Electronic Supplementary Material (ESI) for Green Chemistry

DABCO-Promoted three-component regioselective synthesis of functionalized chromen-5-ones and pyrano[3,2-*c*]chromen-5-ones via direct annulation of α-oxoketene-N,S-arylaminoacetals under solvent-free conditions

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Table of Content

General

All reagents were commercial and purchased from Merck, Aldrich and Fluka and were used as received. All ^{1}H and ^{13}C NMR spectra were recorded on JEOL AL 300 and FT-NMR spectrometer. Chemical shifts are given as δ value with reference to tetramethylsilane (TMS) as the internal standard. The IR spectra were recorded on Varian 3100 FT-IR spectrophotometer. Mass spectra were recorded on Waters Acquity Ultra Performance LC spectrometer. The C, H, and N analyses were performed from microanalytical laboratory with an Exeter Analytical Inc. "Model CE-400 CHN Analyzer". X-ray diffraction was measured on Xcalibur Oxford CCD Diffractometer. All the reactions were monitored by TLC using precoated sheets of silica gel G/UV-254 of 0.25 mm thickness (Merck $60F_{254}$) using UV light (254 nm/365 nm) for visualization. Melting points were determined with Büchi B-540 melting point apparatus and are uncorrected.

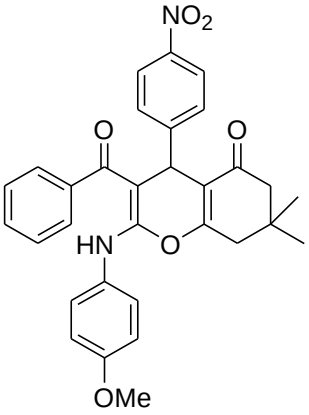
General Procedure for synthesis of tetrahydrochromen-5-one (6a-r) and pyrano[3,2-*c*]chromen-5-one (7a-i)

The aldehyde (1.0 mmol), cyclic 1,3-dicarbonyl compound (1.0 mmol), α-oxoketene-N,S-acetal (1.0 mmol) and DABCO were (1.0 mmol) mixed thoroughly in a 10 ml round bottom flask and the whole reaction mixture was heated in an oil bath at 100 ^{o}C for the stipulated period of time till the completion of the reaction (monitored by TLC). Ethanol (2 mL) was added to the reaction mixture. The product was appeared as solid which was filtered out and washed with another 2 ml of EtOH to remove the DABCO and other impurities. Finally the products were recrystallized from ethanol.

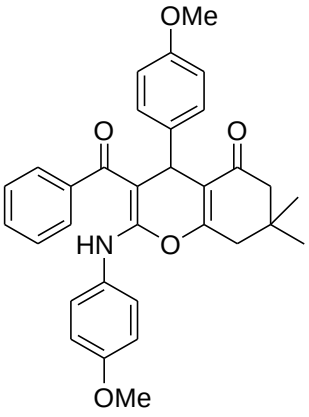
General procedure for the synthesis of pyrano[3,2-*c*]chromenoquinolines 8a-b

To a 5 ml dimethylformamide solution of 3-(2-halobenzoyl)-pyrano[3,2-*c*]chromen-5-one (**7h o**r **7i**) (1.0 mmol), K_2CO_3 (0.138 g, 1 mmol) was added and the reaction mixture was heated to 100 ^{o}C. After completion of the reaction as indicated by TLC (about 40 min), the mixture was cooled to room temperature and cold water was added to precipitate the product, which was then collected by filtration and washed with cold water to afford pure **8**.

Characterization data of the isolated compounds

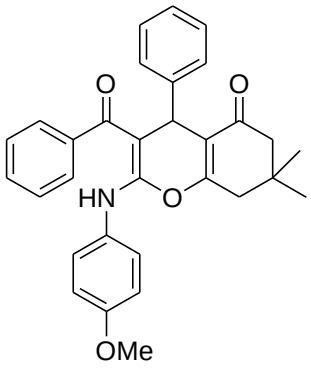


3-Benzoyl-2-(4-methoxyphenylamino)-7,7-dimethyl-4-(4-nitrophenyl)-4,6,7,8-tetrahydrochromen-5-one (6a): White solid; mp 256-257 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.14 (s, 1H), 7.91 (d, J = 8.7 Hz, 2H), 7.38 (d, J = 7.5 Hz, 1H), 7.34-7.25 (m, 4H), 7.06 (d, J = 7.2 Hz, 2H), 6.96-6.88 (m, 4H), 4.94 (s, 1H), 3.85 (s, 3H), 2.54 (d, J = 18.0 Hz, 1H), 2.44 (d, J = 18.0 Hz, 1H), 2.27 (d, J = 16.2 Hz, 1H), 2.15 (d, J = 16.2 Hz, 1H), 1.12 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.8, 194.7, 161.3, 157.9, 157.2, 152.6, 146.1, 140.5, 129.4, 129.2, 128.6, 128.3, 126.0, 124.3, 123.2, 116.3, 114.4, 88.6, 55.5, 50.5, 40.3, 35.5, 32.2, 29.1, 27.1. IR (KBr, cm^{-1}): 3055, 2954, 1683, 1666, 1631, 1590, 1562, 1373; MS: m/z = 547 (M^++Na). Anal. Calcd for $C_{31}H_{28}N_2O_6$: C, 70.98; H, 5.38; N, 5.34. Found: C, 70.74; H, 5.53; N, 5.47.

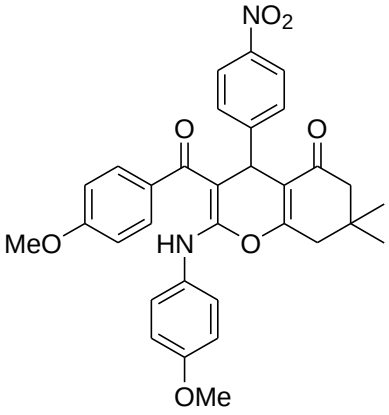


3-Benzoyl-4-(4-methoxyphenyl)-2-(4-methoxyphenylamino)-7,7-dimethyl-4,6,7,8-tetrahydrochromen-5-one (6b): White solid; mp 160-161 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.1 (s, 1H), 7.37-7.28 (m, 5H), 7.10 (d, J = 7.2 Hz, 2H), 6.92 (d, J = 8.7 Hz, 2H), 6.71 (d, J = 8.7 Hz, 2H), 6.60 (d, J = 8.4 Hz, 2H), 4.74 (s, 1H), 3.84 (s, 3H), 3.71 (s, 3H), 2.52-2.39 (m, 2H), 2.24 (d, J = 16.2 Hz, 1H), 2.15 (d, J = 16.2 Hz, 1H), 1.10 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.1, 194.9, 160.5, 158.1, 157.7, 156.9, 140.8, 137.7, 129.8, 129.0, 128.6, 128.0, 126.3, 124.1, 118.0, 114.3, 113.3, 90.1, 55.4, 55.0, 50.7, 40.3, 34.2, 32.2, 29.2, 27.1. IR (KBr, cm^{-1}): 3057, 2975, 1683, 1667, 1625,

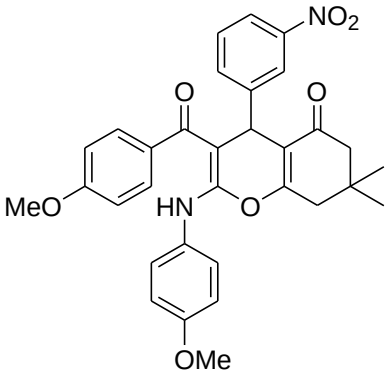
1581, 1559, 1401; MS: *m/z* = 532 (M^++Na). Anal. Calcd for $C_{32}H_{31}NO_5$: C, 75.42; H, 6.13; N, 2.75. Found: C, 75.58; H, 5.98; N, 2.63.



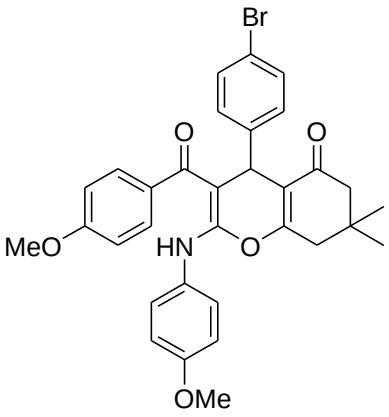
3-Benzoyl-2-(4-methoxyphenylamino)-7,7-dimethyl-4-phenyl-4,6,7,8-tetrahydro chromen-5-one (6c): White solid; mp 182-183 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.13 (s, 1H), 7.37-7.25 (m, 6H), 7.11-7.05 (m, 4H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 5.7 Hz, 2H), 4.81 (s, 1H), 3.84 (s, 3H), 2.53-2.40 (m, 2H), 2.25 (d, *J* = 15 Hz, 1H), 2.16 (d, *J* = 15 Hz, 1H), 1.10 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.1, 195.0, 160.8, 158.3, 157.0, 145.4, 140.9, 129.9, 129.2, 128.2, 128.1, 127.7, 126.4, 126.2, 124.3, 118.0, 114.4, 90.1, 55.6, 50.8, 40.5, 35.1, 32.4, 29.3, 27.2. IR (KBr, cm^{-1}): 3041, 2929, 1675, 1670, 1624, 1571, 1558, 1385; MS: *m/z* = 502 (M^++Na). Anal. Calcd for $C_{31}H_{29}NO_4$: C, 77.64; H, 6.10; N, 2.92. Found: C, 77.82; H, 6.01; N, 2.83.



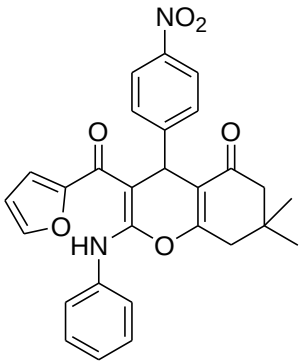
3-(4-Methoxybenzoyl)-2-(4-methoxyphenylamino)-7,7-dimethyl-4-(4-nitrophenyl)-4,6,7,8-tetrahydrochromen-5-one (6d): White solid; mp 209-210 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.05 (s, 1H), 7.93 (d, *J* = 8.7 Hz, 2H), 7.27 (d, *J* = 9.3 Hz, 2H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.97-6.92 (m, 4H), 6.84 (d, *J* = 8.4 Hz, 2H), 5.05 (s, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 2.53 (d, *J* = 17.7 Hz, 1H), 2.45 (d, *J* = 17.7 Hz, 1H), 2.28 (d, *J* = 16.2 Hz, 1H), 2.17 (d, *J* = 16.2 Hz, 1H), 1.13 (s, 3H), 0.92 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.9, 194.2, 161.5, 160.6, 157.7, 157.1, 152.7, 146.2, 133.0, 129.4, 128.5, 128.2, 124.2, 123.3, 116.4, 114.4, 113.6, 88.6, 55.5, 55.3, 50.5, 40.3, 35.6, 32.3, 29.2, 27.1. IR (KBr, cm^{-1}): 3056, 2978, 1688, 1661, 1628, 1589, 1559, 1368; MS: *m/z* = 577 (M^++Na). Anal. Calcd for $C_{32}H_{30}N_2O_7$: C, 69.30; H, 5.45; N, 5.05. Found: C, 69.13; H, 5.60; N, 5.12.



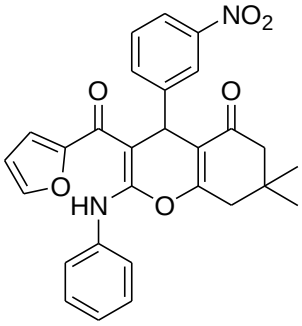
3-(4-Methoxybenzoyl)-2-(4-methoxyphenylamino)-7,7-dimethyl-4-(3-nitrophenyl)-4,6,7,8-tetrahydrochromen-5-one (6e): White solid; mp 199-200 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.02 (s, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.58 (s, 1H), 7.29-7.18 (m, 3H), 7.10-7.05 (m, 3H), 6.93 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.4 Hz, 2H), 5.03 (s, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 2.51 (s, 2H), 2.27 (d, J = 16.2 Hz, 1H), 2.16 (d, J = 16.2 Hz, 1H), 1.13 (s, 3H), 0.94 (s, 3H); 13C NMR (75 MHz, $CDCl_3$): δ 196.0, 193.3, 166.3, 165.4, 164.7, 163.8, 155.3, 149.1, 139.5, 135.9, 134.0, 132.4, 128.0, 124.4, 118.3, 116.4, 116.3, 114.4, 113.7, 110.2, 91.7, 55.5, 55.3, 50.6, 40.3, 35,5, 32.3, 29.6, 27.2. IR (KBr, cm^{-1}): 3072, 2925, 1685, 1664, 1629, 1593, 1561, 1362; MS: *m/z* = 577 (M^{+}+Na). Anal. Calcd for $C_{32}H_{30}N_2O_7$: C, 69.30; H, 5.45; N, 5.05. Found: C, 69.09; H, 5.38; N, 5.13.



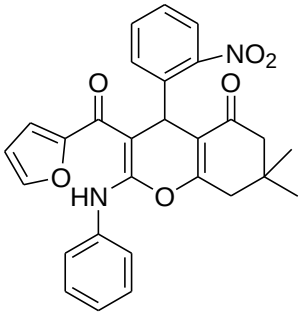
4-(4-Bromophenyl)-3-(4-methoxybenzoyl)-2-(4-methoxyphenylamino)-7,7-dimethyl-4,6,7,8-tetrahydrochromen-5-one (6f): White solid; mp 205-206 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.03 (s, 1H), 7.60 (s, 1H), 7.13 (d, J = 8.7 Hz, 2H), 6.93-6.82 (m, 6H), 6.73-6.70 (m, 3H), 4.89 (s, 1H), 3.83 (s, 6H), 2.53-2.42 (m, 2H), 2.29-2.17 (m, 2H), 1.11 (s, 3H), 0.92 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.1, 195.0, 161.3, 133.3, 131.2, 129.4, 128.4, 124.2, 117.4, 114.4, 113.6, 90.1, 55.6, 55.4, 50.7, 40.5, 32.4, 31.0, 29.3, 27.2. IR (KBr, cm^{-1}): 3052, 2974, 1691, 1656, 1620, 1579, 1552, 1357; MS: *m/z* = 610 (M^{+}+Na). Anal. Calcd for $C_{32}H_{30}BrNO_5$: C, 65.31; H, 5.14; N, 2.38. Found: C, 65.53; H, 5.01; N, 2.19.



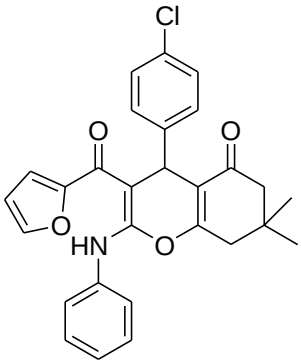
3-(2-Furoyl)-7,7-dimethyl-4-(4-nitrophenyl)-2-phenylamino-4,6,7,8-tetrahydro chromen-5-one (6g): White solid; mp 210-211 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.74 (s, 1H), 8.04 (d, *J* = 8.7 Hz, 2H), 7.54-7.35 (m, 7H), 7.21 (t, *J* = 6.9 Hz, 1H), 7.01 (d, *J* = 3.6 Hz, 1H), 6.45 (d, *J* = 1.5 Hz, 1H), 5.88 (s, 1H), 2.54 (d, *J* = 17.7 Hz, 1H), 2.46 (d, *J* = 17.7 Hz, 1H), 2.32 (d, *J* = 16.2 Hz, 1H), 2.23 (d, *J* = 16.2 Hz, 1H), 1.13 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.9, 178.0, 161.5, 159.0, 153.4, 153.0, 146.3, 144.4, 136.6, 129.3, 128.5, 125.2, 123.5, 122.6, 116.9, 116.8, 112.0, 88.5, 50.6, 40.4, 33.1, 32.3, 29.1, 27.1. IR (KBr, cm^{-1}): 3054, 2925, 1688, 1665, 1619, 1572, 1556, 1383; MS: *m/z* = 507 (M^++Na). Anal. Calcd for $C_{28}H_{24}N_2O_6$: C, 69.41; H, 4.99; N, 5.78. Found: C, 69.25; H, 5.10; N, 5.88.



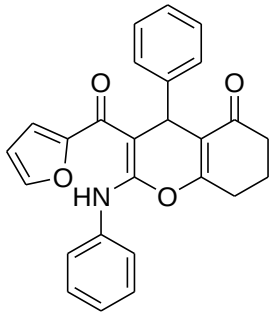
3-(2-Furoyl)-7,7-dimethyl-4-(3-nitrophenyl)-2-phenylamino-4,6,7,8-tetrahydro chromen-5-one (6h): White solid; mp 201-202 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.71 (s, 1H), 8.14 (s, 1H), 7.94 (d, *J* = 7.5 Hz, 1H), 7.65-7.58 (m, 2H), 7.43-7.31 (m, 5H), 7.21 (t, *J* = 6.9 Hz, 1H), 7.02 (d, *J* = 3.6 Hz, 1H), 6.45 (s, 1H), 5.89 (s, 1H), 2.52 (s, 2H), 2.32 (d, *J* = 16.2 Hz, 1H), 2.23 (d, *J* = 16.2 Hz, 1H), 1.13 (s, 3H), 0.92 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.0, 178.1, 161.3, 158.9, 153.5, 148.1, 147.8, 144.4, 136.6, 134.0, 129.2, 128.9, 125.2, 122.7, 122.7, 121.5, 116.9, 112.0, 88.7, 50.6, 40.3, 33.0, 32.3, 29.1, 27.1. IR (KBr, cm^{-1}): 3054, 2976, 1686, 1666, 1624, 1583, 1551, 1388; MS: *m/z* = 507 (M^++Na). Anal. Calcd for $C_{28}H_{24}N_2O_6$: C, 69.41; H, 4.99; N, 5.78. Found: C, 69.19; H, 5.10; N, 5.87.



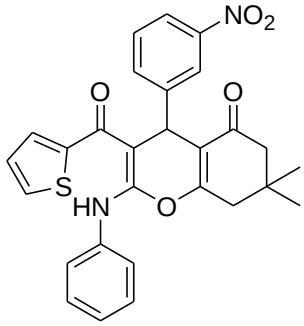
3-(2-Furoyl)-7,7-dimethyl-4-(2-nitrophenyl)-2-phenylamino-4,6,7,8-tetrahydro chromen-5-one (6i): White solid; mp 159-160 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.25 (s, 1H), 7.52-7.30 (m, 8H), 7.20-7.15 (m, 2H), 6.91 (d, J = 3.3 Hz, 1H), 6.40 (s, 1H), 6.18 (s, 1H), 2.49 (br, 2H), 2.26 (br, 2H), 1.11 (s, 3H), 0.98 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.3, 180.6, 164.6, 160.6, 158.4, 157.4, 146.4, 144.5, 136.9, 136.6, 129.6, 125.2, 125.1, 121.2, 120.8, 118.9, 118.3, 115.0, 112.7, 95.6, 49.3, 42.6, 36.8, 36.5, 33.8, 30.3. IR (KBr, cm^{-1}): 3061, 2931, 1682, 1666, 1621, 1576, 1554, 1375; MS: *m/z* = 507 (M^++Na). Anal. Calcd for $C_{28}H_{24}N_2O_6$: C, 69.41; H, 4.99; N, 5.78. Found: C, 69.63; H, 4.84; N, 5.64.



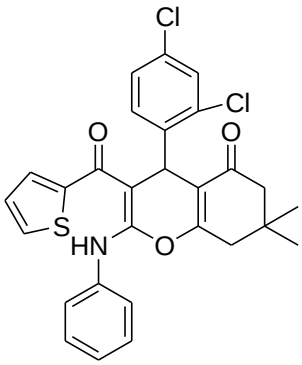
4-(4-Chlorophenyl)-3-(2-furoyl)-7,7-dimethyl-2-phenylamino-4,6,7,8-tetrahydro chromen-5-one (6j): White solid; mp 199-200 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.72 (s, 1H), 7.54 (s, 1H), 7.42-7.35 (m, 5H), 7.25-7.13 (m, 4H), 6.98 (d, J = 3.3 Hz, 1H), 6.44 (q, J = 1.5 Hz, 1H), 5.71 (s, 1H), 2.54-2.41 (m, 2H), 2.31 (d, J = 16.2 Hz, 1H), 2.23 (d, J = 16.2 Hz, 1H), 1.12 (s, 3H), 0.92 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.1, 178.2, 161.0, 159.1, 153.2, 144.4, 144.0, 136.8, 131.9, 129.2, 128.9, 128.4, 124.9, 122.4, 117.7, 116.6, 111.8, 89.3, 50.7, 40.3, 32.3, 29.1, 27.1. IR (KBr, cm^{-1}): 3065, 2926, 1679, 1656, 1618, 1574, 1558, 1370; MS: *m/z* = 496 (M^++Na). Anal. Calcd for $C_{28}H_{24}ClNO_4$: C, 70.96; H, 5.10; N, 2.96. Found: C, 71.14; H, 4.98; N, 2.85.



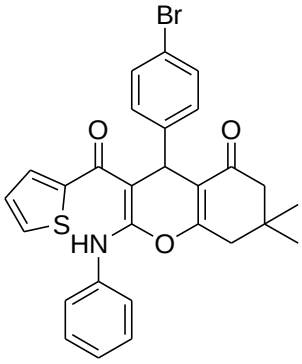
3-(2-Furoyl)-4-phenyl-2-phenylamino-4,6,7,8-tetrahydrochromen-5-one (6k): White solid; mp 187-188 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.7 (s, 1H), 7.54 (s, 1H), 7.38-7.10 (m, 10H), 6.96 (d, J = 3.3 Hz, 1H), 6.42 (s, 1H), 5.73 (s, 1H), 2.63-2.61 (m, 2H), 2.43-2.38 (m, 2H), 2.05-2.01 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.4, 178.4, 162.7, 159.3, 153.2, 145.6, 144.5, 137.1, 129.3, 128.4, 127.6, 126.4, 124.9, 122.5, 119.6, 116.6, 111.8, 89.8, 36.9, 32.8, 26.8, 20.1. IR (KBr, cm^{-1}): 3071, 2923, 1672, 1654, 1620, 1581, 1556, 1361; MS: *m/z* = 434 (M^++Na). Anal. Calcd for $C_{26}H_{21}NO_4$: C, 75.90; H, 5.14; N, 3.40. Found: C, 75.75; H, 5.28; N, 3.48.



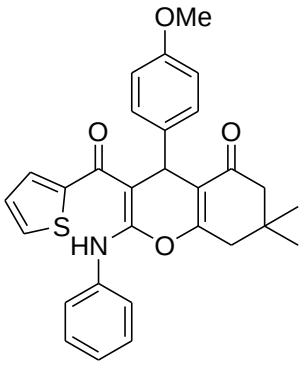
7,7-Dimethyl-4-(3-nitrophenyl)-2-phenylamino-3-(2-thienoyl)-4,6,7,8-tetrahydro chromen-5-one (6l): White solid; mp 217-218 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.43 (s, 1H), 7.99-7.96 (m, 2H), 7.53-7.32 (m, 8H), 7.21 (t, J = 6.6 Hz, 1H), 7.03 (t, J = 4.2 Hz, 1H), 5.54 (s, 1H), 2.55 (d, J = 18.6 Hz, 1H), 2.48 (d, J = 18.6 Hz, 1H), 2.33 (d, J = 16.5 Hz, 1H), 2.24 (d, J = 16.5 Hz, 1H), 1.13 (s, 3H), 0.92 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.9, 184.3, 161.8, 158.8, 148.3, 146.9, 143.5, 136.4, 133.9, 130.0, 129.2, 128.8, 127.3, 125.2, 122.6, 122.3, 121.7, 116.8, 88.8, 50.5, 40.3, 34.3, 32.3, 29.1, 27.1. IR (KBr, cm^{-1}): 3073, 2952, 1689, 1670, 1619, 1591, 1564, 1381; MS: *m/z* = 523 (M^++Na). Anal. Calcd for $C_{28}H_{24}N_2O_5S$: C, 67.18; H, 4.83; N, 5.60. Found: C, 67.26; H, 4.63; N, 5.39.



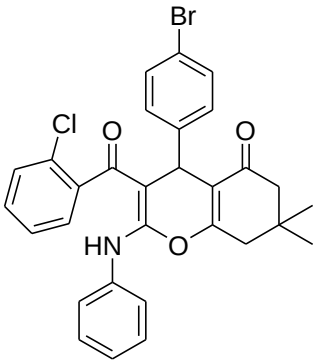
4-(2,4-Dichlorophenyl)-7,7-dimethyl-2-phenylamino-3-(2-thienoyl)-4,6,7,8-tetra-hydrochromen-5-one (6m): White solid; mp 155-156 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.02 (s, 1H), 7.41-7.31 (m, 6H), 7.21-7.16 (m, 2H), 7.04 (t, *J* = 4.2 Hz, 1H), 6.87 (m, 1H), 6.74 (d, *J* = 8.7 Hz, 1H), 5.50 (s, 1H), 2.55 (d, *J* = 17.4 Hz, 1H), 2.47 (d, *J* = 17.4 Hz, 1H), 2.28 (d, *J* = 16.5 Hz, 1H), 2.19 (d, *J* = 16.5 Hz, 1H), 1.14 (s, 3H), 1.01 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.2, 186.1, 161.4, 157.9, 142.7, 138.7, 136.6, 133.7, 133.3, 132.6, 130.1, 129.2, 128.7, 127.9, 126.8, 126.2, 125.0, 122.6, 114.0, 88.4, 50.6, 40.3, 35.1, 32.1, 29.2, 27.3. IR (KBr, cm^{-1}): 3056, 2943, 1684, 1671, 1621, 1586, 1561, 1380; MS: *m/z* = 546 (M^++Na). Anal. Calcd for $C_{28}H_{23}Cl_2NO_3S$: C, 64.12; H, 4.42; N, 2.67. Found: C, 64.29; H, 4.27; N, 2.59.



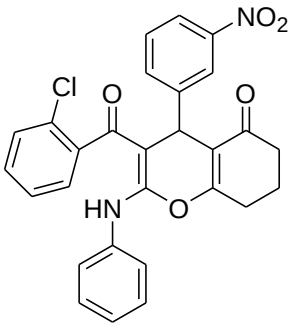
4-(4-Bromophenyl)-7,7-dimethyl-2-phenylamino-3-(2-thienoyl)-4,6,7,8-tetrahydro chromen-5-one (6n): White solid; mp 207-208 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.55 (s, 1H), 7.45 (d, *J* = 1.5 Hz, 1H), 7.39-7.32 (m, 7H), 7.21-7.12 (m, 3H), 7.00 (t, *J* = 4.2 Hz, 1H), 5.40 (s, 1H), 2.53-2.39 (m, 2H), 2.34-2.22 (m, 2H), 1.11 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.1, 183.8, 161.5, 159.2, 144.1, 143.7, 136.7, 131.6, 130.1, 129.2, 129.1, 127.4, 125.0, 122.4, 120.4, 117.8, 89.2, 50.7, 40.3, 33.5, 32.3, 29.2, 27.0. IR (KBr, cm^{-1}): 3035, 2942, 1687, 1670, 1629, 1592, 1563; MS: *m/z* = 558 (M^++Na). Anal. Calcd for $C_{28}H_{24}BrNO_3S$: C, 62.92; H, 4.53; N, 2.62. Found: C, 63.13; H, 4.42; N, 2.51.



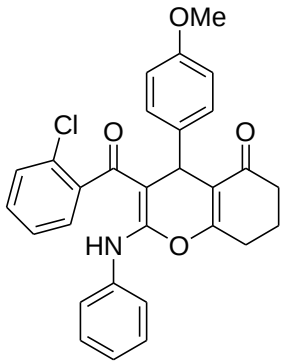
4-(4-Methoxyphenyl)-7,7-dimethyl-2-phenylamino-3-(2-thienoyl)-4,6,7,8-tetrahydro chromen-5-one (6o): White solid; mp 175-176 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.59 (s, 1H), 7.44 (d, *J* = 5.1 Hz, 1H), 7.38-7.35 (m, 5H), 7.20-7.17 (m, 3H), 6.98 (t, *J* = 4.2 Hz, 1H), 6.77-6.74 (m, 2H), 5.37 (s, 1H), 3.73 (s, 3H), 2.51-2.39 (m, 2H), 2.33-2.22 (m, 2H), 1.10 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 196.3, 183.8, 161.1, 159.4, 158.0, 144.4, 136.9, 130.0, 129.5, 129.2, 128.3, 127.5, 124.8, 122.4, 118.7, 113.9, 89.9, 55.1, 50.8, 40.3, 33.0, 32.3, 29.2, 27.0. IR (KBr, cm^{-1}): 3059, 2927, 1685, 1673, 1620, 1581, 1562, 1383; MS: *m/z* = 508 (M^++Na). Anal. Calcd for $C_{29}H_{27}NO_4S$: C, 71.73; H, 5.60; N, 2.88. Found: C, 71.56; H, 5.81; N, 3.01.



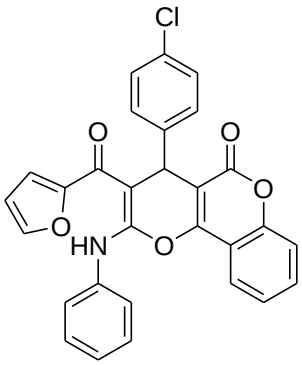
4-(4-Bromophenyl)-3-(2-chlorobenzoyl)-7,7-dimethyl-2-phenylamino-4,6,7,8-tetra-hydrochromen-5-one (6p): White solid; mp 235-236 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.08 (s, 1H), 7.41-7.01 (m, 10H), 6.62-6.44 (m, 3H), 4.44 (s, 1H), 2.56 (d, *J* = 18.0 Hz, 1H), 2.46 (d, *J* = 18.0 Hz, 1H), 2.26 (d, *J* = 16.5 Hz, 1H), 2.14 (d, *J* = 18.0 Hz, 1H), 1.15 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.7, 192.4, 160.3, 157.9, 136.5, 130.8, 129.8, 129.2, 126.6, 125.1, 122.5, 120.1, 117.1, 90.8, 50.5, 40.3, 34.7, 32.2, 29.2, 27.0. IR (KBr, cm^{-1}): 3053, 2941, 1684, 1670, 1627, 1593, 1561; MS: *m/z* = 584 (M^++Na). Anal. Calcd for $C_{30}H_{25}BrClNO_3$: C, 64.01; H, 4.48; N, 2.49. Found: C, 64.12; H, 4.29; N, 2.57.



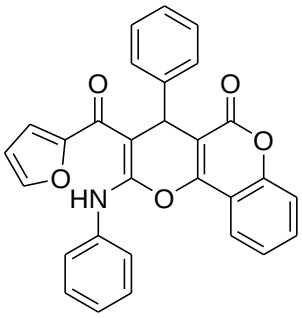
3-(2-Chlorobenzoyl)-4-(3-nitrophenyl)-2-phenylamino-4,6,7,8-tetrahydrochromen-5-one (6q): White solid; mp 240-241 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.09 (s, 1H), 7.93 (d, J = 7.2 Hz, 1H), 7.58-6.91 (m, 12H), 4.66 (s, 1H), 2.70-2.66 (m, 2H), 2.34-2.32 (m, 2H), 2.10-1.97 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 195.8, 192.3, 162.4, 157.6, 147.8, 136.2, 134.6, 130.1, 129.2, 128.5, 126.6, 125.4, 123.1, 122.7, 121.4, 117.5, 90.2, 36.6, 35.3, 26.7, 20.0. IR (KBr, cm^{-1}): 3060, 2931, 1684, 1673, 1621, 1593, 1555, 1376; MS: *m/z* = 523 (M^++Na). Anal. Calcd for $C_{28}H_{21}ClN_2O_5$: C, 67.14; H, 4.23; N, 5.59. Found: C, 67.02; H, 4.45; N, 5.50.



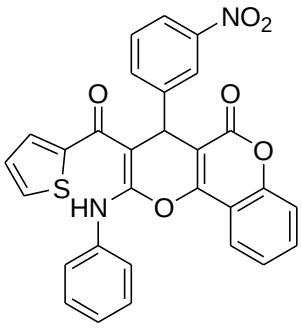
3-(2-Chlorobenzoyl)-4-(4-methoxyphenyl)-2-phenylamino-4,6,7,8-tetrahydrochromen-5-one (6r): White solid; mp 190-192 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.05 (s, 1H), 7.40-7.25 (m, 7H), 6.68-6.58 (m, 6H), 4.43 (s, 1H), 3.72 (s, 3H), 2.64 (br, 2H), 2.33 (br, 2H), 2.06-1.90 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): 193.9, 186.4, 161.5, 157.9, 136.8, 129.6, 129.2, 126.4, 124.9, 122.4, 119.2, 113.2, 86.6, 55.1, 36.8, 29.6, 26.7, 20.1. IR (KBr, cm^{-1}): 3067, 2935, 1685, 1671, 1620, 1595, 1557; MS: *m/z* = 508 (M^++Na). Anal. Calcd for $C_{29}H_{24}ClNO_4$: C, 71.67; H, 4.98; N, 2.88. Found: C, 71.85; H, 4.89; N, 2.78.



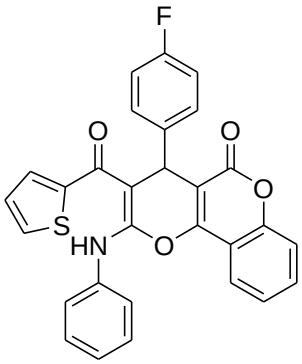
4-(4-Chlorophenyl)-3-(2-furoyl)-2-phenylamino-4*H*-pyrano[3,2-*c*]chromen-5-one (7a): White solid; mp 232-233 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.62 (s, 1H), 7.57-7.17 (m, 14H), 7.07 (d, J = 3.0 Hz, 1H), 6.47 (d, J = 1.8 Hz, 1H), 5.96 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.2, 159.1, 158.4, 153.2, 152.8, 152.6, 144.6, 142.7, 141.5, 136.2, 132.7, 132.4, 129.3, 129.2, 128.6, 125.9, 124.5, 123.9, 122.3, 117.2, 116.9, 112.0, 108.5, 88.5, 34.2. IR (KBr, cm^{-1}): 3056, 2976, 1751, 1739, 1690, 1606, MS: *m/z* = 518 (M^++Na). Anal. Calcd for $C_{29}H_{18}ClNO_5$: C, 70.24; H, 3.66; N, 2.82. Found: C, 70.43; H, 3.49; N, 2.72.



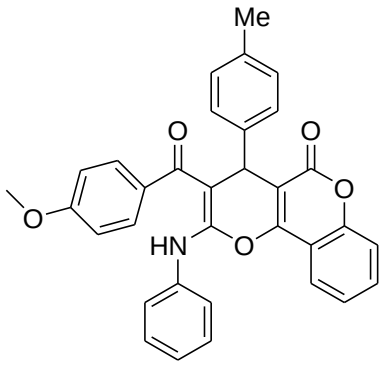
3-(2-Furoyl)-4-phenyl-2-phenylamino-4*H*-pyrano[3,2-*c*]chromen-5-one (7b): White solid; mp 215-216 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.64 (s, 1H), 7.58-7.43 (m, 9H), 7.33-7.21 (m, 5H), 7.16-7.05 (m, 2H), 6.45 (t, J = 1.8 Hz, 1H), 5.97 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.3, 160.7, 158.6, 153.2, 152.8, 152.5, 144.6, 144.1, 136.3, 132.2, 129.3, 128.5, 127.7, 127.0, 125.8, 124.4, 123.9, 122.2, 117.0, 116.8, 113.5, 111.8, 109.1, 88.9, 34.7. IR (KBr, cm^{-1}): 3076, 2939, 1755, 1742, 1686, 1609, 1571; MS: *m/z* = 483 (M^++Na). Anal. Calcd for $C_{29}H_{19}NO_5$: C, 75.48; H, 4.15; N, 3.04. Found: C, 75.31; H, 4.33; N, 2.91.



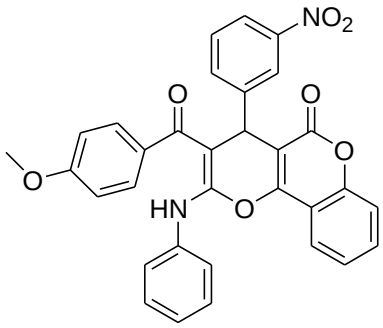
4-(3-Nitrophenyl)-2-phenylamino-3-(2-thienoyl)-4*H*-pyrano[3,2-*c*]chromen-5-one (7c): White solid; mp 203-204 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.33 (s, 1H), 8.12 (s, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.57-7.29 (m, 12H), 7.06 (t, J = 4.2 Hz, 1H), 5.74 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 184.5, 160.5, 158.2, 153.5, 152.6, 148.4, 145.5, 143.0, 135.8, 134.1, 132.8, 130.3, 129.4, 129.3, 129.0, 127.4, 126.2, 124.7, 124.1, 122.6, 122.5, 122.2, 116.9, 113.0, 107.4, 88.1, 36.3. IR (KBr, cm^{-1}): 3075, 2924, 1752, 1741, 1681, 1601, 1582; MS: *m/z* = 545 (M^++Na). Anal. Calcd for $C_{29}H_{18}N_2O_6S$: C, 66.66; H, 3.47; N, 5.36. Found: C, 66.78; H, 3.61; N, 5.19.



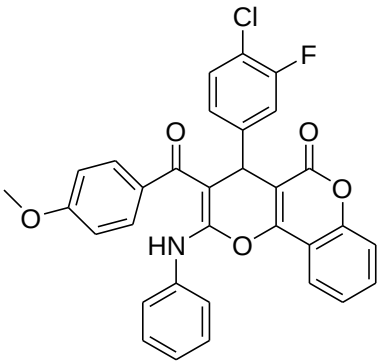
4-(4-Fluorophenyl)-2-phenylamino-3-(thienoyl)-4*H*-pyrano[3,2-*c*]chromen-5-one (7d): White solid; mp 203-204 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.45 (s, 1H), 7.56-7.23 (m, 13H), 7.04-6.92 (m, 3H), 5.61 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.2, 160.7, 158.6, 153.1, 152.5, 143.7, 139.2, 136.1, 132.4, 130.4, 129.4, 129.3, 129.1, 127.5, 125.9, 124.6, 123.9, 122.3, 116.9, 115.8, 115.5, 113.3, 108.8, 88.8, 35.4. IR (KBr, cm^{-1}): 3054, 2971, 1750, 1734, 1684, 1610, 1591; MS: *m/z* = 518 (M^++Na). Anal. Calcd for $C_{29}H_{18}FN_4S$: C, 70.29; H, 3.66; N, 2.83. Found: C, 70.10; H, 3.54; N, 3.04.



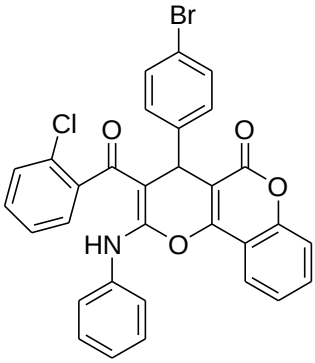
3-(4-Methoxybenzoyl)-2-phenylamino-4-p-tolyl-4H-pyrano[3,2-c]chromen-5-one (7e): White solid; mp 187-188 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.99 (s, 1H), 7.60-7.47 (m, 6H), 7.32-7.21 (m, 5H), 6.98-6.85 (m, 6H), 5.11 (s, 1H), 3.86 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.8, 160.8, 157.3, 152.9, 152.5, 140.9, 136.6, 136.5, 132.8, 132.1, 131.3, 129.2, 129.1, 128.5, 127.6, 125.5, 124.4, 123.6, 122.3, 116.8, 113.6, 113.5, 109.1, 89.8, 55.3, 36.6, 21.0. IR (KBr, cm^{-1}): 3065, 2936, 1753, 1738, 1680, 1608, 1578; MS: *m/z* =538 (M^++Na). Anal. Calcd for $C_{33}H_{25}NO_5$: C, 76.88; H, 4.89; N, 2.72. Found: C, 77.05; H, 4.75; N, 2.63.



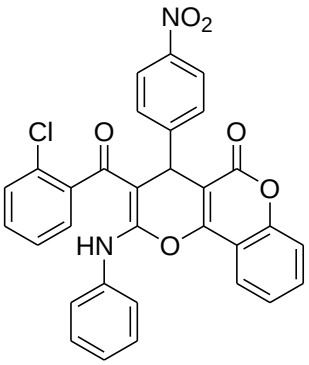
3-(4-Methoxybenzoyl)-4-(3-nitrophenyl)-2-phenylamino-4H-pyrano[3,2-c]chromen-5-one (7f): White solid; mp 210-212 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.97 (s, 1H), 7.95 (d, *J* = 7.2 Hz, 1H), 7.71 (s, 1H), 7.62-7.47 (m, 7H), 7.34-7.24 (m, 5H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 2H), 5.27 (s, 1H), 3.87 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$+DMSO-d_6): δ 193.6, 160.0, 159.2, 155.6, 152.3, 151.6, 146.7, 145.0, 135.1, 133.3, 132.0, 131.6, 128.4, 128.3, 127.1, 124.9, 123.9, 122.7, 122.0, 121.6, 120.8, 115.9, 112.7, 112.0, 105.7, 87.8, 54.4, 28.5. IR (KBr, cm^{-1}): 3067, 2934, 1757, 1738, 1681, 1601, 1582; MS: *m/z* = 569 (M^++Na). Anal. Calcd for $C_{32}H_{22}N_2O_7$: C, 70.32; H, 4.06; N, 5.13. Found: C, 70.14; H, 4.19; N, 5.26.



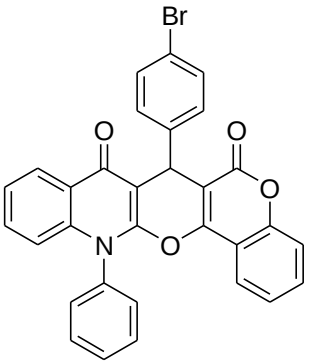
4-(4-Chloro-3-fluoro-phenyl)-3-(4-methoxybenzoyl)-2-phenylamino-4H-pyrano[3,2-c]chromen-5-one (7g): White solid; mp 226-227 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 12.95 (s, 1H), 7.59-7.43 (m, 6H), 7.34-7.12 (m, 6H), 6.88 (d, J = 8.1 Hz, 2H), 6.78-6.70 (m, 2H), 5.14 (s, 1H), 3.87 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 194.8, 161.0, 160.4, 157.1, 153.2, 152.6, 144.8, 144.7, 136.2, 132.6, 130.2, 129.3, 128.3, 125.8, 124.6, 124.2, 123.8, 122.4, 117.0, 116.2, 115.9, 113.7, 113.2, 111.2, 107.6, 88.7, 55.4, 36.7. IR (KBr, cm^{-1}): 3089, 2954, 1743, 1745, 1689, 1603, 1582; MS: *m/z* = 576 (M^++Na). Anal. Calcd for $C_{32}H_{21}ClFNO_5$: C, 69.38; H, 3.82; N, 2.53. Found: C, 69.20; H, 3.98; N, 2.61.



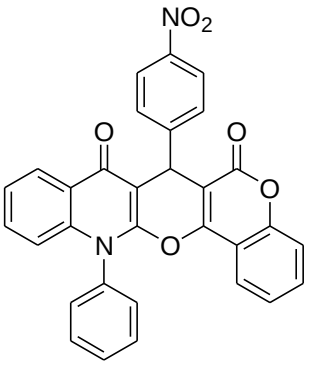
4-(4-Bromophenyl)-3-(2-chlorobenzoyl)-2-phenylamino-4*H*-pyrano[3,2-*c*]chromen-5-one (7h): White solid; mp 202-204 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.0 (s, 1H), 7.59-7.51 (m, 6H), 7.31-7.03 (m, 8H), 6.76-6.46 (m, 3H), 4.67 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.7, 160.1, 157.3, 152.5, 152.4, 135.8, 132.5, 131.1, 130.1, 129.3, 126.7, 126.1, 124.6, 124.0, 122.4, 120.8, 116.9, 113.2, 108.0, 89.8, 36.3. IR (KBr, cm^{-1}): 2978, 1750, 1737, 1679, 1606, 1583; MS: *m/z* = 606 (M^++Na). Anal. Calcd for $C_{31}H_{19}BrClNO_4$: C, 63.66; H, 3.27; N, 2.39. Found: C, 63.75; H, 3.04; N, 2.50.



3-(2-Chlorobenzoyl)-4-(4-nitrophenyl)-2-phenylamino-4*H*-pyrano[3,2-c]chromen-5-one (7i): White solid; mp 265-266 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 13.04 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 2H), 7.61-7.25 (m, 12H), 7.04 **(**m, 2H**),** 6.41 (s, 1H), 4.86 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.4, 160.0, 157.2, 152.8, 152.7, 146.7, 135.5, 132.9, 130.3, 129.4, 126.8, 126.4, 124.7, 124.1, 123.2, 122.5, 117.0, 112.9, 107.0, 89.2, 36.9. IR (KBr, cm^{-1}): 2967, 1746, 1725, 1683, 1599; MS: *m/z* = 573 (M^++Na). Anal. Calcd for $C_{31}H_{19}ClN_2O_6$: C, 67.58; H, 3.48; N, 5.08. Found: C, 67.77; H, 3.24; N, 5.21.

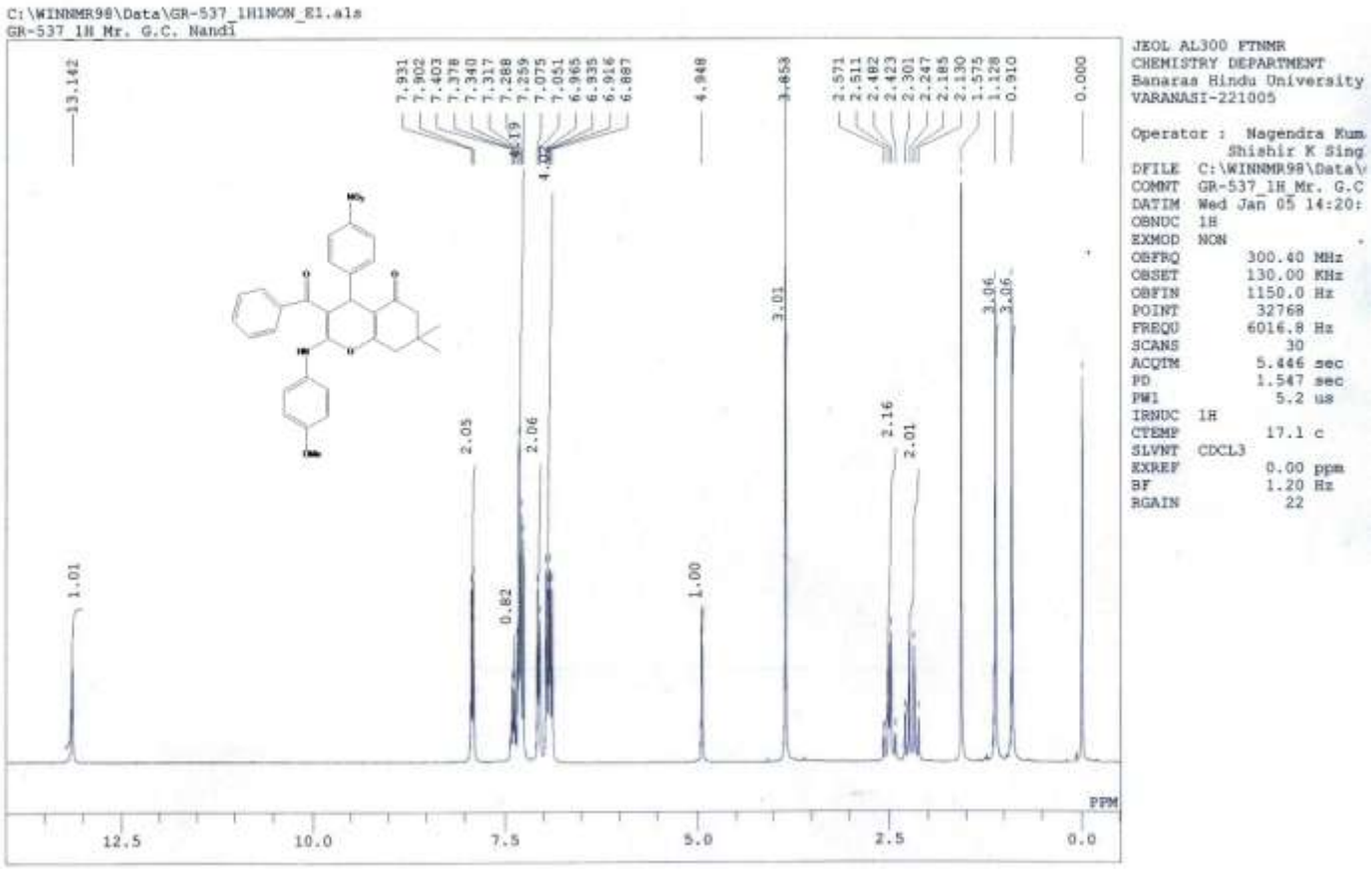


7-(4-Bromophenyl)-13-phenyl-7,13-dihydro-5,14-dioxa-13-aza-benzo[a]naphthacene-6,8-dione (8a): White solid; mp >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.26 (d, *J* = 7.5 Hz, 1H), 8.17 (d, *J* = 7.5 Hz, 1H), 7.67-7.35 (m, 13H), 7.17 (d, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 5.27 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.4, 160.4, 156.8, 156.7, 154.2, 152.6, 144.8, 131.4, 131.2, 130.8, 130.2. 129.1, 128.8, 124.5, 122.7, 122.5, 122.2, 116.3, 110.8, 105.9, 34.8. IR (KBr, cm^{-1}): 3091, 2926, 1743, 1668, 1618, 1591, 1541, 1366; MS: *m/z* = 570 (M^++Na). Anal. Calcd for $C_{31}H_{18}BrNO_4$: C, 67.90; H, 3.31; N, 2.55. Found: C, 68.11; H, 3.21; N, 2.40.

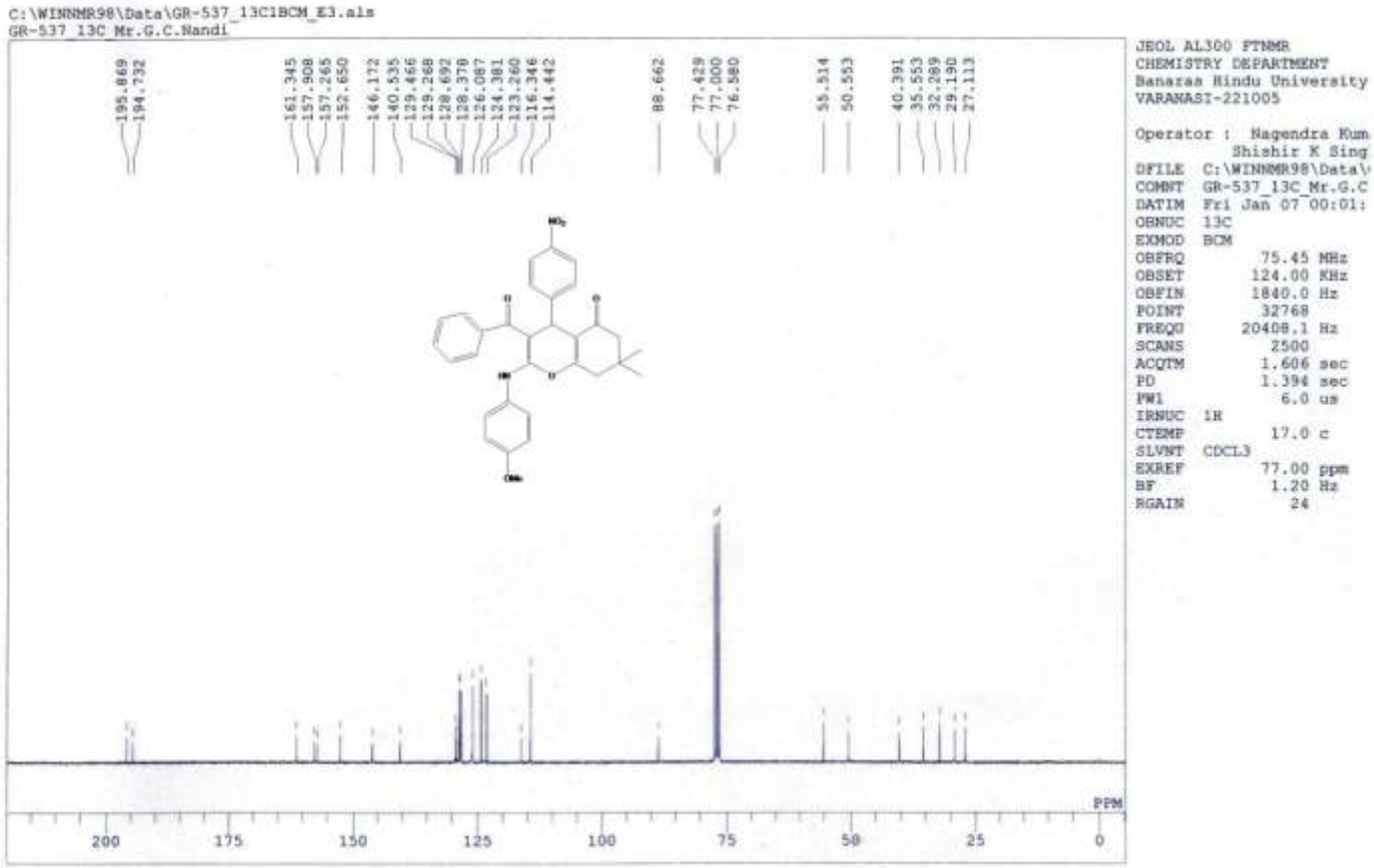


7-(4-Nitrophenyl)-13-phenyl-7,13-dihydro-5,14-dioxa-13-aza-benzo[a]naphthacene-6,8-dione (8b): White solid; mp >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.28 (d, J = 7.5 Hz, 1H), 8.19 (d, J = 7.5 Hz, 1H), 8.12-8.09 (m, 2H), 7.67-7.41 (m, 11H), 7.14 (d, J = 6.9 Hz, 1H), 6.76 (d, J = 8.4 Hz, 1H), 5.40 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.9, 169.1, 159.4, 150.8, 147.6, 146.2, 139.5, 137.4, 135.4, 134.4, 129.4, 125.7, 124.1, 123.3, 122.2, 118.4, 117.8, 116.0, 115.8, 108.6, 36.9. IR (KBr, cm^{-1}): 3063, 2954, 1749, 1663, 1610, 1581, 1550, 1363; MS: m/z = 537 (M^{+}+23). Anal. Calcd for $C_{31}H_{18}N_2O_6$: C, 72.37; H, 3.53; N, 5.44. Found: C, 72.42; H, 3.31; N, 5.63.

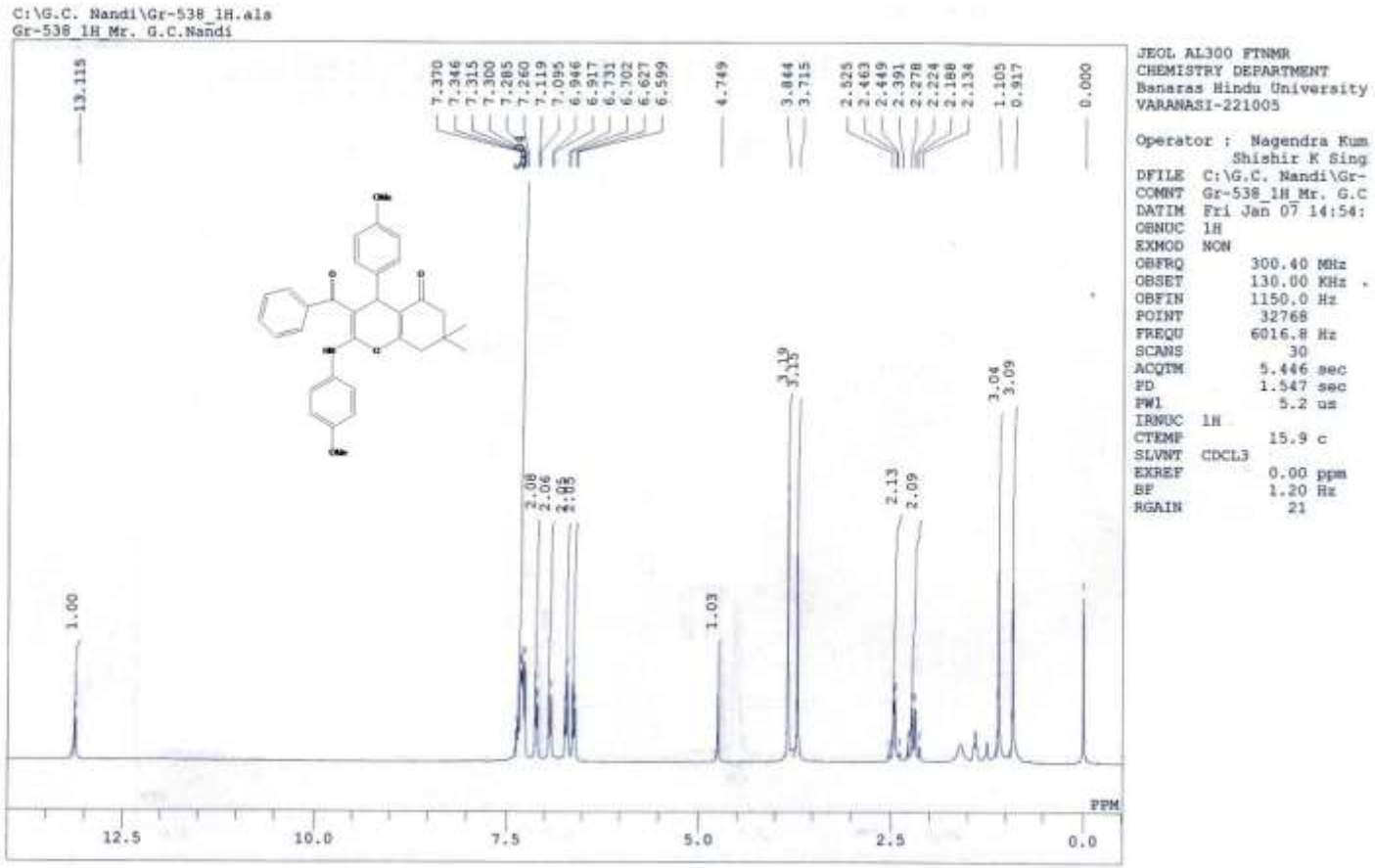
^{1}H spectrum of 6a



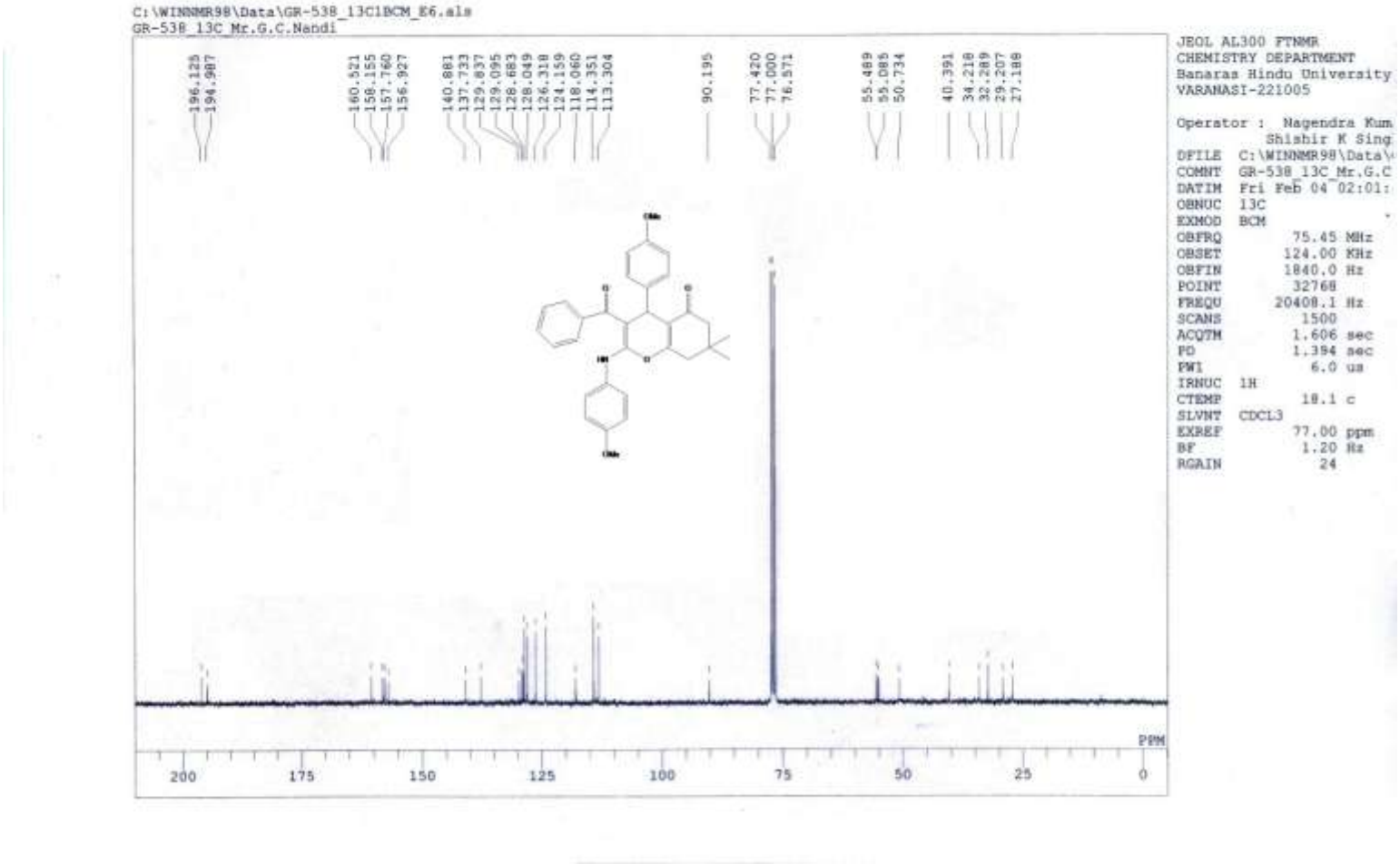
^{13}C spectrum of 6a



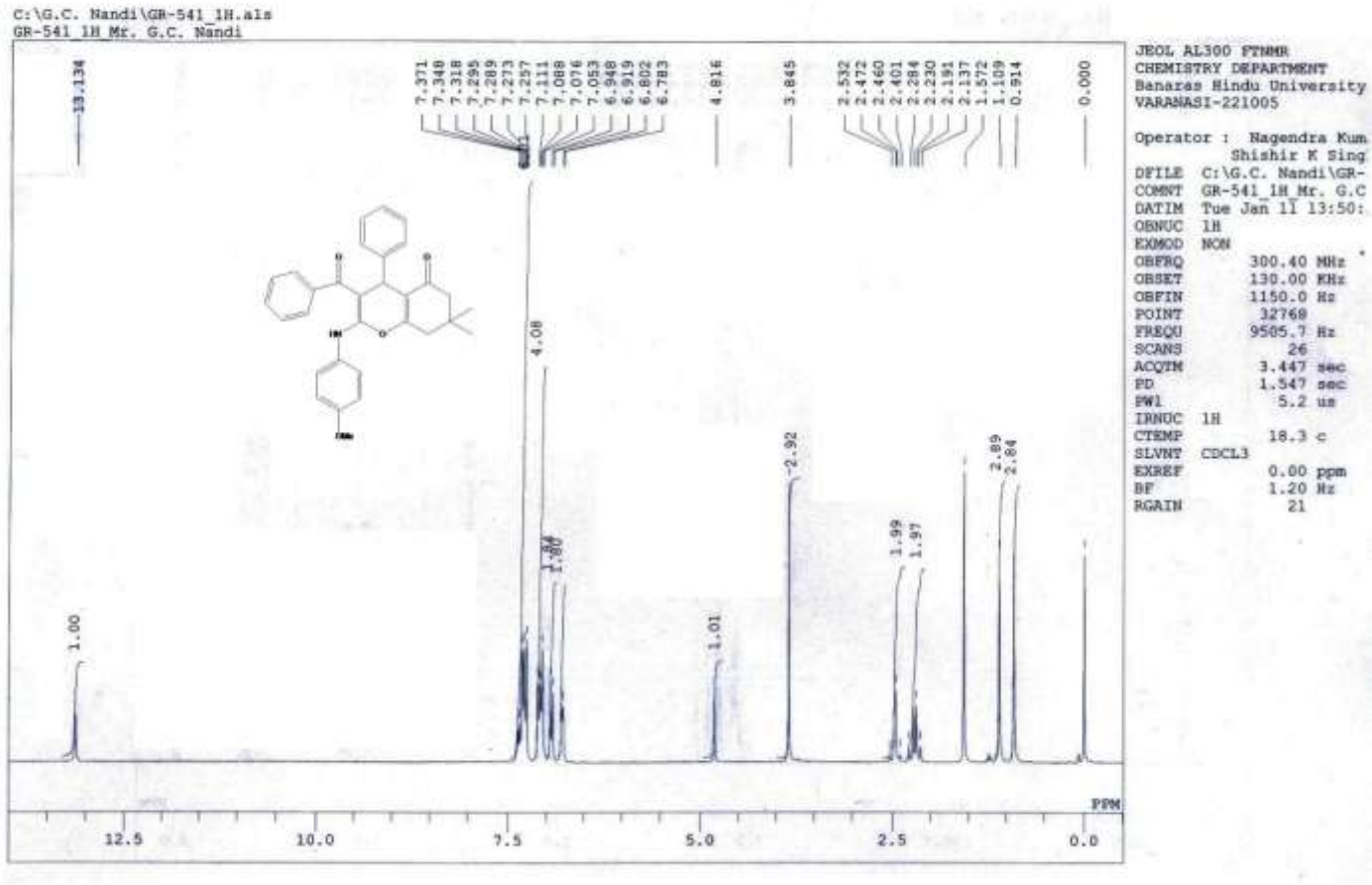
^{1}H spectrum of 6b



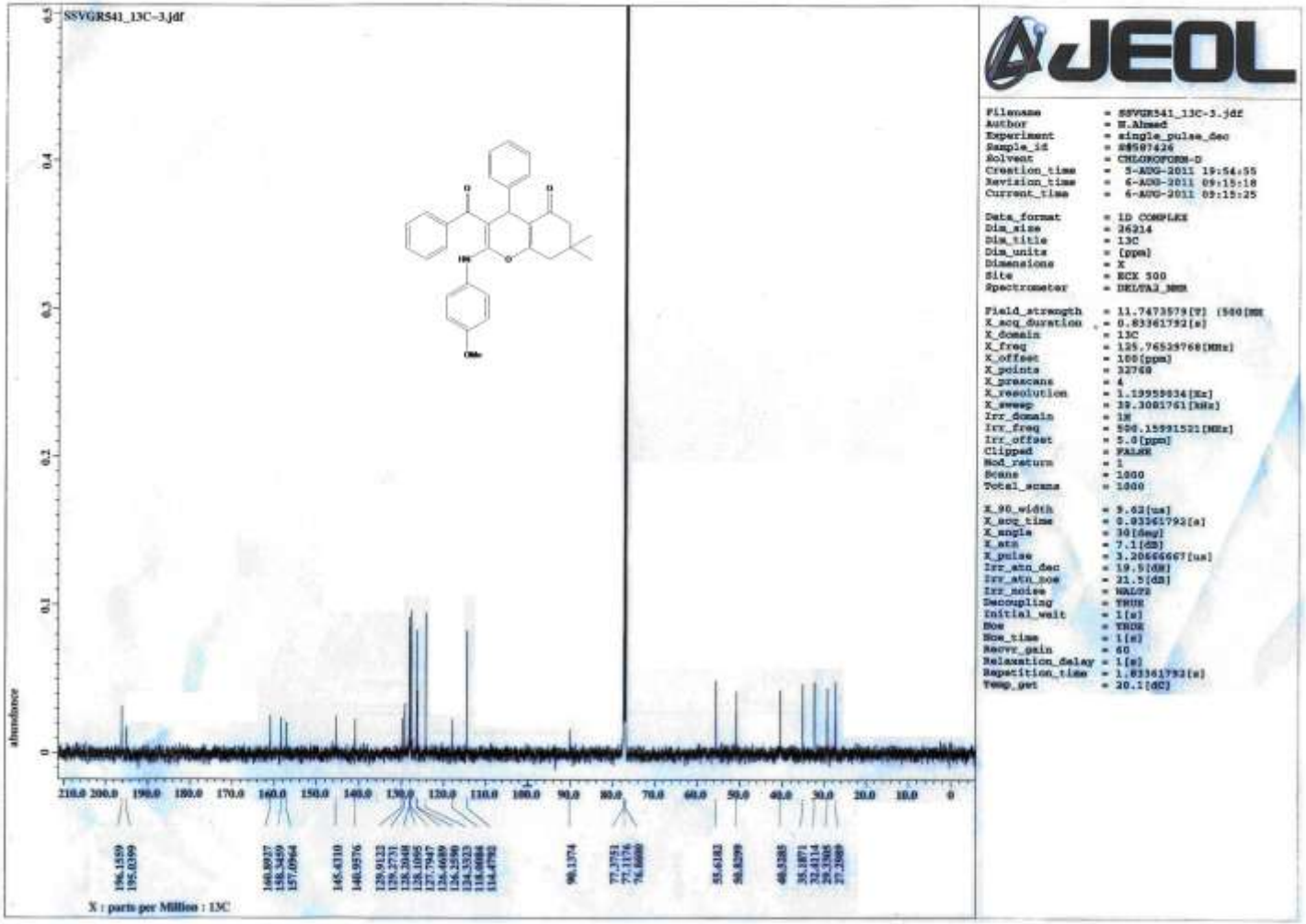
^{13}C spectrum of 6b



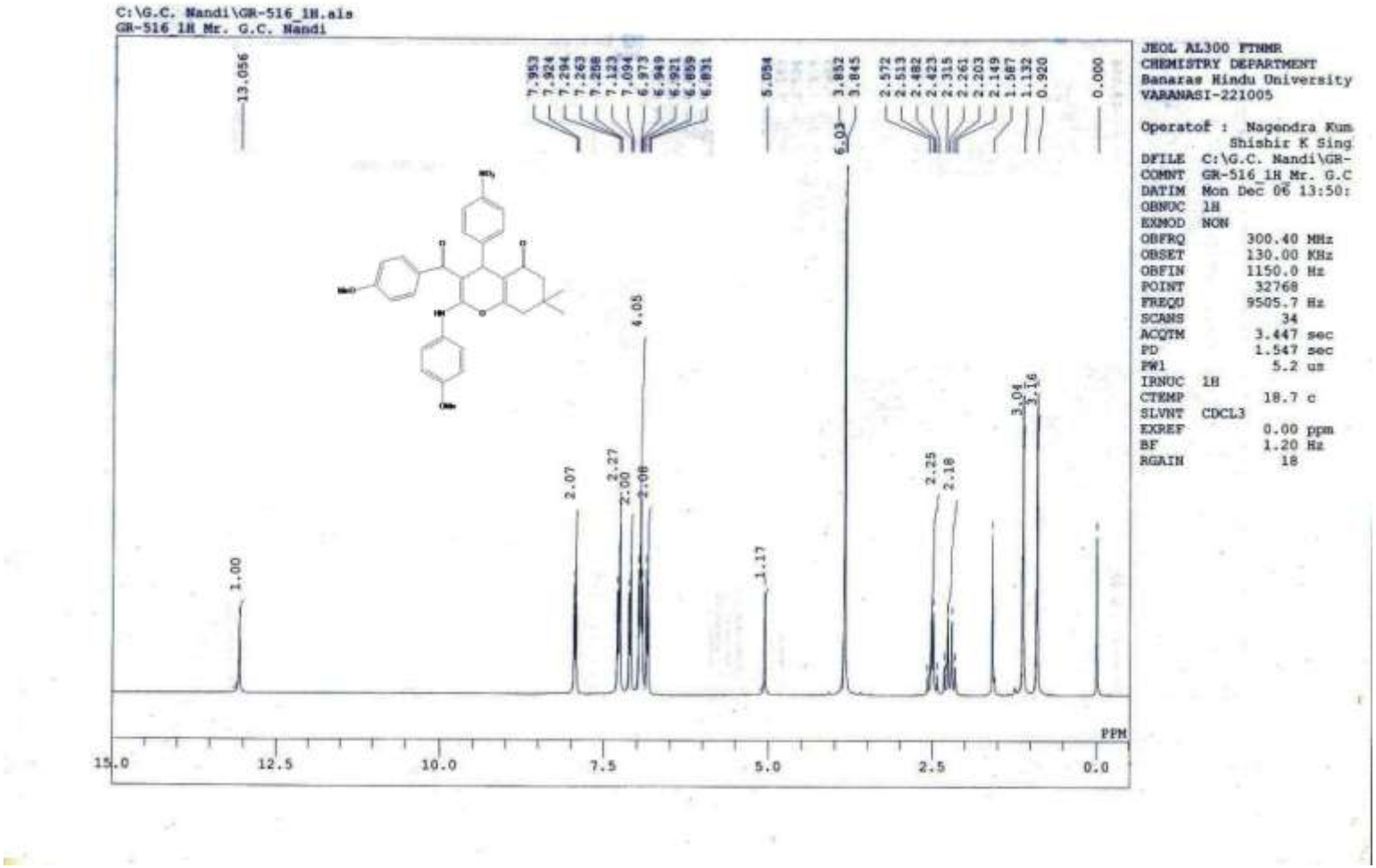
^{1}H spectrum of 6c



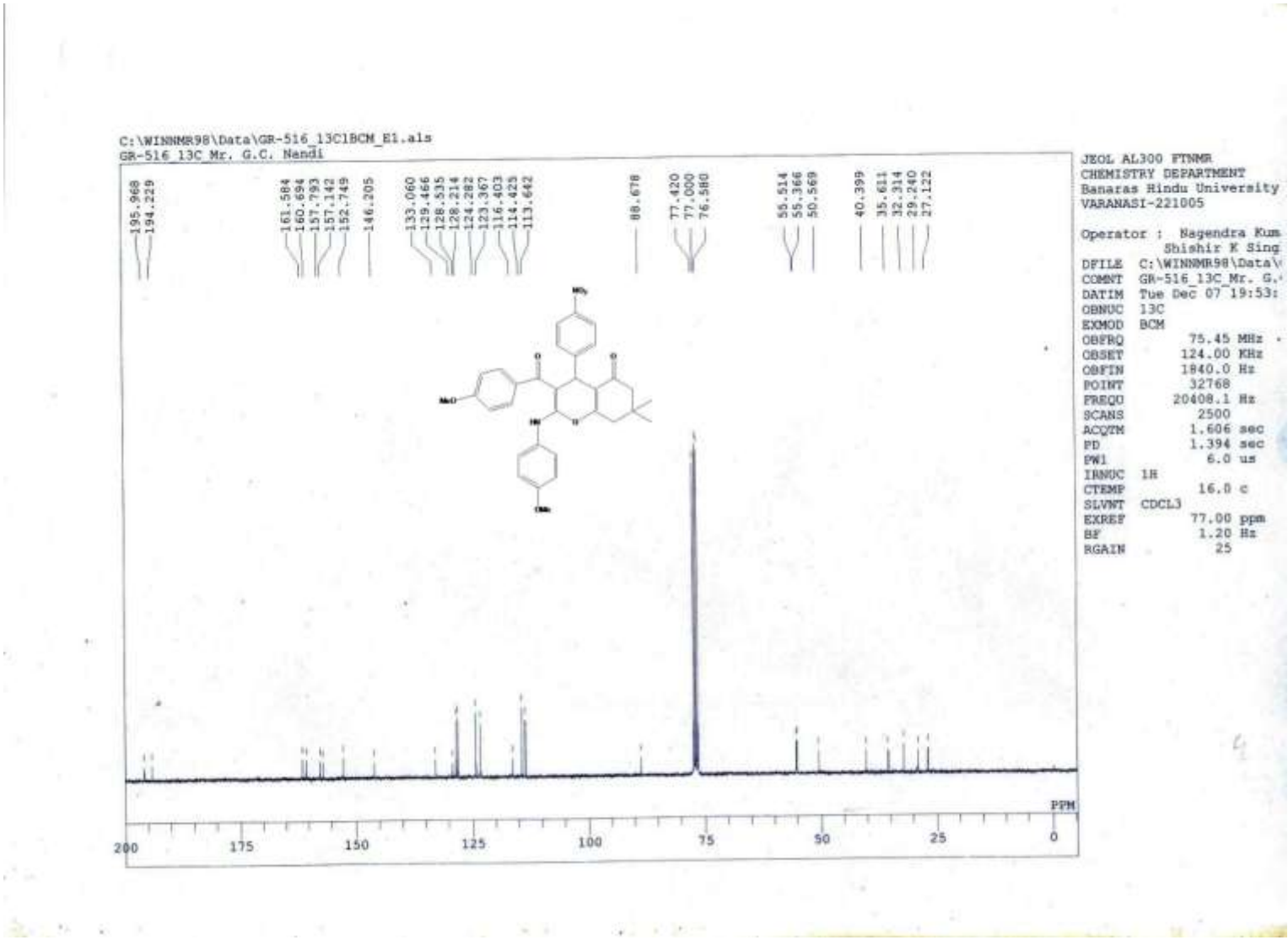
^{13}C spectrum of 6c



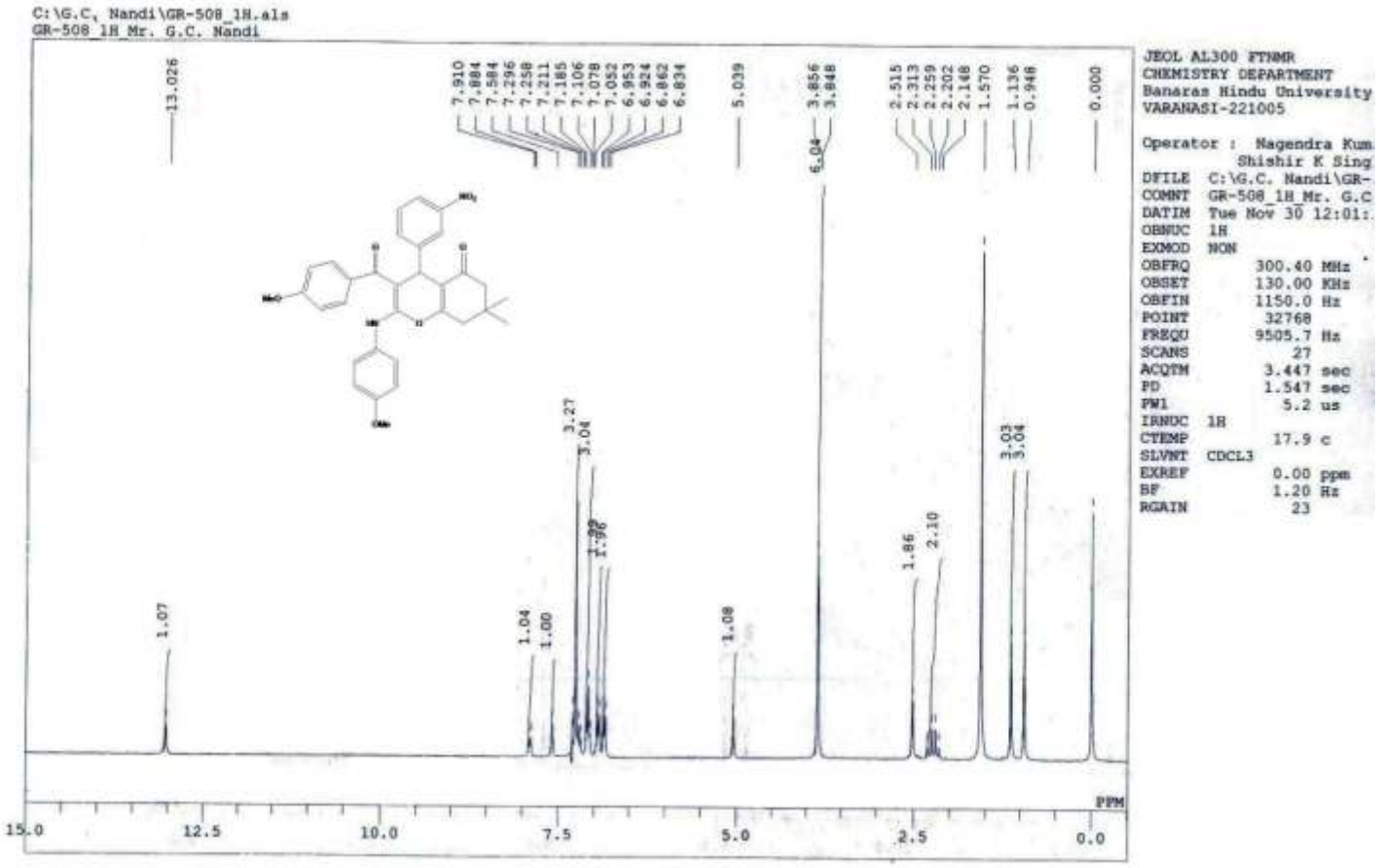
^{1}H spectrum of 6d



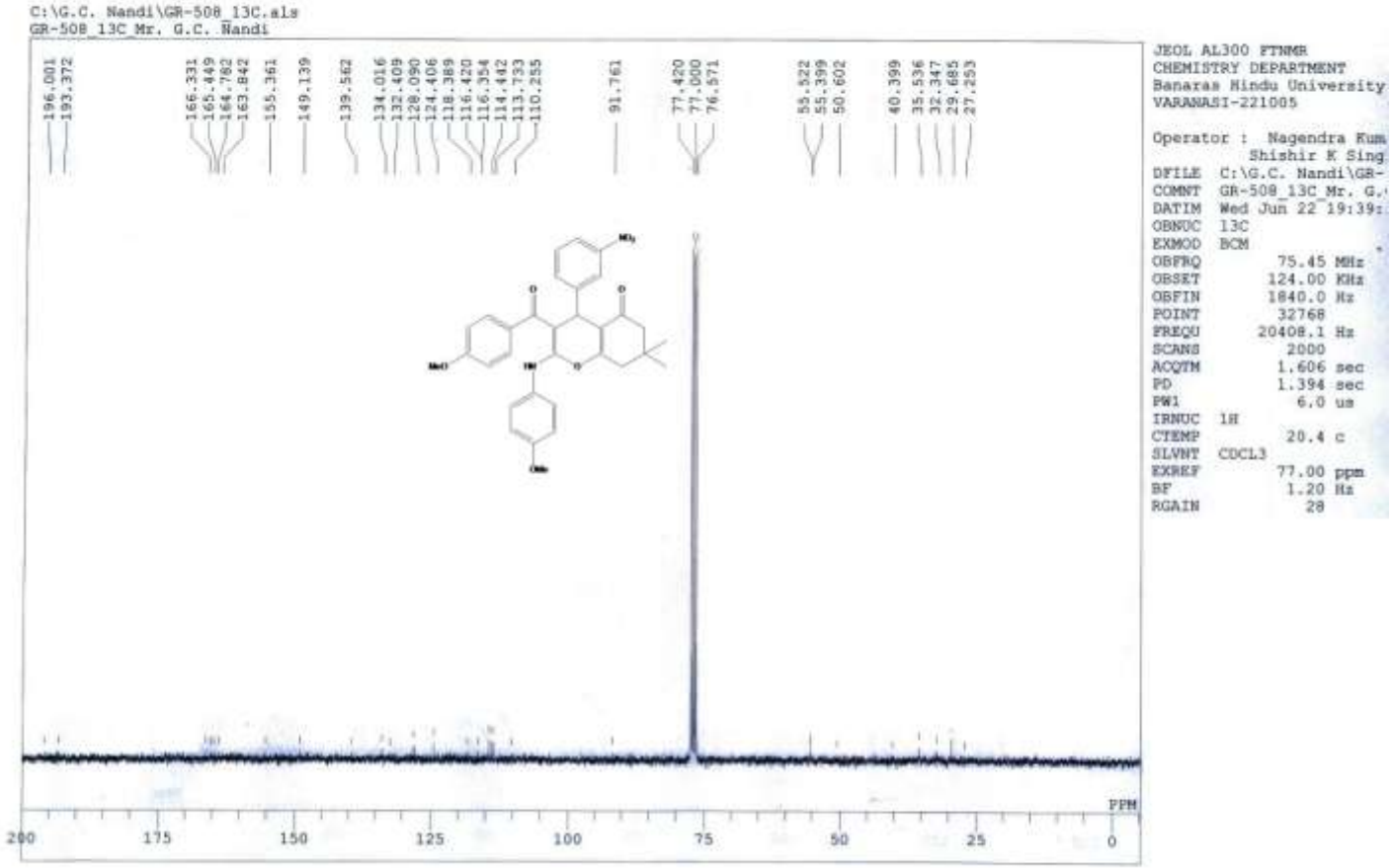
^{13}C spectrum of 6d



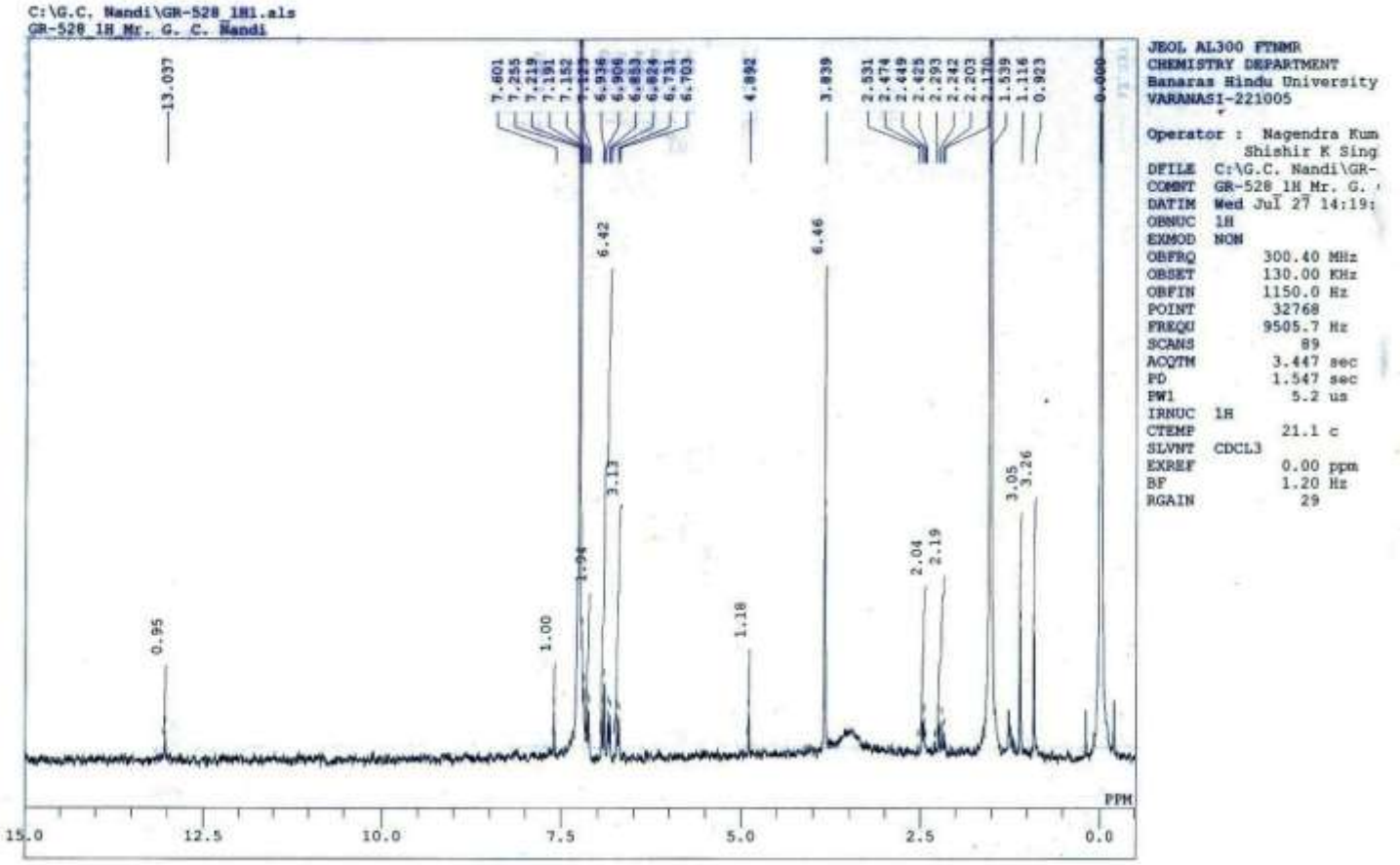
^{1}H spectrum of 6e



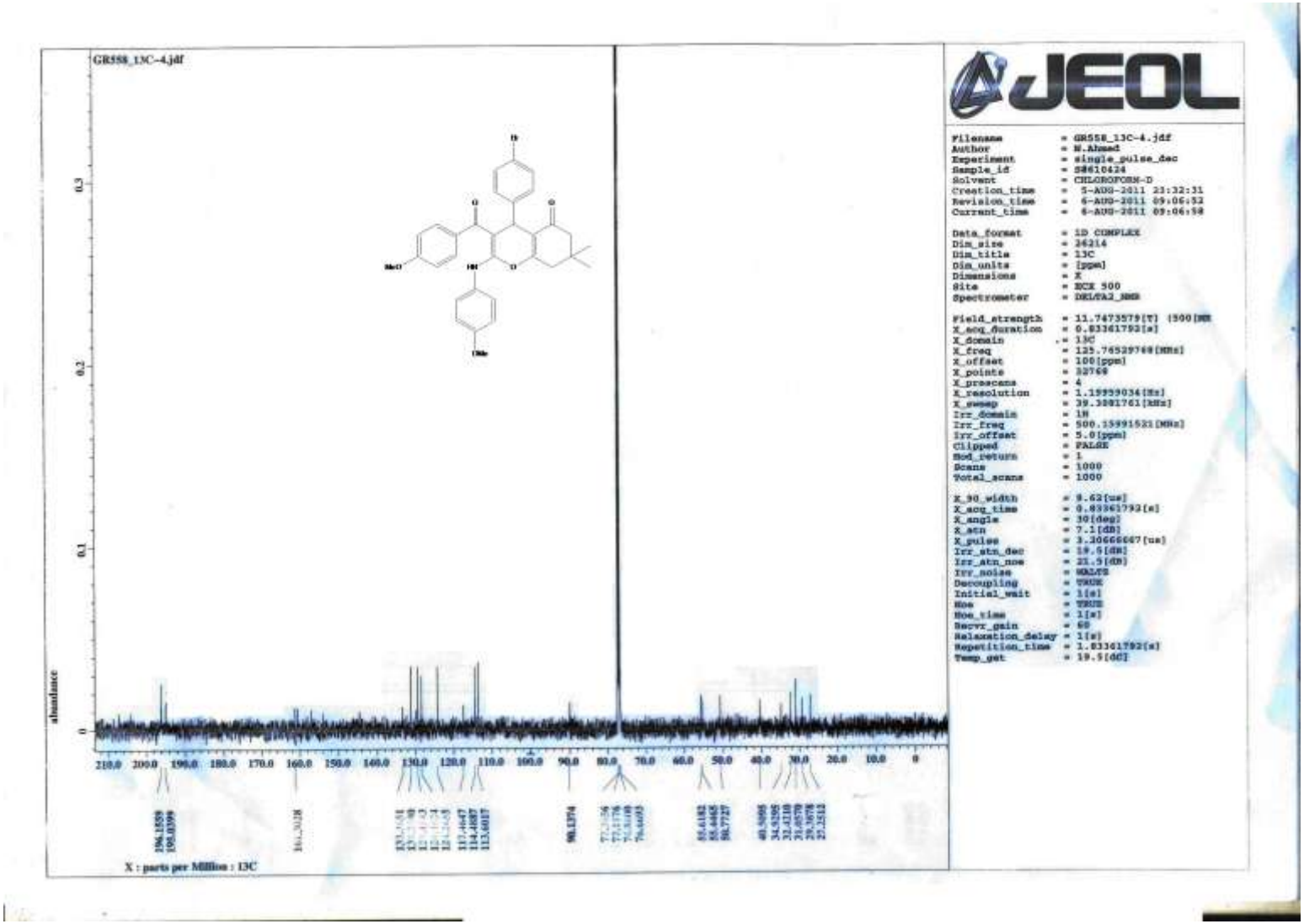
^{13}C spectrum of 6e



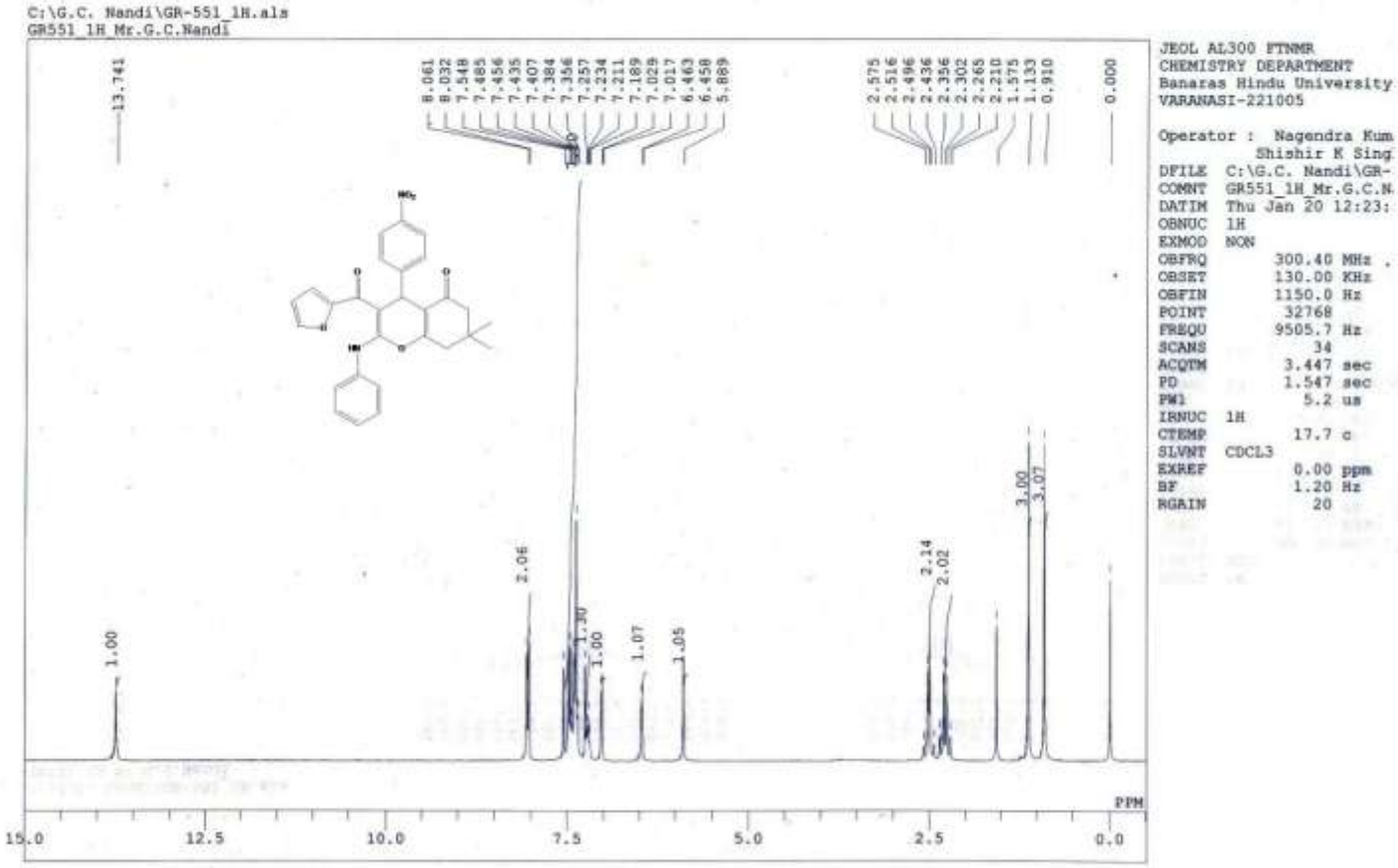
^{1}H spectrum of 6f



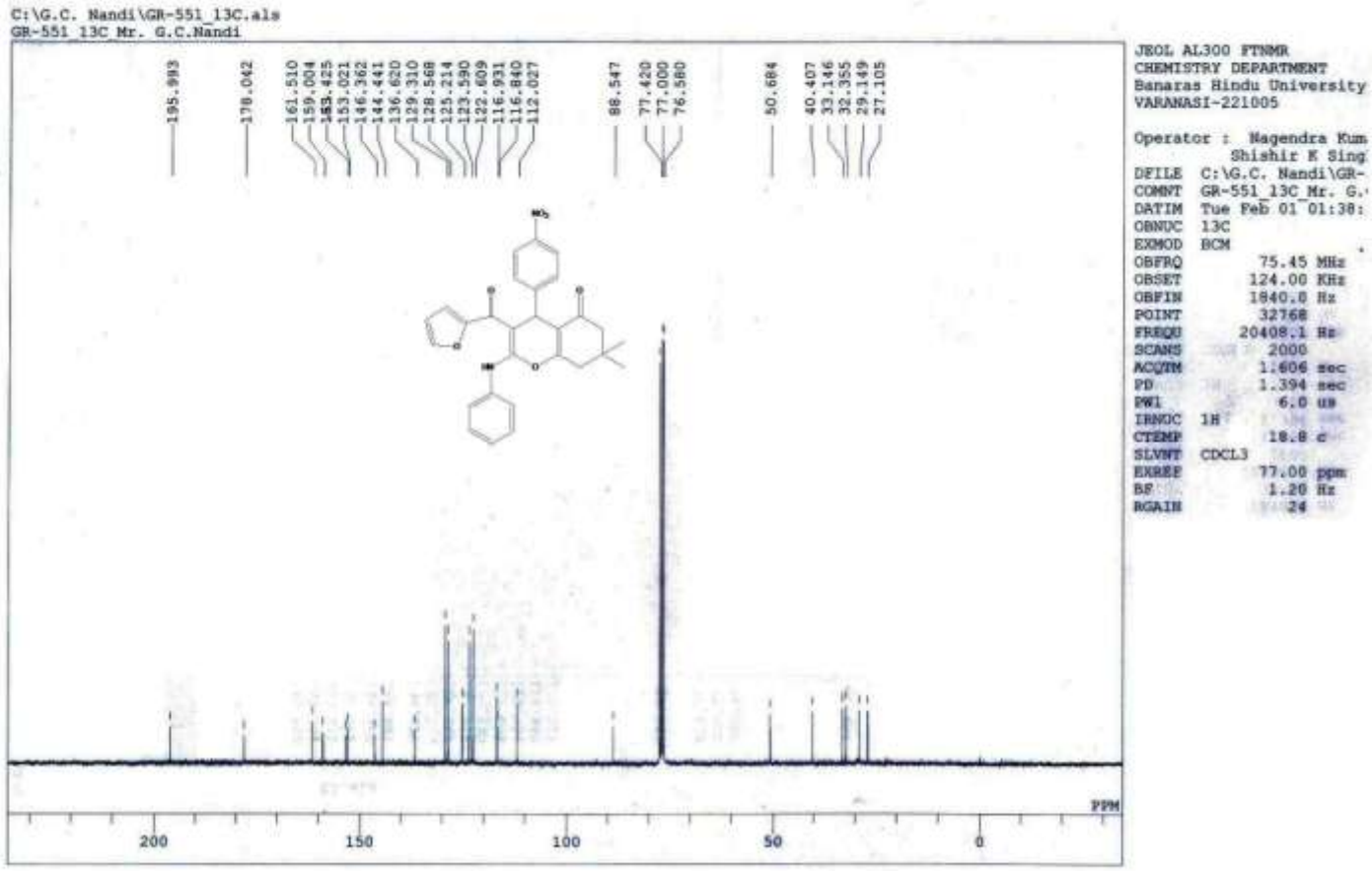
^{13}C spectrum of 6f



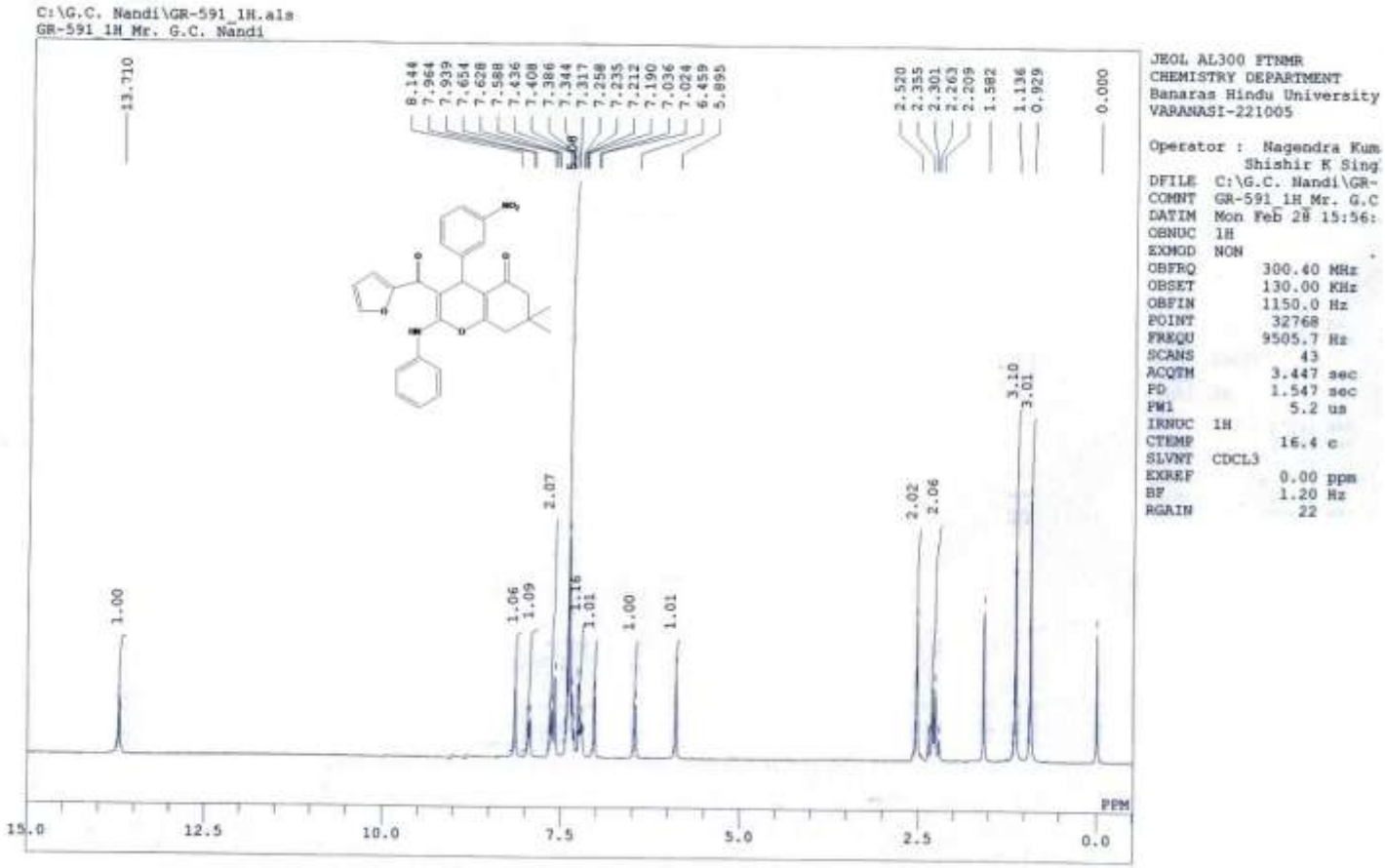
^{1}H spectrum of 6g



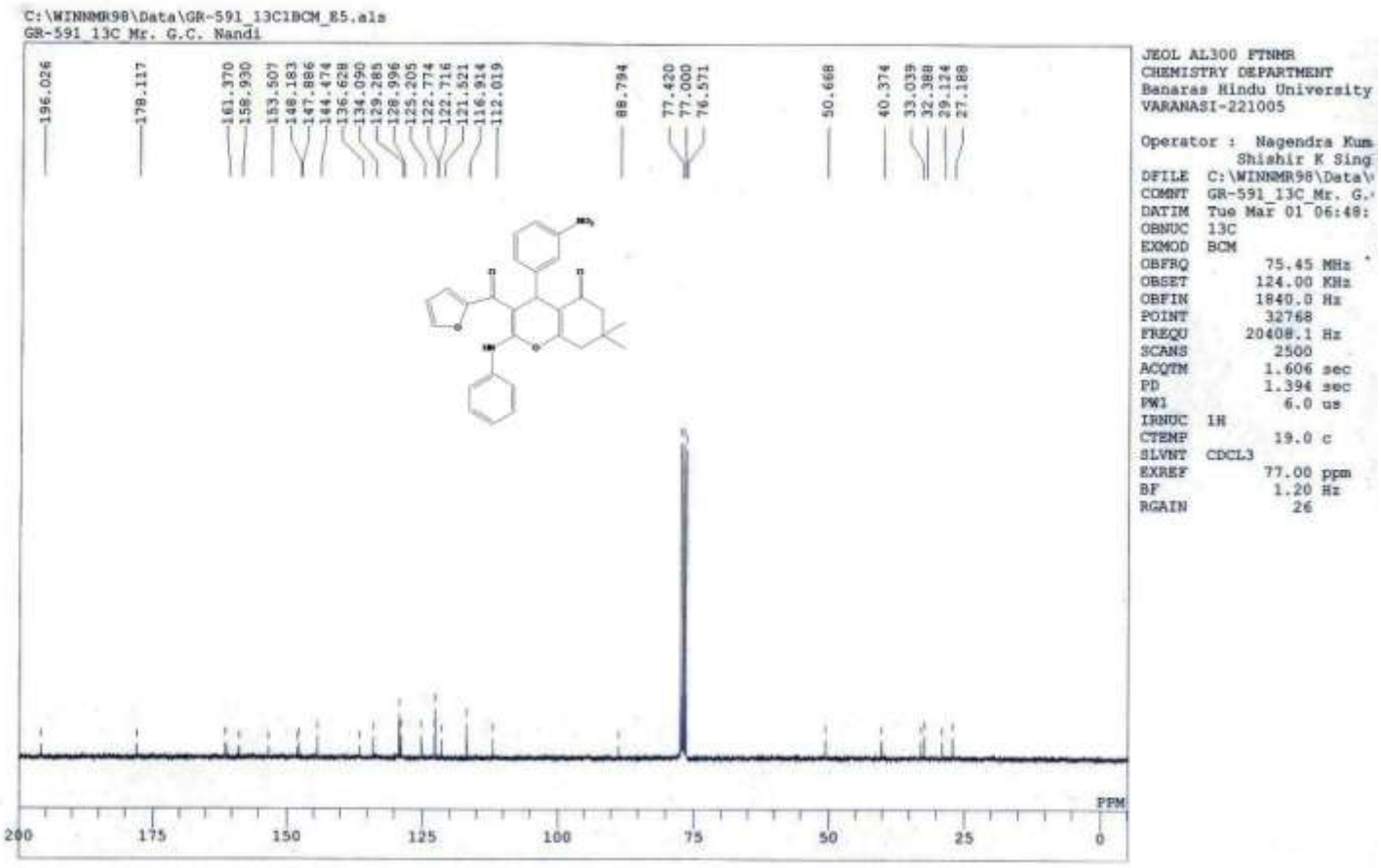
^{13}C spectrum of 6g



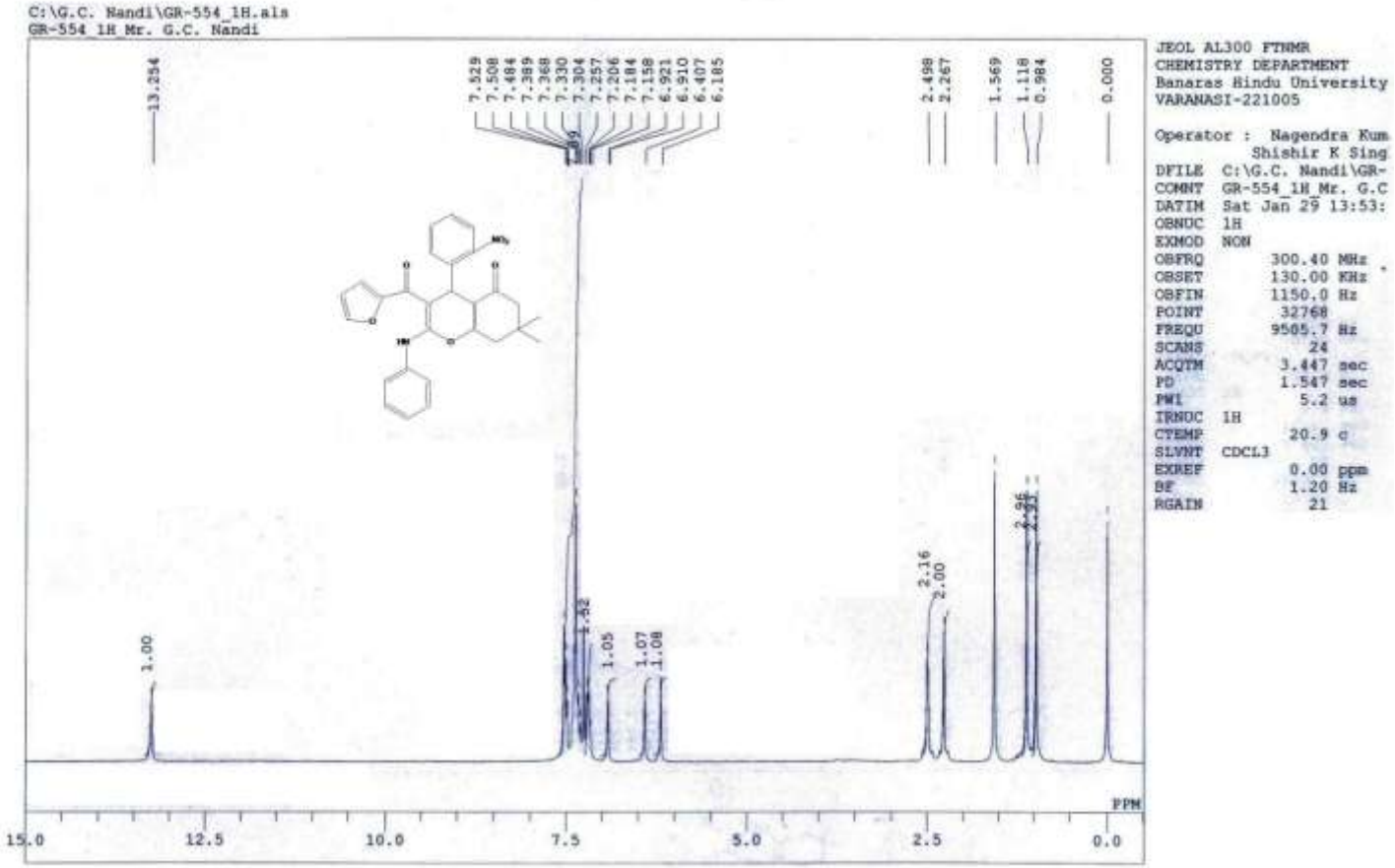
^{1}H spectrum of 6h



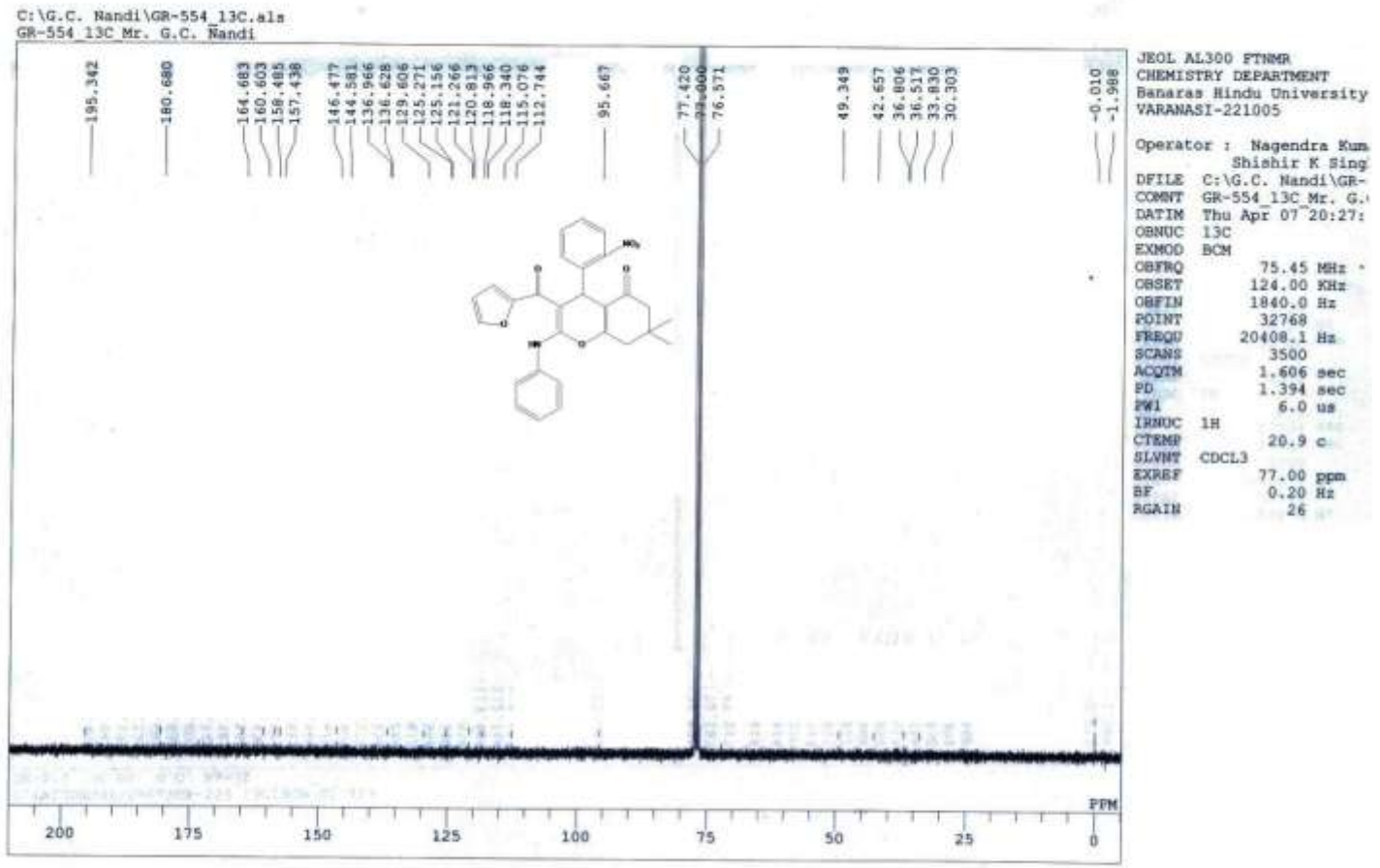
^{13}C spectrum of 6h



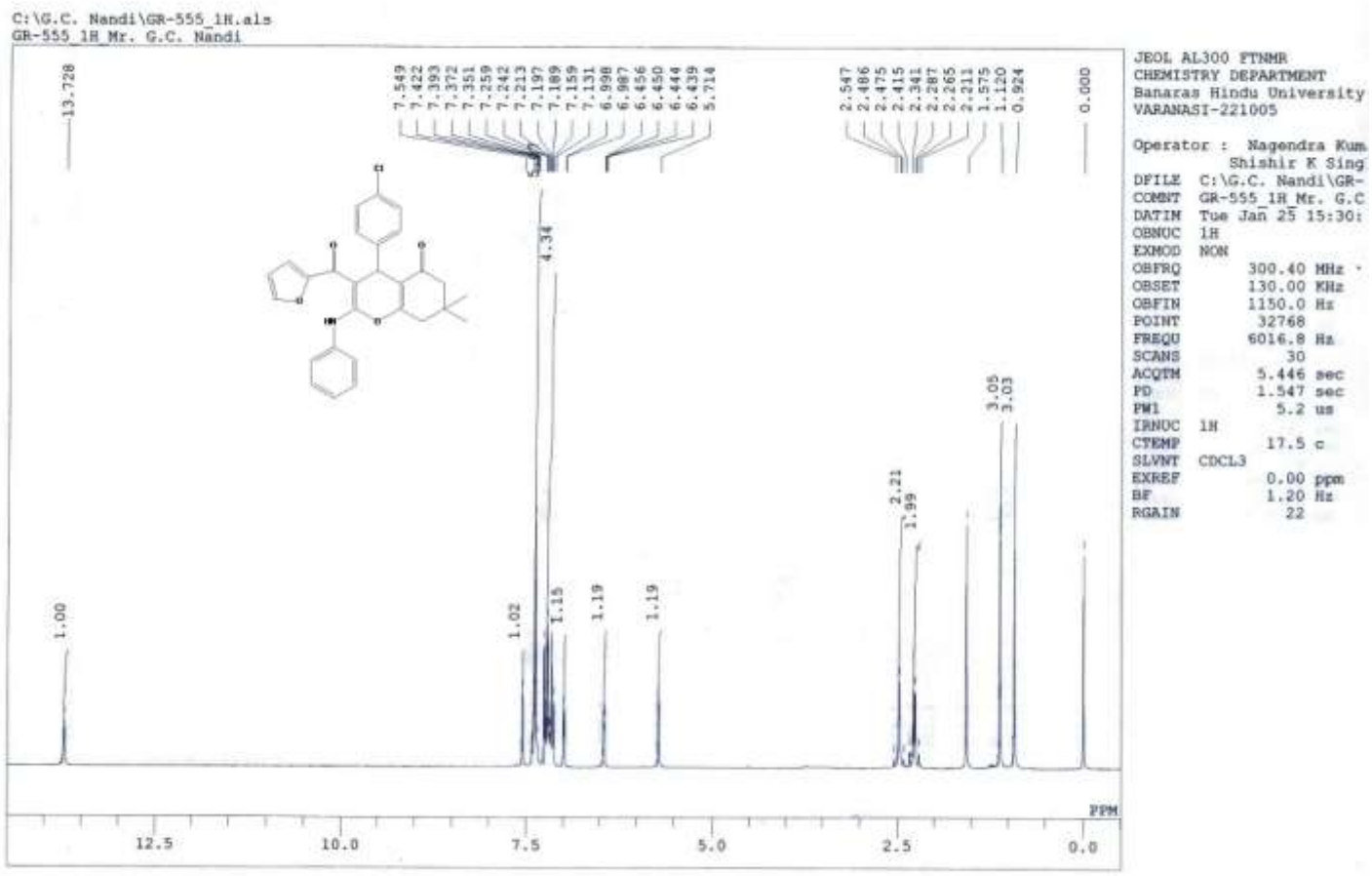
^{1}H spectrum of 6i



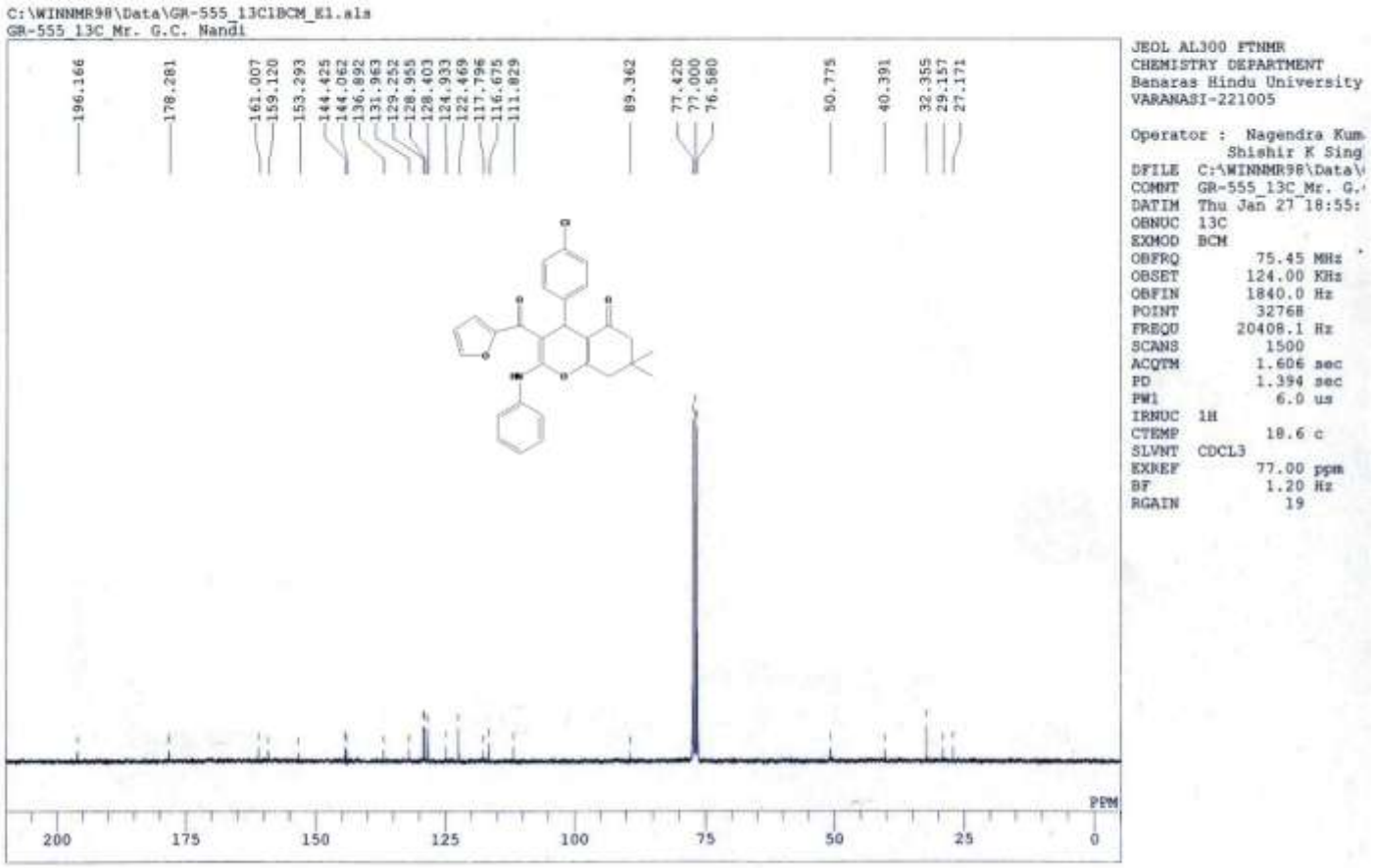
^{13}C spectrum of 6i



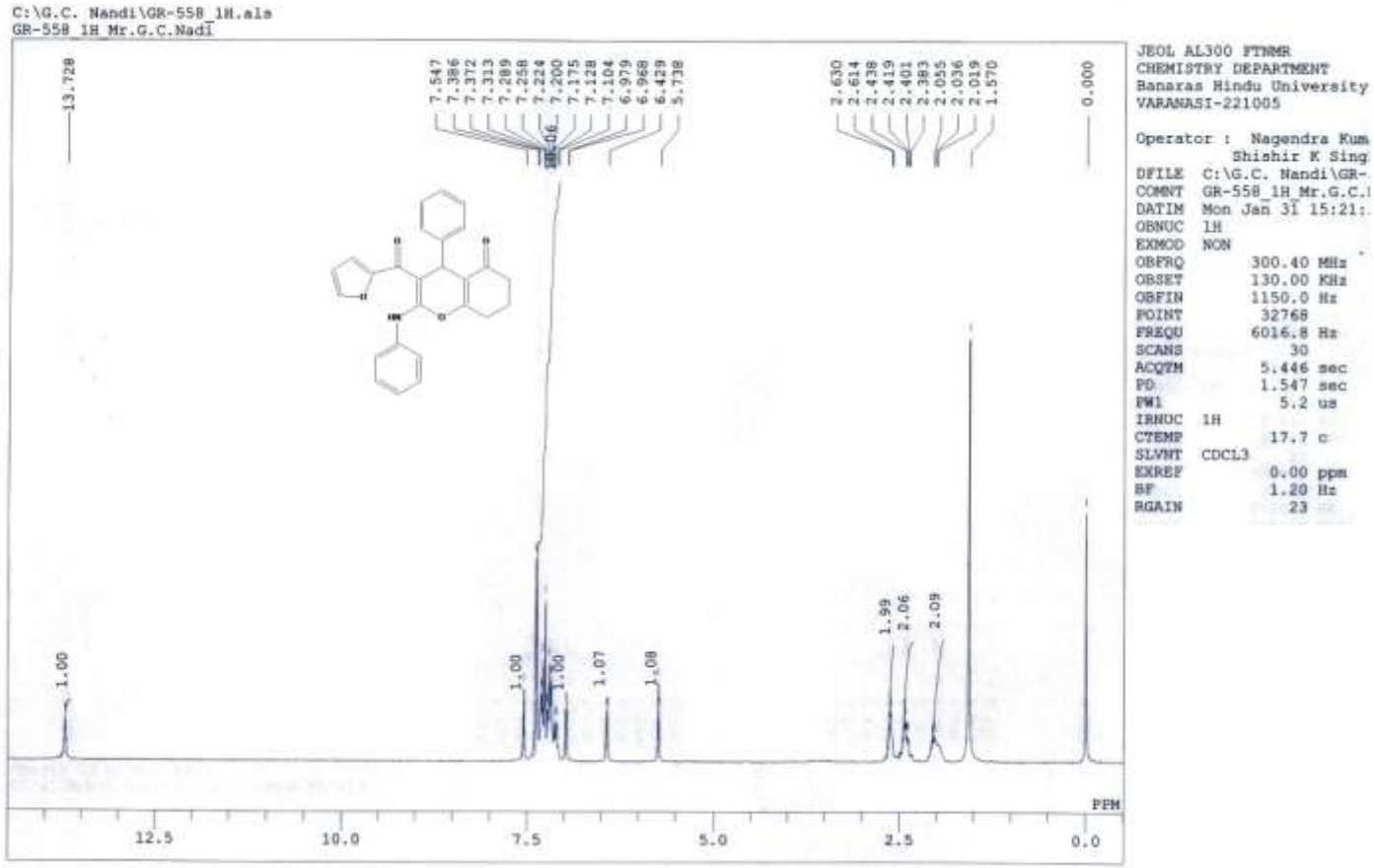
^{1}H spectrum of 6j



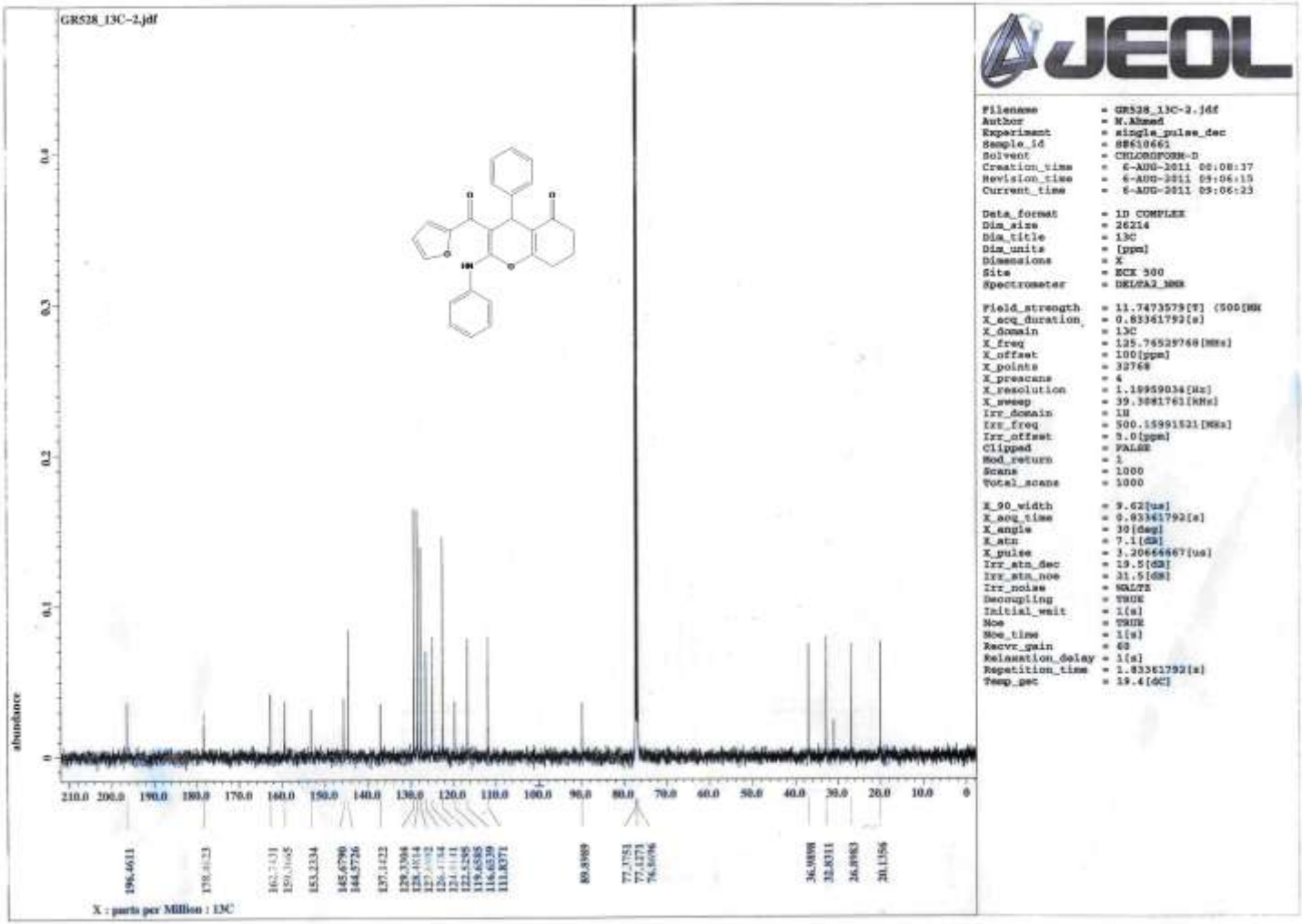
^{13}C spectrum of 6j



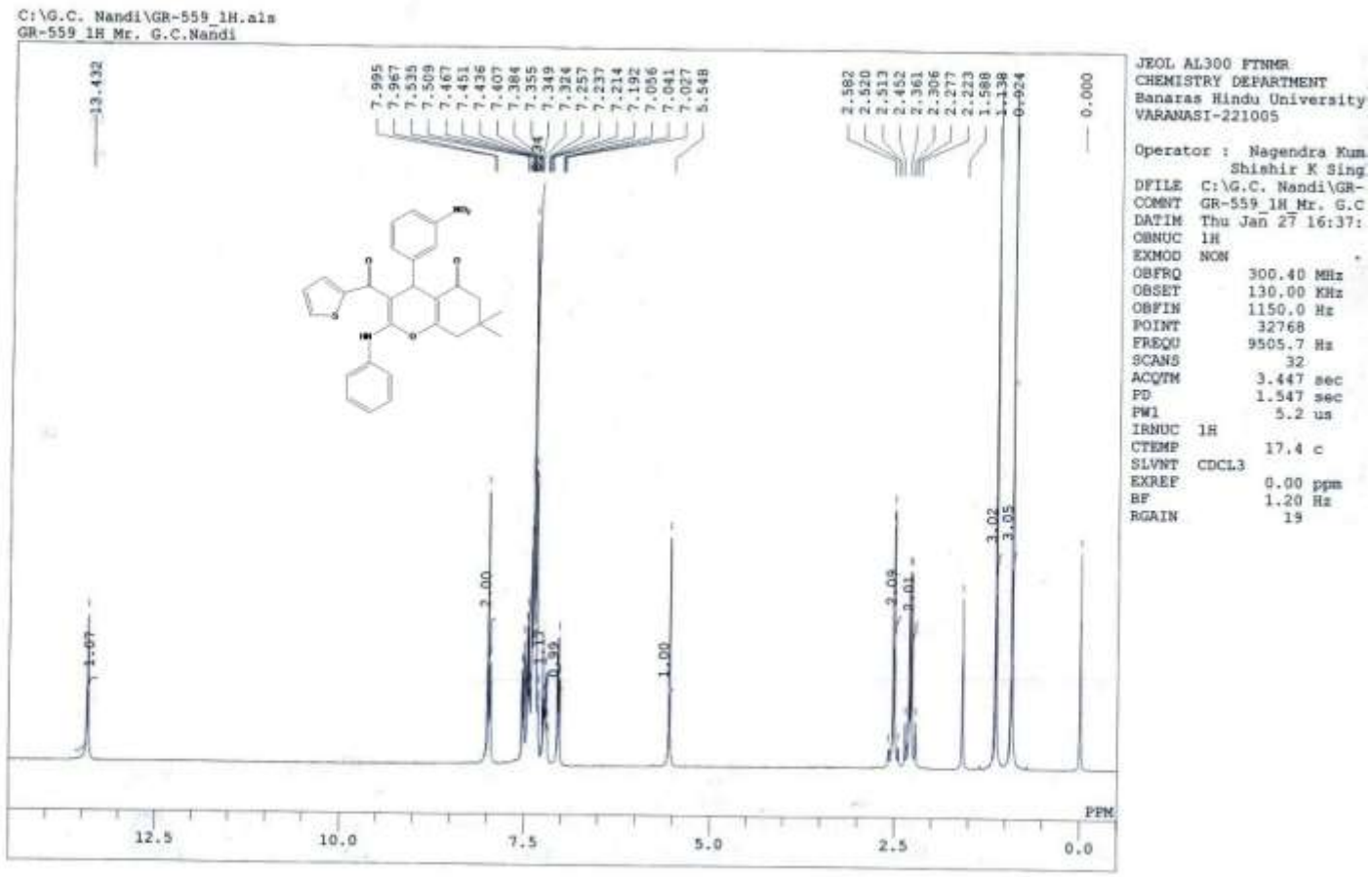
^{1}H spectrum of 6k



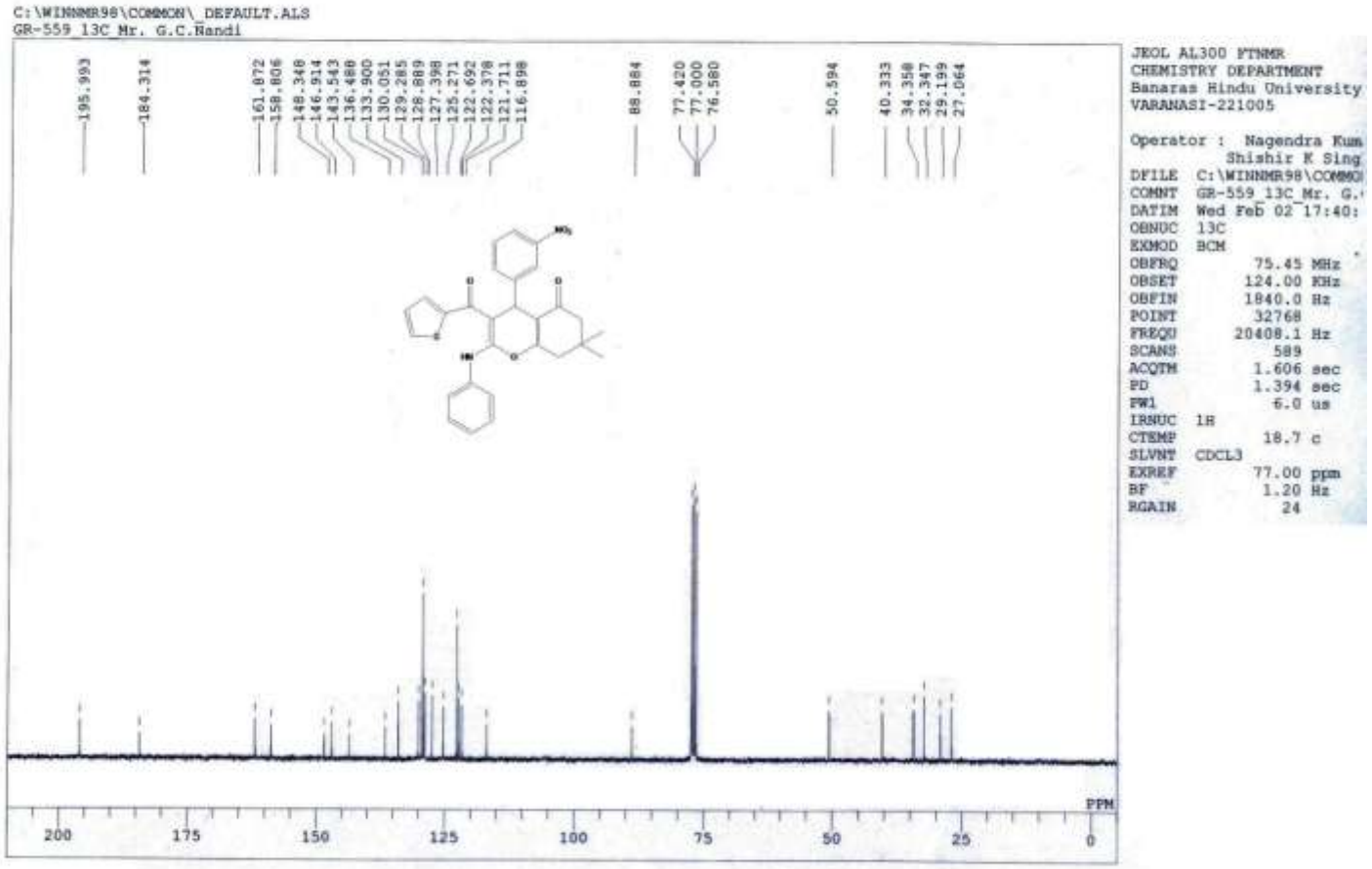
^{13}C spectrum of 6k



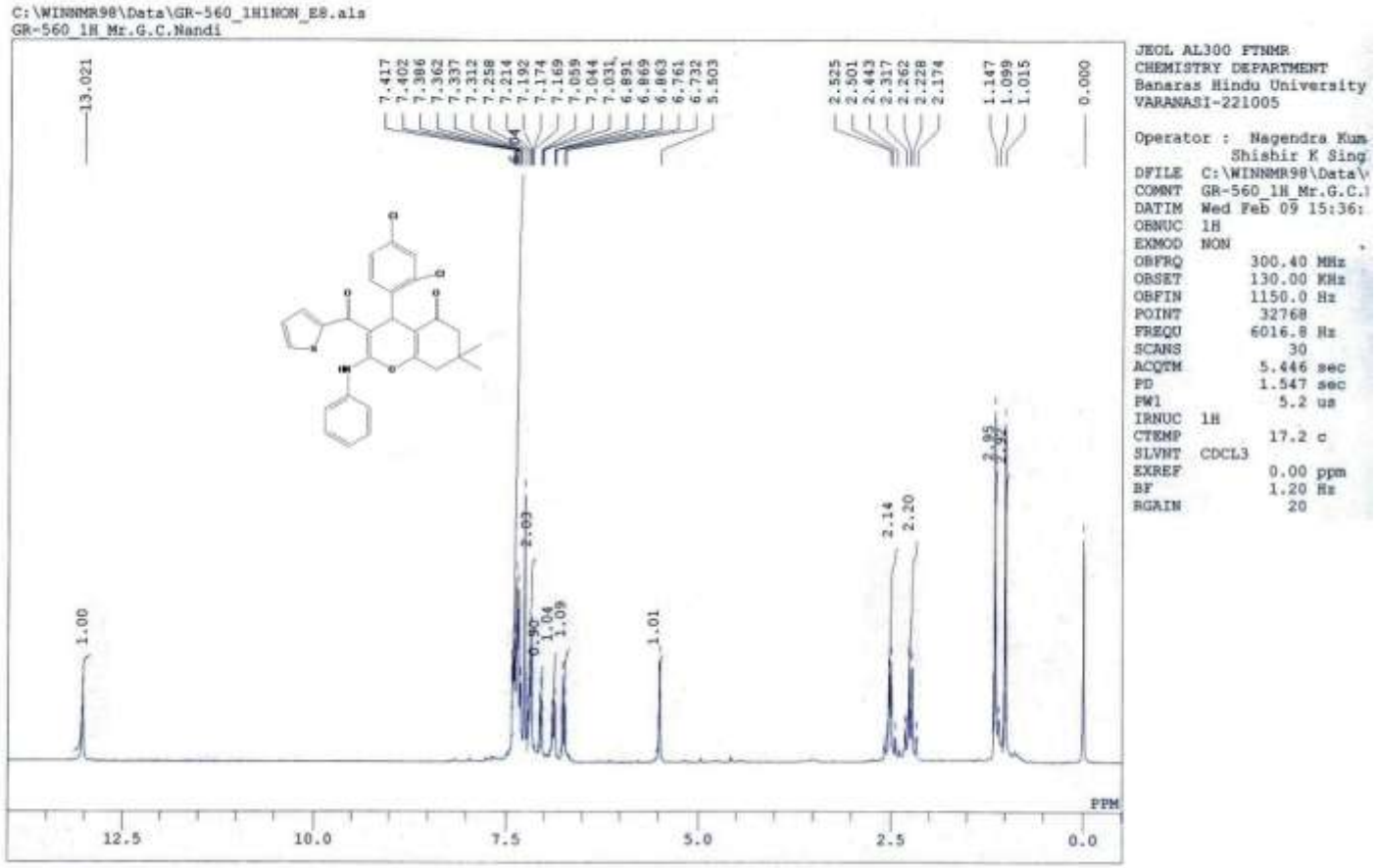
^{1}H spectrum of 6l



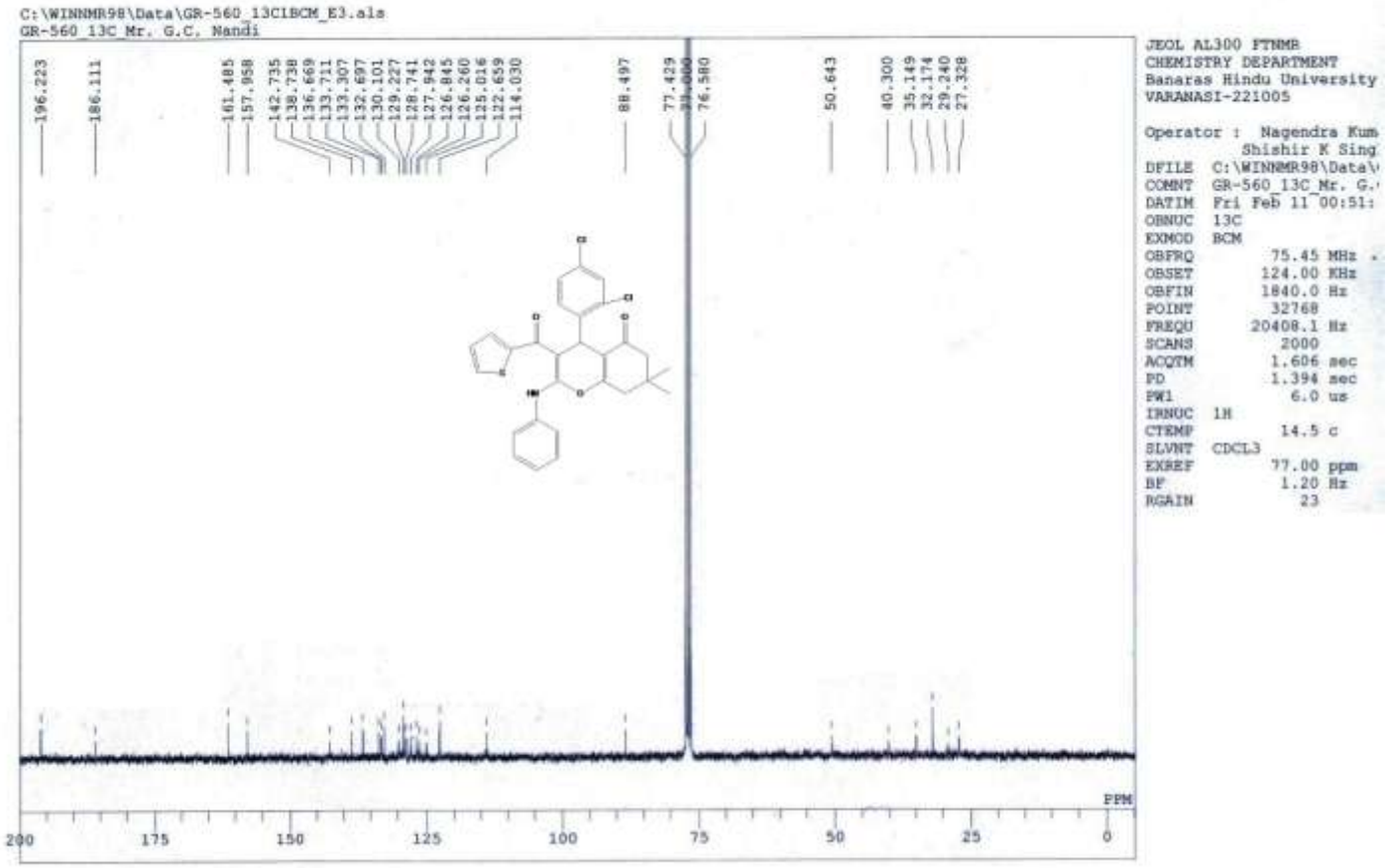
^{13}C spectrum of 6l



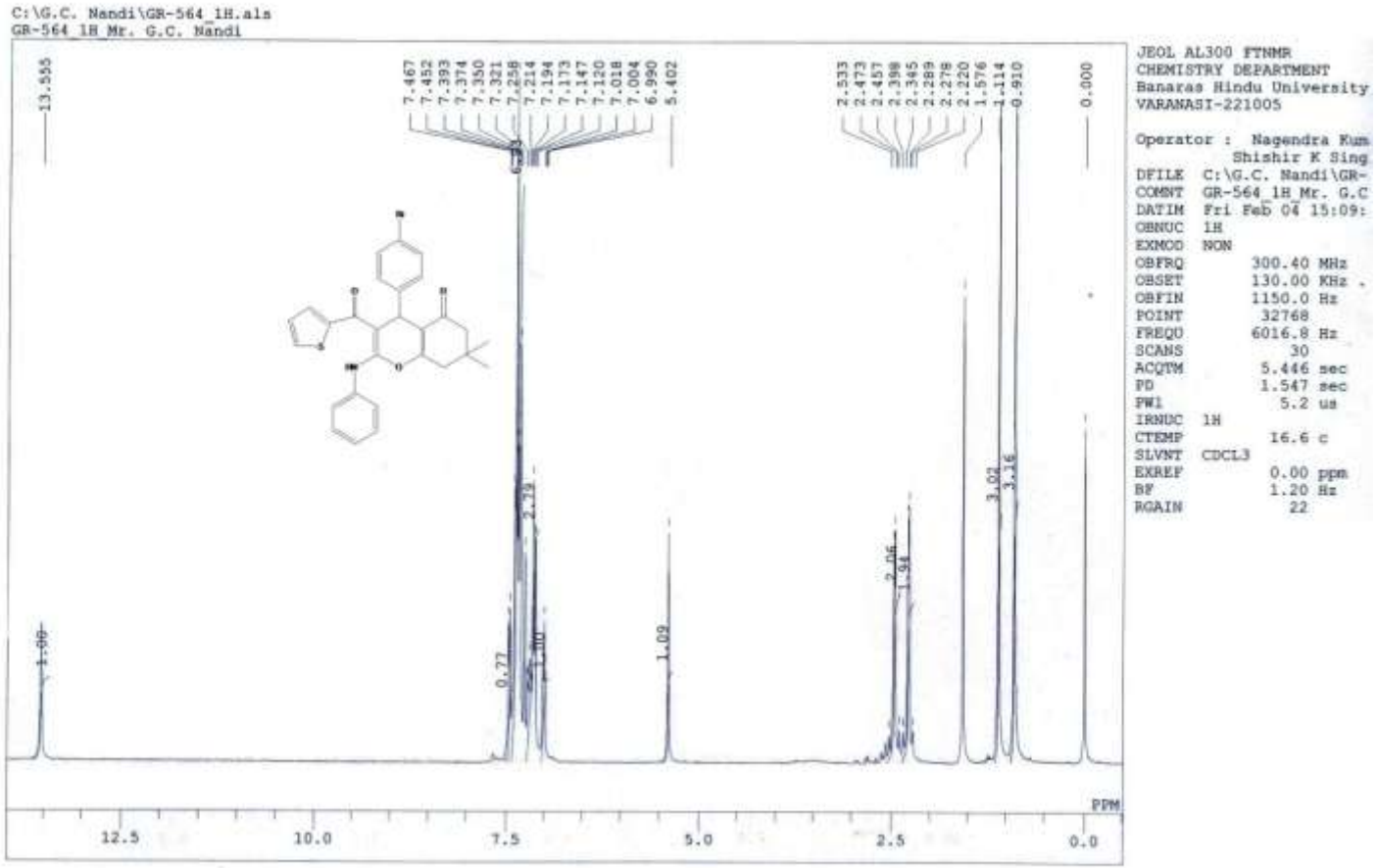
^{1}H spectrum of 6m



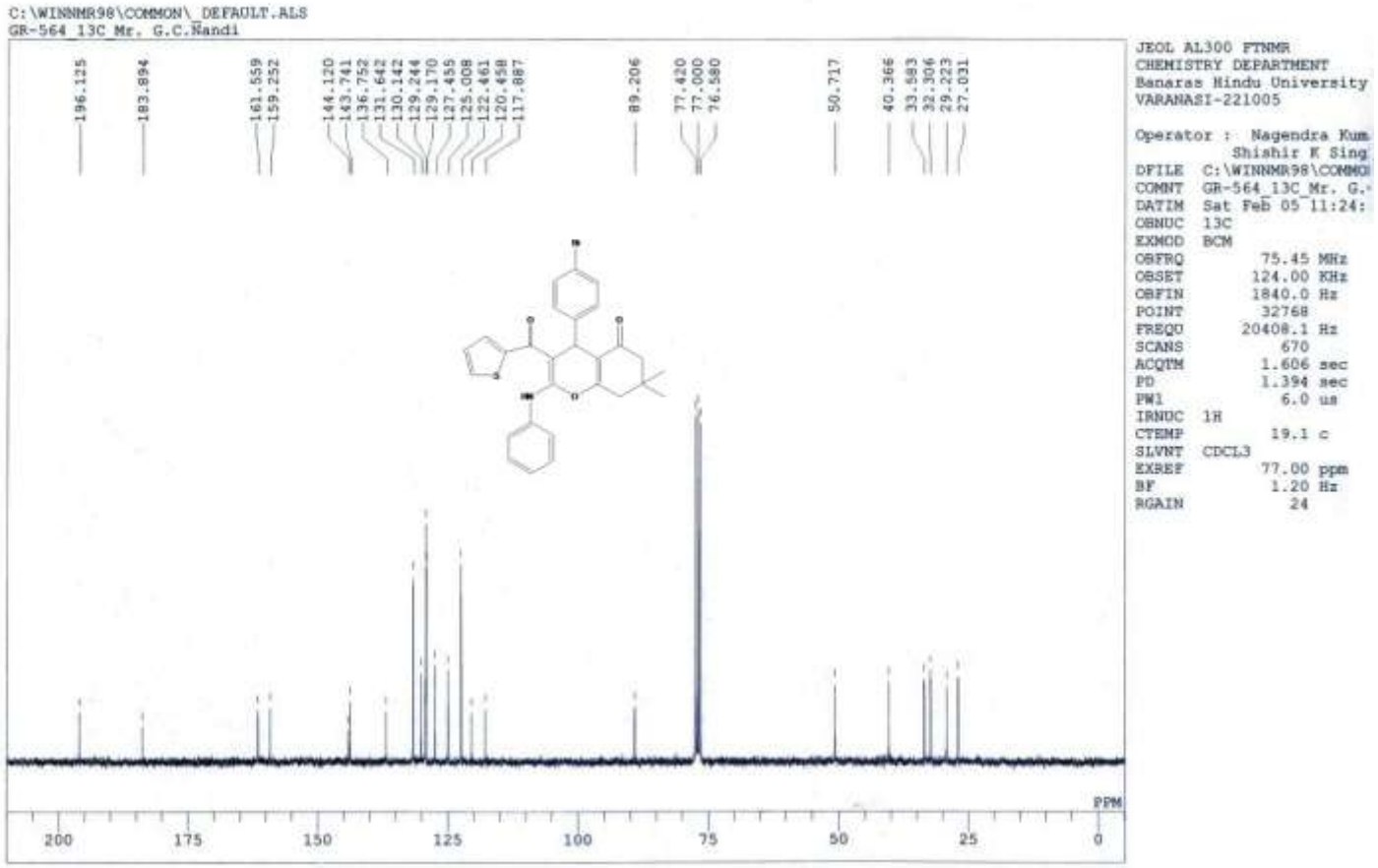
^{13}C spectrum of 6m



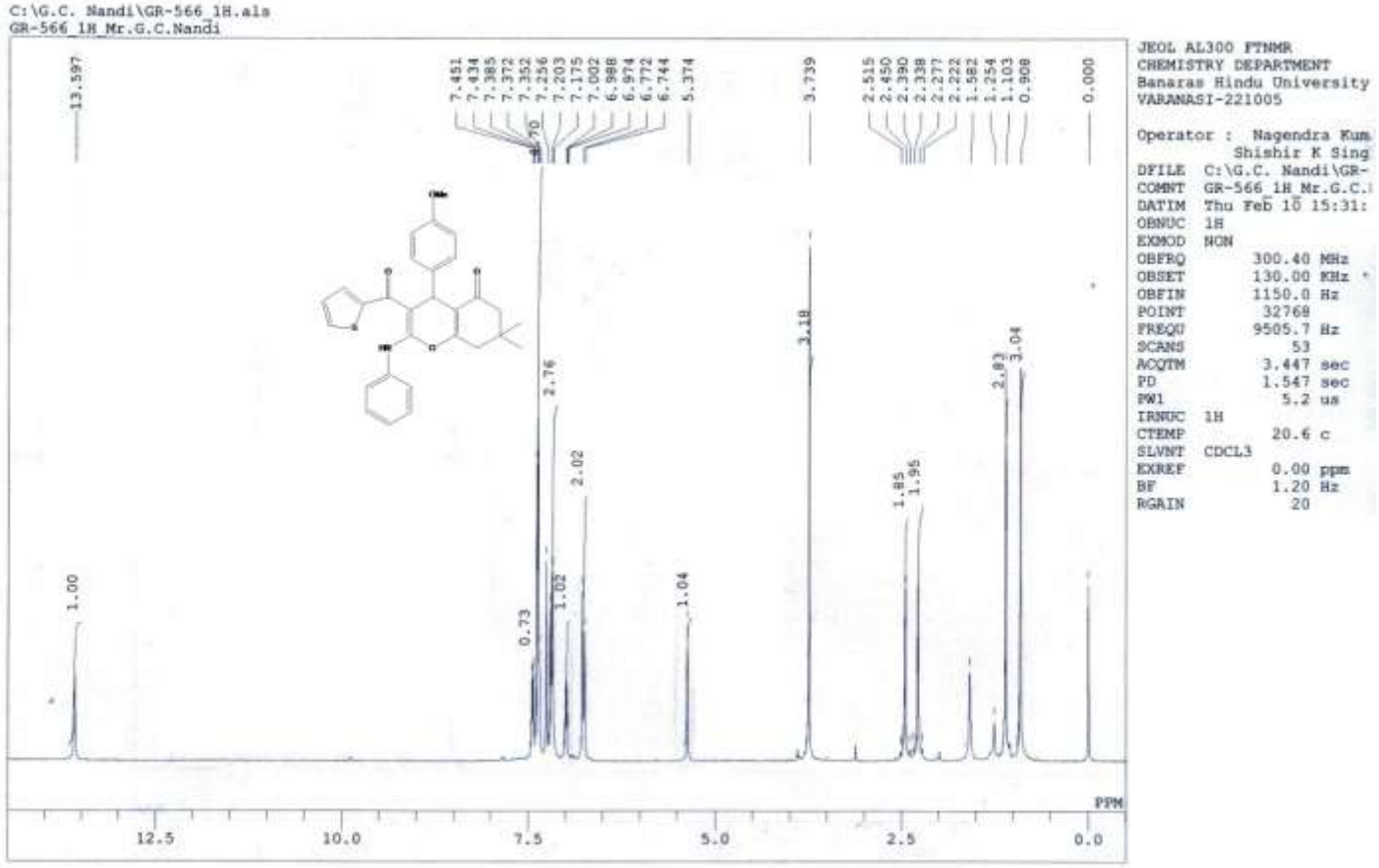
^{1}H spectrum of 6n



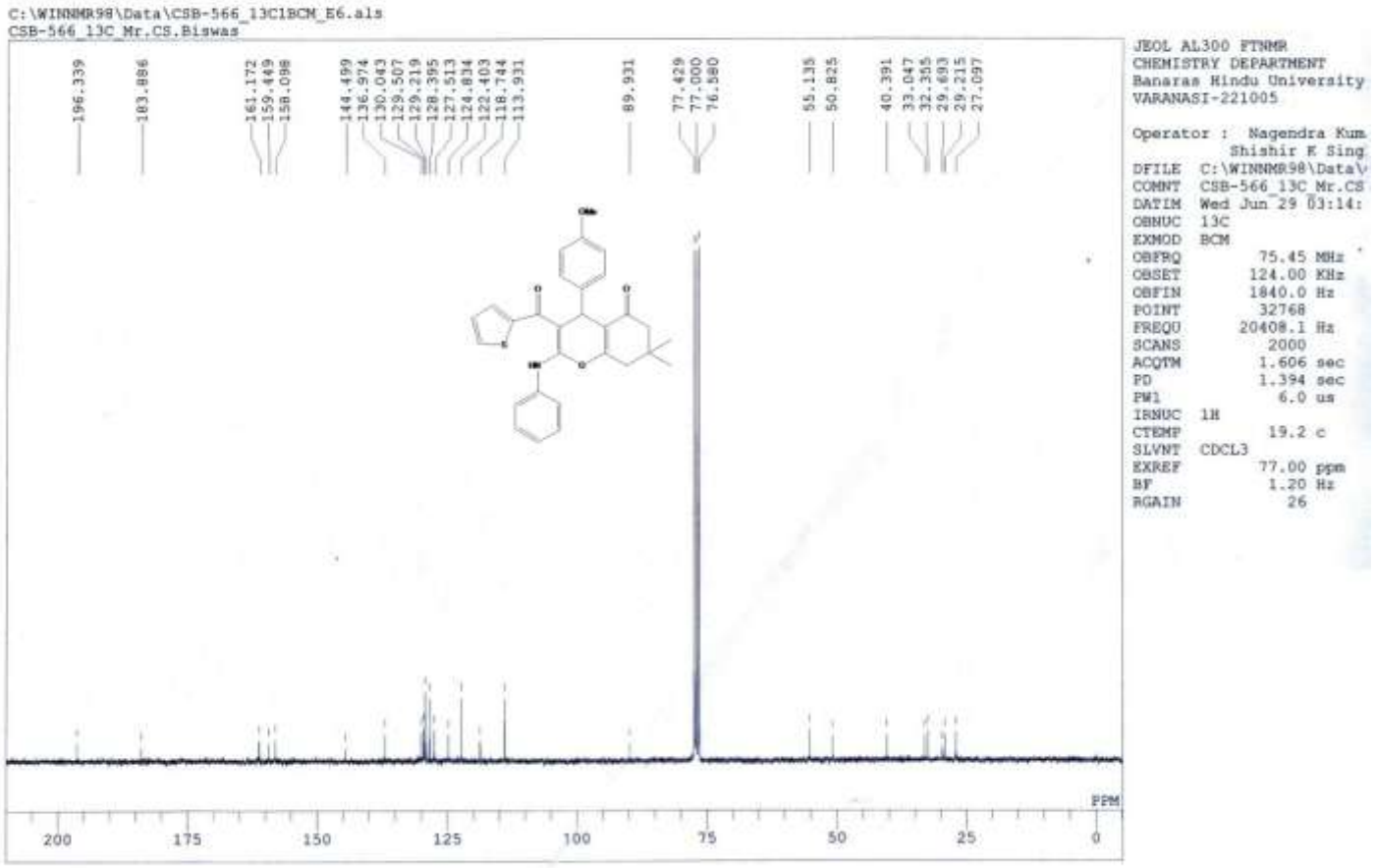
^{13}C spectrum of 6n



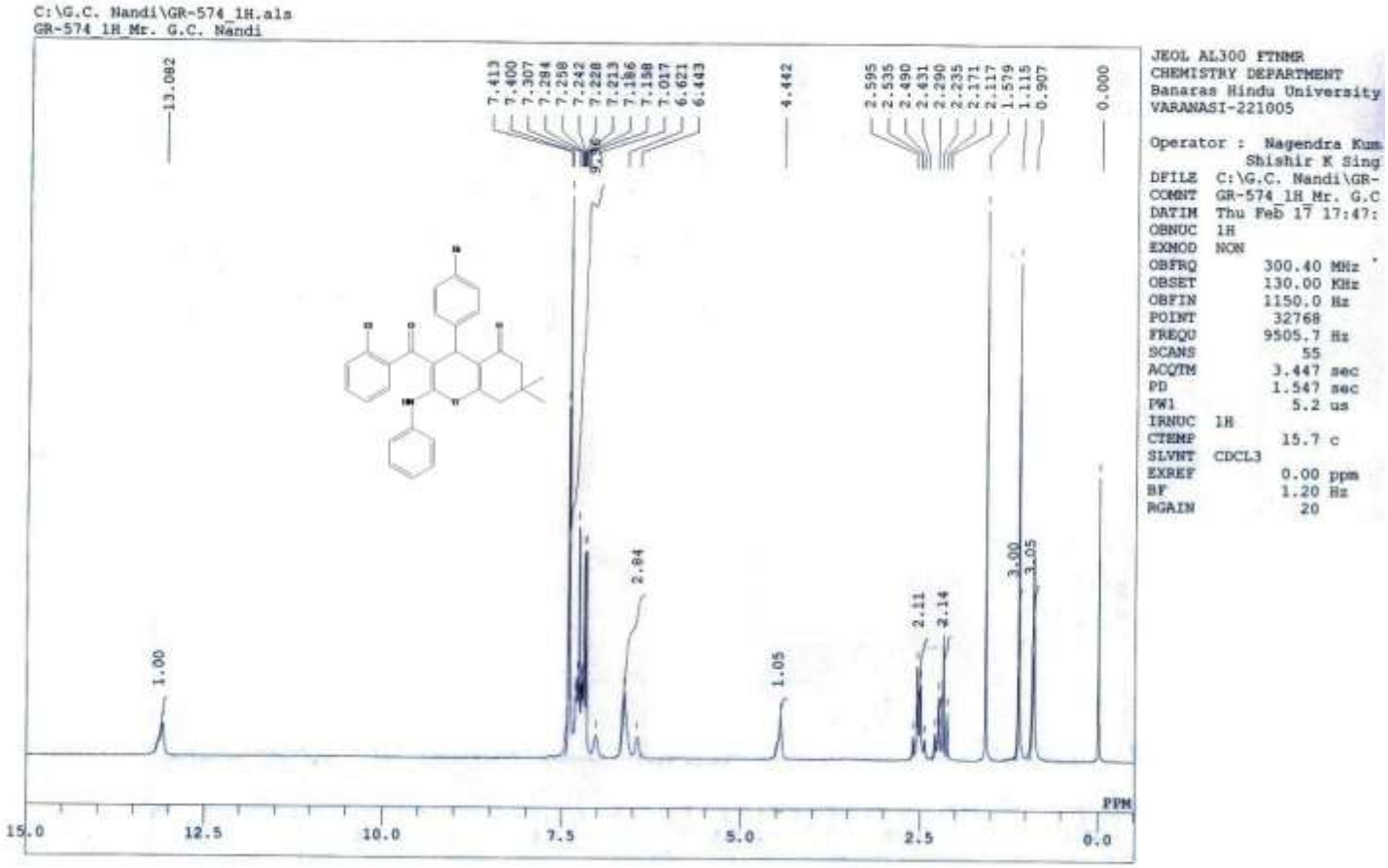
^{1}H spectrum of 6o



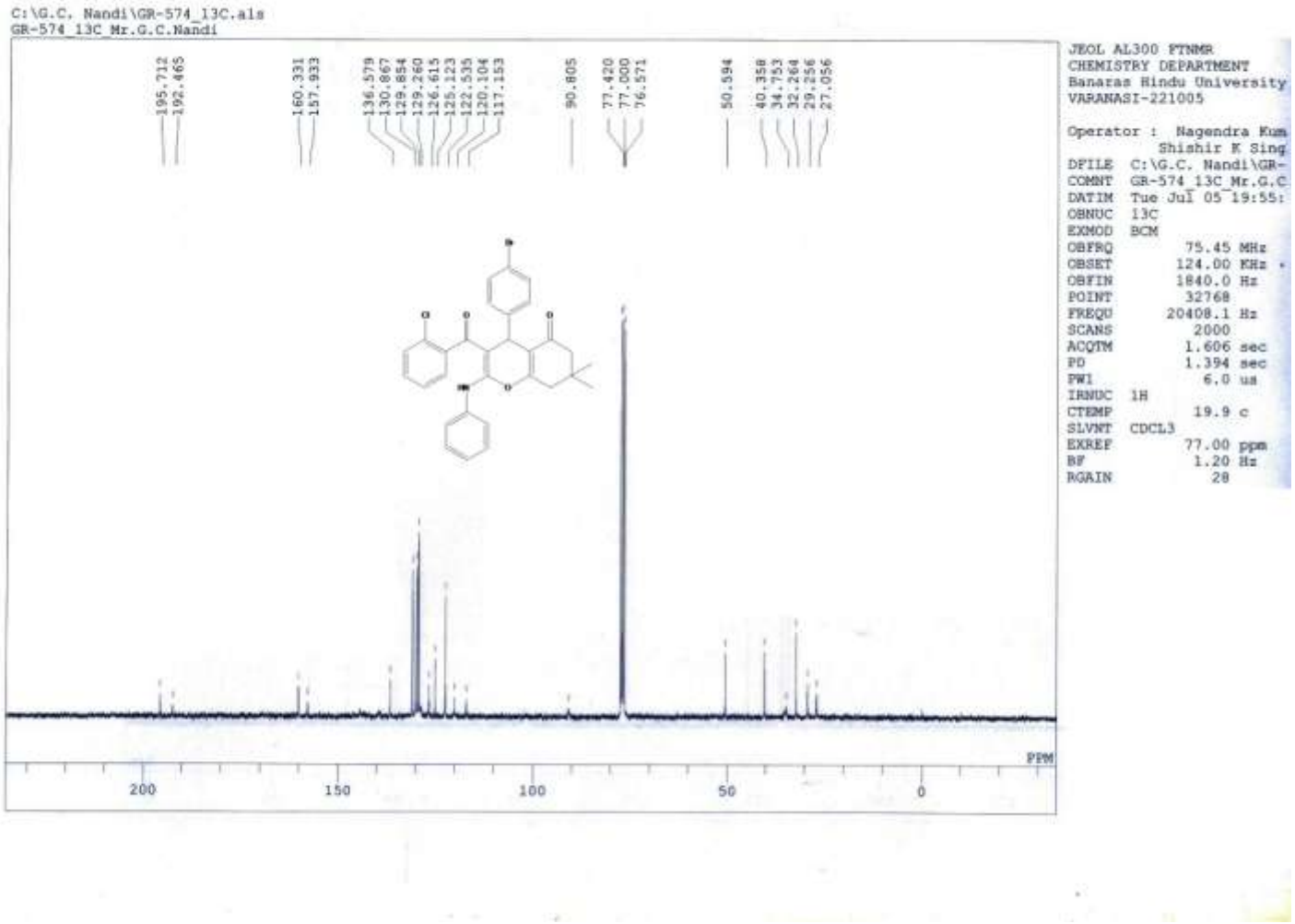
^{13}C spectrum of 6o



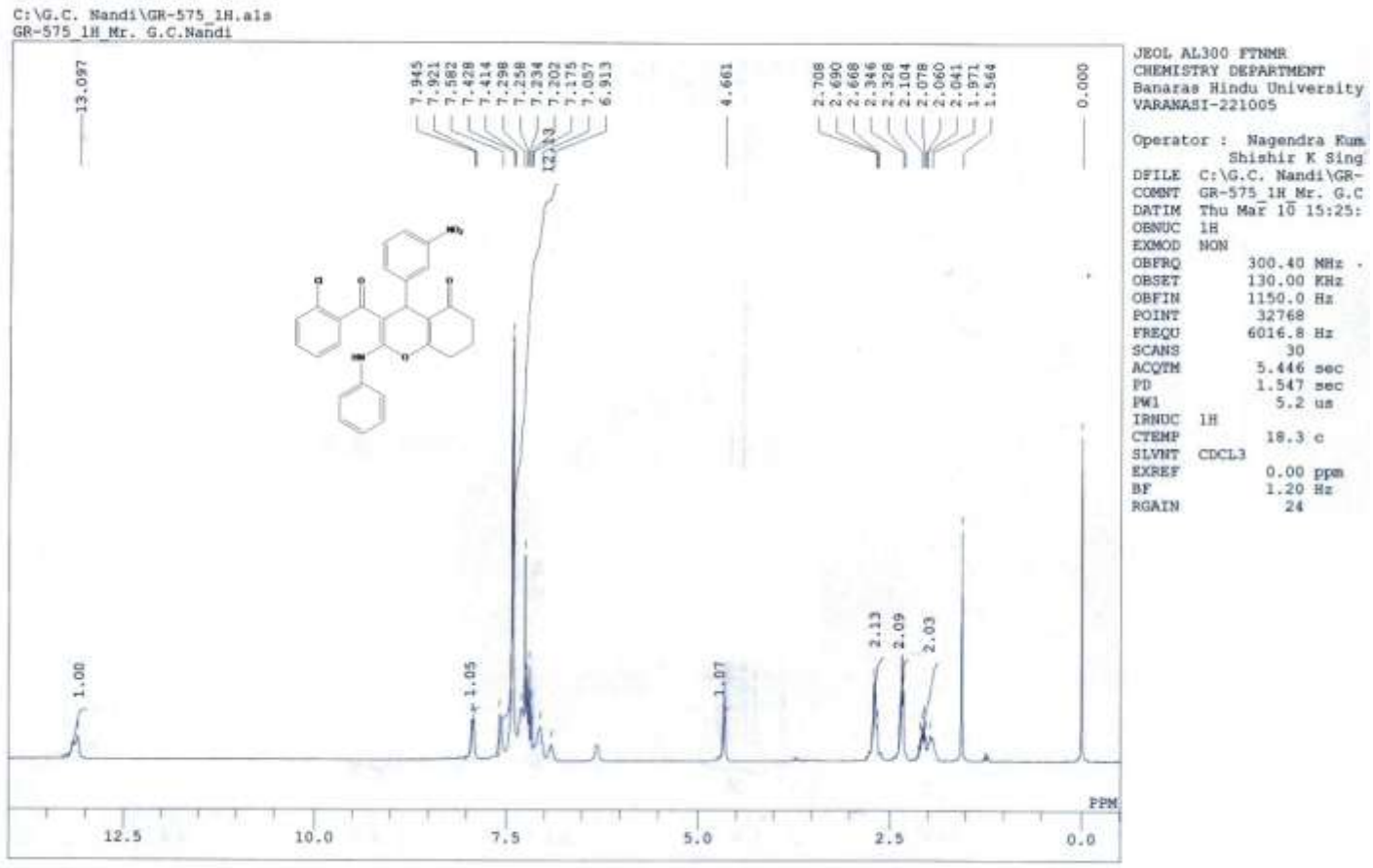
^{1}H spectrum of 6p



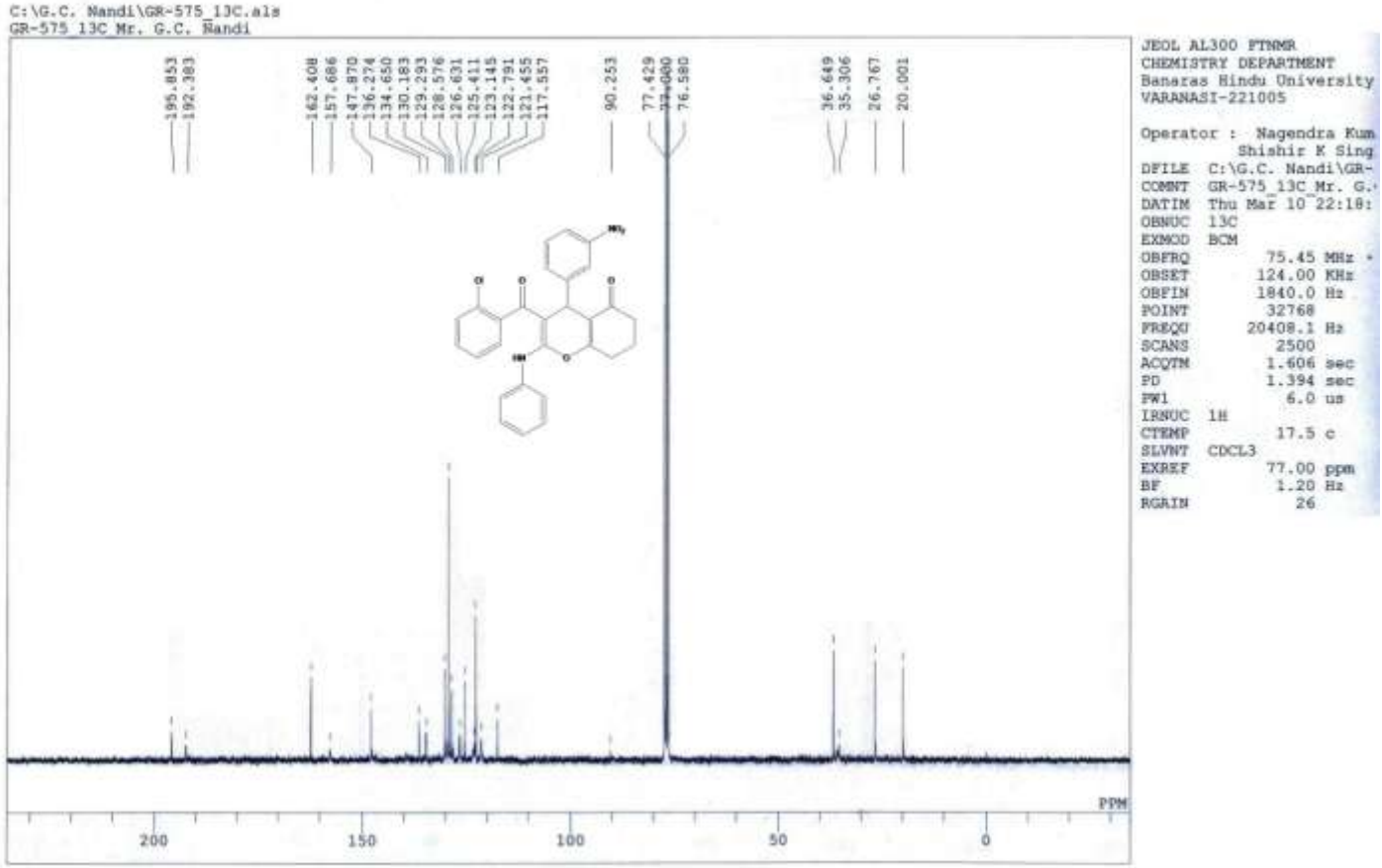
^{13}C spectrum of 6p



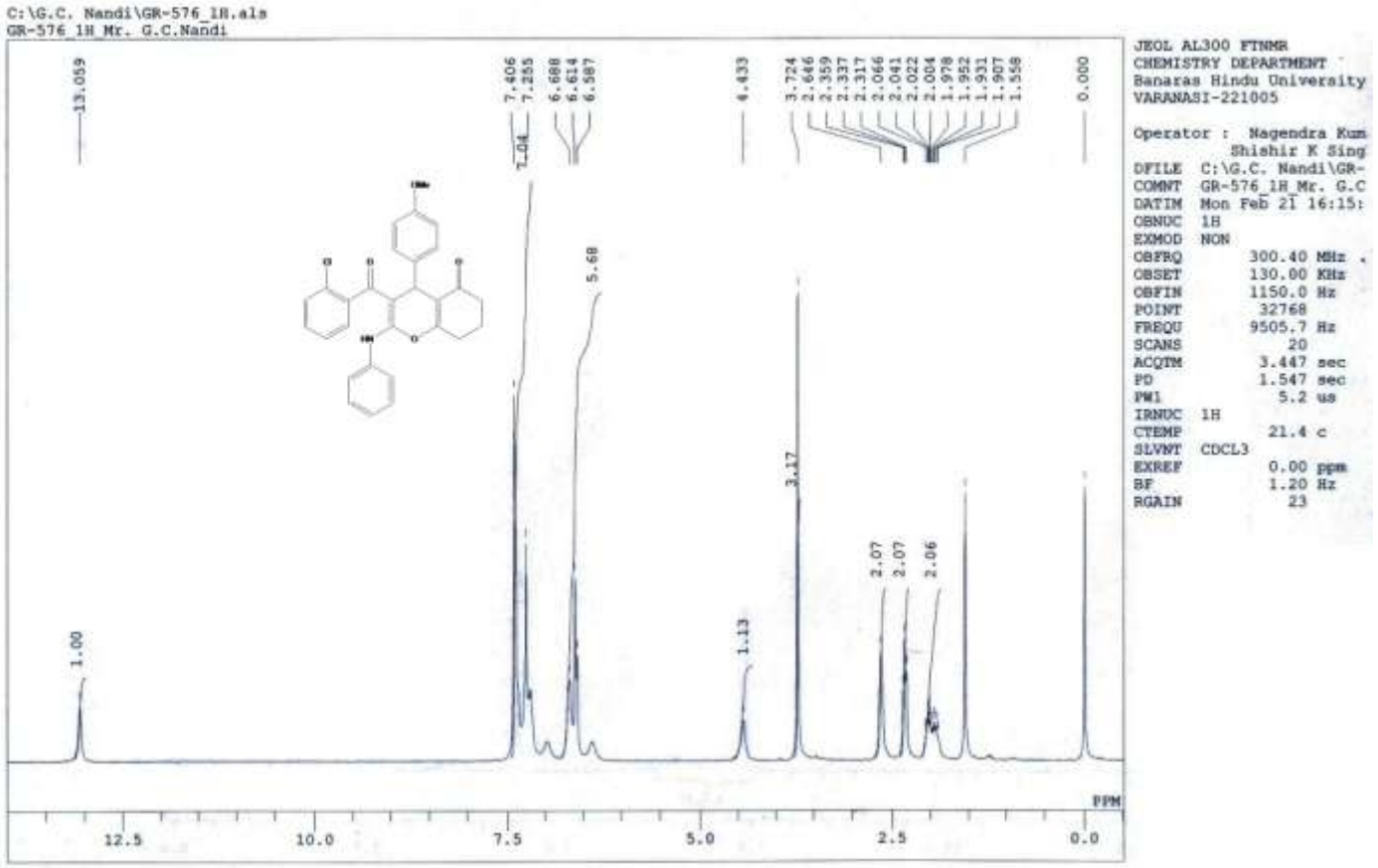
^{1}H spectrum of 6q



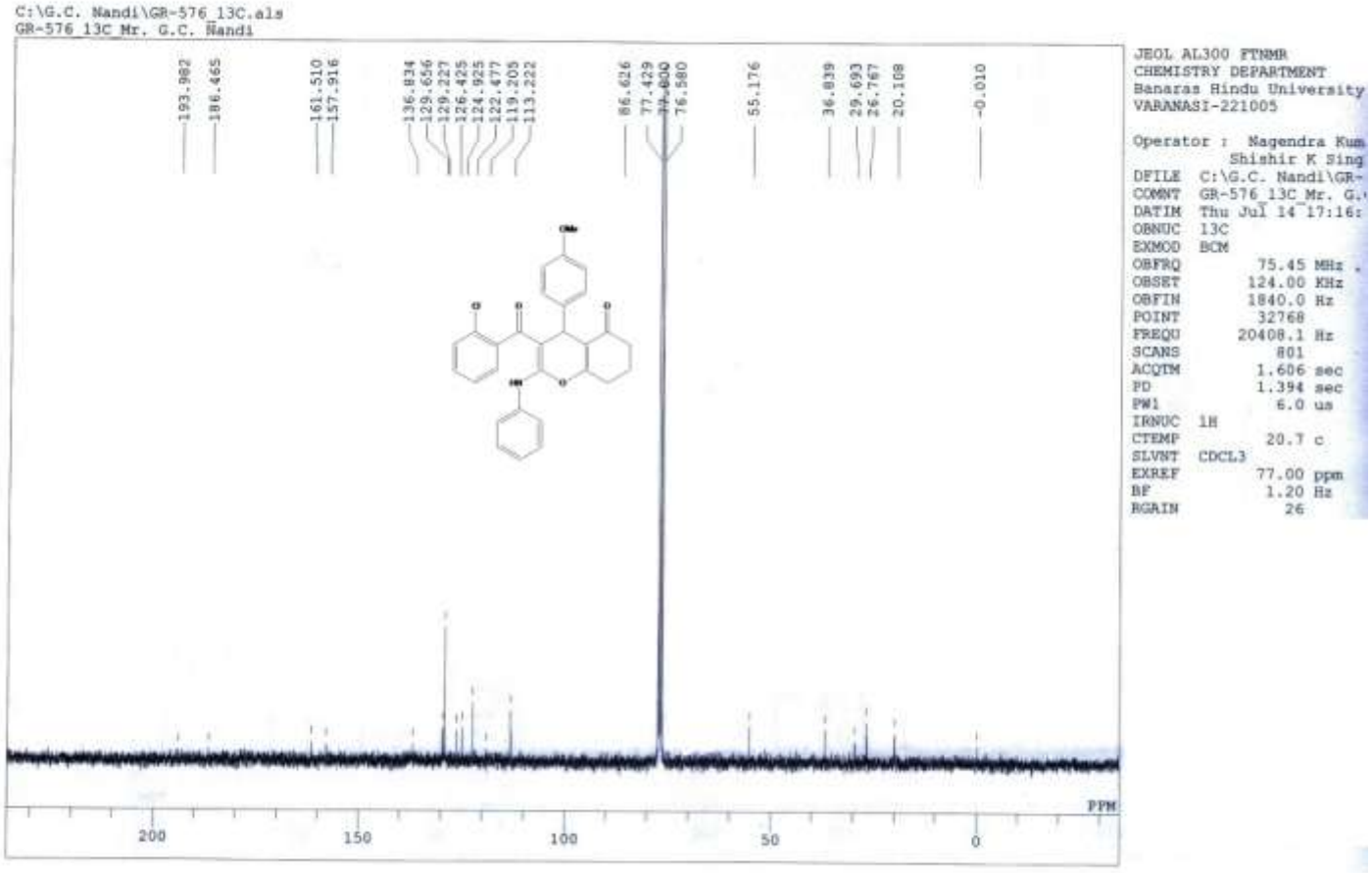
^{13}C spectrum of 6q



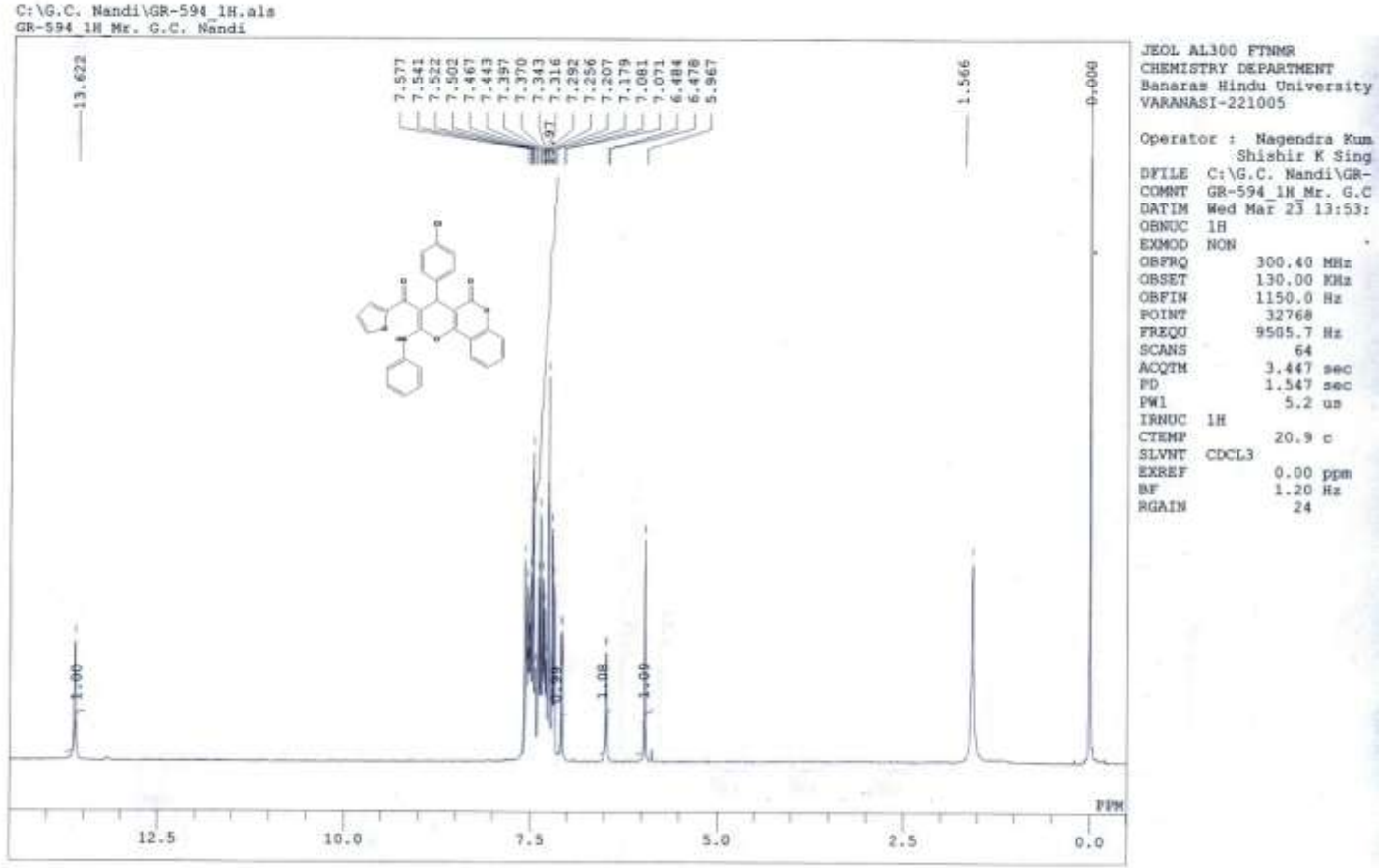
^{1}H spectrum of 6r



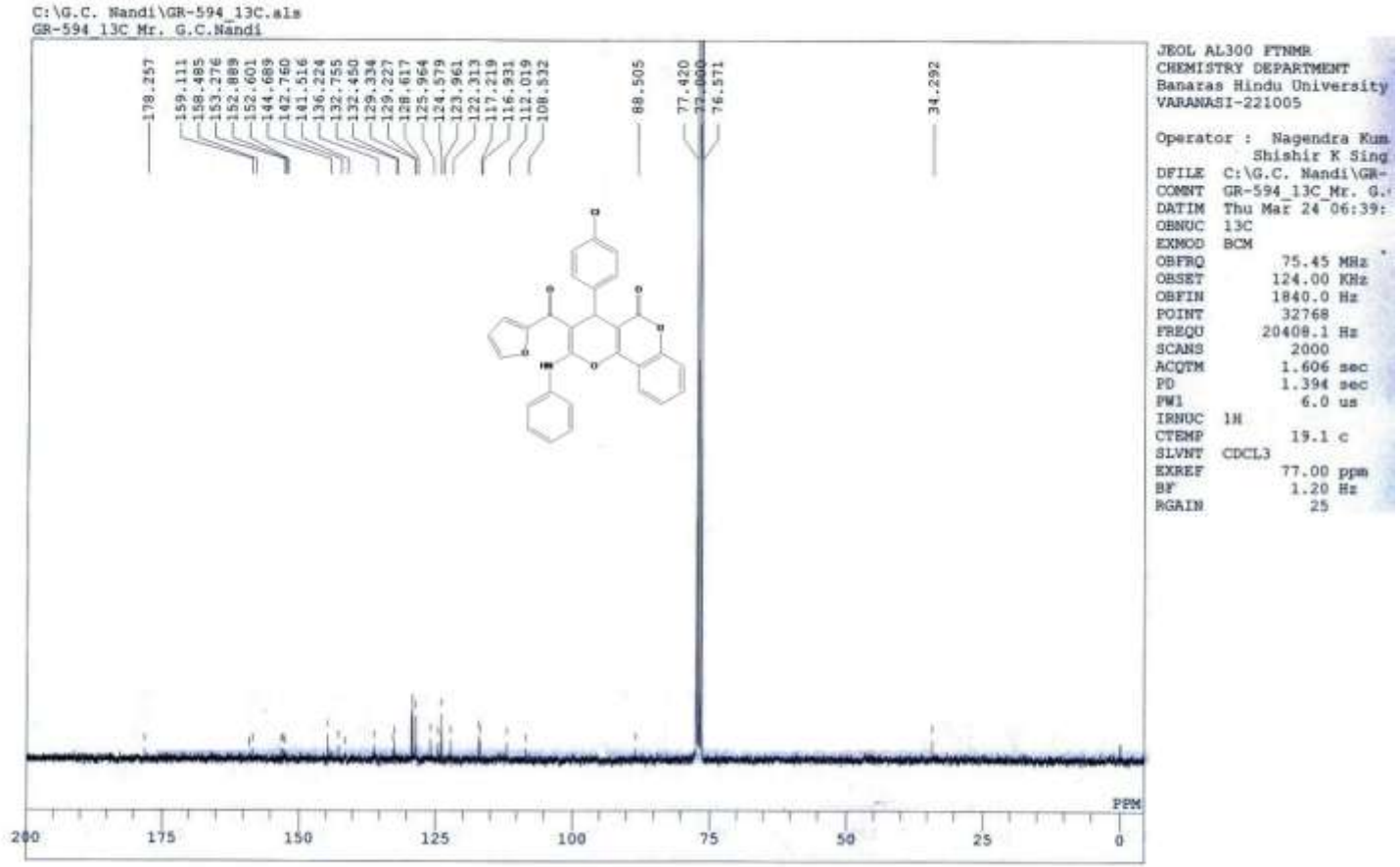
^{13}C spectrum of 6r



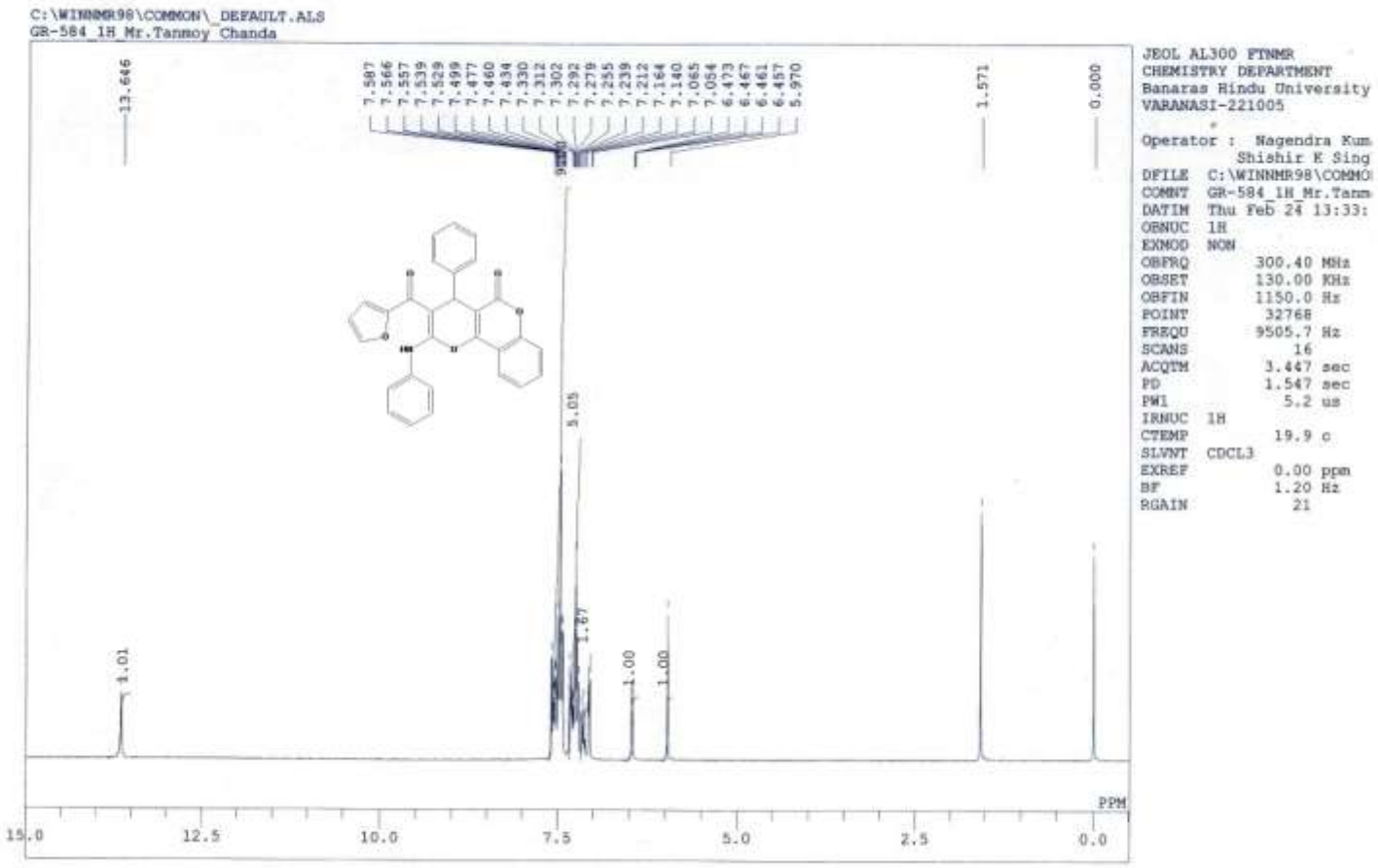
^{1}H spectrum of 7a



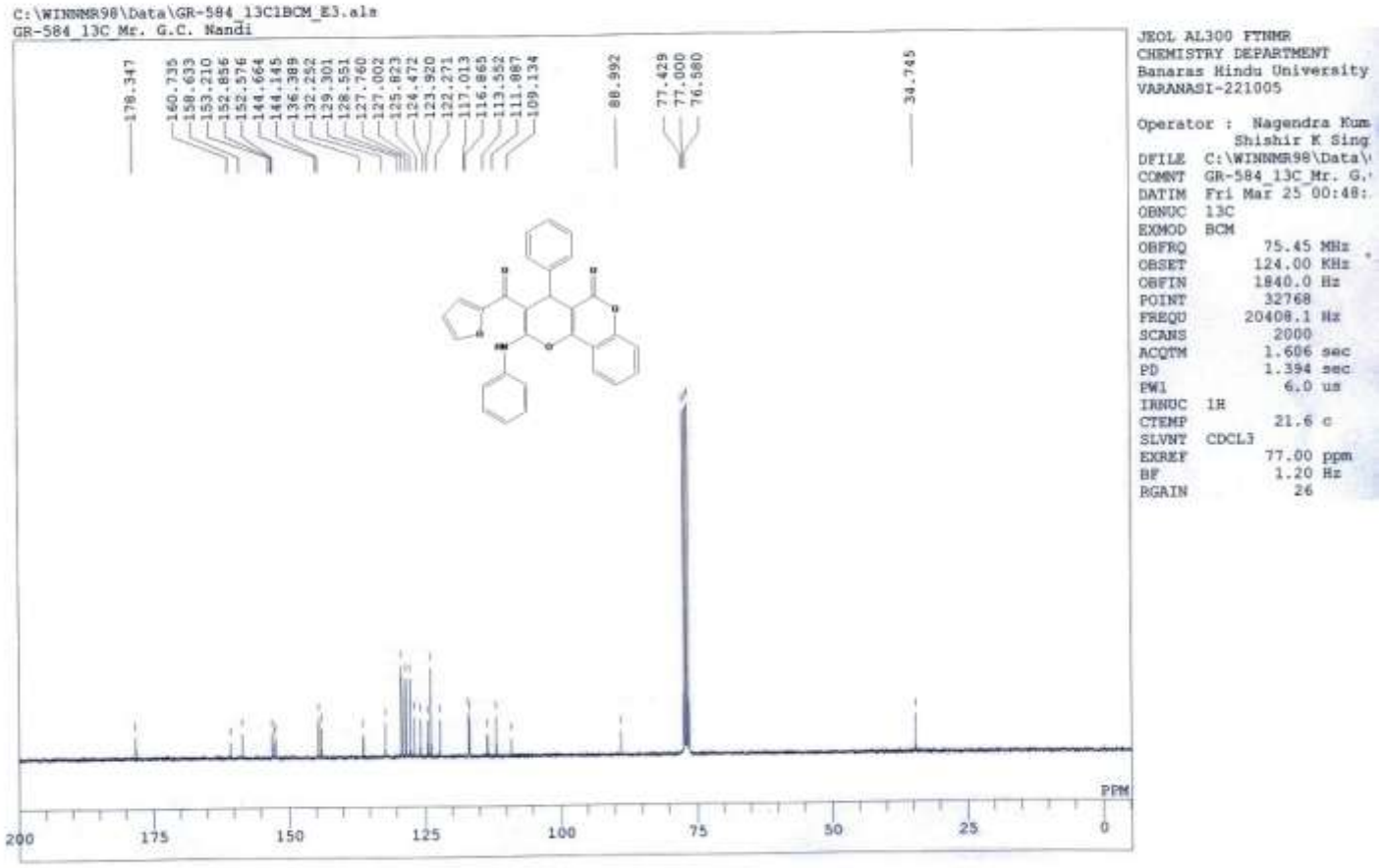
^{13}C spectrum of 7a



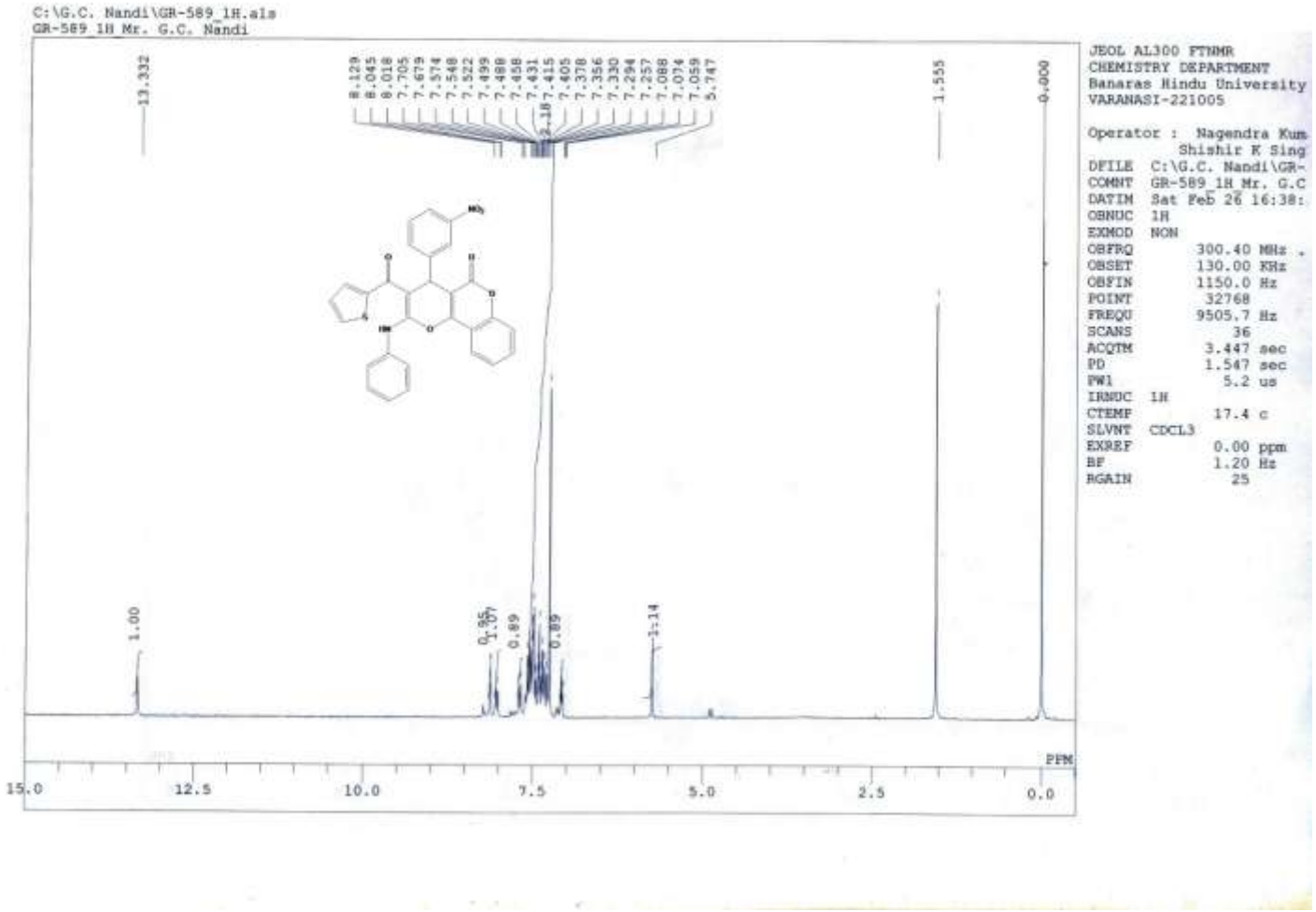
^{1}H spectrum of 7b



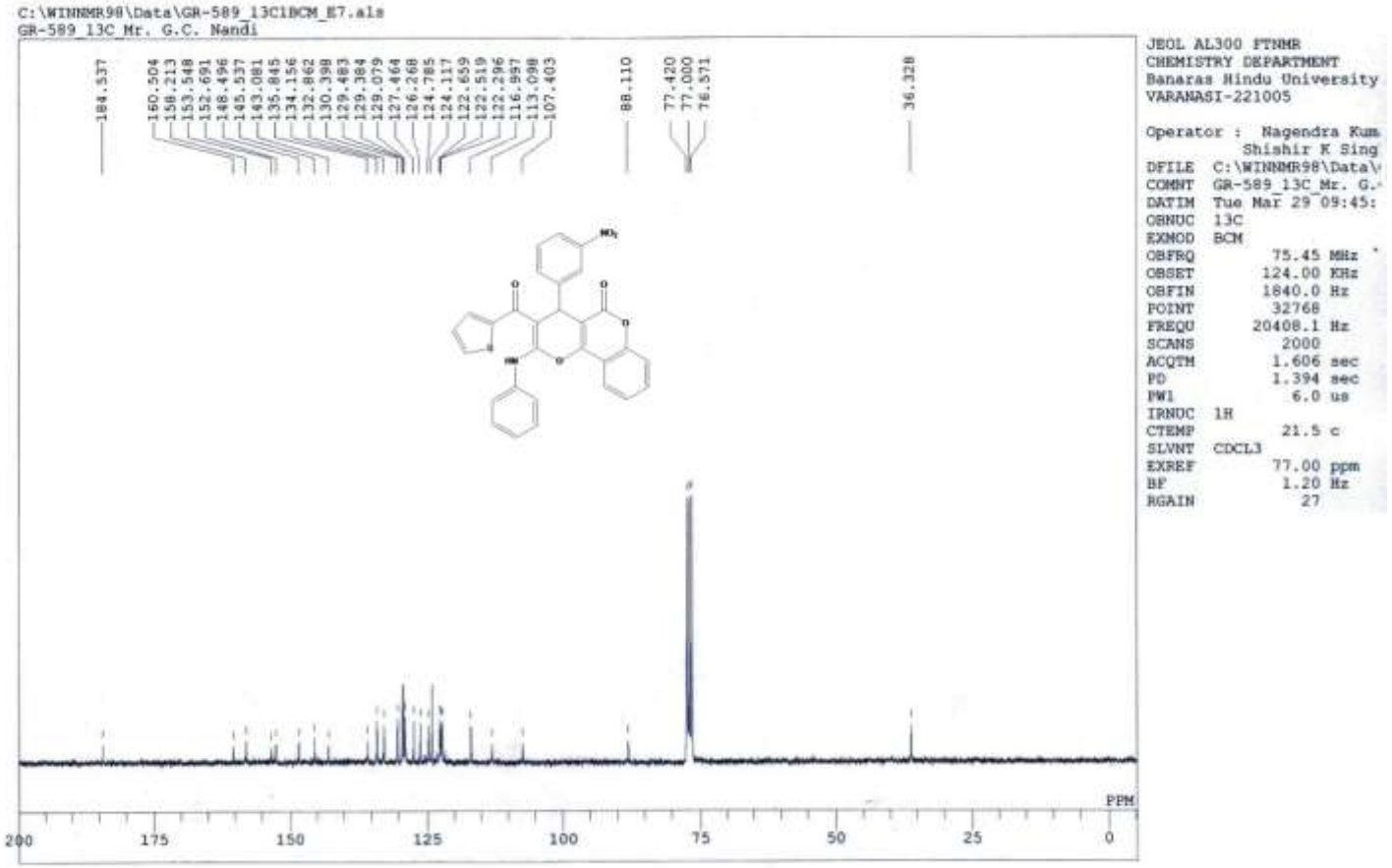
^{13}C spectrum of 7b



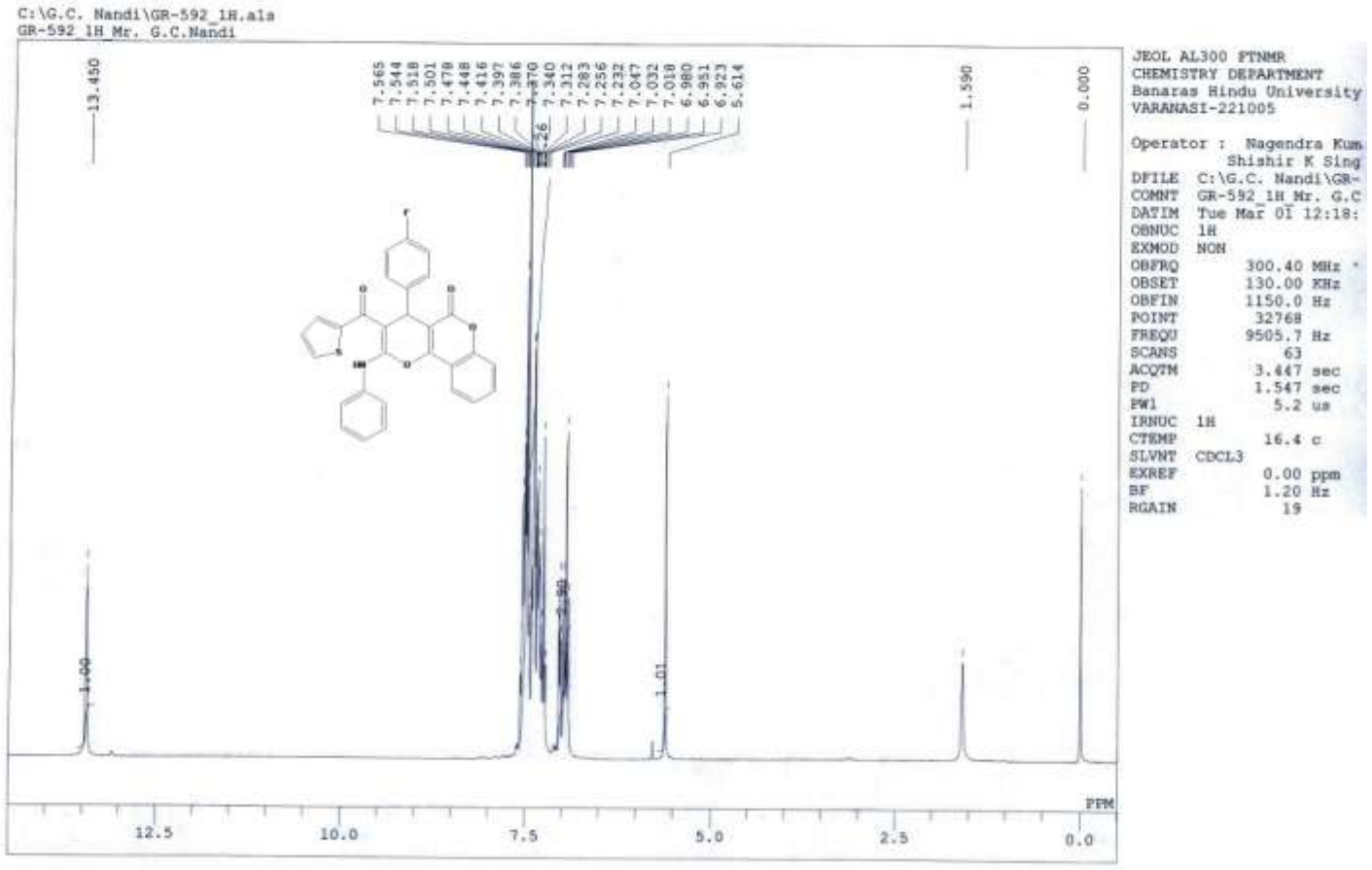
^{1}H spectrum of 7c



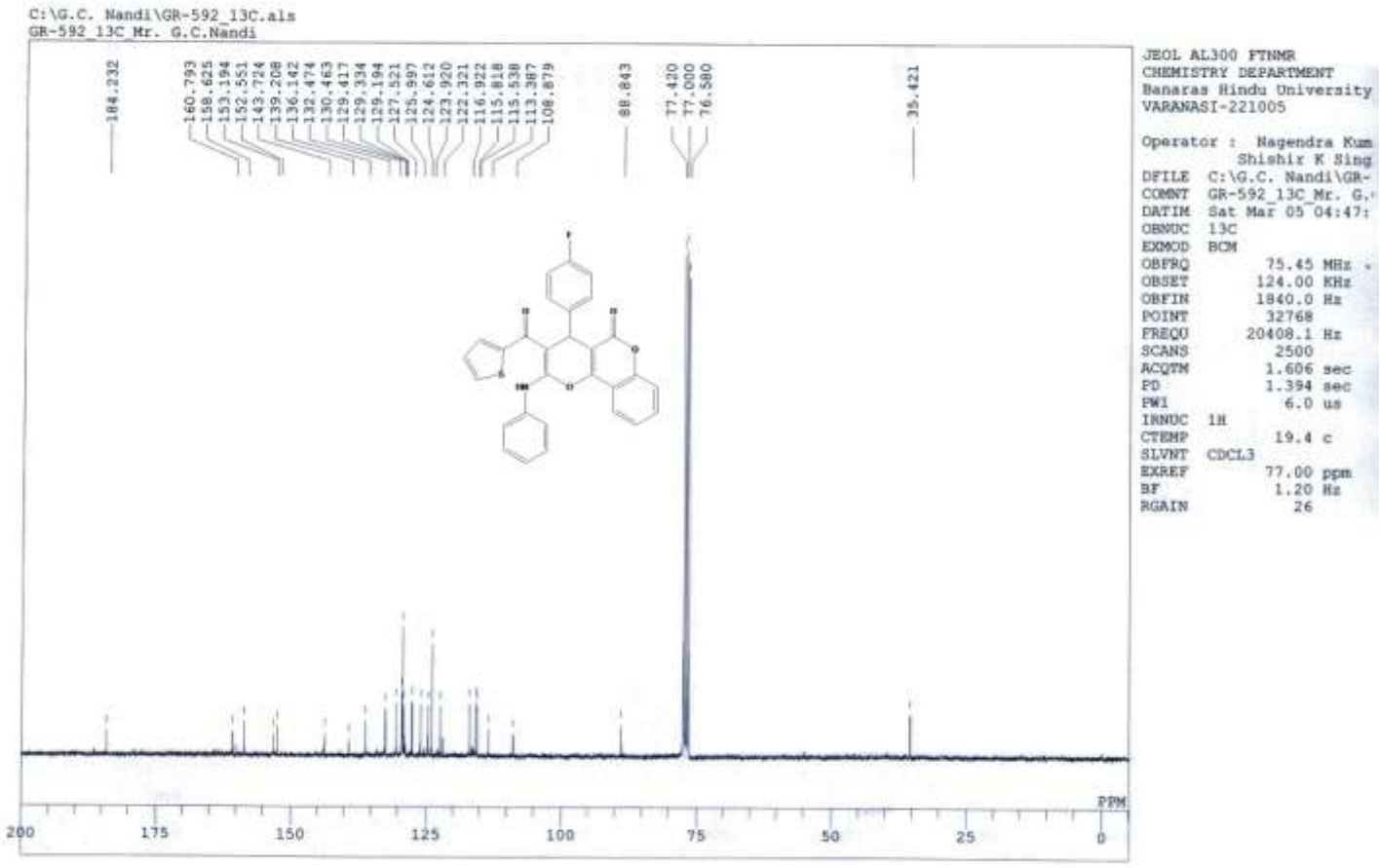
^{13}C spectrum of 7c



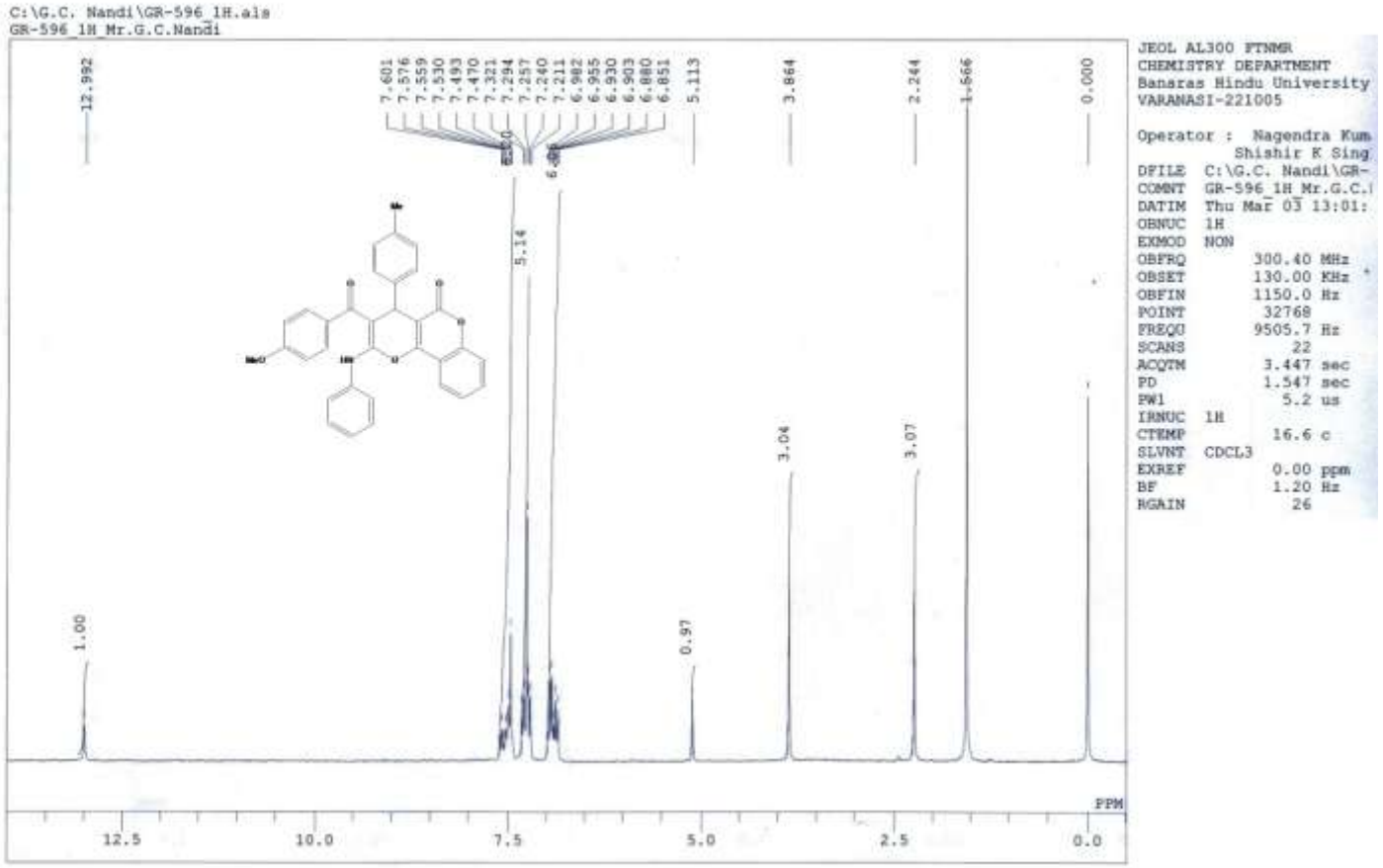
^{1}H spectrum of 7d



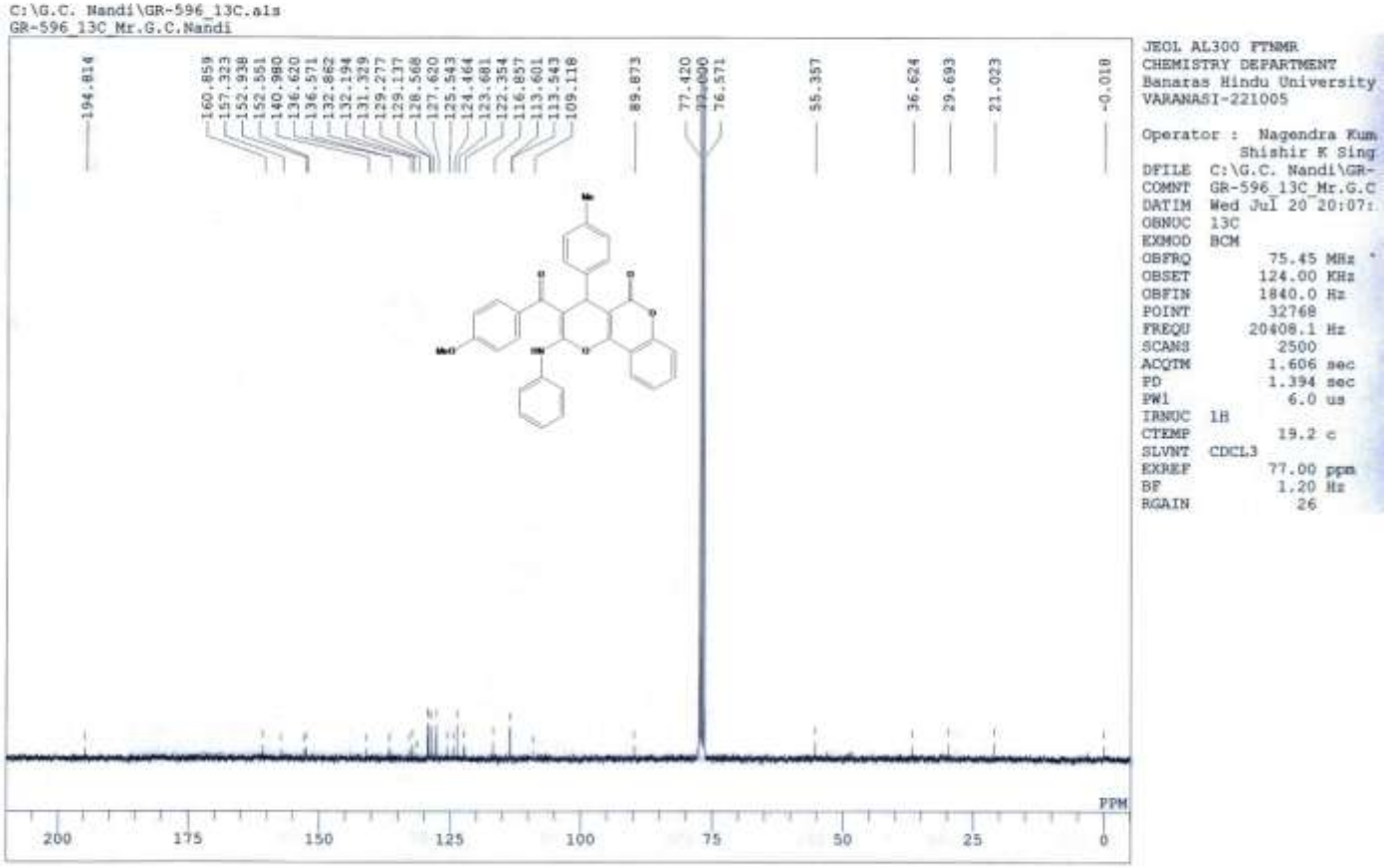
^{13}C spectrum of 7d



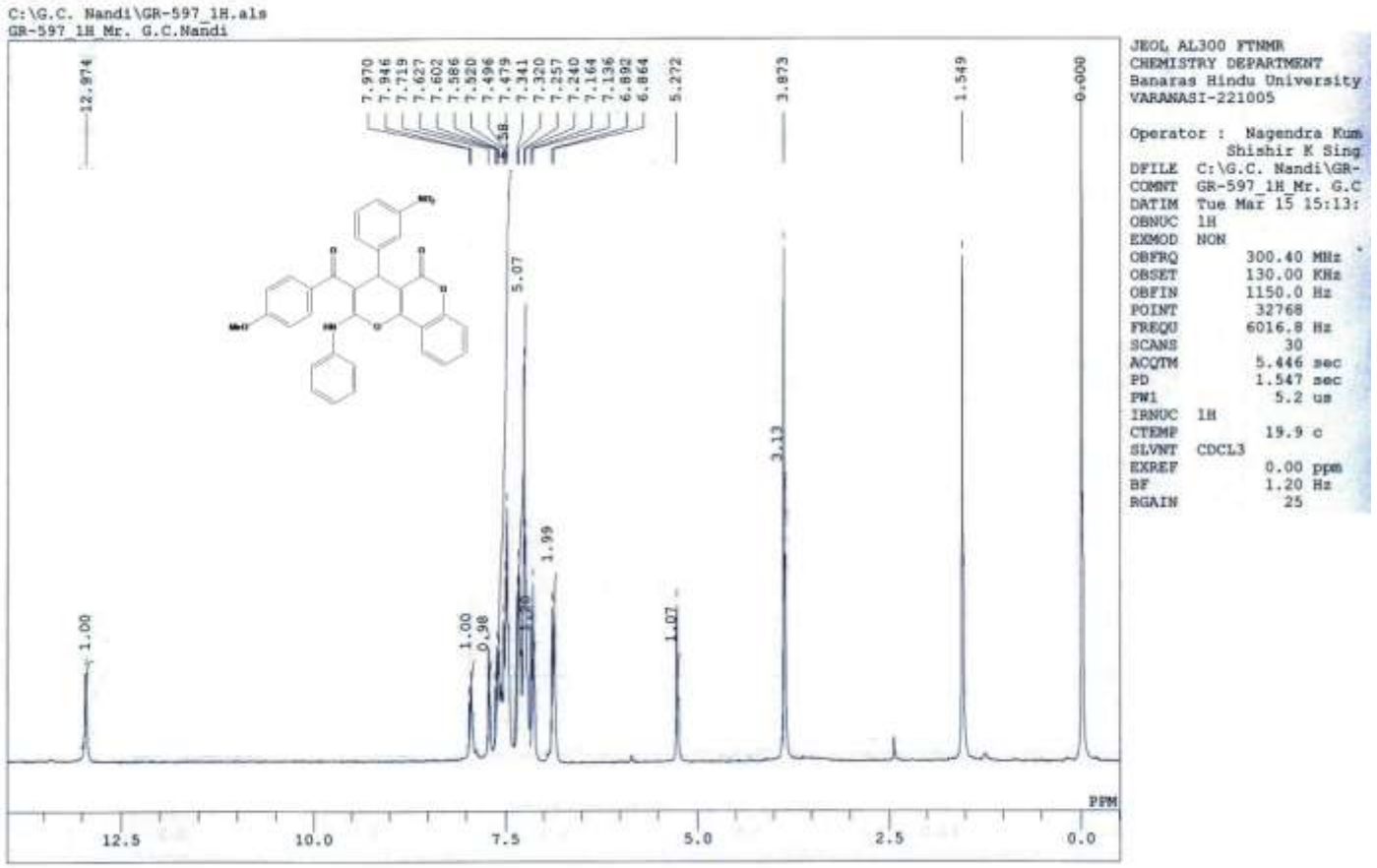
^{1}H spectrum of 7e



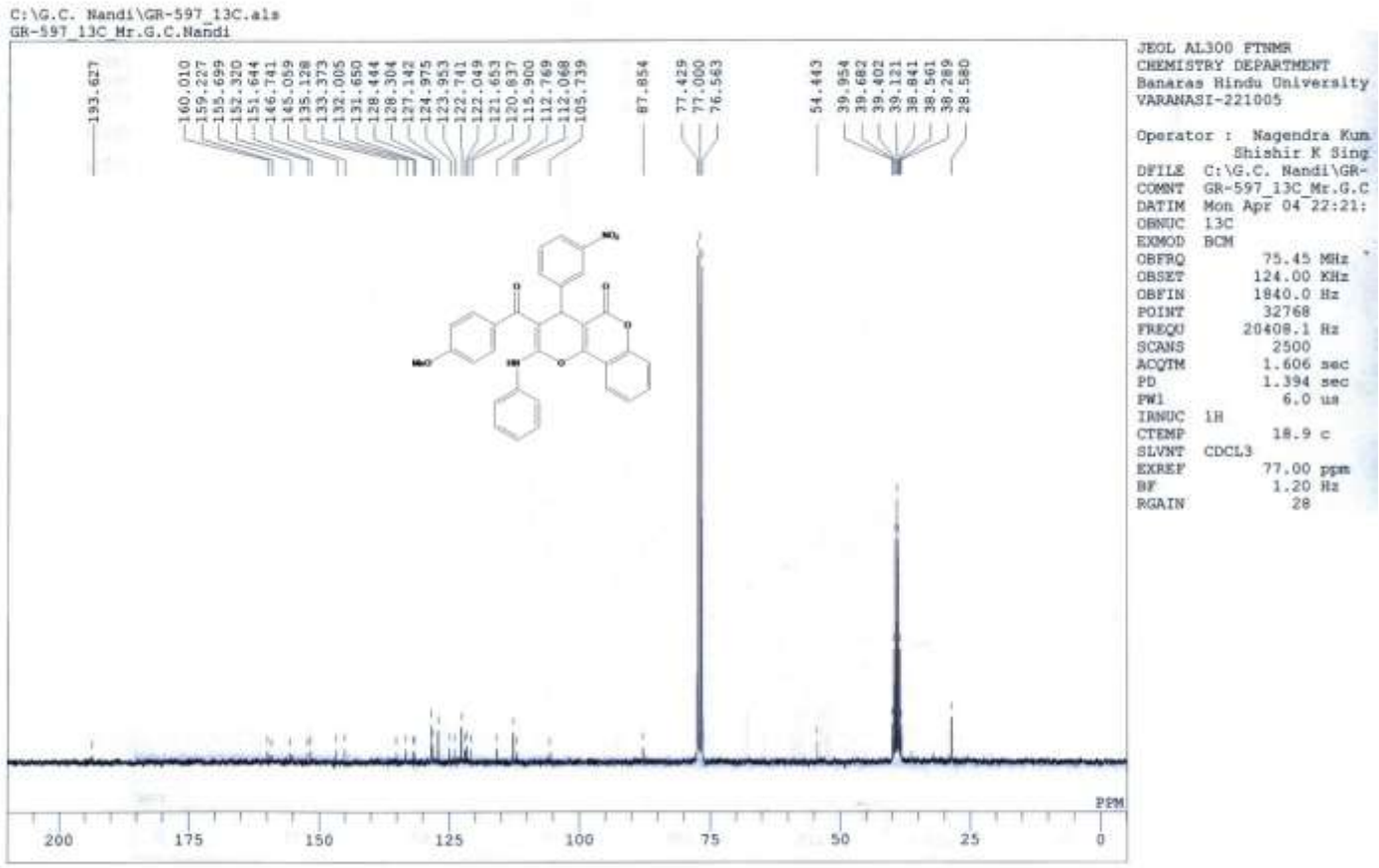
^{13}C spectrum of 7e



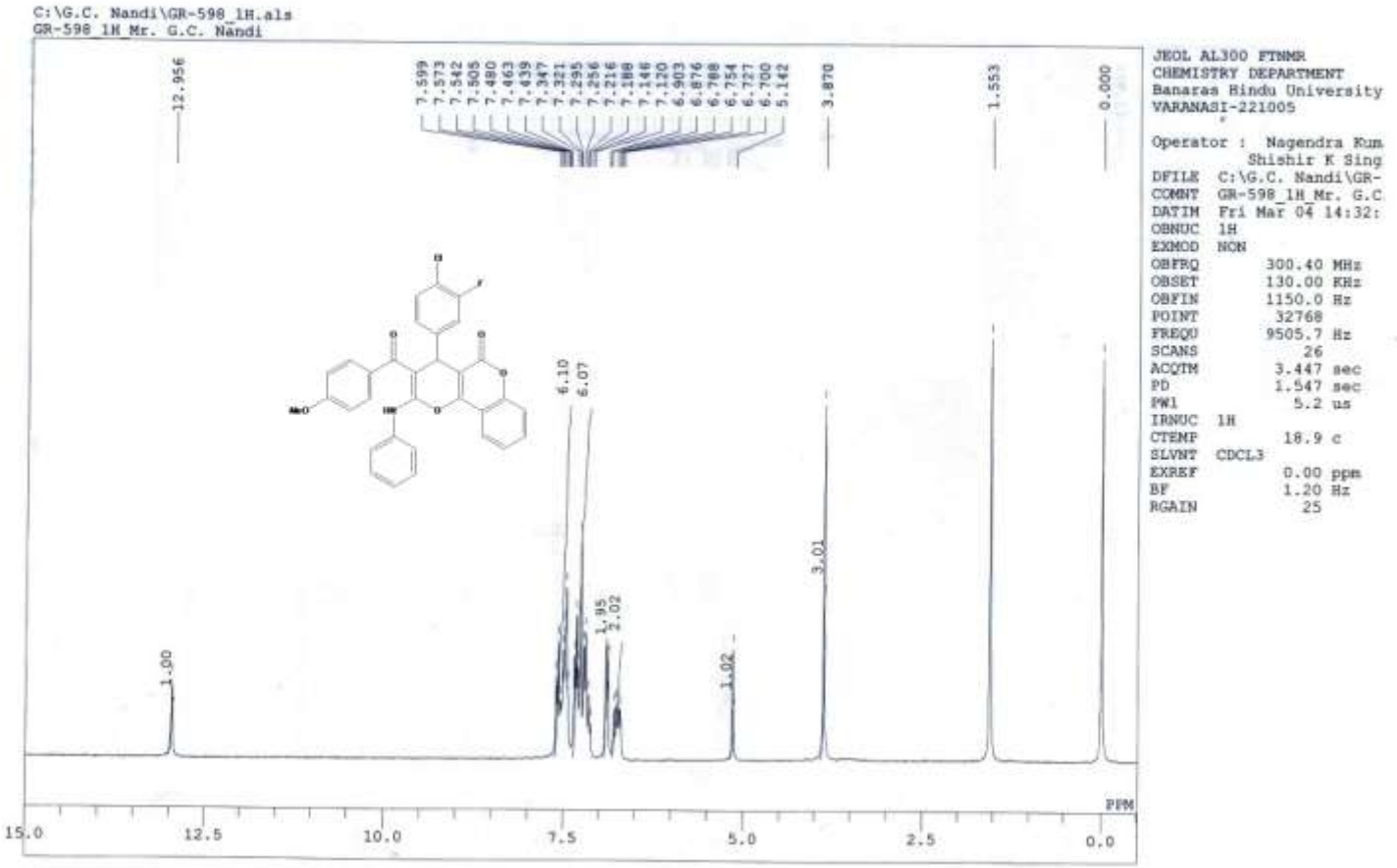
^{1}H spectrum of 7f



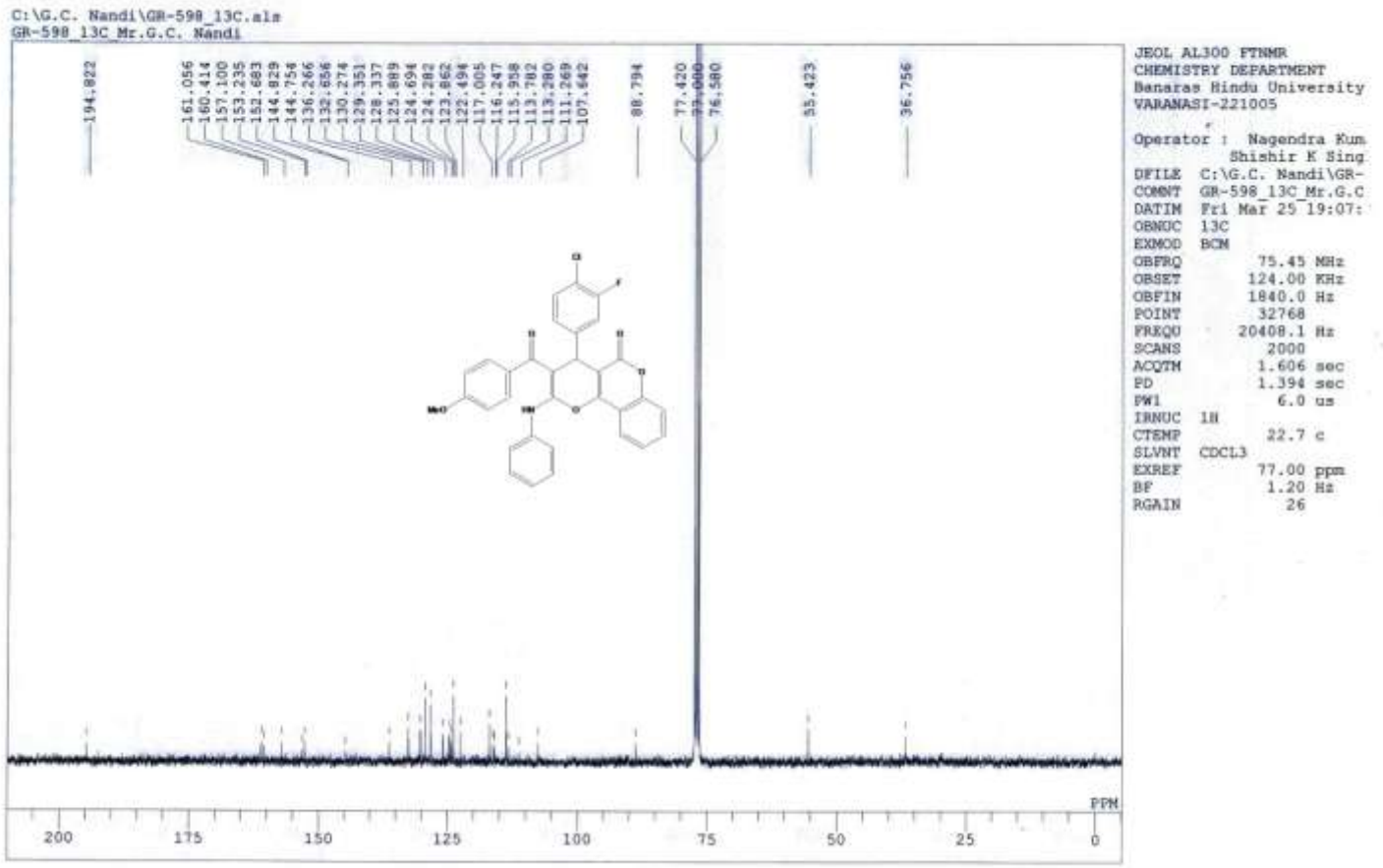
^{13}C spectrum of 7f



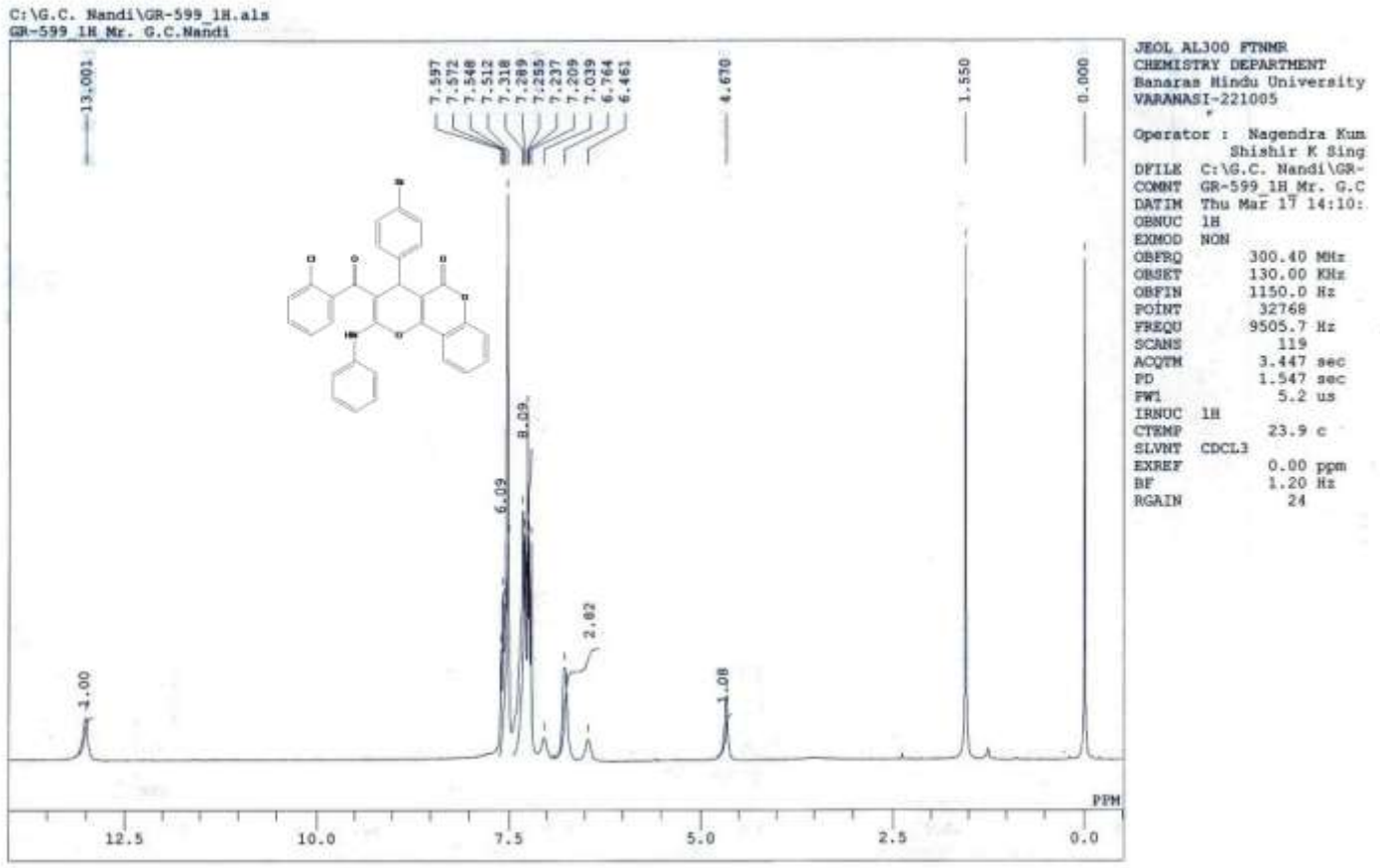
^{1}H spectrum of 7g



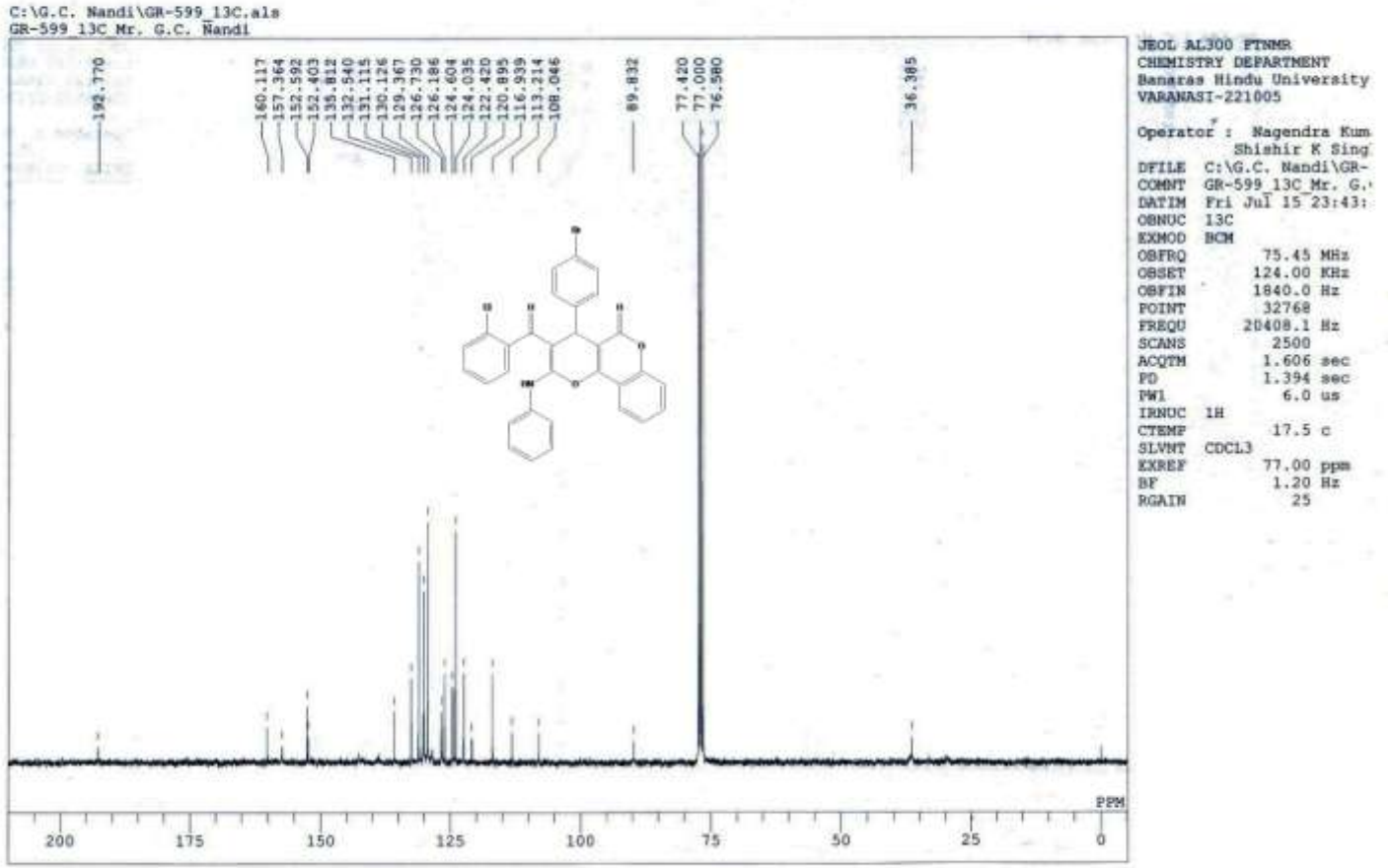
^{13}C spectrum of 7g



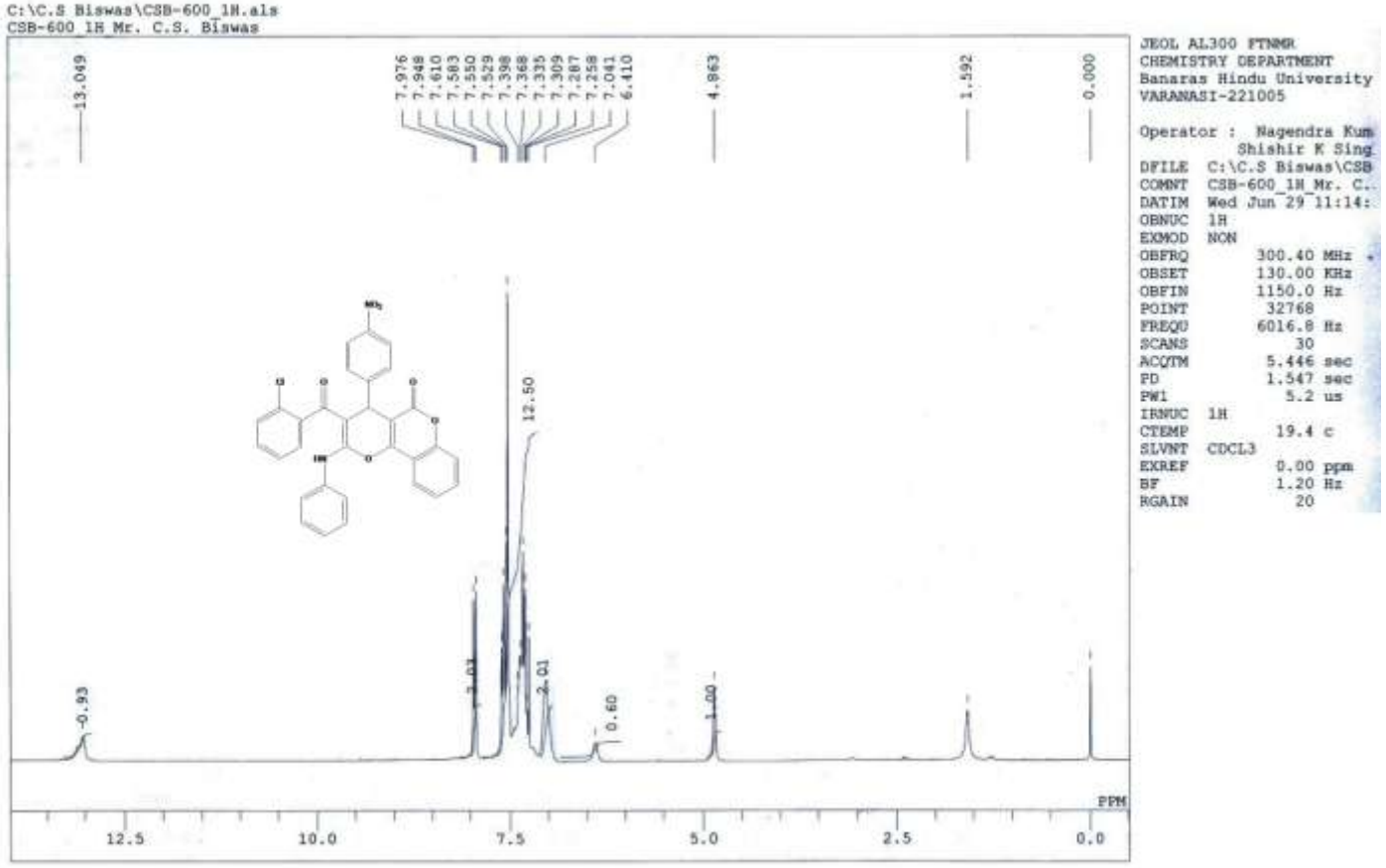
^{1}H spectrum of 7b



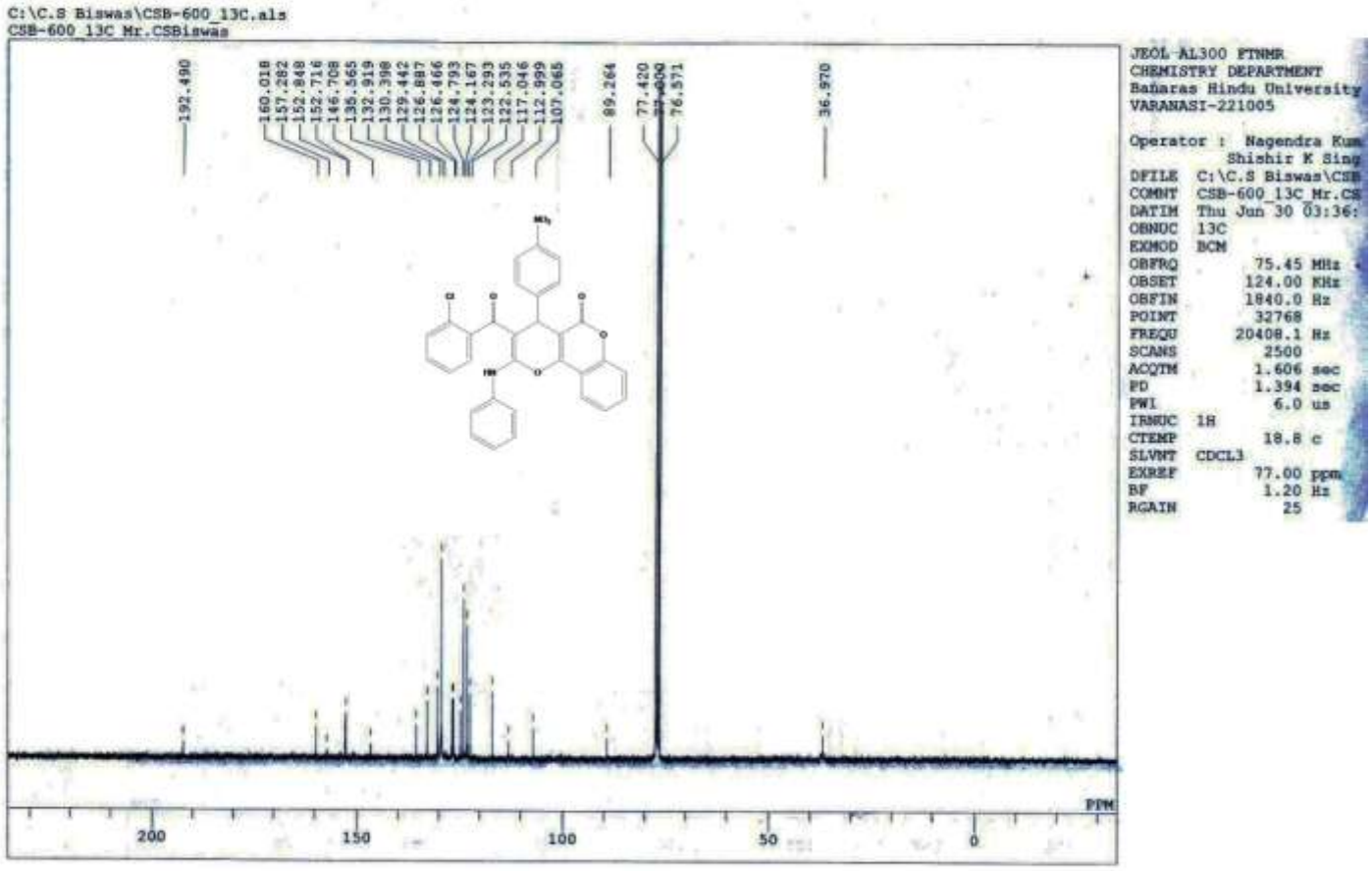
^{13}C spectrum of 7h



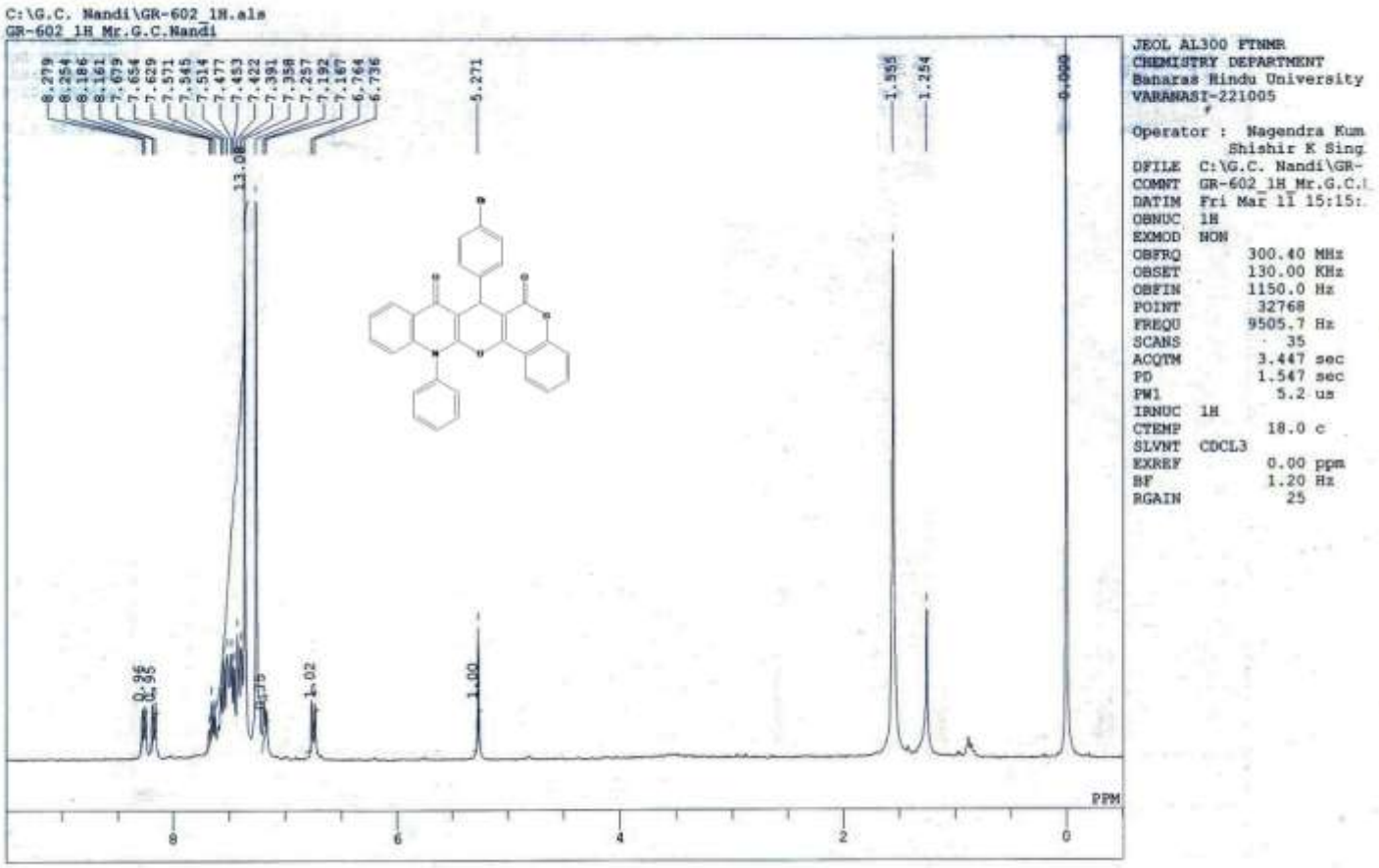
^{1}H spectrum of 7i



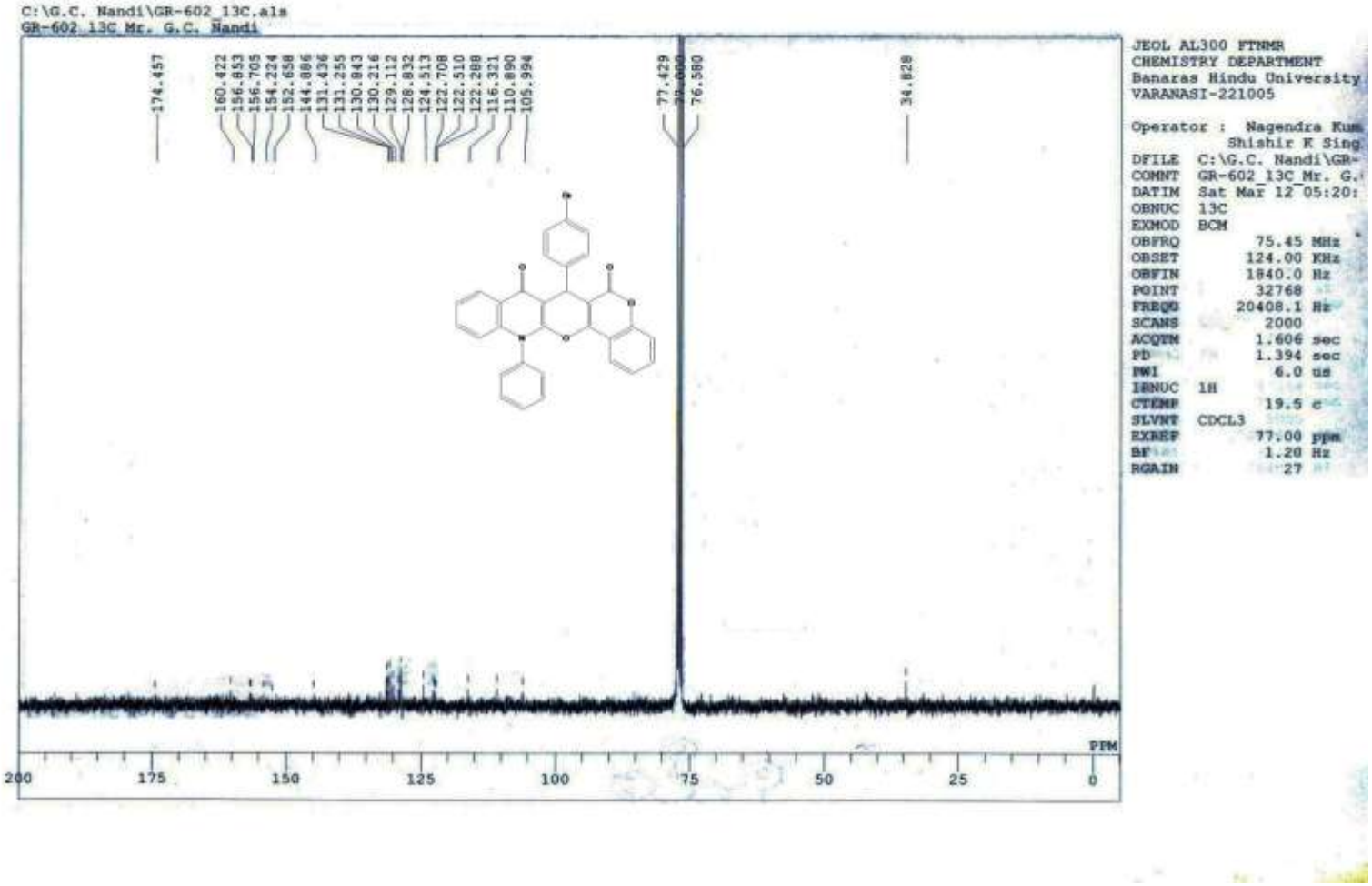
^{13}C spectrum of 7i



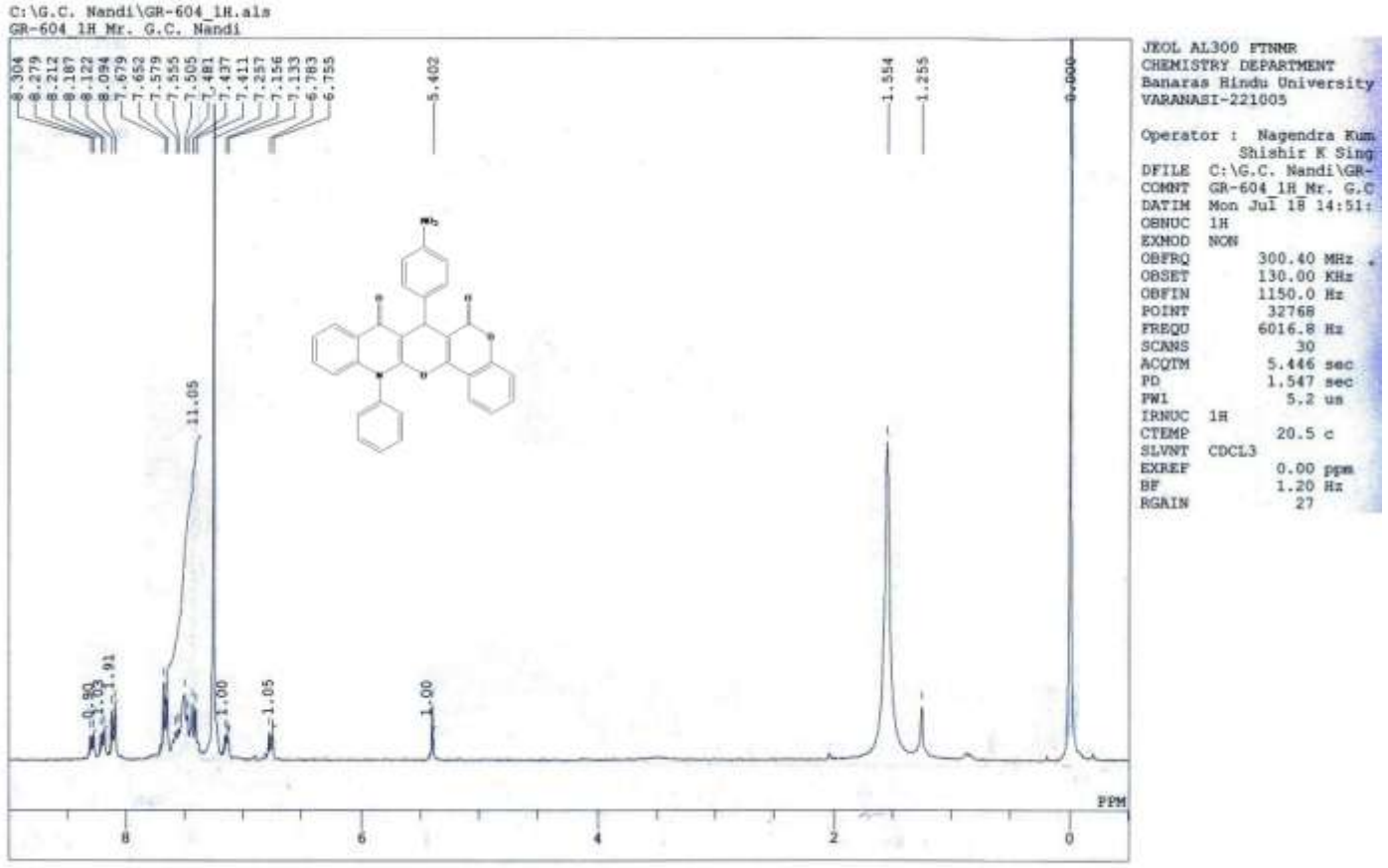
^{1}H spectrum of 8a



^{13}C spectrum of 8a



^{1}H spectrum of 8b



^{13}C spectrum of 8b