Electronic Supplementary Material (ESI) for RSC Advances.

ONO Pincer type Pd(II) complexes: Synthesis, crystal structure and catalytic activity towards C-2 arylation of quinoline scaffolds

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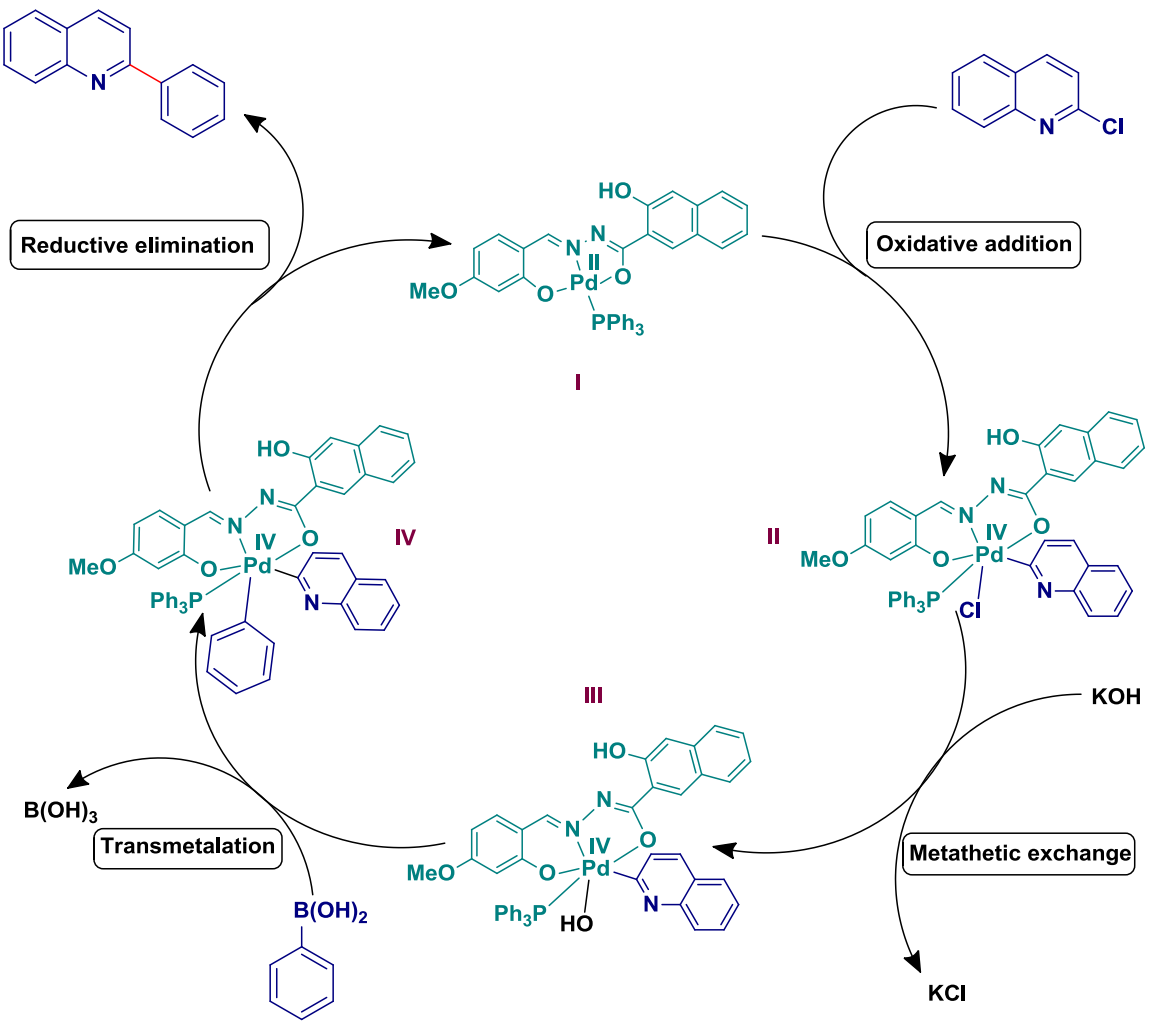
MECHANISM FOR THE SMC REACTION

In general, the pincer type ligand can increase the electron density at palladium(II) centers and promote the generation of the Pd(IV) species. Therefore, Pd(IV) intermediates are considered as the reactive species in the mechanism of the SMC reaction of aryl halides at above room-temperature. In addition, Pd(II)/Pd(IV) cycle helps facile reductive elimination from Pd(IV) intermediate. However, Pd(IV) intermediates are unstable and hence, could not be isolated.[1] In view of these facts and previous reports,[2,3] a plausible mechanism for this reaction has been proposed in Scheme **2.** In the first step, the active Pd(II) species **I** undergoes an oxidative addition of 2-chloroquinoline to form a Pd(IV) intermediate **II** followed by a metathetic exchange upon the addition of KOH to the intermediate **II** resulting in the formation of KCl and intermediate **III**. Subsequent transmetalation between Pd(IV) and the phenylboronic acid yielded intermediate **IV** that underwent a reductive elimination to afford respective 2-phenylquinoline *via* C–C sigma bond formation and regeneration of the active Pd(II) species.



Scheme 2. Plausible mechanism for SMC reaction of 2-chloroquinoline with phenylboronic acid.

References

1) (a) H. Zhang and A. Lei, *Dalton Trans*., 2011, **40,** 8745. (b) J. L. Bolliger, O. Blacque, C. M. Frech, *Chem. Eur. J*., 2008, **14**, 7969.
2) A. Vignesh, W. Kaminsky, N. S. P. Bhuvanesh, N. Dharmaraj, *RSC Adv*., 2015**, 5**, 59428.
3) (a) N. Miyaura and A. Suzuki, *Chem. Rev*., 1995, **95,** 2457. (b) A. J. J. Lennox and G. C. L. Jones, *Chem. Soc. Rev*., 2014, **43,** 412

Table1. Selected bond lengths (Å) and angles (°) for the complexes **1 and 2**

Complex	**1**	**2**
Pd(1) – N(1)	1.995(2)	1.990(4)
Pd(1) – O(1)	1.9830(18)	1.976(2)
Pd(1) – O(2)	1.9998(18)	1.988(3)
Pd(1) – P(1)	2.2801(7)	2.2814(13)
N(1) – C(7)	1.274(4)	1.285(5)
O(1) – C(1)	1.320(3)	1.325(5)
O(2) – C(8)	1.301(3)	1.299(5)
N(1) – N(2)	1.401(3)	1.404(4)
N(2) – C(8)	1.324(4)	1.316(5)
C(7) – C(6)	1.438(4)	1.442(6)
C(1) – C(6)	1.420(4)	1.418(6)
N(1) – Pd(1)– O(1)	93.85(8)	94.33(12)
N(1) – Pd(1)– O(2)	80.44(8)	80.37(12)
O(1) – Pd(1)– O(2)	174.29(8)	174.30(13)
N(1) – Pd(1)– P(1)	174.77(7)	173.09(9)
O(1) – Pd(1)– P(1)	90.50(6)	91.38(10)
O(2) – Pd(1)– P(1)	95.20(6)	94.05(10)
C(7) – N(1) – Pd(1)	126.86(19)	126.4(3)
N(2) – C(8)– O(2)	125.3(2)	125.4(4)
N(2) – N(1)– Pd(1)	113.67(17)	113.8(2)

Table 2. Selected bond lengths (Å) and angles (°) for the complex **3**

Complex	**3**
Pd(1) – N(1)	1.9858(16)
Pd(1) – O(1)	2.0055(14)
Pd(1) – O(2)	1.9686(14)
Pd(1) – P(1)	2.2950(5)
N(1) – C(8)	1.2780(3)
O(1) – C(9)	1.3070(2)
O(2) – C(1)	1.3170(2)
N(1) – N(2)	1.4040(2)
N(2) – C(9)	1.317(3)
C(8) – C(6)	1.420(3)
C(1) – C(6)	1.427(3)
N(1) – Pd(1)– O(1)	80.11(6)
N(1) – Pd(1)– O(2)	85.31(4)

O(1) – Pd(1)– O(2)	174.37(6)
N(1) – Pd(1)– P(1)	179.17(5)
O(1) – Pd(1)– P(1)	100.31(4)
O(2) – Pd(1)– P(1)	85.31(4)
C(8) – N(1) – Pd(1)	125.99(14)
N(2) – C(9)– O(1)	124.54(18)
N(2) – N(1)– Pd(1)	114.15(12)

Table 3. Selected bond lengths (Å) and angles (°) for the complex **4**

Complex	**4**
Pd(1) – N(1)	1.993(4)
Pd(1) – O(1)	1.969(4)
Pd(1) – O(3)	1.991(4)
Pd(1) – P(1)	2.2885(14)
N(1) – C(1)	1.277(7)
O(1) – C(3)	1.311(6)
O(3) – C(9)	1.293(6)
N(1) – N(2)	1.395(6)
N(2) – C(9)	1.316(7)
C(1) – C(2)	1.430(8)
C(2) – C(3)	1.421(8)
N(1) – Pd(1)– O(1)	94.23(19)
N(1) – Pd(1)– O(3)	80.15(18)
O(1) – Pd(1)– O(3)	173.74(15)
N(1) – Pd(1)– P(1)	172.74(13)
O(1) – Pd(1)– P(1)	90.35(11)
O(3) – Pd(1)– P(1)	80.15(18)
C(1) – N(1) – Pd(1)	125.3(4)
N(2) – C(9)– O(3)	125.7(6)
N(2) – N(1)– Pd(1)	113.8(3)

Table 4. Crystal data and structure refinement for complexes **1- 4**

Complex	**1**	**2**	**3**	**4**
CCDC number	**1047924**	**1047925**	**1047926**	**1047927**
Empirical formula	$C_{32}H_{25}N_2O_3PPd$	$C_{36}H_{27}N_2O_3PPd$	$C_{33}H_{27}N_2O_4PPd$	$C_{37}H_{29}N_2O_4PPd$
Formula weight	622.91	672.97	652.94	702.99
Temperature (K)	130(2)	130(2)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P -1	P 2_1/a	P 2_1/c	P 2_1/c
Unit cell dimensions				
a (Å)	9.2348(5)	8.8683(4)	11.0075(5)	15.087(2)
b (Å)	10.1529(5)	21.5484(10)	28.2609(12)	21.144(3)
c (Å)	15.3801(10)	15.2026(7)	8.8037(4)	9.3879(15)
α (°)	97.685(4)	90	90	90
β (°)	90.359(4)	96.079(3)	92.227(2)	94.528(8)
γ (°)	110.319(4)	90	90	90
Volume (Å^3)	1338.00(13)	2888.8(2)	2736.6(2)	2985.5(8)
Z	2	4	4	4
Density(calculated) (Mg m^{-3})	1.546	1.547	1.585	1.564
Absorption coefficient (mm^{-1})	0.791	0.739	0.780	0.721
F(000)	632	1368	1328	1432
Crystal size (mm^3)	0.35 x 0.30 x 0.09	0.40 x 0.25 x 0.20	0.30 x 0.15 x 0.10	0.45 x 0.15 x 0.02
Reflections collected	10984	12436	127872	40321
Independent reflections	6588[R(int)= 0.0576]	7108 [R(int) = 0.1187]	6828 [R(int) =0.0271]	5156 [R(int) = 0.0930]

Max. and min. transmission	0.9322 and 0.7693	0.8663 and 0.7564	0.9261 and 0.7997	0.9857 and 0.7373
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	6588 / 0 / 355	7108 / 0 / 389	6828 / 0 / 374	5156 / 0 / 410
Goodness-of-fit on	1.051	0.935	1.174	1.082
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0413, wR2 = 0.0917	R1 = 0.0585, wR2 = 0.1137	R1 = 0.0286, wR2 = 0.0642	R1 = 0.0568, wR2 = 0.1004
R indices (all data)	R1 = 0.0559, wR2 = 0.0978	R1 = 0.1147, wR2 = 0.1310	R1 = 0.0301, wR2 = 0.0650	R1 = 0.0964, wR2 = 0.1155
Largest diff. peak and hole ($e.Å^{-3}$)	1.256 and -1.367	2.350 and -1.764	0.601 and -0.607	0.728 and -0.808

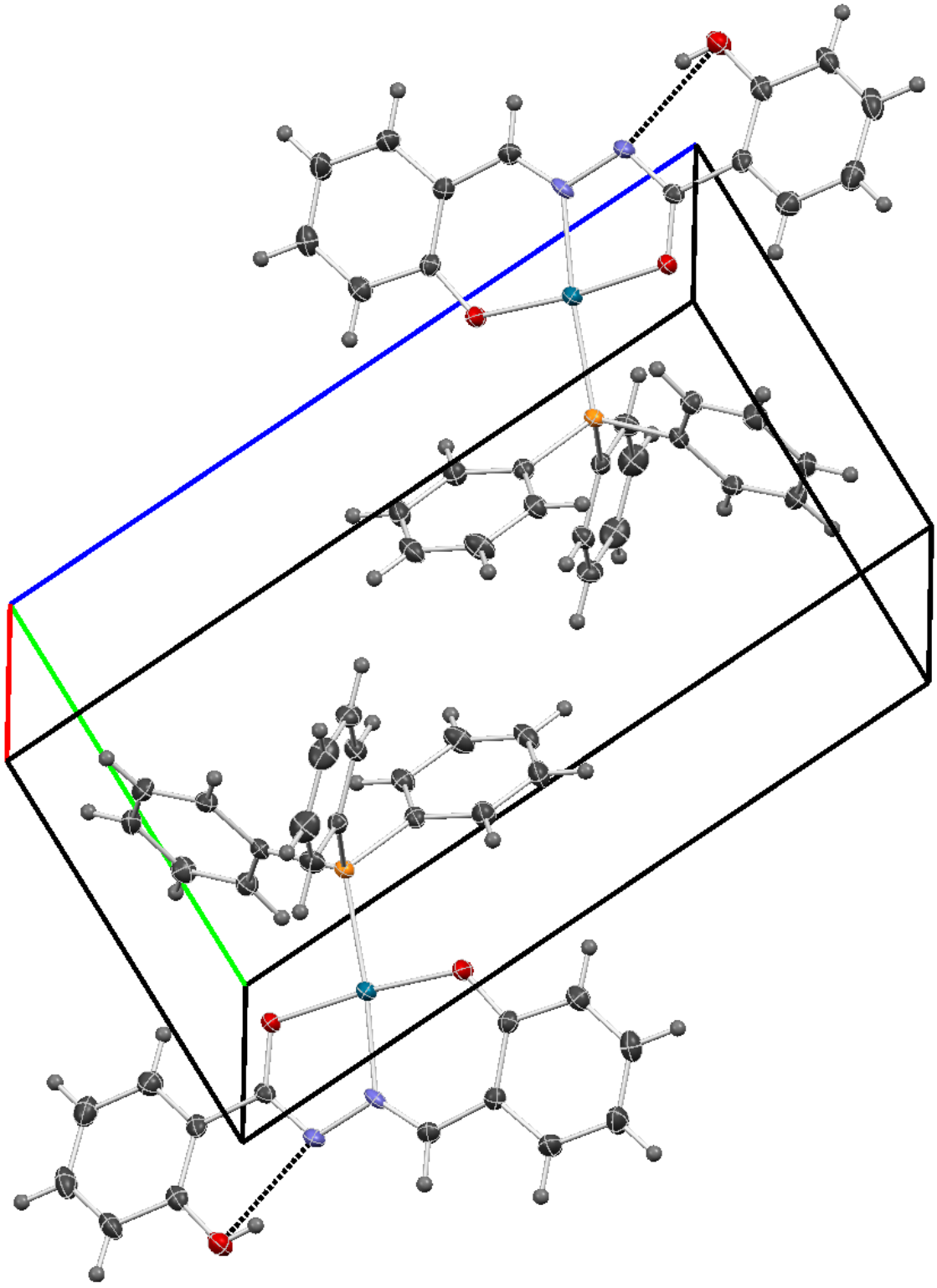


Fig. 1. Unit cell packing diagram of complex **1** with intra molecular hydrogen bonding.

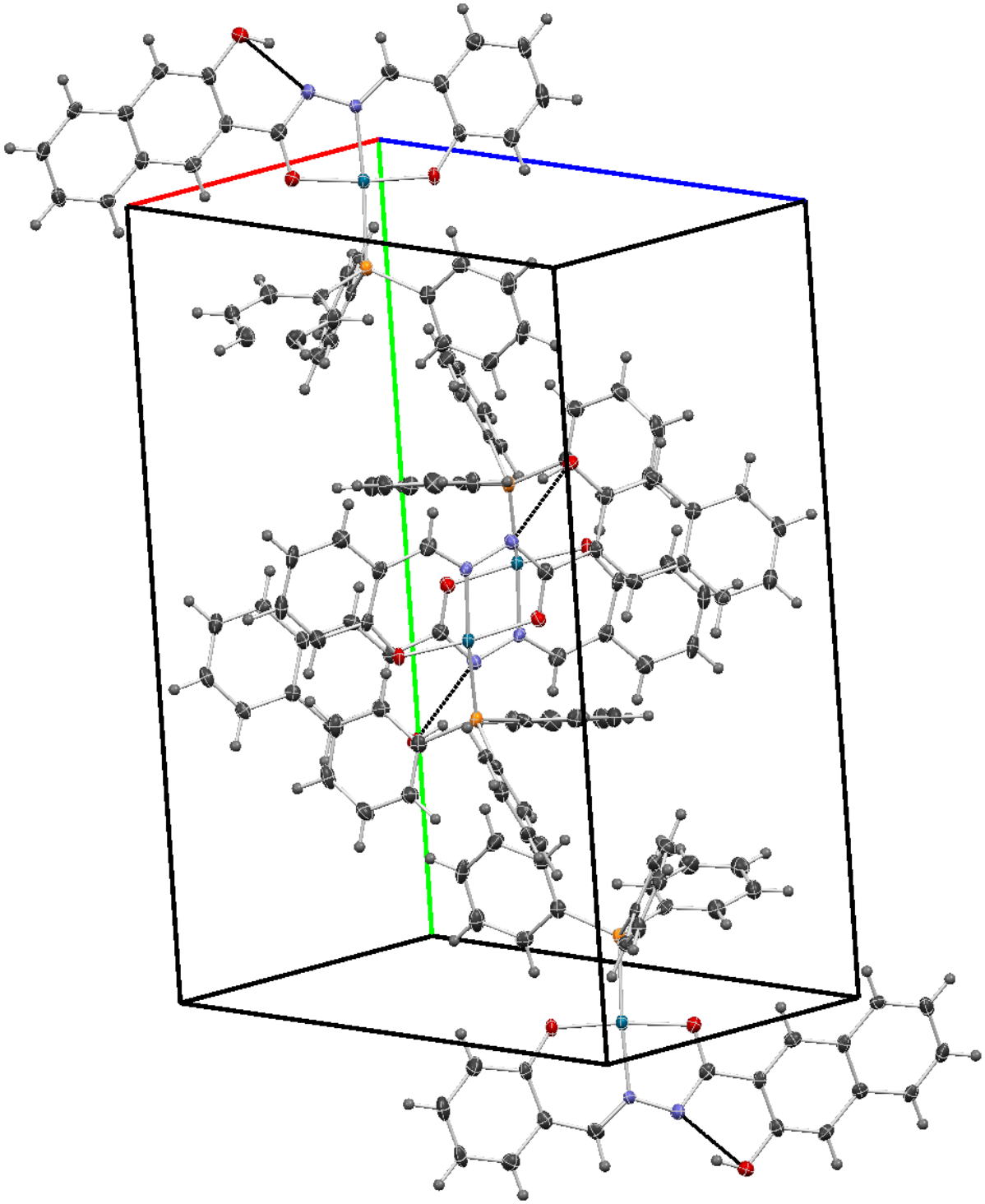


Fig. 2. Unit cell packing diagram of complex **2** with intra molecular hydrogen bonding.

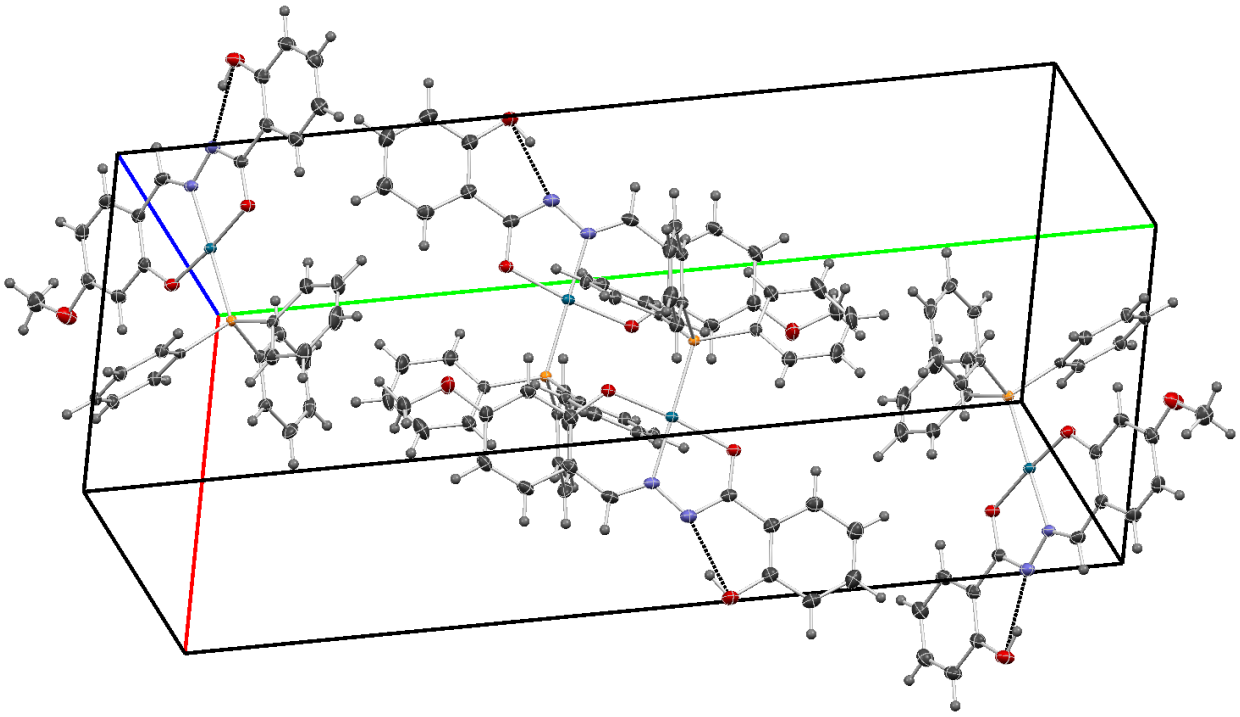


Fig. 3. Unit cell packing diagram of complex **3** with intra molecular hydrogen bonding.

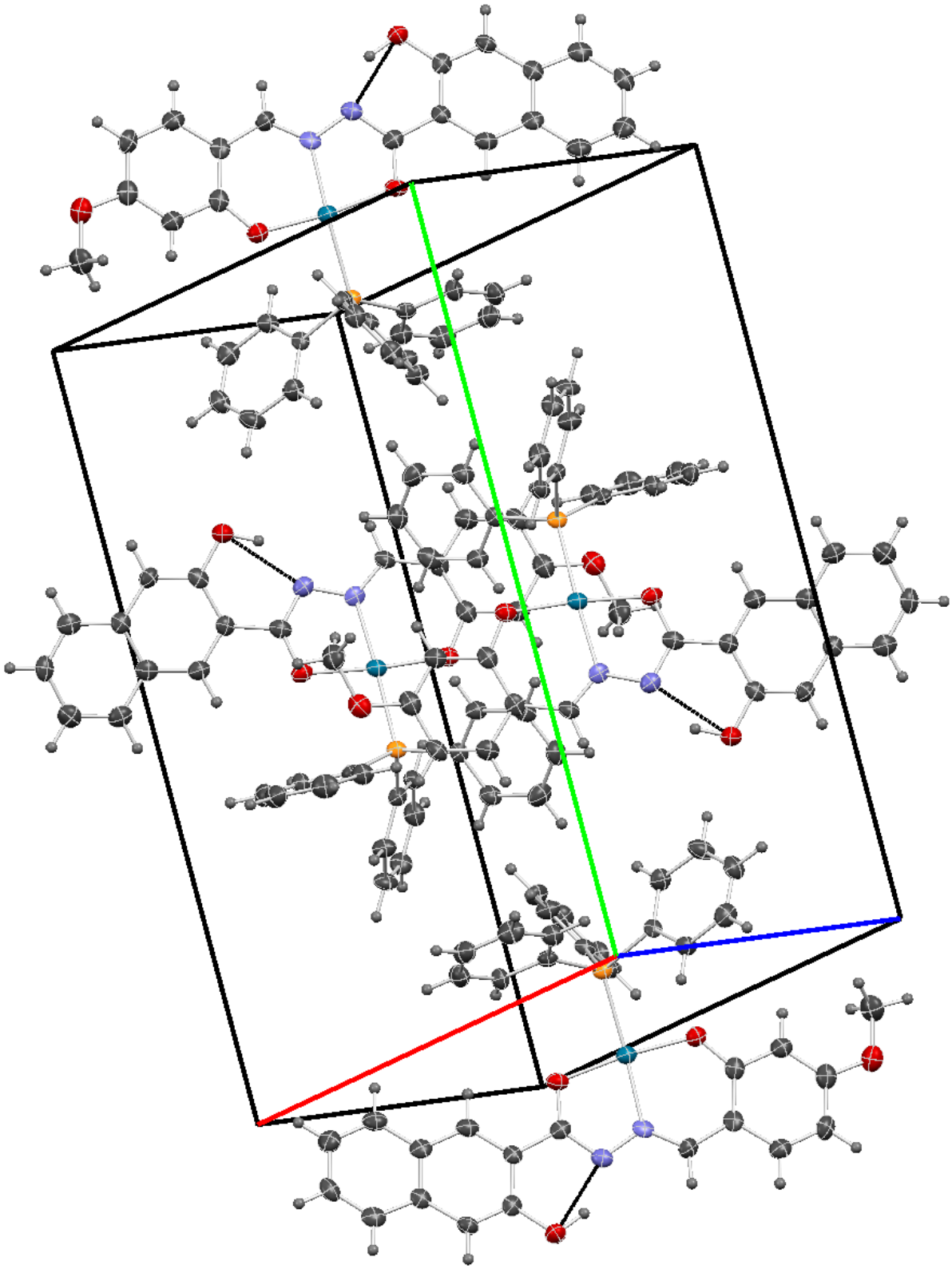


Fig. 4. Unit cell packing diagram of complex **4** with intra molecular hydrogen bonding.

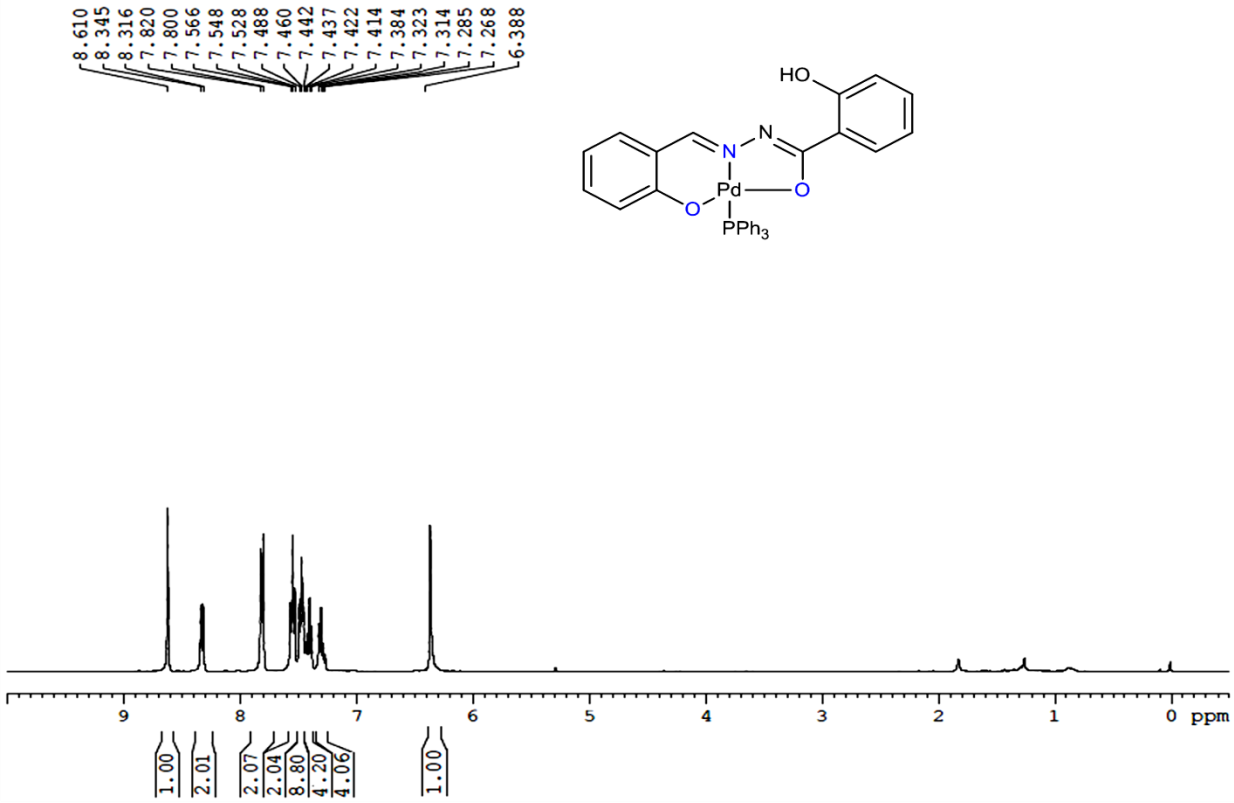


Fig. 5. ^{1}H NMR spectrum of complex **1**

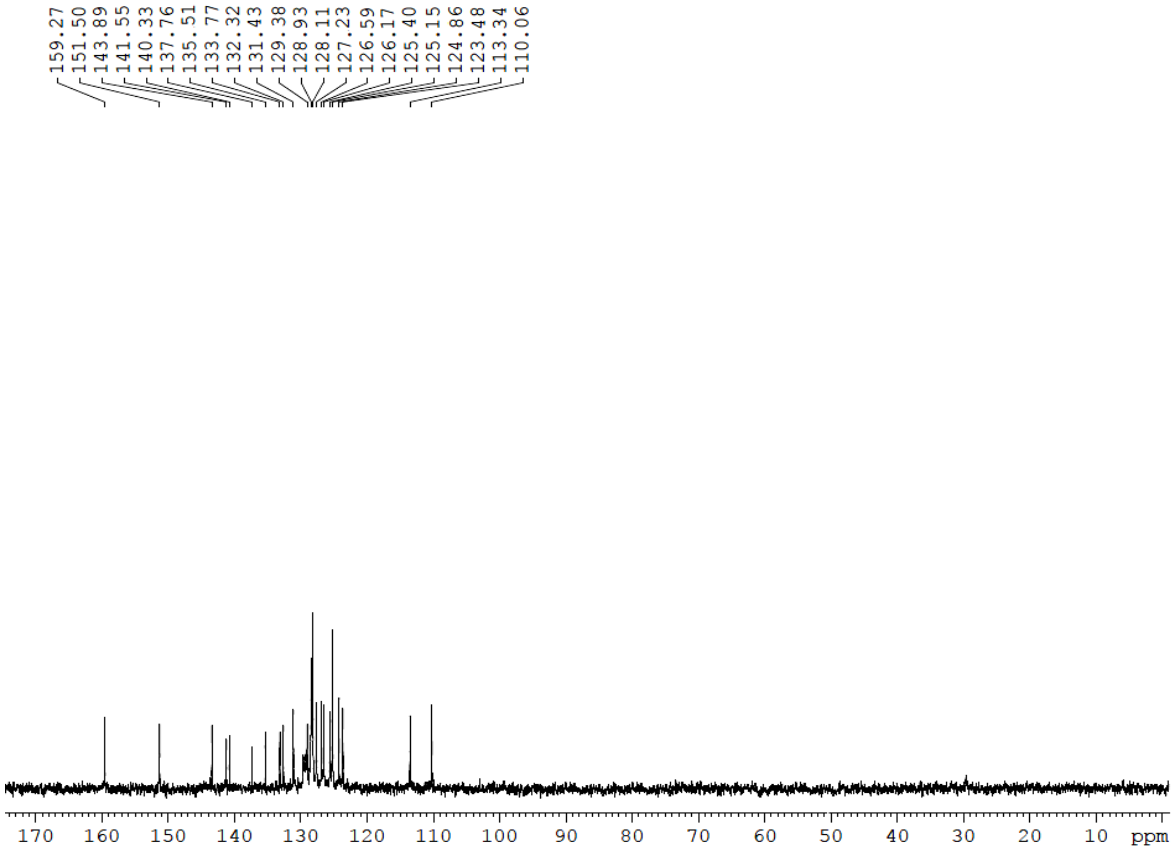


Fig. 6. ^{13}C NMR spectrum of complex **1**

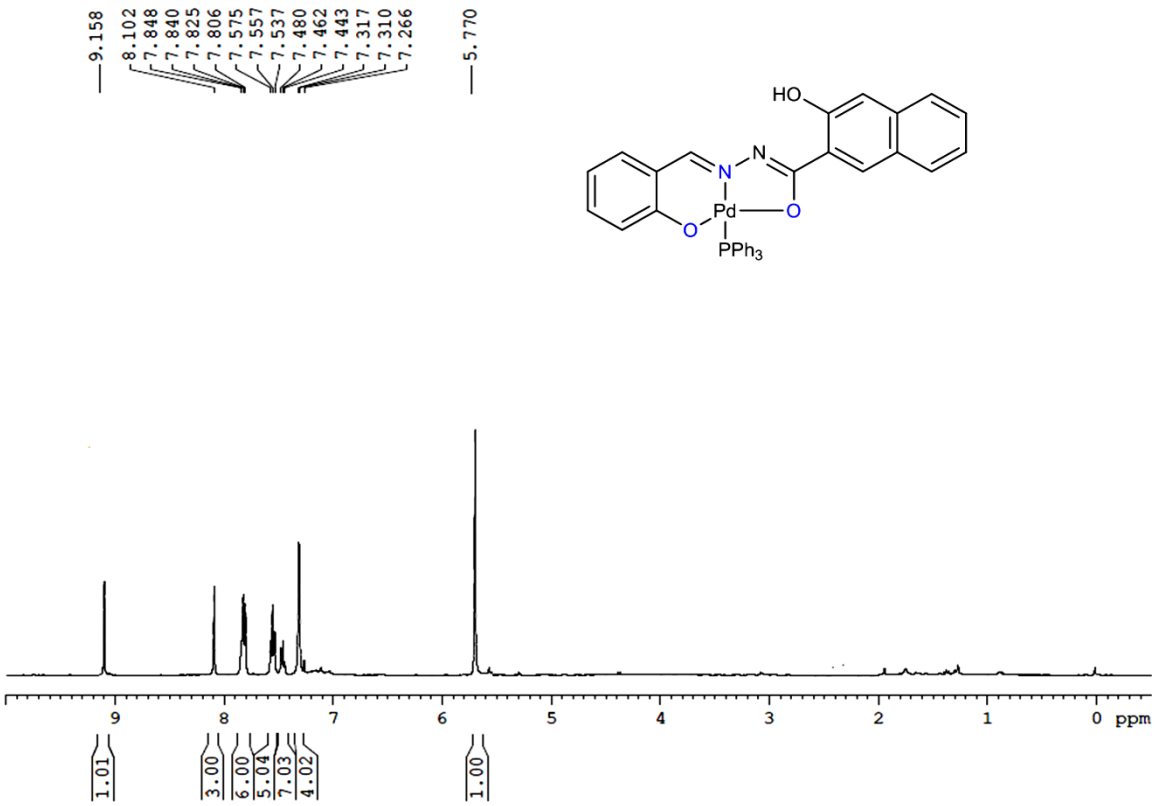


Fig. 7. ^{1}H NMR spectrum of complex **2**

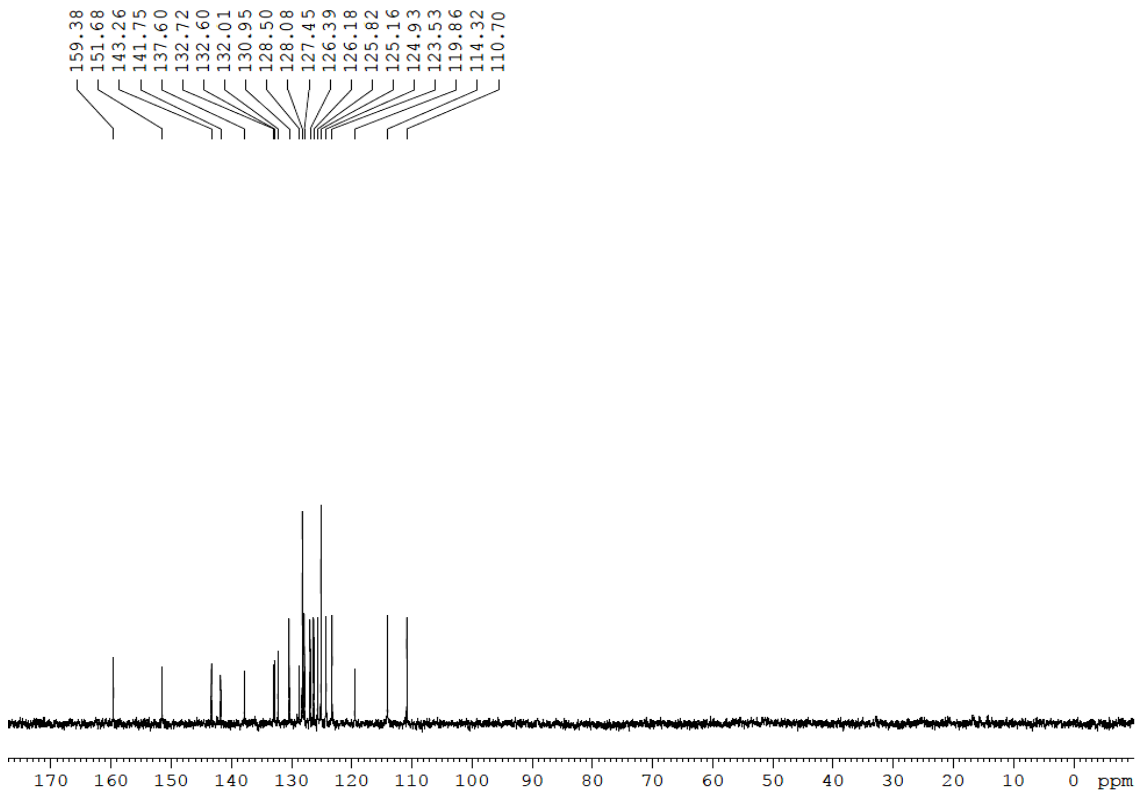


Fig. 8. ^{13}C NMR spectrum of complex **2**

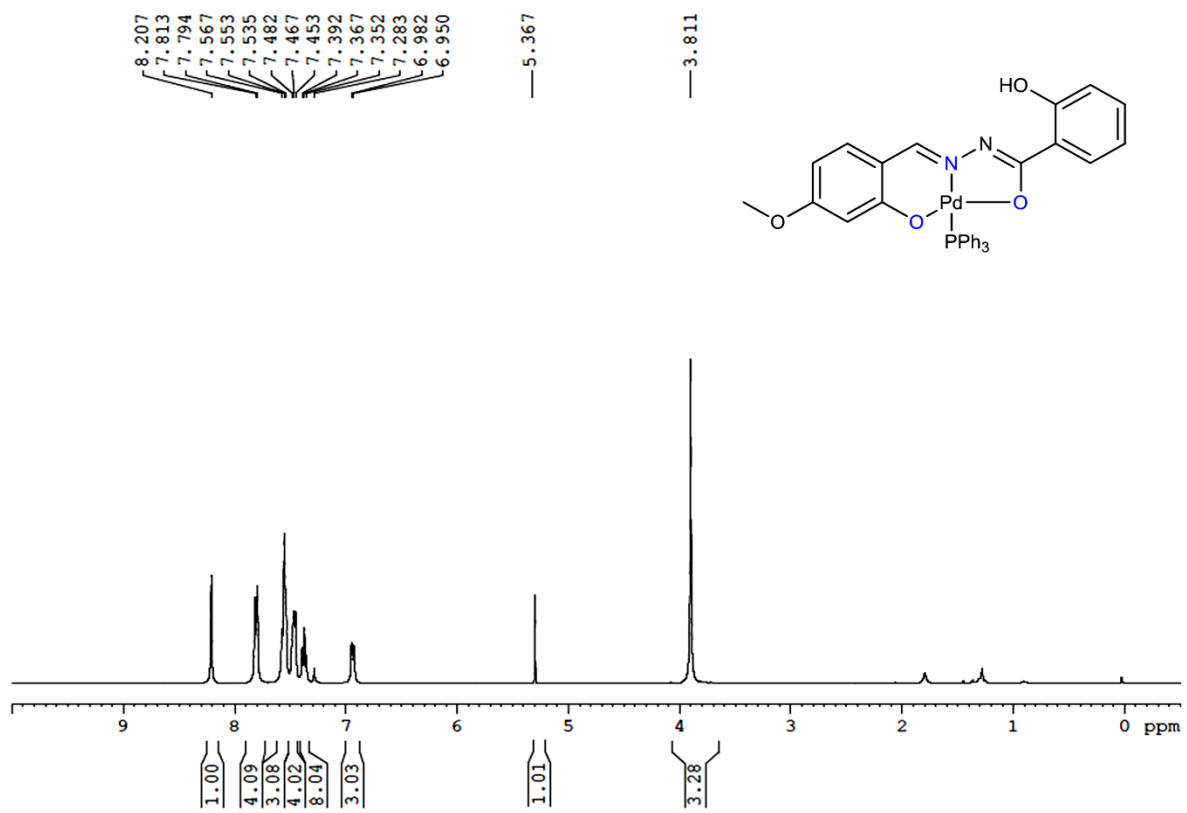


Fig. 9. ^{1}H NMR spectrum of complex **3**

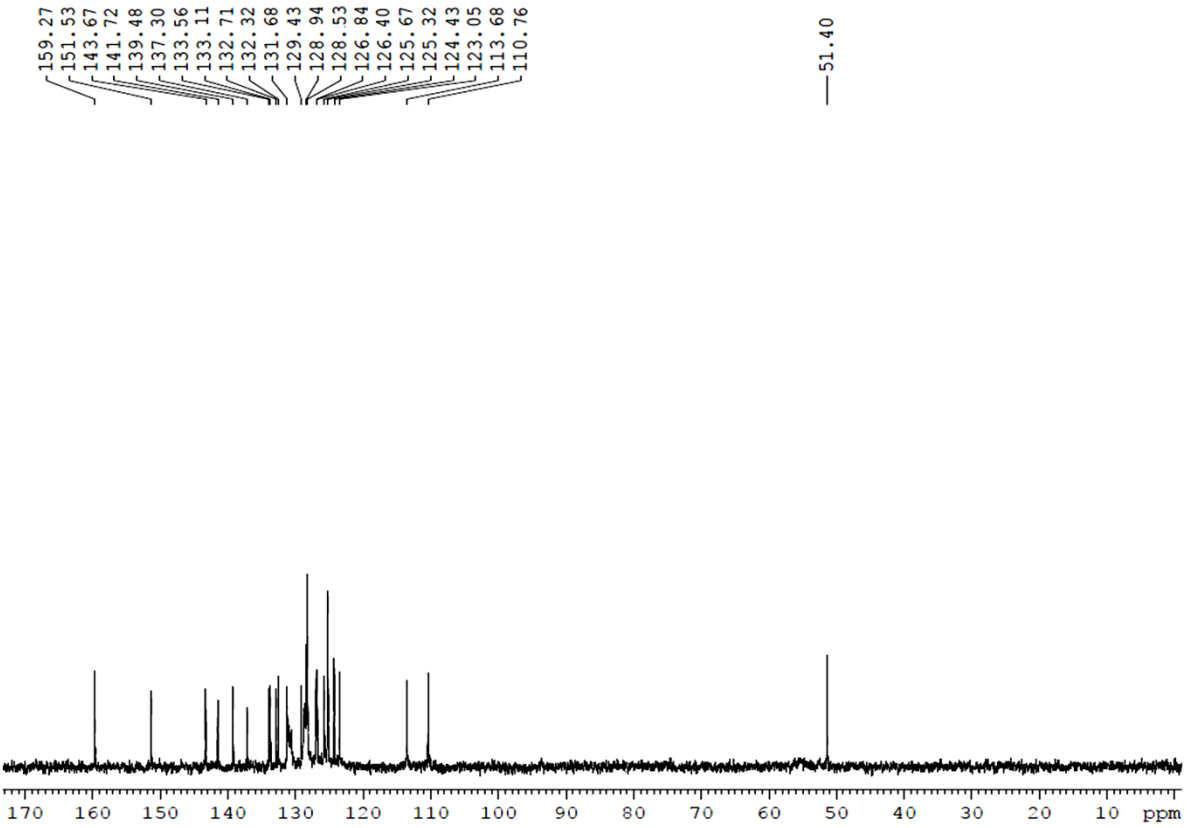


Fig. 10. ^{13}C NMR spectrum of complex **3**

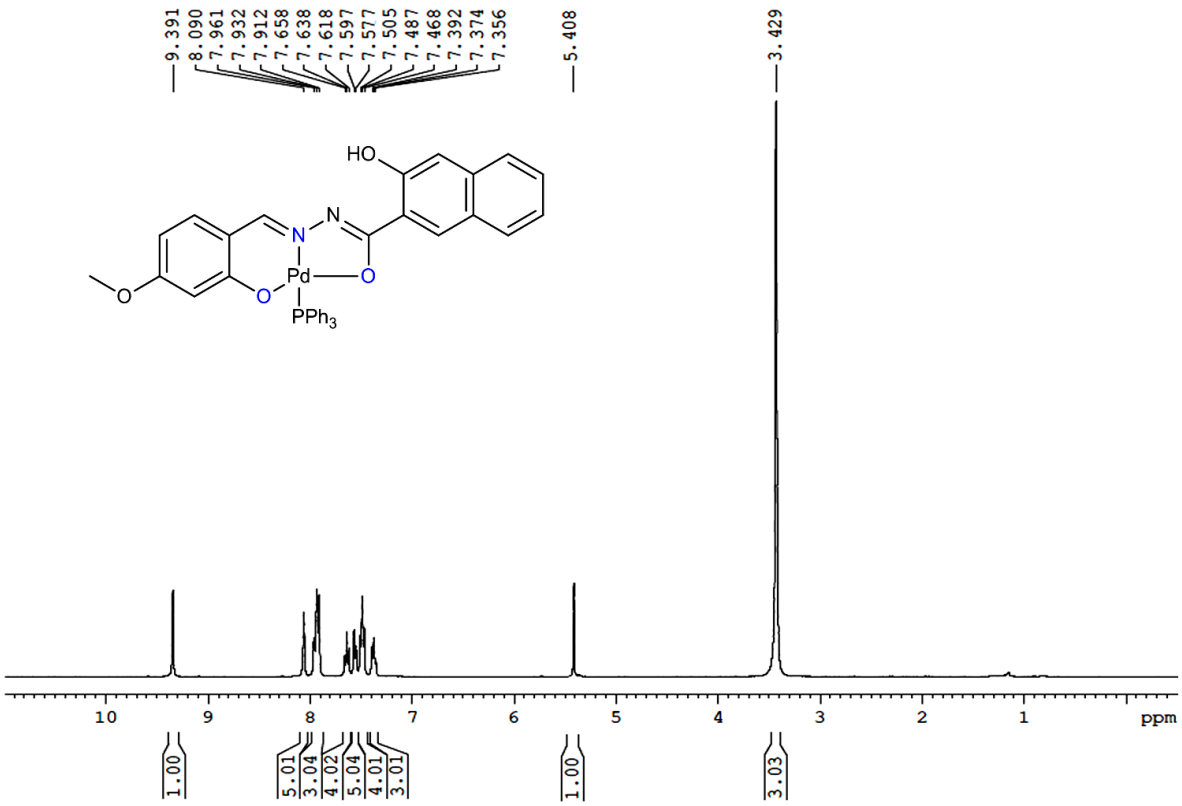


Fig. 11. ^{1}H NMR spectrum of complex **4**

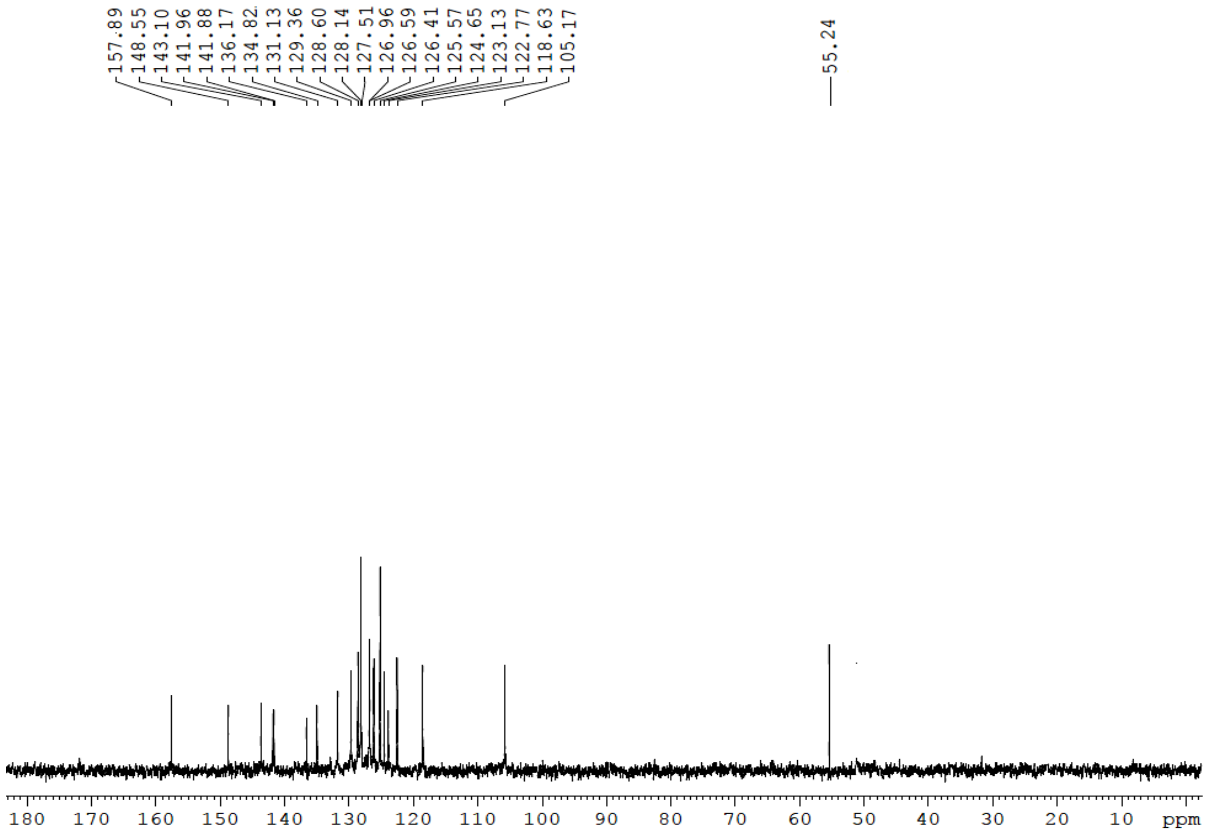


Fig. 12. ^{13}C NMR spectrum of complex **4**

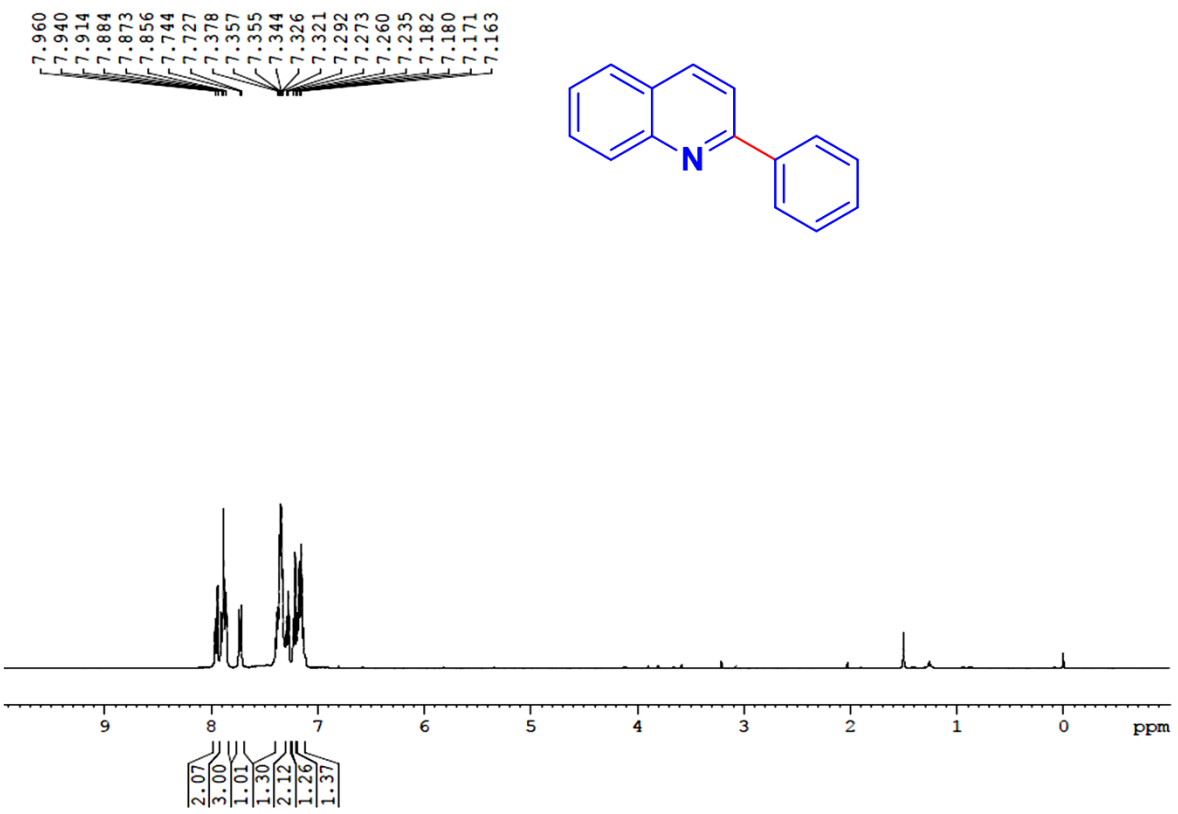


Fig. 13. ^{1}H NMR spectrum of 2-phenyl-quinoline (1a)

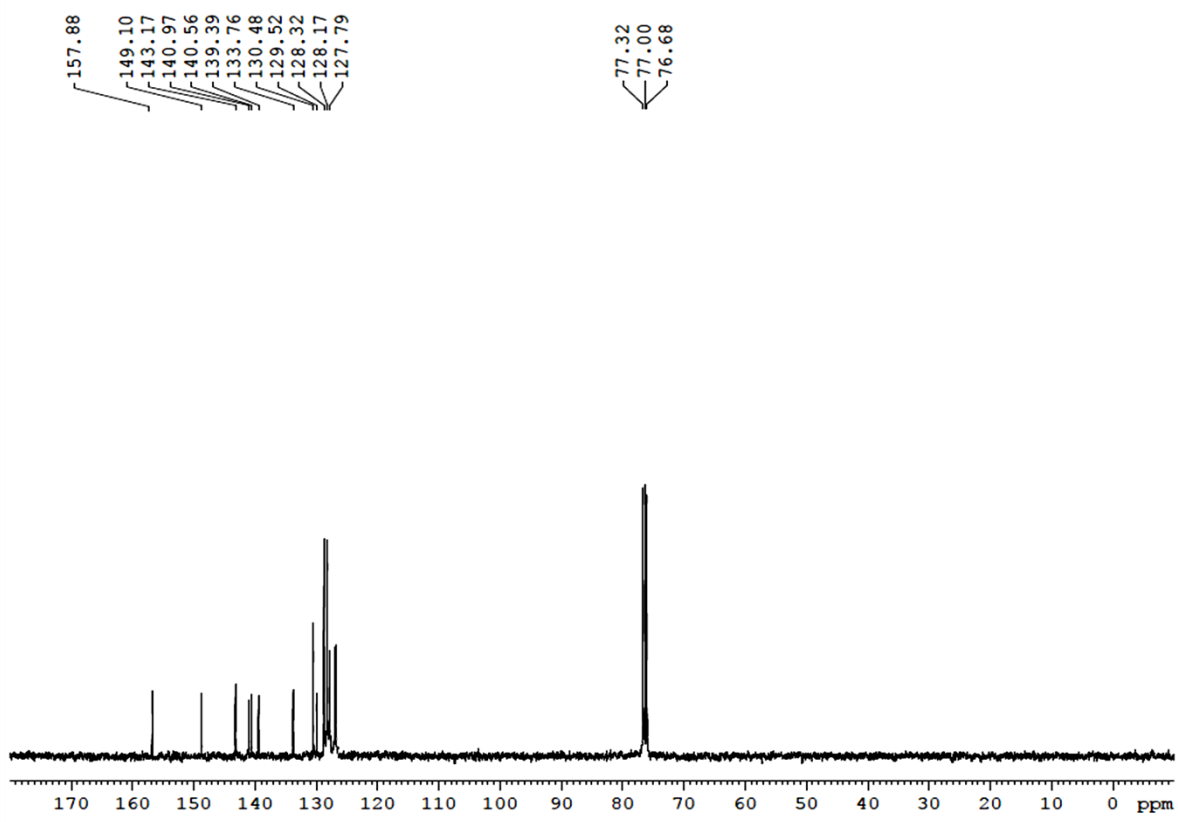


Fig. 14. ^{13}C NMR spectrum of 2-phenyl-quinoline (1a)

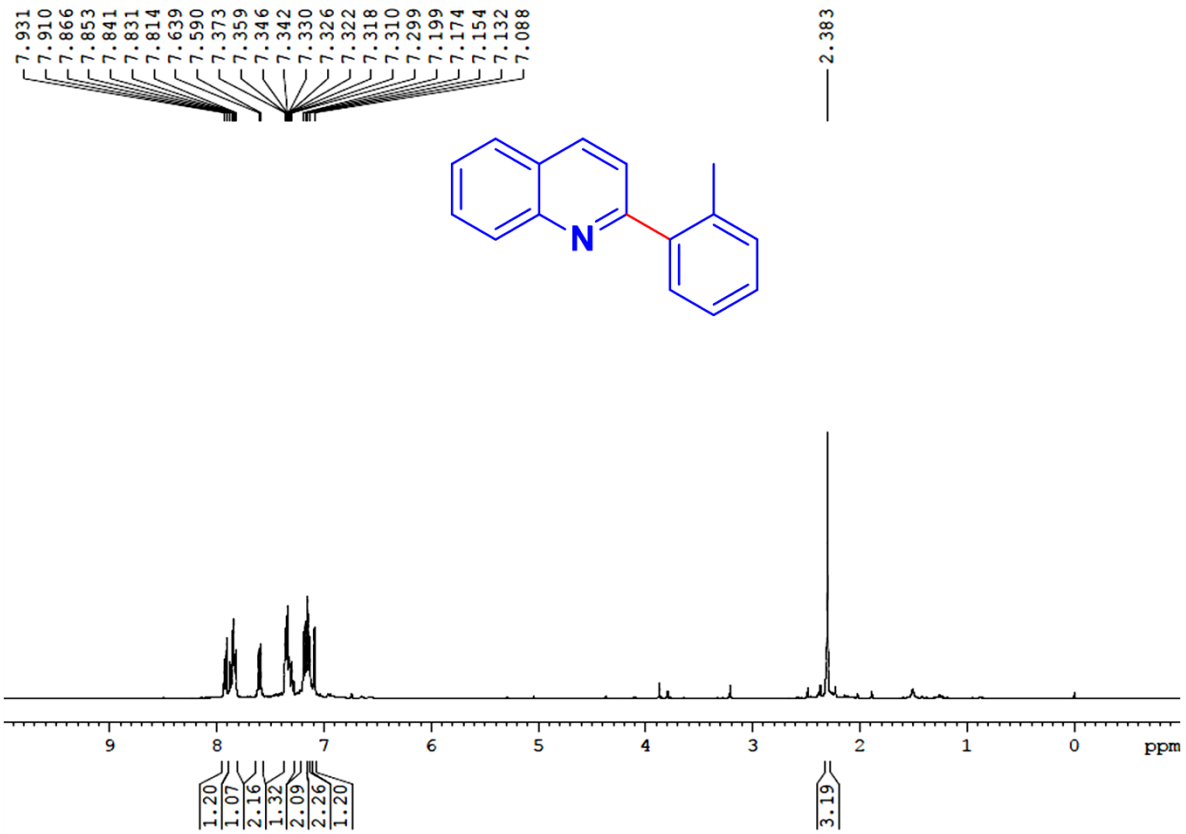


Fig. 15. ^{1}H NMR spectrum of 2-*o*-tolylquinoline (1b)

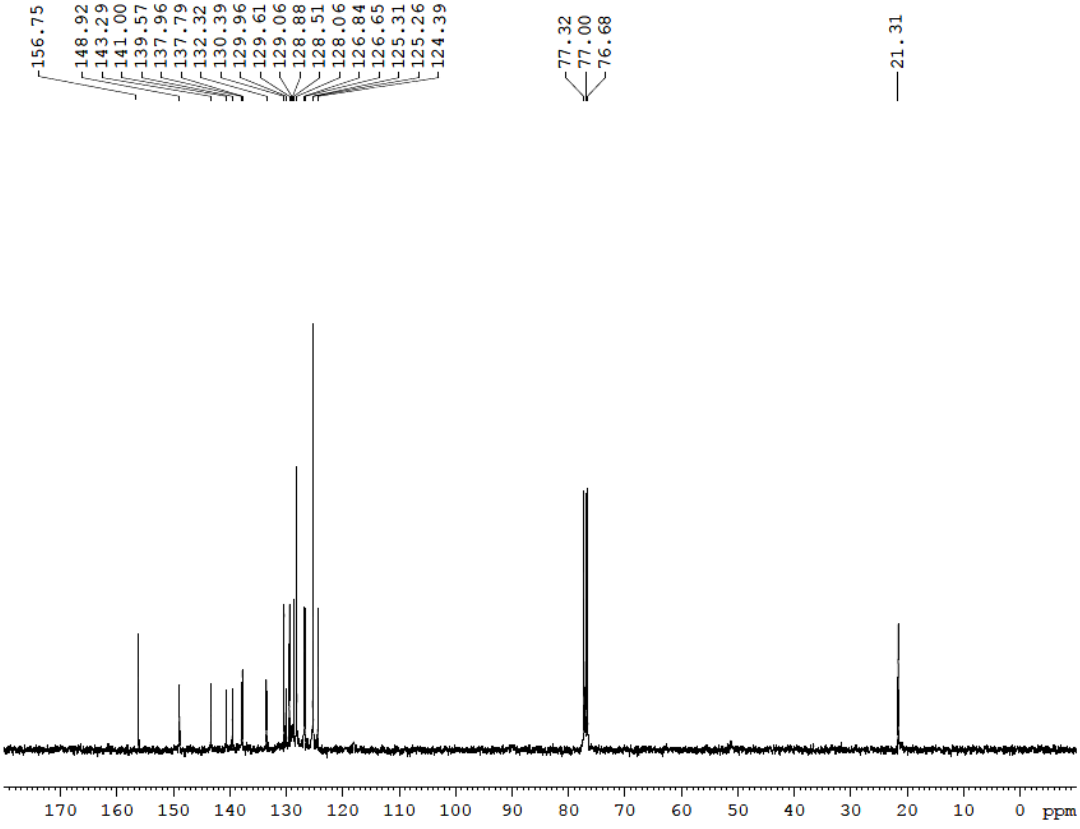


Fig. 16. ^{13}C NMR spectrum of 2-*o*-tolylquinoline (1b)

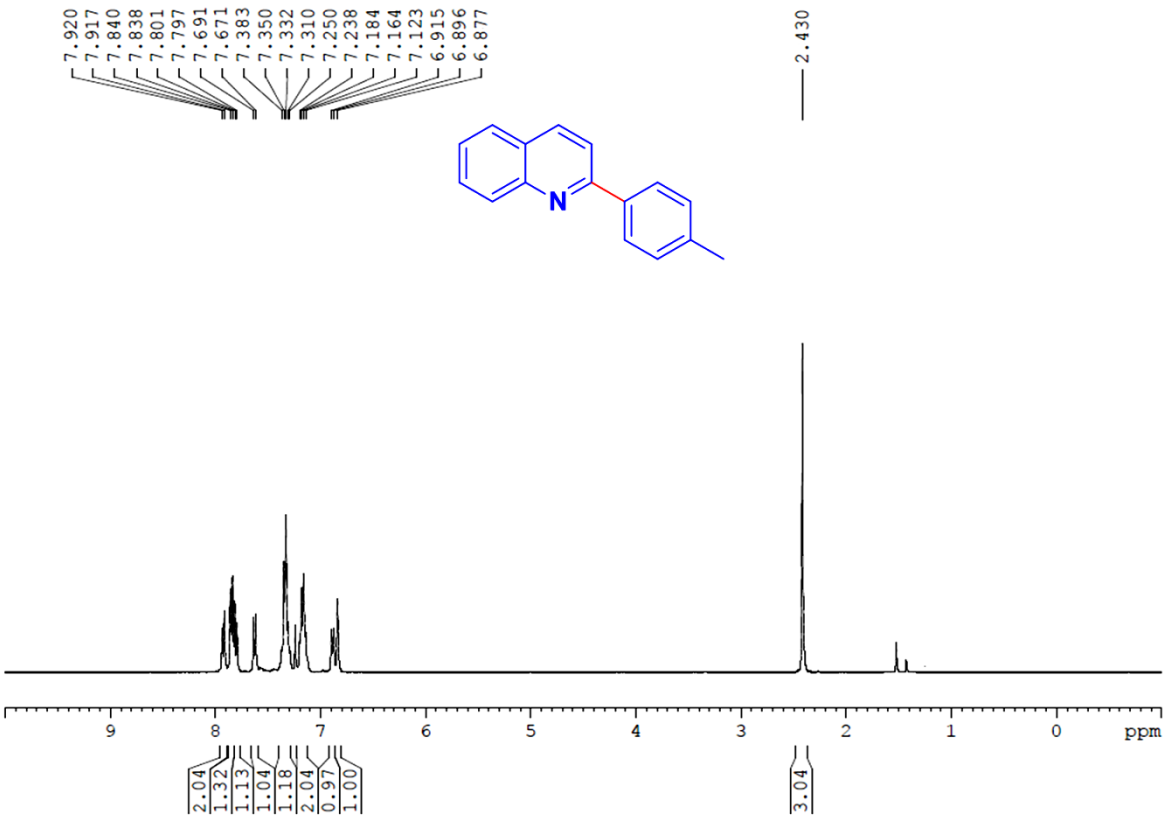


Fig. 17. ^{1}H NMR spectrum of 2-*p*-tolylquinoline (1c)

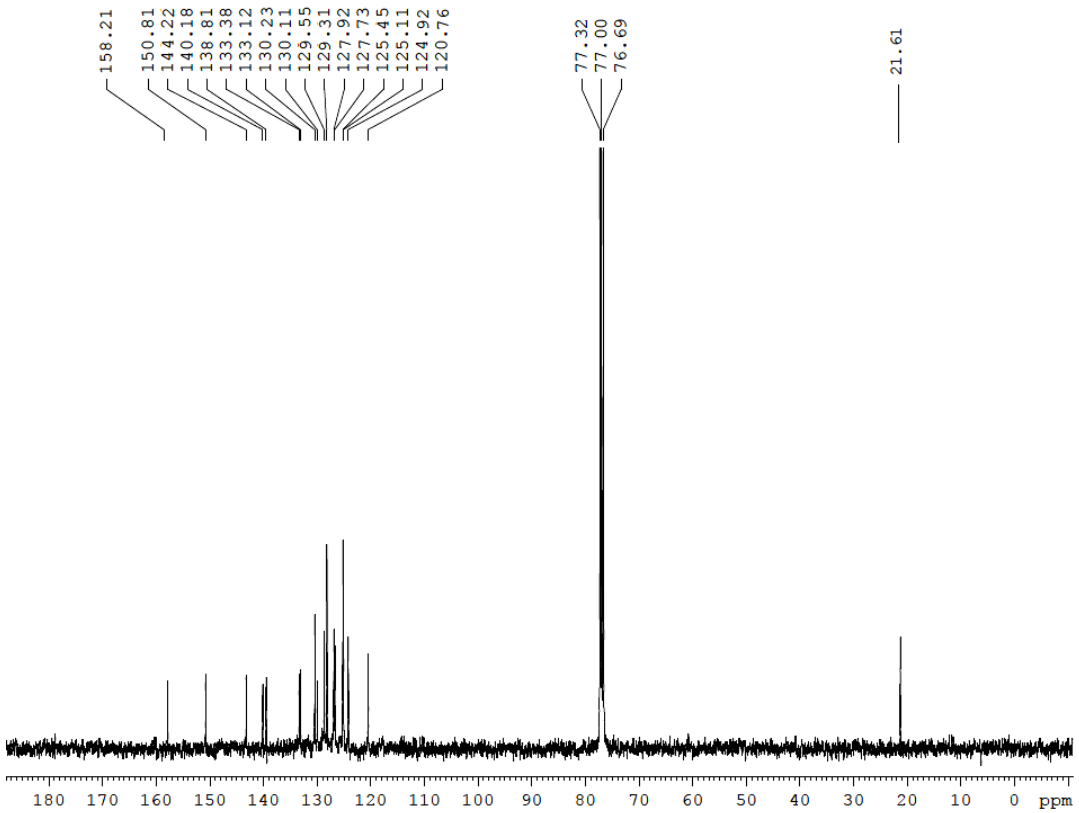


Fig. 18. ^{13}C NMR spectrum of 2-*p*-tolylquinoline (1c)

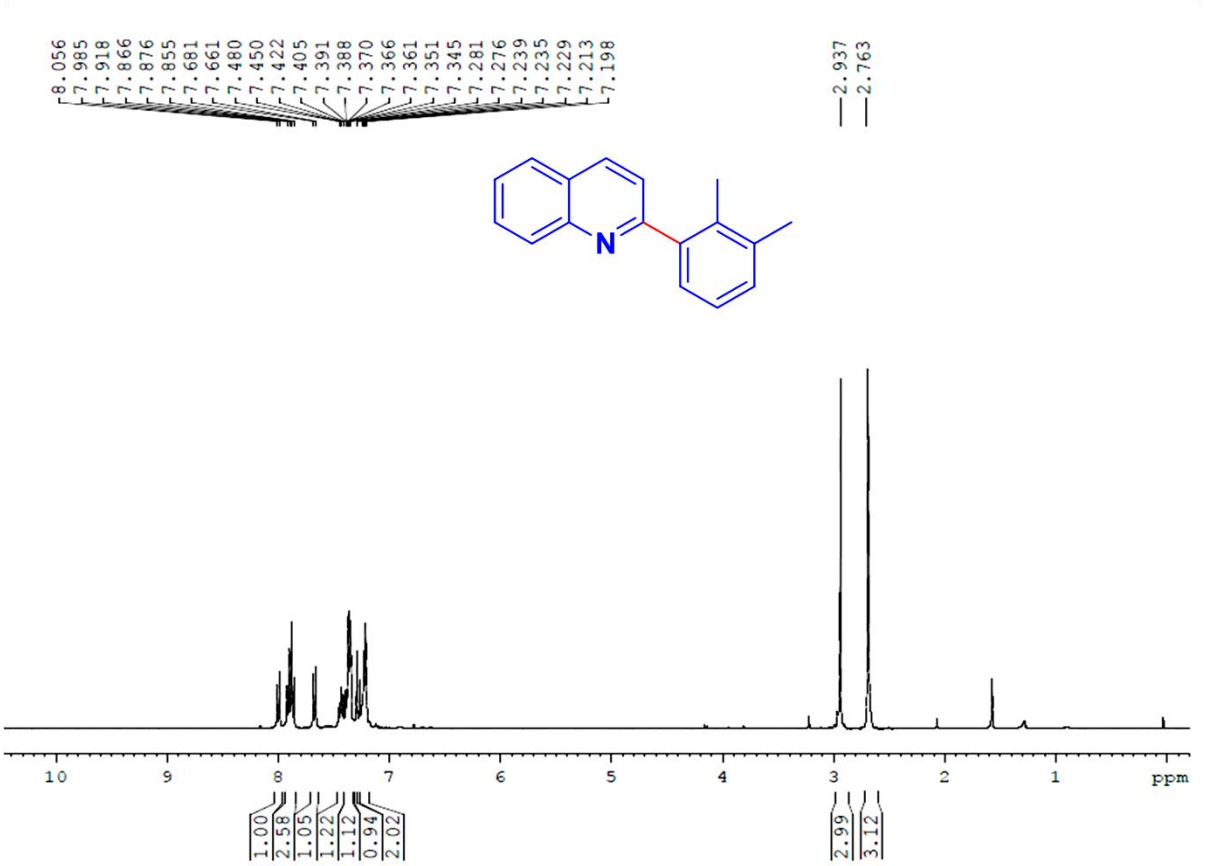


Fig. 19. ^{1}H NMR spectrum of 2-(2, 3-dimethyl-phenyl)-quinoline (1d)

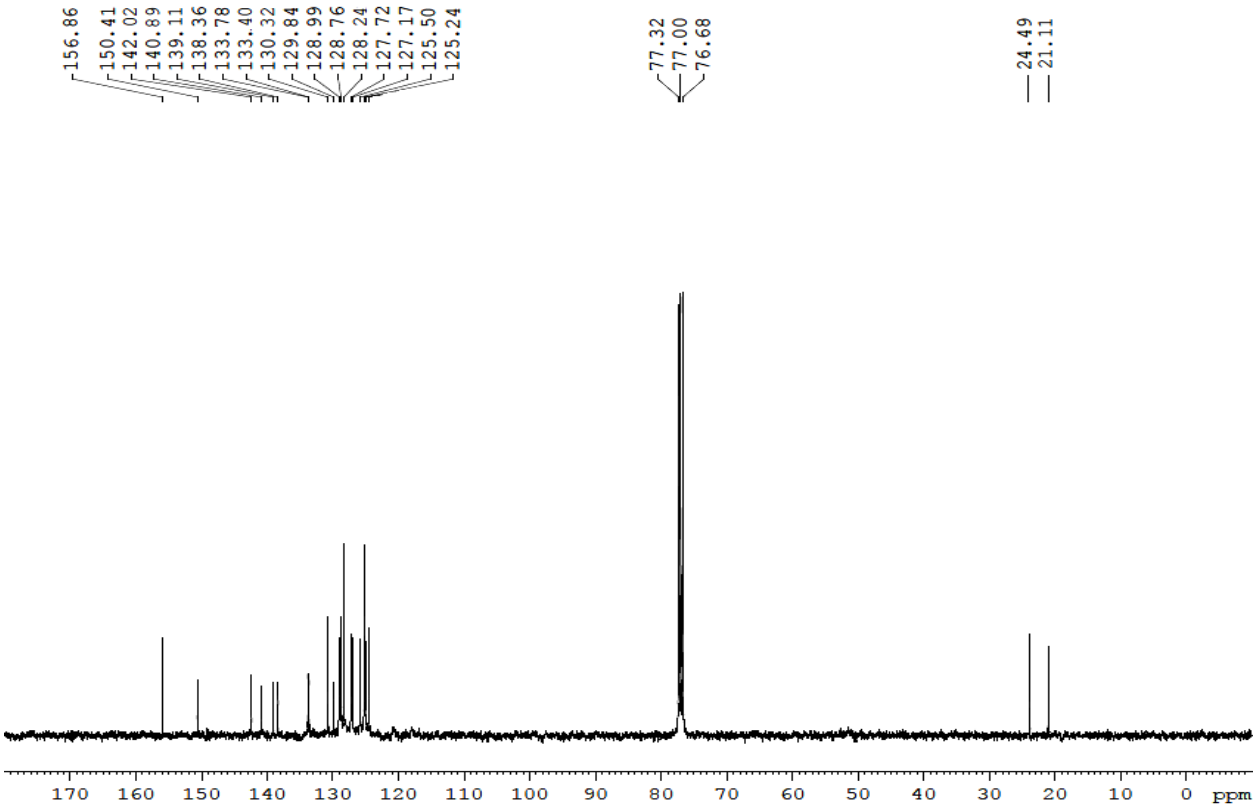


Fig. 20. ^{13}C NMR spectrum of 2-(2, 3-dimethyl-phenyl)-quinoline (1d)

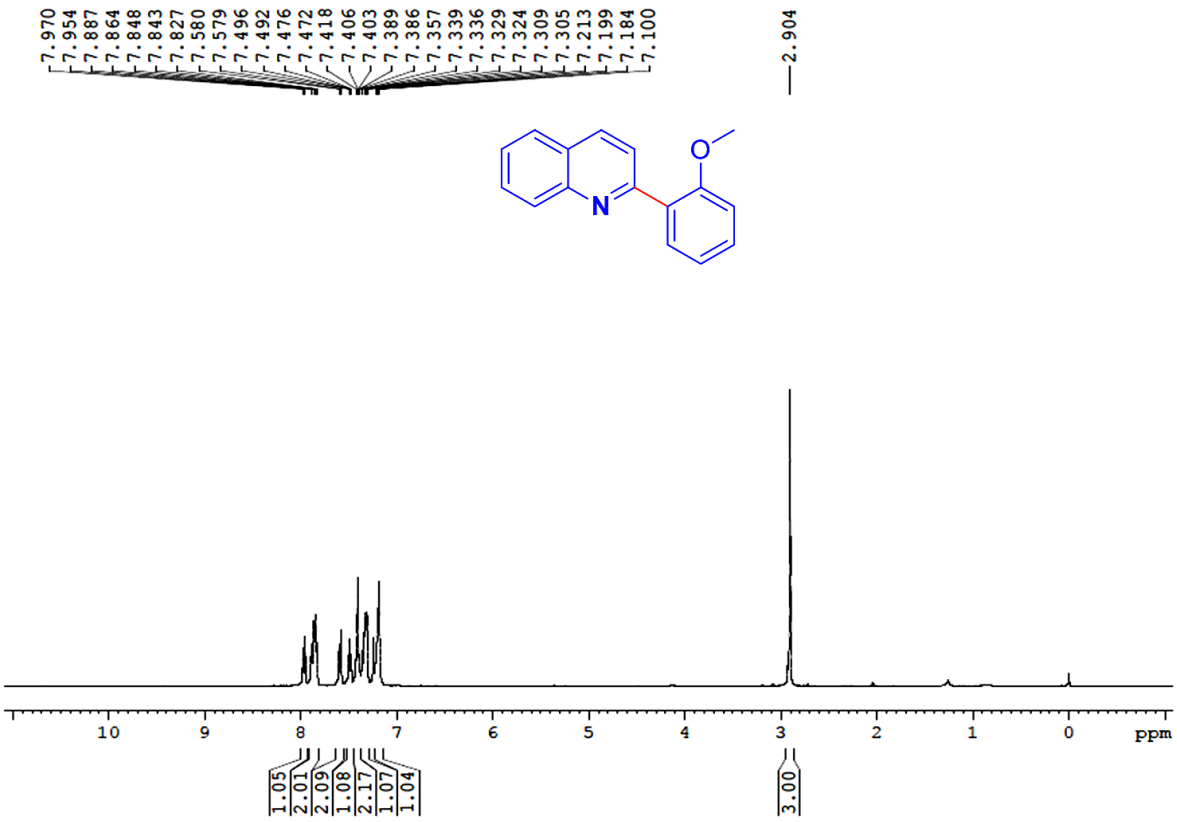


Fig. 21. ^{1}H NMR spectrum of 2-(2-methoxy-phenyl)-quinoline (1e)

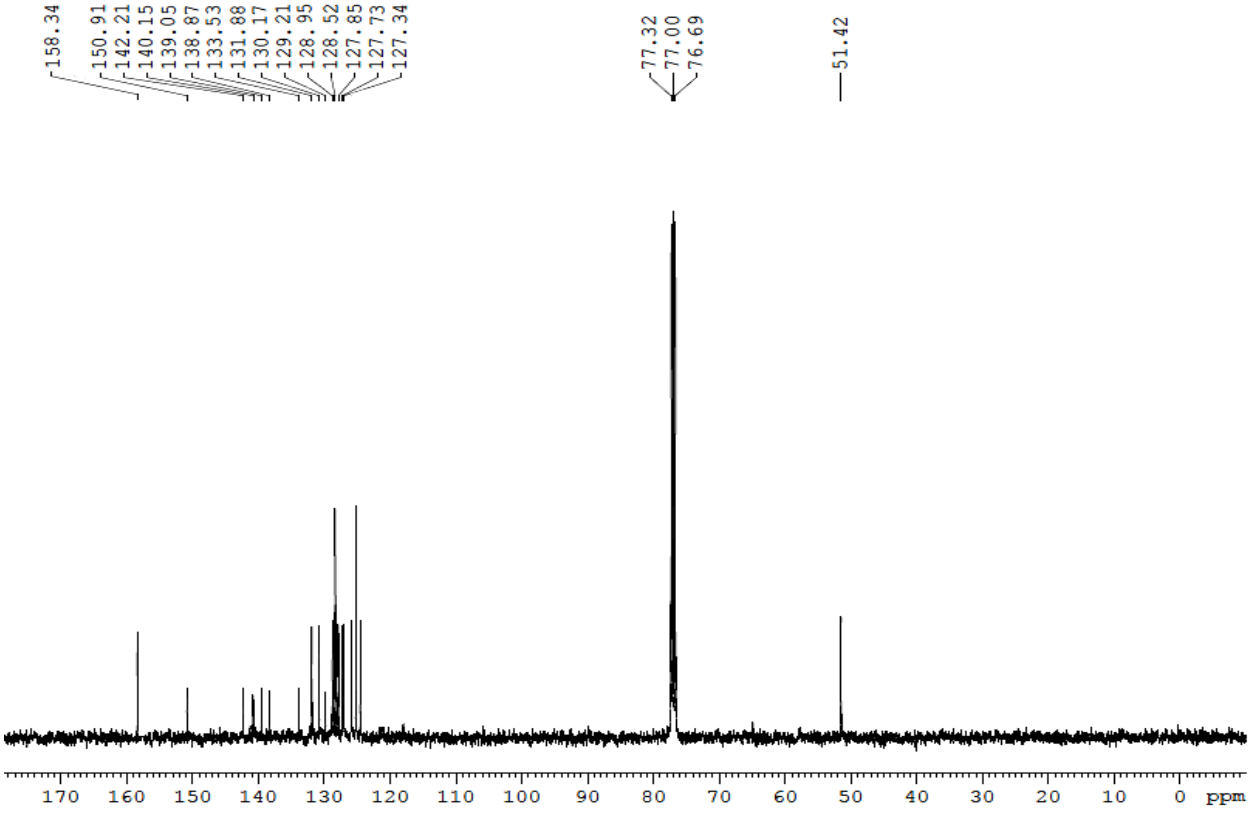


Fig. 22. ^{13}C NMR spectrum of 2-(2-methoxy-phenyl)-quinoline (1e)

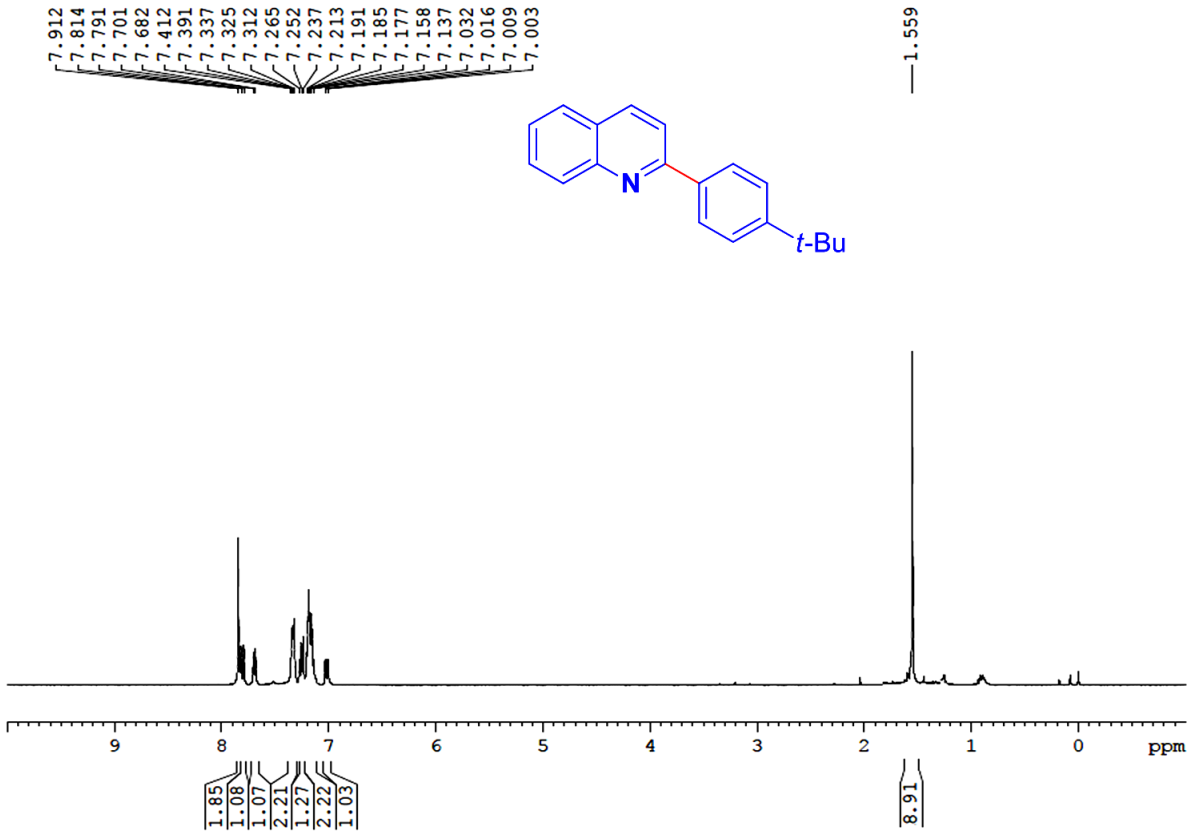


Fig. 23. ^{1}H NMR spectrum of 2-(4-*tert*-butyl-phenyl)-quinoline (1f)

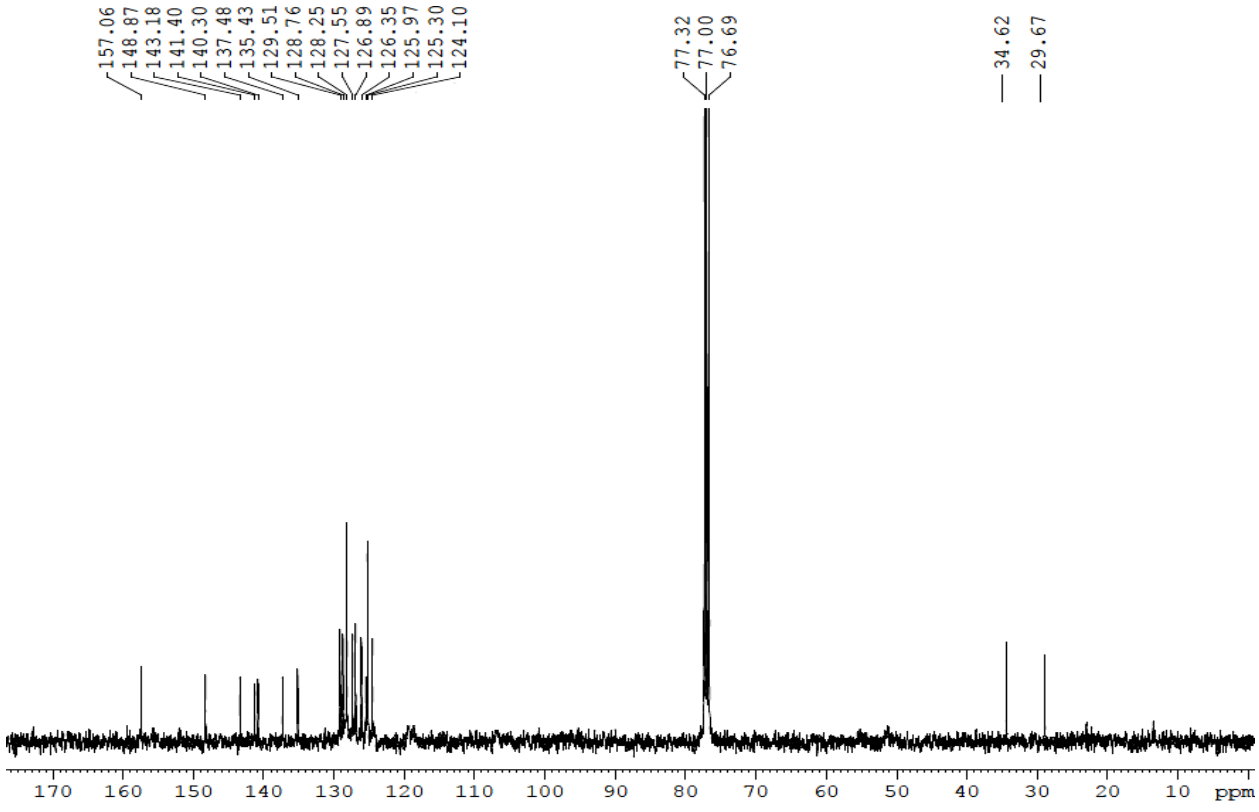


Fig. 24. ^{13}C NMR spectrum of 2-(4-*tert*-butyl-phenyl)-quinoline (1f)

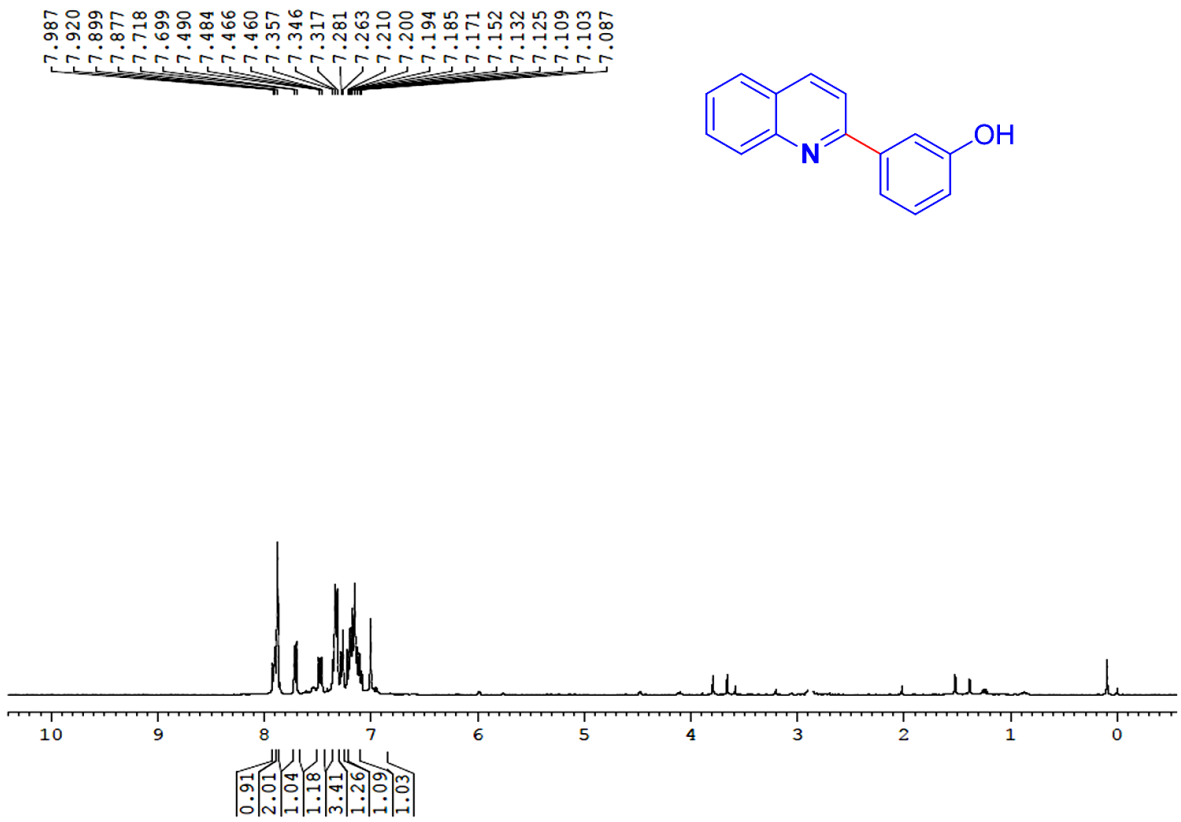


Fig. 25. ^{1}H NMR spectrum of 3-quinolin-2-yl-phenol (1g)

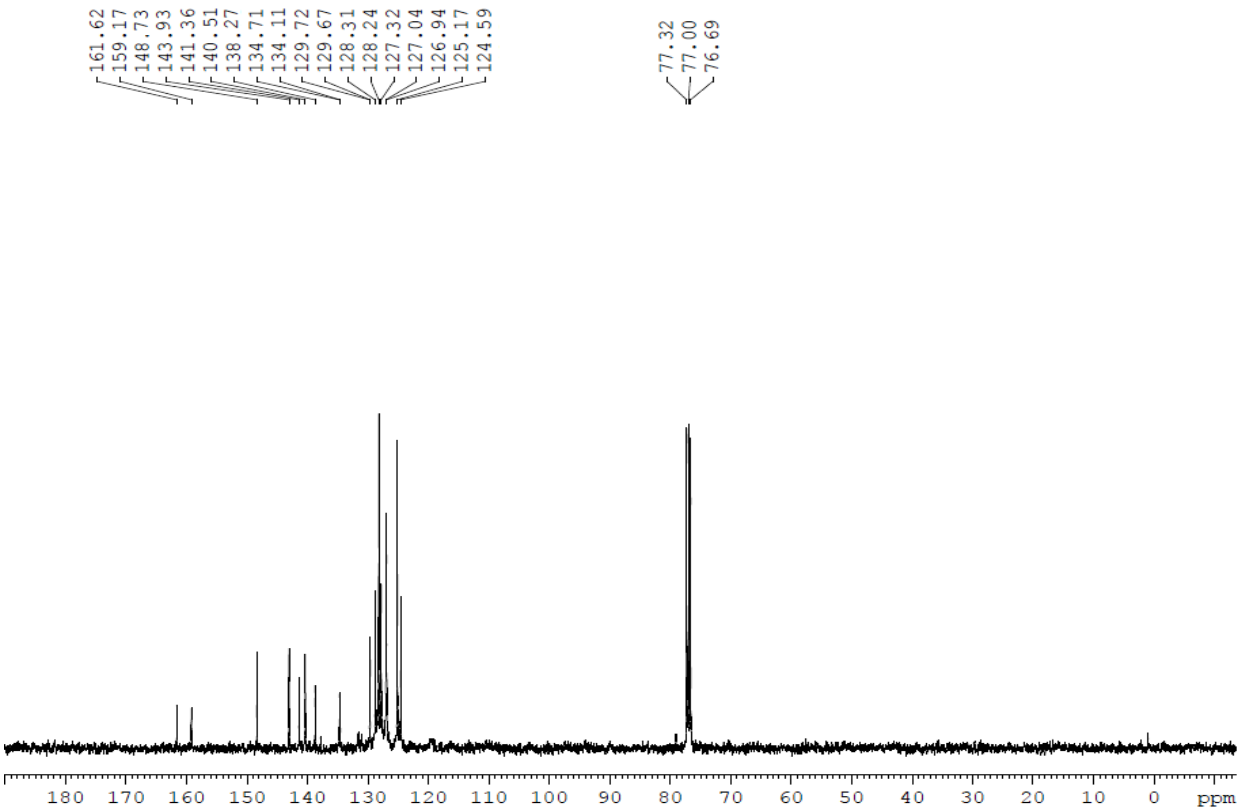


Fig. 26. ^{13}C NMR spectrum of 3-quinolin-2-yl-phenol (1g)

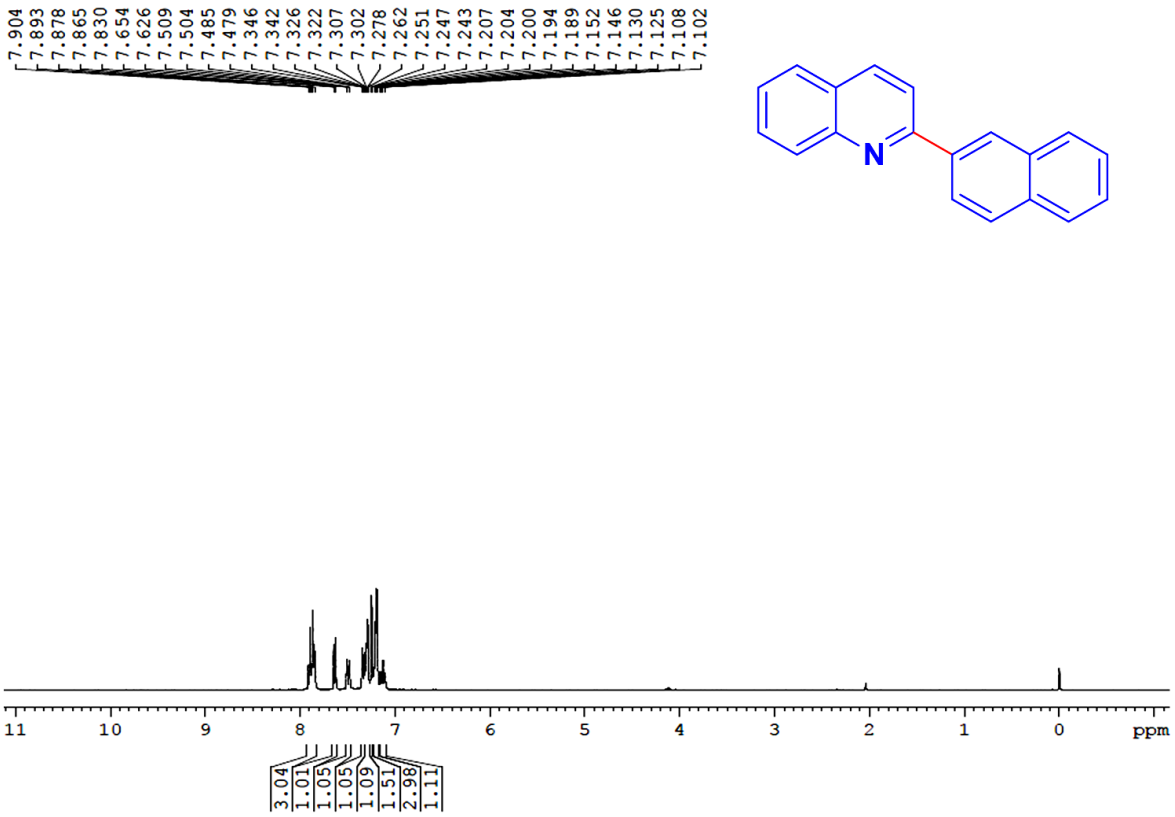


Fig. 27. ^{1}H NMR spectrum of 2-naphthalen-2-yl-quinoline (1h)

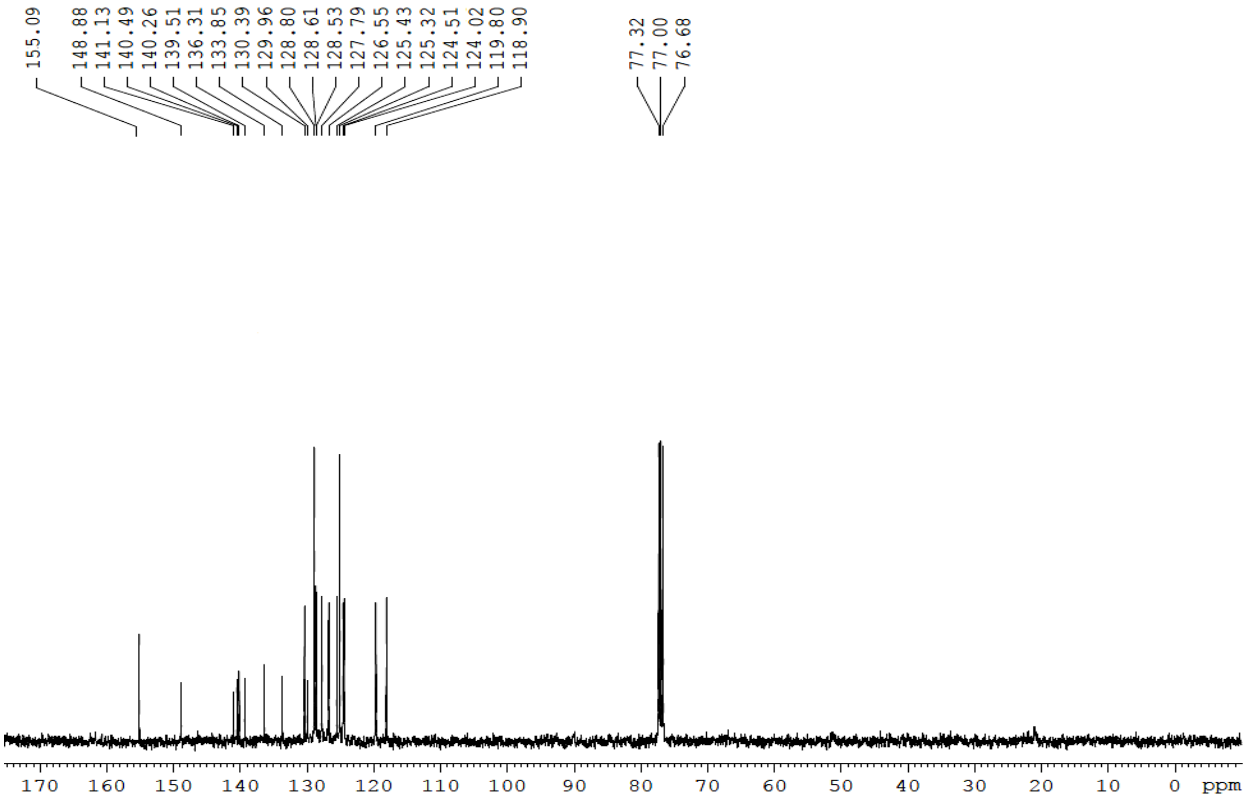


Fig. 28. ^{13}C NMR spectrum of 2-naphthalen-2-yl-quinoline (1h)

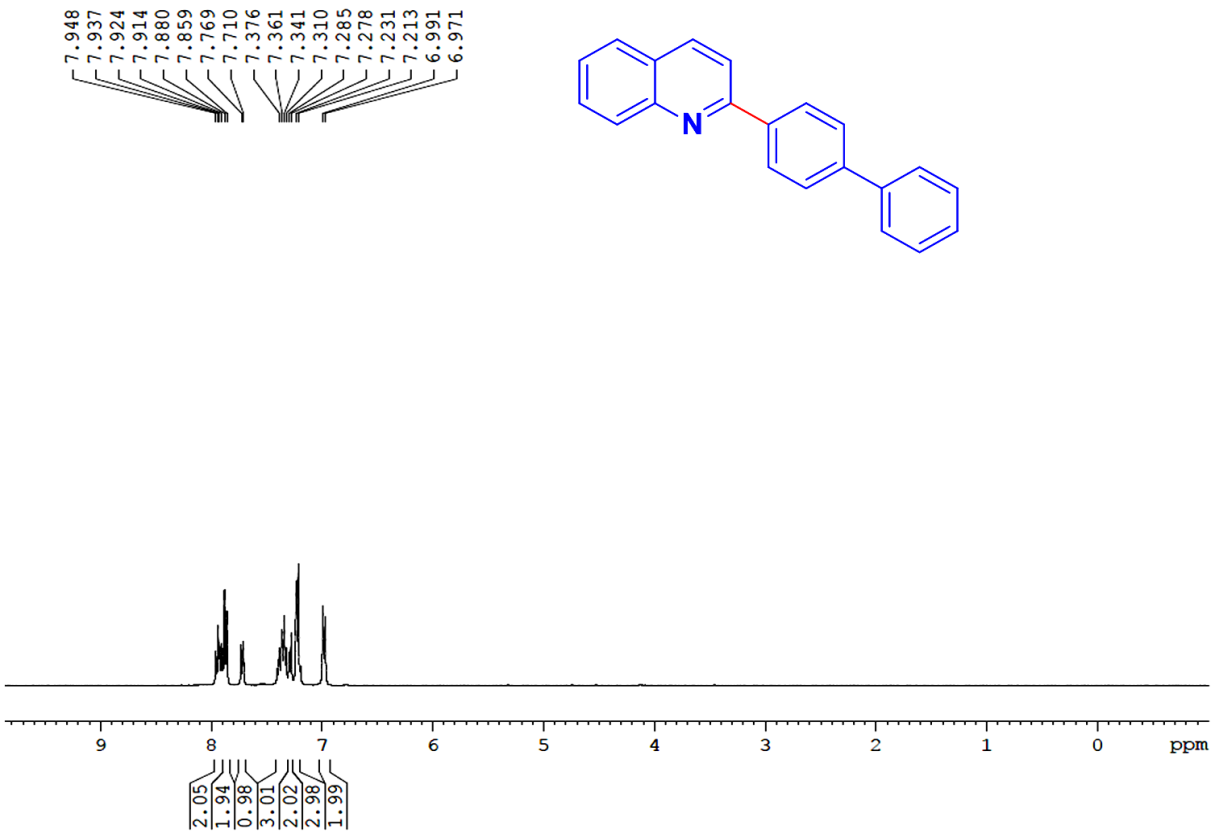


Fig. 29. ^{1}H NMR spectrum of 2-biphenyl-4-yl-quinoline (1i)

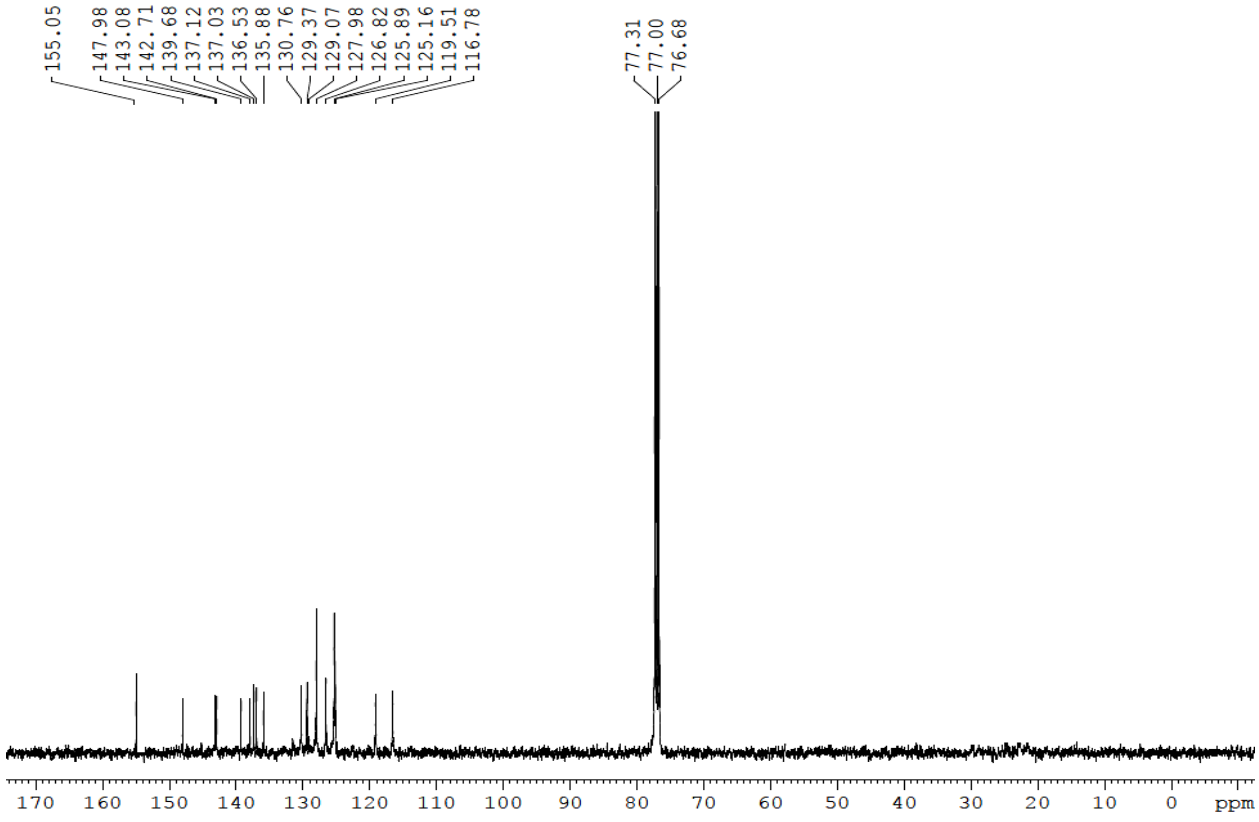


Fig. 30. ^{13}C NMR spectrum of 2-biphenyl-4-yl-quinoline (1i)

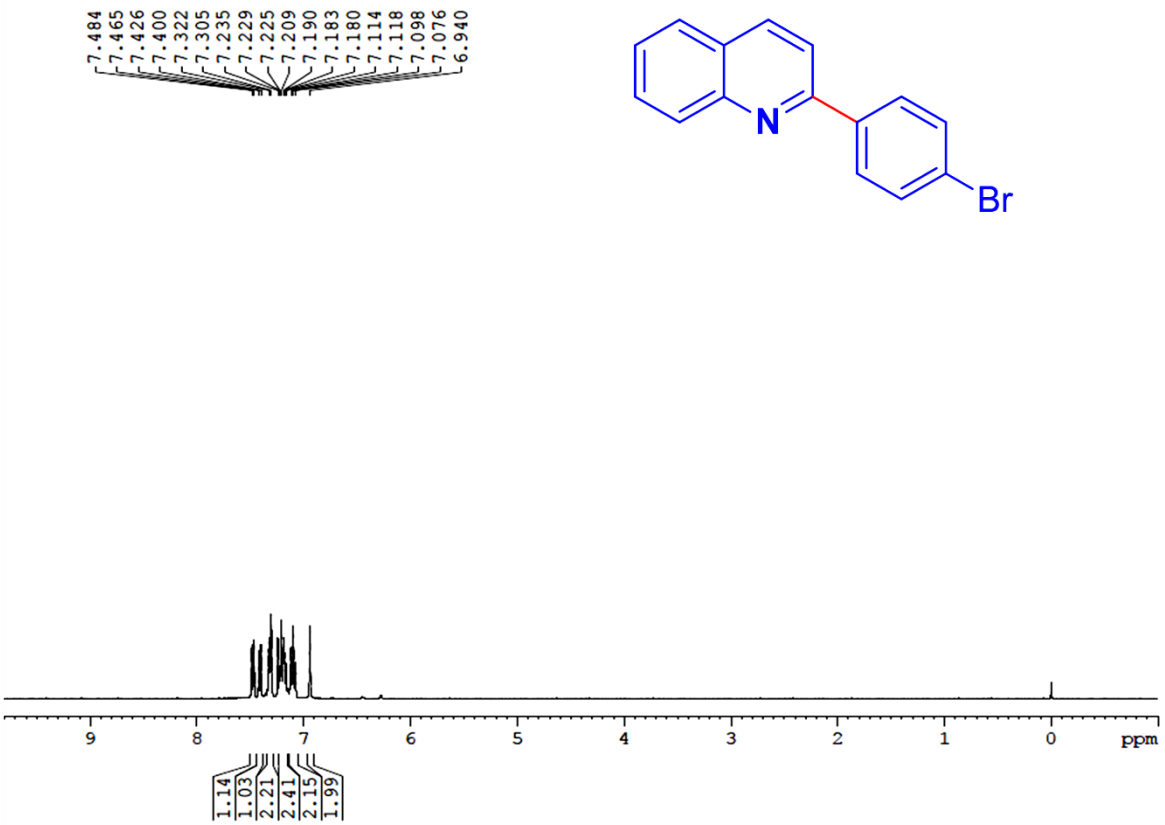


Fig. 31. ^{1}H NMR spectrum of 2-(4-bromo-phenyl)-quinoline (1j)

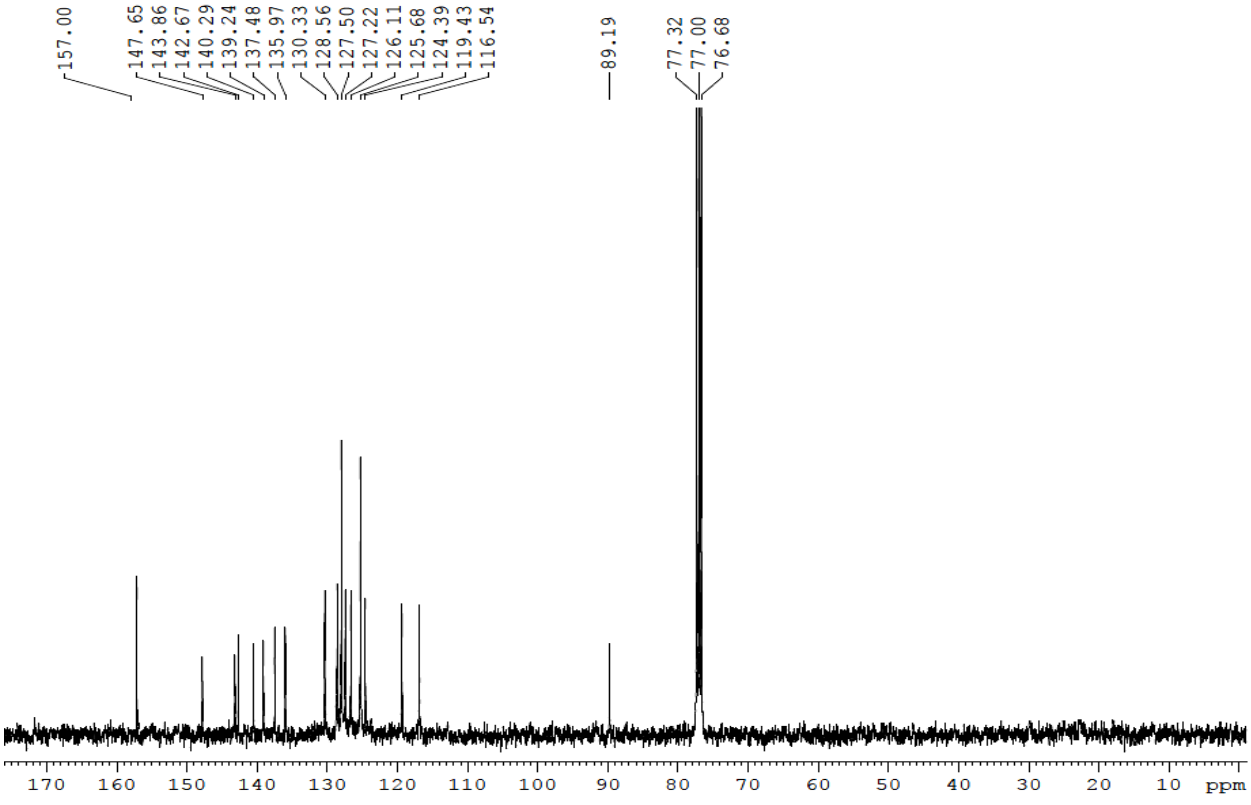


Fig. 32. ^{13}C NMR spectrum of 2-(4-bromo-phenyl)-quinoline (1j)

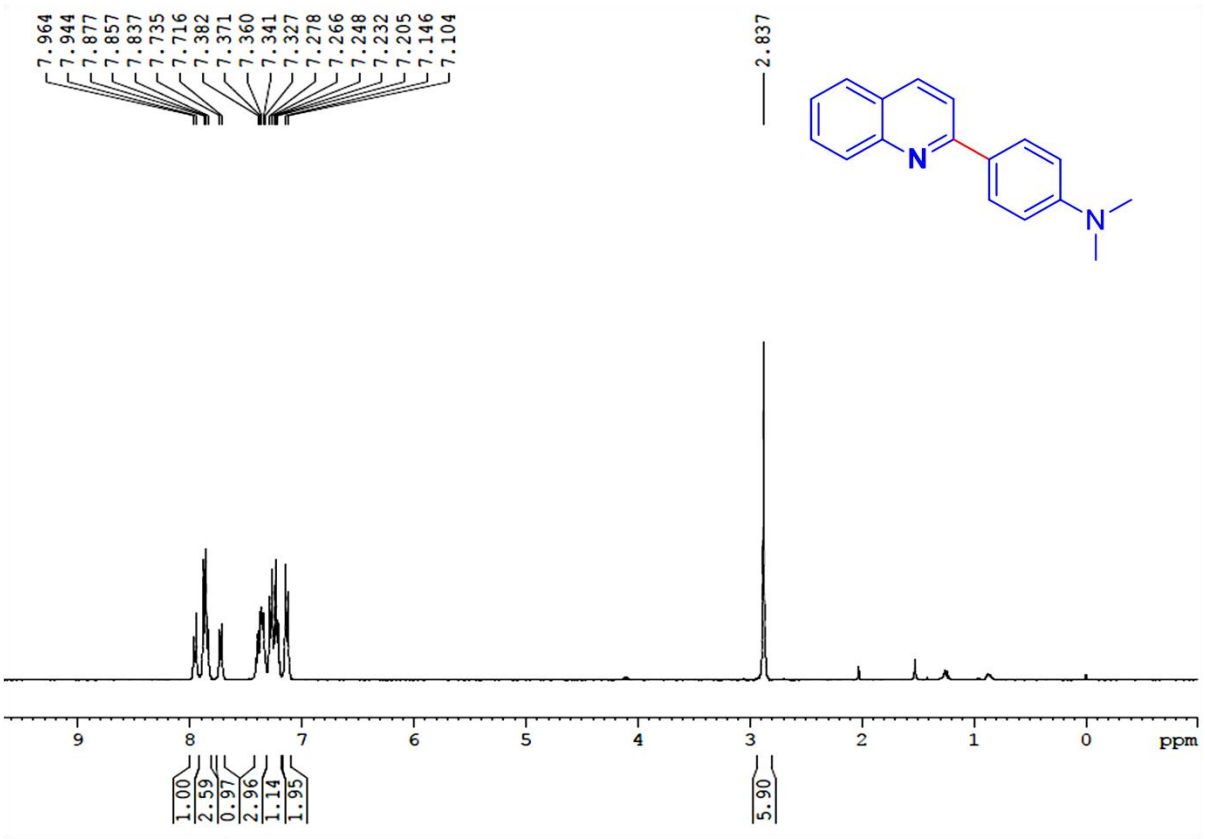


Fig. 33. ^{1}H NMR spectrum of dimethyl-(4-quinolin-2-yl-phenyl)-amine (1k)

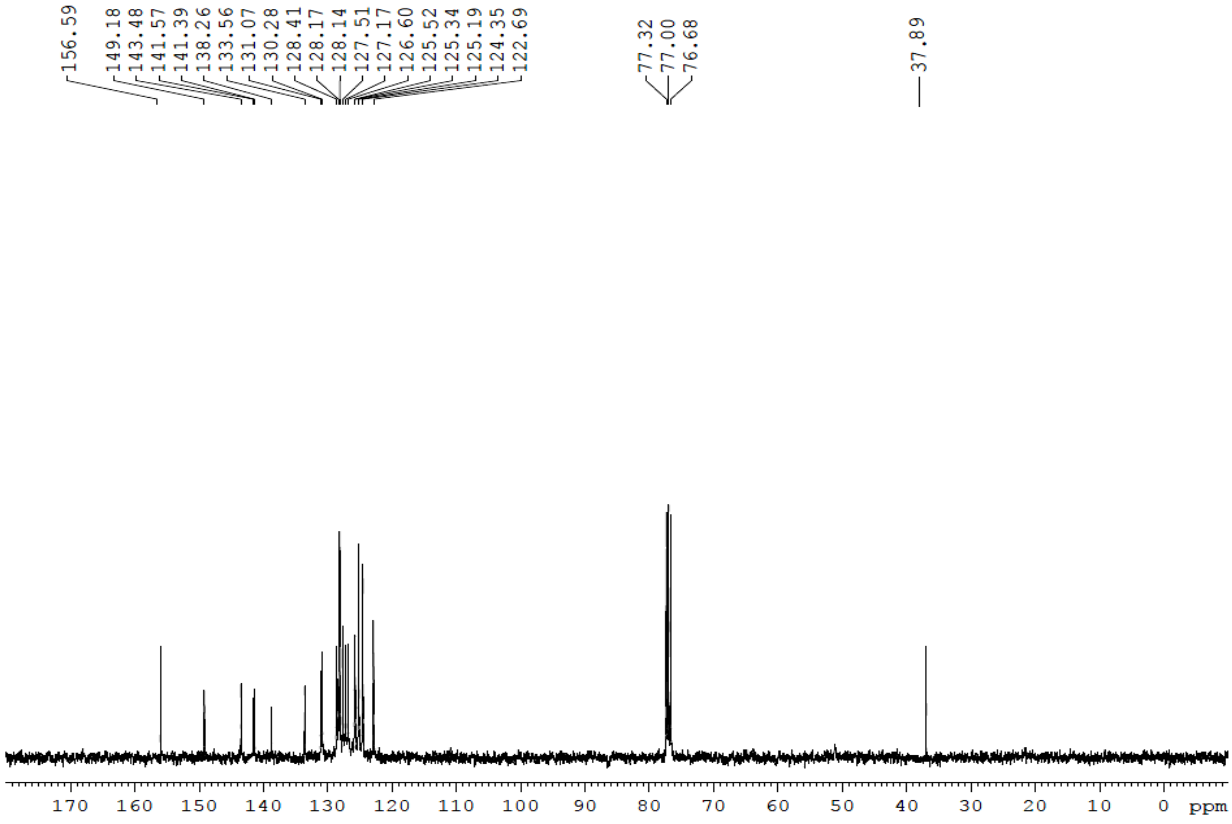


Fig. 34. ^{13}C NMR spectrum of dimethyl-(4-quinolin-2-yl-phenyl)-amine (1k)

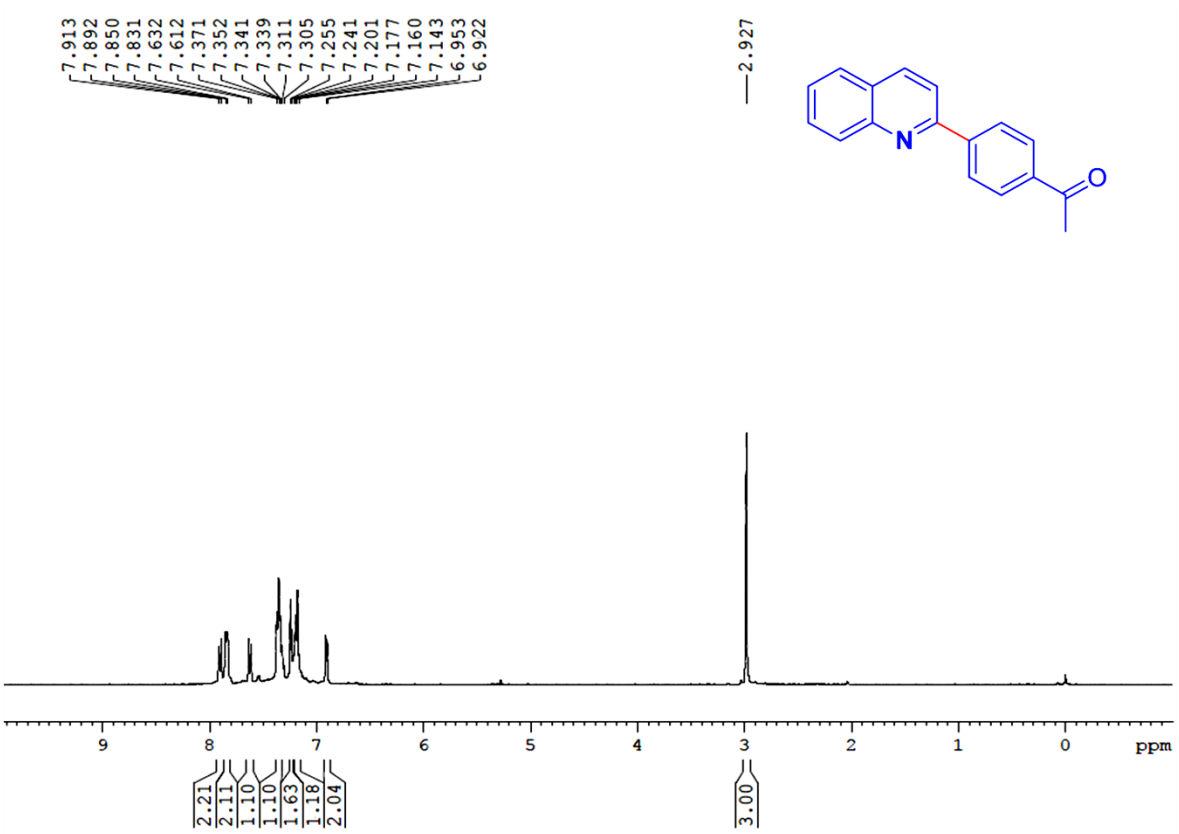


Fig. 35. ^{1}H NMR spectrum of 1-(4-quinolin-2-yl-phenyl)-ethanone (1*l*)

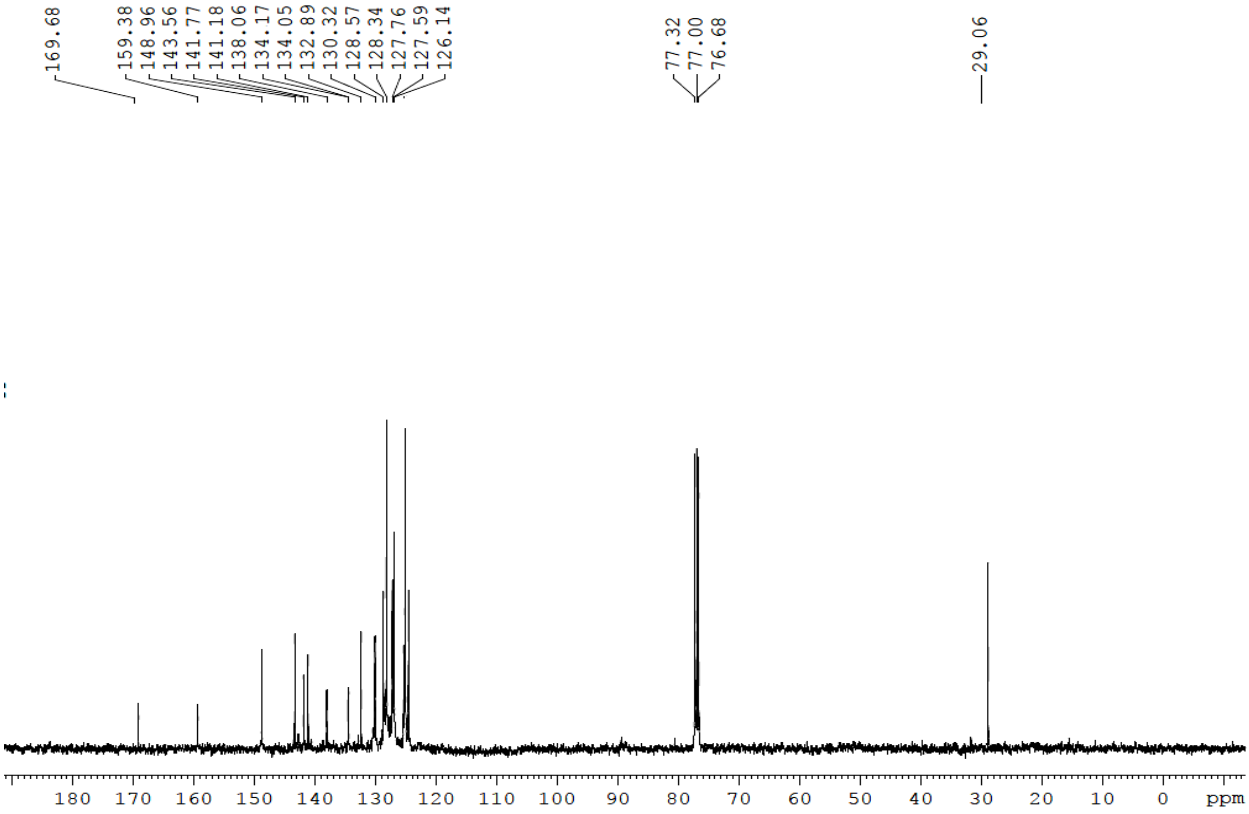


Fig. 36. ^{13}C NMR spectrum of 1-(4-quinolin-2-yl-phenyl)-ethanone (1*l*)

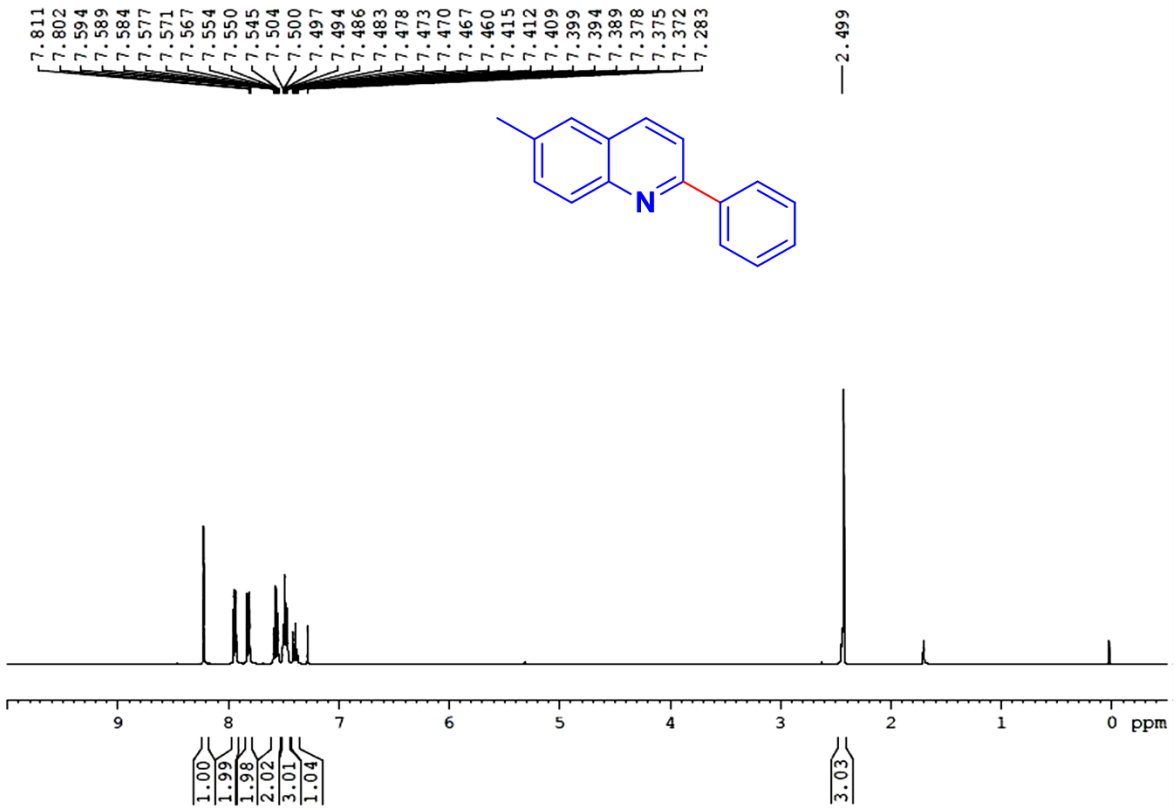


Fig. 37. ^{1}H NMR spectrum of 6-methyl-2-phenyl-quinoline (2a)

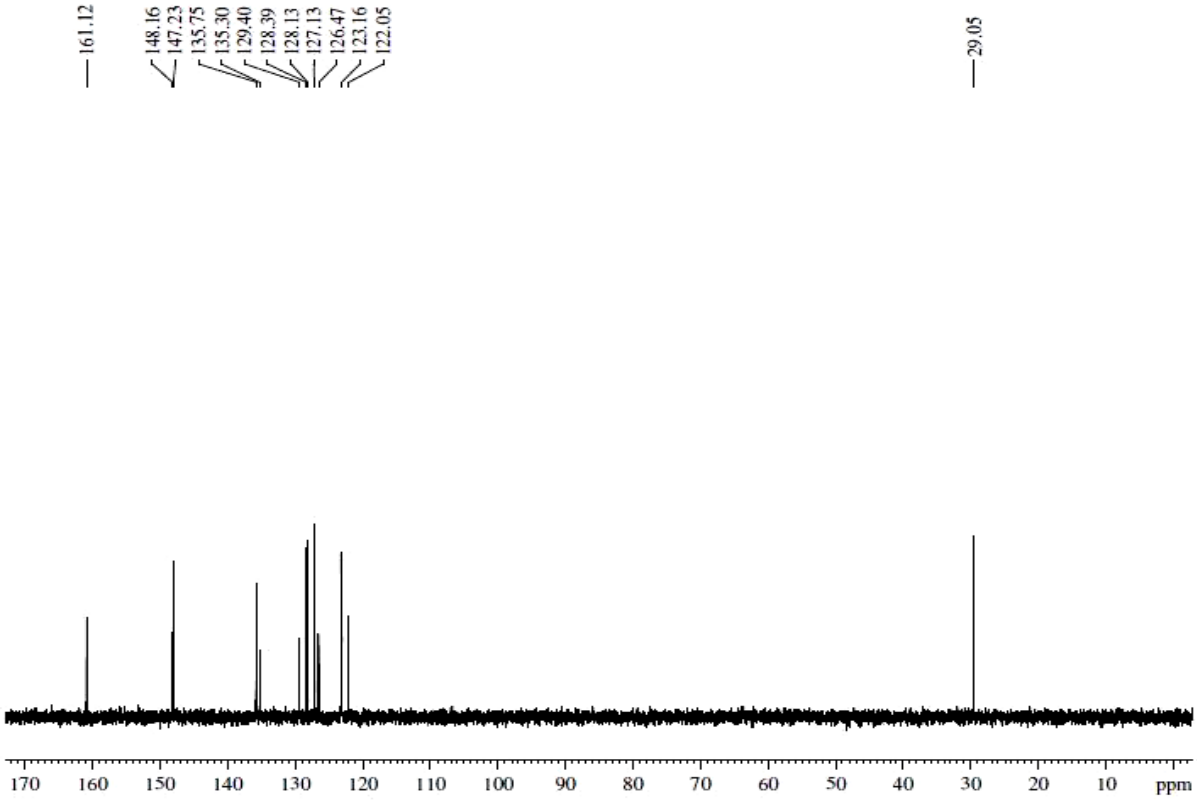


Fig. 38. ^{13}C NMR spectrum of 6-methyl-2-phenyl-quinoline (2a)

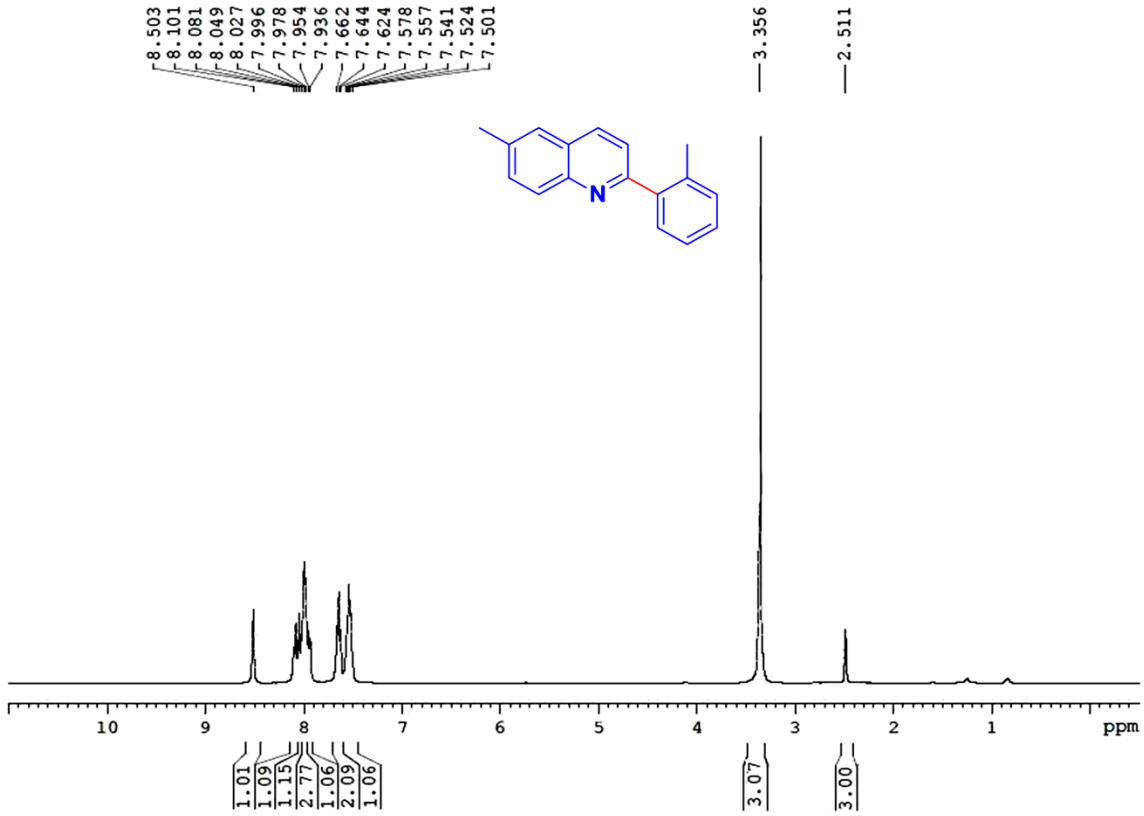


Fig. 39. ^{1}H NMR spectrum of 6-methyl-2-*o*-tolyl-quinoline (2b)

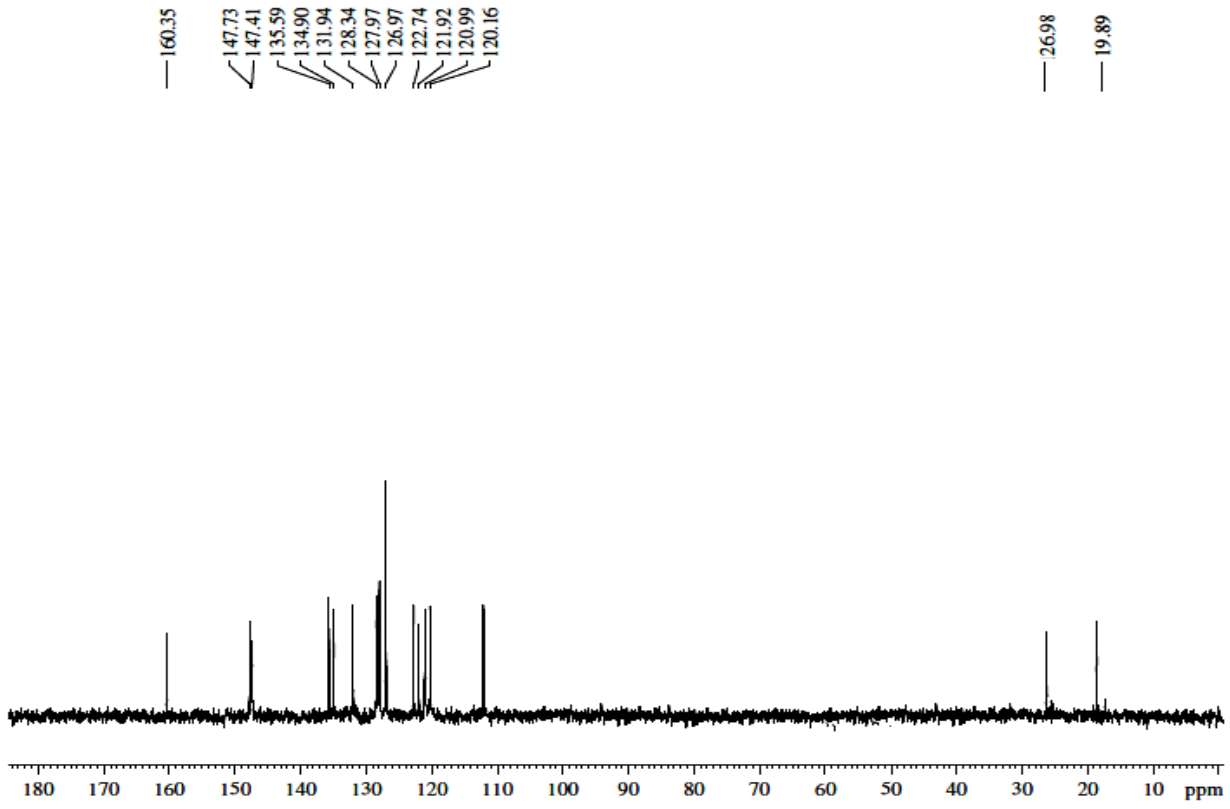


Fig. 40. ^{13}C NMR spectrum of 6-methyl-2-*o*-tolyl-quinoline (2b)

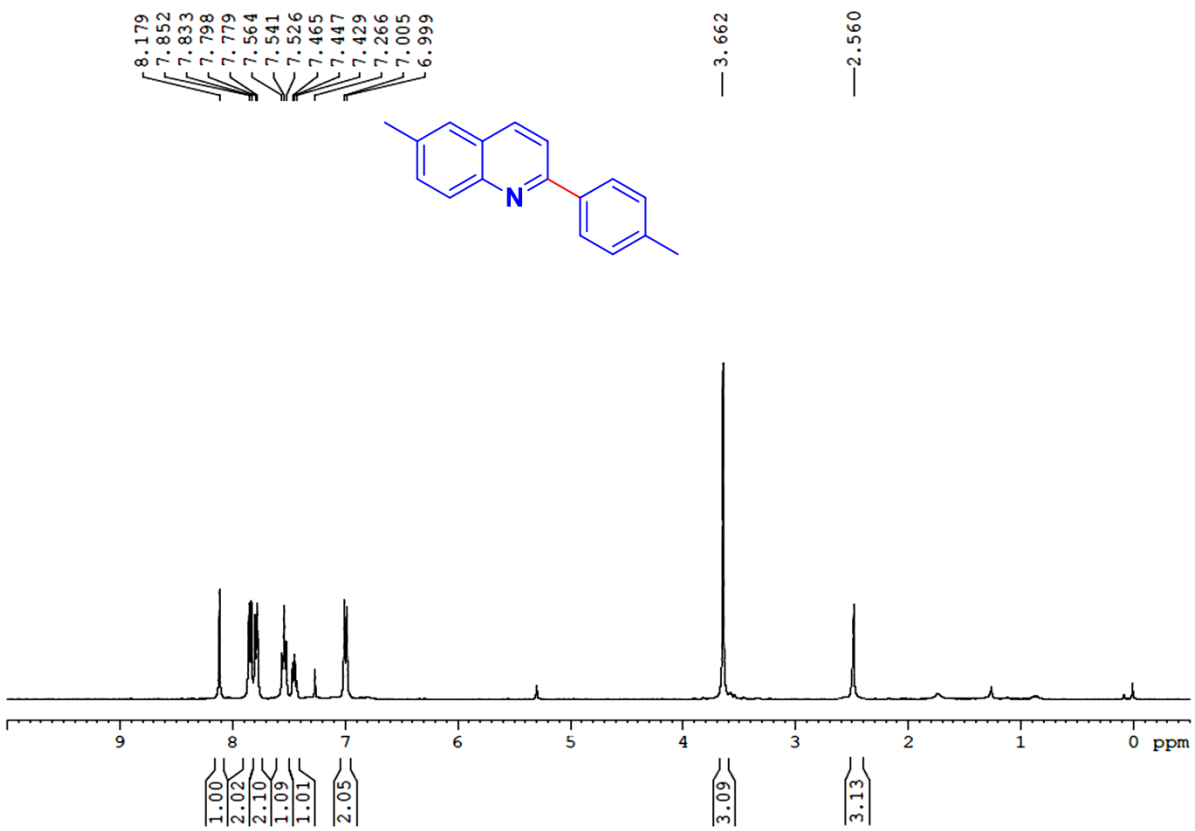


Fig. 41. ^{1}H NMR spectrum of 6-methyl-2-*p*-tolyl-quinoline (2c)

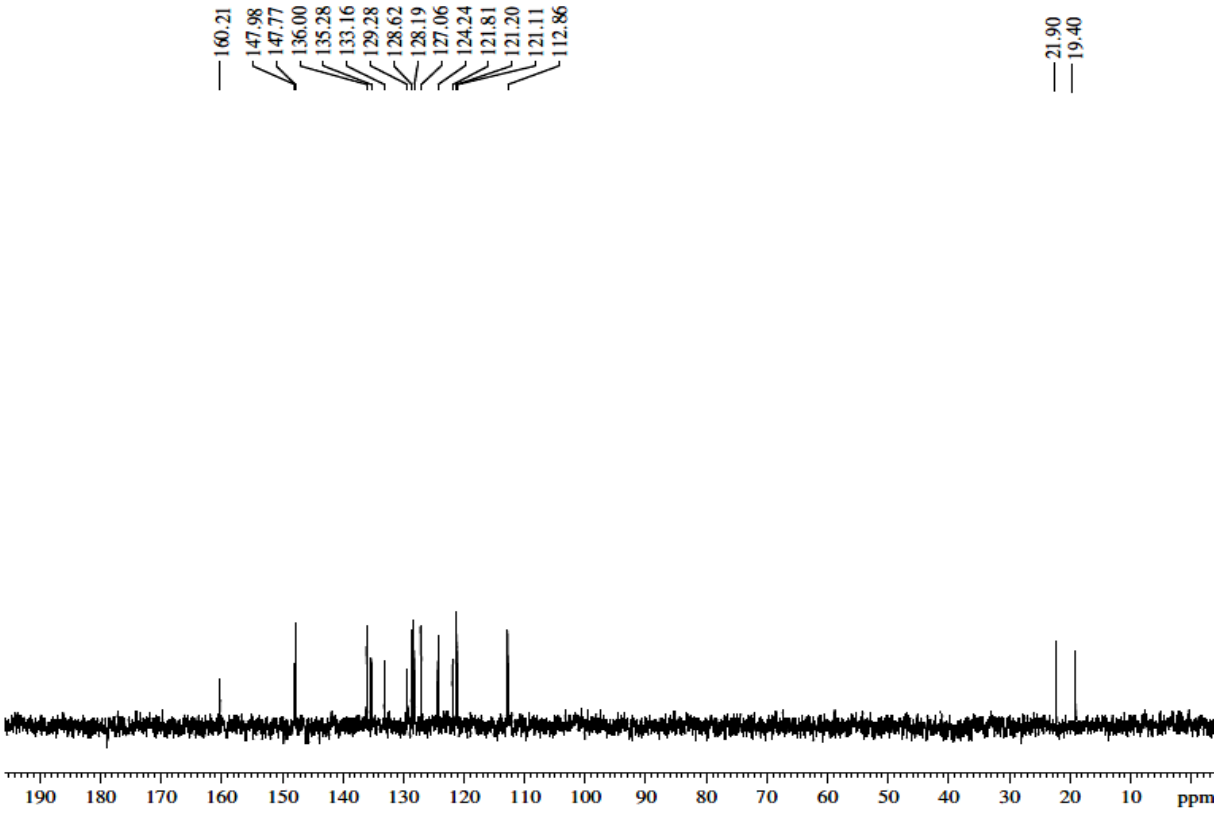


Fig. 42. ^{13}C NMR spectrum of 6-methyl-2-*p*-tolyl-quinoline (2c)

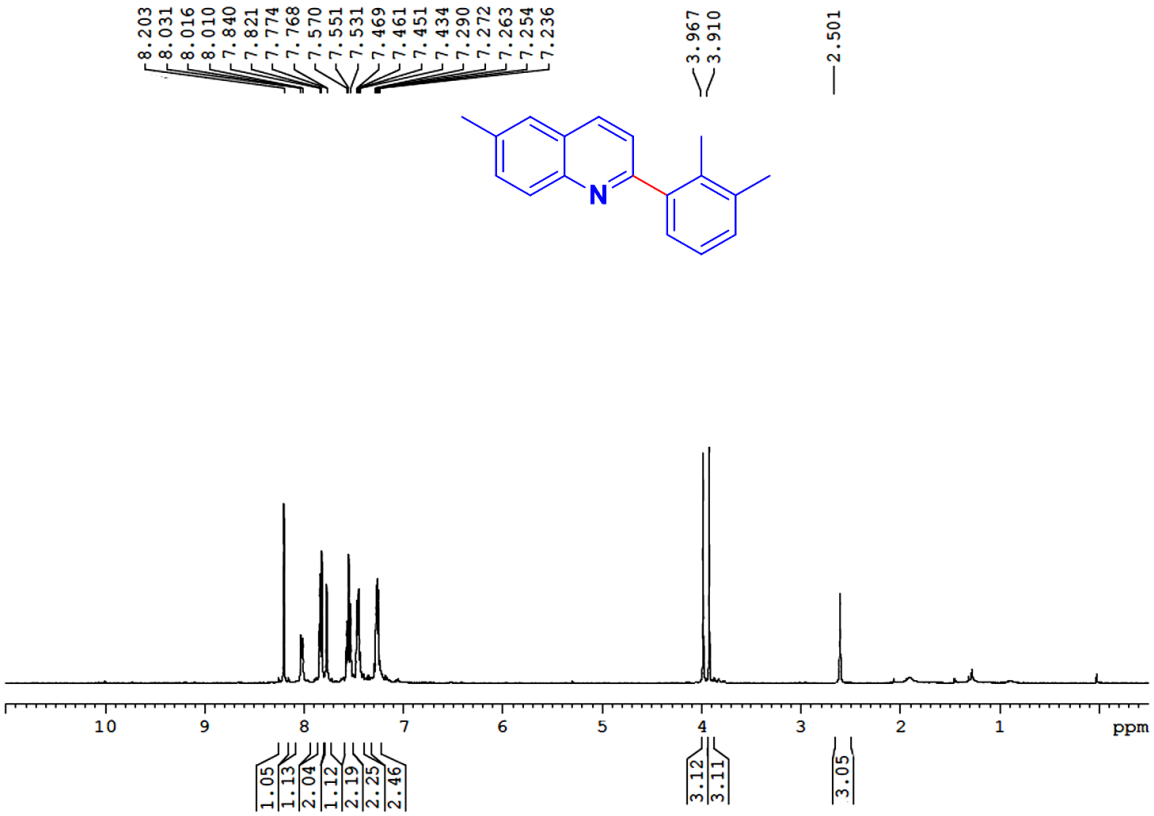


Fig. 43. ^{1}H NMR spectrum of 2-(2, 3-dimethyl-phenyl)-6-methyl-quinoline (2d)

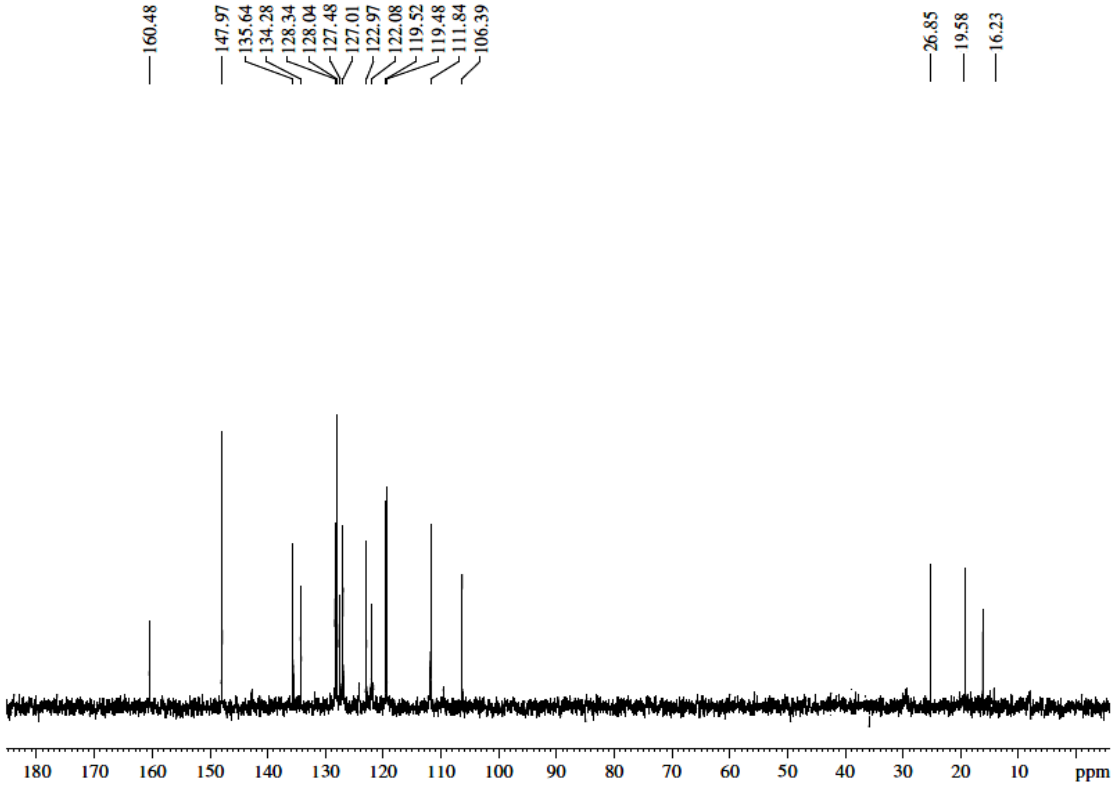


Fig. 44. ^{13}C NMR spectrum of 2-(2, 3-dimethyl-phenyl)-6-methyl-quinoline (2d)

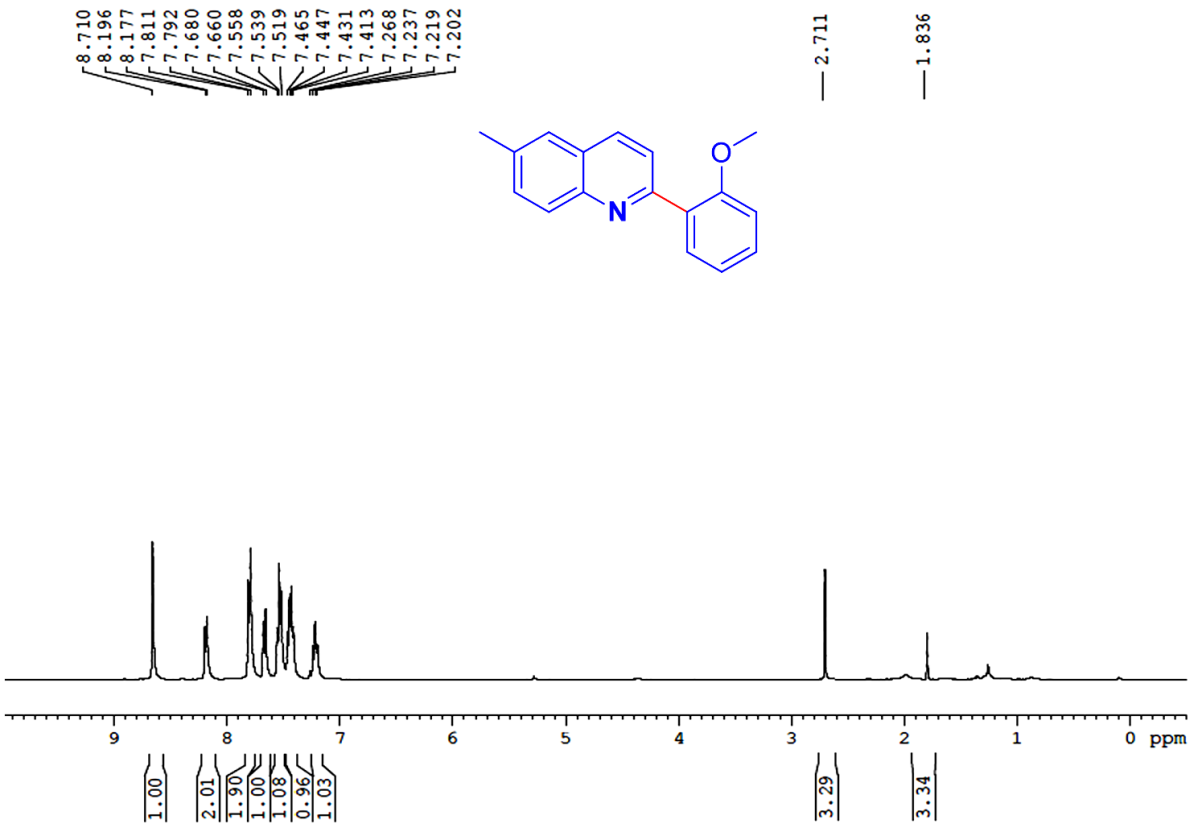


Fig. 45. ^{1}H NMR spectrum of 2-(2-methoxy-phenyl)-6-methyl-quinoline (2e)

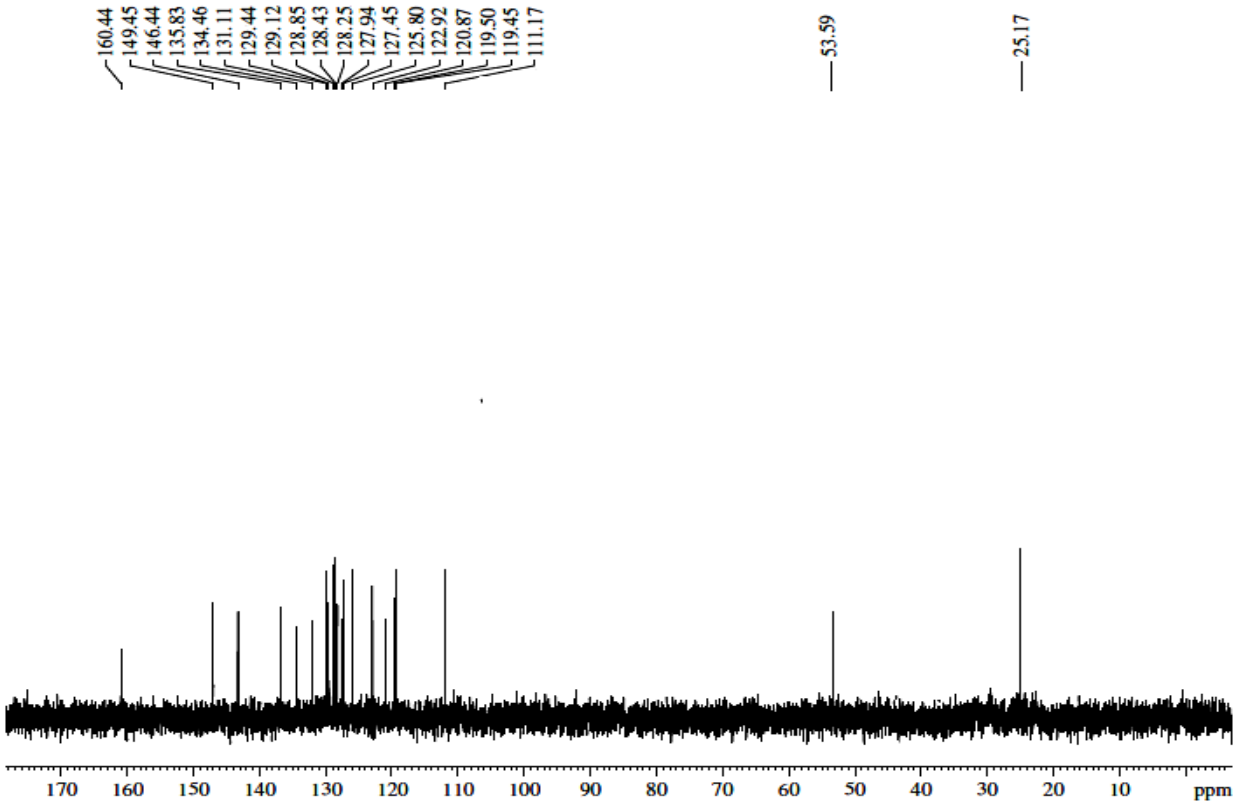


Fig. 46. ^{13}C NMR spectrum of 2-(2-methoxy-phenyl)-6-methyl-quinoline (2e)

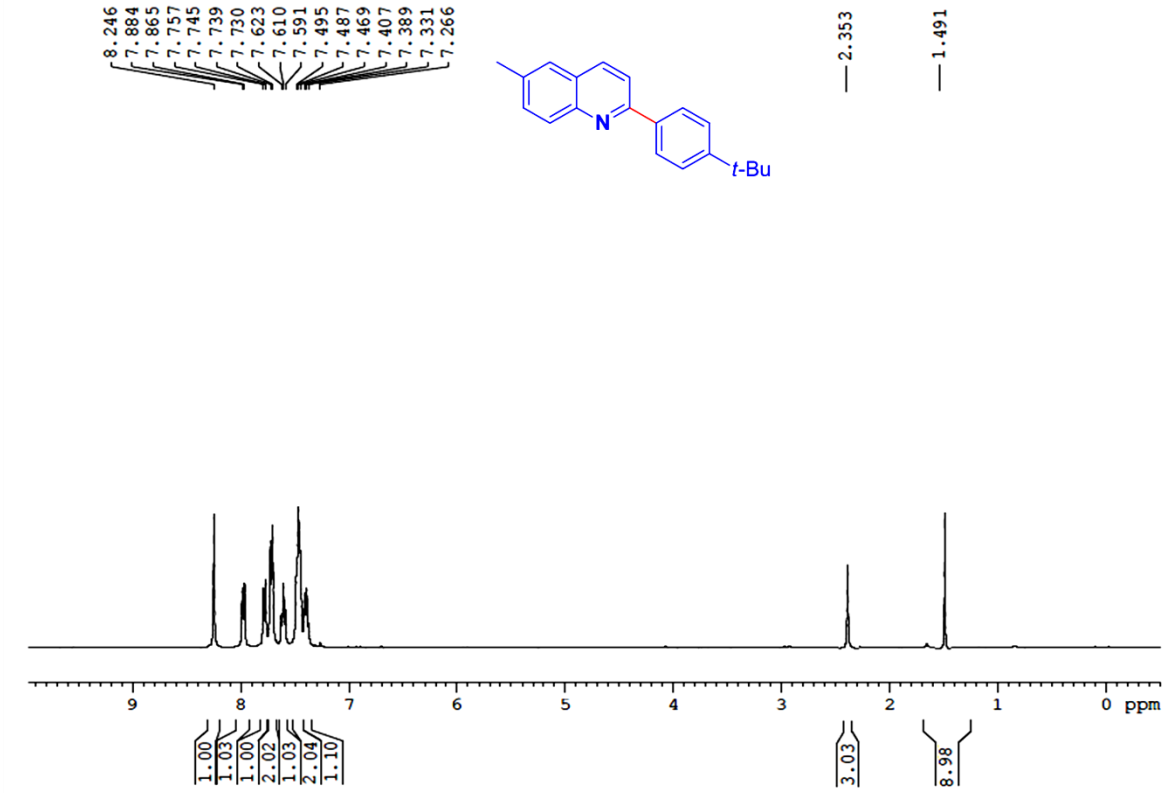


Fig. 47. [1]H NMR spectrum of 2-(4-*tert*-butyl-phenyl)-6-methyl-quinoline (2f)

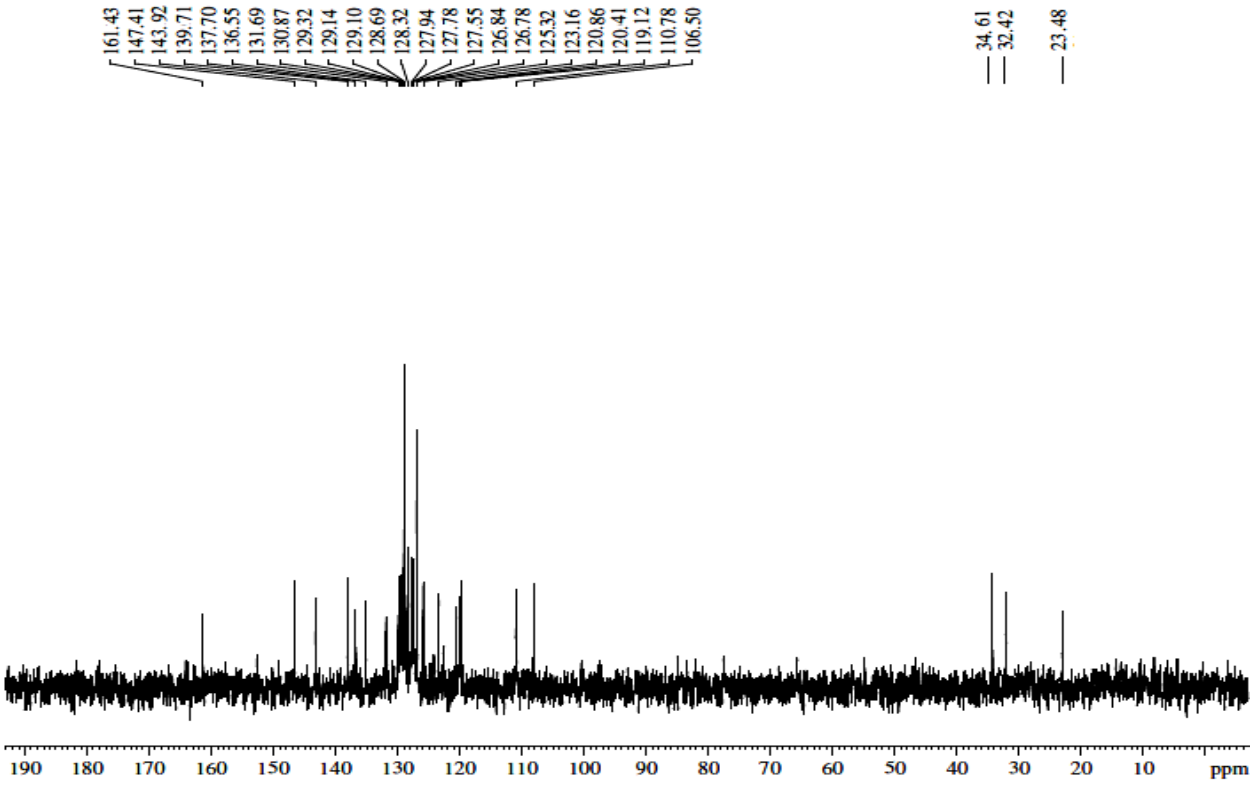


Fig. 48. [13]C NMR spectrum of 2-(4-*tert*-butyl-phenyl)-6-methyl-quinoline (2f)

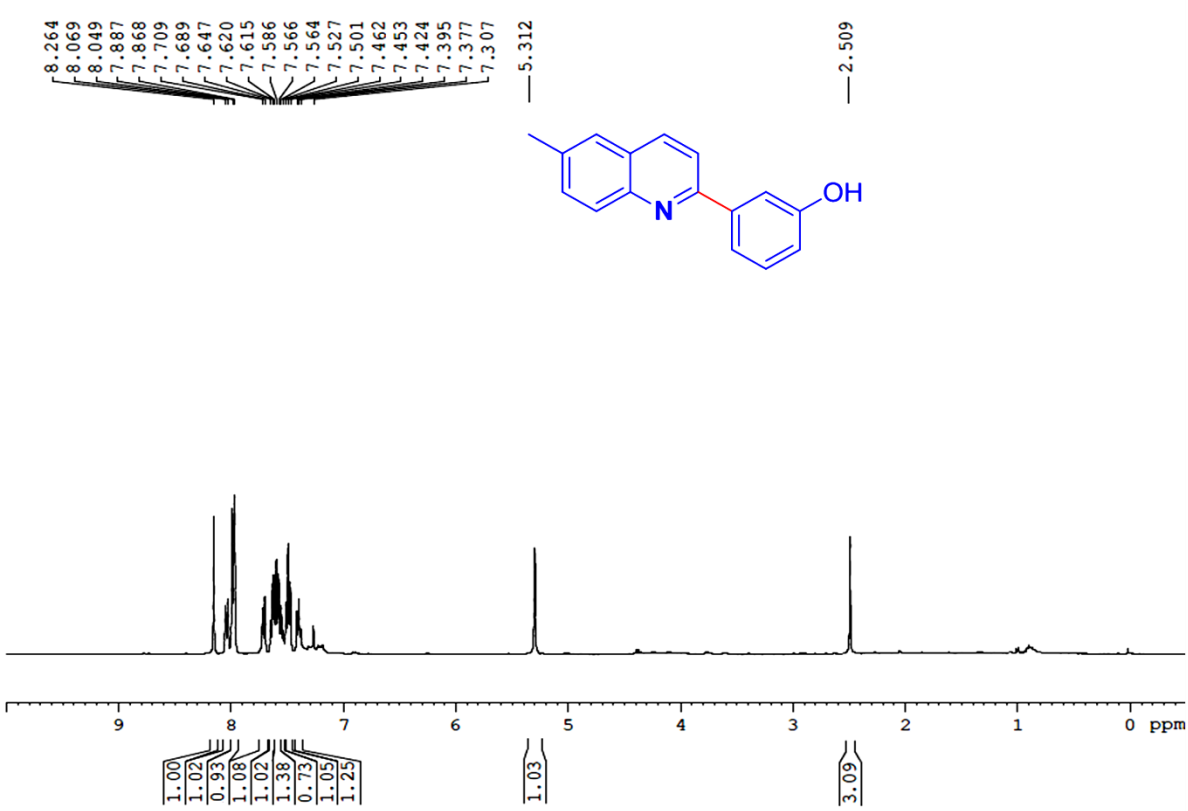


Fig. 49. ^{1}H NMR spectrum of 3-(6-methyl-quinolin-2-yl)-phenol (2g)

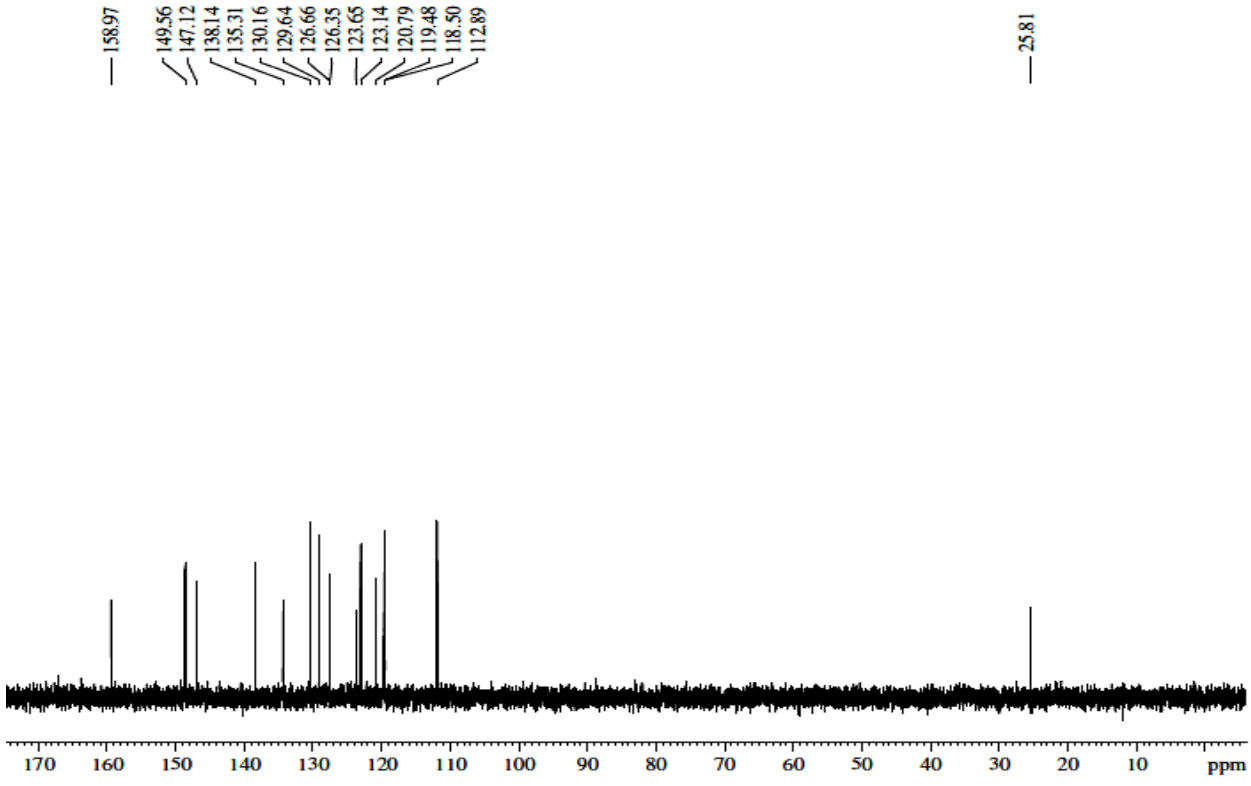


Fig. 50. ^{13}C NMR spectrum of 3-(6-methyl-quinolin-2-yl)-phenol (2g)

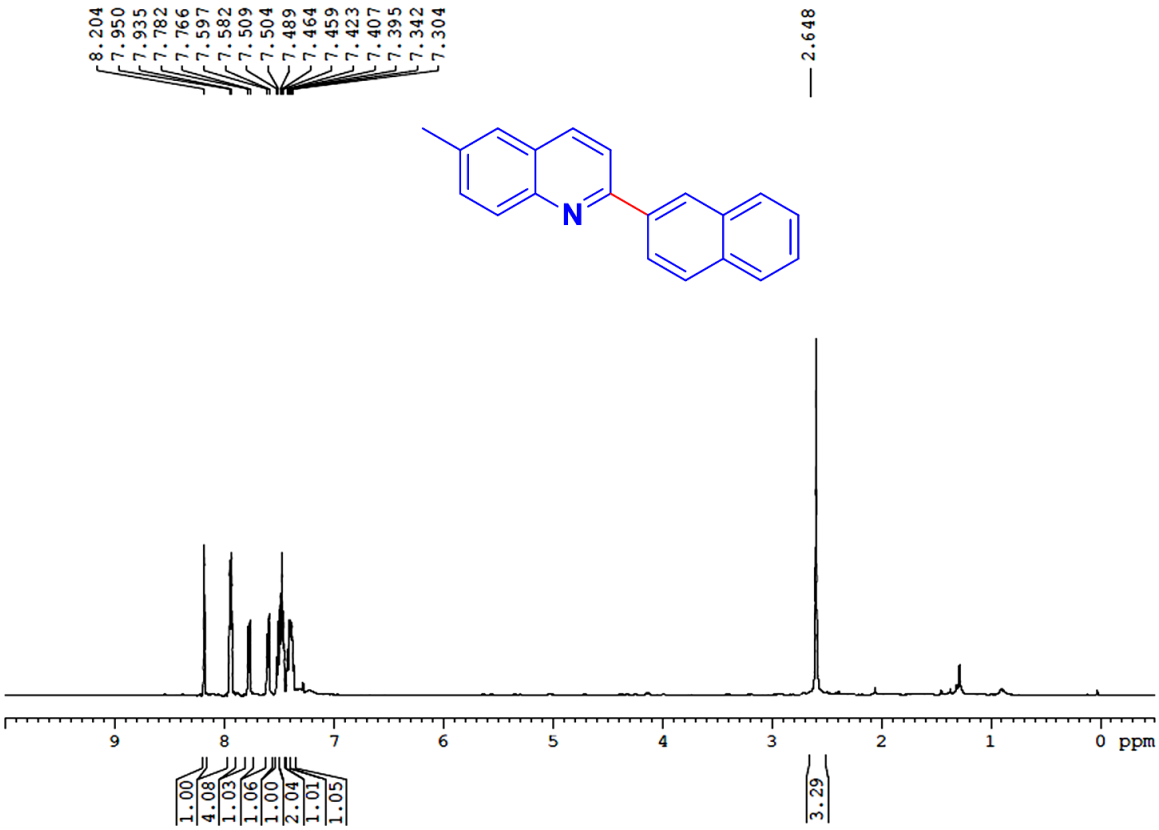


Fig. 51. ^{1}H NMR spectrum of 6-methyl-2-naphthalen-2-yl-quinoline (2h)

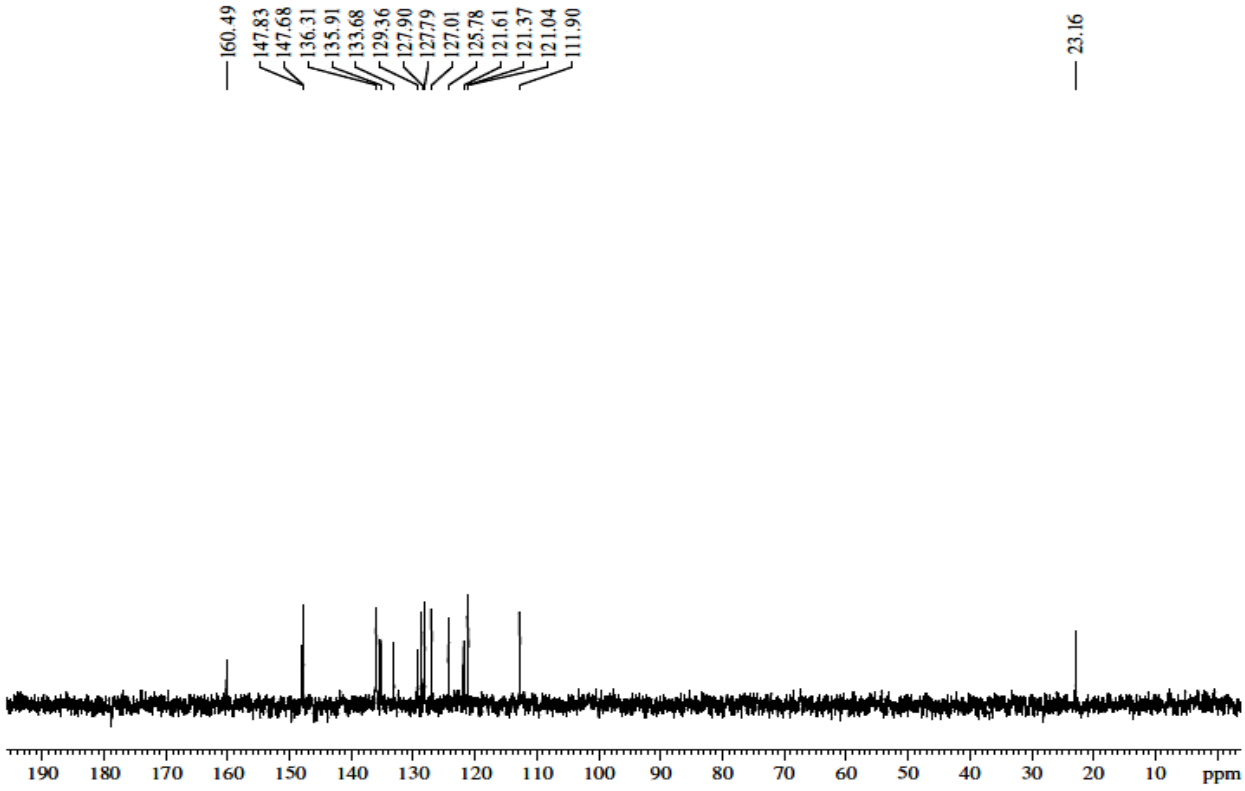


Fig. 52. ^{13}C NMR spectrum of 6-methyl-2-naphthalen-2-yl-quinoline (2h)

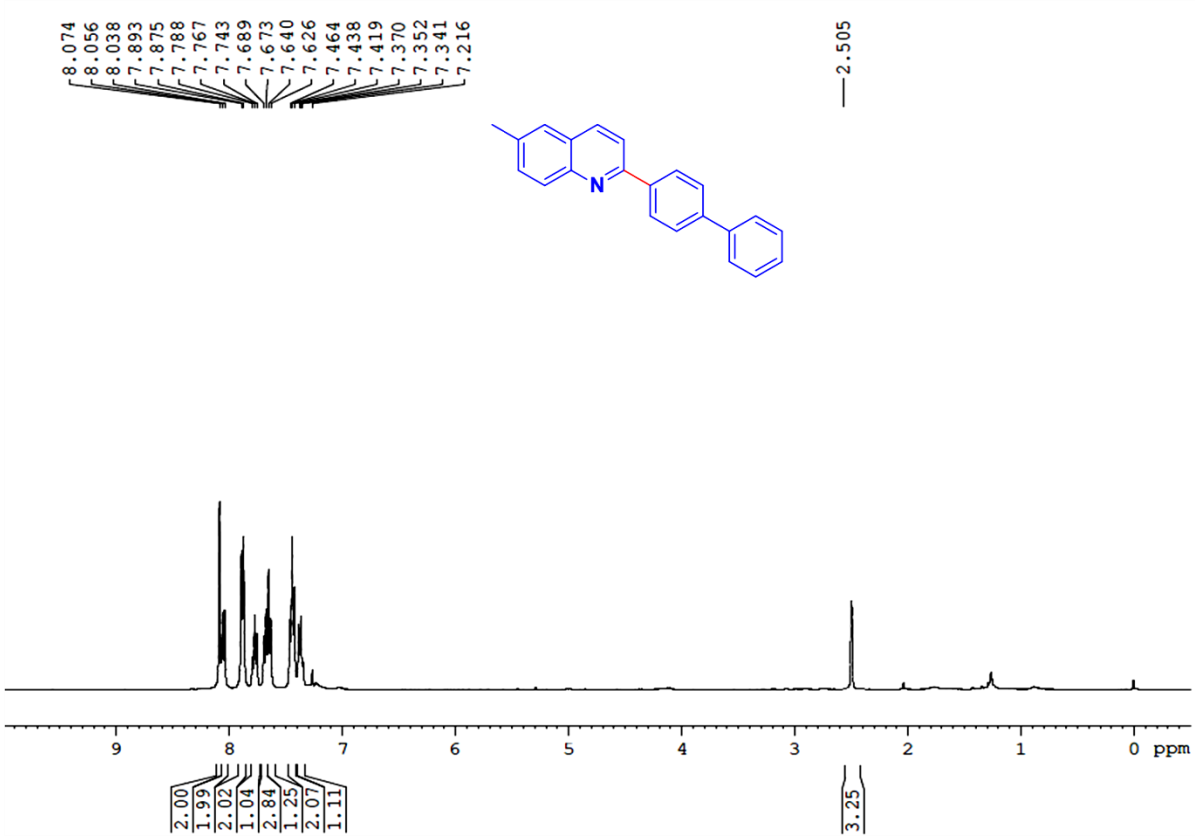


Fig. 53. ^{1}H NMR spectrum of 2-biphenyl-4-yl-6-methyl-quinoline (2i)

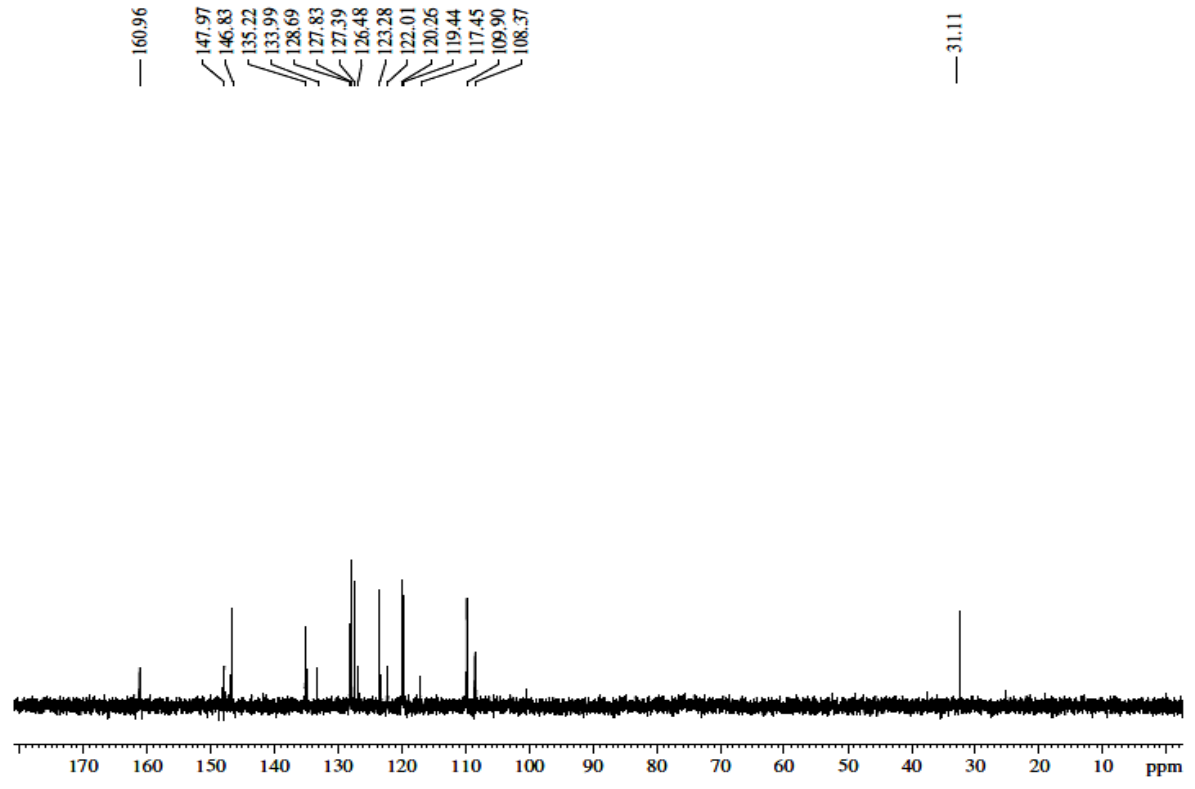


Fig. 54. ^{13}C NMR spectrum of 2-biphenyl-4-yl-6-methyl-quinoline (2i)

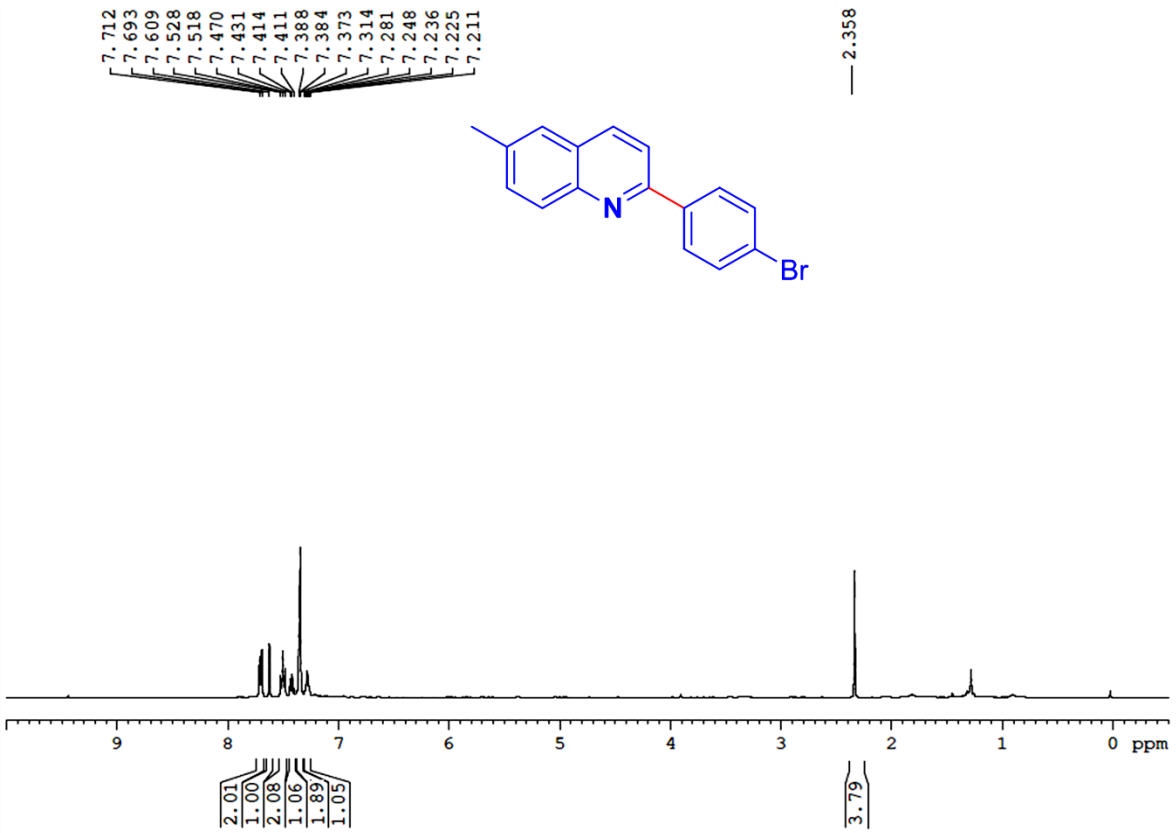


Fig. 55. ^{1}H NMR spectrum of 2-(4-bromo-phenyl)-6-methyl-quinoline (2j)

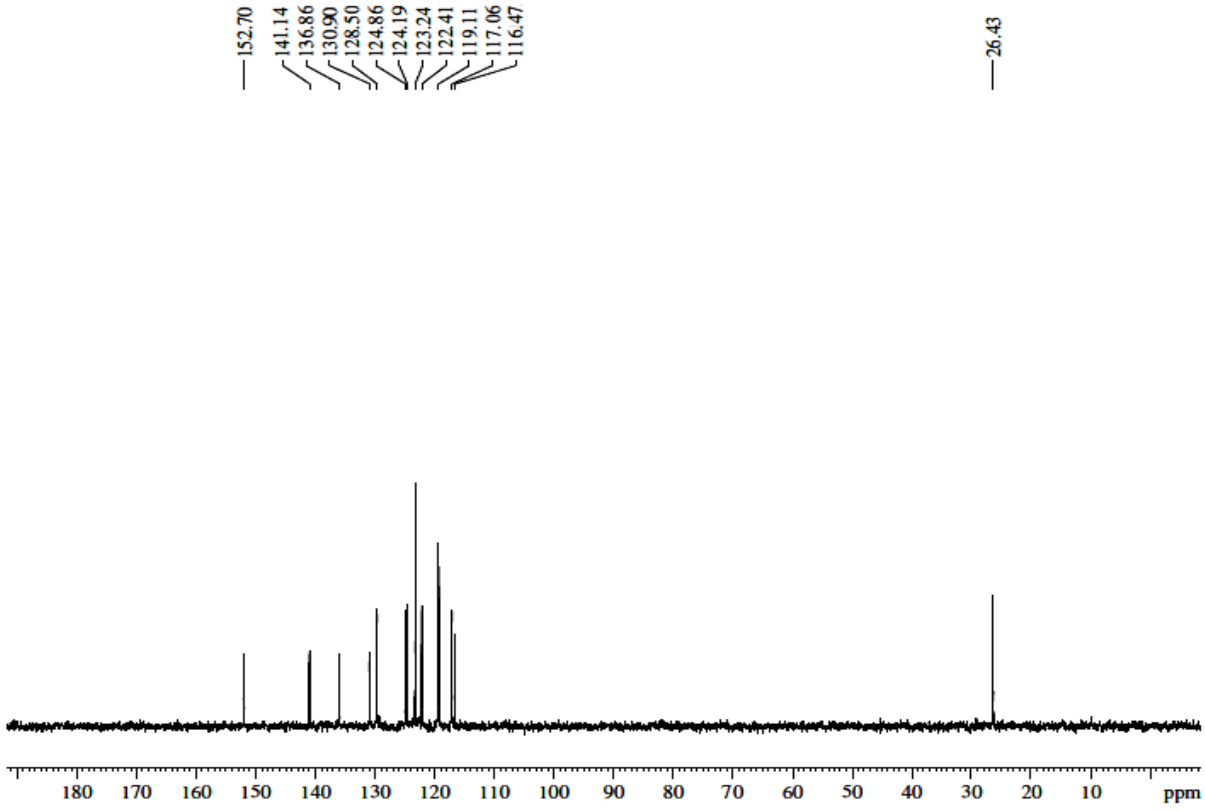


Fig. 56. ^{13}C NMR spectrum of 2-(4-bromo-phenyl)-6-methyl-quinoline (2j)

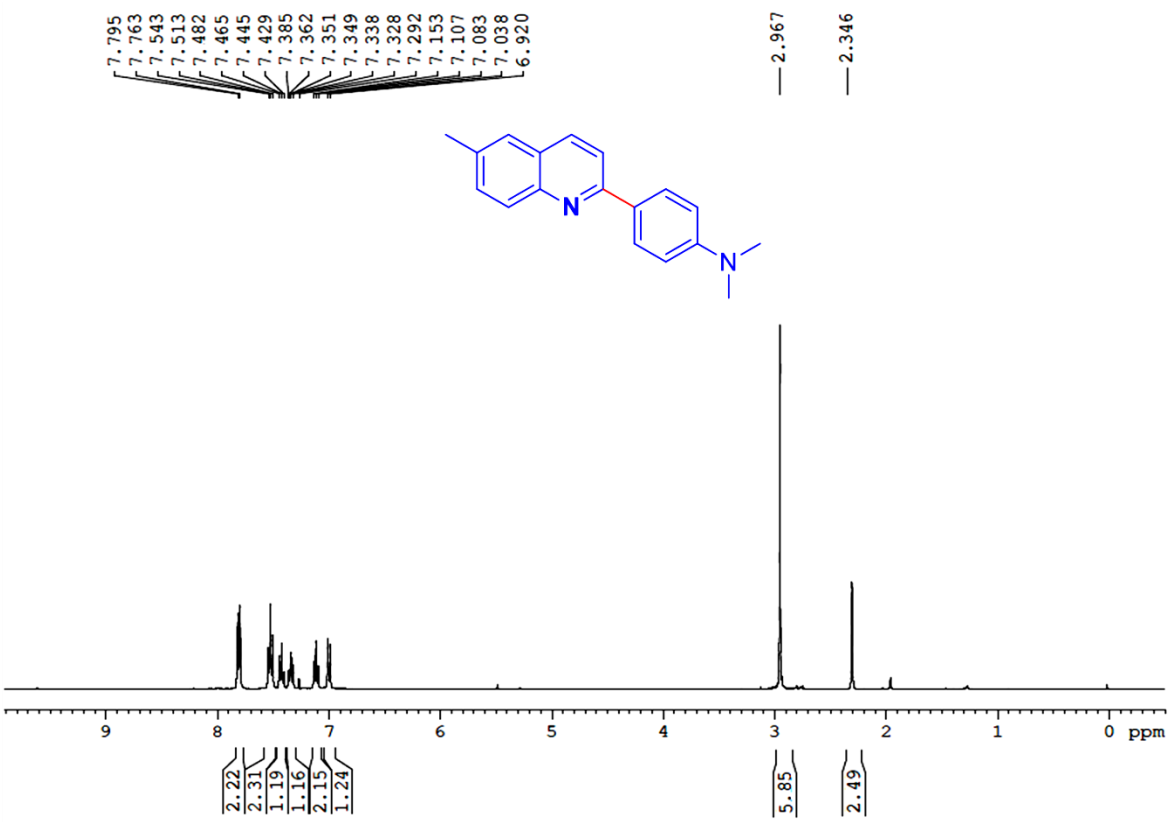


Fig. 57. [1]H NMR spectrum of dimethyl-[4-(6-methyl-quinolin-2-yl)-phenyl]-amine (2k)

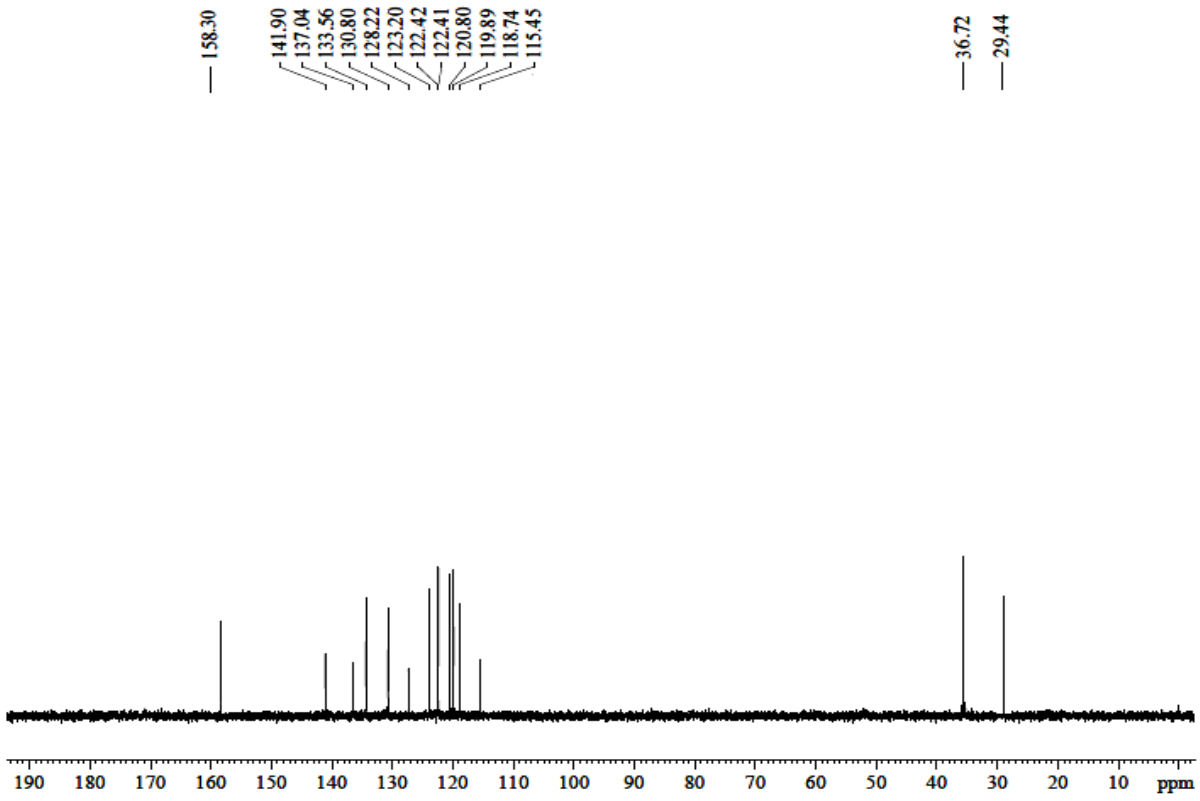


Fig. 58. [13]C NMR spectrum of dimethyl-[4-(6-methyl-quinolin-2-yl)-phenyl]-amine (2k)

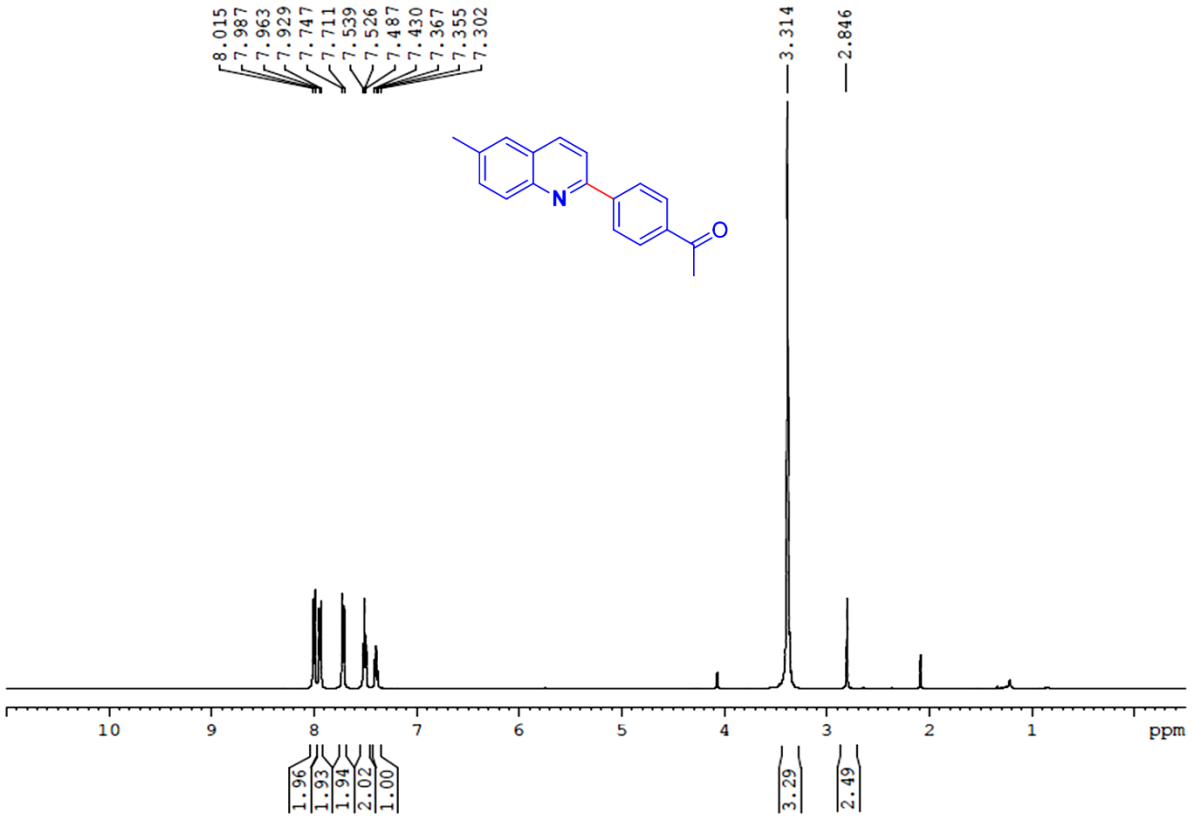


Fig. 59. ^{1}H NMR spectrum of dimethyl-[4-(6-methyl-quinolin-2-yl)-phenyl]-amine (2l)

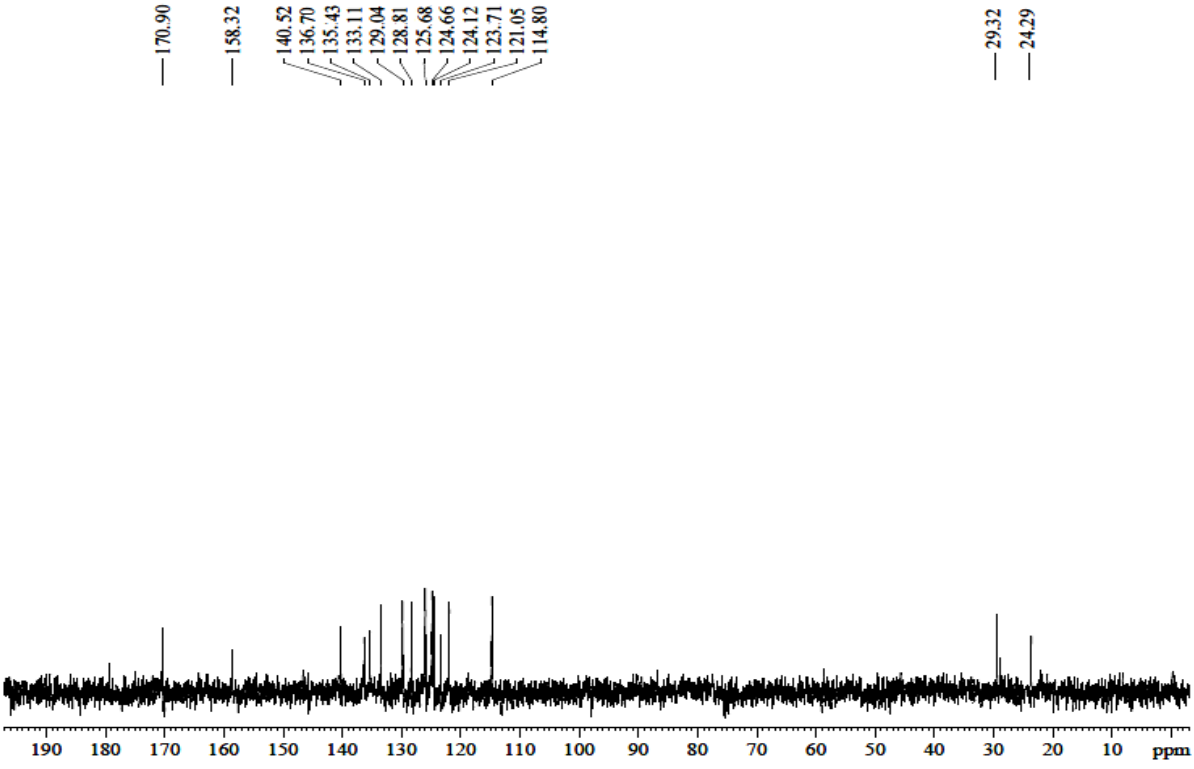


Fig. 60. ^{13}C NMR spectrum of dimethyl-[4-(6-methyl-quinolin-2-yl)-phenyl]-amine (2l)