a- General preparation of N-substituted benzimidazole (A-C)

To a solution of 5,6-dimethylbenzimidazole (3 mmol, 4.38 g) dissolved in 25 mL EtOH, (4 mmol, 2.5 g), KOH was added and the reaction mixture was stirred for 15 min at room temperature. The corresponding aryl chlorides or bromides (3 mmol) were added slowly and the resulting mixture was stirred at room temperature for 1 h and then heated for 8 h at 50°C, after it was heated under reflux for 16 h. Solution was cooled to room temperature and the solvent was removed under reduced pressure. The yellow solid that formed was resolved with DCM (40 mL) and filtered. DCM was evaporated and the isolated product was characterized by NMR spectroscopy.

1-(3, 5-dimethylbenzyl)-5, 6-dimethylbenzimidazole (A)
Yield: 95 %; m.p. 138 °C; FT-IR (KBr) ν, cm⁻¹: 1611 (C=N); 1226 (C-N).

¹H NMR (DMSO-d₆, 400 MHz) δ (ppm): 8.20 (s, 1H, H2); 7.42 (s, 1H, H4); 7.25 (s, 1H, H7); 6.89 (s, 1H, H5′); 6.86 (s, 2H, H3′,7′); 5.33 (s, 2H, H1′); 2.27 (s, 6H, Ha,b); 2.20 (s, 6H, Hc,d).

¹³C NMR (DMSO-d₆, 100 MHz) (δ (ppm)): 143.37 (C2, NCN); 142.17 126.93 (C4', 6', arom.Cq); 137.71 (C2', arom.Cq); 137.07 (C9, arom.Cq); 132.31 (C6, arom.Cq); 130.97 (C8, arom.Cq); 129.87 (C5, arom.Cq); 129.05 (C5', arom.CH); 124.86 (C3', γ, arom. CH); 119.50 (C4, arom. CH); 110.55 (C7, arom. CH); 47.42 (C1', CH2); 20.86 (C, a,b,2×CH3); 20.12 (C, a,b, 2×CH3).

1-(4-methylbenzyl)-5, 6-dimethylbenzimidazole (B)
Yield: 98 %; m.p. = 118 °C; FT-IR (KBr) ν, cm⁻¹: 1684 (C=N); 1285 (C-N).

¹H NMR (CDCl₃, 300 MHz) δ (ppm): 7.83 (s, 1H, H2, NCHN); 7.58 (s, 1H, H4, arom. CH); 7.12 (s, 2H, H3', γ, arom. CH); 7.07 (s, 2H, H4', 6', arom. CH); 7.05 (s, 1H, H7, arom. CH); 5.26 (s, 2H, H1', CH2); 2.36 (s, 3H, H₈,CH₃); 2.33 (s, 6H, Hₐ,b, 2×CH₃).

¹³C NMR (DMSO-d₆, 100 MHz) δ (ppm): 149.85 (C2, NCN); 143.11 (C9, arom.Cq); 142.18 (C5', arom.Cq); 134.23 (C2', arom.Cq); 132.25 (C6, arom.Cq); 130.96 (C8, arom.Cq); 129.85 (C5, arom.Cq); 126.93 (C4', 6', arom.CH); 125.39 (C3', γ, arom. CH); 119.49 (C4, arom. CH); 110.53 (C7, arom. CH); 47.03 (C1', CH2); 31.01 (C, c, 2×CH₃).

1-(4-tertbutylbenzyl)-5, 6-dimethylbenzimidazole (C)
Yield: 92 %; m.p. = 170 °C; FT-IR (KBr) v, cm\(^{-1}\): 1717 (C=N); 1271 (C-N); \(^1\)H NMR (DMSO-d6, 400 MHz) \(\delta\) (ppm): 8.23 (s, 1H, H2CHN); 7.42-7.41 (d, 2H, H4, 6', arom. CH); 7.33-7.31 (d, 2H, H3, 7', arom. CH); 7.18 (s, 2H, H4, 7', arom. CH); 5.39-5.37 (d, 2H, H1', CH2); 2.37; 2.28 (s, 6H, Ha, b, 2×CH3); 1.23 (s, 9H, Ha, b, c, d, e, 3×CH3); 13C NMR (DMSO-d6, 100 MHz) (\(\delta\) (ppm)): 150.03 (C2, NCN); 143.28 (C5', arom.Cq); 142.18 (C9, arom.Cq); 134.29 (C2', arom.Cq); 132.25 (C6, arom.Cq); 130.96 (C8, arom.Cq); 129.87 (C5, arom.Cq); 126.93 (C4', 6', arom.CH); 125.39 (C3', 7', arom. CH); 119.49 (C4, arom. CH); 110.57 (C7, arom. CH); 47.09 (C1', CH2); 34.20 (C(CH3)3, Cq); 31.05 (Cc, d, e, 3×CH3); 20.11 (Ca, b, 2×CH3).

**b- General preparation of Benzimidazolium salts (2a-e)**

To a solution of 5, 6-dimethylbenzimidazole (3 mmol, 4.38 g) resolved in 25 mL EtOH, (4 mmol, 2.5 g), KOH was added and the reaction mixture was stirred for 15 min at room temperature. The corresponding aryl chlorides or bromides (3 mmol) were added slowly and the resulting mixture was stirred at room temperature for 1h and then heated for 8h at 50°C, after it was heated under reflux for 16h. Solution was cooled to room temperature and the solvent was removed under reduced pressure. The yellow solid that formed was resolved with DCM (40 mL) and filtered. DCM was evaporated and the isolated product was characterized by NMR spectroscopy. A mixture of crude product (1g) and corresponding aryl chlorides or bromides in DMF (2 mL) was stirred and heated at 70°C for 48h. The white solid that formed was washed with diethyl ether (30 mL), filtrated and dried under vacuum.

**1-(3,5-dimethylbenzyl)-3-(4-tet-buthylbenzyl)-5,6-dimethylbenzimidazolium bromide (2a)**

Yield: 90 %; m.p.232°C; FT-IR (KBr) v, cm\(^{-1}\): 1566 (C= N); 1357 (C-N); \(^1\)H NMR (CDCl3, 300 MHz) \(\delta\) (ppm): 11.58 (s, 1H, H2CHN); 7.44 (d, 2H, H4, 6', arom. CH, \(3J_{HH}=7.43\) Hz); 7.37 (s, 1H, H3', arom. CH); 7.35 (d, 2H, H5, 7', arom. CH, \(3J_{HH}=7.34\) Hz); 7.27 (s, 1H, H3', arom. CH); 7.01 (s, 2H, H4, 7', arom. CH); 6.94 (s, 1H, H4, 7', arom. CH); 5.76 (s, 2H, H1',CH2); 5.67 (s, 2H, H1',CH2); 2.32 (s, 6H, Ha,b, 2×CH3); 2.26 (s, 6H, Hc,d, 2×CH3); 1.25 (s, 9H, Hx, f, g, 3×CH3); \(^13\)C NMR (CDCl3, 75 MHz) (\(\delta\) (ppm)): 152.81 (C2, NCN); 142.37 (C4', 6', arom.Cq); 139.59 (C2', arom.Cq); 137.84 (C3', arom. CH); 133.11 (C2', arom.Cq); 131.35 (C5, 6, arom.Cq); 130.45 (C8, 9, arom.Cq); 128.53
(C₄, 6', arom. CH); 126.77 (C₃', 5', 7', arom. CH); 126.23 (C₃, 7', arom. CH); 113.82 (C₄, 7, arom. CH); 51.80 (C₁', CH₂); 51.43 (C₁', CH₂); 35.17 (C₂, d, 2×CH₃); 31.70 (C₃, CH₃); 21.75 (C₅, b, 2×CH₃); 21.22 (C₆, g, 2×CH₃). Anal. Calc. for C₂₉H₃₅N₂Br: C, 70.866%; H, 7.178%; N, 5.700%. Found: C, 70.9; H, 7.2; N, 5.8%.

1-(3,5-dimethylbenzyl)-3-(2,3,5,6-tetramethylbenzyl)-5,6-dimethyl benzimidazolium chloride (2b)

Yield: 92%; m.p = 244°C; FT-IR (KBr) ν, cm⁻¹: 1547 (C=N); 1193 (C-N); 1H NMR (CDCl₃, 300 MHz) δ (ppm): 11.17 (s, 1H, H₂, NCHN); 7.24 (s, 2H, H₃, 7’, arom. CH); 7.07 (s, 1H, H₅, arom. CH); 6.98 (s, 1H, H₆, arom. CH); 6.91 (s, 2H, H₄, 7, arom. CH); 5.83 (s, 2H, H₁', CH₂); 5.77 (s, 2H, H₁', CH₂); 2.31 (s, 3H, H₆, CH₃); 2.26 (s, 3H, H₇, CH₃); 2.25 (s, 18H, H₈, d, e, f, g, b, 6×CH₃); 13C NMR (CDCl₃, 75 MHz) (δ (ppm)): 142.95 (C₂, NCN); 139.42 (C₂', 6, arom.Cq); 137.48 (C₄, 6', arom.Cq); 135.58 (C₂', arom.Cq); 134.61 (C₄, 6', arom.Cq); 134.02 (C₅, 6, arom.Cq); 133.71 (C₃', 7', arom.Cq); 131.08 (C₈, 9, arom.Cq); 130.68 (C₃', arom. CH); 128.47 (C₃', 7', arom. CH); 125.97 (C₅', arom. CH); 113.79 (C₄, 7', arom. CH); 51.75 (C₁', CH₂); 48.08 (C₁', CH₂); 21.77 (C₅, d, 2×CH₃); 21.34 (C₅, g, 2×CH₃); 21.11 (C₅, b, 2×CH₃); 16.68 (C₆, h, 2×CH₃); Anal. Calc. for C₂₉H₃₅N₂Cl: C, 77.912%; H, 7.891%; N, 6.266%. Found: C, 77.9; H, 7.9; N, 6.4%.

1-(3,5-dimethylbenzyl)-3-(4-methylbenzyl)-5,6-dimethyl benzimidazolium bromide (2c)

Yield: 93%; m.p. 256°C; FT-IR (KBr) ν, cm⁻¹: 1566 (C=N); 1357 (C-N); 1H NMR (CDCl₃, 300 MHz) δ (ppm): 11.54 (s, 1H, H₂, NCHN); 7.34 – 7.32 (d, 2H, H₄, 6, arom. CH); 7.26 – 7.22 (d, 2H, H₃, 7, arom. CH); 7.12 – 7.09 (d, 2H, H₅, 7, arom. CH); 6.96 (s, 2H, H₄, 7, arom. CH); 6.90 (s, 1H, H₆, arom. CH); 5.72 (s, 2H, H₁, CH₂); 5.63 (s, 2H, H₁, CH₂); 2.28 (s, 6H, H₆, b, 2×CH₃); 2.26 (s, 3H, H₆, CH₃); 2.23 (s, 6H, H₇,d, 2×CH₃); 13C NMR (CDCl₃, 75 MHz) (δ (ppm)): 141.86 (C₂, NCN); 139.24 (C₄, 6, arom.Cq); 139.20 (C₂', arom.Cq); 137.41 (C₅', arom.Cq); 132.70 (C₂', arom.Cq); 130.95 (C₅, 6, arom.Cq); 130.09 (C₈, 9, arom.Cq); 130.01 (C₄, 6, arom. CH); 128.34 (C₃, 5, 7, arom. CH); 125.83 (C₃, 7, arom. CH); 113.39 (C₄, 7, arom. CH); 51.43 (C₁', CH₂); 51.25 (C₁, CH₂); 21.35 (C₆, d, 2×CH₃); 21.28 (C₆, CH₃); 20.80 (C₆, b, 2×CH₃); Anal. Calc. for C₂₉H₂₉N₂Br: C, 69.484%; H, 6.504%; N, 6.233%. Found: C, 69.8; H, 6.5; N, 6.4%.

1, 3-Bis (4-ter-buthylbenzyl)-5, 6-dimethyl benzimidazolium bromide (2d)
Yield: 96%; m.p. 270°C; FT-IR (KBr) ν, cm⁻¹: 1670 (C=N); 1388 (C-N); ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 11.63 (s, 1H, NCHN); 7.14 (m, 4H, H₄, 6', 4', 6'; arom. CH, J_HH = 6 Hz); 7.38 (m, 4H, H₃, 7', 3', 7', arom. CH, J_HH = 9MHz); 7.31 (s, 2H, H₄, 7, arom. CH); 5.74 (s, 4H, 2H₁', 2'CH₂); 2.94 (s, 3H, H₃, CH₃); 2.87 (s, 3H, H₅, CH₃); 2.33 (s, 6H, H_a,b, 2×CH₃); 1.25 (s, 12H, H_c, e, f, h, 4×CH₃); ¹³C NMR (CDCl₃, 75 MHz) (δ (ppm)): 163.06 (C₂, NCN); 152.82 (C₅', 5'', arom.Cq); 142.31 (C₂', 2'', arom.Cq); 137.82 (C₅, 6, arom.Cq); 130.35 (C₈, 9, arom.Cq); 128.52 (C₄', 6', 4', 6'; arom. CH); 126.81 (C₃', 7', 3', 7'; arom. CH); 113.80 (C₄, 7, arom. CH); 51.49 (C₁', 1'', 2×CH₂); 35.18 (C₁', 1'', 2×CH₂); Anal. Calc. for C₃₁H₃₉N₂Br: C, 71.663%; H, 7.566%; N, 5.392%; Found: C, 71.7; H, 7.6; N, 5.4%.

1, 3-Bis (4-methylbenzyl) - 5, 6-dimethyl benzimidazolium bromide (2e):

Yield: 89%; m.p. 268 °C; FT-IR (KBr) ν, cm⁻¹: 1559 (C=N); 1357 (C-N); ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 11.57 (s, 1H, NCHN); 7.36-7.33 (d, 4H, H₄', 6', 4'', 6''; arom. CH); 7.28 (s, 2H, H₄, 7, arom. CH); 7.14-7.12 (d, 4H, H₃, 7', 3', 7'; arom. CH); 5.72 (s, 4H, 2H₁', 2'CH₂); 2.30 (s, 6H, H_a,b, 2×CH₃); 2.28 (s, 6H, H_c,d, 2×CH₃). ¹³C NMR (CDCl₃, 75 MHz) (δ (ppm)): 141.66 (C₂, NCN); 139.16 (C₅', 5'', arom.Cq); 137.40 (C₂', 2'', arom.Cq); 130.04 (C₄', 6', 4', 6''); arom. CH); 129.92 (C₅, 6, arom.Cq); 129.88 (C₈, 9, arom.Cq); 128.23 (C₃', 7', 3', 7'; arom. CH); 113.38 (C₄, 7, arom. CH); 51.15 (C₁', 1'', 2×CH₂); 21.26 (C_c, d, 2×CH₂); 20.76 (C_a, b, 2×CH₃); Anal. Calc. for C₂₅H₂₇N₂Br: C, 68.964%; H, 6.250%; N, 6.434%; Found: C, 68.9; H, 6.4; N, 6.5%.

c- General preparation of PEPPSI complexes (3a – e)

A Schlenk was charged with 5,6-dimethylbenzimidazolium salts (1 mmol), PdCl₂ (0.5 mmol; 0.09g), K₂CO₃ (0.6g) and a stir bar under argon. Dried THF (25 ml) was then added as a solvent. The mixture was heated under reflux and stirred for 24h at 100°C. After completion, the reaction mixture was cooled at r.t and the solvents were removed under vacuum. The solid formed was solved in DCM and purified by flash column, eluting with DCM until the product was completely recovered. DCM was removed under reduce pressure and the white solid was characterized by NMR spectroscopy. Further purification was done using recrystallization (DCM - Hexane) to get pure complexes for analysis and catalysis.

Dichloro[1-(3,5-dimethylbenzyl)-3-(4-tert-buthylbenzyl)-5, 6-dimethylbenzimidazole-2-ylidene] pyridine palladium (II)(3a)
Yield: 96 %; m.p. 204 °C; FT-IR (KBr) ν, cm⁻¹:1613 (C-N); ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 8.99 (dd, 2H, H₂α, H₂β, arom. CH, ¹JHH = 3 MHz); 7.77 (s, 1H, H₄α, arom. CH); 7.55 (d, 2H, H₃α, 5α, arom. CH, ¹JHH = 6 MHz); 7.31 (m, 2H, H₄α, 6α, arom. CH, ¹JHH = 7.5 MHz); 7.40 (d, 4H, H₃β, 7β, arom. CH, ¹JHH = 9 MHz); 7.30 (m, 2H, H₃β, 5β, arom. CH, ¹JHH = 6 MHz); 6.93 (s, 1H, H₅α, arom. CH); 6.86 (s, 2H, H₆α, arom. CH); 6.16 - 6.13 (s, 2H, H₁τ, CH₂); 6.07 (s, 2H, H₁′, CH₂); 2.30 (s, 6H, H₂a, 2×CH₃); 1.40 (s, 6H, H₂b, 3×CH₃); ¹³C NMR (CDCl₃, 75 MHz) (δ (ppm)): 162.47 (C₂, NCN); 153.20 (C₂α, 6α, arom. CH); 152.6 (C₈, 9, arom.Cq); 151.87 (C₄α, 6α, arom.Cq); 151.43 (C₄β, arom. CH); 138.85 (C₅α, arom.Cq); 138.45 (C₅β, arom.Cq); 135.76 (C₂β, arom.Cq); 133.79 (C₃α, arom. CH); 132.78 (C₃β, 7α, arom. CH); 130.20 (C₄α, 6α, arom. CH); 128.23 (C₃β, 7α, arom. CH); 126.25 (C₅, 6, arom.Cq); 124.99 (C₃β, 5α, arom. CH); 112.12 (C₄, 7, arom. CH); 53.48 (C₁′, 2×CH₂); 35.12 (C₄, 2×CH₂); 31.88 (C₄, CH₃); 21.85 (C₂a, 2×CH₂); 20.79 (C₂b, 2×CH₂); Anal. Calc. for C₃H₄₀N₃PdCl₂: C, 61.130%; H, 6.035%; N, 6.290%. Found: C, 61.2; H, 6.1; N, 6.3%.

**Dichloro[I-(3, 5-dimethylbenzyl)-3-(2, 3, 5, 6-tetramethylbenzyl)-5, 6-dimethylbenzimidazol-2-ylidene] pyridine palladium (II)(3b)**

Yield: 95 %; m.p. 200 °C; FT-IR (KBr) ν, cm⁻¹:1597 (C-N); ¹H NMR (CDCl₃, 300 MHz) δ (ppm): 8.90 (d, 2H, H₂α, 6α, arom. CH, ¹JHH = 3 MHz); 7.75 (m, 1H, H₄α, arom. CH, ¹JHH = 7.5 MHz); 7.30 (m, 2H, H₃α, 5α, arom. CH, ¹JHH = 7.5 MHz); 7.26 (s, 1H, H₅α, arom. CH); 7.22 (s, 2H, H₆α, arom. CH); 7.08 (s, 1H, H₅β, arom. CH); 6.92 (s, 1H, H₇α, arom. CH); 6.86 (s, 1H, H₇β, arom. CH); 6.21 (s, 2H, H₁′, CH₂); 6.08 (s, 2H, H₁τ, CH₂); 2.29 (s, 12H, H₂α, H₂β, 4×CH₃); 2.26 (s, 6H, H₂a, 2×CH₃); 2.19 (s, 3H, H₄, CH₃); 2.06 (s, 3H, H₆, CH₃); ¹³C NMR (CDCl₃, 75 MHz) (δ (ppm)): 162.14 (C₁, NCN); 151.38 (C₂α, 6α, arom. CH); 138.36 (C₈, 9, arom.Cq); 138.03 (C₄α, arom.Cq); 135.52 (C₄β, arom.Cq); 135.21 (C₄, arom. CH); 134.33 (C₂β, arom.Cq); 133.77 (C₄α, 6α, arom.Cq); 133.23 (C₃α, 7α, arom. CH); 132.39 (C₅α, arom. CH); 131.99 (C₅β, arom. CH); 131.14 (C₃β, 7α, arom. CH); 129.69 (C₅, 6, arom.Cq); 124.47 (C₃β, 5α, arom. CH); 111.46 (C₄, 7, arom. CH); 52.96 (C₁′, CH₂); 50.40 (C₁′, CH₂); 21.44 (C₂a, 2×CH₂); 20.72 (C₁β, 2×CH₂); 20.28 (C₂b, 2×CH₂); 16.70 (C₂b, 2×CH₂); Anal. Calc. for C₃H₄₀N₃PdCl₂: C, 61.130%; H, 6.035%; N, 6.290%. Found: C, 61.2; H, 6.1; N, 6.3%.

**Dichloro[I-(3, 5-dimethylbenzyl)-3-(4-methylbenzyl)-5, 6-dimethylbenzimidazol-2-ylidene] pyridine palladium (II)(3c)**
Yield: 98 %; m.p. 190 °C; FT-IR (KBr) ν, cm\(^{-1}\): 1614 (C-N), \(^1\)H NMR (CDCl\(_3\), 300 MHz) δ (ppm): 8.94 (d, 2H, H\(_3\)\(_6\), arom. CH, \(^4\)J\(_{HH} = 3\) MHz); 7.68 (s, 1H, H\(_4\)\(_6\), arom. CH); 7.47 (d, 2H, H\(_3\)\(_7\), arom. CH, \(^4\)J\(_{HH} = 9\) MHz); 7.26 (s, 2H, H\(_3\)\(_7\), arom. CH); 7.20 (s, 2H, H\(_5\), arom. CH); 7.15 (d, 1H, H\(_4\), 6", arom. CH); 6.90 (s, 1H, H\(_5\), arom. CH); 6.85 (s, 2H, H\(_4\), arom. CH); 6.12 (s, 2H, H\(_1\)\(_1\), CH\(_2\)); 6.03 (s, 2H, H\(_1\)\(_1\), CH\(_2\)); 2.29 (s, 3H, H\(_e\), CH\(_3\)); 2.26 (s, 6H, H\(_{a,b}\), 2×CH\(_3\)); 2.14 (s, 6H, H\(_c\), d, 2×CH\(_3\)); \(^1\)C NMR (CDCl\(_3\), 75 MHz) (δ (ppm)): 161.88 (C\(_2\), NCN); 152.75 (C\(_2\)\(_6\), 6", arom. CH); 152.16 (C\(_8\), 9, arom. C\(_q\)); 151.42 (C\(_4\), 6", arom. C\(_q\)); 153.32 (C\(_2\), arom. C\(_q\)); 138.42 (C\(_4\), arom. CH); 137.77 (C\(_5\), arom. C\(_q\)); 129.58 (C\(_4\), 6", arom. CH); 127.98 (C\(_3\), arom. CH); 129.77 (C\(_3\), 7", arom. CH); 124.55 (C\(_3\), 5", arom. CH); 117.40 (C\(_7\), arom. CH); 53.39 (C\(_1\), CH\(_2\)); 53.11 (C\(_1\), CH\(_2\)); 21.41 (C\(_d\), 2×CH\(_3\)); 20.35 (C\(_a\), b, 2×CH\(_3\)); Anal. Calc. for C\(_3\)H\(_3\)N\(_3\)PdCl\(_2\): C, 59.483%; H, 5.475%; Found: C, 59.5; H, 5.5; N, 6.8%.

**Dichloro[I, 3-bis- (4-tert-buthylbenzyl)-5, 6-dimethylbenzimidazole-2-ylidene] pyridine palladium (II)(3d)**

Yield: 89 %; m.p. 177 °C; FT-IR (KBr) ν, cm\(^{-1}\): 1612(C-N); \(^1\)H NMR (CDCl\(_3\), 300 MHz) δ (ppm): 9.01 (s, 2H, C\(_5\)H\(_3\)N); 7.75 (m, 1H, C\(_5\)H\(_3\)N); 7.57 (d, 4H, H\(_4\), 6", 4", 6", C\(_2\)C\(_6\)H\(_3\)(CH\(_3\))\(_2\)-3,5); 7.40 (d, 4H, H\(_3\), 7", 3", 7", C\(_2\)C\(_6\)H\(_3\)(CH\(_3\))\(_2\)-3,5); 7.31 (m, 2H, H\(_3\), 5", C\(_5\)H\(_3\)N); 6.84 (s, 2H, H\(_4\), C\(_6\)H\(_2\)(CH\(_3\))\(_2\)-5,6); 6.16 (s, 4H, H\(_1\), 1", 2×CH\(_2\)); 2.10 (s, 6H, H\(_a,b\), 2×CH\(_3\)); 1.22 (s, 18H, H\(_c\), d, e, f, g, h, 6×CH\(_3\)); \(^1\)C NMR (CDCl\(_3\), 75 MHz) (δ (ppm)): 153.22 (C\(_2\), NCN); 152.64 (C\(_2\), 6", arom. CH); 151.90 (C\(_8\), 9, arom. C\(_q\)); 151.45 (C\(_4\), arom. CH); 138.38 (C\(_5\), 5", arom. C\(_q\)); 133.86 (C\(_2\), 2", arom. C\(_q\)); 132.78 (C\(_3\), 7", 3", 7", arom. CH); 128.22 (C\(_4\), 6", 4", 6", arom. CH); 126.29 (C\(_5\), 6, arom. C\(_q\)); 125.01 (C\(_3\), 5", arom. CH); 114.28 (C\(_4\), 7, arom. CH); 53.47 (C\(_1\), 1", 2×CH\(_2\)); 35.13 (C\(_d\), g, 2×CH\(_3\)); 31.89 (C\(_a\), b, 2×CH\(_3\)); 20.76 (C\(_c\), e, f, h, 4×CH\(_3\)); Anal. Calc. for C\(_3\)H\(_3\)N\(_3\)PdCl\(_2\): C, 62.028%; H, 6.507%; N, 6.028%; Found: C, 62.1; H, 6.5; N, 6.1%.

**Dichloro[I, 3-bis- (4-methylbenzyl)-5, 6-dimethylbenzimidazole-2-ylidene] pyridine palladium (II)(3e)**

Yield: 91 %; m.p. 195 °C; FT-IR (KBr) ν, cm\(^{-1}\): 1609(C-N); \(^1\)H NMR (CDCl\(_3\), 300 MHz) δ (ppm): 8.99 (s, 2H, C\(_5\)H\(_3\)N); 7.74 (s, 1H, H\(_4\), C\(_5\)H\(_3\)N); 7.50 (d, 4H, H\(_4\), 6", 4", 6", C\(_2\)C\(_6\)H\(_3\)(CH\(_3\))\(_2\)-3,5); 7.30 (m, 2H, H\(_3\), 5", C\(_5\)H\(_3\)N); 7.18 (d, 2H, H\(_3\), 7", 3", 7", C\(_2\)C\(_6\)H\(_3\)(CH\(_3\))\(_2\)-3,5); 6.84 (s, 1H, H\(_4\), C\(_6\)H\(_2\)(CH\(_3\))\(_2\)-5,6); 6.12 (s, 4H, H\(_1\), 1", 2×CH\(_2\)); 2.33 (s, 6H, H\(_a,b\), 2×CH\(_3\)); 2.17 (s, 6H, H\(_c\), d, 2×CH\(_3\)); \(^1\)C NMR (CDCl\(_3\), 75 MHz) (δ
(ppm): 161.97 (C₂, NCN); 152.76 (C₂, 6", C₅H₅N); 152.18 (C₈, 9); 151.43 (C₄", C₅H₅N); 137.80 (C₅', 5", arom. Cq); 133.39 (C₂', 2", arom. Cq); 132.39 (C₃', 7', 3", 7" arom. CH); 129.60 (C₄', 6', 4", 6", arom. CH); 127.96 (C₅, 6, arom. Cq); 124.59 (C₃", 5", C₅H₅N); 111.79 (C₄, 7, arom. CH); 53.08 (C₁', 1", 2×CH₂); 21.35 (C₉, d, 2×CH₃); 20.37 (C₇, a, b, 2×CH₃); Anal. Calc. for C₃₀H₃₂N₃PdCl₂: C, 58.884%; H, 5.271%; N, 6.867%, Found: C, 58.9; H, 5.3; N, 6.9%.

The suzuki miyaura reaction, the cytotoxic and the antibacterial activities were prepared according to the reported procedures.[44]

d- The general procedure for the Suzuki Miyaura reaction

Under argon atmosphere, arylbromides (0.6 mmol), palladium catalyst (0.5 mol%), KOTBU (0.6 mmol) and DMF (5 mL) were added to a schlenck containing a magnetic stir bar, followed by (0.6 mmol) of phenylacetylene. The resulting mixture was placed in an oil bath preheated to 100 °C and stirred vigorously for the indicated time. Upon completion, the mixture was cooled to room temperature, was partitioned between 30 mL of water and 20 mL of diethylether or ethyl acetate and the combined organic layer was further washed with 2 × 20 Ml of diethylether or ethyl acetate and was dried over MgSO₄. The extraction was done with DCM when 2,6-dibromopyridine was used as a substrate. The filtrate was sampled at intervals for GC analysis to check the purity and the conversions are based on arylbromides. We measure the conversion of the product and by-product compared to the corresponding starting material, the peak area of the product is divided into the sum of the areas.

e- Agar well diffusion method

Agar well diffusion method was employed for the determination of the antibacterial activity of the synthesized compounds according to.[56] The antibacterial activity was assayed by measuring in millimeters the diameter of the inhibition zone formed around the well. This determination was done in triplicate and obtained results were very similar. The reported diameter of inhibition is the average of the three tests.

f- MIC determination

The minimum inhibitory concentration (MICs) in accordance with NCCLS guideline M7-A6 and M38-P.[56] The test was performed in sterile 96-well microplates according to the literature.[44]
g- synthesis of the ligand 4

The N-heterocyclic carbene ligand precursor 4 was obtained in quantitative yield by reaction of sodium sulfonate bromide (10 mmol) and 1-methyl-4,5-dihydro-1H-imidazole (11 mmol) in DMC at 90°C for 24 h. After evaporation of solvent under high vacuum, the white solid was recrystallised in methanol to gave compound 4 as white crystals (3.5 g, % 95). $^1$H NMR (300 MHz, DMSO-d$_6$) $\delta =$ 9.75 (s, 1H, NCHN), 2.10–2.45 ppm (m, 4H, CH$_2$CH$_2$), 2.25(s,3H,CH$_3$), 3.64 (s,2H). $^{13}$C NMR (75 MHz, DMSO-d$_6$) $\delta =$ 153.6, 36.5,57,3,60.2,76.5.

Silver(I)-N heterocyclic carbene (Ag-NHC) complex 5 was obtained in quantitative yield by reaction of 3 (1 mmol) and Ag$_2$O/AgOCOCH$_3$ (1.2 mmol) in water/methanol mixture (1:1) at room temperature for 24 h in leading to the desired silver(I)-NHC complex. After reaction, the solution was filtered with celite and solvent was removed under high vacuum, the residue washed with diethyl ether and dried under high vacuum to gave compound 5. (3.1 g, % 90). $^1$H NMR (300 MHz, CD$_3$OD) $\delta =$ 2.13–2.57 ppm (m, 4H, CH$_2$CH$_2$), 2.22(s,3H,CH$_3$), 3.64 (s,2H,CH$_2$). $^{13}$C NMR (75 MHz, CD$_3$OD) $\delta =$ 188.2,185.4, 35.5,58,2,62.3,77.4.
Figure 1: 1H NMR Spectrum of Salt 2a Recorded in CDCl₃ at 300 MHz.
Figure 2: 13C NMR spectrum of salt 2a recorded in CDCl$_3$ in 75 MHz complete proton decoupling.
Figure 3: 1H NMR Spectrum of Salt 2e Recorded in CDCl$_3$ at 300 MHz.

Figure 4: 13C NMR spectrum of salt 2e recorded in CDCl$_3$ in 75 MHz complete proton decoupling.

Figure 5: Mass spectrum in DART-TOF-MS mode of salt 2e.

Figure 6: Mass spectrum in DART-TOF-MS mode of salt 2e.
Figure 7: FT-IR spectrum of complex 3b recorded in solid dispersion in KBr.

Figure 8: 1H NMR spectrum of the 3b complex recorded in CDCl₃ at 300 MHz.
Figure 9: 13C NMR spectrum of 3b complex recorded in CDCl₃ in 75MHz proton decoupling.

Figure 10: MS spectra DART-TOF-MS of complex 3b.
Scheme 6: Mechanism of fragmentation leading to the peak m / z = 409.

Scheme 7: Mechanism of fragmentation leading to the peak m/z = 263.

Complex 3d

Figure 11: 1H NMR spectrum of the 3d complex recorded in CDCl₃ at 300 MHz.
**Figure 12:** 13C NMR spectrum of 3d complex recorded in CDCl$_3$ in 75MHz proton decoupling.

**Figure 13:** Chromatogram of the product of the 3b catalyzed Suzuki reaction: (a) control; (b) coupling product.
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Sample Type: Unknown
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Sample ID:
Sample Type: Unknown
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