Supporting Information

Na_2S mediated synthesis of terminal alkynes from *gem*-dibromoalkenes

Radhey M. Singh,[a*] Durgesh Nandini,[a,b] Kishor Chandra Bharadwaj,[a] Tanu Gupta[a] and Raj Pal Singh[b]

[a]Department of Chemistry, Institute of Science, Banaras Hindu University, Varanasi, India.

[b]Centre for Fire Explosive and Environment Safety, Defense Research Development Organization, New Delhi, India

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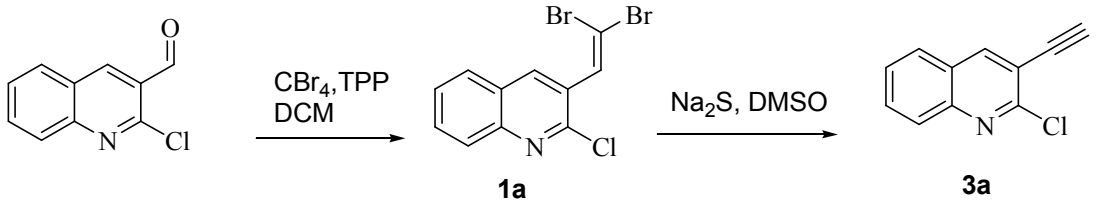
General Information

All the chemicals and reagents were purchased from Sigma-Aldrich. All reagents were used directly without further purification. Common solvents for chromatographic separations were distilled prior to use. Silica gel (100-200 mesh) was used for column chromatography. Reactions were monitored by thin layer chromatography (TLC) which was performed on silica gel coated on aluminum plates (Merck, silica gel 60, F254) and visualized under UV light or iodine chamber. Melting points were measured using Buchi Melting-point apparatus and are uncorrected. ^{1}H (300/400 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on JEOL spectrometer. HRMS (ESI) measurements were performed on an Agilent 1969A TOF mass spectrometer.

General procedure

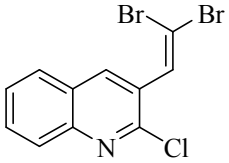


1a **3a**

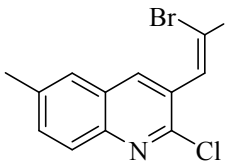
To a solution of 2-chloro-3-formylquinolines (0.191 g, 1.0 mmol) in DCM (3 mL) were added CBr_4 (0.662 g, 2.0 mmol) & PPh_3 (0.524 g, 2.0 mmol) at 0 °C and stirred for 60 min. After completion of reaction, DCM was evaporated and the residue obtained was purified by column chromatography using ethyl acetate and hexane (1:99) to yield 0.292 g of **1a** in 85% yield.

To a solution of 2-chloro-3-(2,2-dibromo-vinyl)-quinoline **1a** (344 mg, 1.00 mmol) in DMSO (2.0 mL) at 20 °C was added $Na_2S.9H_2O$ (120.0 mg, 0.5 mmol) and reaction mixture was stirred for 2h. After complete consumption of starting material (monitored by TLC), water was added along with few drops of AcOH. The reaction mixture was extracted using ethyl acetate. Organic phase was washed with water, dried over anhydrous Na_2SO_4, and concentrated. The residue obtained was purified by column chromatography using hexane-ethyl acetate (1:99) to obtain 2-chloro-3-ethynyl quionline **3a** (140.6 mg, 75% yield) as colorless solid.

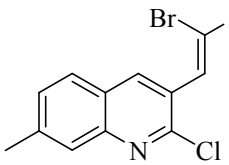
Compounds **3l, 3p-3r** were purified by distillation. After the completion of reaction diethyl ether was added to reaction mixture and the organic phase was washed thrice by water. Ether was removed and the residue obtained was purified by distillation. For **3l, 3p, 3r** distillation was performed under reduced pressure. **3q** was purified by distillation under argon atmosphere.



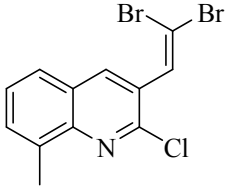
2-chloro-3-(2,2-dibromo-vinyl)-quinoline(1a) white solid; yield: 85%; mp 100 °C; IR (KBr): 3030, 1617, 1139, 832 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.58(t, *J*=8.1 Hz, 1H), 7.65(s, 1H), 7.77(t, *J*=7.8Hz, 1H), 7.85(d, *J*= 8.1 Hz, 1H), 8.01(d, *J*= 8.1 Hz,1H), 8.46(s,1H); ^{13}C NMR (75 MHz, $CDCl_3$,): δ 94.6, 126.5, 127.6, 128.3, 130.3, 132.6, 134.5, 138.6, 141.6, 146.9,148.7.



2-chloro-3-(2,2-dibromo-vinyl)-6-methyl quinoline (1b) White solid; yield: 89%; mp 96 °C; IR (KBr): 3021, 1052, 821 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.54 (s, 3H), 7.57-7.63 (m, 3H), 7.89 (d, *J=8.4*, 1H), 8.36 (s,1H); ^{13}C NMR (75 MHz, $CDCl_3$,): δ 21.5, 94.3, 126.6, 126.7, 128.0, 132.8, 133.0, 133.4, 137.6, 138.0, 145.5, 147.8.

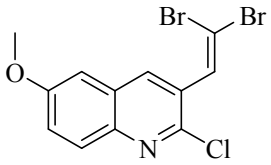


2-chloro-3-(2,2-dibromo-vinyl)-7-methyl quinoline (1c) White solid; Yield: 88%; mp 82 °C; IR (KBr): 3022, 1045, 799 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.56(s, 3H), 7.41(d,*J*=8.4 Hz,1H), 7.63(s,1H), 7.73(s,1H), 7.77(d, *J*=6.3 Hz,1H), 8.41(s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.0, 94.1, 124.5, 127.1, 127.4, 129.7, 132.7, 135.5, 138.2, 141.9, 147.1, 148.7.

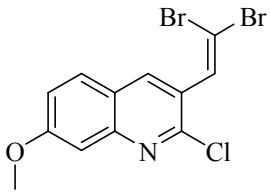


2-chloro-3-(2,2-dibromo-vinyl)-8-methyl-quinoline(1d) White solid; Yield: 84%; mp 85 °C ; IR (KBr): 3022, 1085, 831 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.76 (s, 3H), 7.45 (t, *J*= 7.8Hz, 1H), 7.59 (d, *J*=6.9 Hz, 1H), 7.65

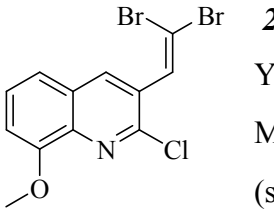
(s, 1H), 7.67 (d, J=8.1 Hz, 1H), 8.40 (s,1H); ^{13}CNMR (75 MHz, $CDCl_3$): δ 17.7, 94.2, 125.7, 126.6, 127.2, 127.8, 131.2, 132.8, 136.6, 138.8, 146.1, 147.6.



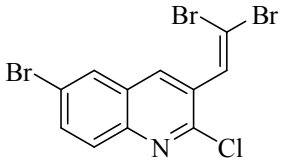
2-chloro-3-(2,2-dibromo-vinyl)-6-methoxy-quinoline(1e) White solid; Yield: 87%; mp 125 °C; IR (KBr): 3038, 1050, 823 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.93(s, 3H), 7.09(s, 1H), 7.39 (d, *J*=6.6 Hz,1H), 7.63 (s,1H), 7.85(d, *J*= 8.1 Hz,1H), 8.34 (s,1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.6, 94.3, 105.1, 123.8, 127.7, 128.3, 129.7, 132.8, 137.2, 143.0, 146.1, 158.4.



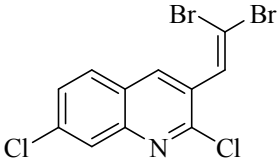
2-chloro-3-(2,2-dibromo-vinyl)-7-methoxy-quinoline(1f) White solid; Yield: 92%; mp 130 °C; IR (KBr): 2995, 1131, 816 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.93 (s, 3H), 7.20 (d, *J*= 8.7 Hz, 1H), 7.31 (s, 1H), 7.61 (s, 1H), 7.70 (d, *J*= 9.0 Hz, 1H), 8.36 (s,1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.6, 93.6, 106.5, 121.6, 125.5, 128.7, 132.6, 134.5, 138.0, 139.4, 148.8, 162.1.



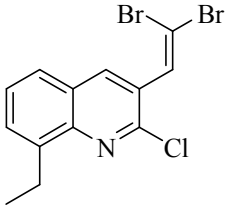
2-chloro-3-(2,2-dibromo-vinyl)-8-methoxy-quinoline(1g) White solid; Yield: 82%; mp 160 °C; IR (KBr): 3014, 1118, 828 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.94(s, 3H), 7.23(t, *J*=7.8 Hz,1H), 7.57-7.72 (m, 3H), 8.35 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$):δ 55.5, 93.4, 106.4, 120.8, 125.8, 129.9, 131.6, 133.8, 137.9, 139.8, 147.9, 161.9.



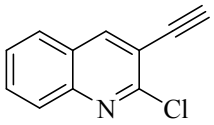
6-Bromo-2-chloro-3-(2,2-dibromo-vinyl)-quinoline (1h) White solid; Yield: 89%; mp 180 °C; IR (KBr): 3035, 1074, 829 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63(s, 1H), 7.82(d, *J*=9.0 Hz, 1H), 7.87(d, *J*=8.7 Hz, 1H) 8.02(s, 1H), 8.36(s,1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 94.9, 120.8, 122.3, 127.2, 128.6, 129.4, 131.8, 134.0, 137.1, 144.9, 148.5.



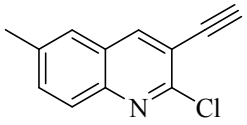
2,7-dichloro-3-(2,2-dibromo-vinyl)-quinoline(1i) White solid; Yield: 87%; mp 180 °C ; IR (KBr): 3035, 1074, 829 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.53 (d, *J*=7.2 Hz, 1H), 7.62 (s, 1H), 7.78 (d, *J*=8.7 Hz, 1H), 7.99 (s, 1H), 8.43 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 95.0, 124.9, 127.5, 128.9, 132.3, 134.2, 137.2, 137.7, 138.2, 147.1, 150.0.



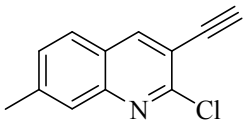
2-chloro-3-(2,2-dibromo-vinyl)-8-ethyl-quinoline (1j) White solid; Yield: 80%; mp 98-99 °C; IR (KBr): 3021, 1079, 832 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.35 (t, *J*=7.2 Hz, 3H), 3.23 (q, *J*=7.5 Hz, 2H), 7.48 (t, *J*=7.5 Hz, 1H), 7.59 (d, *J*=6.9 Hz, 1H), 7.63 (s, 1H), 7.65 (d, *J*=8.1 Hz, 1H), 8.38 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.8, 24.1, 94.1, 125.6, 126.6, 127.3, 129.5, 130.9, 132.8, 138.8, 142.3, 145.5, 147.5.



2-chloro-3-ethynyl-quinolines (3a); colorless solid (75% yield). m.p. 114-115 °C; ^1H NMR (300 MHz, $CDCl_3$) δ/ppm: 3.49 (s, 1H), 7.56-7.61 (m, 1H), 7.73-7.80 (m, 2H), 8.01 (d, *J*= 8.4 Hz, 1H), 8.34 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$)δ/ppm: 78.9, 83.4, 116.2, 126.4, 127.6, 128.6, 130.9, 131.4, 138.5, 146.3, 149.2; HRMS (ESI): *m/z* $[M+H]^+$ found : 188.0272 $C_{11}H_6ClNH$ calculated 188.0267.

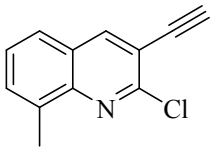


2-chloro-3-ethynyl-6-methyl quinoline (3b); colorless solid (81% yield); m.p. 128-129 °C; ^1H NMR (300 MHz, $CDCl_3$)δ/ppm:2.53 (s, 3H), 3.48 (s, 1H), 7.54-7.59 (m, 2H), 7.89 (d, *J*=8.7 Hz, 1H), 8.24 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$)δ/ppm:21.5, 79.0, 84.5, 115.9, 123.8, 127.2, 127.8, 131.1, 132.2, 147.2, 150.2; HRMS (ESI): *m/z* $[M+H]^+$ found : 202.0421 $C_{12}H_8ClNH$ calculated 202.0424.

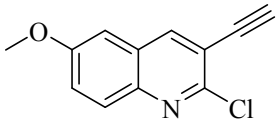


2-chloro-3-ethynyl-7-methyl quinoline (3c); colorless solid (83% yield); m.p. 125-126 °C; ^1H NMR (300 MHz, $CDCl_3$)δ/ppm:2.56 (s, 3H), 3.46 (s,

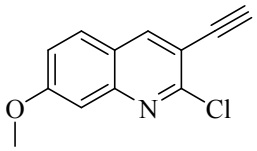
1H), 7.40 (d, *J*=8.1 Hz, 1H), 7.63 (s, 1H), 7.76 (d, *J*=7.5 Hz, 1H), 8.40 (s, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm:22.0, 79.1, 83.4, 114.12, 124.6, 129.7, 132.8, 138.2, 142.0, 142.3, 147.2, 148.7; HRMS (ESI): *m/z* $[M+H]^+$ found : 202.0417 $C_{12}H_8ClNH$ calculated 202.0424.



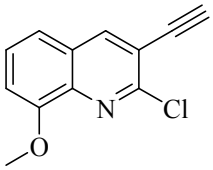
2-chloro-3-ethynyl-8-methyl quinoline (3d); Colorless solid (78% yield); m.p. 109-110 °C;^{1}H NMR (300 MHz, $CDCl_3$)δ/ppm:2.75 (s, 3H), 3.47 (s, 1H), 7.43-7.48 (m, 1H), 7.58-7.63 (m, 2H), 8.30 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm:17.2, 78.5, 84.3, 115.2, 125.6, 126.7, 129.2, 132.8, 134.4, 138.0, 145.5, 147.8; HRMS (ESI): *m/z* $[M+H]^+$ found : 202.0420 $C_{12}H_8ClNH$ calculated 202.0424.



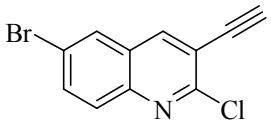
2-chloro-3-ethynyl-6-methoxy quinoline (3e); Colorless solid (82% yield); m.p. 107-108 °C; ^{1}H NMR (300 MHz, $CDCl_3$)δ/ppm:3.48 (s, 1H), 3.92 (s, 3H), 7.02 (d, *J*= 2.4 Hz, 1H), 7.36-7.37 (m, 1H), 7.89 (d, *J*=9.3 Hz, 1H), 8.22 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$)δ/ppm: 55.6, 79.0, 83.8, 104.6, 116.8, 124.7, 127.4, 129.8, 141.2, 142.7, 147.8, 158.5; HRMS (ESI): *m/z* $[M+H]^+$ found : 218.0382 $C_{12}H_8ClNOH$ calculated 218.0373.



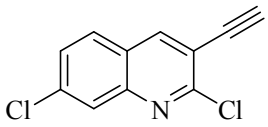
2-chloro-3-ethynyl-7-methoxy quinoline (3f); Colorless solid (83% yield); m.p. 90-91°C; ^{1}H NMR (300 MHz, $CDCl_3$)δ/ppm:3.45 (s, 1H), 3.94 (s, 3H), 7.25-7.32 (m, 1H), 7.64-7.67 (m, 2H), 8.24 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$)δ/ppm: 51.7, 79.2, 84.0, 117.3, 125.6, 127.2, 128.0, 138.0, 141.4, 144.5, 148.8, 159.1; HRMS (ESI): *m/z* $[M+H]^+$ found : 218.0375 $C_{12}H_8ClNOH$ calculated 218.0373.



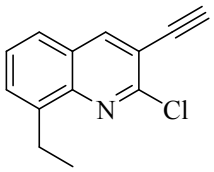
2-chloro-3-ethynyl-8-methoxy quinoline (3g); Colorless solid (74% yield); m.p. 131-132°C; ^{1}H NMR (300 MHz, $CDCl_3$)δ/ppm: 3.49 (s, 1H), 4.06 (s, 3H), 7.10 (d, *J*=7.5 Hz, 1H), 7.34 (d, *J*=8.1 Hz, 1H), 7.47-7.52 (m, 1H), 8.30 (s, 1H);^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 56.1, 78.2, 84.1, 109.7, 118.8, 126.6, 126.7, 127.9, 130.8, 142.5, 145.0, 155.8; HRMS (ESI): *m/z* $[M+H]^+$ found : 218.0378 $C_{12}H_8ClNOH$ calculated 218.0373.



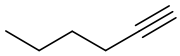
6-bromo-2-chloro-3-ethynylquinoline (3h); Colorless solid (68% yield); m.p. 128°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.53 (s, 1H), 7.80 (d, *J*=7.6 Hz, 1H), 7.82 (d, *J*=7.2 Hz, 1H), 7.94 (s, 1H), 8.22 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$,) δ/ppm: 82.5, 84.2, 84.8, 118.2, 127.2, 129.1, 130.1, 134.7, 141.3, 145.1, 152.6; HRMS (ESI): *m/z* $[M+H]^+$ found : 265.9379 $C_{11}H_5BrClNH$ calculated 265.9372.



2,7-dichloro-3-ethynylquinoline (3i); Colorless solid (70% yield); m.p. 125°C; ^{1}H NMR (300 MHz, $CDCl_3$)δ/ppm: 3.51 (s, 1H), 7.53 (d, *J*= 8.7 Hz, 1H), 7.72 (d, *J*=8.7 Hz, 1H), 8.01 (s, 1H), 8.30 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 81.6, 84.0, 117.5, 123.8, 127.7, 128.3, 129.7, 137.2, 143.0, 146.1, 158.4; HRMS (ESI): *m/z* $[M+H]^+$ found : 221.9870 $C_{11}H_5Cl_2NH$ calculated 221.9877.



8-ethyl-2-chloro-3-ethynylquinoline (3j); Colorless solid (71% yield); m.p. 130°C; ^{1}H NMR (300 MHz, $CDCl_3$)δ/ppm: 1.35 (t, *J*= 7.5 Hz, 3H), 3.23 (q, *J*=7.2 Hz, 2H), 3.47 (s, 1H), 7.50 (d, *J*=7.5 Hz, 1H), 7.60 (s, 2H), 8.30 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm: 14.9, 23.8, 79.1, 83.5, 83.6, 125.0, 126.2, 127.4, 129.9, 142.5, 142.9, 142.93, 145.2 HRMS (ESI): *m/z* $[M+H]^+$ found : 216.0610 $C_{13}H_{10}ClNH$ calculated 216.0580.



Hexyne-1 (3q); Colorless liquid (42% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm: 0.91 (t, *J*= 7.2 Hz, 3H), 1.39-1.57 (m, 4H), 1.92-1.93 (m, 1H), 2.16-2.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm: 13.1, 18.1, 21.9, 30.6, 68.0, 84.8.

Compounds 3l-3r are known compounds.[1]

1 (*a*) S. Liu, X. Chen, Y. Hu, L. Yuan, S. Chen, P. Wu, W. Wang, S. Zhang and W. Zhang, *Adv. Synth. Catal*., 2015, **357**, 553; (*b*) K. Park, T. Palani, A. Pyo and S. Lee *Tetrahedron Lett*., 2012, **53**, 733; (*c*) M. Beshai, B. Dhudshia, R. Mills, A. N. Thadani, *Tetrahedron Lett*., 2008, **49**, 6794; (*d*) P. R. Serwinski and P. M. Lahti *Org. Lett*., 2003, **5**, 2099; (*e*) P. Vinczer, T. Kovacs, L. Novak, and C. Szantay *Org. Prep. Proc. Int.*, 1989, **21**, 232.

1. Single crystal structure of 3b

The single crystal X-ray crystallographic analysis of **3b** further supported the structure of cyclized products. An ORTEP representation of the molecule **3b** is given in figure 1.

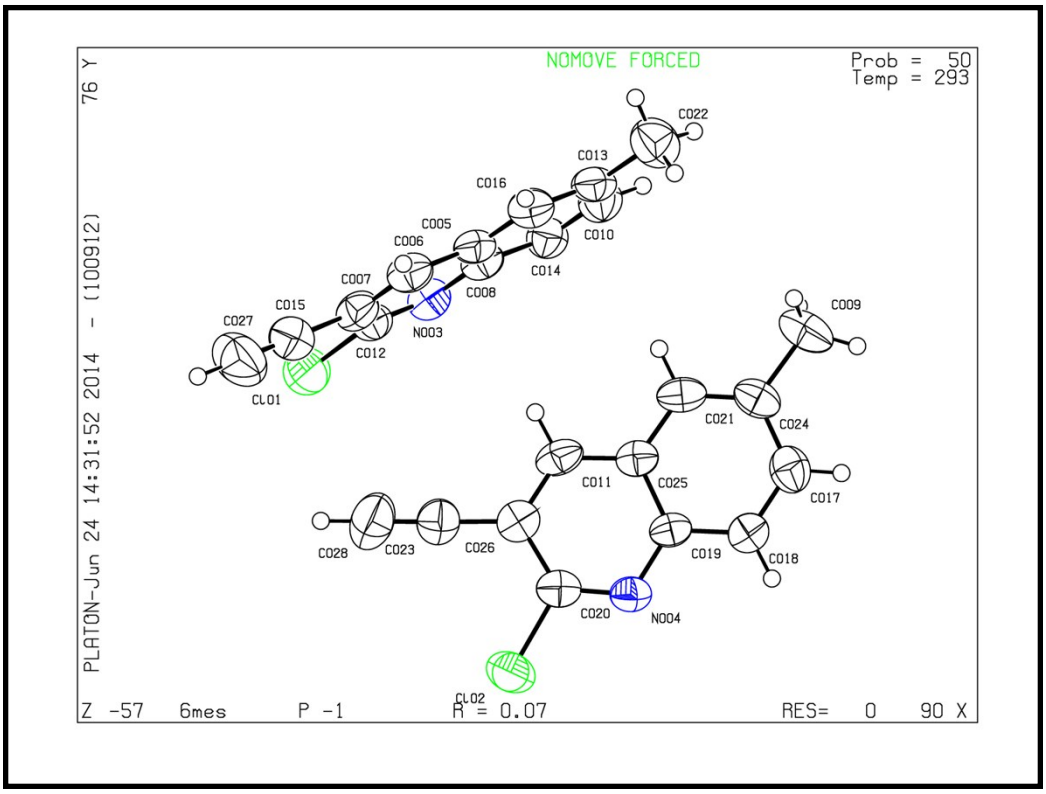


Figure 1. ORTEP drawing of the X-ray structure of **3b**

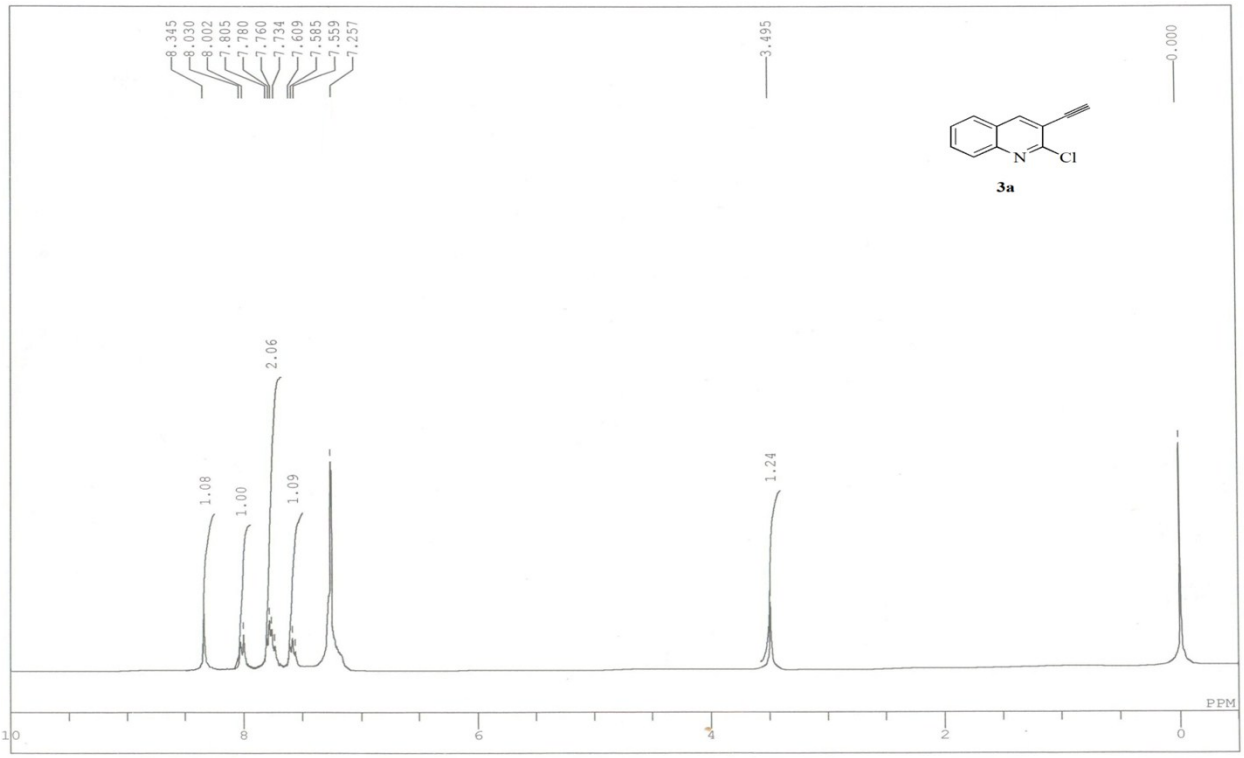
The crystal structure was deposited at the Cambridge Crystallographic Data Centre. The data have been assigned the deposition numbers: **CCDC 1413348**.

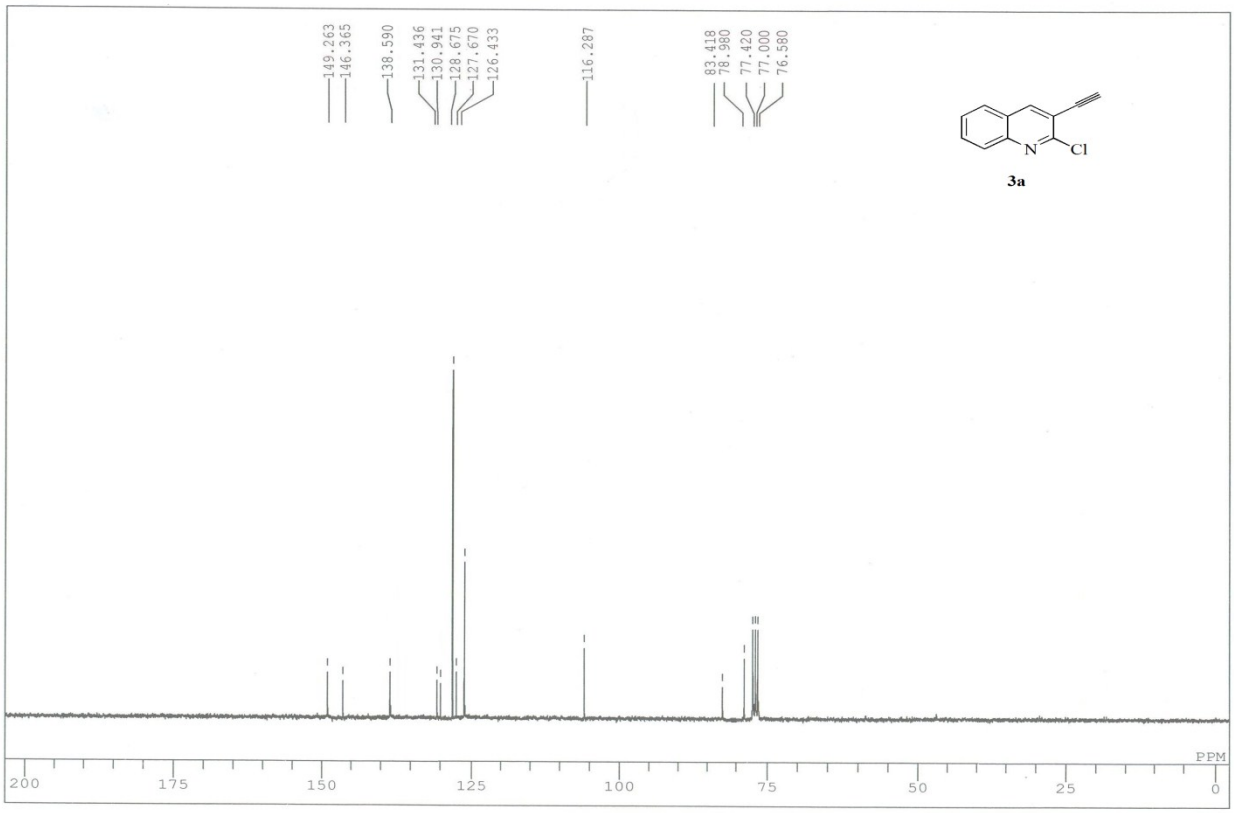
Table 2. Summary of Crystallographic data for compound **3b**

Parameters	**3b**
Empirical Formula	$C_{12}H_8ClN$
Formula Weight	201.64

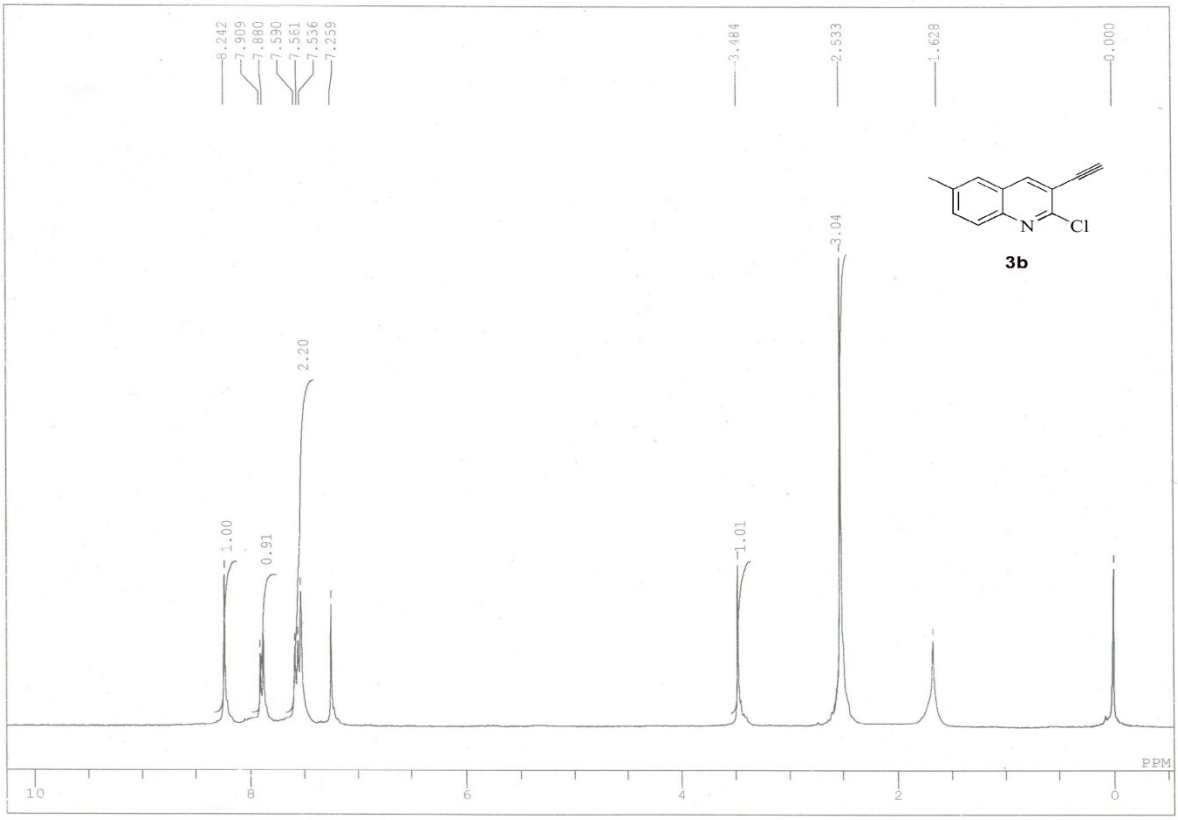
Crystal system	Triclinic
Temperature/K	293(2) K
Space group	P-1
a/ Å	7.060(3)
b/ Å	11.3973(17)
c/ Å	13.353(3)
α (°)	70.012(19)
β (°)	84.34(3)
γ (°)	84.46(2)
V/ Å^3	1002.5(5)
Z	4
D_c/ mg·m^{-3}	1.336
F_{000}	416.0
$F_{000'}$	416.72
h,k,l_{max}	9,15,18
Theta(max)	28.990
R(*int*)	0.0681(2004)
wR_2(Reflections)	0.1624(3296)

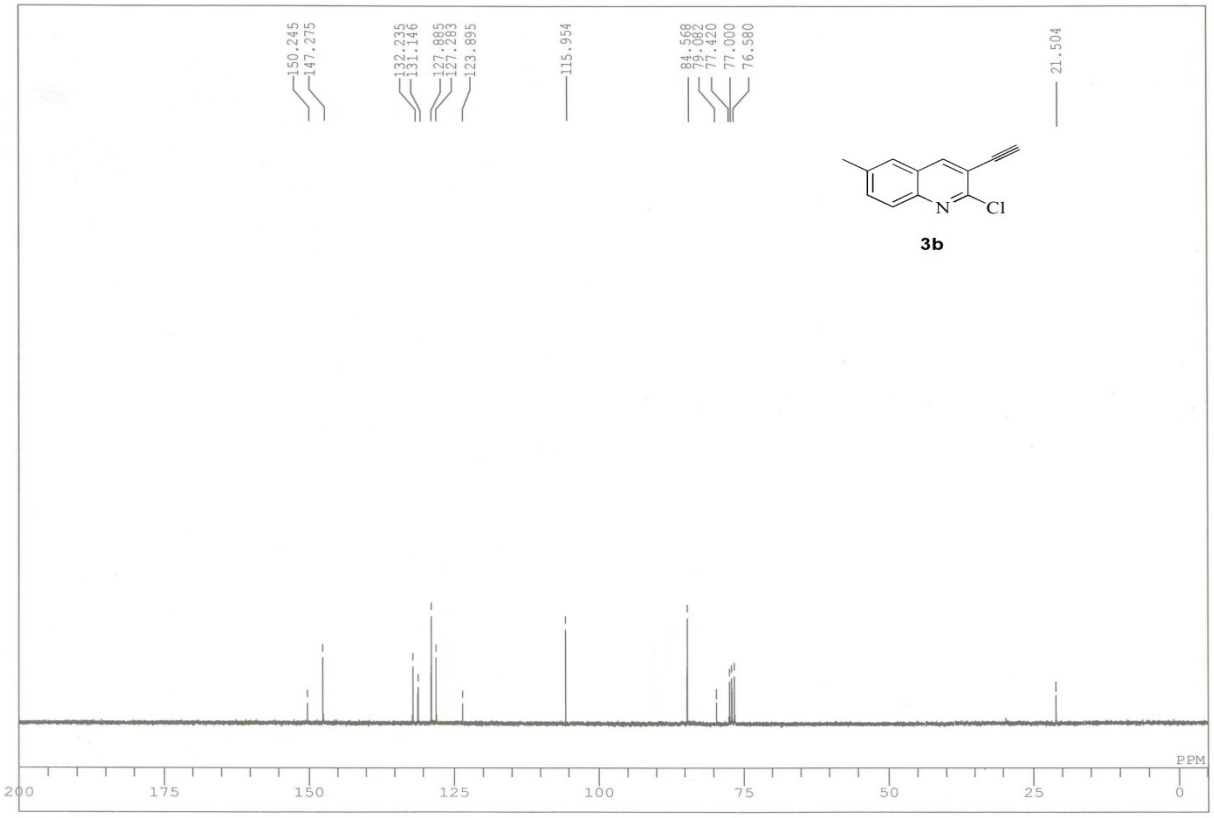
1. ^{1}H & ^{13}C NMR spectra of 2-chloro-3-ethynyl-quinoline (3a)



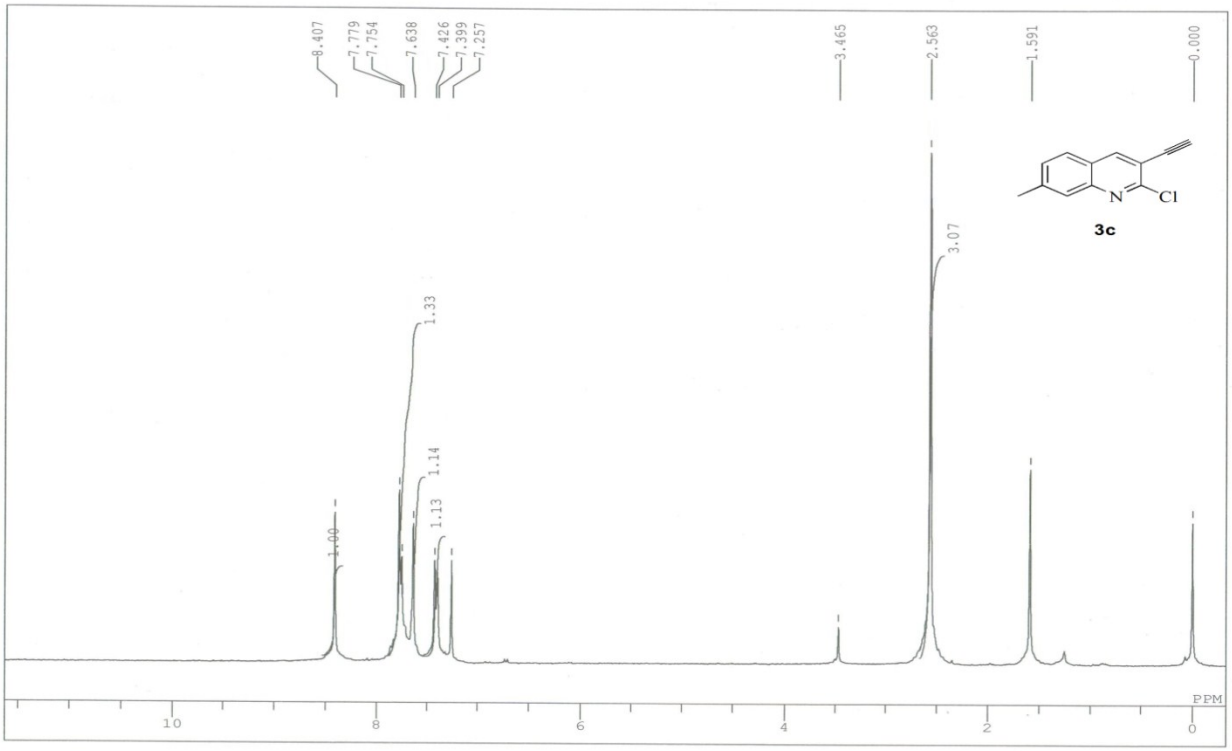


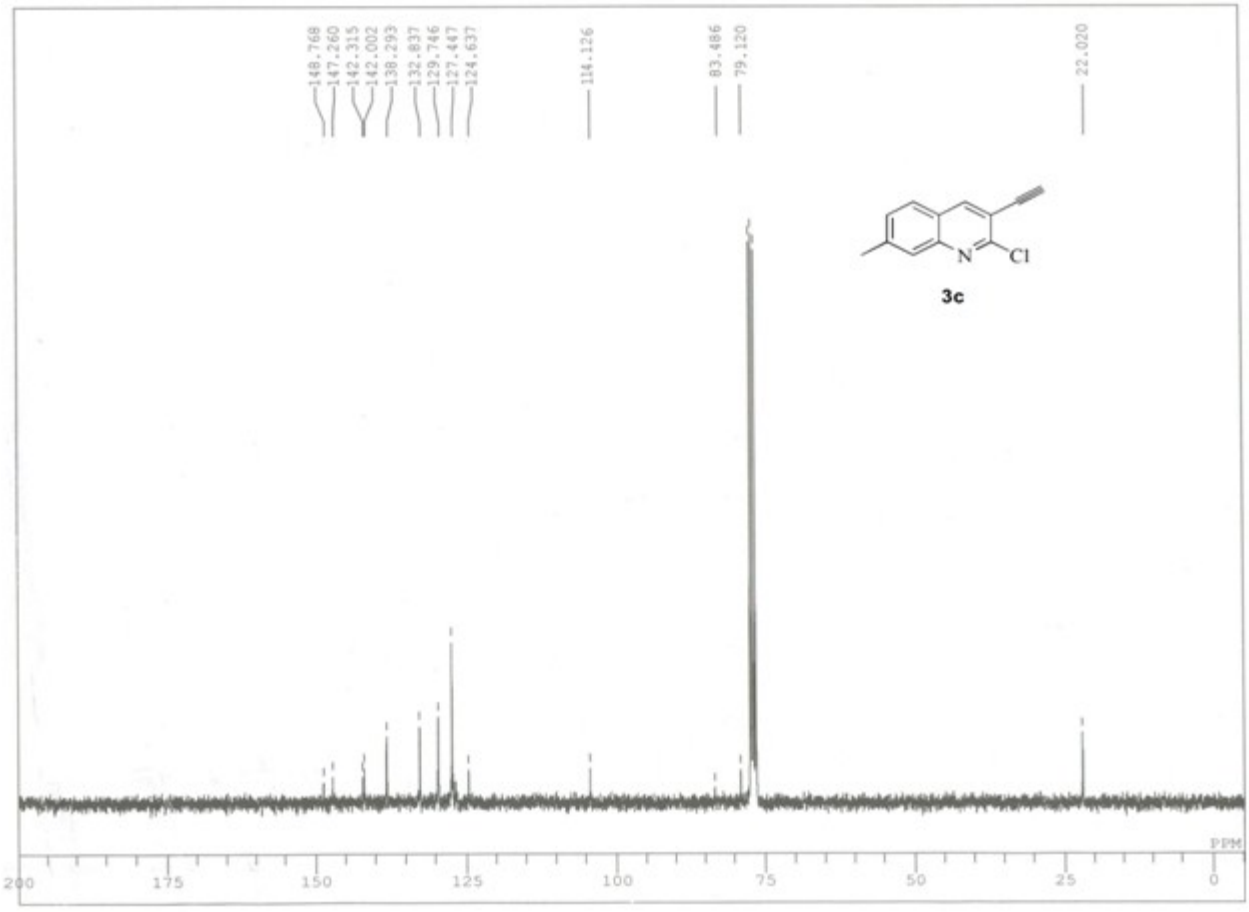
2. ^{1}H & ^{13}C NMR spectra of 2-chloro-3-ethynyl-6-methyl quinoline (3b)



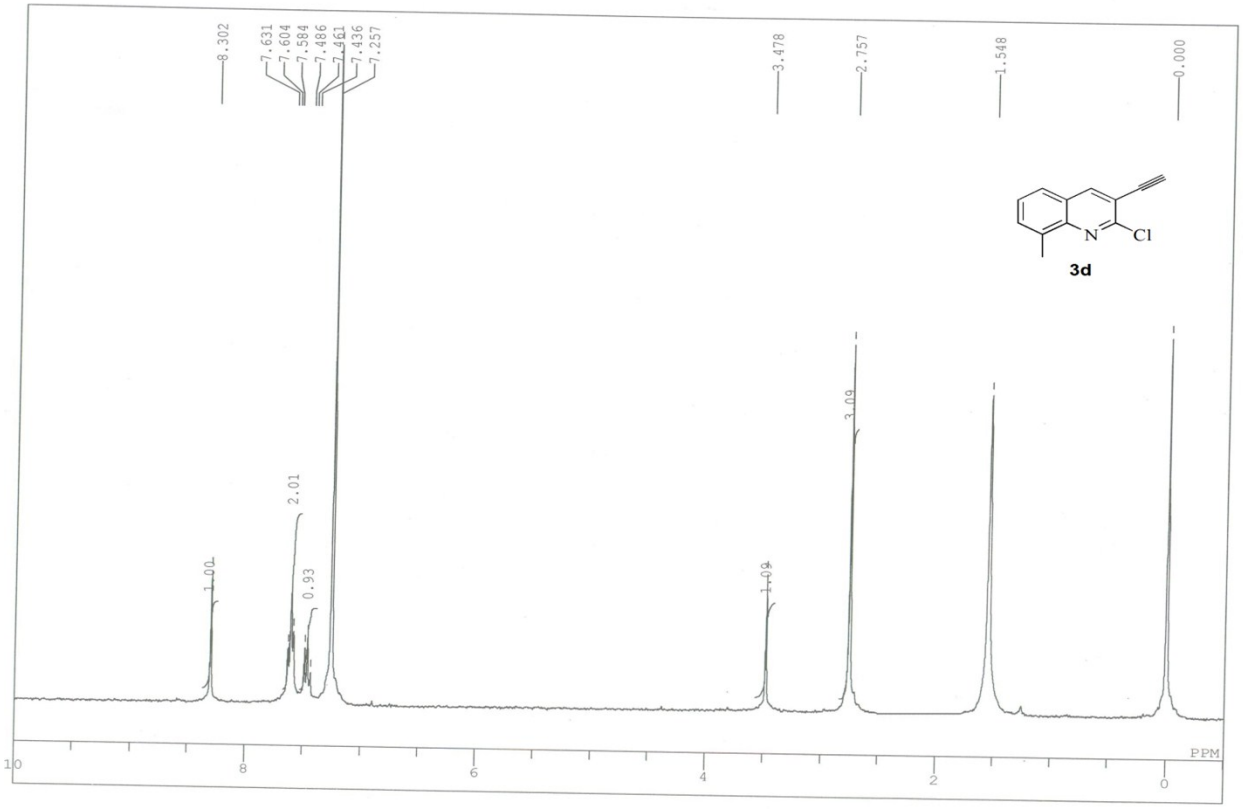


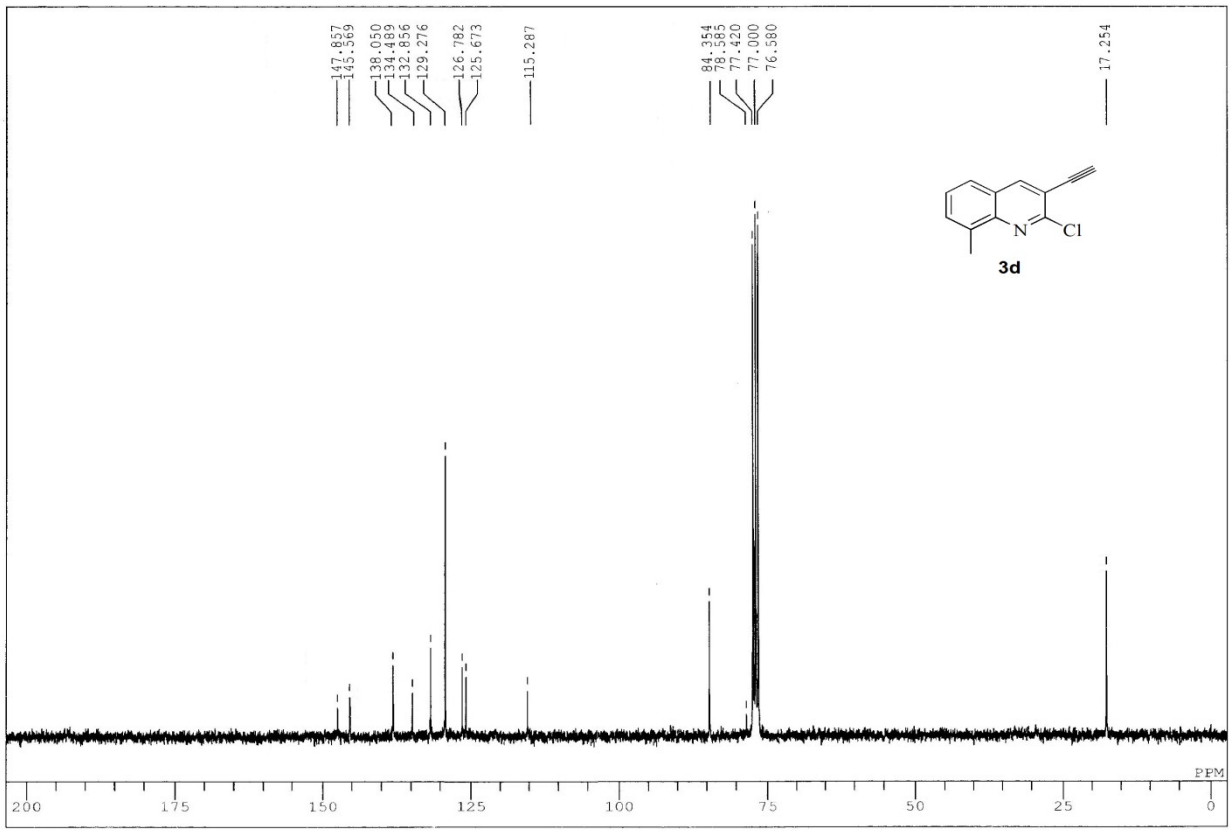
3. ^{1}H & ^{13}C NMR spectra of 2-chloro-3-ethynyl-7-methyl quinoline (3c)



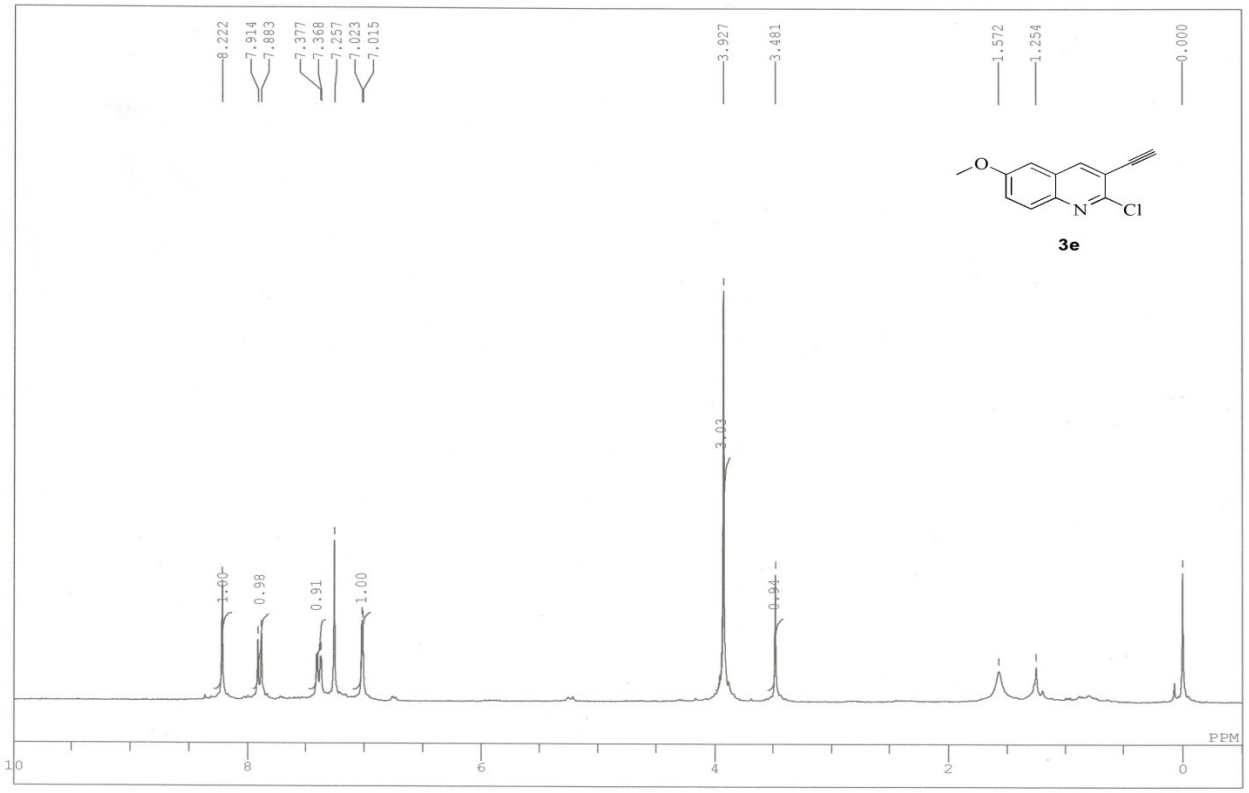


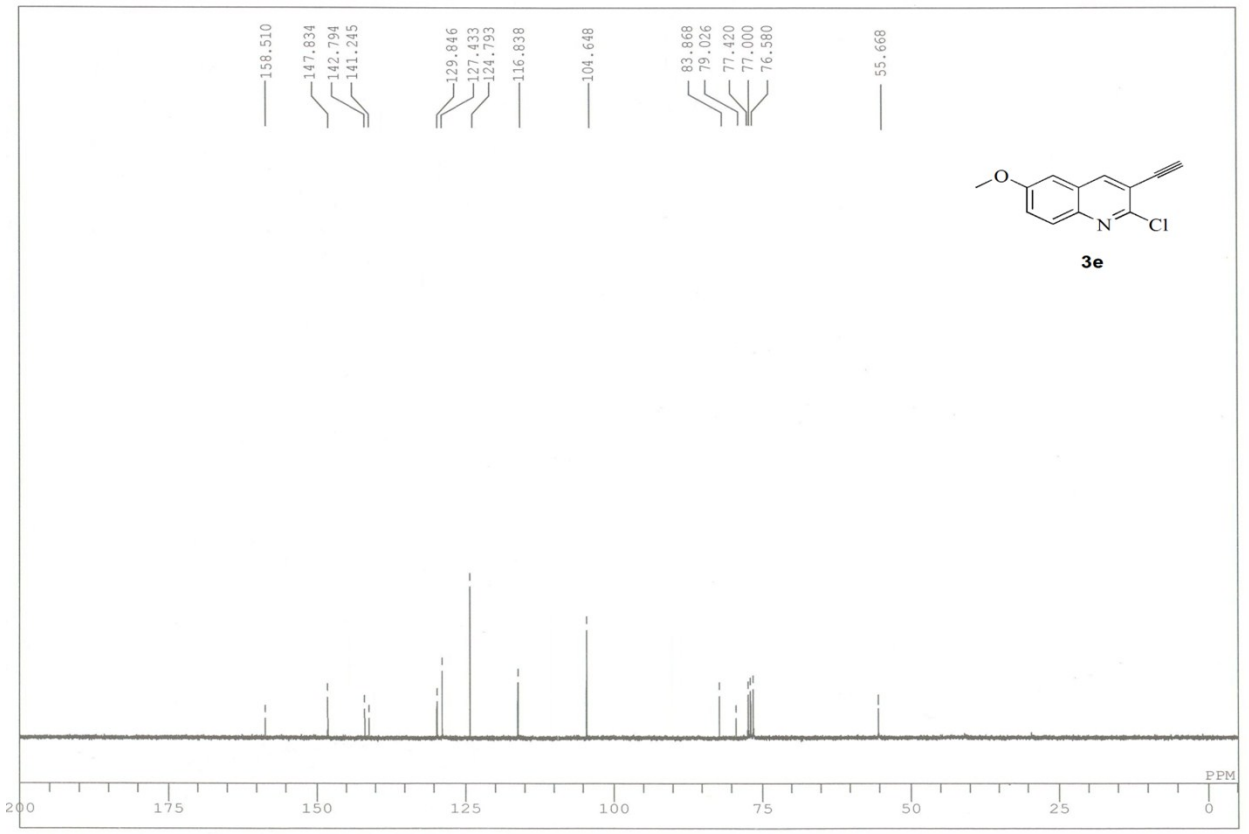
4. ^{1}H & ^{13}C NMR spectra of 2-chloro-3-ethynyl-8-methyl quinoline (3d)



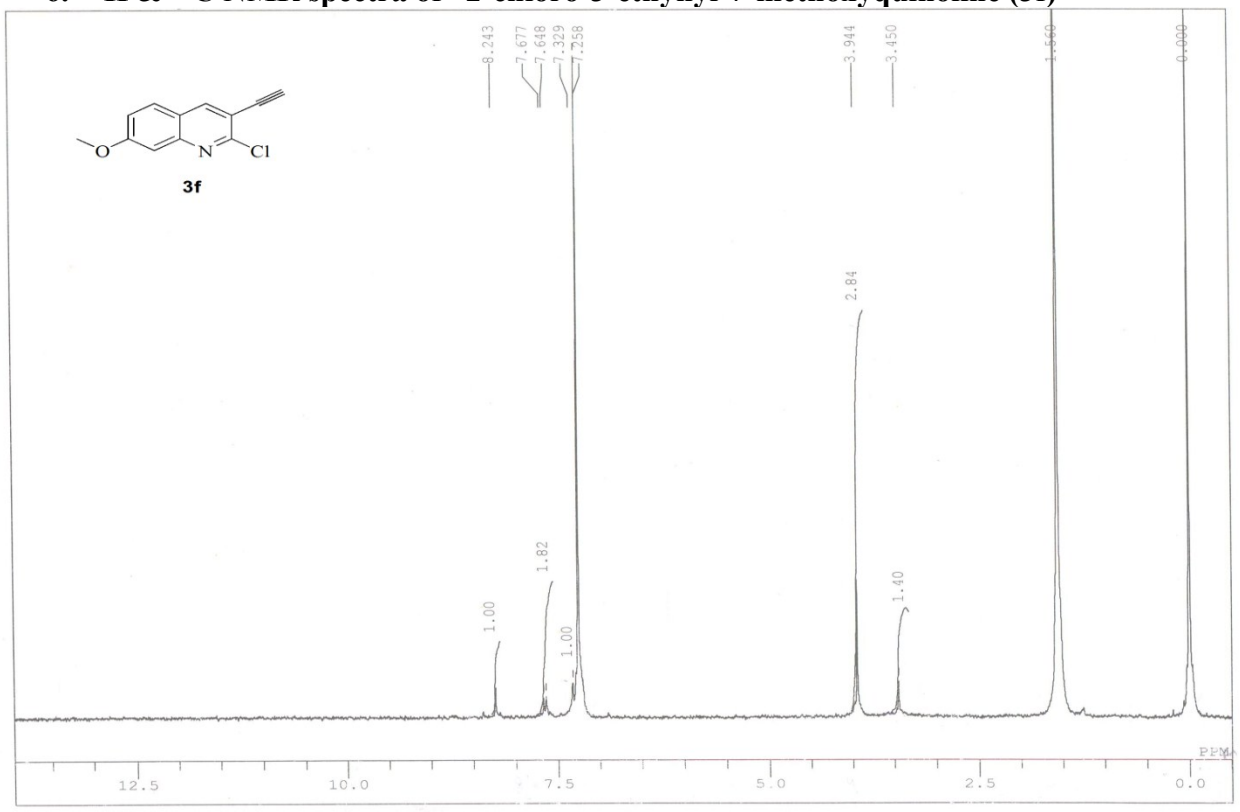


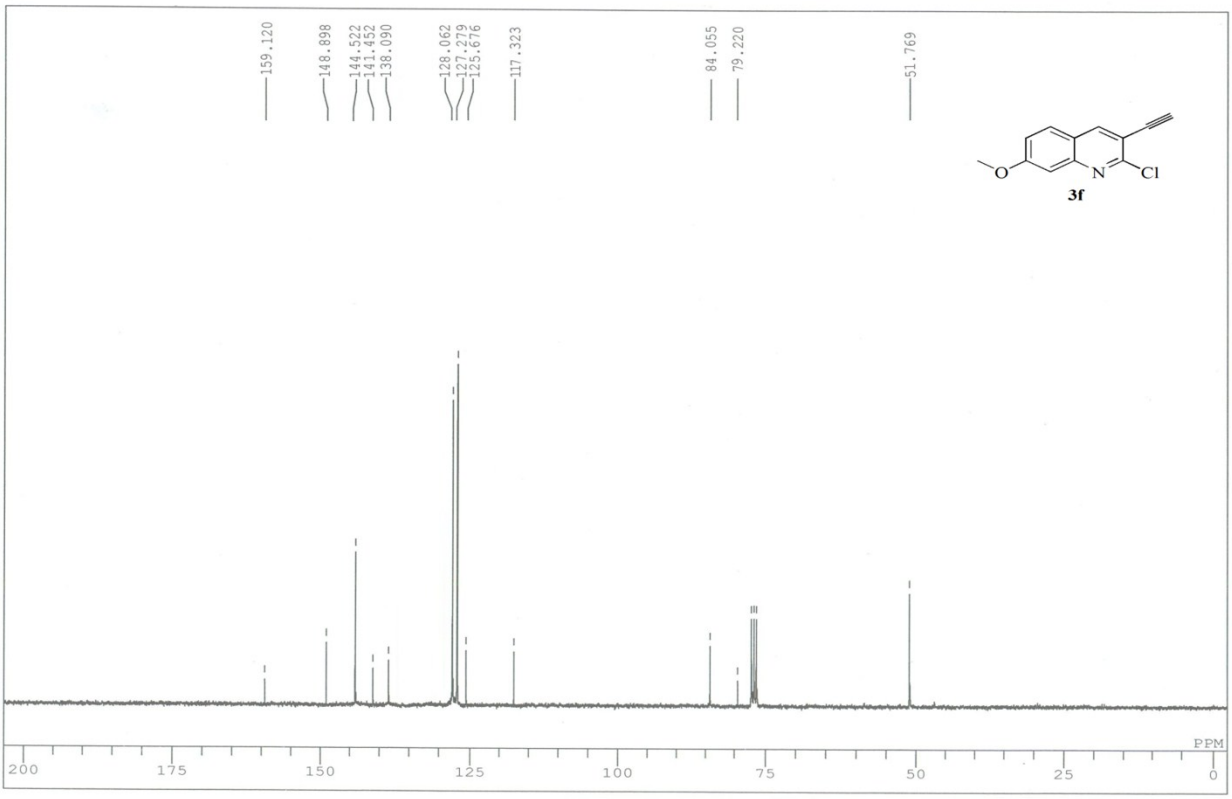
5. ^{1}H & ^{13}C NMR spectra of 2-chloro-3-ethynyl-6-methoxyquinoline (3e)



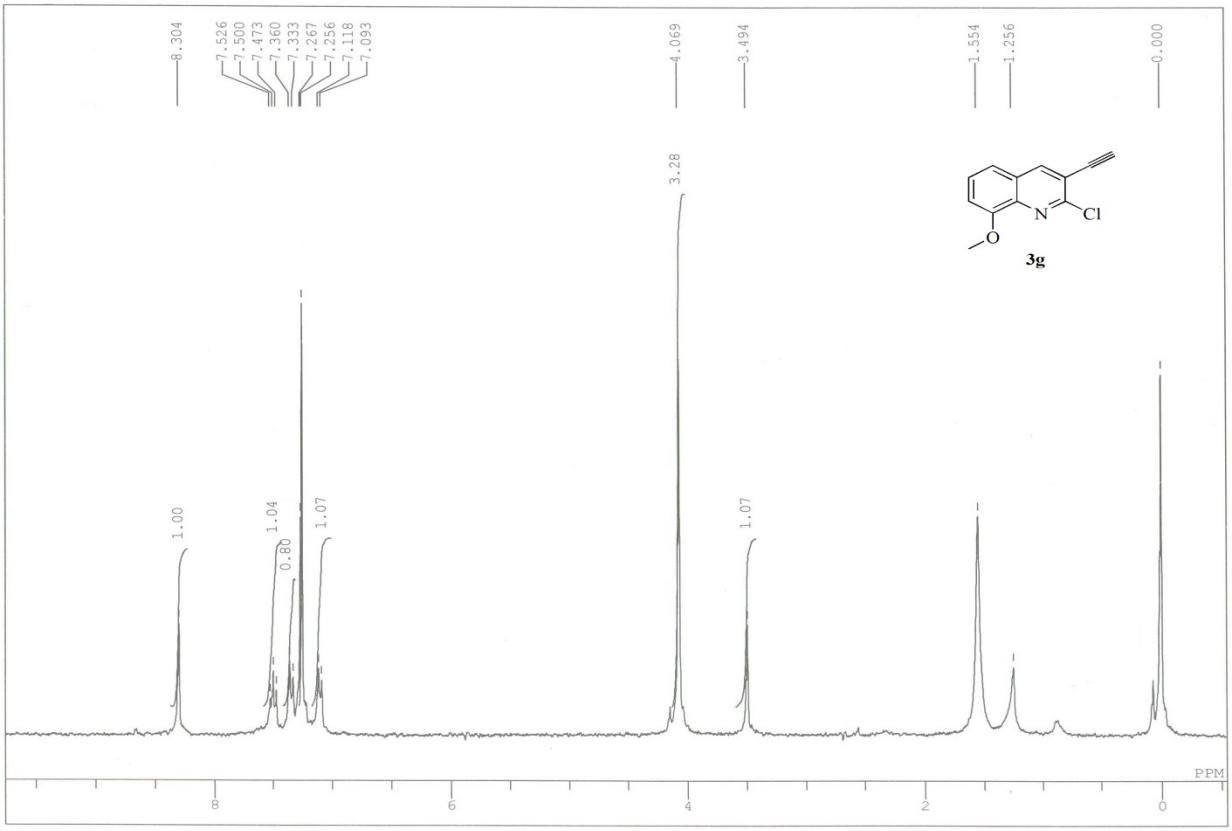


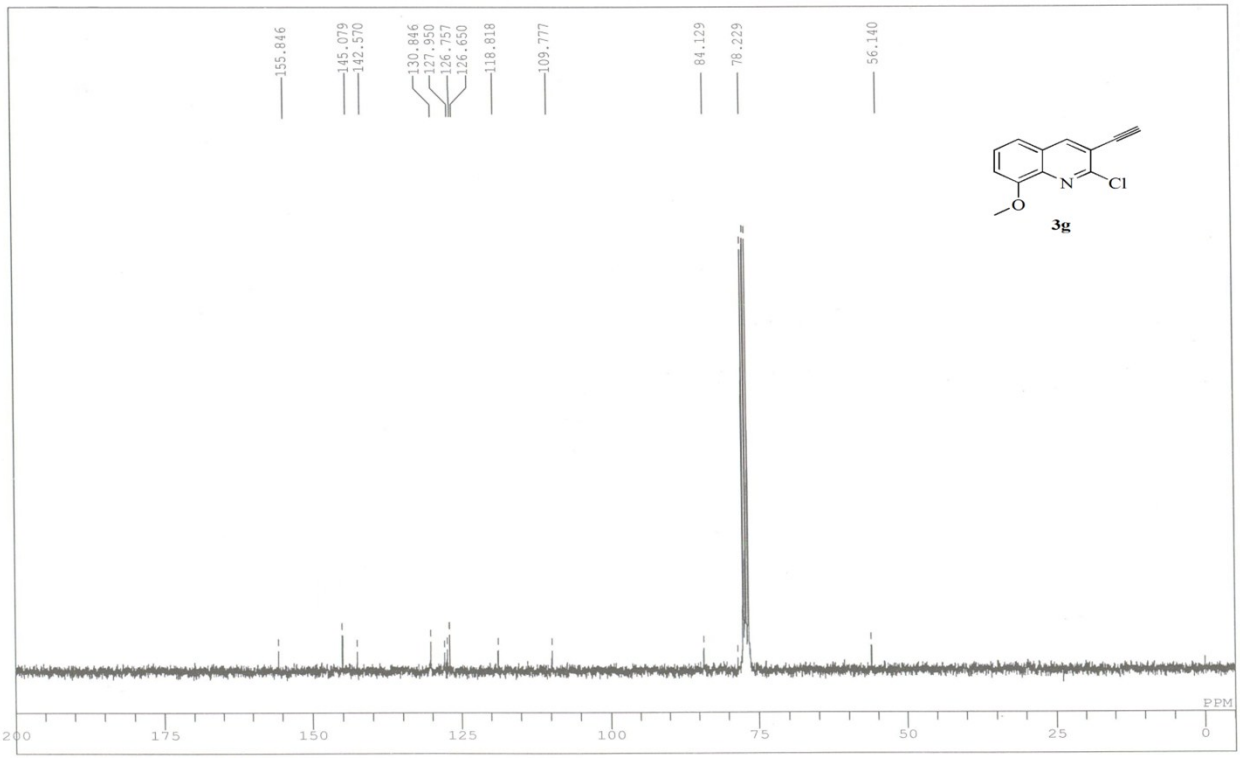
6. ^{1}H & ^{13}C NMR spectra of 2-chloro-3-ethynyl-7-methoxyquinoline (3f)



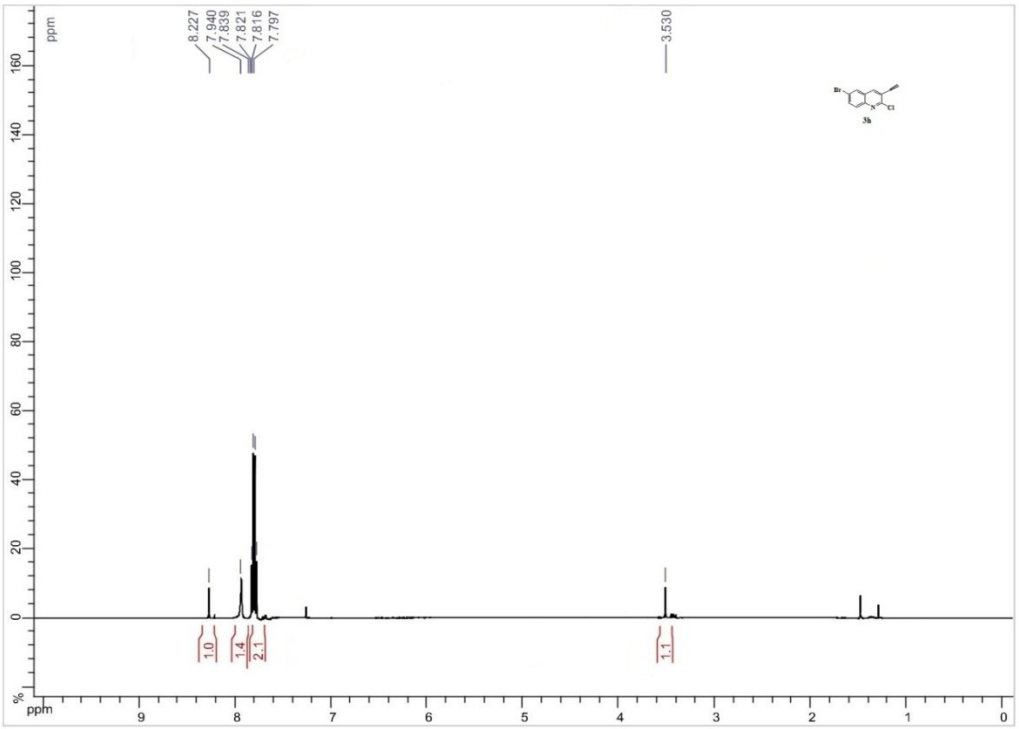


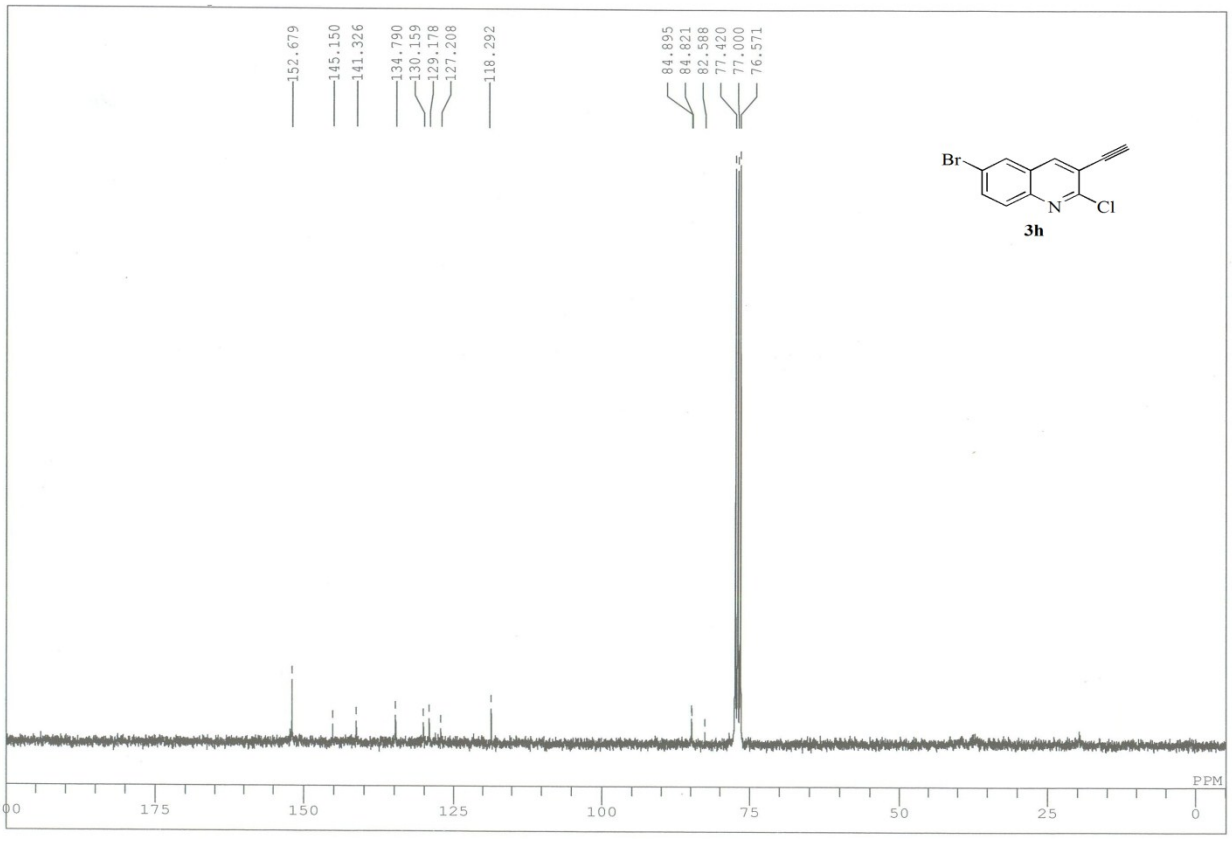
7. ^{1}H & ^{13}C NMR spectra of 2-chloro-3-ethynyl-8-methoxyquinoline (3g)



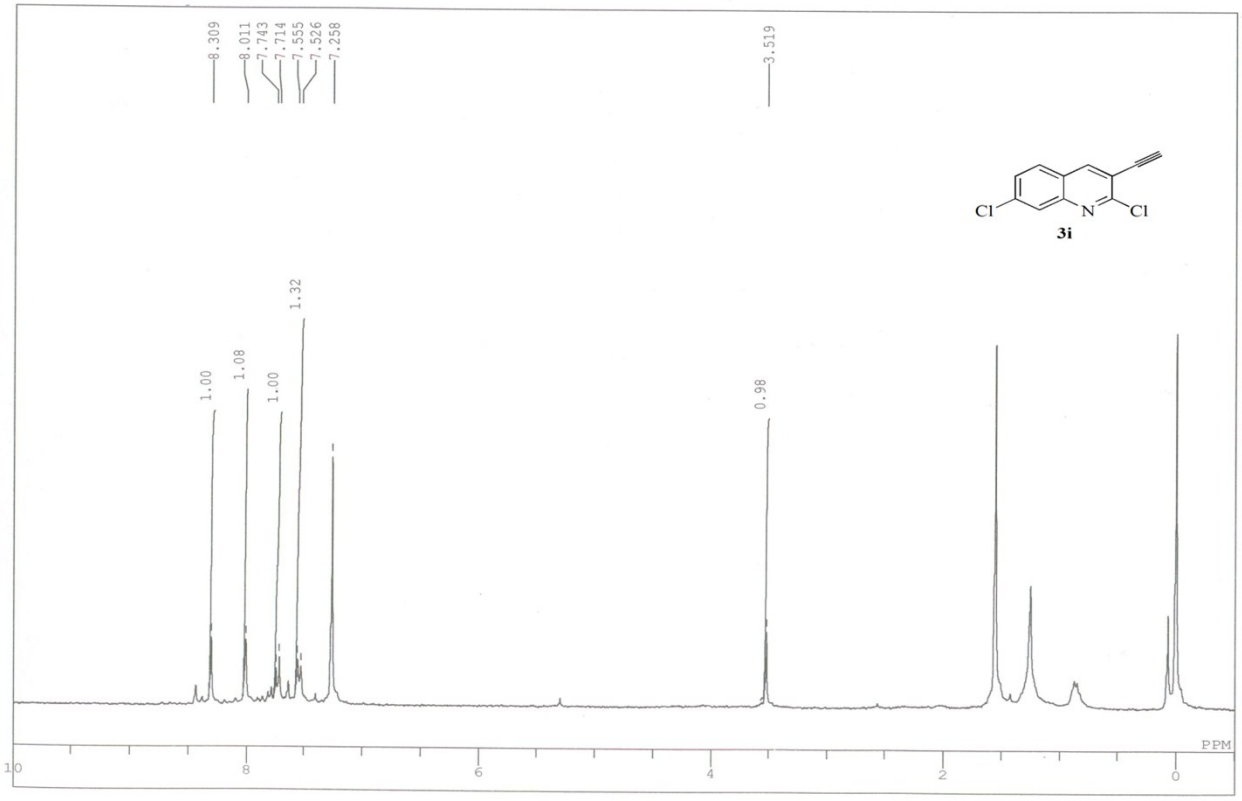


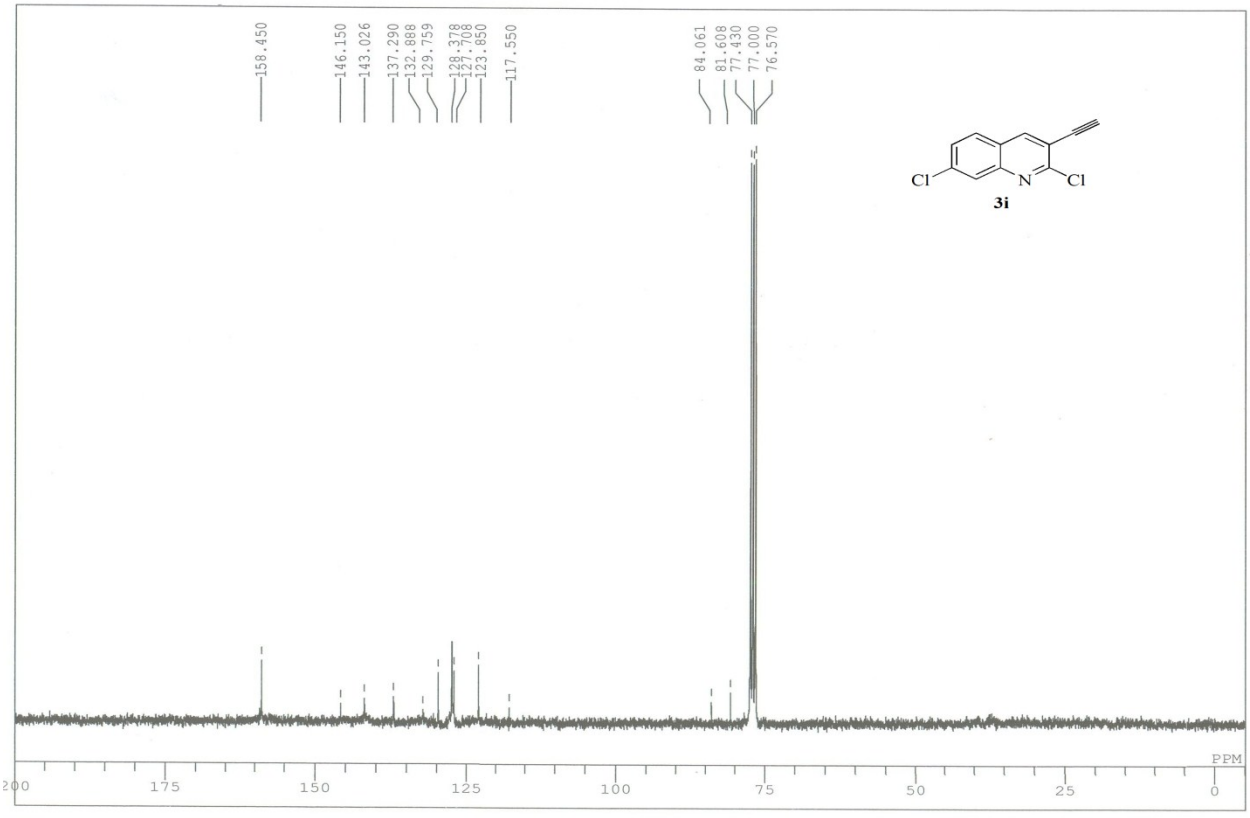
8. ^{1}H & ^{13}C NMR spectra of 6-bromo-2-chloro-3-ethynylquinoline (3h)





9. ^{1}H & ^{13}C NMR spectra of 2,7-dichloro-3-ethynylquinoline (3i)





10. **^{1}H & ^{13}C NMR spectra of 8-ethyl-2-chloro-3-ethynylquinoline (3j)**