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First Noscapine Glycoconjugates inspired by Click Chemistry

Kunj B. Mishra[1], **Ram C. Mishra,**[2] and **Vinod K. Tiwari**[*1]

[1]Department of Chemistry, Centre of Advanced Study, Banaras Hindu University, Varanasi-, India
[2]College of Pharmacy, University of Georgia, Athens, GA 30605, USA

*Corresponding authors: E-mail: rcmishra@uga.edu, Tel: +1-706-542-5395; Fax: +1-706-542-5358 (RCM); and E-mail: tiwari_chem@yahoo.co.in (VKT), Tel.: +91-542-6702466; Fax: +91-542-236817

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1. General methods

All of the reactions were executed using anhydrous solvents under an argon atmosphere in one-hour oven-dried glassware at 100°C. All reagents and solvents were of pure analytical grade. Thin-layer chromatography (TLC) was performed on 60 F254 silica gel, pre-coated on aluminum plates and revealed with either a UV lamp (λ_{max} = 254 nm) or a specific color reagent (iodine vapors) or by spraying with methanolic H_2SO_4 solution and subsequent charring by heating at 100°C. ^{1}H and ^{13}C NMR were recorded at 300 and 75 MHz, respectively. Chemical shifts given in ppm downfield from internal TMS; *J* values in Hz. Mass spectra recorded using electrospray ionization mass spectrometry (ESI-MS). Infrared spectra recorded as Nujol mulls in KBr plates. Single-crystal Xray data collected on Xcalibur Eos (Oxford) CCD-diffractometer.

2. Synthesis of novel tosyl sugar (5i-j):

1,2-*O*-isopropylidene-3-*O*-Propyl-6-*O*-tosyl-α-D-glucofuranose (5i). A stirring solution of 3-1,2-*O*-isopropylidene-*O*-Propyl-α-D-glucofuranose (1.34 g, 5.1 mmol) in pyridine (15 mL) was treated with *p*-toluene sulphonyl chloride (1.0 g, 5.1 mmol) at 0 ^{0}C under anhydrous condition followed by stirring for 12 h at 5-10 ^{0}C afforded viscous liquid (1.3 g, 62%); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 5.86 (d, *J* = 3.6 Hz, 1H), 4.52 (d, *J* = 3.6 Hz, 1H), 4.28-3.96 (m, 5H), 3.57 (dd, *J* = 6.6 and 15.6 Hz, 1H), 3.43 (dd, *J* = 6.6 and 15.6 Hz, 1H), 2.52-2. 44 (m, 4H), 1.62-1.30 (m, 8H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 144.9, 132.5, 129.9, 128.0, 111.8, 105.0, 82.7, 81.9, 79.0, 72.1, 67.5, 26.7, 26.1, 22.8, 21.6, 10.5 ppm.

3-*O*-*iso*-pentyl-1,2-*O*-isopropylidene-6-*O*-tosyl-α-D-glucofuranose (5j). A stirring solution of 3-*O*-isopentyl-1,2-*O*-isopropylidene-α-D-glucofuranose (1.6 g, 5.7 mmol) in pyridine (15 mL) was treated with *p*-toluene sulphonyl chloride (1.08 g, 5.7 mmol) at 0 ^{0}C under anhydrous condition followed by stirring for 12 h at 10 ^{0}C afford the title compound as viscous liquid (1.5 g, 60%); ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.79 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 5.85 (d, J = 3.6 Hz, 1H), 4.52 (d, J = 3.6 Hz, 1H), 4.26-3.95 (m, 5H), 3.64 (dd, J = 6.6, 15.6 Hz, 1H), 3.49 (dd, J = 6.6, 15.9 Hz, 1H), 2.88 (d, J = 5.57 Hz, 1H) 2.44 (s, 3H), 1.69-1.23 (m, 13H), 0.91 (d, J = 6.6Hz, 6H); ^{13}C NMR (75 MHz, CDCl$_3$): 144.9, 132.5, 129.9, 128.0, 111.8, 105.0, 82.8, 81.9, 79.0, 72.2, 68.9, 67.5, 38.4, 26.7, 26.2, 24.9, 22.5, 21.6 ppm.

3. Synthesis ofnovel sugar azides (6i-k):

6-Azido-6-deoxy-1,2-*O*-isopropylidene-3-*O*-propyl-α-D-glucofuranose (6i): Reaction of compound **5j** (1.34 g, 3.2 mmol) with NaN$_3$ (0.62 g, 9.6 mmol) in DMF (15 mL) at 80 ^{0}C afforded compound **6i** as viscous liquid (0.81 g, 88 % yield); IR (KBr) cm^{-1}: 3453, 2964, 2935, 2878, 2103, 1633, 1455, 1080;^{1}H NMR (300 MHz, CDCl$_3$): δ5.91 (d, J = 3.6 Hz, 1H), 4.57 (d, J = 3.9 Hz, 1H), 4.10 (m, 2H), 4.00 (s, 1H), 3.66-3.43 (m, 4H), 2.74 (s, 1H), 1.65-1.56 (m, 2H), 1.49 (s, 3H), 1.32 (s, 3H), 0.94 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, CDCl$_3$):δ 111.8, 105.0, 82.8, 81.9, 79.7, 72.0, 68.9, 54.5, 26.7, 26.2, 22.9, 10.5 ppm.

6-Azido-6-deoxy-3-*O*-*iso*pentyl-1,2-*O*-isopropylidene-α-D-glucofuranose (6j): Reaction of compound **5j** (1.5 g, 3.3 mmol) with NaN$_3$ (1.67 g, 10.0 mmol) in DMF (15 mL) at 80 ^{0}C afforded compound **6j** as viscous liquid (0.98 g, 92 % yield); IR (KBr) cm^{-1}: 3472, 2958, 2872, 2104, 1711, 1633, 1466, 1081;^{1}H NMR (300 MHz, CDCl$_3$): δ 5.90 (d, J = 3.6 Hz, 1H), 4.56 (d, J = 3.6 Hz, 1H), 4.10-3.98 (m, 3H), 3.72-3.43 (m, 4H), 2.62 (s, 1H), 1.72-1. 61 (m, 2H), 1.49, 1.32 (each s, 6H), 0.92-0.90 (m, 7H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 111.8, 105.1, 82.9, 81.9, 79.8, 68.9, 68.8, 54.6, 38.4, 26.8, 26.2, 25.0, 22.5, 22.4 ppm.

4. General procedure for the synthesis of glycosyl epoxides (5k-m): A solution of orthogonally protected sugar **4k-m** having one free hydroxyl group (1.0 mmol) in anhydrous

DMF (15 mL) was cooled to 0 ºC and sodium hydride (2.0 equiv.) was added portionwise. The reaction mixture was stirred at 0 ºC under argon atmosphere for 20 minutes. Epichlorohydrin (1.2 mmol) was added at 0 ºC and allowed to stir for 12 hour at room temperature. Upon completion of the reaction (monitor by TLC), excess of sodium hydride was quenched by adding water under inert atmosphere, the solvent was removed under reduced pressure, extracted with ethyl acetate. The organic layer was washed with brine solution, separated, dried over anhydrous Na_2SO_4, filtered, concentrated under vacuum, which on flash chromatography (ethyl acetate: hexane) afforded desired glycosyl epoxide **5k-m**.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-(oxirane-2-ylmethoxy)-α-D-glucofuranose (5k): Reaction of compound 1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (1.0 g, 3.8 mmol) with epichlorohydrin (0.41 ml, 5.0 mmol) in presence of NaH (0.26, 11.4 mmol) in DMF (10 mL) 12 h afforded compound **5k** as colourless liquid (1.02 g, 85 % yield);^{1}H NMR (300 MHz, $CDCl_3$): δ5.86 (d,J = 4.5 Hz, 1H), 4.56 (dd, J = 3.6, 13.8Hz, 1H), 4.34-4.27 (m, 1H), 4.11-3.84 (m, 5H), 3.66-3.44 (m, 1H), 3.13 (m, 1H), 2.82-2.77 (m, 1H), 2.64-2.61 (m, 1H), 1.49, 1.42, 1.34, 1.31 (each s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$):δ 111.7, 108.9, 105.1, 82.9, 82.5, 81.0, 72.2, 70.5, 67.3, 50.4, 44.0, 26.8, 26.7, 26.1, 25.2 ppm.

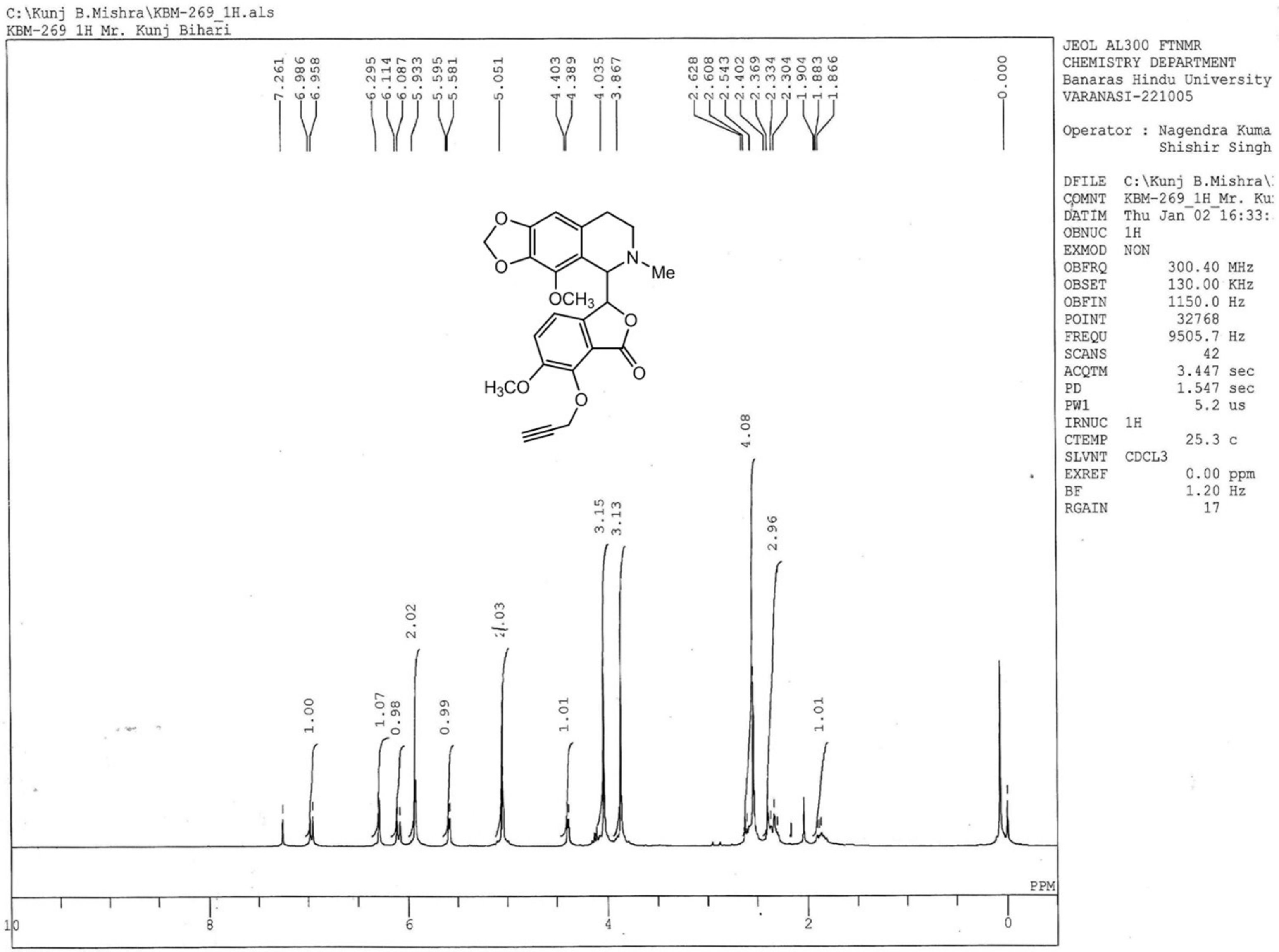
1,2:3,4-Di-*O*-isopropylidene-6-*O*-(oxirane-2-ylmethoxy)-α-D-galactopyranose (5l): Reaction of compound 1,2:3,4-Di-*O*-isopropylidene-α-D-galactopyranose (1.5 g, 5.7 mmol) with epichlorohydrin (0.60 ml, 7.4 mmol) in presence of NaH (0.39 g, 17.1 mmol) in DMF (10 ml) for 12 h afforded compound **5l** as colourless liquid (1.49 g, 82 % yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.53 (d, J = 4.5 Hz, 1H), 4.60 (d, J = 7.5 Hz, 1H), 4.32-4.26 (m, 2H), 4.24-3.98 (m, 1H), 3.97-3.60 (m, 3H), 3.53-3.40 (m, 1H), 3.17 (m, 1H), 2.78 (t, J = 4.2 Hz, 1H), 2.62 (d, J =

5.7 Hz, 1H), 1.58-1.33 (merged four s, 12H); ^{13}C NMR (75 MHz, CDCl$_3$): δ 109.2, 108.5, 96.4, 71.0, 70.6, 70.4, 50.4, 44.3, 26.0, 26.7, 24.8, 24.4 ppm.

5. General procedure for the synthesis of glycosyl azido alcohols from epoxides (6k-m): A solution of the compounds **5k-m** in EtOH/H$_2$O (1:1) treated with NaN$_3$ and NH$_4$Cl at 65 ºC for 8 h. Upon completion of the reaction, the solvent was removed under reduced pressure, extracted with ethyl acetate and water. The organic layer was dried over anhydrous Na$_2$SO$_4$, filtered, concentrated under vacuum, followed by flash chromatography (ethyl acetate: hexane) afforded the desired glycosyl azido alcohol **6k-m** in good yields.

3-*O*-(3-Azido-2-hydroxypropoxy)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (6k): Reaction of compound **5k** (1.0 g, 3.1 mmol) with NaN$_3$ (0.31 g, 4.7 mmol) in presence of NH$_4$Cl (0.16 g, 3.1 mmol) in EtOH/H$_2$O (1:1, 10 mL) at 65 ºC for 12 h afforded the title compound **6k** as viscous liquid (0.96 g, 86 % yield); IR (KBr) cm^{-1}: 3456, 2988, 2936, 2103, 1667, 1456, 1075; ^{1}H NMR (300 MHz, CDCl$_3$): δ 5.90 (d, J = 3.3 Hz, 1H), 4.56 (s, 1H), 4.32-4.29 (m, 1H), 4.15-3.75 (m, 6H), 3.59-3.32 (m, 3H), 1.49, 1.44, 1.37, 1.32 (each s, 12H); ^{13}C NMR (75 MHz, CDCl$_3$): δ111.9, 109.4, 105.4, 84.3, 82.8, 82.3, 81.1, 72.7, 71.3, 70.1, 68.7, 67.7, 53.0, 52.6, 26.7, 26.0, 25.0 ppm.

6-*O*-(3-Azido-2-hydroxypropoxy)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (6l): Reaction of compound **5l** (1.5 g, 4.7 mmol) with NaN$_3$ (0.46 g, 7.1 mmol) in presence of NH$_4$Cl (0.25 g, 4.7 mmol) in EtOH/H$_2$O (1:1, 10 mL) at 65 ºC for 12 h afforded compound **6l** as viscous liquid (1.41 g, 84 % yield); IR (KBr) cm^{-1}: 3434, 2989, 2935, 2103, 1643, 1455, 1383, 1257, 1070; ^{1}H NMR (300 MHz, CDCl$_3$): δ 5.53 (d, J = 3.9 Hz, 1H), 4.62 (d, J = 8.1 Hz, 1H), 4.33-4.22 (m, 2H), 3.98-3.88 (m, 2H), 3.70-3.48 (m, 4H), 3.35-3.34 (m, 2H), 3.07 (s, 1H), 1.54, 1.45, 1.38, 1.33 (each s, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 109.4, 108.7, 96.2, 72.9, 72.6, 71.1, 70.6, 70.5, 70.4, 69.9, 69.3, 66.5, 53.2, 25.9, 24.8, 24.4 ppm.



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CHEMISTRY DEPARTMENT
Banaras Hindu University
VARANASI-221005

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Figure 1: ^{1}H NMR of compound 3

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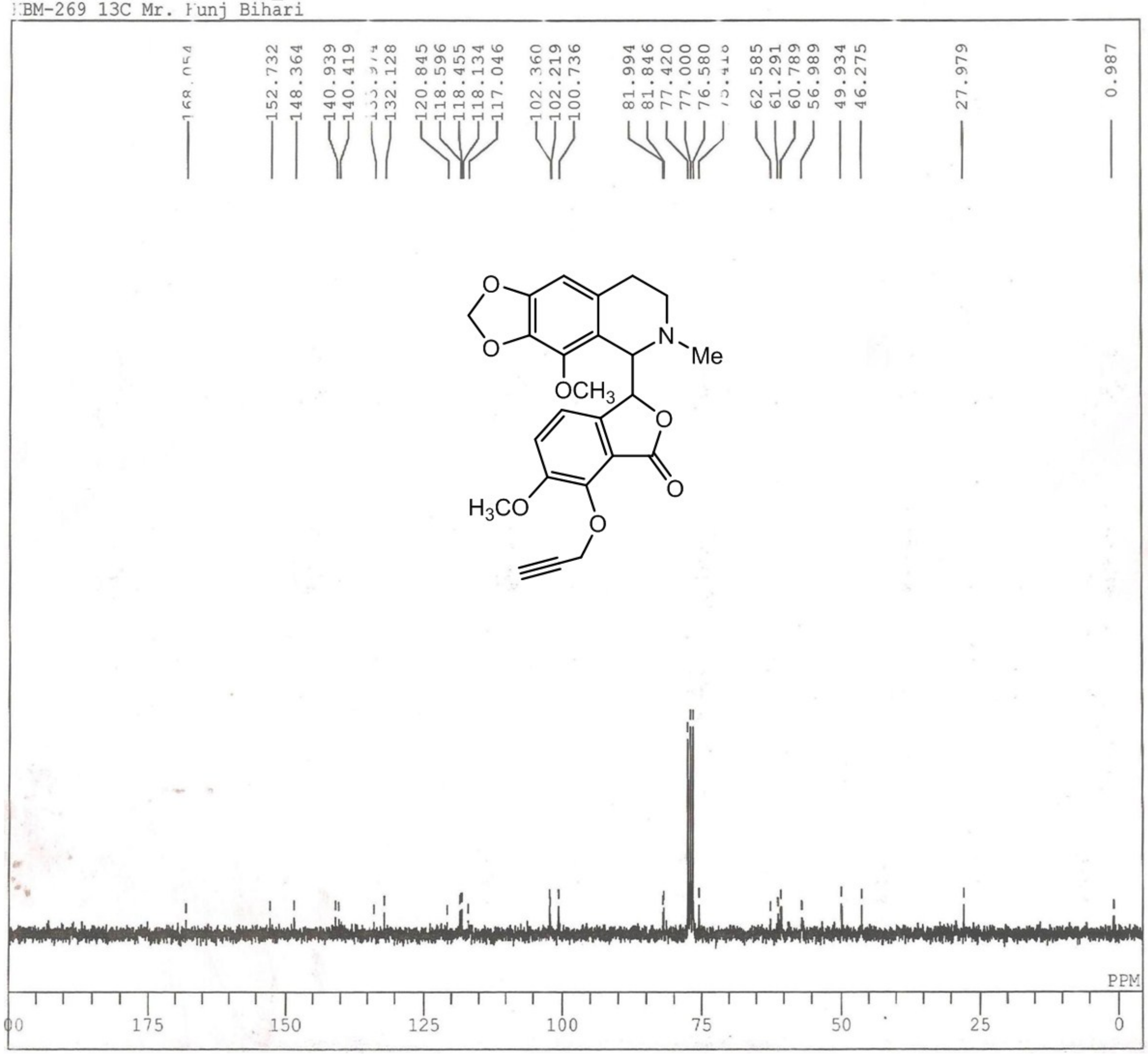

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Banaras Hindu University,
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Figure 2: ^{13}C NMR of compound 3

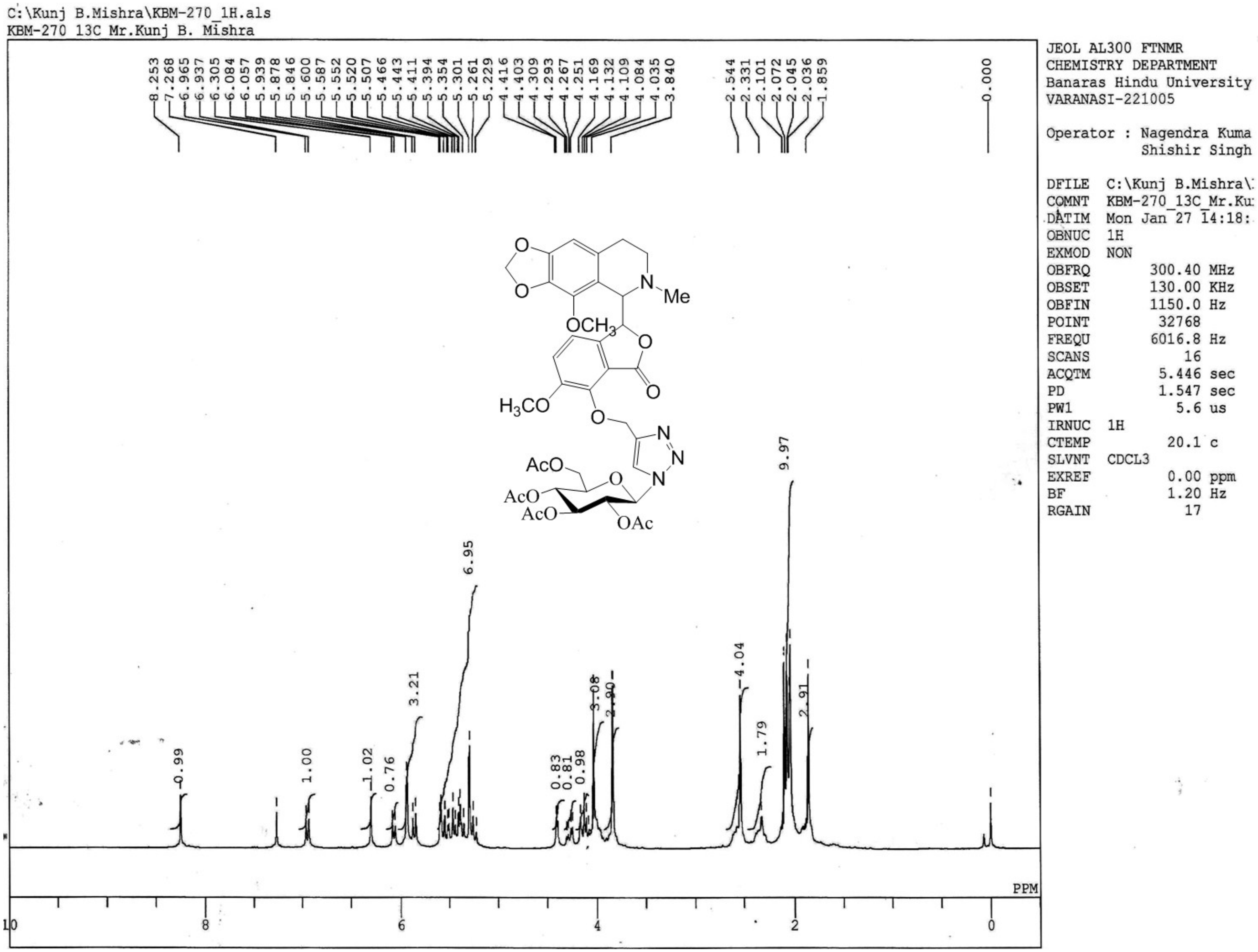

Figure 3: ^{1}H NMR of compound 8a

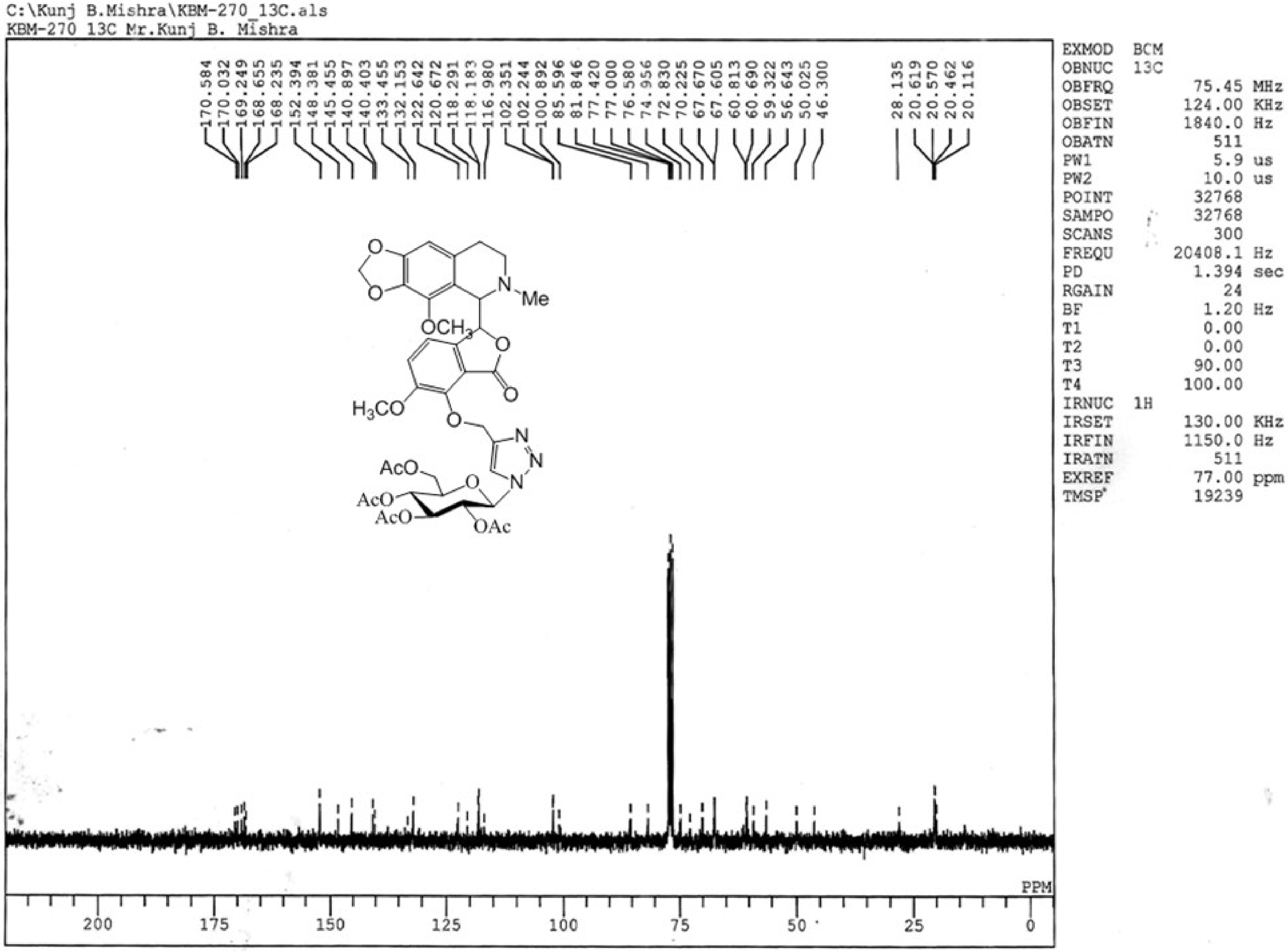

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Figure 4: ^{13}C NMR of compound 8a

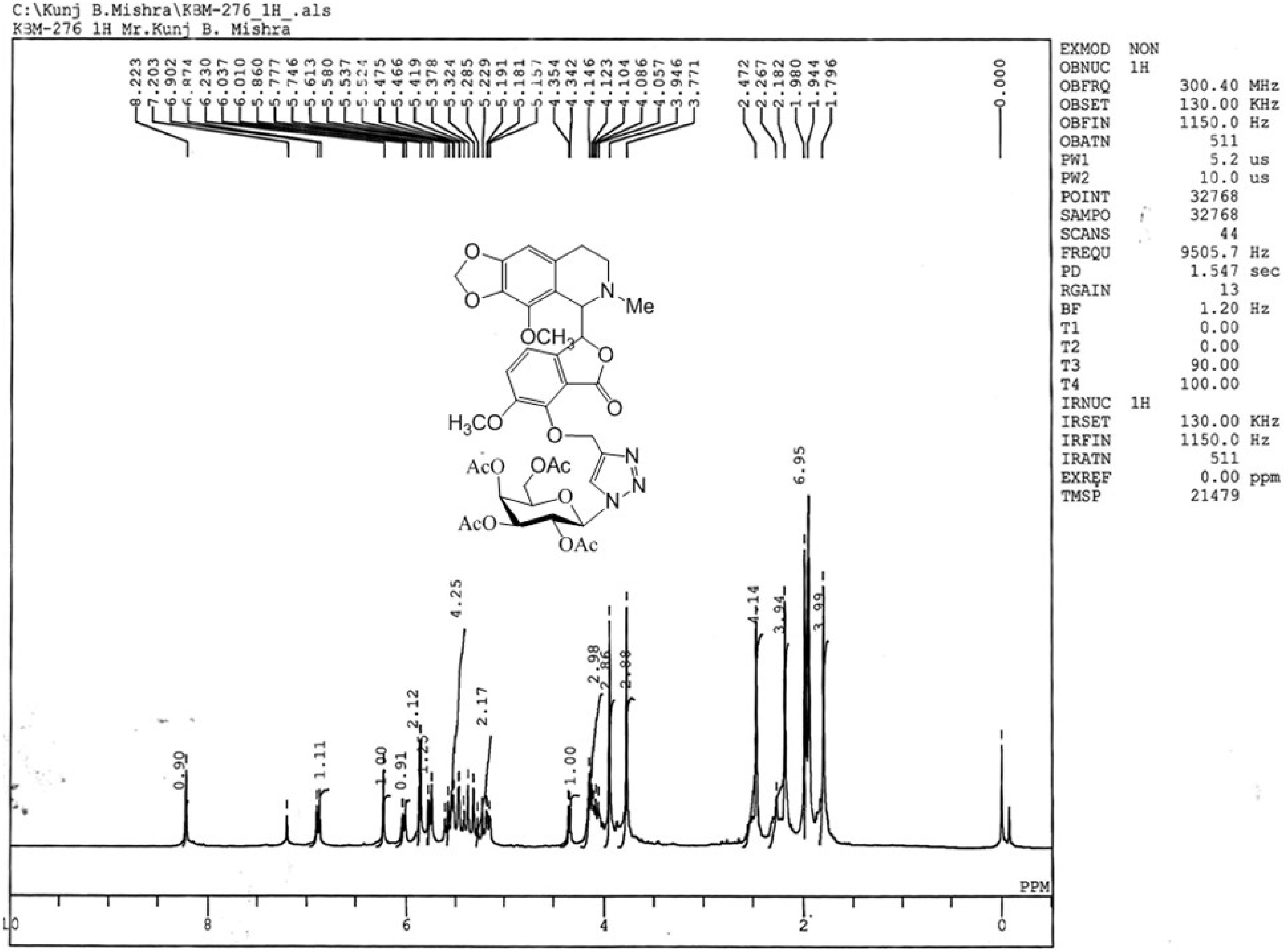

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Figure 5:^{1}HNMR of compound 8b

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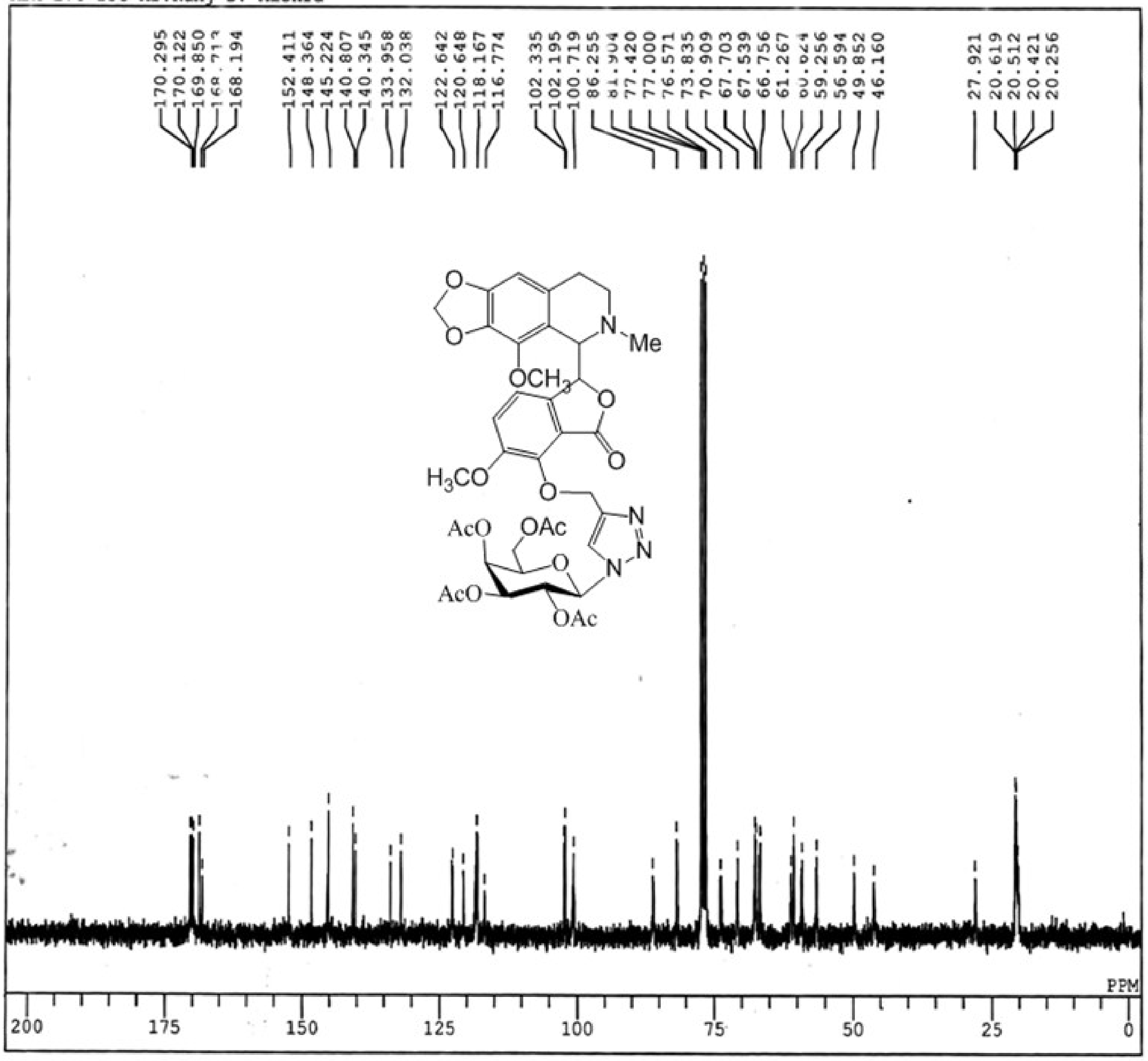

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CHEMISTRY DEPARTMENT
Banaras Hindu University,
VARANASI-221005

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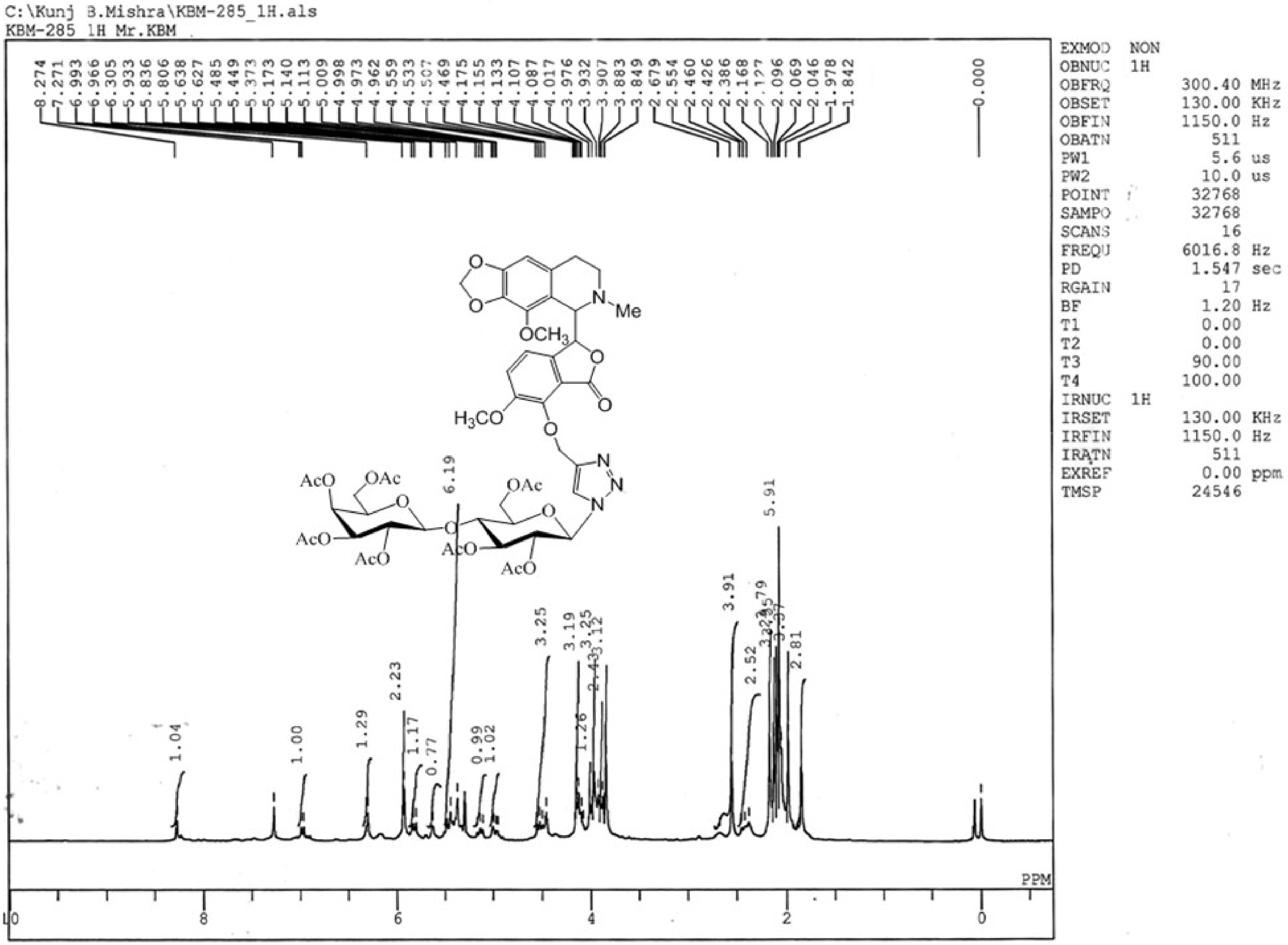
Figure 6:^{13}C NMR of compound 8b



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T4           100.00
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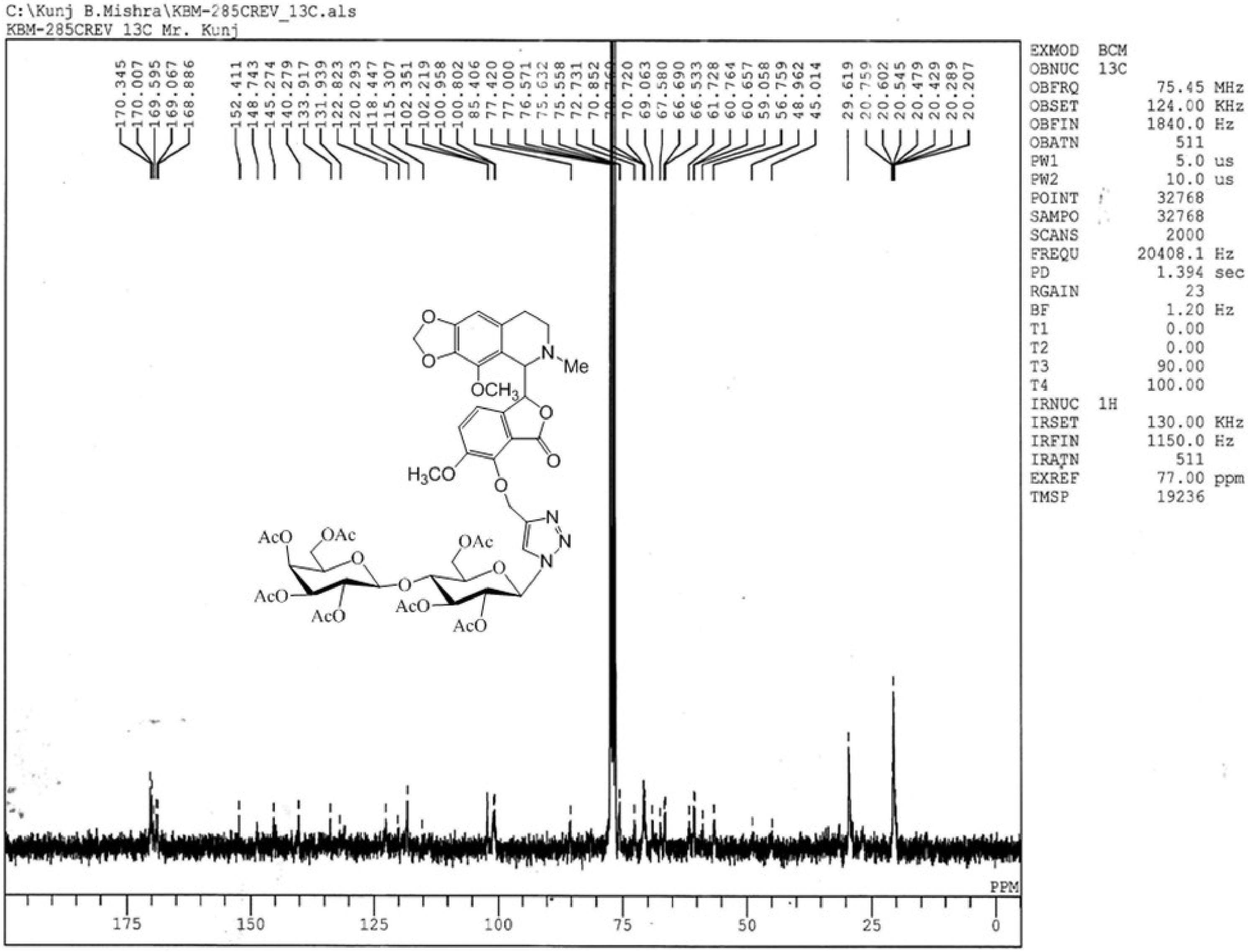
Figure 7:^{1}HNMR of compound 8c



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KBM-285CREV 13C Mr. Kunj
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RGAIN           23
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IRNUC  1H
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Figure 8:^{13}C NMR of compound 8c

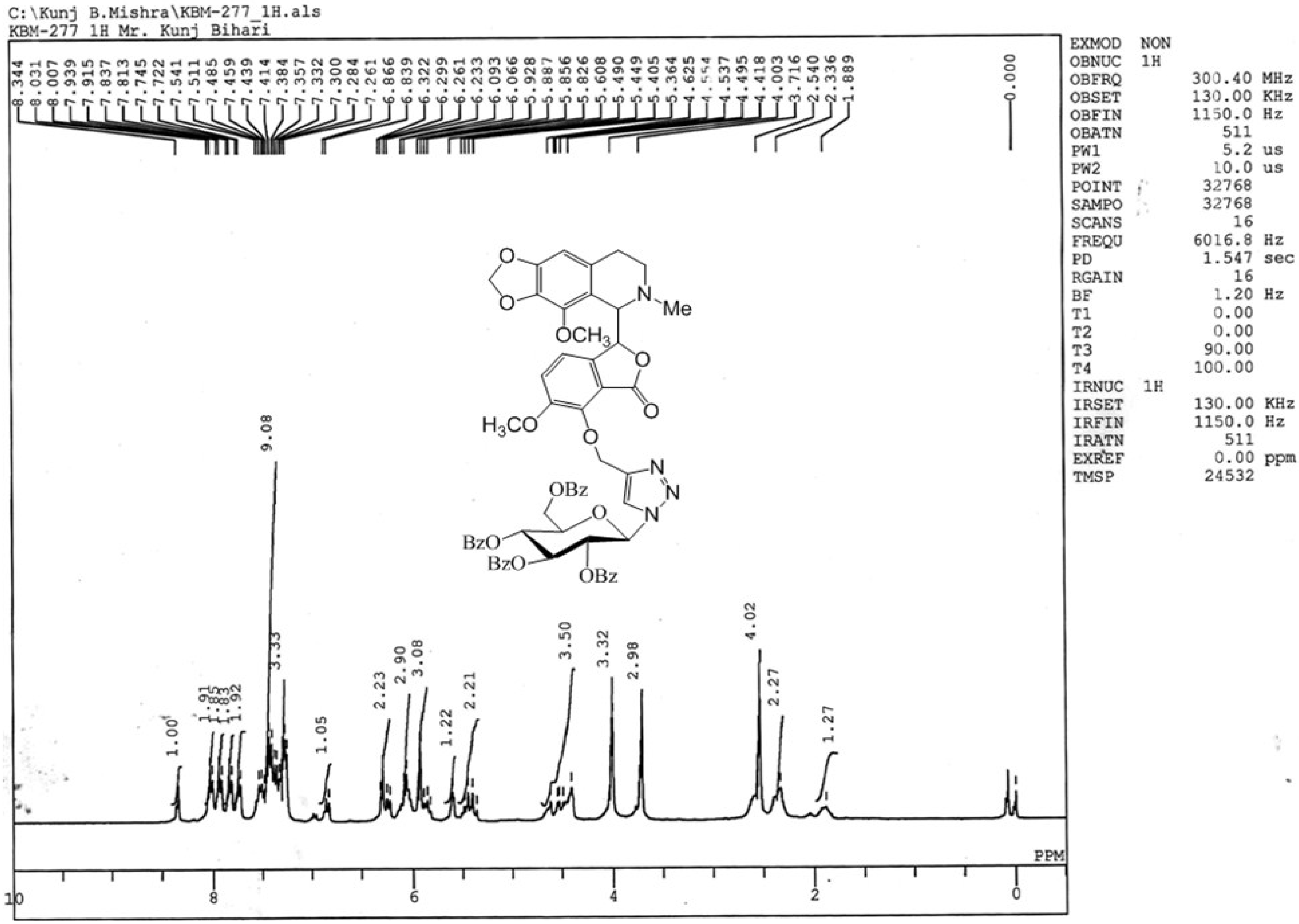

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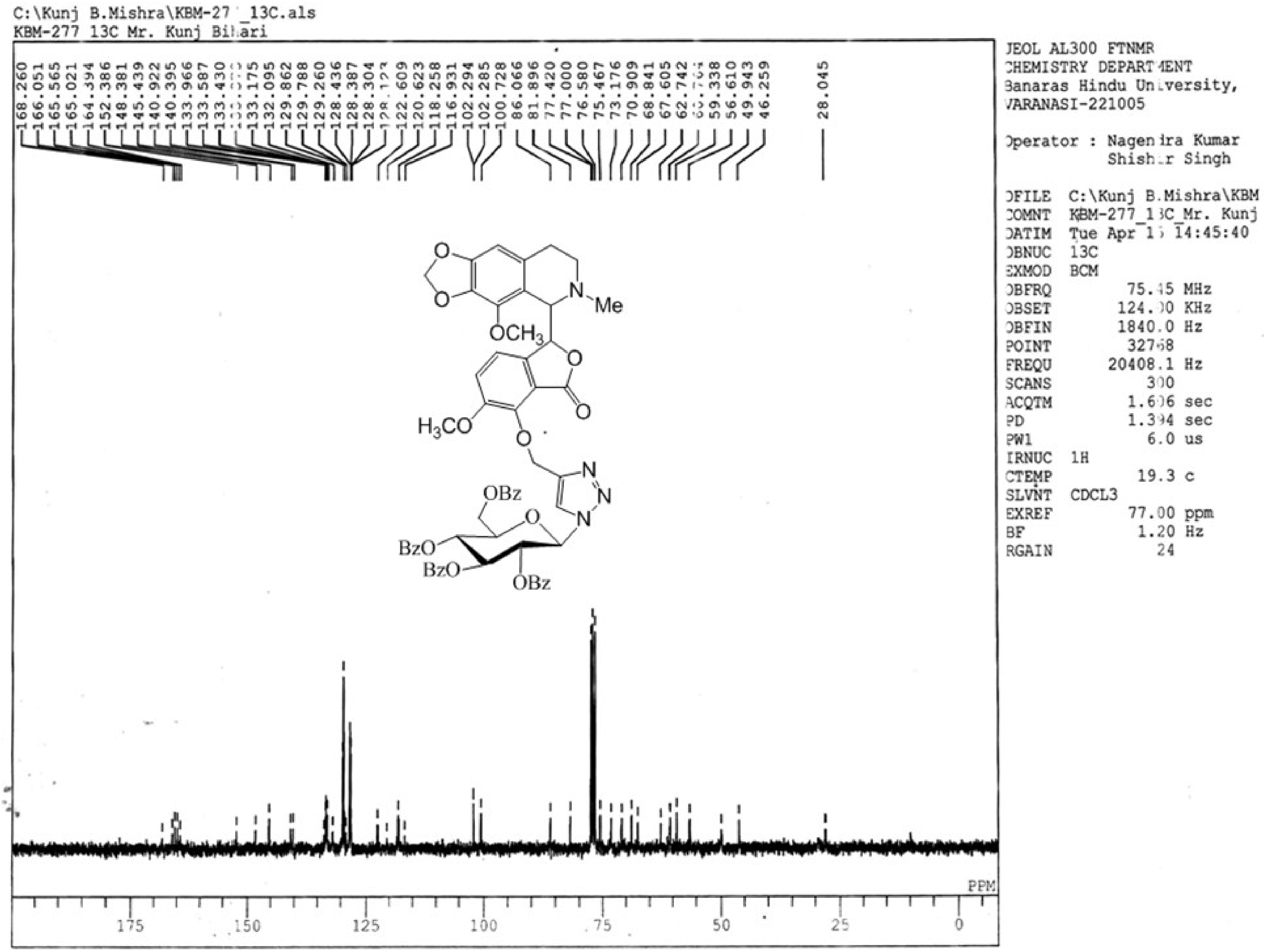
Figure 9:^{1}HNMR of compound 8d



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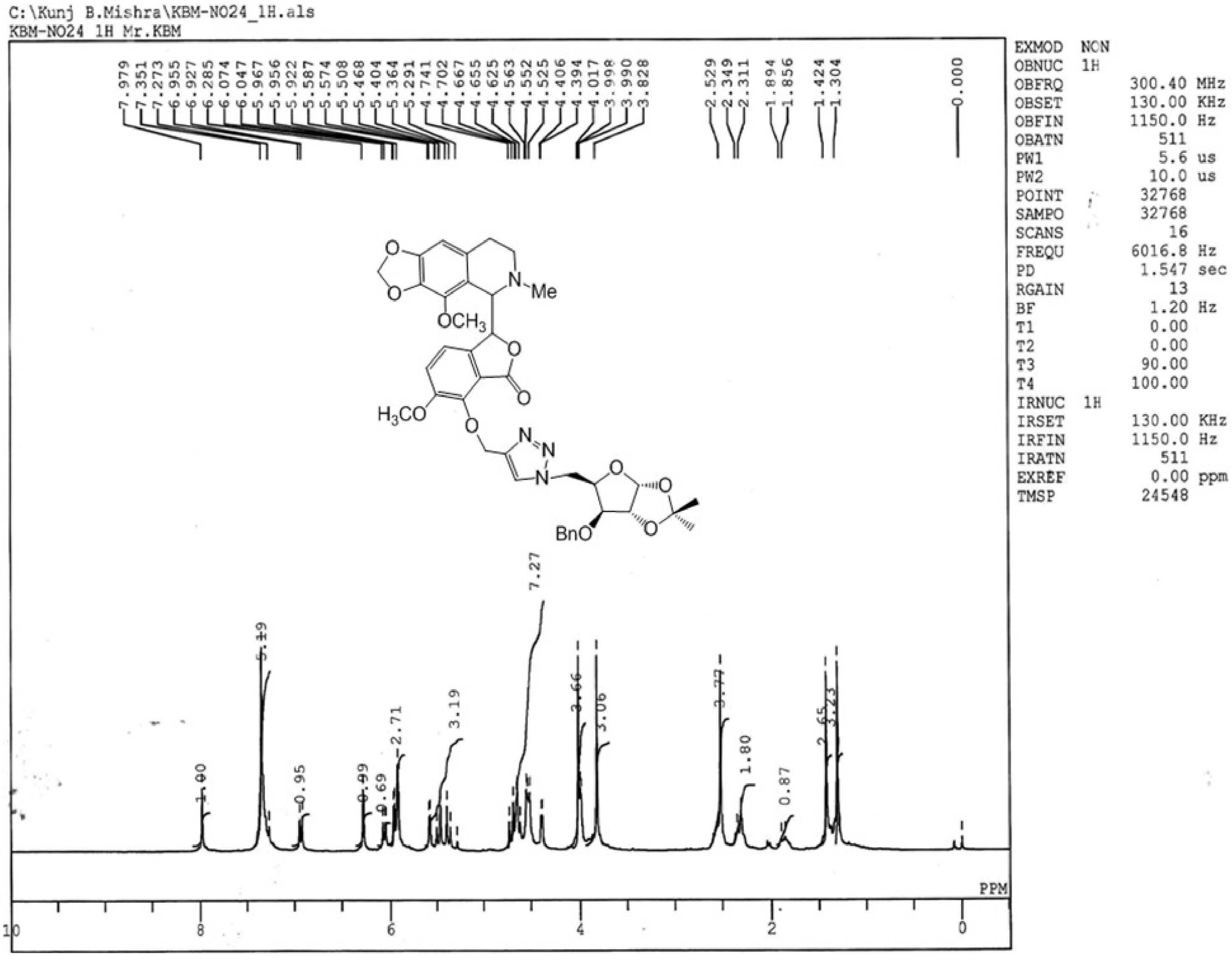
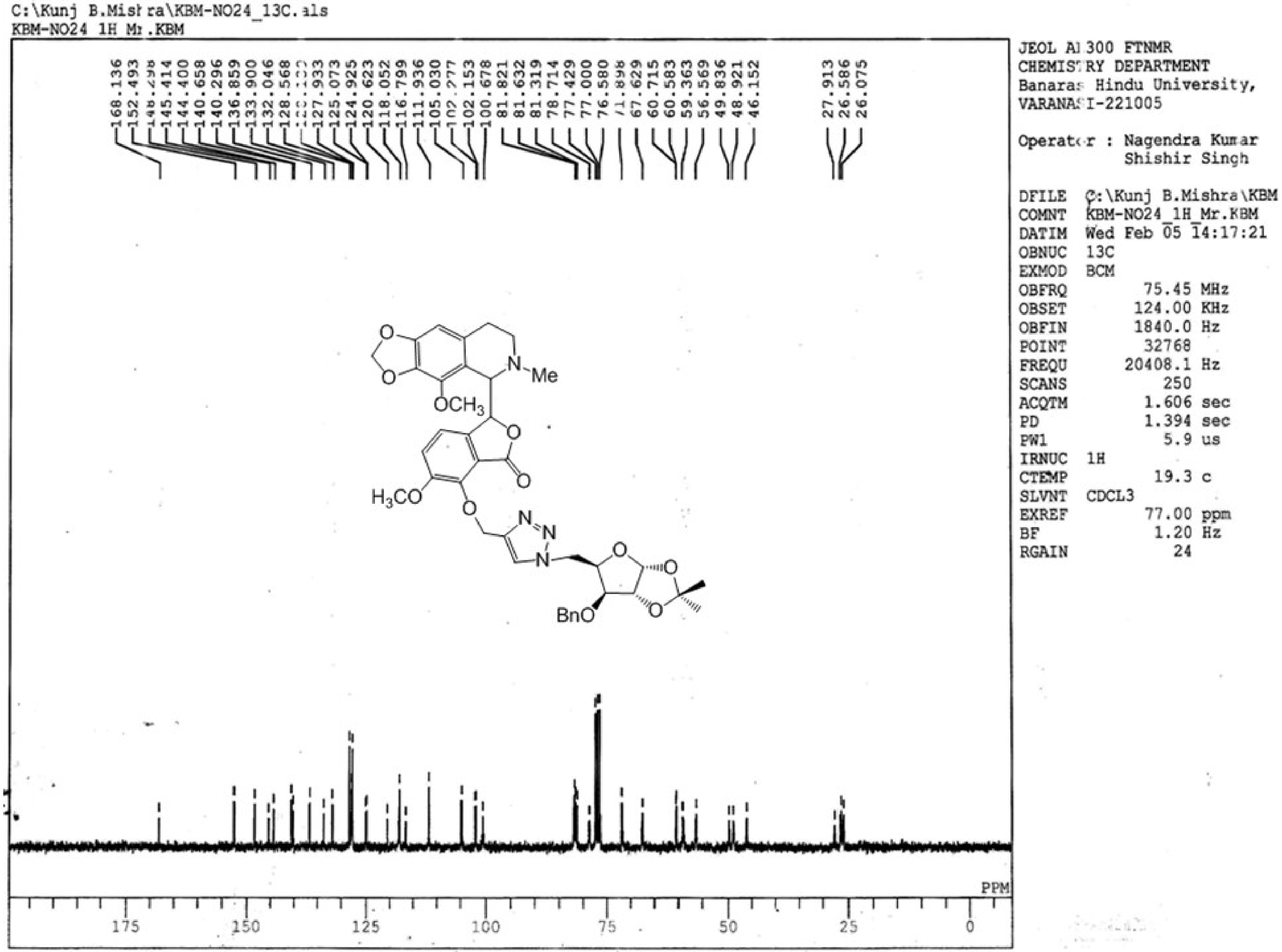


Figure 11:^{1}HNMR of compound 8e



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

Operator : Nagendra Kumar
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Figure 12:^{13}C NMR of compound 8e

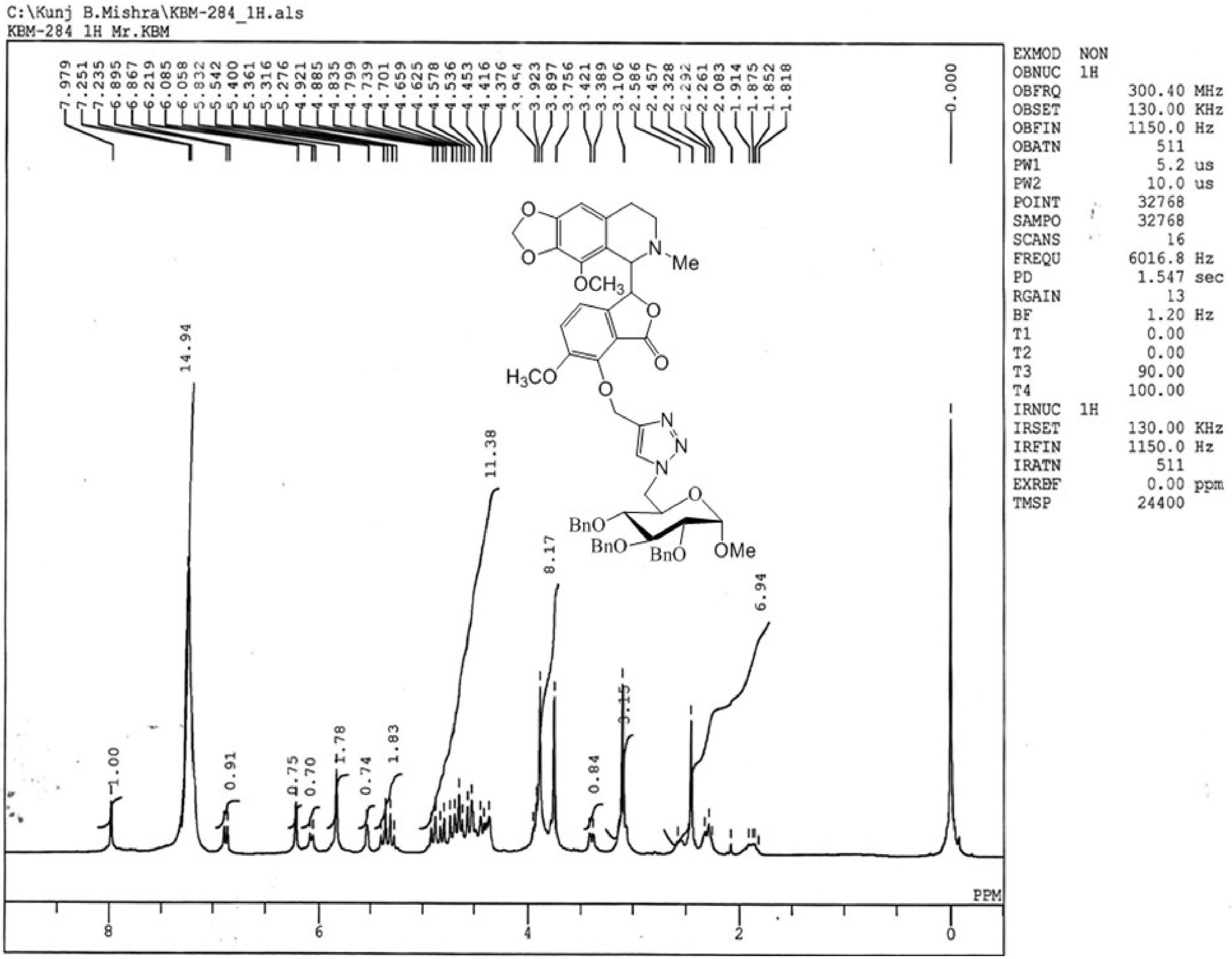
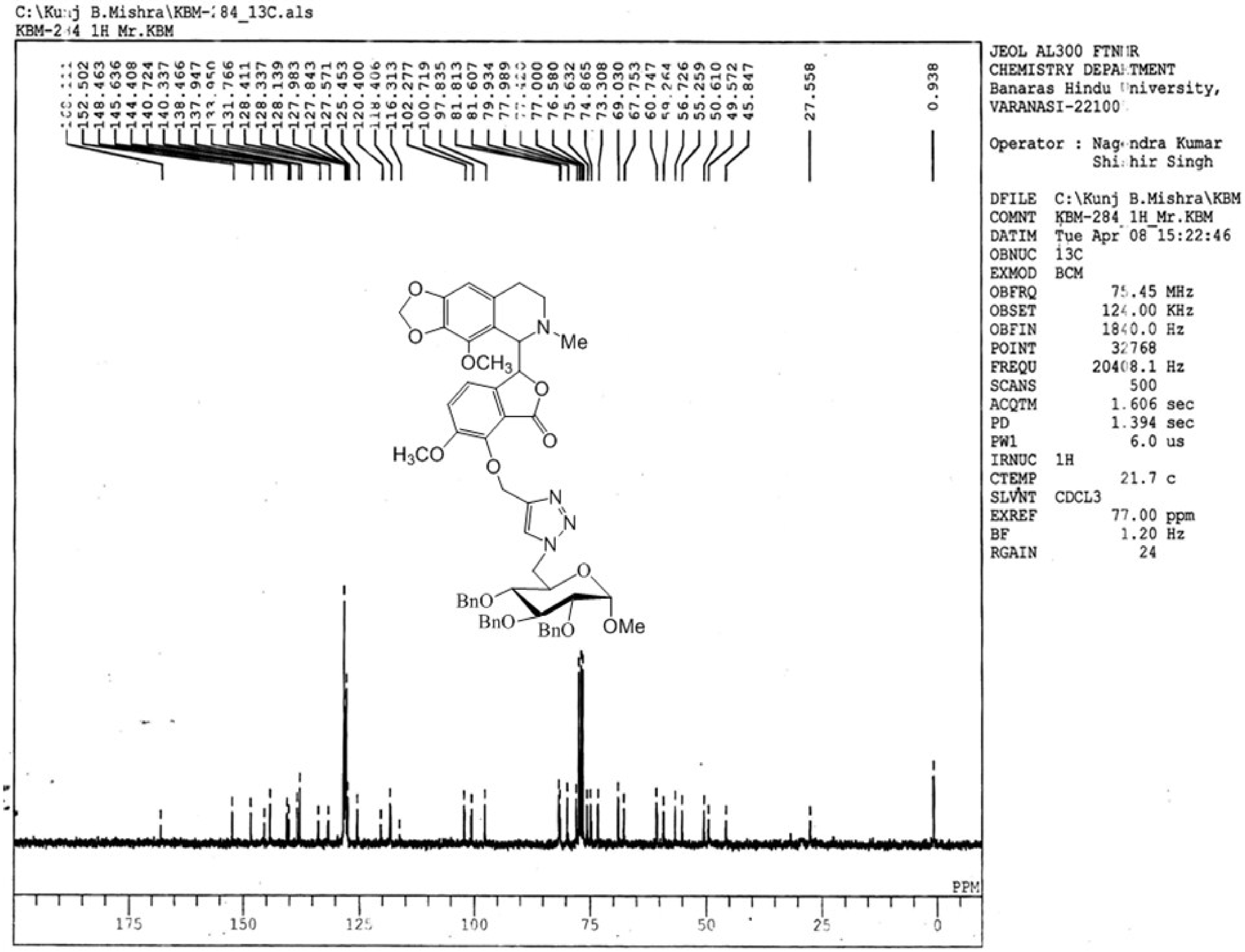


Figure 13:^{1}HNMR of compound 8f



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SCANS          500
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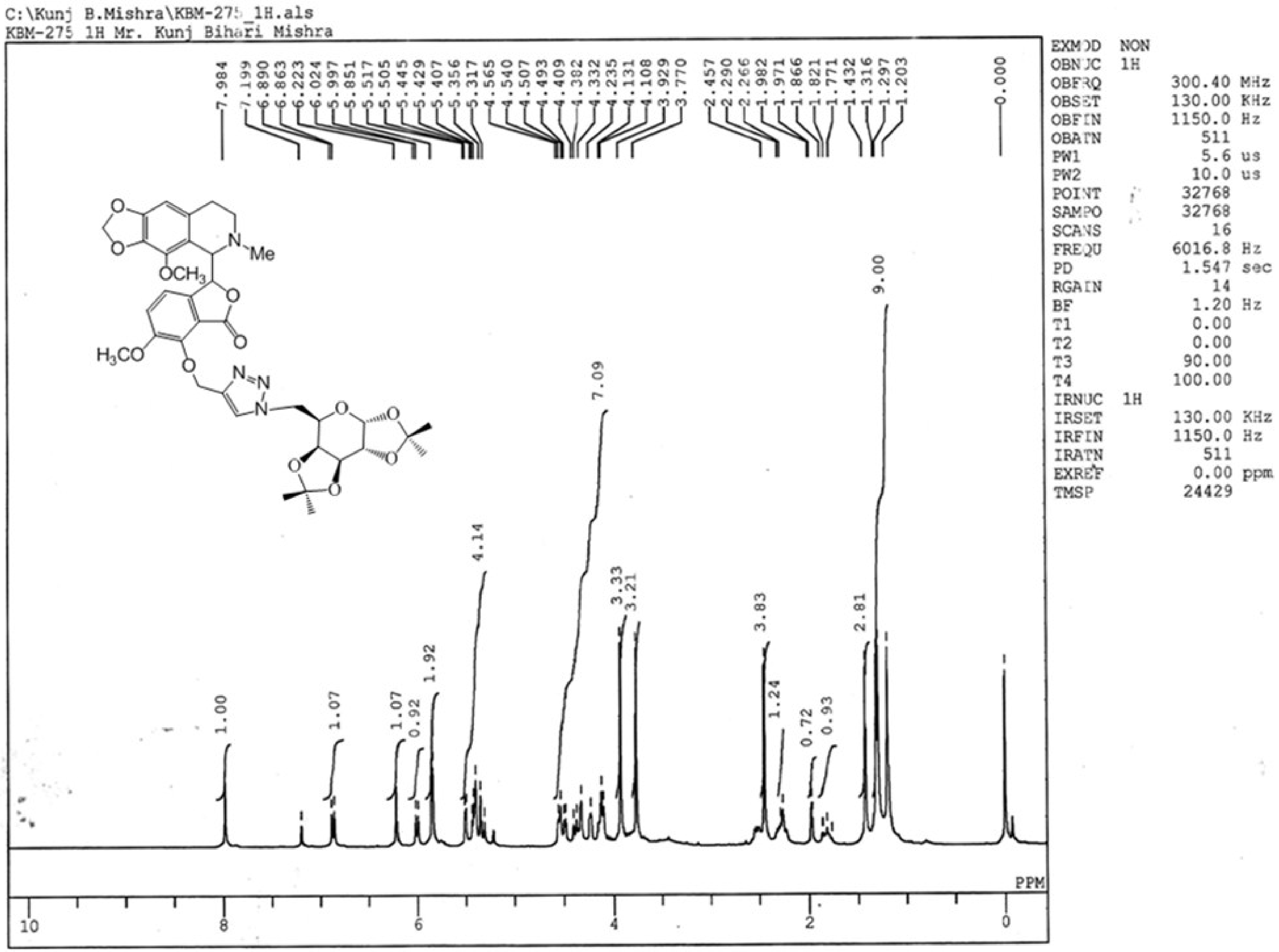
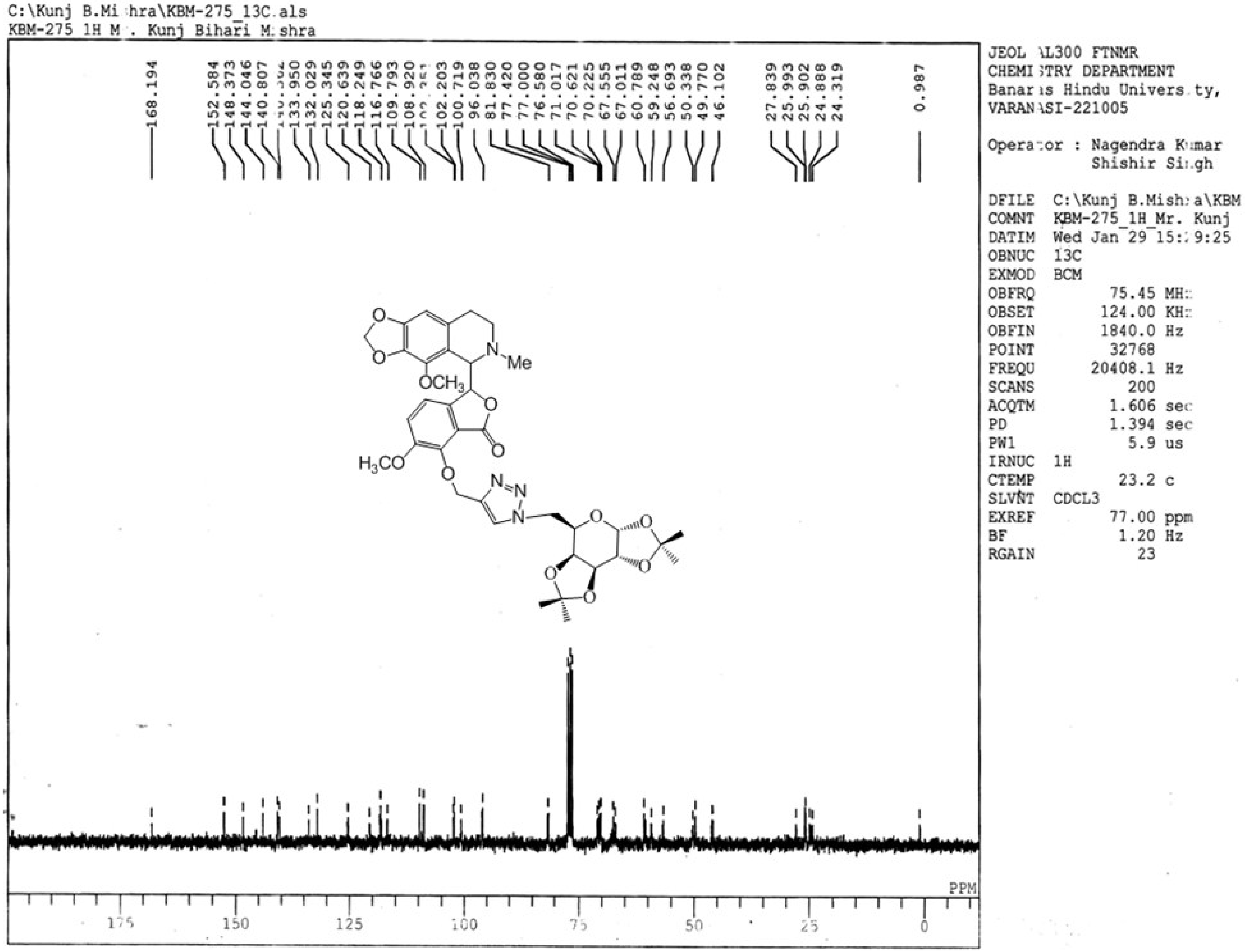
PD           1.394 sec
PW1            6.0 us
IRNUC  1H
CTEMP         21.7 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            1.20 Hz
RGAIN           24
```

Figure 14: ^{13}C NMR of compound 8f



```
EXMOD   NON
OBNUC   1H
OBFRQ         300.40 MHz
OBSET         130.00 KHz
OBFIN         1150.0 Hz
OBATN            511
PW1              5.6 us
PW2             10.0 us
POINT          32768
SAMPO          32768
SCANS             16
FREQU         6016.8 Hz
PD             1.547 sec
RGAIN             14
BF              1.20 Hz
T1              0.00
T2              0.00
T3             90.00
T4            100.00
IRNUC   1H
IRSET         130.00 KHz
IRFIN         1150.0 Hz
IRATN            511
EXREF           0.00 ppm
TMSP           24429
```

Figure 15:^{1}HNMR of compound 8g



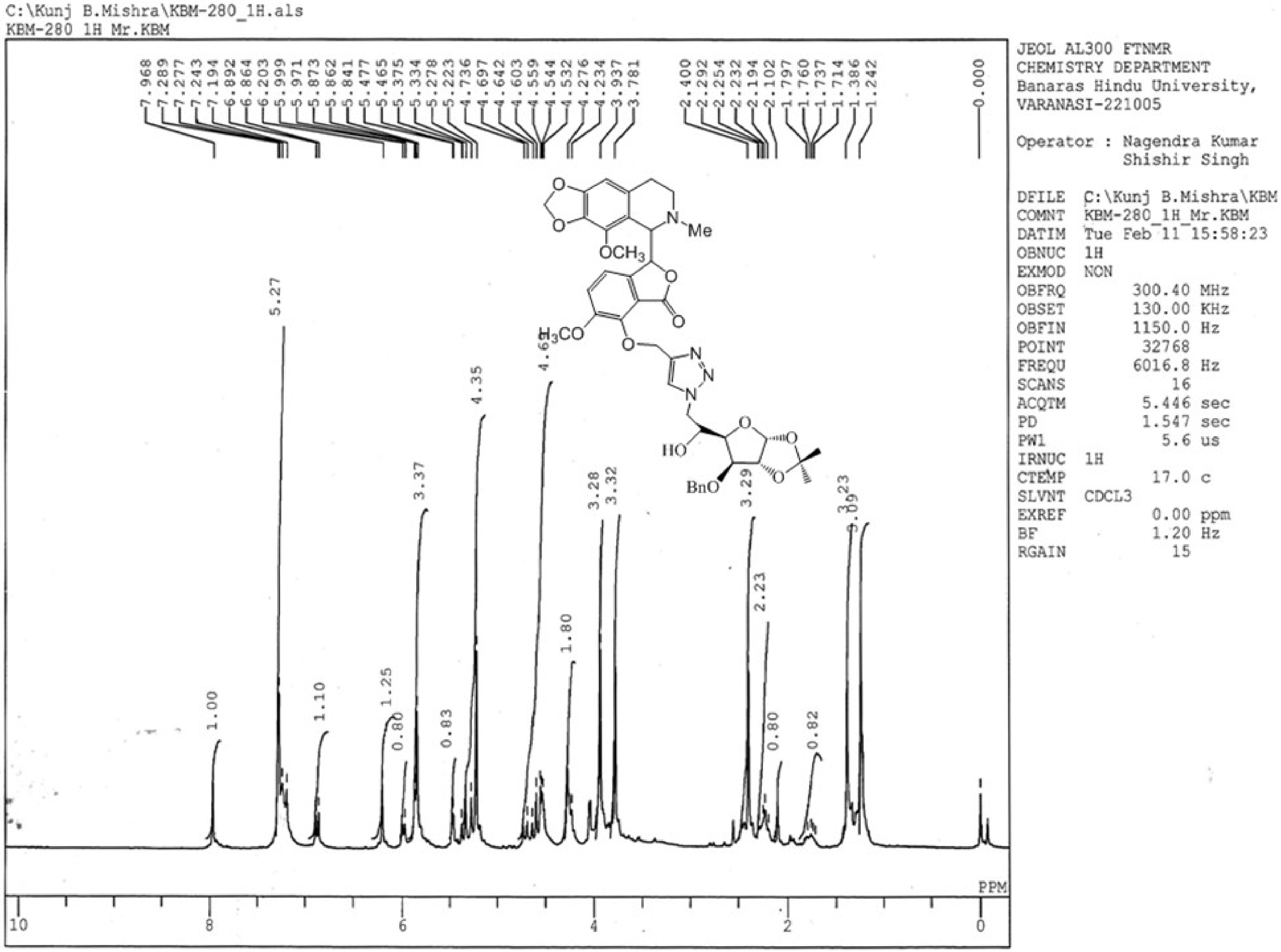
C:\Kunj B.Mi hra\KBM-275_13C.als
KBM-275 1H M . Kunj Bihari M shra

JEOL L300 FTNMR
CHEMI TRY DEPARTMENT
Banar s Hindu Univers ty,
VARAN SI-221005

Opera or : Nagendra K mar
Shishir Si gh

```
DFILE   C:\Kunj B.Mish a\KBM
COMNT   KBM-275_1H_Mr. Kunj
DATIM   Wed Jan 29 15: 9:25
OBNUC   13C
EXMOD   BCM
OBFRQ          75.45 MH
OBSET         124.00 KH
OBFIN         1840.0 Hz
POINT          32768
FREQU        20408.1 Hz
SCANS            200
ACQTM          1.606 se
PD             1.394 sec
PW1              5.9 us
IRNUC   1H
CTEMP           23.2 c
SLVNT   CDCL3
EXREF          77.00 ppm
BF              1.20 Hz
RGAIN             23
```

Figure 16:^{13}CNMR of compound 8g

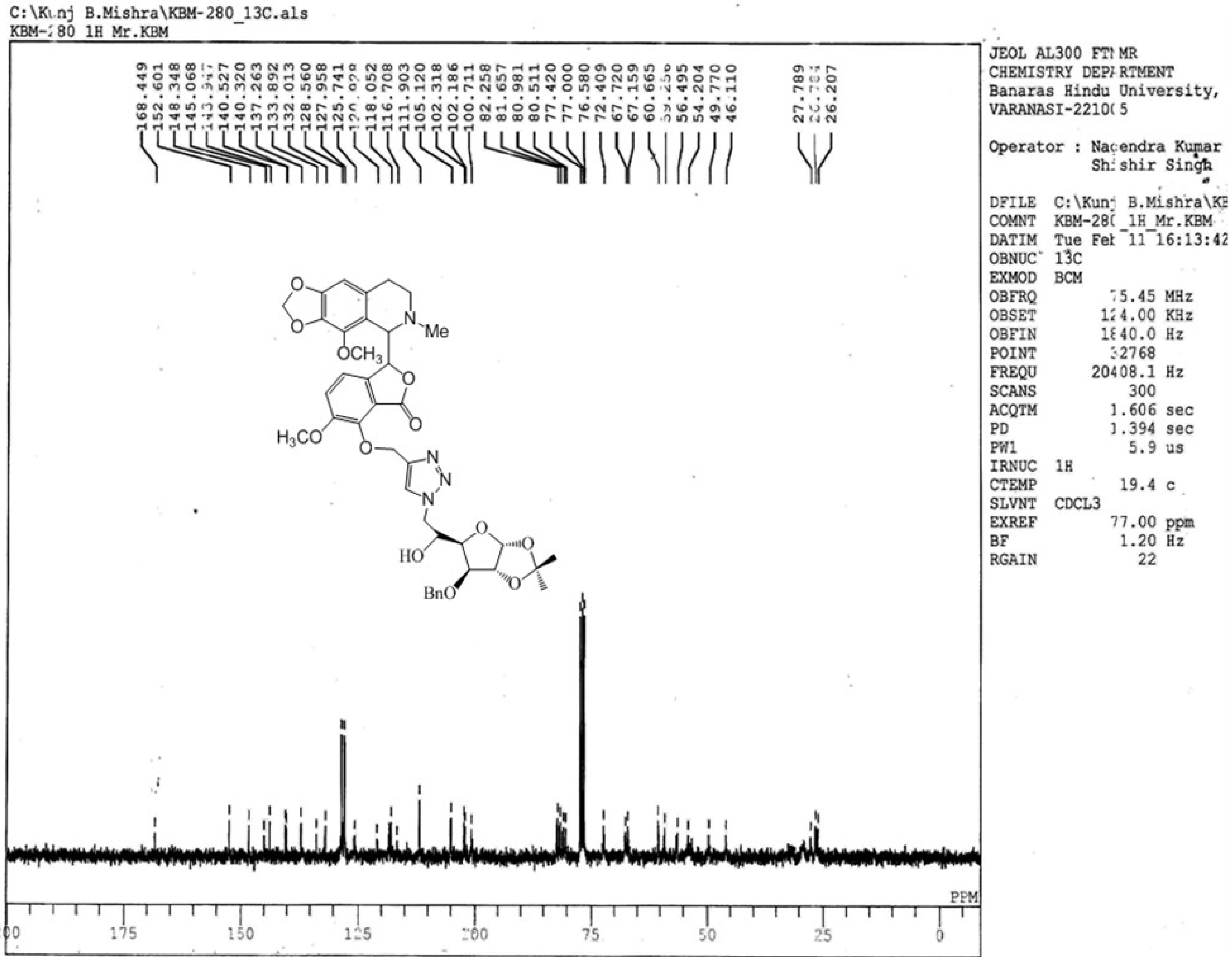


JEOL AL300 FTNMR
CHEMISTRY DEPARTMENT
Banaras Hindu University,
VARANASI-221005

Operator : Nagendra Kumar
Shishir Singh

DFILE C:\Kunj B.Mishra\KBM
COMNT KBM-280_1H_Mr.KBM
DATIM Tue Feb 11 15:58:23
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6016.8 Hz
SCANS 16
ACQTM 5.446 sec
PD 1.547 sec
PW1 5.6 us
IRNUC 1H
CTEMP 17.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 15

Figure 17:^{1}HNMR of compound 8h



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

Operator : Nagendra Kumar
           Shishir Singh

DFILE  C:\Kunj B.Mishra\KB
COMNT  KBM-280_1H_Mr.KBM
DATIM  Tue Feb 11 16:13:42
OBNUC  13C
EXMOD  BCM
OBFRQ         75.45 MHz
OBSET        124.00 KHz
OBFIN        1840.0 Hz
POINT         32768
FREQU       20408.1 Hz
SCANS           300
ACQTM         1.606 sec
PD            1.394 sec
PW1             5.9 us
IRNUC  1H
CTEMP          19.4 c
SLVNT  CDCL3
EXREF         77.00 ppm
BF             1.20 Hz
RGAIN            22
```

Figure 18: ^{13}C NMR of compound 8h

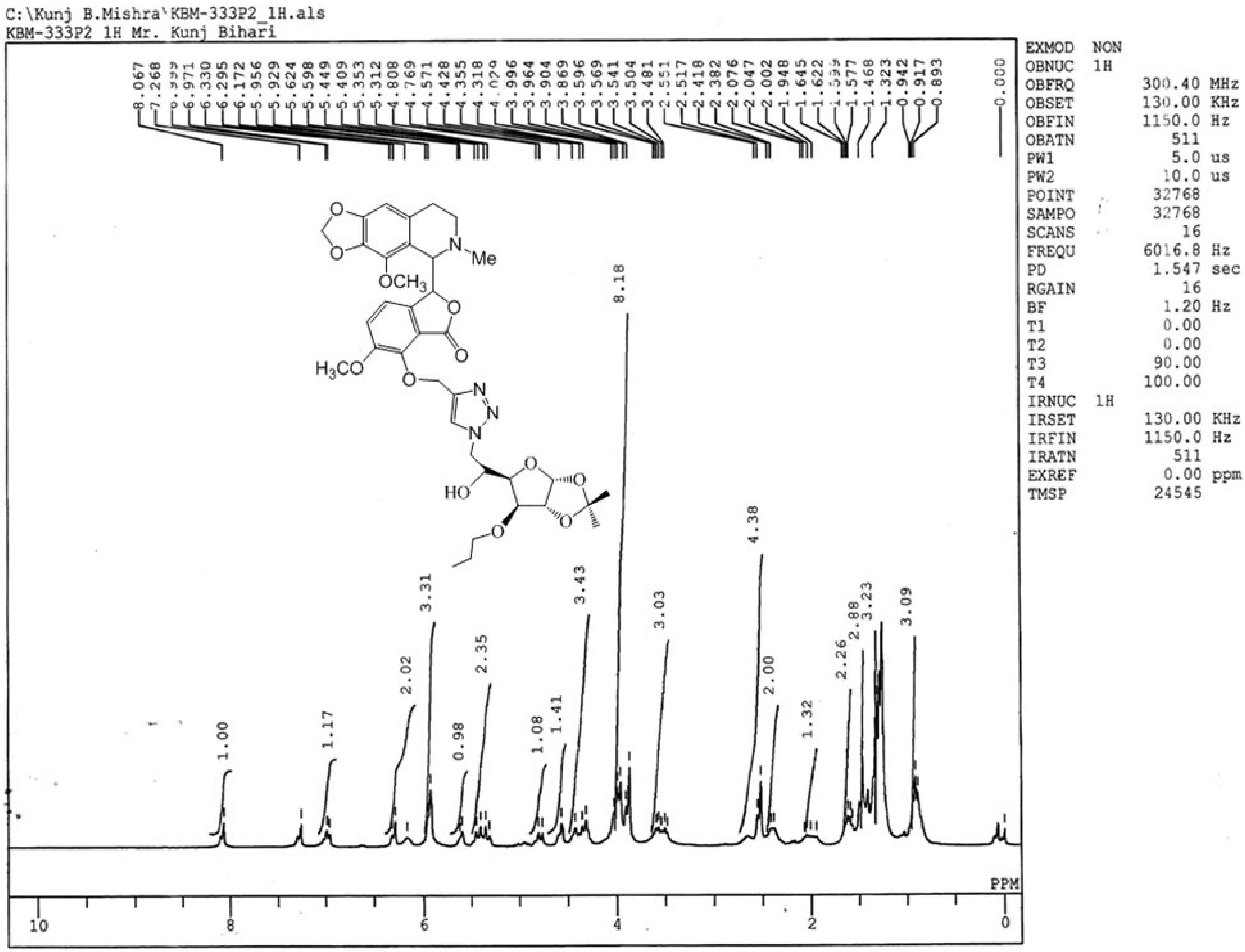
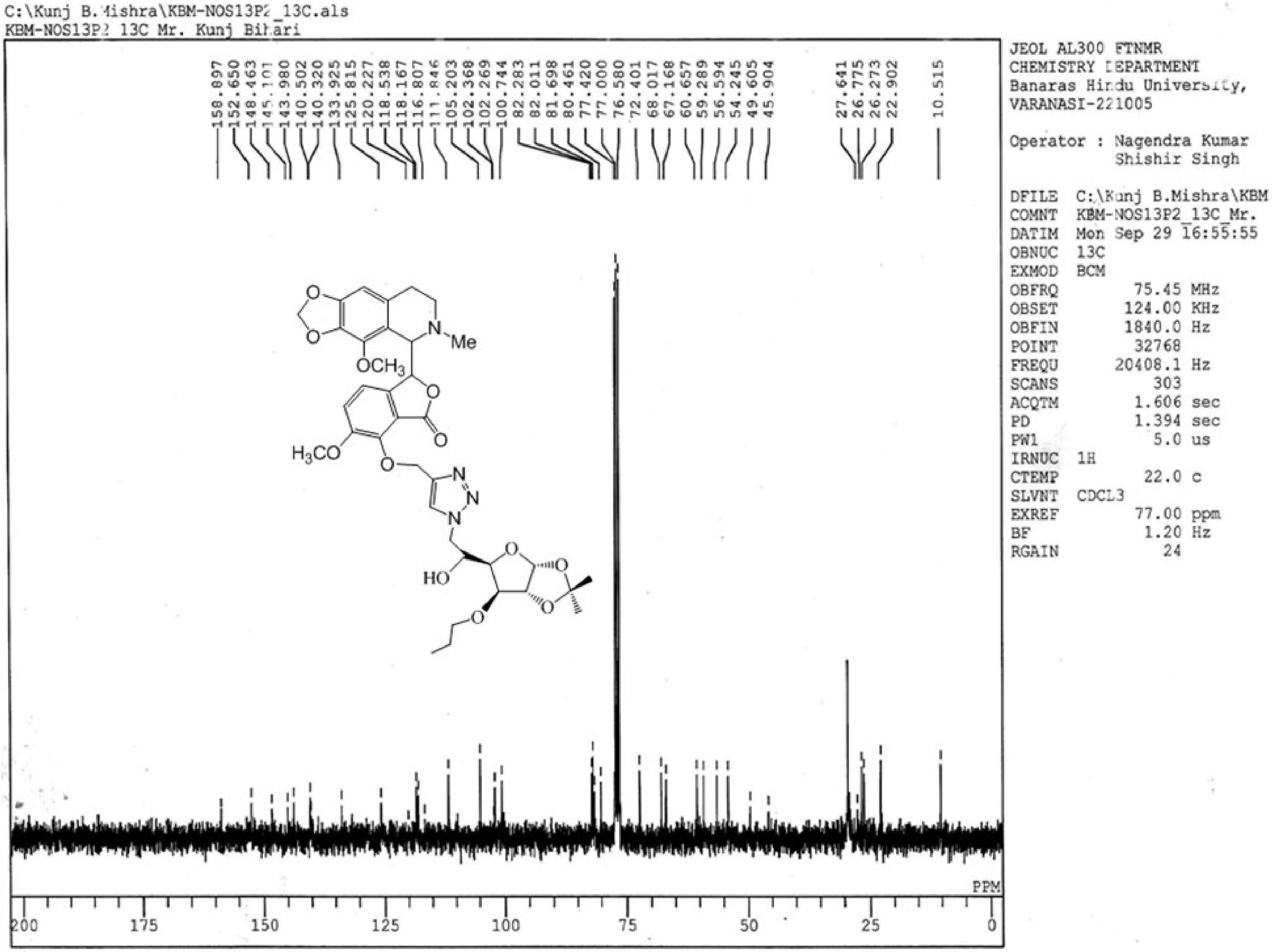


Figure 19:^{1}HNMR of compound 8i



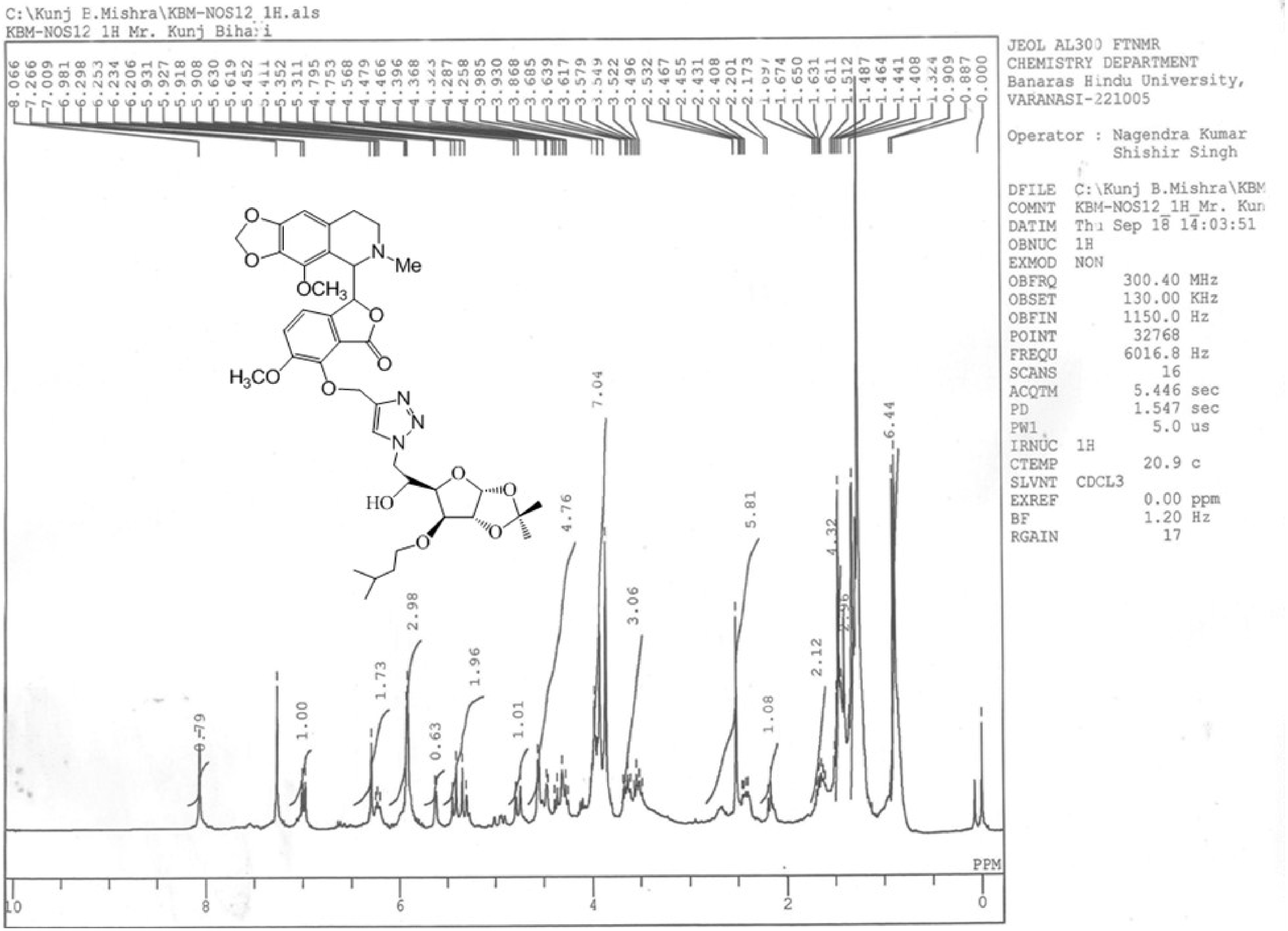
C:\Kunj B.Mishra\KBM-NOS13P2_13C.als
KBM-NOS13P2 13C Mr. Kunj Bihari

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

Operator : Nagendra Kumar
Shishir Singh

DFILE	C:\Kunj B.Mishra\KBM	
COMNT	KBM-NOS13P2_13C_Mr.	
DATIM	Mon Sep 29 16:55:55	
OBNUC	13C	
EXMOD	BCM	
OBFRQ	75.45	MHz
OBSET	124.00	KHz
OBFIN	1840.0	Hz
POINT	32768	
FREQU	20408.1	Hz
SCANS	303	
ACQTM	1.606	sec
PD	1.394	sec
PW1	5.0	us
IRNUC	1H	
CTEMP	22.0	c
SLVNT	CDCL3	
EXREF	77.00	ppm
BF	1.20	Hz
RGAIN	24	

Figure 20:^{13}C NMR of compound 8i



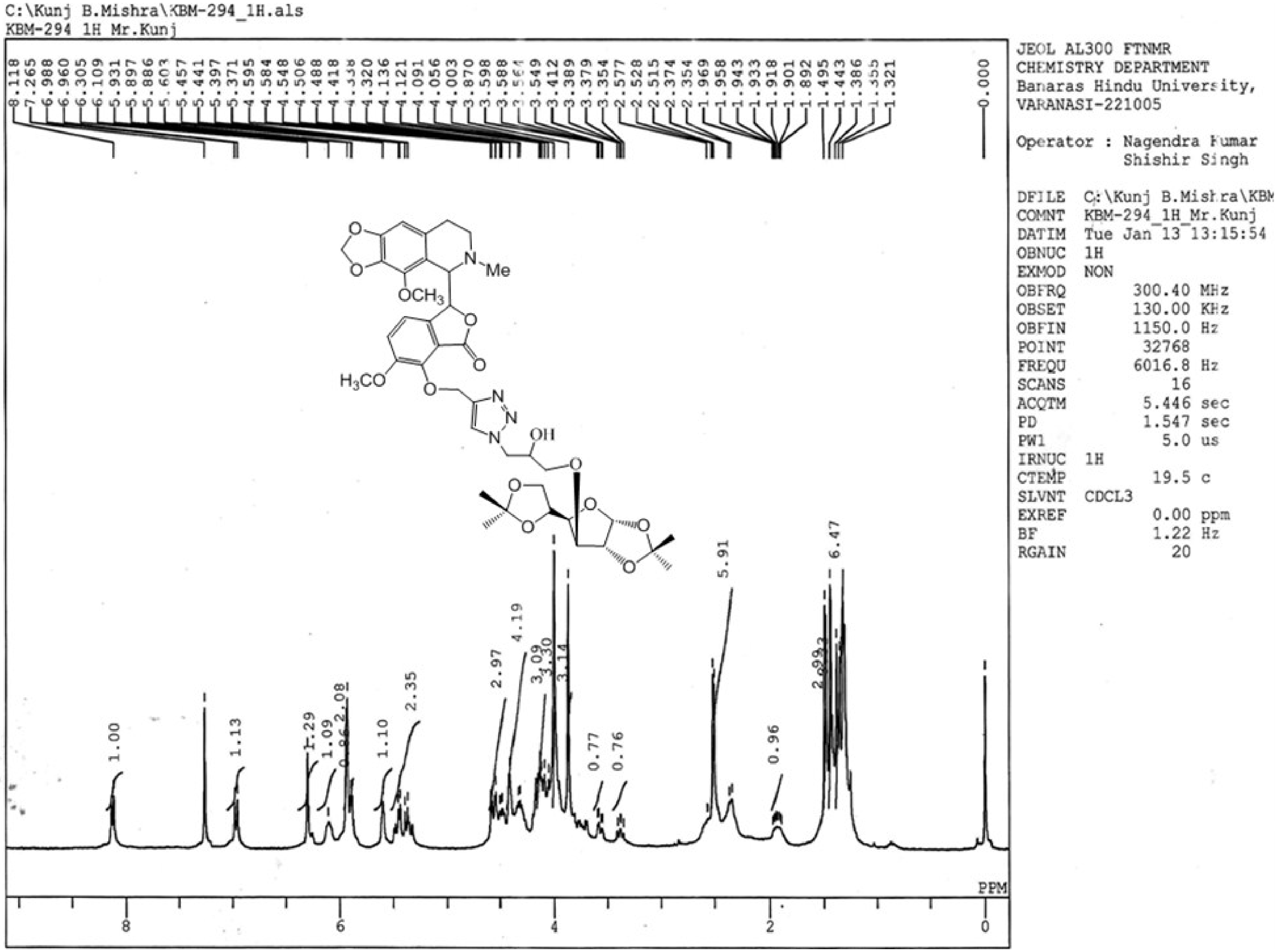
C:\Kunj B.Mishra\KBM-NOS12_1H.als
KBM-NOS12_1H Mr. Kunj Bihari

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

Operator : Nagendra Kumar
Shishir Singh

DFILE C:\Kunj B.Mishra\KBM
COMNT KBM-NOS12_1H_Mr. Kun
DATIM Thu Sep 18 14:03:51
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6016.8 Hz
SCANS 16
ACQTM 5.446 sec
PD 1.547 sec
PW1 5.0 us
IRNUC 1H
CTEMP 20.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.20 Hz
RGAIN 17

Figure 21:^{1}HNMR of compound 8j

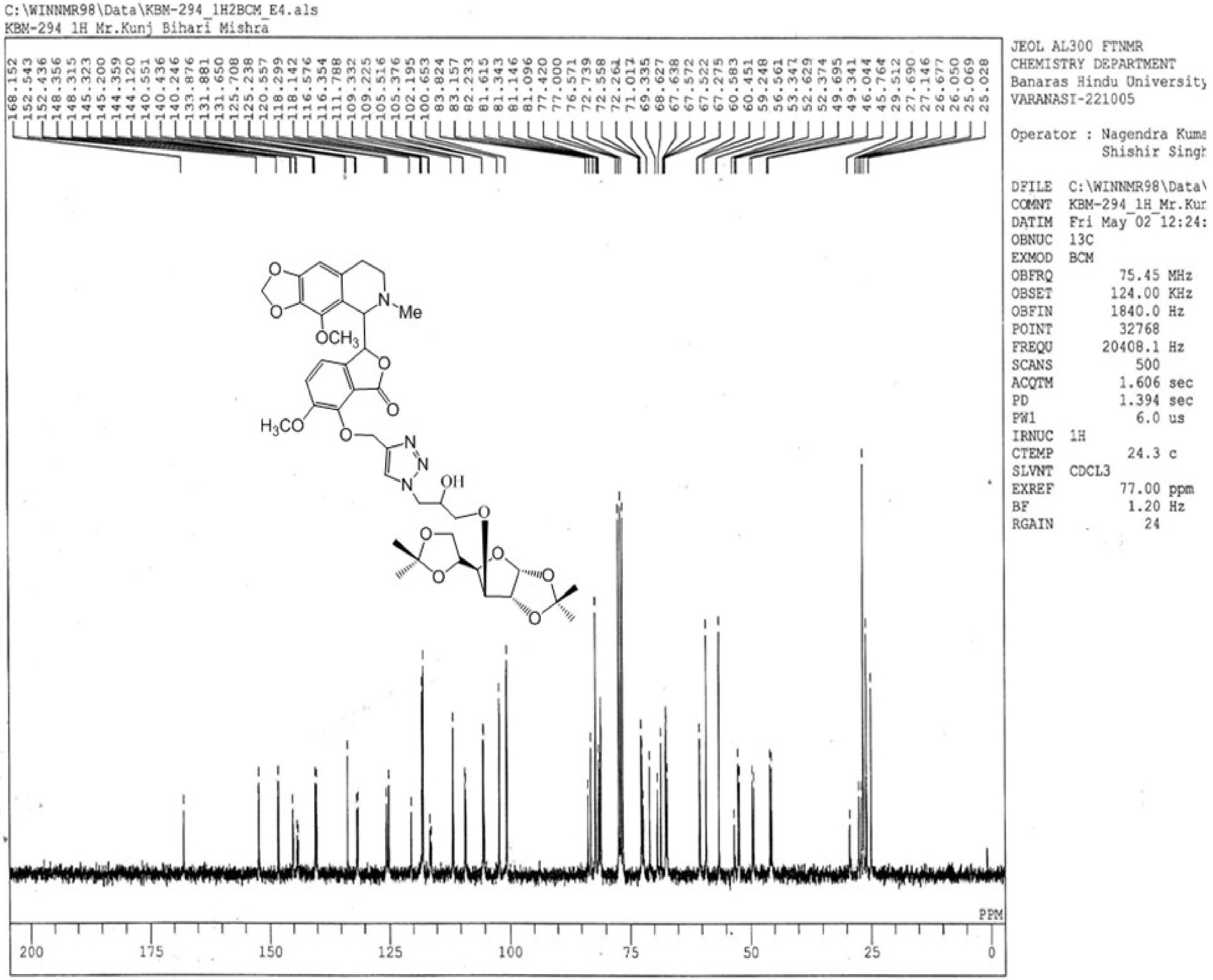


JEOL AL300 FTNMR
CHEMISTRY DEPARTMENT
Banaras Hindu University,
VARANASI-221005

Operator : Nagendra Kumar
Shishir Singh

DFILE C:\Kunj B.Mishra\KBM
COMNT KBM-294_1H_Mr.Kunj
DATIM Tue Jan 13 13:15:54
OBNUC 1H
EXMOD NON
OBFRQ 300.40 MHz
OBSET 130.00 KHz
OBFIN 1150.0 Hz
POINT 32768
FREQU 6016.8 Hz
SCANS 16
ACQTM 5.446 sec
PD 1.547 sec
PW1 5.0 us
IRNUC 1H
CTEMP 19.5 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 1.22 Hz
RGAIN 20

Figure 23:^{1}HNMR of compound 8k



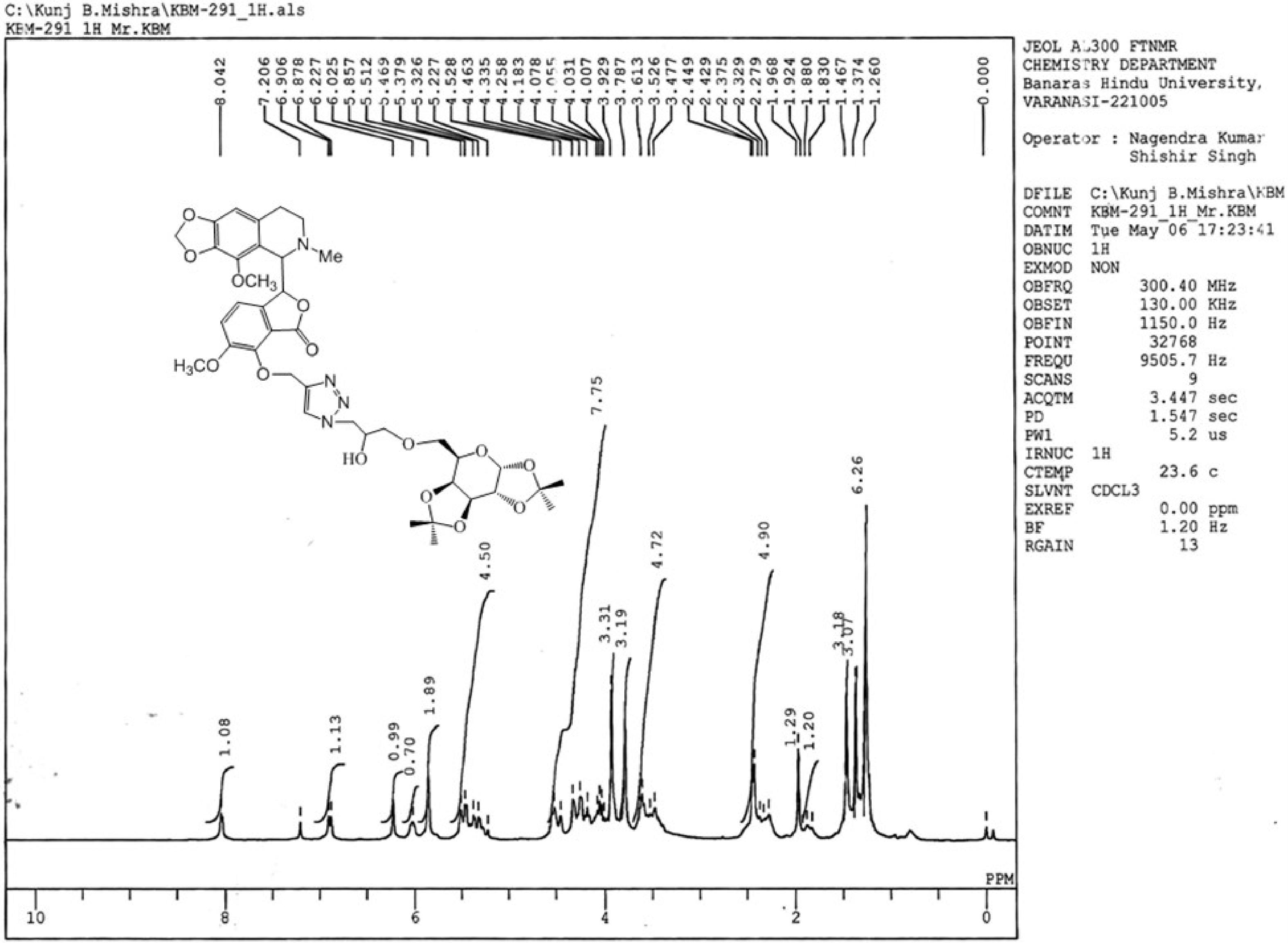
```
C:\WINNMR98\Data\KBM-294_1H2BCM_E4.als
KBM-294 1H Mr.Kunj Bihari Mishra

JEOL AL300 FTNMR
CHEMISTRY DEPARTMENT
Banaras Hindu Universit
VARANASI-221005

Operator : Nagendra Kum
           Shishir Sing

DFILE  C:\WINNMR98\Data\
COMNT  KBM-294_1H_Mr.Ku
DATIM  Fri May 02 12:24:
OBNUC  13C
EXMOD  BCM
OBFRQ        75.45 MHz
OBSET       124.00 KHz
OBFIN       1840.0 Hz
POINT        32768
FREQU      20408.1 Hz
SCANS          500
ACQTM        1.606 sec
PD           1.394 sec
PW1            6.0 us
IRNUC  1H
CTEMP         24.3 c
SLVNT  CDCL3
EXREF        77.00 ppm
BF            1.20 Hz
RGAIN           24
```

Figure 24:^{13}C NMR of compound 8k



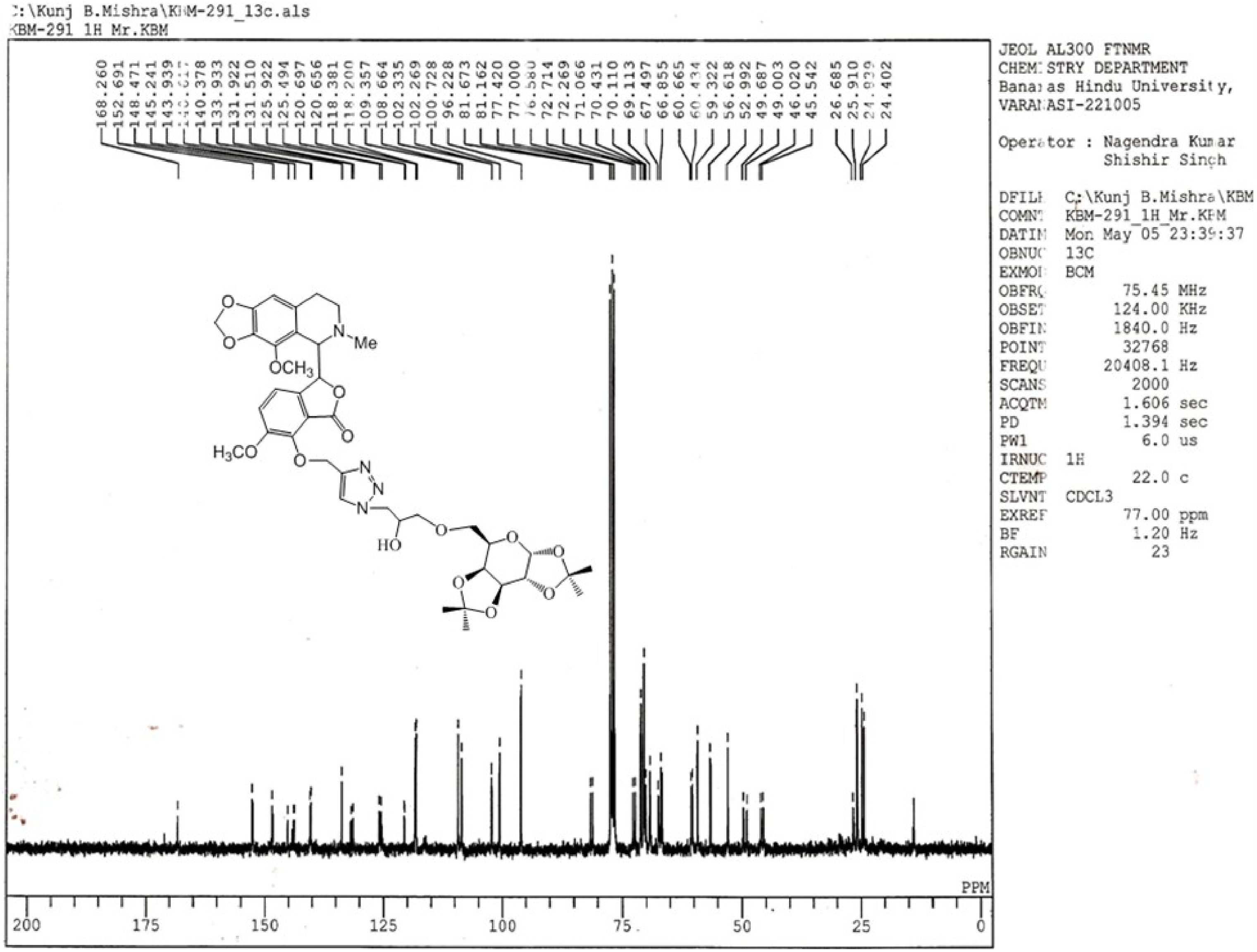
```
C:\Kunj B.Mishra\KBM-291_1H.als
KBM-291 1H Mr.KBM
```

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

Operator : Nagendra Kumar
           Shishir Singh

DFILE  C:\Kunj B.Mishra\KBM
COMNT  KBM-291_1H_Mr.KBM
DATIM  Tue May 06 17:23:41
OBNUC  1H
EXMOD  NON
OBFRQ       300.40 MHz
OBSET       130.00 KHz
OBFIN       1150.0 Hz
POINT        32768
FREQU       9505.7 Hz
SCANS            9
ACQTM        3.447 sec
PD           1.547 sec
PW1            5.2 us
IRNUC  1H
CTEMP         23.6 c
SLVNT  CDCL3
EXREF         0.00 ppm
BF            1.20 Hz
RGAIN           13
```

Figure 25:^{1}HNMR of compound 8l

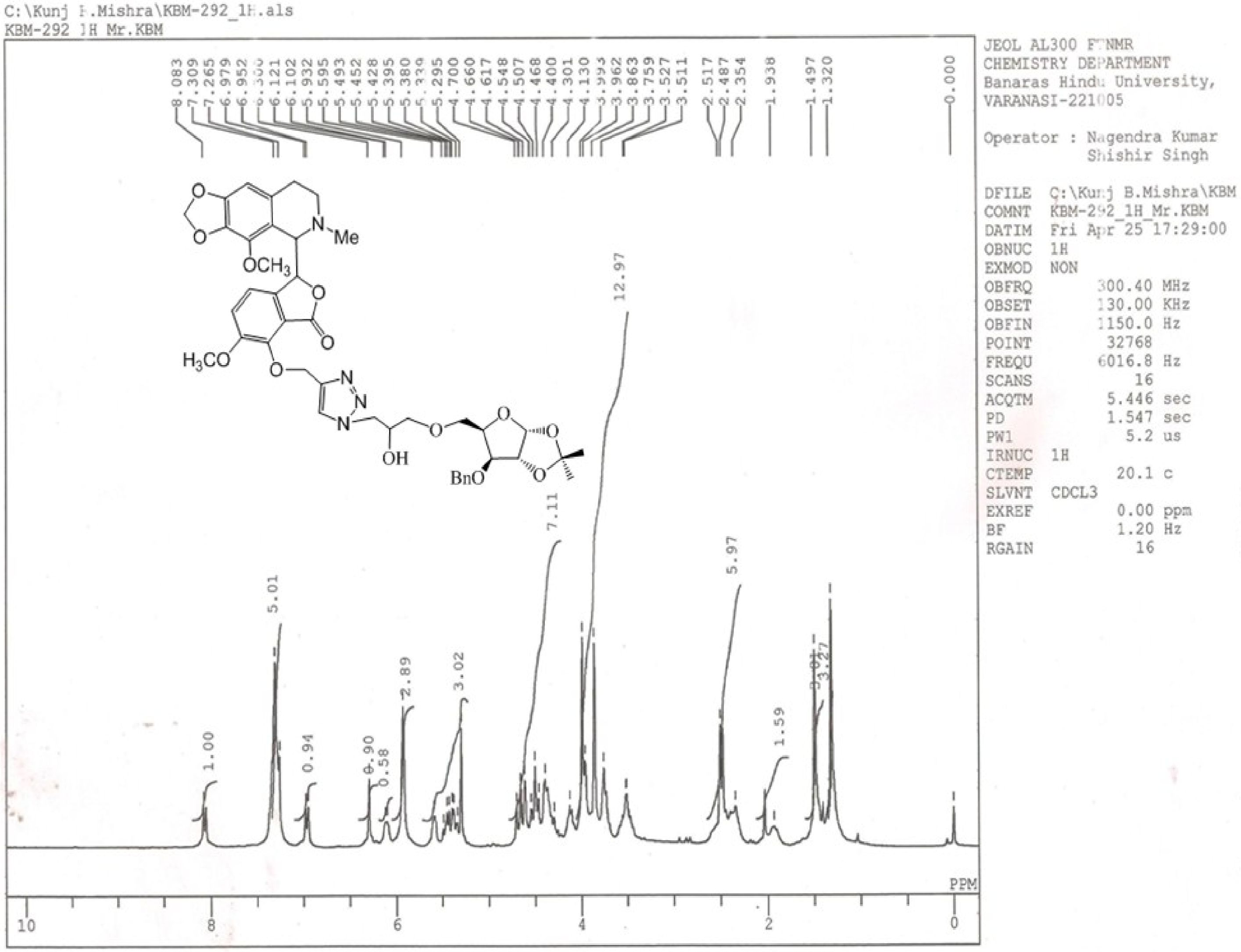


```
JEOL AL300 FTNMR
CHEMISTRY DEPARTMENT
Banaras Hindu University,
VARANASI-221005

Operator : Nagendra Kumar
           Shishir Singh

DFILE  C:\Kunj B.Mishra\KBM
COMNT  KBM-291_1H_Mr.KBM
DATIM  Mon May 05 23:39:37
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           6.0 us
IRNUC  1H
CTEMP        22.0 c
SLVNT  CDCL3
EXREF       77.00 ppm
BF           1.20 Hz
RGAIN          23
```

Figure 26: ^{13}CNMR of compound 8l



C:\Kunj B.Mishra\KBM-292_1H.als
KBM-292 1H Mr.KBM

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

Operator : Nagendra Kumar
Shishir Singh

```
DFILE  C:\Kunj B.Mishra\KBM
COMNT  KBM-292_1H_Mr.KBM
DATIM  Fri Apr 25 17:29:00
OBNUC  1H
EXMOD  NON
OBFRQ       300.40 MHz
OBSET       130.00 KHz
OBFIN       1150.0 Hz
POINT        32768
FREQU       6016.8 Hz
SCANS           16
ACQTM        5.446 sec
PD           1.547 sec
PW1            5.2 us
IRNUC  1H
CTEMP         20.1 c
SLVNT  CDCL3
EXREF         0.00 ppm
BF            1.20 Hz
RGAIN           16
```

Figure 27:^{1}HNMR of compound 8m

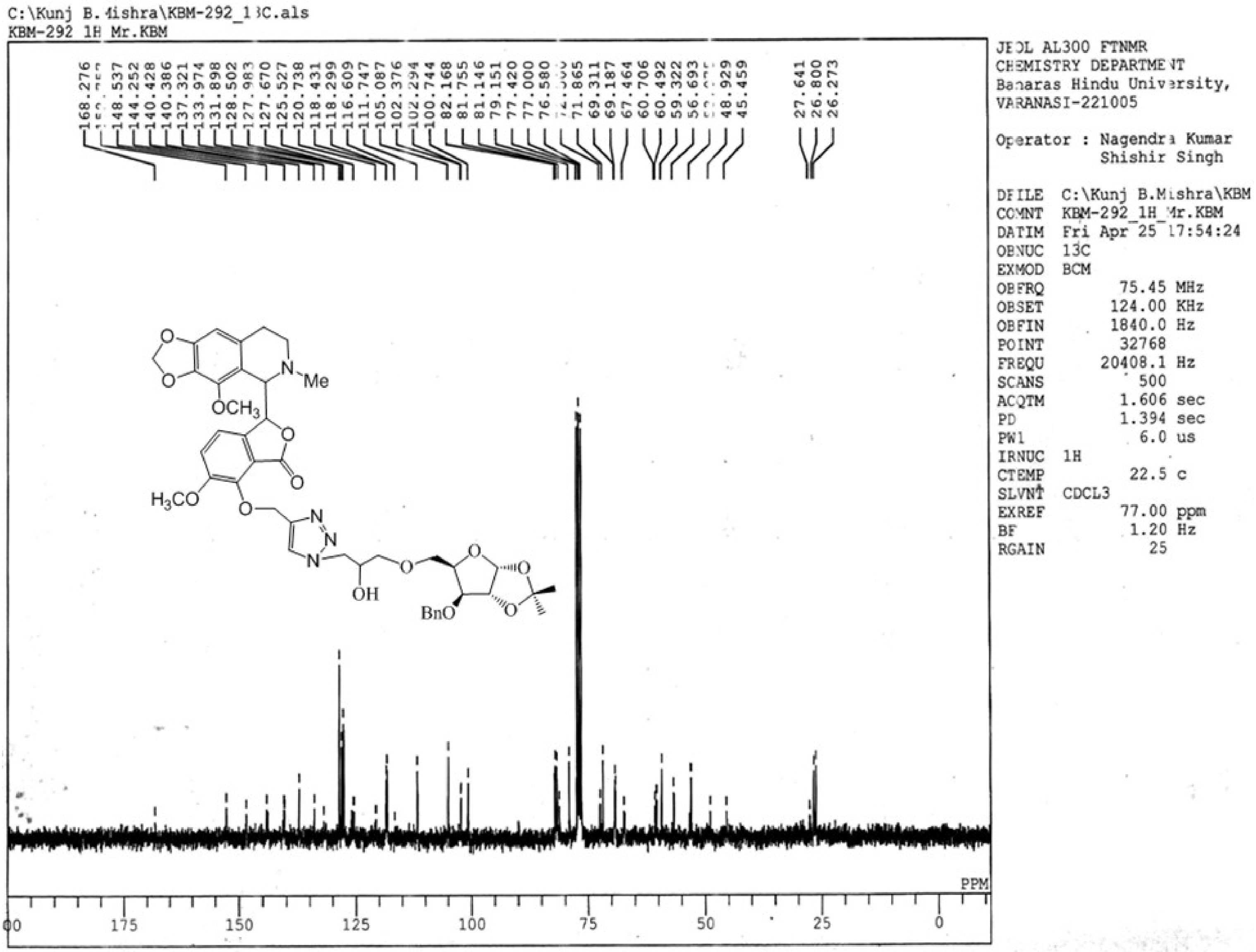


Figure 28: ^{13}C NMR of compound 8m

Single Crystal X-ray data

Single-crystal X-ray data of compound**5a** was collected on Xcalibur Eos (Oxford) CCD diffractometer using graphite monochromated Mo*K*α radiation (λ = 0.71073 Å). The data integration and reduction were processed with CrysAlis Pro software. The structures were solved by the direct method and then refined on F^2 by the full matrix least-squares technique with the SHELX-97 set of softwareusing the WinGX (version 1.80.05) program package. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were treated as riding atoms using SHELX default parameters. Molecular structures have drawn using ORTEP software given in Figure S-1. Further information on the crystal structure determination (excluding structure factors) has been deposited in the Cambridge Crystallographic Data Centre as supplementary publications no.**949197**. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033. e-mail: deposit@ccdc.cam.ac.uk) or via internet.

Table S1. Crystallographic refinement data for compound **3a**

Compound	**3**
Empirical Formula	$C_{24}H_{23}NO_7$
Formula Weight	437.44
Crystal System	Monoclinic
Space group	P 21
a (Å)	8.5515(14)
b (Å)	11.720(3)
c (Å)	11.059(2)
β (°)	100.720(17)
V (Å^3)	1089.0(4)
Z	2
Density (calc)	1.334
F(000), F'(000)	460.0,460.26
μ (mm^{-1})	0.099
Crystal Size [mm]	0.09 x 0.11x 0.14
Temperature (K)	293
Radiation	Mo$K\alpha$ 0.71073
θ Min-Max [°]	3.3, 29.190
h, k, l	-10:11; -11:16; -17:12
Tot.,UniqData, R(int)	4714, 3367, 0.106

Obs. data [I > 2.0 σ(I)]	1873
Nref, Npar	5882, 289
R1, wR2, S	0.0976, 0.2378, 1.191
CCDC	**1022189**

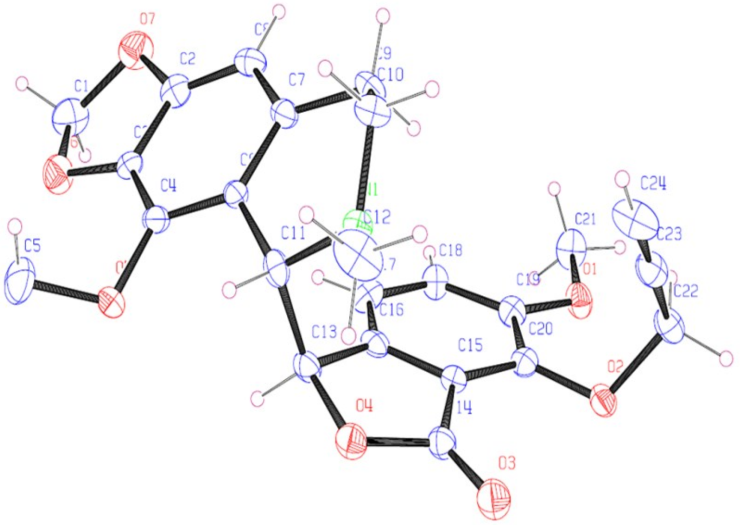


Figure S1. Molecular structure of **3a**. Thermal ellipsoids of C, N, and O are set at 40 % probability