HYDROGENATION OF α,β-UNSATURATED CARBONYL COMPOUNDS CATALYZED BY RUTHENIUM(II) COMPLEXES

S. Nandhini,[1#] B. Mugesh,[1#] S. Hema,[1] G. Prabusankar[2] and R. Prabhakaran[1*]

[1]Department of Chemistry, Bharathiar University, Coimbatore - 641 046, India.

[2]Department of Chemistry, Indian Institute of Technology, Hyderabad - 502285, India.

**Corresponding author's E-mail:*rpnchemist@gmail.com ; rpnchemist@buc.edu.in

[#] Author's contributed equally.

EXPERIMENTAL SECTION

All the reagents used were of Analar or chemically pure grade. Solvents were purified and dried according to the literature procedure.[1] The starting compounds 8-methyl-2-oxo-1, 2-dihydroquinoline-3-carbaldehyde,and ruthenium precursor [$RuHCl(CO)(PPh_3)_3$], were prepared by the literature method.[2,3]Melting points of the complexes were recorded by RAAGA melting point apparatus. FT-IR spectra of the ligands and complexes have been recorded as KBr pellets with a JASCO FT-IR 4100 instrument in the range 400-4000 cm^{-1}. Electronic spectra of the ligands and complexes were recorded in DMSO using JASCO V-630 UV-Vis Spectrometer in the 200-800 nm range. ^1H NMR spectra were taken in DMSO-d^6 by using Bruker 400 MHz instrument with TMS as standard. Mass spectrum was recorded with a high-resolution Q-TOF mass spectrometer. Single crystal data collections and corrections for the complexes **2-4** were done at 293 K with CCD Kappa Diffractometer using graphite monochromated Mo Ka (k = 0.71073 A) radiation.[4] The structural solution was done by using SHELXS-97[5] and refined by full matrix least square on F^2using SHELXL-2014.[6]The catalyst have been regenerated by separation technique using methanol and chloroform as solvents. For Gas chromatography-mass spectroscopic analysis, AGILENT 5977C GC/MSD was used with split-mode injector (split ratio-1:100), the interpretation of the mass spectra was done by using National Institute Standards and Technology (NIST23).The CD spectrum were recorded in JASCO J-1500 with ethyl acetate as standard solution.

Preparation of new ruthenium(II) complexes

To a solution of [$RuHCl(CO)(PPh_3)_3$] (0.05 g, 0.052 mmol) in chloroform (10 cm^3), was added to a methanolic solution (10 cm^3)of**(HL^{1-4})** (0.013-0.017 g, 0.052 mmol) and the reaction mixture was refluxed for 5 h. It was subjected to thin layer chromatography where two spots were identified and isolated by silica gel column chromatography using benzene–methanol as solvent mixture. The yellow band was eluted with 98:2 benzene: methanol and complex **1-**

4was isolated from a reddish-brown band by using 85:15 benzene: methanol as eluent, and was crystallized by using chloroform-ethyl acetate mixture afforded red semi crystals.

[RuH8MT] (1) - Yield: 82%. mp: >280 °C. Anal. Calcd for $C_{49}H_{42}ClN_4O_2P_2RuS$: C,61.99; H, 4.46; N, 5.90; S, 3.38. Found: C, 61.96; H, 4.42; N, 5.86; S, 3.33%. FT-IR (ν, cm^{-1}) in KBr: ν(C=O) 1644, ν(C=N) 1479, ν(C−S) 746. UV−vis(DMSO), λ_{max}, nm (ε, $dm^3\ mol^{-1}\ cm^{-1}$) 274 (11,2401) (Intra ligand transition), 359 (34,3007) (LMCT), 413 (47,5989) (MLCT). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm, J Hz):11.64 (s, 1H, N(1)H), 10.47 (s, 1H, N(4)H), 9.14 (s, 1H, -CH=N), 8.78 (s, 1H, C(4)H), 7.78 (s, 1H, *J* =8 Hz, C(5)H), 7.63-7.64 (d, 1H, *J* = 4 Hz, C(7)H), 7.60-7.61 (t, 1H, *J* = 4 Hz,C(6)H), 6.44-6.48 (d, 2H, *J* = 16 Hz, terminal –NH_2), 7.46-7.48 (m, 15H, *J* = 8 Hz, -PPh_3), 7.40-7.42 (m, 15H, *J* = 8 Hz, -PPh_3), 2.70 (s, 3H, -CH_3, quinoline methyl at C(8) position).^{13}C NMR(DMSO,δppm):150.07,148.33,144.56, 143.97,141.97,139.87,138.79,138.20,135.20,135.01,134.68,134.05,133.90,133.84,133.67,133 .47,132.94,131.78,130.91,130.48,130.05,129.94,129.81,129.64,129.12,129.06,128.73,128.32, 128.14,127.65,127.57,126.78,126.58,126.25,125.90,125.82,125.77,125.48,125.20,125.01,124 .73,124.55,124.39,124.07,123.97,123.76,123.53,120.74,30.03.ESI: *m/z* calcd. for $C_{49}H_{42}ClN_4O_2P_2RuS$, 958.2; found, 949.2$[M+0.5H_2O]^+$.

[RuH8MMT] (2) - Yield: 79%. mp: >280 °C. Anal. Calcd for $C_{50}H_{44}ClN_4O_2P_2RuS$: C,61.99; H, 4.60; N, 5.82; S, 3.33. Found: C, 61.95; H, 4.58; N, 5.80; S, 3.30%. FT-IR (ν, cm^{-1}) in KBr: ν(C=O) 1644, ν(C=N) 1481, ν(C−S) 747. UV−vis(DMSO), λ_{max}, nm (ε, $dm^3\ mol^{-1}\ cm^{-1}$) 266 (11,8311) (Intra ligand transition),359 (43,2710) (LMCT), 409 (55,6890) (MLCT). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm, J Hz): 11.16(s, 1H, N(1)H), 10.79 (s, 1H, N(4)H), 9.26 (s, 1H, -CH=N), 8.83 (s, 1H, C(4)H), 7.41-7.44 (d, 1H, *J* = 12 Hz, C(5)H), 7.32-7.33(d, 1H, *J* = 4 Hz, C(7)H), 7.26-7.28(t, 1H, *J* = *8* Hz, C(6)H), 7.60-7.65 (m, 15H, *J* = 20 Hz, -PPh_3), 7.54-7.58 (m, 15H, *J* = 16 Hz, -PPh_3), 2.25-2.27 (t, 3H, *J* = 8 Hz, terminal -CH_3), 2.70 (s, 3H, quinoline -CH_3 at C(8) position).^{13}C NMR(DMSO,δppm):150.29, 146.31, 145.14, 144.71, 141.92, 138.71, 138.11, 137.56, 137.43, 137.40, 137.19, 134.69, 134.56, 133.98, 133.91, 133.79, 133.10, 133.02, 132.47, 130.80, 130.58, 130.37, 129.51, 129.12, 129.07, 129.02, 128.77, 128.32, 128.25, 127.85, 127.76, 127.61, 127.58, 127.37, 127.11, 127.08, 126.60, 126.42, 126.27, 126.06, 126.03, 125.89, 125.84,125.34, 124.64, 124.62, 123.68, 123.42, 30.09, 21.55. ESI: *m/z*calcd. for $C_{50}H_{44}ClN_4O_2P_2RuS$, 1026.13; found, 962.13 $[M+2CH_3OH]^+$.

[RuH8MET] (3) - Yield: 73%. mp: >280 °C. Anal. Calcd for$C_{51}H_{46}ClN_4O_2P_2RuS$: C,62.67; H, 4.74; N, 5.73; S, 3.28. Found: C, 62.72; H, 4.68; N, 5.80; S, 3.32%. FT-IR (ν, cm^{-1}) in KBr: ν(C=O) 1646, ν(C=N) 1481, ν(C−S) 743. UV−vis(DMSO), λ_{max}, nm (ε, $dm^3\ mol^{-1}\ cm^{-1}$) 268 (11,3221) (Intra ligand transition), 360 (43,3710) (LMCT), 410 (55,9802) (MLCT). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm, J Hz):11.17 (s, 1H, N(1)H), 10.79 (s, 1H, N(4)H), 8.32 (s,1H,-CH=N), 7.79 (s, 1H, C(4)H), 7.63–7.64 (d, 1H, *J* = 4 Hz, C(5)H), 7.56-7.58 (t, 1H, *J* = 8 Hz, C(7)H), 7.40-7.41 (t, 1H, *J* = 4 Hz, C(6)H), 7.30-7.37 (m, 15H, *J* = 28 Hz, -PPh_3), 7.24-7.27 (m, 15H, *J* = 12 Hz, -PPh_3), 1.18-1.26 (p, 2H, *J* = 32 Hz, terminal -CH_2), 2.42 (s, 3H, terminal -CH_3), 2.28 (s, 3H, quinoline -CH_3 at C(8) position).^{13}CNMR(DMSO,δppm):150.29, 148.59, 146.29, 145.17, 144.73, 143.29, 141.36, 141.32, 141.06, 140.31, 139.48, 138.47, 137.61, 137.50, 137.40, 137.23, 137.12, 136.61, 136.30, 136.17, 134.53, 133.98, 133.93, 133.52, 133.06, 132.42, 132.86, 131.08, 129.93, 129.87, 129.54, 129.27, 129.22, 129.04, 128.39, 127.80, 127.78, 127.66, 127.62, 127.08, 126.91, 126.80, 126.68, 126.62, 126.24, 126.01, 123.96, 122.81, 29.66, 21.57, 21.15 ESI: *m/z* calcd. for $C_{51}H_{46}ClN_4O_2P_2RuS$, 1085.46; found, 976.46 $[M+DMF+2H_2O]^+$.

[RuH8MPT] (4) - Yield: 70%. mp: >280 °C. Anal. Calcd for $C_{55}H_{46}ClN_4O_2P_2RuS$: C,64.42; H, 4.52; N, 5.46; S, 3.13. Found: C, 64.38; H, 4.60; N, 5.53; S, 3.18%. FT-IR (ν, cm^{-1}) in KBr: ν(C=O) 1646, ν(C=N) 1528, ν(C−S) 744. UV−vis(DMSO), λ_{max}, nm (ε, $dm^3\ mol^{-1}\ cm^{-1}$) 269 (11,8756) (Intra ligand transition), 364 (38,8361) (LMCT), 418 (56,2910) (MLCT). ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm, J Hz): 11.41 (s, 1H, N(1)H), 10.28 (s, 1H, N(4)H), 9.22 (s, 1H, -CH=N), 8.51 (s, 1H, C(4)H), 7.40-7.41 (d, 1H, *J* = 4 Hz, C(5)H), 7.36-7.37 (d, 1H, *J* = 4 Hz, C(7)H), 7.25-7.29 (t, 1H, *J* = 16 Hz, C(6)H), 7.61-7.68 (m, 15H, *J* = 28 Hz, -PPh_3), 7.51-7.58 (m, 15H, *J* = 28 Hz, -PPh_3),7.22-7.24 (t, 1H, *J* = 8 Hz, phenyl proton), 7.18-7.20(t, 2H, *J* = 8 Hz, phenyl proton), 7.14-7.16 (d, 2H, *J* = 8 Hz, phenyl proton), 2.46 (s, 3H, -CH_3, quinoline methyl at C(8) position).^{13}CNMR(DMSO,δppm):150.45, 150.07, 149.66, 148.37, 147.73, 146.49, 146.36, 144.71, 144.61, 144.47, 144.39, 144.00, 143.45, 139.38, 139.24, 138.05, 136.42, 136.34, 135.56, 135.01, 134.92, 134.78, 134.65, 134.23, 133.94, 133.68, 133.56, 133.47, 130.01, 129.88, 129.58, 129.31, 128.81, 128.76, 128.67, 128.54, 128.29, 128.10, 127.65, 127.61, 127.51, 127.29, 126.98, 126.38, 126.20, 126.02, 125.79, 125.75, 125.30, 125.18, 124.99, 124.14, 124.11, 124.03, 123.07, 29.65.ESI: *m/z*calcd. for $C_{55}H_{46}ClN_4O_2P_2RuS$, 1065.55 ; found, 1024.51 $[M+CH_3CN]^+$.

Infrared spectroscopy

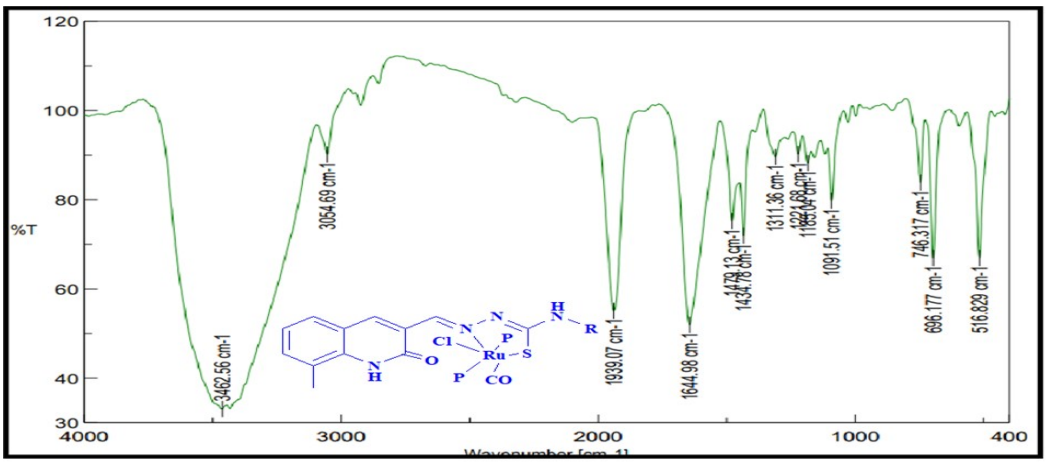


Fig.S1. FT-IR spectrum of the complex **[RuH8MT)] (1)**

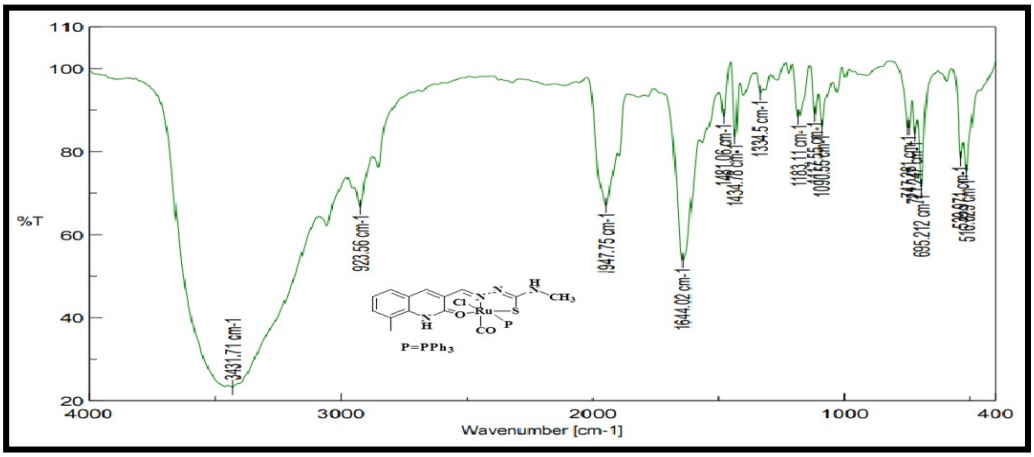


Fig.S2. FT-IR spectrum of the complex **[RuH8MMT)] (2)**

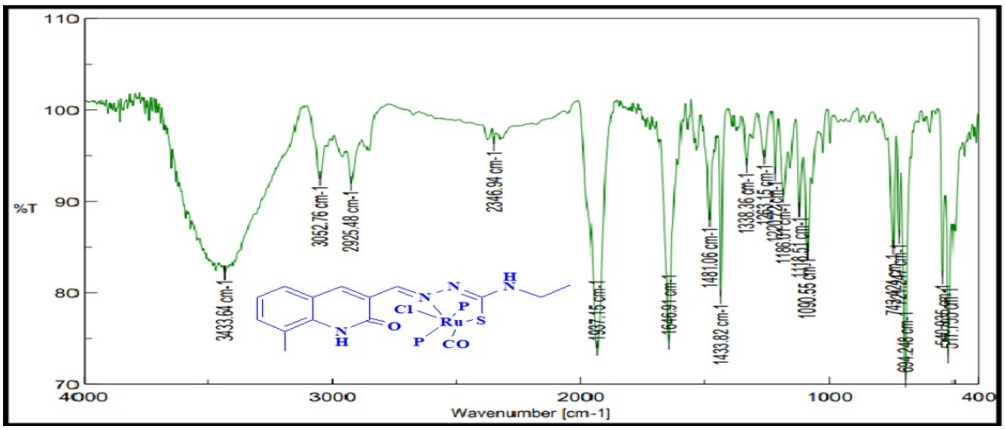


Fig.S3. FT-IR spectrum of the complex **[RuH8MET] (3)**

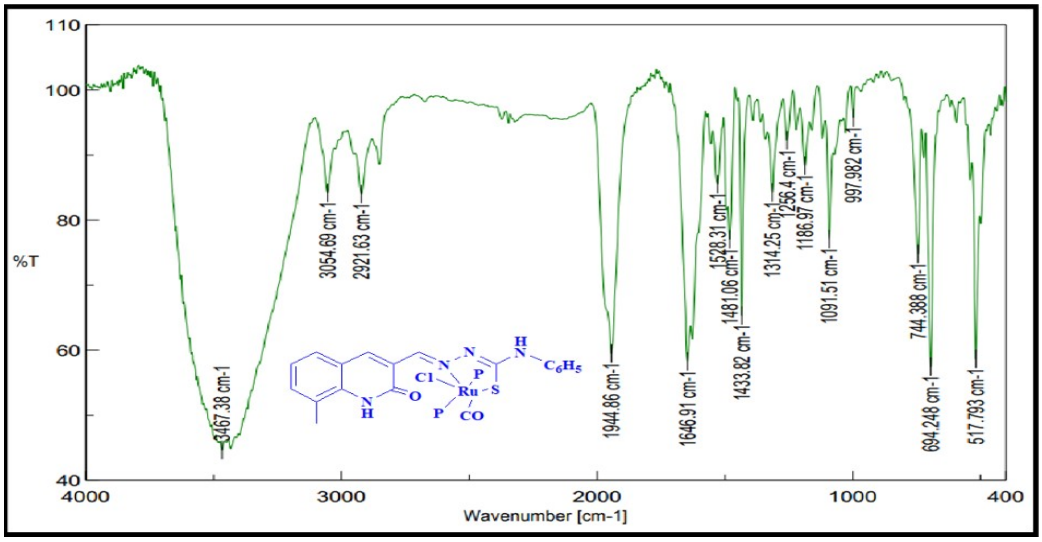
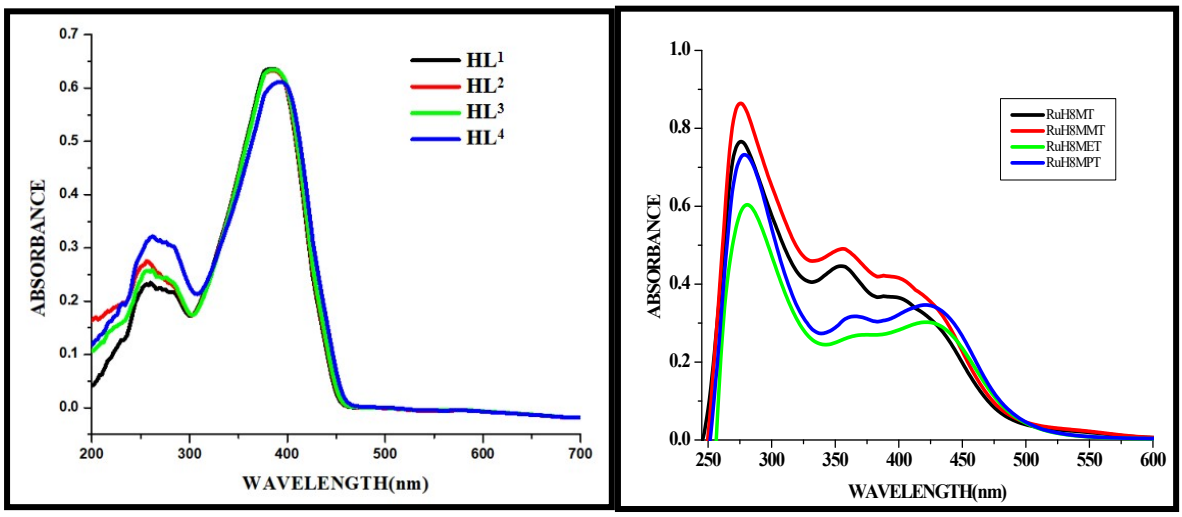


Fig.S4. FT-IR spectrum of the complex **[RuH8MPT] (4)**

Electronic spectroscopy



A **B**

Fig. S5. Electronic spectra of ligands (HL^{1-4}) and the complexes (1-4)

Procedure for catalytic transfer hydrogenation of alkenes

The alkene (0.030 mg; 1mmol) and catalyst (0.005 mmol) were dissolved in 10 cm^3 of methanol, to this sodium borohydride ($NaBH_4$) (0.225 mg; 6 mmol) was added under ice cold condition with stirring. Further, the reaction mixture was stirred in room temperature for 6 h. The reaction was monitored by thin layer chromatography before prior to the next step. After the completion of the reaction, the reaction mixture was worked up with chloroform and water where the organic layer was collected, passed through anhydrous Na_2SO_4, distilled and

dried. The product was isolated by using column chromatography with petroleum ether (60-80 °C) and ethyl acetate as eluents.

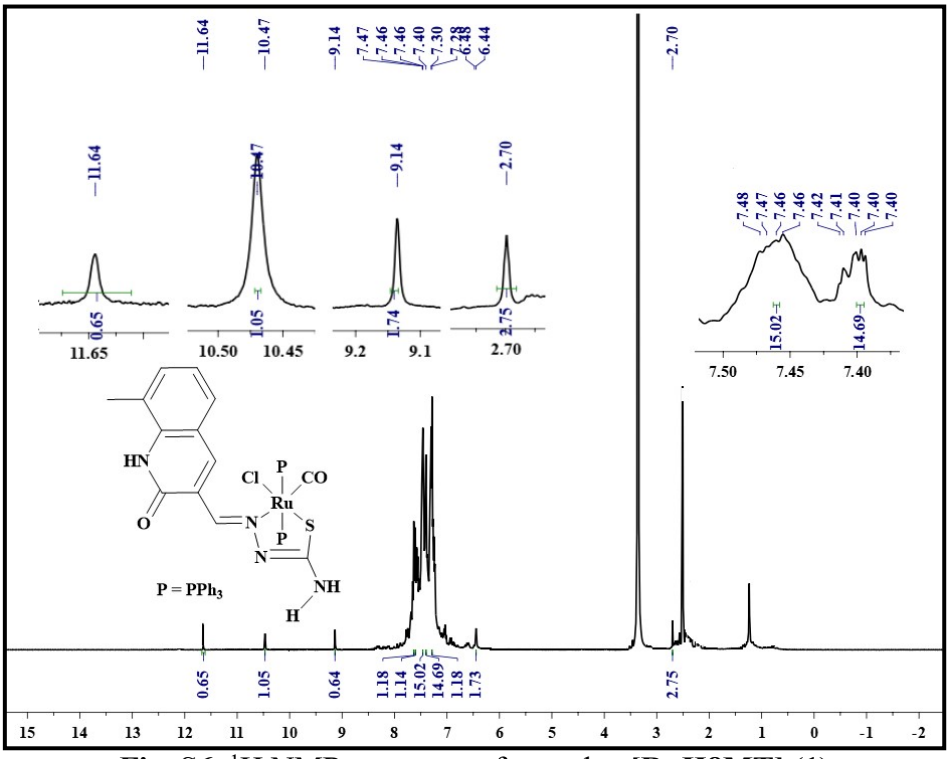


Fig. S6. ^{1}H NMR spectrum of complex **[RuH8MT] (1)**

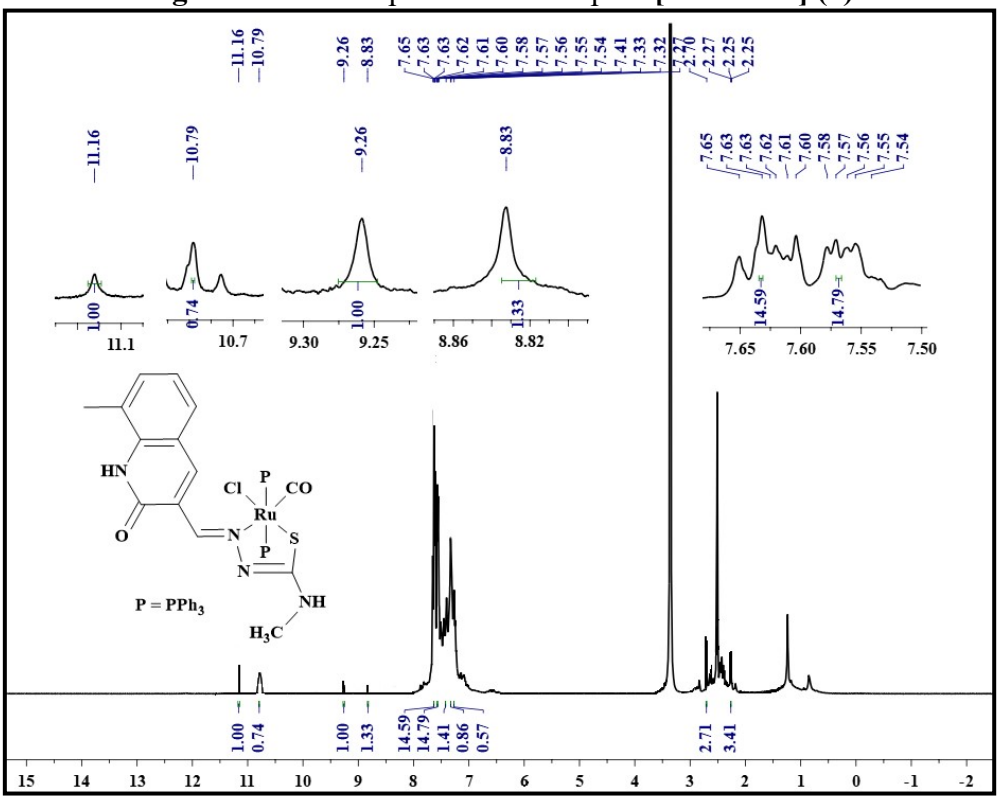


Fig. S7. ^{1}H NMR spectrum of complex **[RuH8MMT] (2)**

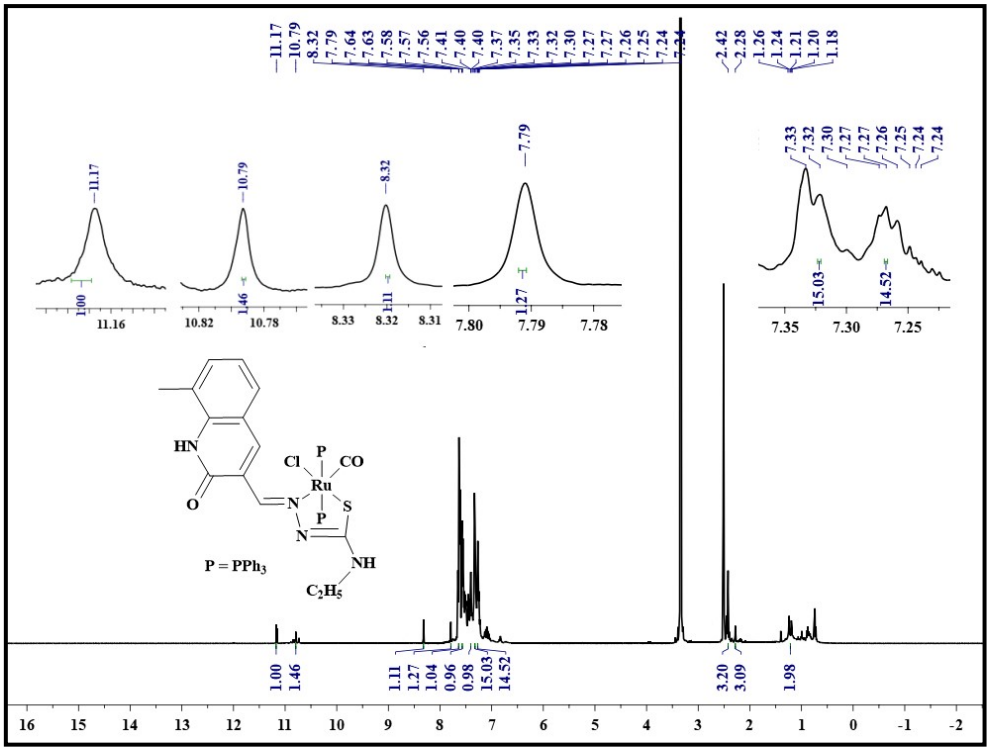


Fig. S8. ^{1}H NMR spectrum of complex **[RuH8MET] (3)**

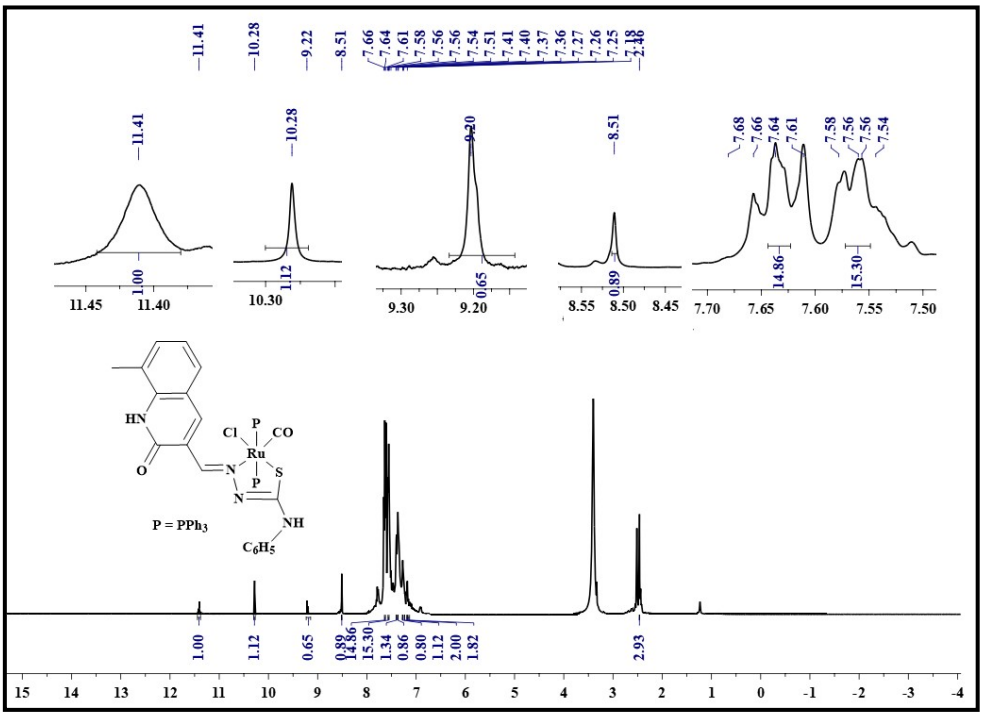


Fig. S9. ^{1}H NMR spectrum of complex **[RuH8MPT] (4)**

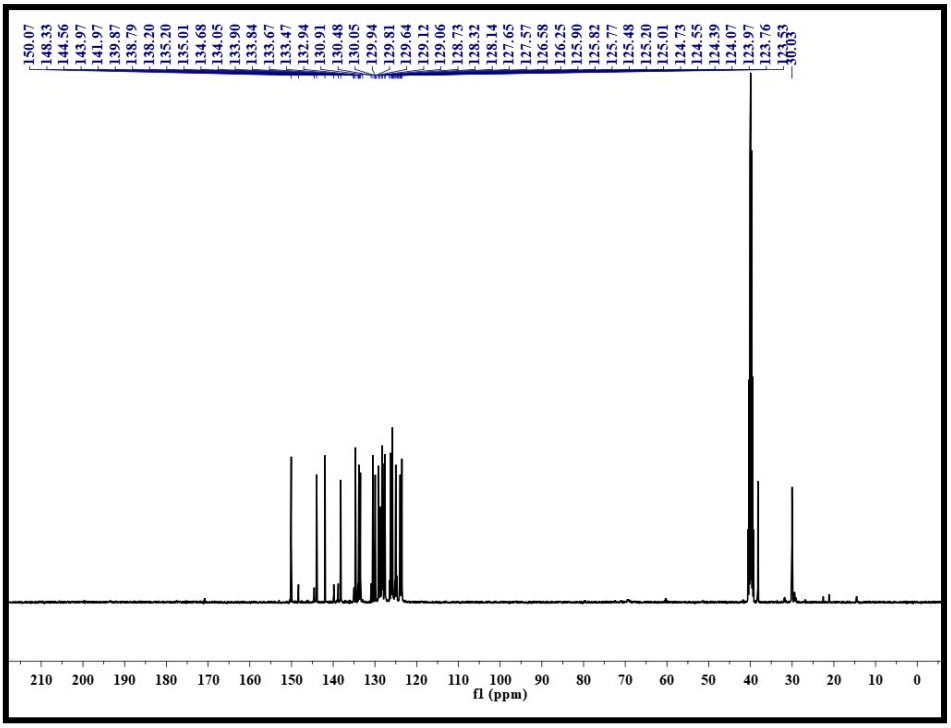


Fig. S10. ^{13}CNMR spectrum of complex **[RuH8MT] (1)**

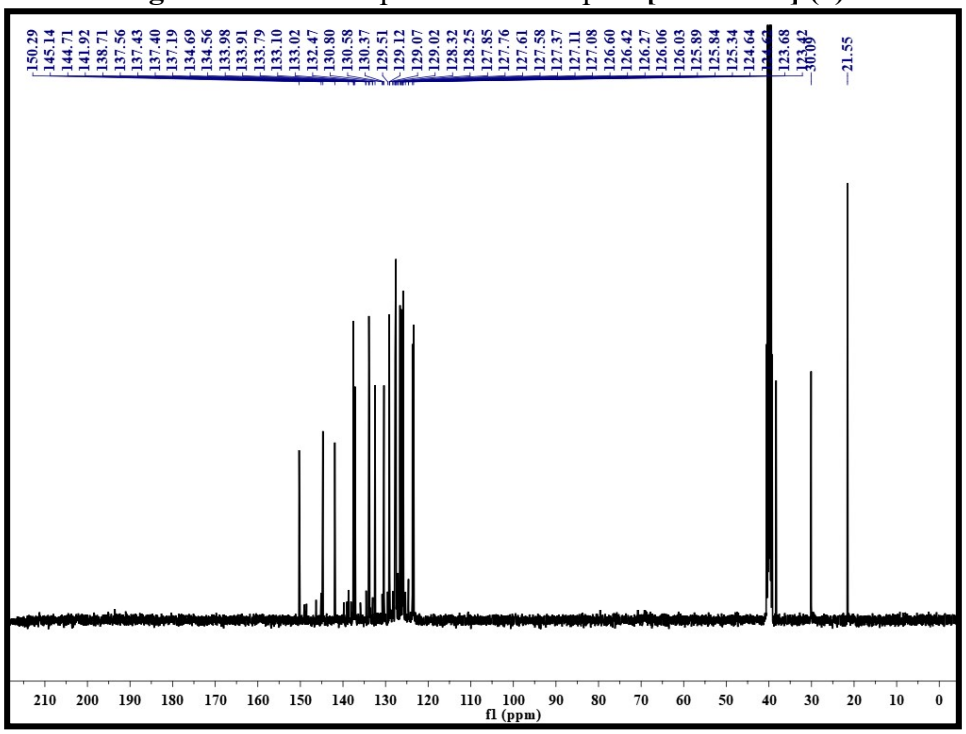


Fig. S11. ^{13}CNMR spectrum of complex **[RuH8MMT] (2)**

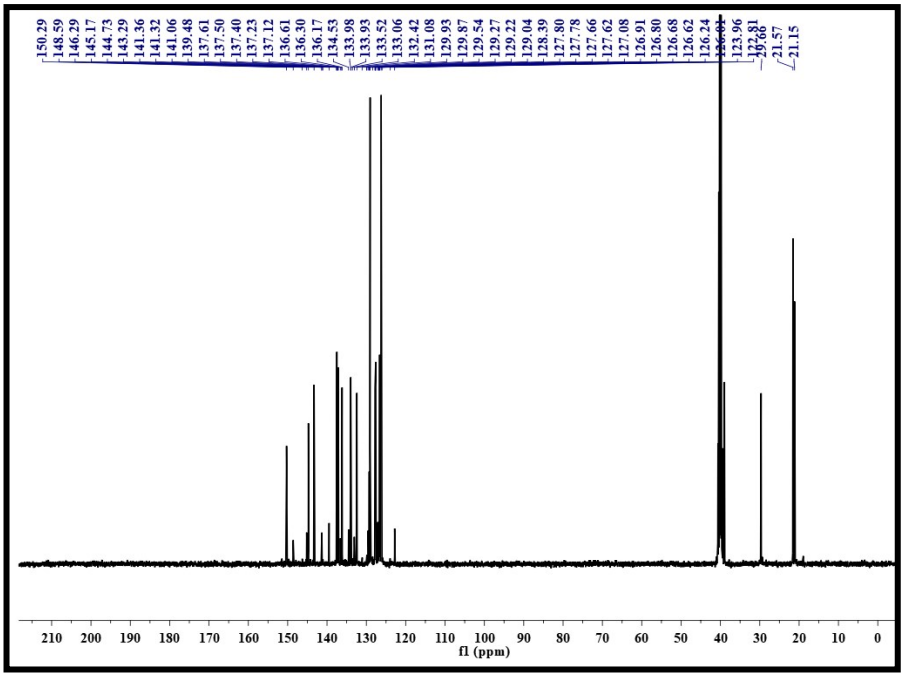


Fig. S12. ^{13}CNMR spectrum of complex **[RuH8MET] (3)**

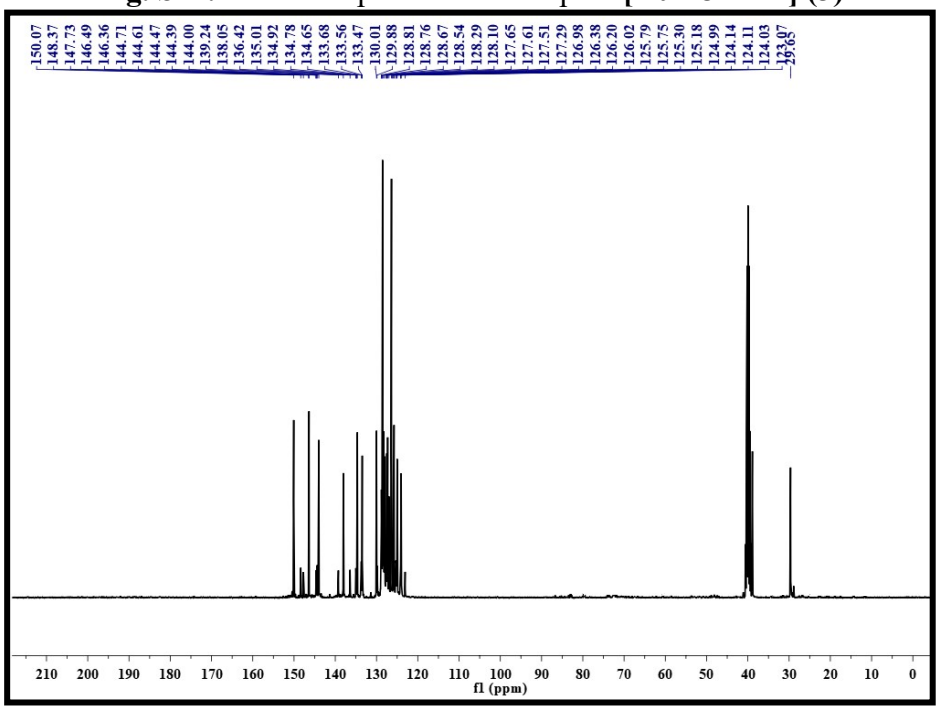


Fig. S13. ^{13}CNMR spectrum of complex **[RuH8MPT] (4)**

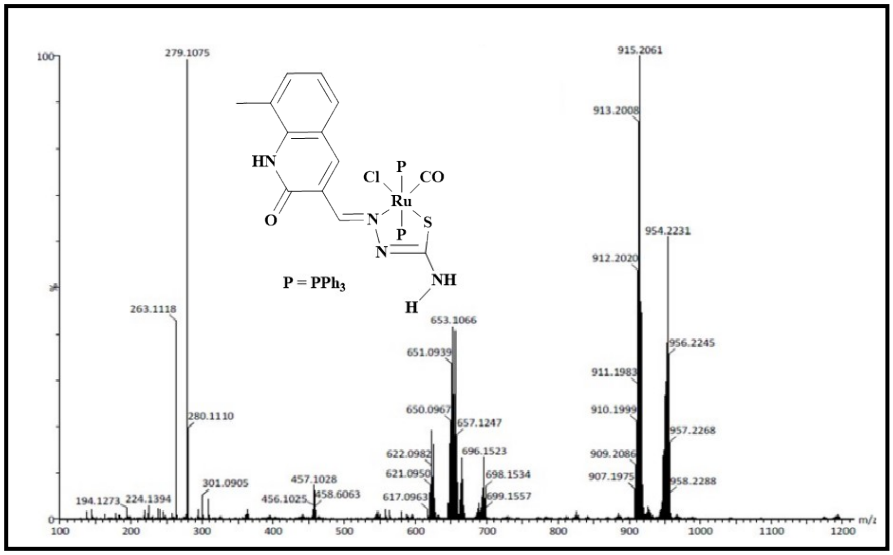


Fig. S14. Mass spectrum of the complex **[RuH8MT)]** (**1**)

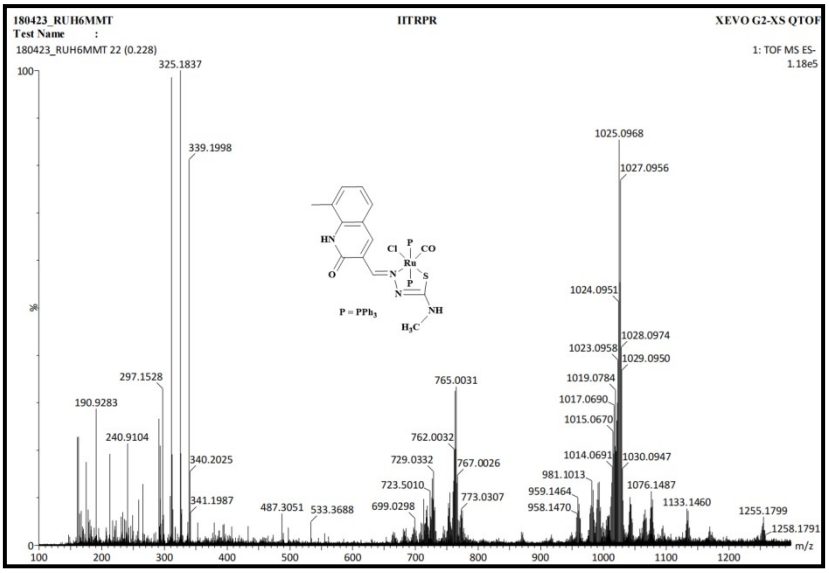


Fig. S15. Mass spectrum of the complex **[RuH8MMT)]** (**2**)

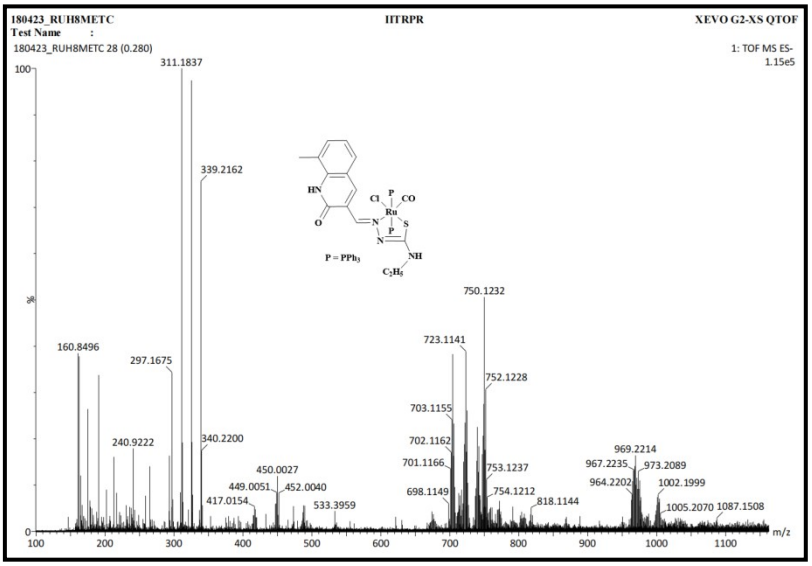


Fig. S16. Mass spectrum of the complex **[Ru8MET)]** (**3**)

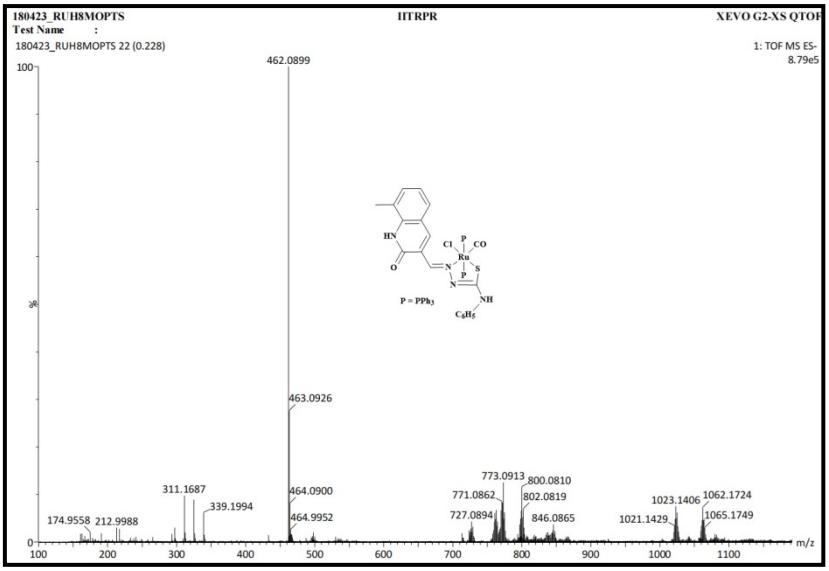


Fig. S17. Mass spectrum of the complex **[Ru8MPT)]** (**4**)

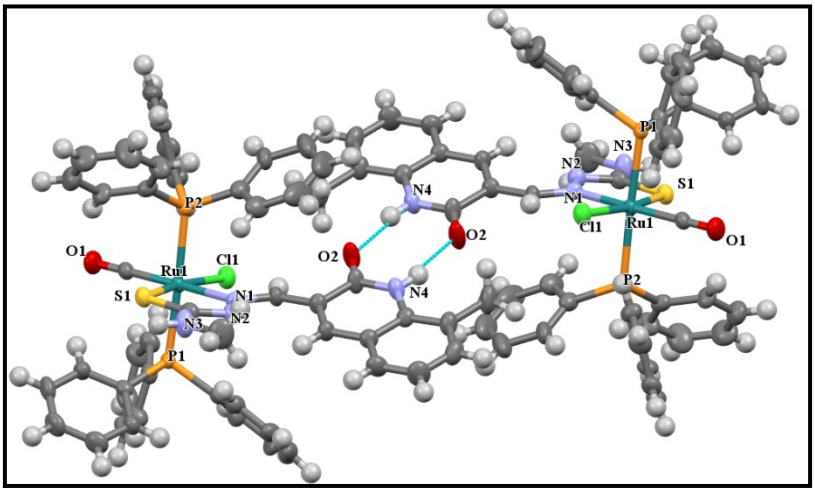


Fig. S18. ORTEP diagram of complex **2**with hydrogen bonding

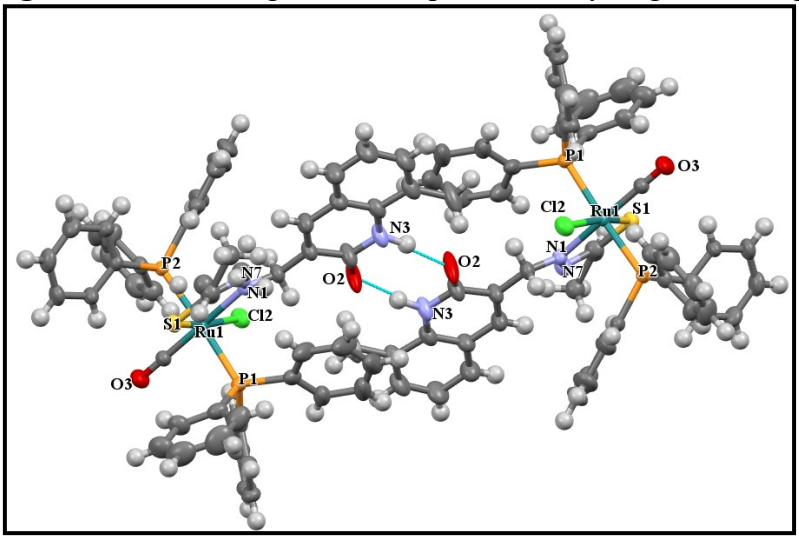


Fig. S19. ORTEP diagram of complex **3**with hydrogen bonding

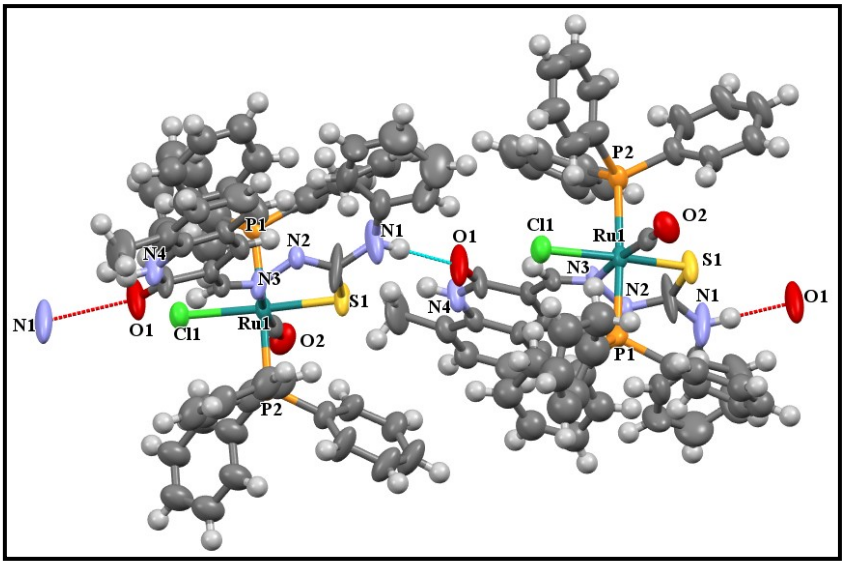


Fig. S20. ORTEP diagram of complex **4** with hydrogen bonding

Table S1. Crystallographic data and structure refinement of new Ru(II) complexes

Compound	**2**	**3**	**4**
Empirical formula	$C_{50}H_{44}ClN_4O_2P_2RuS$	$C_{51}H_{46}ClN_3O_2P_2RuS$	$C_{55}H_{46}ClN_3O_2P_2RuS$
Formula weight	1041.517	961.41	1026.99
Temperature(K)	273 K	298 K	298 K
Wavelength(Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	P -1	P -1	P 21 21 21
a (Å)	12.243(2)	12.2178(5)	14.1817(9)
b (Å)	13.080(3)	13.2469(6)	19.1965(13)
c (Å)	16.249(3)	16.3505(8)	19.3673(13)
α (°)	89.777(6)	89.348(2)	90
β (°)	74.454(5)	74.1690(10)	90
γ (°)	89.408(6)	89.295(2)	90
Volume ($Å^3$)	2506.8(8)	2545.6(2)	5272.5(6)
Z	2	2	4
Absorption co-efficient (mm^{-1})	0.522	0.503	0.491
F(000)	1071.029	988	2118
Theta range for data collection (°)	2.03 to 27.21	2.33 to 23.26	2.37 to 26.73
Index ranges	15 <=h<=-13, 16<=k<=-16, 20<=l<=0	15<=h<=-15 17<=k<=-16, 20<=l<=-20	18<=h<=-18, 24<=k<=-24, 24<=l<=-24
Refinement method	olex2.refine 1.5 (Bourhis et al., 2015)	XL (Sheldrick, 2008)	XL (Sheldrick, 2008)
Final *R* indices [$I>2\sigma(I)$] *R* indices (all data)	R1 = 0.0698 (4939), wR2 = 0.1619 (8631)	R1 = 0.0534 (7291), wR2 = 0.1564 (11250)	R1 = 0.0683 (7787), wR2 = 0.2020 (11631)

Table S2. Selected bond lengths (Å) and angles (°) of new Ru(II) complexes

BOND LENGTH					
Complex 2		**Complex 3**		**Complex 4**	
Ru1-P1	2.395(19)	Ru1-P1	2.403(10)	Ru1-P1	2.416(3)
Ru1-P2	2.397(19)	Ru1-P2	2.468(11)	Ru1-P2	2.382(3)
Ru1-S1	2.354(18)	Ru1-S1	2.355(11)	Ru1-S1	2.348(3)
Ru1-C1	1.853(7)	Ru1-C32	2.389(10)	Ru1-C57	1.838(10)
Ru1-N1	2.153(5)	Ru1-N1	2.156(3)	Ru1- N008	2.162(8)
Ru1-Cl1	2.463(19)	Ru1-Cl2	1.846(4)	Ru1-Cl1	2.434(3)
BOND ANGLE					
Complex 2		**Complex 3**		**Complex 4**	
S1-Ru1-Cl1	169.34(6)	S1-Ru1-Cl2	169.44(4)	S1-Ru1-Cl1	171.21(10)
S1-Ru1-C1	94.38(2)	S1-Ru1-C32	95.83(13)	S1-Ru1-C57	94.4(3)
S1-Ru1-N1	80.20(15)	S1-Ru1-N1	80.29(9)	S1-Ru1-N008	79.6(2)
S1-Ru1-P1	90.79(6)	S1-Ru1-P1	89.31(4)	S1-Ru1-P1	93.67(12)
S1-Ru1-P2	89.43(6)	S1-Ru1-P2	88.78(4)	S1-Ru1-P2	89.56(12)
P1-Ru1-C1	88.92(2)	P1-Ru1-C32	88.29(12)	P1-Ru1-C57	90.4(3)

P1-Ru1-N1	91.75(15)	P1-Ru1-N1	90.93(9)	P1-Ru1- N008	88.2(3)
P1-Ru1-P2	177.56(6)	P1-Ru1-P2	176.76(4)	P1-Ru1-P2	176.77(11)
P1-Ru1-Cl1	87.17(6)	P1-Ru1-Cl2	91.61(4)	P1-Ru1-Cl1	86.94(10)
P2-Ru1-Cl1	93.05(6)	P2-Ru1-Cl2	90.73(4)	P2-Ru1-Cl1	89.86(10)
P2-Ru1-N1	90.68(15)	P2-Ru1-N1	91.31(9)	P2-Ru1- N008	92.3(3)
P2-Ru1-C1	88.63(2)	P2-Ru1-C32	89.26(12)	P2-Ru1-C57	89.5(3)
N1-Ru1-C1	174.54(2)	N1-Ru1-C32	176.07(15)	N1-Ru1-C57	173.7(4)
N1-Ru1-Cl1	89.40(15)	N1-Ru1-Cl2	89.18(9)	N1-Ru1-Cl1	91.7(2)
C1-Ru1-Cl1	96.04(2)	C32-Ru1-Cl2	94.71(13)	C57-Ru1-Cl1	94.4(3)

Table S3. Hydrogen bonds for **complexes (2 - 4)** [Å and °]

RuH8MMT				
D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
N(4)···O(2)	1.991	0.861	2.833	165.53
Symmetry operation: **(x, y, z); (-x, -y, -z)**				
RuH8MET				
N(3)···O(2)	1.801	1.035	2.828	171.07
Symmetry operation: **(x, y, z); (-x, -y, -z)**				
RuH8MPT				
N(1)···O(1)	0.861	1.897	2.754	173.33
Symmetry operation: **(x, y, z); (-x+1/2, -y, z+1/2); (-x, y+1/2, -z+1/2); (x+1/2, -y+1/2, -z)**				

Spectral studies of substrates

The substrate scope was extended with different substituent under optimal hydrogenation conditions (**Fig. 4 (1A-5E)**). The ^{1}H NMR and ^{13}C NMR spectral data of the products obtained are provided in (**Fig. S21. - Fig. S70)**. The GC and GC-MS chromatograms of the products are provided in (**Fig. S71−S79)**. The products were analysed by CD spectrum in ethyl acetate solvent at 10μM concentration, to determine their enantiomeric nature. The CD spectra of representative hydrogenated products have been shown in (**Fig. S80−S84)**.[7-9]

^{1}H NMR of the products

1A:^{1}HNMR(400MHz,DMSO,δppm,*J*Hz):8.25(s,1H),8.19-8.21(t,1H, *J* =8 Hz),7.95-7.97(d,1H,*J* = 8Hz),7.90-7.92(d,1H,*J* = 8Hz),7.84-7.86(t,1H,*J* = 8 Hz),7.72-7.76(t,1H,*J* = 16Hz),7.51-7.61(m,6H,*J* = 40Hz),5.75-5.76(d,1H,*J* = 4 Hz),5.54-5.58(q,1H,*J* = 16Hz),3.05-3.21(m,2H, *J*=64Hz),2.14-2.36(dp,2H,*J* = 88Hz).^{13}CNMR(DMSO,δppm):151.25,146.14,142.00,138.25,134.07,133.79, 130.42, 130.37,129.12,128.01,127.62,127.60,126.28,125.89,125.85,123.73, 123.42,69.16,38.24,30.09.

1B:[1]HNMR(400MHz,DMSO,δppm,*J*Hz):8.14(s,1H),8.09-8.12(d,1H,*J* = 12 Hz),7.91-7.94(dd,1H,*J* = 12Hz),7.85-7.86(d,1H,*J* = 4Hz),7.80-7.82(d,1H,*J* = 8 Hz),7.73-7.77 (t,1H,*J* = 16Hz),7.66-7.67(d,1H,*J* = 4Hz),7.64(s,1H),7.47-7.55(m, 4H, *J* = 32Hz),5.62-5.65(d,1H,*J* = 12Hz),5.43-5.46(q,1H,*J* = 12Hz),3.39(s,3H), 2.96-3.11(m,2H,*J* = 92Hz),2.06-2.25(dp,2H,*J* = 76Hz),[13]CNMR(DMSO,δppm): 150.29,144.71,141.92,137.19,133.91,133.79,132.47,130.37,129.12,128.32, 127.76,127.58,127.08,126.60,126.27,125.89,125.84,123.68,123.42,69.16,38.30, 30.09, 21.55.

1C:[1]HNMR(400MHz,DMSO,δppm,*J*Hz):8.19(s,1H),8.09-8.11(d,1H,*J* = 8Hz),7.90-7.92(dd,1H,*J* = 8Hz),7.79-7.81(d,1H,*J* = 8Hz),7.73-7.77(t,1H,*J* =16 Hz),7.67(s, 1H),7.51-7.53(d,1H,*J* = 8Hz), 7.47-7.49(m,2H,*J* = 8Hz), 7.39-7.40(d, 1H,*J* =4Hz),7.37-7.38(d,1H,*J* = 4Hz),5.63-5.64(d, 1H,*J* =4Hz),5.43-5.46(q,1H,*J* = 12Hz). [13]CNMR(DMSO,δppm):151.15, 146.43,141.99,140.40,137.91,135.01,133.79,133.01,130.85,130.39,129.65,129.12,127.59,126.80,126.40,126.25, 125.88,125.83,123.70,123.42,69.18,30.03,29.55.

1D:[1]H NMR (400 MHz, DMSO, δ ppm, *J* Hz): 8.24 (s, 1H), 8.13-8.16 (d, 1H, *J* = 12Hz),7.93-7.95(dd,1H,*J* = 8Hz),7.82-7.84(d,1H,*J* = 8Hz),7.74-7.77(t,1H,*J* =12 Hz), 7.56-7.58(d,1H, *J* = 8Hz),7.538-7.539(d,1H,*J* = 4Hz),7.45-7.52(m,4H),5.63 (s,1H),5.46-5.48(t, 1H,*J* =8 Hz),3.00-3.15(m,2H),2.09-2.29(dp,2H),2.64(s,3H).[13]CNMR(DMSO,δppm):150.33,145.24,141.97,138.42,135.61,133.80, 133.75,130.41,130.23,129.11,128.24,127.77,127.60,127.24,126.25,125.82,125.78,124.64,123.73,123.46,69.25,30.02,29.43.

1E:[1]HNMR(400MHz,DMSO,δppm,*J*Hz):8.90-8.92(d,1H,*J* = 8Hz),8.06(s, 1H),7.71-7.73(d,1H,*J* = 8Hz),7.82-7.89(m,4H),7.61-7.62(dd,1H,*J* = 8Hz), 7.64-7.66 (d,1H,*J* = 8 Hz),7.44-7.55(m,4H),5.76-5.78(d,1H,*J* =8Hz),5.50-5.52 (q, 1H,*J* =8 Hz),2.98-3.14(m,2H),2.10-2.34(dp,2H).[13]CNMR(DMSO,δppm): 150.07, 143.97, 141.97, 138.20, 134.68, 133.84, 133.47, 130.48, 129.94, 129.12, 128.73, 128.32, 128.14, 127.65, 127.57, 126.25, 125.90, 125.82, 125.77, 125.01, 123.97, 123.76, 123.53, 69.37, 38.19, 30.03.

2A:[1]HNMR(400MHz,DMSO,δppm,*J*Hz):8.23(s,1H),7.98-8.01(d,1H,*J*= 12 Hz),7.91-7.93(d,1H,*J*= 8Hz),7.71-7.77(dd,1H,*J*= 36Hz),7.62-7.64(t,1H,*J*=8Hz), 7.12-7.30(m,5H,*J*=72Hz),5.56-5.60(d,2H,16Hz),5.22-5.25(t,1H,*J* =12Hz), 4.52-4.58(q,2H,J=36Hz),2.05-2.19(dp,2H,*J*=56Hz).[13]CNMR(DMSO,δppm):152.21,145.67,135.46,134.68,130.56,129.29,128.57,128.49, 128.03,127.63,127.56,127.33,127.19,126.37,126.22,72.14,71.25,29.18.

2B:[1]HNMR(400MHz,DMSO,δppm,*J*Hz):8.40(s,1H),8.02(s,1H),7.73-7.75 (d,1H,*J* =8 Hz),7.57-7.60(d,1H,*J* = 12 Hz),7.48-7.49(d,1H,*J* =4Hz),7.38-7.40(d, 1H,*J* = 8Hz),7.31-

7.35(t, 1H,*J* =16Hz),7.21-7.26(p,2H,*J* =20Hz),5.41-5.42(d, 1H,*J* = 4Hz),4.65-4.68(t,1H,*J* = 3Hz),2.73-2.95(dp,2H,*J* = 88Hz),2.41(s,3H), 1.97-2.02(q,2H,*J* = 20Hz).[13]CNMR(DMSO,δppm):150.07,144.03,143.26,
138.58,136.20,134.89,133.60,129.97,129.05,128.50,128.36,127.79,126.25,
125.96,125.20,123.95,72.09,38.90,29.60.

2C:[1]HNMR(400MHz,DMSO,δppm,*J*Hz):7.99(s,1H),7.65-7.66(d,1H,*J* = 4 Hz),7.50-7.48(d,1H,*J* = 8Hz),7.24-7.39(m,6H,*J* = 60Hz),5.64-5.65(d,1H,*J* = 4 Hz),4.74-4.80 (t,1H,*J*=6Hz),2.81-3.04 (dp,2H,*J* = 92Hz),2.42(s,3H),2.10-2.11 (q, 2H,
J = 4Hz).[13]CNMR(DMSO,δppm):151.22,146.48,146.39,140.04,137.48,
133.00,129.34,128.72,128.48,127.99,127.36,127.23,126.88,126.37,125.77,
72.50,39.07,29.74,21.78.

2D:[1]HNMR(400MHz,DMSO,δppm,*J*Hz):9.04(s,1H),7.84-7.86(d,1H,*J* = 8Hz),7.70-7.73(d,1H,*J* = 12Hz),7.64-7.68(t, 1H,*J* = 8Hz),7.51-7.54(t,1H,*J* = 12Hz),
7.38-7.41(m,3H,*J* = 12Hz),7.30-7.32(d,1H,*J* = 8Hz),5.65-5.67(d,1H,*J* = 8Hz), 4.82-4.83(q,1H,*J* = 4 Hz),2.82-3.05(dp,2H,*J* = 92Hz),2.58(s,3H),2.12-2.14(q,2H,
J = 8 Hz). [13]C NMR (DMSO, δ ppm): 150.29, 146.14, 144.45, 139.06, 134.99, 133.80, 131.10, 129.18, 128.95, 128.25, 127.95, 127.20, 126.23, 125.48, 124.22, 120.70, 71.54, 38.72, 29.45.

2E:[1]HNMR(400MHz,DMSO,δppm,*J*Hz):7.76(s,1H),7.61-7.63(d,1H,*J* = 8 Hz),7.47-7.50(d,1H,*J* = 12Hz),7.32-7.34 (d, 1H,*J* = 8Hz),7.23-7.25 (d,1H, *J* = 8 Hz),
7.37-7.44(m,5H,*J* =28Hz),7.13-7.16(t,1H,*J* = 12Hz),7.01-7.05(t,1H,*J* = 16Hz),
5.36-5.37(d,1H,*J* = 4Hz),4.50-4.54(q,1H,*J* = 16Hz),2.55-2.79(dp,2H,*J* = 96Hz), 1.79-1.87(q,2H,*J* = 32Hz).[13]CNMR(DMSO,δppm):150.07,146.36,140.00,
138.05,134.65,133.47,130.01,128.81,128.67,128.54,128.29,128.10,127.51,
127.29,126.98,126.38,125.75,124.99,124.03,72.47,38.90,29.65.

3A:[1]HNMR(400MHz,DMSO,δppm,*J*Hz):8.29(s,1H),7.97-7.99(s,1H,*J* = 8Hz),
7.91-7.93(d,1H,*J* = 8Hz),7.73-7.77(t,1H,*J* = 16Hz),7.60-7.64(t,1H,*J* = 16Hz),
7.26-7.28(d,2H,*J* = 8Hz),7.13-7.15(d,2H,*J* = 8Hz),5.33-5.34(d,1H,*J* = 4Hz),
4.60-4.64 (q,1H,*J* = 16Hz),2.77-2.99(dp,2H,*J* = 88Hz),2.28(s,3H),1.98-2.03(q, 2H,
J = 20Hz).[13]CNMR(DMSO,δppm):151.25,146.55,146.15,143.30,138.06,
136.16,134.08,130.24,129.03,127.92,127.89,127.78,127.46,126.82,126.25,
72.11,38.92,29.69,21.15.

3B:[1]HNMR(400MHz,DMSO,δppm,*J*Hz):8.14(s,1H),7.79-7.81(d,1H,*J* = 8 Hz),
7.69(s,1H),7.56-7.58(d,1H,*J* = 8Hz),7.34-7.36(d,1H,*J* = 8Hz),7.27-7.29(d, 1H,

J = 8Hz),5.35-5.37(d,1H,*J* =8Hz),4.61-4.64(t,1H,*J* = 12Hz),2.75-2.96(dp, 2H, *J* = 84 Hz), 2.48 (s, 3H), 2.29 (s, 3H), 1.97-2.03 (q, 2H, *J* = 24 Hz). ^{13}C NMR (DMSO,δppm):150.29,144.73,143.29,137.50,137.12,136.17,133.98,132.42,129.27, 129.04,127.80,127.62,126.80,126.62,126.24,72.04,38.97,29.66,21.57,21.15.

3C: ^{1}HNMR(400 MHz,DMSO,δppm,*J*Hz):8.00(s,1H),7.65-7.68(d,1H,*J*=12 Hz),7.34-7.35(d,2H,*J*=4Hz),7.27-7.29(d,2H,*J*=8Hz),7.12-7.14(d,2H,*J*=8 Hz), 5.52-5.53(d,1H,*J*=4Hz),4.74-4.75(t,1H,*J*=4Hz),2.08-2.09(q,2H,*J*=4Hz), 2.81-2.99(dp,2H, *J*=72 Hz).^{13}CNMR(DMSO,δppm):152.14,149.51,146.46, 143.34,140.03,137.50,136.16,133.05,129.34,129.05,127.92,127.37,126.87, 126.29,125.78,72.32,37.81,29.75,21.74,21.14.

3D: ^{1}HNMR(400MHz,DMSO,δppm,*J*Hz):7.81(s,1H),7.40-7.42(d,1H,*J* = 8 Hz),7.21-7.22(d,2H,*J* = 4Hz),7.09-7.17(dd,1H,*J* = 32Hz),6.95-6.97(d,1H,*J* = 8 Hz), 6.90-6.92(d,2H,*J* = 8Hz),5.24-5.28(d,1H,*J* = 16Hz),4.487-4.49(t,1H,*J* = 1.2 Hz),2.56-2.79(dp,2H,*J* = 92Hz),2.39(s,3H),2.05(s,3H),1.80-1.88(q,2H,*J* = 32Hz).
^{13}C NMR (DMSO, δ ppm): 150.28, 145.21, 143.22, 138.09, 136.17, 135.59, 133.69, 129.99, 129.24, 129.01, 127.67, 127.00, 126.81, 126.23, 125.61, 72.24, 38.91, 29.65, 21.10, 17.79.

3E: ^{1}HNMR(400MHz,DMSO,δppm,*J*Hz):8.00(s,1H),7.84-7.86(d,1H,*J*=8 Hz),7.73-7.75(d,1H,*J*=8 Hz),7.55-7.71(m,4H,*J*= 64 Hz),7.34-7.36(d,2H,*J*=8 Hz), 7.13-7.15(d,2H,*J*= 8Hz),4.84-4.85(d,1H,*J*=4Hz),4.72-4.75(q,1H,*J*=12 Hz), 2.82-3.04(dp,2H,*J*=88Hz),2.05-2.13(q,2H,*J*= 32Hz).^{13}CNMR(DMSO,δppm):150.10,144.04,143.33,138.06,136.23,134.73,133.49,130.07,129.09,128.64, 128.28,128.09,127.49,126.93,126.32,125.78,124.99,124.06,72.35,38.93,29.72, 21.18.

4A: ^{1}HNMR(400MHz,DMSO,δppm,*J*Hz):8.23 (s,1H),8.01-7.99 (d,2H,*J* = 8 Hz), 7.94-7.91 (d,2H,*J* = 12 Hz),7.77-7.75 (t,1H,*J* = 8 Hz),7.40-7.39 (t,1H,*J* = 4 Hz), 7.15-7.14 (d,2H,*J* = 4 Hz),5.56 (s,1H),2.14-2.13 (d, 2H,*J* = 4 Hz),2.05-2.01 (t,2H, *J* = 16 Hz), 3.94 (s, 1H). ^{13}C NMR (DMSO, δ ppm): 151.02, 146.78, 146.15, 140.38, 137.88, 132.83, 129.08, 128.72, 128.24, 127.49, 126.03, 125.99, 125.77, 79.93, 72.73, 21.78, 21.40.

4B: ^{1}HNMR(400MHz,DMSO,δppm,*J*Hz):8.40 (s,1H),8.02 (s,1H),7.60-7.57 (d, 2H,*J* = 12 Hz),7.49-7.48 (d,2H,*J* = 4 Hz),7.25-7.23 (d,1H,*J* = 8Hz),7.06-7.03 (d,1H, *J* = 12 Hz),5.54 (s,1H),4.46 (s,1H),2.95-2.89 (m,2H),2.79-2.75 (m,2H),2.42 (s,3H).
^{13}CNMR(DMSO,δppm):150.39,146.15,144.28,138.43,134.92,133.68,129.88, 128.81,128.76,127.54,127.12,126.91,126.23,125.61,125.18,124.14,72.66,29.39, 28.98.

4C: ^{1}HNMR(400MHz,DMSO,δppm,*J*Hz):7.99 (s,1H),7.66-7.65 (d,2H,*J* = 4 Hz), 7.39-7.35 (d, 2H,*J* = 16 Hz),7.28-7.26 (d,1H,*J* = 8 Hz),7.50-7.48 (d,1H, *J* = 8 Hz),5.65 (s, 1H), 4.80 (s,1H),3.85 (s,1H), 3.04-2.81 (m,2H),2.11-2.10 (d,2H, *J* = 4 Hz),2.42 (s,3H).^{13}CNMR(DMSO,δppm):150.39,145.27,143.35,137.70,137.23,136.52,134.19, 129.43,128.84,128.39,126.91,126.80,126.16,72.97,72.04,29.66,28.76.

4D: ^{1}HNMR(400MHz,DMSO,δppm,*J*Hz):8.19 (s,1H),8.11-8.09 (d,1H,*J* = 8 Hz), 7.92-7.91 (d,1H,*J* = 4 Hz),7.81-7.79 (d,2H,*J* = 8 Hz), 7.77-7.73 (t,1H,*J* = 16 Hz), 7.53-7.51 (d,1H,*J* = 8 Hz),7.40-7.38 (d,1H,*J* = 8 Hz),7.45-7.43 (d,1H,*J* = 8 Hz),5.63 (s,1H), 3.09-2.99 (m,2H),2.22-2.07 (m,2H),2.23 (s,2H).^{13}CNMR(DMSO,δppm):150.59, 145.59,143.97,130.49,136.61,135.44,135.17,133.95,130.56,129.30,128.88, 127.84,126.66,125.61,125.45,73.76,72.24,29.65,29.11.

4E: ^{1}HNMR(400 MHz,DMSO,δppm,*J*Hz):8.72-8.70 (d,1H, *J* = 8 Hz),8.20-8.15 (d, 1H,*J* = 20 Hz),7.63-7.61(d,1H,*J* = 8 Hz),7.41-7.39 (d,1H,*J* = 8 Hz),7.76 (s,1H),7.50 (s, 1H),7.47 (s,1H),7.34 (s,1H),7.25-7.23 (d,1H,*J* = 8 Hz),7.05-7.01 (t,1H,*J* =16 Hz), 7.16-7.13 (t, 1H, *J* = 12 Hz), 5.37 (s, 1H), 4.53 (s, 1H), 2.79-2.55 (m, 2H), 1.85-1.83 (d, 2H, *J* = 8 Hz).^{13}CNMR(DMSO,δppm):150.23,146.70,145.43,145.22,138.59,135.59, 134.37,133.60, 132.92,132.35,131.62,131.36,130.36,129.02,128.56,127.75, 127.38,125.79,120.20,71.55,29.33,17.77.

5A: ^{1}HNMR(400MHz, DMSO,δppm,*J*Hz):8.40 (s,1H), 7.60-7.57 (d,1H,*J* = 12 Hz), 7.49-7.48 (d, 1H, *J* = 4 Hz), 7.31-7.21 (m, 2H), 7.35-7.33 (d,1H, *J* = 8 Hz), 7.06-7.03 (d,1H, *J* = 12 Hz),6.67-6.63 (t,1H,*J* = 16 Hz),5.48 (s,1H),4.68-4.65 (t,1H,*J* = 12 Hz),2.95-2.73 (m,4H). ^{13}CNMR(DMSO,δppm):150.05,145.73,144.08,138.65,134.73, 133.62,131.38,129.98,128.59,127.81,125.97,125.20,123.97,120.20,71.54,29.45.

5B: ^{1}HNMR(400MHz,DMSO,δppm,JHz): 9.02 (s,1H),7.99-7.84 (dd, 2H, *J* = 60 Hz),7.70 (s,1H),7.43-7.38 (d,2H,*J* = 20 Hz),7.54-7.51 (t,1H,*J* = 12 Hz),5.67 (s, 1H),4.83 (s,1H),3.09-2.79 (m,4H),2.14 (s,3H).^{13}CNMR(DMSO,δppm):150.66, 150.23,144.76,137.69,137.25,133.70,132.54,128.65,127.78,127.61,127.03, 126.63,124.61,123.50,68.30,22.54,21.56.

5C: ^{1}HNMR(400MHz,DMSO,δppm,*J*Hz):8.19 (s,1H),8.11-8.09 (d,1H,*J* = 8 Hz), 7.92-7.91 (d,1H,*J* = 4 Hz),7.75-7.73 (d,1H,*J* = 8 Hz),7.67 (s,1H),7.53-7.51 (d,1H, *J* = 8 Hz),7.40-7.38 (t,1H,*J* = 8 Hz),5.63 (s,1H),5.45-5.43 (d,1H,*J* = 8 Hz),3.11-2.98 (m, 2H), 2.25-2.03 (m, 2H),2.47 (s,3H).^{13}CNMR(DMSO,δppm):151.20,146.46, 143.46,143.34,140.03,137.50,136.16,133.05,129.34,129.05,127.37,126.87, 126.29,125.78,72.32,21.74,21.14.

5D:[1]HNMR(400MHz, DMSO,δppm,*J*Hz):7.99 (s,1H), 7.67-7.62 (d,2H,*J* = 20 Hz), 7.46-7.44 (t,1H,*J* = 8 Hz),7.35-7.33 (d,1H,*J* = 8 Hz),7.29-7.26(d,1H,*J* =12 Hz), 7.16- 7.12 (t,1H,*J* =16 Hz),5.54 (s,1H),4.74 (s,1H),3.02-2.79 (m,2H),2.15-2.08 (m,2H), 2.26 (s,3H).[13]CNMR(DMSO,δppm):151.22,146.48,146.39,140.04,137.48, 133.00,129.34,128.78,128.48,127.36,127.23,126.88,126.37,125.77,72.50,22.62, 21.78.

5E:[1]HNMR(400MHz,DMSO,δppm,*J*Hz):8.48 (s,1H),8.14 (s,1H),7.94-7.91 (t, 2H,*J* = 12 Hz),7.75-7.73 (d,2H,*J* = 8 Hz),7.64 (s,1H),7.55-7.53 (d,2H,*J* = 8 Hz),7.50- 7.48 (t,1H,*J* = 8 Hz),5.62 (s,1H),5.46-5.43 (t,1H,*J* = 12 Hz),3.08-3.00 (m,2H),2.24- 2.19 (m,2H).[13]CNMR(DMSO,δppm):150.07,146.36,144.00,138.05,134.65, 133.47,130.01,128.54,128.29,128.10,127.51,127.29,126.98,126.38,125.75, 124.99,124.03,72.47,29.65,29.00.

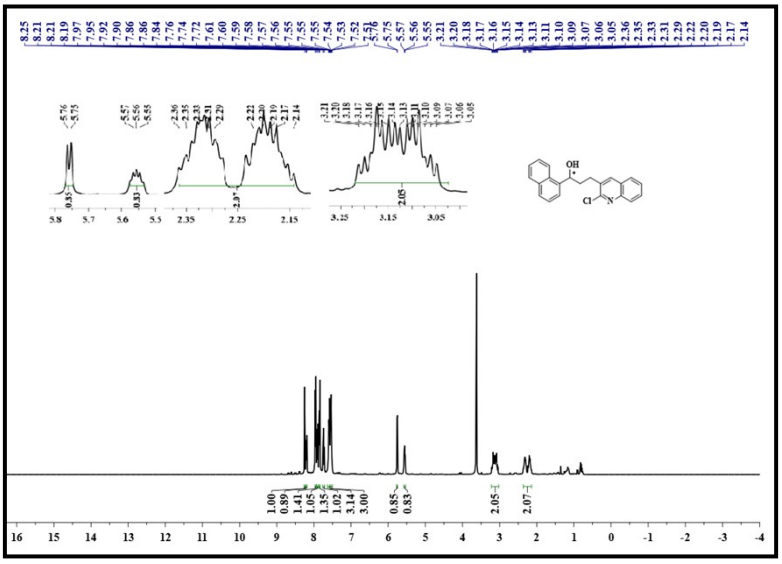


Fig. S21. [1]H NMR spectrum of **1A**

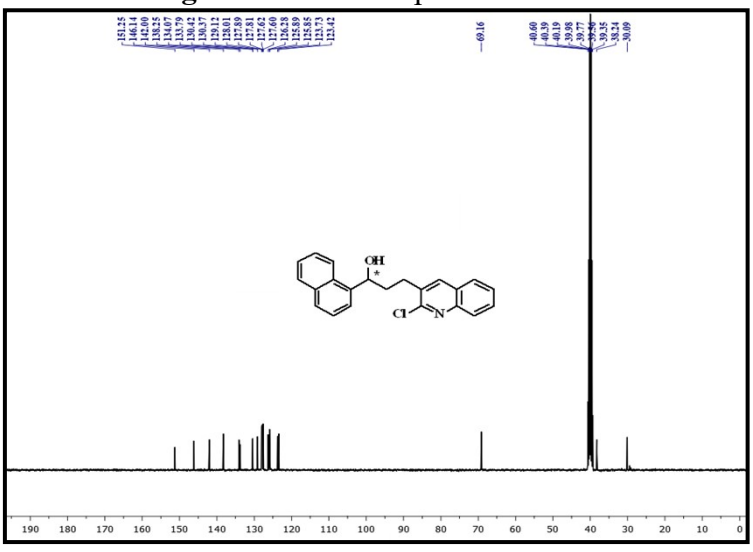


Fig. S22. [13]C NMR spectrum of **1A**

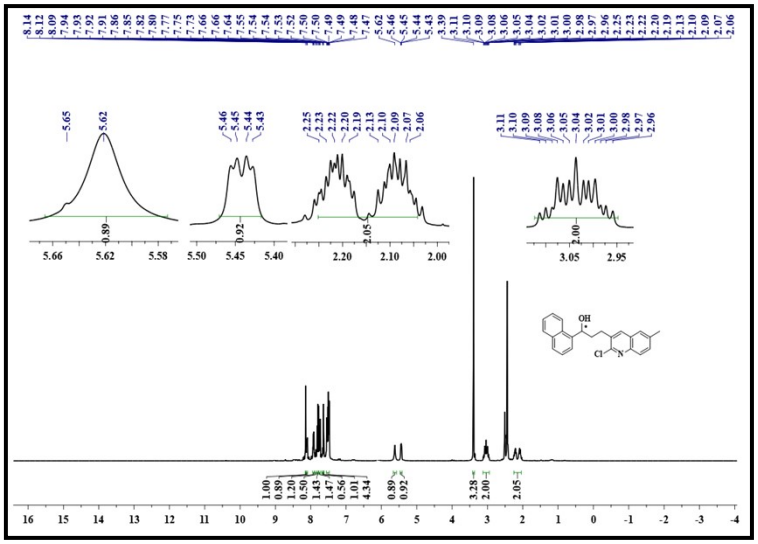


Fig. S23. ^{1}H NMR spectrum of **1B**

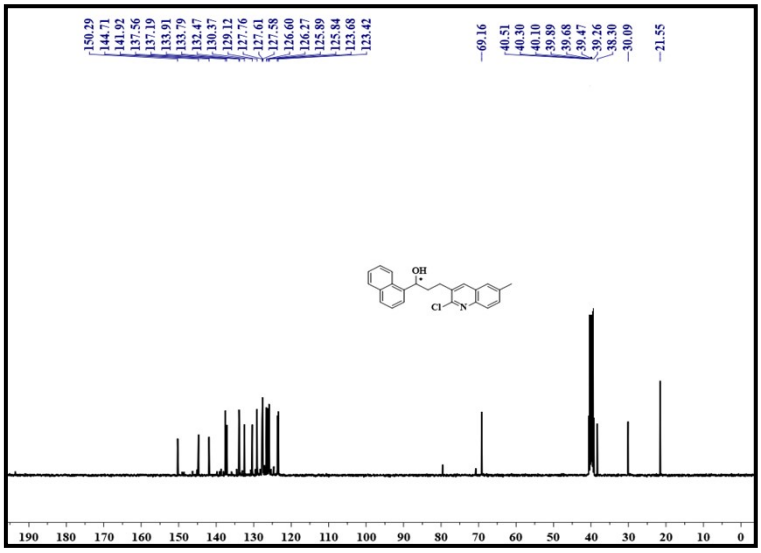


Fig. S24. ^{13}C NMR spectrum of **1B**

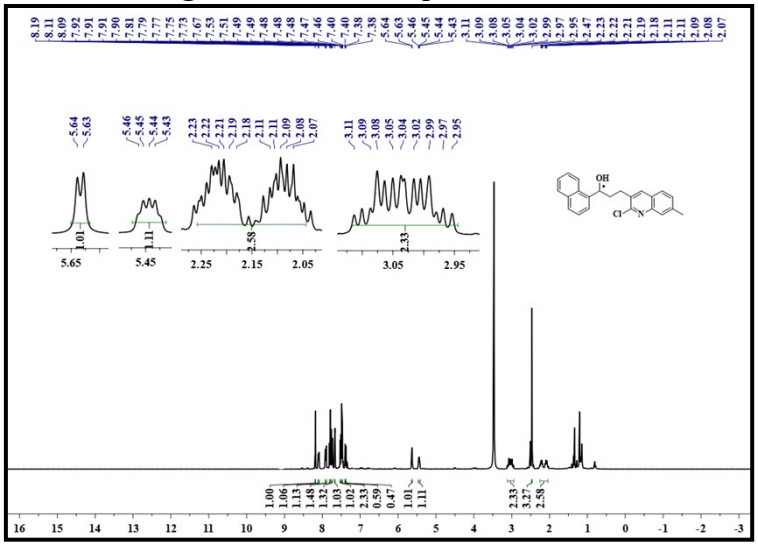


Fig. S25. ^{1}H NMR spectrum of **1C**

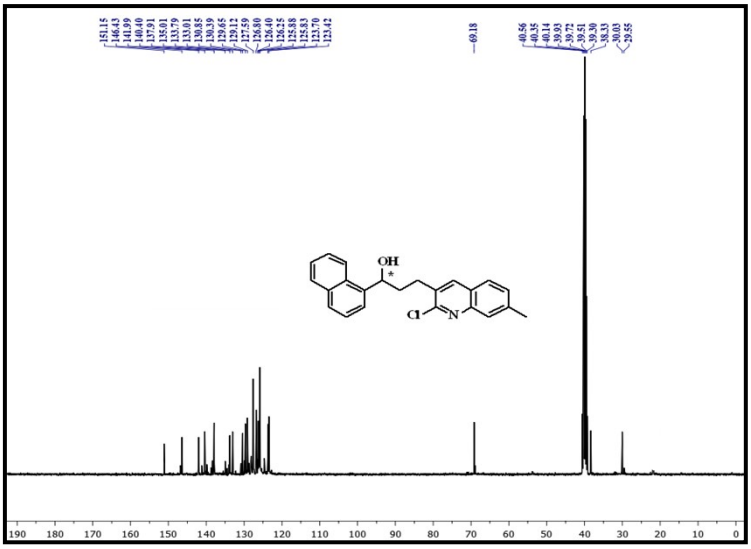


Fig. S26. ^{13}C NMR spectrum of **1C**

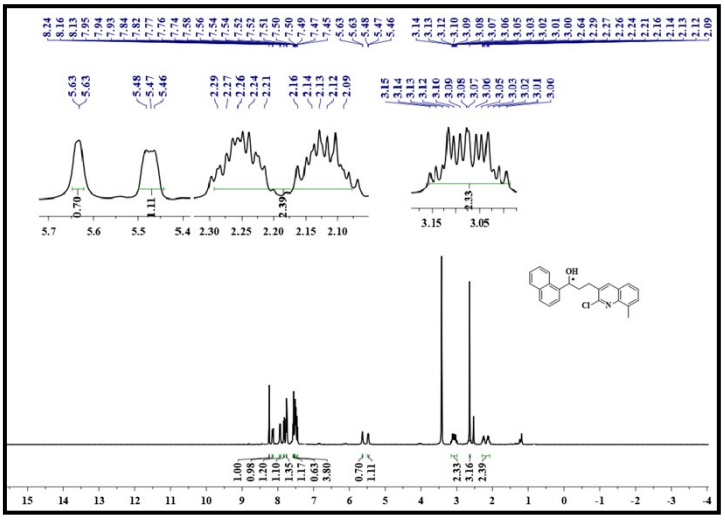


Fig. S27. ^{1}H NMR spectrum of **1D**

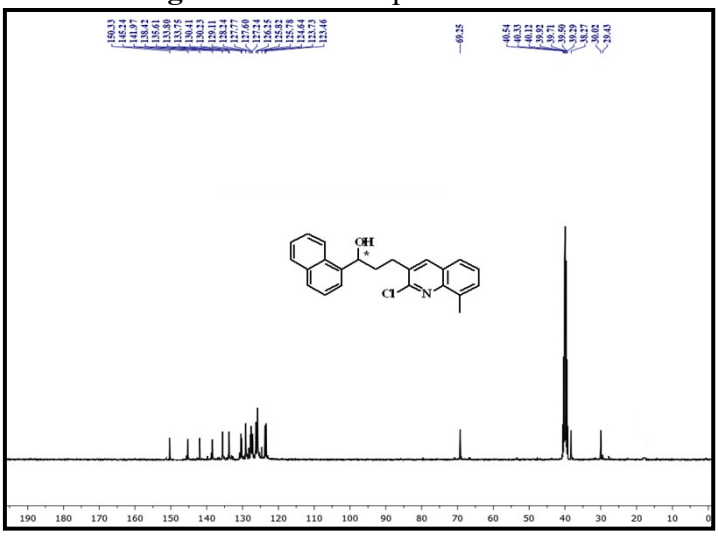


Fig. S28. ^{13}C NMR spectrum of **1D**

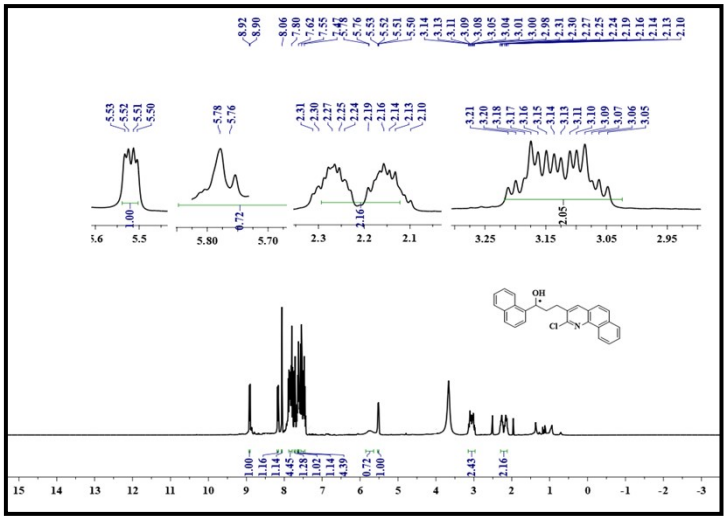


Fig. S29. ^{1}H NMR spectrum of **1E**

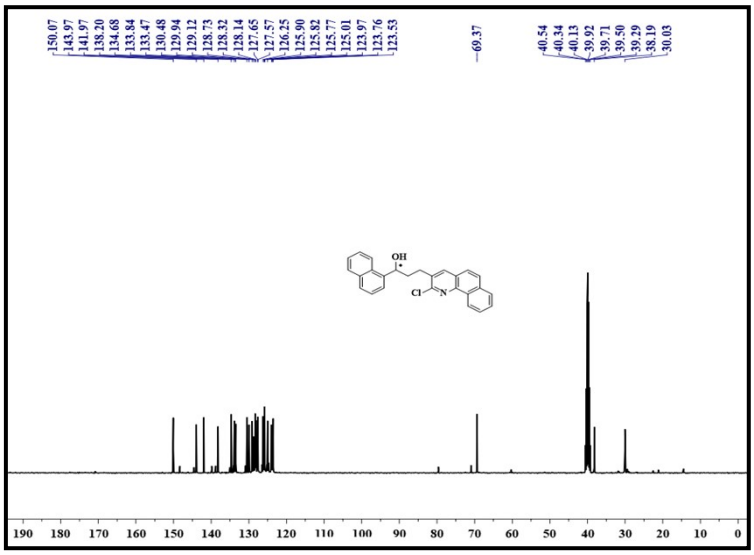


Fig. S30.^{13}C NMR spectrum of **1E**

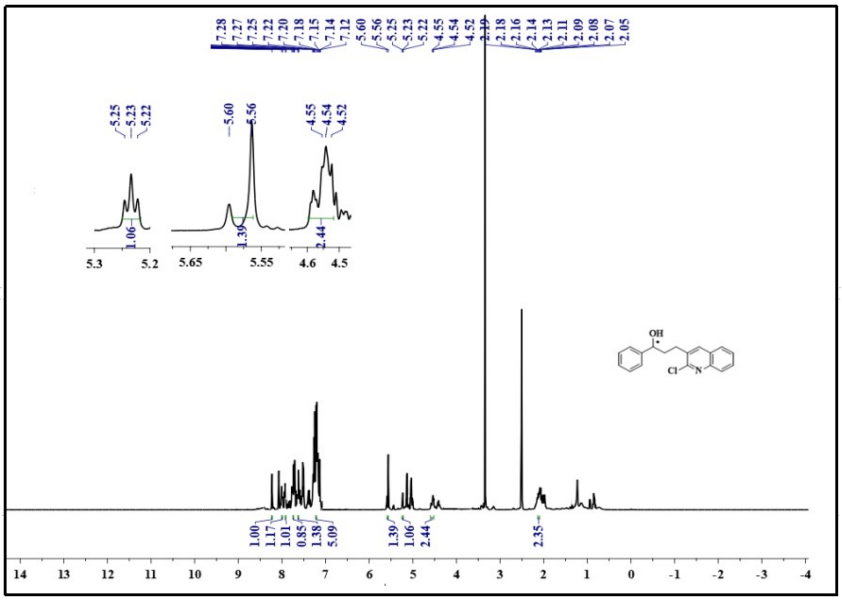


Fig. S31. ^{1}H NMR spectrum of **2A**

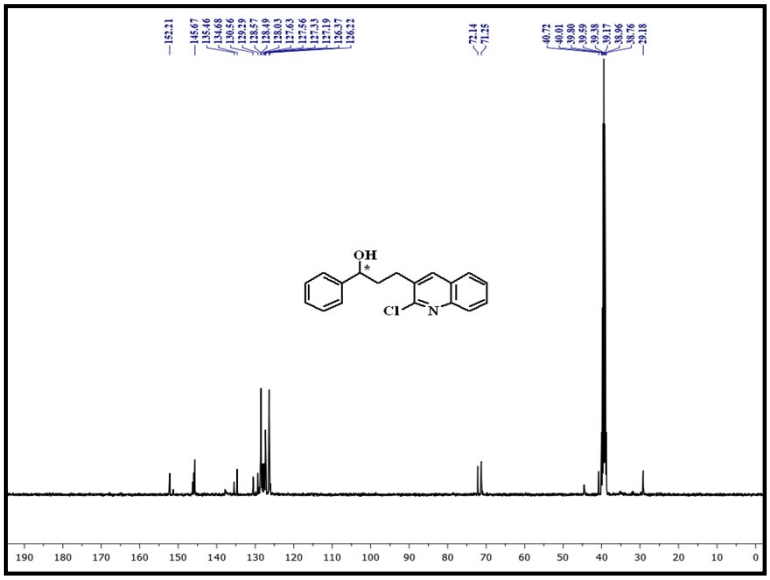


Fig. S32. ^{13}C NMR spectrum of **2A**

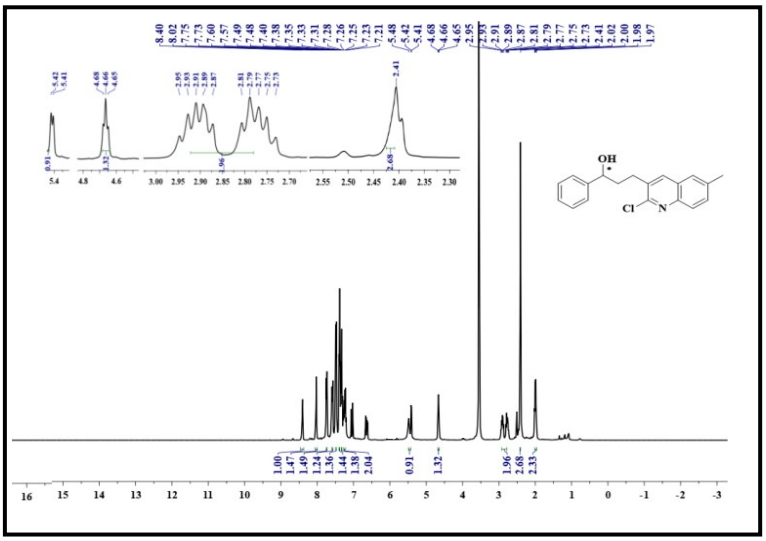


Fig. S33. ^{1}H NMR spectrum of **2B**

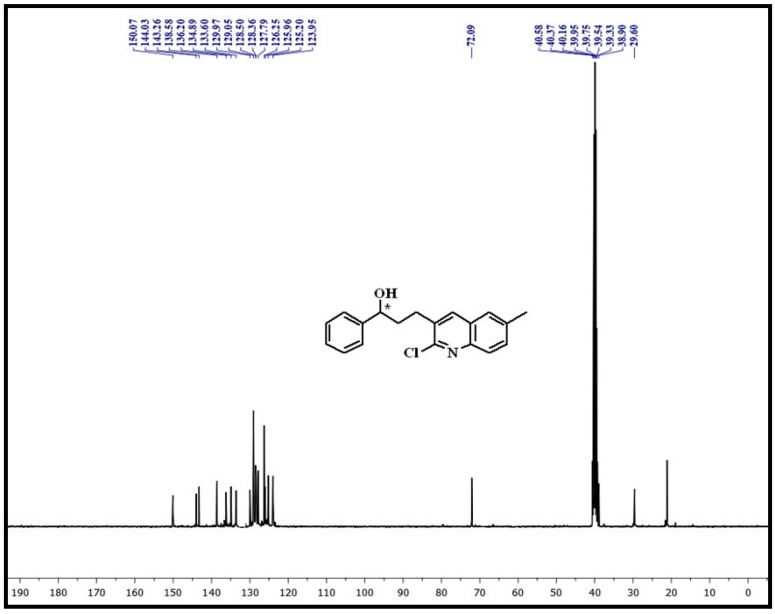


Fig. S34. ^{13}C NMR spectrum of **2B**

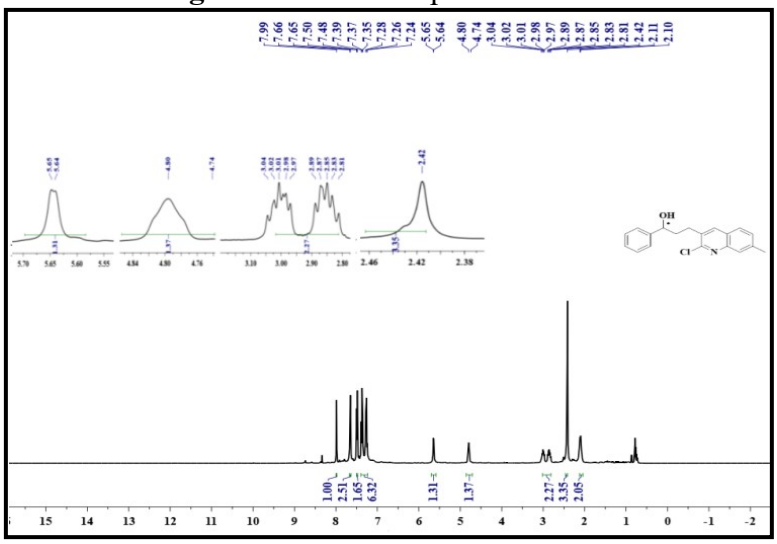


Fig. S35. ^{1}H NMR spectrum of **2C**

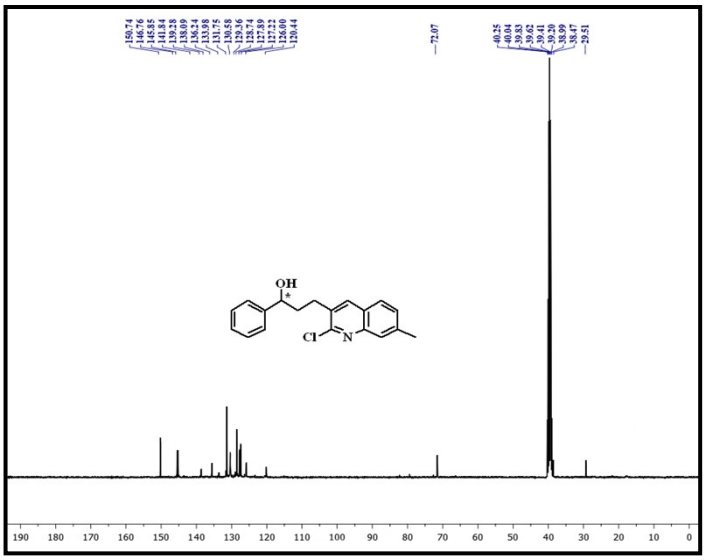


Fig. S36. ^{13}C NMR spectrum of **2C**

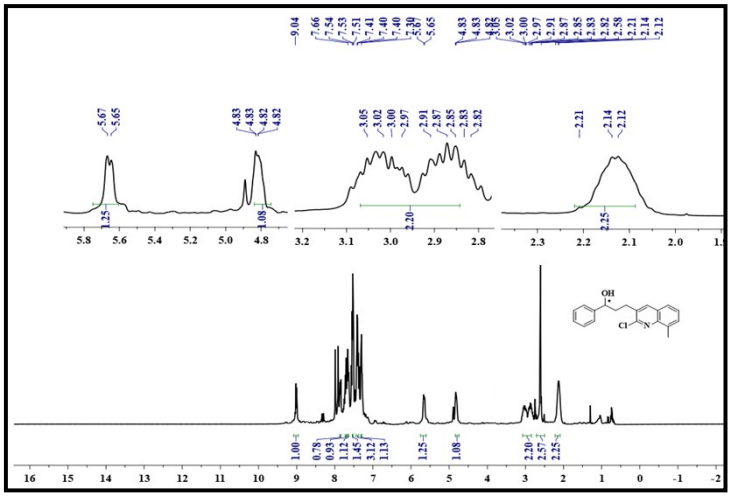


Fig. S37. ^{1}H NMR spectrum of **2D**

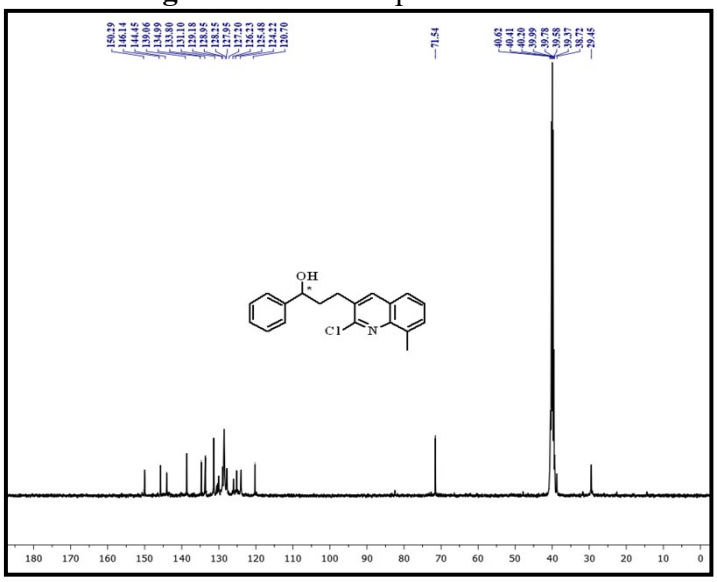


Fig. S38. ^{13}C NMR spectrum of **2D**

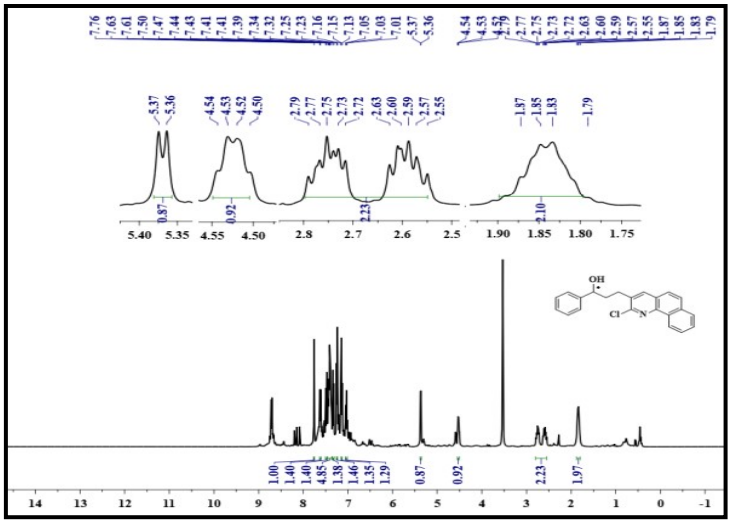


Fig. S39. ^{1}H NMR spectrum of **2E**

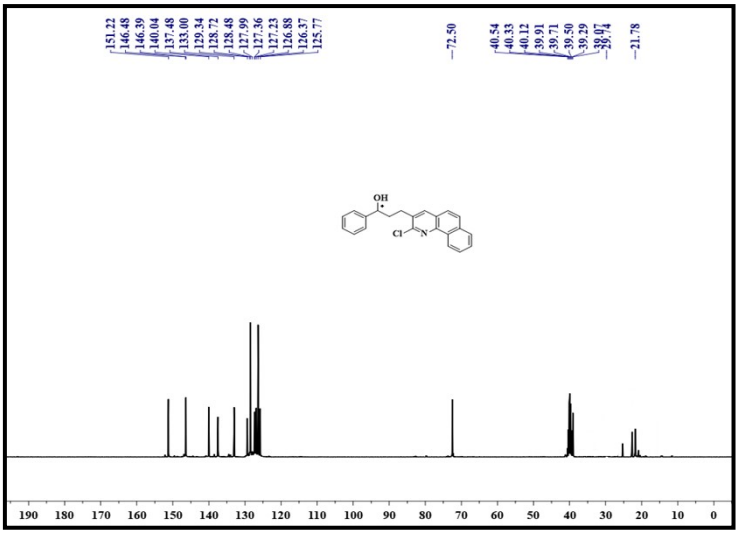


Fig. S40. ^{13}C NMR spectrum of **2E**

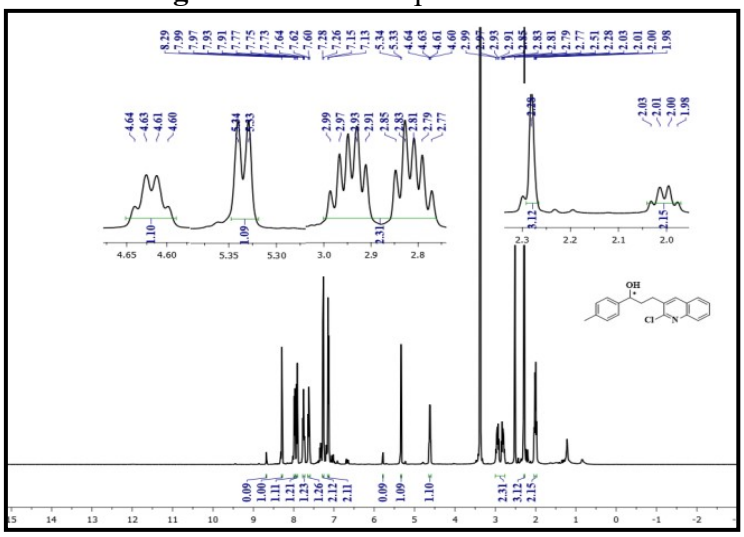


Fig. S41. ^{1}H NMR spectrum of **3A**

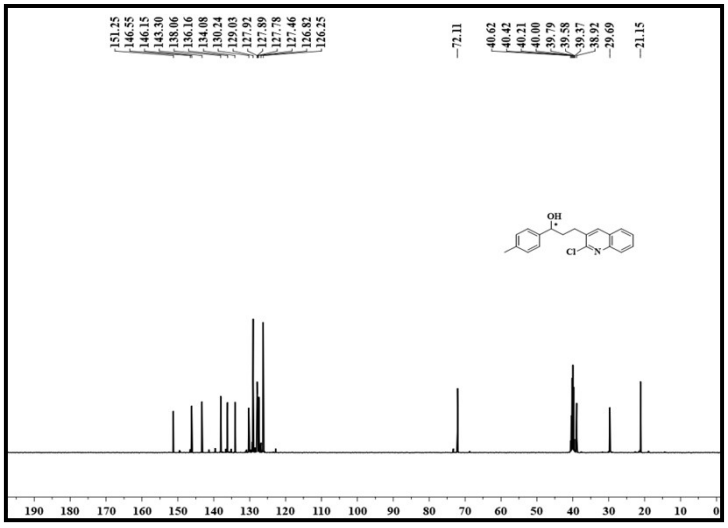


Fig. S42. ^{13}C NMR spectrum of **3A**

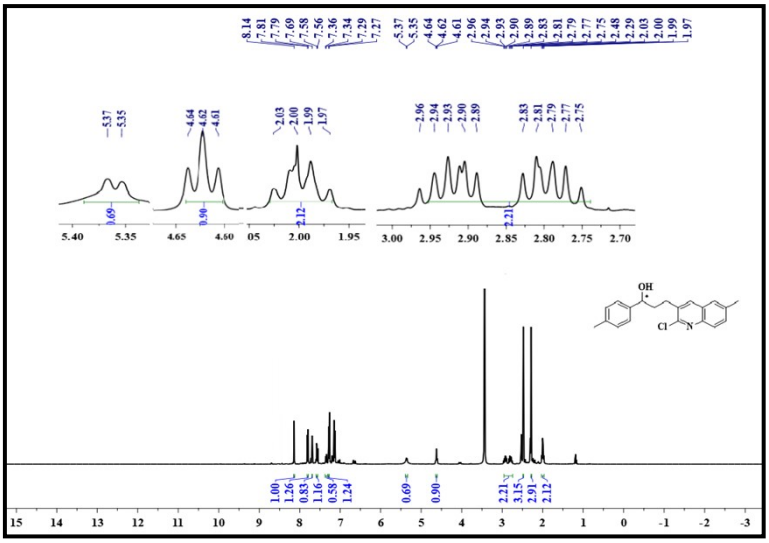


Fig. S43. ^{1}H NMR spectrum of **3B**

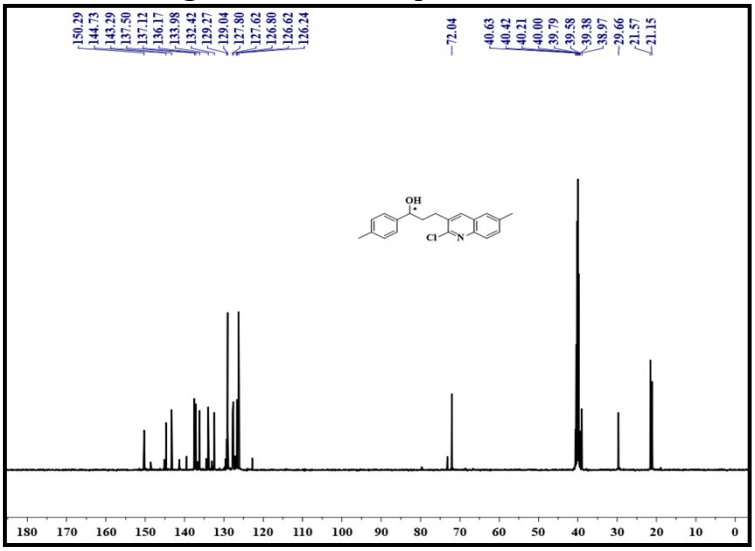


Fig. S44. ^{13}C NMR spectrum of **3B**

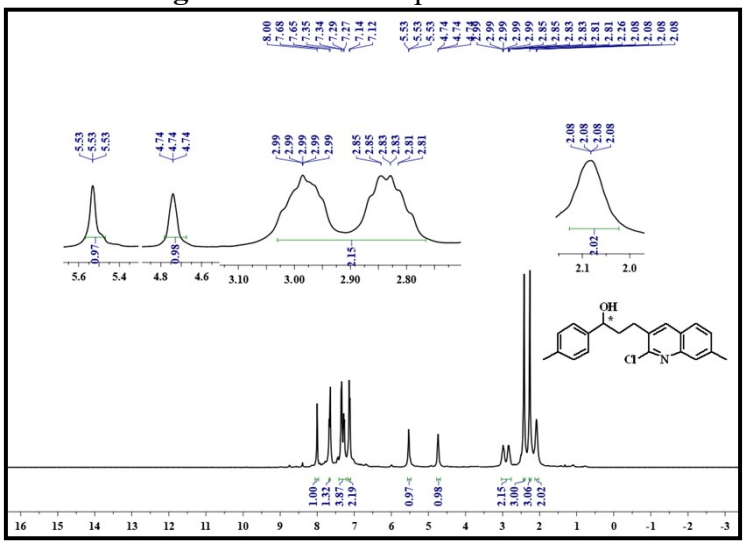


Fig. S45. ^{1}H NMR spectrum of **3C**

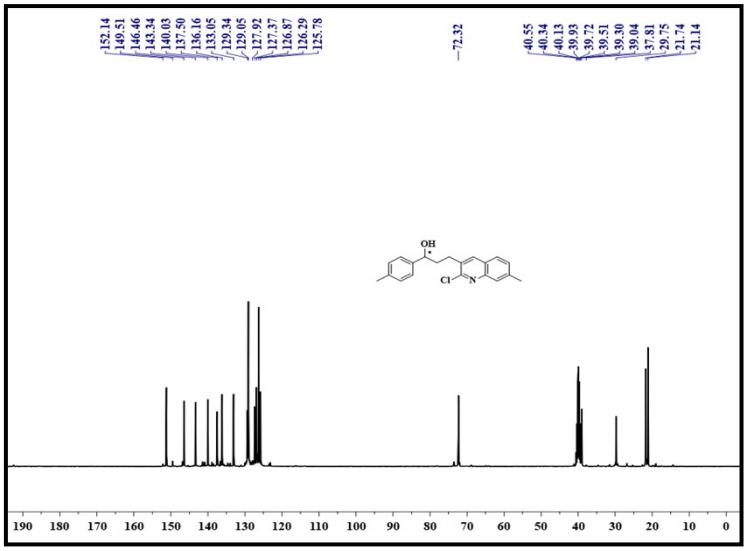


Fig. S46. ^{13}C NMR spectrum of **3C**

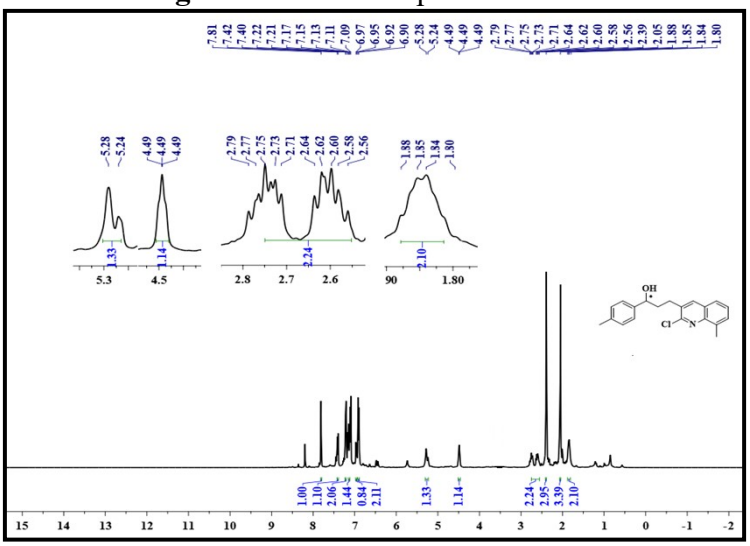


Fig. S47. ^{1}H NMR spectrum of **3D**

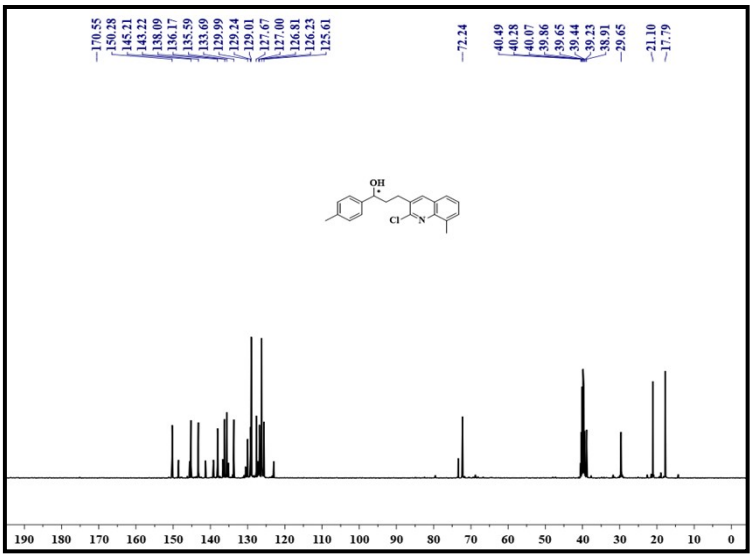


Fig. S48. ^{13}C NMR spectrum of **3D**

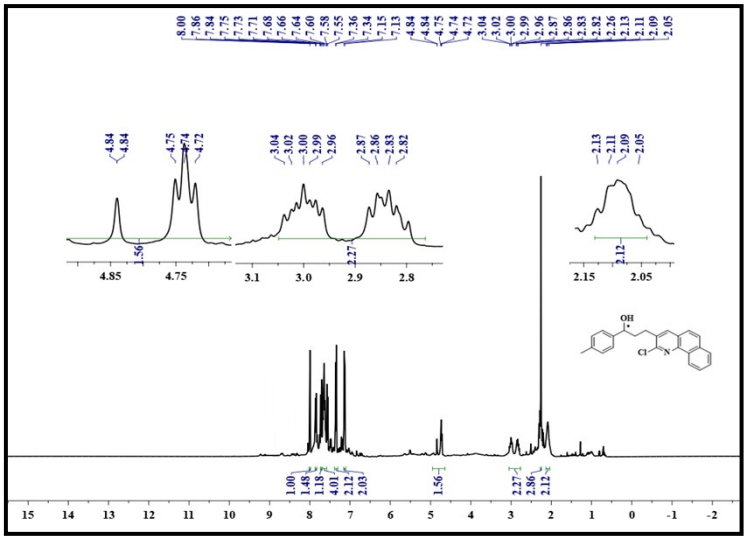


Fig. S49. ^{1}H NMR spectrum of **3E**

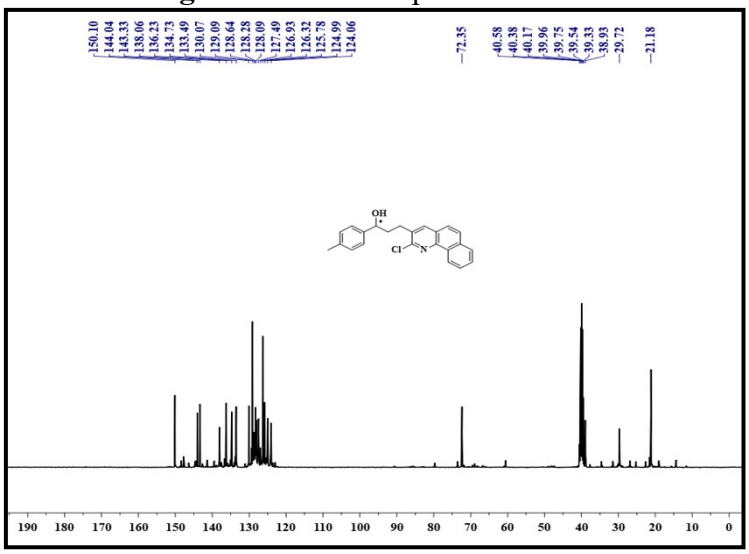


Fig. S50. ^{13}C NMR spectrum of **3E**

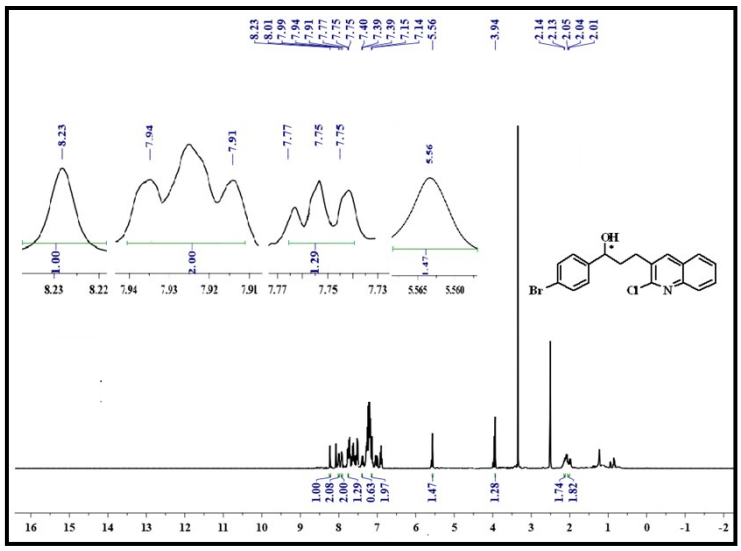


Fig. S51. ^{1}H NMR spectrum of **4A**

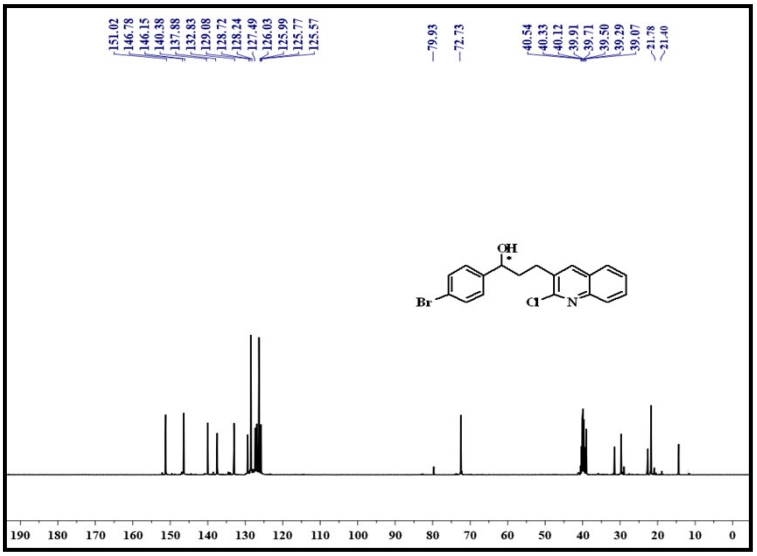


Fig. S52. ^{13}C NMR spectrum of **4A**

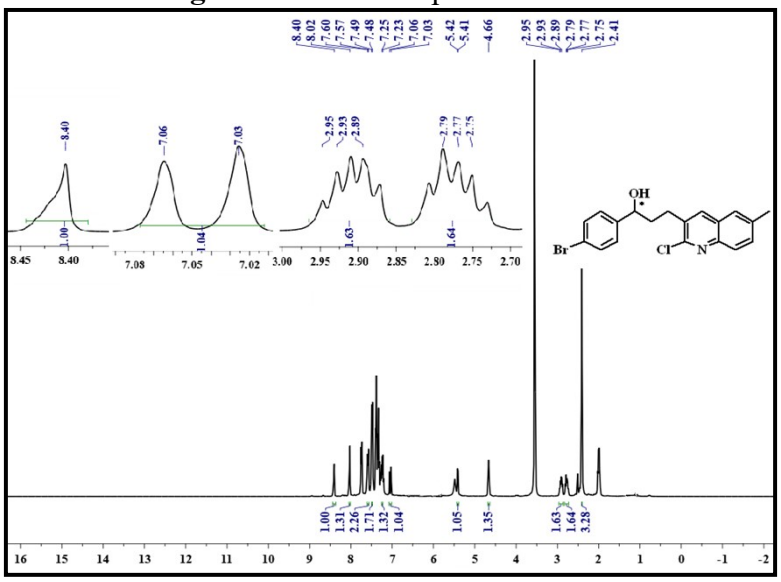


Fig. S53. ^{1}H NMR spectrum of **4B**

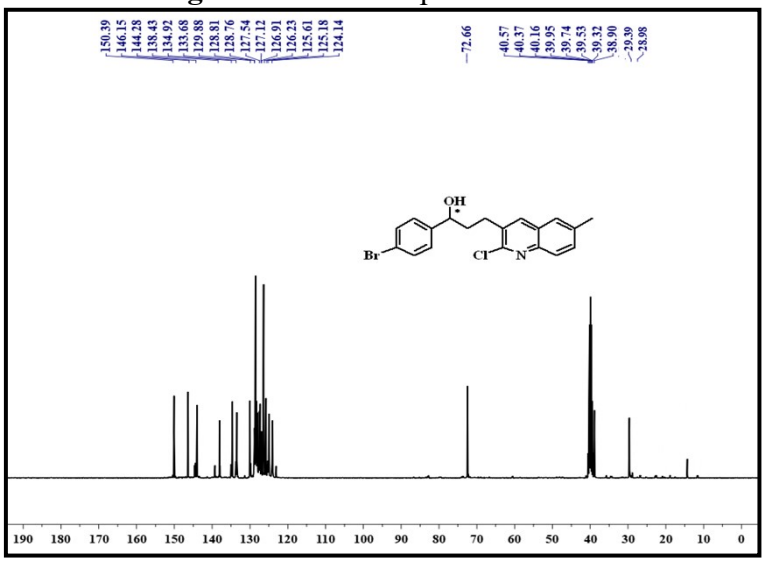


Fig. S54. ^{13}C NMR spectrum of **4B**

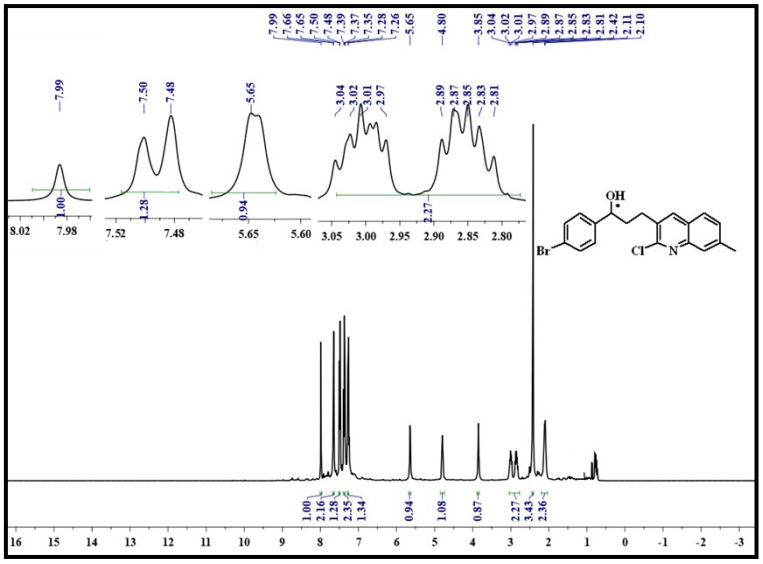


Fig. S55. ^{1}H NMR spectrum of **4C**

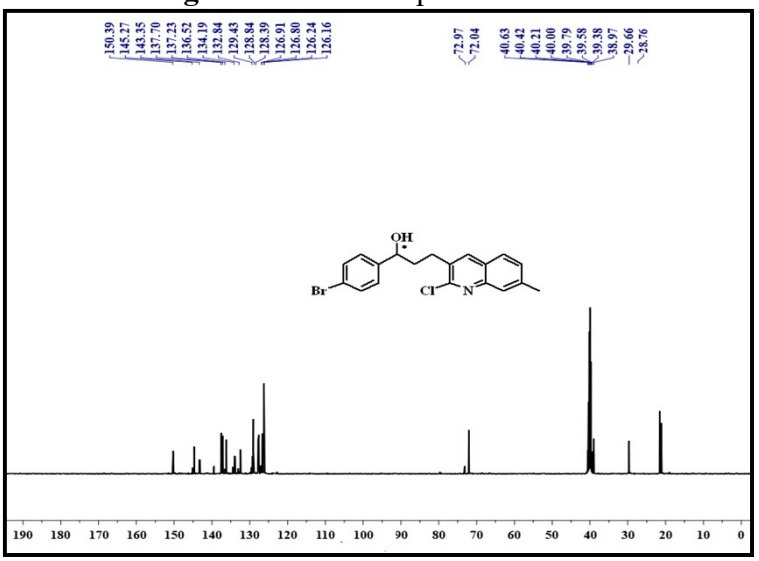


Fig. S56. ^{13}C NMR spectrum of **4C**

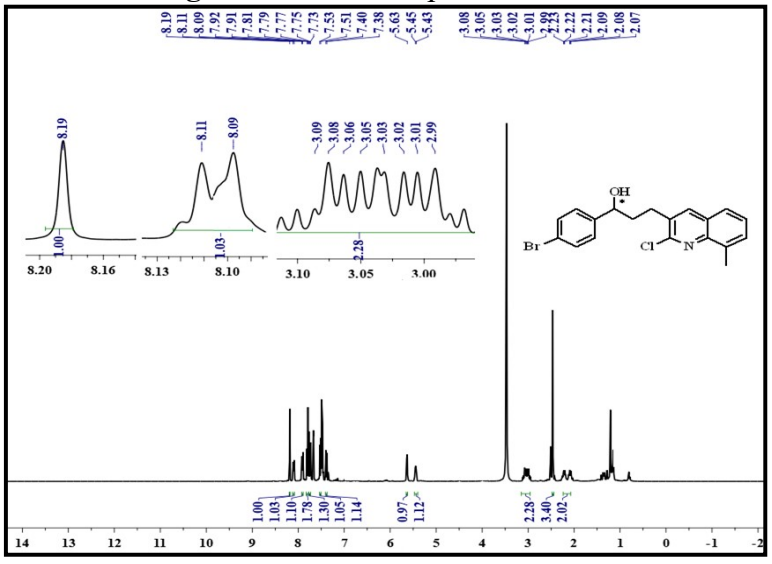


Fig. S57. ^{1}H NMR spectrum of **4D**

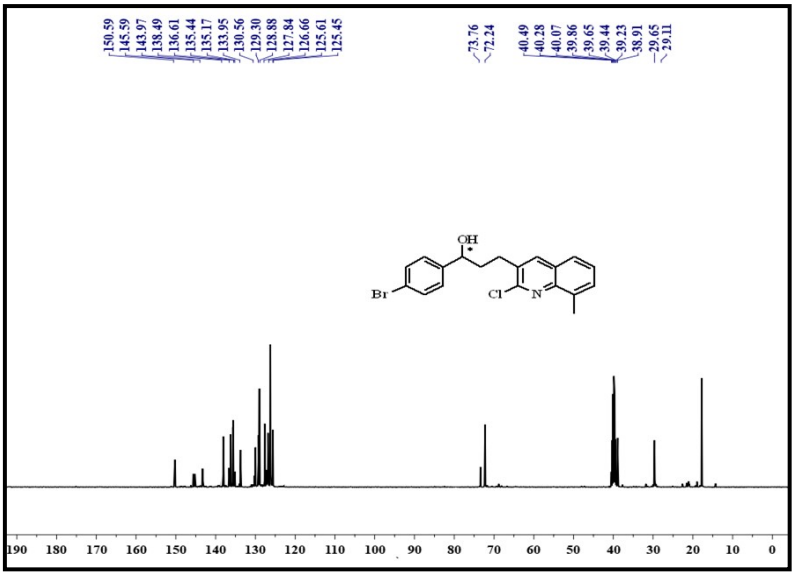


Fig. S58. ^{13}C NMR spectrum of **4D**

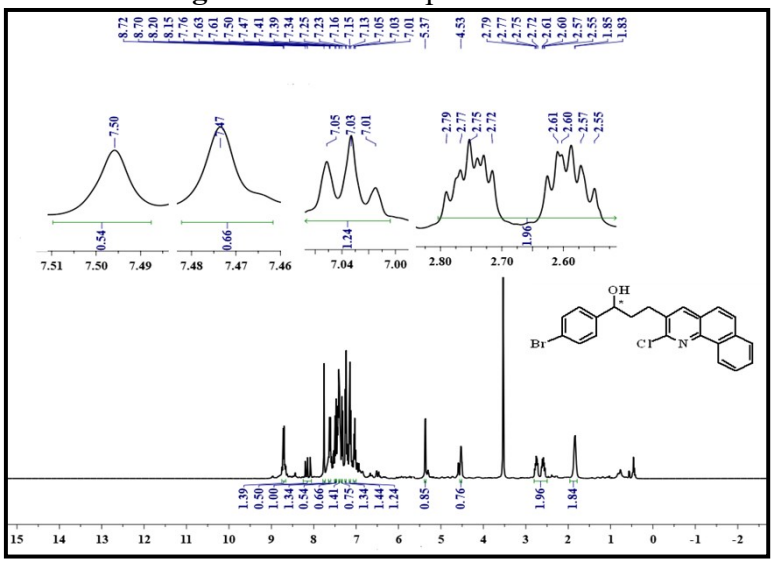


Fig. S59. ^{1}H NMR spectrum of **4E**

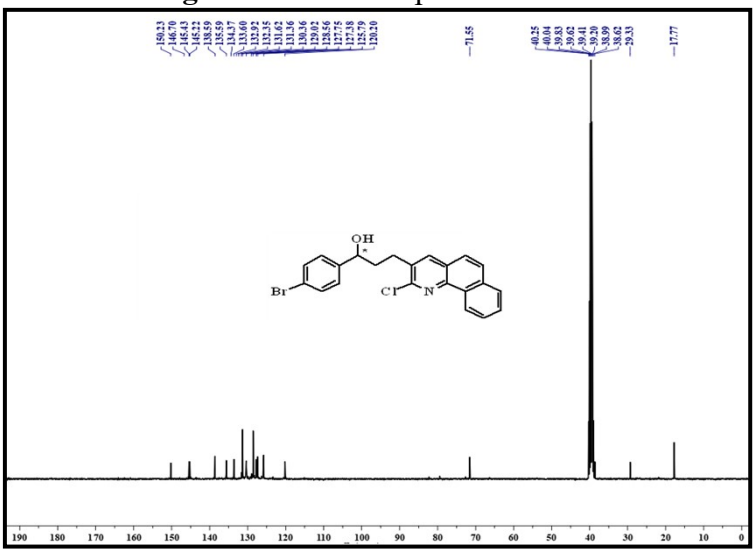


Fig. S60. ^{13}C NMR spectrum of **4E**

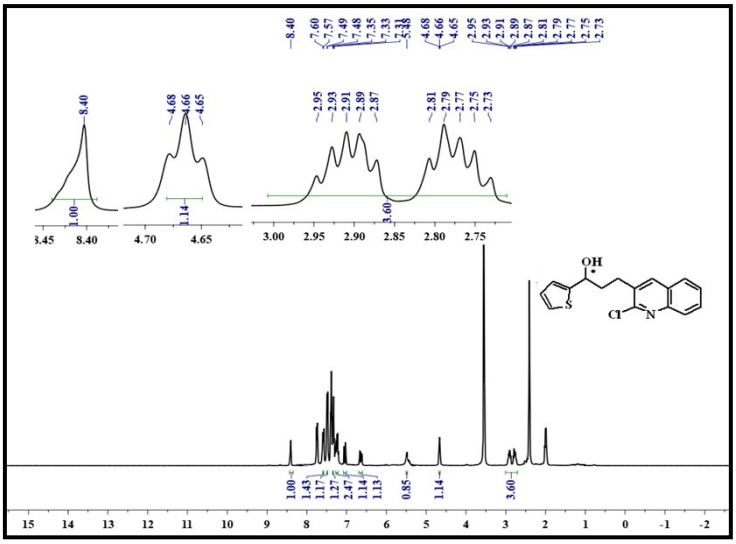


Fig. S61. ^{1}H NMR spectrum of **5A**

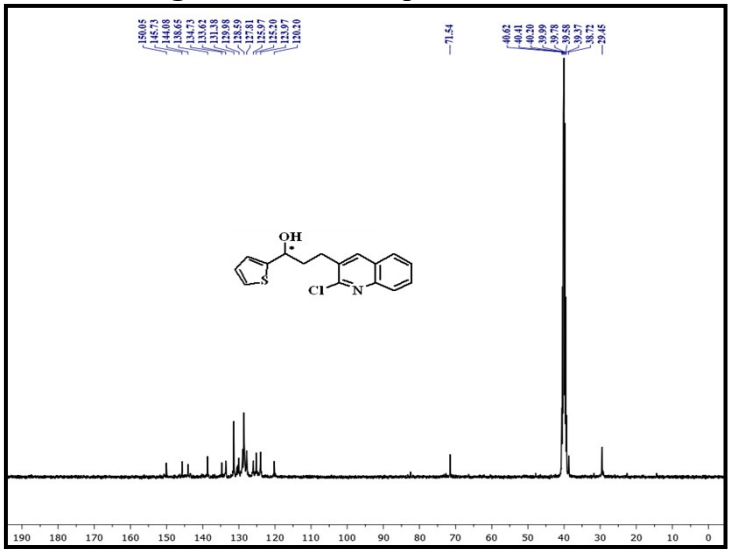


Fig. S62. ^{13}C NMR spectrum of **5A**

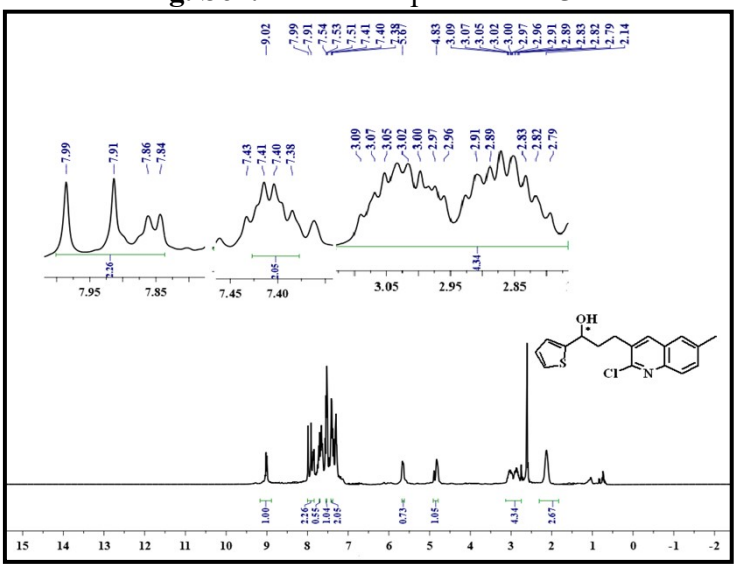


Fig. S63. ^{1}H NMR spectrum of **5B**

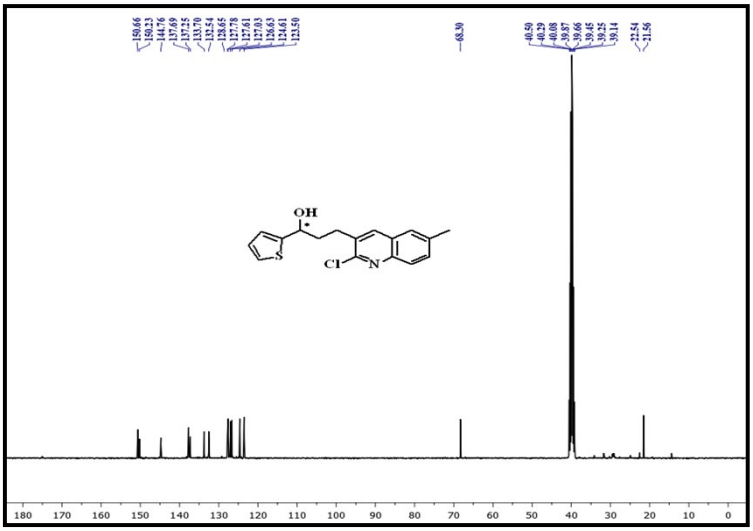


Fig. S64. ^{13}C NMR spectrum of **5B**

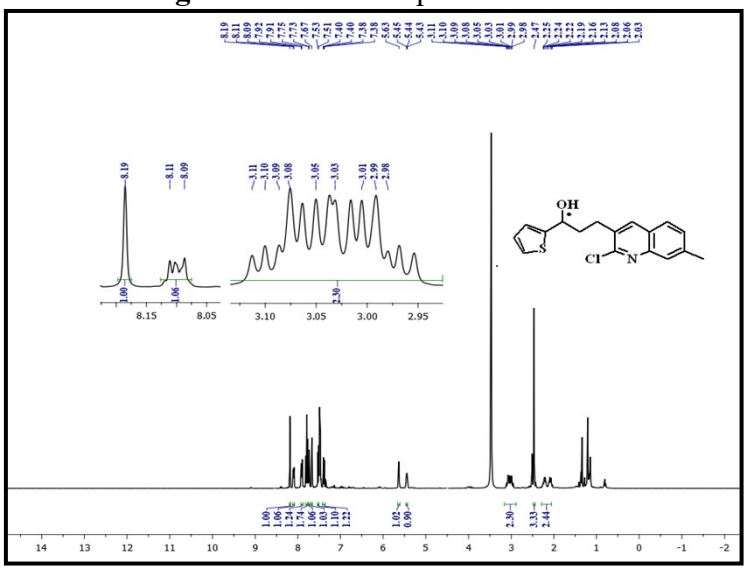


Fig. S65. ^{1}H NMR spectrum of **5C**

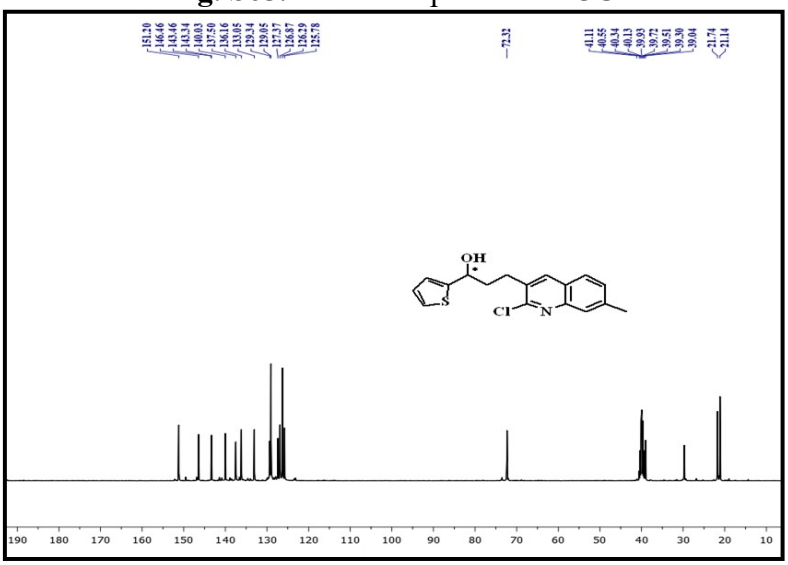


Fig. S66. ^{13}C NMR spectrum of **5C**

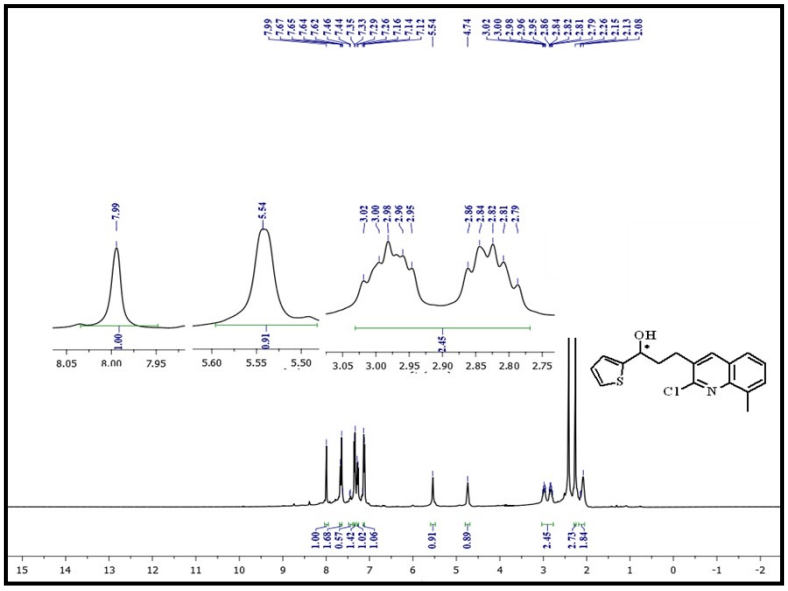


Fig. S67. ^{1}H NMR spectrum of **5D**

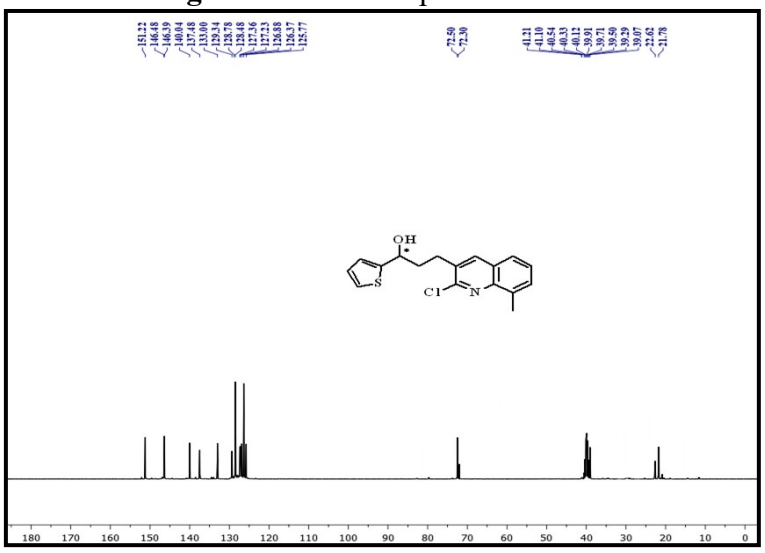


Fig. S68. ^{13}C NMR spectrum of **5D**

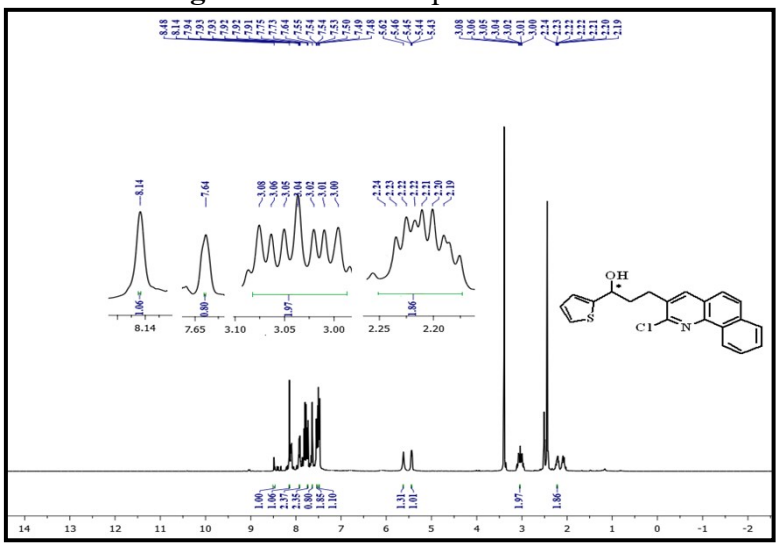


Fig. S69. ^{1}H NMR spectrum of **5E**

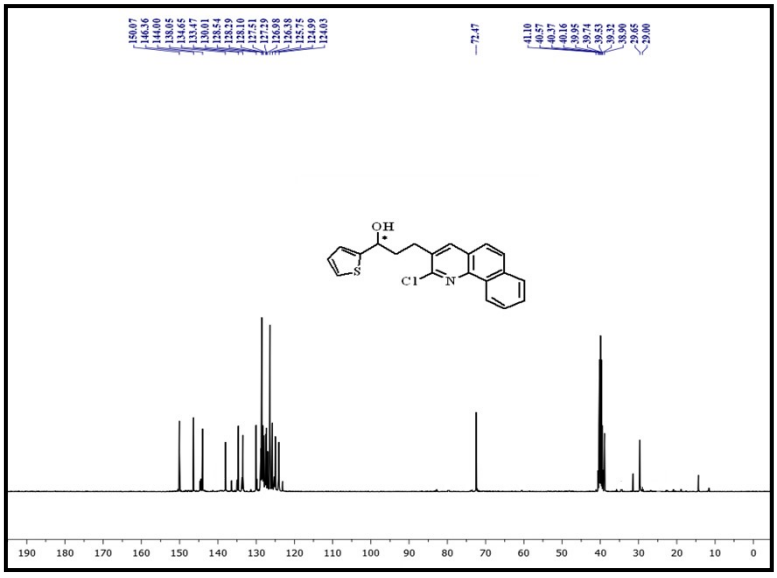
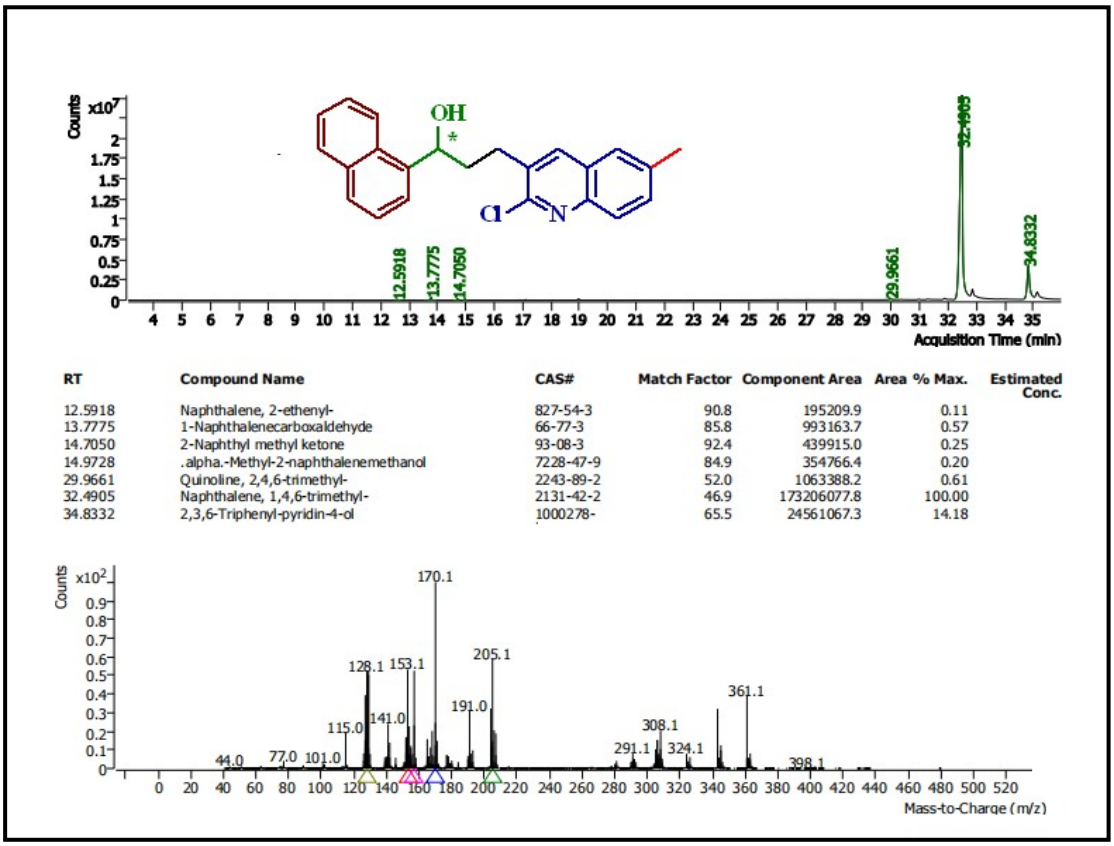
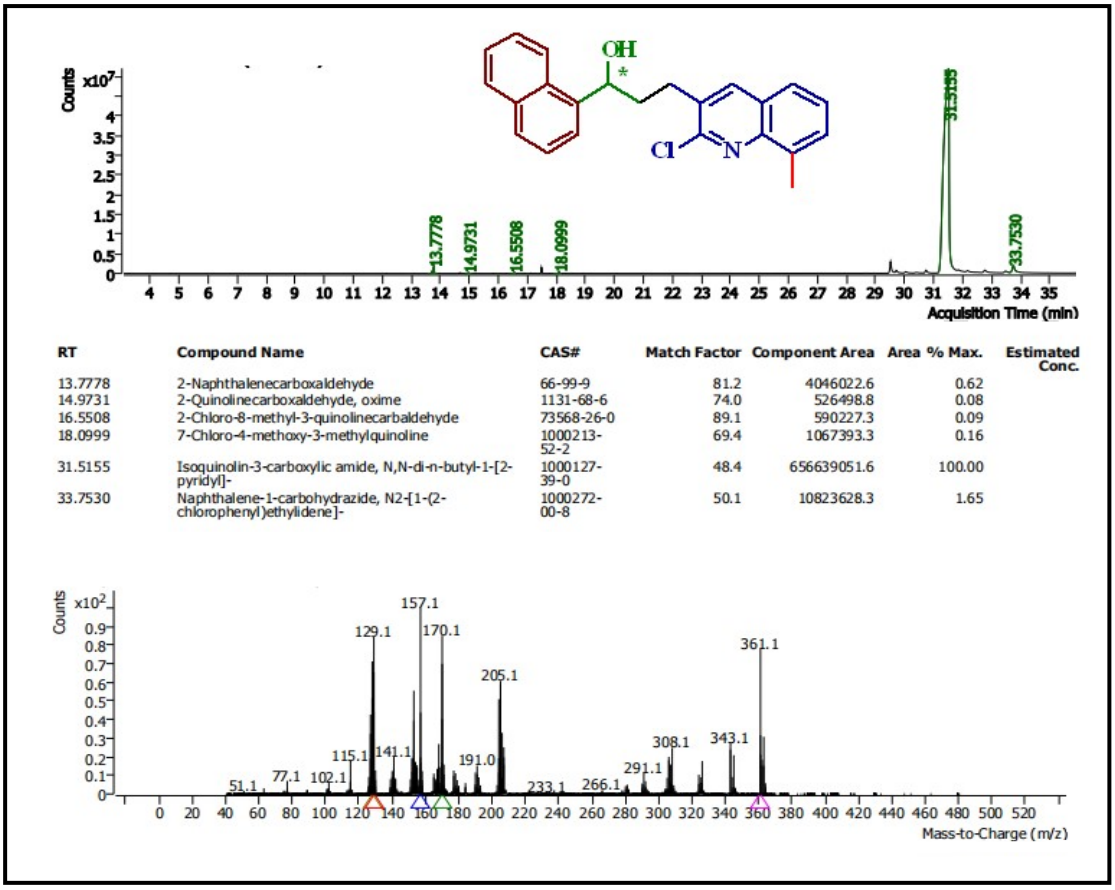


Fig. S70. ^{13}C NMR spectrum of **5E**



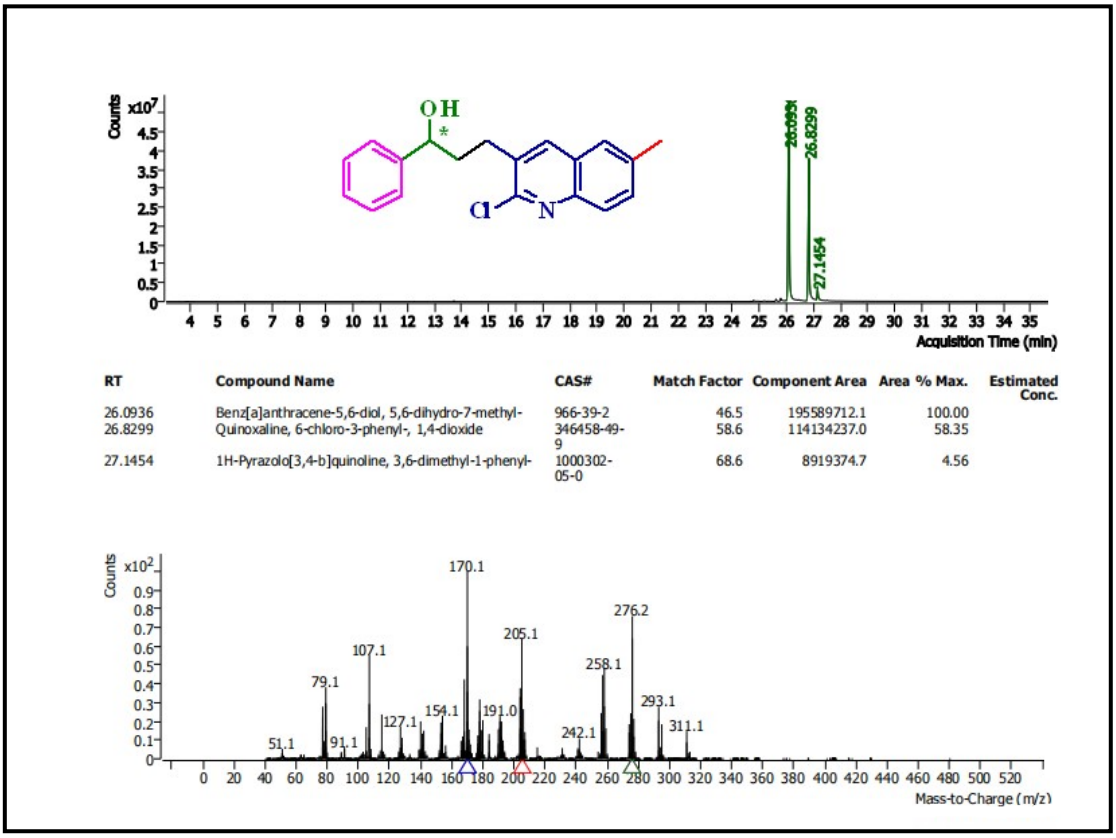
RT	Compound Name	CAS#	Match Factor	Component Area	Area % Max.	Estimated Conc.
12.5918	Naphthalene, 2-ethenyl-	827-54-3	90.8	195209.9	0.11	
13.7775	1-Naphthalenecarboxaldehyde	66-77-3	85.8	993163.7	0.57	
14.7050	2-Naphthyl methyl ketone	93-08-3	92.4	439915.0	0.25	
14.9728	.alpha.-Methyl-2-naphthalenemethanol	7228-47-9	84.9	354766.4	0.20	
29.9661	Quinoline, 2,4,6-trimethyl-	2243-89-2	52.0	1063388.2	0.61	
32.4905	Naphthalene, 1,4,6-trimethyl-	2131-42-2	46.9	173206077.8	100.00	
34.8332	2,3,6-Triphenyl-pyridin-4-ol	1000278-	65.5	24561067.3	14.18	

Fig. S71. GCMS of **1B**



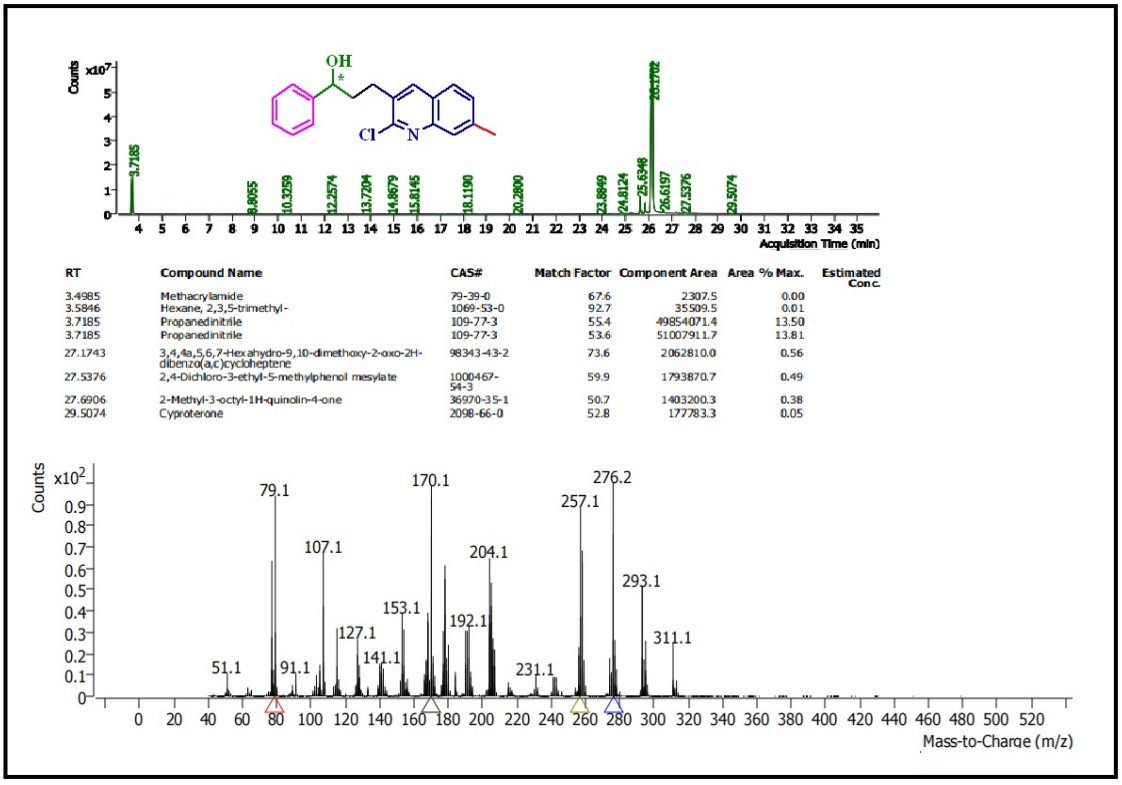
RT	Compound Name	CAS#	Match Factor	Component Area	Area % Max.	Estimated Conc.
13.7778	2-Naphthalenecarboxaldehyde	66-99-9	81.2	4046022.6	0.62	
14.9731	2-Quinolinecarboxaldehyde, oxime	1131-68-6	74.0	526498.8	0.08	
16.5508	2-Chloro-8-methyl-3-quinolinecarbaldehyde	73568-26-0	89.1	590227.3	0.09	
18.0999	7-Chloro-4-methoxy-3-methylquinoline	1000213-52-2	69.4	1067393.3	0.16	
31.5155	Isoquinolin-3-carboxylic amide, N,N-di-n-butyl-1-[2-pyridyl]-	1000127-39-0	48.4	656639051.6	100.00	
33.7530	Naphthalene-1-carbohydrazide, N2-[1-(2-chlorophenyl)ethylidene]-	1000272-00-8	50.1	10823628.3	1.65	

Fig. S72. GCMS of **1D**



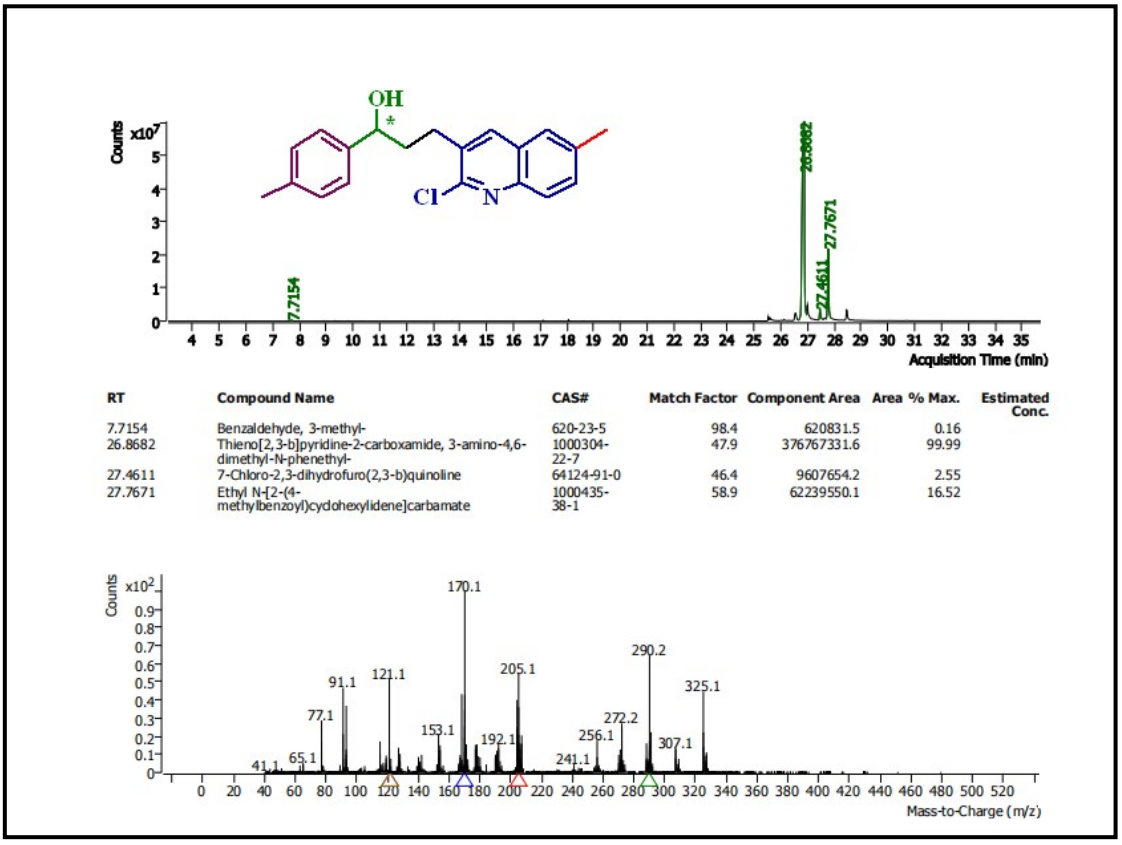
RT	Compound Name	CAS#	Match Factor	Component Area	Area % Max.	Estimated Conc.
26.0936	Benz[a]anthracene-5,6-diol, 5,6-dihydro-7-methyl-	966-39-2	46.5	195589712.1	100.00	
26.8299	Quinoxaline, 6-chloro-3-phenyl-, 1,4-dioxide	346458-49-9	58.6	114134237.0	58.35	
27.1454	1H-Pyrazolo[3,4-b]quinoline, 3,6-dimethyl-1-phenyl-	1000302-05-0	68.6	8919374.7	4.56	

Fig. S73. GCMS of **2B**



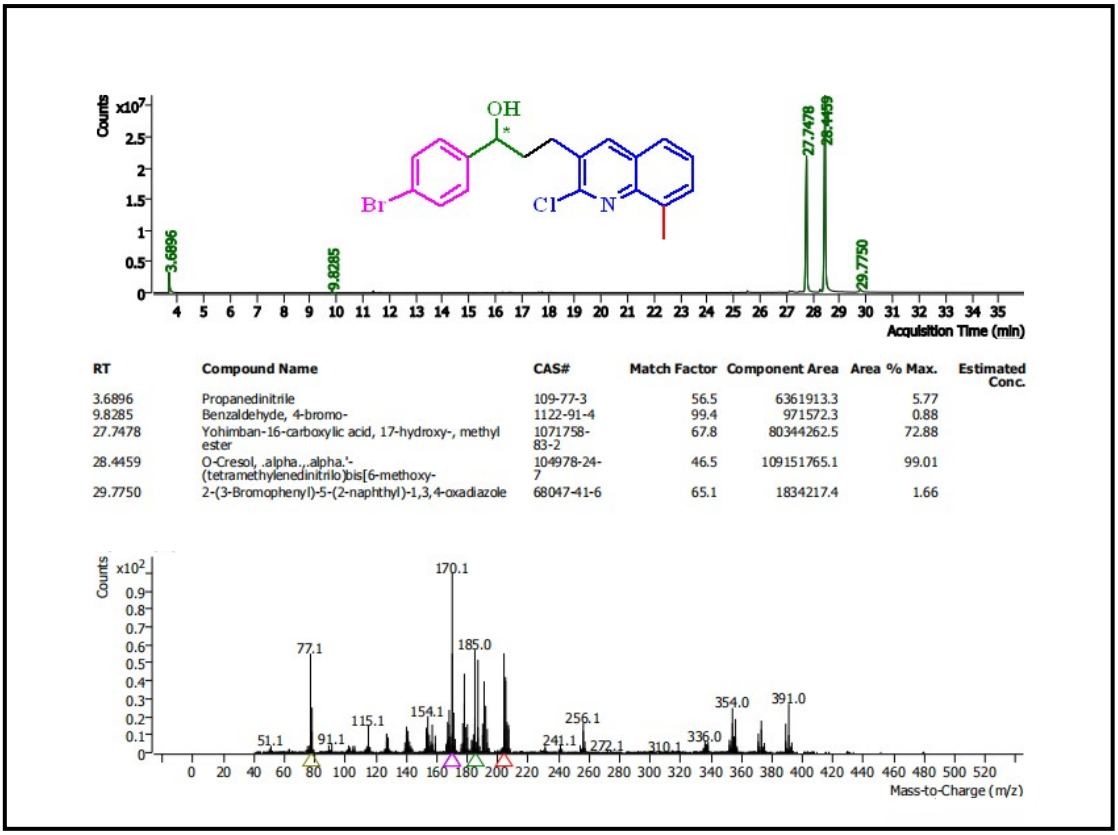
RT	Compound Name	CAS#	Match Factor	Component Area	Area % Max.	Estimated Conc.
3.4985	Methacrylamide	79-39-0	67.6	2307.5	0.00	
3.5846	Hexane, 2,3,5-trimethyl-	1069-53-0	92.7	35509.5	0.01	
3.7185	Propanedinitrile	109-77-3	55.4	49854071.4	13.50	
3.7185	Propanedinitrile	109-77-3	53.6	51007911.7	13.81	
27.1743	3,4,4a,5,6,7-Hexahydro-9,10-dimethoxy-2-oxo-2H-dibenzo(a,c)cycloheptene	98343-43-2	73.6	2062810.0	0.56	
27.5376	2,4-Dichloro-3-ethyl-5-methylphenol mesylate	1000467-54-3	59.9	1793870.7	0.49	
27.6906	2-Methyl-3-octyl-1H-quinolin-4-one	36970-35-1	50.7	1403200.3	0.38	
29.5074	Cyproterone	2098-66-0	52.8	177783.3	0.05	

Fig. S74. GCMS of **2C**



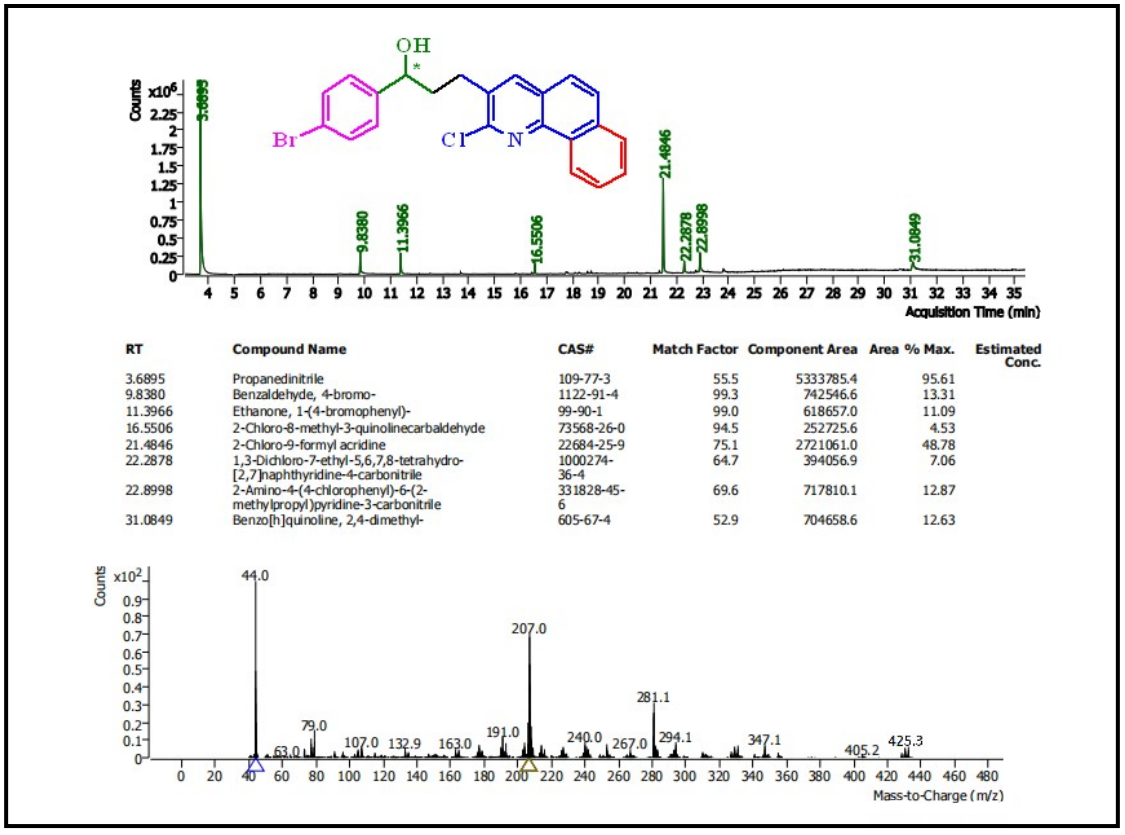
RT	Compound Name	CAS#	Match Factor	Component Area	Area % Max.	Estimated Conc.
7.7154	Benzaldehyde, 3-methyl-	620-23-5	98.4	620831.5	0.16	
26.8682	Thieno[2,3-b]pyridine-2-carboxamide, 3-amino-4,6-dimethyl-N-phenethyl-	1000304-22-7	47.9	376767331.6	99.99	
27.4611	7-Chloro-2,3-dihydrofuro(2,3-b)quinoline	64124-91-0	46.4	9607654.2	2.55	
27.7671	Ethyl N-[2-(4-methylbenzoyl)cyclohexylidene]carbamate	1000435-38-1	58.9	62239550.1	16.52	

Fig. S75. GCMS of **3B**



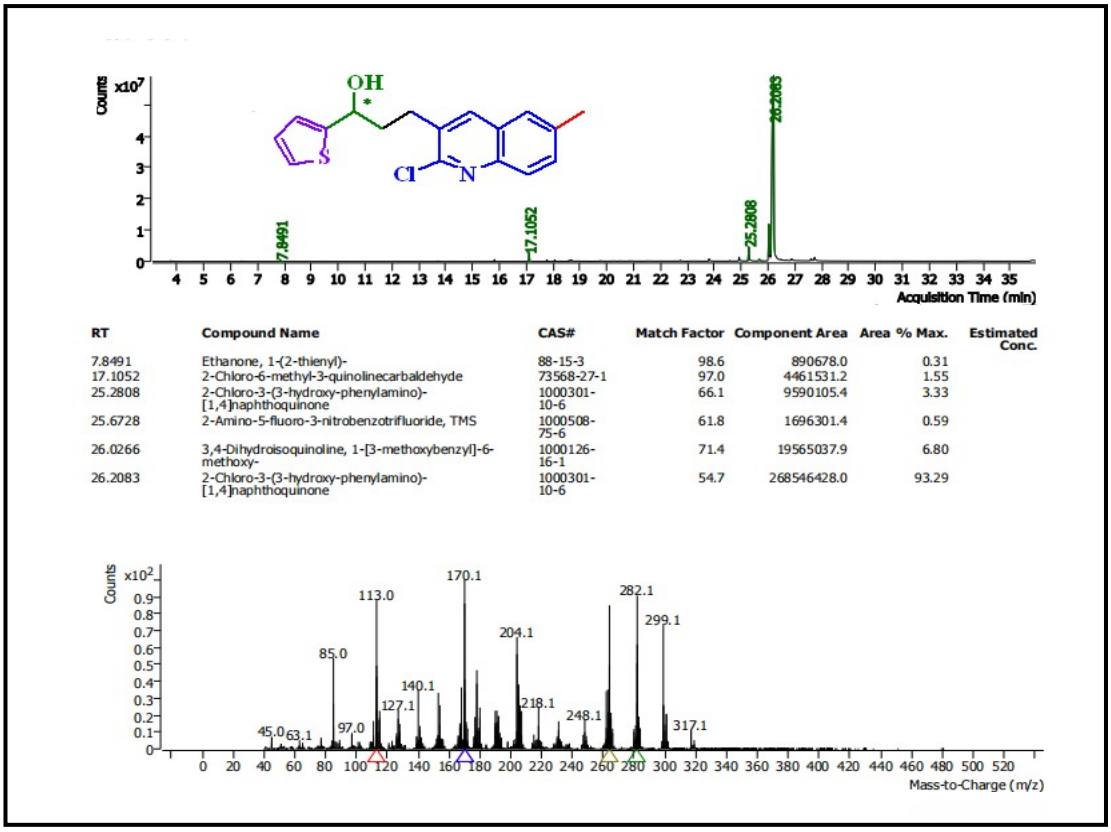
RT	Compound Name	CAS#	Match Factor	Component Area	Area % Max.	Estimated Conc.
3.6896	Propanedinitrile	109-77-3	56.5	6361913.3	5.77	
9.8285	Benzaldehyde, 4-bromo-	1122-91-4	99.4	971572.3	0.88	
27.7478	Yohimban-16-carboxylic acid, 17-hydroxy-, methyl ester	1071758-83-2	67.8	80344262.5	72.88	
28.4459	O-Cresol, .alpha.,.alpha.'-(tetramethylenedinitrilo)bis[6-methoxy-	104978-24-7	46.5	109151765.1	99.01	
29.7750	2-(3-Bromophenyl)-5-(2-naphthyl)-1,3,4-oxadiazole	68047-41-6	65.1	1834217.4	1.66	

Fig. S76. GCMS of **4D**



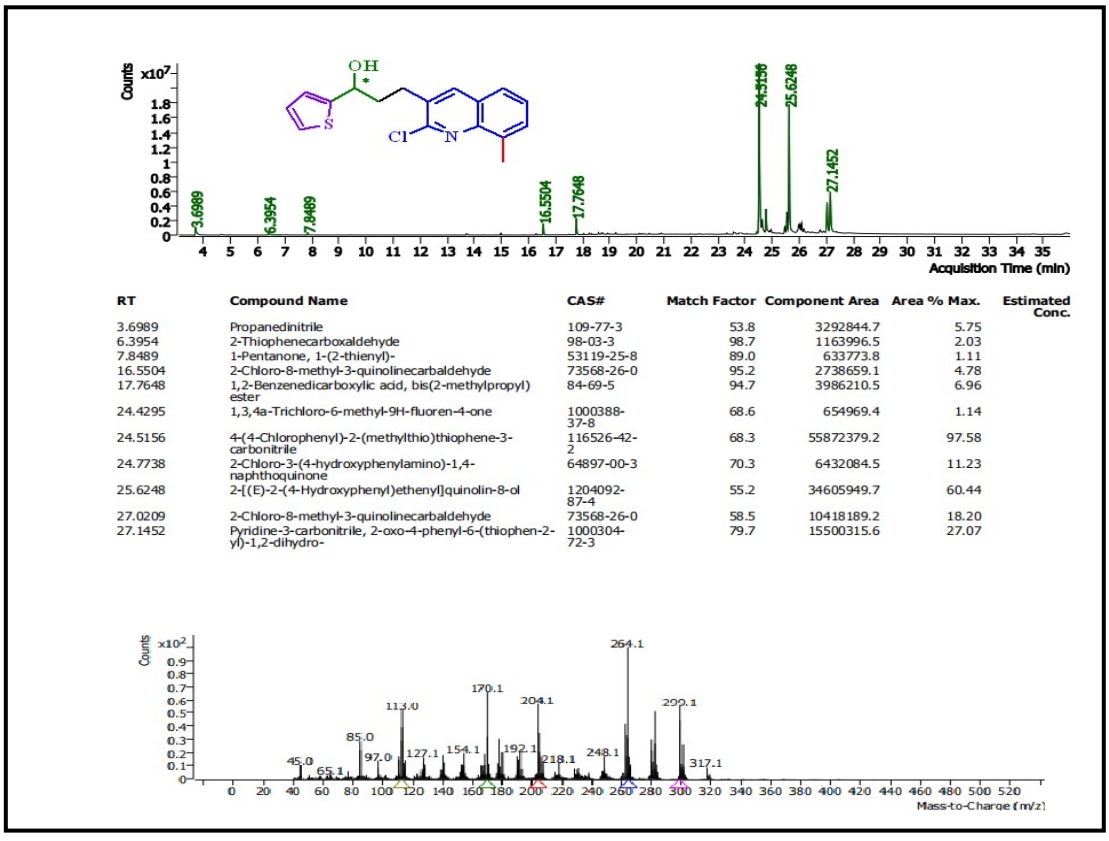
RT	Compound Name	CAS#	Match Factor	Component Area	Area % Max.	Estimated Conc.
3.6895	Propanedinitrile	109-77-3	55.5	5333785.4	95.61	
9.8380	Benzaldehyde, 4-bromo-	1122-91-4	99.3	742546.6	13.31	
11.3966	Ethanone, 1-(4-bromophenyl)-	99-90-1	99.0	618657.0	11.09	
16.5506	2-Chloro-8-methyl-3-quinolinecarbaldehyde	73568-26-0	94.5	252725.6	4.53	
21.4846	2-Chloro-9-formyl acridine	22684-25-9	75.1	2721061.0	48.78	
22.2878	1,3-Dichloro-7-ethyl-5,6,7,8-tetrahydro-[2,7]naphthyridine-4-carbonitrile	1000274-36-4	64.7	394056.9	7.06	
22.8998	2-Amino-4-(4-chlorophenyl)-6-(2-methylpropyl)pyridine-3-carbonitrile	331828-45-6	69.6	717810.1	12.87	
31.0849	Benzo[h]quinoline, 2,4-dimethyl-	605-67-4	52.9	704658.6	12.63	

Fig. S77. GCMS of **4E**



RT	Compound Name	CAS#	Match Factor	Component Area	Area % Max.	Estimated Conc.
7.8491	Ethanone, 1-(2-thienyl)-	88-15-3	98.6	890678.0	0.31	
17.1052	2-Chloro-6-methyl-3-quinolinecarbaldehyde	73568-27-1	97.0	4461531.2	1.55	
25.2808	2-Chloro-3-(3-hydroxy-phenylamino)-[1,4]naphthoquinone	1000301-10-6	66.1	9590105.4	3.33	
25.6728	2-Amino-5-fluoro-3-nitrobenzotrifluoride, TMS	1000508-75-6	61.8	1696301.4	0.59	
26.0266	3,4-Dihydroisoquinoline, 1-[3-methoxybenzyl]-6-methoxy-	1000126-16-1	71.4	19565037.9	6.80	
26.2083	2-Chloro-3-(3-hydroxy-phenylamino)-[1,4]naphthoquinone	1000301-10-6	54.7	268546428.0	93.29	

Fig. S78. GCMS of **5B**



RT	Compound Name	CAS#	Match Factor	Component Area	Area % Max.	Estimated Conc.
3.6989	Propanedinitrile	109-77-3	53.8	3292844.7	5.75	
6.3954	2-Thiophenecarboxaldehyde	98-03-3	98.7	1163996.5	2.03	
7.8489	1-Pentanone, 1-(2-thienyl)-	53119-25-8	89.0	633773.8	1.11	
16.5504	2-Chloro-8-methyl-3-quinolinecarbaldehyde	73568-26-0	95.2	2738659.1	4.78	
17.7648	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester	84-69-5	94.7	3986210.5	6.96	
24.4295	1,3,4a-Trichloro-6-methyl-9H-fluoren-4-one	1000388-37-8	68.6	654969.4	1.14	
24.5156	4-(4-Chlorophenyl)-2-(methylthio)thiophene-3-carbonitrile	116526-42-2	68.3	55872379.2	97.58	
24.7738	2-Chloro-3-(4-hydroxyphenylamino)-1,4-naphthoquinone	64897-00-3	70.3	6432084.5	11.23	
25.6248	2-[(E)-2-(4-Hydroxyphenyl)ethenyl]quinolin-8-ol	1204092-87-4	55.2	34605949.7	60.44	
27.0209	2-Chloro-8-methyl-3-quinolinecarbaldehyde	73568-26-0	58.5	10418189.2	18.20	
27.1452	Pyridine-3-carbonitrile, 2-oxo-4-phenyl-6-(thiophen-2-yl)-1,2-dihydro-	1000304-72-3	79.7	15500315.6	27.07	

Fig. S79. GCMS of **5D**

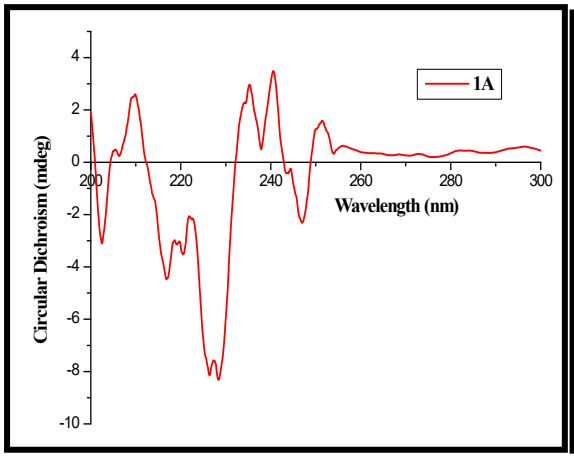


Fig. S80. CD spectrum of 1A

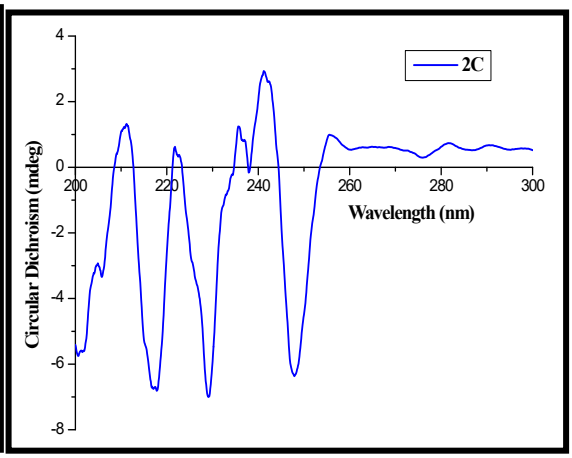


Fig. S81. CD spectrum of 2C

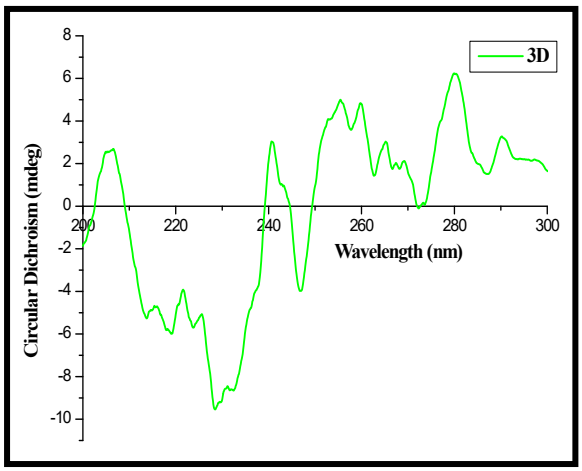


Fig. S82. CD spectrum of 3D

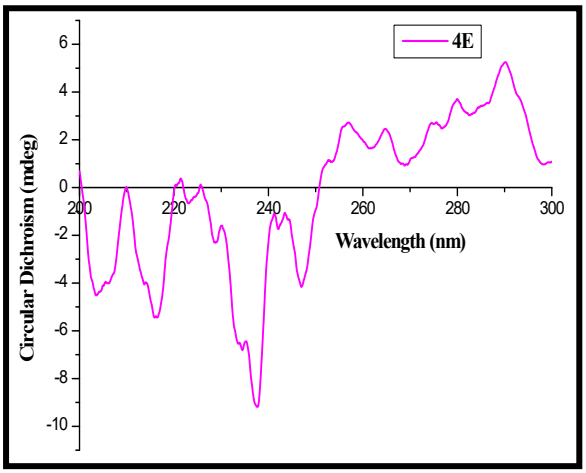


Fig. S83. CD spectrum of 4E

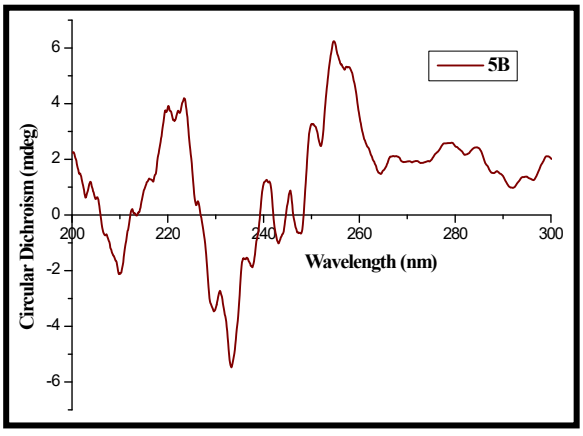


Fig. S84. CD spectrum of 5B

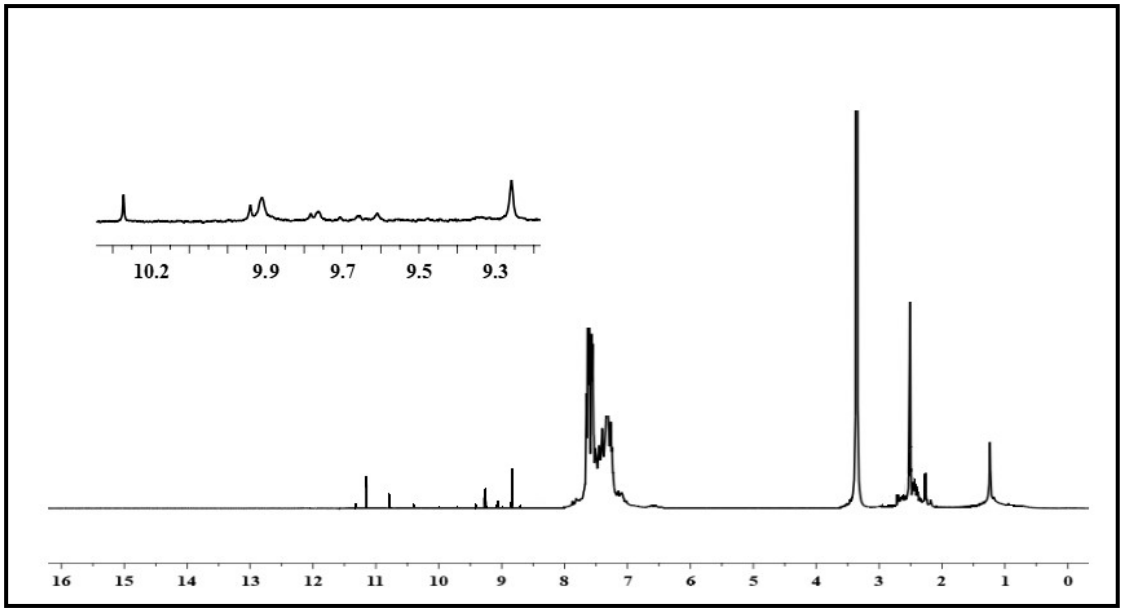


Fig. 85.^{1}H NMR spectrum of the catalyst regenerated after 1st cycle (**C1**)

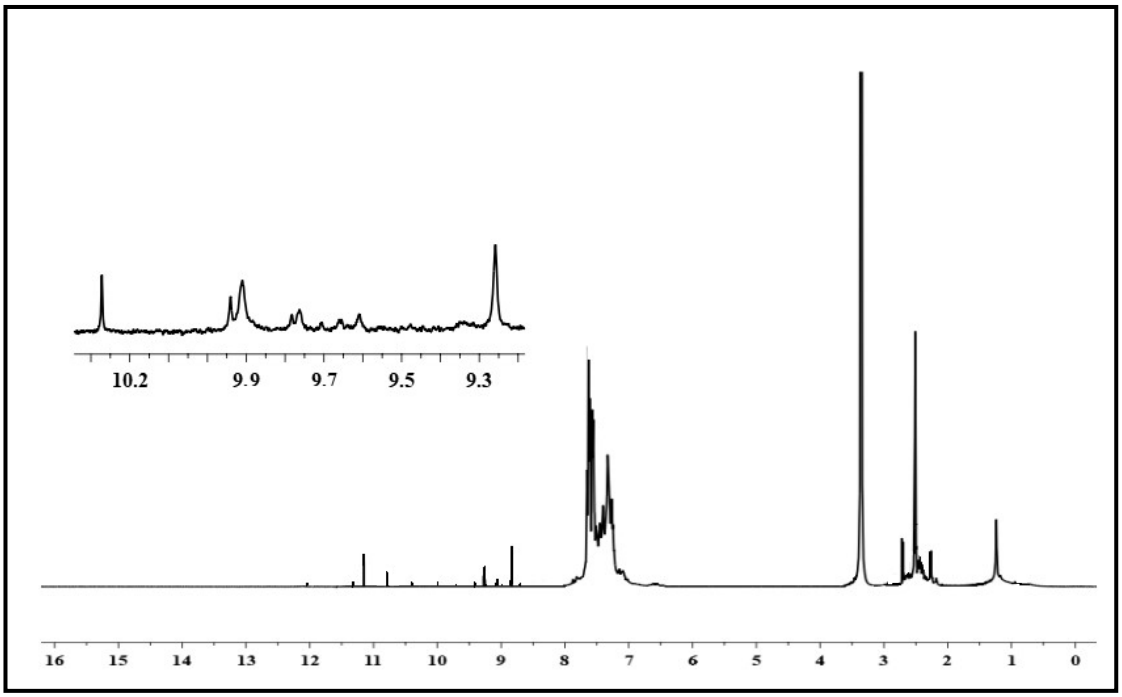


Fig. 86.^{1}H NMR spectrum of the catalyst regenerated after 4th cycle (**C4**)

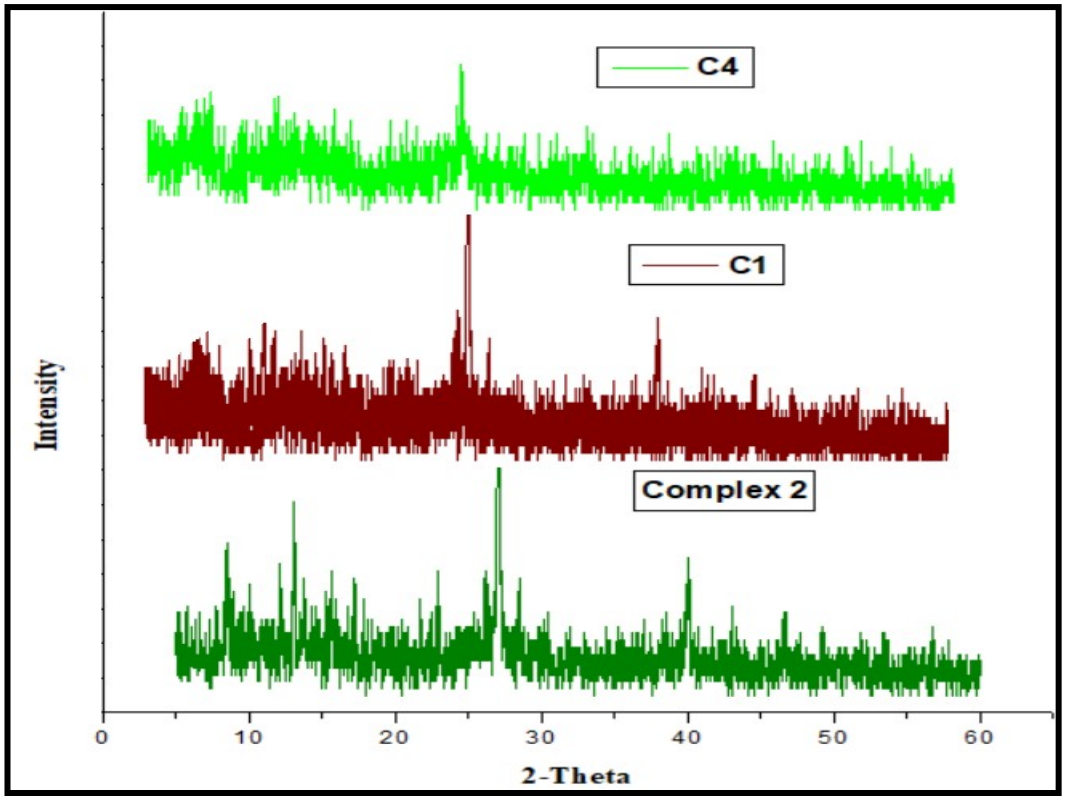


Fig. S87. PXRD patterns of the catalysts before usage in catalytic reaction (**Complex 2**) and regenerated after1st (**C1**) and 4th (**C4**) cycles

References

1. Vogel, Text Book of Practical Organic Chemistry, 1989, **5**, 268.
2. W.S. Hamama, M.E. Ibrahim, A.A. Gooda and H.H. Zoorob, *RSC Adv.*, 2018, **8**, 8484.
3. N. Ahmad, J.J. Levision, S.D. Robinson and M.F. Uttley, *Inorg. Synth.,* 1974, **15**, 45.
4. R.H. Blessing, *Acta Crystallo. Sect. A.*, 1995, **51**, 33.
5. G.M. Sheldrick, SHELXTL Version 5.1, *An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data, Siemens Analytical X-ray Instruments*, Madison, WI, 1990.
6. G.M. Sheldrick, Shelxl-97, *A Program for Crystal Structure Refinement Release 97-2, Institut fur AnorganischeChemie der Universitat Gottingen, Tammanstrasse 4, D-3400*, Gottingen, Germany, 1998.
7. F.Y.Ling, F.Ye, X.J.Fang,X.H.Zhou,W.S.Huang,Z.Xu,and L.W. Xu,2023, *Chem. Sci.*, **14**(5), 1123-1131.
8. L. I. Pilkington and D.Barker, *J. Org. Chem.*2012,**77**, 8166.
9. J. S. Formen,J. R. Howard, E. V. Anslyn andC. Wolf, *Angew. Chem. Int. Ed.,*2024, **63**(19), e202400767.