Supplementary Information

Pyridine-2-carboxylic acid as an effectual catalyst for rapid multi-component synthesis of pyrazolo[3,4-b]quinolinones

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1. General experimental information

All chemicals were purchased from commercially available sources and were used without further purification. The progress of the reaction was monitored by silica gel 60 F254 (Merck) coated TLC plates. Reported R_f values correspond to elution with 1:1 (n-hexane: ethyl acetate) mobile phase. Melting points were determined by the open capillary tube method which was uncorrected. ^{1}H NMR and ^{13}C $\{^{1}H\}$-APT spectral analyses were recorded using a BRUKER AVANCE II 400 NMR spectrometer. Splitting patterns of an apparent multiplet associated with an averaged coupling constant were designated as: s = singlet, d = doublet, t = triplet, dd = double doublet, q= quartet, m = multiplet. The chemical shifts are expressed in parts per million. Mass spectra were measured on Xevo G2-XS QTof mass spectrometer.

2. General procedure for the synthesis of pyrazolo[3,4-b]quinolinones 4(a-u)

To 50 ml round-bottom flak, 1 mmol aldehydes **1(a-j)**, 1 mmol cyclic 1,3-diones **2(a-b)**, and 1 mmol 5-amino-pyrazole derivatives **3(a-b)** were added with 10% mol of pyridine-2-carboxaldehyde and 3 mL ethanol. Reaction mixture is heated at 60 °C for appropriate time (2-10 min). After completion of reaction, which was monitored by TLC, reaction mixture was cooled to room temperature then 5 ml of water was added. Precipitated product was separated by gravitational filtration. Crude product was washed with 20% aqueous solution of ethanol (5 mL ×2).

3-methyl-1,4-diphenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4a): White solid, mp: 122-126 °C, R_f value (1:1, Ethyl acetate:n-hexane): 0.26. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.96-2.01 (m, 2H), 2.03 (s, 3H), 2.86-2.34 (m, 2H), 2.53 (t, *J*= 5.2 Hz, 2H), 5.19 (s, 1H), 6.78 (s, 1H), 7.13 (t, *J*= 7.2 Hz, 1H), 7.24-7.28 (m, 2H), 7.30-7.34 (m, 2H), 7.35-7.39 (m, 1H), 7.43-7.53 (m, 4H) ppm; ^{13}C{^{1}H} APT (100 MHz, $CDCl_3$): δ = 12.6, 21.1, 28.8, 36.0, 37.2, 103.4, 114.1, 123.3, 127.3, 128.6, 128.7, 128.8, 130.0, 133.4, 137.1, 138.0, 146.4, 149.2, 195.4 ppm.

1,3,4-triphenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4b): White solid, mp: 134-138 °C, R_f value (1:1, Ethyl acetate:n-hexane): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.97 (t, *J*= 5.2 Hz, 2H), 2.30-2.36 (m, 2H), 2.51 (t, *J*= 5.2 Hz, 2H), 5.60 (s, 1H), 6.79 (s, 1H), 7.11 (d, *J*= 7.2 Hz, 1H), 7.21 (t, *J*= 7.6 Hz, 2H), 7.28-7.41 (m, 4H), 7.42-45 (m, 2H) 7.48-7.56 (m, 2H), 7.60-7.68 (m, 4H) ppm; ^{13}C{^{1}H} APT (100 MHz, $CDCl_3$): δ = 21.1, 28.8, 36.0, 37.2, 103.4, 114.1, 123.3, 124.5, 126.1, 127.3, 128.2, 128.3, 128.5, 129.5, 130.0, 132.9, 137.1, 138.0, 146.4, 149.2, 150.1, 195.4 ppm.

3,7,7-trimethyl-1,4-diphenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4c): White solid, mp: 128-132 °C, R_f value (1:1, Ethyl acetate:n-hexane): 0.24. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (s, 3H), 1.09 (s, 3H), 2.05 (s, 3H), 2.22 (d, *J*= 7.2 Hz, 2H), 2.40 (s, 2H), 5.16 (s, 1H), 6.52 (s, 1H), 7.14 (t, *J*= 7.2 Hz, 1H), 7.24-7.32 (m, 4H), 7.37-7.41 (m, 1H), 7.52 (t, *J*= 2.8 Hz, 4H) ppm; ^{13}C{^{1}H} APT (100 MHz, $CDCl_3$): δ = 12.1, 27.4, 29.0, 32.6, 36.1, 42.5, 50.9, 104.9, 112.2, 122.9, 126.9, 127.6, 127.9, 128.1, 130.0, 135.1, 138.0, 146.3, 147.6, 148.7, 195.4 ppm.

4-(4-bromophenyl)-3-methyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4d): White solid, MP: 182-186 °C, R_f value (1:1, Ethyl acetate:n-hexane): 0.34. ^{1}H-NMR: δ = 1.26 (t, *J*= 7.2 Hz, 2H), 2.02 (s, 3H), 2.33-2.37 (m, 2H), 2.54 (t, *J*= 6.0 Hz, 2H), 5.18 (s, 1H), 6.52 (s, 1H), 7.21 (dd, *J*= 6.8, 1.6 Hz, 2H), 7.36-7.42 (m, 3H), 7.51-7.53 (m, 4H) ppm; ^{13}C-APT: δ = 12.2, 21.2, 29.0, 35.8, 37.2, 104.1, 113.1, 119.8, 122.9, 127.5, 129.5, 129.9 130.0, 131.2, 135.4, 138.0, 145.5, 147.6, 150.4, 195.6 ppm.

4-(4-bromophenyl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4e): White solid, mp: 206-210 °C, R_f value (1:1, Ethyl acetate:n-hexane): 0.28. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.02 (s, 3H), 1.09 (s, 3H), 2.02 (s, 3H), 2.19 (d, *J*= 16.4 Hz, 1H), 2.25 (d, *J*= 16.4 Hz, 1H), 2.37 (d, *J*= 16.8 Hz, 1H), 2.42 (d, *J*= 17.2 Hz, 1H), 5.14 (s,1H), 6.44 (s, 1H), 7.19 (d, *J*= 8.4 Hz, 2H), 7.36 (d, *J*= 8.4 Hz, 3H), 7.49 (t, *J*= 8.2 Hz, 4H) ppm; ^{13}C{^{1}H} APT (100 MHz, $CDCl_3$): δ = 12.2, 27.4, 29.0, 32.6, 35.8, 42.6, 50.8, 104.2, 111.8, 119.8, 122.8, 127.5, 129.8, 130.0, 131.2, 135.5, 138.0, 145.5, 147.6, 148.7, 195.3 ppm.

4-(4-bromophenyl)-7,7-dimethyl-1,3-diphenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4f): White solid, mp: 216-220 °C, R_f value (1:1, Ethyl acetate:n-hexane): 0.24. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.97 (s, 3H), 1.09 (s, 3H), 2.21 (d, *J*= 16.4 Hz, 1H), 2.27 (d, *J*= 16.4 Hz, 1H), 2.36 (d, *J*= 16.4 Hz, 1H), 2.43 (4, *J*= 16.4 Hz, 1H), 5.55 (s,1H), 6.51 (s, 1H), 7.20 (d, *J*= 8.4 Hz, 2H), 7.32 (dd, *J*= 7.8, 10.6 Hz, 4H), 7.36 (t, *J*= 2.0 Hz, 1H), 7.46 (t, *J*= 7.2 Hz, 1H), 7.57-7.67 (m, 6H)ppm; ^{13}C{^{1}H} APT (100 MHz, $CDCl_3$): δ = 27.2, 29.1, 32.7, 35.7, 42.5, 50.9, 102.8, 112.4, 119.9, 123.2, 127.2, 128.0, 128.1, 128.4, 129.9, 130.1, 131.1, 132.7, 137.0, 137.9, 145.1, 148.3, 149.2, 195.1 ppm.

4-(3-chlorophenyl)-3-methyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4g): White solid, mp: 202-204 °C, R_f value (1:1, Ethyl acetate:n-hexane): 0.42. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.93-1.96 (m, 2H), 2.01 (s, 3H), 2.22-2.30 (m, 2H), 2.46-2.56 (m, 2H), 5.12 (s, 1H), 6.62 (s, 1H) 7.12 (m, 1H), 7.14-7.26 (m, 3H), 7.33-7.36 (m, 1H), 7.44 (d, *J*= 2.8 Hz, 4H) ppm. ^{13}C-APT: δ = 12.3, 21.2, 28.7, 36.1, 37.1, 104.0, 112.5, 123.1, 126.3, 126.5, 127.5, 128.1, 129.2, 129.8, 134.0, 135.6, 137.9, 147.5, 148.7, 151.5, 195.7 ppm; MS(ESI-TOF) m/z calcd. for $C_{23}H_{20}ClN_3O$ $(M+H)^+$; 390.14, Found; 390.16.

4-(3-chlorophenyl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4h): White solid, mp: 212-216 °C, R_f value (1:1, Ethyl acetate:n-hexane): 0.46. ^{1}H NMR: δ = 1.04 (s, 3H), 1.09 (s, 3H), 2.04 (s, 3H), 2.23 (d, *J*= 4.4 Hz, 2H),

2.41 (s, 2H), 5.15 (s, 1H), 6.53 (s, 1H), 7.11 (d, *J*= 7.6 Hz, 2H), 7.18-7.27 (m, 2H), 7.40 (t, *J*= 6.4, 4.4 Hz, t), 7.52 (d, *J*= 6.4 Hz, 5H) ppm, $^{13}C\{^{1}H\}$ APT (100 MHz, $CDCl_3$): δ = 12.3, 27.5, 28.9, 32.7, 36.1, 42.6, 50.8, 104.1, 111.6, 122.9, 126.3, 126.4, 127.5, 128.1, 129.3, 130.0, 134.0, 135.5, 138.0, 147.6, 148.5, 148.9, 195.3 ppm.

4-(4-methoxyphenyl)-3-methyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4i): Light orange solid, mp: 124-128 °C, R_f value (1:1, Ethyl acetate:n-hexane): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.98 (t, *J*= 5.6 Hz, 2H), 2.03 (s, 3H), 2.33-2.37 (m, 2H), 2.51 (d, *J*= 5.2 Hz, 2H), 3.77 (s, 3H), 5.15 (s, 1H), 6.72 (s, 1H), 6.79 (d, *J*= 8.8 Hz, 2H), 7.23 (d, *J*= 8.8 Hz, 2H), 7.36-7.39 (m, 1H), 7.48 (d, *J*= 4.0 Hz, 4H) ppm; $^{13}C\{^{1}H\}$ APT (100 MHz, $CDCl_3$): δ = 12.2, 21.2, 28.9, 35.2, 37.2, 55.2, 104.84, 112.3, 113.4, 122.9, 128.5, 129.0, 129.9, 135.5, 138.1, 139.0, 147.6, 150.4, 157.7, 195.8 ppm; MS(ESI-TOF) m/z calcd. for $C_{24}H_{23}N_3O_2$ $(M+H)^+$: 386.19, found: 386.21.

4-(4-methoxyphenyl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4j): Light orange solid, mp: 166-170 °C, R_f value (1:1, Ethyl acetate:n-hexane): 0.28. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (s, 3H), 1.09 (s, 3H), 2.04 (s, 3H), 2.22 (d, *J*= 5.2 Hz, 2H), 2.39 (s, 2H) 3.77 (s, 3H), 5.13 (s, 1H), 6.40 (s, 1H), 6.79 (d, *J*= 8.4 Hz, 2H), 7.23 (d, *J*= 8.8 Hz, 2H), 7.39 (d, *J*= 6.4 Hz, 1H), 7.51 (t, *J*= 6.4 Hz, 4H) ppm; $^{13}C\{^{1}H\}$ APT (100 MHz, $CDCl_3$): δ = 12.2, 27.4, 29.0, 32.6, 35.2, 42.6, 50.9, 55.2, 104.8, 112.4 113.5, 122.8, 127.4, 128.9, 130.0, 138.9, 148.3, 151.0, 157.7, 195.8 ppm; MS(ESI-TOF) m/z calcd. for $C_{26}H_{27}N_3O_2$ $(M+H)^+$: 414.22, found: 414.24.

4-(3-methoxyphenyl)-3-methyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4k): Light orange solid, mp: 184-190 °C, R_f value (1:1, Ethyl acetate:n-hexane): 0.24. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.97 (t, *J*= 5.2 Hz, 2H), 2.06 (s, 3H), 2.31 (d, *J*= 5.2 Hz, 2H), 2.48-2.53 (m, 2H), 3.79 (s, 3H), 5.16 (s, 1H), 6.62 (s,1H) 6.69 (dd, *J*= 8.0, 2.0 Hz, 1H), 6.87 (s, 1H), 6.93 (d, *J*= 7.6 Hz, 1H), 7.17 (d, *J*= 7.8 Hz, 1H), 7.33 (dd, *J*= 8.4, 4.0 Hz, 1H) 7.45 (d, *J*= 4.0 Hz, 4H) ppm, $^{13}C\{^{1}H\}$ APT (100 MHz, $CDCl_3$): δ = 12.3, 21.2, 28.8, 36.1, 37.2, 55.1, 104.6, 110.7, 113.1, 114.5, 120.6, 122.9, 127.4, 128.9, 129.9, 135.5, 138.0, 147.6, 148.3, 151.0, 159.4, 195.7 ppm.

4-(3-methoxyphenyl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4l): Light orange solid, mp: 192-196 °C, R_f value (1:1, Ethyl acetate:n-hexane): 0.26. ^{1}H NMR: δ = 1.05 (s, 3H), 1.08 (s, 3H), 2.06 (s, 3H), 2.21 (d, *J*= 3.2 Hz, H), 2.38 (s, 2H), 3.78 (s, 3H), 5.13 (s, 1H), 6.56 (s, 1H), 6.68 (dd, *J*= 8.0, 2.0 Hz, 1H),

6.86 (s,1H), 6.92 (d, *J*= 7.6 Hz, 1H), 7.18 (d, *J*= 8.0 Hz, 1H), 7.37 (s, 1H), 7.49 (s, 4H) ppm; $^{13}C\{^{1}H\}$ APT (100 MHz, $CDCl_3$): δ = 12.3, 27.5, 29.0, 32.6, 36.2, 42.5, 50.8, 55.1, 104.7, 110.9, 112.0, 114.2, 120.6, 122.9, 127.4, 129.0, 129.9, 135.5, 138.0, 147.6, 148.2, 148.9, 159.5, 195.5 ppm.

4-(2,5-dimethoxyphenyl)-3-methyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4m): Light orange solid, mp: 186-190 °C, R_f value (1:1, Ethyl acetate:n-hexane): 0.32. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.01 (t, *J*= 5.6 Hz, 2H), 2.06 (s, 3H), 2.33 (t, *J*= 7.4 Hz, H), 2.52 (d, *J*= 6.8 Hz, 2H), 3.72 (s, 3H), 3.90 (s,3H), 5.55 (s, 1H), 6.60 (s, 1H), 6.64 (dd, *J*= 8.8 Hz, 3.2 Hz, 1H), 6.73 (d, *J*= 3.2 Hz, 1H), 6.82 (d, *J*= 8.8 Hz, 1H), 7.35 (t, *J*= 6.6 Hz, 1H) 7.46 (d, *J*= 6.4 Hz, 4H) ppm; $^{13}C\{^{1}H\}$ APT (100 MHz, $CDCl_3$): δ = 12.1, 21.4, 28.9, 29.7, 37.2, 55.5, 56.8, 104.46, 110.4, 112.3, 113.1, 116.4, 122.9, 127.3, 129.9, 135.6, 137.2, 138.16, 147.8, 150.8, 151.2, 153.8, 195.4 ppm; MS(ESI-TOF) m/z calcd. for $C_{25}H_{25}N_3O_3$ $(M+H)^+$; 416.20, found; 416.22.

4-(2,5-dimethoxyphenyl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4n): Light orange solid, mp: 194-198 °C, R_f value (1:1, Ethyl acetate:n-hexane): 0.36. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.10 (s, 3H), 1.16 (s, 3H), 2.07 (s, 3H), 2.41 (s, 2H), 2.53 (d, *J*= 2.4 Hz, 2H), 3.73 (s, 3H), 3.81 (s, 3H), 5.53 (s, 1H), 6.33 (s, 1H), 6.64-6.74 (m, 2H), 6.71 (d, *J*= 8.8 Hz, 1H), 6.96 (d, *J*= 2.4 Hz, 1H), 7.49-7.54 (m, 4H) ppm; $^{13}C\{^{1}H\}$ APT (100 MHz, $CDCl_3$): δ = 12.8, 28.9, 29.7, 32.6, 35.2, 42.6, 53.8, 55.7, 56.7, 104.8, 111.8, 113.4, 114.8, 121.1, 122.9, 125.9, 129.0, 136.6, 138.1, 147.8, 151.2, 154.0, 195.4 ppm; MS(ESI-TOF) m/z calcd. for $C_{27}H_{29}N_3O_3$ $(M+H)^+$: 444.23, found: 444.25.

4-(3,4-dimethoxyphenyl)-3-methyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4o): Light orange solid, MP: 146-150 °C, R_f value (1:1, Ethyl acetate:n-hexane): 0.34. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.0 (t, *J*= 4.8 Hz, 2H), 2.06 (s, 3H), 2.37 (d, *J*= 8 Hz, 2H), 2.54 (d, *J*= 5.2 Hz, 2H), 3.83 (s, 3H), 3.88 (s, 3H), 5.17 (s, 1H), 6.61 (s, 1H), 6.77 (d, *J*= 2.0 Hz, 2H), 6.96 (s, 1H), 7.37-7.40 (m, 1H), 7.51 (t, *J*= 2.6 Hz, 4H) ppm; $^{13}C\{^{1}H\}$ APT (100 MHz, $CDCl_3$): δ = 12.3, 21.2, 28.9, 35.5, 37.3, 55.8, 55.9, 104.7, 111.0, 111.9, 113.6, 120.0, 122.8, 127.4, 129.6, 135.5, 138.1, 139.5, 147.2, 147.6, 148.4, 150.3, 195.8 ppm; MS(ESI-TOF) m/z calcd. for $C_{25}H_{25}N_3O_3$ $(M+H)^+$: 416.20, found: 416.22.

4-(3,4-dimethoxyphenyl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4p): Light orange solid. mp: 174-178 °C, R_f value (1:1, Ethyl

acetate:n-hexane): 0.32. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05 (s, 3H), 1.09 (s, 3H), 2.07 (s, 3H), 2.24 (d, *J*= 3.2 Hz, 2H), 2.39 (d, *J*= 10 Hz,2H) 3.83 (s, 3H), 3.86 (s, 3H), 5.13 (s, 1H), 6.52 (s, 1H), 6.77 (q, *J*= 8.2 Hz, 2H), 6.91 (s, 1H), 7.38 (s, 1H), 7.50 (s, 4H), ppm; ^{13}C{^{1}H} APT (100 MHz, $CDCl_3$): δ = 12.3, 27.3, 29.1, 32.6, 35.6, 42.5, 50.9, 55.9, 104.8, 110.9, 111.7, 112.3, 119.9, 122.8, 124.1, 127.4, 129.6, 135.5, 138.1, 139.5, 147.2, 147.7, 148.5, 148.6, 195.6 ppm; MS(ESI-TOF) m/z calcd. for $C_{27}H_{29}N_3O_3$ $(M+H)^+$: 444.23, found: 444.25.

3-methyl-4-(2-nitrophenyl)-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4q): Yellow solid, mp: 148-152 °C, R_f value (1:1, Ethyl acetate:n-hexane): 0.16. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.14-2.17 (m, 2H), 2.08 (s, 3H), 2.25 (t, *J*= 3.4 Hz, 2H), 2.51 (t, *J*= 2.8 Hz, 2H), 5.91 (s, 1H), 6.72 (s, 1H), 7.34 (d, *J*= 7.2 Hz, 2H), 7.49 (d, *J*= 2.4 Hz, 1H), 7.52-7.59 (m, 5H), 7.74 (dd, *J*= 8.0, 1.2 Hz, 1H) ppm; ^{13}C{^{1}H} APT (100 MHz, $CDCl_3$): δ = 12.4, 21.2, 28.8, 31.5, 36.7, 103.1, 112.9, 123.1, 124.3, 126.6, 127.6, 129.1, 129.6, 130.0, 136.0, 137.9, 145.2, 148.3, 149.2, 153.1, 195.3 ppm; MS(ESI-TOF) m/z calcd. for $C_{23}H_{20}N_4O_3$ $(M+H)^+$: 401.16, found: 401.19.

3,7,7-trimethyl-4-(2-nitrophenyl)-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4r): Yellow solid, mp: 162-166 °C, R_f value (1:1, Ethyl acetate:n-hexane): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.24 (3H, s), 1.26 (3H, s), (3H, s), 2.10 (3H, s), 2.17 (s, 2H), 2.18 (s, 2H), 5.93 (s, 1H), 6.41 (s, 1H), 7.43 (d, *J*= 6.8 Hz, 2H), 7.49 (d, *J*= 6.8 Hz, 1H), 7.54-7.59 (m, 5H), 7.76 (d, *J*= 8.0 Hz, 1H) ppm. ^{13}C-APT: δ = 12.2, 27.4, 28.8, 32.7, 36.0, 42.5, 50.3, 102.9, 123.4, 124.4, 126.7, 127.7, 129.1, 129.7, 130.1, 136.1, 137.9, 145.2, 148.4, 149.7, 153.9, 195.4 ppm; MS(ESI-TOF) m/z calcd. for $C_{25}H_{24}N_4O_3$ $(M+H)^+$: 429.19, found: 429.21.

4-(3-hydroxyphenyl)-3-methyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4s): Light pink solid, mp: 172-176 °C, R_f value (1:1, Ethyl acetate:n-hexane): 0.44. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.94-1.97 (m, 2H), 2.02 (s, 3H), 2.35 (d, *J*= 6.0 Hz, 2H), 2.48 (t, *J*= 6.4 Hz, 2H), 5.14 (s, 1H), 6.59 (s, 1H), 7.08 (t, *J*= 8.0 Hz, 2H), 7.38 (t, *J*= 7.8 Hz, 2H), 7.44-7.49 (m, 5H), 9.89 (s, 1H) ppm. ^{13}C{^{1}H} APT (100 MHz, $CDCl_3$): δ = 12.2, 21.1, 28.8, 35.8, 37.1, 104.6, 113.3, 115.2, 123.0, 124.2, 127.5, 129.5, 129.9, 135.3, 137.9, 142.7, 147.7, 148.1, 148.3, 156.0, 196.2 ppm; MS(ESI-TOF) m/z calcd. for $C_{23}H_{21}N_3O_2$ $(M+H)^+$: 372.17, found: 372.19.

4-(3-hydroxyphenyl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4t): Light pink solid, mp: 176-180 °C, R_f value (1:1, Ethyl acetate:n-

hexane): 0.46. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (s, 3H), 1.08 (s, 3H), 2.04 (s, 3H), 2.17 (d, *J*= 4.8 Hz, 2H), 2.24 (d, *J*= 2.0 Hz, 2H), 5.13 (s, 1H), 6.45 (s, 1H), 7.08 (t, *J*= 8.0 Hz, 2H), 7.38 (d, *J*= 7.2 Hz, 2H), 7.49-7.56 (m, 5H), 9.91 (s, 1H), ppm; $^{13}C\{^{1}H\}$ APT (100 MHz, $CDCl_3$): δ = 12.2, 27.5, 28.9, 32.7, 35.9, 42.6, 50.8, 104.6, 113.2, 115.2, 122.9, 124.3, 127.5, 129.2, 130.0, 135.5, 138.0, 142.7, 147.7, 148.1, 155.8, 195.7 ppm; MS(ESI-TOF) m/z calcd. for $C_{25}H_{25}N_3O_2$ $(M+H)^+$: 400.20, found: 400.22.

4-([1,1'-biphenyl]-4-yl)-3,7,7-trimethyl-1-phenyl-6,7,8,9-tetrahydro-1H-pyrazolo[3,4-b]quinolin-5(4H)-one (4u): Light red solid, mp: 134-138 °C, R_f value (1:1, Ethyl acetate:n-hexane): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03 (s, 3H), 1.08 (s, 3H), 2.07 (s, 3H), 2.20 (d, *J*= 5.2 Hz, 2H), 2.39 (s, 2H), 5.19 (s, 1H), 6.80 (s, 1H), 7.36-7.43(m, 4H), 7.49 (d, *J*= 8.8 Hz, 6H), 7.56 (d, *J*= 7.2 Hz, 4H) ppm; $^{13}C\{^{1}H\}$ APT (100 MHz, $CDCl_3$): δ = 12.3, 27.4, 29.1, 32.6, 35.9, 42.5, 50.8, 104.7, 112.0, 122.9, 126.9, 127.0, 127.4, 128.3, 128.6, 129.9, 135.6, 138.0, 138.8, 141.1, 145.6, 147.6, 149.1, 195.5 ppm; MS(ESI-TOF) m/z calcd. for $C_{31}H_{29}N_3O$ $(M+H)^+$: 460.24, found: 460.26

^{1}H NMR and ^{13}C{^{1}H} APT spectra of **4a-4u**

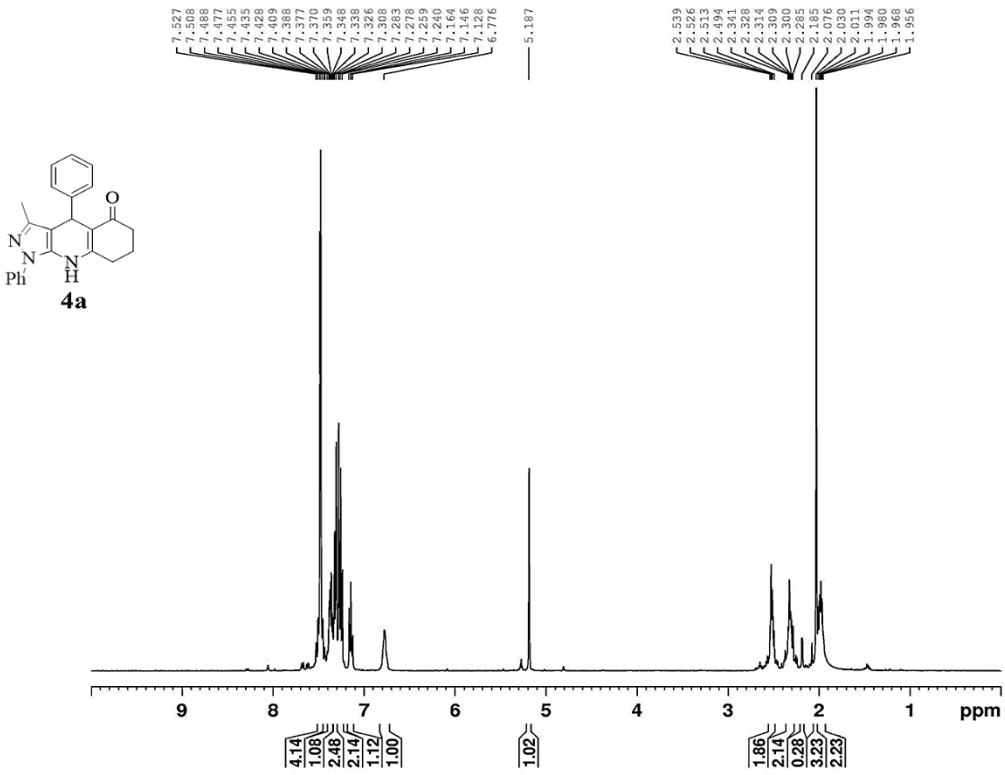


Figure 1. ^{1}H NMR spectrum of compound **4a** at 400 MHz in $CDCl_3$

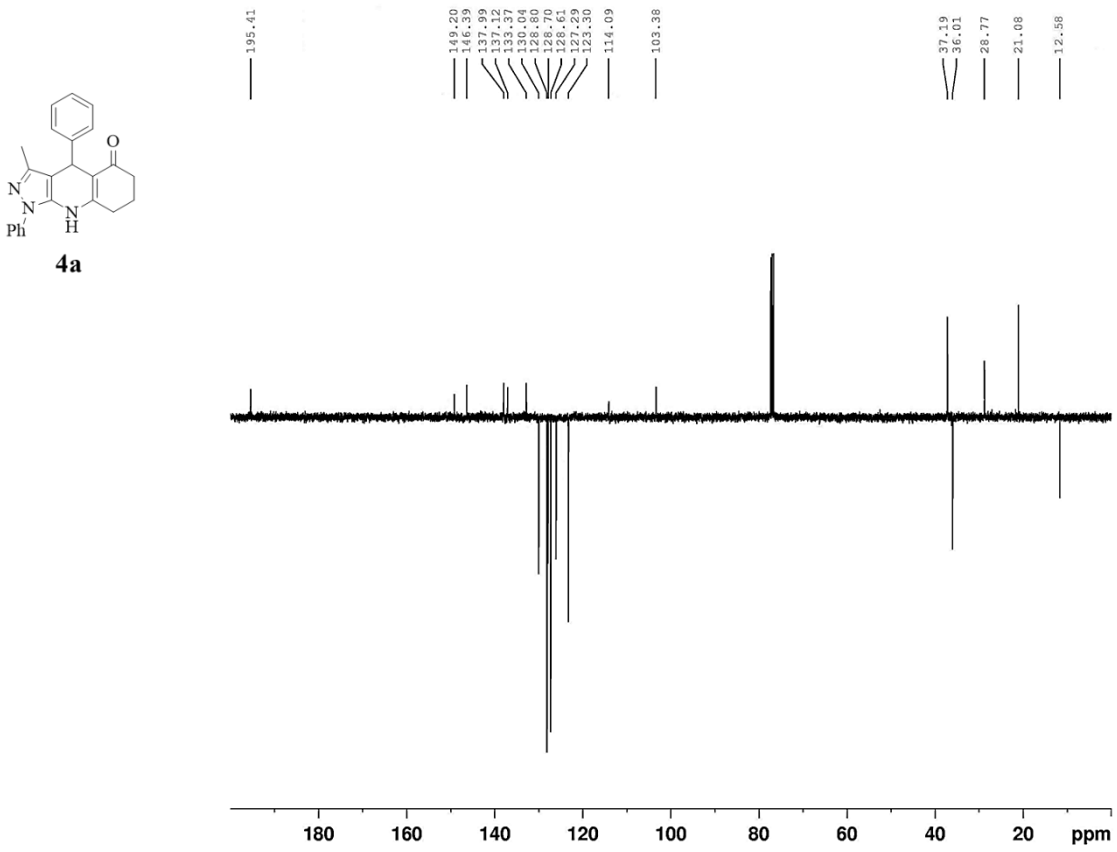


Figure 2. ^{13}C{^{1}H} APT spectrum of compound **4a** at 100 MHz in $CDCl_3$

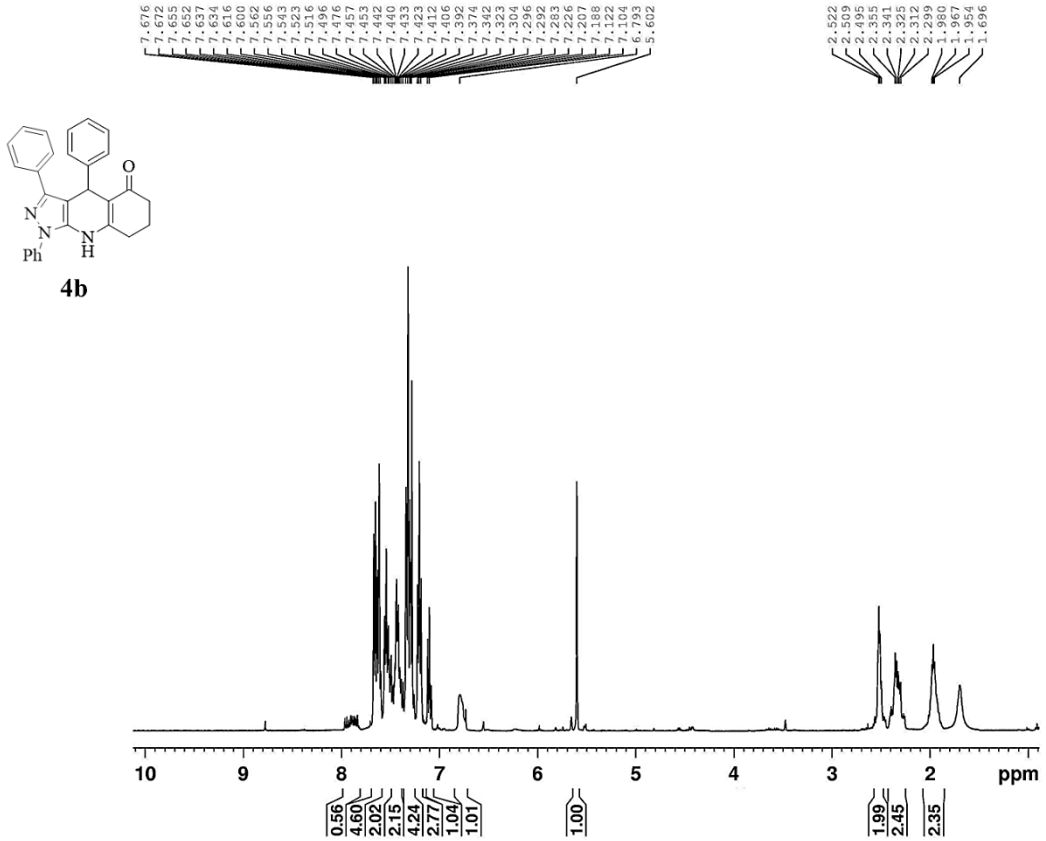


Figure 3. ^{1}H NMR spectrum of compound **4b** at 400 MHz in $CDCl_3$

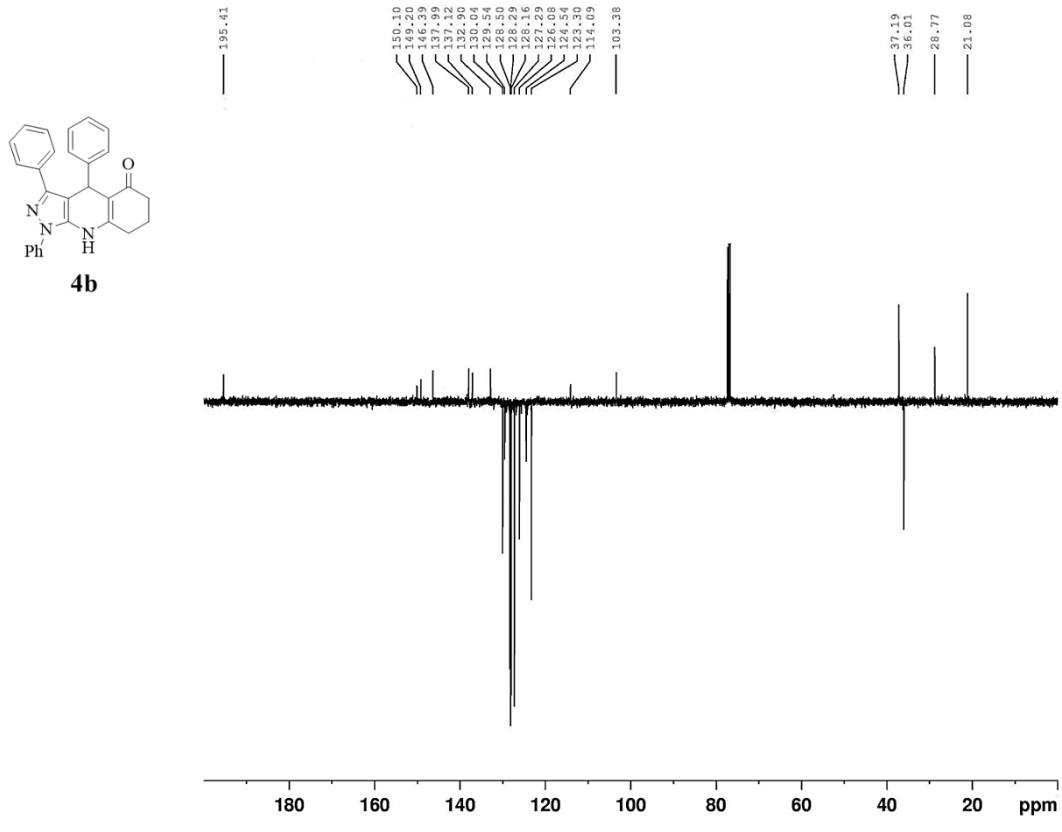


Figure 4. $^{13}C\{^{1}H\}$ APT spectrum of compound **4b** at 100 MHz in $CDCl_3$

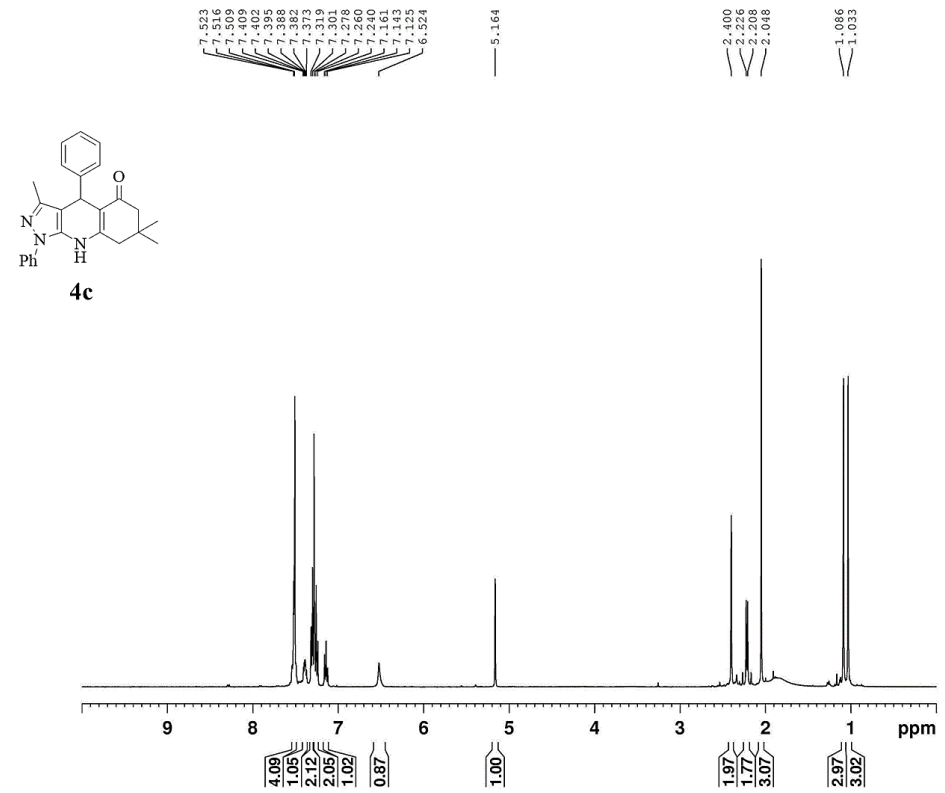


Figure 5. ^{1}H NMR spectrum of compound **4c** at 400 MHz in $CDCl_3$

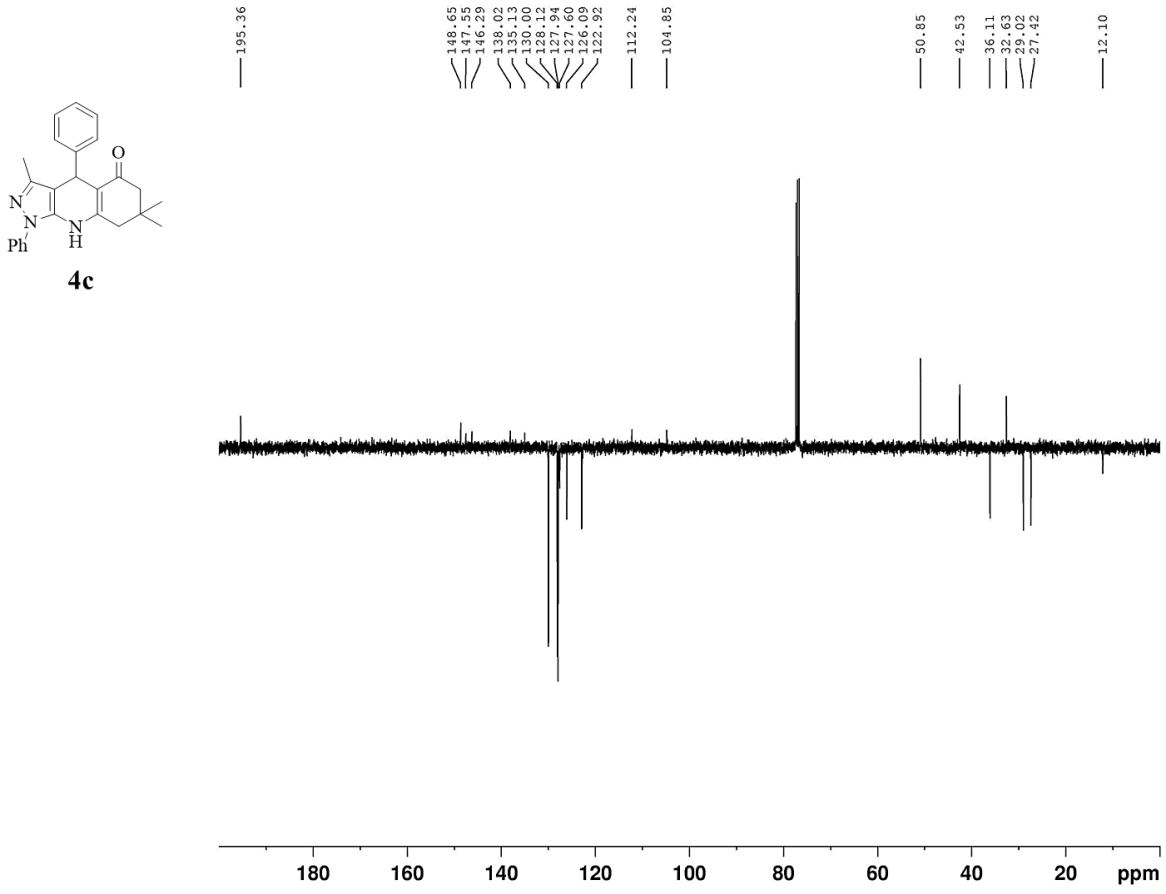


Figure 6. $^{13}C\{^{1}H\}$ APT spectrum of compound **4c** at 100 MHz in $CDCl_3$

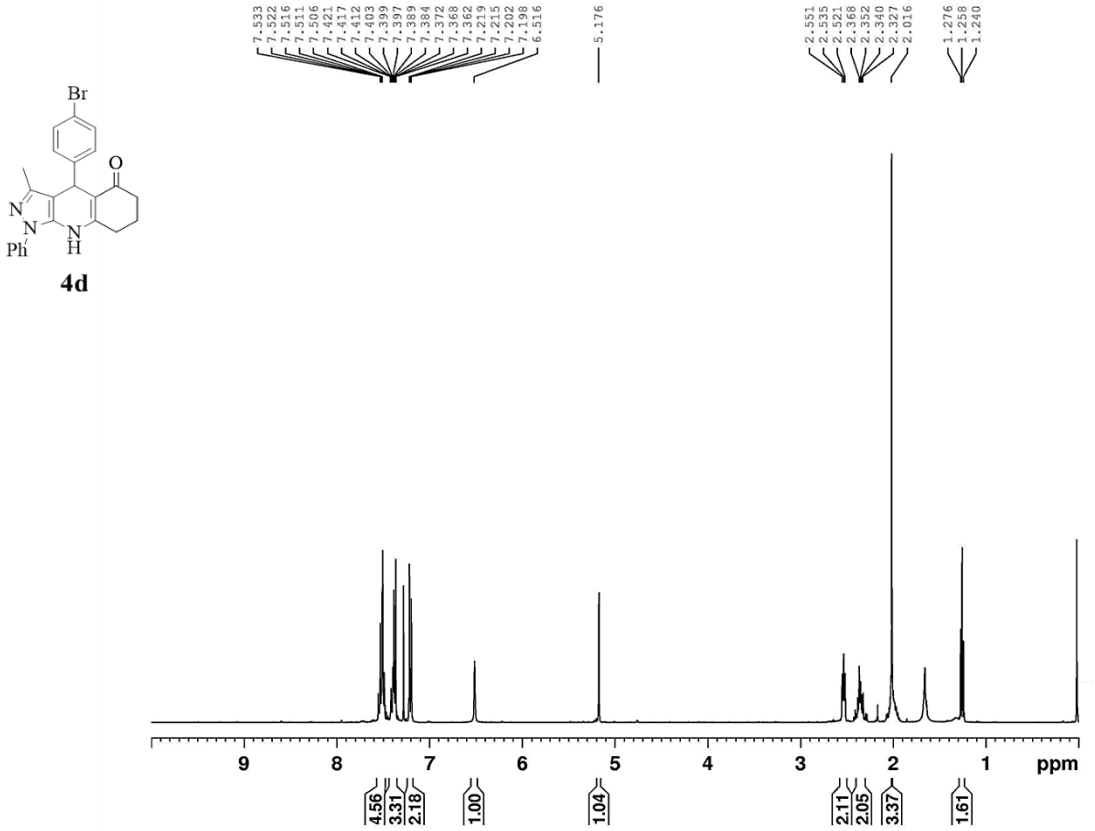


Figure 7. ^{1}H NMR spectrum of compound **4d** at 400 MHz in $CDCl_3$

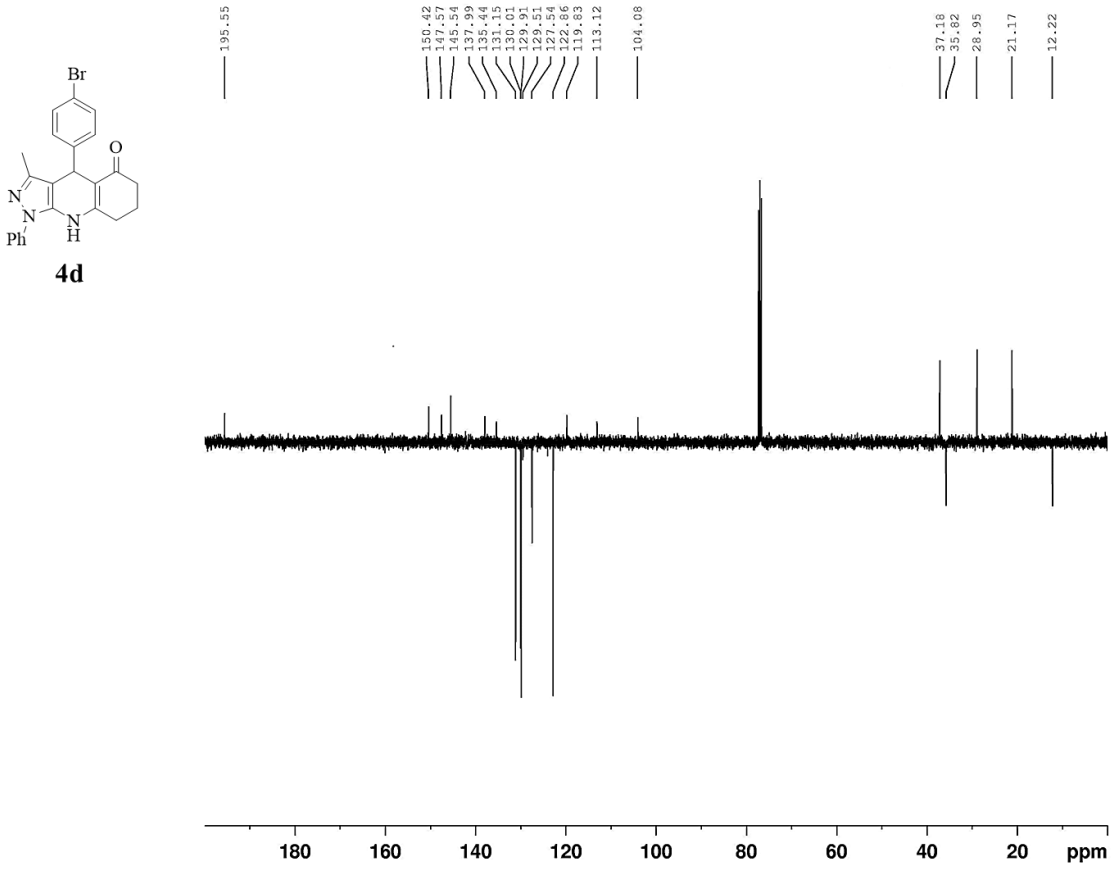


Figure 8. $^{13}C\{^{1}H\}$ APT spectrum of compound **4d** at 100 MHz in $CDCl_3$

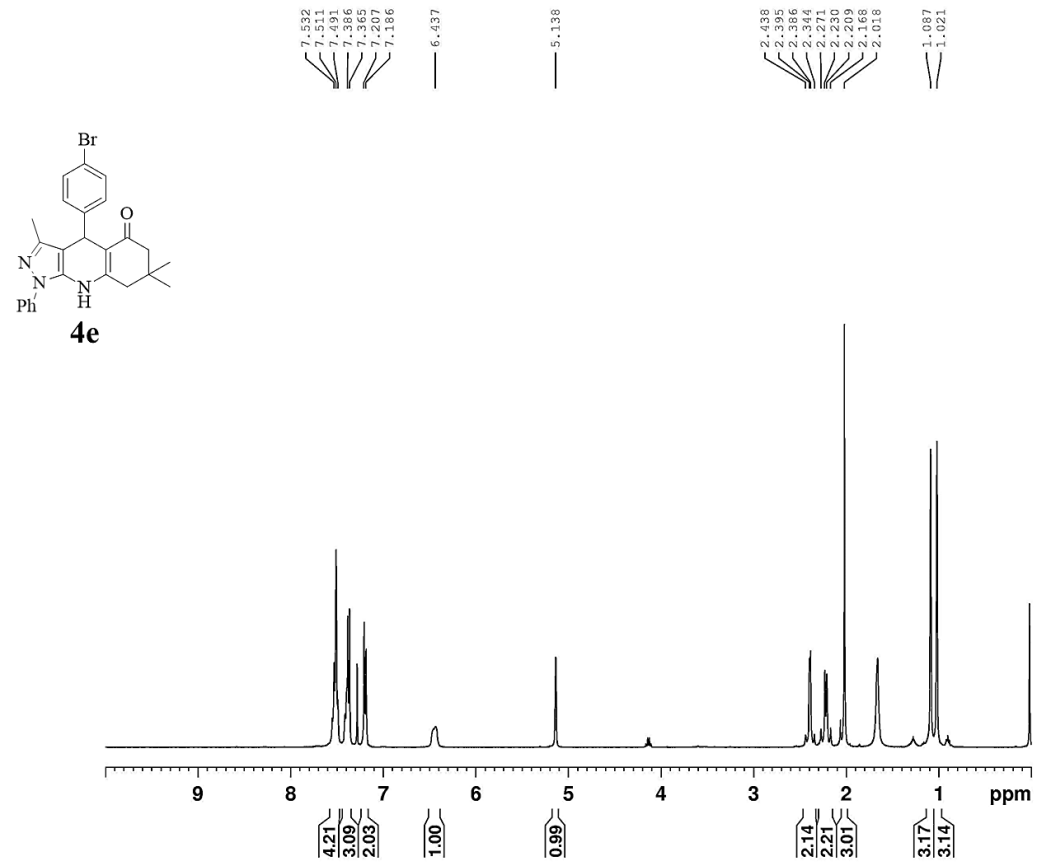


Figure 9. ^{1}H NMR spectrum of compound **4e** at 400 MHz in $CDCl_3$

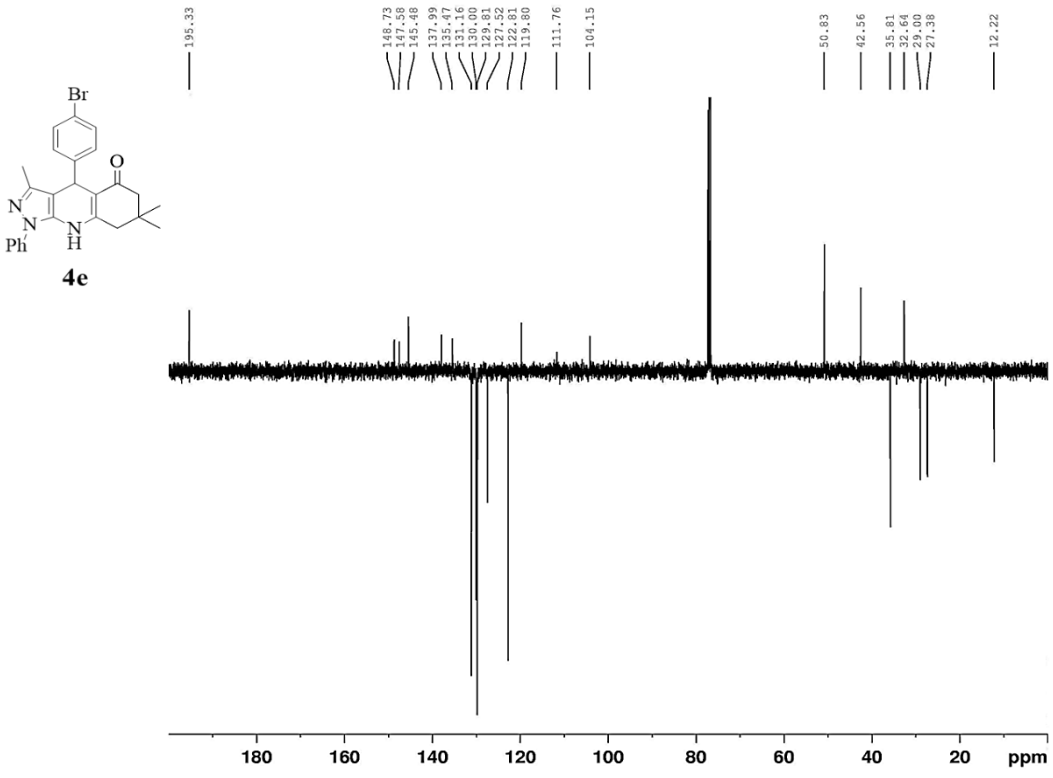


Figure 10. $^{13}C\{^{1}H\}$ APT spectrum of compound **4e** at 100 MHz in $CDCl_3$

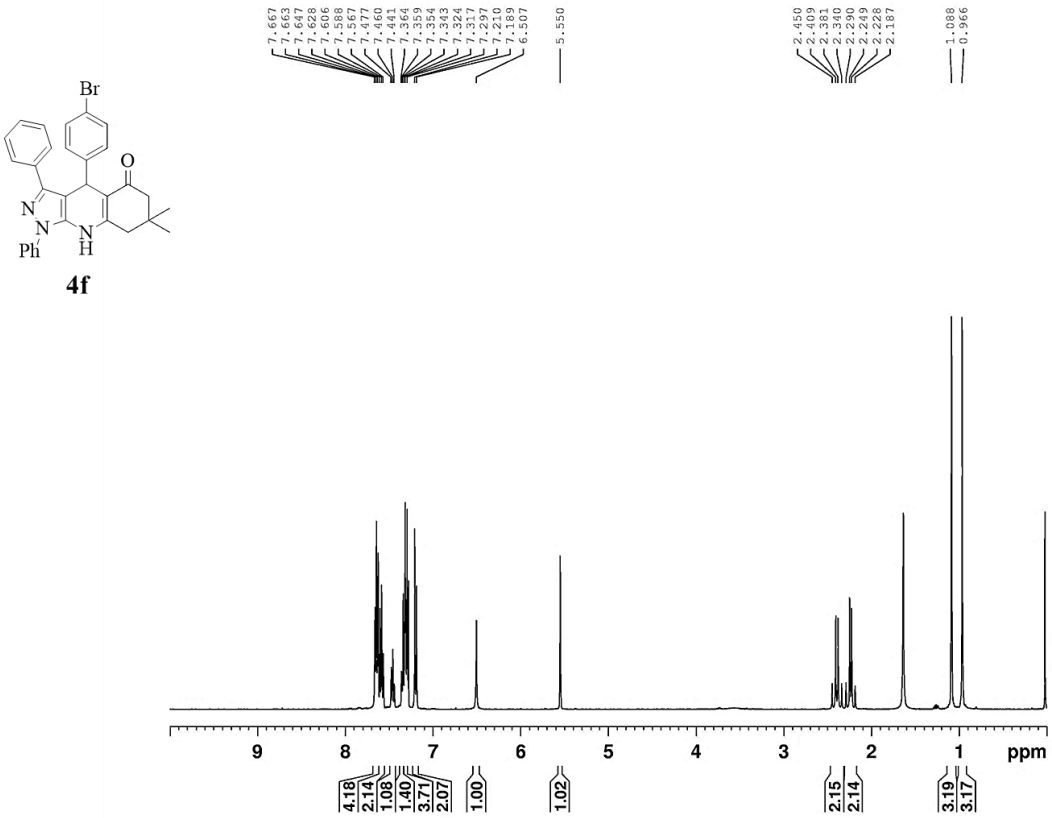


Figure 11. ^{1}H NMR spectrum of compound **4f** at 400 MHz in $CDCl_3$

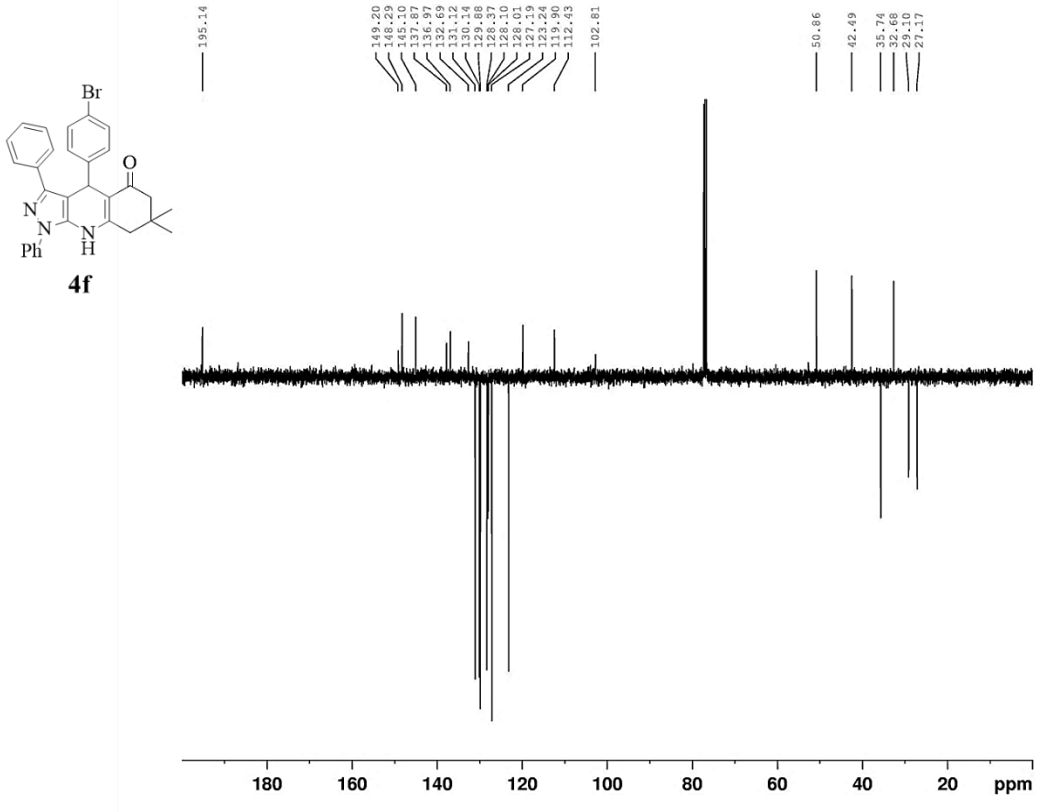


Figure 12. ^{13}C{^{1}H} APT spectrum of compound **4f** at 100 MHz in $CDCl_3$

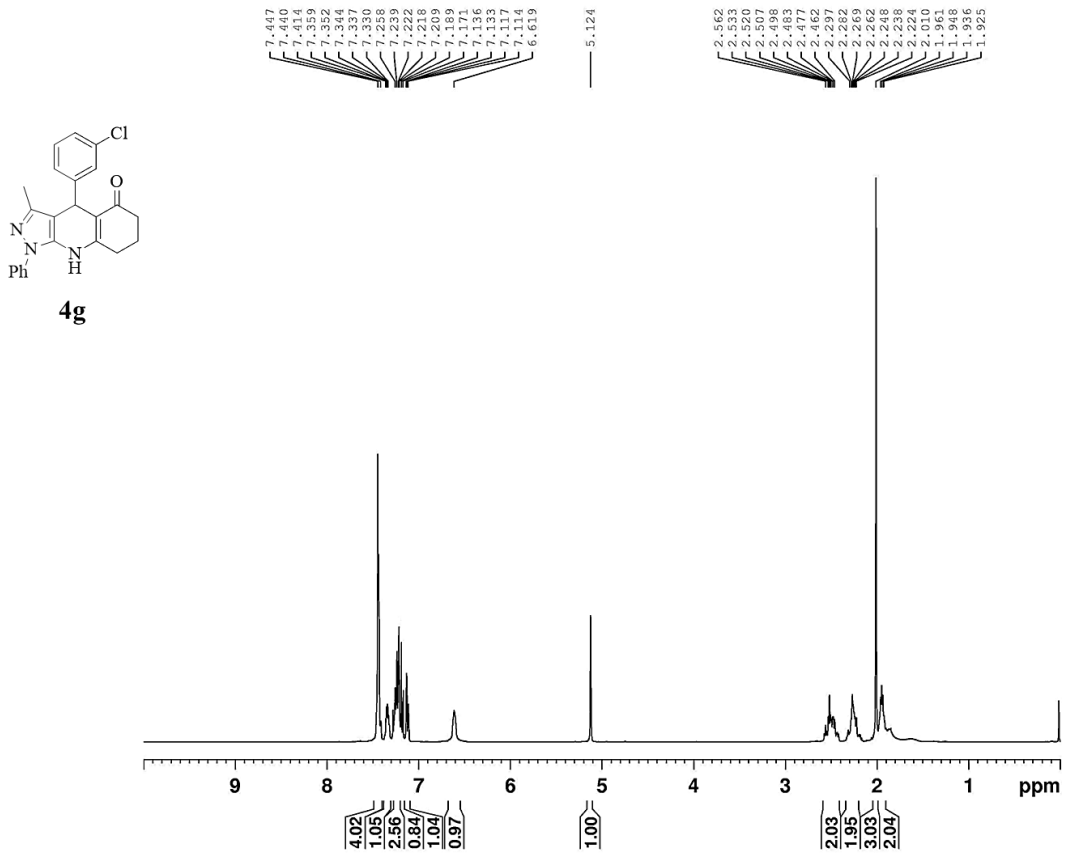


Figure 13. ^{1}H NMR spectrum of compound **4g** at 400 MHz in $CDCl_3$

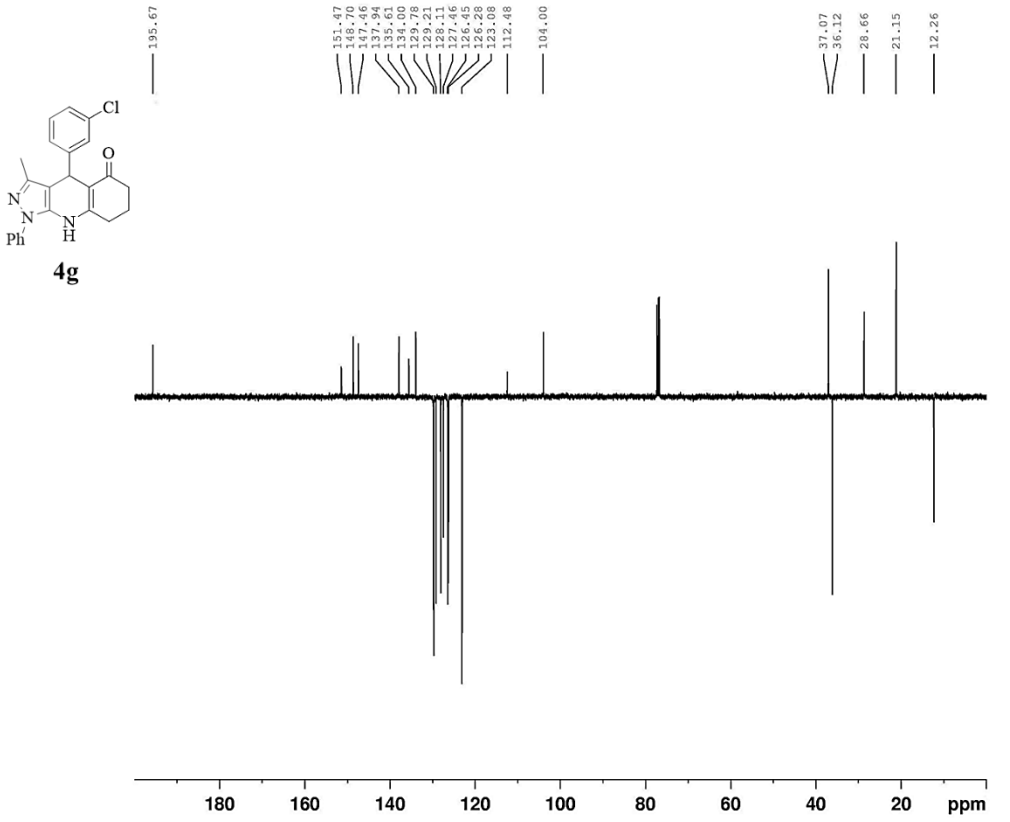


Figure 14. $^{13}C\{^{1}H\}$ APT spectrum of compound **4g** at 100 MHz in $CDCl_3$

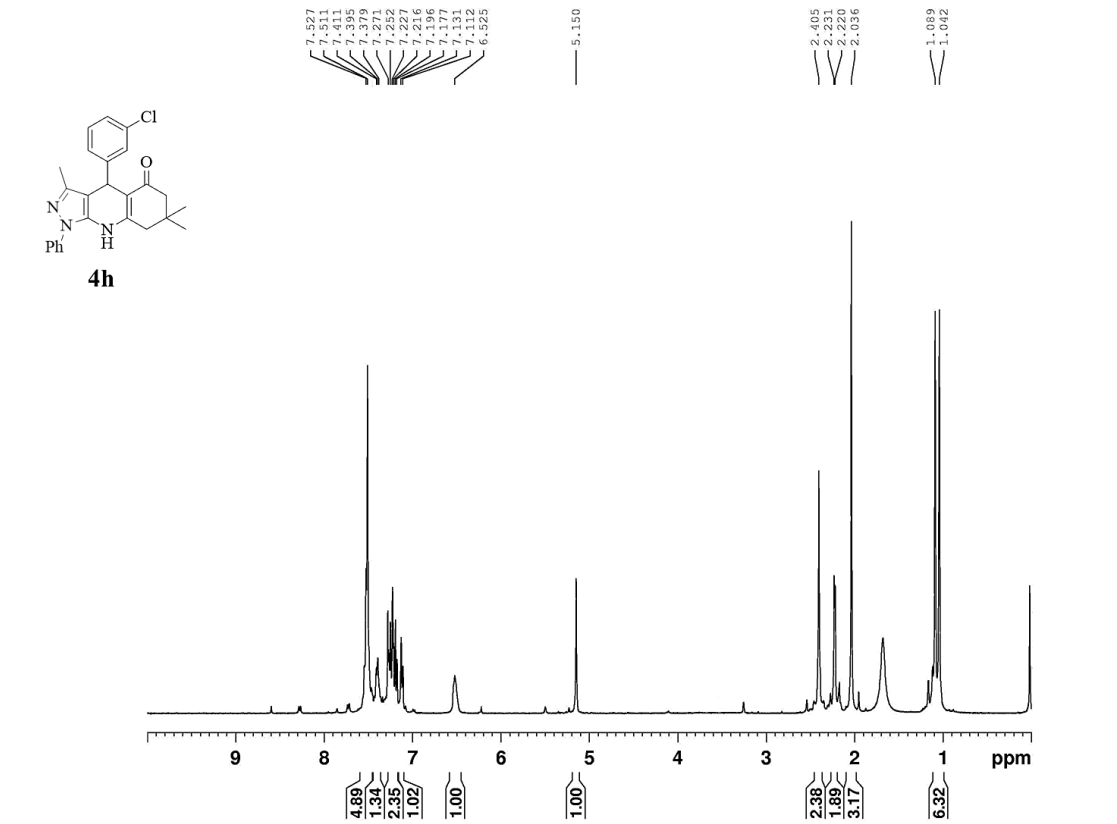


Figure 15. ^{1}H NMR spectrum of compound **4h** at 400 MHz in $CDCl_3$

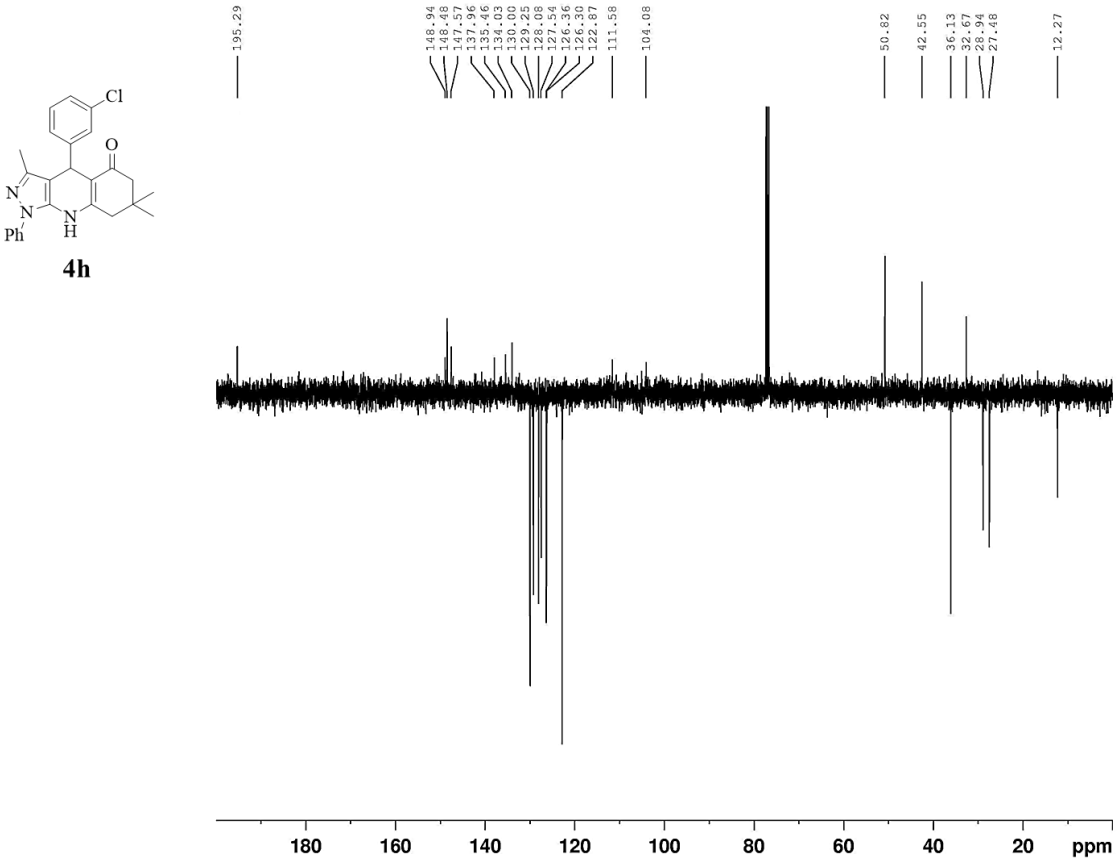


Figure 16. $^{13}C\{^{1}H\}$ APT spectrum of compound **4h** at 100 MHz in $CDCl_3$

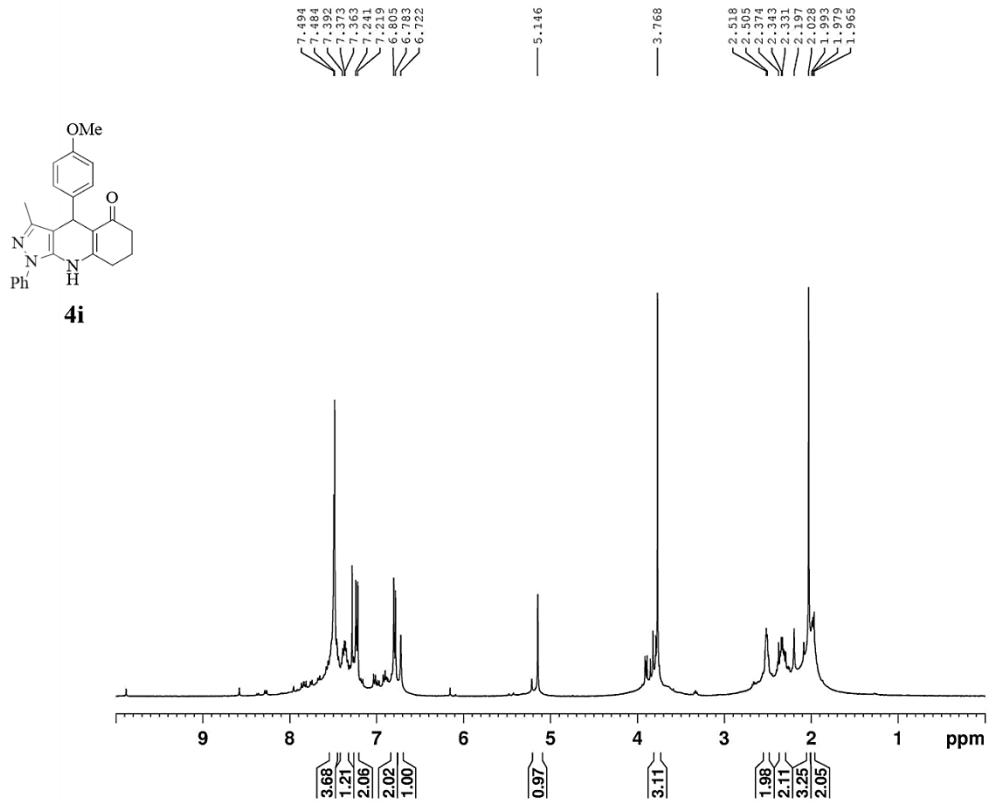


Figure 17. ^{1}H NMR spectrum of compound **4i** at 400 MHz in $CDCl_3$

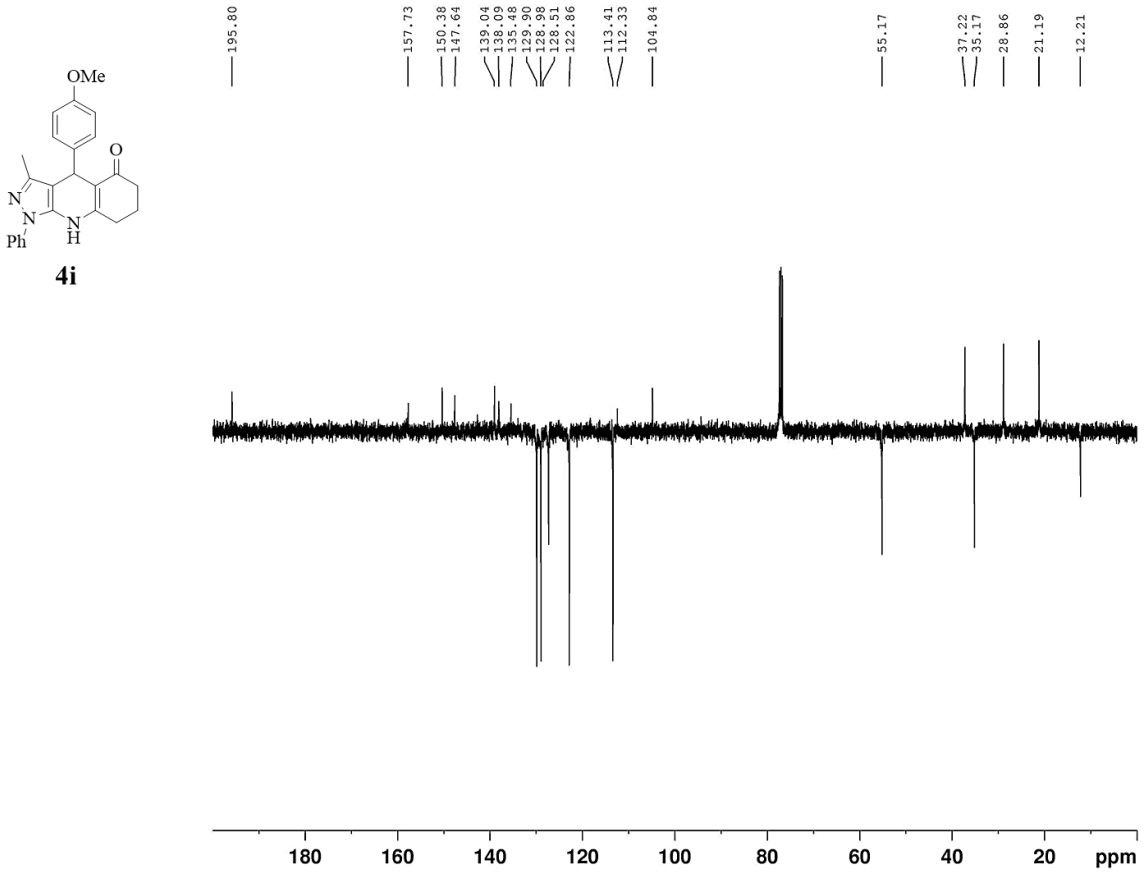


Figure 18. $^{13}C\{^{1}H\}$ APT spectrum of compound **4i** at 100 MHz in $CDCl_3$

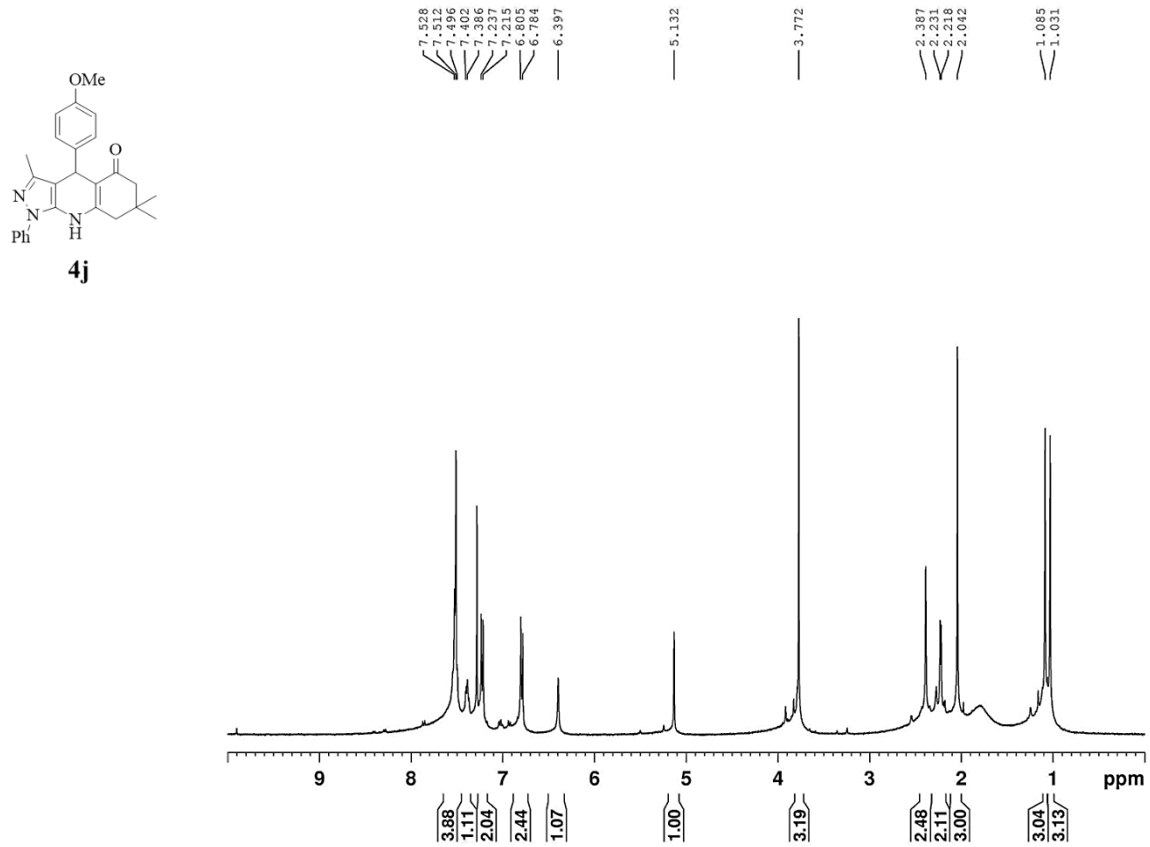


Figure 19. ^{1}H NMR spectrum of compound **4j** at 400 MHz in $CDCl_3$

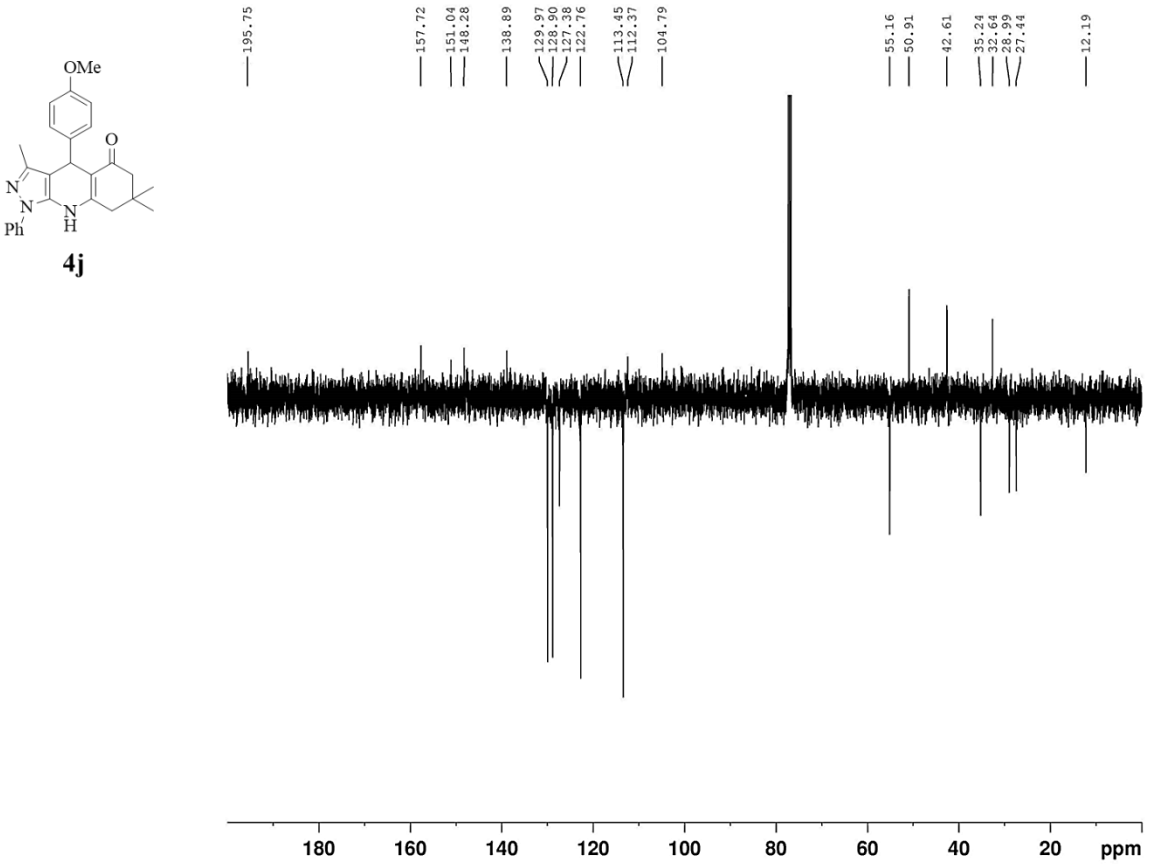


Figure 20. ^{13}C{^{1}H} APT spectrum of compound **4j** at 100 MHz in $CDCl_3$

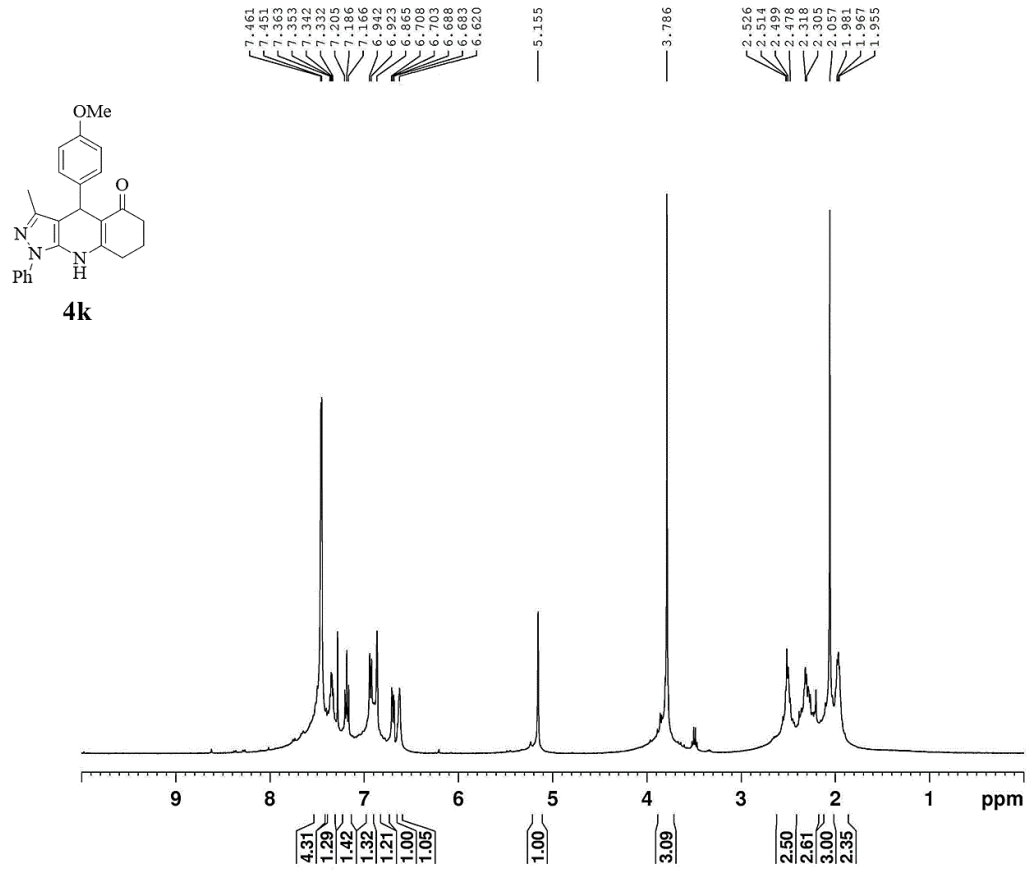


Figure 21. ^{1}H NMR spectrum of compound **4k** at 400 MHz in $CDCl_3$

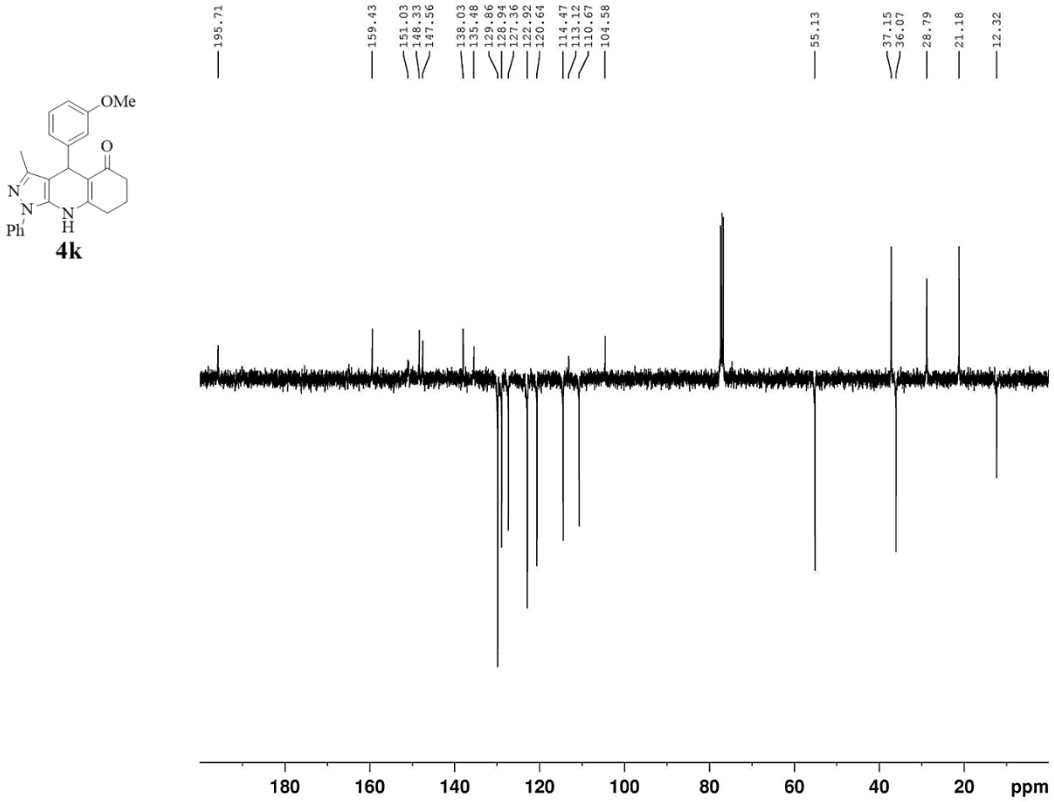


Figure 22. $^{13}C\{^{1}H\}$ APT spectrum of compound **4k** at 100 MHz in $CDCl_3$

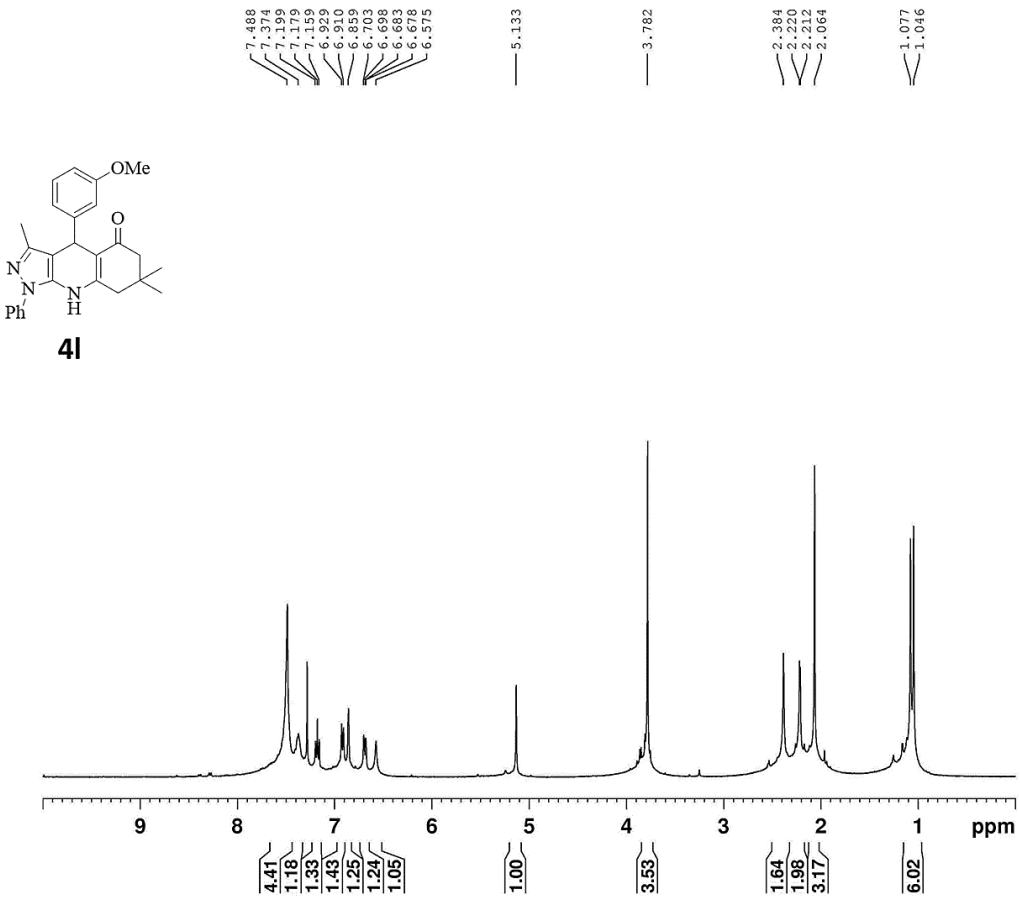


Figure 23. ^{1}H NMR spectrum of compound **4l** at 400 MHz in $CDCl_3$

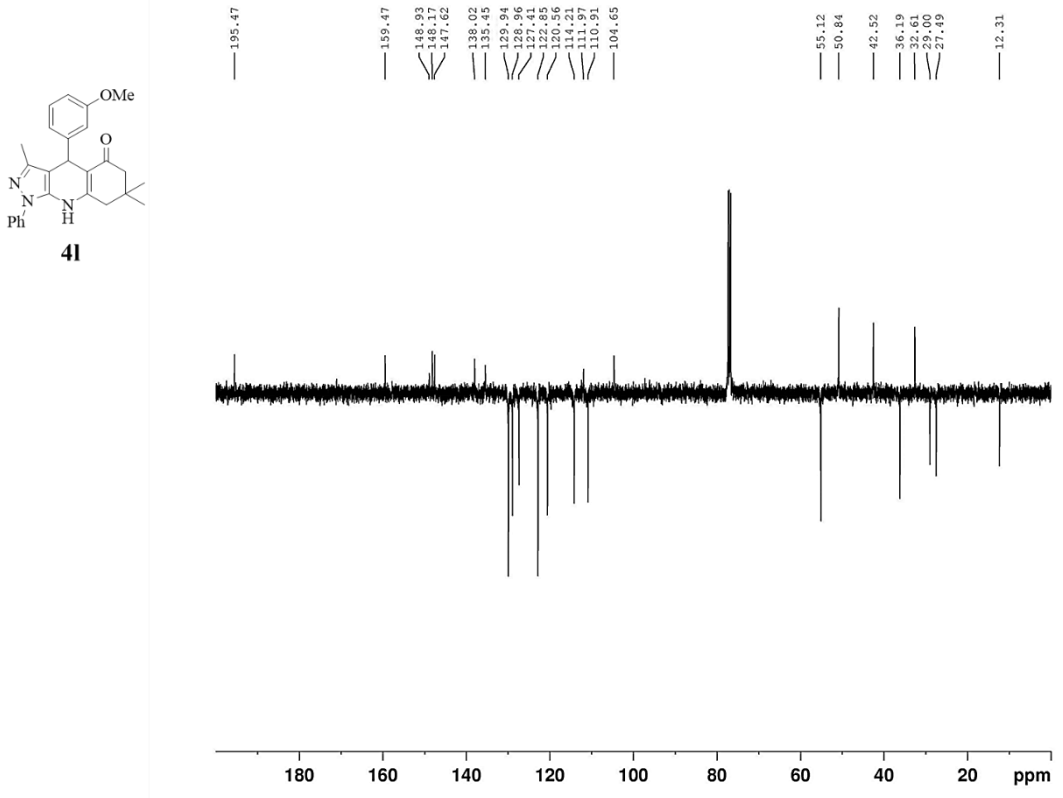


Figure 24. $^{13}C\{^{1}H\}$ APT spectrum of compound **4l** at 100 MHz in $CDCl_3$

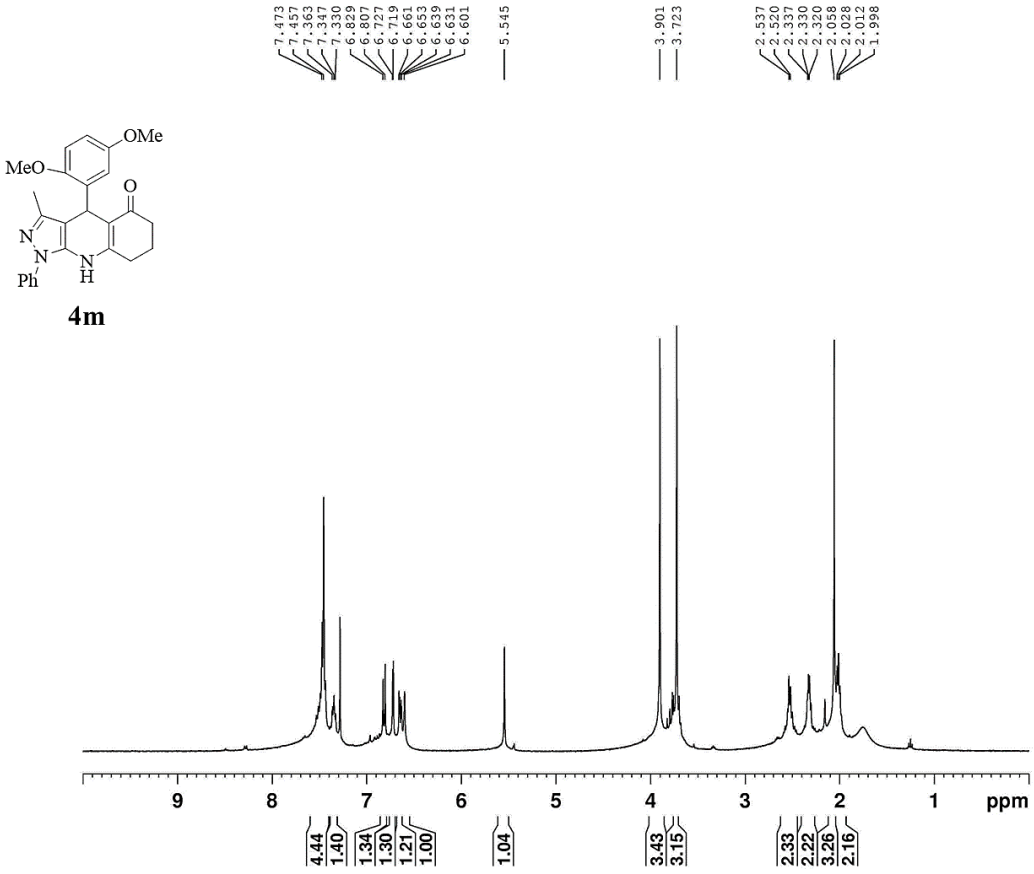


Figure 25. ^{1}H NMR spectrum of compound **4m** at 400 MHz in $CDCl_3$

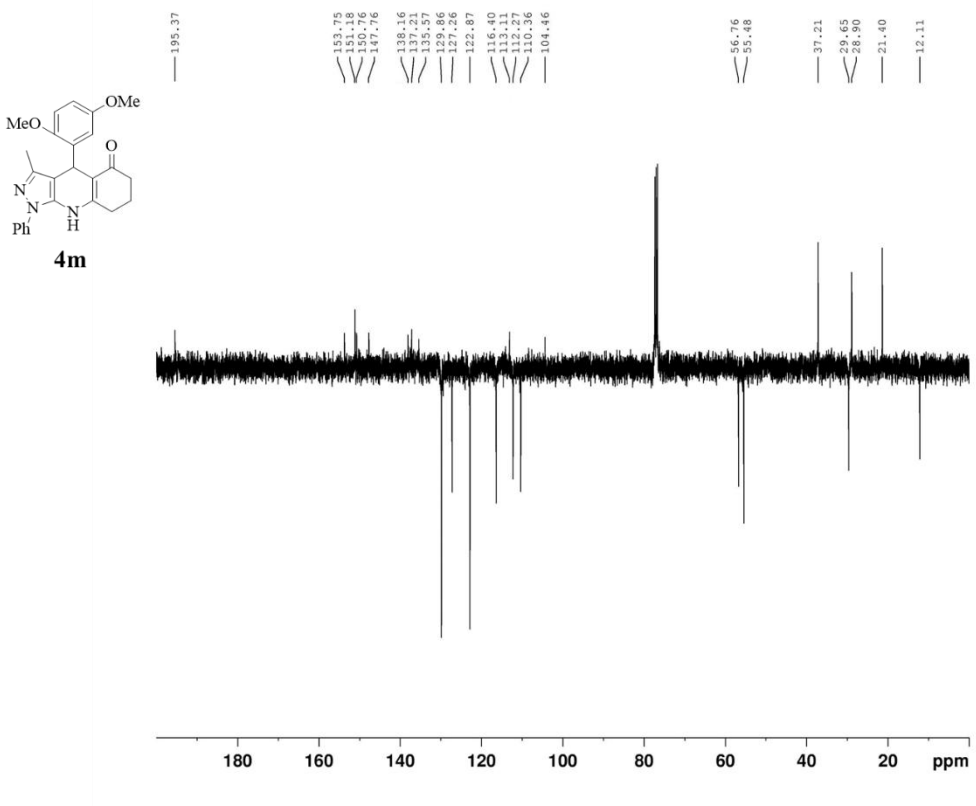


Figure 26. $^{13}C\{^{1}H\}$ APT spectrum of compound **4m** at 100 MHz in $CDCl_3$

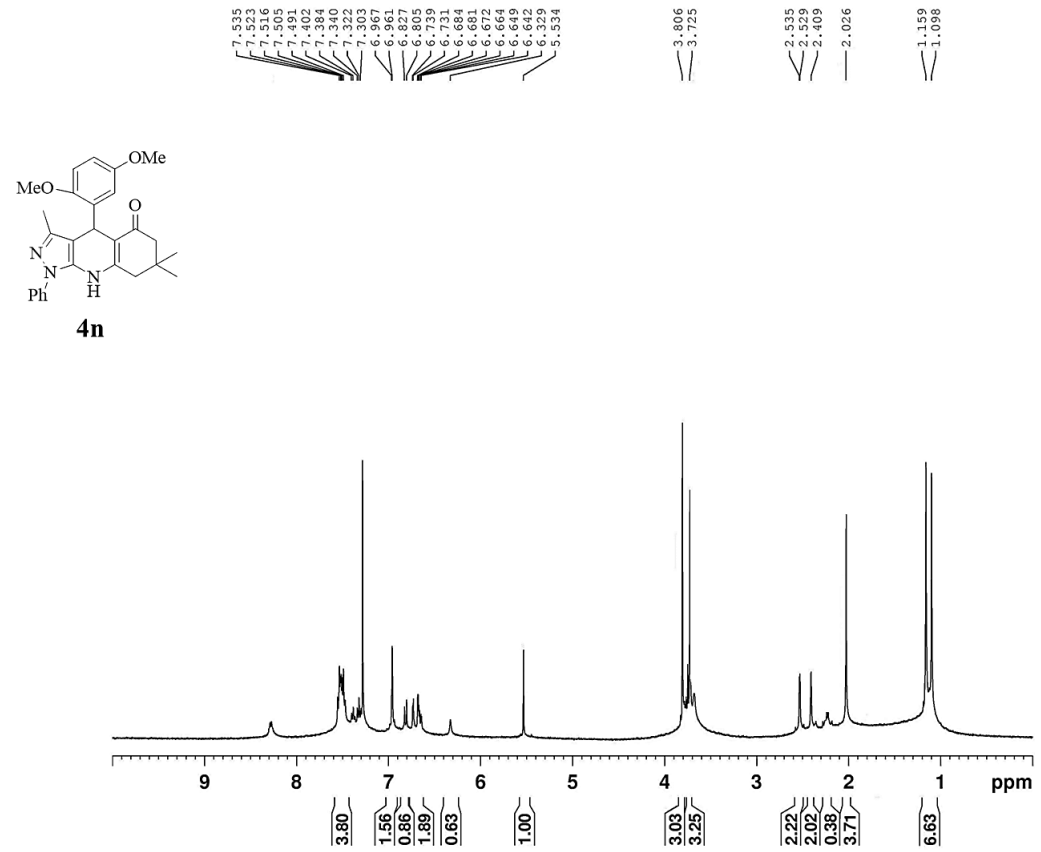


Figure 27. ^{1}H NMR spectrum of compound **4n** at 400 MHz in $CDCl_3$

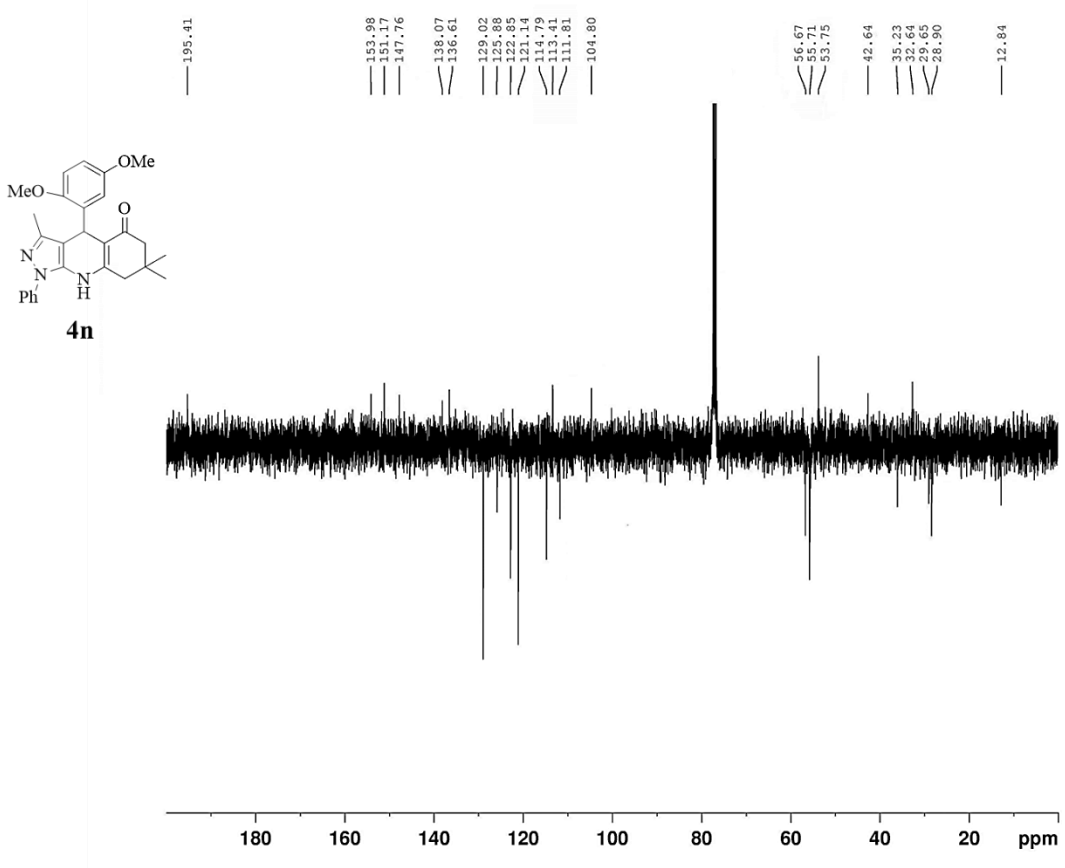


Figure 28. $^{13}C\{^{1}H\}$ APT spectrum of compound **4n** at 100 MHz in $CDCl_3$

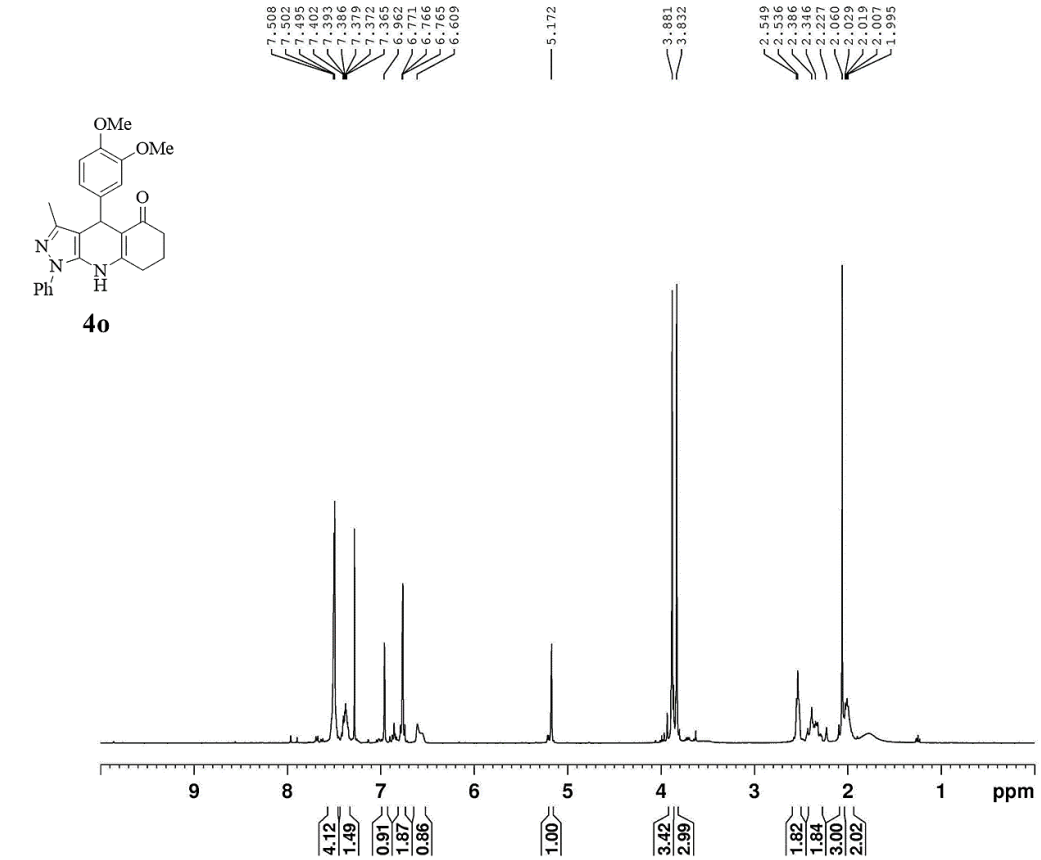


Figure 29. ^{1}H NMR spectrum of compound **4o** at 400 MHz in $CDCl_3$

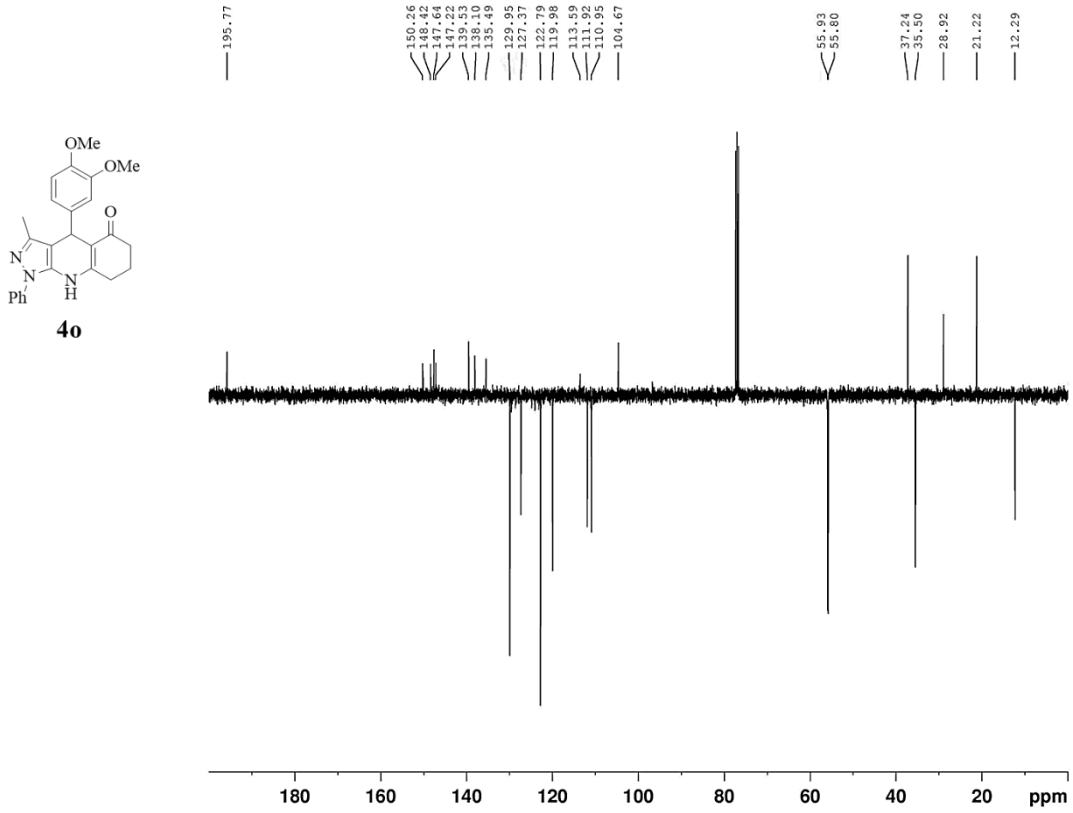


Figure 30. $^{13}C\{^{1}H\}$ APT spectrum of compound **4o** at 100 MHz in $CDCl_3$

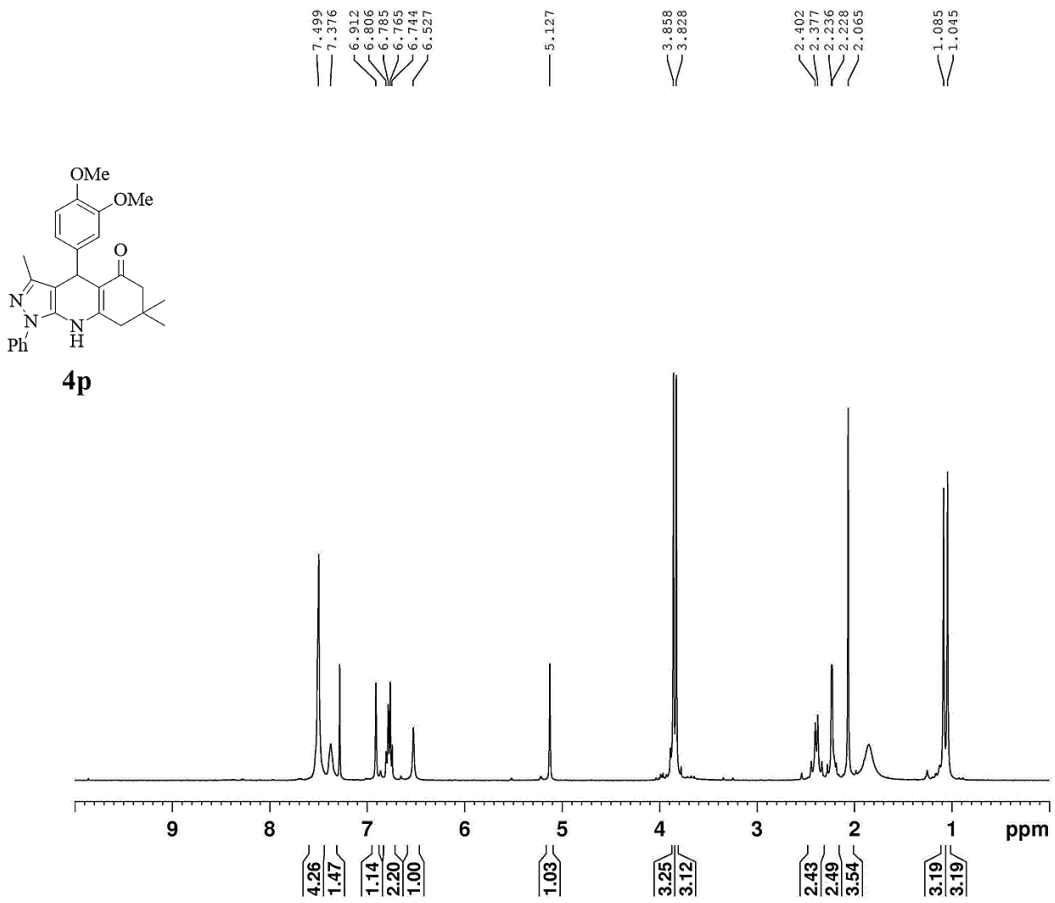


Figure 31. ^{1}H NMR spectrum of compound **4p** at 400 MHz in $CDCl_3$

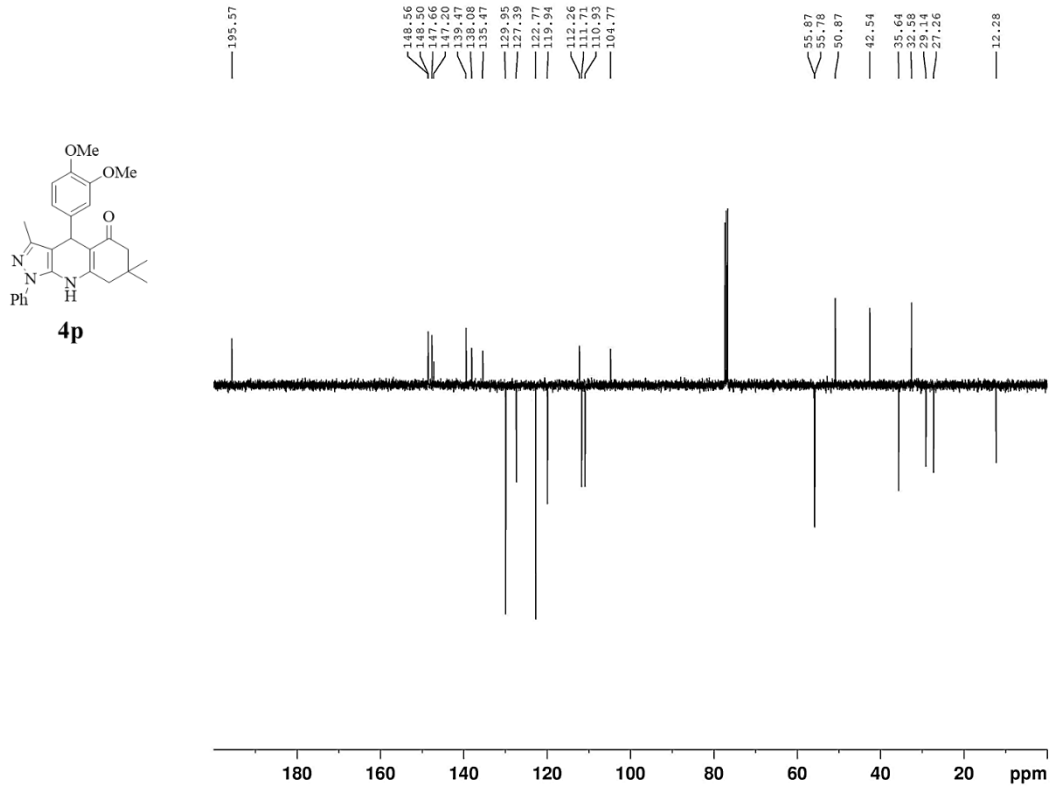
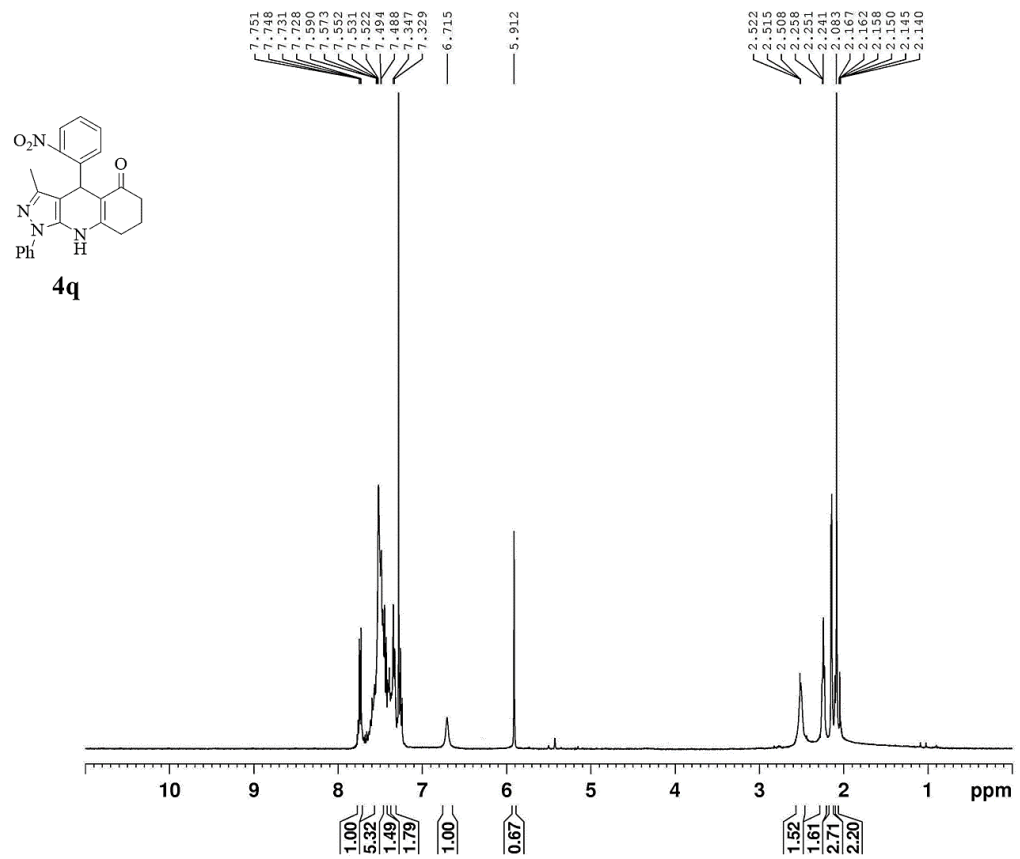
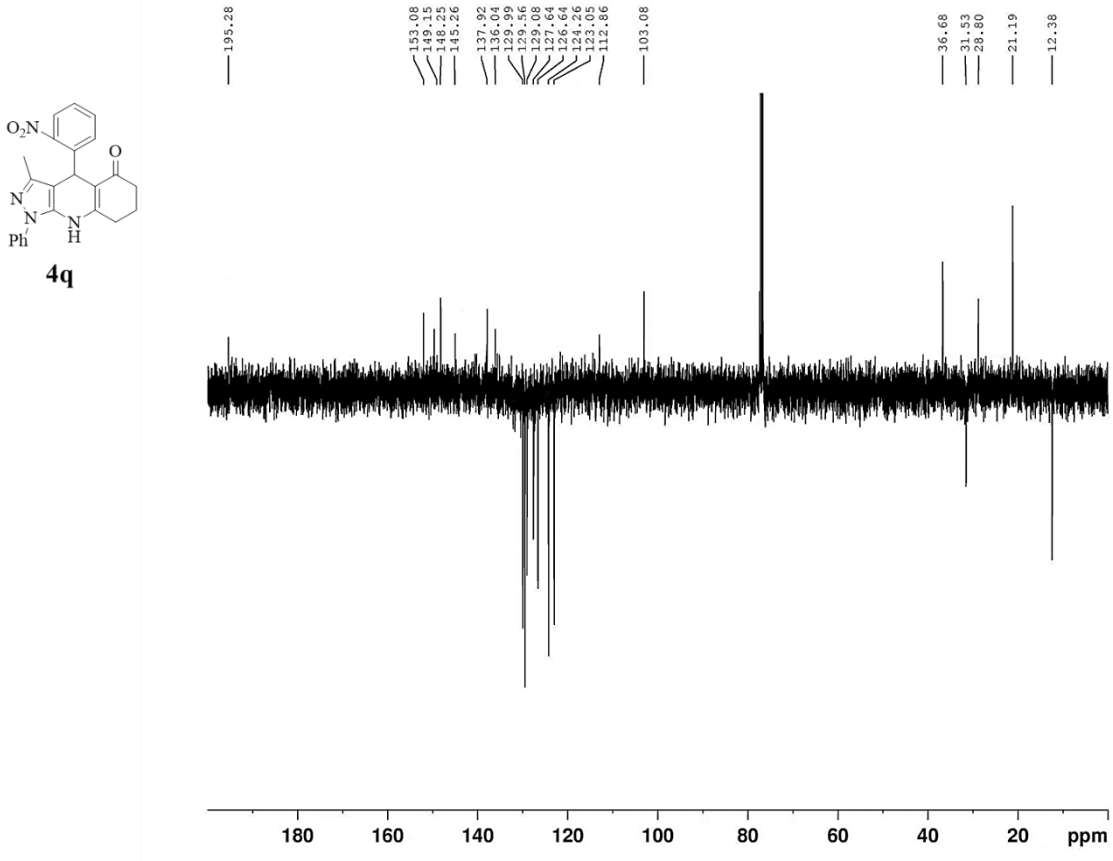


Figure 32. $^{13}C\{^{1}H\}$ APT spectrum of compound **4p** at 100 MHz in $CDCl_3$



4q

Figure 33. ^{1}H NMR spectrum of compound **4q** at 400 MHz in $CDCl_3$



4q

Figure 34. $^{13}C\{^{1}H\}$ APT spectrum of compound **4q** at 100 MHz in $CDCl_3$

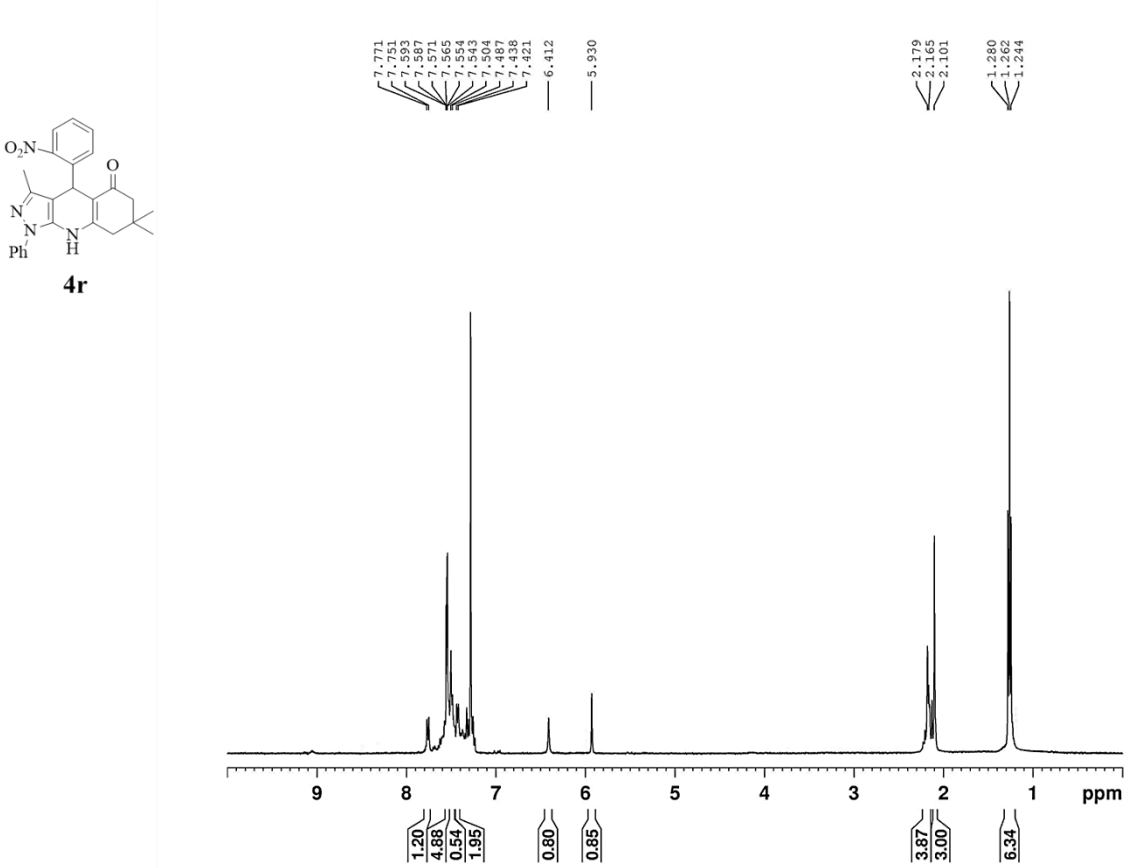


Figure 35. ^{1}H NMR spectrum of compound **4r** at 400 MHz in $CDCl_3$

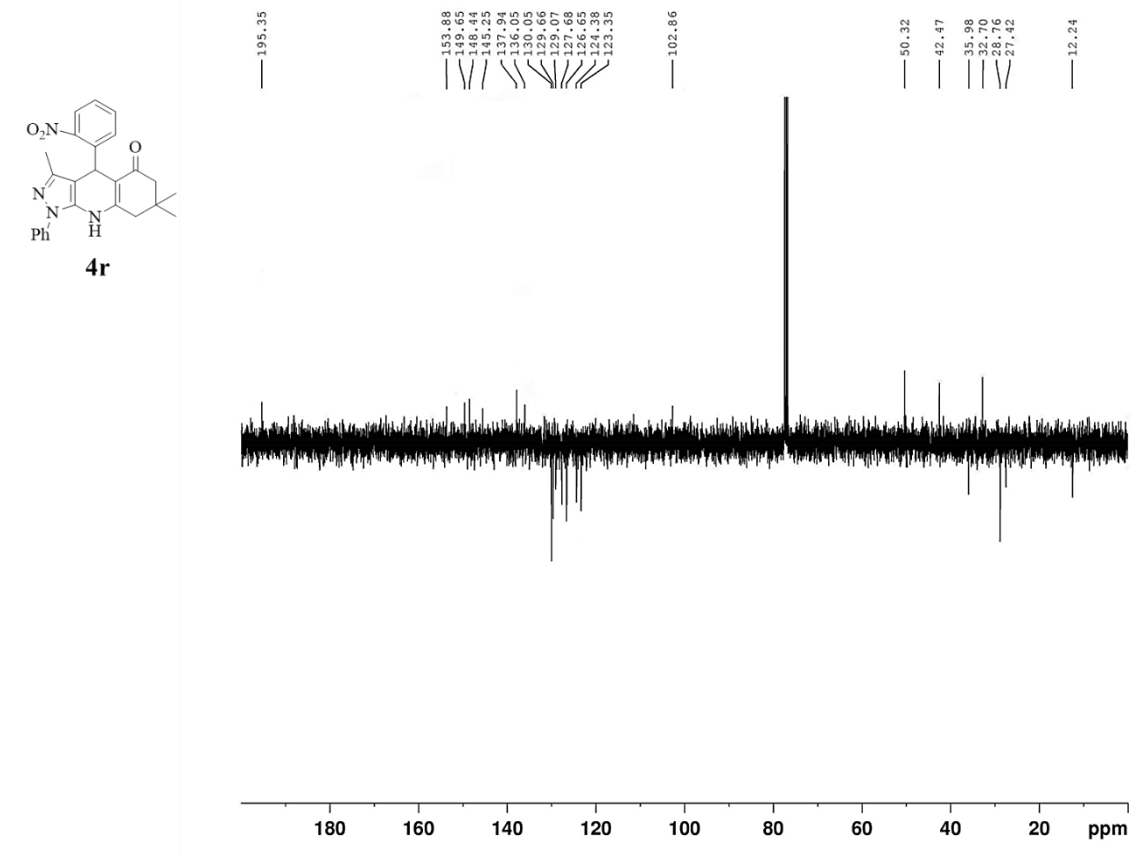


Figure 36. $^{13}C\{^{1}H\}$ APT spectrum of compound **4r** at 100 MHz in $CDCl_3$

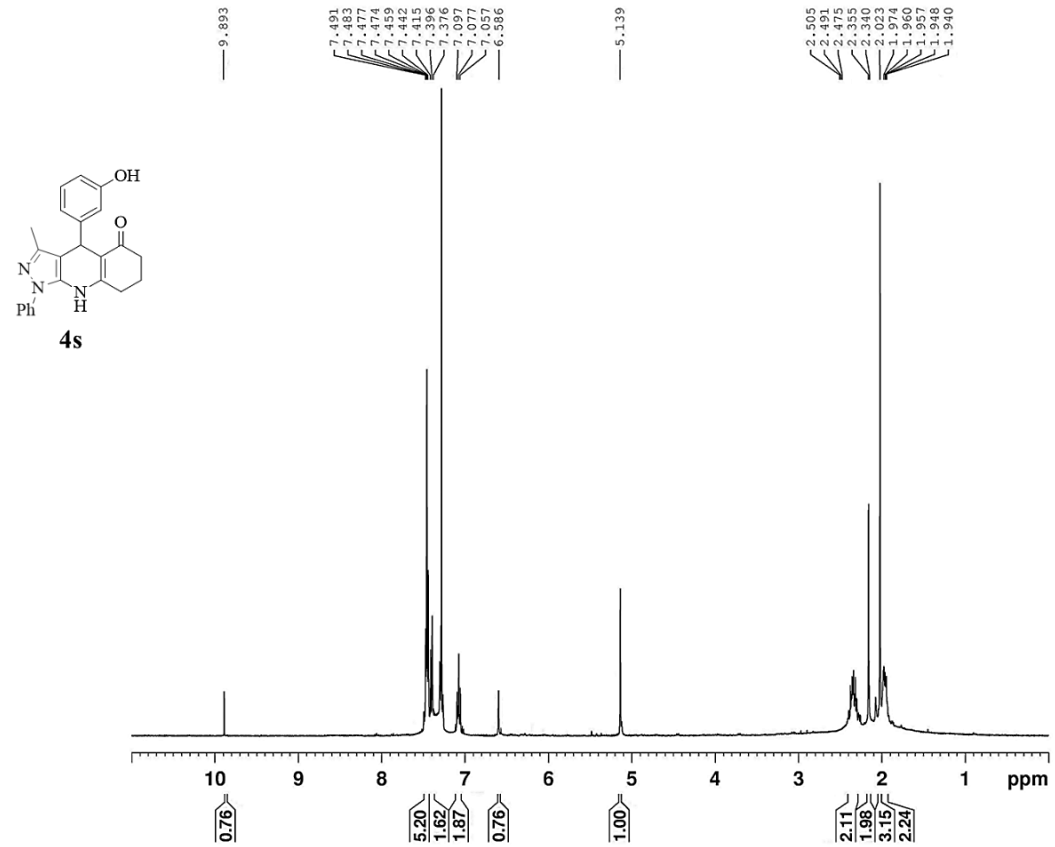


Figure 37. ^{1}H NMR spectrum of compound **4s** at 400 MHz in $CDCl_3$

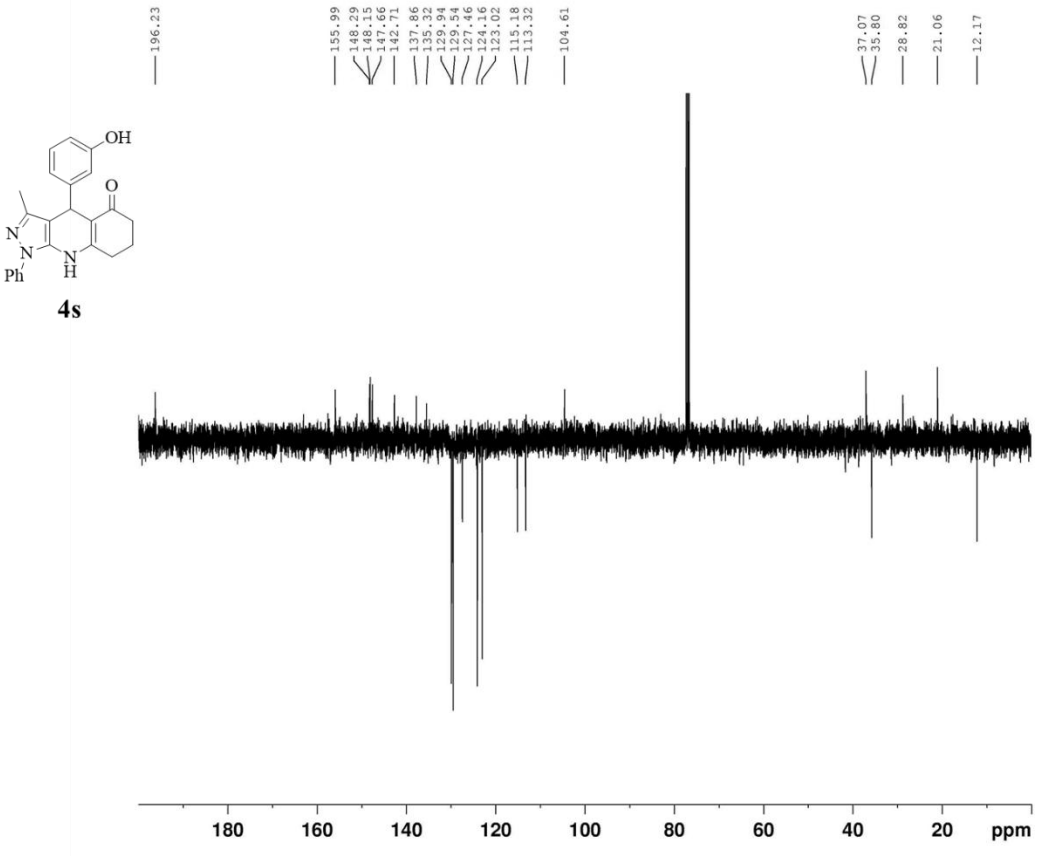


Figure 38. $^{13}C\{^{1}H\}$ APT spectrum of compound **4s** at 100 MHz in $CDCl_3$

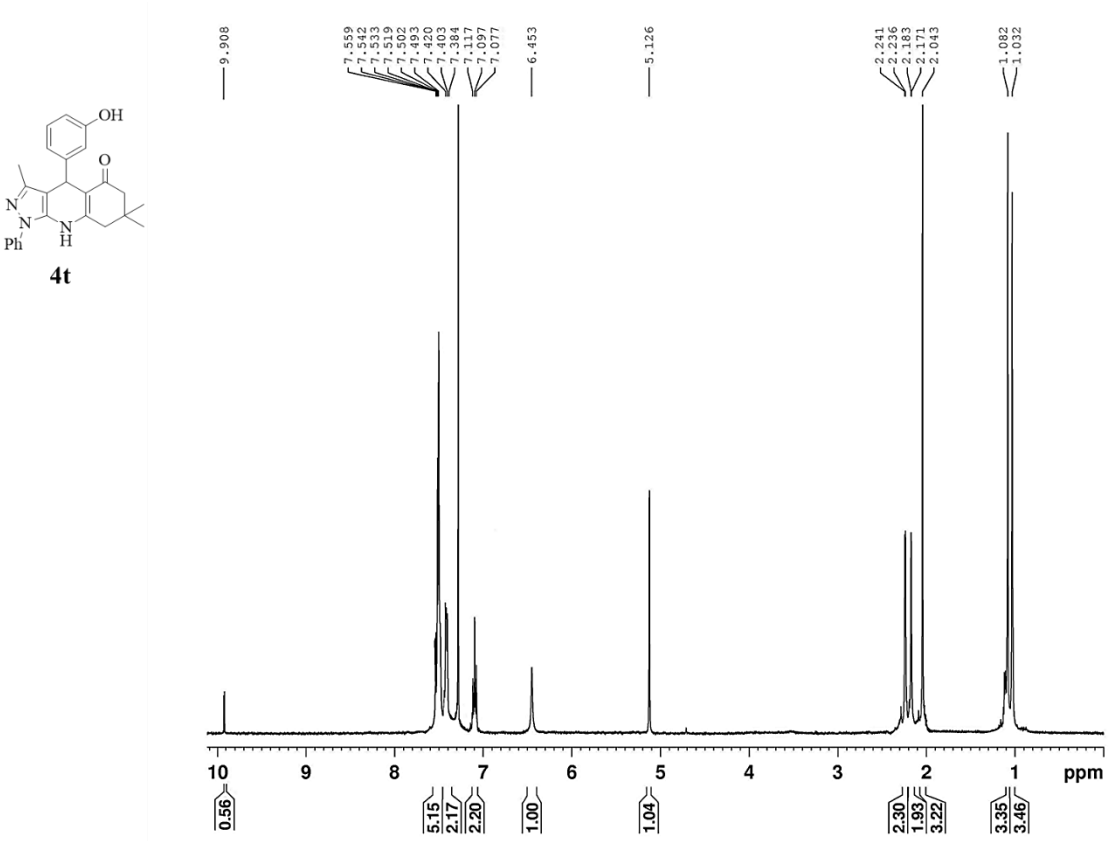


Figure 39. ^{1}H NMR spectrum of compound **4t** at 400 MHz in $CDCl_3$

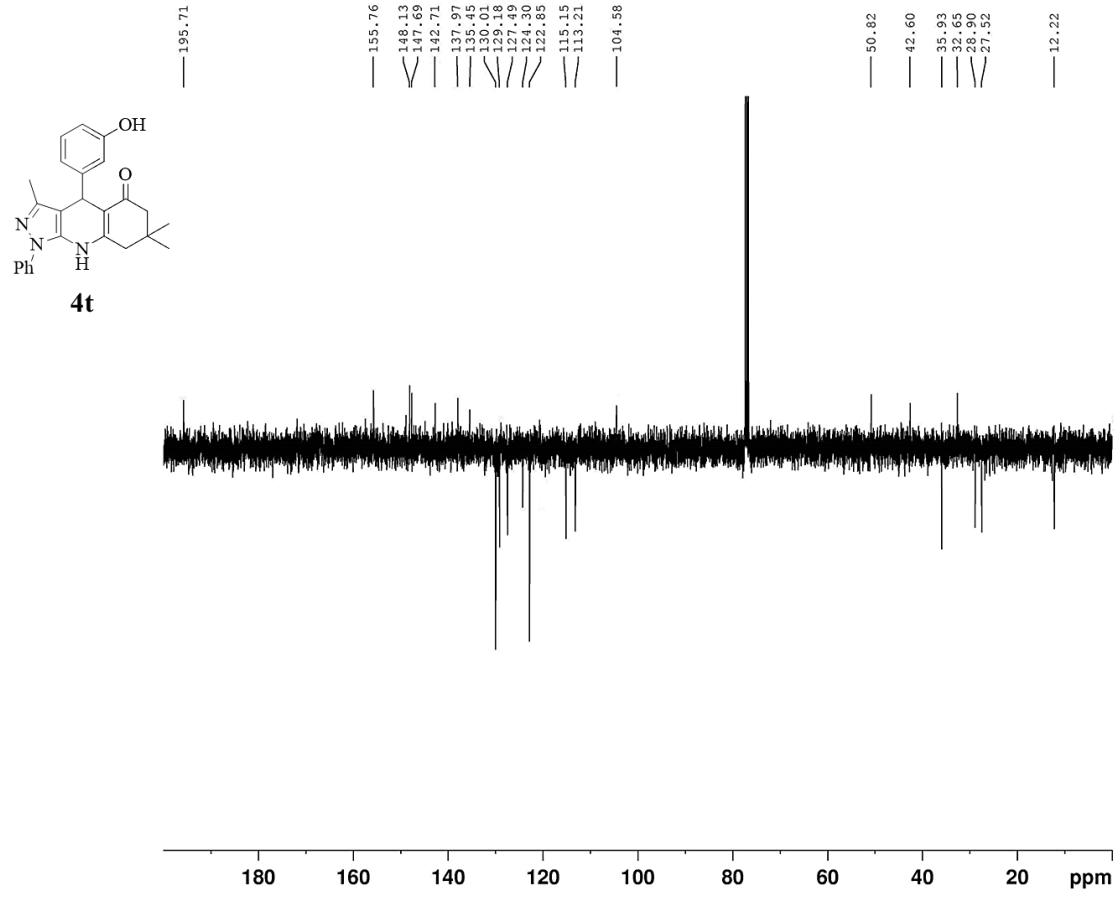


Figure 40. $^{13}C\{^{1}H\}$ APT spectrum of compound **4t** at 100 MHz in $CDCl_3$

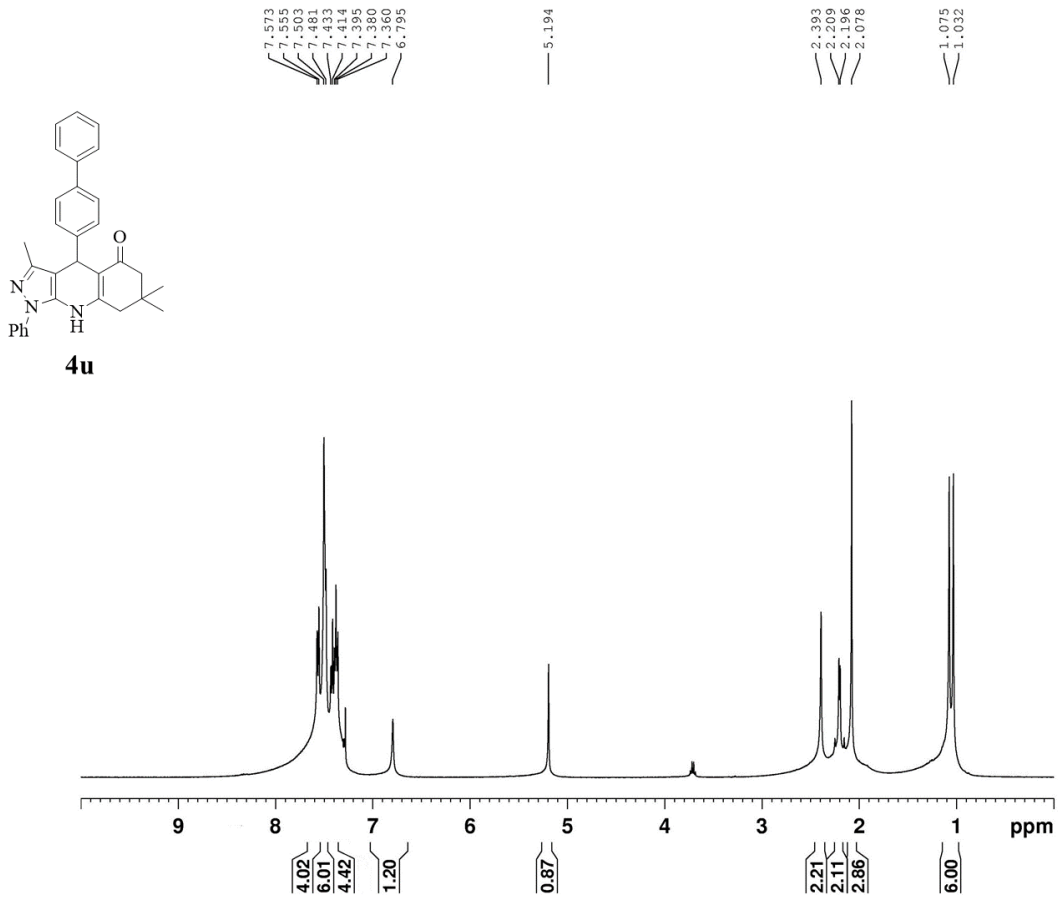


Figure 41. ^{1}H NMR spectrum of compound **4u** at 400 MHz in $CDCl_3$

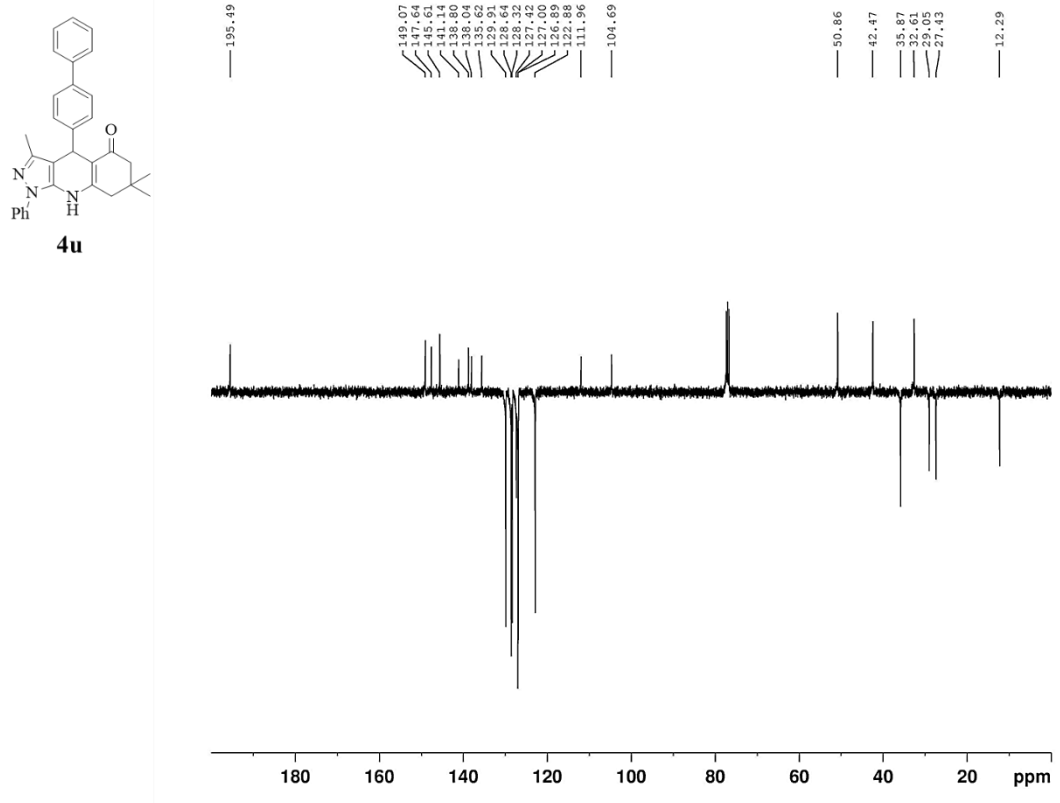


Figure 42. $^{13}C\{^{1}H\}$ APT spectrum of compound **4u** at 100 MHz in $CDCl_3$

Mass spectra of selected compounds

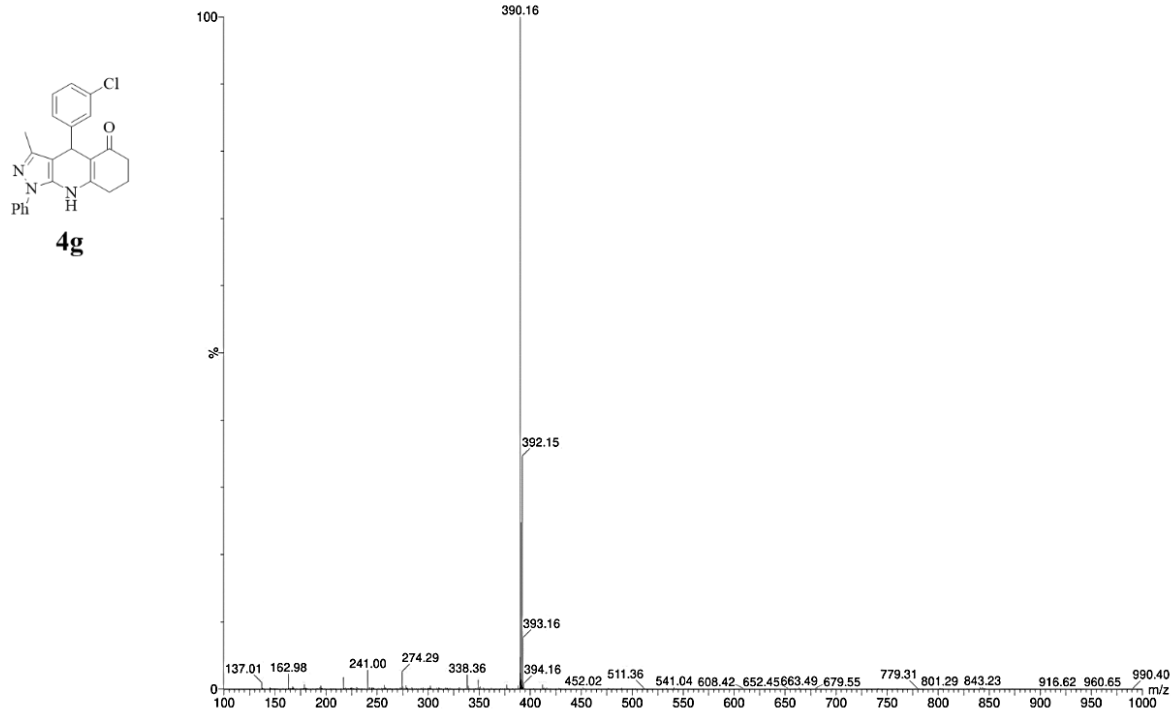


Figure 42. ESI-MS spectrum of compound **4g**

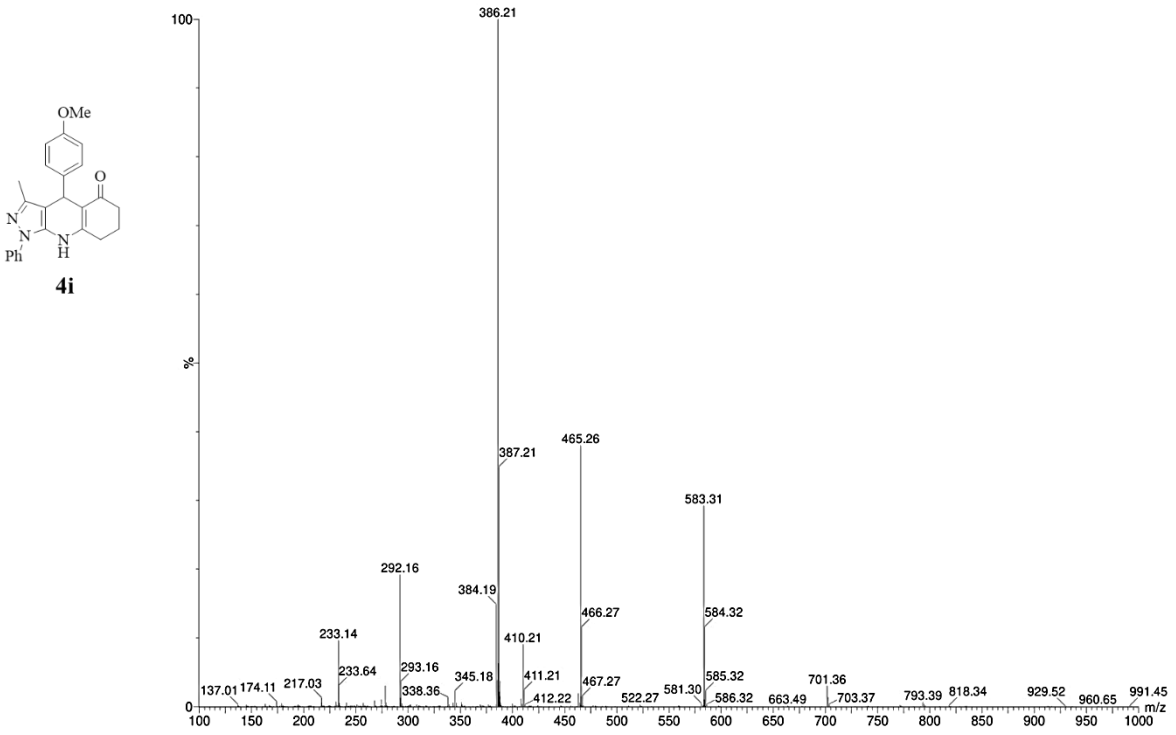


Figure 43. ESI-MS spectrum of compound **4i**

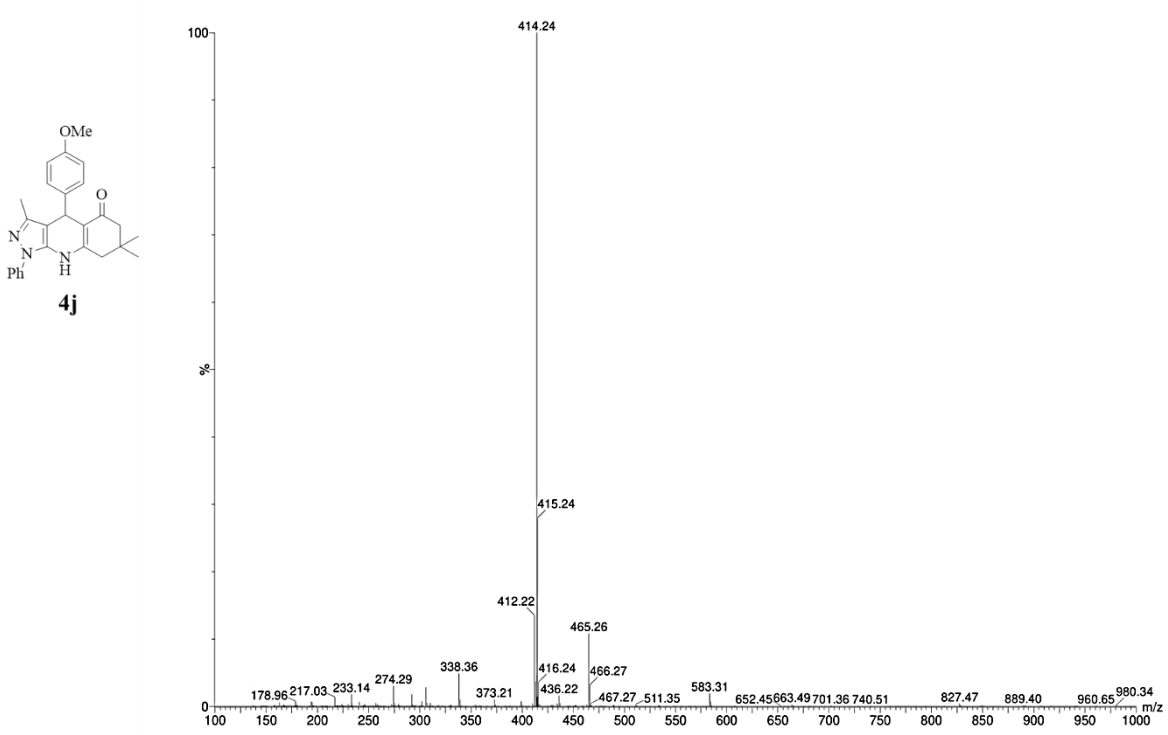


Figure 44. ESI-MS spectrum of compound **4j**

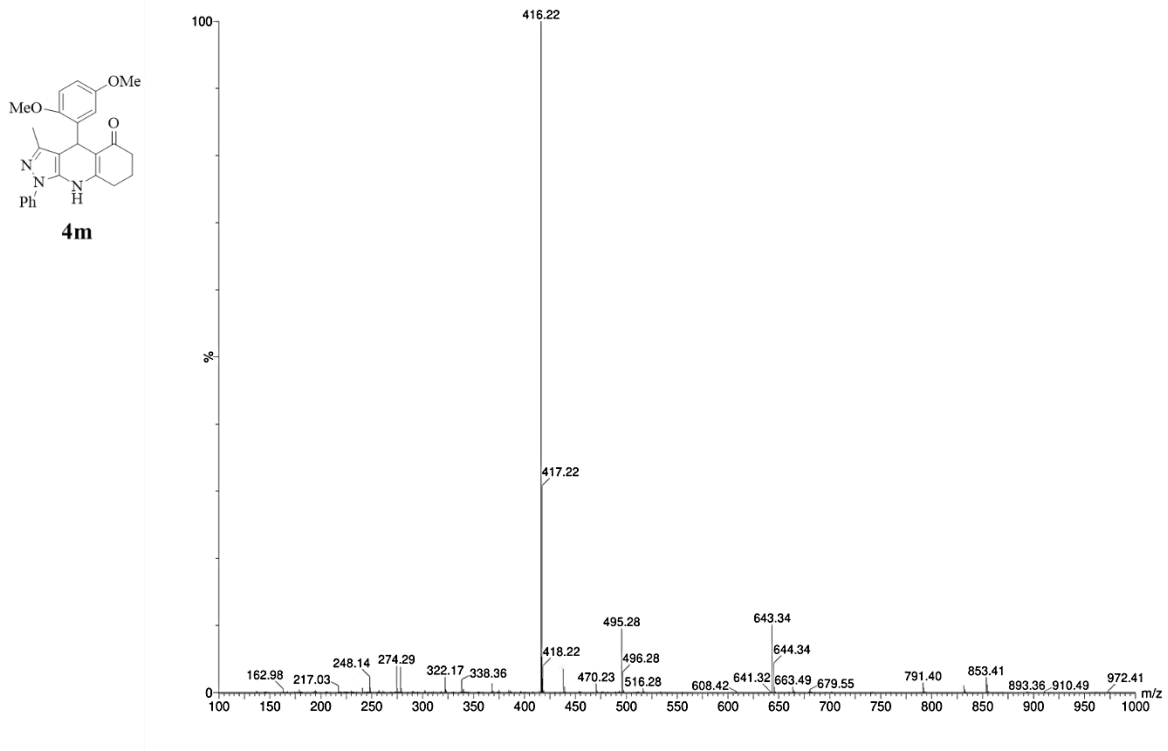
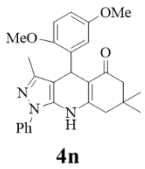


Figure 45. ESI-MS spectrum of compound **4m**



4n

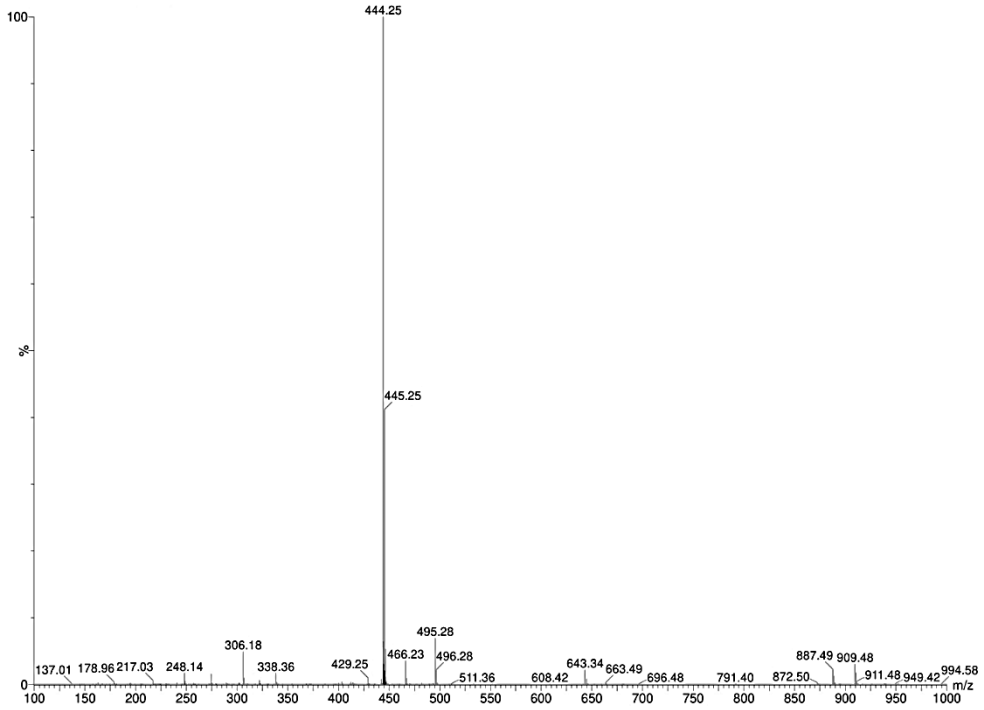
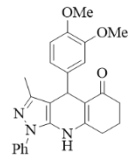


Figure 46. ESI-MS spectrum of compound **4n**



4o

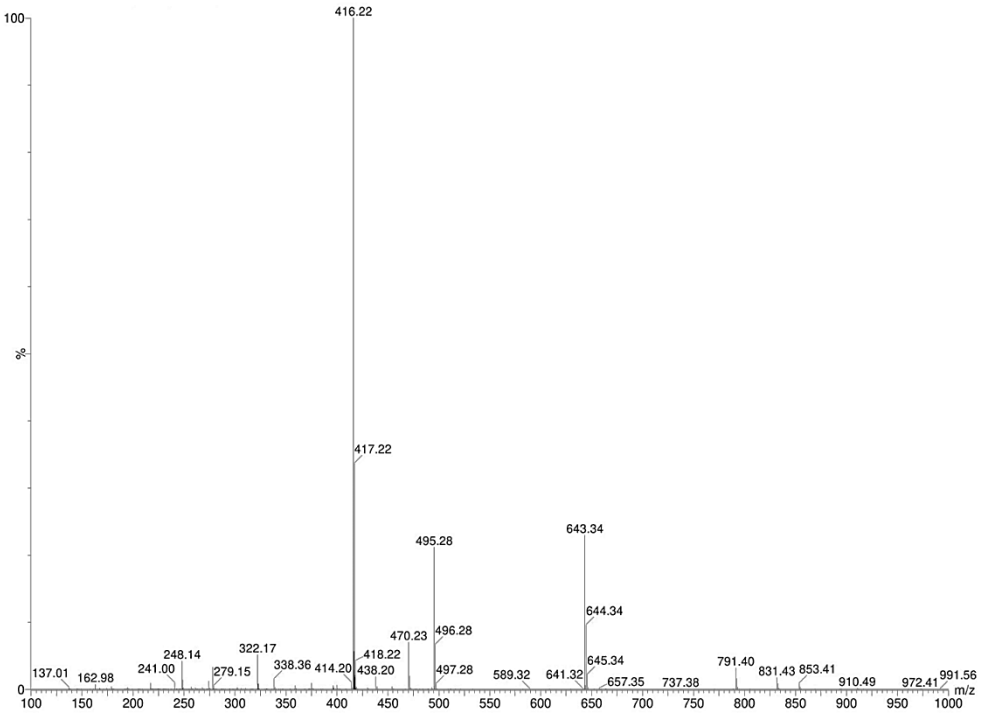
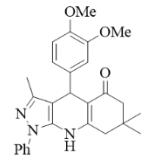


Figure 47. ESI-MS spectrum of compound **4o**



4p

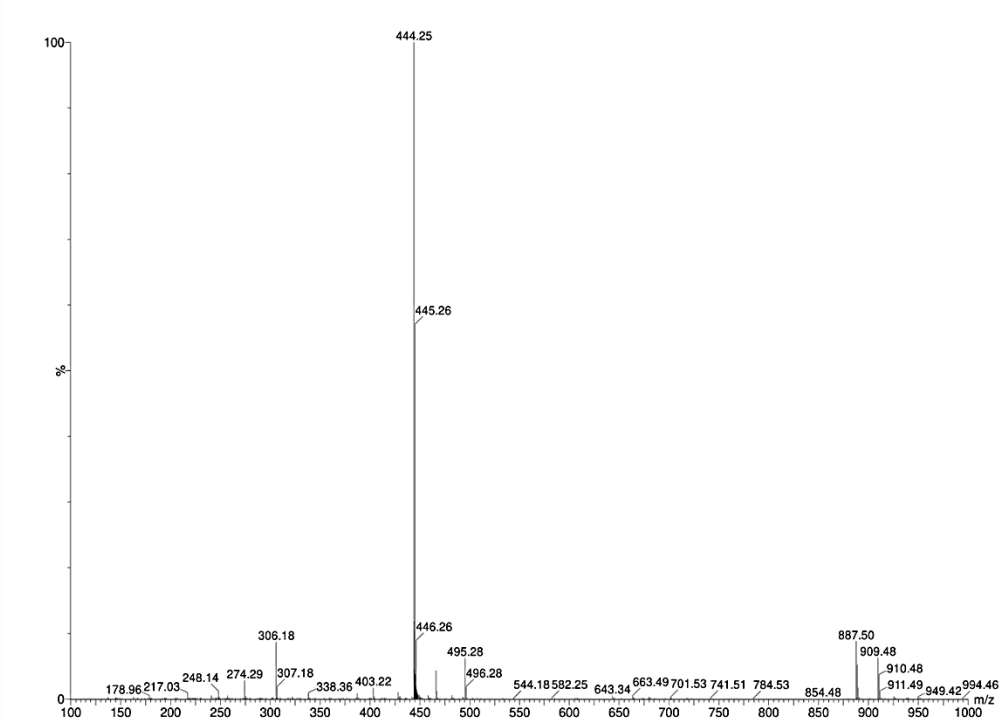
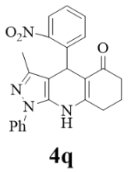


Figure 48. ESI-MS spectrum of compound **4p**



4q

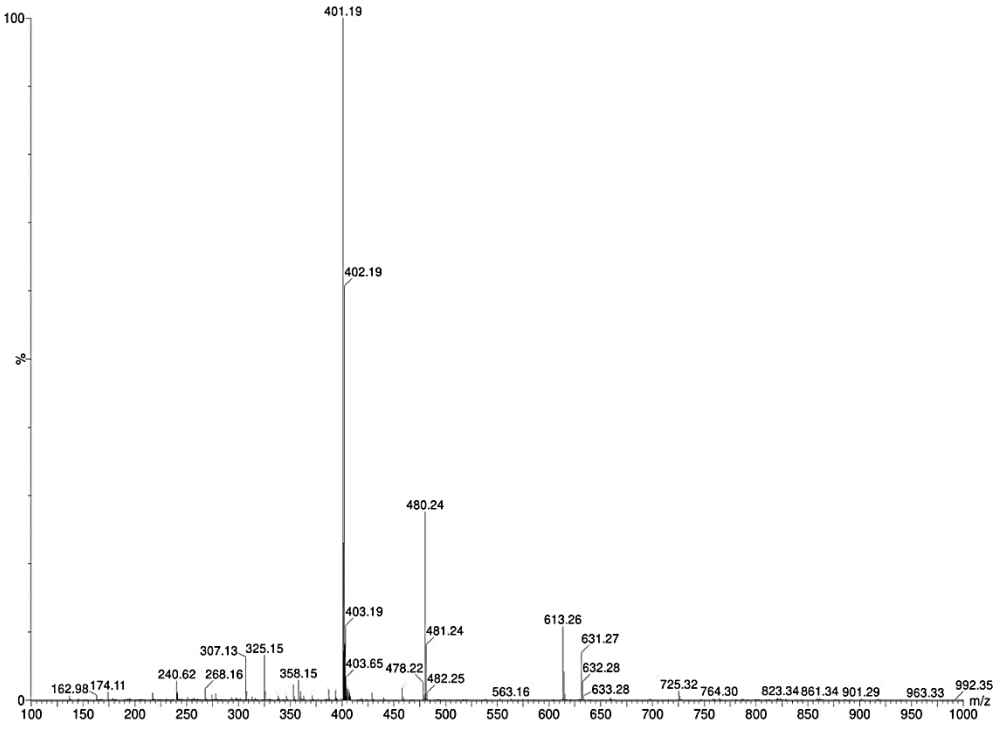


Figure 49. ESI-MS spectrum of compound **4q**

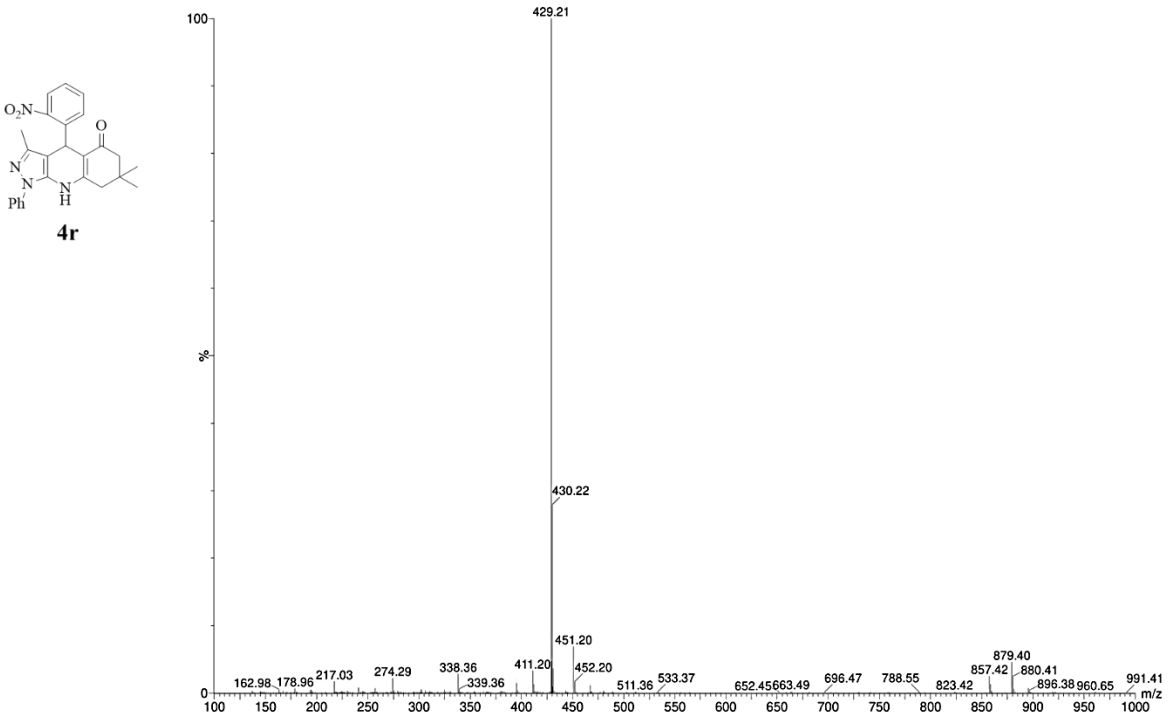


Figure 50. ESI-MS spectrum of compound **4r**

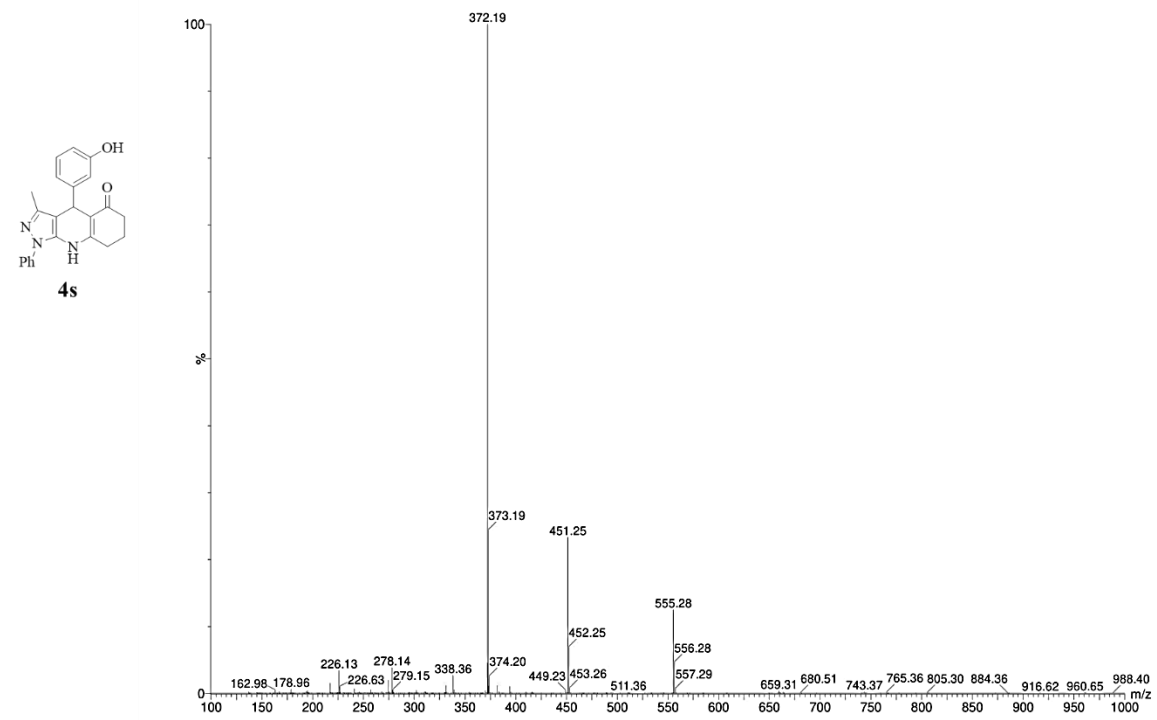
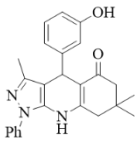


Figure 51. ESI-MS spectrum of compound **4s**



4t

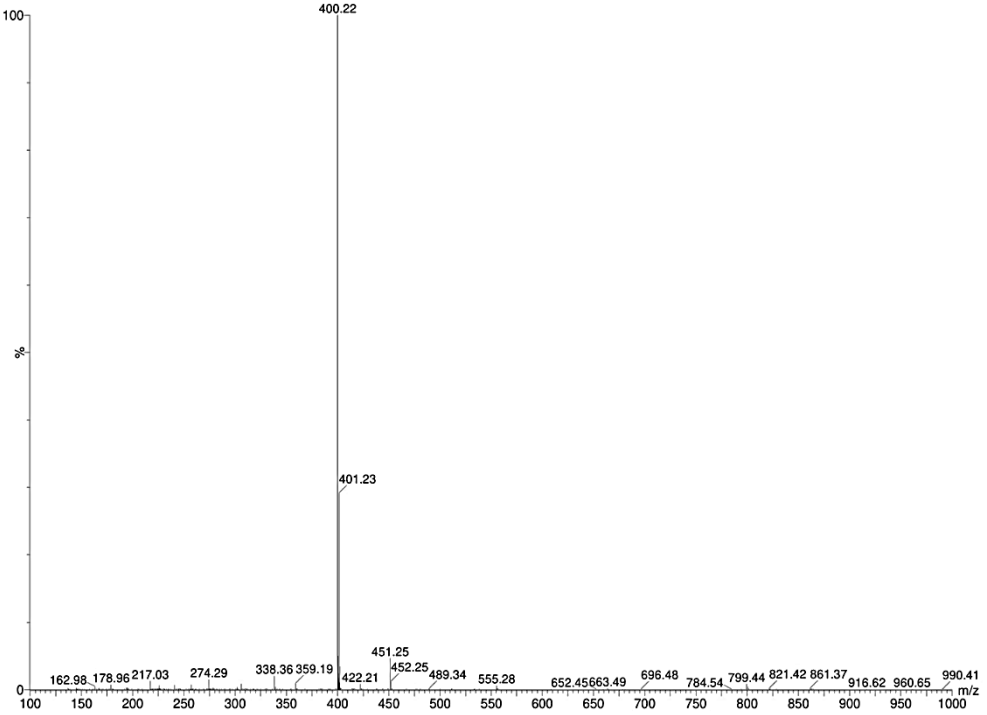
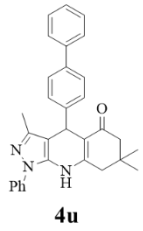


Figure 52. ESI-MS spectrum of compound **4t**



4u

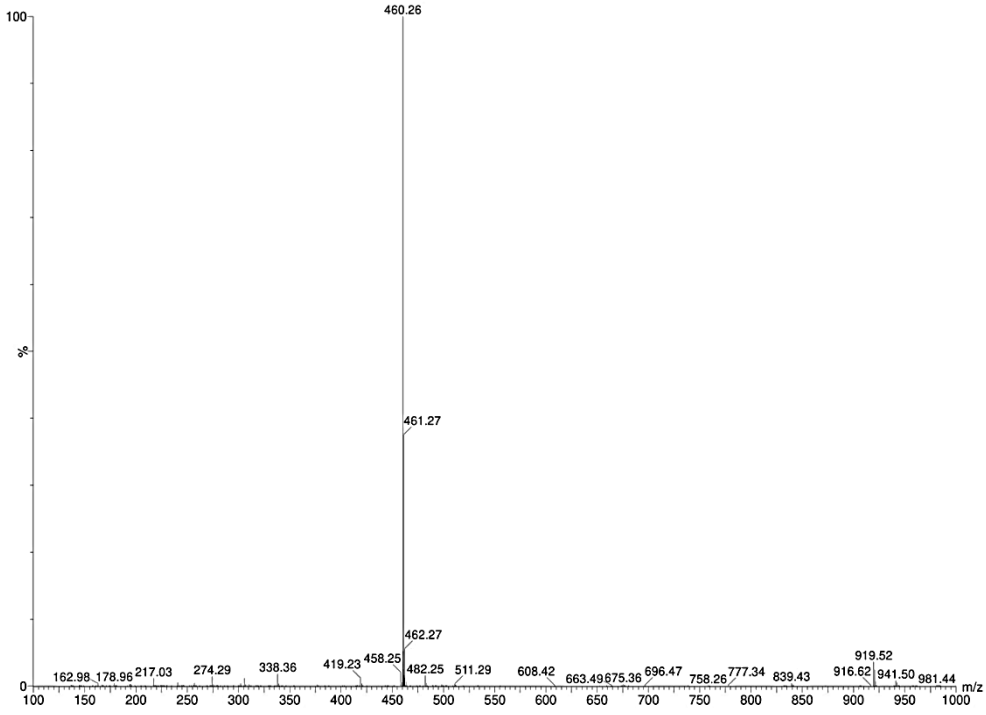


Figure 53. ESI-MS spectrum of compound **4u**