Bromoamination of α,β-unsaturated keto alkenes by palladium(II) metalallocycles: experimental and theoretical approach

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Experimental section

General

All reagents and chemicals used in this study were purchased from authentic chemical suppliers. A standard literature procedure was followed for drying the solvents.[1] In accordance with the previous literature, 8-methyl-2-chloroquinoline-3-carboxaldehyde, its corresponding oxo compound,[2-4] and potassium tetrachloropalladate(II) $K_2[PdCl_4]$ were synthesized.[5] The melting points were confirmed by using a RAAGA melting point. JASCO FT-IR 4100 instrument was used to record infrared spectra in the form of KBr pellet in the range of 400-4000 cm^{-1}. With the aid of a JASCO V-630 spectrophotometer, UV-VIS spectra of the ligands and complexes were obtained. The NMR spectra were recorded with a Bruker DRX-500 advance spectrometer at 400MHz using DMSO-d^6 and TMS as internal references. The thermal stability of the complex were performed under nitrogen atmosphere where temperature range of 0-550 and 10 °C/min heating rate was determined using a Pyris Diamond TG-DTA Analyzer. Mass spectrum was recorded with a high-resolution Q-TOF mass spectrometer.The CD spectrum were recorded in JASCO J-1500 with ethyl acetate as standard solution.

FT-IR spectroscopy

FT-IR spectra of the *N*-heterocyclic thiosemicarbazone ligands **8MOQHL$^{1-4}$** and their corresponding complexes **Pd(8MOQL$^{1-4}$)Cl** were compared in the region of 400-4000 cm^{-1}. The ligands **8MOQHL$^{1-4}$** showed a broad band at 1646-1652 cm^{-1} corresponding to the stretching of oxo (C=O) group. However, in the spectra of the complexes **Pd(8MOQL$^{1-4}$)Cl,** oxo (C=O) group was shifted to lower frequencies (1619-1645 cm^{-1}) indicating the coordination of oxo group to the palladium ion.[6,7]A sharp band at 1538-1606 cm^{-1} corresponding to azomethine (C=N) group in the ligands **8MOQHL$^{1-4}$** was shifted to lower frequencies (1529-1540 cm^{-1}) in the complexes

Pd(8MOQL$^{1-4}$)Cl, which may be attributed to the involvement of azomethine group in coordination to the palladium ion. The C=S stretching observed at 800-854 cm^{-1} in the ligands **8MOQHL$^{1-4}$** disappeared in the complexes **Pd(8MOQL$^{1-4}$)Cl** and a new band was appeared at 750-776 cm^{-1} showing the thione-thiol tautomerization prior to coordination with the metal centre.[8,9]

Electronic spectroscopy

The electronic absorption spectra of the ligands **8MOQHL$^{1-4}$** and complexes **Pd(8MOQL$^{1-4}$)Cl** were recorded in DMSO. The ligands **8MOQHL$^{1-4}$** exhibited two absorption bands in the region 267-391 nm. The absorption bands at 267-269 nm were assigned to π→π* transitions and the bands at 361-391 nm have been assigned to n→π* transitions.[10] Conversely, in the complexes bathochromically shifted bands were observed as a result of extensive conjugation of π-electrons due to the coordination of Schiff bases to the palladium metal centre.[11] The absorption spectra of the Pd(II) complexes **Pd(8MOQL$^{1\&2}$)Cl** exhibited strong bands in the region 239-270 nm and 394-395 nm corresponding to intra ligand transition and ligand to metal charge transfer (LMCT) transition. A third weak band was observed at 414 and 419 nm which can be assigned to metal to ligand charge transfer transition (MLCT).[12,13] The complex **Pd(8MOQL^{3})Cl** showed absorption at 243-267 nm corresponding to intra ligand transition and 410 nm attributable to metal to ligand charge transfer (MLCT). Whereas, the complex **Pd(8MOQL^{4})Cl** exhibited three bands centred at 240-269 nm, 393 nm and 418 nm corresponding to intra ligand transition, ligand to metal charge transfer (LMCT) and metal to ligand charge transfer transition (MLCT) transitions.[12,13]

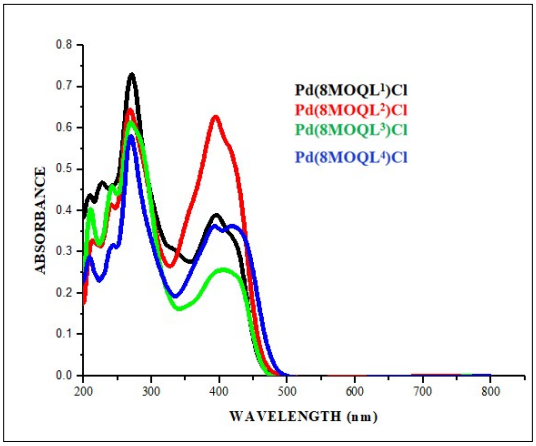

Fig. S1. Electronic spectra of the complexes **Pd(8MOQL$^{1-4}$)Cl**

Thermogravimetric analysis

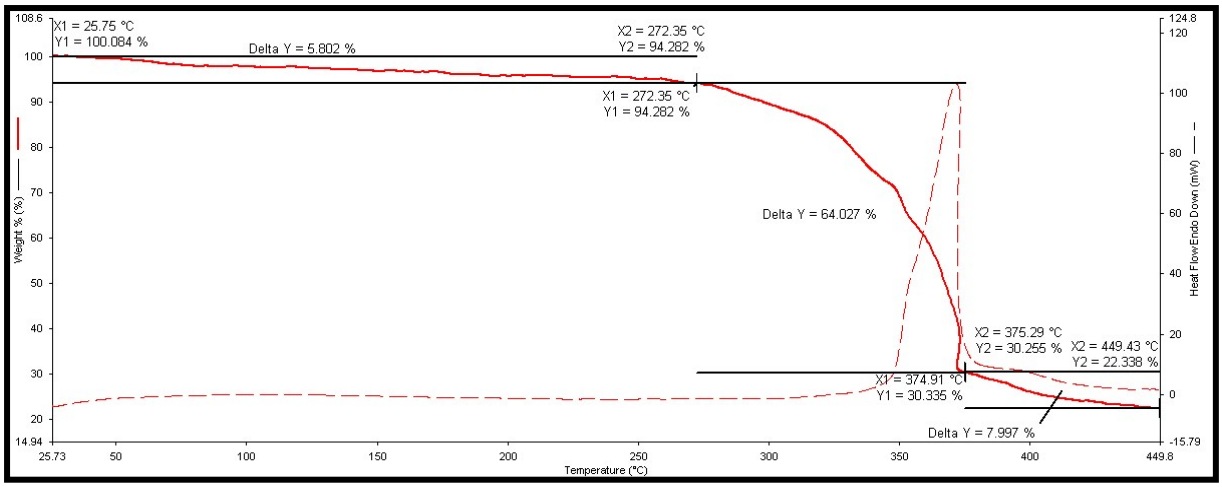

Fig. S2. TG-DTA plots of **Pd(8MOQL^{1})Cl**

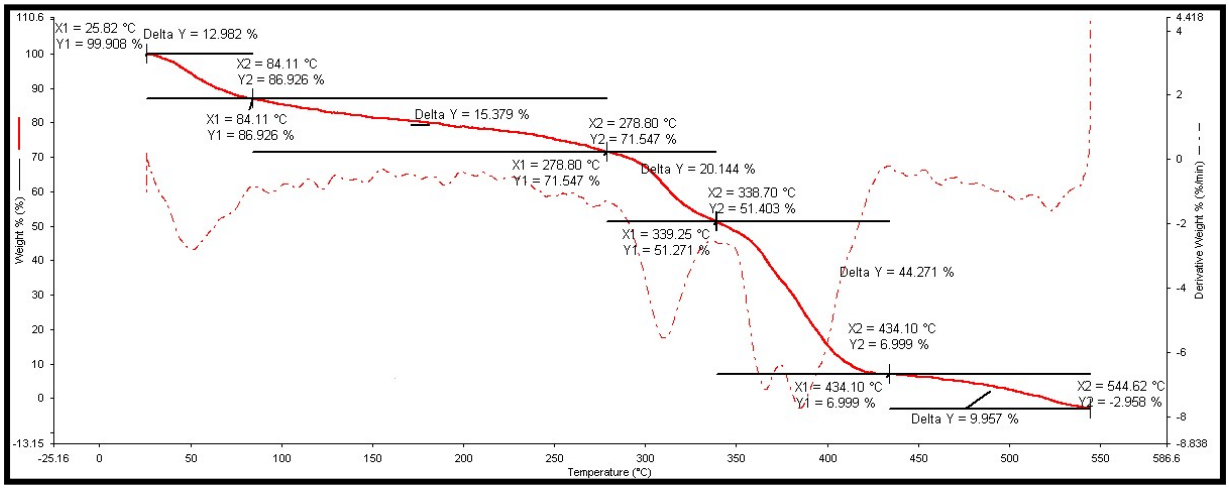

Fig. S3.TG-DTA plots of **Pd(8MOQL^{2})Cl**

^{1}H NMR Spectroscopy

The ^{1}H NMR spectra of the ligands **8MOQHL$^{1\text{-}4}$** and complexes **Pd(8MOQL$^{1\text{-}4}$)Cl** were recorded in DMSO-d^{6} and the corresponding data were presented in **Fig. S2-S5**. The ligands exhibited two singlets in the region δ 11.61-12.01 ppm and δ 10.26-11.18 ppm analogous to quinoline N(1)H and imine N(3)H protons respectively.[9] In the complexes **Pd(8MOQL$^{1\text{-}4}$)Cl**, quinoline N(1)H appeared at δ 13.01-13.14 ppm but there were no signals for N(3)H indicating the enolization and deprotonation of the –NH-C=S group prior to coordination of thiolate sulphur.[8,10] The ligands displayed a singlet at δ 8.75-8.67 ppm corresponding to the azomethine (HC=N) proton.[7] However, in the complexes **Pd(8MOQL$^{1\text{-}4}$)Cl**, azomethine proton was found at δ 8.36-9.01 ppm.[8,10] A doublet appeared at δ 8.29 ppm analogous to terminal N(4)H$_2$ protons in the ligand **8MOQHL^{1}**. However, in the complex **Pd(8MOQL^{1})Cl**, terminal N(4)H$_2$ protons singlet was found

atδ 10.48 ppm. In the ligands **8MOQHL$^{2,3\&4}$**, a singlet resonance signal appeared at δ 8.61-10.16 ppm assigned to terminal N(4)H proton and this was found at δ 8.67-8.85 ppm in the complexes **Pd(8MOQL$^{2,3\&4}$)Cl**.[10] A sharp singlet was found at δ 8.30 ppm and δ 8.42 ppm corresponding to C(4)H protons of the ligands **8MOQHL$^{1-4}$** whereas in the complexes **Pd(8MOQL$^{1-4}$)Cl**, the C(4)H protons resonated at δ 8.67-9.38 ppm.[11] In the ligand **8MOQHL^{2}**, triplet resonance signal was observed at δ 3.05-3.66 ppm for the terminal methyl protons and in the complex **Pd(8MOQL^{2})Cl** at δ 2.80-2.81 ppm.[8,12] In ligand **8MOQHL^{3}**, a triplet was observed at δ 1.17-1.20 ppm for terminal methyl protons and a pentet at δ 3.60-3.66 ppm for methylene protons.[7] In complex **Pd(8MOQL^{3})Cl**, terminal methyl protons were shown at δ 1.09-1.13 ppm and methylene protons at δ 3.17-3.30 ppm.[8] In the ligand **8MOQHL^{4}**, aromatic protons of quinoline moiety and terminal phenyl protons were appeared as multiple resonance signals in the range δ 7.14-7.60 ppm,[9] and in the complex **Pd(8MOQL^{4})Cl** these appeared as multiple signals around δ 6.99-7.82 ppm.[8,10] A singlet corresponding to quinoline methyl protons -$CH_3$was observed at δ 2.43 and δ 2.62 ppm.

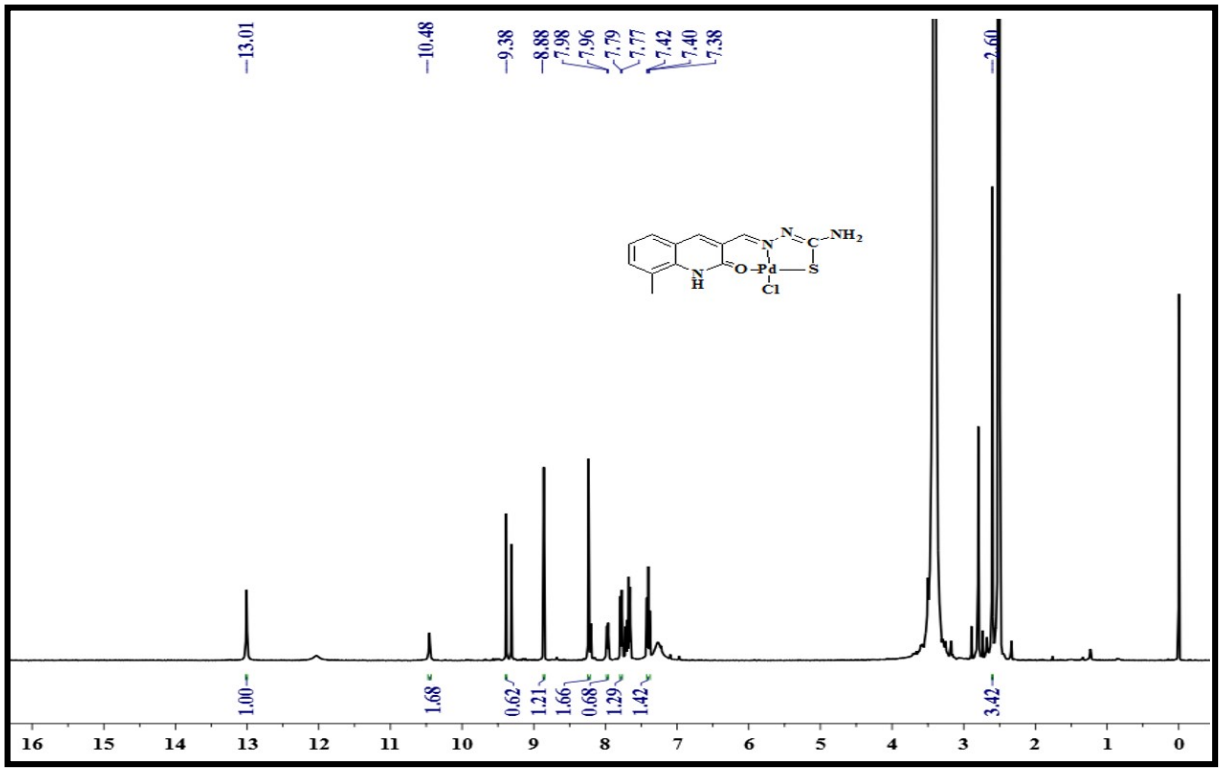

Fig. S4. ^{1}H NMR spectrum of the complex **Pd(8MOQL^{1})Cl**

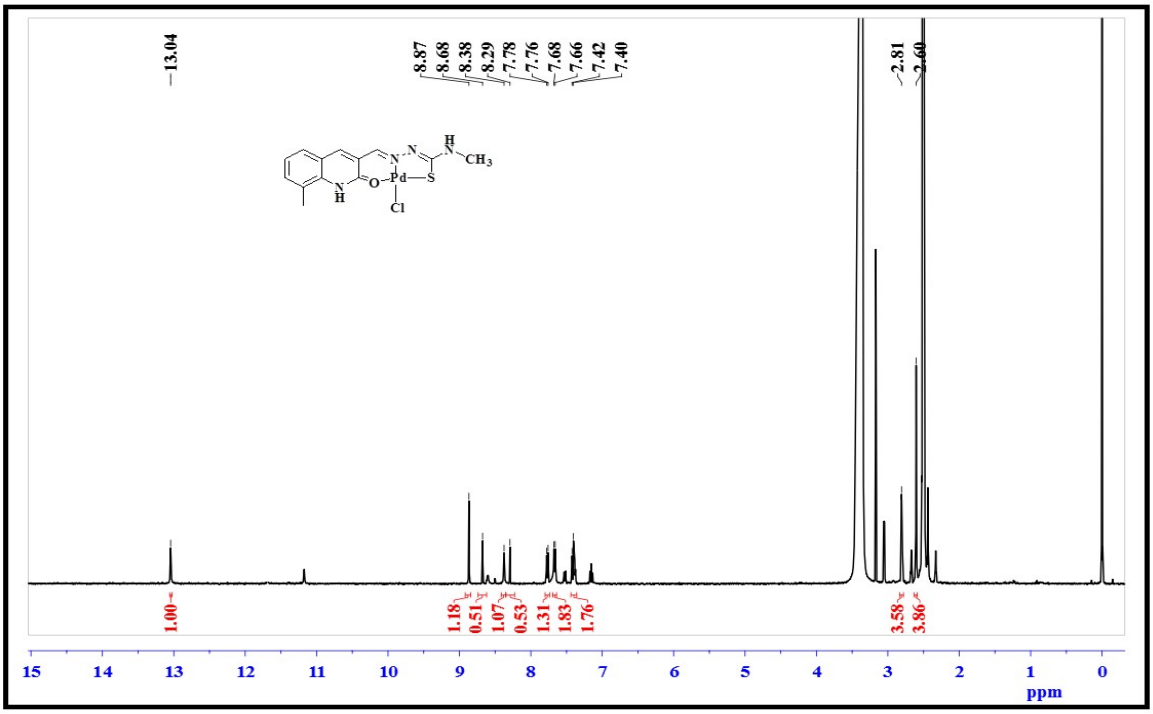

Fig. S5. ^{1}H NMR spectrum of the complex **Pd(8MOQL^{2})Cl**

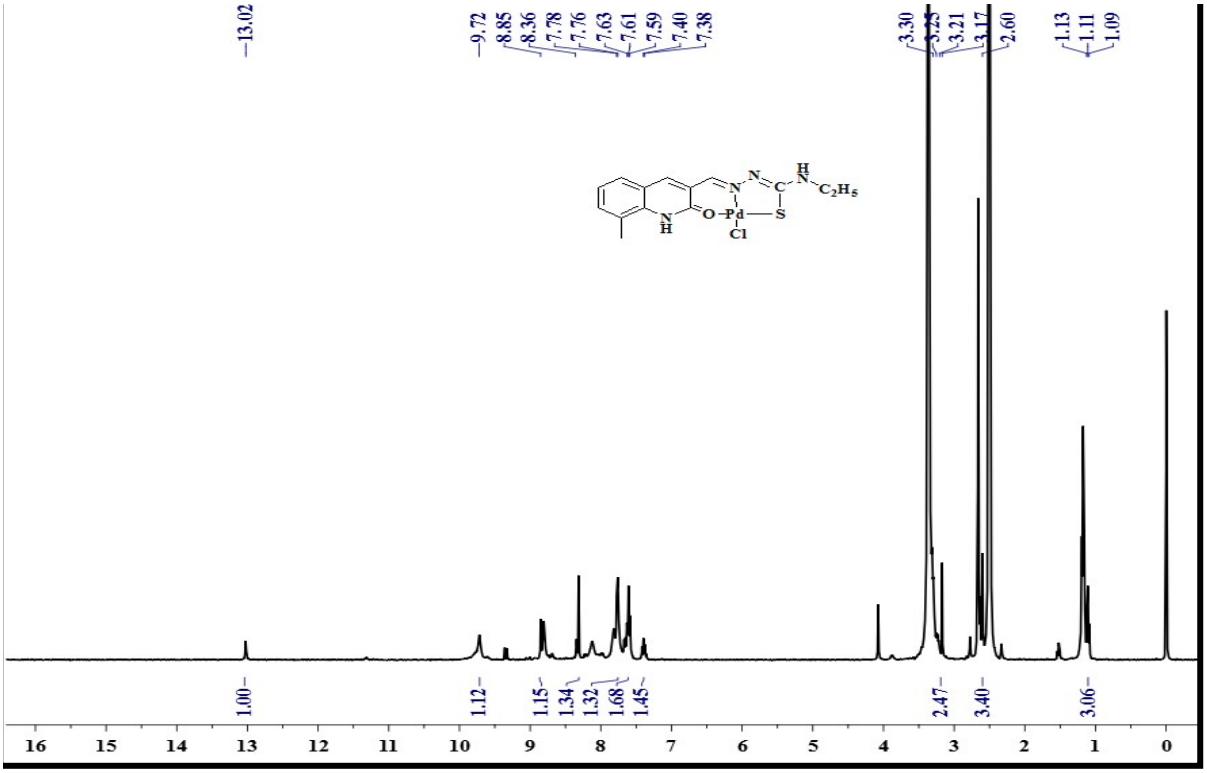

Fig. S6. ^{1}H NMR spectrum of the complex **Pd(8MOQL^{3})Cl**

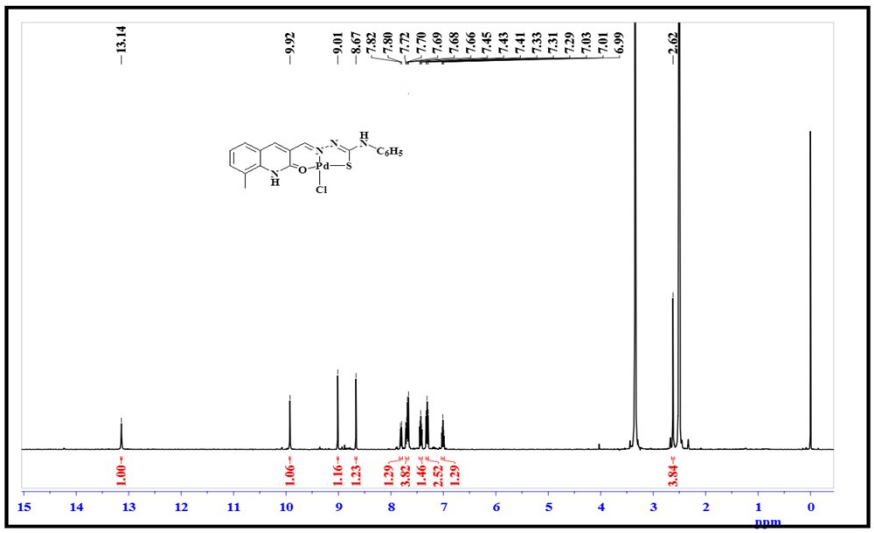

Fig. S7. ^{1}H NMR spectrum of the complex **Pd(8MOQL^{4})Cl**

Mass Spectroscopy

Continuous efforts to obtain suitable crystals of **Pd(8MOQL^{3})Cl** were unsuccessful. Hence, the stoichiometry of the complex was confirmed by mass spectral analyses.The [M+2] peak arises due to the presence of naturally occurring isotopes, particularly heavier isotopes of chlorine (^{37}Cl) element, in the molecule being analyzed.The complex showed a peak at m/z Calcd. (Exper.):-429.23(433.99) corresponding to **[Pd(8MOQL^{3})(CH$_3$CN)]$^{+}$** ion (**Fig. S6**).

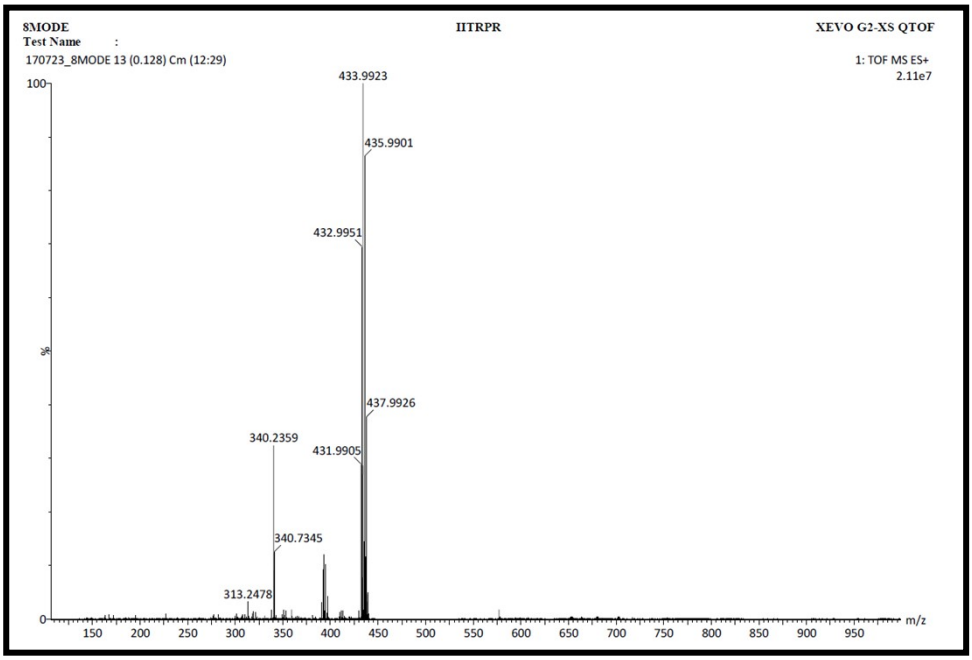

Fig. S8. Mass spectrum of the complex **Pd(8MOQL^{3})Cl**

Synthesis of Pd(II) complexes

A solution of the ligands **8MOQHL$^{1-4}$** (87-124 mg, 35 mmol) in methanol (10 cm^3) was added to $K_2[PdCl_4]$ (100 mg, 35 mmol) in 10 cm^3 of chloroform and refluxed for 1 h. Dark brown precipitates were cooled and separated by filtration, washed with ethanol and dried under room temperature. For X-ray analysis, the complexes were recrystallized from methanol and dimethylformamide (MeOH/DMF) in a 4:1 ratio.

[Pd(8MOQL^1)Cl] Yield:(124 mg, 88%). Melting point: >240°C. Elemental analyses Calc. (Found)%:-C, 35.93(36.05); N, 13.97(13.80); H, 2.76(2.88);O, 3.99(3.92) FT-IR (ν, cm^{-1}) in KBr: ν(C=O)1622, ν(C=N) 1540, ν(C−S) 771.UV-Vis (DMSO), λ_{max} nm (ε, dm^3 $mol^{-1}cm^{-1}$): 269 (11,447) (Intra ligand transition), 382 (66,476) (LMCT), 431 (52,283) (MLCT). ^{1}H NMR (400 MHz, DMSO-d^6, δ ppm, J Hz):13.01(s, 1H, N(1)H),10.48 (s, 1H,terminal –NH_2), 9.38 (s, 1H, N(4)H), 8.85 (s, 1H, -CH=N), 8.68 (s, 1H, C(4)H),7.95-7.98 (d, 1H, *J*=12.0 Hz, C(5)H),7.38-7.40 (t, 1H, *J*=8.0 Hz, C(6)H),7.76-7.78 (d, 1H, *J*=8.0 Hz, C(7)H),2.60 (s, 3H, -CH_3, quinoline methyl at C(8) position).

[Pd(8MOQL^2)Cl] Yield:(131 mg, 90%). Melting point: >240°C. Elemental analyses Calc. (Found)%:- C, 37.61 (37.70); N, 13.49(13.40); H, 3.16(3.25);O, 3.85(3.98).FT-IR (ν, cm^{-1}) in KBr: ν(C=O) 1645, ν(C=N) 1529, ν(C−S) 750.UV-Vis (DMSO), λ_{max} nm (ε, dm^3 $mol^{-1}cm^{-1}$):267 (64,245) Intraligand transition, 394 (62,697) LMCT transition. ^{1}H NMR (400 MHz, DMSO-d^6, δ ppm, J Hz):13.03 (s, 1H, N(1)H), 8.87 (s, 1H, N(4)H), 8.38 (s, 1H, -CH=N), 8.68 (s, 1H, C(4)H),δ 7.76-7.78 (t, 1H, *J*=8.0 Hz, C(5)H), 7.40-7.42 (t, 2H, *J*=8.0 Hz, C(6)), δ 7.66-7.68 (d, 1H, *J*=8.0Hz, C(7)H), δ 2.80-2.81 (d, 3H, *J*=4.0 Hz, terminal -CH_3),δ 2.60 (s, 3H, quinoline -CH_3 at C(8) position).

[Pd(8MOQL^3)Cl] Yield:(138 mg, 92%). Melting point: >240°C. Elemental analyses Calc. (Found)%:- C, 39.17 (39.10); N, 13.05(13.10); H, 3.52(3.55);O, 3.73(3.80). FT-IR (ν, cm^{-1}) in KBr: ν(C=O) 1623, ν(C=N) 1536, ν(C−S) 776.UV-Vis (DMSO), λ_{max} nm (ε, dm^3 $mol^{-1}cm^{-1}$): 269 (11,447) (Intra ligand transition), 382 (66,476) (LMCT), 421 (53,565) (MLCT). ^{1}H NMR (400 MHz, DMSO-d^6, δ ppm, J Hz):13.02 (s, 1H, N(1)H), 9.72 (s, 1H, N(4)H), 8.36 (s, 1H, -CH=N), 8.85 (s, 1H, C(4)H), 7.76-7.78(d, 1H, *J* = 8Hz, C(5)H), 7.38-7.40 (d, 1H, *J* = 12.0 Hz, C(7)H), 7.59-7.62 (t, 1H, *J* = 12.0 Hz, C(6)H), 3.17-3.30 (q, 2H, *J* = 16.0 Hz, terminal -CH_2),1.09-1.13 (t, 3H, *J* = 16.0 Hz, terminal -CH_3), 2.60 (s, 3H, quinoline -CH_3 at C(8) position).

[Pd(8MOQL^4)Cl] Yield:(145 mg, 87%). Melting point: >240°C. Elemental analyses Calc. (Found)%:- C, 45.30 (45.10); N, 11.74(11.80); H, 3.17(3.20);O, 3.35(3.30). FT-IR (ν, cm^{-1}) in KBr: ν(C=O) 1619, ν(C=N) 1531, ν(C−S) 753.UV-Vis (DMSO), λ_{max} nm (ε, dm^3 $mol^{-1}cm^{-1}$):269

(61,168) (Intraligand transition), 390 (35,937) LMCT transition, 415 (36,427) MLCT transition. ^{1}H NMR (400 MHz, DMSO-d^{6}, δ ppm, J Hz):13.14(s, 1H, N(1)H), 9.92 (s, 1H, N(4)H), 9.01(s, 1H, -CH=N), 8.67(s, 1H, C(4)H),δ 7.76-7.78 (d, 1H, *J* = 8.0 Hz, C(5)H), δ 7.37-7.40 (d, 1H, *J* = 12.0 Hz, C(7)H), δ 7.59-7.62 (t, 1H, *J* = 12.0 Hz,C(6)H), δ 3.17-3.30 (q, 2H, *J* = 52.0 Hz, terminal -CH_2), δ 1.09-1.13 (t, 3H, *J* = 16.0 Hz, terminal -CH_3), δ 2.62(s, 3H, quinoline -CH_3 at C(8) position).

Procedure for bromoamination reaction

A dry round bottom flask was charged with NBS (0.11mmol), chalcone (0.1mmol), and catalyst (16 mol%), followed by 5 cm^3 of acetonitrile. After refluxing the mixture for 5 minutes, *p*-toluenesulfonamide (0.11mmol) was added. Further, the reaction mixture was continued to reflux for 6 h. The reaction progress was monitored using thin layer chromatography (TLC). Afterwards, ethyl acetate was used to work up the reaction mixture, and then the organic layer was collected and dried over anhydrous sodium sulphate. The crude product was purified using column chromatography with petroleum ether and ethyl acetate as eluents.

Spectral data of the coupled products

1B

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, *J* Hz): 8.34 (s, 1H, C4-H), 7.77-7.78 (d, *J* = 4 Hz, 1H, C5-H),7.56-7.57 (t, *J* = 2 Hz, 1H, C6-H), 7.75-7.76 (t, *J* = 4Hz, 1H, C7-H), 7.80-7.81 (t, *J* = 4 Hz, 1H, C8-H), 4.71 (s, 1H, chiral-CH-NH), 5.70 (s, 1H, chiral-CH-Br), 6.83-6.85 (d, *J* = 8 Hz, 1H, *p*-toluene-NH-), 7.79-7.81 (d, *J* = 4 Hz, 2H, *p*-toluene phenyl protons), 7.37-7.38 (d, *J* = 8Hz, 2H, *p*-toluene phenyl protons), 2.14 (s, 3H, *p*-toluene-CH_3), 7.83-7.85 (d, *J* = 8 Hz, 2H, phenyl ring protons), 7.39-7.41 (m, 3H, phenyl ring protons).^{13}C NMR (100 MHz, $CDCl_3$, δ ppm, *J* Hz): 196.60, 143.72, 142.44, 139.13, 136.68, 136.16, 134.12, 133.78, 130.50, 129.72, 129.43, 128.61, 127.61, 127.83, 127.10, 126.83, 126.67, 126.58, 126.45, 125.47, 125.12, 124.52, 124.19, 124.00, 62.86, 51.95, 21.53.

2B

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, *J* Hz): 8.28 (s, 1H, C4-H), 7.59 (s, *J* = 4 Hz, 1H, C5-H),7.572-7.569 (d, *J* = 8 Hz, 1H, C7-H), 7.99-8.00 (d, *J* = 4 Hz, 1H, C8-H), 4.84 (s, 1H, chiral-CH-NH), 5.73 (s, 1H, chiral-CH-Br), 6.84-6.86 (d, *J* = 8 Hz, 1H, *p*-toluene-NH-),7.80-7.82 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons),7.29-7.31 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons), 2.14 (s, 3H, *p*-toluene-CH_3), 7.83-7.85 (d, 2H), 7.38-7.42 (m, 3H, naphthalene protons), 2.54 (s, 3H, -CH_3, C6-H quinoline methyl protons).^{13}C NMR (100 MHz, $CDCl_3$, δ ppm, *J* Hz): 194.77, 147.67, 145.86,

143.64, 137.65, 136.37, 135.33, 134.26, 133.73, 129.70, 129.42, 129.36, 129.22, 128.91, 128.65, 127.79, 127.02, 126.71, 126.58, 126.45, 61.03, 50.12, 21.60, 21.37.

3B

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, *J* Hz): 8.30 (s, 1H, C4-H), 7.72-7.74 (d, *J* = 8 Hz, 1H, C5-H), 7.61-7.63 (d, *J* = 4 Hz, 1H, C6-H), 8.07 (s, 1H, C8-H), 5.19 (s, 1H, chiral-CH-NH), 5.70 (s, 1H, chiral-CH-Br), 6.81-6.83 (d, *J* = 8 Hz, 1H, *p*-toluene-NH-), 7.79-7.81(d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons), 7.47-7.49 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons), 2.12 (s, 3H, *p*-toluene-CH_3), 7.86-7.87 (d, 2H), 7.37-7.41 (m, 3H), 2.56 (s, 3H, -CH_3, C7-H quinoline methyl protons).^{13}C NMR (100 MHz,$CDCl_3$, δ ppm, *J* Hz): 194.15, 148.55, 147.48, 143.55, 143.46,142.26, 139.23, 136.42, 135.36, 134.28, 130.11, 129.77, 129.68, 129.38, 128.94, 128.67, 127.56, 127.35, 127.11, 126.63, 127.48, 126.48, 126.41, 61.14, 50.54, 21.51, 21.34.

4B

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, *J* Hz): 8.29 (s, 1H, C4-H), 7.57-7.59 (d, *J* = 4 Hz, 1H, C5-H), 7.50-7.52 (d, *J* = 4 Hz, 1H, C6-H), 7.54-7.55 (d, 1H, C7-H), 5.10 (s, 1H, chiral-CH-NH), 5.75 (s, 1H, chiral-CH-Br), 6.83-6.85 (d, *J* = 12 Hz, 1H, *p*-toluene-NH-), 7.80-7.82 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons), 7.45-7.46 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons), 2.13 (s, 3H, *p*-toluene-CH_3), 7.85-7.87 (d, 2H), 7.39-7.42 (m, 3H), 2.73 (s, 3H, -CH_3, C8-H quinoline methyl protons).^{13}C NMR (100 MHz, $CDCl_3$, δ ppm, *J* Hz): 192.11, 134.71, 132.89, 132.49, 129.68,129.38, 127.59, 127.20, 127.11, 126.90, 126.79, 126.47, 125.52, 125.30, 124.99, 124.12, 124.02, 56.22, 40.64, 21.04, 19.60.

5B

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, *J* Hz): 8.50 (s, 1H, C4-H), 7.75-7.76 (d, *J* = 4 Hz, 1H, C5-H), 7.55-7.56 (d, *J* = 4 Hz, 1H, C6-H), 7.73-7.74 (d, *J* = 4 Hz, 2H,C7&C10-H), 7.53-7.54 (d, *J* = 8 Hz, 2H,C8&C9-H), 4.85 (s, 1H, chiral-CH-NH), 5.34 (s, 1H, chiral-CH-Br), 6.72-6.74 (d, *J* = 8 Hz, 1H, *p*-toluene-NH-), 7.90-7.91 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons), 7.42-7.44 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons), 2.31 (s, 3H, *p*-toluene-CH_3), 7.92.7.93 (d, *J* = 4 Hz, 2H), 7.37-7.39 (m, 3H).^{13}C NMR (100 MHz, $CDCl_3$, δ ppm, *J* Hz):188.54, 142.32, 139.50, 138.30, 137.90,137.38, 133.59, 133.15, 132.06, 130.74, 128.62,127.44, 127.21, 126.89, 126.84, 126.62, 126.57, 126.12, 125.94, 125.36, 124.85, 124.71, 62.23, 54.45, 20.48.

6B

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, *J* Hz): 8.48 (s, 1H, C4-H), 7.78-7.79 (d, *J* = 4 Hz, 1H, C5-H), 7.75-7.77 (t, *J* = 2 Hz, 1H, C6-H), 7.80-7.81 (t, *J* = 4 Hz, 1H, C7-H), 7.94-7.95 (t, *J* = 4 Hz, 1H,

C8-H), 5.11 (s, 1H, chiral-CH-NH), 5.64 (s, 1H, chiral-CH-Br), 6.87-6.89 (d, *J* = 8 Hz, 1H, *p*-toluene-NH-), 7.92-7.93 (d, *J* = 4 Hz, 2H, *p*-toluene phenyl protons), 7.45-7.47 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons), 2.13 (s, 3H, *p*-toluene-CH_3), 8.11 (s, 1H, naphthalene protons), 8.02-8.04 (d, *J* = 8 Hz,1H, naphthalene protons), 7.96-7.98 (d, *J* = 8 Hz, 1H, naphthalene protons), 7.58-7.64 (m, 4H, naphthalene protons). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm,*J*Hz):195, 145.8, 145.67, 143.50, 141.88, 139.65, 139.36, 137.80, 135.53, 133.21, 132.72, 130.58, 130.21, 128.95, 128.44, 128.03, 127.59, 127.09, 126.75, 126.54, 126.44, 126.12, 125.76, 125.59, 124.56, 124.43, 123.19, 123.96, 61.05, 49.50, 20.8.

7B

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, *J* Hz): 8.45 (s, 1H, C4-H), 7.56-7.57 (d, *J* = 4 Hz, 1H, C5-H), 7.52-7.54 (d, *J* = 8Hz, 1H, C7-H), 7.67-7.68 (d, *J* = 4 Hz, 1H, C8-H), 4.97 (s, 1H, chiral-CH-NH), 5.78 (s, 1H, chiral-CH-Br), 6.93-6.95 (d, *J* = 8 Hz, 1H, *p*-toluene-NH-), 7.70-7.72 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons), 7.47-7.49 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons), 2.13 (s, 3H, *p*-toluene-CH_3), 7.95 (s, 1H, naphthalene protons), 7.89-7.91 (d, 1H, *J* = 8 Hz, naphthalene protons), 7.96-7.98 (d, 1H, *J* = 8 Hz, naphthalene protons), 7.63-7.65 (m, 4H, naphthalene protons), 2.55 (s, 3H, -CH_3, C6-H quinoline methyl protons).^{13}C NMR (100 MHz, $CDCl_3$, δ ppm, *J* Hz): 195.29, 144.38 145.8, 142.65, 142.52, 141.08, 138.11, 136.56, 135.62, 133.22, 133.13, 132.68, 132.43, 131.14, 130.57, 128.58, 128.43, 128.58, 127.44, 126.54, 125.76, 125.61, 125.42, 124.42, 123.20, 122.65,61.80, 49.21, 21.66, 20.49.

8B

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, *J* Hz): 8.41 (s, 1H, C4-H), 7.57-7.59 (d, *J* = 8Hz, 1H, C5-H),7.55-7.56 (d, *J* = 4 Hz, 1H, C6-H), 7.67 (s, 1H, C8-H), 4.75 (s, 1H, chiral-CH-NH), 5.78 (s, 1H, chiral-CH-Br), 6.91-6.93 (d, *J* = 8 Hz, 1H, *p*-toluene-NH-), 7.72-7.74 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons), 7.45-7.47 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons), 2.12 (s, 3H, *p*-toluene-CH_3), 7.95 (s, 1H, naphthalene protons), 7.91-7.93 (d, 1H, *J* = 8 Hz, naphthalene protons), 7.69-7.70 (d, 1H, *J* =4 Hz, naphthalene protons), 7.61-7.65 (m, 4H, naphthalene protons), 2.53 (s, 3H, -CH_3, C7-H quinoline methyl protons).^{13}C NMR (100 MHz, $CDCl_3$, δ ppm, *J* Hz): 196.13, 147.60, 143.87, 142.74, 140.69,137.56, 136.92, 136.28, 134.25,133.45, 131.25, 130.62, 129.73, 129.55, 129.47, 128.62, 128.58, 128.13, 128.00,127.57, 127.48, 127.15, 126.79, 126.63, 125.46, 124.22, 124.04, 62.46, 50.48, 22.79, 21.54.

9B

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, *J* Hz): 8.44 (s, 1H, C4-H), 7.61-7.62 (d, *J* = 4 Hz, 1H, C5-H), 7.56-7.57 (d, *J* = 4 Hz, 1H, C6-H), 7.53-7.54 (d, *J* = 4 Hz ,1H, C7-H), 4.88 (s, 1H, chiral-CH-NH), 5.81 (s, 1H, chiral-CH-Br), 6.96-6.99 (d, *J* = 12 Hz, 1H, *p*-toluene-NH-),7.80-7.82 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons), 7.28-7.30 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons), 2.11 (s, 3H, *p*-toluene-CH_3), 7.93 (s, 1H, naphthalene protons), 7.87-7.89 (d, *J* = 4 Hz 1H, naphthalene protons), 7.68-7.70 (d, *J* = 8 Hz, 1H, naphthalene protons),7.48-7.51 (m, 4H, naphthalene protons), 2.42 (s, 3H, -CH_3, C8-H quinoline methyl protons).^{13}C NMR (100 MHz, $CDCl_3$, δ ppm, *J* Hz): 194.64, 140.07, 136.38, 135.04, 134.18,133.89, 133.69, 13.04, 131.75, 131.41, 129.79,129.66, 129.53, 129.09, 128.65, 128.52,129.93, 127.64, 127.57, 127.50, 127.08, 126.76, 126.52, 126.41, 125.02, 124.54, 124.21, 62.15, 52.23, 21.73, 21.46.

10B

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, *J* Hz): 8.41(s, 1H, C4-H), 7.653-7.649 (d, *J* = 4 Hz, 1H, C5-H), 7.57-7.58 (d, *J* = 4 Hz, 1H, C6-H), 7.59-7.60 (d, *J* = 4 Hz, 2H, C7&C10-H), 7.30-7.32 (d, *J* = 8 Hz, 2H, C8&C9-H), 4.67 (s, 1H, chiral-CH-NH), 5.69 (s, 1H, chiral-CH-Br), 6.82-6.84 (d, *J* = 8 Hz, 1H, *p*-toluene-NH-), 7.82-7.84 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons), 7.39 -7.41 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons), 2.40 (s, 3H, *p*-toluene-CH_3), 7.95 (s, 1H, naphthalene protons), 7.92-7.93 (d, *J* = 4 Hz, 1H, naphthalene protons), 7.72-7.73 (d, *J* = 4 Hz,1H, naphthalene protons), 7.52-7.55 (m, 4H, naphthalene protons).^{13}C NMR (100 MHz, $CDCl_3$, δ ppm, *J* Hz): 195.26, 147.47, 142.49, 140.96, 135.61,135.09, 133.50, 133.11, 132.51, 131.10, 130.63,128.68, 128.38, 128.27, 127.59, 127.50, 126.97, 126.80, 126.47, 125.81, 125.55, 125.37, 124.58, 124.49, 123.81, 123.18, 123.10, 121.07, 122.35, 62.30, 49.69, 21.66.

11B

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, *J* Hz): 7.96 (s, 1H, C4-H), 7.65-7.67 (d, *J* = 4 Hz, 1H, C5-H),7.43-7.47 (t, *J* = 2 Hz, 1H, C6-H), 7.59-7.62 (t, *J* = 4 Hz, 1H, C7-H), 7.80-7.82 (t, *J* = 4 Hz, 1H, C8-H), 5.15 (s, 1H, chiral-CH-NH), 5.54 (s, 1H, chiral-CH-Br), 6.83-6.84 (d, *J* = 8 Hz, 1H, *p*-toluene-NH-), 7.84-7.87 (d, *J* = 4 Hz, 2H, p-toluene phenyl protons), 7.28-7.30 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons), 2.42 (s, 3H, *p*-toluene-CH_3), 7.55-7.56 (d, *J* = 4 Hz,1H, thiophene ring protons), 7.53-7.54 (d, *J* = 4 Hz,1H, thiophene ring protons), 7.50-7.52 (t, *J* = 8 Hz,1H, thiophene ring protons).^{13}C NMR (100 MHz, $CDCl_3$, δ ppm, *J* Hz):196.33, 143.87, 142.74, 140.42, 134.25, 131.55, 131.25, 130.62, 129.73, 129.55, 129.47, 128.62, 128.58, 128.13, 128.00, 127.57, 127.48, 127.15, 126.79, 126.63, 125.46, 124.32, 124.22, 62.76, 50.53, 21.46.

12B

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, *J* Hz): 8.32 (s, 1H, C4-H), 7.83 (s,1H, C5-H),7.53-7.54 (d, *J* = 8 Hz, 1H, C7-H), 7.95-7.98 (d, *J* = 4 Hz, 1H, C8-H), 4.58 (s, 1H, chiral-CH-NH), 5.69 (s, 1H, chiral-CH-Br), 6.90-6.91 (d, *J* = 8 Hz, 1H, *p*-toluene-NH-), 7.92-7.91 (d, *J* = 8Hz, 2H, *p*-toluene phenyl protons), 7.17-7.18 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons), 2.01 (s, 3H, *p*-toluene-CH_3), 7.86-7.88 (d, *J* =8 Hz, 1H), 7.56-7.55 (d, *J* = 4 Hz, 1H), 7.75-7.76 (t, *J* = 4 Hz, 1H), 2.48 (s, 3H, -CH_3, C6-H quinoline methyl protons).^{13}C NMR (100 MHz, $CDCl_3$, δ ppm, *J* Hz): 194.42, 148.60, 147.21, 143.67, 143.51, 140.37, 139.19, 136.37, 135.53, 134.52, 134.28, 131.44, 129.70, 129.38, 129.24, 128.91, 128.67, 128.14, 127.93, 127.53, 126.99, 126.68, 126.53, 126.44, 61.00, 49.88, 21.52, 21.39.

13B

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, *J* Hz): 8.45 (s, 1H, C4-H), 7.77-7.78 (d, *J* = 8 Hz, 1H, C5-H),7.48-7.49 (d, *J* = 4 Hz, 1H, C6-H), 7.92-7.93 (m, 1H, C8-H), 4.73 (s, 1H, chiral-CH-NH), 5.42 (s, 1H, chiral-CH-Br), 7.01-7.03 (d, *J* = 8 Hz, 1H, *p*-toluene-NH-), 8.23-8.27 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons), 7.43-7.46 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons), 2.17 (s, 3H, *p*-toluene-CH_3), 7.80-7.81 (d, *J* = 4 Hz, 1H), 7.30-7.29 (d, *J* = 4 Hz, 1H), 7.73-7.75 (t, *J* = 8 Hz, 1H), 2.49 (s, 3H, -CH_3,C7-H quinoline methyl protons).^{13}C NMR (100 MHz, $CDCl_3$, δ ppm, *J* Hz): 195.21, 145.97, 144.95, 139.67, 137.98,137.86, 137.09, 135.74, 135.18, 133.54, 132.96, 132.57, 131.61, 131.49, 128.20, 127.68, 127.04, 126.49,126.49, 125.59, 124.88, 62.11, 51.55, 21.75, 20.62.

14B

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, *J* Hz): 8.33 (s, 1H, C4-H), 7.67-7.69 (d, *J* = 4 Hz, 1H, C5-H),7.43-7.47 (d, *J* = 4 Hz, 1H, C6-H), 7.51-7.53 (d, 1H, C7-H),4.91 (s, 1H, chiral-CH-NH), 5.62 (s, 1H, chiral-CH-Br), 6.82-6.84 (d, *J* = 12 Hz, 1H, *p*-toluene-NH-),7.80-7.82 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons),7.37-7.39 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons), 2.14 (s, 3H, *p*-toluene-CH_3), 7.72-7.73 (d, *J* = 4 Hz, 1H), 7.29-7.31 (d, *J* = 8 Hz, 1H), 7.57-7.61 (t, *J* = 16 Hz, 1H), 2.42 (s, 3H, -CH_3,C8-H quinoline methyl protons).^{13}C NMR (100 MHz, $CDCl_3$, δ ppm, *J* Hz): 193.49, 143.53, 143.49, 139.15, 137.03,136.47, 134.61, 129.70, 129.31, 129.26, 129.14,128.93, 128.87, 128.74, 128.66, 128.59, 127.86, 126.46, 126.43, 124.50, 60.47, 57.78, 21.52, 20.92.

15B

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm, *J* Hz): 8.34(s, 1H, C4-H), 7.64-7.67 (d, *J* = 4 Hz, 1H, C5-H), 7.57-7.60 (d, *J* = 4 Hz, 1H, C6-H), 7.74-7.77 (d, *J* = 4 Hz, 2H, C7&C10-H), 7.30- 7.32 (d, *J* = 8 Hz, 2H, C8&C9-H), 4.84 (s, 1H, chiral-CH-NH), 5.77 (s, 1H, chiral-CH-Br), 6.71-6.73 (d, *J* = 8 Hz, 1H, *p*-toluene-NH-), 7.91-7.92 (d, *J* = 8 Hz, 2H, *p*-toluene phenyl protons), 7.32-7.35 (d, *J* = 8 Hz,

2H, *p*-toluene phenyl protons), 2.43 (s, 3H, *p*-toluene-$\underline{CH_3}$), 7.83-7.84 (d, J = 4 Hz, 1H, naphthalene protons), 7.81 (s, 1H), 7.50-7.52 (t, J = 4 Hz, 1H, naphthalene protons).^{13}C NMR (100 MHz, $CDCl_3$, δ ppm, J Hz): 195.26, 144.98, 140.96, 135.09, 131.10, 128.68, 128.38, 128.27, 127.59, 127.50, 126.97, 126.80, 126.47, 125.81, 125.55, 125.37, 124.58, 124.49, 123.81, 123.18, 123.10, 62.30, 49.69, 21.66.

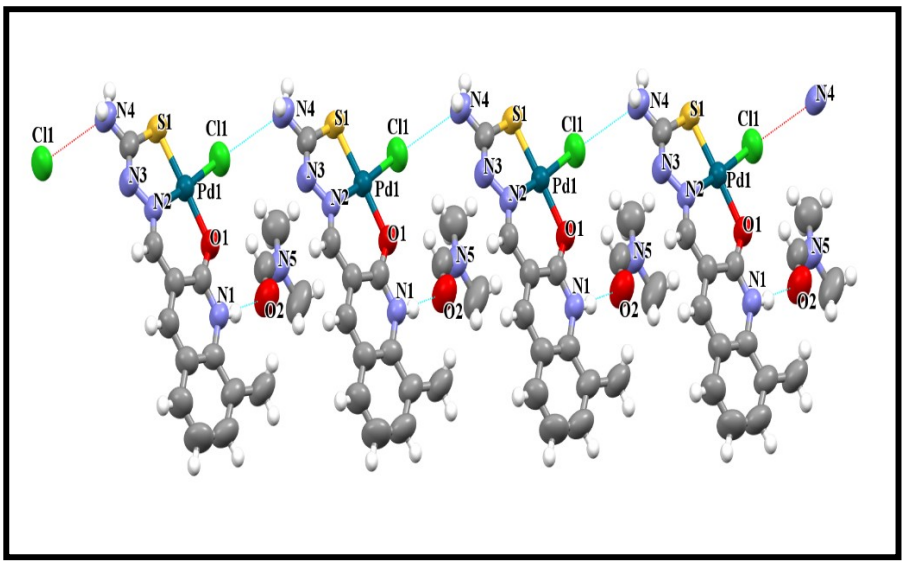

Fig. S9. ORTEP diagram of the complex Pd(8MOQL^1)Cl with hydrogen bonding

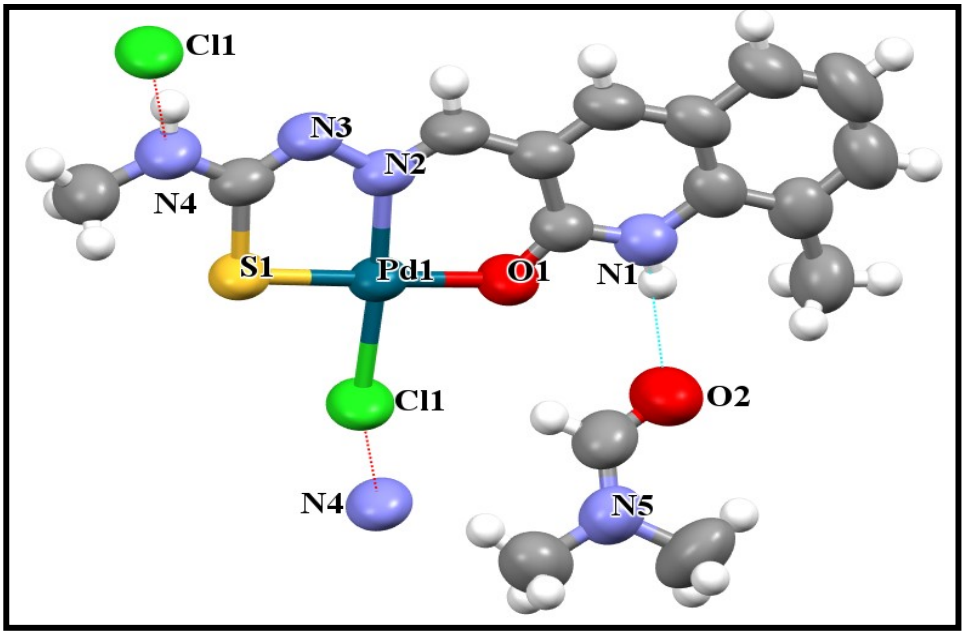

Fig. S10. ORTEP diagram of the complex Pd(8MOQL^2)Cl with hydrogen bonding

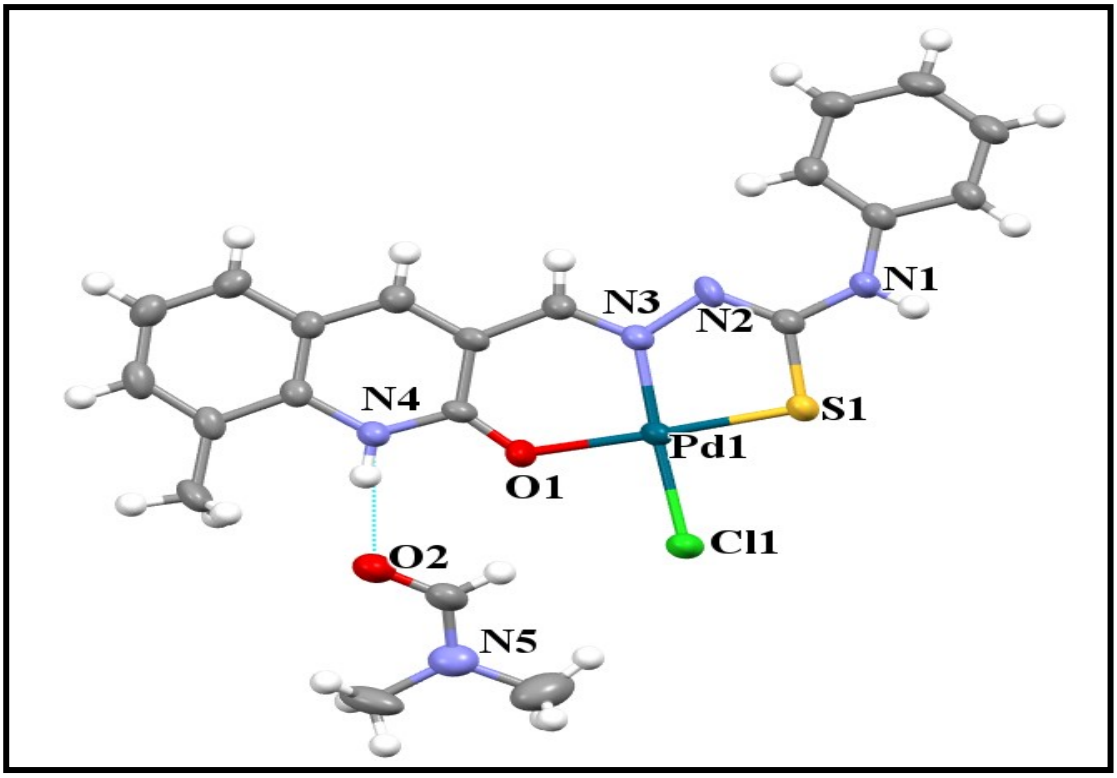

Fig. S11. ORTEP diagram of the complex Pd(8MOQL^4)Cl with hydrogen bonding

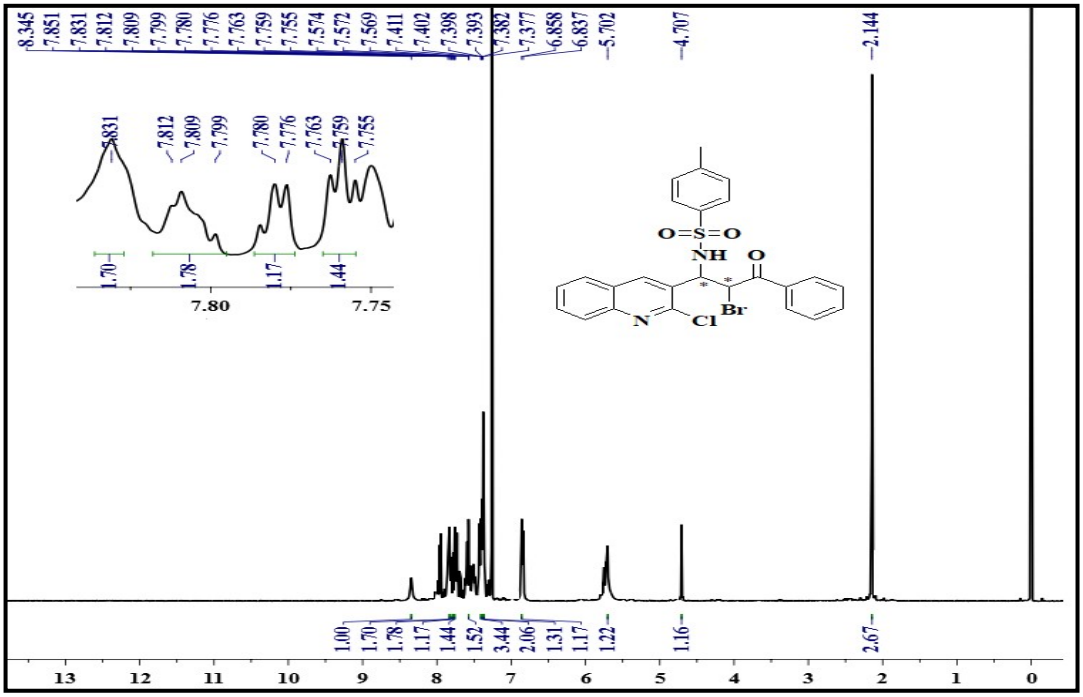

Fig. S12. ^{1}H NMR spectrum of 1B

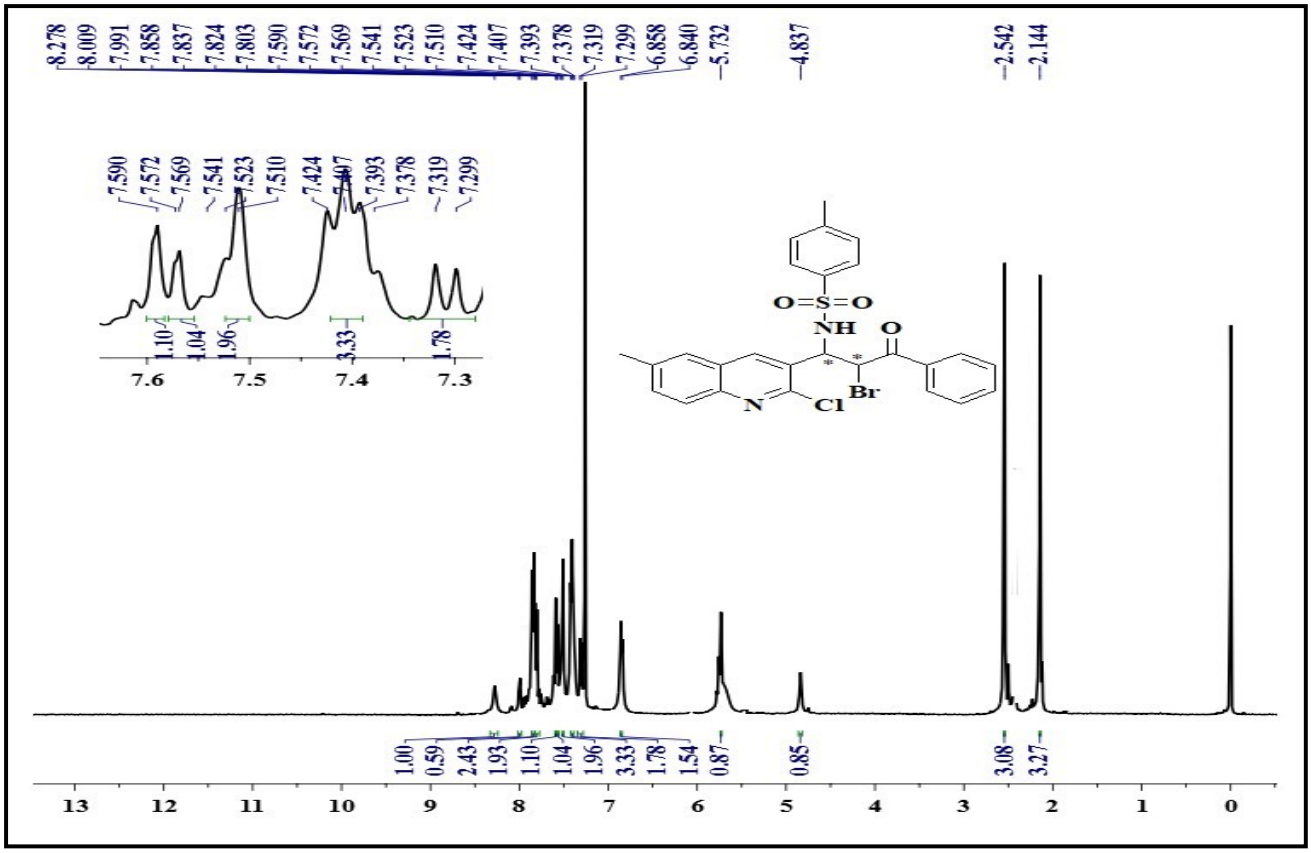

Fig. S13. ^{1}H NMR spectrum of 2B

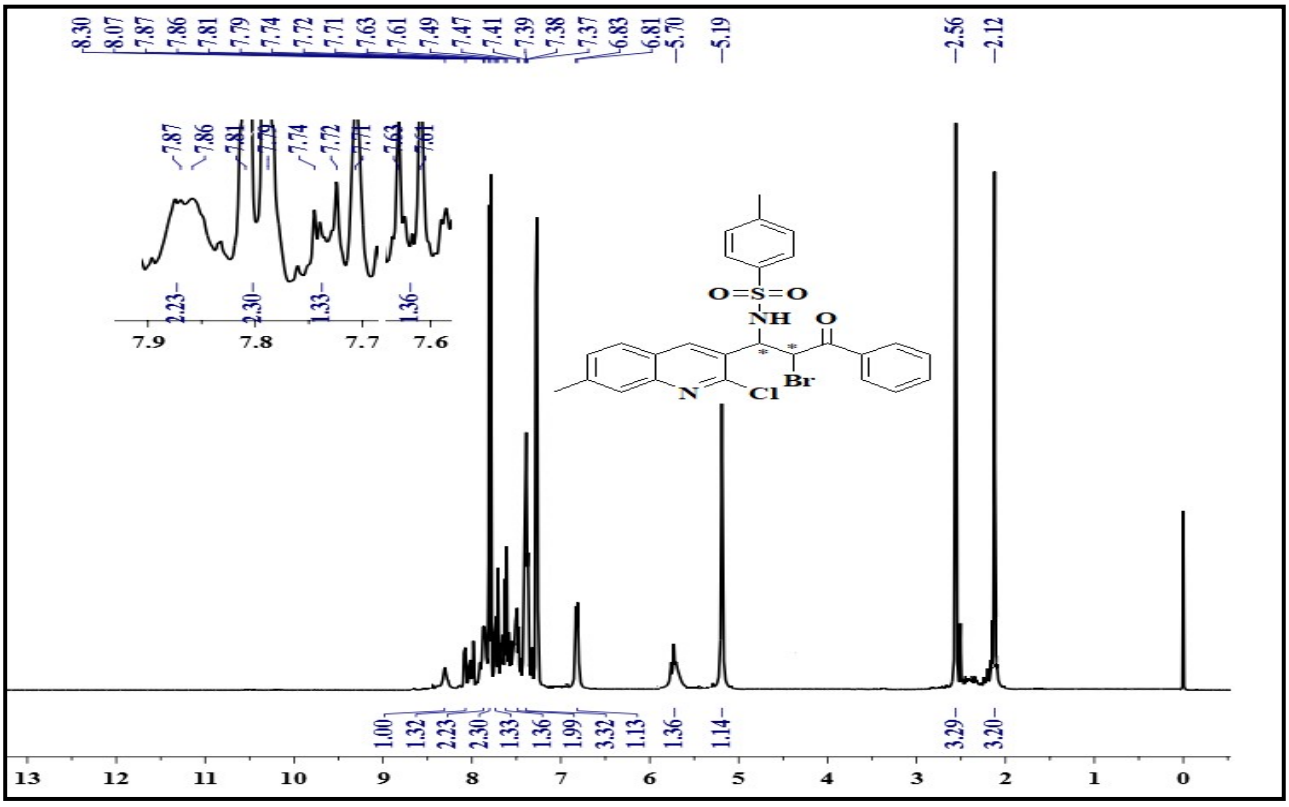

Fig. S14. ^{1}H NMR spectrum of 3B

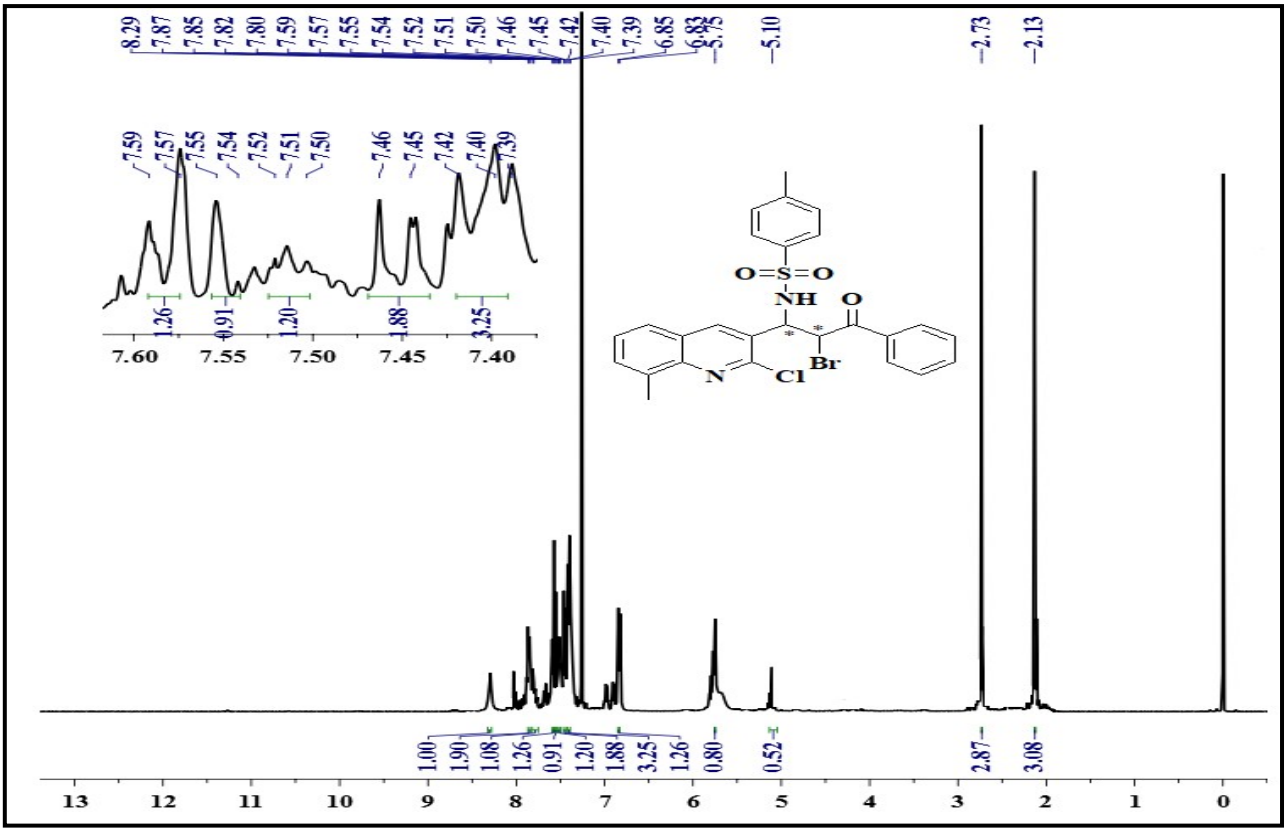

Fig. S15. ^{1}H NMR spectrum of 4B

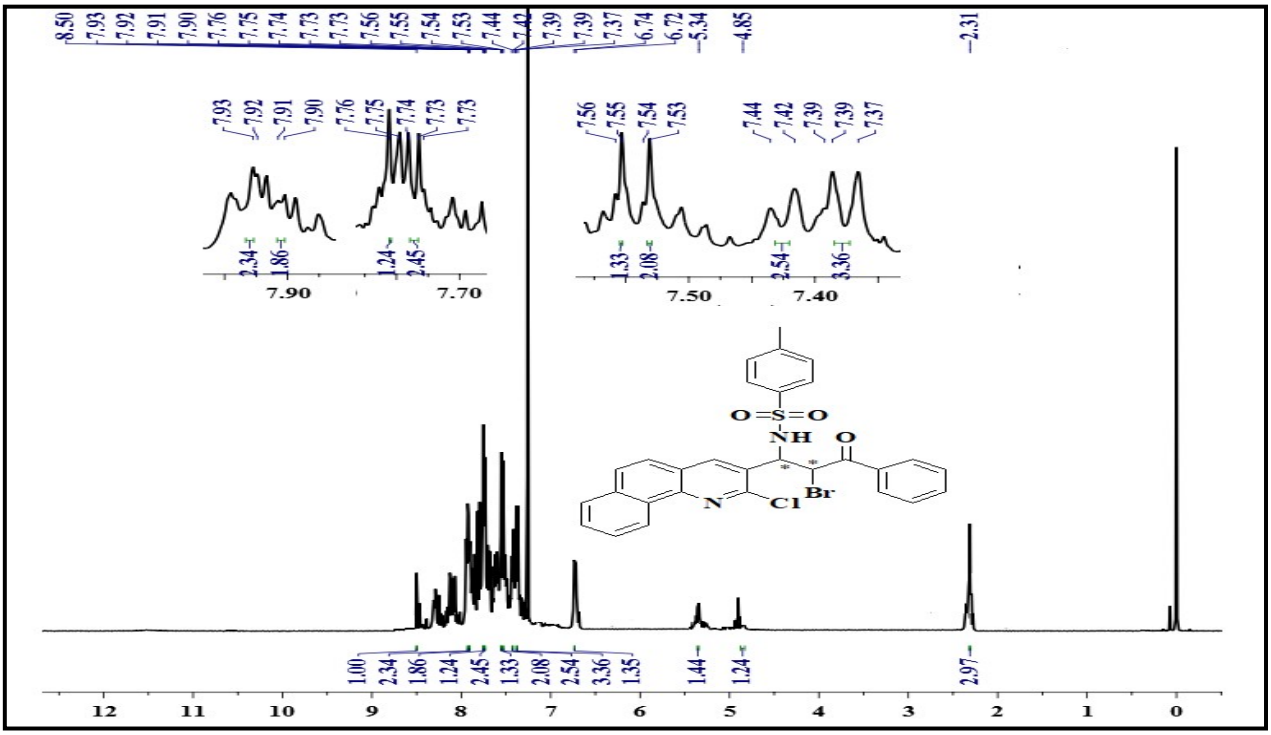

Fig. S16. ^{1}H NMR spectrum of 5B

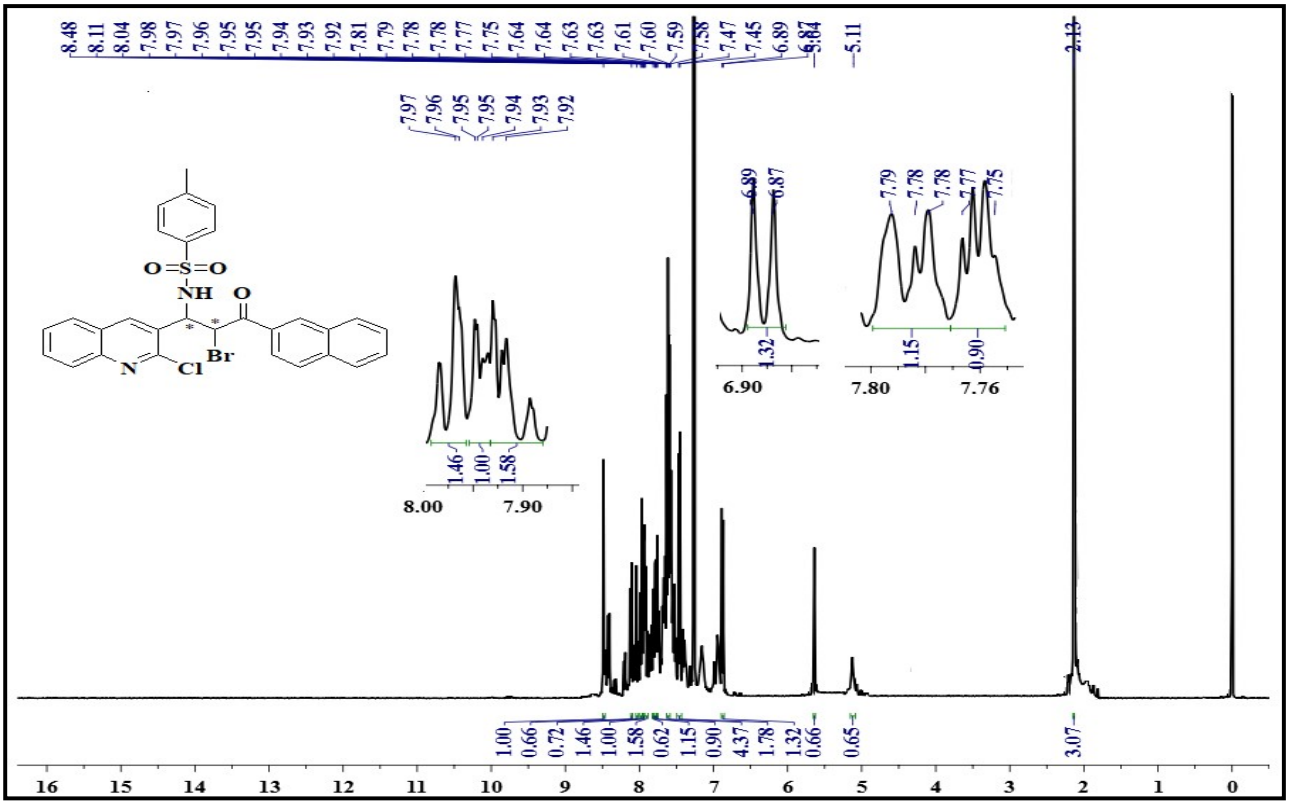

Fig. S17. ^{1}H NMR spectrum of 6B

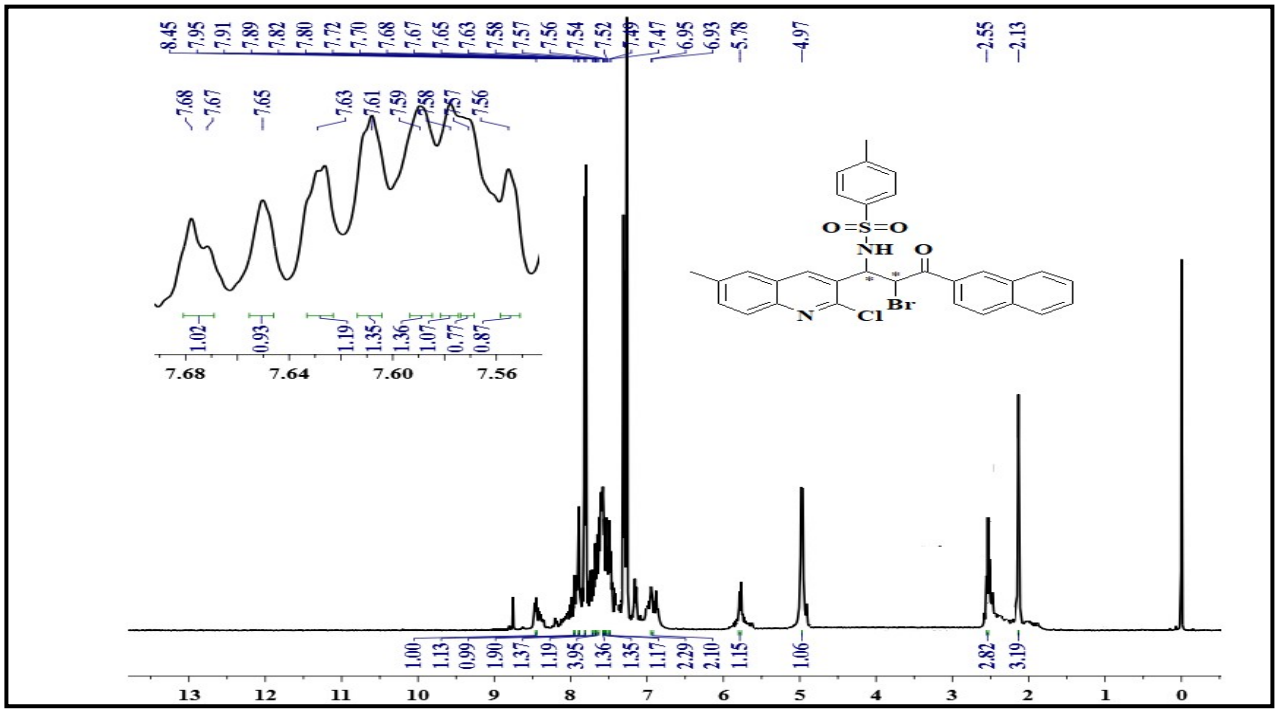

Fig. S18. ^{1}H NMR spectrum of 7B

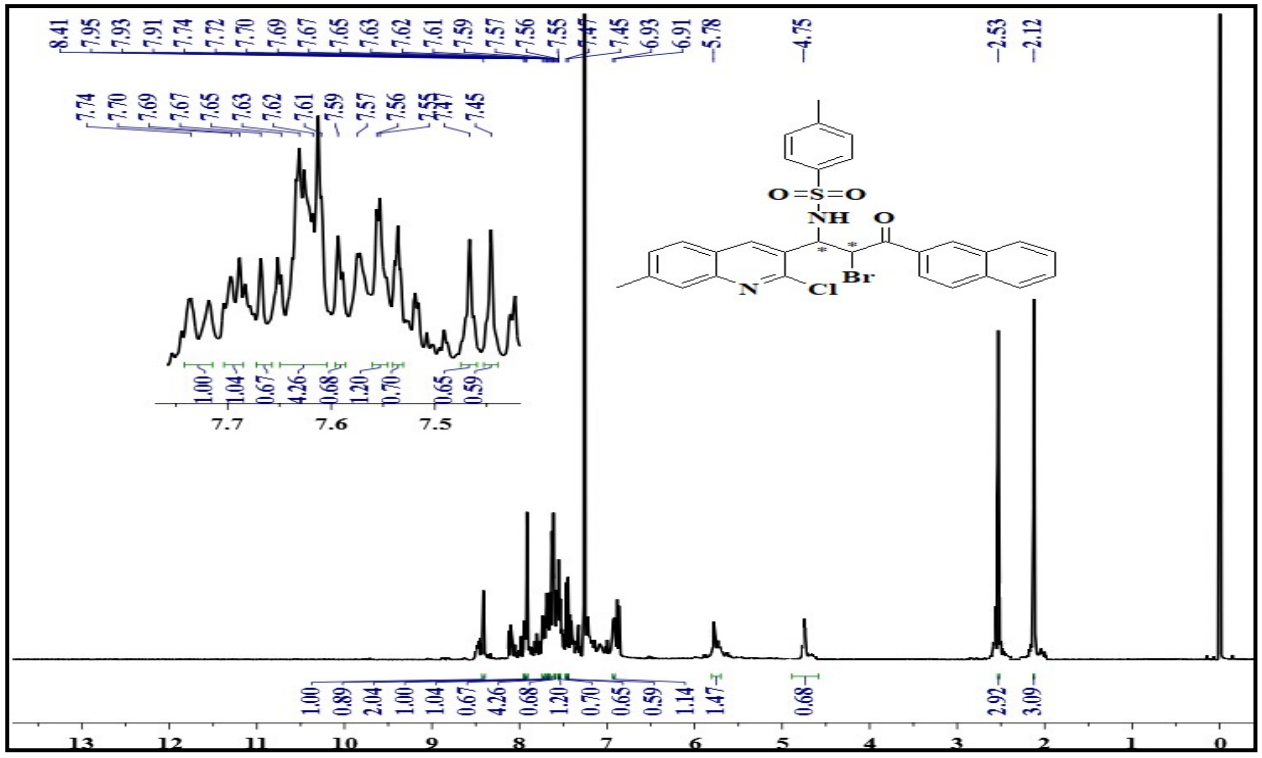

Fig. S19. ^{1}H NMR spectrum of 8B

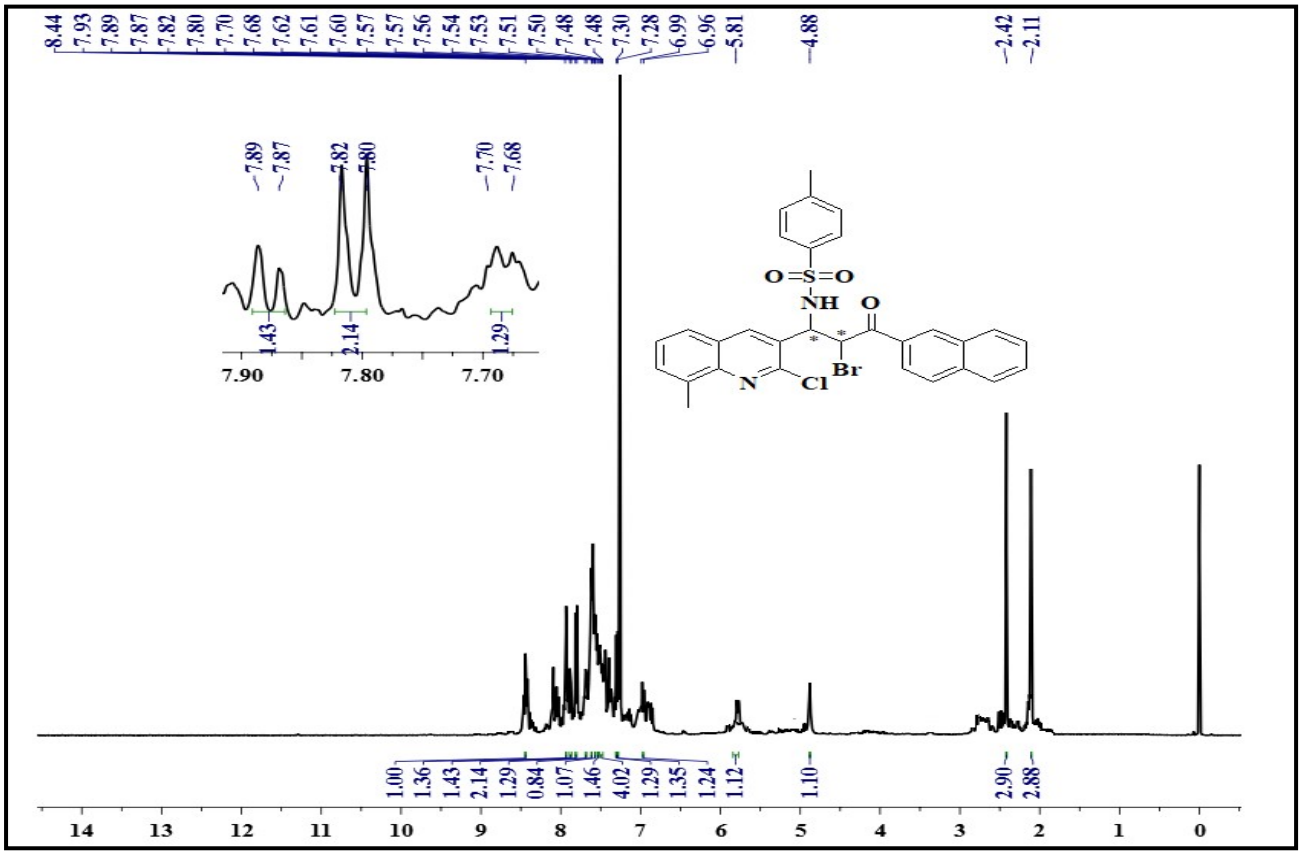

Fig. S20. ^{1}H NMR spectrum of 9B

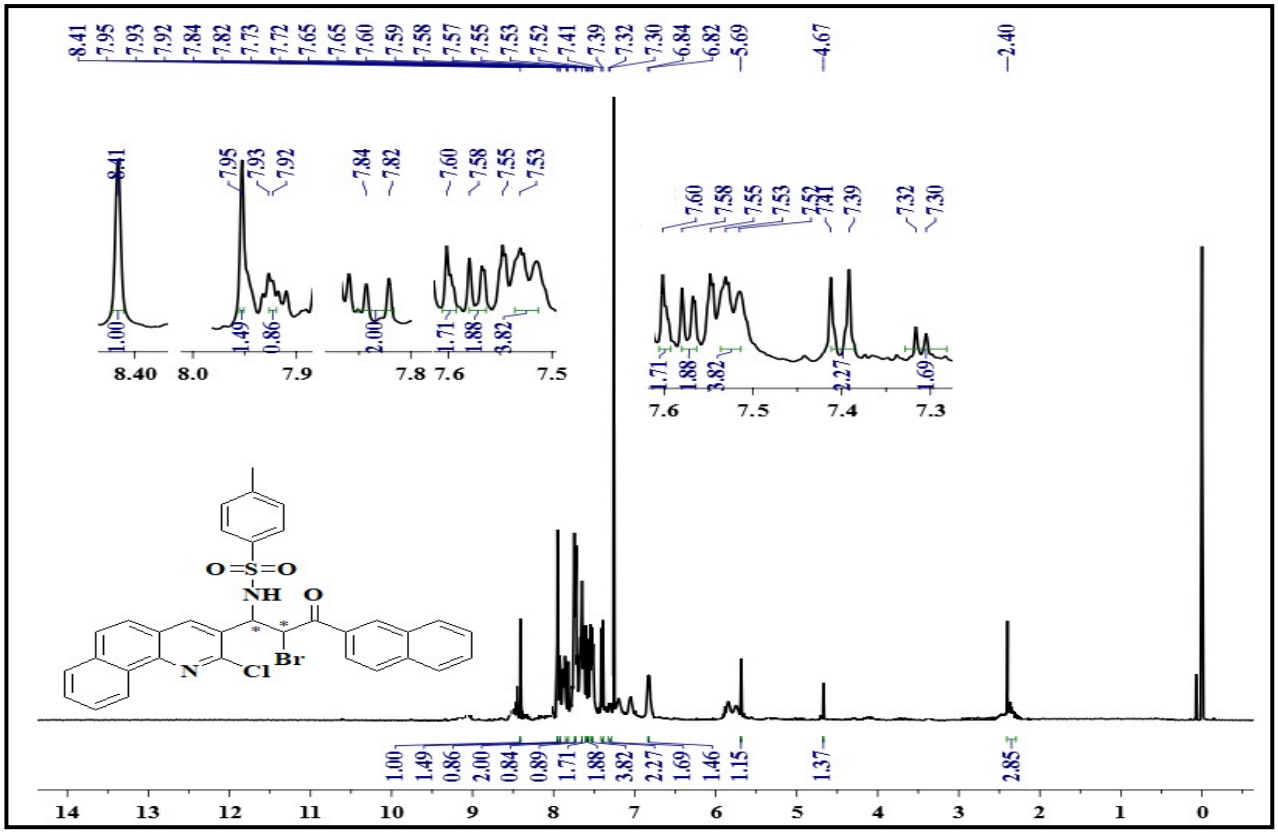

Fig. S21. ^{1}H NMR spectrum of 10B

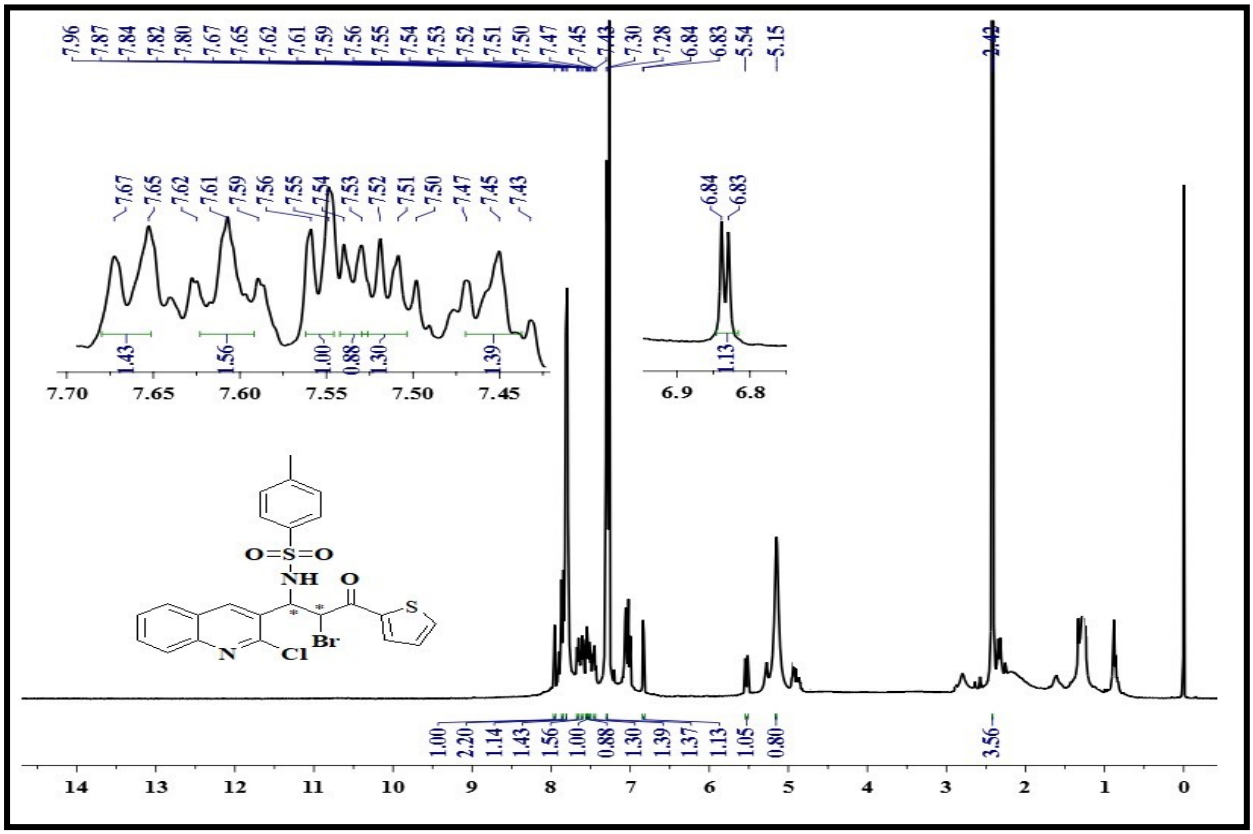

Fig. S22. ^{1}H NMR spectrum of 11B

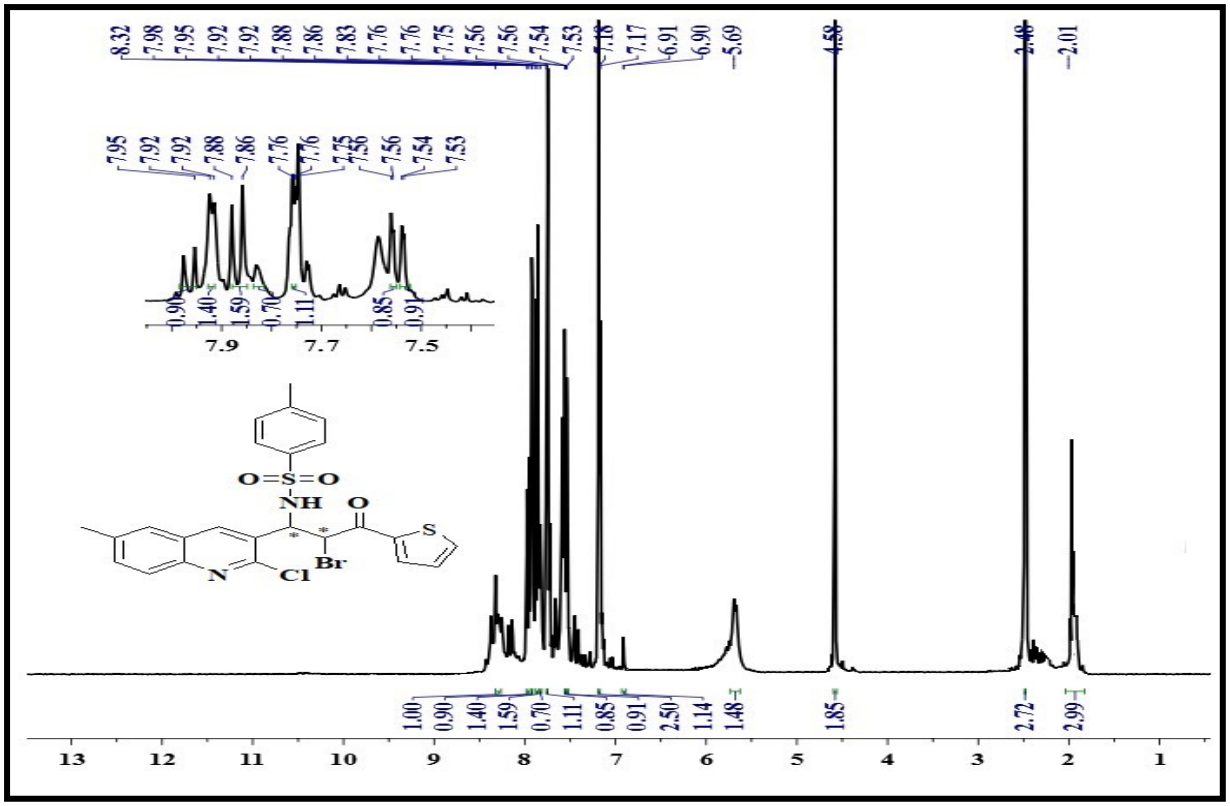

Fig. S23. ^{1}H NMR spectrum of 12B

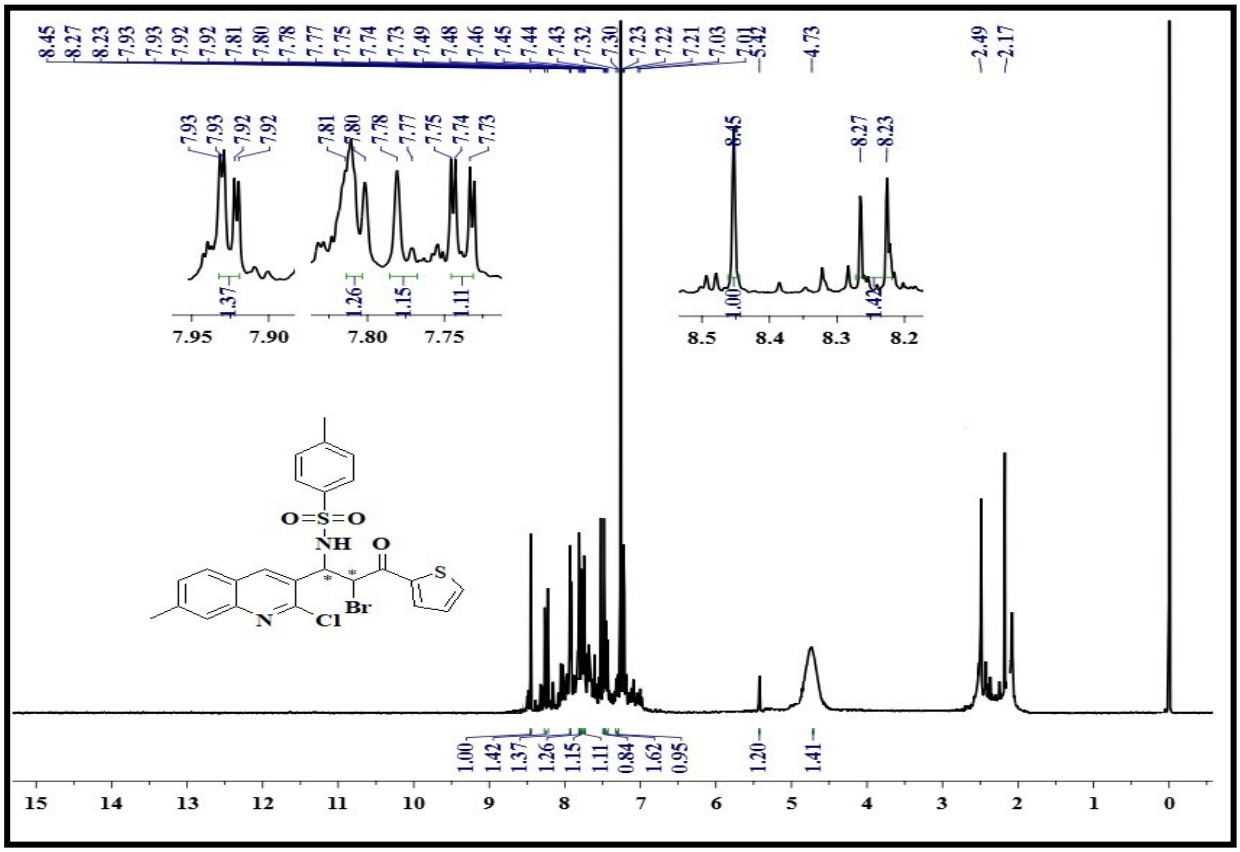

Fig. S24. ^{1}H NMR spectrum of 13B

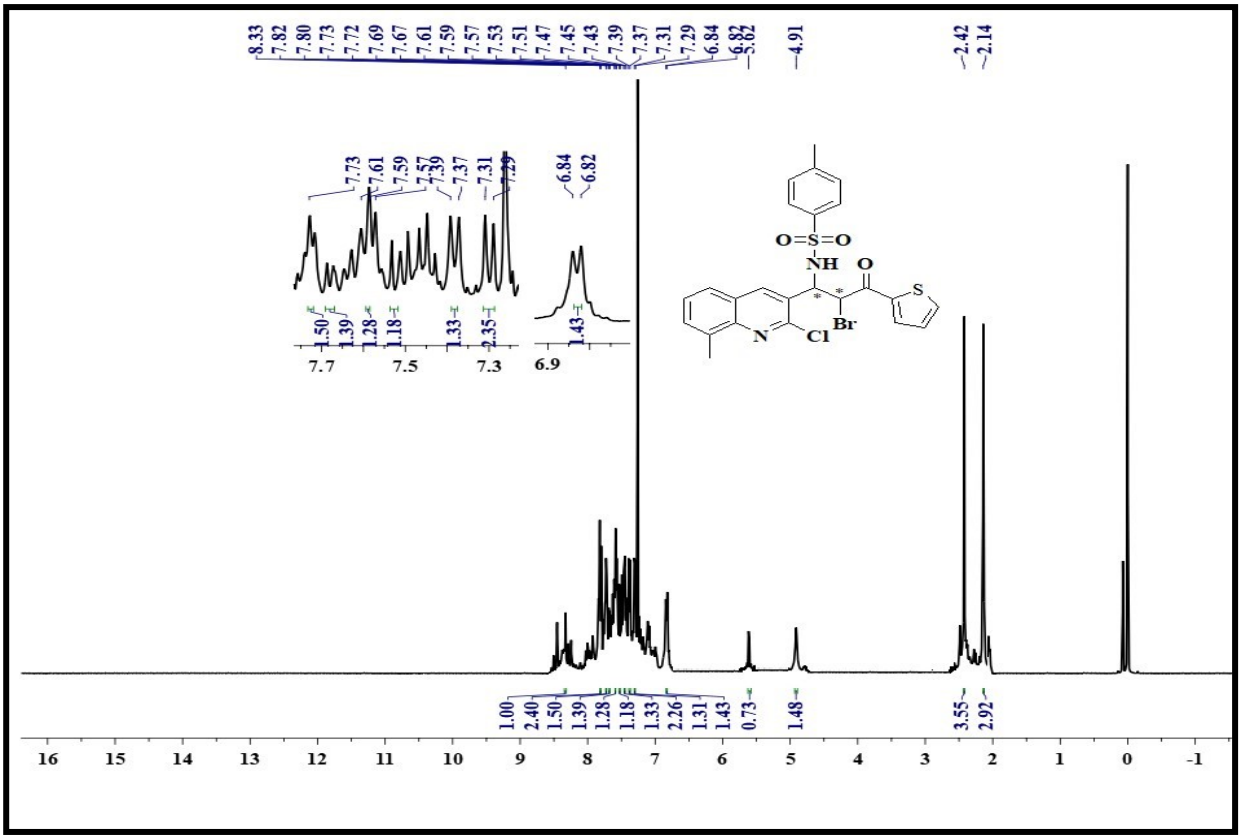

Fig. S25. ^{1}H NMR spectrum of 14B

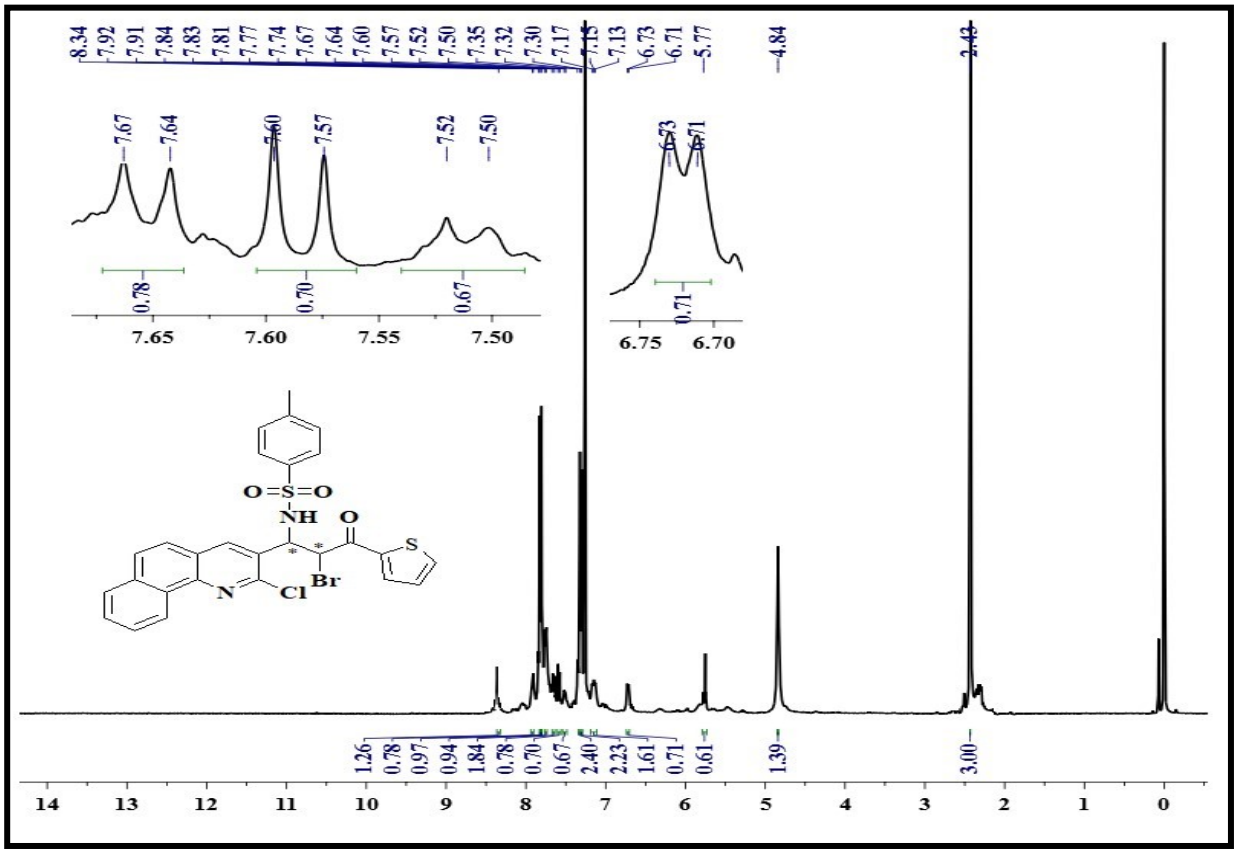

Fig. S26. ^{1}H NMR spectrum of 15B

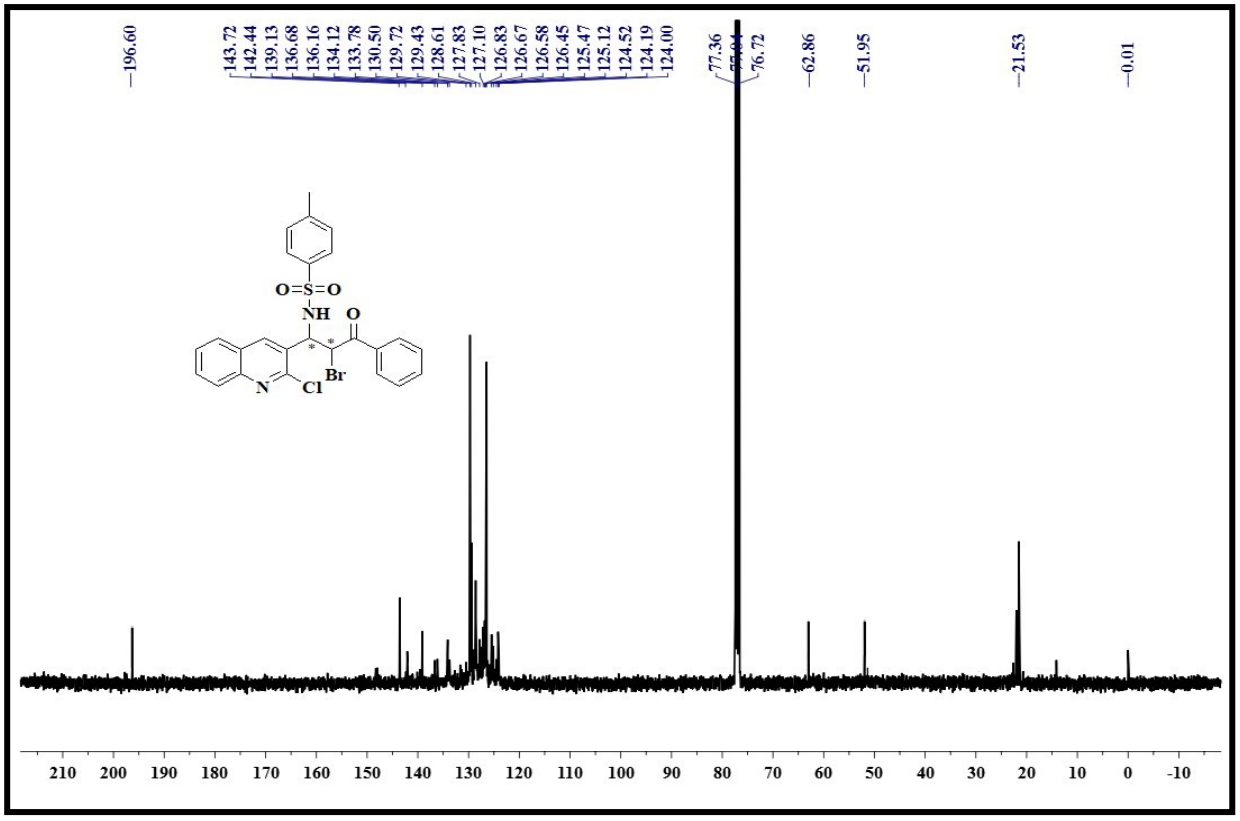

Fig. S27. ^{13}C NMR spectrum of 1B

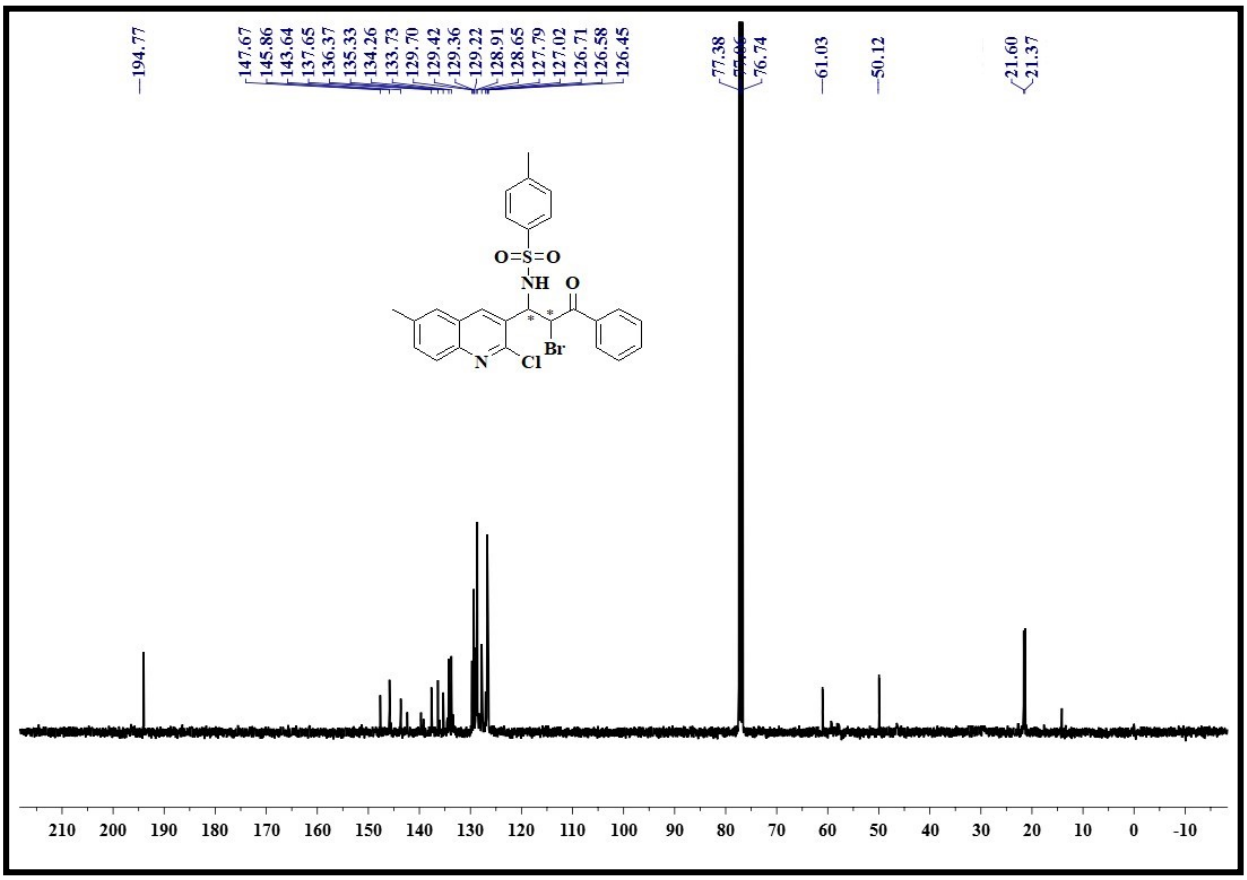

Fig. S28. ^{13}C NMR spectrum of 2B

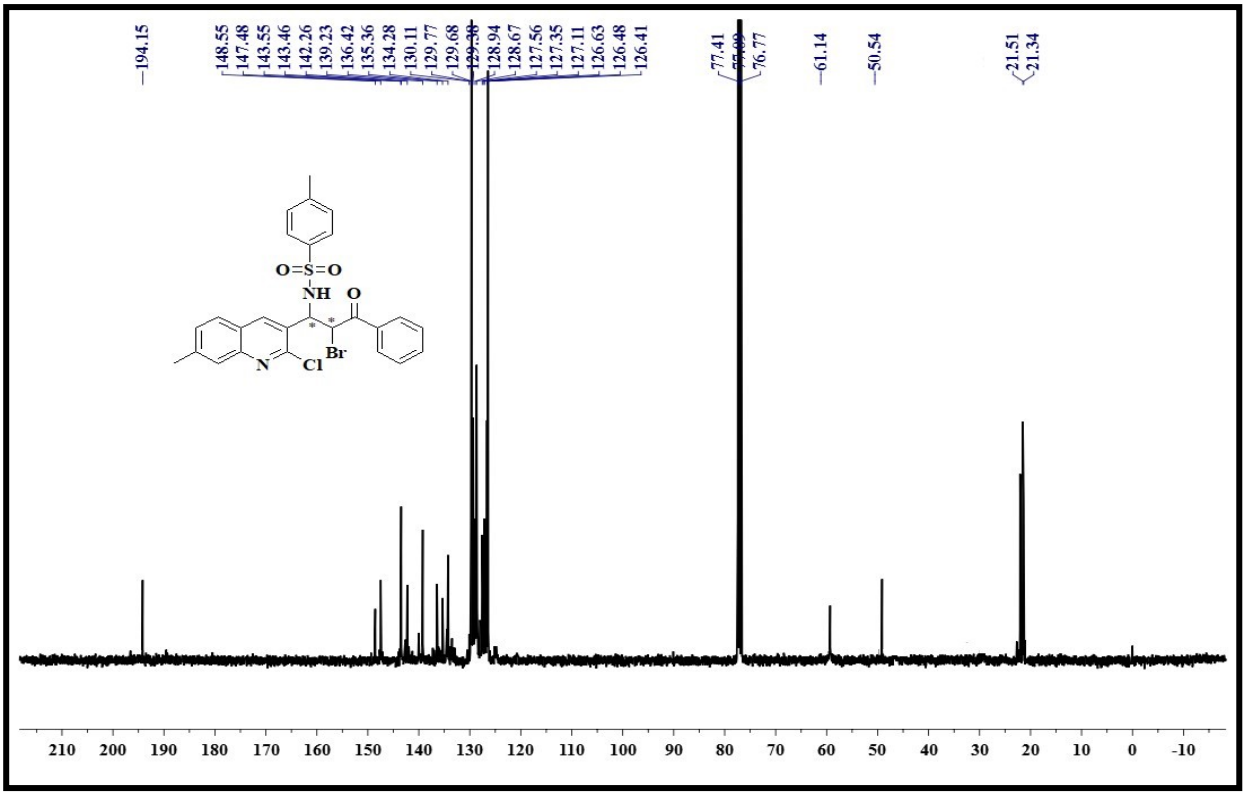

Fig. S29. ^{13}C NMR spectrum of 3B

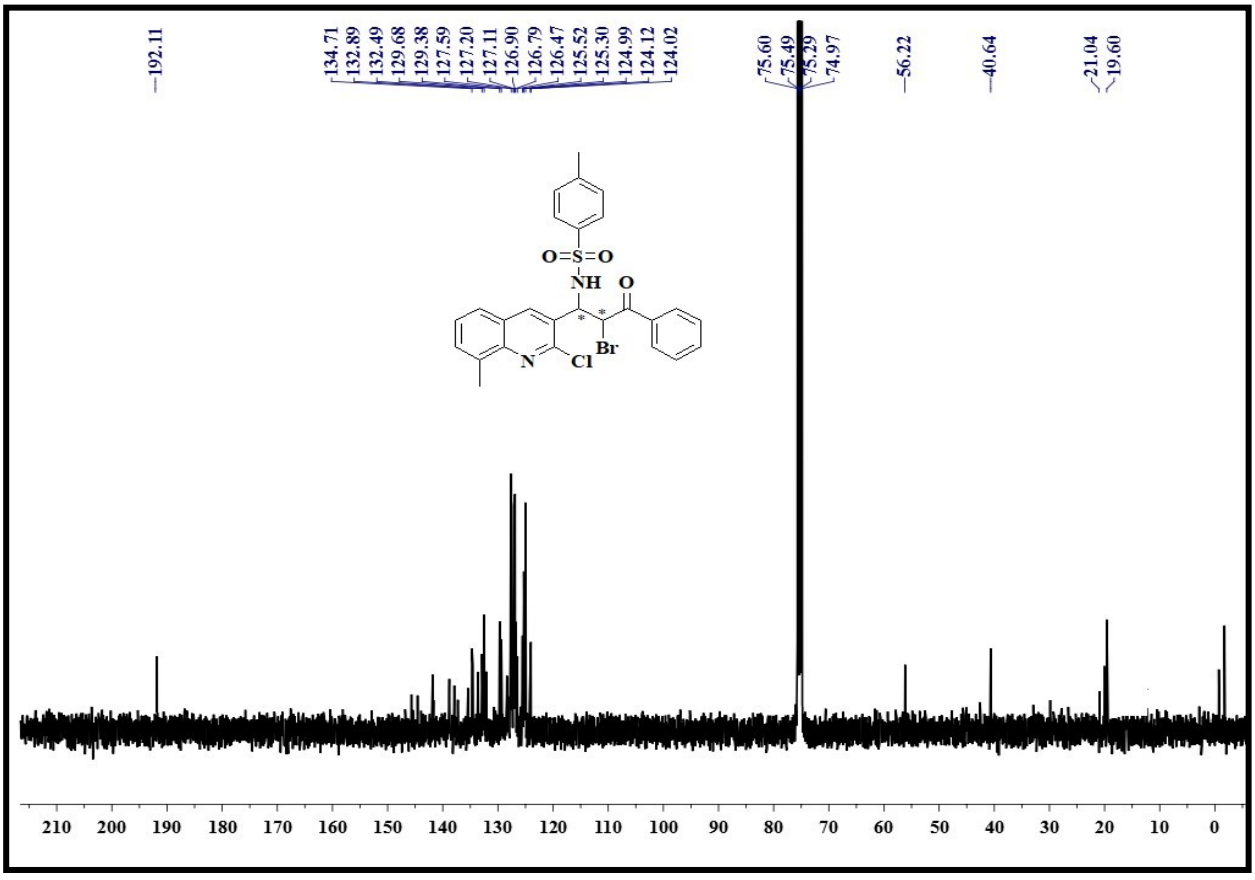

Fig. S30. ^{13}C NMR spectrum of 4B

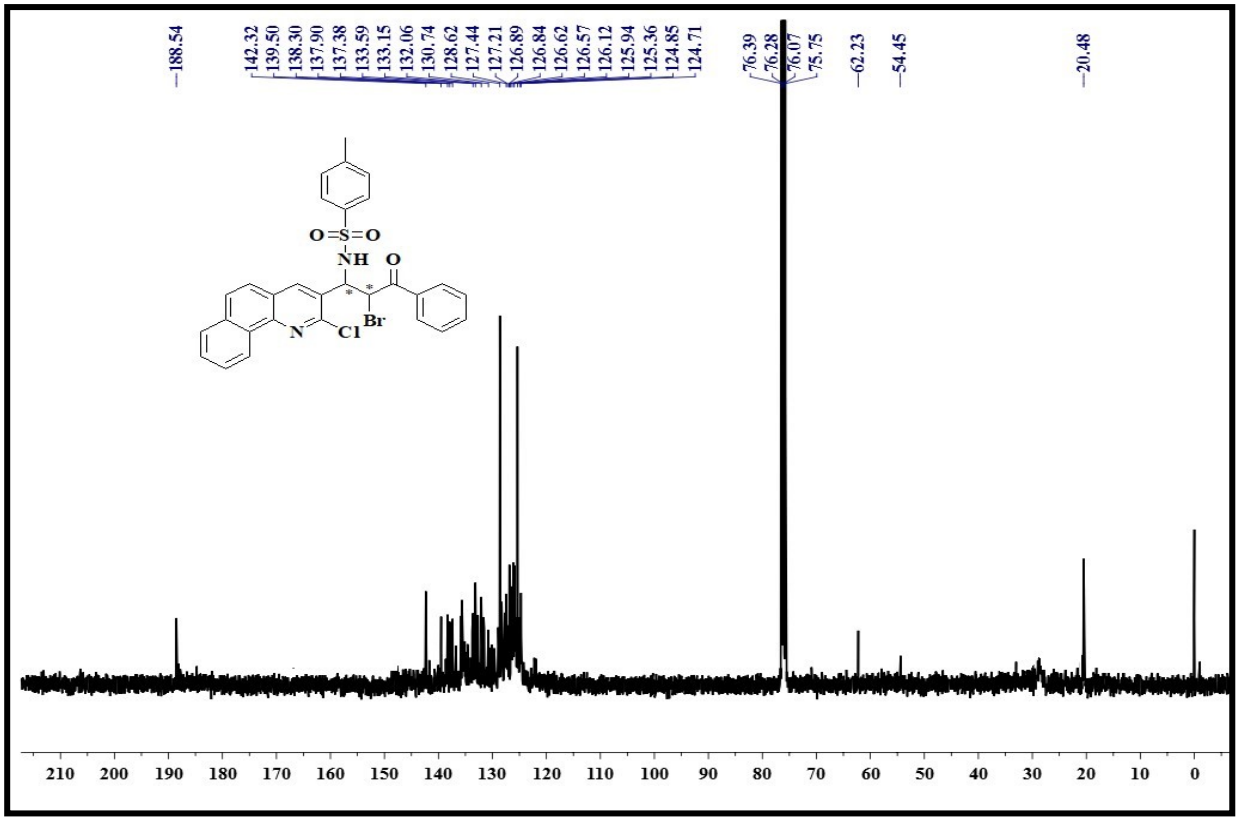

Fig. S31. ^{13}C NMR spectrum of 5B

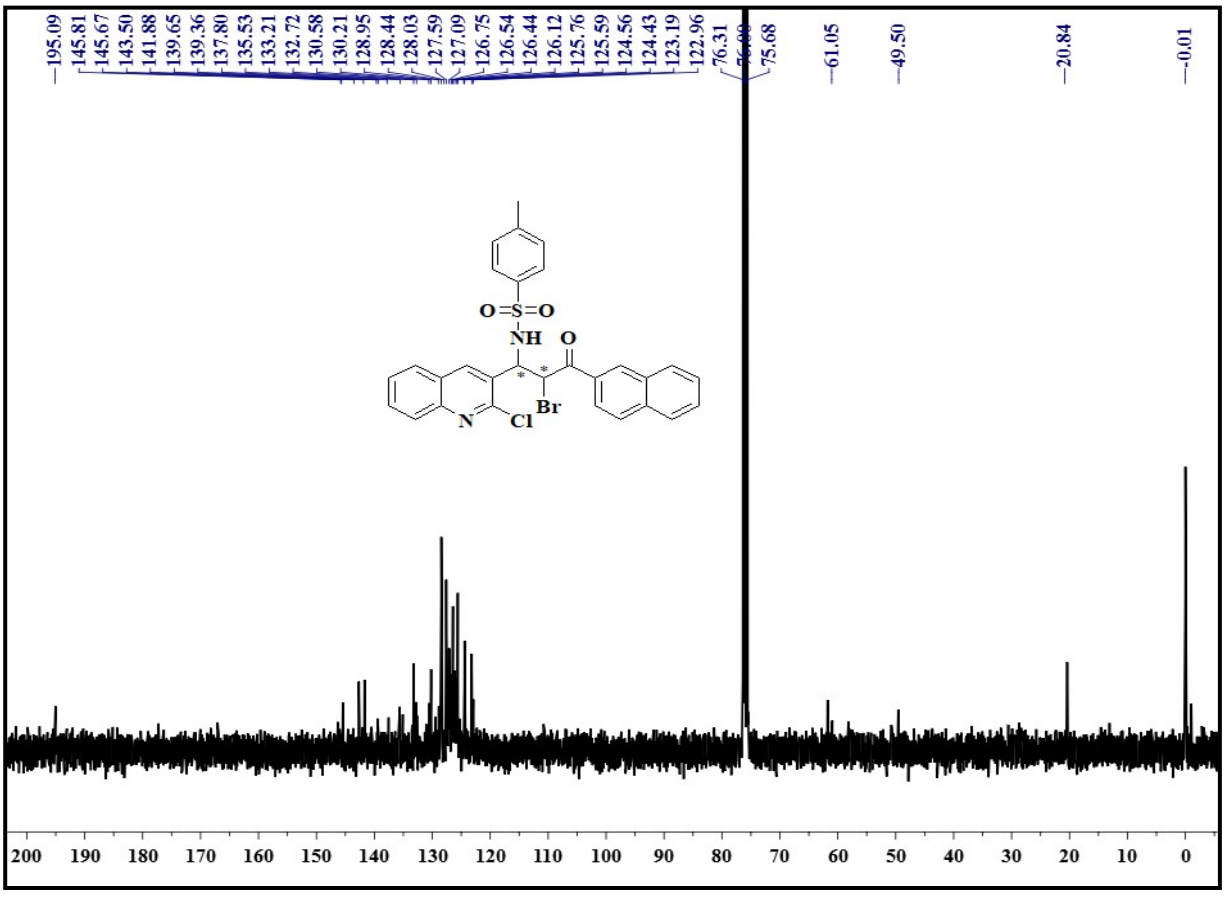

Fig. S32. ^{13}C NMR spectrum of 6B

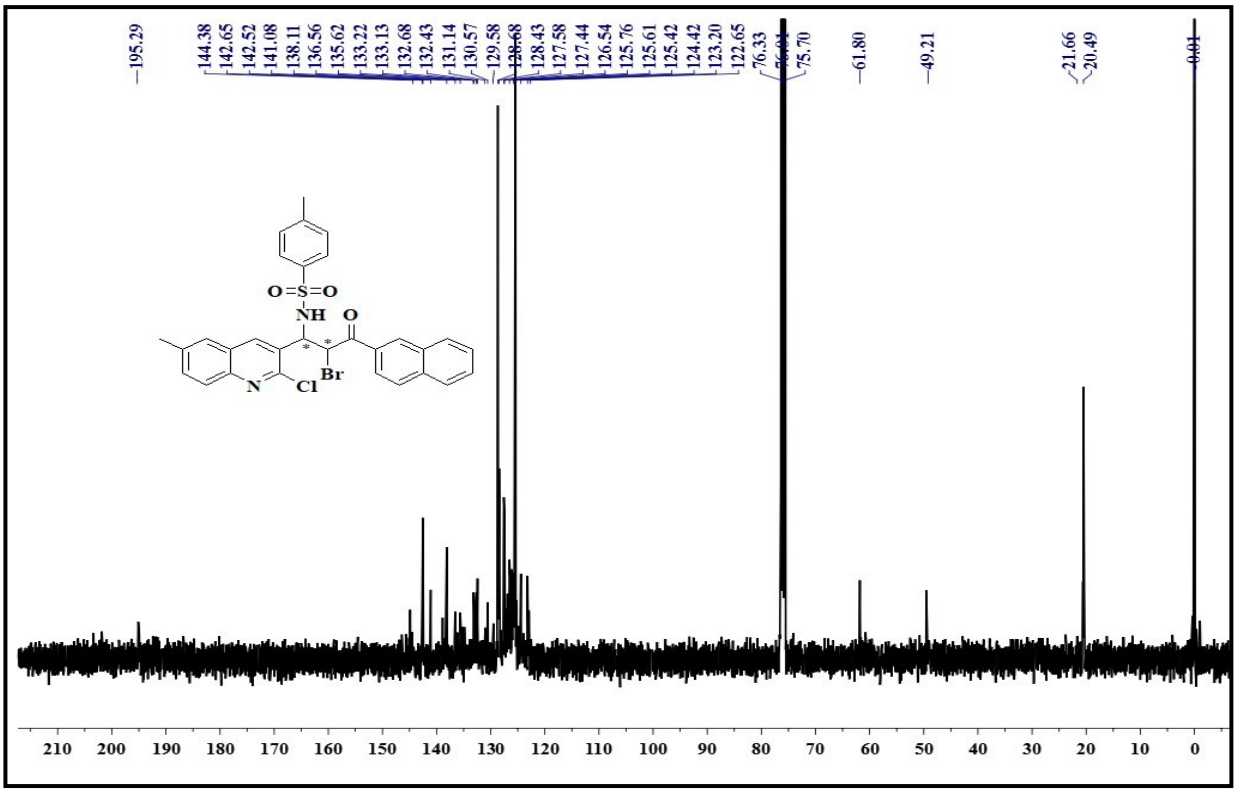

Fig. S33. ^{13}C NMR spectrum of 7B

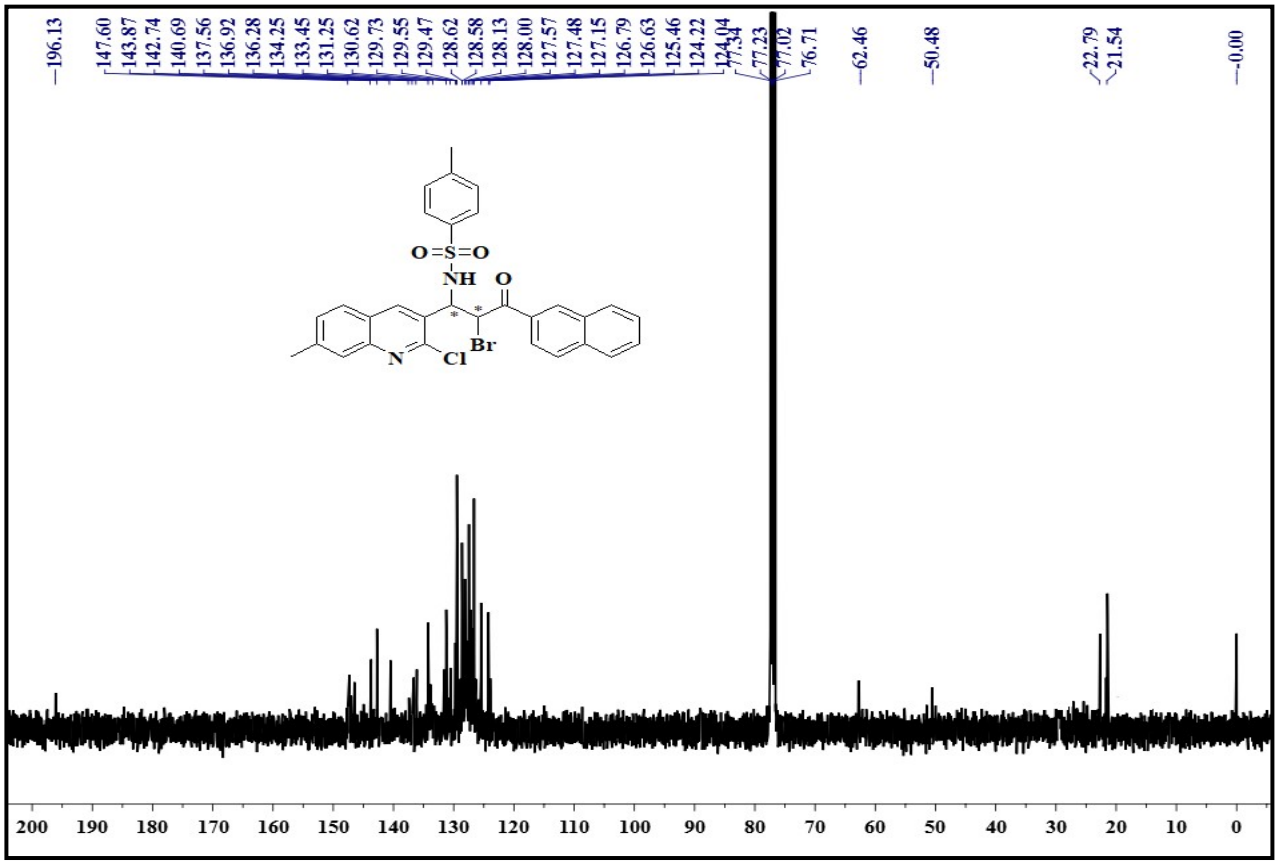

Fig. S34. ^{13}C NMR spectrum of 8B

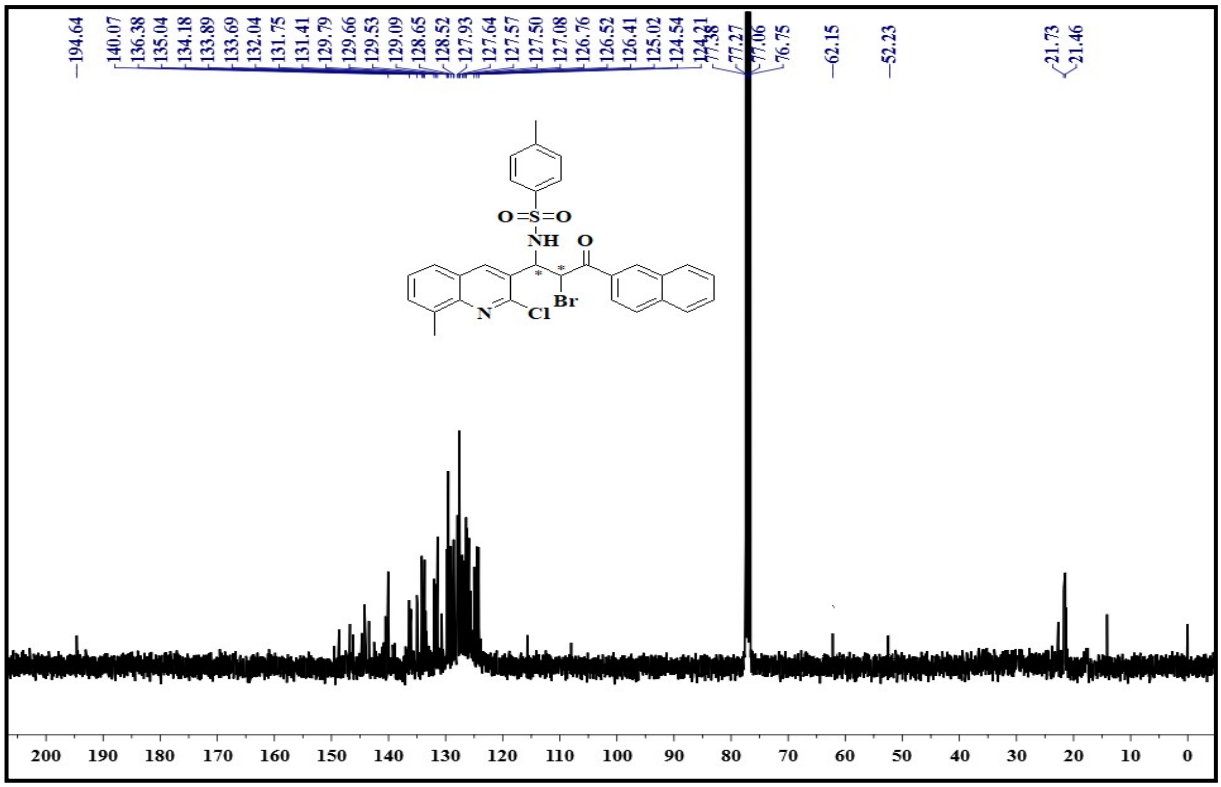

Fig. S35. ^{13}C NMR spectrum of 9B

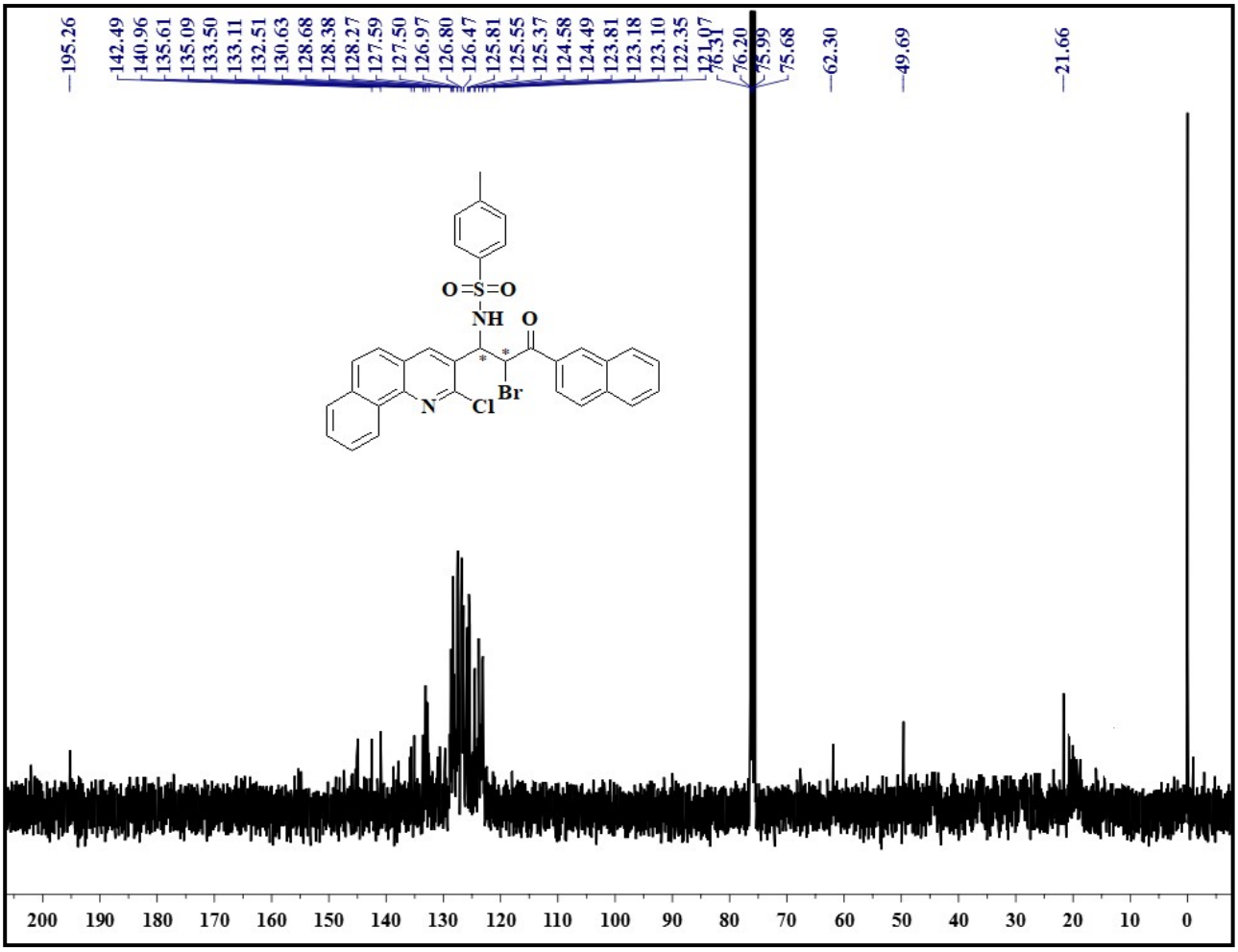

Fig. S36. ^{13}C NMR spectrum of 10B

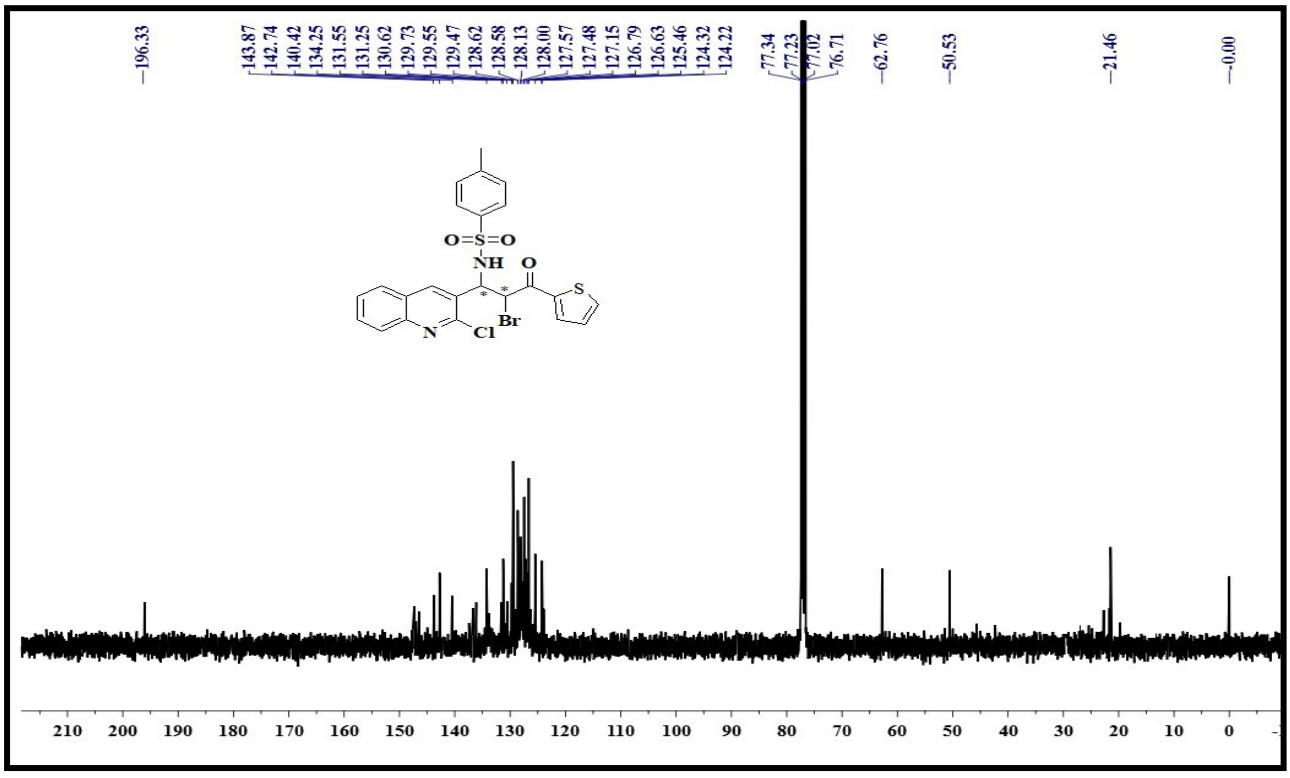

Fig. S37. ^{13}C NMR spectrum of 11B

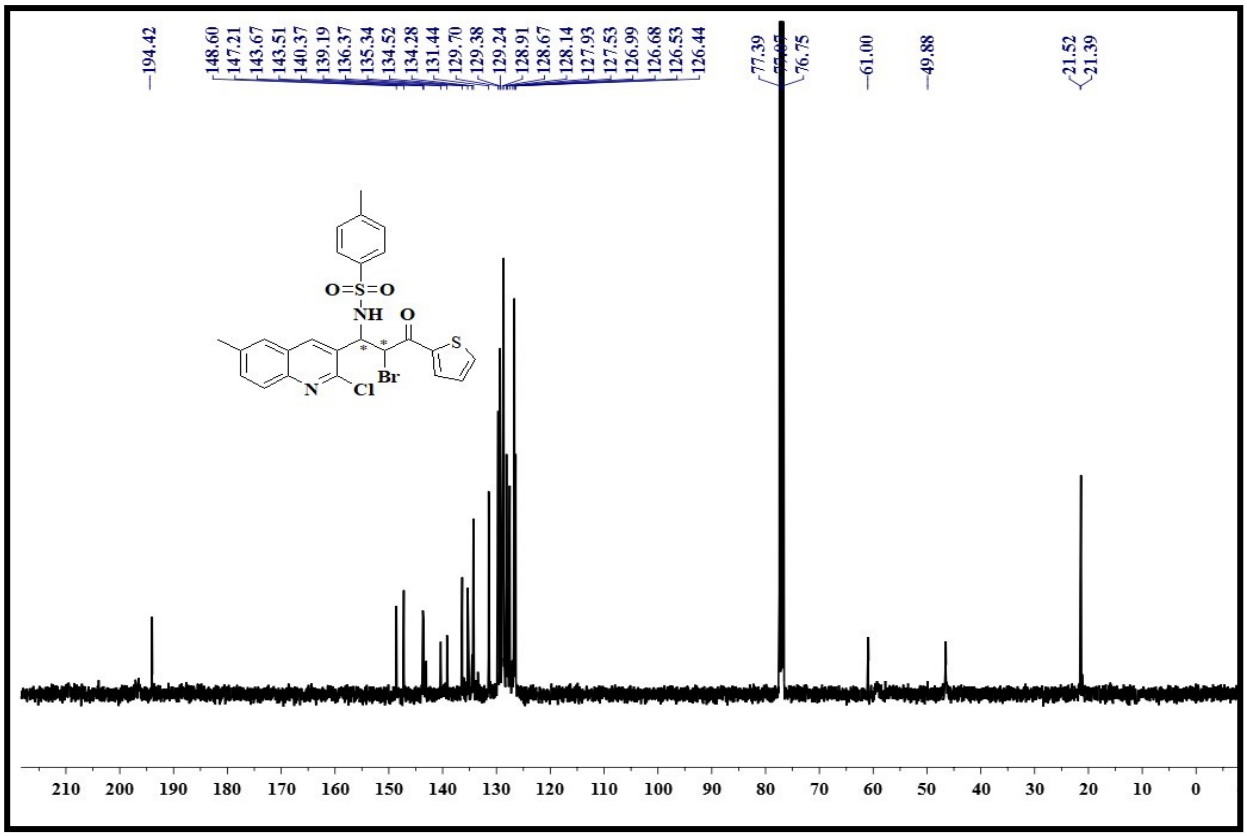

Fig. 38. ^{13}C NMR spectrum of 12B

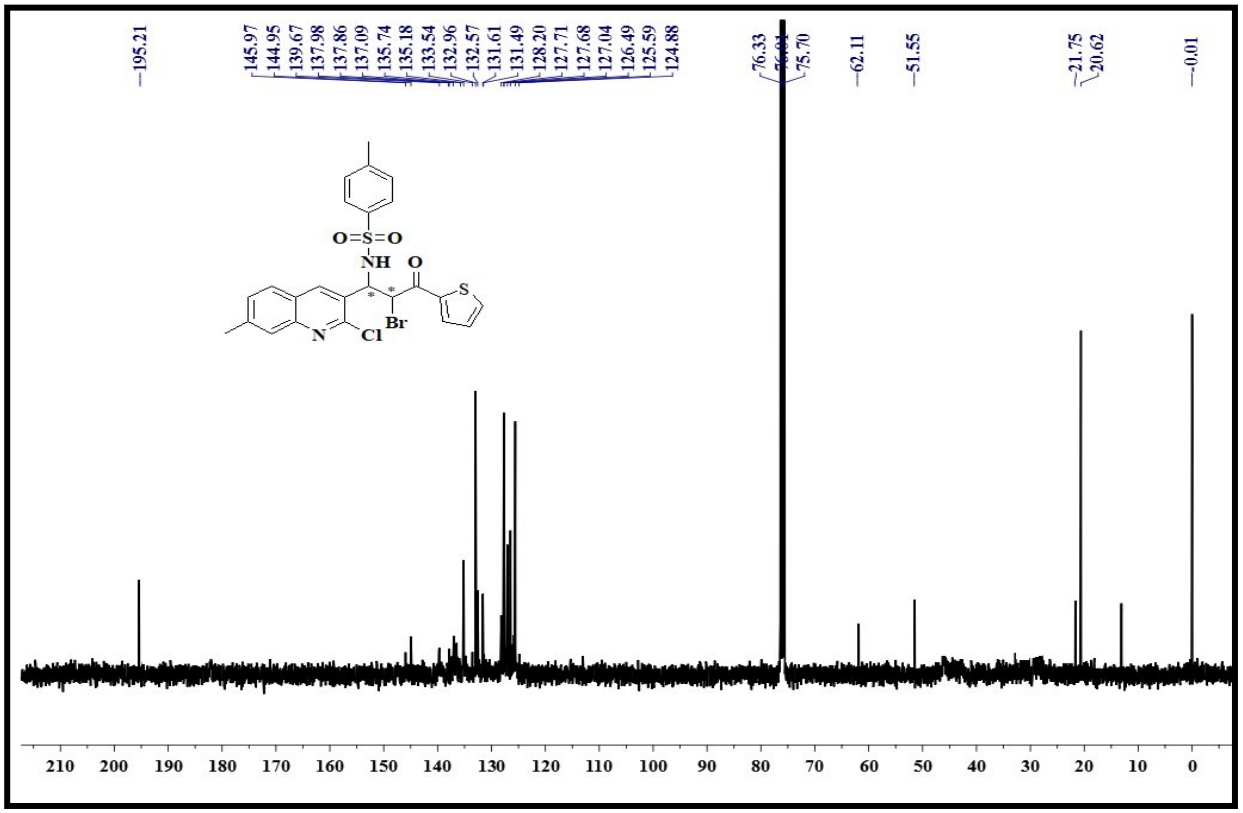

Fig. S39. ^{13}C NMR spectrum of 13B

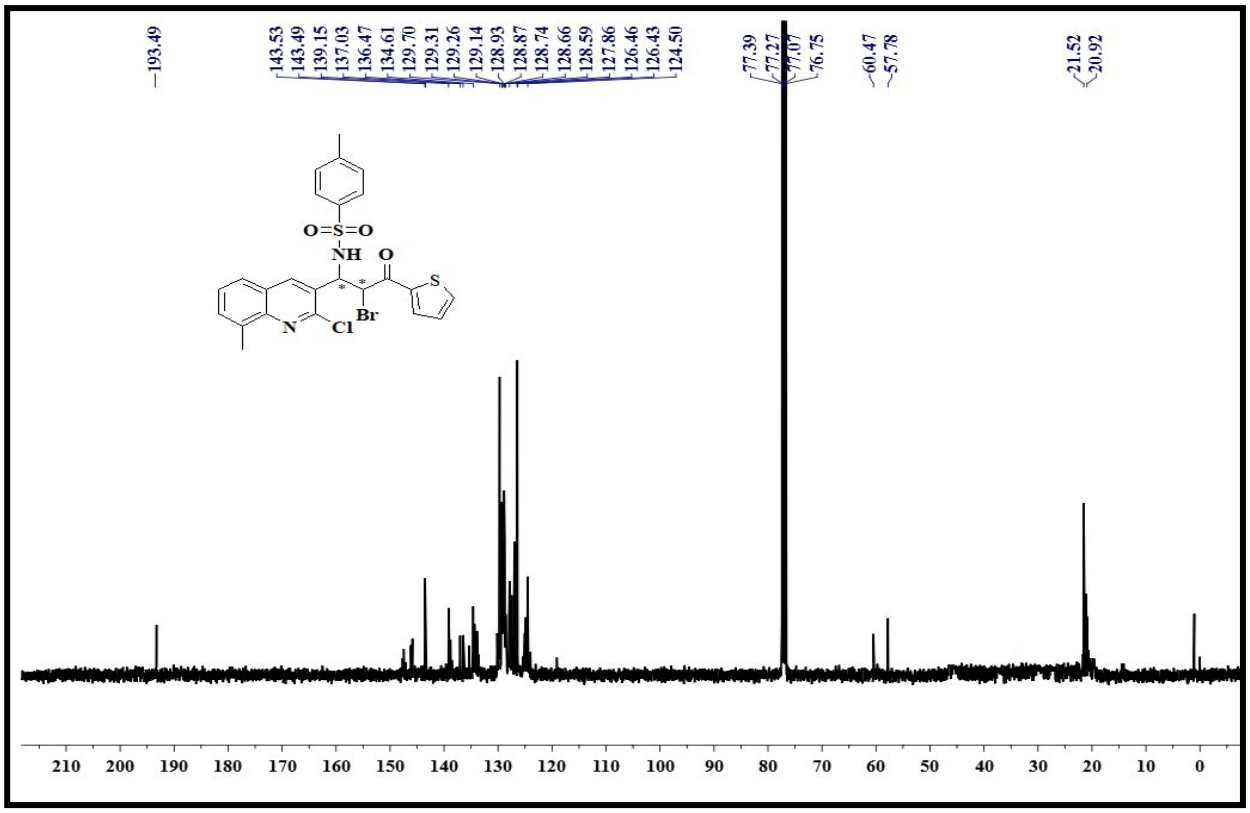

Fig. S40. ^{13}C NMR spectrum of 14B

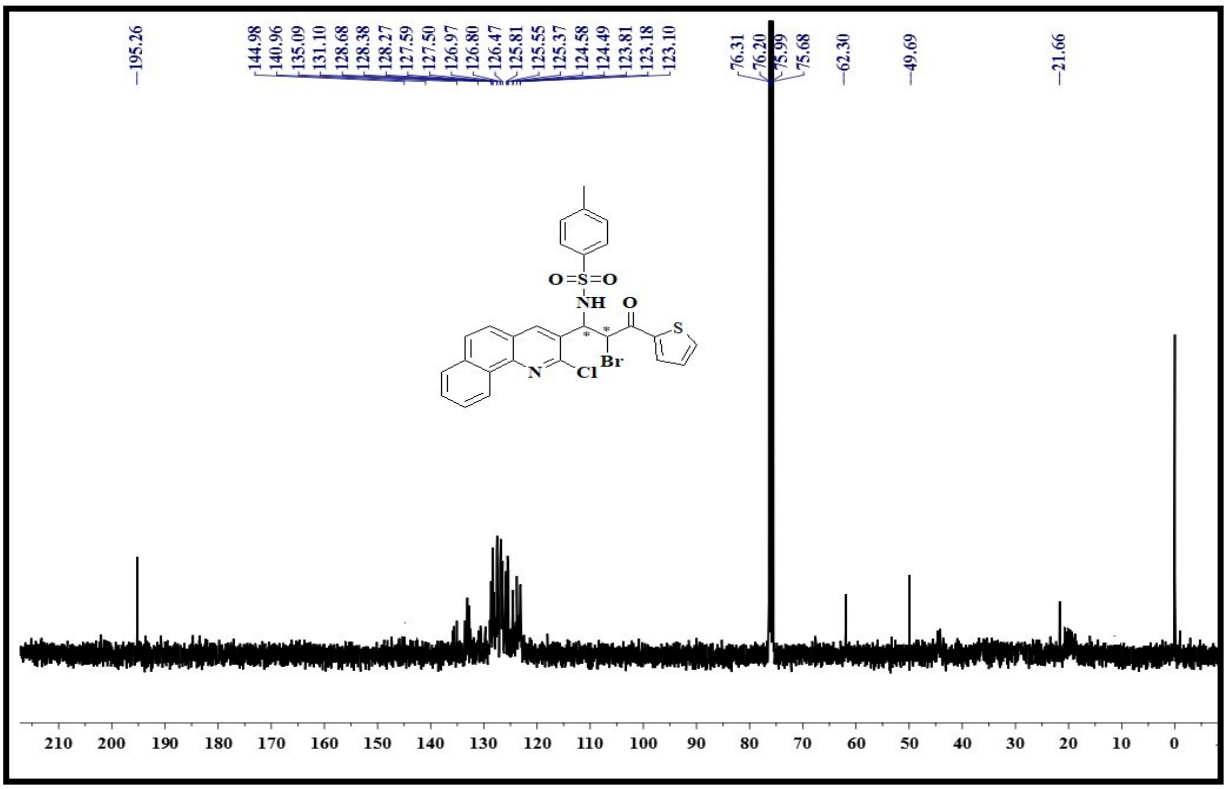

Fig. S41. ^{13}C NMR spectrum of 15B

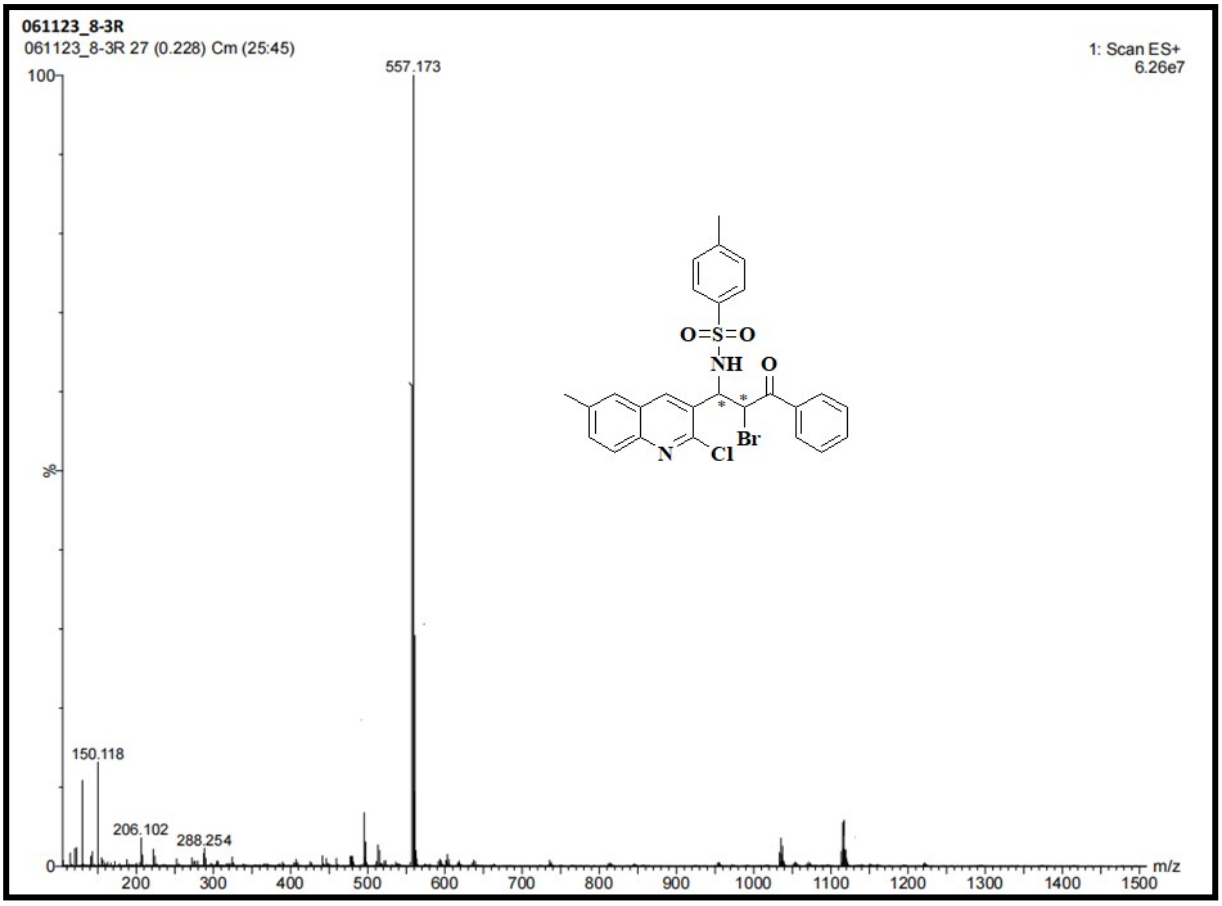

Fig. S42. Mass spectrum of 2B

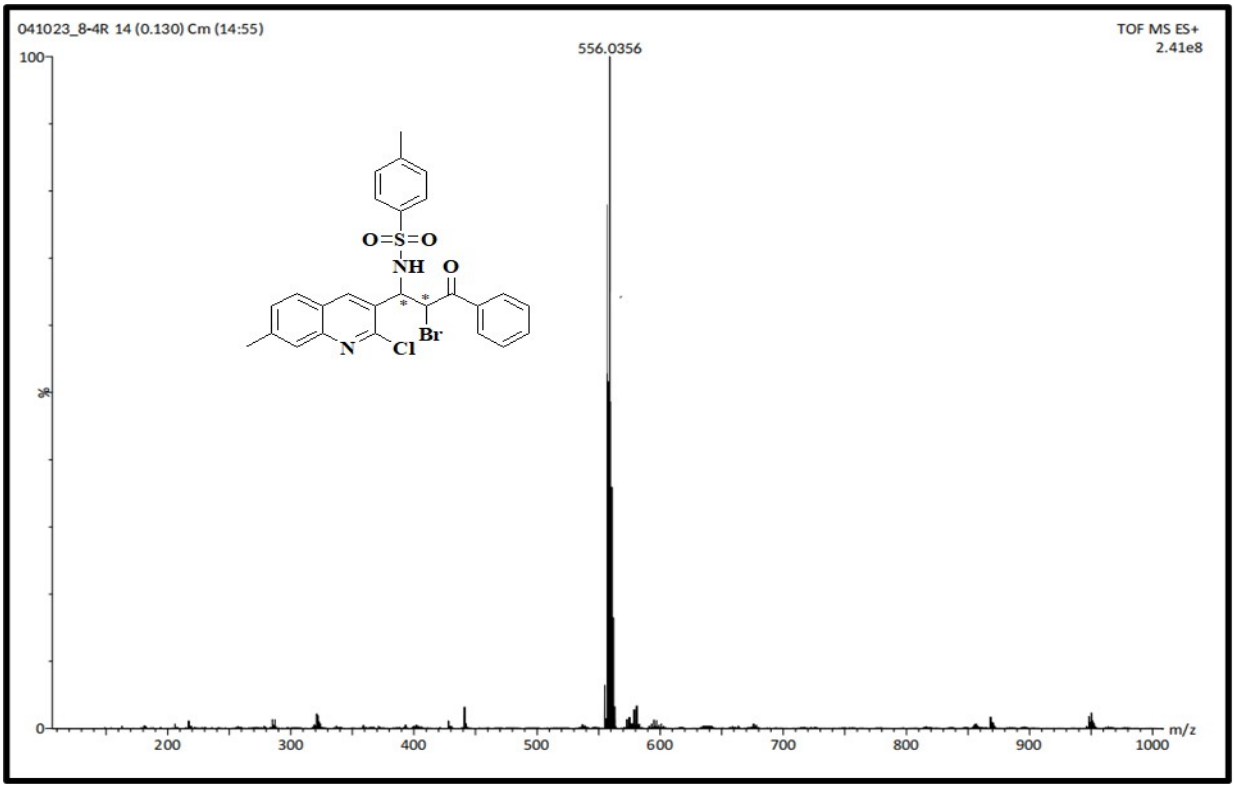

Fig. S43. Mass spectrum of 3B

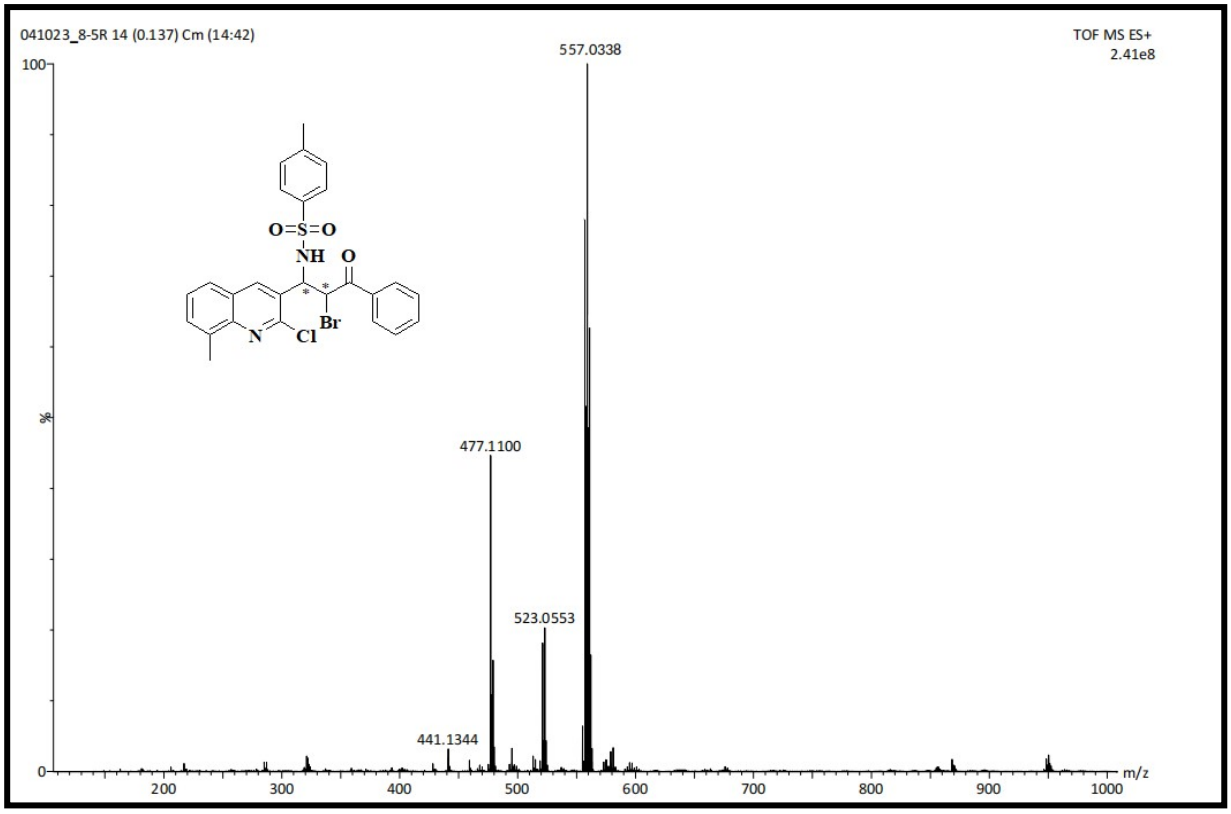

Fig. S44. Mass spectrum of 4B

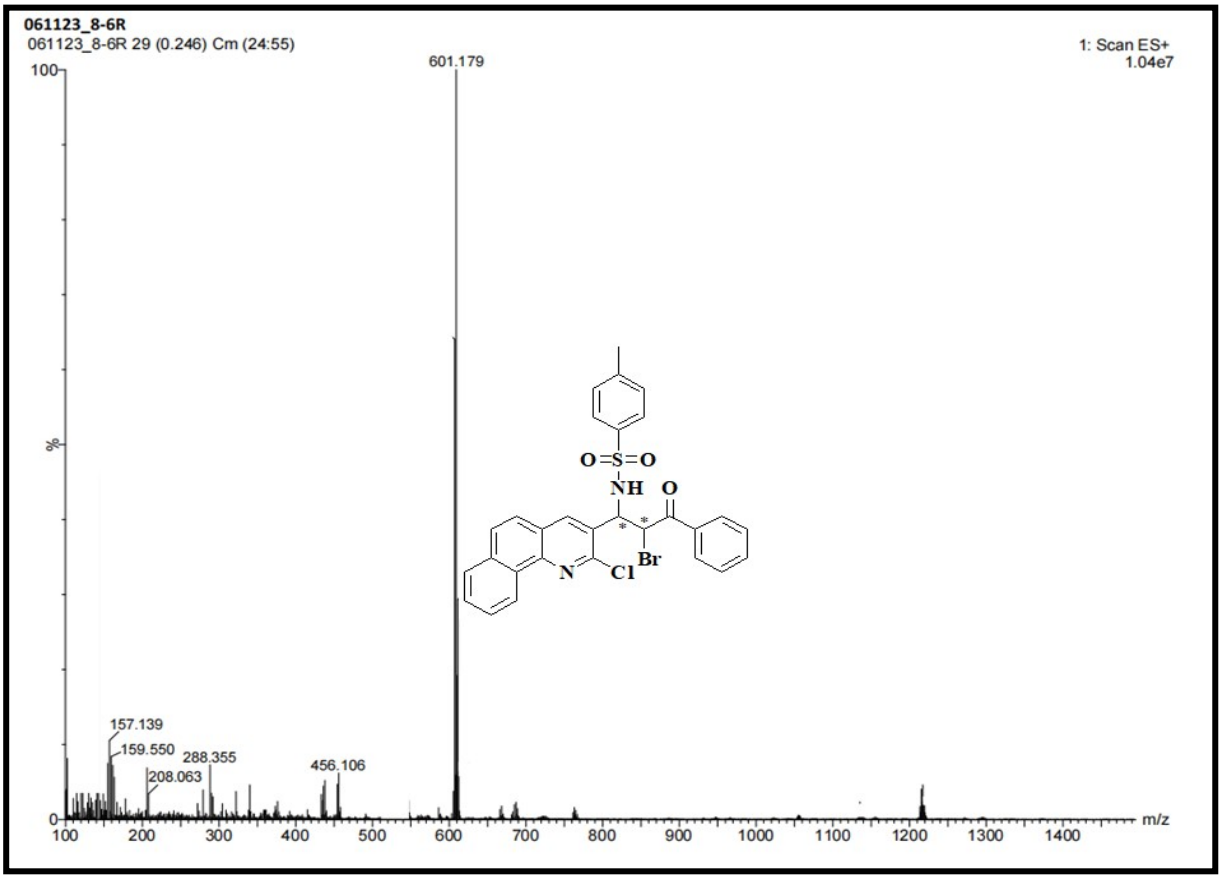

Fig. S45. Mass spectrum of 5B

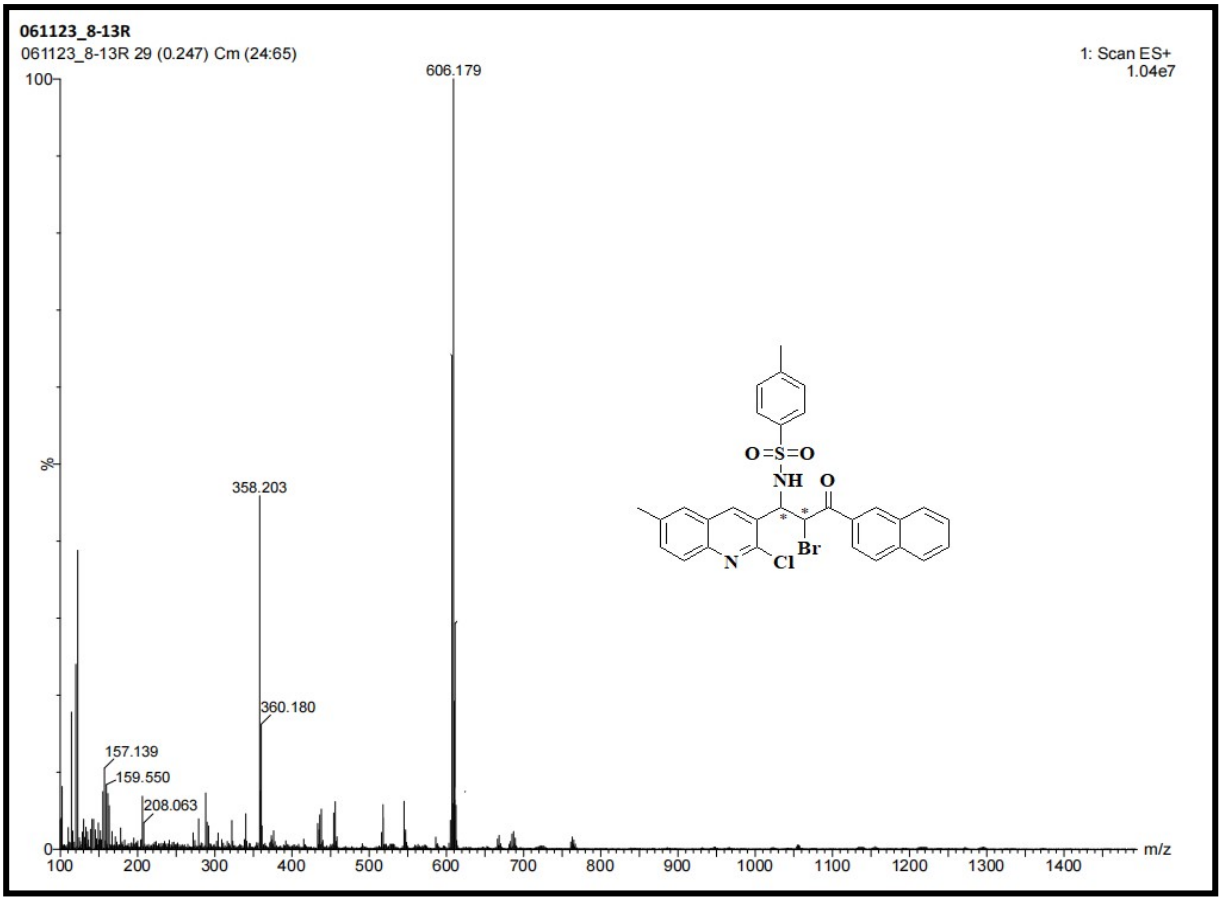

Fig. S46. Mass spectrum of 7B

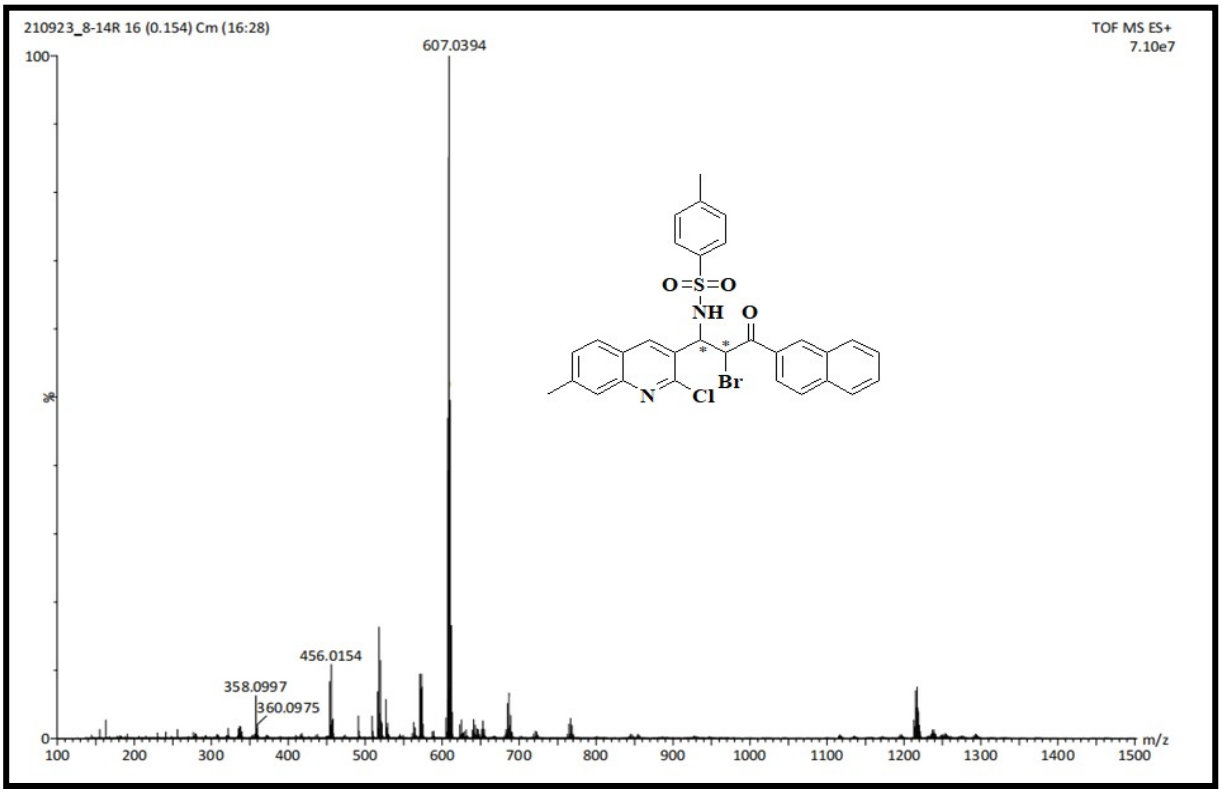

Fig. S47. Mass spectrum of 8B

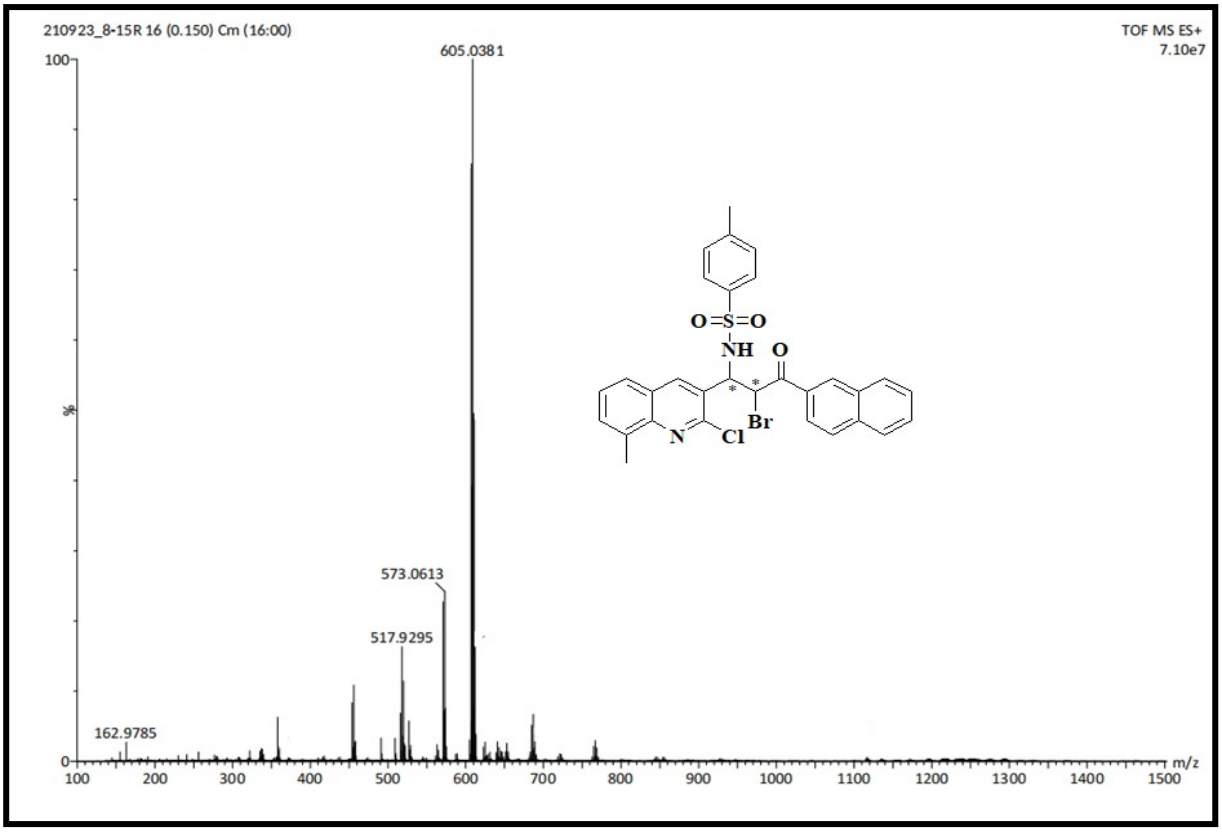

Fig. S48. Mass spectrum of 9B

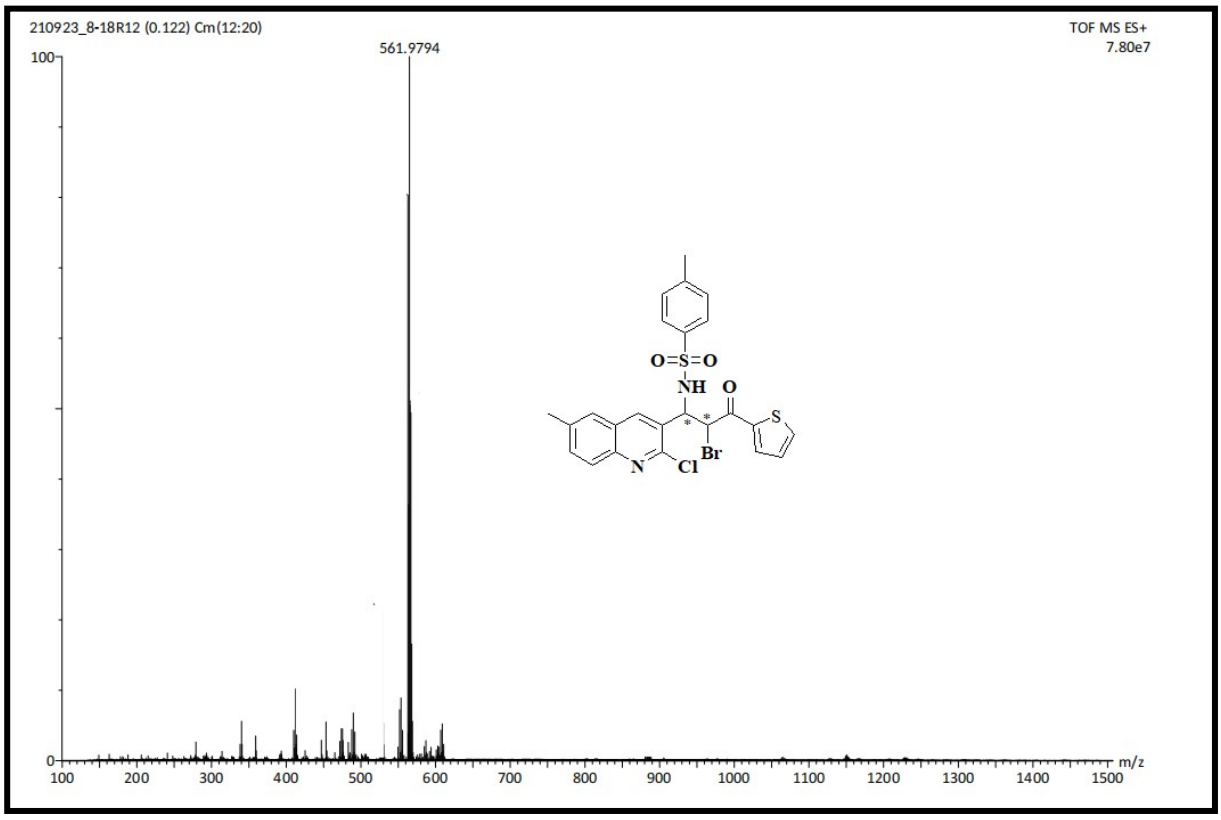

Fig. S49. Mass spectrum of 12B

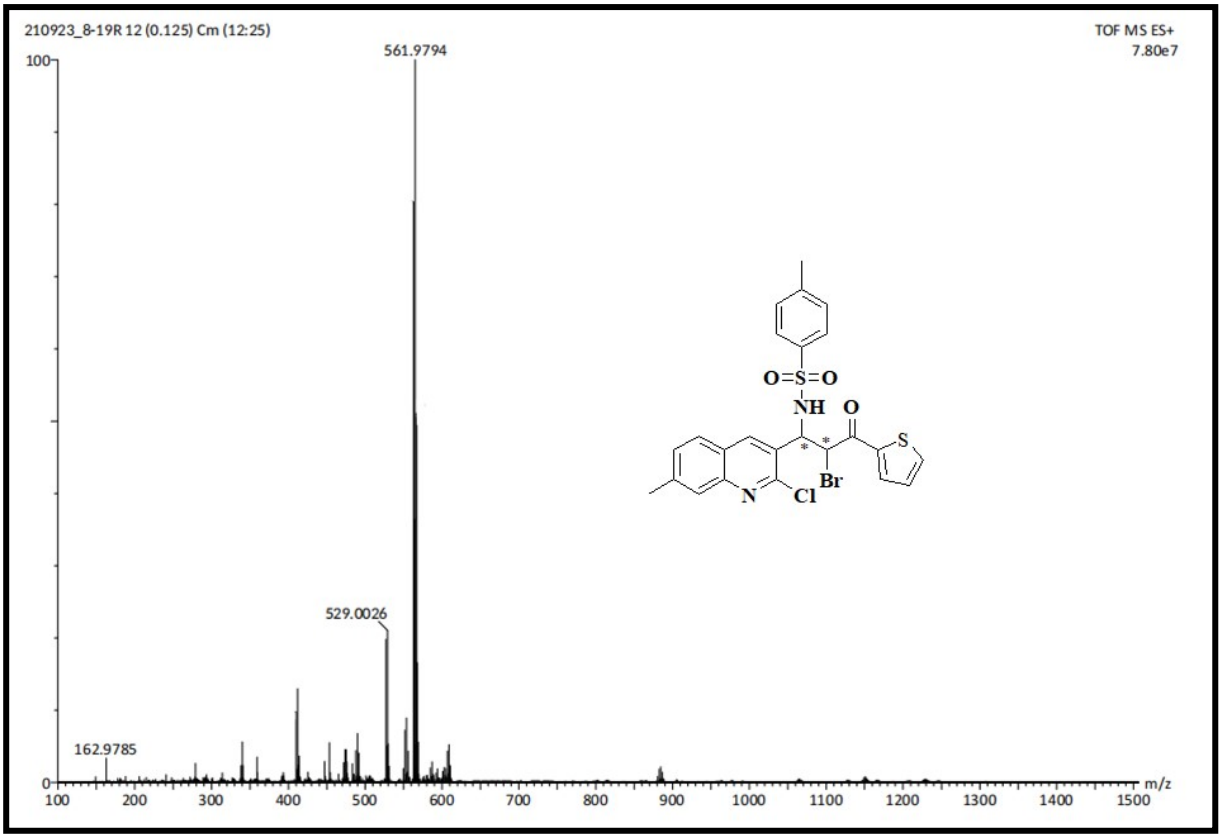

Fig. S50. Mass spectrum of 13B

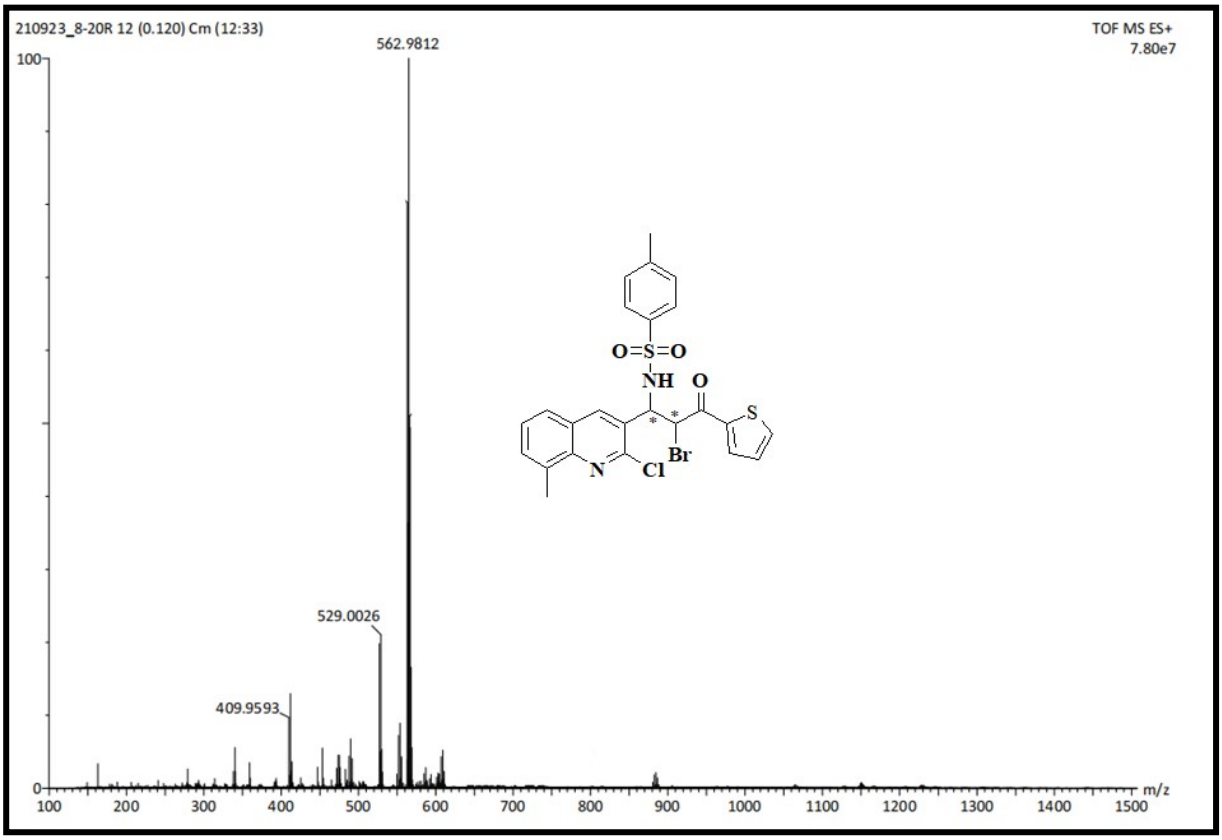

Fig. S51. Mass spectrum of 14B

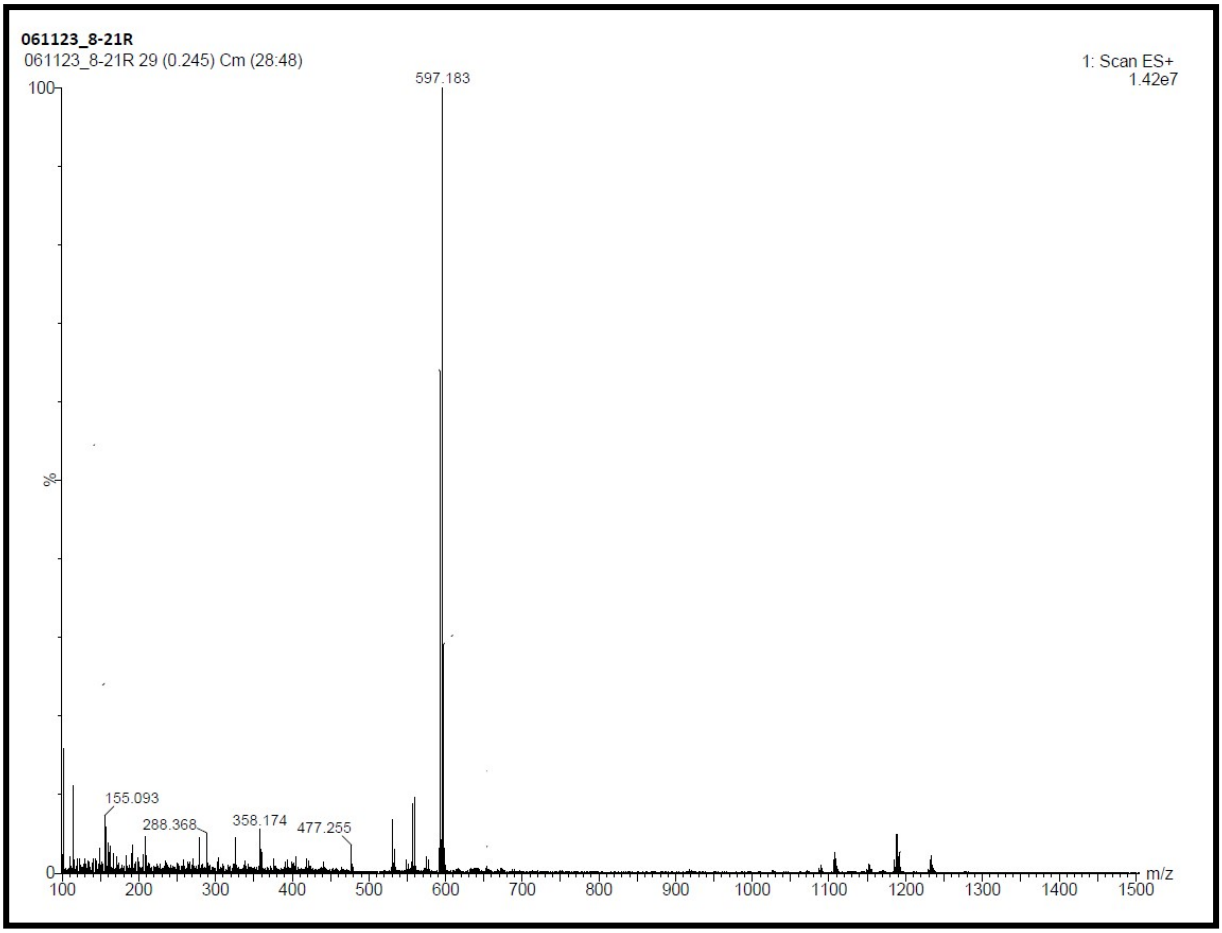

Fig. S52. Mass spectrum of 15B

Table S1 Crystallographic data of complexes [**Pd(8MOQL$^{1,2\&4}$)Cl]**

Compound	**Pd(8MOQL^{1})Cl**	**Pd(8MOQL^{2})Cl**	**Pd(8MOQL^{4})Cl**
Empirical formula	$C_{12}H_{11}ClN_4OPdS$	$C_{13}H_{13}ClN_4OPdS$	$C_{18}H_{15}ClN_4OPdS$
Formula weight	474.28	488.30	549.37
Temperature(K)	295 K	273(2)	295 K
Wavelength(Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	'P -1'	'P -1'	'P -1'
a (Å)	8.4878(8)	8.6492(3)	7.5069(8)
b (Å)	11.0977(11)	10.9746(4)	12.9454(14)
c (Å)	11.1379(11	11.5173(4)	12.9847(14)
α (°)	111.827(3)	69.7100(10)	61.465(3)
β (°)	109.312(3)	68.7380(10)	88.838(4)
γ (°)	93.968(3)	89.2470(10)	85.449(4)
Volume (Å^3)	1753.1(2)	947.64(6)	1104.8(2)
τ_4	0.04517	0.0404	0.0482
Z	2	2	2
Absorption co-efficient (mm^{-1})	1.320	1.252	1.084
F(000)	474.7124	488.7174	552.7431
Theta range for data collection (°)	4.0360 to 27.9030	3.7040 to 29.0320	3.2440 to 75.8430
Index ranges	10<=h<=-10, 14<=k<=-13, 14<=l<=-14	11<=h<=-10, 14<=k<=-13, 14<=l<=0	9<=h<=-19, 16<=k<=-16, 16<=l<=-16
Refinement method	Fsqd	Fsqd	Fsqd
Final *R* indices [$I>2\sigma(I)$]	R1 = 0.0553, wR2 =0.0798	R1 = 0.0301, wR2 = 0.0655	R1 = 0.0980, wR2 = 0.2998
R indices (all data)	R1 = 0.0355, wR2 = 0.0876	R1 = 0.0253, wR2 = 0.0683	R1 = 0.0871, wR2 = 0.3094

Table S2. Selected bond lengths (Å) and angles (°) of complexes [**Pd(8MOQL^1)Cl**], [**Pd(8MOQL^2)Cl**], [**Pd(8MOQL^4)Cl**]

BOND LENGTH					
Complex Pd(8MOQL^1)Cl		**Complex Pd(8MOQL^2)Cl**		**Complex Pd(8MOQL^4)Cl**	
Pd(1)-Cl(1)	2.2995(9)	Pd(1)-Cl(1)	2.3044(5)	Pd(1)-Cl(1)	2.300(3)
Pd(1)-S(1)	2.2100(9)	Pd(1)-S(1)	2.2131(5)	Pd(1)-S(1)	2.223(3)
Pd(1)-O(1)	2.059(2)	Pd(1)-O(1)	2.0647(15)	Pd(1)-O(1)	2.041(9)
Pd(1)-N(2)	1.983(3)	Pd(1)-N(2)	1.9803	Pd(1)-N(3)	1.944(11)
BOND ANGLE					
Complex Pd(8MOQL^1)Cl		**Complex Pd(8MOQL^2)Cl**		**Complex Pd(8MOQL^4)Cl**	
S(1)-Pd(1)-Cl(1)	89.94(3)	S(1)-Pd(1)-Cl(1)	90.12(2)	Cl(1)-Pd(1)-S(1)	92.96(12)
O(1)-Pd(1)-Cl(1)	91.05(6)	O(1)-Pd(1)-Cl(1)	91.01(4)	N(3)-Pd(1)-S(1)	84.6(3)
O(1)-Pd(1)-S(1)	178.35(6)	O(1)-Pd(1)-S(1)	178.85(4)	N(3)-Pd(1)-Cl(1)	176.7(3)
N(2)-Pd(1)-Cl(1)	175.28(8)	N(2)-Pd(1)-Cl(1)	175.43(5)	O(1)-Pd(1)-S(1)	176.2(3)
N(2)-Pd(1)-S(1)	85.34(8)	N(2)-Pd(1)-S(1)	85.46(5)	O(1)-Pd(1)-Cl(1)	89.8(3)
N(2)-Pd(1)-O(1)	93.67(9)	N(2)-Pd(1)-O(1)	93.43(6)	O(1)-Pd(1)-N(3)	92.8(4)
C(1)-S(1)-Pd(1)	95.92(11)	C(1)-S(1)-Pd(1)	96.04(7)	C(7)-S(1)-Pd(1)	96.4(4)
C(11)-O(1)-Pd(1)	124.11(19)	C(13)-O(1)-Pd(1)	124.53(13)	N(2)-N(3)-Pd(1)	123.6(8)
N(3)-N(2)-Pd(1)	120.55(2)	N(3)-N(2)-Pd(1)	120.76(13)	C(8)-N(3)-Pd(1)	126.6(8)
C(2)-N(2)-Pd(1)	124.26(2)	C(3)-N(2)-Pd(1)	124.40(14)	C(18)-O(1)-Pd(1)	126.7(8)

Table S3. Hydrogen bonds for **Pd(8MOQL^1)Cl**, **Pd(8MOQL^2)Cl**and **Pd(8MOQL^4)Cl** [A˚ and °]

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
Complex Pd(8MOQL^1)Cl				
N(1)-H(1)...O(2)	0.860	**1.985**	2.827	**165.86**
N(4)-H...Cl(1)	0.859	**5.726**	**5.815**	**91.68**
Symmetry operation: **x,y,z; -x,-y,-z**				
Complex Pd(8MOQL^2)Cl				
N(1)-H(1)...O(2)	0.860	2.005	2.824	158.76
N(4)-H...Cl(1)	0.860	**6.565**	**5.830**	**29.14**
Symmetry operation: **x,y,z; -x,-y,-z**				
Complex Pd(8MOQL^4)Cl				
N(4)-H(1)...O(2)			2.740	
Symmetry operation: **(x, y, z); x,y,z, -x,-y,-z**				

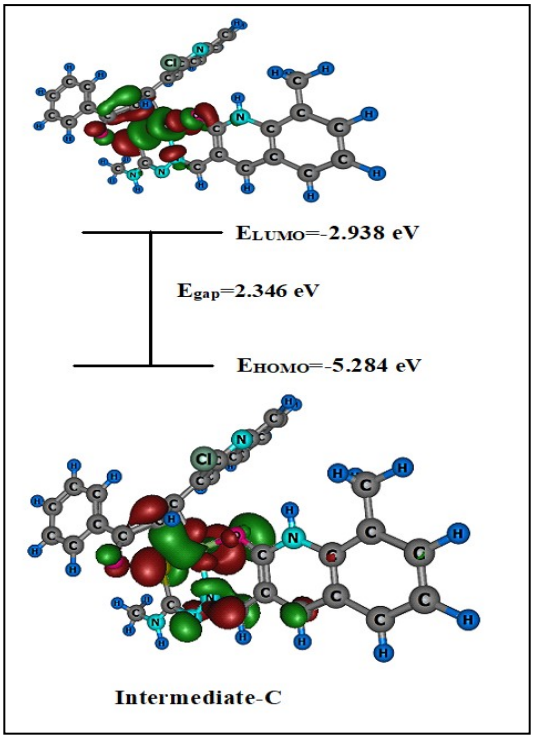

Fig. S53. Energy level diagram between HUMO and LUMO of Intermediate **C**.

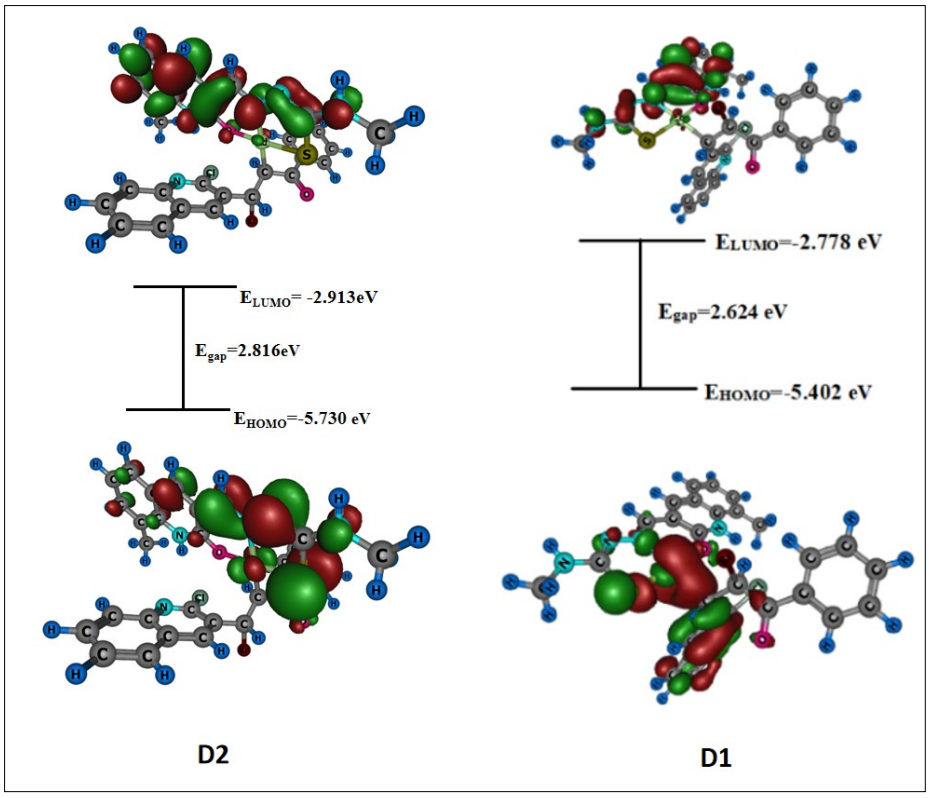

Fig. S54. Energy level diagram between HUMO and LUMO of Intermediate-**D1** and Intermediate-**D2**.

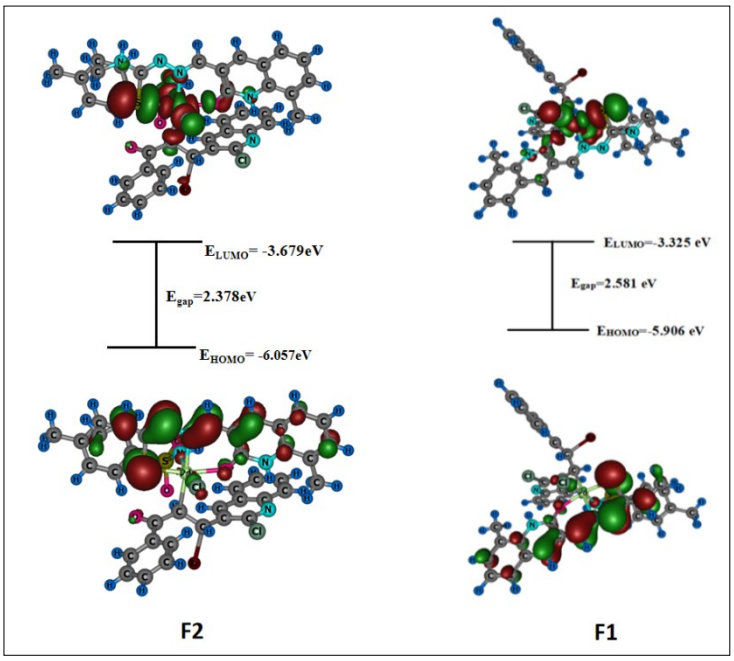

Fig. S55. Energy level diagram between HUMO and LUMO of Intermediate-**F2** and Intermediate-**F1**.

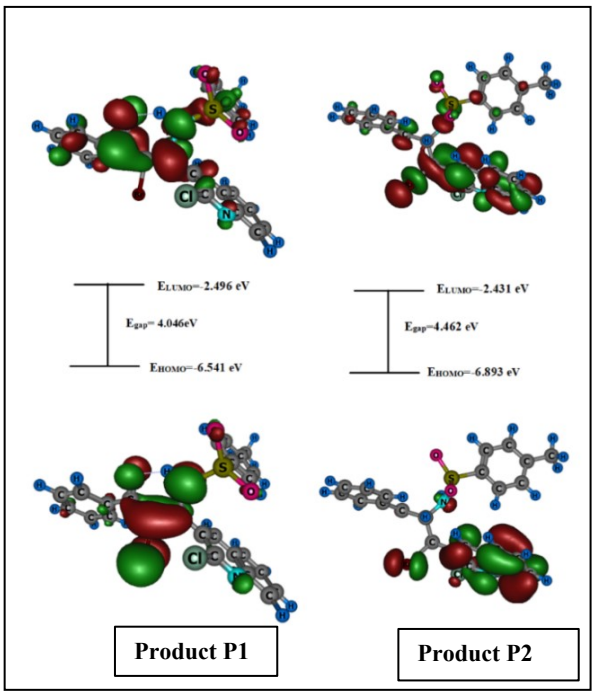

Fig. S56. Energy level diagram between HUMO and LUMO of Product **P1** and Product **P2**.

CD spectrum

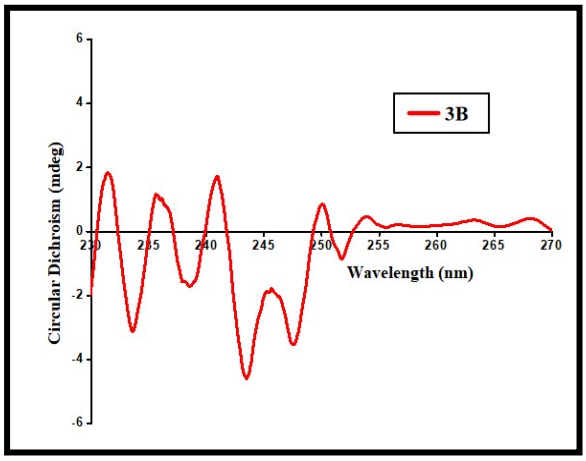

Fig. S57.CD spectrum of **3B**

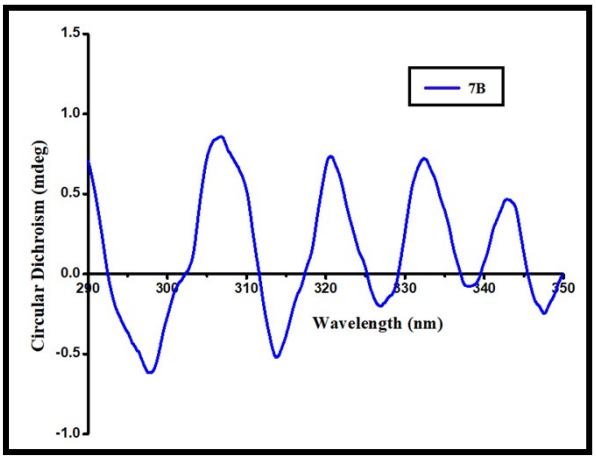

Fig. S58.CD spectrum of **7B**

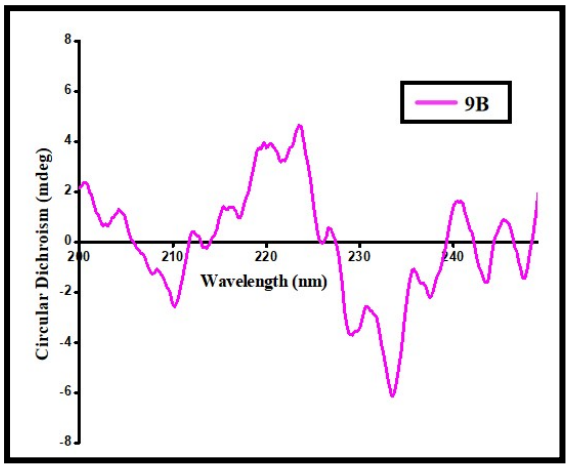

Fig. S59.CD spectrum of **9B**

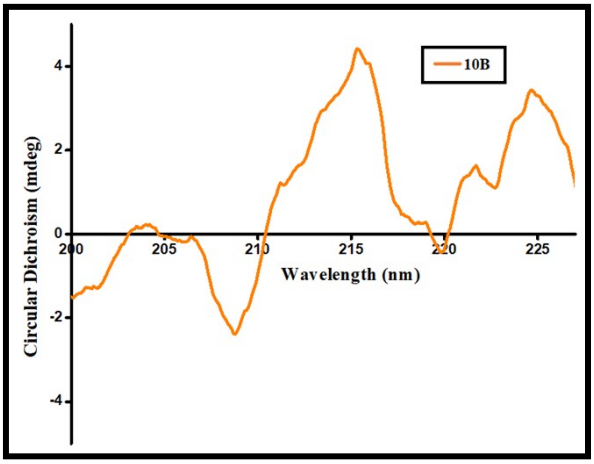

Fig. S60. CD spectrum of **10B**

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