Supporting Information for:

Investigation of structural changes of Cu(I) and Ag(I) complexes utilizing a flexible, yet sterically demanding multidentate phosphine oxide ligand

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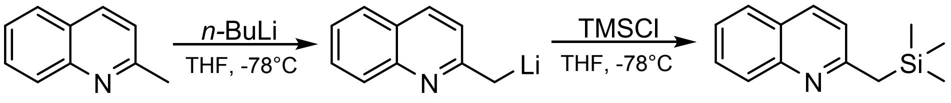
Experimental Details

General Methods. All compounds were handled using Schlenk techniques under dry Ar. Unless otherwise specified, all reagents and solvents were purchased from commercial sources and used as received. The solvents tetrahydrofuran, dichloromethane, acetonitrile and diethyl ether were dried, freshly distilled and degassed prior to use. As drying agents, calcium hydride was used for dichloromethane, SICAPENT® for acetonitrile, and sodium for diethyl ether. The deuterated solvents used ($CDCl_3$, CD_2Cl_2 and MeCN-d_3) were distilled and stored under Ar atmosphere over mol sieves. NMR spectra were recorded on a Bruker Avance III spectrometer operating at 400.1 MHz (^{1}H), 376.4 MHz (^{19}F), 161.9 MHz (^{31}P), 128.4 MHz (^{11}B), 100.6 MHz (^{13}C), 95.8 MHz (^{121}Sb), 79.5 MHz (^{29}Si) and 40.5 MHz (^{15}N). As well as on a JEOL Eclipse 270+ instrument operating at 109.4 MHz (^{31}P). Chemical shifts are in reference to TMS (^{1}H, ^{13}C, ^{29}Si), 85 % H_3PO_4 (^{31}P), $MeNO_2$ (^{15}N), $KSbCl_6$ (^{121}Sb), CCl_3F (^{19}F) and BF_3 in Et_2O (^{11}B) as external standards. All spectra were measured, if not mentioned otherwise, at 25 °C. The assignment of the signals is based on 2D (^{1}H^{1}H–COSY, ^{1}H^{13}C–HMQC, ^{1}H^{13}C–HMBC and ^{1}H^{1}H–NOESY) NMR experiments. Coupling constant (J) values are given in Hertz (Hz). The multiplicity of each resonance observed in the NMR spectra is reported as s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet.
Solid state NMR measurements were recorded on a Bruker Avance-III 500 spectrometer with an 11.7 T magnet, operating at a ^{1}H frequency of 500.25 MHz. The samples were transferred into a 2.5 mm rotor, mounted in a commercial double-resonance MAS probe (Bruker). For all measurements, the ^{1}H resonance of 1 % TMS in $CDCl_3$ was used as an external secondary reference.
The samples for infrared spectroscopy were placed under ambient conditions without further preparation onto a Smith DuraSampLIR II ATR device using a Perkin Elmer BX II FT-IR System spectrometer. Melting points were determined using a Buechi B-540 apparatus using a heating rate of 1°C min. Other melting points were detected using an OZM DTA 552-Ex instrument. The scanning temperature range was set from 293 to 673 K with a scanning rate of 5 K min^{-1}. ESI measurements were done using a Thermo Finnigan LTQ FT Ultra Fourier Transform Ion Cyclotron Resonance Mass Spectrometer. MALDI measurements were done on a Bruker Daltonics Autoflex II Mass Spectrometer using a nitrogen-cartridge-laser with 337 nm and sinapin acid as matrix.
Cyclic voltammetry measurements were performed at room on a µ-Autolab III potentiostat (Metrohm) operated with Nova 1.10 software in a three-electrode setup consisting of a Pt-coil as working electrode, a glassy carbon counter electrode and an Ag/$AgNO_3$ (0.01 M) reference electrode. Cyclic voltammograms were recorded at a scan rate of 50 mV s^{-1} in potential ranges of -1.2 to 0.5 mV and 0 to2 V. A solution of 0.1 M tetrabutylammonium hexfluorophosphate (Sigma-Aldrich) in dry acetonitrile (Sigma-Aldrich) was used as electrolyte. The sample was dissolved in the electrolyte having a concentration of 1 mM.
Elemental analysis was done using an Elementar vario micro cube instrument and an Elementar vario EL instrument. Single crystals of compounds **2**–**6b** suitable for X-ray diffraction measurements could be obtained by diffusion of diethyl ether into the reaction mixture. The crystals were introduced into perfluorinated oil and a suitable single crystal was carefully mounted on top of a thin glass wire. The data collection for compounds **2** and **4** was performed with a Bruker D8 Venture TXS system equipped with a multilayer mirror optics monochromator and a Mo Kα rotating-anode. Data collection for complexes **3**, **5**–**6b** was performed with a Rigaku Oxford Xcalibur 3 diffractometer equipped with a Spellman generator (50 kV, 40 mA) and a Kappa CCD detector, operating with Mo-Kα radiation.
For compounds **2** and **4**, the Bruker SAINT software package utilizing a narrow-frame algorithm was used. Absorption correction using the multi-scan method was applied. Data collection and data reduction for complexes **3**, **5**–**6b** were performed with the CrysAlisPro software. The structures were solved with SIR2014,[1] refined with SHELXL-2018/1[2,3] and finally checked using PLATON[4] integrated in WinGX.[5] Non-hydrogen atoms were refined anisotropically. The finalized CIF files were checked with checkCIF. Crystallographic data and structure refinements are listed in Table S1. Molecular plots were performed with DIAMOND 3.2k.[6] CCDC data can be found provided free of charge by The Cambridge Crystallographic Data Center:

ccdc.cam.ac.uk/structures. Pictures of the crystals were taken using a Leica Stereozoom S9i microscope. Hirshfeld surface analysis were conducted as well as the 2D fingerprint plots of the compounds using CrystalExplorer17 software.[12] The complexes were positioned to highlight specific and significant structural features. Strong intermolecular contacts are visible as red spots in the d_{norm} maps and sharp spikes in the fingerprint plots, respectively.

Synthesis of 2-((trimethylsilyl)methyl)quinoline (**A**)

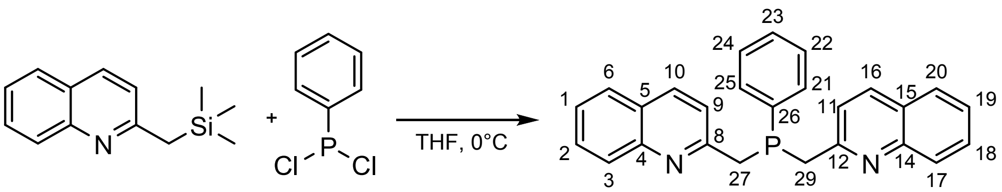


A

2-Methylquinoline (33.9 mL) was dissolved in 150 mL dry, degassed THF and cooled to −78 °C. *n*-BuLi (2.4 M in *n*-hexane, 104.6 mL), was added dropwise to the solution while stirring. The reaction mixture turns dark red. After stirring for one hour, chloro(trimethyl)silane (32.2 mL, 376.4 mmol) was added quickly though dropwise at −78 °C to the mixture and the color changes to a light yellow.[13] After stirring for another 14 hours while letting the mixture warm up to RT, the solvent is evaporated and the left-over liquid is distilled (bp. 65 °C at $2.6 \cdot 10^{-2}$ mbar). A colorless to yellow liquid of **A** is received in 60 % yield (32.4 g, 150.4 mmol).

^{29}Si [$CDCl_3$, 79.495 MHz] ⍰ = 2.6 ($^1J_{Si-C}$ = 25.6 Hz) ppm; **^{1}H** [$CDCl_3$, 400.133 MHz] ⍰ = 0.02 (s, 9H, CH_3, $^2J_{H-Si}$ = 58.9 Hz), 2.49 (s, 2H, CH_2), 6.92 (d, 1H, J = 6.92 Hz, J = 1.5 Hz), 7.26 (t, 1H, J = 8.0 Hz, J = 1.0 Hz), 7.51 (dq, 1H, J = 8.4 Hz, J = 1.5 Hz), 7.55 (d, 1H, J = 8.5 Hz, J = 1.2 Hz), 7.76 (d, 1H, J = 8.3 Hz), 8.02 (d, 1H, J = 8.4 Hz) ppm; **^{13}C{^{1}H}** [$CDCl_3$, 100.623 MHz] ⍰ = −2.0 (s, $^1J_{C-Si}$ = 25.3 Hz; CH_3), 30.9 (s, $^1J_{C-Si}$ = 21.4 Hz; CH_2), 121.0 (s), 124.3 (s), 125.3 (s), 126.9 (s), 128.0 (s), 128.5 (s), 134.9 (s, $^2J_{C-Si}$ = 42.8 Hz), 147.7 (s), 161.2 (s, $^3J_{C-Si}$ = 289.4 Hz) ppm; **IR**: $\tilde{\nu}_{max}$ (cm^{-1}) = 3057 (vw), 2954 (w), 2923 (w), 2852 (vw), 1618 (w), 1599 (m), 1560 (vw), 1501 (m), 1464 (w), 1424 (w), 1375 (vw), 1311 (w), 1248 (m), 1224 (w), 1141 (m), 1118 (w), 1092 (w), 1017 (vw), 950 (vw), 903 (w), 843 (s), 783 (m), 767 (m), 745 (s), 697 (m), 651 (w), 617 (w), 470 (m), 430 (vw).

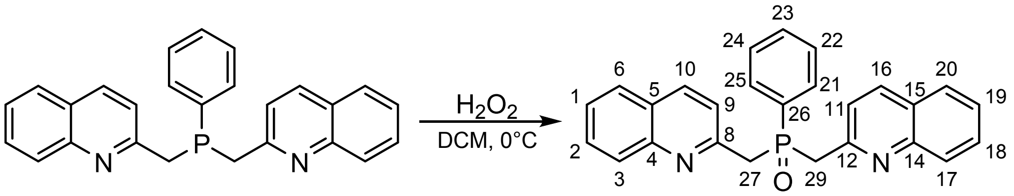
Synthesis of phenylbis(quinolin-2-ylmethyl)phosphine (**1**)



To a solution of 2-((trimethylsilyl)methyl)quinoline (32 mmol) in 50 mL THF at −10 °C, dichlorophenylphosphine (15 mmol) was added slowly, dropwise and further stirred for 18 hours. The color of the solution changes from yellow to orange. The reaction mixture was stripped off of its solvent under vacuum and heated to 80 °C to remove excess 2-((trimethylsilyl)methyl)quinoline. **1** is received as a viscos, brown/orange oil in stochiometric yields. Compound **1** is air and moisture sensitive and must be stored and handled under inert gas atmosphere. It is soluble in common organic solvents like tetrahydrofuran, dichloromethane, acetonitrile and toluene.

^{31}P{^{1}H} [$CDCl_3$, 161.996 MHz] ⍰ = −14.6 (s) ppm; **^{31}P** [$CDCl_3$, 161.996 MHz] ⍰ = −14.6 (quin., $^2J_{P-H}$ = 7.1 Hz) ppm; **^{1}H** [$CDCl_3$, 400.182 MHz] ⍰ = ABX spin system (A = B = H, X = P) 3.58 (m, 4H, $^2J_{A-B}$ = 13.3 Hz, $^2J_{A-X}$ = 1.1 Hz; H27, H29), 7.15 (d, 2H, $^4J_{H-H}$ = 8.2 Hz; H9, H11), 7.28 (m, 3H; H26, H21, H25), 7.40 (m, 2 H, $^3J_{H-H}$ = 8.1 Hz, $^3J_{H-H}$ = 6.9 Hz, $^4J_{H-H}$ = 1.2 Hz; H2, H18), 7.52 (m, 2H; H22, H24), 7.60 (m, 2H, $^3J_{H-H}$ = 6.9 Hz, $^4J_{H-H}$ = 1.5 Hz; H1, H19), 7.65 (d, 2H, $^3J_{H-H}$ = 8.1 Hz; H3, H17), 7.84 (d, 2H, $^3J_{H-H}$ = 8.5 Hz; H10, H16), 7.95 (d_d, 2H, $^3J_{H-H}$ = 8.5 Hz; H6, H20) ppm; **^{13}C{^{1}H}** [$CDCl_3$, 100.636 MHz] ⍰ = 38.6 (d, $^1J_{C-P}$ = 19.3 Hz; C27, C29), 122.2 (d, $^3J_{C-P}$ = 4.9 Hz; C9,C11), 125.7 (d, $^6J_{C-P}$ = 0.7 Hz; C2, C18), 126.50 (d, $^5J_{C-P}$ = 1.4 Hz; C5, C15), 127.4 (d, $^5J_{C-P}$ = 0.7 Hz; C3, C17), 128.3 (d, $^2J_{C-P}$ = 7.0 Hz; C21, C25), 128.8 (s; C6, C20), 129.2 (s; C1, C19), 132.8 (d, $^3J_{C-P}$ = 19.9 Hz; C22, C24), 135.9 (s, C10, C16), 147.9 (d, $^4J_{C-P}$ = 0.5 Hz; C4, C14), 158.6 (d, $^2J_{C-P}$ = 5.9 Hz; C8, C12) ppm.

Synthesis of phenylbis(quinolin-2-ylmethyl)phosphine oxide (**2**)

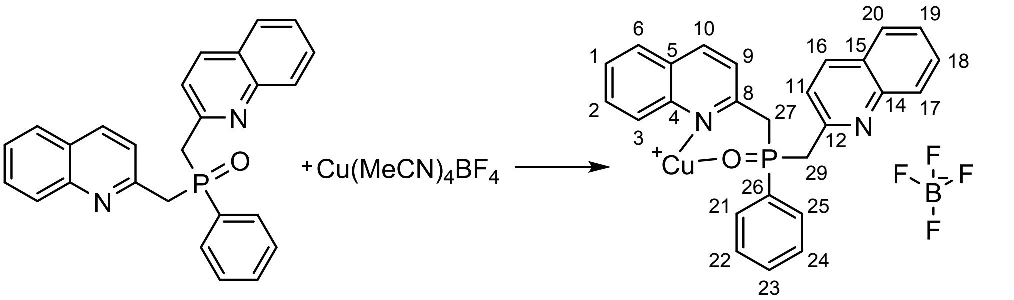


Phenylbis(quinolin-2-ylmethyl)phosphine **1** (5.89 g, 15.0 mmol) is dissolved in 50 mL dichloromethane. Hydrogen peroxide (30 %, 4 mL in 5 mL water) is added dropwise to the mixture while cooling with an ice-bath. After stirring for 4 hours, the solvent was removed and the left-over oil dissolved in ethyl acetate. After extracting the ethyl acetate mixture three times with water, the combined water phases were extracted again three times with ethyl acetate. The combined organic phases were reduced under pressure. The left over solid was dissolved in dry THF and stirred with 4 Å mol sieves in a tea bag to remove any leftover hydrogen peroxide and water. After removal of all volatiles, **2** is received as a white to beige powder. Crystals were received by recrystallization from dichloromethane. Yield: 81.6 %, 5.00 g, 12.2 mmol. The melting point of **2** is 168 °C, decomposition starts at 305 °C, determined from the DTA plot. Compound **2** is soluble in common organic solvents like tetrahydrofuran, dichloromethane and warm acetonitrile.

Elemental Anal. calcd. $C_{26}H_{21}N_2OP$, C: 76.46, H: 5.18, N: 6.86 %; found: C: 76.16, H: 4.80, N: 6.77 %; **ESI HRMS** (positive mode, CH_3CN/H_2O) m/z calcd for $C_{26}H_{21}N_2OP$ $[M+H]^+$: 409.1470 found 409.1461; ^{31}**P{^{1}H}** [$CDCl_3$, 161.976 MHz] δ = 35.0 (s, $^{1}J_{P-C}$ = 28.6 Hz) ppm; ^{31}**P** [$CDCl_3$, 161.976 MHz] δ = 35.0 (hept., $^{2}J_{P-H}$ = 14.0 Hz) ppm; ^{31}**P{^{1}H}** [CD_2Cl_2, 161.976 MHz] δ = 34.0 ($^{1}J_{P-C}$ = 28.4 Hz) ppm; ^{31}**P** [CD_2Cl_2, 161.976 MHz] δ = 34.0 (hept., $^{2}J_{P-H}$ = 14.0 Hz) ppm; ^{31}**P{^{1}H}** [CD_3CN, 161.976 MHz] δ = 33.7 ($^{1}J_{P-C}$ = 28.8 Hz) ppm; ^{31}**P** [CD_3CN, 161.976 MHz] δ = 33.7 (hept., $^{2}J_{P-H}$ = 13.8 Hz) ppm; ^{15}**N** [from $^1H^{15}N$ HMBC, $CDCl_3$, 40.5387 MHz] δ = −91.9 (s) ppm; ^{1}**H** [$CDCl_3$, 400.133 MHz] δ = ABX spin system (A = B = H, X = P) 3.92 (d, 4H, $^{2}J_{A-X}$ = 14.7 Hz; H27, H29), 7.34 (m, 2H, $^{3}J_{H-H}$ = 7.6, $^{4}J_{H-H}$ =1.3 Hz; H21, H25), 7.42 (td, 2H, $^{3}J_{H-H}$ = 8.4 Hz, $^{3}J_{H-H}$ = 7.3 Hz, $^{4}J_{H-H}$ = 1.6 Hz; H1, H19), 7.44 (m, 1H; H23), 7.47 (dd, 2H, $^{3}J_{H-H}$ = 8.4 Hz, $^{4}J_{H-P}$ = 1.3 Hz; H9, H11), 7.63 (ddd, 2 H, $^{3}J_{H-H}$ = 8.4 Hz, $^{3}J_{H-H}$ =6.9 Hz, $^{4}J_{H-H}$ = 1.5 Hz; H2, H18), 7.69 (dd, $^{3}J_{H-H}$ = 8.2 Hz, $^{4}J_{H-H}$ = 1.4 Hz; 2H, H22, H24), 7.70 (dd, 2H, $^{3}J_{H-H}$ = 8.3 Hz, $^{4}J_{H-H}$ = 1.4 Hz; H6, H20), 7.90 (d, 2H, $^{3}J_{H-H}$ = 8.5 Hz; H3, H17), 7.98 (d, 2H, $^{3}J_{H-H}$ = 8.5 Hz; H10, H16) ppm; ^{1}**H** [CD_2Cl_2, 400.133 MHz] δ = ABX spin system (A = B = H, X = P) 3.93 (d, 4H, $^{2}J_{A-B}$ = 14.2 Hz, $^{2}J_{A-X}$ = 15.1 Hz; H27, H29), 7.41 – 7.35 (m, 2H; H21, H25), 7.40 (dd, 2H, $^{3}J_{H-H}$ = 8.5 Hz, $^{4}J_{H-H}$ = 1.3 Hz; H1, H19), 7.54 – 7.43 (m, 3H; H9, H11, H23), 7.72 – 7.62 (m, 4H; H22, H24, H2, H18), 7.77 (dd, 2H, $^{3}J_{H-H}$ = 8.2 Hz, $^{4}J_{H-H}$ = 1.4 Hz; H6, H20), 7.91 (dq, 2H, $^{3}J_{H-H}$ = 8.5 Hz, $^{4}J_{H-H}$ = 0.5 Hz; H3, H17), 8.02 (d, 2H, $^{3}J_{H-H}$ = 8.5 Hz, H10, H16) ppm; ^{1}**H** [CD_3CN, 400.133 MHz] δ = ABX spin system (A = B = H, X = P) 3.97 (d, 4H, $^{2}J_{A-B}$ = 15.6 Hz, $^{2}J_{A-X}$ = 14.2 Hz, H27, H29), 7.36 (dd, 2H, $^{3}J_{H-H}$ = 8.4, $^{4}J_{H-H}$ =1.3 Hz; H22, H24), 7.47 (dq, 2H, $^{3}J_{H-H}$ = 6.7 Hz, $^{4}J_{H-H}$ = 1.7 Hz; H1, H19), 7.44 (m, 1H; H23), 7.52 (ddt, 2H, $^{3}J_{H-H}$ = 8.1 Hz, $^{4}J_{PH}$ = 1.0 Hz; H9, H11), 7.71–7.63 (m, 4H; H22, H24, H2, H18), 7.83 (dd, 2H, $^{3}J_{H-H}$ = 8.3 Hz, $^{4}J_{H-H}$ = 1.4 Hz; H6, H20), 7.86 (ddd, 2H, $^{3}J_{H-H}$ = 8.3 Hz, $^{4}J_{H-H}$ = 1.4 Hz; H3, H17), 8.09 (d, 2H, $^{3}J_{H-H}$ = 8.5 Hz, H10, H16) ppm; ^{13}**C{^{1}H}** [$CDCl_3$, 100.623 MHz] δ = 41.9 (d, $^{1}J_{C-P}$ = 61.0 Hz; C27, C29), 122.9 (d, $^{3}J_{C-P}$ = 2.9 Hz; C9, C11), 126.3 (d, $^{5}J_{C-P}$ = 1.2 Hz; C1, C19), 127.0 (d, $^{5}J_{C-P}$ = 1.8 Hz; C5, C15), 127.6 (d, $^{6}J_{C-P}$ = 1.2 Hz; C6, C20), 128.4 (d, $^{3}J_{C-P}$ = 11.9 Hz; C21, C25), 129.0 (d, $^{5}J_{C-P}$ = 0.9 Hz; C3, C17), 129.6 (d, $^{6}J_{C-P}$ = 0.9 Hz; C2, C18), 131.2 (d, $^{2}J_{C-P}$ = 9.2 Hz; C22, C24), 131.5 (d, $^{1}J_{C-P}$ = 96.9 Hz; C26), 132.0 (d, $^{4}J_{C-P}$ = 2.9 Hz; C23), 136.5 (d, $^{4}J_{C-P}$ = 1.7 Hz; C10, C16), 148.1 (d, $^{4}J_{C-P}$ = 1.9 Hz; C4, C14), 153.6 (d, $^{2}J_{C-P}$ = 7.2 Hz; C8, C12) ppm; ^{13}**C{^{1}H}** [CD_2Cl_2, 100.623 MHz] δ = 42.1 (d, $^{1}J_{C-P}$ = 60.9 Hz; C27, C29), 123.2 (d, $^{3}J_{C-P}$ = 2.9 Hz; C9, C11), 126.5 (d, $^{5}J_{C-P}$ = 1.3 Hz; C1, C19), 127.2 (d, $^{5}J_{C-P}$ = 1.9 Hz; C5, C15), 128.0 (d, $^{6}J_{C-P}$ = 1.4 Hz; C6, C20), 128.7 (d, $^{3}J_{C-P}$ = 11.9 Hz; C21, C25), 129.2 (d, $^{5}J_{C-P}$ = 0.8 Hz; C3, C17), 129.8 (d, $^{6}J_{C-P}$ = 0.8 Hz; C2, C18), 131.4 (d, $^{2}J_{C-P}$ = 8.9 Hz; C22, C24), 132.1 (d, $^{4}J_{C-P}$ = 2.7 Hz; C23), 132.4 (d, $^{1}J_{C-P}$ = 96.3 Hz; C26), 136.5 (d, $^{4}J_{C-P}$ = 1.6 Hz; C10, C16), 148.4 (d, $^{4}J_{C-P}$ = 1.9 Hz; C4, C14), 154.2 (d, $^{2}J_{C-P}$ = 7.6 Hz; C8, C12) ppm; ^{13}**C{^{1}H}** [CD_3CN, 100.623 MHz] δ = 42.3 (d, $^{1}J_{C-P}$ = 61.2 Hz; C27, C29), 123.9 (d, $^{3}J_{C-P}$ = 3.1 Hz; C9, C11), 127.2 (d, $^{5}J_{C-P}$ = 1.3 Hz; C1, C19), 127.7 (d, $^{5}J_{C-P}$ = 1.9 Hz; C5, C15), 128.7 (d, $^{6}J_{C-P}$ = 1.2 Hz; C6, C20), 129.2 (d, $^{3}J_{C-P}$ = 11.6

Hz; C21, C25), 129.5 (d, $^{5}J_{C-P}$ = 1.1 Hz; C3, C17), 130.5 (d, $^{6}J_{C-P}$ = 1.1 Hz; C2, C18), 132.0 (d, $^{2}J_{C-P}$ = 8.9 Hz; C22, C24), 132.7 (d, $^{4}J_{C-P}$ = 2.8 Hz; C23), 133.4 (d, $^{1}J_{C-P}$ = 95.9 Hz; C26), 137.0 (d, $^{4}J_{C-P}$ = 1.6 Hz; C10, C16), 148.8 (d, $^{4}J_{C-P}$ = 2.3 Hz; C4, C14), 155.3 (d, $^{2}J_{C-P}$ = 7.9 Hz; C8, C12) ppm; **IR**: $\tilde{\nu}_{max}$ (cm^{-1}) = 3062 (vw), 2864 (w), 1617 (w), 1598 (m), 1558 (w), 1501 (m), 1425 (w), 1398 (w), 1311 (w); 1233 (w), 1205 (m), 1190 (s), 1017 (w), 1111 (m), 955 (w), 856 (s), 844 (s), 760 (s), 744 (vs), 725 (m), 693 (s), 659 (m), 639 (w), 616 (m), 555 (m), 542 (m), 497 (m), 477 (s), 467 (s), 444 (s).

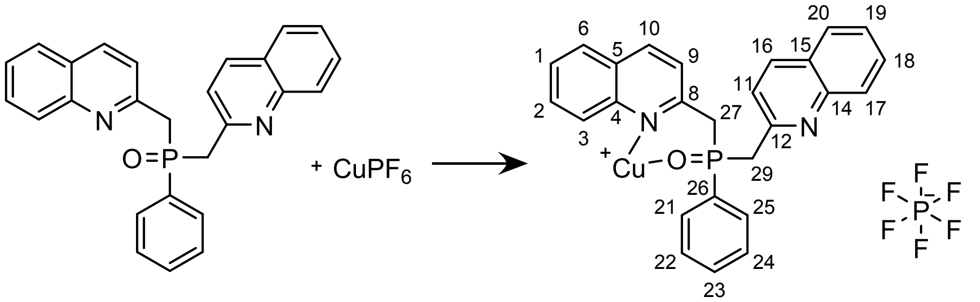
Synthesis of phenylbis(quinolin-2-ylmethyl)phosphine oxide copper(I) tetrafluoroborate (**3**)



A solution of phenylbis(quinolin-2-ylmethyl)phosphine oxide **2** (0.428 g, 1.05 mmol) in 20 mL dry, degassed acetonitrile was added to $Cu(MeCN)_4BF_4$ (0.33 g, 1.05 mmol) and stirred for a few hours. Afterwards, the solvent was removed and the remaining solid dissolved in dry, degassed dichloromethane. After removal of all volatiles, **3** is received as a yellow powder (0.490 g, 0.877 mmol, 84 %). Yellow crystals were received by difussion of diethylether into a solution of **3** in dichloromethane. MP: 195 °C. Compound **3** is soluble in DCM or MeCN. **3** is air and moisture sensitive and should be stored under protective gas.

Elemental Anal. calcd. $C_{26}H_{21}BCuF_4N_2OP$, C: 55.85, H: 3.79, N: 5.01 % found C: 53.81, H: 3.55, N: 5.12 %, C differs due to formation of phosphorus carbide; **ESI HRMS** (positive mode, CH_3CN/H_2O) m/z calcd for $C_{26}H_{21}BCuF_4N_2OP$ [M−BF_4^-]$^+$: 471.0682 found 471.0683; ^{31}**P{**^{1}**H}** [CD_3CN, 161.996 MHz] ⍰ = 36.0 (s) ppm; ^{31}**P** [CD_3CN, 161.996 MHz] ⍰ = 36.0 (s) ppm; ^{31}**P{**^{1}**H}** [CD_2Cl_2, 161.976 MHz] ⍰ = 44.0 (s) ppm; ^{31}**P** [CD_2Cl_2, 161.976 MHz] ⍰ = 44.0 (s) ppm; ^{19}**F{**^{1}**H}** [CD_3CN, 376.508 MHz] ⍰ = −152.58 (s) ppm; ^{19}**F{**^{1}**H}** [CD_2Cl_2, 376.442 MHz] ⍰ = −150.43 (s) ppm; ^{11}**B{**^{1}**H}** [CD_3CN, 128.394 MHz] ⍰ = −2.01 (s) ppm; ^{11}**B{**^{1}**H}** [CD_2Cl_2, 128.378 MHz] ⍰ = −0.75 (s) ppm; ^{1}**H** [CD_3CN, 400.182 MHz] ⍰ = 3.99 (d, 4H, ^{2}J = 40.2 Hz; H27, H29), 7.36 (m, 3H, H23, H9, H11), 7.44 (m, 4H, H22, H24, H1, H19), 7.60 (m, 4H, H21, H25, H2, H18), 7.74 (s, 2H, H3, H17), 8.00 (m, 4H, H10, H16, H6, H20,) ppm; ^{1}**H** [CD_2Cl_2, 400.133 MHz] ⍰ = 4.25 (t, 2H, $^{2}J_{H-H}$ = 16.2 Hz, CH_2), 4.55 (t, 2H, J_{H-H} = 13.3 Hz, CH_2), 7.26 (t, 2H, J = 7.7 Hz), 7.38 (t, 2H, J = 7.5 Hz), 7.49 (m, 1H), 7.60 (t, 1H, J = 7.5 Hz), 7.71 (d, 2H, J = 8.1 Hz), 7.83 (t, 2H, J = 7.8 Hz), 7.97 (d, 2H, J = 8.5 Hz), 8.08 (d, 2H, J = 8.7 Hz), 8.22 (d, 2H, J = 8.5 Hz) ppm; ^{13}**C{**^{1}**H}** [CD_3CN, 100.636 MHz] ⍰ = 127.6 (d; C1, C19), 129.0 (s; C3, C17), 129.6 (s; C23), 130.9 (s; C2, C18), 131.8 (s; C21, C25), 133.3 (s; C22, C24), 137.8 (s; C10, C16), 148.3 (s; C4, C14), 155.0 (s; C8, C12) ppm; **IR**: $\tilde{\nu}_{max}$ (cm^{-1}) = 3059 (vw), 2964 (vw), 2912 (vw), 2286 (vw), 1619 (vw), 1598 (m), 1564 (vw), 1506 (m), 1432 (w), 1400 (vw), 1311 (vw), 1262 (w), 1238 (w), 1162 (w), , 1049 (vs), 1025 (vs), 910 (w), 844 (m), 799 (m), 747 (s), 716 (s), 693 (m), 659 (m), 642 (m), 618 (w), 556 (m), 540 (w), 520 (m), 501 (m), 488 (m), 427 (m).

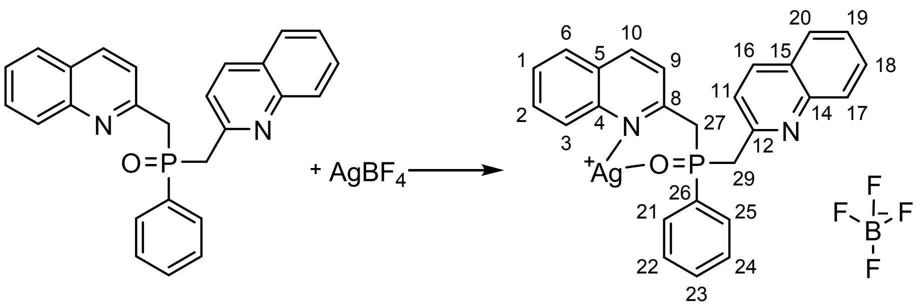
Synthesis of phenylbis(quinolin-2-ylmethyl)phosphine oxide copper(I) hexafluoro-phosphate (**4**)



A solution of phenylbis(quinolin-2-ylmethyl)phosphine oxide **2** (0.166 g, 0.406 mmol) in 20 mL dry, degassed acetonitrile was added to $CuPF_6$ (0.085 mg, 0.406 mmol) and stirred for a few hours. Afterwards, the solvent was removed and the remaining solid dissolved in dry, degassed dichloromethane. After removal of all volatiles, **4** is received as an orange powder (0.215 g, 0.350 mmol, 86 %). Orange crystals were received by difussion of diethylether into a solution of **4** in dichloromethane. The so formed crystals do hardly dissolve in dichloromethane again. Compound **4** is air and moisture sensitive and should be stored under protective gas.

Elemental Anal. calcd. $C_{26}H_{21}CuN_2F_6OP_2$, C: 50.62, H: 3.25, N: 4.54 % found C: 50.56, H: 3.25, N: 4.41 %; **MALDI MS** (positive mode, sinapinic acid) m/z calcd for $C_{26}H_{21}CuN_2F_6OP_2$ $[M{-}PF_6^-]^+$: 471.07 found 471.58; **^{31}P{^{1}H}** [CD_3CN, 161.996 MHz] ⍰ = 36.2 (s), −141.8 (sept, $^1J_{P-F}$ = 710.0 Hz) ppm; **^{19}F{^{1}H}** [CD_3CN, 376.489 MHz] ⍰ = −72.9 (d, $^1J_{F-P}$ = 706.4 Hz) ppm; **^{1}H** [CD_3CN, 400.182 MHz] ⍰ = 3.94 (d, 4H, $^2J_{P-H}$ = 40.0 Hz, CH_2), 7.35 (m, J = 6.6 Hz), 7.45 (m, J = 7.3 Hz), 7.61 (m), 7.78 (m), 7.89 (m), 8.04 (m) ppm; **^{13}C{^{1}H}** [CD_3CN, 100.636 MHz] ⍰ = 127.6 (s), 129.0 (s), 129.4 (d, J = 8.5 Hz), 130.8 (s), 131.9 (s), 133.1 (s), 137.7 (s), 148.3 (s), 155.0 (s) ppm; Due to the broadness of the signals, an assignment was not possible. **IR**: $\tilde{\nu}_{max}$ (cm^{-1}) = 3071 (vw), 2963.56 (vw), 2911 (vw), 1620 (vw), 1599 (w), 1566 (vw), 1509 (m), 1435 (w), 1402 (w), 1379 (vw), 1353 (vw), 1309 (w), 1269 (vw), 1243 (w), 1216 (vw), 1160 (m), 1123 (m), 1099 (m), 1072 (vw), 1026 (vw), 999(vw), 956 (vw), 877 (m), 829 (vs), 780 (s), 748 (vs), 715 (s), 693 (s), 659 (m), 641 (w), 556 (vs), 494 (s), 472 (m), 457 (m), 436 (m).

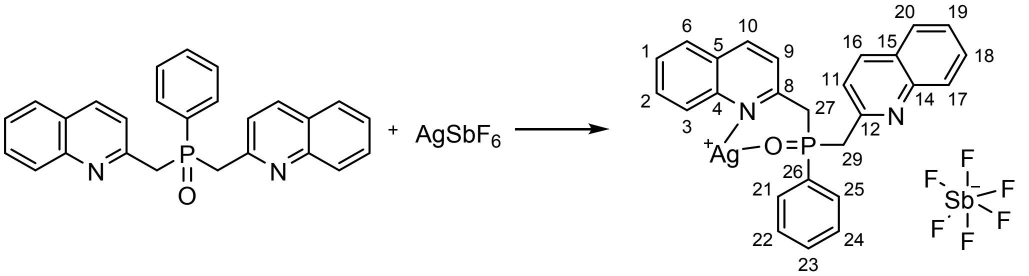
Synthesis of phenylbis(quinolin-2-ylmethyl)phosphine oxide silver(I) tetrafluoroborate (**5**)



A solution of phenylbis(quinolin-2-ylmethyl)phosphine oxide **2** (0.839 g, 2.05 mmol) in 20 mL dry, degassed acetonitrile was added to $AgBF_4$ (0.4 g, 2.05 mmol). A clear orange solution formed, and a colorless percipitate formed after a while of stirring. The solvent was concentrated in vacuo and left to crystallize (1.128 g, 1.870 mmol, 91 %). Colorless to beige crystals were received by diffusion of diethyl ether into a solution of **5** in acetonitrile. MP: 113 °C. Compound **5** is moisture sensitive and should be stored with the exclusion of light.

Elemental Anal. calcd. $C_{26}H_{21}BAgN_2F_4OP$ + CH_3CN, C: 52.21, H: 3.76, N: 6.52 % found C: 52.32, H: 3.99, N: 6.47 %; **MALDI MS** (positive mode, sinapinic acid) m/z calcd for $C_{26}H_{21}BAgN_2F_4OP$ $[M{-}BF_4^-]^+$: 515.0437 found 515.45; ^{31}P{^{1}H} [CD_3CN, 161.976 MHz] ⍰ = 37.9 (s) ppm; **^{31}P{/}** [CD_3CN, 161.976 MHz] ⍰ = 37.9 (quint., $^2J_{P-H}$ = 13.4 Hz) ppm; **^{31}P{^{1}H}** [CD_2Cl_2, 161.976 MHz] ⍰ = 43.6 (s) ppm; **^{19}F{^{1}H}** [CD_3CN, 376.461 MHz] ⍰ = −152.5 (s) ppm; **^{19}F{^{1}H}** [CD_2Cl_2, 376.461 MHz] δ = −153.8 (s) ppm; **^{11}B {^{1}H}** [CD_3CN, 128.378 MHz] δ = −2.0 (s) ppm; **^{1}B {^{1}H}** [CD_2Cl_2, 128.378 MHz] δ = −4.0 (quint., $^{1}J_{B-F}$ = 1.3 Hz) ppm; **^{15}N** [CD_3CN *via* ^{1}H^{15}N HMBC, 40.5371 MHz] δ = −121.4 (s) ppm; **^{15}N** [CD_2Cl_2 *via* ^{1}H^{15}N HMBC, 40.5371 MHz] δ = −133.5 (s), −137.0 (s) ppm; **^{1}H** [CD_3CN, 400.132 MHz] δ = ABX 4.23 (m, 4H, $^{2}J_{H-H}$ = 14.6, $^{2}J_{H-P}$ = 5.2 Hz; H27, H29), 7.33 (d$_d$, 2H, $^{3}J_{H-H}$ = 8.5 Hz, $^{4}J_{H-H}$ = 1.0 Hz; H9, H11), 7.49 (m, 6H, $^{3}J_{H-H}$ = 6.7 Hz, $^{4}J_{H-H}$ = 1.7 Hz; H1,H6, H19, H20, H22, H24), 7.60 (td, 1H, $^{3}J_{H-H}$ = 6.8 Hz, $^{4}J_{H-H}$ = 1.4 Hz; H23), 7.74 (dd, 2H, $^{3}J_{H-H}$ = 7.2, $^{4}J_{H-H}$ = 1.4 Hz; H21, H25), 7.81 (m, 2H, $^{3}J_{H-H}$ = 5.0 Hz, $^{4}J_{H-H}$ = 1.7 Hz; H2, H18), 7.95 (m, 2H, $^{3}J_{H-H}$ = 8.2 Hz; H3, H17), 8.14 (d, 2H, $^{3}J_{H-H}$ = 8.5 Hz; H10, H16) ppm; **^{1}H** [CD_2Cl_2, 400.132 MHz] δ = 4.50 (s, 2H, CH_2; H27, H29), 4.70 (t, 2H, $^{3}J_{H-H}$ = 14.1 Hz; H27, H29), 7.32 (d$_d$, 2H, $^{3}J_{H-H}$ = 8.4 Hz, H9, H11), 7.42 (t, 2H, $^{3}J_{H-H}$ = 7.5 Hz; H10, H16), 7.69 (m, 9H, $^{3}J_{H-H}$ = 8.5 Hz, H1, H3, H6, H17, H19, H20, H22, H23, H24), 8.10 (d, 2H, $^{3}J_{H-H}$ = 8.4; H21, H25), 8.15 (m, 2H; H2, H18) ppm; **^{1}H** [CD_2Cl_2, 400.132 MHz, −80°C] δ = set 1: 8.13 (2H, H10, H16), 7.76 (2H, H6, H20), 7.57 (2H, H3, H17), 7.41 (2H, H1, H19), 7.28 (2H, H2, H18), 7.22 (2H, H9, H11), 4.78 (2H, H27, H29) ppm; set 2: 7.91(2H, H10, H16), 7.65 (2H, H9, H11), 7.55 (2H, H3, H17), 7.50 (2H, H6, H20), 7.33 (2H, H1, H19), 7.15 (2H, H2, H18), 4.53 (1H, $^{2}J_{H-H}$ = 13.6 Hz, H27 o. H29), 4.12 (1H, $^{2}J_{H-H}$ = 17.9, $^{2}J_{H-P}$ = 24.1 Hz, H27 o. H29) ppm; phenyl ring: 8.40 (2H, H21, H25), 7.74 (2H, H22, H24), 7.26 (1H, H23) ppm; **^{13}C{^{1}H}** [CD_3CN, 100.623 MHz] δ = 43.0 (d, $^{1}J_{C-P}$ = 58.9 Hz; C27, C29), 124.8 (d, $^{3}J_{C-P}$ = 3.9 Hz; C9, C11), 128.2 (d, $^{5}J_{C-P}$ = 1.9 Hz; C5, C15), 128.3 (d, $^{3}J_{C-P}$ = 1.1 Hz; C6, C20), 129.2 (d, $^{6}J_{C-P}$ = 1.3 Hz; C2, C18), 129.6 (s; C3, C17), 129.9 (d, $^{2}J_{C-P}$ = 12.2 Hz; C21, C25), 130.5 (d, $^{1}J_{C-P}$ = 99.0 Hz; C26), 131.8 (d, $^{3}J_{C-P}$ = 9.6 Hz; C22, C24), 131.9 (s; C1, C19), 134.0 (d, $^{4}J_{C-P}$ = 2.9 Hz; C23), 139.8 (d, $^{4}J_{C-P}$ = 1.5 Hz; C10, C16), 147.5 (d, $^{4}J_{C-P}$ = 2.2 Hz; C4, C14), 155.8 (d, $^{2}J_{C-P}$ = 8.9 Hz; C8, C12) ppm; **^{13}C{^{1}H}** [CD_2Cl_2, 100.623 MHz] δ = 43.5 (d, $^{1}J_{C-P}$ = 58.5 Hz; C27, C29), 125.0 (s; C9, C11), 128.0 (s; C5, C15), 127.9 (d, $^{3}J_{C-P}$ = 1.5 Hz; C6, C20), 128.0 (s; C2, C18), 128.7 (s; C3, C17), 129.8 (d, $^{2}J_{C-P}$ = 12.7 Hz; C21, C25), 131.7 (d, $^{3}J_{C-P}$ = 10.3 Hz; C22, C24,), 131.9 (s; C1, C19), 134.0 (d, $^{4}J_{C-P}$ = 2.9 Hz; C23), 140.3 (s; C10, C16), 146.3 (s; C4, C14), 155.5 (d; C8, C12, $^{2}J_{C-P}$ = 8.1 Hz); **^{13}C{^{1}H}** [CD_2Cl_2, 100.623 MHz, −80°C] δ = set 1: 153.8 (d, $^{2}J_{C-P}$ = 10.1 Hz), 145.2 (s), 139.4 (s), 130.8 (s), 129.0 (s), 128.0 (s), 127.0 (s), 123.0 (d, broad $^{3}J_{C-P}$ not resolved), 42.5 (s) ppm; set 2: 154.4 (d, $^{2}J_{C-P}$ = 8.9 Hz), 144.4 (s), 139.0 (s), 131.2 (s), 127.4 (s), 127.0 (s), 127.0 (s), 126.2 (s), 123.9 (d, $^{1}J_{C-P}$ = 19.0 Hz), 41.8 (d, $^{2}J_{C-P}$ = 41.9 Hz), phenyl ring: 133.4 (C26), 133.4 (s), 130.8 (s), 130.6 (d) ppm; **IR**: $\tilde{\nu}_{max}$ (cm^{-1}) = 3118 (vw), 3061 (vw), 2964 (vw), 2899(vw), 2895 (vw), 2853 (vw), 1619 (vw), 1598 (w), 1567 (vw), 1509 (w), 1434 (w), 1403 (w), 1377 (vw), 1352 (vw), 1309 (w), 1237 (m), 1167 (m), 1125 (m), 1045 (s), 1033 (vs), 997 (s), 984 (m), 913 (w), 874 (m), 844 (m), 779 (w), 765 (m), 747 (vs), 714 (s), 693 (m), 658 (m), 636 (w), 558 (m), 520 (m), 497 (m), 483 (m), 472 (m), 454 (w), 434 (m).

Synthesis of phenylbis(quinolin-2-ylmethyl)phosphine oxide silver(I) hexafluoro-antimonate (**6**)



A solution of phenylbis(quinolin-2-ylmethyl)phosphine oxide **2** (0.181 g, 0.443 mmol) in 20 mL dry dichloromethane was added to $AgSbF_6$ (0.152 g, 0.443 mmol). A clear beige solution formed, where a colorless percipitate appears after a while of stirring. The solvent was removed in vacuo and a beige solid was received (0.297 g, 0.394 mmol, 89 %). Crystals were received by a diffusion of diethylether into a solution of compound **6** in dichloromethane or acetonitrile. Compound **6** is moisture sensitive and should be stored with the exclusion of light.

Elemental Anal. was not possible due to Sb in the compound. **MALDI MS** (positive mode, sinapinic acid) m/z calcd for $C_{26}H_{21}SbAgN_2F_6OP$ [M+H−SbF_6^-]$^+$: 516.0515 found 516.08; **^{31}P{^{1}H}** [CD_3CN, 161.976 MHz] δ = 41.4 (s) ppm; **^{31}P** [CD_3CN, 161.976 MHz] δ = 41.4 (s) ppm; **^{19}F{^{1}H}** [CD_3CN, 376.461 MHz] δ = −124.1 (m, $^{1}J_{F-Sb}$ = 1935 Hz) ppm; **^{121}Sb** [CD_3CN, 95.753 MHz] δ = 96.6

(septett, $^{1}J_{Sb-F}$ = 1935 Hz) ppm; **^{15}N** [CD_3CN *via* $^{1}H^{15}N$ HMBC, 40.5371 MHz] ⍰ = −127.2 (s) ppm; **^{1}H** [CD_3CN, 400.132 MHz] ⍰ = ABX 4.25 (m, 4H, $^{3}J_{H-H}$ = 14.2; H27, H29), 7.36 (d, 2H, $^{3}J_{H-H}$ = 8.5 Hz; H9, H11), 7.51–7.39 (m, 4H, $^{3}J_{H-H}$ = 6.7 Hz; H1, H19, H6, H20), 7.54 (dd, 2H, $^{3}J_{H-H}$ = 7.6, $^{4}J_{H-H}$ = 3.1 Hz; H21, H25), 7.64 (t, 2H, $^{3}J_{H-H}$ = 7.0; H23), 7.80 (d, 2H, $^{3}J_{H-H}$ = 8.2 Hz; H2, H18), 7.88–7.83 (m, 2H; H22, H24), 7.91 (d, 2H, $^{3}J_{H-H}$ = 8.1 Hz; H3, H17), 8.17 (d, 2H, $^{3}J_{H-H}$ = 8.5 Hz; H10, H16) ppm; **^{13}C{^{1}H}** [CD_3CN, 100.623 MHz] ⍰ = 43.3 (d, $^{1}J_{C-P}$ = 58.7 Hz; C27, C29), 124.8 (d, $^{3}J_{C-P}$ = 4.3 Hz; C9, C11), 128.3 (d, $^{5}J_{C-P}$ = 1.7 Hz; C5, C15), 128.5 (s; C1, C19), 129.3 (s; C2, C18), 129.54 (s; C3, C17), 130.1 (d, $^{2}J_{C-P}$ = 12.2 Hz; C21, C25), 130.2 (C26, second peak missing), 131.9 (d, $^{3}J_{C-P}$ = 9.8 Hz; C22, C24), 132.3 (s; C6, C20), 134.2 (d, $^{4}J_{C-P}$ = 3.0 Hz; C23), 140.4 (s; C10, C16), 147.2 (d, $^{4}J_{C-P}$ = 2.3 Hz; C4, C14), 155.7 (d, $^{2}J_{C-P}$ = 9.2 Hz; C8, C12) ppm.

Crystallographic data

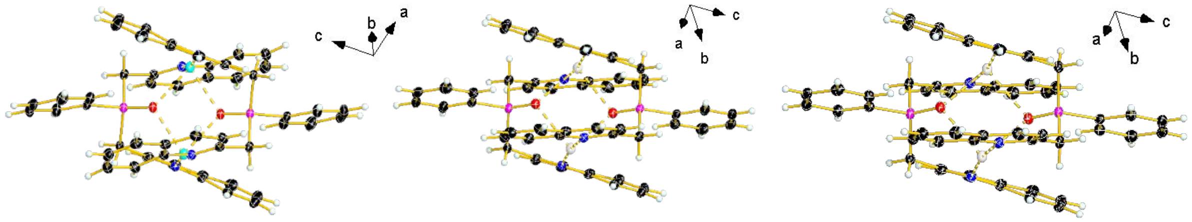


Figure S1. Visualization of the distorted/twisted quinaldinyl rings in **3** (left), **5** (center) and **6b** (right). Thermal ellipsoids are drawn at 50 % probability level. Solvent molecules and anions are omitted.

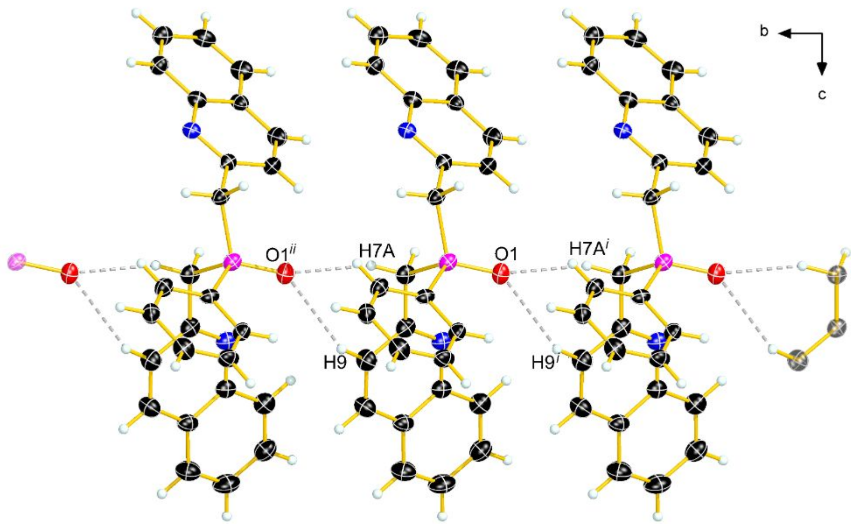


Figure S2. Non-classical hydrogen bonds in the crystal structure of phosphine oxide **2**: H7A^{i}⋯O1 2.437 Å, H9^{i}⋯O1 2.590 Å. Thermal ellipsoids are drawn at 50 % probability level. Symmetry code *i* = *x*, 1+*y*, *z*.

Table S1. Selected bond lengths [Å] and angles [°] of compounds **2**–**6b**.

2			
P1–C1	1.807(2)	C1–P1–C17	105.7(4)
P1–C7	1.805(2)	C7–P1–C17	103.2(3)
P1–C17	1.812(2)	O1–P1–C1	111.6(2)
P1–O1	1.482(2)	O1–P1–C7	114.5(2)
C1–P1–C7	107.4(3)	O1–P1–C17	113.6(2)
3		*i* = 2−*x*, −*y*, 1−*z*	
P1–O1	1.499(2)	Cu1–O1	2.305(2)
P1–C1	1.791(2)	Cu1^i–N2	1.946(2)
P1–C7	1.819(3)	Cu1···Cu1^i	3.607(4)
P1–C17	1.808(3)	O1···O1^i	2.853(2)
Cu1–N1	1.941(2)		
O1–P1–C1	111.9(2)	Cu1–O1–P1	115.1(2)
O1–P1–C7	111.6(2)	Cu1^i–O1–P1	115.6(9)
O1–P1–C17	110.9(2)	O1–Cu1–N2^i	94.8(8)
C1–P1–C7	104.9(2)	Cu1–O1–Cu1^i	103.3(6)
C1–P1–C17	108.0(2)	O1–Cu1–O1^i	76.7(6)
C7–P1–C17	109.4(2)	O1–Cu1–O1^i–Cu1^i	0.0(1)
4		*i* = 1−*x*, 1−*y*, 1−*z*	
P1–O1	1.499(2)	Cu1–O1	2.255(2)
P1–C1	1.798(4)	Cu1–N2^i	1.951(3)
P1–C7	1.823(3)	Cu1···Cu1^i	3.533(5)
P1–C17	1.813(4)	O1···O1^i	2.948(3)
Cu1–N1	1.953(3)		
O1–P1–C1	112.7(2)	Cu1–O1–P1	115.9(2)
O1–P1–C7	111.6(2)	Cu1^i–O1–P1	115.2(2)
O1–P1–C17	110.8(2)	O1–Cu1–N2^i	95.4(2)
C1–P1–C7	105.8(2)	Cu1–O1–Cu^i	100.3(9)
C1–P1–C17	106.1(2)	O1–Cu1–O1^i	79.7(9)
C7–P1–C17	109.9(2)	O1–Cu1–O1^i–Cu^i	0.0(8)
5		*i* = −*x*, 1−*y*, −*z*	
P1–O1	1.494(2)	Ag1–N1	2.230(2)
P1–C1	1.796(2)	Ag1–N2^i	2.228(2)
P1–C7	1.814(2)	Ag1···Ag1^i	3.673(4)
P1–C17	1.817(2)	O1···O1^i	3.349(2)
Ag1–O1	2.491(2)		
O1–P1–C1	111.3(3)	Ag1–O1–P1	116.1(8)
O1–P1–C7	112.6(4)	Ag1^i–O1–P1	119.3(9)
O1–P1–C17	110.9(3)	O1–Ag1–N1	88.9(6)
C1–P1–C7	105.5(4)	O1–Ag1–O1^i	84.7(5)
C1–P1–C17	105.8(4)	Ag1–O1–Ag1^i	95.3(3)
C7–P1–C17	110.4(4)	O1–Ag1–O1^i–Ag1^i	0.0(3)
6a			
P1–O1	1.499(4)	O1–Ag1	2.685(5)
P2–O2	1.504(4)	O1–Ag2	2.605(4)
P1–C1	1.801(7)	Ag1–O2	2.509(4)
P2–C27	1.804(6)	Ag2–O2	2.587(4)
P1–C7	1.810(6)	Ag1–N1	2.228(4)
P2–C33	1.810(6)	Ag2–N2	2.215(5)
P1–C17	1.825(6)	Ag1···Ag2	3.792(7)
P2–C43	1.828(6)	O1···O2	3.199(5)
O1–P1–C1	112.7(3)	C7–P1–C17	102.0(4)

O2–P2–C27	112.4(5)	C33–P2–C43	109.9(4)
O1–P1–C7	113.4(4)	Ag1–O1–P1	106.1(2)
O2–P2–C33	111.1(5)	Ag2–O1–P1	111.8(2)
O1–P1–C17	112.8(5)	O1–Ag1–N1	83.1(3)
O2–P2–C43	112.7(3)	O1–Ag2–N2	88.5(3)
C1–P1–C7	107.5(5)	O1–Ag1–O2	76.0(3)
C27–P2–C33	105.9(5)	Ag1–O1–Ag2	91.6(3)
C1–P1–C17	107.7(4)	Ag1–O2–Ag2	96.1(3)
C27–P2–43	104.5(4)	O1–Ag1–O2–Ag2	−33.5(3)
6b		$i = -x, 1-y, -z$	
P1–O1	1.498(2)	O1–Ag1^i	2.508(2)
P1–C1	1.796(2)	Ag1–N1	2.240(2)
P1–C7	1.816(2)	Ag1–N2^i	2.243(2)
P1–C17	1.816(2)	Ag1···Ag1^i	3.630(4)
O1–Ag1	2.510(2)	O1···O1^i	3.464(2)
O1–P1–C1	112.5(2)	Ag1^i–O1–P1	114.2(9)
O1–P1–C7	110.5(2)	O1^i–Ag1–N1	89.0(6)
O1–P1–C17	113.1(2)	O1–Ag1–N2^i	100.3(6)
C1–P1–C7	106.2(2)	O1–Ag1–O1^i	87.3(5)
C1–P1–C17	103.0(2)	Ag1–O1–Ag1^i	92.7(5)
C7–P1–C17	111.2(2)	O1–Ag1–O1^i–Ag1^i	0.0(2)
Ag1–O1–P1	118.5(9)		

Table S2. Crystallographic and refinement data for compounds **2**–**4**.

	2	**3**	**4**
Formula	$C_{26}H_{21}N_2OP$	$C_{52}H_{42}B_2Cu_2F_8N_4O_2P_2$	$C_{59.09}H_{51.09}Cl_{2.30}Cu_2F_{12}N_4O_2P_4$
Formula weight [g·mol^{-1}]	408.42	1117.53	1409.84
Colour	colorless	yellow	Colorless
Habit	rod	block	block
T [K]	113	129	123
λ [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1$	$P2_1/c$	$P2_1/c$
a [Å]	10.3956(5)	9.1235(3)	11.0193(5)
b [Å]	5.7580(3)	10.7088(3)	9.1541(4)
c [Å]	17.4339(11)	23.9819(6)	29.122(2)
α [°]	90	90	90
β [°]	105.249(2)	95.620(3)	98.310(5)
γ [°]	90	90	90
V [Å^3]	1,006.81(10)	2,331.81(12)	2,906.7(3)
Z	2	2	2
ρ_{calc} [g·cm^{-3}]	1.347	1.592	1.611
μ [mm^{-1}]	0.158	1.061	1.034
F(0 0 0)	428	1136	1429.6
Crystal size [mm]	0.10×0.02×0.02	0.25×0.25×0.20	0.25×0.20×0.10
Θ range [°]	2.721–25.417	3.289–28.281	2.173–26.022
Index ranges	$-11 \leq h \leq 12$ $-6 \leq k \leq 6$ $-21 \leq l \leq 19$	$-12 \leq h \leq 12$ $-7 \leq k \leq 14$ $-31 \leq l \leq 30$	$-13 \leq h \leq 13$ $-11 \leq k \leq 11$ $-32 \leq l \leq 35$
reflns collected	9,090	20,435	22,121
Independent reflns	3,558 [R_{int} = 0.0532]	5,767 [R_{int} = 0.0619]	5,744 [R_{int} = 0.0538]
Completeness to theta	96.7 %	99.8 %	99.9 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/ restraints/ Parameters	3,558 / 1 / 271	5,767 / 0 / 325	5,742 / 5 / 405
Hydrogen atom treatment	constrained	constrained	constrained
R_1/wR_2 (I > 2 σ (I))	0.0536/0.0965	0.0447/0.0875	0.0504/0.1168
R_1/wR_2 (all data)	0.0786/0.1053	0.0697/0.0996	0.0739/0.1294
Goodness-of-fit on F^2	1.038	1.033	1.048
larg. diff peak/hole [e·Å^{-3}]	0.586/−0.295	0.628/−0.379	0.576/−0.446
CCDC No.	2042242	2042245	2042247

Table S3. Crystallographic and refinement data for compounds **5**–**6b**.

	5	**6a**	**6b**
Formula	$C_{56}H_{48}Ag_2B_2F_8N_6O_2P_2$	$C_{55}H_{48}Ag_2Cl_6F_{12}N_4O_2P_2Sb_2$	$C_{56}H_{48}Ag_2F_{12}N_6O_2P_2Sb_2$
Formula weight [g·mol^{-1}]	1,288.30	1,758.85	1,586.18
T [K]	130	123	123
λ [Å]	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	triclinic
Space group	P–1	P–1	P–1
colour	colorless	brown-yellow	colorless
habit	block	block	block
a [Å]	9.9850(4)	10.6785(4)	10.0325(3)
b [Å]	11.3496(5)	12.9834(16)	11.2046(4)
c [Å]	12.7437(6)	24.0750(8)	13.4670(4)
α [°]	76.480(4)	74.980(4)	78.726(3)
β [°]	68.868(4)	82.951(3)	69.530(3)
γ [°]	84.189(4)	73.426(4)	86.217(3)
V [Å^3]	1309.51(11)	3085.6(2)	1390.87(8)
Z	1	2	1
ρ_{calc} [g·cm^{-3}]	1.634	1.893	1.894
μ [mm^{-1}]	0.887	1.884	1.801
F(0 0 0)	648	1716	776
Crystal size [mm]	0.40×0.20×0.20	0.20×0.20×0.05	0.47×0.16×0.05
Θ range [°]	3.246–28.279	2.520–26.372	2.167–30.508
Index ranges	$-13 \le h \le 13$ $-14 \le k \le 15$ $-15 \le l \le 16$	$-13 \le h \le 13$ $-16 \le k \le 14$ $-30 \le l \le 29$	$-14 \le h \le 14$ $-16 \le k \le 15$ $-19 \le l \le 19$
Reflns collected	11,880	25,623	28,183
Independent reflns	6,477 [R_{int} = 0.0299]	12,611 [R_{int} = 0.0486]	8,503 [R_{int} = 0.0330]
Completeness to theta	99.8 %	99.9 %	99.9 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	6,477 / 0 / 376	12,611 / 0 / 799	8,503 / 0 / 371
R_1/wR_2 (l > 2 σ (I))	0.0345/0.0675	0.0509/0.1126	0.0287/0.0634
R_1/wR_2 (all data)	0.0443/0.0732	0.0791/0.1272	0.0418/0.0694
Goodness-of-fit on F^2	1.057	1.031	1.056
larg. diff peak/hole [e·Å^{-3}]	0.635/−0.522	0.971/−1.558	1.201/−0.542
CCDC No.	2042243	2042244	2042246

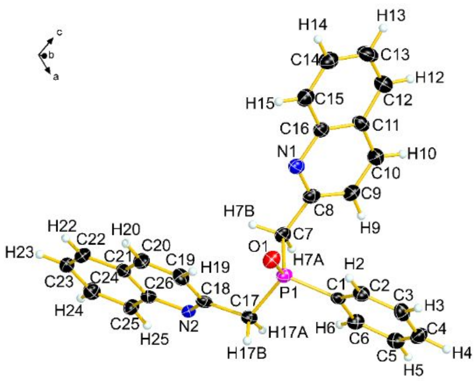


Figure S3. Numbering scheme for compound **2**.

Table S4. Atomic coordinates (·10^{4}) and equivalent isotropic displacement parameters (Å^{2}·10^{3}) for **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	9917(1)	5025(2)	1824(1)	24(1)
C(1)	8685(5)	6981(10)	2020(3)	26(1)
N(1)	7904(4)	5285(8)	3076(2)	27(1)
O(1)	9722(3)	2556(6)	2004(2)	29(1)
C(3)	9177(5)	8779(10)	3381(3)	32(1)
N(2)	7960(4)	6905(7)	−262(2)	21(1)
C(2)	8589(5)	6979(10)	2865(3)	26(1)
C(4)	9019(5)	8838(10)	4127(3)	34(1)
C(19)	6175(5)	8410(9)	−1296(3)	25(1)
C(5)	8277(5)	7089(10)	4379(3)	29(1)
C(20)	6706(5)	6665(9)	−749(3)	24(1)
C(6)	8026(5)	7059(12)	5141(3)	38(2)
C(25)	13559(5)	5197(11)	3355(3)	30(1)
C(8)	6822(5)	3490(11)	4813(3)	36(1)
C(7)	7327(5)	5289(12)	5345(3)	41(2)
C(23)	13359(5)	8777(10)	2645(3)	28(1)
C(9)	7020(5)	3519(10)	4069(3)	33(1)
C(14)	6463(5)	2943(9)	−163(3)	29(1)
C(10)	7749(4)	5321(10)	3836(3)	26(1)
C(11)	9824(5)	5559(9)	786(3)	23(1)
C(24)	14100(5)	7264(10)	3203(3)	31(1)
C(12)	8450(4)	5220(10)	243(3)	21(1)
C(22)	12070(5)	8190(9)	2230(3)	27(1)
C(13)	7727(5)	3168(9)	299(3)	27(1)
C(18)	4899(5)	8260(9)	−1768(3)	29(1)
C(15)	5900(5)	4687(9)	−711(3)	24(1)
C(26)	12284(5)	4586(9)	2934(3)	26(1)
C(16)	4593(5)	4576(10)	−1217(3)	30(1)
C(17)	4094(5)	6337(10)	−1732(3)	30(1)
C(21)	11536(5)	6075(9)	2373(3)	21(1)

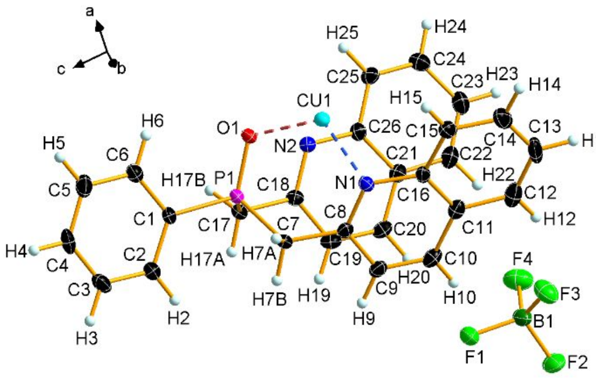


Figure S4. Numbering scheme for compound **3**.

Table S5. Atomic coordinates (·10[4]) and equivalent isotropic displacement parameters (Å[2]·10[3]) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	8512(1)	−1049(1)	4775(1)	17(1)
B(1)	5078(4)	6034(3)	3728(1)	26(1)
P(1)	8621(1)	638(1)	5900(1)	15(1)
F(1)	5028(2)	5666(2)	4283(1)	37(1)
O(1)	9635(2)	−84(2)	5564(1)	17(1)
N(1)	6955(2)	163(2)	4598(1)	16(1)
C(1)	8563(3)	−5(2)	6587(1)	18(1)
F(2)	4015(2)	6951(2)	3601(1)	39(1)
N(2)	10363(2)	2589(2)	5117(1)	17(1)
C(2)	7514(3)	363(3)	6944(1)	25(1)
F(3)	4809(2)	5019(2)	3381(1)	37(1)
C(3)	7444(3)	−250(3)	7447(1)	28(1)
C(4)	8404(3)	−1209(3)	7602(1)	27(1)
F(4)	6462(2)	6512(2)	3660(1)	42(1)
C(5)	9484(3)	−1550(3)	7261(1)	28(1)
C(6)	9557(3)	−950(2)	6751(1)	22(1)
C(7)	6727(3)	578(2)	5584(1)	17(1)
C(8)	6464(3)	933(2)	4976(1)	18(1)
C(9)	5703(3)	2044(2)	4823(1)	21(1)
C(15)	6996(3)	−412(3)	3622(1)	23(1)
C(14)	6789(3)	−97(3)	3069(1)	30(1)
C(16)	6666(3)	465(2)	4035(1)	17(1)
C(13)	6261(3)	1088(3)	2898(1)	34(1)
C(12)	5872(3)	1922(3)	3283(1)	29(1)
C(11)	6028(3)	1625(2)	3861(1)	21(1)
C(10)	5538(3)	2411(2)	4279(1)	22(1)
C(17)	9201(3)	2248(2)	5976(1)	18(1)
C(25)	11674(3)	2993(2)	4310(1)	20(1)
C(24)	11775(3)	3576(2)	3810(1)	24(1)
C(23)	10632(3)	4353(3)	3575(1)	27(1)
C(22)	9444(3)	4579(3)	3860(1)	25(1)
C(26)	10440(3)	3197(2)	4610(1)	18(1)
C(21)	9334(3)	4038(2)	4392(1)	19(1)
C(20)	8204(3)	4339(2)	4732(1)	21(1)
C(19)	8205(3)	3802(2)	5246(1)	21(1)
C(18)	9276(3)	2903(2)	5422(1)	17(1)

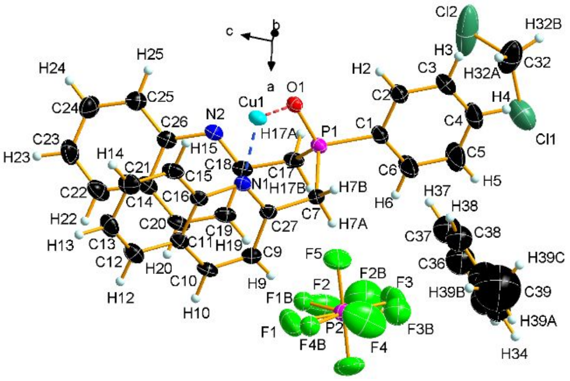


Figure S5. Numbering scheme for compound **4**.

Table S6. Atomic coordinates (·10⁴) and equivalent isotropic displacement parameters (Å²·10³) for **4**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	6011(1)	6443(1)	4917(1)	24(1)
P(1)	5547(1)	3755(1)	4207(1)	23(1)
N(1)	7555(2)	5362(3)	5009(1)	23(1)
O(1)	4870(2)	4734(2)	4496(1)	23(1)
C(1)	4912(3)	3799(4)	3603(1)	32(1)
C(3)	3506(4)	4906(5)	2996(2)	45(1)
C(2)	3997(3)	4805(4)	3457(1)	33(1)
N(2)	5206(2)	2004(3)	5202(1)	23(1)
C(4)	3912(4)	3993(6)	2674(2)	57(1)
C(6)	5322(4)	2878(5)	3277(2)	57(1)
C(5)	4817(5)	2968(6)	2813(2)	73(2)
C(7)	7146(3)	4303(4)	4234(1)	26(1)
C(27)	7864(3)	4359(4)	4713(1)	24(1)
C(9)	8840(3)	3373(4)	4834(1)	27(1)
C(10)	9480(3)	3398(4)	5270(1)	28(1)
C(11)	9192(3)	4439(4)	5594(1)	26(1)
C(15)	8000(3)	6557(4)	5751(2)	33(1)
C(14)	8645(3)	6660(5)	6186(2)	41(1)
C(13)	9578(4)	5658(5)	6339(2)	41(1)
C(12)	9843(3)	4568(4)	6049(1)	35(1)
C(24)	5073(4)	1547(4)	6440(2)	44(1)
C(23)	6229(4)	938(5)	6600(2)	50(1)
C(22)	7031(4)	659(5)	6294(2)	43(1)
C(21)	6709(3)	971(4)	5817(1)	31(1)
C(20)	7442(3)	574(4)	5479(2)	32(1)
C(19)	7027(3)	814(4)	5023(1)	29(1)
C(18)	5903(3)	1557(3)	4890(1)	25(1)
C(17)	5462(3)	1867(4)	4389(1)	28(1)
C(16)	8241(3)	5442(4)	5446(1)	24(1)
C(26)	5558(3)	1637(3)	5659(1)	26(1)
C(25)	4752(3)	1901(4)	5987(2)	33(1)
F(1)	9371(4)	33(6)	4304(1)	86(2)
F(2)	8160(3)	-1662(5)	3938(2)	90(2)
F(3)	8033(4)	-437(6)	3273(1)	81(2)
F(4)	9273(4)	1250(4)	3616(2)	114(2)
F(5)	7591(3)	743(4)	3886(1)	86(1)
F(6)	9888(2)	−1047(3)	3674(1)	71(1)
P(2)	8715(1)	−185(1)	3777(1)	34(1)
F(1B)	8380(30)	−980(40)	4158(11)	33(8)

F(2B)	7880(60)	−1340(80)	3540(30)	140(30)
F(3B)	8530(40)	250(50)	3256(16)	66(13)
F(4B)	9580(30)	700(30)	4139(13)	36(9)
F(5B)	7591(3)	743(4)	3886(1)	86(1)
F(6B)	9888(2)	−1047(3)	3674(1)	71(1)
P(2B)	8715(1)	−185(1)	3777(1)	34(1)
Cl(2)	570(4)	871(5)	2666(1)	132(2)
Cl(1)	2513(3)	650(3)	2081(1)	73(1)
C(32)	1357(10)	1784(12)	2258(4)	75(3)
C(33)	9013(9)	6037(8)	2586(3)	95(5)
C(34)	9354(7)	4728(10)	2399(3)	55(3)
C(35)	8748(8)	3442(8)	2480(3)	82(4)
C(36)	7802(8)	3465(9)	2748(3)	76(4)
C(37)	7461(8)	4773(12)	2935(3)	68(4)
C(38)	8067(9)	6059(9)	2854(3)	61(4)
C(39)	9685(19)	7460(30)	2501(6)	195(12)

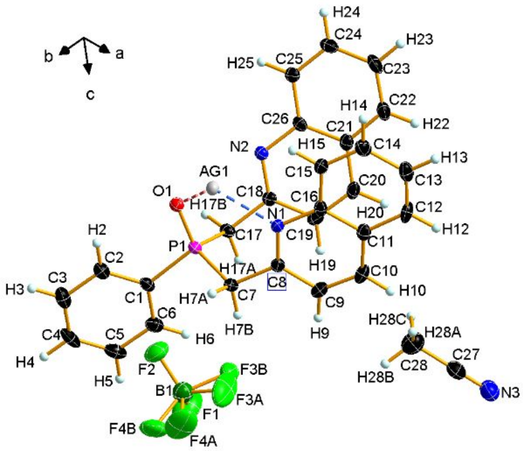


Figure S6. Numbering scheme for compound **5**.

Table S7. Atomic coordinates ($\cdot 10^4$) and equivalent isotropic displacement parameters ($Å^2 \cdot 10^3$) for **5**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ag(1)	1462(1)	5951(1)	−137(1)	18(1)
F(1)	250(2)	6964(2)	4792(2)	76(1)
O(1)	−989(2)	5377(1)	1253(1)	19(1)
N(1)	2379(2)	4585(2)	1003(2)	17(1)
C(1)	-2498(2)	5633(2)	3443(2)	20(1)
P(1)	−1103(1)	4872(1)	2474(1)	17(1)
C(10)	3765(3)	2973(2)	2324(2)	25(1)
C(6)	−2889(3)	5279(2)	4634(2)	25(1)
C(7)	526(2)	5062(2)	2733(2)	20(1)
C(24)	1255(3)	1043(2)	−1278(2)	25(1)
C(3)	−4291(3)	7231(2)	3651(3)	30(1)
C(2)	−3200(2)	6605(2)	2953(2)	23(1)
N(2)	−588(2)	2498(2)	1151(2)	16(1)
F(2)	636(2)	8064(2)	2980(2)	53(1)
C(22)	2464(3)	412(2)	92(2)	26(1)
C(5)	−3990(3)	5911(3)	5322(2)	30(1)
C(4)	−4673(3)	6878(3)	4835(3)	32(1)
C(21)	1439(2)	1063(2)	852(2)	20(1)
C(20)	1407(3)	1040(2)	1971(2)	23(1)

C(19)	411(2)	1713(2)	2638(2)	22(1)
C(8)	1859(2)	4374(2)	2147(2)	18(1)
C(18)	−557(2)	2470(2)	2189(2)	18(1)
C(9)	2528(2)	3565(2)	2832(2)	23(1)
C(17)	−1589(2)	3286(2)	2906(2)	19(1)
C(11)	4333(2)	3145(2)	1118(2)	21(1)
C(12)	5600(2)	2529(2)	524(2)	26(1)
C(13)	6095(2)	2731(2)	−645(2)	26(1)
C(14)	5351(3)	3536(2)	−1284(2)	26(1)
C(15)	4141(2)	4138(2)	−729(2)	21(1)
C(16)	3601(2)	3958(2)	471(2)	18(1)
C(23)	2375(3)	410(2)	−949(2)	28(1)
C(25)	277(3)	1709(2)	−581(2)	20(1)
B(1)	1148(3)	7743(3)	3873(3)	31(1)
N(3)	3797(3)	−852(2)	6559(2)	39(1)
C(28)	2463(3)	548(3)	5322(3)	43(1)
C(27)	3219(3)	−242(3)	6024(2)	30(1)
C(26)	371(2)	1765(2)	486(2)	18(1)
F(4A)	1950(30)	8580(9)	3985(16)	91(6)
F(3A)	2500(10)	7330(20)	3554(7)	83(5)
F(4B)	957(12)	8780(4)	4322(4)	61(2)
F(3B)	2150(30)	6806(18)	3482(9)	41(5)

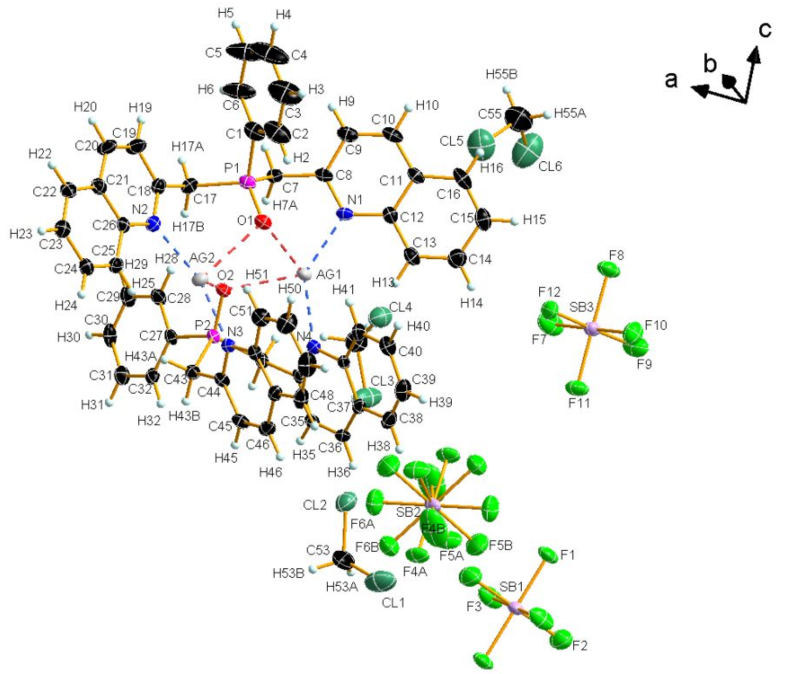


Figure S7. Numbering scheme for compound **6a**.

Table S8. Atomic coordinates (·10⁴) and equivalent isotropic displacement parameters (Å²·10³) for **6a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sb(1)	0	5000	0	23(1)
Cl(1)	5045(3)	3315(2)	174(1)	72(1)
P(1)	8220(2)	8245(1)	3652(1)	24(1)
O(1)	7352(4)	8573(3)	3156(2)	23(1)
N(1)	6271(5)	6502(4)	3942(2)	21(1)
C(1)	7743(7)	9189(6)	4119(3)	35(2)
Sb(2)	0	10000	0	26(1)

Cl(2)	6742(2)	2894(2)	1112(1)	47(1)
P(2)	9553(1)	6168(1)	2046(1)	19(1)
O(2)	9196(3)	6739(3)	2535(2)	21(1)
N(2)	9904(4)	9590(4)	2547(2)	23(1)
C(2)	6589(8)	10019(7)	4021(3)	53(2)
C(20)	10949(7)	10791(6)	3092(3)	35(2)
Sb(3)	281(1)	3500(1)	3987(1)	27(1)
Cl(3)	7223(2)	2087(2)	2617(1)	75(1)
N(3)	7569(4)	8688(4)	1495(2)	18(1)
C(3)	6168(11)	10721(8)	4401(4)	74(3)
Ag(1)	6989(1)	6691(1)	3022(1)	24(1)
Ag(2)	8667(1)	8866(1)	2169(1)	24(1)
N(4)	6447(4)	6434(4)	2208(2)	21(1)
Cl(4)	6372(2)	3638(2)	3353(1)	49(1)
C(4)	6916(12)	10606(8)	4853(4)	85(4)
F(12)	839(4)	4798(4)	3817(2)	47(1)
C(12)	5056(6)	6336(5)	4121(2)	23(1)
C(34)	7191(5)	5686(5)	1937(2)	17(1)
C(8)	6954(6)	6735(5)	4302(2)	22(1)
F(8)	144(4)	3504(4)	4774(2)	47(1)
C(6)	8485(9)	9073(6)	4581(3)	55(2)
F(6A)	1814(7)	9777(7)	−121(3)	53(3)
F(4A)	−216(10)	10623(7)	−788(3)	42(3)
F(5A)	171(11)	8591(6)	−100(3)	44(4)
F(6B)	1234(10)	9654(11)	−586(4)	64(4)
F(4B)	−893(15)	11240(17)	−512(7)	100(9)
F(5B)	−1039(16)	9222(15)	−176(5)	87(7)
Cl(6)	6067(3)	-1387(2)	6895(1)	89(1)
C(32)	11841(6)	4903(5)	1582(3)	26(1)
C(15)	2570(6)	5981(6)	4464(3)	35(2)
F(1)	-626(3)	4988(4)	768(1)	39(1)
C(21)	10726(6)	11194(6)	2502(2)	27(1)
F(7)	2008(4)	2661(4)	4063(2)	63(2)
C(7)	8286(5)	6872(5)	4094(2)	22(1)
C(44)	8034(5)	7896(5)	1207(2)	20(1)
C(18)	10176(5)	9217(5)	3101(2)	25(1)
C(39)	2645(6)	8092(6)	1677(3)	34(2)
C(13)	4359(6)	6057(6)	3745(3)	30(2)
C(10)	5235(6)	6690(5)	5045(2)	31(2)
C(11)	4495(6)	6422(5)	4678(2)	24(1)
F(11)	383(4)	3490(4)	3206(1)	43(1)
F(2)	-872(4)	3968(4)	-28(2)	56(1)
C(24)	10214(6)	11886(5)	1335(3)	26(1)
C(36)	5474(5)	5820(5)	1344(2)	25(1)
C(25)	9940(5)	10934(6)	1647(2)	27(1)
C(42)	5183(5)	6959(5)	2032(2)	20(1)
C(16)	3230(6)	6253(6)	4837(3)	36(2)
F(3)	1469(4)	3860(4)	264(2)	50(1)
C(30)	13790(6)	4060(6)	2098(3)	33(2)
C(27)	11244(5)	5381(5)	2037(2)	20(1)
C(45)	7339(6)	7757(5)	785(2)	24(1)
C(19)	10690(7)	9830(6)	3387(3)	36(2)
C(23)	10752(6)	12511(5)	1595(3)	28(1)
F(10)	−1441(3)	4376(4)	3906(2)	44(1)
F(9)	−326(4)	2227(4)	4172(2)	51(1)

C(9)	6439(6)	6847(5)	4863(2)	30(2)
C(22)	11000(6)	12164(5)	2163(2)	27(1)
C(31)	13107(6)	4252(5)	1609(3)	29(1)
C(5)	8055(12)	9805(7)	4943(3)	80(4)
Cl(5)	6061(2)	912(2)	6357(1)	78(1)
C(26)	10185(5)	10554(5)	2241(2)	21(1)
C(54)	7594(7)	2495(7)	3191(3)	45(2)
C(53)	6632(7)	2653(9)	437(3)	60(3)
C(52)	6344(5)	9412(5)	1361(2)	22(1)
C(51)	5859(6)	10272(6)	1648(3)	32(2)
C(50)	4640(6)	11003(6)	1524(3)	37(2)
C(49)	3888(7)	10896(6)	1112(3)	40(2)
C(48)	4358(6)	10071(6)	834(3)	31(2)
C(47)	5590(6)	9309(5)	952(2)	24(1)
C(46)	6128(6)	8450(5)	658(2)	28(1)
C(43)	9374(5)	7140(5)	1341(2)	22(1)
C(17)	9936(5)	8135(5)	3421(2)	26(1)
C(33)	8600(5)	5192(5)	2103(2)	21(1)
C(38)	3368(6)	7267(6)	1426(3)	32(2)
C(35)	6720(6)	5347(5)	1507(2)	23(1)
C(37)	4665(5)	6673(5)	1598(2)	21(1)
C(40)	3178(6)	8358(6)	2115(3)	32(2)
C(14)	3155(6)	5881(6)	3912(3)	36(2)
C(41)	4413(5)	7805(5)	2289(2)	27(1)
C(29)	13219(6)	4528(6)	2548(3)	35(2)
C(28)	11939(6)	5197(6)	2520(2)	29(2)
C(55)	5694(10)	−26(8)	6983(4)	69(3)

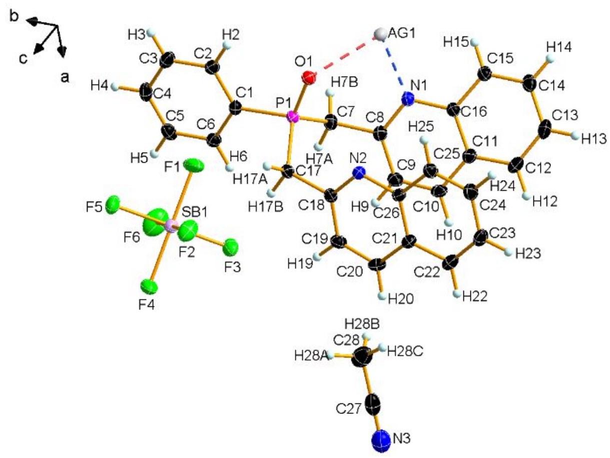


Figure S8. Numbering scheme for compound **6b**.

Table S9. Atomic coordinates (·10⁴) and equivalent isotropic displacement parameters (Å²·10³) for **6b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sb(1)	1559(1)	8000(1)	3766(1)	20(1)
Ag(1)	−1454(1)	4075(1)	60(1)	17(1)
F(1)	672(2)	8038(2)	2749(2)	43(1)
O(1)	−1039(2)	5433(1)	1201(1)	18(1)
N(1)	−605(2)	2513(2)	979(2)	17(1)
C(28)	2612(3)	500(3)	5471(3)	41(1)
C(1)	−2486(2)	5620(2)	3311(2)	17(1)
P(1)	−1148(1)	4894(1)	2337(1)	16(1)

N(2)	2323(2)	4574(2)	1024(2)	17(1)
F(2)	3171(2)	8740(2)	2684(1)	35(1)
C(2)	−3253(3)	6574(2)	2932(2)	20(1)
C(4)	−4527(3)	6825(2)	4757(2)	25(1)
F(4)	2442(2)	7944(2)	4792(1)	34(1)
C(3)	−4271(3)	7178(2)	3665(2)	25(1)
N(3)	3921(3)	−908(3)	6604(2)	42(1)
F(3)	2317(2)	6466(1)	3509(1)	30(1)
F(5)	818(2)	9527(1)	4018(1)	33(1)
C(5)	−3775(3)	5871(2)	5135(2)	25(1)
C(6)	−2748(3)	5270(2)	4413(2)	21(1)
F(6)	−25(2)	7231(2)	4860(2)	53(1)
C(8)	−588(3)	2516(2)	1965(2)	18(1)
C(7)	−1649(3)	3299(2)	2654(2)	20(1)
C(27)	3350(3)	−288(3)	6107(3)	32(1)
C(9)	397(3)	1833(2)	2377(2)	21(1)
C(10)	1445(3)	1203(2)	1727(2)	22(1)
C(13)	2431(3)	465(2)	−1015(2)	27(1)
C(12)	2516(3)	528(2)	−42(2)	25(1)
C(11)	1473(3)	1178(2)	678(2)	19(1)
C(17)	458(2)	5097(2)	2617(2)	20(1)
C(18)	1803(2)	4428(2)	2087(2)	18(1)
C(19)	2469(3)	3691(2)	2756(2)	22(1)
C(20)	3689(3)	3082(2)	2302(2)	23(1)
C(21)	4247(3)	3178(2)	1174(2)	19(1)
C(22)	5483(3)	2545(2)	646(2)	25(1)
C(23)	5965(3)	2654(2)	−454(2)	24(1)
C(24)	5245(3)	3397(2)	−1065(2)	25(1)
C(25)	4057(3)	4034(2)	−579(2)	21(1)
C(26)	3528(2)	3936(2)	552(2)	17(1)
C(16)	384(2)	1806(2)	343(2)	17(1)
C(15)	302(3)	1694(2)	−659(2)	21(1)
C(14)	1290(3)	1026(2)	−1314(2)	24(1)

Table S10. Bond lengths [Å] and bond angles [°] of non-classical hydrogen bonds of compounds **2**–**6b** calculated using PLATON.

Bond	d(D–H)	d(H···A)	d(D···A)	<(D–H···A)
2				
C2–H2···O1	0.95	2.53	2.969(6)	108
C6–H6···O1	0.95	2.76	3.454(6)	130
C7–H7A···O1	0.99	2.44	3.389(7)	161
C9–H9···O1	0.95	2.59	3.396(6)	143
C17–H17B···N2	0.99	2.43	3.418(7)	178
C19–H19···O1	0.95	2.52	3.165(6)	125
C24–H24···N1	0.95	2.69	3.399(7)	131
3				
C2–H2···F2	0.95	2.50	3.403(1)	158
C3–H3···F3	0.95	2.53	3.454(1)	164
C3–H3···F4	0.95	2.86	3.454(1)	117
C4–H4···F4	0.95	2.54	3.253(1)	132
C6–H6···O1	0.95	2.59	3.003(1)	107
C7–H7B···F2	0.99	2.51	3.398(1)	149
C9–H9···F1	0.95	2.46	3.370(1)	159
C10–H10···F1	0.95	2.66	3.515(1)	150
C10–H10···F3	0.95	2.73	3.550(1)	145

C12–H12···F3	0.95	2.61	3.474(1)	151
C13–H13···F2	0.95	2.75	3.694(1)	179
C13–H13···F3	0.95	2.63	3.329(1)	131
C15–H15···F4	0.95	2.57	3.335(1)	138
C17–H17A···F2	0.99	2.42	3.310(1)	149
C19–H19···F1	0.95	2.43	3.310(1)	154
C20–H20···F1	0.95	2.41	3.310(1)	159
C22–H22···F4	0.95	2.51	3.415(1)	158
C24–H24···F3	0.95	2.70	3.415(1)	132
4				
C2–H2···O1	0.95	2.62	3.041(2)	107
C4–H4···F3	0.95	2.40	3.283(2)	154
C6–H6···F5	0.95	2.54	3.455(2)	161
C7–H7A···F5	0.99	2.67	3.468(2)	138
C9–H9···F1	0.95	2.64	3.512(2)	153
C9–H9···F4B	0.95	2.41	3.351(2)	171
C10–H10···F1	0.95	2.73	3.542(2)	144
C10–H10···F2	0.95	2.76	3.586(2)	146
C10–H10···F1B	0.95	2.56	3.478(2)	162
C12–H12···F2	0.95	2.57	3.449(2)	154
C12–H12···F6	0.95	2.69	3.324(2)	125
C13–H13···Cl1	0.95	3.12	3.812(3)	131
C14–H14···F4	0.95	2.78	2.978(2)	93
C17–H17B···F5	0.99	2.19	3.113(2)	154
C19–H19···F1	0.95	2.71	3.624(2)	162
C19–H19···F5	0.95	2.67	3.456(2)	141
C19–H19···F1B	0.95	2.59	3.514(2)	165
C20–H20···F1	0.95	2.63	3.522(2)	157
C20–H20···F4B	0.95	2.56	3.509(2)	172
C22–H22···F6	0.95	2.68	3.402(2)	133
C24–H24···F2B	0.95	2.64	3.274(2)	125
C25–H25···F2	0.95	2.55	3.255(2)	131
C25–H25···F1B	0.95	2.85	3.513(2)	127
C32–H32A···F3	0.99	2.64	3.102(2)	108
C32–H32B···F3	0.99	2.80	3.102(2)	98
C32–H32B···F6	0.99	2.60	3.482(2)	148
5				
C2–H2···O1	0.95	2.54	2.975(1)	108
C3–H3···F3A	0.95	2.75	3.240(2)	113
C4–H4···N3	0.95	2.79	3.638(2)	148
C6–H6···F1	0.95	2.72	3.622(2)	159
C6–H6···F3A	0.95	2.53	3.390(2)	150
C6–H6···F3B	0.95	2.31	3.191(2)	153
C7–H7A···F2	0.99	2.61	3.510(2)	151
C7–H7A···F3B	0.99	2.58	3.178(1)	119
C7–H7B···F1	0.99	2.49	3.324(2)	142
C9–H9···F1	0.95	2.48	3.264(2)	140
C10–H10···N3	0.95	2.75	3.668(2)	162
C13–H13···F2	0.95	2.85	3.739(2)	155
C13–H13···F3B	0.95	2.87	3.339(2)	112
C14–H14···F3A	0.95	2.47	3.223(2)	136
C14–H14···F3B	0.95	2.34	3.083(1)	134
C15–H15···O1	0.95	2.72	3.413(2)	131
C17–H17A···F1	0.99	2.75	3.583(2)	142
C17–H17B···N3	0.99	2.90	3.496(2)	119

C19–H19···F4B	0.95	2.66	3.537(2)	153
C20–H20···F4B	0.95	2.84	3.381(2)	117
C20–H20···F4A	0.95	2.73	3.469(2)	136
C23–H23···N3	0.95	2.73	3.552(2)	145
C24–H24···F2	0.95	2.57	3.292(2)	132
C28–H28A···N3	0.98	2.88	3.637(2)	135
C28–H28B···F2	0.98	2.61	3.539(2)	159
C28–H28B···F4B	0.98	2.78	3.312(2)	114
C28–H28C···F4B	0.98	2.36	3.332(2)	172
C28–H28C···F4A	0.98	2.41	3.285(2)	149
6a				
C2–H2···Cl5	0.95	3.00	3.668(2)	129
C2–H2···Cl6	0.95	2.74	3.563(2)	145
C2–H2···O1	0.95	2.63	3.042(1)	107
C4–H4···Cl5	0.95	2.97	3.719(2)	137
C5–H5···F9	0.95	2.83	3.475(2)	126
C6–H6···F8	0.95	2.55	3.289(2)	135
C7–H7A···F10	0.99	2.56	3.313(2)	133
C7–H7A···F12	0.99	2.55	3.379(2)	141
C7–H7B···F8	0.95	2.24	3.231(1)	175
C9–H9···F7	0.95	2.58	3.516(2)	169
C10–H10···Cl4	0.95	3.07	3.994(2)	164
C13–H13···Cl4	0.95	3.07	3.545(2)	113
C14–H14···F12	0.95	2.52	3.231(1)	132
C15–H15···F8	0.95	2.47	3.230(1)	137
C16–H16···F10	0.95	2.57	3.416(2)	148
C17–H17B···O2	0.99	2.61	3.420(2)	139
C20–H20···Cl6	0.95	2.88	3.493(2)	123
C20–H20···F11	0.95	2.82	3.459(2)	126
C22–H22···F1	0.95	2.63	3.300(2)	128
C23–H23···F1	0.95	2.65	3.343(2)	130
C23–H23···F3	0.95	2.63	3.343(2)	132
C24–H24···F5A	0.95	2.49	3.285(2)	141
C24–H24···F5B	0.95	2.78	3.374(2)	122
C25–H25···F4A	0.95	2.40	3.182(1)	140
C25–H25···F6B	0.95	2.47	3.321(2)	148
C28–H28···F12	0.95	2.43	3.165(1)	134
C28–H28···O2	0.95	2.62	3.042(1)	107
C29–H29···Cl4	0.95	3.01	3.826(2)	145
C30–H30···Cl3	0.95	3.05	3.959(2)	161
C32–H32···F1	0.95	2.57	3.432(2)	152
C33–H33A···F1	0.99	2.54	3.277(2)	131
C33–H33B···F11	0.99	2.59	3.371(2)	136
C35–H35···Cl2	0.95	2.87	3.545(2)	129
C35–H35···F1	0.95	2.52	3.139(1)	123
C36–H36···Cl1	0.95	2.96	3.598(2)	126
C39–H39···F4A	0.95	2.48	3.337(2)	151
C39–H39···F4B	0.95	2.70	3.350(2)	126
C40–H40···N2	0.95	2.86	3.555(2)	130
C41–H41···Cl5	0.95	3.15	3.948(2)	143
C43–H43A···F4A	0.99	2.38	3.195(1)	139
C43–H43A···F4B	0.99	2.39	3.164(1)	134
C43–H43B···N3	0.99	2.59	3.421(2)	141
C43–H43B···Cl5	0.99	2.85	3.798(2)	161
C45–H45···F1	0.95	2.85	3.639(2)	141

C45–H45···F3	0.95	2.67	3.582(2)	161
C46–H46···Cl1	0.95	3.11	3.933(2)	146
C53–H53A···F6A	0.99	2.48	3.351(2)	147
C53–H53A···F6B	0.99	2.39	3.169(1)	135
C53–H53A···F2	0.99	2.61	3.485(2)	147
C54–H54A···F11	0.99	2.63	3.575(2)	159
C55–H55A···O1	0.99	2.39	3.269(2)	148
6b				
C2–H2···O1	0.95	2.61	3.029(1)	107
C3–H3···F2	0.95	2.63	3.504(1)	153
C3–H3···F4	0.95	2.76	3.248(1)	113
C4–H4···F4	0.95	2.66	3.199(1)	117
C4–H4···N3	0.95	2.92	3.781(1)	152
C6–H6···F3	0.95	2.49	3.226(1)	134
C6–H6···F4	0.95	2.83	3.576(1)	136
C7–H7A···F4	0.99	2.30	3.280(1)	169
C7–H7B···N3	0.99	2.85	3.396(1)	116
C9–H9···F5	0.95	2.71	3.165(1)	110
C10–H10···F2	0.95	2.59	3.437(1)	149
C10–H10···F5	0.95	2.73	3.159(1)	108
C13–H13···N3	0.95	2.80	3.628(1)	146
C14–H14···F1	0.95	2.56	3.211(1)	126
C15–H15···F1	0.95	2.64	3.244(1)	122
C17–H17A···F1	0.99	2.43	3.360(1)	156
C17–H17A···F3	0.99	2.69	3.153(1)	109
C19–H19···F6	0.95	2.49	3.305(1)	144
C20–H20···N3	0.95	2.85	3.762(1)	161
C24–H24···F3	0.95	2.49	3.325(1)	147
C25–H25···O1	0.95	2.66	3.402(1)	135
C28–H28B···F4	0.98	2.78	3.204(1)	107
C28–H28B···F5	0.98	2.74	3.438(1)	129
C28–H28B···F5	0.98	2.43	3.266(1)	143
C28–H28C···N3	0.98	2.80	3.610(1)	141

Additional solution NMR pictures

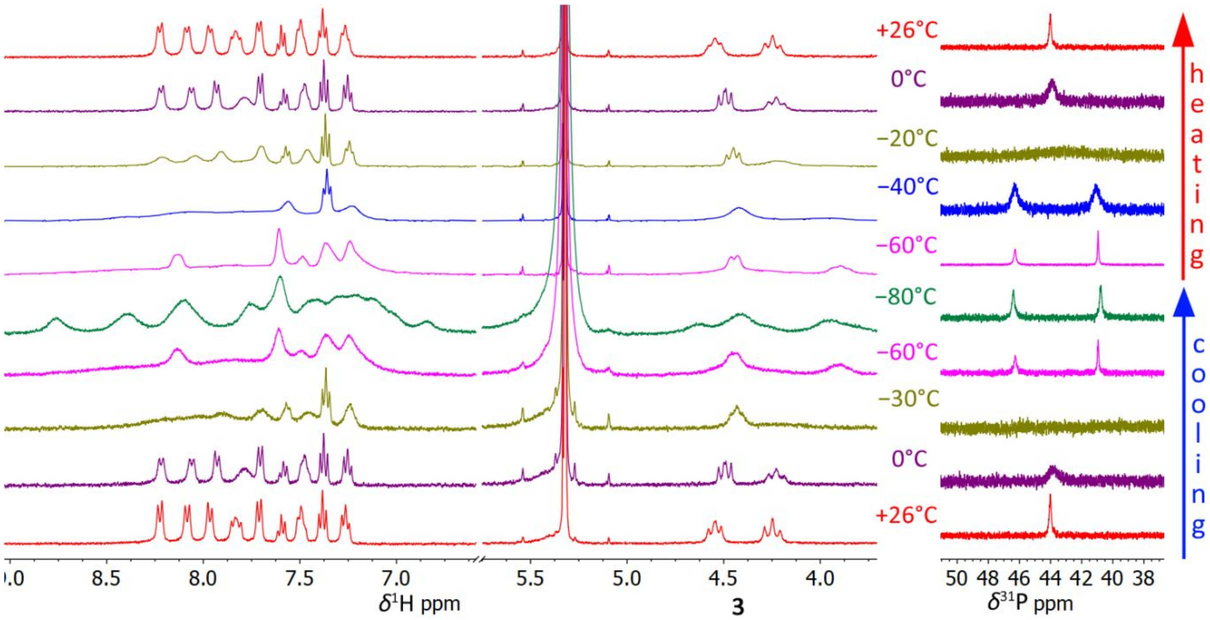


Figure S9. ^{31}P (right) and ^{1}H NMR (left) of compound **3** in CD_2Cl_2 at different temperatures.

Cyclic voltammetry

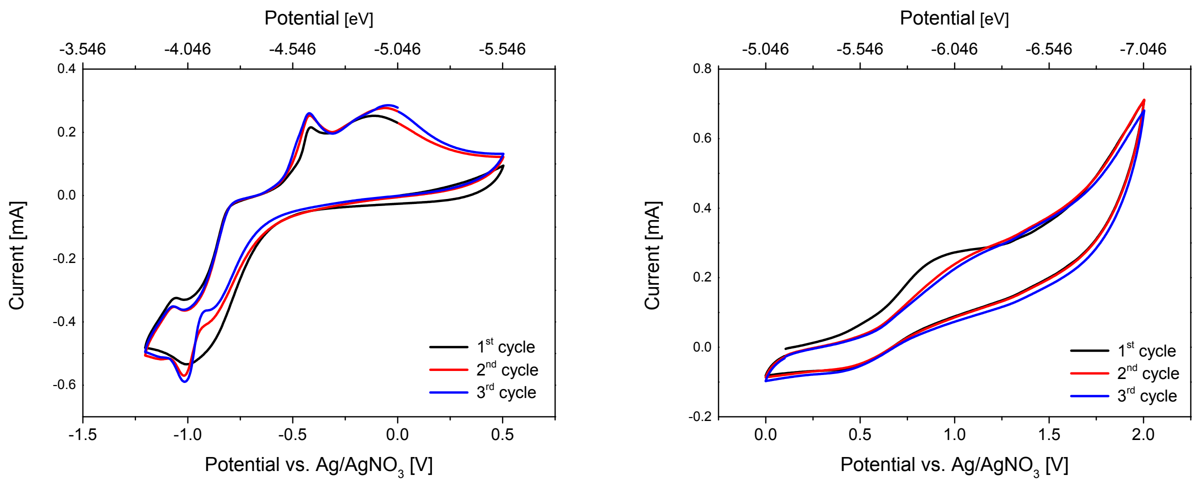


Figure S10. CV curves of complex **3** recorded between −1.2-0.5 V (left) and 0-2 V (right).

Hirshfeld surface analysis

To gain more insight into the intermolecular interactions of the presented compounds **2**–**6b** in the crystal, quantitative Hirshfeld surface analysis was conducted (Figure 2, S11). In all structures of the complexes, attractive intermolecular (N⋯H–C, F⋯H–C) interactions (25.4–35.6%) and weak π-π-interactions (23–29.5%) are present to roughly the same extent (Figure 9–11). The only complex, that shows additional O⋯H–C interactions (0.5%) is **6a** due to the different coordination geometry and the resulting more exposed oxygen atom. All complexes show strong intermolecular interactions with the fluorine containing counterion indicated by sharp spikes in the fingerprint plots. Contrary to the complexes, in the structure of the free ligand **2**, weak π-π-interactions (C⋯C, C⋯H–C) are predominant (38.6%). The shortest C⋯H–C contacts originate from the CH_2 groups, as indicated by red dots in the d_{norm} maps.

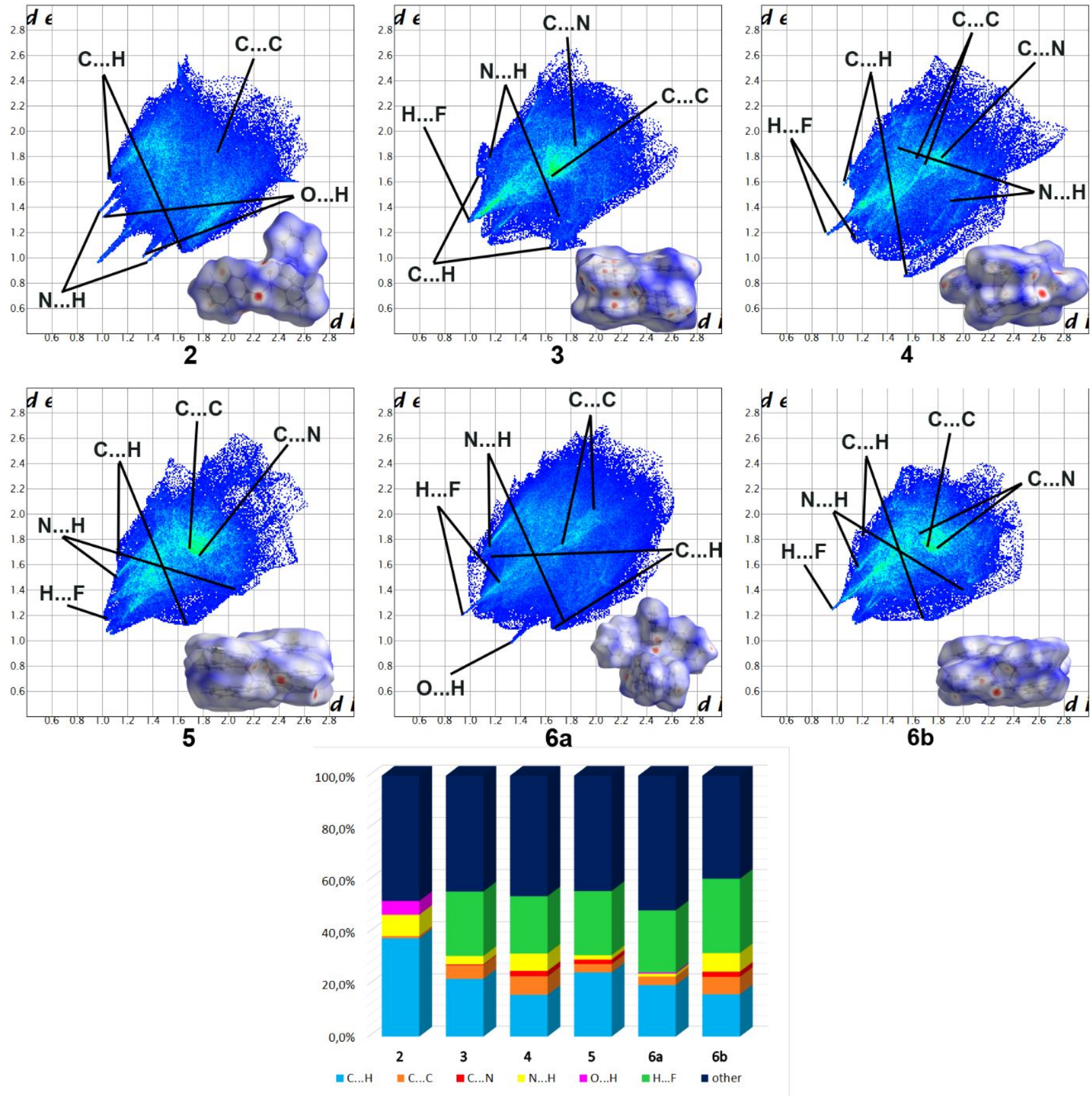
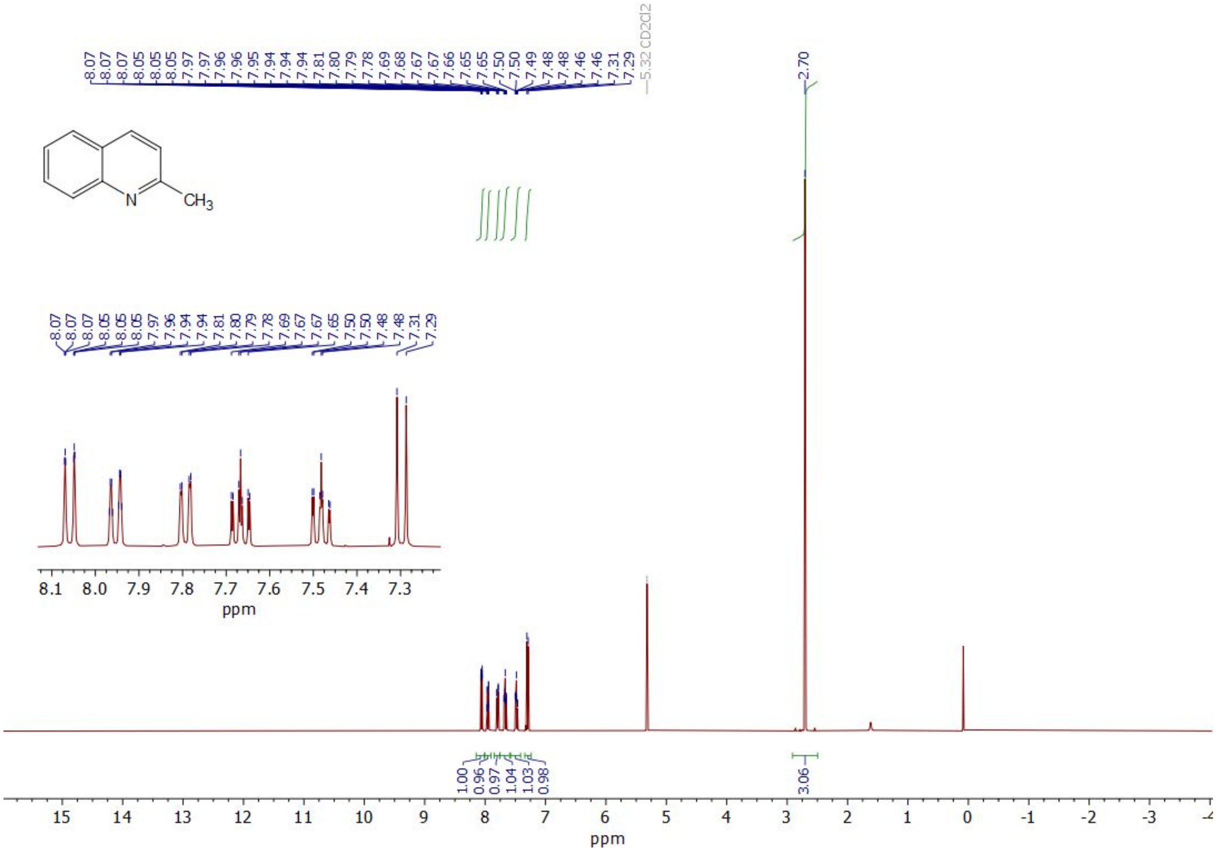


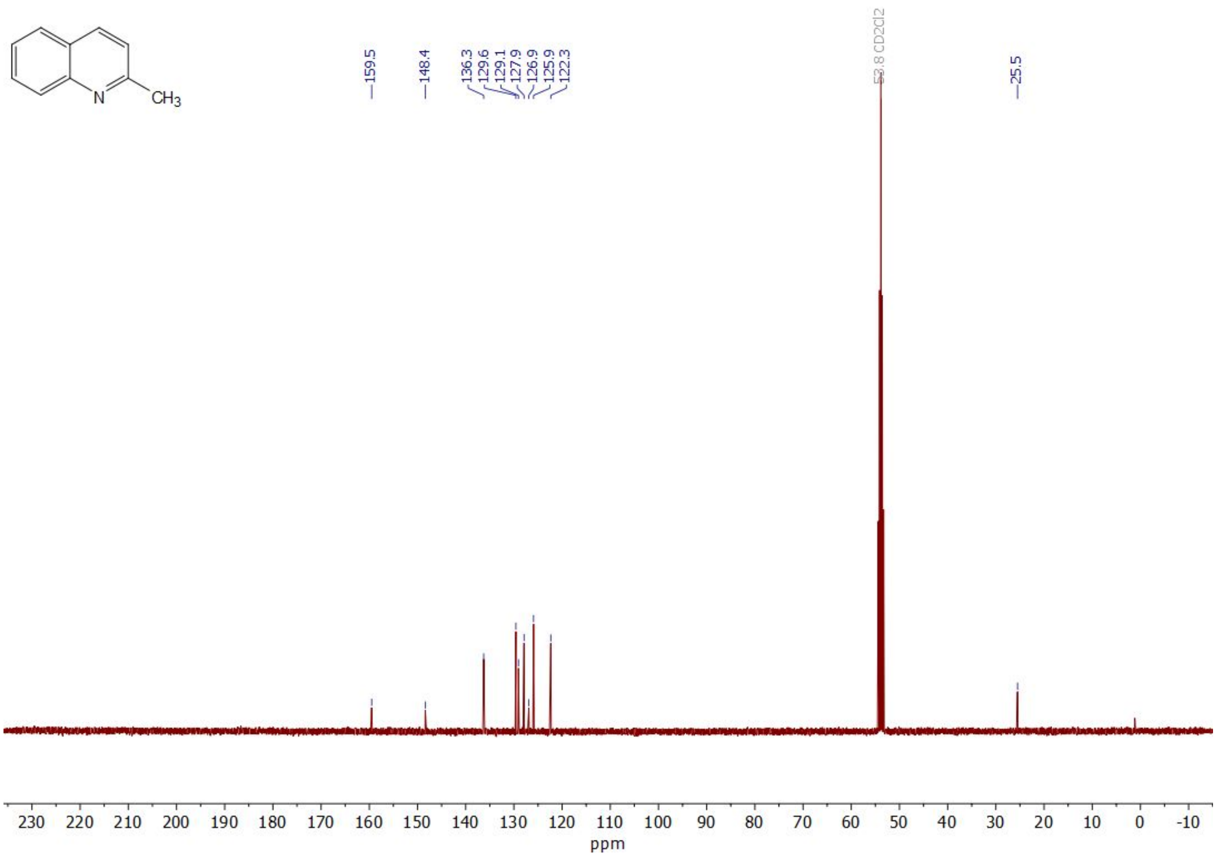
Figure S11. d_{norm} maps and fingerprint plots of compounds **2**–**6b**. The diagram on the bottom is showing the close contacts of compounds **2**–**6b** in the crystal packing.

Solution NMR spectra

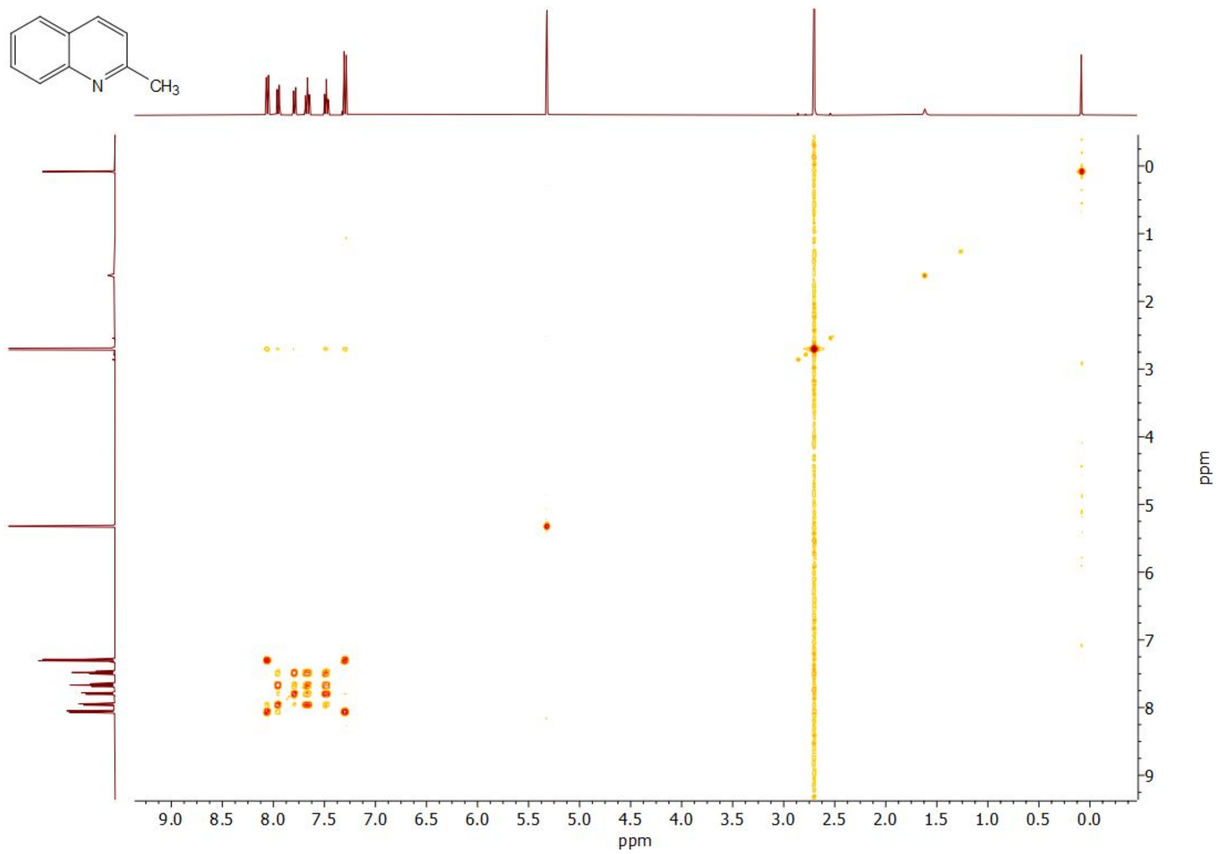
^{1}H NMR of **quinaldine** in CD_2Cl_2, 400.182 MHz.



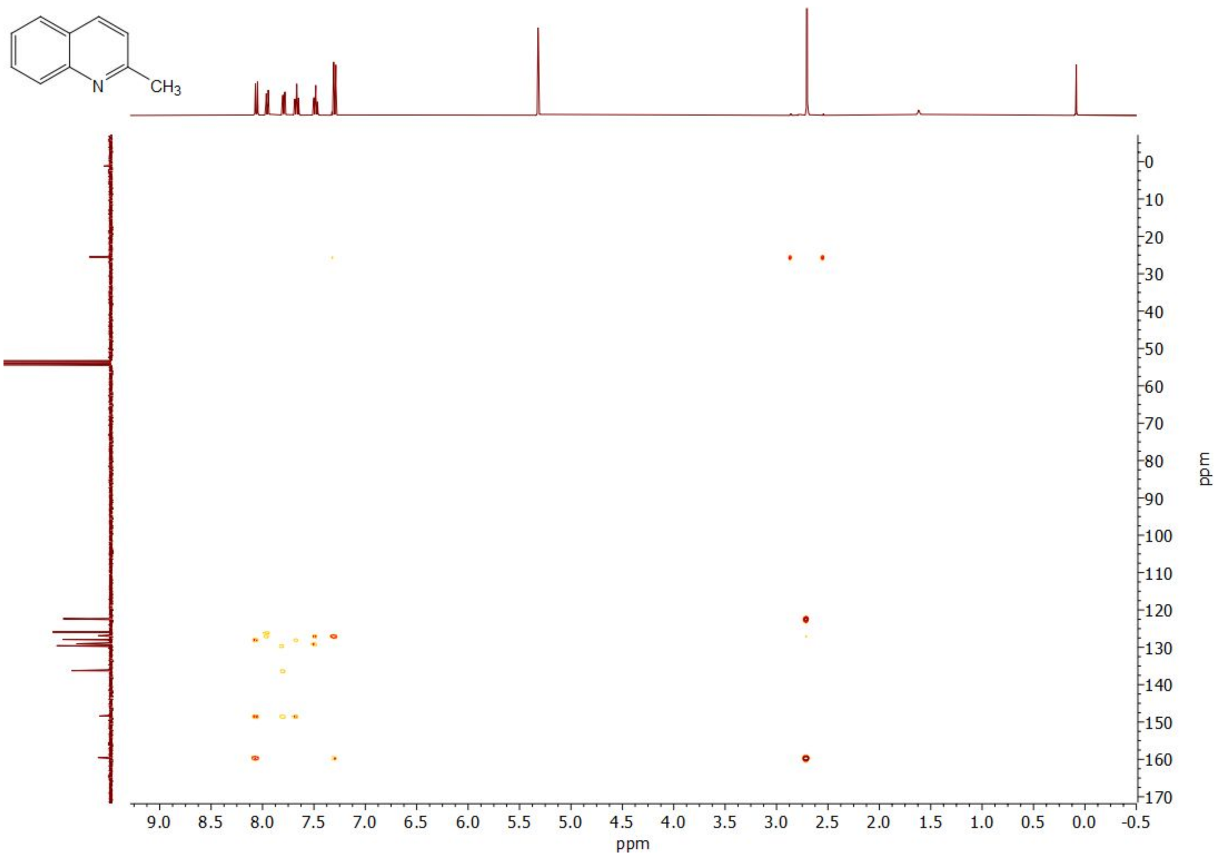
^{13}C NMR of **quinaldine** in CD_2Cl_2, 100.636 MHz.



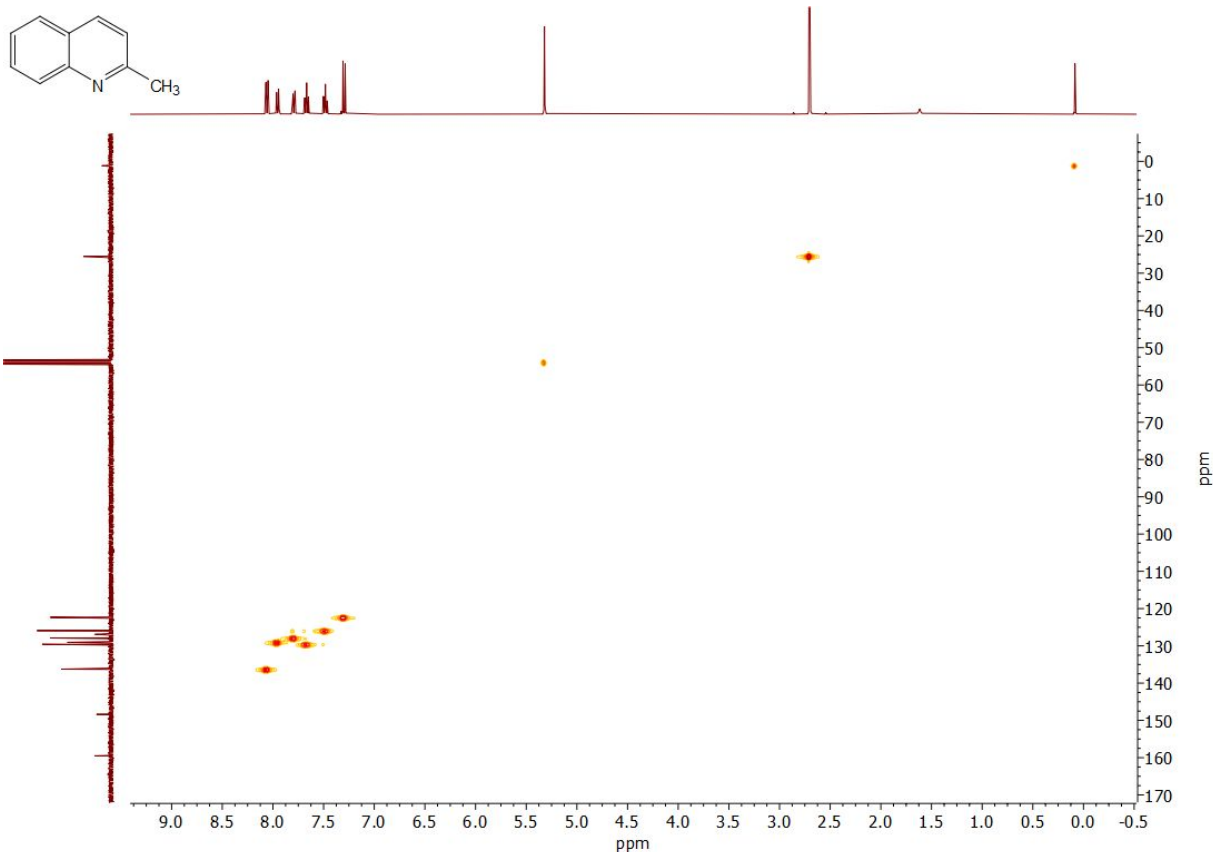
$^{1}H,^{1}H$–COSY$_{45}$ of **quinaldine** in CD_2Cl_2



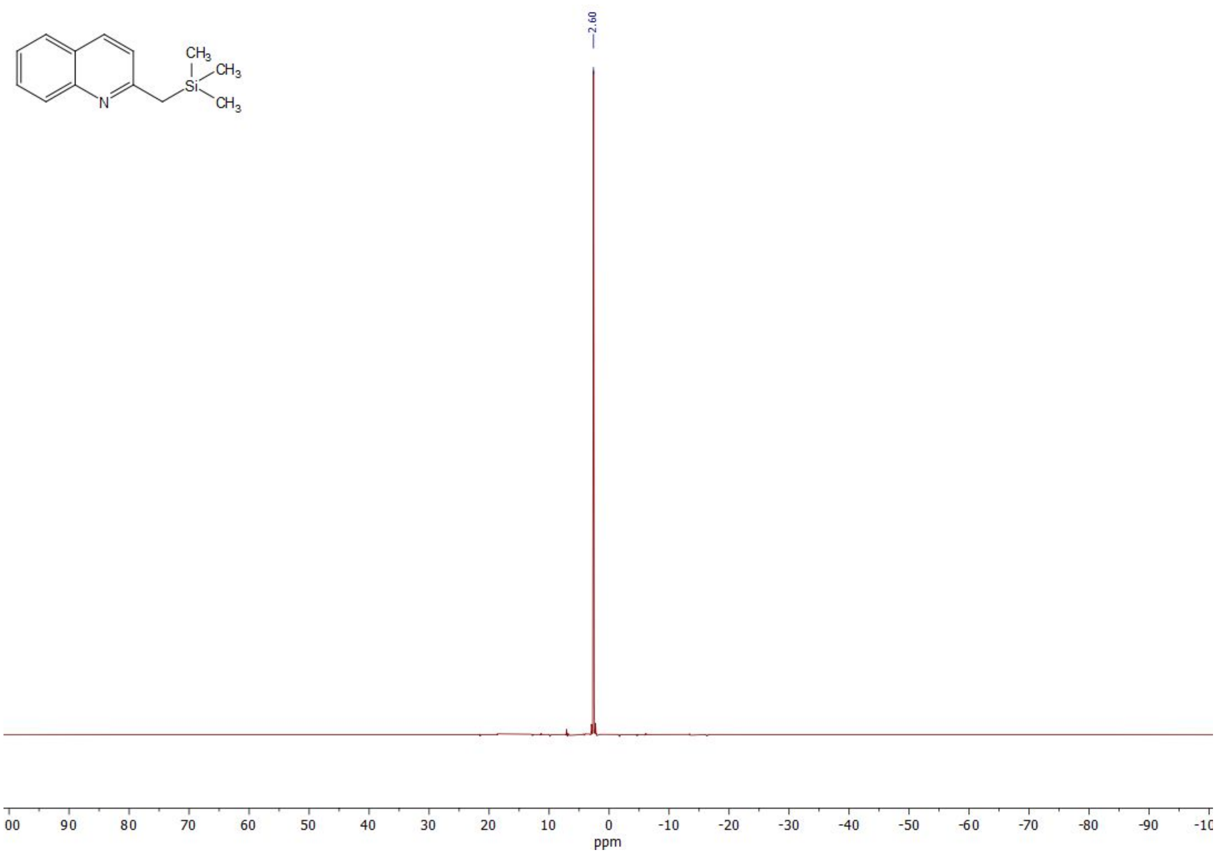
$^{1}H,^{13}C$–HMBC of **quinaldine** in CD_2Cl_2



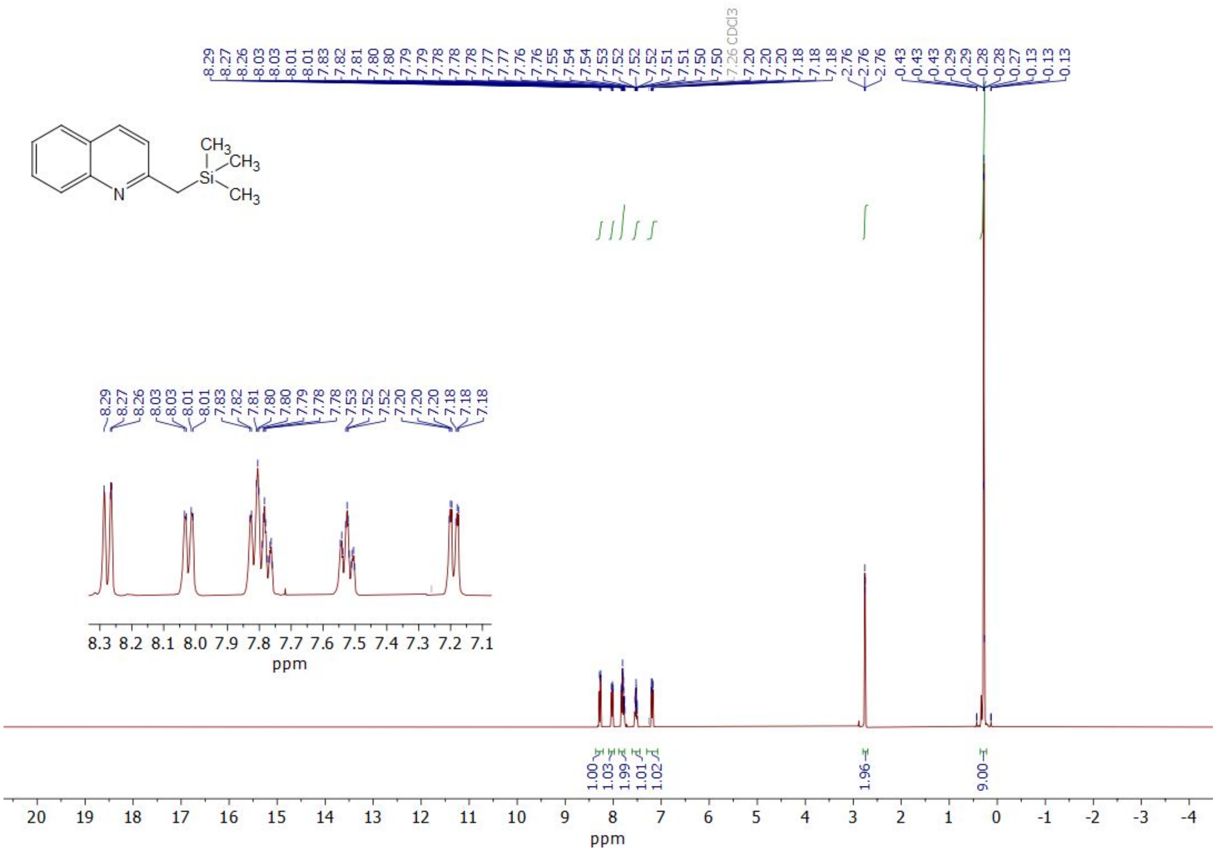
$^{1}H,^{13}C$–HSQC of **quinaldine** in CD_2Cl_2



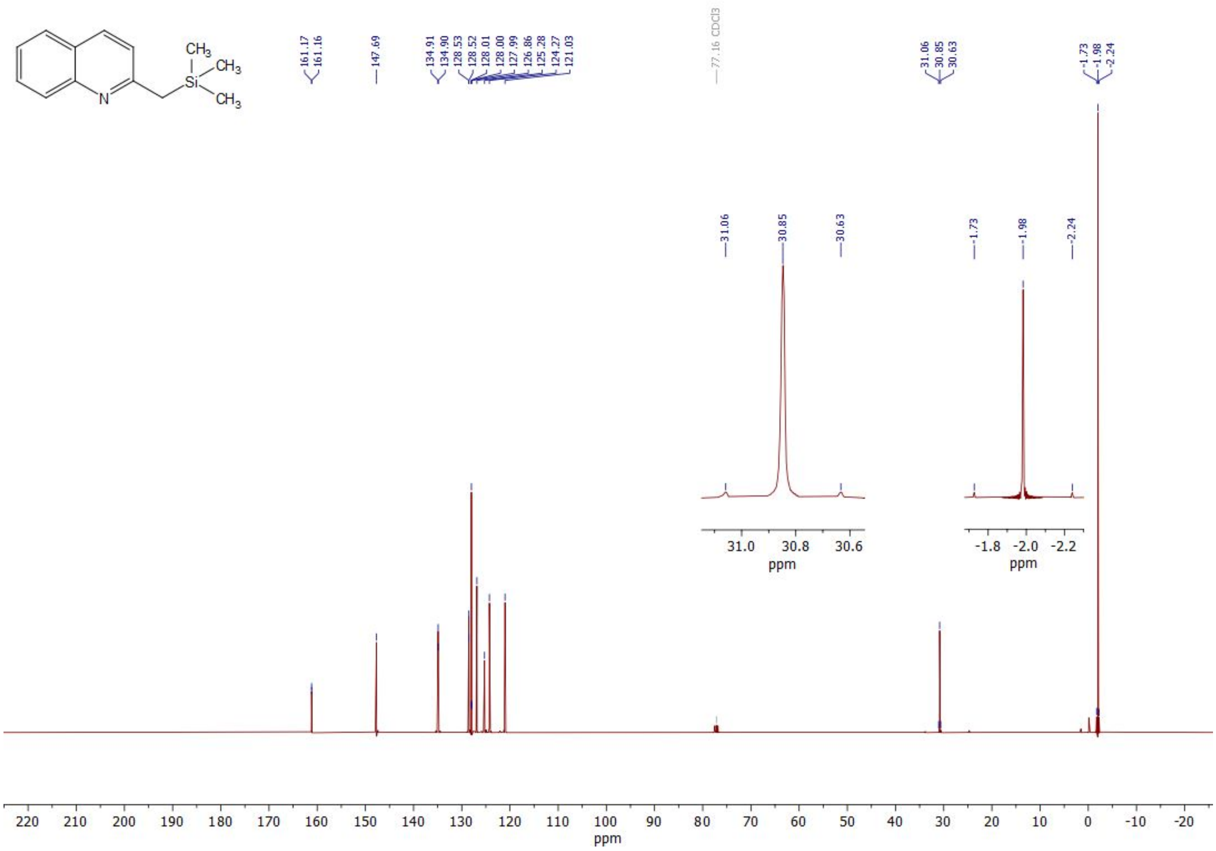
^{29}Si INEPT NMR of **A** in $CDCl_3$, 79.495 MHz.



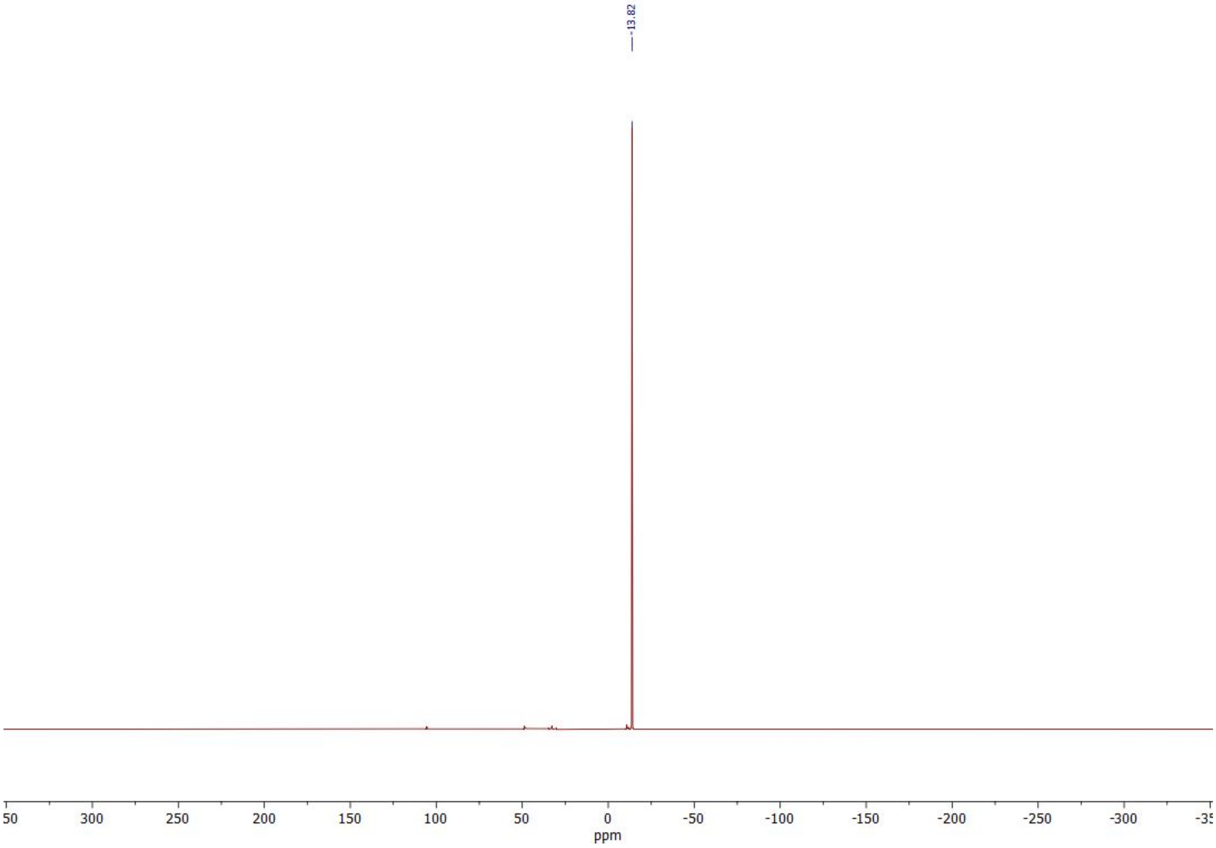
^{1}H NMR of **A** in $CDCl_3$, 400.133 MHz.



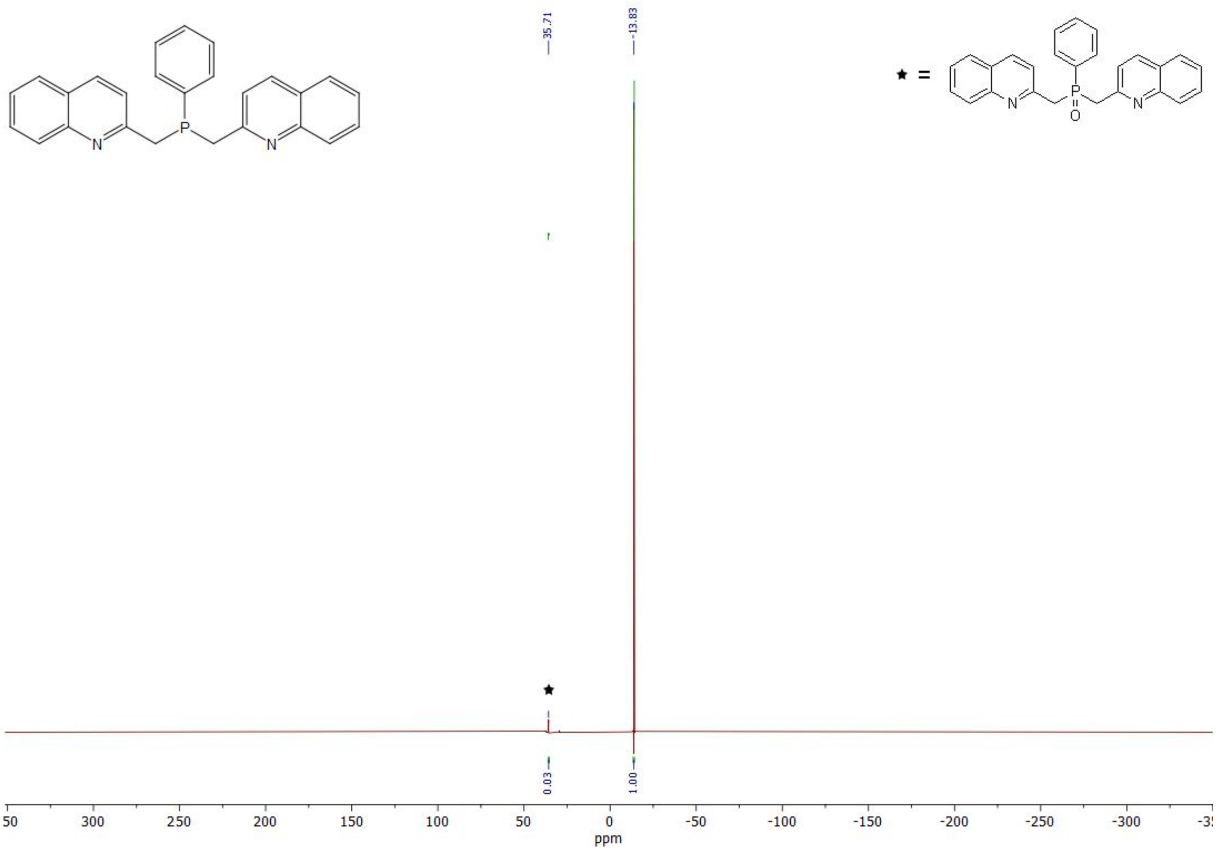
^{13}C NMR of **A** in $CDCl_3$, 100.623 MHz.



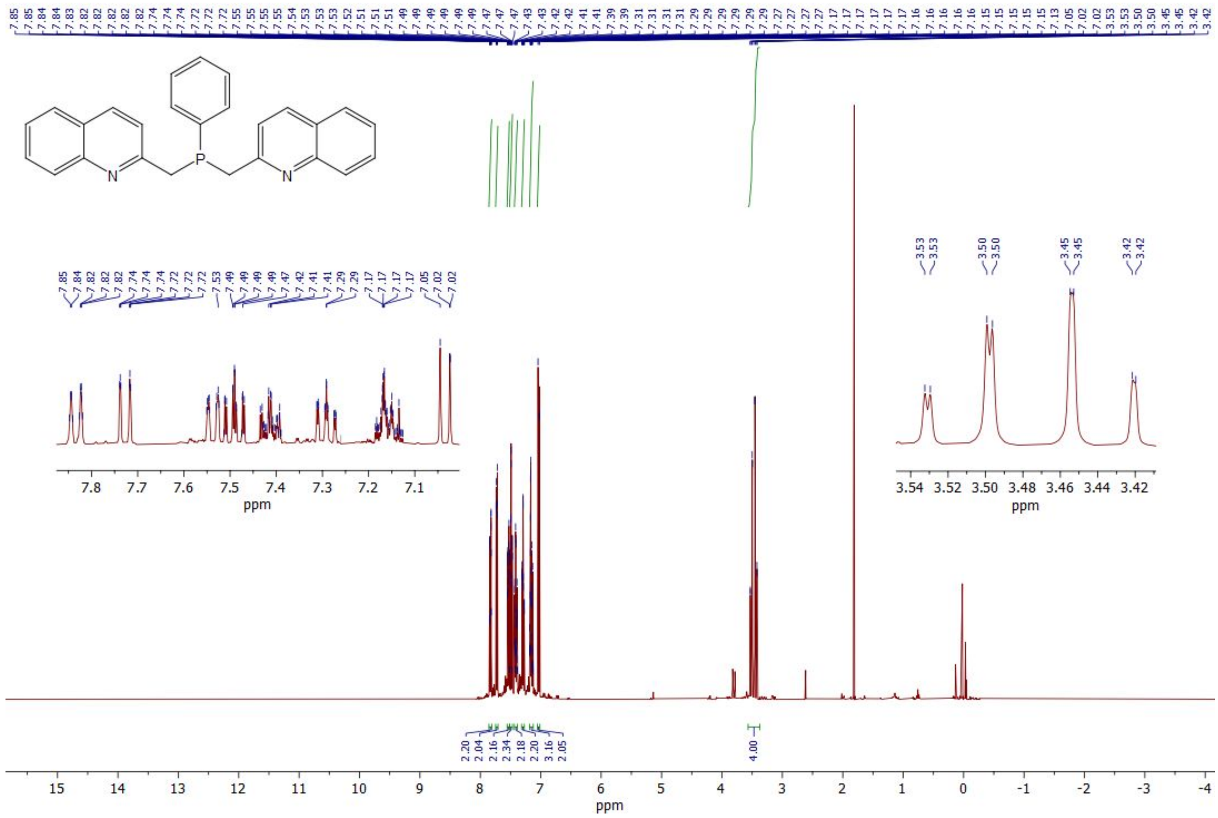
$^{31}P\{^{1}H\}$ NMR of **1** in the reaction mixture, 109.365 MHz.



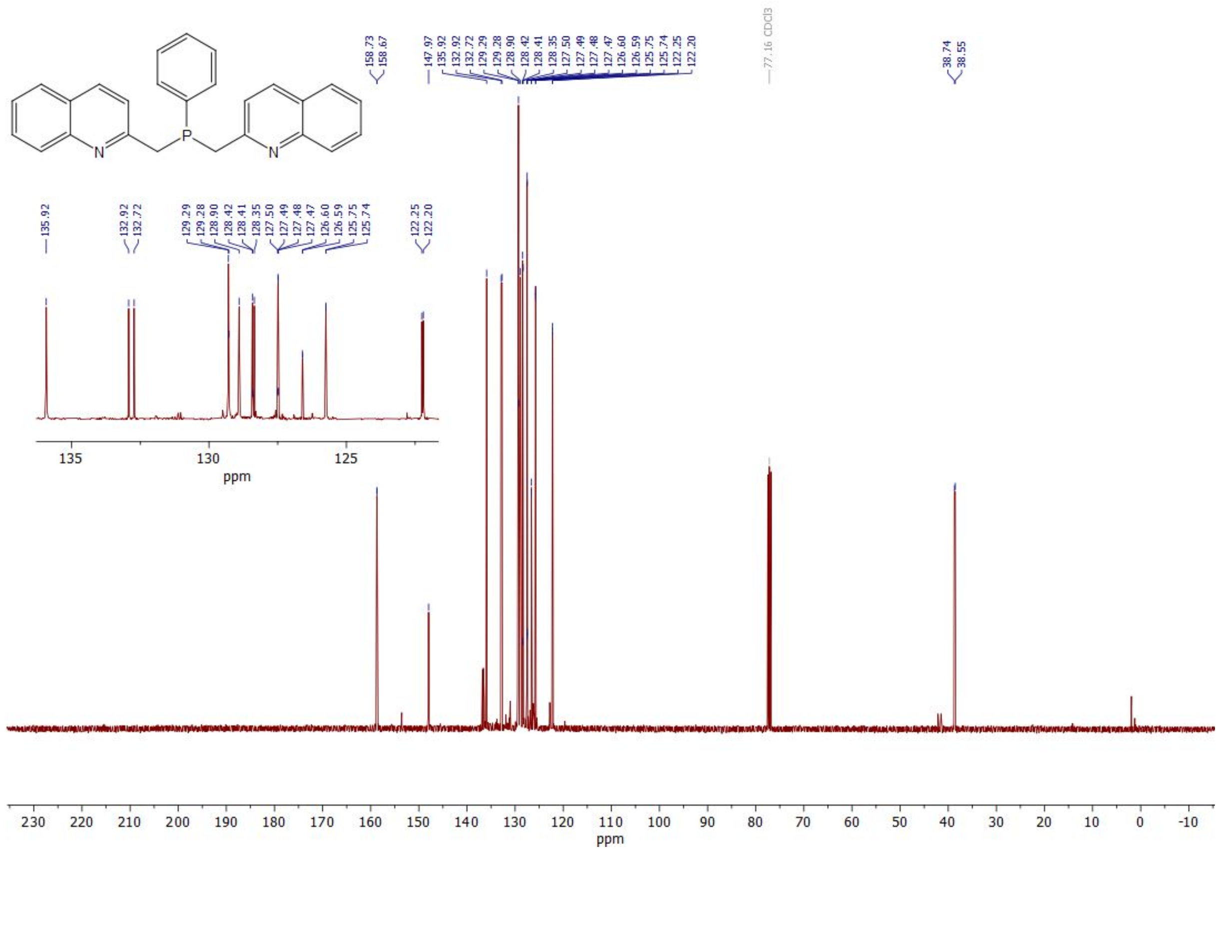
$^{31}P\{^{1}H\}$ NMR of **1** in $CDCl_3$, 161.996 MHz.



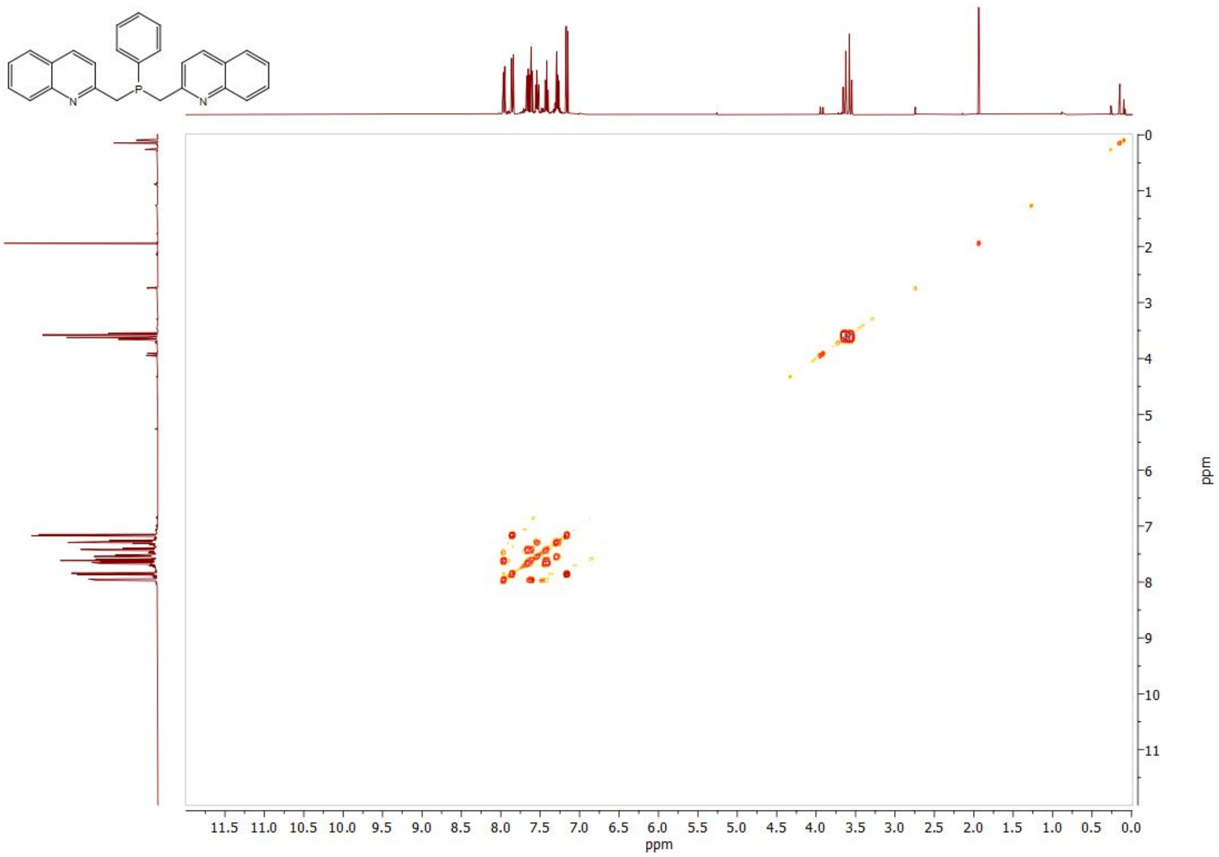
^{1}H NMR of **1** in $CDCl_3$, 400.133 MHz.



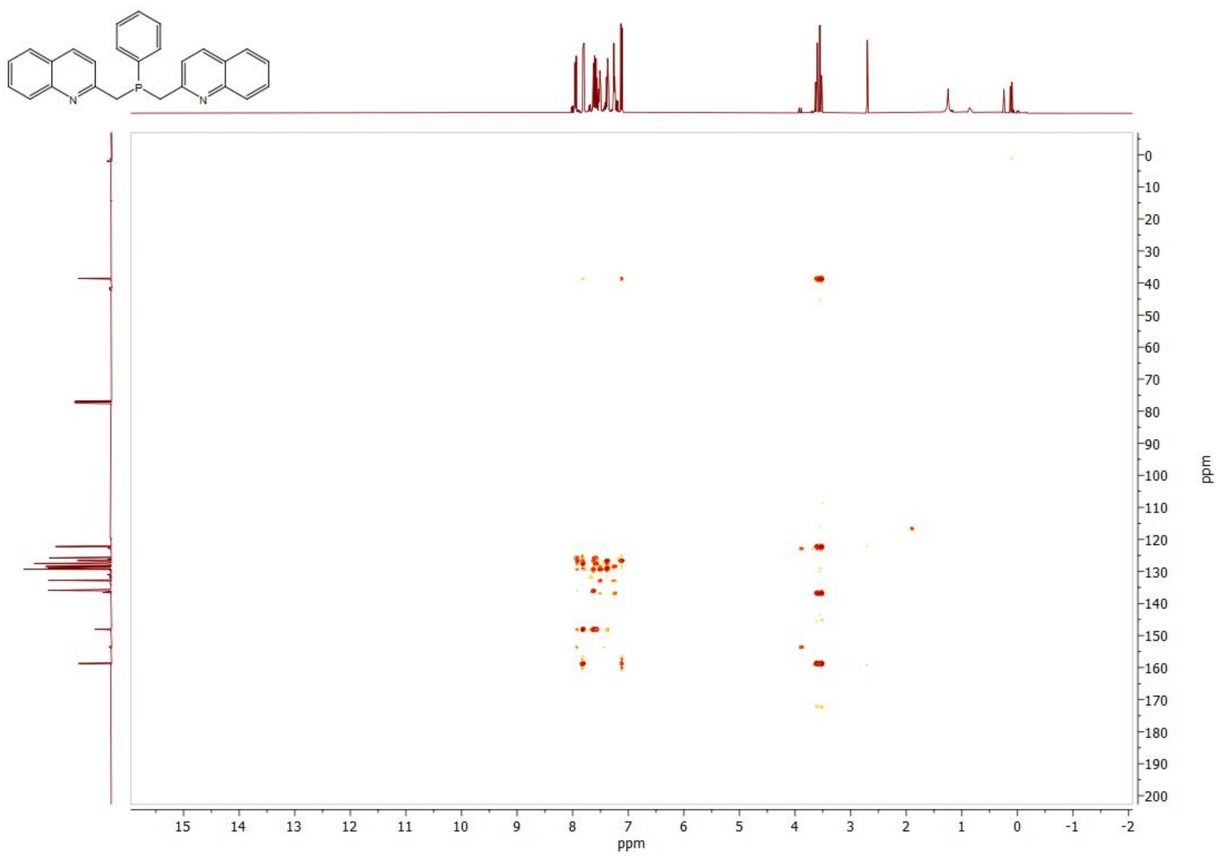
^{13}C NMR of **1** in $CDCl_3$, 100.623 MHz.



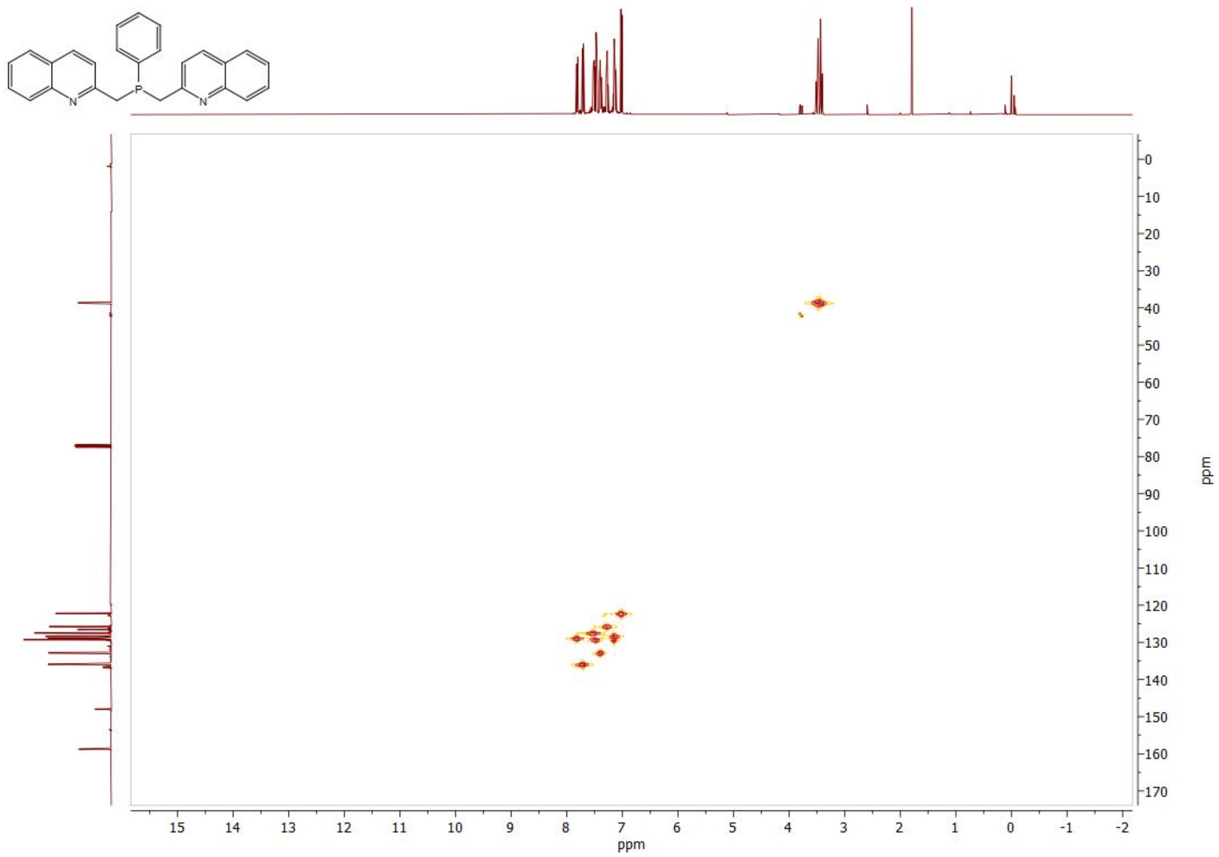
$^{1}H,^{1}H$–COSY$_{45}$ of **1** in $CDCl_3$



$^{1}H,^{13}C$–HMBC of **1** in $CDCl_3$

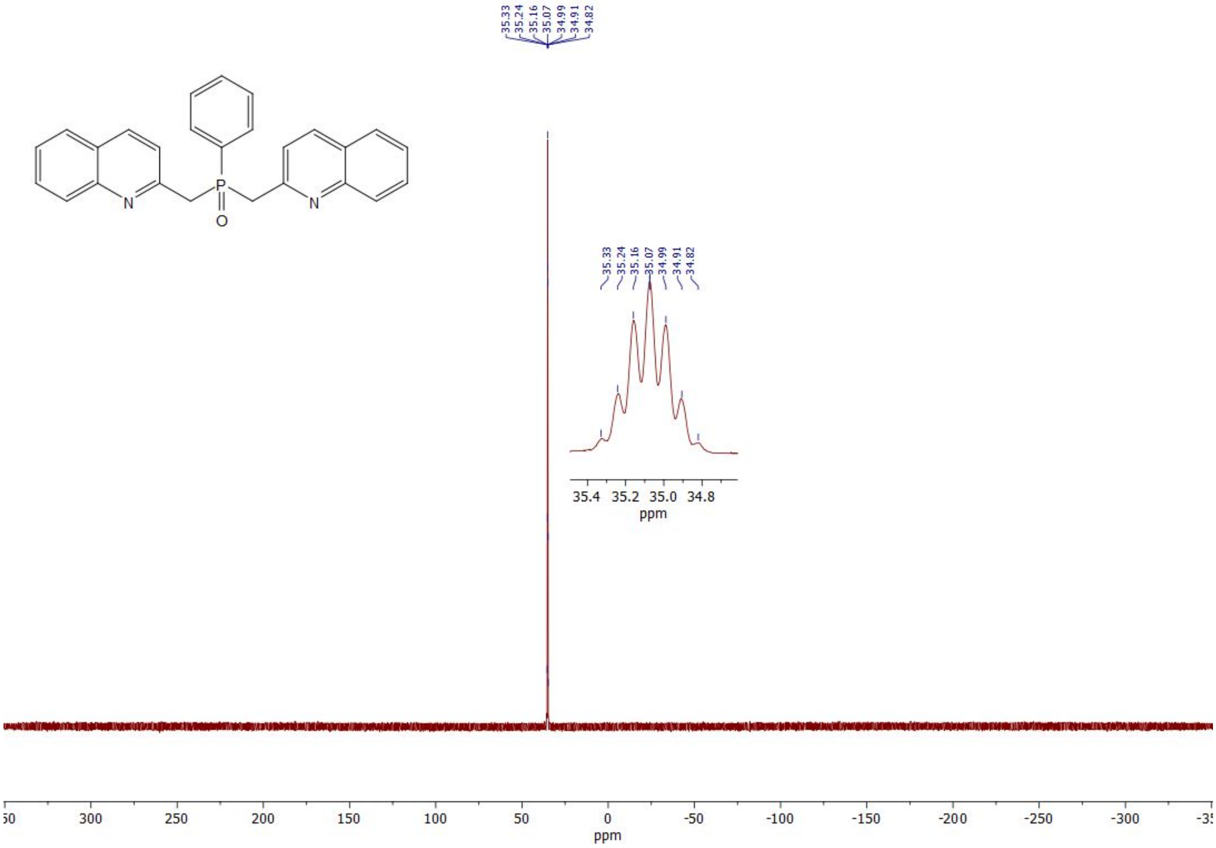


$^{1}H,^{13}C$–HMQC of **1** in $CDCl_3$

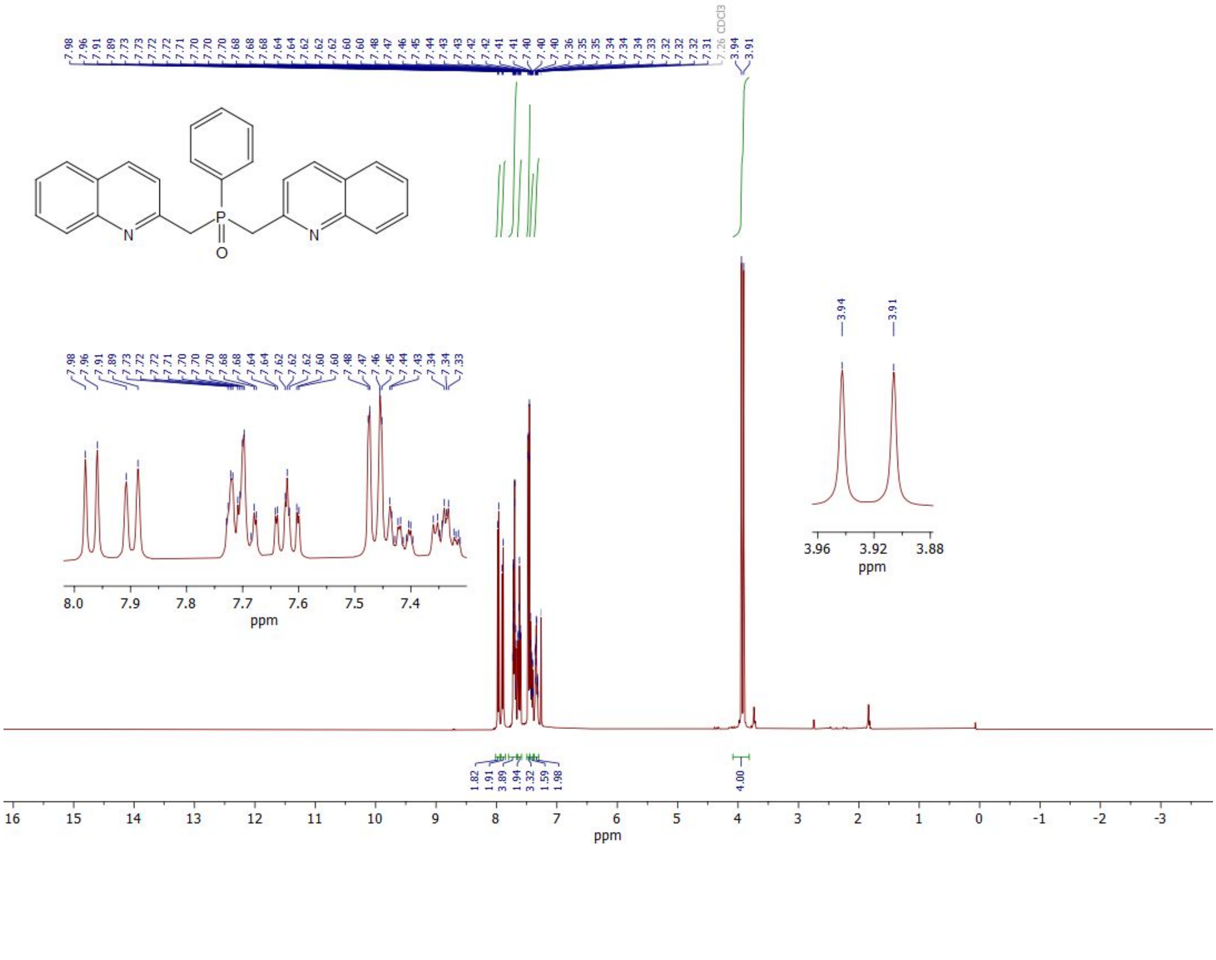


$^{31}P\{^{1}H\}$ NMR of **2** in $CDCl_3$, 161.976 MHz.

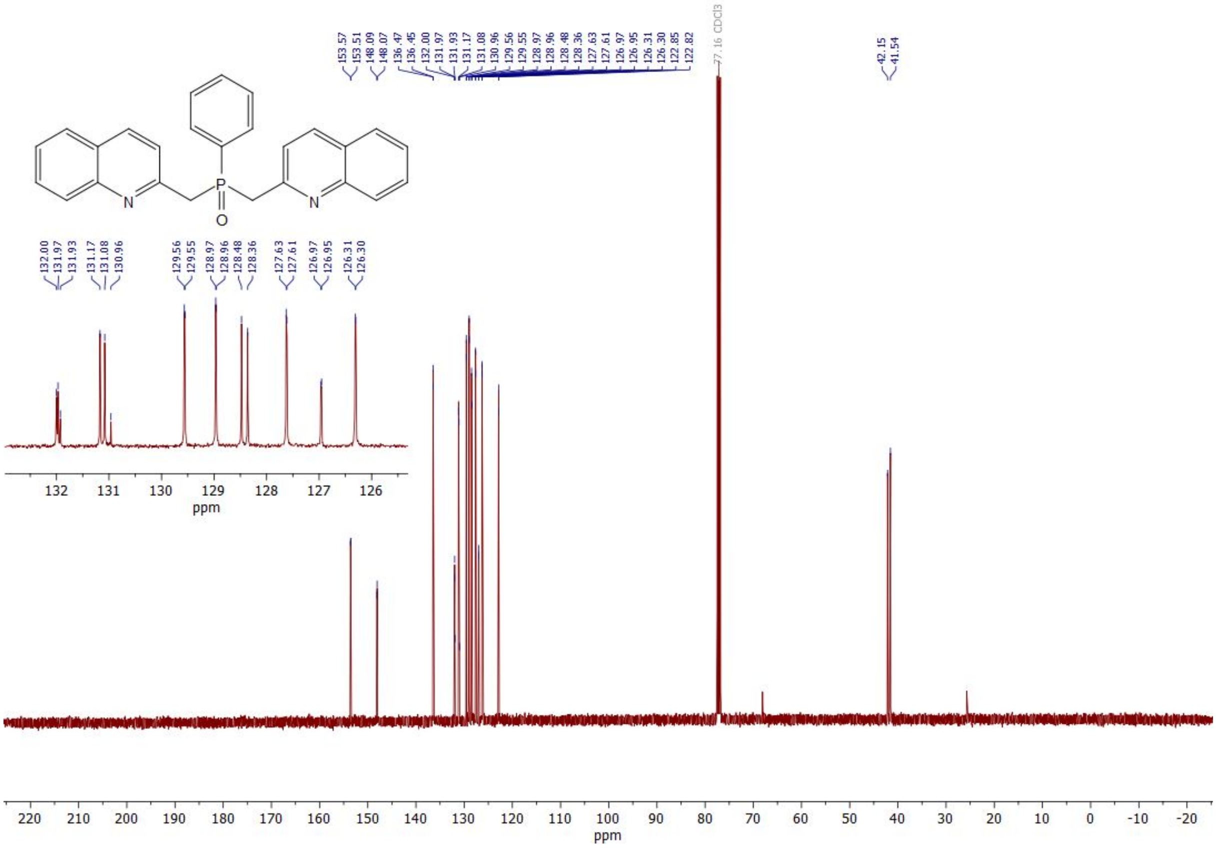
$^{31}P\{/\}$ NMR of **2** in $CDCl_3$, 161.976 MHz.



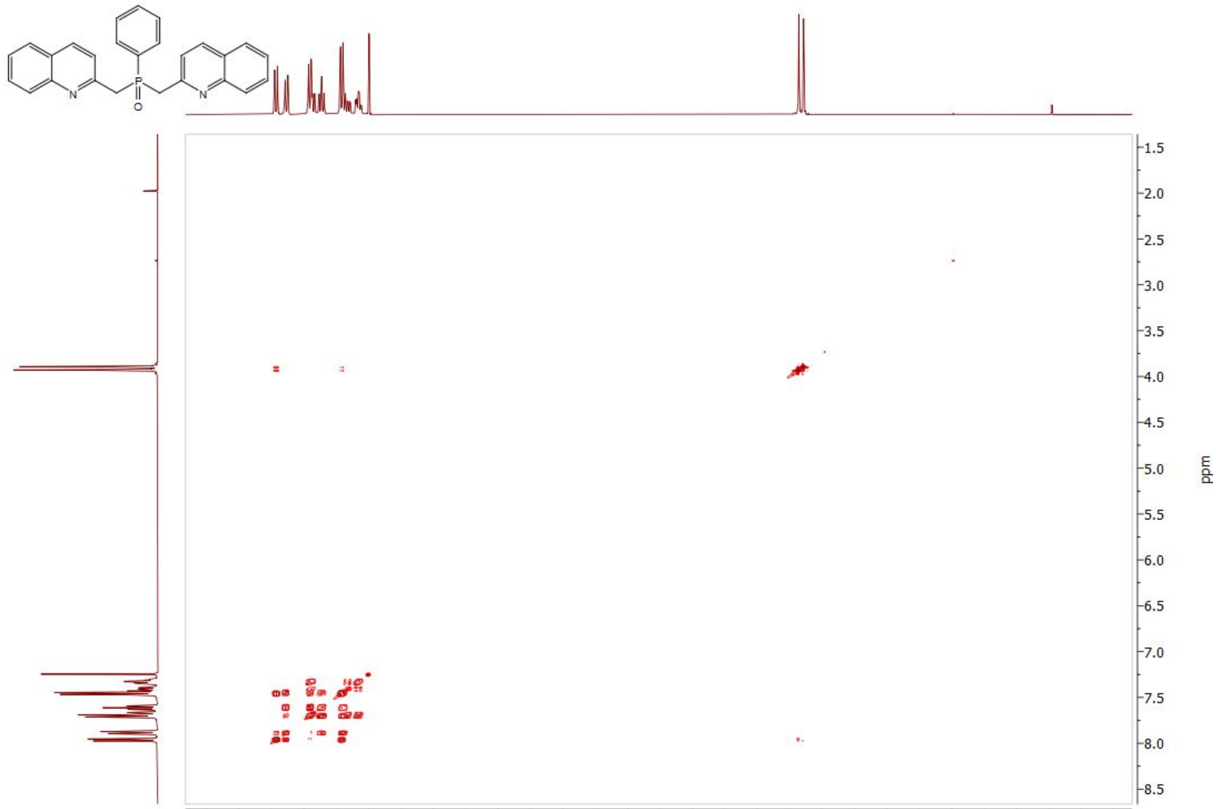
^{1}H NMR of **2** in $CDCl_3$, 400.133 MHz.



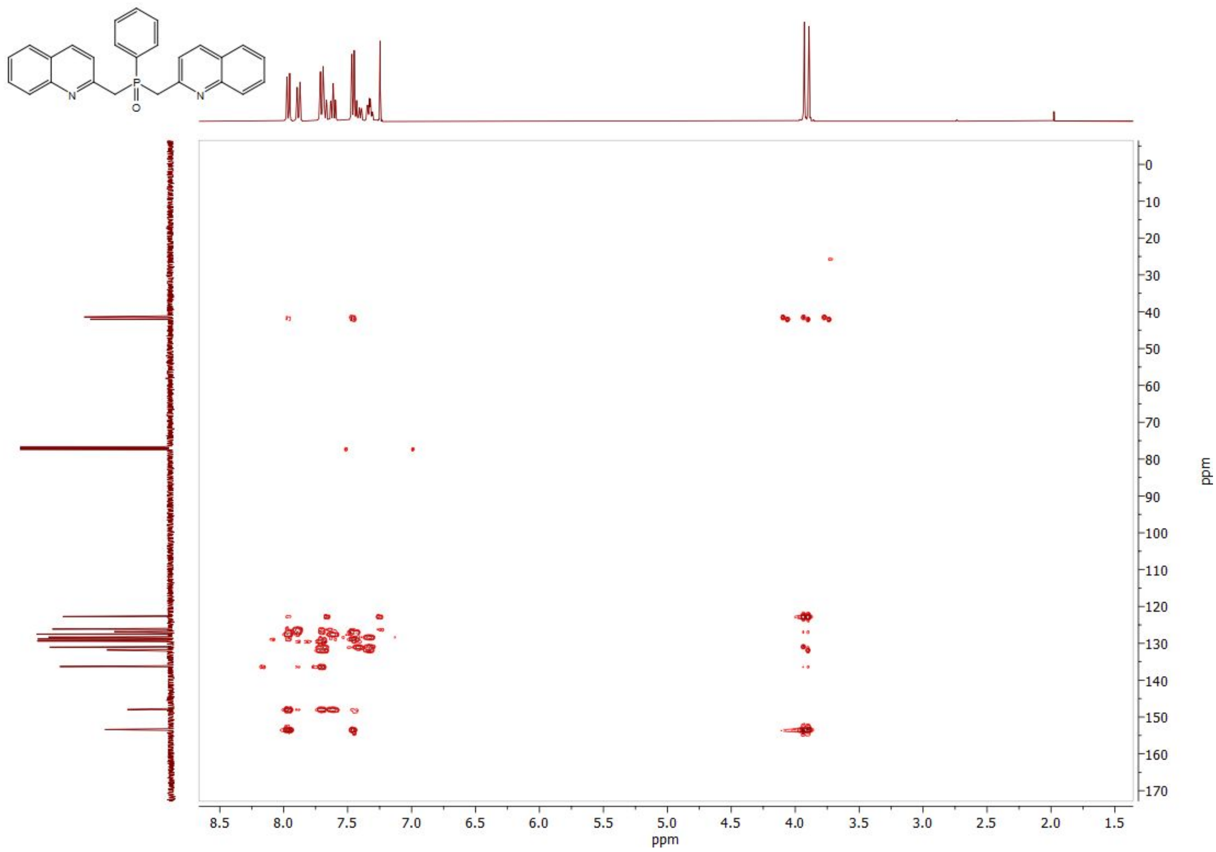
^{13}C NMR of **2** in $CDCl_3$, 100.623 MHz.



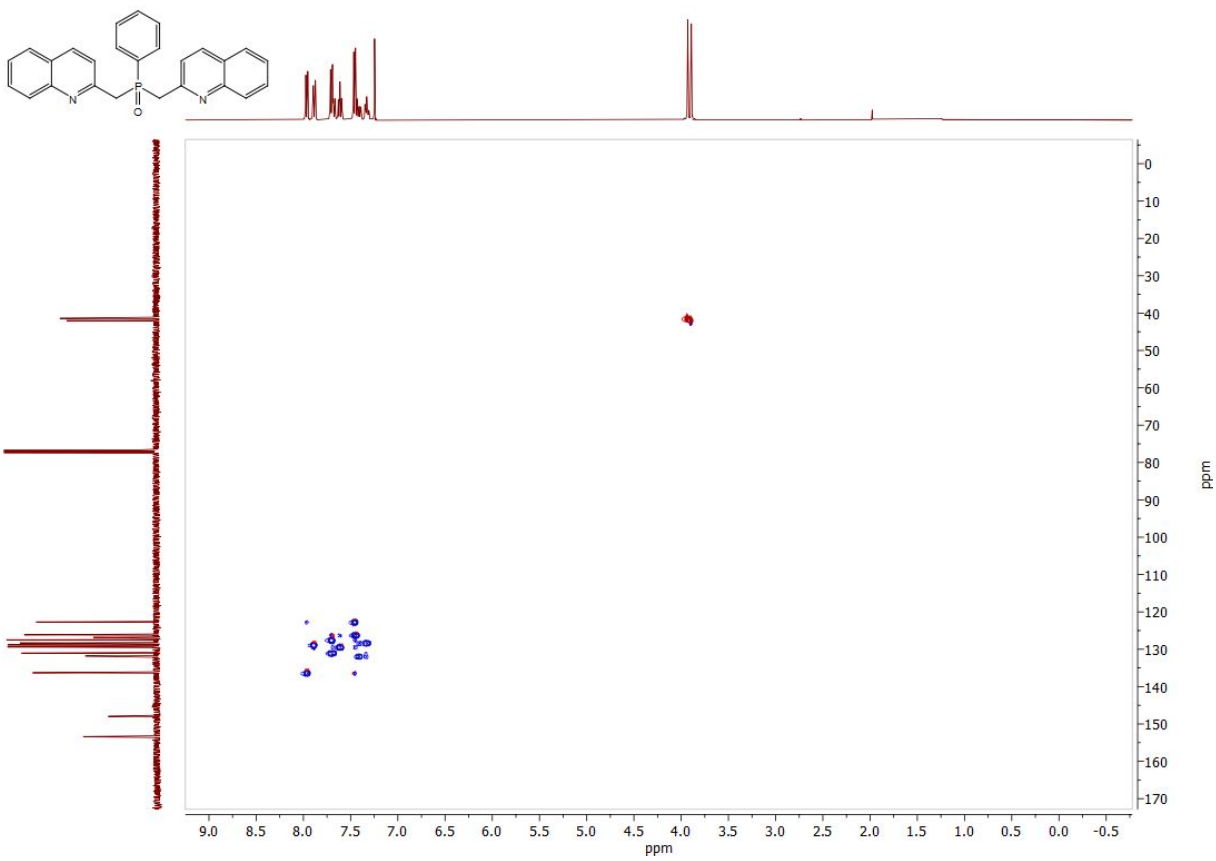
$^{1}H,^{1}H$–$COSY_{45}$ of **2** in $CDCl_3$



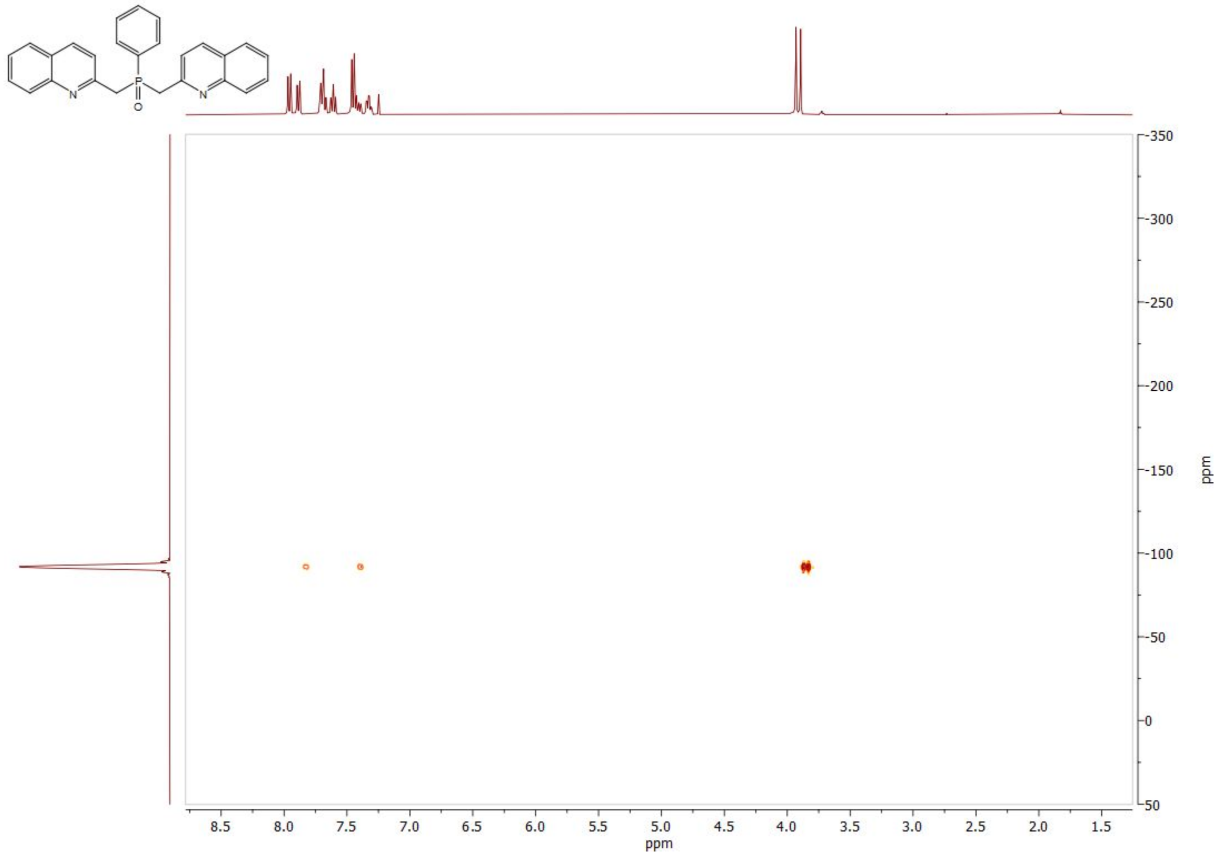
$^{1}H,^{13}C$–HMBC of **2** in $CDCl_3$



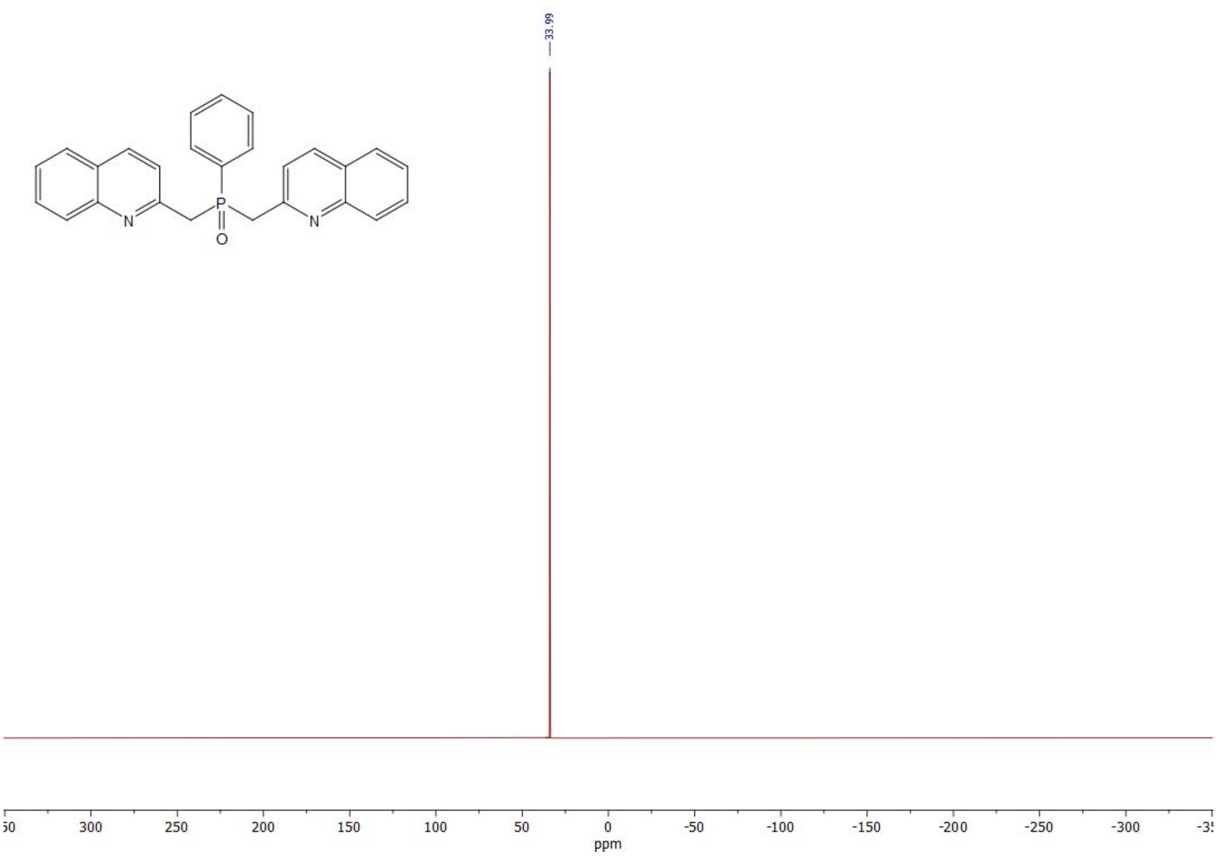
$^{1}H,^{13}C$–HSQC of **2** in $CDCl_3$



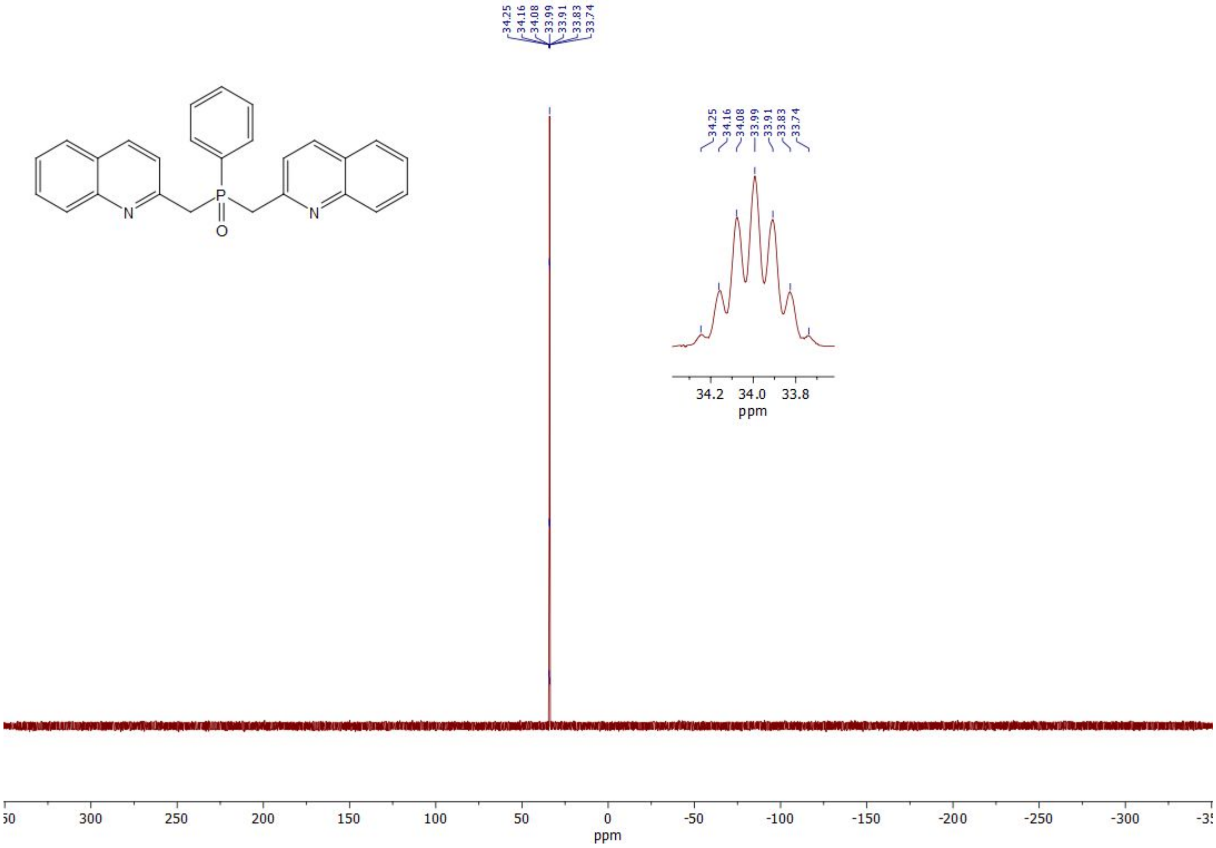
$^{1}H,^{15}N$–HMBC of **2** in $CDCl_3$



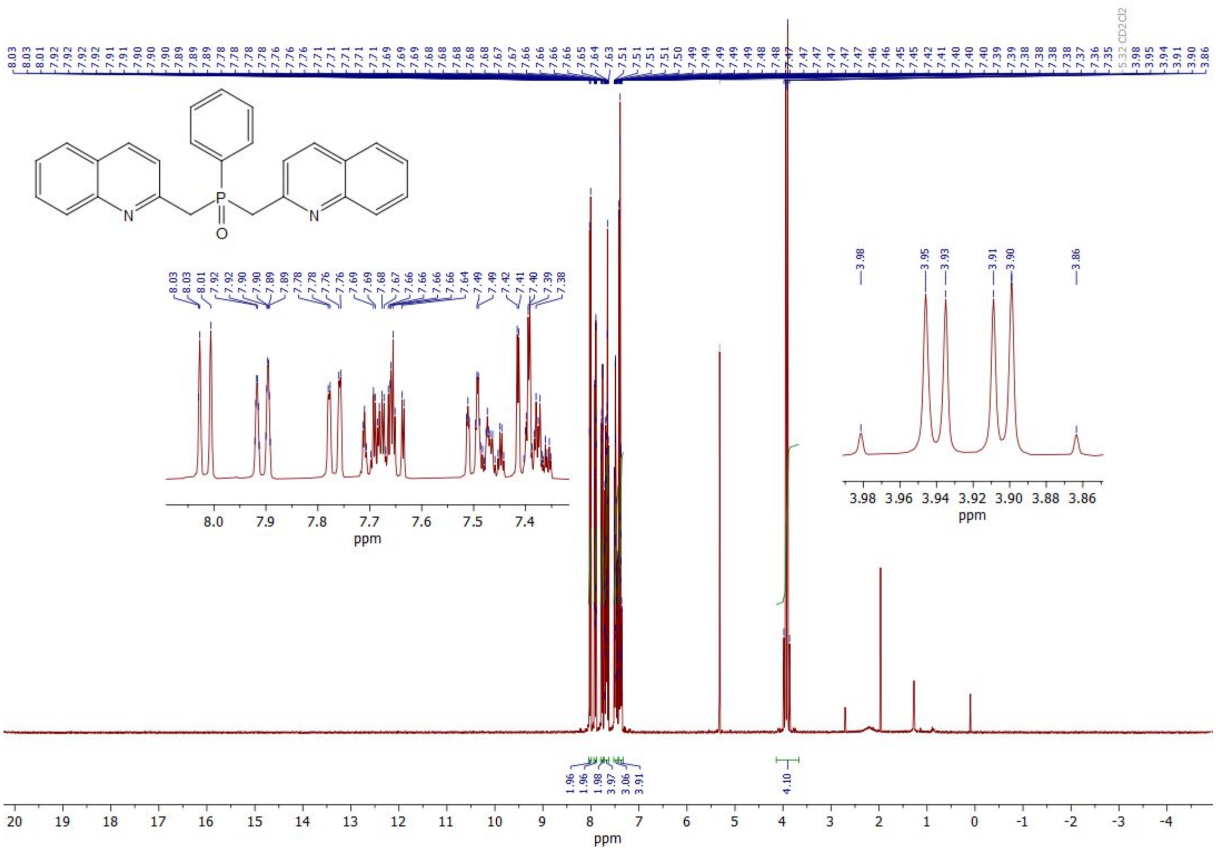
$^{31}P\{^{1}H\}$ NMR of **2** in CD_2Cl_2, 161.976 MHz.



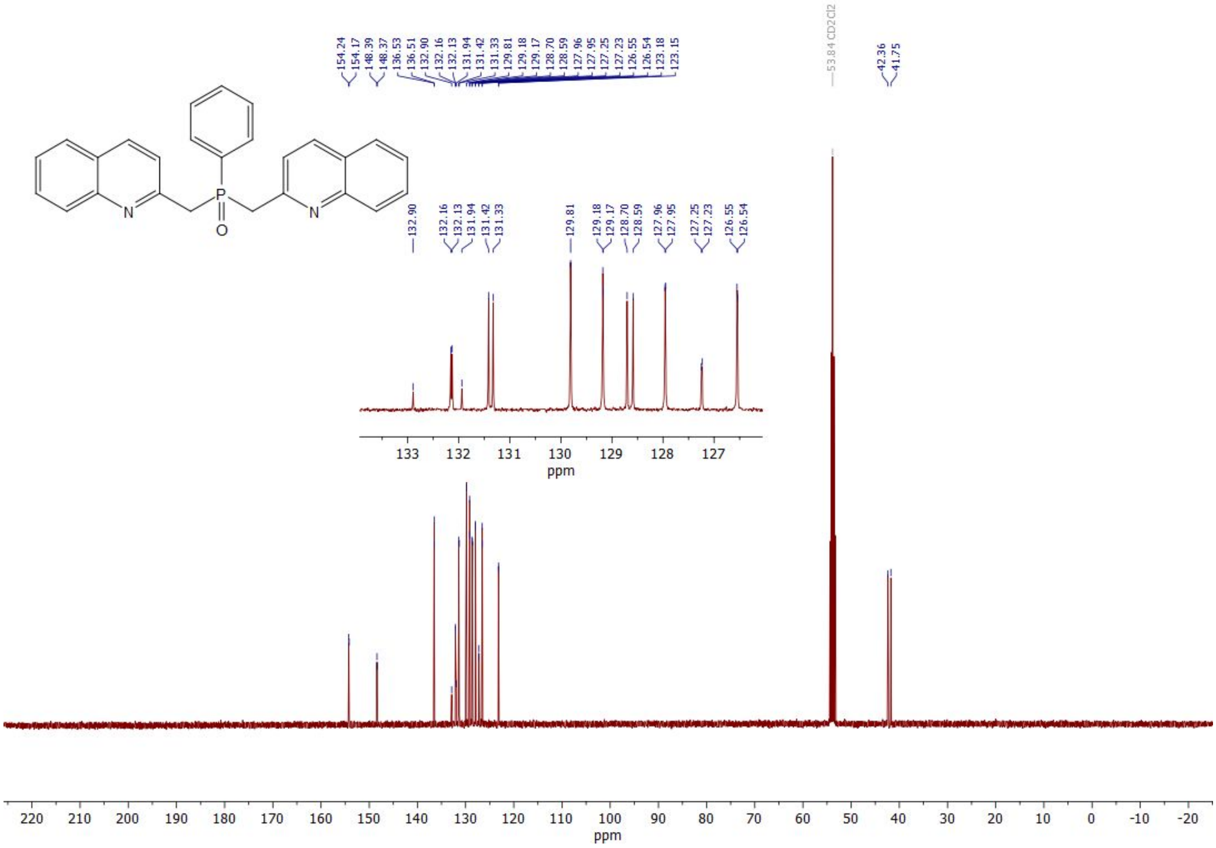
$^{31}P\{/\}$ NMR of **2** in CD_2Cl_2, 161.976 MHz.



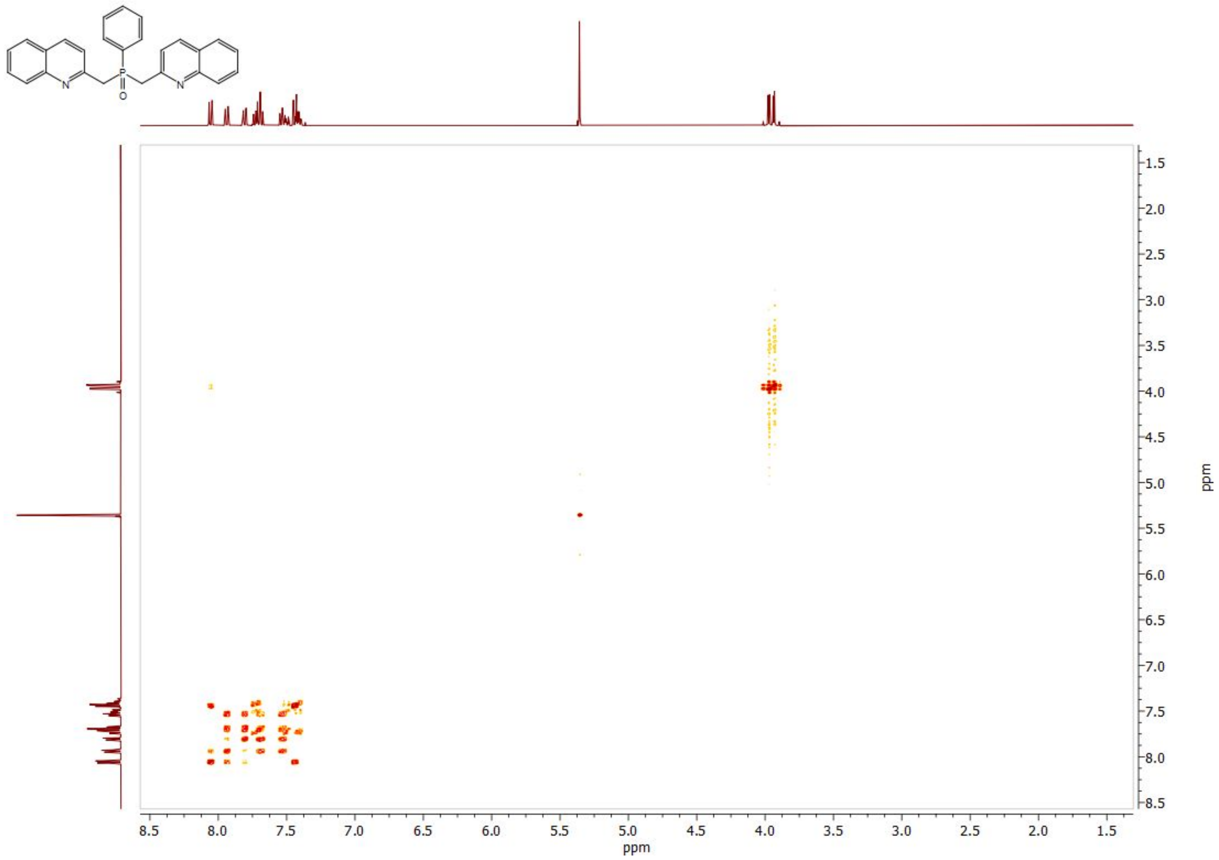
^{1}H NMR of **2** in CD_2Cl_2, 400.133 MHz.



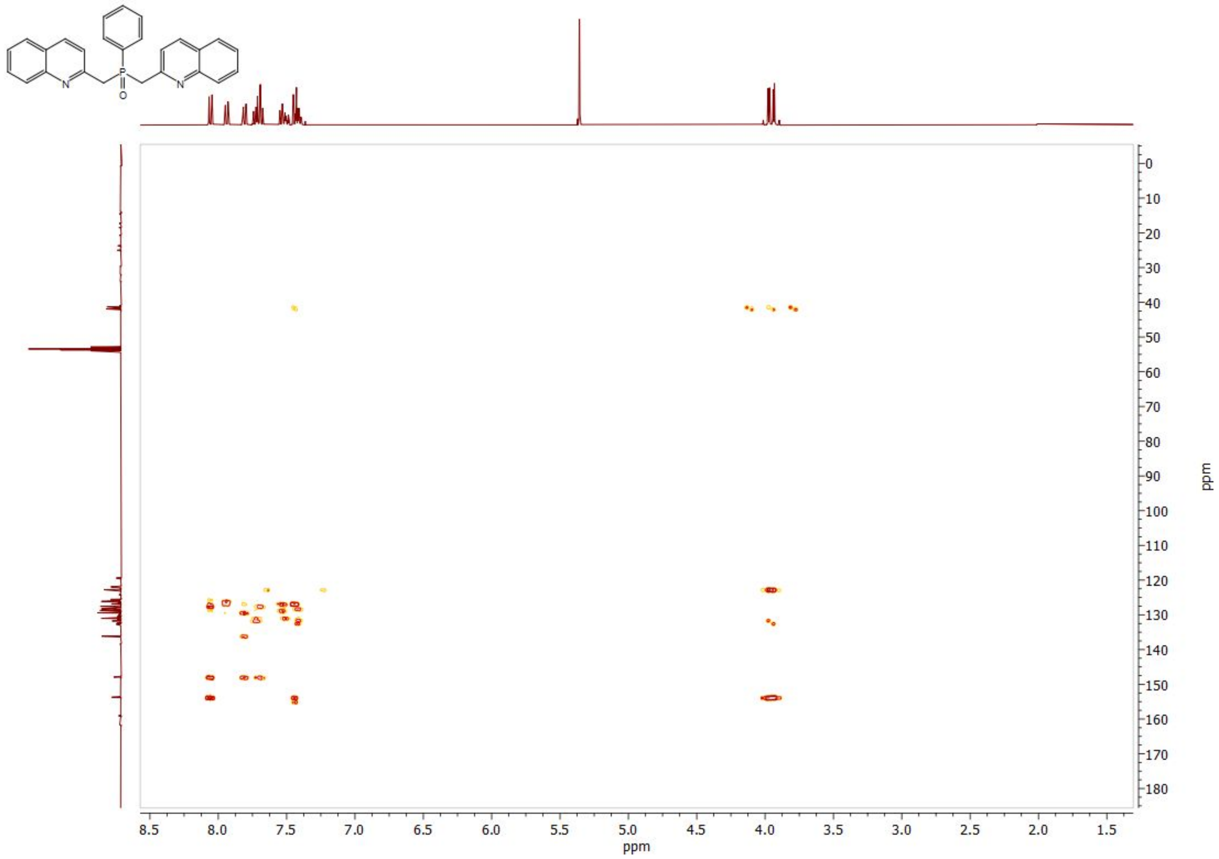
^{13}C NMR of **2** in CD_2Cl_2, 100.623 MHz.



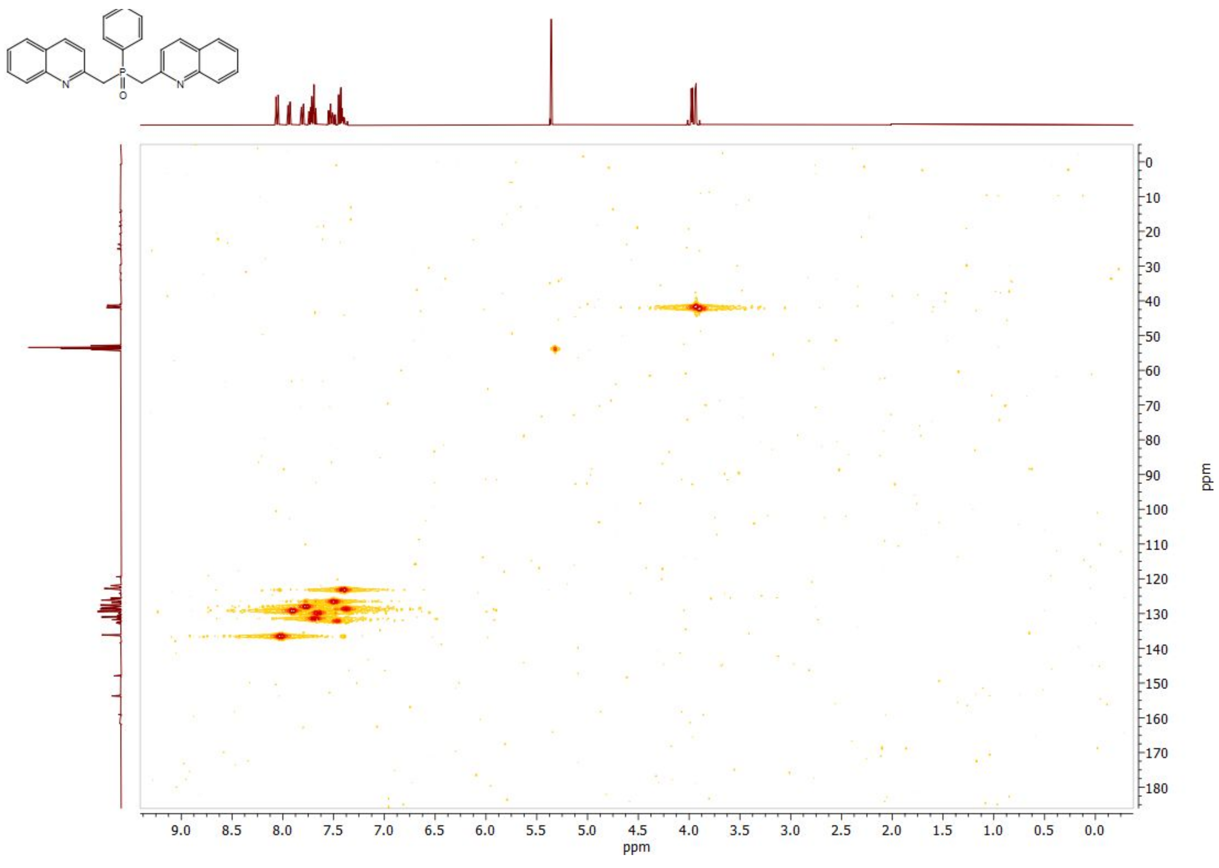
$^{1}H,^{1}H$–$COSY_{45}$ of **2** in CD_2Cl_2



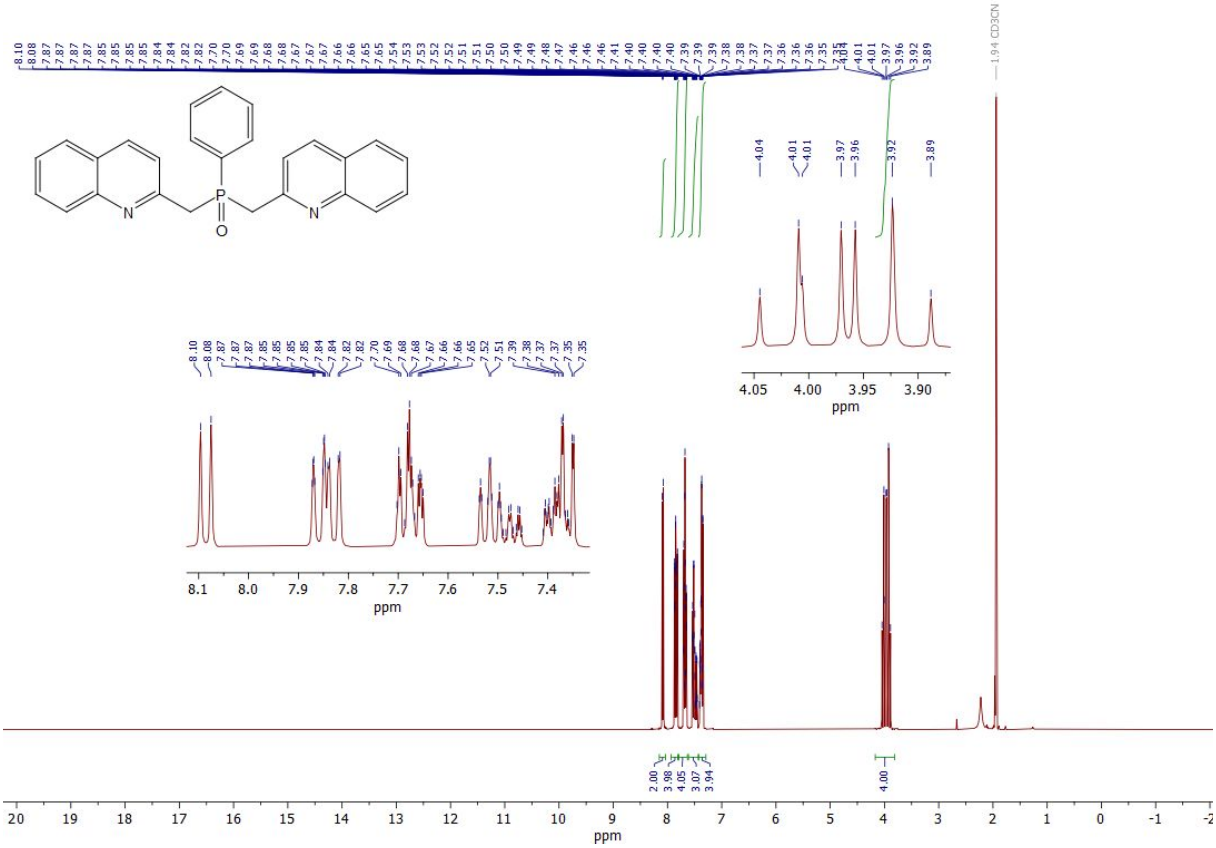
$^{1}H,^{13}C$–HMBC of **2** in CD_2Cl_2



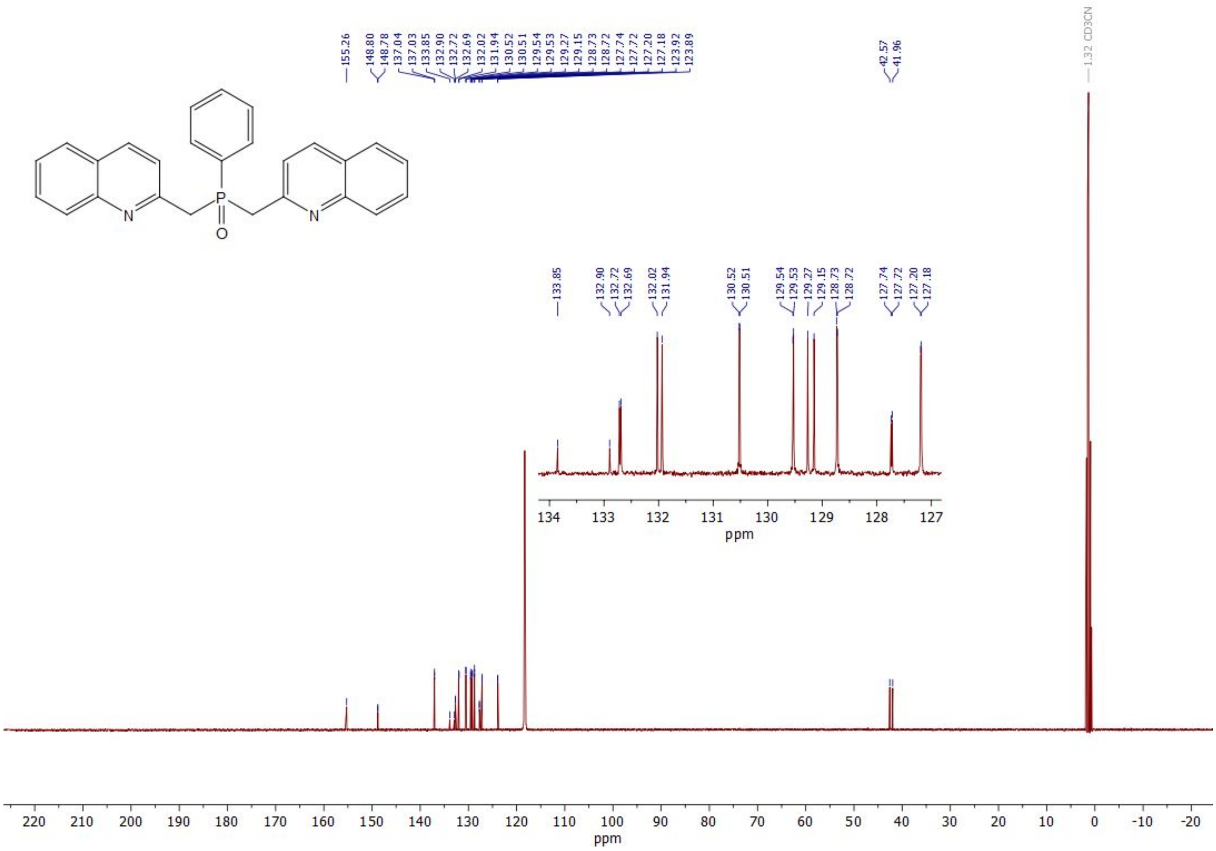
$^{1}H,^{13}C$–HSQC of **2** in CD_2Cl_2



^{1}H NMR of **2** in CD_3CN, 400.133 MHz.

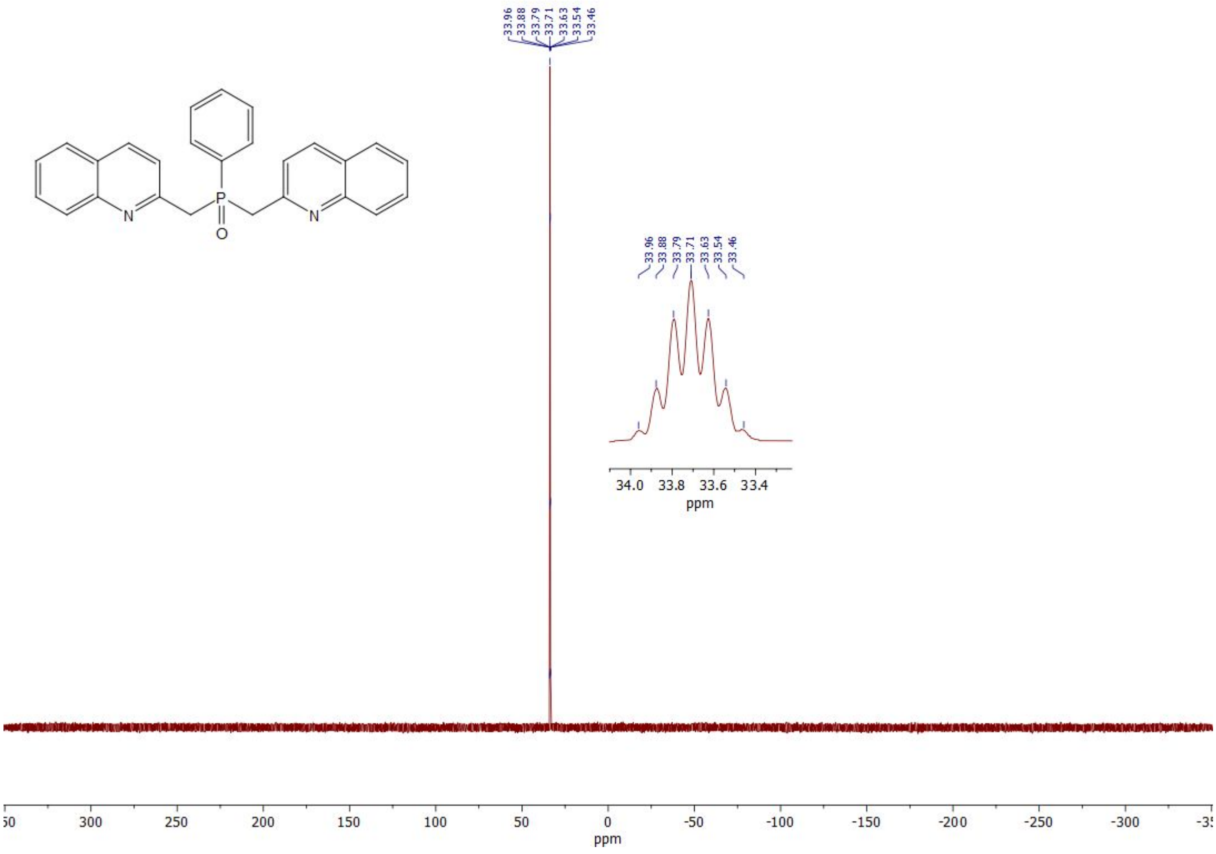


^{13}C NMR of **2** in CD_3CN, 100.623 MHz.

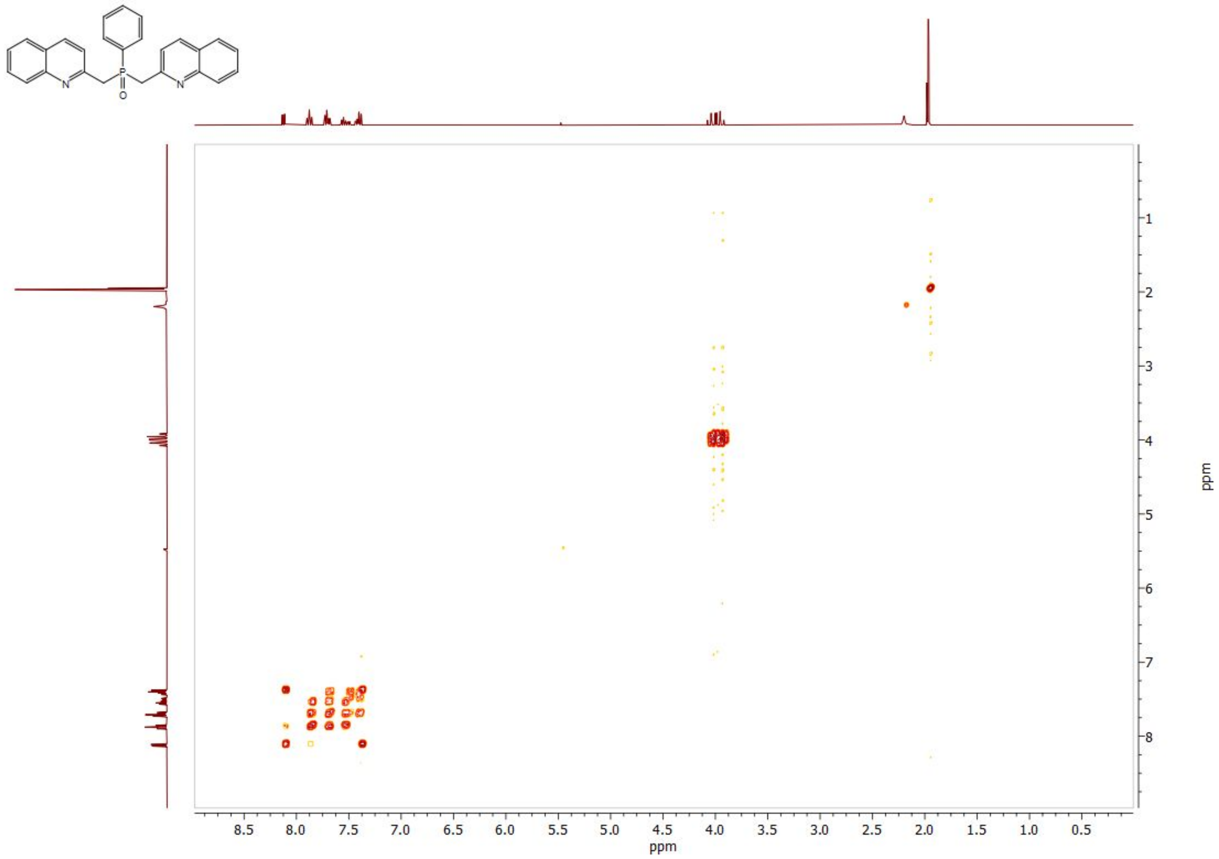


$^{31}P\{^1H\}$ NMR of **2** in CD_3CN, 161.976 MHz.

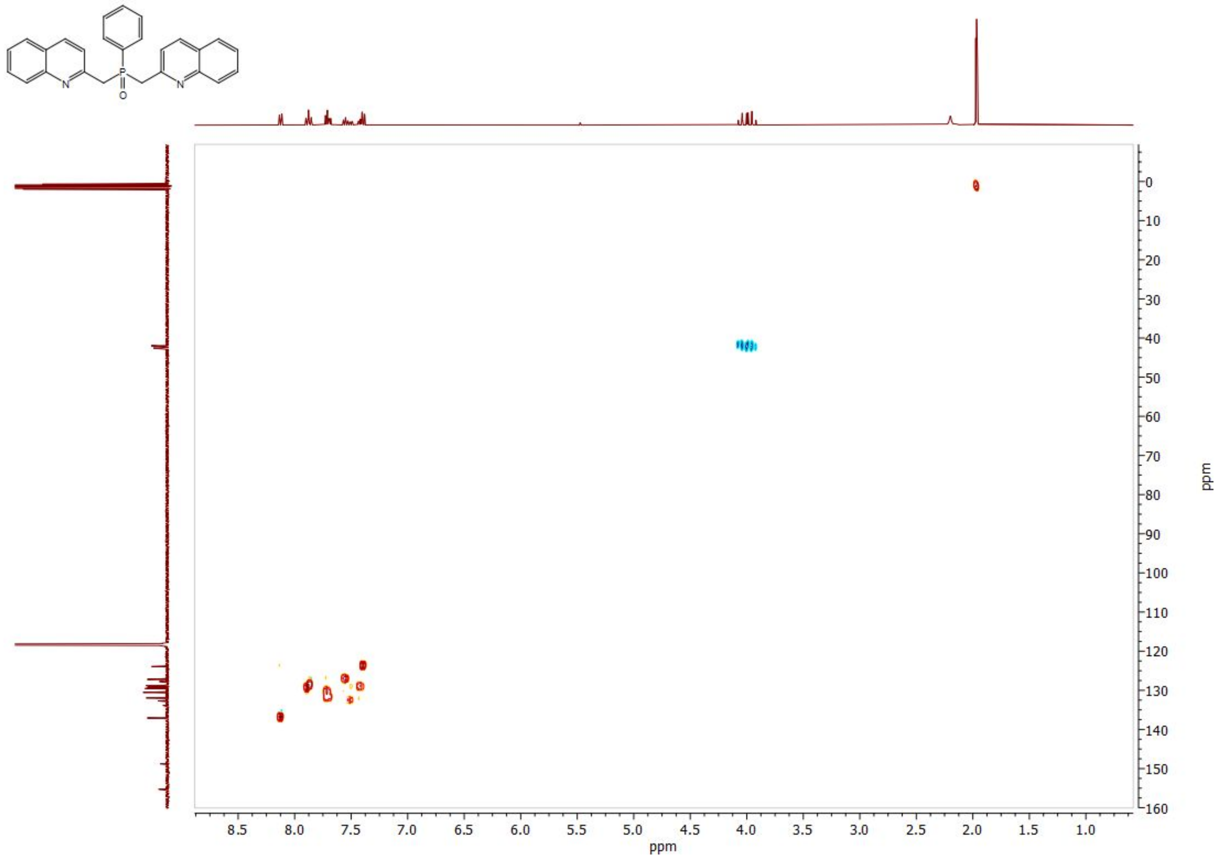
$^{31}P\{/\}$ NMR of **2** in CD_3CN, 161.976 MHz.



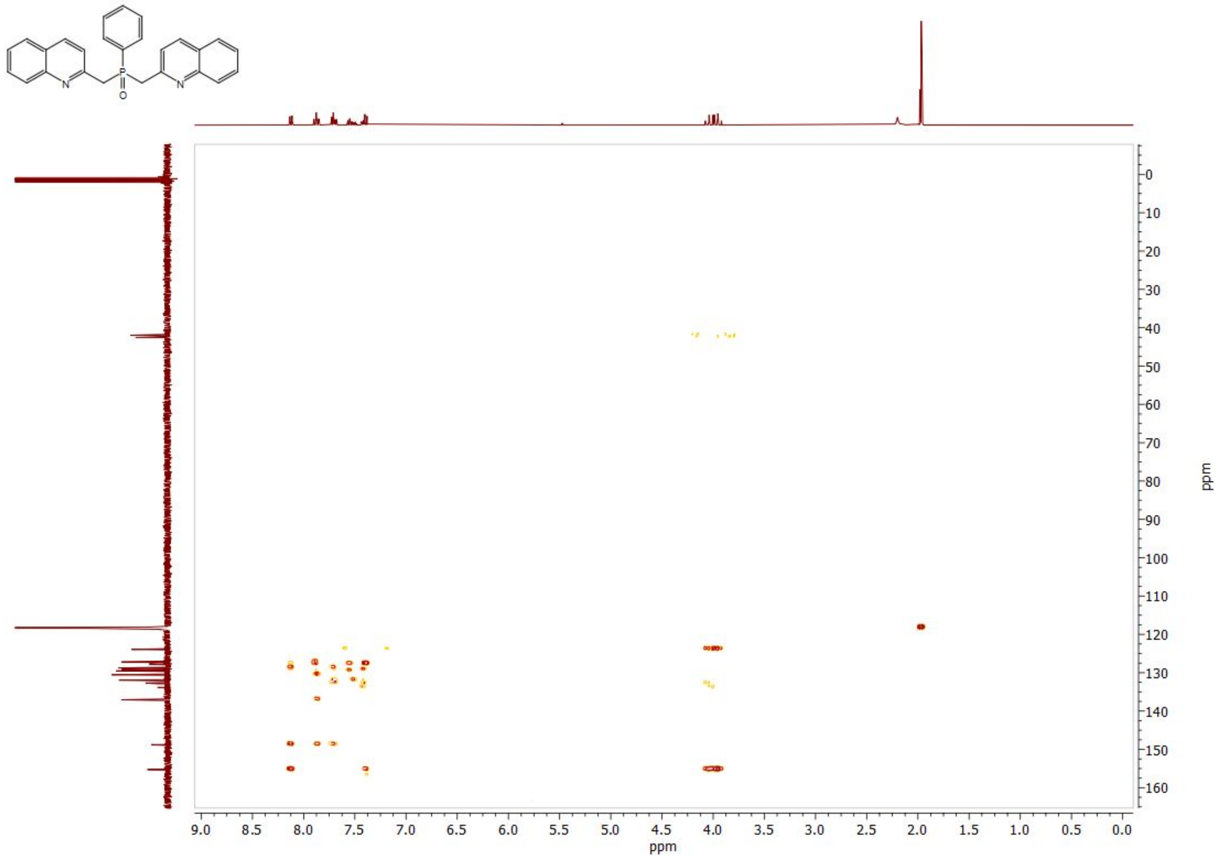
$^{1}H,^{1}H$–COSY$_{45}$ of **2** in CD_3CN



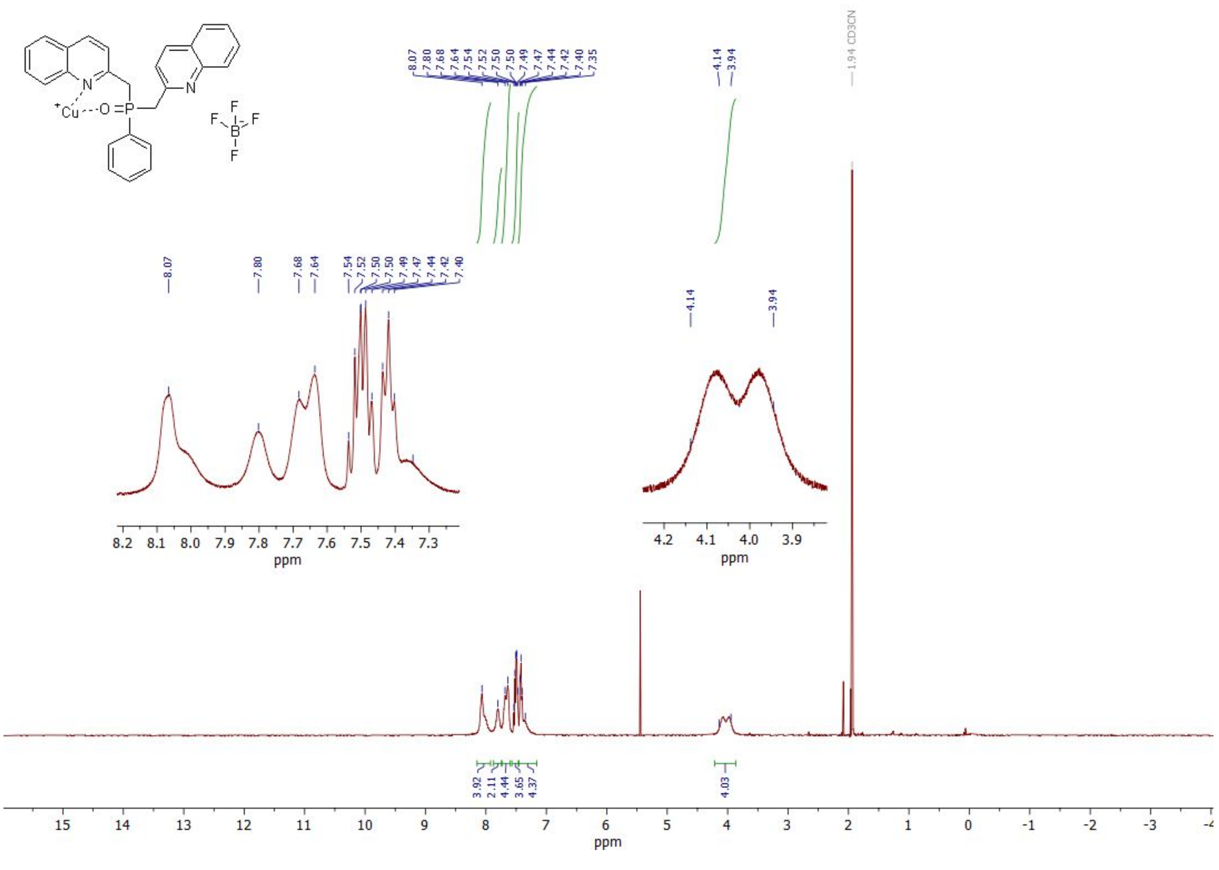
$^{1}H,^{13}C$–HSQC-AIDA of **2** in CD_3CN



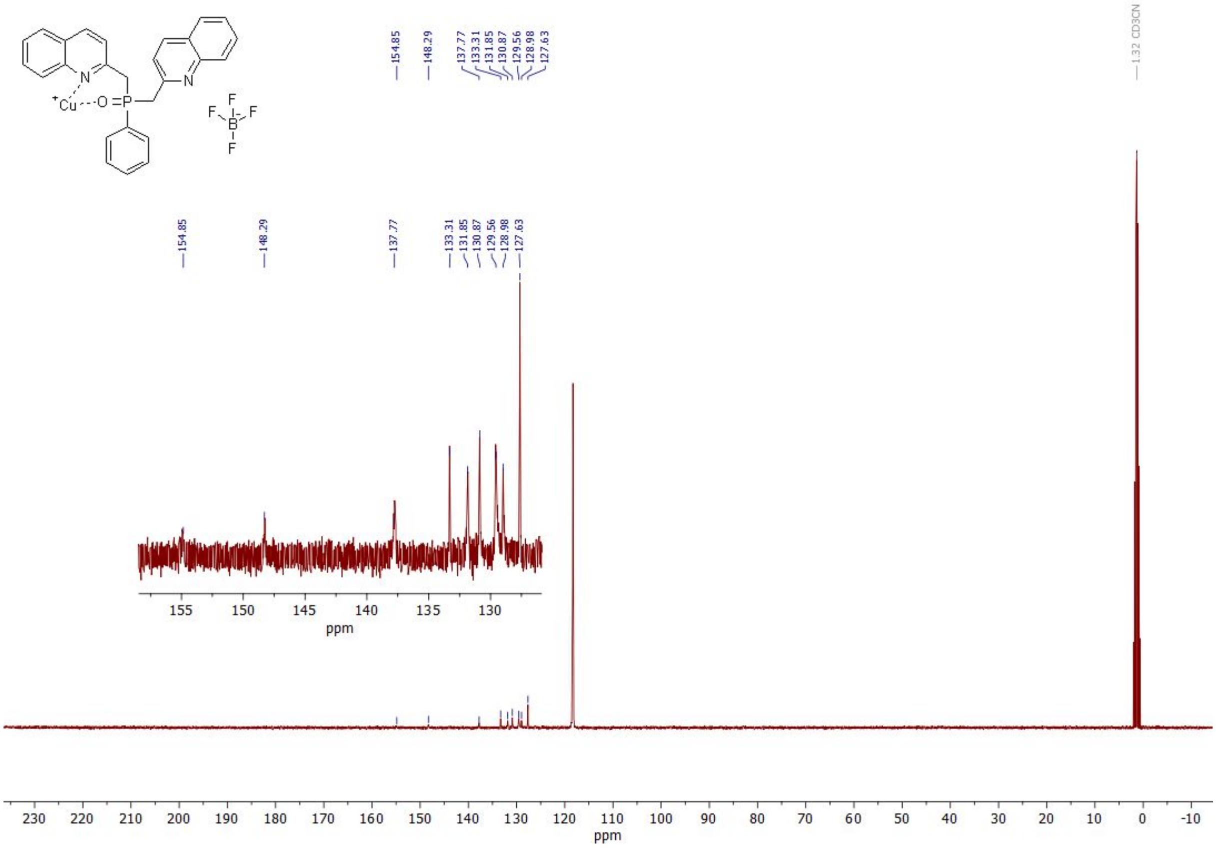
$^{1}H,^{13}C$–HMBC of **2** in CD_3CN



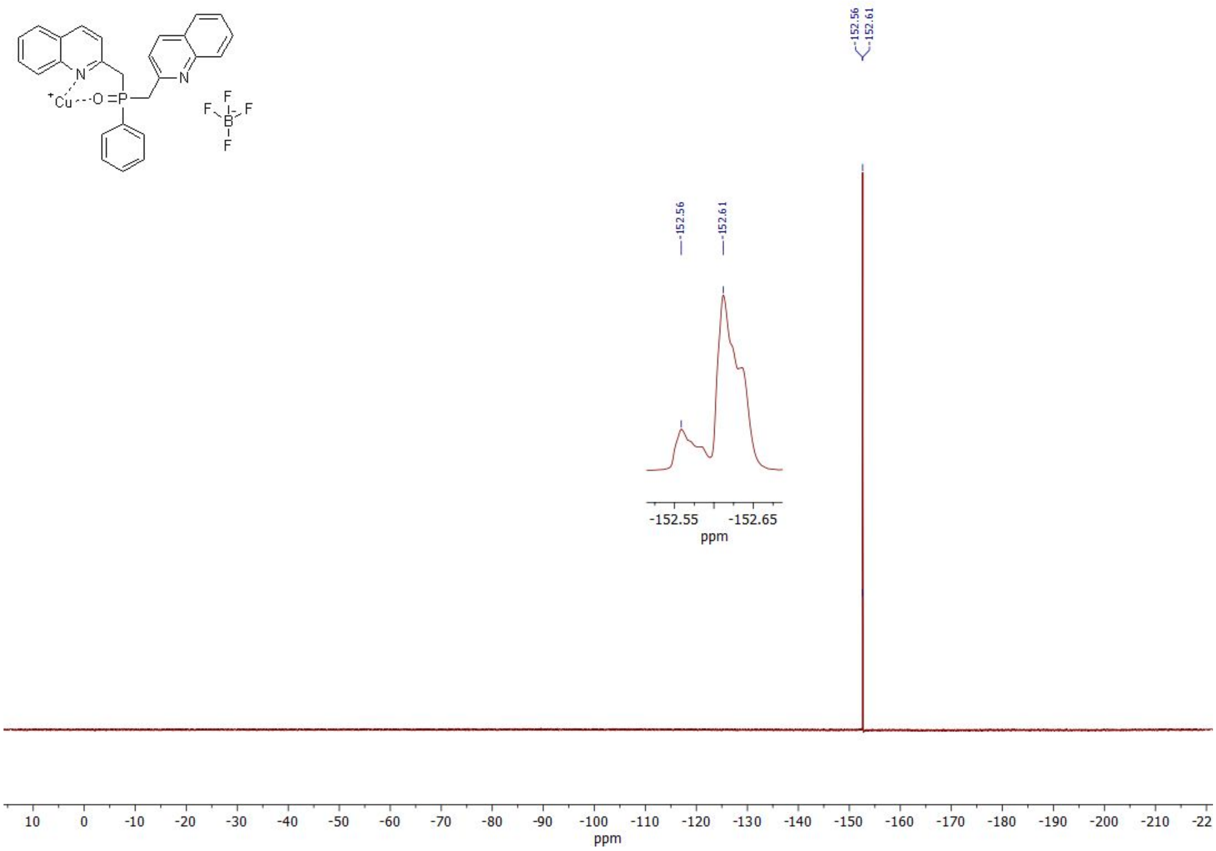
^{1}H NMR of **3** in CD_3CN, 400.133 MHz.



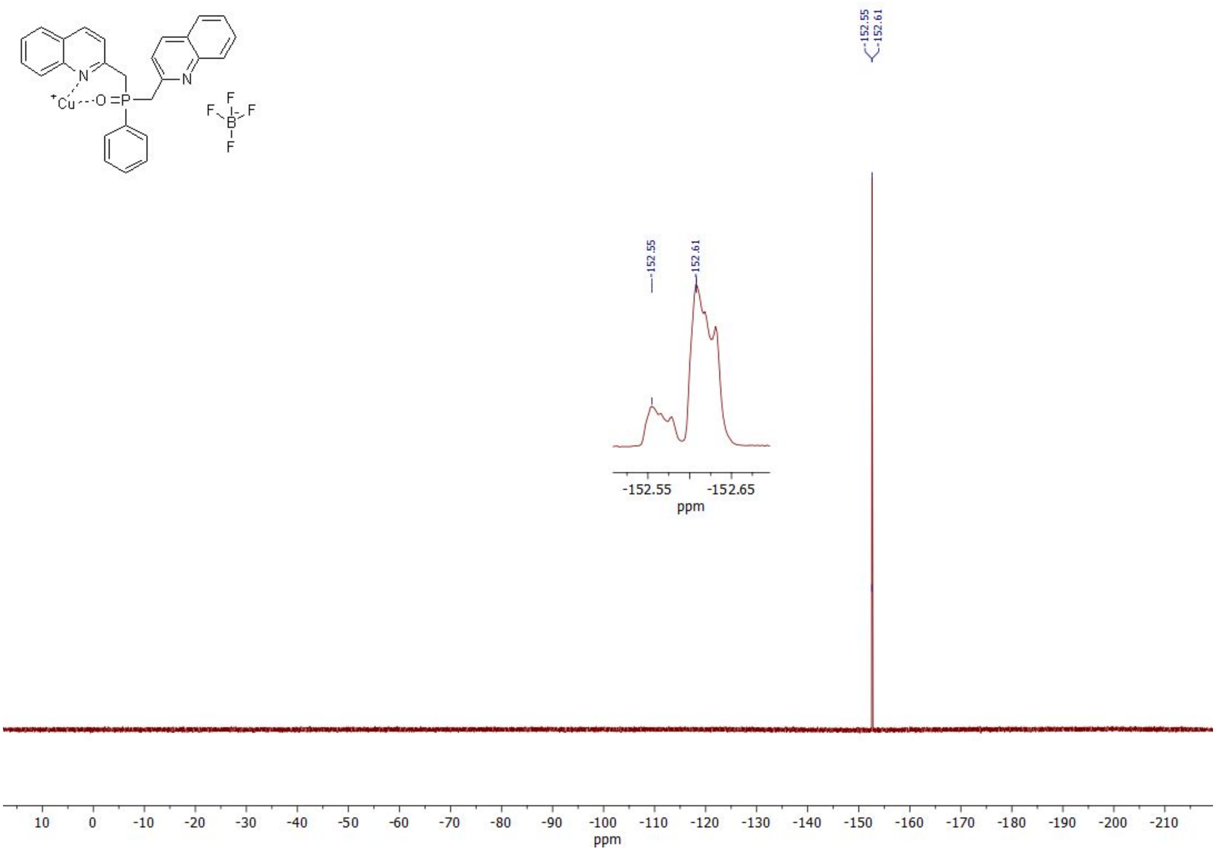
^{13}C NMR of **3** in CD_3CN, 100.623 MHz.



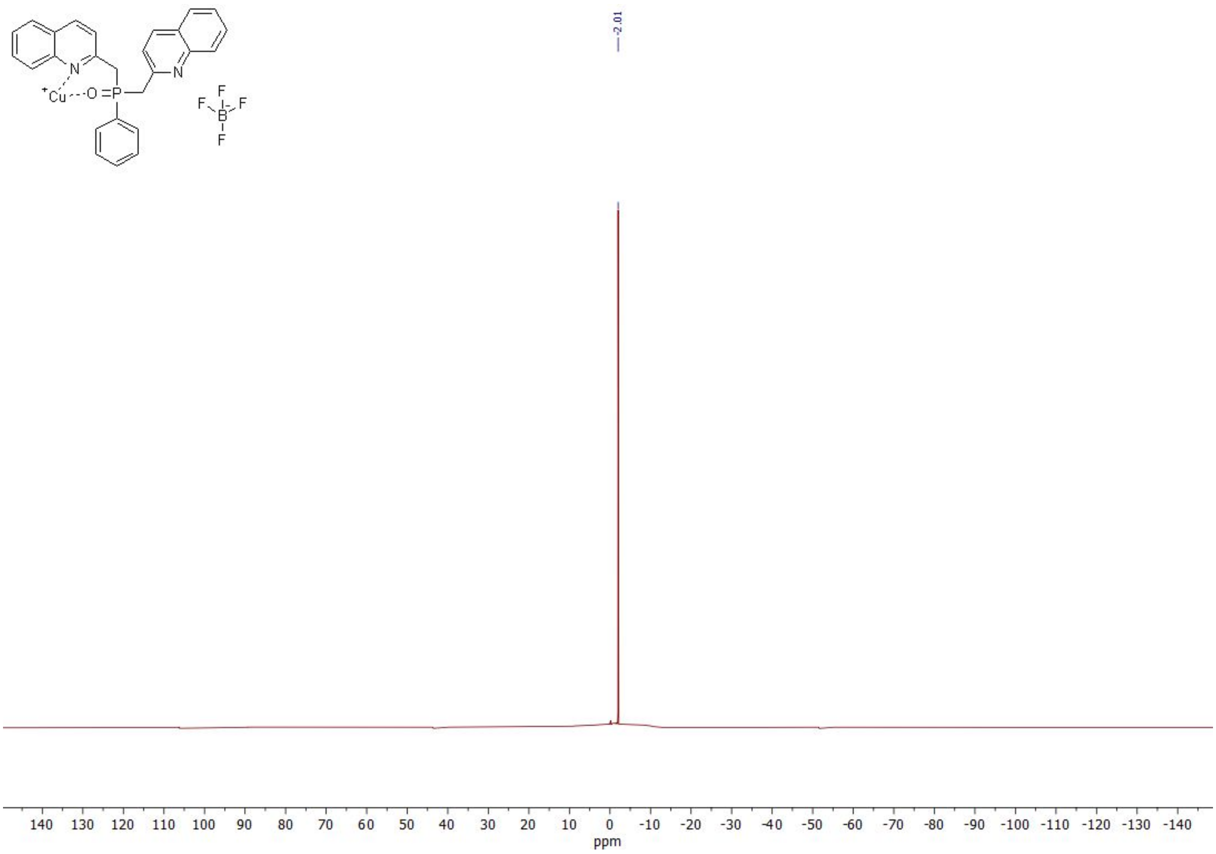
$^{19}F\{^1H\}$ NMR of **3** in CD_3CN, 376.508 MHz.



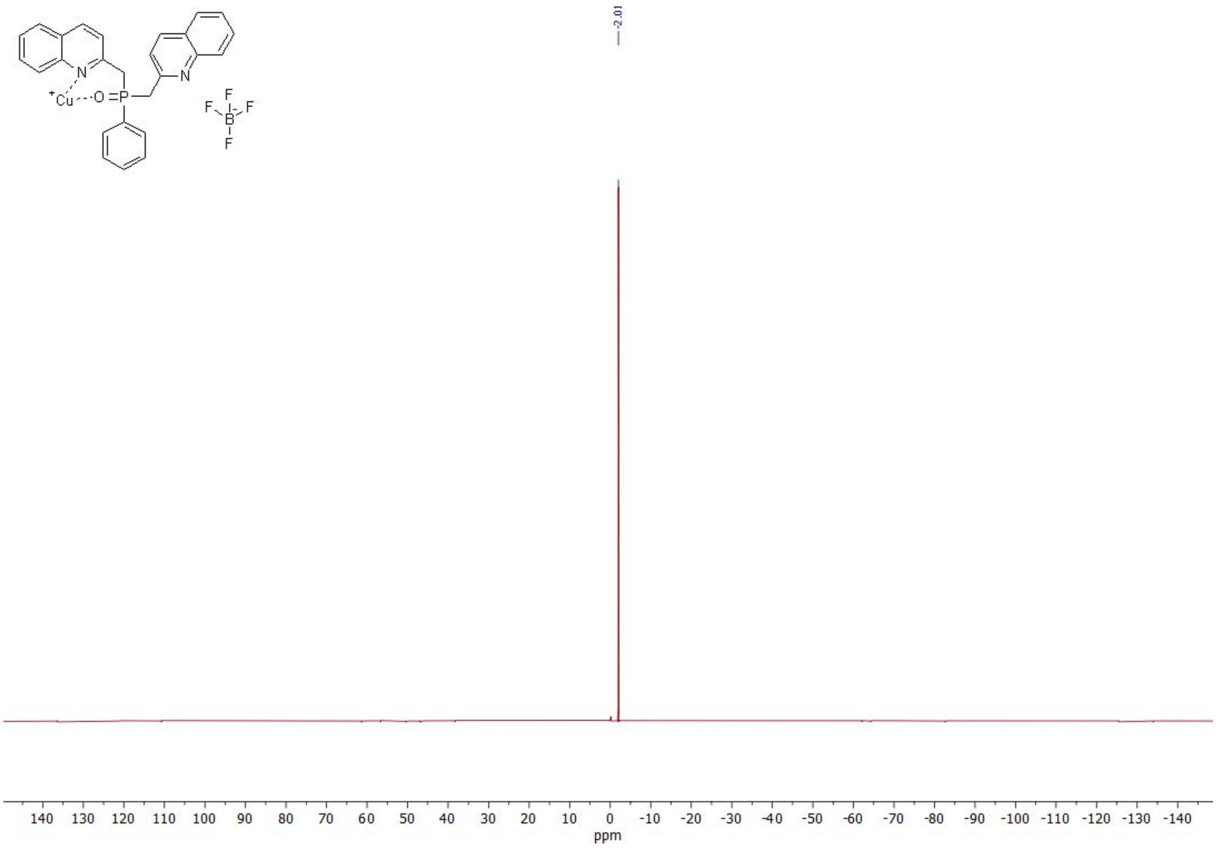
$^{19}F\{/\}$ NMR of **3** in CD_3CN, 376.508MHz.



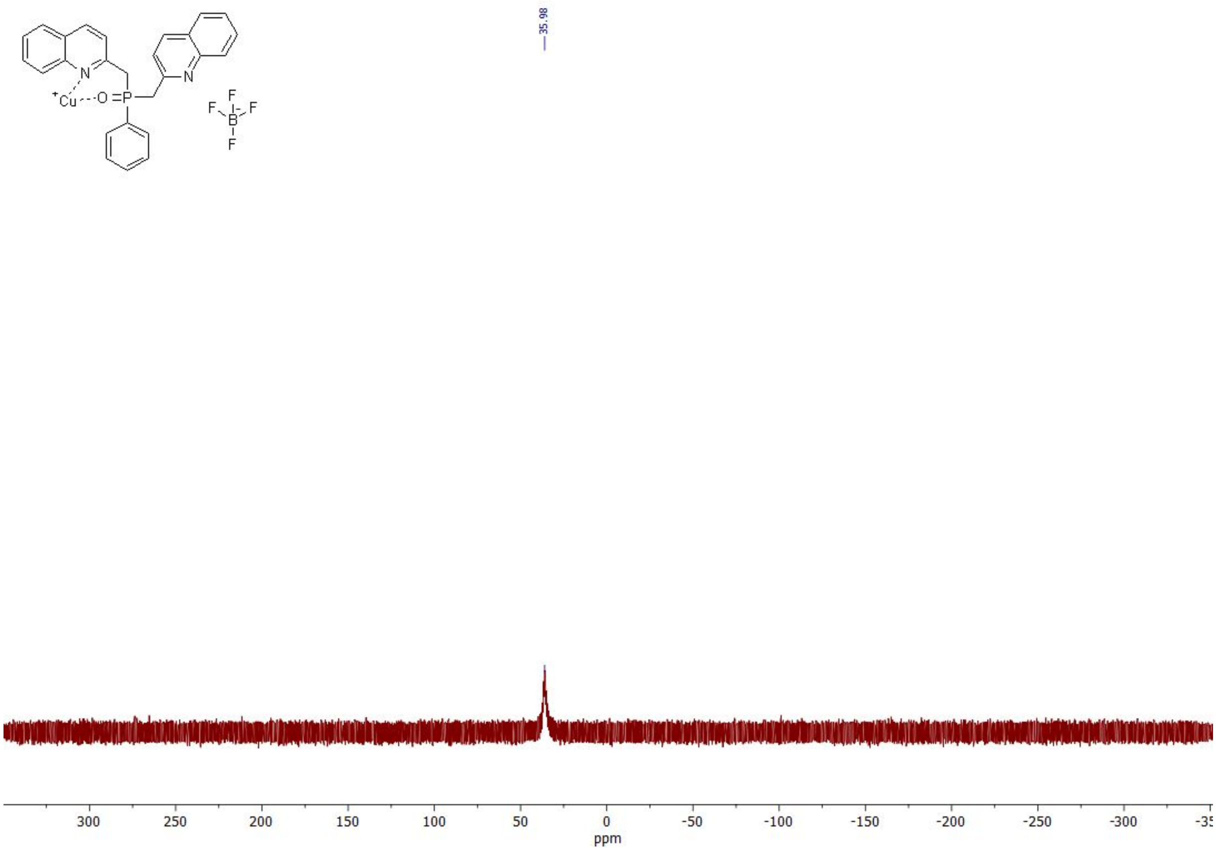
$^{11}B\{^1H\}$ NMR of **3** in CD_3CN, 128.394 MHz.



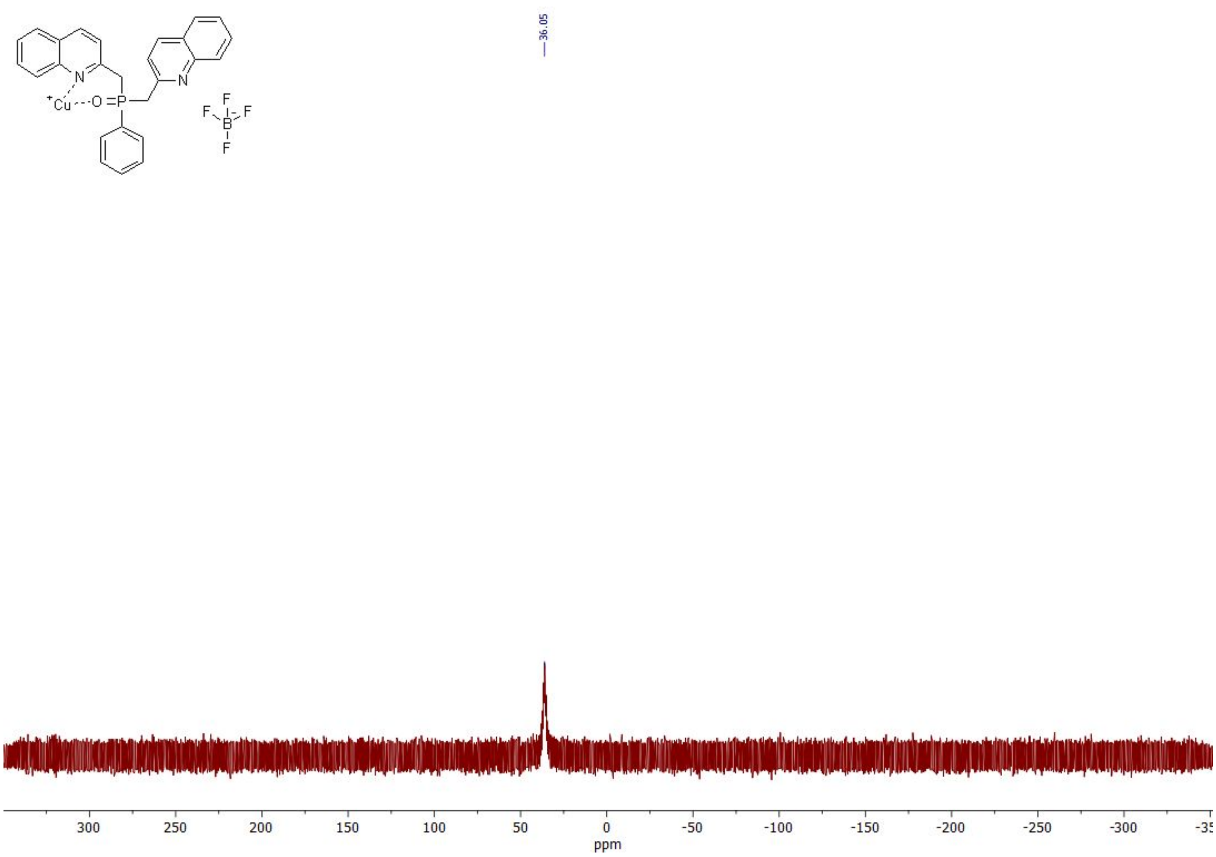
$^{11}B\{/\}$ NMR of **3** in CD_3CN, 128.394 MHz.



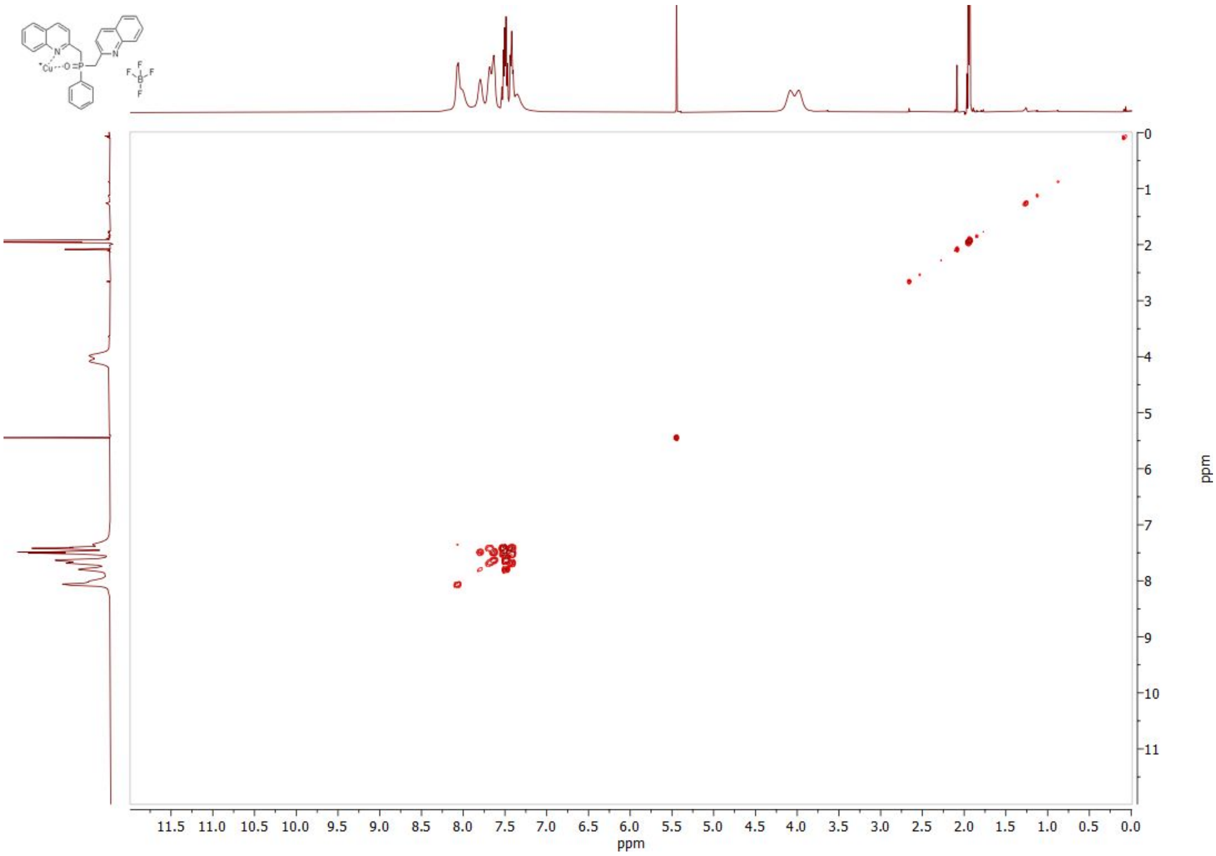
$^{31}P\{^{1}H\}$ NMR of **3** in CD_3CN, 161.996 MHz.



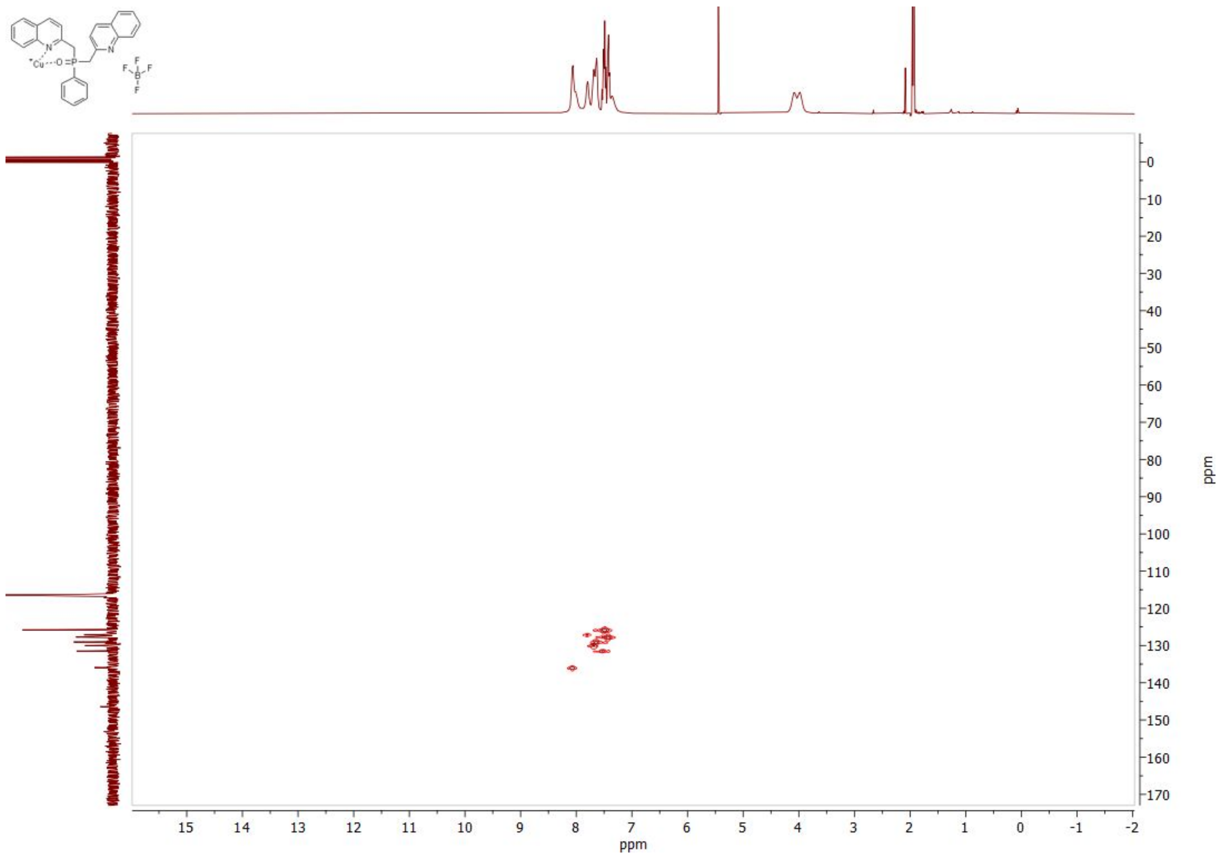
^{31}P{/} NMR of **3** in CD_3CN, 161.996 MHz.



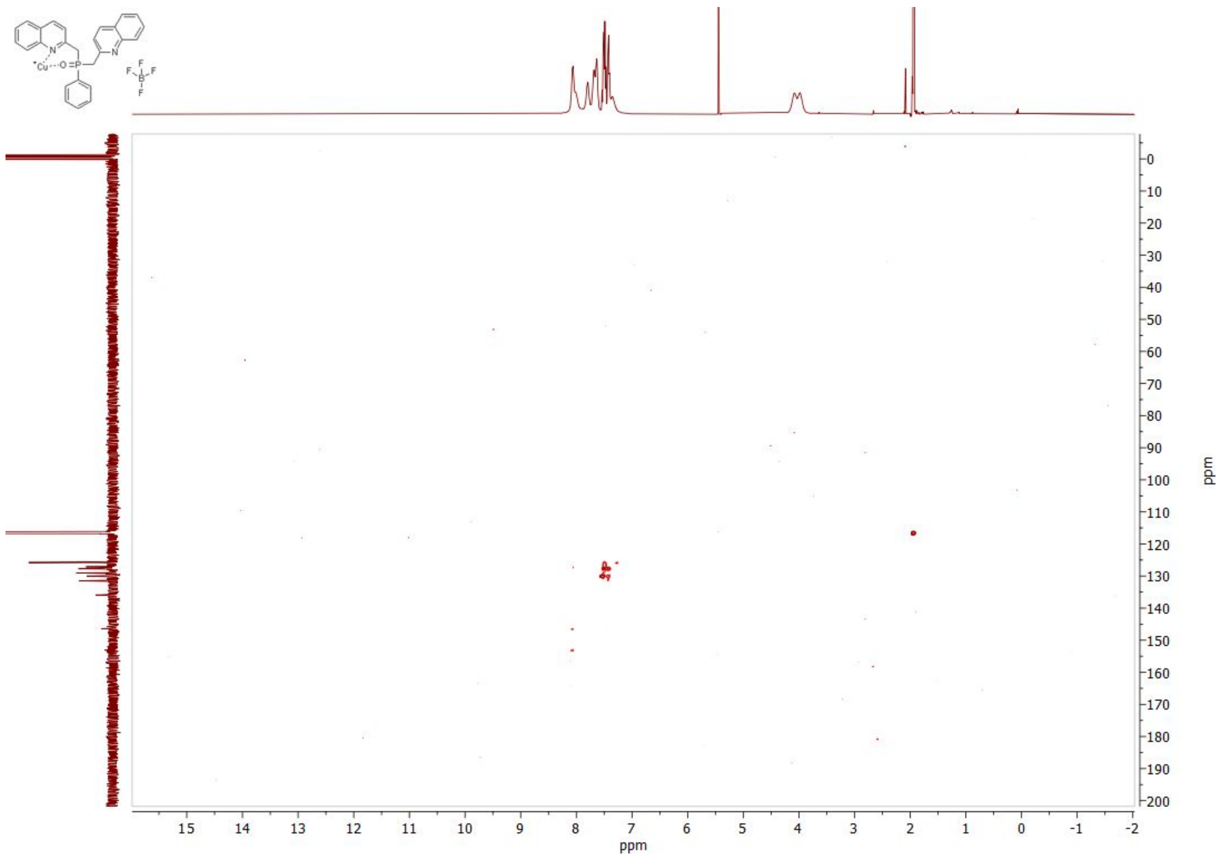
^{1}H,^{1}H–COSY$_{45}$ of **3** in CD_3CN.



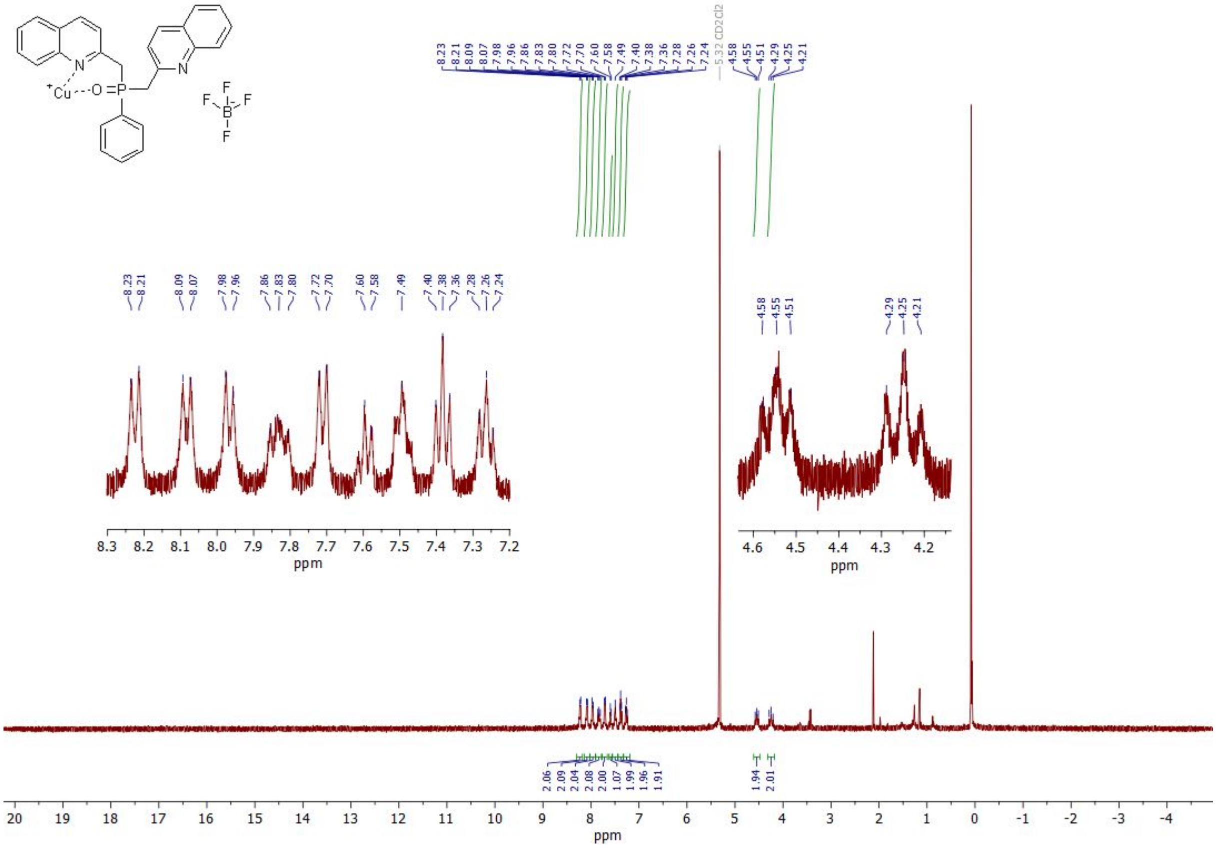
$^{1}H,^{13}C$–HMQC of **3** in CD_3CN



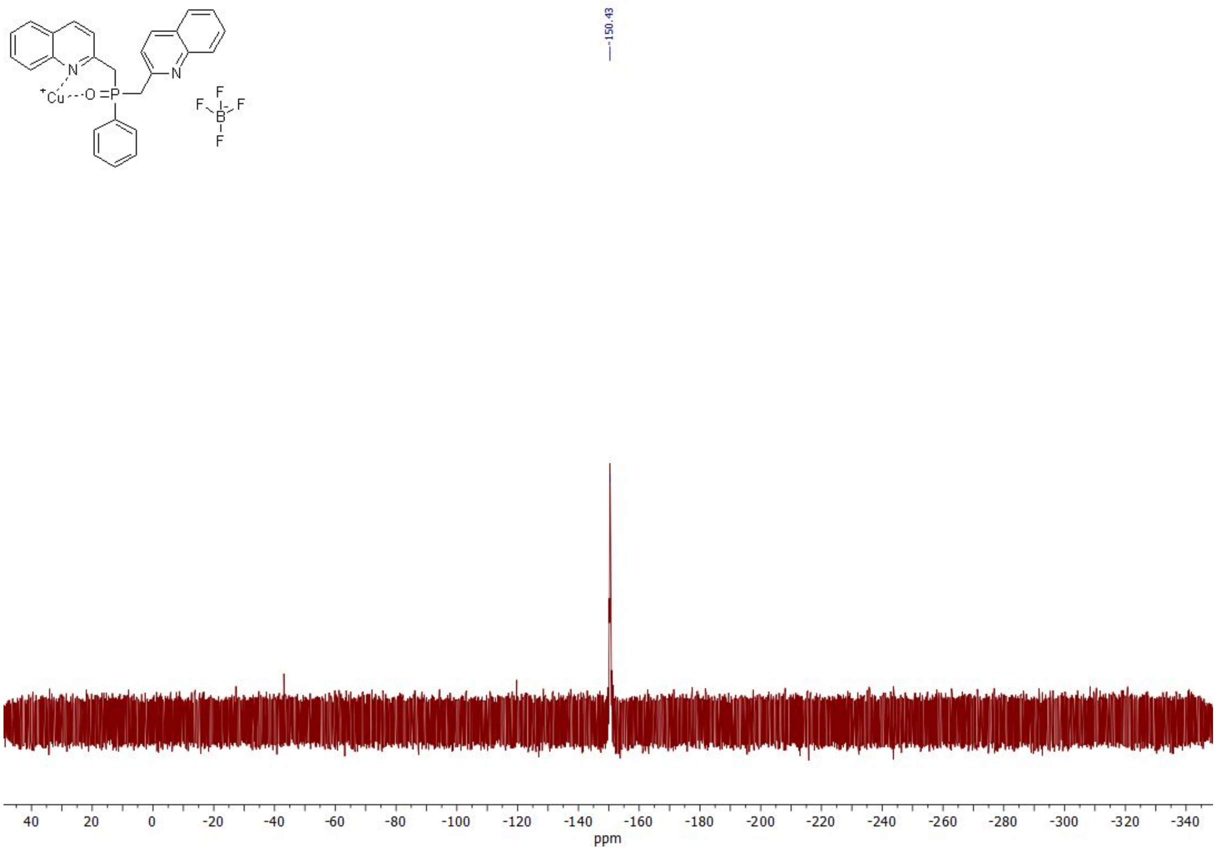
$^{1}H,^{13}C$–HMBC of **3** in CD_3CN



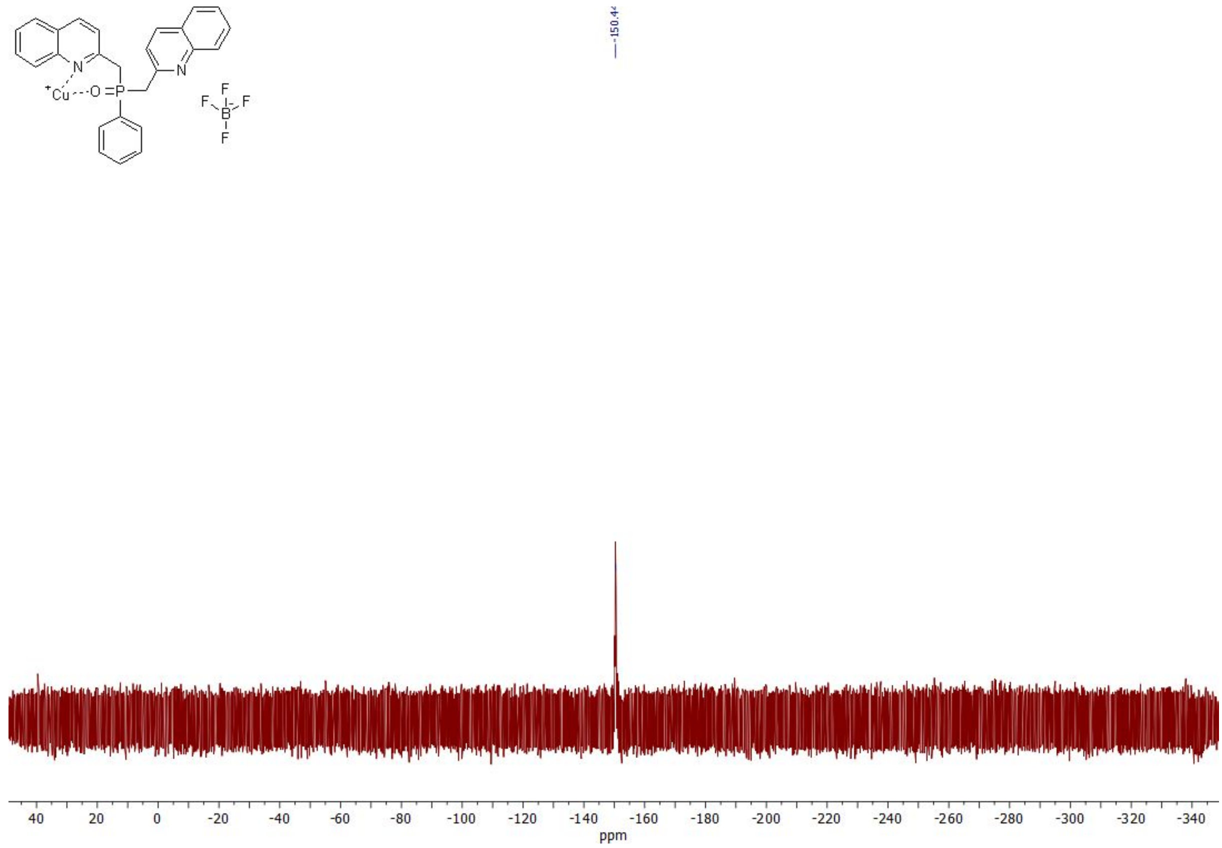
^{1}H NMR of **3** in CD_2Cl_2, 400.133 MHz



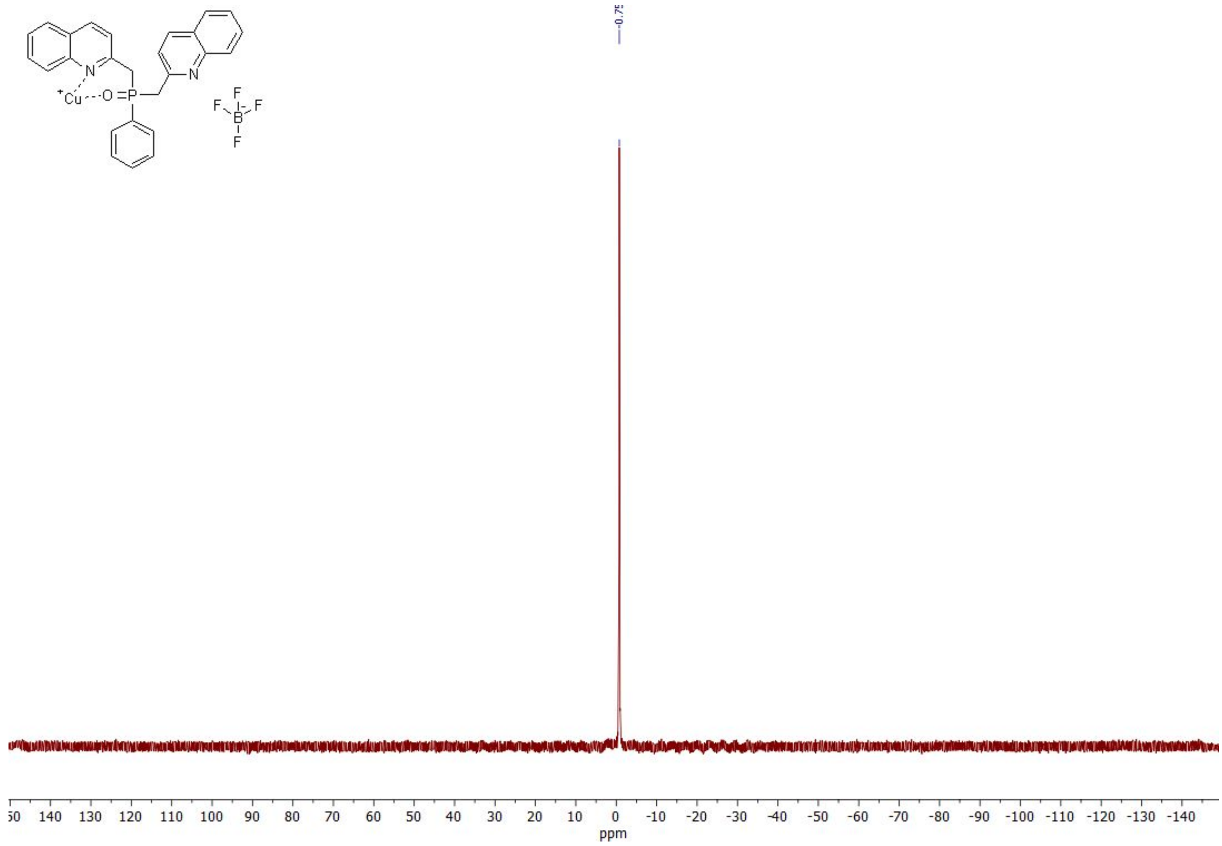
^{19}F{^{1}H} NMR of **3** in CD_2Cl_2, 376.442 MHz



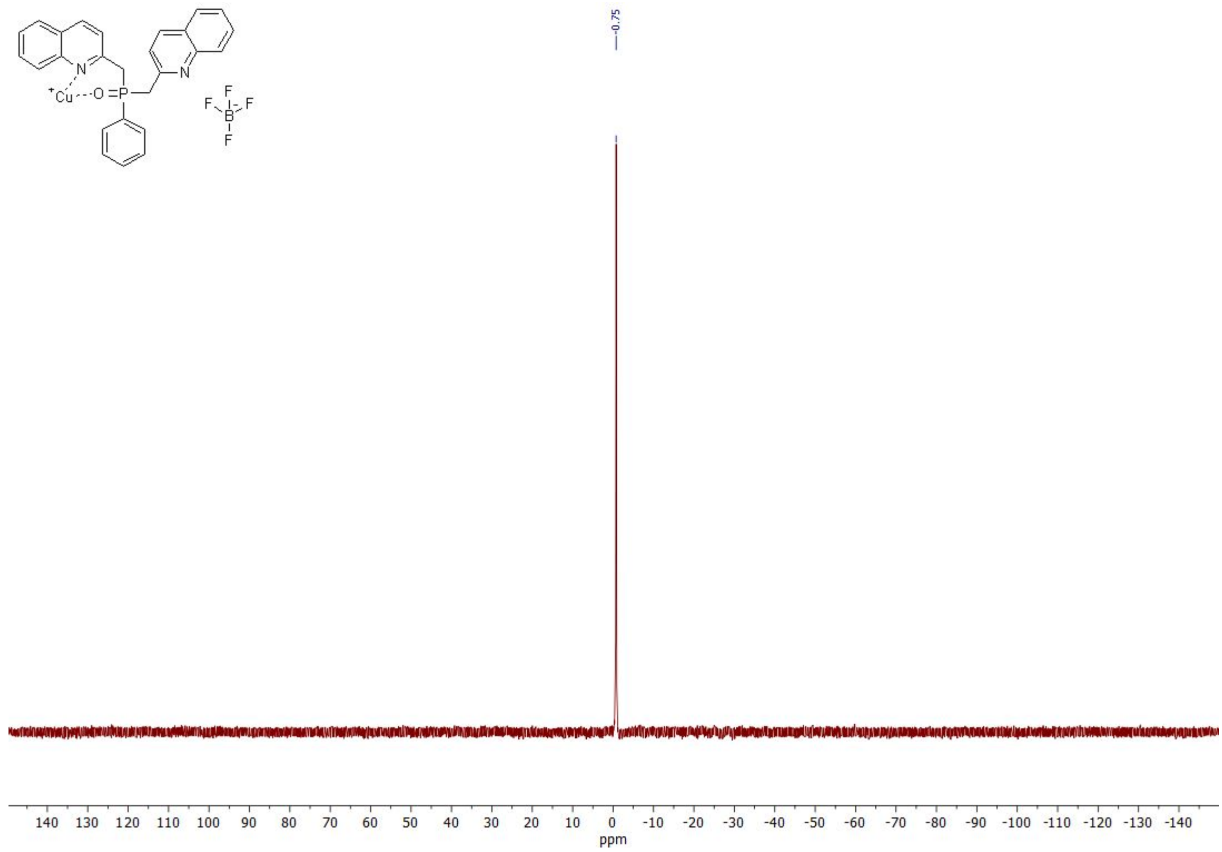
$^{19}F\{/\}$ NMR of **3** in CD_2Cl_2, 376.442 MHz.



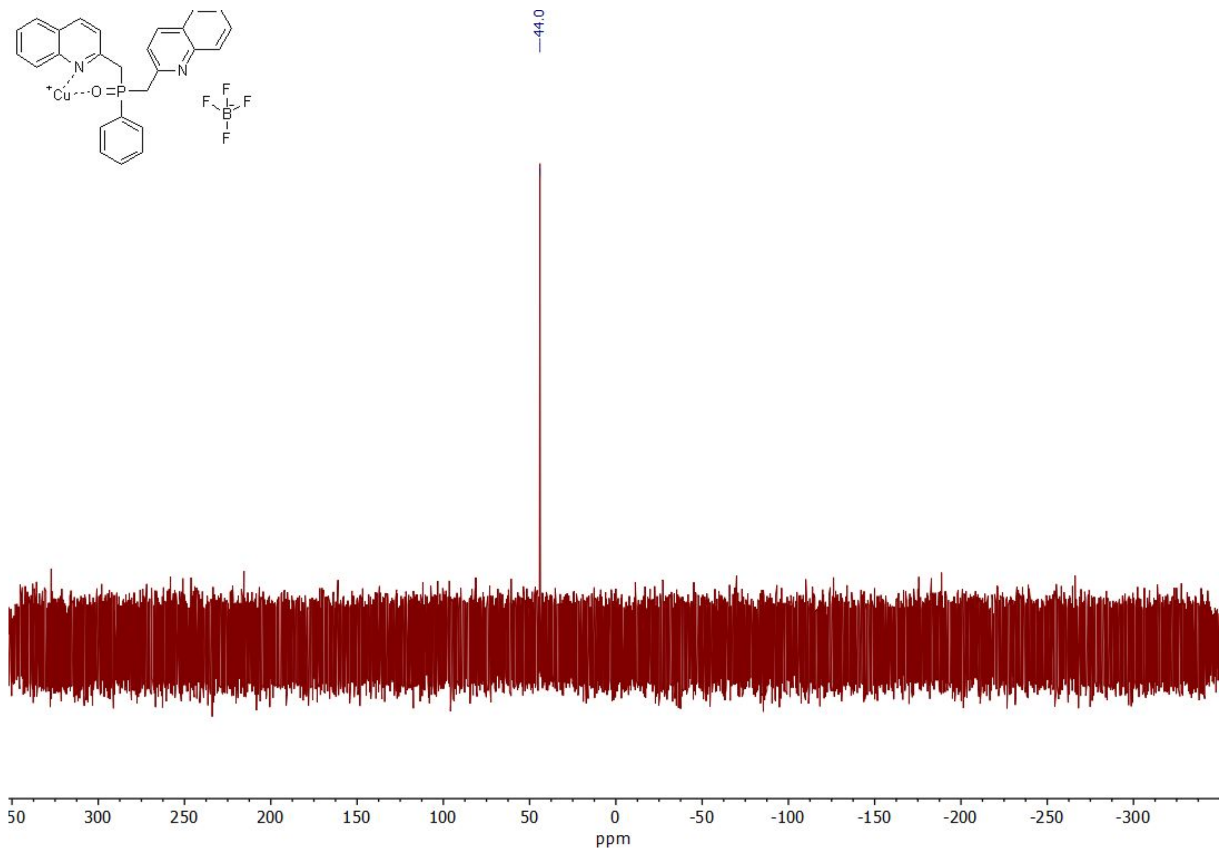
$^{11}B\{^1H\}$ NMR of **3** in CD_2Cl_2, 128.378 MHz.



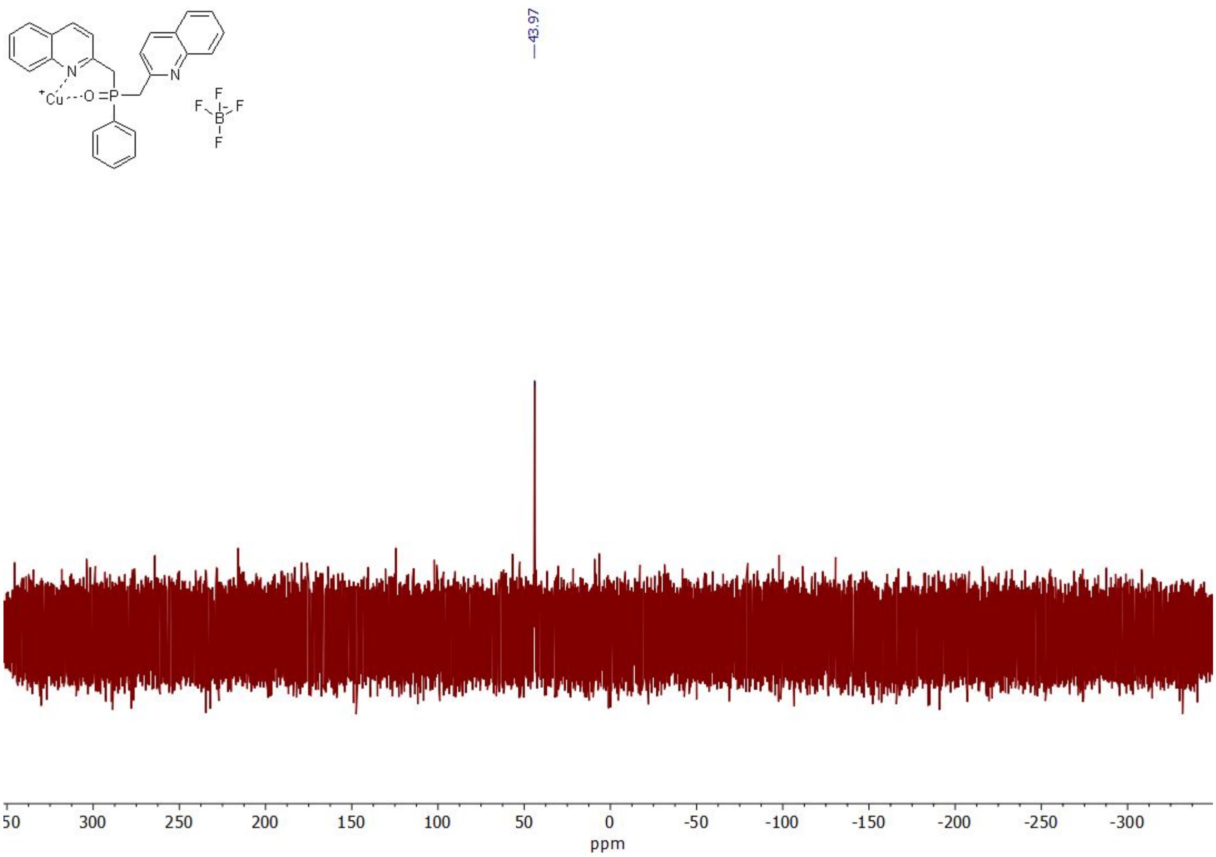
^{11}B{/} NMR of **3** in CD_2Cl_2, 128.378 MHz.



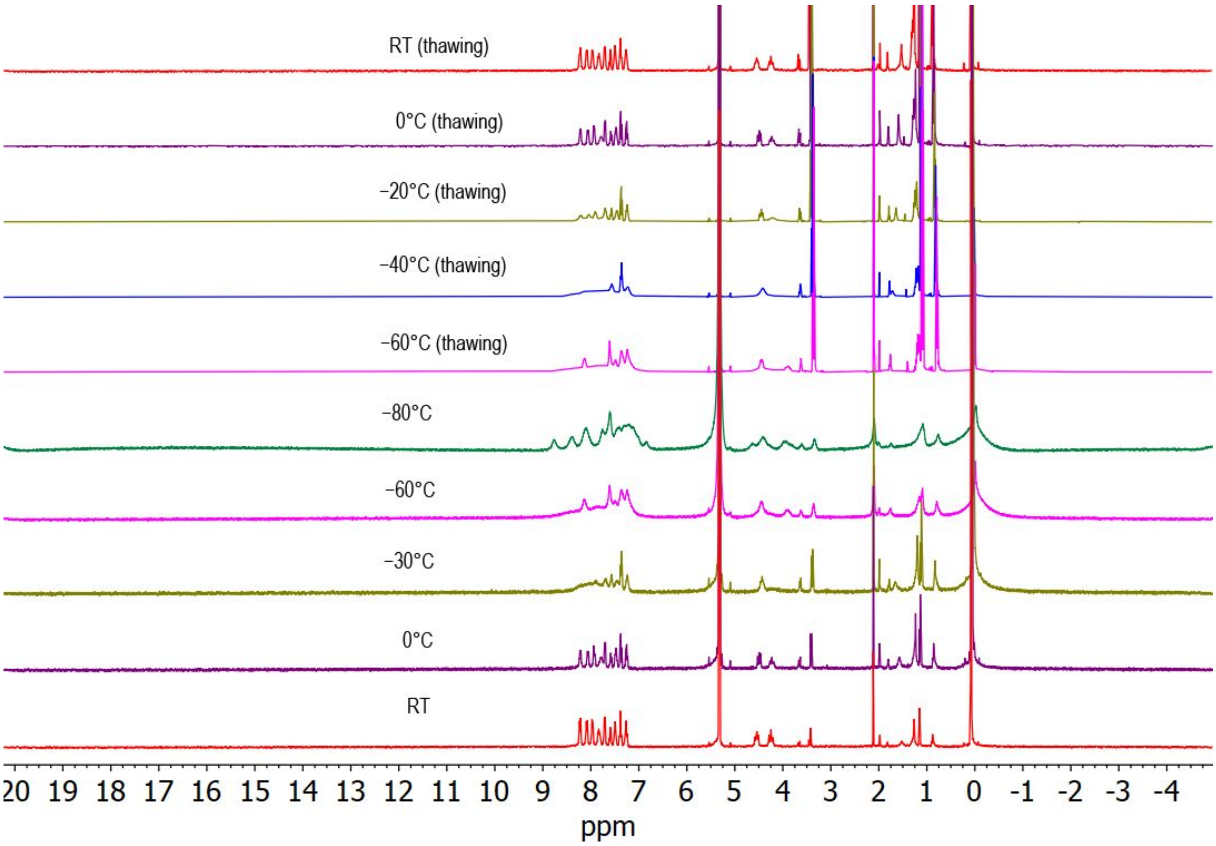
^{31}P{^{1}H} NMR of **3** in CD_2Cl_2, 161.976 MHz.



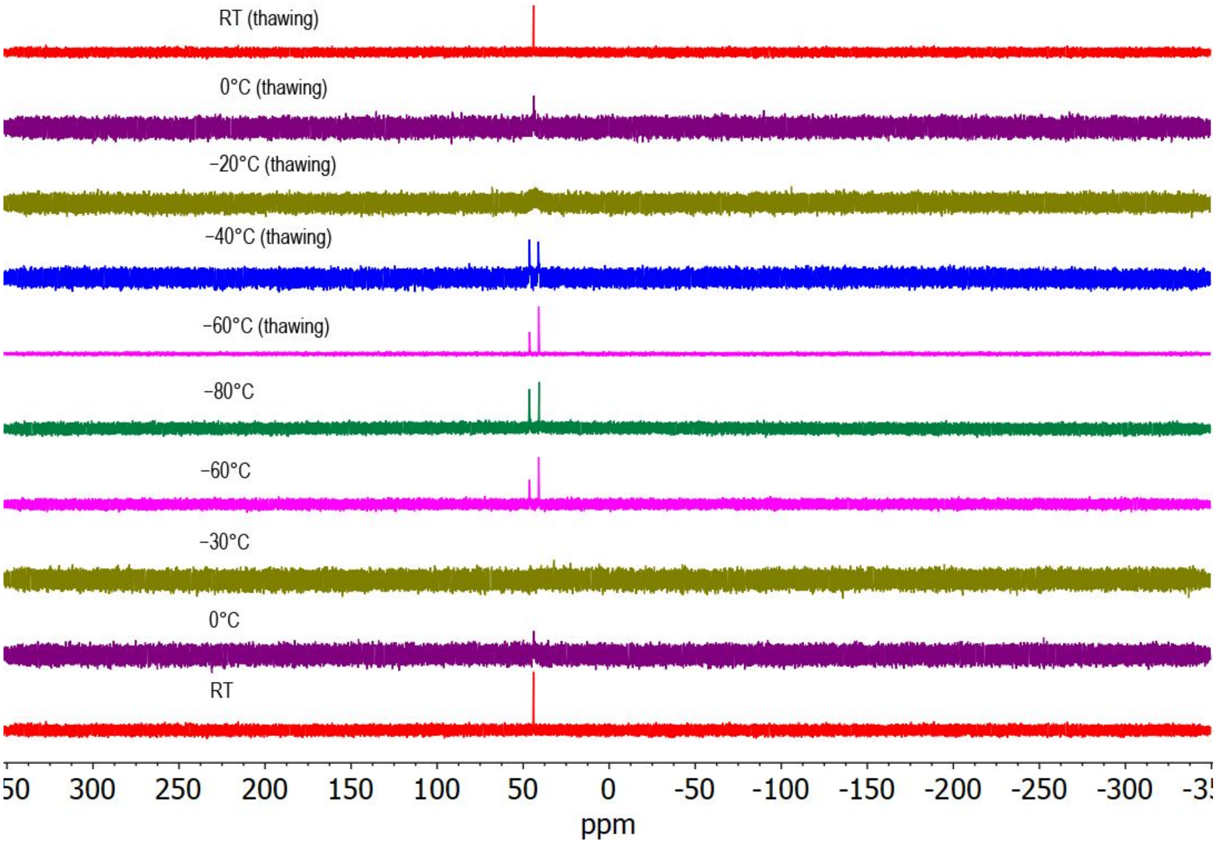
$^{31}P\{/\}$ NMR of **3** in CD_2Cl_2, 161.976 MHz.



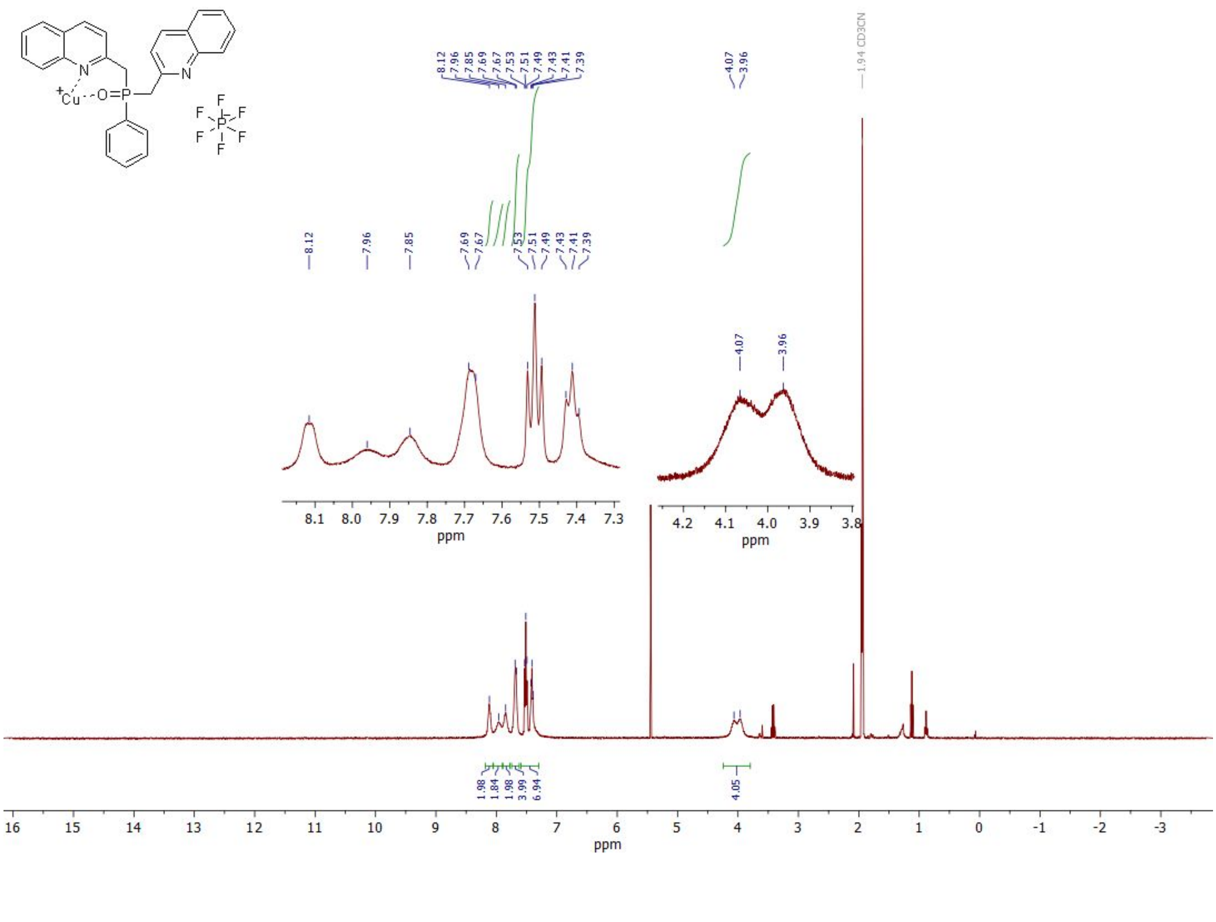
^{1}H NMR of **3** at varying temperatures in CD_2Cl_2, 400.133 MHz.



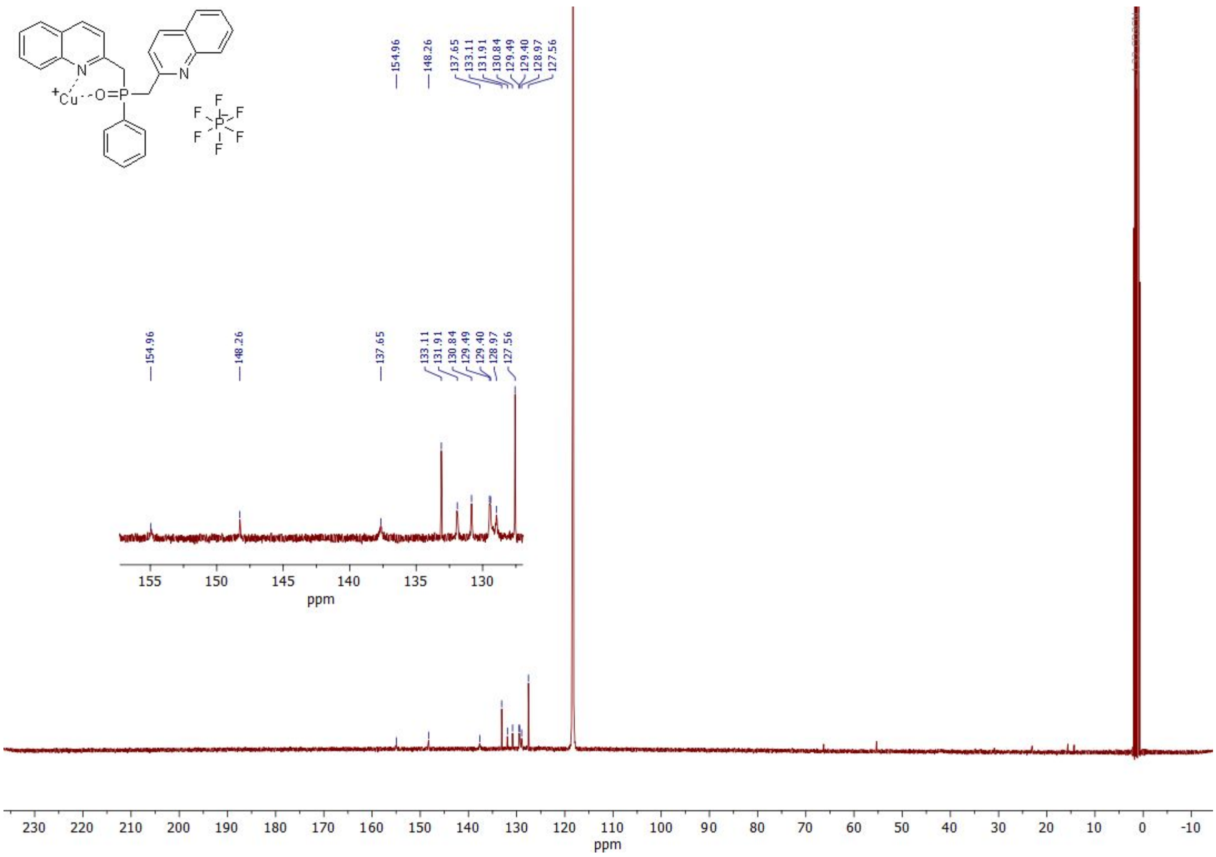
^{31}P NMR of **3** at varying temperatures in CD_2Cl_2, 400.133 MHz.



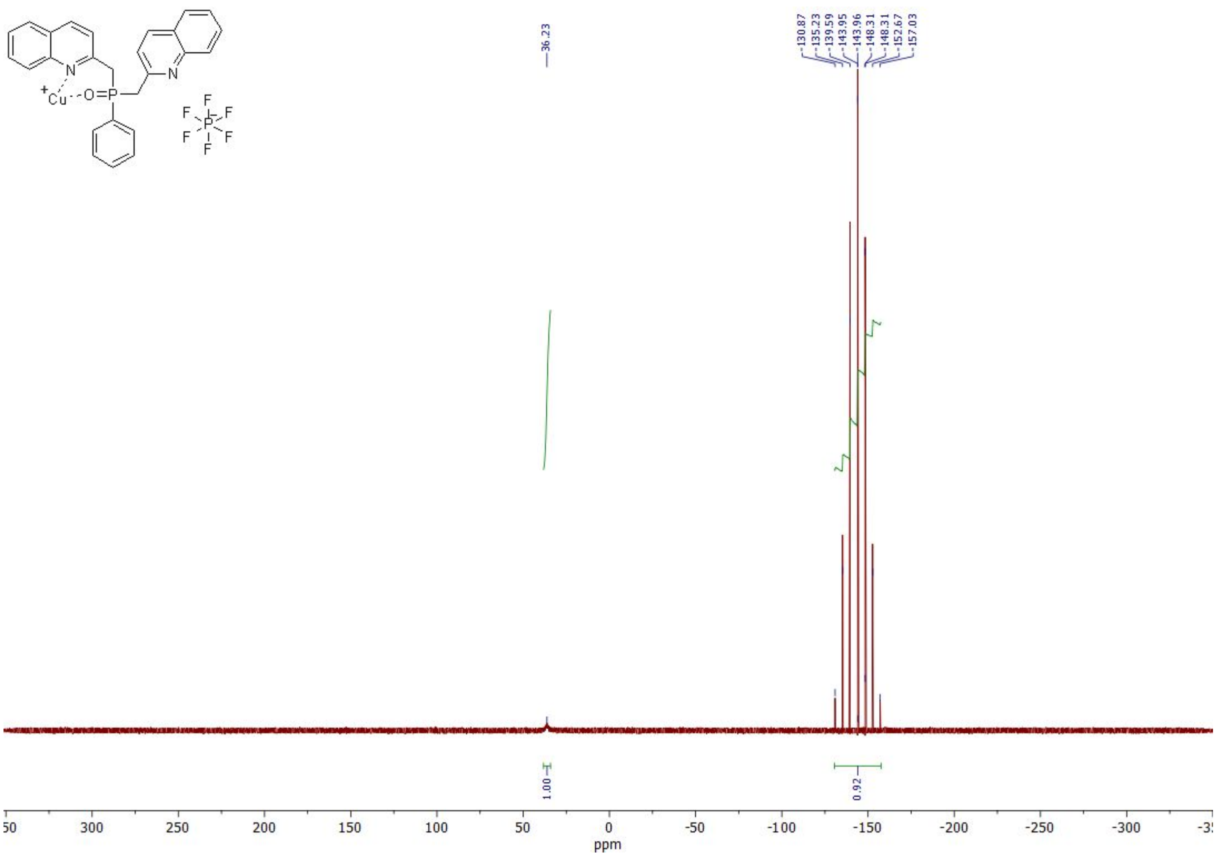
^{1}H NMR of **4** in CD_3CN, 400.133 MHz



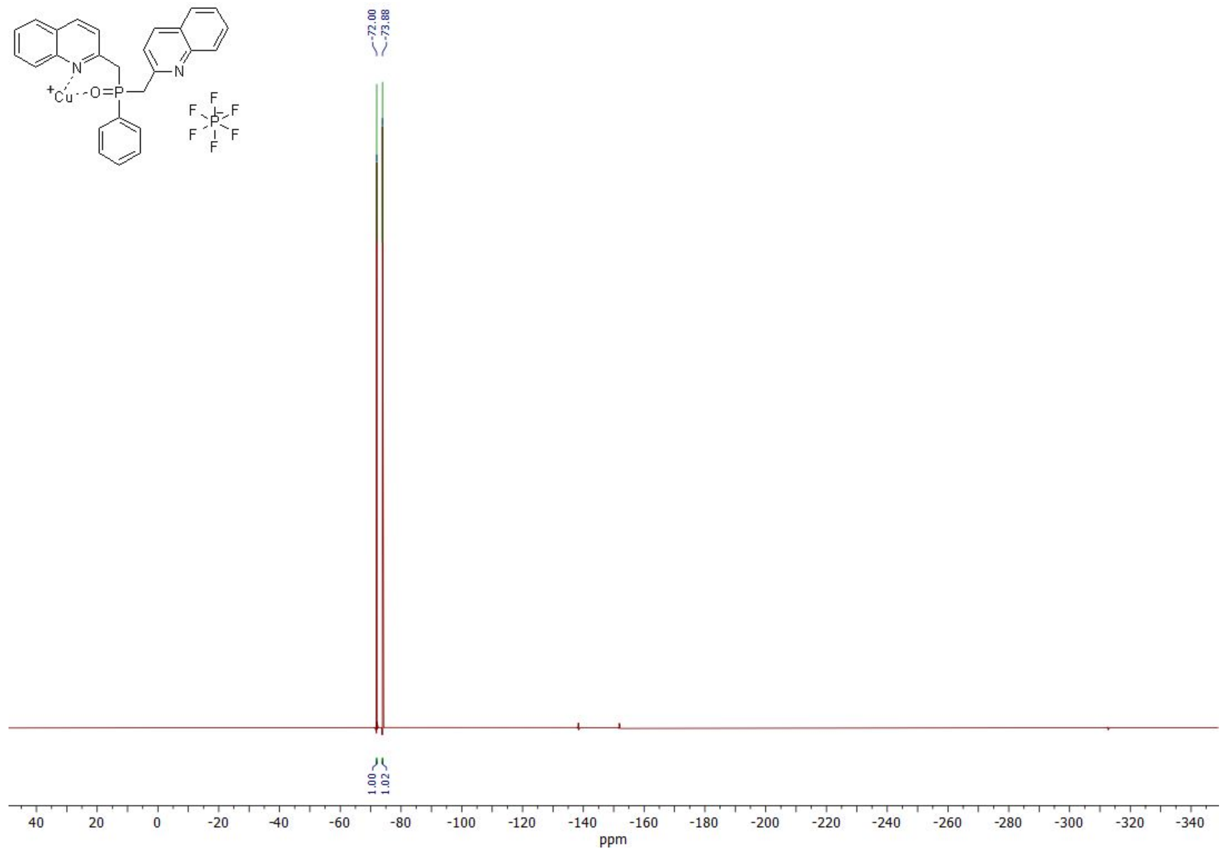
^{13}C NMR of **4** in CD_3CN, 100.623 MHz.



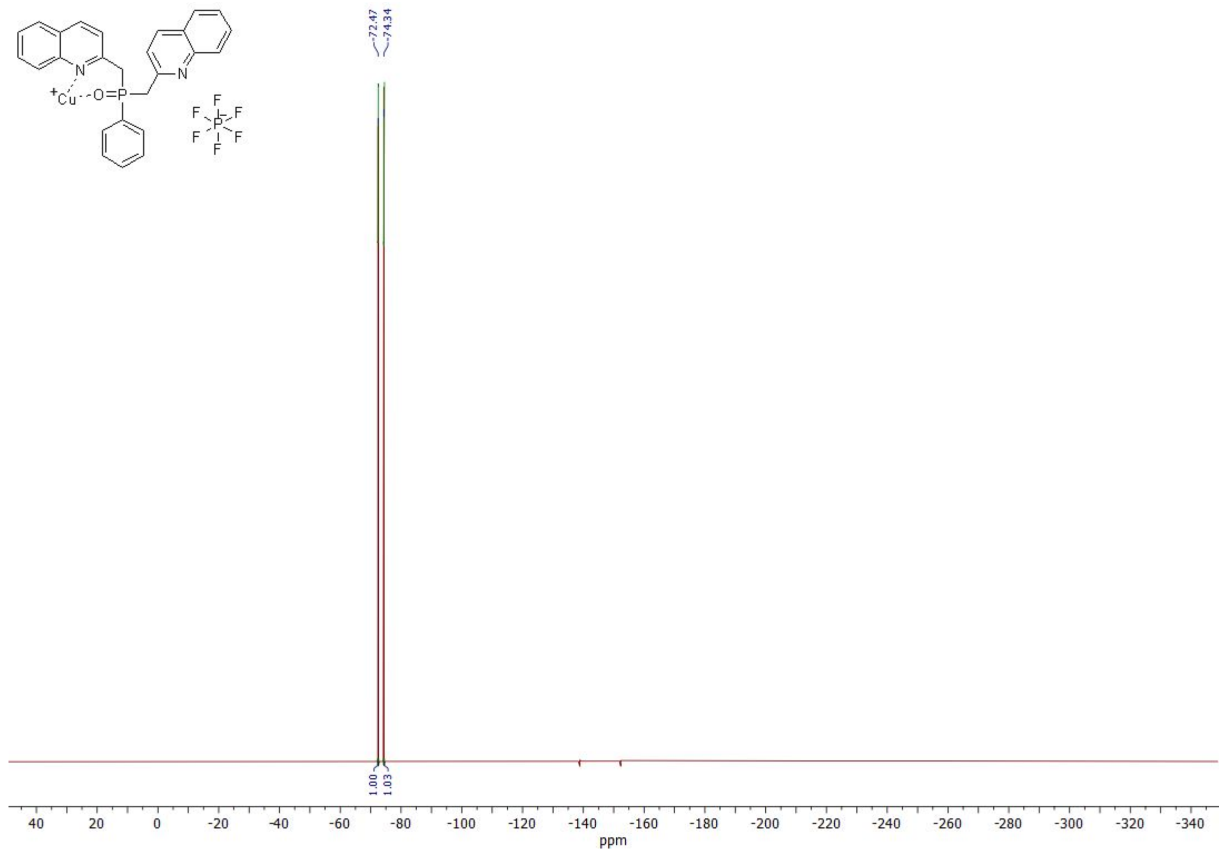
$^{31}P\{^1H\}$ NMR of **4** in CD_3CN, 161.976 MHz.



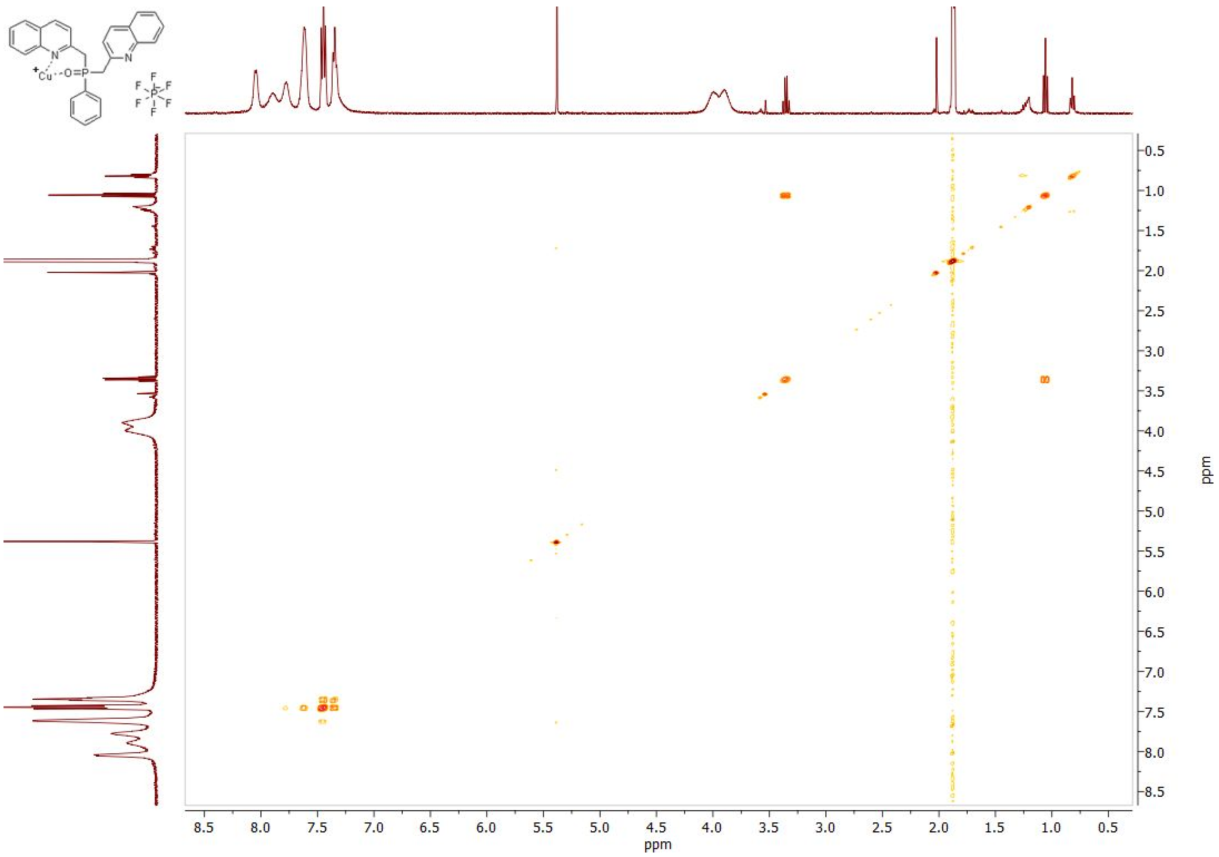
$^{19}F\{^{1}H\}$ NMR of **4** in CD_3CN, 376.442 MHz.



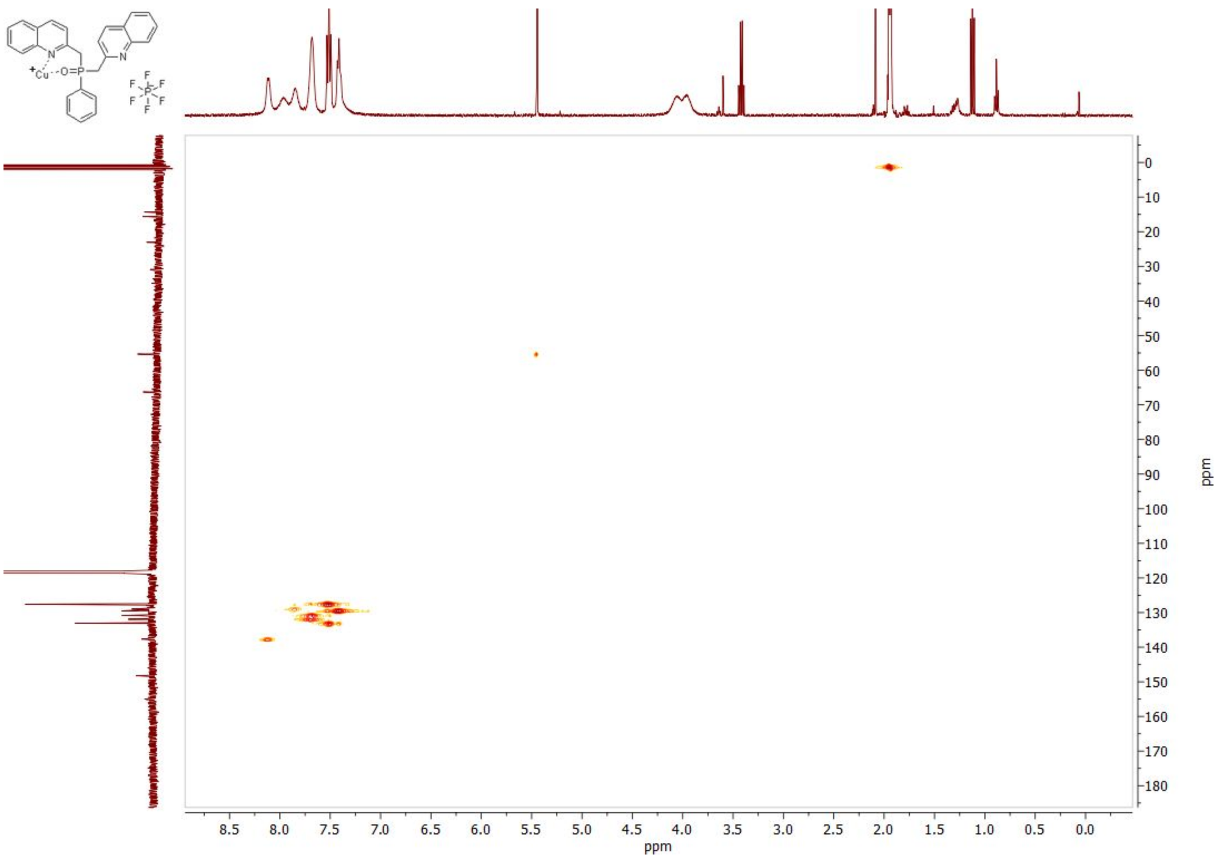
$^{19}F\{/\}$ NMR of **4** in CD_3CN, 376.442 MHz.



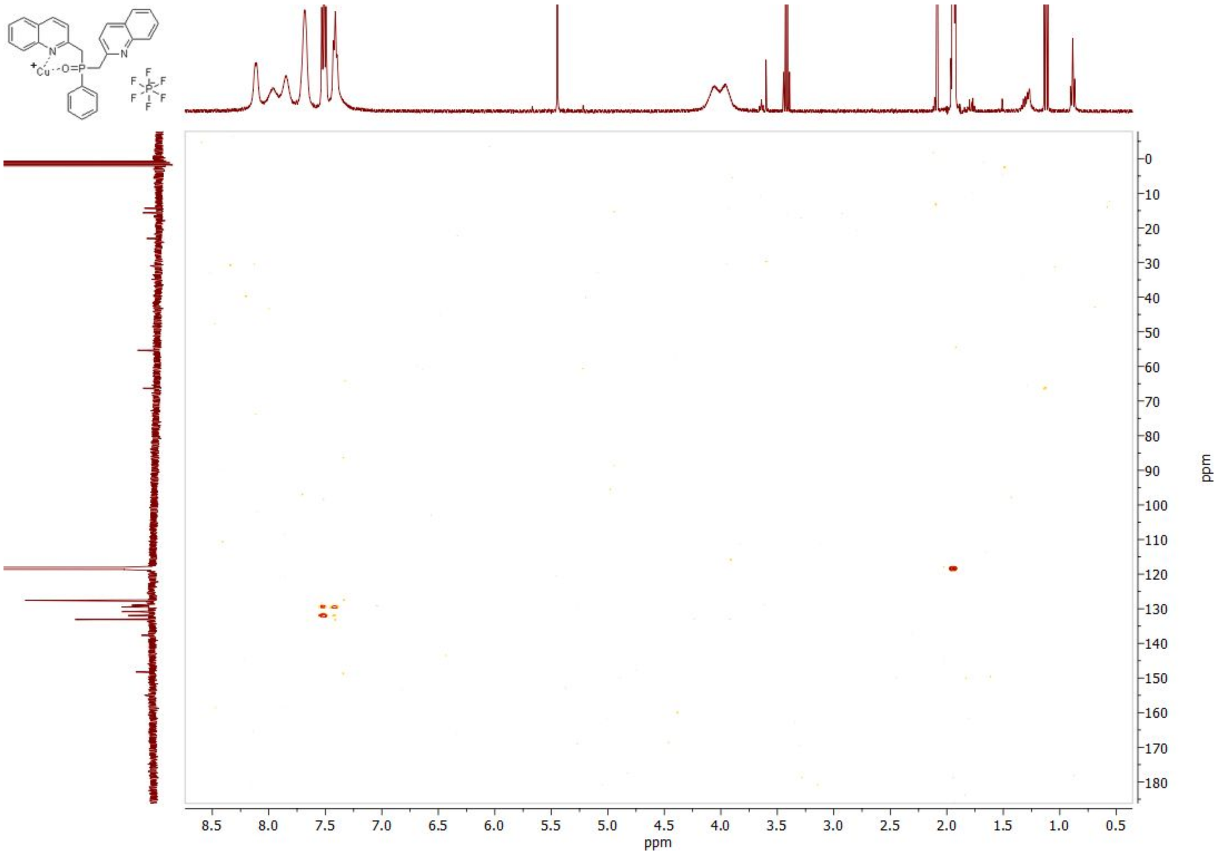
$^{1}H,^{1}H$–COSY$_{45}$ of **4** in CD_3CN.



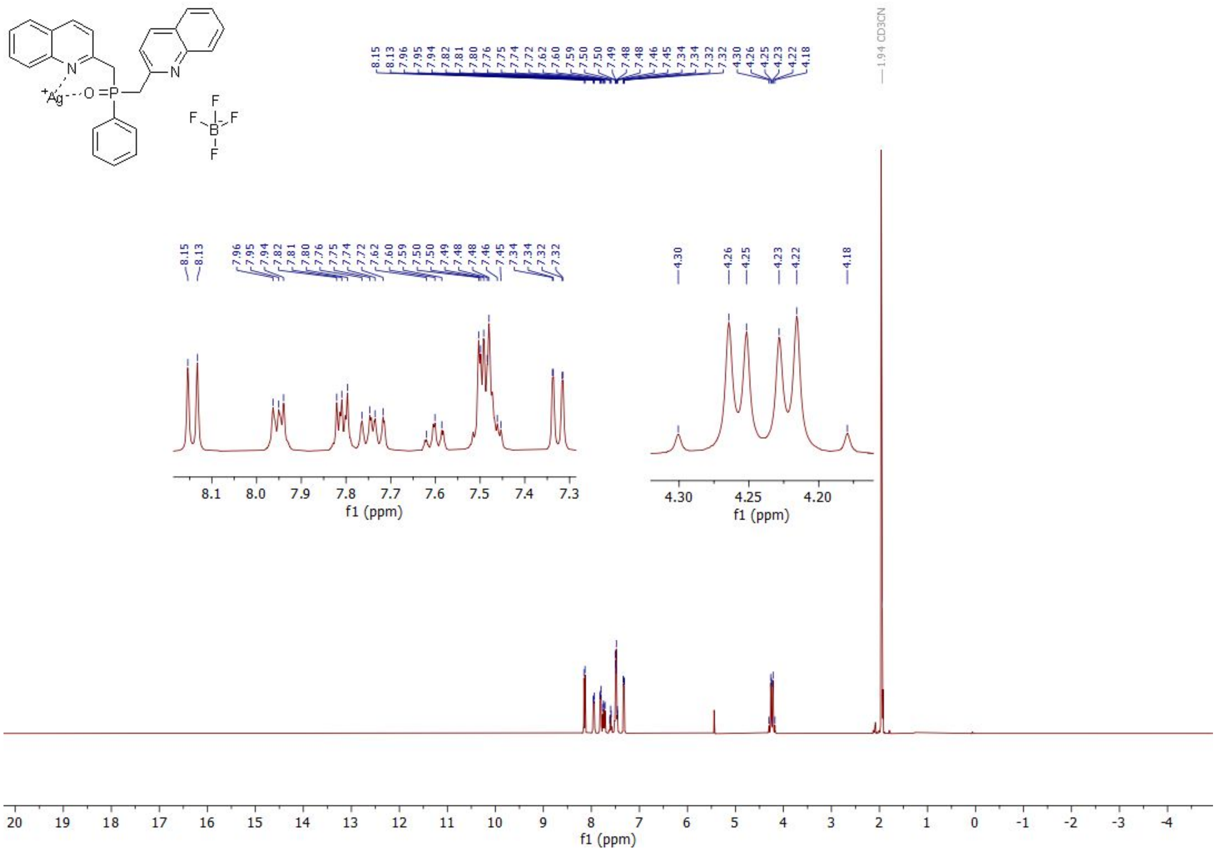
$^{1}H,^{13}C$–HSQC of **4** in CD_3CN



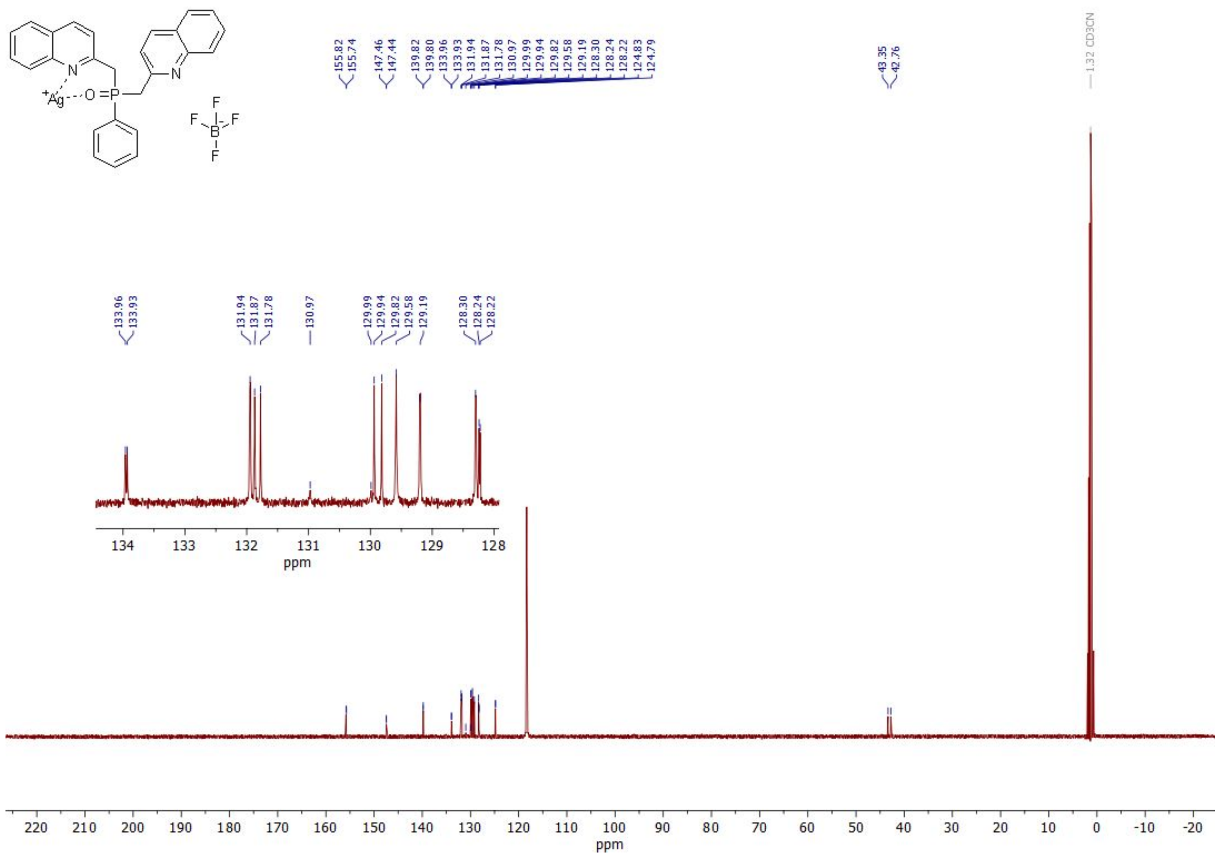
$^{1}H,^{13}C$–HMBC of **4** in CD_3CN



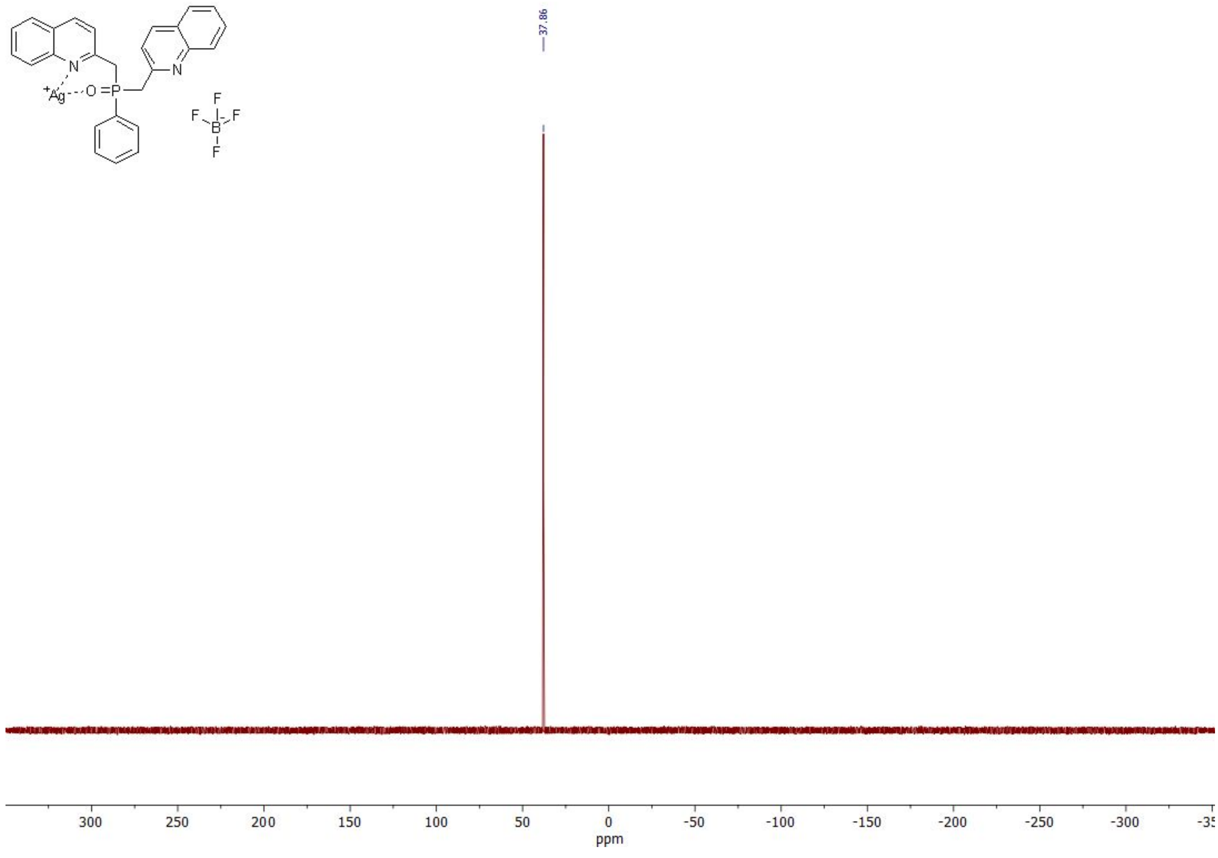
^{1}H NMR of **5** in CD_3CN, 400.133 MHz.



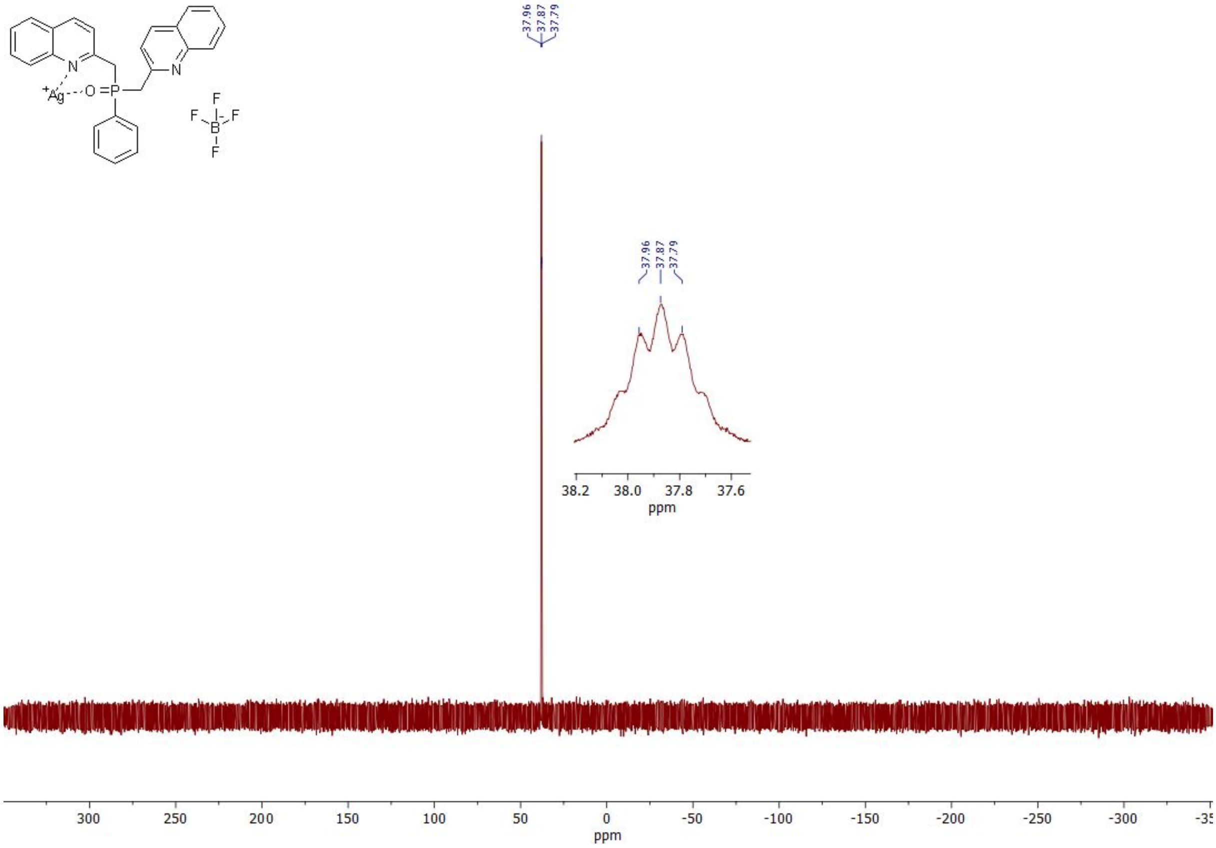
^{13}C NMR of **5** in CD_3CN, 100.623 MHz.



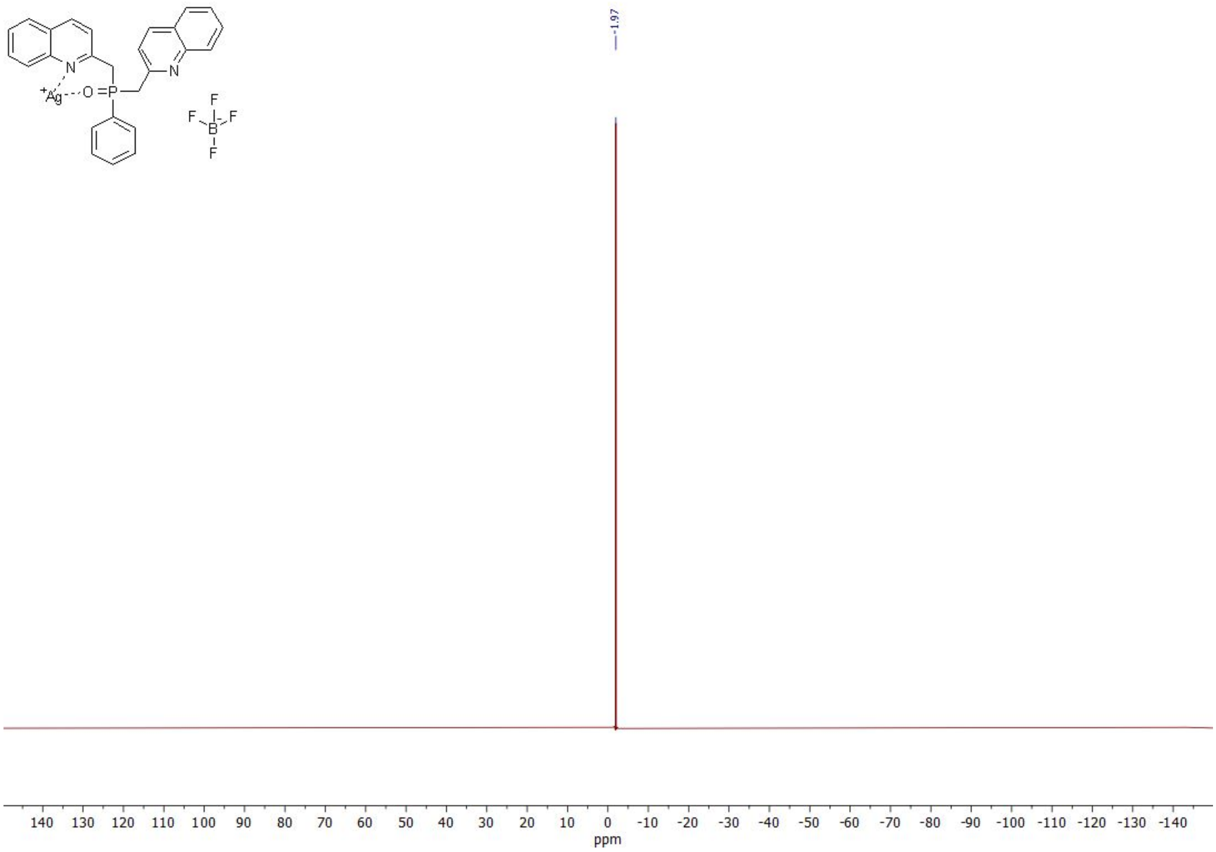
$^{31}P\{^1H\}$ NMR of **5** in CD_3CN, 161.996 MHz.



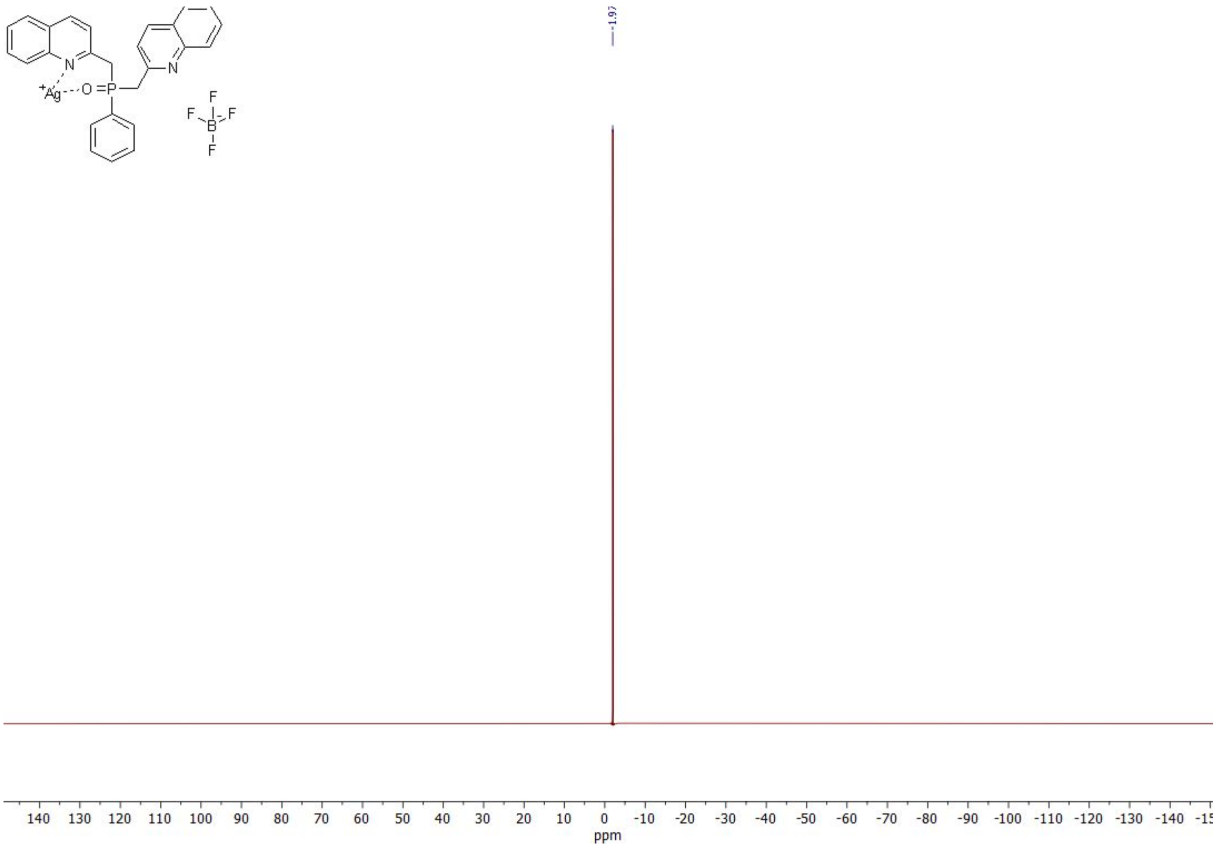
^{31}P{/} NMR of **5** in CD_3CN, 161.996 MHz.



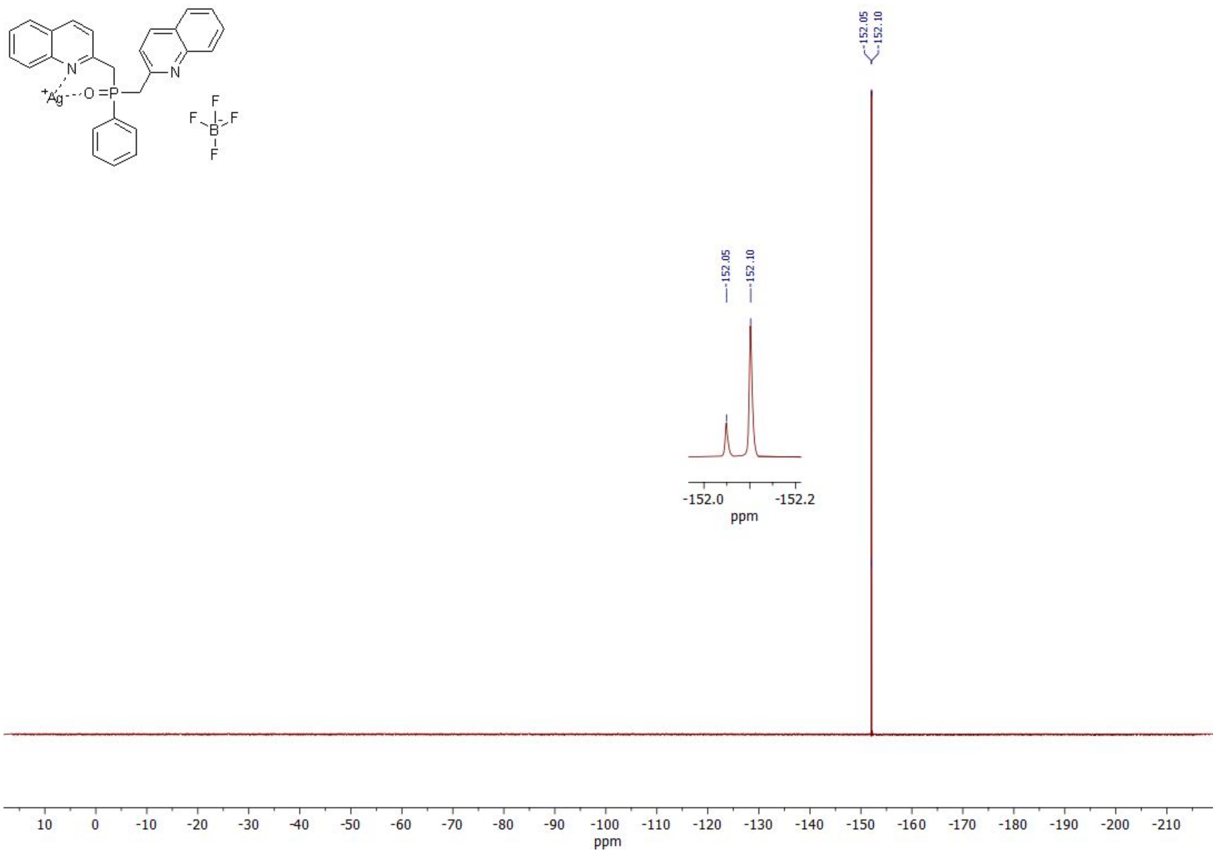
^{11}B{^{1}H} NMR of **5** in CD_3CN, 128.394 MHz.



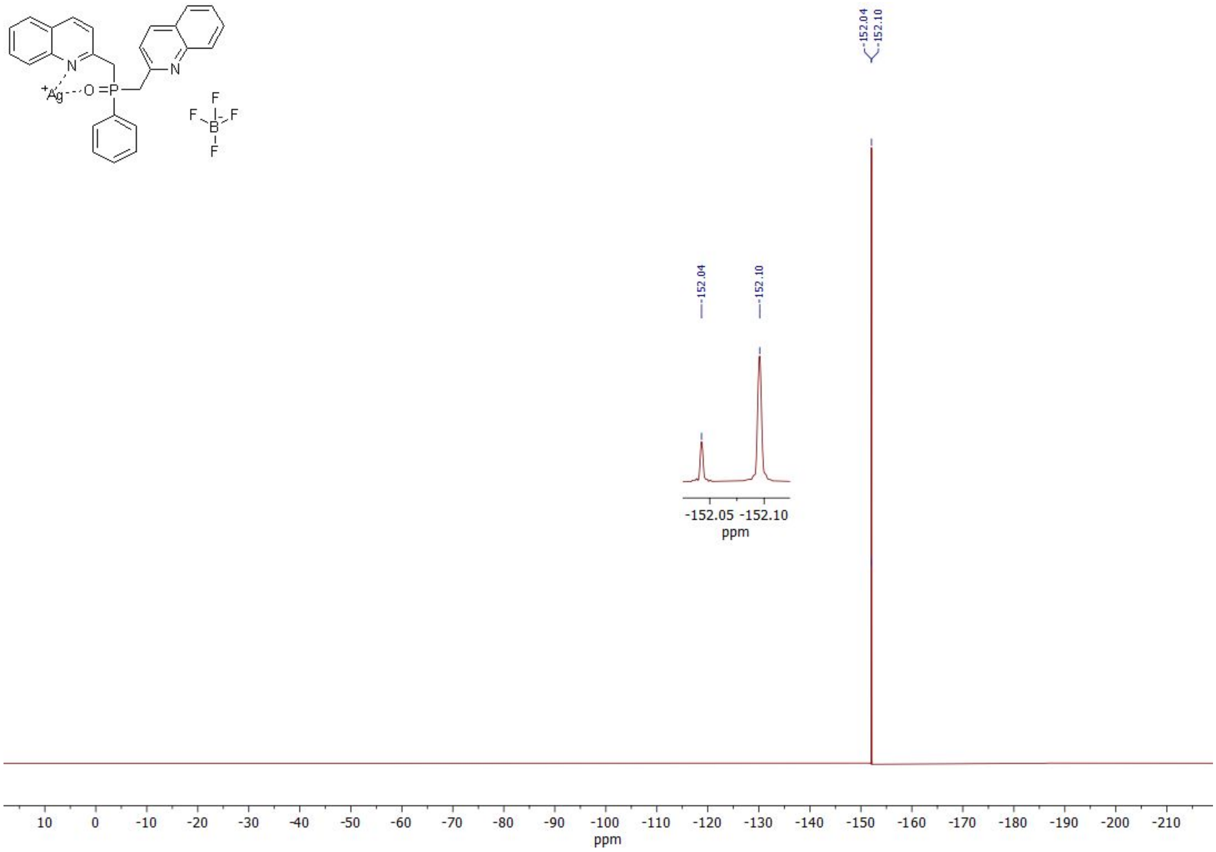
$^{11}B\{/\}$ NMR of **5** in CD_3CN, 128.394 MHz.



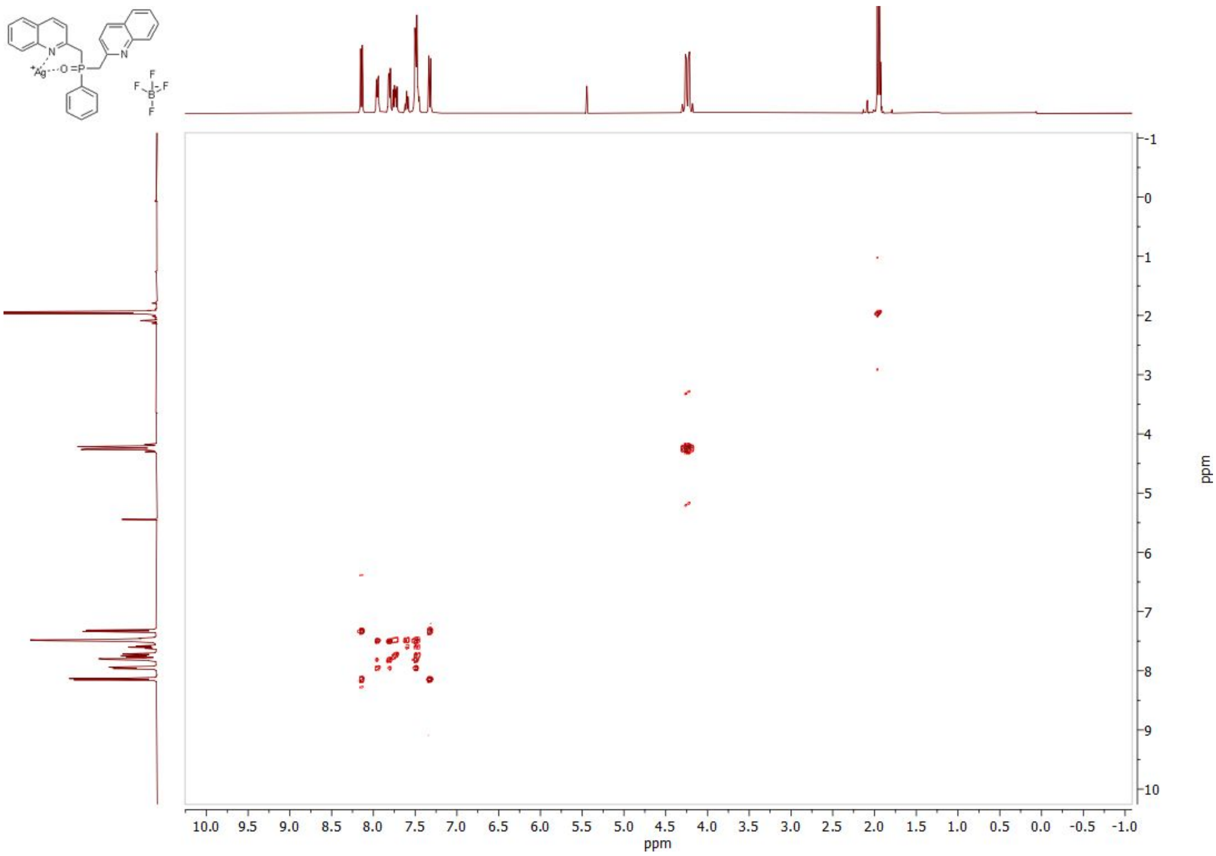
$^{19}F\{^{1}H\}$ NMR of **5** in CD_3CN, 376.442 MHz.



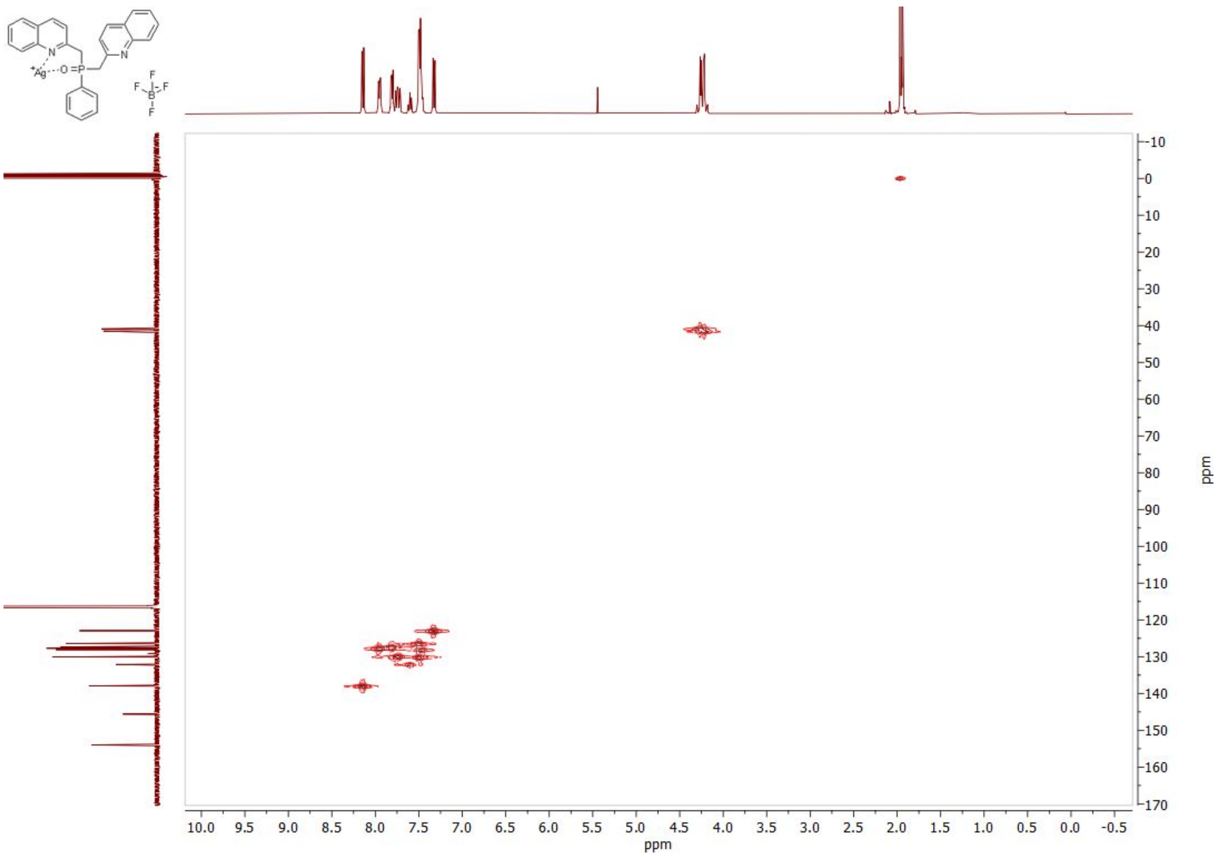
^{19}F{/} NMR of **5**in CD_3CN, 376.442 MHz.



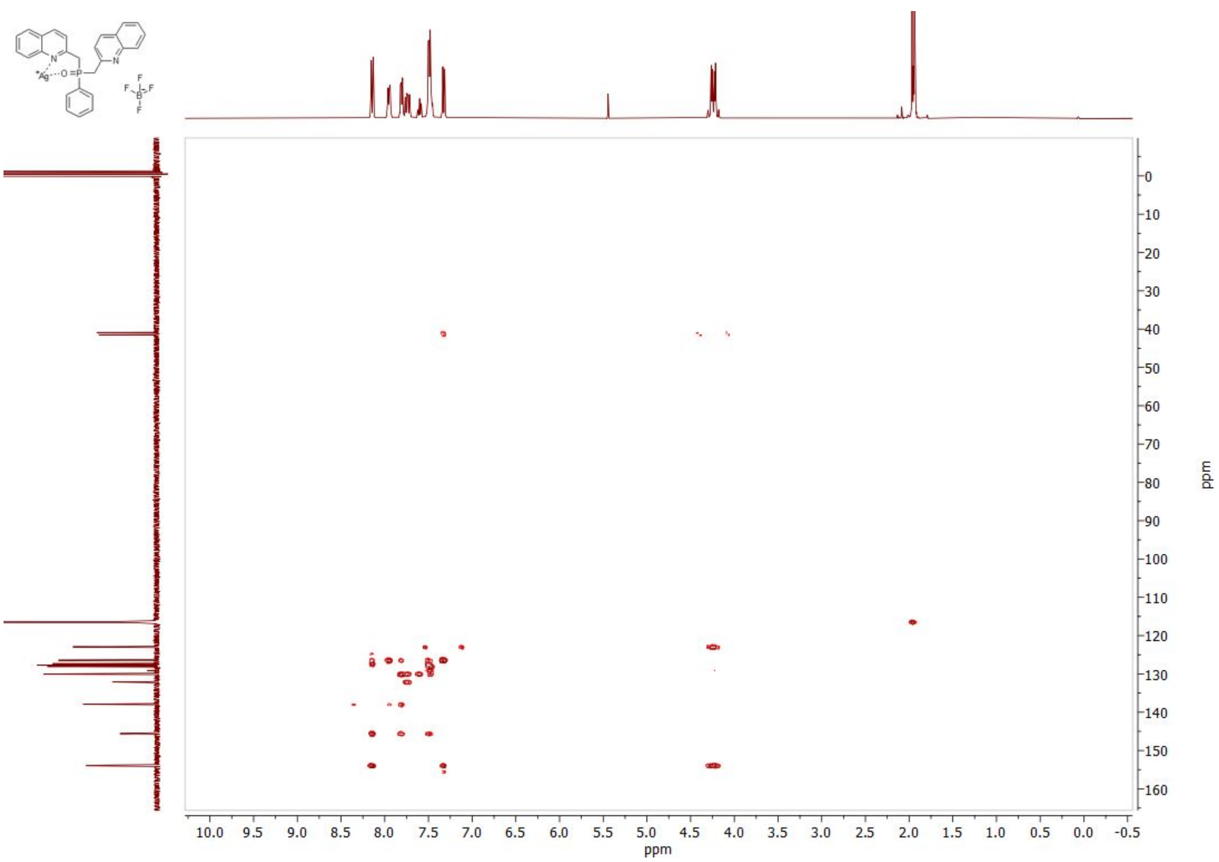
^{1}H,^{1}H–COSY$_{45}$ of **5** in CD_3CN.



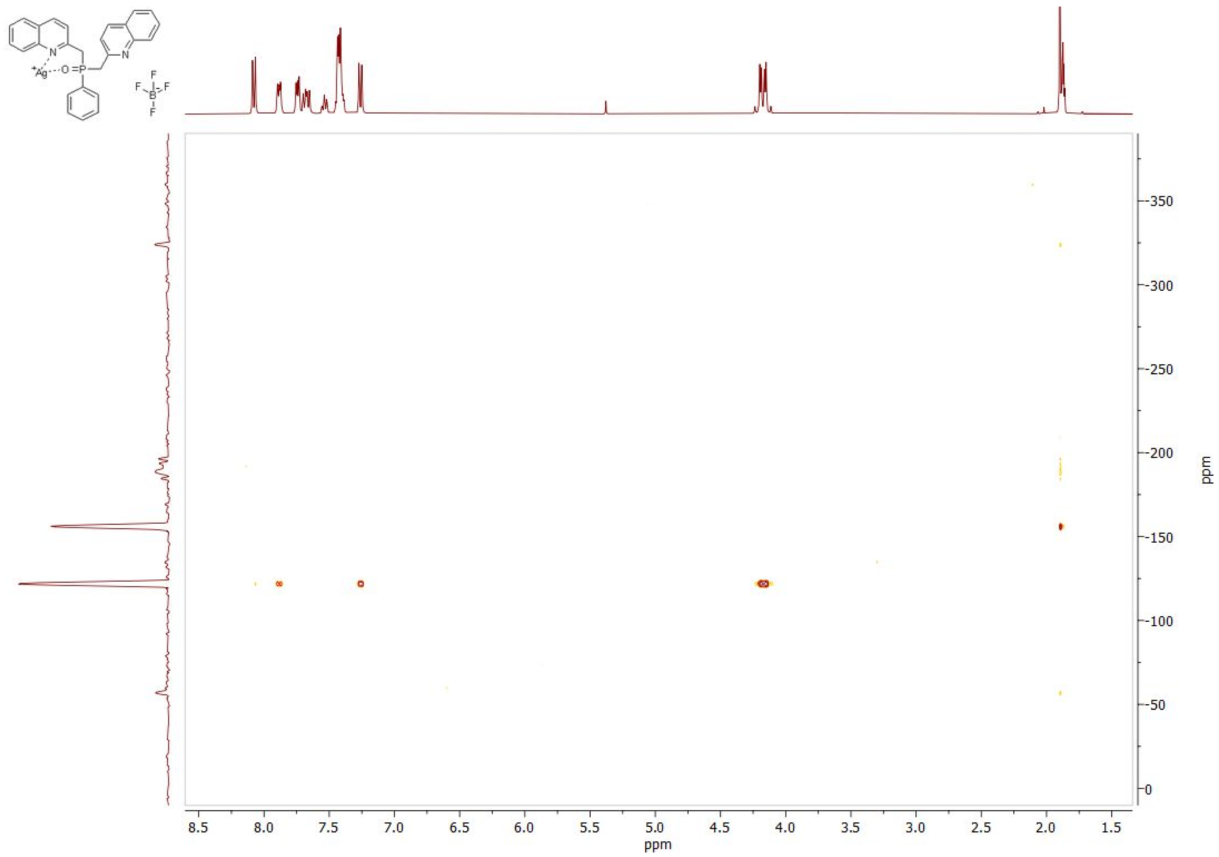
$^{1}H,^{13}C$–HMQC of **5** in CD_3CN



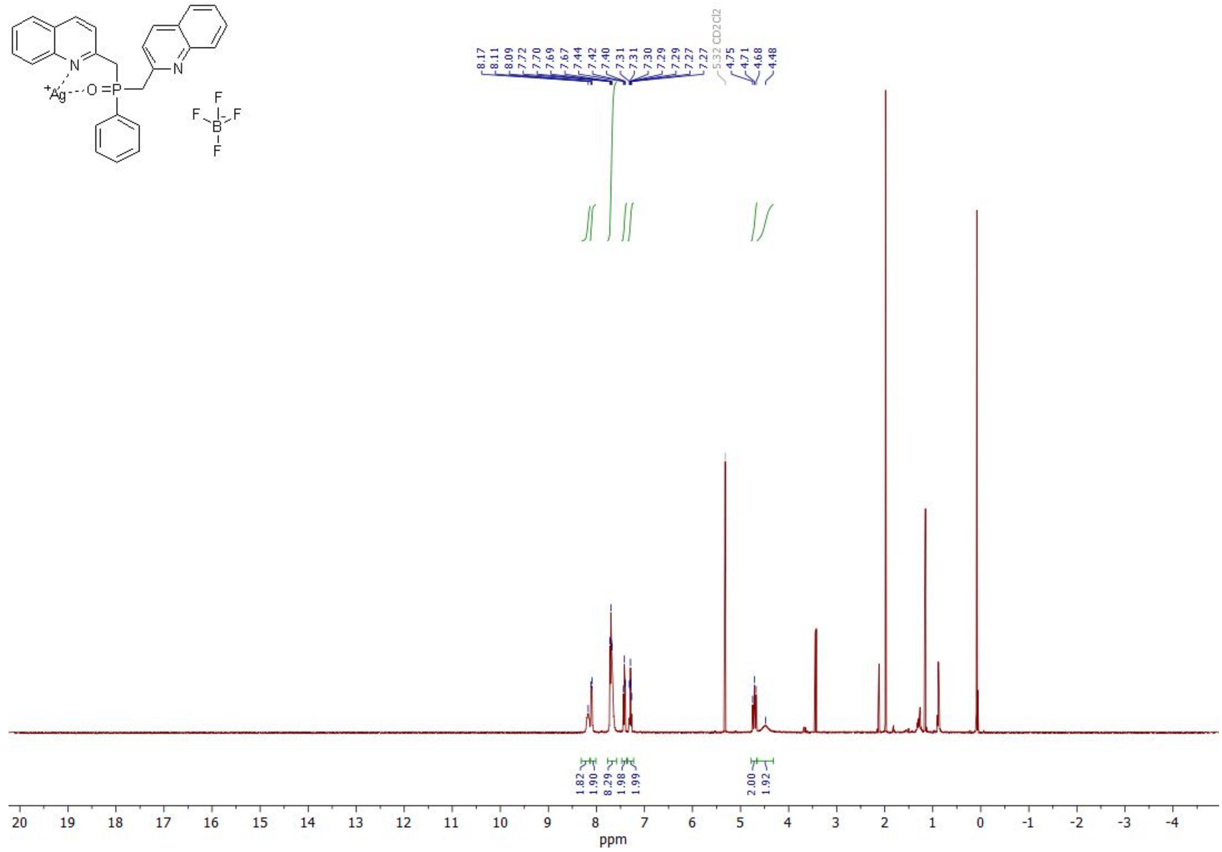
$^{1}H,^{13}C$–HMBC of **5** in CD_3CN



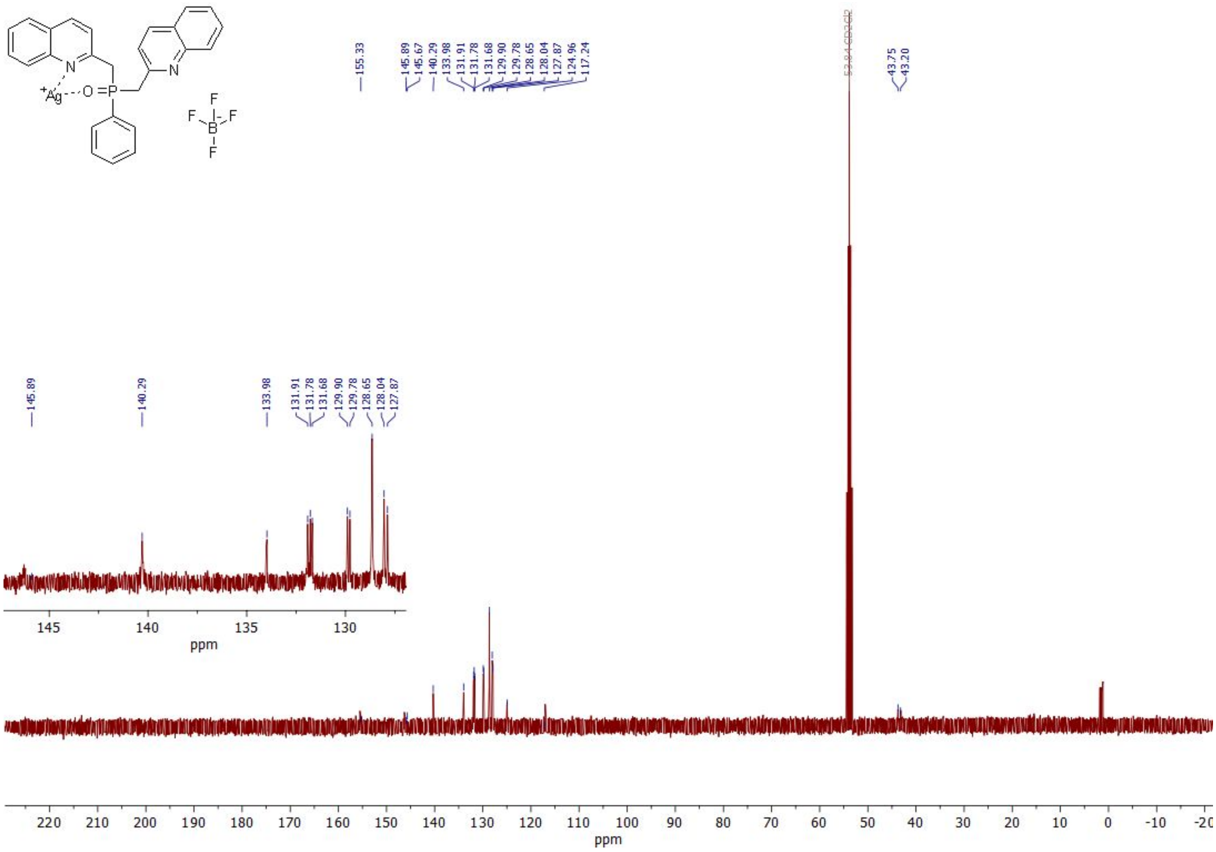
$^1H,^{15}N$–HMBC of **5** in CD_3CN



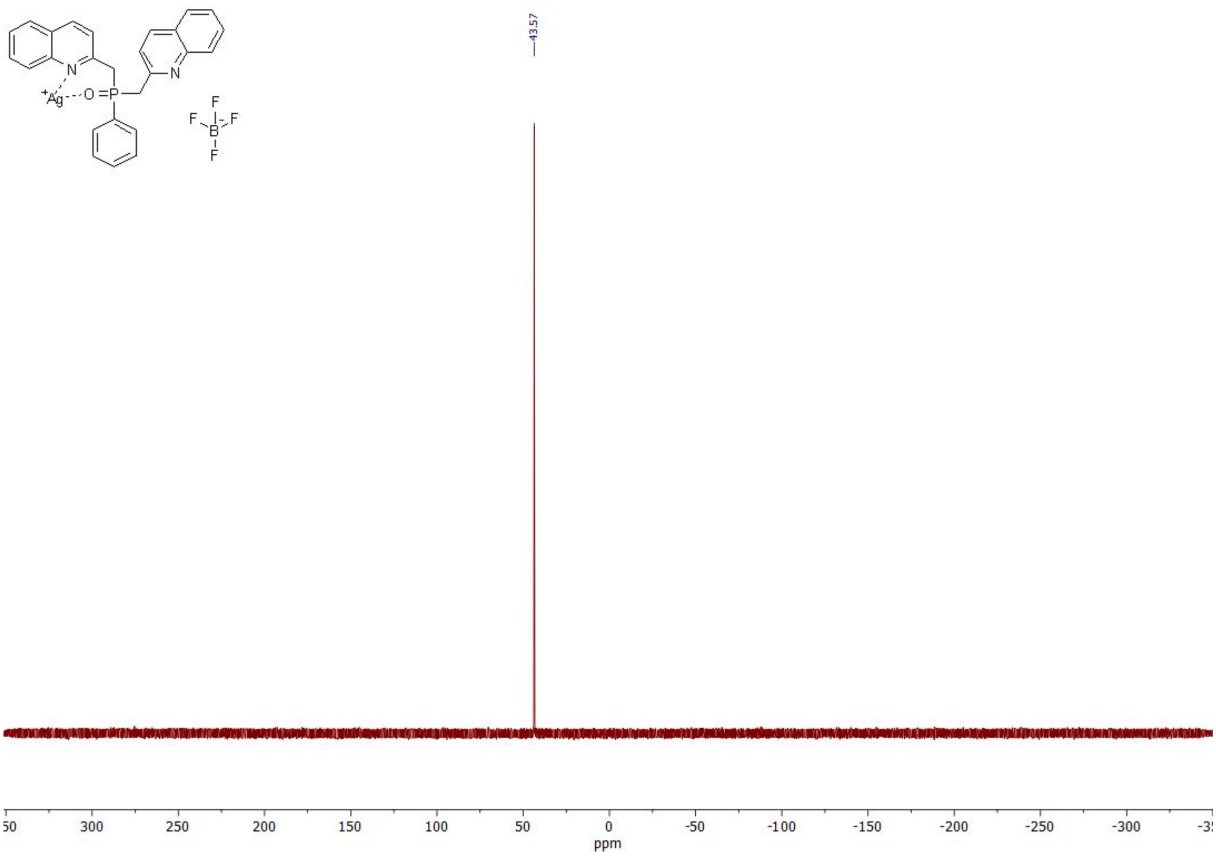
^1H NMR of **5** in CD_2Cl_2, 400.133 MHz.



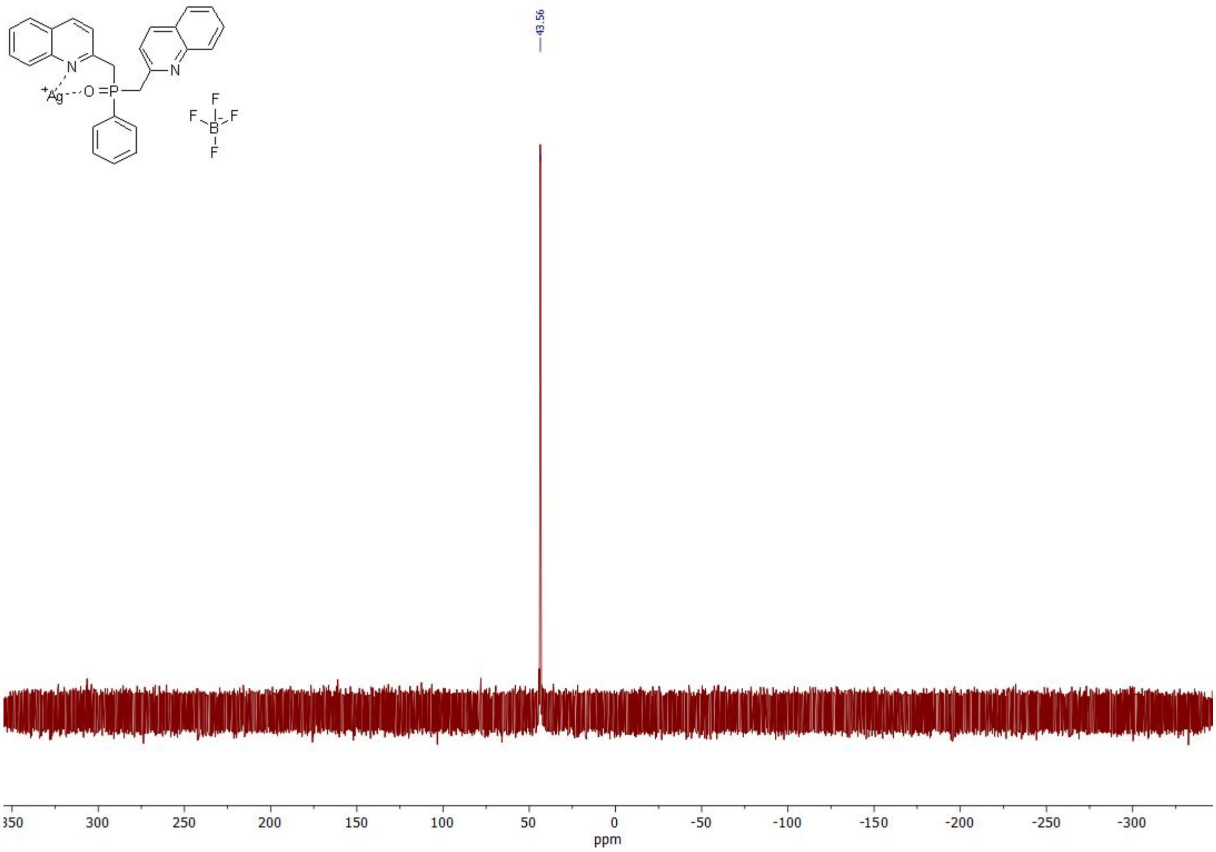
^{13}C NMR of **5** in CD_2Cl_2, 100.623 MHz.



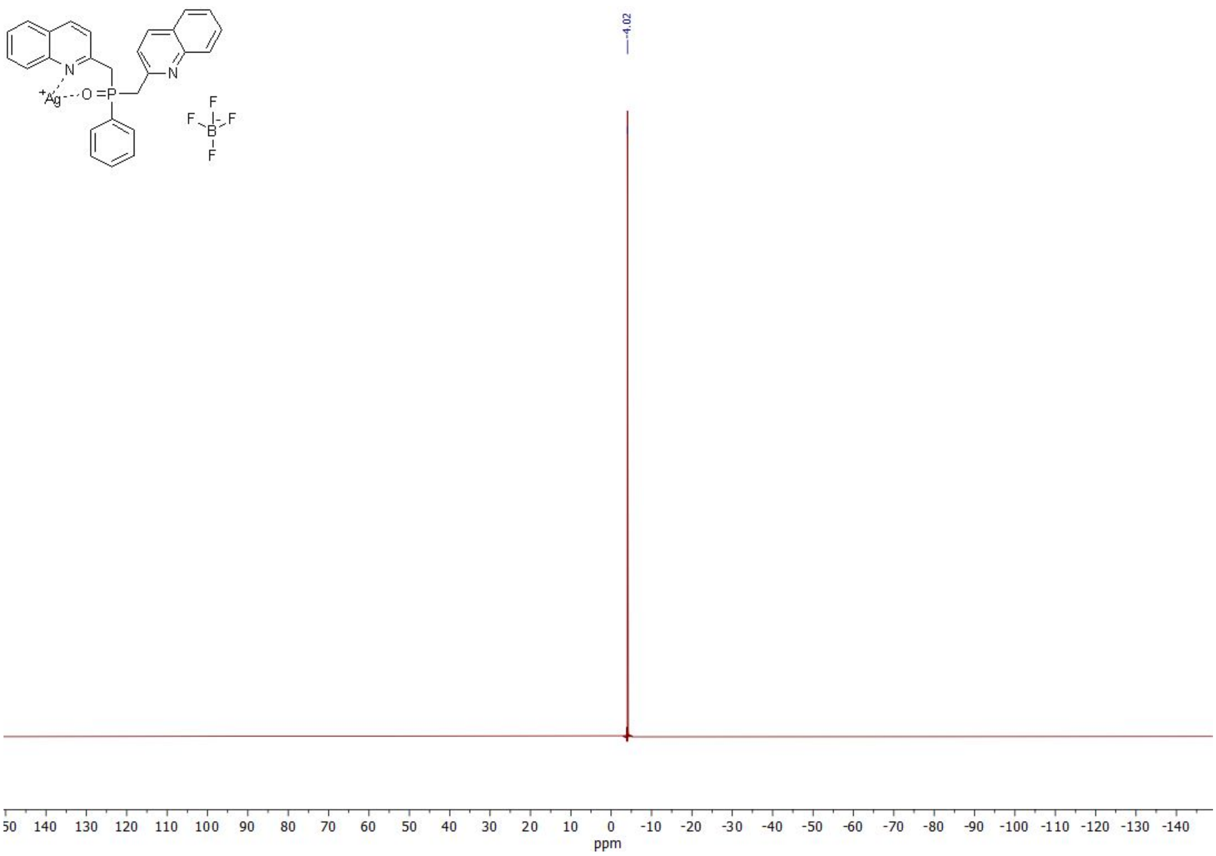
$^{31}P\{^1H\}$ NMR of **5** in CD_2Cl_2, 161.996 MHz.



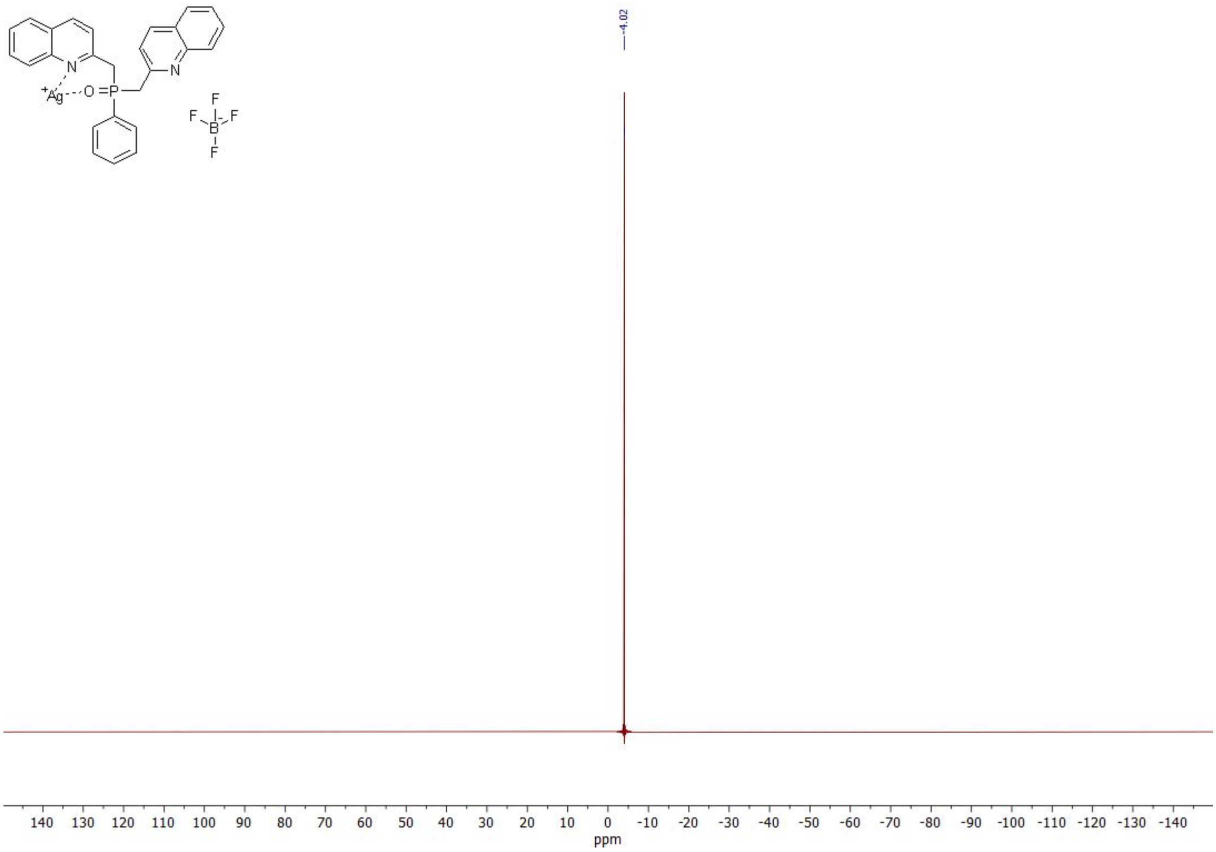
$^{31}P\{/\}$ NMR of **5** in CD_2Cl_2, 161.996 MHz.



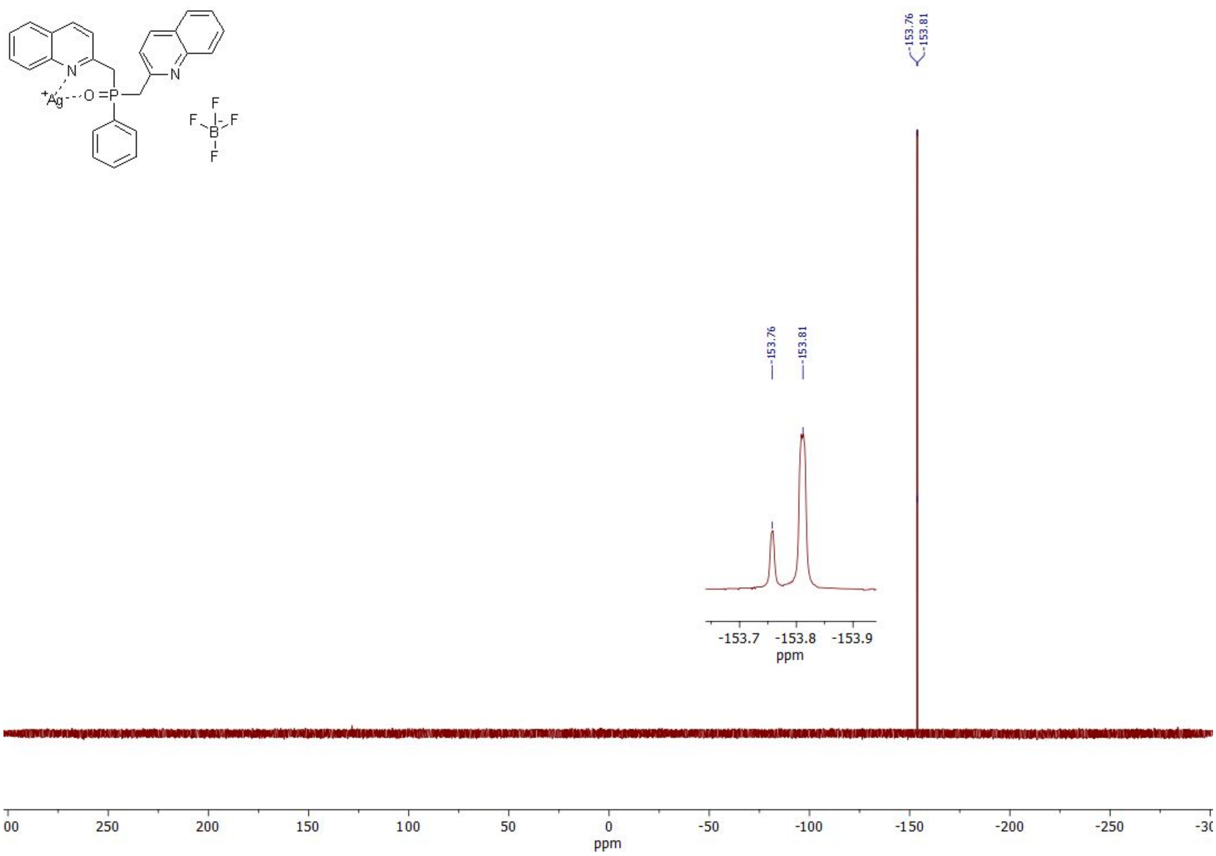
$^{11}B\{^1H\}$ NMR of **5** in CD_2Cl_2, 128.394 MHz.



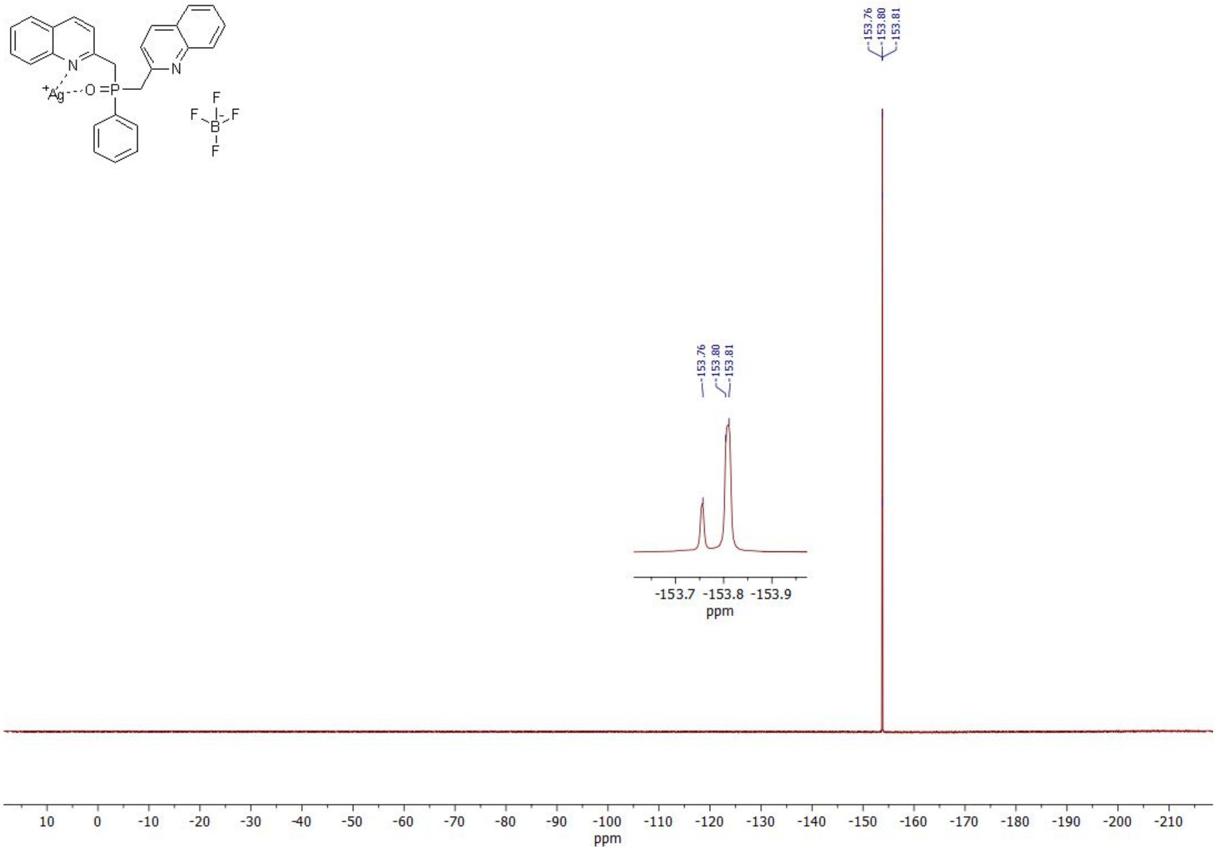
$^{11}B\{/\}$ NMR of **5** in CD_2Cl_2, 128.394 MHz.



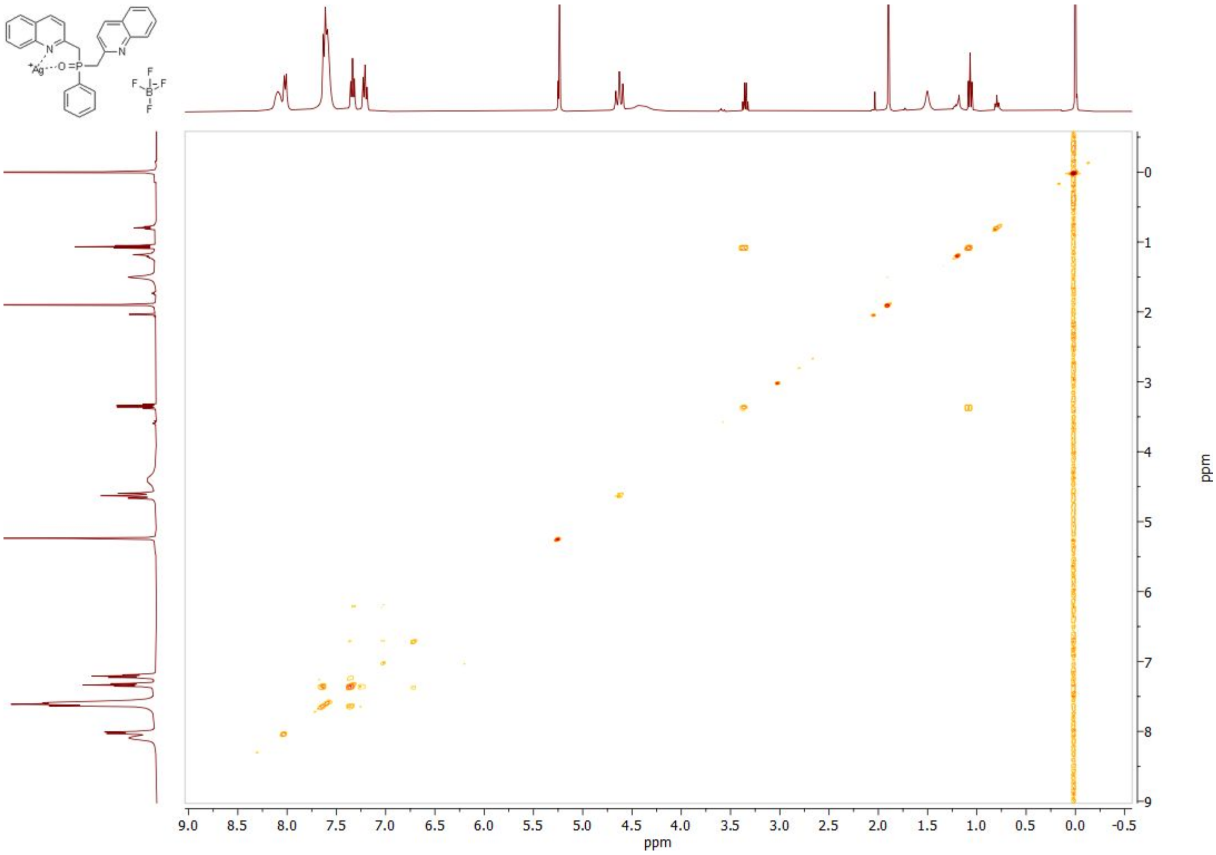
$^{19}F\{^1H\}$ NMR of **5** in CD_2Cl_2, 376.442 MHz.



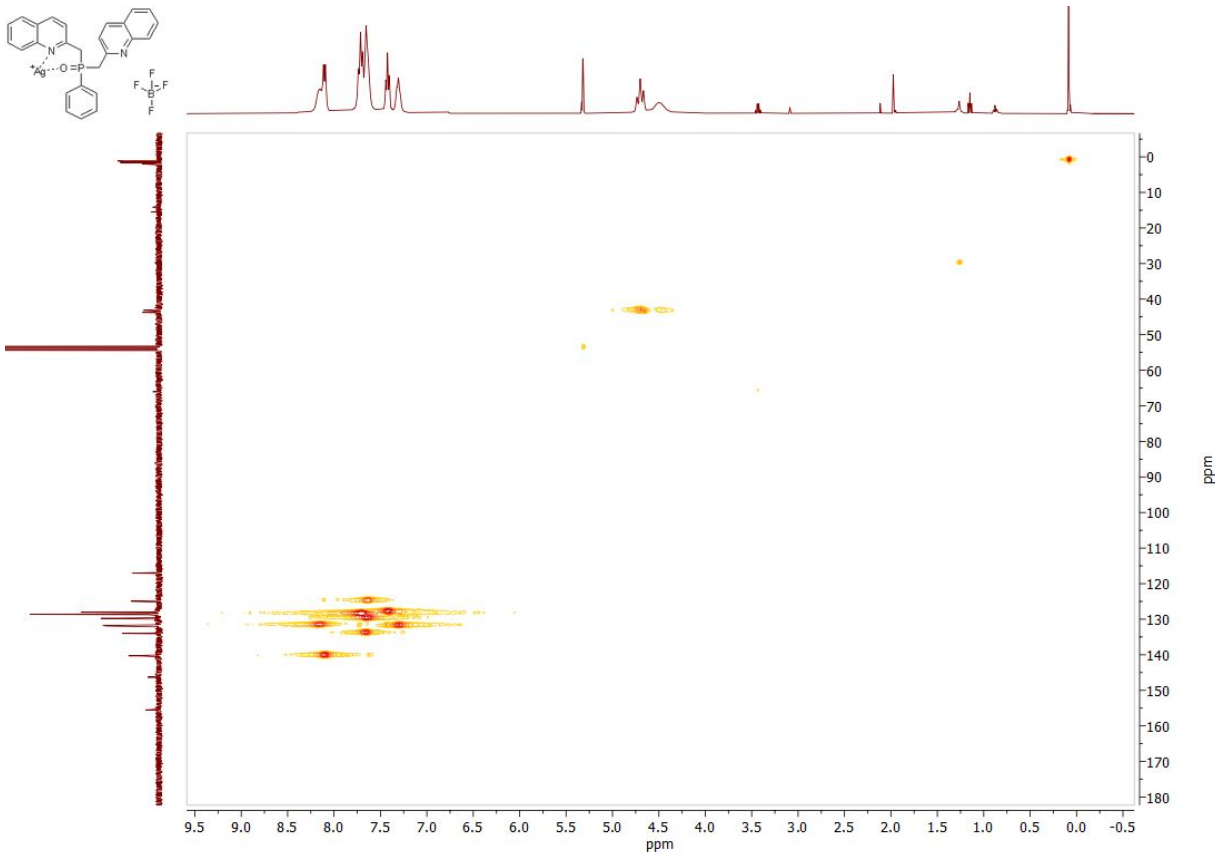
$^{19}F\{/\}$ NMR of **5**in CD_2Cl_2, 376.442 MHz.



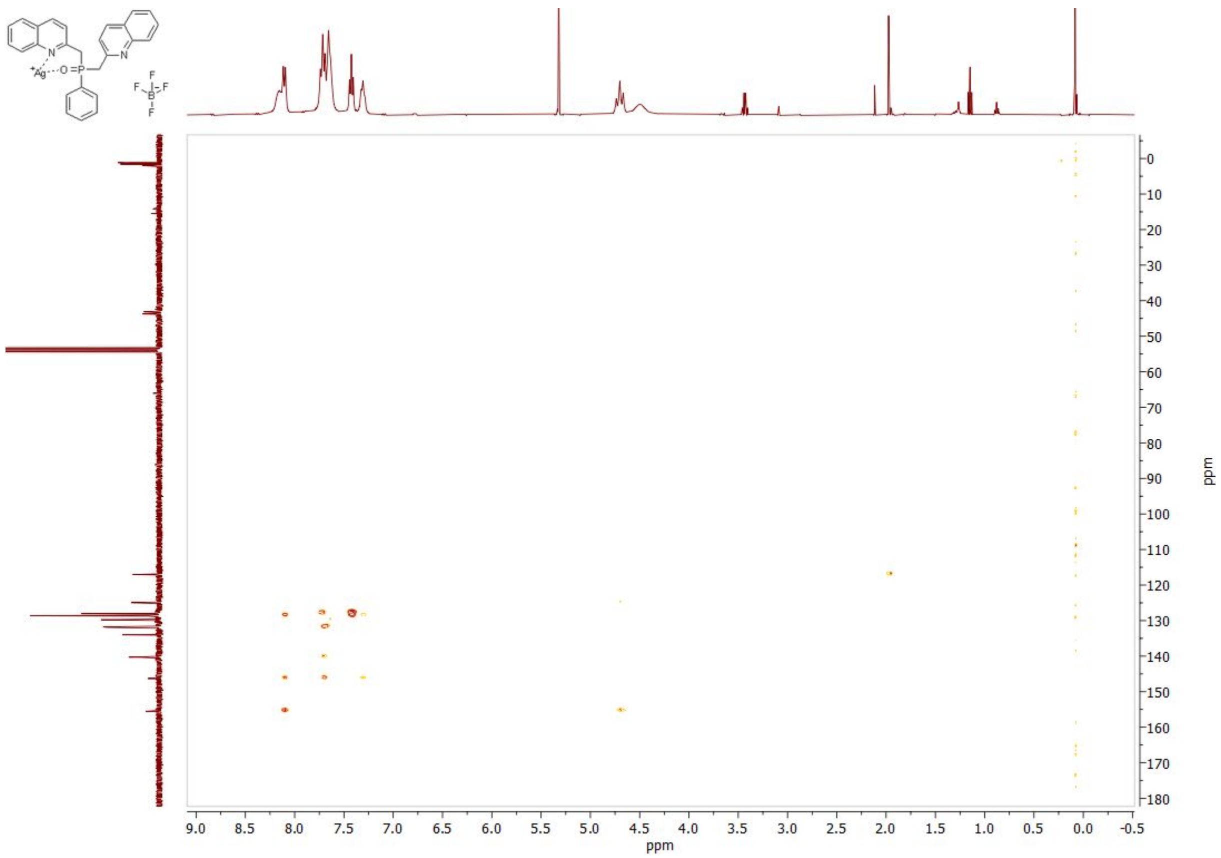
$^{1}H,^{1}H$–COSY$_{45}$ of **5** in CD_2Cl_2.



^1H,^{13}C–HSQC of **5** in CD_2Cl_2



^1H,^{13}C–HMBC of **5** in CD_2Cl_2



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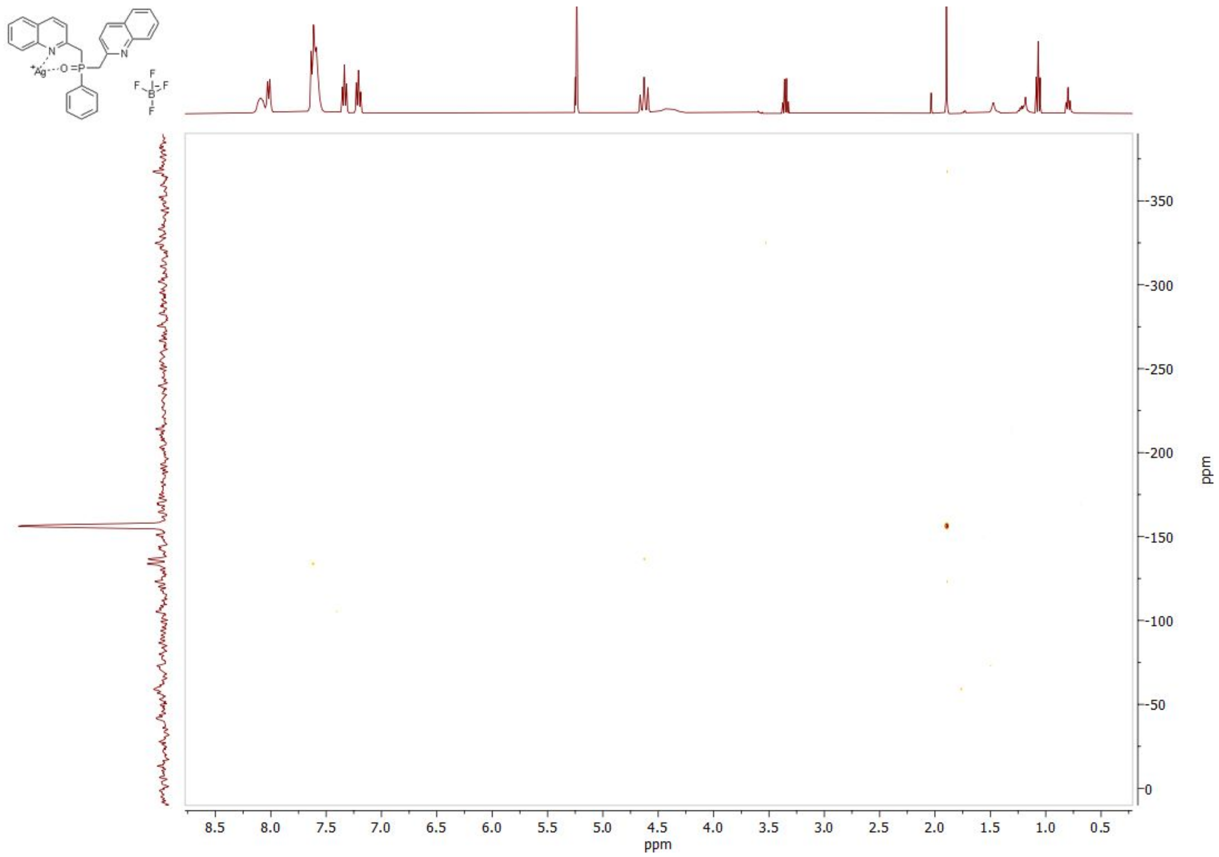
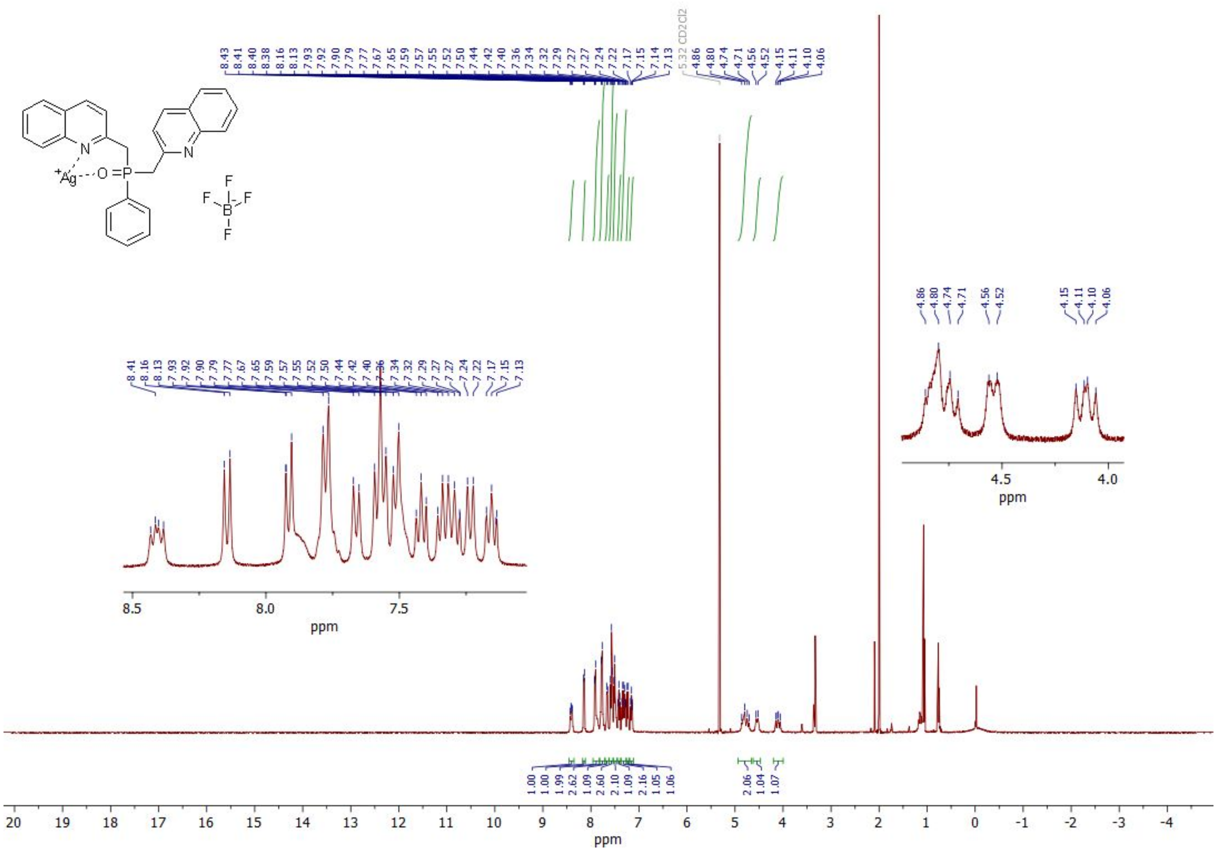
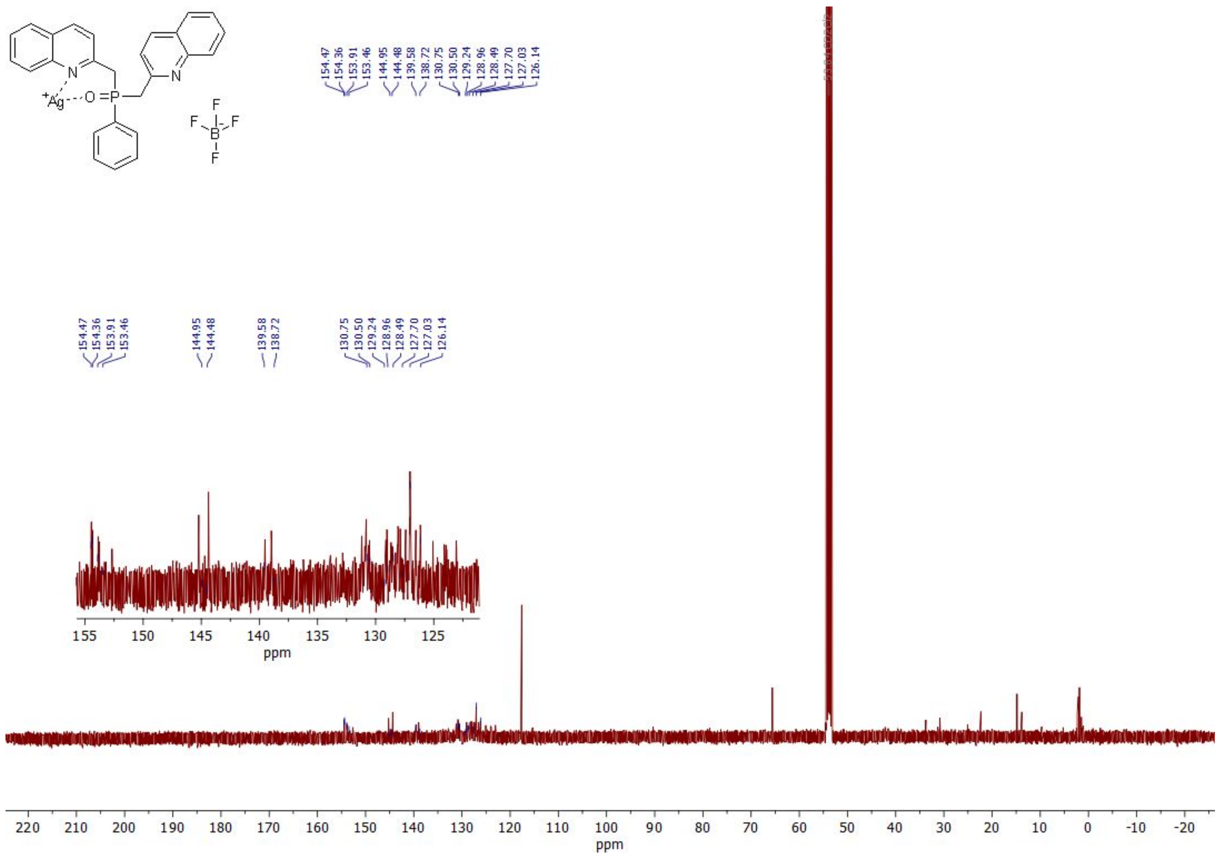


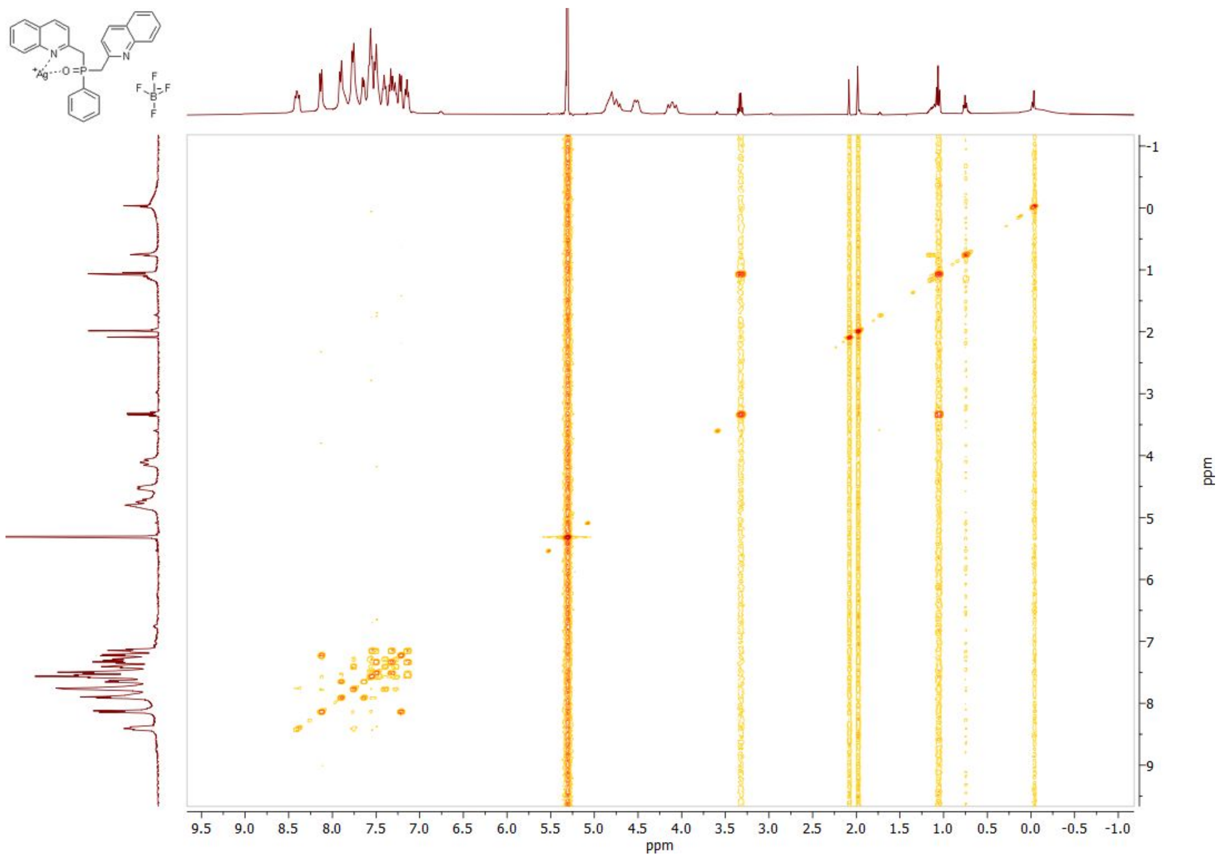
^{1}H NMR of **5** at −80°C in CD_2Cl_2, 400.133 MHz.



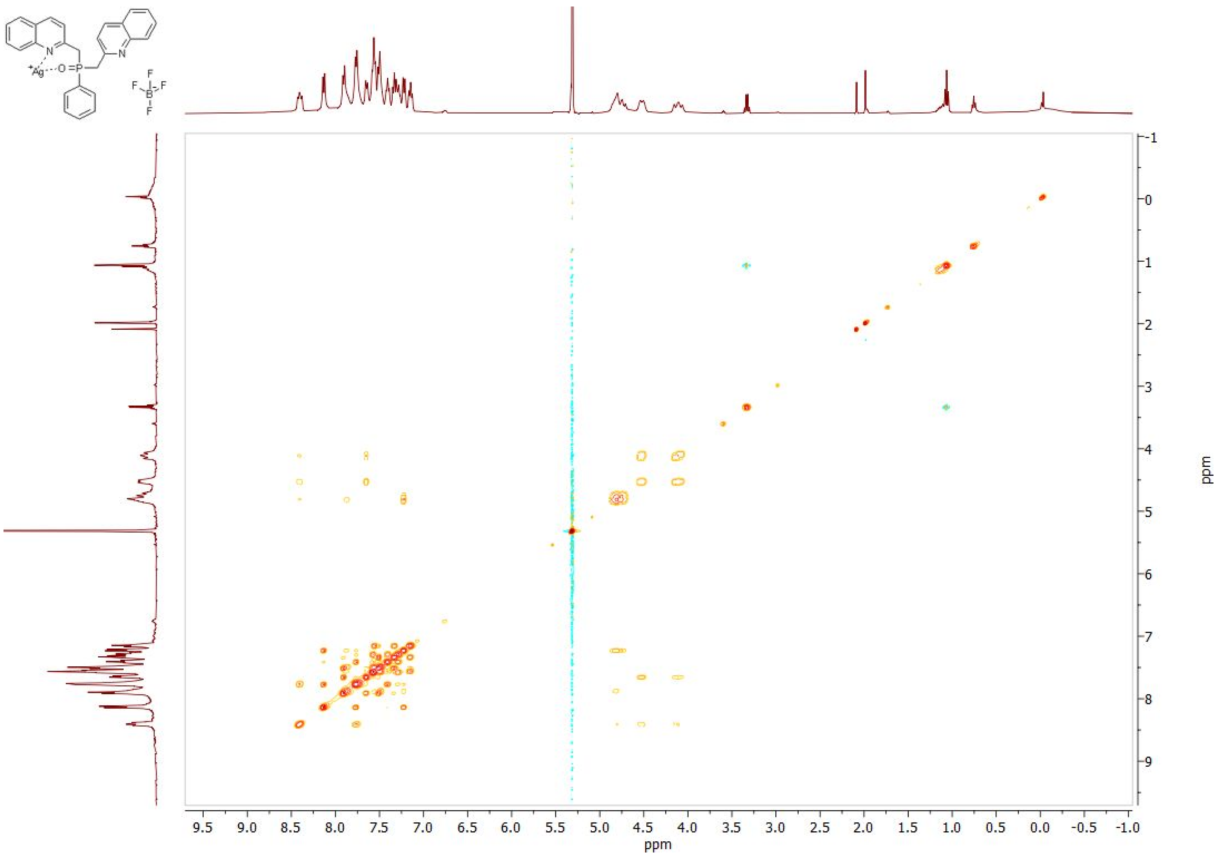
^{13}C NMR of **5** at −80°C in CD_2Cl_2, 100.623 MHz.



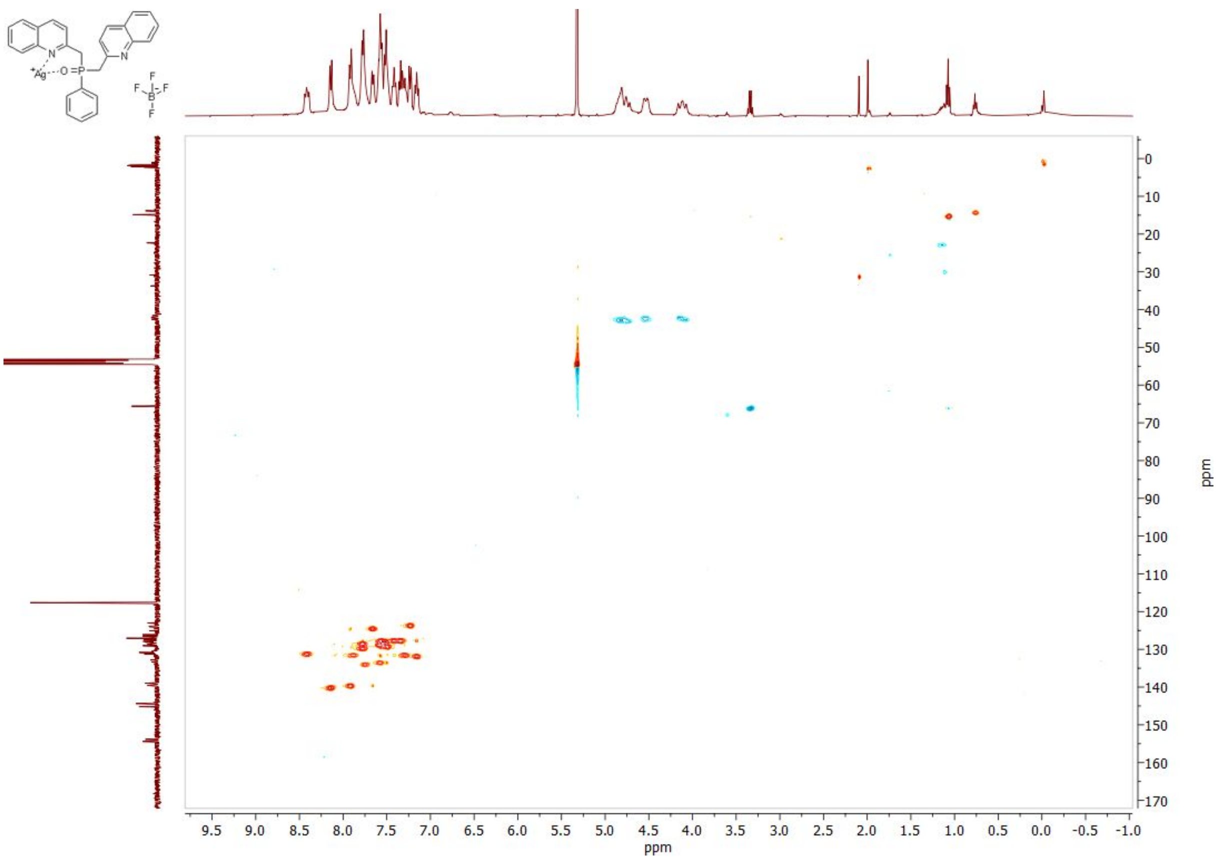
$^1H,^1H$–$COSY_{45}$ of **5** at −80°C in CD_2Cl_2.



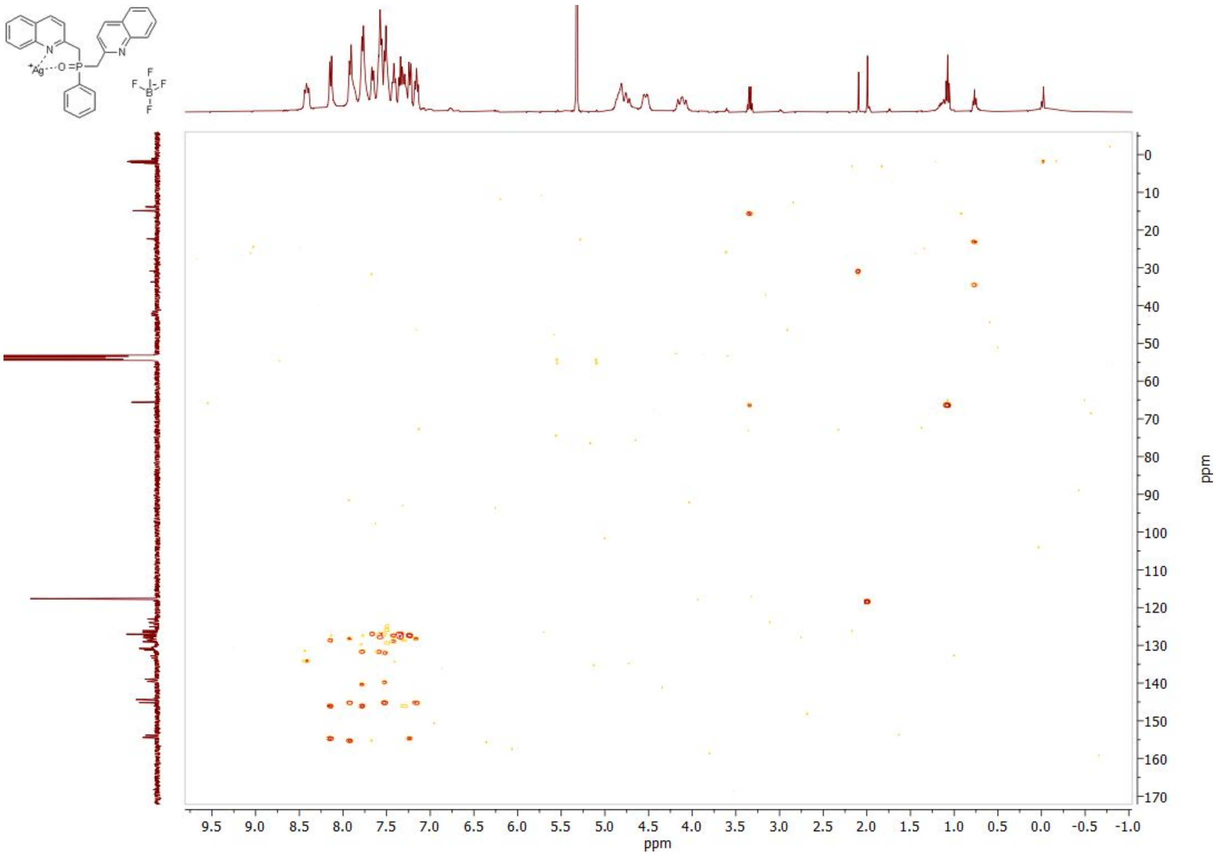
$^{1}H,^{1}H$–NOESY$_{45}$ of **5** at −80°C in CD_2Cl_2.



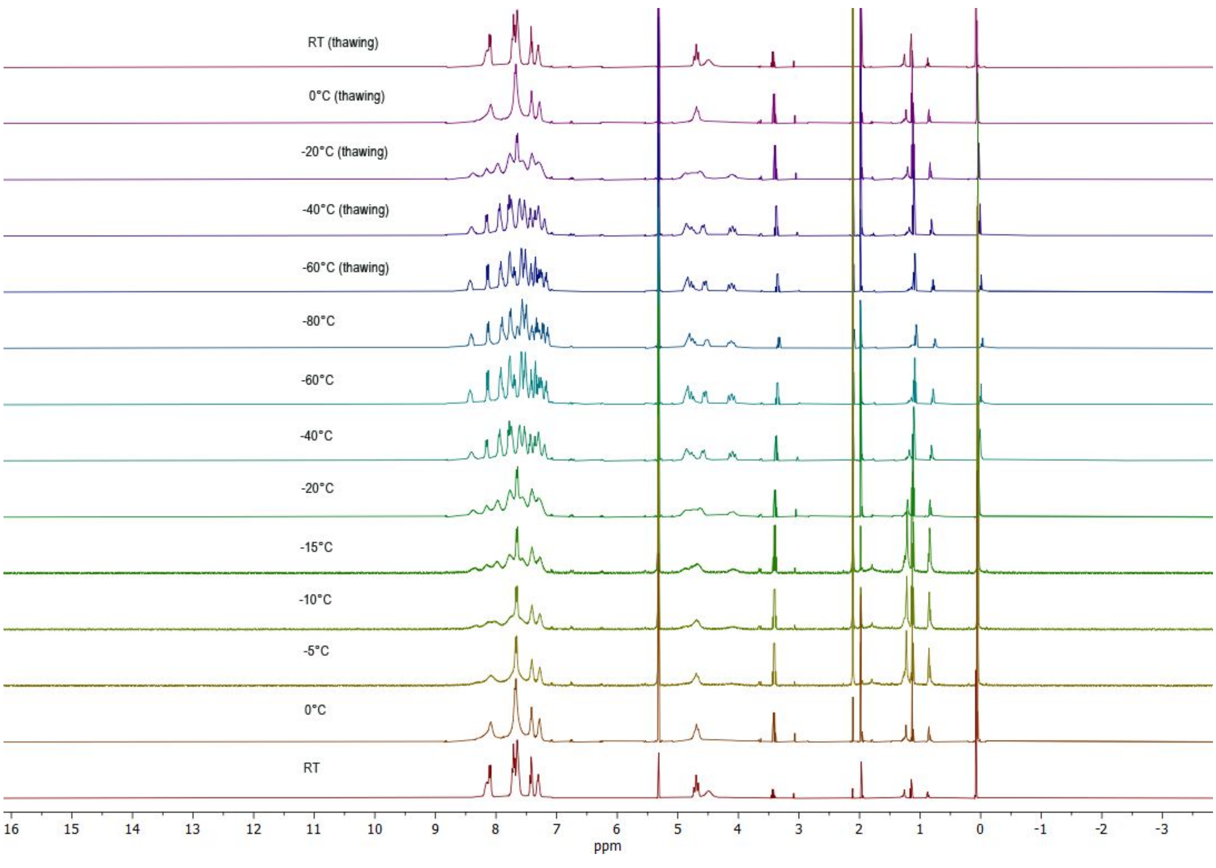
$^{1}H,^{13}C$–HSQC of **5** at −80°C in CD_2Cl_2



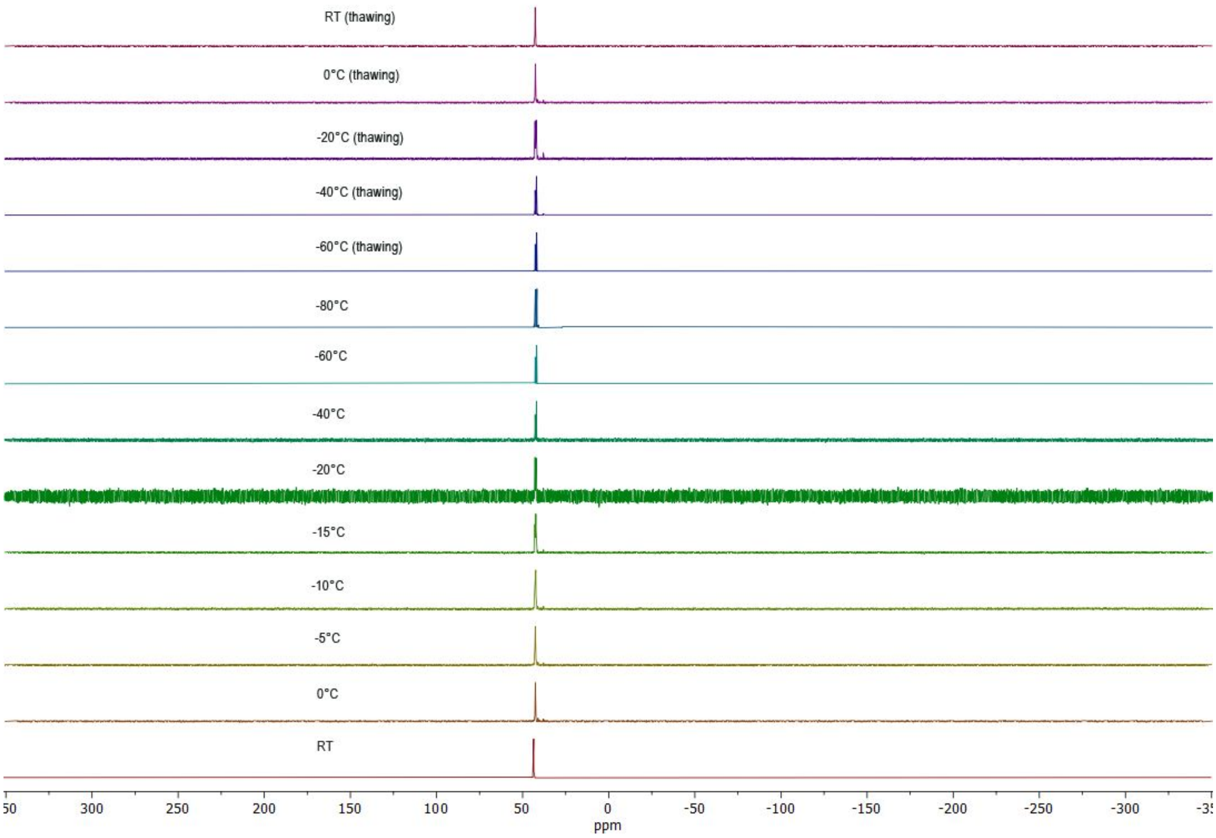
$^{1}H,^{13}C$–HMBC of **5** at −80°C in CD_2Cl_2



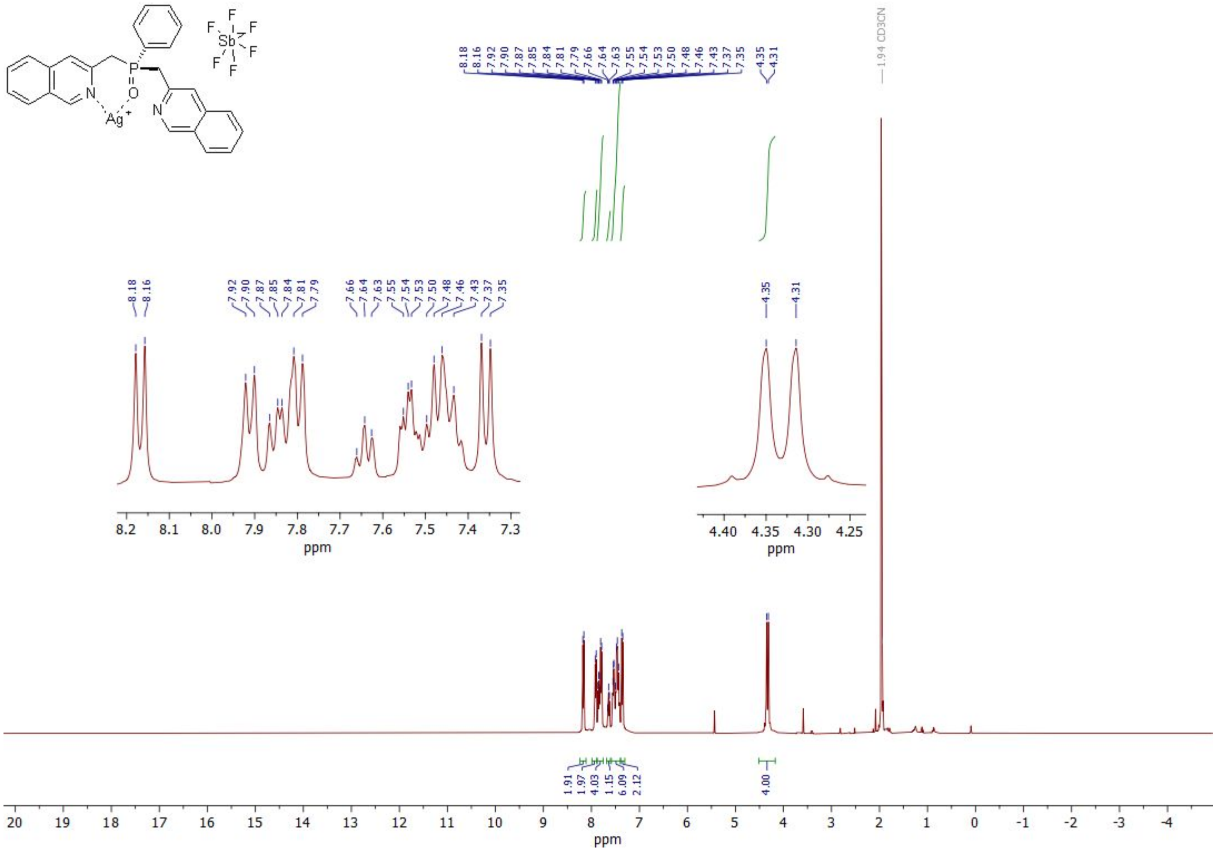
^{1}H NMR of **5** at varying temperatures in CD_2Cl_2, 400.133 MHz.



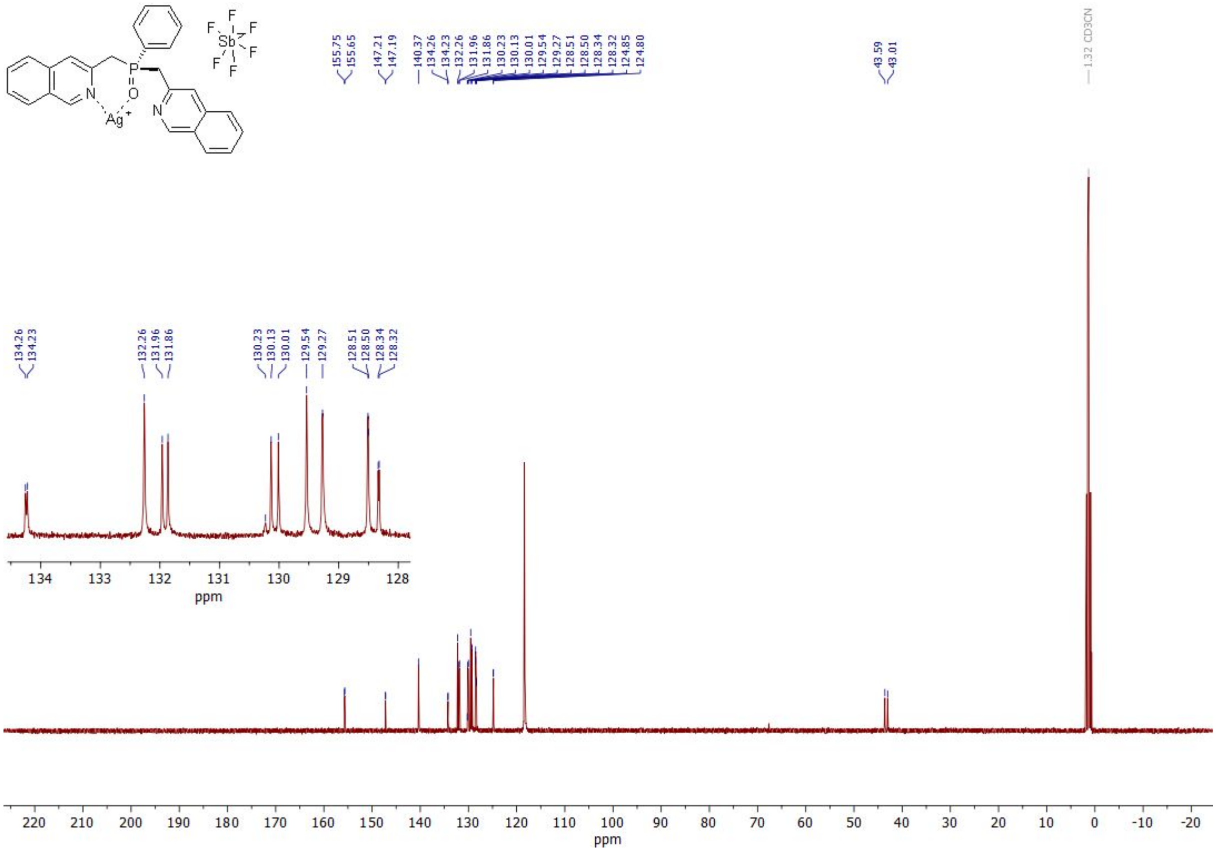
$^{31}P\{^{1}H\}$ NMR of **5** at variable temperatures in CD_2Cl_2, 161.996 MHz.



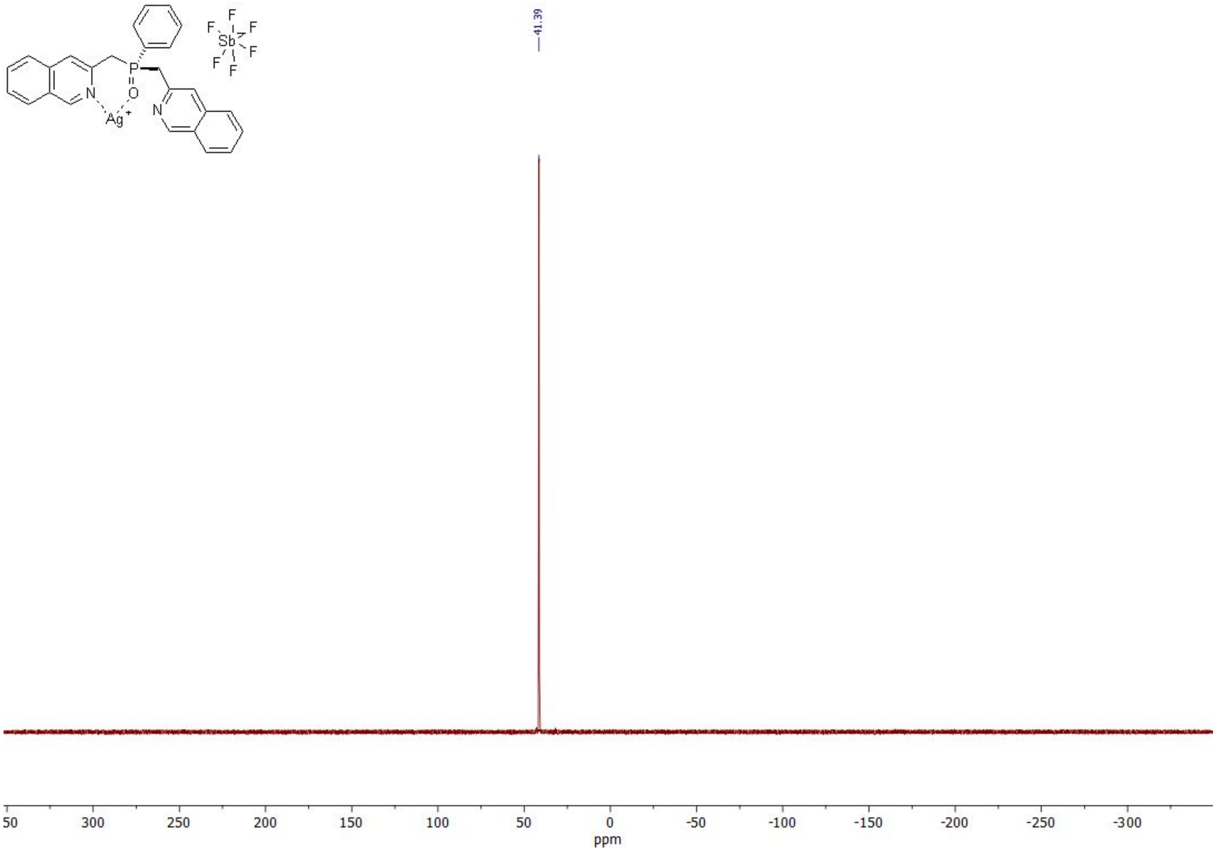
^{1}H NMR of **6** in CD_3CN, 400.133 MHz.



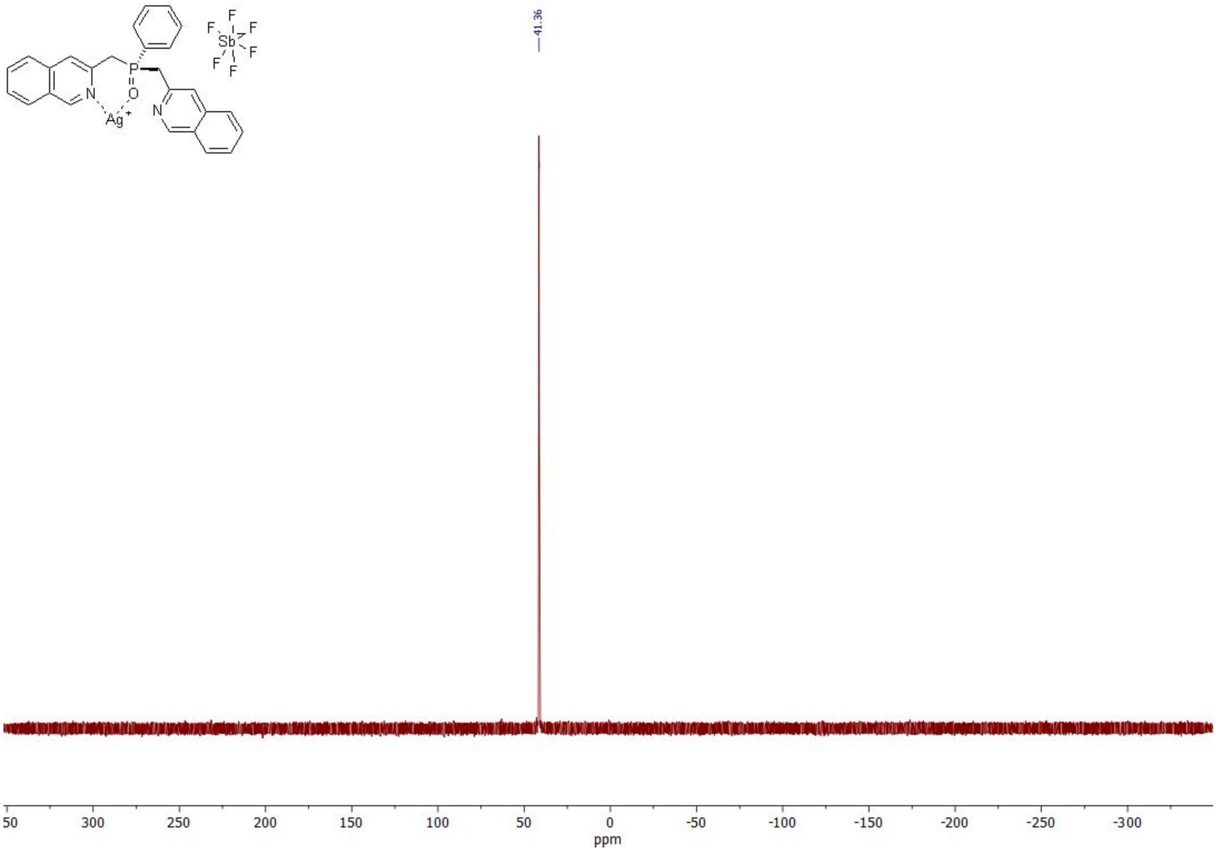
^{13}C NMR of **6** in CD_3CN, 100.623 MHz.



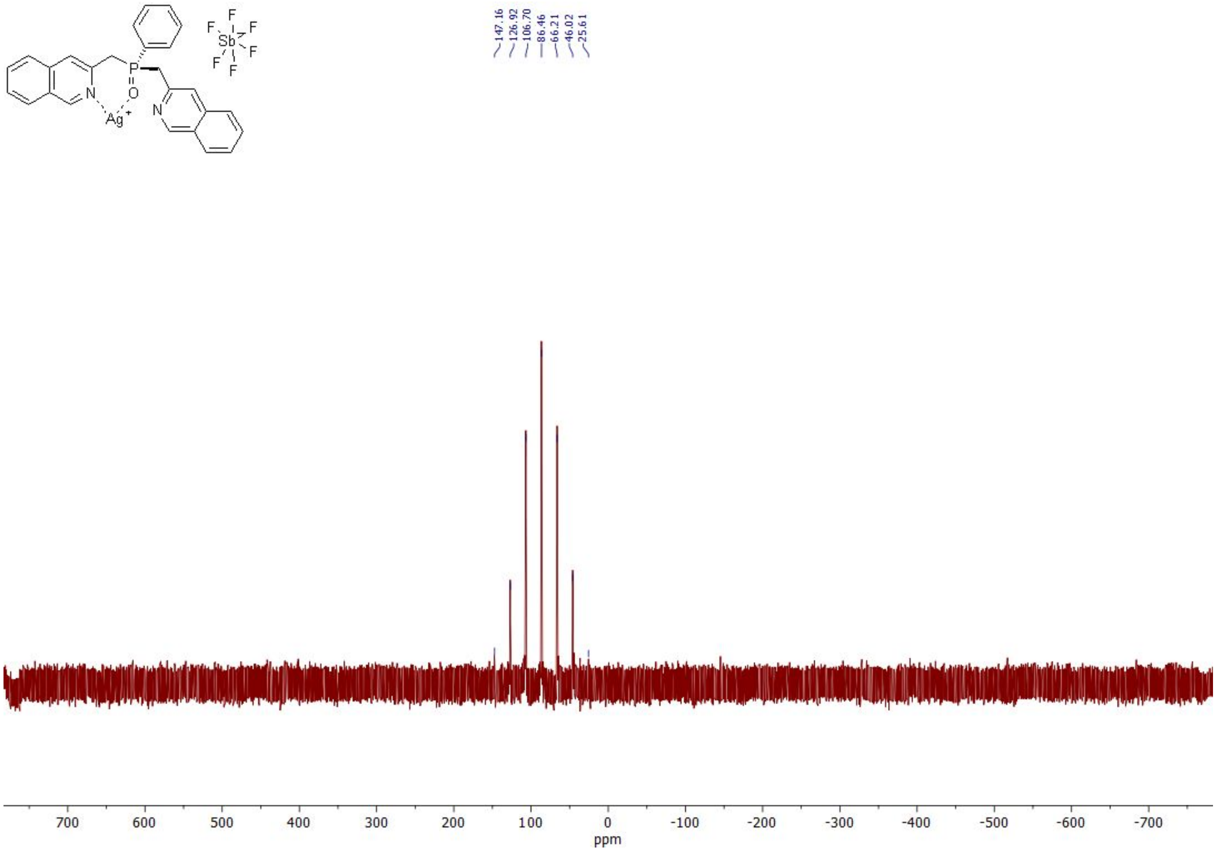
$^{31}P\{^1H\}$ NMR of **6** in CD_3CN, 161.996 MHz.



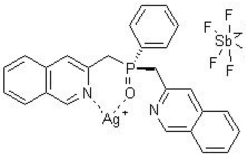
$^{31}P\{/\}$ NMR of **6** in CD_3CN, 161.996 MHz.

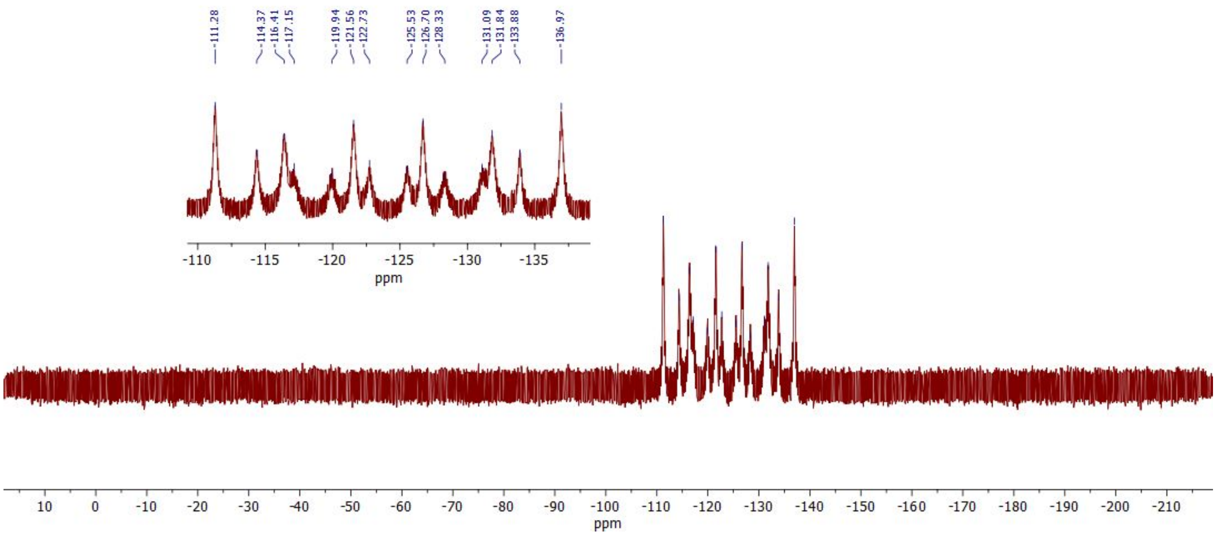


^{121}Sb NMR of **6** in CD_3CN, 95.753 MHz.

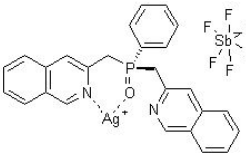


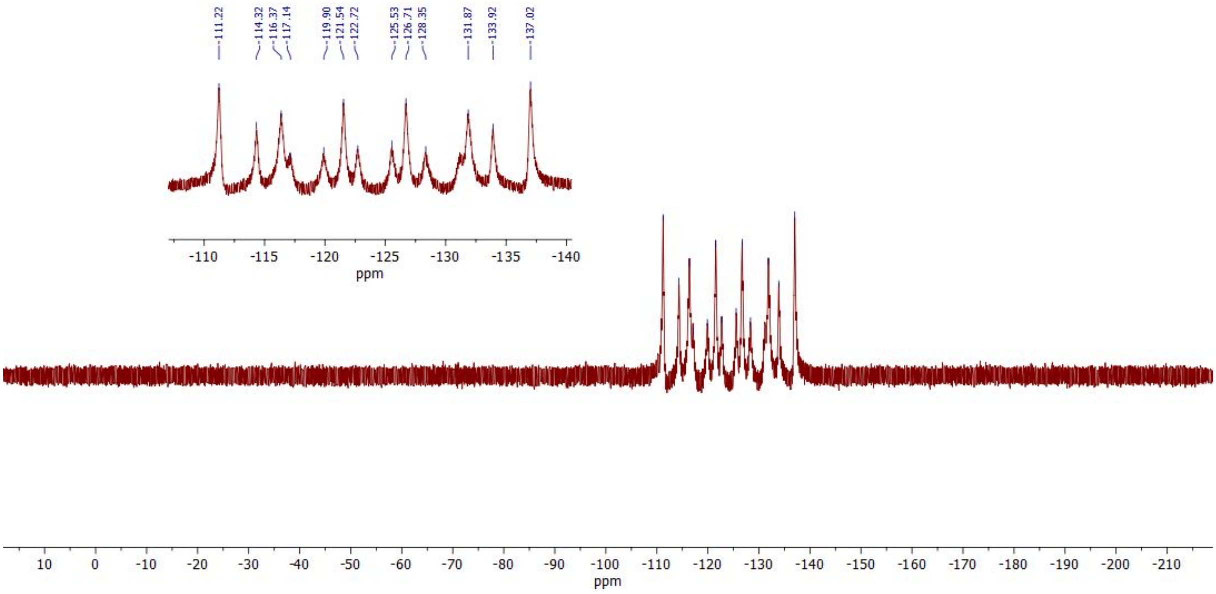
$^{19}F\{^{1}H\}$ NMR of **6** in CD_3CN, 376.442 MHz.



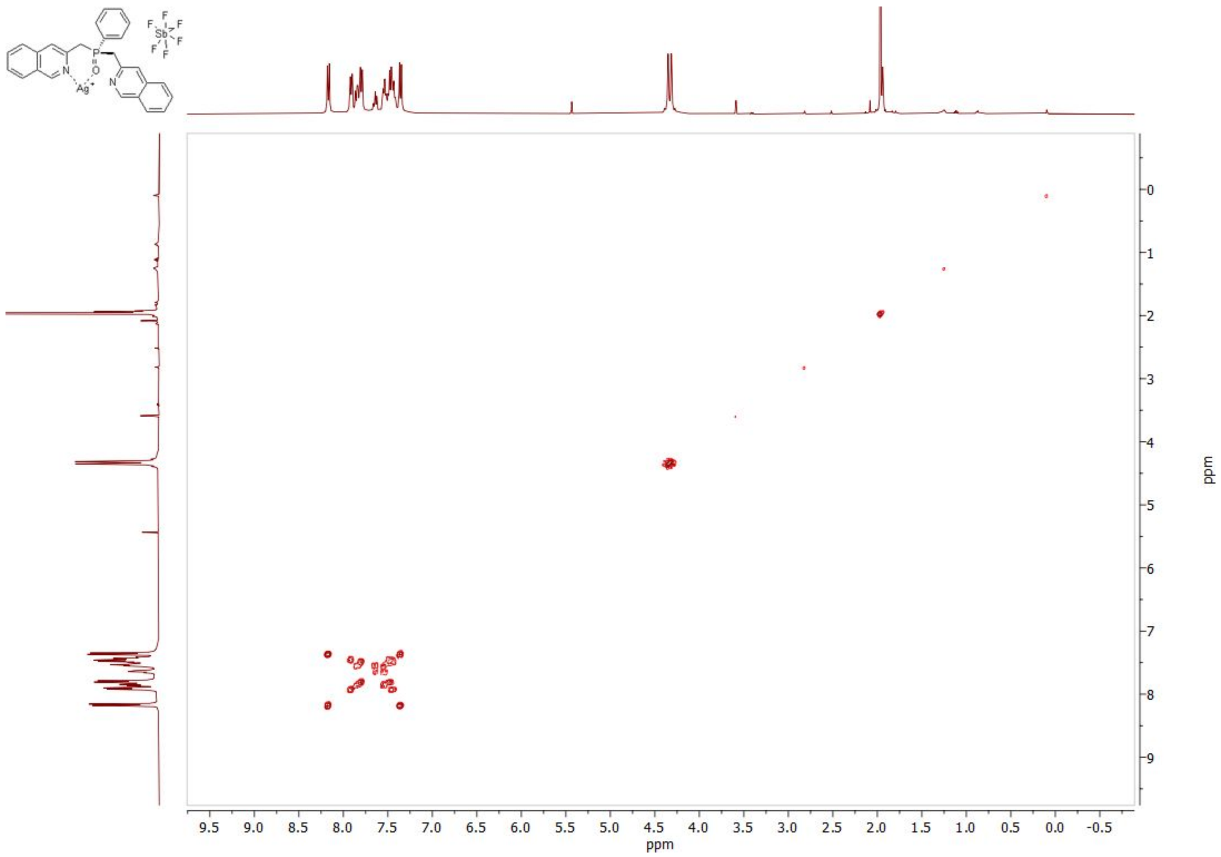


$^{19}F\{/\}$ NMR of **6**in CD_3CN, 376.442 MHz.

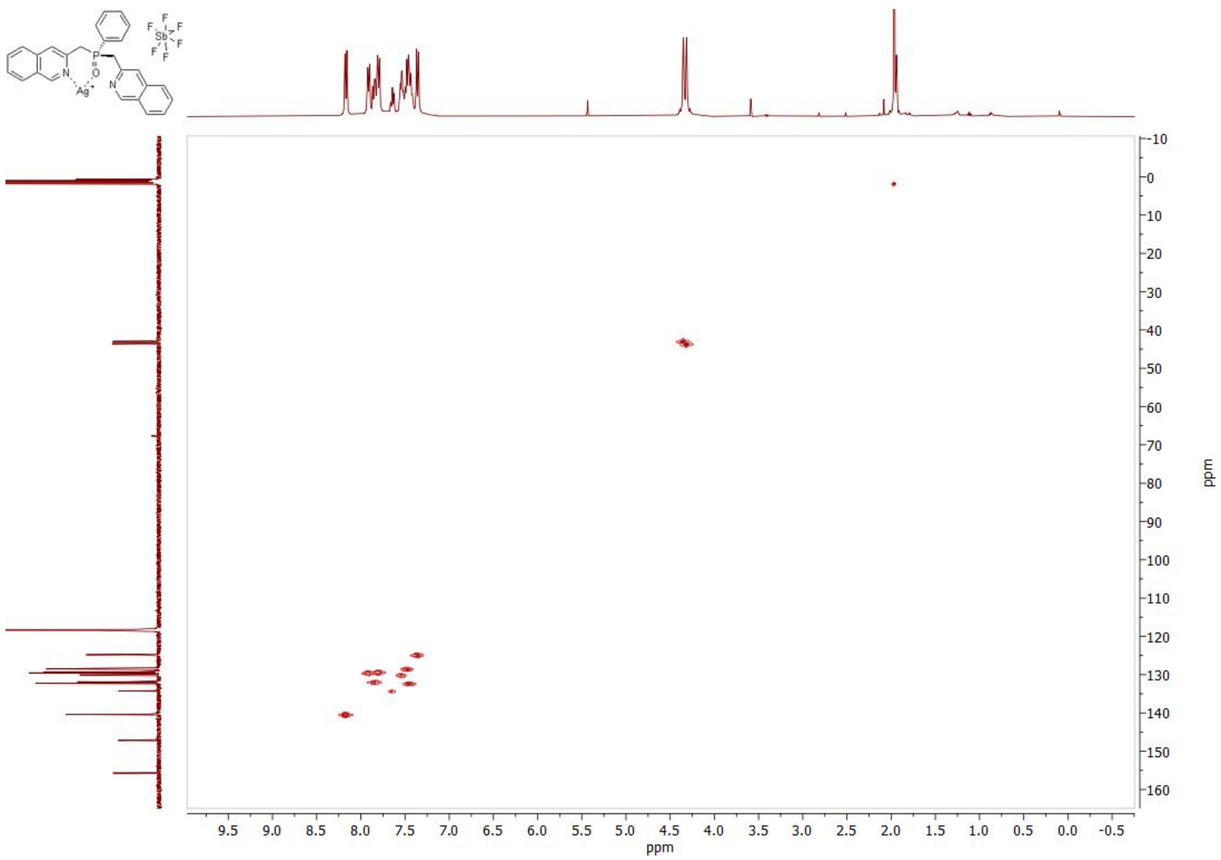




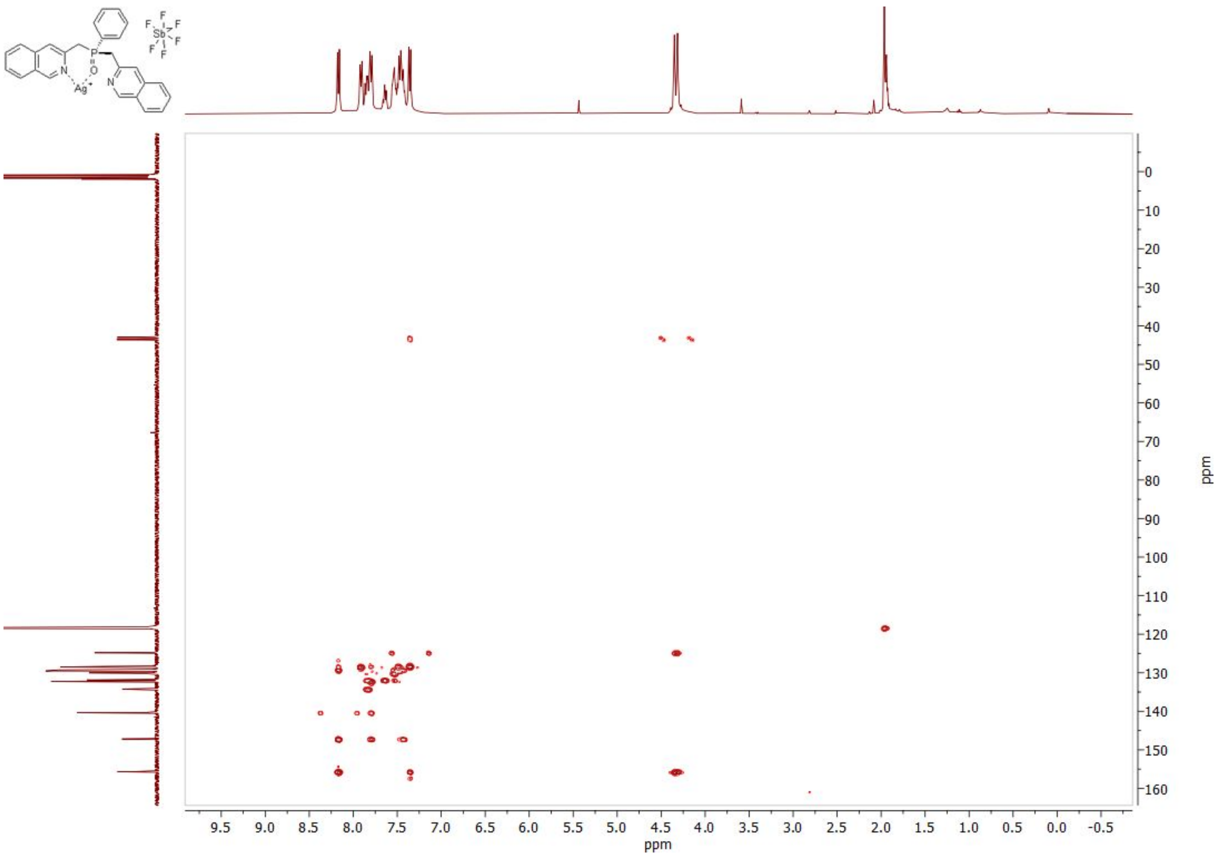
$^1H,^1H$–COSY$_{45}$ of **6** in CD_3CN.



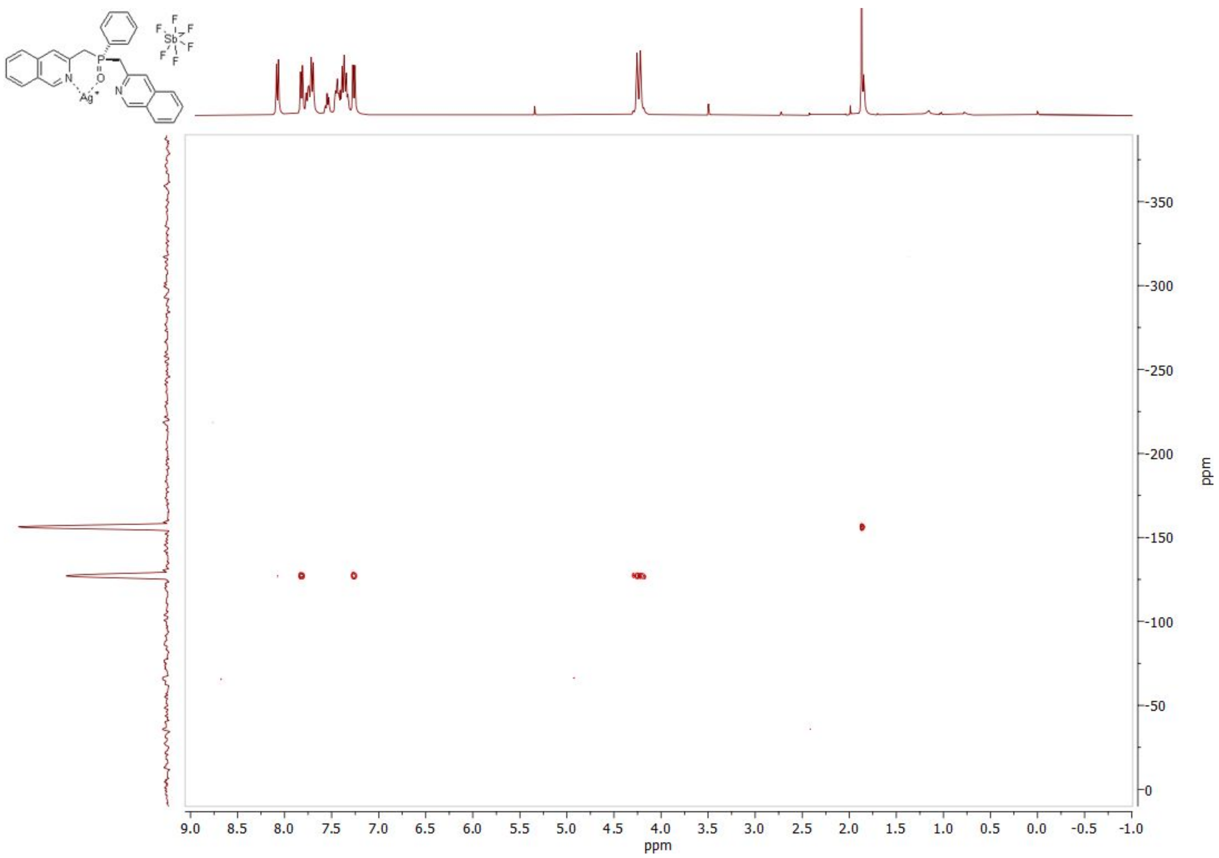
$^1H,^{13}C$–HMQC of **6** in CD_3CN



$^{1}H,^{13}C$–HMBC of **6** in CD_3CN

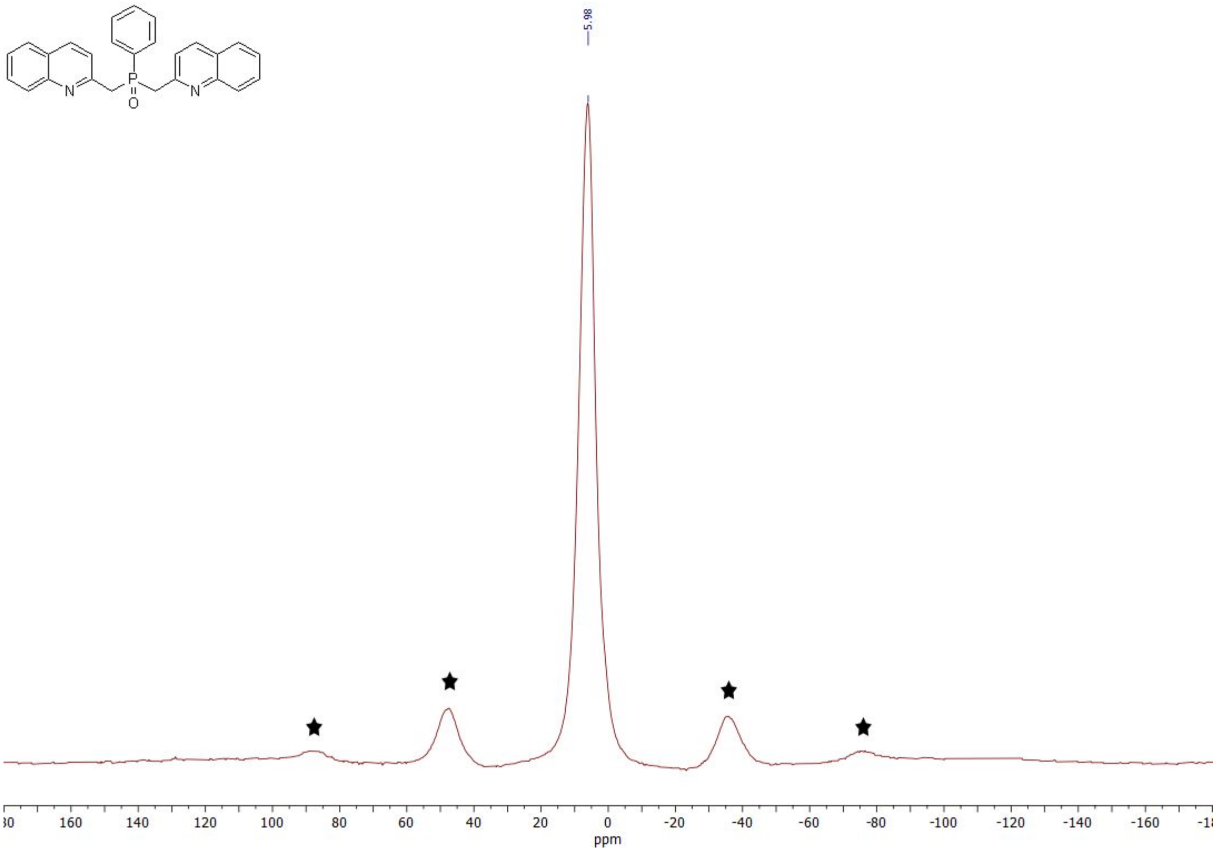


$^{1}H,^{15}N$–HMBC of **6** in CD_3CN

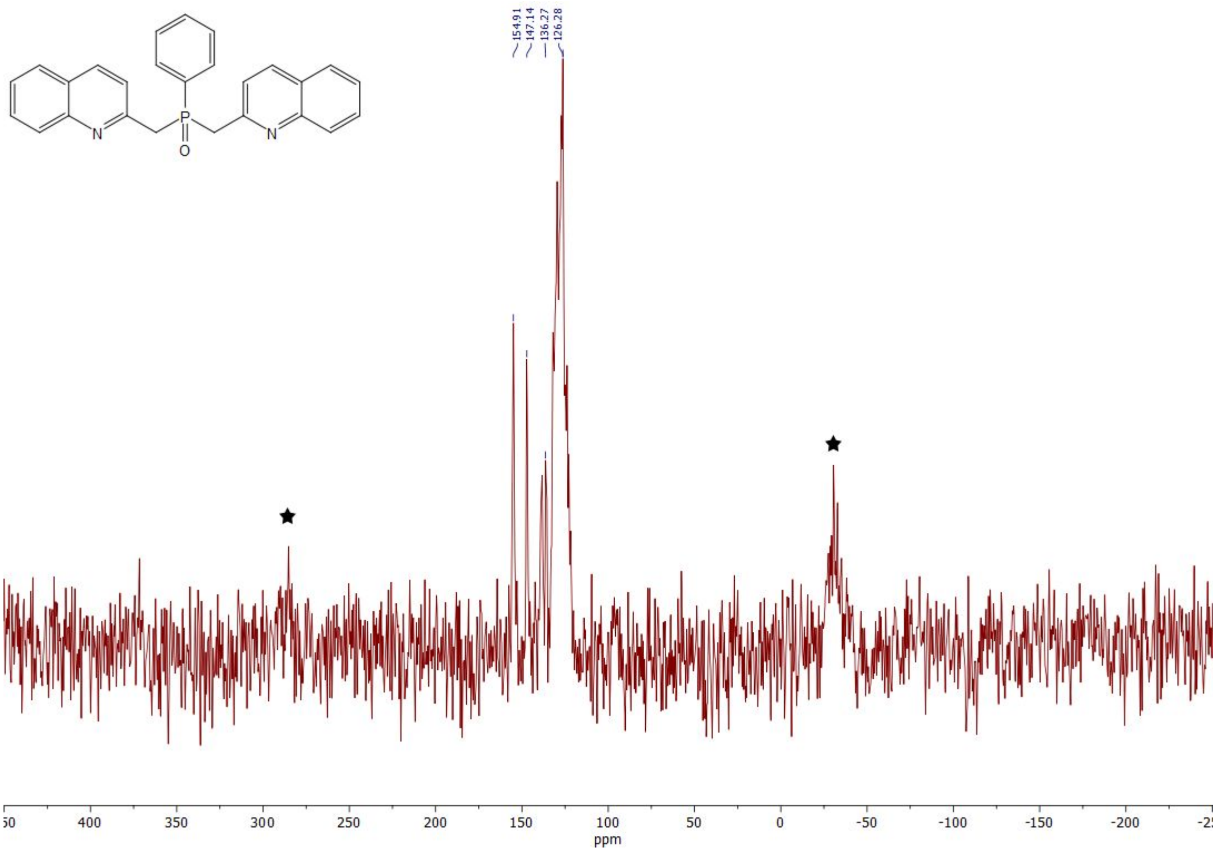


Solid-State NMR data

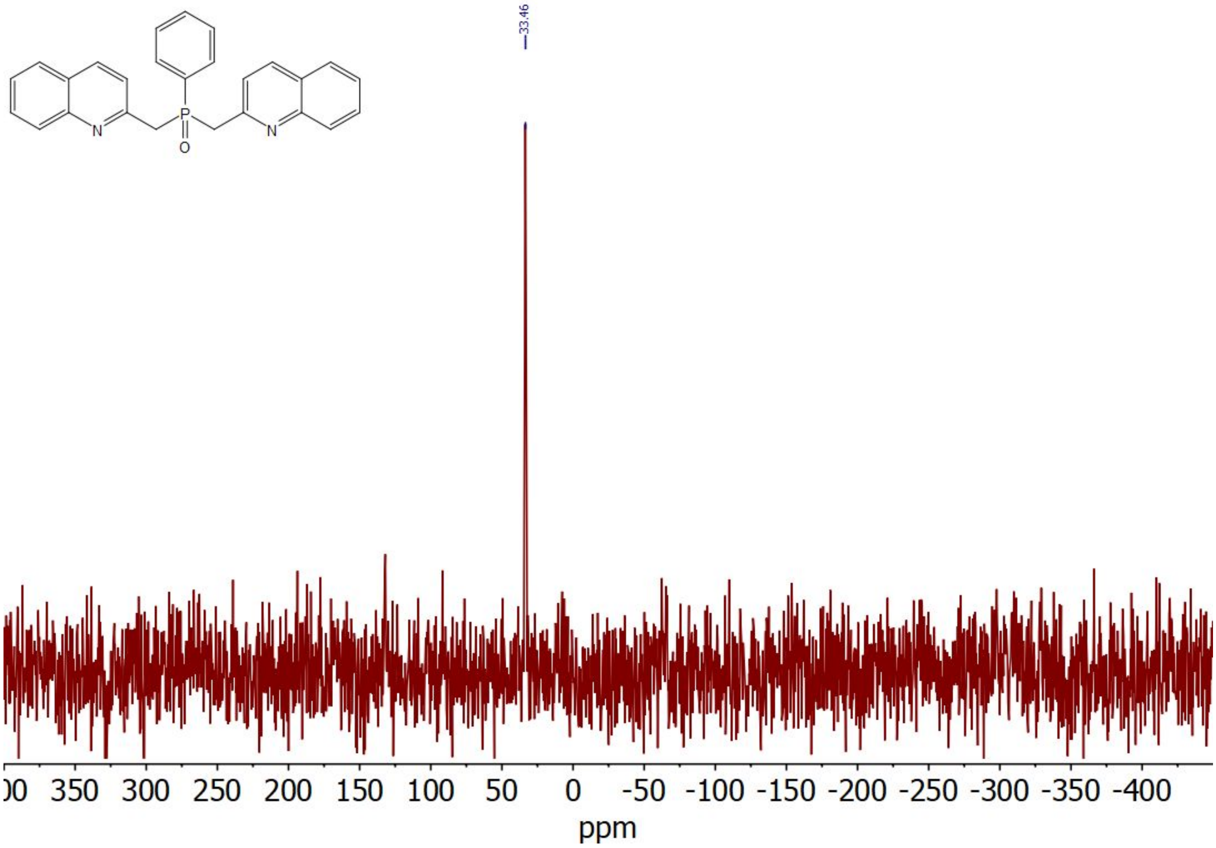
^1H CP MAS NMR of **2**, 300 K



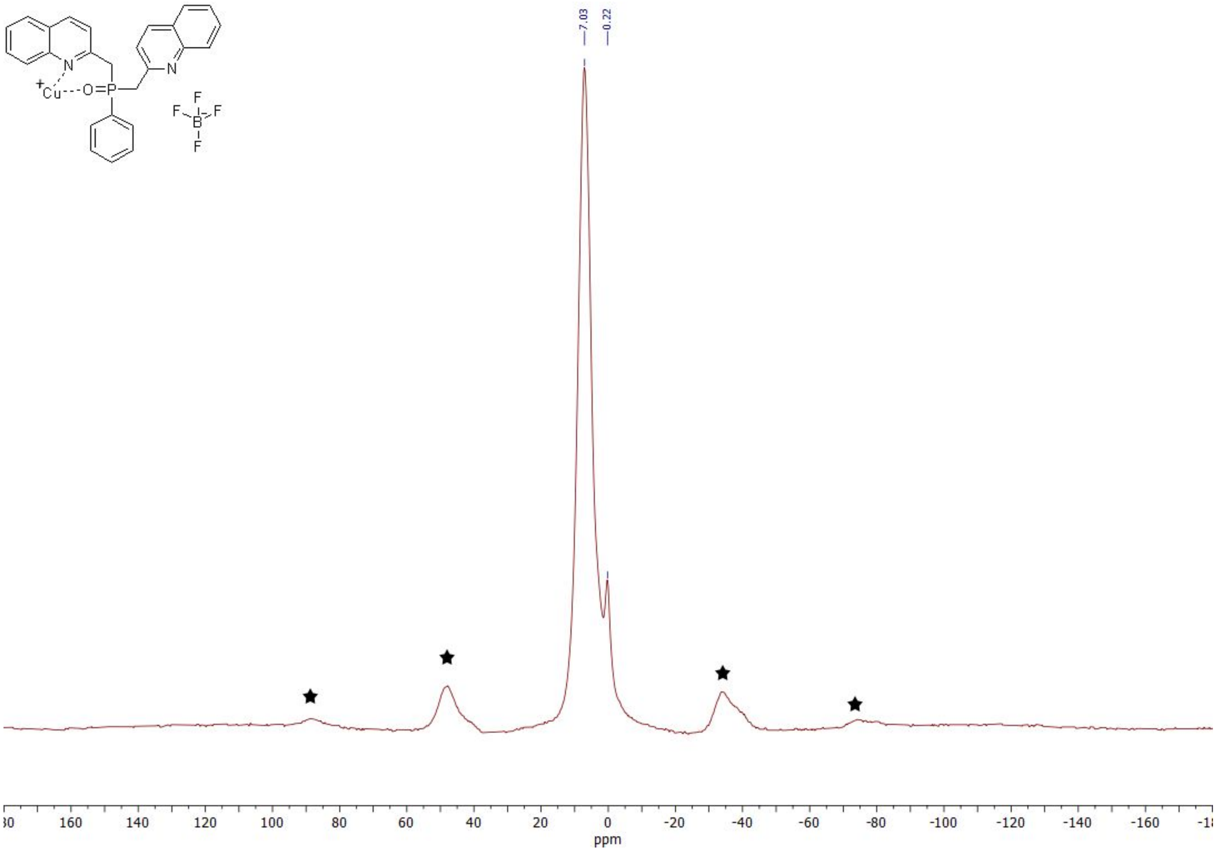
^{13}C CP MAS NMR of **2**, 300 K



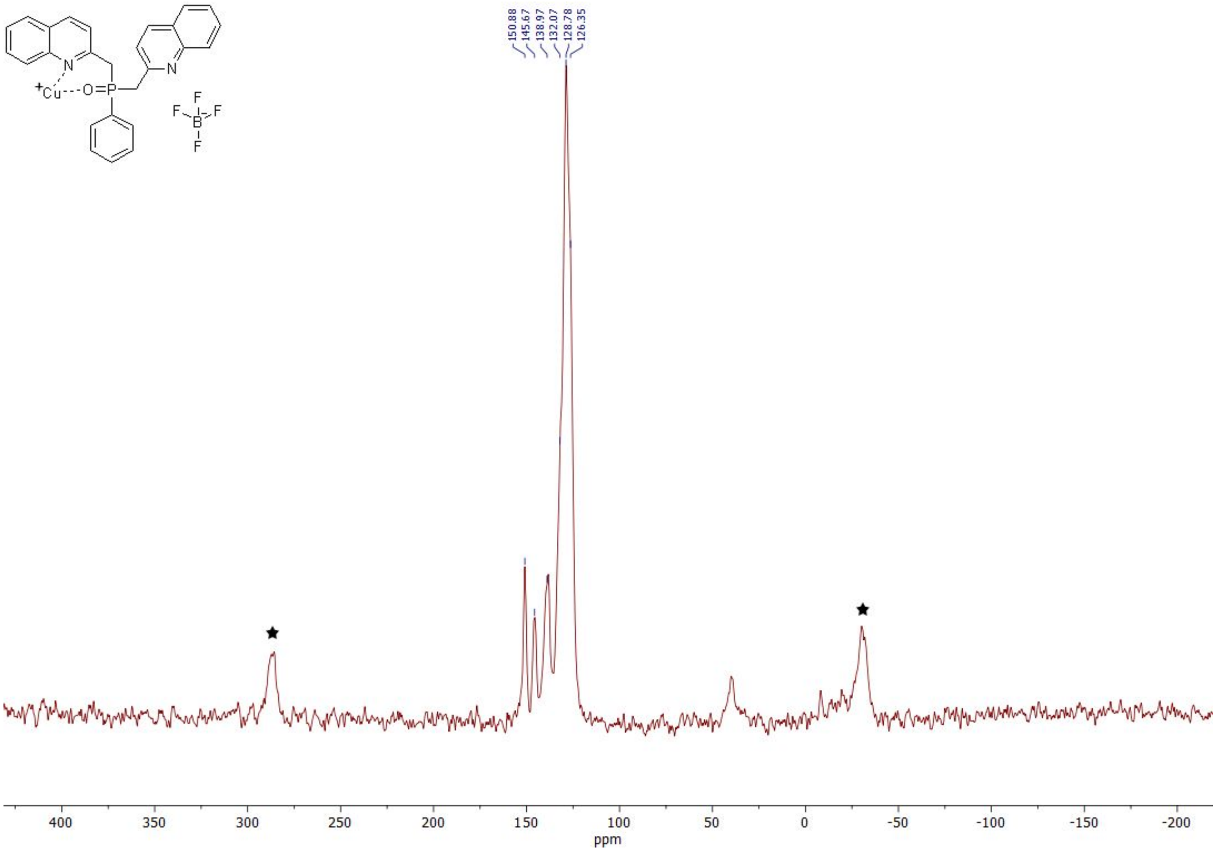
^{31}P CP MAS NMR of **2**, 300 K



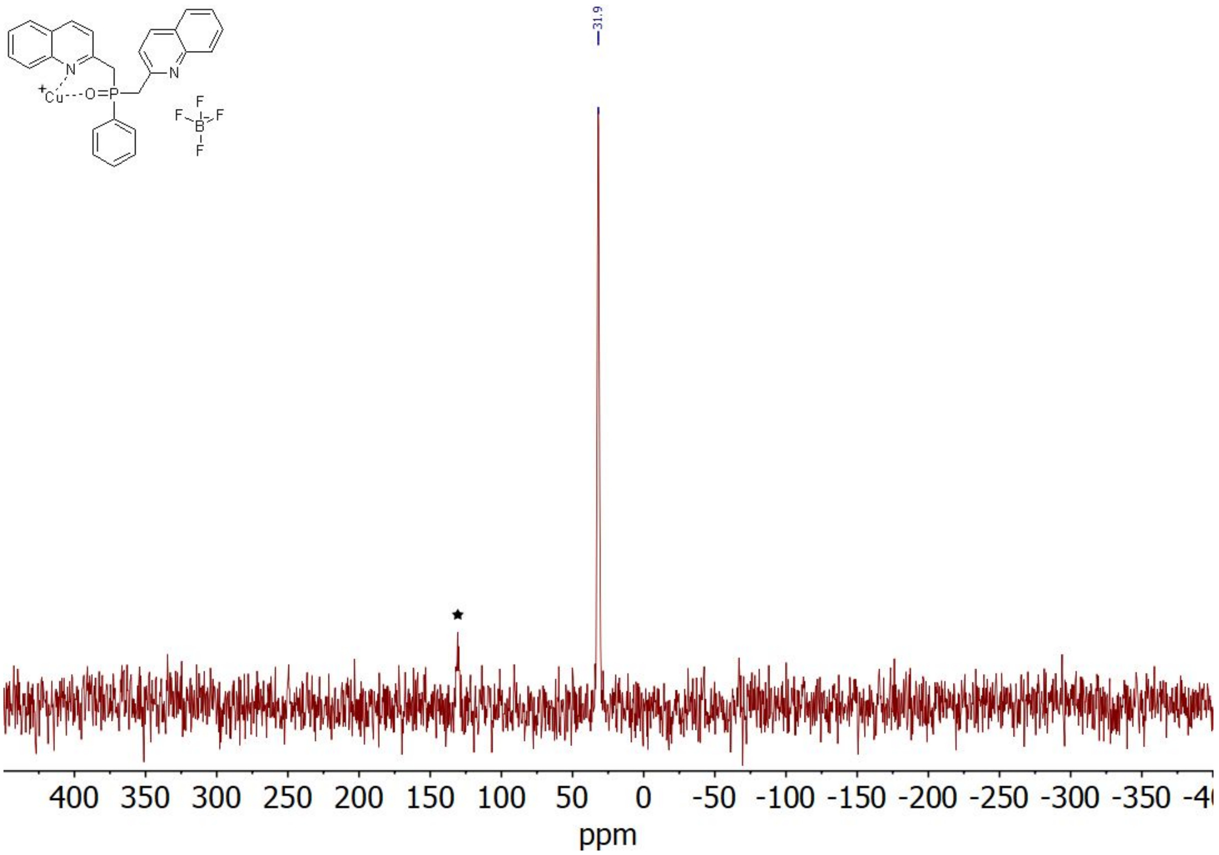
^{1}H CP MAS NMR of **3**, 300 K



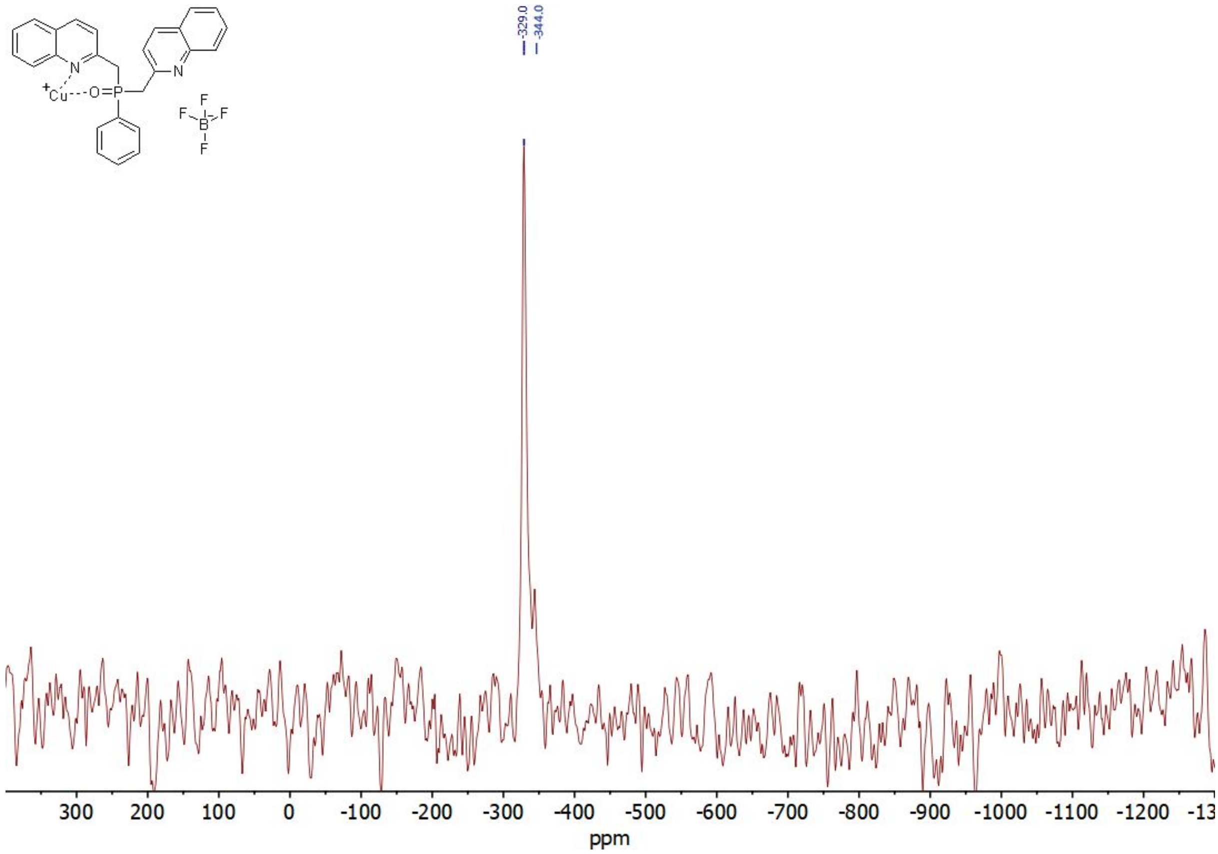
^{13}C CP MAS NMR of **3**, 300 K



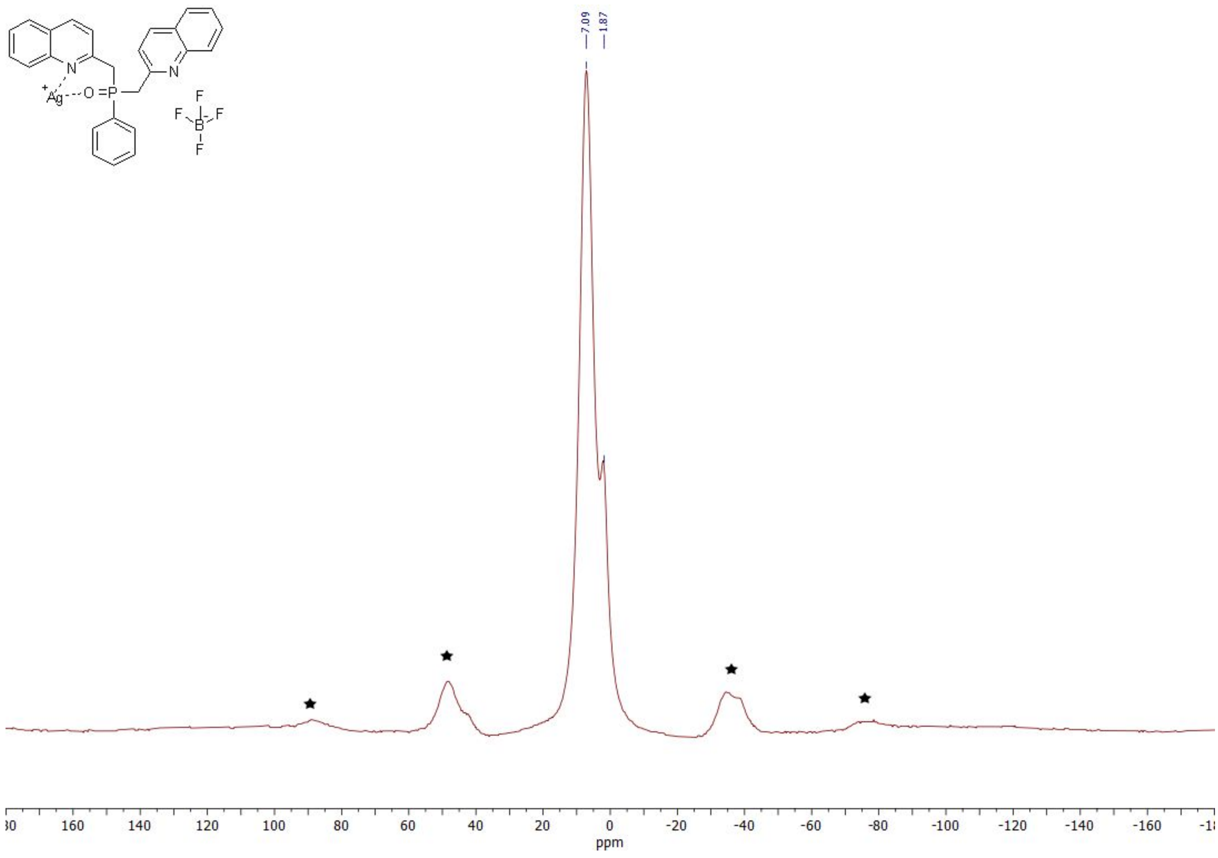
^{31}P CP MAS NMR of **3**, 300 K



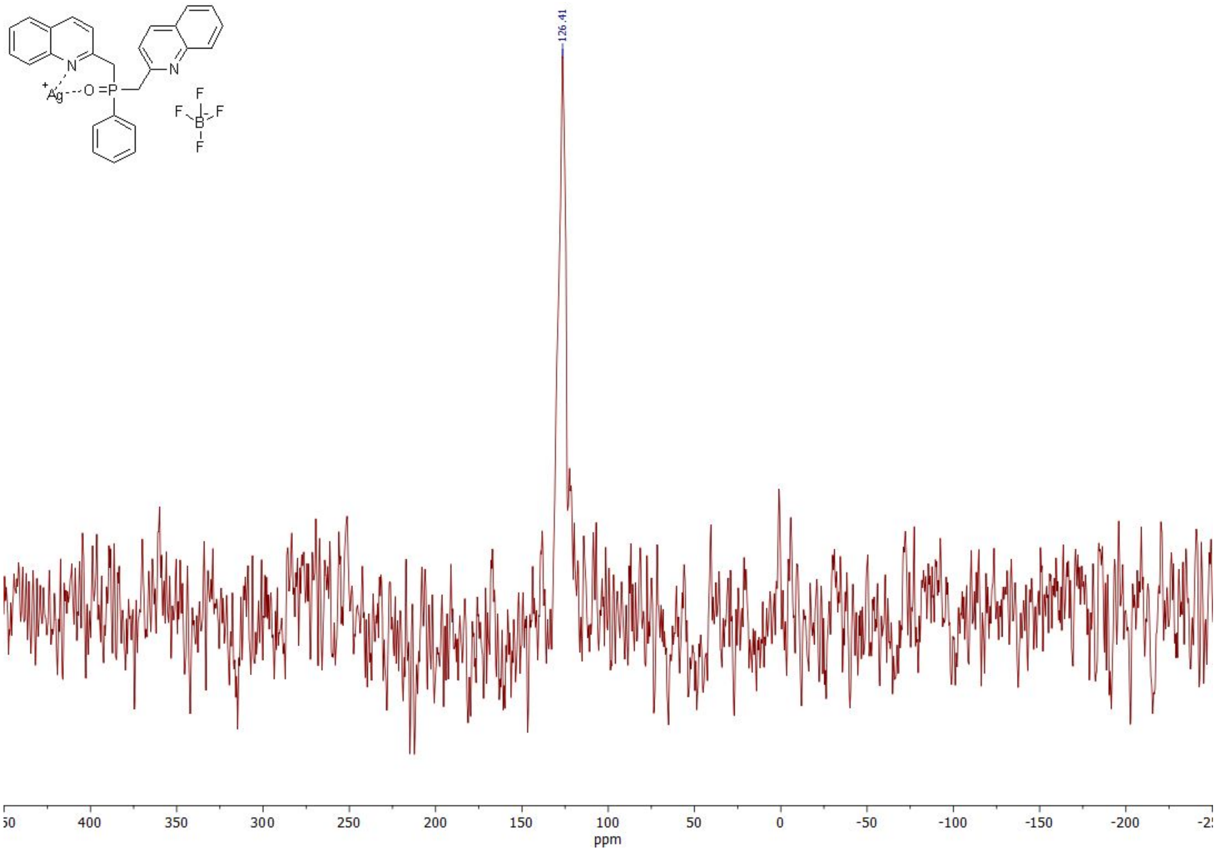
^{63}Cu CP MAS NMR of **3**, 300 K



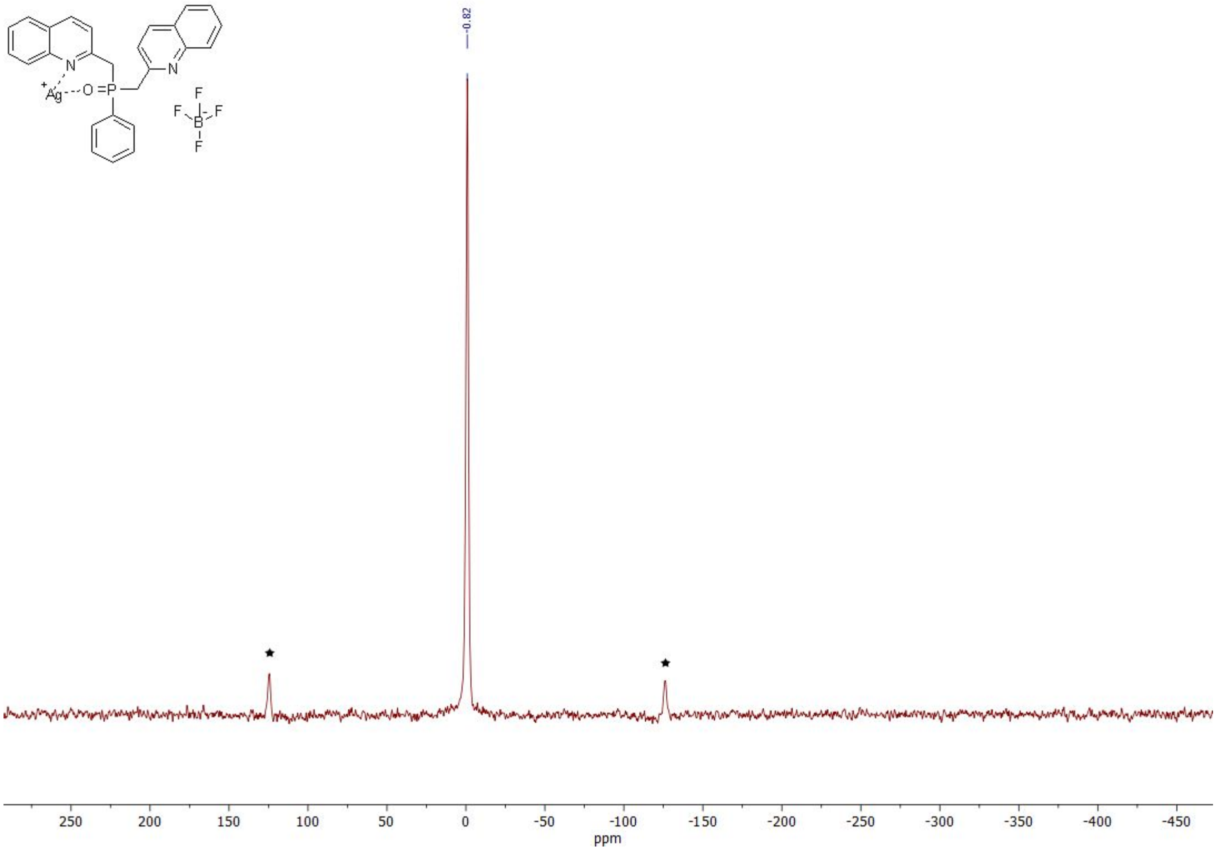
^{1}H CP MAS NMR of **5**, 300 K



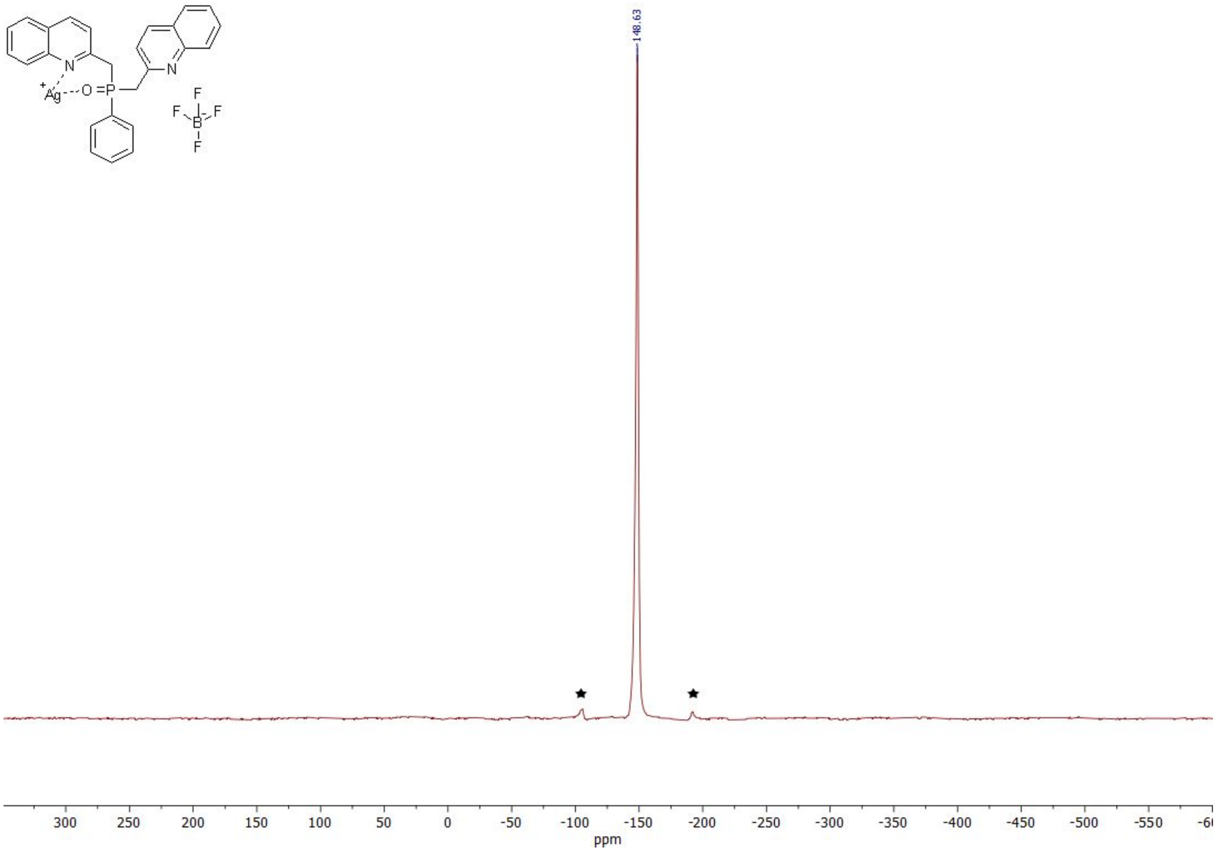
^{13}C CP MAS NMR of **5**, 300 K



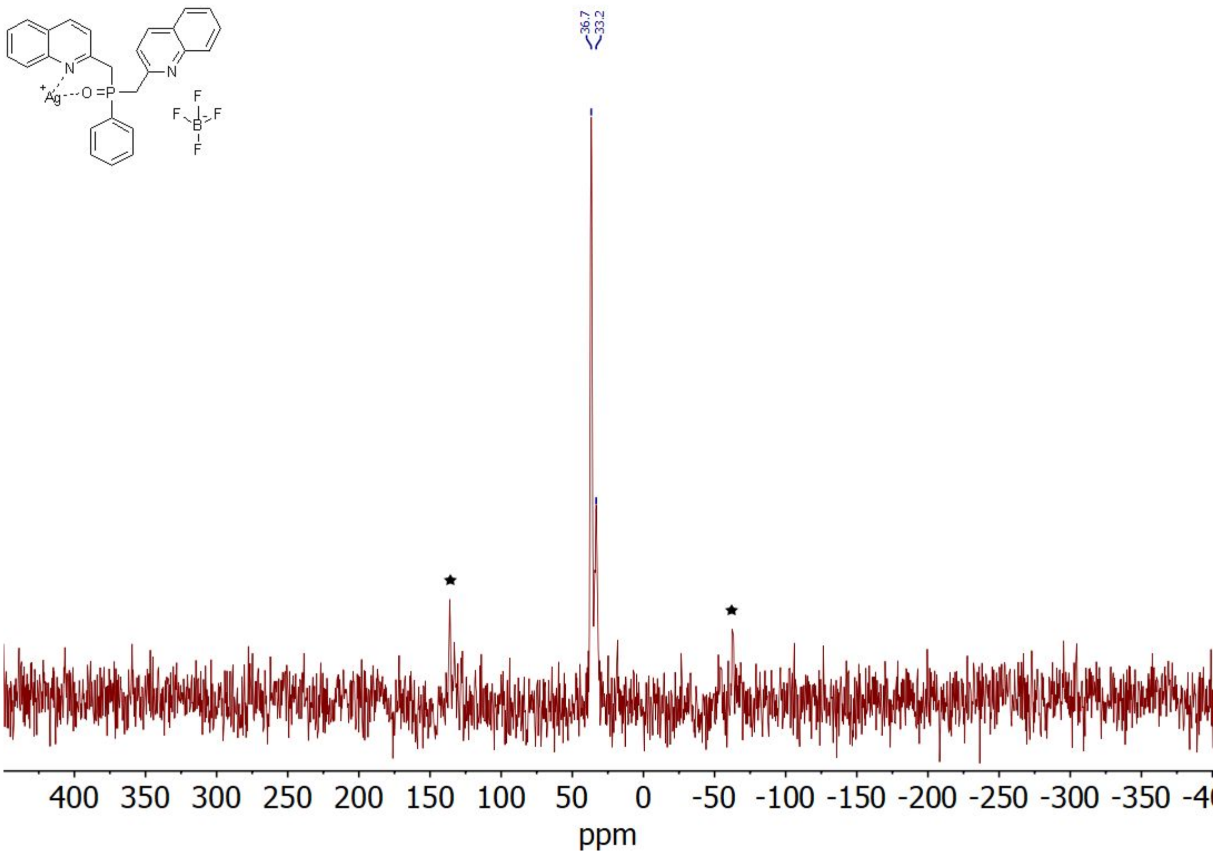
^{11}B CP MAS NMR of **5**, 300 K



^{19}F CP MAS NMR of **5**, 300 K



^{31}P CP MAS NMR of **5**, 300 K



DTA plots

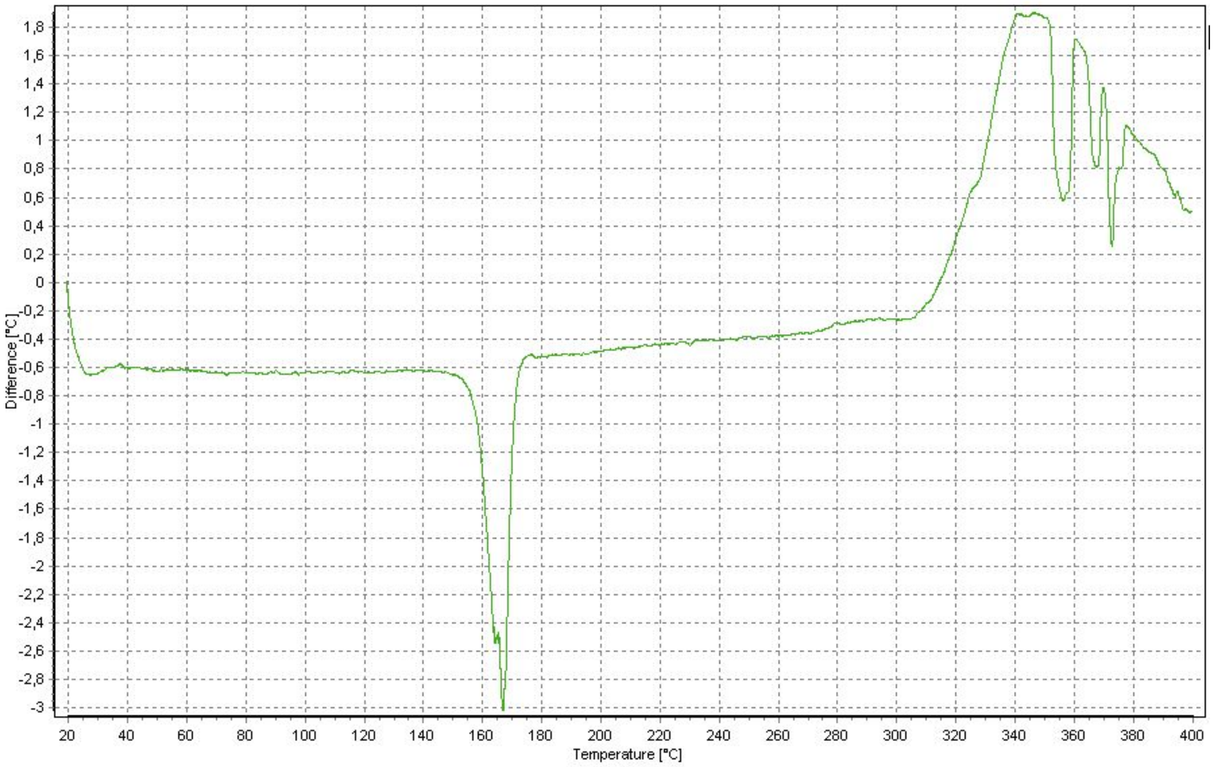


Figure S13. DTA plot of compound **2**.

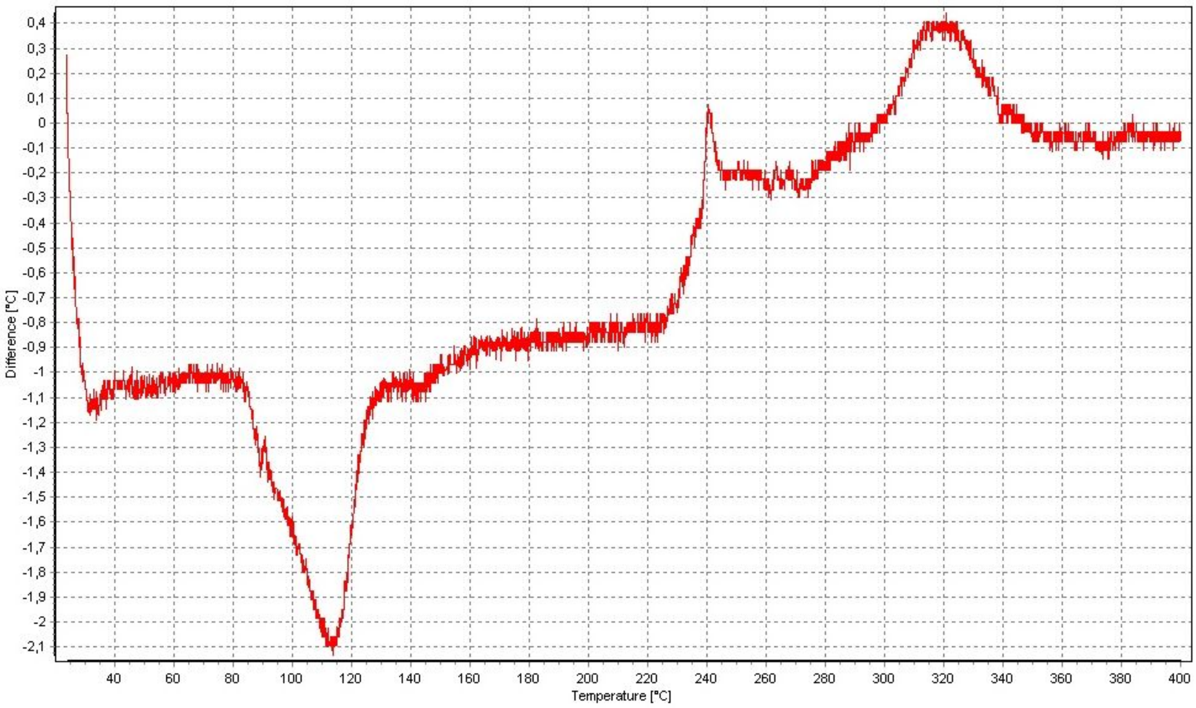


Figure S14. DTA plot of compound **5**.

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