Supporting Information

Cyano-Substituted Phenoxazine Moiety as an Organophotoredox Catalyst for C–C, C–B and C–P Coupling Reactions with Aryl Halides

Aditi Das[a] and Chandan Mukherjee*[a]

***Corresponding address:**

Dr. Chandan Mukherjee, Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati, 781039, Assam, India.
Email: cmukherjee@iitg.ac.in
Phone No. +91-361-258-2327, Fax: +91-361-258-2349

Materials: Chemicals and solvents were purchased from commercial sources as supplied. 2-Aminobenzonitrile, 3,5-di-*tert*-butylcatechol, $P(OEt)_3$ and $MnCl_2 \bullet 4H_2O$ were purchased from Sigma–Aldrich. Solvents were obtained from Merck (India). Methyl 4-chlorobenzoate, 4-chlorobenzonitrile, 4-iodoanisole, 3-bromoquinoline, N-methylpyrrole, Bis(pinacolato)diborane, and DBU were purchased from BLD Pharmatech Ltd., and N,N-diisopropylethylamine was purchased from Spectrochem, India. Mass spectra were measured in HPLC-grade acetonitrile solvent.

Physical methods: IR spectra were recorded on a Perkin Elmer Instrument from 4000 cm^{-1} to 400 cm^{-1} at room temperature (25 °C) on a diamond tip. ^1H and ^{13}C-NMR spectra of the ligand were recorded in a BRUKER 600 MHz NMR machine. Mass spectral (MS) data were acquired from a quadrupole time-of-flight (QTOF)-MS spectrometer. UV-Vis spectra and spectroelectrochemical data were recorded on a Perkin Elmer Lambda 750 by preparing a known concentration of the samples in HPLC Grade dichloromethane (CH_2Cl_2; DCM) at room temperature (25 °C) using a cuvette of 1 cm width. Cyclic voltammograms (CVs) of the compound were being recorded in acetonitrile solutions containing 0.10 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte at a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode. The experiments were performed at different scan rates. Emission spectra and photoluminescence quenching experiment were recorded on Fluoromax-4C (Horiba Model), and lifetime data were measured on TCSPC Lifetime system (Horiba Jobin, Model: Ultrafast-01-DD) by preparing a known concentration of the samples in DMSO at room temperature (25 °C) using a cuvette of 1 cm width. A Chanzon 395 nm purple LED (50 W) was used as a light source.

Experimental Section

Synthesis of [$C_{21}H_{26}N_2O$], Compound 1: In a 100 mL round-bottomed flask, 3,5-di-*tert*-butyl catechol (945 mg, 4.25 mmol) was taken in hexane (6 mL), and then 4 mL of acetic acid was added under stirring conditions at room temperature. 2-aminobenzonitrile (503 mg, 4.25 mmol) in dichloromethane (8 mL) was added dropwise to the mixture and allowed to stir for 2 days. Upon completion of the reaction, hexane (2 mL) was added to the mixture to induce white precipitation. After filtration, the residue was washed with hexane (5-6 times) to remove excess acetic acid. The white solid was obtained. Yield = 890 mg, 65%. FT-IR (cm^{-1}): 3416, 3357, 2950, 2218, 1599, 1576, 1503, 1480, 1458, 1421, 1359, 1314, 1218, 973, 762. ^1H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.50-7.52 (dd, J_1 = 7.82 Hz, J_2 = 1.2 Hz, 1H), 7.34 (t, J = 7.84 Hz, 1H), 7.29 (d, J = 2.2 Hz, 1H), 7.01-7.02 (d, J = 2.16 Hz, 1H), 6.85 (t, J = 7.4 Hz, 1H), 6.49-

6.51 (d, J = 8.52 Hz, 1H), 5.98 (s, O-H), 5.82 (s, N-H), 1.44 (s, 9H), 1.28 (s, 9H). ^{13}C-NMR ($CDCl_3$, 125 MHz) δ (ppm): 149.82, 149.37, 143.02, 136.28, 134.51, 125.29, 123.42, 122.14, 119.39, 117.60, 114.08, 97.98, 35.25, 34.56, 31.69, 29.65. ESI-MS (+) *m/z* for $[C_{21}H_{26}N_2O + H]^+$ calcd., 323.2118; found, 323.2102.

Synthesis of $[C_{21}H_{24}N_2O]$, Compound 2: Compound 2 was prepared according to the reported procedure.[1] **Compound 1** (161 mg, 0.50 mmol) was dissolved in acetonitrile (10 mL) in an oven-dried 50 mL round-bottomed flask, and 4 mol% $MnCl_2$•$4H_2O$ (4 mg, 0.02 mmol) was added under stirring conditions at room temperature. After adding Et_3N (0.10 mL), the solution immediately turns reddish-brown, and the mixture was refluxed for 12 h. The solution was filtered and allowed to slowly evaporate. A faint-yellow crystalline compound was obtained. Yield = 96 mg, 60%. FT-IR (cm^{-1}): 3316, 2954, 2227, 1626, 1577, 1532, 1471, 1437, 1362, 1319,1281, 1243,1001, 854,774, 722, 651, 584,518. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 6.91-6.93 (d, J = 7.52 Hz, 1H), 6.80-6.84 (m, 2H), 6.61-6.65 (t, J = 7.72 Hz, 1H), 6.44 (s, 1H), 5.82 (s, N-H), 1.38 (s, 9H),1.26 (s, 9H). ^{13}C-NMR ($CDCl_3$, 125 MHz) δ (ppm): 146.60,144.10, 139.40, 136.93, 129.23, 125.79, 120.83, 119.17, 117.86, 116.44, 110.23, 94.89, 34.96, 34.59, 31.42, 29.96. ESI-MS (+) *m/z* for $[C_{21}H_{24}N_2O + H]^+$ calcd., 321.1961; found, 321.1950.

Synthesis of $[C_{23}H_{28}N_2O]$, PC-A: In an oven-dried 50 mL two-neck round-bottomed flask, **Compound 2** (250 mg, 0.78 mmol) and NaOH (300 mg, 7.8 mmol) were taken in dry THF (10 mL) under inert conditions (N_2 atmosphere). The reaction mixture was stirred for 30 min at room temperature, and then ethyl bromide (0.086 mL, 1.17 mmol) was added to the mixture with continuous stirring. The reaction was refluxed for 36 h. Upon completion of the reaction, the reaction mixture was diluted with ethyl acetate and washed with brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated by rotary evaporation to obtain a brown residue, which was purified by column chromatography using 1% ethyl acetate in hexane. The light-yellow crystalline product was obtained. Yield = 235 mg, 86%. FT-IR (cm^{-1}): 2959, 2218, 1592, 1443, 1365, 1255, 1050, 995, 782, 727. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.12-7.14 (dd, J_1 = 7.92 Hz, J_2 = 1.4 Hz, 1H), 6.95-6.98 (dd, J_1 = 7.88 Hz, J_2 = 1.4 Hz, 1H), 6.92-6.93 (d, J = 2.16 Hz, 1H), 6.78-6.82 (t, J = 7.92, 1H), 6.76-6.77 (d, J = 2.16, 1H), 4.03-4.08 (q, J = 7 Hz, 2H), 1.40 (s, 9H), 1.29-1.33 (t, J = 7 Hz, 3H), 1.29 (s, 9H). ^{13}C-NMR ($CDCl_3$, 125 MHz) δ (ppm): 150.56, 146.33, 145.26, 139.79, 136.82, 133.91, 128.88, 122.22, 119.57, 118.49, 118.41, 113.65, 110.32, 47.11, 34.86, 34.78, 31.57, 30.10, 13.60. ESI-MS (+) *m/z* for $[C_{23}H_{28}N_2O + H]^+$ calcd., 349.2278; found, 349.2270.

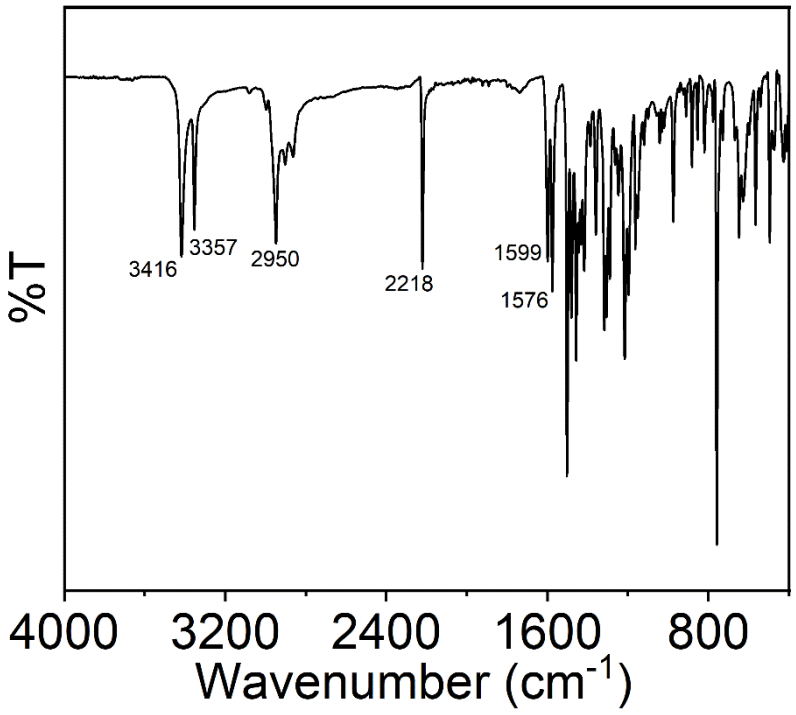


Figure S1. FTIR plot of **Compound 1**.

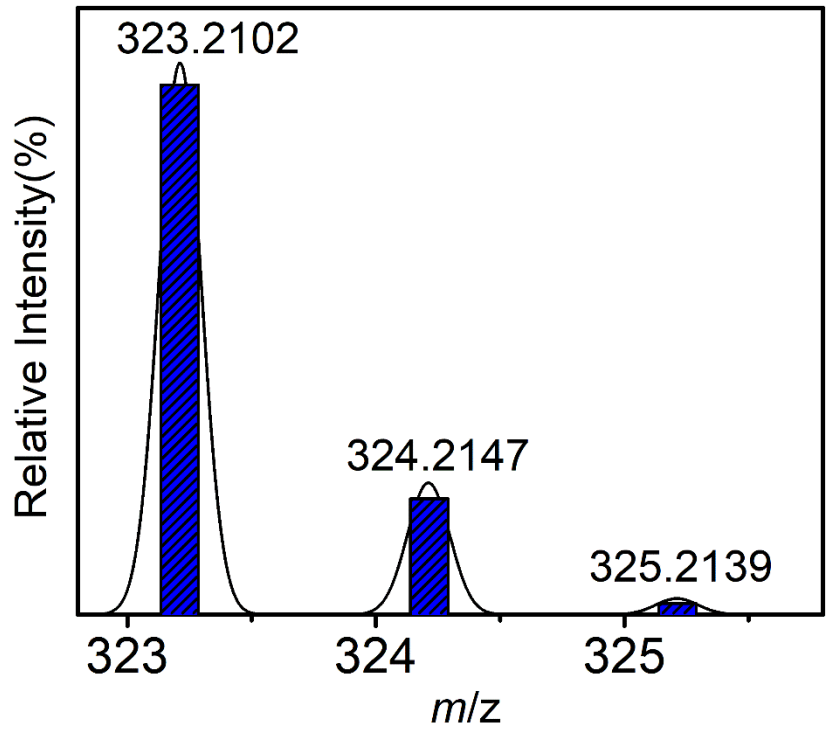


Figure S2. ESI-MS (+ve) mass spectrum of **Compound 1**. Experimental data in the column and theoretical isotopic distribution in the wave.

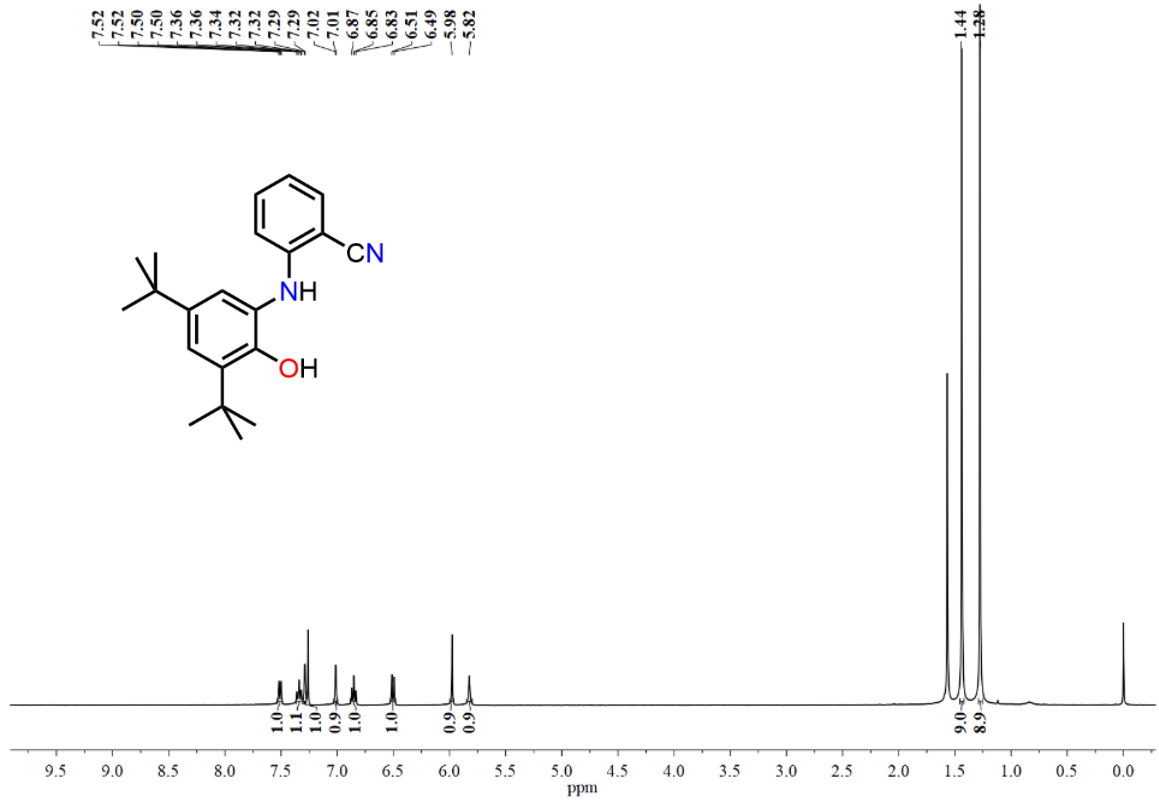


Figure S3. ^{1}H-NMR spectrum of **Compound 1** in $CDCl_3$ solvent.

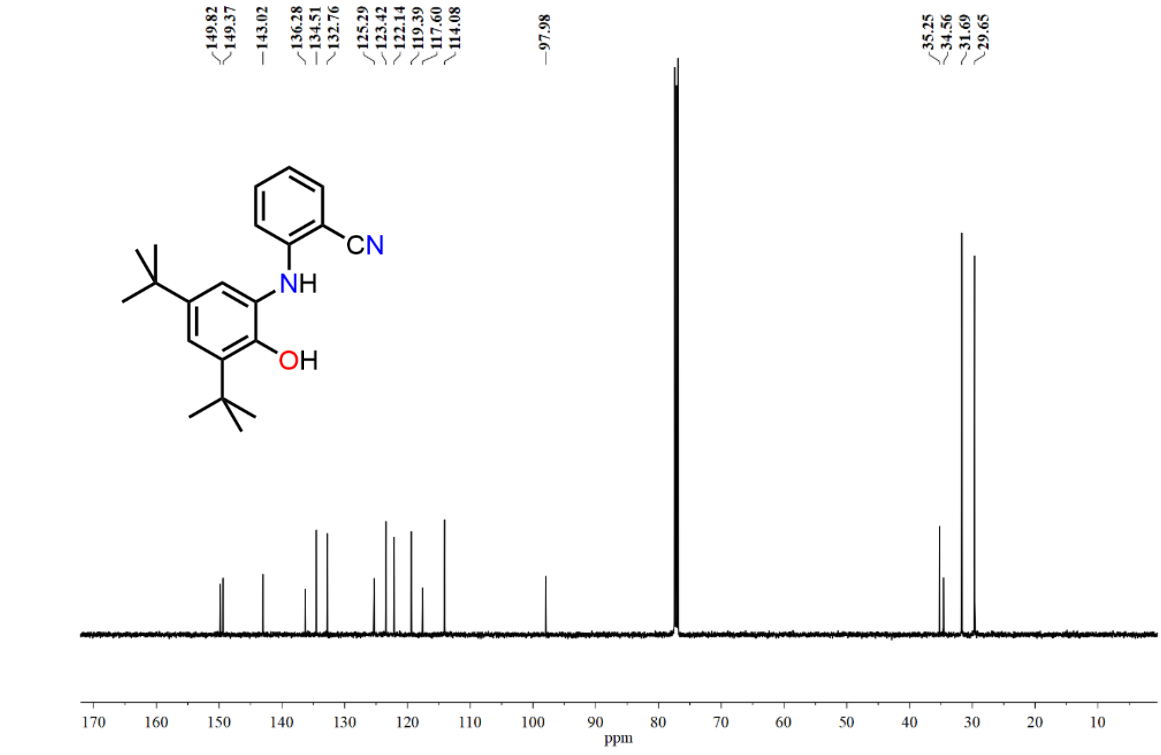


Figure S4. ^{13}C-NMR spectrum of **Compound 1** in $CDCl_3$ solvent.

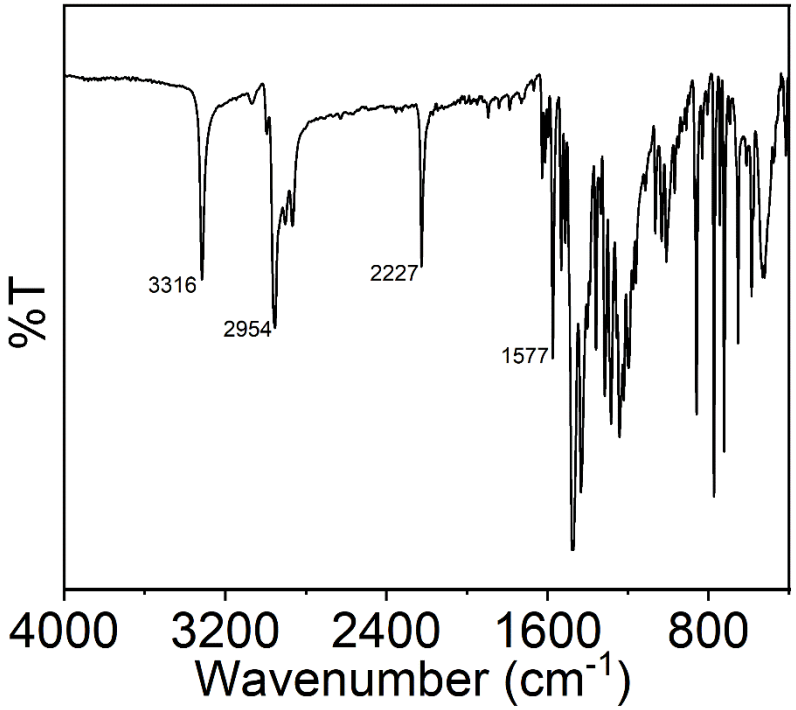


Figure S5. FTIR plot of **Compound 2**.

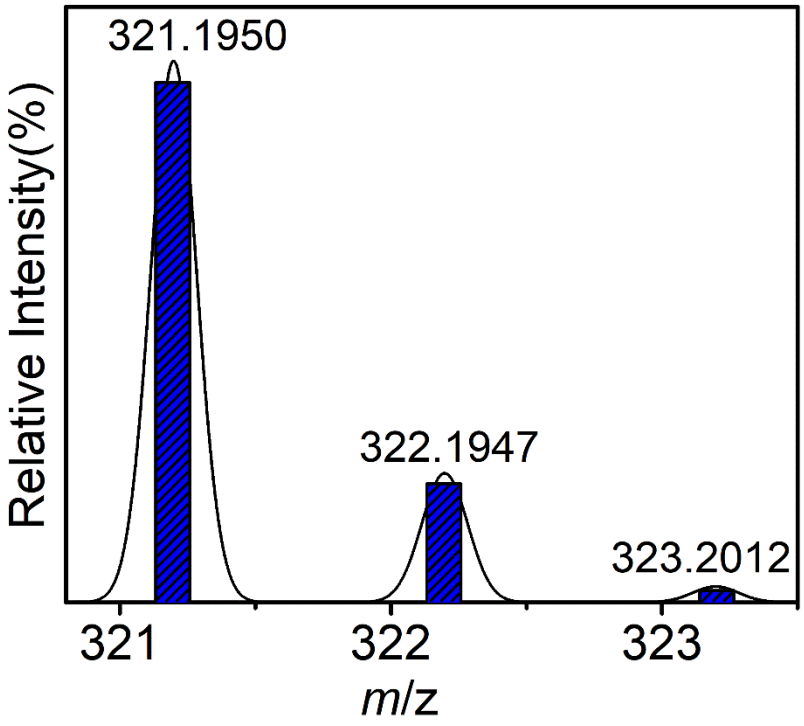


Figure S6. ESI-MS (+ve) mass spectrum of **Compound 2**. Experimental data in the column and theoretical isotopic distribution in line.

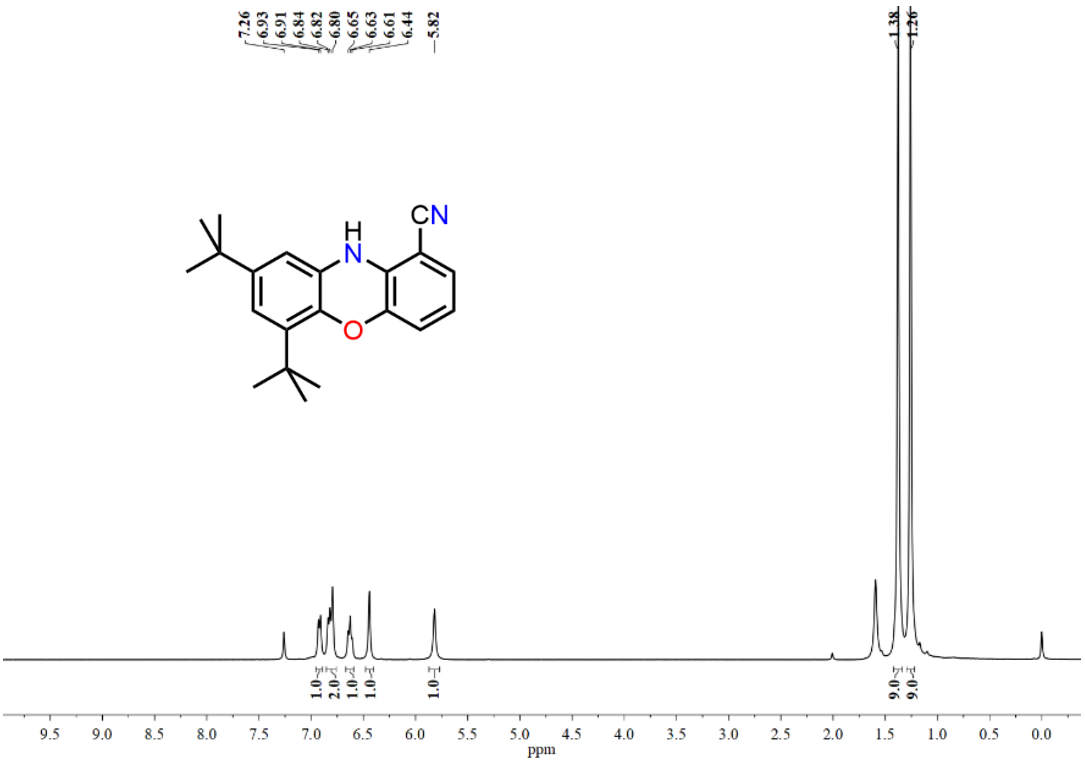


Figure S7. ^{1}H-NMR spectrum of **Compound 2** in $CDCl_3$ solvent.

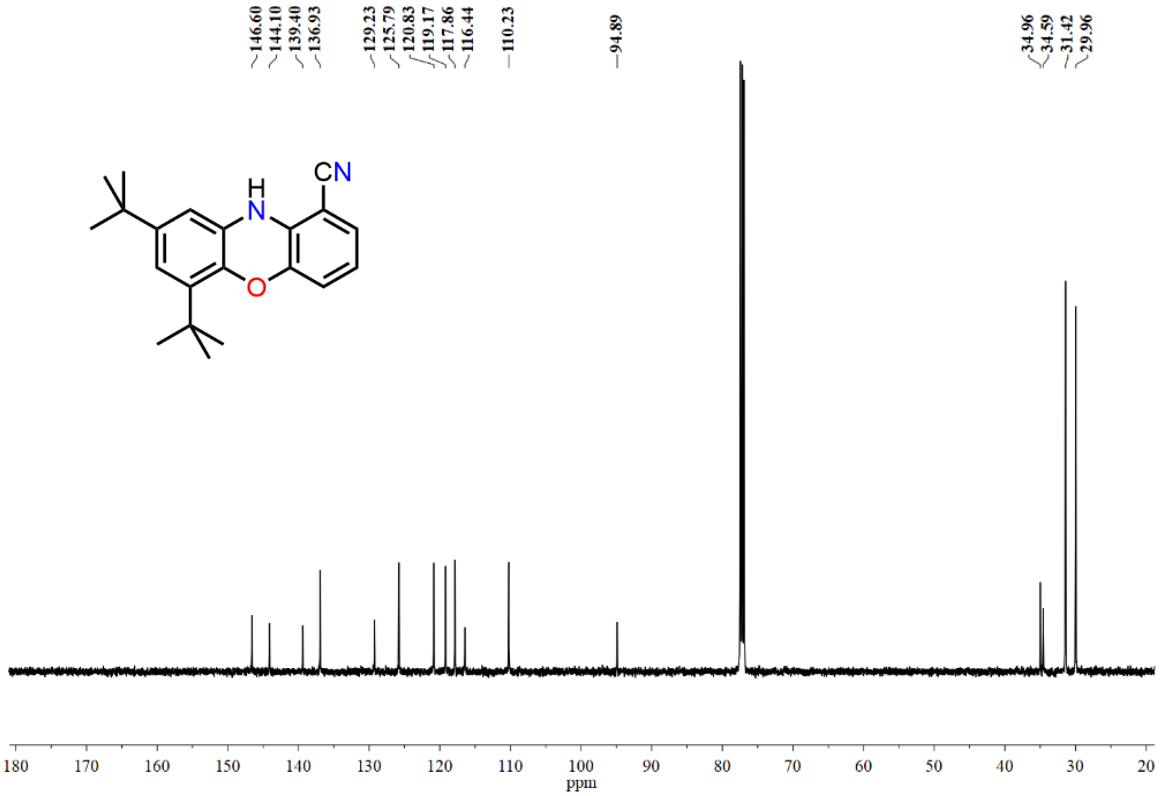


Figure S8. ^{13}C-NMR spectrum of **Compound 2** in $CDCl_3$ solvent.

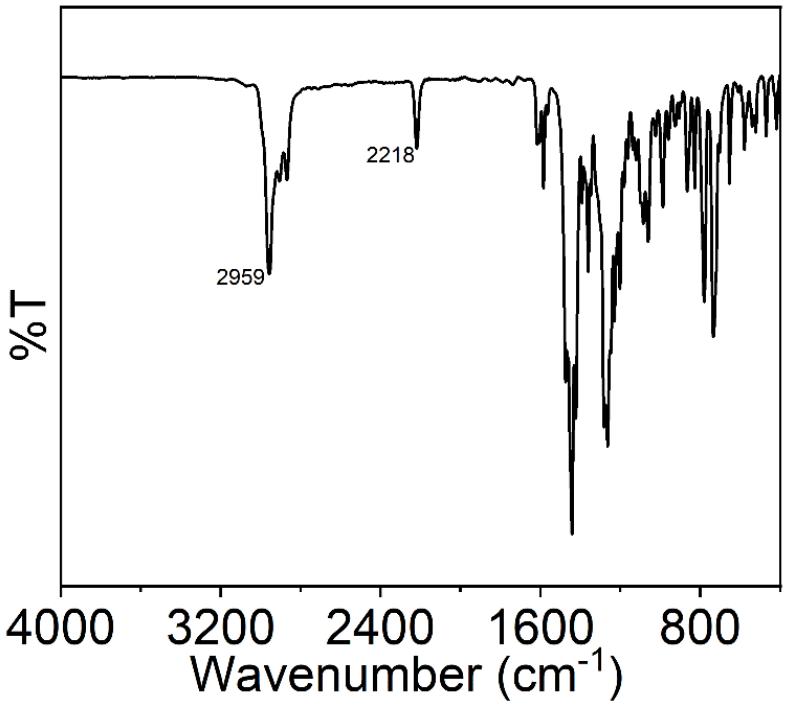


Figure S9. FTIR plot of **PC-A**.

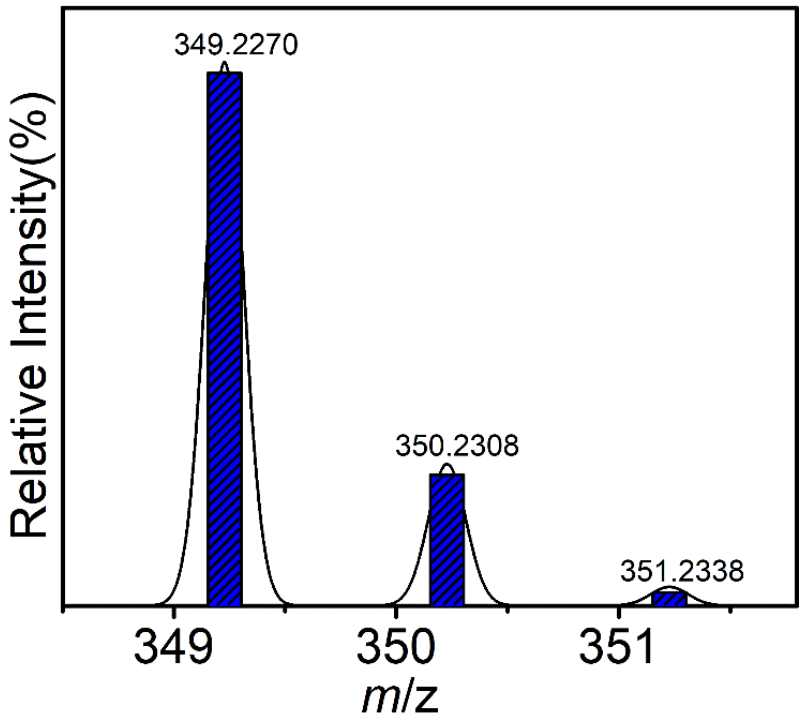


Figure S10. ESI-MS (+ve) mass spectrum of **PC-A**. Experimental data in the column and theoretical isotopic distribution in line.

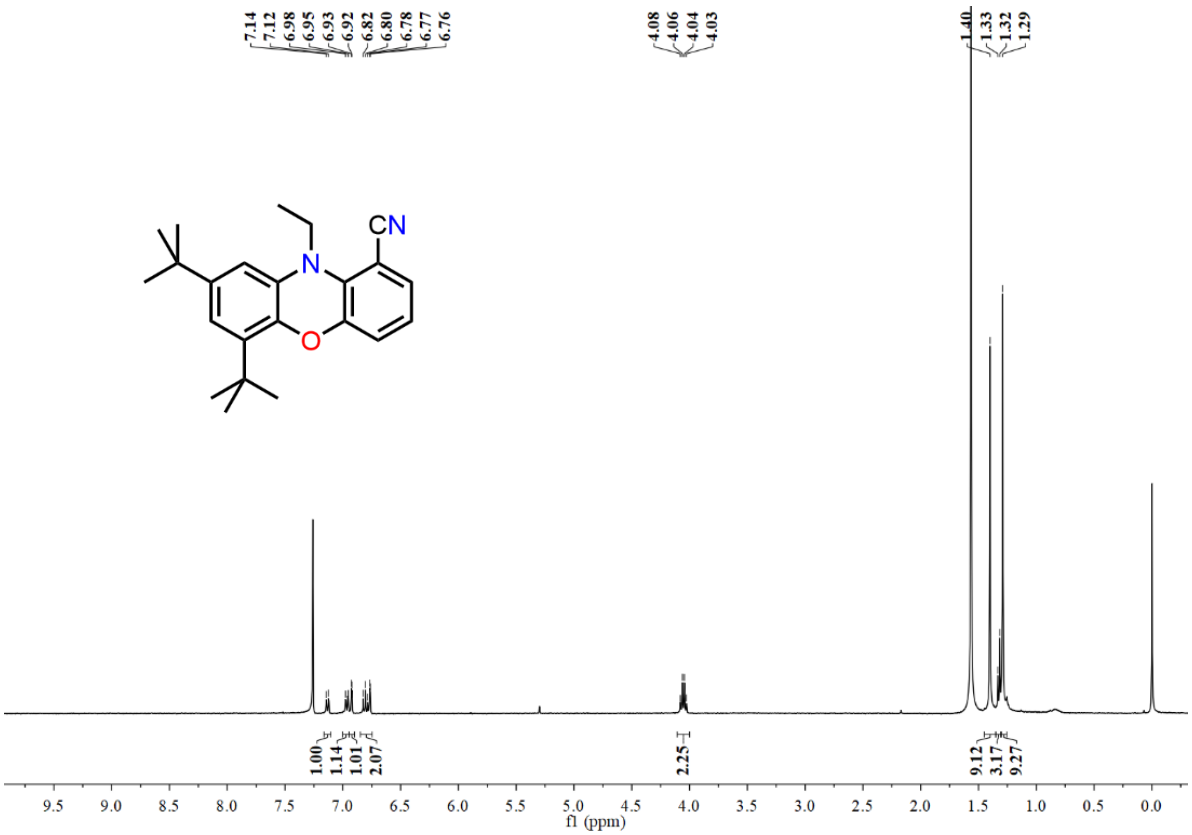


Figure S11. ^{1}H-NMR spectrum of **PC-A** in $CDCl_3$ solvent.

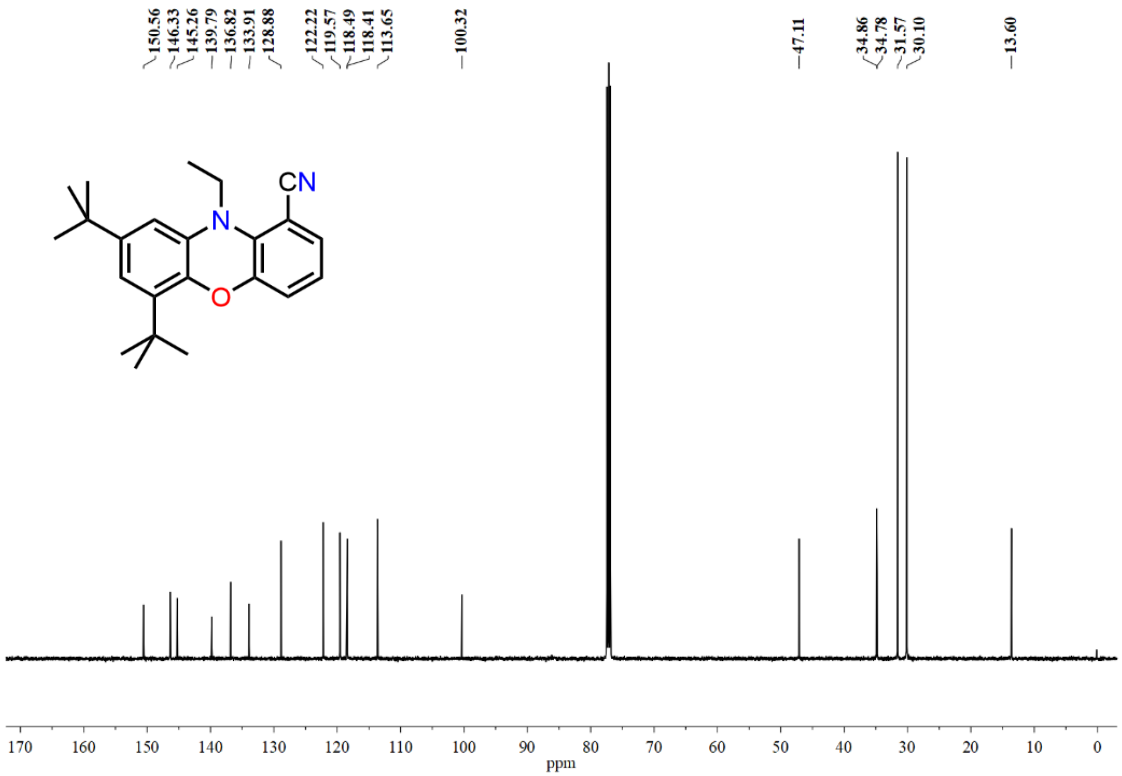


Figure S12. ^{13}C-NMR spectrum of **PC-A** in $CDCl_3$ solvent.

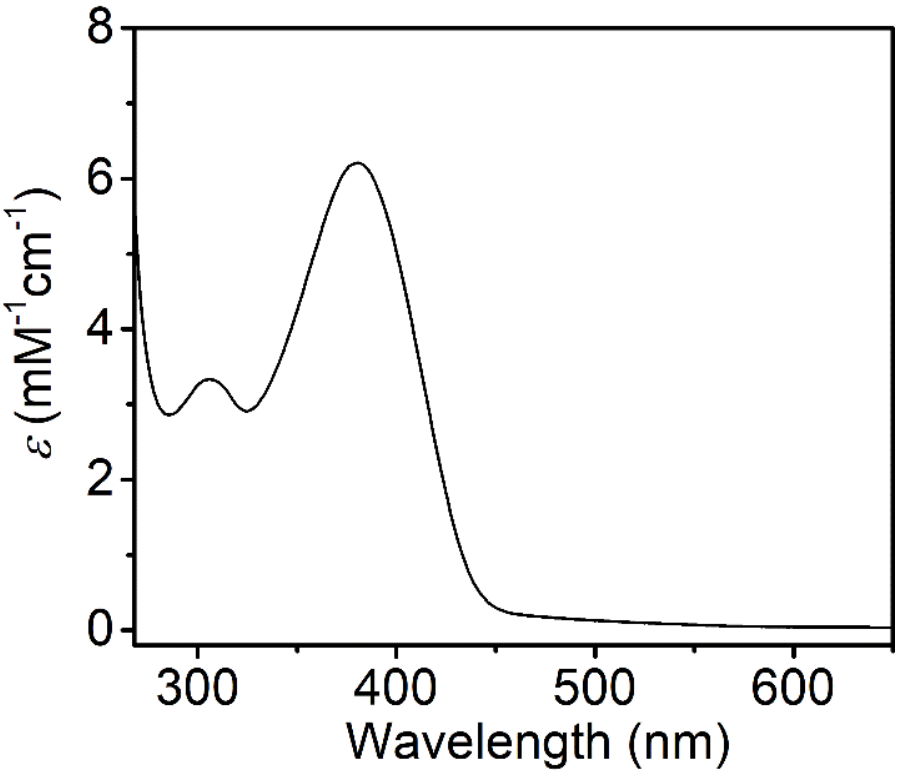


Figure S13. UV-Vis spectra of **PC-A** (0.1 mM) in DMSO.

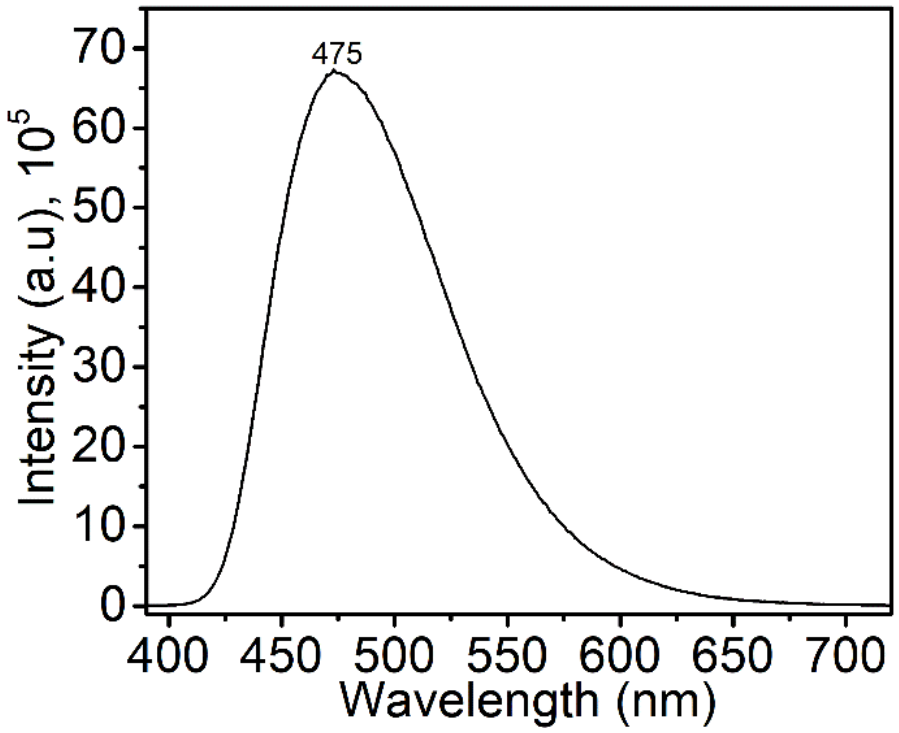


Figure S14. Fluorescence emission spectra of **PC-A** (0.1 mM) in DMSO.

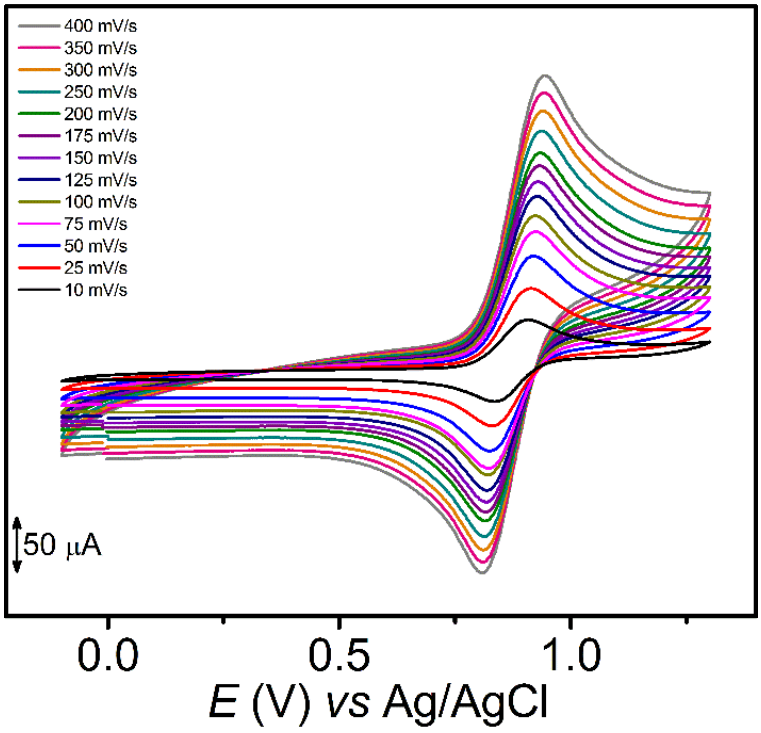


Figure S15. Cyclic voltammograms of 1 mM **PC-A** in 0.1 M $TBAPF_6$ in MeCN.

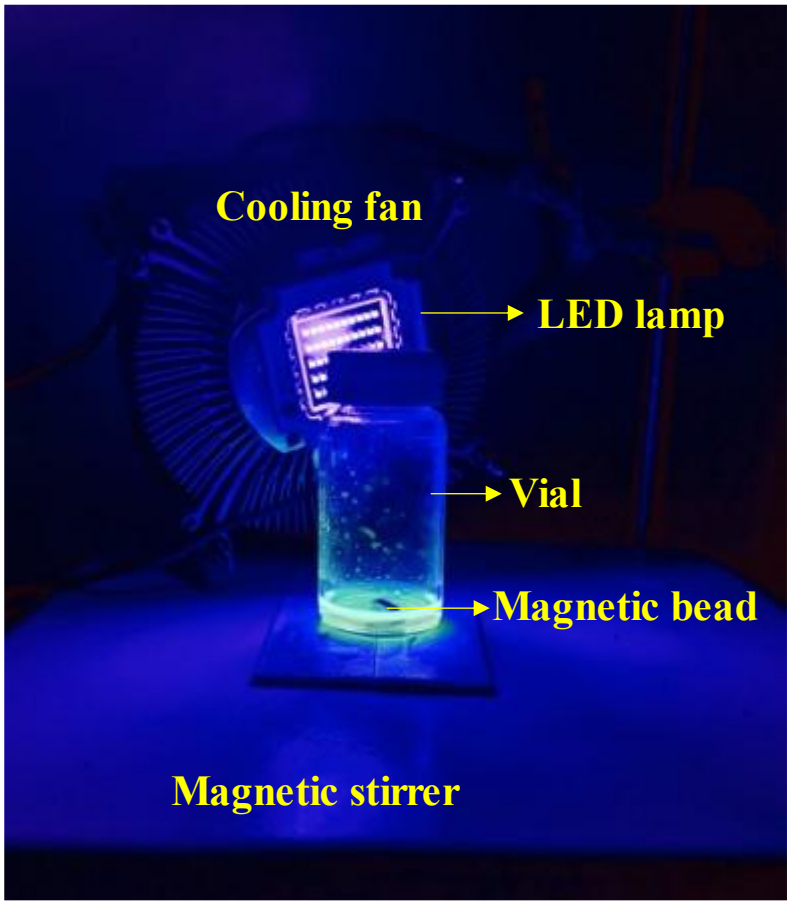


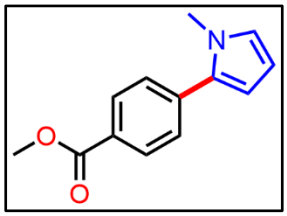
Figure S16. Set up for photoredox reactions.

General procedure for C–C coupling reactions: In an oven-dried 10 mL vial, aryl halide **1** (0.3 mmol), N-methylpyrrole (**2a**, 3 mmol), base DIPEA (1.2 mmol), and 5 mol% catalyst **PC-A** were added in a 0.1 M DMSO solution. Then, N_2 was bubbled for 15 minutes to make it inert. The mixture was stirred for 6 h at room temperature under the LED light. After completion, the mixture was diluted by adding CH_2Cl_2 (15 mL) and washed with ice water. The organic layer was separated and dried over Na_2SO_4, filtered, and evaporated to yield a residue, which was then purified by column chromatography using hexane and ethyl acetate to give the corresponding C–C bonded product (**3**).

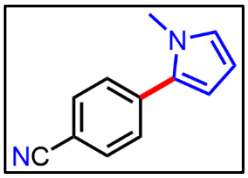
General procedure for C–B coupling reactions: In an oven-dried 10 mL vial, aryl halide **1** (0.3 mmol), bis(pinacoloto)diboron (**2b**, 0.9 mmol), base DBU (0.6 mmol), and 5 mol% catalyst were added in a 0.1 M DMSO solution. Then N_2 was bubbled for 15 min to make it inert. The mixture was stirred for 6 h at room temperature under the LED light. After completion, the mixture was diluted by adding CH_2Cl_2 (15 mL) and washed with ice water. The organic layer was separated and dried over Na_2SO_4, filtered, and evaporated to obtain a residue, which was then purified by column chromatography using hexane and ethyl acetate to give the corresponding C–B bonded product (**4**).

General procedure for C–P coupling reactions: In an oven-dried 10 mL vial, aryl halide **1** (0.3 mmol), triethyl phosphite (**2c**, 3 mmol), DBU (0.6 mmol), and 5 mol% **PC-A** catalyst were added in a 0.1 M DMSO solution. Then N_2 was bubbled for 15 min to make it inert. The mixture was stirred for 6 h at room temperature under the LED light. After completion, the mixture was diluted by adding CH_2Cl_2 (15 mL) and washed with ice water. The organic layer was separated and over Na_2SO_4, filtered, and evaporated to get a residue, which was then purified by column chromatography using hexane and ethyl acetate to give the corresponding C–P bonded product (**5**).

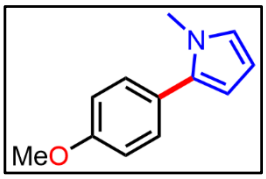
Analytical data for synthesised compounds:



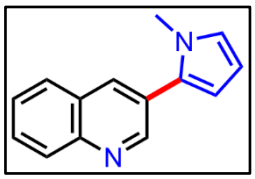
Methyl 4-(1-methyl-1*H*-pyrrol-2-yl)benzoate (3aa): The reaction mixture was purified by column chromatography on silica gel using Hexane/EtOAc as eluent. Product **3aa** (50 mg, 77% yield) was obtained as a pale green solid. R_f = 0.5 (Hexane: EtOAc = 95:5). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.07-8.05(d, J = 8 Hz, 2H), 7.49-7.46 (d, J = 1.2 Hz, 2H), 6.77-6.75 (m, 1H), 6.34-6.33 (m, 1H), 6.23-6.22 (m,1H), 3.93 (s, 3H), 3.71 (s, 3H). ^{13}C-NMR ($CDCl_3$, 126 MHz) δ (ppm): 167.11, 137.89, 133.50, 129.81, 128.06, 127.99, 125.25, 110.18, 108.28, 51.96, 35.66. The obtained data are consistent with the literature reports.[2]



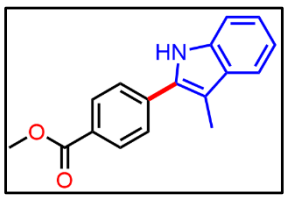
4-(1-Methyl-1*H*-pyrrol-2-yl)benzonitrile (3ba): The reaction mixture was purified by column chromatography on silica gel using Hexane/EtOAc as eluent. Product **3ba** (41 mg, 75% yield) was obtained as a white solid. R_f = 0.5 (Hexane: EtOAc = 95:5). ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.68-7.66(d, J = 10 Hz, 2H), 7.51-7.49 (d, J = 10 Hz, 2H), 6.78-6.77 (m, 1H), 6.35-6.34 (m, 1H), 6.24-6.22 (t, J = 5 Hz, 1H), 3.71 (s, 3H). ^{13}C-NMR ($CDCl_3$, 126 MHz) δ (ppm): 132.42, 128.44, 125.99, 110.90, 109.85, 108.74, 35.61. The obtained data are consistent with the literature reports.[2]



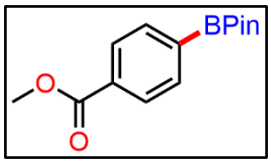
2-(4-methoxyphenyl)-1-methyl-1H-pyrrole (3ca): The reaction mixture was purified by column chromatography on silica gel using Hexane/EtOAc as eluent. Product **3ca** (23 mg, 40% yield) was obtained as a pale green solid. R_f = 0.5 (Hexane: EtOAc = 95:5). ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm): 7.33-7.31(d, J = 12 Hz, 2H), 6.95-6.93 (d, J = 12 Hz, 2H), 6.69 (m, 1H), 6.19-6.18 (m, 1H), 6.15 (m, 1H), 3.84 (s, 3H), 3.63 (s, 3H). ^{13}C-NMR ($CDCl_3$, 151 MHz) δ (ppm): 158.79, 134.52, 130.17, 126.11, 123.11, 113.93, 108.13, 107.69, 55.45, 35.02. The obtained data are consistent with the literature reports.[3]



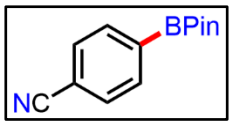
3-(1-Methyl-1*H*-pyrrol-2-yl)quinoline (3da): The reaction mixture was purified by column chromatography on silica gel using Hexane/EtOAc as eluent. Product **3da** (48 mg, 77% yield) was obtained as a pale yellow solid. R_f = 0.5 (Hexane: EtOAc = 95:5). ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm): 9.03-9.02(d, J = 6 Hz, 1H), 8.13-8.12 (m, 2H), 7.85-7.83 (d, J = 12 Hz, 1H), 7.75-7.70 (m, 1H), 7.59-7.56 (m, 1H), 6.83-6.82 (m, 1H), 6.42 (m,1H), 6.29-6.28 (t, J = 6 Hz, 1H), 3.76 (s, 3H). ^{13}C-NMR ($CDCl_3$, 151 MHz) δ (ppm): 151.11, 146.82, 133.94, 131.15, 129.40, 127.93, 127.21, 126.65, 125.11, 110.41, 108.58, 35.41. The obtained data are consistent with the literature reports.[2]



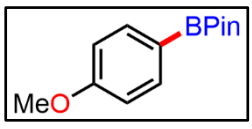
Methyl 4-(3-methyl-1H-indol-2-yl)benzoate (3ea): The reaction mixture was purified by column chromatography on silica gel using Hexane/EtOAc as eluent. Product **3ea** (45 mg, 56% yield) was obtained as a white solid. R_f = 0.5 (Hexane: EtOAc = 95:5). ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm): 8.15-8.13 (d, *J* = 12 Hz, 2H), 8.11(brs, 1H), 7.67-7.65 (d, *J* = 12 Hz, 2H), 7.63-7.62 (d, *J* = 6 Hz, 1H), 7.39-7.38 (d, *J* = 6 Hz, 1H), 7.24-7.23 (d, *J* = 6 Hz, 1H), 7.18-7.15 (m, 1H), 3.95 (s, 3H), 2.50 (s, 3H). ^{13}C-NMR ($CDCl_3$, 126 MHz) δ (ppm): 167.00, 137.88, 136.33, 132.90, 130.27, 130.10, 128.66, 127.36, 123.21, 119.95, 119.43, 110.97, 110.72, 52.35, 10.05. The obtained data are consistent with the literature reports.[2]



Methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (4ab): The reaction mixture was purified by column chromatography on silica gel using Hexane/EtOAc as eluent. Product **4ab** (64 mg, 80% yield) was obtained as a white solid. R_f = 0.5 (Hexane: EtOAc = 95:5). ^{1}H-NMR (600 MHz, $CDCl_3$) *δ* (ppm): 8.02-8.01(d, *J* = 6 Hz, 2H), 7.87-7.86 (d, *J* = 6 Hz, 2H), 3.92 (s, 3H), 1.35 (s, 12H). ^{13}C-NMR ($CDCl_3$, 151 MHz) *δ* (ppm): 167.30, 134.81, 132.44, 128.74, 84.33, 52.30, 25.03. The obtained data are consistent with the literature reports.[4]

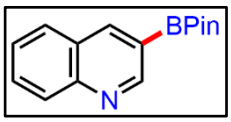


4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (4bb): The reaction mixture was purified by column chromatography on silica gel using Hexane/EtOAc as eluent. Product **4bb** (55 mg, 80% yield) was obtained as a white solid. R_f = 0.5 (Hexane: EtOAc = 20:1). ^{1}H-NMR (500 MHz, $CDCl_3$) *δ* (ppm): 7.89-7.87 (d, *J* = 10 Hz, 2H), 7.65-7.63 (d, *J* = 10 Hz, 2H), 1.35 (s, 12H). ^{13}C-NMR ($CDCl_3$, 126 MHz) *δ* (ppm): 135.25, 131.30, 119.03, 114.69, 84.65, 25.00. The obtained data are consistent with the literature reports.[5]

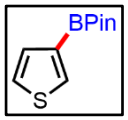


2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4cb): The reaction mixture was purified by column chromatography on silica gel using Hexane/EtOAc as eluent. Product **4cb** (40 mg, 57% yield) was obtained as a pale-yellow solid. R_f = 0.5 (Hexane: EtOAc = 95:5). ^{1}H-NMR (500 MHz, $CDCl_3$) *δ* (ppm): 7.76-7.74(d, *J* = 10 Hz, 2H), 6.90-6.89 (d, *J* = 5 Hz, 2H), 3.83 (s, 3H), 1.33 (s, 12H).

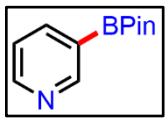
^{13}C-NMR ($CDCl_3$, 126 MHz) δ (ppm): 162.28, 136.65, 113.45, 83.70, 55.24, 25.00. The obtained data are consistent with the literature reports.[4]



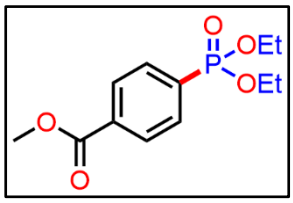
3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)quinoline (4db): Product **4db** was obtained as a yellow crude. The overall yield (70% yield) was determined from ^{1}H-NMR analysis. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 9.19 (d, J = 5 Hz, 1H), 8.63 (s, 1H), 8.11 (m, 1H), 7.83 (m, 1H), 7.76 (m, 1H), 7.56 (m, 1H), 1.39 (s, 12H). The obtained data are consistent with the literature reports.[6]



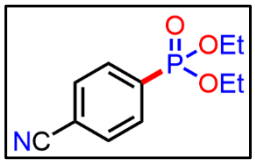
4,4,5,5-tetramethyl-2-(thiophen-3-yl)-1,3,2-dioxaborolane (4eb): Product **4eb** was obtained as a yellow crude. The overall yield (60% yield) was determined from ^{1}H-NMR analysis. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.92-7.91 (d, J = 4 Hz, 1H), 7.41-7.40 (d, J = 4 Hz, 1H), 7.34-7.32 (m, 1H), 1.33 (s, 12H). The obtained data are consistent with the literature reports.[9]



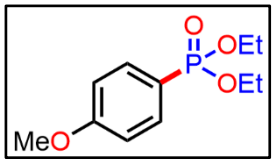
3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (4fb): Product **4fb** was obtained as a yellow crude. The overall yield (40% yield) was determined from ^{1}H-NMR analysis. ^{1}H-NMR (600 MHz, $CDCl_3$) δ (ppm): 8.94 (s, 1H), 8.66 (m, 1H), 8.08 (m, 1H), 7.31 (m, 1H), 1.35 (s, 12H). The obtained data are consistent with the literature reports.[9]



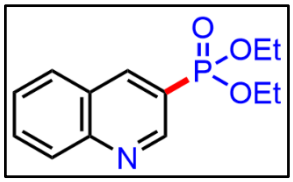
Methyl 4-(diethoxyphosphoryl)benzoate (5ac): The reaction mixture was purified by column chromatography on silica gel using Hexane/EtOAc as eluent. Product **5ac** (64 mg, 78% yield) was obtained as a colourless oil. R_f = 0.5 (Hexane: EtOAc = 10:3). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.13-8.10 (m, 2H), 7.91-7.86 (m, 2H), 4.22-4.05 (m, 4H), 3.95 (s, 3H), 1.35-1.31 (t, J = 8 Hz, 6H). ^{13}C-NMR ($CDCl_3$, 126 MHz) δ (ppm): 166.41, 133.69 (d, J = 3.8 Hz), 132.67, 131.99 (d, J = 10.1 Hz), 129.64 (d, J = 15.1 Hz), 62.60 (d, J = 6.3 Hz), 52.62, 16.49 (d, J = 6.3 Hz). ^{31}P-NMR ($CDCl_3$, 202 MHz) δ (ppm): 17.03. The obtained data are consistent with the literature reports.[7]



Diethyl (4-cyanophenyl)phosphonate (5bc): The reaction mixture was purified by column chromatography on silica gel using Hexane/EtOAc as eluent. Product **5bc** (52 mg, 73% yield) was obtained as a colourless oil. R_f = 0.5 (Hexane: EtOAc = 10:3). ^{1}H-NMR (500 MHz, $CDCl_3$) δ (ppm): 7.94-7.90 (m, 2H), 7.76-7.74 (m, 2H), 4.22-4.07 (m, 4H), 1.33 (t, J = 8 Hz, 6H). ^{13}C-NMR ($CDCl_3$, 126 MHz) δ (ppm): 134.83, 133.33, 132.45 (d, J = 10.1 Hz), 132.21 (d, J = 15.1 Hz), 117.99, 116.17 (d, J = 3.8 Hz), 62.86 (d, J = 5 Hz), 16.49 (d, J = 6.3 Hz). ^{31}P-NMR ($CDCl_3$, 202 MHz) δ (ppm): 15.37. The obtained data are consistent with the literature reports.[7]



Diethyl (4-methoxyphenyl)phosphonate (5cc): The reaction mixture was purified by column chromatography on silica gel using Hexane/EtOAc as the eluent. Product **5cc** (43 mg, 59% yield) was obtained as a colourless oil. R_f = 0.5 (Hexane: EtOAc = 10:3). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 7.77-7.72 (m, 2H), 6.98-6.95 (m, 2H), 4.17-3.99 (m, 4H), 3.85 (s, 3H), 1.33-1.29 (t, J = 8 Hz, 6H). ^{13}C-NMR ($CDCl_3$, 101 MHz) δ (ppm): 163.01 (d, J = 3 Hz), 133.98 (d, J = 11.1 Hz), 120.65, 114.23 (d, J = 16.2 Hz), 62.09 (d, J = 6.1 Hz), 55.47, 16.49 (d, J = 6.1 Hz). ^{31}P-NMR ($CDCl_3$, 202 MHz) δ (ppm): 19.74. The obtained data are consistent with the literature reports.[7]



Diethyl quinolin-3-ylphosphonate (5dc): The reaction mixture was purified by column chromatography on silica gel using Hexane/EtOAc as eluent. Product **5dc** (57 mg, 72% yield) was obtained as a colourless oil. R_f = 0.5 (Hexane: EtOAc = 10:3). ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 9.16-9.14 (m, 1H), 8.73-8.69 (m, 1H), 8.18-8.15 (d, J = 12 Hz, 1H), 7.93-7.91 (d, J = 8 Hz, 1H), 7.87-7.85 (m, 1H), 7.66-7.63 (m, 1H), 4.29-4.11 (m, 4H), 1.38-1.34 (t, J = 8 Hz, 6H). ^{13}C-NMR ($CDCl_3$, 101 MHz) δ (ppm): 150.8 (d, J = 13.1 Hz), 149.51, 142.25 (d, J = 8.1 Hz), 132.02, 129.65, 128.86, 127.77, 126.93 (d, J = 13.1 Hz), 122.97, 62.79 (d, J = 6.1 Hz), 16.55 (d, J = 6.1 Hz). ^{31}P-NMR ($CDCl_3$, 202 MHz) δ (ppm): 16.15. The obtained data are consistent with the literature reports.[6]

Mechanistic studies:

a) Radical trapping with TEMPO:

To a solution of **PC-A** (0.015 mmol), **1a** (0.3 mmol), **2a** (3 mmol), and DIPEA (1.2 mmol) in N_2-saturated DMSO (0.1 M, 1mL), radical quencher TEMPO (1.5 equivalents, 0.45 mmol) was added, and the mixture was stirred for 6 h under purple-LED light at room temperature. The reaction entirely ceased as found from TLC, and no desired C–C coupling product was observed. TEMPO adduct was detected from HRMS, which confirms the generation of a free radical in the reaction.

For the borylation reaction, **PC-A** (0.015 mmol), **1a** (0.3 mmol), **2b** (0.9 mmol), and DBU (0.6 mmol) and for phosphorylation reaction **PC-A** (0.015 mmol), **1a** (0.3 mmol), **2c** (3 mmol), and DBU (0.6 mmol) was used in N_2-saturated DMSO (0.1 M, 1mL) along with radical quencher TEMPO (1.5 equivalents, 0.45 mmol) and both the mixture was stirred for 6 h under purple-LED light at room temperature. And in both cases, no C–B and C–P bonded product was observed.

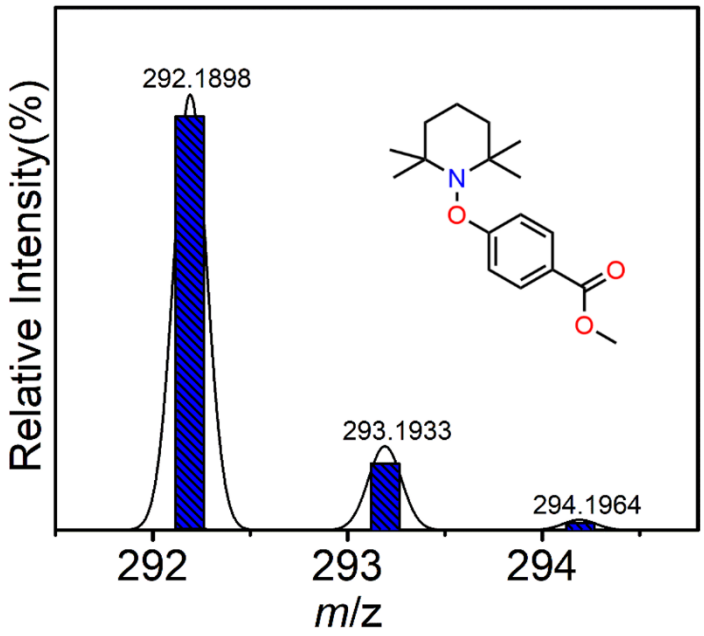


Figure S17. ESI-MS (+ve) mass spectrum of TEMPO-adducted product. Experimental data in the column and theoretical isotopic distribution in line.

b) Stern-Volmer study (Fluorescence quenching experiment):

Fluorescence quenching experiments were carried out on catalyst **PC-A** ([**PC-A**] = 50 μM) by varying the concentration of quencher ([Q]/[**PC-A**] = 5/100, 10/100, 15/100, and 20/100) at room temperature in N_2-saturated DMSO solution. All the solutions were irradiated at 370 nm,

and emission intensity was recorded at 475 nm. Stern-Volmer plots were generated between the concentration of quencher and I_0/I (emission values without and with quencher at 475 nm) to calculate K_{sv}.

For the C-C coupling reaction, fluorescence quenching was performed with **PC-A** for both 1a and DIPEA (**Figure S18**). Stern-Volmer analysis showed that both **1a** and DIPEA quenched the excited state **PC-A***, and the photoluminescence quenching of substrate **1a** occurred at a higher rate than DIPEA (K_{sv} for **1a** is 0.94 mM^{-1} and DIPEA is 0.62 mM^{-1}).

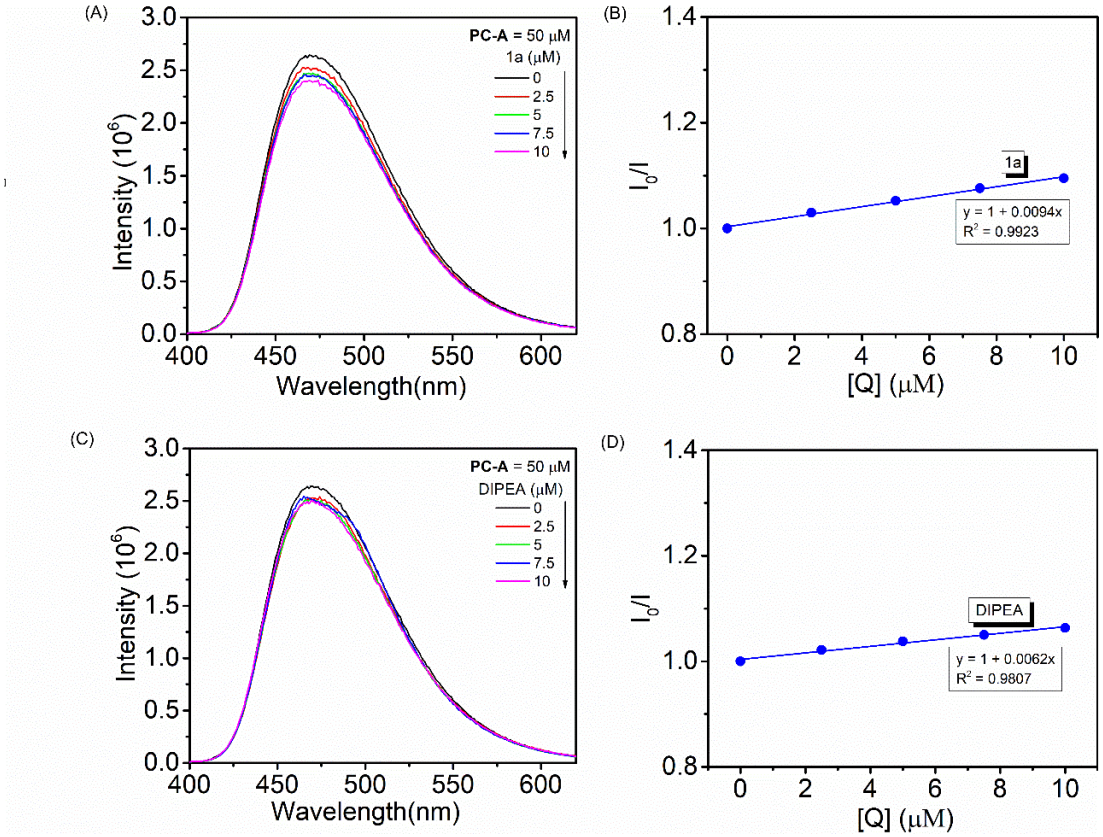


Figure S18. (A) and (C) Quenching experiment using **1a** and DIPEA, respectively. (C) and (D) Stern-Volmer plot based on quenching of **1a** and DIPEA, respectively.

For borylation and phosphorylation reactions, photoluminescence quenching was conducted with **PC-A** and a 1:1 mixture of both B_2Pin_2 and $P(OEt)_3$ with base DBU (**Figure S19**). Here, also substrate **1a** quenched the excited state **PC-A*** more rapidly than these two mixtures (K_{sv} for [B_2Pin_2 + DBU] is 0.56 mM^{-1} and [$P(OEt)_3$ + DBU] is 0.92 mM^{-1}), which proved that electron transfer always occurs from the catalyst **PC-A** to the substrate **1a** by formation of an aryl radical.

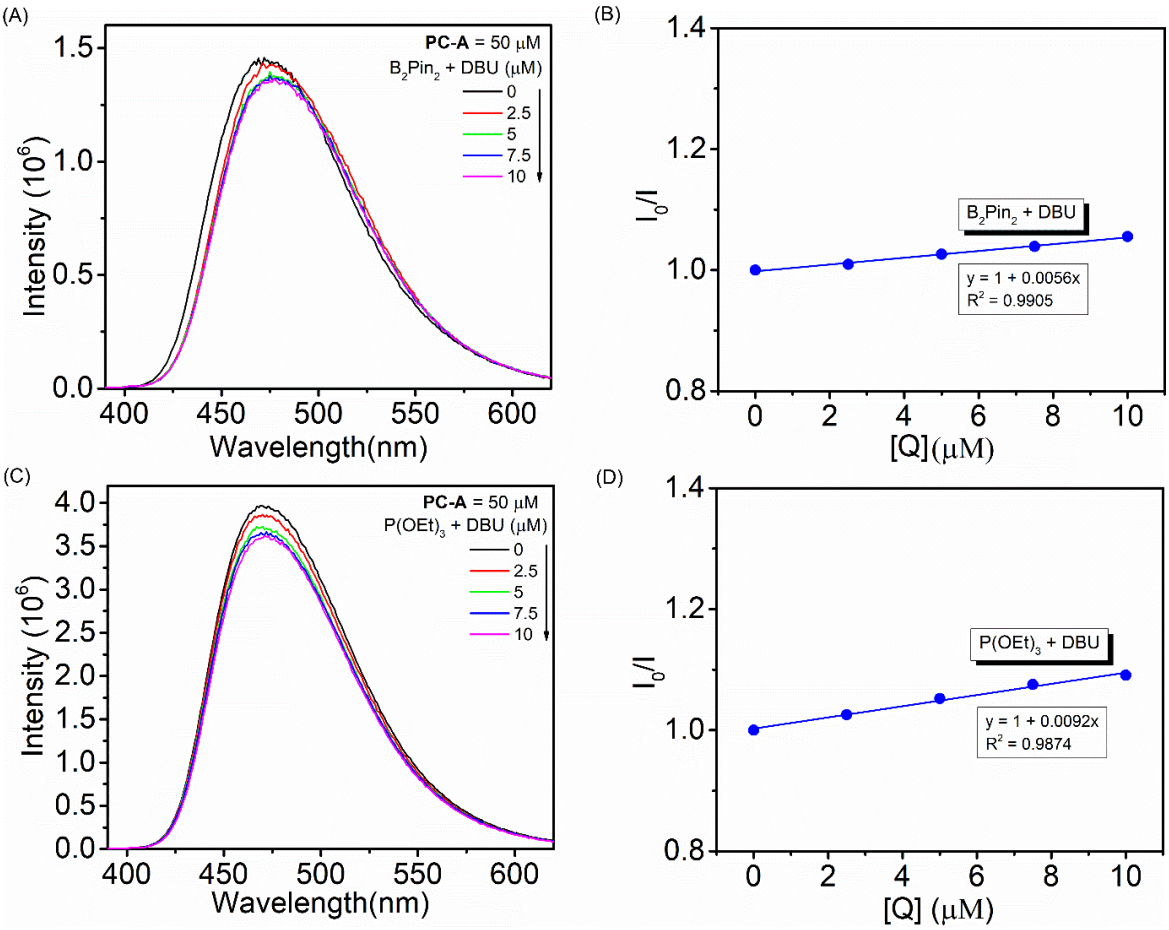


Figure S19. (A) and (C) Quenching experiment using 1:1 mixture of B_2Pin_2, DBU and $P(OEt)_3$, DBU, respectively. (B) and (D) Stern-Volmer plot based on quenching of B_2Pin_2 + DBU and $P(OEt)_3$ + DBU respectively. Experiments with B_2Pin_2 were carried out in CH_3CN.

Table 1. Photophysical and electrochemical parameters of the photo-catalyst **PC-A** in DMSO.

λ_{abs} (nm)	λ_{em} (nm)	Φ_{PL} (%)	τ_{obs} (ns)	k_{nr} (10^5 s^{-1})	k_r (10^6 s^{-1})	E_{ox} (V vs SCE)	E_{ox}* (V vs SCE)	E_{ox}* (V vs SCE) (theoretical)
380	470	0.98	6.84	1.4	2.92	0.854	-2.03	-2.10

The change in Gibbs free energy for one electron transfer was evaluated.[6] The calculated values, ΔG_{ET} = +61.8 kcal mol^{-1} (ground state electron transfer) and ΔG_{PET} = –6.92 kcal mol^{-1} (excited state electron transfer), clearly confirm that the electron transfer process is feasible only in the excited state.

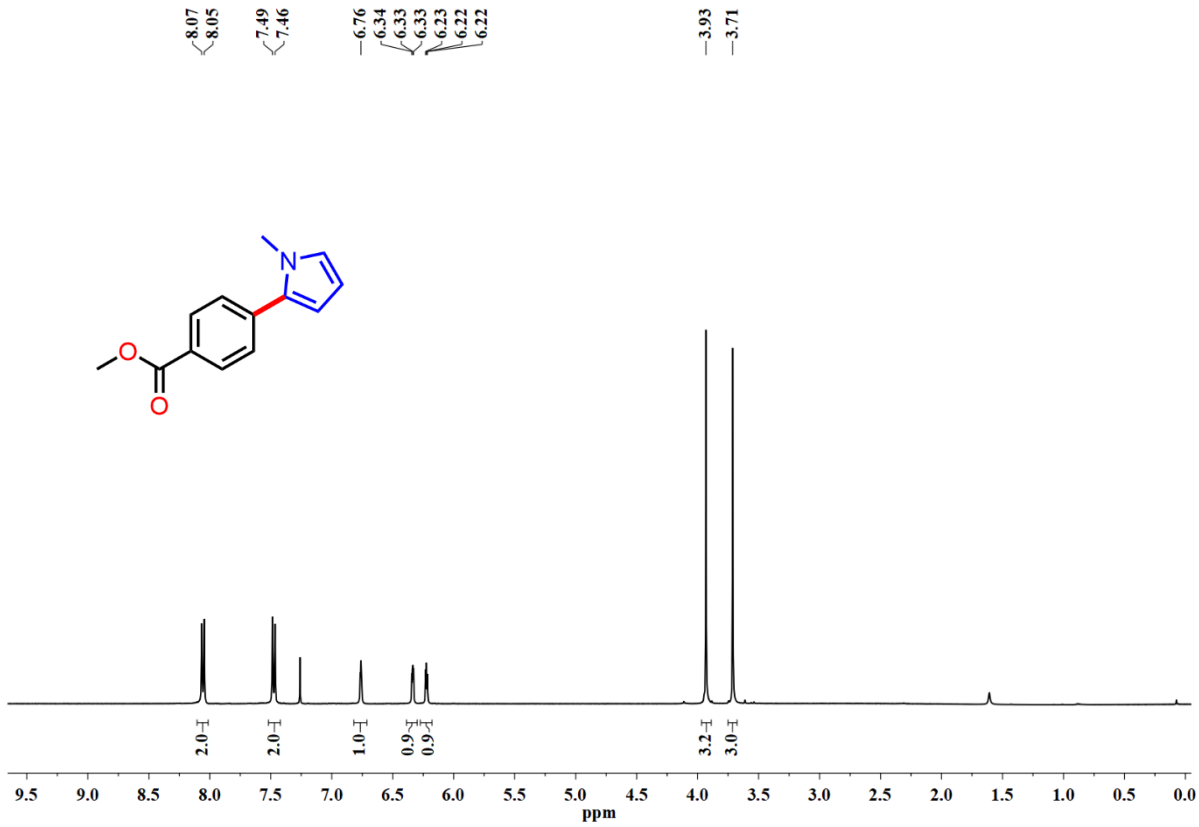


Figure S20. ^{1}H-NMR spectrum of **3aa** in $CDCl_3$ solvent.

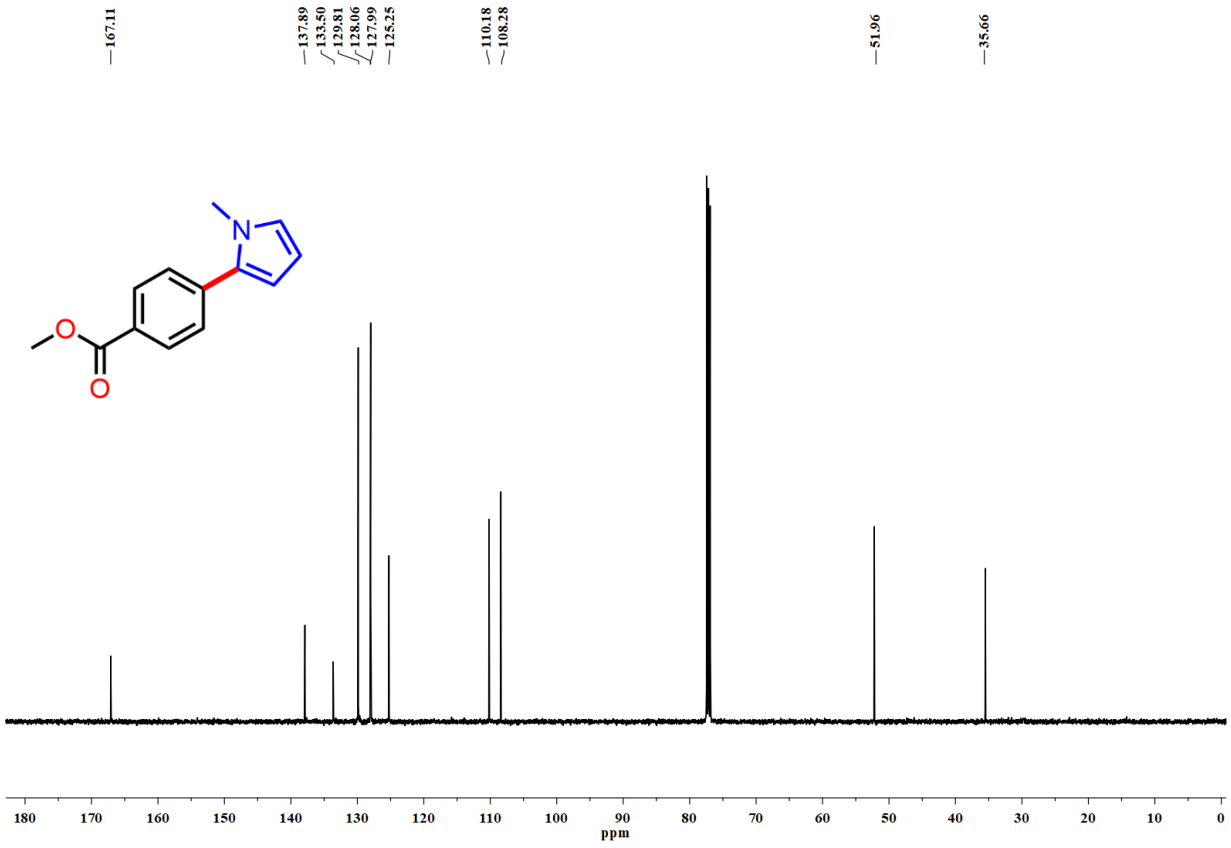


Figure S21. ^{13}C-NMR spectrum of **3aa** in $CDCl_3$ solvent.

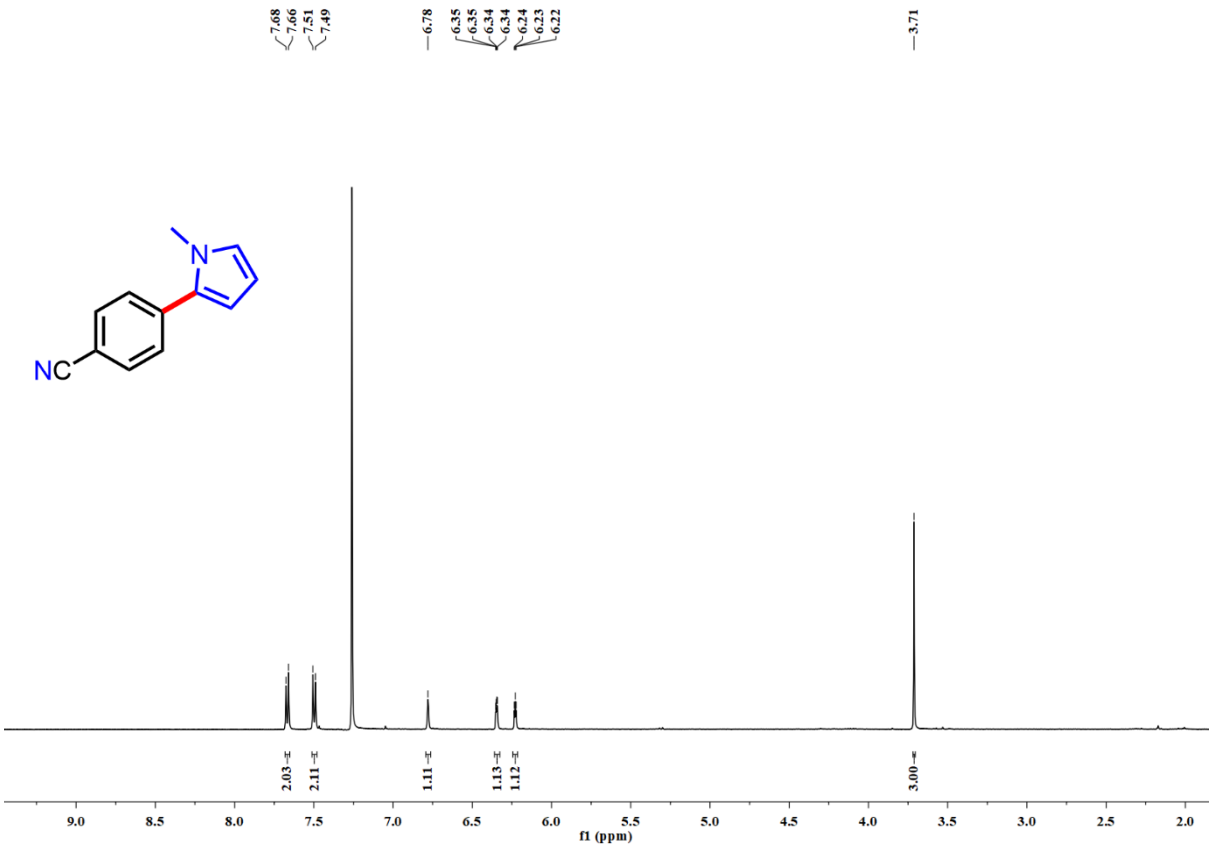


Figure S22. ^{1}H-NMR spectrum of **3ba** in $CDCl_3$ solvent.

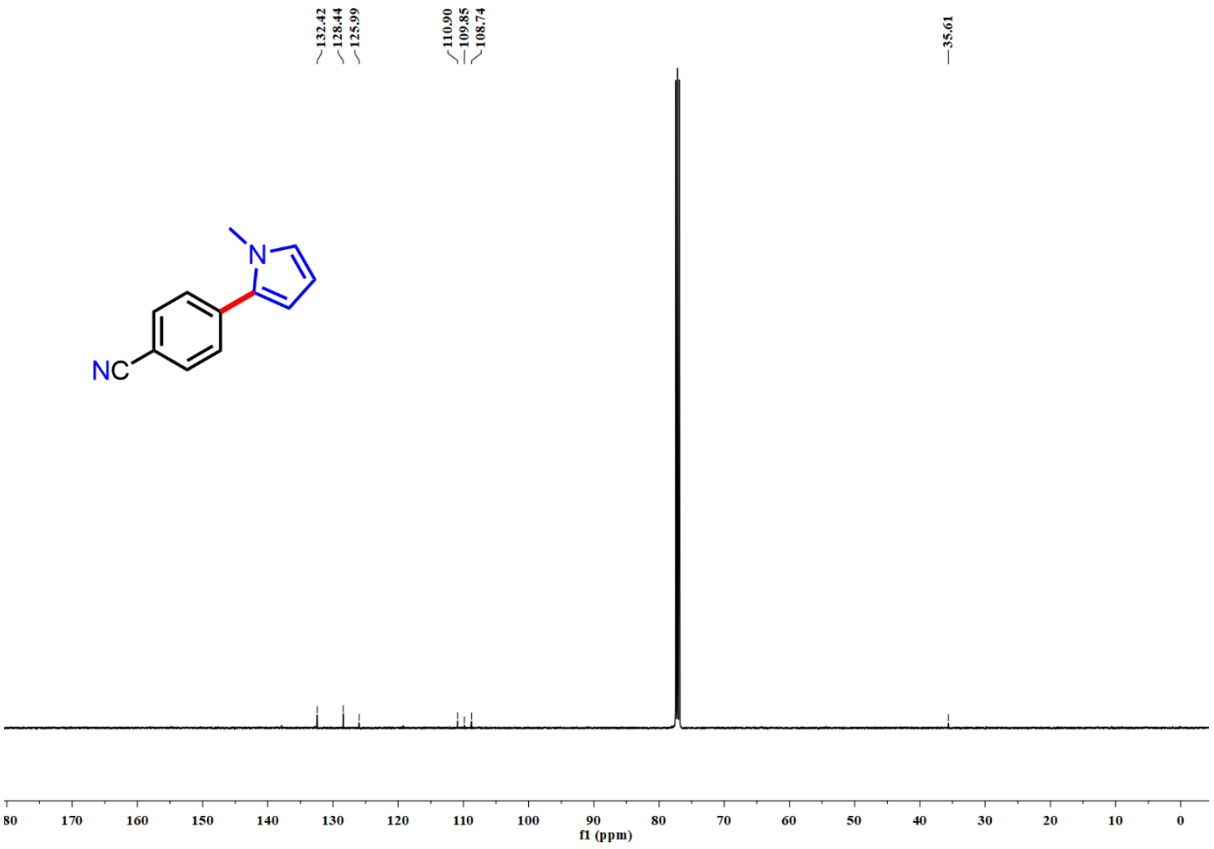


Figure S23. ^{13}C-NMR spectrum of **3ba** in $CDCl_3$ solvent.

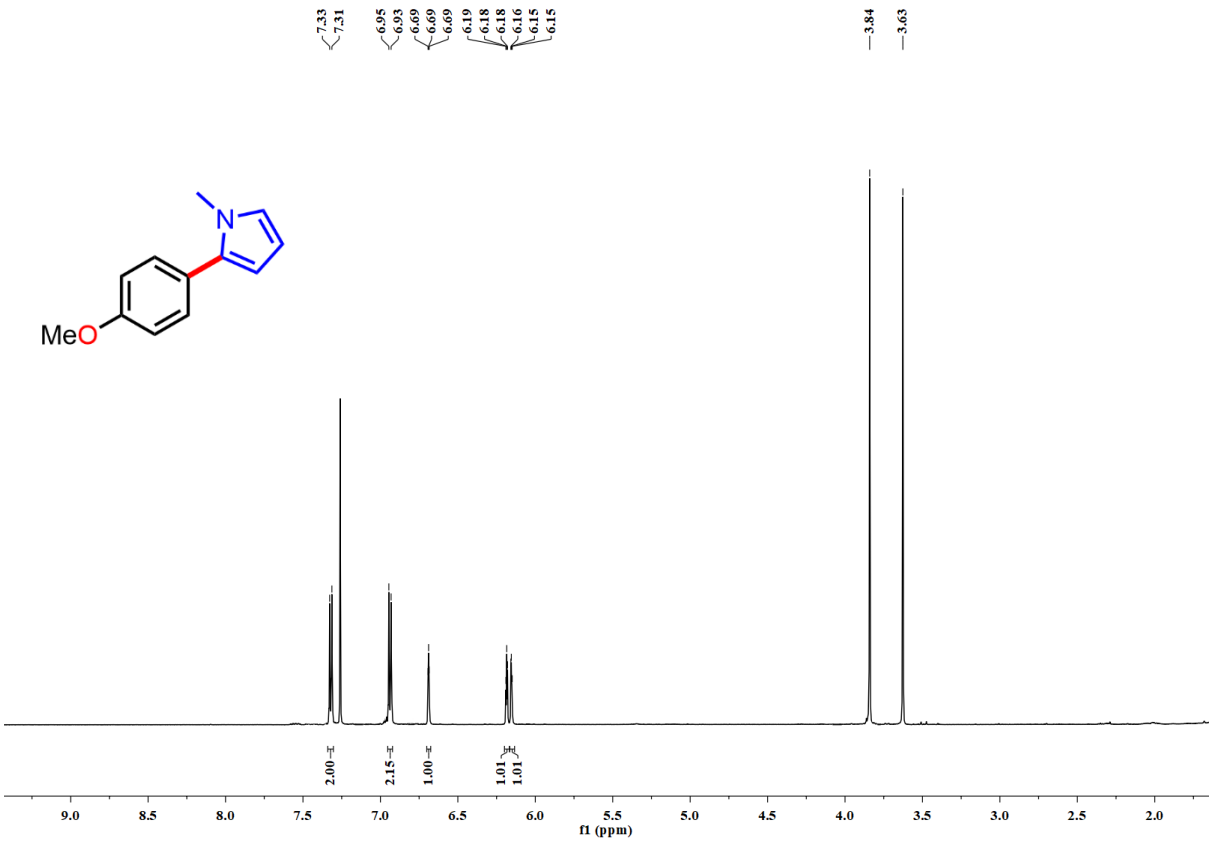


Figure S24. ^{1}H-NMR spectrum of **3ca** in $CDCl_3$ solvent.

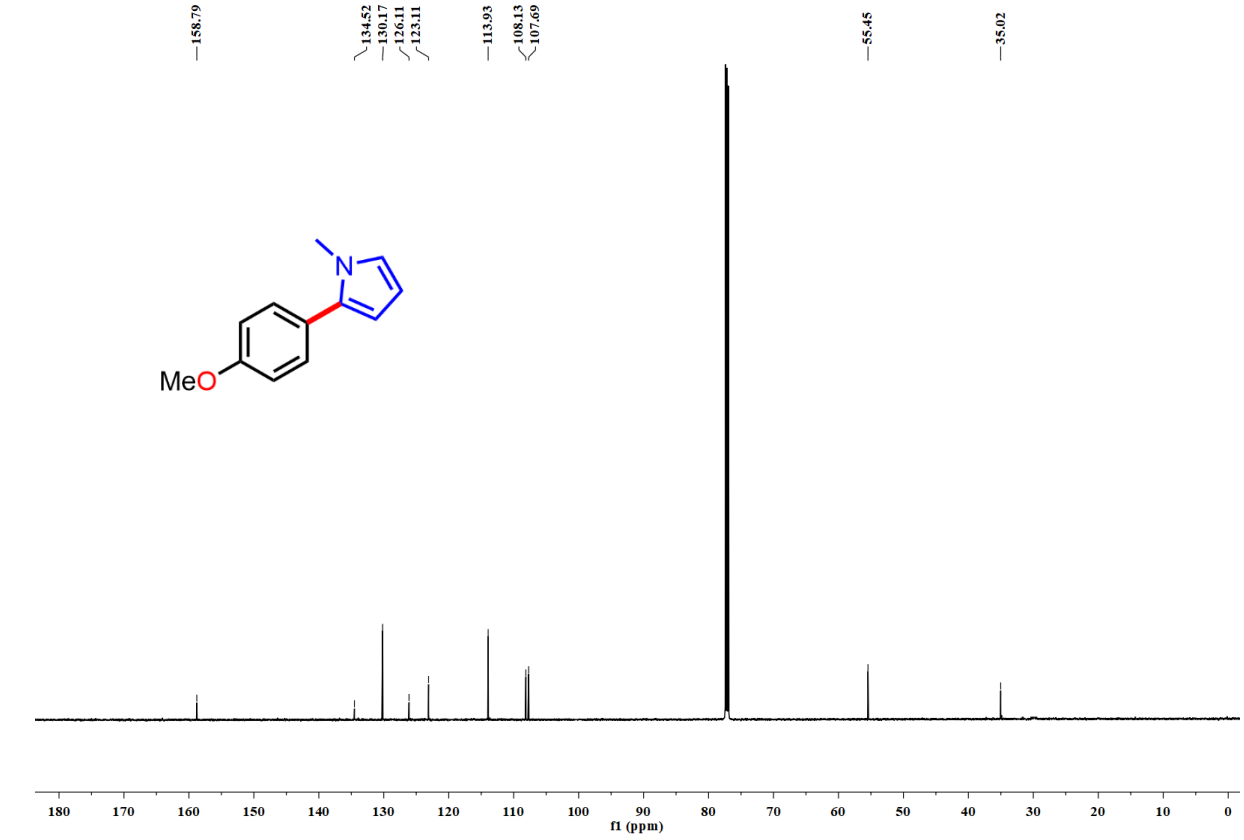


Figure S25. ^{13}C-NMR spectrum of **3ca** in $CDCl_3$ solvent.

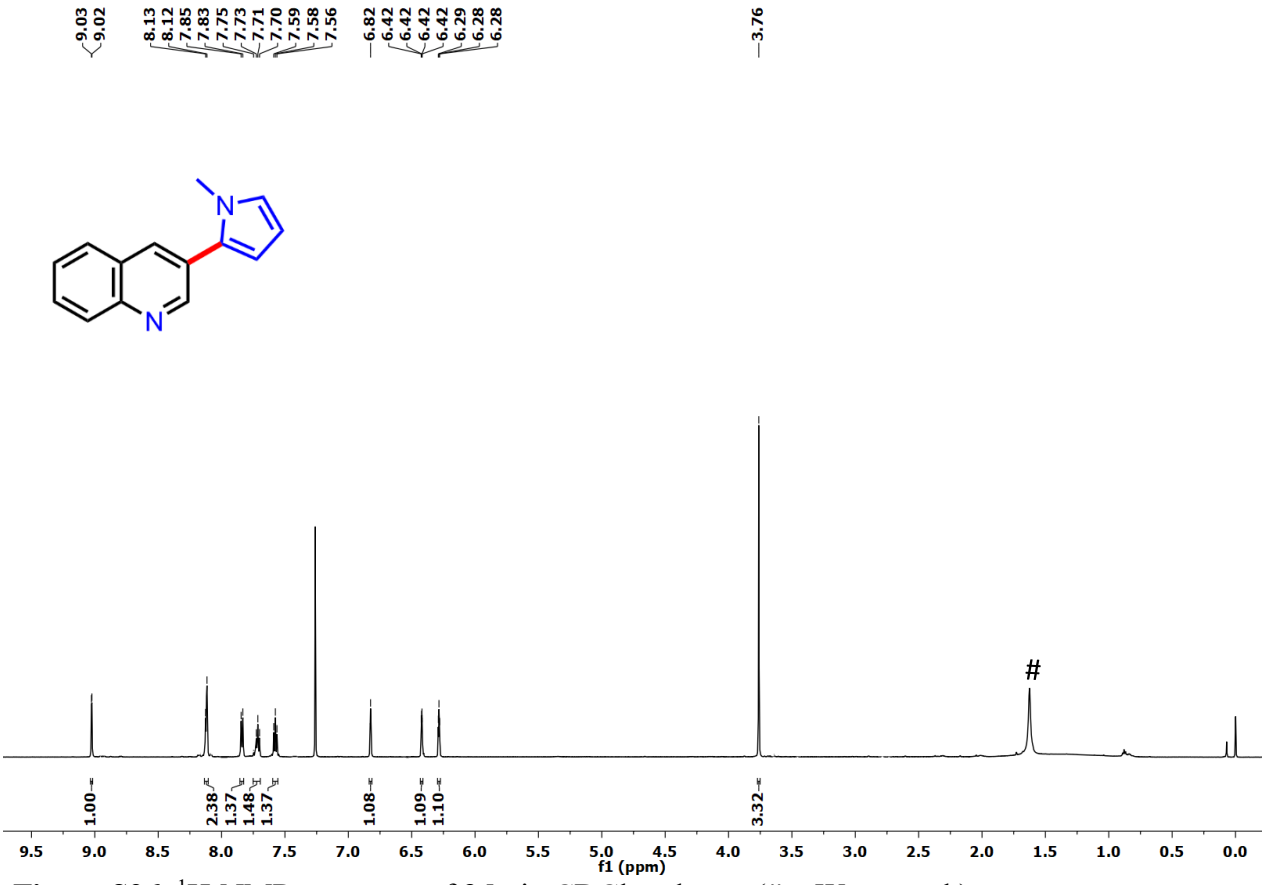


Figure S26. ^{1}H-NMR spectrum of **3da** in $CDCl_3$ solvent. (# = Water peak)

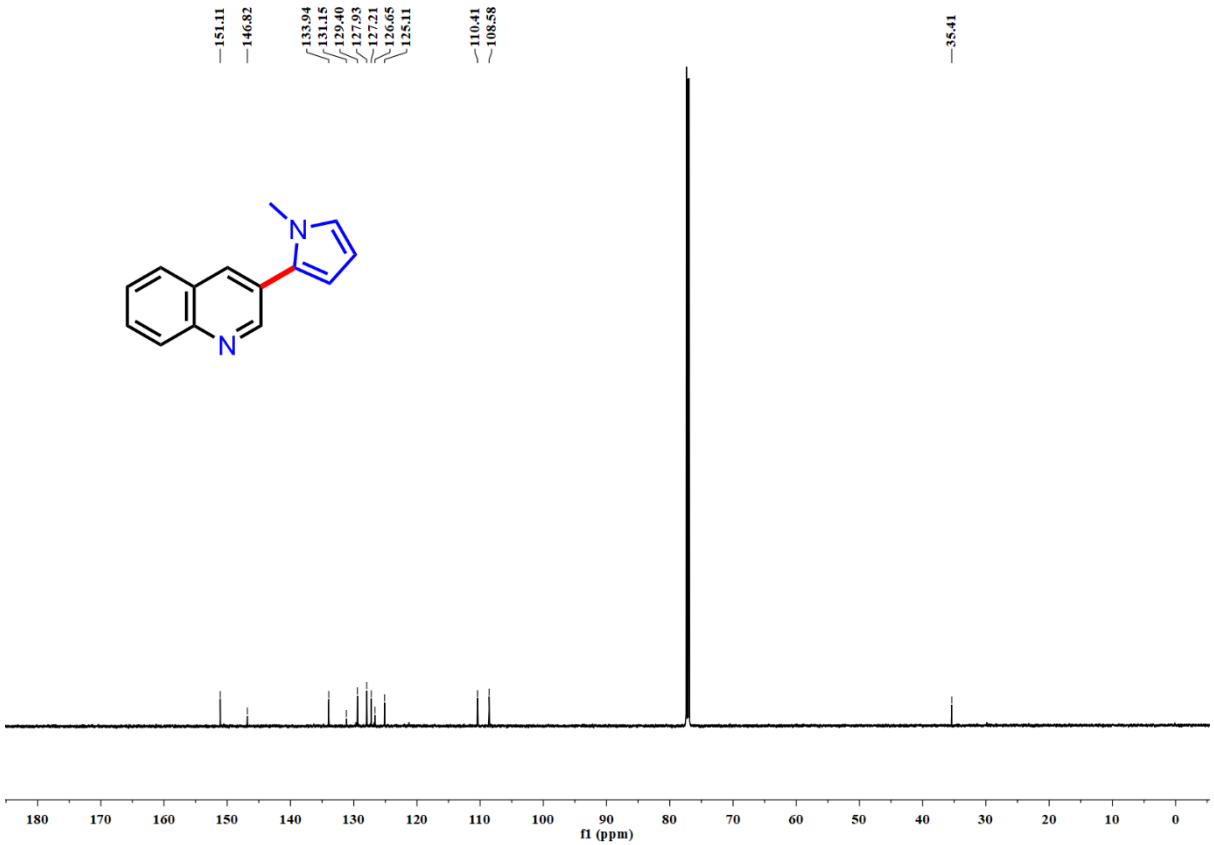


Figure S27. ^{13}C-NMR spectrum of **3da** in $CDCl_3$ solvent.

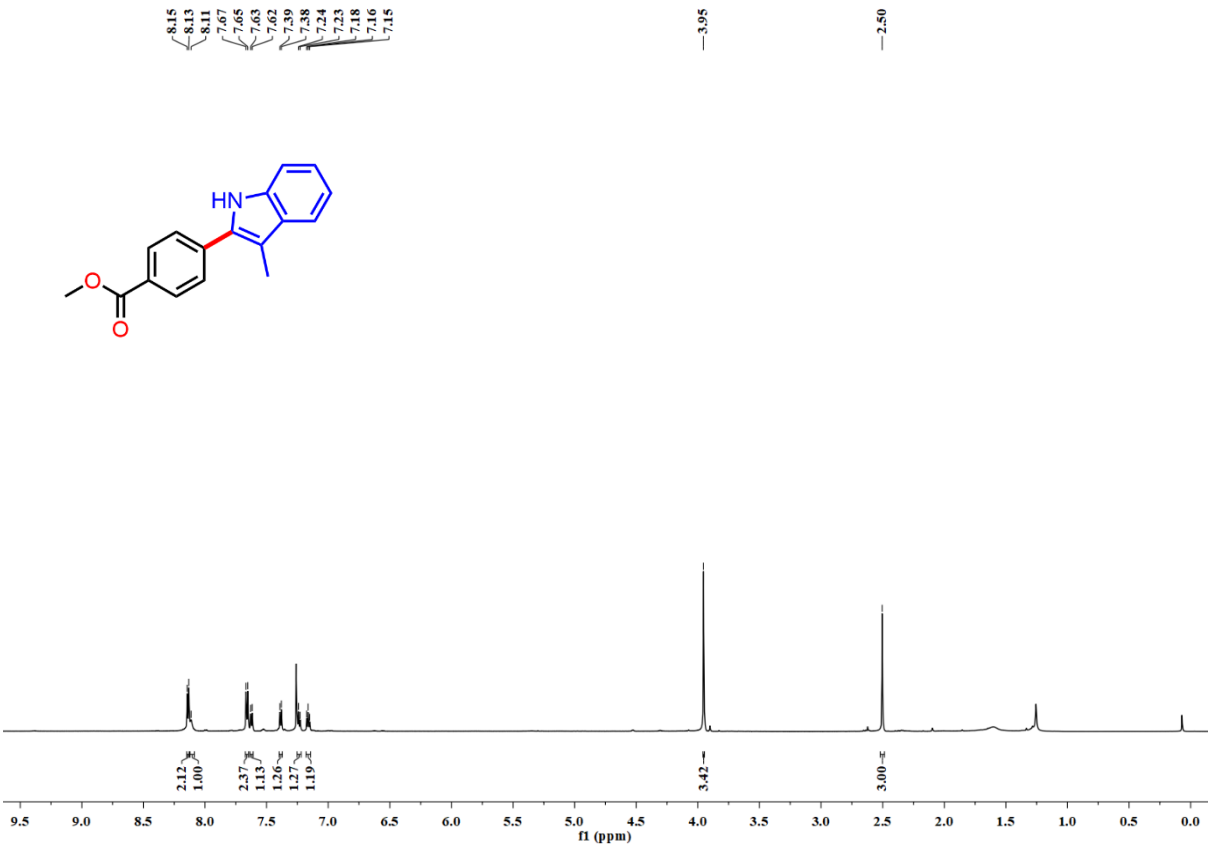


Figure S28. ^{1}H-NMR spectrum of **3ea** in $CDCl_3$ solvent.

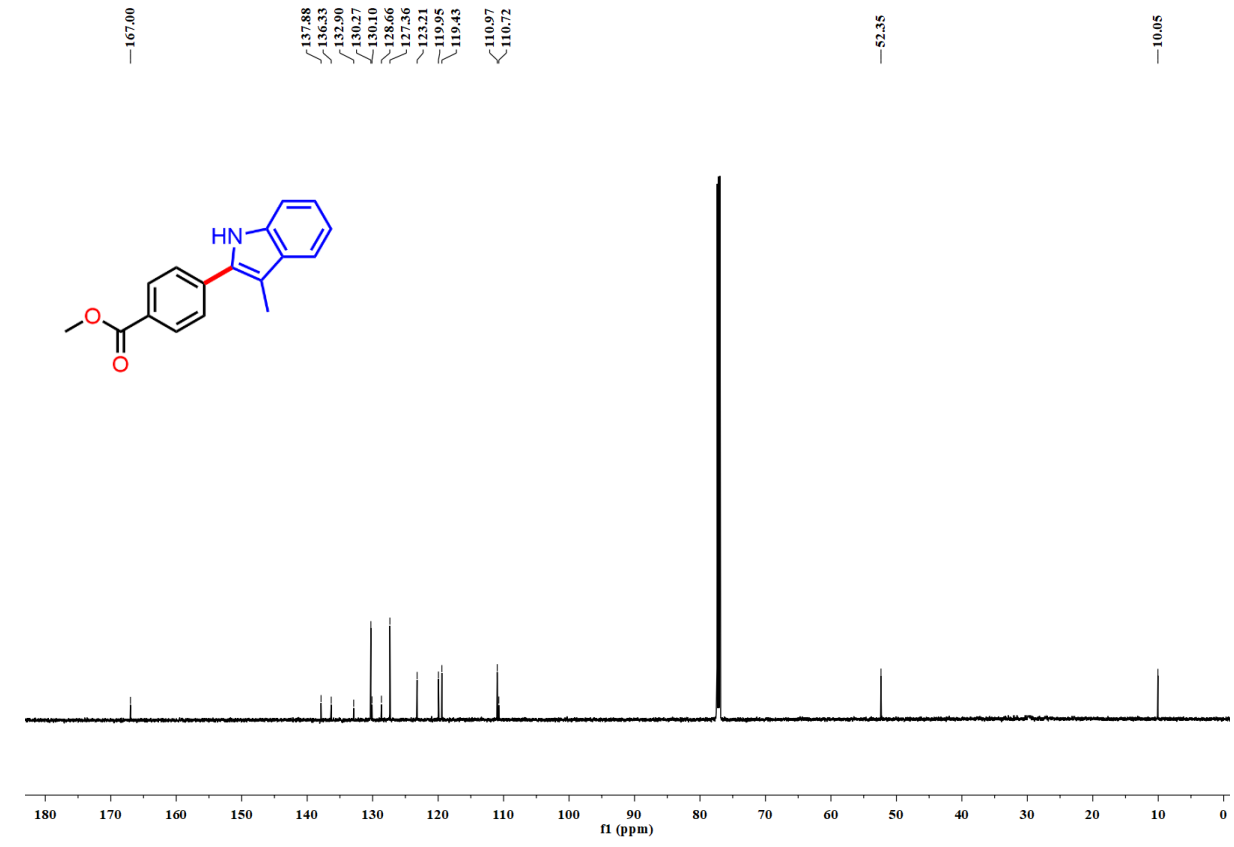


Figure S29. ^{13}C-NMR spectrum of **3ea** in $CDCl_3$ solvent.

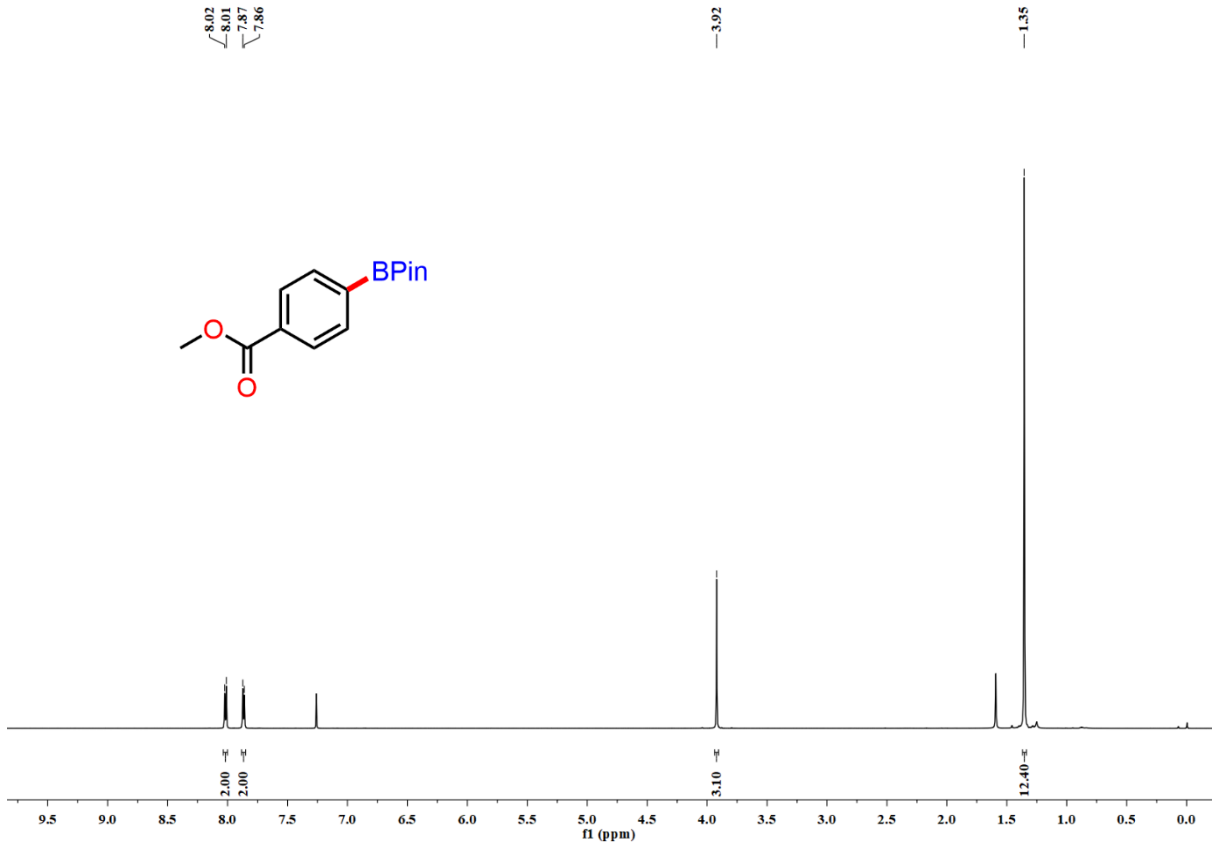


Figure S30. ^{1}H-NMR spectrum of **4ab** in $CDCl_3$ solvent.

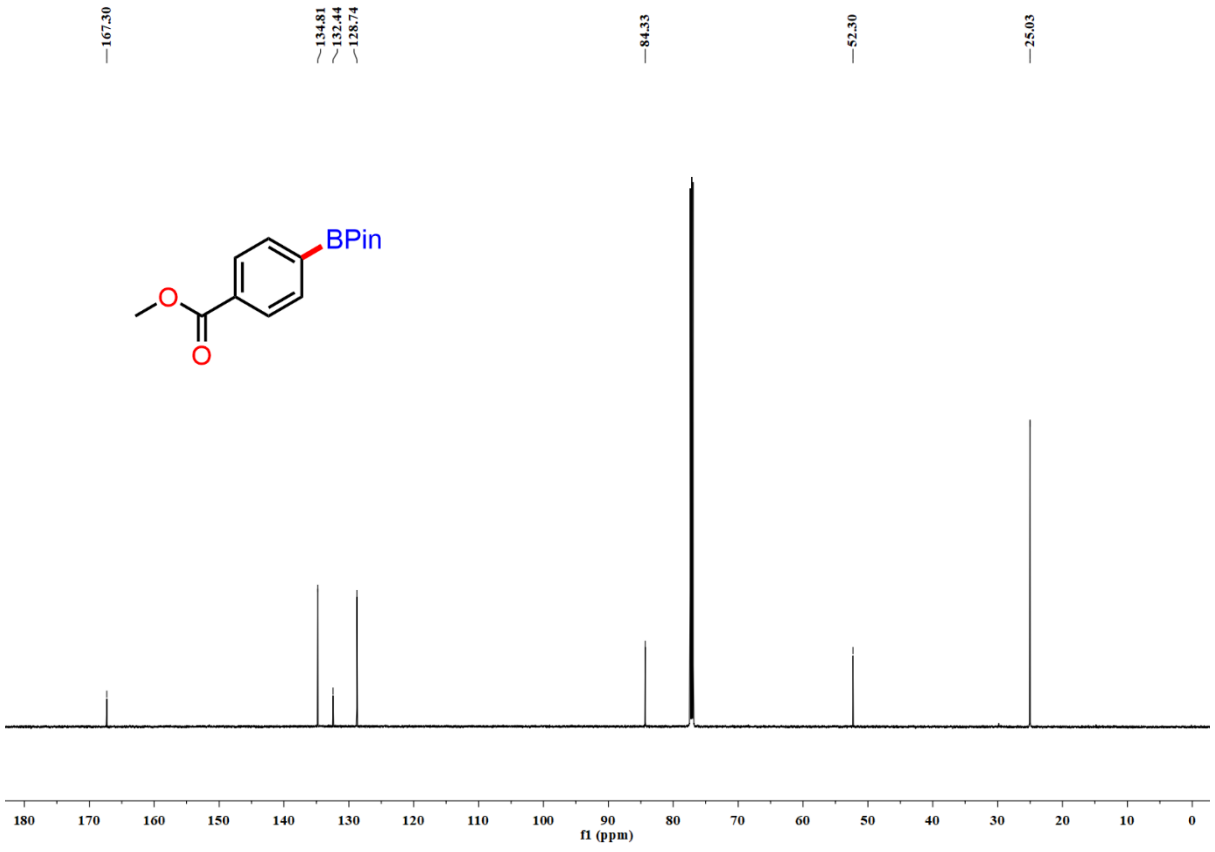


Figure S31. ^{13}C-NMR spectrum of **4ab** in $CDCl_3$ solvent.

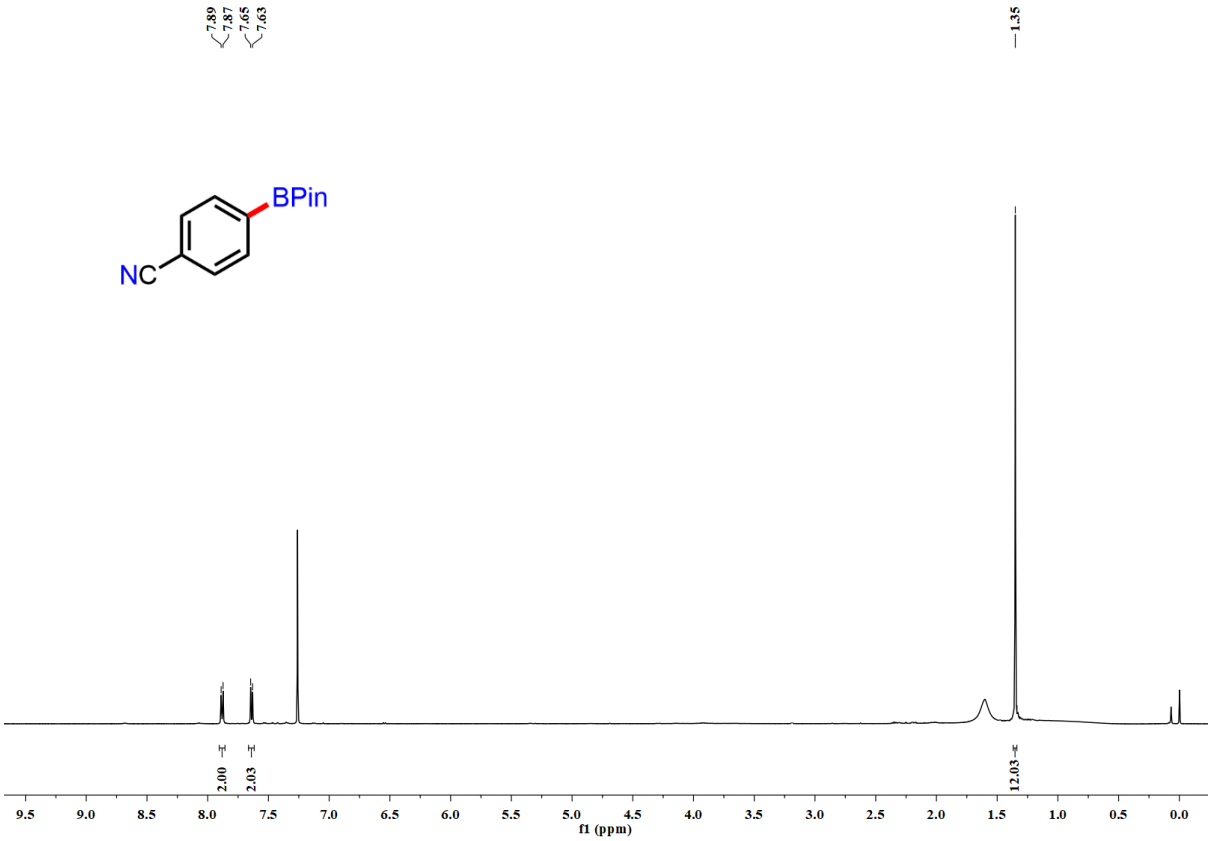


Figure S32. ^{1}H-NMR spectrum of **4bb** in $CDCl_3$ solvent.

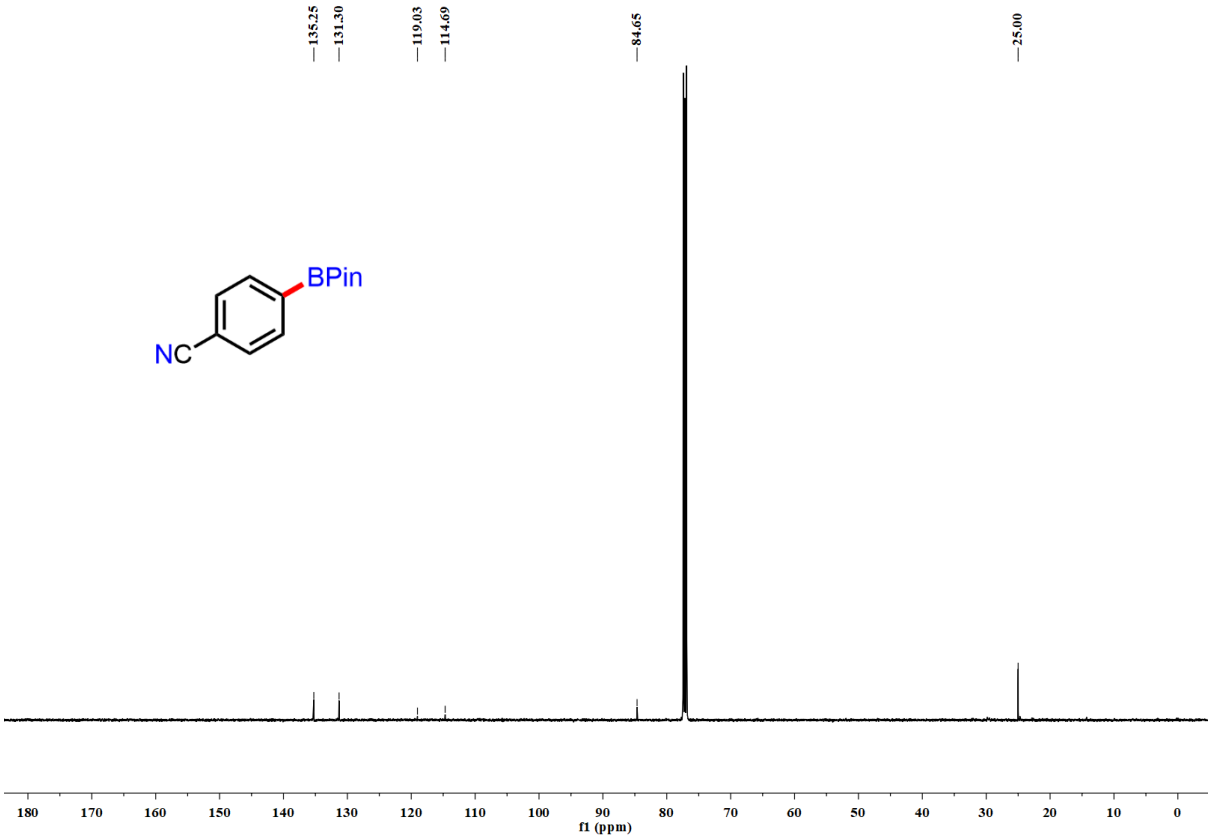


Figure S33. ^{13}C-NMR spectrum of **4bb** in $CDCl_3$ solvent.

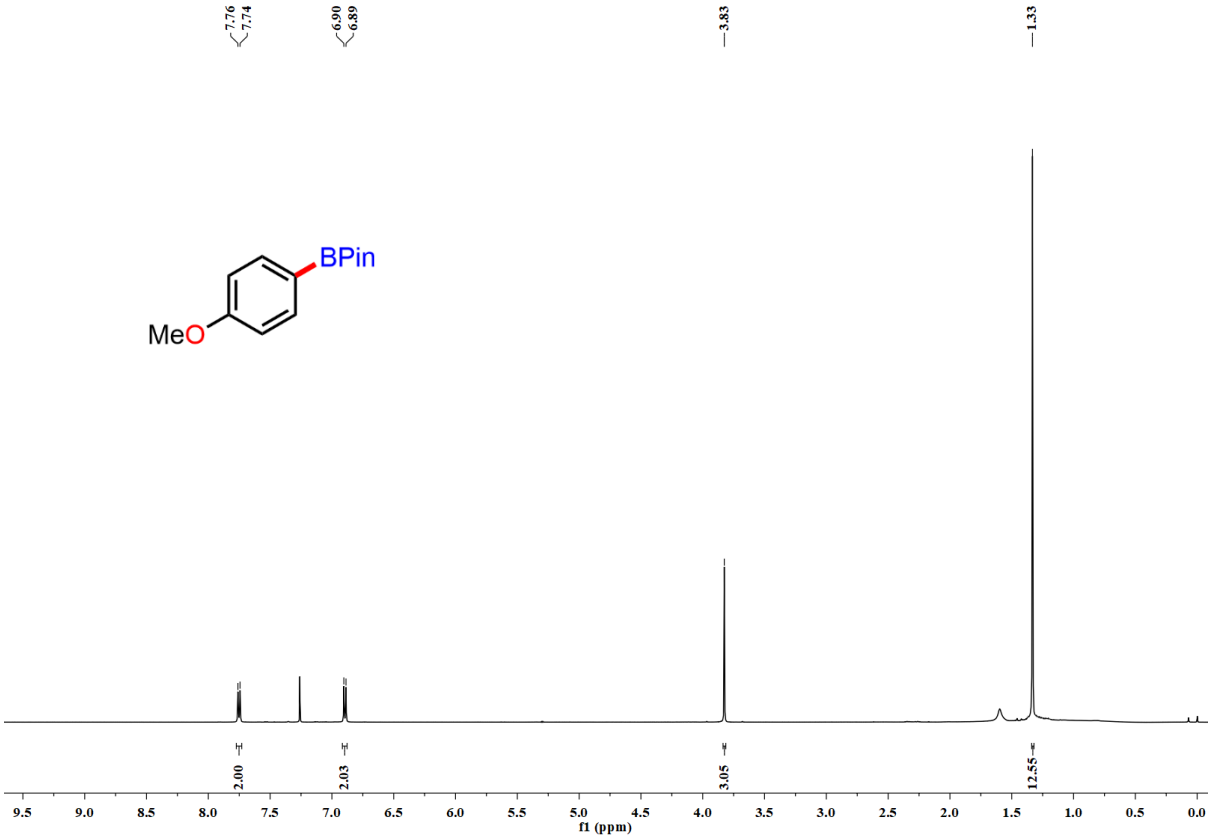


Figure S34. ^{1}H-NMR spectrum of **4cb** in $CDCl_3$ solvent.

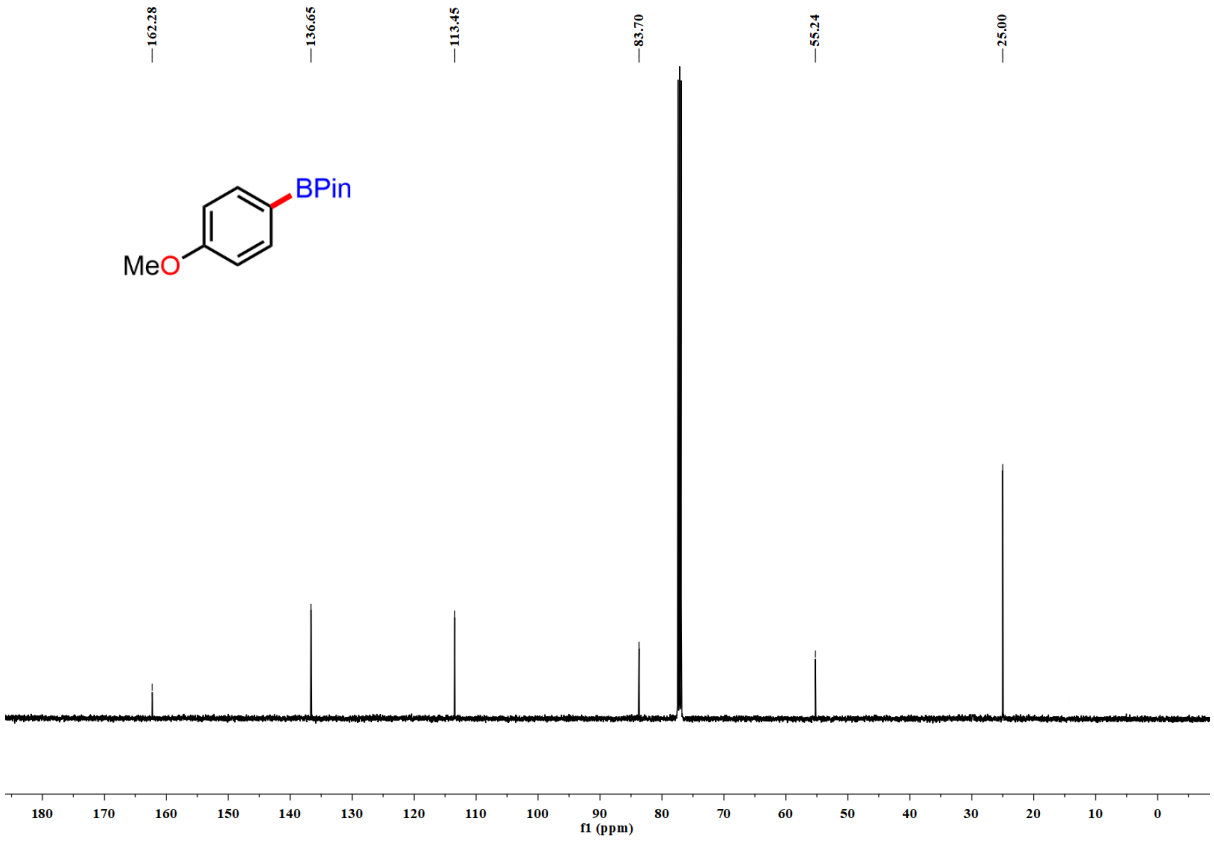


Figure S35. ^{13}C-NMR spectrum of **4cb** in $CDCl_3$ solvent.

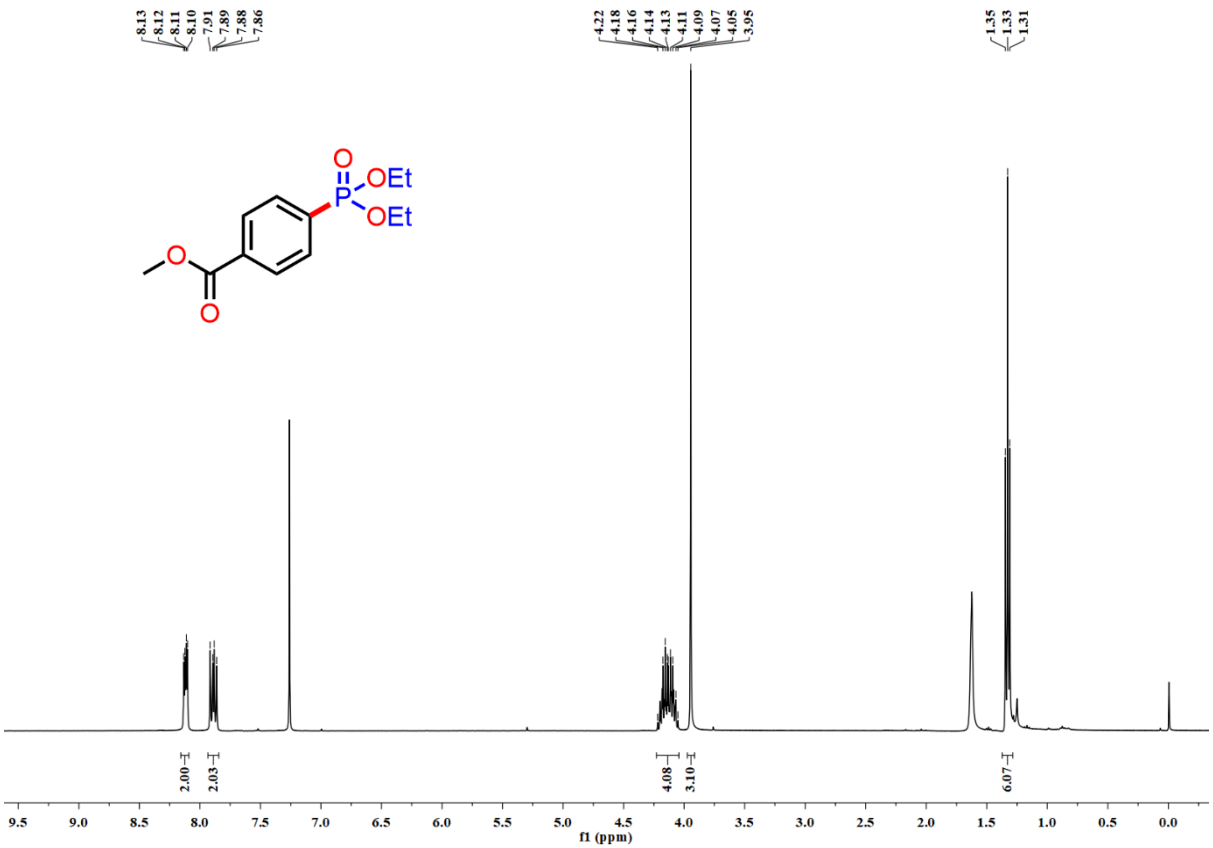


Figure S36. ^{1}H-NMR spectrum of **5ac** in $CDCl_3$ solvent.

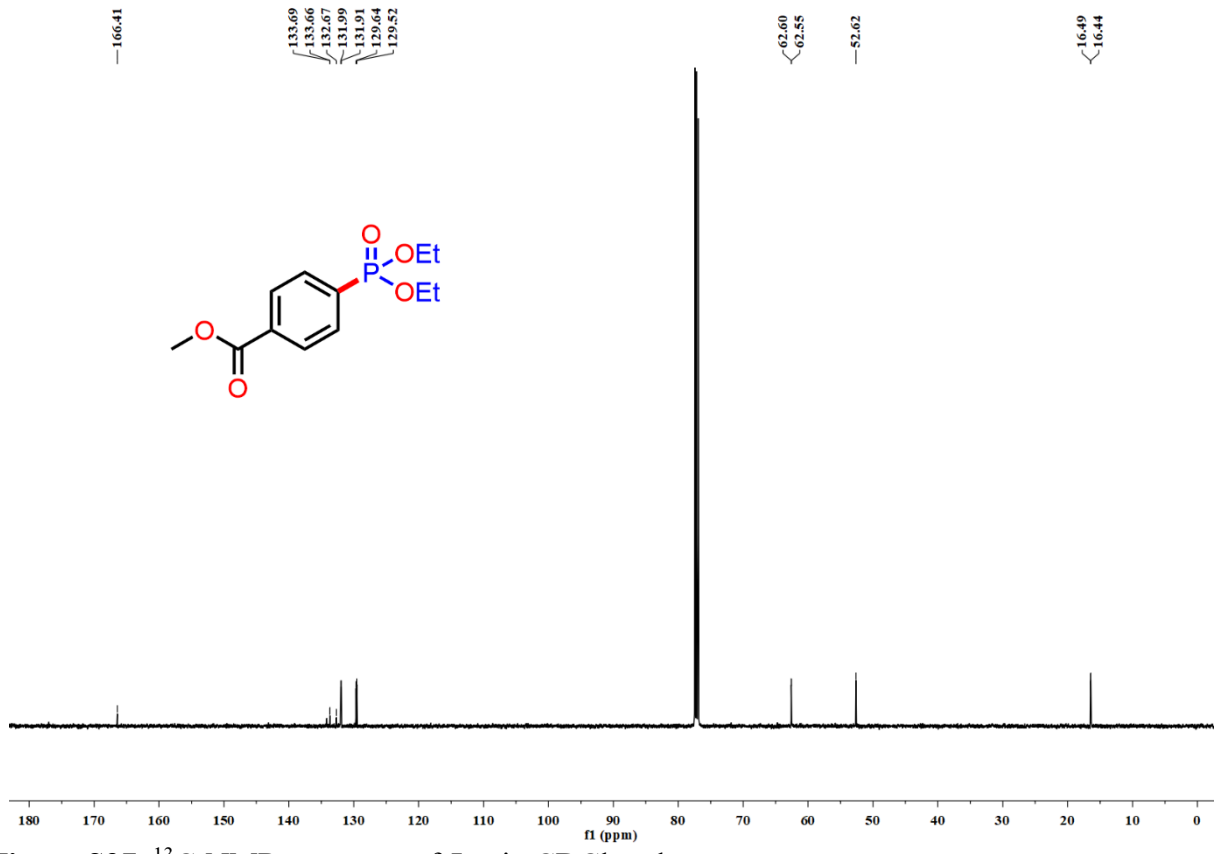


Figure S37. ^{13}C-NMR spectrum of **5ac** in $CDCl_3$ solvent.

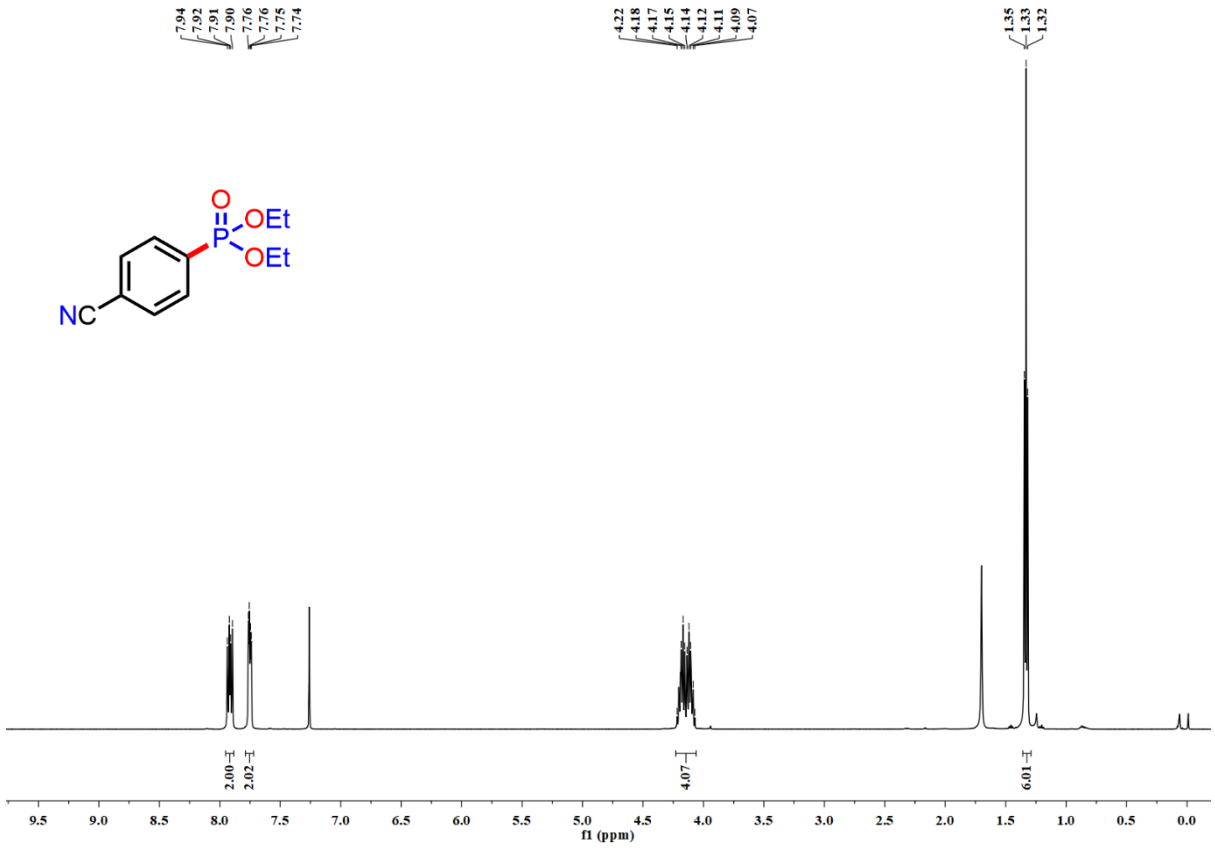


Figure S38. ^{1}H-NMR spectrum of **5bc** in $CDCl_3$ solvent.

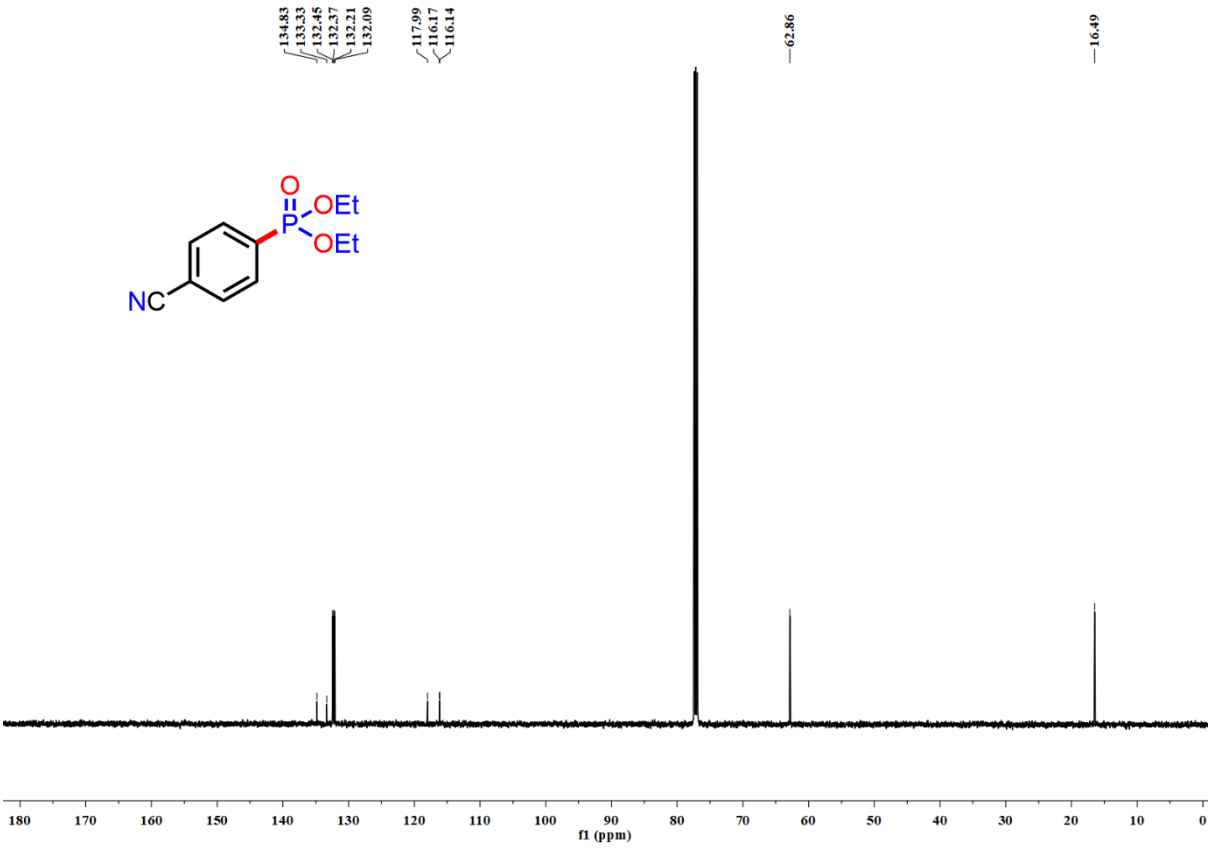


Figure S39. ^{13}C-NMR spectrum of **5bc** in $CDCl_3$ solvent.

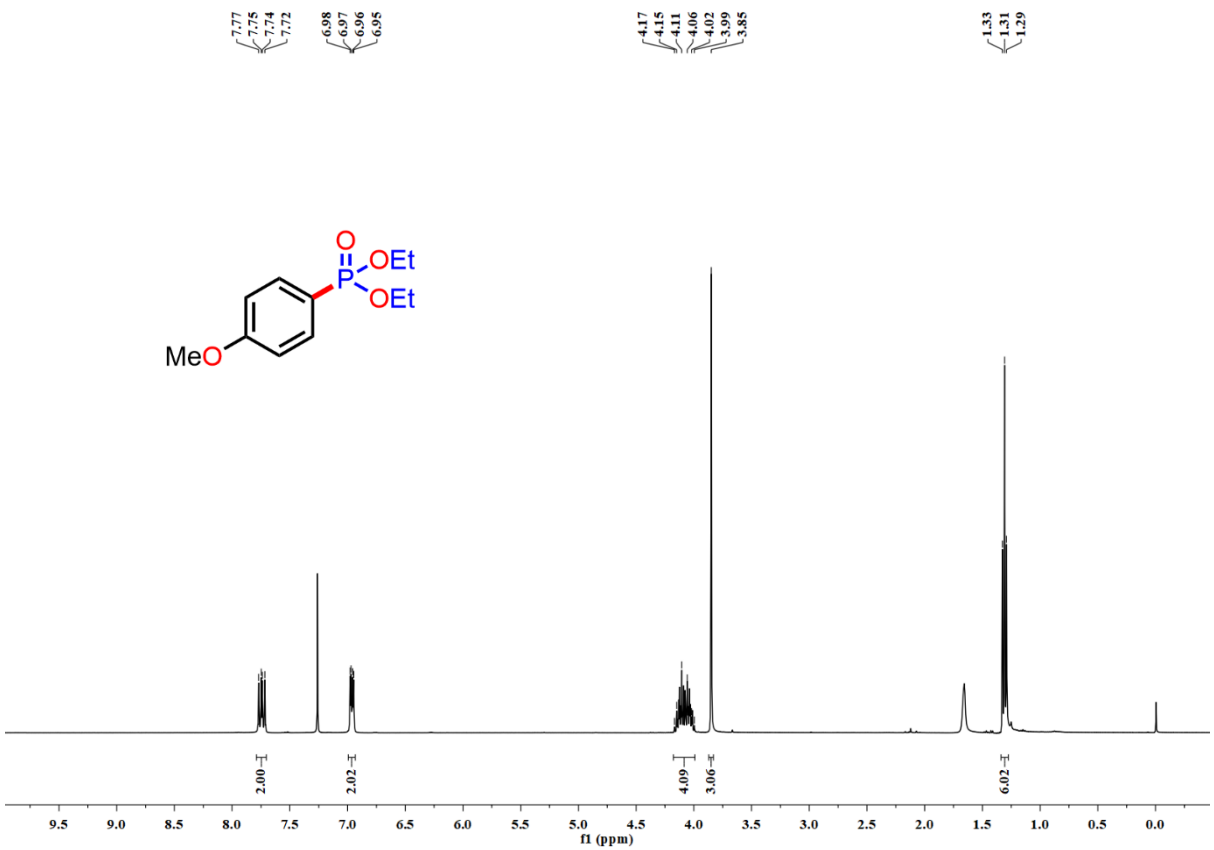


Figure S40. ^{1}H-NMR spectrum of **5cc** in $CDCl_3$ solvent.

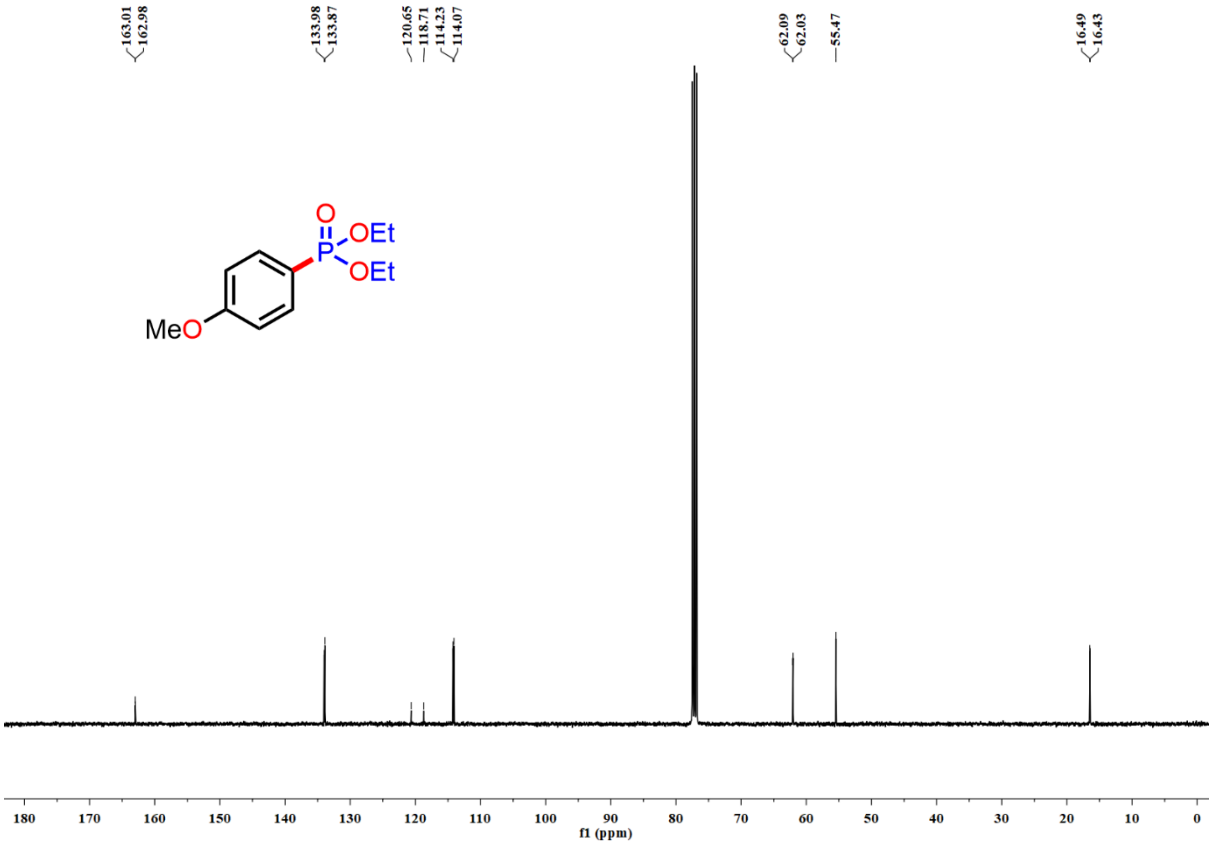


Figure S41. ^{13}C-NMR spectrum of **5cc** in $CDCl_3$ solvent.

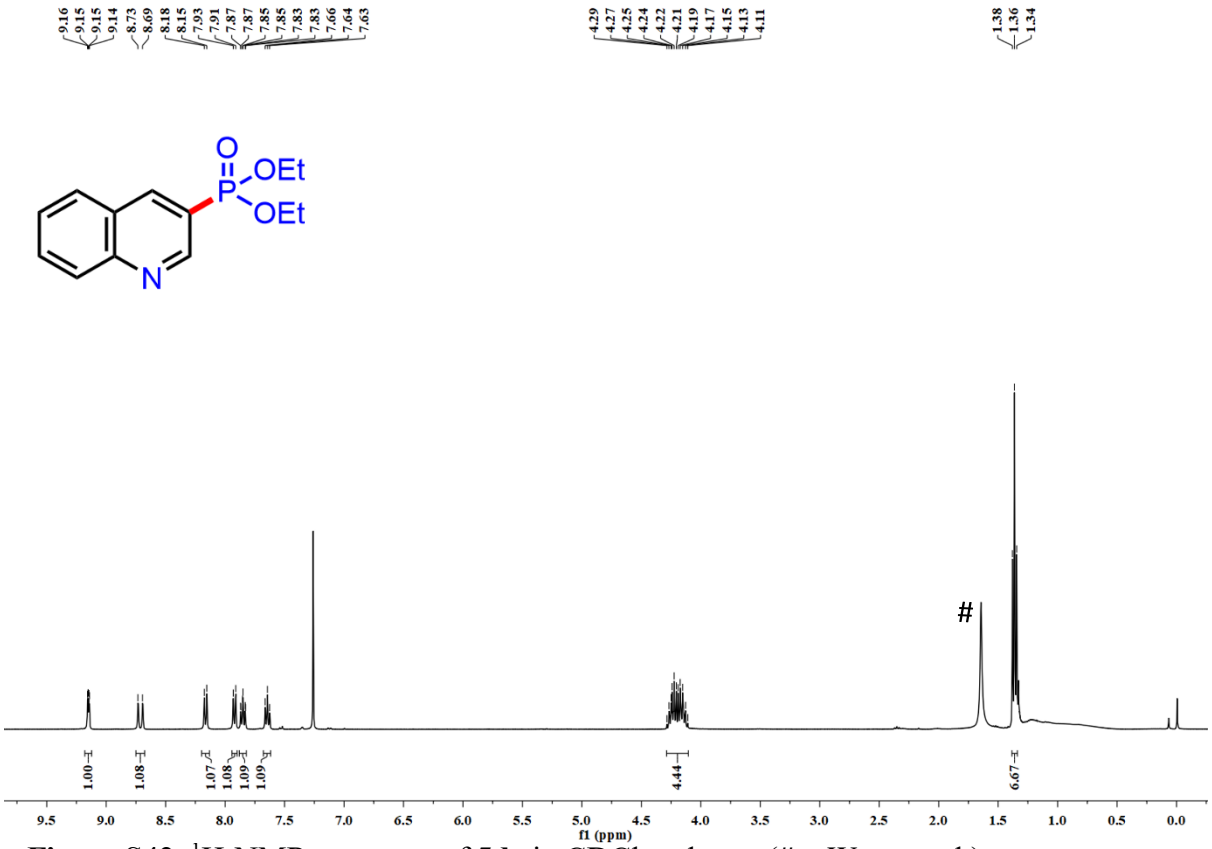


Figure S42. ^{1}H-NMR spectrum of **5dc** in $CDCl_3$ solvent. (# = Water peak)

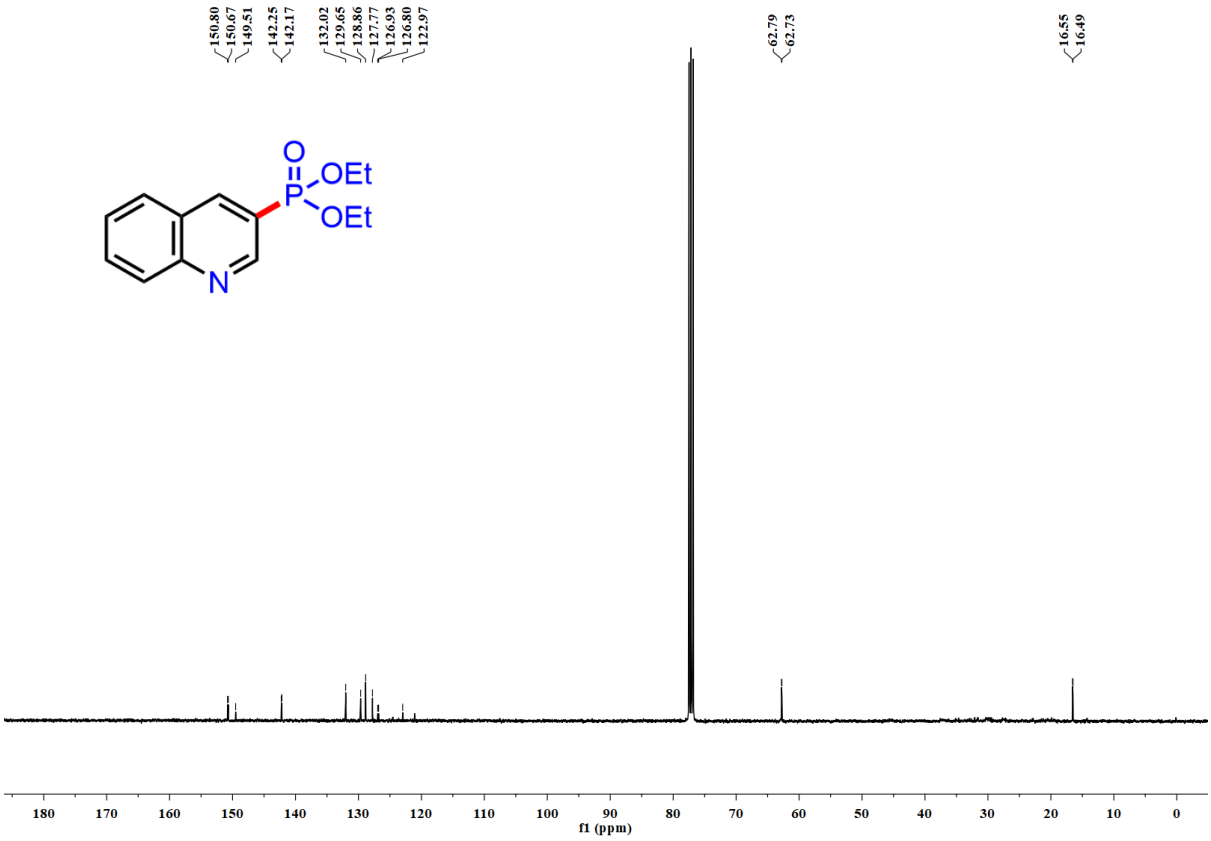


Figure S43. ^{13}C-NMR spectrum of **5dc** in $CDCl_3$ solvent.

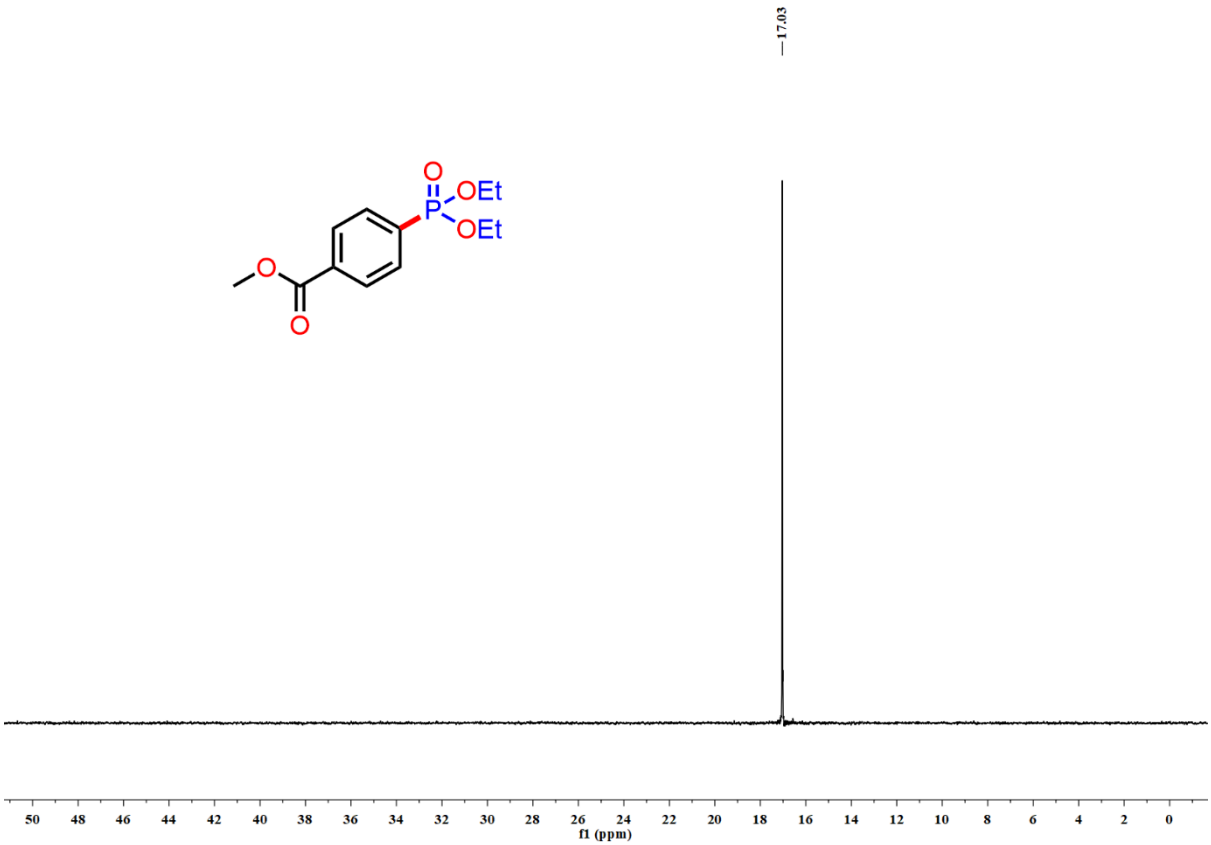


Figure S44. ^{31}P-NMR spectrum of **5ac** in $CDCl_3$ solvent.

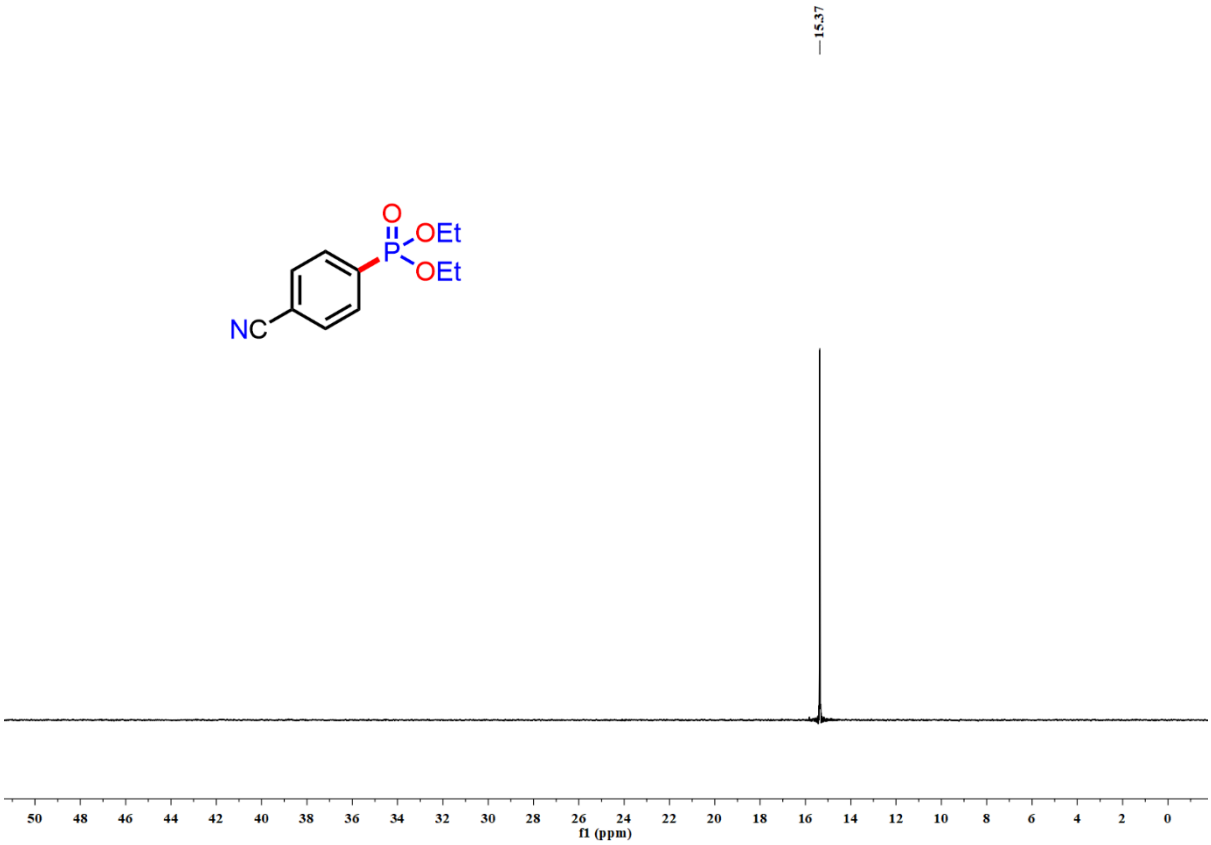


Figure S45. ^{31}P-NMR spectrum of **5bc** in $CDCl_3$ solvent.

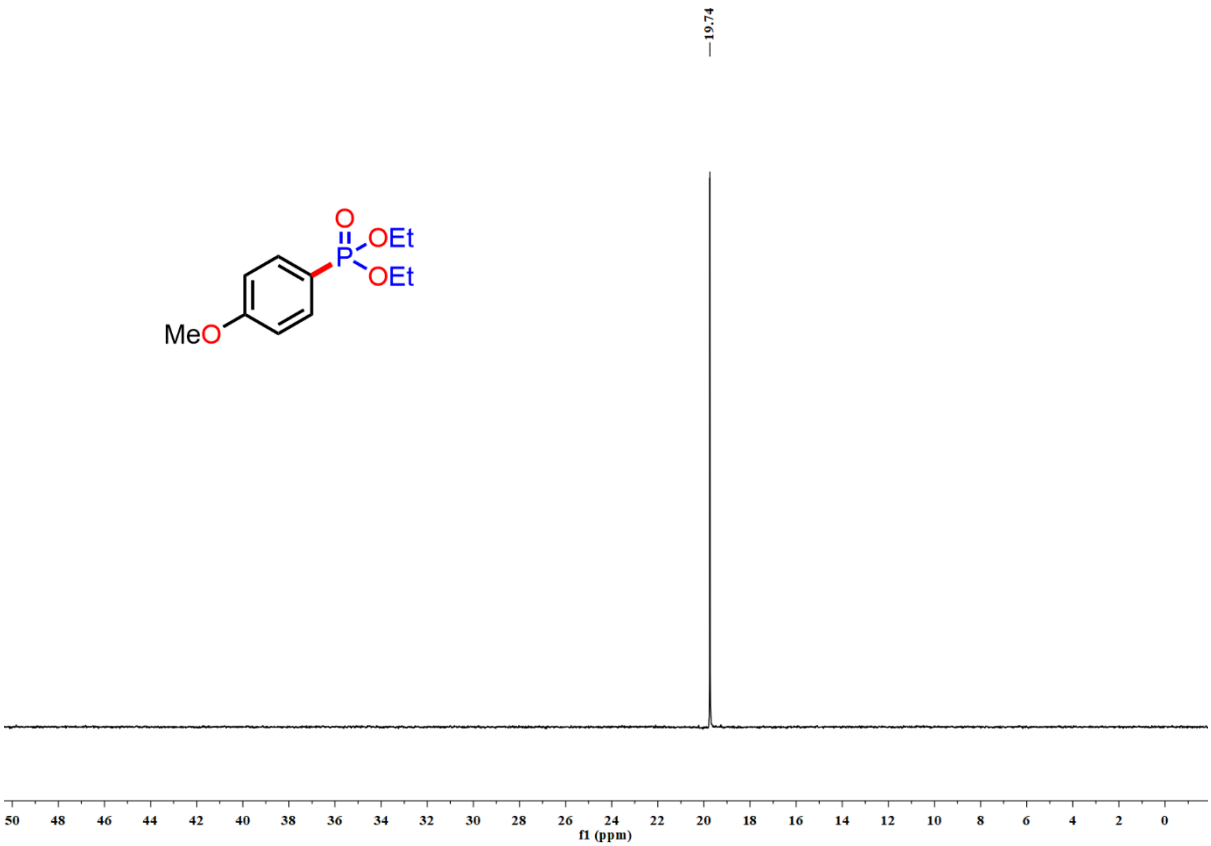


Figure S46. ^{31}P-NMR spectrum of **5cc** in $CDCl_3$ solvent.

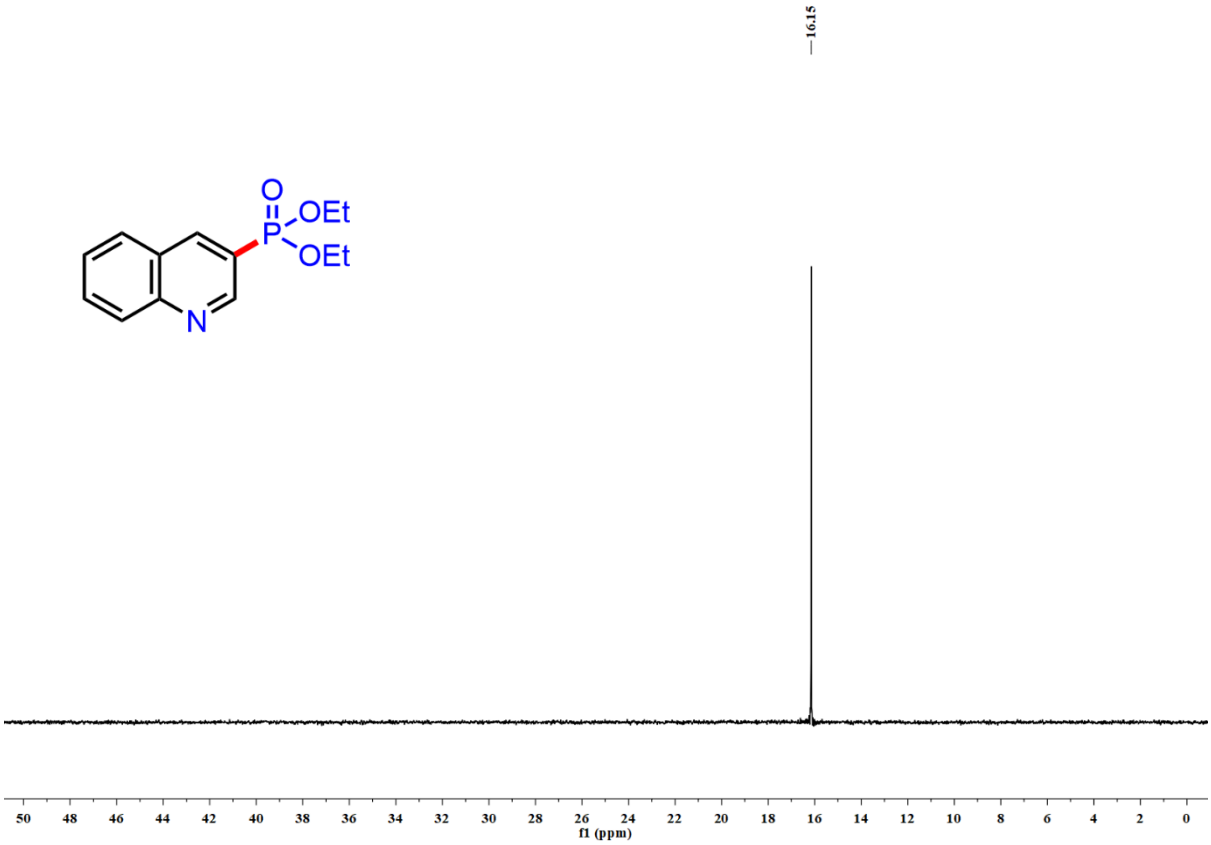


Figure S47. ^{31}P-NMR spectrum of **5dc** in $CDCl_3$ solvent.

References:

1. S. S. Bag, S. Ghorai, S. Jana and C. Mukherjee, *RSC Adv*., 2013, **3**, 5374–5377.
2. B. H. Jhun, J. Jang, S. Lee, E. J. Cho and Y. You, *Nat. Commun*., 2024, **15**, 6586.
3. H. Li, X. Tang, J. H. Pang, X. Wu, E. K. L. Yeow, J. Wu and S. Chiba, *J. Am. Chem. Soc*., 2021, **143**, 481–487.
4. D. S. Lee, C. S. Kim, N. Iqbal, G. S. Park, K.-S. Son and E. J. Cho, *Org. Lett*., 2019, **21**, 9950–9953.
5. S. K. Bose and T. B. Marder, *Org. Lett*., 2014, **16**, 4562–4565.
6. D. Bhattacharya and A. Studer, *Angew. Chem. Int. Ed*., 2025, **64**, e202423512.
7. V. J. Roy and S. R. Roy, *Org. Lett*., 2023, **25**, 923–927.
8. Y. Toda, R. Yamaguchi, S. Fuwa, M. Iwasaki and H. Suga, *Chem. Commun*., 2025, **61**, 16254–16257.
9. P. K. Verma, S. Mandal and K. Geetharani, *ACS Catal*., 2018, **8**, 4049–4054.