenaphthylen-1(2*H*)-one (**16**).



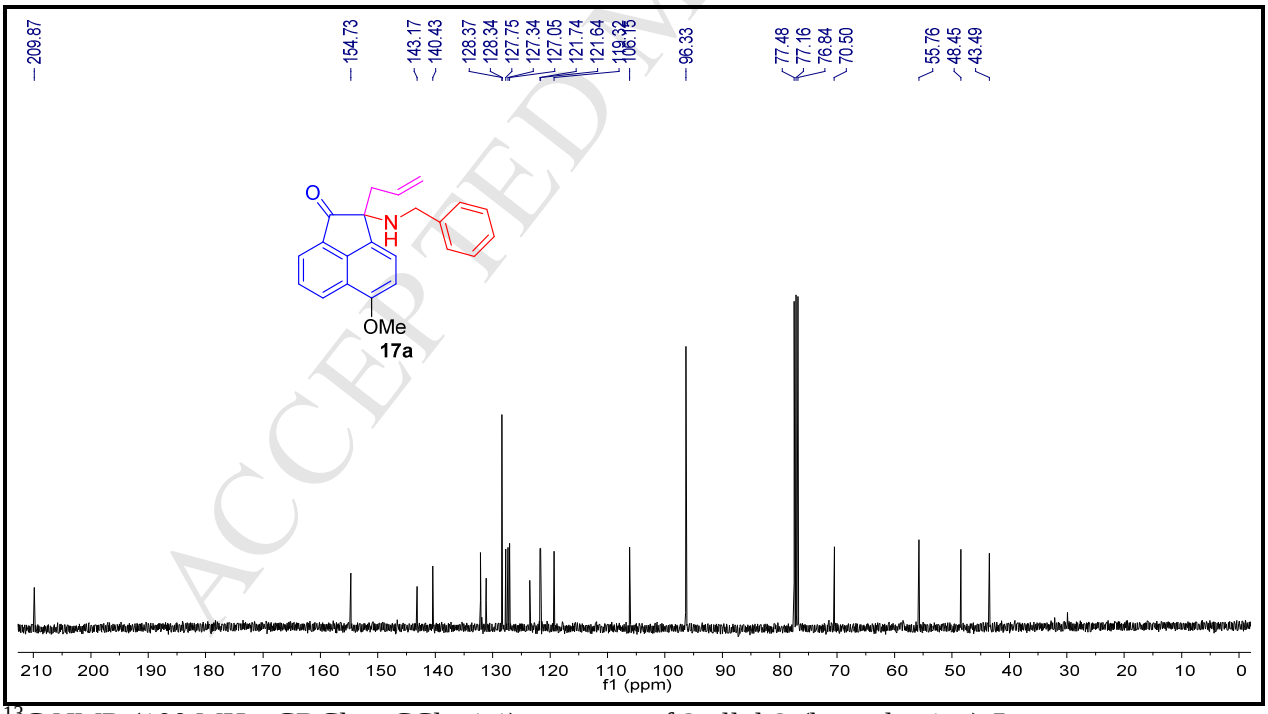
DEPT-135 NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-hydroxy-5-nitroacenaphthylen-1(2*H*)-one (**16**).



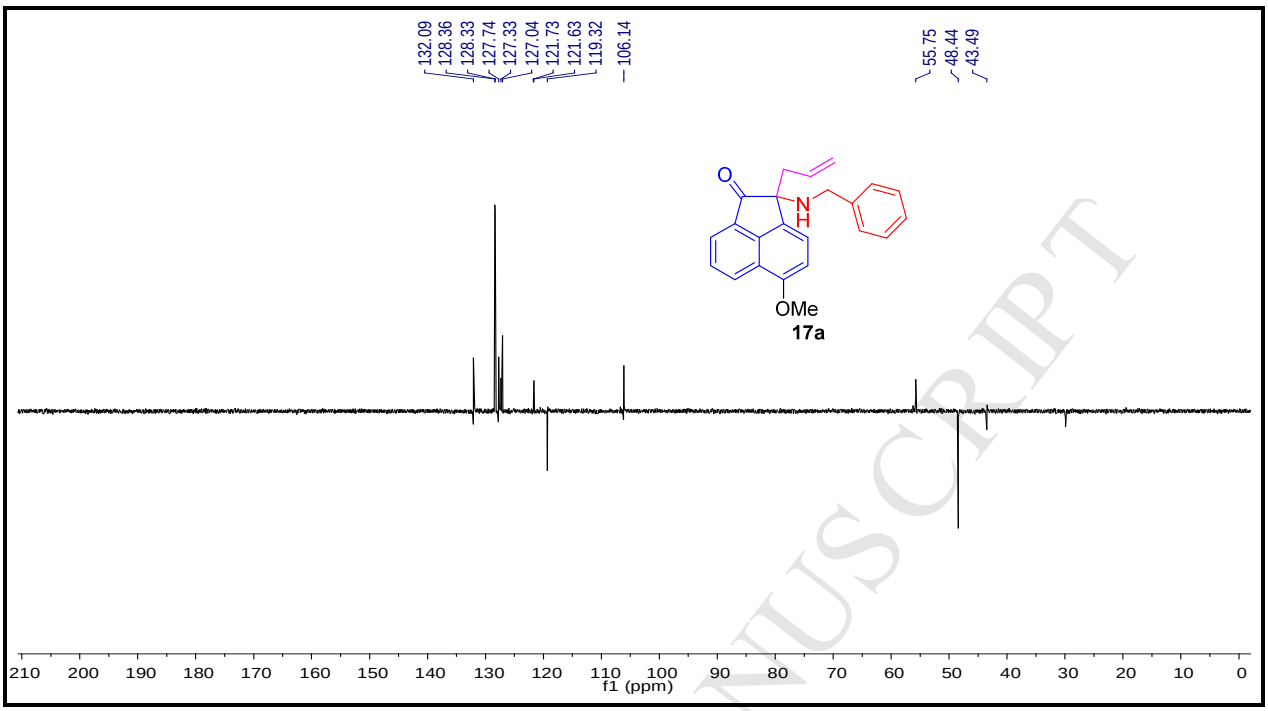
HRMS spectrum of 2-allyl-2-hydroxy-5-nitroacenaphthylen-1(2*H*)-one (**16**).



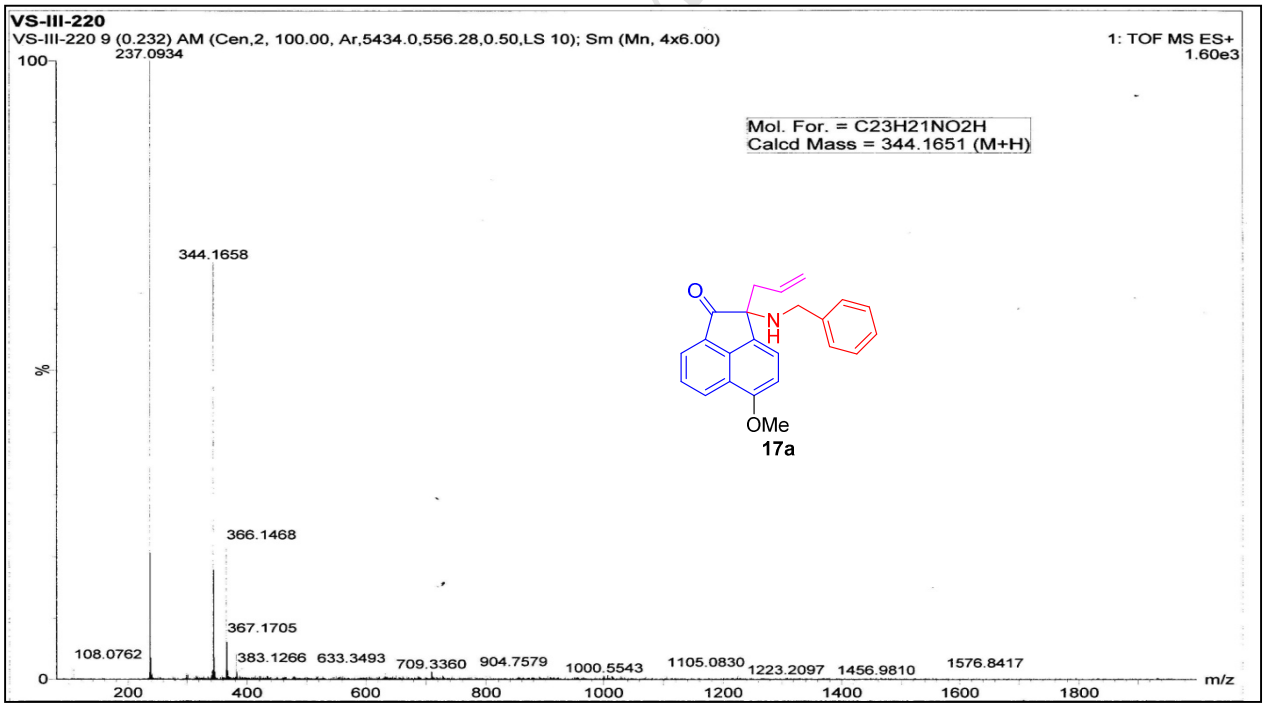
^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-(benzylamino)-5-methoxyacenaphthylen-1(2*H*)-one (**17a**).



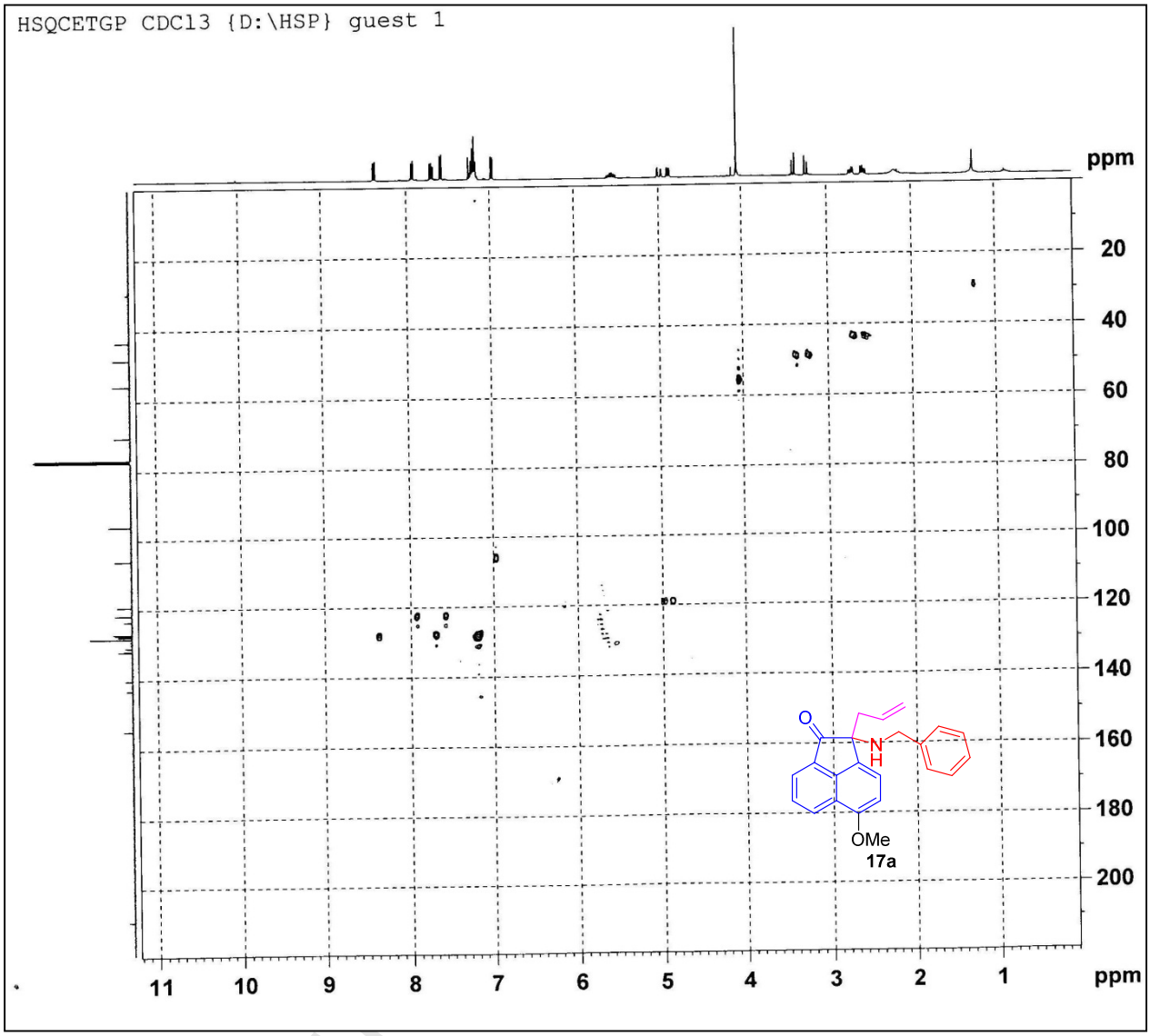
^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-(benzylamino)-5-methoxyacenaphthylen-1(2*H*)-one (**17a**).



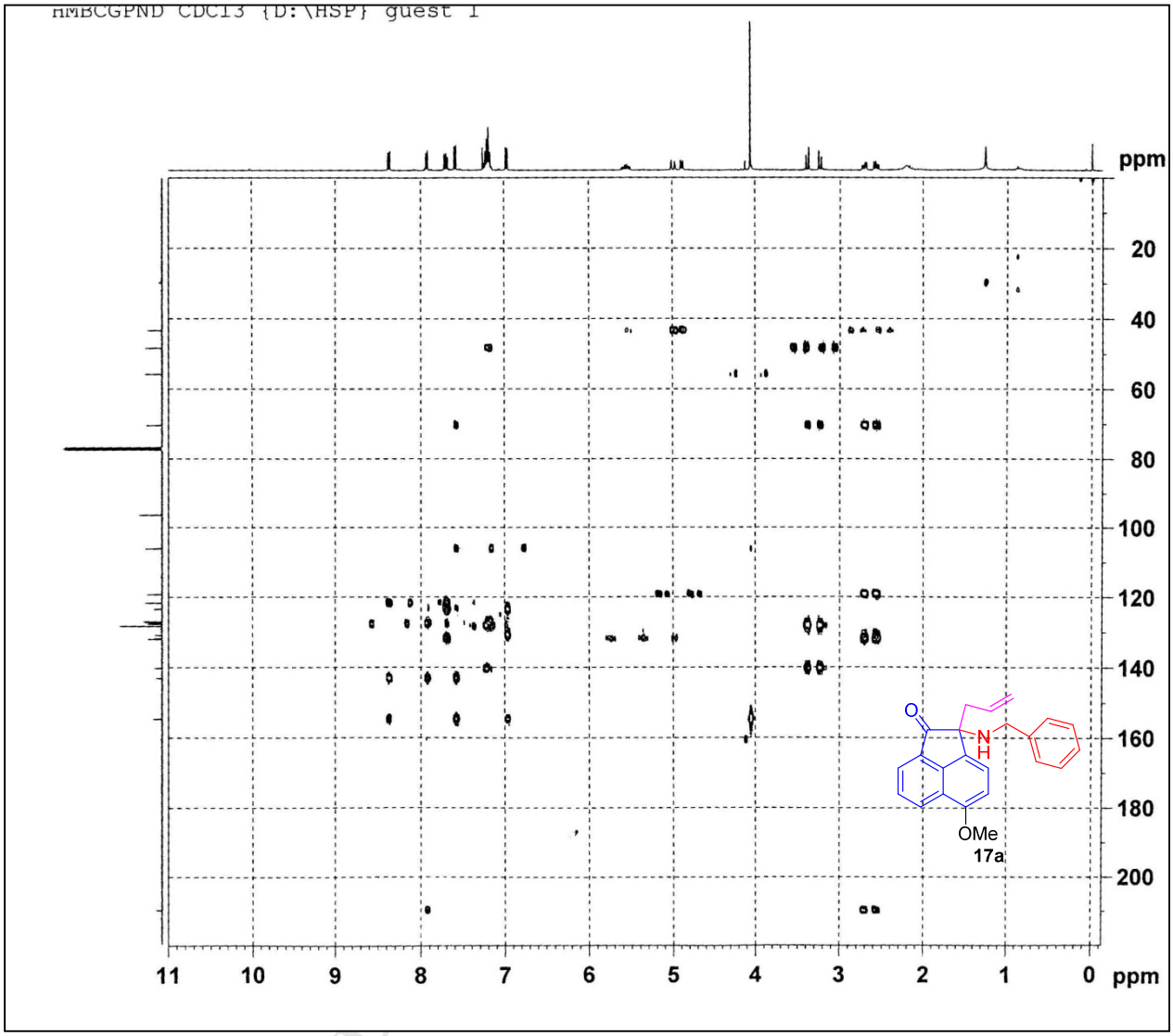
DEPT-135 NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-(benzylamino)-5-methoxyacenaphthylen-1(2*H*)-one (**17a**).



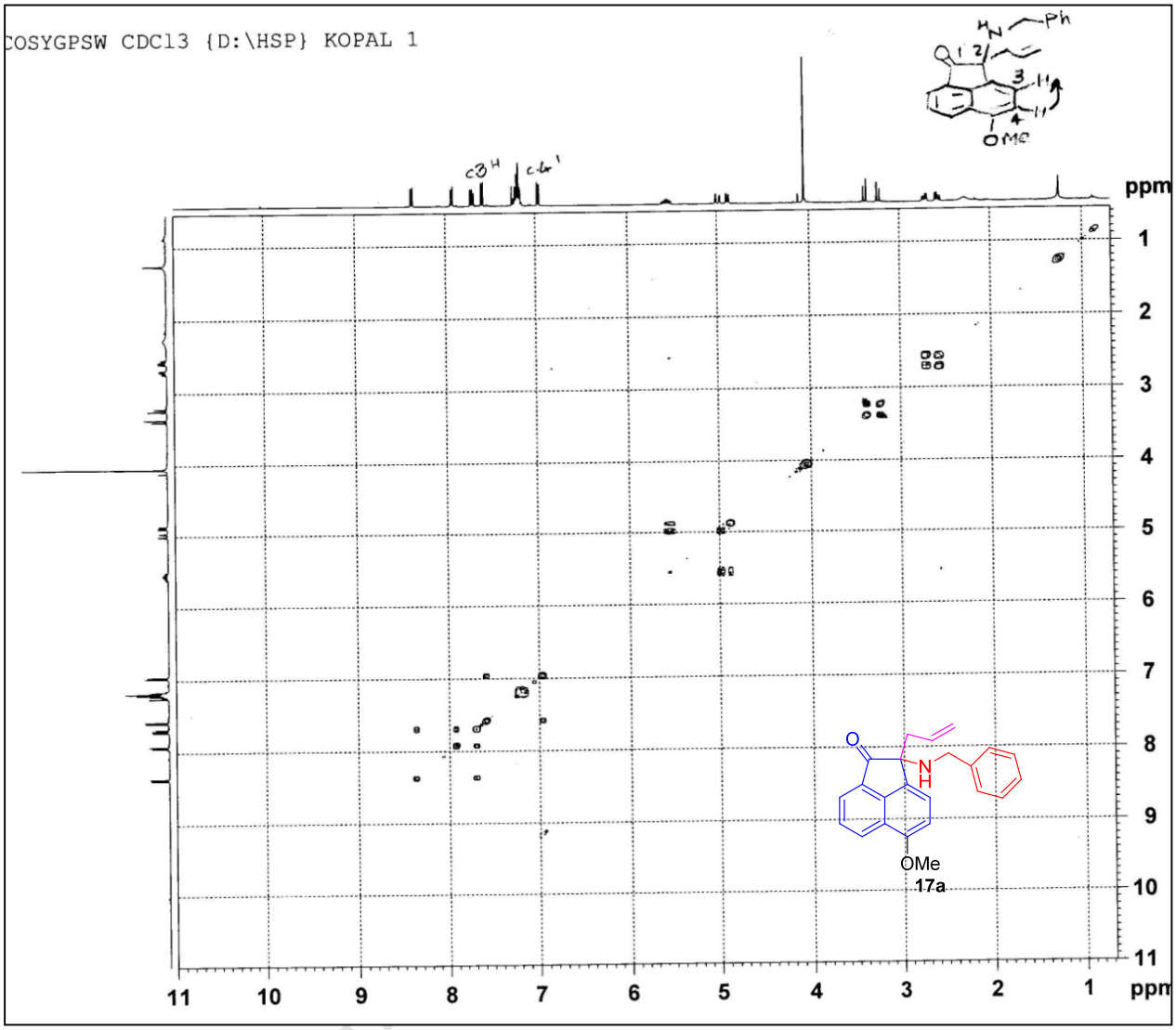
HRMS spectrum of 2-allyl-2-(benzylamino)-5-methoxyacenaphthylen-1(2*H*)-one (**17a**).



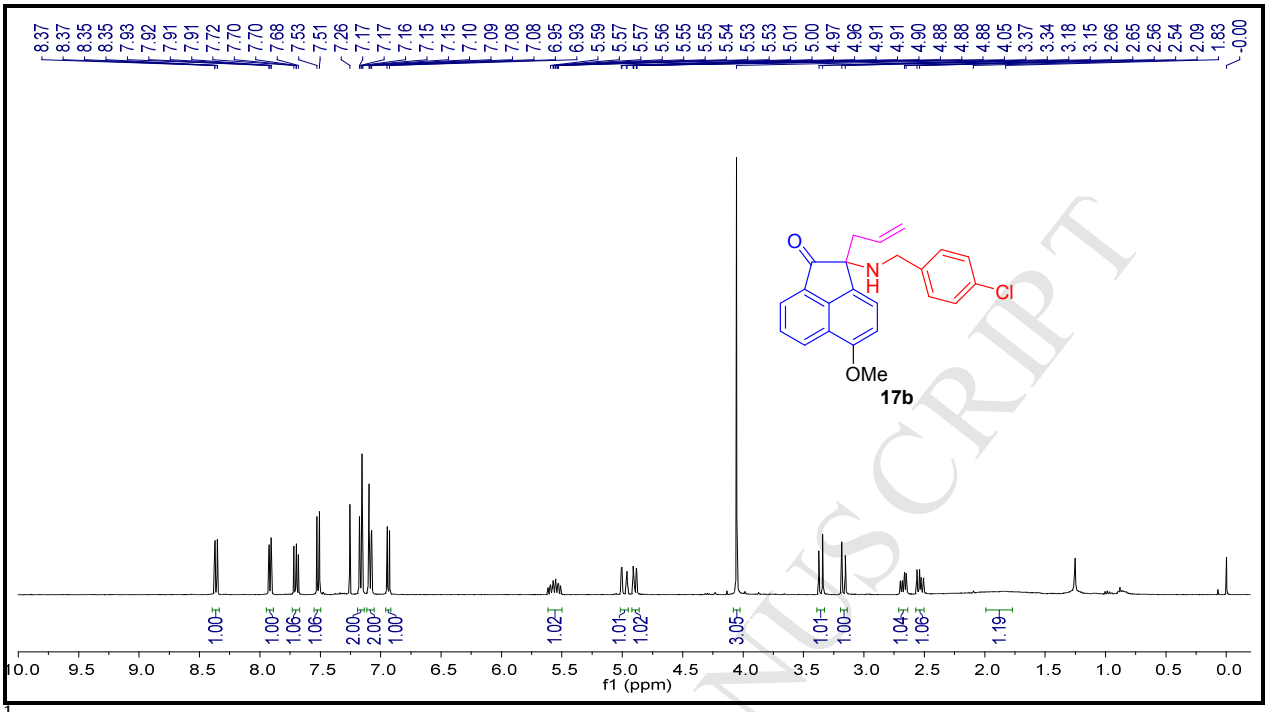
HSQC spectrum of 2-allyl-2-(benzylamino)-5-methoxyacenaphthylen-1(2*H*)-one (**17a**).



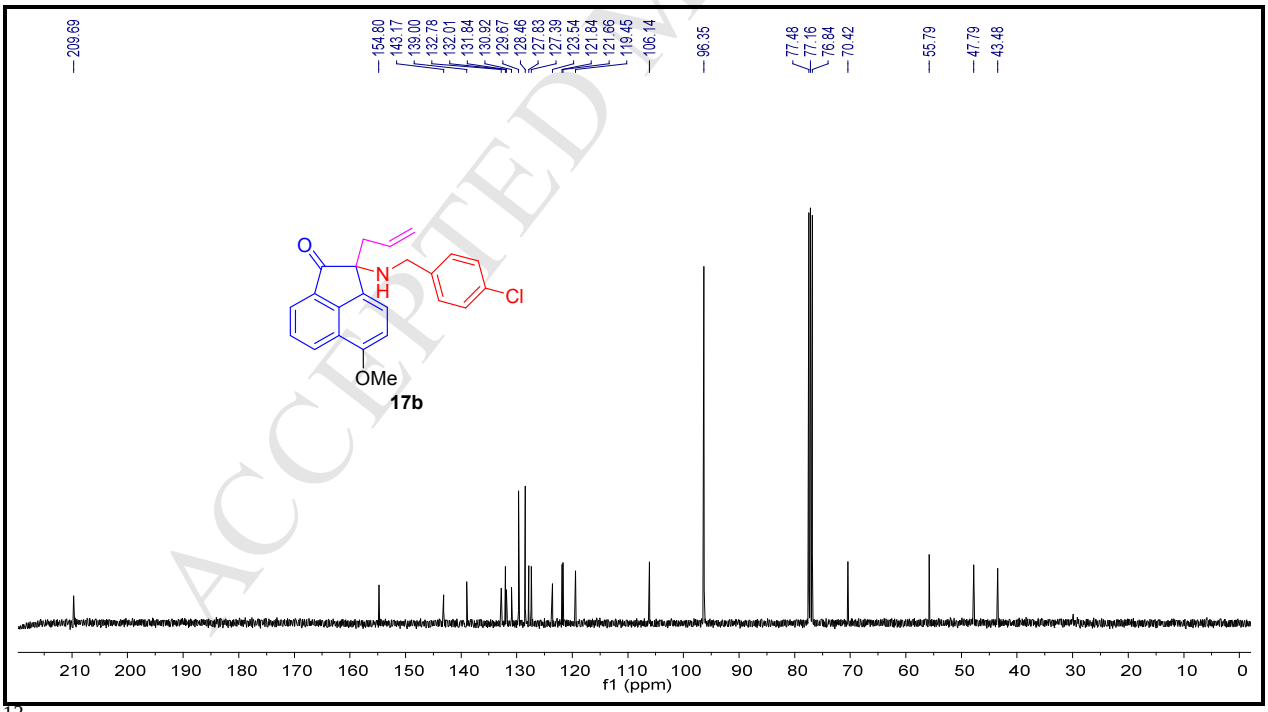
HMBC spectrum of 2-allyl-2-(benzylamino)-5-methoxyacenaphthylen-1(2*H*)-one (**17a**).



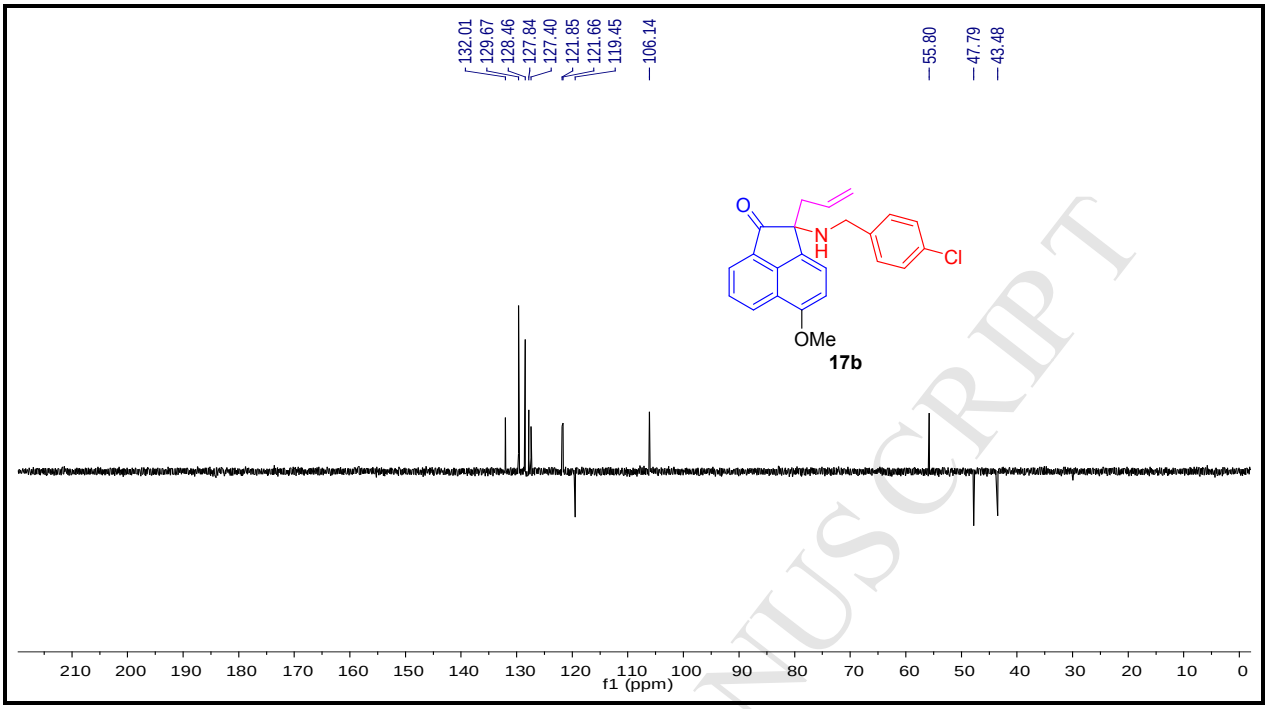
COSY spectrum of 2-allyl-2-(benzylamino)-5-methoxyacenaphthylen-1(2*H*)-one (**17a**).



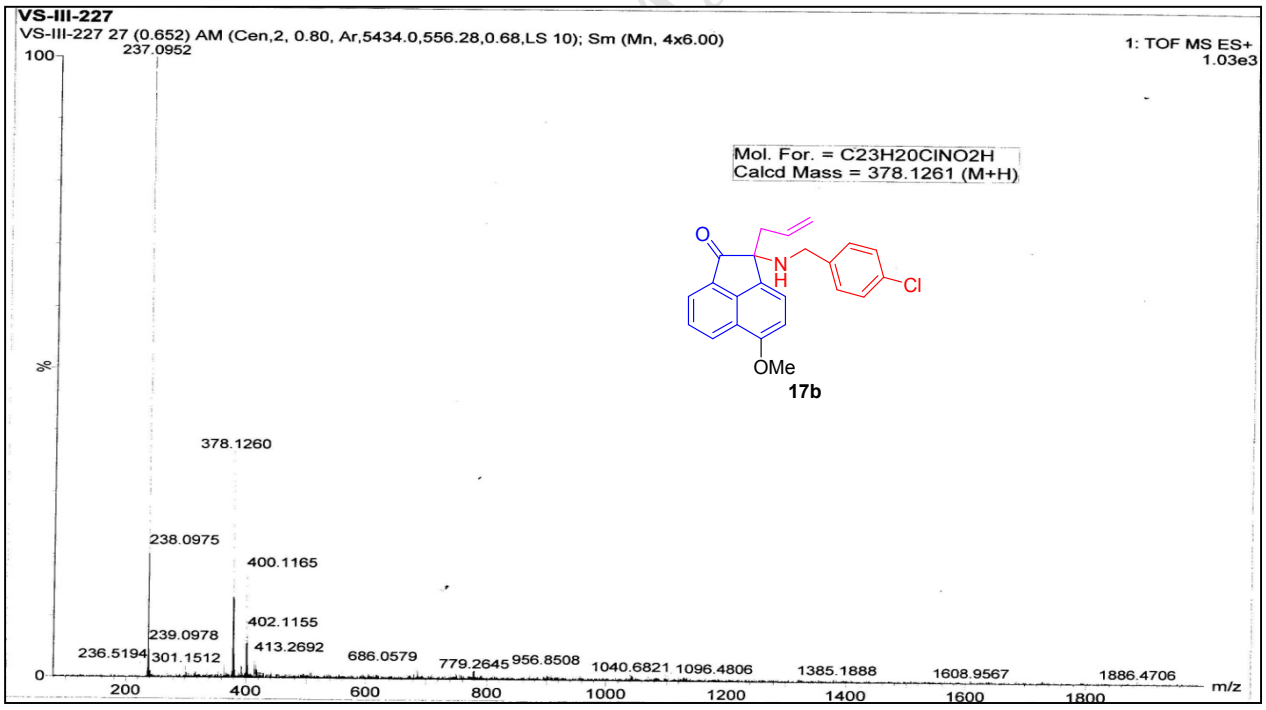
^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-((4-chlorobenzyl)amino)-5-methoxyacenaphthylen-1(2*H*)-one (**17b**).



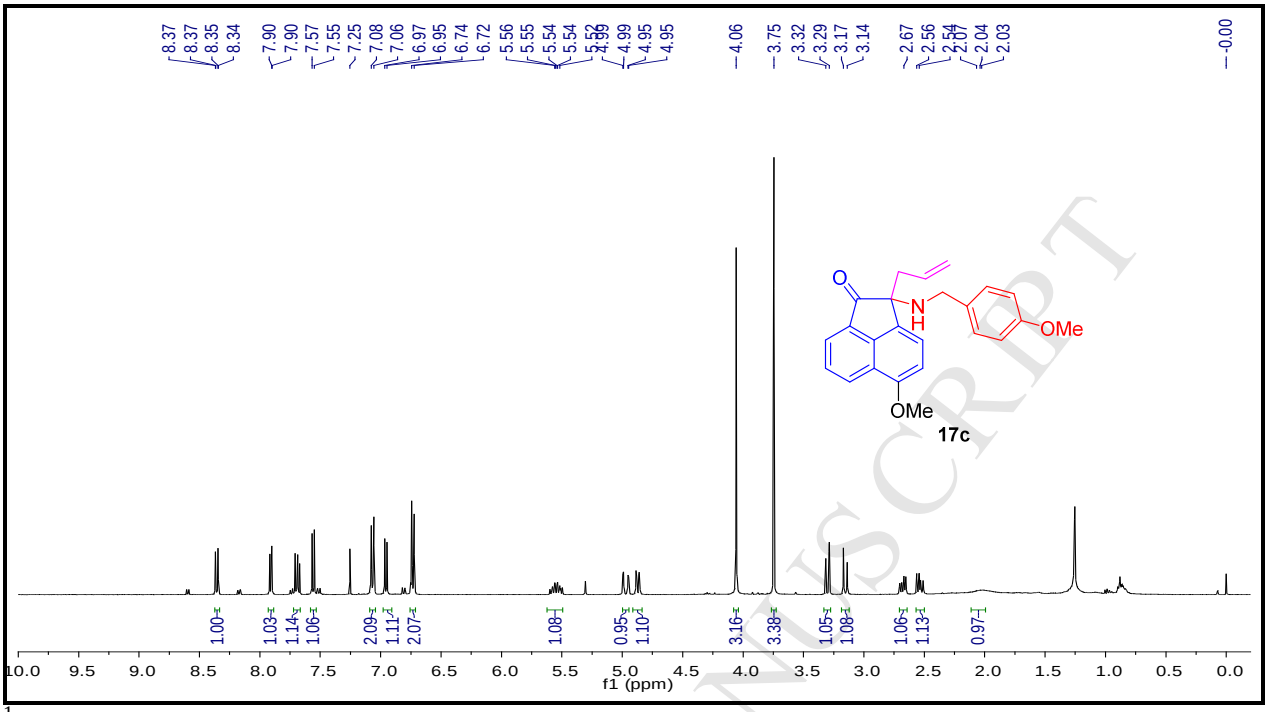
^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-((4-chlorobenzyl)amino)-5-methoxyacenaphthylen-1(2*H*)-one (**17b**).



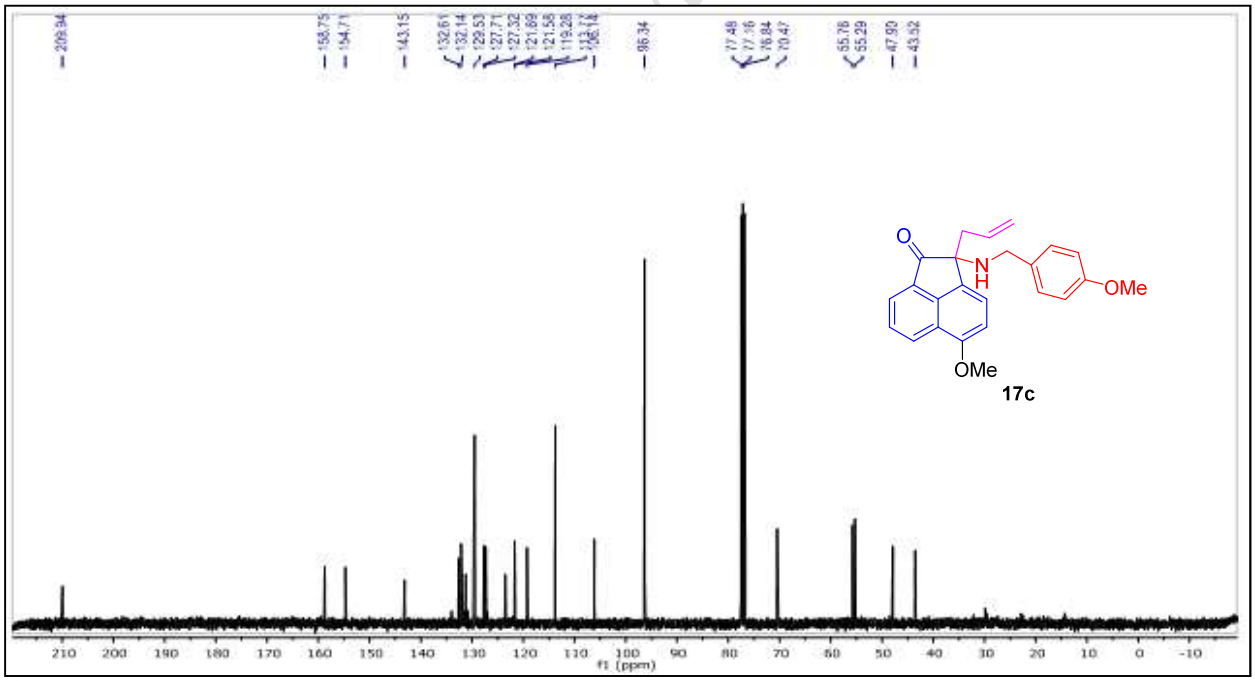
DEPT-135 NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-((4-chlorobenzyl)amino)-5-methoxyacenaphthylen-1(2*H*)-one (**17b**).



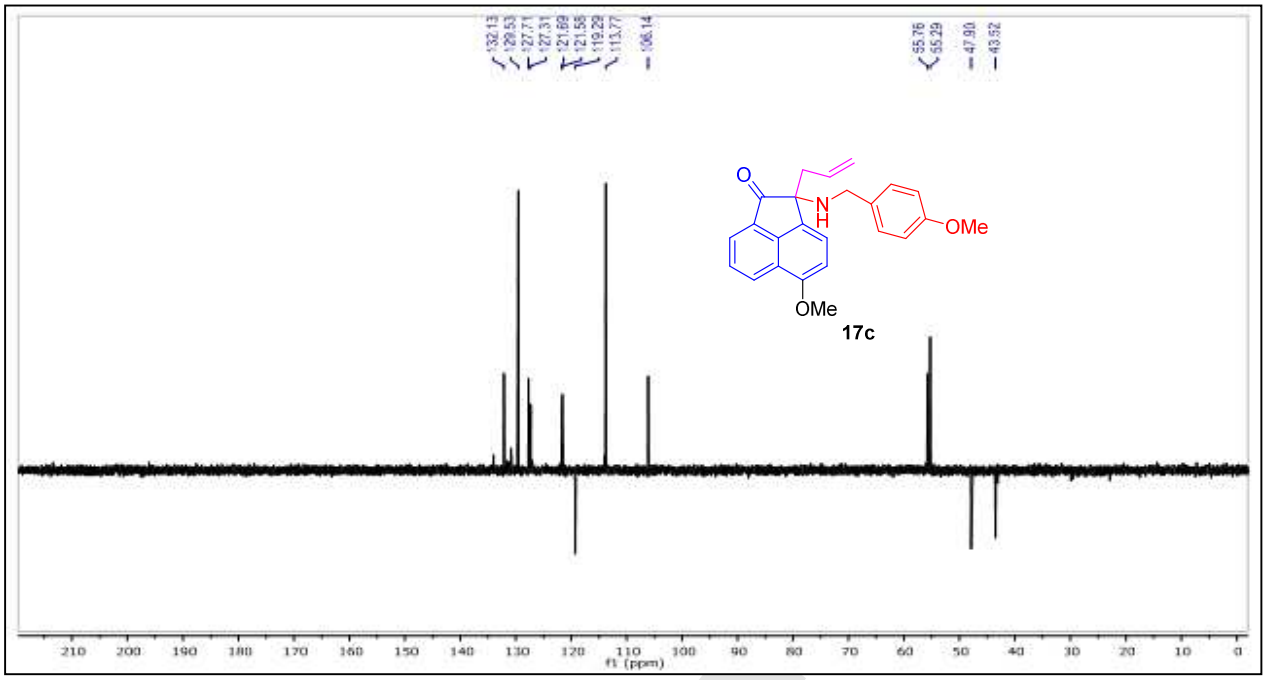
HRMS spectrum of 2-allyl-2-((4-chlorobenzyl)amino)-5-methoxyacenaphthylen-1(2*H*)-one (**17b**).



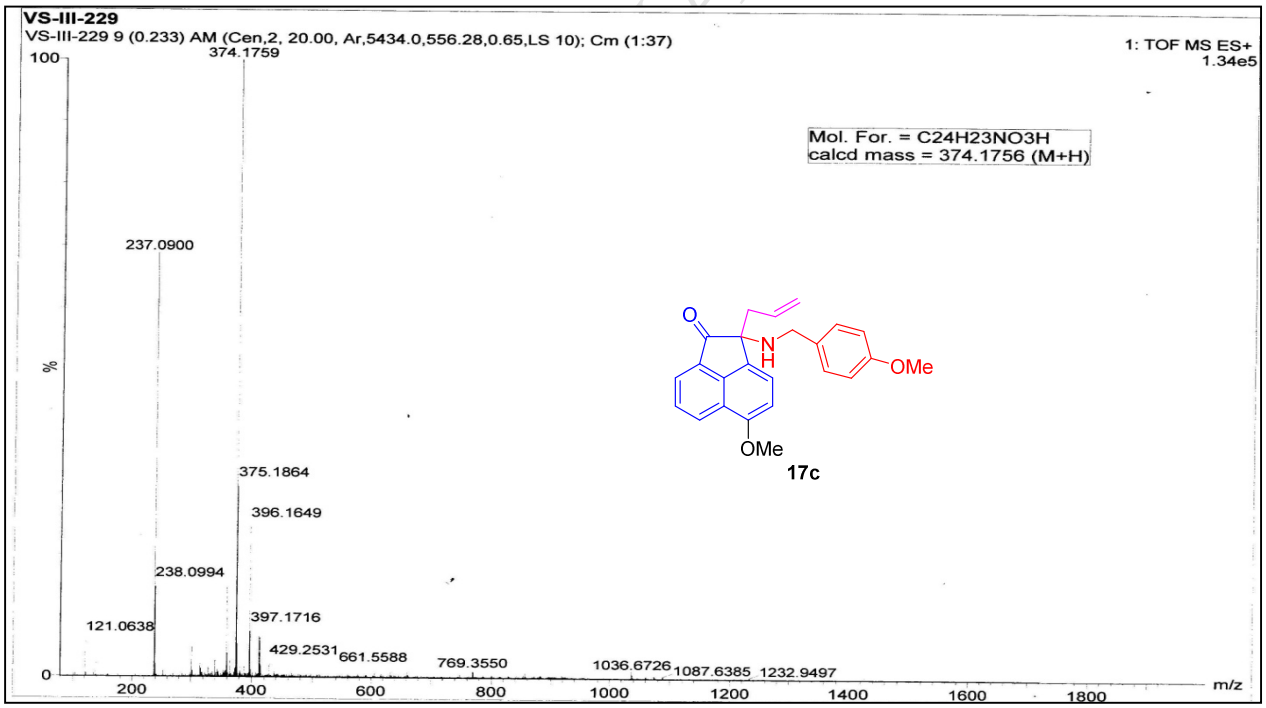
^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-((4-methoxybenzyl)amino)-5-methoxyacenaphthylen-1(2*H*)-one (**17c**).



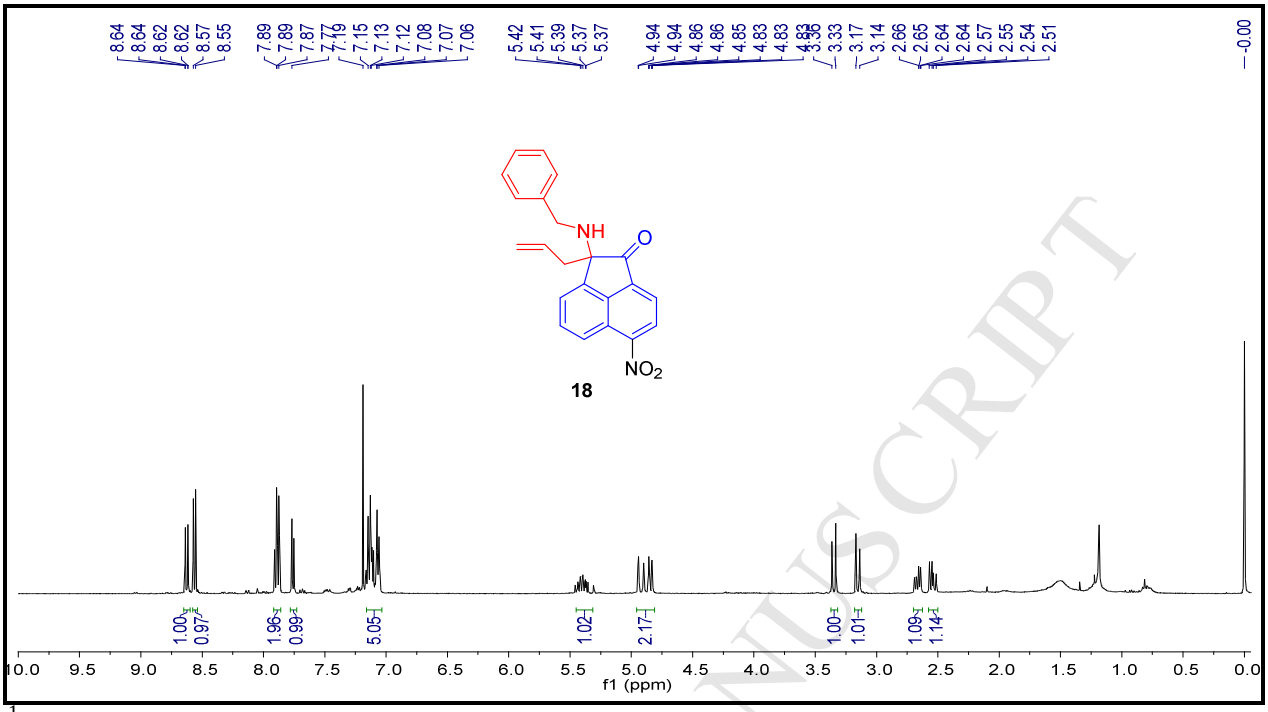
^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-((4-methoxybenzyl)amino)-5-methoxyacenaphthylen-1(2*H*)-one (**17c**).



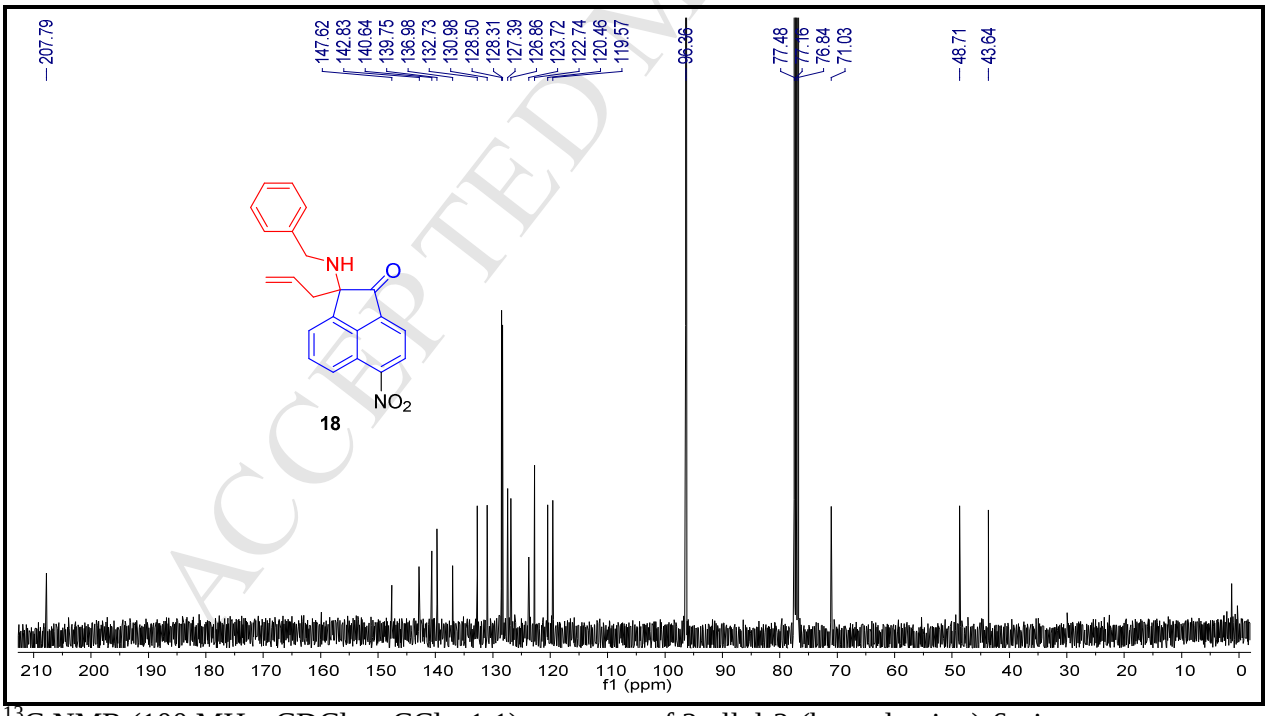
DEPT-135 NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-((4-methoxybenzyl)amino)-5-methoxyacenaphthylen-1(2*H*)-one (**17c**).



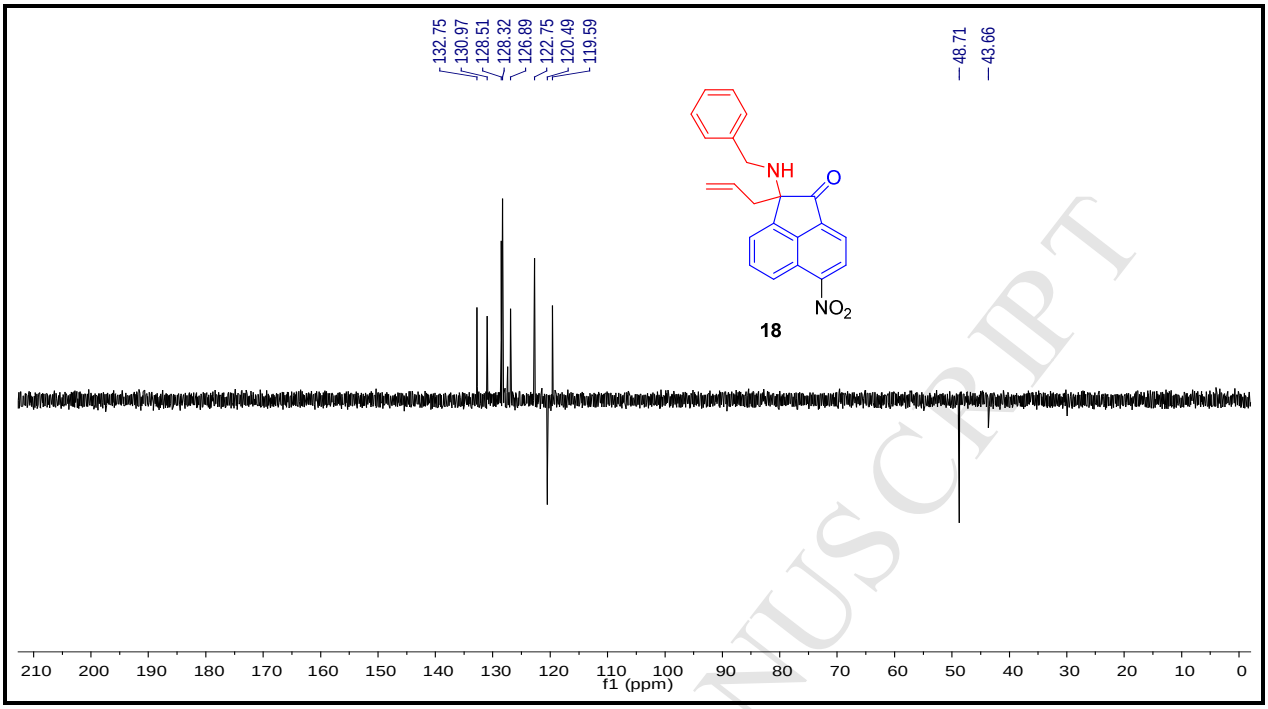
HRMS spectrum of 2-allyl-2-((4-methoxybenzyl)amino)-5-methoxyacenaphthylen-1(2*H*)-one (**17c**).



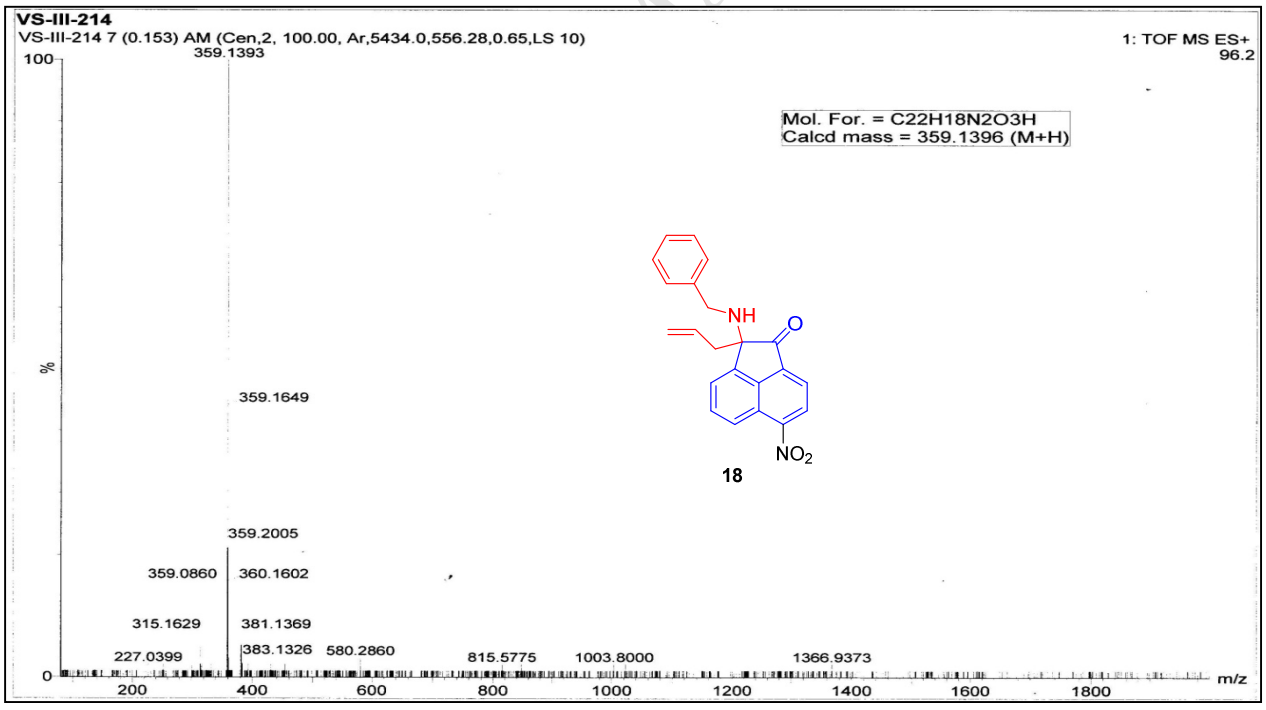
^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-(benzylamino)-6-nitro acenaphthylen-1(2*H*)-one (**18**).



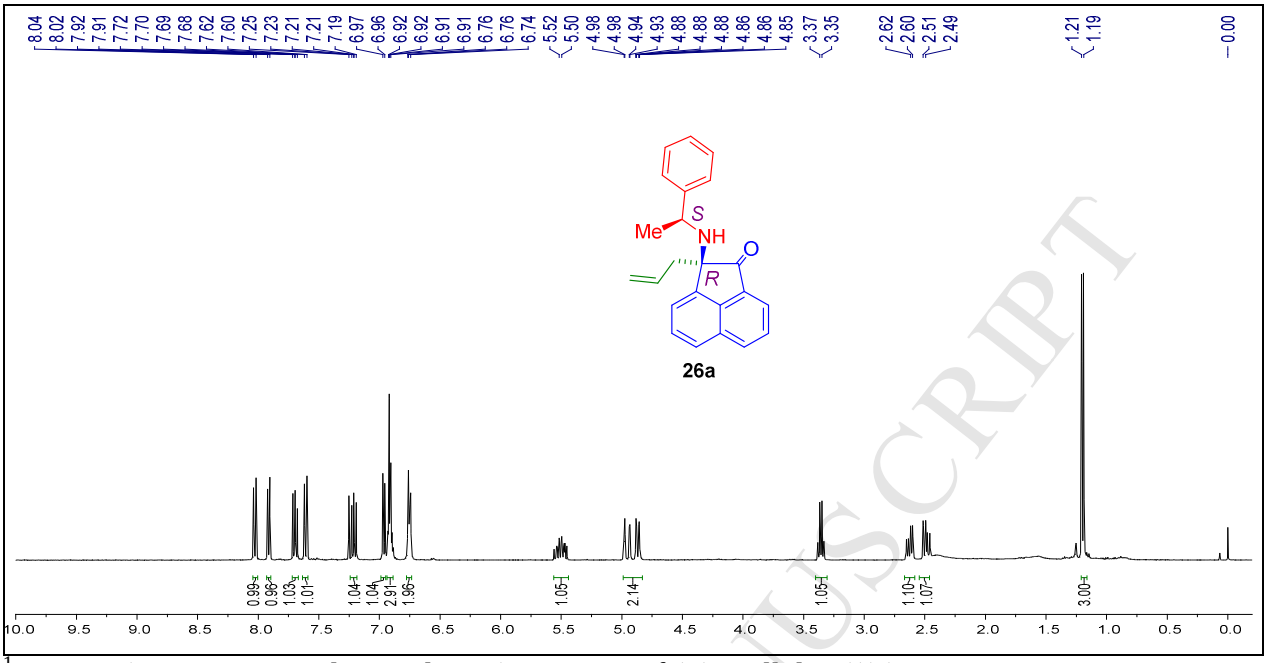
^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-(benzylamino)-6-nitro acenaphthylen-1(2*H*)-one (**18**).



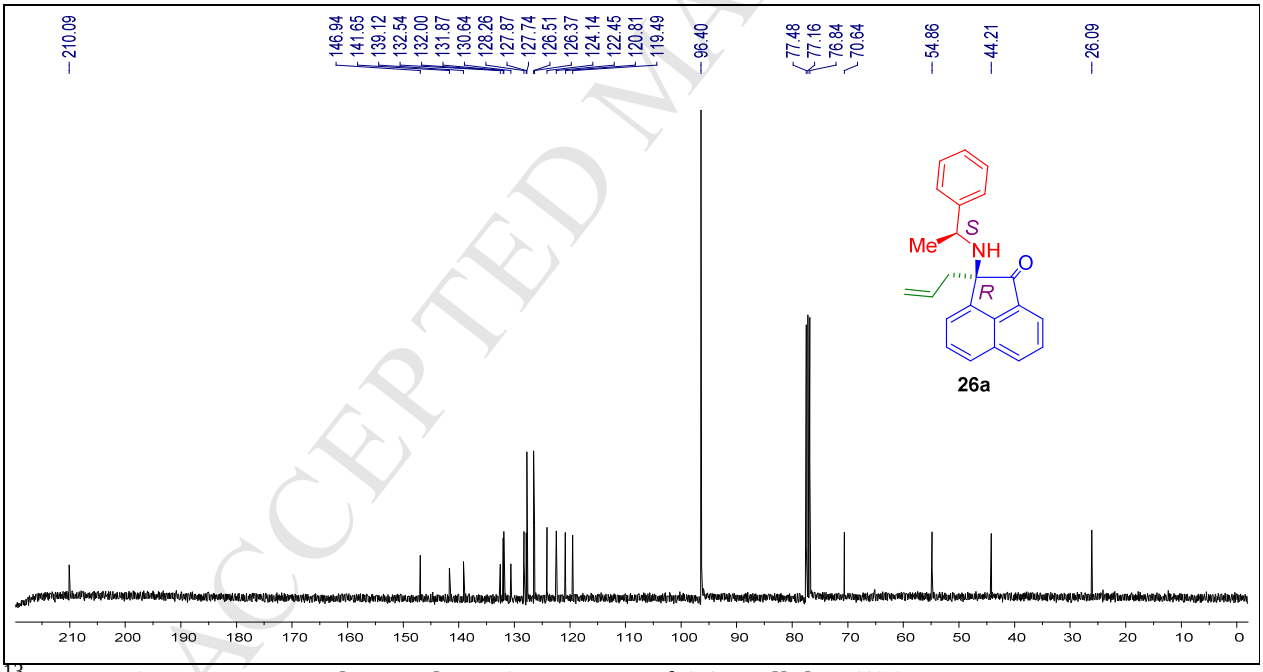
DEPT-135 NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 2-allyl-2-(benzylamino)-6-nitro acenaphthylen-1(2*H*)-one (**18**).



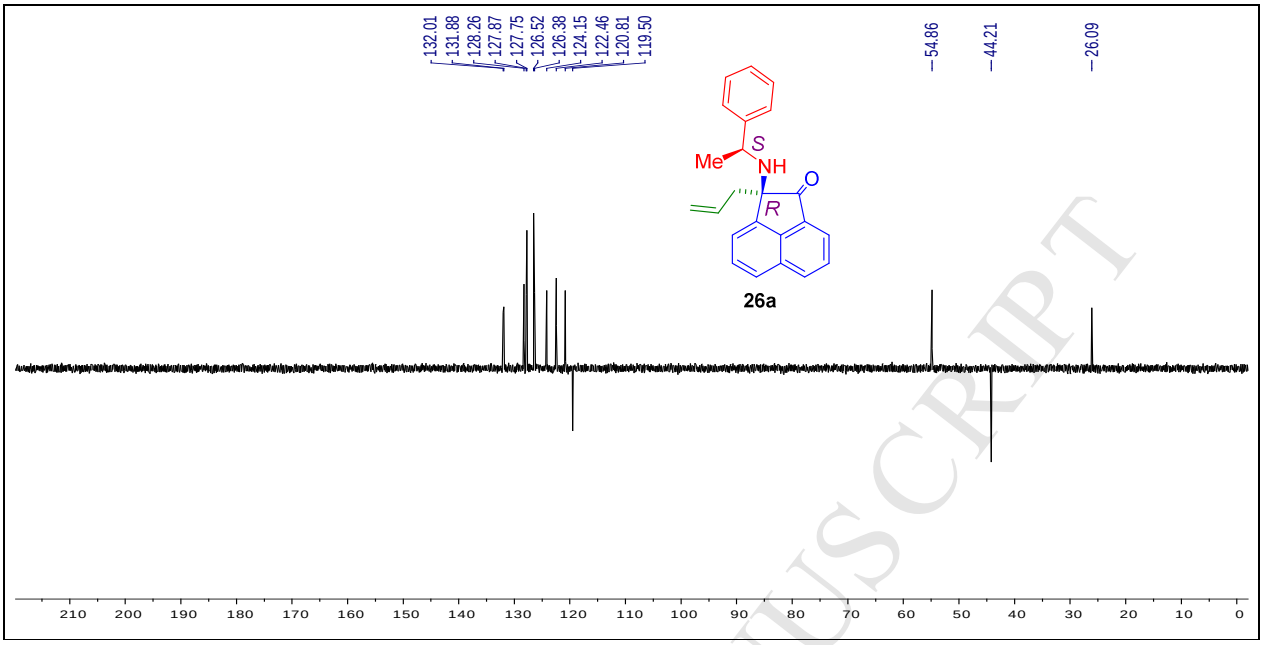
HRMS spectrum of 2-allyl-2-(benzylamino)-6-nitro acenaphthylen-1(2*H*)-one (**18**).



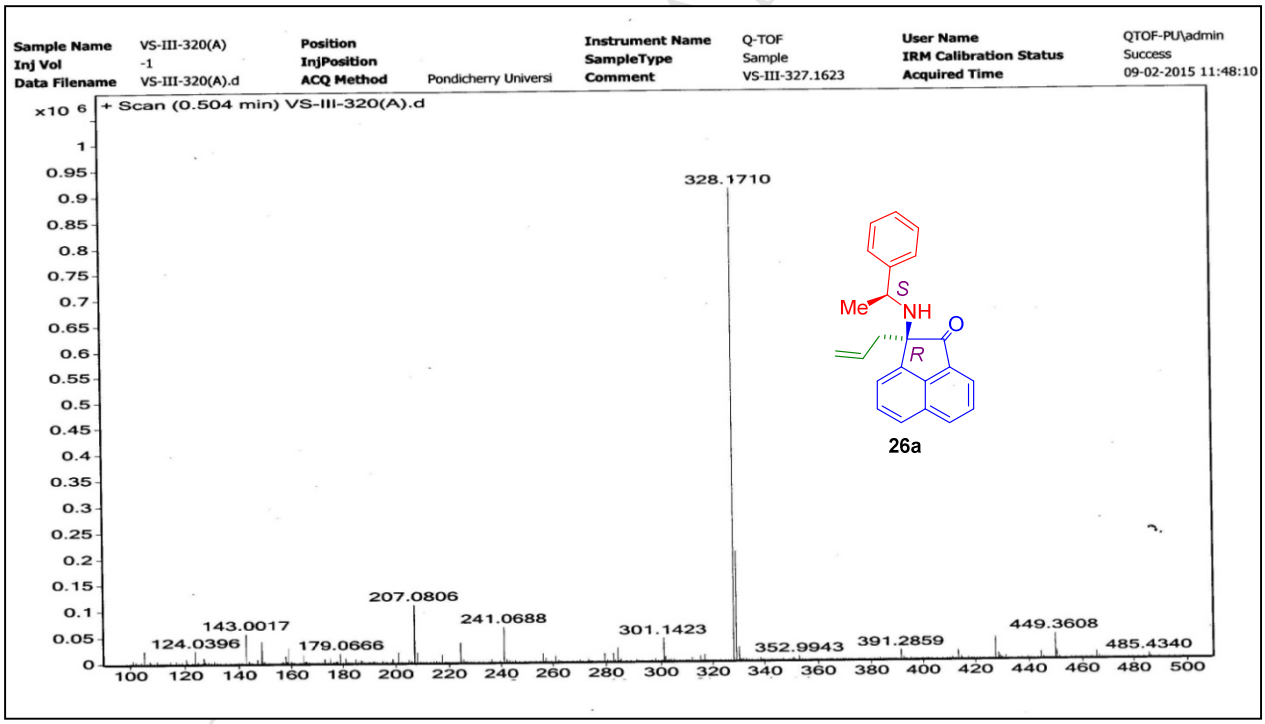
^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of (*R*)-2-allyl-2-(((*S*)-1-phenylethyl)amino)acenaphthylen-1(2*H*)-one (**26a**).



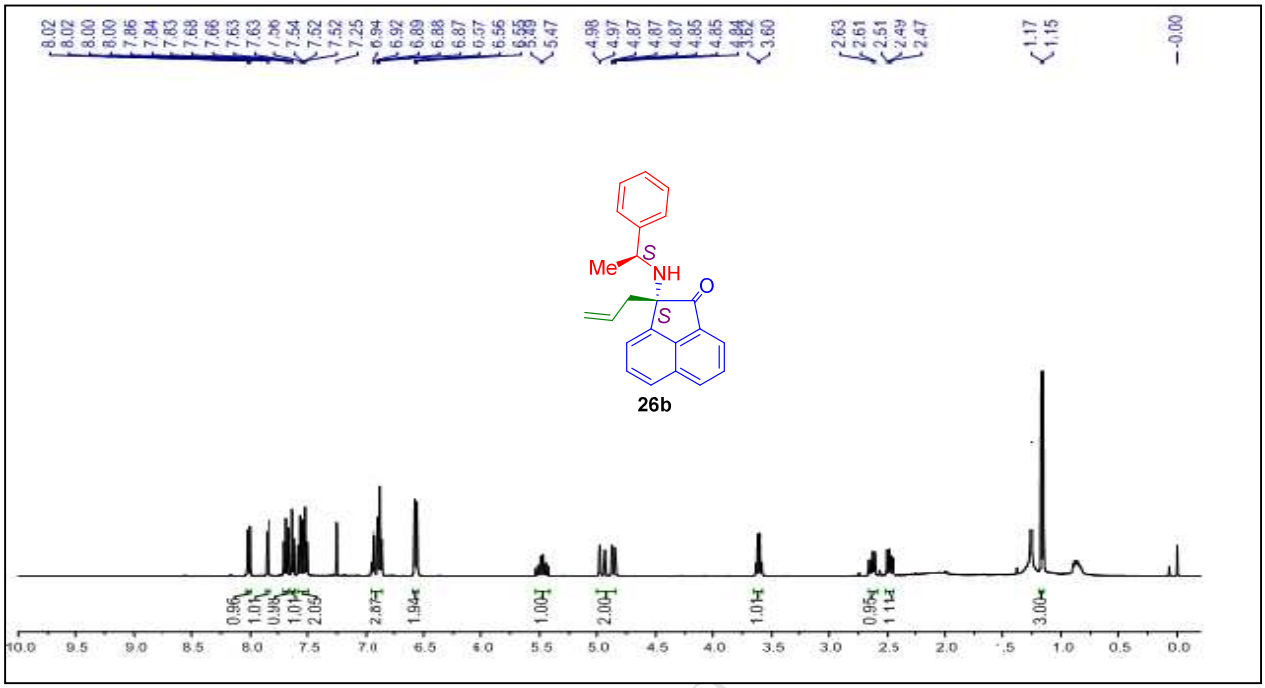
^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of (*R*)-2-allyl-2-(((*S*)-1-phenylethyl)amino)acenaphthylen-1(2*H*)-one (**26a**).



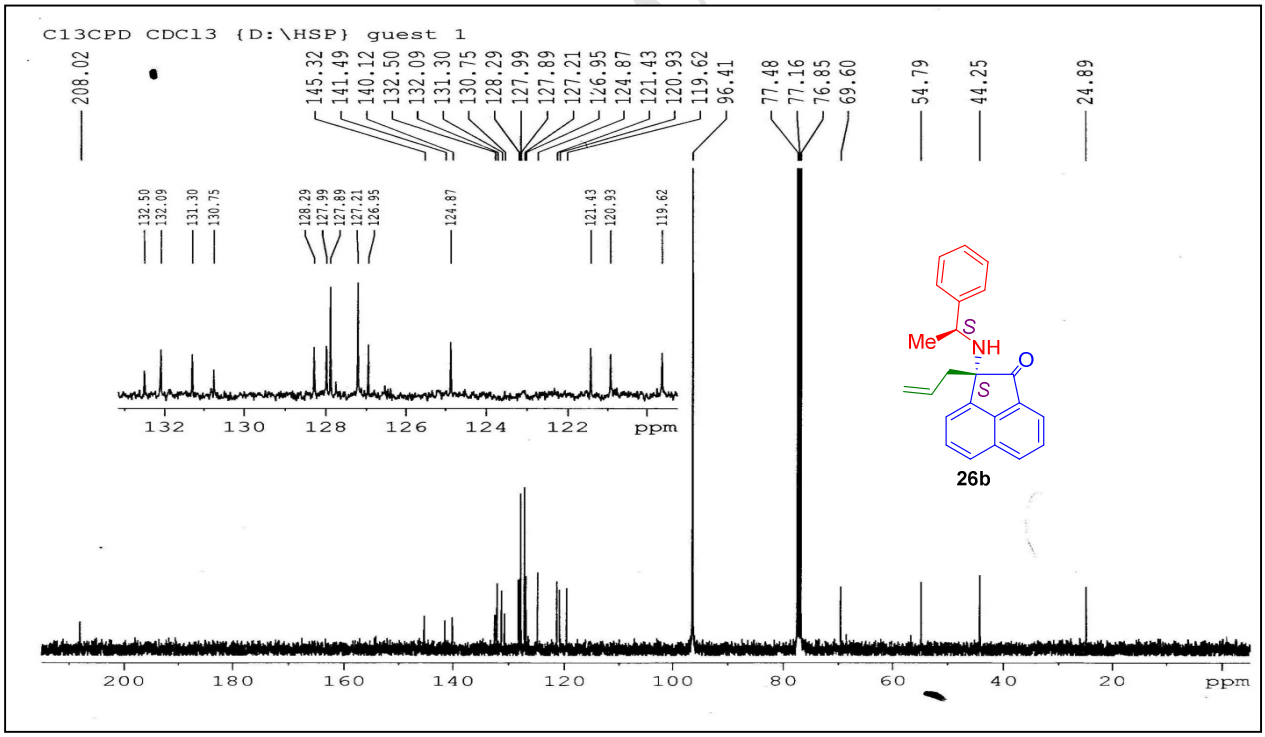
DEPT-135 NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of (*R*)-2-allyl-2-(((*S*)-1-phenylethyl)amino)acenaphthylen-1(2*H*)-one (**26a**).



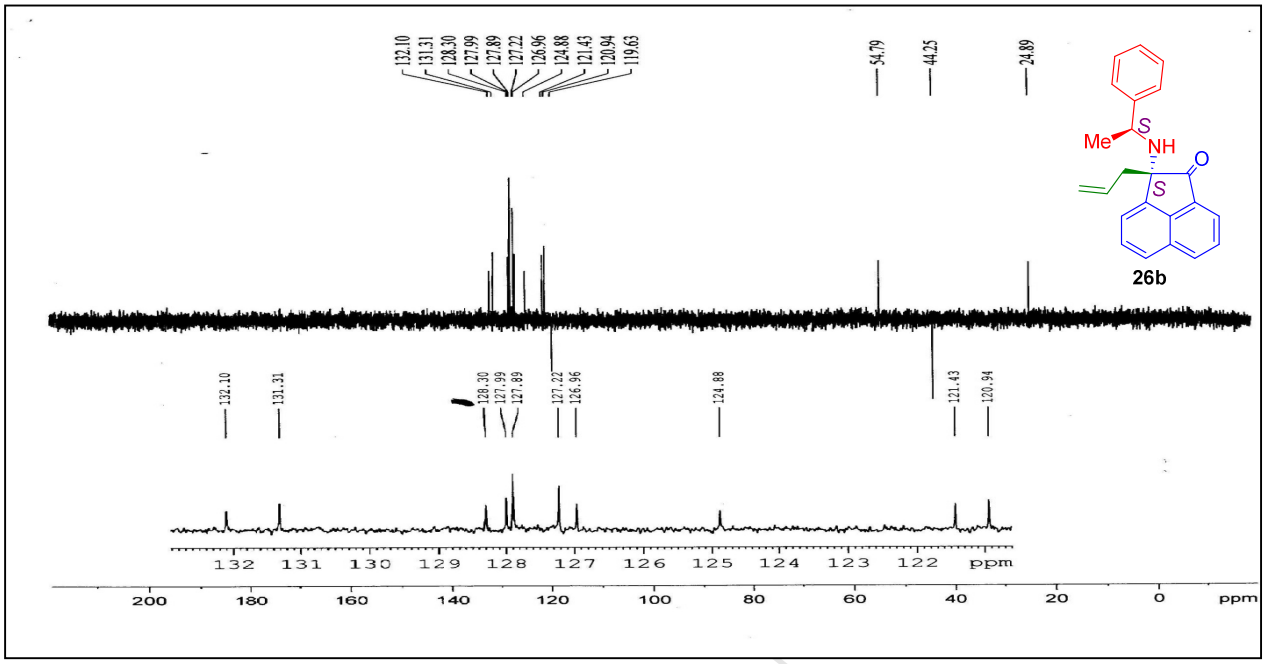
HRMS spectrum of (*R*)-2-allyl-2-(((*S*)-1-phenylethyl)amino)acenaphthylen-1(2*H*)-one (**26a**).



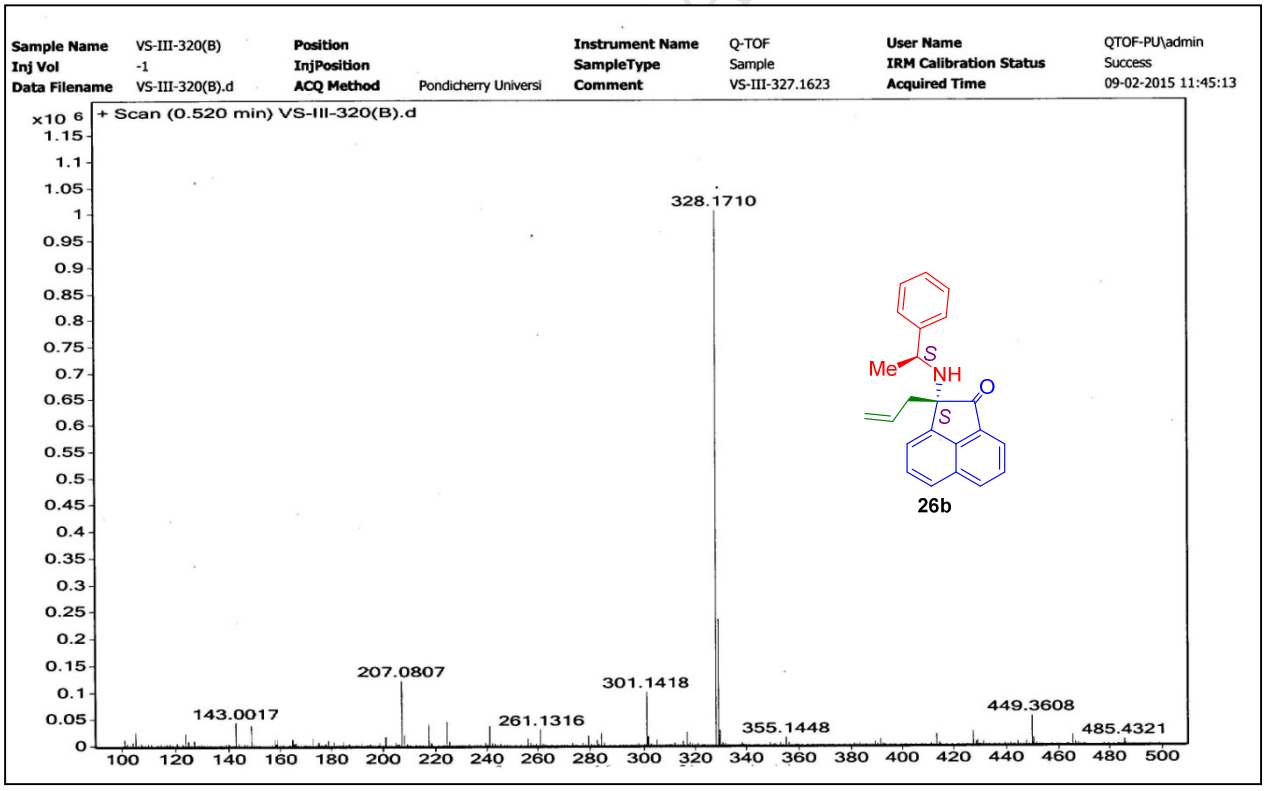
^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of (*S*)-2-allyl-2-(((*S*)-1-phenylethyl)amino)acenaphthylen-1(2*H*)-one (**26b**).



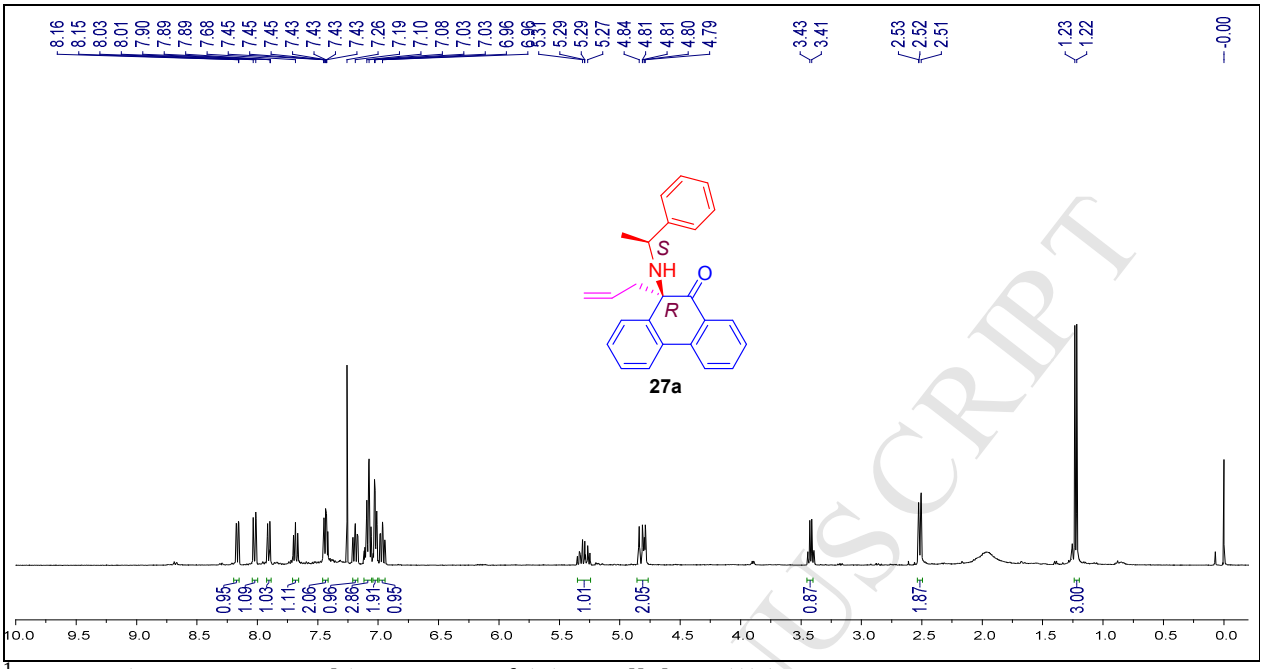
^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of (*S*)-2-allyl-2-(((*S*)-1-phenylethyl)amino)acenaphthylen-1(2*H*)-one (**26b**).



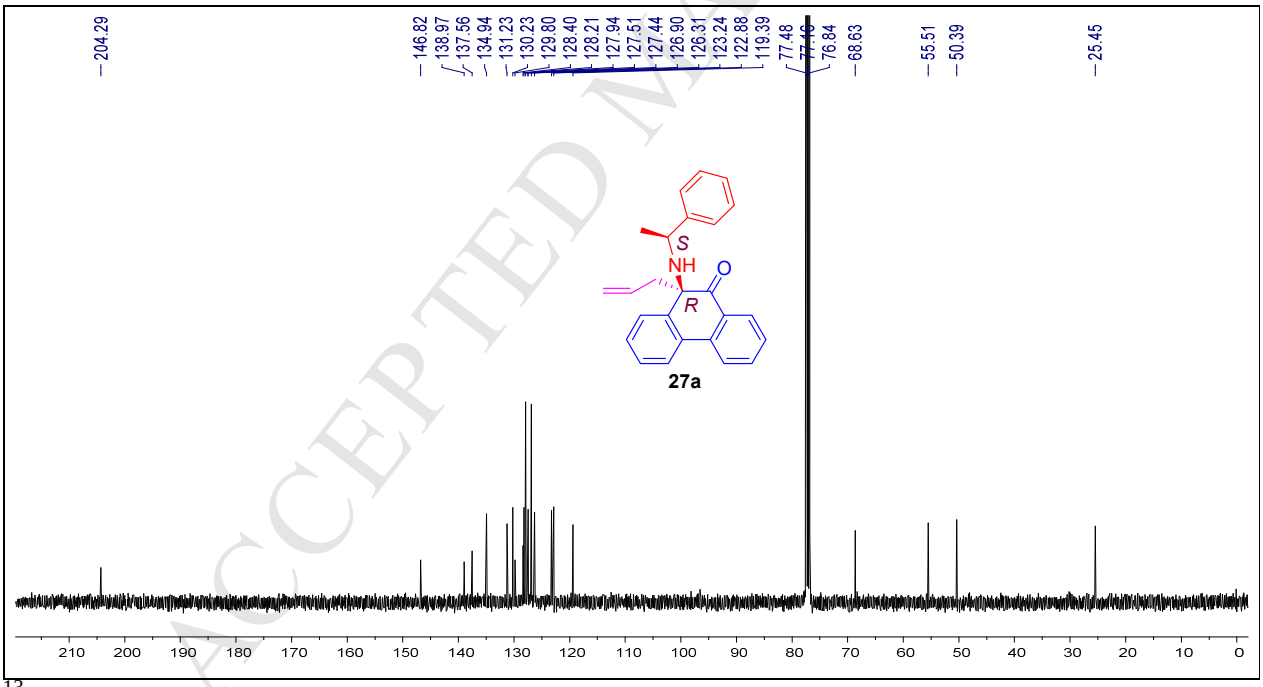
DEPT-135 NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of (*S*)-2-allyl-2-(((*S*)-1-phenylethyl)amino)acenaphthylen-1(2*H*)-one (**26b**).



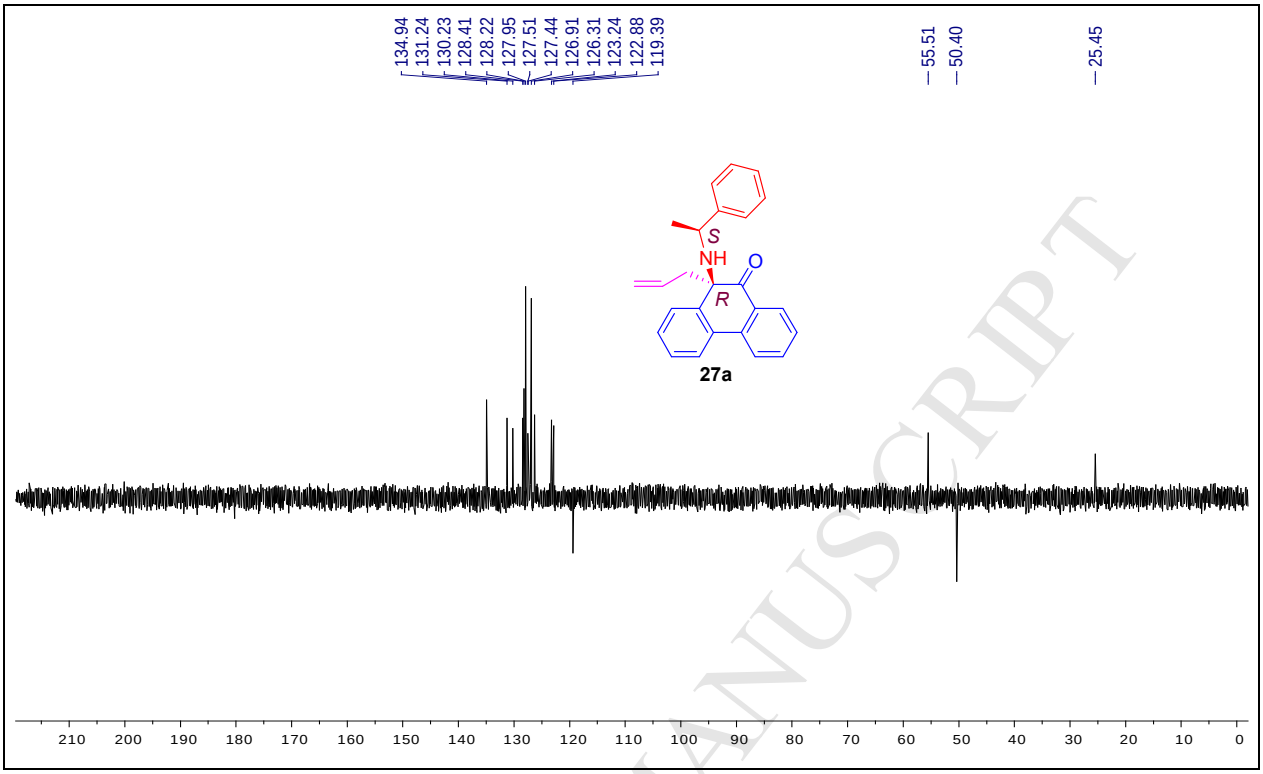
HRMS spectrum of (*S*)-2-allyl-2-(((*S*)-1-phenylethyl)amino)acenaphthylen-1(2*H*)-one (**26b**).



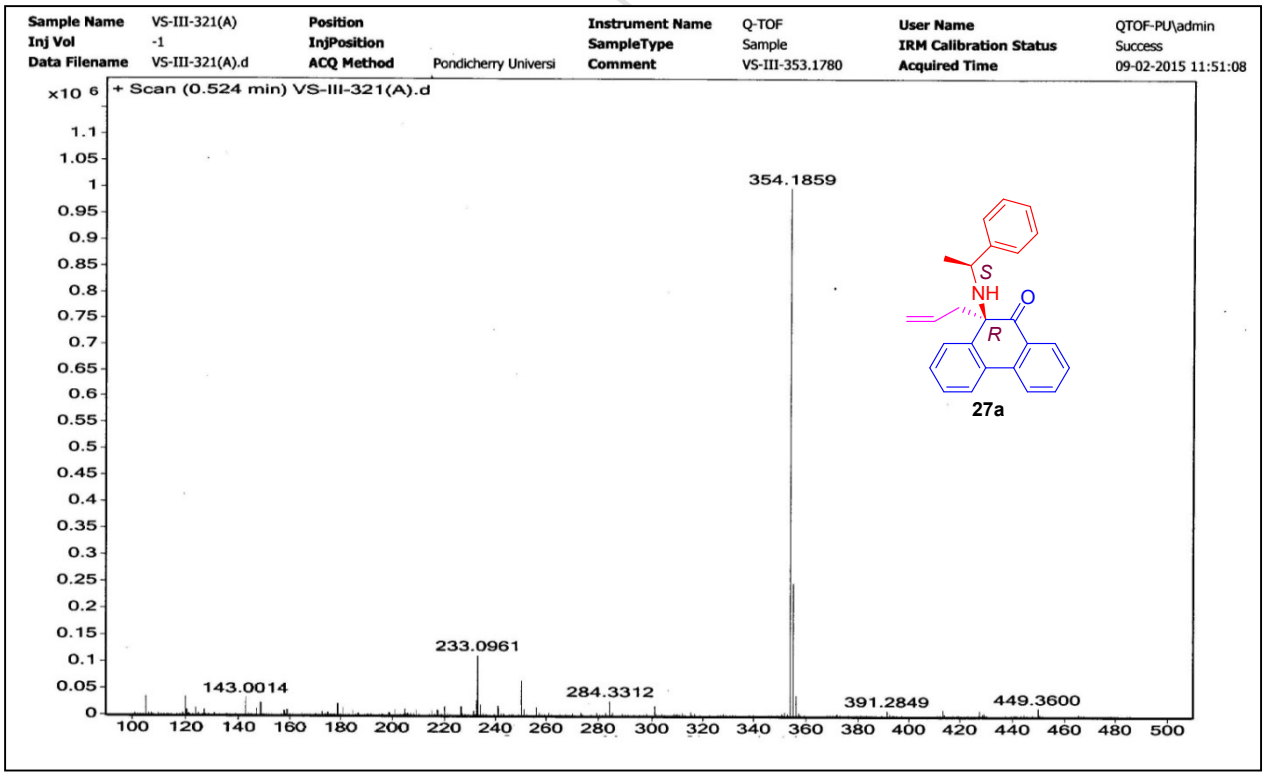
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (*R*)-10-allyl-10-(((*S*)-1-phenylethyl)amino)phenanthren-9(10*H*)-one (**27a**).



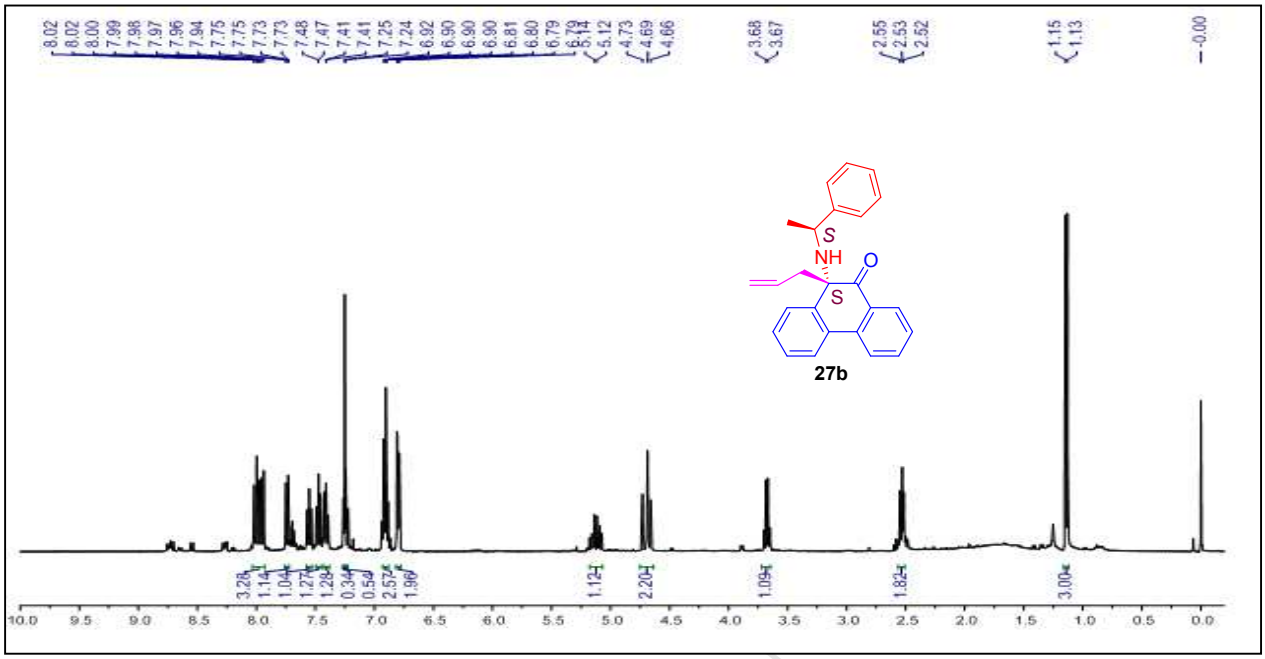
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-10-allyl-10-(((*S*)-1-phenylethyl)amino)phenanthren-9(10*H*)-one (**27a**).



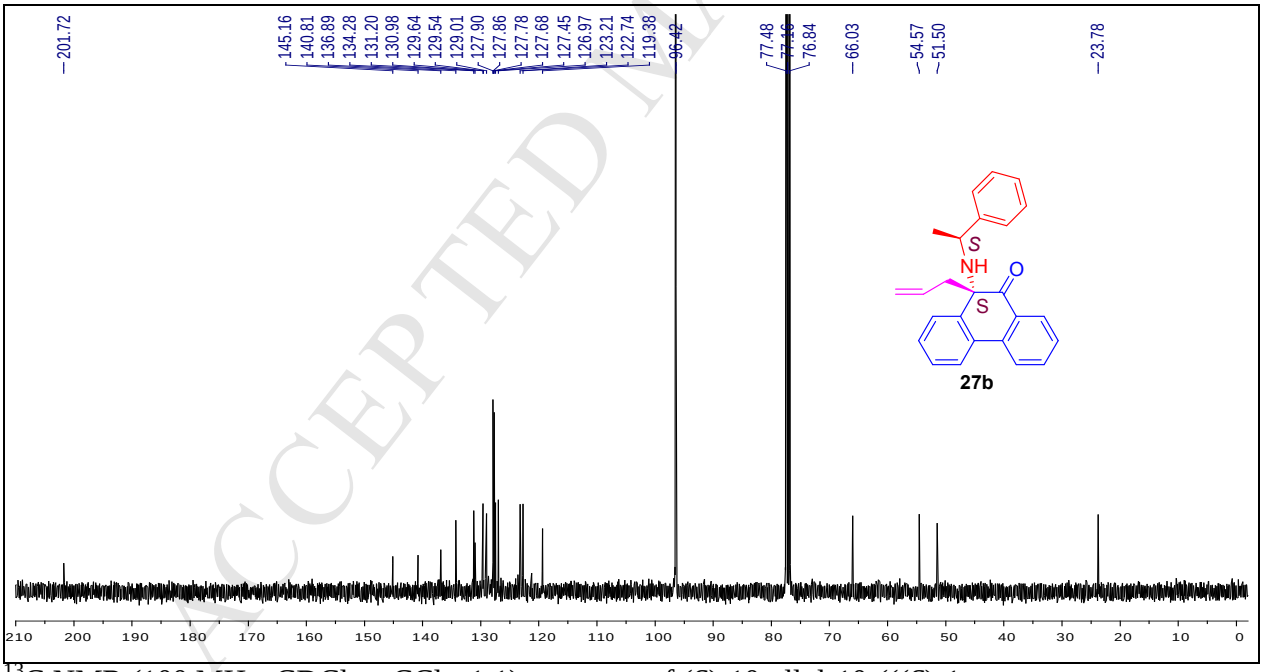
DEPT-135 NMR (100 MHz, $CDCl_3$) spectrum of (*R*)-10-allyl-10-(((*S*)-1-phenylethyl)amino)phenanthren-9(10*H*)-one (**27a**).



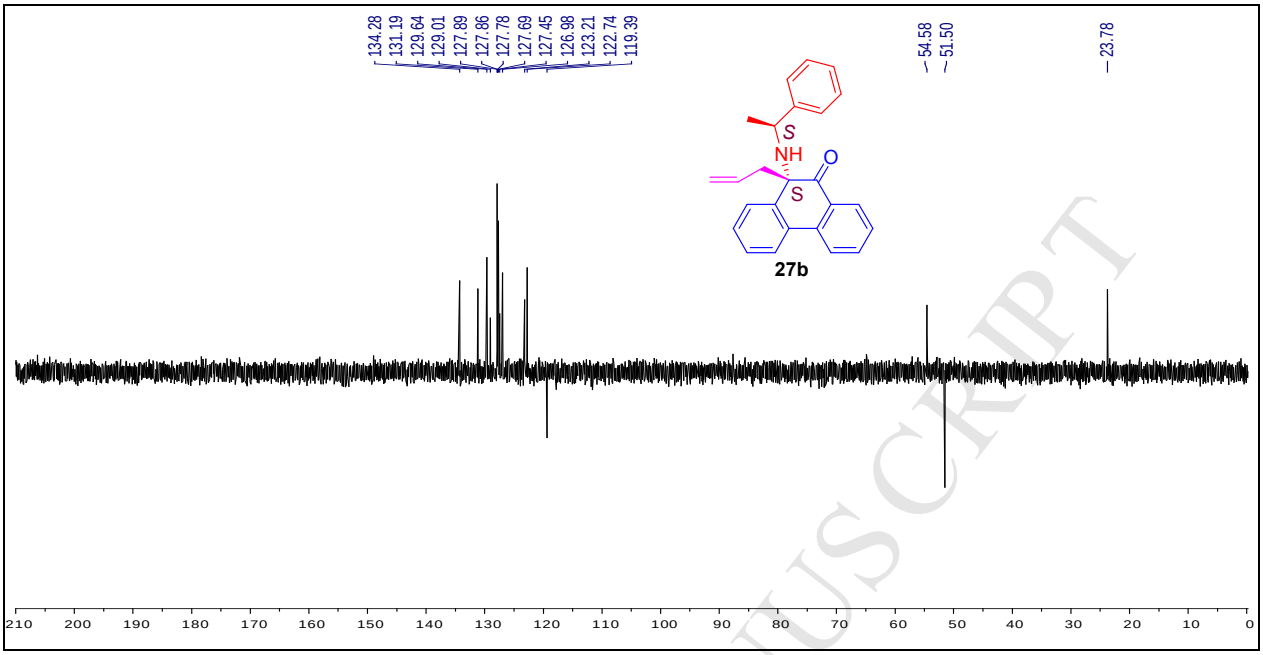
HRMS spectrum of (*R*)-10-allyl-10-(((*S*)-1-phenylethyl)amino)phenanthren-9(10*H*)-one (**27a**).



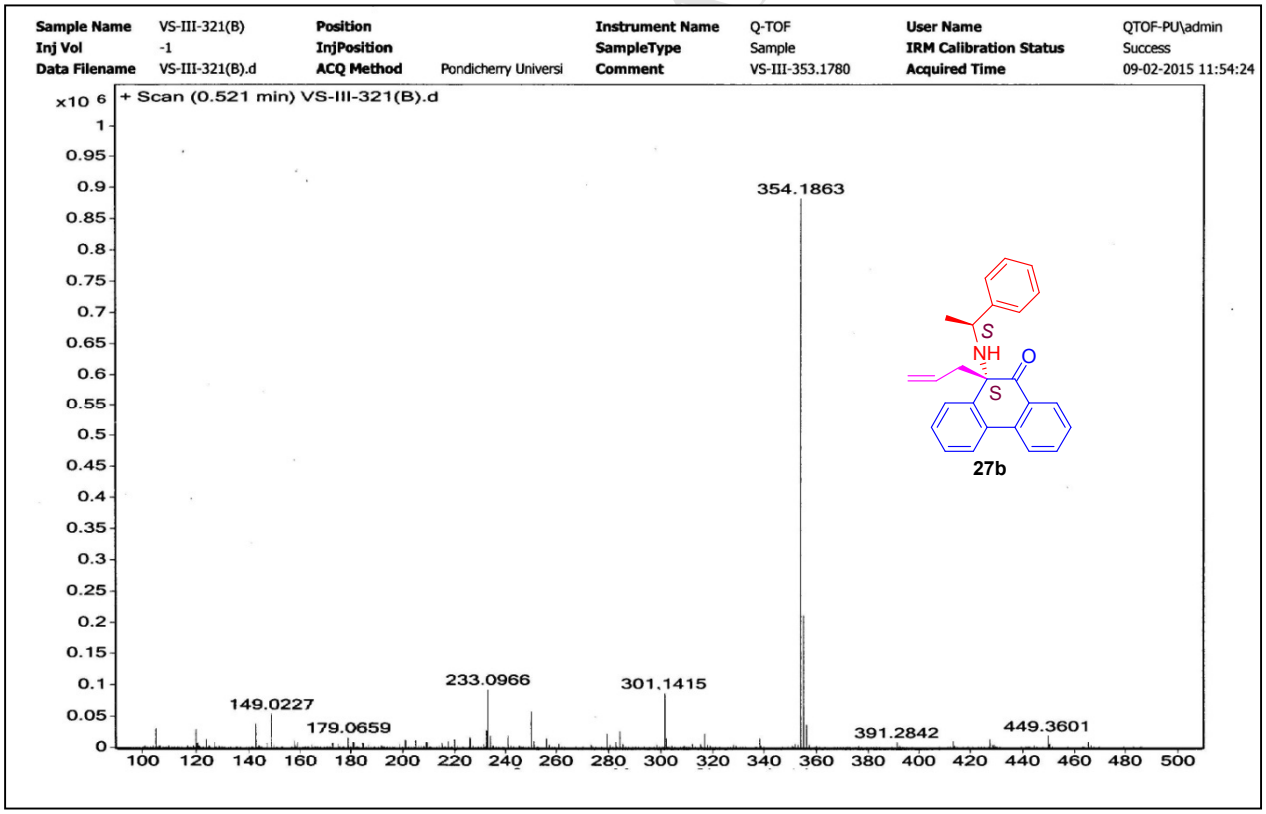
^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of (*S*)-10-allyl-10-(((*S*)-1-phenylethyl)amino)phenanthren-9(10*H*)-one (**27b**).



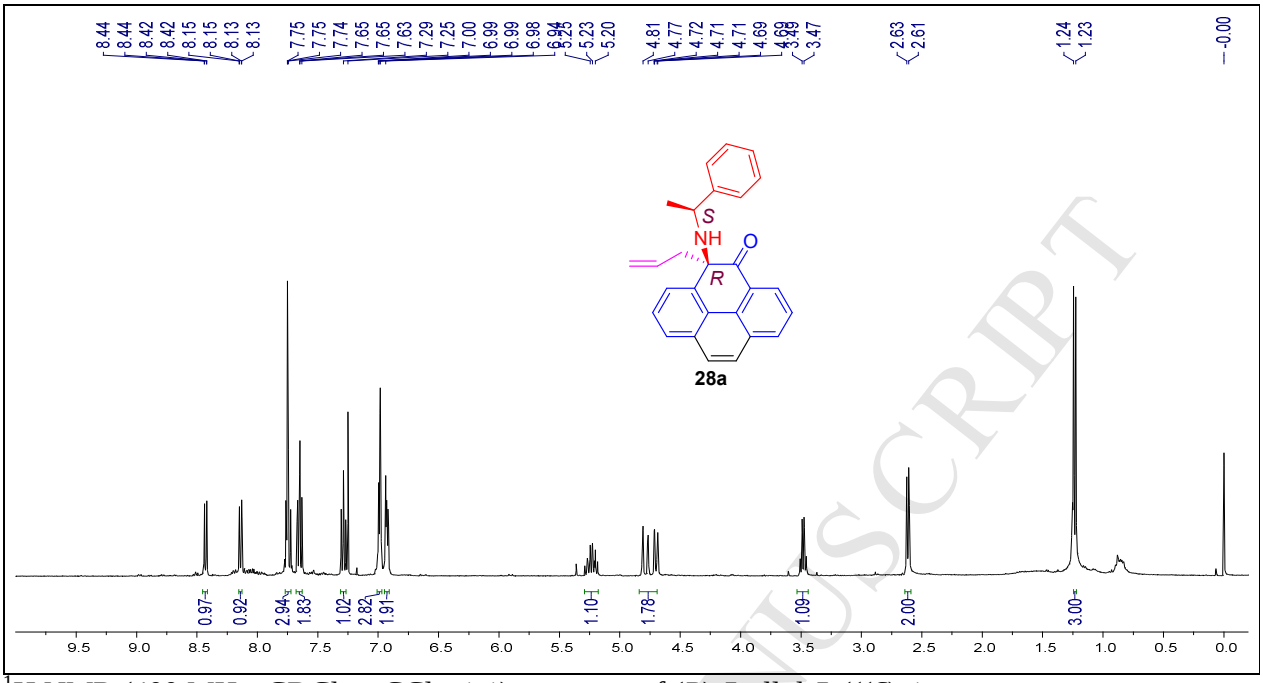
^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of (*S*)-10-allyl-10-(((*S*)-1-phenylethyl)amino)phenanthren-9(10*H*)-one (**27b**).



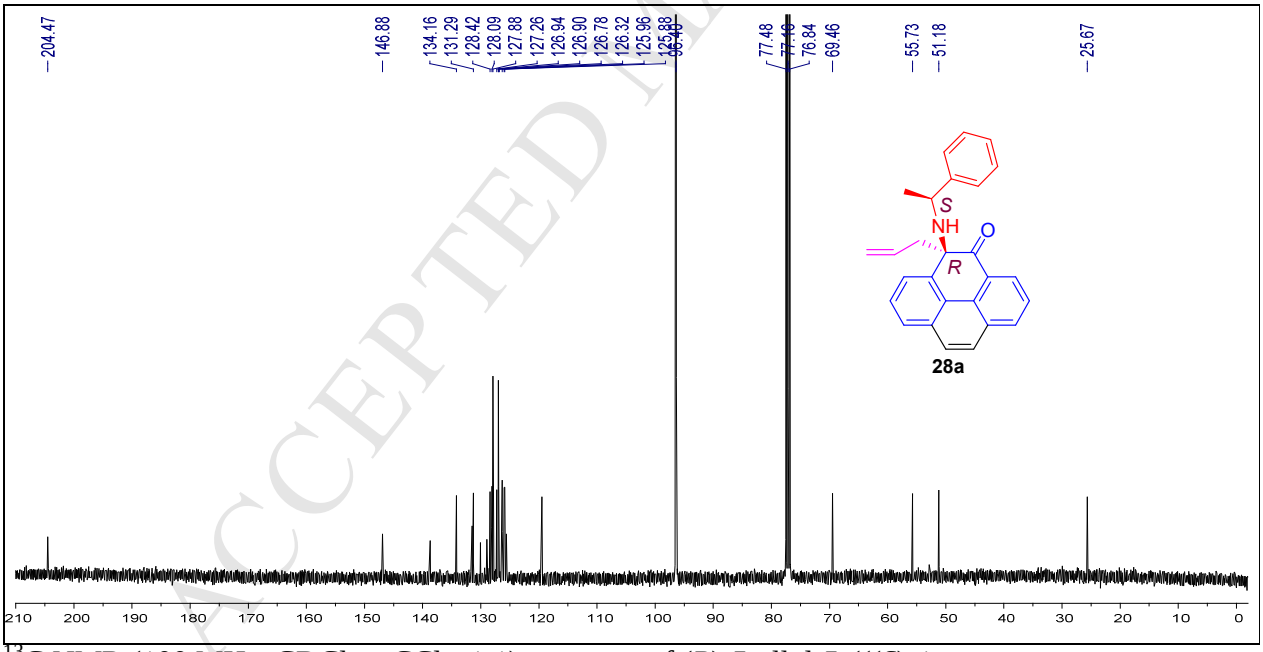
DEPT-135 NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of (*S*)-10-allyl-10-(((*S*)-1-phenylethyl)amino)phenanthren-9(10*H*)-one (**27b**)



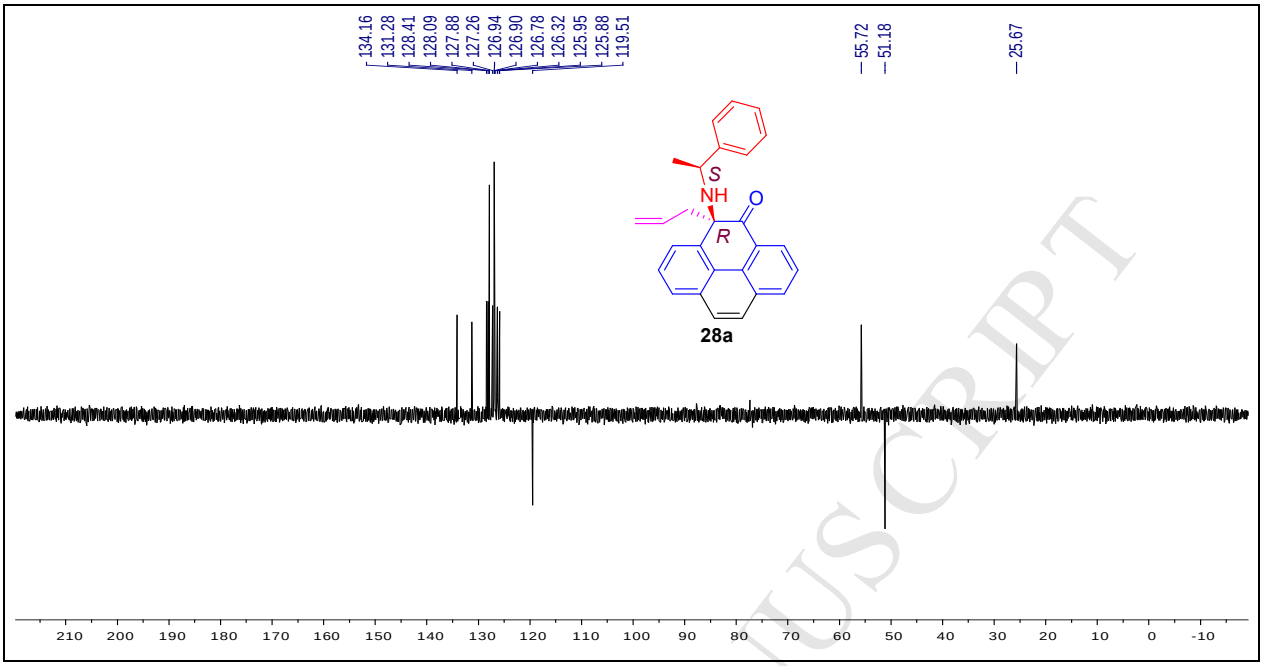
HRMS spectrum of (*S*)-10-allyl-10-(((*S*)-1-phenylethyl)amino)phenanthren-9(10*H*)-one (**27b**).



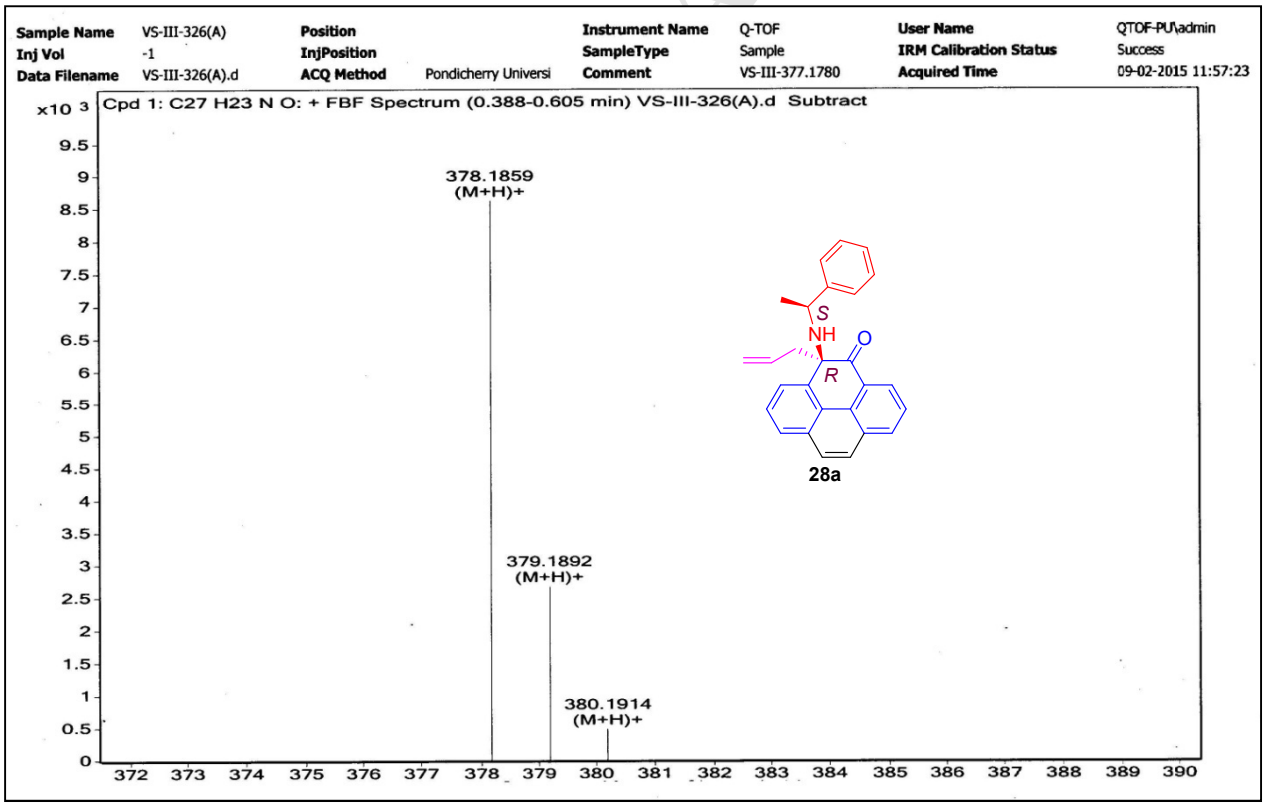
^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of (*R*)-5-allyl-5-(((*S*)-1-phenylethyl)amino)pyren-4(5*H*)-one (**28a**).



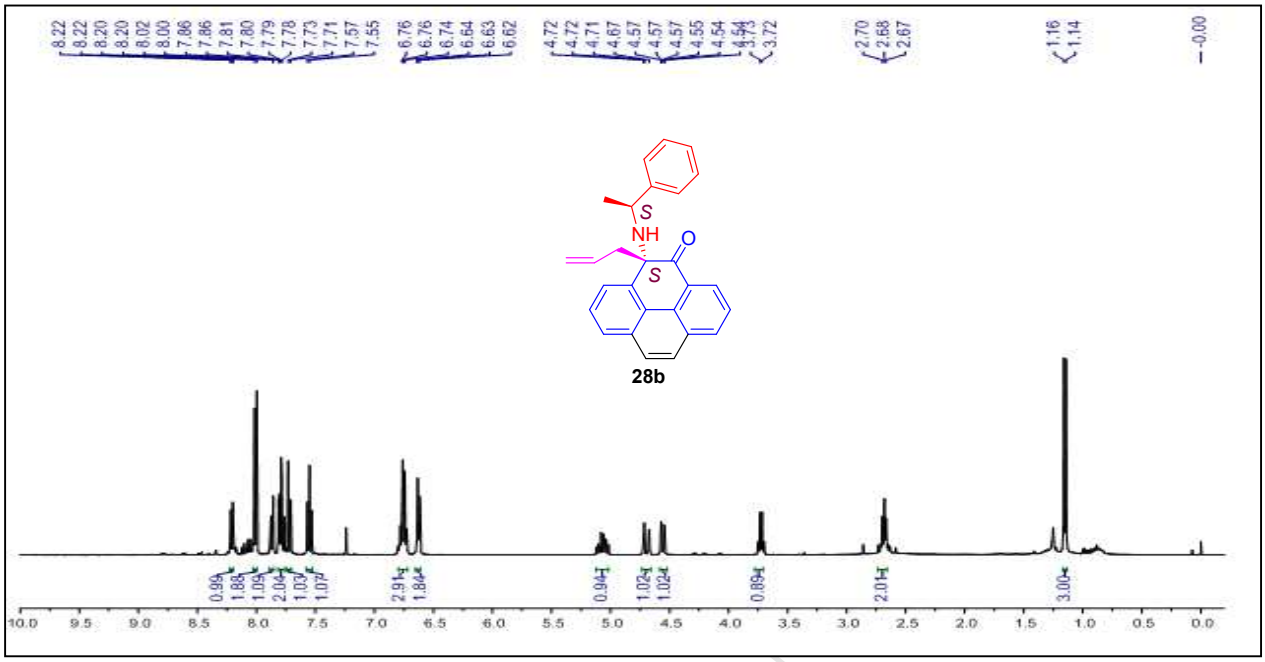
^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of (*R*)-5-allyl-5-(((*S*)-1-phenylethyl)amino)pyren-4(5*H*)-one (**28a**).



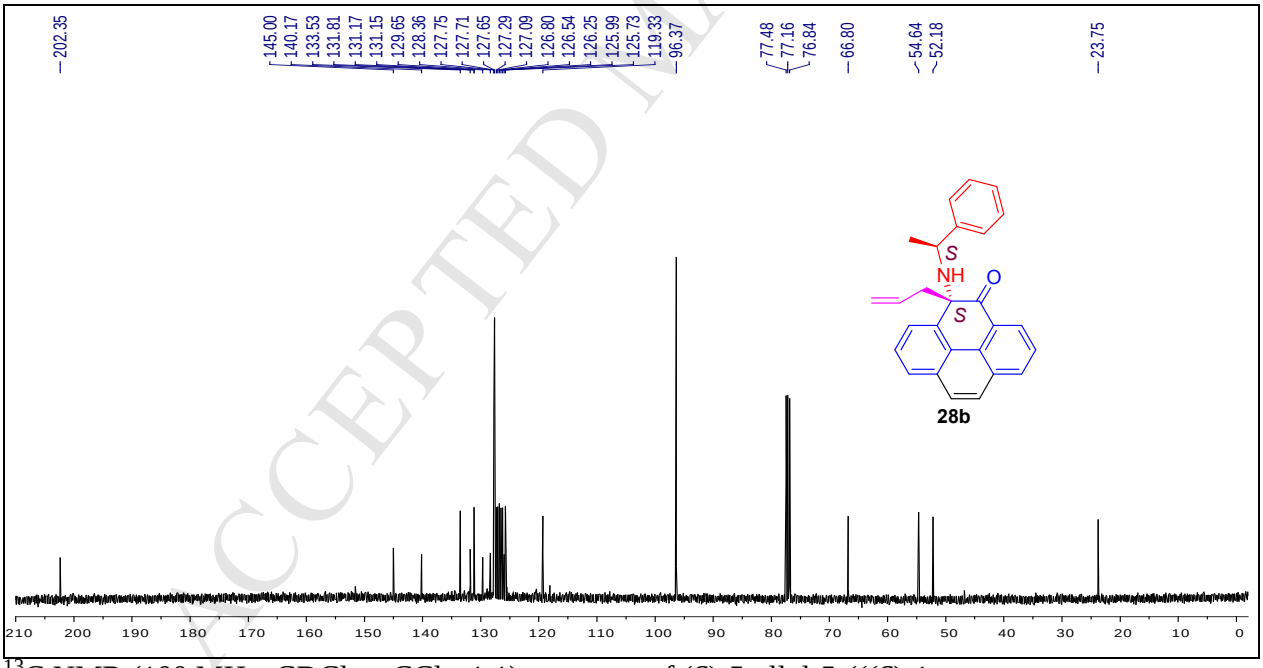
DEPT-135 NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of (*R*)-5-allyl-5-(((*S*)-1-phenylethyl)amino)pyren-4(5*H*)-one (**28a**).



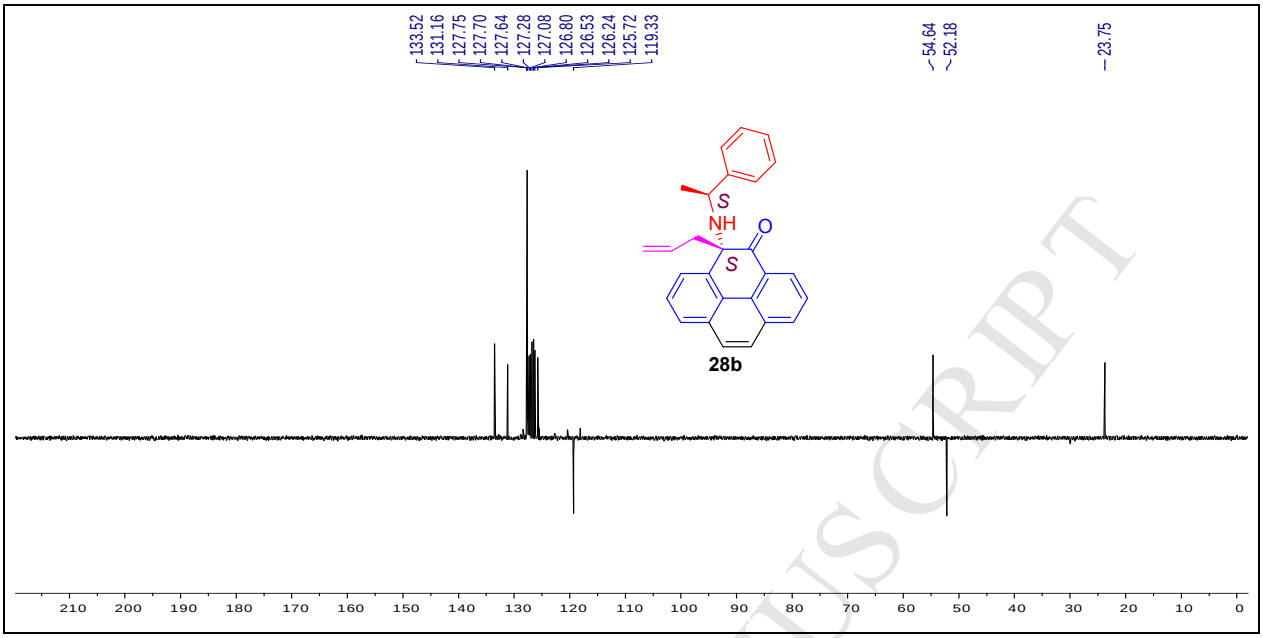
HRMS spectrum of (*R*)-5-allyl-5-(((*S*)-1-phenylethyl)amino)pyren-4(5*H*)-one (**28a**).



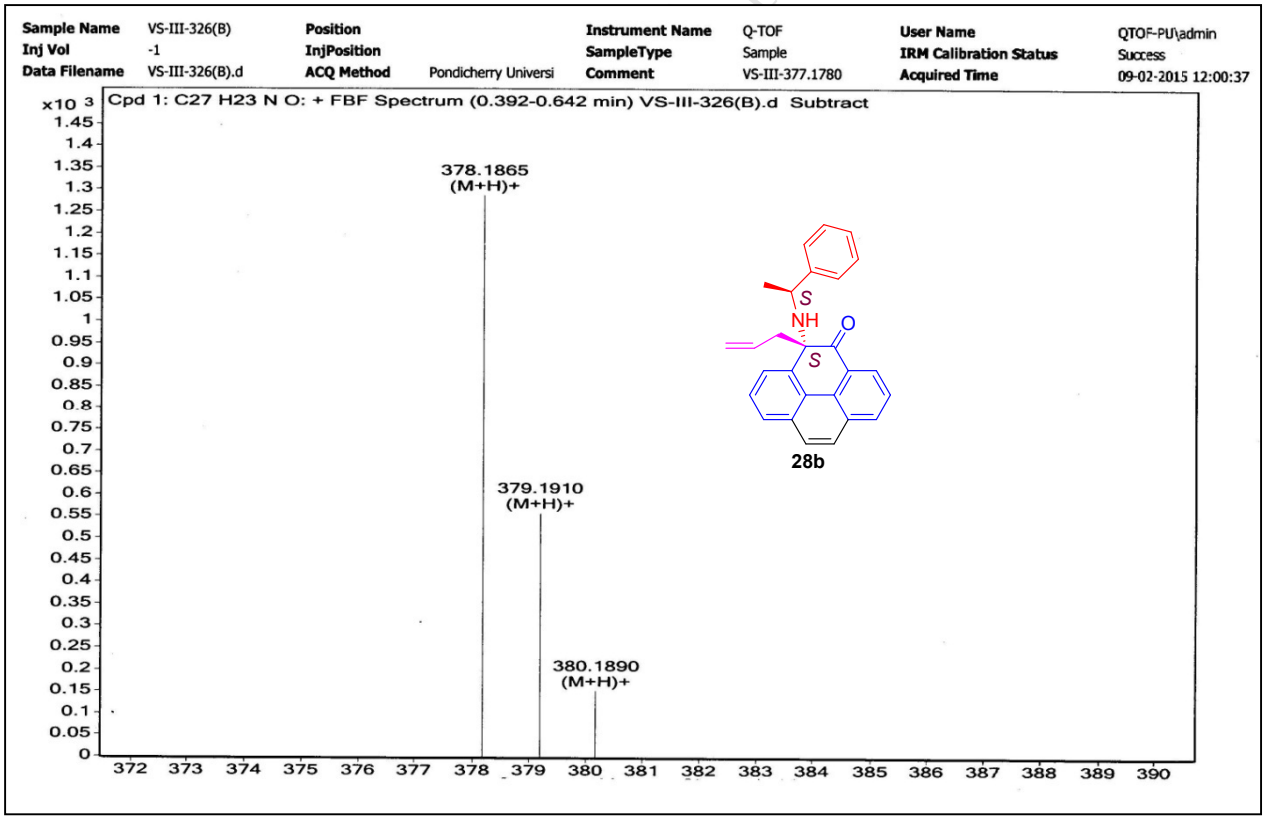
^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of (*S*)-5-allyl-5-(((*S*)-1-phenylethyl)amino)pyren-4(5*H*)-one (**28b**).



^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of (*S*)-5-allyl-5-(((*S*)-1-phenylethyl)amino)pyren-4(5*H*)-one (**28b**).



DEPT-135 NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of (*S*)-5-allyl-5-(((*S*)-1-phenylethyl)amino)pyren-4(5*H*)-one (**28b**).

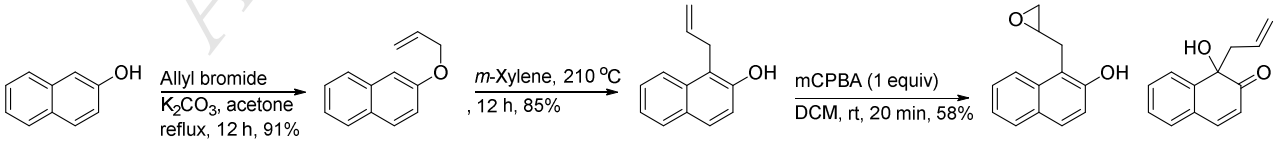


HRMS spectrum of (*S*)-5-allyl-5-(((*S*)-1-phenylethyl)amino)pyren-4(5*H*)-one (**28b**).

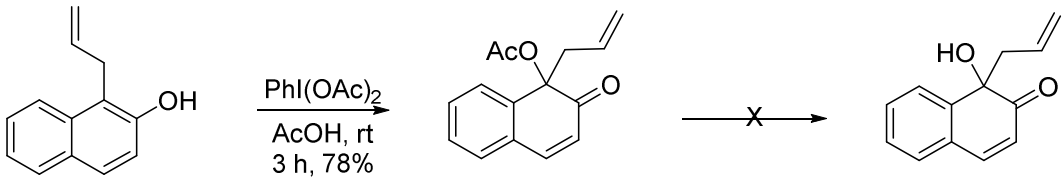
Appendix I

Attempted synthesis of 1-hydroxy-1-allyl-2-naphthalenone by following Barton's protocol.

According to the honorable referee suggestion, we went through the paper of late Professor Barton and coworkers which appeared in *Bull Soc Chim Fr*, **1988**, 681-687. The paper is in French language and we got it translated by using web-based resources. The authors reported the synthesis of 1-hydroxy-1-allyl-2-naphthalenone from 1-allyl-2-naphthol by using disodium peroxymolybdate or *m*-chloroperbenzoic acid, but never isolated it in pure form. In both the instances, the authors mentioned that 1-hydroxy-1-allyl-2-naphthalenone is unstable. Therefore they converted it into 4-nitrobenzoic acid ester. In the oxidation with mCPBA the researchers found three products out of which one could be 1-hydroxy-1-allyl-2-naphthalenone. Formation of 1-hydroxy-1-allyl-2-naphthalenone was deduced by comparing NMR spectrum of the crude product with that of its ester with 4-nitrobenzoic acid. When we attempted the conversion of 1-allyl-2-hydroxynaphthalene to 1-hydroxy-1-allyl-2-naphthalenone by employing mCPBA we isolated epoxide, 1-(oxiran-2-ylmethyl)naphthalen-2-ol as the only product (Scheme 1). Following this failure, we attempted oxidation of 1-hydroxy-1-allyl-2-naphthalenone with phenyl-λ^3-iodanediyl diacetate (bis(acetoxy)iodobenzene, BAIB). The reaction provided 1-allyl-2-oxo-1,2-dihydronaphthalen-1-yl acetate (Scheme 2). Hydrolysis of the acetate did not yield desired 1-hydroxy-1-allyl-2-naphthalenone. Next, we tried the Voight reaction on 1-allyl-2-oxo-1,2-dihydronaphthalen-1-yl acetate with benzyl amine, formic acid, assuming that formic acid would hydrolyze acetate into required *tert*-alcohol and the product would undergo Voight rearrangement. Unfortunately, this reaction did not work; under room temperature, the starting acetate remained more or less unchanged even after 24 h. At 60 ^{o}C, the reaction provided an inseparable mixture. Similarly attempted *in situ* hydrolysis and the Voight reaction on 1-allyl-2-oxo-1,2-dihydronaphthalen-1-yl acetate with aniline and *p*-toluenesulfonic acid also did not work.



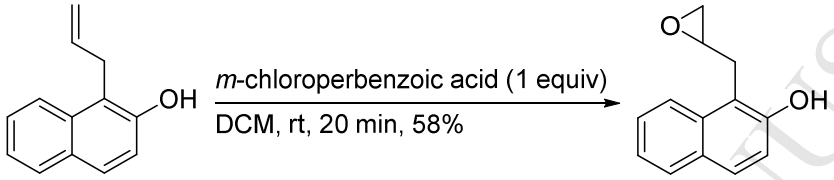
Scheme 1. Attempted synthesis of 1-hydroxy-1-allyl-2-naphthalenone by following Barton's protocol.



Scheme 2. Attempted alternate synthesis of 1-hydroxy-1-allyl-2-naphthalenone.

Experimental Section

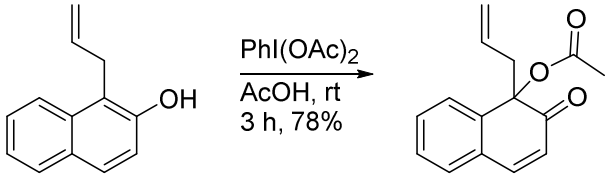
Synthesis of 1-(oxiran-2-ylmethyl)naphthalen-2-ol



Experimental procedure: 1-Allylnaphthalen-2-ol was prepared according to literature procedure (Angewandte Chemie, International Edition, **2011**, *50*, 5834-5838). 1-Allylnaphthalen-2-ol (100.2 mg, 0.54 mmol) was dissolved in dichloromethane (DCM) and then *m*-chloroperbenzoic acid (92.8 mg, 0.54 mmol) was added under nitrogen atmosphere and stirred at room temperature for 20 min, and then added DCM (20 mL) to the reaction mixture and DCM layer was washed with 0.1 *N* sodium bicarbonate solution (20 mL), brain (20 mL) and then dried over anhydrous sodium sulfate. Then the concentrated crude product was purified by column chromatography using silica gel (60-120 mesh SRL chemicals) using increasing amounts of ethyl acetate (5 to 10%) in hexanes to afford 1-(oxiran-2-ylmethyl)naphthalen-2-ol (62.9 mg) as a liquid in 58% yield; R_f (90% Hexane/EtOAc) 0.5; IR (KBr, cm^{-1}) 3395, 3061, 2927, 1630, 1589, 1517, 1460, 1379, 1249, 1158, 1046, 1010, 972, 900, 810, 750; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 7.79 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 8.7 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.49-7.42 (m, 1H), 7.33-7.27 (m, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 5.14-5.05 (m, 1H), 3.94-3.87 (m, 1H), 3.85-3.78 (m, 1H), 3.56-3.48 (m, 1H), 3.29-3.22 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) δ 156.8 (C), 131.0 (C), 129.5 (C), 129.3 (CH), 128.9 (CH), 126.9 (CH), 123.2 (CH), 122.8 (CH), 118.3 (C), 112.1 (CH), 84.0 (CH), 65.3 (CH_2), 30.4 (CH_2) ppm; HRMS (ESI) calcd for $C_{13}H_{12}O_2Na$ (M + Na) 223.0730, found 223.0721.

Attempted alternate synthesis of 1-hydroxy-1-allyl-2-naphthalenone

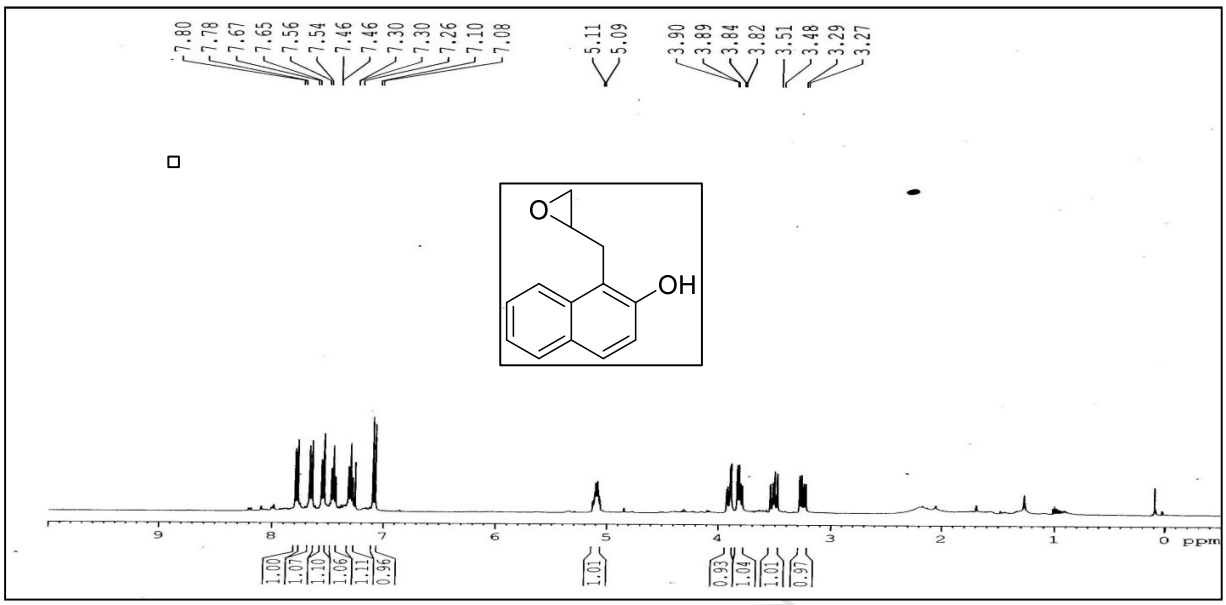
Synthesis of 1-allyl-2-oxo-1,2-dihydronaphthalen-1-yl acetate



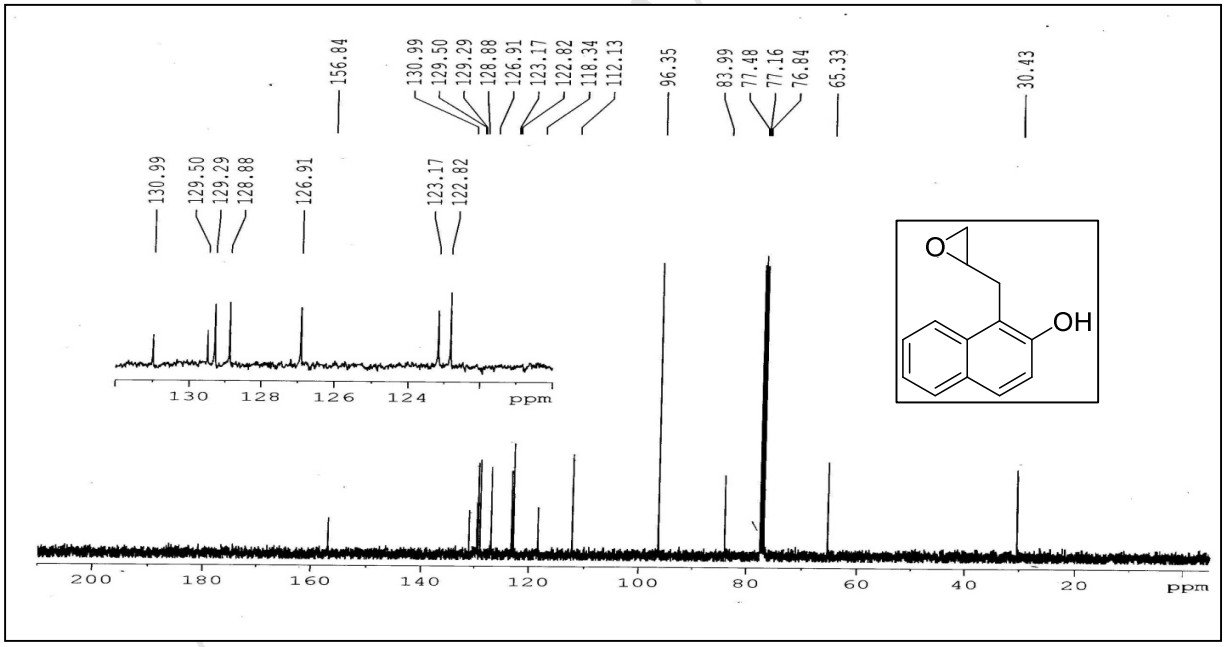
Experimental procedure: 1-Allylnaphthalen-2-ol (98.2 mg, 0.54 mmol) was dissolved in acetic acid and then phenyl-λ^3-iodanediyl diacetate $PhI(OAc)_2$ (216.9 mg, 0.65 mmol) was added to the reaction mixture under nitrogen atmosphere and stirred at room temperature for 3 h, until the starting material was disappeared. Afterthat acetic acid was evaporated under reduced pressure and the crude product was subjected to column chromatography using silica gel (60-120 mesh SRL chemicals) using increasing amounts of ethyl acetate (5 to 10%) in hexanes to yield 1-allyl-2-oxo-1,2-dihydronaphthalen-1-yl acetate as a liquid (101.3 mg) in 78% yield; R_f (90% Hexane/EtOAc) 0.5; IR (KBr, cm^{-1}) 2920, 1739, 1681, 1458, 1372, 1240, 1028, 835, 751, 681; ^1H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 7.42-7.36 (m, 3H), 7.33-7.30 (m, 2H), 6.21 (d, *J* = 9.9 Hz, 1H), 5.51-5.39 (m, 1H), 5.00-4.85 (m, 2H), 2.74-2.59 (m, 2H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) δ 196.9 (C=O), 169.0 (C), 144.6 (CH), 142.3 (C), 130.3(C), 130.2 (CH), 129.5 (CH), 129.4 (CH), 128.2 (CH), 125.5 (CH), 125.0 (CH), 120.3 (CH_2), 81.5 (C), 46.3 (CH_2), 20.9 (CH_3) ppm; HRMS (ESI) calcd for $C_{15}H_{15}O_3$ (M + H) 243.1016, found 243.1016.

Previously, Miller and co-worker (*J. Org. Chem.* **1978**, *43*, 4441-4446) reported unsuccessful attempt in the hydrolysis of the acetate group in 1-allyl-2-oxo-1,2-dihydronaphthalen-1-yl acetate to corresponding alcohol. We tried to hydrolyze acetate group to the corresponding alcohol by using alternate methods such as K_2CO_3/MeOH, KOH/MeOH, NaOMe/MeOH and $CuCl_2$/MeOH, but we failed to get the required hydroxy ketone. Then, we tried Voight reaction on 1-allyl-2-oxo-1,2-dihydronaphthalen-1-yl acetate with benzylamine in the presence of formic acid in methanol and with aniline in the presence of *p*-toluenesulfonic acid monohydrate in toluene. In both the cases, the reaction did not work.

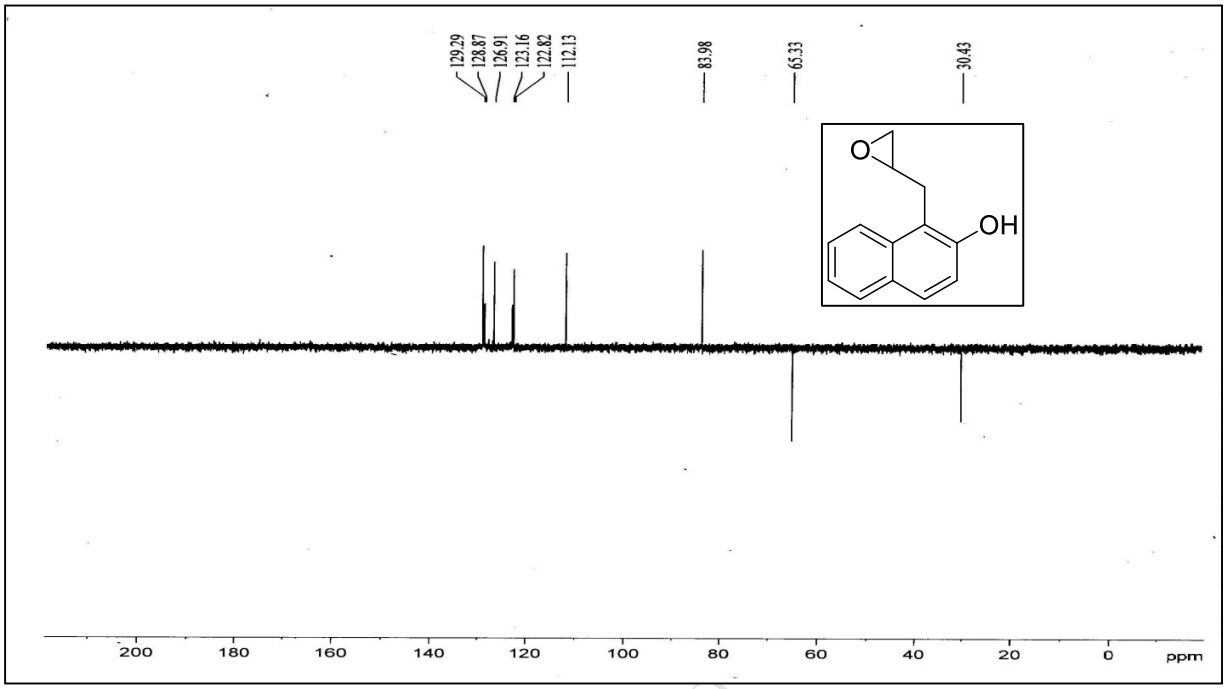
Spectra



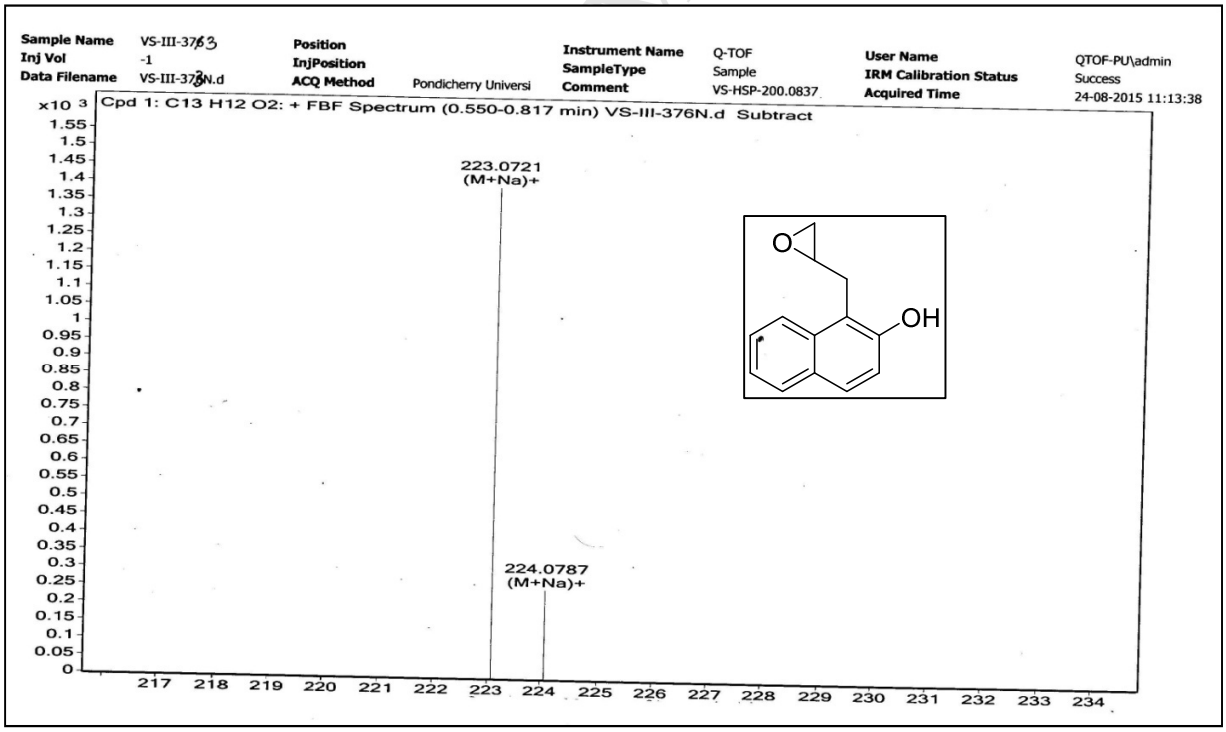
^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 1-(oxiran-2-ylmethyl)naphthalen-2-ol.



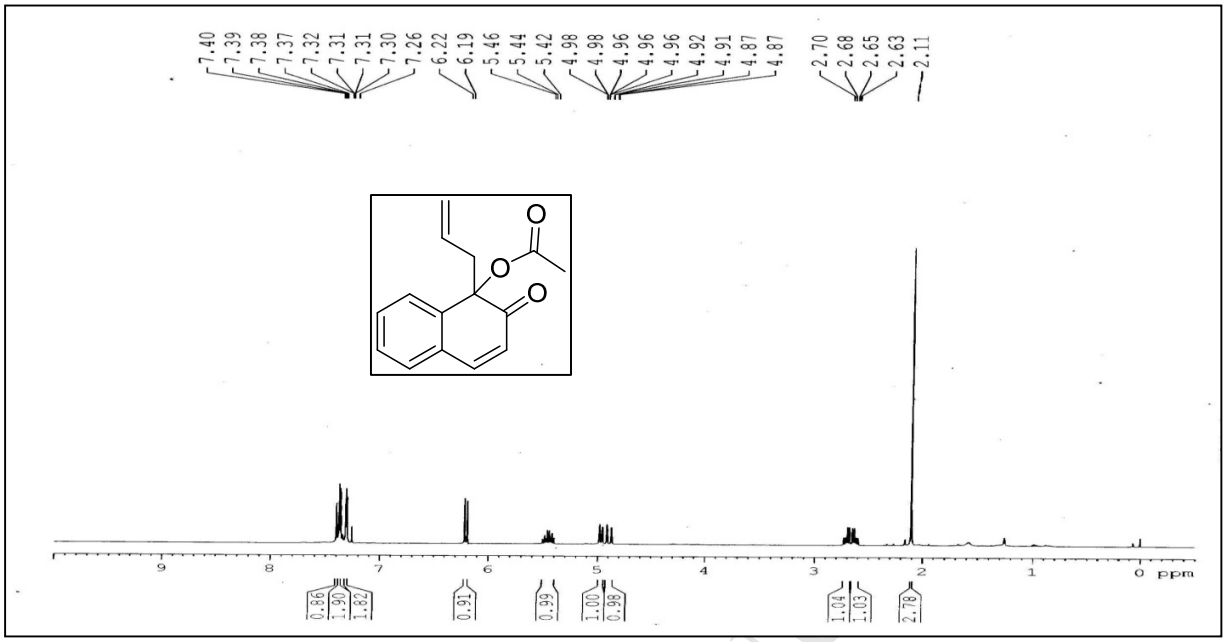
^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 1-(oxiran-2-ylmethyl)naphthalen-2-ol.



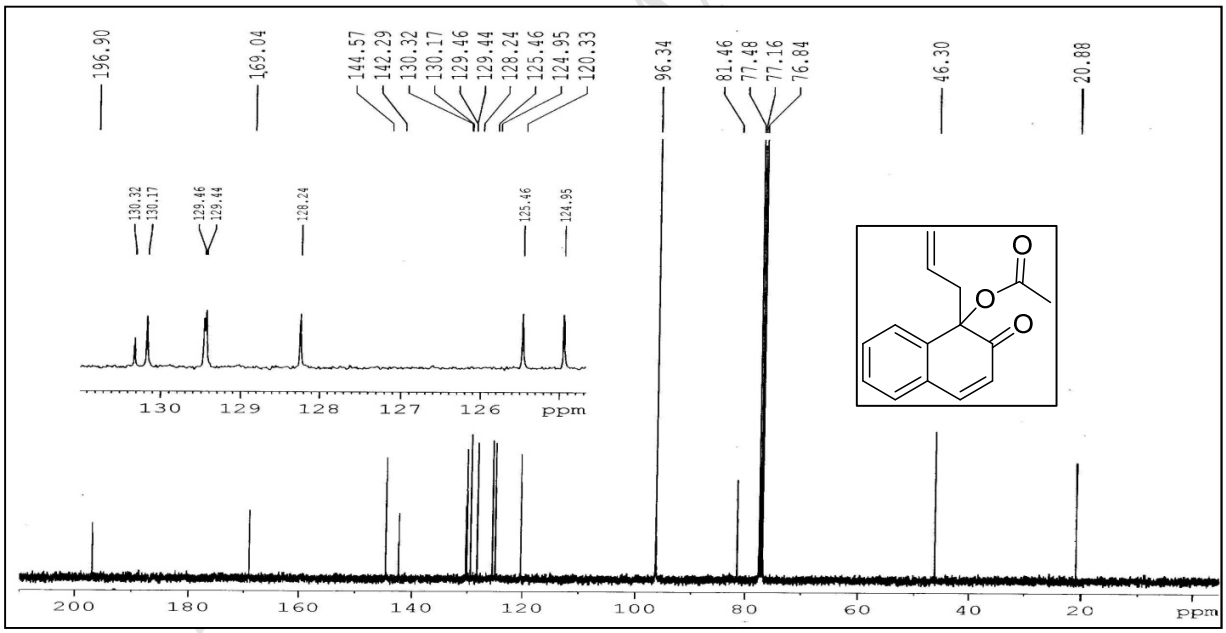
DEPT-135 NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 1-(oxiran-2-ylmethyl)naphthalen-2-ol.



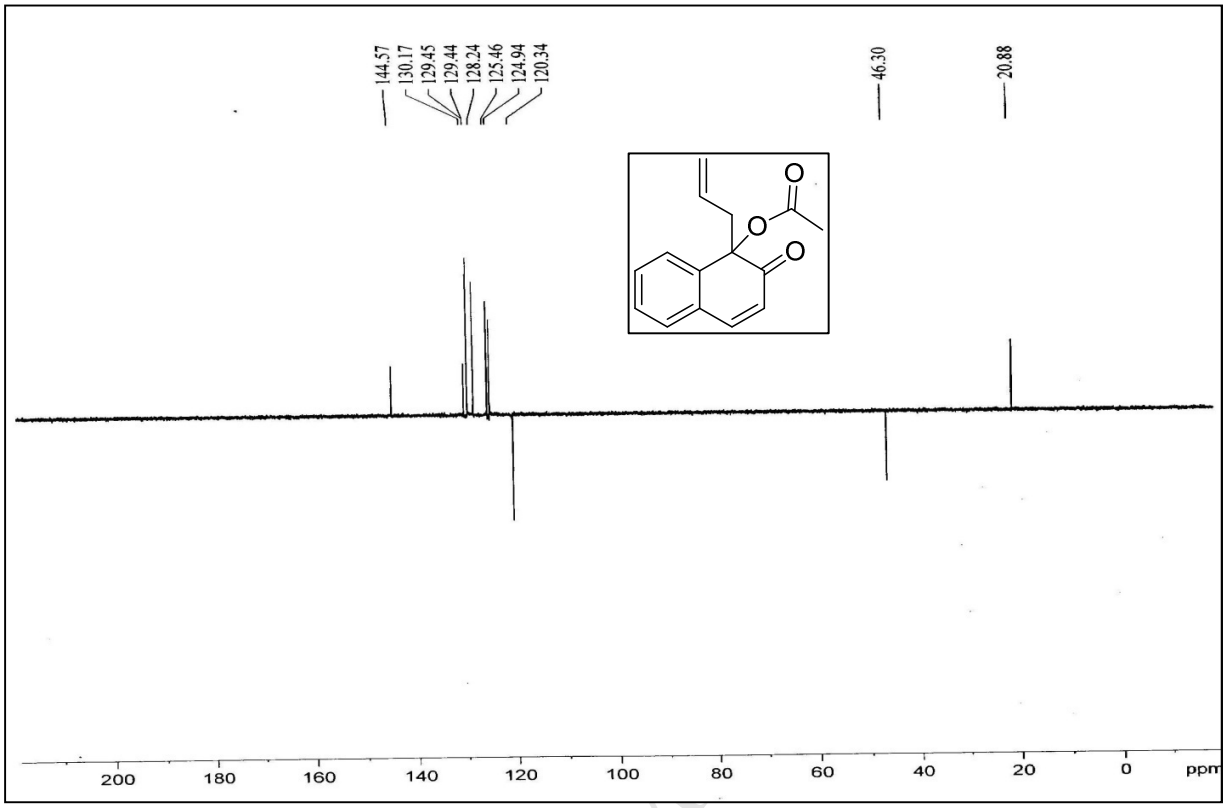
HRMS spectrum of 1-(oxiran-2-ylmethyl)naphthalen-2-ol.



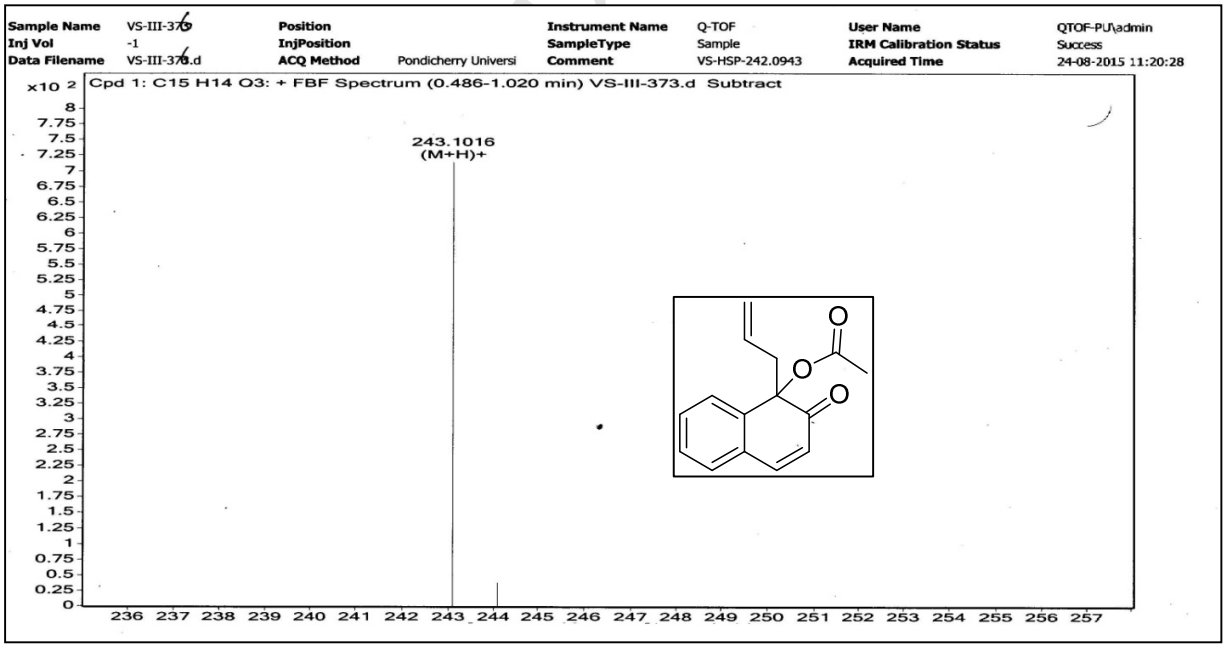
^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 1-allyl-2-oxo-1,2-dihydronaphthalen-1-yl acetate.



^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 1-allyl-2-oxo-1,2-dihydronaphthalen-1-yl acetate.

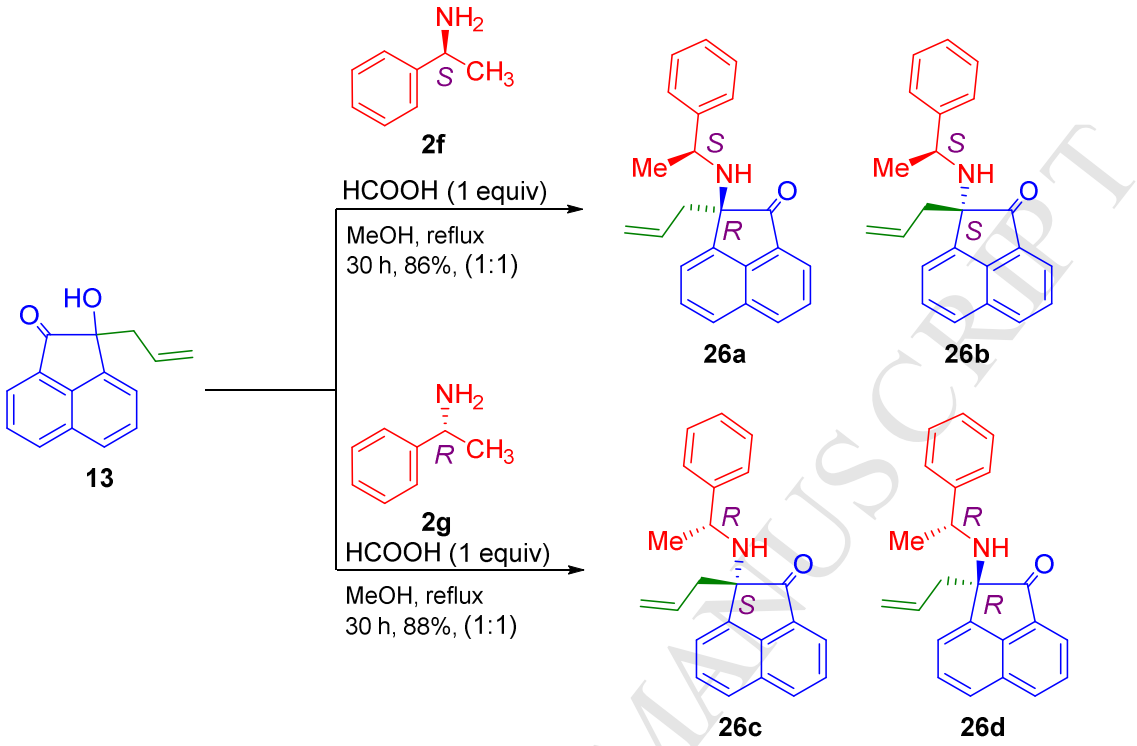


DEPT-135 NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of 1-allyl-2-oxo-1,2-dihydronaphthalen-1-yl acetate.



HRMS spectrum of 1-allyl-2-oxo-1,2-dihydronaphthalen-1-yl acetate.

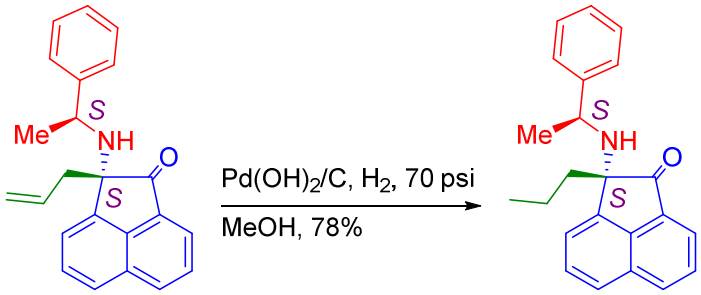
Appendix II



Scheme 3. Voight reaction of *tert*-α-hydroxy ketone present on acenaphthylene motif **13** with chiral amines **2f-g** to corresponding *tert*-α-amino ketones **26a-d**.

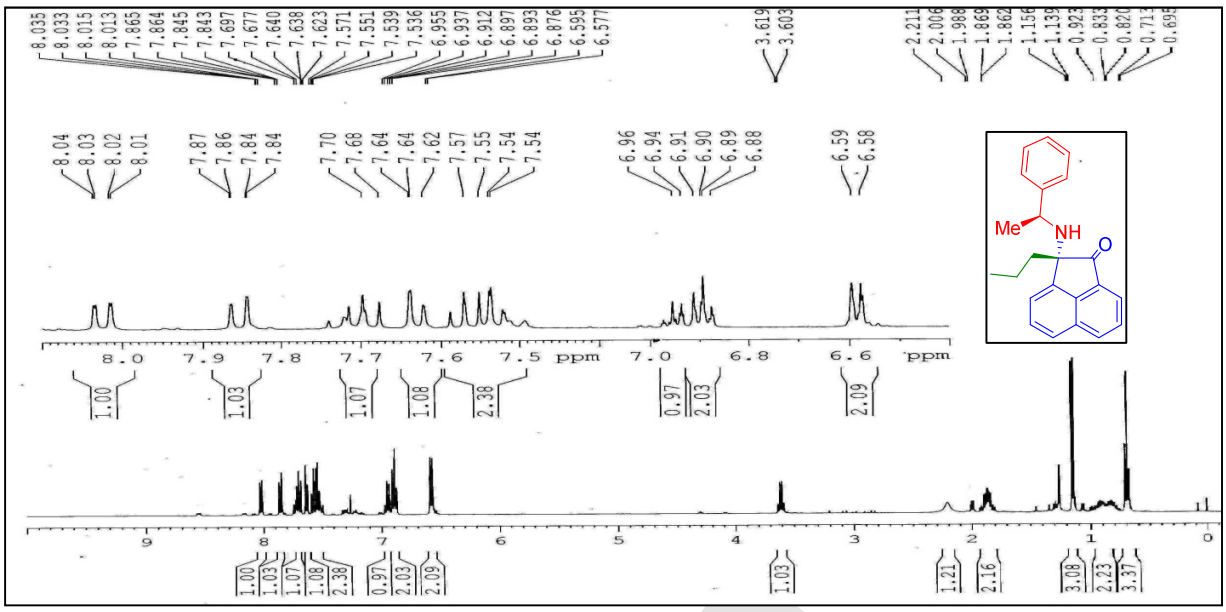
The product as given in Scheme 3 is a mixture of diastereomers. We separated the diasteromeric mixture into optically active tertiary-α-amino ketones. Removal of the chiral auxiliary (ethylbenzene moiety) will provide optically active primary amino ketone. But, in tertiary-α-amino ketones like **26** there are multiple benzylic C-N bonds as well as an allyl group, all of which are prone for reduction / reductive cleavage under hydrogenation with palladium catalysts. Still, we attempted reductive removal of ethylbenzene moiety selectively by hydrogenolysis using Pd/C (10%) or $Pd(OH)_2/C$ (20%). In both the instances, we isolated the double bond reduced product (allyl to propyl) without reductive cleavage of α-methylbenzyl group. At higher pressures (300 psi) the reaction provided an inseparable mixture.

Synthesis of (*S*)-2-(((*S*)-1-phenylethyl)amino)-2-propylacenaphthylen-1(2*H*)-one

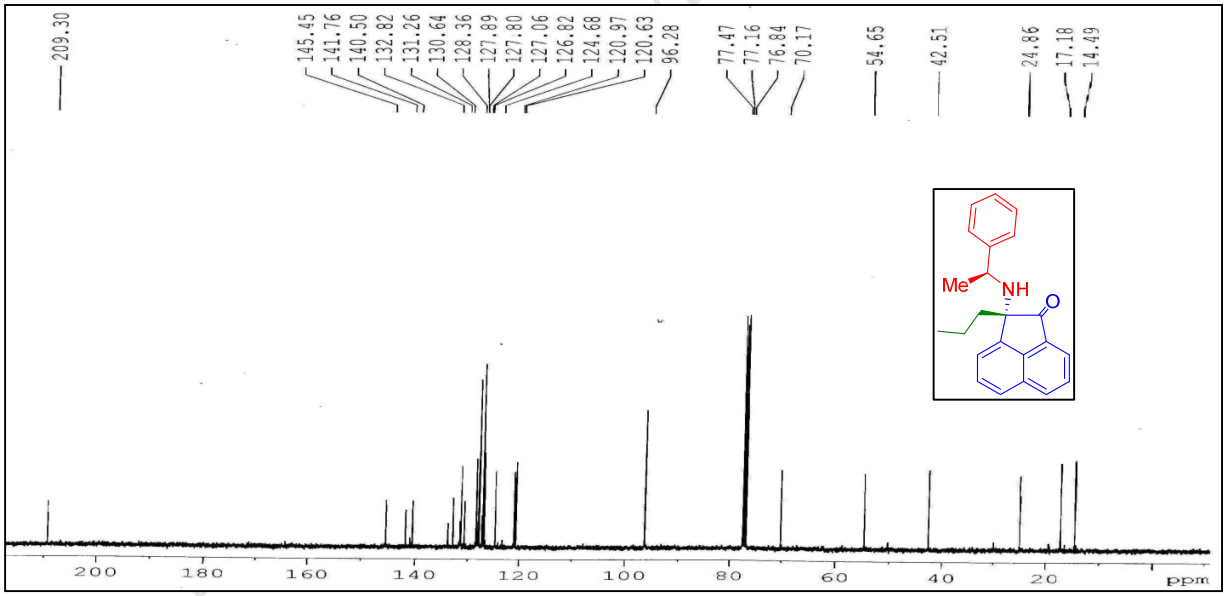


Experimental procedure: (*S*)-2-allyl-2-(((*S*)-1-phenylethyl)amino)acenaphthylen-1(2*H*)-one (100.1 mg, 0.31 mmol) was taken in a hydrogenator, dissolved in methanol (5 mL) and then 20% $Pd(OH)_2/C$ (4.2 mg, 0.03 mmol) was added. The reaction was done at 70 psi for 12 h. After completion of starting material in the reaction mixture, filter the Pd/C through celite and concentrated the mother liquor. Then the crude product was subjected to column chromatography using neutral alumina using hexanes as eluent to afford (*S*)-2-(((*S*)-1-phenylethyl)amino)-2-propylacenaphthylen-1(2*H*)-one (78.2 mg) as a semi solid in 78% yield, R_f (98% Hexane/EtOAc) 0.7; $[\alpha]_D^{22}$ = -85° (c = 1, methanol); IR (KBr, cm^{-1}) 3443, 2955, 2928, 2865, 1721, 1603, 1457, 1377, 1263, 1072, 1026, 971, 779, 700; ^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) δ 8.02 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.73-7.68 (m, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.59-7.52 (m, 2H), 6.95 (d, *J* = 7.2 Hz, 1H), 6.91-6.86 (m, 2H), 6.59 (d, *J* = 7.2 Hz, 2H), 3.61 (q, *J* = 6.6 Hz, 1H), 2.21 (s, 1H), 1.99-1.86 (m, 2H), 1.15 (d, *J* = 6.6 Hz, 3H), 0.92-0.71 (m, 2H), 0.71 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) 209.3 (C=O), 145.5 (C), 141.8 (C), 140.5 (C), 132.8 (C), 131.3 (CH), 130.6 (C), 128.4 (CH), 127.9 (CH), 127.8 (CH), 127.1 (CH), 126.8 (CH), 124.7 (CH), 121.0 (CH), 120.6 (CH), 70.2 (C), 54.7 (CH), 42.5 (CH_2), 24.9 (CH_3), 17.2 (CH_2), 14.5 (CH_3) ppm; HRMS (ESI) calcd for $C_{23}H_{24}NO$ (M + H) 330.1852, found 330.1854.

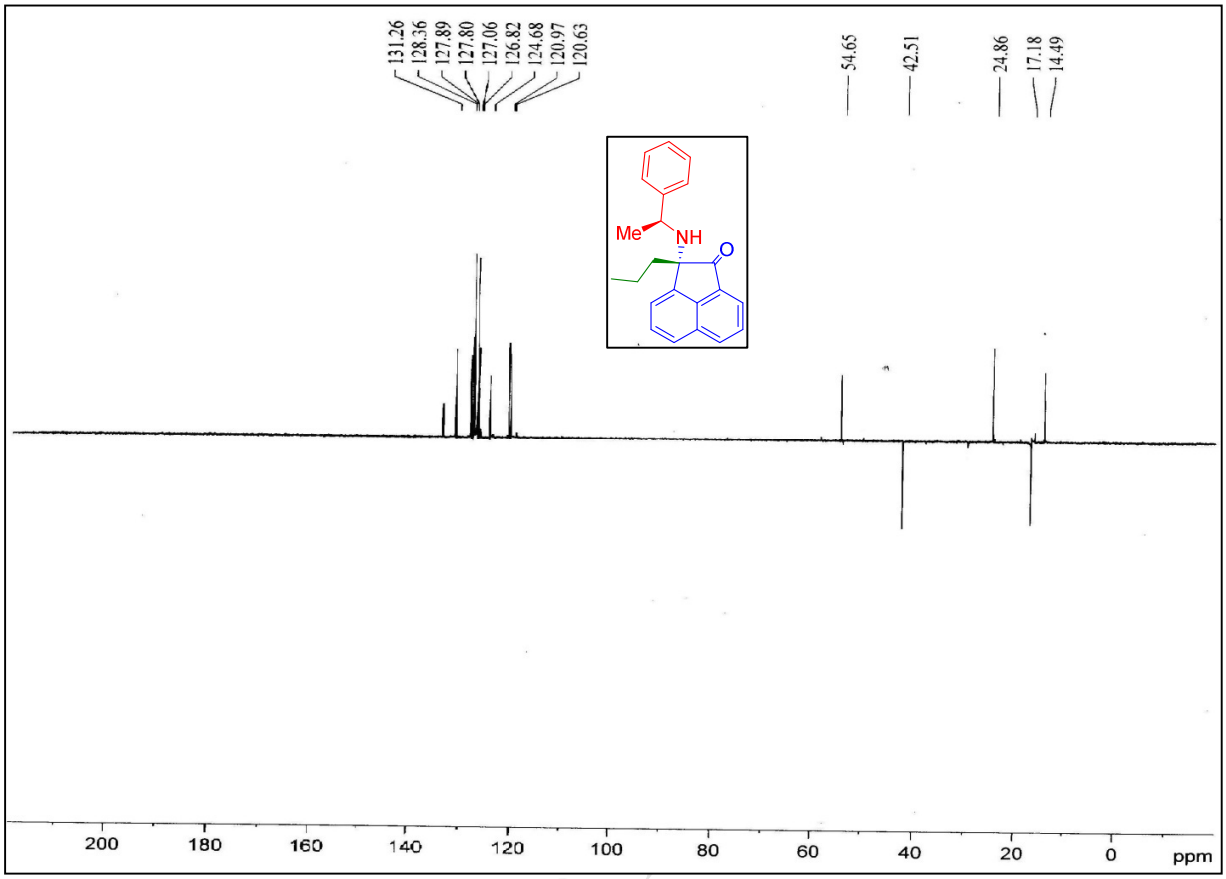
Spectra



^{1}H NMR (400 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of (*S*)-2-(((*S*)-1-phenylethyl)amino)-2-propylacenaphthylen-1(2*H*)-one.



^{13}C NMR (100 MHz, $CDCl_3$ + CCl_4; 1:1) spectrum of (*S*)-2-(((*S*)-1-phenylethyl)amino)-2-propylacenaphthylen-1(2*H*)-one.



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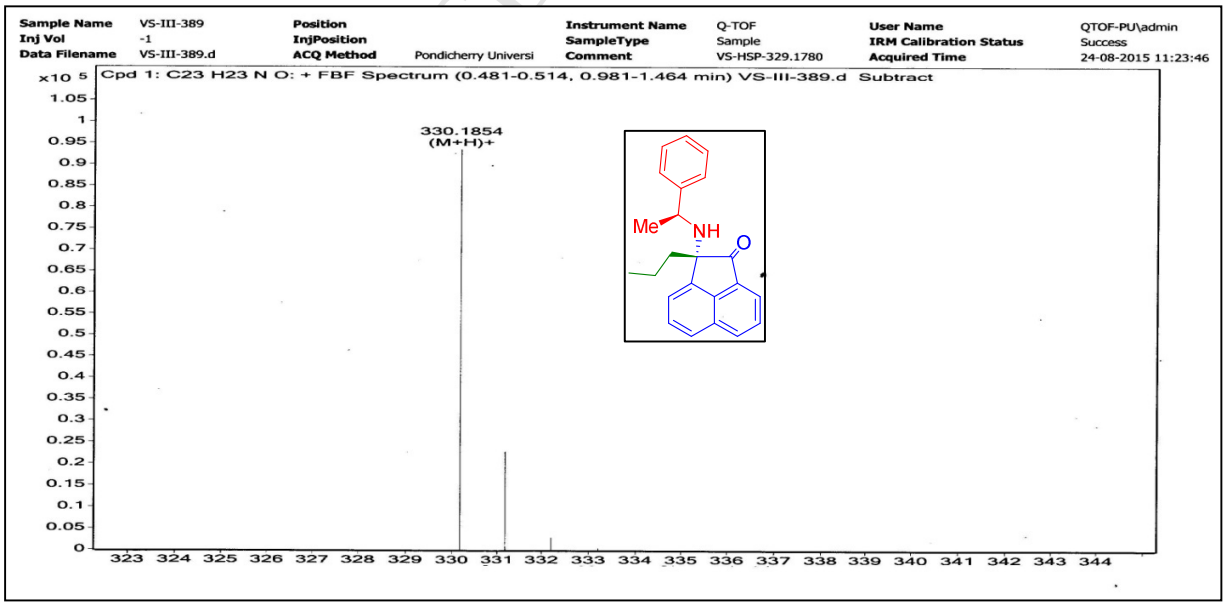

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