Supporting Information

Facile Synthesis of 2-Substituted Quinolines and 3-Alkynyl-2-Aryl-2*H*-Indazole *via* $SnCl_2$-Mediated Reductive Cyclization

Narayanasamy Sudhapriya,[a]Avanashiappan Nandakumar[a] and Paramasivan Thirumalai Perumal[a*]

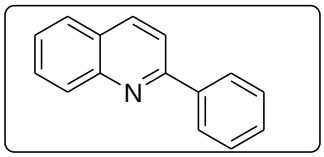
Organic Chemistry Division, CSIR- Central Leather Research Institute, Adyar, Chennai-600020

E-mail: ptperumal@gmail.com

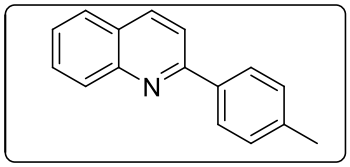
General information:

Reagents and solvents were purchased from commercial sources (Aldrich and Merck) and used without further purification. Copper (I) iodide (99.999 % purity) and Stannous chloride dihydrate (>99.99 % purity) were purchased from Sigma-Aldrich and used as such without further purification. All reactions were carried out in reaction vessels with magnetic stirring and no special precautions were taken to exclude air from the reaction vessels. The reactions were monitored by thin layer chromatography. Analytical TLC was performed on pre-coated aluminium sheets of silica gel $60F_{254}$ of 0.2 mm thickness (Merck,Germany). Flash column chromatography was performed on silica gel (230-400mesh), SRL. India. Melting points were determined on Gallenkamp meltingpoint apparatus using capillary tubes and are uncorrected. ^{1}HNMR (400MHz) and ^{13}CNMR (100MHz) spectra were recorded in $CDCl_3$/ TMS solution with TMS as internal standard on a Bruker spectrometer. Mass spectra were recorded using ESI/HRMS at 60000 resolutions in Thermo scientific Exactive mass spectrometer.Elemental analyses were recorded using a Thermo Finnigan FLASH EA1112 CHN analyzer.

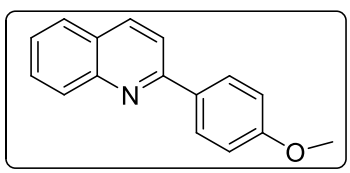
Typical experimental procedure for the preparation of quinoline (4a-m): N-alkyl propargylamines were prepared according to the similar procedure as reported.[15d] A mixture of copper iodide (15 mol %), 2-nitrobezaldehyde **1** (1.0 mmol), piperidine **2**(1.2 mmol) and alkyne **3** (1.2 mmol) in toluene was heated at 100°C for 3h. Then the reaction mixture was cooled to rt and the solvent was removed then used directly without further purification. The reaction mixture of N-alkyl propargylamine **5** was dissolved in 5 ml of ethanol and added $SnCl_2.2H_2O$ (4.0 mmol) then heated at 70°C for 2h. After the completion of reaction it was filtered through celite by washing with ethylacetate and added water (50ml) extracted with same solvent (2x20ml). The combined organic layer washed with saturated NaOH and brine solution and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel using petroleum ether/ ethyl acetate (5-20%) to afford quinoline derivatives in 62-89 % yield. All the prepared compounds were characterized by NMR and Mass spectroscopy techniques.



2-phenylquinoline (4a). White solid; yield:85%; mp: 82-84°C;^{1}H NMR (400MHz, $CDCl_3$/ TMS):δ (ppm) 7.44-7.48 (m, 1H), 7.51-7.54 (m, 3H), 7.69-7.74 (m, 1H), 7.82 (d, *J*= 8.4 Hz,1H), 7.87 (d, *J*=8.8 Hz, 1H), 8.15-8.17 (m, 3H), 8.20-8.22 (m,1H);^{13}C NMR (100MHz, $CDCl_3$/ TMS):δ(ppm) 119.0, 126.3, 127.5, 127.6, 128.9, 129.3, 129.7, 129.8, 130.9, 136.8, 139.7, 148.3, 157.4;HRMS (ESI) calc for $C_{15}H_{11}N[M+H]^+$: 206.0964, found: 206.0968.

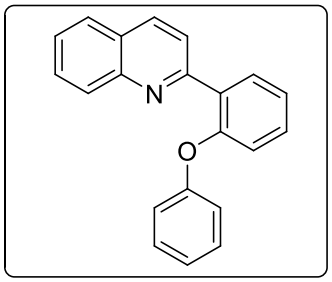


2-p-tolylquinoline (4b). White solid;yield: 87%; mp: 79-81°C;^{1}H NMR (400MHz, $CDCl_3$/ TMS):δ (ppm) 2.41 (s, 3H), 7.31 (d, *J*= 8.0 Hz,2H), 7.48 (t,*J*= 7.4 Hz, 1H), 7.70 (t, *J*=7.6 Hz,1H), 7.78 (d, *J*= 8.0 Hz, 1H), 7.82 (d,*J*= 8.4 Hz,1H), 8.06 (d, *J*= 8Hz, 2H), 8.16(d, *J*= 8.4Hz, 2H);^{13}C NMR (100MHz, $CDCl_3$/ TMS) δ (ppm) 21.3, 118.9, 126.1, 127.1, 127.4, 129.6, 129.7, 136.8, 136.9, 139.4, 148.3, 157.3;HRMS (ESI) calculated for $C_{16}H_{13}N$ $[M+H)^+$:220.1121, found: 220.1125.

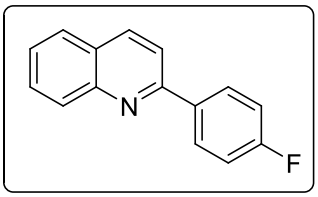


2-(4-methoxyphenyl)quinoline (4c).White solid;yield: 83%; mp 119-121°C;^{1}H NMR (400MHz, $CDCl_3$/ TMS) δ (ppm) 3.88 (s, 3H), 7.04 (d,*J*= 8.4 Hz, 2H), 7.49 (t, *J*=7.6 Hz, 1H), 7.70 (t, *J*= 7.8

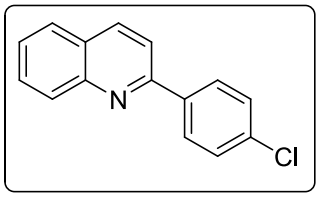
Hz,1H), 7.78-7.84 (m, 2H), 8.12-8.18 (m,4H);^{13}C NMR (100MHz, $CDCl_3$/ TMS) δ (ppm) 55.4, 114.2, 118.6, 125.9, 126.9, 127.4, 128.9, 129.5, 129.6, 132.2, 136.7, 148.3, 156.9, 160.8;MS (ESI)for $C_{16}H_{13}NO$:m/z236 $[M+H]^+$; Elemental analysis calc for$C_{16}H_{13}NO$: C 81.68, H 5.57, N 5.95, O 6.80; found C 81.70, H5.53, N 5.92, O 6.79.



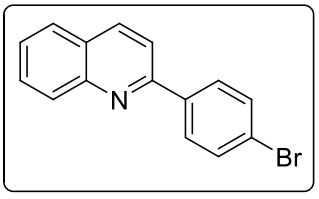
2-(2-phenoxyphenyl)quinoline (4d).White solid;yield: 81%; mp 88-89°C;^{1}H NMR (400MHz, $CDCl_3$/ TMS) δ (ppm) 6.97-7.04 (m, 4H), 7.24-7.33 (m, 3H), 7.40 (t, *J*= 7.8 Hz, 1H), 7.50 (t,*J*= 7.4 Hz,1H), 7.69 (t,*J*= 7.6 Hz,1H), 7.78 (d, *J*= 8.0 Hz, 1H), 7.94 (d, *J*= 8.4 Hz, 1H), 8.08 (td, J_1= 20.8 Hz, J_2 = 7.6 Hz, 3H);^{13}C NMR (100MHz, $CDCl_3$/ TMS) δ (ppm) 118.3, 119.9, 122.9, 123.0, 124.5, 126.4, 127.1, 127.4, 129.4, 129.7, 129.8, 130.5, 131.9, 132.5, 135.6, 148.3, 154.4, 156.1, 157.4;HRMS (ESI) calculated for $C_{21}H_{15}NO[M+ H)^+$: 298.1226, found: 298.1232.



2-(4-fluorophenyl)quinoline (4e). White solid;yield: 78%; mp 90-91°C;^{1}H NMR (400MHz, $CDCl_3$/ TMS) δ (ppm) 7.02 (t, *J*= 8.6 Hz, 2H), 7.34 (t, *J*= 7.4 Hz, 1H), 7.54 (t, *J*= 7.6 Hz, 1H), 7.64 (d, *J*= 8.8 Hz, 2H), 7.97 (t,*J*= 7.6 Hz, 3H), 8.03 (d, *J*= 8.8 Hz, 1H);^{13}C NMR (100MHz, $CDCl_3$/ TMS) δ (ppm) 115.7 (d, J_{CF}= 22 Hz), 115.9, 118.7, 126.4, 127.1, 127.5, 129.4 (d, J_{CF}= 9 Hz), 129.7, 129.8, 135.8(d,J_{CF}= 3 Hz), 136.9, 148.2, 156.3, 162.6, 165.1;MS (ESI)for $C_{15}H_{10}FN$: m/z 224 $[M+H]^+$; Elemental analysis calc for$C_{15}H_{10}FN$: C 80.70, H 4.51, F 8.51, N 6.27; found: C 80.74, H, 4.56, F 8.48, N 6.25.

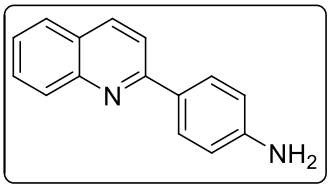


2-(4-chlorophenyl)quinoline(4f).White solid;yield: 75%; mp 114-116°C;^{1}H NMR (400MHz, $CDCl_3$/ TMS) δ (ppm) 7.49-7.56 (m, 3H), 7.74 (t, *J*= 7.6 Hz, 1H), 7.82-7.86 (m, 2H), 8.11-8.16(m, 3H), 8.23 (d,*J*=8.4 Hz, 1H);^{13}C NMR (100MHz, $CDCl_3$/ TMS) δ (ppm) 118.6, 126.5, 127.2, 127.5, 128.8, 129.0, 129.7, 129.9, 135.6, 136.9, 138.1, 148.3, 156.1;HRMS (ESI) calculated for $C_{15}H_{10}ClN[M+ H)^+$:240.0575, found:240.0580.

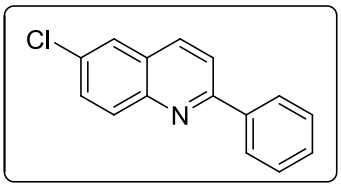


2-(4-bromophenyl)quinoline (4g).White solid; yield: 72%; mp 120-122°C;^{1}HNMR (400MHz, $CDCl_3$/ TMS) δ (ppm) 7.53-7.56 (m, 1H),

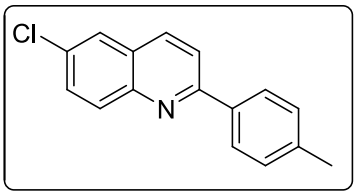
7.65 (d, *J*= 7.6 Hz, 2H), 7.74 (t, *J*= 7.8 Hz, 1H), 7.84 (dd,J_1= 8.0 Hz, J_2= 3.2 Hz,2H), 8.06 (d,*J*=7.6 Hz, 2H), 8.15 (d,*J*= 8.8 Hz, 1H), 8.23 (d,*J*= 8.8 Hz, 1H);^{13}C NMR (100MHz, $CDCl_3$/ TMS) δ (ppm) 118.6, 123.9, 126.6, 127.3, 127.5, 129.1, 129.7, 129.9, 132.0, 138.5, 139.1, 148.3, 156.1;MS (ESI)for $C_{15}H_{10}BrN$: m/z 284 $[M+H]^+$; Elemental analysis calc for$C_{15}H_{10}BrN$: C 63.40, H 3.55, Br 28.12, N 4.93; found C 63.41, H, 3.52, Br 28.13, N 4.90.



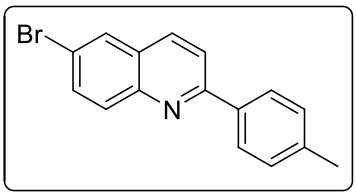
2-(4-amino)phenylquinoline (4h). White solid;yield: 70%; mp193-194°C;^{1}H NMR (400MHz, $CDCl_3$/ TMS) δ (ppm) 3.88 (s , 2H, -NH_2, D_2O exchangeable), 6.80 (d, *J*= 8.4 Hz, 2H), 7.46 (t, *J*= 7.6 Hz, 1H), 7.68 (t, *J*= 7.6 Hz, 1H), 7.79 (t,*J*= 9.2 Hz, 2H), 8.02 (d,*J*=8.0 Hz, 2H), 8.12 (t,*J*=10.0 Hz, 2H);^{13}C NMR (100MHz, $CDCl_3$/ TMS) δ (ppm) 115.1, 118.3, 125.6, 126.8, 127.4, 128.8, 129.4, 129.5, 129.9, 136.5, 147.8, 148.3, 157.3;HRMS (ESI) calculated for $C_{15}H_{12}N_2$[M+ H)$^+$:221.1073, found: 221.1080.



6-chloro-2-phenylquinoline (4i).White solid;yield: 63%; mp 108-110°C;^{1}H NMR (400MHz, $CDCl_3$/ TMS) δ (ppm) 7.45-7.49 (m, 1H), 7.53 (t, *J*= 7.2 Hz, 2H), 7.66 (d, *J*= 8.8 Hz, 1H), 7.81 (s, 1H), 7.90 (d,*J*=8.4 Hz, 1H), 8.09-8.15 (m, 4H);^{13}C NMR (100MHz, $CDCl_3$/ TMS) δ (ppm) 119.8, 126.1, 127.5, 127.8, 128.8, 129.6, 130.6, 130.9, 131.3, 135.9, 139.2, 146.7, 157.6;MS (ESI)for $C_{15}H_{10}ClN$: m/z 240 $[M+H]^+$; Elemental analysis calc for$C_{15}H_{10}ClN$: C 75.16, H 4.21, Cl 14.79, N 5.84; found: C 75.21, H, 4.18, Cl 14.80, N 5.88.

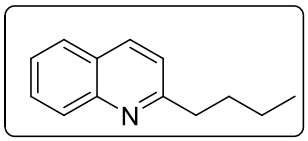


6-chloro-2-p-tolylquinoline (4j).White solid;yield: 66%; mp 140-142°C;^{1}H NMR (400MHz, $CDCl_3$/ TMS) δ (ppm) 2.43 (s, 3H), 7.33 (d, *J*= 8.0 Hz, 2H), 7.64 (d, *J*= 8.8 Hz, 1H), 7.79 (s, 1H), 7.88 (d,*J*= 8.8 Hz, 1H), 8.05 (d,*J*=8.4 Hz, 2H), 8.11 (d, *J*= 9.6 Hz, 2H);^{13}C NMR (100MHz, $CDCl_3$/ TMS) δ (ppm) 21.3, 119.7, 126.1, 127.4, 127.7, 129.7, 130.5, 131.3, 135.7, 136.4, 139.7, 146.7, 157.6;HRMS (ESI) calculated for $C_{16}H_{12}ClN$[M+ H)$^+$:254.0731, found: 254.0737.

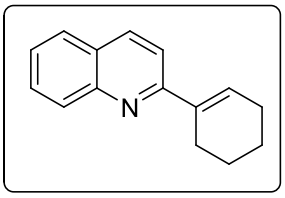


6-bromo-2-p-tolylquinoline (4k).White solid;yield: 62%; mp 158-160°C;^{1}H NMR (400MHz, $CDCl_3$/ TMS) δ (ppm) 2.43 (s, 3H),

7.33 (d, *J*= 7.6 Hz, 2H), 7.77 (d, *J*= 8.8 Hz, 1H), 7.88 (d, *J*= 8.4 Hz, 1H), 7.97 (s, 1H), 8.02 (d,*J*=8.8 Hz, 1H), 8.05 (d, *J*= 7.7 Hz, 2H), 8.10 (d, *J*= 8.4 Hz, 1H);^{13}C NMR (100MHz, $CDCl_3$/ TMS) δ (ppm) 21.4, 119.7, 119.8, 127.4, 128.2, 129.5, 131.4, 133.0, 135.7, 136.4, 139.8, 146.9, 157.7;HRMS (ESI) calculated for $C_{16}H_{12}BrN[M+H)^+$: 298.0226, found: 298.0236.



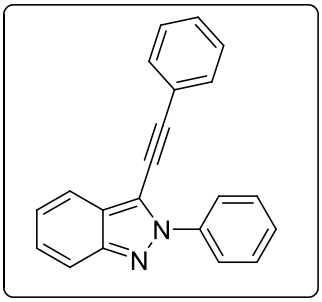
2-butylquinoline (4l). Yellow oil;yield: 89%;^{1}H NMR (400MHz, $CDCl_3$/ TMS) δ (ppm) 0.86 (t, *J*= 7.2 Hz, 3H), 1.29-1.39 (m, 2H), 1.65-1.73 (m, 2H), 2.87 (t, *J*= 7.8 Hz, 2H), 7.17 (d,*J*= 8.4 Hz, 1H), 7.36 (t, *J*= 7.6 Hz, 1H), 7.56 (t, *J*= 7.6 Hz, 1H), 7.65 (d, *J*= 8.4 Hz,1H), 7.94 (t, *J*= 9.2 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$/ TMS) δ (ppm) 14.0, 22.6, 32.2, 39.0, 121.3, 125.6, 126.7, 127.4, 128.7, 129.3, 136.1, 147.8, 163.1; HRMS (ESI) calculated for $C_{13}H_{15}N$ $[M+H]^+$: 186.1277, found: 186.1280.



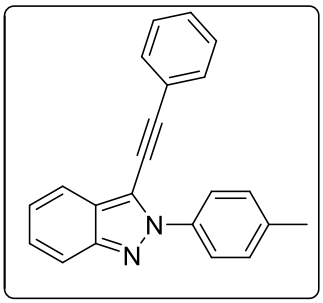
2-cyclohexenylquinoline (4m).Yellow oil; yield: 76%;^{1}H NMR (400MHz, $CDCl_3$/ TMS) δ (ppm) 1.71-1.75(m, 2H), 1.81-1.85 (m, 2H), 2.30-2.34 (m, 2H), 2.68-2.72 (m, 2H), 6.75-6.78 (m,1H), 7.45 (t, *J*= 7.3 Hz, 1H), 7.57 (d, *J*= 8.6 Hz, 1H), 7.66 (t, *J*= 7.7 Hz,1H), 7.75 (d, *J*= 8.2 Hz, 1H), 8.05 (dd, J_1= 8.4 Hz, J_2= 3.6 Hz, 2H); ^{13}C NMR (100MHz, $CDCl_3$/ TMS) δ (ppm) 22.1, 22.8, 26.0, 26.2, 118.0, 125.7, 127.0, 127.3, 129.2, 129.4, 130.3, 135.8, 137.7, 147.8, 159.2; MS (ESI)for $C_{15}H_{15}N$: m/z 210 $[M+H]^+$; Elemental analysis calc for$C_{15}H_{15}N$: C 86.08, H 7.22, N 6.69; found: C 86.12, H 7.23, N 6.67.

General Procedure for the preparation of 3-alkynyl-2-aryl-2H-indazole (10a-f): A mixture of the aldehyde **1** (1.0 mmol) and aniline **8** (1.2 mmol) was heated at 60°C for about 2h. Then $RuCl_3$ (3 mol %), CuBr (30 mol%), alkyne **3** (1.2 mmol), and water (flashed with nitrogen) (2ml) were added into the reaction mixture under nitrogen. The mixture was stirred at rt for 10 min and then at 40°C overnight. After the completion of the reaction it was extracted with ethylacetate and then purified by column chromatography. Then the pure N-arylpropargylamine **9** was dissolved in 5 ml of ethanol and added $SnCl_2.2H_2O$ (4.0 mmol) then heated at 70°C for 2h. After the completion of reaction it was concentrated to remove the solvent and extracted with ethylacetate. The organic layer washed with saturated NaOH and brine solution and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel using petroleum ether/ ethyl acetate (5-20%) to afford

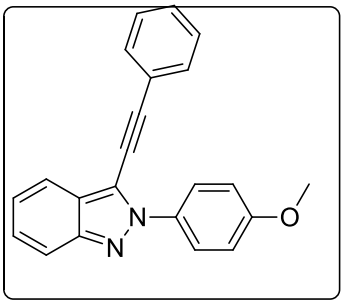
indazole derivatives **(10a-f)** in 58-81% yield. All the prepared compounds were characterized by NMR and Mass spectroscopy techniques



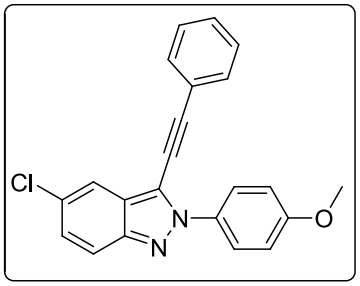
2-phenyl-3-(phenylethynyl)-2H-indazole (10a).White solid;yield: 72%; mp 73-74°C;^{1}H NMR (400MHz, $CDCl_3$/ TMS) δ (ppm) 7.21 (t, *J*= 7.6 Hz, 1H), 7.35-7.38 (m, 4H), 7.43-7.49 (m, 3H), 1H), 7.54 (t,*J*=7.6 Hz, 2H), 7.82 (t,*J*=8.2 Hz, 2H), 8.00 (d, *J*= 8.0 Hz, 2H);^{13}C NMR (100MHz, $CDCl_3$/ TMS) δ (ppm) 78.2, 100.4, 118.4, 120.3, 122.3, 123.3, 124.5, 125.7, 127.4, 128.6, 128.6, 129.0, 129.1, 131.4, 140.2, 148.8;HRMS (ESI) calculated for $C_{21}H_{14}N_2$[M+ H)$^+$: 295.1230, found: 295.1237.



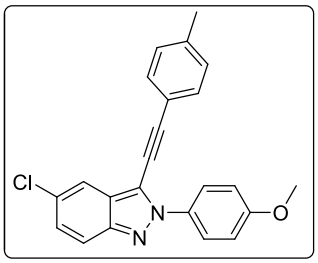
3-(phenylethynyl)-2-p-tolyl-2H-indazole (10b).Whitesolid;yield: 79%;mp94-95°C;^{1}H NMR (400MHz, $CDCl_3$/ TMS) δ (ppm) 2.45 (s, 3H), 7.19 -7.24 (m, 1H), 7.34-7.36 (m, 6H), 7.50-7.51 (m, 2H), 7.82 (t,*J*=8.8 Hz, 2H), 7.88 (d, *J*=8.0 Hz, 2H);^{13}C NMR (100MHz, $CDCl_3$/ TMS) δ (ppm) 21.3, 78.3, 100.2, 118.3, 120.2, 122.4, 123.2, 124.3, 125.6, 127.3, 128.6, 129.0, 129.6, 131.4, 137.8, 138.7, 148.6;HRMS (ESI) calculated for $C_{22}H_{16}N_2$[M+ H)$^+$: 309.1386, found: 309.1394.



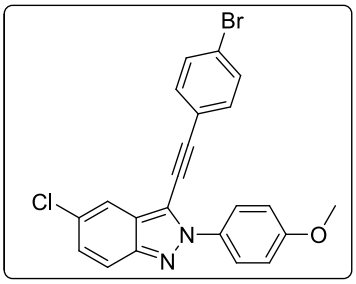
2-(4-methoxyphenyl)-3-(phenylethynyl)-2H-indazole(10c).White solid;yield: 81%; mp 98-100°C;^{1}H NMR (400MHz, $CDCl_3$/ TMS) δ (ppm) 3.89 (s, 3H), 7.06 (d, *J*=8.8 Hz, 2H), 7.21 (t, *J*=7.4 Hz, 1H), 7.35-7.37 (m, 4H), 7.49-7.51 (m, 2H), 7.82 (t,*J*=9.6 Hz, 2H), 7.90 (d, *J*=8.8 Hz, 2H);^{13}C NMR (100MHz, $CDCl_3$/ TMS) δ (ppm) 55.6, 78.2, 100.1, 114.7, 118.2, 120.1, 122.3, 123.1, 125.4, 125.8, 127.1, 128.5, 128.9, 131.3, 133.4, 148.5, 159.7;HRMS (ESI) calculated for $C_{22}H_{16}N_2O$[M+ H)$^+$: 325.1335, found: 325.1342.



5-chloro-2-(4-methoxyphenyl)-3-(phenylethynyl)-2H-indazole(10d). White solid;yield: 64%; mp 185-186°C;^{1}H NMR (400MHz, $CDCl_3$/ TMS) δ (ppm) 3.90 (s, 3H), 7.06 (d, *J*=8.8 Hz, 2H), 7.30 (d, *J*=9.2 Hz, 1H), 7.37-7.39 (m, 3H), 7.49-7.51 (m, 2H), 7.73 (d,*J*=9.2 Hz, 1H), 7.81 (s, 1H), 7.88 (d, *J*= 8.8 Hz, 2H);^{13}C NMR (100MHz, $CDCl_3$/ TMS) δ (ppm) 55.6, 77.6, 100.6, 114.2, 117.9, 119.0, 119.7, 122.1, 125.7, 125.8, 128.5, 128.6, 128.9, 129.2, 131.4, 133.1, 146.8, 159.9;MS (ESI)for $C_{22}H_{15}ClN_2O$: m/z 359 $[M+H]^+$; Elemental analysis calc for$C_{22}H_{15}ClN_2O$: C 73.64, H 4.21, Cl 9.88, N, 7.81, O 4.46; found: C 73.60, H 4.23,Cl 9.86, N 7.85, O 4.44.

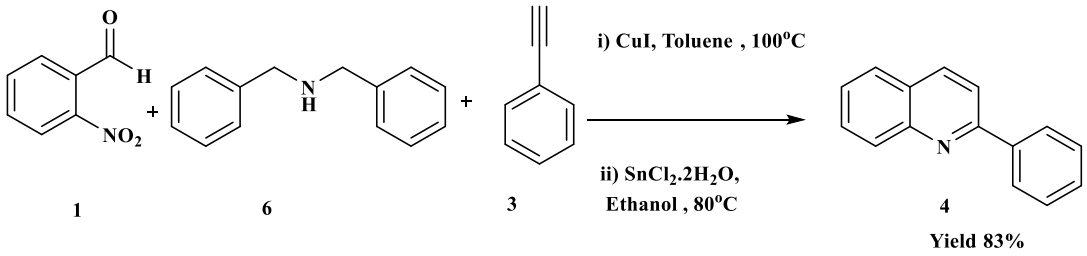


5-chloro-2-(4-methoxyphenyl)-3-(p-tolylethynyl)-2H-indazole(10e). White solid;yield: 66%; mp 148-150°C;^{1}H NMR (400MHz, $CDCl_3$/ TMS) δ (ppm) 2.39 (s, 3H), 3.90 (s, 3H), 7.06 (d, *J*= 8.8 Hz, 2H), 7.19 (d, *J*= 7.6 Hz, 2H), 7.29 (d, *J*= 8.8 Hz, 1H), 7.40 (d, *J*= 7.6 Hz, 2H), 7.72 (d,*J*= 9.2 Hz, 1H), 7.80 (s, 1H), 7.88 (d, *J*= 8.8 Hz, 2H);^{13}C NMR (100MHz, $CDCl_3$/ TMS) δ (ppm) 30.9, 55.6, 77.5, 100.8, 114.1, 118.9, 119.0, 119.6, 125.7, 125.8, 128.5, 128.7, 129.3, 131.3, 133.2, 139.5, 146.8, 159.9;HRMS (ESI) calculated for $C_{23}H_{17}ClN_2O[M+ H)^+$: 373.1102, found: 373.1104.



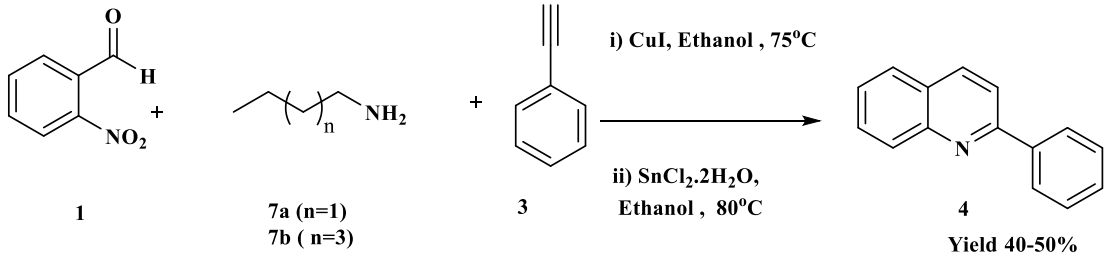
3-((4-bromophenyl)ethynyl)-5-chloro-2-(4-methoxyphenyl)-2H-indazole(10f). White solid;yield: 58%; mp 173-175°C;^{1}H NMR (400MHz, $CDCl_3$/ TMS) δ (ppm) 3.90 (s, 3H), 7.06 (d, *J*= 8.8 Hz, 2H), 7.31 (d, *J*= 8.8 Hz, 1H), 7.35 (d, *J*= 8.4 Hz, 2H), 7.51 (d, *J*=8.4 Hz, 2H), 7.74 (d,*J*= 9.2 Hz, 1H), 7.79 (s, 1H), 7.85 (d, *J*= 8.8 Hz, 2H);^{13}C NMR (100MHz, $CDCl_3$/ TMS) δ (ppm) 55.6, 78.7, 114.8, 118.9, 119.7, 120.9, 123.5, 125.7, 125.8, 128.6, 129.1, 131.9, 132.7, 133.0, 136.0, 146.8, 159.9;MS (ESI)for $C_{22}H_{14}BrN_2O$: m/z 437 $[M+H]^+$.Elemental analysis calc for$C_{22}H_{14}BrN_2O$: C 60.37, H 3.22, Br 18.25, Cl 8.10, N, 6.40, O 3.66; found: C 60.39, H 3.19,Br 18.28, Cl 8.14, N 6.45, O3.69.

Typical experimental procedure for the preparation of propargylamine from dibenzylamine and its conversion to quinoline



A mixture of copper iodide (15 mol %),2-nitrobezaldehyde **1**(1.0mmol), dibenzylamine**6**(1.2 mmol) and alkyne**3** (1.2 mmol) in toluene was heated at 100°C for 3h. Then the reaction mixture was cooled to rt and the solvent was removed then used directly without further purification.The reaction mixture of N-alkyl propargylamine was dissolved in 5 ml of ethanol and added $SnCl_2.2H_2O$ (4.0 mmol) then heated at 70°C for 2h. After the completion of reaction it was filtered through celite by washing with ethylacetate and added water (50ml) extracted with same solvent (2x20ml). The combined organic layer washed with saturated NaOH and brine solution and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel using petroleum ether/ ethyl acetate (5-20%) to afford quinoline derivatives in 83 % yield.

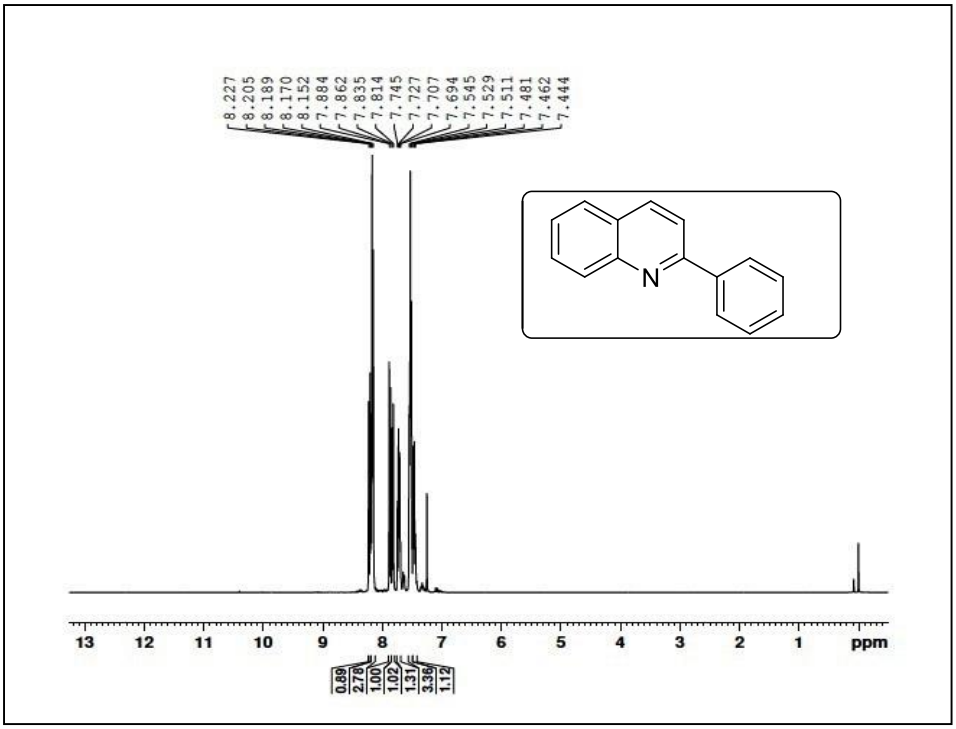
Typical experimental procedure for the preparation of propargylamine from n-butylamine and its conversion to quinoline



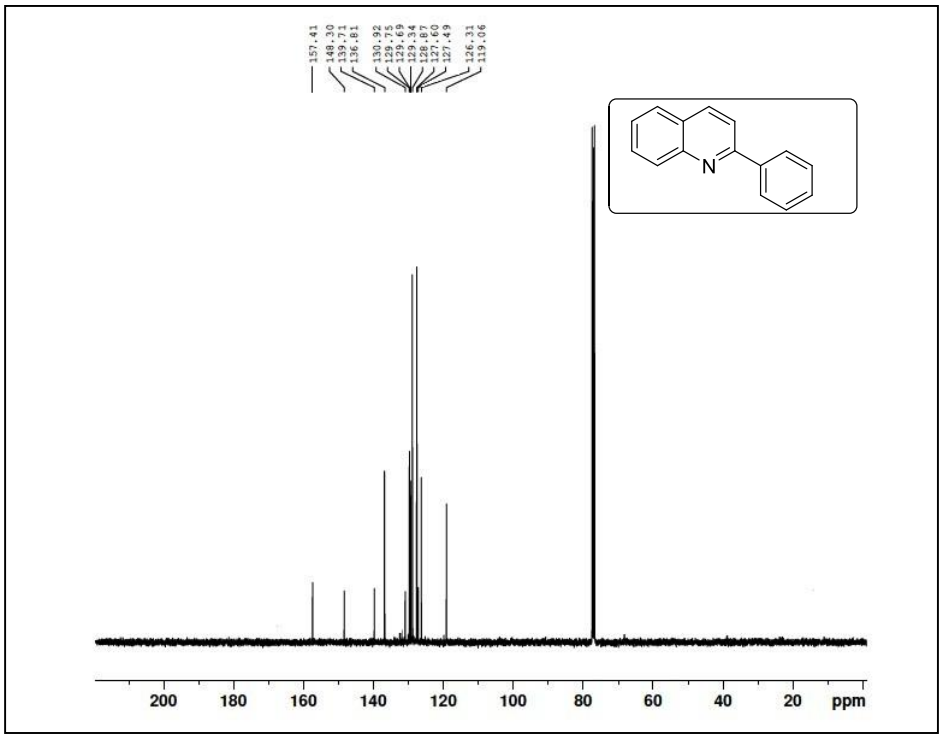
In a 50ml RB flask was added CuI (15 mol %). The reaction vessel was sealed and flushed with N_2. Then added EtOH (0.15 mL), aldehyde **1**(1.0 mmol), and amine **7a/ 7b** (1.2mmol).

Thereaction mixture was allowed to stir at room temperature for approximately 30 sec. and then alkyne **3** (1.2mmol) was added. The RB was placed in an oil bath set at75^{o}C and was allowed to stir overnight. The reaction mixture was allowed to cool to roomtemperature and was purified by silica gel column chromatography to provide the propargylamine as pale yellow oil. It was then dissolved in 5 ml of ethanol and added $SnCl_2.2H_2O$ (4.0 mmol) then heated at 70°C for 2h. After the completion of reaction it was filtered through celite by washing with ethylacetate and added water (50ml) extracted with same solvent (2x20ml). The combined organic layer washed with saturated NaOH and brine solution and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel using petroleum ether/ ethyl acetate (5-20%) to afford quinoline in 40-50 % yield.

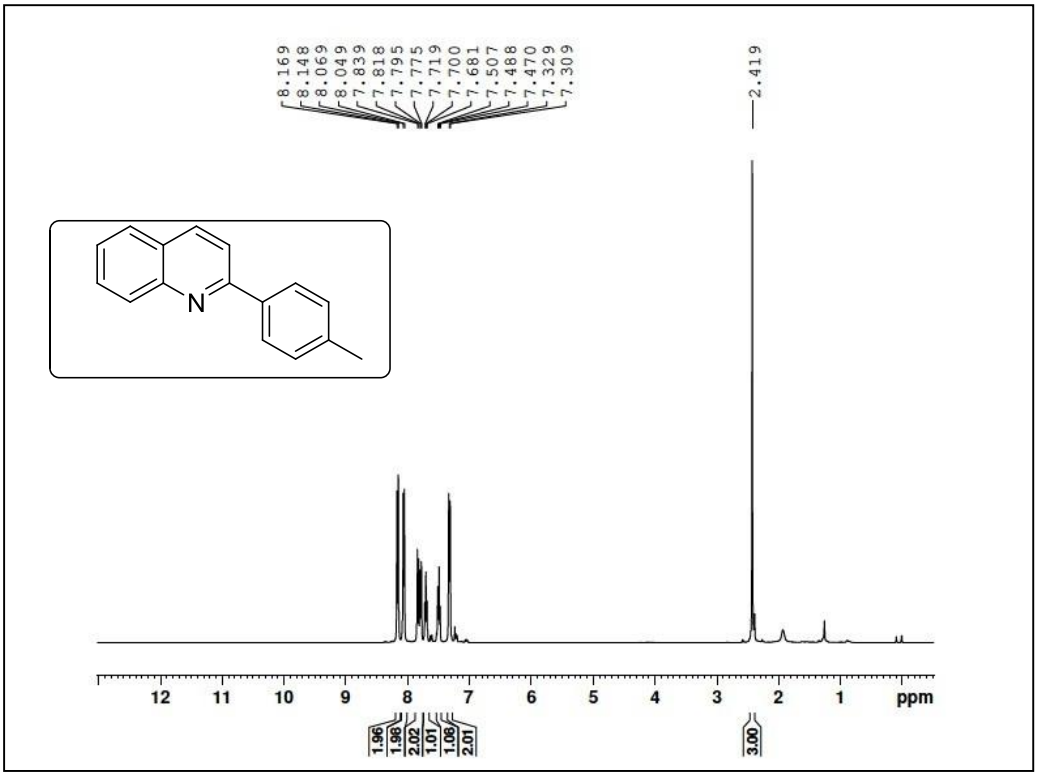
NMR and Mass Spectra of prepared compounds



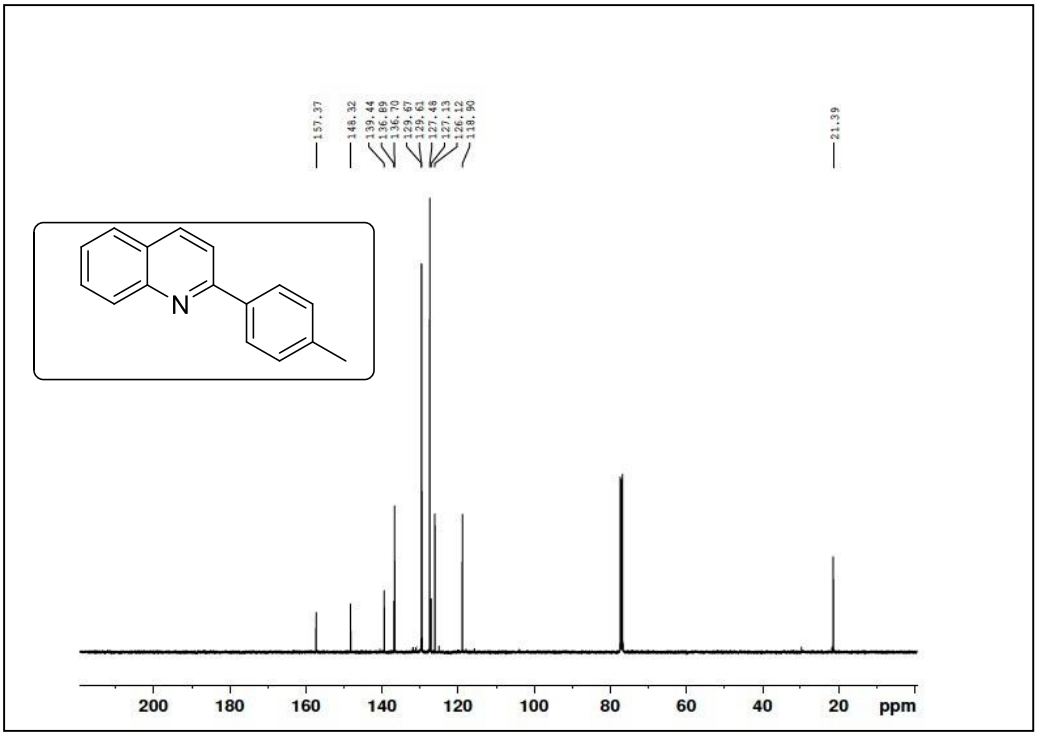
^{1}H NMR spectrum of **4a**



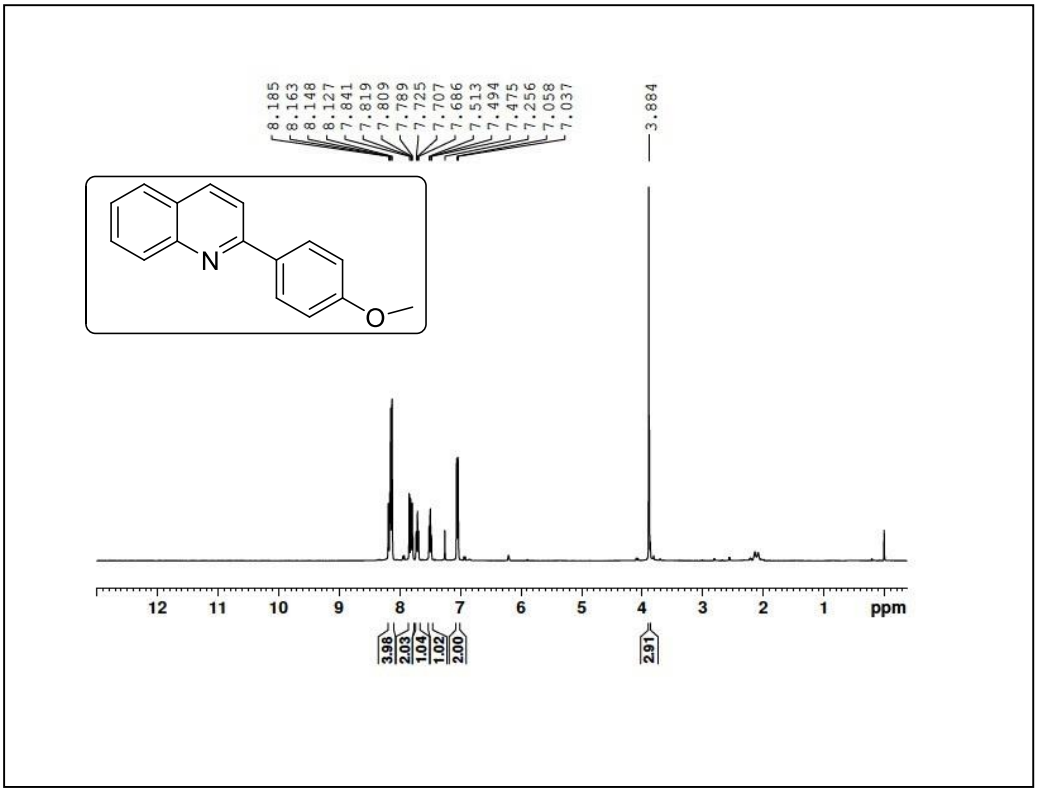
^{13}C NMR of spectrum of **4a**



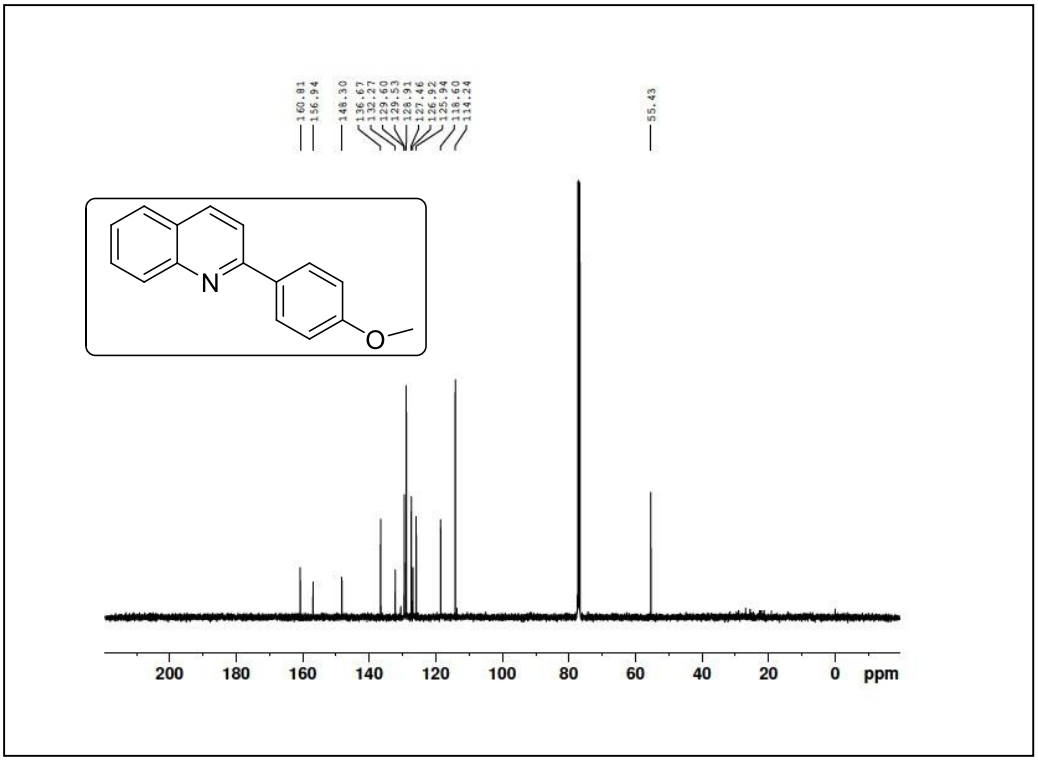
^{1}H NMR spectrum of **4b**



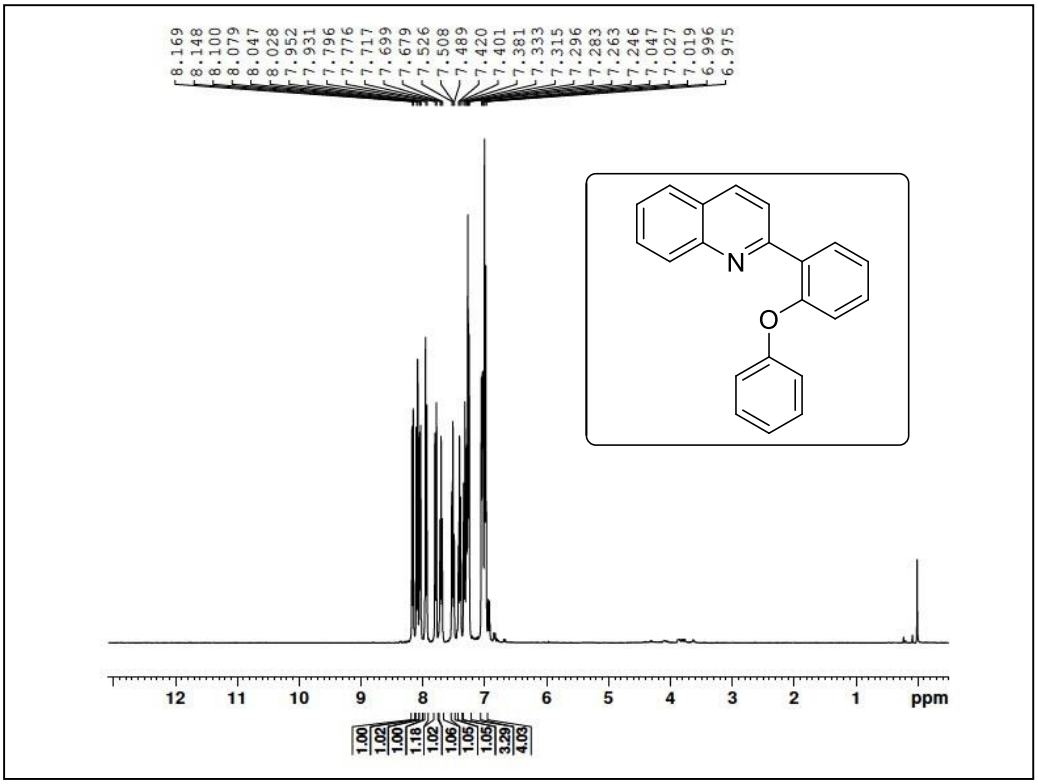
^{13}C NMR of spectrum of **4b**



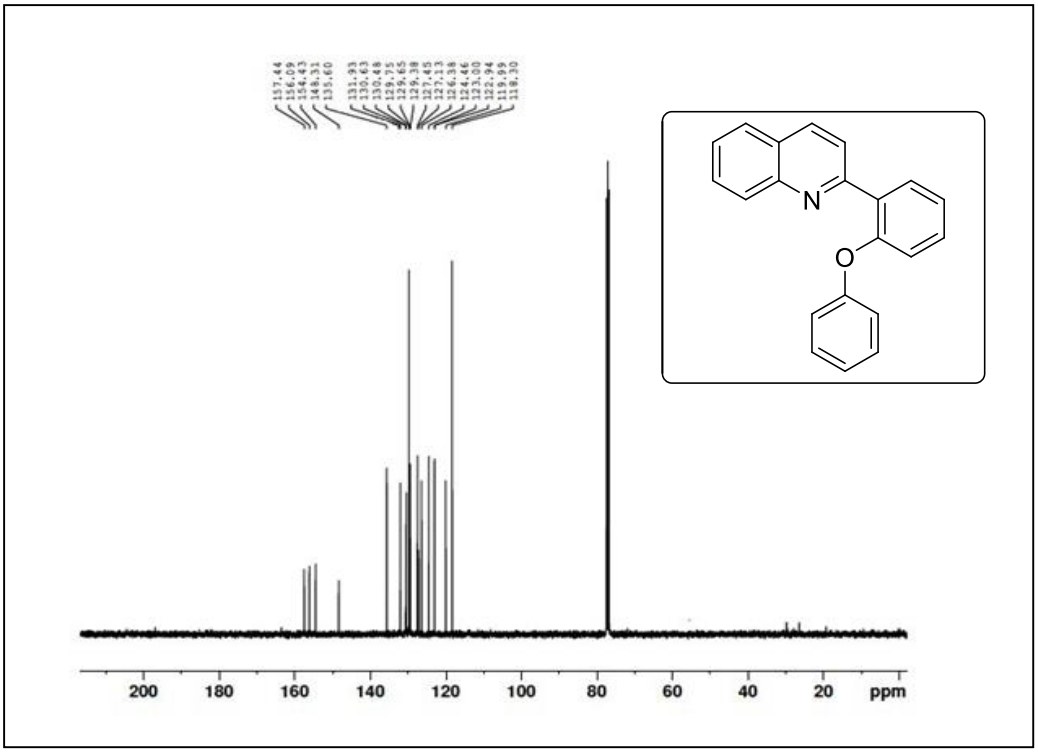
^{1}H NMR spectrum of **4c**



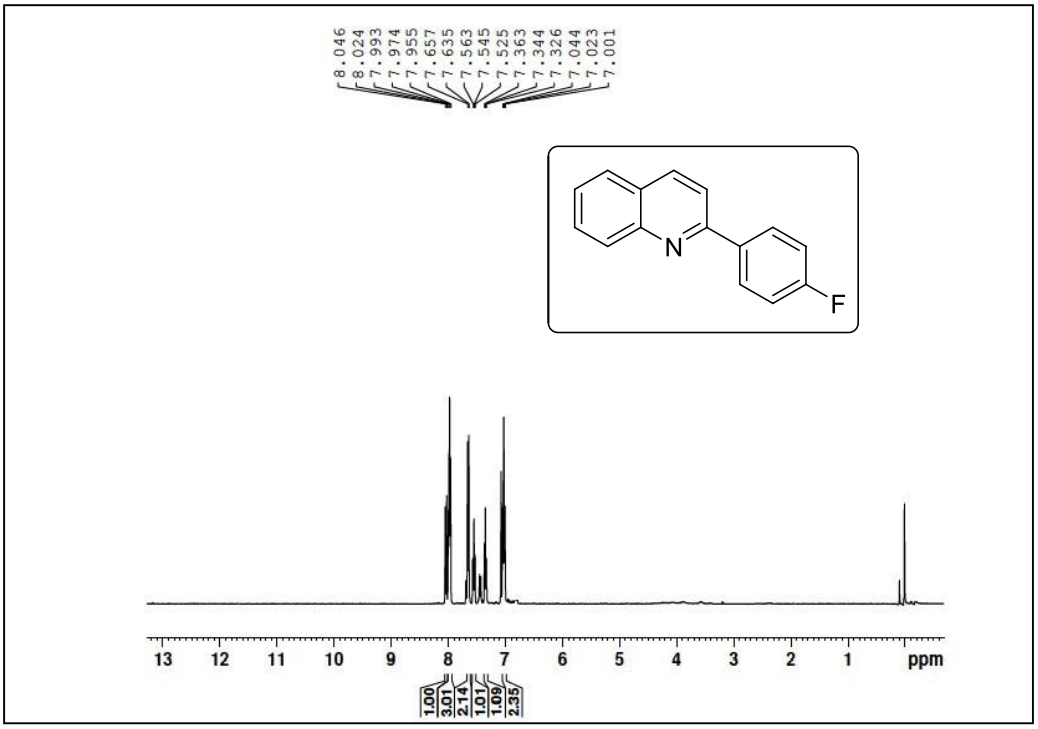
^{13}C NMR spectrum of **4c**



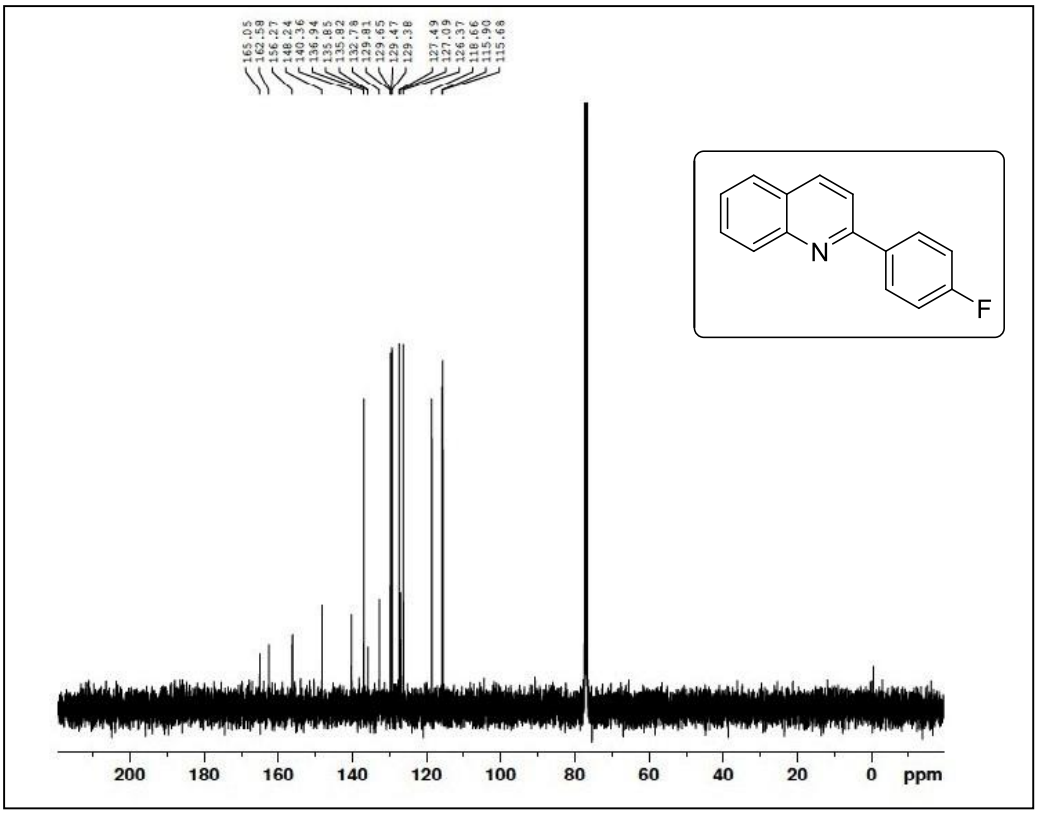
^{1}H NMR spectrum of **4d**



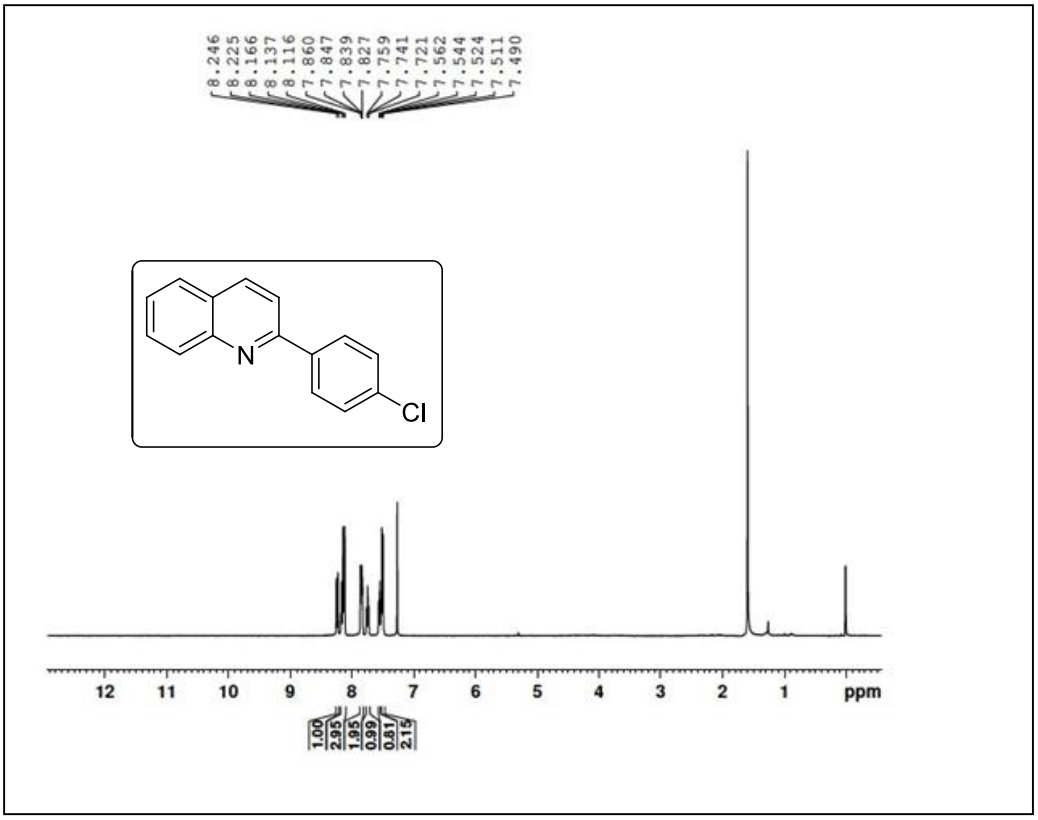
^{13}C NMR spectrum of **4d**



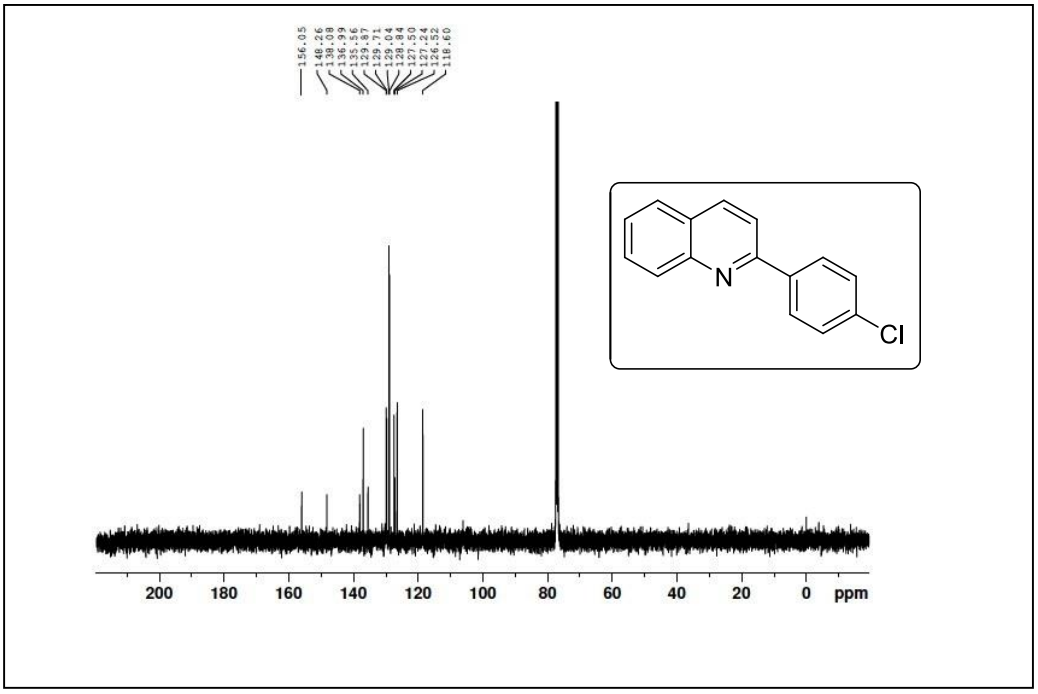
^{1}H NMR spectrum of **4e**



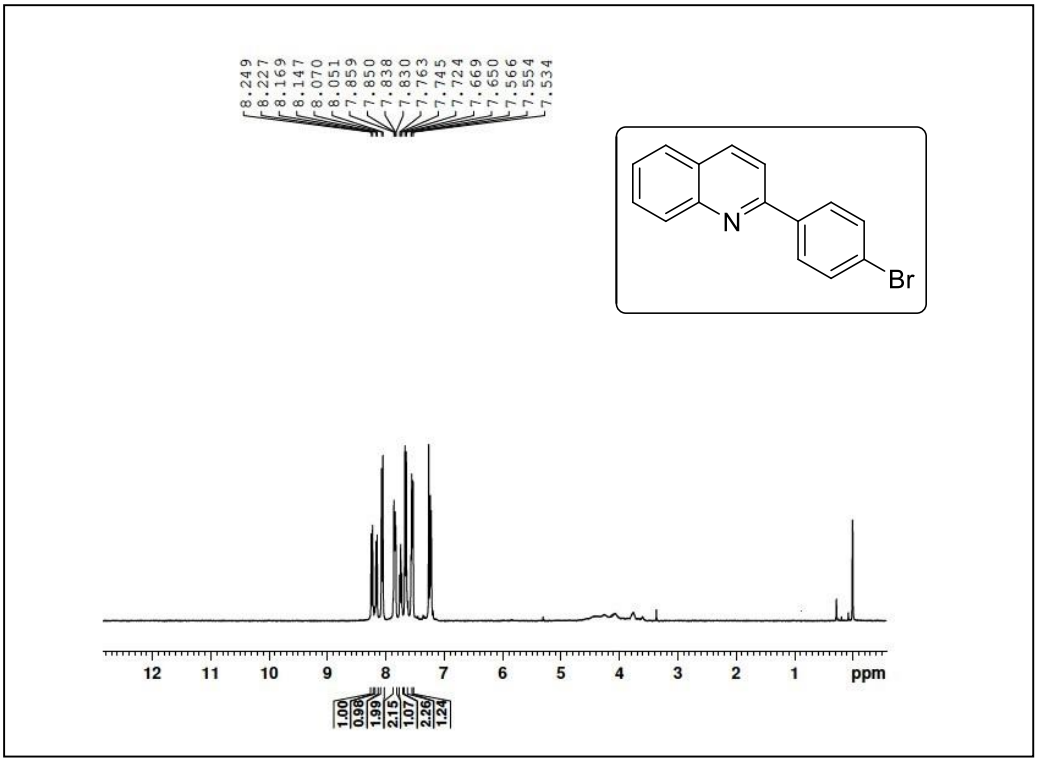
^{13}C NMR spectrum of **4e**



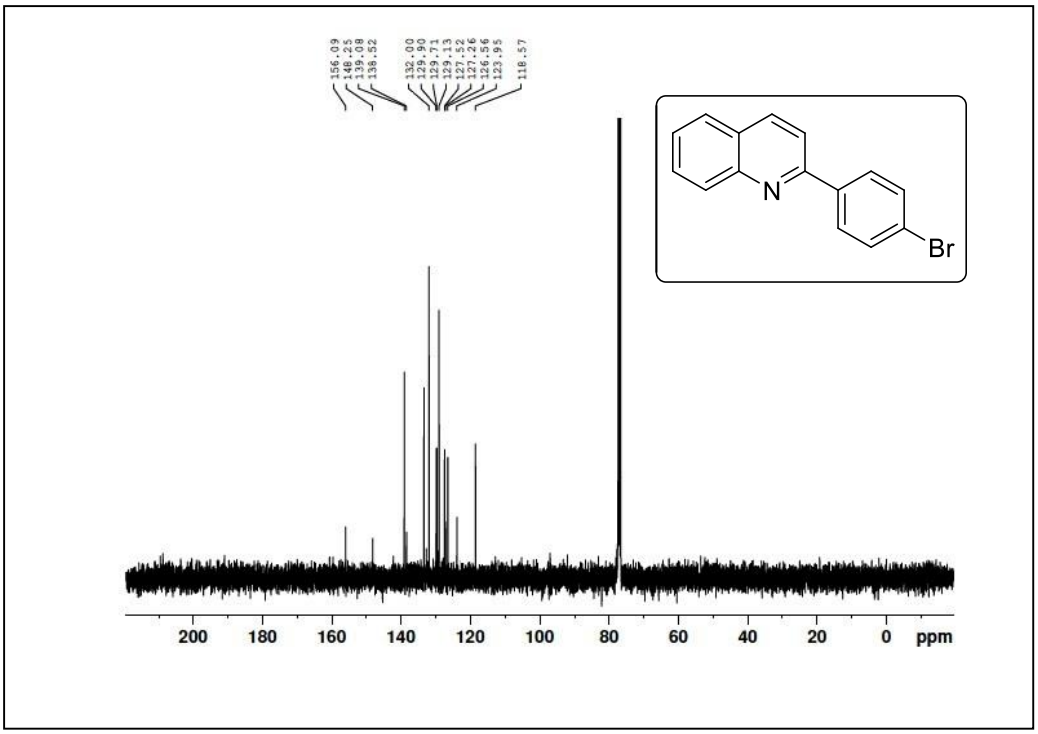
^{1}H NMR spectrum of **4f**



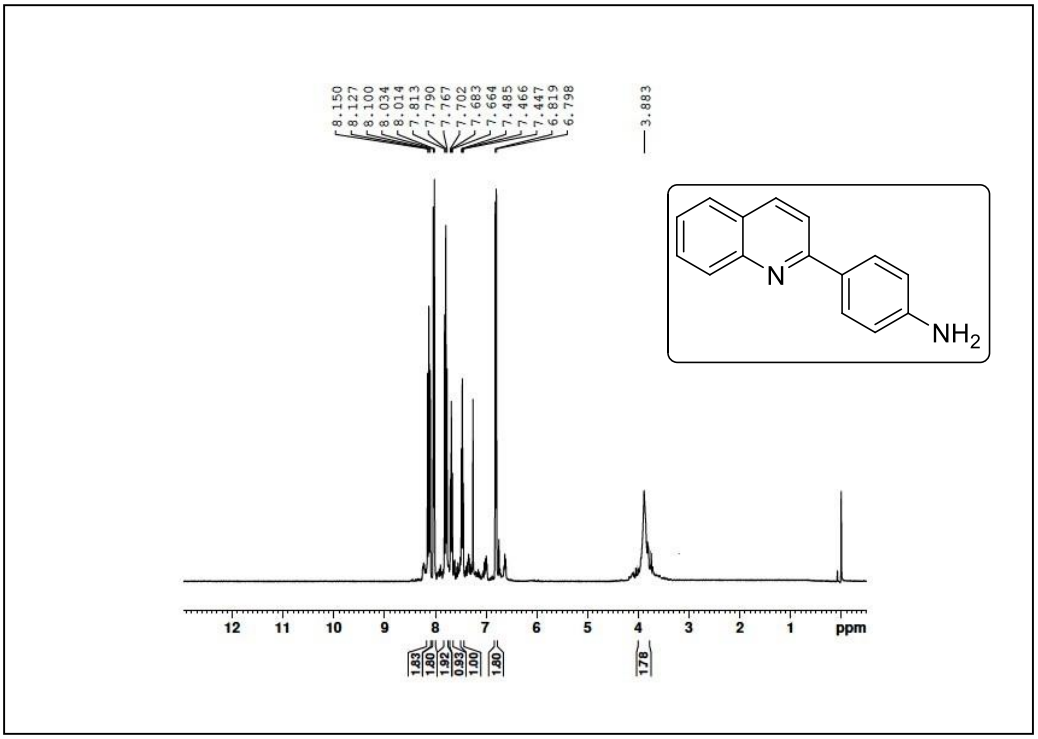
^{13}C NMR spectrum of **4f**



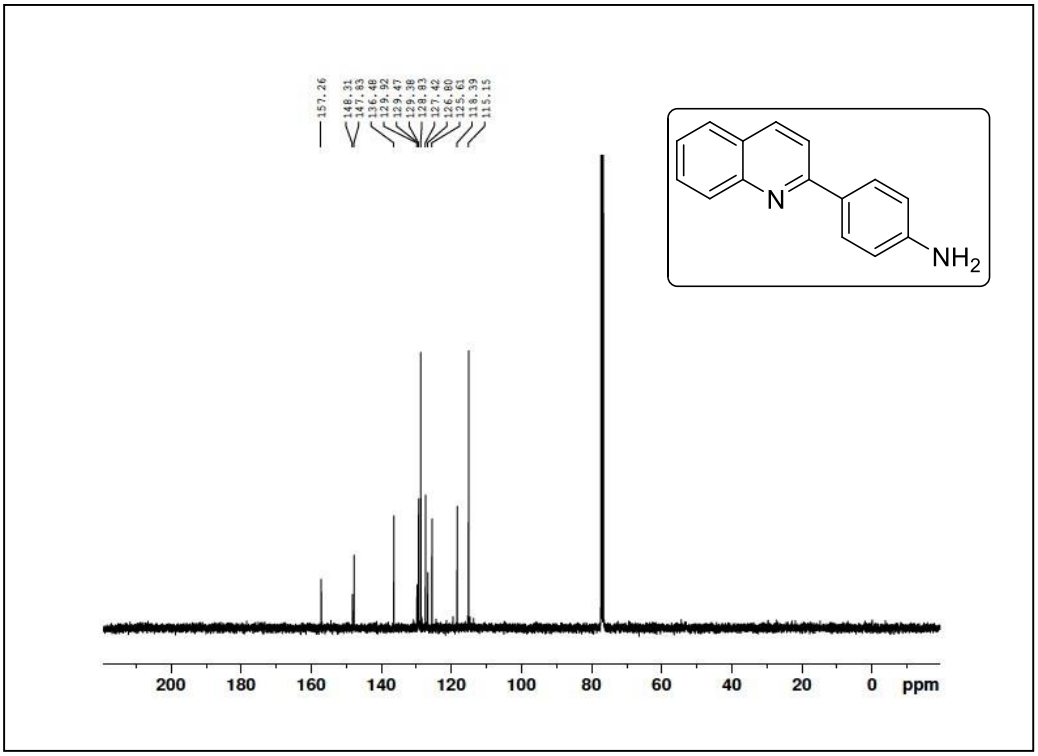
^{1}H NMR spectrum of **4g**



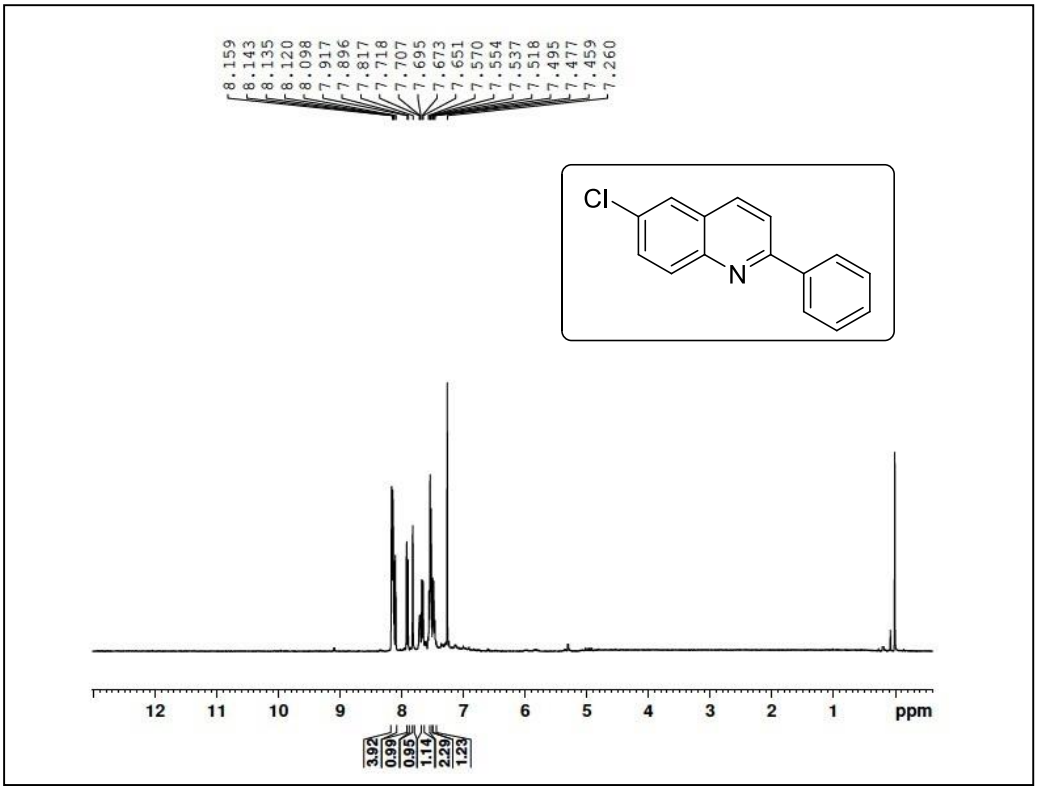
^{13}C NMR spectrum of **4g**



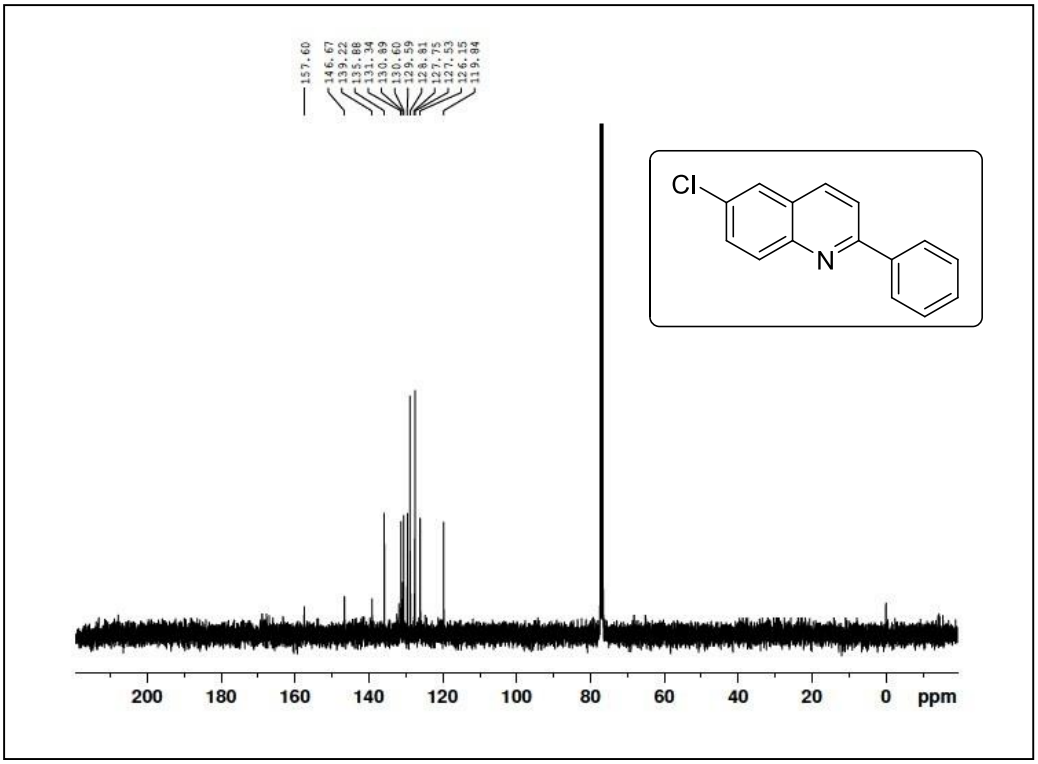
^{1}H NMR spectrum of **4h**



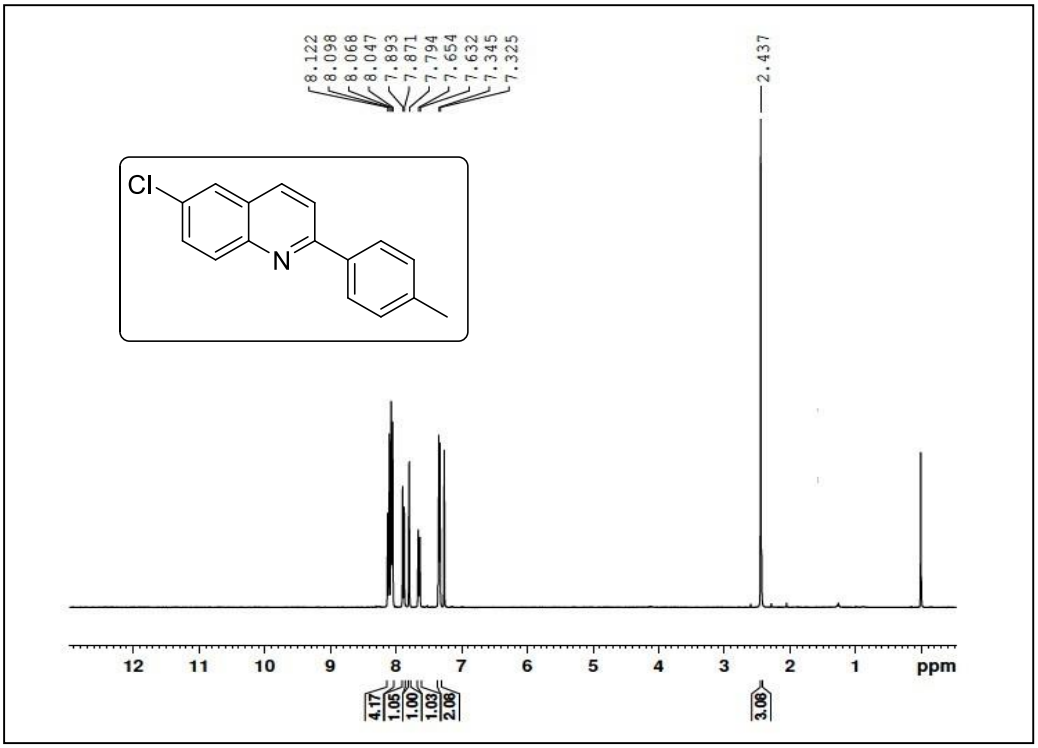
^{13}C NMR spectrum of **4h**



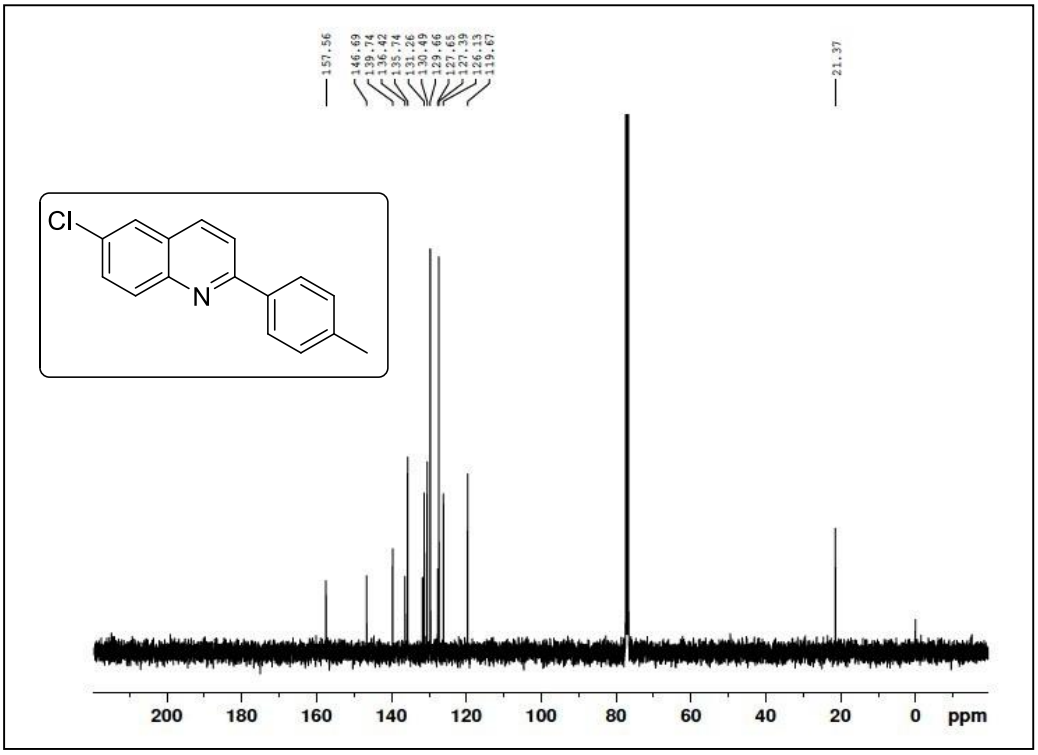
^{1}H NMR spectrum of **4i**



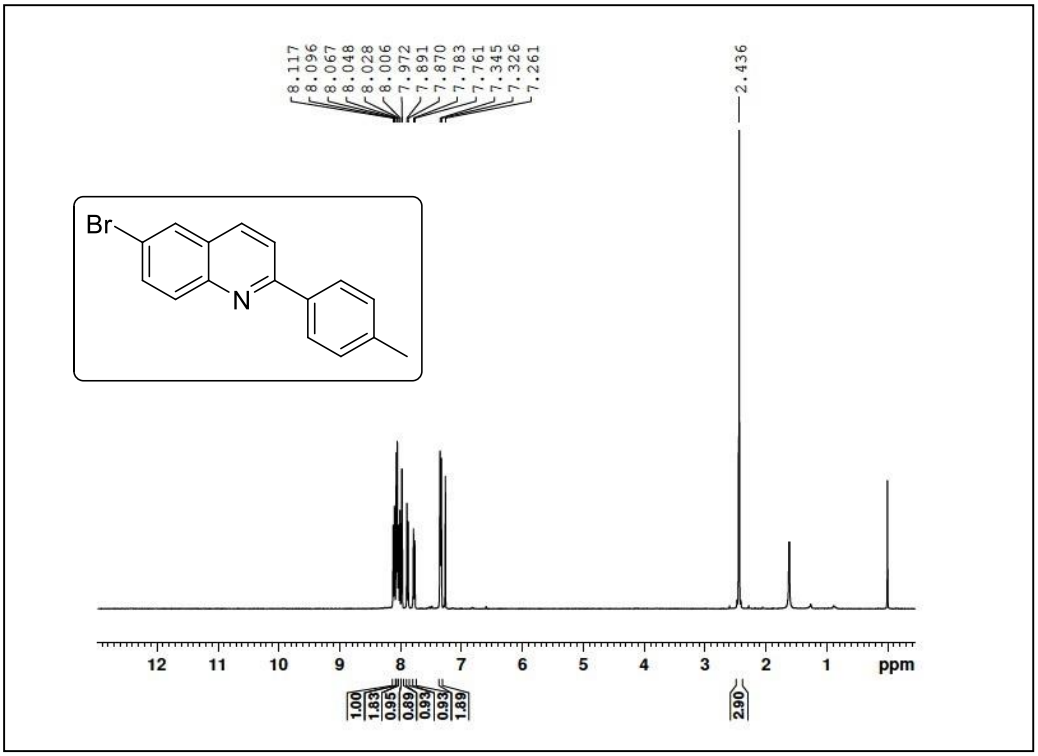
^{13}C NMR spectrum of **4i**



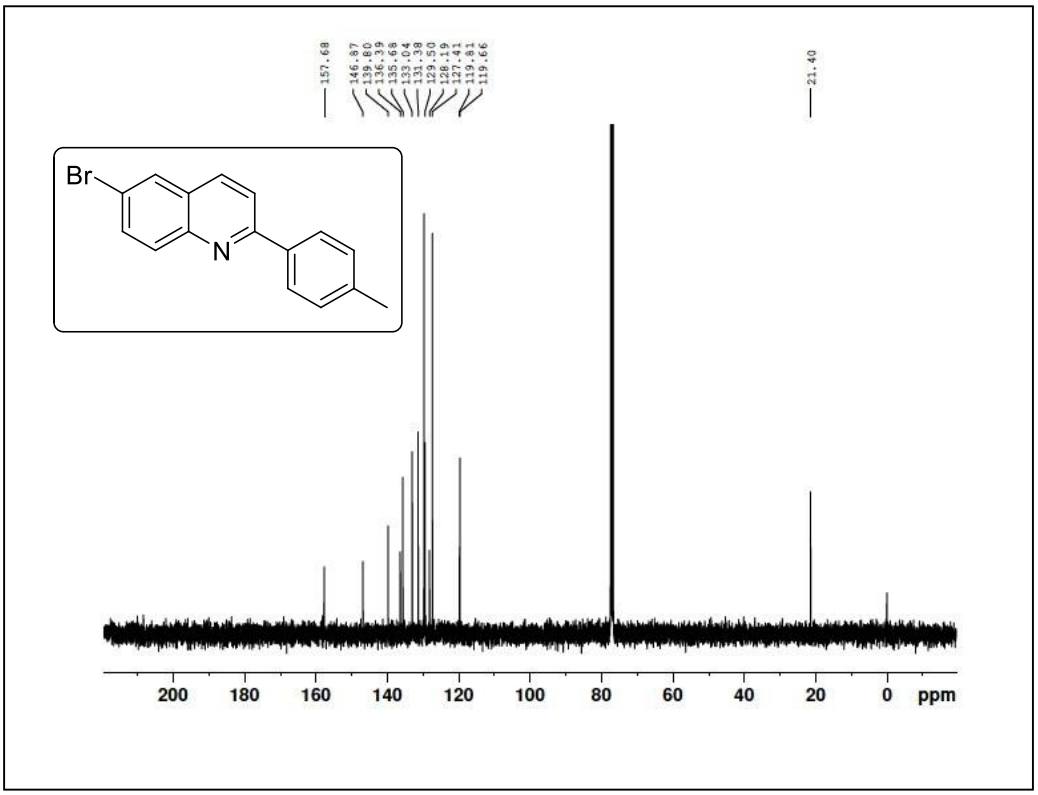
^{1}H NMR spectrum of **4j**



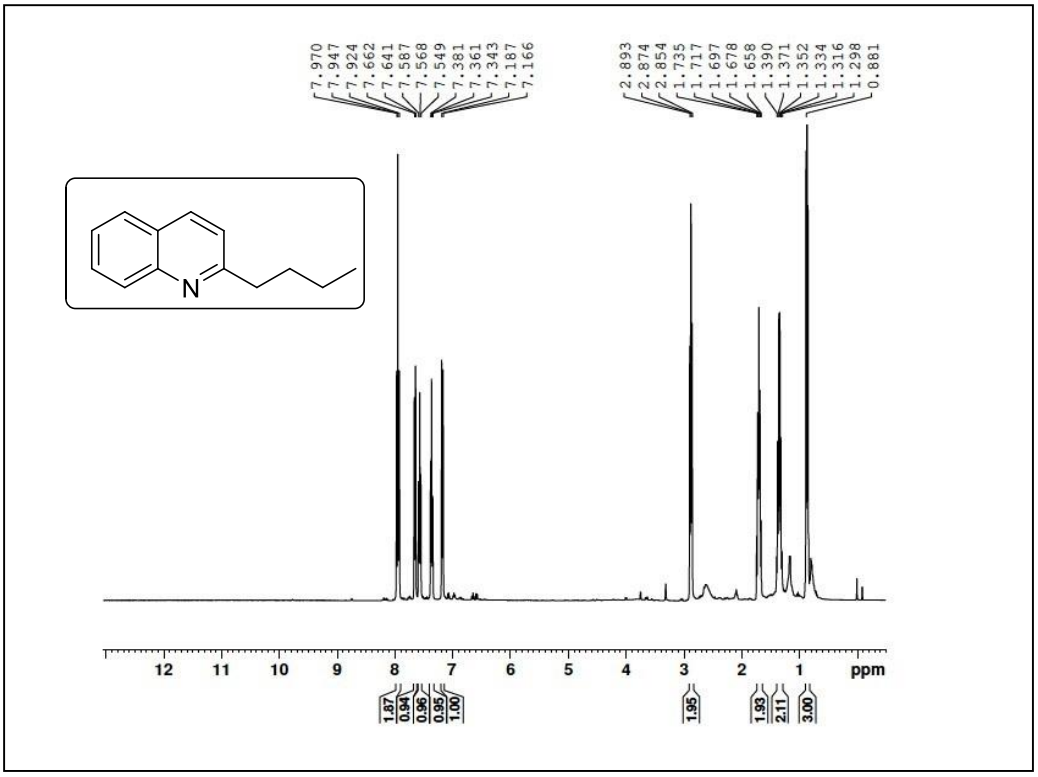
^{13}C NMR spectrum of **4j**



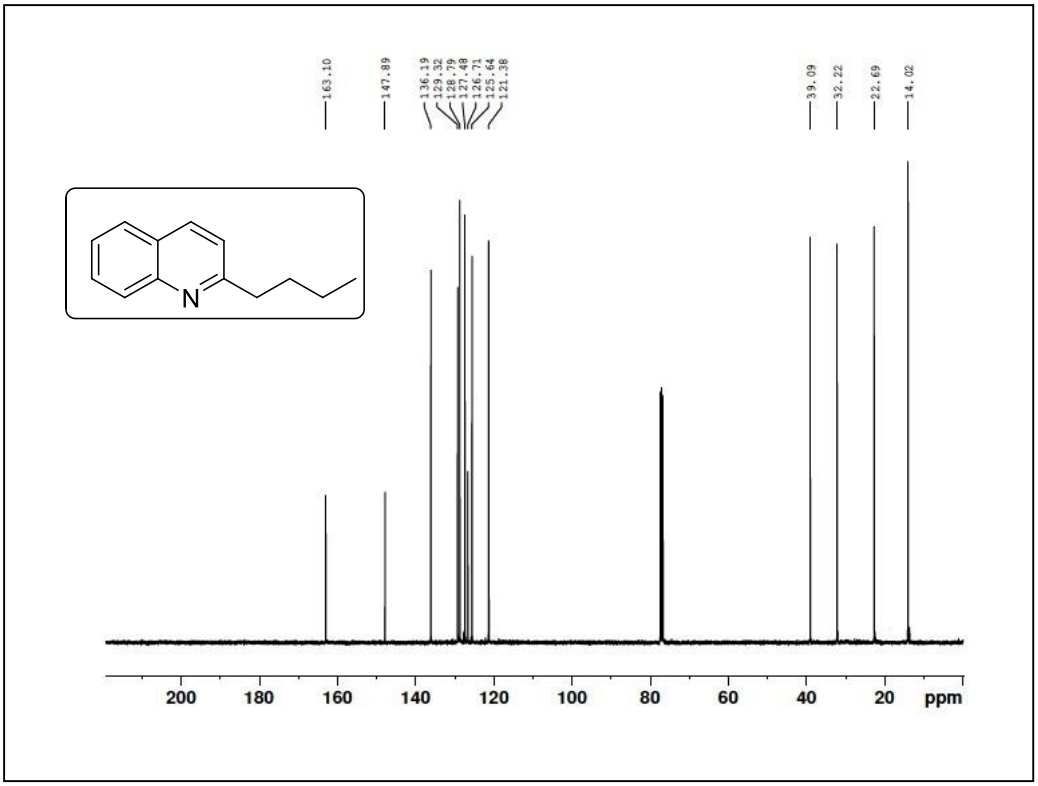
^{1}H NMR spectrum of **4k**



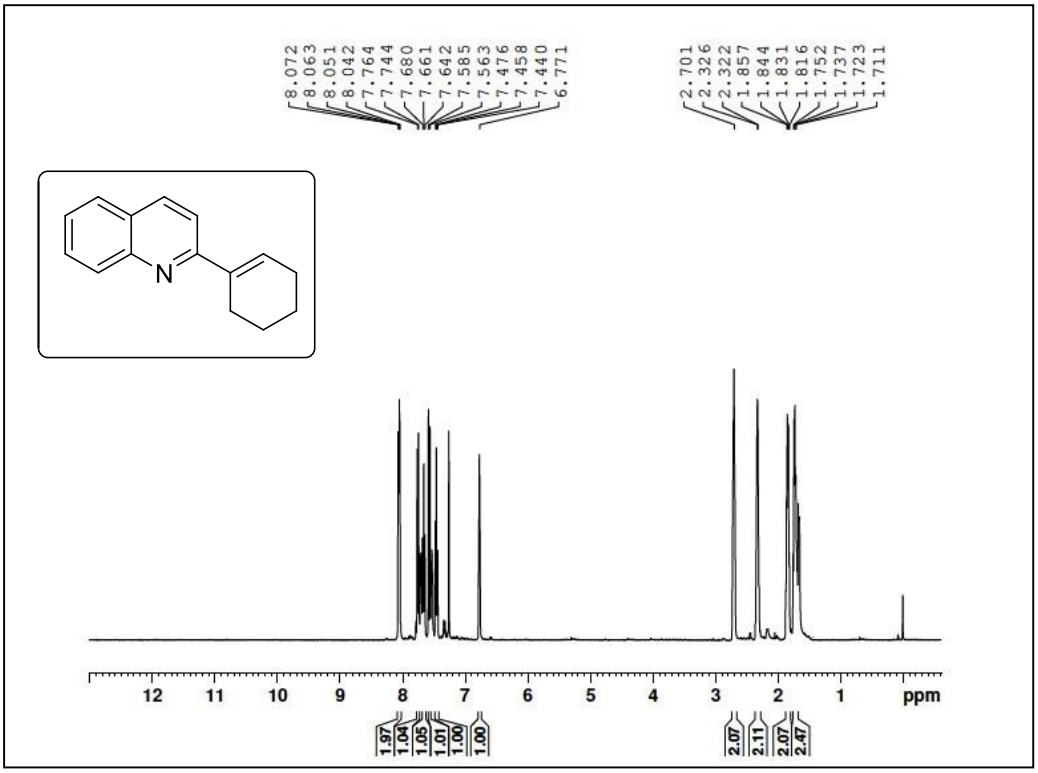
^{13}C NMR spectrum of **4k**



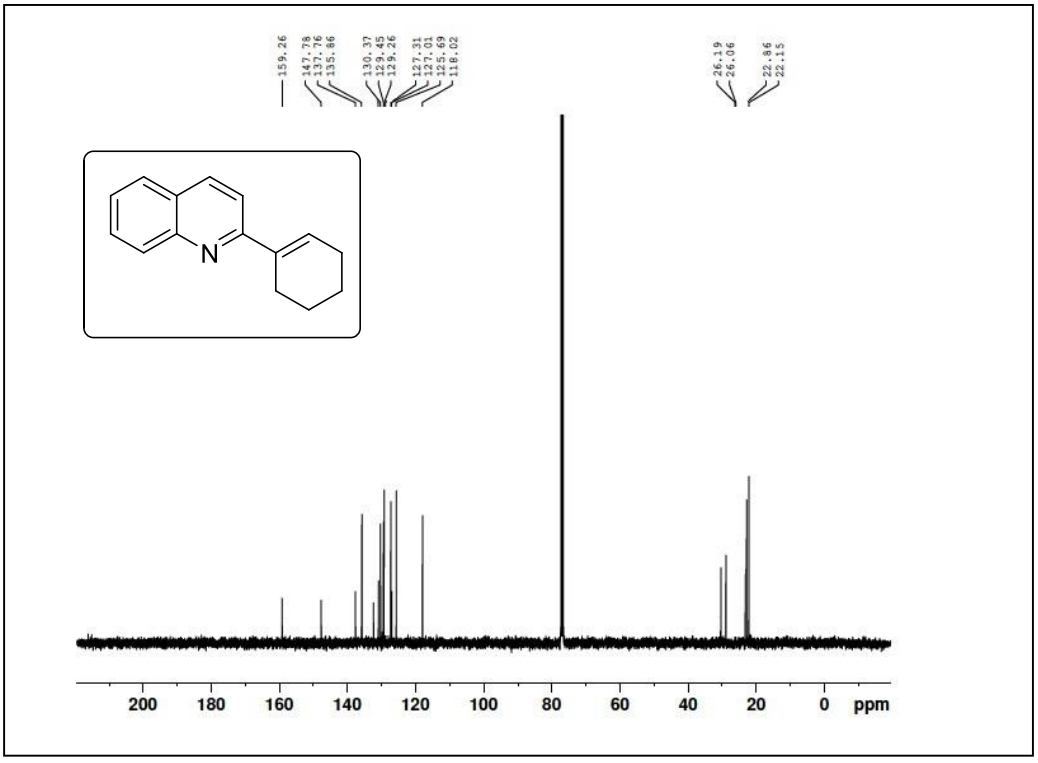
^{1}H NMR spectrum of **4l**



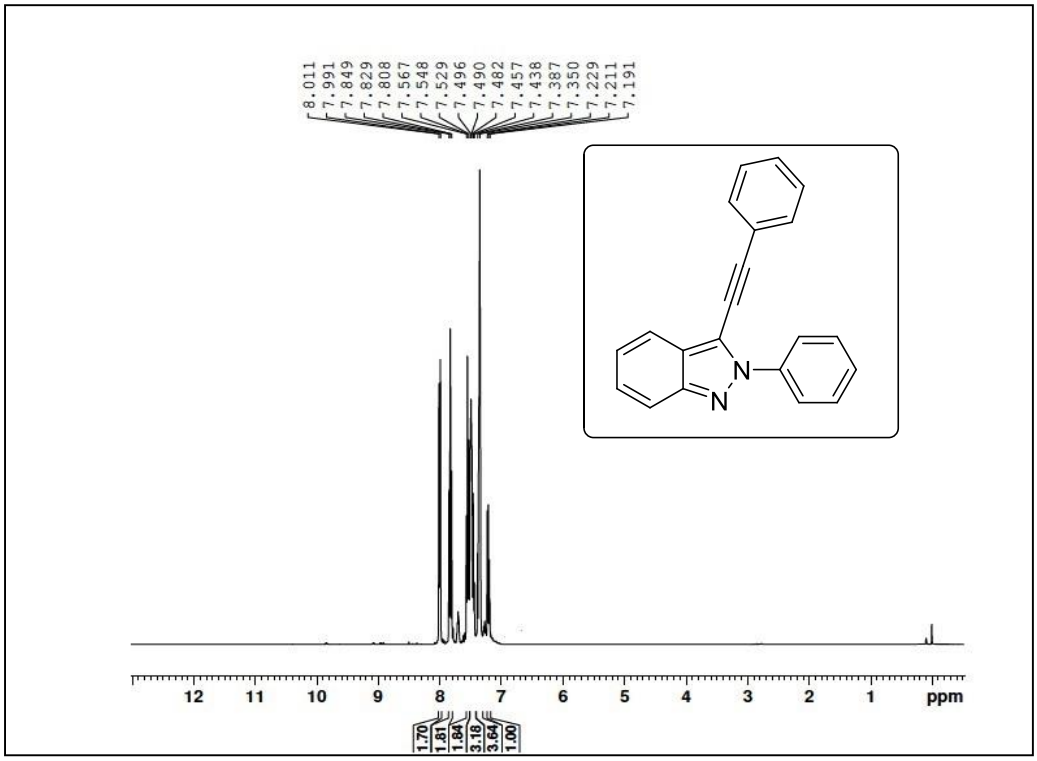
^{13}C NMR spectrum of **4l**



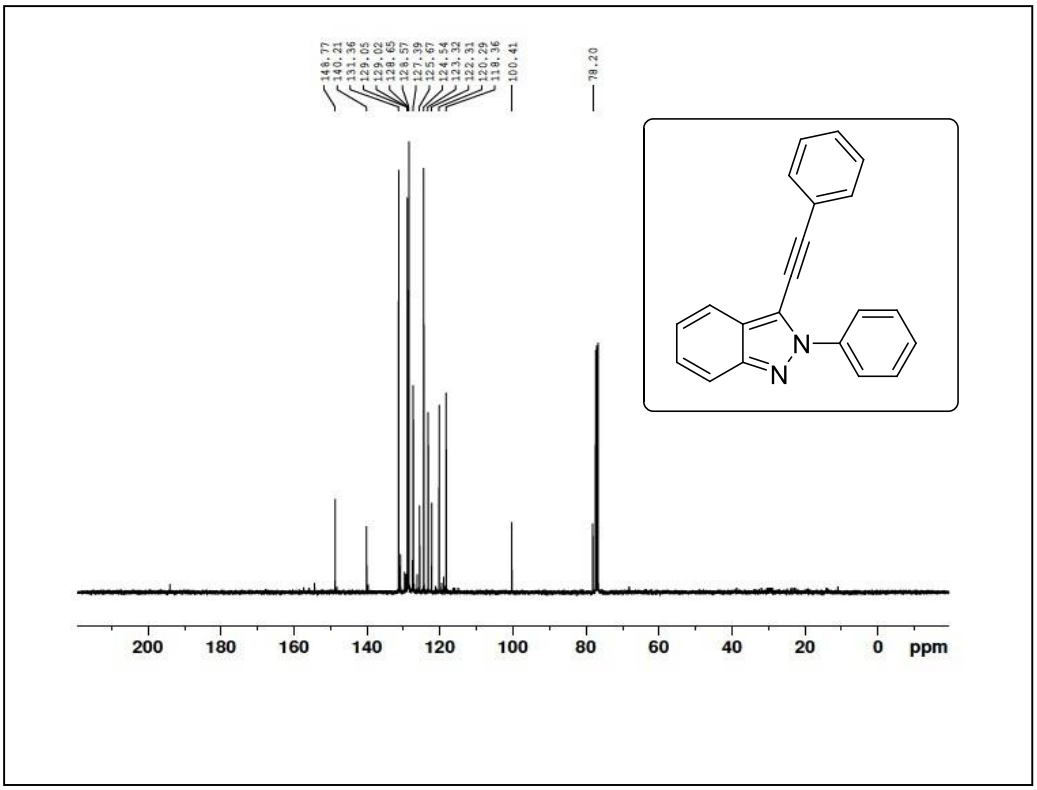
^{1}H NMR spectrum of **4m**



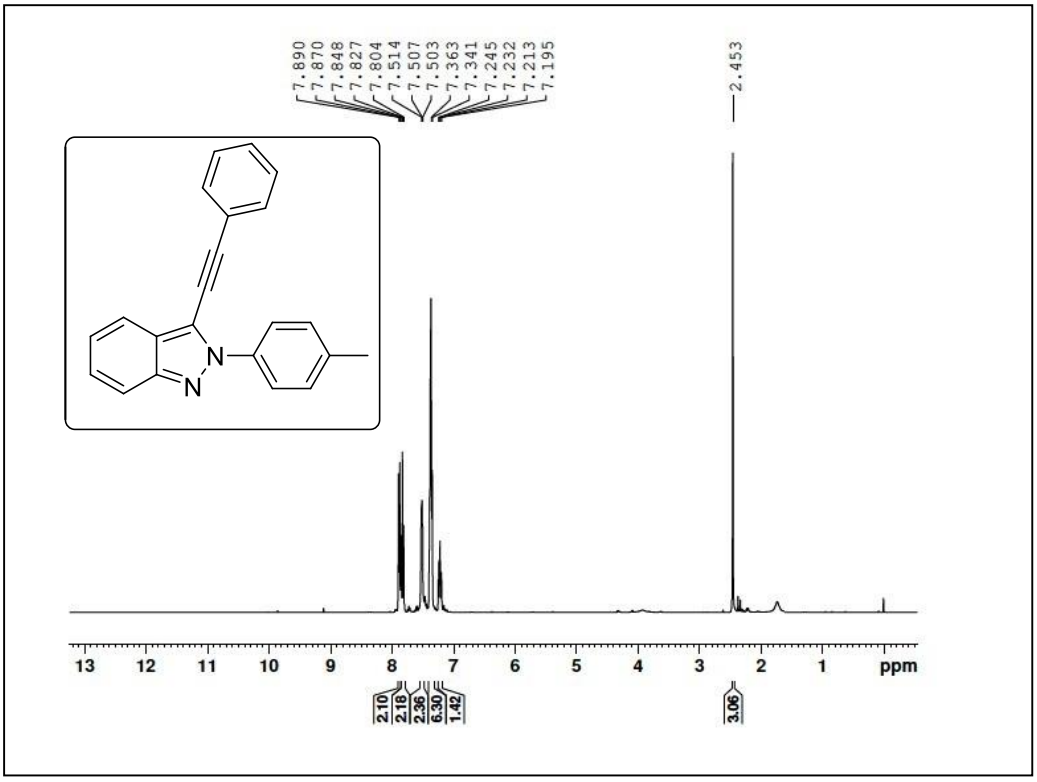
^{13}C NMR spectrum of **4m**



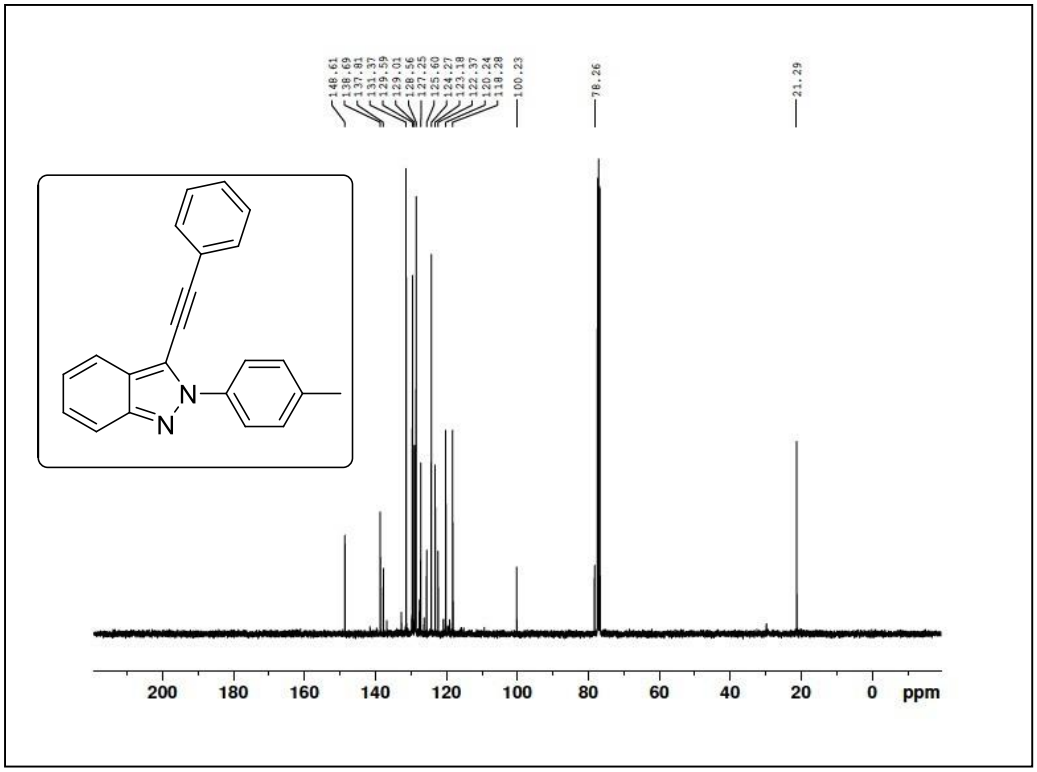
^{1}H NMR spectrum of **10a**



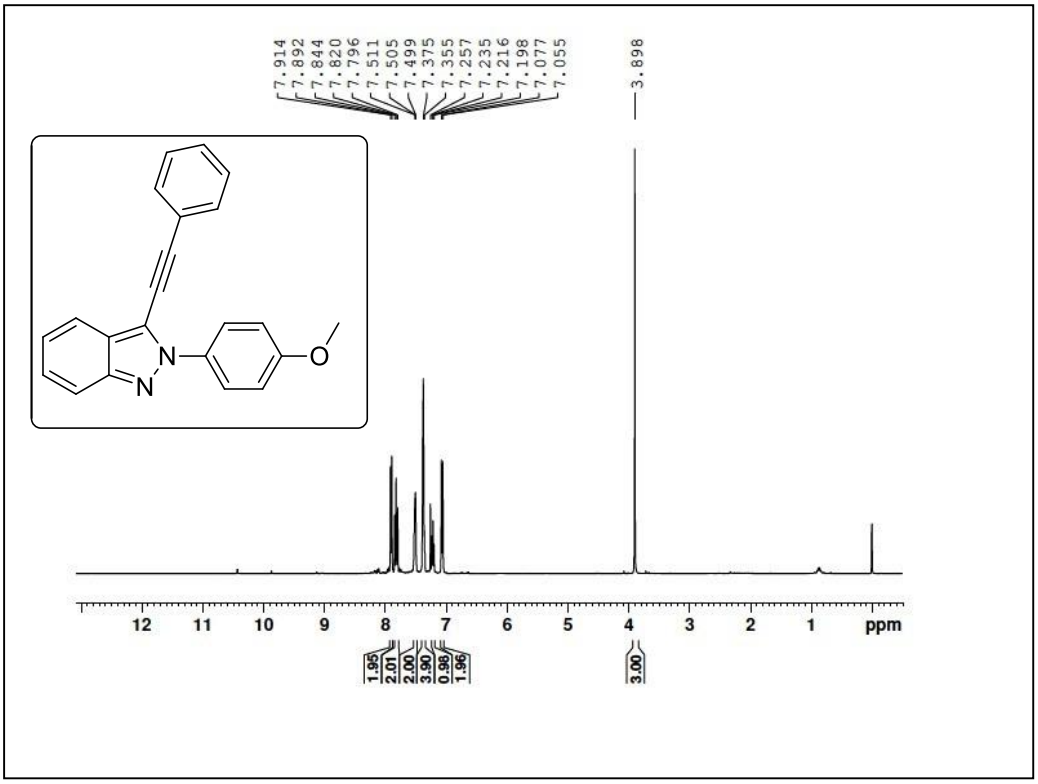
^{13}C NMR spectrum of **10a**



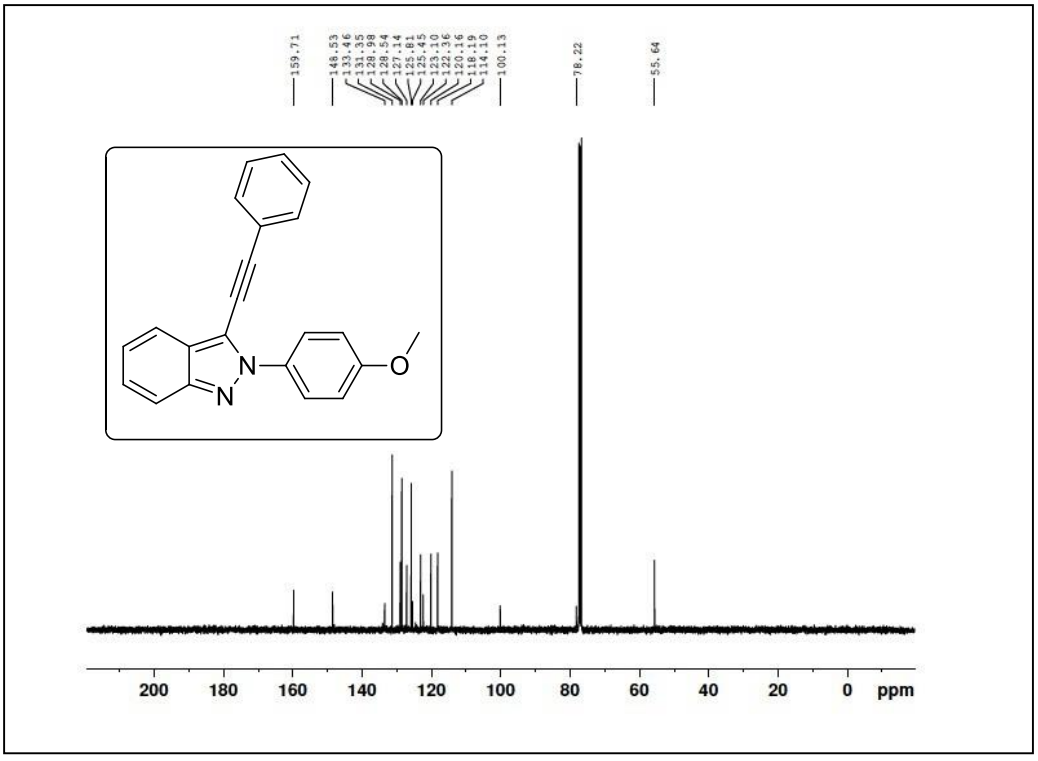
^{1}H NMR spectrum of **10b**



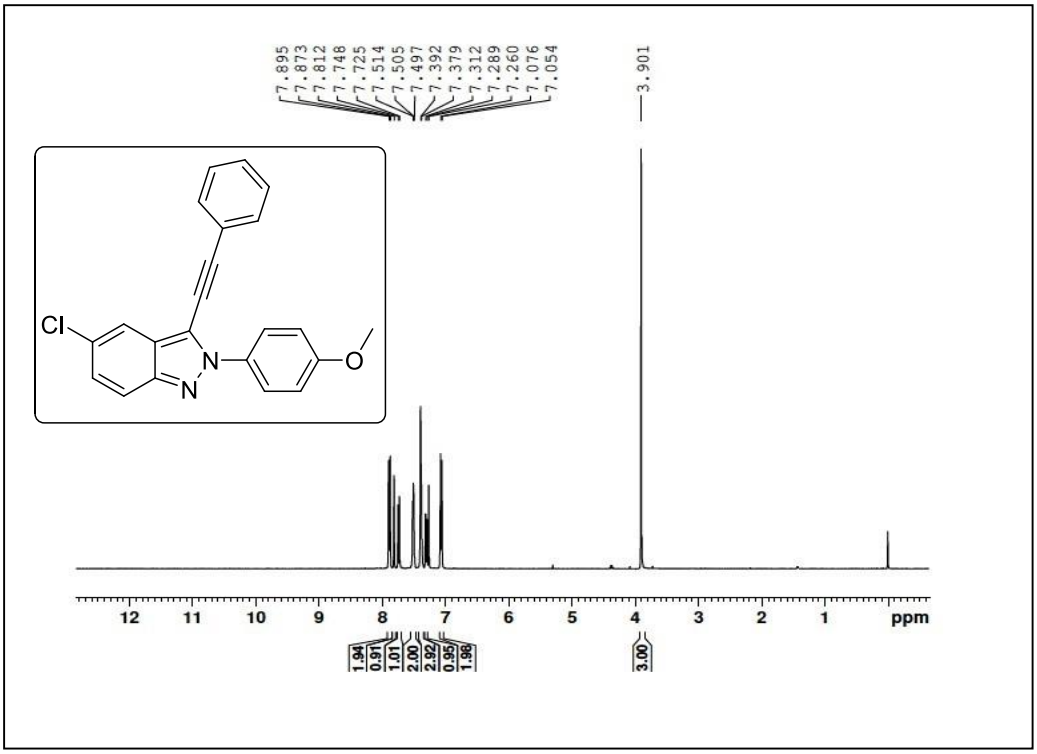
^{13}C NMR spectrum of **10b**



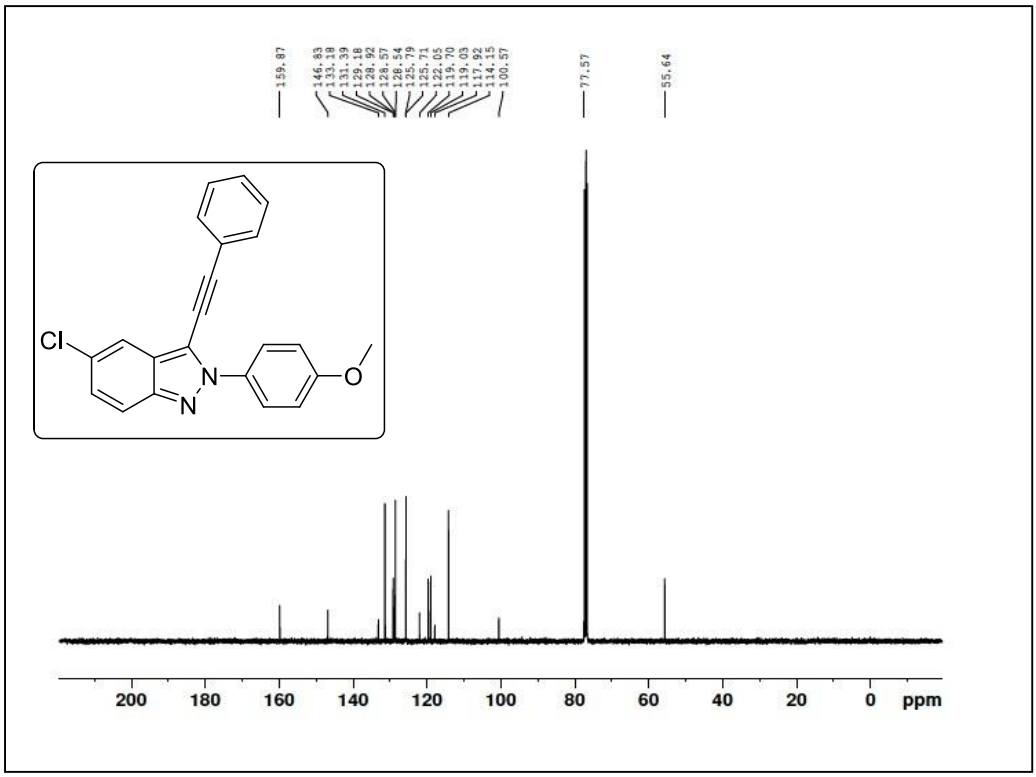
^{1}H NMR spectrum of **10c**



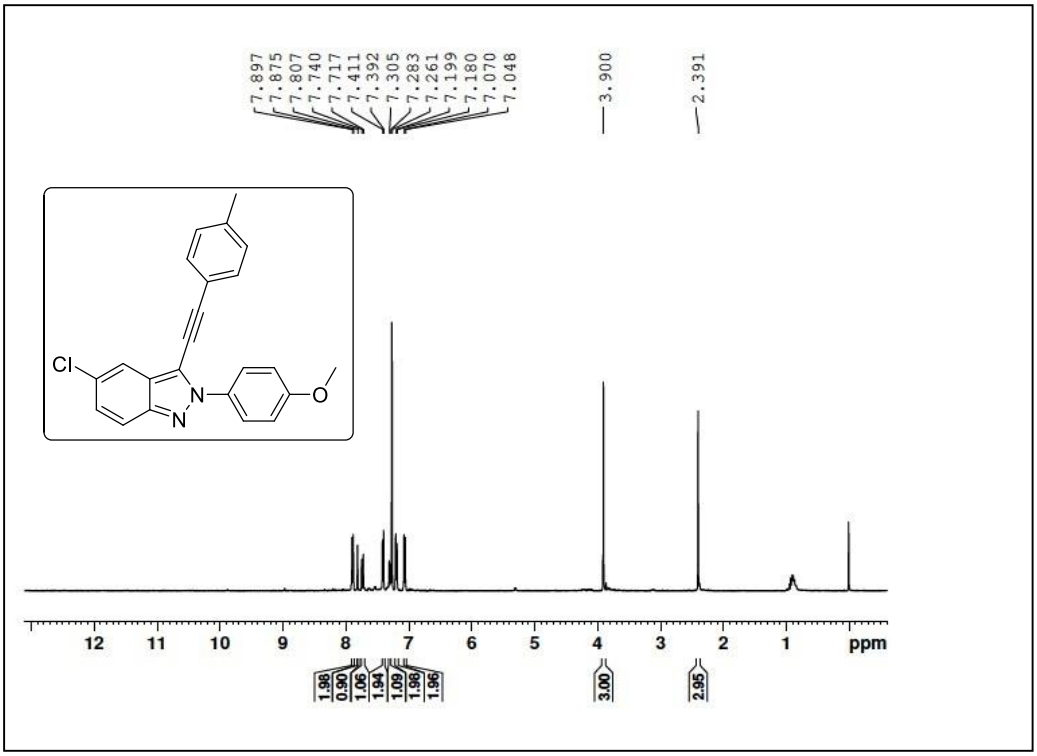
^{13}C NMR spectrum of **10c**



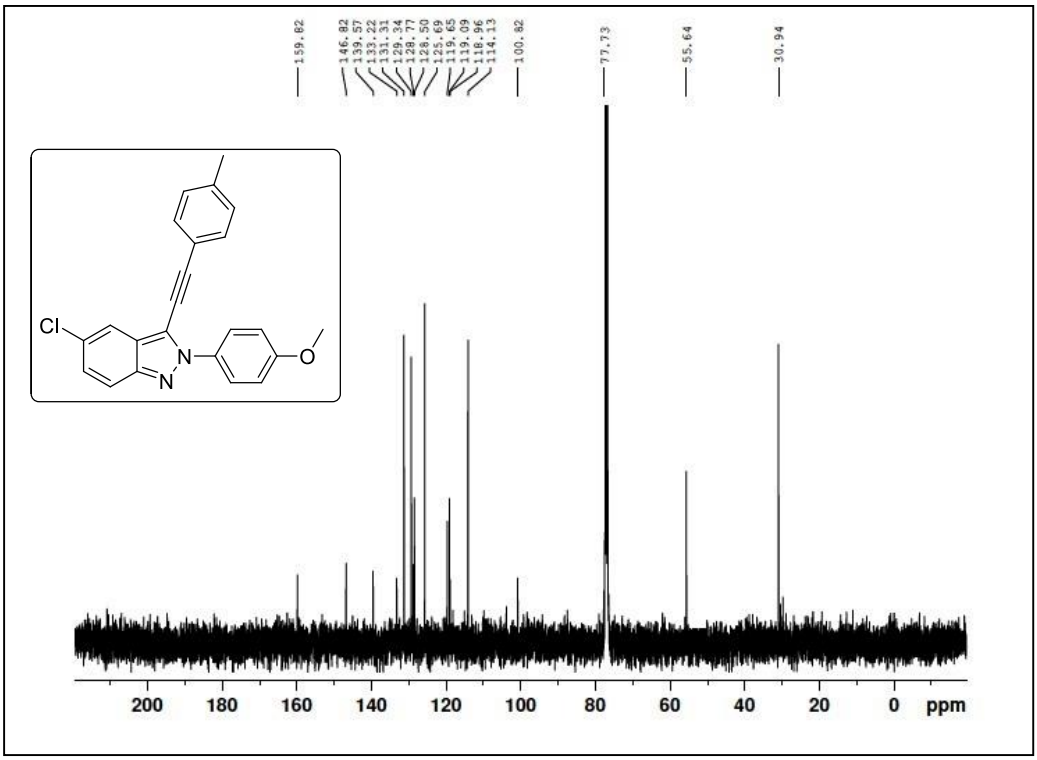
^{1}H NMR spectrum of **10d**



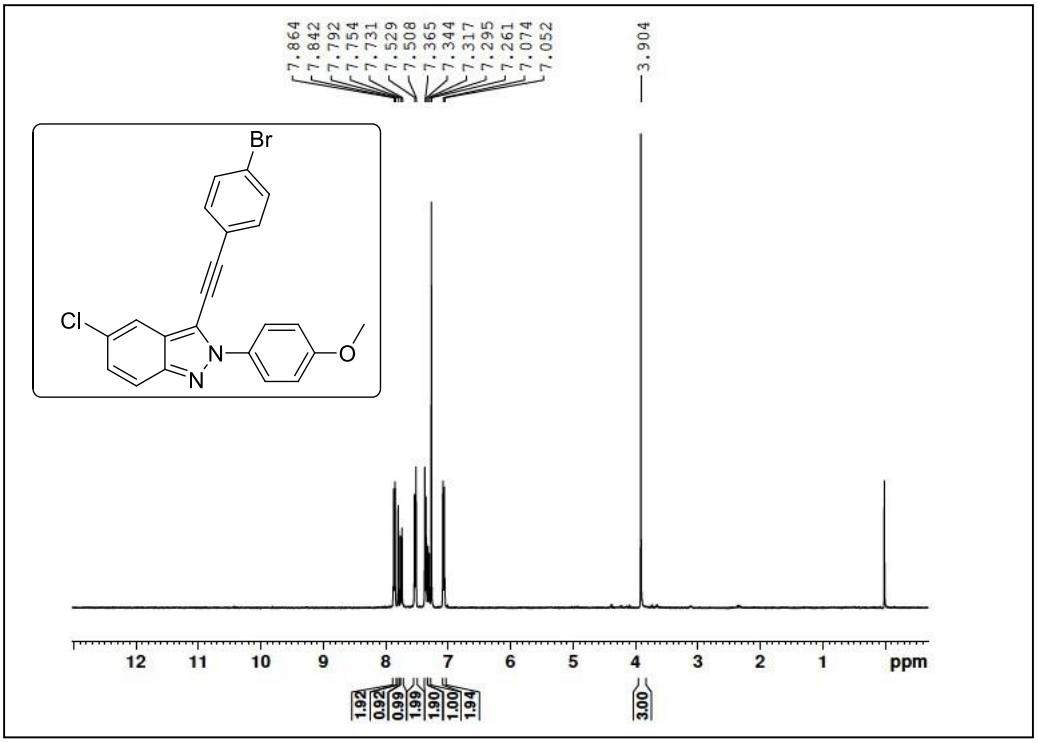
^{13}C NMR spectrum of **10d**



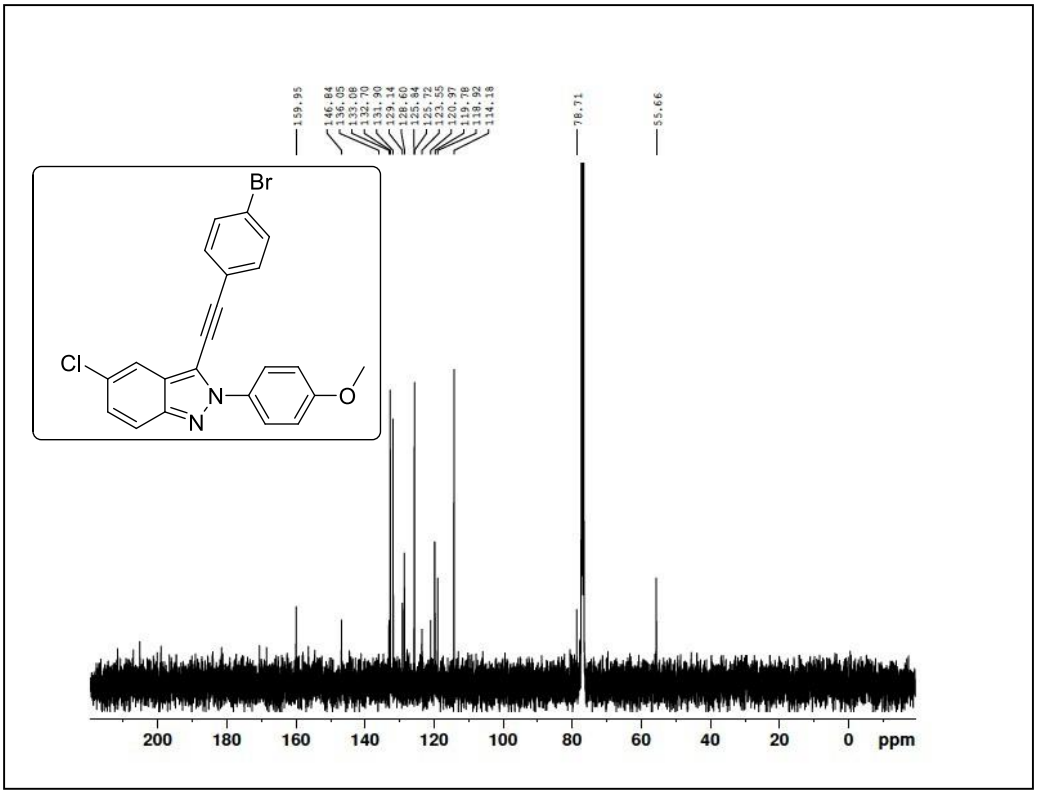
^{1}H NMR spectrum of **10e**



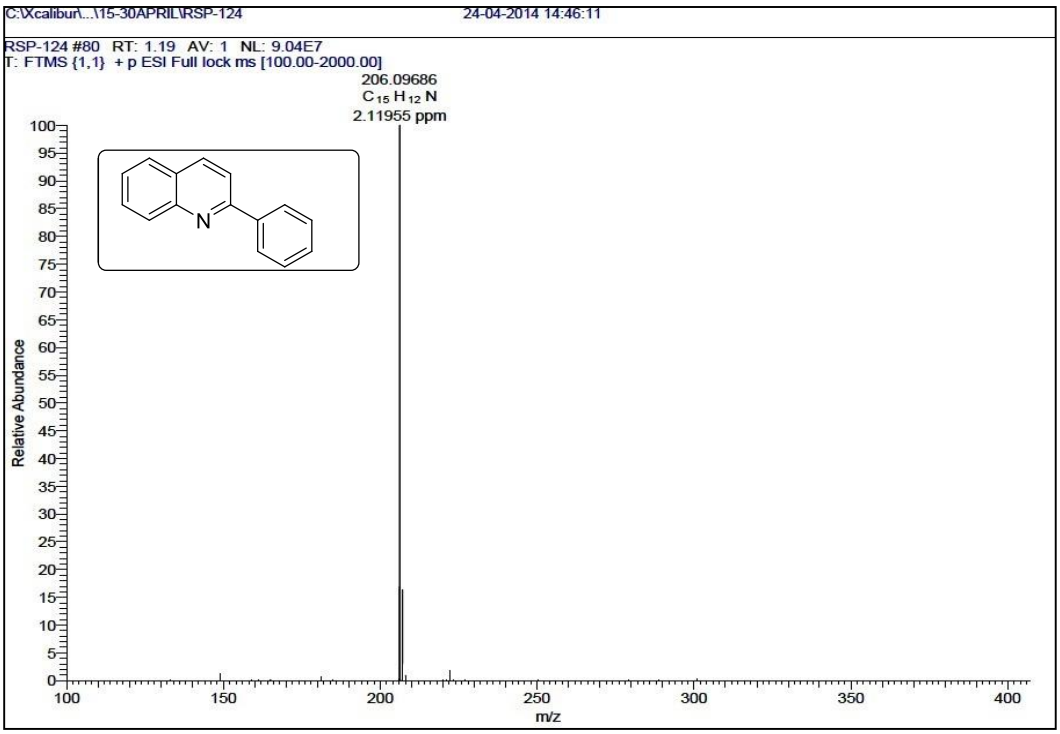
^{13}C NMR spectrum of **10e**



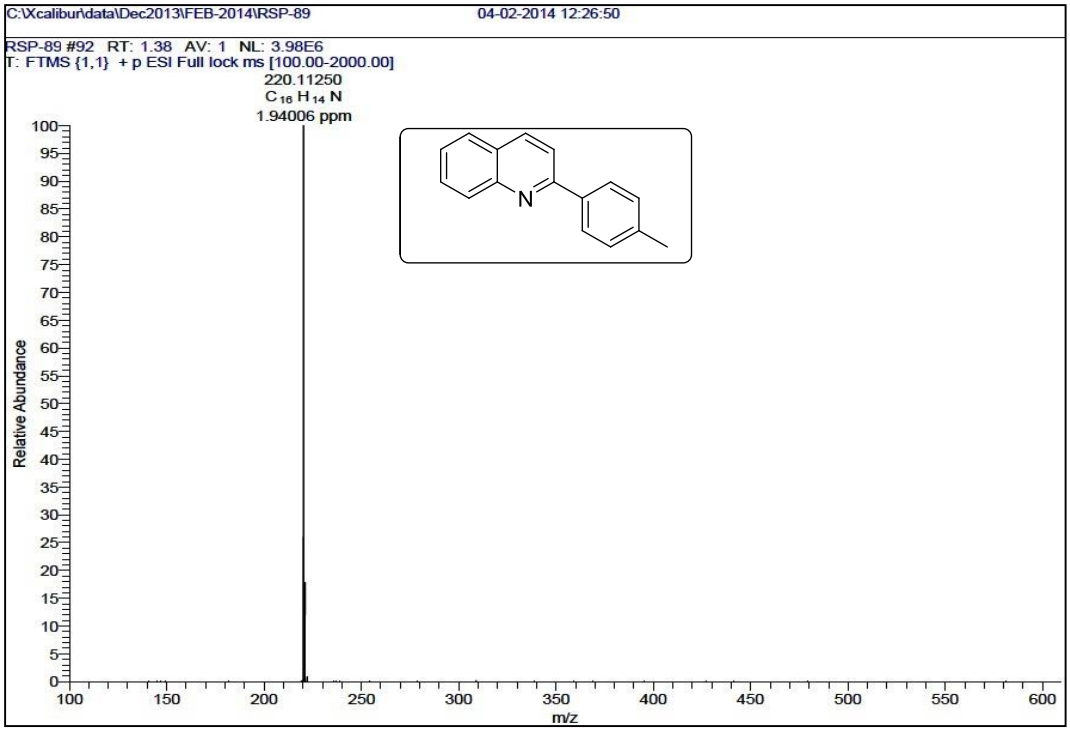
^{1}H NMR spectrum of **10f**



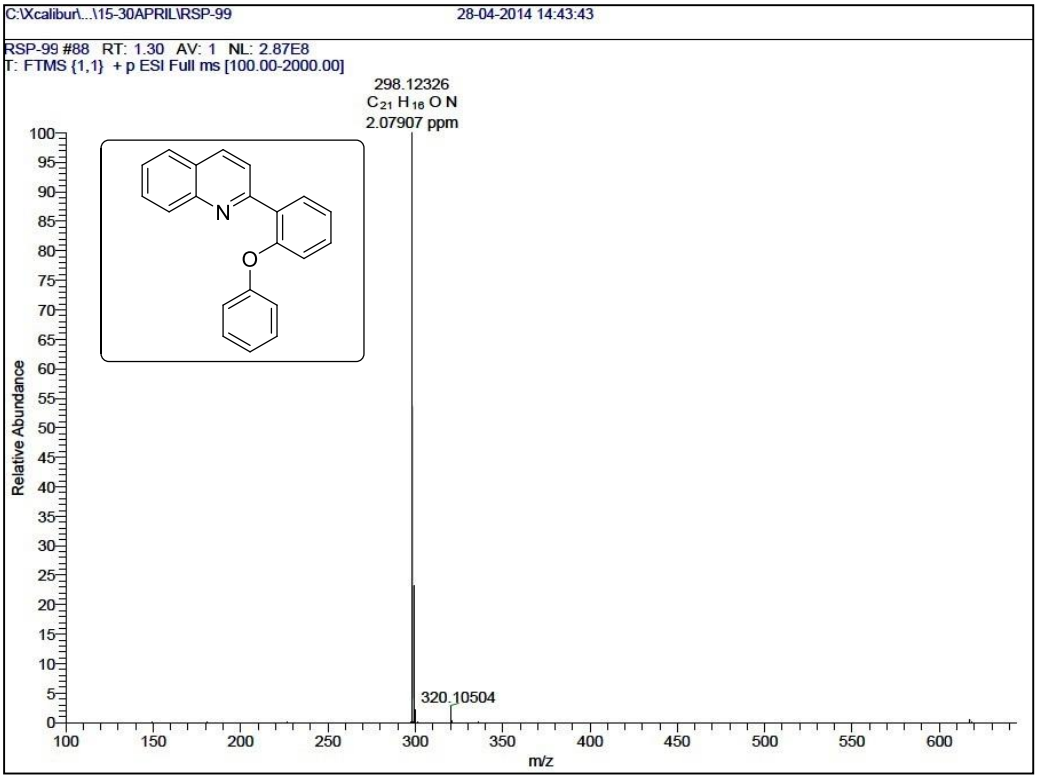
^{13}C NMR spectrum of **10f**



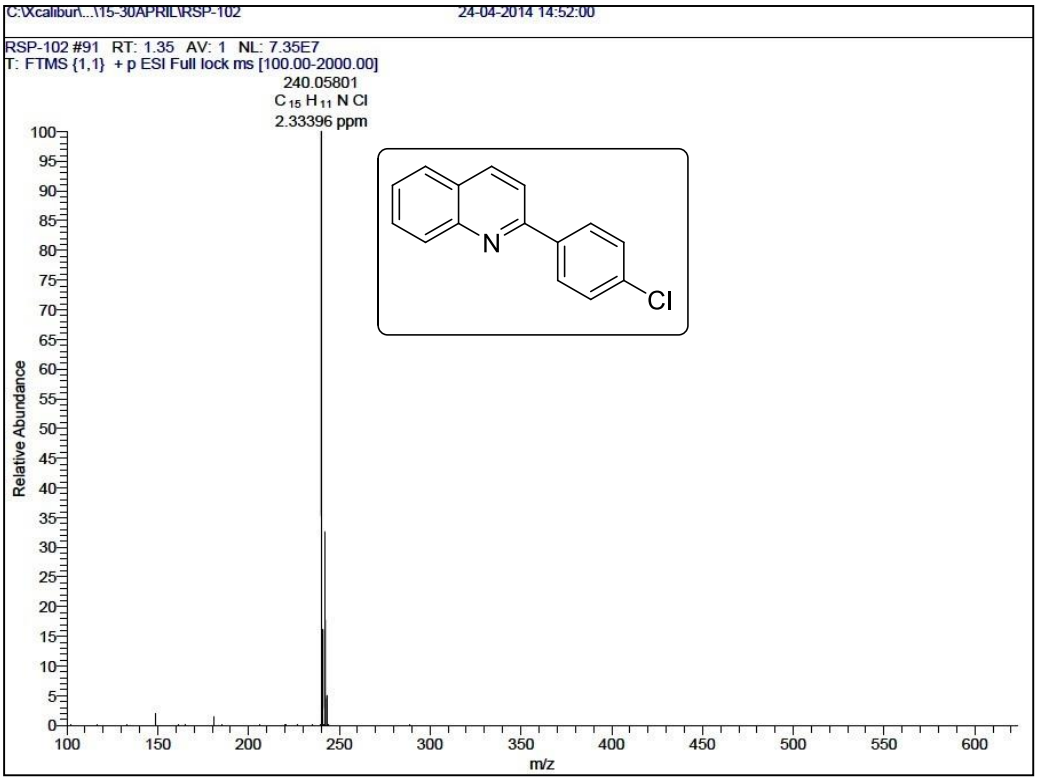
Mass spectrum of **4a**



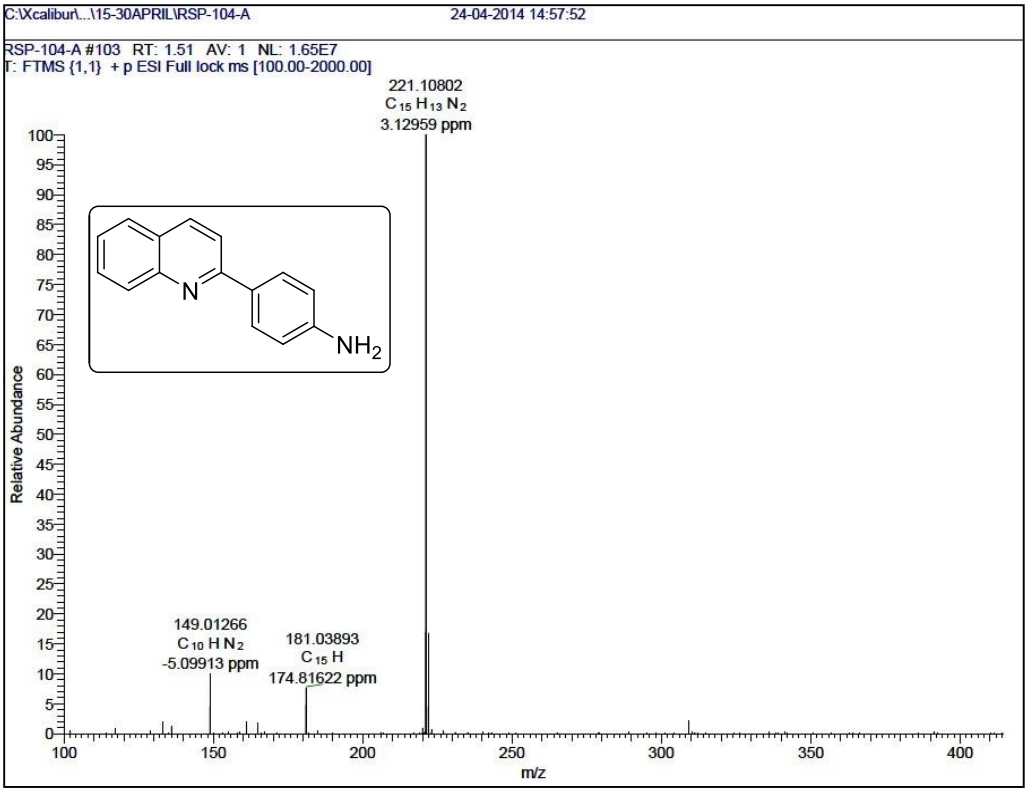
Mass spectrum of **4b**



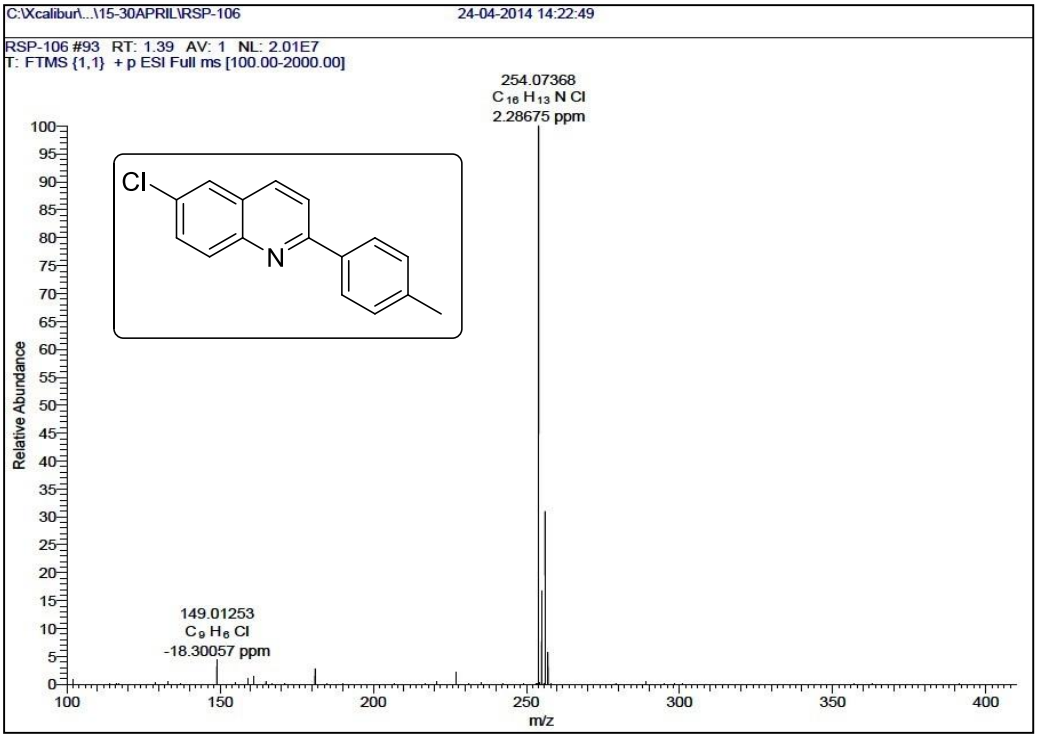
Mass spectrum of **4d**



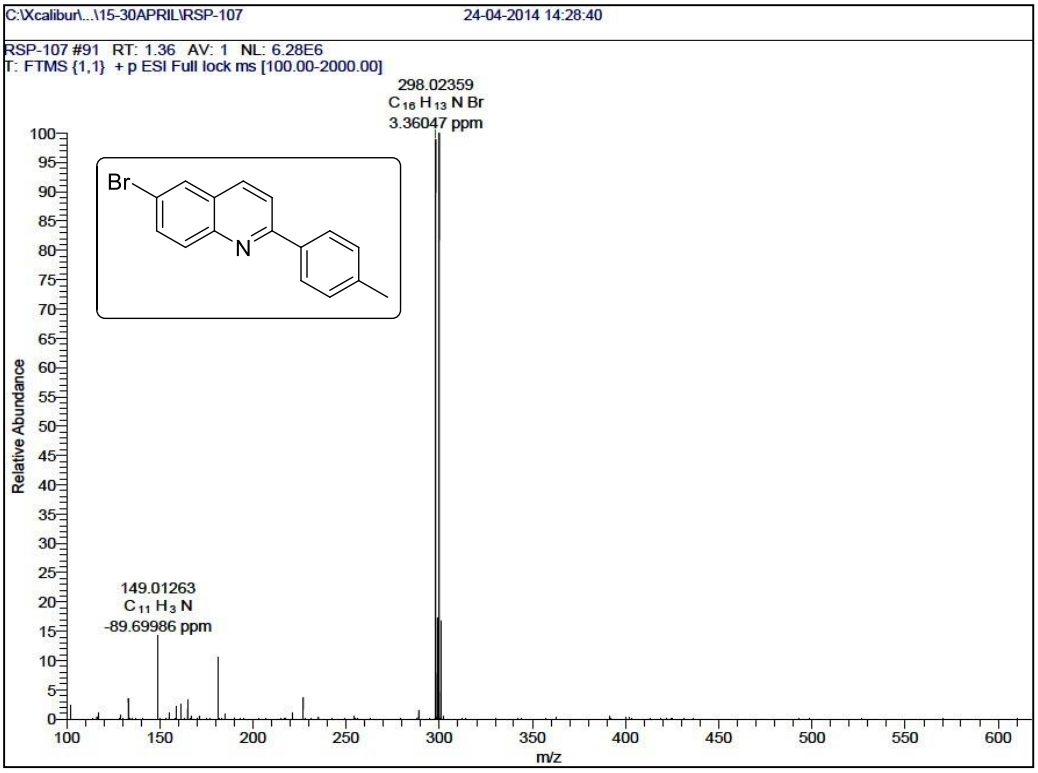
Mass spectrum of **4f**



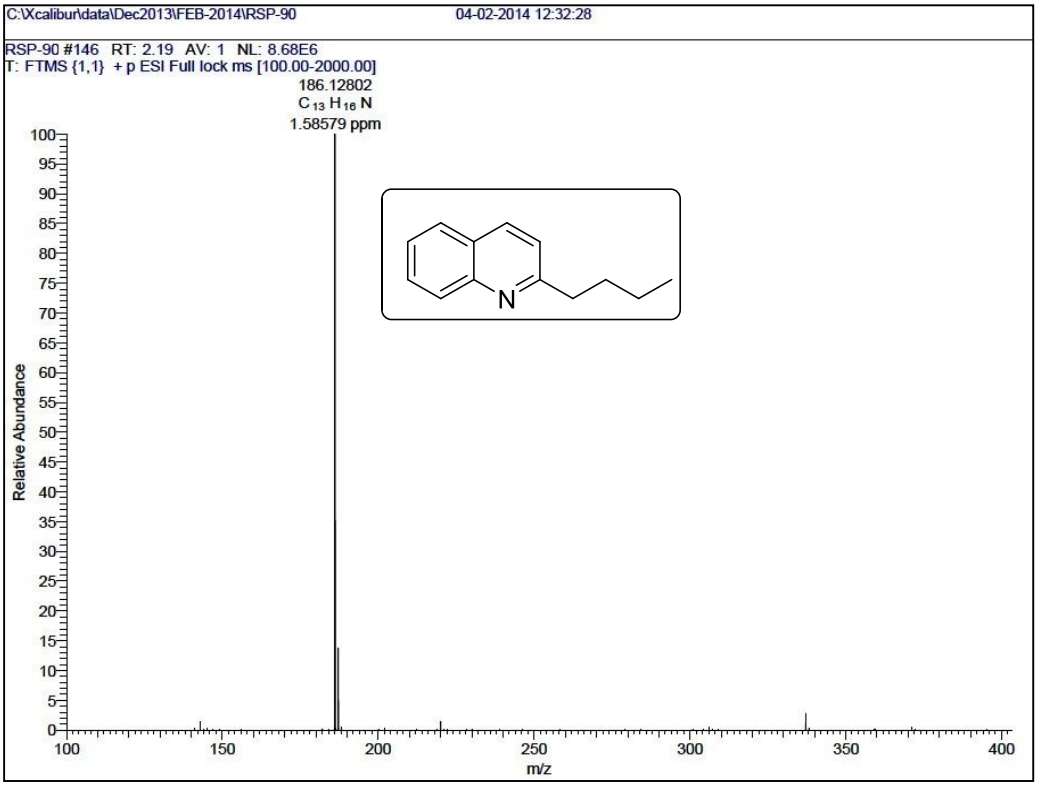
Mass spectrum of **4i**



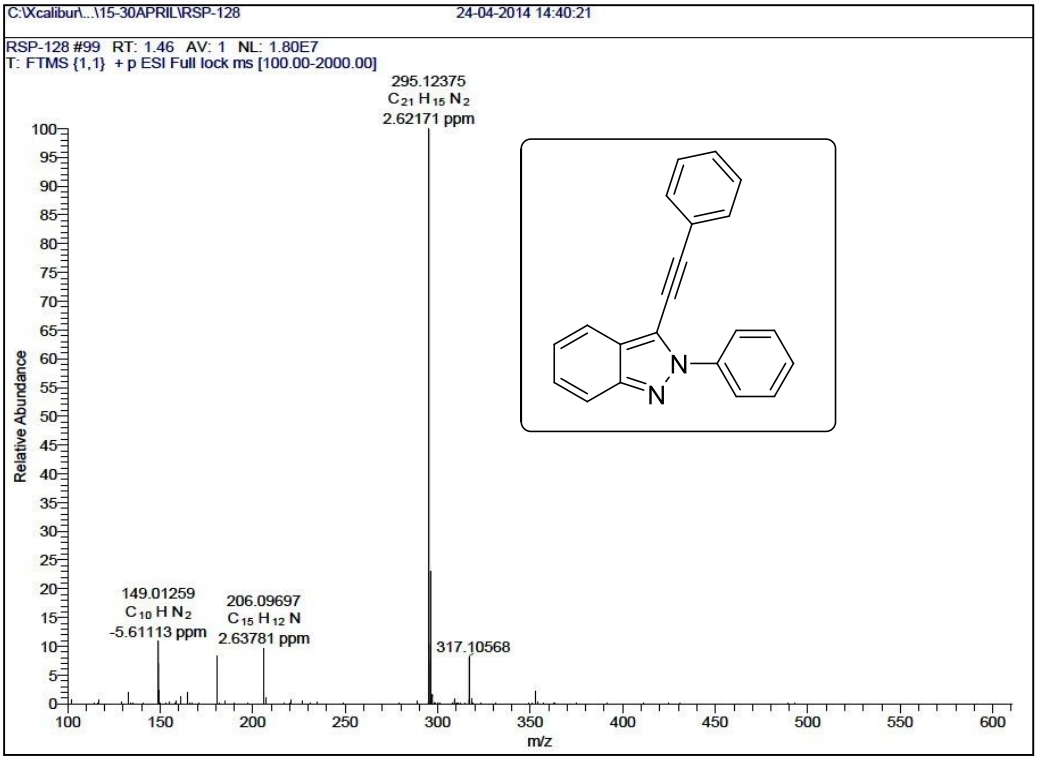
Mass spectrum of **4k**



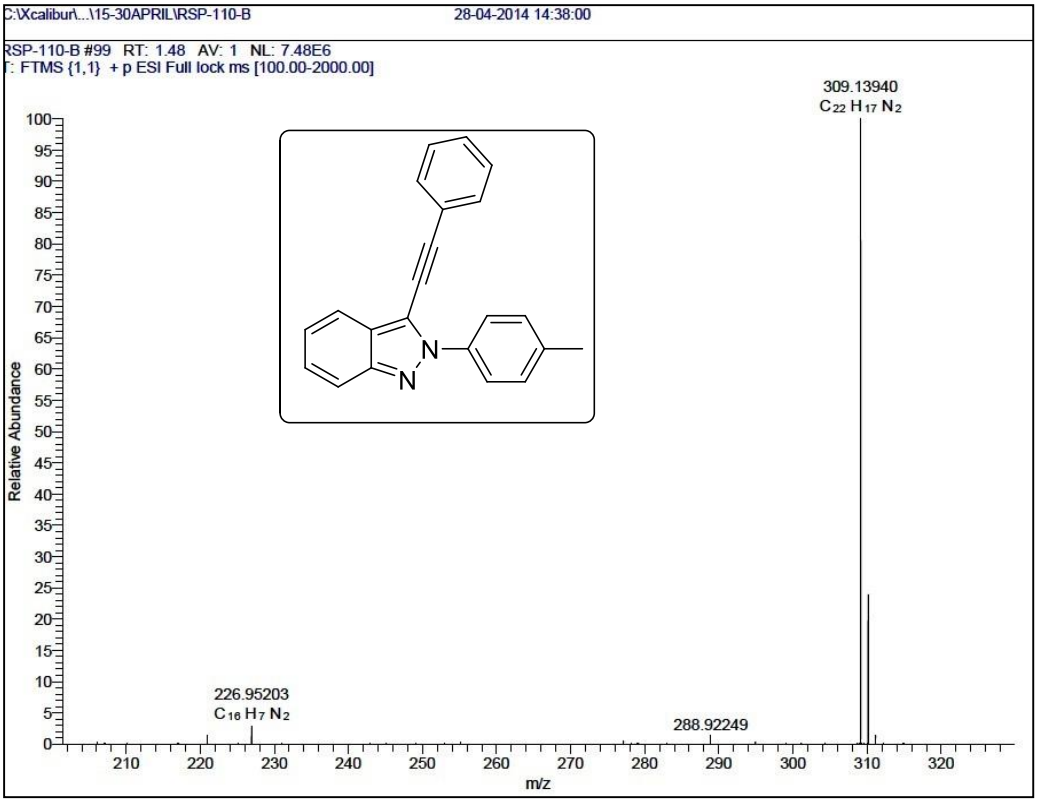
Mass spectrum of **4l**



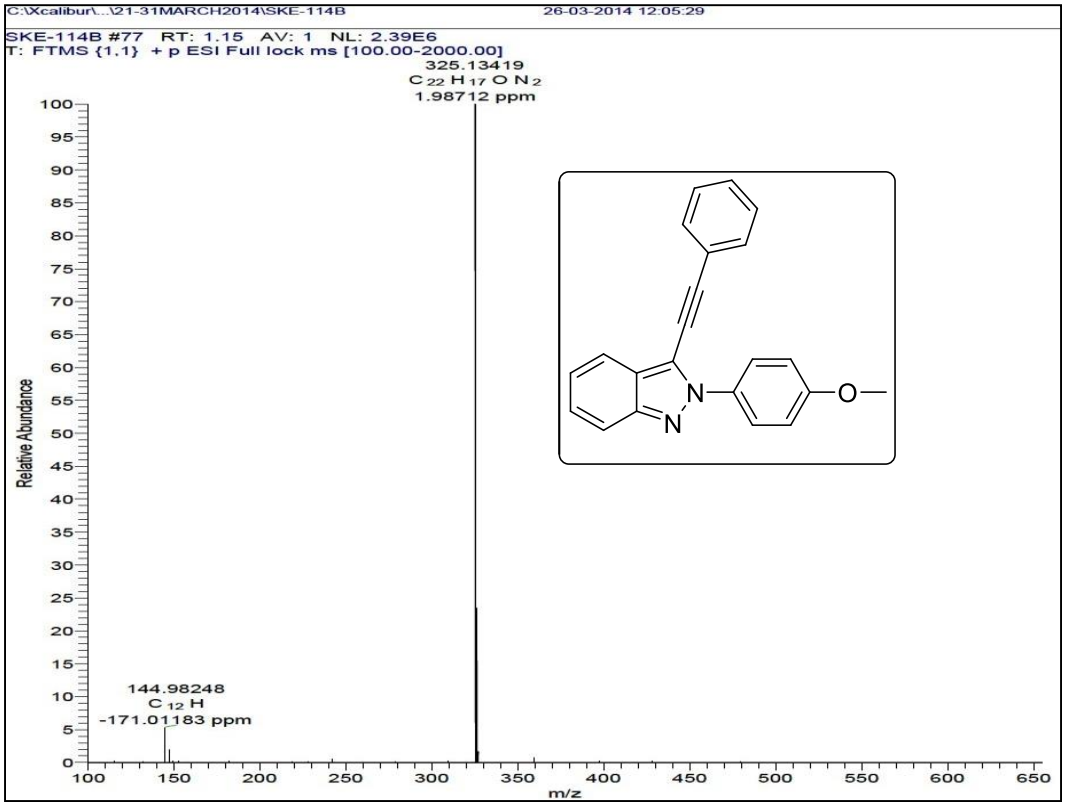
Mass spectrum of **4m**



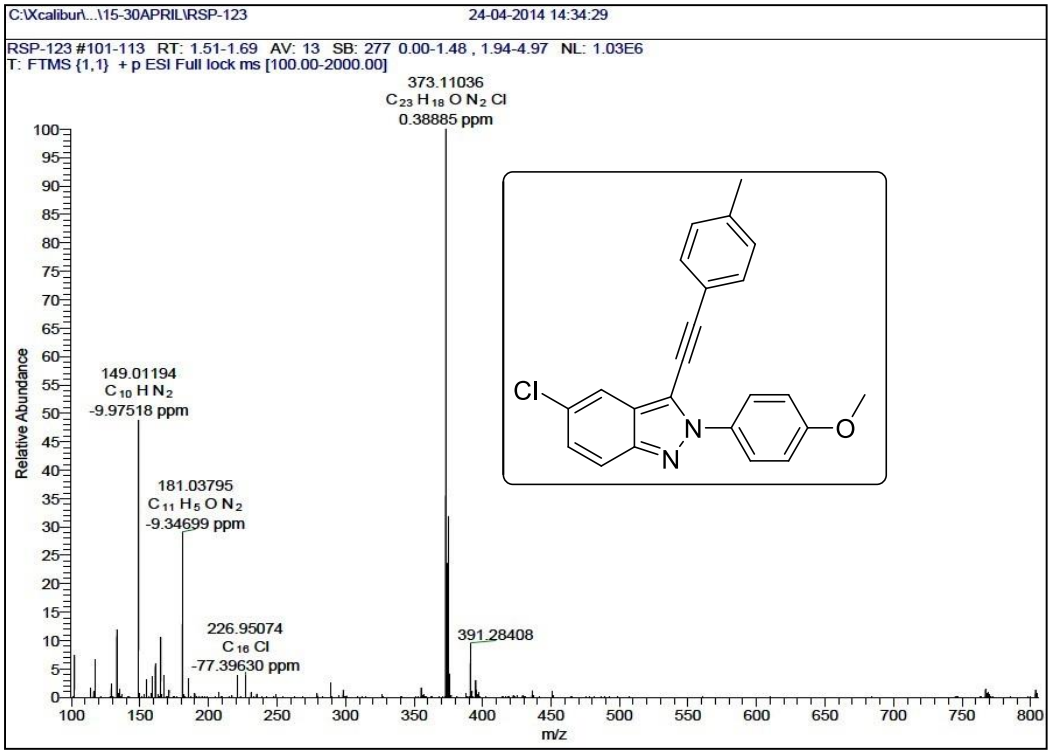
Mass spectrum of **10a**



Mass spectrum of **10b**



Mass spectrum of **10c**



Mass spectrum of **10e**