Electronic Supplementary Material (ESI) for Green Chemistry
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Supporting Information 1

A new MCM-41 supported HPF_6 catalyst for the library synthesis of highly substituted 1,4-dihydropyridines and oxidation to pyridines: report of one-dimensional packing towards LMSOMs and studies on their photophysical properties

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Materials and Methods

All solvents were dried by standard methods. Chemicals were purchased from Aldrich, USA and Spectrochem, India and used without further purification. TLC was done on glass sheets pre-coated with silica gel (with binder, 300 mesh, Spectrochem). The ^{1}H- and ^{13}C-NMR analysis were carried out on Bruker-Advance Digital 300 MHz and 75.5 MHz instruments in D_6-DMSO and $CDCl_3$ with TMS as an internal reference. The chemical shifts were reported as δ values (ppm) relative to TMS. IR spectra were recorded in KBr pellets in reflection mode on a Perkin Elmer RX-1 FTIR spectrophotometer. CHN analysis was performed using a Perkin-Elmer 2400 Series II CHN analyzer. X-ray diffraction patterns of the powder sample were obtained with a Seifert P3000 diffractometer using Cu Kα (λ = 0.15406 nm) radiation. Nitrogen adsorption/desorption isotherms were obtained using a Quantachrome Autosorb 1C at 77 K. Prior to gas adsorption, all the samples were degassed for 2 h at 403 K. Transmission electron microscopic images were recorded on a JEOL 2010 TEM operated at 200 kV in Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India. The 29Si MAS NMR was referenced with respect to external TMS using 7mm zirconia rotor and 2.5–3.5 kHz speed for more than 5 h, scanning around 5000 scans in NMR Research Centre, IISc, Bangalore-560012.

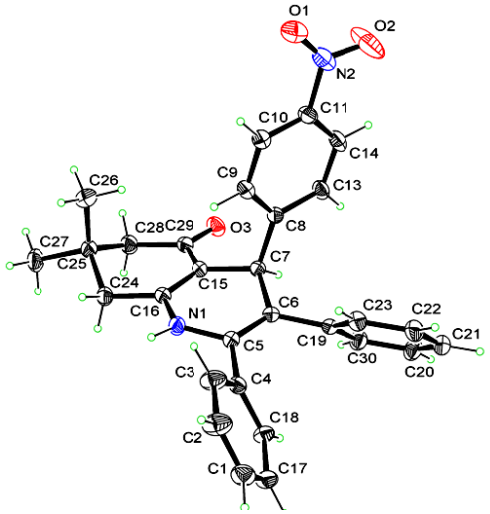

Figure 1. Ortep diagram of **5d** showing the crystallographic numbering (**CCDC 853740**).

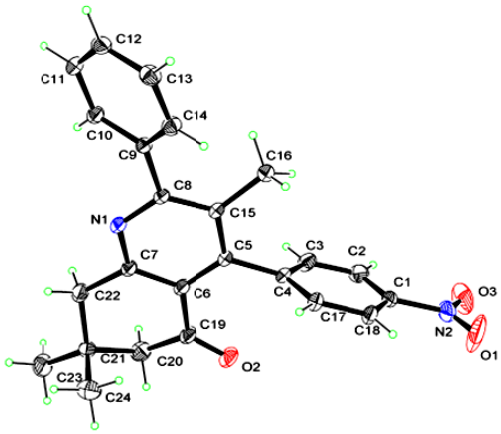

Figure 2. Ortep diagram of of (**6i**) showing the crystallographic numbering (**CCDC 884043**).

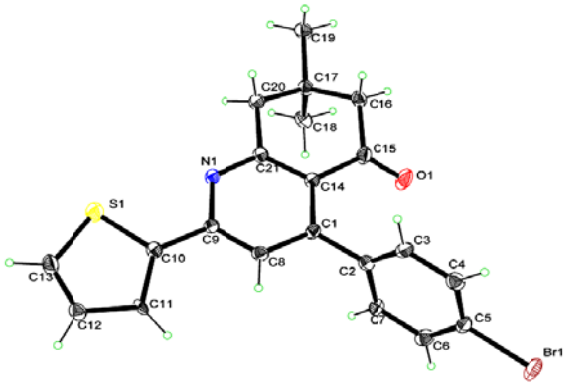

Figure 3. Ortep diagram of of (**6r**) showing the crystallographic numbering (**CCDC 853739**).

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General synthetic procedure for the preparation of 5a-5w

All the reactions were carried out in a round bottom flask equipped with a magnetic stirrer. In a typical reaction a solution of ketone (1 mmol), 1,3-diketoneone (1 mmol), aldehyde (1 mmol), and ammonium carbonate (1.2 mmol) in water (2 ml) were stirred at room temperature till completion using 40 mg of silica-HPF_6 catalyst. The completion of the reaction was indicated by the disappearance of the starting material in thin layer chromatography. After completion of the reaction the crude product was taken in dichloromethane and filtered to separate the products as filtrate from the catalyst (residue). The solvent was evaporated in rotary evaporator and the crude product was further purified by silica gel column chromatography (25% ethyl acetate/75% petroleum ether). The products were characterized by IR, ^{1}H NMR, ^{13}NMR, CHN and X-ray single crystal analysis. The spectral and analytical data of all the novel 1,4-dihydropyridine compounds are given below.

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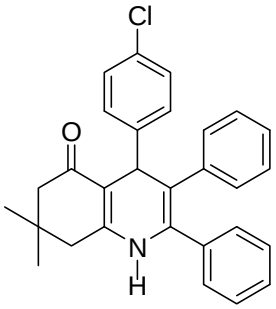
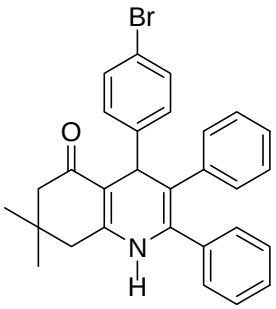
Spectroscopic characterization for 5a-5w:



4-(4-chlorophenyl)-7,8-dihydro-7,7-dimethyl-2,3-diphenylquinolin-5(1H,4H,6H)-one (**5a**):

Yellow solid, mp 240-242 °C; IR ν_{max} (KBr) 3435, 3012, 2962, 1685, 1573, 1518, 1457, and 1238 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.27 (2H, d, J = 8.1 Hz), 7.17-7.11 (7H, m), 6.93 (3H, brs), 6.78 (2H, d, J = 3.6 Hz), 5.99 (1H, s), 4.90 (1H, s), 2.42-2.06 (4H, m), 1.03 (3H, s), 0.83 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 195.1, 149.4, 144.8, 139.4, 136.4, 132.7, 131.6, 129.8, 129.6, 129.2, 129.0, 128.7, 128.5, 127.7, 127.6, 126.2, 118.2, 116.4, 50.7, 41.7, 41.5, 32.6, 29.8, 26.7; Anal. Calcd for $C_{29}H_{26}ClNO$: C, 79.17; H, 5.96; N, 3.18. Found C, 79.34; H, 6.00; N, 3.26.



4-(4-bromophenyl)-7,8-dihydro-7,7-dimethyl-2,3-diphenylquinolin-5(1H,4H,6H)-one (**5b**):

Yellow solid, mp 280-282 °C; IR ν_{max} (KBr) 3434, 3011, 2968, 1681, 1573, 1510, 1458, and 1238 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.30-7.15 (9H, m), 6.94-6.01 (3H, m), 6.80-6.74 (2H, m), 4.89 (1H, s), 2.53-2.11 (4H, m), 1.04 (3H, s), 0.84 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 193.0, 150.1, 145.6, 139.4, 135.2, 133.6, 130.4, 130.0, 129.8, 129.2, 129.0, 128.6, 127.6, 127.0, 126.8, 125.2, 118.2, 113.1, 106.0, 49.8, 40.9, 31.3, 29.0, 25.4; Anal. Calcd for $C_{29}H_{26}BrNO$: C, 71.90; H, 5.41; N, 2.89. Found C, 71.61; H, 5.43; N, 2.60.

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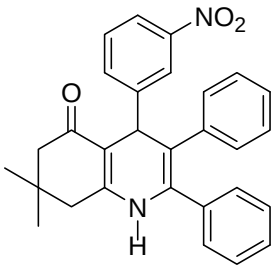
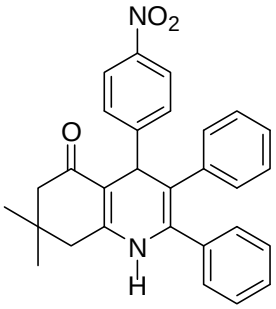


7,8-dihydro-7,7-dimethyl-4-(3-nitrophenyl)-2,3-diphenylquinolin-5(1H,4H,6H)-one (**5c**):

Yellow solid, mp 206-208 °C; IR ν_{max} (KBr) 3434, 3050, 2970, 1685, 1573, 1518, 1457, and 1244 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.28 (1H, d, J = 1.8 Hz), 7.99 (1H, dd, J = 7.2 Hz and J = 1.2 Hz), 7.34 (1H, t, J = 7.8 Hz), 7.27 (5H, brs), 7.02-7.00 (3H, m), 6.86-6.83 (2H, m, aromatic-H), 5.99 (1H, s), 5.17 (1H, s), 2.51-2.16 (4H, m), 1.12 (3H, s), 0.92 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 194.5, 153.7, 150.1, 146.3, 139.0, 136.1, 134.6,129.5, 129.0, 128.7, 128.6, 127.9, 126.5, 122.5, 121.3, 115.9, 108.1, 50.6, 42.8, 41.5, 32.6, 29.7, 26.7; Anal. Calcd for $C_{29}H_{26}N_2O_3$: C, 77.31; H, 5.82; N, 6.22. Found C, 77.31; H, 5.90; N, 6.41.



7,8-dihydro-7,7-dimethyl-4-(4-nitrophenyl)-2,3-diphenylquinolin-5(1H,4H,6H)-one (**5d**) (Table 1, entry 1):yellow solid, mp 254-256 °C; IR ν_{max} (KBr) 3434, 3012, 2949, 1685, 1573, 1518, 1457, and 1244 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.10 (2H, d, J = 8.4 Hz), 7.56 (2H, d, J = 8.4 Hz), 7.26 (5H, d, J = 2.4 Hz), 7.02-7.00 (3H, m), 6.84-6.81 (2H, m), 6.16 (1H, brs), 5.14 (1H, s), 2.53-2.04 (4H, m), 1.12 (3H, s), 0.91 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 194.9, 153.5, 150.1, 146.3, 139.0, 136.0, 133.3,129.4, 128.9, 128.7, 127.8, 126.5, 123.6, 122.7, 115.9, 108.1, 50.6, 42.8, 41.5, 32.6, 29.7, 26.7; Anal. Calcd for $C_{29}H_{26}N_2O_3$: C, 77.31; H, 5.82; N, 6.22. Found C, 77.60; H, 5.92; N, 6.02.

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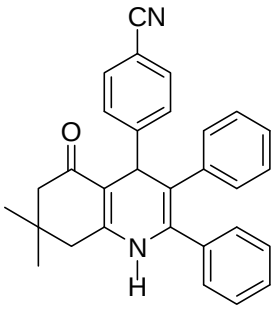
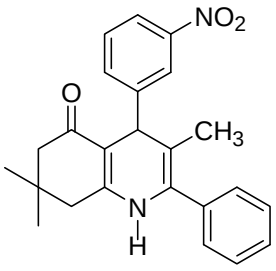


4-(7,7-Dimethyl-5-oxo-2,3-diphenyl-1,4,5,6,7,8-hexahydro-quinolin-4-yl)-benzonitrile (**5e**):

Yellow solid, mp 288-290 °C; IR ν_{max} (KBr) 3432, 3018, 2960, 1685, 1561, 1518, 1451, and 1245 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-D_6) δ: 9.04 (1H, s), 7.68 (2H, d, J = 7.8 Hz), 7.42 (2H, d, J = 8.4 Hz), 7.24 (5H, br s), 6.95-6.94 (3H, m), 6.73-6.70 (2H, m), 4.86 (1H, s), 2.51-1.91 (4H, m), 0.98 (3H, s), 0.73 (3H, s); ^{13}C NMR (75 MHz, DMSO-D_6) δ: 193.6, 152.2, 151.3, 139.8, 135.7, 134.6, 132.3, 129.7, 129.2, 128.5, 128.3, 127.8, 126.0, 119.1, 113.4, 108.7, 106.1, 50.4, 42.6, 32.0, 29.6, 26.1; Anal. Calcd for $C_{30}H_{26}N_2O$: C, 83.69; H, 6.09; N, 6.51. Found C, 83.95; H, 6.17; N, 6.56.



3,7,7-Trimethyl-4-(3-nitro-phenyl)-2-phenyl-4,6,7,8-tetrahydro-1H-quinolin-5-one (**5f**):

Wellowish white solid, mp 250-252 °C (CH_2Cl_2 + EtOAc, equal volumes); IR ν_{max} (KBr) 3432, 3061, 2972, 1684, 1572, 1518, 1458, and 1241 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.23 (1H, s), 8.02 (2H, dd, J = 8.1 Hz and J = 1.2 Hz), 7.77 (2H, d, J = 7.5 Hz), 7.45-7.33 (6H, m), 6.22 (1H, br s), 4.64 (1H, s), 2.43-1.99 (4H, m), 1.52 (3H, s), 1.08 (3H, s), 0.93 (3H, s); ^{13}C NMR (75 MHz, DMSO-D_6) δ: 192.8, 151.0, 148.7, 147.2, 134.9, 133.7, 130.8, 128.9, 128.6, 127.8, 127.7, 127.5, 121.3, 120.4, 109.4, 104.249.6, 42.3, 31.3, 28.8, 27.3, 25.7, 16.7; Anal. Calcd for $C_{24}H_{24}N_2O_3$: C, 74.21; H, 6.23; N, 7.40. Found C, 74.51; H, 6.30; N, 7.40.

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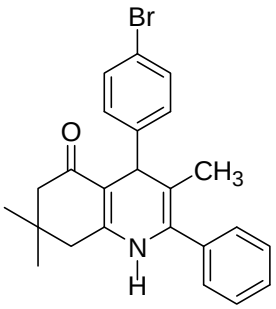
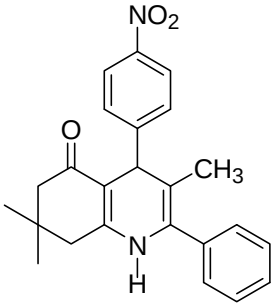


4-(4-Bromo-phenyl)-3,7,7-trimethyl-2-phenyl-4,6,7,8-tetrahydro-1H-quinolin-5-one (**5g**):

Yellowish white solid, mp 140-142 °C (CH_2Cl_2 + EtOAc, equal volumes); IR ν_{max} (KBr) 3438, 3010, 2961, 1688, 1574, 1512, 1458, and 1231 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.37-7.20 (9H, m), 6.03 (1H, br s), 4.40 (1H, s), 2.34-1.91 (4H, m), 1.46 (3H, s), 1.01 (3H, s), 0.93 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 196.8, 160.8, 158.8, 148.8, 139.2, 138.2, 131.9, 130.5, 130.2, 129.8, 129.1, 128.8, 128.6, 128.5, 127.9, 127.7, 127.5, 127.4, 122.9, 119.6, 52.5, 45.8, 31.7, 27.2, 16.7; Anal. Calcd for $C_{24}H_{24}BrNO$: C, 68.25; H, 5.73; N, 3.32. Found C, 68.20; H, 5.77; Br, N, 3.32.



7,8-dihydro-3,7,7-trimethyl-4-(4-nitrophenyl)-2-phenylquinolin-5(1H,4H,6H)-one (**5h**):

Yellow solid, mp 244-246 °C (CH_2Cl_2 + EtOAc, equal volumes); IR ν_{max} (KBr) 3430, 3068, 2951, 2869, 1681, 1576, 1530, and 1347 cm^{-1}; ^1H NMR (300 MHz, DMSO-D_6) δ: 8.74 (1H, s), 8.16 (2H, dd, J = 6.9 Hz and J = 1.8 Hz), 7.57 (2H, dd, J = 6.9 Hz and J = 1.8 Hz), 7.47-7.32 (7H, m), 4.53 (1H, s), 2.51-1.90 (4H, m), 1.40 (3H, s), 1.00 (3H, s), 0.85 (3H, s); ^{13}C NMR (75 MHz, DMSO-D_6) δ: 192.7, 154.2, 150.9, 145.2, 134.9, 130.7, 128.6, 128.2, 127.8, 127.7, 123.1, 122.7, 109.2, 104.1, 49.6, 42.7, 31.3, 28.8, 25.9, 16.8; Anal. Calcd for $C_{24}H_{24}N_2O_3$: C, 74.21; H, 6.23; N, 7.40. Found C, 74.44; H, 6.30; N, 7.21.

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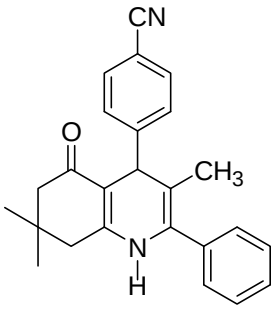
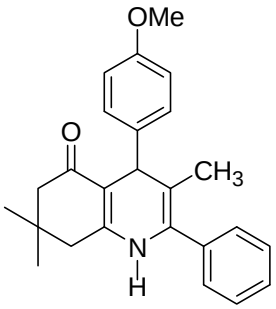


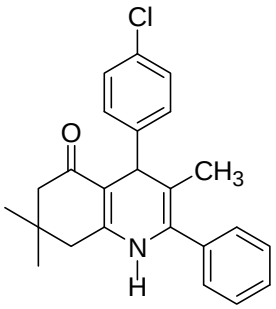
4-(1,4,5,6,7,8-hexahydro-3,7,7-trimethyl-5-oxo-2-phenylquinolin-4-yl)benzonitrile (**5i**):

Yellowish white solid, mp 244-250 °C (CH_2Cl_2 + EtOAc, equal volumes); IR ν_{max} (KBr) 3434, 3067, 2951, 2869, 1681, 1576, 1530, 1349, and 1245 cm^{-1}; ^1H NMR (300 MHz, DMSO-D_6) δ: 8.70 (1H, s), 7.74 (2H, dd, J = 6.6 Hz and J = 1.8 Hz), 7.50-7.31 (7H, m), 4.45 (1H, s), 2.49-1.86 (4H, m), 1.39 (3H, s), 1.06 (3H, s), 0.84 (3H, s); ^{13}C NMR (75 MHz, DMSO-D_6) δ: 192.7,152.0, 151.0, 134.9, 131.4, 130.7, 128.6, 128.5, 128.0, 127.8, 127.7, 127.5, 118.5, 109.3, 108.0, 104.1, 49.7, 42.8, 31.3, 28.8, 25.9, 16.9; Anal. Calcd for $C_{25}H_{24}N_2O$: C, 81.49; H, 6.57; N, 7.60. Found C, 81.88; H, 6.66; N, 7.62.



7,8-dihydro-4-(4-methoxyphenyl)-3,7,7-trimethyl-2-phenylquinolin-5(1H,4H,6H)-one (**5j**):

Yellowish white solid, mp 194-196 °C (CH_2Cl_2 + EtOAc, equal volumes); IR ν_{max} (KBr) 3434, 3067, 2951, 2869, 1681, 1576, 1530, and 1349 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.52-7.20 (9H, m), 6.15 (1H, s), 4.45 (1H, s), 2.45-1.94 (4H, m), 1.53 (3H, s), 1.05 (3H, s), 0.94 (3H, s); Anal. Calcd for $C_{25}H_{27}NO_2$: C, 80.40; H, 7.29; N, 3.75. Found C, 80.10; H, 7.38; N, 3.71.



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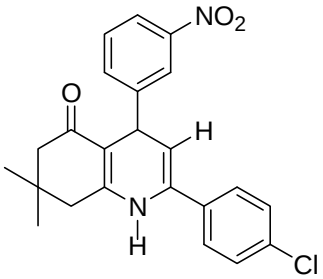
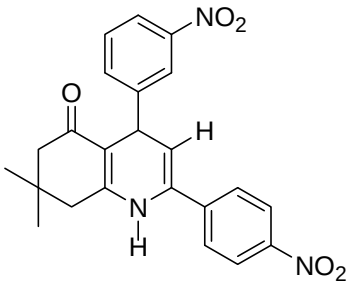
4-(4-chlorophenyl)-7,8-dihydro-3,7,7-trimethyl-2-phenylquinolin-5(1H,4H,6H)-one (**5k**):

Yellowish white solid, mp 200-202 °C; IR ν_{max} (KBr) 3434, 3059, 2959, 2869, 1681, 1576, 1526, and 1344 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.40-7.29 (7H, m), 7.80 (2H, d, J = 7.8 Hz), 6.25 (1H, s), 4.42 (1H, s), 3.75 (3H, s), 2.36-1.98 (4H, m), 1.54 (3H, s), 1.09 (3H, s), 0.92 (3H, s); Anal. Calcd for $C_{24}H_{24}ClNO$: C, 76.28; H, 6.40; N, 3.71. Found C, 76.28; H, 6.49; N, 3.58.



2-(4-Chloro-phenyl)-3,7,7-trimethyl-4-(3-nitro-phenyl)-4,6,7,8-tetrahydro-1H-quinolin-5-one (**5l**):

Yellow solid, mp 268-270 °C (CH_2Cl_2 + EtOAc, equal volumes); IR ν_{max} (KBr) 3170, 3074, 1666, 1588, 1531, 1499, 1388, and 1349 cm^{-1}; ^1H NMR (300 MHz, DMSO-D_6) δ: 8.77 (1H, s), 8.00-7.95 (2H, m), 7.67 (1H, d, J = 7.8 Hz), 7.56-7.41 (5H, m), 5.25 (1H, d, J = 5.1 Hz), 4.72 (1H, d, J = 5.1 Hz), 2.19-1.95 (4H, m), 1.00 (3H, s), 0.92 (3H, s); ^{13}C NMR (75 MHz, DMSO-D_6) δ: 194.0, 153.0, 150.3, 147.9, 134.4, 134.3, 133.7, 133.1, 129.7, 128.5, 127.6, 121.8, 120.9, 105.3, 50.3, 37.3, 32.0, 29.2, 26.8; Anal. Calcd for $C_{23}H_{21}ClN_2O_3$: C, 67.56; H, 5.18; N, 6.85. Found C, 67.86; H, 5.20; N, 7.00.



7,8-dihydro-7,7-dimethyl-4-(3-nitrophenyl)-2-(4-nitrophenyl)quinolin-5(1H,4H,6H)-one (**5m**):

Yellow solid, mp 294-296 °C (CH_2Cl_2 + EtOAc, equal volumes); IR ν_{max} (KBr) 3188, 3074, 2964, 1661, 1589, 1531, 1499, 1388, and 1345 cm^{-1}; ^1H NMR (300 MHz, DMSO-D_6) δ: 9.90 (1H, s), 8.64 (2H, d, J = 8.7 Hz), 8.45-8.33 (3H, m), 8.19 (2H, d, J = 9.0 Hz), 8.12 (1H, d, J = 7.5 Hz), 8.03-7.98 (2H, m), 5.92 (1H, d, J = 4.2 Hz), 5.20 (1H, d, J = 5.1 Hz), 2.65-2.37 (4H, m), 1.45 (3H, s), 1.37 (3H, s); ^{13}C NMR (75 MHz, DMSO-D_6) δ: 193.5, 152.4, 149.5, 149.2, 148.6, 147.2, 146.8, 146.6, 140.3, 133.9, 133.7, 133.4, 133.2, 129.2, 1218.6, 128.1, 126.2, 123.1, 121.4, 121.2,

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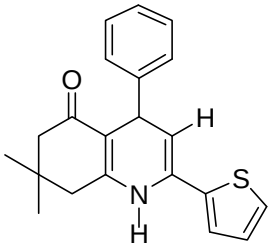
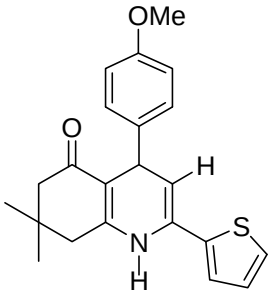
120.4, 120.1, 110.0, 107.6, 104.6, 49.6, 36.8, 33.0, 31.6, 28.5, 28.4, 27.2, 26.2; Anal. Calcd for $C_{23}H_{21}N_3O_5$: C, 65.86; H, 5.05; N, 10.02. Found C, 66.06; H, 5.15; N, 10.00.

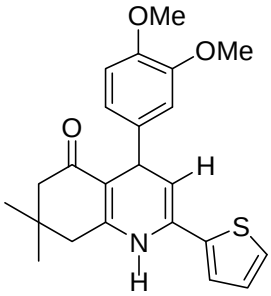


7,8-dihydro-7,7-dimethyl-4-phenyl-2-(thiophen-2-yl)quinolin-5(1H,4H,6H)-one (**5n**): yellowish white solid, mp 194-196 °C; IR ν_{max} (KBr) 3432, 3067, 2951, 2859, 1686, 1576, 1526, and 1344 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.32 (2H, d, J = 7.5 Hz), 7.24 (2H, t, J = 7.5 Hz), 7.19-7.10 (2H, m), 7.07 (1H, d, J = 2.4 Hz), 6.96 (1H, t, J = 3.6 Hz), 6.22 (1H, brs), 5.35(1H, d, J = 5.1 Hz), 4.68 (1H, d, J = 5.1 Hz), 2.38-2.10 (4H, m), 1.06 (3H, s), 0.98 (3H, s); Anal. Calcd for $C_{22}H_{23}NOS$: C, 75.61; H, 6.63; N, 4.01. Found C, 75.90; H, 6.70; N, 4.21.



7,8-dihydro-4-(4-methoxyphenyl)-7,7-dimethyl-2-(thiophen-2-yl)quinolin-5(1H,4H,6H)-one (**5o**):

Yellowish white solid, mp 212-214 °C; IR ν_{max} (KBr) 3432, 3067, 2951, 2869, 1681, 1576, 1530, and 1344 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.26 (2H, d, J = 8.7 Hz), 7.20 (1H, d, J = 5.1 Hz), 7.06 (1H, d, J = 5.4, Hz), 6.99 (1H, t, J = 4.2 Hz), 6.80 (2H, d, J = 8.7 Hz), 6.07 (1H, s), 5.36-5.34 (1H, m), 4.64 (1H, d, J = 5.1 Hz), 3.77 (3H, s), 2.38-2.12 (4H, m), 1.07 (3H, s), 0.99 (3H, s); Anal. Calcd for $C_{22}H_{23}NO_2S$: C, 72.30; H, 6.34; N, 3.83; O. Found CC, 72.30; H, 6.34; N, 3.83; O.



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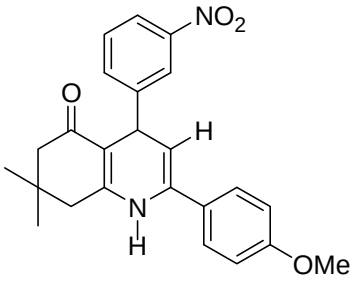
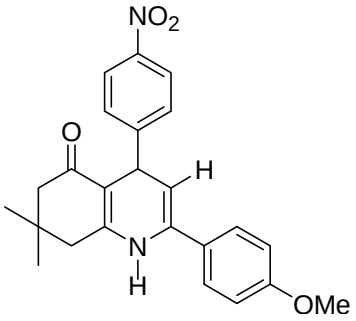
7,8-dihydro-4-(3,4-dimethoxyphenyl)-7,7-dimethyl-2-(thiophen-2-yl)quinolin-5(1H,4H,6H)-one (**5p**):

Yellowish white solid, mp 222-224 °C; IR ν_{max} (KBr) 3438, 3057, 2951, 2869, 1681, 1579, 1530, and 1346 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 7.20 (1H, d, J = 5.1 Hz), 7.10 (1H, d, J = 3.3, Hz), 6.98 (1H, t, J = 4.5 Hz), 6.86 (1H, d, J = 8.1 Hz), 6.77 (1H, d, J = 8.4 Hz), 6.19 (1H, s), 5.38-5.36 (1H, m), 4.65 (1H, d, J = 5.4 Hz), 3.80 (3H, s), 3.76 (3H, s), 2.40-2.04 (4H, m), 1.08 (3H, s), 1.01 (3H, s) ; Anal. Calcd for $C_{23}H_{25}NO_3S$: C, 69.84; H, 6.37; N, 3.54. Found C, 70.03; H, 6.47; N, 3.54.



7,8-dihydro-2-(4-methoxyphenyl)-7,7-dimethyl-4-(3-nitrophenyl)quinolin-5(1H,4H,6H)-one (**5q**):

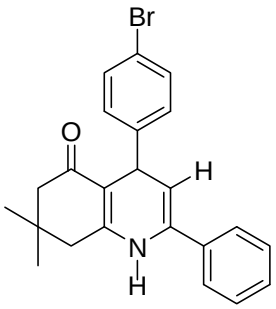
Yellow solid, mp 184-186 °C (CH_2Cl_2 + EtOAc, equal volumes); IR ν_{max} (KBr) 3180, 3074, 2964, 1661, 1589, 1531, 1499, 1388, and 1345 cm^{-1}; ^1H NMR (300 MHz, DMSO-D_6) δ: 8.69 (1H, s), 8.00-7.93 (2H, m), 7.67 (1H, d, J = 7.5 Hz), 7.58-7.48 (1H, m), 7.39 (2H, d, J = 8.7 Hz), 6.91 (2H, d, J = 9.0 Hz), 5.11 (1H, d, J = 6.6 Hz), 4.70 (1H, d, J = 5.4 Hz), 3.72 (3H, s), 2.19-1.93 (4H, m), 1.00 (3H, s), 0.95 (3H, s); ^{13}C NMR (75 MHz, DMSO-D_6) δ: 193.9, 159.6, 155.0, 150.7, 147.8, 135.1, 134.2, 129.6, 127.3, 127.1, 122.5, 121.8, 120.7, 120.4, 113.9, 111.9, 105.4, 103.3, 55.3, 50.3, 37.3, 31.7, 29.2, 28.0, 26.8; Anal. Calcd for $C_{24}H_{24}N_2O_4$: C, 71.27; H, 5.98; N, 6.93. Found C, 71.51; H, 5.88; N, 6.90.



7,8-dihydro-2-(4-methoxyphenyl)-7,7-dimethyl-4-(4-nitrophenyl)quinolin-5(1H,4H,6H)-one (**5r**):

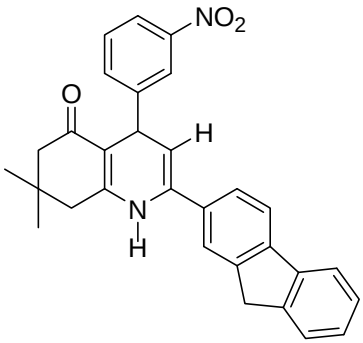
Yellow solid, mp 194-196 °C (CH_2Cl_2 + EtOAc, equal volumes); IR ν_{max} (KBr) 3431, 3069, 2951, 2869, 1681, 1576, 1530, and 1333 cm^{-1}; ^1H NMR (300 MHz, DMSO-D_6) δ: 8.34 (1H, s), 8.13 (2H, d, J = 8.4 Hz), 7.50-7.41 (4H, m), 6.95 (2H, d, J = 8.7 Hz), 5.10 (1H, d, J = 4.5 Hz), 4.72 (1H, d, J = 5.4 Hz), 3.77 (3H, s), 2.21-1.98 (4H, m), 1.04

(3H, s), 0.95 (3H, s); ^{13}C NMR (75 MHz, DMSO-D_6) δ: 193.2, 158.9, 155.4, 152.4, 145.0, 134.4, 128.9, 128.4, 127.9, 126.7, 126.4, 122.9, 122.3, 113.7, 113.2, 104.5, 102.4, 54.7, 49.7, 37.1, 31.3, 28.5, 27.2, 26.4; Anal. Calcd for $C_{24}H_{24}N_2O_4$: C, 71.27; H, 5.98; N, 6.93. Found C, 71.57; H, 5.91; N, 6.71.



4-(4-Bromo-phenyl)-3,7,7-trimethyl-2-phenyl-4,6,7,8-tetrahydro-1H-quinolin-5-one (**5s**):

Yellow solid, mp 164-166 °C (CH_2Cl_2 + EtOAc, equal volumes); IR ν_{max} (KBr)) 3434, 3067, 2951, 2869, 1681, 1577, 1525, and 1335 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.38-7.36 (7H, m), 7.25-7.22 (2H, m), 5.96 (1H, br s), 5.23 (1H, d, J = 4.8 Hz), 4.70 (1H, d, J = 5.1 Hz), 2.42-2.04 (4H, m), 1.00 (3H, s), 0.91 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 195.4, 162.3, 150.7, 146.6, 135.6, 134.4, 131.3, 129.7, 128.9, 125.1, 119.8, 108.1, 106.4, 50.7, 42.1, 37.3, 32.5, 29.4, 27.4; Anal. Calcd for $C_{24}H_{24}BrNO$: C, 68.25; H, 5.73; N, 3.32. Found C, 68.25; H, 5.73; N, 3.32.



2-(9H-fluoren-2-yl)-7,8-dihydro-7,7-dimethyl-4-(3-nitrophenyl)quinolin-5(1H,4H,6H)-one (**5t**):

Yellow solid, mp 194-196 °C; IR ν_{max} (KBr) 3433, 3067, 2951, 2869, 1681, 1577, 1525, and 1344 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.21 (1H, s), 8.00 (1H, dd, J = 8.1 Hz and J = 1.2 Hz), 7.80-7.73 (3H, m), 7.59-7.54 (2H, m), 7.45-7.30 (4H, m), 6.06 (1H, s), 5.29-5.26(1H, m), 5.14 (1H, d, J = 5.1 Hz), 3.90 (2H, s), 2.55-2.15 (4H, m), 1.12 (3H, s), 1.04 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 194.5, 149.7, 148.7, 144.0, 143.4, 142.7, 140.8, 135.4, 134.2, 133.7, 129.0, 127.3, 127.0, 125.1, 124.0, 122.8, 122.0, 121.2, 120.2, 107.2, 105.4, 50.6, 42.1, 38.0, 36.9, 32.6, 29.3, 27.4; Anal. Calcd for $C_{14}H_{16}N_2O_3S$: C, 57.52; H, 5.52; N, 9.58. Found C, 57.70; H, 5.60; N, 9.70.

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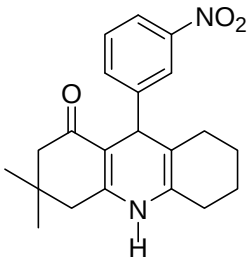
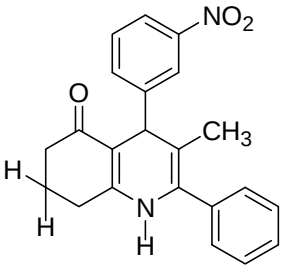


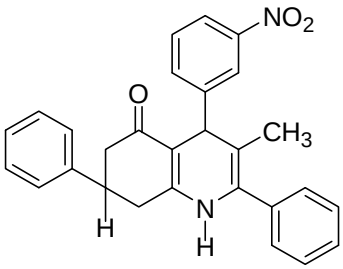
3,3-Dimethyl-9-(3-nitro-phenyl)-3,4,5,6,7,8,9,10-octahydro-2H-acridin-1-one (**5u**):

Brown liquid, IR ν_{max} (Neat) 3434, 3067, 2951, 2869, 1681, 1576, 1530, and 1349 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-D_6) δ: 8.34 (1H, s), 7.96-7.93 (2H, m), 7.60 (2H, d, J = 7.5 Hz), 7.49 (1H, t, J = 7.8 Hz), 4.30 (1H, s), 2.37-2.21 (2H, m), 2.10-2.05 (3H, m), 1.90-1.85 (1H, m), 1.79-1.74 (1H, m), 1.63 (2H, br s), 1.44 (3H, br s), 0.97 (3H, s), 0.84 (3H, s); ^{13}C NMR (75 MHz, DMSO-D_6) δ: 193.2, 151.4, 149.8, 147.7, 134.3, 129.3, 128.3, 121.8, 120.7, 110.4, 105.1, 50.2, 42.3, 32.0, 29.2, 26.7, 25.6, 22.4, 22.0; Anal. Calcd for $C_{21}H_{24}N_2O_3$: C, 71.57; H, 6.86; N, 7.95. Found C, 71.70; H, 6.86; N, 7.90.



7,8-dihydro-3-methyl-4-(3-nitrophenyl)-2-phenylquinolin-5(1H,4H,6H)-one (**5v**):

Yellow solid, mp 236-238 °C (CH_2Cl_2 + EtOAc, equal volumes); IR ν_{max} (KBr) 3438, 3077, 2961, 1681, 1576, 1530, and 1325 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.35 (1H, s), 8.04 (1H, d, J = 6.6 Hz), 7.82 (1H, d, J = 7.8 Hz), 7.47-7.36 (6H, m), 5.89 (1H, br s), 4.71 (1H, s), 2.52-2.46 (2H, m), 2.36-2.32 (2H, m), 2.09-1.85 (2H, m), 1.54 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 195.5, 151.6, 148.7, 135.8, 134.8, 130.8, 128.8, 122.7, 121.3, 111.9, 108.4, 43.1, 36.9, 27.9, 21.4, 17.5; Anal. Calcd for $C_{22}H_{20}N_2O_3$: C, 73.32; H, 5.59; N, 7.77. Found C, 73.32; H, 5.59; N, 7.77.



7,8-dihydro-3-methyl-4-(3-nitrophenyl)-2,7-diphenylquinolin-5(1H,4H,6H)-one (**5w**):

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Yellow solid, mp 200-202 °C (CH_2Cl_2 + EtOAc, equal volumes); IR ν_{max} (KBr)) 3432, 3071, 2951, 2868, 1681, 1577, 1525, and 1344 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.15 (1H, d, J = 1.8 Hz), 7.99 (1H, dd, J = 9.9 Hz and J = 0.9 Hz), 7.72 (1H, d, J = 7.5 Hz), 7.45-7.08 (11H, m), 5.86 (1H, br s), 4.66 (1H, s), 3.47-3.42 (1H, m), 2.84-2.48 (4H, m), 1.49 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 194.3, 150.5, 148.7, 148.2, 142.6, 135.7, 134.7, 130.7, 128.9, 128.8, 128.6, 126.9, 126.7, 122.7, 121.3, 112.1, 108.2, 43.4, 39.3, 35.2, 30.9, 17.5; Anal. Calcd for $C_{28}H_{24}N_2O_3$: C, 77.04; H, 5.54; N, 6.42. Found C, 77.14; H, 5.54; N, 6.58.

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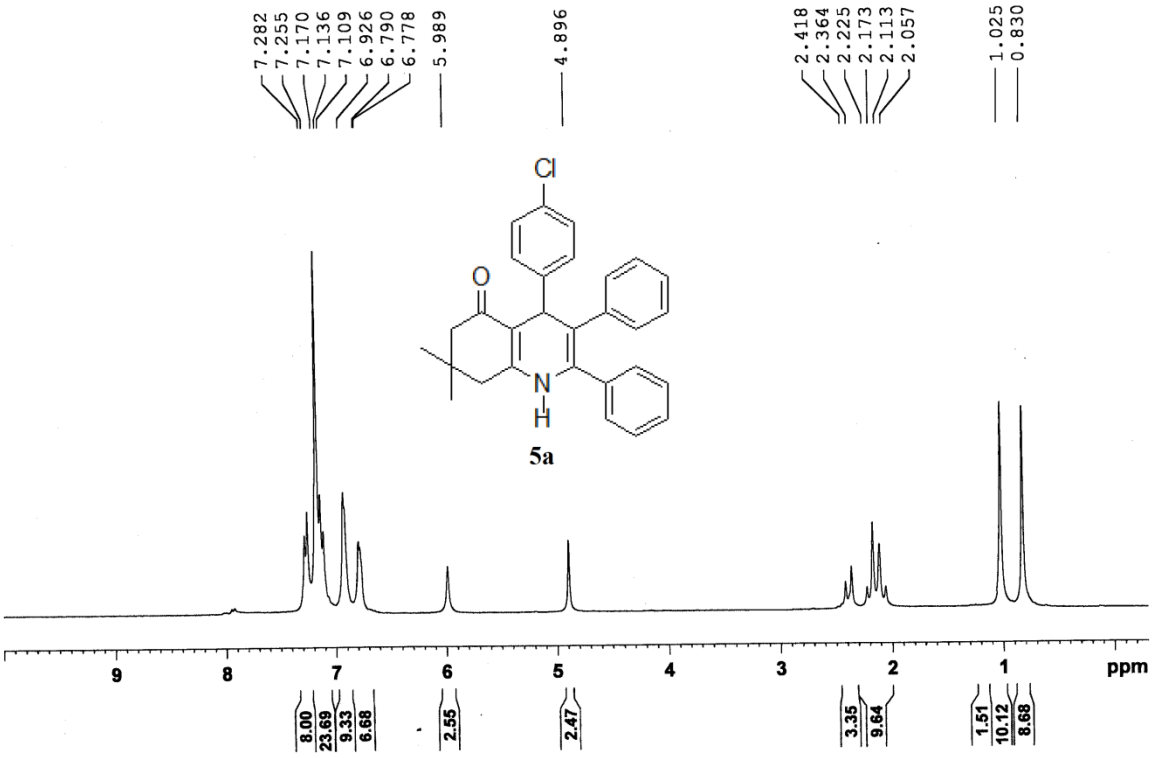
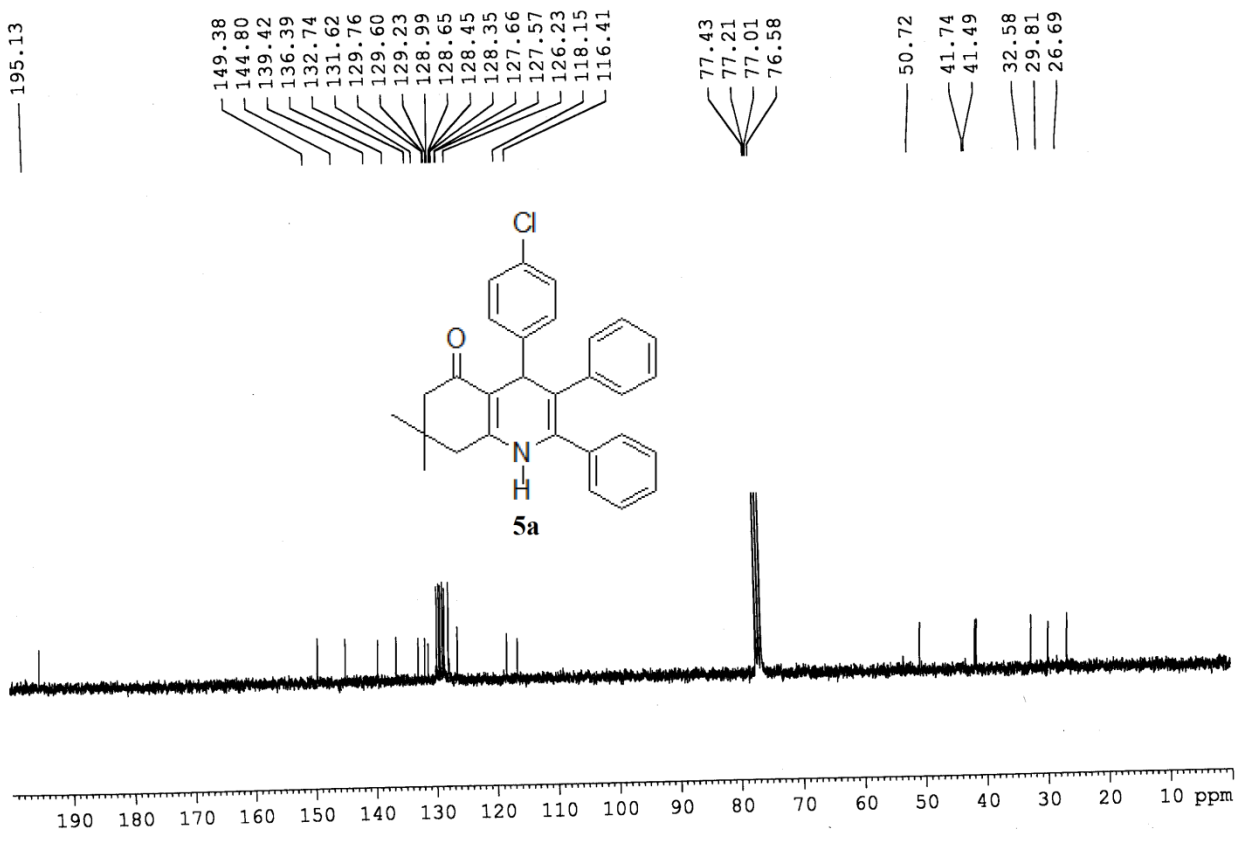
1H NMR and 13C NMR spectra for 5a-5w





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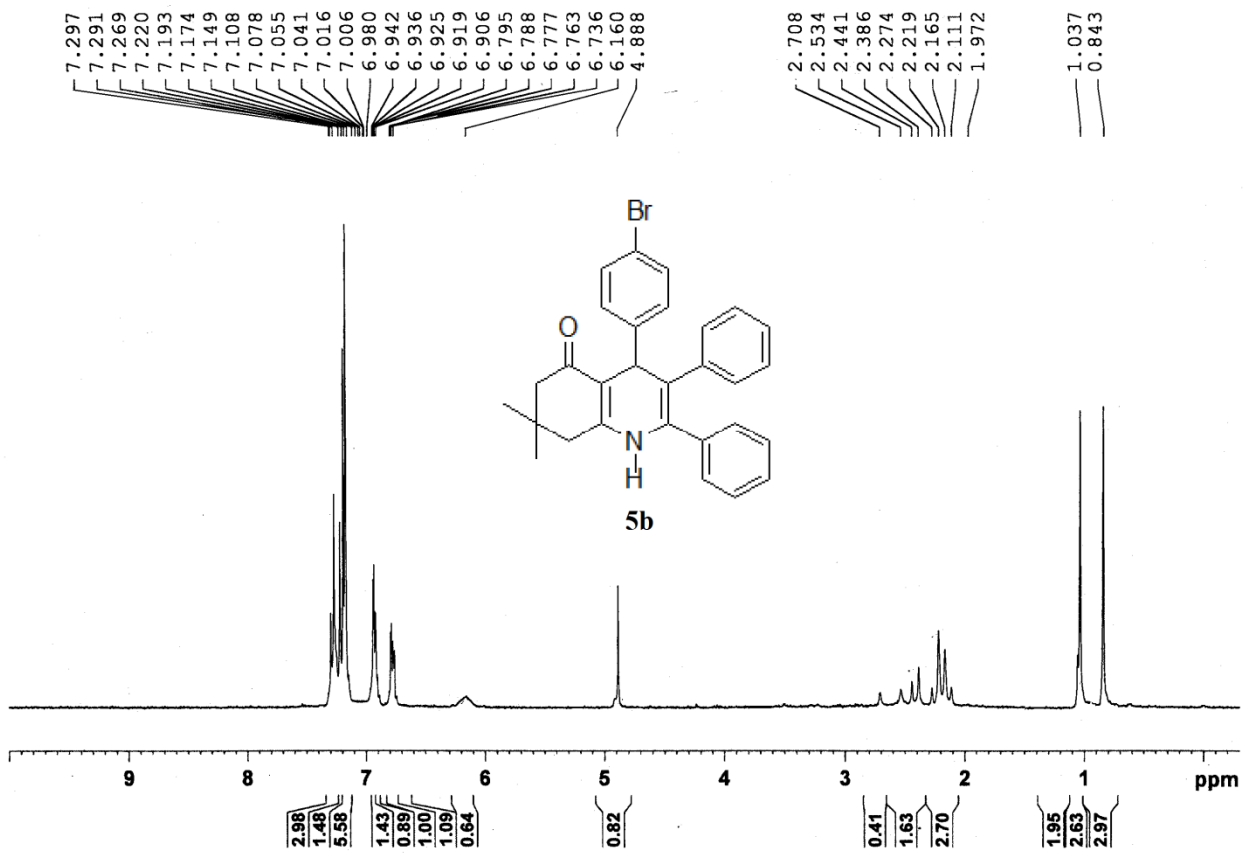

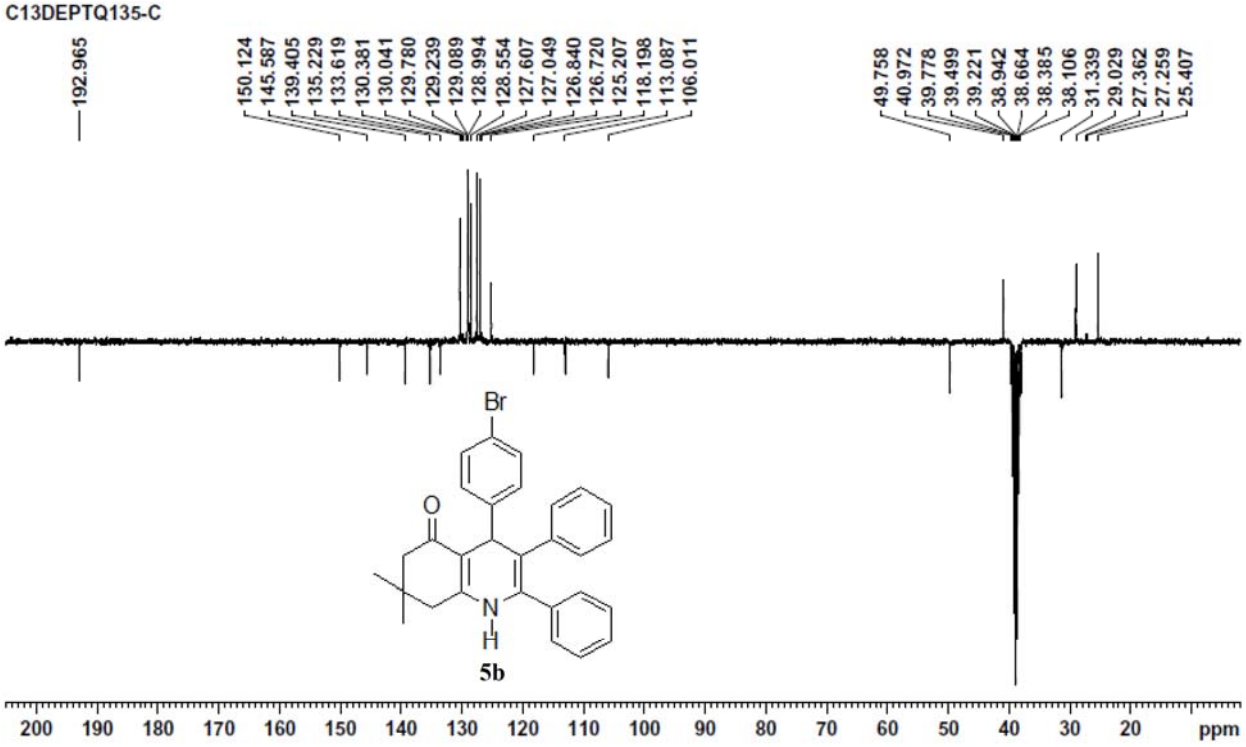

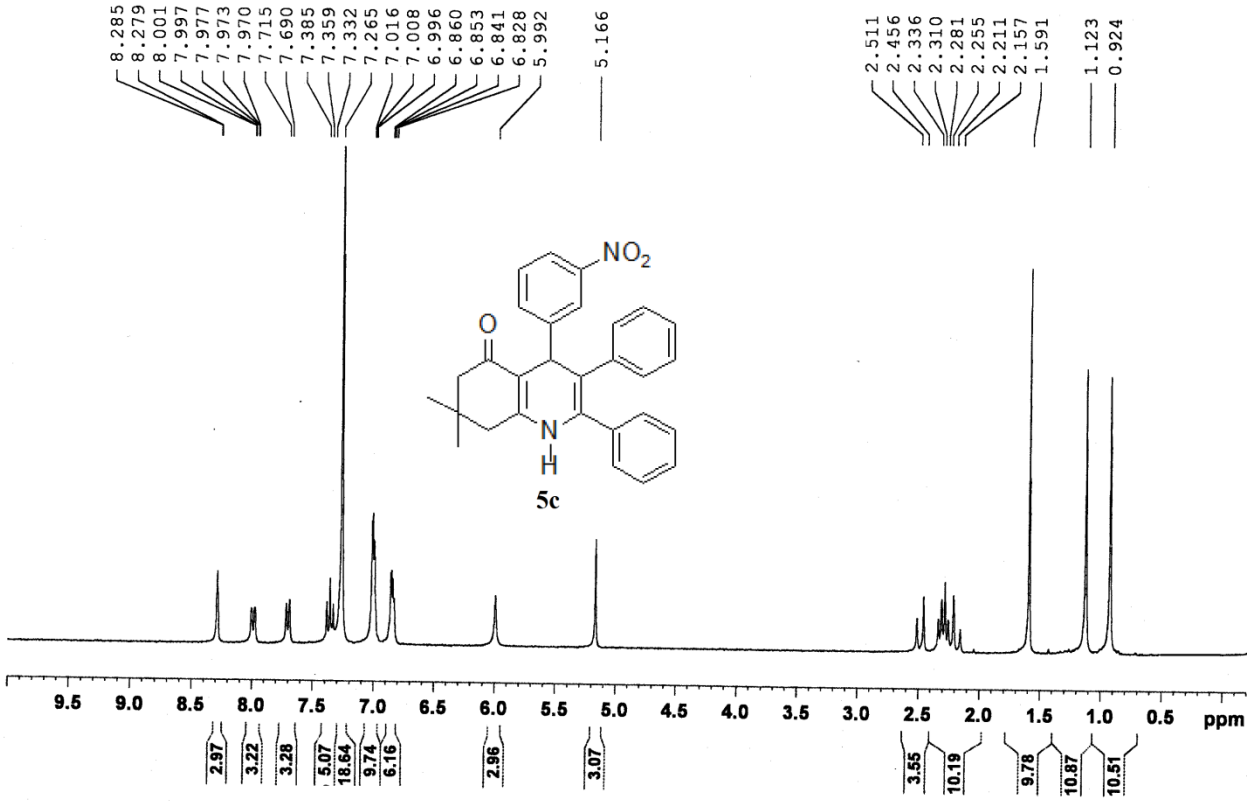

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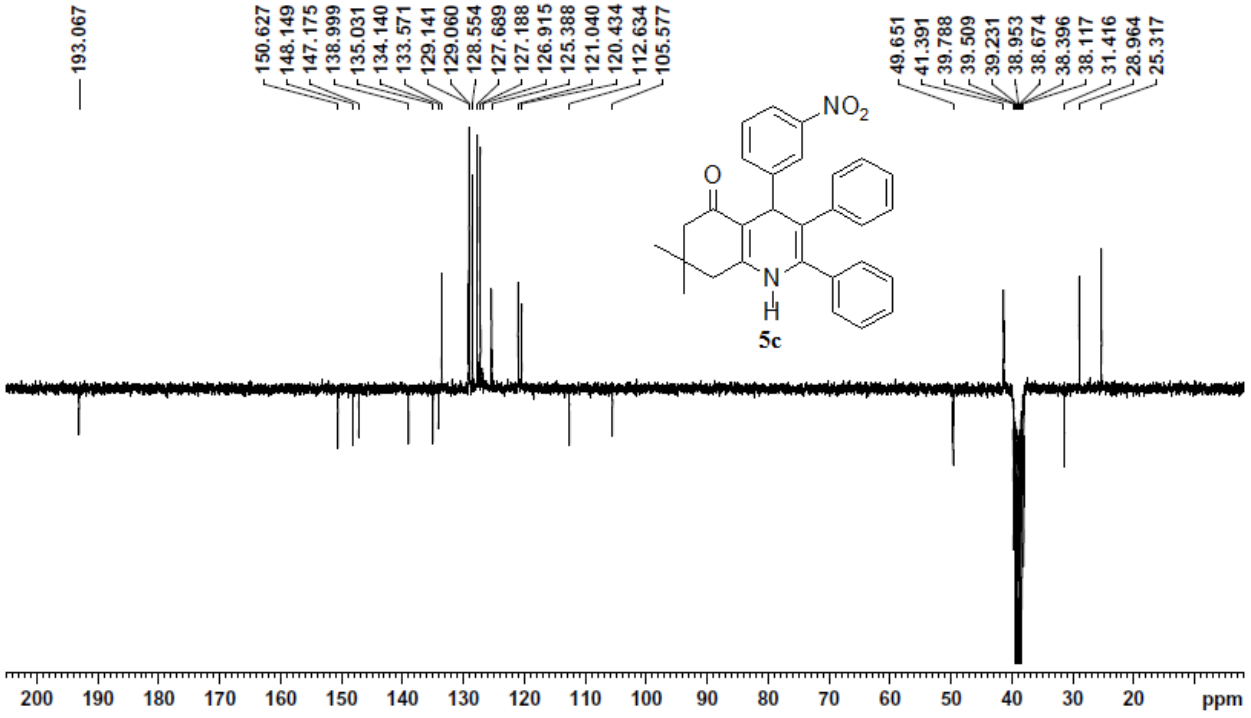

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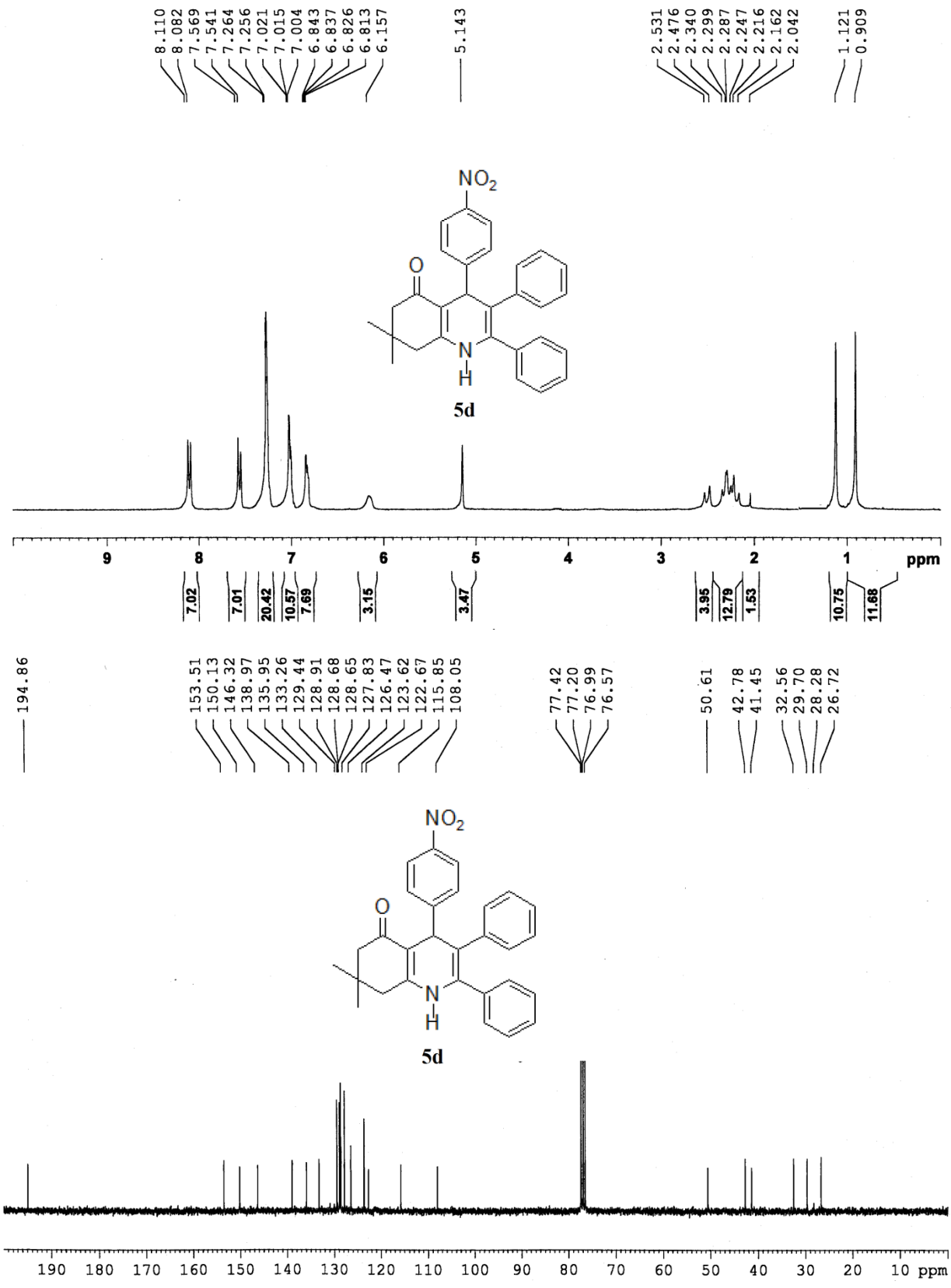

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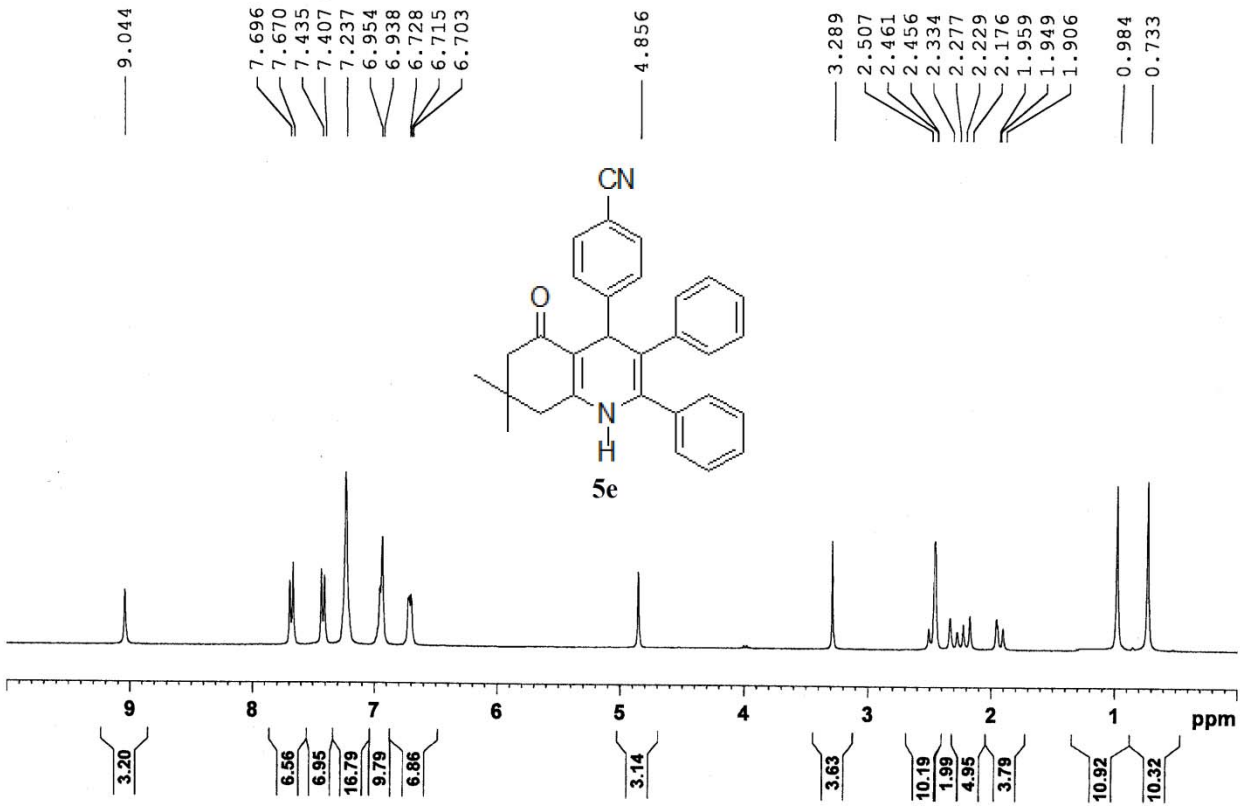

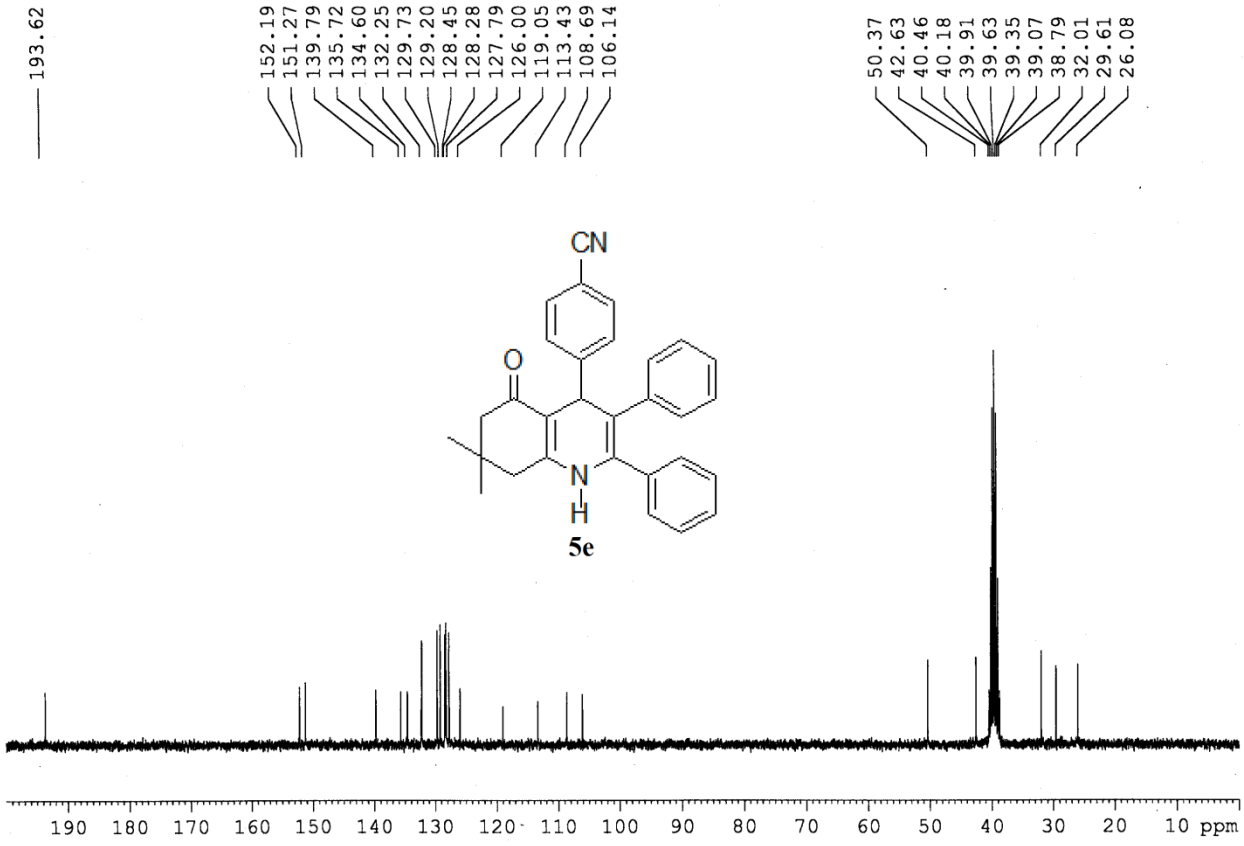

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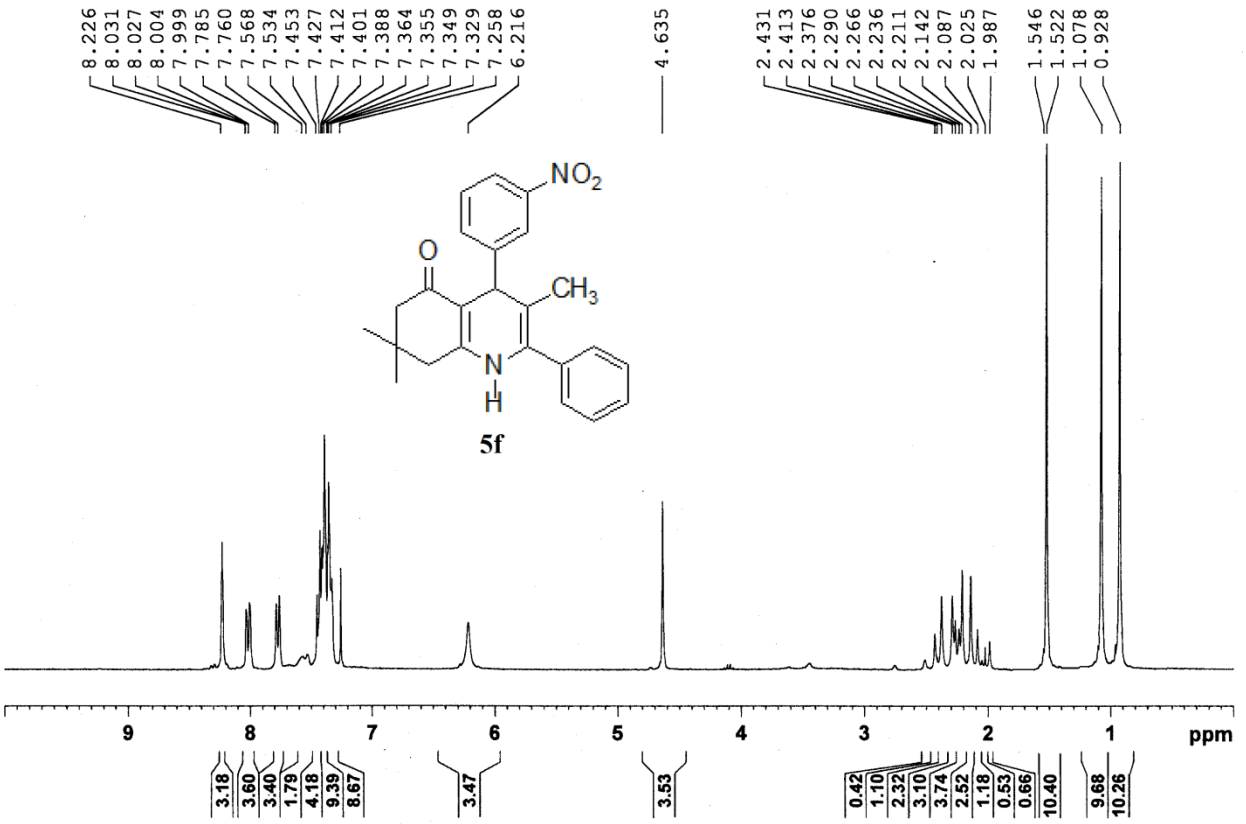

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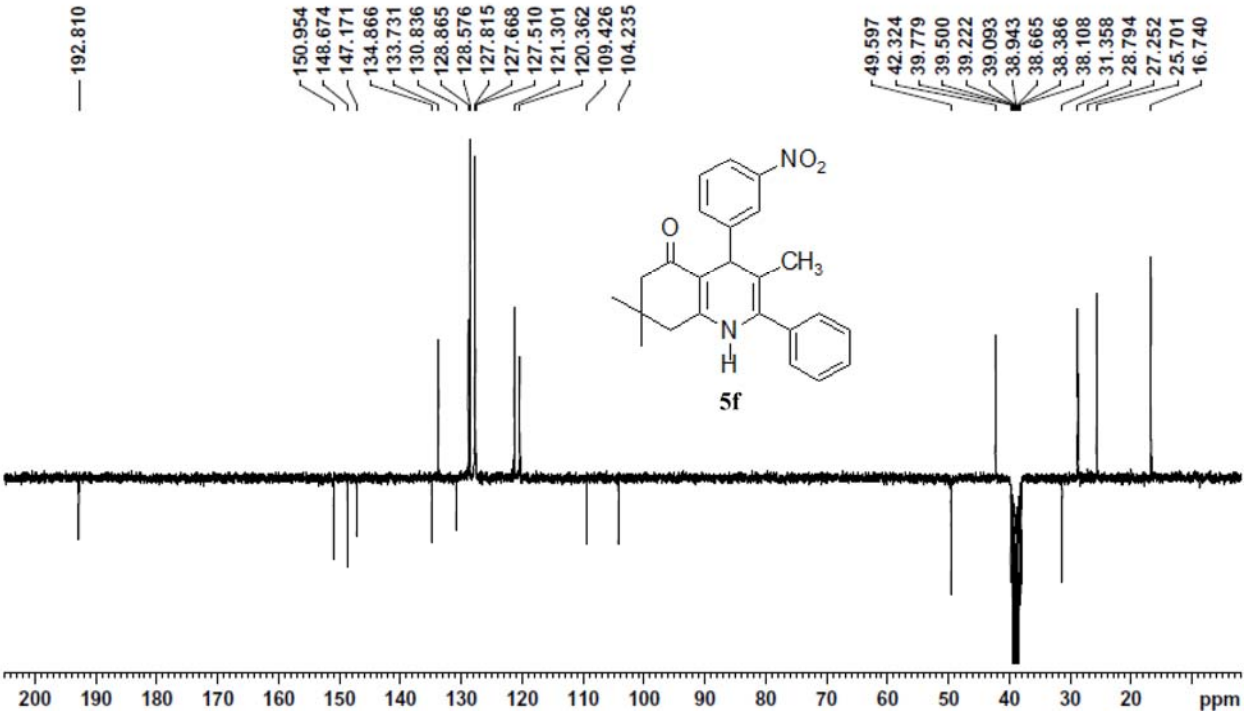

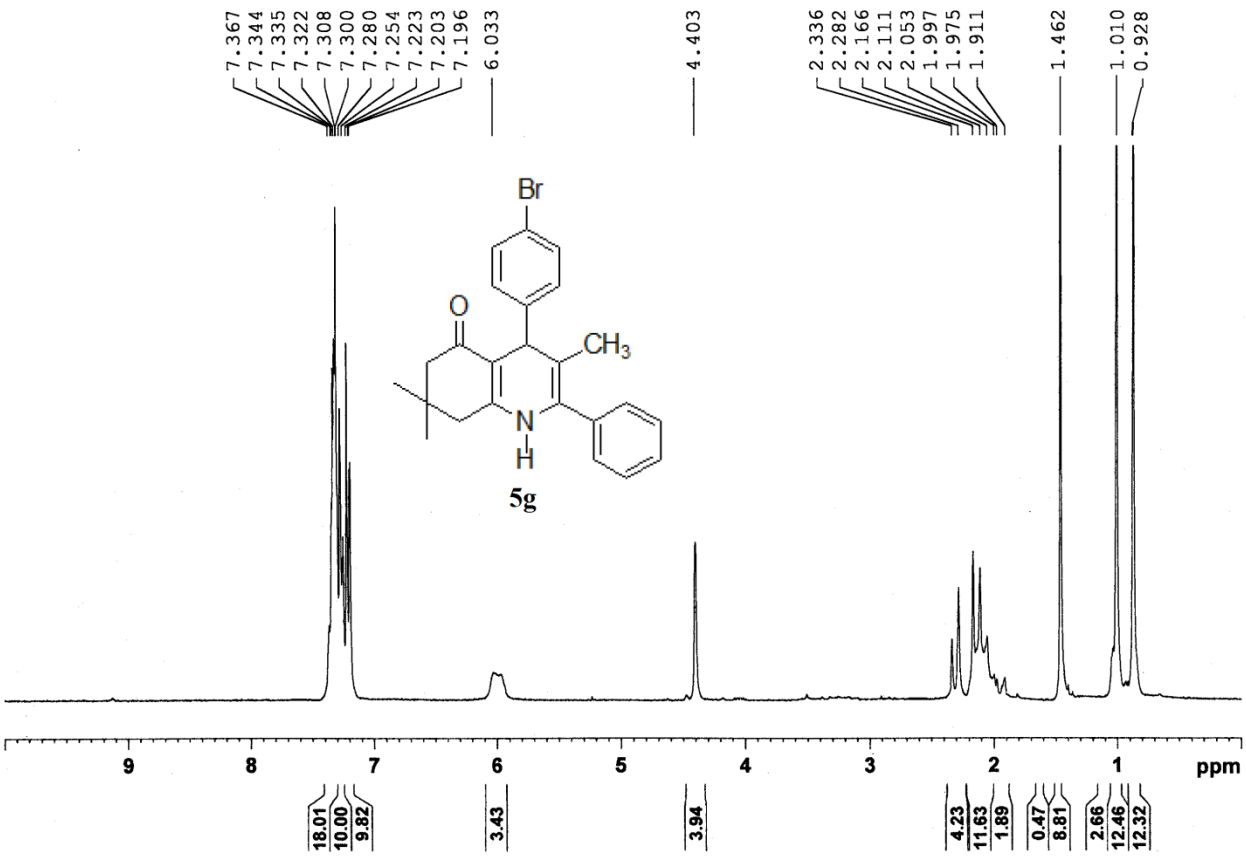

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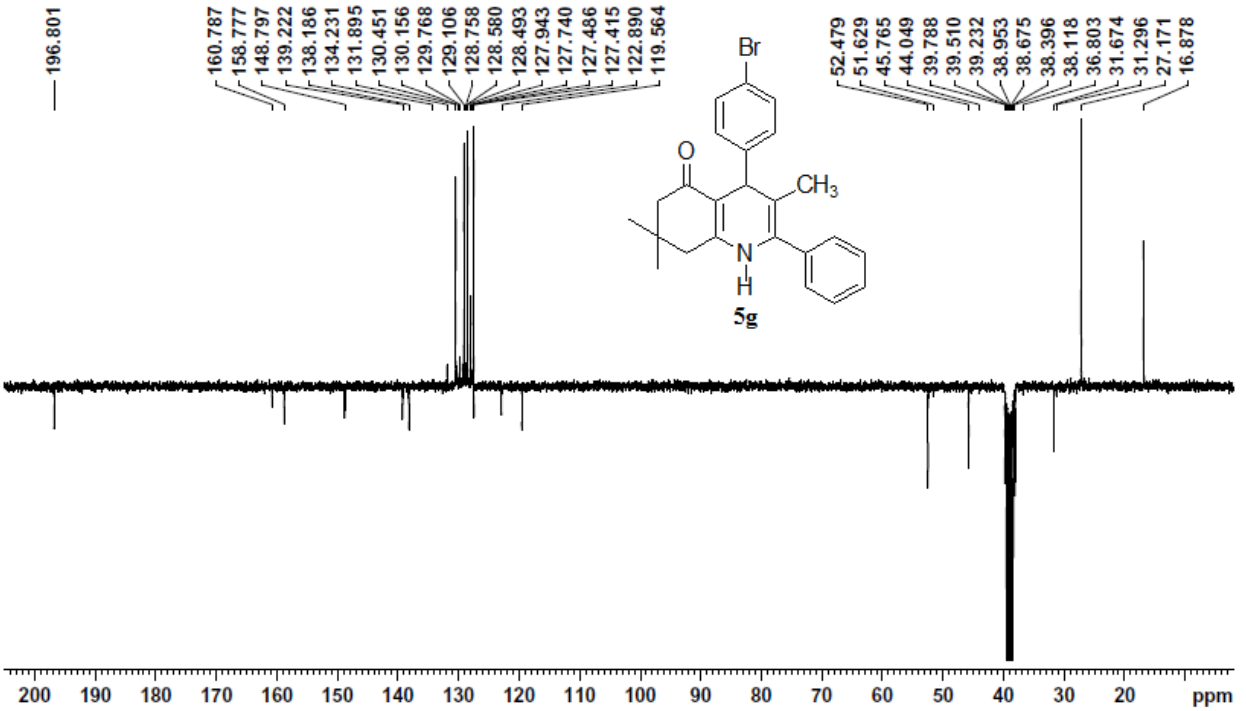

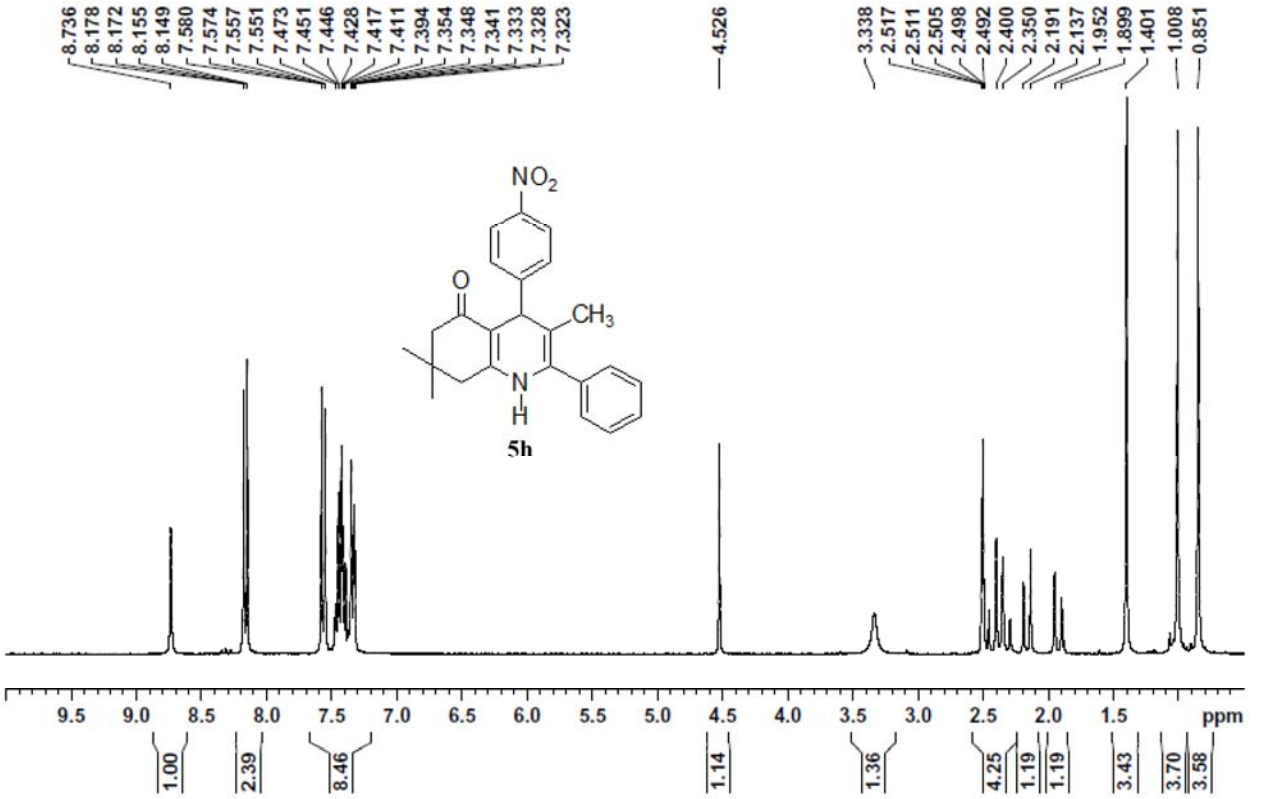
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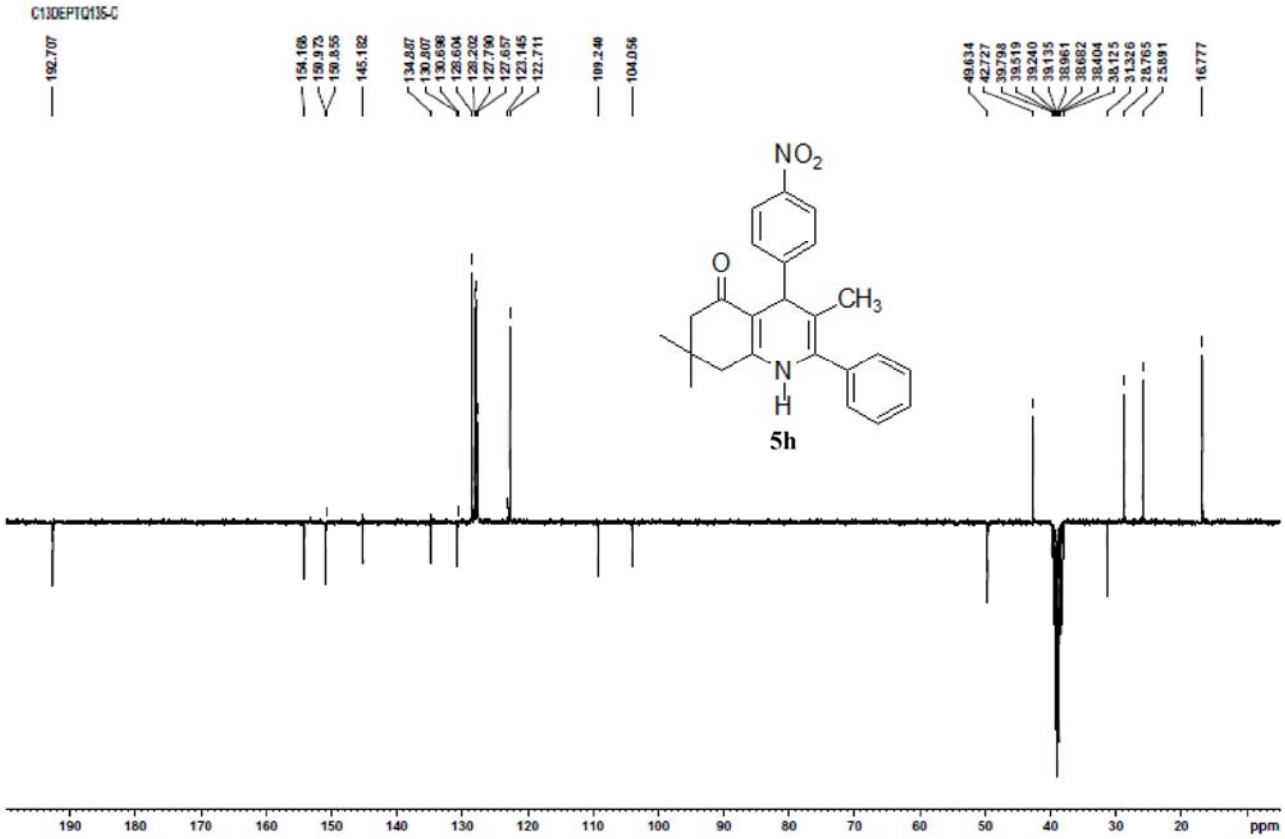
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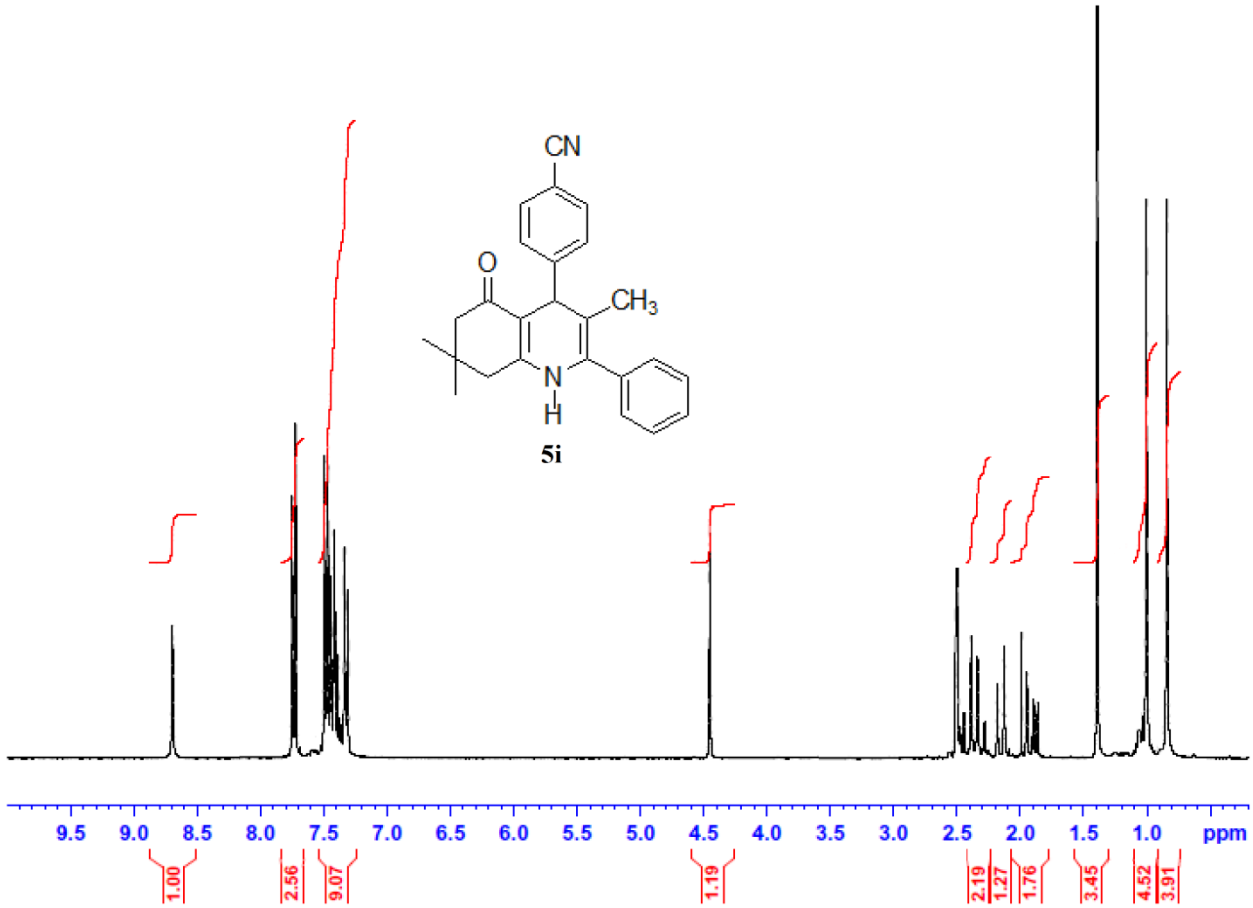
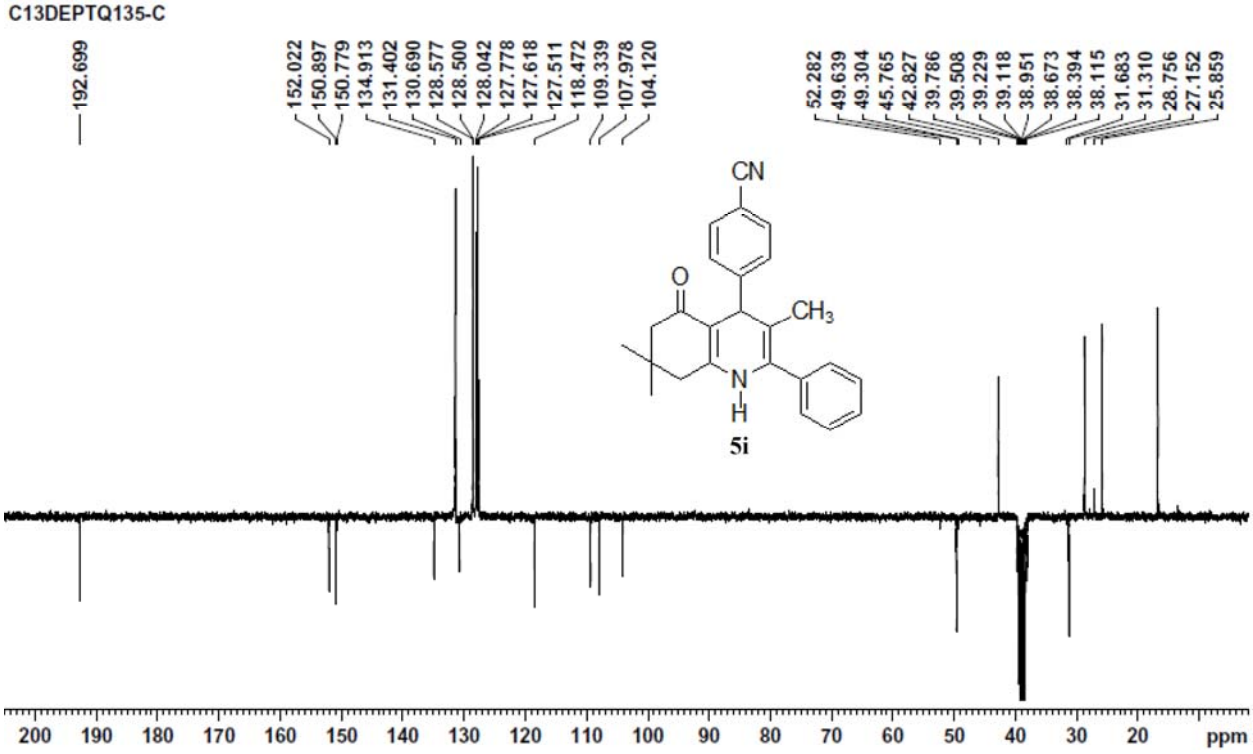
20
ppm


CN
O
CH3
N
H
5i
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.00 2.56 9.07 1.19 2.19 1.27 1.76 3.45 4.52 3.91


C13DEPTQ135-C
192.699
152.022 150.897 150.779 134.913 131.402 130.690 128.577 128.500 128.042 127.778 127.618 127.511 118.472 109.339 107.978 104.120
52.282 49.639 49.304 45.765 42.827 39.786 39.508 39.229 39.118 38.951 38.673 38.394 38.115 31.683 31.310 28.756 27.152 25.859
CN
O
CH3
N
H
5i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

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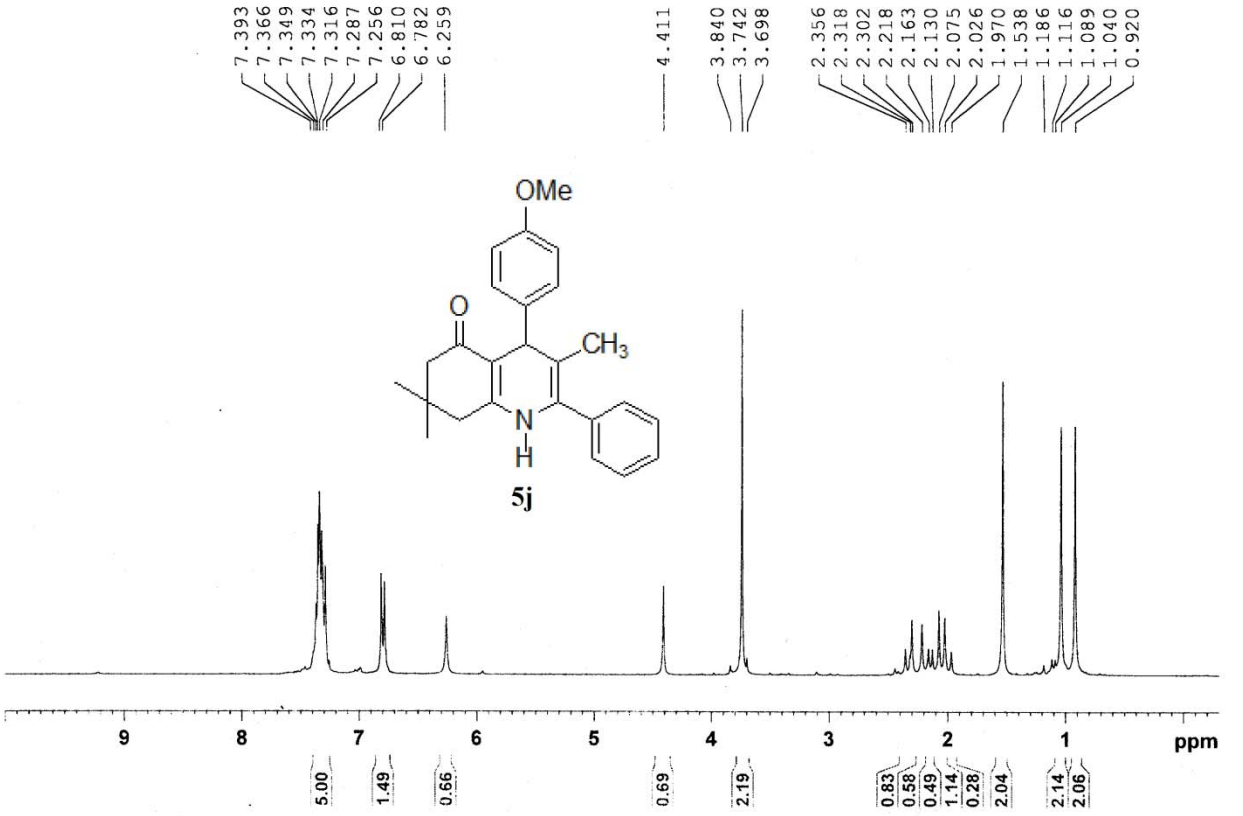

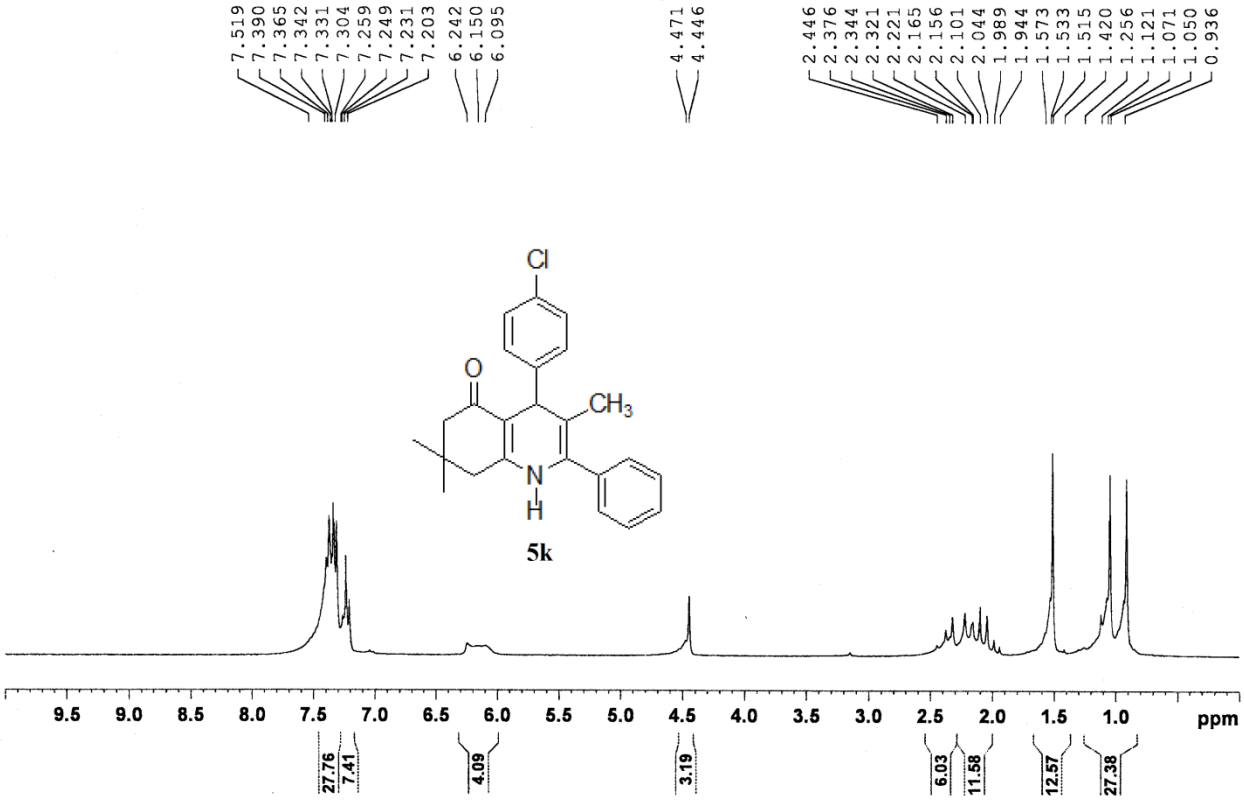

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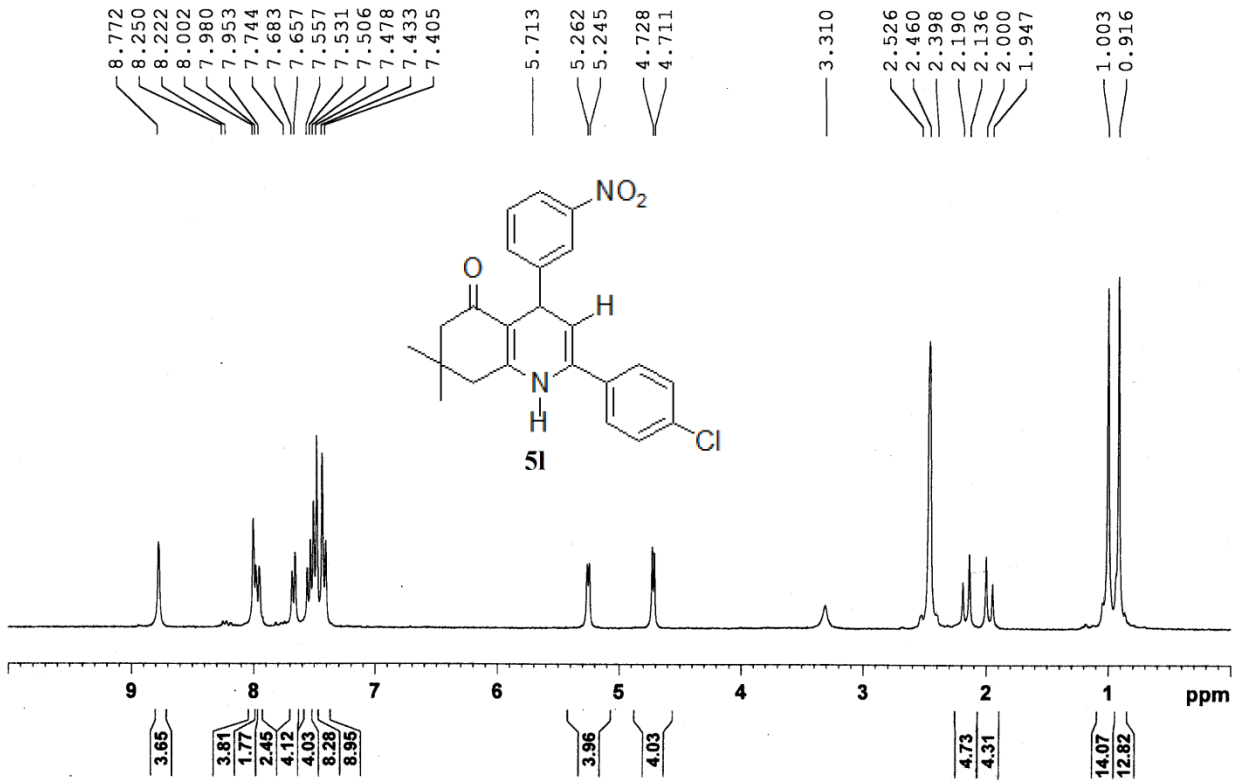

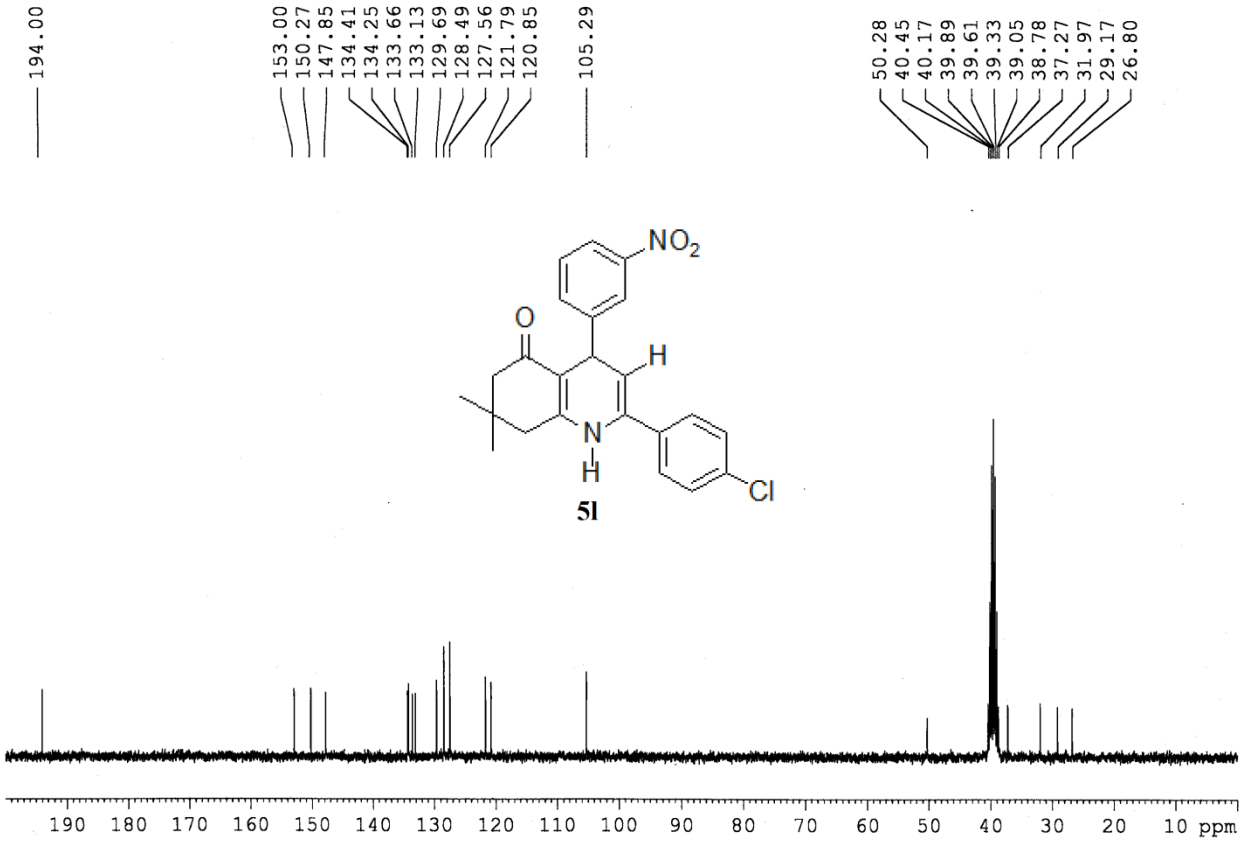

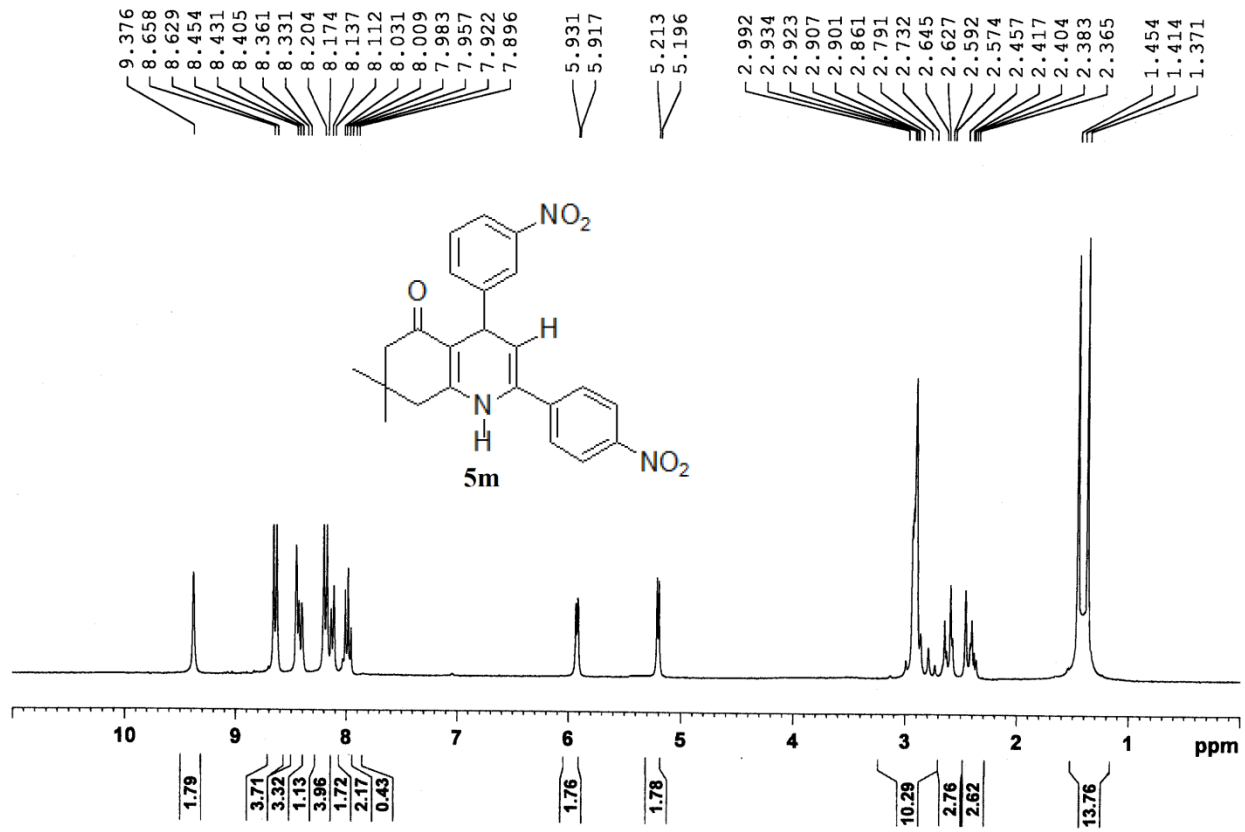

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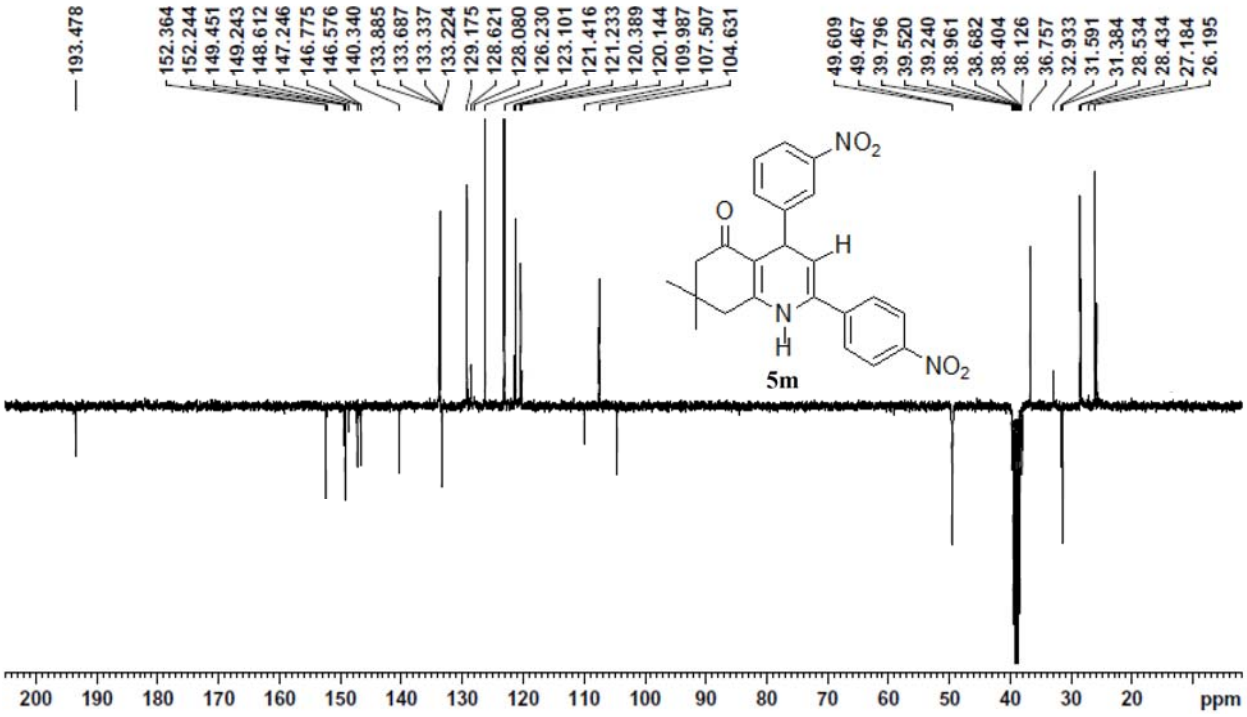
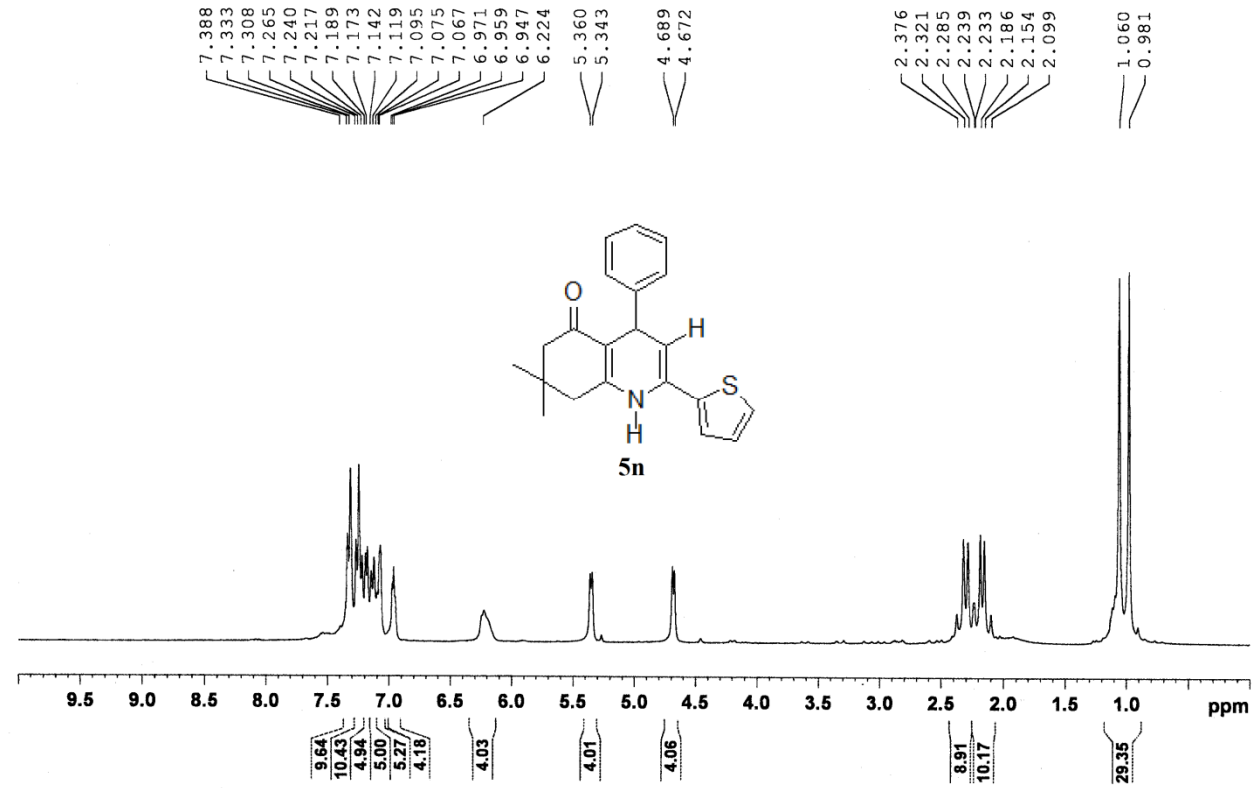
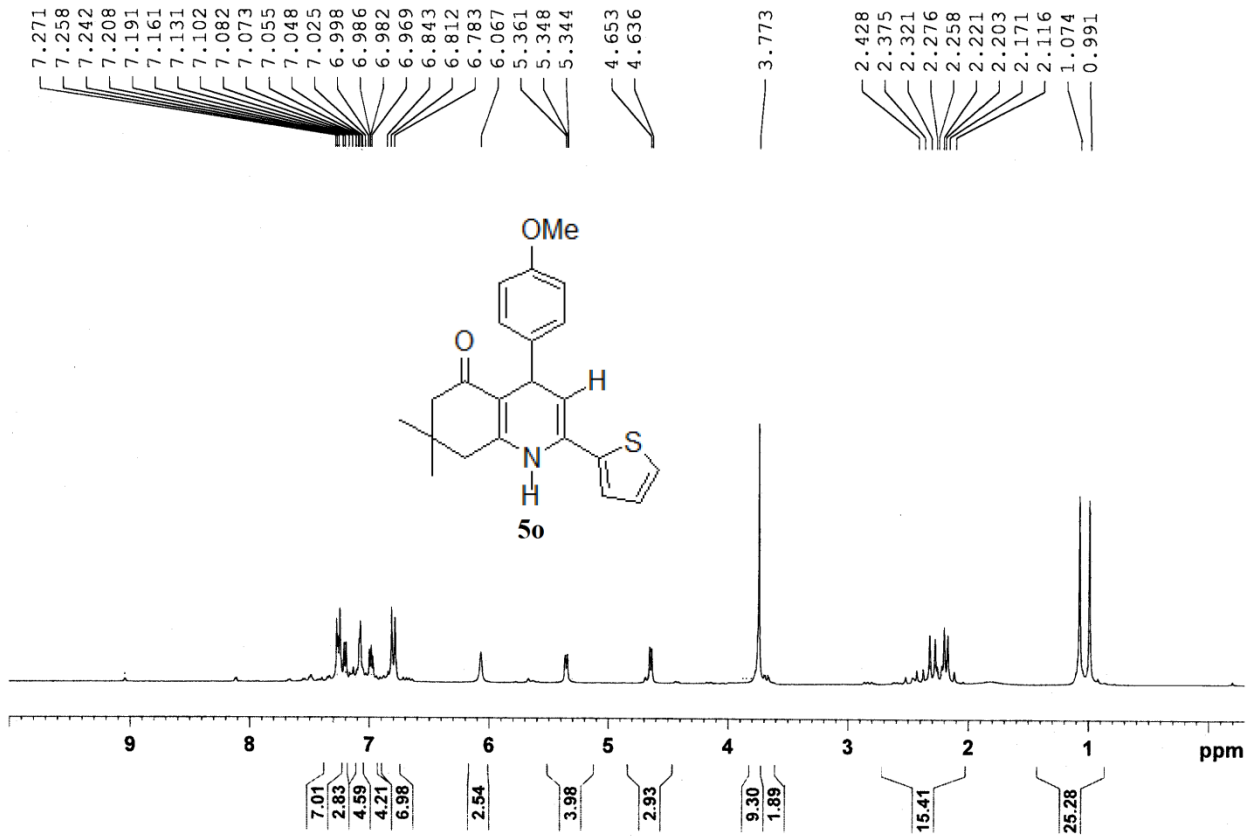



7.388
7.333
7.308
7.265
7.240
7.217
7.189
7.173
7.142
7.119
7.095
7.075
7.067
6.971
6.959
6.947
6.224
5.360
5.343
4.689
4.672
2.376
2.321
2.285
2.239
2.233
2.186
2.154
2.099
1.060
0.981
O
H
N
H
S
5n
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
9.64
10.43
4.94
5.00
5.27
4.18
4.03
4.01
4.06
8.91
10.17
29.35


7.271
7.258
7.242
7.208
7.191
7.161
7.131
7.102
7.082
7.073
7.055
7.048
7.025
6.998
6.986
6.982
6.969
6.843
6.812
6.783
6.067
5.361
5.348
5.344
4.653
4.636
3.773
2.428
2.375
2.321
2.276
2.258
2.221
2.203
2.171
2.116
1.074
0.991
OMe
O
H
N
H
S
5o
9 8 7 6 5 4 3 2 1 ppm
7.01
2.83
4.59
4.21
6.98
2.54
3.98
2.93
9.30
1.89
15.41
25.28

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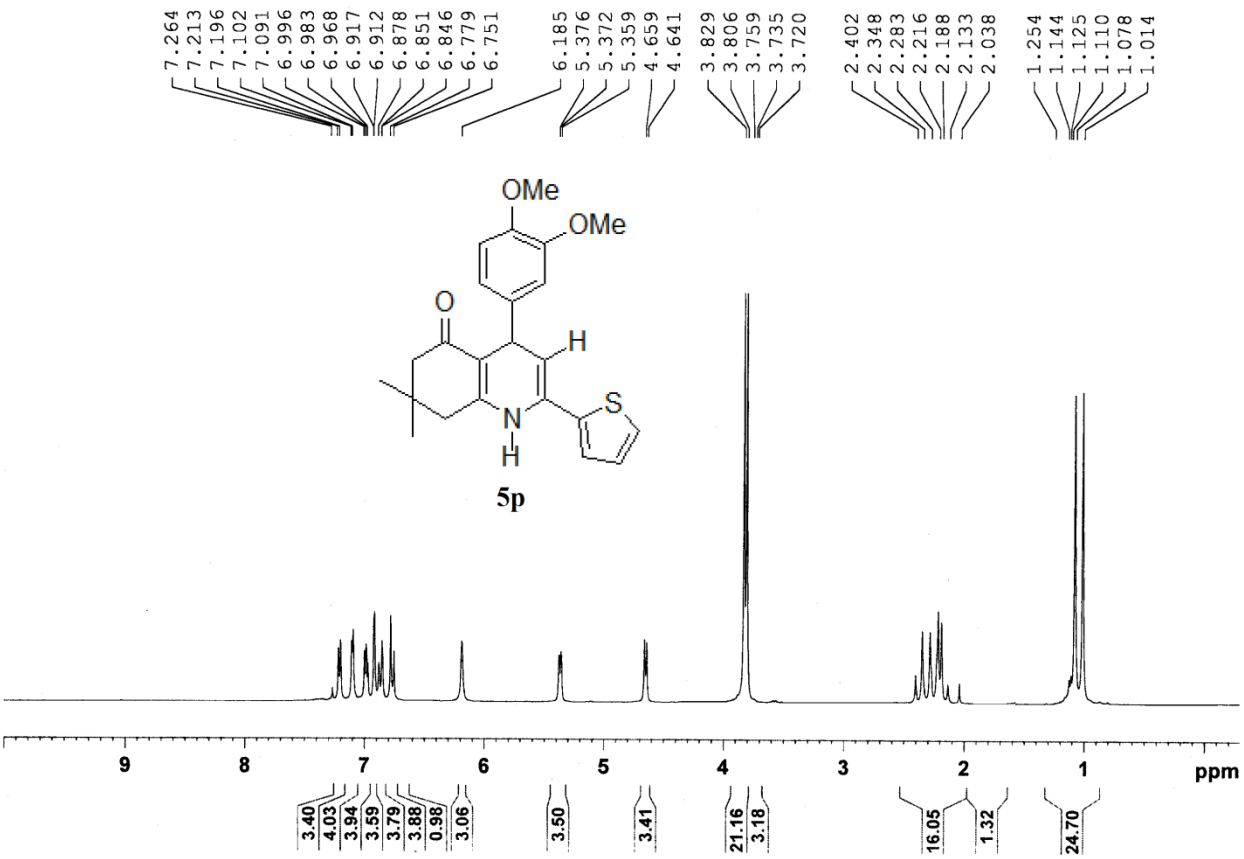

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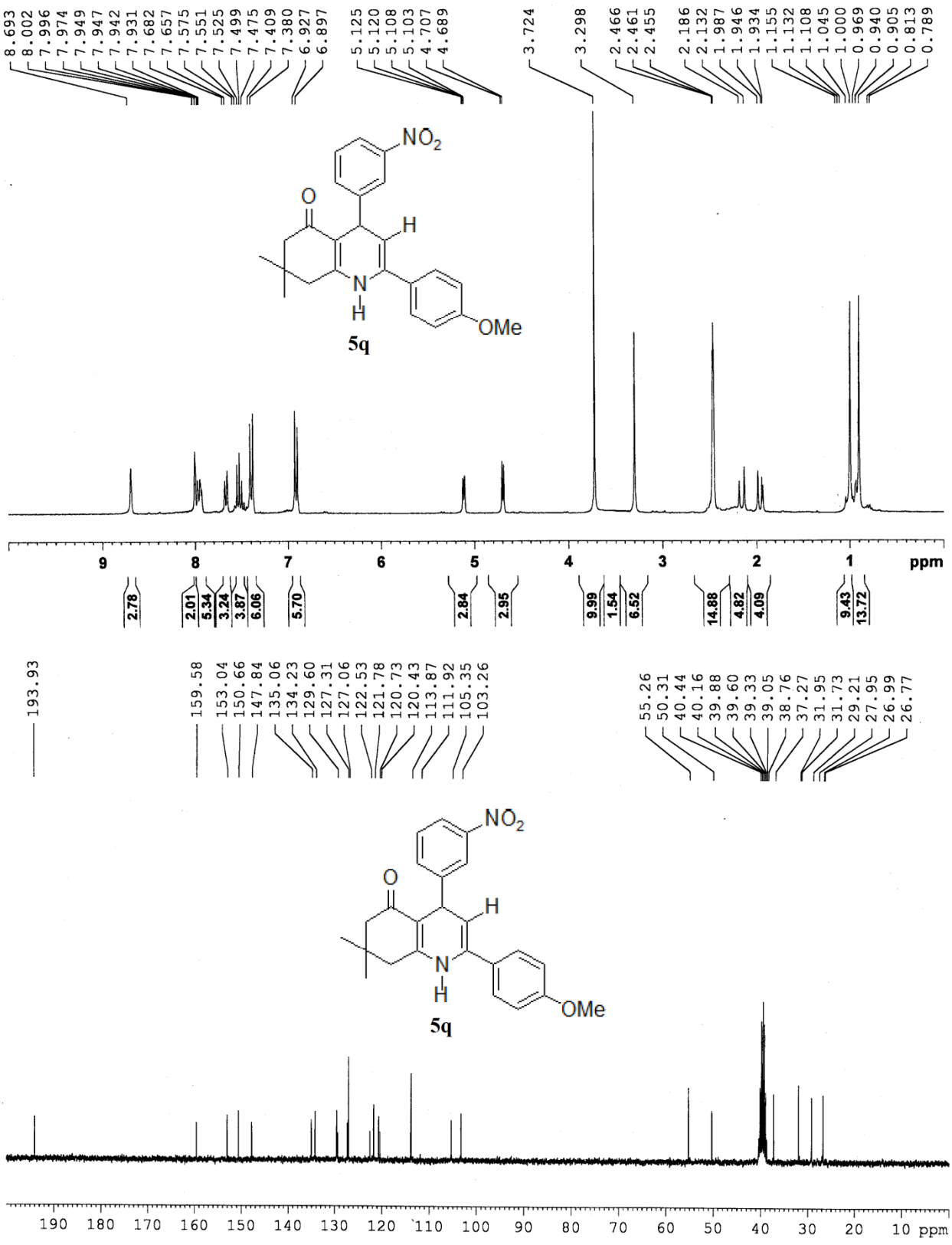

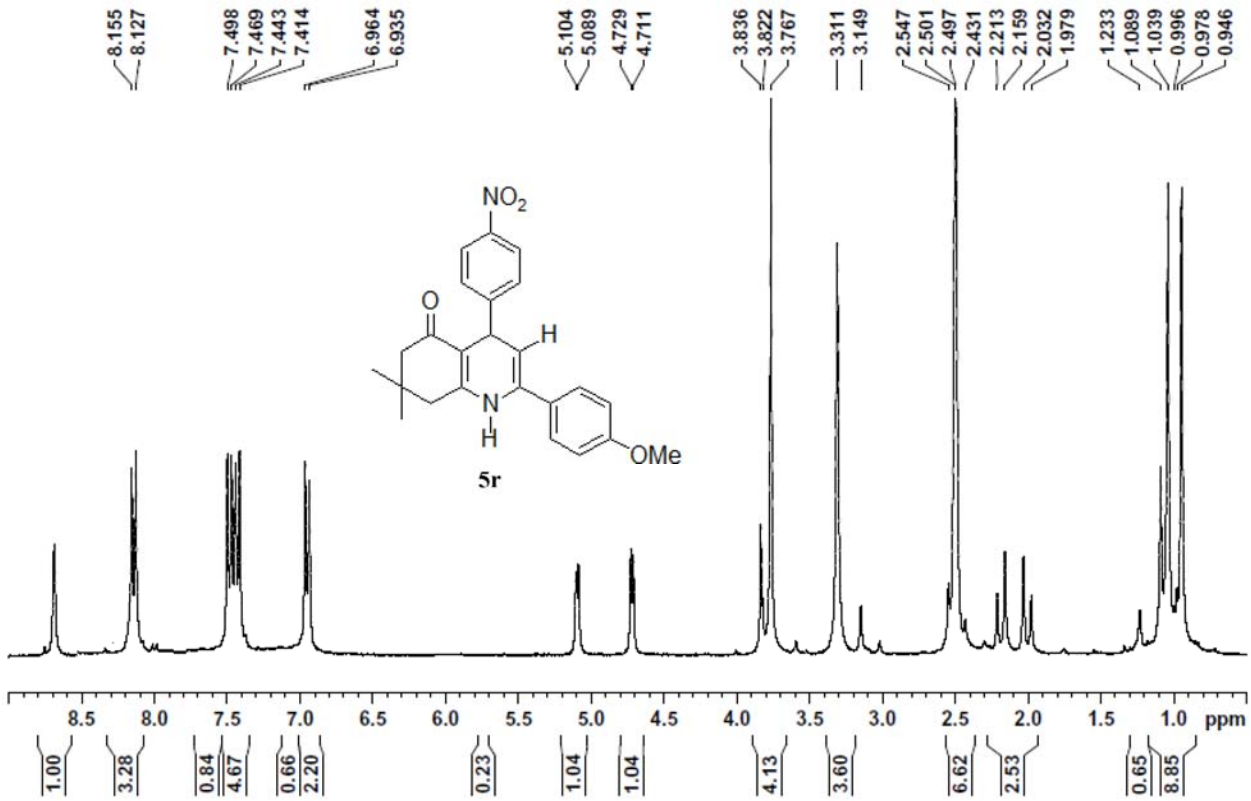
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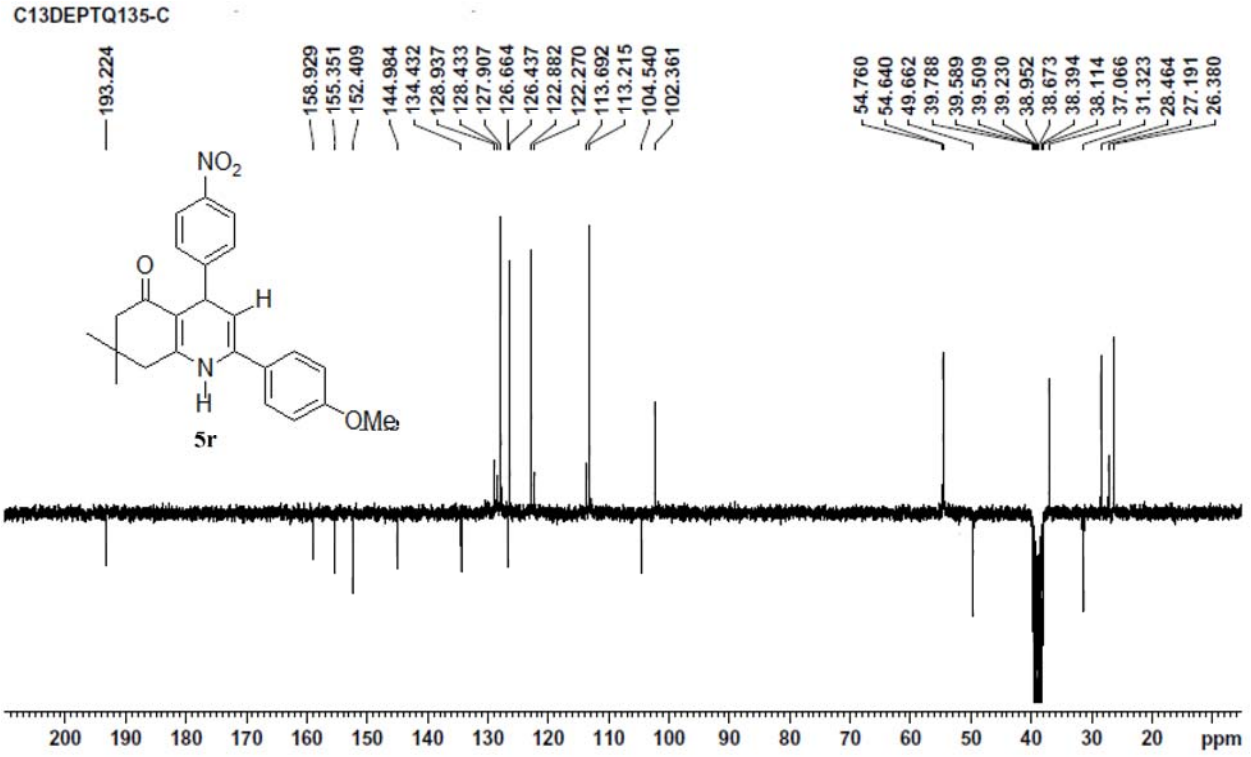
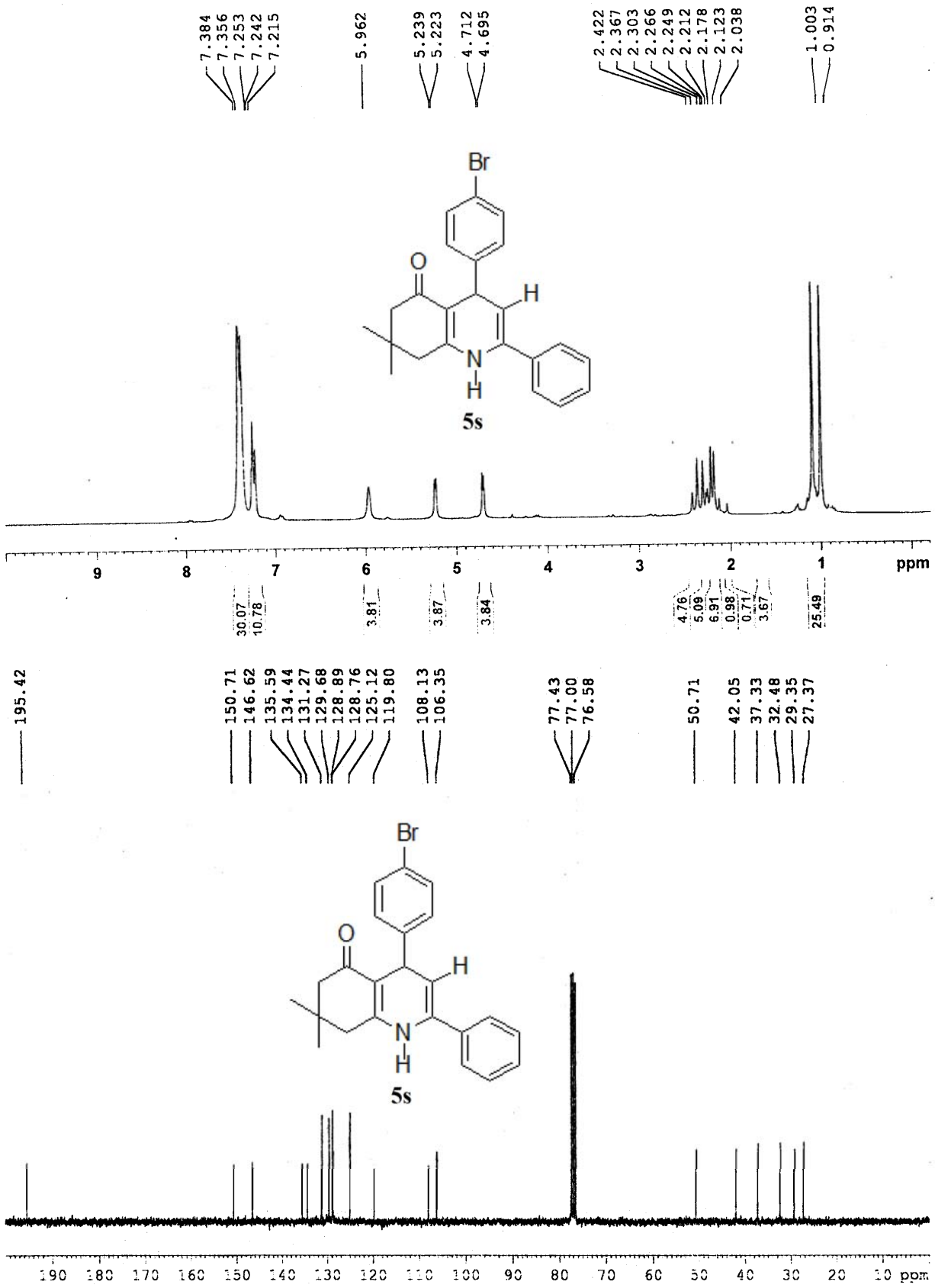
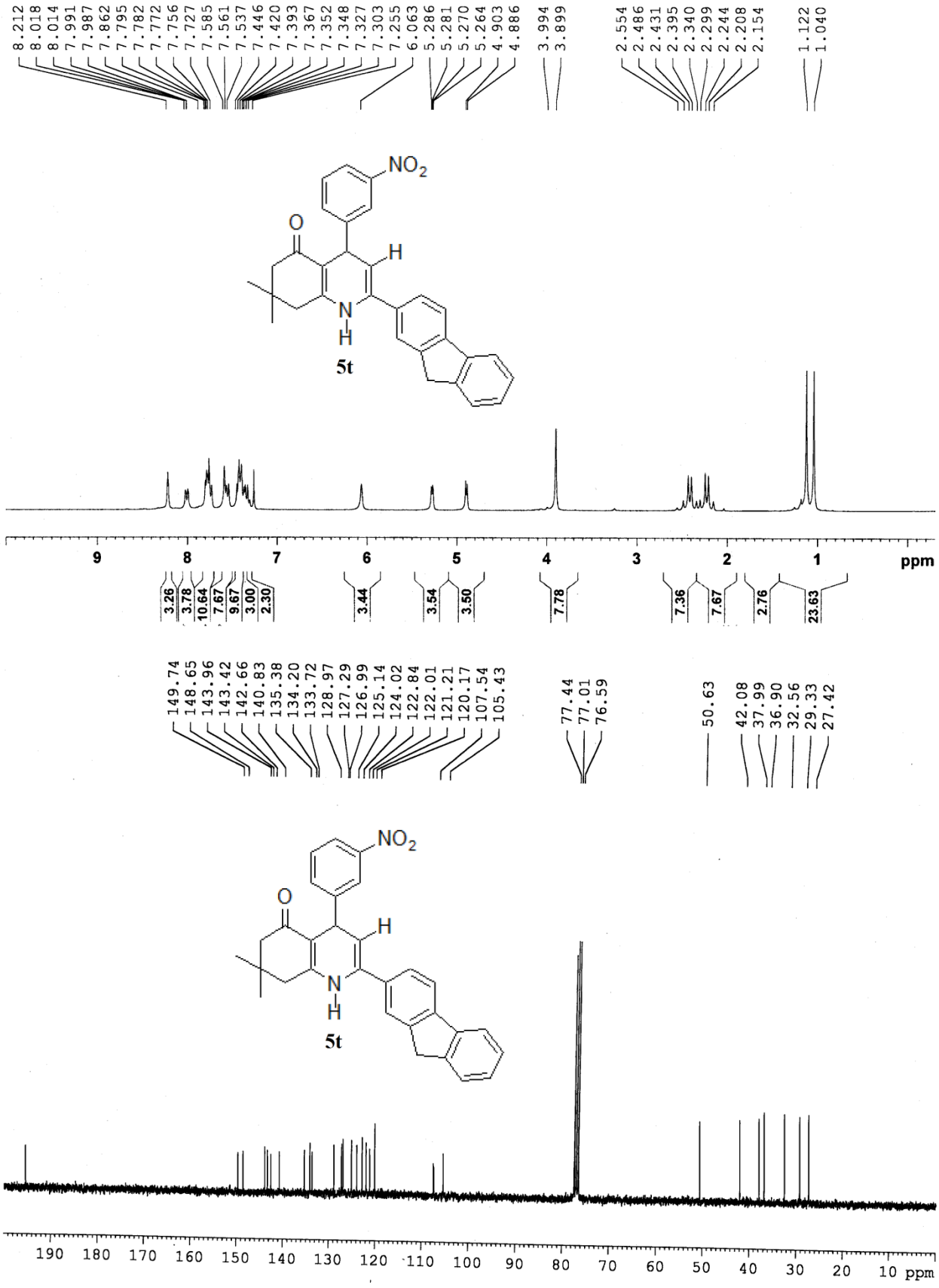
8.127
7.498
7.469
7.443
7.414
6.964
6.935
5.104
5.089
4.729
4.711
3.836
3.822
3.767
3.311
3.149
2.547
2.501
2.497
2.431
2.213
2.159
2.032
1.979
1.233
1.089
1.039
0.996
0.978
0.946
NO2
O
H
N
H
OMe
5r
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
3.28
0.84
4.67
0.66
2.20
0.23
1.04
1.04
4.13
3.60
6.62
2.53
0.65
8.85


C13DEPTQ135-C
193.224
158.929
155.351
152.409
144.984
134.432
128.937
128.433
127.907
126.664
126.437
122.882
122.270
113.692
113.215
104.540
102.361
54.760
54.640
49.662
39.788
39.589
39.509
39.230
38.952
38.673
38.394
38.114
37.066
31.323
28.464
27.191
26.380
NO2
O
H
N
H
OMe
5r
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.384
7.356
7.253
7.242
7.215
5.962
5.239
5.223
4.712
4.695
2.422
2.367
2.303
2.266
2.249
2.212
2.178
2.123
2.038
1.003
0.914
Br
O
H
N
H
5s
ppm
30.07
10.78
3.81
3.87
3.84
4.76
5.09
6.91
0.98
0.71
3.67
25.49
195.42
150.71
146.62
135.59
134.44
131.27
129.68
128.89
128.76
125.12
119.80
108.13
106.35
77.43
77.00
76.58
50.71
42.05
37.33
32.48
29.35
27.37
Br
O
H
N
H
5s
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.212
8.018
8.014
7.991
7.987
7.862
7.795
7.782
7.772
7.756
7.727
7.585
7.561
7.537
7.446
7.420
7.393
7.367
7.352
7.348
7.327
7.303
7.255
6.063
5.286
5.281
5.270
5.264
4.903
4.886
3.994
3.899
2.554
2.486
2.431
2.395
2.340
2.299
2.244
2.208
2.154
1.122
1.040
NO2
O
H
N
H
5t
9
8
7
6
5
4
3
2
1
ppm
3.26
3.78
10.64
7.67
9.67
3.00
2.30
3.44
3.54
3.50
7.78
7.36
7.67
2.76
23.63
149.74
148.65
143.96
143.42
142.66
140.83
135.38
134.20
133.72
128.97
127.29
126.99
125.14
124.02
122.84
122.01
121.21
120.17
107.54
105.43
77.44
77.01
76.59
50.63
42.08
37.99
36.90
32.56
29.33
27.42
NO2
O
H
N
H
5t
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

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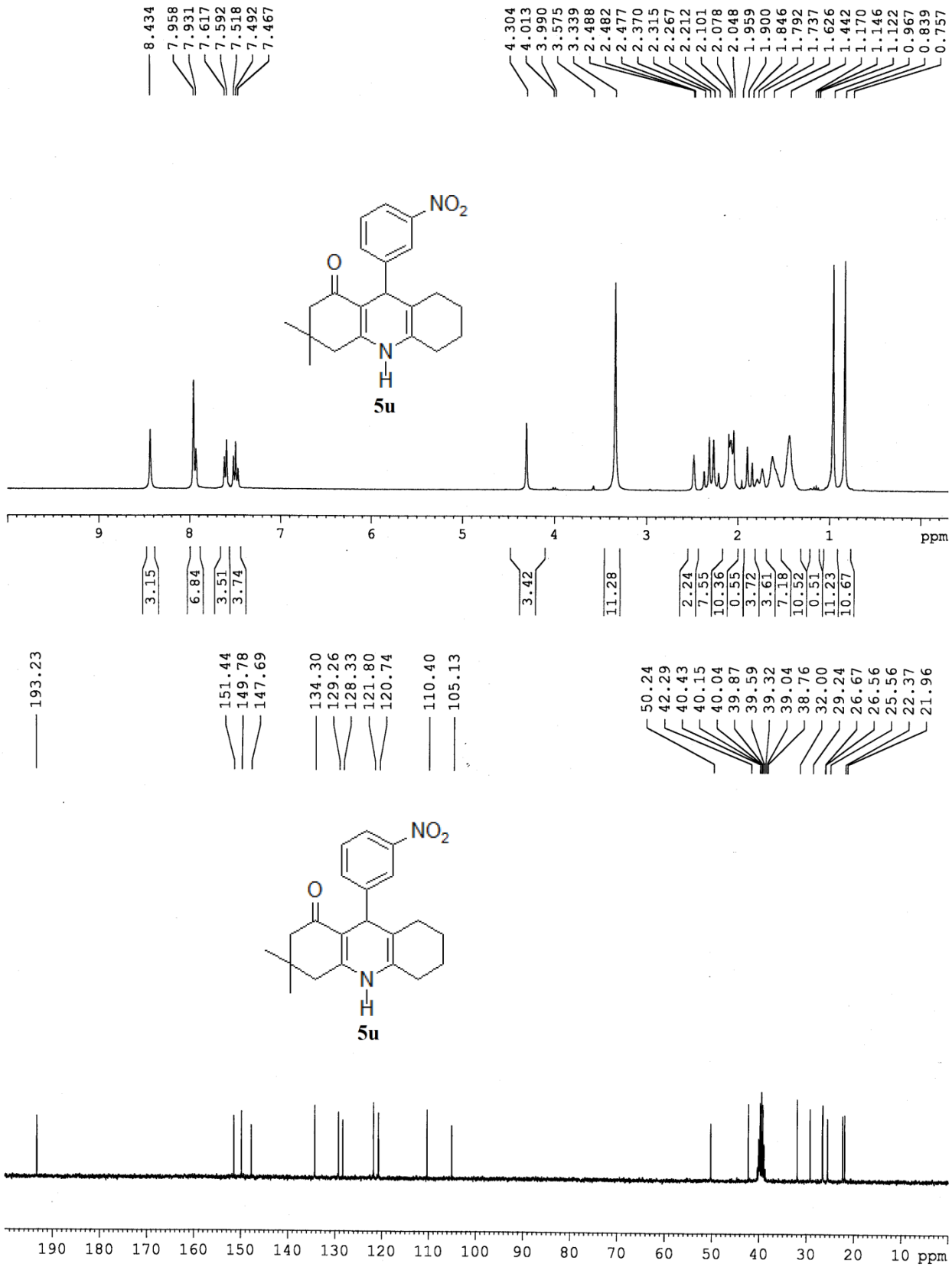
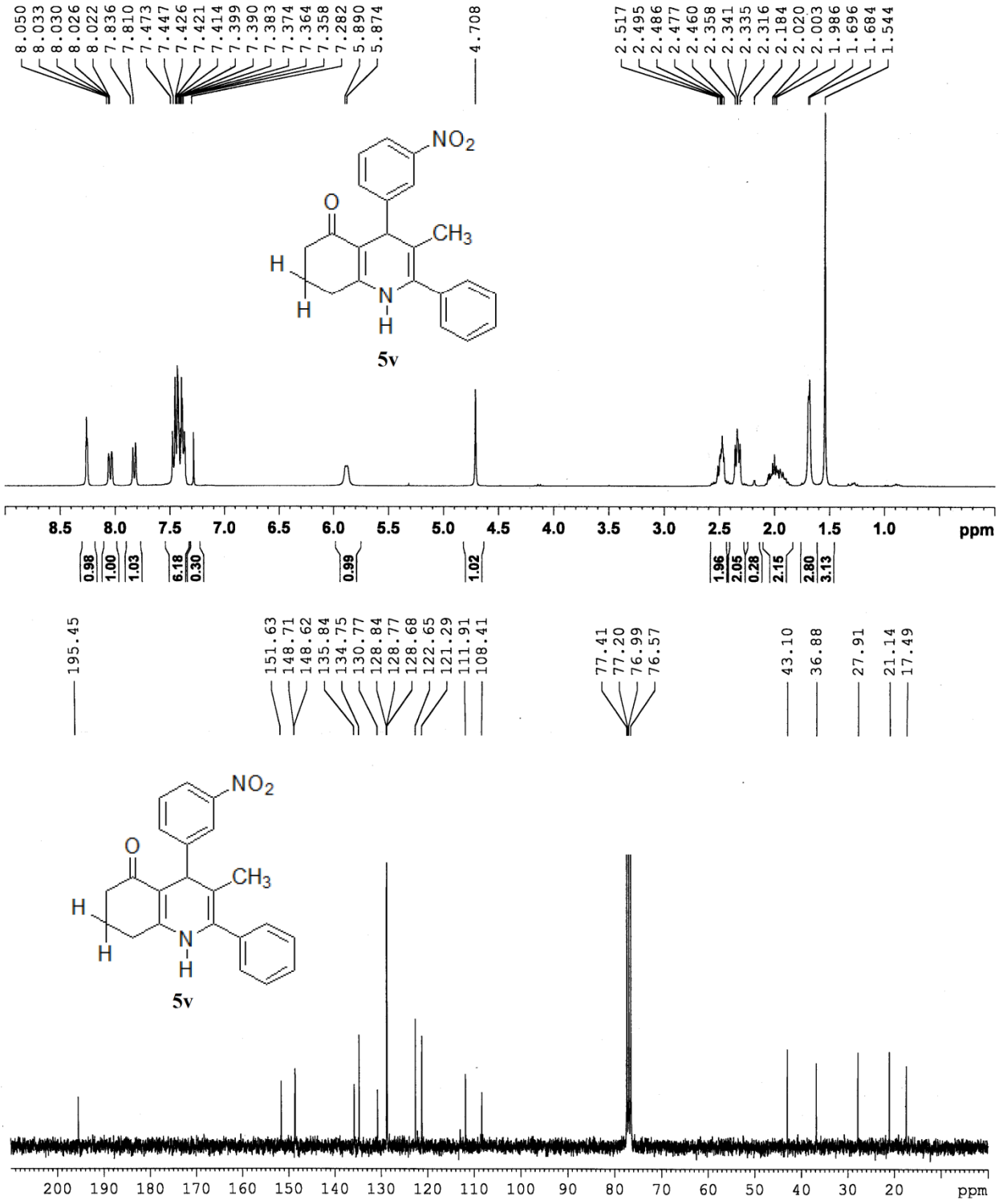
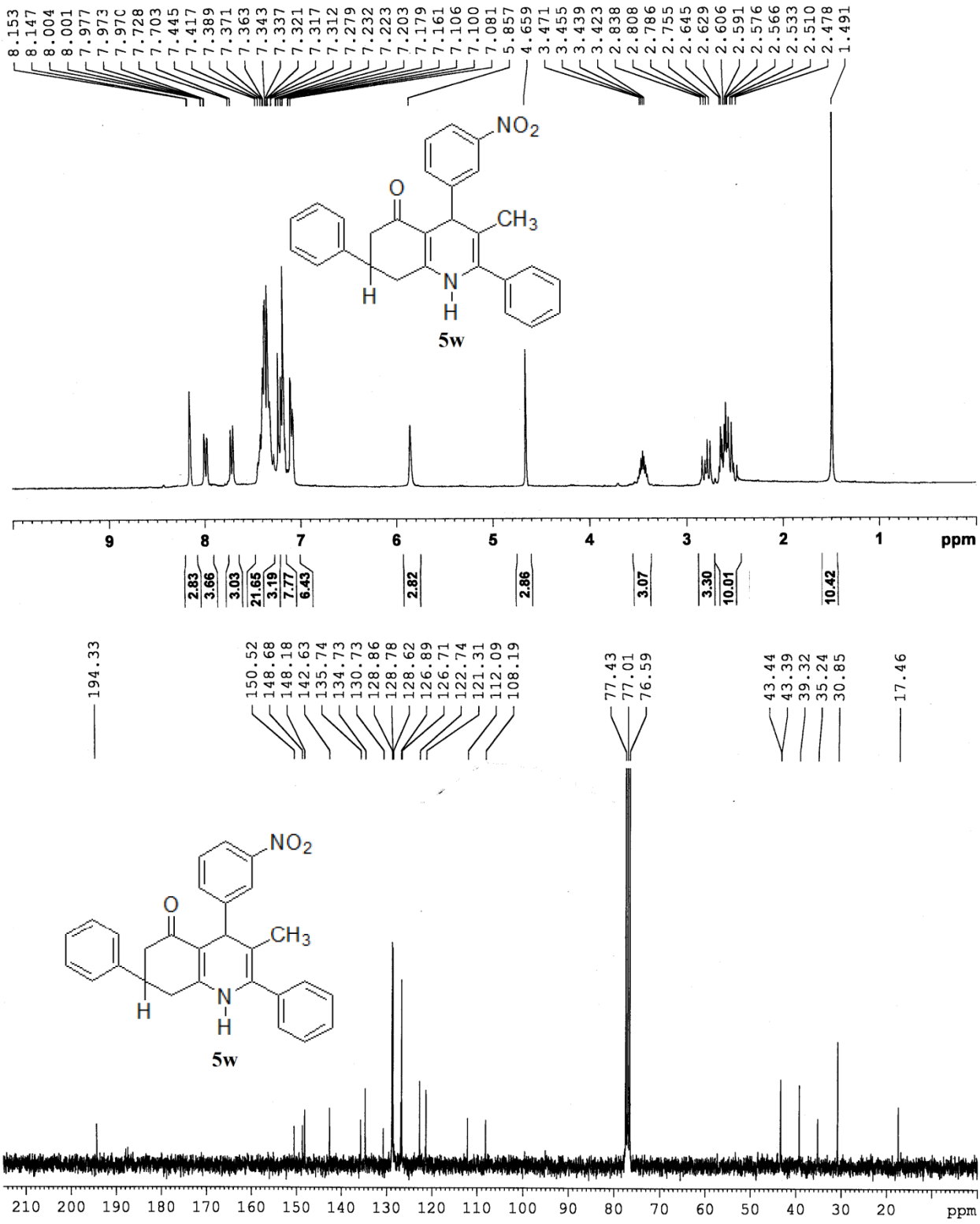



8.050
8.033
8.030
8.026
8.022
7.836
7.810
7.473
7.447
7.426
7.421
7.414
7.399
7.390
7.383
7.374
7.364
7.358
7.282
5.890
5.874
4.708
2.517
2.495
2.486
2.477
2.460
2.358
2.341
2.335
2.316
2.184
2.020
2.003
1.986
1.696
1.684
1.544
NO2
O
CH3
H
N
H
H
5v
ppm
0.98
1.00
1.03
6.18
0.30
0.99
1.02
1.96
2.05
0.28
2.15
2.80
3.13
195.45
151.63
148.71
148.62
135.84
134.75
130.77
128.84
128.77
128.68
122.65
121.29
111.91
108.41
77.41
77.20
76.99
76.57
43.10
36.88
27.91
21.14
17.49
NO2
O
CH3
H
N
H
H
5v
ppm


8.153
8.147
8.004
8.001
7.977
7.973
7.970
7.728
7.703
7.445
7.417
7.389
7.371
7.363
7.343
7.337
7.321
7.317
7.312
7.279
7.232
7.223
7.203
7.179
7.161
7.106
7.100
7.081
5.857
4.659
3.471
3.455
3.439
3.423
2.838
2.808
2.786
2.755
2.645
2.629
2.606
2.591
2.576
2.566
2.533
2.510
2.478
1.491
NO2
O
CH3
N
H
H
5w
9
8
7
6
5
4
3
2
1
ppm
2.83
3.66
3.03
21.65
3.19
7.77
6.43
2.82
2.86
3.07
3.30
10.01
10.42
194.33
150.52
148.68
148.18
142.63
135.74
134.73
130.73
128.86
128.78
128.62
126.89
126.71
122.74
121.31
112.09
108.19
77.43
77.01
76.59
43.44
43.39
39.32
35.24
30.85
17.46
NO2
O
CH3
N
H
H
5w
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

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Preparation of MCM-41 supported HPF_6 catalyst

MCM-41 was synthesized according to the literature method[1] by the hydrolysis of the structure directing agent CTAB (cetyltrimethylammonium bromide) and tetraethyl orthosilicate (TEOS), in basic solution with a molar composition of the reactants 1.0 CTAB:7.5 TEOS:1.8 NaOH:500 H_2O. The gelatinous mixture was then hydrothermally treated at 110 °C for 60 h in a Teflon lined autoclave. After cooling to room temperature the resultant solid was recovered by filtration, washed with deionized water and dried in air. The collected product was calcined at 823 K for 8 h to remove the occluded polymeric surfactants. 2.0 g of the as prepared MCM-41 was dispersed in water (10 mL) in a round bottom flask. 10 mmol of HPF_6 was added to the mixture through a constant-pressure dropping funnel under stirring over a period of 30 min at room temperature. After the addition was completed, the mixture was stirred for another 24 h at room temperature. The white solid was collected by filtration. The residue was thoroughly washed with water (10 times) and acetone (5 times). The obtained solid was then dried in vacuum at 80 °C for 2h and kept in vacuum desiccators. A white precipitate was obtained on treatment of barium chloride solution with the aqueous extract of the solid after first washing. This precipitate was soluble in excess hydrochloric acid. This proved the presence of F^- in the first washing. However no such precipitate was obtained on same treatment with the aqueous extract of the solid after washing it ten times with distilled water. The aforesaid observation conclusively proved the absence of F^- on the solid catalyst after thorough washing with distilled water.

Reference

1 S. Bhunia, R. Sen, S. Koner, *Inorganica Chimica Acta*, 2010, **363**, 3993.