Supporting information

Silver-catalyzed Tandem *5*- and *6-endo*-cyclizations via Concomitant Yne-ol-imine Activation: Selective Entry to 2-Arydihydrofuroquinolines

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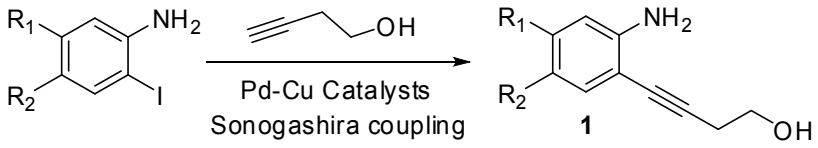
I. General Details

Unless otherwise stated, solvents and reagents were purchased from recognized commercial suppliers (Sigma-Aldrich, Merck, etc.) and were used without further purification. Solvents were dried and distilled following standard procedures. TLC analyses were carried out on aluminium sheets coated with silica gel 60 F254. All chemical reactions were run under argon atmosphere in flame-dried glassware. Flash chromatography was done using Merck silica gel 60 (partial size 0.04-0.063 mm). ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Bruker NMR Spectrometer at 25 ^{o}C (100 MHz for ^{13}C). All ^{13}C NMR spectra were proton decoupled. Chemical shifts were reported in δ units, parts per million (ppm) referenced to 0.00 ppm for tetramethylsilane. Data for ^{1}H NMR spectra are provided as follows: chemical shift (δ shift), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, brs = broad singlet), integration, coupling constant (J in Hz). Perkin Elmer FT-IR Spectrometer was used for recording Infrared (IR) spectra.

II. General procedure for the synthesis of starting alkynes 1a-c.

Alkyne-amines (**1a-c**) were synthesized in gram-scale from 2-iodoaniline and 3-butyn-1-ol employing palladium-copper catalyzed Sonogashira coupling reaction.



1a: R_1, R_2 = H; **1b**: R_1 = Cl; R_2 = H; **1c**: R_1 = H; R_2 = Cl

Procedure for the synthesis of 4-(2-aminophenyl)but-3-yn-1-ol (1a):

$PdCl_2(PPh_3)_2$ (0.064 g, 0.09 mmol), CuI (0.036 g, 0.19 mmol) and 2-Iodoaniline (2 gm, 9.13 mmol) were taken in a round bottom flask previously flushed with argon, and triethylamine (15 mL) was added to it at room temperature. After that, 3-butyn-1-ol (0.645 gm, 9.2 mmol) was added dropwise. The reaction mixture was stirred for 12 hours at room temperature. After completion, Et_2O and water were added and product was extracted with Et_2O. The organic layer was washed with water and brine, dried over Na_2SO_4, filtered and evaporated. The residue was purified by column chromatography on silicagel (Hexane-Ethylacetate; 6:1) to afford 1.24 gm (7.7 mmol) of 4-(2-aminophenyl)but-3-yn-1-ol in 84% yield.

III. General procedure for the catalysis

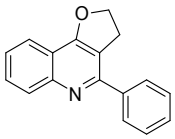
a) General procedure for syntheses of the products 3a-i.

Procedure for synthesis of 3a: Combination of DMA (15 mg, 0.12 mmol)-TEA (6 mg, 0.06 mmol) (20 mol%: 10 mol% w. r. t. alkyne) was taken into a sealed tube at 25 °C. A mixture of 4-(2-aminophenyl)but-3-yn-1-ol **1a** (100 mg, 0.62 mmol) and benzalaldehyde **2a** (99 mg, 0.93 mmol) in toluene (0.5 mL) was then added dropwise via a cannula into the sealed tube and the reaction mixture was placed on a pre-heated oil bath at 120 °C and was stirred for 10 minutes. After that, AgOTf (6 mg, 0.02 mmol, 3 mol % with respect to alkyne **1**) was taken in anhydrous toluene (0.5 mL) and was added dropwise into the reaction mixture by a syringe under argon atmosphere. It was monitored by TLC. Upon completion, the solvent was removed under vacuum and the crude product was subjected to flash column chromatography (5% EA/ hexane) to afford the pure product **3a** (116 mg, 0.47 mmol) in 76% yield. The following products (**3a-i**) are obtained from this study and their spectral data are included.

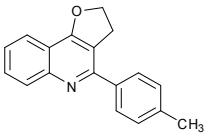
b) General procedure for syntheses of the products 3j-n (Gram-scale synthesis of 3j)

Procedure for syntheses of 3j: 4-(2-aminophenyl)but-3-yn-1-ol **1a** (1g, 6.2 mmol) and *N*-benzyl-indole-3-carbaldehyde **2j** (2.18 g, 9.3 mmol) were added into a mixture of DMA (10 mL) and TEA (0.12 g, 1.2 mmol, 20 mol% with respect to alkyne) in a sealed tube. The reaction mixture was placed on a pre-heated oil bath at 140 ºC and was stirred for 10 minutes. After that, AgOTf (60 mg, 0.2 mmol, 3 mol % with respect to alkyne **1**) was added into the reaction mixture. It was monitored by TLC. Upon completion, the solvent was removed under vacuum and the crude product was subjected to flash column chromatography (10% EA/ hexane) to afford the pure product **3j** (1.5 g, 4 mmol) in 65% yield. The following products **3k-n** are obtained from this study and their spectral data are included. Some aldehyde-DMA adduct (15~20 % with respect to aldehyde) was formed during each transformation.

IV. List of new compounds prepared



3a (76%)



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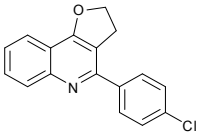
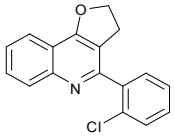
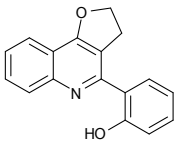


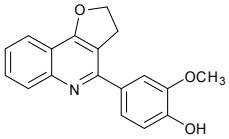
3c (74%)



3d (60%)



3e (68%)



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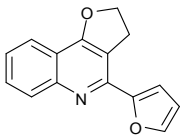

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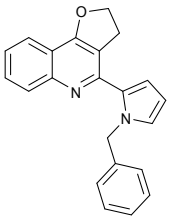
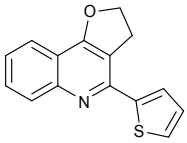
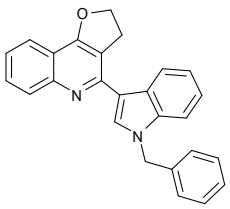


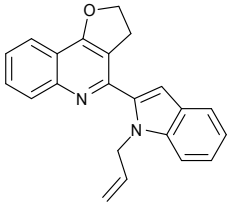
3h (55%)



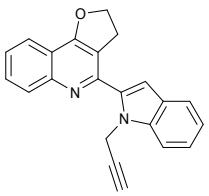
3i (76%)



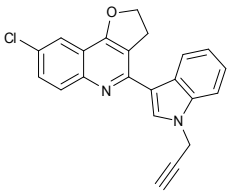
3j (65%)



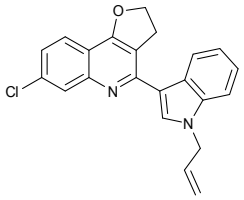
3k (52%)



3l (60%)

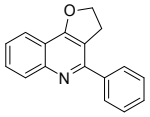


3m (47%)



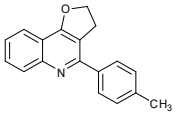
3n (51%)

V. Spectroscopic data of compounds 3a-n



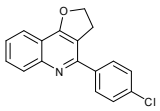
4-phenyl-2, 3-dihydrofuro[3,2-c]quinoline (**3a**)

White crystalline solid, mp. 58-60 ºC. IR (neat, cm^{-1}): 3056, 2960, 2916, 1630, 1588, 1551, 1506, 1493, 1411, 1342, 1267, 1086, 918, 906, 760, 701. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.8 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.83-7.79 (m, 2H), 7.60-7.56 (m, 1H), 7.44-7.33 (m, 4H), 4.78 (t, J = 9 Hz, 2H), 3.47 (t, J = 9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 155.6, 149.2, 139.9, 129.7, 129.3, 128.8, 128.6, 128.3, 125.4, 121.4, 116.0, 115.1, 73.1, 30.1; Elemental analysis observed: C, 82.38; H, 5.19; N, 5.51;calcd for $C_{17}H_{13}NO$: C, 82.57; H, 5.30; N, 5.66.



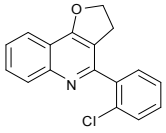
4-p-tolyl-2, 3-dihydrofuro[3,2-c]quinoline (**3b**)

According to the general procedure **IIIa**, **1a** (100 mg, 0.62mmol), **2b** (112 mg, 0.93 mmol) and AgOTf (6 mg, 0.02 mmol, 3 mol %) were used to obtain **3b** (115 mg, 0.44 mmol), which was isolated by flash chromatography (6 % EA/Hexane) in 71% yield. White crystalline solid, mp. 85-87 ºC. IR (neat, cm^{-1}) : 3085, 2994, 2905, 1631, 1588, 1549, 1498, 1425, 1340, 1272, 1085, 926, 818, 749; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 8 Hz, 2H), 7.61-7.57 (m, 1H), 7.38 (t, J = 7.4 Hz, 1H), 7.24 (d, J = 8 Hz, 2H), 4.81 (t, J = 8.8 Hz, 2H), 3.51 (t, J = 8.8 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 155.5, 149.0, 138.9, 137, 129.7, 129.3, 129.1, 128.3, 125.3, 121.4, 115.9, 115.0, 73.1, 30.2, 21.4; Elemental analysis observed: C, 82.55; H, 5.62; N, 5.23;calcd for $C_{18}H_{15}NO$:C, 82.73; H, 5.79; N, 5.36.



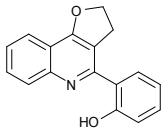
4-(4-chlorophenyl)-2, 3-dihydrofuro[3,2-c]quinoline (**3c**)

According to the general procedure **IIIa**, **1a** (100 mg, 0.62mmol), **2c** (131 mg, 0.93 mmol) and AgOTf (6 mg, 0.02 mmol, 3 mol %) were used to obtain **3c** (130 mg, 0.46 mmol), which was isolated by flash chromatography (6 % EA/Hexane) in 74% yield. White crystalline solid, mp. 121-123 ºC. IR (neat, cm^{-1}) : 2961, 2920, 2854, 1629, 1589, 1572, 1548, 1488, 1410, 1390, 1337, 1261, 1086, 1012, 845, 812, 763; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.8 Hz, 2H), 7.61-7.57 (m, 1H), 7.41-7.37 (m, 3H), 4.80 (t, J = 9 Hz, 2H), 3.47 (t, J = 9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 154.2, 149.1, 138.3, 134.9, 129.9, 129.7, 129.2, 128.7, 125.6, 121.4, 116.0, 114.9, 73.1, 30.1; Elemental analysis observed: C, 72.29; H, 4.20; N, 4.85; calcd for $C_{17}H_{12}ClNO$: C, 72.47; H, 4.29; N, 4.97.



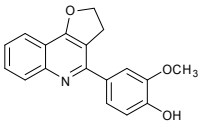
4-(2-chlorophenyl)-2,3-dihydrofuro[3,2-c]quinoline (**3d**)

According to the general procedure **IIIa**, **1a** (100 mg, 0.62 mmol), **2d** (131 mg, 0.93 mmol) and AgOTf (6 mg, 0.02 mmol, 3 mol %) were used to obtain **3d** (104 mg, 0.37 mmol), which was isolated by flash chromatography (6 % EA/Hexane) in 60% yield. White crystalline solid, mp. 117-119 ºC. IR (neat, cm^{-1}) : 3060, 2973, 2923, 2863, 1632, 1598, 1552, 1508, 1477, 1405, 1277, 1260, 1088, 1059, 913, 760, 643; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 8.4 Hz, 1H), 7.62-7.57 (m, 1H), 7.44-7.38 (m, 3H), 7.32-7.27 (m, 2H), 4.79 (t, J = 9 Hz, 2H), 3.21 (t, J = 9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 155.1, 148.9, 139.1, 132.3, 130.7, 129.8, 129.7, 129.3, 127.1, 125.8, 121.4, 117.2, 116.2, 73.4, 28.7; Elemental analysis observed: C, 72.32; H, 4.18; N, 4.83;calcd for $C_{17}H_{12}ClNO$:C, 72.47; H, 4.29; N, 4.97.



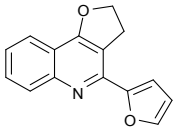
2-(2,3-dihydrofuro[3,2-c]quinolin-4-yl)phenol (**3e**)

According to the general procedure **IIIa**, **1a** (100 mg, 0.62 mmol), **2e** (114 mg, 0.93 mmol) and AgOTf (6 mg, 0.02 mmol, 3 mol %) were used to obtain **3e** (110 mg, 0.42 mmol), which was isolated by flash chromatography (10% EA/Hexane) in 68% yield. Yellow crystalline solid, mp. 142-144 ºC. IR (neat, cm^{-1}) : 3424, 2923, 1635, 1609, 1584, 1500, 1418, 1251, 1090, 755, 737; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.85 (m, 2H), 7.69 (d, J = 8 Hz, 1H), 7.63-7.59 (m, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.26 (t, J = 7.6 Hz, 2H), 7.02 (d, J = 8.4 Hz, 1H), 6.82 (t, J = 7.6 Hz, 1H), 4.85 (t, J = 9 Hz, 2H), 3.69 (t, J = 9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 161.3, 155.4, 145.4, 131.4, 130.6, 128.1, 126.7, 125.7, 121.5, 119.9, 118.6, 118, 115.6, 113.6, 73, 31.6; Elemental analysis observed: C, 77.29; H, 4.90; N, 5.16; calcd for $C_{17}H_{13}NO_2$: C, 77.55; H, 4.98; N, 5.32.



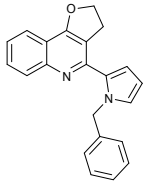
4-(2,3-dihydrofuro[3,2-c]quinolin-4-yl)-2-methoxyphenol (**3f**)

According to the general procedure **IIIa**, **1a** (100 mg, 0.62 mmol), **2f** (141 mg, 0.93 mmol) and AgOTf (6 mg, 0.02 mmol, 3 mol %) were used to obtain **3f** (132 mg, 0.45 mmol), which was isolated by flash chromatography (10 % EA/Hexane) in 72% yield. Greyish White crystalline solid, mp. 175-177 ºC. IR (neat, cm^{-1}) : 3444, 2921, 2853, 1626, 1587, 1538, 1495, 1387, 1368, 1291, 1181, 1057, 971, 845, 733, 697; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.61-7.56 (m, 2H), 7.38 (t, J = 7.4 Hz, 1H), 7.27 (dd, J = 2, J = 8 Hz, 1H), 6.93 (d, J = 8 Hz, 1H), 4.82 (t, J = 9 Hz, 2H), 3.94 (s, 3H), 3.52 (t, J = 9 Hz, 2H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 164, 154.8, 148.6, 148.3, 147.9, 130.9, 130.2, 129.1, 125.6, 121.9, 121.6, 115.7, 115.6, 112.7, 73.6, 56.1, 30.3; Elemental analysis observed: C, 73.57; H, 5.08; N, 4.66; calcd for $C_{18}H_{15}NO_3$: C, 73.71; H, 5.15; N, 4.78.



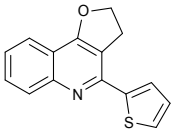
4-(furan-2-yl)-2,3-dihydrofuro[3,2-c]quinoline (**3g**)

According to the general procedure **IIIa**, **1a** (100 mg, 0.62 mmol), **2g** (89 mg, 0.93 mmol) and AgOTf (6 mg, 0.02 mmol, 3 mol %) were used to obtain **3g** (115 mg, 0.48 mmol), which was isolated by flash chromatography (5 % EA/Hexane) in 77% yield. Greyish White crystalline solid, mp. 77-79 ºC. IR (neat, cm^{-1}) : 2961, 2924, 1632, 1590, 1504, 1424, 1345, 1248, 1088, 1034, 885, 808, 748, 657; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.8 Hz, 1H), 7.81 (d, J = 8 Hz, 1H), 7.58-7.54 (m, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 3.2 Hz, 1H), 6.51 (t, J = 1.6 Hz, 1H), 4.82 (t, J = 9 Hz, 2H), 3.57 (t, J = 9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 153.6, 149.0, 145.9, 143.9, 129.8, 128.9, 125.2, 121.3, 115.9, 113.3, 111.9, 111.1, 73.2, 29.9; Elemental analysis observed: C, 75.86; H, 4.59; N, 5.79; calcd for $C_{15}H_{11}NO_2$: C, 75.94; H, 4.67; N, 5.90.



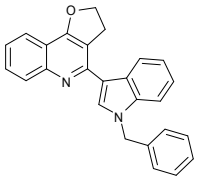
4-(1-benzyl-1H-pyrrol-2-yl)-2, 3-dihydrofuro[3,2-c]quinoline (**3h**)

According to the general procedure **IIIa**, **1a** (100 mg, 0.62 mmol), **2h** (172 mg, 0.93 mmol) and AgOTf (6 mg, 0.02 mmol, 3 mol %) were used to obtain **3h** (110 mg, 0.34 mmol), which was isolated by flash chromatography (7 % EA/Hexane) in 55% yield. Pale Yellow crystalline solid, mp. 68-70 ºC. IR (neat, cm^{-1}) : 3060, 2921, 2850, 1630, 1591, 1501, 1476, 1438, 1420, 1327, 1262, 1087, 1043, 906, 764, 720; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 4.8 Hz, 1H), 7.79 (d, J = 8 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.14-7.05 (m, 3H), 6.96 (d, J = 7.2 Hz, 2H), 6.82 (s, 1H), 6.58-6.56 (m, 1H), 6.22 (t, J = 3.2 Hz, 1H), 5.82 (s, 2H), 4.77 (t, J = 9 Hz, 2H), 3.41 (t, J = 9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 149.2, 148.5, 139.8, 130.7, 129.4, 128.7, 128.4, 126.9, 126.8, 126.2, 124.8, 121.3, 115.5, 114.8, 112.8, 108.1, 72.9, 52.4, 30.6; Elemental analysis observed: C, 80.73; H, 5.47; N, 8.44; calcd for $C_{22}H_{18}N_2O$: C, 80.96; H, 5.56; N, 8.58.



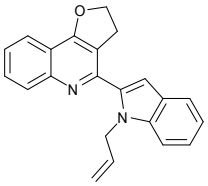
4-(thiophen-2-yl)-2, 3-dihydrofuro[3,2-c]quinoline (**3i**)

According to the general procedure **IIIa**, **1a** (100 mg, 0.62 mmol), **2i** (104 mg, 0.93 mmol) and AgOTf (6 mg, 0.02 mmol, 3 mol %) were used to obtain **3i** (120 mg, 0.47 mmol), which was isolated by flash chromatography (5 % EA/Hexane) in 76% yield. Greyish White crystalline solid, mp. 114-116 ºC. IR (neat, cm^{-1}): 2961, 2922, 2855, 1628, 1587, 1552, 1503, 1370, 1344, 1261, 1080, 1024, 804, 761, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.8 Hz, 1H), 7.78 (d, J = 8 Hz, 1H), 7.57-7.53 (m, 1H),7.47 (brs, 1H), 7.38 (dd, J=2, J=4.8 Hz, 1H), 7.34-7.30 (m, 1H), 7.08-7.05 (m, 1H), 4.84-4.78 (m, 2H), 3.54-3.48 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 149.3, 148.9, 144.8, 129.8, 128.8, 128.3, 127.9, 126.7, 125.1, 121.3, 115.9, 113.1, 72.9, 30.3; Elemental analysis observed: C, 70.95; H, 4.30; N, 5.41;calcd for $C_{15}H_{11}NOS$: C, 71.12; H, 4.38; N, 5.53.



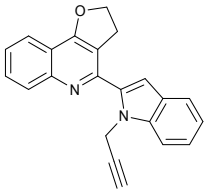
4-(1-benzyl-1H-indol-3-yl)-2, 3-dihydrofuro[3,2-c]quinoline (**3j**)

White crystalline solid, mp. 180-182 ºC. IR (neat, cm^{-1}) : 3137, 2964, 2920, 1629, 1593, 1540, 1504, 1393, 1366, 1297, 1058, 921, 894, 772, 731; ^1H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 5.6 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.60-7.56 (m, 1H) 7.49 (s, 1H), 7.36-7.32 (m, 1H), 7.26-7.19 (m, 6H), 7.08 (d, J=2 Hz, 1H), 7.07 (s, 1H), 5.32 (s, 2H), 4.81 (t, J = 9 Hz, 2H), 3.43 (t, J = 9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 152.4, 149.4, 137.1, 129.4, 129.3, 129, 128.9, 127.9, 127.6, 126.8, 124.5, 123.7, 123.1, 121.3, 116.2, 115.6, 113.9, 109.7, 72.8, 50.4, 30.7; Elemental analysis observed: C, 82.76; H, 5.27; N, 7.29; calcd for $C_{26}H_{20}N_2O$: C, 82.95; H, 5.35; N, 7.44.



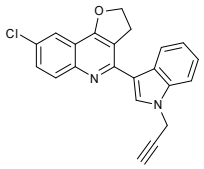
4-(1-allyl-1H-indol-2-yl)-2,3-dihydrofuro[3,2-c]quinoline (**3k**)

According to the general procedure **IIIb**, **1a** (100 mg, 0.62 mmol), **2k** (172 mg, 0.93 mmol) and AgOTf (6 mg, 0.02 mmol, 3 mol %) were used to obtain **3k** (104 mg, 0.32 mmol), which was isolated by flash chromatography (10 % EA/Hexane) in 52% yield. Greyish white crystalline solid, mp. 159-161 ºC. IR (neat, cm^{-1}) : 3285, 2923, 2851, 1610, 1519, 1461, 1344, 1185, 1162, 1121, 1058, 943, 812, 744, 658; ^1H NMR (400 MHz, $CDCl_3$) δ 8.80 (brs, 1H), 8.08 (d, J = 8.8 Hz, 1H), 7.82 (d, J = 8 Hz, 1H), 7.61-7.55 (m, 1H) 7.39 (s, 1H), 7.28-7.21 (m, 3H), 5.97-5.88 (m, 1H), 5.15 (d, J=10.4 Hz, 1H), 5.04 (dd, J = 8 Hz, J = 1 Hz, 1H), 4.77 (t, J = 9 Hz, 2H), 4.68-4.66 (m, 2H), 3.41 (t, J = 9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 152.3, 149.2, 136.7, 132.9, 129.3, 128.8, 128.7, 127.3, 124.3, 123.4, 122.7, 121.2, 121.1, 117.7, 115.7, 115.4, 113.8, 109.5, 72.6, 49, 30.6; Elemental analysis observed: C, 80.79; H, 5.48; N, 8.41; calcd for $C_{22}H_{18}N_2O$: C, 80.96; H, 5.56; N, 8.58.



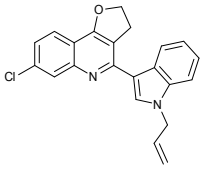
4-(1-(prop-2-ynyl)-1H-indol-2-yl)-2,3-dihydrofuro[3,2-c]quinoline (**3l**)

According to the general procedure **IIIb**, **1a** (100 mg, 0.62 mmol), **2l** (170 mg, 0.93 mmol) and AgOTf (6 mg, 0.02 mmol, 3 mol %) were used to obtain **3l** (120 mg, 0.37 mmol), which was isolated by flash chromatography (10 % EA/Hexane) in 60% yield. Pale Yellow crystalline solid, mp. 148-150 ºC. IR (neat, cm^{-1}) : 3271, 2962, 2909, 2123, 1628, 1587, 1542, 1504, 1390, 1296, 1191, 1059, 895, 735, 655; ^1H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, J = 7.2 Hz, 1H), 8.10 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8 Hz, 1H), 7.59 (d, J = 7.2 Hz, 1H), 7.56 (s, 1H), 7.36-7.32 (m, 2H), 7.30-7.23 (m, 2H), 4.84 (d, J = 2.4, 2H), 4.81 (t, J = 9 Hz, 2H), 3.46 (t, J = 9 Hz, 2H), 2.39 (t, J = 2.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 151.9, 149.1, 136.2, 129.3, 128.8, 128.1, 127.5, 124.4, 123.7, 122.9, 121.3, 121.2, 116.1, 115.4, 113.8, 109.1, 74.1, 72.6, 35.9, 30.4; Elemental analysis observed: C, 81.22; H, 4.88; N, 8.48; calcd for $C_{22}H_{16}N_2O$: C, 81.46; H, 4.97; N, 8.64.



8-chloro-4-(1-(prop-2-ynyl)-1H-indol-3-yl)-2, 3-dihydrofuro[3,2-c]quinoline (**3m**)

According to the general procedure **IIIb**, **1b** (100 mg, 0.51 mmol), **2m** (139 mg, 0.76 mmol) and AgOTf (6 mg, 0.02 mmol, 3 mol %) were used to obtain **3m** (86 mg, 0.24 mmol), which was isolated by flash chromatography (8% EA/Hexane) in 47% yield. Yellow crystalline solid, mp. 163-165 ºC. IR (neat, cm^{-1}) : 3096, 2922, 2817, 1652, 1526, 1468, 1401, 1386, 1175, 1136, 1038, 990, 928, 747; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 6.8 Hz, 1H), 7.99 (d, J = 8.8 Hz, 1H), 7.79 (d, J = 2.4 Hz, 1H), 7.54 (s, 1H), 7.49 (dd, J = 2 Hz, J = 8.8 Hz, 1H), 7.35 (d, J = 6.8 Hz, 1H), 7.30-7.24 (m, 2H), 4.85 (d, J = 2.4 Hz, 2H), 4.81 (t, J = 9 Hz, 2H), 3.45 (t, J = 9 Hz, 2H), 2.39 (t, J = 2.4 Hz, 1H);^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 152.4, 146.3, 132.3, 136.5, 130.5, 130.4, 130.1, 128.4, 127.6, 123.8, 123.3, 121.7, 120.5, 116.1, 114.7, 109.4, 74.5, 72.9, 36.3, 30.7; Elemental analysis observed: C, 73.31; H, 4.12; N, 7.65; calcd for $C_{22}H_{15}ClN_2O$: C, 73.64; H, 4.21; N, 7.81.

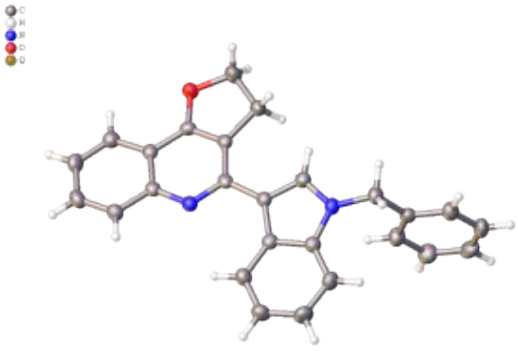


4-(1-allyl-1H-indol-3-yl)-7-chloro-2,3-dihydrofuro[3,2-c]quinoline (**3n**)

According to the general procedure **IIIb**, **1c** (100 mg, 0.51 mmol), **2n** (141 mg, 0.76 mmol) and AgOTf (6 mg, 0.02 mmol, 3 mol %) were used to obtain **3n** (94 mg, 0.26 mmol), which was isolated by flash chromatography (10 % EA/Hexane) in 51% yield. Greyish white crystalline solid, mp. 160-162 ºC IR (neat, cm^{-1}): 2941, 1624, 1585, 1537, 1494, 1417, 1306, 1286, 1213, 1054, 909, 748; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (brs, 1H), 8.07 (brs, 1H), 7.76-7.72 (m, 1H), 7.39 (s, 1H), 7.26-7.19 (m, 4H), 5.99-5.89 (m, 1H), 5.17 (d, J = 10.4 Hz, 1H), 5.06 (d, J = 16.8 Hz, 1H), 4.81-4.76 (m, 2H), 4.69 (d, J = 1.2 Hz, 2H), 3.43-3.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 153.5, 149.7, 136.9, 135.3, 132.9, 129.3, 127.8, 127.4, 125.3, 123.8, 123, 122.8, 121.4, 117.9, 114.1, 113.9, 109.7, 72.9, 49.2, 30.8; Elemental analysis observed: C, 73.11; H, 4.66; N, 7.81; calcd for $C_{22}H_{17}ClN_2O$: C, 73.23; H, 4.75; N, 7.76.

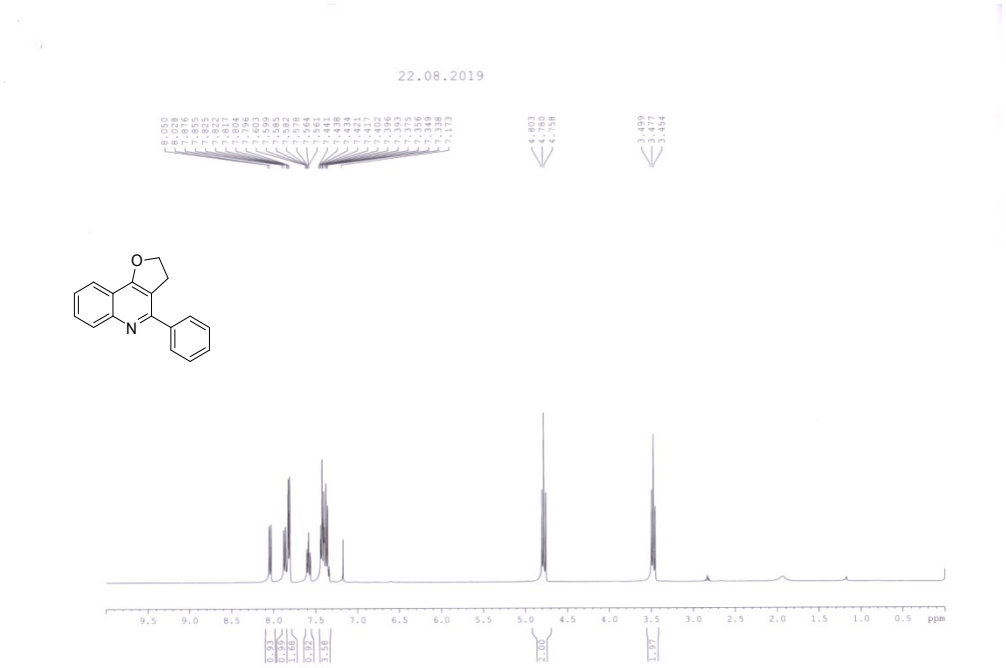
VI. **X-ray structure of 3j**:

CCDC Deposition number 1952336 was allocated. Data Block Name: data_d8_n_0m_a. Unit cell parameters: a 11.6475 (8); b 12.5986 (10); c 26.1644 (19) Pbca.

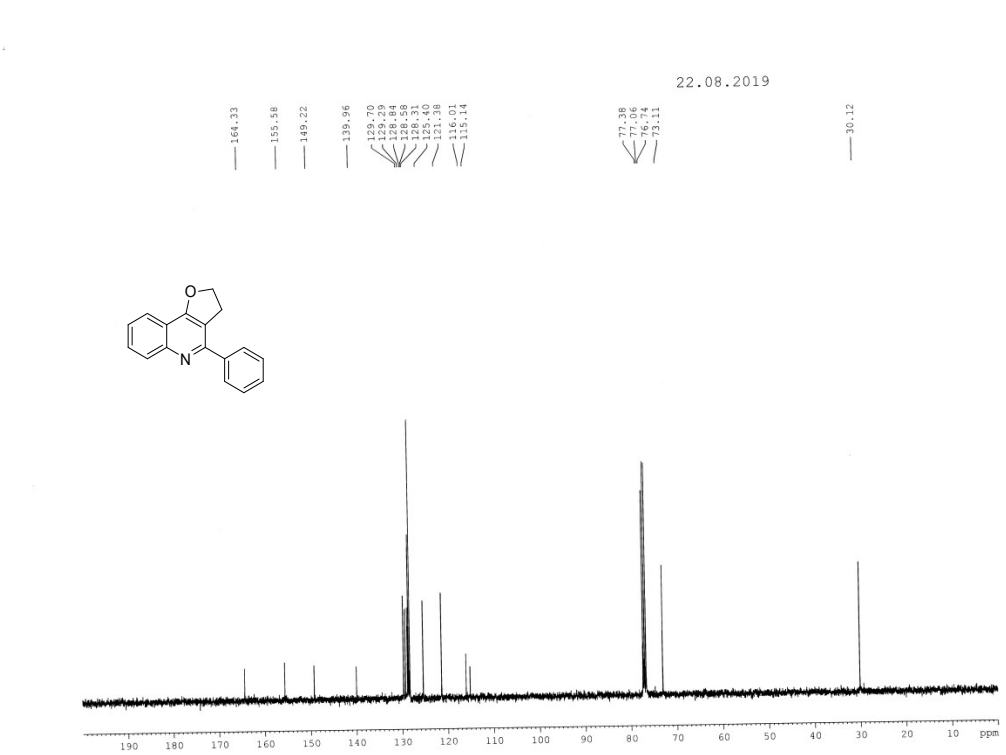


VII. ^{1}H and ^{13}C NMR spectra of compounds 3a-y

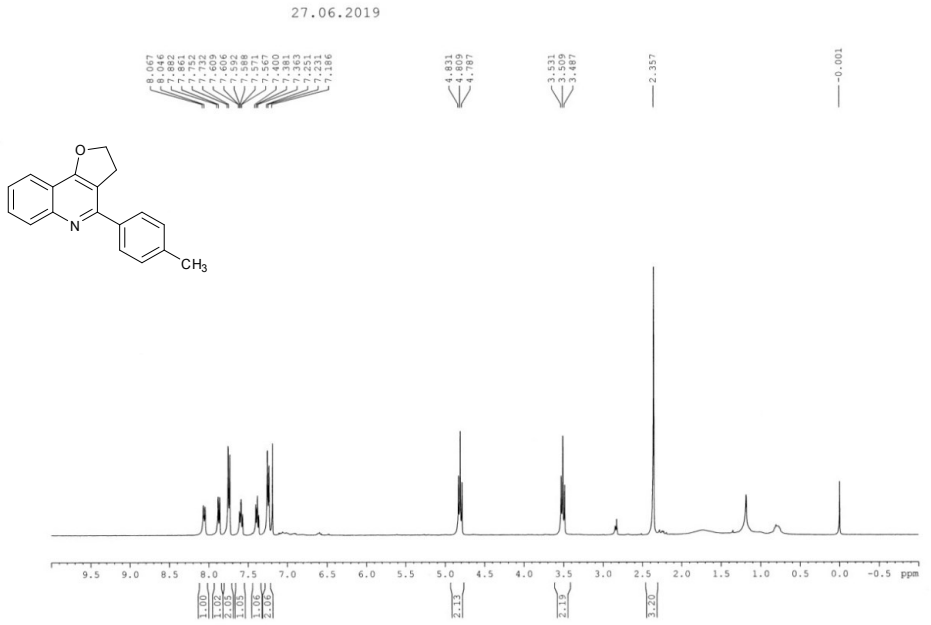
^{1}H NMR Spectrum of **3a**



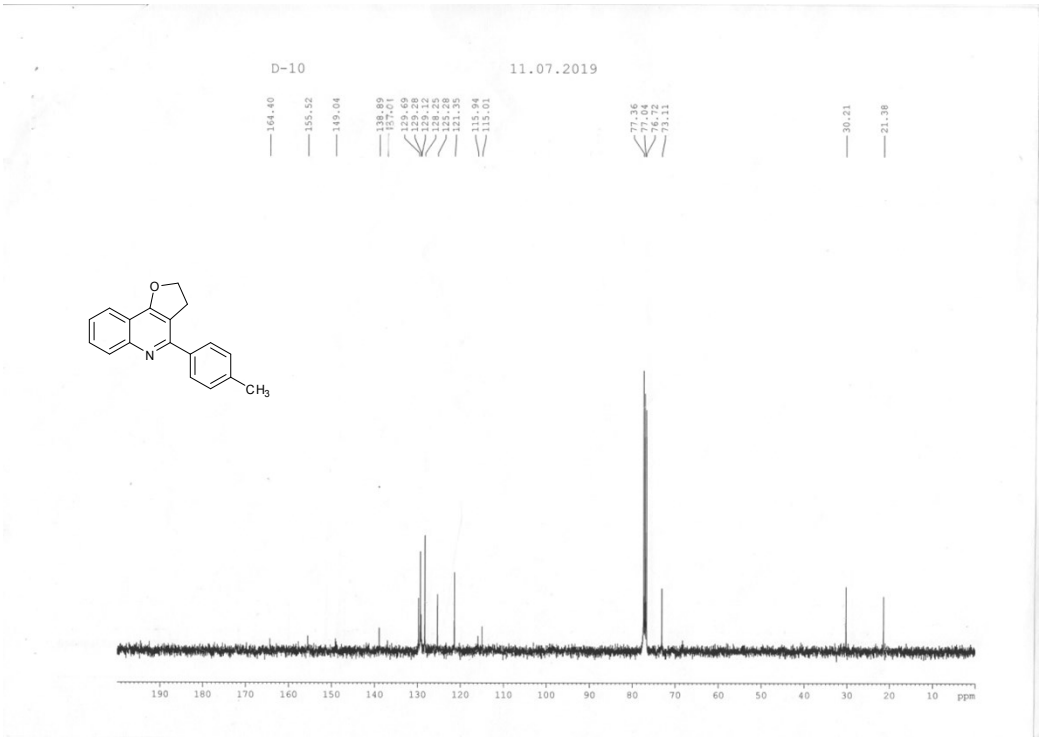
^{13}C NMR Spectrum of **3a**



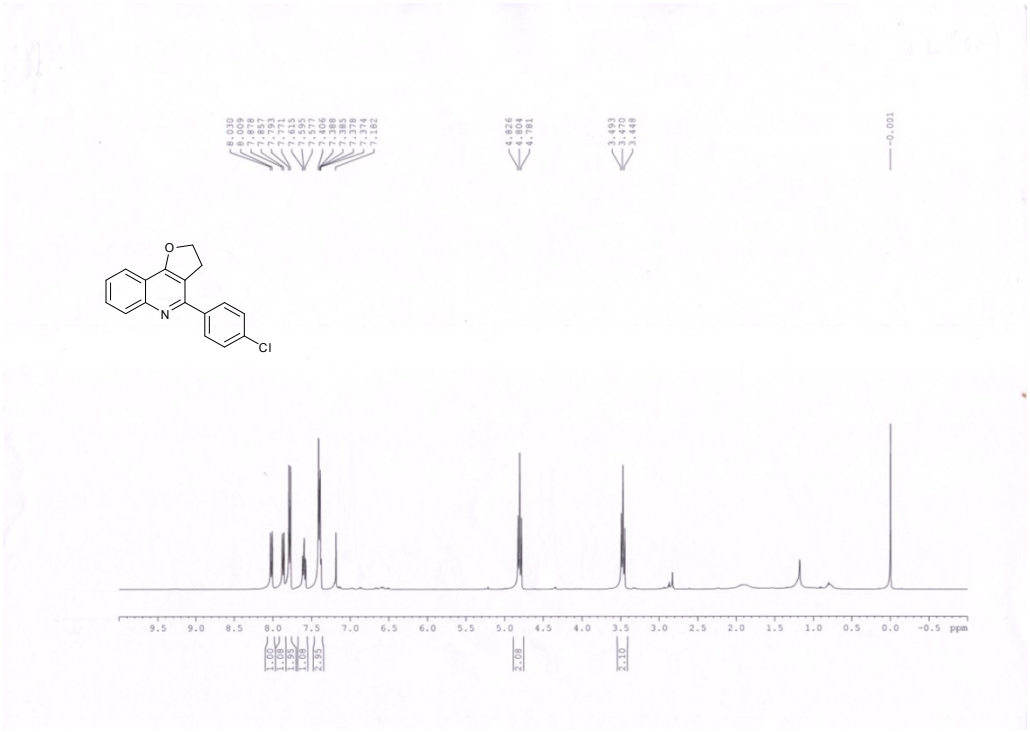
^{1}H NMR Spectrum of **3b**



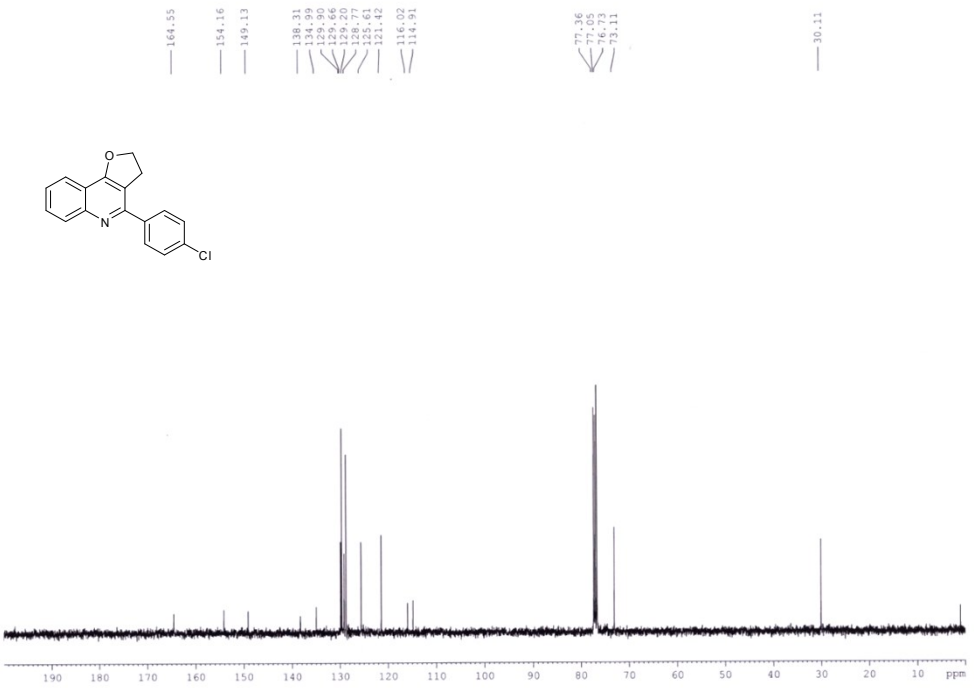
^{13}C NMR Spectrum of **3b**



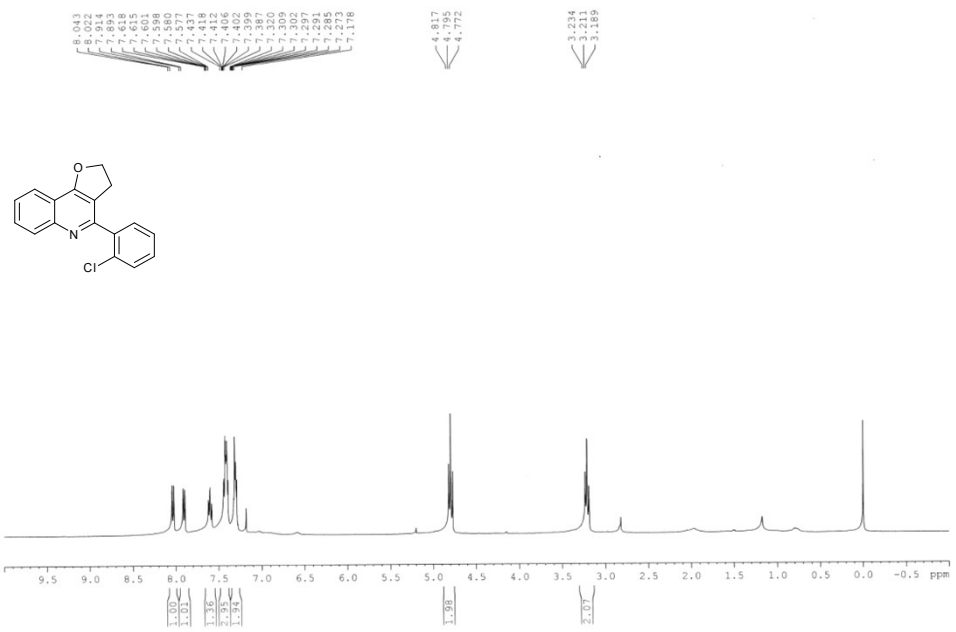
^{1}H NMR Spectrum of **3c**



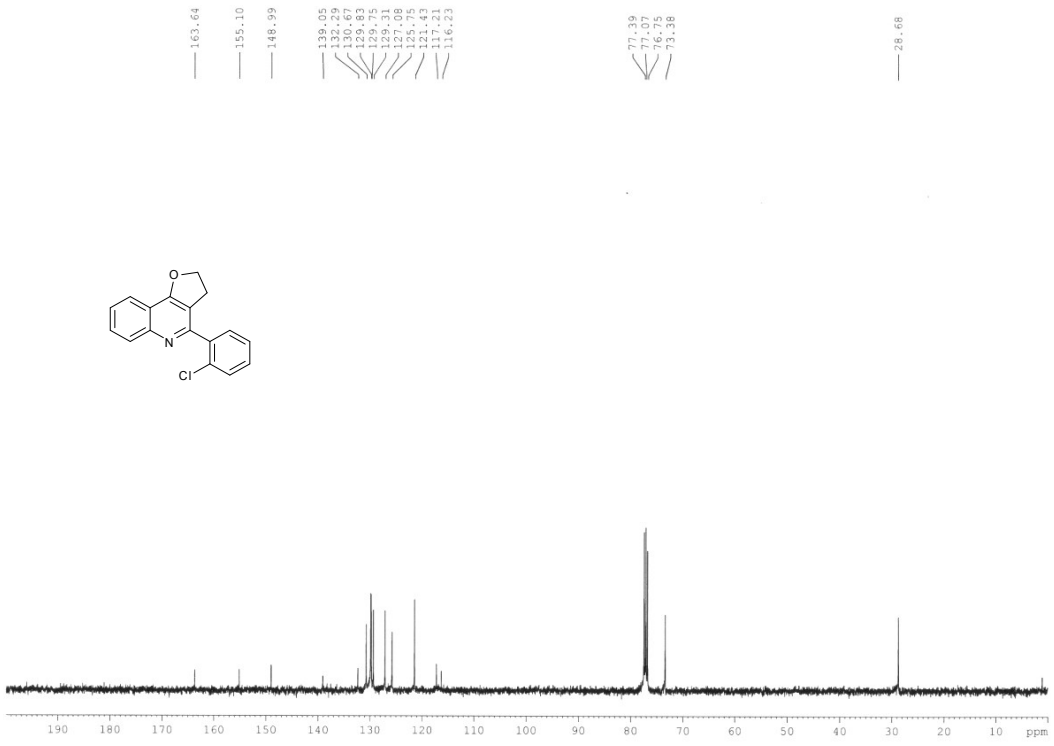
^{13}C NMR Spectrum of **3c**



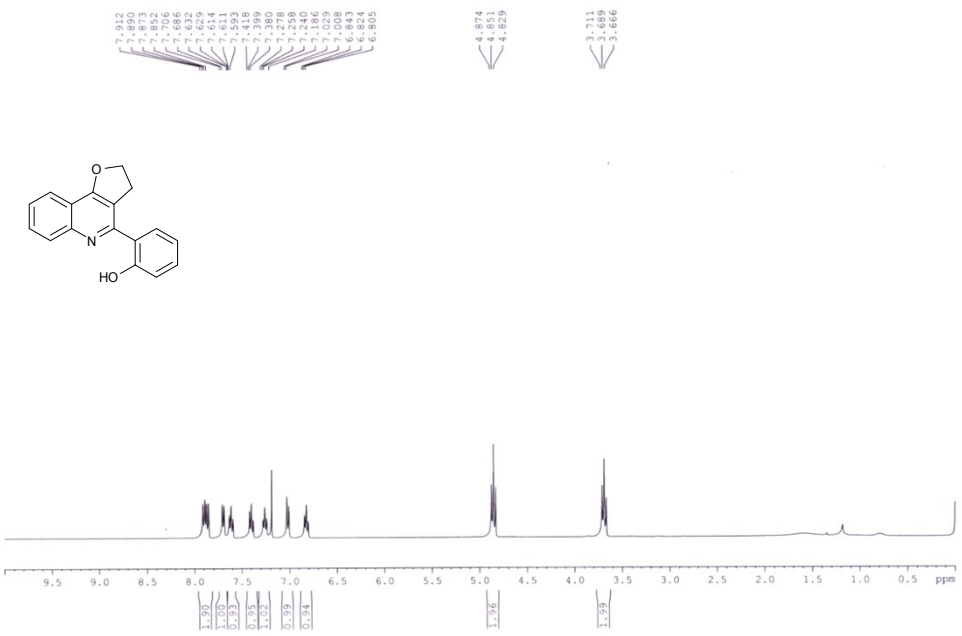
[1]H NMR Spectrum of **3d**



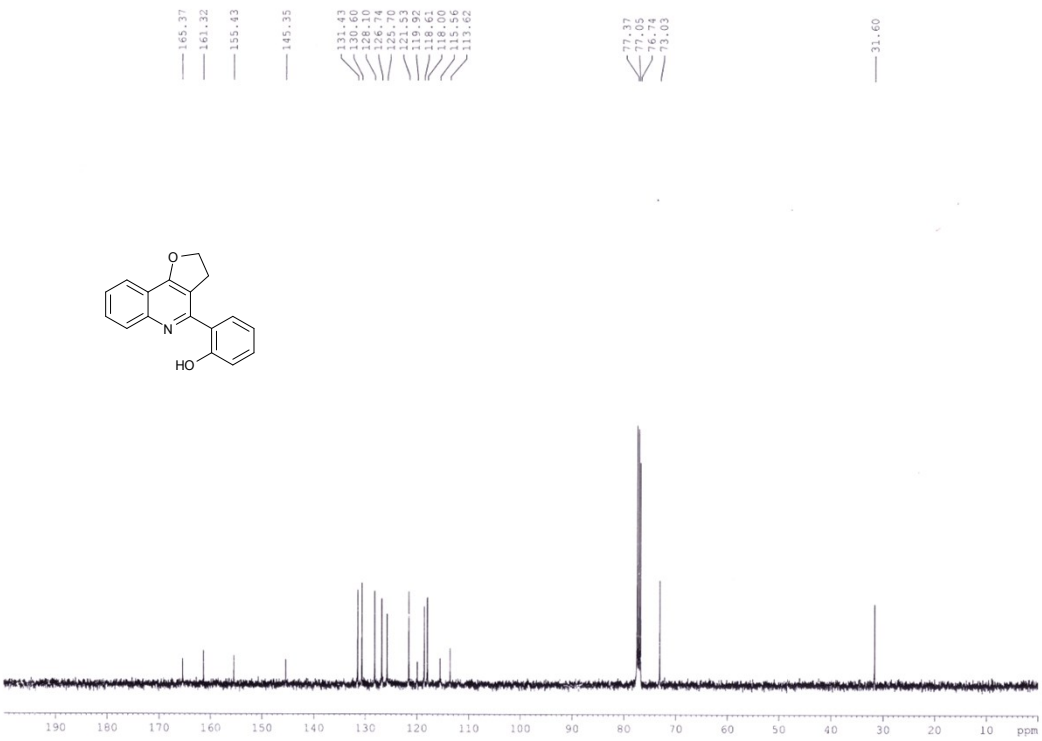
[13]C NMR Spectrum of **3d**



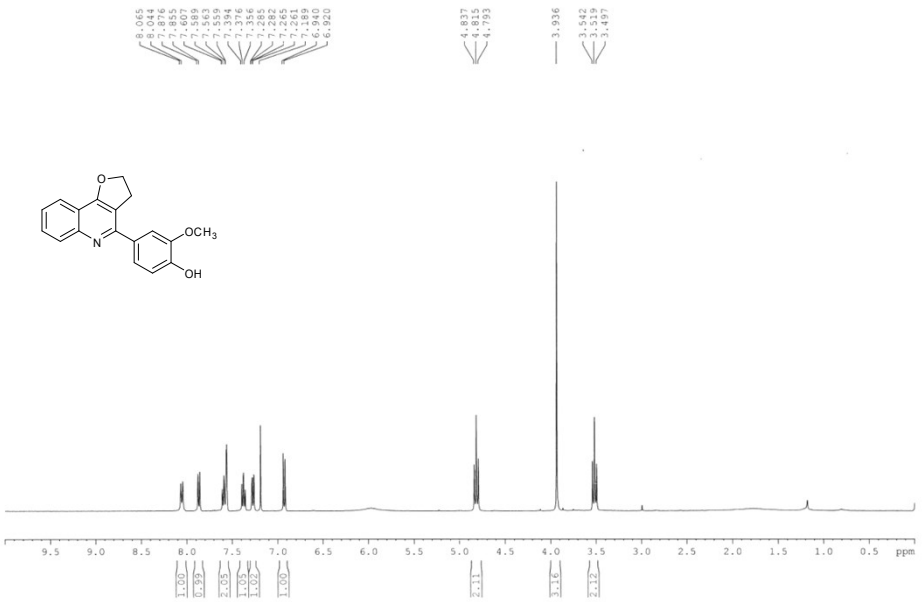
^{1}H NMR Spectrum of **3e**



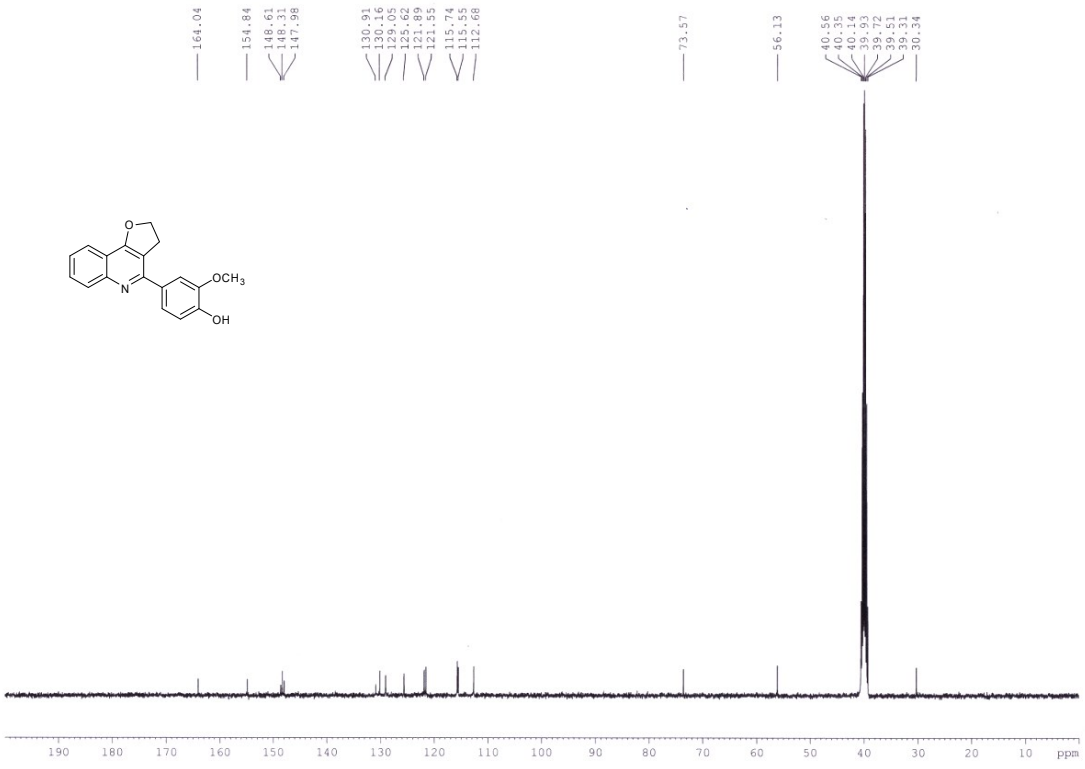
^{13}C NMR Spectrum of **3e**



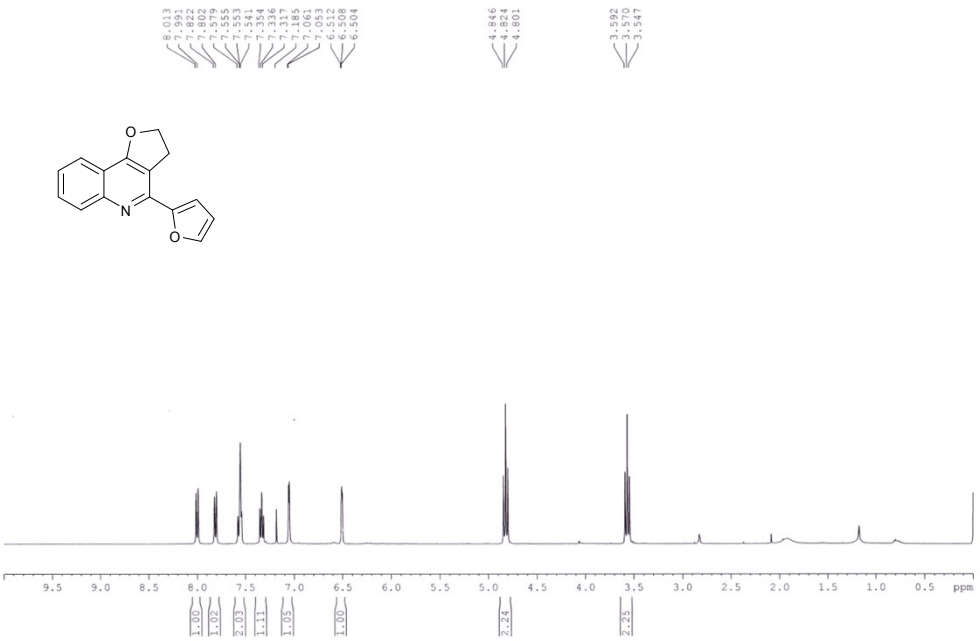
^{1}H NMR Spectrum of **3f**



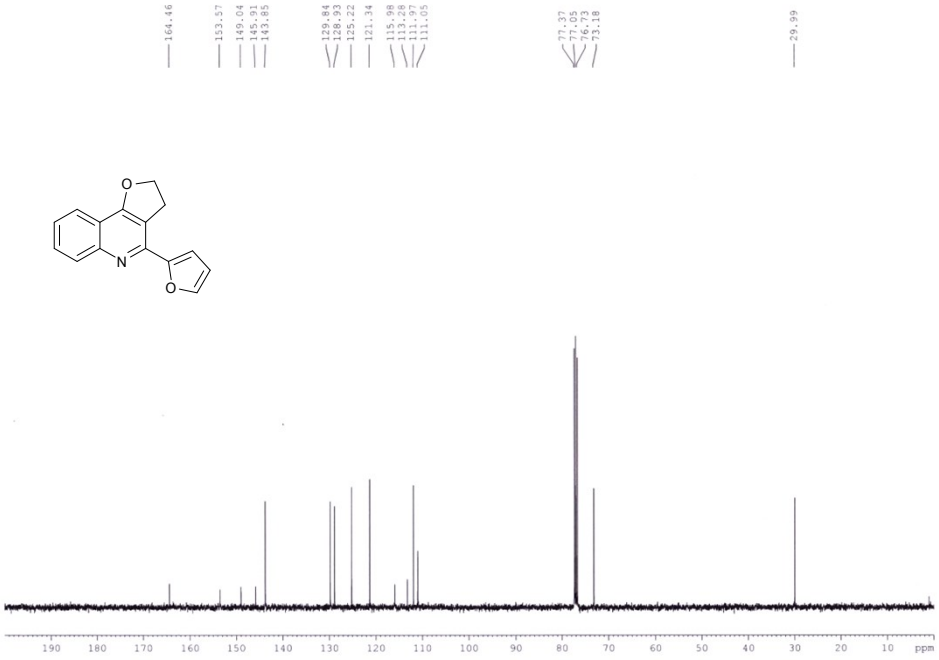
^{13}C NMR Spectrum of **3f**



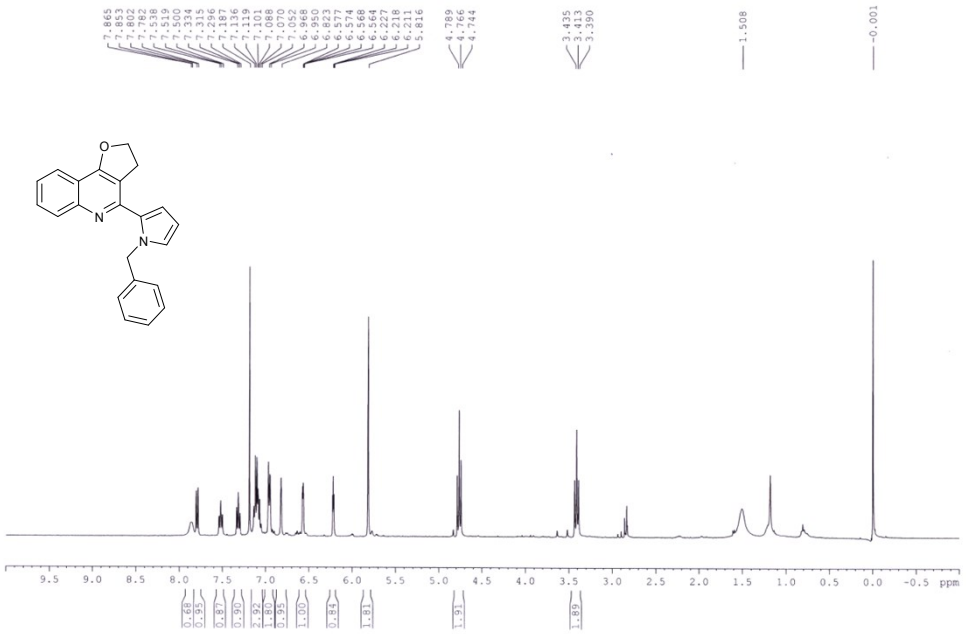
[1]H NMR Spectrum of **3g**



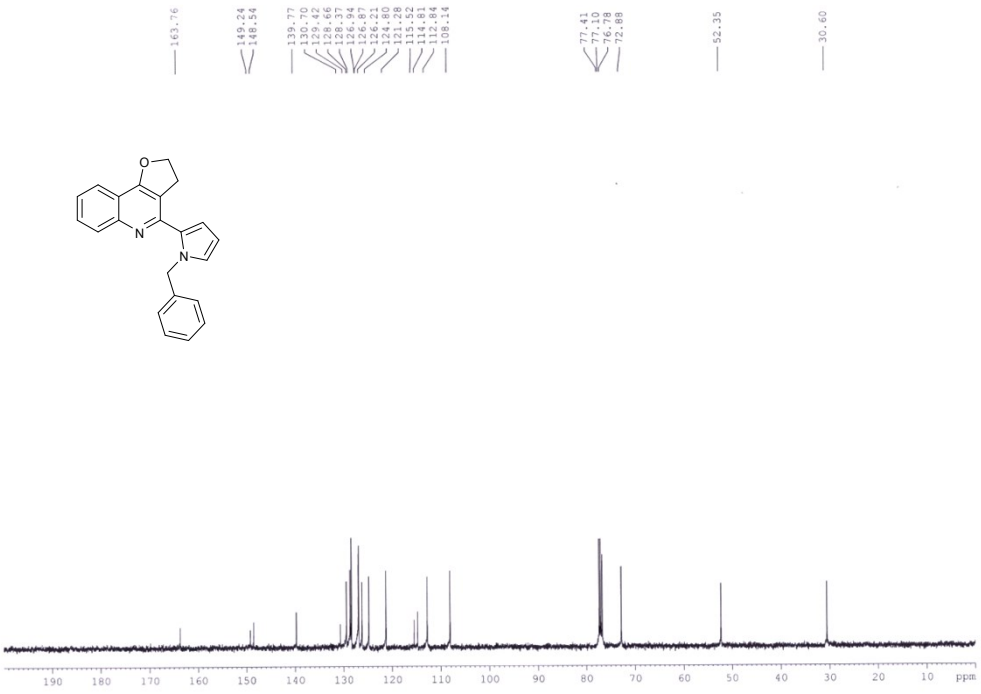
[13]C NMR Spectrum of **3g**



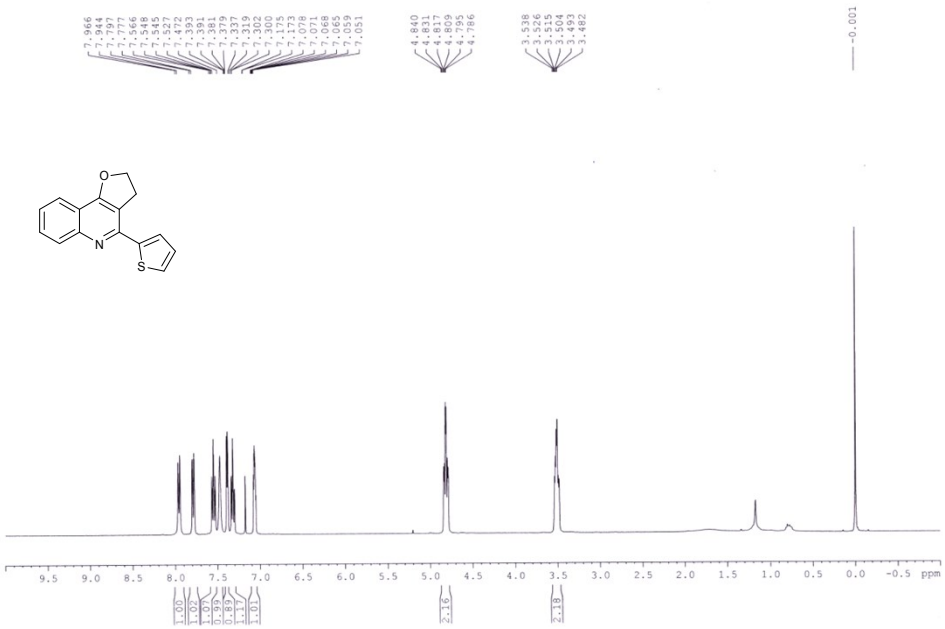
^{1}H NMR Spectrum of **3h**



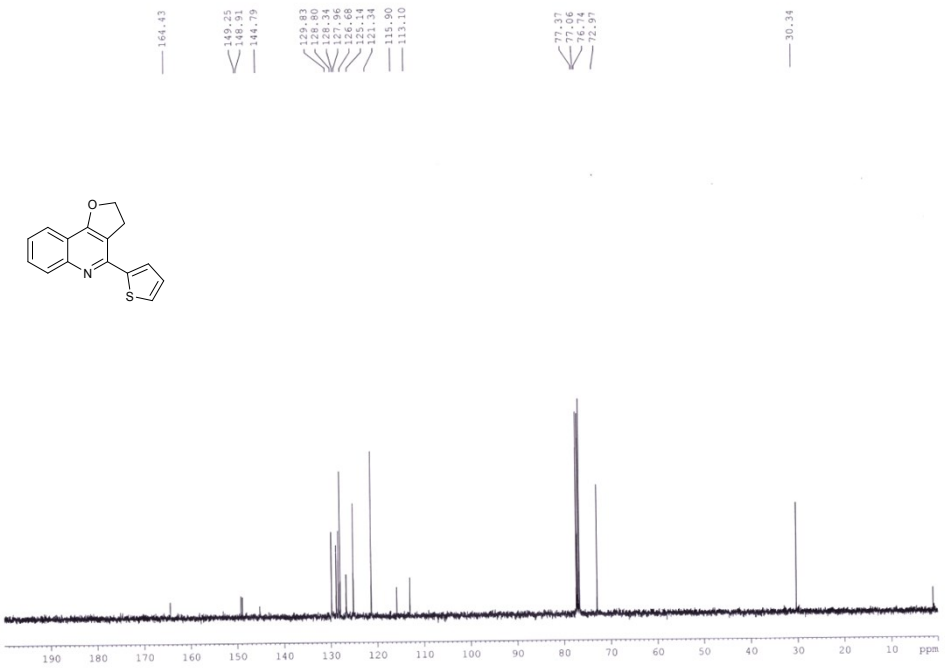
^{13}C NMR Spectrum of **3h**



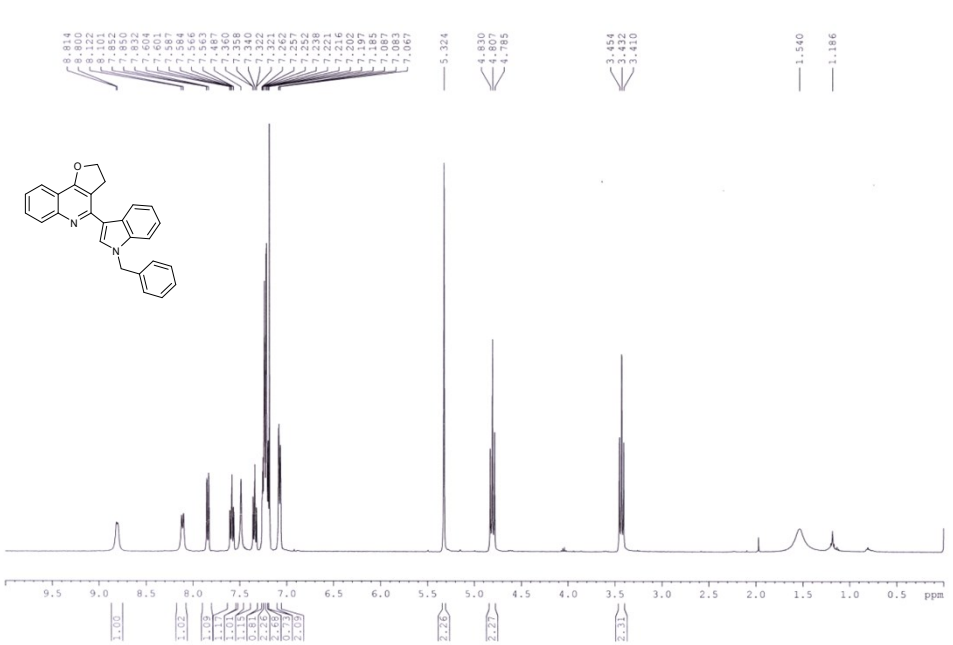
^{1}H NMR Spectrum of **3i**



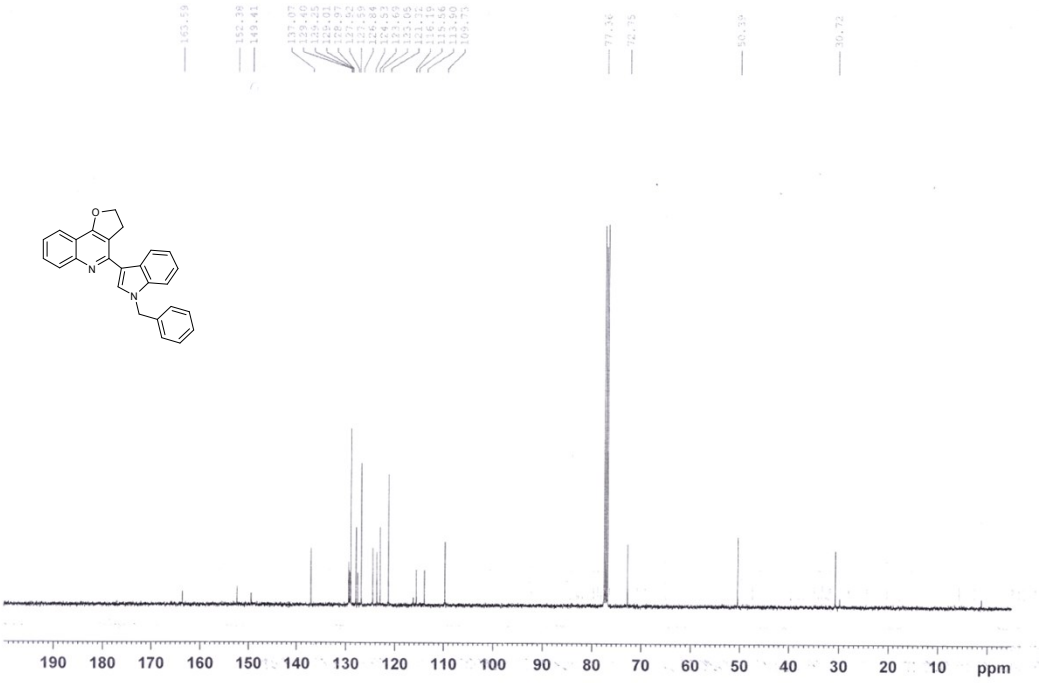
^{13}C NMR Spectrum of **3i**



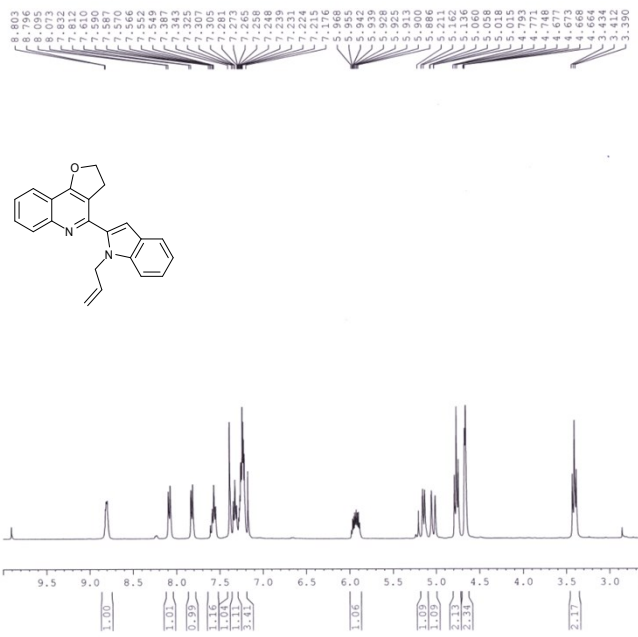
^{1}H NMR Spectrum of **3j**



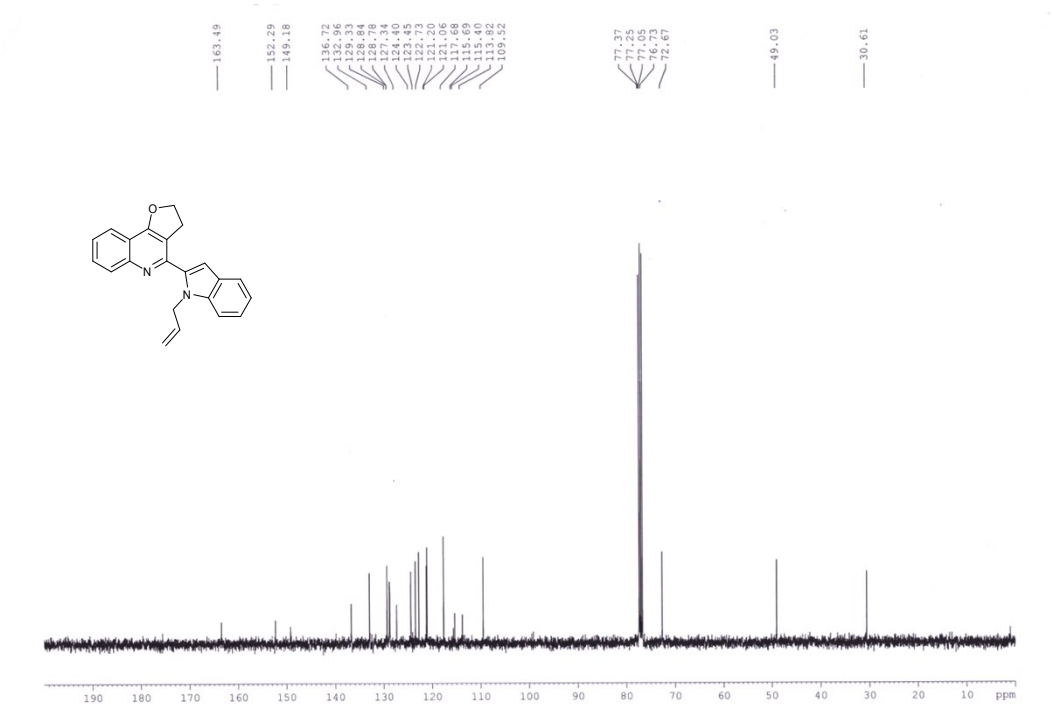
^{13}C NMR Spectrum of **3j**



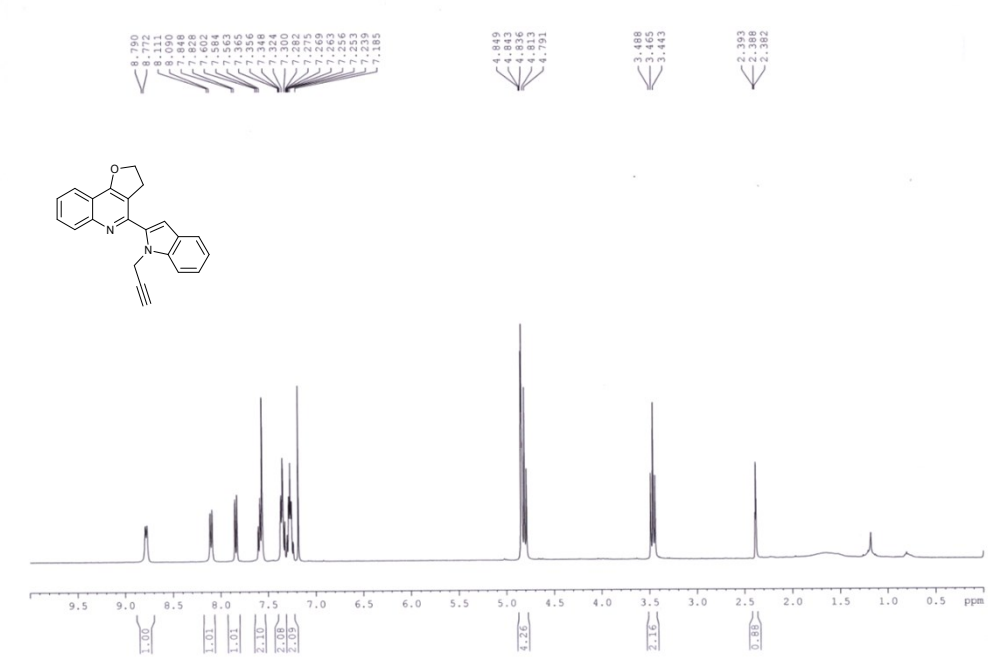
^{1}H NMR Spectrum of **3k**



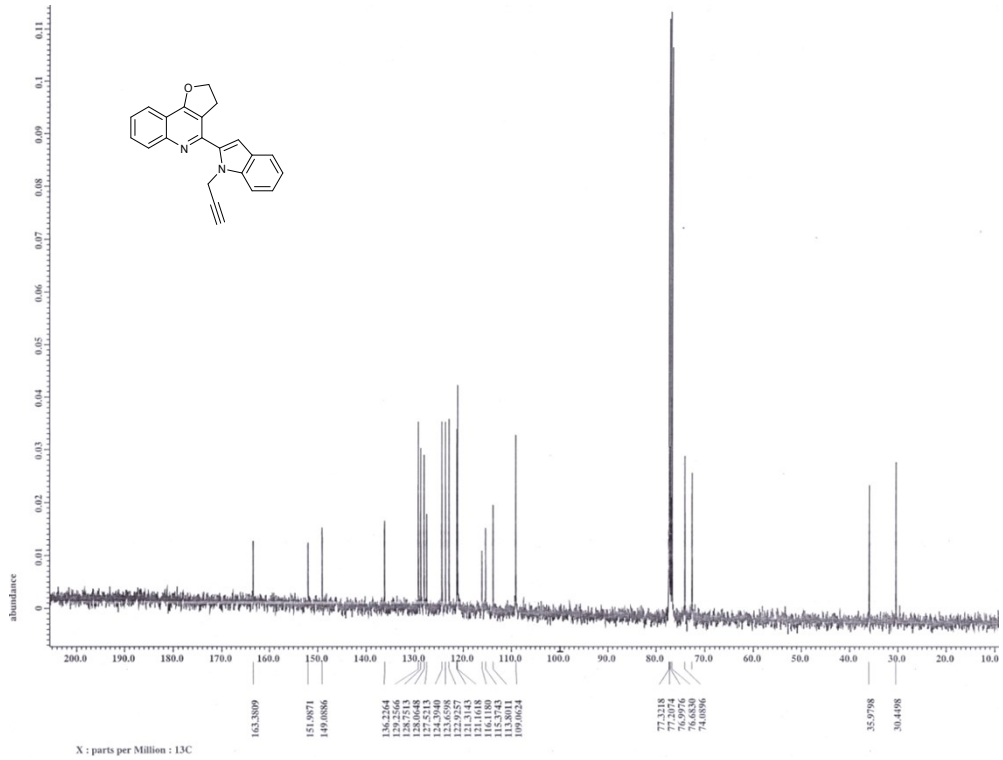
^{13}C NMR Spectrum of **3k**



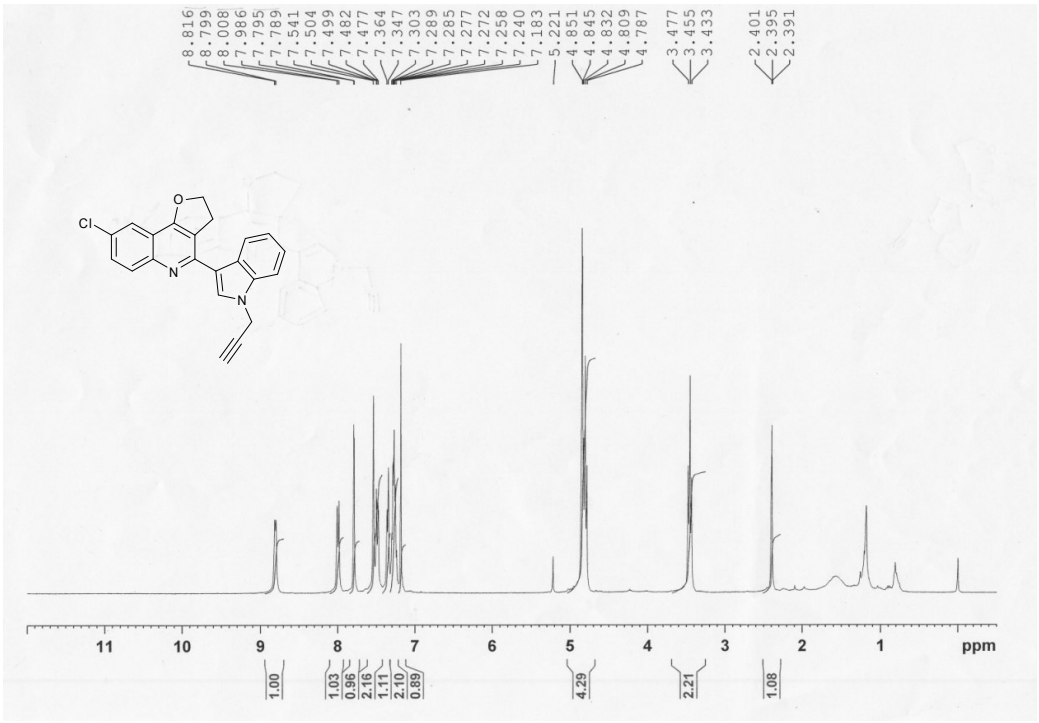
^{1}H NMR Spectrum of **3l**



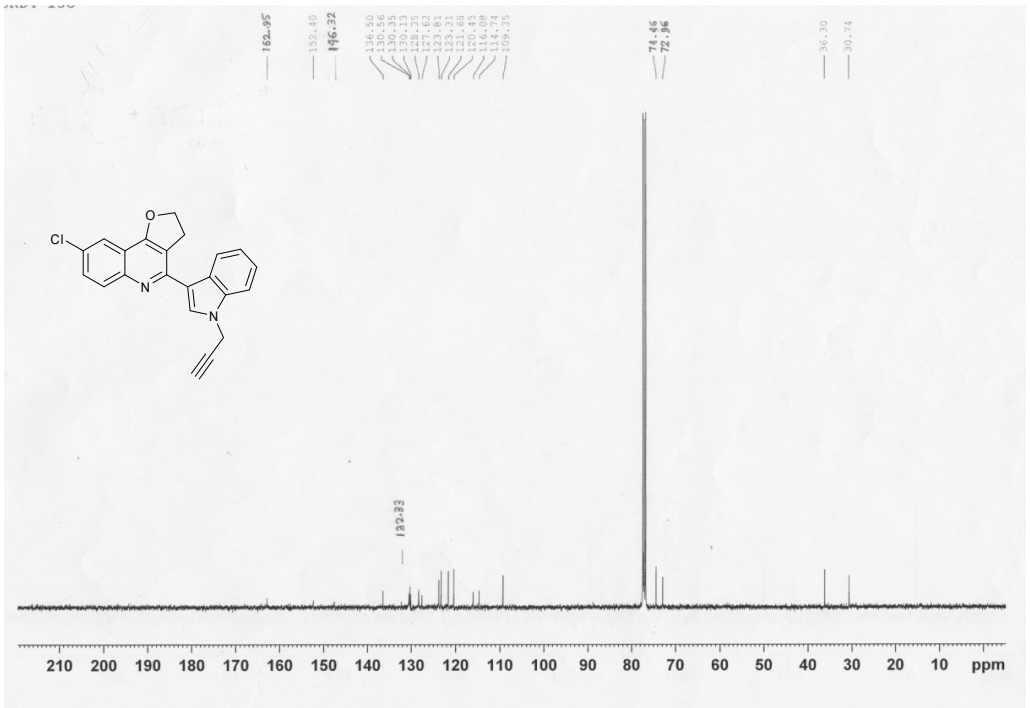
^{13}C NMR Spectrum of **3l**



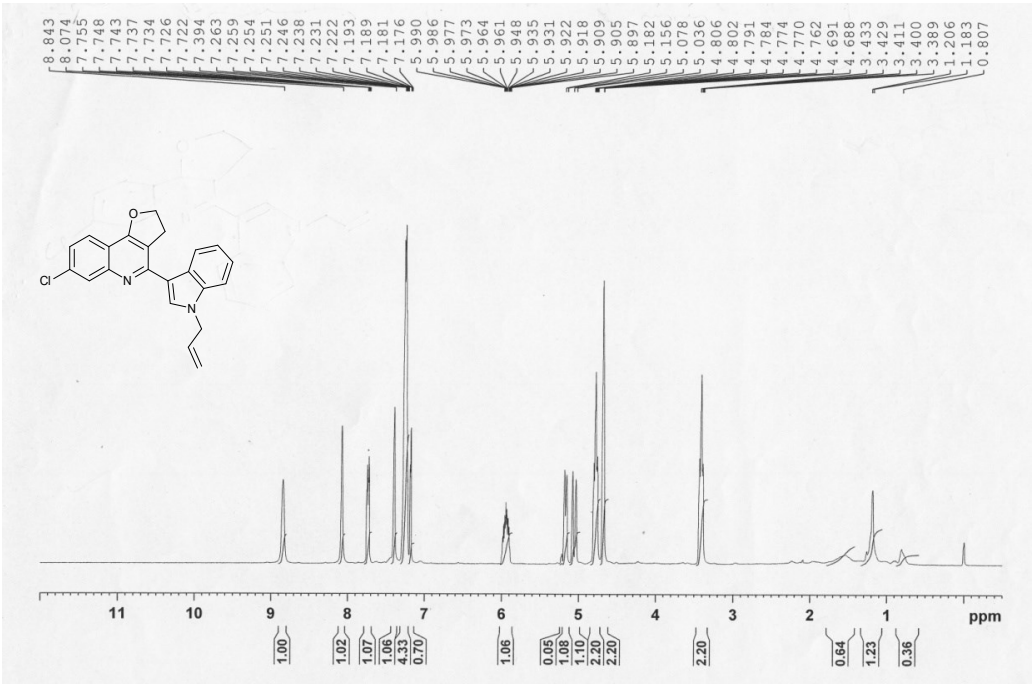
^{1}H NMR Spectrum of **3m**



^{1}H NMR Spectrum of **3m**



[1]H NMR Spectrum of **3n**



[13]C NMR Spectrum of **3n**