Supporting Information

A Nickel-Catalyzed anti-Carbometallative Cyclization of Alkyne-Azides With Organoboronic Acids: Synthesis of 2,3-Diarylquinolines

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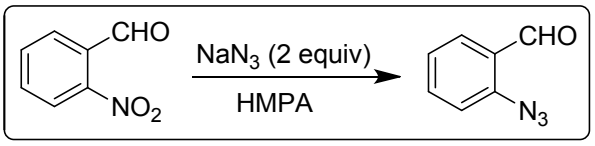
I. General Information and methods

All reagents and solvents were purchased from commercial sources and used without purification. NMR spectra were recorded with 400 MHz spectrometers for ^{1}H NMR and 100 MHz for ^{13}C NMR. Chemical shifts δ are given in ppm relative to the residual signals of tetramethylsilane in $CDCl_3$ or deuterated solvent DMSO-d_6 for ^{1}H and ^{13}C NMR. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of triplets (dt), triplet (t), quartet (q), multiplet (m), broad singlet (bs). HRMS were obtained using the electro spray ionization (ESI) technique and a time-of-flight (TOF) analyzer. Column chromatography was performed using silica gel (100-200 mesh) as the stationary phase. All reactions were monitored by thin layer chromatography (TLC). The purity and characterization of these compounds were further established using HR/ESI Mass spectroscopy. Melting points were measured on a capillary melting point apparatus and are uncorrected.

II. General Procedure for the Preparation of Starting Materials and Final Compounds

General procedure for the synthesis of azido benzaldehydes:

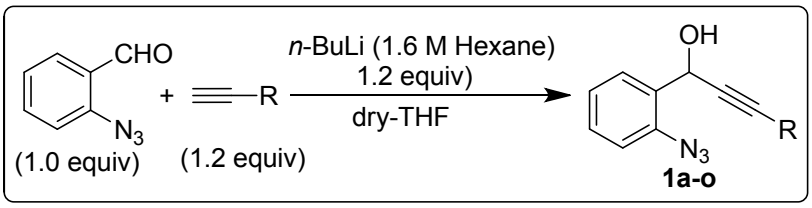
The requisite *ortho*-azidobenzaldehydes derivatives were synthesized from their corresponding commercially available *ortho*-nitrobenzaldehydes with sodium azide in HMPA following the reported procedure[1]. Yields were not optimized.



To a stirred solution of 2-nitrobenzaldehyde (1.0 equiv) in HMPA was added sodium azide (2.0 equiv) and reaction mixture was stirred at ambient temperature for overnight. After completion of the reaction (as indicated by TLC), the mixture was diluted with water, extracted with ethyl acetate and washed with brine. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. Crude product was purified by column chromatography (silica gel 100-200 mesh, 1-2% EtOAc in Hexanes).

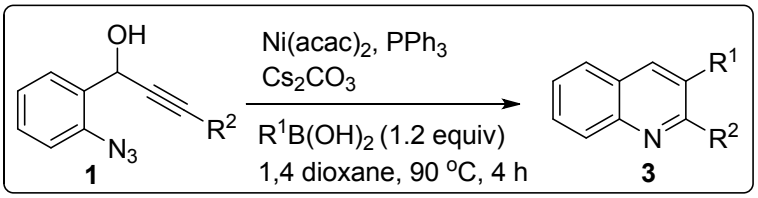
General procedure for the synthesis of azido propargyl alcohols (1):

The required *ortho*-azido propargyl alcohols were prepared by following the literature procedure[2]. To a stirred solution of phenylacetylene (1.2 equiv) in dry THF at -78 °C was added *n*-BuLi (1.6 *M* solution in hexane, 1.2 equiv) drop wise. The reaction was stirred at -78 °C for one hour.



After that the solution of *ortho*-azidobenzaldehyde (1.0 equiv) in dry THF was added slowly and stirred for addition 3 hours at the same temperature. After completion of the reaction, saturated NH_4Cl solution was added at 0 °C. The THF layer was separated and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. Crude product was purified by column chromatography (silica gel 100-200 mesh, 10-20% EtOAc in Hexanes).These azido propargyl alcohols found unstable and immediately taken for the next step.

General procedure for the synthesis of 3:

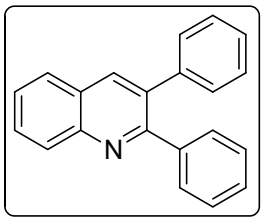


A mixture of azido-propargyl alcohol **1** (0.5 mmol), boronic acid **2** (0.6 mmol), $Ni(acac)_2$ (0.1 equiv), triphenylphosphine (0.1 equiv) and cesium carbonate (0.2 equiv) was stirred in 1,4-Dioxane (5 ml) at 90 °C for 4 h in reaction vial under the atmosphere of nitrogen. After completion of the reaction (as indicated by TLC), the reaction mixture was quenched by

saturated water and extracted with EtOAc. Organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Crude product was purified by column chromatography (silica gel, 4-5% EtOAc in Hexanes) to get pure final products **3**.

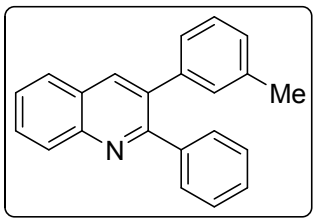
III. Characteristic data of final compounds

2,3-diphenylquinoline (3aa)[3]: Yield = 114 mg (92%); gram scale 970 mg (86%); Yellow



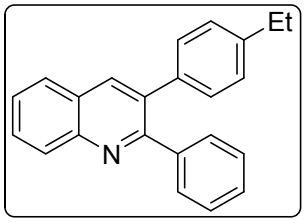
solid; mp 88-90 °C (Lit.[3] 88-91.5 °C); $\underline{R_f}$ = 0.50 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.2 Hz, 1H), 8.17 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.75-7.71 (m, 1H), 7.58-7.54 (m, 1H), 7.46-7.44 (m, 2H), 7.29-7.23 (m, 8H), 7.20-7.14 (m, 4H), 2.68 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 147.3, 140.4, 139.9, 137.5, 134.5, 129.9, 129.7, 129.5, 129.4, 128.2, 127.9, 127.8, 127.4, 127.2, 127.1, 126.7 ppm; HRMS (ESI-TOF) calcd for $C_{21}H_{16}N$ $[M + H]^+$ 282.1282 found 282.1280.

2-phenyl-3-(*m*-tolyl)quinoline (3ab): Yield = 101 mg (81%); Yellow oil; R_f = 0.60 (10%



ethyl acetate/hexane);^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.2 Hz, 1H), 8.19 (s, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.78-7.73 (m, 1H), 7.61-7.7.57 (m, 1H), 7.49-7.47 (m, 2H), 7.32-7.28 (m, 3H), 7.20-7.11 (m, 3H), 7.02 (d, *J* = 7.5 Hz, 1H), 2.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 147.3, 140.5, 139.9, 137.9, 137.5, 134.7, 130.4, 130.0, 129.5, 129.4, 128.0, 127.9, 127.8, 127.5, 127.3, 127.0, 126.7, 21.4 ppm; HRMS (ESI-TOF) calcd for $C_{22}H_{18}N$ $[M + H]^+$ 296.1439 found 296.1421.

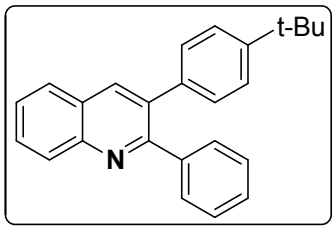
3-(4-ethylphenyl)-2-phenylquinoline (3ac): Yield = 104 mg (84%); Yellow oil; R_f = 0.50



(10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.2 Hz, 1H), 8.19 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.71-7.73 (m, 1H), 7.60-7.56 (m, 1H), 7.51-7.48 (m, 2H), 7.32-7.28 (m,

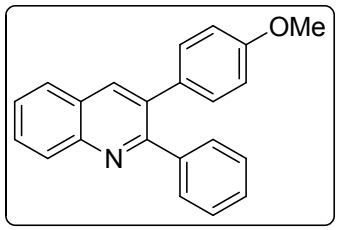
3H), 7.20-7.14 (m, 4H), 2.68 (q, J = 7.6 Hz, 2H), 1.27 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 147.3, 143.3, 140.6, 137.5, 137.3, 134.6, 130.1, 129.7, 129.5, 128.0, 127.9, 127.8, 127.4, 127.3, 126.7, 28.5, 15.4 ppm; HRMS (ESI-TOF) calcd for $C_{23}H_{20}N$ $[M + H]^+$ 310.1596 found 310.1592.

3-(4-(*tert*-butyl)phenyl)-2-phenylquinoline (3ad)[4]: Yield = 102 mg (82%); Pale yellow oil;



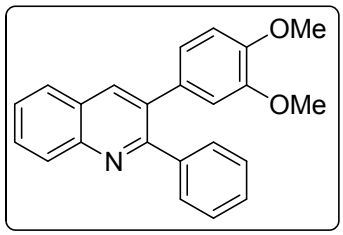
R_f = 0.50 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 8.4 Hz, 1H), 8.17 (s, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.78-7.73 (m, 1H), 7.59-7.56 (m, 1H), 7.51-7.49 (m, 2H), 7.35-7.28 (m, 5H), 7.22-7.19 (m, 2H), 1.36 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 150.2, 147.3, 140.6, 137.5, 136.9, 134.5, 130.1, 129.5, 129.4, 128.0, 127.9, 127.5, 127.3, 126.7, 125.2, 34.6, 31.4 ppm; HRMS (ESI-TOF) calcd for $C_{25}H_{24}N$ $[M + H]^+$ 338.1909 found 338.1894.

3-(4-methoxyphenyl)-2-phenylquinoline (3ae)[4]: Yield = 93 mg (75%); Pale yellow solid;



mp 126-128 °C; R_f = 0.40 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 8.0 Hz, 1H), 8.16 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.76-7.72 (m, 1H), 7.59-7.56 (m, 1H), 7.50-7.48 (m, 2H), 7.33-7.31 (m, 3H), 7.190 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 3.84 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 158.5, 147.2, 140.7, 137.2, 134.2, 132.3, 130.9, 130.0, 129.5, 129.4, 128.0, 127.9, 127.4, 127.3, 126.7, 113.8, 55.2 ppm; HRMS (ESI-TOF) calcd for $C_{22}H_{18}NO$ $[M + H]^+$ 312.1388 found 312.1370.

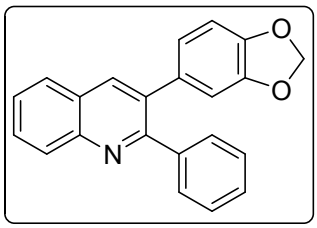
3-(3,4-dimethoxyphenyl)-2-phenylquinoline (3af): Yield = 85 mg (68%); Golden yellow



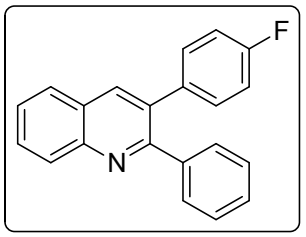
solid; mp 117-119 °C; R_f = 0.30 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, J = 9.5 Hz, 2H), 7.87 (d, J = 8.1 Hz, 1H), 7.72 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 (d, J = 3.5 Hz, 2H), 7.30 (d, J = 3.0 Hz, 3H), 6.92 (d, J =

8.2 Hz, 1H), 6.85 (d, J = 8.2 Hz, 1H), 6.61 (s, 1H), 3.90 (s, 3H), 3.58 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 148.4, 148.4, 147.2, 140.7, 137.0, 134.2, 132.4, 129.9, 129.5, 129.4, 128.0, 127.9, 127.4, 127.3, 126.7, 121.9, 113.5, 111.0, 55.8, 55.7 ppm; HRMS (ESI-TOF) calcd for $C_{23}H_{20}NO_2$ $[M + H]^+$ 342.1494 found 342.1471.

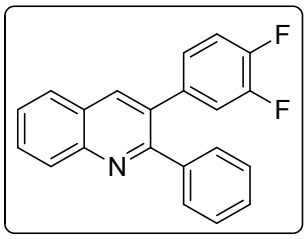
3-(benzo[*d*][1,3]dioxol-5-yl)-2-phenylquinoline (3ag): Yield = 91 mg (73%); Pale yellow solid; mp 127-129 °C; R_f = 0.40 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 8.4 Hz, 1H), 8.15 (s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.77-7.73 (m, 1H), 7.59-7.56 (m, 1H), 7.52-7.49 (m, 2H), 7.34-7.32 (m, 3H), 6.79-6.73 (m, 3H), 5.98 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 147.5, 147.2, 146.9, 140.5, 137.4, 134.2, 133.9, 129.9, 129.5, 129.4, 128.1, 128.0, 127.4, 127.2, 126.8, 123.5, 110.2, 108.2, 101.1 ppm; HRMS (ESI-TOF) calcd for $C_{22}H_{16}NO_2$ $[M + H]^+$ 326.1181 found 326.1170.



3-(4-fluorophenyl)-2-phenylquinoline (3ah)[4]: Yield = 106 mg (85%); Pale yellow solid; mp 101-103 °C; R_f = 0.60 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 8.4 Hz, 1H), 8.17 (s, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.79-7.75 (m, 1H), 7.62-7.58 (m, 1H), 7.47-7.44 (m, 2H), 7.33-7.30 (m, 3H), 7.25-7.21 (m, 2H), 7.03-6.99 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2 (d, J = 251.0 Hz), 158.3, 147.4, 140.3, 137.5, 136.0 (d, J = 3.3 Hz), 133.5, 131.4 (d, J = 8.0 Hz), 130.0, 129.7, 129.5, 128.1, 128.0, 127.4, 127.2, 126.9, 115.3 (d, J = 21.3 Hz) ppm; HRMS (ESI-TOF) calcd for $C_{21}H_{15}NF$ $[M + H]^+$ 300.1189 found 300.1172.

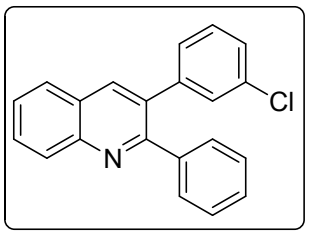


3-(3,4-difluorophenyl)-2-phenylquinoline (3ai): Yield = 90 mg (72%); Pale yellow solid; mp 120-122 °C; R_f = 0.50 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 8.4 Hz, 1H), 8.17 (s, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.79-7.75 (m, 1H), 7.62-7.58 (m, 1H), 7.47-



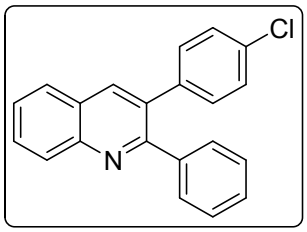
7.44 (m, 2H), 7.33-7.30 (m, 3H), 7.25-7.21 (m, 2H), 7.03-6.99 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 151.1 (dd, J_1 = 247.9 Hz, J_2 = 13.7 Hz), 148.7 (dd, J_1 = 247.9 Hz, J_2 = 13.9 Hz), 147.5, 139.9, 137.6, 136.9, 132.4, 130.0, 129.9, 129.5, 128.3, 128.2, 127.5, 127.0, 125.9, 118.7 (d, J = 17.5 Hz), 117.2 (d, J = 17.5) ppm; HRMS (ESI-TOF) calcd for $C_{21}H_{14}NF_2$ $[M + H]^+$ 318.1094 found 318.1082.

3-(3-chlorophenyl)-2-phenylquinoline (3aj): Yield = 96 mg (77%); Pale yellow solid; mp



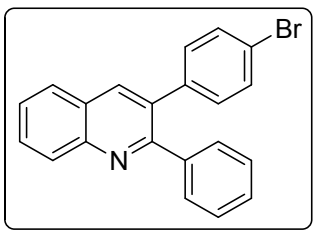
112-114 °C; R_f = 0.50 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 8.2 Hz, 1H), 8.19 (s, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.80-7.76 (m, 1H), 7.63-7.59 (m, 1H), 7.48-7.46 (m, 2H), 7.35-7.28 (m, 5H), 7.20 (t, J = 7.8 Hz, 1H), 7.07 (d, J = 7.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 147.5, 141.9, 140.0, 137.6, 134.2, 133.1, 130.0, 129.9, 129.6, 129.5, 129.4, 128.3,128.2, 128.1, 127.5, 127.3, 127.1, 126.9 ppm; HRMS (ESI-TOF) calcd for $C_{21}H_{15}NCl$ $[M + H]^+$ 316.0893 found 316.0876.

3-(4-chlorophenyl)-2-phenylquinoline (3ak)[4]: Yield = 98 mg (79%); Pale yellow solid; mp



147-149 °C (Lit.[4] 146-147 °C);; R_f = 0.50 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 8.5 Hz, 1H), 8.17 (s, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.79-7.75 (m, 1H), 7.62-7.58 (m, 1H), 7.48-7.45 (m, 2H), 7.34-7.28 (m, 5H), 7.21-7.19 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 147.4, 140.2, 138.5, 137.5, 133.4, 133.3, 131.0, 130.0, 129.9, 129.5, 128.5, 128.2, 128.1, 127.5, 127.1, 126.9 ppm; HRMS (ESI-TOF) calcd for $C_{21}H_{15}NCl$ $[M + H]^+$ 316.0893 found 316.0878.

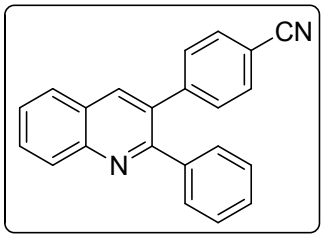
3-(4-bromophenyl)-2-phenylquinoline (3al): Yield = 109 mg (88%); Pale yellow solid; mp



152-154 °C; R_f = 0.50 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 8.2 Hz, 1H), 8.17 (s, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.79-7.75 (m, 1H), 7.62-7.58 (m, 1H), 7.47-7.44 (m,

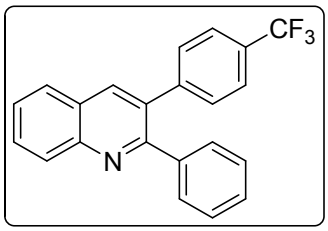
4H), 7.34-7.32 (m, 3H), 7.14 (d, J = 8.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 147.4, 140.1, 138.9, 137.5, 133.3, 131.5, 131.4, 130.0, 129.9, 129.5, 128.2, 128.1, 127.5, 127.1, 126.9, 121.6 ppm; HRMS (ESI-TOF) calcd for $C_{21}H_{15}NBr$ $[M + H]^+$ 360.0388 found 360.0365.

4-(2-phenylquinolin-3-yl)benzonitrile (3am)[4]: Yield = 88 mg (71%); Pale yellow solid; mp



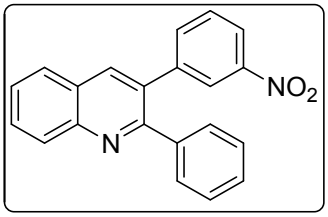
198-200 °C; R_f = 0.40 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, J = 8.4 Hz, 1H), 8.2 (s, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.83-7.79 (m, 1H), 7.65-7.60 (m, 3H), 7.44-7.28 (m, 7H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 147.7, 144.9, 139.7, 137.8, 132.6, 132.0, 130.5, 130.4, 130.0, 129.5, 128.5, 128.3, 127.6, 127.2, 126.9 ppm; HRMS (ESI-TOF) calcd for $C_{22}H_{15}N_2$ $[M + H]^+$ 307.1235 found 307.1215.

2-phenyl-3-(4-(trifluoromethyl)phenyl)quinoline (3an): Yield = 92 mg (74%); Pale yellow



solid; mp 125-127 °C; R_f = 0.50 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, J = 8.5 Hz, 1 H), 8.21 (s, 1H), 7.92 (d, J = 7.8 Hz, 1H), 7.82-7.78 (m, 1H), 7.64-7.57 (m, 3H), 7.46-7.44 (m, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.34-7.32 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 147.6, 143.8, 139.9, 137.8, 133.1, 130.1, 130.0, 130.0, 129.5, 129.2, 128.3, 128.2, 127.6, 127.0, 125.5, 125.2 (q, J = 2.8 Hz), 122.8 ppm; HRMS (ESI-TOF) calcd for $C_{22}H_{15}NF_3$ $[M + H]^+$ 350.1157 found 350.1142.

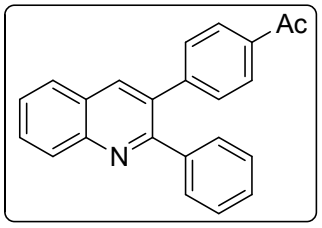
3-(3-nitrophenyl)-2-phenylquinoline (3ao): Yield = 93 mg (75%); Golden yellow solid; mp



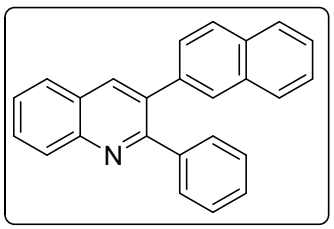
113-115 °C; R_f = 0.40 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, J = 8.2 Hz, 1H), 8.19 (s, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.80-7.76 (m, 1H), 7.63-7.59 (m, 1H), 7.48-7.46 (m, 2H), 7.35-7.28 (m, 5H), 7.20 (t, J = 7.8 Hz, 1H), 7.07 (d, J = 7.7 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9, 148.3, 147.7, 141.7, 139.6, 137.9,

135.9, 132.0, 130.4, 130.0, 129.5, 129.0, 128.5, 128.3, 127.6, 127.2, 127.0, 124.4, 121.2 ppm; HRMS (ESI-TOF) calcd for $C_{21}H_{15}N_2O_2$ $[M + H]^+$ 327.1134 found 327.1118.

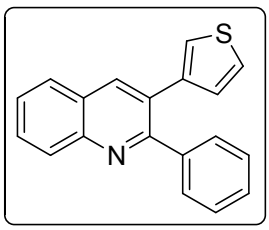
1-(4-(2-phenylquinolin-3-yl)phenyl)ethan-1-one (3ap): Yield = 107 mg (86%); Pale yellow solid; mp 160-162 °C; R_f = 0.40 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25-8.21 (m, 3H), 7.91 (d, J = 8.5 Hz, 3H), 7.81-7.77 (m, 1H), 7.63-7.59 (m, 1H), 7.47-7.45 (m, 2H), 7.38 (d, J = 8.5 Hz, 2H), 7.33-7.31 (m, 3H), 2.62 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 158.0, 147.6, 144.9, 140.1, 137.7, 135.7, 133.4, 130.1, 130.0, 129.9, 129.5, 128.3, 128.1, 127.6, 127.0, 26.6 ppm; HRMS (ESI-TOF) calcd for $C_{23}H_{18}NO$ $[M + H]^+$ 324.1388 found 324.1373.



3-(naphthalen-2-yl)-2-phenylquinoline (3aq): Yield = 100 mg (80%); Pale yellow solid; mp 137-139 °C; R_f = 0.60 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (s, 1H), 8.26 (d, J = 8.4 Hz, 1H), 7.94-7.92 (m, 2H), 7.85-7.83 (m, 2H), 7.81-7.76 (m, 1H), 7.70 (d, J = 8.6 Hz, 1H), 7.63-7.59 (m, 1H), 7.53-7.51 (m, 4H), 7.29-7.22 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 147.5, 140.5, 138.0, 137.8, 134.5, 133.5, 132.4, 130.1, 129.7, 129.5, 128.5, 128.2, 128.1, 128.0, 127.4, 127.6, 127.3, 126.8, 126.3, 126.2 ppm; HRMS (ESI-TOF) calcd for $C_{25}H_{18}N$ $[M + H]^+$ 332.1439 found 332.1422.

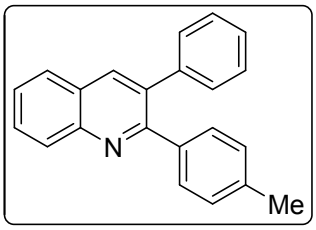


2-phenyl-3-(thiophen-3-yl)quinoline (3ar): Yield = 80 mg (64%); Pale yellow solid; mp 137-139 °C; R_f = 0.50 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 8.21 (d, J = 9.1 Hz, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.77-7.73 (m, 1H), 7.61-7.57 (m, 1H), 7.53-7.51 (m, 2H), 7.37-7.35 (m, 3H), 7.25-7.23 (m, 1H), 7.19-7.18 (m, 1H), 6.84 (dd, J_1 = 5.0 Hz, J_2 = 1.3 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 147.2, 140.6, 140.3,

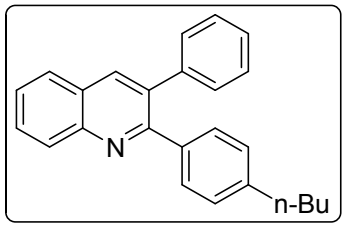


136.9, 129.7, 129.6, 129.5, 129.4, 128.9, 128.2, 128.1, 127.4, 127.2, 126.8, 125.3, 123.7 ppm; HRMS (ESI-TOF) calcd for $C_{19}H_{14}NS$ $[M + H]^+$ 288.0847 found 288.0850.

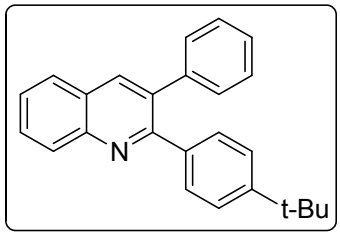
3-phenyl-2-(*p*-tolyl)quinoline (3ba): Yield = 110 mg (84%); Yellow oil; R_f = 0.60 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.19 (d, J = 8.4 Hz, 1H), 8.15 (s, 1H); 7.85 (d, J = 8.0 Hz, 1H), 7.72 (t, J = 8.0 Hz, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.35 (d, J = 7.5 Hz, 1H), 7.30-7.26 (m, 5H), 7.08 (d, J = 7.8 Hz, 2H), 2.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.5, 147.4, 140.3, 137.9, 137.6, 134.6, 130.0, 129.8, 129.6, 129.5, 128.7, 128.3, 127.5, 127.2, 126.6, 21.3 ppm; HRMS (ESI-TOF) calcd for $C_{22}H_{18}N$ $[M + H]^+$ 296.1439, found 296.1424.



2-(4-butylphenyl)-3-phenylquinoline (3ca): Yield = 120 mg (79%); Yellow oil; R_f = 0.60 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.19 (d, J = 8.5 Hz, 1H), 8.15 (s, 1H); 7.85 (d, J = 8.0 Hz, 1H), 7.72 (t, J = 8.0 Hz, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.28-7.26 (m, 5H), 7.08 (d, J = 7.7 Hz, 2H), 2.58 (t, J = 7.6 Hz, 2H), 1.57-1.53 (m, 2H), 1.37-1.30 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.6, 147.4, 142.9, 140.3, 137.8, 137.6, 134.6, 130.0, 129.8, 129.6, 129.5, 128.3, 128.1, 127.5, 127.2, 127.2, 126.6, 35.5, 33.5, 22.3, 14.0 ppm; HRMS (ESI-TOF) calcd for $C_{25}H_{24}N$ $[M + H]^+$ 338.1909, found 338.1894.

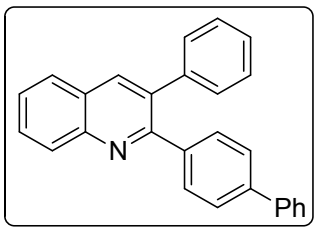


2-(4-(*tert*-butyl)phenyl)-3-phenylquinoline (3da): Yield = 114 mg (75%); Pale yellow solid; mp 84-86 ^{o}C; R_f = 0.50 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (d, J = 8.5 Hz, 1H), 8.15 (s, 1H), 7.86 (d, J = 7.7 Hz, 1H), 7.74-7.70 (m, 1H), 7.56-7.52 (m, 1H), 7.39 (d, J = 8.5 Hz, 2H), 7.31-7.27 (m, 7H), 1.30 (s, 9H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.5, 151.1, 147.5, 140.3, 137.6, 134.6, 129.9, 129.8,



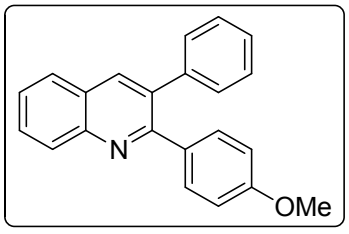
129.6, 129.5, 128.3, 127.5, 127.2, 127.2, 126.7, 125.0, 34.7, 31.4 ppm; HRMS (ESI-TOF) calcd for $C_{25}H_{24}N$ $[M + H]^+$ 338.1909, found 338.1897.

2-([1,1'-biphenyl]-4-yl)-3-phenylquinoline (3ea): Yield = 154 mg (95%); White solid; mp



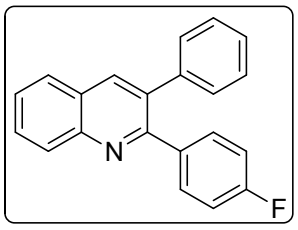
141-143 °C; R_f = 0.50 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.23-8.19 (m, 2H,); 7.88 (d, *J* = 8.1 Hz, 1H); 7.77-7.72 (m, 1H); 7.61-7.53 (m, 7H); 7.43 (t, *J* = 7.2 Hz, 2H,); 7.35-7.31 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.1, 147.5, 140.8, 140.8, 140.1, 139.5, 137.7, 134.6, 130.6, 129.9, 129.7, 129.6, 128.8, 128.4, 127.6, 127.5, 127.3, 127.2, 126.9, 126.8 ppm; HRMS (ESI-TOF) calcd for $C_{27}H_{20}N$ $[M + H]^+$ 358.1596, found 358.1590.

2-(4-methoxyphenyl)-3-phenylquinoline (3fa): Yield = 113 mg (81%); Colorless oil; R_f =



0.40 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.5 Hz, 1H), 8.13 (s, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.74-7.70 (m, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.41(d, *J* = 8.5 Hz, 2H), 7.32-7.26 (m, 5H), 6.80 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.7, 158.0, 147.4, 140.4, 137.7, 134.5, 132.9, 131.5, 129.8, 129.6, 129.3, 128.4, 127.5, 127.2, 127.1, 126.6, 113.5, 55.3 ppm; HRMS (ESI-TOF) calcd for $C_{22}H_{18}NO$ $[M + H]^+$ 312.1388, found 312.1383.

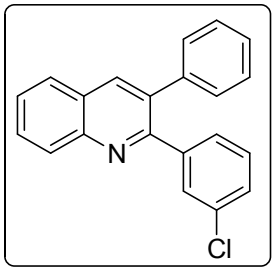
2-(4-fluorophenyl)-3-phenylquinoline (3ga): Yield = 92 mg (69%); Pale yellow solid; mp



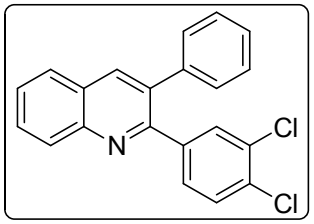
101-103 °C; R_f = 0.50 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22-8.19 (m, 2H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.79-7.75 (m, 1H), 7.62-7.58 (m, 1H), 7.48-7.45 (m, 2H), 7.35-7.33 (m, 3H), 7.28-7.25 (m, 2H), 7.01-6.97 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.7 (d, *J* = 247.0 Hz), 157.3, 147.3, 139.9, 137.7, 136.5 (d. *J* = 3.0 Hz),

134.4, 131.9 (d, J = 8.0 Hz), 129.7, 129.4, 128.4, 127.5, 127.3, 127.2, 126.9, 114.9 (d, J = 22.0 Hz) ppm; HRMS (ESI) calcd for $C_{21}H_{15}NF$ [M + H] 300.1189 found 300.1172.

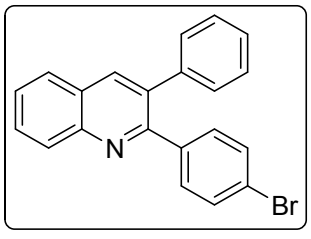
2-(3-chlorophenyl)-3-phenylquinoline (3ha): Yield = 112 mg (79%); Yellow oil; R_f = 0.60 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24-8.21 (m, 2H), 7.90 (d, J = 7.8 Hz, 1H), 7.80-7.76 (m, 1H), 7.63-7.59 (m, 2H), 7.36-7.34 (m, 3H), 7.30-7.23 (m, 4H), 7.19-7.15 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 147.3, 142.2, 139.5, 137.7, 134.4, 134.0, 130.1, 129.8, 129.7, 129.0, 128.4, 128.3, 128.1, 127.5, 127.5, 127.4, 127.1 ppm; HRMS (ESI) calcd for $C_{21}H_{15}NCl$ [M + H] 316.0893 found 316.0880.



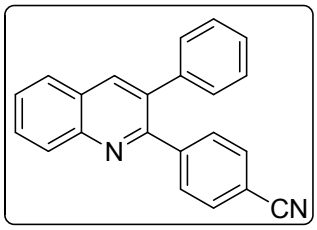
2-(3,4-dichlorophenyl)-3-phenylquinoline (3ia): Yield = 102 mg (64%); Pale yellow solid; mp 96-98 ^{o}C; R_f = 0.50 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19-8.17 (m, 2H), 7.88 (d, J = 8.0 Hz, 1H), 7.78-7.74 (m, 1H), 7.71 (d, J = 2.0 Hz, 1H), 7.61-7.57 (m, 1H), 7.35-7.34 (m, 3H), 7.27-7.23 (m, 3H), 7.17-7.14 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 155.7, 147.4, 140.5, 139.4, 128.0, 134.4, 132.5, 132.4, 132.1, 130.1, 129.8, 129.5, 128.7, 127.7, 127.6, 127.5, 127.3 ppm; HRMS (ESI-TOF) calcd for $C_{21}H_{14}Cl_2N$ $[M + H]^+$ 350.0503, found 350.0494.



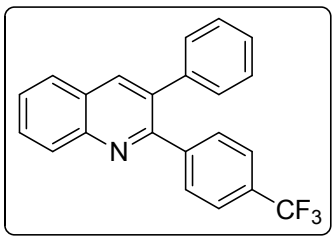
2-(4-bromophenyl)-3-phenylquinoline (3ja): Yield = 95 mg (58%); Colorless oil; R_f = 0.60 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 8.4 Hz, 1H), 8.17 (s, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.76-7.72 (m, 1H), 7.58-7.54 (m, 1H), 7.48-7.46 (m, 2H), 7.30-7.28 (m, 5H), 7.27-7.24 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.5, 147.4, 140.5, 140.1, 137.6, 134.6, 130.1, 129.8, 129.7, 129.5, 128.3, 128.1, 128.0, 127.5, 127.3, 127.2, 126.8 ppm; HRMS (ESI-TOF) calcd for $C_{21}H_{15}BrN$ $[M + H]^+$ 360.0388, found 360.0365.



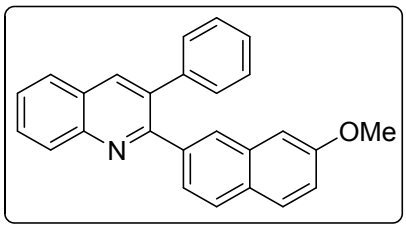
4-(3-phenylquinolin-2-yl)benzonitrile (3ka): Yield = 99 mg (72%); Pale yellow solid; mp 130-132 °C; R_f = 0.40 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (s, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.82-7.78 (m, 1H), 7.66-7.59 (m, 5H), 7.36-7.35 (m, 3H), 7.28-7.23 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 147.3, 144.9, 139.1, 138.0, 134.3, 131.7, 130.8, 130.1, 129.7, 129.4, 128.6, 127.7, 127.6, 127.5, 118.8, 115.5, 111.7 ppm; HRMS (ESI) calcd for $C_{22}H_{15}N_2$ [M + H] 307.1235 found 307.1223.



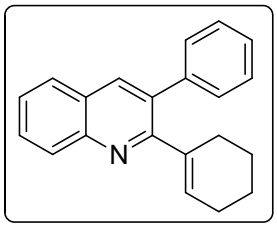
3-phenyl-2-(4-(trifluoromethyl)phenyl)quinoline (3la): Yield = 117 mg (74%); Colorless oil; R_f = 0.60 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21-8.19 (m, 2H), 7.90-7.88 (m, 1H), 7.78-7.74 (m, 1H), 7.62-7.53 (m, 5H), 7.34-7.30 (m, 3H), 7.26-7.22 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.8, 147.4, 144.1, 139.5, 137.9, 134.5, 130.5, 130.2, 130.0, 129.8, 128.6, 127.6, 127.5, 127.3, 125.6, 125.0(q, *J*= 2.8 Hz), 122.9 ppm; HRMS (ESI-TOF) calcd for $C_{22}H_{15}F_3N$ $[M + H]^+$ 350.1157, found 350.1145.



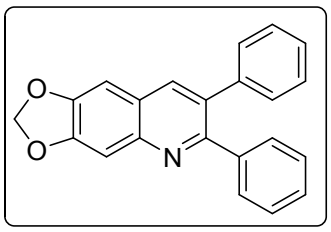
2-(7-methoxynaphthalen-2-yl)-3-phenylquinoline (3ma): Yield = 146 mg (89%); Pale yellow solid; mp 150-152 °C; R_f = 0.50 (20% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.24 (d, *J* = 8.5Hz, 1H), 8.20 (s, 1H), 8.00 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.75 (t, *J* = 7.5 Hz, 1H); 7.67 (d, *J* = 8.8 Hz, 1H); 7.59-7.55 (m, 2H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.27-7.26 (m, 5H), 7.12-7.09 (m, 2H), 3.91 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3, 158.2, 147.5, 140.2, 137.7, 135.8, 134.7, 134.3, 130.2, 129.8, 129.7, 129.5, 128.7, 128.4, 128.3, 127.6, 127.3, 126.7, 126.2, 118.8, 105.3, 55.3 ppm; HRMS (ESI-TOF) calcd for $C_{26}H_{20}NO$ $[M + H]^+$ 362.1545, found 362.1533.



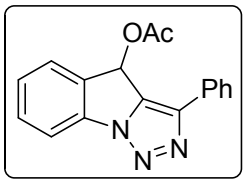
2-(cyclohex-1-en-1-yl)-3-phenylquinoline (3na)[3]: Yield = 90 mg (71%); Yellow oil; R_f = 0.60 (10% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15 (d, J = 8.4 Hz, 1H,), 8.03 (s, 1H), 7.80 (d, J = 7.9 Hz, 1H), 7.71-7.66 (m, 1H), 7.52-7.47 (m, 3H), 7.44-7.34 (m, 3H), 5.94 (s, 1H), 2.12-2.11 (m, 4H), 1.58-1.56 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.4, 147.0, 140.4, 138.9, 137.0, 134.2, 131.1, 129.4, 129.3, 129.2, 128.2, 127.5, 127.4, 127.2, 126.4, 28.2, 25.7, 22.7, 21.8 ppm; HRMS (ESI-TOF) calcd for $C_{21}H_{20}N$ $[M + H]^+$ 286.1596, found 286.1586.



6,7-diphenyl-[1,3]dioxolo[4,5-g]quinoline (3oa)[3]: Yield = 133 mg (91%); Off-white solid; mp 160-162 °C; R_f = 0.40 (20% ethyl acetate/hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (s, 1H), 7.48 (s, 1H), 7.42-7.40 (m, 2H), 7.28-7.25 (m, 6H); 7.23-7.20 (m, 2H), 7.10 (s, 1H), 6.12 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.0, 150.9, 148.1, 145.6, 140.6, 140.2, 136.6, 132.8, 130.1, 129.8, 128.2, 127.9, 127.8, 127.0, 124.3, 105.9, 102.4, 101.8 ppm; HRMS (ESI-TOF) calcd for $C_{22}H_{16}NO_2$ $[M + H]^+$ 326.1181 found 326.1175.



3-phenyl-4*H*-[1,2,3]triazolo[1,5-a]indol-4-yl acetate (4): Yield = 129 mg (89%); Off-white solid; mp 160-162 °C; R_f = 0.40 (20% ethyl acetate/hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.87 (t, J = 8.4 Hz, 3H), 7.68 (d, J = 7.6 Hz, 1H), 7.56 (t, J = 7.7 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.38 (dd, J_1 = 13.9 Hz, J_2 = 7.0 Hz, 2H), 7.12 (s, 1H), 2.21 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.7, 143.2, 136.9, 135.5, 134.0, 130.8, 129.7, 128.9, 128.7, 128.0, 127.9, 126.2, 112.6, 65.4, 20.7 ppm; HRMS (ESI-TOF) calcd for $C_{17}H_{14}N_3O_2$ $[M + H]^+$ 292.1086 found 292.1084.



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2. N. Zhou, Z. Yan, H. Zhang, Z. Wu and C. Zhu, *J. Org. Chem.,* 2016, **81**, 12181.

3. R. K. Saunthwal, M. Patel and A. K. Verma, *Org. Lett.* 2016, **18**, 2200.

4. X. Ji, H. Huang, Y. Li, H. Chen and H. Jiang, *Angew. Chem. Int. Ed.* 2012, **51**, 7292.

IV. Copies of ^{1}H and ^{13}C NMR

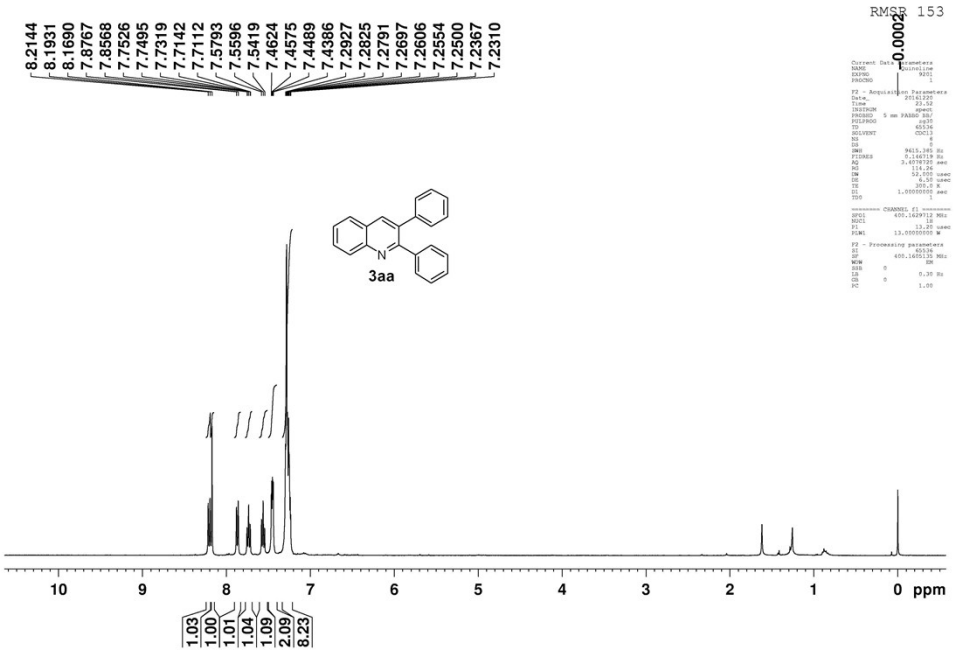

Fig. S1 ^{1}H NMR of **3aa**

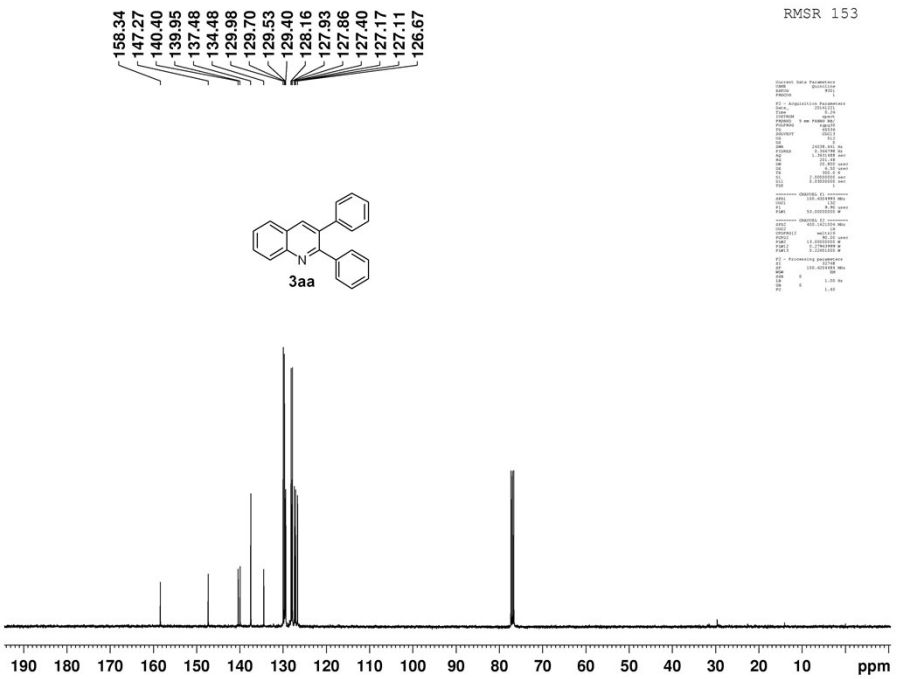

Fig. S2 ^{13}C NMR of **3aa**

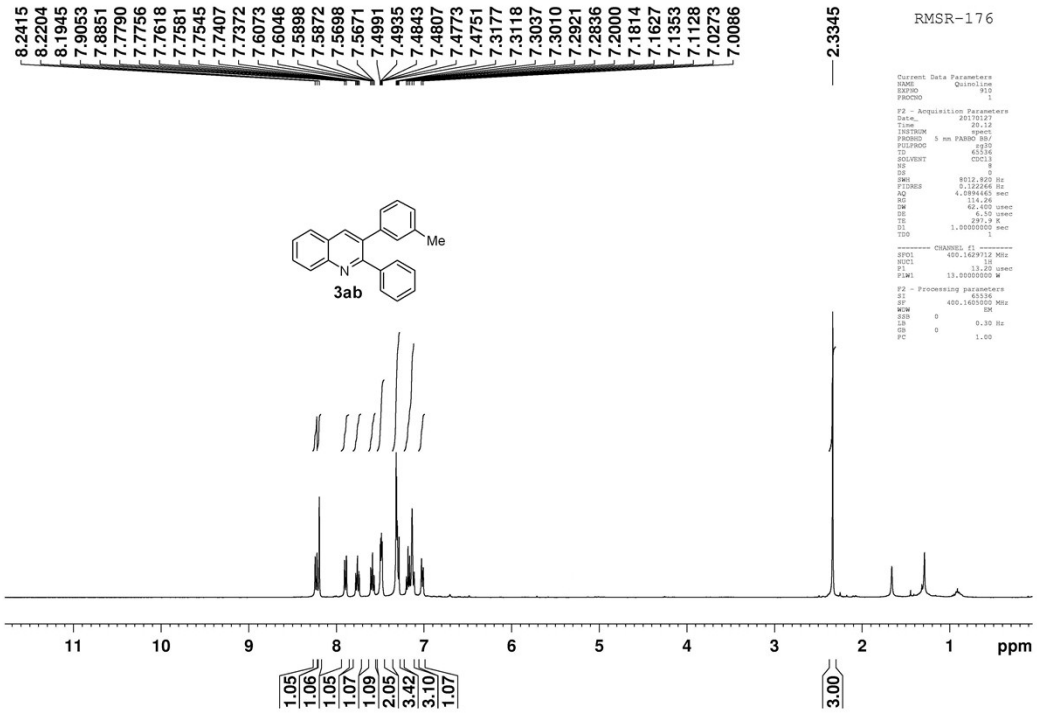

Fig. S3 ^{1}H NMR of **3ab**

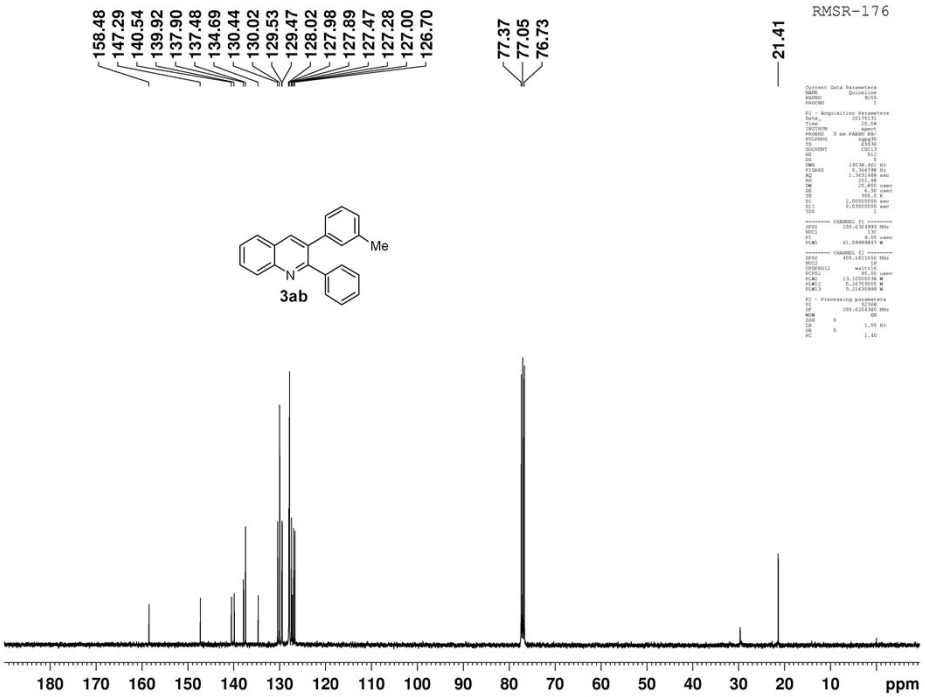

Fig. S4 ^{13}C NMR of **3ab**

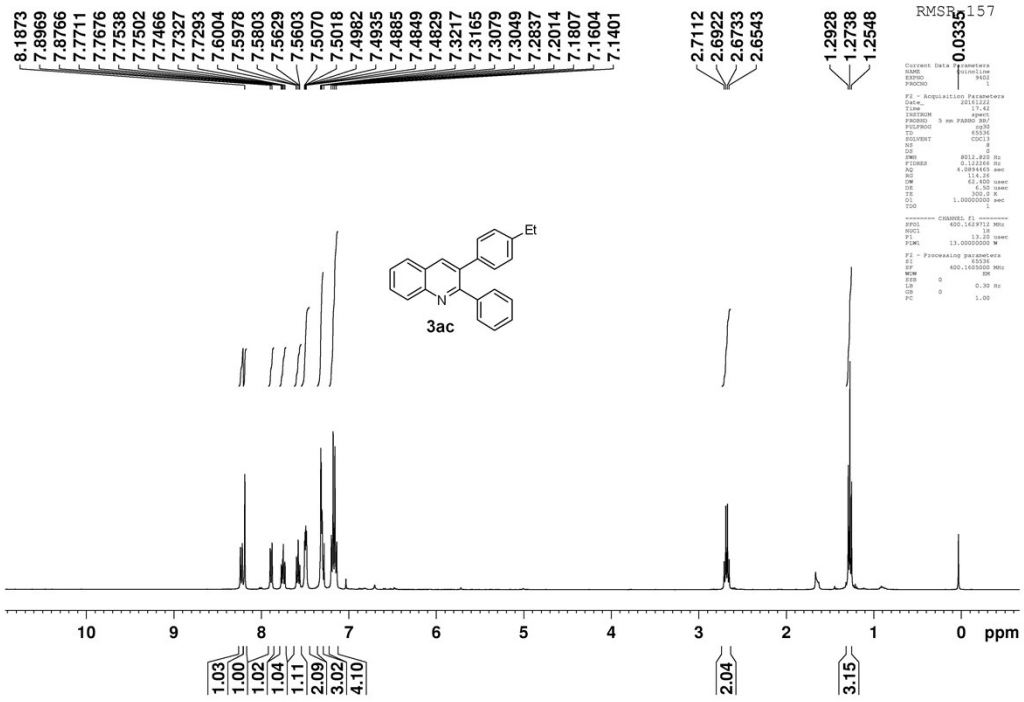

Fig. S5 ^{1}H NMR of **3ac**

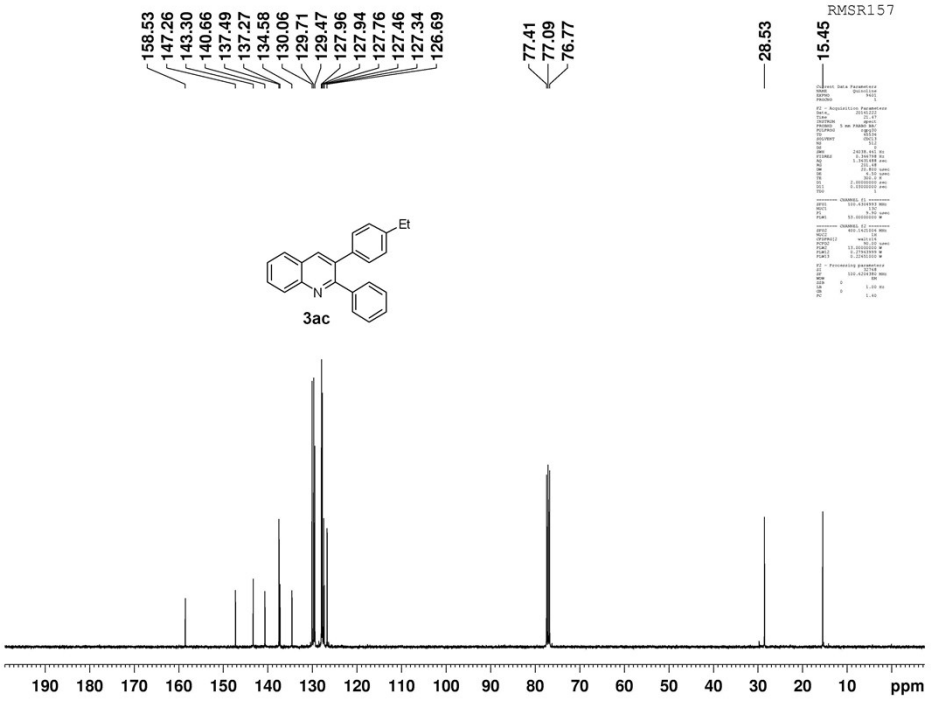

Fig. S6 ^{13}C NMR of **3ac**

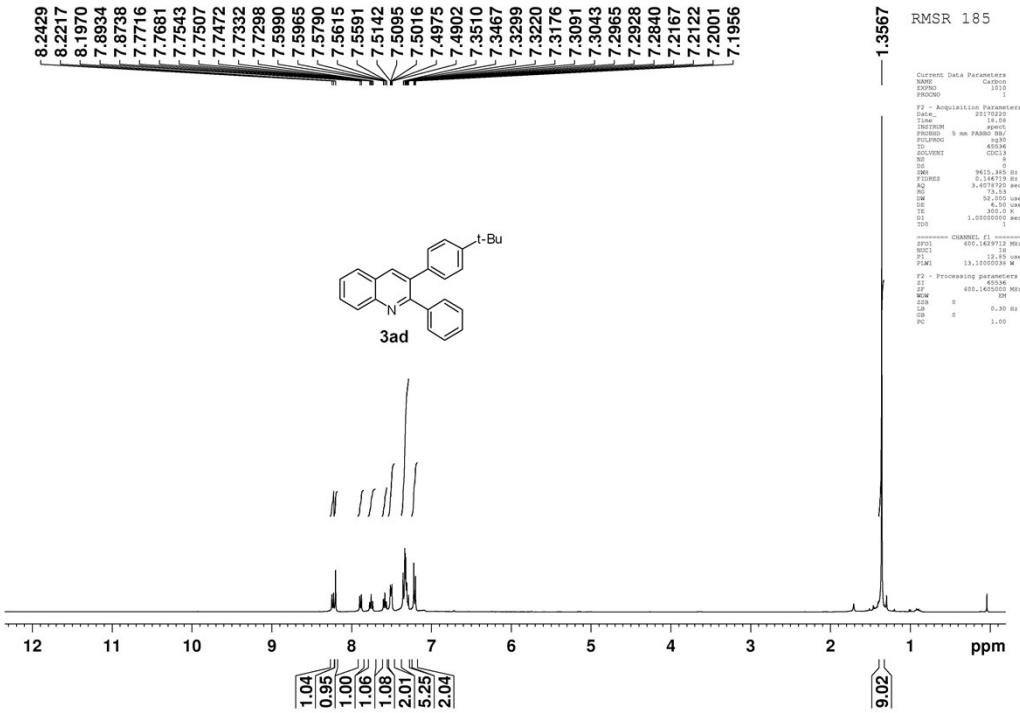

Fig. S7 ^{1}H NMR of **3ad**

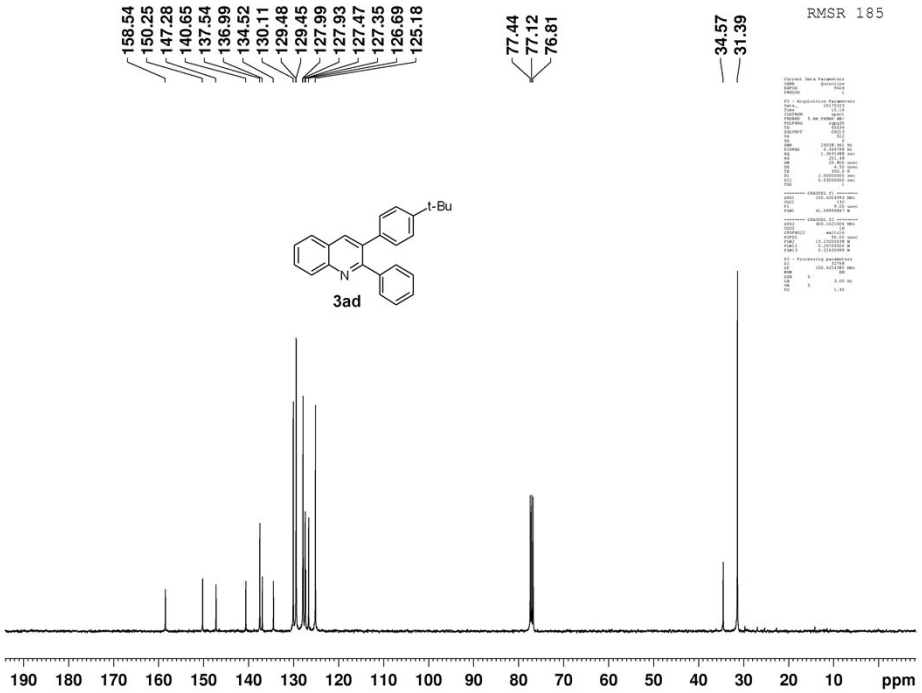

Fig. S8 ^{13}C NMR of **3ad**

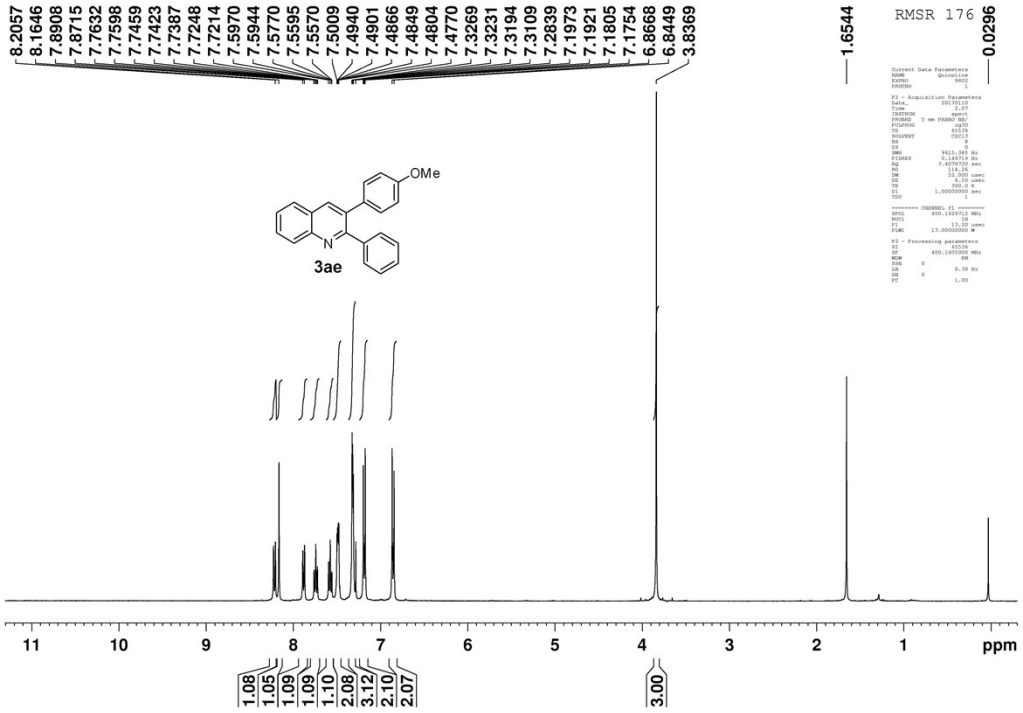

Fig. S9 ^{1}H NMR of **3ae**

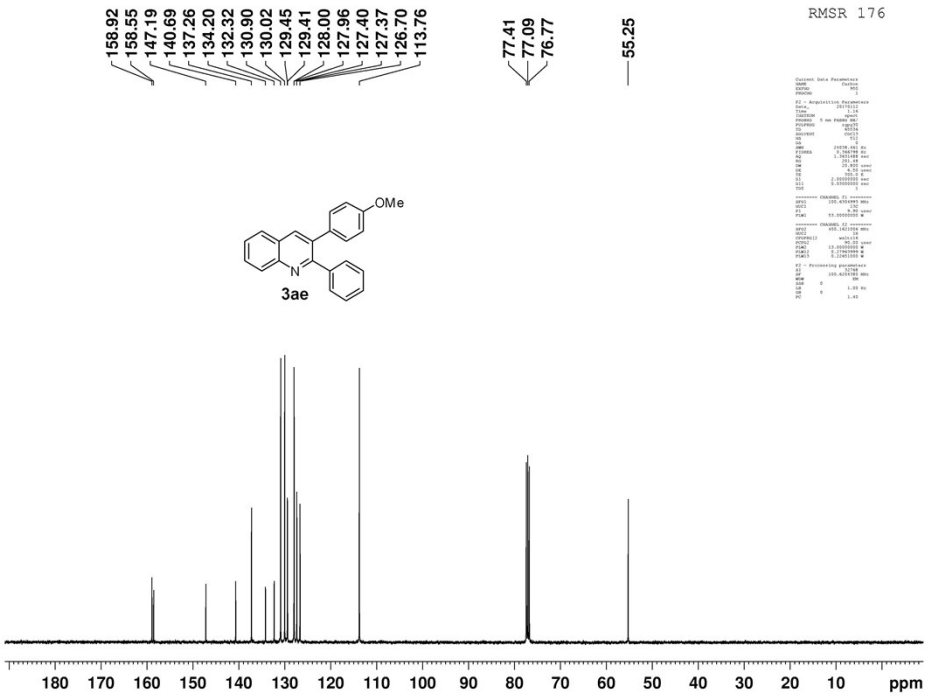

Fig. S10 ^{13}C NMR of **3ae**

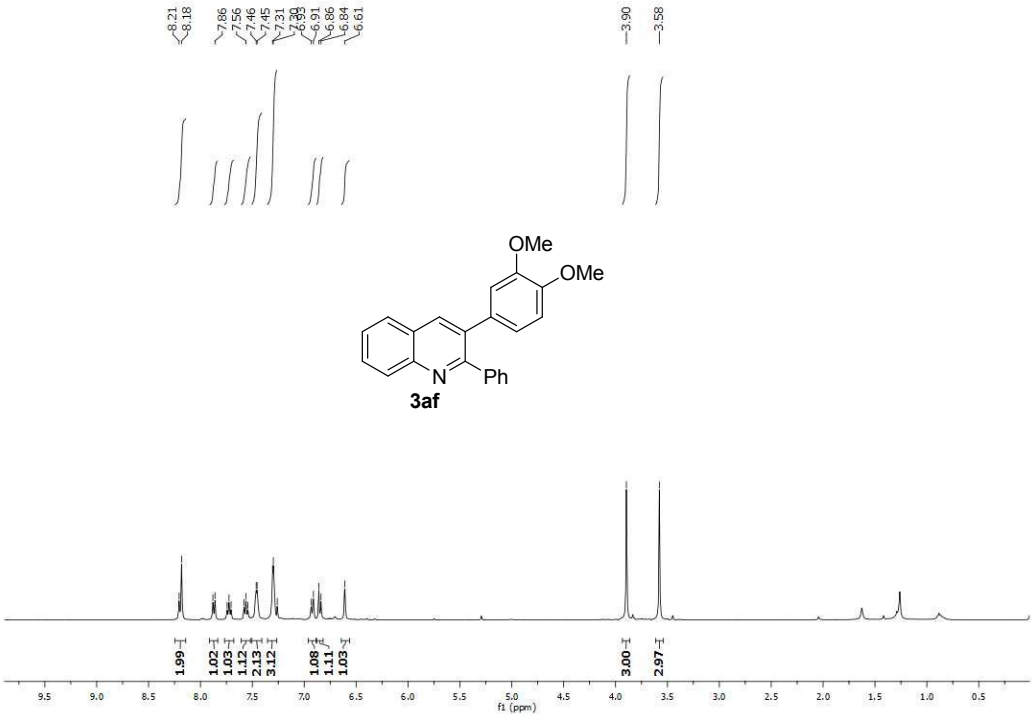

Fig. S11 ^{1}H NMR **of 3af**

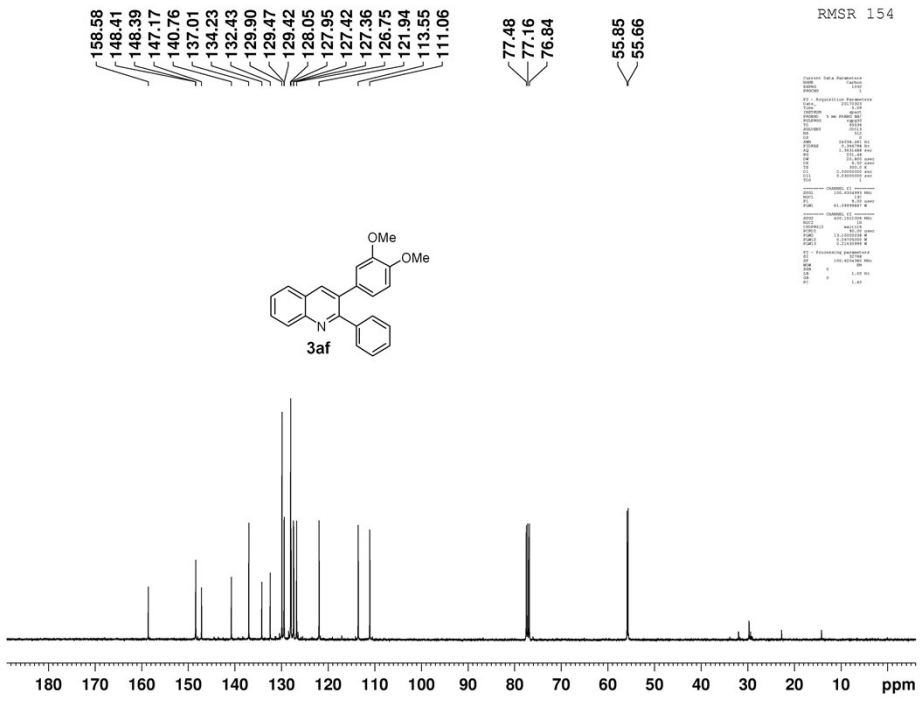

Fig. S12 ^{13}C NMR of **3af**

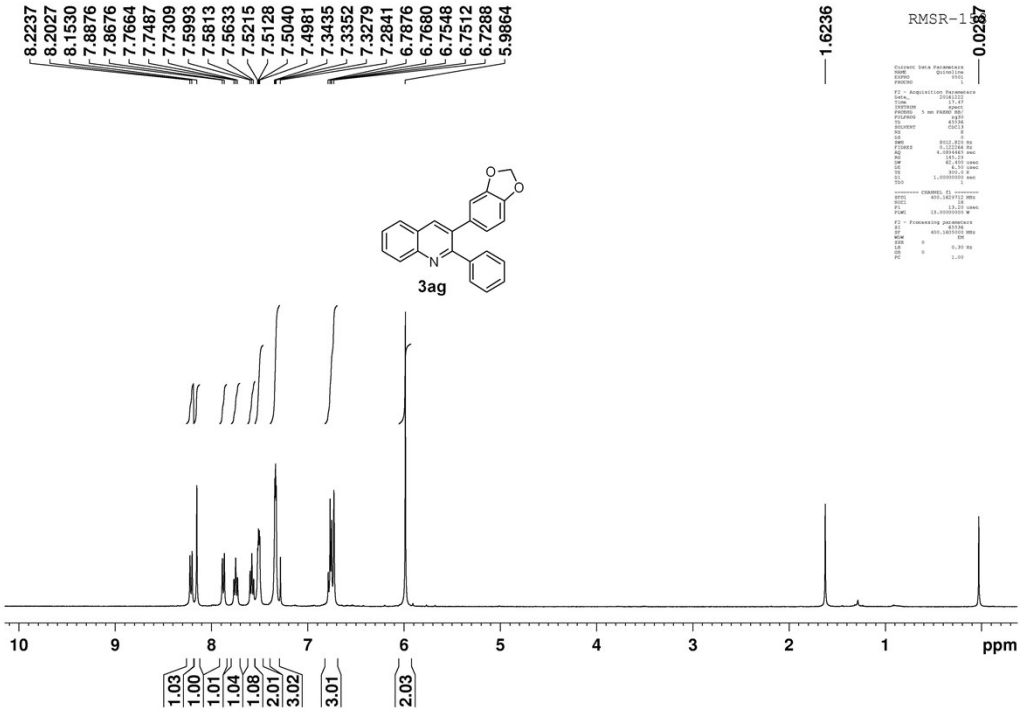

Fig. S13 ^{1}H NMR of **3ag**

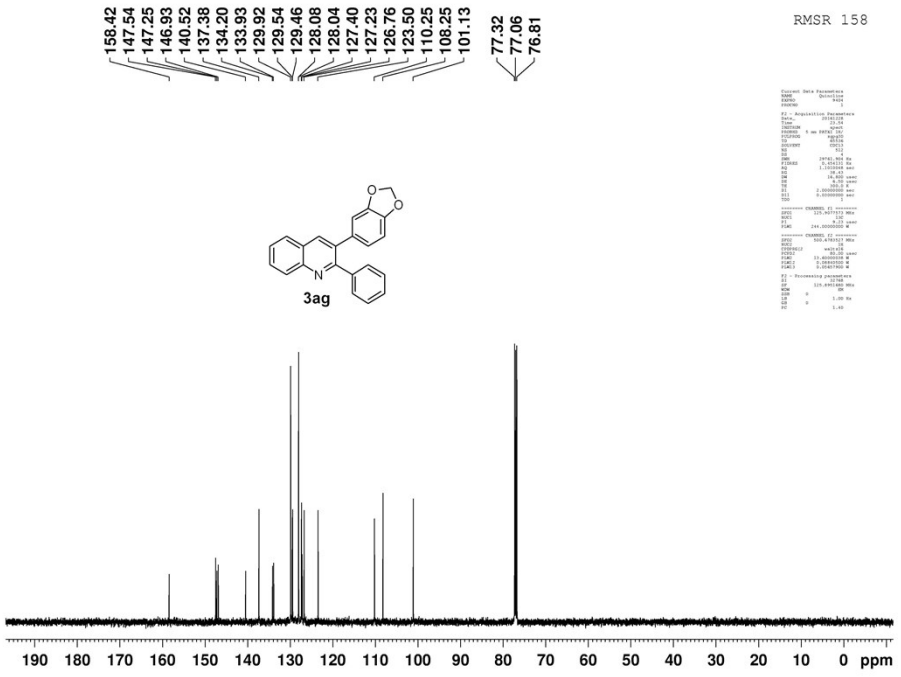

Fig. S14 ^{13}C NMR of **3ag**

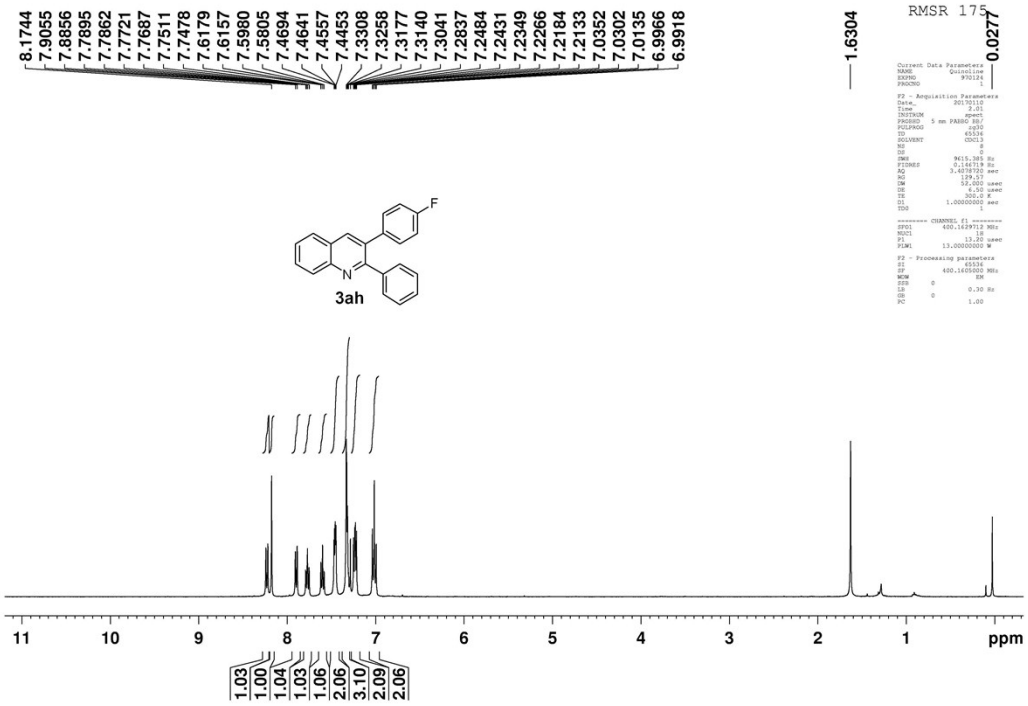

Fig. S15 ^{1}H NMR of **3ah**

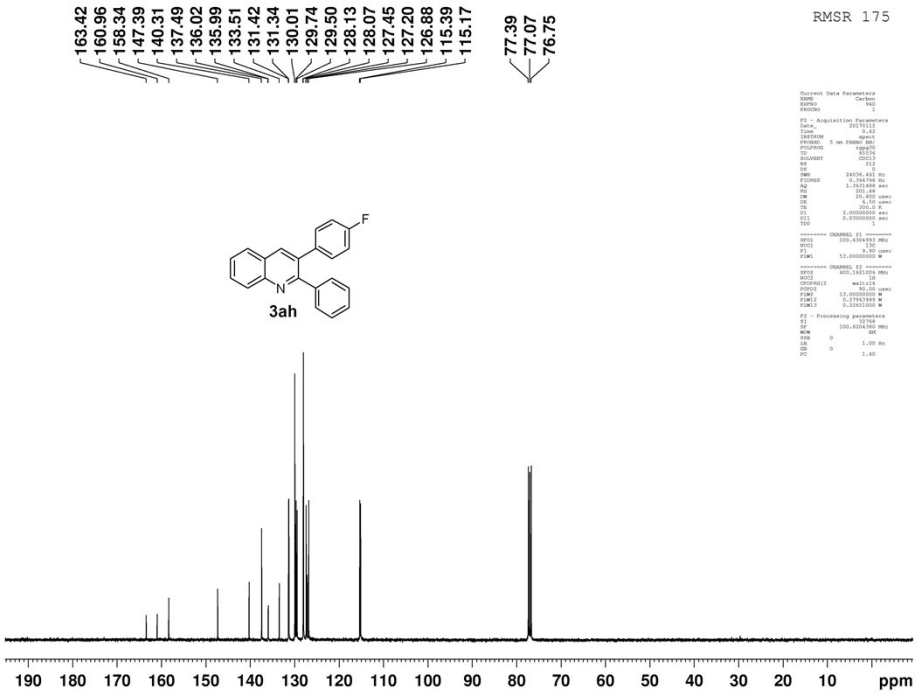

Fig. S16 ^{13}C NMR of **3ah**

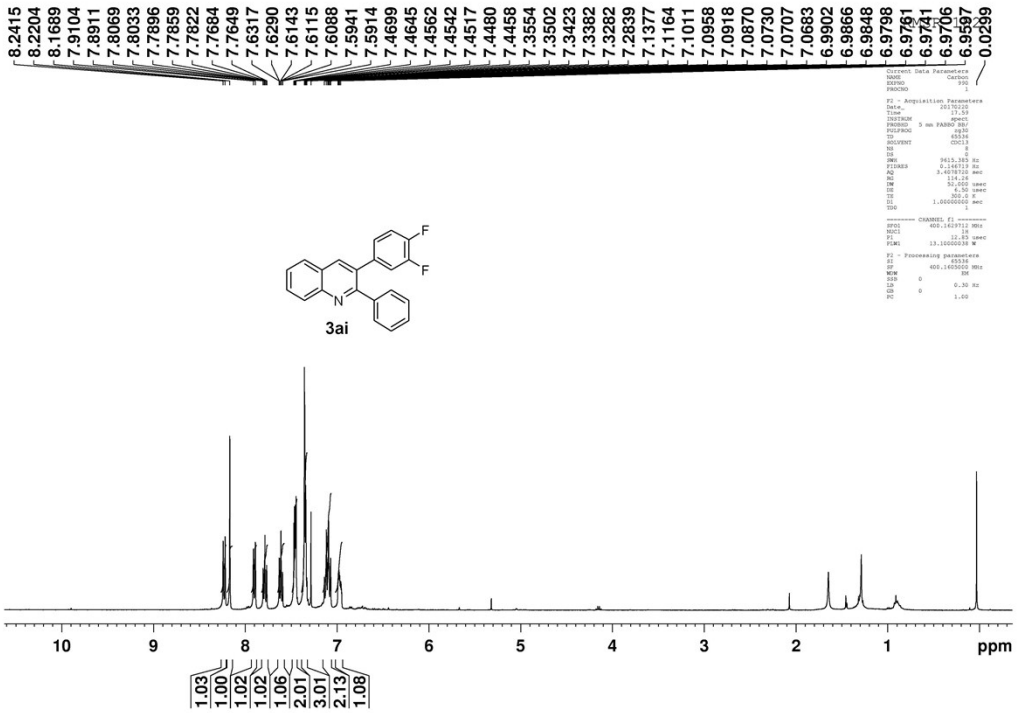

Fig. S17 ^{1}H NMR of **3ai**

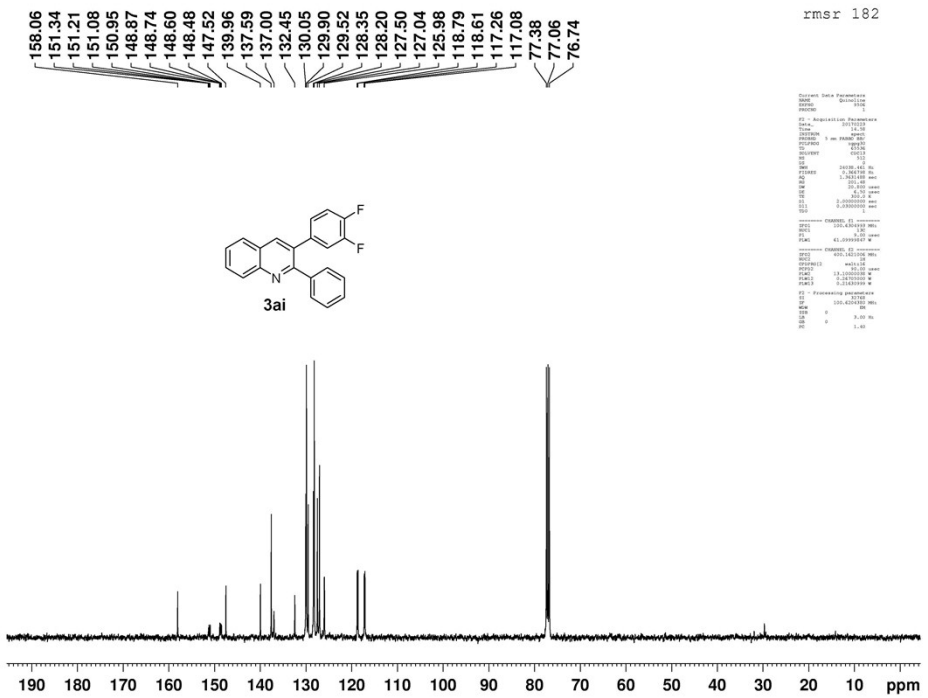

Fig. S18 ^{13}C NMR of **3ai**

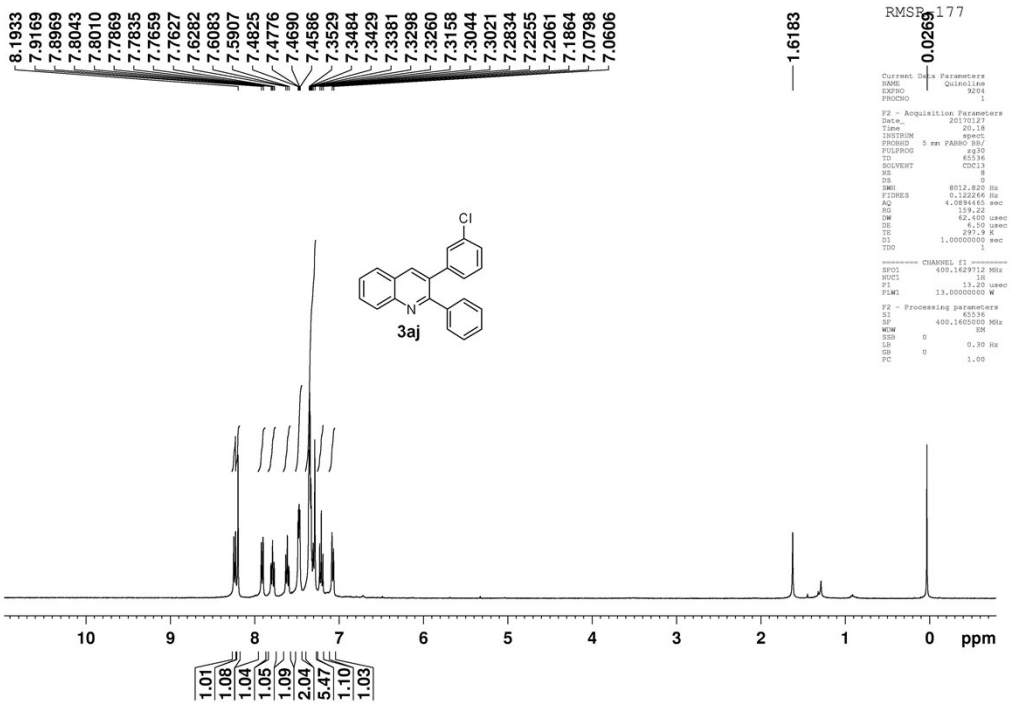

Fig. S19 ^{1}H NMR of **3aj**

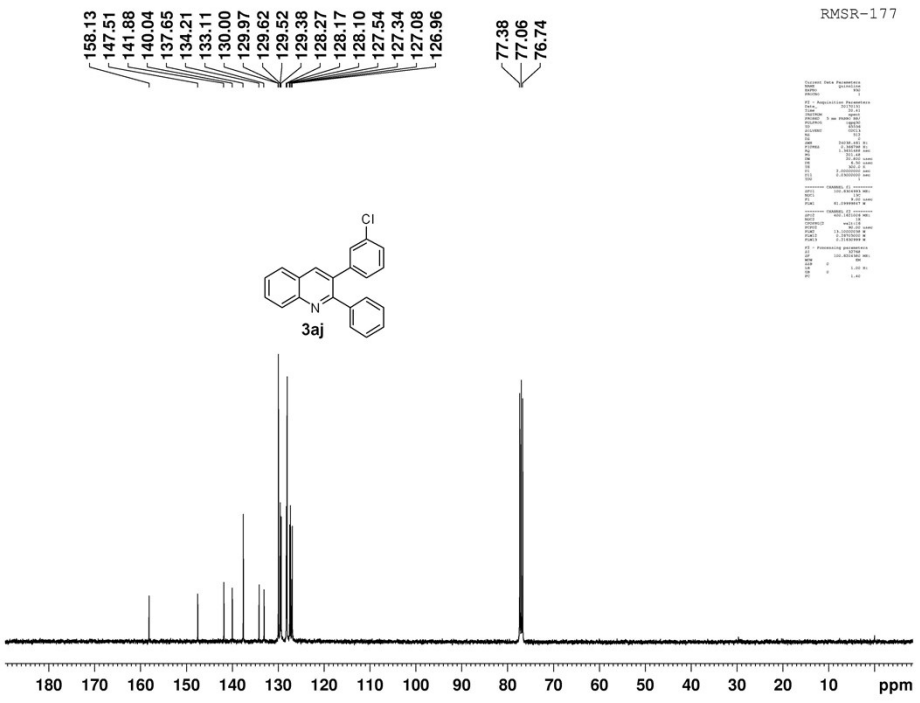

Fig. S20 ^{13}C NMR of **3aj**

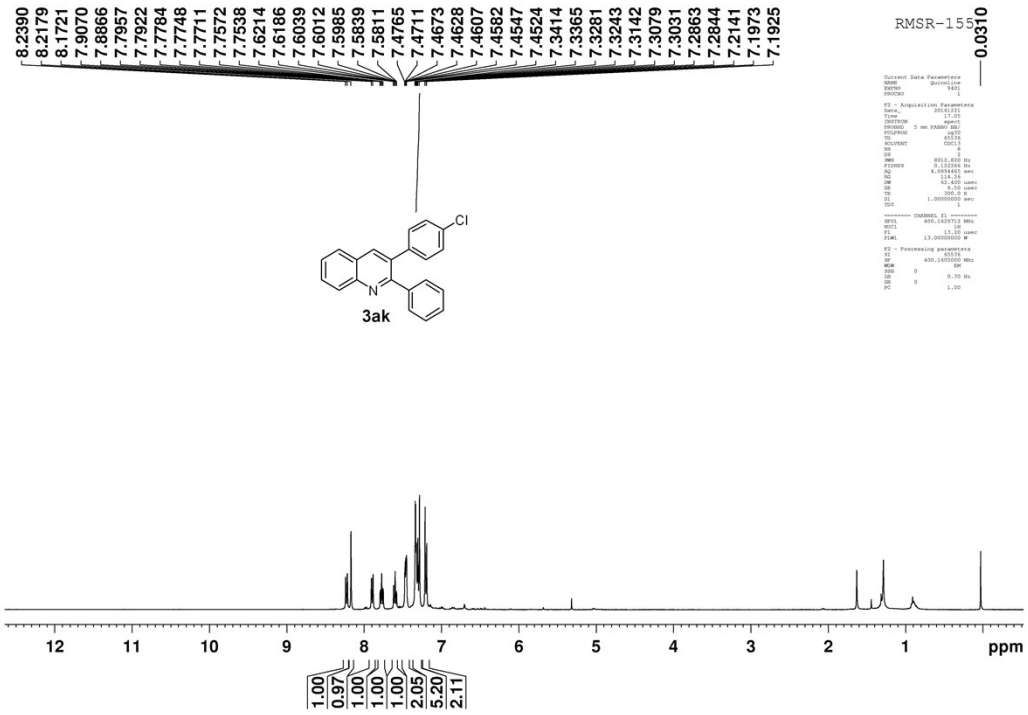

Fig. S21 ^{1}H NMR of **3ak**

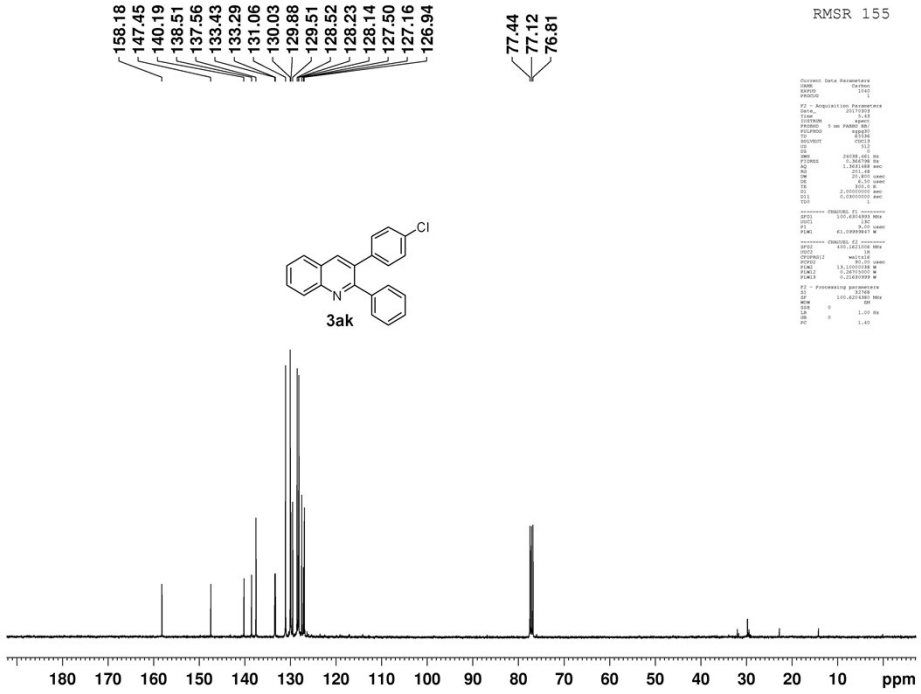

Fig. S22 ^{13}C NMR of **3ak**

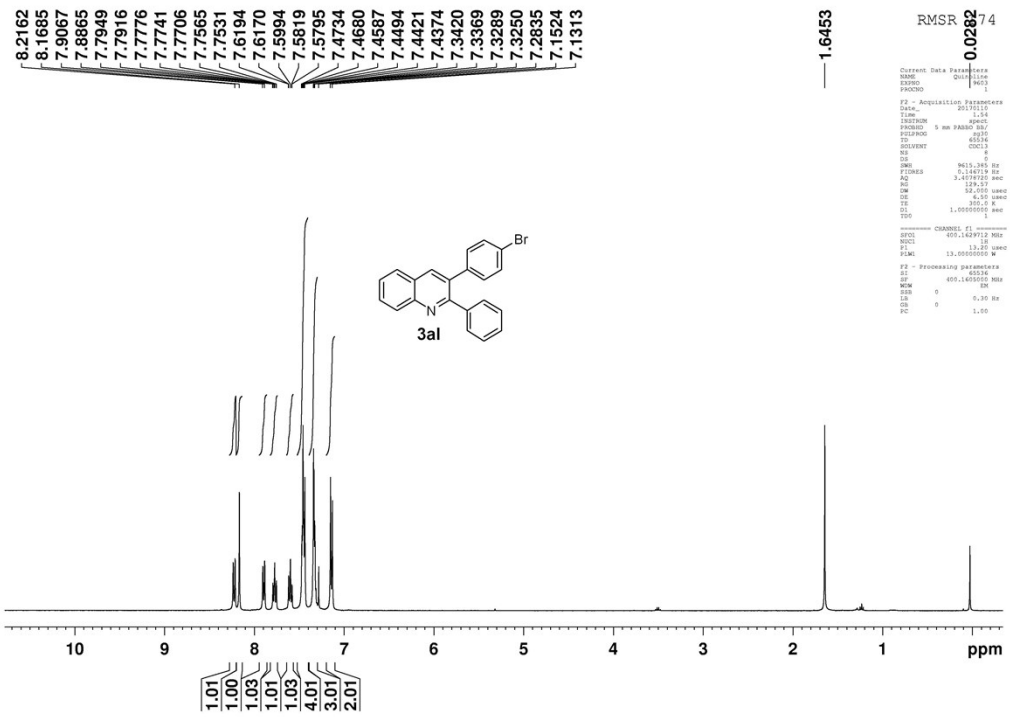

Fig. S23 ^{1}H NMR of **3al**

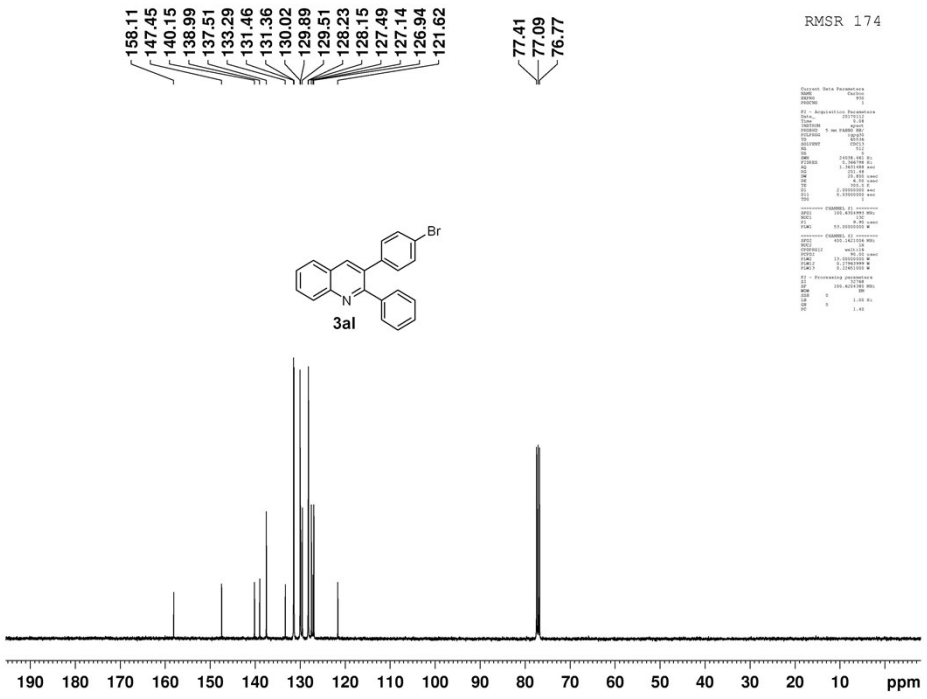

Fig. S24 ^{13}C NMR of **3al**

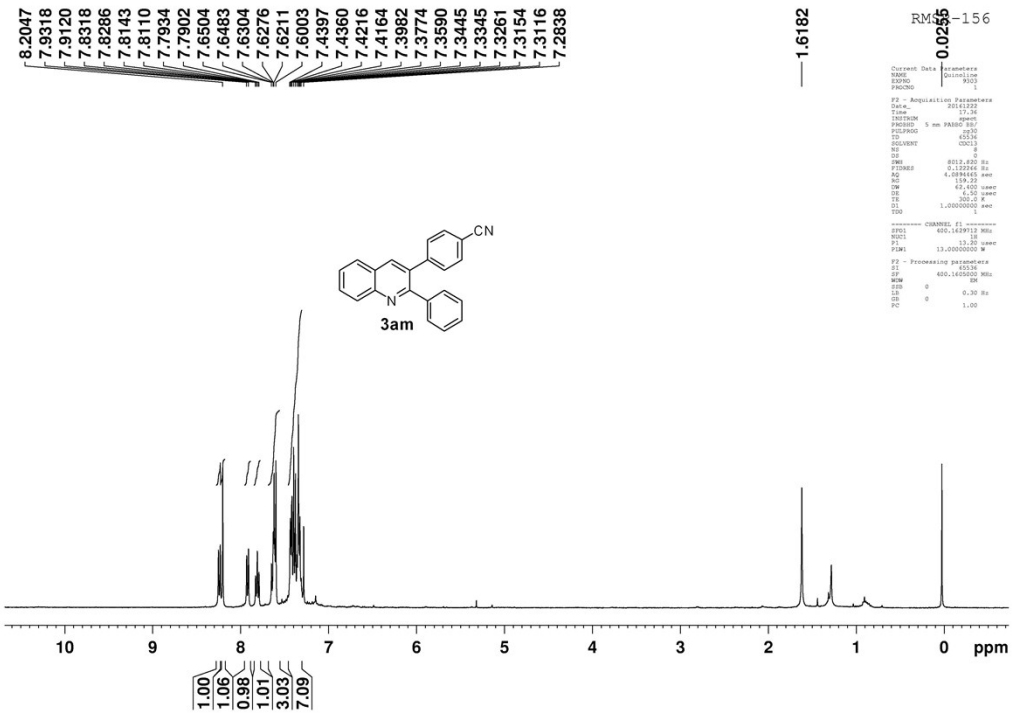

Fig. S25 ^{1}H NMR of **3am**

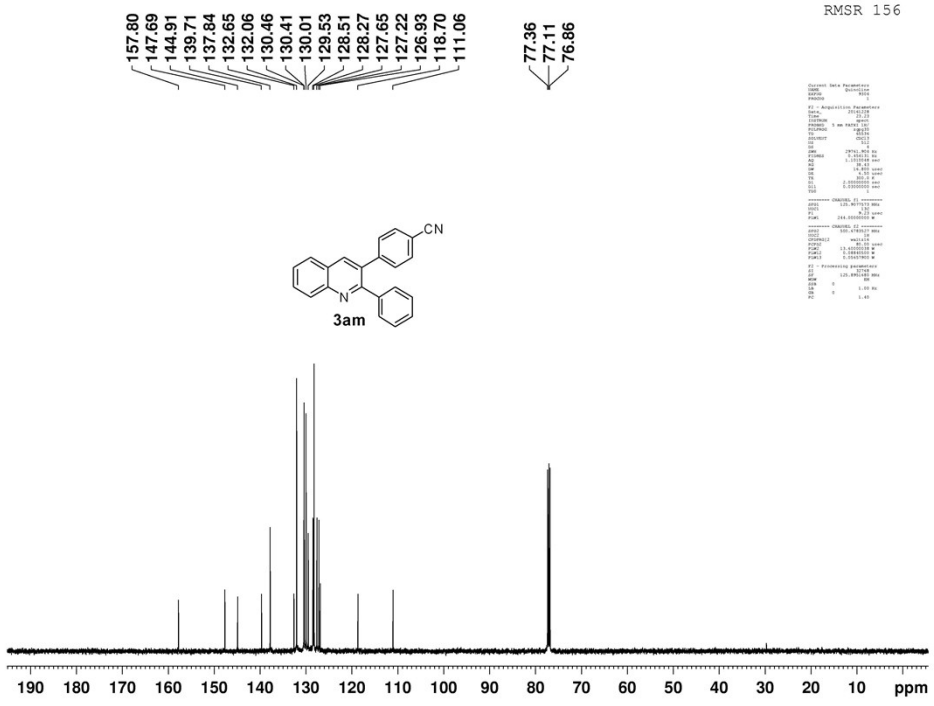

Fig. S26 ^{13}C NMR of **3am**

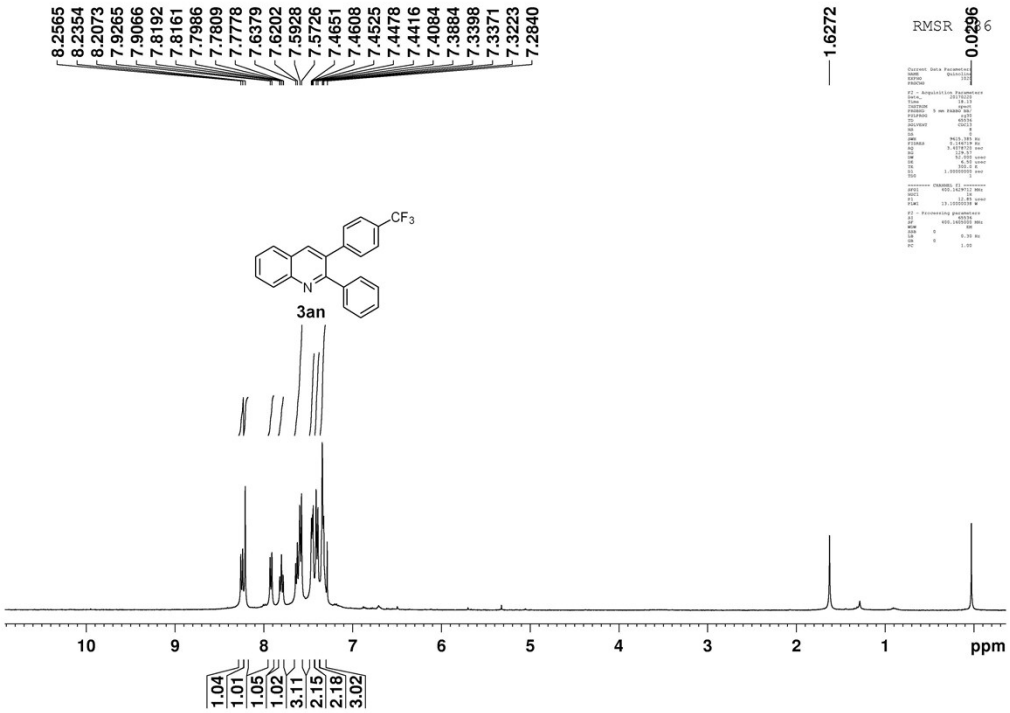

Fig. S27 ^{1}H NMR of **3an**

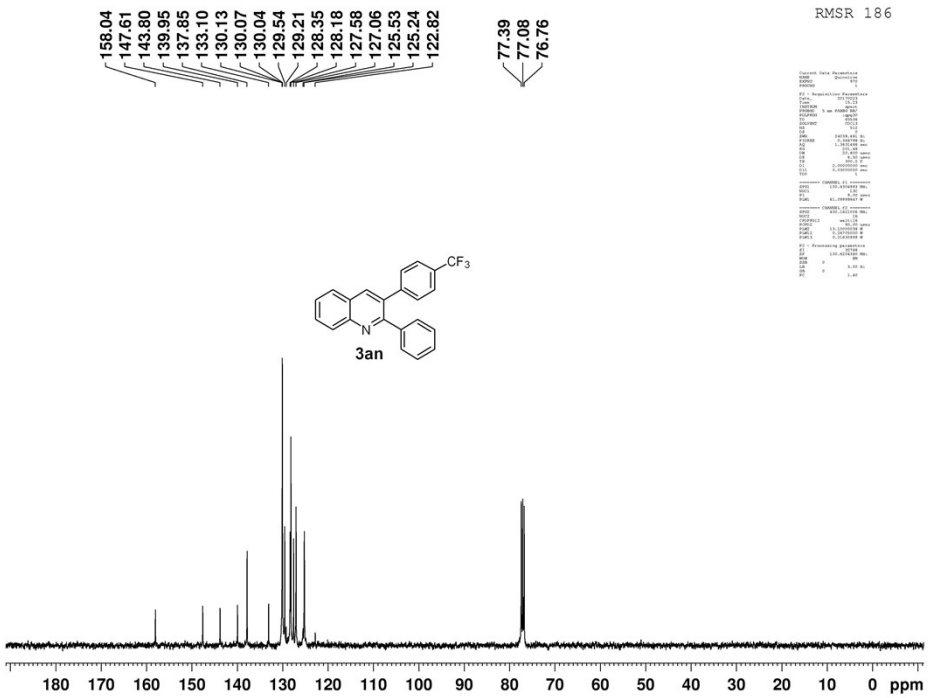

Fig. S28 ^{13}C NMR of **3an**

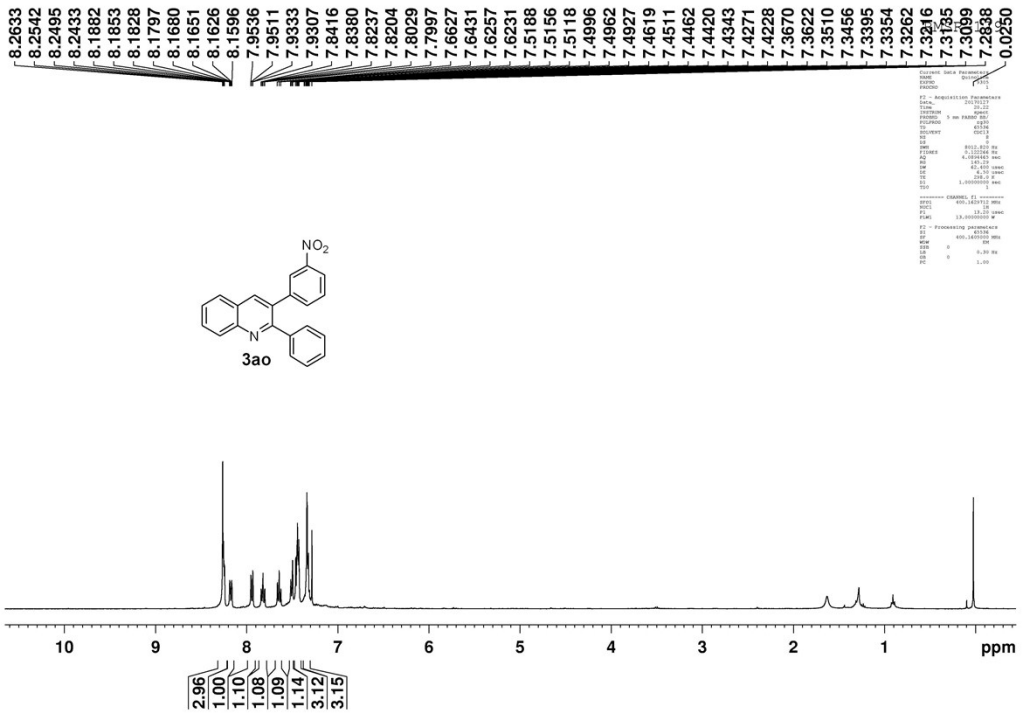

Fig. S29 ^{1}H NMR of **3ao**

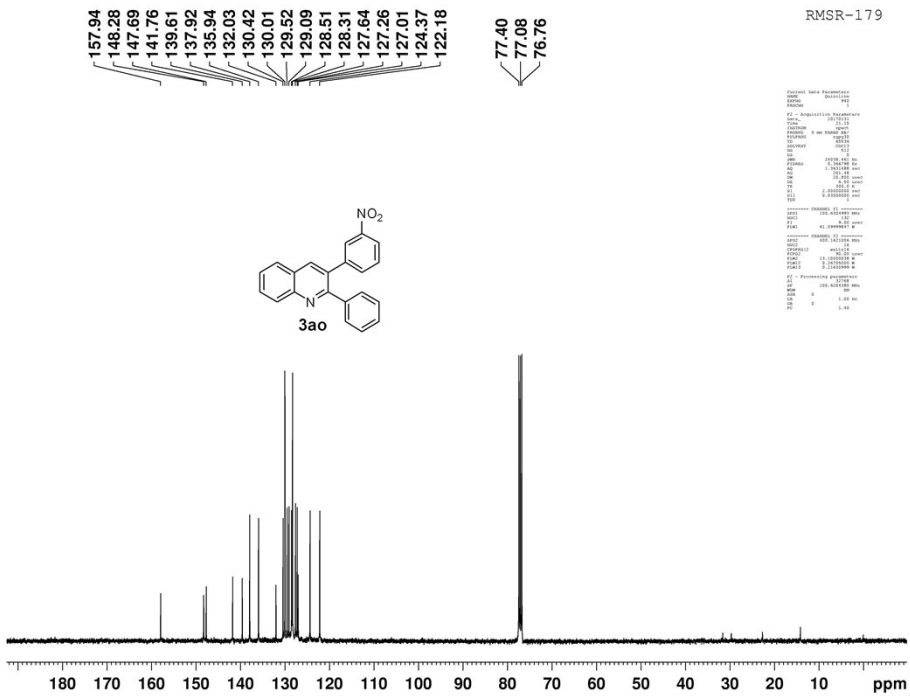

Fig. S30 ^{13}C NMR of **3ao**

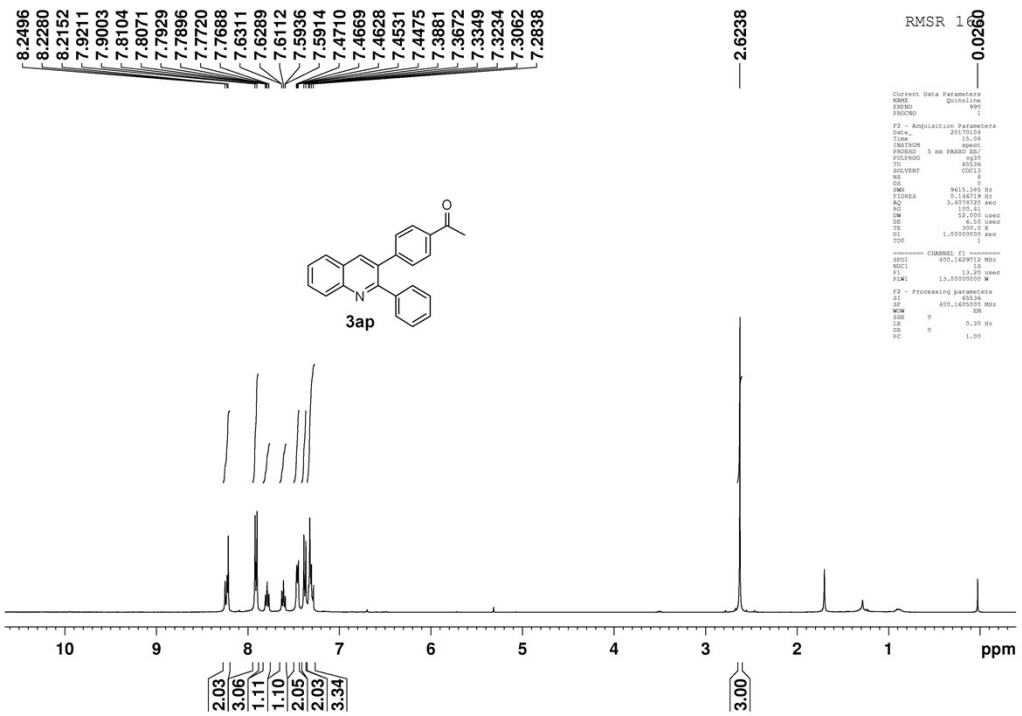

Fig. S31 ^{1}H NMR of **3ap**

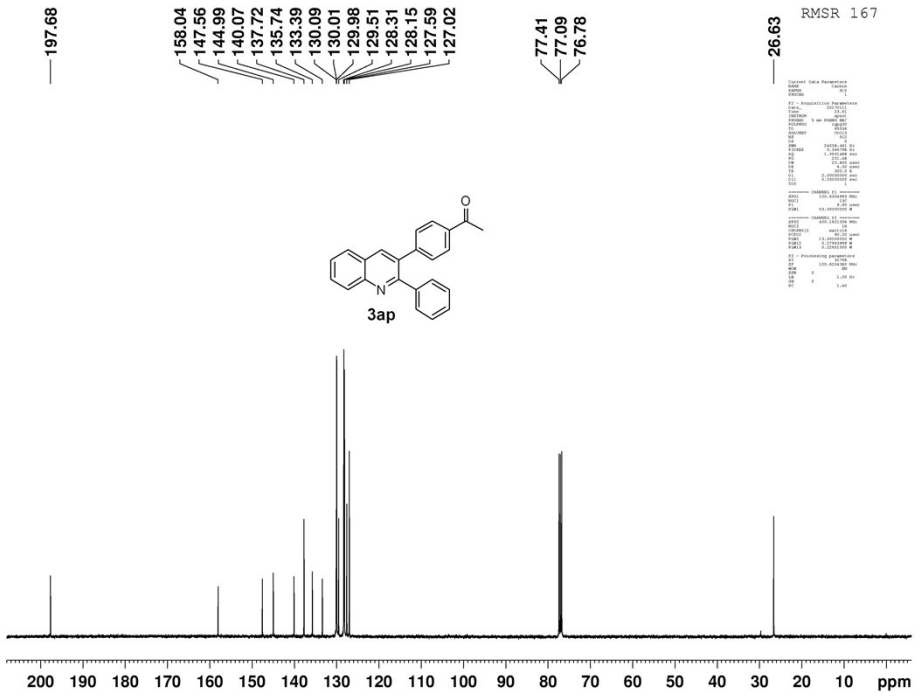

Fig. S32 ^{13}C NMR of **3ap**

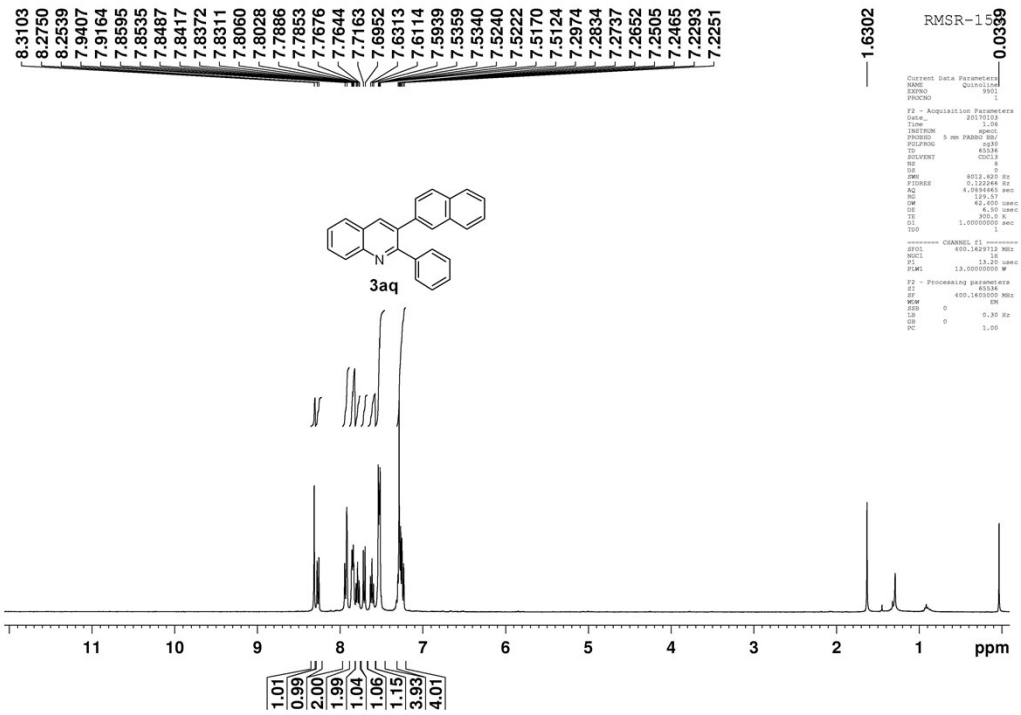

Fig. S33 ^{1}H NMR of **3aq**

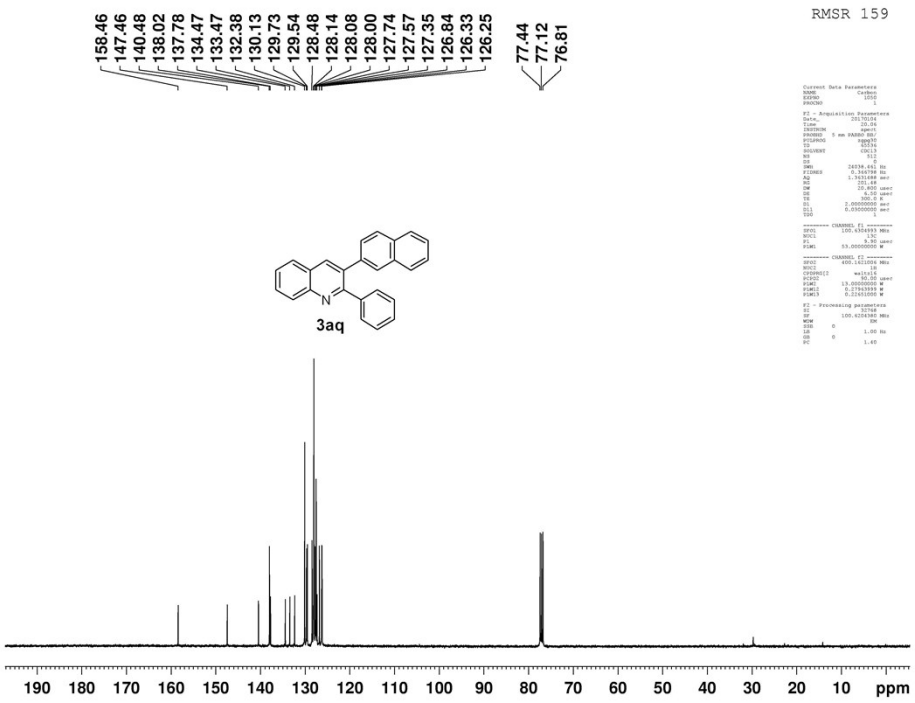

Fig. S34 ^{13}C NMR of **3aq**

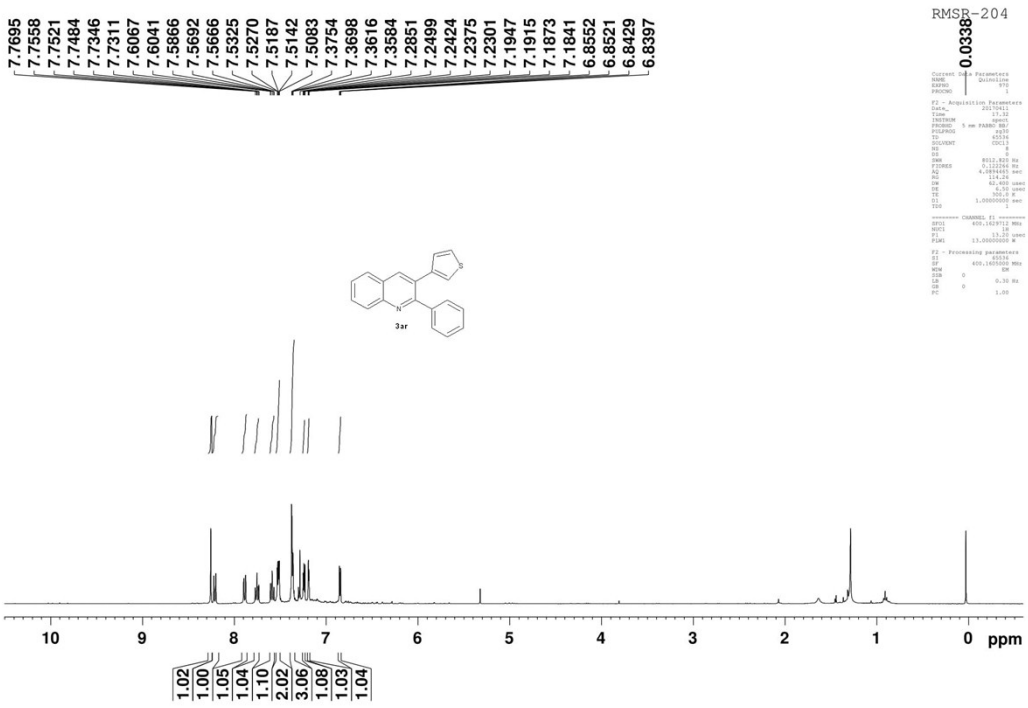

Fig. S35 ^{1}H NMR of **3ar**

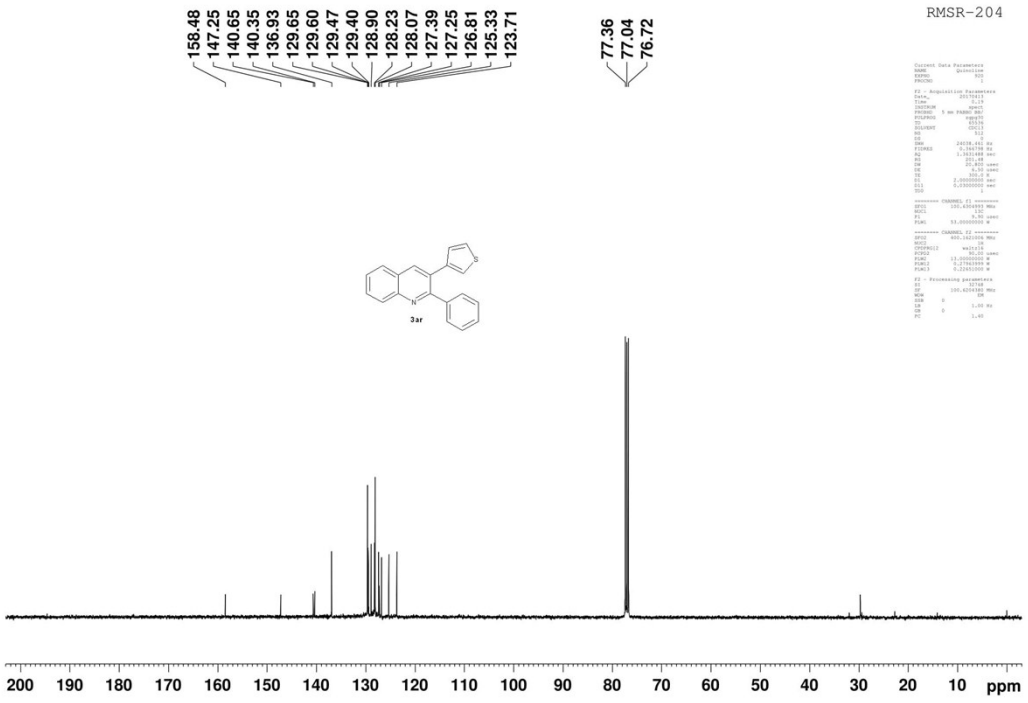

Fig. S36 ^{13}C NMR of **3ar**

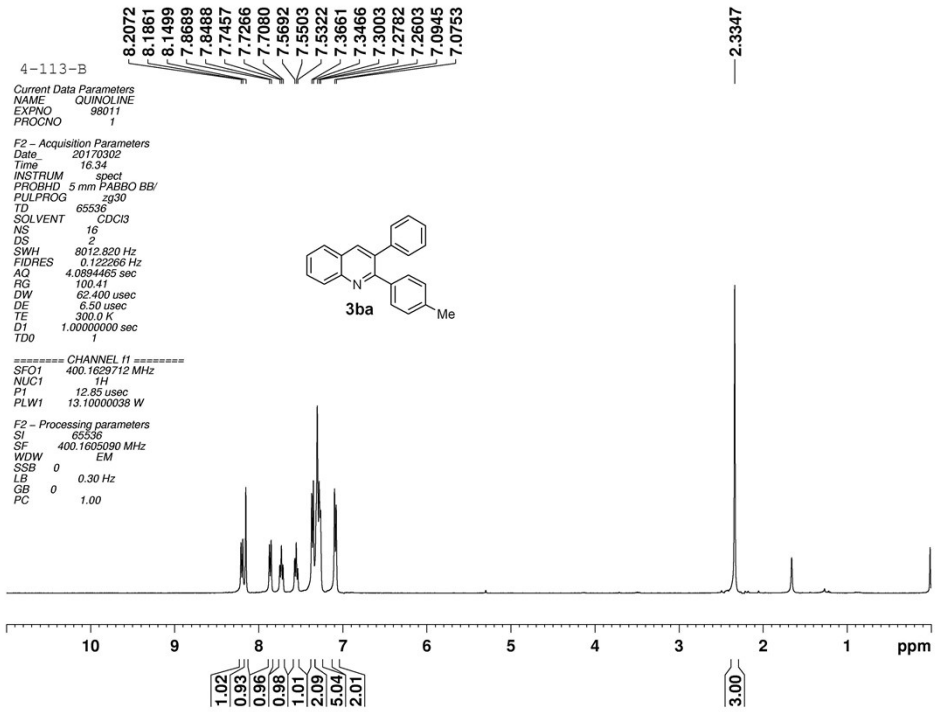

Fig. S37 ^{1}H NMR of **3ba**

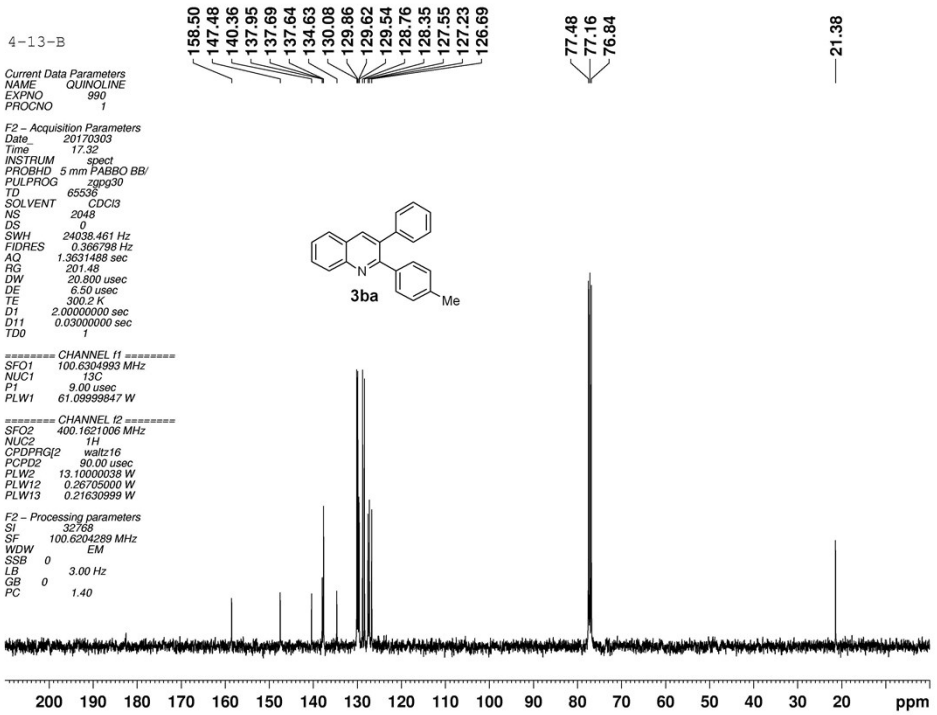

Fig. S38 ^{13}C NMR of **3ba**

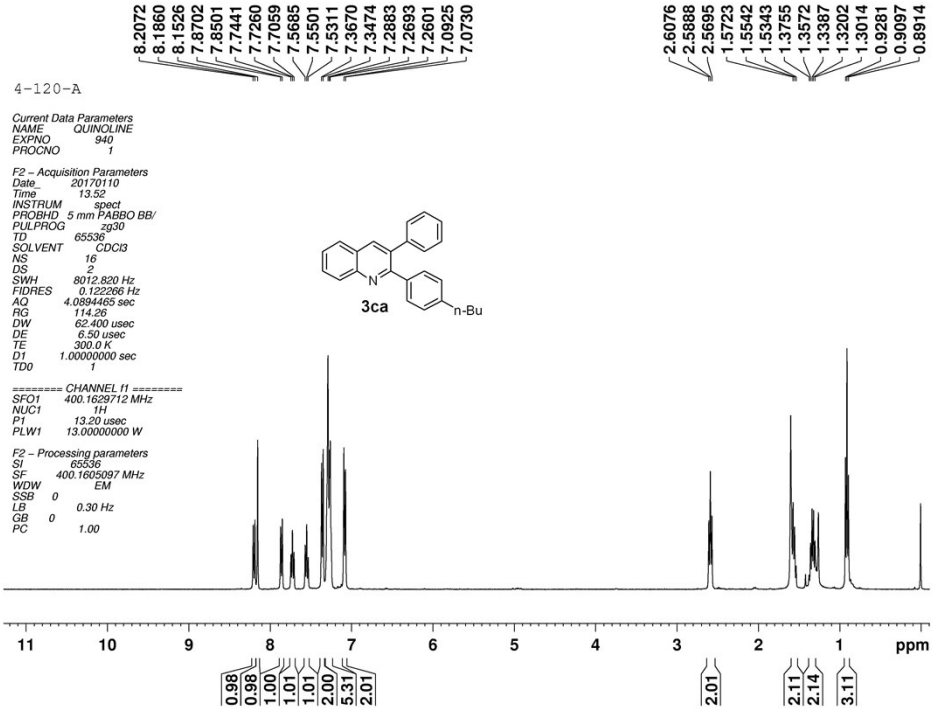

Fig. S39 ^{1}H NMR of **3ca**

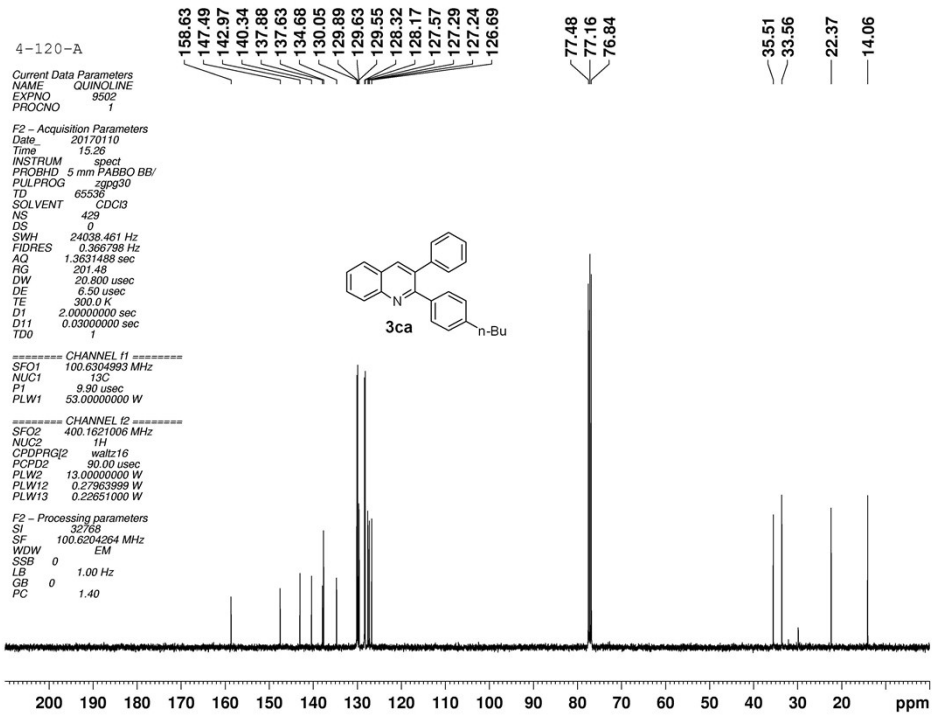

Fig. S40 ^{13}C NMR of **3ca**

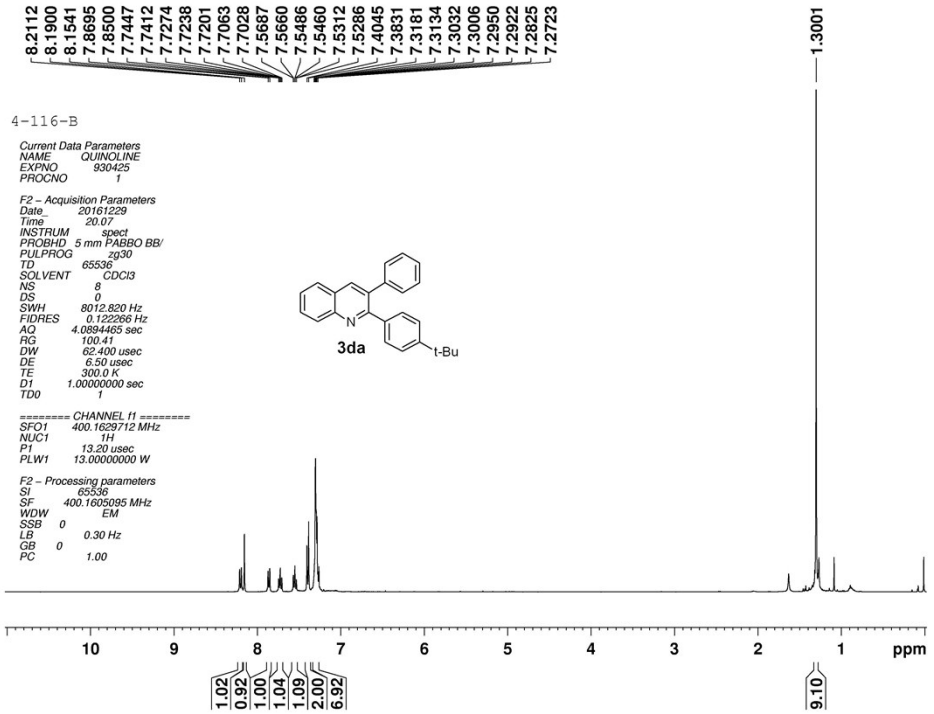

Fig. S41 ^{1}H NMR of **3da**

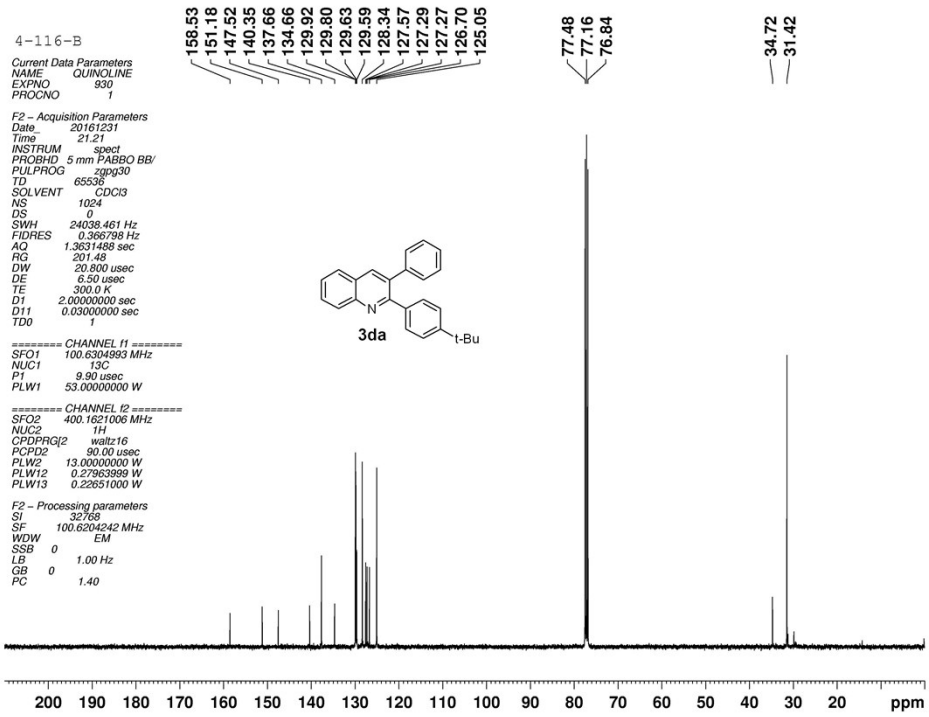

Fig. S42 ^{13}C NMR of **3da**

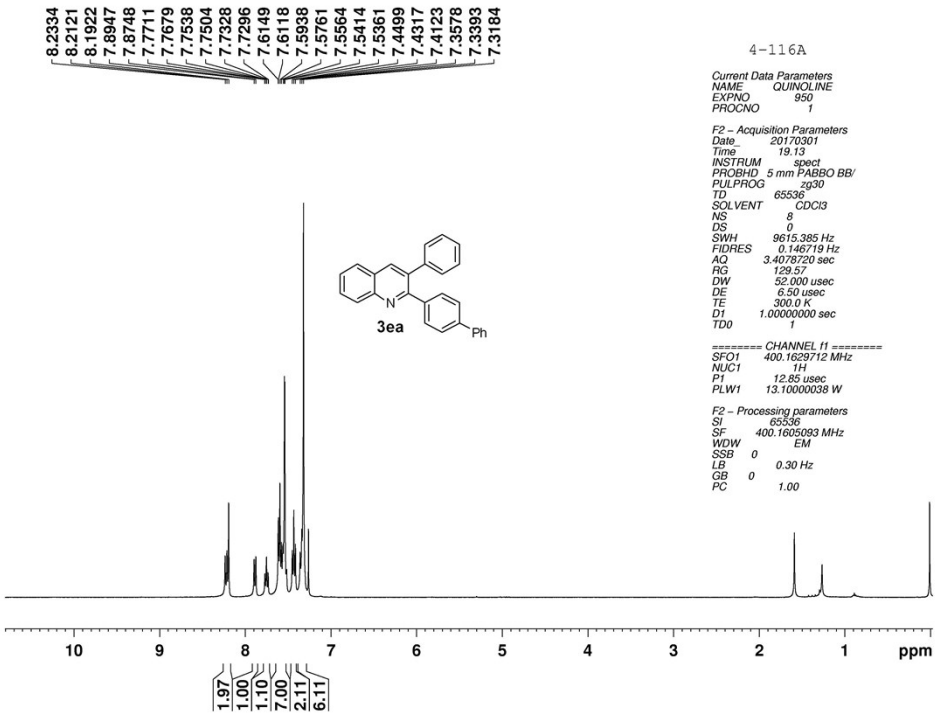

Fig. S43 ^{1}H NMR of **3ea**

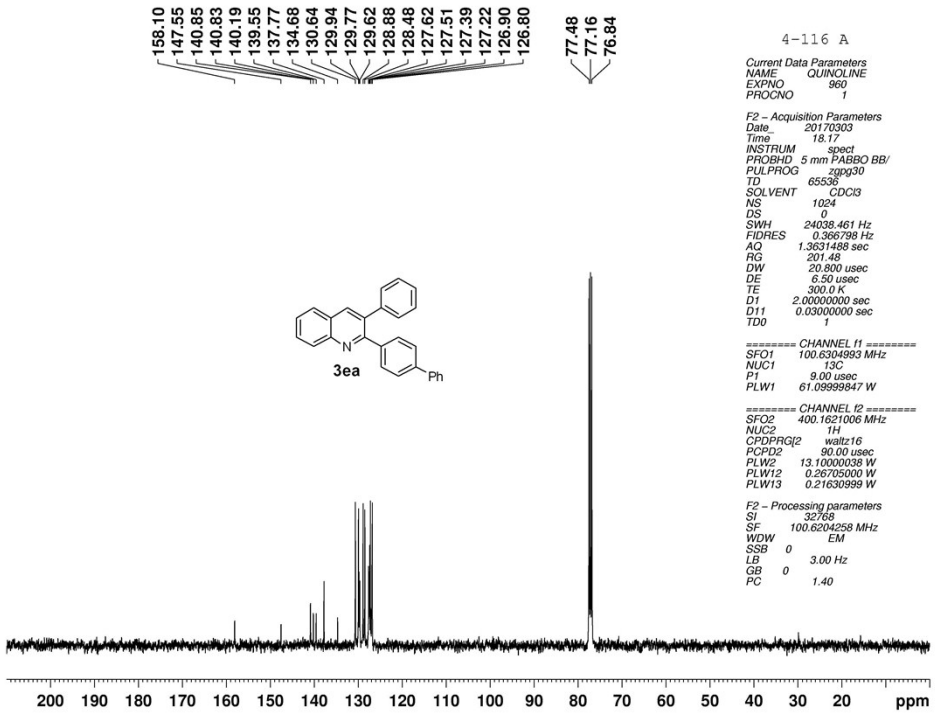

Fig. S44 ^{13}C NMR of **3ea**

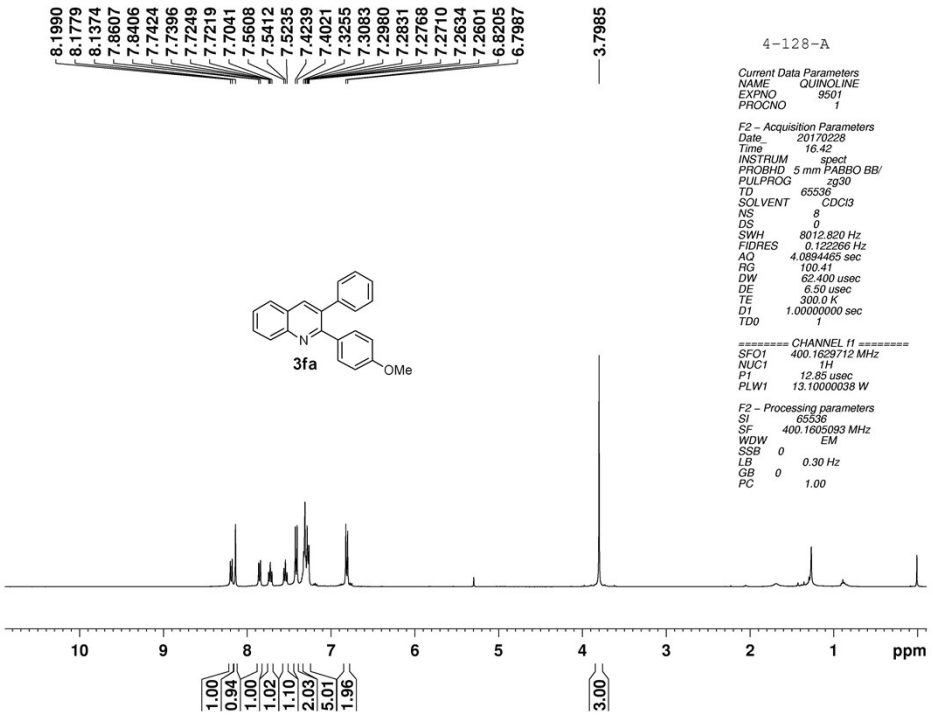

Fig. S45 ^{1}H NMR of **3fa**

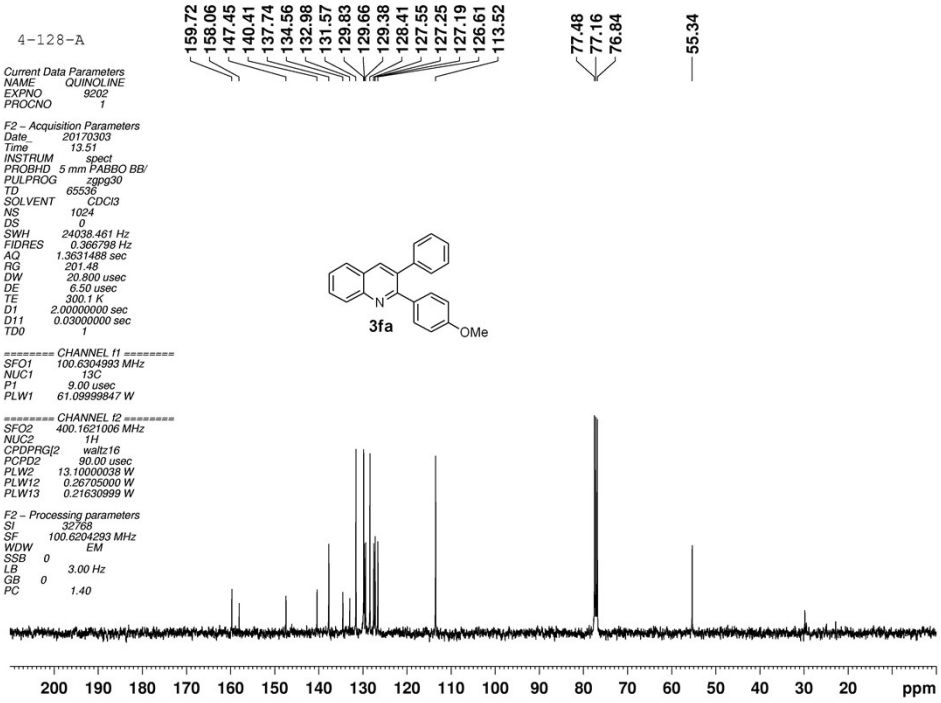

Fig. S46 ^{13}C NMR of **3fa**

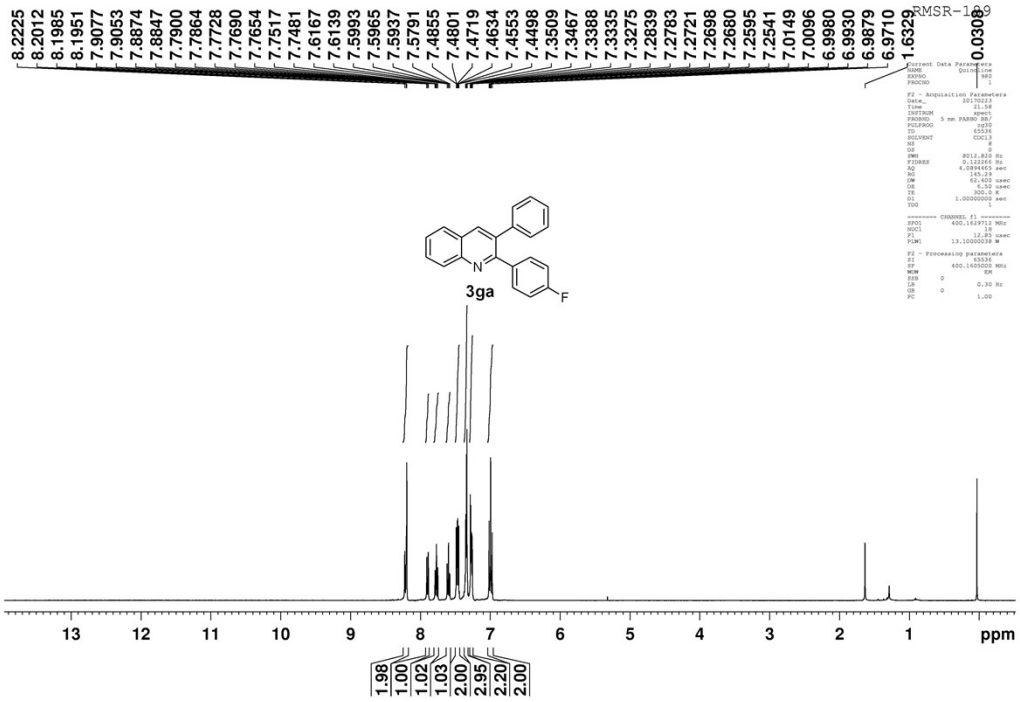

Fig. S47 ^{1}H NMR of **3ga**

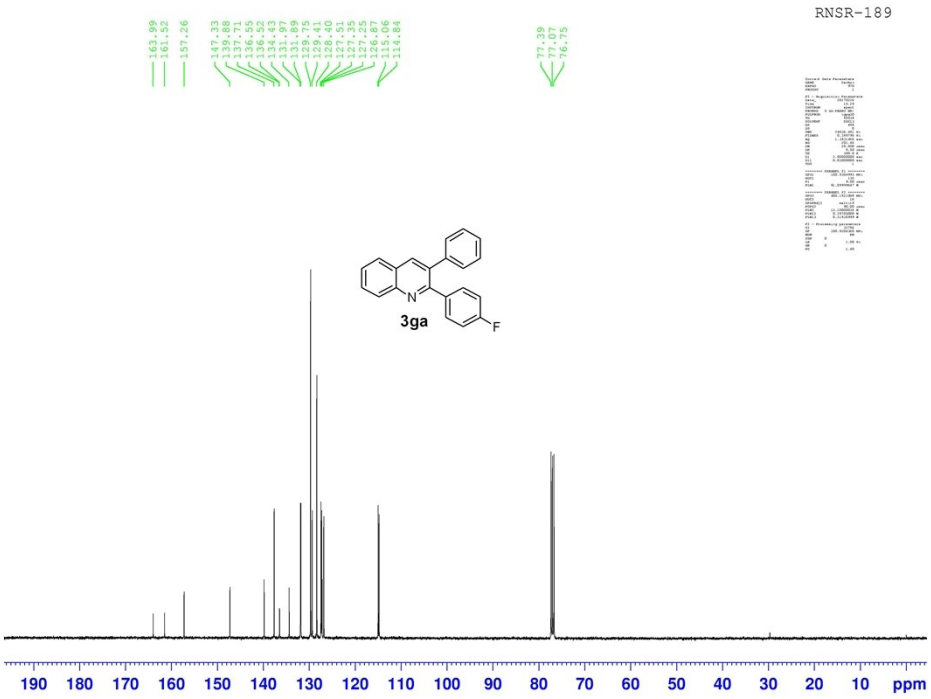

Fig. S48 ^{13}C NMR of **3ga**

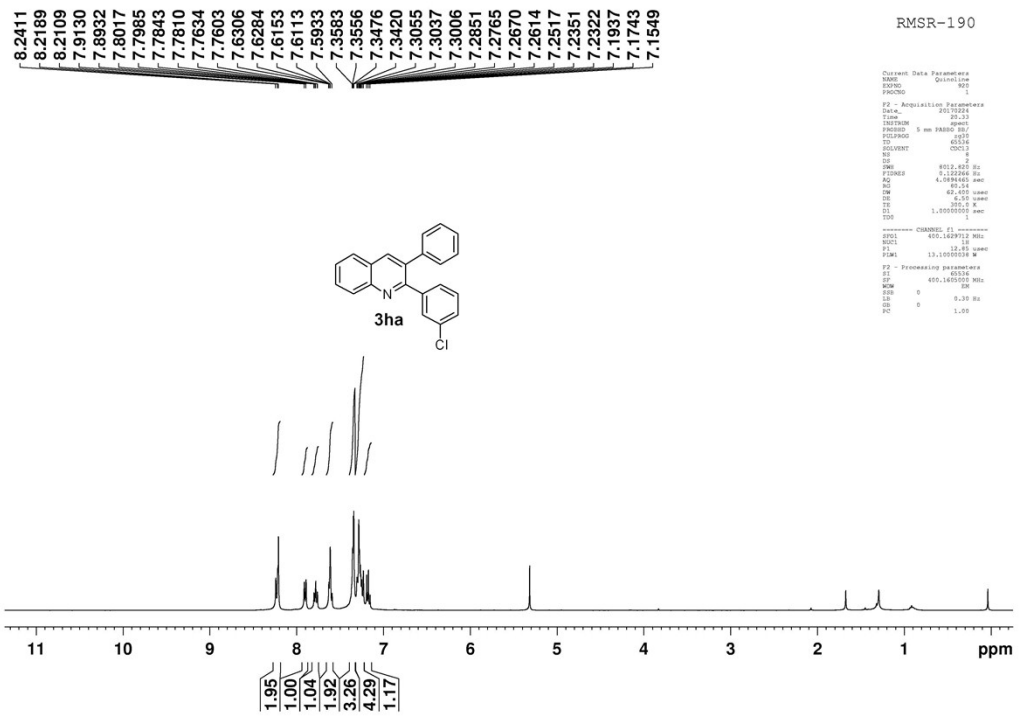

Fig. S49 ^{1}H NMR of **3ha**

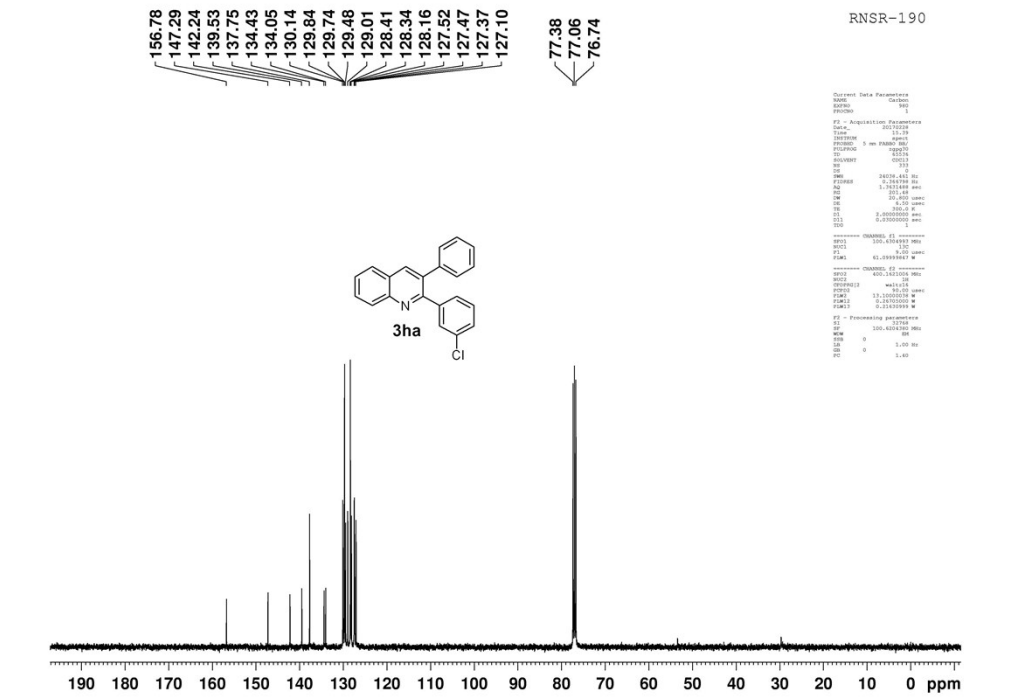

Fig. S50 ^{13}C NMR of **3ha**

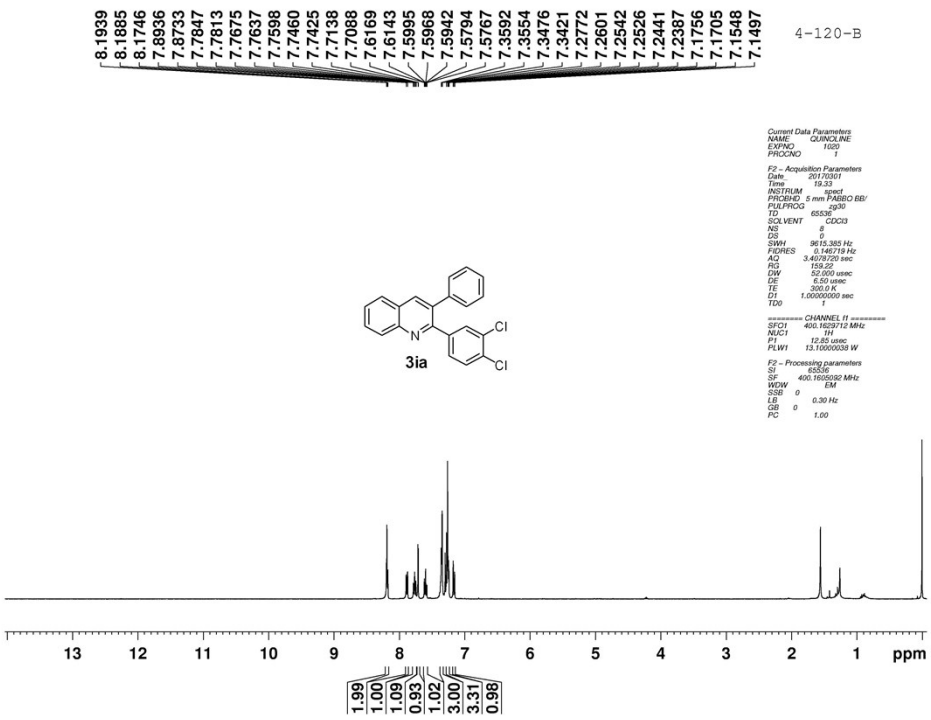

Fig. S51 ^{1}H NMR of **3ia**

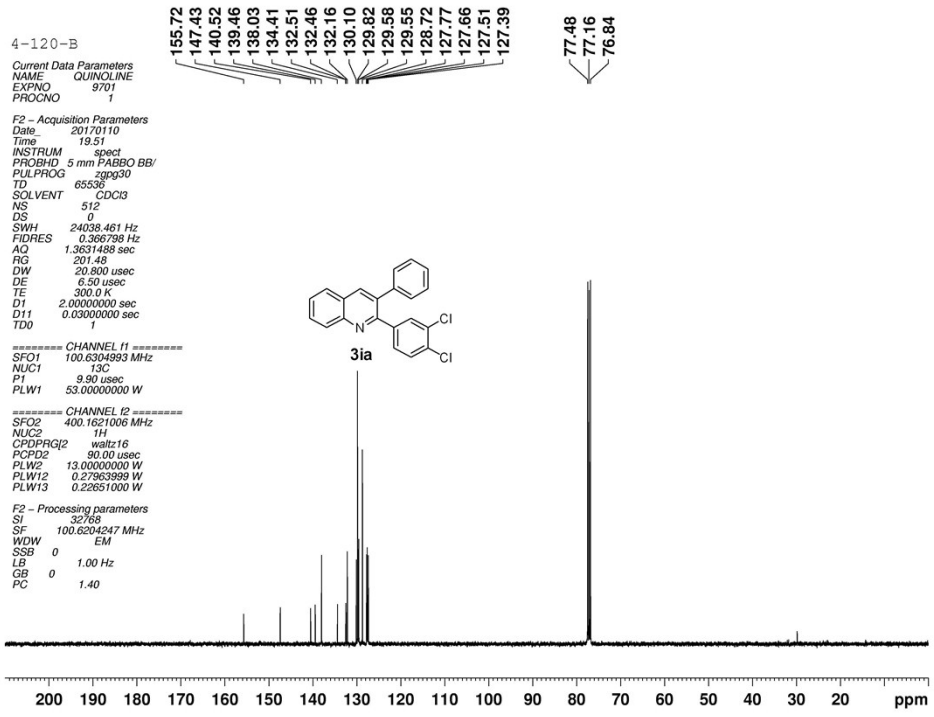

Fig. S52 ^{13}C NMR of **3ia**

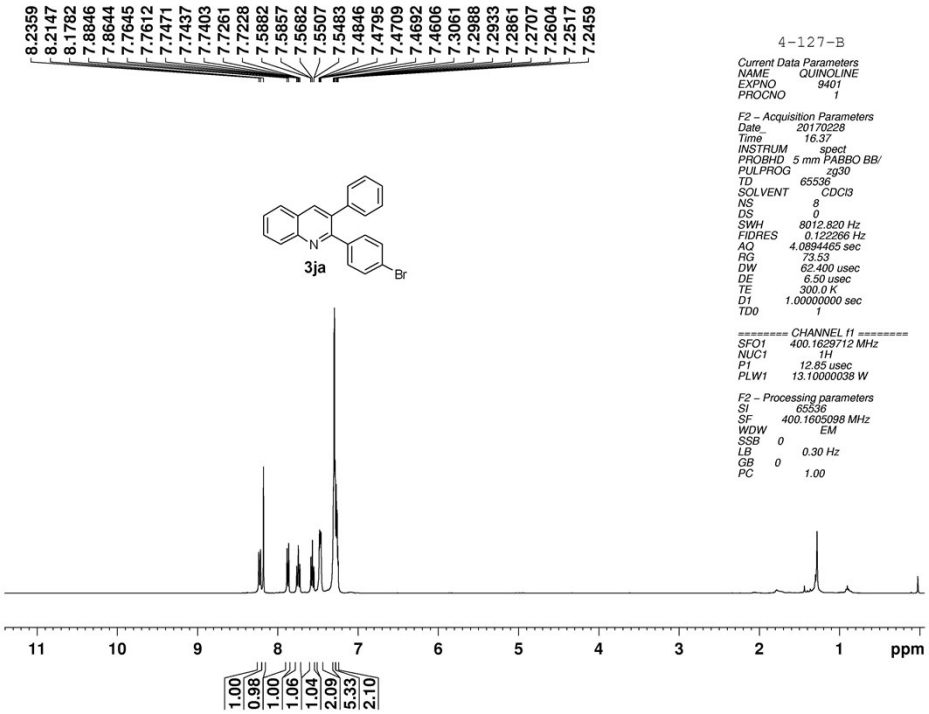

Fig. S53 ^{1}H NMR of **3ja**

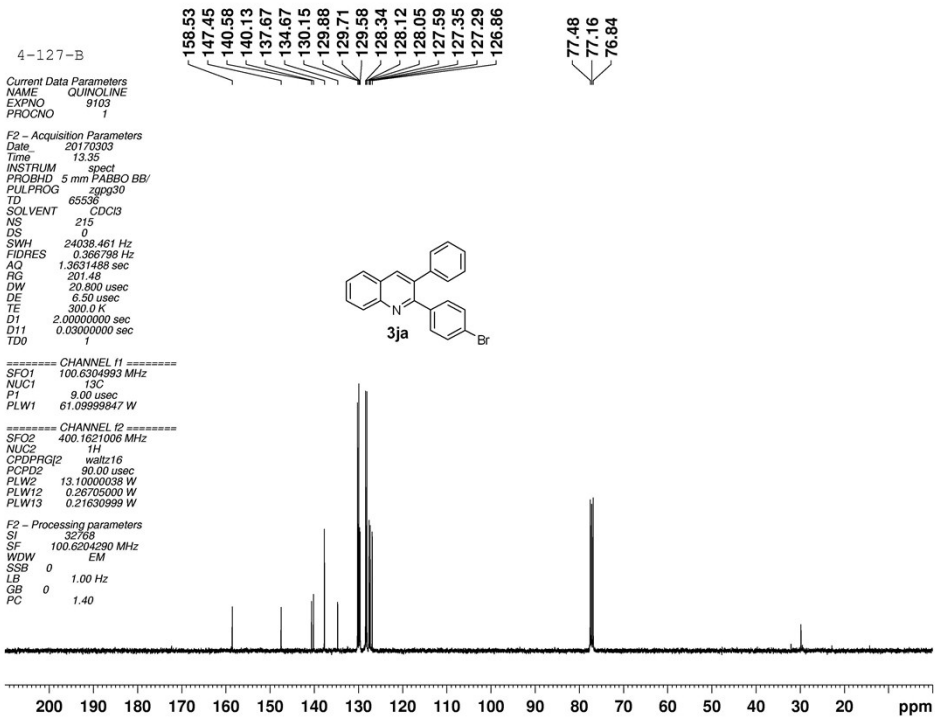

Fig. S54 ^{13}C NMR of **3ja**

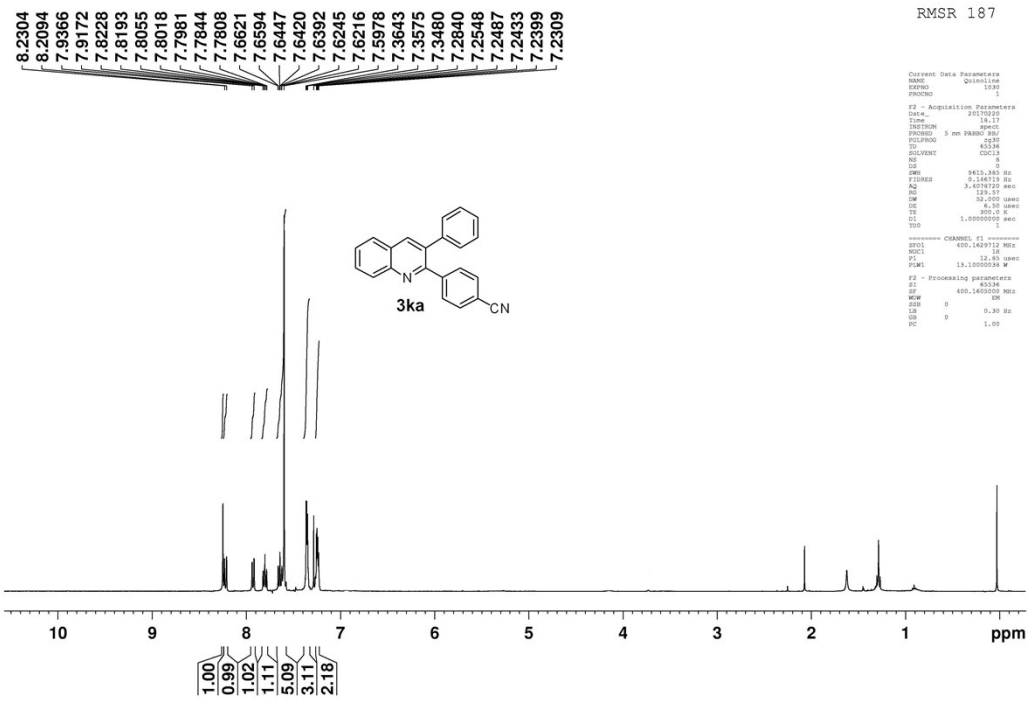

Fig. S55 ^{1}H NMR of **3ka**

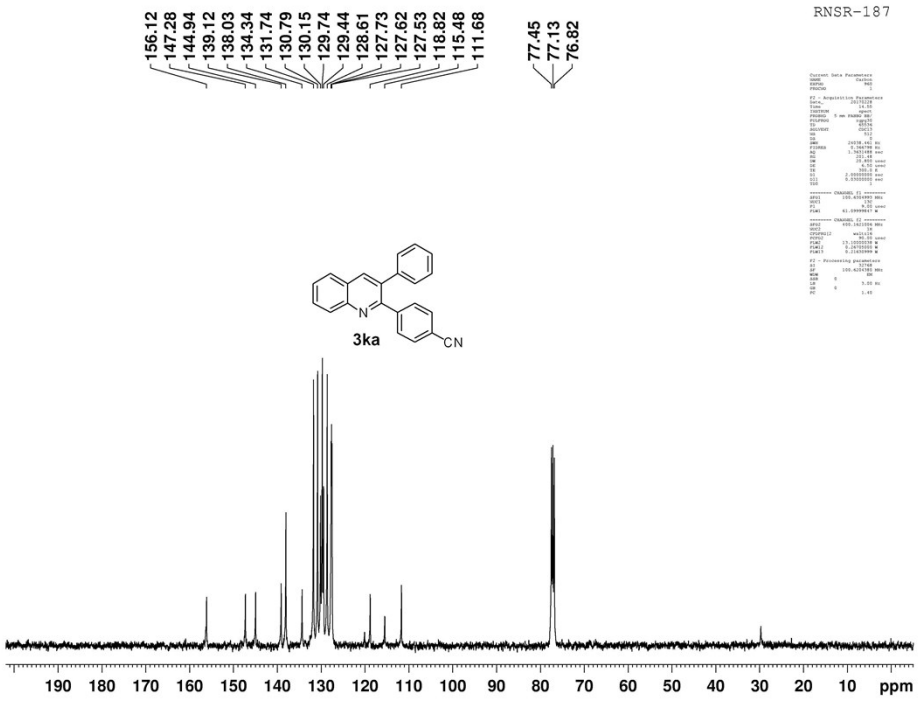

Fig. S56 ^{13}C NMR of **3ka**

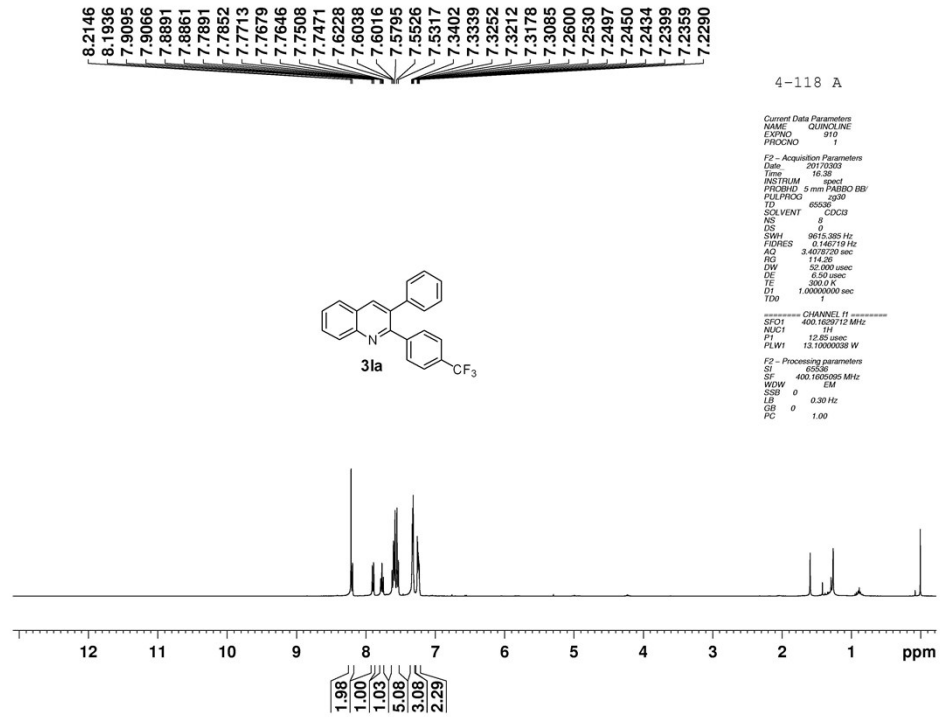

Fig. S57 ^{1}H NMR of **3la**

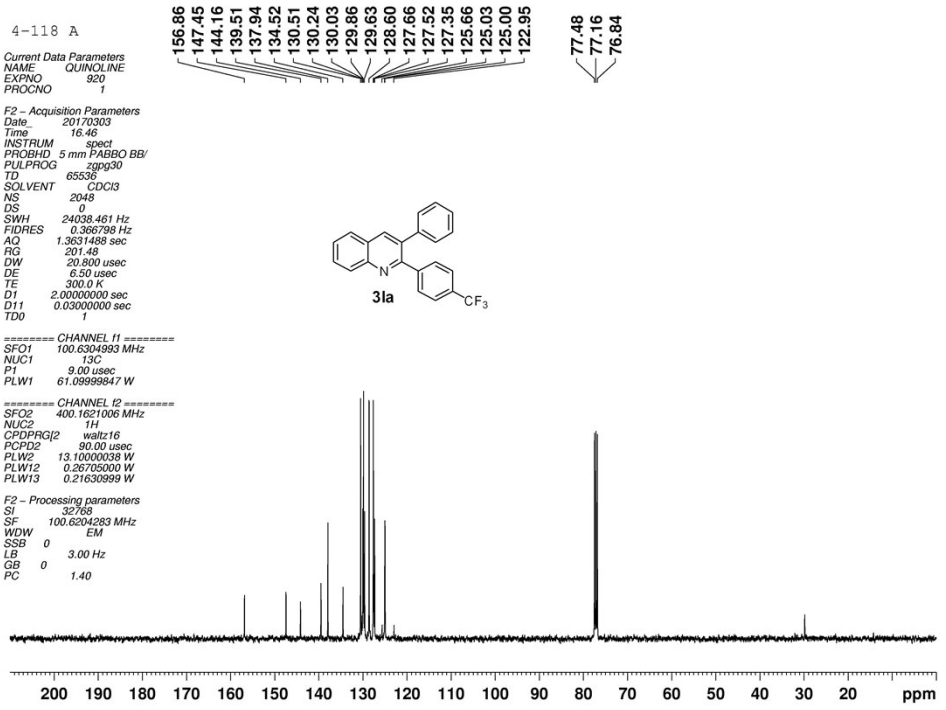

Fig. S58 ^{13}C NMR of **3la**

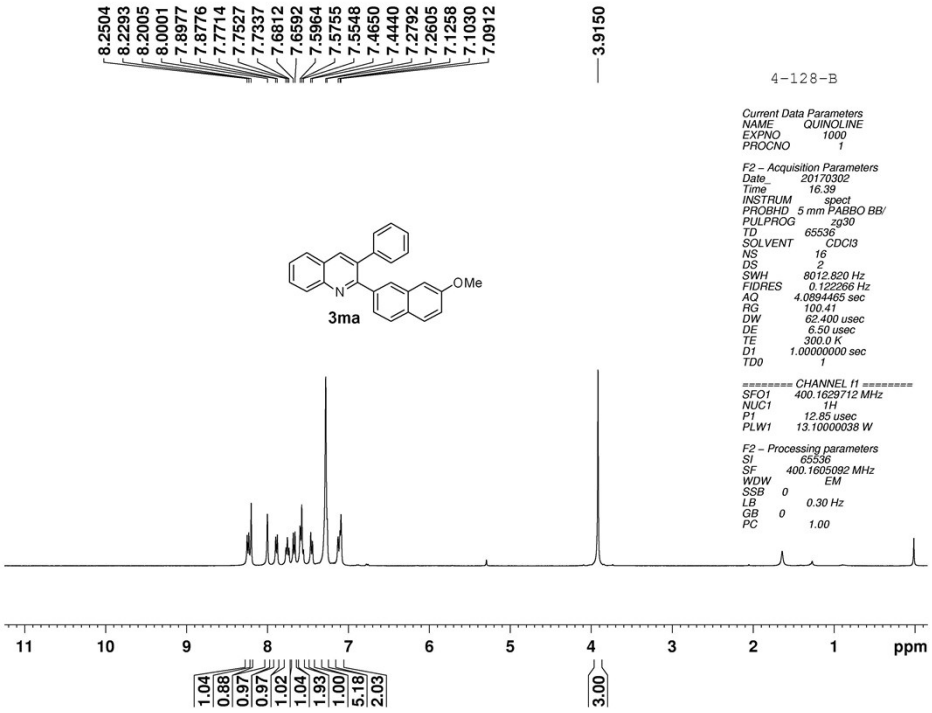

Fig. S59 ^{1}H NMR of **3ma**

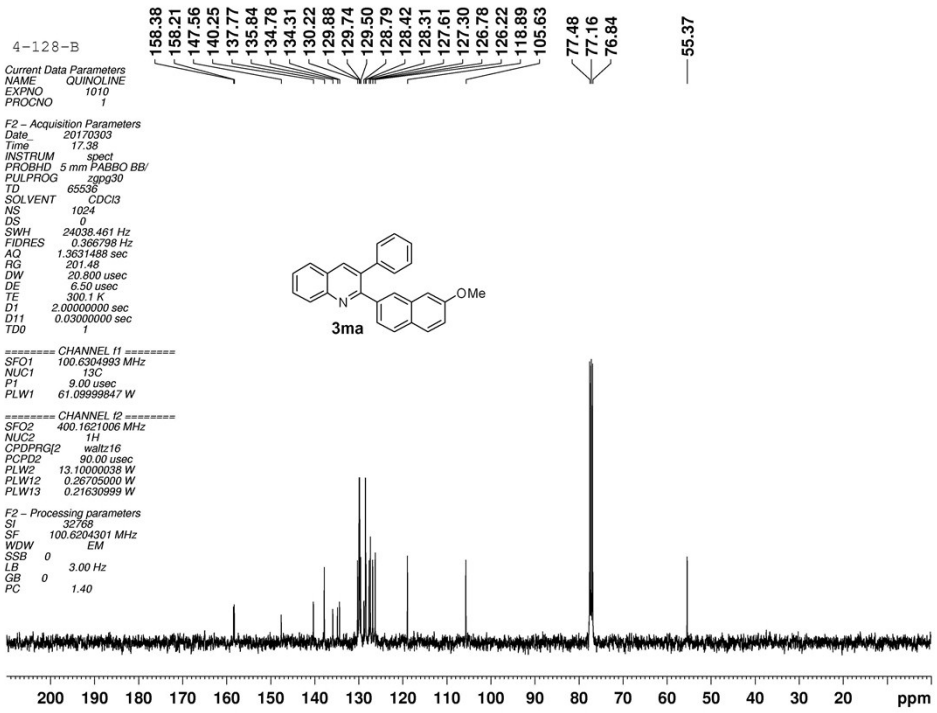

Fig. S60 ^{13}C NMR of **3ma**

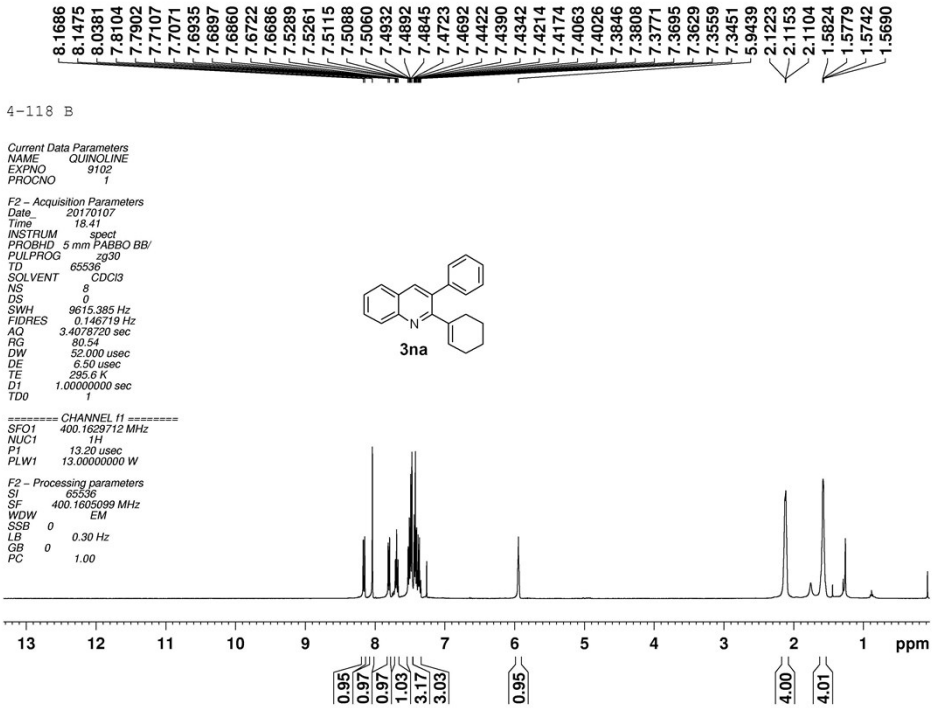

Fig. S61 ^{1}H NMR of **3na**

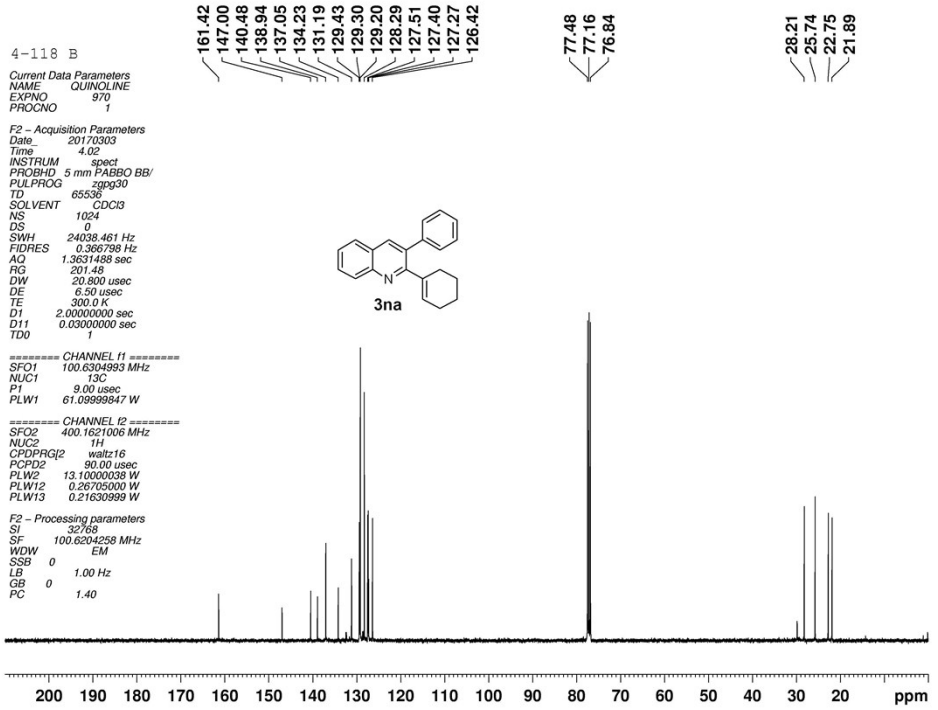

Fig. S62 ^{13}C NMR of **3na**

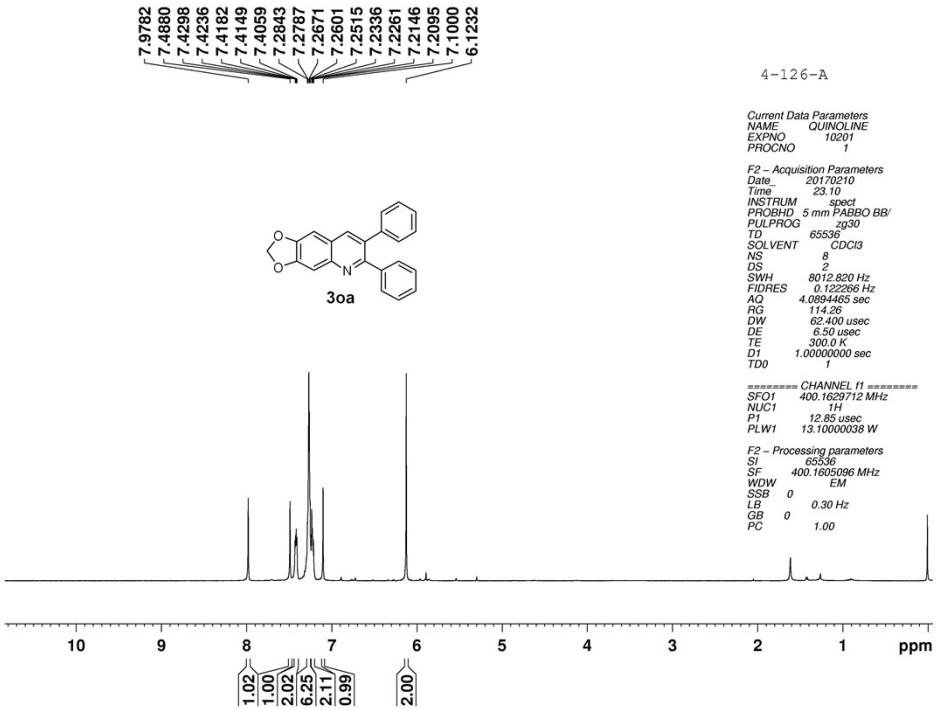

Fig. S63 ^{1}H NMR of **3oa**

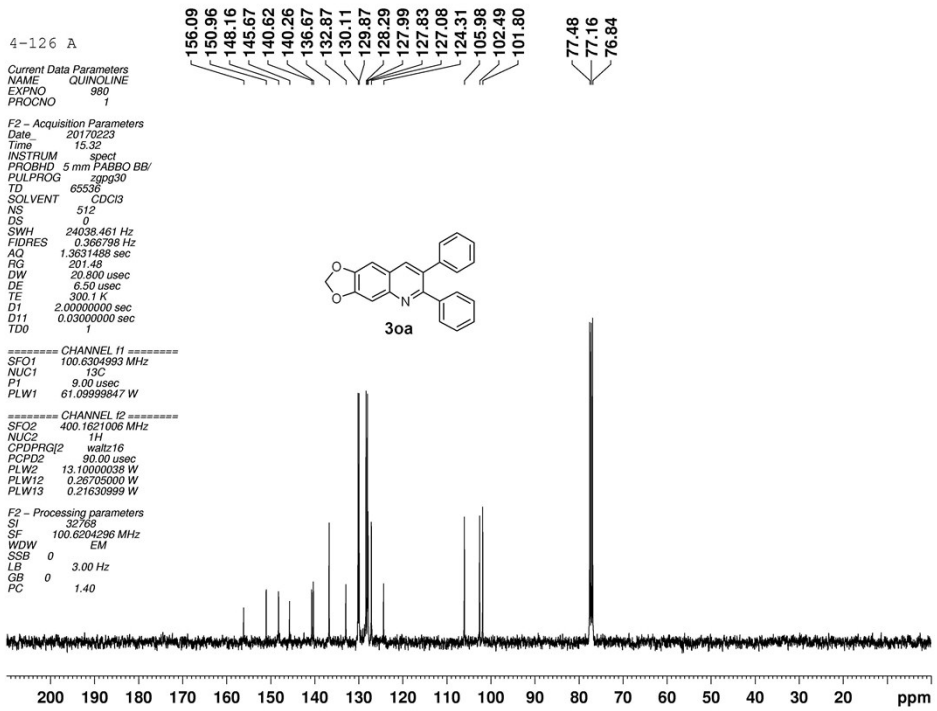

Fig. S64 ^{13}C NMR of **3oa**

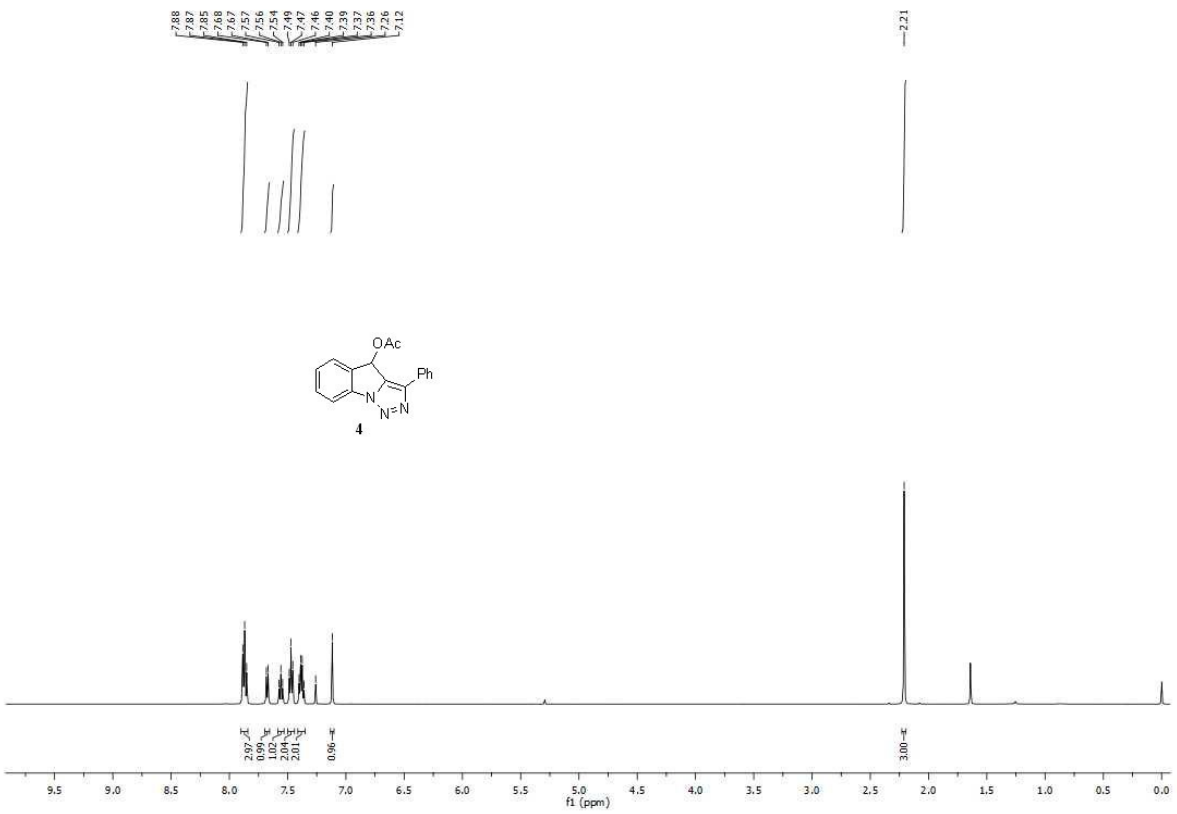

Fig. S65 ^{1}H NMR of **4**

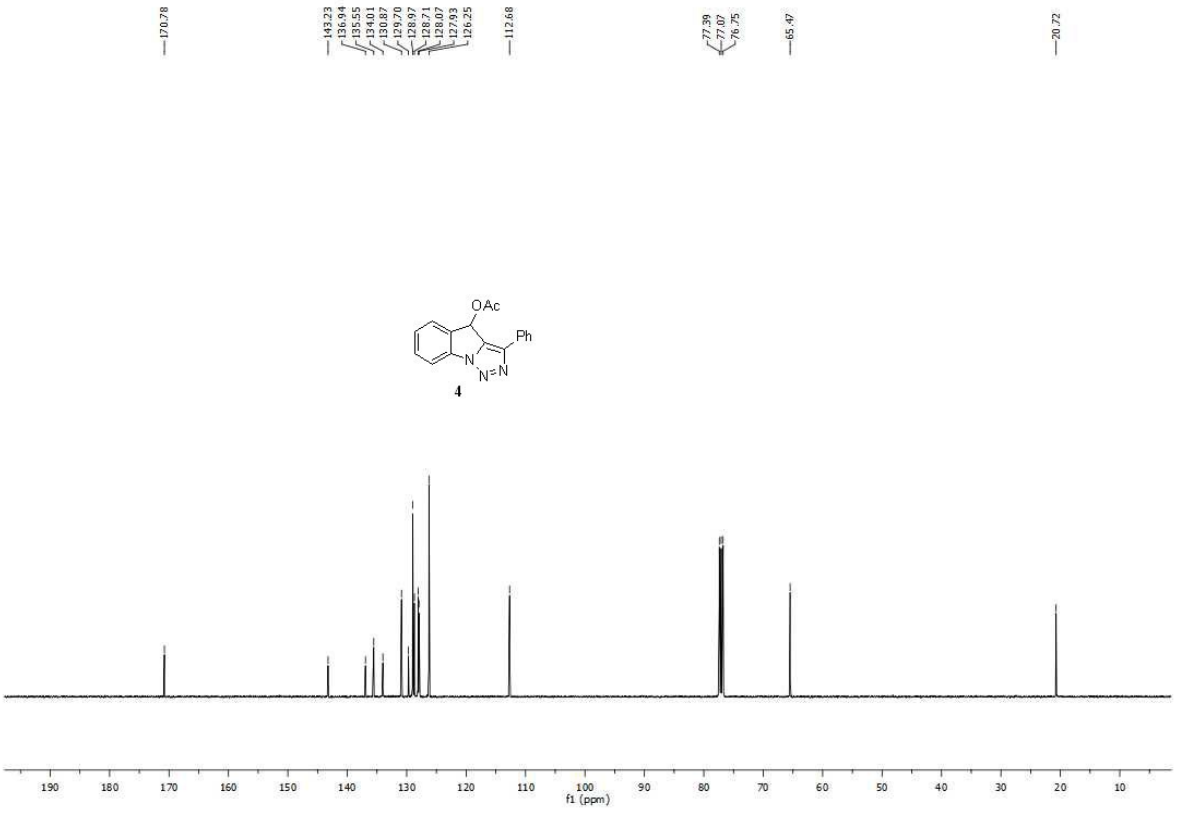

Fig. S66 ^{13}C NMR of **4**