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Supporting Information

Synthesis of Zwitterionic Palladium Complexes and Their Application as Catalysts in Cross-Coupling Reactions of Aryl, Heteroaryl and Benzyl Bromides with Organoboron Reagents in Neat Water

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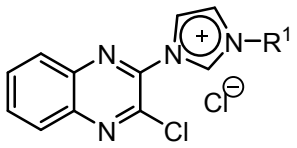
General considerations. All manipulations, except syntheses of Pd(II) complexes, were carried out under open atmosphere. *N*-Substituted imidazoles were prepared by following literature procedures.[1] All commercially available chemicals including aryl bromides and arylboronic acids were used as received (Sigma-Aldrich, Avra and Alfa Aesar). THF, toluene (from Na/benzophenone ketyl) acetonitrile and chloroform (from CaH_2) were distilled fresh as and when required. Thin-layer chromatography was performed using pre-coated silica gel 60 F_{254} plates and UV light at 254 nm. ^{1}H, ^{13}C and ^{31}P spectra were recorded on a Bruker 400 MHz instrument. HR-MS were recorded on Agilent 6540 UHD Q-TOF mass spectrometer. Elemental analyses were performed using a Thermo Scientific Flash 2000 CHNS analyser.

Experimental procedures

General procedure for the synthesis of *N*-(3-chloro-2-quinoxalinyl)-*N*′-aryl substituted imidazolium salts. 2,3-Dichloroquinoxaline (1 equiv) and excess of *N*-aryl substituted imidazole (1.5 equiv) were taken in a pressure tube, closed tight and heated at 140 °C for 90 min. The mixture was allowed to cool to ambient temperature, diethyl ether was added and ultrasonicated for 30 min. The suspension was filtered, the solid residue was washed with diethyl ether and dried under high vacuum.

***N*-(3-Chloro-2-quinoxalinyl)-*N*′-(2,6-diisopropylphenyl)imidazolium chloride**, [**HL1Cl**]**Cl**.

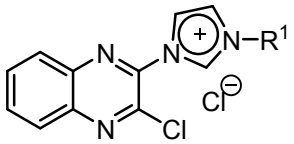


R^1 = 2,6-Diisopropylphenyl, **[HL1Cl]Cl**

2,3-Dichloroquinoxaline (0.995 g, 5.0 mmol), 1-(2,6-diisopropylphenyl)-1H-imidazole (1.712 g, 7.5 mmol). White solid. Yield: 92% (1.950 g). mp: 264 – 268 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.80 (s, 1H, imidazole-NC*H*N), 8.81 (d, 1H, imidazole-NC*H*CHN), 8.64 (d, 1H, imidazole-NCHC*H*N), 8.19 (m, 4H, quino-H), 7.67 (m, 3H, Ph-H), 2.49 [m, 2H, C*H*(CH_3)$_2$], 1.29 [d, 12H, CH(C*H*$_3$)$_2$]

ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 144.84, 141.54, 139.92, 139.83, 138.47, 133.53, 132.53, 131.76, 130.29, 128.85, 128.02, 125.42, 124.53, 124.28, 28.34, 23.76, 23.64 ppm. HRMS (ESI): *m/z* calcd for $C_{23}H_{24}ClN_4$ [M − Cl]$^+$ 391.1689, found 391.1682.

***N*-(3-Chloro-2-quinoxalinyl)-*N′*-(2,4,6-trimethylphenyl)imidazolium chloride**, [**HL2Cl]Cl**.



R^1 = Mesityl, **[HL2Cl]Cl**

2,3-Dichloroquinoxaline (0.850 g, 4.3 mmol), 1-mesityl-1H-imidazole (1.192 g, 6.3 mmol). Brown solid. Yield: 93% (1.521 g). mp: 227 – 231 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.60 (s, 1H, imidazole-NC*H*N), 8.70 (d, 1H, imidazole-NC*H*CHN), 8.41 (d, 1H, imidazole-NCHC*H*N),8.31 (m, 2H, quino-H), 8.14 (m, 2H, quino-H), 7.22 (s, 2H, Ph-H), 2.36 (s, 3H, *p*-CH_3), 2.16 (s, 6H, *o*-CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 141.64, 141.57, 140.62, 139.85, 139.61, 138.48, 134.16, 133.52, 132.53, 130.90, 129.36, 128.84, 128.03, 124.35, 124.15, 20.62, 17.06 ppm. HRMS (ESI): *m/z* calcd for $C_{20}H_{18}ClN_4$ [M − Cl]$^+$ 349.1219, found 349.1214.

***N*-(3-Chloro-2-quinoxalinyl)-*N′*-(2,6-diisopropylphenyl)imidazolium hexafluorophosphate**, [**HL1Cl]PF$_6$**.

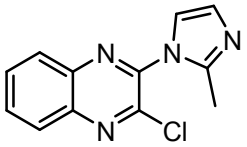
To a solution of *N*-(3-chloro-2-quinoxalinyl)-*N'*-(2,6-diisopropylphenyl)imidazolium chloride (0.854 g, 2 mmol) in water (10 mL) was added a filtered saturated aqueous solution of KPF_6 (0.460 g, 2.5 mmol). The pale yellow precipitate, which formed immediately was collected by filtration, washed with water and diethyl ether, and dried under vacuum. Yield: 90% (0.962 g). mp: 251 – 253 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.40 (s, 1H, imidazole-NC*H*N), 8.70 (s, 1H, imidazole-N*CH*CHN), 8.53 (s, 1H, imidazole-NCH*CH*N), 8.37 – 8.32 (m, 2H, quino-H), 8.21 – 8.14 (m, 2H, quino-H), 7.77 – 7.73 (m, 2H, Ph-H), 7.59 (m, 2H, Ph-H), 2.42 [m, 2H, C*H*$(CH_3)_2$], 1.20 [dd, 12H, CH(C*H*$_3$)$_2$] ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 144.99, 141.65, 141.27,

139.88, 139.71, 138.61, 133.39, 132.75, 131.95, 130.4, 128.95, 128.13, 125.54, 124.68, 124.27, 28.47, 23.80 ppm. HRMS (ESI): *m/z* calcd for $C_{23}H_{24}ClN_4$ $[M - PF_6]^+$ 391.1689, found 391.1681.

***N*-(3-Chloro-2-quinoxalinyl)-*N′*-(2,4,6-trimethylphenyl)imidazolium hexafluorophosphate, [HL2Cl]PF_6.**

The same procedure as mentioned for the synthesis of *N*-(3-chloro-2-quinoxalinyl)-*N′*-(2,6-diisopropylphenyl)imidazolium hexafluorophosphate was followed. *N*-(3-Chloro-2-quinoxalinyl)-*N′*-(2,4,6-trimethylphenyl)imidazolium chloride (0.770 mg, 2.0 mmol), KPF_6 (0.644 mg, 3.5 mmol), in water (10 mL). The brown precipitate was collected by filtration. Yield: 91% (0.902 g). mp: 242 – 244 ºC. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.17 (s, 1H, imidazole-NC*H*N), 8.58 (s, 1H, imidazole-NC*H*CHN), 8.25 (m, 3H, quino-H), 8.14 (m, 2H, quino-H), 7.19 (s, 2H, Ph-H), 2.41 (s, 3H, *p*-CH_3), 2.18 (s, 6H, *o*-CH_3) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 141.62, 141.04, 140.66, 139.53, 139.13, 138.50, 134.06, 133.34, 132.37, 130.81, 129.33, 128.70, 127.91, 124.26, 124.04, 20.65, 17.03 ppm. HRMS (ESI): *m/z* calcd for $C_{20}H_{18}ClN_4$ $[M - PF_6]^+$ 349.1219, found 349.1211.

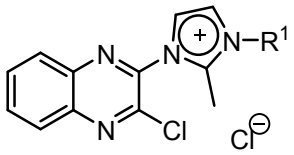
2-Chloro-3-(2-methyl-1H-imidazol-1-yl)quinoxaline.



2-Methylimidazole (0.412 g, 5.02 mmol), potassium hydroxide (0.338 g, 6.03 mmol), tetrabutylammonium bromide (0.023 g, 0.07 mmol) and 2,3-dichloroquinoxaline (1.000 g, 5.02 mmol) were placed in a round-bottomed flask and suspended in 20 mL of THF. The mixture was stirred at 70 ºC for 2 h. The resulting mixture was allowed to cool to room temperature, and the solvent was removed under vacuum. Water was added to the residue and extracted three times with 100 mL of dichloromethane. After washing with water, the combined organic phases were dried over anhydrous $MgSO_4$, filtered, and volatiles

were removed under reduced pressure. The crude solid was purified by column chromatography (silica gel, hexane/ethyl acetate: 12/88) to afford white solid. Yield: 52% (0.632 g). mp: 149 - 153 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (m, 2H, quino-H), 7.89 (m, 2H, quino-H), 7.24 (d, 1H, imidazole-NC*H*CHN), 7.10 (d, 1H, imidazole-NCHC*H*N), 2.41 (s, 3H, imidazole-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.05, 143.45, 142.85, 141.81, 139.96, 132.26, 132.13, 131.66, 129.46, 129.13, 128.98, 128.41, 120.05, 14.08 ppm. HRMS (ESI): *m/z* calcd for $C_{12}H_{10}ClN_4$ [M + H]$^+$ 245.0594, found 245.0586.

***N*-(3-Chloro-2-quinoxalinyl)-2-methyl-*N'*-benzylimidazolium chloride**, **[L3Cl]Cl**.

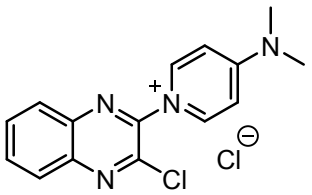


R^1 = Benzyl, **[L3Cl]Cl**

Excess of benzyl chloride (0.909 g, 7.1 mmol) was added to 2-chloro-3-(2-methyl-1H-imidazol-1-yl)quinoxaline (0.244 g, 1 mmol) in a 13 mm X 90 mm test tube and the mixture was stirred for 1 h at 120 °C. A white precipitate started to form during the course of the reaction. After cooling to ambient temperature, the solid was collected by filtration and washed thoroughly with diethyl ether and dried under vacuum. Yield: 62% (0.231 g). mp: 237 - 240 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, 1H, imidazole-NC*H*CHN), 8.19 (m, 2H, quino-H), 8.02 (m, 2H, quino-H), 7.73 (d, 1H, imidazole-NCHC*H*N), 7.54 (m, 2H, Ph-H), 7.41 (m, 2H, Ph-H), 6.12 (s, 2H, benzyl-CH_2), 2.85 (s, 3H, imidazole-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.16, 142.88, 141.80, 139.47, 138.82, 134.11, 133.06, 132.74, 129.46, 129.34, 128.92, 128.57, 124.23, 122.13, 122.07, 53.15, 12.05 ppm. HRMS (ESI): *m/z* calcd for $C_{19}H_{16}ClN_4$ [M – Cl]$^+$ 335.1063, found 335.1056.

1-(3-Chloro-2-quinoxalinyl)-4-(dimethylamino)pyridinium chloride, **[L4Cl]Cl**.

A mixture of 2,3-dichloroquinoxaline (0.398 g, 2 mmol) and *N*,*N*-dimethyl-4-aminopyridine (0.366 g, 3 mmol) in 5 mL of toluene



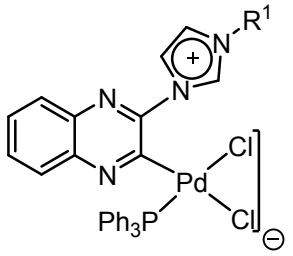
[L4Cl]Cl

was refluxed for 2 h to afford a light yellow solid, which was collected by filtration, washed with diethyl ether and dried under vacuum. Yield: 85% (0.542 g). mp: 278 – 282 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.70 (d, 2H, Py-H), 8.26 – 8.23 (m, 2H, quino-H), 8.13 – 8.05 (m, 2H, quino-H), 7.37 (d, 2H, Py-H), 3.36 [s, 6H, N(CH_3)$_2$] ppm. ^{13}C NMR (100 MHz, DMSO-d_6): δ 156.70, 144.63, 142.10, 141.53, 141.12, 138.80, 133.12, 132.25, 128.81, 127.92, 107.50, 40.45 ppm. HRMS (ESI): *m/z* calcd for $C_{15}H_{14}ClN_4$ [M – Cl]$^+$ 285.0907, found 285.0898.

General procedure for the synthesis of anionic zwitterionic palladium(II) complexes. A Schlenk flask was charged with imidazolium salt (1 equiv) and Pd(PPh_3)$_4$ (1.2 equiv) (**Path-1**) or Pd_2(dba)$_3$ (0.6 equiv) and PPh_3 (1.2 equiv) (**Path-2**), in 20 mL of THF. The mixture was stirred under N_2 atmosphere for 6 h at 50 °C. A yellow precipitate started to form during the course of reaction. After cooling to room temperature, the solid was collected by filtration, washed thoroughly with 10 mL of chloroform/toluene (1:1) mixture and dried under vacuum. Recrystallization from acetonitrile gave pale yellow crystals at 0 °C.

[Pd(HL1)(PPh_3)Cl_2] (I)

Path-1: [HL1Cl]Cl (0.213 g, 0.5 mmol), Pd(PPh_3)$_4$ (0.693 g, 0.6 mmol). Yield: 92% (0.365 g). **Path-2:** [HL1Cl]Cl (0.185 g, 0.43 mmol), Pd_2(dba)$_3$ (0.237 g, 0.26 mmol) and PPh_3 (0.136 g, 0.52 mmol), Yield: 90% (0.310 g). Yellow solid. mp: 183 – 187 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.52 (s, 1H, imidazole-NC*H*N), 9.88 (s, 1H, imidazole-NC*H*CHN), 8.52 (s, 1H, imidazole-NCHC*H*N) 7.89 – 7.65 (m, 5H, quino-H), 7.52 – 7.48 (m, 8H, Ph-H), 7.28 – 7.21 (m, 9H, Ph-H), 2.31 [m, 2H, C*H*(CH_3)$_2$], 1.21 – 1.04 [m, 12H, CH(C*H*$_3$)$_2$] ppm. ^{31}P (100 MHz, DMSO-d_6): δ 26.31. HRMS (ESI): *m/z* calcd for $C_{41}H_{39}ClN_4PPd$ [M – Cl]$^+$ 759.1636, found 759.1654. Anal. Calcd for $C_{41}H_{39}Cl_2N_4PPd$: C, 61.86; H, 4.94; N, 7.04.

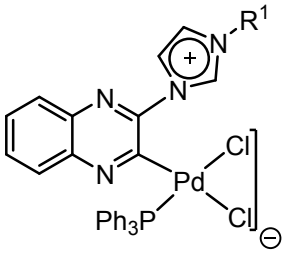


[Pd(HL1)(PPh_3)Cl_2]

R^1 = 2,6-Diisopropylphenyl

Found: C, 62.02; H, 4.93; N, 7.27. The complex is only sparingly soluble in DMSO and hence a ^{13}C NMR spectrum could not be obtained.

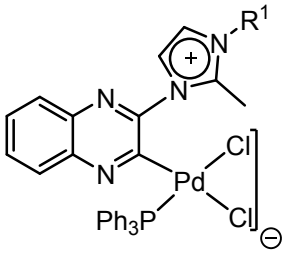
[Pd(HL2)(PPh$_3$)Cl$_2$] (II)



[Pd(HL2)(PPh$_3$)Cl$_2$]
R^1 = Mesityl

Path-1: [HL2Cl]Cl (0.205 g, 0.53 mmol), Pd(PPh$_3$)$_4$ (0.737 g, 0.63 mmol). Yield: 92% (0.369 g). **Path-2:** [HL2Cl]Cl (0.185 g, 0.43 mmol), Pd$_2$(dba)$_3$ (0.264 g, 0.28 mmol) and PPh$_3$ (0.151 g, 0.57 mmol), Yield: 90% (0.326 g). Yellow solid. mp: 187 – 191 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.64 (s, 1H, imidazole-NC*H*N), 9.37 (s, 1H, imidazole-NC*H*CHN), 8.35 (s, 1H, imidazole-NCHC*H*N), 7.81 – 7.66 (m, 4H, quino-H), 7.50 – 7.45 (m, 6H, Ph-H), 7.29 – 7.21 (m, 11H, Ph-H), 2.39 (s, 3H, *p*-CH$_3$), 2.22 (s, 3H, *o*-CH$_3$), 1.98 (s, 3H, *o*-CH$_3$) ppm. ^{31}P (100 MHz, DMSO-d_6): δ 26.58 ppm. HRMS (ESI): *m/z* calcd for $C_{38}H_{33}ClN_4PPd$ [M – Cl]$^+$ 717.1166, found 717.1181. Anal. Calcd for $C_{38}H_{33}Cl_2N_4PPd$: C, 60.53; H, 4.41; N, 7.43. Found: C, 60.09; H, 4.42; N, 7.79. The complex is only sparingly soluble in DMSO and hence a ^{13}C NMR spectrum could not be obtained.

[Pd(L3)(PPh$_3$)Cl$_2$] (V)



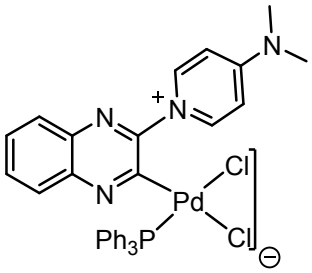
[Pd(L3)(PPh$_3$)Cl$_2$]
R^1 = Benzyl

[L3Cl]Cl (0.175 g, 0.47 mmol), Pd(PPh$_3$)$_4$ (0.653 g, 0.56 mmol). Yellow solid**.** Yield: 88% (0.307 g). mp: 224 – 229 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.32 (d, 1H, imidazole-NC*H*CHN), 8.33 (d, 1H, imidazole-NCHC*H*N), 7.87 – 7.83 (m, 1H, quino-H), 7.77 (dd, 2H, quino-H), 7.68 (d, 1H, quino-H), 7.41 – 7.30 (m, 15H, Ph-H), 7.19 – 7.15 (m, 5H, Ph-H), 5.58 (q, 2H, benzyl-CH$_2$), 2.14 (s, 3H, imidazole-CH$_3$) ppm. ^{31}P (100 MHz, DMSO-d_6): δ 26.75 ppm. HRMS (ESI): *m/z* calcd for $C_{37}H_{31}ClN_4PPd$ [M – Cl]$^+$ 703.1010, found 703.1017. Anal. Calcd for $C_{37}H_{31}Cl_2N_4PPd$: C, 60.06; H, 4.22; N, 7.57. Found: C, 60.02; H, 4.47;

N, 7.51. The complex is only sparingly soluble in DMSO and hence a ^{13}C NMR spectrum could not be obtained.

[Pd(L4)(PPh$_3$)Cl$_2$] (VI)

[L4Cl]Cl (0.168 g, 0.52 mmol), Pd(PPh$_3$)$_4$ (0.725 g, 0.62 mmol). Yellow solid**.** Yield: 92% (0.332 g). mp: 241 – 243 ^{o}C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.16 (d, 2H, Py-H), 7.90 (d, 1H, quino-H), 7.77 – 7.65 (m, 3H, quino-H), 7.33 – 7.27 (m, 11H, Ph-H), 7.19 – 7.15 (m, 6H, Ph-H), 3.39 [s, 6H, N(CH$_3$)$_2$] ppm. ^{31}P (100 MHz, DMSO-d_6): δ 33.14. HRMS (ESI): *m/z* calcd for $C_{33}H_{29}ClN_4PPd$ [M – Cl]$^+$ 653.0859, found 653.0865. Anal. Calcd for $C_{33}H_{29}Cl_2N_4PPd$: C, 57.45; H, 4.24; N, 8.12. Found: C, 58.03; H, 4.28; N, 8.22. The complex is only sparingly soluble in DMSO and hence a ^{13}C NMR spectrum could not be obtained.

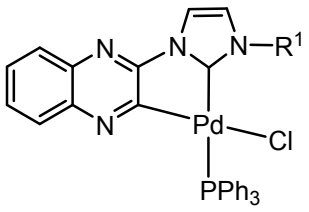


[Pd(L4)(PPh$_3$)Cl$_2$]

Synthesis of cyclometalated NHC-phosphine-Pd(II) complexes.

A Schlenk tube (13 mm X 90 mm) was charged with zwitterionic Pd(II) complex (1 equiv) and DMAP (1.1 equiv) in acetonitrile (10 mL). The mixture was stirred under N_2 atmosphere for 10 min at room temperature. The volatiles were removed under vacuum, the residue was washed with 10 mL of 20% HCl and extracted with chloroform (3 X 10 mL). After drying the solution with Na_2SO_4, volatiles were removed under vacuum. Recrystallization of the residue from acetone gave colorless crystals of [Pd(L1)(PPh$_3$)Cl$_2$] at 0 °C.

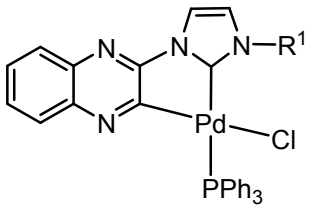
[Pd(L1)(PPh$_3$)Cl] (III) [Pd(HL1)(PPh$_3$)Cl$_2$] (0.156 g, 0.19 mmol), DMAP (0.026 g, 0.21 mmol). White solid. Yield: 85% (0.126 g). mp: 256 – 258 ^{o}C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.98 (d, 1H, imidazole-NC*H*CHN), 7.75 (s, 1H, quino-H), 7.70 – 7.64 (m, 6H, Ph-H), 7.46 –



[Pd(L1)(PPh$_3$)Cl]
R^1 = 2,6-Diisopropylphenyl

7.42 (m, 2H, quino-H), 7.31 – 7.21 (m, 13H, Ph-H), 7.03 – 7.00 (m, 2H, Ph-H), 2.77 [m, 2H, C*H*$(CH_3)_2$], 1.45 [d, 6H, CH(C*H*$_3$)$_2$], 1.17 [d, 6H, CH(C*H*$_3$)$_2$] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.11, 137.65, 135.20, 135.13, 132.62, 132.17, 130.19, 129.54, 128.07, 127.86, 127.81, 127.76, 127.66, 126.00, 123.84, 114.53, 28.93, 24.72, 24.02 ppm. ^{31}P (100 MHz, $CDCl_3$): δ 31.99 ppm. HRMS (ESI): *m/z* calcd for $C_{41}H_{38}N_4PPd$ [M – Cl]$^+$ 723.1868, found 723.1865. Anal. Calcd for $C_{41}H_{38}ClN_4PPd$: C, 64.83; H, 5.04; N, 7.38. Found: C, 64.64; H, 5.03; N, 7.52.

[Pd(L2)(PPh$_3$)Cl] (IV) [Pd(HL2)(PPh$_3$)Cl$_2$] (0.162 g, 0.21 mmol), DMAP (0.028 g, 0.23 mmol). Pale yellow solid. Yield: 82% (0.126 g). mp: 262 – 265 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, 1H, imidazole-NC*H*CHN), 7.75 (s, 1H, quino-H), 7.68 – 7.63 (m, 6H, Ph-H), 7.46 – 7.42 (m, 1H, quino-H), 7.31 – 7.21 (m, 11H, Ph-H), 6.98 – 6.93 (m, 3H, Ph-H), 2.30 (s, 3H, *p*-CH_3), 2.21 (s, 6H, *o*-CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.99, 137.57, 135.76, 135.32, 135.21, 134.75, 132.41, 131.95, 129.62, 129.10, 128.05, 127.90, 127.73, 127.62, 124.90, 114.94, 21.40, 18.42 ppm. ^{31}P (100 MHz, $CDCl_3$): δ 32.33 ppm. HRMS (ESI): *m/z* calcd for $C_{38}H_{32}N_4PPd$ [M – Cl]$^+$ 681.1399, found 681.1396. Anal. Calcd for $C_{38}H_{32}ClN_4PPd$: C, 63.61; H, 4.50; N, 7.81. Found: C, 62.95; H, 4.62; N, 7.75.



[Pd(L2)(PPh$_3$)Cl]
R^1 = Mesityl

General procedure for Suzuki-Miyaura cross-coupling reactions: To a test tube (13 mm X 90 mm) with a stir bar were added arylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), Pd catalyst (0.5 mol%), aryl bromide (1/n mmol, n = number of bromine atoms on aryl ring) and water (3 mL). The resulting mixture was stirred vigorously at room temperature or heated in an oil bath at 70 °C in open atmosphere. The progress of the reaction was monitored by TLC and ^{1}H NMR spectroscopy. Most of the reactions were completed in 3 h. The reaction mixture was cooled to room temperature and mixed with water (5 mL). If the product was solid it was separated by simple

filtration using a frit and if the product was a semi-solid or an oily substance it was extracted with diethyl ether (3 X 10 mL). In the case of hydrophilic biaryl derivatives, 20 mL of 20% HCl was added to the reaction mixture and the product was either filtered or extracted with ethyl acetate (3 X 10 mL), the resulting organic portions were combined and dried over Na_2SO_4. The volatiles were removed using a rotary evaporator. The crude product was subjected to ^{1}H NMR study. In case of impure products, purification was done by column chromatography (eluting with hexane/ethyl acetate) on silica gel (230-400 mesh). The identity of products was confirmed by NMR (^{1}H NMR) spectroscopy. Many biaryls have already been reported and the data was compared with the literature data.

Hg poisoning test

To a 13 X 90 mm test tube were added catalyst (0.5 mol%), a drop of Hg (>500 equiv per Pd atom) and water (3 mL). The mixture was stirred for 10 min at room temperature before the addition of phenylboronic acid (1.2 mmol), K_2CO_3 (2 mmol) and 4-bromoacetophenone (1.0 mmol). The reaction mixture was stirred vigorously at room temperature or heated in an oil bath at 70 °C for 3 h. The work up was done as per the procedure given for carrying out Suzuki-Miyaura cross-coupling reactions. The yield of the product (4-acetylbiphenyl) was determined by ^{1}H NMR. The Hg was recovered and stored safely.

PPh_3 poisoning test

Triphenylphosphine (2 mmol, at t = 0 min) was taken along with the catalyst (0.5 mol%), K_2CO_3 (2 mmol) and the coupling reagents [phenylboronic acid (1.2 mmol) and 4-bromoacetophenone (1.0 mmol)] in water (3 mL). The reaction mixture was stirred vigorously at room temperature or heated in an oil bath at 70 °C for 3 h under open atmosphere. The work up was done as per the

procedure given for carrying out Suzuki-Miyaura cross-coupling reactions. The yield of the product (4-acetylbiphenyl) was analyzed by ^{1}H NMR.

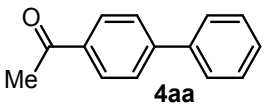
Two-phase test

A mixture of 4-bromoacetophenone (0.199 g, 1 mmol), phenylboronic acid (0.304 g, 2.5 mmol), catalyst **I** (0.5 mol%) and K_2CO_3 (0.552 g, 4 mmol) in water (3 mL) was magnetically stirred in the presence of freshly prepared immobilized aryl bromide[2] (0.200 g) at 70 °C for 3 h. The reaction mixture was cooled to room temperature and filtered through a G-4 frit. The residue was washed with 20 mL of water and then 20 mL of diethyl ether. The filtrate and the washings were collected together and mixed with water (10 mL). The resulting mixture was extracted with 20 mL of diethyl ether. The solvent from the organic extract was evaporated on a rotary evaporator and the white residue thus obtained was identified by ^{1}H NMR. The residue collected on G-4 frit was hydrolyzed with KOH (1.68 g dissolved in 5 mL of water + 10 mL of EtOH) at 90 °C for 3 days. The reaction mixture was neutralized with aqueous HCl (20% v/v). The products were extracted with dichloromethane (30 mL), followed by ethyl acetate (40 mL). The organic extracts were combined together and the solvents were evaporated off under vacuum. The resulting residue was subjected to ^{1}H NMR to identify the products.

Analytical data

1. **4-Acetylbiphenyl** (entry 1 of table 3)[3]

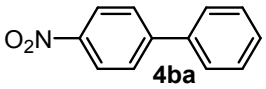
   ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, 2H), 7.68 (d, 2H), 7.63 (dd, 2H), 7.46 (m, 2H), 7.41 (m, 1H), 2.64 (s, 3H) ppm.



4aa

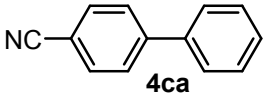
2. **4-Nitrobiphenyl** (entry 2 of table 3)[3]

   ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 – 8.27 (d, 2H), 7.73 – 7.72 (d, 2H), 7.63 – 7.61 (m, 2H), 7.52 – 7.43 (m, 3H) ppm



4ba

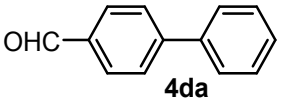
3. **Biphenyl-4-carbonitrile** (entry 3 of table 3)[3]



4ca

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 – 7.67 (m, 4H), 7.60 – 7.58 (m, 2H), 7.50 – 7.42 (m, 3H) ppm.

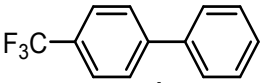
4. **Biphenyl-4-carbaldehyde** (entry 4 of table 3)[3]



4da

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.06 (s, 1H), 7.97 – 7.94 (d, 2H), 7.77 – 7.75 (d, 2H), 7.65 – 7.63 (m, 2H), 7.51 – 7.47 (m, 2H), 7.44 – 7.41 (m, 1H) ppm.

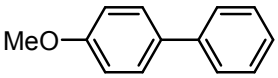
5. **4-(Trifluoromethyl)biphenyl** (entry 5 of table 3)[4]



4ea

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (s. 4H), 7.61 – 7.59 (m, 2H), 7.49 – 7.46 (m, 2H), 7.42 – 7.39 (m, 1H) ppm.

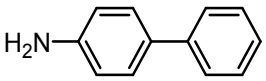
6. **4-Methoxybiphenyl** (entry 6 of table 3)[5]



4fa

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 – 7.52 (m, 4H), 7.44 – 7.40 (t, 2H), 7.32 – 7.30 (t, 1H), 6.99 – 6.97 (d, 2H), 3.85 (s, 3H) ppm.

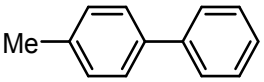
7. **Biphenyl-4-amine** (entry 7 of table 3)[3]



4ga

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.52 (m, 2H), 7.43 – 7.37 (m, 4H), 7.29 – 7.26 (t, 1H), 6.77 – 6.75 (d, 2H), 3.72 (s, 2H) ppm.

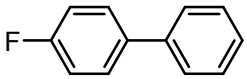
8. **4-Methylbiphenyl** (entry 8 of table 3)[4]



4ha

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.50 (t, 2H), 7.45 – 7.43 (t, 2H), 7.42 – 7. 37 (m, 2H), 7.35 – 7.24 (m, 1H), 7.19 – 7.11 (d, 2H), 2.33 (s, 3H) ppm

9. **4-Fluorobiphenyl** (entry 9 of table 3)[5]

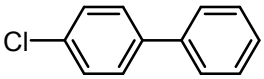


4ia

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.53 (m, 4H), 7.45 – 7.41 (m, 2H), 7.36 – 7.34 (m, 1H), 7.15 – 7.09 (m, 2H) ppm.

10. **4-Chlorobiphenyl** (entry 10 of table 3)[5]

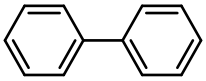
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.51 (m, 4H), 7.46 – 7.36 (m, 5H) ppm.



4ja

11. **Biphenyl** (entry 11 of table 3)[6]

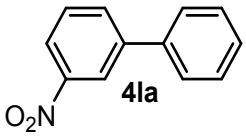
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, 4H), 7.44 (t, 4H), 7.36 (t, 2H) ppm.



4ka

12. **3-Nitro-biphenyl** (entry 12 of table 3)[7]

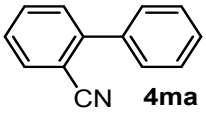
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, 1H), 8.22 – 8.19 (dd, 1H), 7.93 – 7.91 (d, 1H), 7.64 – 7.59 (m, 3H), 7.52 – 7.40 (m, 3H) ppm.



4la

13. **Biphenyl-2-carbonitrile** (entry 13 of table 3)[8]

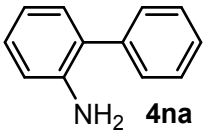
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, 1H), 7.63 (t, 1H), 7.55 (m, 2H), 7.49 (m, 3H), 7.43 (m, 2H) ppm.



4ma

14. **2-Aminobiphenyl** (entry 14 of table 3)[6]

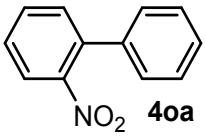
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 – 7.46 (m, 4H), 7.39 – 7.36 (m, 1H), 7.19 – 7.14 (m, 2H), 6.86 (m, 1H), 6.79 (m, 1H), 3.66 (s, 2H) ppm.



4na

15. **2-Nitro-biphenyl** (entry 15 of table 3)[6]

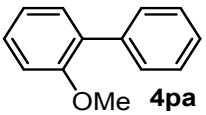
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, 1H), 7.64 – 7.60 (m, 1H), 7.50 – 7.40 (m, 5H), 7.33 – 7.31 (m, 2H) ppm.



4oa

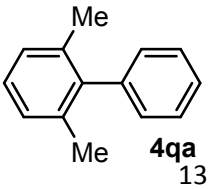
16. **2-Methoxybiphenyl** (entry 16 of table 3)[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.53 (m, 2H), 7.44 – 7.40 (m, 2H), 7.35 – 7.32 (m, 3H), 7.02 (d, 1H), 6.99 (d, 1H), 3.82 (s, 3H) ppm.



4pa

17. **2,6-Dimethyl-biphenyl** (entry 17 of table 3)[4]

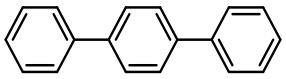


4qa

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (t, 2H), 7.36 – 7.32 (m, 1H), 7.19 – 7.11 (m, 5H), 2.04 (s, 6H) ppm.

18. **1,4-Diphenylbenzene** (entry 18 of table 3)[5]

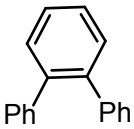
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 – 7.65 (m, 8H), 7.49 – 7.46 (m, 4H), 7.39 – 7.36 (m, 2H) ppm.



4ra

19. ***o*-Terphenyl** (entry 19 of table 3)[5]

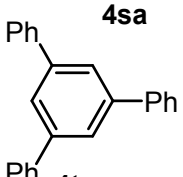
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (m, 4H), 7.12 – 7.04 (m, 10H) ppm.



4sa

20. **1,3,5-Triphenyl benzene** (entry 20 of table 3)[5]

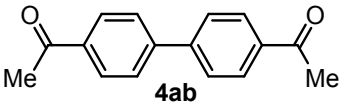
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (s, 3H), 7.70 (d, 6H), 7.49 (m, 6H), 7.40 (m, 3H) ppm.



4ta

21. **4,4'-Diacetylbiphenyl** (entry 1 of table 4)[9]

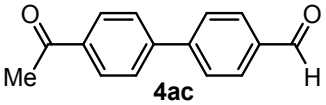
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 – 8.04 (d, 4H), 7.73 – 7.71 (d, 4H), 2.65 (s, 6H) ppm.



4ab

22. **4-Acetylbiphenyl-4-carboxaldehyde** (entry 2 of table 4)[9]

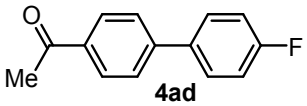
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.08 (s, 1H), 8.08 – 8.05 (d, 2H), 7.99 – 7.97 (d, 2H), 7.80 – 7.78 (d, 2H), 7.74 – 7.72 (d, 2H), 2.65 (s, 3H) ppm.



4ac

23. **1-(4'-Fluoro-biphenyl-4-yl)-ethanone** (entry 3 of table 4)[10]

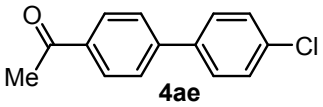
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, 2H), 7.64 (d, 2H), 7.63 – 7.57 (m, 2H), 7.16 (t, 2H), 2.64 (s, 3H) ppm.



4ad

24. **1-(4'-Chlorobiphenyl-4-yl)ethanone** (entry 4 of table 4)[11]

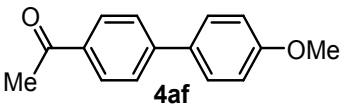
^{1}H NMR: (400 MHz, $CDCl_3$): δ 8.02 (d, 2H); 7.64 (d, 2H); 7.55 (d, 2H); 7.43 (d, 2H); 2.63 (s, 3H) ppm.



4ae

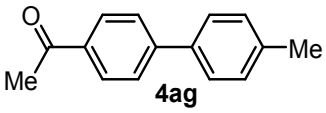
25. **4-Acetyl-4methoxybiphenyl** (entry 5 of table 4)[10]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 – 7.99 (d, 2H), 7.65 – 7.63 (d, 2H), 7.59 – 7.57 (d, 2H), 7.01 – 6.99 (d, 2H), 3.86 (s, 3H), 2.63 (s, 3H) ppm.



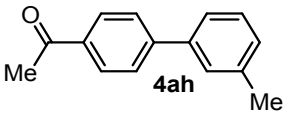
26. **4-Acetyl-(4-methyl)biphenyl** (entry 6 of table 4)[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 – 8.01 (d, 2H), 7.68 – 7.66 (d, 2H), 7.55 – 7.52 (d, 2H), 7.29 – 7.26 (d, 2H), 2.63 (s, 3H), 2.41 (s, 3H) ppm.



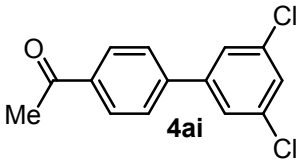
27. **4-Acetyl-3'-methylbiphenyl** (entry 7 of table 4)[10]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, 2H), 7.68 (d, 2H), 7.44 – 7.36 (m, 3H), 7.23 – 7.21 (m, 1H), 2.64 (s, 3H), 2.43 (s, 3H) ppm.



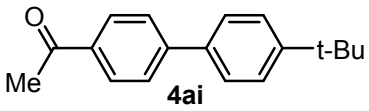
28. **3,5-Dichlorobiphenyl** (entry 8 of table 4)[11]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 – 8.03 (d, 2H), 7.64 – 7.62 (d, 2H), 7.49 – 7.48 (d, 2H), 7.40 – 7.38 (m, 1H), 2.64 (s, 3H) ppm.



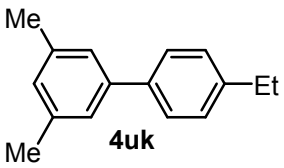
29. **4-Tert-butylphenylacetophenone** (entry 9 of table 4)[12]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, 2H), 7.68 (d, 2H), 7.59 – 7.49 (m, 4H), 2.63 (s, 3H), 1.37 (s, 9H) ppm.



30. **4'-Ethyl-3,5-dimethyl-1,1'-biphenyl** (entry 10 of table 4)

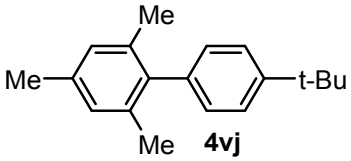
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 5.1 Hz, 2H), 6.88 (s, 1H), 2.60 (q, J = 7.6 Hz, 2H), 2.28 (s, 6H), 1.18 (t, J = 7.6 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.31, 141.36, 138.97, 138.30, 128.75, 128.33,



127.14, 125.10, 28.64, 21.54, 15.72 ppm. HRMS (ESI): *m/z* calcd for $C_{16}H_{19}$ $[M + H]^+$ 211.1486, found 211.1479.

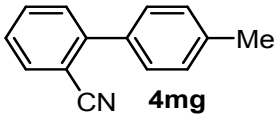
31. **4'-Tert-butyl-2,4,6-trimethylbiphenyl** (entry 11 of table 4)[13]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, 2H), 7.08 (d, 2H), 6.96 (s, 2H), 2.35 (s, 3H), 2.04 (s, 6H), 1.39 (s, 9H) ppm.



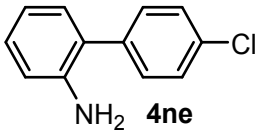
32. **4'-Methylbiphenyl-2-carbonitrile** (entry 12 of table 4)[6]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, 1H), 7.62 (t, 1H), 7.50 – 7.39 (m, 4H), 7.30 (d, 2H), 2.42 (s, 3H) ppm.



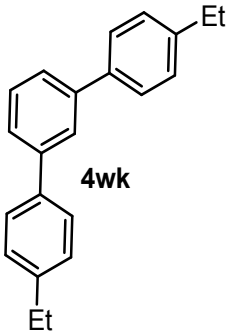
33. **4'-Chlorobiphenyl-2-amine** (entry 13 of table 4)[3]

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.40 (s, 4H), 7.20 – 7.16 (t, 1H), 7.11 – 7.09 (d, 1H), 6.88 – 6.84 (t, 1H), 6.81 – 6.79 (d, 1H) ppm.



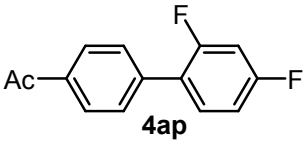
34. ***m*-Terphenyl, 4,4''-diethyl** (entry 14 of table 4)[14]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (s, 1 H), 7.58 (m, 6H), 7.51 – 7.44 (m, 1H), 7.31 (d, 4H), 2.73 (q, 4H), 1.31 (t, 6H) ppm.



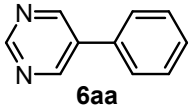
35. **4'-(2,4-Difluorophenyl)acetophenone** (entry 15 of table 4)[11]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, 2H), 7.60 (d, 2H), 7.46 – 7.40 (m, 1H), 7.00 – 6.90 (m, 2H), 2.63 (s, 3H) ppm.



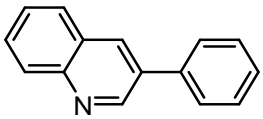
36. **5-Phenylpyrimidine** (entry 1 of table 5)[5]

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.23 (s, 1H), 9.00 (s, 2H), 7.60 – 7.58 (d, 2H), 7.55 – 7.48 (m, 3H) ppm.



37. **3-Phenylquinoline** (entry 2 of table 5)[3]

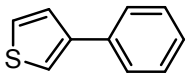
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.19 – 9.18 (d, 1H), 8.33 (d, 1H), 8.18 (d, 1H), 7.89 (d, 1H), 7.76 – 7.70 (m, 3H), 7.61 – 7.51 (m, 3H), 7.46 – 7.43 (m, 1H) ppm.



6ba

38. **3-Phenylthiophene** (entry 3 of table 5)[15]

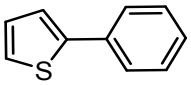
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, 2H), 7.46 – 7.38 (m, 5H), 7.31 – 7.28 (m, 1H) ppm.



6ca

39. **2-Phenylthiophene** (entry 4 of table 5)[3]

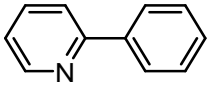
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 – 7.63 (d, 2H), 7.41 – 7.38 (t, 2H), 7.34 – 7.29 (m, 3H), 7.11 – 7.09 (m, 1H) ppm.



6da

40. **2-Phenylprydine** (entry 5 of table 5)[8]

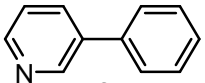
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (d, 1H), 8.10 – 7.98 (m, 2H), 7.76 – 7.72 (m, 2H), 7.50 – 7.40 (m, 3H), 7.25 – 7.21 (m, 1H) ppm.



6ea

41. **3-Phenylpyridine** (entry 6 of table 5)[3]

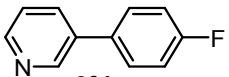
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.88 (s, 1H), 8.62 (d, 1H), 7.88 (d, 1H), 7.58 (d, 2H), 7.48 (t, 2H), 7.43 – 7.36 (m, 2H) ppm.



6fa

42. **3-(4-Fluorophenyl)pyridine** (entry 7 of table 5)[16]

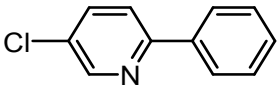
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 1H), 8.58 (dd, 1H), 7.87 – 7.85 (m, 1H), 7.55 – 7.52 (m, 2H), 7.37 (dd, 1H), 7.19 – 7.13 (m, 2H) ppm.



6fd

43. **5-Chloro-2-phenylpyridine** (entry 8 of table 5)[17]

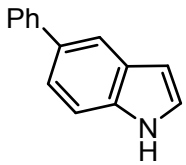
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, 1H), 7.95 (m, 2H), 7.73 – 7.66 (m, 2H), 7.49 – 7.42 (m, 3H) ppm.



6ga

44. **5-Phenyl-1H-indole** (entry 9 of table 5)[8]

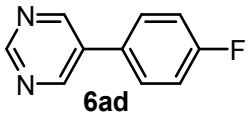
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.77 (m, 1H), 7.58 – 7.56 (m, 2H), 7.42 – 7.33 (m, 4H), 7.24 – 7.20 (m, 1H), 7.14 – 7.11 (m, 1H), 6.51 (m, 1H) ppm.



6ha

45. **5-(4-Fluorophenyl)pyrimidine** (entry 10 of table 5)[18]

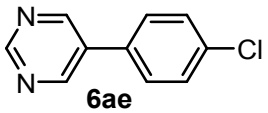
^{1}H NMR (400 MHz, CDCl3): δ 9.22 (s, 1H), 8.94 (s, 2H), 7.58 – 7.54 (m, 2H), 7.25 – 7.20 (m, 2H) ppm.



6ad

46. **5-(4-Chlorophenyl)pyrimidine** (entry 11 of table 5)[18]

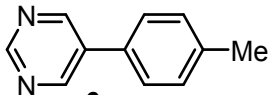
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.23 (s, 1H), 8.95 (s, 2H), 7.51 (m, 4H) ppm.



6ae

47. **5-(4-Methyl phenyl)pyrimidine** (entry 12 of table 5)[18]

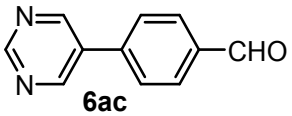
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.19 (s, 1H), 8.96 (s, 2H), 7.48 (d, 2H), 7.33 (d, 2H), 2.42 (s, 3H) ppm.



6ag

48. **4-(5-pyrimidinyl)benzaldehyde** (entry 13 of table 5)[19]

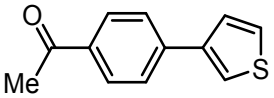
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.10 (s, 1H), 9.28 (s, 1H), 9.02 (s, 2H), 8.06 (d, 2H), 7.78 (d, 2H) ppm.



6ac

49. **1-(4-(Thiophen-3-yl)phenyl)ethanone** (entry 14 of table 5)[12]

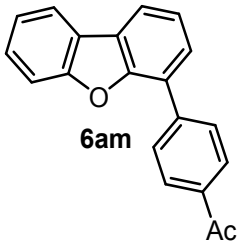
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, 2H), 7.69 (d, 2H), 7.58 (dd, 1H), 7.43 (m, 2H), 2.62 (s, 3H) ppm.



6al

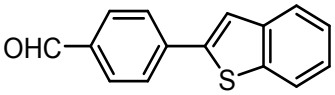
50. **4-(4'-Acetylphenyl)dibenzofuran** (entry 15 of table 5)[20]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, 2H), 8.04 – 7.98 (m, 4H), 7.65 – 7.60 (m, 2H), 7.51 – 7.36 (m, 3H), 2.68 (s, 3H) ppm.



6am

51. **4-(Benzo[b]thiophen-2-yl)benzaldehyde** (entry 16 of table 5)[21]

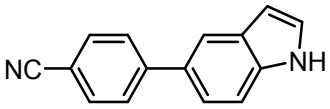


6dn

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.04 (s, 1H), 7.96 – 7.82 (m, 6H), 7.71 (s, 1H), 7.40 – 7.37 (m, 2H) ppm.

52. **4-(1H-Indol-5-yl)benzonitrile** (entry 17 of table 5)[22]

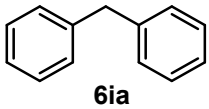
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 1H), 7.88 (d, 1H), 7.72 (m, 4H), 7.50 (d, 1H), 7.44 (m, 1H), 7.28 (m, 1H), 6.64 (m, 1H) ppm.



6co

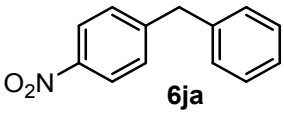
53. **Diphenylmethane** (entry 1 of table 6)[23]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 – 7.16 (m, 4H), 7.11 – 7.08 (m, 6H), 3.88 (s, 2H) ppm.


6ia

54. **1-Benzyl-4-nitrobenzene** (entry 2 of table 6)[24]

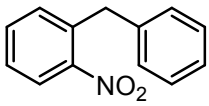
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, 2H), 7.34 (m, 4H), 7.24 (m, 1H), 7.16 (d, 2H), 4.07 (s, 2H) ppm.



6ja

55. **1-Benzyl-2-nitrobenzene** (entry 3 of table 6)[24]

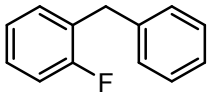
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (dd, 1H), 7.50 (m, 1H), 7.36 (m, 1H), 7.30 – 7.21 (m, 4H), 7.19 – 7.13 (m, 2H), 4.30 (s, 2H) ppm.



6ka

56. **1-Benzyl-2-fluorobenzene** (entry 4 of table 6)[23]

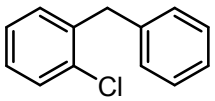
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.31 (m, 2H), 7.31 – 7.16 (m, 5H), 7.15 – 7.04 (m, 2H), 4.07 (s, 2H) ppm.



6la

57. **2-Chlorodiphenylmethane** (entry 5 of table 6)[25]

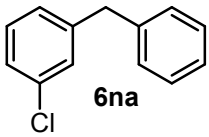
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 – 7.25 (m, 9H), 4.21 (s, 2H) ppm.



6ma

58. **3-Chlorodiphenylmethane** (entry 6 of table 6)[26]

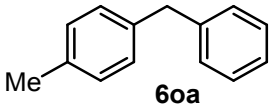
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 – 7.13 (m, 2H), 7.09 – 7.01 (m, 6H), 6.93 – 6.91 (m, 1H), 3.82 (s, 2H) ppm.



6na

59. **1-Benzyl-4-methylbenzene** (entry 7 of table 6)[25]

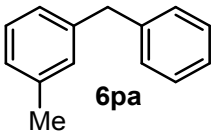
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.32 (m, 2H), 7.32 – 7.22 (m, 3H), 7.22 – 7.12 (m, 4H), 4.03 (s, 2H), 2.40 (s, 3H) ppm.



6oa

60. **1-Benzyl-3-methylbenzene** (entry 8 of table 6)[25]

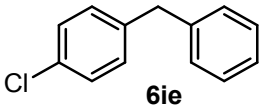
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 – 7.26 (m, 2H), 7.21 – 7.15 (m, 4H), 7.01 – 6.98 (m, 3H), 3.94 (s, 2H), 2.30 (s, 3H) ppm.



6pa

61. **4-Chlorobenzylbenzene** (entry 10 of table 6)[25]

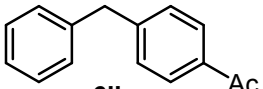
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.29 – 7.15 (m, 5H), 7.13 – 7.11 (m, 2H), 7.06 – 7.04 (m, 2H), 3.92 (s, 2H) ppm.



6ie

62. **4-Benzyl-acetophenone** (entry 11 of table 6)[27]

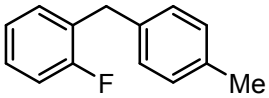
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, 2H), 7.35 – 7.17 (m, 7H), 4.03 (s, 2H), 2.57 (s, 3H) ppm.



6ib

63. **1-Methyl-4-(2-fluorobenzyl)benzene** (entry 12 of table 6)[23]

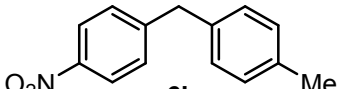
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 – 7.07 (m, 6H), 7.05 – 7.01 (m, 2H), 3.98 (s, 2H), 2.33 (s, 3H) ppm.



6lg

64. **1-Methyl-4-(4-nitrobenzyl)benzene** (entry 13 of table 6)[28]

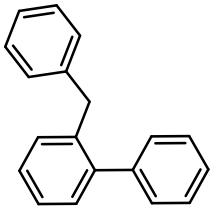
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, 2H), 7.32 (d, 2H), 7.12 (d, 2H), 7.05 (d, 2H), 4.03 (s, 2H), 2.33 (s, 3H) ppm.



6jg

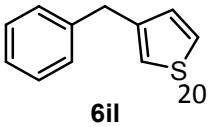
65. **2-Benzylbiphenyl** (entry 14 of table 6)[25]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.11 (m, 12H), 6.97 (d, 2H), 3.94 (s, 2H) ppm.



6qa

66. **3-Benzylthiophene** (entry 15 of table 6)[29]

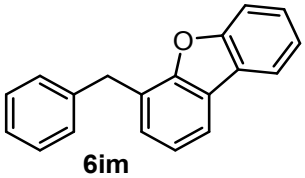


6il

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 – 7.32 (m, 6H), 6.90 – 6.91 (m, 2H), 3.98 (s, 2H) ppm.

67. **4-Benzyldibenzo[b,d]furan** (entry 16 of table 6)[29]

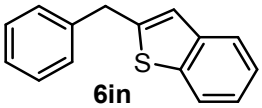
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 – 7.90 (m, 1H), 7.79 (dd, 1H), 7.57 (m, 1H), 7.45 – 7.41 (m, 1H), 7.33 – 7.17 (m, 8H), 4.33 (s, 2H) ppm.



6im

68. **2-Benzylbenzo[b]thiophene** (entry 17 of table 6)[30]

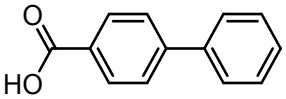
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 – 7.63 (d, 1H), 7.56 (d, 1H), 7.35 – 7.13 (m, 7H), 6.91 (s, 1H), 4.14 (s, 2H) ppm.



6in

69. **4-Carboxybiphenyl** (entry 1 of table 7)[5]

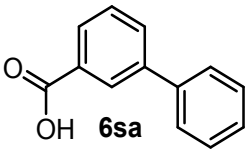
^{1}H NMR (400 MHz, DMSO-d_6): δ 12.96 (s, 1H), 8.02 (d, 2H), 7.79 (d, 2H), 7.73 (d, 2H), 7.50 (t, 2H), 7.43 (t, 1H) ppm.



6ra

70. **Biphenyl-3-ylcarboxylic acid** (entry 2 of table 7)[31]

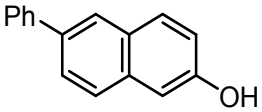
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (s, 1H), 8.11 (d, 1H), 7.85 (d, 1H), 7.65 – 7.54 (m, 3H), 7.50 – 7.39 (m, 3H) ppm.



6sa

71. **6-Phenylnaphthalen-2-ol** (entry 3 of table 7)[32]

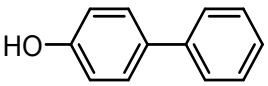
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.82 – 7.69 (m, 5H), 7.48 (t, 2H), 7.37 (t, 1H), 7.20 – 7.12 (m, 2H) ppm.



6ta

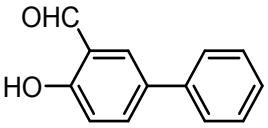
72. **4-Phenylphenol** (entry 4 of table 7)[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.53 (m, 2H), 7.49 – 7.46 (m, 2H), 7.43 – 7.39 (m, 2H), 7.32 – 7.28 (m, 1H), 6.92 – 6.90 (m, 2 H) ppm.



6ua

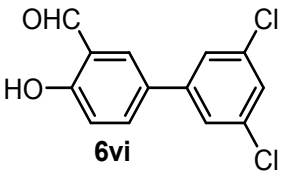
73. **5-Phenyl salicylaldehyde** (entry 5 of table 7)[9]



6va

^{1}H NMR (400 MHz, $CDCl_3$): δ 11.02 (s, 1H), 9.98 (s, 1H), 7.80 – 7.75 (m, 2H), 7.59 – 7.53 (m, 2H), 7.50 – 7.42 (m, 2H), 7.38 (m, 1H), 7.09 (d, 1H) ppm.

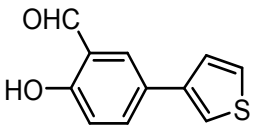
74. **3',5'-Dichloro-4-hydroxy-[1,1'-biphenyl]-3-carbaldehyde** (entry 6 of table 7)



6vi

White solid. mp: 166 – 168 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.07 (s, 1H), 9.98 (s, 1H), 7.75 – 7.68 (m, 2H), 7.42 (d, J = 1.5 Hz, 2H), 7.35 (s, 1H), 7.10 (d, J = 8.3 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.75, 160.87, 140.64, 135.31, 131.22, 128.47, 126.90, 126.01, 120.77, 119.97, 118.30 ppm. HRMS (ESI): *m/z* calcd for $C_{13}H_9Cl_2O_2$ $[M + H]^+$ 266.9978, found 266.9969.

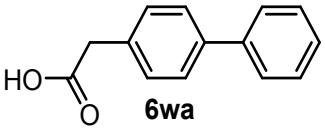
75. **2-Hydroxy-5-(thiophen-3-yl)benzaldehyde** (entry 7 of table 7)



6vl

White solid. mp: 117 – 119 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.98 (s, 1H), 9.96 (s, 1H), 7.79 – 7.75 (m, 2H), 7.43 – 7.39 (m, 2H), 7.35 (d, J = 4.8 Hz, 1H), 7.04 (d, J = 8.3 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.75, 160.87, 140.64, 135.31, 131.22, 128.47, 126.90, 126.01, 120.77, 119.97, 118.30 ppm. HRMS (ESI): *m/z* calcd for $C_{11}H_9O_2S$ $[M + H]^+$ 205.0323, found 205.0337.

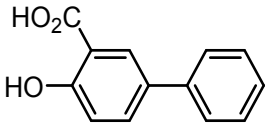
76. **4-Biphenylacetic acid**, **Felbinac** (entry 8 of table 7)[33]



6wa

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 – 7.55 (m, 4H), 7.44 (m, 2H), 7.37 – 7.32 (m, 3H), 3.70 (s, 2H) ppm.

77. **4-Hydroxy-[1,1'-biphenyl]-3-carboxylic acid** (entry 9 of table 7)[31]

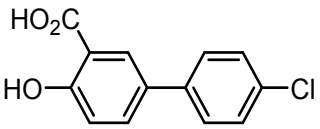


6xa

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.13 (d, 1H), 7.80 (t, 1H), 7.62 (t, 2H), 7.43 (m, 2H), 7.33 (m, 1H), 7.04 (d, 1H) ppm.

78. **4'-Chloro-4-hydroxy-[1,1'-biphenyl]-3-carboxylic acid** (entry 10 of table 7)[34]

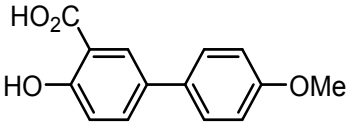
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.01 (d, 1H), 7.81 (t, 1H), 7.63 (t, 2H), 7.47 (m, 2H), 7.04 (d, 1H) ppm.



6xe

79. **4-Hydroxy-4'-methoxy-[1,1'-biphenyl]-3-carboxylic acid** (entry 11 of table 7)[34]

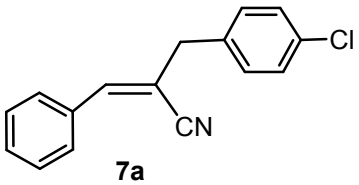
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.08 (d, 1H), 7.77 (t, 1H), 7.55 (t, 2H), 7.02 – 6.99 (m, 3H), 3.82 (s, 3H) ppm.



6xf

80. **2-(4-Chlorobenzyl)-3-phenylacrylonitrile**

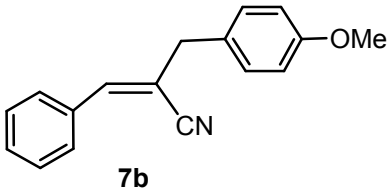
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 – 7.71 (m, 2H), 7.42 (dd, J = 5.1, 2.1 Hz, 3H), 7.35 – 7.32 (m, 2H), 7.24 – 7.21 (m, 2H), 6.97 (s, 1H), 3.68 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.46, 135.04, 133.46, 130.45, 130.38, 129.85, 129.21, 129.04, 129.00, 128.84, 118.60, 110.30, 41.66 ppm. HRMS (ESI): *m/z* calcd for $C_{16}H_{12}ClNNa$ [M + Na]$^+$ 276.0555, found 276.0577.



7a

81. **2-(4-Methoxybenzyl)-3-phenylacrylonitrile**

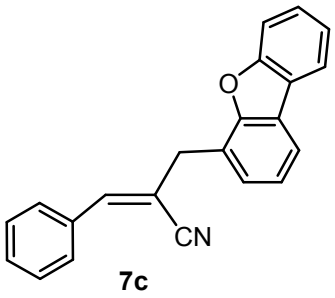
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 – 7.71 (m, 2H), 7.40 – 7.38 (m, 3H), 7.21 – 7.19 (m, 2H), 6.94 – 6.89 (m, 3H), 3.81 (s, 3H), 3.65 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.01, 143.75, 133.72, 130.18, 130.14, 128.92, 128.78, 128.51, 118.89, 114.43, 111.38, 55.41, 41.52 ppm. HRMS (ESI): *m/z* calcd for $C_{17}H_{16}NO$ [M + H]$^+$ 250.1231, found 250.1254.



7b

82. **2-(Dibenzo[b,d]furan-4-ylmethyl)-3-phenylacrylonitrile**

White solid. Mp: 100 – 102 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 – 7.94 (m, 1H), 7.91 (dd, J = 7.6, 1.3 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.59 (d, J = 8.2 Hz, 1H), 7.49 – 7.44 (m, 1H), 7.42 – 7.33 (m, 6H), 7.13 (s, 1H), 4.09 (s, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.11, 154.56, 144.65, 133.58, 130.13, 128.79, 128.73, 127.74, 127.29, 124.48, 124.31, 123.16, 122.89, 120.82, 120.46, 119.98, 118.75, 111.79, 109.21, 35.97 ppm. HRMS (ESI): *m/z* calcd for $C_{22}H_{16}NO$ $[M + H]^+$ 310.1231, found 310.1255.



7c

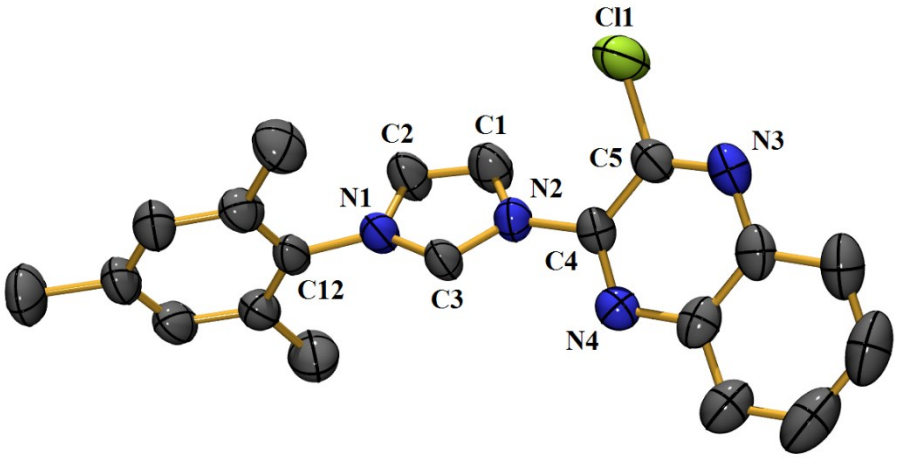


Figure S1. Molecular structure of **[HL2Cl](PF_6)**. All hydrogen atoms and the counter anion have been removed for clarity. Thermal ellipsoids are drawn at 50% probability level. Selected bond lengths [Å]: Cl1−C5 1.732(6), C12−C13 1.368(7), N1−C12 1.450(6), N1−C3 1.334(6), N2−C3 1.340(6), N2−C4 1.428(6), C4−C5 1.420(7), N3−C5 1.281(7). Selected bond angles [°]: N3−C5−Cl1 116.0(4), N3−C5−C4 122.8(5), C4−N4−Cl1 117.1(4), C1−N2−C4 127.0(4), N4−C4−N2 115.5(4), C3−N1−C12 128.0(4), C3−N2−C4 124.6(4), C2−N1−C12 122.8(4).

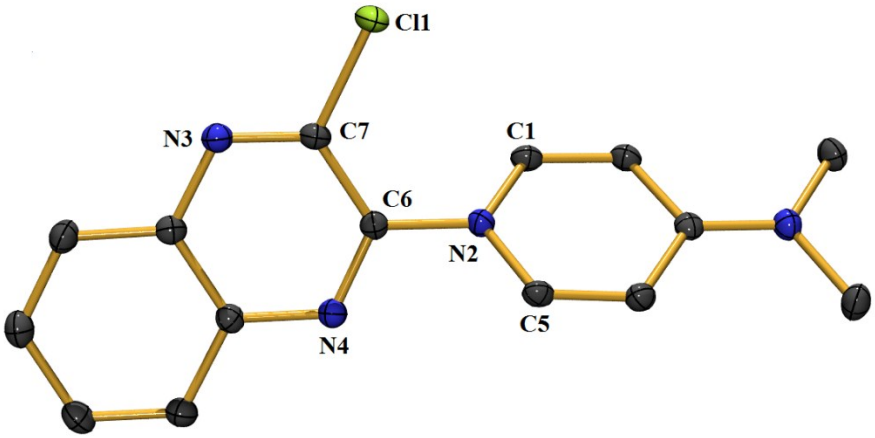


Figure S2. Molecular structure of **[L4Cl]Cl**. All hydrogen atoms, solvent molecules and counter anion have been removed for clarity. Thermal ellipsoids are drawn at 50% probability level. Selected bond lengths [Å]: Cl1−C7 1.734(15), N3−C7 1.295(2), C7−C6 1.431(2), N4−C6

1.302(19), N2−C6 1.428(19), N2−C1 1.370(19), N2−C5 1.371(19). Selected bond angles [°]: N3−C7−Cl1 116.23(11), C6−C7−Cl1 121.05(12), N2−C6−C7 122.54(13), N4−C6−N2 116.30.

Table S1 Suzuki-Miyaura coupling reaction of 4-bromoacetophenone at different catalyst loading[a]

Entry	Complex	Catalyst (mol%)	Time/h	[b]Yield (%)	TON	TOF
1	I	0.5	3	98	196	65
	II	0.5	3	98	196	65
2	I	0.06	5	97	1,616	323
	II	0.06	5	95	1,583	316
3	I	0.02	8	95	4,750	593
	II	0.02	8	92	4,600	575
4	I	0.005	12	72[c] (95)[d]	14,400 (19,000)	1,200 (1,583)
	II	0.005	12	69[c] (92)[d]	13,800 (18,400)	1,150 (1,533)
5	I	0.001	24	82[c,d]	82,000	3,416
	II	0.001	24	80[c,d]	80,000	3,333

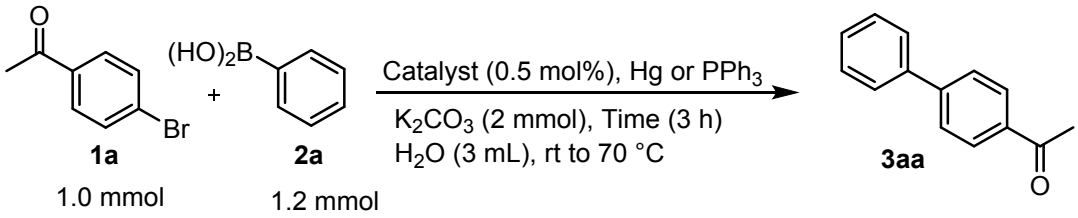
[a]Reaction conditions: 4-bromoacetophenone (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), H_2O (3 mL), 0.5 mol% [Pd], at room temperature, in air. [b]Isolated yield (the purity of the isolated product was confirmed by ^{1}H NMR). [c]Isolated yield after column chromatography. [d]Temperature of oil bath 70 ºC.

Investigations into the nature of the catalysis (homogeneous *vs* heterogeneous)

There are several poison tests known in the literature to distinguish between homogeneous and heterogeneous catalysis. The most common method is the addition of mercury, which leads to amalgamation of the metal or adsorption on the metal surface of heterogeneous catalyst. There is another popular method in which a heterogeneous catalyst is poisoned by treating it with ligands like CS_2, PPh_3 or thiophene in substoichiometric amount (less than 1.0 equivalent per metal atom).[35] The poisoning tests *viz* the addition of Hg and the addition of PPh_3 were carried out on **I** and **VI** and the results are furnished in Table S2. Though the room temperature reactions were affected significantly, the reactions conducted at 70 °C afforded excellent yields in both the tests.

It is noteworthy that in case of PPh_3 poison test, even after the addition of 2 equivalents of PPh_3 the yields were almost quantitative, when the reaction was conducted at 70 °C.

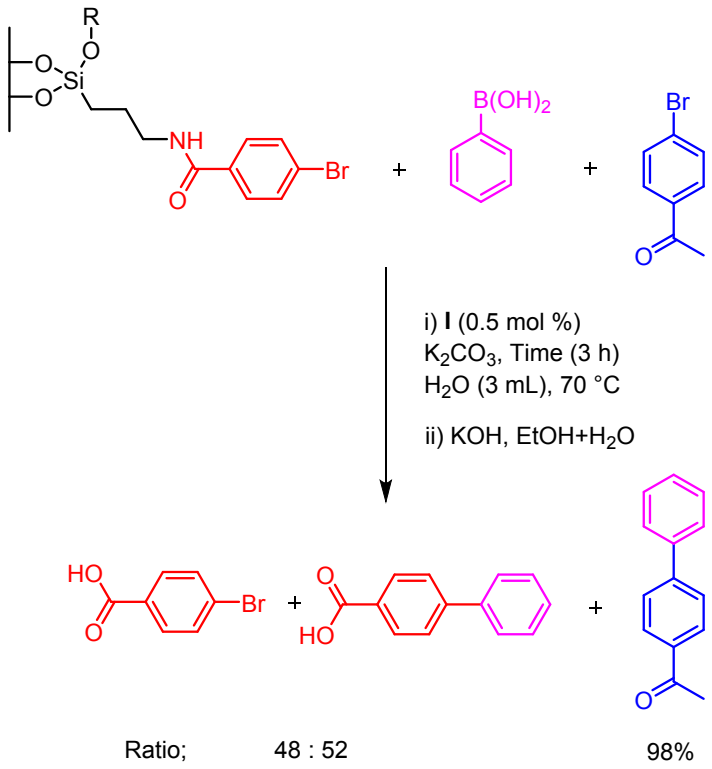
Table S2 Summary of poisoning experiments for complexes **I** and **VI**



Entry	Poisoning additives	% Isolated yield of **3aa** (by ^{1}H NMR)			
		[Pd(HL1)(PPh$_3$)Cl$_2$] (**I**)		[Pd(L4)(PPh$_3$)Cl$_2$] (**VI**)	
		rt	70 ºC	rt	70 ºC
1	Hg (one drop)	45	90	42	82
2	PPh_3 (2 equiv per metal)	38	98	36	98

Further, a two phase test,[36] which is more confirmative in determining the nature of the catalysis (homogeneous *vs* heterogeneous), has also been performed on **I**. In this test, generally an immobilized aryl bromide, an aryl bromide and excess of arylboronic acid are used. If the catalyst is homogeneous, the immobilized aryl bromide will also be converted into product, which is not expected in case of a heterogeneous catalyst. A mixture of 4-bromoacetophenone and freshly prepared immobilized aryl bromide were treated with excess of phenylboronic acid in the presence of **I** as catalyst and K_2CO_3 in water at 70 ºC (Scheme S1). After 3 h of stirring, the mixture was filtered and the precipitate was extracted with ether, and analyzed with ^{1}H NMR. The NMR spectrum showed that a 98% conversion of 4-bromoacetophenone occurred. The residue, which is basically the immobilized amide, was hydrolyzed and the resultant products were analyzed using ^{1}H NMR after work up. The analysis with ^{1}H NMR indicated that the immobilized aryl bromide

was also converted to the cross coupled product to the extent of 52%. These results indicate that the catalysis is largely homogeneous.



Scheme S1 Two phase test

Table S3 Crystal data for Compounds **[HL2Cl](PF$_6$)**, **[L4Cl]Cl**, **I**, **II**, **III** and **V**.

	[HL2Cl](PF$_6$)	**[L4Cl]Cl**	**[Pd(L)(PPh$_3$)Cl] (III)**
empirical formula	$C_{20}H_{18}F_6N_4PCl$	$C_{15}H_{18}Cl_2N_4O_2$	$C_{41}H_{38}N_4PdPCl$
formula wt	494.80	357.23	759.57
temp (K)	150(2)	120(2)	150(2)
cryst syst	Orthorhombic	Triclinic	Triclinic
space group	*Pca2$_1$*	*P–1*	*P–1*
a (Å)	24.3122(14)	7.2346(4)	9.2199(5)
b (Å)	8.5288(6)	9.1795(5)	11.5698(7)

c (Å)	10.4839(8)	13.2726(8)	17.5646(10)
α (deg)	90	86.782(5)	83.401(5)
β (deg)	90	77.574(5)	88.501(5)
γ (deg)	90	70.405(5)	70.238(6)
V (Å^3)	2173.9(3)	810.81(8)	1751.48(18)
Z	4	2	2
ρ_{calcd} (Mg m^{-3})	1.512	1.463	1.440
μ (mm^{-1})	0.316	0.415	0.688
F(000)	1008.0	372.0	780.0
cryst size (mm)	0.31 x 0.28 x 0.18	0.5 × 0.35 × 0.09	0.4 x 0.3 x 0.03
θ range (deg)	7.96 – 58.22	8.88 – 58.22	8 – 57.62
no. of collected/unique rflns	14085/5084 (R(int) = 0.0574)	8635/3752 (R(int) = 0.0240)	16836/7873 (R(int) = 0.0516)
no. of data/restraints/ params	5084/1/292	3752/0/226	7873/0/437
$R1$, $wR2$ ($I > 2\sigma(I)$)[a]	0.0778, 0.1981	0.0336, 0.0821	0.0537, 0.1284
$R1$, $wR2$ (all data)[a]	0.1311, 0.2391	0.0415, 0.0873	0.0761, 0.1406
GOF	1.047	1.050	1.056
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.42/–0.41	0.30/-0.34	2.08/–1.07

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$.

Table S3 *continued*

	[Pd(HL1)(PPh$_3$)Cl$_2$]·2CH$_3$CN (**I**)	**[Pd(HL2)(PPh$_3$)Cl$_2$]**·2CH$_3$CN (**II**)	**[Pd(L3)(PPh$_3$)Cl$_2$]**·CH$_3$CN (**V**)
empirical formula	$C_{45}H_{45}N_6PCl_2Pd$	$C_{42}H_{39}Cl_2N_6PPd$	$C_{39}H_{36}N_5PCl_2Pd$
formula wt	878.14	836.06	783.05
temp (K)	150(2)	150(2)	200(2)
cryst syst	Monoclinic	Triclinic	Triclinic

space group	$P2_1/c$	P–1	P–1
a (Å)	10.5933(3)	13.3244(4)	11.5440(6)
b (Å)	15.7459(4)	15.4366(4)	12.9028(13)
c (Å)	25.1218(15)	20.4811(6)	13.2418(14)
α (deg)	90	87.426(2)	116.569(10)
β (deg)	93.177(3)	88.905(2)	91.069(6)
γ (deg)	90	66.105(3)	99.752(6)
V (Å^3)	4183.9(3)	3847.69(19)	1728.6(3)
Z	4	4	2
ρ_{calcd} (Mg m^{-3})	1.394	1.443	1.5044
μ (mm^{-1})	0.649	0.702	0.775
F(000)	1808.0	1712.0	799.1
cryst size (mm)	0.42 x 0.32 x 0.24	0.5 x 0.4 x 0.25	0.4 x 0.35 x 0.3
θ range (deg)	7.12 – 58.38	7.16 – 58.42	7.2 – 58.26
no. of collected/unique rflns	27806/9765 (R(int) = 0.0350)	40083/17709 (R(int) = 0.0417)	14537/7848 (R(int) = 0.0733)
no. of data/restraints/ params	9765/0/502	17709/0/947	7848/0/434
$R1$, $wR2$ ($I > 2\sigma(I)$)[a]	0.0341, 0.0653	0.0674, 0.1620	0.0793, 0.1828
$R1$, $wR2$ (all data)[a]	0.0518, 0.0702	0.0884, 0.1718	0.1507, 0.2298
GOF	1.052	1.173	1.027
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	0.51/–0.56	0.51/–0.56	2.60/–1.54

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{0.5}$.

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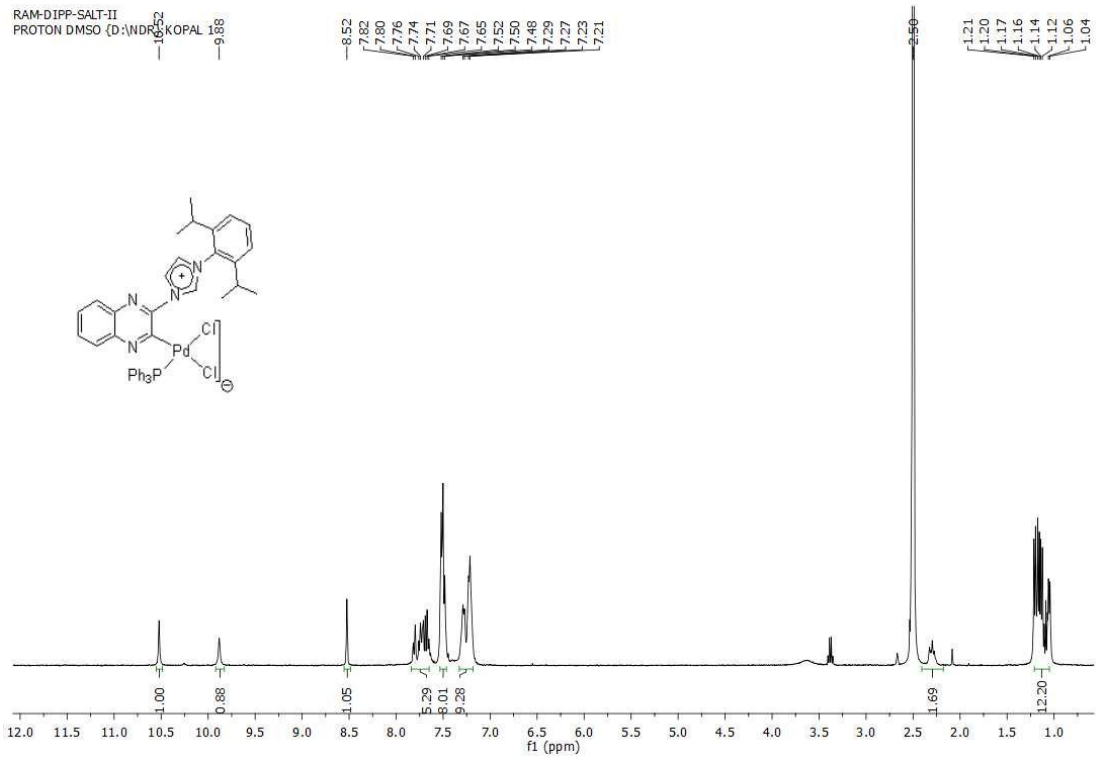


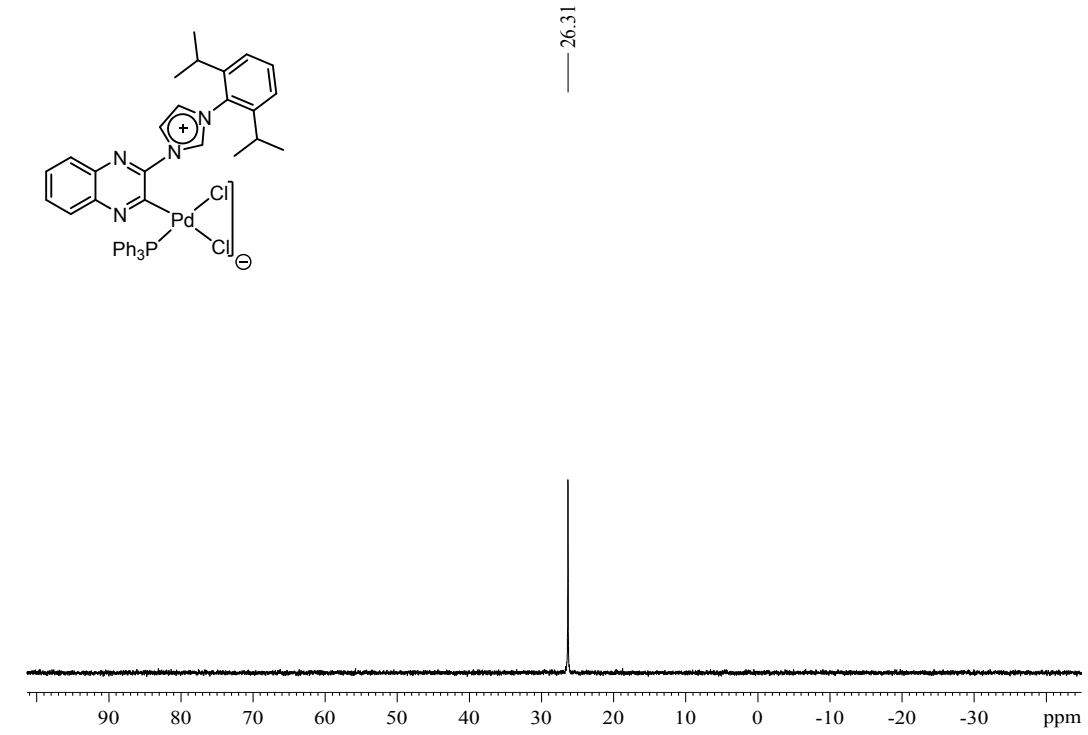
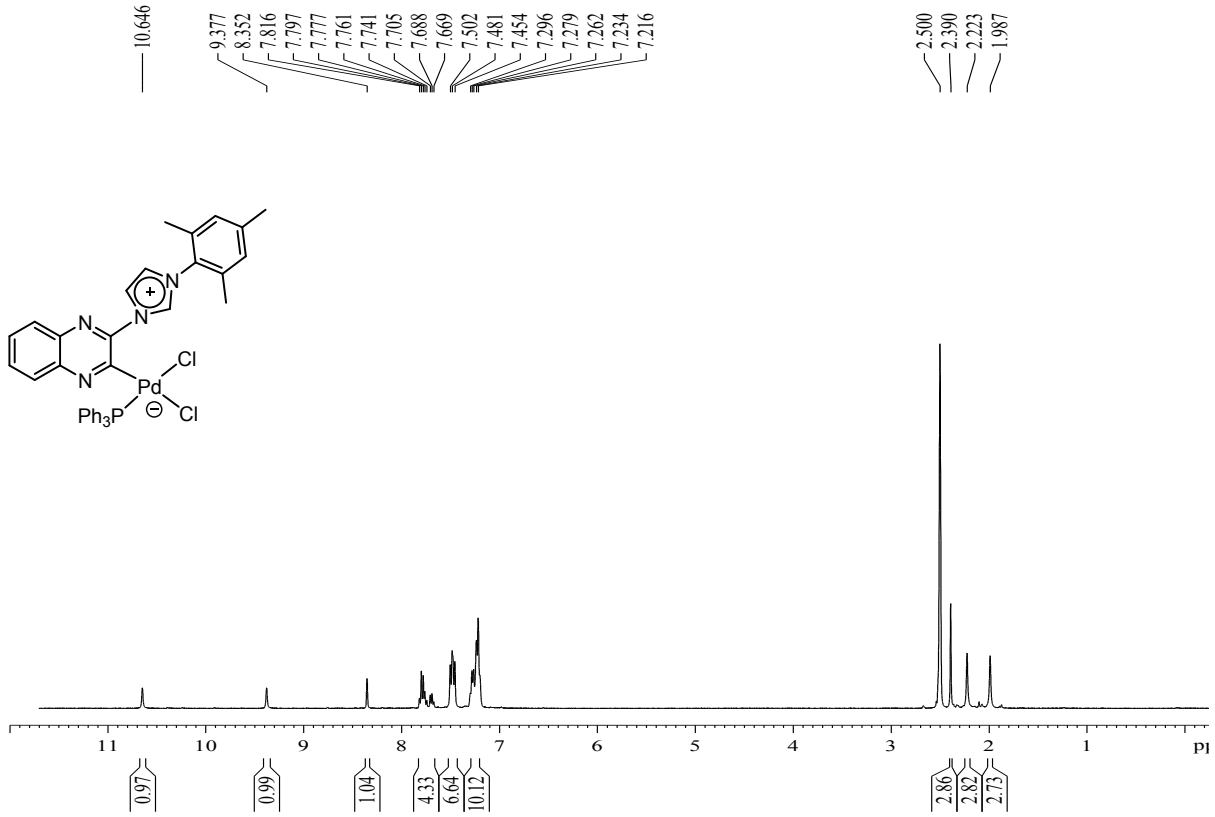


Figure S3. ^{1}H and ^{31}P NMR spectrum of [Pd(HL1)(PPh$_3$)Cl$_2$] **(I)** in DMSO-d_6.



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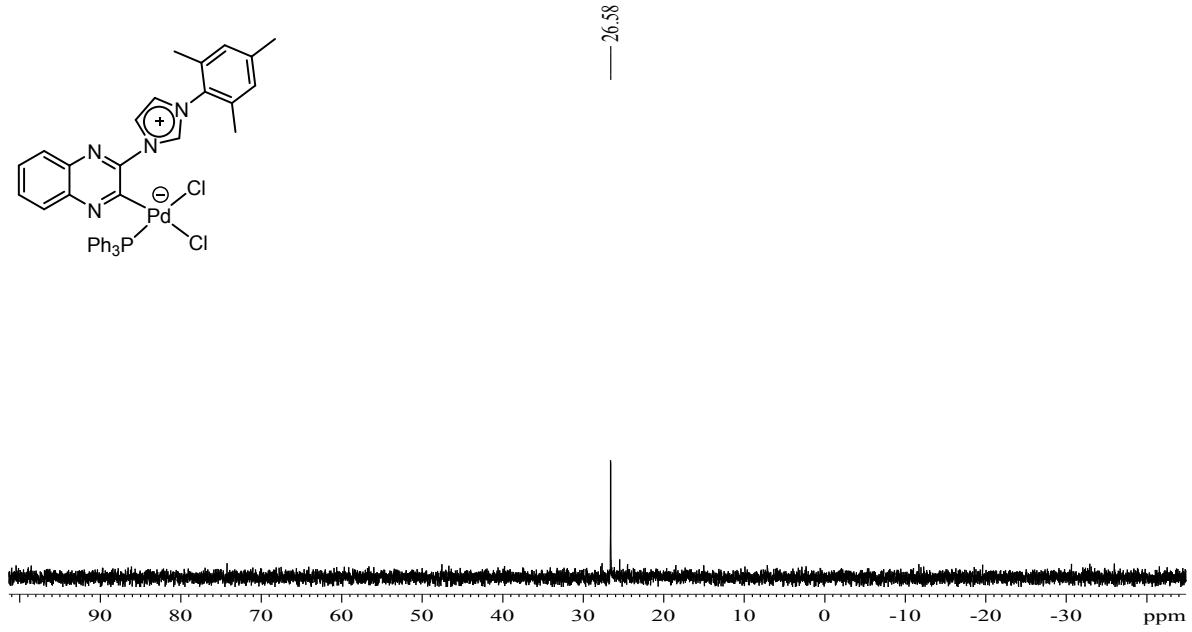
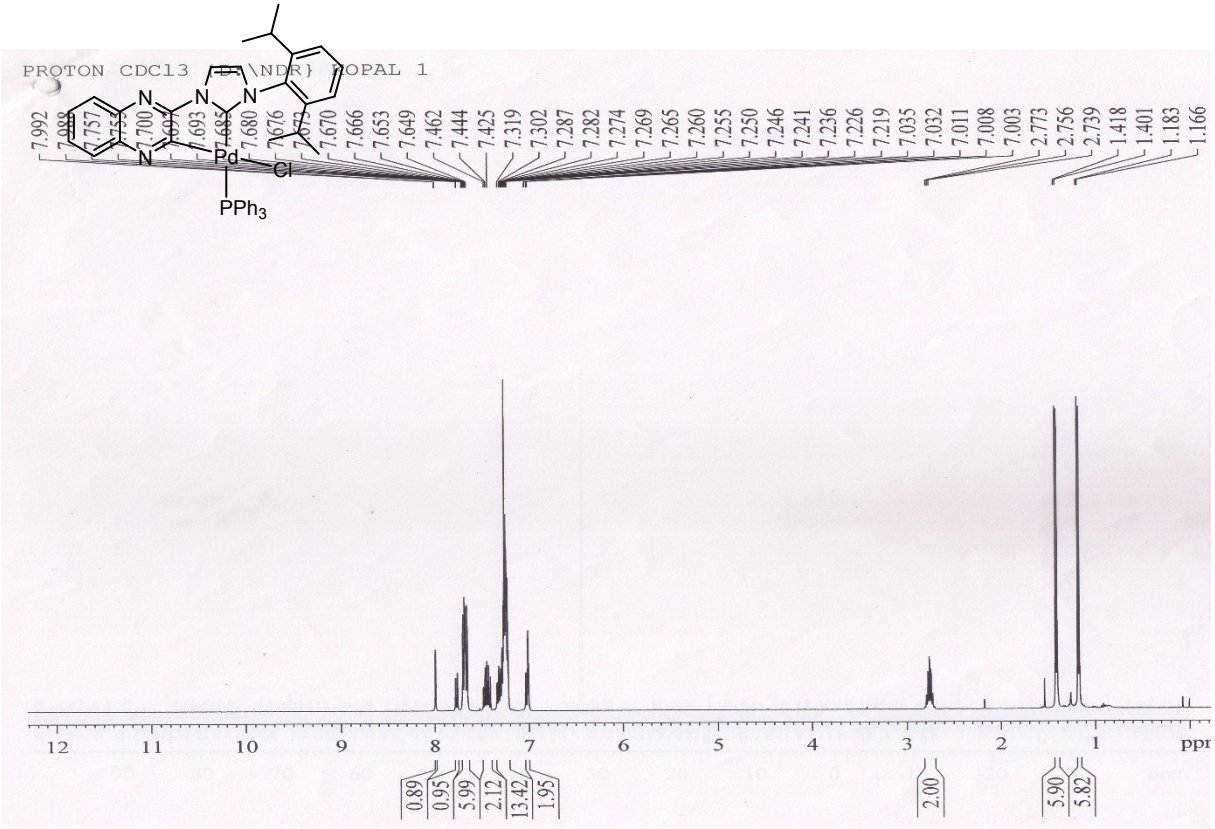


Figure S4. ^{1}H and ^{31}P NMR spectrum of [Pd(HL2)(PPh$_3$)Cl$_2$] **(II)** in DMSO-d_6.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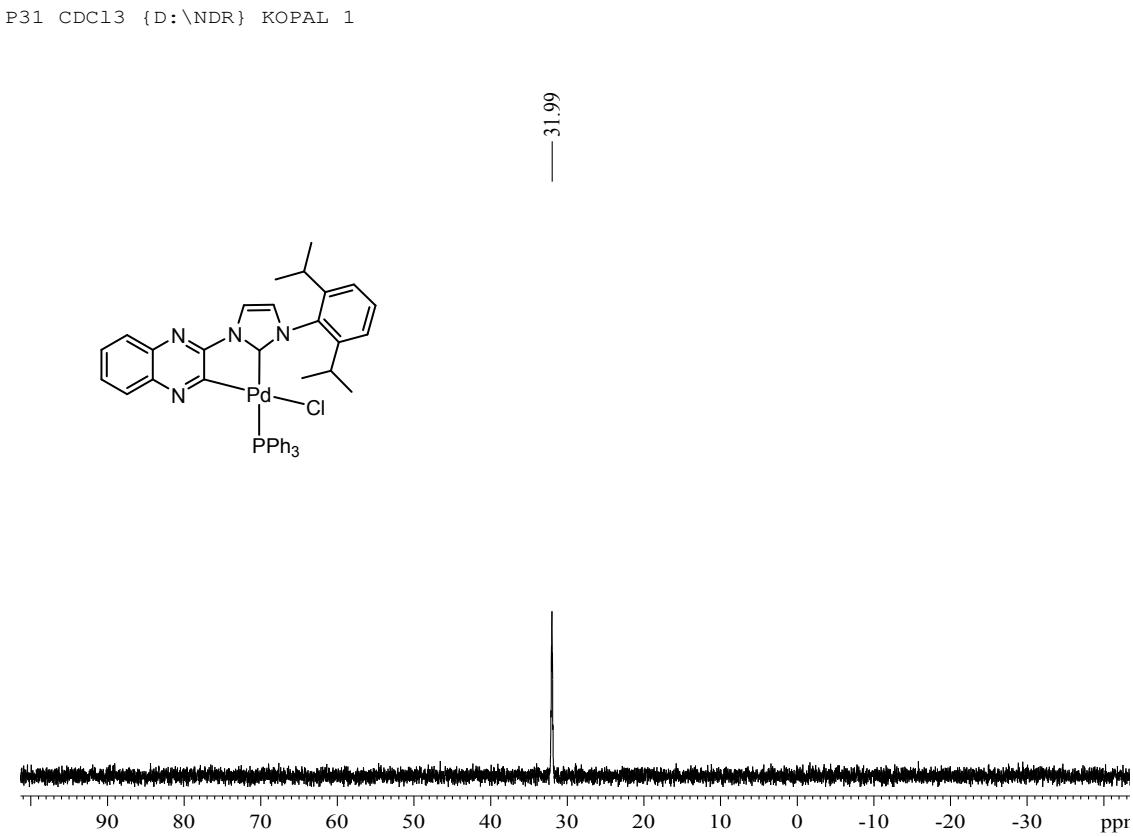


Figure S5. ^{1}H and ^{31}P NMR spectrum of [Pd(L1)(PPh_3)Cl] **(III)** in $CDCl_3$.

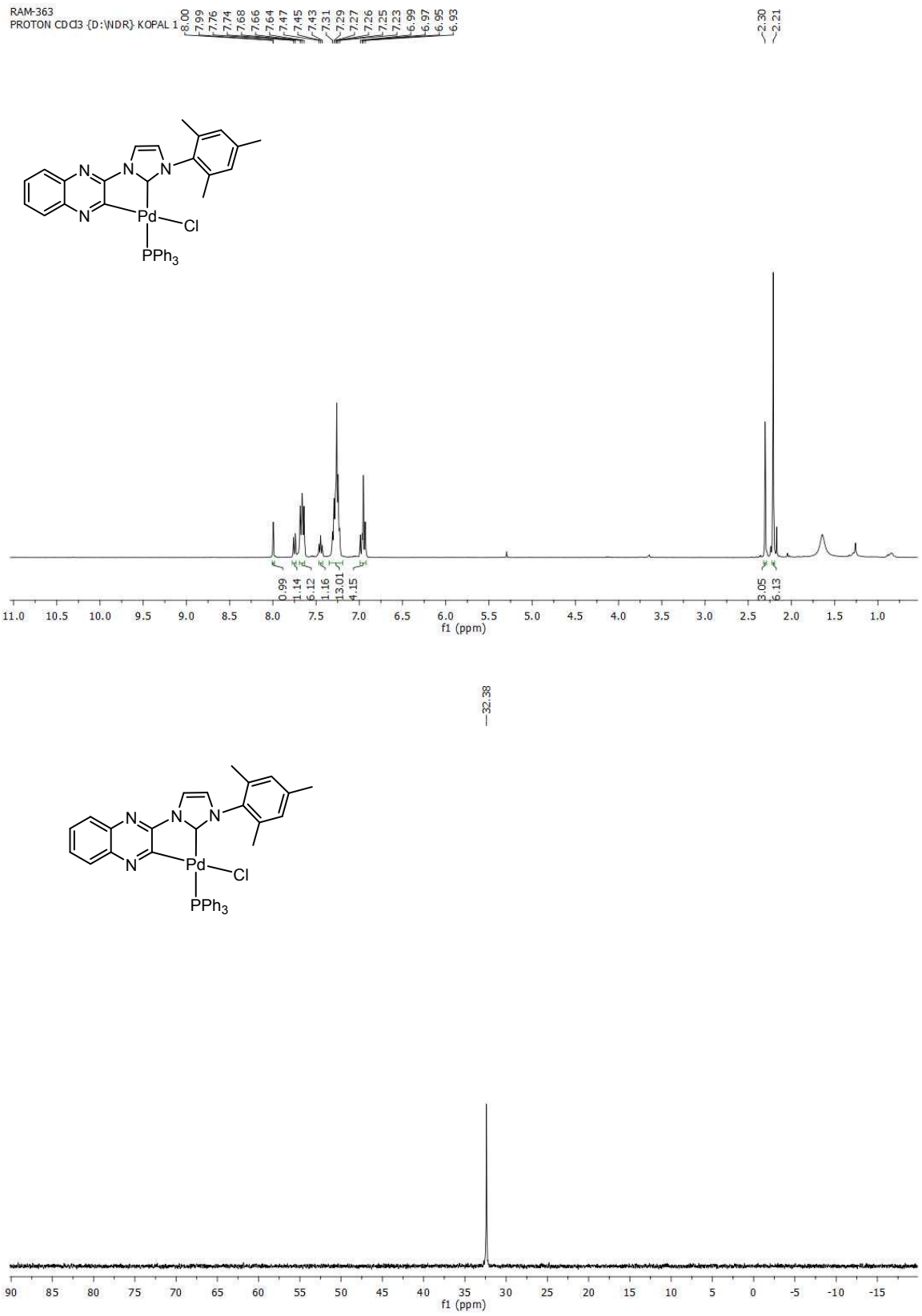


Figure S6. ^{1}H and ^{31}P NMR spectrum of [Pd(L2)(PPh_3)Cl] **(IV)** in $CDCl_3$.

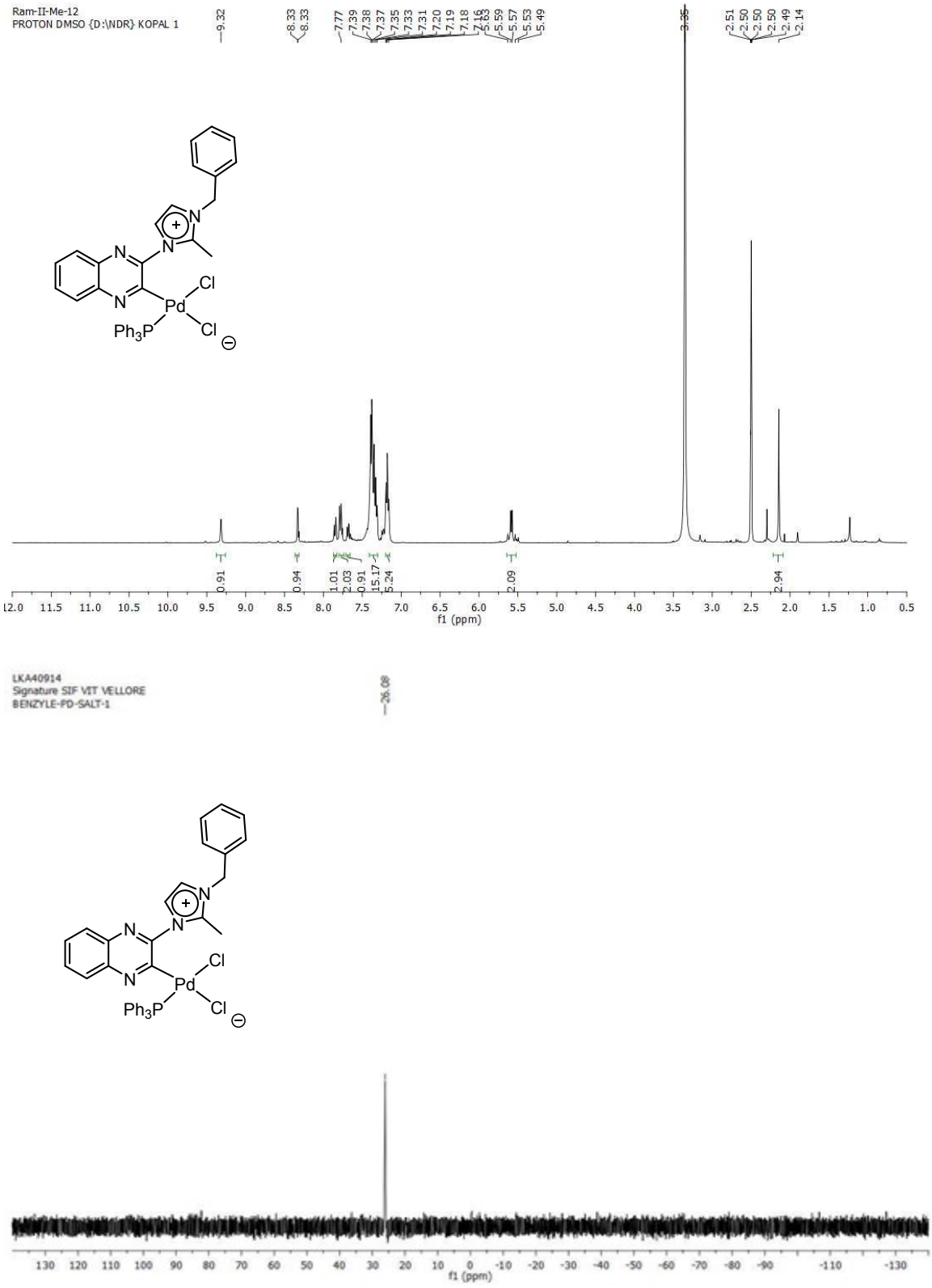


Figure S7. ^{1}H and ^{31}P NMR spectrum of [Pd(L3)(PPh_3)Cl_2] **(V)** in DMSO-d_6.

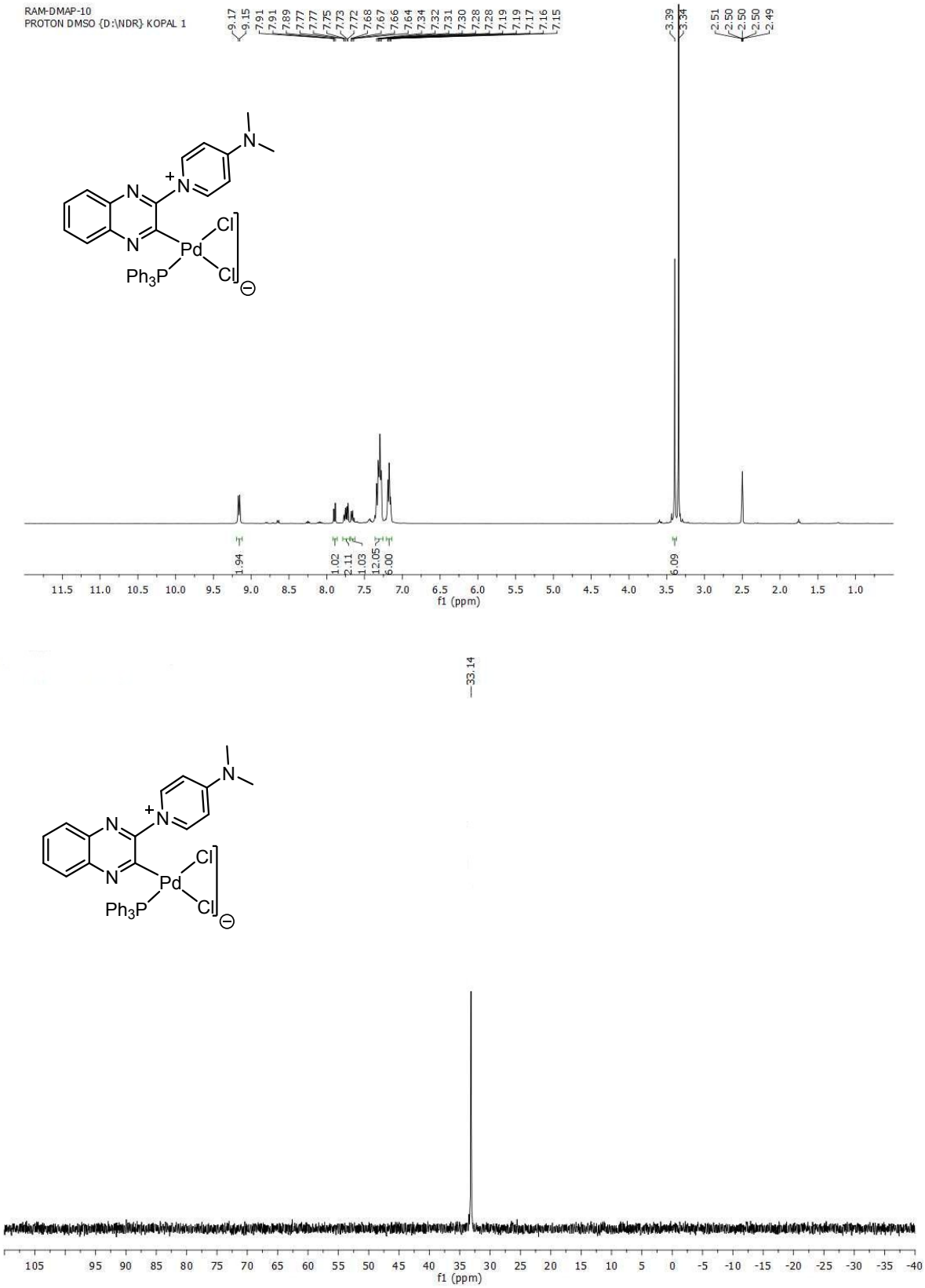


Figure S8. ^{1}H and ^{31}P NMR spectrum of [Pd(L4)(PPh$_3$)Cl$_2$] **(VI)** in DMSO-d_6.

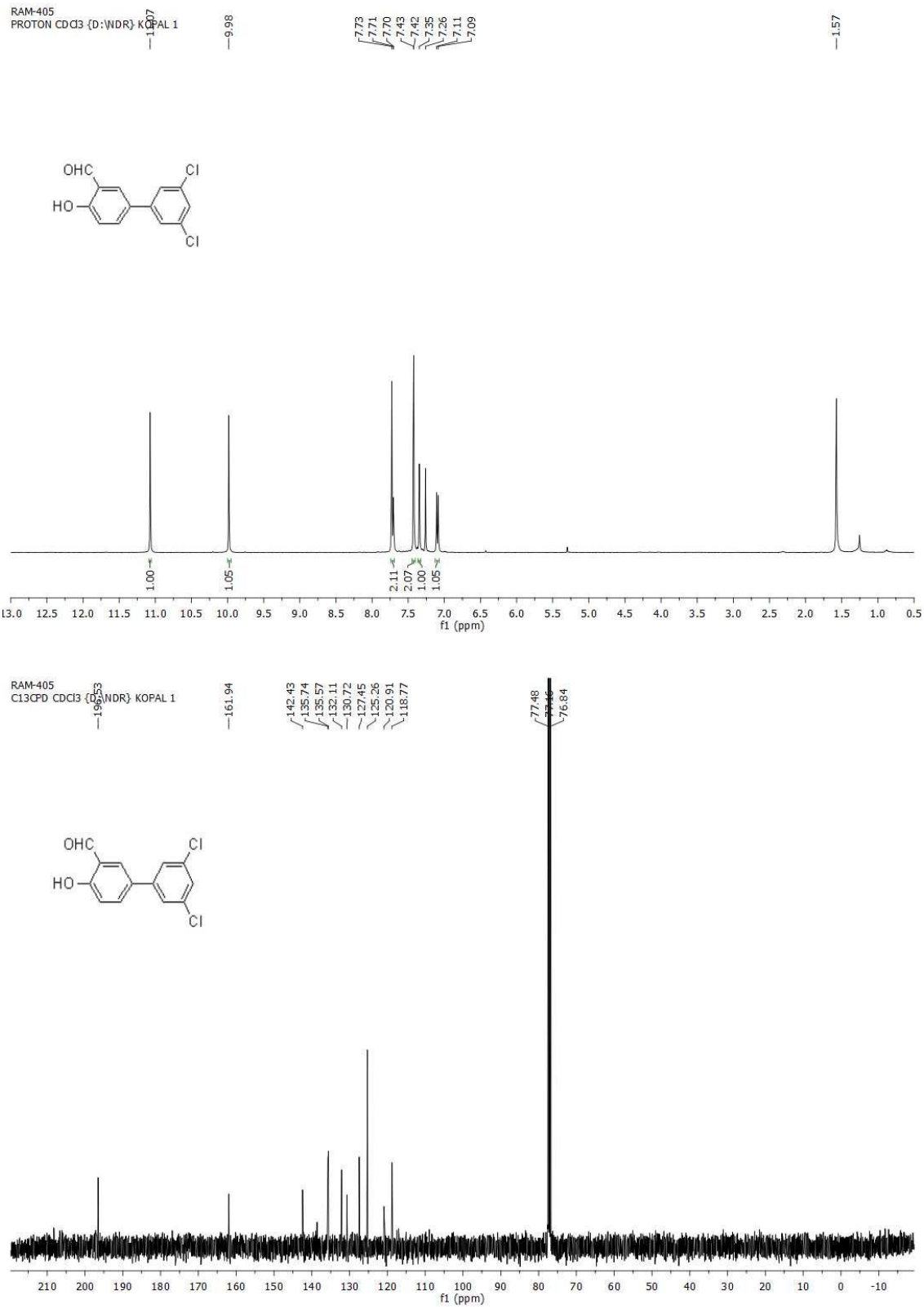


Figure S9. ^{1}H and ^{13}C NMR spectrum of 3',5'-dichloro-4-hydroxy-[1,1'-biphenyl]-3-carbaldehyde in $CDCl_3$.

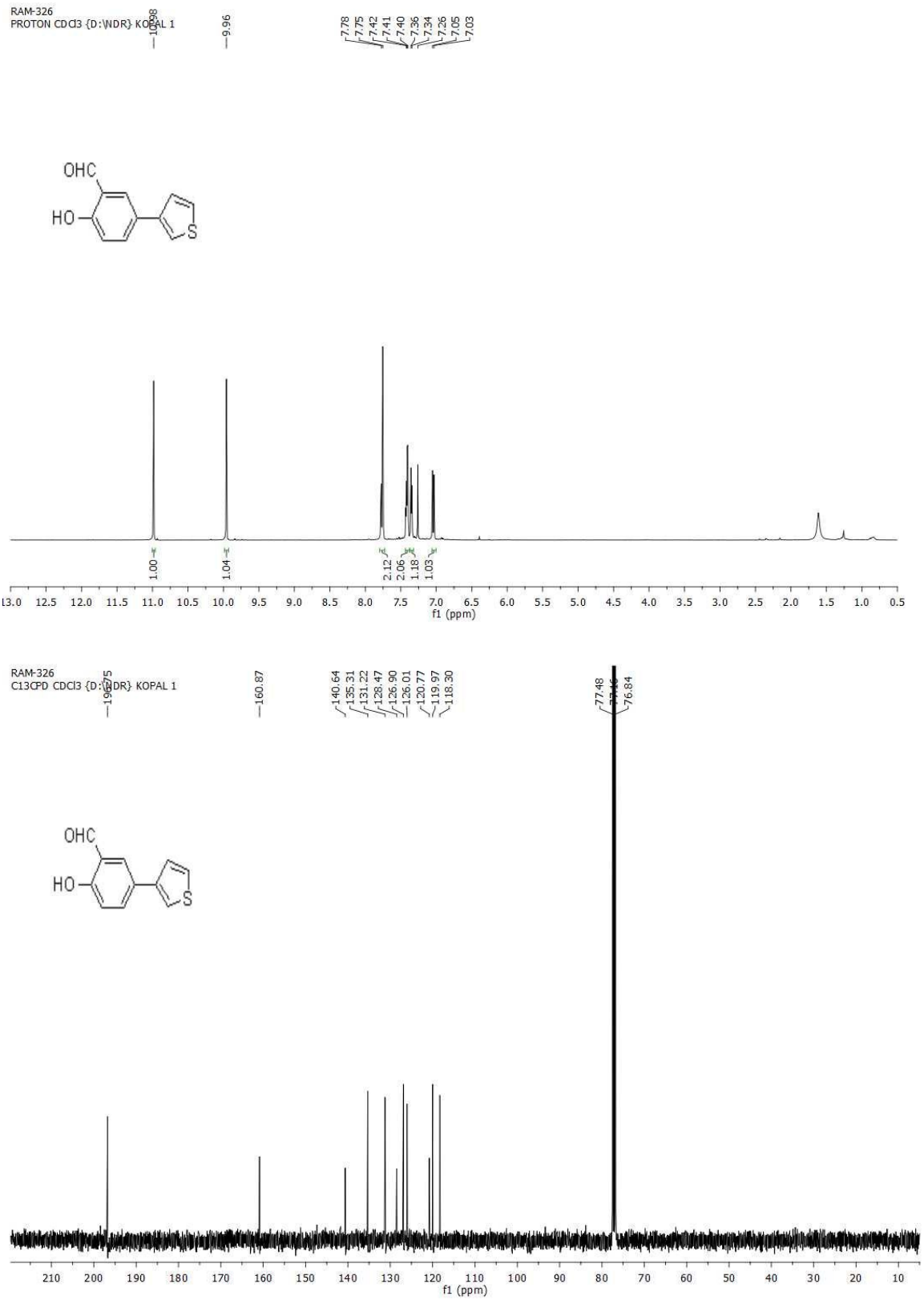


Figure S10. ^{1}H and ^{13}C NMR spectrum of 2-hydroxy-5-(thiophen-3-yl)benzaldehyde in $CDCl_3$.

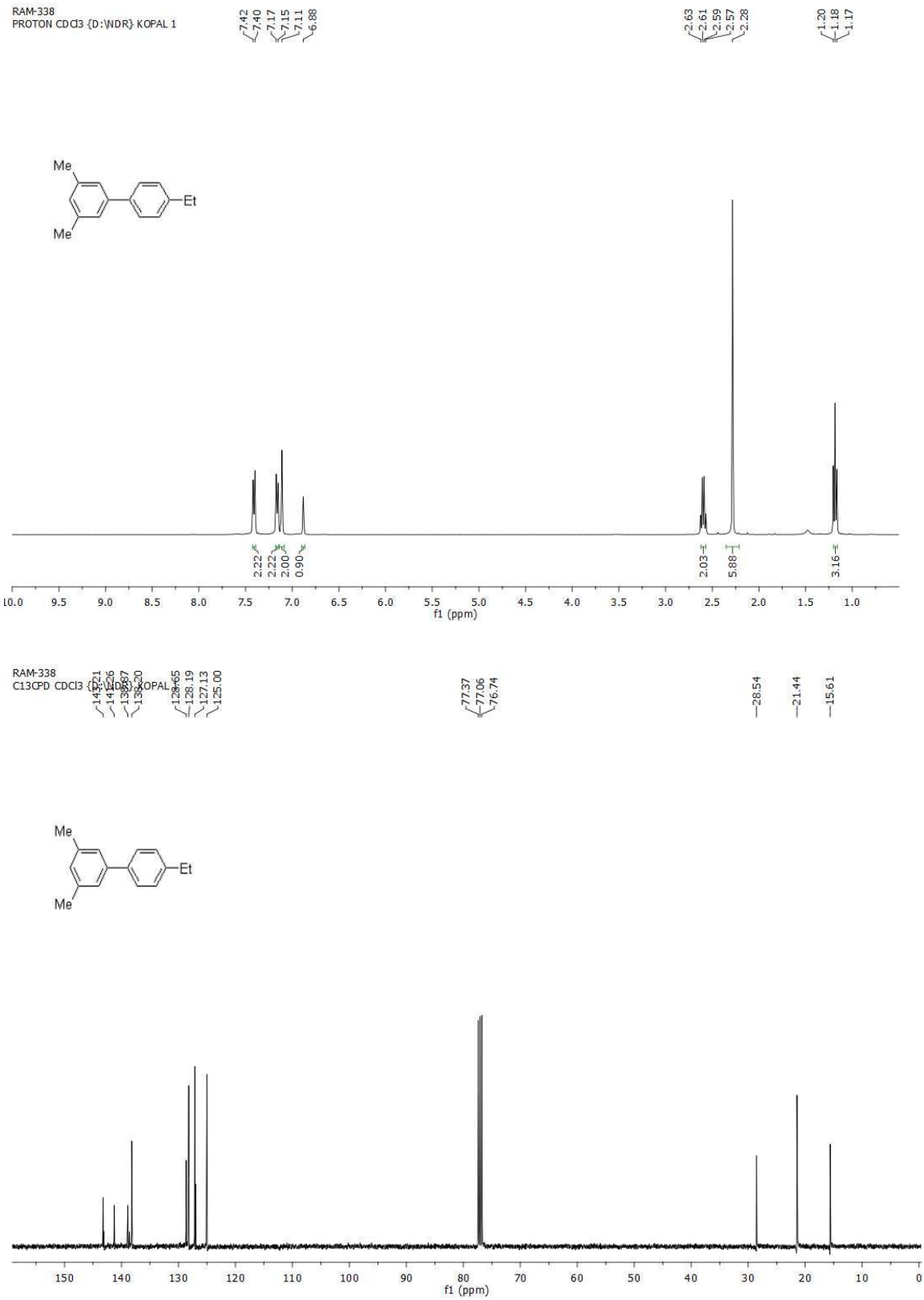


Figure S11. ^{1}H and ^{13}C NMR spectrum of 4'-ethyl-3,5-dimethyl-1,1'-biphenyl in $CDCl_3$.

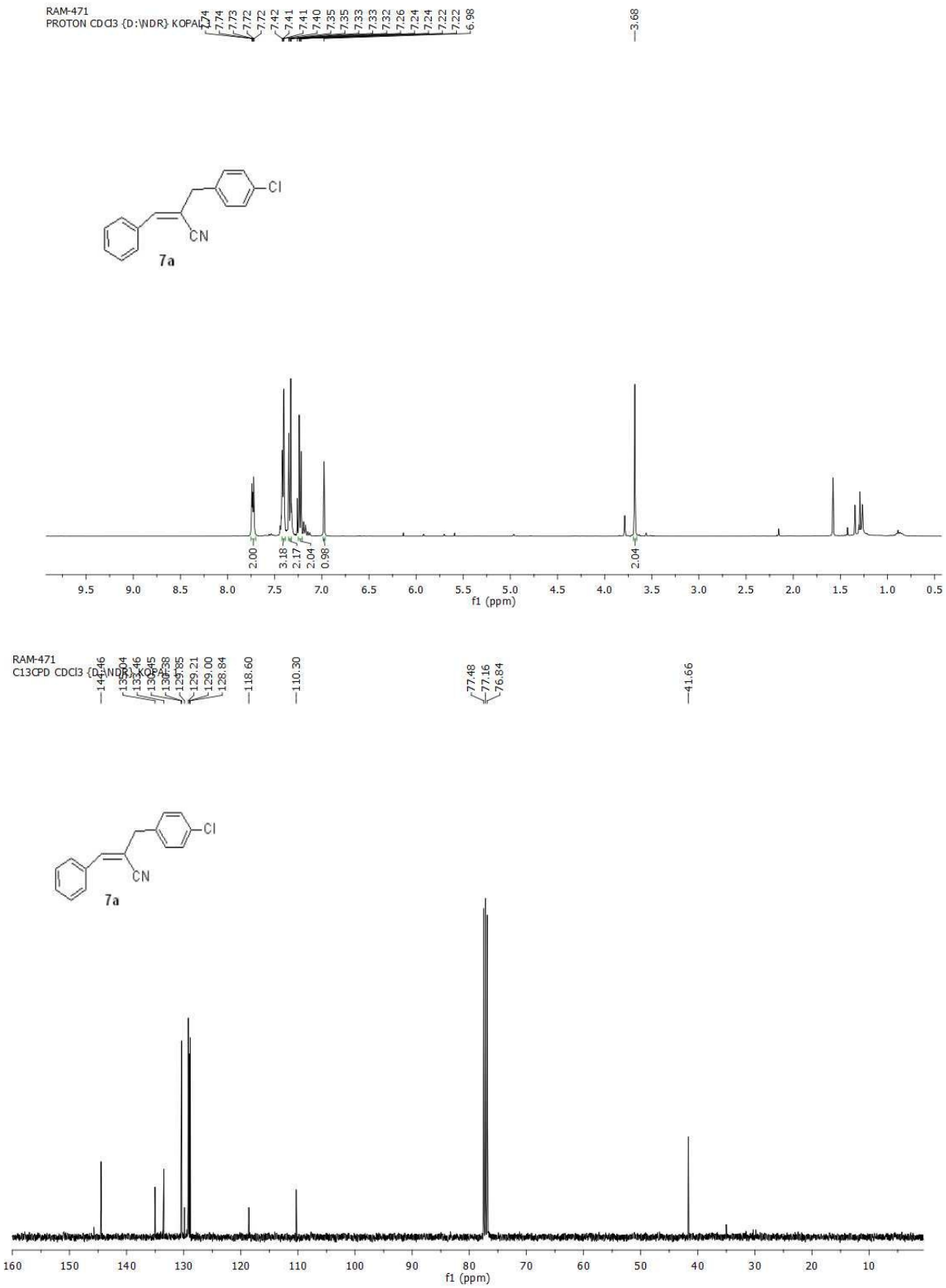
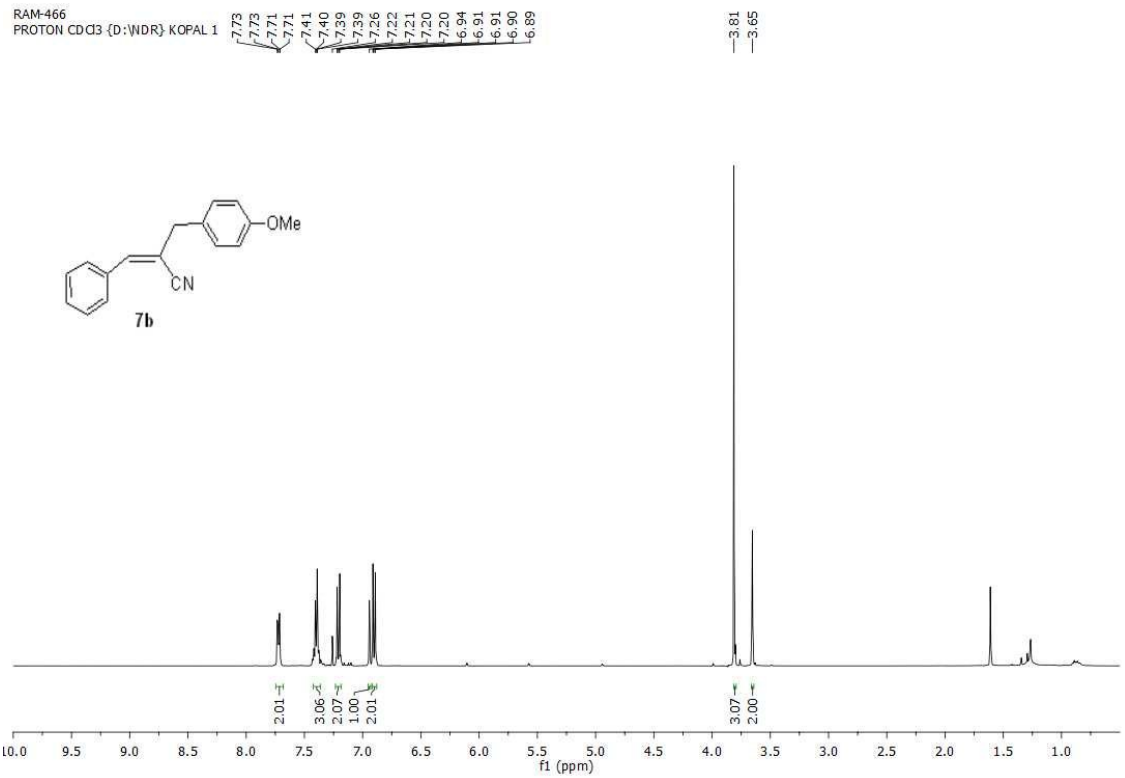


Figure S12. ^{1}H and ^{13}C NMR spectrum of 2-(4-chlorobenzyl)-3-phenylacrylonitrile (**7a**) in $CDCl_3$.



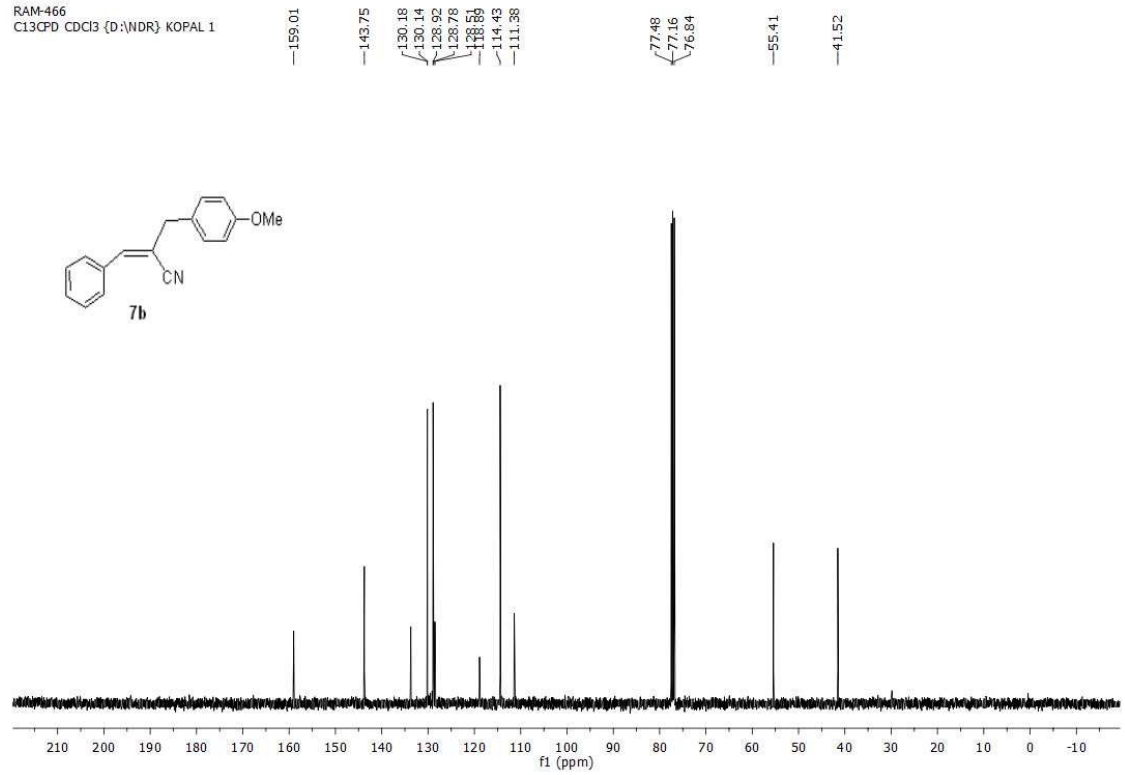


Figure S13. ^{1}H and ^{13}C NMR spectrum of 2-(4-methoxybenzyl)-3-phenylacrylonitrile (**7b**) in $CDCl_3$.

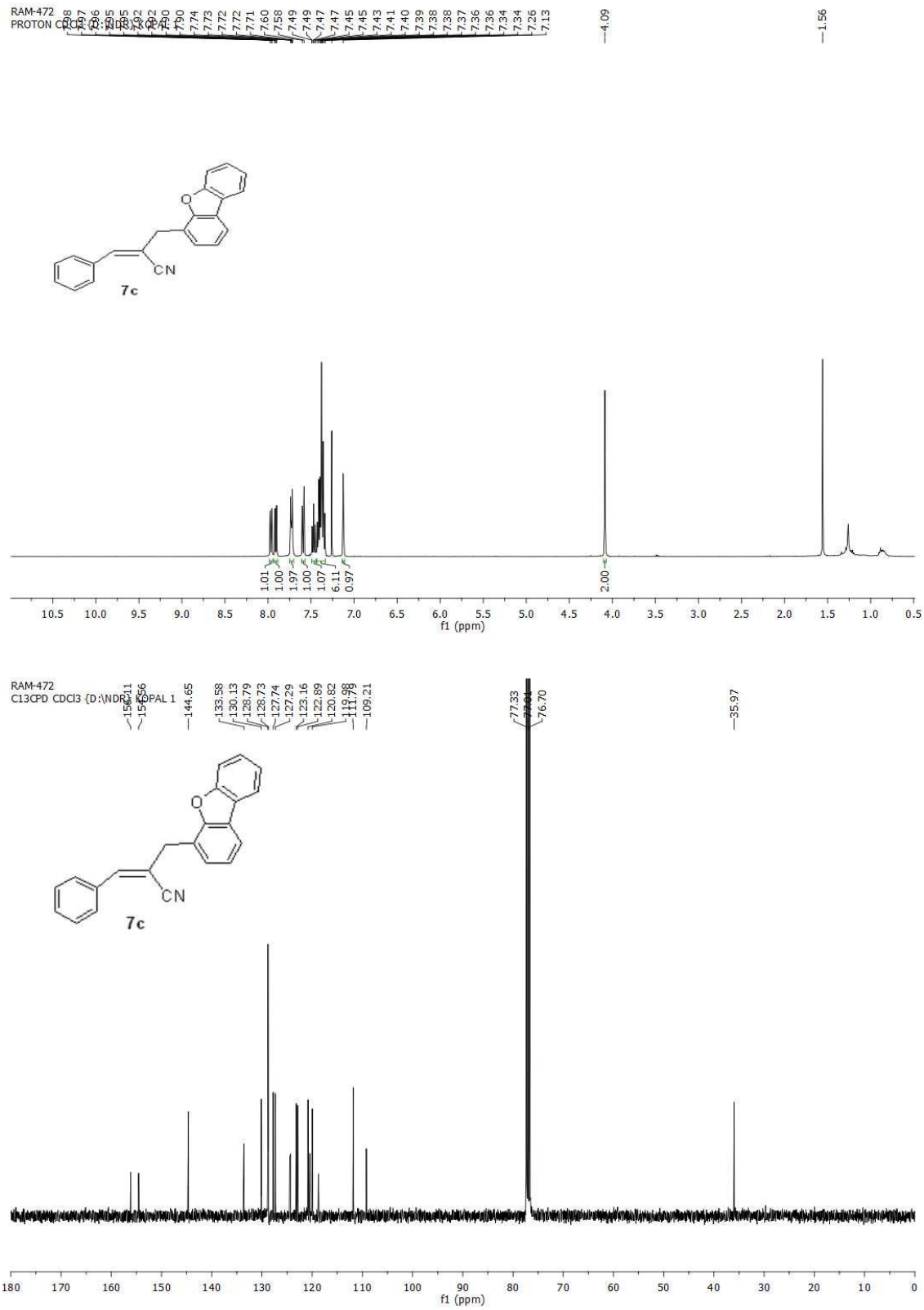


Figure S14. ^{1}H and ^{13}C NMR spectrum of 2-(dibenzo[b,d]furan-4-ylmethyl)-3-phenylacrylonitrile (**7c**) in $CDCl_3$.

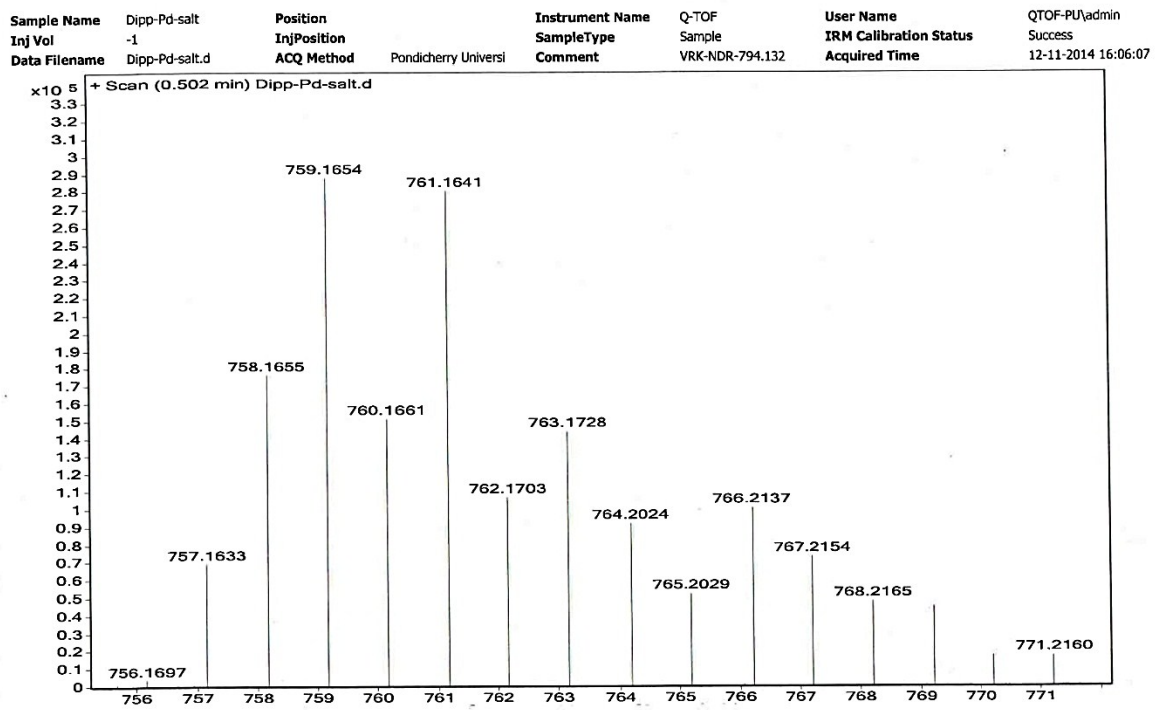


Figure S15. ES-MS spectrum showing isotopic distribution pattern for $[M - Cl]^+$ of $C_{41}H_{39}Cl_2N_4PPd$ (**I**)

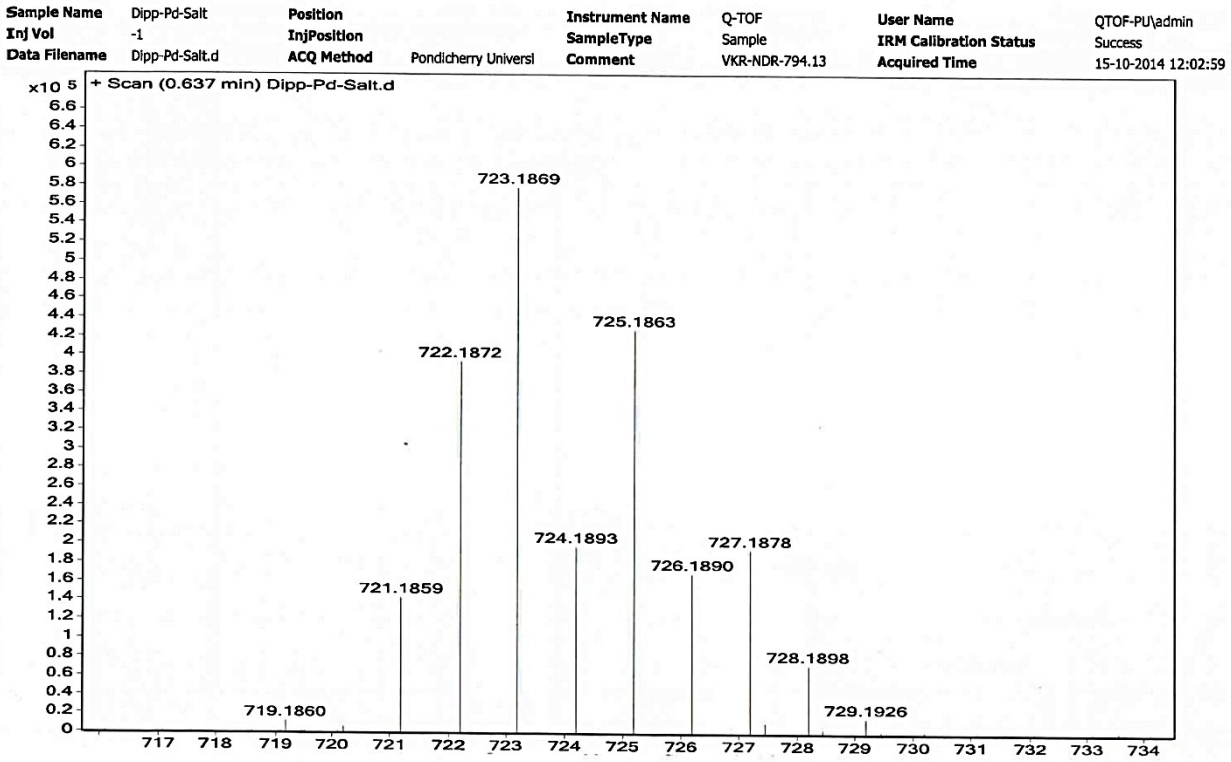


Figure S16. ES-MS spectrum showing isotopic distribution pattern for $[M - 2Cl - H]^+$ of $C_{41}H_{39}Cl_2N_4PPd$ (**I**)

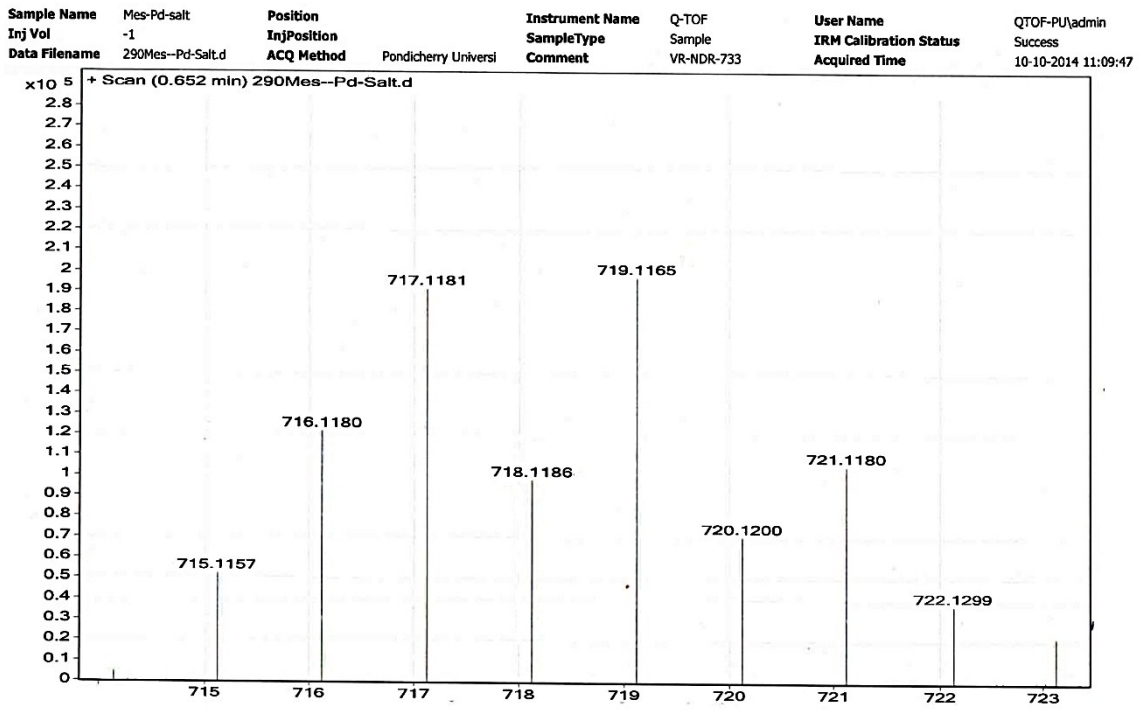


Figure S17. ES-MS spectrum showing isotopic distribution pattern for $[M - Cl]^+$ of $C_{38}H_{33}Cl_2N_4PPd$ (**II**)

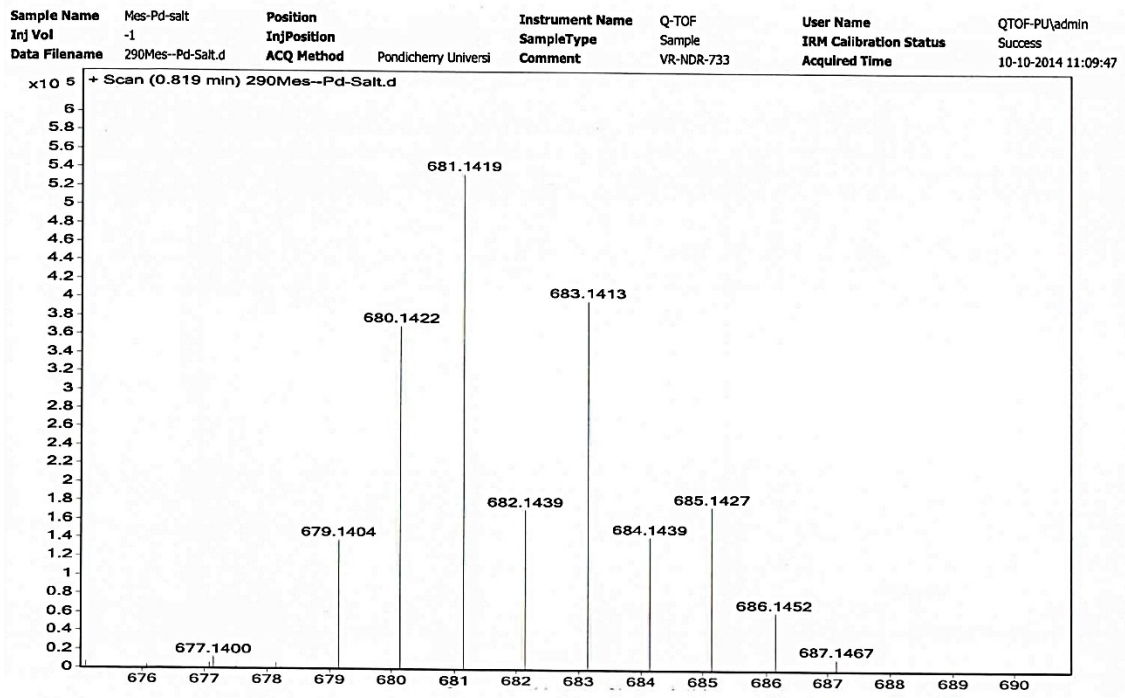


Figure S18. ES-MS spectrum showing isotopic distribution pattern for $[M - 2Cl - H]^+$ of $C_{38}H_{33}Cl_2N_4PPd$ (**II**)

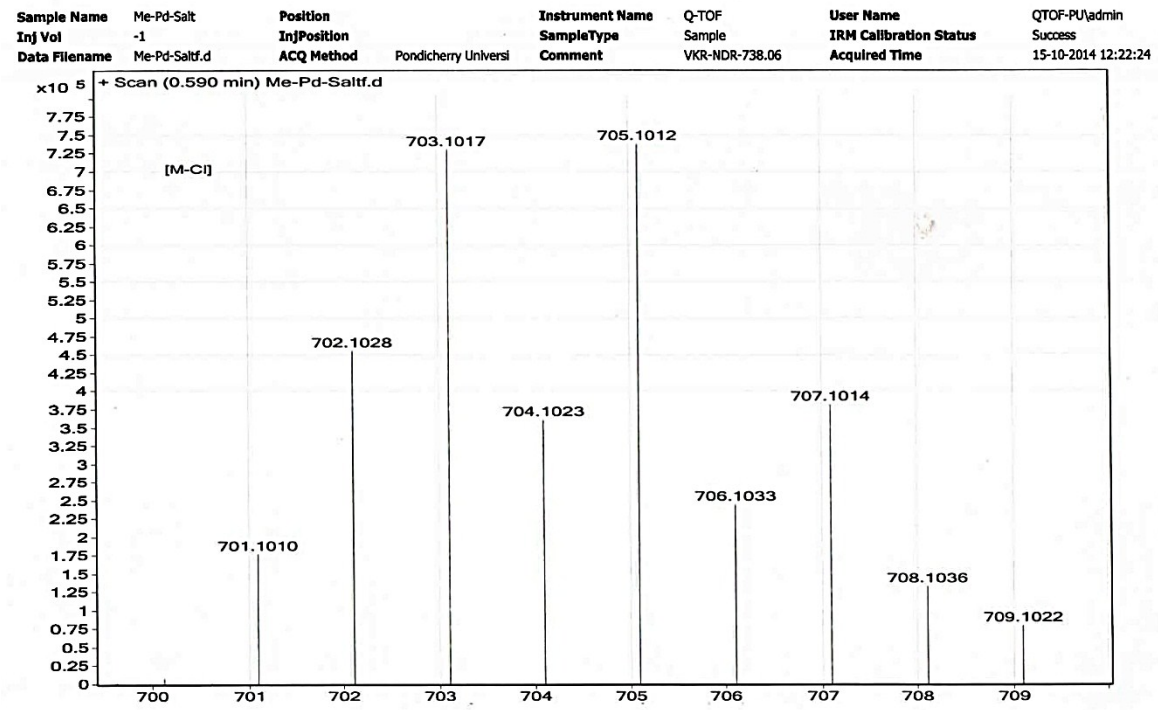


Figure S19. ES-MS spectrum showing isotopic distribution pattern for $[M - Cl]^+$ of $C_{37}H_{31}Cl_2N_4PPd$ (**V**)

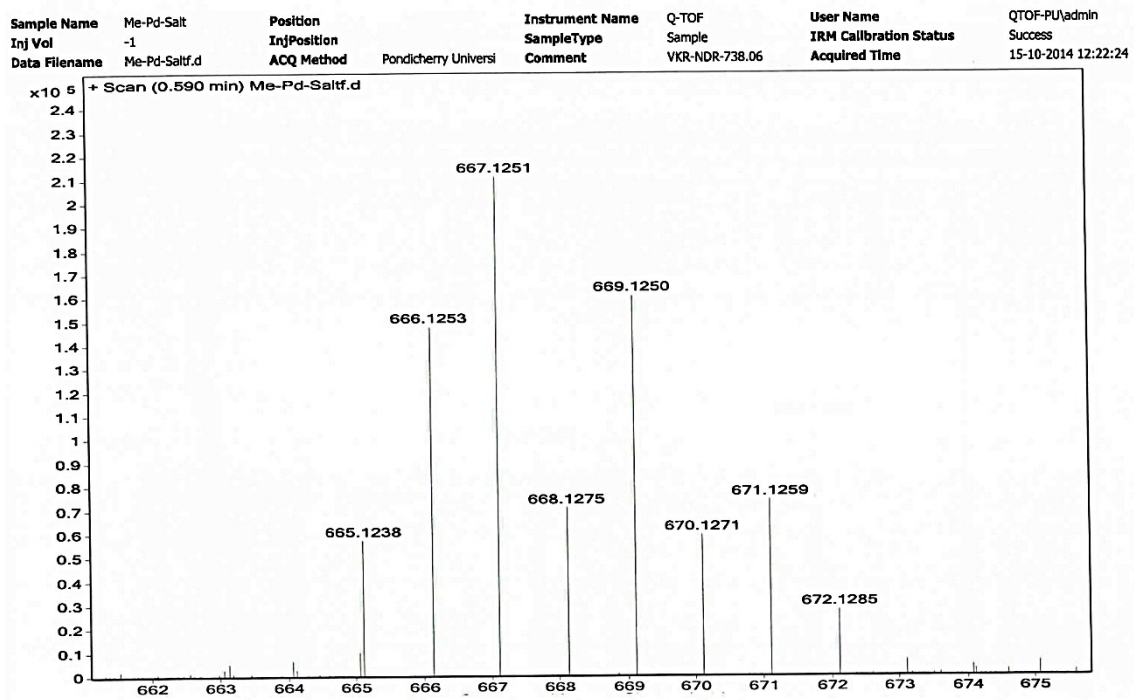


Figure S20. ES-MS spectrum showing isotopic distribution pattern for $[M - 2Cl - H]^+$ of $C_{37}H_{31}Cl_2N_4PPd$ (**V**)

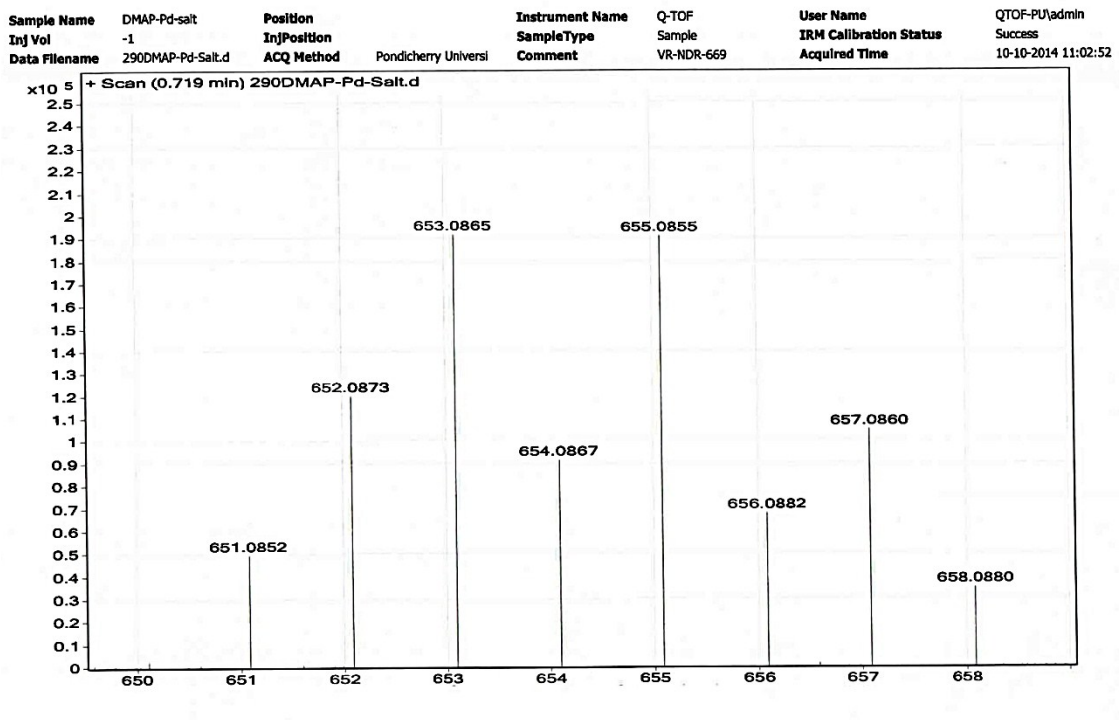


Figure S21. ES-MS spectrum showing isotopic distribution pattern for $[M - Cl]^+$ of $C_{33}H_{29}Cl_2N_4PPd$ (**VI**)

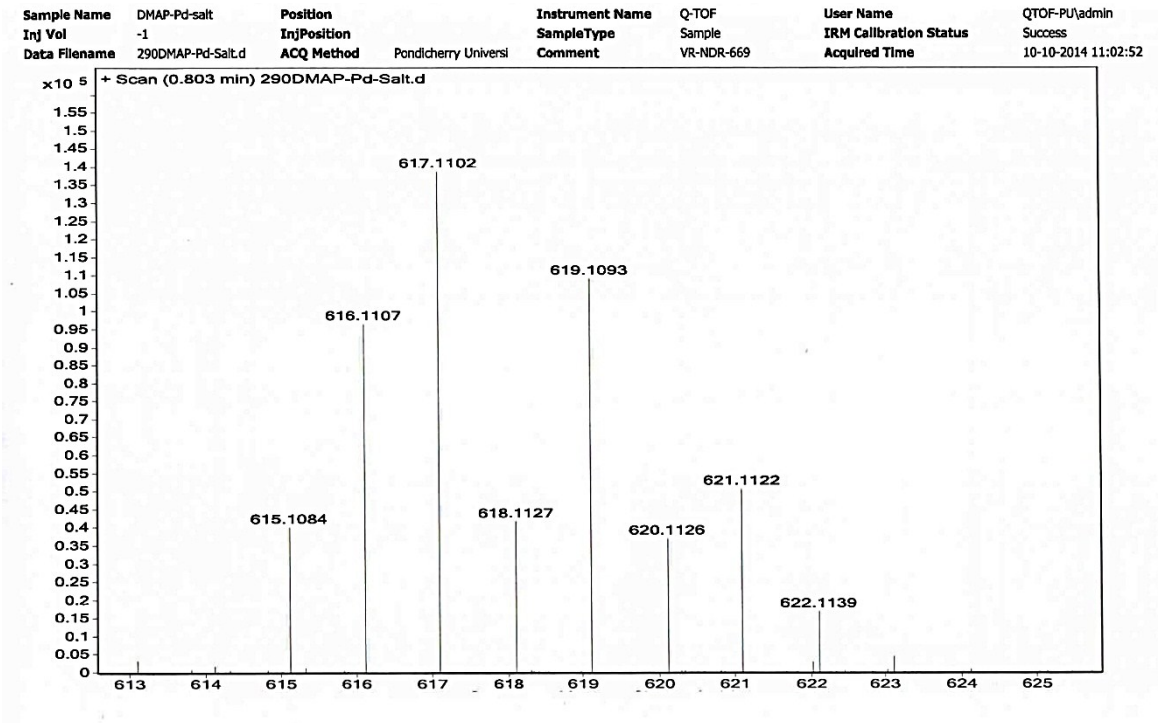


Figure S22. ES-MS spectrum showing isotopic distribution pattern for $[M - 2Cl - H]^+$ of $C_{33}H_{29}Cl_2N_4PPd$ (**VI**)

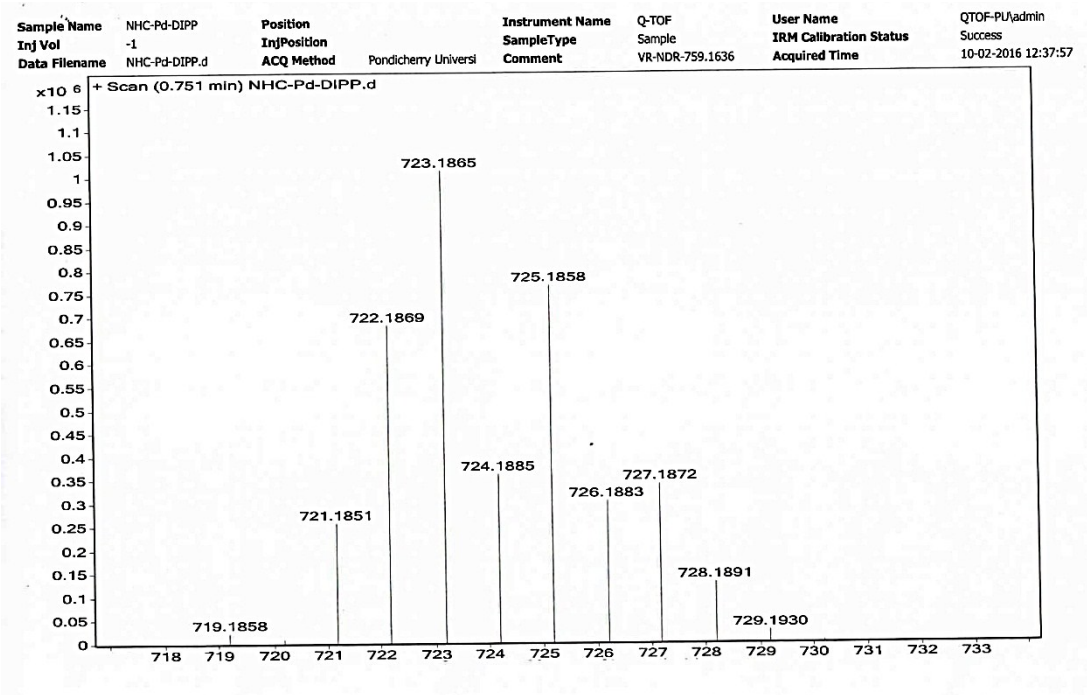


Figure S23. ES-MS spectrum showing isotopic distribution pattern for $[M - Cl]^+$ of $C_{41}H_{38}ClN_4PPd$ (**III**)

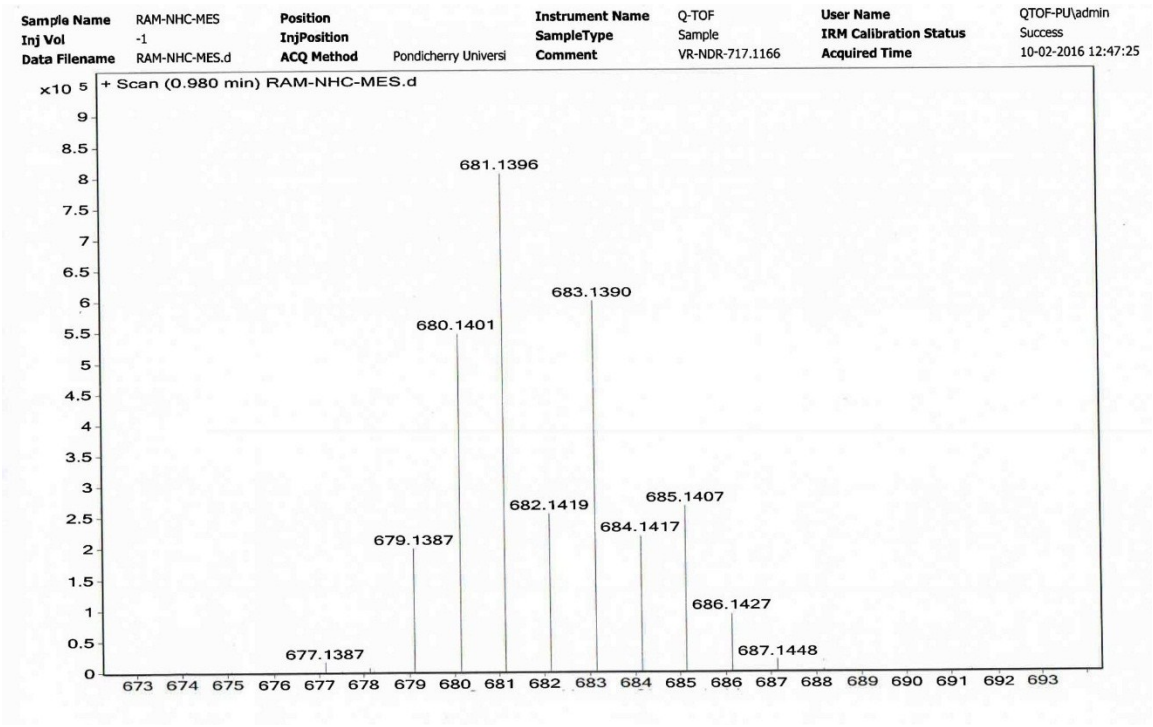


Figure S24. ES-MS spectrum showing isotopic distribution pattern for $[M - Cl]^+$ of $C_{38}H_{32}ClN_4PPd$ (**IV**)