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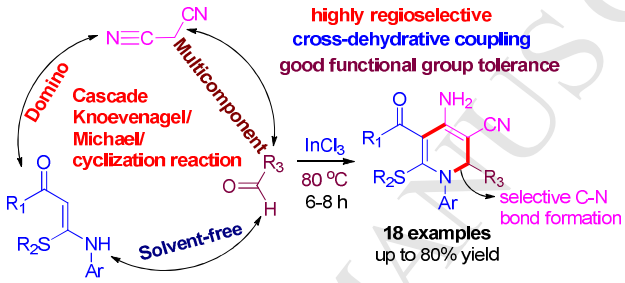

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ABSTRACT

A highly convergent and regioselective one-pot synthesis of hitherto unreported 4-amino-1,2-dihydropyridines has been achieved via three-component domino coupling (3CDC) of α-oxoketene-*N*,*S*-arylaminoacetals, aldehydes, and malononitrile in the presence of $InCl_3$ under solvent-free conditions. The merit of this cascade Knoevenagel condensation/Michael addition/cyclization sequence is highlighted by its atom-economy, efficacy of forming consecutive three new bonds (two C–C and one C–N), and one ring in a single operation. Noteworthy, the presence of nitrile and amino groups at 3- and 4-positions of 1,2-dihydropyridine ring makes these compounds excellent precursors for further synthetic renovations. Remarkably, one of the newly synthesized 4-amino-1,2-dihydropyridine exhibited high selectivity and sensitivity for Fe^{3+} ion over other metal ions.

1. Introduction

To achieve pre-eminent goal of organic synthesis, the development of pot, step, and atom economic sustainable methods is highly desirable. One of the important challenges of synthesis is to design well-organized cascades that provide structural and functional complexity as well as diversity with remarkable properties. One approach to address this challenge involves the development of multicomponent domino reactions[1-3] (MDRs), particularly those performed in aqueous media or under solvent-free conditions. Due to their simplified reaction design, convergent nature, extensive minimization of waste, labor, time, energy and cost, the MDRs have emerged as one of the important tools for modern organic synthesis, and have realized exponential growth over the past two decades.[4,5] As a consequence, solvent-free MDRs and related reactions are witnessing a new spring.[6,7]

For the past several decades, the synthesis of nitrogen heterocycles has been a key goal because of their ubiquitous presence in natural products and drugs.[8] Pyridines, one of the prominent and privileged N-heterocyclic pharmacophore, exhibit diverse biological and therapeutic activities, and constitute the core structural motif of numerous natural products.[9] Furthermore, pyridine based derivatives have broad applications in coordination chemistry,[10a] supra-molecular chemisty,[10b,c] artificial photosynthesis systems,[10d] luminescent sensor materials,[10e] and non-linear optical materials.[10f] Additionally, pyridines consisting of pendant chiral substituents, often used as ligands in several metal-catalyzed asymmetric syntheses.[11]

In view of above significant applications, synthesis of pyridine derivatives has received much attention. The development of synthetic routes to pyridine derivatives has been the focus for decades and continues to be an active area of research even today.[12] Among the reported methods for the synthesis of pyridine derivatives, the commonly utilized are cycloaddition reactions,[13] condensation of amine with carbonyl compounds,[14] iminoannulation,[15a] coupling of N-vinyl amides with alkenes or alkynes,[15b] ring closing metathesis,[16] and annulations via C–H activation.[17] However, most of the reported methods suffer from some drawbacks like poor yields,[18] use of hazardous solvents/reagents[15b,17a] that are difficult to degrade or remove from the reaction media. Directed toward such challenging goals, we focus our attention toward the use and design of domino reactions for the construction of highly functionalized pyridine derivatives. The planning of domino reactions is like playing chess.

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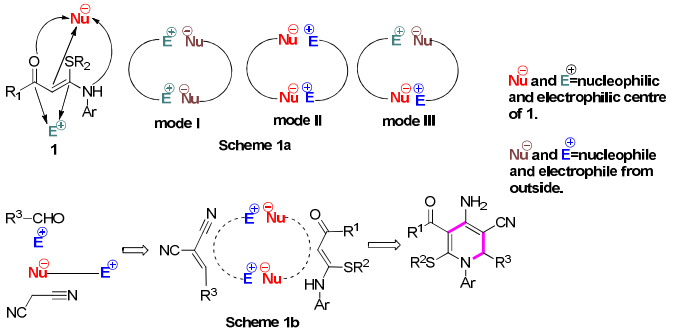
2. Results and discussion

Sustainable development has become one of the hottest terms in the current century. With regard to sustainability, methodologies based on domino raections are a highly efficient strategy for the construction of carbon-carbon and carbon-heteroatom bonds. Ambiphilic synthons have shown a great potential in the development of new reaction pathways. α-Oxoketene-*N*,*S*-arylaminoacetals containing promising structural features have demonstrated incredible utility as versatile intermediates in organic synthesis.[19] Depending upon the reaction conditions and counter reagents, α-oxoketene-*N*,*S*-acetal can apply its reactive centers in different modes[20] as depicted in Scheme 1a.



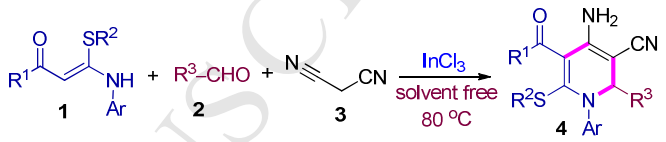
Scheme 1a

Scheme 1b

Scheme 1. (a) Reaction modes of α-oxoketene-*N*,*S*-arylaminoacetals. (b) Synthetic strategy for hexasubstituted 1,2-dihydropyridines.

As a part of our research interest toward the development of new methodologies via MCRs for the synthesis of novel heterocyclic compounds,[21,22] this time, we envisioned to explore α-oxoketene-*N*,*S*-arylaminoacetals (using its C and N nucleophilic centers) for the straightforward construction of 4-aminopyridine derivatives. To the best of our knowledge, there is no report on the synthesis of 4-amino-pentasubstituted 1,2-dihydropyridine derivatives from α-oxoketene-*N*,*S*-arylaminoacetals. With regard to develop a new method for the synthesis of highly functionalized pyridines, we devised a cascade cross-dehydrative coupling strategy as outlined in Scheme 1b. We envisaged that one-pot three-component synthesis of 1,2-dihydropyridine derivatives from simple and easily available synthons such as binucleophilic α-oxoketene-*N*,*S*-arylaminoacetal and bielectrophilic Knoevenagel condensation product derived from aromatic aldehyde and malononitrile could be handy in the present case (Scheme 1b). The precursor α-oxoketene-*N*,*S*-arylaminoacetals are not commercially sourced and have been synthesized by literature methods.[23a] This strategy provided fully substituted 1,2-dihydropyridines by the coupling of α-oxoketene-*N*,*S*-arylaminoacetals, aldehydes, and malononitrile in the presence of Lewis acid under solvent-free conditions at 80 °C. It involves domino Knoevenagel/Michael /cyclization sequence, in which three new σ bonds and one six-membered ring could be straightforwardly formed (Scheme 2).

To optimize the reaction conditions for the synthesis of 4-amino-1,2-dihydropyridines, 3-(methylthio)-1-phenyl-3-(phenylamino)prop-2-en-1-one **1a**, benzaldehyde **2a**, and malononitrile **3** were taken as test substrates. The equimolar amounts of **1a**, **2a**, and **3** were examined under the array of different conditions and the results are listed in Table 1. Initially, one-pot three-component reaction of **1a**, **2a**, and **3** was performed in EtOH at room temperature. Unfortunately, the reaction did not proceed at all even after 24 h of stirring, and the starting materials remained completely unconsumed (Table 1, entry 1). Next, upon increasing the temperature of the above reaction to reflux, the Knoevenagel condensation product between aldehyde **2a** and malononitrile **3** was obtained whereas the *N*,*S*-acetal **1a** remained unconsumed even after 24 h (Table 1, entry 2). Next, the above model reaction was carried out in ethanol under reflux in the presence of $InCl_3$ (10 mol % with respect to **1a**). In this case also the reaction stopped at the Knoevenagel condensation step (Table 1, entry 3). A brief screen of some polar aprotic solvents like CH_3CN and THF also did not provide any further improvement (Table 1, entries 4 and 5). With above failures, we next performed the model reaction in the non-polar solvents like toluene and benzene in the presence of 10 mol % of $InCl_3$ (Table 1, entries 6 and 7). Notably, the workup of the reaction provided the desired pyridine **4a** in 40% and 32% yields, respectively along with Knoevenagel product as predominant one.



1a: R^1=Ph, R^2=Me, Ar=Ph; **1b**: R^1=2-ClC_6H_4, R^2=Me, Ar=2-BrC_6H_4;
1c: R^1=2-furyl, R^2=Et, Ar=Ph; **1d**: R^1=2-thienyl, R^2=*n*-Pr, Ar=Ph;
1e: R^1=3-OMeC_6H_4, R^2=*n*-Bu, Ar=Ph; **1f**: R^1=4-MeC_6H_4, R^2=Me, Ar=Ph;
1g: R^1=4-MeOC_6H_4, R^2=Me, Ar=Ph; **1h**: R^1=4-MeOC_6H_4, R^2=*n*-Pent, Ar=Ph
2a: R^3=Ph; **2b**: R^3=2-BrC_6H_4; **2c**: R^3=2-furyl; **2d**: R^3=3-ClC_6H_4;
2e: R^3=3-$NO_2C_6H_4$; **2f**: R^3=4-MeC_6H_4; **2g**: R^3=4-MeOC_6H_4;
2h: R^3=4-FC_6H_4; **2i**: R^3=4-BrC_6H_4; **2j**: R^3=4-$NO_2C_6H_4$;
2k: R^3=2,4-$Cl_2C_6H_3$; **2l**: R^3=2-F-4-ClC_6H_3; **2m**: R^3=cyclohexyl;
2n: R^3=*n*-heptyl

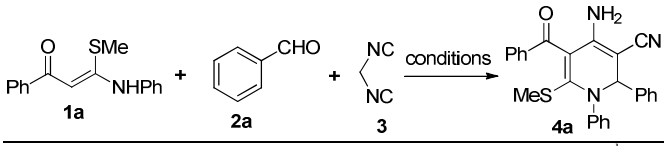
Scheme 2. Synthesis of 4-amino-1,2-dihydropyridines.

Solvent-free reactions play an ever-increasing and important role in organic synthesis. Interestingly, the power of solvent-free reactions is even more visible in the area of domino reactions, so we decided to carry out the reaction under solvent-free conditions. Thus, the above MCR was performed under solvent-free conditions at 80 °C in the presence of 10 mol % of $InCl_3$. To our pleasure, the desired product **4a** was obtained in 80% yield within 6 h (Table 1, entry 8). With a view to optimize the reaction conditions, experiments were conducted by varying Lewis acid catalysts and temperature. However, increasing or decreasing the reaction temperature showed no improvement (Table 1, entries 9 and 10). Next, some other common Lewis acids such as $FeCl_3$, $AlCl_3$, $InBr_3$, $Sc(OTf)_3$, and $Y(OTf)_3$ were also screened to check their competence (Table 1, entries 11-15) but none of them provided better result than $InCl_3$. Thus, $InCl_3$ was found to be most efficient and effective Lewis acid for the current MCR.

With $InCl_3$ Lewis acid as good promoter in hand, next we intended to optimize its loading, and it was found that the use of 10 mol % of $InCl_3$ provided the best result (Table 1, entry 8). Reducing the mol % of $InCl_3$ in the reaction increased the reaction time and lowered the yield, and increasing the catalyst loading did not show any improvement (Table 1, entries 16 and 17). Next, to see the feasibility of this one-pot three-component cascade coupling in water, we performed the model reaction in water at 100 °C, but the reaction stopped at its intermediate Knoevenagel condensation step (Table 1, entry 18). Obviously, screening of various parameters revealed that the reaction

proceeded well in the presence of $InCl_3$ under solvent-free conditions. Thus, the optimum reaction condition for the synthesis of **4a** was found to be equimolar amounts of **1a**, **2a**, and **3** in the presence of 10 mol % of $InCl_3$ at 80 °C under solvent-free conditions (Table 1, entry 8).

Table 1
Optimization of reaction conditions for the synthesis of **4a**[a]



Entry	Catalyst (mol %)	Solvent	Temp (° C)	Time (h)	Yield[b] (%)
1	none	EtOH	rt	24	nr[c]
2	none	EtOH	reflux	24	Kp[d]
3	$InCl_3$ (10)	EtOH	reflux	24	Kp[d]
4	$InCl_3$ (10)	CH_3CN	reflux	24	Kp[d]
5	$InCl_3$ (10)	THF	reflux	24	Kp[d]
6	$InCl_3$ (10)	Toluene	reflux	24	40
7	$InCl_3$ (10)	Benzene	reflux	24	32
8	$InCl_3$ (10)	none	80	6	80
9	$InCl_3$ (10)	none	90	6	76
10	$InCl_3$ (10)	none	70	12	65
11	$FeCl_3$ (10)	none	80	24	30
12	$AlCl_3$ (10)	none	80	24	38
13	$InBr_3$ (10)	none	80	24	72
14	$Sc(OTf)_3$ (10)	none	80	24	52
15	$Y(OTf)_3$ (10)	none	80	24	59
16	$InCl_3$ (5)	none	80	10	61
17	$InCl_3$ (20)	none	80	6	80
18	$InCl_3$ (10)	H_2O	reflux	24	Kp[d]

[a] All reactions were carried out using 1.0 mmol of each **1a**, **2a**, and **3** in 5 mL of each solvent.

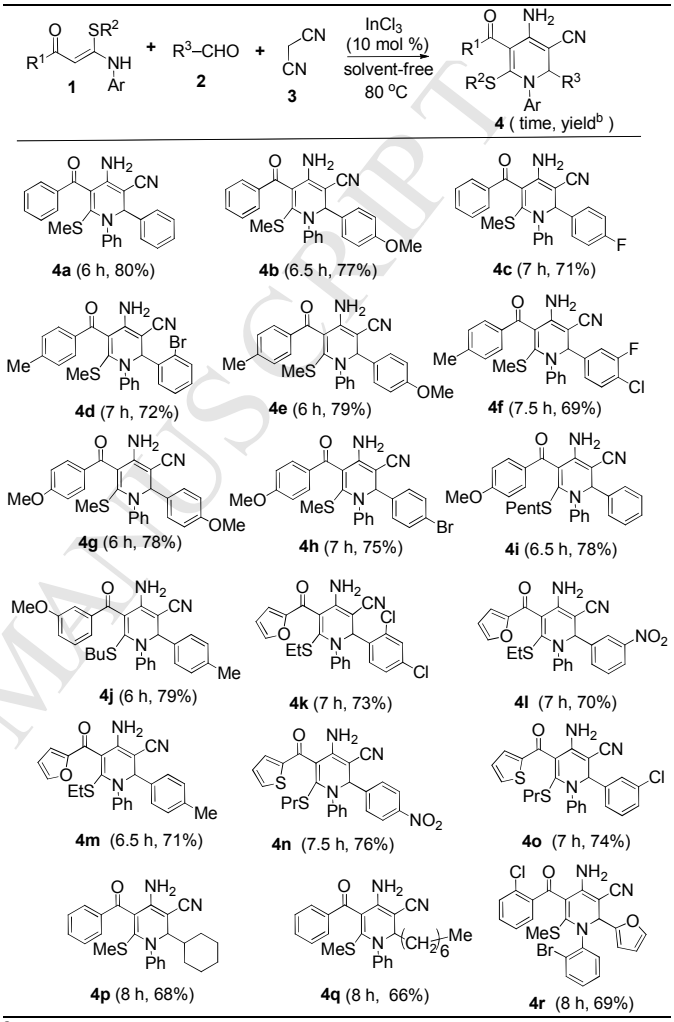
[b] Isolated pure yield.

[c] No reaction.

[d] Intermediate Knoevenagel condensation product of **2a** and **3**.

Experiments probing the scope and generality of this one-pot three-component cross-dehydrative coupling reaction between α-oxoketene-*N*,*S*-acetals **1**, aldehydes **2**, and malononitrile **3** under optimized conditions are summarized in Table 2. A broad spectrum of α-oxoketene-*N*,*S*-acetals **1**, bearing R^1 as aryl (containing both electron-donating and electron-withdrawing groups) and hetaryl, and R^2 as methyl, ethyl, *iso*-propyl, *n*-butyl and *n*-pentyl groups could be employed to afford 1,2-dihydropyridines **4** in good to excellent yields. As can be seen from Table 2, all reactions proceeded smoothly resulting the corresponding products **4** in high yields. Steric and electronic effects of the substituents had no noticeable impact on the yield as well as on the rate of the reaction. In all products 6-thioalkyl substituent that stem from α-oxoketene-*N*,*S*-acetals was also well tolerated under these reaction conditions and was kept constant. To illustrate the broad synthetic utility and generality of our developed methodology, diverse aromatic aldehydes (**4a–o**), aliphatic aldehydes (**4p, q**), and one heteroaromatic aldehyde (**4r**) were examined and tolerated well under the optimized reaction conditions to give the desired products **4**.

Table 2
Substrates scope for the synthesis of **4**[a]



[a] All reactions were performed using 1.0 mmol of each **1**, **2** and **3**.

[b] Isolated pure yield.

To prove the intermediacy of the Knoevenagel product (obtained from the corresponding aldehyde and malononitrile),[23b] we isolated it and allowed to react with α-oxoketene-*N*,*S*-arylaminoacetal under the previously optimized reaction conditions. As per our expectation, the fully substituted 1,2-dihydropyridine was obtained almost in comparable yield to that of three-component reaction. To explore the scope and limitations of the $InCl_3$ catalyst, and to add further diversity to the 1,2-dihydropyridine framework, we used methyl/ethyl cyanoacetate as a coupling partner instead of malononitrile under optimized reaction conditions. To our surprise, a number of overlapping inseparable spots were observed on the TLC plate and no desired product was observed, thus limiting the scope and generality of this protocol to some extent. To overcome the above problems, the test reaction was performed under a variety of conditions, but to no avail.

The structures of all 1,2-dihydropyridines **4a–r** were deduced from their satisfactory spectroscopic data (IR, ^{1}H, & ^{13}C NMR and MS) and unequivocally established by the X-ray single crystal diffraction analysis of some representative molecules such as **4b** (Figure 1), **4d**, **4j** and **4m** (see supporting information).[24] The introduction of nitrile and amino functional groups at 3-and 4-positions of the newly formed 1,2-dihydropyridine is of special interest as it can act as an effective chemical handle for further functionalization and diversification.

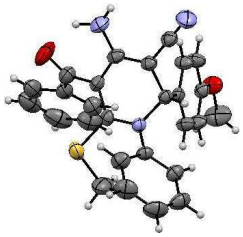
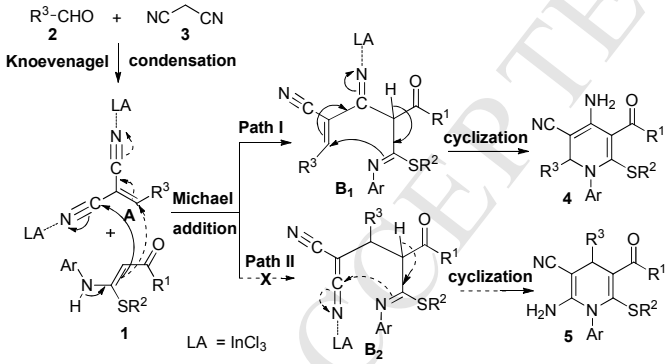


Fig. 1. ORTEP diagram of **4b**.

Taking into consideration the entire outcome, a plausible mechanistic pathway for the one-pot three-component cross-dehydrative coupling protocol is depicted in Scheme 3. The first step would be the Knoevenagel condensation between aldehyde **2** and malononitrile **3** to give the Knoevenagel product **A**, which could serve as Michael acceptor. In the next step, Michael acceptor **A** reacts with α-oxoketene-*N*,*S*-acetal **1** in a Lewis-acid assisted Michael addition process. It is likely that the attack of α-oxoketene-*N*,*S*-acetal can take place in two ways (path **I** & **II**) to furnish the open chain intermediates $\mathbf{B_1}$ and $\mathbf{B_2}$, respectively. The intermediates $\mathbf{B_1}$ and $\mathbf{B_2}$ immediately would undergo intramolecular *N*-cyclization to furnish compounds **4** and **5**. But during our investigation, we did not observe even a trace of **5**, and **4** was obtained exclusively suggesting that the protocol is highly regioselective.



Scheme 3. Plausible reaction scenario for the formation of **4**.

Following a comprehensive investigation for the one-pot synthesis of 4-amino-1,2-dihydropyridine, we became interested to find out its application in metal sensing. To do that we involved one of the 4-amino-1,2-dihydropyridine **4f** in metal ion sensing. Figure 1 shows UV-vis spectra of **4f** measured in CH_3CN-H_2O (9:1) with respective metal cations. Because of the non-fluorescent nature of **4f**, we executed the whole sensing experiment with the help of UV-vis spectroscopy over a wide range of metal ions like Na^+, K^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, Cu^{2+}, Pb^{2+}, Al^{3+}, Cr^{3+} and Fe^{3+}. To our pleasure, **4f** senses the Fe^{3+} ion selectively over the other metal ions (Figure 2). Due to the maximum abundance of iron in biological systems among the transition metals and attributable to its important role in many biological processes,[25] it is very much necessary to find out a suitable sensor for iron, which can be applied for several realistic purposes. In this circumstance our new discovery about the selective Fe^{3+} sensing ability of 4-amino-1,2-dihydropyridine possibly will find potential application in the advancement of different metal sensors.

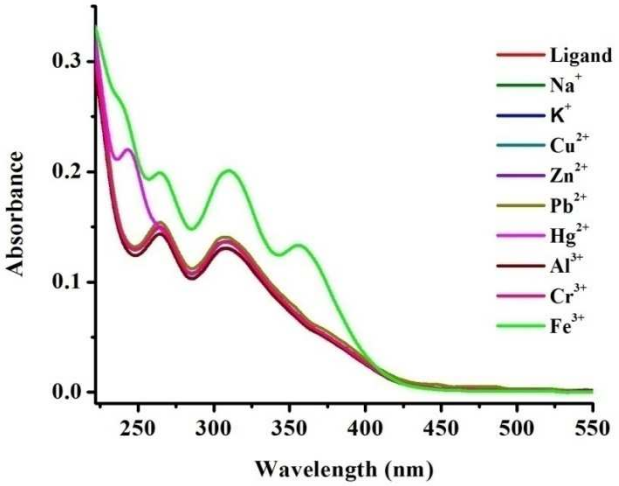


Figure 2. Changes in the absorption spectra of **4f** (1.1 X 10^{-5} M) in the presence of different metal ions in CH_3CN-H_2O (9:1).

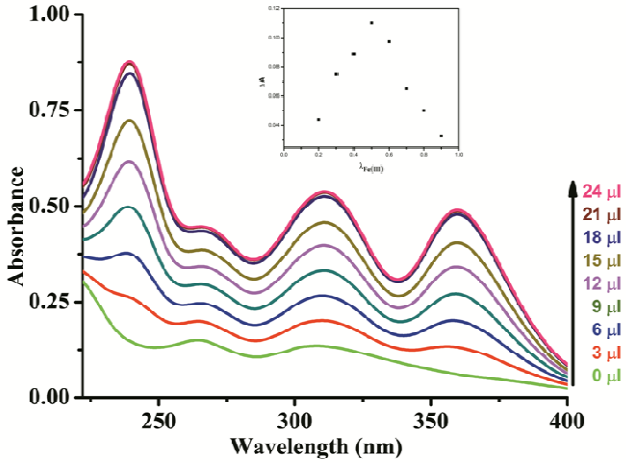


Figure 3. Changes in the absorption spectra of **4f** (1.1 X 10^{-5} M) in CH_3CN-H_2O (9:1) upon titration with (1.1 X 10^{-2} M) of Fe^{III} (0-16 equiv have been employed). Inset: plots according to the method for continuous variations indicating the 1:1 stoichiometry for **4f**-Fe^{III} (the total concentration of **4f** and Fe^{3+} is 3mL).

3. Conclusion

In summary, we have developed a highly efficient and regioselective synthesis of 4-amino-5-aroyl-6-thioalkyl-1,2-disubstituted-1,6-dihydropyridine-3-carbonitrile frameworks through three-component cross-dehydrative coupling of α-oxoketene-*N*,*S*-acetals, aldehydes, and malononitrile in the presence of $InCl_3$ under solvent-free conditions. This atom-economic domino protocol involves Knoevenagel condensation/Michael addition/cyclization sequence forming three new bonds (two C–C and one C–N), and one stereocenter in a single operation with all reactants efficiently being utilized. Cheap and easily available $InCl_3$ worked efficiently with diversly substituted α-oxoketene-*N*,*S*-acetals and aromatic aldehydes. The remarkable renovation of these pyridine derivatives could be

achieved toward their diversification for variety of purposes. Importantly, the selective Fe^{3+} sensing capability of one of its representative compound may be of value for both synthetic and material chemists for academic research and practical applications.

4. Experimental section

4.1. General

The commercially available starting materials were used as received without further purification. α-Oxoketene-*N*,*S*-arylaminoacetals **1** were prepared by the known procedure.[23a] Thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates. Infrared (IR) spectra are measured in KBr, and wavenumber ($\bar{\upsilon}$) are reported in cm^{-1}. ^1H and ^{13}C NMR spectra were recorded on NMR spectrometers operating at 300 and 75 MHz, respectively. Chemical shifts (δ) are given in parts per million (ppm) using the residue solvent peaks as reference relative to TMS. *J* values are given in Hz. Mass spectra were recorded using electrospray ionization (ESI) mass spectrometry. The melting points are uncorrected.

4.2. General procedure for the synthesis of the 4-amino-1,2-dihydropyridine (**4a-r**):

To a mixture of α-oxoketene-*N*,*S*-arylaminoacetals (1.0 mmol), aldehyde (1.0 mmol) and malononitrile (1.0 mmol), $InCl_3$ (0.1 mmol) was added and the reaction mixture was heated at 80 °C till the completion of the reaction. After completion of the reaction (monitored by TLC), water (20 mL) was added to the reaction mixture followed by extraction with ethyl acetate (2 × 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuo. The crude residue thus obtained was purified by column chromatography over silica gel using ethyl acetate/hexane as eluent to afford pure 4-amino-1,2-dihydropyridines **4**.

*4.2.1. 4-Amino-5-benzoyl-6-methylthio-1,2-diphenyl-1,2-dihydropyridine-3-carbonitrile (**4a**).*

Yellow solid, mp 173-175 °C; FT IR (KBr, cm^{-1}): 3471, 3354, 2936, 2157, 1643, 1438, 1057; ^1H NMR (300 MHz, $CDCl_3$): δ 7.62 (d, *J* = 6.3 Hz, 2H, Ar), 7.42-7.24 (m, 9H, Ar), 7.04-6.99 (m, 2H, Ar), 6.88 (d, *J* = 7.2 Hz, 2H, Ar), 5.89 (br, 2H, D_2O Exchangeable, NH_2), 5.47 (s, 1H, Chiral CH), 2.10 (s, 3H, SCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.06, 154.54, 152.60, 144.16, 140.86, 131.93, 129.47, 128.73, 128.65, 128.47, 128.32, 127.85, 126.97, 125.19, 120.41, 114.78, 65.33, 63.05, 15.74; HRMS $[M+H]^+$ calcd. For $C_{26}H_{22}N_3OS$ 424.1483, found 424.1490.

*4.2.2. 4-Amino-5-benzoyl-2-(4-methoxyphenyl)-6-methylthio-1-phenyl-1,2-dihydropyridine-3-carbonitrile (**4b**).*

Yellow solid, mp 170-172 °C; FT IR (KBr, cm^{-1}): 3482, 3337, 2932, 2160, 1628, 1446, 1025; ^1H NMR (300 MHz, $CDCl_3$): δ 7.58-7.31 (m, 8H, Ar), 7.17-6.98 (m, 6H, Ar), 5.92 (br, 2H, NH_2), 5.48 (s, 1H, Chiral CH), 3.86 (s, 3H, OCH_3), 1.71 (s, 3H, SCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.02, 159.79, 154.38, 152.55, 144.16, 140.05, 132.50, 131.94, 129.44, 128.73, 128.28, 127.82, 126.94, 125.23, 120.40, 114.72, 113.74, 65.00, 63.19, 55.45, 15.80; HRMS $[M+Na]^+$ calcd. For $C_{27}H_{23}N_3O_2SNa$ 476.1403, found 476.1389.

*4.2.3. 4-Amino-5-benzoyl-2-(4-fluorophenyl)-6-methylthio-1-phenyl-1,2-dihydropyridine-3-carbonitrile (**4c**).*

Yellow solid, mp 145-147 °C; FT IR (KBr, cm^{-1}): 3463, 3348, 2922, 2139, 1651, 1436, 1021; ^1H NMR (300 MHz, $CDCl_3$): δ 7.64 (t, *J* = 6.4 Hz, 2H, Ar), 7.40-7.33 (m, 6H, Ar), 7.20-7.10 (m, 4H, Ar), 7.00 (d, *J* = 7.5 Hz, 2H, Ar), 5.95 (br, 2H, NH_2), 5.48 (s, 1H, Chiral CH), 1.73 (s, 3H, SCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.89, 154.61, 152.58, 144.16, 139.87, 136.66, 132.17, 129.56, 128.85, 128.63, 127.94, 127.17, 125.25, 120.21, 115.36 (d, J_{CF} = 21.7Hz), 114.80, 114.75, 65.03, 63.06, 15.95 ; HRMS $[M+H]^+$ calcd. For $C_{26}H_{21}FN_3OS$ 442.1389, found 442.1410.

*4.2.4. 4-Amino-2-(2-bromophenyl)-5-(4-methylbenzoyl)-6-methylthio-1-phenyl-1,2-dihydropyridine-3-carbonitrile (**4d**).*

Yellow solid, mp 209-211 °C; FT IR (KBr, cm^{-1}): 3472, 3353, 2935, 2158, 1644, 1436, 1067; ^1H NMR (300 MHz, $CDCl_3$): δ 7.68-7.63 (m, 2H, Ar), 7.51 (d, *J* = 8.1 Hz, 2H, Ar), 7.30-7.23 (m, 7H, Ar), 7.12 (d, *J* = 7.8 Hz, 2H, Ar), 5.94 (br, 2H, NH_2), 5.84 (s, 1H, Chiral CH), 2.37 (s, 3H, CH_3), 1.82 (s, 3H, SCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.95, 158.55, 153.48, 144.31, 143.26, 138.59, 137.07, 134.03, 130.44, 130.21, 129.34, 129.11, 128.87, 127.68, 127.57, 127.15, 123.35, 119.87, 112.46, 64.75, 63.45, 21.55, 17.33; HRMS $[M+Na]^+$ calcd. For $C_{27}H_{22}BrN_3OSNa$ 538.0559, found 538.0563.

*4.2.5. 4-Amino-2-(4-methoxyphenyl)-5-(4-methylbenzoyl)-6-methylthio-1-phenyl-1,2-dihydropyridine-3-carbonitrile (**4e**).*

Yellow solid, mp 168-169 °C; FT IR (KBr, cm^{-1}): 3438, 3328, 2925, 2180, 1623, 1413, 1058; ^1H NMR (300 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.1 Hz, 2H, Ar), 7.34-7.18 (m, 5H, Ar), 6.93-6.84 (m, 6H, Ar), 5.80 (br, 2H, NH_2), 5.40 (s, 1H, Chiral CH), 3.79 (s, 3H, OCH_3), 2.22 (s, 3H, CH_3), 1.18 (s, 3H, SCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.86, 174.92, 159.83, 152.50, 144.30, 137.21, 132.61, 129.66, 129.45, 129.31, 129.15, 129.02, 128.63, 128.30, 126.93, 126.89, 125.32, 113.80, 64.92, 63.24, 55.44, 21.50, 15.78; HRMS $[M+H]^+$ calcd. For $C_{28}H_{26}N_3O_2S$ 468.1745, found 468.1760.

*4.2.6. 4-Amino-2-(4-chloro-3-fluorophenyl)-5-(4-methylbenzoyl)-6-methylthio-1-phenyl-1,2-dihydropyridine-3-carbonitrile (**4f**).*

Yellow solid, mp 161-163 °C; FT IR (KBr, cm^{-1}): 3479, 3350, 2923, 2173, 1624, 1471, 1033; ^1H NMR (300 MHz, $CDCl_3$): δ 7.53-7.31 (m, 9H, Ar), 6.95 (br, 3H, Ar), 5.92 (br, 2H, NH_2), 5.45 (s, 1H, Chiral CH), 2.32 (s, 3H, CH_3), 1.79 (s, 3H, SCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.32, 159.76, 156.44, 154.15, 152.53, 143.94, 143.35, 142.69, 136.79, 130.57, 129.57, 128.73, 127.20, 125.11, 123.36, 120.01, 115.33 (d, J_{CF} = 22.9Hz), 114.78, 111.73, 64.74, 62.51, 21.53, 15.97; HRMS $[M+H]^+$ calcd. For $C_{27}H_{22}ClFN_3OS$ 490.1156, found 490.1168.

*4.2.7. 4-Amino-5-(4-methoxybenzoyl)-2-(4-methoxyphenyl)-6-methylthio-1-phenyl-1,2-dihydropyridine-3-carbonitrile (**4g**).*

Yellow sticky solid; FT IR (KBr, cm^{-1}): 3452, 3332, 2937, 2168, 1629, 1447, 1021; ^1H NMR (300 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.4 Hz, 2H, Ar), 7.41 (d, *J* = 4.5 Hz, 4H, Ar), 7.32-7.25 (m, 1H, Ar), 7.00-6.97 (m, 4H, Ar), 6.60 (d, *J* = 8.7 Hz, 2H, Ar), 5.83 (br, 2H, NH_2), 5.47 (s, 1H, Chiral CH), 3.85 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 1.77 (s, 3H, SCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.59, 162.94, 159.81, 153.09, 152.37, 144.33, 132.73, 132.31, 131.24, 129.40, 128.37, 126.77, 125.23, 120.38, 115.02, 113.76, 113.08, 64.86, 63.39, 55.53, 55.25, 15.83; HRMS $[M+H]^+$ calcd. For $C_{28}H_{26}N_3O_3S$ 484.1695, found 484.1713.

*4.2.8. 4-Amino-2-(4-bromophenyl)-5-(4-methoxybenzoyl)-6-methylthio-1-phenyl-1,2-dihydropyridine-3-carbonitrile (**4h**).*

Yellow solid, mp 171-173 °C; FT IR (KBr, cm^{-1}): 3475, 3351, 2939, 2152, 1674, 1432, 1064; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54-7.46 (m, 4H, Ar), 7.32-7.18 (m, 5H, Ar), 6.87 (br, 2H, Ar), 6.56 (d, J = 8.7 Hz, 2H, Ar), 5.75 (br, 2H, NH_2), 5.38 (s, 1H, Chiral CH), 3.73 (s, 3H, OCH_3), 1.72 (s, 3H, SCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.35, 163.16, 153.01, 152.40, 144.06, 140.41, 131.84, 131.55, 131.11, 129.52, 128.96, 126.96, 125.08, 122.31, 120.12, 115.23, 113.22, 64.83, 62.82, 55.31, 15.83; HRMS $[M+Na]^+$ calcd. For $C_{27}H_{22}BrN_3O_2SNa$ 554.0514, found 554.0552.

*4.2.9. 4-Amino-5-(4-methoxybenzoyl)-6-pentylthio-1,2-diphenyl-1,2-dihydropyridine-3- carbonitrile (**4i**).*

Yellow solid, mp 69-71 °C; FT IR (KBr, cm^{-1}): 3486, 3342, 2931, 2163, 1648, 1444, 1025; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (br, 2H, Ar), 7.45-7.40 (m, 7H, Ar), 7.25 (br, 1H, Ar), 6.95 (br, 2H, Ar), 6.55 (d, J = 8.4 Hz, 2H, Ar), 5.82 (br, 2H, NH_2), 5.51 (s, 1H, Chiral CH), 3.76 (s, 3H, OCH_3), 2.44-2.36 (m, 1H), 2.23-2.15 (m, 1H), 1.02-0.92 (m, 4H), 0.84-0.67 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.96, 162.83, 153.35, 152.51, 144.58, 141.02, 132.56, 131.18, 129.34, 128.42, 128.35, 127.10, 126.75, 125.46, 120.48, 115.22, 113.06, 65.33, 62.88, 55.24, 33.17, 30.31, 28.02, 21.85, 13.63; HRMS $[M+H]^+$ calcd. For $C_{31}H_{32}N_3O_2S$ 510.2210, found 510.2216.

*4.2.10. 4-Amino-6-butylthio-5-(3-methoxybenzoyl) -1-phenyl-2-(p-tolyl)-1,2-dihydropyridine-3-carbonitrile (**4j**).*

Yellow solid, mp 214-216 °C; FT IR (KBr, cm^{-1}): 3462, 3349, 2923, 2138, 1652, 1435, 1025; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 (d, J = 7.5 Hz, 2H, Ar), 7.43-7.37 (m, 4H, Ar), 7.33-7.25 (m, 3H, Ar), 6.90-6.84 (m, 3H, Ar), 6.34 (s, 1H, Ar), 5.92 (br, 2H, NH_2), 5.48 (s, 1H, Chiral CH), 3.66 (s, 3H, OCH_3), 2.42-2.29 (m, 4H), 2.21-2.10 (m, 1H), 0.98-0.82 (m, 4H), 0.60 (t, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.48, 159.40, 152.69, 144.68, 143.89, 141.92, 138.27, 137.64, 129.49, 129.40, 129.18, 128.63, 127.10, 127.00, 125.64, 121.71, 118.29, 114.86, 112.90, 65.31, 62.86, 55.30, 33.05, 30.22, 21.32, 13.17, 12.94; HRMS $[M+H]^+$ calcd. For $C_{31}H_{32}N_3O_2S$ 510.2215, found 510.2237.

*4.2.11. 4-Amino-2-(2,4-dichlorophenyl)-6-ethylthio-5-(2-furoyl)-1-phenyl-1,2-dihydropyridine-3-carbonitrile (**4k**).*

Yellow sticky solid; FT IR (KBr, cm^{-1}): 3481, 3350, 2916, 1645, 1439, 1053; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97-7.92 (m, 1H, Ar), 7.51-7.18 (m, 8H, Ar), 7.06 (d, J = 3.6 Hz, 1H, Ar), 6.54 (t, J = 1.5 Hz, 1H, Ar), 5.89-5.79 (m, 3H, NH_2 & Chiral CH), 2.55-2.46 (m, 1H, SCH_2), 2.23-2.14 (m, 1H, SCH_2), 0.82 (t, J = 7.5 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.15, 158.31, 154.01, 152.34, 145.01, 144.50, 136.66, 134.74, 132.75, 130.30, 129.84, 129.34, 127.99, 127.30, 126.61, 119.57, 117.36, 112.80, 110.42, 63.15, 62.49, 28.81, 14.00; HRMS $[M+H]^+$ calcd. For $C_{25}H_{20}Cl_2N_3O_2S$ 496.0653, found 496.0653.

*4.2.12. 4-Amino-6-ethylthio-5-(2-furoyl)-2-(3-nitrophenyl)-1-phenyl-1,2-dihydropyridine-3-carbonitrile (**4l**).*

Yellow solid, mp 157-159 °C; FT IR (KBr, cm^{-1}): 3456, 3327, 2923, 2181, 1643, 1416, 1059; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.59 (s, 1H, Ar), 8.23 (d, J = 7.5 Hz, 1H, Ar), 7.91 (d, J = 7.5 Hz, 1H, Ar), 7.60 (t, J = 8.1 Hz, 1H, Ar), 7.42-7.33 (m, 6H, Ar), 6.84 (d, J = 1.8 Hz, 1H, Ar), 6.43 (dd, J_1 = 1.2 Hz, J_2 = 3.0 Hz, 1H, Ar), 5.91 (br, 2H, NH_2), 5.52 (s, 1H, Chiral CH), 2.82-2.75 (m, 1H, SCH_2), 2.37-2.31 (m, 1H, SCH_2), 0.85 (t, J = 7.5 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.24, 156.73, 153.63, 152.16, 148.15, 145.80, 144.37, 143.60, 132.95, 129.92, 129.67, 127.85, 125.75, 123.07, 120.48, 120.19, 117.17, 112.62, 112.50, 65.22, 63.17, 28.11, 13.71; HRMS $[M+H]^+$ calcd. For $C_{25}H_{21}N_4O_4S$ 473.1283, found 473.1302.

*4.2.13. 4-Amino-6-ethylthio-5-(2-furoyl)-1-phenyl-2-(p-tolyl)-1,2-dihydropyridine-3- carbonitrile (**4m**).*

Yellow solid, mp 165-166 °C; FT IR (KBr, cm^{-1}): 3456, 3342, 2934, 2158, 1622, 1451, 1043; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50-7.20 (m, 10H, Ar), 6.29 (d, J = 1.8 Hz, 1H, Ar), 6.08 (br, 1H, Ar), 5.76 (br, 2H, NH_2), 5.41 (s, 1H, Chiral CH), 2.54-2.23 (m, 5H, SCH_2 & tolyl CH_3), 0.77 (t, J = 7.5 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.51, 155.08, 153.63, 151.91, 145.84, 144.58, 138.04, 137.69, 129.37, 129.08, 127.21, 126.88, 126.73, 125.84, 120.26, 117.67, 111.87, 65.56, 63.45, 27.88, 21.06, 13.54; HRMS $[M+Na]^+$ calcd. For $C_{26}H_{23}N_3O_2SNa$ 464.1403, found 464.1406.

*4.2.14. 4-Amino-2-(4-nitrophenyl)-1-phenyl-6-propylthio-5-(2-thienoyl)-1,2- dihydropyridine-3-carbonitrile (**4n**).*

Yellow solid, mp 163-165 °C; FT IR (KBr, cm^{-1}): 3478, 3351, 2924, 2172, 1654, 1463, 1032; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.33 (d, J = 8.4 Hz, 2H, Ar), 7.85 (d, J = 8.4 Hz, 2H, Ar), 7.47-7.35 (m, 6H, Ar), 6.81 (t, J = 4.2 Hz, 1H, Ar), 6.70 (d, J = 3.0 Hz, 1H, Ar), 5.83 (br, 2H, NH_2), 5.52 (s, 1H, Chiral CH), 2.54-2.46 (m, 1H, SCH_2), 2.36-2.28 (m, 1H, SCH_2), 1.20-1.00 (m, 1H, CH_2), 0.93-0.82 (m, 1H, CH_2), 0.56 (t, J = 7.3 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.07, 172.42, 152.21, 148.54, 145.24, 144.28, 133.67, 132.62, 129.66, 127.93, 127.85, 127.62, 127.57, 125.77, 123.80, 123.69, 119.84, 114.76, 65.16, 62.15, 35.89, 21.56, 12.80; HRMS $[M+H]^+$ calcd. For $C_{26}H_{23}N_4O_3S_2$ 503.1206, found 503.1214.

*4.2.15. 4-Amino-2-(3-chlorophenyl)-1-phenyl-6-propylthio-5-(2-thienoyl)-1,2- dihydropyridine-3-carbonitrile (**4o**).*

Yellow solid, mp 77-78 °C; FT IR (KBr, cm^{-1}): 3480, 3346, 2933, 1641, 1434, 1048; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 (br, 1H, Ar), 7.49 (d, J = 5.1 Hz, 1H, Ar), 7.39-7.25 (m, 8H, Ar), 6.82 (t, J = 4.3 Hz, 1H, Ar), 6.57 (d, J = 3.0 Hz, 1H, Ar), 5.74 (br, 2H, NH_2), 5.45 (s, 1H, Chiral CH), 2.54-2.46 (m, 1H, SCH_2), 2.31-2.22 (m, 1H, SCH_2), 1.19-1.01 (m, 1H, CH_2), 0.89-0.85 (m, 1H, CH_2), 0.55 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.56, 153.89, 151.94, 145.71, 144.30, 143.24, 134.59, 133.45, 132.91, 129.96, 129.49, 128.47, 127.43, 127.23, 126.93, 126.89, 125.62, 125.25, 120.09, 115.10, 65.19, 62.79, 35.54, 21.67, 12.83; HRMS $[M]^+$ calcd. For $C_{26}H_{22}ClN_3OS_2$ 491.0888, found 491.0887.

*4.2.16. 4-Amino-5-benzoyl-2-cyclohexyl-6-methylthio-1-phenyl-1,2-dihydropyridine-3-carbonitrile (**4p**).*

Yellow solid, mp 212-214 °C; FT IR (KBr, cm^{-1}): 3476, 3352, 2938, 2147, 1664, 1442, 1066; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, J = 7.5 Hz, 2H, Ar), 7.50-7.22 (m, 8H, Ar), 5.90 (br, 2H, NH_2), 3.88 (d, J = 10.2 Hz, 1H, Chiral CH), 2.17-2.05 (m, 5H), 1.85-1.72 (m, 4H), 1.36-1.25 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.26, 156.53, 151.67, 145.20, 140.58, 132.03, 129.24, 128.83, 128.18, 127.10, 126.35, 120.90, 113.46, 69.63, 63.21, 41.33, 31.67, 29.85, 26.31, 26.00, 16.69; HRMS $[M+H]^+$ calcd. For $C_{26}H_{28}N_3OS$ 476.1948, found 476.1956.

*4.2.17. 4-Amino-5-benzoyl-2-heptyl-6-methylthio-1-phenyl-1,2-dihydropyridine-3-carbonitrile (**4q**).*

Yellow sticky solid; FT IR (KBr, cm^{-1}): 3482, 3349, 2912, 1665, 1435, 1054; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, J = 6.9 Hz, 2H, Ar), 7.49-7.25 (m, 8H, Ar), 5.86 (br, 2H, NH_2), 4.26 (t, J = 7.3 Hz, 1H, Chiral CH), 1.70 (s, 3H, SCH_3), 1.41-1.25 (m, 12H), 0.89 (t, J = 5.1 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.73, 169.10, 151.77, 144.94, 140.84, 132.01, 129.30, 129.05, 128.77, 128.18, 127.84, 127.20, 125.92, 125.22, 63.78, 36.58, 34.89, 31.83, 29.66, 29.25, 26.00, 25.86, 22.61, 14.05; HRMS $[M+H]^+$ calcd. For $C_{27}H_{32}N_3OS$ 446.2266, found 446.2287.

*4.2.18. 4-Amino-1-(2-bromophenyl)-5-(2-chlorobenzoyl)-2-(furan-2-yl)-6-methylthio-1,2-dihydropyridine-3-carbonitrile (**4r**).*

Yellow solid, mp 226-228 °C; FT IR (KBr, cm^{-1}): 3472, 3381, 2957, 2166, 1664, 1435, 1061; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 (d, J = 7.8 Hz, 1H, Ar), 7.61 (t, J = 7.9 Hz, 2H, Ar), 7.44 (t, J = 7.5 Hz, 1H, Ar), 7.34-7.17 (m, 2H, Ar), 6.96 (t, J = 7.3 Hz, 1H, Ar), 6.33 (dd, J_1 = 1.2 Hz, J_2 = 7.5 Hz, 1H, Ar), 6.50 (br, 2H, NH_2), 5.31 (s, 1H, Chiral CH), 1.53 (s, 3H, SCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.14, 159.05, 154.90, 152.46, 147.64, 143.13, 141.27, 134.13, 133.28, 130.67, 130.57, 129.96, 129.83, 129.77, 129.65, 128.70, 125.61, 123.46, 119.36, 110.56, 61.30, 59.85, 17.19; HRMS $[M+H]^+$ calcd. For $C_{24}H_{18}BrClN_3O_2S$ 525.9986, found 525.9999.

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† Dedication

This paper is dedicated to Prof. Ganesh Pandey on the occasion of his 60th birthday.

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Supplementary Material

^{1}H and ^{13}C NMR spectra of all new compounds, experimental procedures and supplementary data associated with this article can be found in the online version, at

Lewis-acid mediated three-component one-flask regioselective synthesis of densely functionalized 4-amino-1,2-dihydropyridines via cascade Knoevenagel/Michael/cyclization sequence

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Supporting Information

1. EXPERIMENTAL SECTION

General Methods: The commercially available starting materials were used as received without further purification. α-Oxoketene-*N*,*S*-arylaminoacetals **1** were prepared following the known procedure (Ref. 23a in main manuscript). Thin-layer chromatography (TLC) was performed using silica gel 60 F254 precoated plates. Infrared (IR) spectra are measured in KBr, and wavenumber ($\bar{\upsilon}$) are reported in cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded on NMR spectrometer operating at 300 and 75 MHz, respectively. Chemical shifts (δ) are given in parts per million (ppm) using the residue solvent peaks as reference relative to TMS. *J* values are given in hertz. Electronic absorption spectra at 25 °C were acquired on a Shimadzu UV-1701 spectrophotometer, in CH_3CN-H_2O (9 : 1, v/v; *c*, 10 μM). Mass spectra were recorded using electrospray ionization (ESI) mass spectrometry. The melting points are uncorrected.

General Procedure for the Synthesis of the 1,2-Dihydropyridine (4a-r):

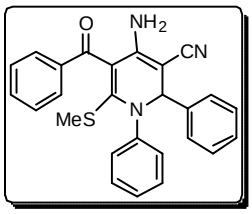
To a mixture of α-oxoketene-*N*,*S*-arylaminoacetals **1** (1.0 mmol), aldehyde (1.0 mmol) **2** and malononitrile **3** (1.0 mmol), $InCl_3$ (0.1 mmol) was added and the reaction mixture was heated at 80 ^{o}C till the completion of the reaction (Table-2 of main manuscript). After completion of the reaction (monitored by TLC), water (20 mL) was added to the reaction mixture followed by extraction with ethyl acetate (2 X 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and then evaporated in vacuo. The crude residue was purified by column chromatography over silica gel using ethyl acetate/hexane as eluent to afford pure 1,2-dihydropyridine **4**.

UV-vis Study:

For electronic absorption study the stock solution of ligand was prepared in CH_3CN-H_2O (9 : 1, v/v; *c*, 10 μM), while for various metal ions (Na^{+}, K^{+}, Fe^{3+}, Al^{3+}, Cr^{3+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Pb^{2+}) by dissolving respective nitrates in triply distilled water (10 mM) containg phosphate buffered saline (PBS).

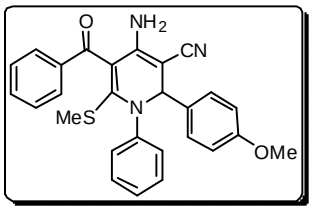
2. Characterization Data of New Compounds:

4-Amino-5-benzoyl-6-methylthio-1,2-diphenyl-1,2-dihydropyridine-3-carbonitrile (4a).



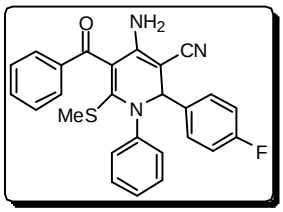
Yellow solid, mp 173-175 °C; FT IR (KBr, cm^{-1}): 3471, 3354, 2936, 2157, 1643, 1438, 1057; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 (d, J = 6.3 Hz, 2H, Ar), 7.42-7.24 (m, 9H, Ar), 7.04-6.99 (m, 2H, Ar), 6.88 (d, J = 7.2 Hz, 2H, Ar), 5.89 (br, 2H, D_2O Exchangeable, NH_2), 5.47 (s, 1H, Chiral CH), 2.10 (s, 3H, SCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.06, 154.54, 152.60, 144.16, 140.86, 131.93, 129.47, 128.73, 128.65, 128.47, 128.32, 127.85, 126.97, 125.19, 120.41, 114.78, 65.33, 63.05, 15.74; HRMS $[M+H]^+$ calcd. For $C_{26}H_{22}N_3OS$ 424.1483, found 424.1490.

4-Amino-5-benzoyl-2-(4-methoxyphenyl)-6-methylthio-1-phenyl-1,2-dihydropyridine-3-carbonitrile (4b).



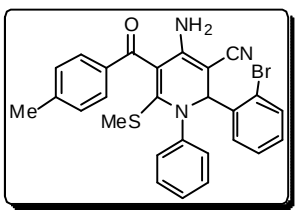
Yellow solid, mp 170-172 °C; FT IR (KBr, cm^{-1}): 3482, 3337, 2932, 2160, 1628, 1446, 1025; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58-7.31 (m, 8H, Ar), 7.17-6.98 (m, 6H, Ar), 5.92 (br, 2H, NH_2), 5.48 (s, 1H, Chiral CH), 3.86 (s, 3H, OCH_3), 1.71 (s, 3H, SCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.02, 159.79, 154.38, 152.55, 144.16, 140.05, 132.50, 131.94, 129.44, 128.73, 128.28, 127.82, 126.94, 125.23, 120.40, 114.72, 113.74, 65.00, 63.19, 55.45, 15.80; HRMS $[M+Na]^+$ calcd. For $C_{27}H_{23}N_3O_2SNa$ 476.1403, found 476.1389.

4-Amino-5-benzoyl-2-(4-fluorophenyl)-6-methylthio-1-phenyl-1,2-dihydropyridine-3-carbonitrile (4c).



Yellow solid, mp 145-147 °C; FT IR (KBr, cm^{-1}): 3463, 3348, 2922, 2139, 1651, 1436, 1021; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64 (t, J = 6.4 Hz, 2H, Ar), 7.40-7.33 (m, 6H, Ar), 7.20-7.10 (m, 4H, Ar), 7.00 (d, J = 7.5 Hz, 2H, Ar), 5.95 (br, 2H, NH_2), 5.48 (s, 1H, Chiral CH), 1.73 (s, 3H, SCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.89, 154.61, 152.58, 144.16, 139.87, 136.66, 132.17, 129.56, 128.85, 128.63, 127.94, 127.17, 125.25, 120.21, 115.36 (d, J_{CF} = 22.9Hz), 114.80, 114.75, 65.03, 63.06, 15.95; HRMS $[M+H]^+$ calcd. For $C_{26}H_{21}FN_3OS$ 442.1389, found 442.1410.

4-Amino-2-(2-bromophenyl)-5-(4-methylbenzoyl)-6-methylthio-1-phenyl-1,2-dihydropyridine-3-carbonitrile (4d).



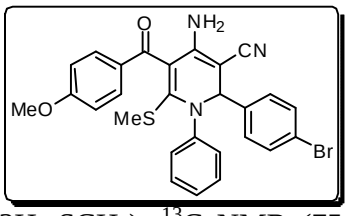
Yellow solid, mp 209-211 °C; FT IR (KBr, cm^{-1}): 3472, 3353, 2935, 2158, 1644, 1436, 1067; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68-7.63 (m, 2H, Ar), 7.51 (d, J = 8.1 Hz, 2H, Ar), 7.30-7.23 (m, 7H, Ar), 7.12 (d, J = 7.8 Hz, 2H, Ar), 5.94 (br, 2H, NH_2), 5.84 (s, 1H, Chiral CH), 2.37 (s, 3H, CH_3), 1.82 (s, 3H,

SCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.95, 158.55, 153.48, 144.31, 143.26, 138.59, 137.07, 134.03, 130.44, 130.21, 129.34, 129.11, 128.87, 127.68, 127.57, 127.15, 123.35, 119.87, 112.46, 64.75, 63.45, 21.55, 17.33; HRMS $[M+Na]^+$ calcd. For $C_{27}H_{22}BrN_3OSNa$ 538.0559, found 538.0563.

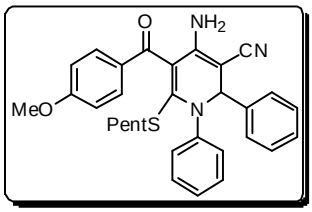
4-Amino-2-(4-methoxyphenyl)-5-(4-methylbenzoyl)-6-methylthio-1-phenyl-1,2-dihydropyridine-3-carbonitrile (4e). Yellow solid, mp 168-169 °C; FT IR (KBr, cm^{-1}): 3438, 3328, 2925, 2180, 1623, 1413, 1058; ^1H NMR (300 MHz, $CDCl_3$): δ 7.50 (d, J = 8.1 Hz, 2H, Ar), 7.34-7.18 (m, 5H, Ar), 6.93-6.84 (m, 6H, Ar), 5.80 (br, 2H, NH_2), 5.40 (s, 1H, Chiral CH), 3.79 (s, 3H, OCH_3), 2.22 (s, 3H, CH_3), 1.18 (s, 3H, SCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.86, 174.92, 159.83, 152.50, 144.30, 137.21, 132.61, 129.66, 129.45, 129.31, 129.15, 129.02, 128.63, 128.30, 126.93, 126.89, 125.32, 113.80, 64.92, 63.24, 55.44, 21.50, 15.78; HRMS $[M+H]^+$ calcd. For $C_{28}H_{26}N_3O_2S$ 468.1745, found 468.1760.

4-Amino-2-(4-chloro-3-fluorophenyl)-5-(4-methylbenzoyl)-6-methylthio-1-phenyl-1,2-dihydropyridine-3-carbonitrile (4f). Yellow solid, mp 161-163 °C; FT IR (KBr, cm^{-1}): 3479, 3350, 2923, 2173, 1624, 1471, 1033; ^1H NMR (300 MHz, $CDCl_3$): δ 7.53-7.31 (m, 9H, Ar), 6.95 (br, 3H, Ar), 5.92 (br, 2H, NH_2), 5.45 (s, 1H, Chiral CH), 2.32 (s, 3H, CH_3), 1.79 (s, 3H, SCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.32, 159.76, 156.44, 154.15, 152.53, 143.94, 143.35, 142.69, 136.79, 130.57, 129.57, 128.73, 127.20, 125.11, 123.36, 120.01, 115.33 (d, J_{CF} = 22.9Hz), 114.78, 111.73, 64.74, 62.51, 21.53, 15.97; HRMS $[M+H]^+$ calcd. For $C_{27}H_{22}ClFN_3OS$ 490.1156, found 490.1168.

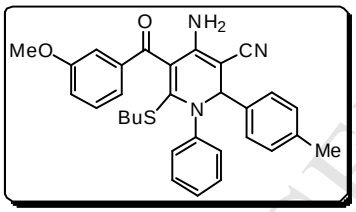
4-Amino-5-(4-methoxybenzoyl)-2-(4-methoxyphenyl)-6-methylthio-1-phenyl-1,2-dihydropyridine-3-carbonitrile (4g). Yellow sticky solid; FT IR (KBr, cm^{-1}): 3452, 3332, 2937, 2168, 1629, 1447, 1021; ^1H NMR (300 MHz, $CDCl_3$): δ 7.58 (d, J = 8.4 Hz, 2H, Ar), 7.41 (d, J = 4.5 Hz, 4H, Ar), 7.32-7.25 (m, 1H, Ar), 7.00-6.97 (m, 4H, Ar), 6.60 (d, J = 8.7 Hz, 2H, Ar), 5.83 (br, 2H, NH_2), 5.47 (s, 1H, Chiral CH), 3.85 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 1.77 (s, 3H, SCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.59, 162.94, 159.81, 153.09, 152.37, 144.33, 132.73, 132.31, 131.24, 129.40, 128.37, 126.77, 125.23, 120.38, 115.02, 113.76, 113.08, 64.86, 63.39, 55.53, 55.25, 15.83; HRMS $[M+H]^+$ calcd. For $C_{28}H_{26}N_3O_3S$ 484.1695, found 484.1713.

4-Amino-2-(4-bromophenyl)-5-(4-methoxybenzoyl)-6-methylthio-1-phenyl-1,2-dihydropyridine-3-carbonitrile (4h). 

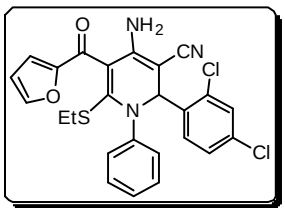
Yellow solid, mp 171-173 °C; FT IR (KBr, cm^{-1}): 3475, 3351, 2939, 2152, 1674, 1432, 1064; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54-7.46 (m, 4H, Ar), 7.32-7.18 (m, 5H, Ar), 6.87 (br, 2H, Ar), 6.56 (d, J = 8.7 Hz, 2H, Ar), 5.75 (br, 2H, NH_2), 5.38 (s, 1H, Chiral CH), 3.73 (s, 3H, OCH_3), 1.72 (s, 3H, SCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.35, 163.16, 153.01, 152.40, 144.06, 140.41, 131.84, 131.55, 131.11, 129.52, 128.96, 126.96, 125.08, 122.31, 120.12, 115.23, 113.22, 64.83, 62.82, 55.31, 15.83; HRMS $[M+Na]^+$ calcd. For $C_{27}H_{22}BrN_3O_2SNa$ 554.0514, found 554.0552.

4-Amino-5-(4-methoxybenzoyl)-6-pentylthio-1,2-diphenyl-1,2-dihydropyridine-3-carbonitrile (4i). 

Yellow solid, mp 69-71 °C; FT IR (KBr, cm^{-1}): 3486, 3342, 2931, 2163, 1648, 1444, 1025; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66 (br, 2H, Ar), 7.45-7.40 (m, 7H, Ar), 7.25 (br, 1H, Ar), 6.95 (br, 2H, Ar), 6.55 (d, J = 8.4 Hz, 2H, Ar), 5.82 (br, 2H, NH_2), 5.51 (s, 1H, Chiral CH), 3.76 (s, 3H, OCH_3), 2.44-2.36 (m, 1H), 2.23-2.15 (m, 1H), 1.02-0.92 (m, 4H), 0.84-0.67 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.96, 162.83, 153.35, 152.51, 144.58, 141.02, 132.56, 131.18, 129.34, 128.42, 128.35, 127.10, 126.75, 125.46, 120.48, 115.22, 113.06, 65.33, 62.88, 55.24, 33.17, 30.31, 28.02, 21.85, 13.63; HRMS $[M+H]^+$ calcd. For $C_{31}H_{32}N_3O_2S$ 510.2215, found 510.2216.

4-Amino-6-butylthio-5-(3-methoxybenzoyl)-1-phenyl-2-(p-tolyl)-1,2-dihydropyridine-3-carbonitrile (4j). 

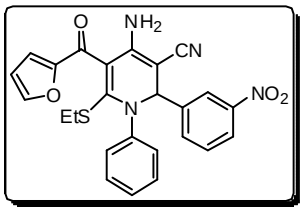
Yellow solid, mp 214-216 °C; FT IR (KBr, cm^{-1}): 3462, 3349, 2923, 2138, 1652, 1435, 1025; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 (d, J = 7.5 Hz, 2H, Ar), 7.43-7.37 (m, 4H, Ar), 7.33-7.25 (m, 3H, Ar), 6.90-6.84 (m, 3H, Ar), 6.34 (s, 1H, Ar), 5.92 (br, 2H, NH_2), 5.48 (s, 1H, Chiral CH), 3.66 (s, 3H, OCH_3), 2.42-2.29 (m, 4H), 2.21-2.10 (m, 1H), 0.98-0.82 (m, 4H), 0.60 (t, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.48, 159.40, 152.69, 144.68, 143.89, 141.92, 138.27, 137.64, 129.49, 129.40, 129.18, 128.63, 127.10, 127.00, 125.64, 121.71, 118.29, 114.86, 112.90, 65.31, 62.86, 55.30, 33.05, 30.22, 21.32, 13.17, 12.94; HRMS $[M+H]^+$ calcd. For $C_{31}H_{32}N_3O_2S$ 510.2215, found 510.2237.

4-Amino-2-(2,4-dichlorophenyl)-6-ethylthio-5-(2-furoyl)-1-phenyl-1,2-dihydropyridine-3-carbonitrile (4k). 

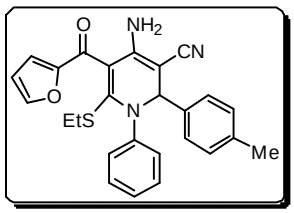
Yellow sticky solid; FT IR (KBr, cm^{-1}): 3481, 3350, 2916, 1645, 1439, 1053; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97-7.92 (m, 1H, Ar), 7.51-7.18 (m, 8H, Ar), 7.06 (d, J = 3.6 Hz, 1H, Ar), 6.54 (t, J =

1.5 Hz, 1H, Ar), 5.89-5.79 (m, 3H, NH_2 & Chiral CH), 2.55-2.46 (m, 1H, SCH_2), 2.23-2.14 (m, 1H, SCH_2), 0.82 (t, J = 7.5 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.15, 158.31, 154.01, 152.34, 145.01, 144.50, 136.66, 134.74, 132.75, 130.30, 129.84, 129.34, 127.99, 127.30, 126.61, 119.57, 117.36, 112.80, 110.42, 63.15, 62.49, 28.81, 14.00; HRMS $[M+H]^+$ calcd. For $C_{25}H_{20}Cl_2N_3O_2S$ 496.0653, found 496.0653.

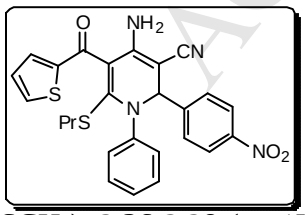
4-Amino-6-ethylthio-5-(2-furoyl)-2-(3-nitrophenyl)-1-phenyl-1,2-dihydropyridine-3-carbonitrile (4l). Yellow solid, mp 157-159 °C; FT IR (KBr, cm^{-1}): 3456, 3327, 2923, 2181, 1643, 1416, 1059; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.59 (s, 1H, Ar), 8.23 (d, J = 7.5 Hz, 1H, Ar), 7.91 (d, J = 7.5 Hz, 1H, Ar), 7.60 (t, J = 8.1 Hz, 1H, Ar), 7.42-7.33 (m, 6H, Ar), 6.84 (d, J = 1.8 Hz, 1H, Ar), 6.43 (dd, J_1 = 1.2 Hz, J_2 = 3.0 Hz, 1H, Ar), 5.91 (br, 2H, NH_2), 5.52 (s, 1H, Chiral CH), 2.82-2.75 (m, 1H, SCH_2), 2.37-2.31 (m, 1H, SCH_2), 0.85 (t, J = 7.5 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.24, 156.73, 153.63, 152.16, 148.15, 145.80, 144.37, 143.60, 132.95, 129.92, 129.67, 127.85, 125.75, 123.07, 120.48, 120.19, 117.17, 112.62, 112.50, 65.22, 63.17, 28.11, 13.71; HRMS $[M+H]^+$ calcd. For $C_{25}H_{21}N_4O_4S$ 473.1283, found 473.1302.



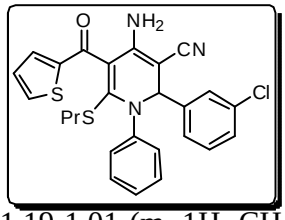
4-Amino-6-ethylthio-5-(2-furoyl)-1-phenyl-2-(p-tolyl)-1,2-dihydropyridine-3- carbonitrile (4m). Yellow solid, mp 165-166 °C; FT IR (KBr, cm^{-1}): 3456, 3342, 2934, 2158, 1622, 1451, 1043; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50-7.20 (m, 10H, Ar), 6.29 (d, J = 1.8 Hz, 1H, Ar), 6.08 (br, 1H, Ar), 5.76 (br, 2H, NH_2), 5.41 (s, 1H, Chiral CH), 2.54-2.23 (m, 5H, SCH_2 & tolyl CH_3), 0.77 (t, J = 7.5 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 181.51, 155.08, 153.63, 151.91, 145.84, 144.58, 138.04, 137.69, 129.37, 129.08, 127.21, 126.88, 126.73, 125.84, 120.26, 117.67, 111.87, 65.56, 63.45, 27.88, 21.06, 13.54; HRMS $[M+Na]^+$ calcd. For $C_{26}H_{23}N_3O_2SNa$ 464.1403, found 464.1406.



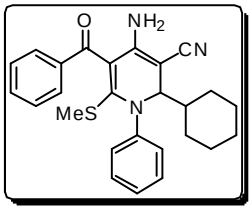
4-Amino-2-(4-nitrophenyl)-1-phenyl-6-propylthio-5-(2-thienoyl)-1,2-dihydropyridine-3-carbonitrile (4n). Yellow solid, mp 163-165 °C; FT IR (KBr, cm^{-1}): 3478, 3351, 2924, 2172, 1654, 1463, 1032; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.33 (d, J = 8.4 Hz, 2H, Ar), 7.85 (d, J = 8.4 Hz, 2H, Ar), 7.47-7.35 (m, 6H, Ar), 6.81 (t, J = 4.2 Hz, 1H, Ar), 6.70 (d, J = 3.0 Hz, 1H, Ar), 5.83 (br, 2H, NH_2), 5.52 (s, 1H, Chiral CH), 2.54-2.46 (m, 1H, SCH_2), 2.36-2.28 (m, 1H, SCH_2), 1.20-1.00 (m, 1H, CH_2), 0.93-0.82 (m, 1H, CH_2), 0.56 (t, J = 7.3 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.07, 172.42, 152.21, 148.54, 145.24, 144.28, 133.67, 132.62, 129.66, 127.93, 127.85, 127.62, 127.57, 125.77, 123.80, 123.69, 119.84,



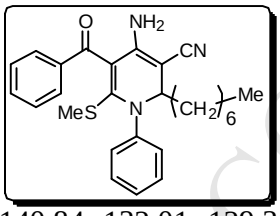
114.76, 65.16, 62.15, 35.89, 21.56, 12.80; HRMS $[M+H]^+$ calcd. For $C_{26}H_{23}N_4O_3S_2$ 503.1206, found 503.1214.

4-Amino-2-(3-chlorophenyl)-1-phenyl-6-propylthio-5-(2-thienoyl)-1,2-dihydropyridine-3-carbonitrile (4o). 

Yellow solid, mp 77-78 °C; FT IR (KBr, cm^{-1}): 3480, 3346, 2933, 1641, 1434, 1048; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63 (br, 1H, Ar), 7.49 (d, J = 5.1 Hz, 1H, Ar), 7.39-7.25 (m, 8H, Ar), 6.82 (t, J = 4.3 Hz, 1H, Ar), 6.57 (d, J = 3.0 Hz, 1H, Ar), 5.74 (br, 2H, NH_2), 5.45 (s, 1H, Chiral CH), 2.54-2.46 (m, 1H, SCH_2), 2.31-2.22 (m, 1H, SCH_2), 1.19-1.01 (m, 1H, CH_2), 0.89-0.85 (m, 1H, CH_2), 0.55 (t, J = 7.2 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.56, 153.89, 151.94, 145.71, 144.30, 143.24, 134.59, 133.45, 132.91, 129.96, 129.49, 128.47, 127.43, 127.23, 126.93, 126.89, 125.62, 125.25, 120.09, 115.10, 65.19, 62.79, 35.54, 21.67, 12.83; HRMS $[M]^+$ calcd. For $C_{26}H_{22}ClN_3OS_2$ 491.0888, found 491.0887.

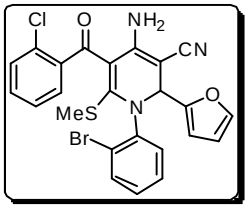
4-Amino-5-benzoyl-2-cyclohexyl-6-methylthio-1-phenyl-1,2-dihydropyridine-3-carbonitrile (4p). 

Yellow solid, mp 212-214 °C; FT IR (KBr, cm^{-1}): 3476, 3352, 2938, 2147, 1664, 1442, 1066; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, J = 7.5 Hz, 2H, Ar), 7.50-7.22 (m, 8H, Ar), 5.90 (br, 2H, NH_2), 3.88 (d, J = 10.2 Hz, 1H, Chiral CH), 2.17-2.05 (m, 5H), 1.85-1.72 (m, 4H), 1.36-1.25 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.26, 156.53, 151.67, 145.20, 140.58, 132.03, 129.24, 128.83, 128.18, 127.10, 126.35, 120.90, 113.46, 69.63, 63.21, 41.33, 31.67, 29.85, 26.31, 26.00, 16.69; HRMS $[M+H]^+$ calcd. For $C_{26}H_{28}N_3OS$ 476.1948, found 476.1956.

4-Amino-5-benzoyl-2-heptyl-6-methylthio-1-phenyl-1,2-dihydropyridine-3-carbonitrile (4q). 

Yellow sticky solid; FT IR (KBr, cm^{-1}): 3482, 3349, 2912, 1665, 1435, 1054; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, J = 6.9 Hz, 2H, Ar), 7.49-7.25 (m, 8H, Ar), 5.86 (br, 2H, NH_2), 4.26 (t, J = 7.3 Hz, 1H, Chiral CH), 1.70 (s, 3H, SCH_3), 1.41-1.25 (m, 12H), 0.89 (t, J = 5.1 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.73, 169.10, 151.77, 144.94, 140.84, 132.01, 129.30, 129.05, 128.77, 128.18, 127.84, 127.20, 125.92, 125.22, 63.78, 36.58, 34.89, 31.83, 29.66, 29.25, 26.00, 25.86, 22.61, 14.05; HRMS $[M+H]^+$ calcd. For $C_{27}H_{32}N_3OS$ 446.2266, found 446.2287.

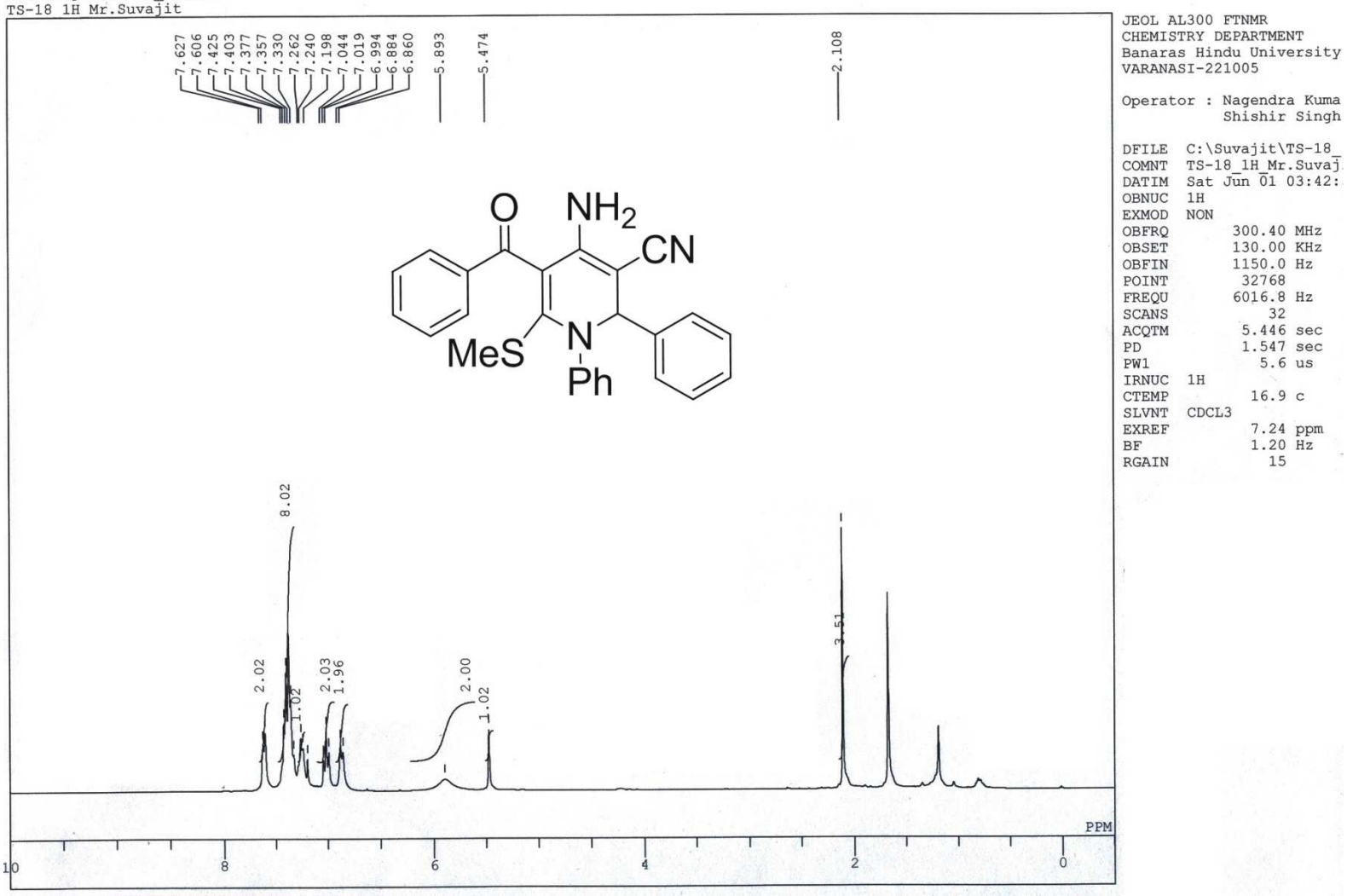
4-Amino-1-(2-bromophenyl)-5-(2-chlorobenzoyl)-2-(2-furyl)-6-methylthio-1,2-dihydropyridine-3-carbonitrile (4r). Yellow solid, mp 226-228 °C; FT IR (KBr, cm^{-1}): 3472, 3381, 2957, 2166, 1664, 1435, 1061; ^{1}H NMR (300



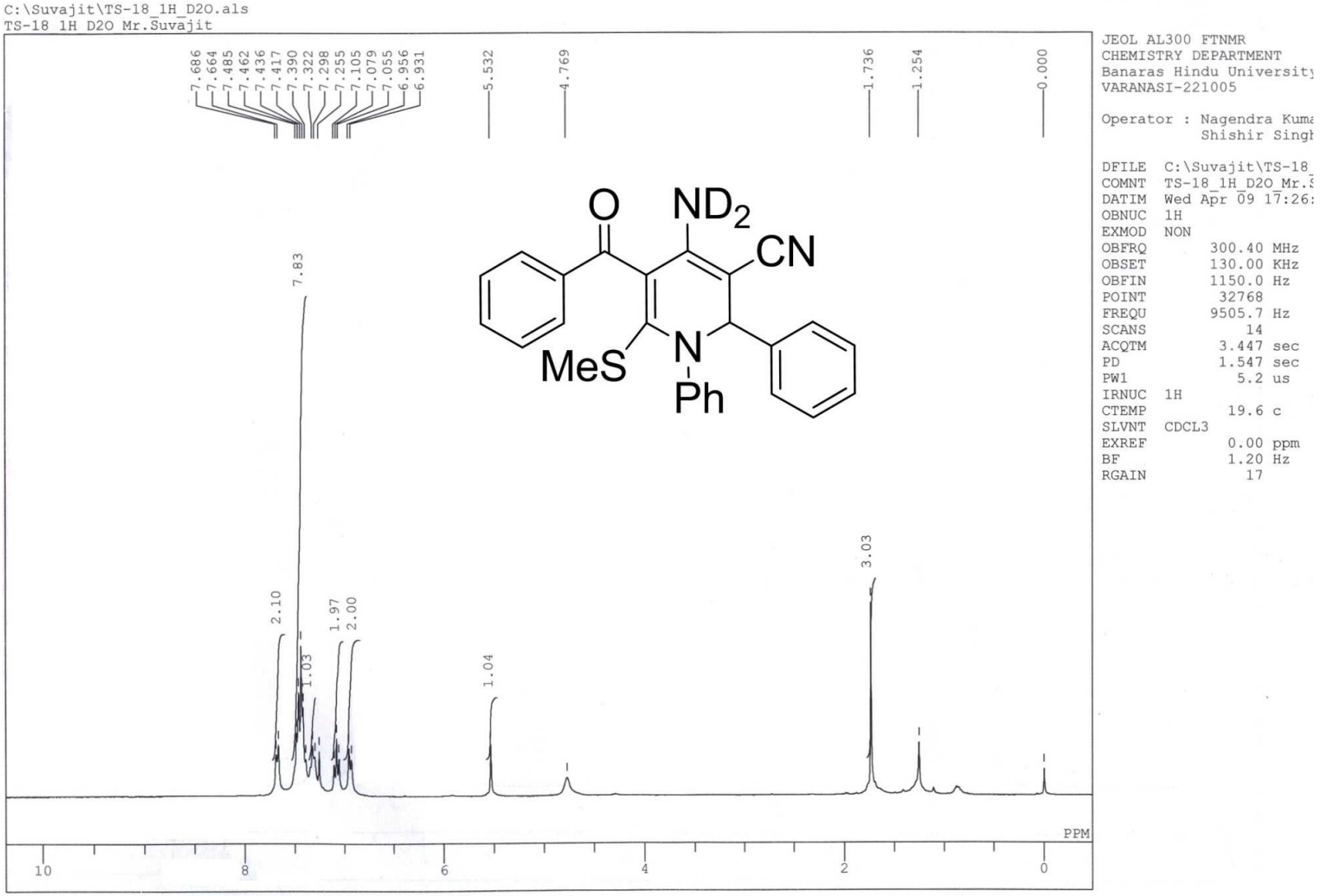
MHz, $CDCl_3$): δ 7.94 (d, J = 7.8 Hz, 1H, Ar), 7.61 (t, J = 7.9 Hz, 2H, Ar), 7.44 (t, J = 7.5 Hz, 1H, Ar), 7.34-7.17 (m, 2H, Ar), 6.96 (t, J = 7.3 Hz, 1H, Ar), 6.33 (dd, J_1 = 1.2 Hz, J_2 = 7.5 Hz, 1H, Ar), 6.50 (br, 2H, NH_2), 5.31 (s, 1H, Chiral CH), 1.53 (s, 3H, SCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.14, 159.05, 154.90, 152.46, 147.64, 143.13, 141.27, 134.13, 133.28, 130.67, 130.57, 129.96, 129.83, 129.77, 129.65, 128.70, 125.61, 123.46, 119.36, 110.56, 61.30, 59.85, 17.19; HRMS $[M+H]^+$ calcd. For $C_{24}H_{18}BrClN_3O_2S$ 525.9986, found 525.9999.

3. Copies of the ^{1}H and ^{13}C NMR Spectra of the Compounds 4a-r:

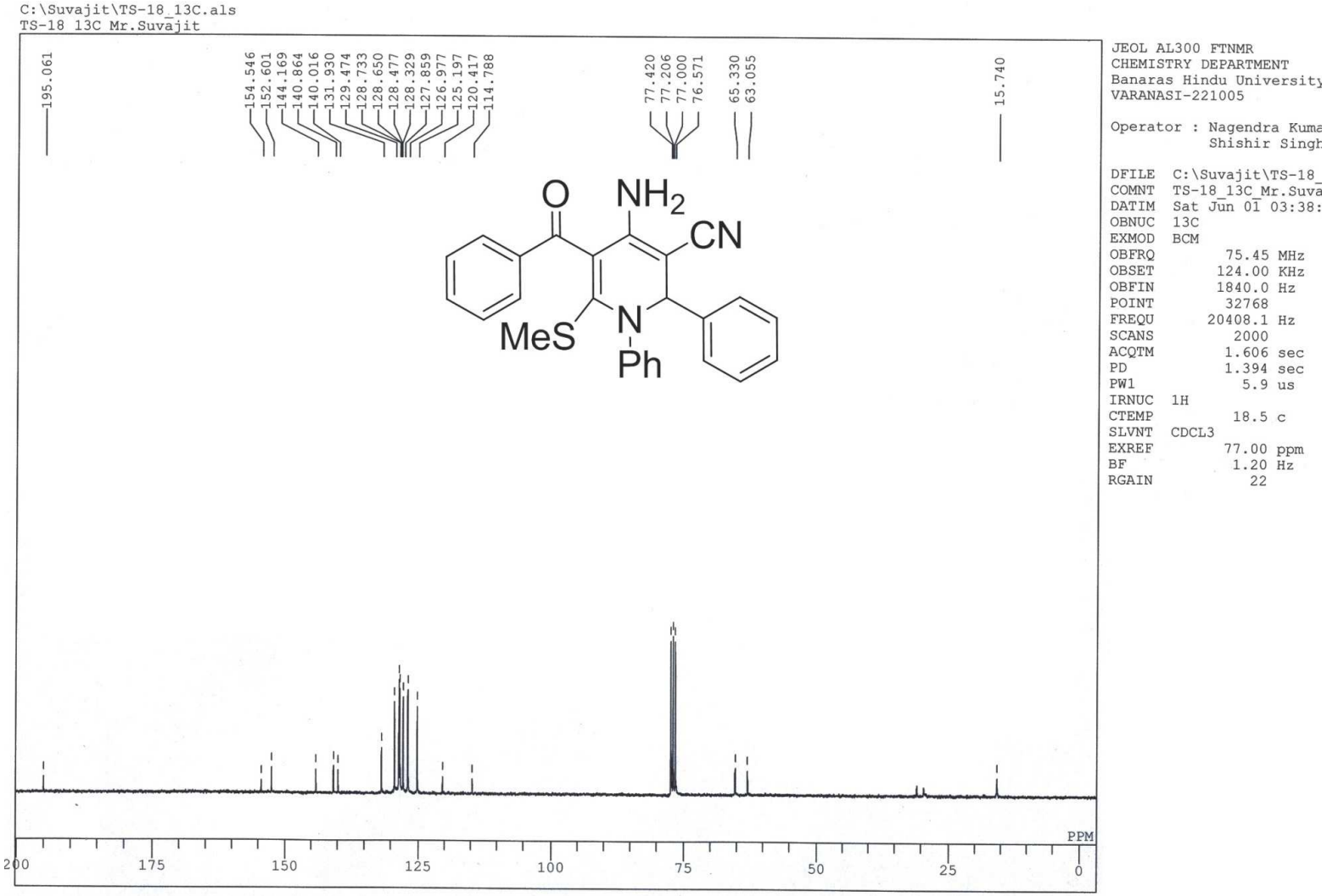
^{1}H NMR Spectrum of the Compound 4a:



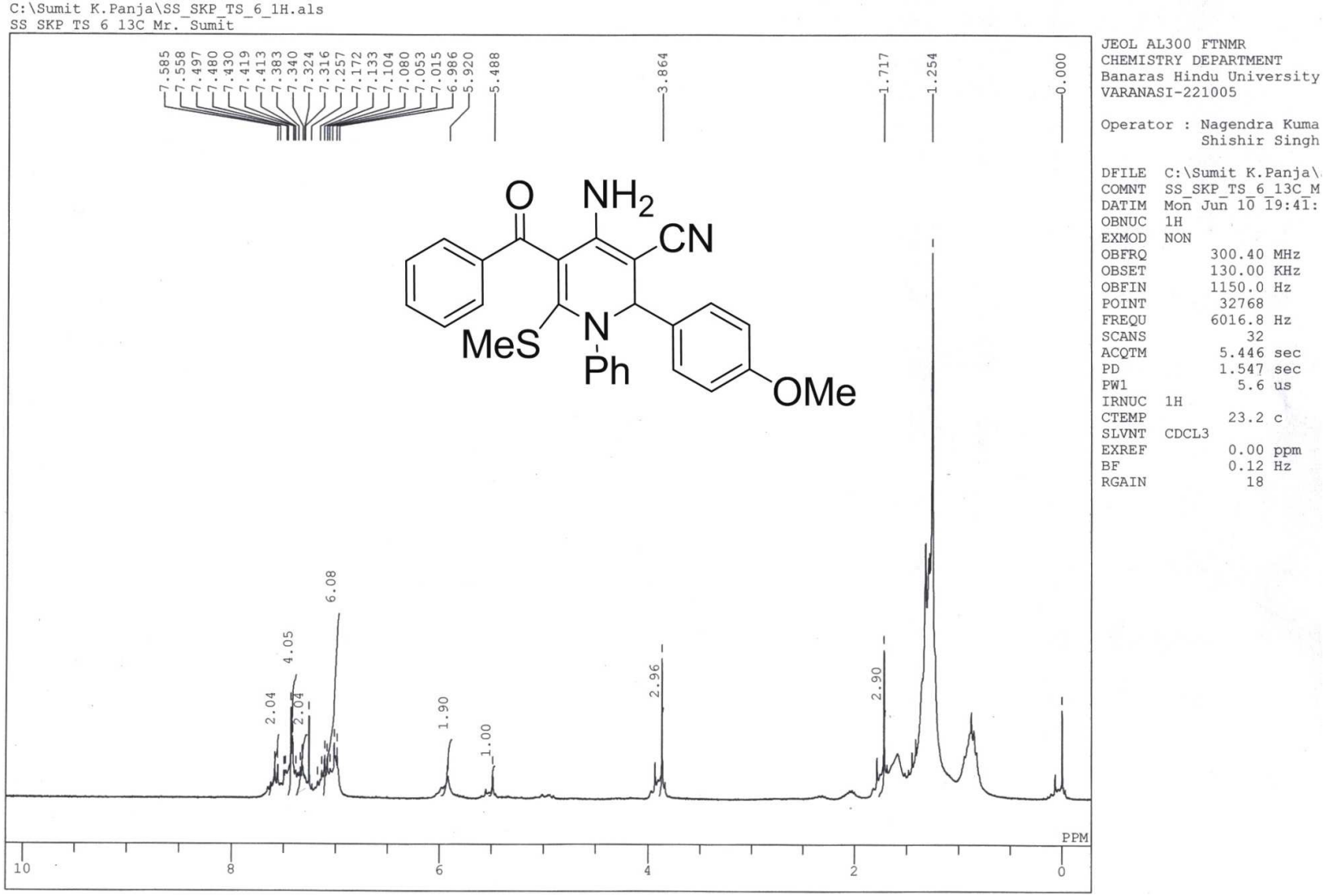
D_2O Exchanged ^1H NMR Spectrum of the Compound 4a:



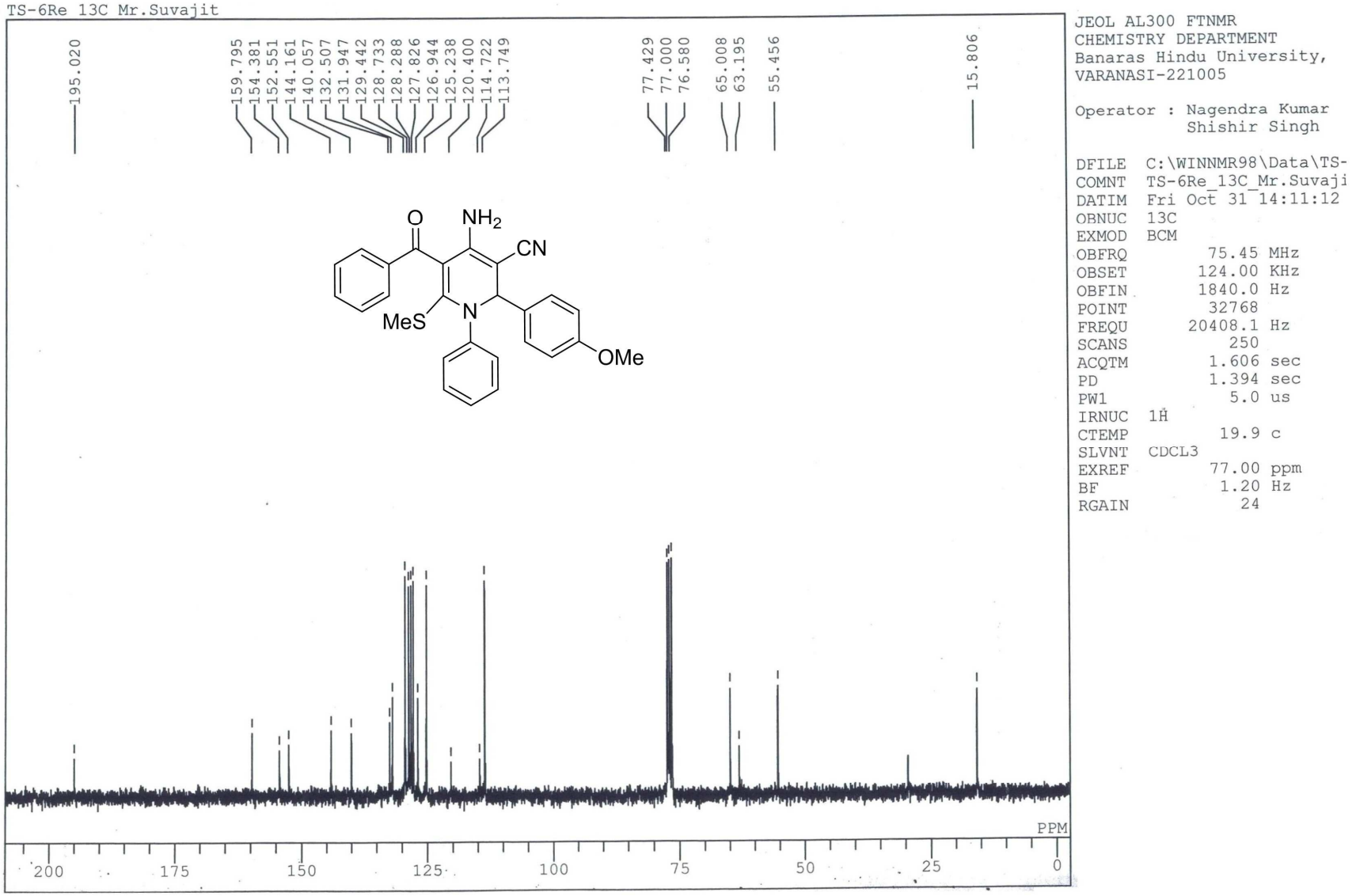
^{13}C NMR Spectrum of the Compound 4a:



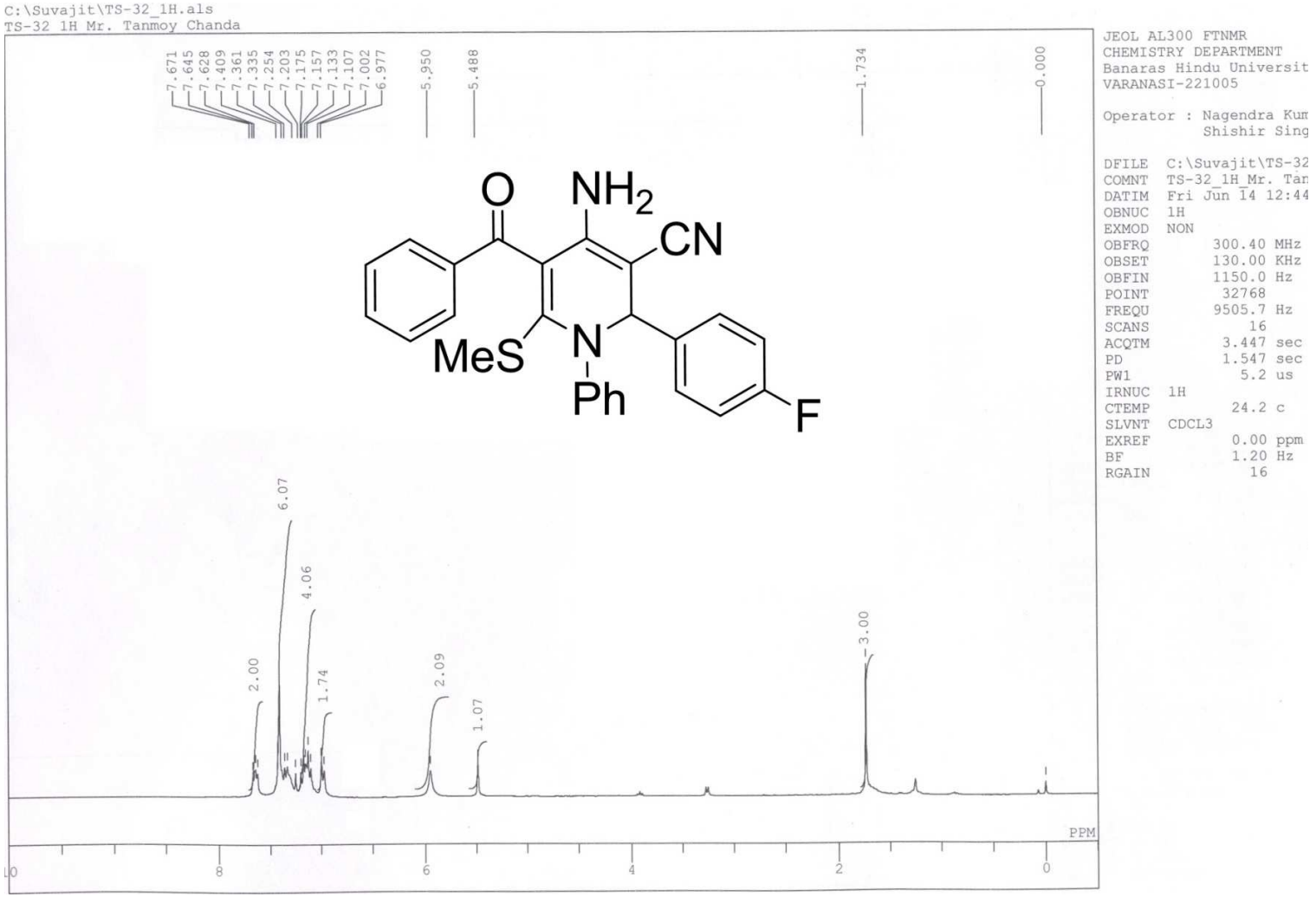
^{1}H NMR Spectrum of the Compound 4b:



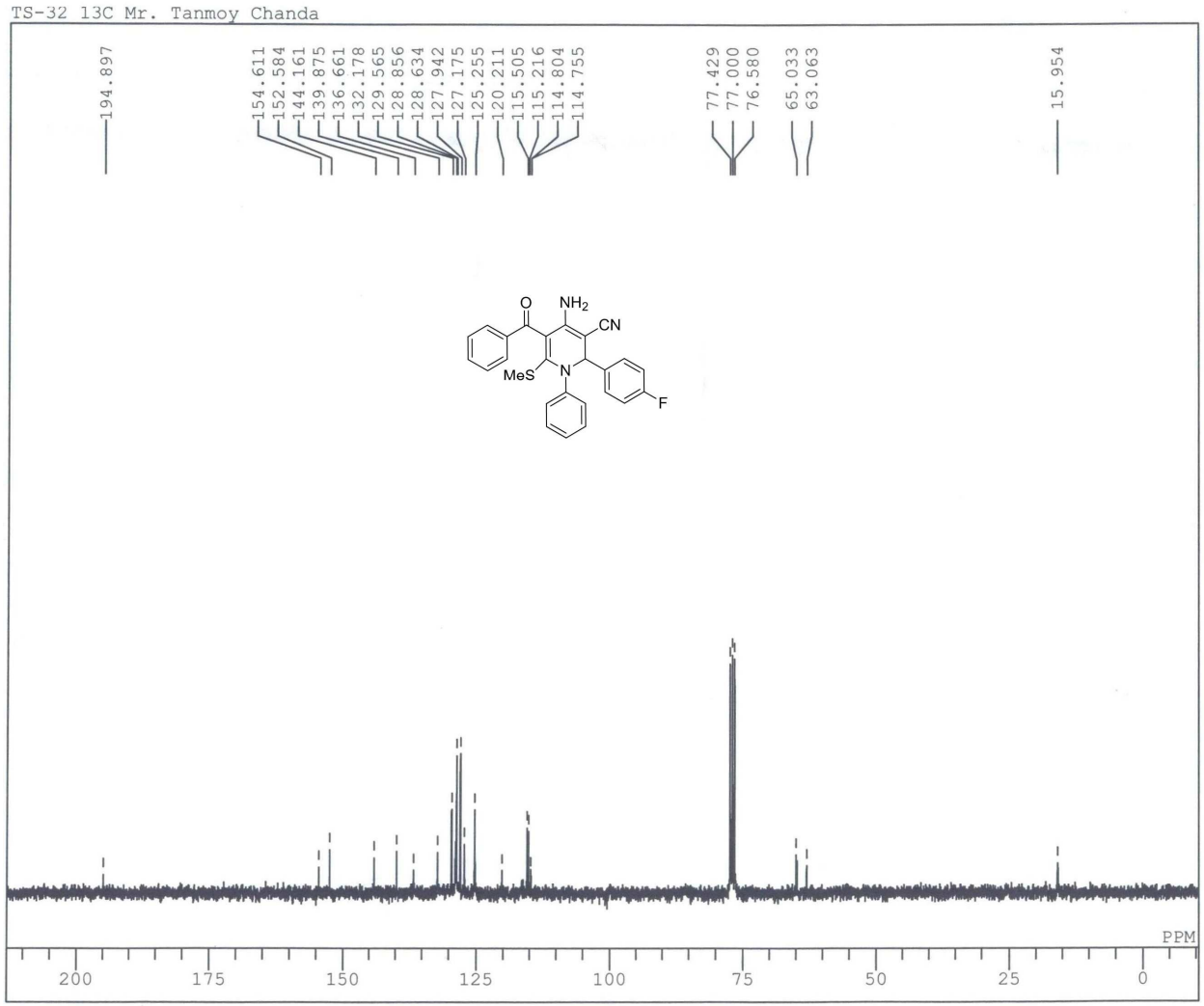
^{13}C NMR Spectrum of the Compound 4b:



^{1}H NMR Spectrum of the Compound 4c:



^{13}C NMR Spectrum of the Compound 4c:




```
JEOL AL300 FTNMR
CHEMISTRY DEPARTMENT
Banaras Hindu University,
VARANASI-221005

Operator : Nagendra Kumar
           Shishir Singh

DFILE  C:\Suvajit\TS-32_13C
COMNT  TS-32_13C_Mr. Tanmoy
DATIM  Fri Jun 14 12:40:49
OBNUC  13C
EXMOD  BCM
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN       1840.0 Hz
POINT        32768
FREQU       20408.1 Hz
SCANS          247
ACQTM        1.606 sec
PD           1.394 sec
PW1            5.9 us
IRNUC  1H
CTEMP         23.3 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            1.20 Hz
RGAIN           24
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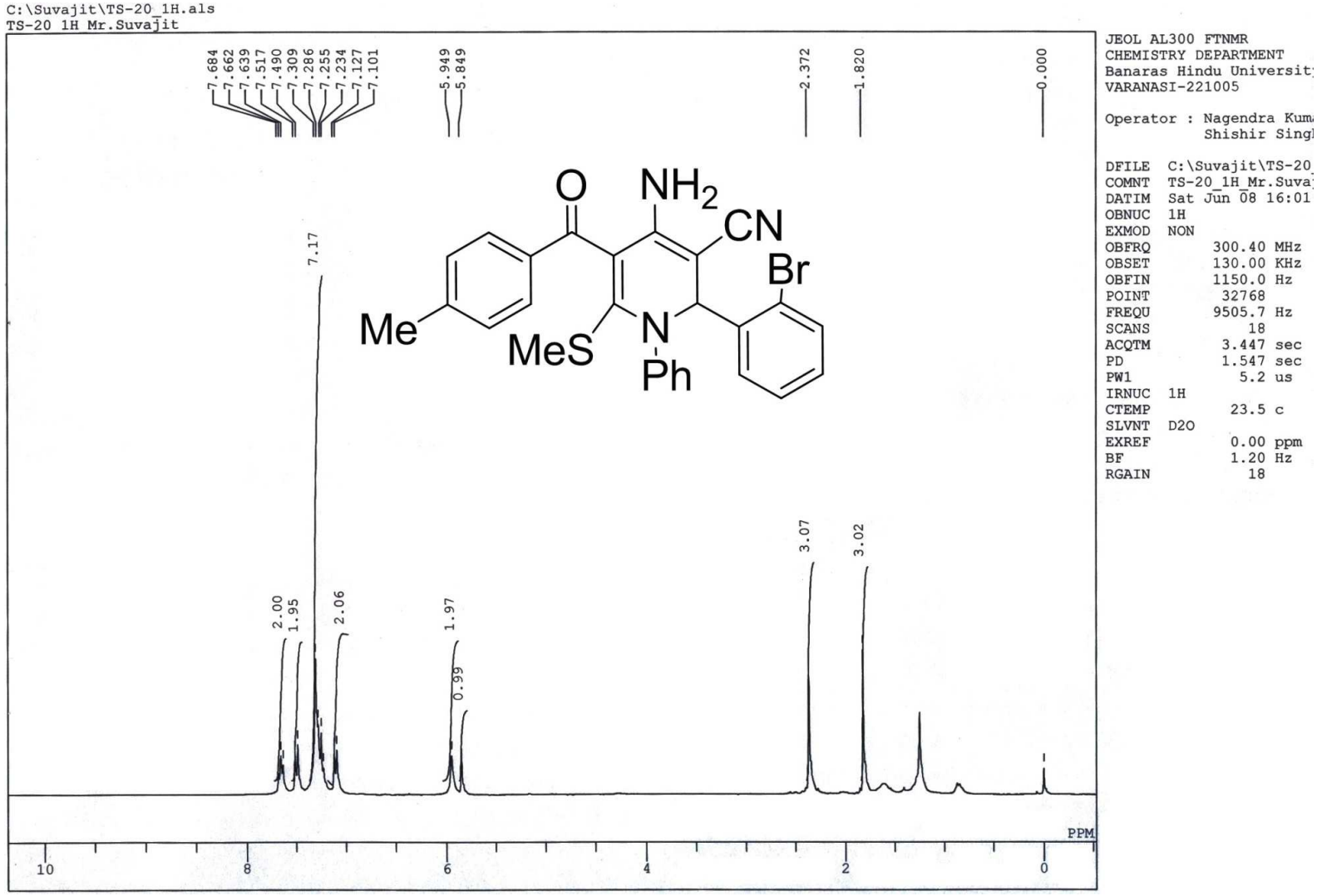
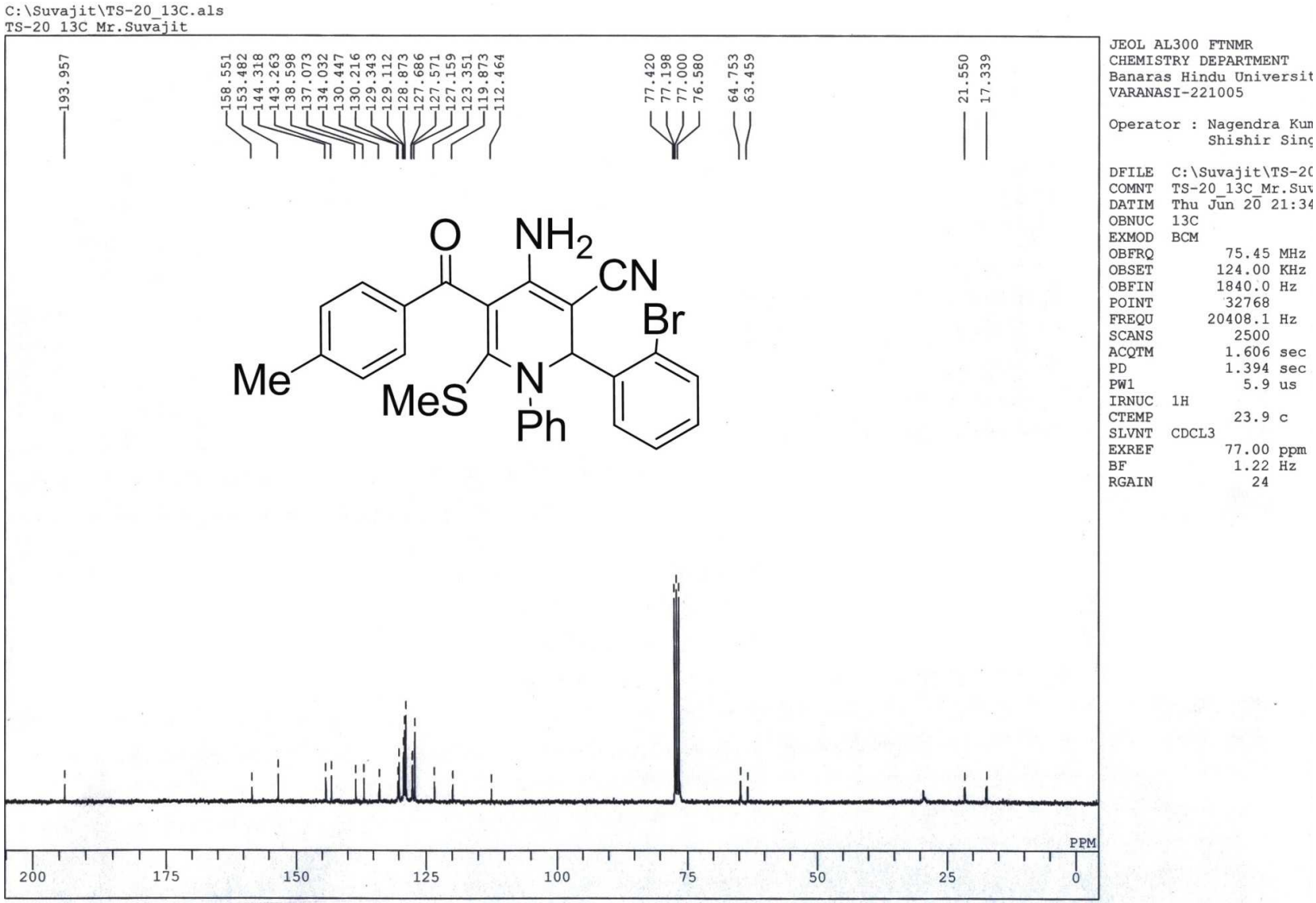
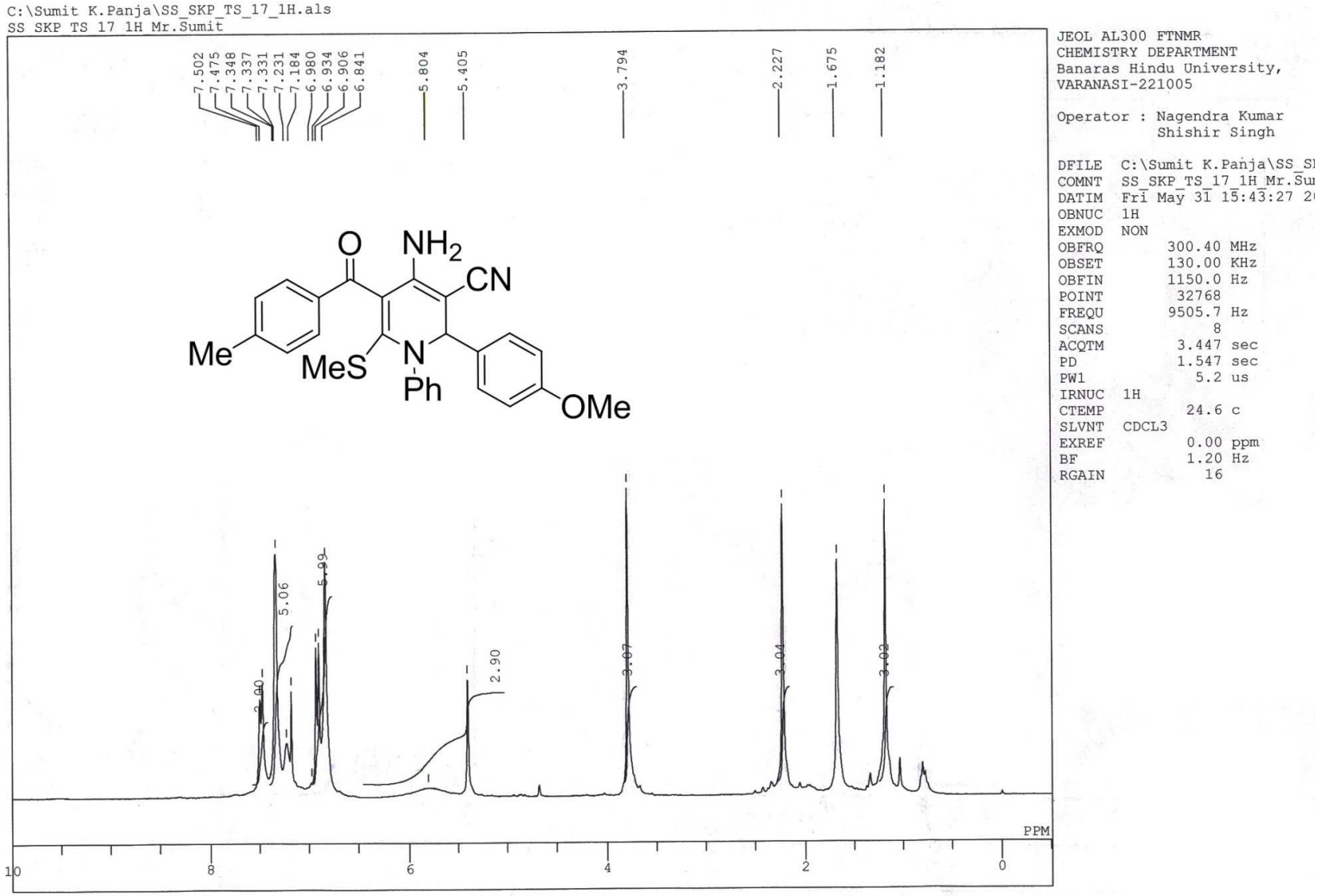
[1]H NMR Spectrum of the Compound 4d:



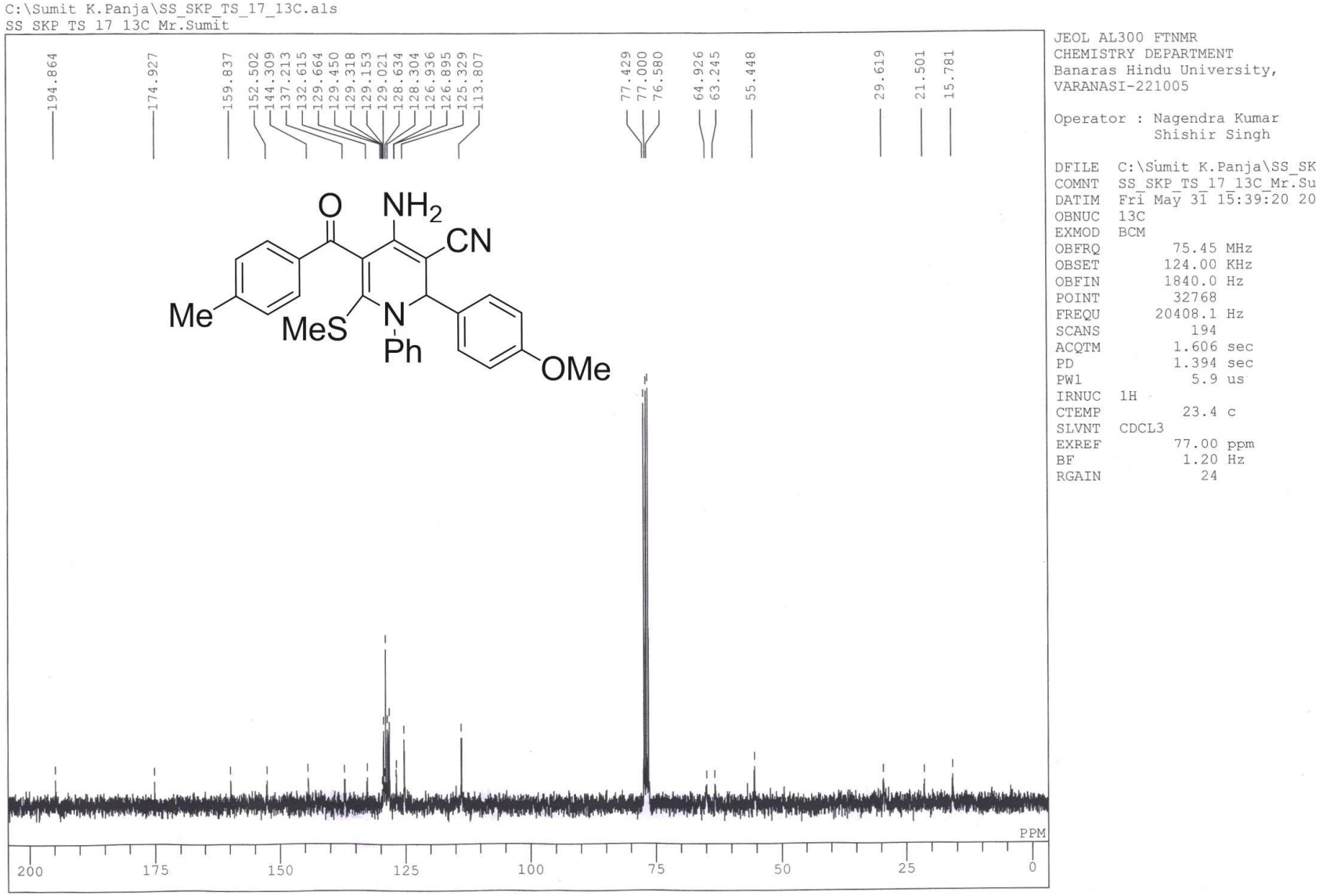
^{13}C NMR Spectrum of the Compound 4d:



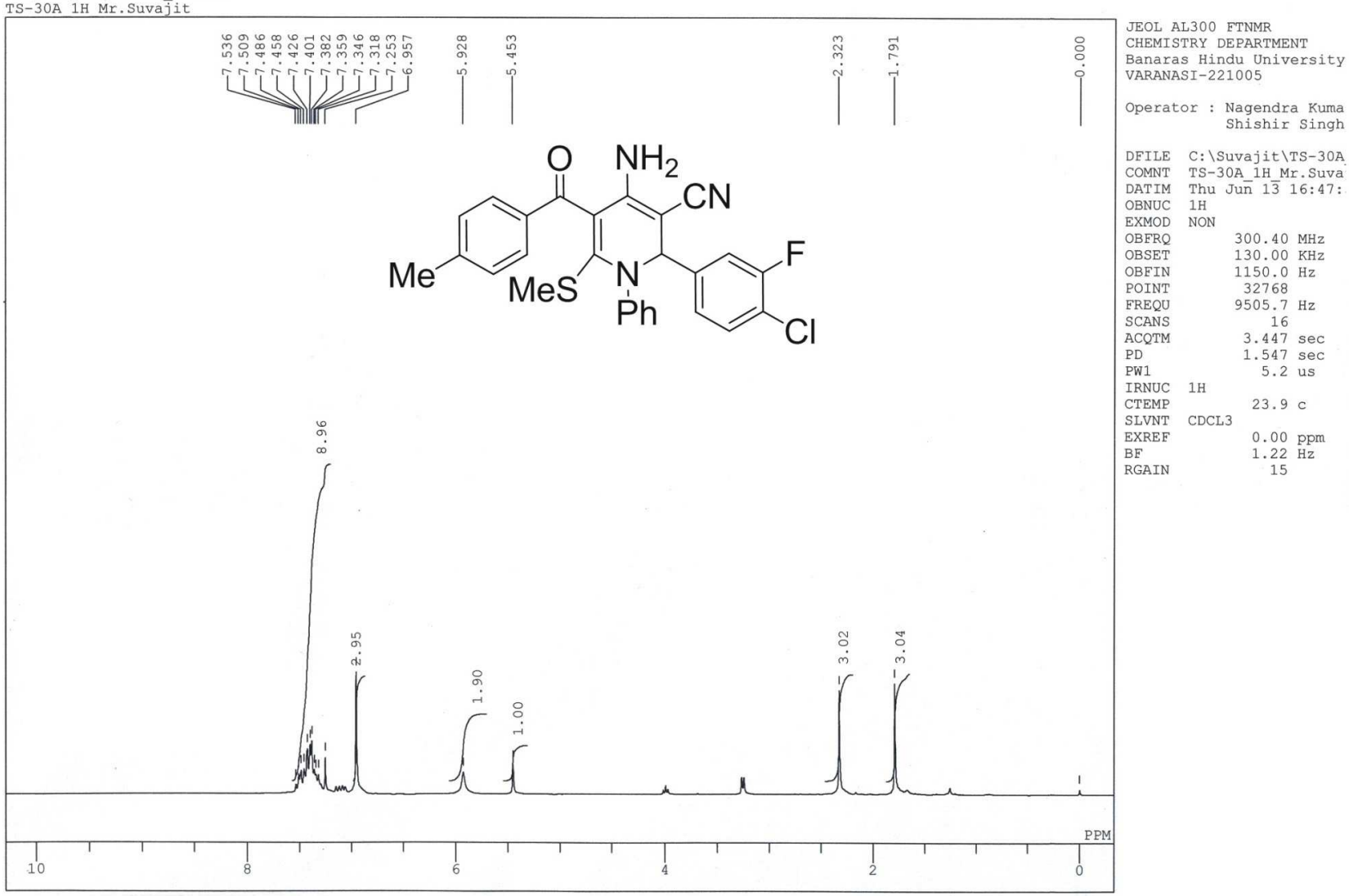
^{1}H NMR Spectrum of the Compound 4e:



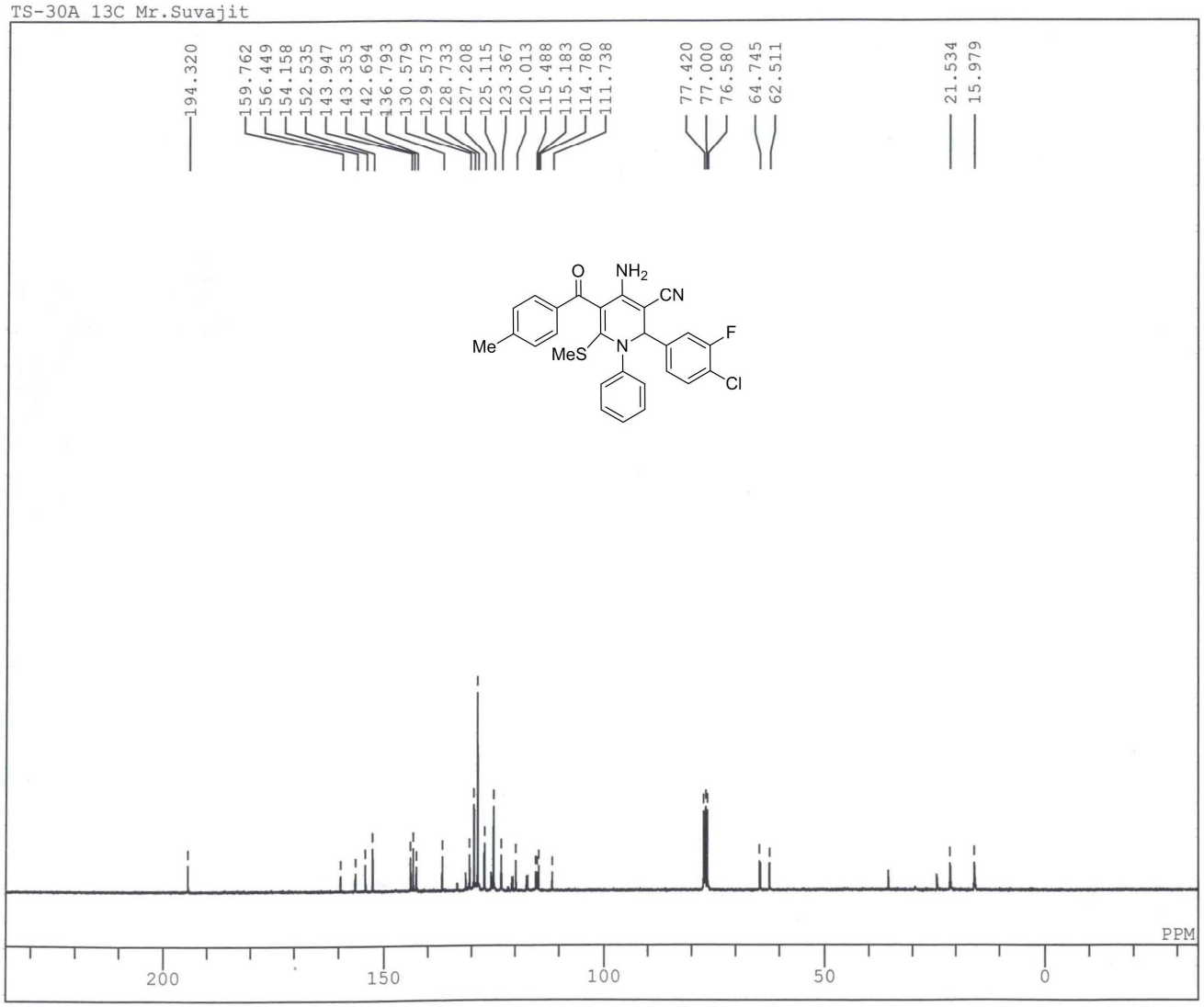
^{13}C NMR Spectrum of the Compound 4e:



^{1}H NMR Spectrum of the Compound 4f:



^{13}C NMR Spectrum of the Compound 4f:

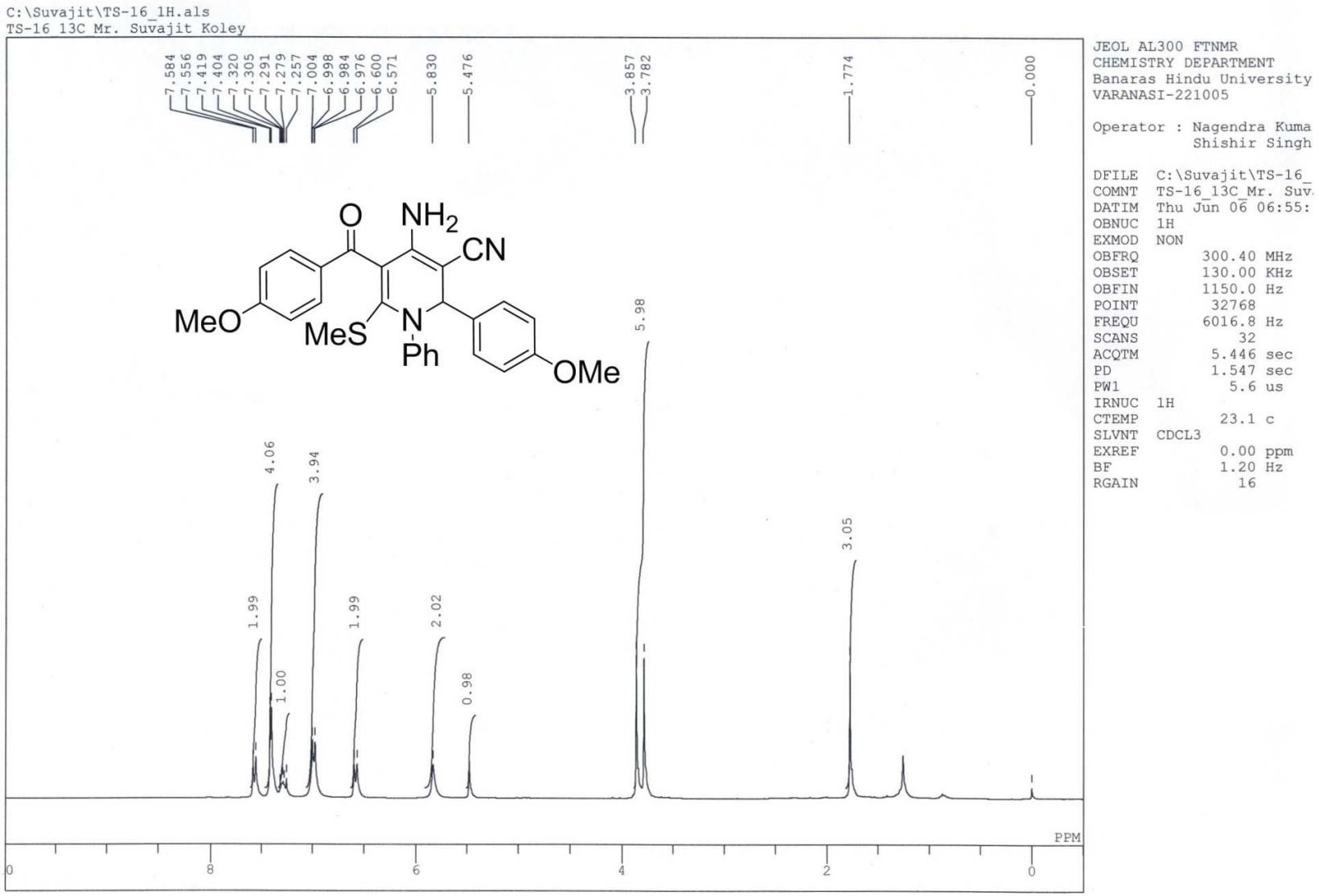



```
JEOL AL300 FTNMR
CHEMISTRY DEPARTMENT
Banaras Hindu University,
VARANASI-221005

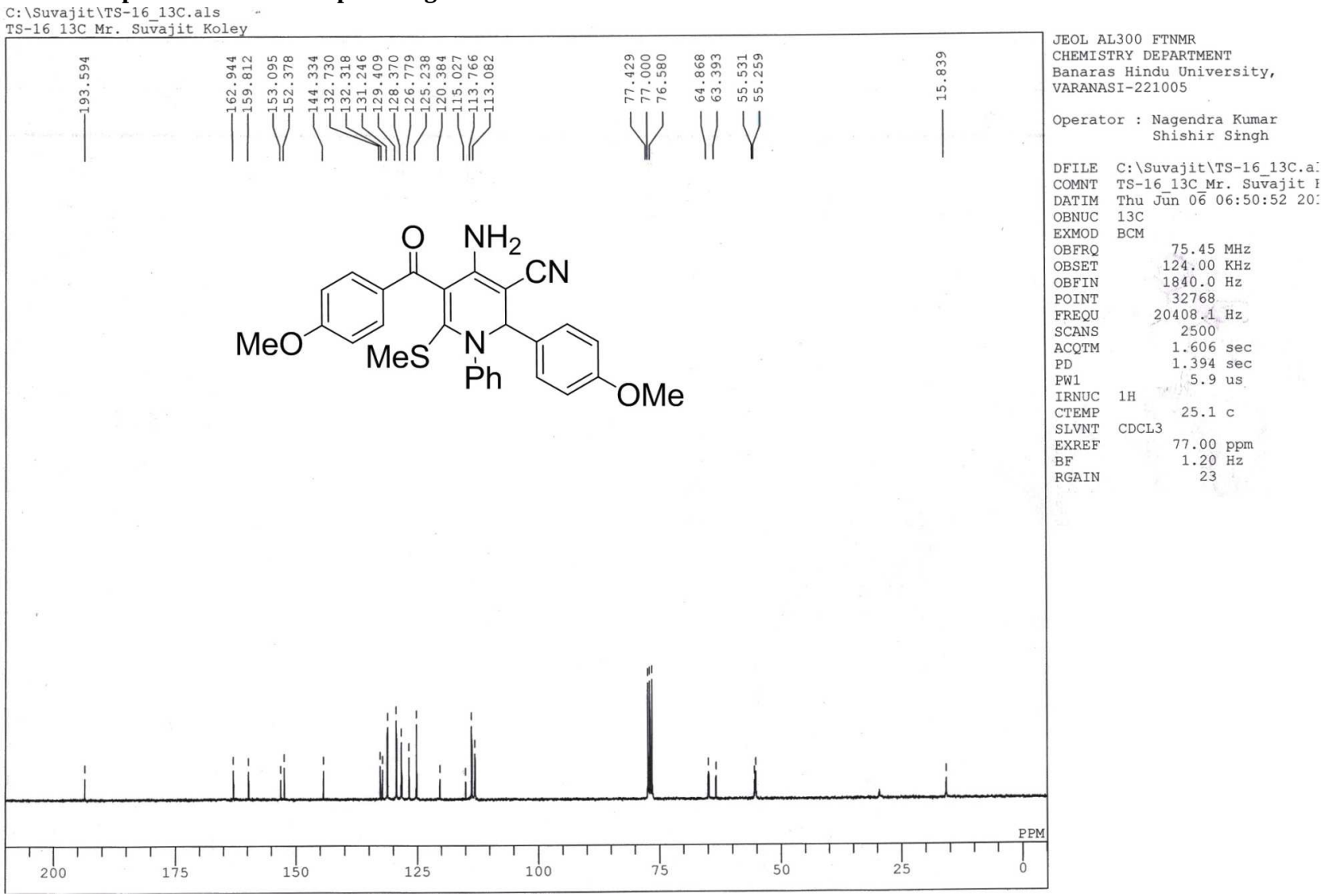
Operator : Nagendra Kumar
           Shishir Singh

DFILE  C:\Suvajit\TS-30A_13
COMNT  TS-30A_13C_Mr.Suvaji
DATIM  Thu Jun 20 19:17:40
OBNUC  13C
EXMOD  BCM
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN       1840.0 Hz
POINT        32768
FREQU       20408.1 Hz
SCANS          2000
ACQTM        1.606 sec
PD           1.394 sec
PW1            5.9 us
IRNUC  1H
CTEMP         23.4 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            1.20 Hz
RGAIN           24
```

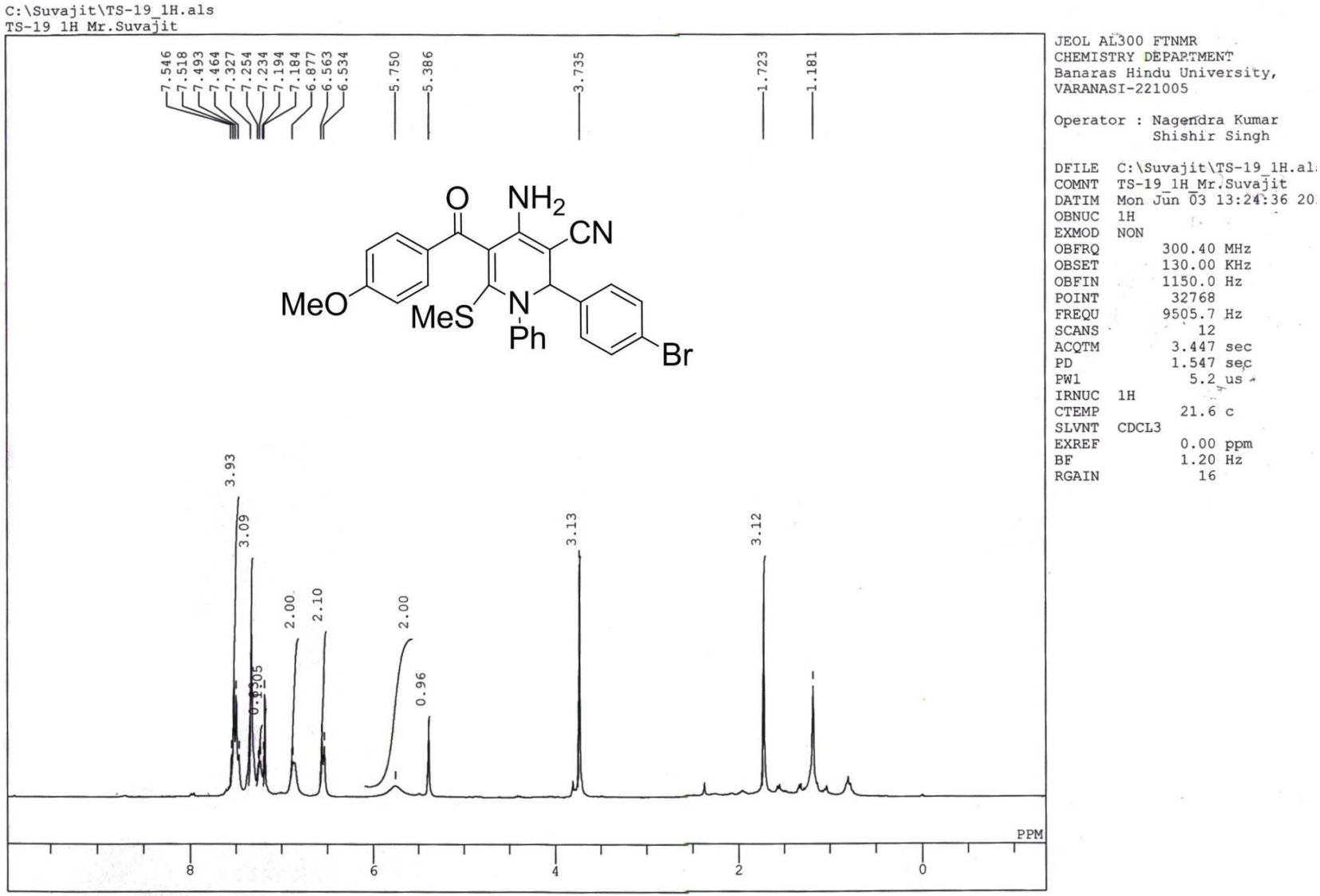
^{1}H NMR Spectrum of the Compound 4g:



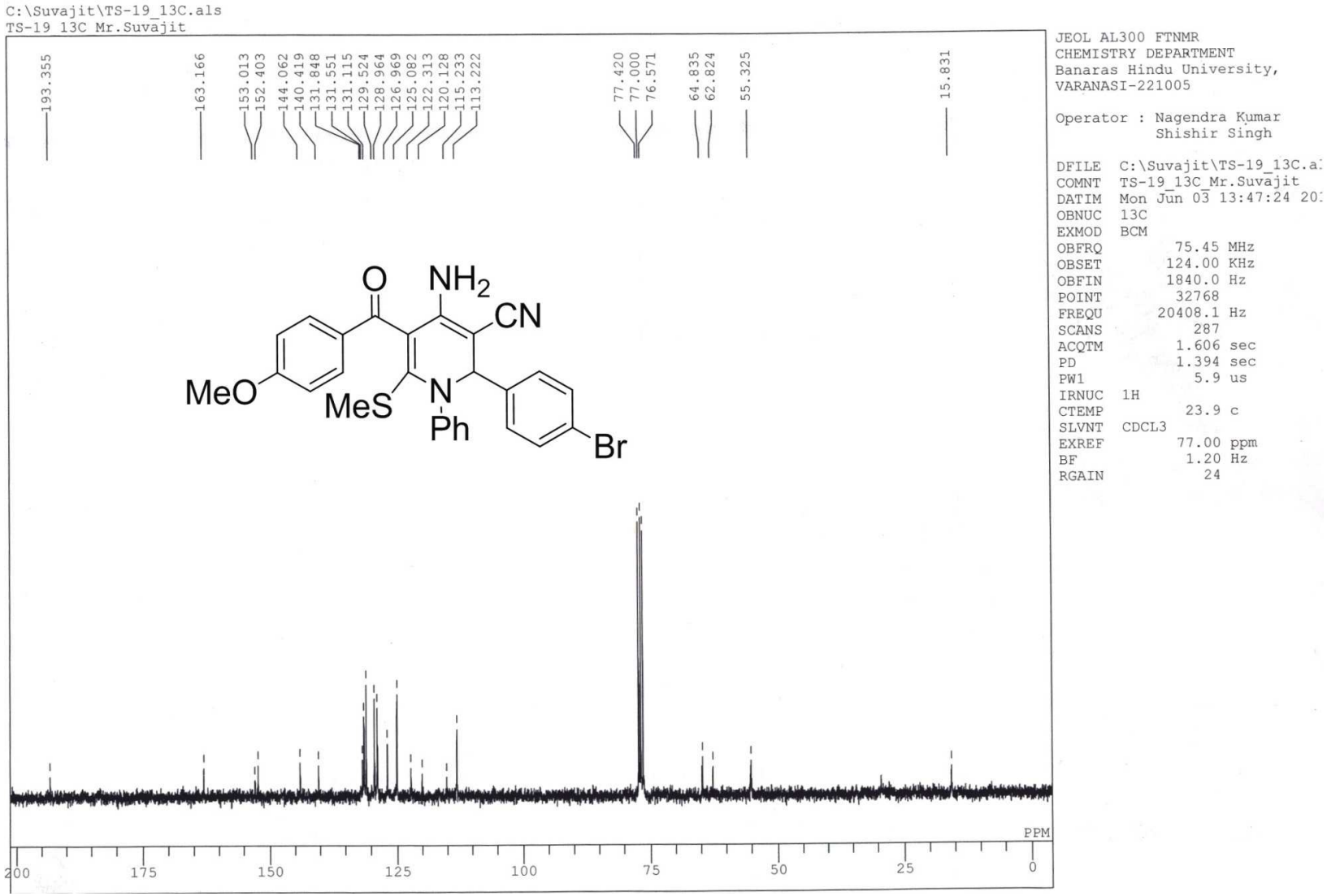
^{13}C NMR Spectrum of the Compound 4g:



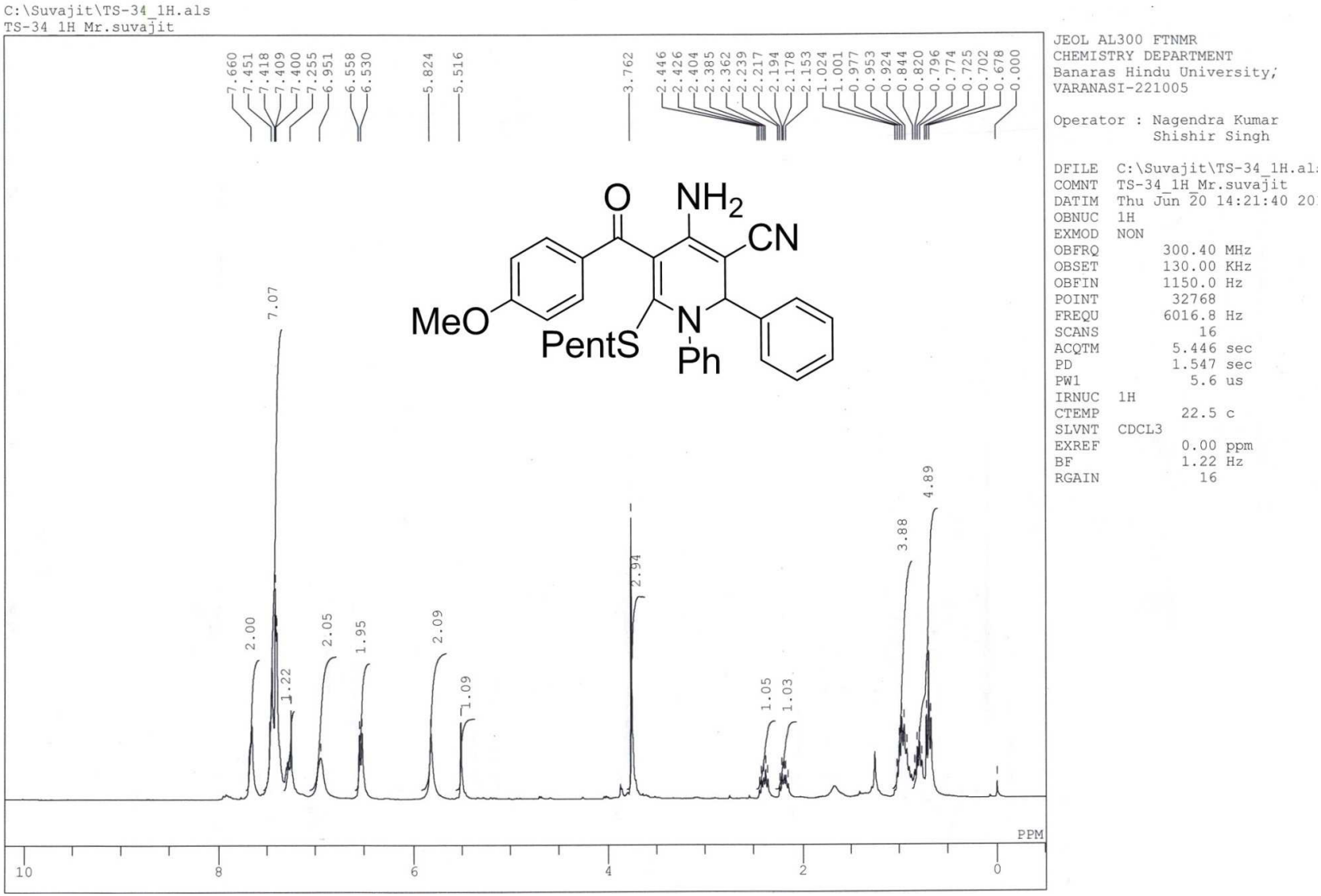
^{1}H NMR Spectrum of the Compound 4h:



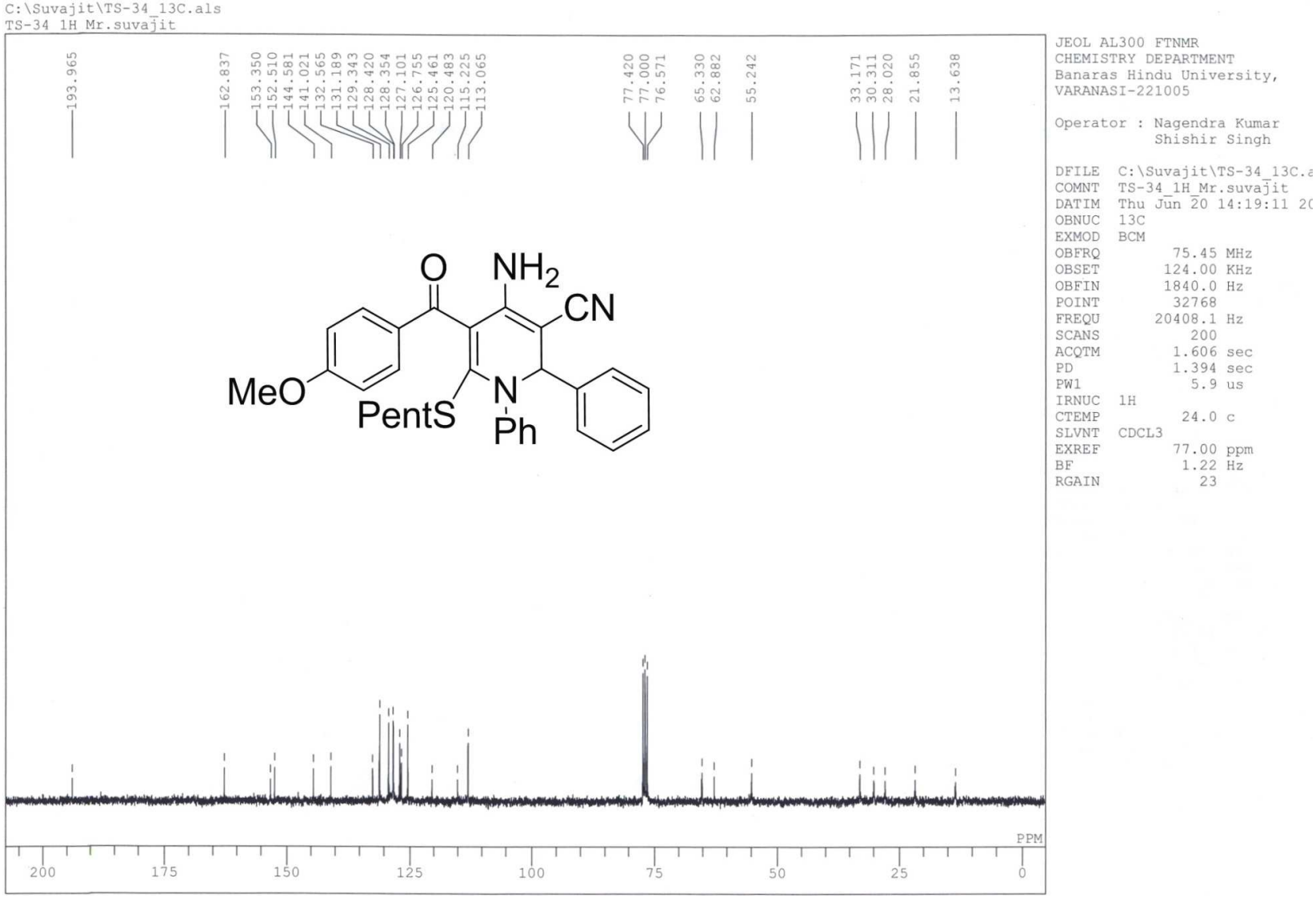
^{13}C NMR Spectrum of the Compound 4h:



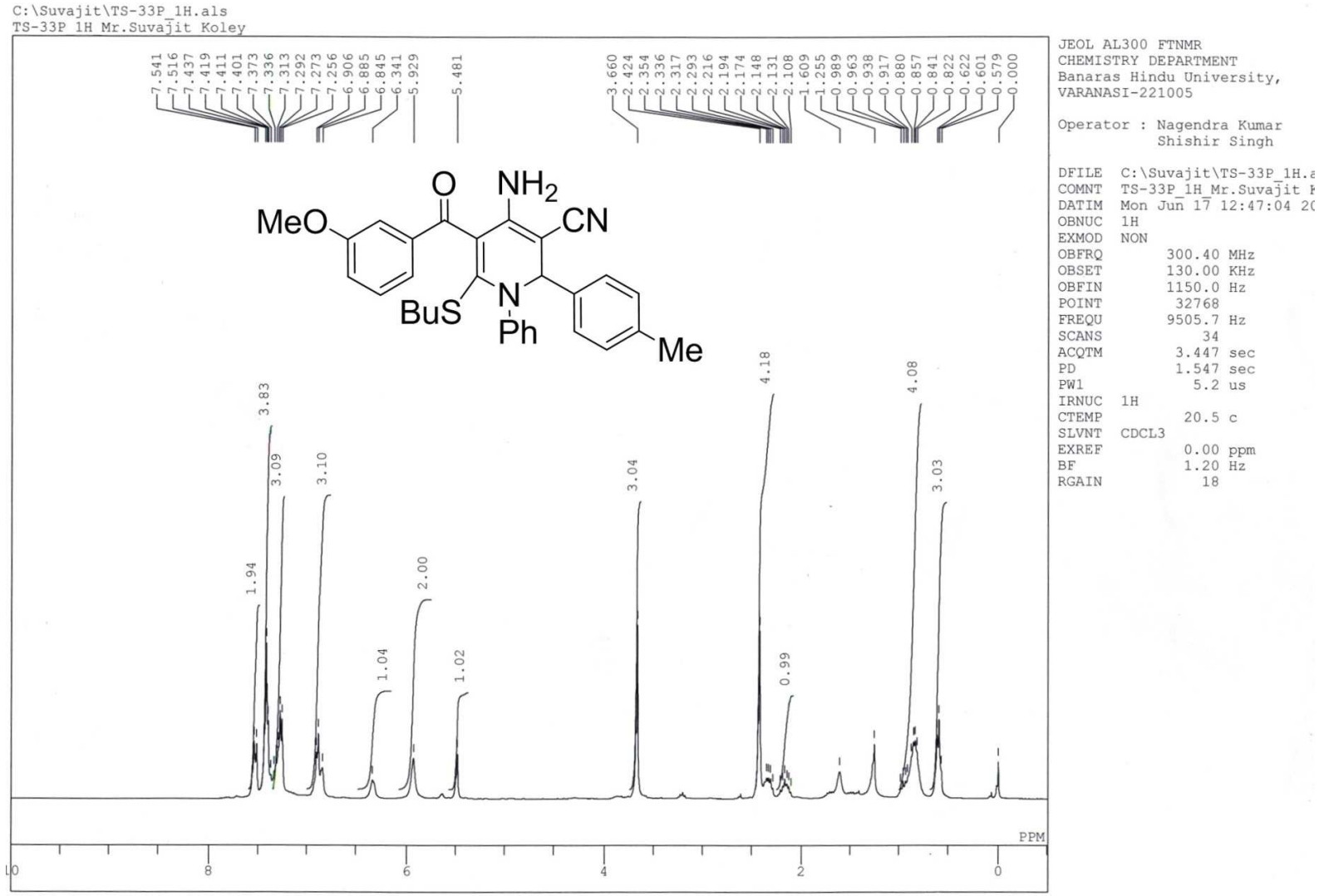
^{1}H NMR Spectrum of the Compound 4i:



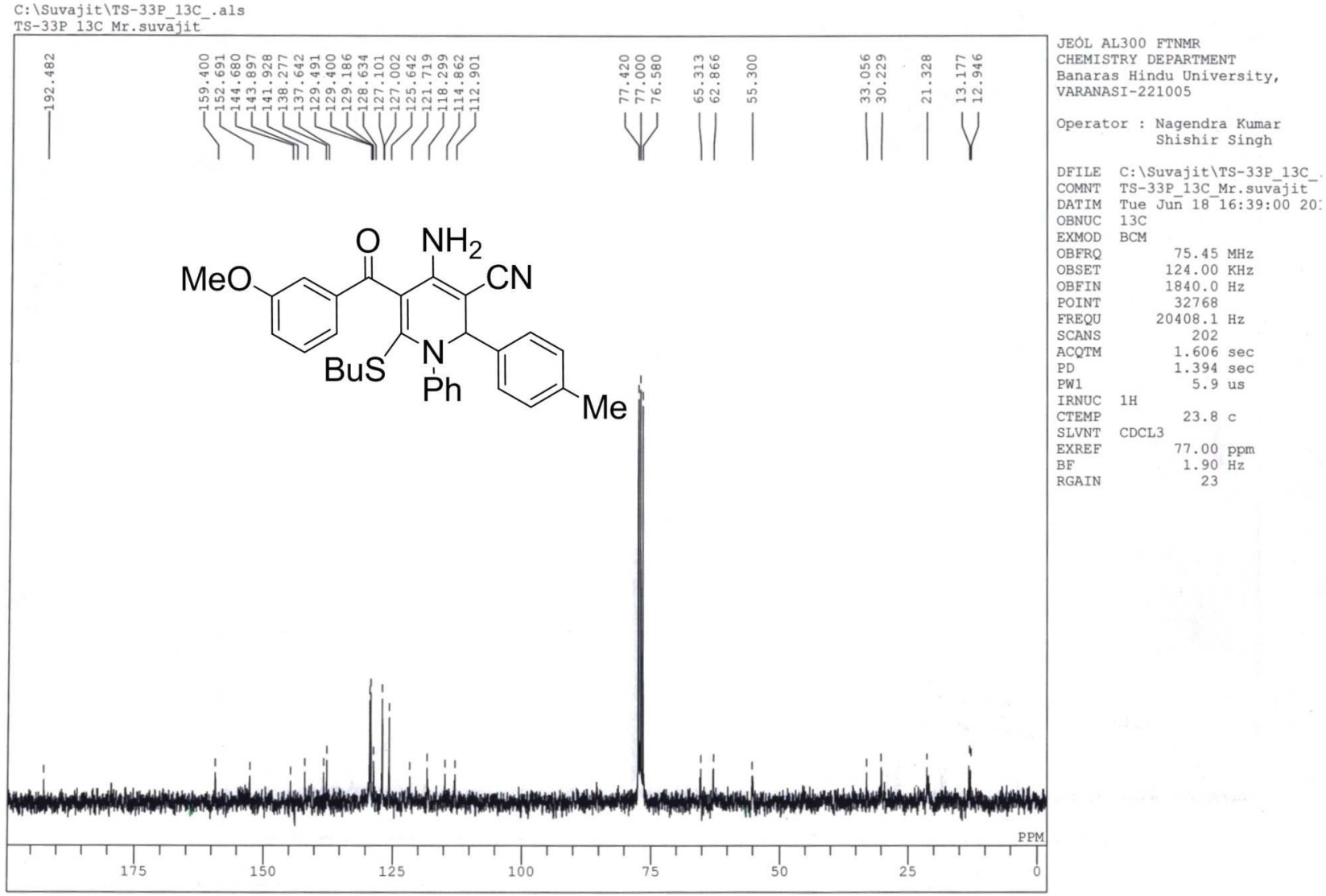
^{13}C NMR Spectrum of the Compound 4i:



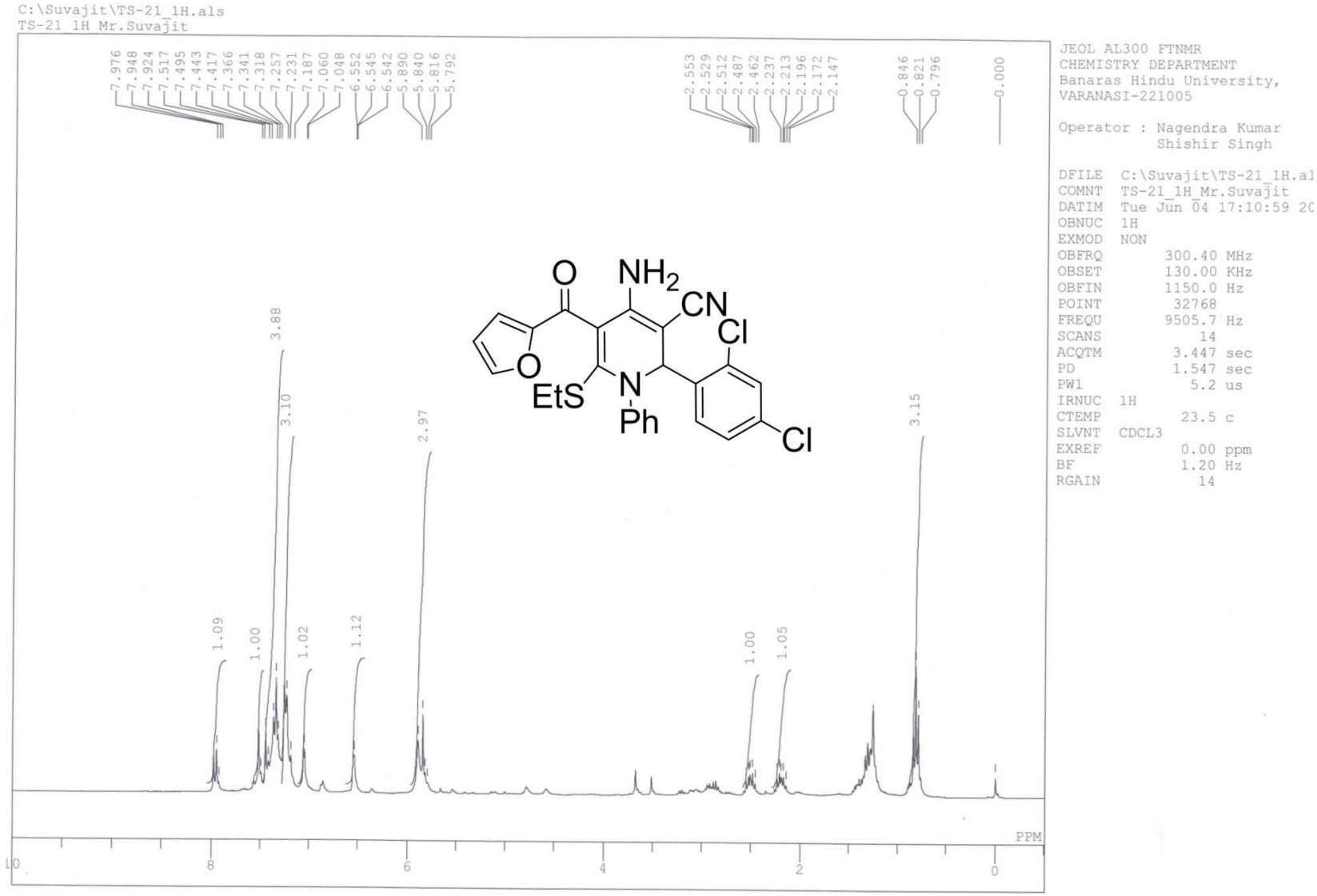
^{1}H NMR Spectrum of the Compound 4j:



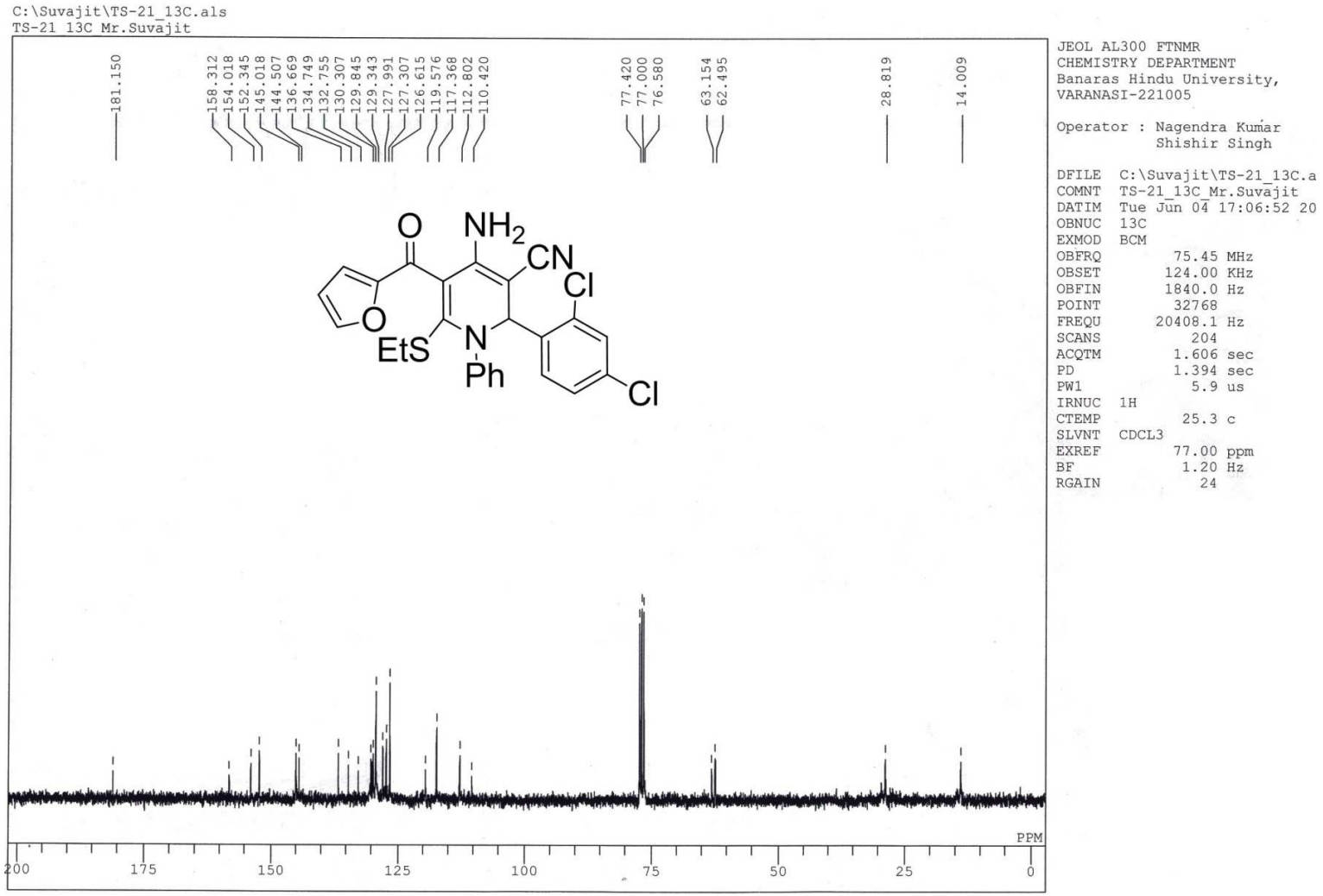
^{13}C NMR Spectrum of the Compound 4j:



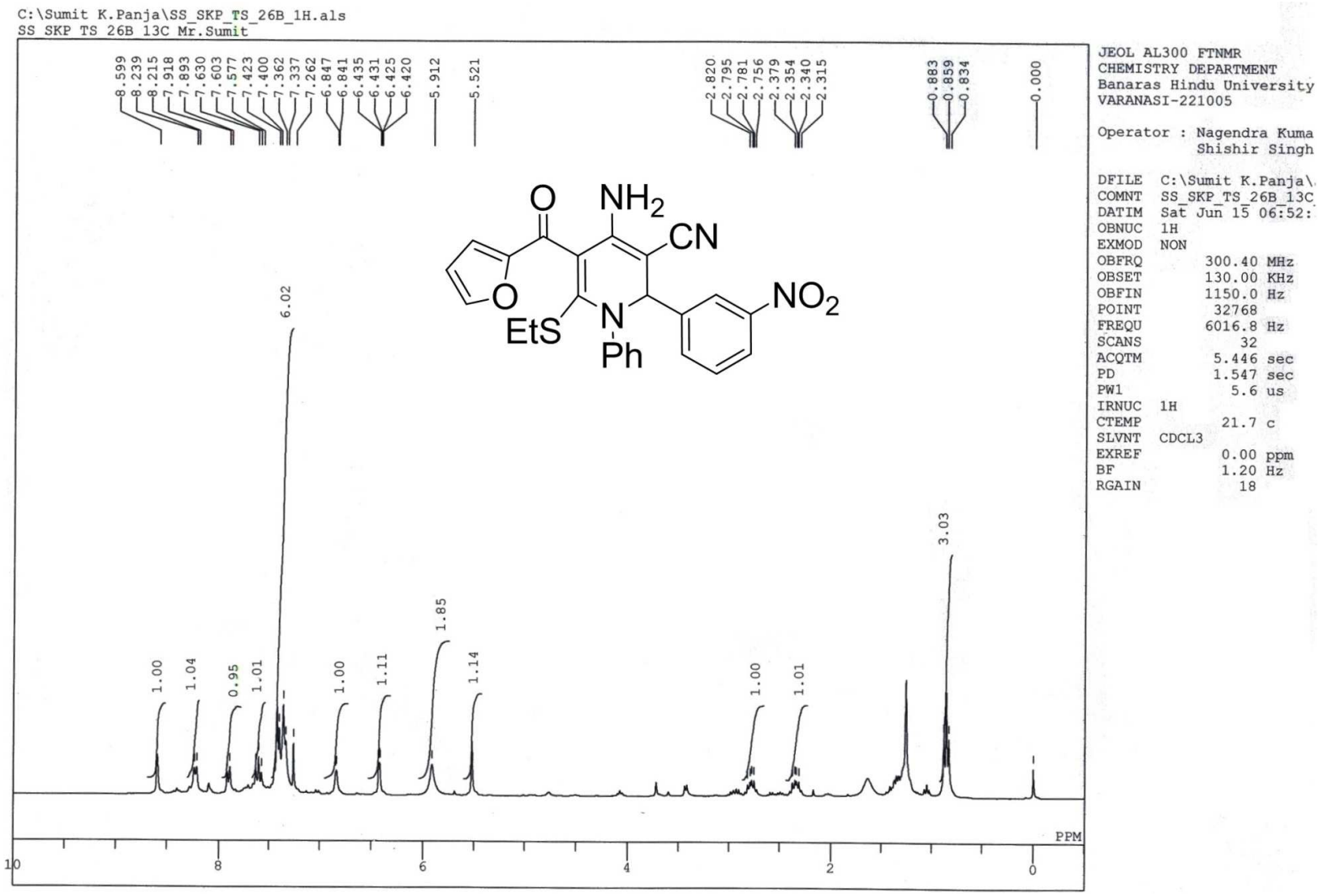
^{1}H NMR Spectrum of the Compound 4k:



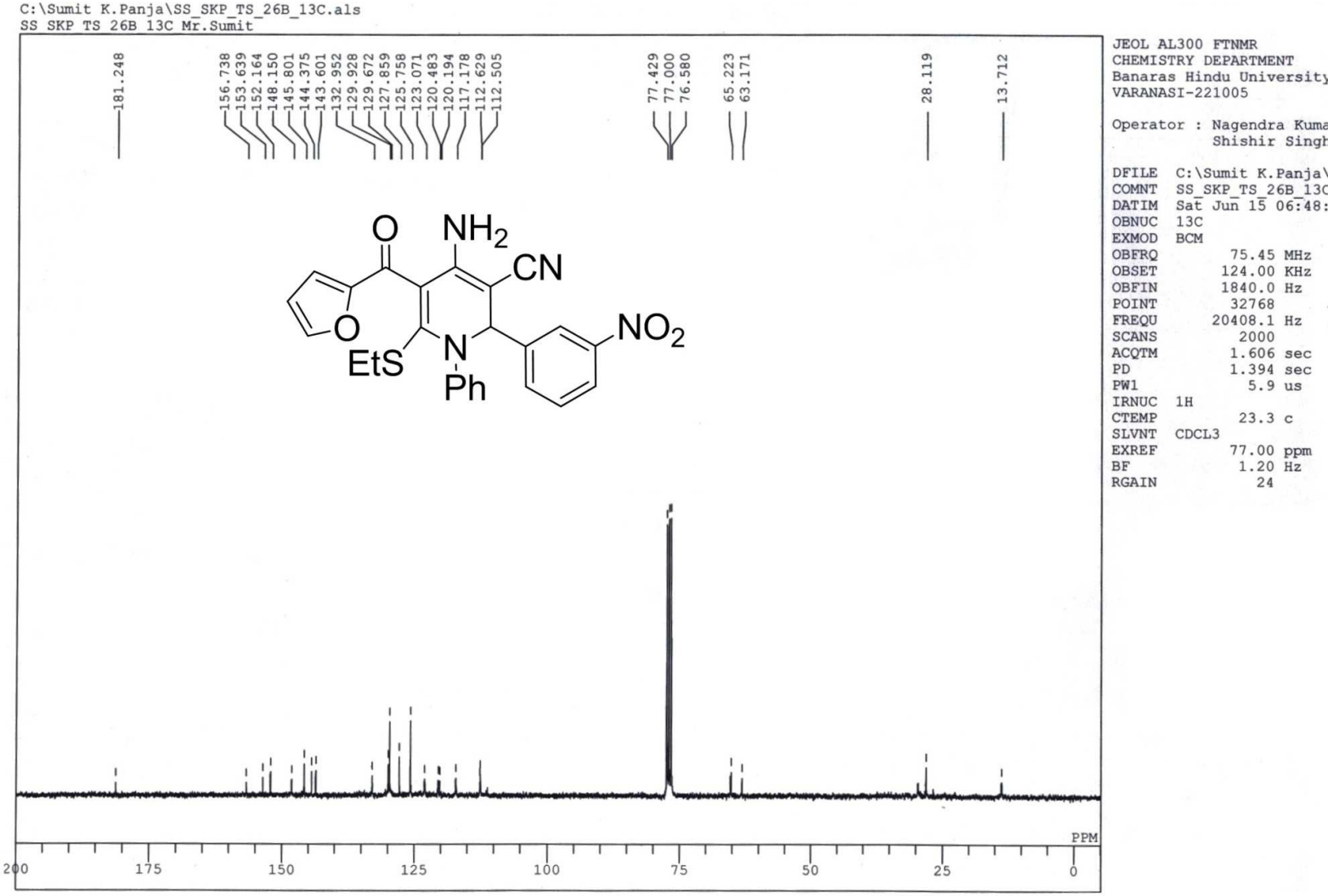
^{13}C NMR Spectrum of the Compound 4k:



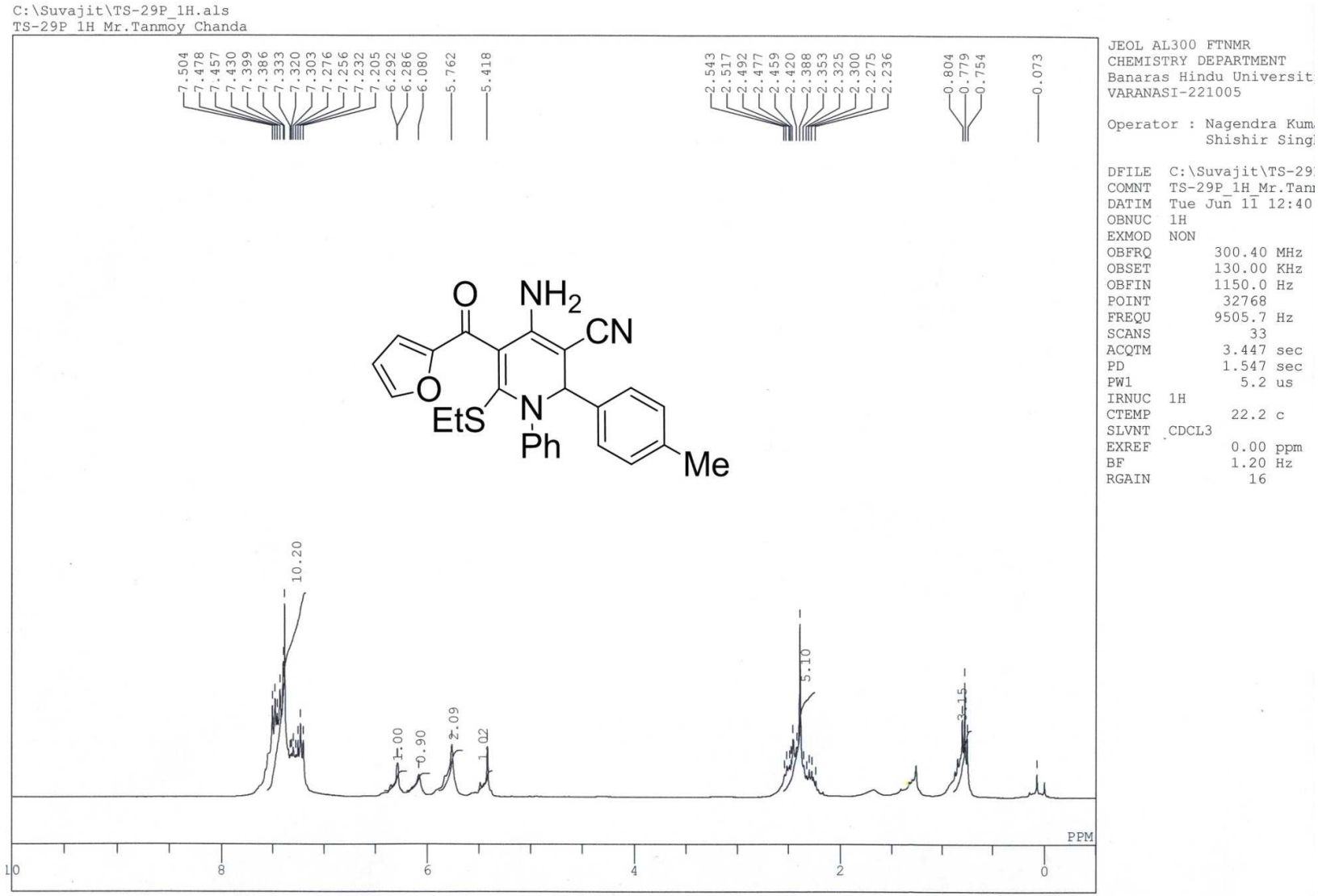
^{1}H NMR Spectrum of the Compound 4l:



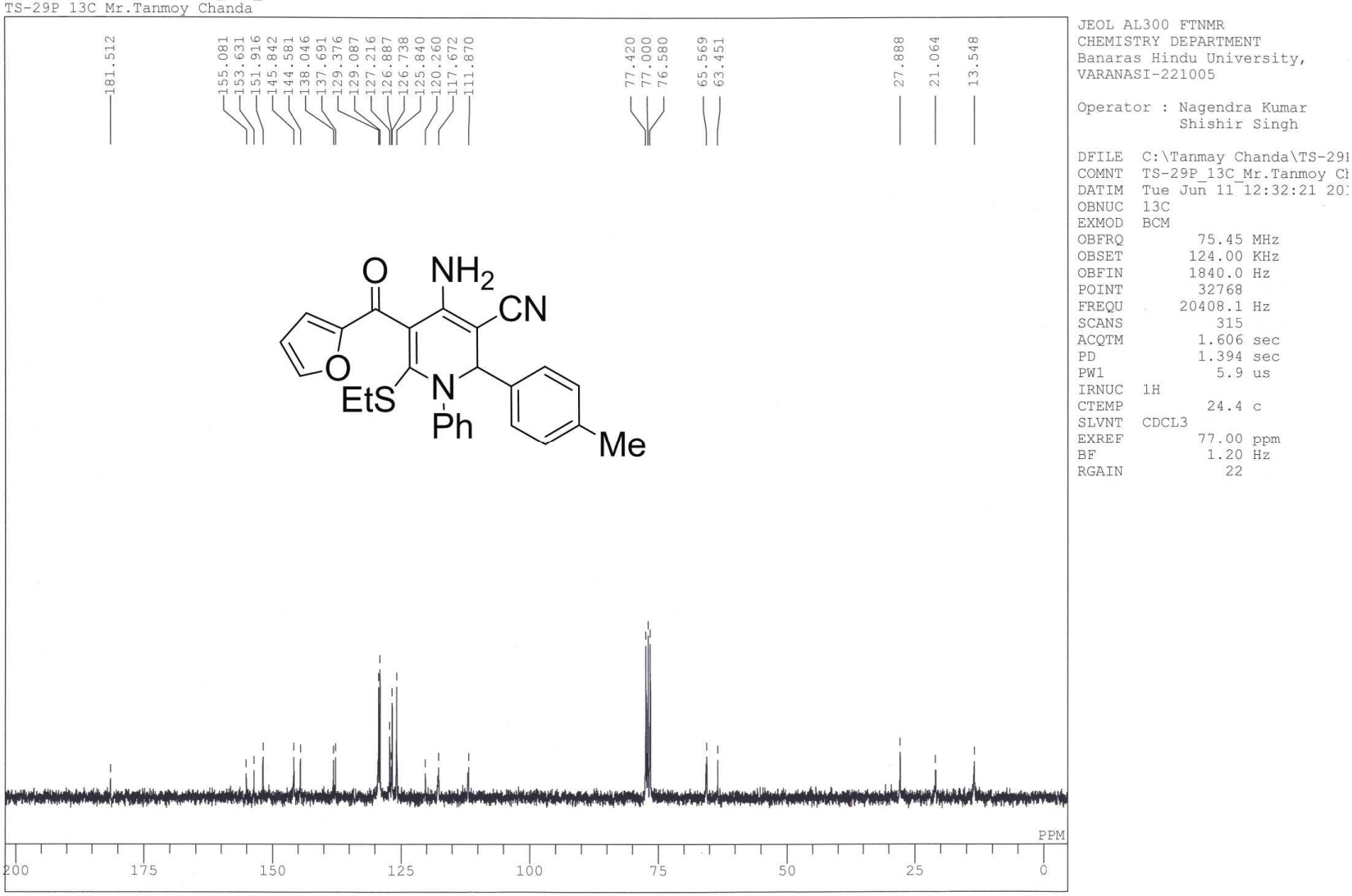
^{13}C NMR Spectrum of the Compound 4l:



^{1}H NMR Spectrum of the Compound 4m:



^{13}C NMR Spectrum of the Compound 4m:




```
JEOL AL300 FTNMR
CHEMISTRY DEPARTMENT
Banaras Hindu University,
VARANASI-221005

Operator : Nagendra Kumar
           Shishir Singh

DFILE   C:\Tanmay Chanda\TS-29I
COMNT   TS-29P_13C_Mr.Tanmoy Ch
DATIM   Tue Jun 11 12:32:21 20:
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OBSET        124.00 KHz
OBFIN        1840.0 Hz
POINT         32768
FREQU       20408.1 Hz
SCANS           315
ACQTM         1.606 sec
PD            1.394 sec
PW1             5.9 us
IRNUC   1H
CTEMP          24.4 c
SLVNT   CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            22
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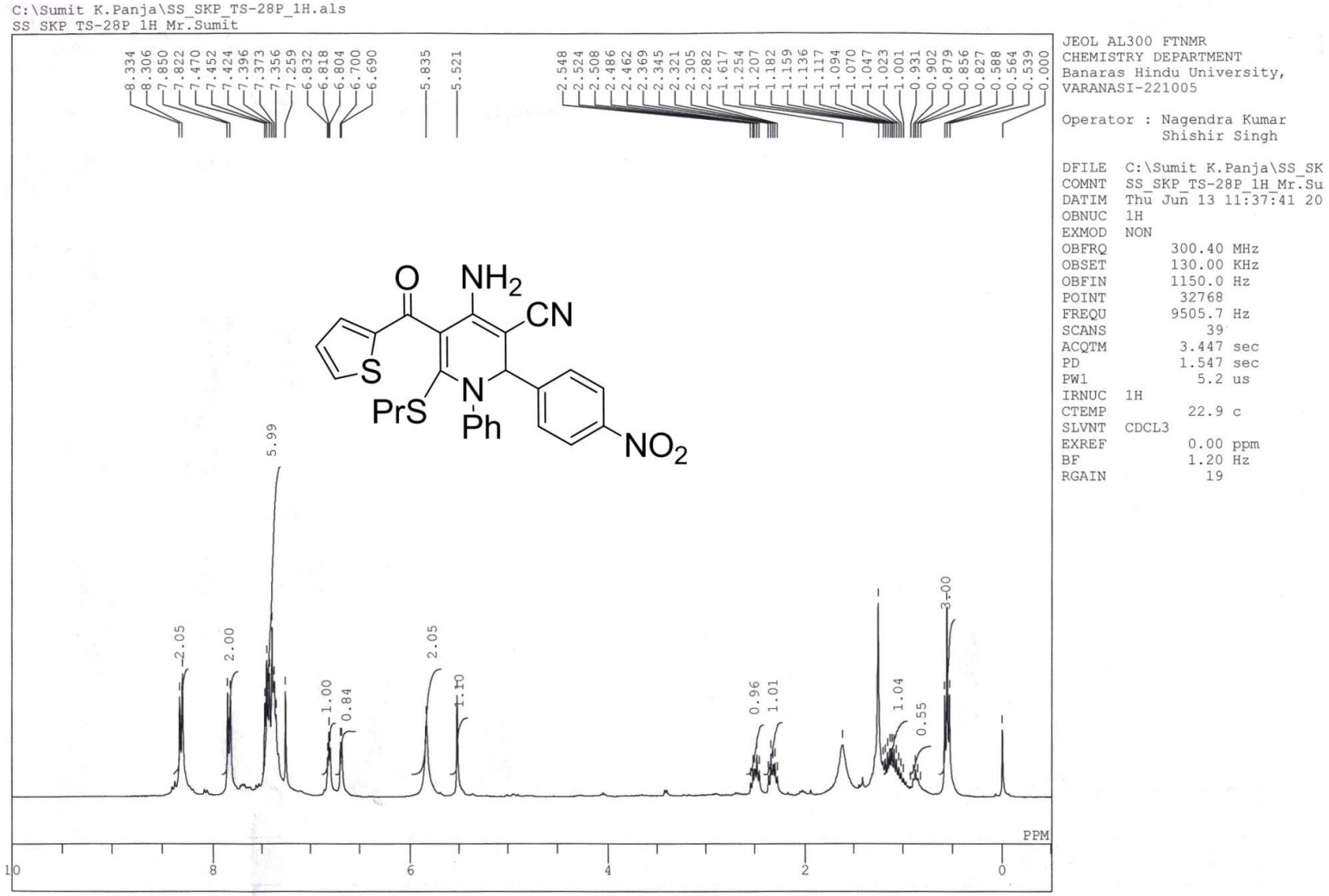
^{1}H NMR Spectrum of the Compound 4n:



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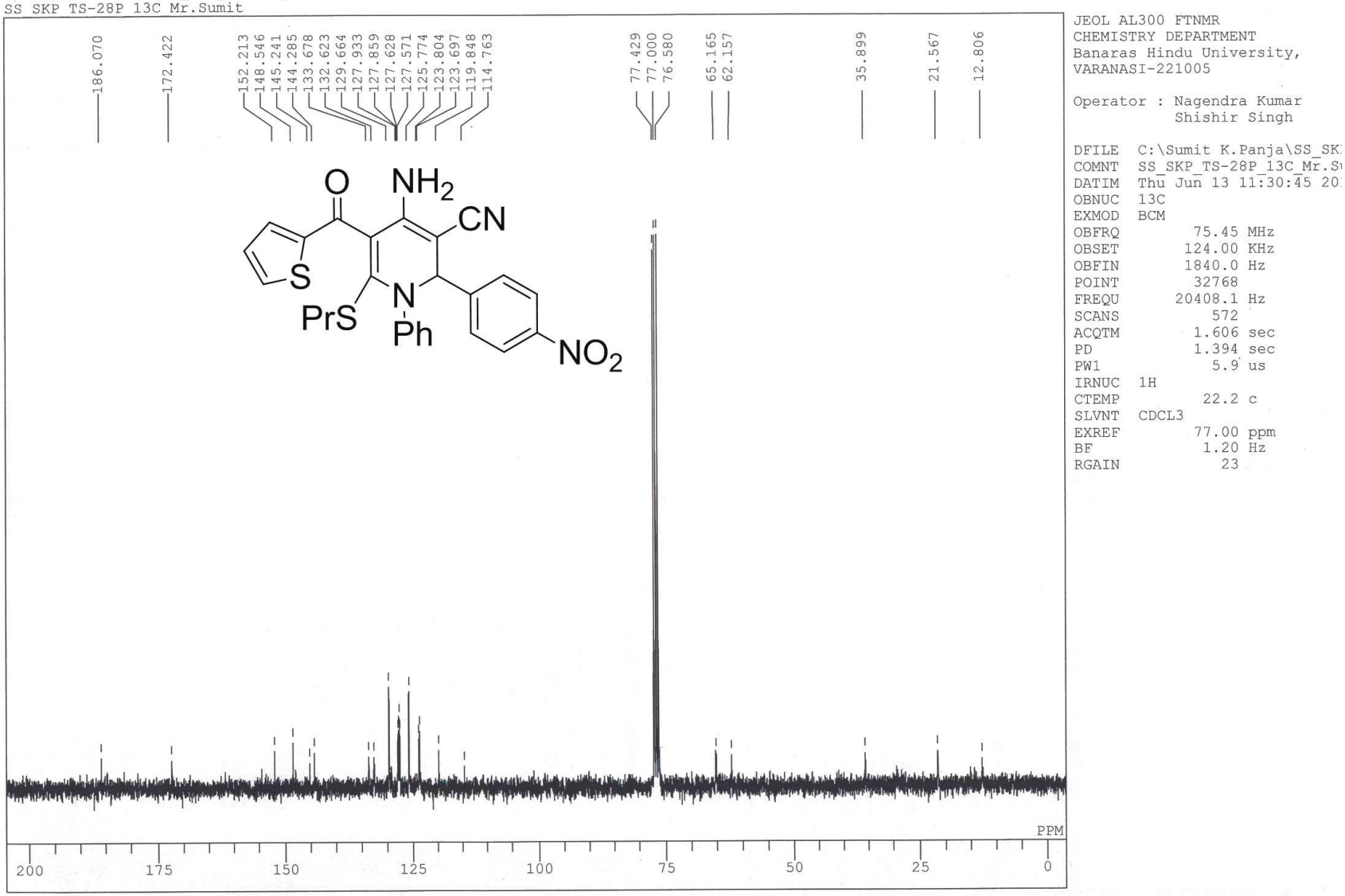
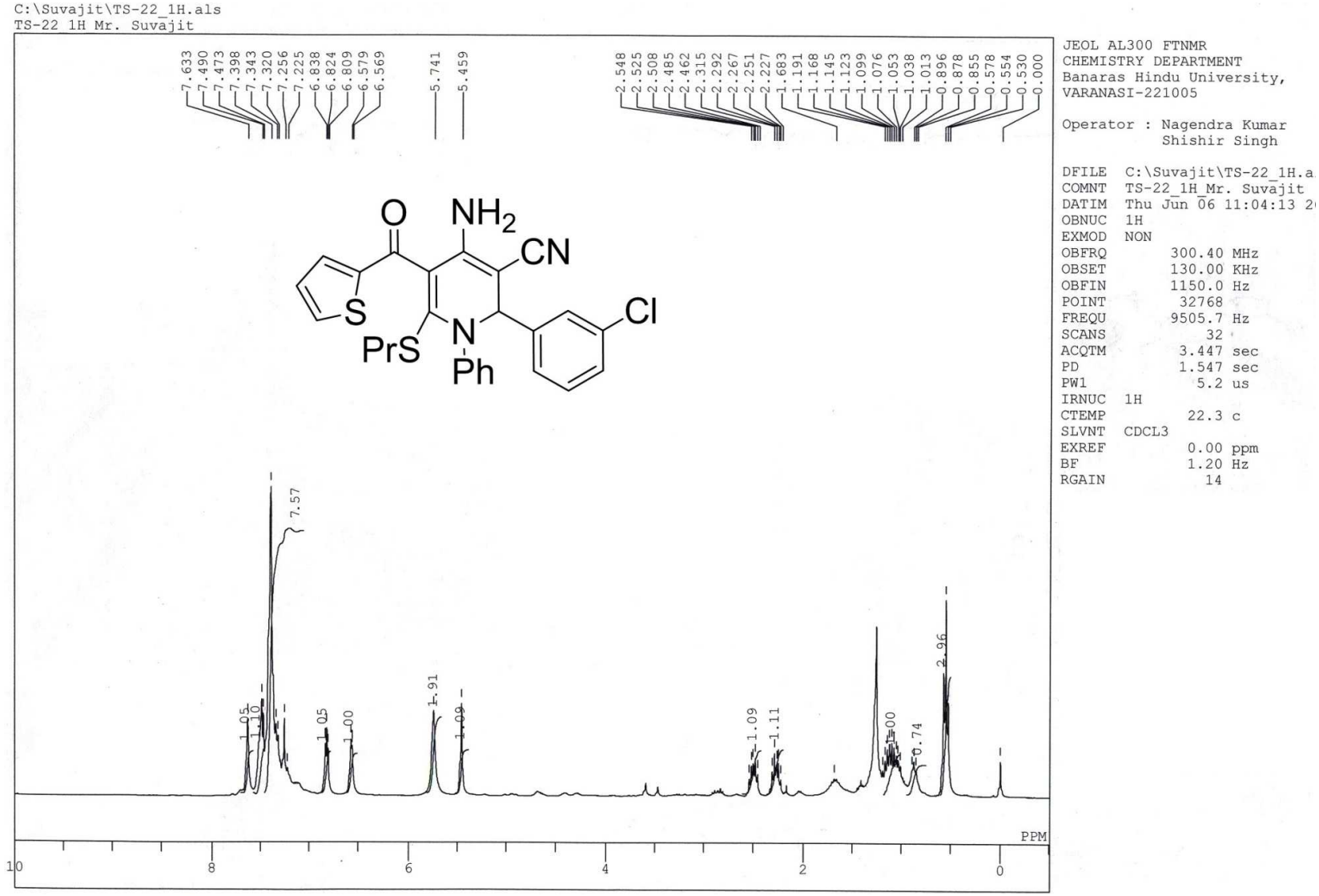
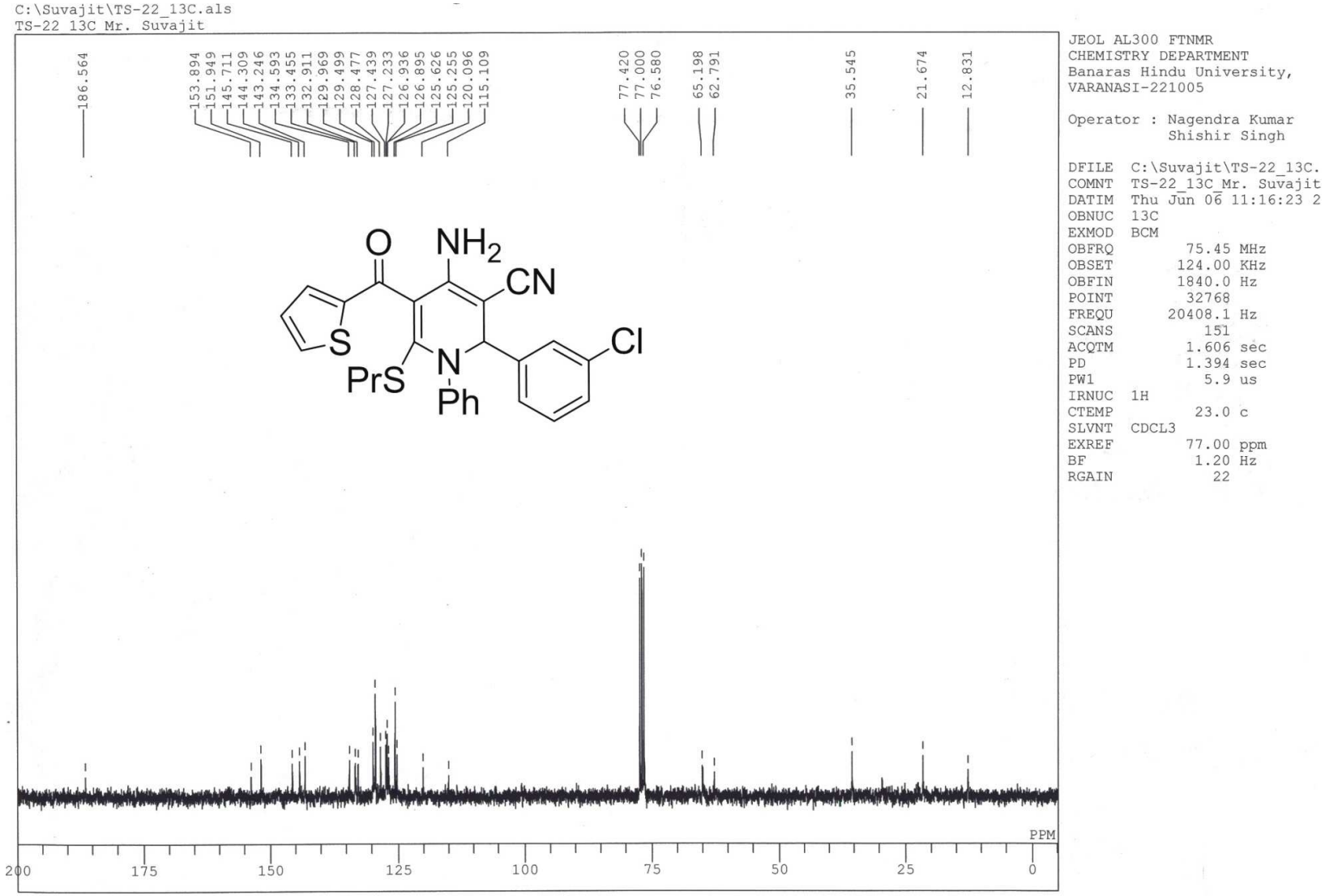


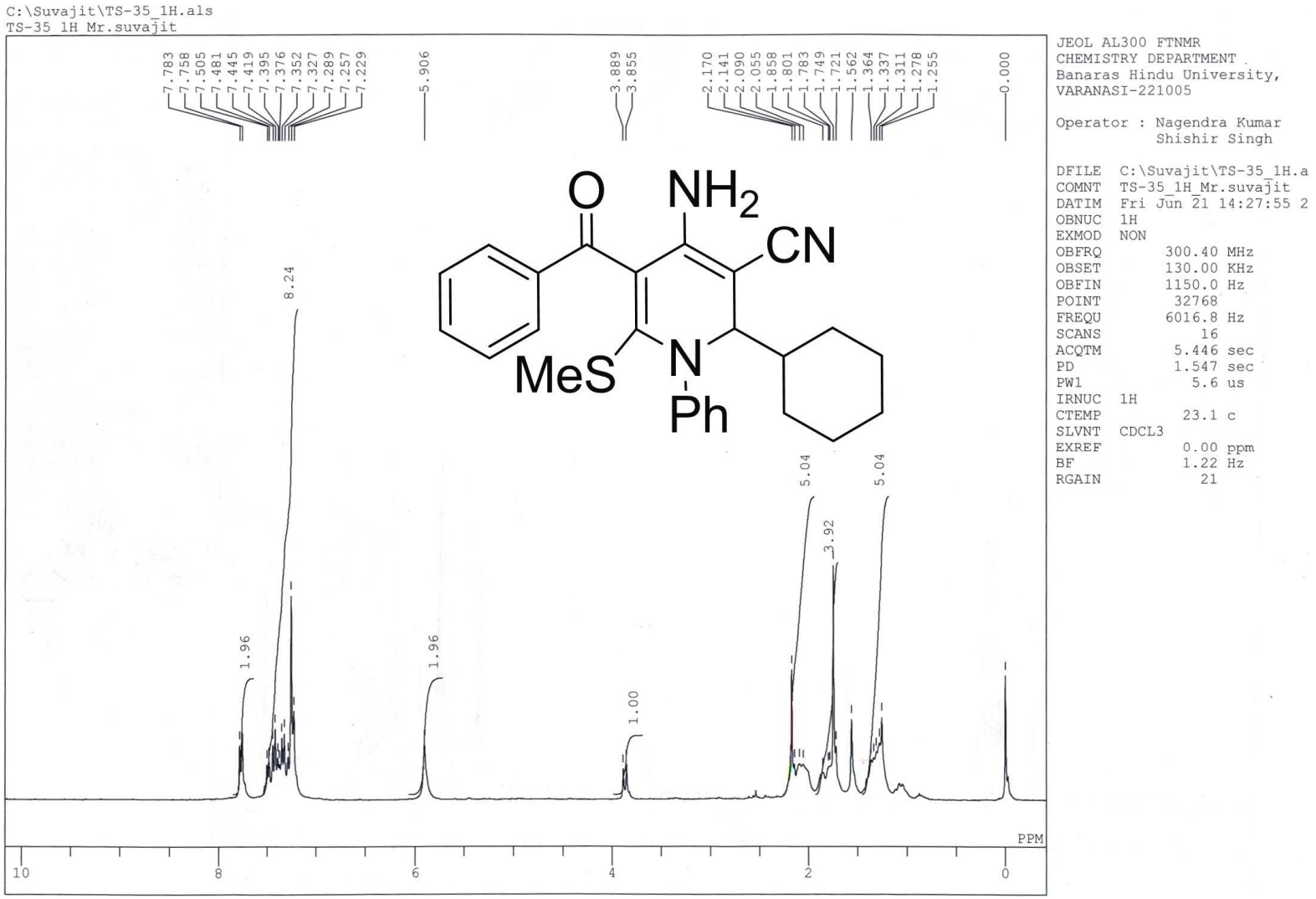
^{1}H NMR Spectrum of the Compound 4o:



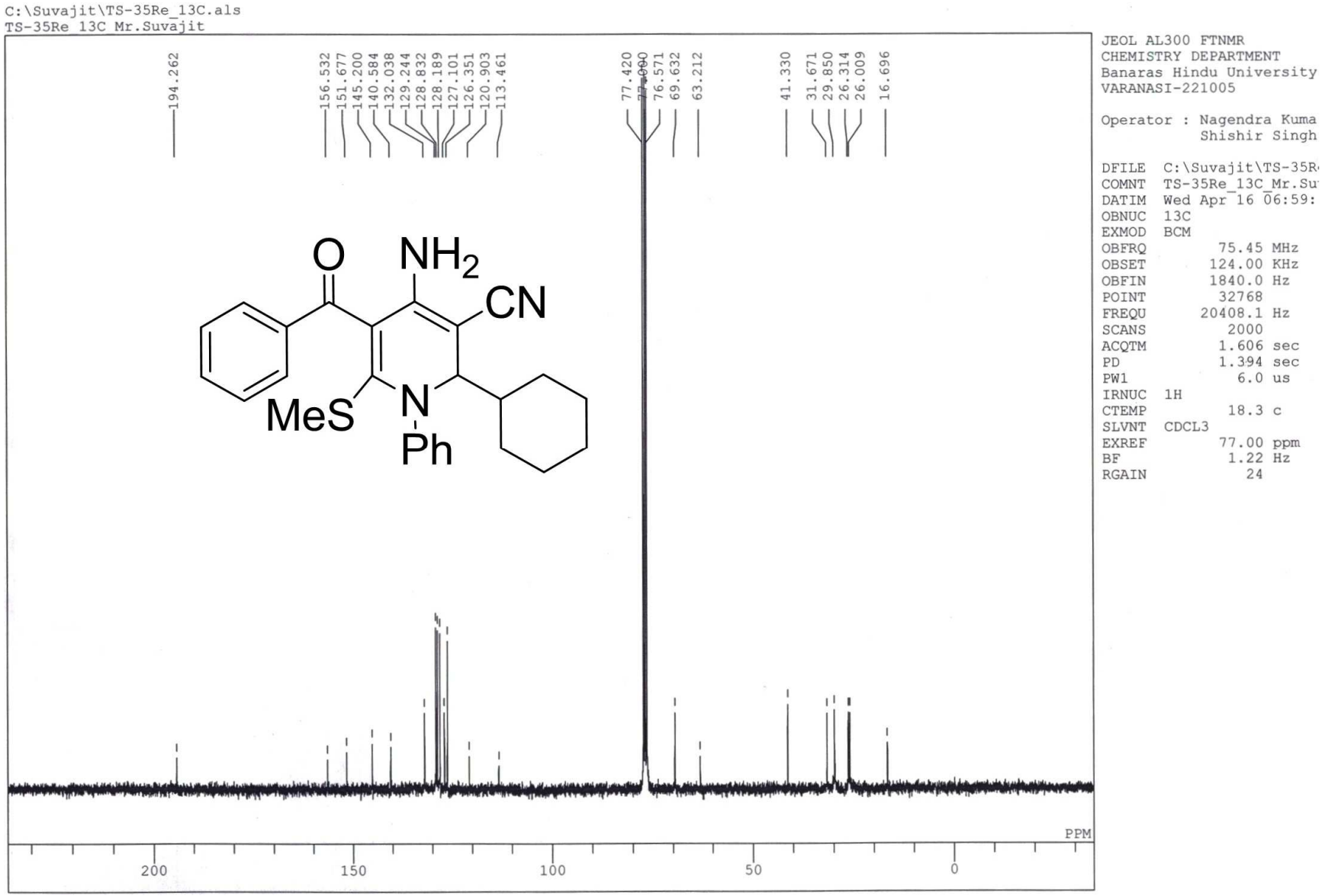
^{13}C NMR Spectrum of the Compound 4o:



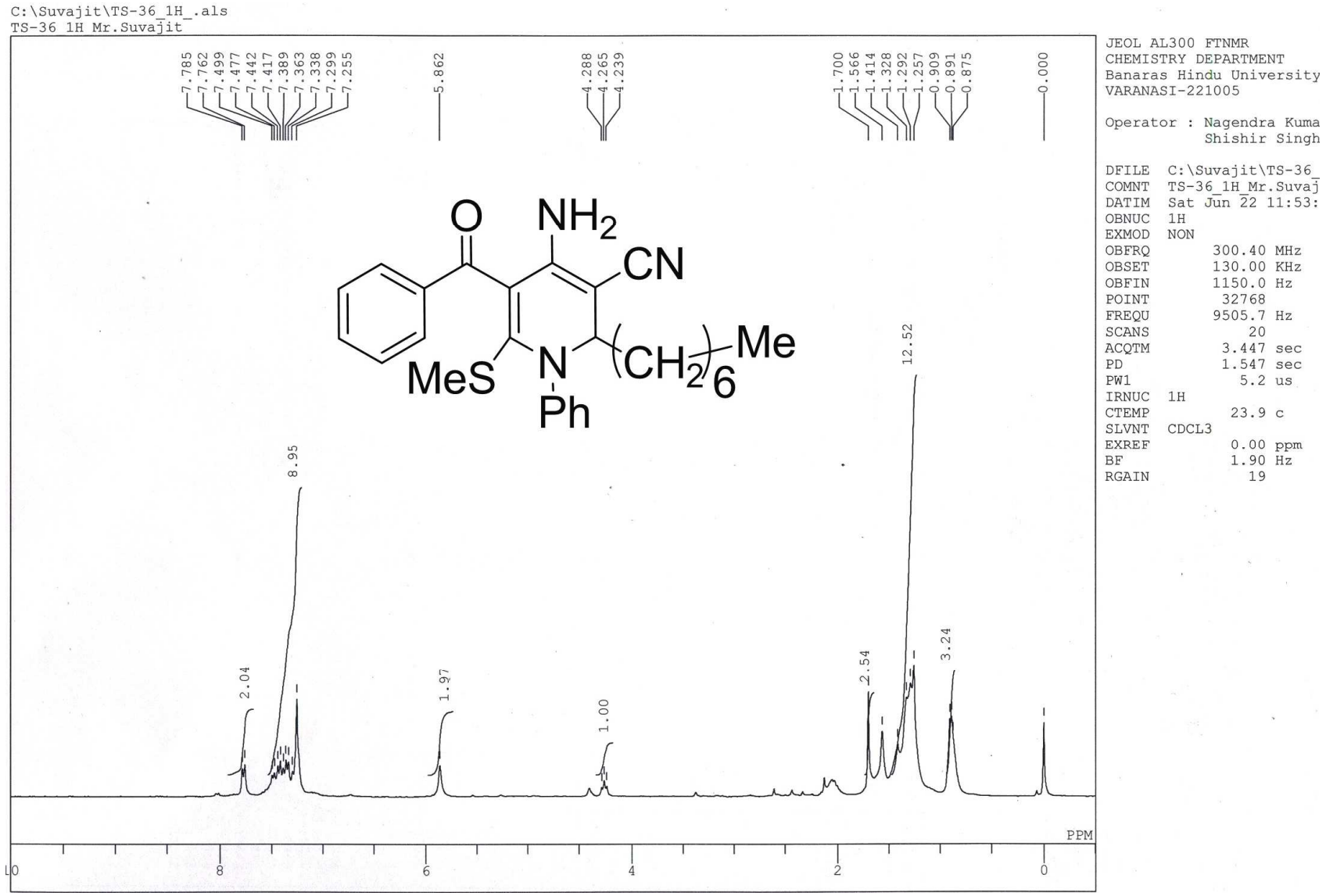
^{1}H NMR Spectrum of the Compound 4p:



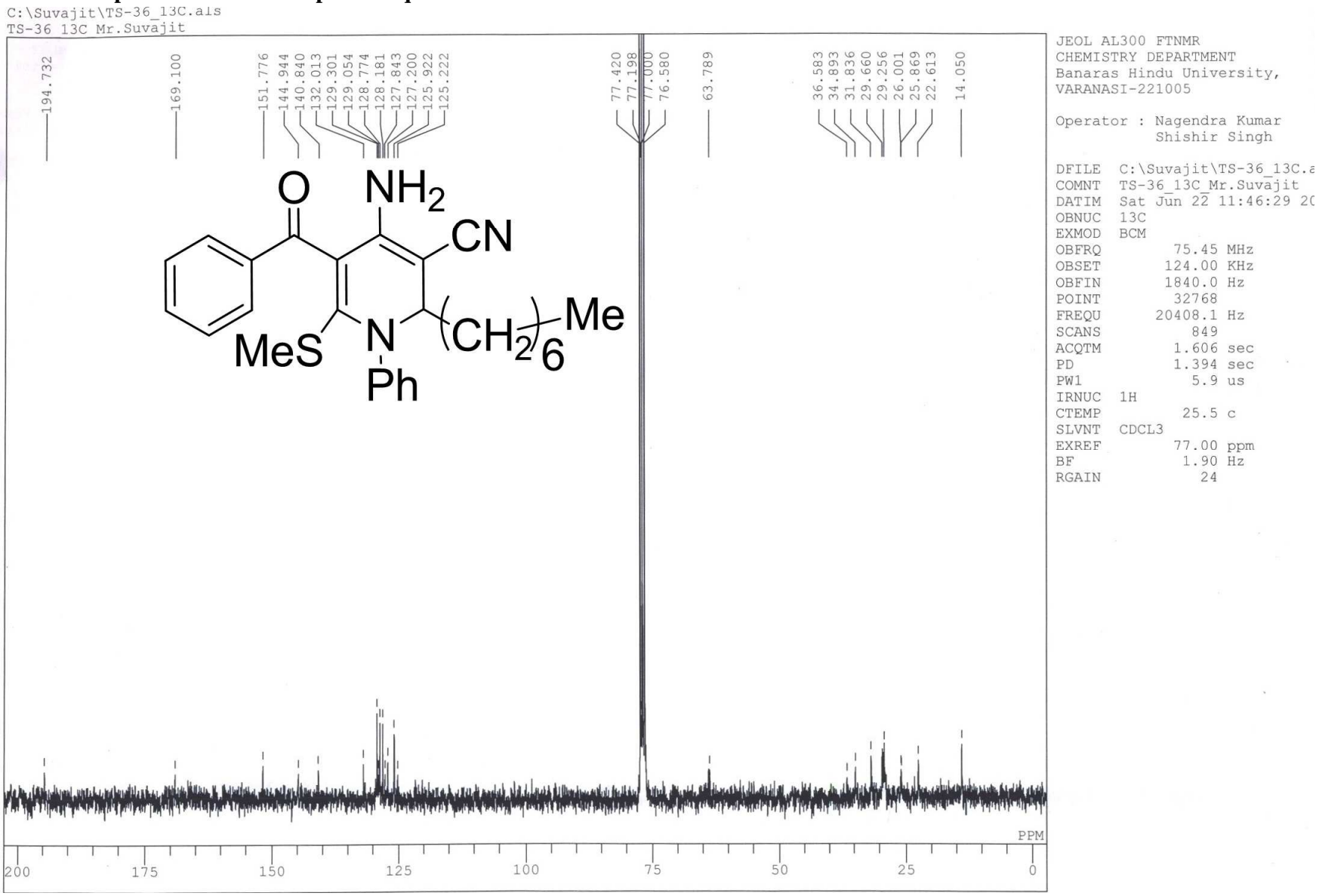
^{13}C NMR Spectrum of the Compound 4p:



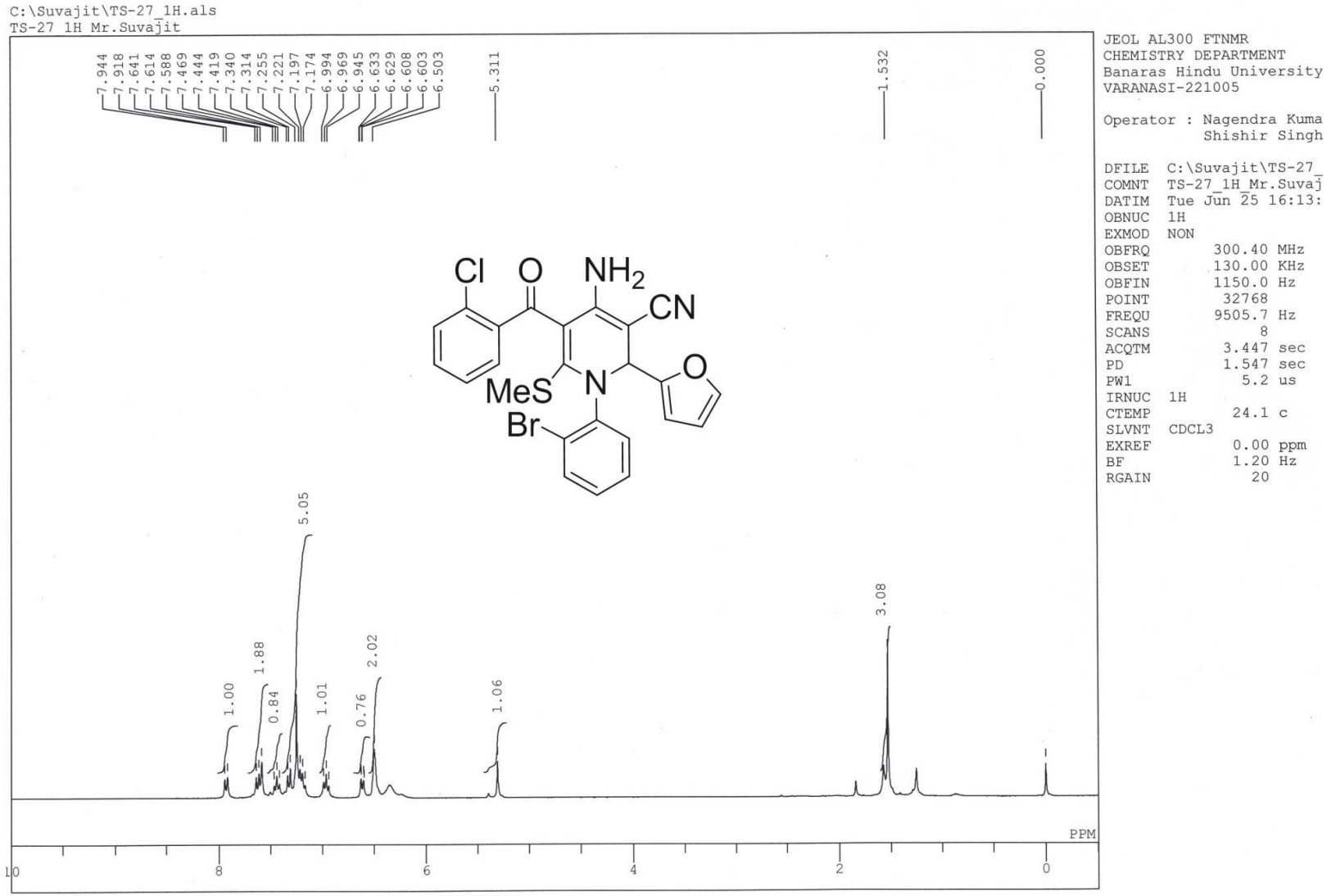
^{1}H NMR Spectrum of the Compound 4q:



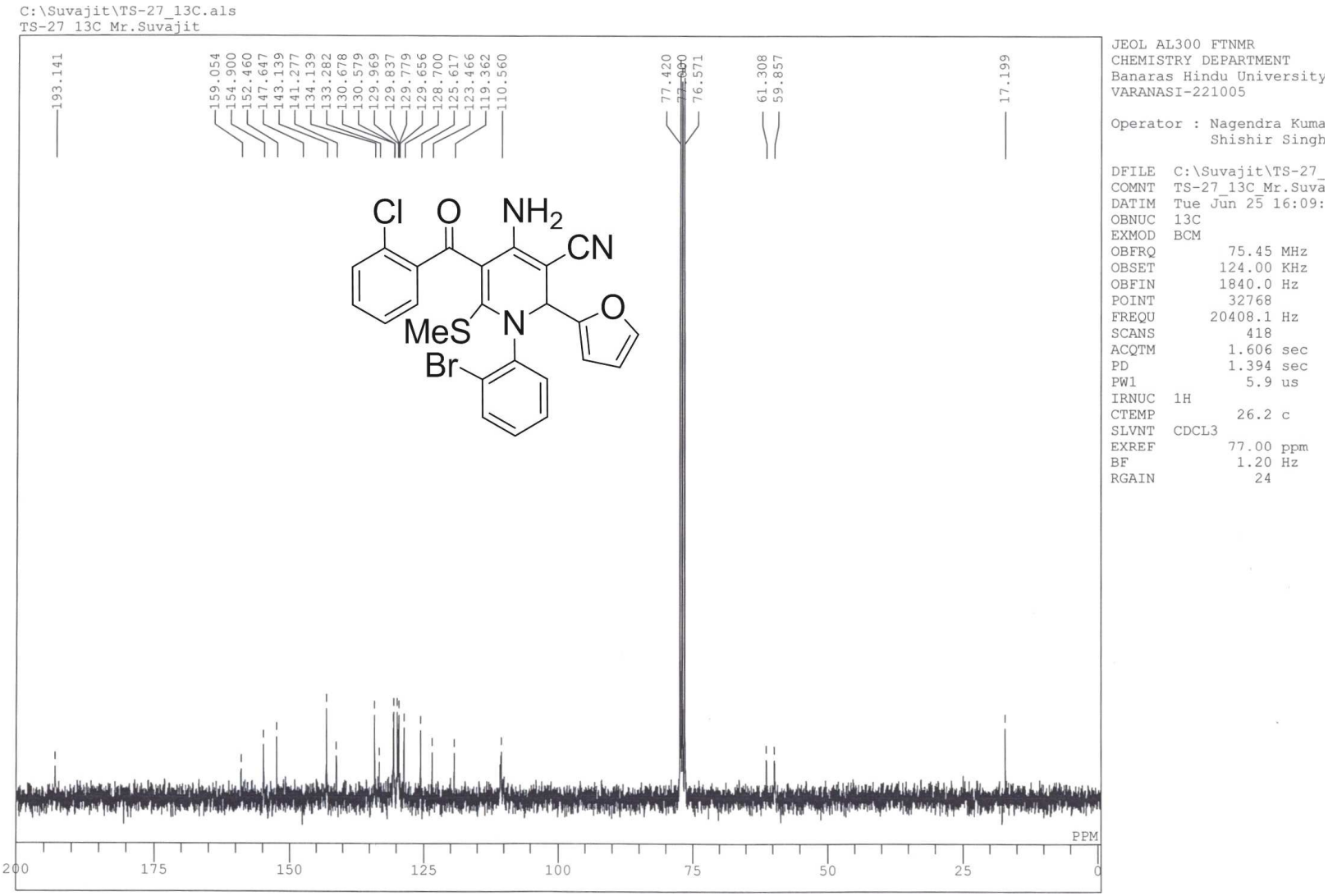
^{13}C NMR Spectrum of the Compound 4q:



^{1}H NMR Spectrum of the Compound 4r:

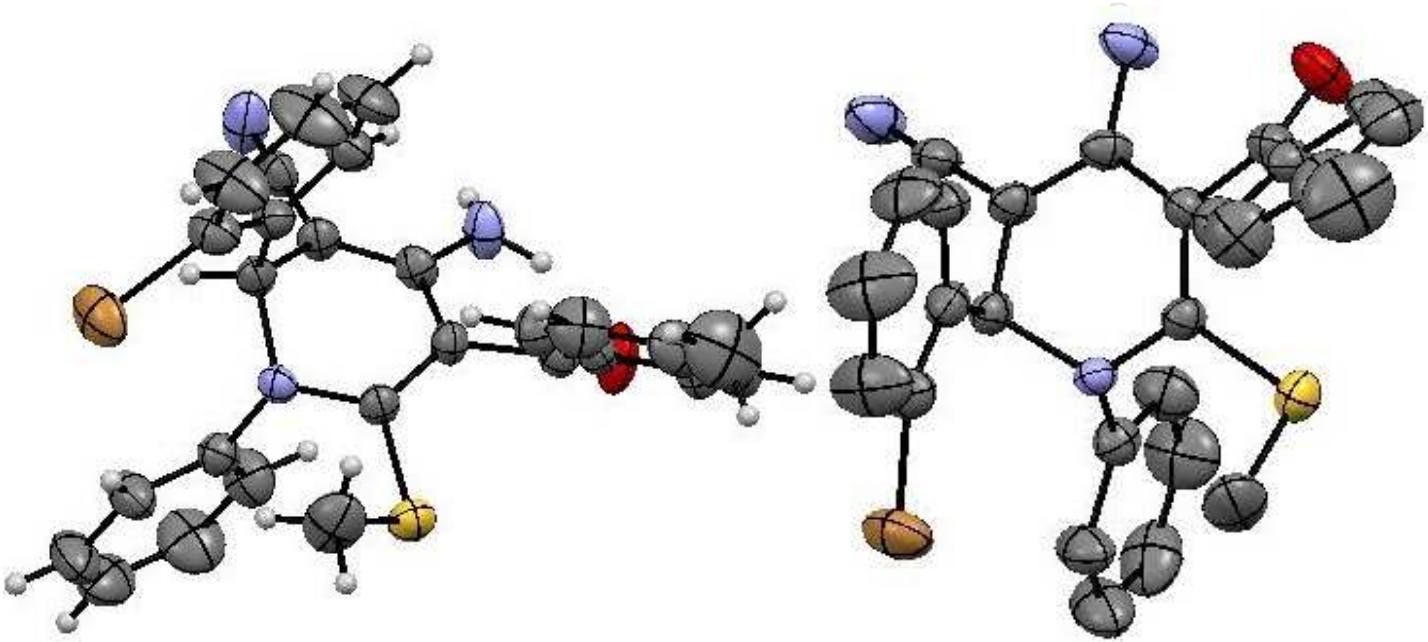


^{13}C NMR Spectrum of the Compound 4r:



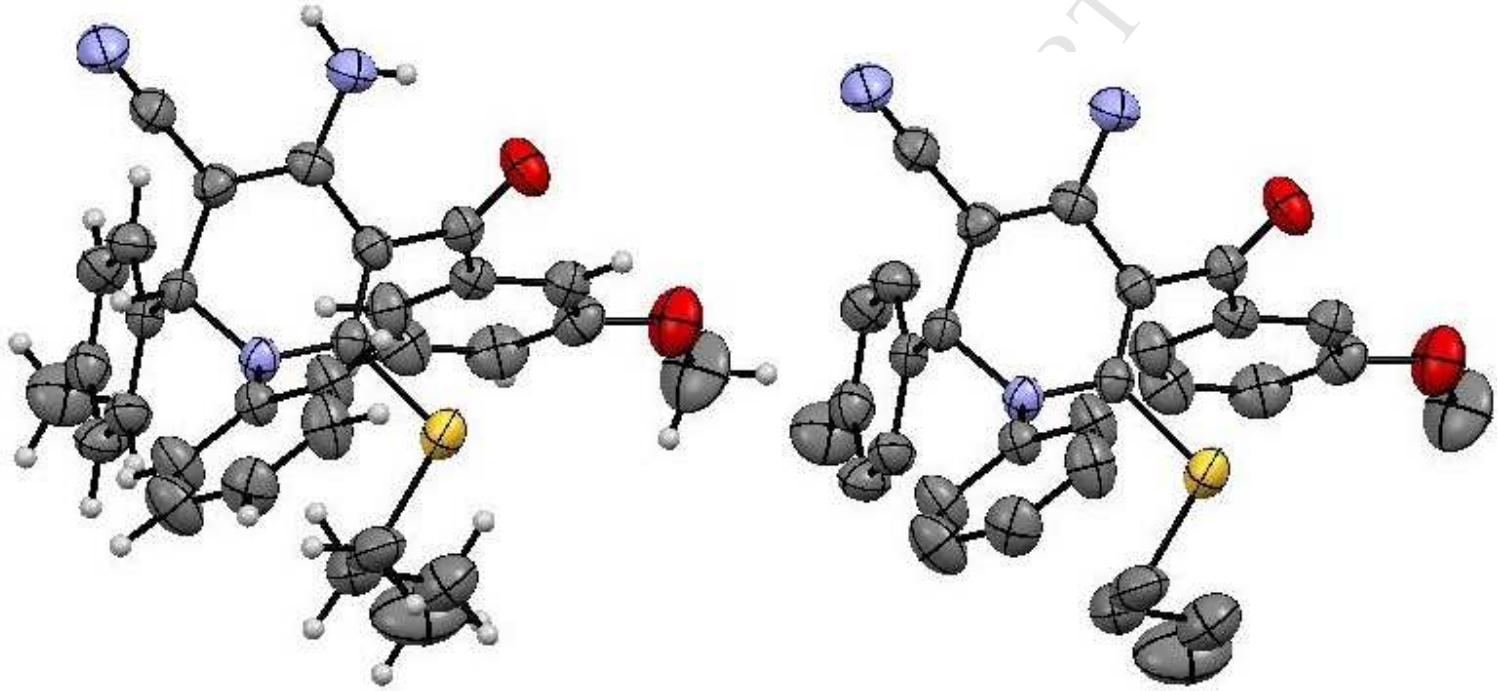
ORTEP Diagrams of 4d:

CCDC No.: 1024367



ORTEP Diagrams of 4j:

CCDC No.: 1024825



ORTEP Diagrams of 4m:

CCDC No.: 1024366